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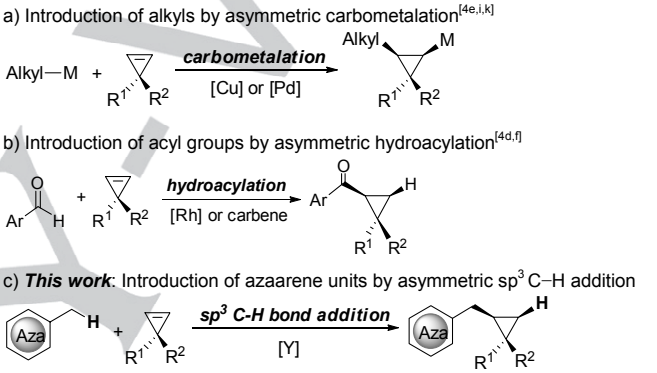
Asymmetric Yttrium-Catalyzed C(sp^3)−H Addition of 2-Methyl Azaarenes to Cyclopropenes

Yong Luo,[a] Huai-Long Teng,[b] Masayoshi Nishiura,[a,b] and Zhaomin Hou*[a,b]

Abstract: The enantioselective C−H addition to a C=C double bond represents the most atom-efficient route for the construction of chiral carbon−carbon skeletons, a central research topic in organic synthesis. We report here the enantioselective yttrium-catalyzed C(sp^3)−H bond addition of 2-methyl azaarenes such as 2-methyl pyridines to various substituted cyclopropenes and norbornenes. This protocol efficiently afforded a new family of chiral pyridylmethyl-functionalized cyclopropane and norbornane derivatives in high yields and high enantioselectivity (up to 97% ee).

Cyclopropanes have constantly attracted interest in the organic chemistry community and related fields, as the unique three-membered carbocycles are not only important components in a large number of biologically active natural products and pharmaceuticals,[1] but they can also serve as synthetically useful precursors through selective C−C bond cleavage.[2] The development of efficient and selective routes for the synthesis of enantioenriched cyclopropane derivatives represents a persistent challenge in chemical research. Among possible approaches to chiral cyclopropane structures,[3] the asymmetric addition of nucleophiles to substituted cyclopropenes has received much recent attention.[4] In this context, the transition-metal-catalyzed enantioselective carbozincation,[4e,i] carbomagnesation,[4k] and hydroacylation[4d,f] of various substituted cyclopropenes have been reported as convenient routes for the asymmetric formation of a C−C bond with the cyclopropene moieties (Schemes 1a and 1b). In principle, the enantioselective C−H addition of an organic compound to cyclopropenes may serve as the most atom-efficient method for the synthesis of chiral C-substituted cyclopropane derivatives. However, such asymmetric C−H bond activation approach has remained unexplored to date, except for the hydroacylation reactions.[4d,f] This is probably due to the lack of suitable catalysts that can not only effectively promote C−H bond activation, but also show high activity and enantioselectivity for cyclopropene insertion without causing ring-cleavage.[5]

We have recently found that half-sandwich rare earth alkyl complexes can serve as efficient catalysts for the C−H addition of heteroatom-containing aromatic compounds such as anisoles, pyridines, and *N*,*N*-dimethylanilines to various alkenes.[6,7] By using some chiral half-sandwich rare-earth catalysts, we have also achieved the enantioselective sp^2 C−H addition of pyridines to 1-alkenes[8] and the enantioselective intermolecular hydroamination of cyclopropenes with amines.[4j] These results encouraged us to examine whether chiral half-sandwich rare earth catalysts could be employed for the asymmetric C−H addition of pyridines to cyclopropenes. Pyridine moieties are among the most important heterocyclic structural motifs, widely existing in natural products, pharmaceuticals, ligands, and functional materials.[9] Hence, the efficient synthesis of pyridine-functionalized chiral cyclopropane derivatives is of great interest and importance.



Scheme 1. Enantioselective C−C bond forming reactions with cyclopropenes leading to chiral cyclopropane derivatives.

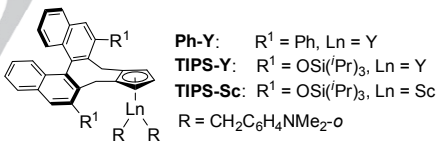


Chart 1. Chiral half-sandwich rare earth dialkyl complexes.

We report here the enantioselective sp^3 C−H addition of 2-methyl azaarenes such as 2-methyl pyridines to cyclopropenes by a chiral half-sandwich yttrium catalyst (Scheme 1c). This protocol constitutes a 100% atom-efficient route for the synthesis of a series of chiral pyridylmethyl-functionalized cyclopropane derivatives in high yields and high enantioselectivity. The enantioselective sp^3 C−H addition of 2-methyl pyridines to norbornenes has also been achieved in a similar fashion. This work represents the first example of asymmetric sp^3 C−H addition of an organic compound to a cyclopropene moiety as well as the first example of asymmetric sp^3 C−H addition of a pyridine compound to an alkene.[10]

At first, we examined the reaction of 2,6-lutidine (**1a**) with 3-methyl-3-phenylcyclopropene (**2a**) as a model reaction by using the yttrium complex **Ph-Y** (Chart 1) as a catalyst. The neutral complex **Ph-Y** alone was not effective for the C−H addition of **1a** to **2a** (Table 1, entry 1), although it showed excellent activity and enantioselectivity for the hydroamination of cyclopropenes with amines.[4j] In the presence of [Ph$_3$C][B(C$_6$F$_5$)$_4$] as a cocatalyst,

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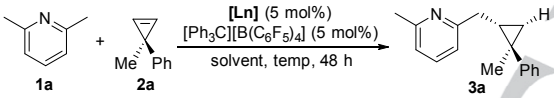
Ph-Y showed moderate activity for the sp^3 C−H addition of **1a** to **2a**, affording the pyridylmethylation product **3a** in 76% yield at room temperature in 48 h, albeit with poor stereoselectivity (1.1:1 dr with 41% and 31% ee, respectively) (Table 1, entry 2). When the reaction was carried out at −20°C, the enantioselectivity was significantly improved to 86% ee, though the diastereoselectivity was still poor (1.3:1 dr) (Table 1, entry 3). When the slightly bulkier complex **TIPS-Y** was used in place of **Ph-Y**, the target product **3a** was obtained in 88% yield with high enantioselectivity (90% ee) and significantly improved diastereoselectivity (7.5:1 dr) (Table 1, entry 4). When the reaction was carried out at a further lower temperature (−40 °C), the product yield was dropped significantly (40%), while a higher stereoselectivity (10:1 dr, 91% ee) was achieved (Table 1, entry 5). Under the similar conditions, the scandium analogue **TIPS-Sc** did not show an activity for the present sp^3 C−H addition of **1a** to **2a** (Table 1, entry 6), though it exhibited high activity for the enantioselective sp^2 C−H addition of pyridines to 1-alkenes.[8] These results demonstrate that the activity and stereoselectivity of the C−H addition reactions are significantly influenced not only by the catalyst ancillary ligands and metal ions but also by the C−H bond type.[11,12] The use of chlorobenzene or xylene instead of toluene as a solvent did not show much influence on the reaction (Table 1, entries 4, 8, and 9).

Table 1. Asymmetric sp^3 C−H addition of 2,6-lutidine to 3-methyl-3-phenylcyclopropene by chiral half-sandwich rare-earth catalysts.[a]

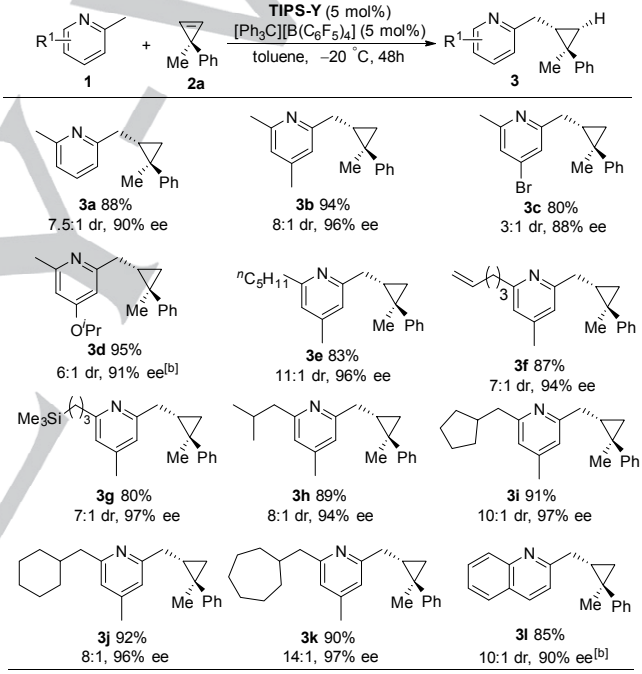


entry	[Ln]	solvent	temp (°C)	yield (%)[b]	Dr[c]	ee (%)[d]
1[e]	**Ph-Y**	toluene	rt	-	-	-
2	**Ph-Y**	toluene	rt	76	1.1:1	41; 31
3	**Ph-Y**	toluene	−20	84	1.3:1	86; 76
4	**TIPS-Y**	toluene	−20	88	7.5:1	90
5	**TIPS-Y**	toluene	−40	40	10:1	91
6	**TIPS-Sc**	toluene	−20	-	-	-
7	**TIPS-Y**	chloroben zene	−20	83	8:1	86
8	**TIPS-Y**	xylene	−20	87	7.5:1	89

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), **[Ln]** (5 mol %), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (5 mol %), toluene (1 mL), 48 h, unless otherwise noted. [b] Combined isolated yield of both diastereomers. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by chiral HPLC. [e] Without [Ph$_3$C][B(C$_6$F$_5$)$_4$].

With the optimized reaction conditions in hand, we then examined the scope of the pyridine substrates in the reaction with **2a** by using **TIPS-Y**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] at −20 ºC in toluene (Table 2). Similar to 2,6-lutidine (**1a**), the reaction of 2,4,6-trimethylpyridine with **2a** gave the ortho sp^3 C−H cyclopropylation product **3b** in high yield (94%) and high stereoselectivity (96% ee, 8:1 dr). 4-Bromo-2,6-dimethylpyridine also afforded the target product **3c** in good yield (80%) and high enantioselectivity (88% ee), albeit with a lower diastereoselectivity (3:1 dr). Debromination was not observed. In the case of 4-isopropoxy-2,6-dimethyl pyridine, the target product **3d** was obtained in high yield (95%) and high stereoselectivity (91% ee, 6:1 dr) at 0 °C. Various substituents (both linear and branched) at the 6-position of the 2-methylpyridne substrates were compatible with the enantioselective ortho methyl C−H cyclopropylation, giving the desired products such as **3e**–**3h** in high yields (80–89%) and excellent enantioselectivity (94–97% ee). The alkenyl (**3f**) and $SiMe_3$ (**3g**) groups survived the reaction conditions. Substrates with a bulky five-, six-, or seven-membered ring in the ortho substituents (6 position) all gave the desired products (**3i**, **3j**, and **3k**) in high yields (90–92%) and excellent enantioselectivity (96–97% ee). 2-Methylquinoline was also a suitable substrate, affording the desired product **3l** in 85% yield and 90% ee.

Table 2. Asymmetric sp^3 C−H addition of various 2-methylpyridines to 3-methyl-3-phenylcyclopropene by **TIPS-Y**.[a]



[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), **TIPS-Y** (5 mol%), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (5 mol%), toluene (1 mL), −20 °C, 48 h, combined isolated yield of both diastereomers; dr and ee determined by ^{1}H NMR analysis of the crude reaction mixture and chiral HPLC, respectively. [b] 0 °C .

To examine the scope of the cyclopropene substrates, 2,4,6-trimethylpyridine (**1b**) was used to react with various substituted cyclopropenes (Table 3). In a series of 3-methyl-3-phenyl-disubstitued cyclopropenes, the substrates containing either electron-donating (such as OMe) or electron-withdrawing (such as F and Cl) groups at either the para or meta or ortho position of the phenyl substituent all afforded the desired products (such as **3m**–**3r**) in good yields (78−86%) and excellent enantioselectivity (92−97% ee). A heterocycle (such as thiophene)-substituted cyclopropene compound was also suitable, giving the desired product **3s** in 69% yield and 95% ee. The spirocycle-containing cyclopropenes (**3t** and **3u**) showed

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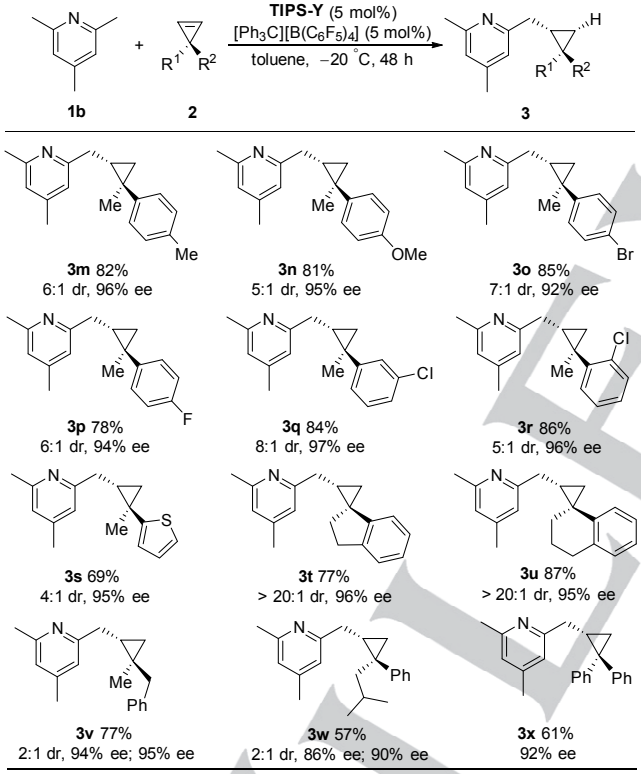
remarkably high diastereoselectivity (>20:1) and excellent enantioselectivity (95−96% ee), probably due to the influence of the rigid spiro structure. In the case of 3-methyl-3-benzylcyclopropene and 3-isopropyl-3-phenylcyclopropene, the target products **3v** and **3w** were obtained in a relatively lower diastereoselectivity (2:1) probably because of the smaller difference in steric hindrance between the two substituents, but the enantioselectivity remained high (90−95% ee). In the case of 3,3-diphenylcyclopropene, the single-stereoceneter-containing target product **3x** was isolated in 61% yield and 92% ee. The absolute configuration of **3t** was determined by the X-ray diffraction analysis of a single crystal of the anilinium salt **3t·HBr** prepared by treatment of **3t** with HBr (see supporting information). It was confirmed that the predominant configuration was formed by addition of the 2-pyridylmethyl unit *syn* to the smaller substituent in the cyclopropene skeleton through a *re*-face (vide infra).

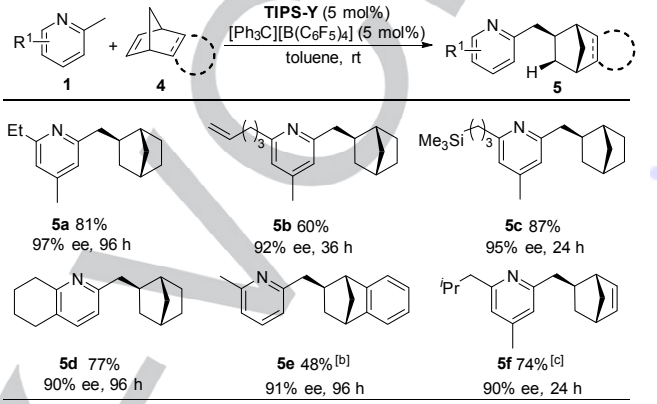
Table 3. Asymmetric sp^3 C−H addition of 2,4,6-trimethylpyridine to various substituted cyclopropenes by **TIPS-Y**.[a]



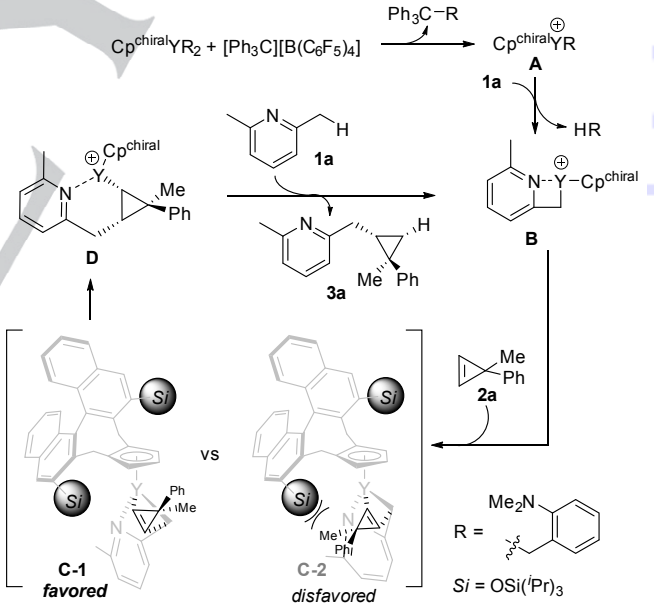
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), **TIPS-Y** (5 mol%), $[Ph_3C][B(C_6F_5)_4]$ (5 mol%), toluene (1 mL), −20 °C, 48 h, combined isolated yield of both diastereomers; dr and ee determined by ^{1}H NMR analysis of crude reaction mixture and chiral HPLC, respectively.

The combination of **TIPS-Y** and $[Ph_3C][B(C_6F_5)_4]$ also served as an efficient catalyst for the enantioselective sp^3 C−H addition of various 2-methylpyridines to norbonenes, affording the corresponding pyridylmethyl-functionalized norbornane derivatives such as **5a**–**5e** with high enantioselectivity (90−97% ee) and moderate to high yields at room temperature (Table 4). The chiral pyridylmethyl-functionalized norbornene compound **5f**, which contains a reactive C=C double bond that may allow further functionalizations,[13] was selectively obtained in high enantioselectivity (90% ee) by reaction with norbornadiene under appropriate conditions. Pyridylmethyl-functionalized norbornane moieties were known to serve as a core structure of useful chiral ligands.[14]

Table 4. Asymmetric sp^3 C−H addition of 2-methylpyridines to norbornenes by **TIPS-Y**.[a]



[a] Reaction conditions: **1** (0.2 mmol), **4** (0.3 mmol), **TIPS-Y** (5 mol%), $[Ph_3C][B(C_6F_5)_4]$ (5 mol%), toluene (1 mL), rt, isolated yield, ee determined by chiral HPLC. [b] **1** (0.3 mmol), **4** (0.2 mmol). [c] **1** (0.2 mmol), **4** (0.4 mmol).



Scheme 2. Proposed mechanism for the enantioselective sp^3 C−H addition of **1a** to **2a**.

A possible reaction mechanism for the enantioselective C(sp^3)−H bond addition of 2,6-dimethyllutidine (**1a**) to 3-methyl-3-phenylcyclopropene (**2a**) is shown in Scheme 2. The cationic chiral yttrium alkyl species **A** generated from the reaction of the dialkyl precursor **TIPS-Y** with $[Ph_3C][B(C_6F_5)_4]$ may undergo deprotonative C(sp^3)−H activation of **1a** to give intermediate **B** with the assistance of interaction between the metal center and the pyridine nitrogen atom.[7c] The coordination of the

cyclopropene unit in **2a** to the metal center in **B** could afford two possible transition states **C-1** and **C-2**, in which **C-1** is favored as it has less steric repulsion between the substituents of the cyclopropene skeleton in **2a** and the catalyst ligand. The insertion of the cyclopropene unit into the pyridylmethyl−Y bond in **C-1** would give **D**, which after deprotonation of another molecule of **1a** by the cyclopropyl−Y bond affords the final product **3a** and regenerates the active species **B**. The kinetic isotope effect (KIE) studies suggest that C(sp^3)−H bond cleavage is involved in the rate-determining step (see supporting information).

In summary, we have achieved for the first time the enantioselective C(sp^3)−H bond addition of 2-methyl azaarenes to various cyclopropenes and norbornenes by using a chiral half-sandwich rare-earth metal catalyst such as **TIPS-Y**. This protocol has afforded a series of chiral pyridylmethyl-functionalized cyclopropane and norbornane derivatives in high yields and excellent enantioselectivity in a 100% atom-efficient manner. Functional groups such as $SiMe_3$, linear alkenyl, and aryl halides are compatible. This unique catalytic transformation could be ascribed to the strong heteroatom affinity of the rare-earth metal ions and the high activity of the cationic rare-earth metal alkyl species towards both C–H activation and C=C double bond insertion, as well as to the well-defined chiral Cp ligand environment. Studies on the synthesis and application of chiral half-sandwich rare-earth alkyl catalysts for asymmetric C–H transformations and related reactions can be fruitfully prospected.

Acknowledgements

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Keywords: cyclopropenes • sp^3 C-H bond addition • chiral yttrium catalyst • pyridine• norbornene

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[11] When 2-methyl pyridine was used instead of 2,6-lutidine (**1a**) to react with **2a**, the ortho sp^2 (rather than sp^3) C-H addition product was obtained, but the yield and enantioselectivity were lower.

[12] When an excess molar amount of **2a** was used in the reaction with **1a**, the cyclopropylation took place at both methyl groups of **1a**, but the resulting diastereoisomers, which have four chiral centers, were difficult to separate.

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C(sp^3)−H Addition

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Asymmetric Yttrium-Catalyzed C(sp^3)−H Addition of 2-Methyl Azaarenes to Cyclopropenes

The enantioselective C(sp^3)−H bond addition of 2-methyl azaarenes such as 2-methylpyridines to various substituted cyclopropenes and norbornenes has been achieved for the first time by using a chiral half-sandwich yttrium catalyst. This protocol afforded a series of chiral pyridylmethyl-functionalized cyclopropane and norbornane derivatives in high yields, high enantioselectivity, and 100% atom-efficiency.