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Enantioselective Palladium-Catalyzed Allylic Substitution of Sodium Benzotriazolide

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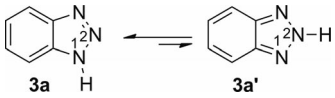
Chiral allylic benzotriazole-containing regioisomers **4** and **5** were synthesized by enantioselective palladium-catalyzed allylation of sodium benzotriazolide with a range of allylic carbonates in 50–89 % yields, regioselectivities of 2.2:1 to 1:3.4, and *ee* values of up to 95 %.

The palladium-catalyzed asymmetric allylic alkylation (AAA) has been developed as a useful tool for the preparation of chiral allylic compounds[1] and, during the past several decades, a wide range of nitrogen nucleophiles[2] have been studied in Tsuji–Trost allylation reactions. In this context, the use of benzotriazole (BtH) as a pronucleophile in asymmetric reactions of this type has not yet been reported. The asymmetric reaction of BtH has been extensively investigated for organocatalytic applications,[3] and the aluminum-catalyzed enantioselective Michael reaction has also been described.[4] In addition, Bt-containing compounds may have a broad potential in drug discovery and organic synthesis,[5] and, as a result, new synthetic methods for the preparation of chiral Bt-substituted compounds is the subject of considerable interest.[6] Benzotriazole, which is an important fragment of many pharmaceuticals,[7] contains a relatively acidic N–H bond (pK_a = 8.6) and exists in two tautomeric forms (**3a** and **3a′**) in solution (Scheme 1).[8]



Scheme 1. Tautomers of benzotriazole in solution.

Tautomer **3a** has a greater aromatic character[9] and predominates in the equilibrium both in solution[9] and in the solid phase.[10] The repulsion of electronic pairs between the N-2 and N-1 atoms has a destabilizing effect.[11] The larger dipolar moment of **3a** favors the interactions between benzotriazole molecules in the solid state and between **3a** and a polar solvent in solution. However, **3a′** is by 4 kcal/mol more stable than **3a** in the gas phase.[12] An initial study on the palladium-catalyzed allylation of BtH with cinnamyl ethyl carbonate as an allylating agent provided good yields of allylic Bt-containing regioisomers, albeit with poor regioselectivities.[13] Herein, we report the formation of chiral Bt-containing allylic compounds through Pd-catalyzed asymmetric allylation of sodium benzotriazolide (BtNa) with structurally diverse allyl carbonates.

Results and Discussion

In an exploratory study, we began with a reaction between BtH, which has two different nucleophilic positions, and *rac*-1,3-diphenylallyl ethyl carbonate (**2a**) in the presence of $[Pd_2(dba)_3{\cdot}CHCl_3]$ and (*S*)-PHOX (**1a**) in tetrahydrofuran (THF) at room temperature under argon; unfortunately, under these conditions, a complex mixture of products was obtained. Interestingly, when BtNa was used rather than BtH under the same reaction conditions, a mixture of allylic N-1 regioisomer **4a** and N-2 regioisomer **5a** was achieved in overall 62 % yield with 77 % *ee* of **4a** and 94 % of **5a**, although unsurprisingly with a low regioselectivity (**4a**/**5a** = 1:1.2; Table 1, Entry 1), which is in agreement with results obtained with the palladium-catalyzed allylation of BtH.[13] Solvent screening revealed that THF was an optimal solvent (Table 1, Entry 1); poor results were obtained when the reaction was conducted in dioxane, diethyl ether, or toluene (Table 1, Entries 2–3, 5). The reaction in dichloromethane gave rise to moderate yields and *ee* values of **4a** and **5a** (Table 1, Entry 4). Additionally, varyiation of the ratio of **2a**/**3b** was found to have a considerable influence on the outcome of the allylation reaction; it was found that a twofold excess of **3b** produced the highest yield and *ee* of **4a** and **5a** (Table 1, Entries 1, 6, 7). Change of the reaction temperature had a drastic effect on the efficiency, regioselectivity, and enantioselectivity (Table 1, Entries 1, 8,

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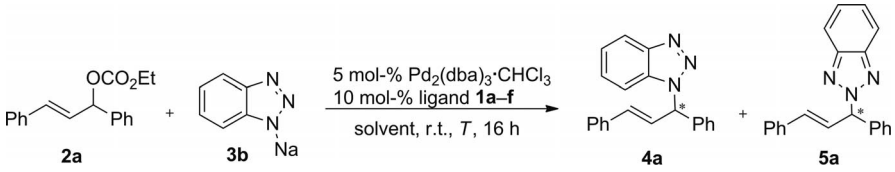
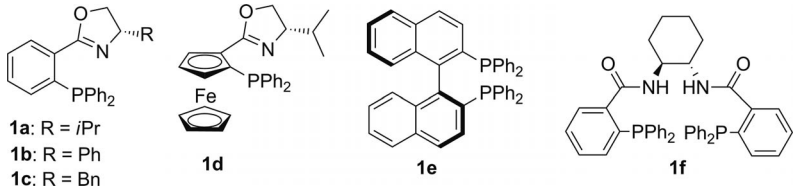
Table 1. Optimizing reaction conditions for Pd-catalyzed asymmetric allylation of BtNa.[a]



Entry	Ligand	2a/3b	Solvent	*T* [°C]	Overall yield [%][b]	4a/5a	*ee* [%][c] 4a	5a
1	**1a**	1.2:1	THF	r.t.	62	1:1.2	77	94
2	**1a**	1.2:1	dioxane	r.t.	42	1:1.2	–	
3	**1a**	1.2:1	Et_2O	r.t.	28	1.5:1	–	
4	**1a**	1.2:1	CH_2Cl_2	r.t.	67	2:1	41	59
5	**1a**	1.2:1	toluene	r.t.	30	2:1	–	
6	**1a**	2:1	THF	r.t.	60	1:1.2	77	94
7	**1a**	1:2	THF	r.t.	72	1:1.3	77	91
8	**1a**	1:2	THF	0	46	1:1.3	20	65
9	**1a**	1:2	THF	35	64	1:1.2	75	85
10	**1b**	1:2	THF	r.t.	65	1:1.1	4	11
11	**1c**	1:2	THF	r.t.	67	1:1.1	67	80
12	**1d**	1:2	THF	r.t.	68	1.2:1	34	75
13	**1e**	1:2	THF	r.t.	53	1.5:1	9	35
14[d]	**1f**	1:2	THF	r.t.	38	1:1.1	0	14

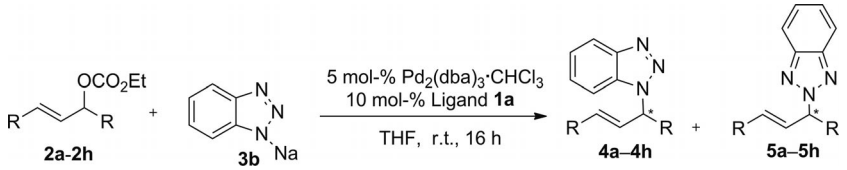
[a] Reagents and conditions: **3b** (0.2 mmol, 1.0 equiv.), catalyst (5 mol-%), solvent (2 mL), argon. [b] Isolated yield. [c] Determined by HPLC analysis using Diacel CHIRALPAK AD-H. [d] Reaction time 60 h.



Scheme 2. Chiral ligands **1a**–**f**.

9). Further investigations were performed with a range of chiral ligands, including **1a**,[14–16] **1b**,[14–16] **1c**,[14–16] **1d**,[17] **1e**,[18] and Trost ligand **1f**[19] (Scheme 2) to evaluate how the structural variation of the ligands may affect the enantioselectivity. Ligand **1a** gave the best results (overall 72% yield with 77% *ee* of **4a** and 91% *ee* of **5a**) in favor of the N-2 regioisomer **5a** (**4a**/**5a** = 1:1.3; Table 1, Entry 7). The palladium complexes generated from **1b** and **1d**–**f** gave

Table 2. Pd-catalyzed asymmetric allylation of BtNa with various allyl carbonates.[a]



Entry	R	Product	Overall yield [%][b]	4/5	*ee* [%][c] 4	5
1	Ph	**4a**, **5a**	72	1:1.3	77	91
2	2-MeC_6H_4	**4b**, **5b**	69	1.8:1	–46	–72
3	3-MeC_6H_4	**4c**, **5c**	89	1.3:1	95	95
4	4-MeC_6H_4	**4d**, **5d**	87	2.2:1	65	80
5	4-BrC_6H_4	**4e**, **5e**	60	2:1	40	68
6[d]	2-naphthyl	**4f**, **5f**	50	1:1	44	73
7[e]	Et	**4g**, **5g**	80	1:3.4	–72	78
8[e]	Me	**4h**, **5h**	73	1:1.9	–61	71

[a] Reagents and conditions: carbonate **2a**–**h** (0.2 mmol, 1.0 equiv.), **3b** (0.4 mmol, 2.0 equiv.), catalyst (5 mol-%), THF (2 mL), argon. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase. [d] OCO_2Et was replaced by OAc due to decomposition. [e] 10 mol-% of catalyst was used; the ratio of **2**/**3b** was 2:1.

either poor yields or *ee* values (Table 1, Entries 10, 12–14). Use of ligand **1c** led to the formation of **4a** (32% yield and 67% *ee*) and **5a** (35% yield and 80% *ee*) with a 1:1 ratio of **4a**/**5a** (Table 1, Entry 9). Therefore, the conditions presented in Table 1, Entry 7 were chosen as the standard.

With the optimized reaction conditions in hand, the scope of the enantioselective Pd-catalyzed allylation of BtNa was further examined with a range of allyl carbonates (Table 2). It can be seen that the variation of substituents in the symmetrical allyl carbonates **2a**–**h** strongly influences both the regio- and enantioselectivity. The reaction of diarylallyl carbonates with electron-donating or electron-attracting groups (*o*-Me, *m*-Me, *p*-Me; or *p*-Br) on the phenyl ring gave Bt-substituted regioisomers (**4b**–**e** and **5b**–**e**) in 60–89% overall yields and 40–95% *ee*, with regioselectivities in the range 2.3:1–1.8:1, except for bis(2-naphthyl)allyl carbonate, which gave a 1:1 ratio of **4f**/**5f** (Table 2, Entries 2–6). The reaction of bis(phenyl- and alkyl)allyl carbonates led to the formation of the corresponding Bt-containing regioisomers (**4a**, **4g**, **4h** and **5a**, **5g**, **5h**) in 72–80% overall yields and 61–91% *ee*, with regioselectivities in the range of 1:1.9–1:3.4. It should be noted that diarylallyl carbonate **2c**, with a *meta*-methyl group on the phenyl rings, gave rise to both **4a** and **5a** with the highest *ee* value (95% *ee*; Table 2, Entry 3). Further study on this reaction indicated that no isomerization occurred between **5a** and **4a** with $[Pd_2(dba)_3{\cdot}CHCl_3]$ and **1a** in THF at room temperature within 12 h.

Conclusions

We have developed an efficient $[Pd_2(dba)_3{\cdot}CHCl_3]$/(*S*)-PHOX (**1a**) catalyst system for the asymmetric allylic amination of benzotriazole with a range of carbonates. The allylic Bt-containing regioisomers were obtained in good overall yields with regioselectivities in the range of 2.2:1–1:3.4 and *ee* of up to 95%. To the best of our knowledge, this is the first example of a transition-metal-catalyzed asymmetric allylation of BtH. Further studies aimed at improving the regioselectivity and enantioselectivity of this AAA is in progress.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ with a Bruker NMR (400 MHz) spectrometer. The chemical shifts are reported in δ units downfield from the Me_4Si internal reference. Optical rotations were determined with a JASCO P-2200 instrument. HPLC analyses were carried out on chiral columns (Chiralcel AD-H, OJ-H) with a Shimadzu 150 instrument fitted with a multi-wavelength detector. Low-resolution electron-impact (EI) mass spectra were obtained with an Agilent MSD Chemstation, and high-resolution mass spectra were obtained with a Finnigan VG Platform or a Finnigan MAT 95S. Carbonates **2a**–**h** were prepared according to known procedures.[2a]

Sodium Benzotriazolide (3b): BtH (6.0 g, 0.1 mol) was dissolved in THF and cooled to 0 °C in an ice bath. NaH (1.2 g, 0.1 mol) was added, and the mixture was stirred for 2 h, then THF was removed by rotary evaporation. The white solid was washed with CH_2Cl_2, and the solvent was removed under vacuum. $[Pd_2(dba)_3{\cdot}CHCl_3]$ (0.01 mmol, 11.5 mg) and ligand (0.02 mmol) were dissolved in THF (2.0 mL) and stirred in a dry Schlenk tube filled with argon for 30 min. Allylic carbonate **2** (0.20 mmol) and sodium benzotriazolide (0.40 mmol, 56.4 mg) were added, and the reaction mixture was stirred at room temperature. The crude reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:20) to give the desired products.

(*E*)-1,3-Di-*m*-tolylallyl Ethyl Carbonate (2c): Yield: 1.0 g (70%). Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.21 (m, 3 H), 7.20–7.16 (m, 3 H), 7.12 (d, *J* = 6.7 Hz, 1 H), 7.07–7.02 (m, 1 H), 6.65 (d, *J* = 15.8 Hz, 1 H), 6.34 (dd, *J* = 15.3, 6.5 Hz, 1 H), 6.21 (d, *J* = 6.8 Hz, 1 H), 4.19 (qd, *J* = 6.3, 4.3 Hz, 2 H), 2.35 (s, 3 H), 2.31 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 138.8, 138.4, 138.2, 136.1, 133.0, 129.2, 129.0, 128.6, 128.5, 127.7, 127.5, 126.9, 124.1, 124.0, 80.2, 64.1, 21.5, 21.4, 14.3 ppm. MS (EI): *m*/*z* (%) = 220 (100), 310 $[M]^+$. HRMS (EI): calcd. for $C_{20}H_{22}O_3$ $[M]^+$ 310.1569; found 310.1570. IR (KBr): $\tilde{\nu}_{max}$ = 3037, 2917, 2847, 1650, 1606, 1508, 1457, 1378, 1270, 1235, 1156, 1140, 1083, 973, 916, 811, 792, 740, 498 cm^{-1}.

(*E*)-1,3-Bis(4-bromophenyl)allyl Ethyl Carbonate (2e): Yield: 1.2 g (90%). Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.59 (d, *J* = 15.8 Hz, 1 H), 6.30 (dd, *J* = 15.8, 6.7 Hz, 1 H), 6.18 (d, *J* = 6.7 Hz, 1 H), 4.20 (qd, *J* = 7.1, 3.1 Hz, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 137.6, 134.8, 132.1, 131.9, 131.8, 128.8, 128.3, 127.2, 122.6, 122.2, 79.0, 64.4, 14.3 ppm. MS (EI): *m*/*z* (%) = 269 (100), 438 $[M]^+$. HRMS (EI): calcd. for $C_{18}H_{16}Br_2O_3$ $[M]^+$ 437.9466; found 437.9469. IR (KBr): $\tilde{\nu}_{max}$ = 2986, 2917, 1742, 1486, 1406, 1368, 1302, 1242, 1074, 1004, 960, 807, 849, 846, 830, 564, 510 cm^{-1}.

General Procedure for the Pd-Catalyzed Asymmetric Allylic Alkylation of Benzotriazole: $[Pd_2(dba)_3{\cdot}CHCl_3]$ (0.01 mmol, 11.5 mg) and ligand (0.02 mmol) were dissolved in THF (2.0 mL) and stirred in a dry Schlenk tube filled with argon for 30 min. Allylic carbonate **2** (0.20 mmol) and sodium benzotriazolide (0.40 mmol, 56.4 mg) were added, and the reaction mixture was stirred at room temperature. The crude reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1: 20) to give the desired products.

(*E*)-1-(1,3-Diphenylallyl)-1*H*-benzo[*d*][1,2,3]triazole (4a): Yield: 19.9 mg (32%). White solid; m.p. 169–170 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.08 (m, 1 H), 7.46–7.40 (m, 3 H), 7.39–7.36 (m, 5 H), 7.36–7.27 (m, 5 H), 7.02 (dd, *J* = 15.9, 7.2 Hz, 1 H), 6.80 (d, *J* = 7.2 Hz, 1 H), 6.63 (d, *J* = 15.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 137.9, 135.8, 134.6, 132.5, 129.1, 128.7, 128.6, 128.5, 127.4, 127.3, 126.9, 125.6, 124.0, 120.2, 110.4, 65.6 ppm. MS (EI): *m*/*z* (%) =193 (100), 311 $[M]^+$. HRMS (EI): calcd. for $C_{21}H_{17}N_3$ $[M]^+$ 311.1422; found 311.1423. IR (KBr): $\tilde{\nu}_{max}$ = 3062, 3015, 2923, 1655, 1448, 1381, 1273, 1223, 1153, 1064, 966, 742, 691, 532 cm^{-1}. The enantiomeric excess of the product (77%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 14.24 (minor), 18.67 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 80:20; 1.0 mL/min]. $[\alpha]_D^{20}$ = –21.0 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(1,3-Diphenylallyl)-2*H*-benzo[*d*][1,2,3]triazole (5a): Yield: 24.9 mg (40%). White solid; m.p. 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.90 (dd, *J* = 6.6, 3.1 Hz, 2 H), 7.52–7.46 (m, 3 H), 7.46–7.39 (m, 5 H), 7.39–7.27 (m, 4 H), 7.09 (dd, *J* = 15.9, 7.9 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 6.71 (d, *J* = 15.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 138.4, 135.9, 134.6, 128.9, 128.7, 128.6, 128.4, 127.4, 127.0, 126.5, 126.2, 118.3, 72.6 ppm. MS (EI): *m*/*z* (%) =193 (100), 311 $[M]^+$. HRMS (EI): calcd. for $C_{21}H_{17}N_3$ $[M]^+$ 311.1422; found 311.1420. IR (KBr): $\tilde{\nu}_{max}$ = 3062, 3021, 2923, 1653, 1492, 1448, 1381, 1308, 1201, 967, 887, 745, 694, 548, 482 cm^{-1}. The enantiomeric excess of the product (91%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 10.52 (minor), 11.35 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 80:20; 1.0 mL/min]. $[\alpha]_D^{20}$ = –55.0 (*c* = 1.0, $CHCl_3$).

(*E*)-1-(1,3-Di-*o*-tolylallyl)-1*H*-benzo[*d*][1,2,3]triazole (4b): Yield: 29.8 mg (44%). White solid; m.p. 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 5.7, 3.0 Hz, 1 H), 7.60–7.54 (m, 1 H), 7.38 (t, *J* = 3.8 Hz, 3 H), 7.34–7.25 (m, 4 H), 7.24–7.13 (m, 3 H), 7.02 (d, *J* = 6.2 Hz, 1 H), 6.84 (dd, *J* = 15.7, 6.2 Hz, 1 H), 6.66 (d, *J* = 15.8 Hz, 1 H), 2.38 (s, 3 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 136.5, 135.8, 135.8, 135.1, 132.8, 131.8, 131.2, 130.4, 128.8, 128.3, 127.6, 127.3, 126.9, 126.7, 126.3, 126.1, 124.0, 120.2, 110.5, 62.9, 19.7, 19.3 ppm. MS (EI): *m*/*z* (%) = 221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1737. IR (KBr): $\tilde{\nu}_{max}$ = 3031, 2910, 2857, 1736, 1612, 1486, 1448, 1321, 1267, 960, 795, 687, 441 cm^{-1}. The enantiomeric excess of the product (–46%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 6.20 (major), 6.63 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = 34.4 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(1,3-Di-*o*-tolylallyl)-2*H*-benzo[*d*][1,2,3]triazole (5b): Yield: 17.0 mg (25%). White solid; m.p. 71–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 6.5, 3.1 Hz, 2 H), 7.54 (dd, *J* = 5.2, 3.8 Hz, 1 H), 7.40–7.33 (m, 3 H), 7.22 (dd, *J* = 7.2, 5.1 Hz, 3 H), 7.18–7.10 (m, 3 H), 6.98 (d, *J* = 6.9 Hz, 1 H), 6.85 (dd, *J* = 15.6, 6.9 Hz, 1 H), 6.77 (d, *J* = 15.7 Hz, 1 H), 2.43 (s, 3 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 136.6, 135.9, 135.9, 135.1, 131.9, 130.9, 130.4, 128.6, 128.2, 127.3, 127.2, 126.7, 126.4, 126.2, 126.2, 118.3, 69.4, 19.7, 19.4 ppm. MS (EI): *m*/*z* (%) =221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1738. IR (KBr): $\tilde{\nu}_{max}$ = 3322, 2926, 2853, 1732, 1457, 1254, 1004, 884, 745, 435 cm^{-1}. The enantiomeric excess of the product (–72%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 5.42 (major), 12.51 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = 20.8 (*c* = 1.0, $CHCl_3$).

(*E*)-1-(1,3-Di-*m*-tolylallyl)-1*H*-benzo[*d*][1,2,3]triazole (4c): Yield: 33.9 mg (50%). White solid; m.p. 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.8 Hz, 1 H), 7.42–7.35 (m, 3 H), 7.30–7.22 (m, 4 H), 7.19–7.10 (m, 4 H), 7.01 (dd, *J* = 15.8, 7.2 Hz, 1 H), 6.75 (d, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 15.8 Hz, 1 H), 2.36 (s, 3 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 138.9, 138.3, 137.9, 135.8, 134.5, 132.5, 129.3, 129.2, 128.9, 128.6, 128.0, 127.5, 127.3, 125.5, 124.4, 124.1, 124.0, 120.2, 110.5, 65.6, 21.5, 21.4 ppm. MS (EI): *m*/*z* (%) =221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1737. IR (KBr): $\tilde{\nu}_{max}$ = 3019, 2933, 2847, 1609, 1486, 1451, 1267, 1372, 1156, 1061, 967, 786, 741, 688, 434 cm^{-1}. The enantiomeric excess of the product (95%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 11.16 (minor), 14.91 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 80:20; 1.0 mL/min]. $[\alpha]_D^{20}$ = –22.2 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(1,3-Di-*m*-tolylallyl)-2*H*-benzo[*d*][1,2,3]triazole (5c): Yield: 26.4 mg (39%). White solid; m.p. 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 6.6, 3.0 Hz, 2 H), 7.37 (dd, *J* = 6.6, 3.0 Hz, 2 H), 7.29–7.26 (m, 1 H), 7.25–7.16 (m, 5 H),7.13–7.07 (m, 2 H), 7.03 (dd, *J* = 15.8, 7.9 Hz, 1 H), 6.70 (d, *J* = 8.0 Hz, 1 H), 6.64 (d, *J* = 15.8 Hz, 1 H), 2.32 (s, 3 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 138.7, 138.4, 138.2, 135.9, 134.5, 129.4, 129.2, 128.8, 128.6, 128.0, 127.6, 126.4, 126.0, 124.5, 124.2, 118.4, 72.7, 21.5, 21.4 ppm. MS (EI): *m*/*z* (%) =221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1737. IR (KBr): $\tilde{\nu}_{max}$ = 3060, 2917, 2850, 1711, 1612, 1492, 1451, 1369, 1277, 1229, 1153, 1068, 960, 754, 447 cm^{-1}. The enantiomeric excess of the product (95%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 9.46 (minor), 11.81 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = –10.9 (*c* = 1.0, $CHCl_3$).

(*E*)-1-(1,3-Di-*p*-tolylallyl)-1*H*-benzo[*d*][1,2,3]triazole (4d): Yield: 40.7 mg (60%). White solid; m.p. 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.8 Hz, 1 H), 7.37–7.26 (m, 5 H), 7.20 (d, *J* = 7.7 Hz, 2 H), 7.17–7.08 (m, 4 H), 6.91 (dd, *J* = 15.8, 7.1 Hz, 1 H), 6.72 (d, *J* = 7.1 Hz, 1 H), 6.54 (d, *J* = 15.8 Hz, 1 H), 2.32 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 138.4, 135.0, 134.3, 133.1, 132.5, 129.7, 129.4, 127.3, 127.2, 126.8, 124.7, 123.9, 120.2, 110.6, 65.5, 21.3, 21.2 ppm. MS (EI): *m*/*z* (%) =221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1736. IR (KBr): $\tilde{\nu}_{max}$ = 3028, 2923, 2860, 1742, 1615, 1511, 1451, 1384, 1273, 1156, 969, 808, 748, 498 cm^{-1}. The enantiomeric excess of the product (65%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 23.29 (minor); 35.12 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 80:20; 1.0 mL/min]. $[\alpha]_D^{20}$ = –29.6 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(1,3-Di-*p*-tolylallyl)-2*H*-benzo[*d*][1,2,3]triazole (5d): Yield: 18.3 mg (27%). White solid; m.p. 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 6.5, 2.9 Hz, 2 H), 7.36 (dd, *J* = 6.6, 2.8 Hz, 2 H), 7.34–7.28 (m, 4 H), 7.16 (d, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 7.7 Hz, 2 H), 6.97 (dd, *J* = 15.8, 7.9 Hz, 1 H), 6.70 (d, *J* = 7.9 Hz, 1 H), 6.62 (d, *J* = 15.8 Hz, 1 H), 2.32 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 138.4, 138.3, 135.6, 134.3, 133.2, 129.5, 129.3, 127.4, 126.9, 126.3, 125.3, 118.3, 72.5, 21.3, 21.2 ppm. MS (EI): *m*/*z* (%) =221 (100), 339 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{21}N_3$ $[M]^+$ 339.1735; found 339.1736. IR (KBr): $\tilde{\nu}_{max}$ = 3021, 2920, 1654, 1518, 1451, 1372, 1318, 1258, 1182, 970, 887, 798, 745, 504 cm^{-1}. The enantiomeric excess of the product (80%) was determined by HPLC analysis (214 nm, 25 °C): t_R = 7.52 (minor), 8.26 min (major) [Diacel CHIRALPAK OD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = –19.0 (*c* = 1.0, $CHCl_3$).

(*E*)-1-[1,3-Bis(4-bromophenyl)allyl]-1*H*-benzo[*d*][1,2,3]triazole (4e): Yield: 37.4 mg (40%). White solid; m.p. 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 7.44–7.33 (m, 3 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 6.95 (dd, *J* = 15.9, 7.0 Hz, 1 H), 6.69 (d, *J* = 7.0 Hz, 1 H), 6.54 (d, *J* = 15.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 136.7, 134.5, 133.7, 132.3, 132.3, 131.9, 129.0, 128.4, 127.6, 125.9, 124.2, 122.8, 122.6, 120.4, 110.0, 64.7 ppm. MS (EI): *m*/*z* (%) =349 (100), 467 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{15}Br_2N_3$ $[M]^+$ 466.9633; found 466.9639. IR (KBr): $\tilde{\nu}_{max}$ = 3056, 2923, 2847, 1660, 1584, 1486, 1448, 1406, 1264, 1156, 1064, 1001, 963, 811, 748, 700, 545, 491 cm^{-1}. The enantiomeric excess of the product (41%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 17.94 (minor), 30.25 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm);

hexane/2-propanol, 70:30; 1.0 mL/min]. $[\alpha]_D^{20}$ = –55.6 (*c* = 1.0, $CHCl_3$).

(*E*)-2-[1,3-Bis(4-bromophenyl)allyl]-2*H*-benzo[*d*][1,2,3]triazole (5e): Yield: 18.7 mg (20%). White solid; m.p. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 6.6, 3.1 Hz, 2 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.42 (dd, *J* = 6.6, 3.1 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.00 (dd, *J* = 15.9, 7.7 Hz, 1 H), 6.71 (d, *J* = 7.7 Hz, 1 H), 6.60 (d, *J* = 15.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 137.1, 134.6, 133.7, 132.1, 131.9, 129.2, 128.5, 126.7, 126.4, 122.9, 122.5, 118.3, 71.7 ppm. MS (EI): *m*/*z* (%) = 349 (100), 467 $[M]^+$. HRMS (EI): calcd. for $C_{23}H_{15}Br_2N_3$ $[M]^+$ 466.9633; found 466.9636. IR (KBr): $\tilde{\nu}_{max}$ = 3066, 2920, 2841, 1732, 1598, 1486, 1410, 1308, 1258, 1261, 1188, 1071, 1004, 969, 890, 821, 738, 540, 494 cm^{-1}. The enantiomeric excess of the product (68%) was determined by HPLC analysis (276 nm, 25 °C): t_R = 6.85 (minor), 7.69 min (major) [Diacel CHIRALPAK OD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = –26.2 (*c* = 1.0, $CHCl_3$).

(*E*)-1-[1,3-Bis(naphthalen-2-yl)allyl]-1*H*-benzo[*d*][1,2,3]triazole (4f): Yield: 20.6 mg (25%). White solid; m.p. 160–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 5.3, 2.6 Hz, 1 H), 7.84 (d, *J* = 3.4 Hz, 2 H), 7.82–7.72 (m, 6 H), 7.65 (d, *J* = 8.5 Hz, 1 H), 7.49 (dd, *J* = 5.4, 2.7 Hz, 2 H), 7.46–7.31 (m, 6 H), 7.19 (dd, *J* = 15.8, 6.9 Hz, 1 H), 6.97 (d, *J* = 6.9 Hz, 1 H), 6.78 (d, *J* = 15.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 135.3, 134.8, 133.5, 133.4, 133.2, 132.6, 129.2, 128.5, 128.2, 128.1, 127.8, 127.8, 127.5, 127.3, 126.7, 126.5, 126.4, 125.8, 125.0, 124.1, 123.6, 120.3, 110.5, 65.8 ppm. MS (EI): *m*/*z* (%) = 293 (100), 411 $[M]^+$. HRMS (EI): calcd. for $C_{29}H_{21}N_3$ $[M]^+$ 411.1735; found 411.1737. IR (KBr): $\tilde{\nu}_{max}$ = 3053, 2932, 2853, 1723, 1593, 1505, 1480, 1394, 1267, 1251, 1077, 960, 862, 814, 786, 741, 707, 662, 475 cm^{-1}. The enantiomeric excess of the product (44%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 16.83 (minor), 30.83 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 50:50; 1.0 mL/min]. $[\alpha]_D^{20}$ = –8.4 (*c* = 1.0, $CHCl_3$).

(*E*)-2-[1,3-Bis(naphthalen-2-yl)allyl]-2*H*-benzo[*d*][1,2,3]triazole (5f): Yield: 20.6 mg (25%). White solid; m.p. 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.89 (m, 3 H), 7.86–7.74 (m, 7 H), 7.68 (d, *J* = 8.6 Hz, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.49–7.41 (m, 4 H), 7.38 (dd, *J* = 6.6, 3.0 Hz, 2 H), 7.25 (dd, *J* = 15.4, 7.2 Hz, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 6.85 (d, *J* = 15.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 135.8, 134.8, 133.5, 133.4, 133.3, 133.3, 128.9, 128.4, 128.3, 128.2, 127.7, 127.4, 126.8, 126.6, 126.5, 126.4, 126.3, 125.0, 123.8, 118.4, 72.8 ppm. MS (EI): *m*/*z* (%) = 293 (100), 411 $[M]^+$. HRMS (EI): calcd. for $C_{29}H_{21}N_3$ $[M]^+$ 411.1735; found 411.1736. IR (KBr): $\tilde{\nu}_{max}$ = 3053, 3027, 2930, 1739, 1650, 1619, 1569, 1508, 1441, 1368, 1334, 1226, 1033, 960, 852, 808, 741, 691, 475 cm^{-1}. The enantiomeric excess of the product (78%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 19.61 (minor), 23.00 min (major) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 50:50; 1.0 mL/min]. $[\alpha]_D^{20}$ = –28.5 (*c* = 1.0, $CHCl_3$).

(*E*)-1-(Hept-4-en-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (4g): Yield: 7.7 mg (18%). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.3 Hz, 1 H), 7.55 (d, *J* = 8.3 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 5.87–5.71 (m, 2 H), 5.20 (dd, *J* = 14.7, 6.7 Hz, 1 H), 2.39–2.22 (m, 1 H), 2.13–2.00 (m, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H), 0.88 (t, *J* = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 136.3, 132.4, 126.8, 126.6, 123.7, 120.1, 110.2, 63.9, 27.6, 25.2, 13.2, 10.8 ppm. MS (EI): *m*/*z* (%) = 143 (100), 215 $[M]^+$. HRMS (EI): calcd. for $C_{13}H_{17}N_3$ $[M]^+$ 215.1422; found 215.1424. IR (KBr): $\tilde{\nu}_{max}$ = 2990, 2920, 2835, 1705, 1468, 1390, 1278, 1200, 1089, 978, 750, 740 cm^{-1}. The enantiomeric excess of the product (–72%) was determined by HPLC analysis (214 nm, 25 °C): t_R = 6.79 (major), 7.84 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = 20.5 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(Hept-4-en-3-yl)-2*H*-benzo[*d*][1,2,3]triazole (5g): Yield: 26.7 mg (62%). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 6.5, 3.1 Hz, 2 H), 7.37 (dd, *J* = 6.5, 3.1 Hz, 2 H), 5.91–5.78 (m, 2 H), 5.23 (dd, *J* = 14.7, 6.9 Hz, 1 H), 2.38–2.24 (m, 1 H), 2.24–2.10 (m, 1 H), 2.07 (dt, *J* = 12.3, 6.2 Hz, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 136.9, 126.9, 126.0, 118.1, 71.3, 28.9, 25.2, 13.1, 10.6 ppm. MS (EI): *m*/*z* (%) = 143 (100), 215 $[M]^+$. HRMS (EI): calcd. for $C_{13}H_{17}N_3$ $[M]^+$ 215.1422; found 215.1423. IR (KBr): $\tilde{\nu}_{max}$ = 3003, 2989, 2910, 2860, 2801, 1720, 1550, 1440, 1368, 1250, 1090, 1020, 783, 660 cm^{-1}. The enantiomeric excess of the product (78%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 7.92 (minor), 9.47 min (major) [Diacel CHIRALPAK IC (0.46 cm × 25 cm); hexane/2-propanol, 99:1; 1.0 mL/min]. $[\alpha]_D^{20}$ = 40.7 (*c* = 1.0, $CHCl_3$).

(*E*)-1-(Pent-3-en-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4h): Yield: 9.4 mg (25%). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.3 Hz, 1 H), 7.55 (d, *J* = 8.3 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 5.84 (dd, *J* = 15.4, 6.3 Hz, 1 H), 5.74 (dq, *J* = 18.2, 5.9 Hz, 1 H), 5.49 (quint, *J* = 6.4 Hz, 1 H), 1.84 (d, *J* = 7.0 Hz, 3 H), 1.73 (d, *J* = 6.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.5, 132.2, 130.0, 128.6, 126.9, 123.7, 120.1, 110.3, 57.4, 20.1, 17.6 ppm. MS (EI): *m*/*z* (%) = 144 (100), 187 $[M]^+$. HRMS (EI): calcd. for $C_{11}H_{13}N_3$ $[M]^+$ 187.1109; found 187.1108. IR (KBr): $\tilde{\nu}_{max}$ = 2980, 2923, 2850, 1606, 1451, 1384, 1267, 1159, 1074, 960, 776, 745 cm^{-1}. The enantiomeric excess of the product (–61%) was determined by HPLC analysis (214 nm, 25 °C): t_R = 6.86 (major), 7.56 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 90:10; 1.0 mL/min]. $[\alpha]_D^{20}$ = 8.3 (*c* = 1.0, $CHCl_3$).

(*E*)-2-(Pent-3-en-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (5h): Yield: 18.0 mg (48%). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 6.5, 3.1 Hz, 2 H), 7.37 (dd, *J* = 6.5, 3.1 Hz, 2 H), 5.90 (dd, *J* = 15.8, 7.2 Hz, 1 H), 5.85–5.75 (m, 1 H), 5.51 (quint, *J* = 6.9 Hz, 1 H), 1.82 (d, *J* = 6.9 Hz, 3 H), 1.73 (d, *J* = 6.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 130.2, 129.2, 126.1, 118.1, 64.7, 21.1, 17.7 ppm. MS (EI): *m*/*z* (%) = 187 (100), 187 $[M]^+$. HRMS (EI): calcd. for $C_{11}H_{13}N_3$ $[M]^+$ 187.1109; found 187.1110. IR (KBr): $\tilde{\nu}_{max}$ = 2964, 2929, 2863, 1726, 1441, 1378, 1251, 1080, 1023, 792, 666 cm^{-1}. The enantiomeric excess of the product (71%) was determined by HPLC analysis (254 nm, 25 °C): t_R = 9.50 (major), 10.26 min (minor) [Diacel CHIRALPAK AD-H (0.46 cm × 25 cm); hexane/2-propanol, 98:2; 1.0 mL/min]. $[\alpha]_D^{20}$ = 48.8 (*c* = 1.0, $CHCl_3$).

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of new substances and chiral HPLC charts.

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