JOC The Journal of Organic Chemistry

Featured Article

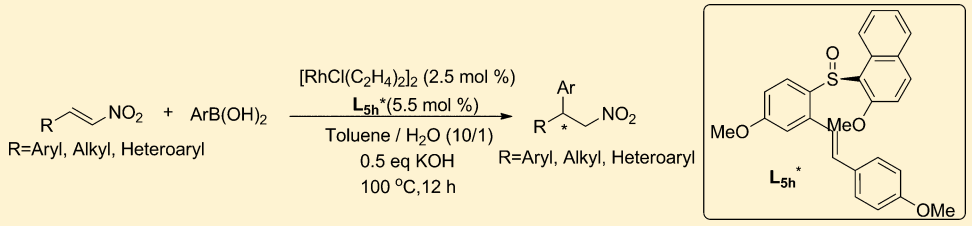
pubs.acs.org/joc

Rhodium-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Nitroalkenes Using Olefin−Sulfoxide Ligands

Feng Xue, Dongping Wang, Xincheng Li, and Boshun Wan*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Supporting Information



ABSTRACT: An efficient rhodium/olefin−sulfoxide catalyzed asymmetric conjugate addition of organoboronic acids to a variety of nitroalkenes has been developed, where 2-methoxy-1-naphthyl sulfinyl functionalized olefin ligands have shown to be highly effective and are applicable to a broad scope of aryl, alkyl, and heteroaryl nitroalkenes.

INTRODUCTION

Over the past few years, the Rh-catalyzed enantioselective conjugate addition of organoboron reagents to electron deficient olefins has been established as a powerful and straightforward method for the construction of new carbon−carbon bonds and has become increasingly explored.[1] Although many exciting results have been achieved in the asymmetric addition to α,β-unsaturated carbonyl compounds[2] and related aldimines,[3] there were few reports with respect to nitroalkenes,[4,5] likely because of the challenge in control of the reaction stereoselectivity. Since Hayashi's pioneering work was reported in the asymmetric addition to cyclic nitroalkenes using a rhodium/binap (Figure 1, **1**) catalyst in 2000,[4a] little progress has been made in the reaction of cyclic nitroalkenes,[4b,c] and related examples focusing on 2-nitrostyrenes were only reported with low levels of enantioselectivities (<50% ee).[5a−c] No significant progress has been made until Lin[5d] and Liao[5e] recently reported efficient rhodium-catalyzed asymmetric addition reactions to 2-nitroarylstyrenes using diene ligand **3** and sulfoxide−phosphine ligand **4**, respectively (Figure 1). Nevertheless, little study on 2-nitroalkylstyrenes[5d] and 2-nitroheteroarylstyrenes[5f] has yet been made. Given the wide applicability of nitro compounds in organic transformations,[6] it is still highly desirable to develop effective catalytic systems for asymmetric addition to a broad scope of nitroalkenes using the readily available ligands.

We have recently devolped a series of simple and modular chiral olefin−sulfoxide ligands for the Rh-catalyzed enantioselective addition of arylboronic acids to enones.[7] While other sulfinyl-based olefin ligands have also been successfully developed and applied in the Rh-catalyzed enantioselective addition reactions,[8] there still lie some drawbacks and limitations: (i) the sulfinyl moieties of the reported sulfinyl-based olefin ligands were mostly limited to *tert*-butyl substitution, and the incorporation of alkenes with other sulfinyl groups remains less explored;[8a] (ii) the application of the reported olefin−sulfoxide ligands were also mostly restricted to the Rh-catalyzed enantioselective addition of arylboronic acids to enones.[8a−g] To the best of our knowledge, there has been no report of such kind of ligands in the conjugate addition to nitroalkenes. Herein, we present our studies on the Rh-catalyzed asymmetric addition of organoboronic acids to challenging nitroalkenes using olefin−sulfoxide ligands bearing various sulfinyl groups.

RESULTS AND DISCUSSION

The olefin−sulfoxide ligands were prepared via a facile three-step synthesis by following a related literature procedure (Scheme 1).[7] Horner−Wadsworth−Emmons reaction of phosphonates **7** with corresponding aldehyde provided *trans*-stilbene derivatives **8**. Treatment of **8** with *n*BuLi at −78 °C, followed by addition of commercially available (*S*)-sulfinate derivatives, led to the desired ligands **5** in 43−71% yield.

Initially, we evaluated ligand **5a**[7] in Rh-catalyzed conjugate addition of *para*-anisylboronic acid **10** to *trans*-β-nitrostyrene **9**. The reaction was conducted at 100 °C in the presence of **5a** (5.5 mol %) under aqueous KOH/toluene for 12 h, yielding the corresponding product **11a** in both low yield (32%) and low enantioselectivity (14% ee) (Table 1, entry 1).

Ligands (Scheme 2, **5b**−**5e**) bearing different sulfinyl moieties were subsequently screened, and we were pleased to find that the reaction afforded improved yield (68%) and enantioselectivity (72% ee) (Table 1, entry 5) with ligand **5e** bearing a 2-methoxy-1-naphthyl sulfinyl moiety. Encouraged by the results, we next embarked on the synthesis of a series of olefin−sulfoxide ligands bearing 2-methoxy-1-naphthyl sulfinyl moieties (**5f**−**5t**).[9] When ligand **5f** was employed, which possesses an electron-donating *para*-methoxy group on the

Received: February 24, 2012
Published: March 24, 2012

   dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071−3081

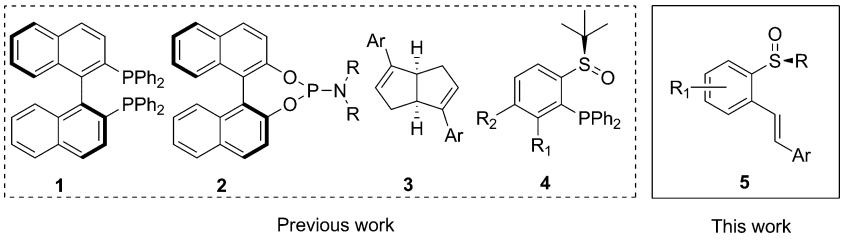


Figure 1. Ligands used in the asymmetric addition reaction of arylboronic acids to nitroalkenes.

Scheme 1. Synthesis of Olefin–Sulfoxide Ligands 5

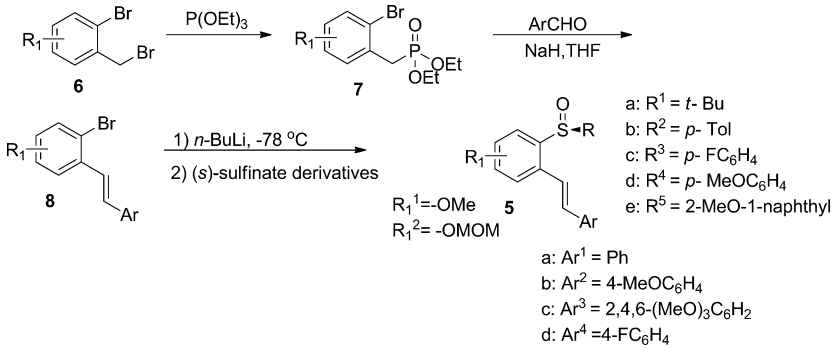
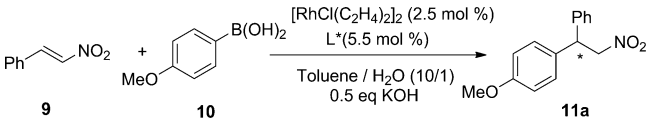


Table 1. Screening of Ligands in the Conjugate Addition[a]



entry	ligand	yield[b] (%)	ee[c] (%)
1	**5a**	32	14
2	**5b**	46	56
3	**5c**	50	7
4	**5d**	59	40
5	**5e**	68	72
6	**5f**	80	72
7	**5g**	87	69
8	**5h**	89	90
9	**5i**	88	84
10	**5j**	82	86
11	**5k**	80	79
12	**5l**	81	64
13	**5m**	87	83
14	**5n**	80	85
15	**5o**	81	80
16	**5p**	80	84
17	**5q**	70	82
18	**5r**	75	79
19	**5s**	77	66
20	**5t**	76	78
21[d]	**5h**	86	83

[a]The reaction was carried out with *trans*-β-nitrostyrene (0.30 mmol), *para*-anisylboronic acid (0.90 mmol), $[RhCl(C_2H_4)_2]_2$ (0.0075 mmol), ligand (0.0165 mmol, 1.1 equiv to Rh), and 0.75 M aq KOH (0.20 mL) in toluene (2.0 mL) at 100 °C for 12 h. [b]Yield based on *trans*-β-nitrostyrene. [c]Determined by HPLC analysis. [d]The reaction was conducted at 80 °C for 12 h.

terminal benzene ring, the catalytic reactivity further increased (80% yield), but the enantioselectivity (72% ee) remained (Table 1, entry 6). In comparison, ligand **5g** with a *para*-fluorine group on the terminal benzene ring resulted in higher yield (87%) and a slight decrease of enantioselectivity (69% ee) (Table 1, entry 7). At this point, we speculated that the electronic property of the substitutes at the olefin–sulfoxide ligands should have a significant effect on the reactivity and enantioselectivity.[10] Accordingly, the substitution effects on the central benzene ring moiety were carefully examined. Great improvement in enantioselectivity (Table 1, entry 8, 90% ee) was observed when a methoxy group was introduced into the 4-position of the central benzene moiety (ligand **5h**). Interestingly, ligand with an electron-donating group on the terminal benzene ring proved superior to its analogues with electron-withdrawing group in most cases (Table 1, entries 6–11) with exception to ligands **5l** and **5m** (Table 1, entries 12–13). However, further modification on the substituent failed to afford better results (Table 1, entries 14–20). In addition, decrease of the reaction temperature to 80 °C in the presence of ligand **5h** led to a loss in both yield and enantioselectivity (Table 1, entry 21).

After ligand **5h** was established as the optimal ligand, the reaction conditions were further explored (see Table 2). A survey of inorganic bases such as K_3PO_4, K_2HPO_4, KF, and organic base such as Et_3N did not improve the enantioselectivity of the reaction (Table 2, entries 1–4). When the reaction was conducted under aqueous KHF_2/toluene, where a potassium aryltrifluoroborate can be generated in situ,[5d] no increase of reactivity and enantioselectivity was observed (Table 2, entry 5). Morever, other solvents such as CH_2Cl_2, Et_2O, and DCE did not improve the reactivity and enantioselectivity (Table 2, entries 6–8). In contrast, no desired product was generated when water-soluble solvents such as THF, dioxane, and MeOH were used (Table 2, entries 9–11).

With the optimal reaction conditions in hand, we set out to define the scope of this reaction, a variety of representative boronic acids were tested with aromatic nitroalkenes (Table 3). The desired products were obtained in moderate to high yields (50–96%) and high enantioselectivities (82–91% ee). In general, the electronic properties of the substituent on the substrates did not affect the reaction stereoselectivity significantly. However, the steric hindrance of the substituents

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071–3081

Scheme 2. Olefin−Sulfoxide Ligands with Diverse Structures

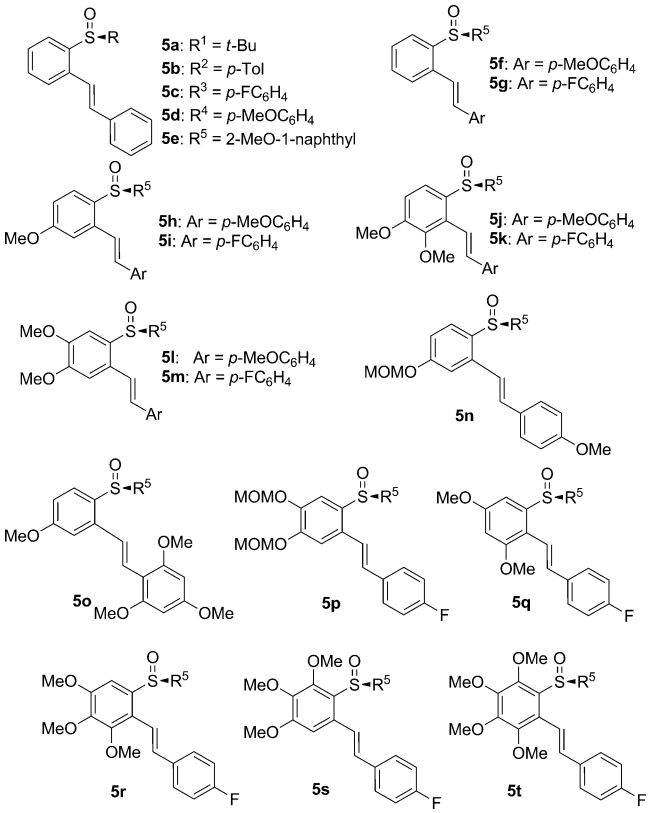


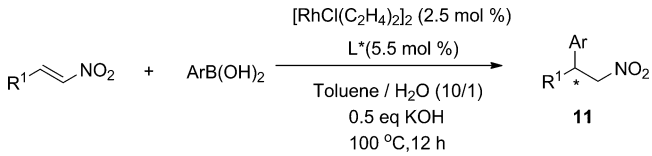
Table 2. Optimization of the Reaction Conditions[a]

entry	solvent	additive	yield[b] (%)	ee[c] (%)
1	toluene	K_3PO_4	80	79
2	toluene	K_2HPO_4	83	84
3	toluene	KF	83	84
4[d]	toluene	Et_3N	67	75
5[e]	toluene	KHF_2	81	83
6[f]	CH_2Cl_2	KOH	85	83
7[f]	Et_2O	KOH	84	82
8[g]	DCE	KOH	77	76
9	THF	KOH	trace	nd[h]
10	dioxane	KOH	trace	nd[h]
11	MeOH	KOH	trace	nd[h]

[a]The reaction was carried out with *trans*-β-nitrostyrene (0.30 mmol), *para*-anisylboronic acid (0.90 mmol), $[RhCl(C_2H_4)_2]_2$ (0.0075 mmol), ligand **5h** (0.0165 mmol, 1.1 equiv to Rh), and additive (0.75 M aq, 0.20 mL, 0.5 equiv) in the indicated solvent (2 mL) at 100 °C for 12 h unless otherwise stated. [b]Yield based on *trans*-β-nitrostyrene. [c]Determined by HPLC analysis. [d]Et_3N (22 μL, 0.5 equiv). [e]KHF_2 (4.5 M aq, 0.20 mL, 3 equiv). [f]The reaction proceeded at 40 °C. [g]The reaction proceeded at 80 °C. [h]Not determined.

on the aromatic ring had a significant impact on the activity, but little effect on the enantioselectivity, as in the reaction of 1-naphthylboronic acid and *o*-MeO-2-nitrostyrene (Table 3, entries 7−8 and entries 9−11). For electron-deficient nitrostyrenes, the electron-rich boronic acids had a slightly negative effect on the enantioselectivity, but a positive effect on the activity, for example, *p*-F-2-nitrostyrene (Table 3, entry 13, 83% yield, 87% ee versus entry 18, 90% yield, 87% ee) and *p*-CF_3-2-nitrostyrene (Table 3, entry 15, 79% yield, 87% ee versus entry 20, 85% yield, 82% ee).

Table 3. Scope of the Rh-Catalyzed Asymmetric Addition of Arylboronic Acids to 2-Nitroarylalkenes[a]



entry	R^1	Ar	yield[b] (%)	ee[c] (%)
1	Ph	4-$MeOC_6H_4$	89 (**11a**)	90 (*S*)
2	Ph	3-$MeOC_6H_4$	85 (**11b**)	91 (*S*)
3	Ph	3-MeC_6H_4	80 (**11c**)	86 (*S*)
4	Ph	4-FC_6H_4	85 (**11d**)	87 (*S*)
5	Ph	4-*t*BuC_6H_4	79 (**11e**)	85 (*S*)
6	Ph	3,4-diMeC_6H_3	86 (**11f**)	86 (*S*)
7	Ph	1-naph	55 (**11g**)	91 (*S*)
8	Ph	2-naph	83 (**11h**)	88 (*S*)
9	2-$MeOC_6H_4$	Ph	50 (**11i**)	84 (*R*)
10	3-$MeOC_6H_4$	Ph	76 (**11b′**)	85 (*R*)
11	4-$MeOC_6H_4$	Ph	85 (**11a′**)	88 (*R*)
12	4-MeC_6H_4	Ph	80 (**11j**)	87 (*R*)
13	4-FC_6H_4	Ph	83 (**11d′**)	87 (*R*)
14	4-ClC_6H_4	Ph	81 (**11k**)	88 (*R*)
15	4-$CF_3C_6H_4$	Ph	79 (**11l**)	87 (*R*)
16	3,4-di$MeOC_6H_3$	Ph	87 (**11m**)	87 (*R*)
17	4-$Me_2NC_6H_4$	Ph	81 (**11n**)	88 (*R*)
18	4-FC_6H_4	4-$MeOC_6H_4$	90 (**11o**)	87 (*S*)
19	4-BrC_6H_4	4-$MeOC_6H_4$	86 (**11p**)	85 (*S*)
20	4-$CF_3C_6H_4$	4-$MeOC_6H_4$	85 (**11q**)	82 (*S*)
21	2-naph	4-$MeOC_6H_4$	96 (**11r**)	90 (*S*)
22	3,4-di$MeOC_6H_3$	4-$MeOC_6H_4$	92 (**11s**)	88 (*S*)
23	4-BnO-3-$MeOC_6H_3$	4-$MeOC_6H_4$	77 (**11t**)	89 (*S*)
24	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	65 (**11u**)	90 (*S*)
25	3,5-diClC_6H_3	4-$MeOC_6H_4$	91 (**11v**)	89 (*S*)
26	3,4-di$MeOC_6H_3$	3-$MeOC_6H_4$	84 (**11w**)	89 (*S*)
27	4-BnO-3-$MeOC_6H_3$	3-$MeOC_6H_4$	80 (**11x**)	87 (*S*)
28	4-$Me_2NC_6H_4$	3-$MeOC_6H_4$	75 (**11y**)	91 (*S*)
29	3,5-diClC_6H_3	3-$MeOC_6H_4$	90 (**11z**)	85 (*S*)

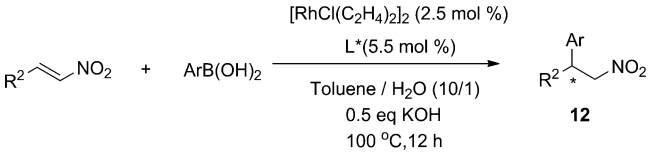
[a]The reaction was carried out with nitroalkenes (0.30 mmol), arylboronic acids (0.90 mmol), $[RhCl(C_2H_4)_2]_2$ (0.0075 mmol), ligand **5h** (0.0165 mmol, 1.1 equiv to Rh), and 0.75 M aq KOH (0.20 mL) in toluene (2.0 mL) at 100 °C for 12 h. [b]Yield based on nitroalkenes. [c]Determined by HPLC analysis.

In addition, like the one with a dimethylamino group, substrates bearing two alkoxyl or two chloro groups on the aromatic ring afforded the corresponding products with high ee-values (Table 3, entries 16, 17, and 22−29).

To further define the scope of this addition reaction, aliphatic nitroalkenes and heteroaryl nitroalkenes were next studied (Table 4). To our delight, when aliphatic and heteroaromatic nitroalkenes were subjected to the conjugate addition, the same level of enantioselectivity was also retained. It is worth mentioning that when it comes to challenging aliphatic nitroalkenes, higher enantioselecitivities were obtained than those in previously reported work (Table 4, entry 2, 85% ee versus 61% ee[5d] and entry 10, 89% ee versus 84% ee[5d]). Electron-poor boronic acids tended to give higher enantioselectivity (Table 4, entry 4, 88% ee and entry 7, 90% ee, respectively). In addition to aliphatic nitroalkenes, 2-nitroheteroarylstyrenes, such as (*E*)-2-(2-nitrovinyl)furan and (*E*)-2-(2-nitrovinyl)thiophene, were also applicable, and the desired products were obtained in good to high enantioselectivities (75−87% ee, Table 4, entries 12−16).

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071−3081

Table 4. Scope of the Rh-Catalyzed Asymmetric Addition of Arylboronic Acids to 2-Nitroalkylstyrenes and 2-Nitroheteroarylstyrenes[a]



entry	R^2	Ar	yield[b] (%)	ee[c] (%)
1	*n*Bu	Ph	61 (**12a**)	87 (*S*)
2	*n*Bu	4-MeOC$_6$H$_4$	78 (**12b**)	85 (*S*)
3	*n*Bu	4-MeC$_6$H$_4$	85 (**12c**)	87 (*S*)
4	*n*Bu	4-FC$_6$H$_4$	83 (**12d**)	88 (*S*)
5	*i*Pr	Ph	70 (**12e**)	86 (*S*)
6	*i*Pr	4-MeOC$_6$H$_4$	56 (**12f**)	87 (*S*)
7	*i*Pr	4-FC$_6$H$_4$	60 (**12g**)	90 (*S*)
8	*i*Pr	4-MeC$_6$H$_4$	85 (**12h**)	88 (*S*)
9	*c*-C$_6$H$_{11}$	Ph	81 (**12i**)	88 (*S*)
10	*c*-C$_6$H$_{11}$	4-MeOC$_6$H$_4$	65 (**12j**)	89 (*S*)
11	*c*-C$_6$H$_{11}$	4-MeC$_6$H$_4$	71 (**12k**)	90 (*S*)
12	2-furyl	4-MeOC$_6$H$_4$	57 (**12l**)	79
13	2-thienyl	4-MeOC$_6$H$_4$	84 (**12m**)	87
14	2-thienyl	3,4-diMeC$_6$H$_3$	60 (**12n**)	75
15	2-furyl	3,4-diMeOC$_6$H$_3$	63 (**12o**)	83
16	2-thienyl	3,4-diMeOC$_6$H$_3$	74 (**12p**)	86

[a]The reaction was carried out with nitroalkenes (0.30 mmol), arylboronic acids (0.90 mmol), $[RhCl(C_2H_4)_2]_2$ (0.0075 mmol), ligand **5h** (0.0165 mmol, 1.1 equiv to Rh), and 0.75 M aq KOH (0.20 mL) in toluene (2.0 mL) at 100 °C for 12 h. [b]Yield based on nitroalkenes. [c]Determined by HPLC analysis.

Compared to (*E*)-2-(2-nitrovinyl)furan, (*E*)-2-(2-nitrovinyl)-thiophene showed better reactivity and enantioselectivity in this reaction (Table 4, entries 13 and 16).

The stereochemical outcome of the Rh-complex catalyzed 1,4-addition can be rationalized as depicted in Figure 2. There tends to be a $\pi-\pi$ stacking between the phenyl ring of the ligand terminus and the metalated phenyl ring of phenylboronic acid in the reaction transition state. The Rh-complex recognizes the alkene moiety of the nitroalkenes as a result of the steric repulsion between the 2-methoxy-1-naphthyl group of the ligand and nitro group of the nitroalkene. Thus, coordination of the nitroalkene from the less steric hindered side is more favorable, which leads to the *S* isomer and is consistent with the observed stereochemistry.

In conclusion, we have developed an efficient rhodium/olefin–sulfoxide catalyzed asymmetric conjugate addition of organoboronic acids to nitroalkenes with moderate to high yields and good enantioselectivities. A wide range of nitroalkenes can be tolerated in this process. In particular, alkyl- and heteroaryl-substituted nitroalkenes are applicable substrates for this asymmetric addition. The recently developed olefin–sulfoxide ligands were successfully extended to asymmetric addition to nitroalkenes and provided an alternative method for the synthesis of chiral nitro compounds, where 2-methoxy-1-naphthyl sulfinyl-based olefin ligands have proved to be more effective than the *tert*-butyl sulfinyl-based ones. Further investigations on the reaction mechanism and extensions of olefin–sulfoxide hybrid ligands to other asymmetric catalysis are currently underway.

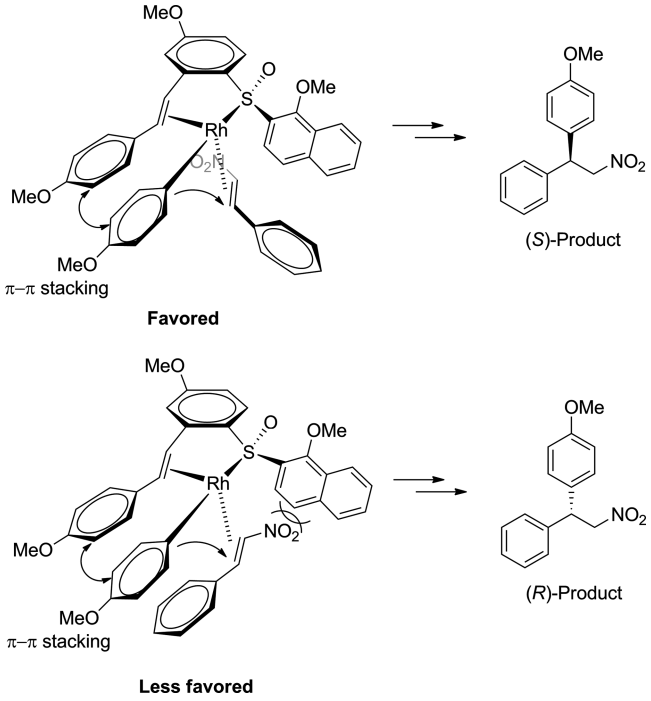


Figure 2. Proposed stereochemical pathway for the asymmetric 1,4-addition.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.2 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (300–400 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

Commercially available reagents were used throughout without further purification other than those detailed below. THF, Et_2O and toluene were distilled over sodium benzopheneone ketyl under nitrogen. Methylene chloride was distilled over calcium hydride. Arylboronic acids were recrystallized from water.

General Procedures for the Synthesis of *trans*-Stilbene Derivatives 8. To a suspension of NaH (60% in oil, 0.44 mg, 11.0 mmol) in THF (5 mL) at 0 °C, diethyl 2-bromobenzylphosphonate derivatives 7 (10.0 mmol) prepared by the similar procedure[11] from 1-bromo-2-(bromomethyl)benzene derivatives **6** was slowly added. The resulting suspension was stirred for additional 1 h at room temperature. The reaction mixture was cooled to 0 °C, then a solution of aldehyde (10.0 mmol) in THF (5 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight, the reaction was quenched with ice water, and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate as eluent) to give products **8**.

*(E)-1-Bromo-4-methoxy-2-(4-methoxystyryl)benzene (**8a**).* White solid: 2.23 g, 70% yield; mp 29–31 °C; R_f = 0.38 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 16.2 Hz, 1H), 7.15 (d, *J* = 3.0 Hz, 1H), 6.96 (d, *J* = 16.2 Hz, 1H), 6.90 (t, *J* = 5.7 Hz, 2H), 6.67 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.1, 138.2, 133.6, 131.1, 129.9, 128.3, 125.5, 114.9, 114.8, 114.3, 111.6, 55.6, 55.4; HRMS (ESI, *m/z*) calcd for $C_{16}H_{15}BrO_2Na$ $[M + Na]^+$ 341.0153, found 341.0161.

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071–3081

*(E)-1-Bromo-2-(4-fluorostyryl)-4-methoxybenzene (**8b**).* White solid: 2.30 g, 75% yield; mp 66−68 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.4 Hz, 2H), 7.46 (d, J = 8.8 Hz, 1H), 7.38 (dd, J = 14.5, 5.5 Hz, 2H), 7.33−7.25 (m, 1H), 7.18 (s, 1H), 7.02 (d, J = 16.1 Hz, 1H), 6.71 (dd, J = 8.7, 2.6 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.9, 137.1, 133.7, 131.7, 128.9, 128.3, 127.7, 127.0, 115.2, 115.1, 111.9, 55.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.13 (s, 1F); HRMS (ESI, m/z) calcd for $C_{15}H_{12}BrFONa$ $[M + Na]^+$ 328.9953, found 328.9961.

*(E)-1-Bromo-3,4-dimethoxy-2-(4-methoxystyryl)benzene (**8c**).* Colorless oil: 2.41 g, 69% yield; R_f = 0.33 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 16.5 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 16.5 Hz, 1H), 6.89 (d, J = 8.2 Hz, 2H), 6.65 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.7, 148.2, 135.0, 131.6, 130.6, 128.2, 128.0, 121.8, 115.3, 114.2, 111.8, 60.0, 56.1, 55.3; HRMS (ESI, m/z) calcd for $C_{17}H_{17}BrO_3Na$ $[M + Na]^+$ 371.0259, found 371.0268.

*(E)-1-Bromo-2-(4-fluorostyryl)-3,4-dimethoxybenzene (**8d**).* White solid: 2.40 g, 71% yield; mp 53−55 °C; R_f = 0.37 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.9, 5.7 Hz, 2H), 7.39 (d, J = 16.5 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.07 (dd, J = 20.0, 12.1 Hz, 3H), 6.70 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5, 152.8, 148.4, 134.4, 134.1 134.0, 131.3, 128.5, 128.4, 128.3, 123.8, 123.7, 115.8, 115.6, 115.3, 112.3, 60.2, 56.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.39 (s, 1F); HRMS (ESI, m/z) calcd for $C_{16}H_{14}BrFO_2Na$ $[M + Na]^+$ 359.0059, found 359.0061.

*(E)-1-Bromo-4,5-dimethoxy-2-(4-methoxystyryl)benzene (**8e**).* White solid: 3.01 g, 86% yield; mp 93−95 °C; R_f = 0.15 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.6 Hz, 2H), 7.29−7.21 (m, 1H), 7.13 (s, 1H), 7.03 (s, 1H), 6.94−6.83 (m, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.2, 148.8, 130.1, 129.8, 129.2, 128.0, 125.4, 115.6, 114.7, 114.3, 108.7, 56.3, 56.2, 55.5; HRMS (ESI, m/z) calcd for $C_{17}H_{17}BrO_3Na$ $[M + Na]^+$ 371.0259, found 371.0262.

*(E)-1-Bromo-2-(4-fluorostyryl)-4,5-dimethoxybenzene (**8f**).* White solid: 2.56 g, 76% yield; mp 107−109 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.6, 5.7 Hz, 2H), 7.30 (d, J = 16.2 Hz, 1H), 7.12 (s, 1H), 7.10−7.01 (m, 3H), 6.88 (d, J = 16.1 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.4, 149.6, 148.8, 133.6, 133.5, 129.3, 128.4, 128.3, 128.2, 127.3, 127.2, 115.9, 115.7, 125.6, 115.0, 108.9, 56.3, 56.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.50 (s, 1F); HRMS (ESI, m/z) calcd for $C_{16}H_{14}BrFO_2Na$ $[M + Na]^+$ 359.0059, found 359.0055.

*(E)-1-Bromo-4-(methoxymethoxy)-2-(4-methoxystyryl)benzene (**8g**).* Colorless oil: 2.36 g, 68% yield; R_f = 0.29 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 14.3, 8.6 Hz, 3H), 7.32 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 16.2 Hz, 1H), 6.97 (d, J = 16.1 Hz, 1H), 6.89 (d, J = 8.3 Hz, 2H), 6.80 (dd, J = 8.8, 2.1 Hz, 1H), 5.17 (s, 2H), 3.81 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.8, 138.3, 133.7, 131.3, 130.4, 129.8, 128.3, 125.3, 116.9, 116.1, 114.3, 114.1, 113.7, 94.7, 56.2, 55.4; HRMS (ESI, m/z) calcd for $C_{17}H_{17}BrO_3Na$ $[M + Na]^+$ 371.0259, found 371.0260.

*(E)-2-(2-Bromo-5-methoxystyryl)-1,3,5-trimethoxybenzene (**8h**).* White solid: 2.15 g, 57% yield; mp 90−92 °C; R_f = 0.21 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 16.5 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 16.4 Hz, 1H), 7.23 (d, J = 3.0 Hz, 1H), 6.64 (dd, J = 8.7, 3.0 Hz, 1H), 6.16 (s, 2H), 3.89 (s, 6H), 3.83 (d, J = 2.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 159.9, 159.1, 140.4, 133.4, 128.7, 122.5, 115.0, 113.9, 111.7, 108.1, 90.9, 55.9, 55.7, 55.5; HRMS (ESI, m/z) calcd for $C_{18}H_{19}BrO_4Na$ $[M + Na]^+$ 401.0364, found 401.0362.

*(E)-Bromo-2-(4-fluorostyryl)-4,5-bis(methoxymethoxy)benzene (**8i**).* White solid: 3.36 g, 85% yield; mp 69−71 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.4, 5.6 Hz, 2H), 7.41 (d, J = 27.4 Hz, 2H), 7.32−7.22 (m, 1H), 7.04 (t, J = 8.6 Hz, 2H), 6.88 (d, J = 16.2 Hz, 1H), 5.27 (s, 2H), 5.23 (s, 2H), 3.54 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.4, 147.6, 147.0, 133.5, 133.4, 131.1, 129.1, 128.4, 128.3, 127.0, 126.9, 120.7, 116.5, 115.9, 115.7, 114.2, 95.8, 95.6, 56.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.39 (s, 1F); HRMS (ESI, m/z) calcd for $C_{18}H_{18}BrFO_4Na$ $[M + Na]^+$ 419.0270, found 419.0268.

*(E)-1-Bromo-2-(4-fluorostyryl)-3,5-dimethoxybenzene (**8j**).* White solid: 0.78 g, 23% yield; mp 93−95 °C; R_f = 0.34 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.4, 5.6 Hz, 2H), 7.29 (t, J = 13.2 Hz, 1H), 7.15 (d, J = 16.4 Hz, 1H), 7.03 (t, J = 8.6 Hz, 2H), 6.80 (d, J = 2.2 Hz, 1H), 6.46 (d, J = 2.0 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.5, 159.5, 134.8, 134.7, 132.2, 128.1, 128.0, 126.0, 124.2, 124.1, 119.2, 115.7, 115.5, 109.8, 98.8, 55.9, 55.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −115.49 (s, 1F); HRMS (ESI, m/z) calcd for $C_{16}H_{14}BrFO_2Na$ $[M + Na]^+$ 359.0059, found 359.0058.

*(E)-1-Bromo-2-(4-fluorostyryl)-3,4,5-trimethoxybenzene (**8k**).* White solid: 1.61 g, 44% yield; mp 47−49 °C; R_f = 0.26 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.45 (m, 2H), 7.32 (d, J = 16.4 Hz, 1H), 7.10−7.01 (m, 3H), 6.96 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.3, 153.1, 152.9, 142.6, 134.4, 132.6, 128.1, 128.0, 124.2, 123.9, 118.6, 115.8, 115.6, 112.6, 61.1, 60.7, 56.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.92 (s, 1F); HRMS (ESI, m/z) calcd for $C_{17}H_{16}BrFO_3Na$ $[M + Na]^+$ 389.0165, found 389.0167.

*(E)-2-Bromo-1-(4-fluorostyryl)-3,4,5-trimethoxybenzene (**8l**).* White solid: 3.13 g, 85% yield; mp 76−79 °C; R_f = 0.21 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.47 (m, 2H), 7.37 (d, J = 16.1 Hz, 1H), 7.11−7.02 (m, 2H), 6.98 (s, 1H), 6.89 (d, J = 16.1 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5, 152.9, 151.2, 143.2, 133.3, 132.8, 129.6, 128.5, 128.4, 127.7, 127.6, 115.9, 115.8, 105.3, 61.4, 61.1, 56.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.13 (s, 1F); HRMS (ESI, m/z) calcd for $C_{17}H_{16}BrFO_3Na$ $[M + Na]^+$ 389.0165, found 389.0174.

*(E)-1-Bromo-2-(4-fluorostyryl)-3,4,5,6-tetramethoxybenzene (**8m**).* White solid: 3.06 g, 77% yield; mp 71−73 °C; R_f = 0.34 (petroleum ether/ethyl acetate = 15/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.47 (m, 2H), 7.31 (d, J = 16.5 Hz, 1H), 7.13−7.03 (m, 3H), 3.96 (d, J = 3.1 Hz, 6H), 3.87 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.4, 149.0, 147.7, 147.0, 146.8, 134.2, 134.1, 133.6, 128.3, 128.2, 126.8, 123.7, 115.8, 115.6, 114.3, 61.6, 61.5, 61.0, 60.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.60 (s, 1F); HRMS (ESI, m/z) calcd for $C_{18}H_{18}BrFO_4Na$ $[M + Na]^+$ 419.0270, found 419.0269.

General Procedures for the Synthesis of Ligands 5. At −78 °C, *n*-BuLi (5.25 mmol) was added dropwise to a solution of **8** (5.0 mmol) in THF (15 mL). The resulting mixture was stirred for 1 h at −78 °C, and a solution of (*S*)-(L)-menthyl 2-methoxy-1-naphthalensulfinate[12] (1.89 g, 5.25 mmol) in THF (10 mL) was slowly added. After stirring for additional 1 h at −78 °C, the solution was allowed to warm to room temperature, stirred for another 1 h, and then quenched with cold saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by flash chromatography (petroleum ether/ethyl acetate as eluent) to afford the ligands **5**.

The synthesis of **5a** and **5g** has been reported. Please see reference 7 for details.

*(S,E)-1-Styryl-2-(p-tolylsulfinyl)benzene (**5b**).*[8e] Following the similar procedure with (1*S*,2*R*,5*S*)-(+)-menthyl-(*S*)-*p*-Tol-sulfinate in place of (*S*)-(L)-menthyl 2-methoxy-1-naphthalensulfinate. White solid: 0.97 g, 61% yield; R_f = 0.44 (petroleum ether/ethyl acetate = 2/1); mp 80−81 °C; $[\alpha]^{20}_D$ = −278.7 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 3.7 Hz, 1H), 7.53 (s, 1H), 7.47−7.33 (m, 7H), 7.29 (t, J = 7.4 Hz, 2H), 7.18 (dd, J = 23.3, 7.7 Hz, 1H), 7.07 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 16.0 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.1, 141.5, 136.6, 135.9, 132.5, 131.1, 130.0, 128.9, 128.6, 128.5, 126.9, 126.1, 125.3, 124.6, 123.0, 21.4; HRMS (ESI, m/z) calcd for $C_{21}H_{18}OSNa$ $[M + Na]^+$ 341.0976, found 341.0970.

dx.doi.org/10.1021/jo3003562 | *J. Org. Chem.* 2012, 77, 3071−3081

*(S,E)-1-(4-Fluorophenylsulfinyl)-2-styrylbenzene (**5c**).* Following the similar procedure with 1,2:5,6-di-*O*-isopropylidene-a-D-glucofuranosyl (*S*)-4-fluorophenylsulfinate[13] in place of (*S*)-(L)-menthyl 2-methoxy-1-naphthalensulfinate. Colorless oil: 0.84 g, 52% yield; R_f = 0.31 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{20}_D$ = +45.6 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.93 (m, 1H), 7.68−7.61 (m, 1H), 7.61−7.44 (m, 7H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.12−6.94 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 136.6, 136.2, 133.0, 131.5, 129.0, 128.8, 128.7, 127.6, 127.5, 126.9, 126.4, 124.6, 122.9, 116.8, 116.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −109.03 (s, 1F); HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{15}FOSNa$ $[M + Na]^+$ 345.0725, found 345.0737.

*(S,E)-1-(4-Methoxyphenylsulfinyl)-2-styrylbenzene (**5d**).* Following the similar procedure with (*S*)-(L) menthyl *p*-methoxybenzenesulfinate[14] in place of (*S*)-(L)-menthyl 2-methoxy-1-naphthalensulfinate. White solid: 0.77 g, 46% yield; mp 101−103 °C; R_f = 0.29 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{25}_D$ = −326.6 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.01 (m, 1H), 7.68−7.58 (m, 1H), 7.54−7.49 (m, 2H), 7.46 (dd, *J* = 10.0, 6.5 Hz, 5H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.91−6.83 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 143.1, 136.7, 136.5, 135.9, 132.5, 131.1, 129.0, 128.7, 128.5, 127.6, 126.9, 126.2, 124.4, 123.1, 114.9, 55.6; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{18}O_2SNa$ $[M + Na]^+$ 357.0925, found 357.0919.

*(R,E)-2-Methoxy-1-(2-styrylphenylsulfinyl)naphthalene (**5e**).* White solid: 0.98 g, 51% yield; mp 64−66 °C; R_f = 0.44 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −136.4 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.60−7.47 (m, 3H), 7.39 (dd, *J* = 14.9, 7.3 Hz, 2H), 7.23−7.15 (m, 3H), 7.09−6.98 (m, 4H), 6.69 (d, *J* = 15.9 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 141.5, 136.7, 135.2, 134.9, 132.4, 131.5, 130.0, 129.3, 129.0, 128.6, 128.5, 128.0, 127.4, 126.8, 126.7, 125.8, 124.5, 124.0, 122.8, 113.4, 56.6; HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{20}O_2SNa$ $[M + Na]^+$ 407.1082, found 407.1089.

*(R,E)-2-Methoxy-1-(2-(4-methoxystyryl)phenylsulfinyl)-naphthalene (**5f**).* White solid: 1.24 g, 60% yield; mp 81−84 °C; R_f = 0.39 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −180.4 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.6 Hz, 1H), 8.41−8.31 (m, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.59−7.45 (m, 3H), 7.38 (td, *J* = 7.3, 3.1 Hz, 2H), 7.08 (d, *J* = 9.1 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 157.6, 141.3, 135.1, 132.4, 130.9, 129.9, 129.6, 129.3, 129.0, 128.5, 128.1, 127.0, 126.6, 125.5, 124.4, 122.8, 121.7, 113.9, 113.5, 56.6, 55.4; HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}O_3SNa$ $[M + Na]^+$ 437.1187, found 437.1190.

*(R,E)-2-Methoxy-1-(4-methoxy-2-(4-methoxystyryl)-phenylsulfinyl)naphthalene (**5h**).* White solid: 1.15 g, 52% yield; mp 116−119 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −216.6 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.6 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 4H), 6.96 (d, *J* = 15.9 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 159.7, 157.4, 136.8, 134.9, 132.5, 131.2, 130.0, 129.6, 129.4. 128.9, 128.5, 128.4, 128.2, 124.4, 122.9, 121.8, 114.0, 113.4, 112.9, 110.7, 110.1, 56.8, 55.8, 55.5; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{24}O_4SNa$ $[M + Na]^+$ 467.1293, found 467.1286.

*(R,E)-1-(2-(4-Fluorostyryl)-4-methoxyphenylsulfinyl)-2-methoxy-naphthalene (**5i**).* White solid: 1.43 g, 66% yield; mp 152−155 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{24}_D$ = −161.5 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.43−7.33 (m, 1H), 7.13−6.94 (m, 6H), 6.89 (t, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.4, 161.2, 157.4, 136.3, 134.9, 133.2, 132.9, 132.4, 130.4, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 124.5, 123.8, 123.7, 122.8, 115.6, 115.4, 113.5, 113.2, 111.0, 56.8, 55.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.96 (s, 1F); HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{21}FO_3SNa$ $[M + Na]^+$ 455.1093, found 455.1089.

*(R,E)-1-(3,4-Dimethoxy-2-(4-methoxystyryl)phenylsulfinyl)-2-methoxynaphthalene (**5j**).* White solid: 1.28 g, 54% yield; mp 60−62 °C; R_f = 0.22 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{26}_D$ = −101.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.38−7.25 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.04−6.97 (m, 3H), 6.88 (d, *J* = 16.3 Hz, 1H), 6.76 (t, *J* = 5.7 Hz, 2H), 6.49 (d, *J* = 16.3 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.65 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 157.5, 154.3, 146.9, 135.4, 134.7, 134.3, 132.3, 130.2, 130.1, 129.3, 128.6, 128.1, 128.0, 124.3, 123.1, 123.0, 120.5, 117.9, 113.9, 113.1, 110.2, 60.2, 56.4, 56.1, 55.5; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{26}O_5SNa$ $[M + Na]^+$ 497.1399, found 497.1408.

*(R,E)-1-(2-(4-Fluorostyryl)-3,4-dimethoxyphenylsulfinyl)-2-methoxy-naphthalene (**5k**).* White solid: 1.45 g, 63% yield; mp 76−78 °C; R_f = 0.24 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −63.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.75−7.63 (m, 1H), 7.38−7.27 (m, 2H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.04−6.97 (m, 3H), 6.93−6.83 (m, 3H), 6.53 (d, *J* = 16.3 Hz, 1H), 3.93 (s, 3H), 3.66 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.1, 157.4, 154.3, 147.0, 134.9, 134.6, 134.3, 133.5, 132.3, 129.2, 128.7, 128.2, 128.1, 124.3, 123.2, 122.9, 119.8, 115.4, 115.2, 113.1, 110.5, 60.2, 56.4, 56.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.44 (s, 1F); HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{23}FO_4SNa$ $[M + Na]^+$ 485.1199, found 485.1204.

*(R,E)-1-(4,5-Dimethoxy-2-(4-methoxystyryl)phenylsulfinyl)-2-methoxynaphthalene (**5l**).* White solid: 1.18 g, 50% yield; mp 100−103 °C; R_f = 0.12 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −165.3 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.7 Hz, 1H), 7.95−7.83 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.62−7.52 (m, 1H), 7.40 (p, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 1H), 7.02−6.94 (m, 3H), 6.94−6.85 (m, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 4.05 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 157.4, 150.5, 148.8, 135.0, 133.2, 132.4, 129.8, 129.3, 129.1, 129.0, 128.5, 128.1, 127.9, 124.5, 122.8, 121.5, 114.0, 113.4, 109.2, 107.8, 56.8, 56.5, 56.2, 55.4; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{26}O_5SNa$ $[M + Na]^+$ 497.1399, found 497.1398.

*(R,E)-1-(2-(4-Fluorostyryl)-4,5-dimethoxyphenylsulfinyl)-2-methoxy-naphthalene (**5m**).* White solid: 1.57 g, 68% yield; mp 175−177 °C; R_f = 0.14 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = −151.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.6 Hz, 1H), 7.94−7.83 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.55 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.44−7.36 (m, 1H), 7.10 (d, *J* = 9.1 Hz, 1H), 6.99−6.84 (m, 6H), 6.58 (d, *J* = 15.9 Hz, 1H), 4.06 (s, 3H), 3.93 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 160.9, 157.4, 150.5, 149.1, 135.0, 133.6, 133.1, 132.4, 129.3, 129.0, 128.5, 128.3, 128.2, 128.1, 127.5, 124.5, 123.5, 122.6, 115.6, 115.4, 113.5, 109.2, 107.9, 56.7, 56.5, 56.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.45 (s, 1F); HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{23}FO_4SNa$ $[M + Na]^+$ 485.1199, found 485.1193.

*(R,E)-2-Methoxy-1-(4-(methoxymethoxy)-2-(4-methoxystyryl)-phenylsulfinyl)naphthalene (**5n**).* White solid: 1.16 g, 49% yield; mp 95−97 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{26}_D$ = −300.7 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.7 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.17−7.11 (m, 2H), 7.07 (d, *J* = 9.1 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 15.8 Hz, 1H), 5.20 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 158.9, 157.3, 136.7, 134.9, 134.0, 132.3, 131.2, 129.4, 129.3, 128.9, 128.4, 128.2, 124.4, 123.0, 122.8, 121.4, 115.0, 113.9, 113.3, 112.6, 94.5, 56.7, 56.3, 55.4; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{26}O_5SNa$ $[M + Na]^+$ 497.1399, found 497.1381.

*(R,E)-2-Methoxy-1-(4-methoxy-2-(2,4,6-trimethoxystyryl)-phenylsulfinyl)naphthalene (**5o**).* White solid: 1.08 g, 43% yield; mp 68−70 °C; R_f = 0.22 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{26}_D$ = −150.9

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071−3081

(c = 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.7 Hz, 1H), 8.15 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 16.1 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 9.1 Hz, 1H), 6.96 (dd, J = 23.3, 14.0 Hz, 3H), 6.07 (s, 2H), 3.83 (d, J = 3.9 Hz, 6H), 3.70 (s, 3H), 3.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 160.8, 159.6, 157.0, 139.8, 134.2, 133.0, 132.8, 129.3, 128.5, 128.4, 127.8, 125.7, 124.2, 123.4, 123. 2, 113.3, 112.5, 110.9, 108.0, 90.6, 90.5, 56.3, 55.7, 55.5, 55.4, 55.1; HRMS (ESI, m/z) calcd for $C_{29}H_{28}O_6SNa$ $[M + Na]^+$ 527.1504, found 527.1498.

*(R,E)-1-(2-(4-Fluorostyryl)-4,5-bis(methoxymethoxy)phenylsulfinyl)-2-methoxynaphthalene (**5p**).* White solid: 1.85 g, 71% yield; mp 105−107 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{26}_D$ = −133.3 (c = 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 8.6 Hz, 1H), 8.14 (s, 1H), 7.87 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.10 (d, J = 9.1 Hz, 1H), 7.03−6.85 (m, 5H), 6.58 (d, J = 15.9 Hz, 1H), 5.45 (d, J = 6.6 Hz, 1H), 5.31 (d, J = 6.6 Hz, 1H), 5.27 (s, 2H), 3.80 (s, 3H), 3.57 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.2, 157.5, 149.1, 146.8, 135.0, 133.1, 132.4, 129.3, 129.1, 129.0, 128.5, 128.3, 128.2, 124.4, 123.2, 122.8, 115.6, 115.3, 115.0, 113.4, 113.1, 95.6, 95.5, 56.7, 56.5, 56.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.40 (s, 1F); HRMS (ESI, m/z) calcd for $C_{29}H_{28}FO_6S$ $[M + H]^+$ 523.1591, found 523.1589.

*(R,E)-1-(2-(4-Fluorostyryl)-3,5-dimethoxyphenylsulfinyl)-2-methoxynaphthalene (**5q**).* White solid: 1.38 g, 60% yield; mp 131−133 °C; R_f = 0.37 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = +23.9 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.6 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.72 (t, J = 7.2 Hz, 1H), 7.65 (s, 1H), 7.34 (dt, J = 22.7, 7.2 Hz, 2H), 7.02 (d, J = 9.1 Hz, 1H), 6.92−6.79 (m, 5H), 6.53 (s, 1H), 6.22 (d, J = 16.4 Hz, 1H), 4.00 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 159.6, 158.7, 145.3, 135.0, 132.7, 132.3, 129.2, 128.8, 128.4, 128.0, 127.9, 124.4, 122.9, 120.2, 116.8, 115.3, 115.1, 113.2, 102.3, 100.8, 56.4, 56.1, 55.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −115.36 (s, 1F); HRMS (ESI, m/z) calcd for $C_{27}H_{23}FO_4SNa$ $[M + Na]^+$ 485.1199, found 485.1198.

*(R,E)-1-(2-(4-Fluorostyryl)-3,4,5-trimethoxyphenylsulfinyl)-2-methoxynaphthalene (**5r**).* White solid: 1.35 g, 55% yield; mp 46−48 °C; R_f = 0.26 (petroleum ether/ethyl acetate = 1/1); $[\alpha]^{25}_D$ = +8.0 (c = 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 7.88 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.41 (dt, J = 23.2, 7.2 Hz, 2H), 7.10 (d, J = 9.1 Hz, 1H), 6.92 (t, J = 6.9 Hz, 2H), 6.86 (t, J = 8.5 Hz, 2H), 6.81 (d, J = 16.2 Hz, 1H), 6.50 (d, J = 16.2 Hz, 1H), 4.06 (s, 3H), 3.91 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.0, 157.7, 152.7, 137.8, 135.0, 133.7, 133.2, 132.4, 129.2, 128.8, 128.4, 128.1, 128.0, 124.4, 122.9, 121.9, 119.8, 119.7, 115.4, 115.2, 113.2, 106.1, 61.2, 60.7, 56.6, 56.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.85 (s, 1F); HRMS (ESI, m/z) calcd for $C_{28}H_{25}FO_5SNa$ $[M + Na]^+$ 515.1304, found 515.1301.

*(S,E)-1-(6-(4-Fluorostyryl)-2,3,4-trimethoxyphenylsulfinyl)-2-methoxynaphthalene (**5s**).* White solid: 1.33 g, 54% yield; mp 89−91 °C; R_f = 0.27 (petroleum ether/ethyl acetate = 2/1); $[\alpha]^{20}_D$ = +18.0 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, J = 8.7 Hz, 1H), 8.50 (d, J = 16.2 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.54−7.46 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 9.1 Hz, 1H), 7.03 (t, J = 8.4 Hz, 2H), 6.98 (s, 1H), 6.93 (d, J = 16.2 Hz, 1H), 3.95 (s, 3H), 3.75(s, 3H), 3.72 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.3, 155.5, 155.0, 151.7, 141.6, 135.3, 133.8, 133.5, 133.4, 128.7, 128.4, 128.4, 128.3, 127.9, 127.5, 125.6, 125.5, 124.3, 123.7, 115.9, 115.7, 113.1, 104.3, 60.9, 60.4, 56.6, 56.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.65 (s, 1F); HRMS (ESI, m/z) calcd for $C_{28}H_{25}FO_5SNa$ $[M + Na]^+$ 515.1304, found 515.1299.

*(S,E)-1-(2-(4-Fluorostyryl)-3,4,5,6-tetramethoxyphenylsulfinyl)-2-methoxynaphthalene (**5t**).* White solid: 1.56 g, 60% yield; mp 49−52 °C; R_f = 0.17 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{24}_D$ = −53.4 (c = 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 16.5 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.56 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H), 7.52−7.44 (m, 2H), 7.43−7.30 (m, 2H), 7.13 (d, J = 9.0 Hz, 1H), 7.06−6.97 (m, 2H), 3.97 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.3, 154.4, 150.2, 148.5, 147.9, 145.7, 134.5, 133.8, 133.3, 133.2, 130.3, 129.5, 128.4, 128.3, 128.2, 127.4, 124.3, 123.6, 120.7, 115.7, 115.5, 114.8, 112.8, 61.4, 61.2, 60.7, 60.6, 56.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −115.05 (s, 1F); HRMS (ESI, m/z) calcd for $C_{29}H_{27}FO_6SNa$ $[M + Na]^+$ 545.1410, found 545.1398.

General Procedure for the Asymmetric Conjugate Addition of Arylboronic Acids to Nitroalkenes. Under nitrogen atmosphere, a mixture of $[RhCl(C_2H_4)_2]_2$ (2.9 mg, 0.0075 mmol) and **5h** (7.4 mg, 0.0165 mmol) in 1 mL of toluene was stirred at room temperature for 1 h, at which time arylboronic acid (0.90 mmol) was added, followed by nitroalkene (0.30 mmol), aqueous KOH (0.75 M in H_2O, 0.20 mL, 0.15 mmol), and toluene (1 mL). The reaction was stirred at 100 °C for 12 h. When the reaction was over, the reaction mixture was concentrated in vacuo and purified by silica gel flash column chromatography (petroleum ether/ethyl acetate as eluent) to afford the product.

*1-Methoxy-4-(2-nitro-1-phenylethyl)benzene (**11a**).*[5d] Colorless oil: 69 mg, 89% yield, 90% ee; R_f = 0.31 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −10.8 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 18.1 min (major) and 21.2 min (minor); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.13 (m, 5H), 7.14 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 4.92 (d, J = 8.3 Hz, 2H), 4.85 (q, J = 8.3 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 139.7, 131.3, 129.1, 128.8, 127.7, 127.6, 114.5, 79.5, 55.3, 48.3.

*1-Methoxy-4-(2-nitro-1-phenylethyl)benzene (**11a′**).*[5d] Colorless oil: 66 mg, 85% yield, 88% ee; R_f = 0.31 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{25}_D$ = +8.9 (c = 1.1, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (72 bar), t_R = 18.1 min (minor) and 20.0 min (major).

*1-Methoxy-3-(2-nitro-1-phenylethyl)benzene (**11b**).*[5e] Colorless oil: 65 mg, 85% yield, 91% ee; R_f = 0.33 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = +1.7 (c = 1.3, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 50/50, flow = 1.0 mL/min (79 bar), t_R = 31.0 min (minor) and 64.7 min (major); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 2H), 7.28−7.21 (m, 4H), 6.89−6.72 (m, 3H), 5.01−4.92 (m, 2H), 4.92−4.82 (m, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 140.9, 139.2, 130.2, 129.2, 127.8, 119.9, 114.1, 112.6, 79.3, 55.3, 49.0.

*1-Methoxy-3-(2-nitro-1-phenylethyl)benzene (**11b′**).*[5e] Colorless oil: 59 mg, 76% yield, 85% ee; R_f = 0.33 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −3.2 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 50/50, flow = 1.0 mL/min (78 bar), t_R = 31.6 min (major) and 59.7 min (minor).

*1-Methyl-3-(2-nitro-1-phenylethyl)benzene (**11c**).* Colorless oil: 58 mg, 80% yield, 86% ee; R_f = 0.19 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = +1.5 (c = 0.9, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 50/50, flow = 1.0 mL/min (79 bar), t_R = 14.8 min (major) and 18.6 min (minor); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.28 (m, 2H), 7.27−7.18 (m, 4H), 7.07−7.02 (m, 3H), 5.04−4.91 (m, 2H), 4.91−4.81 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 139.2, 138.9, 129.1, 129.0, 128.6, 128.5, 127.8, 127.7, 124.7, 79.4, 49.1, 21.6; HRMS (EI, m/z) calcd for $C_{15}H_{15}NO_2$ $[M]^+$ 241.1103, found 241.1097.

*1-Fluoro-4-(2-nitro-1-phenylethyl)benzene (**11d**).*[5d] White solid: 63 mg, 85% yield, 87% ee; mp 92−94 °C; R_f = 0.29 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −9.6 (c = 1.1, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (66 bar), t_R = 13.6 min (major) and 25.6 min (minor); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 2H), 7.30−7.24 (m, 1H), 7.24−7.18 (m, 4H), 7.06−6.96 (m, 2H), 5.05−4.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 139.1, 135.1, 129.5, 129.4, 129.3, 127.9, 127.7, 116.2, 116.0, 79.4, 48.4.

*1-Fluoro-4-(2-nitro-1-phenylethyl)benzene (**11d′**).*[5d] White solid: 61 mg, 83% yield, 87% ee; mp 92−94 °C; R_f = 0.29 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{25}_D$ = +6.9 (c = 0.9, $CHCl_3$); HPLC Chiracel

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071−3081

OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (65 bar), t_R = 13.8 min (minor) and 25.6 min (major).

*1-tert-Butyl-4-(2-nitro-1-phenylethyl)benzene (**11e**).*[5d]* Colorless oil: 67 mg, 79% yield, 85% ee; R_f = 0.22 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{25}_D$ = +3.85 (*c* = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (86 bar), t_R = 11.5 min (major) and 16.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 4H), 7.24−7.20 (m, 3H), 7.18−7.13 (m, 2H), 5.00−4.93 (m, 2H), 4.87 (dd, *J* = 8.9, 7.3 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 139.5, 136.2, 129.1, 127.8, 127.7, 127.4, 126.1, 79.5, 48.7, 34.6, 31.4.

*1,2-Dimethyl-4-(2-nitro-1-phenylethyl)benzene (**11f**).* White solid: 66 mg, 86% yield, 86% ee; mp 49−51 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{25}_D$ = +0.64 (*c* = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (86 bar), t_R = 20.8 min (minor) and 32.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 2H), 7.27−7.20 (m, 3H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.96 (dd, *J* = 11.2, 3.5 Hz, 2H), 5.03−4.89 (m, 2H), 4.90−4.77 (m, 1H), 2.21 (d, *J* = 2.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.4, 136.7, 136.1, 130.3, 129.1, 127.7, 127.6, 124.9, 79.5, 48.8, 20.0, 19.5; HRMS (EI, *m*/*z*) calcd for $C_{16}H_{17}NO_2$ $[M]^+$ 255.1259, found 255.1251.

*1-(2-Nitro-1-phenylethyl)naphthalene (**11g**).*[5d]* Colorless oil: 46 mg, 55% yield, 91% ee; R_f = 0.31 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = +6.6 (*c* = 0.8, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (86 bar), t_R = 40.1 min (major) and 51.9 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.89−7.82 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.54−7.40 (m, 3H), 7.37−7.19 (m, 6H), 5.74 (t, *J* = 8.0 Hz, 1H), 5.19−4.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 134.8, 134.3 131.3, 129.2, 129.1, 128.6, 128.1, 127.8, 126.9, 126.1, 125.3, 124.3, 123.1, 79.2, 44.7.

*2-(2-Nitro-1-phenylethyl)naphthalene (**11h**).*[5d]* Colorless oil: 69 mg, 83% yield, 88% ee; R_f = 0.30 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = +30.7 (*c* = 1.1, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (86 bar), t_R = 32.4 min (minor) and 61.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.4, 3.4 Hz, 3H), 7.68 (s, 1H), 7.52−7.42 (m, 2H), 7.36−7.20 (m, 6H), 5.15−4.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 136.7, 133.5, 132.7, 129.2, 129.0, 128.0, 127.9, 127.8, 126.6, 126.4, 126.2, 126.0, 79.3, 49.1.

*1-Methoxy-2-(2-nitro-1-phenylethyl)benzene (**11i**).*[5e]* Colorless oil: 39 mg, 50% yield, 84% ee; R_f = 0.34 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = +23.5 (*c* = 0.5, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (81 bar), t_R = 9.6 min (minor) and 14.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.19 (m, 6H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.91−6.86 (m, 2H), 5.29−5.25 (m, 1H), 5.05−4.93 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 139.0, 128.9, 128.9, 128.6, 128.1, 127.6, 127.4, 120.9, 111.2, 78.1, 55.6, 43.4.

*1-Methyl-4-(2-nitro-1-phenylethyl)benzene (**11j**).*[5d]* Colorless oil: 58 mg, 80% yield, 87% ee; R_f = 0.20 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −1.5 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min (35 bar), t_R = 35.3 min (minor) and 37.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.28 (m, 2H), 7.24−7.21 (m, 3H), 7.12 (s, 4H), 5.00−4.92 (m, 2H), 4.86 (dd, *J* = 8.8, 7.4 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.4, 136.3, 129.8, 129.1, 127.7, 127.6, 79.5, 48.8, 21.1.

*1-Chloro-4-(2-nitro-1-phenylethyl)benzene (**11k**).*[5d]* White solid: 64 mg, 81% yield, 88% ee; mp 54−56 °C; R_f = 0.28 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{23}_D$ = −0.9 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 16.7 min (minor) and 25.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (m, 5H), 7.22−7.15 (m, 4H), 4.99−4.93 (m, 2H), 4.88 (dd, *J* = 9.1, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.8, 133.7, 129.4, 129.3, 129.2, 128.0, 127.7, 79.1, 48.5.

*1-(2-Nitro-1-phenylethyl)-4-(trifluoromethyl)benzene (**11l**).*[15]* Colorless oil: 70 mg, 79% yield, 87% ee; R_f = 0.30 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −2.7 (*c* = 1.3, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 12.4 min (minor) and 26.3 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.40−7.31 (m, 4H), 7.31−7.26 (m, 1H), 7.24−7.19 (m, 2H), 5.05−4.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.4, 129.4, 128.2, 128.1, 127.7, 126.2 (q, *J* = 3.7 Hz), 78.9, 48.8.

*1,2-Dimethoxy-4-(2-nitro-1-phenylethyl)benzene (**11m**).*[5e]* Colorless oil: 75 mg, 87% yield, 87% ee; R_f = 0.28 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{23}_D$ = +5.1 (*c* = 1.4, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (76 bar), t_R = 21.6 min (minor) and 27.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.30 (m, 2H), 7.29−7.20 (m, 3H), 6.85−6.76 (m, 2H), 6.71 (d, *J* = 1.8 Hz, 1H), 4.99−4.91 (m, 2H), 4.89−4.81 (m, 1H), 3.83 (d, *J* = 7.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.6, 139.5, 131.7, 129.1, 127.67, 127.66, 119.6, 111.5, 111.4, 79.5, 56.01, 55.98, 48.7.

*N,N-Dimethyl-4-(2-nitro-1-phenylethyl)aniline (**11n**).*[5e]* Light yellow oil: 66 mg, 81% yield, 88% ee; R_f = 0.27 (petroleum ether/ethyl acetate = 8/1); $[\alpha]^{24}_D$ = +1.1 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 0.8 mL/min (67 bar), t_R = 17.6 min (minor) and 18.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 2H), 7.22 (dd, *J* = 9.8, 4.0 Hz, 3H), 7.12−7.03 (m, 2H), 6.71−6.62 (m, 2H), 4.97−4.88 (m, 2H), 4.80 (t, *J* = 8.2 Hz, 1H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 140.1, 129.0, 128.5, 127.7, 127.4 126.8, 112.9, 79.7, 48.3, 40.6.

*1-Fluoro-4-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (**11o**).*[5e]* Light yellow oil: 75 mg, 90% yield, 87% ee; R_f = 0.25 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{24}_D$ = −0.5 (*c* = 1.5, $CHCl_3$); HPLC Chiracel OJ-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (72 bar), t_R = 23.7 min (minor) and 27.6 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.15 (m, 2H), 7.15−7.09 (m, 2H), 7.05−6.97 (m, 2H), 6.90−6.83 (m, 2H), 4.94−4.90 (m, 2H), 4.84 (dd, *J* = 9.2, 7.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 159.2, 135.4, 131.1, 129.4, 129.3, 128.8, 116.2, 116.0, 114.6, 79.6, 55.4, 47.7.

*1-Bromo-4-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (**11p**).* Colorless oil: 87 mg, 86% yield, 85% ee; R_f = 0.26 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{23}_D$ = −8.5 (*c* = 1.6, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (49 bar), t_R = 32.7 min (minor) and 36.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.40 (m, 2H), 7.17−7.06 (m, 4H), 6.92−6.80 (m, 2H), 4.96−4.87 (m, 2H), 4.86−4.77 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.7, 132.2, 130.7, 129.4, 128.8, 121.6, 114.6, 79.2, 55.4, 47.8; HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{14}BrNO_3Na$ $[M + Na]^+$ 358.0055, found 358.0062.

*1-Methoxy-4-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)benzene (**11q**).* Light yellow oil: 83 mg, 85% yield, 82% ee; R_f = 0.24 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{24}_D$ = −9.5 (*c* = 1.5, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (72 bar), t_R = 12.3 min (minor) and 18.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.18−7.09 (m, 2H), 6.94−6.83 (m, 2H), 5.03−4.88 (m, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.7, 130.4, 128.8, 128.1, 126.1 (q, *J* = 3.8 Hz), 114.8, 79.1, 55.4, 48.1; HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}F_3NO_3Na$ $[M + Na]^+$ 348.0823, found 348.0818.

*2-(1-(4-Methoxyphenyl)-2-nitroethyl)naphthalene (**11r**).*[5e]* Colorless oil: 89 mg, 96% yield, 90% ee; R_f = 0.23 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{23}_D$ = −45.2 (*c* = 1.8, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (88 bar), t_R = 28.0 min (major) and 64.3 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.73 (m, 3H), 7.66 (d, *J* = 1.1 Hz, 1H), 7.51−7.40 (m, 2H), 7.29 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.22−7.13 (m, 2H), 6.88−6.80 (m, 2H), 5.10−4.97 (m, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 137.1, 133.5, 132.7, 131.2, 129.0, 128.0, 127.8, 126.6, 126.3, 126.0, 114.6, 79.5, 55.4, 48.4.

dx.doi.org/10.1021/jo3003562 | *J. Org. Chem.* 2012, 77, 3071−3081

*1,2-Dimethoxy-4-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (**11s**).*[16] Colorless oil: 88 mg, 92% yield, 88% ee; R_f = 0.22 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{24}_D$ = +0.5 (*c* = 1.7, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (40 bar), t_R = 26.1 min (major) and 29.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.90−6.74 (m, 4H), 6.70 (s, 1H), 4.96−4.85 (m, 2H), 4.79 (t, *J* = 8.1 Hz, 1H), 3.83 (d, *J* = 7.6 Hz, 6H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 149.5, 148.6, 132.2, 131.6, 128.8, 119.5, 114.5, 111.6, 111.4, 79.8, 56.1, 56.0, 55.4, 48.0.

*1-(Benzyloxy)-2-methoxy-4-(1-(4-methoxyphenyl)-2-nitroethyl)-benzene (**11t**).* Light yellow solid: 91 mg, 77% yield, 89% ee; mp 100−102 °C; R_f = 0.28 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = −2.5 (*c* = 1.5, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (49 bar), t_R = 26.9 min (minor) and 32.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.21 (m, 5H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.90−6.76 (m, 3H), 6.76−6.62 (m, 2H), 5.10 (s, 2H), 4.88 (d, *J* = 7.7 Hz, 2H), 4.77 (t, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.0, 147.7, 137.1, 132.6, 131.4, 128.7, 128.7, 128.0, 127.3, 119.4, 114.4, 114.1, 111.8, 79.7, 71.1, 56.1, 55.3, 48.0; HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{23}NO_5Na$ $[M + Na]^+$ 416.1474, found 416.1462.

*4-(1-(4-Methoxyphenyl)-2-nitroethyl)-N,N-dimethylaniline (**11u**).*[5e] Light yellow solid: 58 mg, 65% yield, 90% ee; mp 76−77 °C; R_f = 0.17 (petroleum ether/ethyl acetate = 8/1); $[\alpha]^{24}_D$ = +5.5 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OJ-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 70/30, flow = 1.0 mL/min (50 bar), t_R = 63.3 min (major) and 79.1 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 8.3 Hz, 2H), 4.89 (d, *J* = 8.2 Hz, 2H), 4.76 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 2.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 149.9, 132.1, 128.8, 128.4, 127.2, 114.4, 112.9, 80.0, 55.4, 47.6, 40.6.

*1,3-Dichloro-5-(1-(4-methoxyphenyl)-2-nitroethyl)benzene (**11v**).* Colorless oil: 89 mg, 91% yield, 89% ee; R_f = 0.31 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −9.2 (*c* = 1.6, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 60/40, flow = 1.0 mL/min (62 bar), t_R = 19.5 min (minor) and 30.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.8 Hz, 1H), 7.20−7.04 (m, 4H), 6.95−6.80 (m, 2H), 4.93−4.87 (m, 2H), 4.83−4.75 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 143.1, 135.7, 129.8, 128.8, 128.0, 126.3, 114.9, 78.8, 55.4, 47.8; HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{13}Cl_2NO_3Na$ $[M + Na]^+$ 348.0170, found 348.0161.

*1,2-Dimethoxy-4-(1-(3-methoxyphenyl)-2-nitroethyl)benzene (**11w**).* Colorless oil: 80 mg, 84% yield, 89% ee; R_f = 0.23 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{25}_D$ = +6.2 (*c* = 1.4, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (38 bar), t_R = 28.1 min (minor) and 34.8 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.2 Hz, 1H), 6.87−6.68 (m, 6H), 4.93 (d, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 5.8 Hz, 6H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 149.4, 148.6, 141.1, 131.6, 130.1, 119.8, 119.5, 114.0, 112.5, 111.5, 111.3, 79.4, 56.0, 55.9, 55.3, 48.6; HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{19}NO_5Na$ $[M + Na]^+$ 340.1161, found 340.1167.

*1-(Benzyloxy)-2-methoxy-4-(1-(3-methoxyphenyl)-2-nitroethyl)-benzene (**11x**).* White solid: 94 mg, 80% yield, 87% ee; mp 97−99 °C; R_f = 0.28 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{23}_D$ = +2.5 (*c* = 1.6, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 50/50, flow = 1.0 mL/min (86 bar), t_R = 15.7 min (minor) and 38.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.17 (m, 6H), 6.88−6.64 (m, 6H), 5.10 (s, 2H), 4.90 (d, *J* = 7.8 Hz, 2H), 4.79 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 150.0, 147.8, 141.0, 137.1, 132.1, 130.1, 128.7, 128.0, 127.3, 119.8, 119.5, 114.2, 114.0, 112.5, 111.9, 79.4, 71.1, 56.2, 55.3, 48.6; HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{23}NO_5Na$ $[M + Na]^+$ 416.1474, found 416.1475.

*4-(1-(3-Methoxyphenyl)-2-nitroethyl)-N,N-dimethylaniline (**11y**).* Yellow oil: 68 mg, 75% yield, 91% ee; R_f = 0.19 (petroleum ether/ethyl acetate = 8/1); $[\alpha]^{24}_D$ = +16.1 (*c* = 1.0, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (38 bar), t_R = 22.2 min (minor) and 23.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.18 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.97−4.84 (m, 2H), 4.76 (t, *J* = 8.1 Hz, 1H), 3.75 (s, 3H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 150.0, 141.7, 130.0, 128.4, 126.6, 119.9, 113.9, 112.9, 112.4, 79.7, 55.3, 48.3, 40.6; HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{20}N_2O_3Na$ $[M + Na]^+$ 323.1372, found 323.1368.

*1,3-Dichloro-5-(1-(3-methoxyphenyl)-2-nitroethyl)benzene (**11z**).* Colorless oil: 88 mg, 90% yield, 85% ee; R_f = 0.33 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{24}_D$ = −1.7 (*c* = 1.6, $CHCl_3$); HPLC Chiracel AS-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 80/20, flow = 1.0 mL/min (38 bar), t_R = 12.0 min (minor) and 13.8 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 2H), 7.12 (s, 2H), 6.80 (dd, *J* = 17.4, 8.0 Hz, 2H), 6.72 (s, 1H), 4.92 (d, *J* = 7.7 Hz, 2H), 4.81 (t, *J* = 8.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 142.6, 139.3, 135.7, 130.5, 128.1, 126.4, 119.7, 114.2, 113.0, 78.5, 55.4, 48.3; HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{13}Cl_2NO_3Na$ $[M + Na]^+$ 348.0170, found 348.0172.

*(1-Nitrohexan-2-yl)benzene (**12a**).*[17] Colorless oil: 38 mg, 61% yield, 87% ee; R_f = 0.25 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −19.4 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 95/5, flow = 1.0 mL/min (31 bar), t_R = 11.5 min (minor) and 18.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 2H), 7.28−7.24 (m, 1H), 7.20−7.17 (m, 2H), 4.70−4.45 (m, 2H), 3.56−3.34 (m, 1H), 1.68 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.41−1.08 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 129.0, 127.7, 127.6, 81.2, 44.5, 32.9, 29.2, 22.5, 14.0.

*1-Methoxy-4-(1-nitrohexan-2-yl)benzene (**12b**).*[5d] Colorless oil: 56 mg, 78% yield, 85% ee; R_f = 0.13 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −23.8 (*c* = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 95/5, flow = 1.0 mL/min (33 bar), t_R = 13.6 min (minor) and 21.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.04 (m, 2H), 6.96−6.79 (m, 2H), 4.56−4.45 (m, 2H), 3.79 (s, 3H), 3.50−3.28 (m, 1H), 1.74−1.53 (m, 2H), 1.43−1.07 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 131.6, 128.6, 114.4, 81.4, 55.4, 43.8, 32.9, 29.2, 22.5, 14.0.

*1-Methyl-4-(1-nitrohexan-2-yl)benzene (**12c**).*[18] Colorless oil: 56 mg, 85% yield, 87% ee; R_f = 0.22 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −20.7 (*c* = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 7.2 min (minor) and 11.3 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 4.61−4.42 (m, 2H), 3.39 (p, *J* = 7.5 Hz, 1H), 2.32 (s, 3H), 1.66 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.37−1.10 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.6, 129.7, 127.5, 81.3, 44.1, 32.9, 29.2, 22.5, 21.2, 14.0.

*1-Fluoro-4-(1-nitrohexan-2-yl)benzene (**12d**).* Colorless oil: 56 mg, 83% yield, 88% ee; R_f = 0.23 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −19.9 (*c* = 1.1, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, *n*-hexane/*i*-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 6.9 min (minor) and 7.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 5.6 Hz, 2H), 7.02 (t, *J* = 7.9 Hz, 2H), 4.68−4.39 (m, 2H), 3.44 (dd, *J* = 14.5, 7.1 Hz, 1H), 1.84−1.53 (m, 2H), 1.42−1.03 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.1, 135.4, 129.2, 129.1, 116.1, 115.8, 81.1, 43.8, 32.9, 29.1, 22.5, 13.9; HRMS (EI, *m*/*z*) calcd for $C_{12}H_{16}FNO_2$ $[M]^+$ 225.1165, found 225.1164.

*(3-Methyl-1-nitrobutan-2-yl)benzene (**12e**).*[19] Colorless oil: 41 mg, 70% yield, 86% ee; R_f = 0.26 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −34.5 (*c* = 1.1, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, *n*-hexane/*i*-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 9.0 min (minor) and 14.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.20 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 2H), 4.78−4.74 (m, 1H), 4.64 (t, *J* = 11.1 Hz, 1H), 3.23 (dd, *J* = 15.5, 7.9 Hz, 1H), 1.95 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.81

dx.doi.org/10.1021/jo3003562 | J. Org. Chem. 2012, 77, 3071−3081

(d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 128.7, 128.2, 127.6, 79.2, 51.2, 31.5, 20.7, 20.4.

*1-Methoxy-4-(3-methyl-1-nitrobutan-2-yl)benzene (**12f**).*[20] Colorless oil: 37 mg, 56% yield, 87% ee; R_f = 0.15 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −40.7 (c = 0.8, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 11.3 min (minor) and 13.8 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 4.76−4.71 (m, 1H), 4.59 (t, J = 11.1 Hz, 1H), 3.78 (s, 3H), 3.17 (dd, J = 15.6, 8.0 Hz, 1H), 1.91 (dq, J = 13.5, 6.7 Hz, 1H), 0.99 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 130.6, 129.2, 114.1, 79.4, 55.3, 50.5, 31.5, 20.8, 20.3.

*1-Fluoro-4-(3-methyl-1-nitrobutan-2-yl)benzene (**12g**).* Colorless oil: 38 mg, 60% yield, 90% ee; R_f = 0.20 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{25}_D$ = −29.6 (c = 0.6, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 7.9 min (minor) and 8.7 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 6.0 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 4.77−7.73 (m, 1H), 4.60 (t, J = 11.3 Hz, 1H), 3.22 (dd, J = 15.6, 8.1 Hz, 1H), 1.92 (dq, J = 13.5, 6.7 Hz, 1H), 1.01 (d, J = 6.6 Hz, 3H), 0.79 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 134.6, 129.8, 129.7, 115.8, 115.6, 110.2, 79.3, 50.5, 31.5, 20.7, 20.3; HRMS (EI, m/z) calcd for $C_{11}H_{14}FNO_2$ $[M]^+$ 211.1009, found 211.1006.

*1-Methyl-4-(3-methyl-1-nitrobutan-2-yl)benzene (**12h**).* Colorless oil: 53 mg, 85% yield, 88% ee; R_f = 0.24 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −32.9 (c = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 8.5 min (minor) and 11.1 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 7.5 Hz, 2H), 7.03 (d, J = 7.7 Hz, 2H), 4.75−4.72(m, 1H), 4.62−4.59 (m, 1H), 3.19 (dd, J = 15.5, 7.8 Hz, 1H), 2.31 (s, 3H), 1.93 (dq, J = 13.5, 6.7 Hz, 1H), 0.99 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.6, 129.4, 128.1, 79.3, 50.8, 31.4, 21.2, 20.8, 20.3; HRMS (EI, m/z) calcd for $C_{12}H_{17}NO_2$ $[M]^+$ 207.1259, found 207.1249.

*(1-Cyclohexyl-2-nitroethyl)benzene (**12i**).*[21] White solid: 57 mg, 81% yield, 88% ee; mp 55−57 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 15/1); $[\alpha]^{25}_D$ = −28.9 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 8.7 min (minor) and 14.3 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.29 (m, 3H), 7.22 (d, J = 7.1 Hz, 2H), 4.80−4.76(m, 1H), 4.67−4.56 (m, 1H), 3.31−3.21 (m, 1H), 1.86 (t, J = 13.7 Hz, 2H), 1.79−1.61 (m, 3H), 1.54 (d, J = 12.8 Hz, 1H), 1.40−1.04 (m, 4H), 0.94 (q, J = 11.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 128.7, 128.3, 127.5, 79.0, 50.4, 41.0, 31.1, 30.7, 26.4, 26.3, 26.2.

*1-(1-Cyclohexyl-2-nitroethyl)-4-methoxybenzene (**12j**).*[5d] White solid: 52 mg, 65% yield, 89% ee; mp 47−49 °C; R_f = 0.17 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{25}_D$ = −33.0 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 10.6 min (minor) and 13.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 8.2 Hz, 2H), 4.77−4.73 (m, 1H), 4.62−4.51 (m, 1H), 3.77 (s, 3H), 3.23−3.17 (m, 1H), 1.87−1.38 (m, 7H), 1.36−0.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 130.7, 129.2, 114.0, 79.2, 55.3, 49.6, 41.1, 31.1, 30.6, 26.4, 26.3, 26.2.

*1-(1-Cyclohexyl-2-nitroethyl)-4-methylbenzene (**12k**).*[22] Colorless oil: 52 mg, 71% yield, 90% ee; R_f = 0.32 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{24}_D$ = −31.6 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 214 nm, n-hexane/i-propanol = 95/5, flow = 1.0 mL/min (42 bar), t_R = 8.4 min (minor) and 10.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 7.5 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 4.76 (dd, J = 12.1, 5.6 Hz, 1H), 4.59 (t, J = 11.1 Hz, 1H), 3.22 (dd, J = 15.5, 7.9 Hz, 1H), 2.31 (s, 3H), 1.85−1.40 (m, 6H), 1.32−0.76 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.8, 129.4, 128.1, 79.1, 50.0, 41.0, 31.1, 31.0, 30.6, 26.3, 26.2, 21.2.

*2-(1-(4-Methoxyphenyl)-2-nitroethyl)furan (**12l**).* Colorless oil: 42 mg, 57% yield, 79% ee; R_f = 0.36 (petroleum ether/ethyl acetate = 8/1); $[\alpha]^{25}_D$ = −42.4 (c = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 8.0 min (minor) and 13.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 1.2 Hz, 1H), 7.24−7.16 (m, 2H), 6.92−6.83 (m, 2H), 6.30 (dd, J = 3.2, 1.9 Hz, 1H), 6.09 (d, J = 3.3 Hz, 1H), 4.98 (dd, J = 12.2, 7.6 Hz, 1H), 4.87 (t, J = 7.7 Hz, 1H), 4.76 (dd, J = 12.2, 7.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.55, 142.6, 129.1, 129.0, 114.6, 110.6, 107.4, 78.4, 55.4, 43.0; HRMS (ESI, m/z) calcd for $C_{13}H_{13}NO_4Na$ $[M + Na]^+$ 270.0742, found 270.0743.

*2-(1-(4-Methoxyphenyl)-2-nitroethyl)thiophene (**12m**).* Light yellow oil: 66 mg, 84% yield, 87% ee; R_f = 0.38 (petroleum ether/ethyl acetate = 10/1); $[\alpha]^{24}_D$ = −1.3 (c = 1.2, $CHCl_3$); HPLC Chiracel OD-H Column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 13.1 min (minor) and 19.9 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 3H), 6.95−6.92 (m, 1H), 6.91−6.82 (m, 3H), 5.07 (t, J = 8.0 Hz, 1H), 4.97−7.84 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.1, 130.9, 128.8, 127.1, 125.2, 125.0, 114.6, 80.2, 55.4, 44.1; HRMS (ESI, m/z) calcd for $C_{13}H_{13}NO_3SNa$ $[M + Na]^+$ 286.0514, found 286.0516.

*2-(1-(3,4-Dimethylphenyl)-2-nitroethyl)thiophene (**12n**).* Colorless oil: 45 mg, 60% yield, 75% ee; R_f = 0.23 (petroleum ether/ethyl acetate = 30/1); $[\alpha]^{20}_D$ = +8.02 (c = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 14.2 min (minor) and 36.6 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 5.1 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.06−6.99 (m, 2H), 6.96−6.87 (m, 2H), 5.05 (t, J = 8.0 Hz, 1H), 4.92 (qd, J = 12.6, 8.0 Hz, 2H), 2.23 (d, J = 3.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.5, 136.6, 136.3, 130.4, 129.0, 127.1, 125.2, 125.1, 124.8, 80.2, 44.5, 20.0, 19.5; HRMS (ESI, m/z) calcd for $C_{14}H_{15}NO_2SNa$ $[M + Na]^+$ 284.0721, found 284.0725.

*2-(1-(3,4-Dimethoxyphenyl)-2-nitroethyl)furan (**12o**).* Colorless oil: 52 mg, 63% yield, 83% ee; R_f = 0.33 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{18}_D$ = −35.5 (c = 1.0, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 10.8 min (minor) and 15.5 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.80 (d, J = 19.9 Hz, 3H), 6.32 (s, 1H), 6.12 (d, J = 2.9 Hz, 1H), 4.99 (dd, J = 12.0, 7.5 Hz, 1H), 4.93−4.73 (m, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.4, 148.9, 142.6, 129.4, 120.1, 111.6, 111.1, 110.6, 107.4, 78.3, 56.1, 56.0, 43.3; HRMS (ESI, m/z) calcd for $C_{14}H_{15}NO_5Na$ $[M + Na]^+$ 300.0848, found 300.0844.

*2-(1-(3,4-Dimethoxyphenyl)-2-nitroethyl)thiophene (**12p**).* Light yellow oil: 65 mg, 74% yield, 86% ee; R_f = 0.34 (petroleum ether/ethyl acetate = 4/1); $[\alpha]^{19}_D$ = +3.5 (c = 1.2, $CHCl_3$); HPLC Chiracel OD-H column, detected at 230 nm, n-hexane/i-propanol = 60/40, flow = 1.0 mL/min (70 bar), t_R = 17.1 min (minor) and 22.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 5.1 Hz, 1H), 6.95 (t, J = 4.2 Hz, 1H), 6.90 (s, 1H), 6.87−6.81 (m, 2H), 6.78 (s, 1H), 5.07 (t, J = 8.0 Hz, 1H), 4.99−4.87 (m, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.9, 142.9, 131.3, 127.1, 125.3, 125.1, 119.7, 111.5, 111.0, 80.2, 56.0, 55.9, 44.5; HRMS (ESI, m/z) calcd for $C_{14}H_{15}NO_4SNa$ $[M + Na]^+$ 316.0619, found 316.0614.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR, HRMS, and HPLC spectra of new racemic and chiral compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bswan@dicp.ac.cn.

■ ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (2010CB833300) is gratefully acknowledged.

REFERENCES

(1) (a) *Transition Metals for Organic Synthesis*; Beller, M., Bolm. C., Eds.; Wiley-VCH: Weinheim, 2004. (b) *Multimetallic Catalysts in Organic Synthesis*; Shibasaki, M., Yamamoto, Y., Eds.; Wiley-VCH: Weinheim, 2004. (c) *Transition Metal Catalysed Reactions*; Murahashi, S., Davies., S. G., Eds.; Blackwell Science: Oxford, 1999.

(2) For selected reviews, see: (a) Hayashi, T. *Synlett* **2001**, 879. (b) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (c) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (d) Hayashi, T.; Yoshida, K. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2004; pp 55−78. (e) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. *Synthesis* **2007**, 1279.

(3) (a) Wang, Z. Q.; Feng, C. G.; Xu, M. H.; Lin, G. Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336 and references therein. (b) Cao, Z. P.; Du, H. F. *Org. Lett.* **2010**, *12*, 2602. (c) Shintani, R.; Takeda, M.; Tsuji, T.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 13168. (d) Shintani, R.; Takeda, M.; Soh, Y. T.; Tomoaki, I.; Hayashi, T. *Org. Lett.* **2011**, *13*, 2977. (e) Cui, Z.; Yu, H. J.; Yang, R. F.; Gao, W. Y.; Feng, C. G.; Lin, G. Q. *J. Am. Chem. Soc.* **2011**, *133*, 12394.

(4) Asymmetric addition to cyclic nitroalkenes: (a) Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc.* **2000**, *122*, 10716. (b) Dong, L.; Xu, Y. J.; Cun, L. F.; Cui, X.; Mi, A. Q.; Jiang, Y. Z.; Gong, L. Z. *Org. Lett.* **2005**, *7*, 4285. (c) Dong, L.; Xu, Y. J.; Yuan, W. C.; Cui, X.; Cun, L. F.; Gong, L. Z. *Eur. J. Org. Chem.* **2006**, 4093.

(5) Asymmetric addition to 2-nitrostyrenes: (a) Boiteau, J. G.; Imbos, R.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2003**, *5*, 681. (b) Duursma, A.; Hoen, R.; Schuppan, J.; Hulst, R.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2003**, *5*, 3111. (c) Duursma, A.; Pena, D.; Minnaard, A. J.; Feringa, B. L. *Tetrahedron: Asymmetry* **2005**, *16*, 1901. (d) Wang, Z. G.; Feng, C. G.; Zhang, S. S.; Xu, M. H.; Lin, G. Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 5780. (e) Lang, F.; Chen, G. H.; Li, L. C.; Xing, J. W.; Han, F. Z.; Cun, L. F.; Liao, J. *Chem.—Eur. J.* **2011**, *17*, 5242. (f) Xing, J. W.; Chen, G. H.; Cao, P.; Liao, J. *Eur. J. Org. Chem.* **2012**, 1230.

(6) For selected examples: (a) Askani, R.; Taber, D. F. In *Comprehensive Organic Synthesis*; B. Trost, M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. *6*, Chapter 1.4. (b) Tamura, R.; Kamimura, A.; Ono, N. *Synthesis* **1991**, 423. (c) Fuji, K.; Node, M. *Synlett* **1991**, 603. (d) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: Weinheim, 2001.

(7) Xue, F.; Li, X. C.; Wan, B. S. *J. Org. Chem.* **2011**, *76*, 7256.

(8) (a) Thaler, T.; Guo, L. N.; Steib, A. K.; Raducan, M.; Karaghiosoff, K.; Mayer, P.; Knochel, P. *Org. Lett.* **2011**, *13*, 3182. (b) Jin, S. S.; Wang, H.; Xu, M. H. *Chem. Commun.* **2011**, *47*, 7230. (c) Feng, X. Q.; Wang, Y. Z.; Wei, B. B.; Yang, J.; Du, H. F. *Org. Lett.* **2011**, *13*, 3300. (d) Feng, X. Q.; Wei, B. B.; Yang, J.; Du, H. F. *Org. Biomol. Chem.* **2011**, *9*, 5927. (e) Qi, W. Y.; Zhu, T. S.; Xu, M. H. *Org. Lett.* **2011**, *13*, 3410. (f) Wang, Y. Z.; Feng, X. Q.; Du, H. F. *Org. Lett.* **2011**, *13*, 4954. (g) Chen, G. H.; Gui, J. Y.; Li, L. C.; Liao, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 7681. (h) Zhu, T. S.; Jin, S. S.; Xu, M. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 780. (i) Feng, X. Q.; Nie, Y. Z.; Yang, J.; Du, H. F. *Org. Lett.* **2012**, *14*, 624. (j) Tian, P.; Dong, H. Q.; Lin, G. Q. *ACS Catal.* **2012**, *2*, 95. (k) Jin, S. S.; Wang, H.; Zhu, T. S.; Xu, M. H. *Org. Biomol. Chem.* **2012**, *10*, 1764.

(9) While the preparation of ligands with methoxy groups on the central benzene ring moiety (**5p**−**5t**) (Scheme 2) can be successful, we failed in the synthesis of the analogues with *para*-methoxy on the terminal benzene ring.

(10) Luo, Y. F.; Berry, N. G.; Carnell, A. J. *Chem. Commun.* **2012**, *48*, 3279.

(11) Alexander, J. B.; Mervyn, H.; John, T. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3149.

(12) Pyne, S. G.; Hajipour, A. R.; Prabakaran, K. *Tetrahedron Lett.* **1994**, *35*, 645.

(13) Mariz, R.; Poater, A.; Gatti, M.; Drinkel, E.; Bürgi, J. J.; Luan, X. J.; Blumentritt, S.; Linden, A.; Cavallo, L.; Dorta, R. *Chem.—Eur. J.* **2010**, *16*, 14335.

(14) Herbrandson, H. F.; Dickerson, R. I. Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4102.

(15) Michael, S. A.; Lawrence, A. B.; Peter, G. H.; Stanley, H. B.W. *Synthesis* **1988**, 379.

(16) Kumar, A. S.; Ghosh, S.; Soundararajan, R.; Mehta, G. N. *Synth. Commmun.* **2010**, *40*, 1588.

(17) Schaefer, H.; Seebach, D. *Tetrahedron* **1995**, *51*, 2305.

(18) Alexakis, A.; Benhaim, C. *Org. Lett.* **2000**, *2*, 2579.

(19) (a) Czekelius, C.; Carreira, E. M. *Org. Lett.* **2004**, *6*, 4575. (b) Czekelius, C.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 4793.

(20) Bartoli, G.; Bosco, M.; Sambri, L.; Marcantoni, E. *Tetrahedron Lett.* **1994**, *35*, 8651.

(21) Rimkus, A.; Sewald, N. *Org. Lett.* **2002**, *4*, 3289.

(22) Ohe, T.; Uemura, S. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1423.