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Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to Indolylnitroalkenes

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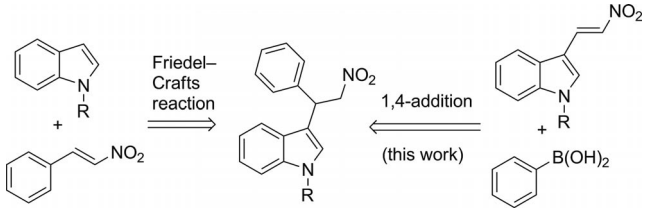
Indolylnitroethanes and their derivatives are key intermediates to many bioactive structures. Most approaches to access chiral indolylnitroethanes involve organocatalyzed or metal-catalyzed asymmetric Friedel–Crafts reaction of indoles with nitroalkenes. We have developed an efficient approach to optically pure α-aryl-3-indolylnitroethanes through rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to indolylnitroalkenes. Excellent yields (up to 99 %) and enantiomeric excesses (up to 99 % *ee*) of chiral indolylnitroethanes were achieved under mild conditions.

Introduction

Indolylnitroethanes and their derivatives, which are key intermediates to many bioactive structures, are an important class of heterocyclic compounds.[1] To date, most approaches to access chiral indolylnitroethanes involve the use of organo- or metal-catalyzed asymmetric Friedel–Crafts reactions of indoles with nitroalkenes;[2–3] other strategies are less developed. Originally developed by Hayashi and Miyaura, rhodium-catalyzed asymmetric 1,4-addition of organoboron reagents to electron-deficient olefins is an efficient transformation for the construction of new carbon–carbon bonds.[4–6] Many successful results have been achieved on the asymmetric addition of organoboron reagents to α,β-unsaturated ketones, esters, amides, and so on. However, less studies have focused on nitroalkenes during the past decade.[7–11] Recently, Lin's group[10] and our group's[11] developed Rh/chiral diene and Rh/chiral sulfoxide–phosphane complexes, respectively, to realize the addition of arylboronic reagents to styrene-type nitroalkenes. To the best of our knowledge, asymmetric catalytic addition of arylboronic acids to heteroarylnitroalkenes has not been reported. The impetus of this work was to find another effective strategy to access chiral indolylnitroethanes (Scheme 1).



Scheme 1. Synthetic strategies for 3-indolylnitroethane.

Results and Discussion

We initially carried out the reaction of *N*-benzyl-protected 3-indolylnitrioalkene (**1a**) with phenylboronic acid (**2a**) in the presence of rhodium/sulfoxide–phosphane complex **L1** (Scheme 2) under our previously reported reaction conditions:[11] ethanol, triethylamine (TEA) as the base, and stirring at 40 °C for 10 h. The expected indolylnitroethane adduct was afforded in excellent yield and enantioselectivity (98 % yield and 97 % *ee*; Table 1, entry 1). The effect of *N*-protecting groups was further evaluated: *N*-methyl showed similar results to the *N*-benzyl protecting group and the *N*-benzenesulfonyl group had a negative effect on the *ee* value (Table 1, entries 2 and 3). Surprisingly, we found that 3-indolylnitroalkene **1d**, which was without an *N*-protecting group, worked well in our system. Compared with styrene-type nitroalkenes, indolylnitroalkenes (without *N*-protecting groups), as a class of *N*-heteroarylnitroalkenes, are more challenging substrates than styrene-type nitroalkenes because the nitrogen atom might ligate to the metal, and therefore, lead to a loss in reactivity.[12] In this reaction, we were pleased to find that the desired product was achieved with excellent results (96 % yield and 98 % *ee*; Table 1, entry 4). Compound **1d** was then chosen as the model substrate for screening of ligands and other conditions. Both sulfoxide–phosphane ligands **L2** and **L3** can generate similar results to **L1**, however, the classical rho-

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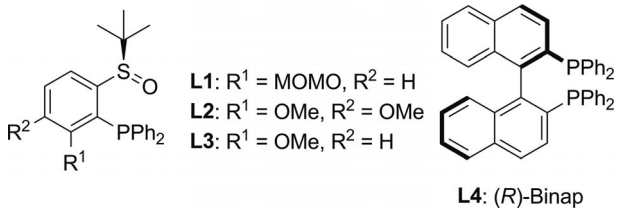
dium–BINAP complex **L4** (BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl) does not work in this transformation (Table 1, entries 5–7). After systematic solvent screening, we found that alcohols were the optimal solvents in terms of yield and *ee* values. The reaction did not work well in CH_3CN, toluene, Et_2O, dioxane, and THF (Table 1, entries 8–18), only trace of product was obtained. Next, various inorganic/organic bases were examined, such as KOH, $KHCO_3$, KF, CsF, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), pyridine and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Table 1, entries 19–26); TEA gave the best yield and *ee* value (Table 1, entry 4).

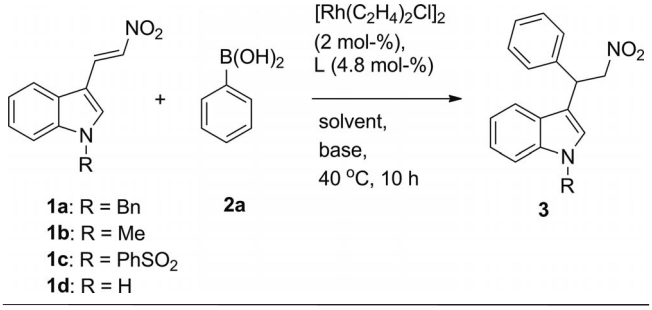


Scheme 2. Ligands for this work.

With the appropriate rhodium catalyst, which was formed in situ from [{$Rh(C_2H_4)_2Cl$}$_2$] and **L1**, and optimal reaction conditions in hand, various 3-indolylnitroalkenes and arylboronic acids were investigated to examine the generality of the reaction. The results are showed in Table 2. Most of the arylboronic acids and 3-indolylnitroalkene reacted smoothly under mild conditions to give the corresponding products in high yields (up to 99%) and excellent enantioselectivities (up to 99% *ee*). Arylboronic acids with different substituents in the *meta* and *para* positions can be all employed successfully to afford the desired products in high yields (95–99%) and excellent enantioselectivities (94–99% *ee*; Table 2, entries 1–5, 7, 9, 10, 12, and 13). In contrast, steric hindrance of the substituents on the arylboronic acids, such as (*o*-methyl-, (*o*-methoxyphenyl)boronic acid, and 1-naphthaleneboronic acid, had a significant effect on the activity and only traces of products were obtained. In addition, electron-withdrawing arylboronic acids had a slightly negative impact on the activity and enantioselectivity (Table 2, entries 6, 8, and 11). Moderate yield (72%) and a slightly decreased enantioselectivity (83% *ee*) was provided with (4-trifluoromethylphenyl)boronic acid (Table 2, entry 8). As expected, electron-donating arylboronic acids are efficient for this reaction. Excellent yields and enantioselectivities were also obtained when phenylboronic acid was treated with substituted 3-indolylnitroalkenes (Table 2, entries 14 and 15). One exception was **1g**, for which a modest yield (62%) was observed (Table 2, entry 16).

To further extend the scope of the reaction, this catalyst system was used in the asymmetric addition of 2-indolylnitroalkenes with arylboronic acids to afford the corresponding 2-indolylnitroethanes, which cannot be realized through direct Friedel–Crafts reactions.[13] Two other five-membered

Table 1. Rhodium-catalyzed asymmetric 1,4-addition of phenylboronic acid to 3-indolylnitroalkene.[a]



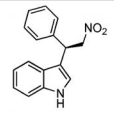
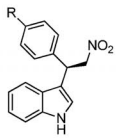
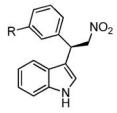
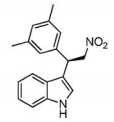
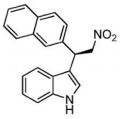
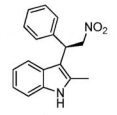
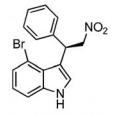
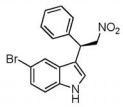
Entry	1	Ligand	Solvent	Base	Yield[b] [%]	*ee*[c] [%]
1	**1a**	**L1**	EtOH	TEA	98	97
2	**1b**	**L1**	EtOH	TEA	96	98
3	**1c**	**L1**	EtOH	TEA	99	86
4	**1d**	**L1**	EtOH	TEA	96	98(*R*)
5	**1d**	**L2**	EtOH	TEA	96	97
6	**1d**	**L3**	EtOH	TEA	95	96
7[d]	**1d**	**L4**	dioxane	KOH	trace	n.d.
8	**1d**	**L1**	CH_2Cl_2	TEA	25	88
9	**1d**	**L1**	acetone	TEA	57	95
10	**1d**	**L1**	EtOAc	TEA	68	96
11	**1d**	**L1**	MeOH	TEA	95	97
12	**1d**	**L1**	*n*PrOH	TEA	93	98
13	**1d**	**L1**	*n*BuOH	TEA	95	98
14	**1d**	**L1**	CH_3CN	TEA	trace	n.d.
15	**1d**	**L1**	toluene	TEA	trace	n.d.
16	**1d**	**L1**	Et_2O	TEA	trace	n.d.
17	**1d**	**L1**	dioxane	TEA	trace	n.d.
18	**1d**	**L1**	THF	TEA	trace	n.d.
19	**1d**	**L1**	EtOH	KOH	trace	n.d.
20	**1d**	**L1**	EtOH	$KHCO_3$	trace	n.d.
21	**1d**	**L1**	EtOH	KF	77	76
22	**1d**	**L1**	EtOH	CsF	trace	n.d.
23	**1d**	**L1**	EtOH	TMEDA	68	97
24	**1d**	**L1**	EtOH	DBU	trace	n.d.
25	**1d**	**L1**	EtOH	Pyridine	trace	n.d.
26	**1d**	**L1**	EtOH	DABCO	47	97

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [{$Rh(C_2H_4)Cl$}$_2$] (1.5 mg, 0.004 mmol), **L** (0.0096 mmol), base (0.1 mmol), and EtOH (1.5 mL) at 40 °C for 10 h. [b] Isolated yield. [c] Determined by HPLC analysis with chiral columns. The absolute configuration was determined by comparison of the specific rotation to literature data.[2a] n.d. = not determined. [d] Reaction temperature 100 °C for 10 h.

heterocyclic substrates, such as 2-nitrovinylfuran and -thiophene, were also chosen in this catalyst system and excellent yields (98–99%) and modest enantioselectivities (50–76% *ee*) were achieved (Table 3).

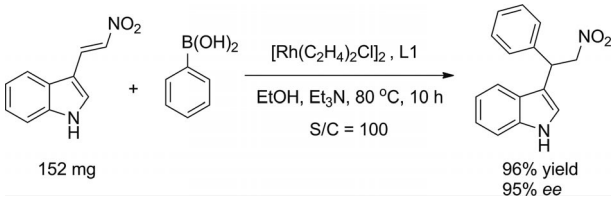
Finally, we investigated the catalyst loading of this transformation. Under the optimized conditions, in the presence of 1 mol-% Rh catalyst, the reaction did not proceed at 40 °C, fortunately, the desired product could be obtained with 96% yield and without loss of enantioselectivity when the temperature was increased to 80 °C (oil bath temperature, Scheme 3). However, continually reducing the catalyst loading to 0.5 mol-% Rh or scaling up the reaction to fivefold in the presence of 1 mol-% Rh led to failure of the transformation. These phenomena indicated that the ac-

Table 2. Scope of the rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to 3-indolylnitroalkenes.[a]

Entry	1	2	3	Yield[b] [%]	*ee*[c] [%]
1	**1d**	**2a**		96	98
2	**1d**	**2b**, R = Me		98	98
3	**1d**	**2c**, R = MeO		98	99
4	**1d**	**2d**, R = MOMO		99	99
5	**1d**	**2e**, R = *t*Bu		96	98
6	**1d**	**2f**, R = Cl		96	94
7	**1d**	**2g**, R = F		95	97
8[d]	**1d**	**2h**, R = CF_3		72	83
9	**1d**	**2i**, R = Me		98	98
10	**1d**	**2j**, R = MeO		98	98
11	**1d**	**2k**, R = Cl		93	90
12	**1d**	**2l**		97	99
13	**1d**	**2m**		98	98
14	**1e**	**2a**		97	99
15	**1f**	**2a**		97	98
16	**1g**	**2a**		62	97

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), [{Rh(C_2H_4)Cl}$_2$] (1.5 mg, 0.004 mmol), **L1** (0.0096 mmol), 50 mol-% TEA, and EtOH (1.5 mL) at 40 °C for 10 h. [b] Isolated yield. [c] Determined by HPLC analysis with chiral columns. [d] Reaction was carried out for 20 h.

tivity of indolylnitroalkene was lower than that of styrene-type nitroalkenes, which could be smoothly converted into adducts with a substrate/catalyst ratio 500 under the same conditions.[11]

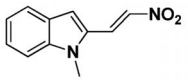
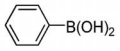
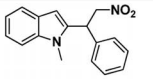
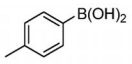
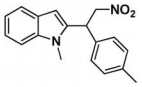
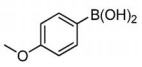
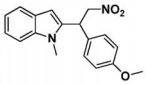
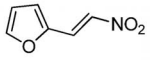
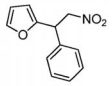
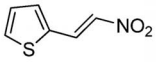
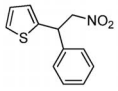


Scheme 3. Catalyst-loading test.

Conclusions

We have developed an efficient rhodium-catalyzed asymmetric addition of arylboronic acids to indolylnitroalkenes by using (*tert*-butylsulfinyl)phosphane as a ligand. The reaction works well with various indolynitroalkenes and arylboronic acids under mild conditions to give excellent yields (up to 99% yield) and enantioselectivities (up to 99% *ee*) of the products. This route provided an efficient option to access optically pure α-aryl-3-indolylnitroethanes. Further studies focused on rhodium-catalyzed asymmetric addition of arylboronic acids to other nitroalkenes are underway in our laboratories.

Table 3. Rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to 2-indolylnitroalkenes and heterocyclnitroalkenes.[a]

Entry	1		2		3		Yield[b] [%]	*ee*[c] [%]
1	**1h**		**2a**				99	50
2	**1h**		**2b**				98	62
3	**1h**		**2c**				98	75
4	**1i**		**2a**				99	60
5	**1j**		**2a**				99	76

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), [{Rh(C_2H_4)Cl}$_2$] (1.5 mg, 0.004 mmol), **L1** (0.0096 mmol), 50 mol-% Et_3N, and EtOH (1.5 mL) at 40 °C for 10 h. [b] Isolated yield. [c] Determined by HPLC analysis with chiral columns.

Experimental Section

General Procedure for the Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to 3-Indolylnitroalkenes: Under an argon atmosphere, at room temperature, [{Rh(C_2H_4)$_2$Cl}$_2$] (1.5 mg, 0.004 mmol) and (*tert*-butylsulfinyl)phosphane ligand **L1** (4.1 mg, 0.0096 mmol), followed by 1.0 mL CH_2Cl_2, were added to a 10 mL Schlenk tube and the mixture was stirred at room temperature for 30 min, then CH_2Cl_2 was removed under reduced pressure and 3-indolylnitroalkenes (0.2 mmol) and arylboronic acids (0.4 mmol) were added, after purging with argon, then ethanol (1.5 mL) and TEA (14.0 μL, 0.1 mmol) were added successively. The mixture was stirred at 40 °C for 10 h, then the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate, 10:1, as the eluent. The *ee* value was determined by HPLC on a chiral phase.

1-Benzyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3aa): Yield 98%. $[\alpha]_D^{20}$ = –38 (*c* = 0.168, $CHCl_3$) for 97% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.9 Hz, 1 H), 7.39–7.19 (m, 10 H), 7.14–7.12 (m, 3 H), 7.02 (s, 1 H), 5.29–5.23 (m, 3 H), 5.11–5.05 (m, 1 H), 5.00–4.93 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.3, 137.2, 136.9, 128.84, 128.75, 127.79, 127.6, 127.5, 126.8, 126.6, 125.7, 122.4, 119.7, 119.1, 113.4, 110.0, 79.5, 50.0, 41.5 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 7.98 (major), 9.13 min (minor).

1-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ba): Yield 96%. $[\alpha]_D^{20}$ = –10 (*c* = 0.172, $CHCl_3$) for 98% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.9 Hz, 1 H), 7.39–7.26 (m, 7 H), 7.12 (t, *J* = 6.8 Hz, 1 H), 6.89 (s, 1 H), 5.24–5.19 (m, 1 H), 5.10–4.99 (m, 1 H), 4.96–4.92 (m, 1 H),3.74 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.4, 137.2, 128.8, 127.7, 127.4, 126.5, 126.3, 122.2, 119.4, 118.9, 112.7, 109.5, 79.5, 41.5, 32.7 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 7.31 (major), 7.74 min (minor).

3-(2-Nitro-1-phenylethyl)-1-(phenylsulfonyl)-1*H*-indole (3ca): Yield 99%. $[\alpha]_D^{20}$ = –17 (*c* = 0.128, $CHCl_3$) for 86% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): 8.00 (d, 1 H, *J* = 8.2 Hz), 7.87–7.84 (m, 2 H), 7.56–7.52 (m, 2 H), 7.45–7.42 (m, 2 H), 7.33–7.25 (m, 7 H), 7.20 (t, 1 H, *J* = 7.2 Hz), 5.10–5.01 (m, 2 H), 4.95–4.88 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 137.7, 137.3, 135.4, 133.9, 129.4, 129.3, 129.1, 128.0, 127.6, 126.6, 125.3, 123.6, 123.1, 121.1, 119.7, 113.8, 78.9, 41.1 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 18.19 (minor), 28.93 min (major). HRMS (EI) for $C_{22}H_{18}N_2NaO_4S$ [M + Na]: calcd. 429.0885; found 429.0861.

3-(2-Nitro-1-phenylethyl)-1*H*-indole (3da): Yield 96%. $[\alpha]_D^{20}$ = –12 (*c* = 0.114, $CHCl_3$) for 98% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (s, 1 H), 7.47 (d, *J* = 7.9 Hz, 1 H), 7.36–7.29 (m, 6 H), 7.26–7.21 (m, 1 H), 7.11 (t, *J* = 7.3 Hz, 1 H), 7.01 (d, *J* = 2.3 Hz, 1 H), 5.20–5.18 (m, 1 H), 5.11–5.04 (m, 1 H), 4.98–4.91 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 136.4, 128.9, 127.7, 127.5, 126.0, 122.6, 121.6, 119.9, 118.9, 114.3, 111.4, 79.5, 41.5 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 15.22 min (major), 16.86 min (minor).

3-[2-Nitro-1-(*p*-tolyl)ethyl]-1*H*-indole (3 db): Yield 98%. $[\alpha]_D^{20}$ = –2 (*c* = 0.150, $CHCl_3$) for 98% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): 8.05 (s, 1 H), 7.87 (d, 1 H, *J* = 7.9 Hz), 7.34 (d, 1 H, *J* = 8.1 Hz), 7.25–7.19 (m, 3 H), 7.15–7.07 (m, 3 H), 6.99 (d, 1 H, *J* = 2.1 Hz), 5.19–5.14 (m, 1 H), 5.09–5.02 (m, 1 H),4.96–4.89 (m, 1 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 137.2, 136.4, 136.1, 129.5, 127.6, 126.0, 122.6, 121.5, 119.8, 114.5, 111.3, 79.6, 41.1, 21.0 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 14.15 (major),16.23 min (minor).

3-[1-(4-Methoxyphenyl)-2-nitroethyl]-1*H*-indole (3dc): Yield 98%. $[\alpha]_D^{20}$ = –9 (*c* = 0.118, $CHCl_3$) for 99% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.39 (d, *J* = 7.9 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 1 H), 7.26–7.23 (m, 3 H), 7.10–7.06 (m, 1 H), 7.00 (d, *J* = 2.0 Hz, 1 H), 6.86–6.83 (m, 2 H), 5.14–5.10 (m, 1 H), 5.05–5.01 (m, 1 H),4.93–4.86 (m, 1 H), 3.77 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 136.4, 131.1, 128.8, 126.0, 122.6, 121.4, 119.9, 118.9, 114.6, 114.2, 111.3, 79.7, 55.2, 40.8 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 75:25, 0.8 mL min^{-1}, 254 nm, retention time: 20.26 (minor), 21.53 min (major).

3-{1-[4-(Methoxymethoxy)phenyl]-2-nitroethyl}-1*H*-indole (3dd): Yield 99%. $[\alpha]_D^{20}$ = –17 (*c* = 0.114, $CHCl_3$) for 99% *ee*. ^{1}H NMR

(300 MHz, $CDCl_3$): 8.11 (s, 1 H), 7.45 (d, 1 H, J = 7.9 Hz), 7.33 (d, 1 H, J = 8.1 Hz), 7.26–7.18 (m, 3 H), 7.10 (t, 1 H, J = 7.1 Hz), 6.99–6.97 (m, 3 H), 5.15–5.12 (m, 3 H), 5.07–5.00 (m, 1 H), 4.92–4.85 (m, 1 H), 3.47 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 156.5, 136.4, 132.4, 128.8, 126.0, 122.6, 121.4, 119.8, 118.9, 116.5, 114.5, 111.3, 94.3, 79.6, 56.0, 40.8 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 13.07 (minor), 14.04 min (major). HRMS (EI) for $C_{18}H_{18}N_2NaO_4$ [M + Na]: calcd. 349.1164; found 349.1156.

3-{1-[4-(*tert*-Butyl)phenyl]-2-nitroethyl}-1*H*-indole (3de): Yield 96%. $[\alpha]_D^{20}$ = +15 (c = 0.126, $CHCl_3$) for 98% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (s, 1 H), 7.50 (d, J = 7.9 Hz, 1 H), 7.36–7.18 (m, 6 H), 7.10 (t, J = 7.3 Hz, 1 H), 7.03 (s, 1 H), 5.21–5.51 (m, 1 H), 5.16–5.02 (m, 1 H), 4.97–4.91 (m, 1 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.3, 136.4, 136.0, 127.3, 126.1, 125.8, 122.6, 121.6, 119.8, 118.9, 114.5, 111.3, 79.5, 41.0, 34.4, 31.3 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 9.74 (major), 11.15 min (minor). HRMS (EI) for $C_{20}H_{22}N_2NaO_2$ [M + Na]: calcd. 345.1579; found 345.1570.

3-[1-(4-Chlorophenyl)-2-nitroethyl]-1*H*-indole (3df): Yield 96%. $[\alpha]_D^{20}$ = –2 (c = 0.128, $CHCl_3$) for 94% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.11 (s, 1 H),7.41 (d, J = 7.9 Hz, 1 H), 7.35 (d, J = 8.1 Hz, 1 H), 7.31–7.20 (m, 5 H), 7.10 (t, J = 7.3 Hz, 1 H), 6.99 (d, 1 H), 5.19–5.14 (m, 1 H), 5.08–5.01 (m, 1 H), 4.93–4.86 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 136.4, 133.3, 129.1, 129.0, 125.8, 122.8, 121.5, 120.0, 118.7, 113.8, 111.5, 79.2, 40.9 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 17.07 (major), 21.41 min (minor).

3-[1-(4-Fluorophenyl)-2-nitroethyl]-1*H*-indole (3dg): Yield 95%. $[\alpha]_D^{20}$ = –29 (c = 0.118, $CHCl_3$) for 97% *ee*. ^1H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1 H), 7.43 (d, 1 H, J = 7.9 Hz), 7.37–7.32 (m, 3 H), 7.32–7.28 (m, 1 H), 7.23–7.10 (m, 1 H), 7.04–7.00 (m, 3 H), 5.18–5.16 (m, 1 H), 5.09–5.02 (m, 1 H), 4.93–4.86 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 162.0 (d, $J_{C\text{-}F}$ = 244.6 Hz), 136.4, 134.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 125.9, 122.7, 121.4, 120.0, 118.8, 115.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.1, 111.4, 79.5, 40.8 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 15.95 (major), 19.52 min (minor).

3-{2-Nitro-1-[4-(trifluoromethyl)phenyl]ethyl}-1*H*-indole (3dh): Yield 72%. $[\alpha]_D^{20}$ = –3 (c = 0.110, $CHCl_3$) for 83% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.58 (d, J = 8.2 Hz, 2 H), 7.48–7.44 (m, 2 H), 7.41–7.36 (m, 2 H), 7.24 (t, J = 7.4 Hz, 1 H), 7.14–7.09 (m, 1 H), 7.02 (d, J = 2.1 Hz, 1 H), 5.26 (t, J = 7.8 Hz, 1 H), 5.12–5.05 (m, 1 H), 4.99–4.92 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3, 136.5, 129.9 (q, $J_{F,C}$ = 32.3 Hz), 128.2, 125. 9 (q, $J_{F,C}$ = 3.8 Hz), 124.0 (q, $J_{F,C}$ = 270.6 Hz), 123.0, 121.6, 120.2, 118.8, 113.5, 111.5, 41.3, 29.7 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time:14.32 (major), 18.06 min (minor).

3-[2-Nitro-1-(*m*-tolyl)ethyl]-1*H*-indole (3di): Yield 98%. $[\alpha]_D^{20}$ = –5 (c = 0.110, $CHCl_3$) for 98% *ee*. ^1H NMR (300 MHz, $CDCl_3$): 8.06 (s, 1 H), 7.50 (d, 1 H, J = 7.8 Hz), 7.35 (d, 1 H, J = 8.0), 7.25–7.08 (m, 6 H), 7.00 (s, 1 H), 5.20–5.15 (m, 1 H), 5.09–5.05 (m, 1 H), 4.97–4.90 (m, 1 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 139.0, 138.5, 136.4, 128.7, 128.5, 128.3, 126.0, 124.6, 122.6, 121.5, 119.8, 118.8, 114.3, 111.3, 79.5, 41.4, 21.4 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 95:5, 0.8 mL min^{-1}, 254 nm, retention time: 29.13 (major), 31.83 min (minor).

3-[1-(3-Methoxyphenyl)-2-nitroethyl]-1*H*-indole (3dj): Yield 98%. $[\alpha]_D^{20}$ = –10 (c = 0.110, $CHCl_3$) for 98% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.49 (d, J = 7.7 Hz, 1 H), 7.33 (d, J = 7.9 Hz, 1 H), 7.28–7.18 (m, 2 H), 7.10 (t, J = 7.0 Hz, 1 H), 6.98–6.89 (m, 3 H), 6.81 (d, J = 7.9 Hz, 1 H), 5.20–5.15 (m, 1 H), 5.08–5.01 (m, 1 H), 4.96–4.89 (m, 1 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 140.8, 136.4, 129.9, 126.0, 122.6, 121.6, 120.0, 119.9, 118.8, 114.1, 114.0, 112.4, 111.4, 79.4, 55.1, 41.4 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 12.65 (minor), 16.77 min (major).

3-[1-(3-Chlorophenyl)-2-nitroethyl]-1*H*-indole (3dk): Yield 93%. $[\alpha]_D^{20}$ = –18 (c = 0.116, $CHCl_3$) for 90% *ee*. ^1H NMR (300 MHz, $CDCl_3$): 8.12 (s, 1 H), 7.45 (d, 1 H, J = 7.9 Hz), 7.37–7.32 (m, 2 H), 7,25–7.20 (m, 4 H), 7.11 (t, 1 H, J = 7.5 Hz), 7.00 (d, 1 H, J = 2.1 Hz), 5.20–5.15 (m, 1 H), 5.07–5.00 (m, 1 H), 4.94–4.87 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 141.3, 136.4,134.7, 130.1, 127.9, 127.8, 125.9, 125.8, 122.8, 121.5, 120.0, 118.7, 113.5, 111.5, 79.1, 41.1 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 14.24 (major), 15.99 min (minor).

3-[1-(3,5-Dimethylphenyl)-2-nitroethyl]-1*H*-indole (3dl): Yield 97%. $[\alpha]_D^{20}$ = –2 (c = 0.128, $CHCl_3$) for 99% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.52 (d, J = 7.9 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 7.26–7.19 (m, 1 H), 7.12 (t, J = 7.1 Hz, 1 H), 7.01–6.91 (m, 4 H), 5.17–5.11 (m, 1 H), 5.08–5.01 (m, 1 H), 4.96–4.89 (m, 1 H), 2.29 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 138.3, 136.4, 129.2, 126.1, 125.5, 122.5, 121.5, 119.8, 118.9, 114.4, 111.3, 79.5, 41.3, 21.3 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 95:5, 0.8 mL min^{-1}, 254 nm, retention time: 21.50 (major), 23.19 min (minor). HRMS (EI) for $C_{18}H_{18}N_2NaO_2$ [M + Na]: calcd. 317.1266; found 317.1254.

3-[1-(Naphthalen-2-yl)-2-nitroethyl]-1*H*-indole (3dm): Yield 98%. $[\alpha]_D^{20}$ = +14 (c = 0.096, $CHCl_3$) for 98% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.81–7.78 (m, 4 H), 7.49–7.42 (m, 4 H), 7.35 (d, J = 8.2 Hz, 1 H), 7.20 (t, J = 7.7 Hz, 1 H), 7.09–7.04 (m, 2 H), 5.40–5.34 (m, 1 H), 5.18–5.02 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6, 136.5, 133.4, 132.7, 128.8, 127.9, 127.6, 126.4, 126.3, 126.1, 125.8, 122.7, 121.7, 120.0, 118.9, 114.3, 111.4, 79.4, 41.6 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 15.42 (minor), 20.41 min (major).

2-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ea): Yield 97%. $[\alpha]_D^{20}$ = +30 (c = 0.112, $CHCl_3$) for 99% *ee*. ^1H NMR (300 MHz, $CDCl_3$): 7.84 (s, 1 H), 7.41 (d, 1 H, J = 7.7 Hz), 7.36–7.23 (m, 6 H), 7.16–7.06 (m, 2 H), 5.26–5.12 (m, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 139.5, 135.3, 132.8, 128.7, 127.2, 127.0, 126. 8, 121.2, 119.7, 118.5, 110.7, 108.7, 78.6, 40.4, 11.9 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 9.43 (major), 28.15 min (minor).

4-Bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3fa): Yield 97%. $[\alpha]_D^{20}$ = +27 (c = 0.100, $CHCl_3$) for 98% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 7.35–7.25 (m, 7 H), 7.02 (t, J = 7.8 Hz, 1 H), 6.91 (s, 1 H), 6.01–5.96 (m, 1 H), 5.18–5.11 (m, 1 H), 4.94–4.86 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.3, 137.7, 128.8, 128.0, 127.4, 124.7, 124.2, 123.5, 114.9, 113.7, 110.8, 79.6, 40.4, 29.6 ppm. HPLC: Daicel Chiralcel, AD-H, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 13.46 (major), 15.74 min (minor).

5-Bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3ga): Yield 62%. $[\alpha]_D^{20}$ = +37 (c = 0.152, $CHCl_3$) for 97% *ee*. ^1H NMR (300 MHz,

$CDCl_3$): 8.17 (s, 1 H), 7.56 (s, 1 H), 7.36–7.24 (m, 6 H), 7.17 (d, 1 H, J = 8.6 Hz), 7.02 (d, 1 H, J = 2.2 Hz), 5.15–5.09 (m, 1 H), 5.04–4.97 (m, 1 H), 4.94–4.87 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 138.6, 135.0, 129.0, 127.8, 127.7, 127.6, 125.5, 122.7, 121.3, 113.8, 113.1, 112.9, 79.3, 41.2 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 13.66 (major), 15.33 min (minor).

1-Methyl-2-(2-nitro-1-phenylethyl)-1*H*-indole (3ha): Yield 99% $[\alpha]_D^{20}$ = –121 (c = 0.12, $CHCl_3$) for 50% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.8 Hz, 1 H), 7.38–7.32 (m, 3 H), 7.28–7.24 (m, 4 H), 7.21–7.15 (m, 1 H), 6.56 (s, 1 H), 5.16–5.08 (m, 2 H), 4.91–4.82 (m, 1 H), 3.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 137.1, 136.9, 129.2, 128.1, 128.0, 127.2, 121.8, 120.5, 119.8, 109.0, 79.0, 99.1, 79.0, 42.0, 29.7 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time:31.67 (minor), 69.17 min (major). HRMS (EI) for $C_{17}H_{16}N_2NaO_2$ [M + Na]: calcd. 303.1109; found 303.1103.

1-Methyl-2-[2-nitro-1-(*p*-tolyl)ethyl]-1*H*-indole (3hb): Yield 98%. $[\alpha]_D^{20}$ = –145 (c = 0.13, $CHCl_3$) for 62% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.8 Hz, 1 H), 7.27–7.22 (m, 2 H), 7.18–7.10 (m, 5 H), 6.53 (s, 1 H), 5.10–5.04 (m, 2 H), 4.87–4.78 (m, 1 H), 3.50 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.9, 137.7, 137.2, 134.1, 129.9, 127.2, 121.7, 120.4, 119.7, 109.0, 99.0, 79.1, 41.69, 29.7, 21.0 ppm. HPLC: Daicel Chiralcel, IB, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 26.61 (minor),52.09 min (major). HRMS (EI) for $C_{18}H_{18}N_2NaO_2$ [M + Na]: calcd. 317.1266; found 317.1262.

2-[1-(4-Methoxyphenyl)-2-nitroethyl]-1-methyl-1*H*-indole (3hc): Yield 98%. $[\alpha]_D^{20}$ = –157 (c = 0.116, $CHCl_3$) for 75% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.8 Hz, 1 H), 7.29–7.22 (m, 2 H), 7.18–7.13 (m, 3 H), 6.86 (d, J = 8.6 Hz, 2 H), 6.51 (s, 1 H), 5.11–5.03 (m, 2 H), 4.86–4.77 (m, 1 H), 3.79 (s, 3 H), 3.49 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 137.7, 137.2, 129.1, 129.0, 127.2, 121.7, 120.4, 119.7, 114.5, 109.0, 99.0, 79.1, 55.2, 41.3, 29.6 ppm. HPLC: Daicel Chiralcel, IA, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, 254 nm, retention time: 10.14 (minor), 11.09 min (major). HRMS (EI) for $C_{18}H_{18}N_2NaO_3$ [M + Na]: calcd. 333.1215; found 333.1207.

3-(2-Nitro-1-phenylethyl)furan (3ia): Yield 99%. $[\alpha]_D^{20}$ = –57 (c = 0.098, $CHCl_3$) for 60% *ee*. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 6 H), 6.33–6.32 (m, 1 H), 6.14–6.13 (m, 1 H), 5.03–4.99 (m, 1 H), 4.96–4.91 (m, 1 H), 4.84–4.81 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0, 142.5, 136.9, 129.0, 128.1, 127.8, 110.4, 107.4, 78.0, 43.5 ppm. HPLC: Daicel Chiralcel, AS-H, *n*-hexane/2-propanol = 90:10, 0.5 mL min^{-1}, 254 nm, retention time: 16.34 (major), 18.04 min (minor).

3-(2-Nitro-1-phenylethyl)thiophene (3ja): Yield 99%. $[\alpha]_D^{20}$ = –7 (c = 0.080, $CHCl_3$) for 76% *ee*. ^1H NMR (300 MHz, CD_3COCD_3): 7.48–7.44 (m, 2 H), 7.40–7.30 (m, 4 H), 7.12–7.11 (m, 1 H), 7.01–6.98 (m, 1 H), 5.28–5.20 (m, 3 H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): 144.1, 140.7, 129.7, 128.6, 128.6, 127.9, 126.0, 125.9, 80.2, 45.4 ppm. HPLC: Daicel Chiralcel, OD-H, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, 254 nm, retention time: 13.61 (minor), 26.03 min (major).

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization of the prepared compounds, copies of the NMR spectra, and chiral HPLC spectra of the Michael addition products.

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