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Reversal of enantioselective Friedel–Crafts C3-alkylation of pyrrole by slightly tuning the amide units of *N*,*N*′-dioxide ligands†

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Chiral Ni(II)-complexes of *N*,*N*′-dioxides show high catalytic activity and enantioselectivity in catalysing the asymmetric Friedel–Crafts C3-alkylation of 2,5-dimethyl pyrrole to β,γ-unsaturated α-ketoesters. A dramatic reversal of enantioselectivity is realized with ligands derived from the same type of chiral source of L-ramipril, by slightly tuning the amide units.

Substituted pyrroles are abundant in both natural products and biologically active molecules.[1] The enantioselective Friedel–Crafts type alkylation reactions of pyrrole are powerful transformations that introduce a substituent onto the C2- or C3-position of this important heterocycle. Despite advances in asymmetric Friedel–Crafts reactions of similar nucleophiles of indoles, sporadical reactions of pyrrole have been documented,[2] likely due to the regioselectivity and reactivity issues. The first enantioselective Friedel–Crafts reaction of pyrrole with α,β-unsaturated aldehydes was reported by MacMillan.[2i] After that, both chiral Lewis acid complexes and organocatalysts have been explored in the nucleophilic addition of pyrrole at its C2-position.[2h–l] Nevertheless, rare examples were reported using the nucleophilicity of the C3-position of pyrroles. Recently, the You group presented an elegant intermolecular asymmetric allylic dearomatization reaction using 2,5-disubstituted pyrroles.[3] Given the regioselective control of the Friedel–Crafts reaction with 3-substituted indoles,[4] we expect to realize the asymmetric Friedel–Crafts alkylation of pyrrole derivatives at the C3-position by the employment of 2,5-dimethyl pyrrole. The multisubstituted pyrrole derivatives, therefore, could be formed regio- and enantioselectively.

Control of the absolute configuration of newly created stereocenters is of special interest in asymmetric catalysis.[5] Synthesis of both enantiomers of the chiral compounds bearing the pyrrole unit is demanded for the purpose of evaluation of biological and pharmaceutical activity. Generally, a switch in enantioselectivity is achieved by the use of enantiomeric ligands. Unfortunately, the two enantiomers of a chiral ligand are not always readily available or economically feasible to synthesize. Alternatively, enantioselectivity of reactions could also be changed with a single ligand by changing the metal sources, solvents, temperature or by other methods.[6] There are also some examples of the reversal of enantioselectivity using ligands with the same chiral backbone simply by modifying subunits of the ligands.[5,7] Prior investigations of chiral *N*,*N*′-dioxide–metal complex catalysts by our group revealed that subtle modification of the ligand moieties, such as the amide substituents, and the amino acid backbone, obviously affects the stereoselection of the reactions.[6v,w,8] As an extension to this approach, we report herein the asymmetric Friedel–Crafts alkylation of 2,5-dimethyl pyrrole with β,γ-unsaturated α-ketoesters,[9] where the reaction occurred at the C3-position of pyrrole. A dramatic switch in the enantioselectivity was realized by slight modification of the substituent at the aniline units of the *N*,*N*′-dioxides. It showed that *N*,*N*′-dioxide–Ni(II) complexes[10] that contain a 2,6-diisopropylaniline or 3,5-ditertbutylaniline substituent imparted good reactivity and reversal of enantioselectivity.

At the outset of this study, 2,5-dimethyl-pyrrole **2a** and β,γ-unsaturated α-ketoester **1a** were employed as the model substrates to study the asymmetric Friedel–Crafts alkylation reaction (Table 1). In the presence of the chiral *N*,*N*′-dioxide ligand **L-PiPh**, derived from L-pipecolic acid and aniline, only the $Ni(OTf)_2$ complex could give the desired C3-alkylation product **3a** in moderate yield, albeit the enantioselectivity was low (74% yield and 15% ee; entries 1–3). To improve the enantioselectivity of the reaction, a series of chiral *N*,*N*′-dioxide ligands was examined. Interestingly, the reaction catalyzed by $Ni(OTf)_2$ complexes of *N*,*N*′-dioxides derived from 2,6-disubstituted anilines displayed the opposite sense of stereoinduction to those observed in the reactions with 3,5-disubstituted ones (entries 3–10 *vs.* entries 11–14). The enantioselectivity gradually increased when the hindrance of the substituents on anilines was raised (entries 4–6). Changing the backbone of the ligands

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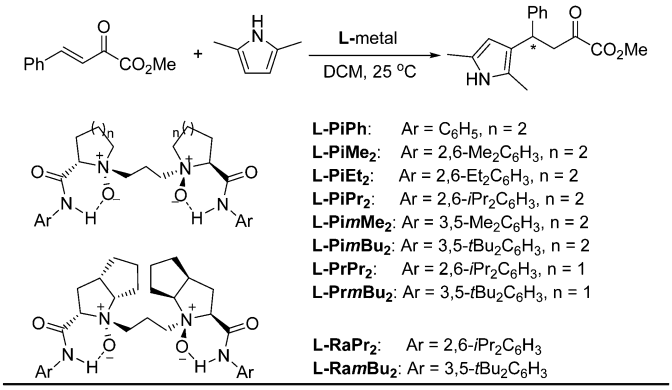
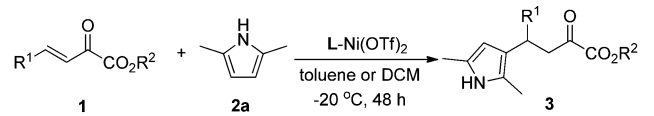
Table 1 Optimization of the reaction conditions

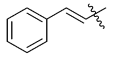
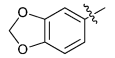


Entry[a]	Ligand	Metal	t (h)	Yield[b] (%)	ee[c] (%)
1	L-**PiPh**	$Sc(OTf)_3$	12	11	14
2	L-**PiPh**	$Cu(OTf)_2$	12	—	—
3	L-**PiPh**	$Ni(OTf)_2$	12	74	15
4	L-**PiMe$_2$**	$Ni(OTf)_2$	12	83	16
5	L-**PiEt$_2$**	$Ni(OTf)_2$	12	84	22
6	L-**PiPr$_2$**	$Ni(OTf)_2$	12	85	55
7	L-**PrPr$_2$**	$Ni(OTf)_2$	12	60	70
8	L-**RaPr$_2$**	$Ni(OTf)_2$	12	79	80
9[d]	L-**RaPr$_2$**	$Ni(OTf)_2$	18	70	90
10[d,e]	L-**RaPr$_2$**	$Ni(OTf)_2$	24	92	92
11	L-**PiMe$_2$**	$Ni(OTf)_2$	15	62	51(−)
12[e]	L-**Pi*m*Bu$_2$**	$Ni(OTf)_2$	24	92	92(−)
13[e]	L-**Pr*m*Bu$_2$**	$Ni(OTf)_2$	24	75	93(−)
14[e]	L-**Ra*m*Bu$_2$**	$Ni(OTf)_2$	24	95	95(−)

[a] Unless otherwise noted, the reaction was carried out with **1a** (0.1 mmol), **2a** (3.0 equiv.) and **L**-metal (10 mol%, 1 : 1) in CH_2Cl_2 (0.5 mL) at 25 °C. [b] Isolated yield of **3a**. [c] Determined by chiral HPLC, and (−) refers to the rotation sign that is opposite to others. [d] In toluene (0.5 mL). [e] At −20 °C.

Table 2 Substrate scope of β,γ-unsaturated α-ketoesters **1**



Entry[a]	R^1	R^2	Yield[b] (%)	ee[c] (%)
1	C_6H_5	Me	92(95)	92(95)
2	C_6H_5	Et	84(85)	95(96)
3	C_6H_5	Bn	91(89)	92(96)
4	C_6H_5	*t*-Bu	89(89)	95(93)
5	2-ClC_6H_4	Me	84(91)	99(67)
6	2-BrC_6H_4	Me	80(78)	98(60)
7	3-ClC_6H_4	Me	89(93)	90(90)
8	4-ClC_6H_4	Me	94(95)	93(93)
9	4-$O_2NC_6H_4$	Me	92(89)	88(92)
10	4-MeC_6H_4	Me	90(93)	93(93)
11	4-PhC_6H_4	Me	92(91)	91(94)
12	3-$MeOC_6H_4$	Me	82(95)	93(93)
13	4-$MeOC_6H_4$	Me	81(78)	96(94)
14	3,4-$Cl_2C_6H_3$	Me	90(92)	91(92)
15	1-Naphthyl	Me	79(80)	95(91)
16	2-Naphthyl	Me	89(89)	93(94)
17	2-Thienyl	Me	84(95)	92(93)
18	2-Furanyl	Me	94(95)	92(96)
19		Me	68(95)	94(91)
20		Me	85(90)	91(95)
21	*c*-Hexyl	Me	78(84)	86(20)

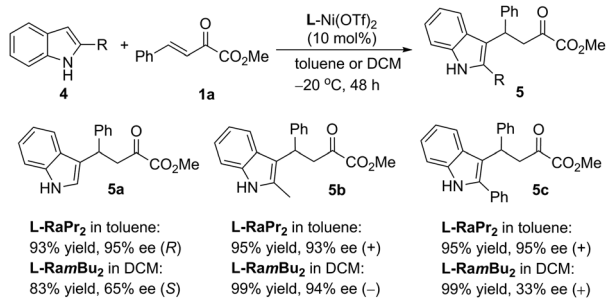
[a] Unless otherwise noted, the reaction was carried out with **1** (0.1 mmol), **2a** (3.0 equiv.) and L-**RaPr$_2$**/$Ni(OTf)_2$ (10 mol%, 1/1) in toluene–DCM (0.5 mL) at −20 °C for 48 h. The data in parentheses was obtained by using L-**Ra*m*Bu$_2$** instead. [b] Isolated yield of **3**. [c] Determined by chiral HPLC. The data in parentheses had opposite configuration.

from L-pipecolic acid to L-proline or L-ramipril, resulted in further improved ee values and yields (Table 1, entries 6–8, and 12–14). The ligand L-**RaPr$_2$** of choice prepared from 2,6-diisopropylaniline and L-ramipril afforded the (+)-**3a** in 79% yield with 80% ee (entry 8). Better results were given when the reaction was performed in toluene and at −20 °C (92% yield, 92% ee; Table 1, entry 10). On the other hand, ligand L-**Ra*m*Bu$_2$**, appropriately combined with 3,5-ditertbutylaniline and L-ramipril, generated (−)-**3a** with 95% ee and 95% yield (entry 14).

To test the generality of the catalytic systems, firstly, the substrate scope for the (+)-enantiomer of pyrrole esters **3** was investigated by using the L-**RaPr$_2$**–$Ni(OTf)_2$ complex as the catalyst. Various β,γ-unsaturated α-ketoesters with 2,5-dimethylpyrrole were evaluated, giving the corresponding adducts with excellent yields and enantioselectivities (up to 94% yield and 99% ee). The ester group had a slight influence on the outcome (Table 2, entries 1–4). γ-Aryl ketoesters bearing a halo-group at the *ortho*-position underwent the reaction with higher enantioselectivity than the others (up to 99% ee; entries 5 and 6). Electron-donating substituents afforded the products sluggishly in comparison with the electron-withdrawing ones (entries 12 and 13 *vs.* 5–10). In addition, naphthyl and 2-thienyl or 2-furanyl substituted ketoesters reacted well with 2,5-dimethyl-pyrrole, delivering the desired products in 92% to 95% ees and 79% to 94% yields, (Table 2, entries 15–18). Remarkably, an aliphatic ketoester was also a suitable candidate for this catalytic system giving 78% yield with 86% ee (Table 2, entry 21).

We next proceeded to prepare the antipodes of the adducts **3** by the employment of the L-**Ra*m*Bu$_2$**–$Ni(OTf)_2$ complex as the catalyst instead. The Friedel–Crafts alkylation reaction with 2,5-dimethylpyrrole was tolerable to various substituted β,γ-unsaturated α-ketoesters, independent of the electron-rich or electron-deficient characteristic of the substituents (Table 2, data in the parentheses). It is noteworthy that the enantioselectivity was fairly similar to its corresponding enantiomer in almost all the cases. The yield was slightly higher than the corresponding enantiomer, such as for 3-methoxylphenyl, 2-thienyl, and (*E*)-phenylethenyl substituted ones (entries 12, 17 and 19). Thus, the two enantiomers of the 2,3,5-trisubstituted pyrrole derivatives could be readily formed from chiral *N*,*N*′-dioxides with subtle modification of the amide units. Scale-up experiments under these reaction conditions with 5 mmol of **1a** afforded both enantiomers in 90% yield, and 92% and 96% ee. Finally, the reaction of *N*-methyl 2,5-dimethyl pyrrole worked well under the standard reaction conditions, thus affording the related enantiomers in 76% yield with 90% ee, and 72% yield with 92% ee. It indicated that there was no interaction between the NH of pyrrole and the catalyst (see ESI† for details).

Encouraged by the above results, we also explored the reaction with 2-substituted indole derivatives as the nucleophile. A reversal



Scheme 1 Substrate scope for indole derivatives.

of enantioselectivity was found upon the ligands and substituents on indoles. As shown in Scheme 1, 2-methyl indole **4b** was a suitable substrate for both catalytic systems, delivering 95% yield with 93% ee, and 99% yield with 94% ee, respectively (Scheme 1, **5b**). The L-**RaPr$_2$**–Ni(OTf)$_2$ complex catalytic system was compatible for the Friedel–Crafts alkylation of indole **4a** and 2-phenyl indole **4c**, giving the desired products in excellent yield and enantioselectivity. Moderate reversed or unreversed enantioselectivity was observed in the presence of the L-**Ra*m*Bu$_2$**–Ni(OTf)$_2$ complex catalyst (Scheme 1, **5a**[11] and **5c**). Additionally, when pyrrole was subjected to the catalytic system of L-**RaPr$_2$**–Ni(OTf)$_2$, the Friedel–Crafts reaction with β,γ-unsaturated α-ketoester **1a** occurred at the C2-position, delivering the 2-substituted pyrrole derivative in 76% yield and 99% ee. A small amount of 2,5-disubstituted pyrrole byproduct was detected.

However, the reaction catalyzed by L-**Ra*m*Bu$_2$**–Ni(OTf)$_2$ was less enantioselective, and the adduct was given in 72% yield and 11% ee with the major enantiomer maintained. It implied that the steric hindrance of the nucleophiles was also crucial for the facial selection (see ESI† for details).

We have been able to obtain the crystal structure of the hydrates of both the L-**RaPr$_2$** and L-**Ra*m*Bu$_2$** complexes of Ni(II)[12] that show a six-coordinate distorted octahedral geometry. Both *N*,*N*′-dioxides act as neutral tetradentate ligands that bind the Ni(II) cation securely through two amine oxide oxygens and two amide oxygens. There are two coordination sites in the equatorial plane that can capture ancillary substrates or solvents. The available spaces in the seesawed amide units of the two catalyst complexes are markedly different (Fig. 1). The torsion angle α (C1–C2–C1′–C2′) of the two amide units of L-**RaPr$_2$** is 147.04°, whereas the corresponding angle in L-**Ra*m*Bu$_2$** is −155.74°. The distance between X and C3 of the center carbon in the substituent in L-**RaPr$_2$** is much shorter than in L-**Ra*m*Bu$_2$** (4.65 Å *vs.* 6.33 Å), but the distance between X and C2′ in L-**RaPr$_2$** is much longer than in L-**Ra*m*Bu$_2$** (5.51 Å *vs.* 4.51 Å).

Fig. 2 shows the side view of two possible catalytic models that rationalize the reversal of the enantioselectivity. The *cis*-auxiliary ligands X/Y (Fig. 1) can be replaced by the bidentate β,γ-unsaturated α-ketoester **1a**. As shown in Fig. 2 (left), the steric hindrance of the *ortho*-isopropyl substituent of the backward amide in L-**RaPr$_2$** is adverse for the *Si*-face attack of indole ($d_{X–C3}$ = 4.65 Å). Therefore, the alkylation reaction dominates from the *Re*-face of the substrate, giving (*R*)-**5a** as the major isomer. In contrast, in the right view (Fig. 2), the *tert*-butyl

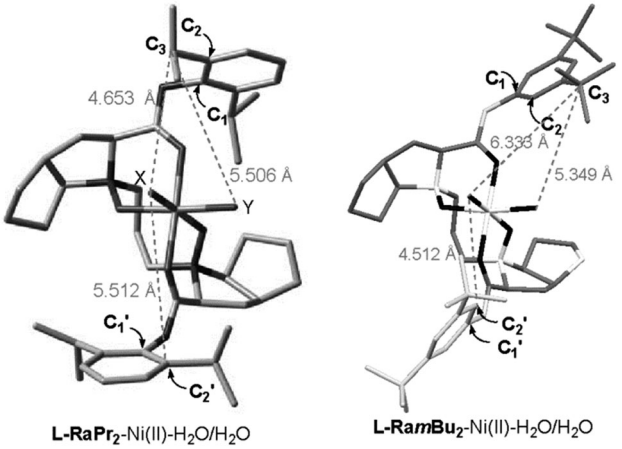


Fig. 1 X-ray crystal structures of the *N*,*N*′-dioxide–Ni(II) complexes (top view).

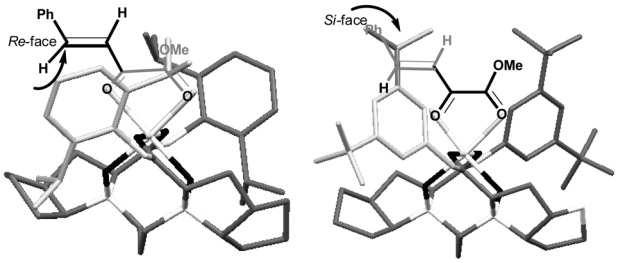


Fig. 2 Possible catalytic models for the switch in enantioselectivity (side view). Left: L-**RaPr$_2$**–Ni(II)–**1a**; right: L-**Ra*m*Bu$_2$**–Ni(II)–**1a**.

substituent of the forward amide in L-**Ra*m*Bu$_2$** efficiently shields the *Re*-face of the substrate ($d_{X–C2'}$ = 4.51 Å). The other amide unit blocks the *Si*-face a little since it is far away from the γ-position of the substrate ($d_{X–C3}$ = 6.33 Å). As a result, the corresponding (*S*)-**5a** is generated as the major enantiomer from the *Si*-face attack. Density functional theory (DFT) calculations at the UM06/[6-31G(d), LanL2DZ] level indicate the preference for the products of L-**RaPr$_2$**-*Re* and L-**Ra*m*Bu$_2$**-*Si* over the products of L-**RaPr$_2$**-*Si* and L-**Ra*m*Bu$_2$**-*Re*, with the differences of the activation energy barriers for the two corresponding competing pathways being 2.5 (L-**RaPr$_2$**-*Re vs.* L-**RaPr$_2$**-*Si*) and 2.9 kJ mol^{-1} (L-**Ra*m*Bu$_2$**-*Si vs.* L-**Ra*m*Bu$_2$**-*Re*) (see ESI† for details).

In summary, we have developed a novel Friedel–Crafts C3-alkylation of 2,5-dimethyl-pyrrole to β,γ-unsaturated α-ketoesters catalysed by chiral *N*,*N*′-dioxide–Ni(OTf)$_2$ complexes. Dramatic reversal of enantioselectivity was accomplished by slightly modifying the subunit of the *N*,*N*′-dioxide. The two enantiomers of 2,3,5-trisubstituted pyrroles were given in high yield and enantioselectivity. A variety of β,γ-unsaturated α-ketoesters, 2,5-dimethyl-pyrrole, pyrrole, and 2-methyl indole could be tolerated in the Friedel–Crafts reaction. X-ray analysis of the two catalysts as well as DFT calculations of the transition states provided a rational explanation for the controllable enantioselectivity.

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