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Asymmetric Friedel−Crafts Alkylations of Indoles with Nitroalkenes Catalyzed by Zn(II)−Bisoxazoline Complexes

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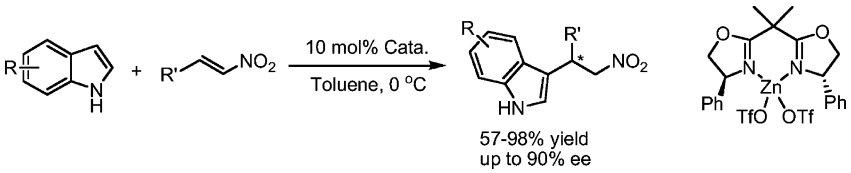

A novel asymmetric Friedel−Crafts alkylation of indoles with nitroalkenes catalyzed by Zn(II)−bisoxazoline complexes has been developed. The nitroalkylated indoles are synthesized in excellent yields and high enantioselectivities (up to 90% ee). The effects of ligand structure, metal salt, and solvent on the reaction are discussed. The substrates of the reaction can be aromatic, heteroaromatic, and even aliphatic nitroalkenes. The high reactivity and selectivity of the reaction are presumptively attributed to the activation and asymmetric induction of chiral Lewis acids coordinated by nitroalkene substrates through a 1,3-metal bonding model.

Introduction

The Friedel−Crafts (F−C) alkylation reaction of arenes with electron-deficient alkenes is one of the most important organic transformations to employ Lewis acid catalysts, and it is a particularly versatile carbon−carbon bond-forming reaction.[1] While an asymmetric version of this reaction can provide access to the important enantiomerically enriched alkylated arene products, to date the successful examples of such processes are limited because of the significant restrictions in the substrates.[2] It is a well-known strategy to use a bidentate chelating substrate to ensure high enantioselectivity in the Lewis acid catalyzed F−C reaction.[3] The suitable substrates, which gave good to excellent enantioselectivities in the F−C alkylation reaction, include β,γ-unsaturated α-ketoesters,[4] alkylidene malonates,[5] acyl phosphonates,[6] α-hydroxy enones,[7] 2-acyl imidazoles,[8] and other acylheterocycle compounds.[9] These substrates are supposed to form 1,4- or 1,5-chelating complexes with metal Lewis acids in the reaction with arene compounds (Figure 1, **A** and **B**). To explore new types of substrates and increase the pool of available templates for catalytic asymmetric Friedel−Crafts reactions, we herein report our efforts in the enantioselective chiral Lewis acid catalyzed F−C reaction with nitroalkenes, which are assumed to form a 1,3-metal bonding species with metal of chiral Lewis acid (Figure 1, **C**).[10]

Nitroalkenes are very attractive Michael acceptors because the nitro group is the strongest electron-withdrawing group known[11] and have been widely used in organic synthesis.[12]

(1) Olah, G. A.; Khrisnamurti, R.; Prakash, G. K. S. In *Comprehensive Organic Synthesis*, 1st ed.; Pergamon: New York, 1991; Vol. 3, pp 293−339.

(2) For reviews, see: (a) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 550. (b) Jørgensen, K. A. *Synthesis* **2003**, 1117.

(3) For asymmetric F−C reaction using nonchelating substrates, see: Bandini, M.; Fagioli, P.; Garavelli, M.; Melloni, A.; Trigari, V.; Umani-Ronchi, A. *J. Org. Chem.* **2004**, *69*, 7511.

(4) Jensen, K. B.; Thorhauge, J.; Mazell, R.-G.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 160.

(5) (a) Zhuang, W.; Hausen, T.; Jørgensen, K. A. *Chem. Commun.* **2001**, 347. (b) Zhou, J.; Tang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 9030. (c) Zhou, J.; Tang, Y. *Chem. Commun.* **2004**, 432. (d) Zhou, J.; Ye, M.-C.; Huang, Z.-Z.; Tang, Y. *J. Org. Chem.* **2004**, *69*, 1309.

(6) Evans, D. A.; Scheidt, K. A.; Frandrick, K. R.; Lam, H. W.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10780.

(7) Palomo, C.; Oiarbide, M.; Kardak, B. G.; Garcia, J. M.; Linden, A. *J. Am. Chem. Soc.* **2005**, *127*, 4154.

(8) Evans, D. A.; Fandrick, K. R.; Song, H. J. *J. Am. Chem. Soc.* **2005**, *127*, 8942.

(9) Bandini, M.; Melloni, A.; Tommasi, S.; Umani-Ronchi, A. *Helv. Chim. Acta* **2003**, *86*, 3753.

(10) For other example of four-membered chelating intermediates of nitroalkenes with Lewis acid, see: Wada, E.; Yoshinaga, M. *Tetrahedron Lett.* **2003**, *44*, 7953.

(11) (a) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: New York, 2001. (b) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1. (c) Calderari, G.; Seebach, D. *Helv. Chim. Acta* **1995**, *68*, 1592.

(12) See review: Berner, O. M.; Tedeschi, L.; Enders, D. *Eur. J. Org. Chem.* **2002**, 1877.

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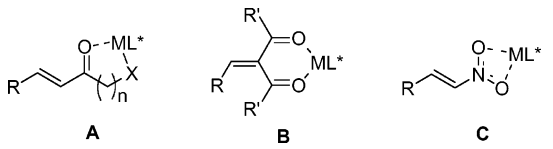


FIGURE 1. Binding models of substrate to catalyst in asymmetric F−C reaction.

Recently, many examples regarding the application of nitroalkenes as Michael acceptors in asymmetric catalytic reactions were reported, such as copper-catalyzed dialkylzinc addition to nitroalkenes,[13] rhodium-catalyzed addition of boronic acids to nitroalkenes,[14] the metal- and organo-catalyzed addition of 1,3-dicarbonyl compounds to nitroalkenes,[15] and conjugated reduction of nitroalkenes.[16] Although the nonasymmetric Friedel−Crafts alkylation reaction of arenes with nitroalkenes was realized by using Lewis acid catalysts,[17] the asymmetric version of this reaction using a chiral Lewis acid catalyst has not been documented.[18] Assuming that nitroakenes form a 1,3-metal binding template with catalysts, we expect that the F−C reaction of nitroalkene catalyzed by a chiral metal Lewis acid can be performed in high enantioselectivity.

Results and Discussion

Selection of Lewis Acids. Indole (**1a**), as an electron-rich heteroaromatic substrate, was chosen to react with *trans*-*β*-nitrostyrene (**2a**) for optimizing reaction conditions. A variety of chiral Lewis acid catalysts generated in situ from metal salts and the ligand 2,2-bis[2-[(*S*)-4-phenyl-4,5-dihydrooxazolyl]]-propane ((*S*)-Ph-bisoxazoline) (**L1**) were evaluated as shown in the illustrated reaction (Scheme 1), and the results are summarized in Table 1. In the absence of catalyst (Table 1, entry 1) or adding 10 mol % of $Fe(ClO_4)_2 \cdot xH_2O$ and 12 mol % of ligand **L1** (entry 2), the reaction did not occur at 15 °C. When CuOTf, $Mg(OTf)_2$, AgOTf, or $Pd(OAc)_2$ was employed as a Lewis acid, the reaction took place slowly, and the enantiomeric excess of the product was zero or negligible, while in the presence of $Cu(OTf)_2$, $Ni(OTf)_2$, or $Zn(OTf)_2$ indole reacted with *trans*-*β*-nitrostyrene smoothly, giving the product 3-(2-nitro-1-phenylethyl)-1*H*-indole (**3aa**) in good yields with high enantioselectivities. In particular, the complex $Zn(OTf)_2$/(*S*)-Ph-bisoxazoline was found to be the best choice of catalyst which gave fast reaction (within 11 h) and excellent yield (97%) (entry 9).

Ligand Effect. With $Zn(OTf)_2$ as Lewis acid different chiral bisoxazoline ligands were subsequently investigated in the reaction. We focused our efforts on the oxazoline-containing ligands displayed in Figure 2 because the typical phosphorus ligands were normally inefficient in this reaction.[19] The bisoxazoline ligands **L1**, **L2**, **L3**, and **L4,** which contain different substituted groups on the oxazoline ring, were first compared, and (*S*)-Ph-bisoxazoline (**L1**) was found to be the best ligand to provide the highest yield and enantioselectivity (Table 2, entries 1−4). Apparently, the phenyl groups on the oxazoline ring are critical for obtaining high enantioselectivity. We accordingly prepared another two bisoxazoline ligands **L5** and **L6** containing phenyl groups. However, both of them gave lower enantioselectivity (27 and 50% ee, respectively) compared to ligand **L1**. Ligand **L7**, which forms a seven-membered chelating ring with zinc ion, also showed lower enantioselectivity (43% ee). Using C_1-symmetric quinoline−oxazoline ligand **L8**[20] led a low reaction rate and low enantioselectivity (entry 8). Finally, the tridentate pyridine−oxazoline ligand **L9** was tested and found to be completely inactive.

Solvent Effect. Solvent screening showed that toluene is a good solvent to provide F−C alkylation product in excellent yield with high enantiomeric excess. For example, in toluene, the $Zn(OTf)_2$/(*S*)-Ph-bisoxazoline catalyzed reaction of indole (**1a**) with *trans*-*β*-nitrostyrene (**2a**) at room temperature produced 3-(2-nitro-1-phenylethyl)-1*H*-indole (**3aa**) in 93% yield with 74% ee (Table 3, entry 1). The enantioselectivity was improved to 84% ee when the reaction was performed at 0 °C (entry 3). However, when the reaction temperature was further lowered to −20 °C, the reaction became very slow and the enantioselectivity was decreased to 62% ee (entry 5). The additives often change the reactivity and enantioselectivity in chiral Lewis acid catalyzed reactions.[3,5d] In this reaction, addition of 10 mol % of NEt_3 dramatically depressed the reaction rate (13% yield was obtained after 60 h). In contrast, addition of 2 equiv of HFIP (1,1,1,3,3,3-hexafluoropropan-2-ol) accelerated the reaction, however, the enantioselectivity was decreased to 71% ee (entry 7). Besides toluene, ether is another solvent in which the reaction proceeded smoothly, and the F−C alkylation product was obtained in a comparable yield and ee (84% yield, 70% ee).

The counterion of catalyst sometimes plays a significant role in both activity and enantioselectivity of catalyst in asymmetric catalysis.[21] In the zinc-catalyzed F−C alkylation of indole with nitroalkene, we found that in addition to $Zn(OTf)_2$ other zinc salts such as $Zn(ClO_4)_2$, $Zn(BF_4)_2$, $Zn(SbF_6)_2$, and $Zn(PF_6)_2$ can also be used as Lewis acids to produce alkylated indole products

(13) (a) Schäfer, H.; Seebach, D. *Tetrahedron* **1995**, *51*, 2305. (b) Alexakis, A.; Benhaim, C. *Org. Lett.* **2000**, *2*, 2579. (c) Duursma, A.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 3700. (d) Sewald, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5794. (e) Choi, H.; Hua, Z.; Ojima, I. *Org. Lett.* **2004**, *6*, 2689. (f) Mampreian, D. M.; Hoveyda, A. H. *Org. Lett.* **2004**, *6*, 2829.

(14) Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716.

(15) (a) Ji, J.-G.; Barnes, D. M.; Zhang, J.; King, S. A.; Wittenberger, S. J.; Morton, H. E. *J. Am. Chem. Soc.* **1999**, *121*, 10215. (b) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672. (c) Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2004**, *126*, 11148. (d) Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906.

(16) (a) Czekelius, C.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4793.

(17) (a) Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F. *Chem. Commun.* **2005**, *6*, 789. (b) Bartoli, G.; Bosco, M.; Giuli, S.; Giuliani, A.; Lucarelli, L.; Marcantoni, E.; Sambri, L.; Torregiani, E. *J. Org. Chem.* **2005**, *70*, 1941. (c) Alam, M. M.; Varala, R.; Adapa, S. R. *Tetrahedron Lett.* **2003**, *44*, 5115. (d) Bandini, M.; Melchiorre, P.; Melloni, A.; Umani-Ronchi, A. *Synthesis* **2002**, 1110. (e) Yadav, J. S.; Abraham, S.; Reddy, B. V. S.; Sabitha, G. *Synthesis* **2001**, 2165. (f) Komoto, I.; Kobayashi, S. *J. Org. Chem.* **2004**, *69*, 680. (g) Harrington, P. E.; Kerr, M. A. *Synlett* **1996**, 1047.

(18) During the revision of this manuscript Jørgensen and Ricci reported respectively enantioselective Friedel−Crafts-type addition of indoles to nitroalkenes using chiral oranocatalyst and achieved up to 64% and 89% ee. See: (a) Zhuang, W.; Hazell, R. G.; Jørgensen, K. A. *Org. Bio. Chem.* **2005**, *3*, 2566. (b) Herrera, R. P.; Sgarzani, V.; Berbardi, L.; Ricci, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6576.

(19) The monophosphoramidite ligand SIPHOS (see: Hu, A.-G.; Fu, Y.; Xie, J.-H.; Zhou, H.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2002**, *41*, 2348), diphosphine ligand BINAP, and P−N ligand PHOX were also investigated in the combination with $Cu(OTf)_2$, and the F−C alkylation product was obtained in very low enantioselectivity (<5% ee).

(20) Wu, X.-Y.; Li, X.-H.; and Zhou, Q.-L. *Tetrahedron: Asymmetry* **1998**, *9*, 4143.

(21) (a) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 798. (b) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325.

SCHEME 1. Asymmetric Catalytic Friedel−Crafts Alkylation of Indole with *trans*-β-Nitrostyrene

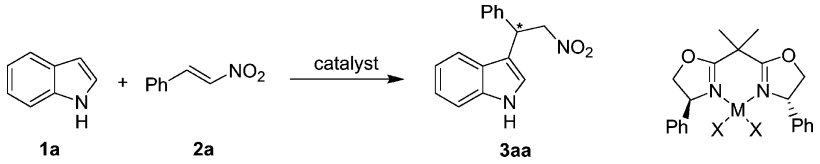


TABLE 1. Asymmetric Friedel−Crafts Alkylation of Indole with *trans*-β-Nitrostyrene Catalyzed by Chiral MXn/(*S*)-Ph-bisoxazoline[a]

entry	MXn	time (h)	yield[b] (%)	ee[c] (%)
1[d]		60		
2[d]	$Fe(ClO_4)_2 \cdot xH_2O$	60		
3[e]	CuOTf	60	49	10
4[e]	$Mg(OTf)_2$	60	34	0
5[e]	AgOTf	60	13	9
6[e]	$Pd(OAc)_2$	60	43	0
7	$Cu(OTf)_2$	60	67	80
8	$Ni(OTf)_2$	20	75	81
9	$Zn(OTf)_2$	11	97	79

[a] The reaction was performed at 15 °C using 0.1 equiv of Lewis acid, 0.12 equiv of (*S*)-Ph-bisoxazoline, 1 equiv of indole, and 2 equiv of *trans*-β-nitrostyrene in toluene under N_2 atmosphere. [b] Isolated yield. [c] Determined by chiral HPLC. The absolute configuration is *S*, ref 18a. [d] No reaction. [e] The starting material was not completely converted.

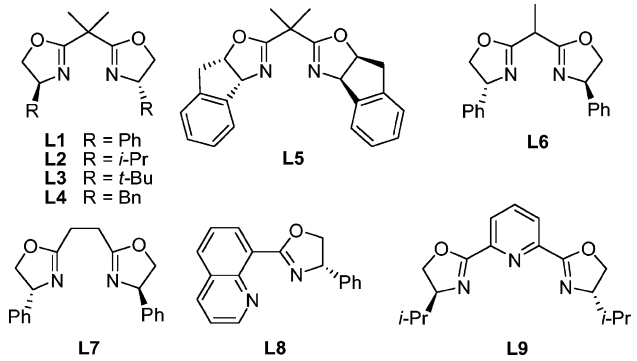


FIGURE 2. Ligands used in the Friedel−Crafts alkylation reaction.

TABLE 2. Effect of Ligand in the $Zn(OTf)_2$-Catalyzed Friedel−Crafts Alkylation Reaction of Indole with *trans*-β-Nitrostyrene[a]

entry	ligand	time (h)	yield (%)	ee (%)
1	L1	11	97	79
2	L2	13	75	15
3[b]	L3	13	53	15
4	L4	13	92	16
5	L5	15	97	−27
6	L6	13	84	−50
7	L7	13	92	−43
8	L8	20	90	9
9[c]	L9	20		

[a] For other reaction conditions, see Table 1. [b] The starting material was not completely converted. [c] No reaction.

in high yields. However, the enantioselectivities of the reaction were sharply reduced to 29−68% ee by using these zinc salts.

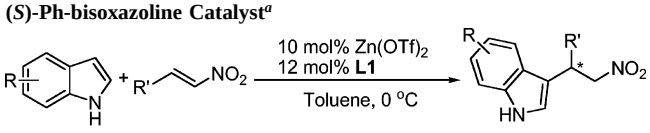
Scope of Substrate. Under the optimal reaction conditions, a variety of nitroalkenes and indoles were investigated, and the results are summarized in Table 4. Most nitroolefins reacted well with indole and its derivatives to produce alkylated indoles in excellent yields and high enantioselectivities. The reactions of nitrostyrenes containing electron-donating groups in the phenyl group had a slightly lower reaction rate than the reaction of nitrostyrenes containing an electron-withdrawing group

TABLE 3. Solvent Effect in the Friedel−Crafts Reaction of Indole with *trans*-β-Nitrostyrene[a]

entry	solvent	*T* (°C)	time (h)	yield (%)	ee (%)
1	toluene	25	5	93	74
2	toluene	15	11	97	79
3	toluene	0	15	97	84
4	toluene	−10	36	88	83
5	toluene	−20	36	31	62
6	toluene + Et_3N (10 mol %)	0	60	13	64
7	toluene + HFIP (2 equiv)	0	3	95	71
8	ether	15	11	84	70
9	CH_2Cl_2	15	11	84	14
10	THF	15	11	88	4

[a] The reaction was performed under N_2 atmosphere, $Zn(OTf)_2$/**L1**/**1a**/**2a** = 0.1/0.12/1/2 (mmol) unless otherwise mentioned. For other reaction conditions and analyses, see Table 1.

TABLE 4. Asymmetric Friedel−Crafts Alkylation Reaction of Indole Derivatives with Nitroalkenes Using $Zn(OTf)_2$/(*S*)-Ph-bisoxazoline Catalyst[a]

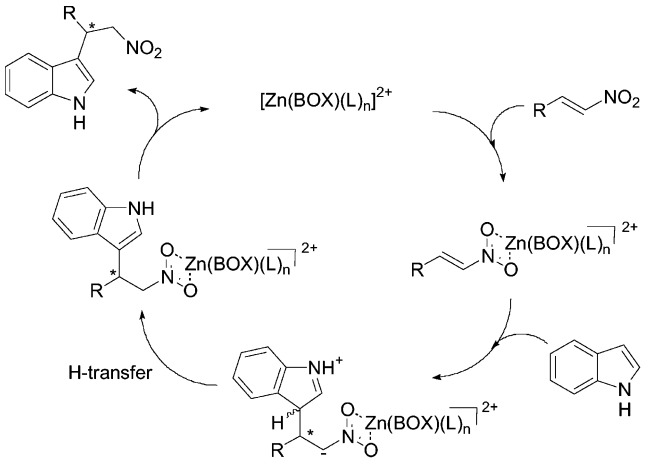


entry	R	R′	product	yield[b] (%)	ee[c] (%)
1	H (**1a**)	Ph (**2a**)	**3aa**	97	84 (*S*)
2	H (**1a**)	4-Me-Ph (**2b**)	**3ab**	98	81
3	H (**1a**)	4-MeO-Ph (**2c**)	**3ac**	91	81
4	H (**1a**)	3-MeO-Ph (**2d**)	**3ad**	79	83
5	H (**1a**)	2-MeO-Ph (**2e**)	**3ae**	87	61
6	H (**1a**)	4-F-Ph (**2f**)	**3af**	96	83
7	H (**1a**)	4-Cl-Ph (**2g**)	**3ag**	98	82
8	H (**1a**)	2-Cl-Ph (**2h**)	**3ah**	97	72
9	H (**1a**)	4-Br-Ph (**2i**)	**3ai**	98	90
10	H (**1a**)	3-Br-Ph (**2j**)	**3aj**	98	86
11	H (**1a**)	4-NO_2-Ph (**2k**)	**3ak**	98	80
12	H (**1a**)	2,4-Cl_2-Ph (**2l**)	**3al**	90	70
13	H (**1a**)	1-Np (**2m**)	**3am**	98	78
14	H (**1a**)	2-thienyl (**2n**)	**3an**	95	82
15	H (**1a**)	2-furyl (**2o**)	**3ao**	98	78
16	H (**1a**)	*n*-propyl (**2p**)	**3ap**	57	70
17	1-Me (**1b**)	Ph (**2a**)	**3ba**	62	31 (*S*)[d]
18	2-Me (**1c**)	Ph (**2a**)	**3ca**	87	21
19	5-MeO (**1d**)	Ph (**2a**)	**3da**	94	79
20	5-Br (**1e**)	Ph (**2a**)	**3ea**	98	80

[a] Reaction was performed at 0 °C for 20 h using 1 equiv of indoles and 2 equiv of nitroalkenes in toluene under N_2. [b] Isolated yield. [c] Determined by HPLC. [d] Determined to be *S* by comparison of optical rotation with that in ref 18b.

(entries 2−5 vs entries 6−12). The ortho-substitution on the phenyl in nitrostyrene, either with electron-donating groups or electron-withdrawing groups, exclusively lowered the reaction rate and the enantiomeric excesses of F−C alkylation products, implying the existence of steric hindrance of ortho-substituents to the reactivity and the enantioselectivity of reaction (entries 5, 8, and 12). In addition to nitrostyrene derivatives, the 1-((*E*)-2-nitrovinyl)naphthalene (**2m**) and heteroaromatic nitroalkenes **2n** and **2o** can also serve as substrates in this reaction, giving

SCHEME 2. Proposed Catalytic Cycle for the Alkylation of Indole with Nitroalkene



the corresponding alkylated indoles in excellent yields and high enantioselectivities (entries 13−15). It was delightful to find that this reaction could be extended to aliphatic nitroalkene, although a longer reaction time was needed. When 1-nitropentene (**2p**) reacted with indole at 0 °C for 72 h, the F−C alkylation product 3-(1-nitromethyl-butyl)-1*H*-indole (**3ap**) was isolated in 57% yield with 70% ee.

The substituent effect on the indole ring was also studied. When a 1-Me or 2-Me was introduced into indole ring the enantioselectivity was dramatically lowered from 84% ee to 31% ee or 21% ee (entries 17 and 18). On the other hand, neither electron-donating group OCH_3 nor electron-withdrawing group Br at the 5-position of indole affected the enantionselectivity of reaction, but the reaction rate was indeed influenced unfavorablely in the case of 5-Br-indole (entries 19 and 20). Moreover, other substrates, such as methyl 1*H*-indole-2-carboxylate, 1,3-dimethoxybenzene, 2-methylfuran, and benzofuran, did not react with *trans*-*β*-nitrostyrene under the same reaction conditions.

Proposed Reaction Mechanism. A mechanism of the Zn(II)(**L1**)-catalyzed Friedel−Crafts reaction between indoles and nitroalkenes is proposed in Scheme 2. The nitroalkene was activated by chelating to Zn(II) to form a four-membered intermediate, which underwent a nucleophilic addition of indole to provide the Friedel−Crafts alkylation adduct. Subsequently, the H-transfer, followed by deassociation, affords the product and regenerates the Zn(II)−bisoxazoline catalyst.

Conclusion

The catalytic asymmetric Friedel−Crafts alkylation reaction of indole and its derivatives with nitroalkenes catalyzed by Zn(II)−bisoxazoline complexes was developed. The nitroalkylated indoles were produced in excellent yields and high enantioselectivities. The new template using nitroalkene for the asymmetric Friedel−Crafts alkylation should have a wide application in other Lewis acid catalyzed asymmetric transformations, and studies are in progress in this laboratory.

Experimental Section

General Procedure for the Catalytic Asymmetric Friedel−Crafts Reaction. (*S*)-3-(2-Nitro-1-phenylethyl)-1*H*-indole (3aa).[17e] To a dried Schlenk tube were added $Zn(OTf)_2$ (18.5 mg, 0.05 mmol) and (*S*)-Ph-bisoxazoline (20 mg, 0.06 mmol) under N_2 atmosphere, followed by addition of the toluene (5 mL). The solution was stirred at room temperature for 2 h under N_2 atmosphere, and the *trans*-*β*-nitrostyrene (**2a**) (149 mg, 1.0 mmol) was added. The mixture was cooled to 0 °C and stirred for 10 min before the indole (**1a**) (57 mg, 0.5 mmol) was added. After the reaction was complete (monitored by TLC), the solvent was removed under vacuum and the residue was chromatographed on silica gel column with ethyl acetate/petroleum ether (1:3, v/v) to afford the product (*S*)-3-(2-nitro-1-phenylethyl)-1*H*-indole (**3aa**) (130 mg, 97% yield) as an oil: $[\alpha]^{20}_D = +25.3$ (*c* 0.9, CH_2Cl_2), 84% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 21.31 min (major) and 27.72 min]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 4.93 (dd, *J* = 8.1, 12.9 Hz, 1H), 5.06 (dd, *J* = 8.1, 12.9 Hz, 1H), 5.19 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.17−7.36 (m, 7H), 7.44 (d, *J* = 8.1 Hz, 1H), 8.09 (s, 1H).

3-[1-(4-Methylphenyl)-2-nitroethyl]-1*H*-indole (3ab): oil; 98% yield; $[\alpha]^{20}_D = +16.4$ (*c* 0.9, CH_2Cl_2), 81% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 20.07 min (major) and 23.14 min]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 2.25 (s, 3H), 4.81 (dd, *J* = 8.1, 11.7 Hz, 1H), 4.93 (dd, *J* = 8.1, 11.7 Hz, 1H), 5.08 (t, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 7.0−7.22 (m, 7H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 21.1, 41.3, 79.7, 111.6, 114.5, 118.9, 119.9, 121.7, 122.6, 126.2, 127.7, 129.7, 136.3, 136.6, 137.3; ESI MS *m*/*z* 279 ($M^- - 1$). Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.74; H, 5.63; N, 10.04.

3-[1-(4-Methoxyphenyl)-2-nitroethyl]-1*H*-indole (3ac): white powder; mp 149−150 °C; 91% yield; $[\alpha]^{20}_D = +26.4$ (*c* 1.1, CH_2Cl_2), 81% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 24.91 min (major) and 30.08 min]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.73 (s, 3H), 4.85 (dd, *J* = 8.4, 12.3 Hz, 1H), 4.99 (dd, *J* = 8.4, 12.3 Hz, 1H), 5.10 (t, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 2.1 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.14−7.22 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 8.01 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 40.9, 55.3, 79.8, 111.4, 114.3, 114.7, 119.0, 119.9, 121.5, 122.7, 126.1, 128.8, 131.3, 136.6, 158.9; ESI MS *m*/*z* 297 ($M^+ + 1$). Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 69.13; H, 5.68; N, 9.73.

3-[1-(3-Methoxyphenyl)-2-nitroethyl]-1*H*-indole (3ad): oil; 79% yield; $[\alpha]^{20}_D = +18.3$ (*c* 0.9, CH_2Cl_2), 83% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 24.31 min (major) and 38.92 min]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.66 (s, 3H), 4.82 (dd, *J* = 8.1, 12.3 Hz, 1H), 4.93 (dd, *J* = 8.1, 12.3 Hz, 1H), 5.09 (t, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.81−6.88 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.1−7.25 (m, 3H), 7.42 (d, *J* = 8.1 Hz, 1H), 8.0 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 41.6, 55.2, 79.5, 111.5, 112.5, 114.1, 114.1, 118.9, 119.9, 120.1, 121.7, 122.6, 126.1, 130.0, 136.5, 141.0, 160.0; ESI MS *m*/*z* 295 ($M^- - 1$). Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.70; H, 5.62; N, 9.70.

3-[1-(2-Methoxyphenyl)-2-nitroethyl]-1*H*-indole (3ae): oil; 87% yield; $[\alpha]^{20}_D = +49.6$ (*c* 0.75, CH_2Cl_2), 61% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 14.15 and 16.30 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.83 (s, 3H), 4.87−5.02 (m, 2H), 5.57 (t, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 2H), 7.1−7.23 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 35.5, 55.6, 78.2, 110.9, 111.4, 113.8, 119.0, 119.7, 120.8, 122.1, 122.4, 126.5, 127.3, 128.7, 128.9, 136.4, 156.9; ESI MS *m*/*z* 295 ($M^- - 1$). Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.68; H, 5.31; N, 9.70.

3-[1-(4-Fluorophenyl)-2-nitroethyl]-1*H*-indole (3af): oil; 96% yield; $[\alpha]^{20}_D = +39.9$ (*c* 0.85, CH_2Cl_2), 83% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 25.14 min (major) and 34.06 min]; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 4.93 (dd, J = 8.4, 11.7 Hz, 1H), 5.08 (dd, J = 8.4, 11.7 Hz, 1H), 5.25 (t, J = 8.4 Hz, 1H), 6.96 (d, J = 1.5 Hz, 1H), 7.06 (t, J = 8.4 Hz, 2H), 7.21 (t, J = 6.9 Hz, 1H), 7.27−7.39 (m, 4H), 7.52 (d, J = 7.5 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.9, 79.6, 111.7, 114.0, 115.7, 116.0, 118.9, 120.0, 121.7, 122.8, 126.0, 129.5, 135.1, 136.6; ESI MS *m*/*z* 283 (M^- − 1). Anal. Calcd for $C_{16}H_{13}FN_2O_2$: C, 67.60; H, 4.61; N, 9.85. Found: C, 67.47; H, 4.82; N, 9.68.

3-[1-(4-Chlorophenyl)-2-nitroethyl]-1*H*-indole (3ag): oil; 98% yield; $[\alpha]^{20}_D$ = +7.5 (*c* 1.2, CH_2Cl_2), 82% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 26.95 min (major) and 35.88 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (dd, J = 8.7, 13.2 Hz, 1H), 5.06 (dd, J = 8.7, 13.2 Hz, 1H), 5.2 (t, J = 8.7 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.24−7.38(m, 6H), 7.47 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.0, 79.3, 111.6, 113.8, 118.8, 120.1, 121.6, 122.8, 125.9, 129.1, 129.2, 133.4, 136.5, 137.8; ESI MS *m*/*z* 301 (M^+ + 1). Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 63.75; H, 4.55; N, 9.52.

3-[1-(2-Chlorophenyl)-2-nitroethyl]-1*H*-indole (3ah): oil; 97% yield; $[\alpha]^{20}_D$ = +76.4 (*c* 0.95, CH_2Cl_2), 72% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 16.95 and 29.34 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.87−4.99 (m, 2H), 5.72 (t, J = 7.8 Hz, 1H), 6.99−7.16 (m, 6H), 7.27 (d, J = 8.4 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.0, 77.7, 111.4, 113.2, 118.9, 120.0, 122.0, 122.8, 126.2, 127.3, 128.8, 129.0, 130.1, 133.8, 136.5; ESI MS *m*/*z* 301 (M^+ + 1). Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 64.03; H, 4.23; N, 9.42.

3-[1-(4-Bromophenyl)-2-nitroethyl]-1*H*-indole (3ai): oil; 98% yield; $[\alpha]^{20}_D$ = −1.7 (*c* 1.0, CH_2Cl_2), 90% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 29.29 min (major) and 37.74 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74 (dd, J = 7.8, 12.3 Hz, 1H), 4.88 (dd, J = 7.8, 12.3 Hz, 1H), 5.01 (t, J = 7.8 Hz, 1H), 6.81 (d, J = 2.1 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 7.04−7.12 (m, 3H), 7.21 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 8.4 Hz, 3H), 8.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.0, 79.2, 111.5, 113.7, 118.8, 120.1, 121.5, 121.6, 122.8, 125.9, 129.5, 132.0, 136.5, 138.3; ESI MS *m*/*z* 345 (M^- + 1). Anal. Calcd for $C_{16}H_{13}BrN_2O_2$: C, 55.67; H, 3.80; N, 8.12. Found: C, 55.95; H, 3.98; N, 8.40.

3-[1-(3-Bromophenyl)-2-nitroethyl]-1*H*-indole (3aj): oil; 98% yield; $[\alpha]^{20}_D$ = +14.7 (*c* 1.3, CH_2Cl_2), 86% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 27.83 min (major) and 41.77 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.90 (dd, J = 7.5, 12.0 Hz, 1H), 5.03 (dd, J = 7.5, 12.0 Hz, 1H), 5.2 (t, J = 7.5 Hz, 1H), 6.95 (s, 1H), 7.15−7.22 (m, 2H), 7.26−7.38 (m, 3H), 7.44 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 8.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.2, 79.2, 111.7, 113.4, 118.7, 120.1, 121.8, 122.8, 123.0, 125.9, 126.5, 130.5, 130.8, 130.9, 136.5, 141.8; ESI MS *m*/*z* 343 (M^- − 1). Anal. Calcd for $C_{16}H_{13}BrN_2O_2$: C, 55.67; H, 3.80; N, 8.12. Found: C, 55.49; H, 4.02; N, 8.27.

3-[2-Nitro-1-(4-nitrophenyl)ethyl]-1*H*-indole (3ak): pale yellow powder; mp 171−172 °C; 98% yield; $[\alpha]^{20}_D$ = −13.3 (*c* 1.3, CH_2Cl_2), 80% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 59.25 min (major) and 80.29 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (dd, J = 9.0, 12.9 Hz, 1H), 5.11 (dd, J = 9.0, 12.9 Hz, 1H), 5.31 (t, J = 9 Hz, 1H), 7.0−7.12 (m, 2H), 7.20−7.26 (m, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 8.7 Hz, 2H), 8.21 (s, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 41.2, 78.7, 111.6, 112.9, 118.5, 120.3, 121.6, 123.1, 124.1, 125.6, 128.7, 136.5, 146.7, 147.3; ESI MS *m*/*z* 310 (M^- − 1). Anal. Calcd for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50. Found: C, 61.49; H, 4.46; N, 13.80.

3-[1-(2,4-Dichlorophenyl)-2-nitroethyl]-1*H*-indole (3al): oil; 90% yield; $[\alpha]^{20}_D$ = +59.5 (*c* 0.8, CH_2Cl_2), 70% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 19.83 and 34.43 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.82−4.96 (m, 2H), 5.64 (t, J = 8.4 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 7.02−7.07 (m, 3H), 7.16 (t, J = 8.1 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.41 (s, 1H), 8.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.6, 77.5, 111.6, 112.7, 118.7, 120.1, 122.0, 122.9, 126.0, 127.6, 129.9, 129.9, 134.0, 134.5, 135.2, 136.5; ESI MS *m*/*z* 333 (M^- − 1). Anal. Calcd for $C_{16}H_{12}Cl_2N_2O_2$: C, 57.33; H, 3.61; N, 8.36. Found: C, 57.19; H, 3.87; N, 8.09.

3-(1-Naphthalen-1-yl-2-nitroethyl)-1*H*-indole (3am): oil; 98% yield; $[\alpha]^{20}_D$ = +22.3 (*c* 1.15, CH_2Cl_2); 78% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 26.52 and 31.17 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96−5.01 (m, 2H), 6.02 (t, J = 7.5 Hz, 1H), 6.78 (s, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.09−7.21 (m, 2H), 7.28 (d, J = 5.4 Hz, 2H), 7.37−7.50 (m, 3H), 7.72 (t, J = 4.5 Hz, 1H), 7.83 (d, J = 6.0 Hz, 2H), 8.23 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.0, 78.6, 111.5, 114.2, 118.8, 120.0, 122.7, 122.7, 124.7, 125.4, 126.0, 126.1, 126.9, 128.4, 129.2, 131.2, 134.2, 134.7, 136.6; ESI MS *m*/*z* 315 (M^- − 1). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.84; H, 5.07; N, 8.78.

3-(2-Nitro-1-thiophene-2-ylethyl)-1*H*-indole (3an): oil; 95% yield; $[\alpha]^{20}_D$ = +24.3 (*c* 1.0, CH_2Cl_2), 82% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 24.47 and 27.23 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.90−5.01 (m, 2H), 5.41 (t, J = 8.7 Hz, 1H), 6.84−6.97 (m, 3H), 7.05−7.2 (m, 3H), 7.27 (d, J = 8.4 Hz, 1H), 7.48(d, J = 8.4 Hz, 1H), 8.03 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.0, 80.0, 111.6, 113.9, 118.8, 120.1, 122.1, 122.7, 124.9, 125.3, 125.7, 127.0, 136.4, 143.0; ESI MS *m*/*z* 271 (M^- − 1). Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.49; H, 4.81; N, 10.18.

3-(1-Furan-2-yl-2-nitroethyl)-1*H*-indole (3ao):[17d] oil; 98% yield; $[\alpha]^{20}_D$ = −78 (*c* 1.0, CH_2Cl_2); 78% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 70:30, 1.0 mL/min, 254 nm; t_R = 14.93 and 21.32 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (dd, J = 7.5 Hz, 12.0 Hz, 1H), 4.91 (dd, J = 7.5 Hz, 12.0 Hz, 1H), 5.11 (t, J = 7.5 Hz, 1H), 6.01 (d, J = 3.0 Hz, 1H), 6.17 (m, 1H), 6.87 (d, J = 2.1 Hz, 1H), 6.98−7.11 (m, 2H), 7.17 (d, J = 8.1 Hz, 1H), 7.24(s, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 77.9, 107.4, 110.5, 111.5, 111.6, 118.7, 120.1, 122.6, 123.8, 125.7, 136.3, 142.3, 152.3; ESI MS *m*/*z* 257 (M^+ + 1). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.44; H, 4.95; N, 11.13.

3-(1-Nitromethylbutyl)-1*H*-indole (3ap): oil; 57% yield; $[\alpha]^{20}_D$ = −51.1 (*c* 0.45, EtOH), 70% ee [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 31.54 and 34.76 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3H), 1.19−1.28 (m, 2H), 1.63−1.82 (m, 2H), 3.7−3.78 (m, 1H), 4.5−4.63 (m, 2H), 6.93 (d, J = 2.1 Hz, 1H), 7.03−7.16 (m, 2H), 7.28 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.3, 34.6, 36.0, 80.5, 111.5, 114.1, 118.7, 119.7, 121.8, 122.4, 126.2, 136.5; ESI MS *m*/*z* 233 (M^+ + 1). Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.43; H, 7.10; N, 12.35.

(*S*)-1-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ba):[17d] oil; 62% yield; $[\alpha]^{20}_D$ = +10.8 (*c* 0.6, CH_2Cl_2), 31% ee [Daicel Chiralcel AS column, *n*-hexane/*i*-PrOH = 98:2, 1.0 mL/min, 254 nm; t_R = 34.41 and 39.17 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (s, 3H), 4.93 (dd, J = 8.1, 12.3 Hz, 1H), 5.05 (dd, J = 8.1, 12.3 Hz, 1H), 5.18 (t, J = 8.1 Hz, 1H), 6.86 (s, 1H), 7.04−7.1 (m, 1H), 7.2−7.34 (m, 7H), 7.45 (d, J = 7.8 Hz, 1H).

2-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ca):[17d] oil; 87% yield; $[\alpha]^{20}_D$ = −13.9 (*c* 0.9, CH_2Cl_2), 21% ee [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 96:4, 1.0 mL/min, 254 nm; t_R = 74.83 min (major) and 79.58 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.08−5.26 (m, 3H), 6.99−7.13 (m, 2H), 7.22−7.38 (m, 7H), 7.86 (s, 1H).

5-Methoxy-3-(2-nitro-1-phenylethyl)-1*H*-indole (3da):[17d] oil; 94% yield; $[\alpha]^{20}_D$ = −25.6 (*c* 1.1, CH_2Cl_2), 79% ee [Daicel

Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 254 nm; t_R = 37.68 and 42.26 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 4.93 (dd, J = 8.1, 12 Hz, 1H), 5.05 (dd, J = 8.1, 12 Hz, 1H), 5.14 (t, J = 8.1 Hz, 1H), 6.84 (s, 1H), 6.86 (d, J = 8.4, 1H), 7.0 (d, J = 2.4 Hz, 1H), 7.23−7.34 (m, 6H), 7.99 (s, 1H).

5-Bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ea):[17d] oil; 98% yield; $[\alpha]^{20}_D$ = −39.2 (*c* 1.15, CH_2Cl_2), 80% ee [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R = 20.97 and 22.96 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88−5.16 (m, 3H), 7.08 (d, J = 2.1 Hz, 1H), 7.21−7.34 (m, 7H), 7.55 (d, J = 2.4 Hz, 1H), 8.16 (s, 1H).

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