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Enantioselective Synthesis of Dihydropyrazoles by Formal [4+1] Cycloaddition of in Situ-Derived Azoalkenes and Sulfur Ylides

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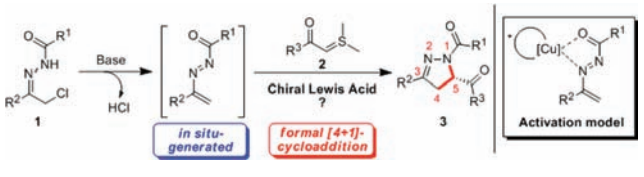
Supporting Information

ABSTRACT: An unprecedented strategy to access highly enantioenriched dihydropyrazoles is described. It involves formal [4+1] cycloadditions of in situ-derived azoalkenes and sulfur ylides catalyzed by a chiral copper/Tol-BINAP complex. A variety of synthetically and biologically important dihydropyrazoles have been obtained with high enantioselectivities (up to 97:3 er) in good yields (83−97%).

Dihydropyrazoles are important five-membered aza-heterocycles, which are present in a wide range of bioactive compounds with anti-depressant, anti-cancer, anti-inflammatory, anti-bacterial, and anti-viral activities.[1,2] Moreover, functionalized dihydropyrazoles are also of significance for the preparation of natural products and applications in asymmetric synthesis. As a result, these aza-heterocycles have become attracting synthetic targets for the development of new chemical reactions. In 2000, Kanemasa and Kanai reported the first enantioselective 1,3-dipolar cycloaddition reactions[3] of diazoalkanes with acrylamides using a magnesium complex as Lewis acid catalyst.[4] Since this pioneering work, catalytic asymmetric [3+2] cycloadditions of diazoalkanes,[5] azomethine imines,[6] nitrile imine dipole precursors,[7] and hydrazones[8] have been established as the most prominent strategies for the synthesis of optically active dihydropyrazole derivatives.[9] Recently, Müller and List reported an alternative method involving phosphoric acids-catalyzed asymmetric 6π electrocyclizations of α,β-unsaturated hydrazones to give dihydropyrazolines in high yields and enantioselectivities.[10a] Furthermore, Brière and co-workers described a powerful domino aza-Michael addition/cyclocondensation reaction for the enantioselective synthesis of 3,5-diaryldihydropyrazoles by phase-transfer catalysis.[10b] While these works stand out as pioneering efforts, wide applications of these methods are impeded by drawbacks such as unsatisfactory yields, poor chemo- and/or stereoselectivities, and limited substrate scope. Therefore, the development of more general strategies for the construction of enantioenriched dihydropyrazole derivatives with functional diversity is still highly desirable.

The formal [4+1] cycloaddition of 1,3-conjugated systems and two-electron, one-carbon synthons has been proven as an attractive but underexploited strategy for the construction of structurally diverse five-membered carbo- and heterocyclic systems.[11] In this context, ylides were identified as versatile 1,1′-dipolar synthons that reacted with a variety of electron-deficient conjugated components, affording multifunctionalized carbo-/heterocyclic motifs.[12] For example, Tang et al. reported formal [4+1] annulations between cinchonidine-derived ammonium salts and nitroolefins, leading to optically active isoxazoline *N*-oxides with excellent diastereo- and enantioselectivities,[12e] and Xiao and co-workers elegantly used an axial-to-central chirality transfer strategy to stereoselectively react stable sulfur ylides with ester-bearing unsaturated imines and nitroolefins.[13] For the current report it is also noteworthy that azoalkenes, which can be readily formed by two-electron oxidation of α-halo-*N*-sulfonyl hydrazones, are highly susceptible to conjugate addition to give the corresponding α-functionalized hydrazones.[14] In the light of all of those findings, we wondered about the possibility of formal asymmetric [4+1] cycloadditions of in situ-generated azoalkenes and sulfur ylides providing optically active dihydropyrazoles under chiral Lewis acid catalysis (Scheme 1). In this scenario, several challenges had to be

Scheme 1. Strategy for the Synthesis of Optically Active Dihydropyrazoles



encountered: (1) the conditions for the generation of the reactive azoalkene should not interfere with the following asymmetric cycloaddition; (2) the Lewis acids should preferentially coordinate with the azoalkene over the sulfur ylide; (3) possible background reactions could be detrimental to the enantioselectivity.[15] The methodological difficulties were mostly expressed by the lack of examples of catalytic asymmetric cycloadditions of sulfur ylides leading to five-membered carbo-/heterocyclic systems.[16] Herein, we report a

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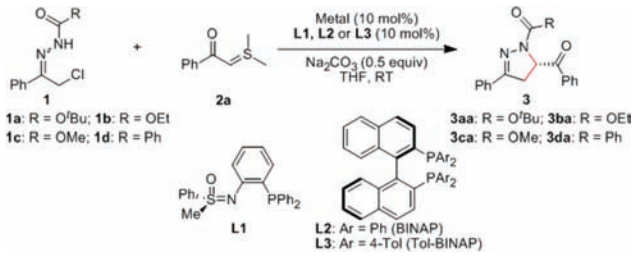
successful introduction of such a strategy using a chiral copper complex for catalytic asymmetric formal [4+1] cycloadditions, providing dihydropyrazoles with high enantioselectivities in good yields (Scheme 1).

Based on our previous work on sulfoximine chemistry,[17,18] we initiated the study by investigating the reaction between *N*-Boc hydrazone **1a** and sulfur ylide **2a** in the presence of the chiral complex formed in situ from sulfoximine **L1**[18] and copper(II) triflate. To our delight, the desired cycloaddition occurred, giving the corresponding product **3aa** in 80% yield, albeit the er was only 58:42 (Table 1, entry 1).[19] Subsequent

Table 1. Asymmetric Formal [4+1] Cycloaddition of in Situ-Derived Azoalkenes 1 with Sulfur Ylide 2a[a]



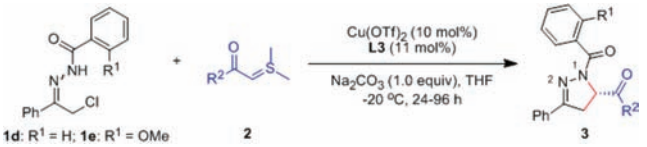
entry	1	metal salt	ligand	*t* (h)	yield (%)	er[b]
1	**1a**	$Cu(OTf)_2$	**L1**	1	80	58:42
2	**1a**	$Cu(OTf)_2$	**L2**	1	80	66:34
3	**1b**	$Cu(OTf)_2$	**L2**	1	85	55:45
4	**1c**	$Cu(OTf)_2$	**L2**	1	72	55:45
5	**1d**	$Cu(OTf)_2$	**L2**	2	90	73:27
6	**1d**	$Cu(OTf)_2$	**L3**	2	80	77:23
7[c]	**1d**	$Cu(OTf)_2$	**L3**	17	89	91:9
8[c,d]	**1d**	$Cu(OTf)_2$	**L3**	36	83	92:8

[a]Reaction conditions: **1** (0.3 mmol, 1.0 equiv), **2a** (0.45 mmol, 1.5 equiv), metal/ligand (10 mol %), Na_2CO_3 (0.5 equiv), THF (10 mL) under Ar. [b]Determined by HPLC using a chiral stationary phase. [c]Performed with 1.0 equiv of Na_2CO_3 and 11 mol % of the ligand at −20 °C. [d]As in footnote *c*, but performed at −30 °C instead of −20 °C.

ligand screening revealed that the use of BINAP increased the er to 66:34 (entry 2). With the goal to induce a more effective stereochemical control by promoting interactions between the azoalkene intermediate and the catalyst, the R substituent at the hydrazone acyl group was varied.[8] As hypothesized, the nature of this group had a significant impact on the enantioselectivity (Table 1, entries 3−5). Notably, the er of the product increased to 73:27 when benzoyl hydrazone **1d** was employed (entry 5). With this substrate, various other ligands were tested. Gratifyingly, the use of Tol-BINAP (**L3**) afforded the product with an er of 77:23 in 80% yield. Changing the metal salt as well as applying other bisphosphines, P,N-ligands, and sulfoximines gave inferior results (for details see Supporting Information). An improvement was possible by optimizing the reaction conditions, and finally [with 10 mol % of $Cu(OTf)_2$, 11 mol % of ligand **L3**, and 1.0 equiv of Na_2CO_3 at −30 °C], the product was obtained with an er of 92:8 in 83% yield (Table 1, entry 8). For the subsequent investigations a temperature of −20 °C was chosen, which allowed us to shorten the reaction time from 36 to 17 h without significantly affecting the er (91:9 for **3da**, entry 7).

Next, the substrate generality with respect to the sulfur ylides was investigated. The results are summarized in Table 2. With

Table 2. Scope of the Sulfur Ylides[a]



entry	1	R^2 (substrate **2**)	3	yield (%)	er[b]
1	**1d**	Ph (**2a**)	**3da**	89	91:9
2	**1d**	4-BrC_6H_4 (**2b**)	**3db**	89 (80)	91:9 (98:2)[c]
3	**1d**	4-ClC_6H_4 (**2c**)	**3dc**	85 (76)	90:10 (98:2)[c]
4	**1d**	3-$NO_2C_6H_4$ (**2d**)	**3dd**	92	92:8
5	**1d**	4-CNC_6H_4 (**2e**)	**3de**	87	92:8
6	**1d**	3-$MeOC_6H_4$ (**2f**)	**3df**	95	90:10
7	**1d**	2-naphthyl (**2g**)	**3dg**	81	90:10
8[d]	**1e**	Ph (**2a**)	**3ea**	84	97:3
9	**1e**	4-BrC_6H_4 (**2b**)	**3eb**	91	97:3
10	**1e**	4-ClC_6H_4 (**2c**)	**3ec**	93	96:4
11[e]	**1e**	3-$NO_2C_6H_4$ (**2d**)	**3ed**	84	92:8
12[e]	**1e**	4-CNC_6H_4 (**2e**)	**3ee**	88	94:6
13	**1e**	3-$MeOC_6H_4$ (**2f**)	**3ef**	95	92:8
14	**1e**	2-naphthyl (**2g**)	**3eg**	92	95:5
15	**1e**	4-FC_6H_4 (**2h**)	**3eh**	93	96:4
16[d]	**1e**	3,4-$Cl_2C_6H_3$ (**2i**)	**3ei**	94	92:8
17[d]	**1e**	4-MeC_6H_4 (**2j**)	**3ej**	92	95:5
18[d]	**1e**	2-furyl (**2k**)	**3ek**	85	93:7
19[d]	**1e**	2-thienoyl (**2l**)	**3el**	88	94:6

[a]Reaction conditions: **1d** or **1e** (0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), $Cu(OTf)_2$ (10 mol %), Tol-BINAP (11 mol %), Na_2CO_3 (1.0 equiv), and THF (10 mL) under Ar at −20 °C. [b]Determined by HPLC using a chiral stationary phase. [c]Values in parentheses are the results after single recrystallizations. [d]With 2.0 equiv of the sulfur ylide. [e]Performed at −15 °C.

N-benzoyl hydrazone **1d**, various electron-poor and -rich sulfur ylides with different substitution patterns on the aromatic ring reacted smoothly, giving the corresponding cyclized products in high yields (85−95%, entries 2−6). The best er ratio was 92:8 (entry 4 and 5). All products were solids, and the er values could be significantly increased (to 98:2) by a single recrystallization (entries 2 and 3). This initial screening also revealed that the presence of a 2-methoxybenzoyl group at N1 of the hydrazone (as in **1e**) substantially improved the enantioselectivity (entry 8 vs entry 1, er ratio of 97:3 vs 91:9). Accordingly, the investigation of the sulfur ylide scope was continued using hydrazone **1e** as substrate (entries 8−19). Also in this case, both electron-withdrawing and -donating groups at the *para*- and *meta*-positions of the phenyl ring were well tolerated. Compared to the previous results with **1d**, use of **1e** as substrate generally led to better enantioselectivities (with er values ranging from 92:8 to 97:3, entries 8−14). Moreover, heterocycle-derived ylides **2k** and **2l** readily participated in this transformation, giving rise to products **3ek** and **3el** with er values of 93:7 and 94:6, respectively (entries 18 and 19).

The relationship between the absolute configurations of the ligand and a product was unambiguously determined by X-ray crystal structure analysis of product (*S*)-**3db** (Figure 1) stemming from a copper catalysis with (*R*)-Tol-BINAP as ligand.[20]

The catalytic asymmetric formal [4+1] cycloaddition was then extended to other hydrazones. As shown in Table 3, an array of α-chloro- and α-bromo *N*-benzoyl hydrazones reacted well, and generally high yields and good enantioselectivities

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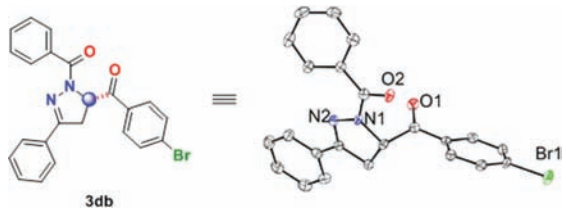
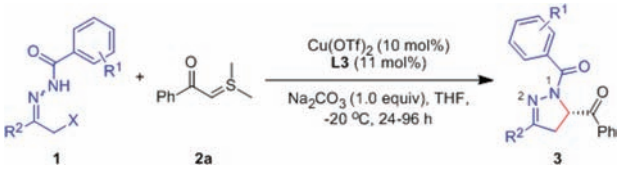


Figure 1. ORTEP diagram of the X-ray crystal structure of **3db**. Platon plot of **3db** (100 K) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Scope of the Hydrazones[a]



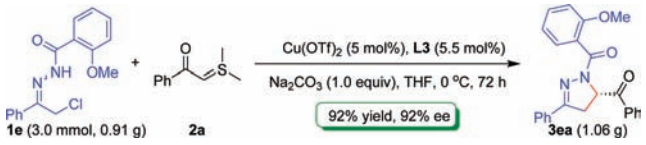
entry	X, R^1, R^2	1	3	yield (%)	er[b]
1	Cl, H, 4-ClC_6H_4	**1f**	**3fa**	94	91:9
2	Cl, H, 4-FC_6H_4	**1g**	**3ga**	97	90:10
3	Br, H, 4-MeC_6H_4	**1h**	**3ha**	95	90:10
4	Cl, 2-MeO, 2,4-$Cl_2C_6H_3$	**1i**	**3ia**	84	93:7
5	Cl, 2-MeO, 4-FC_6H_4	**1j**	**3ja**	92	94:6
6	Br, 2-MeO, 4-BrC_6H_4	**1k**	**3ka**	88	88:12
7	Cl, 2-MeO, 4-ClC_6H_4	**1l**	**3la**	96	88:12
8	Br, 2-MeO, 4-$MeOC_6H_4$	**1m**	**3ma**	86	92:8
9[c]	Cl, 3-OMe, Ph	**1n**	**3na**	83	92:8
10[c]	Cl, 4-OMe, Ph	**1o**	**3oa**	88	91:9
11[c]	Cl, 4-Me, Ph	**1p**	**3pa**	97	90:10
12[d]	Cl, 2-OMe, Me	**1q**	**3qa**	90	77:23
13[e]	Cl, 2-OMe, *t*-Bu	**1r**	**3ra**	93	79:21
14[f]	Br, 2-OMe, *i*-Bu	**1s**	**3sa**	84	87:13
15[f]	Cl, 2-OMe, $PhCH_2CH_2$	**1t**	**3ta**	93	87:13
16[f]	Br, 2-OMe, CO_2Et	**1u**	**3ua**	93	93:7
17[g]	Cl, 2-OMe, Ph-CH=CH	**1v**	**3va**	92	71:29

[a]Reaction conditions: **1** (0.3 mmol, 1.0 equiv), **2a** (0.45 mmol, 1.5 equiv), $Cu(OTf)_2$ (10 mol %), Tol-BINAP (11 mol %), Na_2CO_3 (1.0 equiv), and THF (10 mL) under Ar at −20 °C. [b]Determined by HPLC using a chiral stationary phase. [c]Performed with 2.0 equiv of **2a** at −15 °C. [d]Performed at 0 °C. [e]Performed with 3.0 equiv of **2a** at −10 °C. [f]Performed with 2.5 equiv of **2a** at −40 °C. [g]Performed with 2.5 equiv of **2a** at −30 °C.

were achieved. For example, in the case of hydrazones **1f**−**1h** bearing Cl, F, and Me in the *para*-position of aryl ring, the corresponding products were obtained in 94−97% yield with er values of up to 91:9 (entries 1−3). Also methoxybenzoyl hydrazones **1i**−**1m** with both electron-withdrawing and -donating groups on the phenyl ring reacted efficiently with sulfur ylide **2a** affording the corresponding products in up to 96% yield and er values of up to 94:6 (entries 4−8). Because it is known that the group at *N*1 can significantly affect the biological activities of dihydropyrazoles,[2] a few substrates with different substitution patterns at the *N*1 benzoyl group were applied. Gratifyingly, the reactions of hydrazones **1n**−**1p** having *meta*- or *para*-substituents at the phenyl ring proceeded smoothly, providing the products in high yields and with good enantioselectivities (entries 9−11). Notably, the reaction could also be realized for aliphatic hydrazones. For example, hydrazones **1q** and **1r**, derived from chloroacetone and 1-chloropinacolone, respectively, could be employed, although the er values of the products were only moderate (entries 12 and 13). The less bulky hydrazones **1s** and **1t** gave the corresponding products with er values of 87:13 in up to 93% yield (entries 14 and 15). Interestingly, in the case of ester-substituted hydrazone **1u**, the reaction worked very well, providing product **3ua** with 93:7 er in 93% yield (entry 16). Moreover, the alkenyl-substituted hydrazone **1v** proved to be suitable, and the corresponding product **3va** was isolated in good yield (entry 17).

To demonstrate the synthetic potential of the method, the reaction of hydrazone **1e** and sulfur ylide **2a** was carried out on a gram scale (Scheme 2). To our delight, the catalyst loading

Scheme 2. Gram Scale Experiment



could be reduced to 5 mol % of copper salt combined with 5.5 mol % of ligand, and the corresponding product (**3ea**) was isolated in 92% yield having an er of 96:4.

In summary, we have developed a copper-catalyzed asymmetric formal [4+1] cycloaddition of in situ-generated azoalkenes with sulfur ylides. It provides an efficient, enantioselective access to a variety of optically active dihydropyrazoles. To the best of our knowledge, the current transformation represents the first example of its kind. Further expansion of the reaction scope and mechanistic studies are underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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