JOC*Note*

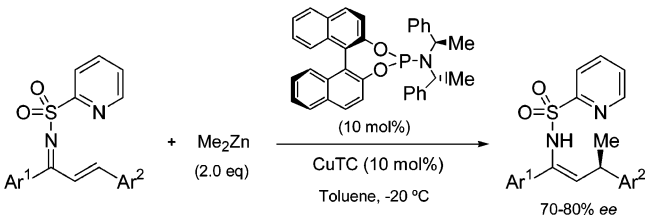
Copper-Catalyzed Enantioselective Conjugate Addition of Dialkylzinc Reagents to (2-Pyridyl)sulfonyl Imines of Chalcones

Jorge Esquivias, Ramon Gómez Arrayás, and Juan C. Carretero*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

juancarlos.carretero@uam.es

Received June 9, 2005



The enantioselective catalytic 1,4-addition to α,β-unsaturated ketimines is an unprecedented process. Herein, we document the copper-catalyzed addition of dialkylzinc reagents to (2-pyridylsulfonyl)imines of chalcones. This process occurs rapidly in the presence of a chiral phosphoramidite ligand to afford exclusively the 1,4-addition product. In the case of addition of dimethylzinc, enantioselectivities in the range 70−80% ee are obtained. The presence of the metal-coordinating 2-pyridylsulfonyl group proved to be essential for this reaction to proceed.

Because of the key importance of the Michael addition in organic synthesis, the development of asymmetric catalytic versions of this reaction has attracted a great deal of attention in the past decade. In particular, highly enantioselective protocols have been described for the conjugate addition of different types of nucleophiles to α,β-unsaturated carbonyl compounds, especially using copper-, rhodium-, and heterobimetallic-based catalysts.[1] In contrast to carbonyl substrates, the enantioselective conjugate addition to α,β-unsaturated imines has been scarcely studied, probably due to the much lower Michael acceptor character of these substrates. To the best of our knowledge, until 2004 the only precedent in this field was the Michael addition of organolithium reagents to α,β-unsaturated *N*-alkyl aldimines in the presence of an excess of a C_2-symmetric chiral diether as a source of asymmetric induction.[2] On the other hand, during the preparation of our manuscript, Tomioka et al. have reported a copper-catalyzed enantioselective conjugate addition of dialkylzinc reagents to β-aryl-α,β-unsaturated *N*-(2,4,6-triisopropylphenyl)sulfonyl aldimines.[3] In connection with our current interest in the use of appropriately functionalized *N*-sulfonyl compounds as versatile substrates in transition-metal-catalyzed reactions,[4] we describe herein the copper-catalyzed enantioselective Michael addition of dialkylzinc reagents to *N*-pyridylsulfonylimines of chalcones, which represents the first protocol of catalytic enantioselective 1,4-addition to α,β-unsaturated ketimines.[5] Taking into account the precedents on conjugate additions of dialkylzinc reagents to α,β-unsaturated ketones, we chose as a model reaction the addition of Me_2Zn to differently substituted *N*-sulfonylimines of chalcone. We envisaged that by combining the high electron-withdrawing character of the sulfonyl group with the use of an appropriate metal-coordinating functionality[6] close to the sulfonyl moiety, the reluctance of α,β-unsaturated ketimines to undergo metal-catalyzed conjugate addition processes could be overcome.

In this pursuit, substrates **1a**−**d** were readily prepared in satisfactory yields (68−86%) by $TiCl_4$-mediated condensation of chalcone with the corresponding sulfonamide in refluxing CH_2Cl_2[7] (Scheme 1). In all cases, the imine formation was completely stereoselective, affording exclusively the (*E*)-ketimine.[8]

Interestingly, while treatment of ketimines **1a**−**c** with Me_2Zn (2 equiv) in toluene at room temperature led to the recovery of unchanged starting material after 60 h, the *N*-(2-pyridyl)sulfonyl derivative **1d** underwent smooth

(1) For recent reviews on enantioselective conjugate addition, see: (a) Tomioka, K. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 2004; Supplement to Chapter 31.1, p 109. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (c) Feringa, B. L.; Naasz, R.; Imbos, R.; Arnold, L. A. In *Modern Organocopper Chemistry*; Krause N., Ed.; Wiley-VCH: Weinheim, 2002; p 224. (d) Alexakis, A.; Benhaim, C. *Eur. J. Org. Chem.* **2002**, 3221. (e) Krause, N.; Hoffmann-Röder, A. *Synthesis* **2001**, 171−196. (f) Sibi, M. P.; Manyem, S. *Tetrahedron* **2000**, *56*, 8033. (g) Feringa, B. L. *Acc. Chem. Res.* **2000**, *33*, 346. Tomioka, K. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2000; Chapter 12. For the Zn−Cu transmetalation and the reaction pathway of the Cu-catalyzed 1,4-addition of organozinc reagenst, see ref 1c.

(2) (a) Shindo, M.; Koga, K.; Tomioka, K. *J. Org. Chem.* **1998**, *63*, 9351. (b) Shindo, M.; Koga, K.; Tomioka, K *J. Am. Chem. Soc.* **1989**, *111*, 8266.

(3) Soeta, T.; Kuriyama, M.; Tomioka, K. *J. Org. Chem.* **2005**, *70*, 297.

(4) (a) Gómez Arrayás, R.; Cabrera, S.; Carretero, J. C. *Org. Lett.* **2005**, *2*, 219. (b) García Mancheño, O.; Gómez Arrayás, R.; Carretero, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 456.

(5) For enantioselective catalytic 1,2-additions to ketimines, see: (a) Jiang, B., Si, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 216. (b) Keith, J.; Jacobsen, E. N. *Org, Lett.* **2004**, *6*, 153. (c) Saaby, S.; Nakama, K.; Lie, M. A.; Hazell, R. G.; Jorgensen, K. A. *Chem. Eur. J.* **2003**, *9*, 6145. (d) Wipf, P.; Sthephenson, R. J. *Org. Lett.* **2003**, *14*, 2449. (e) Masumoto, S.; Usuada, H.; Suzuki, M.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 5634. (f) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536. (g) Byrne, J. J.; Pierre-Yves, M. C.; Vallée, Y. *Tetrahedron Lett.* **2000**, *41*, 873.

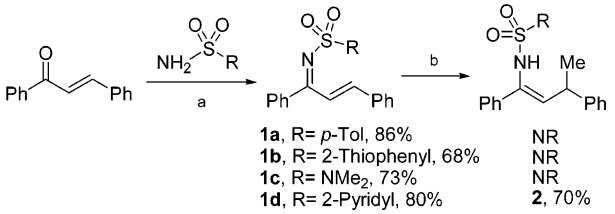
(6) For the concept of controlling stereoselectivity with the aid of a removable reagent-directing group, see: (a) Breit, B. *Chem. Eur. J.* **2000**, *6*, 1519. For recent examples, see: (b) Breit, B.; Breuninger, D. *Synthesis* **2005**, 147. (c) Willis, M. C.; McNally, S. J.; Beswick, P. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 340. (d) Park, Y. J.; Jo, E.-A.; Jun, C.-H. *Chem. Commun.* **2005**, 1185 and refs 9a−c therein.

(7) (a) Ram, R. N., Khan, A. A. *Synth. Commun.* **2001**, *31*, 841. (b) Sandrinelli, F.; Perrio S.; Belsin P. *J. Org. Chem.* **1997**, *62*, 8626. (c) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, *47*, 5561.

(8) The (*E*) stereochemistry of the C=C double bond was established on the basis of the observed coupling constant between the two olefinic protons ($J \approx 16$ Hz in all cases). On the other hand, it is known that the barrier to *E*/*Z* interconversion at the C=N bond is very low for *N*-sulfonylimines (see, for instance: Brown, C.; Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Perkin Trans. 2* **1978**, 822 and references therein).

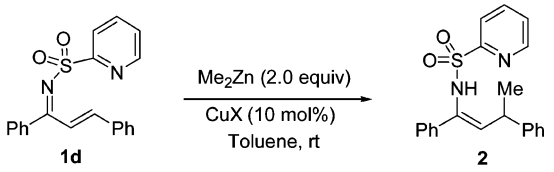
10.1021/jo0511602 CCC: $30.25
Published on Web 08/05/2005

SCHEME 1. Synthesis of *N*-Sulfonyl Ketimines 1 and Reaction with Me_2Zn[a]



[a] Key: (a) $TiCl_4$ (1.0 equiv), Et_3N (2.0 equiv), CH_2Cl_2, reflux, 5 h; (b) Me_2Zn (2.0 equiv), toluene, rt.

TABLE 1. Copper-Catalyzed Conjugate Addition of Me_2Zn to Ketimine 1d



entry	copper salt	time (min)	yield[a] (%)
1	CuCN	90	61
2	CuI	90	69
3	$Cu(OTf)_2$	75	68
4	$Cu(acac)_2$	75	68
5	CuTC	75	90
6	$Cu(CH_3CN)PF_6$	45	70

[a] Isolated product after chromatographic purification.

1,4-addition reaction affording exclusively the product **2** in 70% yield after 15 h, mainly as the (*Z*) stereoisomer at the C−C double bond[9,10] (*Z*/*E* ratio = 95:5). The outstanding reactivity of **1d** clearly suggests that the lone pair of the pyridyl nitrogen could coordinate the highly electrophilic Me_2Zn reagent, promoting the conjugate addition along a pseudo-intramolecular addition process.[11] As expected, this process was greatly accelerated by the presence of a catalytic amount of a Cu(I) or Cu(II) salt, the reaction being complete in 45−90 min at room temperature (Table 1). The highest yield was produced with CuTC[12] as catalyst (entry 5, 90% yield), whereas the fastest reaction was observed in the presence of $Cu(CH_3CN)_4PF_6$ (entry 6, 70% yield). At this point we confirmed the complete lack of reactivity of ketimines **1a**-**c** with Me_2Zn, even in the presence of CuTC (10 mol %) after 48 h at room temperature, highlighting the dramatic role exerted by the metal-coordinating 2-pyridyl unit in the course of the 1,4-addition.[13]

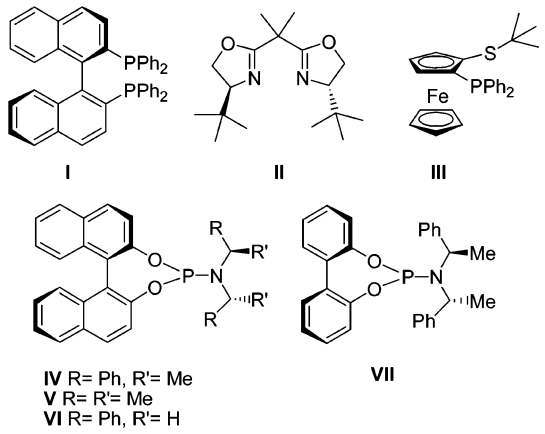


FIGURE 1. Tested chiral ligands.

With these optimal conditions in hand, we undertook the study of the effect of a chiral ligand on the enantioselectivity of the process. Owing to their high efficiency in other copper-catalyzed processes,[14] we selected as chiral ligands BINAP (P,P-ligand **I**), the bisoxazoline **II** (N,N-ligand) and the P,S-ligand **III** (Fesulphos) recently developed in our group,[15] as well as the monodentate Feringa ligand[16] **IV** (Figure 1). As depicted in Table 2, in all cases the presence of ligand produced a slight enhancement in the reaction rate (15−30 min to reach completion). However, the enantioselectivity of the process was extremely low in the case of the bidentate ligands **I**−**III** (entries 1−6). Only the phosphoramidite ligand **IV** afforded **2** with moderate enantioselectivity. The highest asymmetric induction with this ligand, 55% ee (entry 7), was accomplished by applying an inverse addition protocol: slow addition of **1d** to a solution of the complex CuTC−phosphoramidite and Me_2Zn. As the monodentate ligand **IV** proved to be the best ligand, other related chiral phosphoramidites were tested (**V**, **VI**, and **VII**,[17] entries 9−11). Disappointingly, in all cases, the resulting enantioselectivities were lower than those obtained with ligand **IV**.

As the reaction in the presence of the optimal ligand **IV** was fast enough at room temperature, we next studied the effect of the temperature in the enantioselectivity of

(9) The (*Z*) stereochemistry of *N*-sulfonylenamines was assigned by NMR on compound **14**. The observation of a strong NOE signal between the olefinic hydrogen and the ortho-protons on the phenyl group, coupled with the absence of NOE of the latter with the methyl group, was of particular diagnostic value.

(10) For other applications of the (2-pyridyl)sulfonyl group in transition-metal-catalyzed reactions, see: (a) Llamas, T.; Gómez Arrayás, R.; Carretero, J. C. *Adv. Synth. Catal*. **2004**, *346,* 1651. (b) Mauleón, P.; Carretero, J. C. *Org. Lett*. **2004**, *6*, 3195 and ref 4a. (c) Han, H.; Bae, I.; Yoo, E. J.; Lee, J.; Do, Y.; Chang, S. *Org. Lett*. **2004**, *6*, 4109.

(11) Interestingly, under the same reaction conditions, the addition of Me_2Zn to the 2-pyridylsulfonylimine of cinnamaldehyde occurred with complete 1,2-selectivity instead of 1,4-selectivity. For 1,2-addition processes to α,β-unsaturated aldimines, see: Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976.

(12) CuTC = copper thiophene-2-carboxylate: Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc*. **1996**, *118*, 2748.

(13) The same lack of reactivity for substrate **1a** was also observed in the presence of the chiral ligand **IV**.

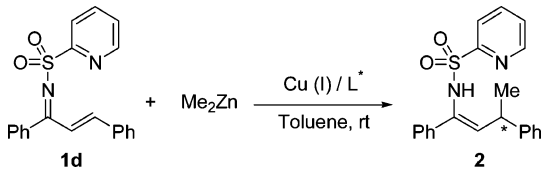
(14) For recent reviews on copper-catalyzed reactions, see: (a) *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, Germany, 2002. (b) Nakamura, E.; Mori, S. *Angew. Chem., Int. Ed*. **2000**, *39*, 3750.

(15) García Mancheño, O.; Priego, J.; Cabrera, S.; Gómez Arrayás, R.; Llamas, T.; Carretero, J. C. *J. Org. Chem.* **2003**, *68*, 3679.

(16) For a review on phosphoramidite ligands in asymmetric catalysis, see: (a) Feringa, B. L. *Acc. Chem. Res*. **2000**, *33*, 346. For recent references on conjugate additions using Cu-phosphoramidite, see: (b) Suárez, R. M.; Peña, D.; Minnaard, A. J.; Feringa, B. L. *Org. Biomol. Chem*. **2005**, *3*, 729. (c) d'Agustin, M.; Palais, L.; Alexakis, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1376. (d) Sebesta, R.; Pizzuti, M. G.; Boersma, A. J.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun*. **2005**, 1711. (e) Shi, M.; Wang, C.-J.; Zhang, C. *Chem. Eur. J*. **2004**, *10*, 5507. (f) Peña, D.; López, F.; Harutyunyan, S. R.; Minaard, A. J.; Feringa, B. L. *Chem. Commun*. **2004**, 1836. (g) Alexakis, A.; Polet, D.; Rosset, S.; March, S. *J. Org. Chem*. **2004**, *69*, 5660. (h) Pfretzschner, T.; Kleeman, L.; Janza, B.; Harms, K.; Schrader, T. *Chem. Eur. J*. **2005**, *10*, 6048. (i) Choi, H.; Hua, Z.; Ojima, I. *Org. Lett*. **2004**, *6*, 2689. (j) Schuppan, J.; Minaard, A. J.; Feringa, B. L. *Chem. Commun*. **2004**, 792. (k) Rimkus, A.; Sewald, N. *Synthesis* **2004**, 135.

(17) Alexakis, A.; Rosset, S.; Allamand, J.; March, S.; Guillen, F.; Benhaim, C. *Synlett* **2001**, 1375.

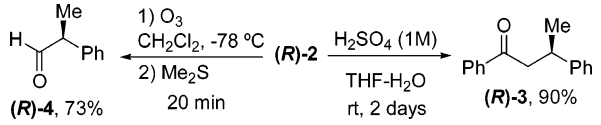
TABLE 2. Copper-Catalyzed Conjugate Addition of Me_2Zn to 1d in the Presence of Chiral Ligands[a]



entry	Cu(I)	L*	time (min)	yield[b] (%)	ee[c] (%)
1	CuTC	**I**	30	85	7
2	$Cu(CH_3CN)_4PF_6$	**I**	30	69	5
3	CuTC	**II**	15	86	5
4	$Cu(CH_3CN)_4PF_6$	**II**	15	72	5
5	CuTC	**III**	30	80	7
6	$Cu(CH_3CN)_4PF_6$	**III**	30	69	5
7	CuTC	**IV**	15	90	42 (55)[d]
8	$Cu(CH_3CN)_4PF_6$	**IV**	15	70	35
9	CuTC	**V**	15	85	37[d]
10	CuTC	**VI**	15	88	50[d]
11	CuTC	**VII**	15	83	26

[a] Reaction conditions: Me_2Zn (2.0 equiv), Cu(I) salt (10 mol %), L* (10 mol %), toluene, rt. [b] Pure product after chromatography. [c] Determined by HPLC. [d] Inverse addition.

SCHEME 2. Hydrolysis and Ozonolysis Reactions of (*R*)-2



the process. Gratifyingly, we observed a large increase on the asymmetric induction at lower temperatures, reaching 80% ee at −20 °C (2 h reaction time). The (*R*) configuration of the major enantiomer **2** was unequivocally established by its transformation into the known products (*R*)-**3** and (*R*)-**4** and comparison of their optical rotation values with those reported in the literature. Thus, smooth acid hydrolysis of (*R*)-**2** (H_2SO_4, THF−H_2O) led to the known ketone (*R*)-**3**,[18] while aldehyde (*R*)-**4**[19] was readily obtained by ozonolysis reaction of (*R*)-**2** (Scheme 2).

Once we optimized the *N*-sulfonyl ketimine (**1d**), the copper catalyst (CuTC), the chiral ligand (**IV**), the solvent[20] (toluene), and the temperature (−20 °C), we applied this new catalyst system to a series of *N*-(2-pyridylsulfonyl)imines derived from substituted chalcones (substrates **5**−**10**). These compounds were readily prepared in satisfactory yields (63−78%) by condensation of 2-pyridylsulfonamide with the corresponding chalcone as previously described for the synthesis of **1d** (Scheme 1).

As shown in Table 3, both the reactivity and the outcome of the process were very homogeneous, regardless of the electronic or steric nature of aryl groups Ar^1 and Ar^2. Chemical yields around 80−90% and enantioselectivities in the range of 70−80% ee were obtained for all conjugate addition products **11**−**16**. By chemical analogy with the reaction of the model substrate **1d**, we supposed for all these products the same (*R*) configuration at the stereogenic center. Additionally, this stereochemical assignment was confirmed in the case of the acid hydrolysis of **14** (H_2SO_4, THF−H_2O, 83%) to the corresponding known chalcone.[21]

Finally, we studied the reaction of Et_2Zn and Bu_2Zn with the model ketimine **1d** in the presence of CuTC/ligand **IV**. In both cases the reaction at room temperature led to the exclusive formation of the conjugate addition products **17** and **18**, respectively (Scheme 3), the process being much faster but significantly less enantioselective than the addition of Me_2Zn. This enhanced reactivity allowed the reaction to be carried out at lower temperature. For instance, the addition of Et_2Zn to **1d** at −78 °C reached completion within 1 h leading to **17** in 89% yield with 60% ee, while the reaction with Bu_2Zn required −40 °C as lowest temperature which afforded **18** in 87% yield and 40% ee after 30 min.

In summary, a catalyst system allowing enantioselective catalytic conjugate addition to α,β-unsaturated ketimines has been described. This protocol is based on the copper-catalyzed addition of dialkylzinc to 2-pyridylsulfonylimines of chalcones in the presence of a chiral ligand. The metal-coordinating (2-pyridyl)sulfonyl moiety at the iminic nitrogen in combination with the Feringa phosphoramidite ligand **IV** are key elements to achieve high chemical yields (80−90%) and enantioselectivities ranging 70−80% ee. The study of the reactivity of sulfonyl ketimines in other enantioselective reactions, as well as the development of synthetic applications, is underway.

Experimental Section[22]

Typical Procedure for the Synthesis of Sulfonylimines of Chalcones. Synthesis of (*E*)-1,3-Diphenyl-*N*-[(2-pyridyl)-sulfonyl]prop-2-en-1-imine (1d). To a solution of 2-pyridylsulfonamide (189.6 mg, 1.2 mmol) and chalcone (250 mg, 1.2 mmol) in CH_2Cl_2 (15 mL), cooled to 0 °C, were successively added Et_3N (336.6 μL, 2.4 mmol) and $TiCl_4$ (131.3 μL, 1.2 mmol). The reaction mixture was heated at reflux overnight. The solution was cooled to room temperature, quenched with water (100 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 2:1) to afford **1d** (334.1 mg, 80%) as a white solid. Mp = 118−119 °C. ^{1}H NMR: δ 8.76 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.91 (ddd, *J* = 7.8, 7.5 and 1.8 Hz, 1H), 7.69−7.40 (m, 12H), 7.10 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR: δ 179.5, 157.9, 149.9, 149.6, 138.3, 137.8, 134.3, 133.4, 131.9, 131.2, 130.0, 129.0, 128.7, 128.3, 126.7, 122.0. MS FAB$^+$ *m/z*: 349 (M^+, 100), 206 (22). EI EMAR for $C_{20}H_{17}N_2O_2S$ (M^+): calcd 349.1011, found 349.1002.

Typical Procedure for the Asymmetric Conjugate Addition of Me_2Zn to *N*-(2-Pyridyl)sulfonylketimines. Synthesis of (1*Z*,3*R*)-1,3-Diphenyl-*N*-[(2-pyridyl)sulfonyl]but-1-en-1-amine (2). A solution of CuTC (1.9 mg, 0.01 mmol) and (*R,S,S*)-**IV** (5.3 mg, 0.011 mmol) in dry toluene (0.5 mL) was stirred at room temperature for 40 min, and then a 2 M solution

(18) $[\alpha]^{20}_D$ = −11.6 (*c* 0.76 CCl_4) for a 80% ee sample of (*R*)-**3**. Literature value for a 93% ee sample of (*R*)-**3**: $[\alpha]^{20}_D$= −14.6, (*c* 1.02 CCl_4), Leitereg, T. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *15*, 4011.

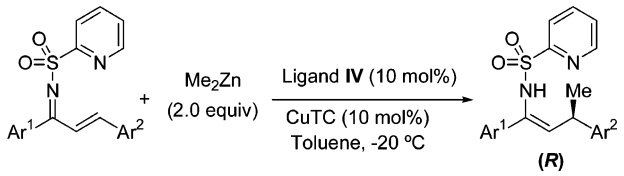
(19) $[\alpha]^{20}_D$= −115.0 (*c* 2 $CHCl_3$) for a 60% ee sample of (*R*)-**4**. Literature value for an optically pure sample of (*S*)-**4**: $[\alpha]^{20}_D$= +130.6, (*c* 10.0 $CHCl_3$), Abidi, S. L.; Wolfhagen, J. L. *J. Org. Chem*. **1979**, *44*, 433.

(20) In chlorinated solvents, such as CH_2Cl_2 and DCE, the reaction occurs with similar yield but lower enantioselectivity.

(21) $[\alpha]^{20}_D$= −10.07 (*c* 0.53 CCl_4) for a 76% ee sample of (*R*)-3-(4-methoxyphenyl)-1-phenylbutan-1-one. Literature value for a 99% ee sample of the (*S*) enantiomer: $[\alpha]^{20}_D$= +21.64, (*c* 9.3 CCl_4), Ollis, W. D.; Rey, M.; Sutherland, I. Q. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1009.

(22) For general remarks, see ref 15.

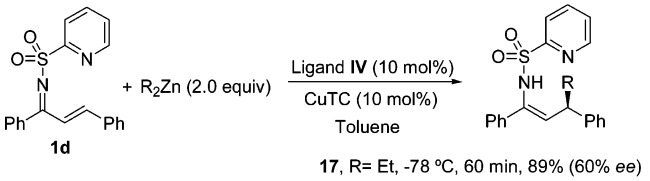
TABLE 3. Enantioselective Copper-Catalyzed Conjugate Addition of Me_2Zn to (2-Pyridylsulfonyl)imines of Substituted Chalcones



entry	imine	Ar^1	Ar^2	time (h)	product	*Z*/*E*[a]	yield[b] (%)	ee[c] (%)
1	**1d**	Ph	Ph	2	**2**	95:5	90	80
2	**5**	*p*-$OMeC_6H_4$	Ph	3	**11**	96:4	88	77
3	**6**	*p*-ClC_6H_4	Ph	4	**12**	95:5	91	70
4	**7**	2-Naph	Ph	2.5	**13**	>98:<2	90	71
5	**8**	Ph	*p*-$OMeC_6H_4$	6	**14**	>98:<2	72[d]	76
6	**9**	Ph	*p*-FC_6H_4	2	**15**	97:3	89	77
7	**10**	Ph	2-Naph	2.5	**16**	83:17	86	74

[a] Determined by ^1H NMR analysis of the crude reaction mixture. [b] Pure product after chromatographic purification. [c] Determined by HPLC. [d] 15% of the starting material was recovered.

SCHEME 3. Enantioselective Copper-Catalyzed Conjugate Addition of Et_2Zn and Bu_2Zn to 1d



of Me_2Zn in toluene (100 μL, 0.2 mmol) was added. The resulting solution was cooled to −20 °C before a solution of ketimine **1d** (34.8 mg, 0.1 mmol) in toluene (0.5 mL) was added. The reaction was followed by TLC analysis until completion, quenched with saturated aqueous NH_4Cl, and extracted several times with CH_2Cl_2. The combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 2:1) to afford **2** (32.7 mg, 90%) as a white solid. Mp = 45−47 °C. ^1H NMR: δ 8.62 (d, J = 5.0 Hz, 1H), 7.67−7.64 (m, 2H), 7.36−7.12 (m, 12H), 5.78 (d, J = 9.7 Hz, 1H), 3.93 (dq, J = 9.7 and 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 3H). ^{13}C NMR: δ 157.2, 149.8, 144.7, 137.5, 132.7, 132.0, 128.7, 128.6, 128.0, 127.9, 127.0, 126.9, 126.6, 126.4, 122.7, 37.3, 22.2. IR (NaCl): ν (cm^{-1}) 3351 (NH), 1580 (C=C), 1256 (S=O). $[\alpha]^{20}_D$ = −21 (c = 0.57, $CHCl_3$). Enantiomeric excess: 80% ee. HPLC (Chiralcel OD column) 0.7 mL/min (*n*-hexane−2-propanol, 91/9): t_R 20.5 (*S*), t_R 24.1 (*R*). MS EI^+ *m*/*z*: 349 (M^+ − Me, 3), 259 (8), 222 (M^+ − SO_2(2-Py), 100), 195 (19), 149 (31), 104 (45), 78 (37).

Acknowledgment. Financial support of this work by the Ministerio de Educación y Ciencia (project BQU2003-0508) and *Consejería de Educación de la Comunidad de Madrid* (project GR/MAT/0016/2004) is gratefully acknowledged. R.G.A. and J.E. also thank the Ministerio de Educación y Ciencia for a Ramón y Cajal contract and a predoctoral fellowship, respectively.

Supporting Information Available: Characterization data for the rest of the chalcone-type sulfonyl ketimines (**1a**−**c** and **5**−**10**) and their addition products (**11**−**18**) and copies of ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0511602