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A chiral cobalt(II) complex catalyzed enantioselective aza-Piancatelli rearrangement/Diels–Alder cascade reaction†

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A chiral *N*,*N*′-dioxide/cobalt(II) complex catalyzed highly diastereoselective and enantioselective tandem aza-Piancatelli rearrangement/intramolecular Diels–Alder reaction has been disclosed. Various valuable hexahydro-2*a*,5-epoxycyclopenta[*cd*]isoindoles bearing six contiguous stereocenters have been obtained in good yields with excellent diastereo- and enantio-selectivities from a wide range of both readily available 2-furylcarbinols and *N*-(furan-2-ylmethyl)anilines.

Introduction

The Piancatelli reaction and its variants,[1] a kind of acid-catalyzed rearrangement of 2-furylcarbinols, allow straightforward access to a large array of 2-substituted cyclopentenones and other structurally complex molecules. Due to the prevalence of cyclopentane structures in major natural product families, as well as in a wealth of biologically active molecules,[2] this reaction has gained great interest in the past decade.[3–7] Although a range of catalytic aza-Piancatelli reactions along with related cascade processes have been developed,[4–6] only a few examples are catalytic enantioselective versions, which are dominated by chiral Brønsted acid catalysts (Scheme 1a). For instance, Rueping's group and Sun's group reported the first catalytic asymmetric aza-Piancatelli reaction with aniline derivatives by using a chiral *N*-triflyl phosphoramide catalyst[6a] and chiral phosphoric acid catalyst,[6b] respectively. Recently, Jiang and coworkers employed chiral phosphoramide to promote an enantioselective aza-Piancatelli rearrangement/Friedel–Crafts alkylation cascade reaction.[6d] In these cases, the chiral Brønsted acids enabled dehydration and regioselective nucleophilic addition, and then the resulting bifunctional chiral anion ensured stereoselection in the key 4π conrotatory electrocyclization of the pentadienyl cation (Scheme 1a). Piancatelli-type reactions are mechanistic analogous to Nazarov cyclization.[8] Although Lewis acids are efficient to accelerate those rearrangements and the following cascade reactions as well,[5] the chiral metal complex catalyzed asymmetric version is still void. Even the well-developed enantioselective Nazarov reaction is usually limited to strong-coordinated bidentate substrates.[9] The major challenge in the asymmetric Piancatelli rearrangement might come from the elusive interaction between chiral metal/ligand and cyclopentadienyl cation, which makes it hard to define the stereochemistry.[6b]

Given the difficulties of aza-Piancatelli rearrangement and its initiated cascade reaction in the synthesis of multicyclic cores, and in connection with our long endeavor in chiral Lewis acid catalysis, we attempt to develop chiral metal complex catalysts to expand the enantioselective aza-Piancatelli-initiated cascade reactions. Chiral *N*,*N*′-dioxide–metal complexes are able to promote a number of asymmetric transformations with high efficiency and stereoselectivity,[10] and are tolerant to water,[11] which is generated in the dehydration step of Piancatelli rearrangement. Very recently, Baskaran disclosed an interesting $Yb(OTf)_3$-catalyzed aza-Piancatelli rearrangement/[4+2] cycloaddition cascade to construct an octahydro-1*H*-cyclopenat[*cd*]isoindole structure, an aza-tricyclic core of a gracilamine alkaloid.[5h] We proposed that the well-characterized chiral pocket of *N*,*N*′-dioxide–metal complex might be able to adopt the hydrocyclopentadienyl cation from 2-furylcarbinol, delivering 3-amino substituted cyclopentenone, which undergoes a Lewis acid-promoted diastereoselective intramolecular Diels–Alder reaction (Scheme 1b). Herein, we report a new chiral *N*,*N*′-dioxide-cobalt(II) complex[12] catalyzed diastereo- and enantioselective aza-Piancatelli rearrangement/Diels–Alder reaction, allowing efficient and direct construction of a number of hexahydro-2*a*,5-epoxycyclopenta[*cd*]isoindole derivatives. The metal salt and the ligand framework were found to be critical for the realization of enantiocontrol.

Results and discussion

In our preliminary investigation, we chose furan-2-yl(phenyl) methanol **1a** and *N*-(furan-2-ylmethyl)aniline **2a** as the model

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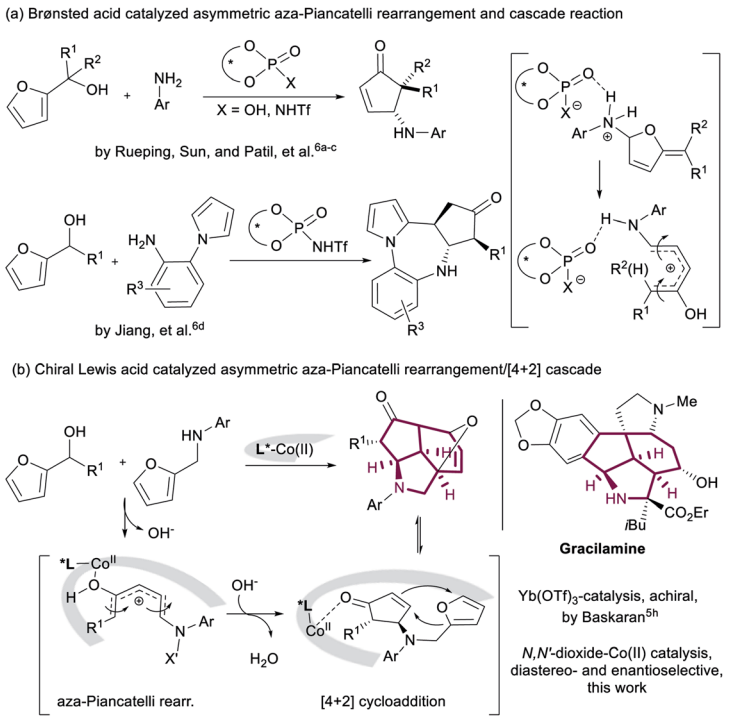
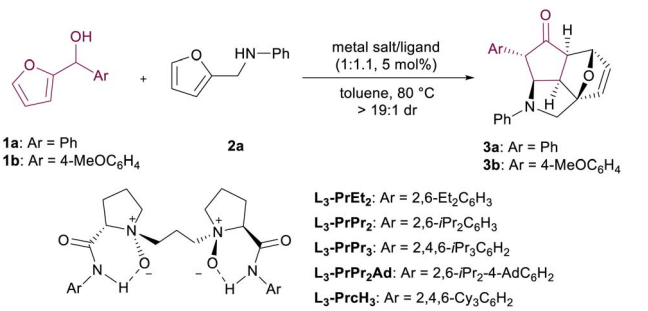
† Electronic supplementary information (ESI) available: ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR, HPLC spectra, and CD spectra (PDF). X-ray crystallographic data for **3m** (CIF). CCDC 1971783. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc00542h



Scheme 1 Asymmetric catalytic aza-Piancatelli rearrangement and cascade reaction.

substrates to optimize the reaction conditions. Various metal salts, including $Yb(OTf)_3$, $Dy(OTf)_3$, and $In(OTf)_3$ as well, which were proven effective for aza-Piancatelli rearrangement, were screened in toluene at 80 °C upon coordination with the chiral *N*,*N*′-dioxide ligand **L_3-PrPr$_2$**. Disappointingly, the corresponding product **3a** was obtained as a nearly racemate with poor to moderate yields, lower reactivity and a longer reaction time than the achiral version[4b,5a,c,h] (Table 1, entries 1–3). We proposed that rare earth metal salts bear large ionic radii and multiple-coordination manners,[13] which might be disadvantageous to create a tight pocket to confine the hydrocyclopentadienyl cation to deliver enantiocontrol in the competition of amine **2**.[14] The existence of water generated in the rearrangement step will accelerate the formation of a poor-enantioselective OH-bridged dimer when indium(III) salt was used.[15] After examining other metal salts, we found that the reaction could be achieved with medium yield and enantioselectivity (36% yield, >19 : 1 dr, 65% ee; Table 1, entry 5) in the presence of $Co(BF_4)_2\cdot 6H_2O$, where the center metal ion Co(II) is soft and bears a small ionic radius, reducing the bonding of the amine nucleophile and forming a suitable chiral pocket with the ligand to define the stereochemistry in the rearrangement of the hydrocyclopentadienyl intermediate. Encouraged by this result, the structure of *N*,*N*′-dioxide ligands was evaluated. It was revealed that the L-proline derived ligand **L_3-PrPr$_2$** gives better enantioselectivity than other amino acid derived ligands (see the ESI† for details). The steric hindrance of the aniline subunits of the ligand has a dramatic influence on the enantioselectivity (Table 1, entries 5–9). Decreasing the steric hindrance, such

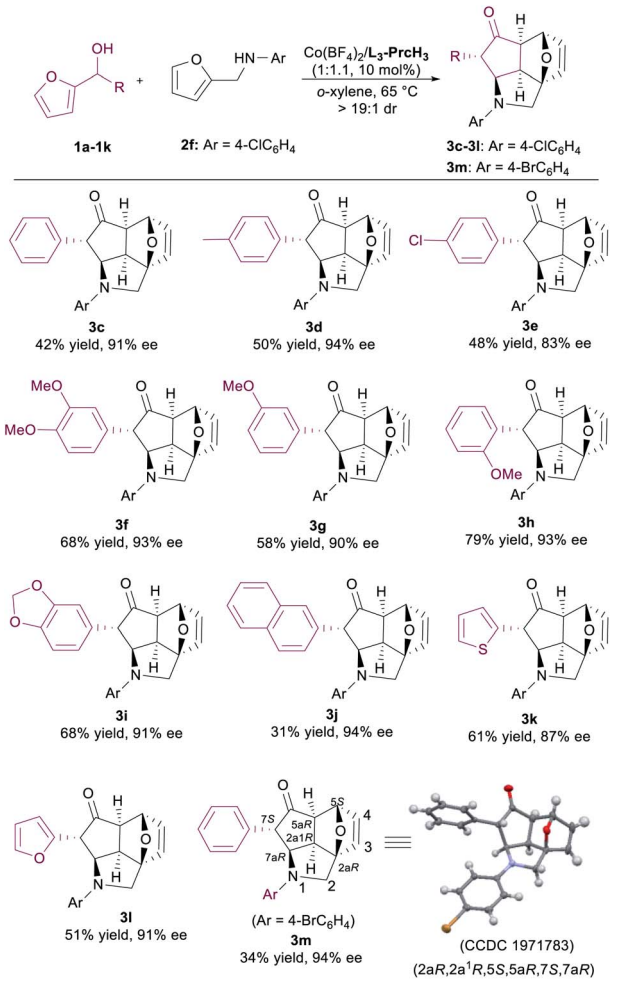
Table 1 Optimization of the reaction conditions[a]



Entry	Metal salt	Ligand	Yield[b] (%)	ee[c] (%)
1	$Yb(OTf)_3$	**L_3-PrPr$_2$**	14	0
2	$Dy(OTf)_3$	**L_3-PrPr$_2$**	<10	−3
3	$In(OTf)_3$	**L_3-PrPr$_2$**	47	4
4	$Co(OTf)_2$	**L_3-PrPr$_2$**	10	57
5	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrPr$_2$**	36	65
6	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrEt$_2$**	60	8
7	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrPr$_3$**	14	81
8	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrPr$_2$Ad**	42	82
9[d]	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrcH$_3$**	55	83
10[d,e]	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrcH$_3$**	63	85
11[d,e,f]	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrcH$_3$**	20	92
12[d,e,f,g]	$Co(BF_4)_2\cdot 6H_2O$	**L_3-PrcH$_3$**	88	90

[a] Unless otherwise noted, the reactions were performed with metal salt/ligand (1 : 1.1, 5 mol%), **1a** (0.10 mmol), and **2a** (1.0 equiv.) in toluene (1.0 mL) at 80 °C for 16 h. [b] Isolated yield, and >19/1 dr was obtained. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Co(II)/ligand (1 : 1.1, 10 mol%). [e] *o*-Xylene (1.0 mL) was used instead of toluene. [f] 65 °C for 16 h. [g] **1b** was used instead of **1a**.

Table 2 Substrate scope of 2-furylcarbinols[a]



[a] Unless otherwise noted, the reactions were performed with $Co(BF_4)_2\cdot 6H_2O$/**L_3-PrcH$_3$** (1 : 1.1, 10 mol%), **1** (0.10 mmol), and **2** (1.0 equiv.), in *o*-xylene (1.0 mL) at 65 °C. >19/1 dr.

as **L_3-PrEt$_2$** containing 2,6-diethyl aniline substituent (Table 1, entry 6).

Bulkier 2,4,6-substitutions, such as **L_3-PrcH$_3$**, bearing a 2,4,6-cyclohexyl aniline moiety, improved the yield to 55% and the ee value to 83% with 10 mol% catalyst loading (Table 1, entry 9). After careful investigation of the solvents, *o*-xylene was proven to be the best choice, and the desired product could be obtained in 63% yield with 85% ee (Table 1, entry 10). When the reaction temperature was reduced to 65 °C, the ee value had an obvious increase (92% ee), but the reaction activity was depressed (Table 1, entry 11). When furan-2-yl(4-methoxyphenyl)methanol **1b** was used as the model substrate instead of **1a**, the related product **3b** could be obtained in 88% yield with 90% ee (Table 1, entry 12). The reason of dramatically increased reactivity might be that the *para*-methoxy group on phenyl of 2-furylcarbinol makes the cyclopentadienyl cation more stable. It is noteworthy that there is a dynamic equilibrium between the desired products **3** and the uncyclized intermediates in the solvent (see the ESI† for details).[5h] Finally, we established the optimized reaction conditions as $Co(BF_4)_2\cdot 6H_2O$/**L_3-PrcH$_3$** (1 : 1.1, 10 mol%) in *o*-xylene at 65 °C for 16 h.

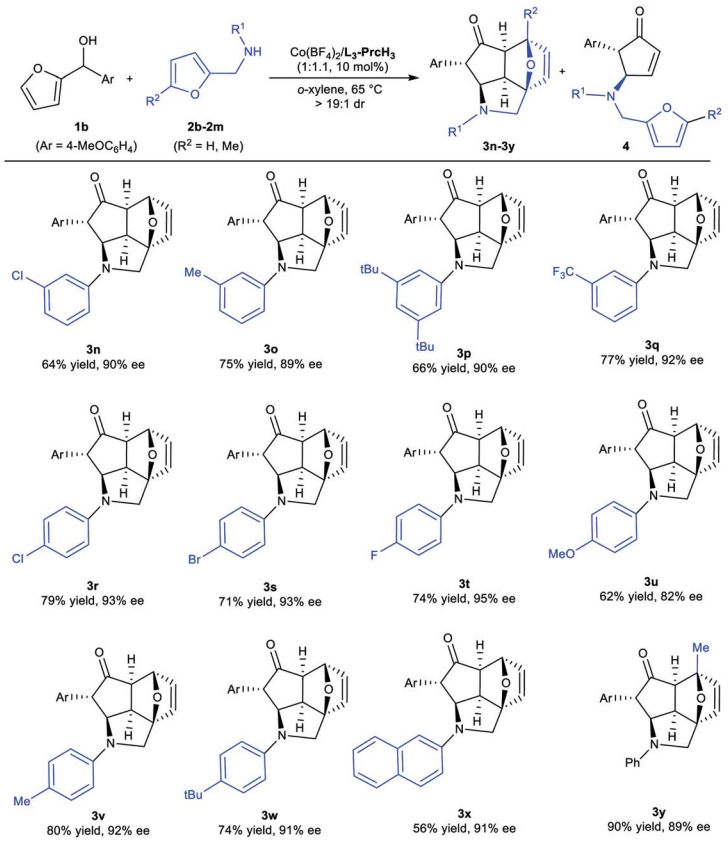
With the optimized conditions in hand, we turned our attention to the scope of 2-furylcarbinols (Table 2). The 2-furylcarbinols containing electron-withdrawing or electron-neutral groups on the aryl moiety had lower reactivity than the standard substrate **1b** in the reaction. The corresponding products **3c–3e** were only achieved in medium yields with excellent ee values after the reaction time was prolonged. The phenyl ring of 2-furylcarbinols bearing electron-donating groups at the *para*, *meta*, or *ortho* position were converted to the desired products **3f–3i** with good yields and enantioselectivities (58–79% yields and 90–93% ee). We were also pleased to find that the reaction was compatible with 2-naphthyl, 2-furyl, and 2-thienyl groups to furnish **3j–3l** in 31–61% yields with 87–94% ee. Moreover, the absolute configuration of the product **3m** was determined to be (2*aR*,2*a*^{1}*R*,5*S*,5*aR*,7*S*,7*aR*) by X-ray crystallography analysis.[16] It is noteworthy that only one diastereoisomer of the epoxycyclopenta[*cd*]isoindole products was isolated in all cases. The absolute configuration of the other products was determined to be uniform by comparing the circular-dichroism spectra with that of **3m**.

Subsequently, we assessed the scope of *N*-(furan-2-ylmethyl) anilines in the reaction with furan-2-yl(4-methoxyphenyl) methanol **1b**, and the results are summarized in Table 3. The electronic properties or steric hindrance of the substituents on the aromatic ring had a little effect on the stereoselectivity of the tandem reaction, and the desired epoxycyclopenta[*cd*]isoindoles **3n–3w** were obtained in good to excellent yields (62–88% yields) with excellent enantioselectivities (82–95% ee). Of note, a 2-naphthyl containing amine was also a suitable substrate, giving the product **3x** in 56% yield with 91% ee. Furthermore, *N*-((5-methylfuran-2-yl)methyl)aniline was converted to the corresponding product **3y** with 90% yield and 89% ee as well.

To show the practicability of this methodology, a gram scale synthesis of the product **3b** was carried out. In the presence of 10 mol% of $Co(BF_4)_2\cdot 6H_2O$/**L_3-PrcH$_3$**, 2-furylcarbinol **1b** (4 mmol) reacted with *N*-(furan-2-ylmethyl)aniline **2a** (4 mmol) smoothly, and delivered **3b** in 79% yield, >19 : 1 dr with 91% ee (Scheme 2a). We also carried out some product derivatization (Scheme 2b–d). For example, the compound **3b** could undergo diastereoselective 1,2-addition with an allyl Grignard reagent or reduction of the carbonyl group, affording the corresponding alcohols in 91% yield with 94% ee (**5**) and 95% yield with 97% ee (**7**). Moreover, phenyloctahydro-2*a*,5-epoxycyclopenta[*cd*]isoindole **6** could be isolated in 90% yield with 95% ee through hydrogenation.

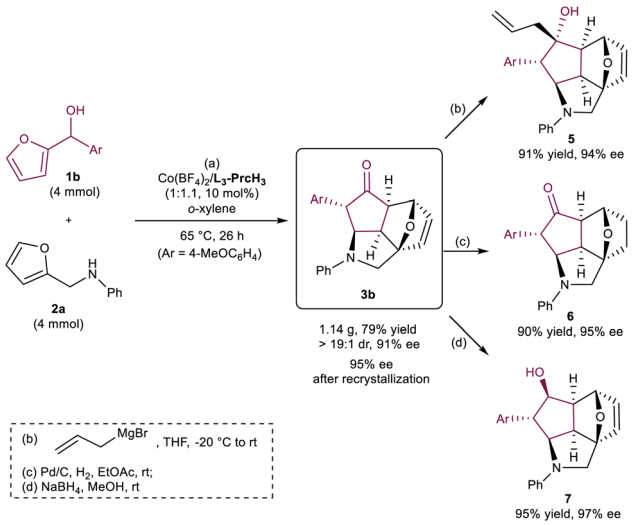
In addition, we tested other amine-type nucleophiles to probe the aza-Piancatelli rearrangement process (Scheme 3). When the substrate *N*-(thiophen-2-ylmethyl)aniline **2n** was used, only the uncyclized product **4bn** could be achieved in 95% yield with 89% ee. It indicates that the high diastereo- and enantio-selectivity come from the 4π conrotatory electrocyclization step. If amine **2o** embodying a 2-furyl substituent

Table 3 Substrate scope of *N*-(furan-2-ylmethyl)anilines[a]

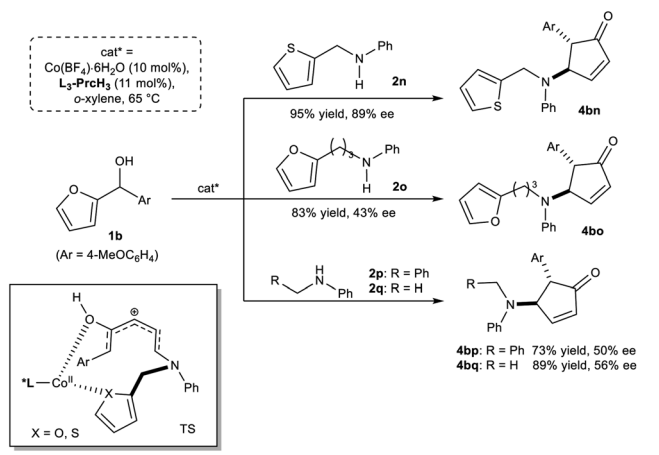


[a] Unless otherwise noted, the reactions were performed with $Co(BF_4)_2 \cdot 6H_2O$/**L_3-PrcH$_3$** (1 : 1.1, 10 mol%), **1b** (0.10 mmol), and **2** (1.0 equiv.) in *o*-xylene (1.0 mL) at 65 °C. >19/1 dr.

with a longer chain was subjected to the reaction, the corresponding aza-Piancatelli rearrangement product **4bo** was isolated in high yield with a medium ee value. Other secondary amines as the nucleophiles yielded the *trans*-substituted cyclopentenone derivatives **4bp** and **4bq** with moderate enantioselectivity, implying that hetero-atoms in furyl or thienyl might also participate in cooperation with the metal center to enhance the enantioselection.



Scheme 2 Gram scale experiment and product derivatization.



Scheme 3 Other amine-type nucleophiles.

Conclusions

We have presented an efficient chiral Lewis acid catalyzed asymmetric aza-Piancatelli rearrangement/Diels–Alder cascade reaction of 2-furylcarbinols with *N*-(furan-2-ylmethyl)anilines. The use of a chiral *N*,*N*′-dioxide-Co$(BF_4)_2\cdot 6H_2O$ complex enabled the construction of a series of hexahydro-2*a*,5-epoxycyclopenta[*cd*]isoindoles bearing six contiguous stereocenters in a wonderful diastereo- and enantio-selective manner. Further investigations on chiral Lewis acid catalyzed other types of rearrangement and electrocyclization reactions as well as the study to probe the secret of enantiocontrol are underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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