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Nickel(II)-catalyzed asymmetric thio-Claisen rearrangement of α -diazo pyrazoleamides with thioindoles

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A nickel(II) catalyzed enantioselective thio-Claisen rearrangement of α -diazo pyrazoleamides with thioindoles was realized with the modified chiral *N*,*N'*-dioxide ligands, affording a variety of C3substituted indole derivatives in high yields (up to 95%) with excellent enantioselectivities (up to 96% ee) under mild reaction conditions. A possible transition state was proposed based on previous reports and X-ray crystal structure of the catalyst.

The thio-Claisen rearrangement¹ as a variation of Claisen rearrangement was first reported by Kwart in 1962² and has been utilized for the synthesis of numerous thiocarbonyl compounds and sulfur-containing heterocycles. Compared with traditional thio-Claisen rearrangement³ of electroneutral allyl vinvl sulfides, the charge-accelerated thio-Claisen rearrangement⁴ utilizing sulfoxides or *in situ* generated sulfonium ylides, could be triggered under relatively mild conditions with a faster reaction rate. This was demonstrated to be a facile and effective means to construct C-C bond in challenging contexts. A great deal of intriguing work in this aspect was reported by several groups, such as Yorimitsu and Oshima,⁵ Rainier⁶, Maulide⁷ and Procter⁸.

Despite the prominent advance of charge-accelerated thio-Claisen rearrangement, asymmetric reports of this kind of reactions were extremely rare. Limited reports revealed that highly enantioselective conversion was achieved through chirality transfer from a sulfur to a carbon stereocenter by the use of chiral sulfoxide substrates.^{7e–f} The only one example of catalytic asymmetric version was presented by Rainier in 2008.^{6e} A key sulfonium ylide intermediate generated from vinyl diazoacetates with 2-thio-3-alkylindoles in the presence of a chiral dirhodium catalyst, and subsequently underwent proton transfer/[3,3] rearrangement/isomerization in sequence, showing high diastereoselectivity but with poor enantioselectivity (Scheme 1a). The low enantioselectivity might be due to the difficulty in fine discrimination of the heterotopic lone pairs of sulfur or the fast inversion of free nonracemic ylide. Therefore, to realize the catalytic asymmetric thio-Claisen rearrangement has aroused our great interest.

(a) Rh(II)-promoted catalytic asymmetric thio-Claisen rearrangement (Rainier's work)⁶





Scheme 1 Asymmetric [3,3]-sigmatropic rearrangements of sulfonium ylide.

Recently, our group achieved the highly enantioselective Doyle–Kirmse reaction,^{9a} [2,3] Stevens and Sommelet–Hauser rearrangements¹⁰ of sulfonium ylides successfully. In these cases, a type of α -diazo pyrazoleamides were designed for the highly efficient [2,3]-sigmatropic rearrangements through the chiral nickel complex bonded ylide intermediates. Encouraged by these works, we conceive that the chiral catalyst would facilitate the formation of sulfonium ylide from vinyl α -diazo pyrazoleamides and 2-thio-indoles in an enantioselective manner (Scheme 1b), then the chiral Lewis acid-bounded ylides

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Electronic Supplementary Information (ESI) available: [¹H, ¹³C[¹H] and ¹⁹F[¹H] NMR, HPLC spectra, CD spectra (PDF). X-ray crystallographic data for **4da**, **9da**, Ni(II)/L₂-**Pi(O/Bu)**₂ (CIF)]. See DOI: 10.1039/x0xx00000x

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might undergo the following proton transfer and [3,3]sigmatropic rearrangement process with good stereocontrol. If the hypothesis mentioned above works, it will provide an efficient solution to catalytic asymmetric [3,3]-sigmatropic rearrangement of sulfonium. Herein, we wish to disclose our efforts in this area. The complex of newly designed chiral *N*,*N'*dioxide ligand¹¹ L₂-**Pi(OiBu)**₂ with nickel(II) salt was found to be highly efficient to promote the asymmetric thio-Claisen rearrangement of vinyl α -diazo pyrazoleamides with 2-thioindoles. Various C3-substituted 2-thio-indoles were generated with good to excellent enantioselectivities (Scheme 1b).

At the beginning of this study, vinyl substituted α -diazo pyrazoleamide **1a** and 2-(methylthio)-1*H*-indole **2a** were chosen as the model substrates. The reaction was performed well in the presence of chiral *N*,*N'*-dioxide-nickel(II) complex catalysts to yield the 3-substituted 2-methylthio indole derivative **3aa** rather than 2-(methylthio)-3*H*-indole isomer^{6e}. However, **3aa** was unstable for storage, for convenience, the isolated **3aa** was oxidized to sulphone **4aa** for further analysis. After intensive screening, the optimized reaction conditions were determined and shown in Table 1, entry 1 (87% yield, 96% ee), using 10 mol% of chiral **L**₂-**Pi(OiBu)**₂/Ni(OTf)₂ complex catalyst in CHCl₃ at -20 °C for 20 hours. We also identified critical parameters during the optimization studies (Table 1). Both nickel(II) source and ligands were essential for promoting the reaction, in the absence of either of them, the reaction did not proceed at all

Table 1 Optimization of the reaction conditions



motal calt	ligand	yield of	yield of	ee
metal salt		3 aa (%) ^b	4aa (%) ^c	(%) ^d
Ni(OTf) ₂	L ₂ -Pi(O <i>i</i> Bu) ₂	94	87	96
Ni(OTf) ₂	—	N.R.	—	—
—	L₂-Pi(O <i>i</i> Bu)₂	N.R.	—	—
Fe(OTf) ₂	L ₂ -Pi(O <i>i</i> Bu) ₂	trace	—	—
Cu(OTf) ₂	L₂-Pi(O <i>i</i> Bu)₂	38	27	37
Co(OTf) ₂	L₂-Pi(O <i>i</i> Bu)₂	82	82	79
$Ni(NTf_2)_2$	L ₂ -Pi(O <i>i</i> Bu) ₂	92	85	95
Ni(DME)Br ₂	L₂-Pi(O <i>i</i> Bu)₂	92	84	94
Ni(OTf) ₂	L ₂ -PiMe ₂	41	24	33
Ni(OTf) ₂	L ₂ -PiEt ₂	99	84	50
Ni(OTf) ₂	L ₂ -PiPr ₂	86	68	61
Ni(OTf) ₂	L ₂ -Pi(OMe) ₂	96	67	58
Ni(OTf) ₂	L ₂ -Pi(OEt) ₂	89	64	62
Ni(OTf) ₂	L ₂ -Pi(O <i>i</i> Pr) ₂	83	61	94
	metal salt Ni(OTf) ₂ Ni(OTf) ₂ Fe(OTf) ₂ Cu(OTf) ₂ Cu(OTf) ₂ Ni(NTf ₂) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂ Ni(OTf) ₂	metal salt ligand Ni(OTf)2 L2-Pi(O/Bu)2 Ni(OTf)2 — L2-Pi(O/Bu)2 — Fe(OTf)2 L2-Pi(O/Bu)2 Cu(OTf)2 L2-Pi(O/Bu)2 Cu(OTf)2 L2-Pi(O/Bu)2 Cu(OTf)2 L2-Pi(O/Bu)2 Ni(NTf2)2 L2-Pi(O/Bu)2 Ni(DME)Br2 L2-Pi(O/Bu)2 Ni(OTf)2 L2-Pi(O/Bu)2 Ni(OTf)2 L2-Pi(O/BU2 Ni(OTf)2 L2-Pi(O/BU2 Ni(OTf)2 L2-Pi(OME)2 Ni(OTf)2 L2-Pi(OME)2	$\begin{array}{c c} \mbox{metal salt} & \mbox{Higand} & \begin{tabular}{lligand} & \be$	$\begin{array}{c c c c c c c } \mbox{Highand} & \begin{tabular}{ c c c c c } \mbox{Highand} & \begin{tabular}{ c c c c c c } \mbox{Highand} & \begin{tabular}{ c c c c c c c } \mbox{Highand} & \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

^{*a*} Unless otherwise noted, the first step of the reactions were carried out with **1a** (0.10 mmol), **2a** (1.2 equiv), Ni(OTf)₂/L₂-Pi(*OiBu*)₂ (1:1, 10 mol%) in CHCl₃ (0.2 M) at -20 °C. ^{*b*} Isolated yield of **3aa**. ^{*c*} Isolated yield of **4aa** after two steps. ^{*d*} The ee value of **4aa** was determined by HPLC analysis on a chiral stationary phase. ^{*e*}N.R. = no reaction. ^{*f*} DME = 1,2-dimethoxyethane.

(entries 2–3). Other metal salts, such as $Fe(OTf)_{2\nu/i}Cu(OTf)_{2ni}OT$ Co(OTf)₂ that may also form metal carbehoids were evaluated (entries 4–6). Iron salt was sluggish, and copper salt was smoothly to promote this reaction but with poorer yields and enantioselectivities. Cobalt salt was slightly worse than nickel salt. The counter anion of the nickel(II) salt showed little effect on the reaction (entries 7–8), Ni(NTf₂)₂ and Ni(DME)Br₂ can give similar results compared with the standard conditions. Additional investigation of chiral ligands indicated that the newly designed *N*,*N*'-dioxide ligands (entries 12–14) containing 2,6-dialkoxy motifs almost exhibited better enantioselectivity than the related 2,6-dialkyl substituted ligands (entries 9–11). Other representative chiral ligands coordinated with Ni(OTf)₂ were also examined, such as BINAP, *t*Bu-box and so on, which couldn't catalyze this reaction (See the ESI for details).

Having established the acceptable reaction conditions, we evaluated the generality of this reaction. Firstly, the substrate scope with respect to vinyl substituted α-diazo pyrazoleamides 1 was explored to react with 2a. As depicted in Table 2, regardless of the electronic nature or steric hindrance of the substituents on the phenyl ring, the pyrazoleamides could be smoothly transformed into the corresponding products 3ba-3na, and further oxidized to 4ba-4na in 51-92% yields with no enantioselectivities (89–95% ee).12 erosion of The heteroaromatic and condensed-ring substrates were also tolerated well in this reaction, readily affording C3-substituted indole derivatives 4oa-4qa with good results (68-88% yields, 92-94% ee). Benzyl substituted substrate 1r was tested under this catalytic system as well, but unfortunately, only poor yield



entry	R ¹ , R ²	yield of 3 (%)	yield of 4 (%)	ee (%)
1	2-FC ₆ H ₄ , H	84 (3ba)	74 (4b a)	93
2	2-CIC ₆ H ₄ , H	84 (3ca)	63 (4ca)	91
3	2-MeC ₆ H ₄ , H	91 (3da)	82 (4da)	92
4	3-FC ₆ H ₄ , H	97 (3ea)	82 (4ea)	93
5	3-ClC ₆ H ₄ , H	96 (3fa)	81 (4fa)	93
6 ^b	3-MeC ₆ H ₄ , H	99 (3ga)	92 (4ga)	95
7	4-FC ₆ H ₄ , H	99 (3ha)	89 (4ha)	94
8	4-CIC ₆ H ₄ , H	86 (3ia)	76 (4ia)	93
9	4-BrC ₆ H ₄ , H	90 (3ja)	82 (4ja)	92
10 ^c	4-IC ₆ H ₄ , H	91 (3ka)	51 (4ka)	95
11 ^c	4-F ₃ CC ₆ H ₄ , H	77 (3la)	71 (4la)	89
12 ^b	4-MeC ₆ H ₄ , H	98 (3ma)	84 (4ma)	94
13 ^c	4-MeOC ₆ H ₄ , H	99 (3na)	86 (4na)	91
14	2-furyl, H	99 (3oa)	68 (4oa)	92
15	3-thienyl, H	99 (3pa)	70 (4pa)	94
16 ^c	2-naphthyl, H	99 (3qa)	88 (4qa)	94
17 ^c	benzyl, H	23 (3ra)	5 (4ra)	78
18 ^c	C ₆ H ₅ , Me	79 (3sa)	39 (4sa)	82

^{*a*} Reaction conditions are identical to those in entry 1 of Table 1. ^{*b*} Ni(NTf₂)₂ was used instead of Ni(OTf)₂. ^{*c*} The isolated product **4** contains a bit of impurities.

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of the product **4ra** (78% ee) was obtained, which may be caused by the low reactivity of **1r** and rapid deterioration of **2a**. The disubstituted vinyl α -diazopyrazoleamide **1s** was subjected to the reaction conditions, and the desired product **3sa** bearing a quaternary carbon centre was obtained successfully.

Subsequently, we turned attention to the scope of thioindoles **2** (Table 3). A variety of aliphatic substituted thioindoles **2b**–**g** reacted with **1a** smoothly to generate **4ab–4ag** with good yields (70–95%) and enantioselectivities (81–92% ee). The phenyl substituted substrate **2h** was also explored, but exhibited very low reactivity and selectivity (62% yield for 30 d, 20% ee of **4ah**). Then substrates with substituents on the indole ring at C5, C6, and C7 positions were examined. Almost all of them could give satisfactory results (**4ai–4an**, 76–93% yields, 94–96% ee) except the C7-position substituted thioindole **2o** exhibited poor selectivity and reactivity (58% yield, 48% ee). Moreover, the C5 and C6 di-substituted thioindole was also applicable, affording **4ap** with 95% yield and 95% ee.

Table 3 Substrate scope of thioindoles^a

$\begin{array}{c} N_2 \\ Ph \\ 1a \\ R^1 \frac{5}{6!} \\ 7 \\ 2b-p \end{array}$	PG NI(OTT) ₂ /L₂-PI(O/Bu) ₂ (1:1, 10 mol%) CHOI ₀ - 20 °C → SR ²	$R^{4} \xrightarrow{PG}_{(2.1e)} K^{2} \xrightarrow{PG}_{(2.1e)} K^{2}$	2BA quuv) min R ¹ al	$PG = \bigvee_{a^{d}}^{a^{d}} N - N$
entry	R ¹ , R ²	yield of 3 (%)	yield of 4 (%)	ee (%)
1	H <i>,</i> Et	87 (3ab)	76 (4ab)	92
2	H <i>, n</i> Pr	94 (3ac)	84 (4ac)	89
3 ^{bd}	H <i>, n</i> Bu	96 (3ad)	95 (4ad)	85
4	H <i>, i</i> Bu	92 (3ae)	70 (4ae)	81
5	H, dodecyl	81 (3af)	70 (4af)	85
6 ^c	H, Bn	82 (3ag)	75 (4ag)	87
7	H, Ph	65 (3ah)	62 (4ah)	20
8 ^{<i>d</i>}	5-Cl, Me	78 (3ai)	76 (4ai)	94
9 ^{bd}	5-Br, Me	98 (3aj)	87 (4aj)	95
10 ^b	5-MeO, Me	99 (3ak)	80 (4ak)	95
11 ^d	6-F, Me	91 (3al)	76 (4al)	96
12 ^b	6-Cl, Me	98 (3am)	93 (4am)	96
13 ^{bd}	6-Br, Me	96 (3an)	87 (4an)	95
14	7-Br, Me	63 (3ao)	58 (4ao)	48
15 ^{bd}		98 (3ap)	95 (4ap)	95

^{*a*} Reaction conditions are identical to those in entry 1 of Table 1. ^{*b*} Ni(NTf₂)₂ was used instead of Ni(OTf)₂. ^{*c*} L₂-Pi(*OiPr*)₂ was used instead of L₂-Pi(*OiBu*)₂. ^{*d*} The isolated product 4 contains a bit of impurities.

To evaluate the practicality of the catalytic system, a scale-up experiment was performed between **1a** (3.0 mmol) and **2a** (3.6 mmol) under the optimized reaction conditions, providing the desired product **4aa** in 85% yield with 97% ee (Scheme 2). Upon treatment of **4aa** with H₂ and Pd/C in methanol, the double bond of the alkyl chain was reduced and gave **5aa** in 87% yield without any loss of enantioselectivity, and **5aa** could be further converted into chiral amide (**6aa**), ester (**7aa**) and alcohol (**8aa**) with high efficiency. Moreover, the thio-Claisen rearrangement product **3aa** underwent oxidation reaction to produce chiral sulfoxide **9aa** in 50% yield, 92:8 dr and 99% ee by using H₂O₂ as the oxidant in the presence of Fe(OTf)₃/L₃-PiPr₂Ad complex¹³.



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Scheme 2 Gram-scale synthesis and further transformations.

Based on our previous works^{9a,10,14}, control experiments (see ESI for details), the absolute configuration of the products and the X-ray crystal structure of Ni(II)/L₂-Pi(OiBu)₂ complex¹⁵, as well as the general mechanism of metal carbene promoted sulfonium [3,3]-sigmatropic rearrangements^{6e}, a possible transition state model was proposed to elucidate the origin of



Scheme 3 Proposed catalytic model

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the stereoselectivity (Scheme 3). The chiral nickel carbene intermediate A was firstly formed when the Ni(II)/L2-Pi(OiBu)2 complex was mixed with diazo compound 1a along with the loss of nitrogen gas. The thioindole 2a preferred to attack the intermediate A from its Re-face because the Si-face was blocked by the below amide unit of the ligand (Int **B** and **B**'). On the other hand, the steric hindrance of indole unit of 1a with the upward amide unit of the ligand enabled the discrimination of the heterotopic lone pairs of sulfur, and resulted in the generation of sulfonium ylide specie **B** with *R* configuration at the sulfurcenter as the major one. According to the mechanism investigated in our previous works,9a,10 the control of chiral N,N'-dioxide ligands as well as the induction of chiral sulfur centre would guide the following proton transfer process in an enantioselective manner to provide the R,R-configured intermediate C. Subsequently, the [3,3]- σ rearrangement took place that C3 of the indole ring attacked the prochiral C3' from its Re-face to produce intermediate D, thus leading to the (R,E)configured product 3aa after isomerization.

Conclusions

In conclusion, we have developed an efficient catalytic thio-Claisen asymmetric rearrangement of α-diazo pyrazoleamides with thioindoles by employing a chiral N,N'dioxide-nickel(II) complex catalyst, providing expedient access to C3-substituted indole derivatives with good to excellent enantioselectivities. Plausible transition state models were proposed to elucidate the origin of chiral induction. Further application of the chiral N, N'-dioxide ligands with metal salts to other enantioselective synthesis are ongoing in our laboratory. We appreciate the National Natural Science Foundation of China (Nos. 21625205 and 21772127) for financial support. Thanks Dr. Yuqiao Zhou and Dr. Daibing Luo for the assistance in X-ray analysis.

Conflicts of interest

There are no conflicts to declare

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The chiral Ni(II) complex catalyzed enantioselective thio-Claisen rearrangement of α -diazo pyrazoleamides with thioindoles.