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Asymmetric α-Amination of 4-Substituted Pyrazolones Catalyzed by a Chiral $Gd(OTf)_3$/N,N′-Dioxide Complex: Highly Enantioselective Synthesis of 4-Amino-5-pyrazolone Derivatives

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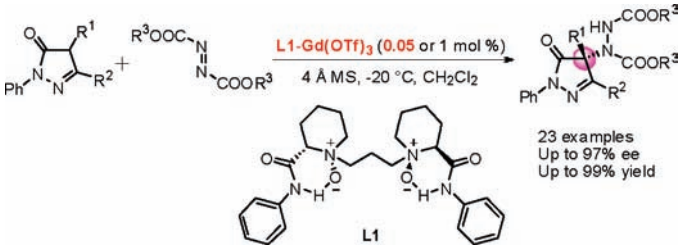
ABSTRACT



The asymmetric α-amination of 4-substituted pyrazolones with azodicarboxylates was investigated for the first time, employing an *N*,*N*′-dioxide gadolinium(III) complex as the catalyst. The novel transformations exhibited high yield, and 4-amino-5-pyrazolone derivatives bearing a chiral quaternary center were obtained in excellent yields (up to 99%) and enantioselectivities (90%−97% ee) for a broad scope of 5-pyrazolones by using 1 mol % or only 0.05 mol % of catalyst.

Pyrazolone derivatives characterized as a five-membered-ring lactam are important frameworks which exhibit a variety of applications as pharmaceutical candidates and biologically important structural components.[1] For example, analgin is used for the treatment of pains of different origin and variable intensity. The development of asymmetric methods to access pyrazolone derivatives with a quaternary stereogenic center[2] at the C4 position has thus given rise to considerable interest. However, relatively fewer examples have been documented for catalytic asymmetric transformations by using pyrazolone as a nucleophile.[3] Recently, the enantioselective α-amination of azodicarboxylates with carbolic nucleophiles represents

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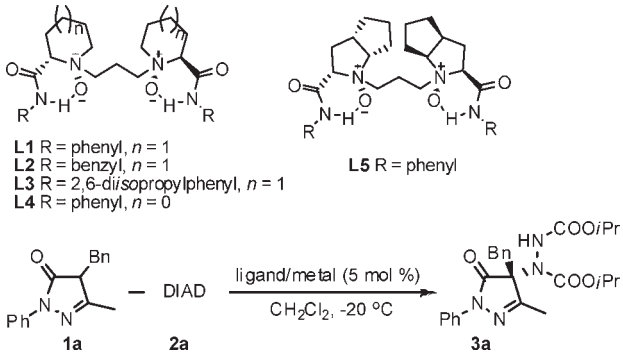
one of the best established strategies for the construction of chiral C−N bonds in organic chemistry.[4,5] Catalytic enantioselective α-amination of pyrazolone has not yet been investigated to conduct optically active 4-amino-5-pyrazolones which are the core frame of numerous pharmaceutical compounds.

In asymmetric catalysis, the contribution of the chiral complex is of leading importance. Our group is endeavoring to develop chiral C_2-symmetric *N,N′*-dioxide into a helpful ligand which could coordinate with a series of cations to form chiral complex catalysts.[6−8] Especially, it could give selective and flexible catalysts with lanthanide metal salts[9] which feature advantages in stability, recovery, the electropositive properties, and high coordination ability. Herein, we wish to report the first highly enantioselective α-amination of 4-substituted 5-pyrazolones with azodicarboxylates using a chiral *N,N′*-dioxide−Gd(III) complex as the catalyst. Excellent yields (up to 99%) and enantioselectivities (up to 97% ee) were achieved for a wide range of pyrazolones at 0.05−1 mol % catalyst loading.

Initially, (*S*)-pipecolic acid derived *N,N′*-dioxide **L1** was complexed with various lanthanide metal salts to catalyze the asymmetric α-amination of 4-benzyl-5-pyrazolone (**1a**) and diisopropylazodicarboxylate (**2a**) in CH_2Cl_2 at −20 °C (Table 1). The central metal ion was found to significantly affect the enantioselectivity of the reaction. As shown in Table 1, when changing the central metal from $La(OTf)_3$ to $Gd(OTf)_3$ in a gradually diminished order of the ionic radii, the enantioselectivity came to increase from 49% to 93% ee and the reactions completed within 36 h to give product **3a** with appropriate yields (Table 1, entries 1−7). In contrast, the enantioselectivity gradually decreased from 93% to 59% ee when the central metal was changed from $Gd(OTf)_3$ to $Lu(OTf)_3$ with the ionic radii continuing to decrease (Table 1, entries 7−14). The results of the influence of the metal cation suggested that Gd^{3+} has relative proper ionic radii to coordinate with the ligand

Table 1. Asymmetric α-Amination of 4-Benzyl-5-pyrazolone Catalyzed by *N,N′*-Dioxide−Metal Complexes[a]



Entry	Metal	Ligand	r_{ion} (Å)[b]	Yield (%)[c]	ee (%)[d]
1	$La(OTf)_3$	**L1**	1.032	98	49
2	$Ce(OTf)_3$	**L1**	1.010	94	76
3	$Pr(OTf)_3$	**L1**	0.990	90	77
4	$Nd(OTf)_3$	**L1**	0.983	94	82
5	$Sm(OTf)_3$	**L1**	0.958	95	91
6	$Eu(OTf)_3$	**L1**	0.947	90	92
7	$Gd(OTf)_3$	**L1**	0.938	95	93
8	$Tb(OTf)_3$	**L1**	0.923	90	92
9	$Dy(OTf)_3$	**L1**	0.912	88	89
10	$Ho(OTf)_3$	**L1**	0.901	97	89
11	$Er(OTf)_3$	**L1**	0.890	96	83
12	$Tm(OTf)_3$	**L1**	0.880	94	75
13	$Yb(OTf)_3$	**L1**	0.868	93	67
14	$Lu(OTf)_3$	**L1**	0.861	85	59
15	$Gd(OTf)_3$	**L2**	0.938	85	72
16	$Gd(OTf)_3$	**L3**	0.938	96	73
17	$Gd(OTf)_3$	**L4**	0.938	91	73
18	$Gd(OTf)_3$	**L5**	0.938	59	48
19[e,f]	$Gd(OTf)_3$	**L1**	0.938	99	96
20[e,g,h]	$Gd(OTf)_3$	**L1**	0.938	98	96
21[e,g,h,i]	$Gd(OTf)_3$	**L1**	0.938	99	95
22[e,g,h,j]	$Gd(OTf)_3$	**L1**	0.938	96	93

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.1 mmol) and **2a** (0.1 mmol) in CH_2Cl_2 (1.0 mL) with catalyst loading of 5 mol % (metal/ligand = 1:1) under nitrogen at −20 °C for 36 h. [b] r_{ion}: ionic radii (Å) of Ln^{3+}.[9b,10] [c] Yield of isolated product. [d] Determined by HPLC using chiral AD-H column. [e] 20 mg of 4 Å molecular sieves (MS) were added. [f] Reaction time: 2 h. [g] Reaction time: 4 h. [h] 1 mol % of catalyst loading was used. [i] Performed at 0 °C. [j] The reaction was carried out under an air atmosphere.

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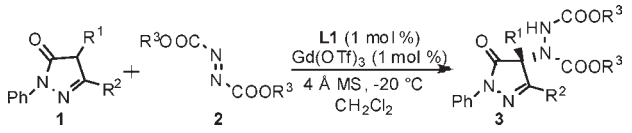
Table 2. α-Amination of 4-Substituted Pyrazolones **1** with Azodicarboxylates **2** Promoted by the Gadolinium Catalyst[a]



Entry	R^1	R^2	R^3	t (h)	Yield (%)[b]	ee (%)[c]
1	Bn	Me	*i*Pr	4	98 (**3a**)	96
2	Bn	Me	Et	1	99 (**3b**)	97[d]
3	Bn	Me	Bn	2	99 (**3c**)	94
4	2-MePhCH$_2$	Me	Et	2	98 (**3d**)	96
5	3-MePhCH$_2$	Me	Et	2	90 (**3e**)	96
6	4-MePhCH$_2$	Me	Et	2	96 (**3f**)	97
7	2-MeOPhCH$_2$	Me	Et	2	94 (**3g**)	96
8	3-MeOPhCH$_2$	Me	Et	2	97 (**3h**)	97
9	4-MeOPhCH$_2$	Me	Et	2	90 (**3i**)	96
10	2-ClPhCH$_2$	Me	Et	2	85 (**3j**)	93
11	3-ClPhCH$_2$	Me	Et	2	98 (**3k**)	94
12	4-ClPhCH$_2$	Me	Et	10	97 (**3l**)	95
13	4-BrPhCH$_2$	Me	Et	2	91 (**3m**)	93
14	2,4-Cl$_2$PhCH$_2$	Me	Et	2	99 (**3n**)	94
15	2-furanylmethyl	Me	Et	2	85 (**3o**)	94
16	2-thienylmethyl	Me	Et	2	98 (**3p**)	92
17	1-naphthylmethyl	Me	Et	2	97 (**3q**)	94
18	2-naphthylmethyl	Me	Et	2	98 (**3r**)	94
19[e]	Me	Ph	*i*Pr	12	92 (**3s**)	90
20[e]	Et	Me	*i*Pr	14	92 (**3t**)	93
21	*n*-propyl	Me	Et	2	94 (**3u**)	92
22	allyl	Me	Et	2	96 (**3v**)	93
23	−(CH$_2$)$_4$−		Et	10	98 (**3w**)	94

[a] Unless otherwise noted, all reactions were carried out with 5-pyrazolone **1** (0.1 mmol), azodicarboxylates **2** (0.1 mmol), and 4 Å MS (20 mg) in CH_2Cl_2 (1.0 mL) with a catalyst loading of 1 mol % **L1**/Gd(OTf)$_3$ (1:1) under nitrogen at −20 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis. [d] The absolute configuration of **3b** was determined by X-ray analysis (see Figure 1a). The other products were assigned by analogy. [e] The catalyst was **L4**/Ho(OTf)$_3$ and in the absence of 4 Å MS.

to form the active catalyst with a strong asymmetric inducing capability.

Further optimization of the reaction conditions was then aimed at the efficiency of Gd(OTf)$_3$ with other *N*, *N*′-dioxide ligands. The results showed that the steric and electronic effects of the amide moiety played a crucial role on the asymmetric induction of the α-amination reaction (Table 1, entries 15,16). Moreover, the chiral backbone of the *N*,*N*′-dioxide had also a significant impact on the enantioselectivity of the reaction. (*S*)-Pipecolic acid derivative *N*,*N*′-dioxide **L1** was superior to L-proline derived **L4** and L-ramipril acid derived **L5** (Table 1, entry 7 vs entries 17 and 18). Remarkably, when 4 Å molecular sieves (20 mg) were employed as an additive, the reaction rate was greatly improved with completed conversion within 2 h to give product **3a**, and the enantioselectivity slightly increased from 93% to 96% ee (Table 1, entry 19). The role of the 4 Å molecular sieves might be helpful for the promotion of the

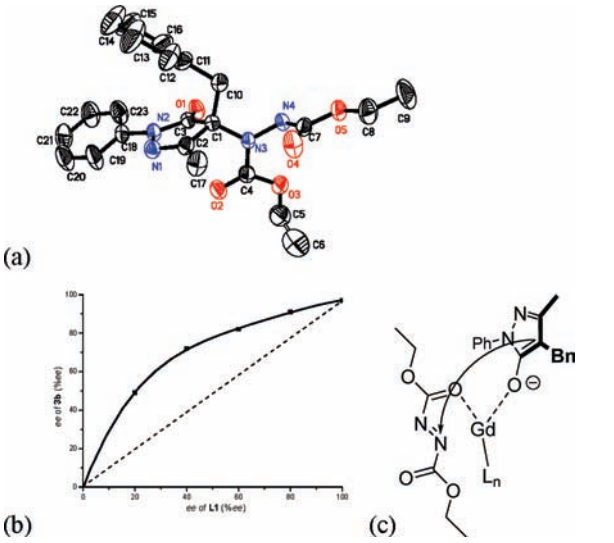


Figure 1. (a) X-ray structure of **3b** with Cu Kα radiation (H atoms omitted for clarity). (b) Nonlinear effect in the amination of **1a** with **2b** catalyzed by the **L1**−Gd(OTf)$_3$ complex. (c) Proposed transition-state model.

equilibrium for the formation of the enolate intermediate and to accelerate the reaction.[5h] Notably, reducing the catalyst loading to 1 mol % led to no loss of yield and enantioselectivity (Table 1, entry 20). Moreover, the enantioselectivity was slightly decreased when the reaction was carried out at 0 °C or under an air atmosphere.

After having established the optimal reaction conditions (Table 1, entry 20), we began to examine the scope of the α-amination reaction. First, the effect of the ester group of the azodicarboxylate was tested for the asymmetric α-amination of 4-benzyl-5-pyrazolone. The ester groups exhibited a slight effect on both the reactivity and enantioselectivity (Table 2, entries 1−3). Diethylazodicarboxylate (DEAD) was the best electrophile for this reaction, and the corresponding product **3b** was obtained in 99% yield with 97% ee after 1 h (Table 2, entry 2). Next, a wide variety of pyrazolones bearing different arylmethyl substituents were investigated for this chiral gadolinium(III) complex catalyzed α-amination reaction (Table 2, entries 4−23). In general, the reactions took place efficiently with excellent levels of enantioselectivity (90−97% ee) and good yields (85−99%). The absolute configuration of **3b** was determined by X- ray crystallography to be *R* (Figure 1a).

The catalytic synthesis of optically active chiral compounds with an extremely low catalyst loading is one of the most valuable advantages for the chemical industry. Although the asymmetric α-amination of the other carbolic nucleophiles with azodicarboxylates had been reported,[4,5] most of these transformations required at least 5 mol % of catalyst loading for sufficient formation of the product and maintenance of the enantioselectivity. The reaction reported herein could be performed without obvious influence upon the enantioselectivity and reactivity even with a catalyst loading of 0.05 mol %, albeit with a somewhat prolonged

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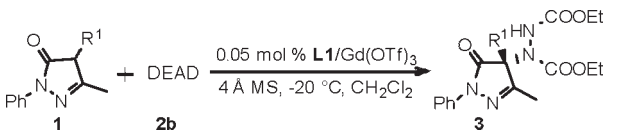
Table 3. α-Amination of 4-Substituted Pyrazolones **1** with Diethylazodicarboxylate **2b** Using 0.05 mol % Catalyst Loading[a]



Entry	R^1	t (h)	Yield (%)[b]	ee (%)[c]
1	Bn	5	96 (**3b**)	93
2	2-MePhCH$_2$	10	97 (**3d**)	96
3	4-MePhCH$_2$	10	95 (**3f**)	90
4	3-MeOPhCH$_2$	10	90 (**3h**)	93
5	2-ClPhCH$_2$	10	96 (**3j**)	93
6	3-ClPhCH$_2$	10	95 (**3k**)	94
7	2,4-Cl$_2$PhCH$_2$	10	94 (**3n**)	90
8	2-thienylmethyl	12	95 (**3p**)	92

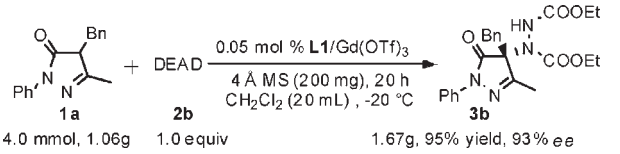
[a] Unless otherwise noted, all reactions were carried out with 5-pyrazolone **1** (0.1 mmol), diethylazodicarboxylate (DEAD) **2b** (0.1 mmol), and 4 Å MS (5 mg) in CH_2Cl_2 (1.0 mL) with 0.05 mol % **L1**/Gd(OTf)$_3$ (1:1) under nitrogen at −20 °C. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis.

reaction time (Table 3). And a relatively wide range of substrates can be tolerated, affording the desired products with 90−97% yield and 90−96% ee. It is noteworthy that this is a rare example of an asymmetric α-amination with azodicarboxylates with such a low amount of catalyst (0.05 mol %).

The low catalyst loading and the inexpensive starting materials and catalyst for this α-amination reaction offered a practical way to scale-up production. As shown in Scheme 1, the reaction proceeded smoothly and the desired addition product **3b** was obtained in 95% yield with 93% ee using only a 0.05 mol % *N,N′*-dioxide **L1**−gadolinium-(III) complex as the catalyst.

The relationship between the enantiomeric excess of the ligand **L1** and the product **3b** was investigated. A positive nonlinear effect was observed (Figure 1b), suggesting that the oligomeric aggregates of **L1**−Gd(OTf)$_3$ might exist in the reaction system. On the basis of the observed absolute configuration of enantiopure **3b** and previous reports of using *N,N′*-dioxide−metal complexes as catalysts,[7c,f] a plausible working model by concerted activation was proposed. As illustrated in Figure 1c, the carbonyl group

Scheme 1. Asymmetric α-Amination of 4-Substituted Pyrazolones **1a** on a Gram Scale



of the pyrazolone would coordinate to the active **L1**−Gd complex to form an enolate. The azodicarboxylate also can coordinate to the central metal ion through an ester carbonyl group. Subsequently, the *Re*-face attack of the electrophilic diethylazodicarboxylate of the enolate would afford the desired adduct **3b** with an *R*-configuration.

In summary, we have successfully presented the first highly stereoselective α-amination of 4-substituted pyrazolones with azodicarboxylates as the nitrogen fragment source. The reactions were catalyzed by an *N,N′*-dioxide gadolinium(III) complex to give the optically active 4-amino-5-pyrazolones in high yields (up to 99%) and excellent enantioselectivities (up to 97% ee). In particular, the procedure is capable of tolerating a relatively wide range of substrates, and excellent results (90%−96% ee) can also be obtained, even in the presence of 0.05 mol % of catalyst loading. Furthermore, excellent ee values and yields can also be obtained in gram-scale, which showed the potential value of the catalyst system. Current studies are underway to investigate the synthetic utility of the α-amination products.

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Supporting Information Available. Experimental procedures and spectral and analytical data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.