JOC The Journal of Organic Chemistry

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Asymmetric Allylic Alkylation of Pyrroles and 4,7-Dihydroindoles with Alkene−Phosphine Ligands

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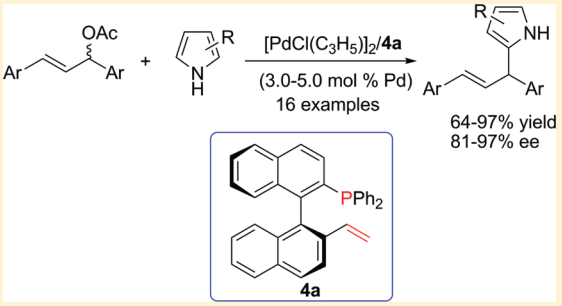
Supporting Information

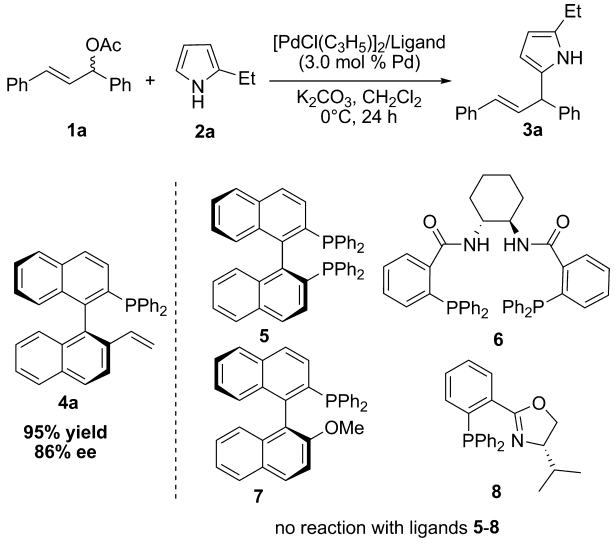
ABSTRACT: A palladium-catalyzed highly enantioselective allylic alkylation of pyrroles and 4,7-dihydroindoles has been successfully developed with the use of chiral alkene-phosphine hybrid ligands to furnish the desired products in high yields with excellent ee's. It is noteworthy that alkene−phosphine ligands are much more effective than some other types of chiral ligands in this catalytic system.



As an important class of electron-rich *N*-containing heterocycles, pyrroles are widely present in biologically active compounds and have also versatile synthetic applications.[1] The acquisition of optically active pyrrole derivatives through asymmetric catalysis represents one of the most challenging and intriguing subjects, and great efforts and progress have been made in this field. However, even for the intensively studied asymmetric Friedel−Crafts alkylations under the catalysis of chiral Lewis acids,[2] Brønsted acids,[3] or secondary amines,[4] there are only limited reports where a wide scope of pyrroles are well tolerated and highly enantioenriched pyrrole derivatives can be furnished. Further exploring highly enantioselective transformations of various pyrroles is still of great interest.

Pd-catalyzed asymmetric allylic alkylation has become an extremely useful synthetic methodology for the stereoselective formation of C−C, C−N, and C−O bonds,[5] whereas such a reaction involving pyrroles still remains as an unsolved problem. In 2006, Bandini, Umani-Ronchi, and co-workers described one example of Pd-catalyzed intramolecular allylic alkylation of substituted pyrrole with 95% enantiomeric excess (ee).[6] However, to the best of our knowledge, Pd-catalyzed intermolecular allylic alkylation of pyrroles[7] and its asymmetric version have seldom been reported. During our previous study on the allylic alkylation of indoles, we were pleased to find that chiral alkene−phosphine hybrid ligand **4a** was also effective for the challenging reaction between 1,3-diphenyl-2-propenyl acetate (**1a**) and 2-ethylpyrrole (**2a**) to give the desired product **3a** in 95% yield with 86% ee (Scheme 1).[8] Several well-established chiral ligands **5**−**8** were examined under the same conditions,[9] but there were no products at all (Scheme 1). These results prompted us to further improve the enantioselectivities and expand the substrate scope. Herein, we report our efforts on Pd-catalyzed asymmetric allylic alkylations of pyrroles and their analogues, 4,7-dihydroindoles, with the use of alkene−phosphine hybrid ligands.[10,11]

Scheme 1. Pd-Catalyzed Asymmetric Allylic Alkylation of Pyrroles

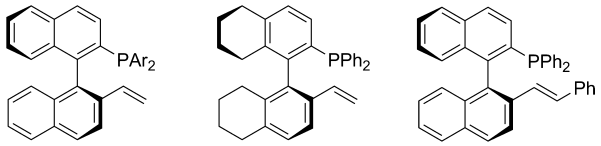


Initially, various reaction conditions were thoroughly examined for the Pd/**4a**-catalyzed asymmetric allylic alkylation of 2-ethylpyrrole (**2a**) with 1,3-diphenyl-2-propenyl acetate (**1a**). Some of the results are summarized in Table 1. We found that all the bases and solvents were suitable for this reaction to give promising reactivity and enantioselectivity (Table 1, entries 1−9). Cs_2CO_3 can give a little higher ee value but a relatively

Received: March 13, 2012
Published: April 11, 2012

   dx.doi.org/10.1021/jo300539y | *J. Org. Chem.* 2012, 77, 4479−4483

Table 1. Optimization of Reaction Conditions and Evaluation of Ligands[a]



4b: Ar = 2-Np
4c: Ar = 3,5-$Me_2C_6H_3$

4d **4e**

entry	ligand	base	solvent	yield[b] (%)	ee[c] (%)
1	**4a**	K_2CO_3	dichloromethane (CH_2Cl_2)	86	86
2	**4a**	Na_2CO_3	CH_2Cl_2	94	84
3	**4a**	Cs_2CO_3	CH_2Cl_2	78	88
4	**4a**	Et_3N	CH_2Cl_2	84	86
5	**4a**	Cs_2CO_3	MeCN	83	88
6	**4a**	Cs_2CO_3	tetrahydrofuran	76	82
7	**4a**	Cs_2CO_3	toluene	86	82
8[d]	**4a**	Cs_2CO_3	CH_2Cl_2/toluene	89	84
9[d]	**4a**	Cs_2CO_3	MeCN/toluene	93	88
10[d]	**4b**	Cs_2CO_3	MeCN/toluene	89	84
11[d]	**4c**	Cs_2CO_3	MeCN/toluene	83	90
12[d]	**4d**	Cs_2CO_3	MeCN/toluene	90	80
13[d]	**4e**	Cs_2CO_3	MeCN/toluene	88	−46
14[d,e]	**4a**	Cs_2CO_3	MeCN/toluene	93	92
15[d,f]	**4a**	K_2CO_3	MeCN/toluene	92	97

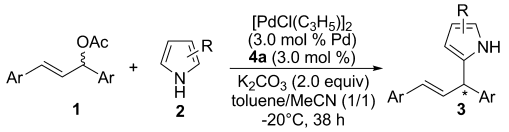
[a]All reactions were carried out with **1a** (0.24 mmol), **2a** (0.2 mmol), Pd/ligand =1/1 (mole ratio, 3 mol % Pd), base (0.40 mmol), and solvent (1.0 mL) at room temperature for 5.5 h unless otherwise stated. [b]Isolated yield based on **2a**. [c]The ee was determined by chiral HPLC. [d]The volume ratio of two solvents was 1/1. [e]The reaction was conducted at −20 °C for 24 h. [f]The reaction was conducted at −20 °C for 38 h.

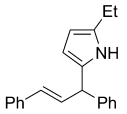
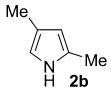
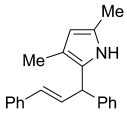
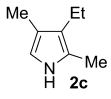
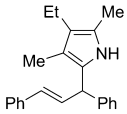
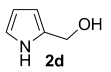
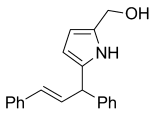
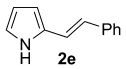
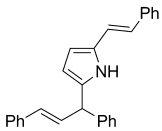
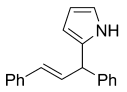
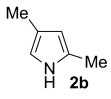
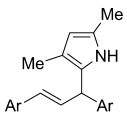
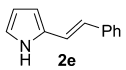
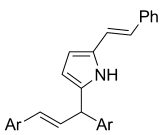
lower yield (Table 1, entry 3). A mixture of acetonitrile (MeCN) and toluene in 1/1 volume ratio seems to be a better solvent (Table 1, entry 9). Chiral alkene−phosphine ligands **4b−e** were then evaluated. Up to 90% ee was obtained with the use of ligand **4c** (Table 1, entry 11). Ligand **4e** containing an internal olefin gave the desired product **3a** in high yield but with a reverse absolute configuration (Table 1, entry 13). In terms of both reactivity and enantioselectivity, ligand **4a** proved to be the optimal ligand. To our pleasure, the ee value was up to 97% when the reaction was carried out at −20 °C with K_2CO_3 as base (Table 1, entry 15).

Asymmetric allylic alkylation of various substituted pyrroles **2a−f** under the catalysis of Pd/**4a** was investigated. As shown in Table 2, all of the reactions proceeded smoothly to furnish the corresponding products **3** in good yields (73−97%) and high enantioselectivities (86−97% ee) (Table 2, entries 1−6). Pyrrole **2d** containing a free hydroxyl group was well tolerated for this transformation to afford a good yield and ee (Table 2, entry 4). Alkylation of pyrroles **2e** or **2f** incorporating *trans*- or *cis*-styryl moieties led to the same product in high yields with 97% ee, which suggests that *cis*-alkene isomerized to *trans*-alkene under the reaction conditions (Table 2, entries 5, 6).[12] With an excess amount of pyrrole (**2g**), the monoalkylated product was obtained in 86% yield with 89% ee (Table 2, entry 7).[8] Moreover, several 1,3-diaryl-2-propenyl acetates were also suitable substrates for this reaction (Table 2, entries 8−11).

4,7-Dihydroindoles are important analogues of pyrroles. Alkylation of 4,7-dihydroindoles followed by a simple oxidation

Table 2. Pd-Catalyzed Asymmetric Allylic Alkylation of Pyrroles[a]



entry	pyrrole (**2**)	product (**3**)	yield (%)[b]	ee (%)[c]
1	 **2a**		92	97
2	 **2b**		97	94
3	 **2c**		93	95
4	 **2d**		73	86
5	 **2e**		91	97
6	 **2f**		93	97
7[d]	 **2g**		86	89
8	 **2b**		89	94
9			95	95
10		Ar = 3-ClC_6H_4 Ar = 4-MeC_6H_4 Ar = 4-ClC_6H_4	64	81
11	 **2e**		81	92

Ar = 3-ClC_6H_4

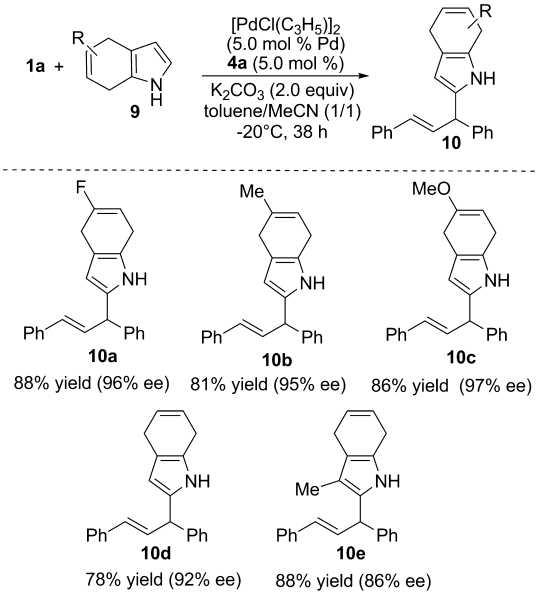
[a]All reactions were carried out with **1** (0.24 mmol), **2** (0.20 mmol), $[PdCl(C_3H_5)]_2$ (0.003 mmol), **4a** (0.006 mmol), and K_2CO_3 (0.40 mmol) in toluene/MeCN (1/1 volume ratio, 1.0 mL) at −20 °C for 38 h. [b]Isolated yield. [c]The ee was determined by chiral HPLC. [d]5.0 equiv of pyrrole (**2g**) was used.

provides a powerful approach for the synthesis of highly desirable 2-substituted indoles which cannot be accessed by direct alkylation of indoles.[13] However, Pd-catalyzed asymmetric allylic alkylation of 4,7-dihydroindoles has been rarely exploited. Therefore, we examined the reaction between 4,7-dihydroindoles **9** and 1,3-diphenyl-2-propenyl acetate (**1a**) under conditions similar to those for the alkylation of pyrroles.

dx.doi.org/10.1021/jo300539y | J. Org. Chem. 2012, 77, 4479−4483

As shown in Scheme 2, all of the reactions proceeded efficiently to give the desired products **10** in 78−88% yield with 86−97% ee.

Scheme 2. Pd-Catalyzed Asymmetric Allylic Alkylation of 4,7-Dihydroindoles



In conclusion, Pd-catalyzed asymmetric allylic alkylation of pyrroles and 4,7-dihydroindoles has been accomplished with the use of a chiral alkene−phosphine ligand to afford the desired pyrrole derivatives in 64−97% yields with 81−97% ee. In comparison with some well-established chiral ligands, the chiral alkene−phosphine hybrid ligands exhibit higher activity and selectivity in this transformation. Further studies of their applications to other asymmetric reactions will be of interest.

EXPERIMENTAL SECTION

Representative Procedure for Pd/4a-Catalyzed Asymmetric Allylic Alkylation of Pyrroles (Table 1, Entry 1). A dried Schlenk flask was charged with $[PdCl(C_3H_5)]_2$ (0.0011 g, 0.003 mmol), chiral alkene−phosphine ligand **4a** (0.0028 g, 0.006 mmol), and MeCN/toluene (1/1 volume ratio) (0.40 mL) under argon. The resulting mixture was stirred at room temperature for 30 min before being cooled to −20 °C. 1,3-Diphenyl-2-propenyl acetate (**1a**) (0.0605 g, 0.24 mmol) in MeCN/toluene (1/1 volume ratio) (0.40 mL), 2-ethylpyrrole (**2a**) (0.0190 g, 0.20 mmol), potassium carbonate (0.0553 g, 0.40 mmol), and MeCN/toluene (1/1 volume ratio) (0.20 mL) were added sequentially. After being stirred at −20 °C for 38 h, the reaction mixture was filtered through a short pad of silica gel (200−300 mesh, 1 cm) and washed with diethyl ether. After removal of solvent, the crude residue was purified by flash chromatography on silica gel (petroleum ether/diethyl ether = 50:1, v/v) to afford the desired product **3a** as a light yellow oil.

(*E*)-2-(1,3-Diphenyl-2-propenyl)-5-ethylpyrrole[8] (Table 2, entry 1): light yellow oil, 0.0526 g, 92% yield; $[\alpha]^{20}_D$ −13.7 (*c* 0.59, CH_2Cl_2) (97% ee) [lit. $[\alpha]^{20}_D$ −11.5 (*c* 1.89, CH_2Cl_2) (86% ee)]; IR (film) 3424, 1598, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (brs, 1H), 7.37−7.18 (m, 10H), 6.58 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 5.84−5.82 (m, 2H), 4.81 (d, *J* = 7.6 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.19 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.3, 134.2, 131.6, 131.5, 131.2, 128.9, 128.7, 128.6, 127.6, 127.0, 126.6, 106.8, 104.3, 48.5, 21.1, 13.7.

(*E*)-3,5-Dimethyl-2-(1,3-diphenyl-2-propenyl)pyrrole (Table 2, entry 2): light yellow oil, 0.0558 g, 97% yield; $[\alpha]^{20}_D$ −18.6 (*c* 0.36, CH_2Cl_2) (94% ee); IR (film) 3435, 1599, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.18 (m, 11H), 6.56 (dd, *J* = 15.6, 6.8 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.71 (s, 1H), 4.94 (d, *J* = 6.8 Hz, 1H), 2.16 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.4, 131.5, 131.2, 128.8, 128.7, 128.6, 127.5, 126.8, 126.5, 126.1, 125.9, 115.5, 108.7, 45.9, 13.2, 11.3; HRMS (TOF-EI) calcd for $C_{21}H_{21}N$ (M) 287.1674, found 287.1677.

(*E*)-4-Ethyl-3,5-dimethyl-2-(1,3-diphenyl-2-propenyl)pyrrole (Table 2, entry 3): light yellow oil, 0.0589 g, 93% yield; $[\alpha]^{20}_D$ −9.3 (*c* 0.14, CH_2Cl_2) (95% ee); IR (film) 3364, 1601, 1494 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.18 (m, 10H), 7.15 (brs, 1H), 6.57 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.94 (d, *J* = 6.8 Hz, 1H), 2.38 (q, *J* = 7.6 Hz, 2H), 2.11 (s, 3H), 1.91 (s, 3H), 1.07 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.5, 131.4, 131.3, 128.8, 128.7, 128.6, 127.5, 126.8, 126.6, 125.0, 121.4, 121.3, 114.3, 46.1, 18.0, 15.9, 11.3, 9.5; HRMS (TOF-EI) calcd for $C_{23}H_{25}N$ (M) 315.1987, found 315.1991.

(*E*)-2-(Hydroxymethyl)-5-(1,3-diphenyl-2-propenyl)pyrrole (Table 2, entry 4): light yellow oil, 0.0420 g, 73% yield; $[\alpha]^{20}_D$ −5.6 (*c* 0.39, CH_2Cl_2) (86% ee); IR (film) 3420, 3328, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (brs, 1H), 7.37−7.19 (m, 10H), 6.56 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.04−6.02 (m, 1H), 5.87−5.85 (m, 1H), 4.81 (d, *J* = 7.6 Hz, 1H), 4.49 (s, 2H), 1.64 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.2, 134.3, 131.6, 131.1, 131.0, 128.9, 128.8, 128.6, 127.7, 127.1, 126.6, 107.6, 107.0, 58.4, 48.5; HRMS (TOF-EI) calcd for $C_{20}H_{19}NO$ (M) 289.1467, found 289.1470.

2-[(*E*)-1,3-Diphenyl-2-propenyl]-5-[(*E*)-styryl]pyrrole (Table 2, entry 5): light red solid, 0.0657 g, 91% yield; mp 150−152 °C, $[\alpha]^{20}_D$ −3.5 (*c* 0.40, CH_2Cl_2) (97% ee); IR (film) 3421, 1597, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (brs, 1H), 7.37−7.33 (m, 6H), 7.31−7.26 (m, 7H), 7.23−7.19 (m, 1H), 7.17−7.14 (m, 1H), 6.87 (d, *J* = 16.4 Hz, 1H), 6.58 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.52 (d, *J* = 16.4 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 5.98 (d, *J* = 2.0 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 137.8, 137.2, 135.0, 131.8, 130.9, 130.8, 129.0, 128.8, 128.6, 127.8, 127.3, 127.0, 126.7, 125.9, 122.9, 119.2, 109.8, 109.1, 48.5; HRMS (TOF-EI) calcd for $C_{27}H_{23}N$ (M) 361.1830, found 361.1834.

2-[(*E*)-1,3-Diphenyl-2-propenyl]-5-[(*E*)-styryl]pyrrole (Table 2, entry 6): light yellow solid, 0.0671 g, 93% yield; mp 150−152 °C, $[\alpha]^{20}_D$ −3.5 (*c* 1.00, CH_2Cl_2) (97% ee); IR (film) 3421, 1597, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (brs, 1H), 7.39−7.34 (m, 6H), 7.31−7.26 (m, 7H), 7.24−7.20 (m, 1H), 7.18−7.14 (m, 1H), 6.88 (d, *J* = 16.4 Hz, 1H), 6.59 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.53 (d, *J* = 16.4 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 5.97 (d, *J* = 2.8 Hz, 1H), 4.87 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 137.8, 137.1, 135.0, 131.8, 130.9, 130.8, 129.0, 128.8, 128.6, 127.8, 127.3, 127.0, 126.6, 125.9, 122.9, 119.2, 109.8, 109.1, 48.5; HRMS (TOF-EI) calcd for $C_{27}H_{23}N$ (M) 361.1830, found 361.1834.

(*E*)-2-(1,3-Diphenyl-2-propenyl)pyrrole[7] (Table 2, entry 7): light yellow oil, 0.0444 g, 86% yield; $[\alpha]^{20}_D$ −11.0 (*c* 0.41, CH_2Cl_2) (89% ee); IR (film) 3430, 2360, 1275, 1261, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (brs, 1H), 7.40−7.21 (m, 10H), 6.74−6.72 (m, 1H), 6.61 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.20−6.18 (m, 1H), 5.99 (s, 1H), 4.89 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.2, 133.3, 131.5, 131.3, 128.9, 128.8, 128.6, 127.7, 127.1, 126.6, 117.4, 108.6, 107.0, 48.3; HRMS (TOF-EI) calcd for $C_{19}H_{17}N$ (M) 259.1361, found 259.1364.

(*E*)-2-[1,3-Bis(3-chlorophenyl)-2-propenyl]-3,5-dimethylpyrrole (Table 2, entry 8): light yellow oil, 0.0633 g, 89% yield; $[\alpha]^{20}_D$ −3.3 (*c* 0.42, CH_2Cl_2) (94% ee); IR (film) 3446, 1593, 1473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (brs, 1H), 7.28−7.17 (m, 7H), 7.12−7.09 (m, 1H), 6.53 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.23 (dd, *J* = 16.0, 1.2 Hz, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 1H), 2.18 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 139.0, 134.8, 134.8, 131.9, 130.8, 130.1, 130.0, 128.6, 127.7, 127.2, 126.7, 126.5, 126.4, 125.0, 124.8, 116.0, 108.9, 45.5, 13.2, 11.3; HRMS (TOF-EI) calcd for $C_{21}H_{19}Cl_2N$ (M) 355.0895, found 355.0899.

dx.doi.org/10.1021/jo300539y | J. Org. Chem. 2012, 77, 4479−4483

(*E*)-3,5-Dimethyl-2-(1,3-di-4-tolyl-2-propenyl)pyrrole (Table 2, entry 9): light yellow oil, 0.0589 g, 95% yield; $[\alpha]^{20}_{D}$ −19.5 (*c* 0.38, CH_2Cl_2) (95% ee); IR (film) 3460, 1602, 1510 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.24 (m, 3H), 7.13−7.08 (m, 6H), 6.49 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 5.70 (d, *J* = 2.4 Hz, 1H), 4.89 (d, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.16 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.3, 136.3, 134.7, 131.2, 130.4, 129.5, 129.4, 128.5, 126.5, 126.4, 125.7, 115.3, 108.6, 45.5, 21.4, 21.2, 13.2, 11.3; HRMS (TOF-EI) calcd for $C_{23}H_{25}N$ (M) 315.1987, found 315.1991.

(*E*)-2-[1,3-Bis(4-chlorophenyl)-2-propenyl)-3,5-dimethylpyrrole (Table 2, entry 10): light yellow oil, 0.0453 g, 64% yield; $[\alpha]^{20}_{D}$ −4.3 (*c* 0.56, CH_2Cl_2) (81% ee); IR (film) 3447, 1592, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.25 (m, 7H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.50 (dd, *J* = 15.6, 6.8 Hz, 1H), 6.23(dd, *J* = 16.0, 1.2 Hz, 1H), 5.72 (d, *J* = 2.4 Hz, 1H), 4.91 (d, *J* = 6.8 Hz, 1H), 2.18 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 135.7, 133.4, 132.7, 131.3, 130.7, 129.9, 129.0, 128.9, 127.8, 126.3, 125.4, 115.8, 108.9, 45.2, 13.2, 11.3; HRMS (TOF-EI) calcd for $C_{21}H_{19}Cl_2N$ (M) 355.0895, found 355.0900.

2-[(*E*)-1,3-Bis(3-chlorophenyl)-2-propenyl)-5-[(*E*)-styryl]-pyrrole (Table 2, entry 11): light red oil, 0.0697 g, 81% yield; $[\alpha]^{20}_{D}$ −1.8 (*c* 0.73, CH_2Cl_2) (92% ee); IR (film) 3433, 1594, 1507 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (brs, 1H), 7.38 (m, 3H), 7.31−7.15 (m, 10H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.59−6.52 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.29 (m, 1H), 5.97 (m, 1H), 4.85(d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.8, 137.7, 134.9, 134.8, 133.6, 131.7, 131.2, 131.0, 130.3, 130.1, 128.9, 128.7, 127.9, 127.6, 127.1, 126.8, 126.6, 126.0, 124.9, 123.4, 119.0, 109.8, 109.3, 48.1; HRMS (TOF-EI) calcd for $C_{27}H_{21}Cl_2N$ (M) 429.1051, found 429.1057.

(*E*)-5-Fluoro-2-(1,3-diphenyl-2-propenyl)-4,7-dihydroindole (10a): light yellow oil, 0.0583 g, 88% yield; $[\alpha]^{20}_{D}$ −10.5 (*c* 1.64, CH_2Cl_2) (96% ee); IR (film) 3421, 1700, 1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (brs, 1H), 7.38−7.20 (m, 10H), 6.57 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.75 (d, *J* = 2.4 Hz, 1H), 5.38−5.31 (m, 1H), 4.82 (d, *J* = 7.6 Hz, 1H), 3.33 (m, 2H), 3.27−3.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, J_{C-F} = 249.0 Hz), 142.3, 137.2, 133.5, 131.5, 131.2, 129.0, 128.8, 128.6, 127.7, 127.2, 126.6, 123.0 (d, J_{C-F} = 2.0 Hz), 113.3 (d, J_{C-F} = 13.0 Hz), 105.6 (d, J_{C-F} = 3.0 Hz), 99.2 (d, J_{C-F} = 20.0 Hz), 48.5, 25.8 (d, J_{C-F} = 28.0 Hz), 22.6 (d, J_{C-F} = 9.0 Hz); HRMS (TOF-EI) calcd for $C_{23}H_{20}FN$ (M) 329.1580, found 329.1583.

(*E*)-5-Methyl-2-(1,3-diphenyl-2-propenyl)-4,7-dihydroindole (10b): light yellow oil, 0.0527 g, 81% yield; $[\alpha]^{20}_{D}$ −7.3 (*c* 0.82, CH_2Cl_2) (95% ee); IR (film) 3423, 1653, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (brs, 1H), 7.39−7.19 (m, 10H), 6.59 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.72 (d, *J* = 2.4 Hz, 1H), 5.51 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 3.17 (m, 2H), 3.07 (m, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.4, 133.3, 132.3, 131.6, 131.3, 128.9, 128.8, 128.7, 127.6, 127.0, 126.6, 124.1, 117.5, 114.9, 105.3, 48.6, 29.9, 24.6, 23.9; HRMS (TOF-EI) calcd for $C_{24}H_{23}N$ (M) 325.1830, found 325.1834.

(*E*)-5-Methoxy-2-(1,3-diphenyl-2-propenyl)-4,7-dihydroindole (10c): light yellow oil, 0.0584 g, 86% yield; $[\alpha]^{20}_{D}$ −7.6 (*c* 0.80, CH_2Cl_2) (97% ee); IR (film) 3421, 1667, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (brs, 1H), 7.38−7.18 (m, 10H), 6.58 (dd, *J* = 16. 0, 7.6 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.81 (d, *J* = 7.6 Hz, 1H), 4.75−4.73 (m, 1H), 3.58 (s, 3H), 3.28−3.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.5, 137.3, 132.8, 131.5, 131.3, 128.9, 128.7, 128.6, 127.6, 127.0, 126.6, 124.0, 114.1, 105.4, 90.2, 54.6, 48.5, 27.6, 23.1; HRMS (TOF-EI) calcd for $C_{24}H_{23}NO$ (M) 341.1780, found 341.1783.

(*E*)-2-(1,3-Diphenyl-2-propenyl)-4,7-dihydroindole (10d): light yellow oil, 0.0485 g, 78% yield; $[\alpha]^{20}_{D}$ −6.6 (*c* 0.35, CH_2Cl_2) (92% ee); IR (film) 3421, 1653, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (brs, 1H), 7.39−7.19 (m, 10H), 6.59 (dd, *J* = 16. 0, 7.6 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.90−5.86 (m, 1H), 5.81−5.77 (m, 1H), 5.73 (d, *J* = 2.8 Hz, 1H), 4.82 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.3, 132.1, 131.5, 131.3, 128.9, 128.8, 128.7, 127.6, 127.0, 126.6, 126.1, 123.8, 123.0, 114.3, 105.6, 48.5, 25.2, 24.2; HRMS (TOF-EI) calcd for $C_{23}H_{21}N$ (M) 311.1674, found 311.1671.

(*E*)-3-Methyl-2-(1,3-diphenyl-2-propenyl)-4,7-dihydroindole (10e): light yellow oil, 0.0572 g, 88% yield; $[\alpha]^{20}_{D}$ −9.3(*c* 0.44, CH_2Cl_2) (86% ee); IR (film) 3424, 1699,1492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.19 (m, 11), 6.58 (dd, *J* = 16.0, 6.8 Hz), 6.34 (d, *J* = 15.6 Hz, 1H), 5.93−5.89 (m, 1H), 5.83−5.79 (m, 1H), 4.99 (d, *J* = 6.8 Hz, 1H), 3.23−3.18 (m, 2H), 3.16−3.11 (m, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.4, 131.6, 131.2, 128.9, 128.8, 128.6, 127.6, 126.8, 126.6, 126.3, 125.8, 123.3, 122.4, 114.7, 112.9, 46.0, 24.4, 24.0, 9.2; HRMS (FT-ICRMS) calcd for $C_{24}H_{23}N$ (M) 325.1814, found 325.1825.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The data for determination of enantiomeric excess along with NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are thankful for financial support from the National Natural Science Foundation of China (21072194, 21172222) and the National Basic Research Program of China (2010CB833300).

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