Asymmetric Syntheses of 3,4-Disubstituted Tetrahydroquinoline Derivatives Using (+)-Sparteine-mediated Electrophilic Substitution

Yun Soo Choi, Kyoung Hee Kang, and Yong Sun Park*

*Department of Chemistry, Konkuk University, Seoul 143-701, Korea. *E-mail: parkyong@konkuk.ac.kr*
Received December 19, 2014, Accepted January 5, 2015, Published online April 28, 2015

Keywords: Heterocycles, Dynamic resolution, Chiral ligand, Asymmetric synthesis, Substitution

Tetrahydroquinolines bearing substituents are frequently found as a substructure in a number of alkaloids and natural products.[1] Since their individual stereoisomers displays different biological activities, it is desirable to develop a highly stereoselective synthetic method for tetrahydroquinolines. While some progress has recently been made toward the development of asymmetric synthetic methods for tetrahydroquinolines, it is still a challenging topic in organic synthesis.[2] In the course of our studies on asymmetric substitution of 2-substituted aniline derivatives, we envisaged a simple and straightforward synthetic method for 3,4-disubstituted tetrahydroquinolines.

The strategy, as shown in Figure 1, involves an asymmetric electrophilic substitution of 2-alkyl aniline with epoxide (step 1) to afford amino alcohol and the subsequent intramolecular cyclization of the amino alcohol (step 2). While epoxides are frequently used in a wide range of nucleophilic ring-opening reactions, the kinetic resolution of racemic epoxide with organolithium species has rarely been reported.[3] Here we report a novel asymmetric synthetic method for *trans*-3,4-disubstituted tetrahydroquinolines via (+)-sparteine-mediated electrophilic substitution of 2-benzyl-*N*-pivaloylanilines, kinetic resolution of racemic epoxide, and Mitsunobu intramolecular cyclization.

We have recently reported (−) or (+)-sparteine-mediated asymmetric lateral substitutions of 2-benzyl-*N*-pivaloyl aniline **1** with various electrophiles.[4] Substitution with ketones, aldehydes, alkyl halides, and α,β-unsaturated esters afforded diverse 2-alkyl-substituted aniline derivatives with high enantioselectivities. We envisioned that the use of epoxide as an electrophile can afford highly enantioenriched amino alcohols suitable for the preparation of tetrahydroquinolines by intramolecular cyclization.

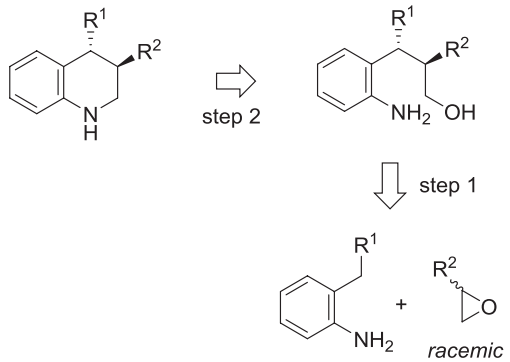
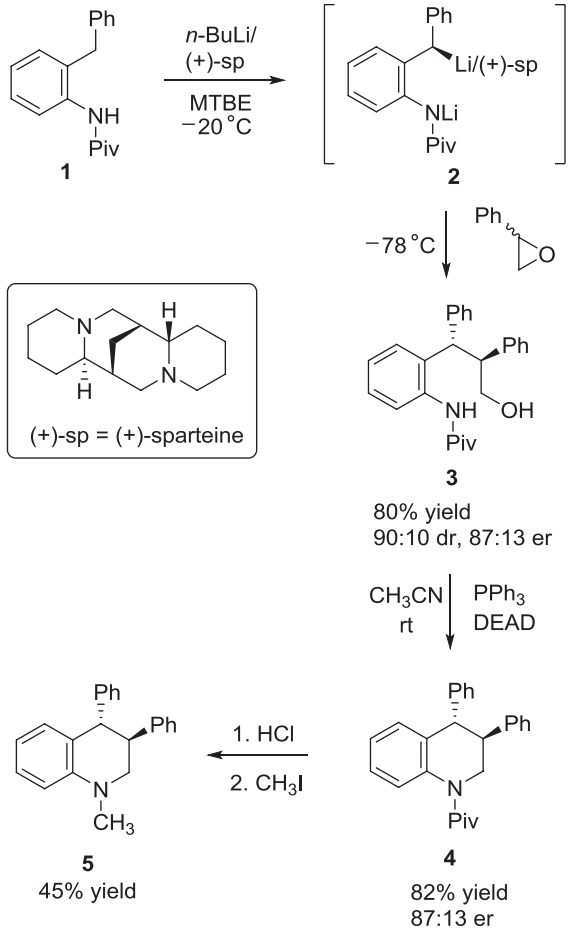


Figure 1. Retrosynthetic analysis for tetrahydroquinoline.

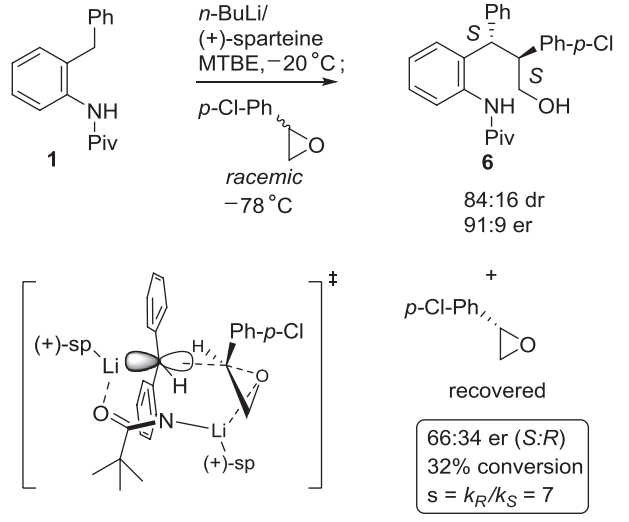
Our first attempt to test the synthetic approach involved the use of phenyloxirane as an electrophile. Lithiation of **1** in the presence of (+)-sparteine in methyl *tert*-butyl ether (MTBE) at −20 °C can provide the highly diastereoenriched lithium intermediate **2** by dynamic thermodynamic resolution.[4d] After adding phenyloxirane (2.5 equiv) at −78 °C, regioselective ring opening occurred at the benzylic position and amino alcohol **3** was obtained in 80% yield as a 90:10 mixture of two inseparable diastereomers. The enantiomeric ratio (er) of the major diastereomer was 87:13, as shown in Scheme 1, and that of the minor diastereomer was 99:1.[5]

When the 90:10 diastereomeric mixture of **3** was treated with PPh_3 and diethyl azodicarboxylate (DEAD) in tetrahydrofuran (THF) at room temperature, the nucleophilic attack by *N*-pivaloyl amide nucleophile provided *trans*-3,4-disubstituted tetrahydroquinoline **4** with 87:13 er; no *cis* product was detected. The *trans* relationship of the two substituents was established after converting **4** to *N*-methyl-substituted tetrahydroquinoline **5**.[6] The results indicated that *trans*-**4** was produced in 82% yield from the major diastereomer of **3** (87:13 er); the minor diastereomer did not cyclize to afford tetrahydroquinoline **4**. We reasoned that the repulsion between two phenyl groups in the transition state formed during the cyclization of the minor diastereomer of **3** prevents the formation of the *cis* product.

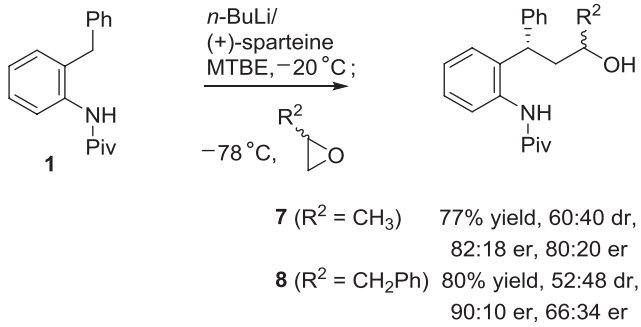
In order to investigate the source of diastereoselection attained in the substitution reaction with a racemic epoxide, we examined the substitution of **2** with an excess amount of racemic *p*-chlorophenyl-substituted oxirane, as shown in Scheme 2. When racemic *p*-chlorophenyloxirane (4.0 equiv) was treated with 2-(α-lithiobenzyl)-*N*-pivaloylaniline (α*R*)-**2**, the reaction of the epoxide proceeded to provide a diastereomeric mixture (84:16 dr) of amino alcohol **6**; the er of the recovered epoxide was 66:34 (*S*:*R*) with 32% conversion. The kinetic resolution in the substitution favoring (*R*)-epoxide proceeded with a selectivity factor (*s*) of 7, as shown in Scheme 2.[7] Based on the *trans* relationship of the two substituents of tetrahydroquinoline **4** and the (*S*)-enantiomer-enriched recovered epoxide, the absolute configurations of the major enantiomer of **6** are assigned as (*S,S*).[8] The



Scheme 1. Asymmetric synthesis of tetrahydroquinoline.



Scheme 2. Kinetic resolution of *p*-chlorophenyloxirane.



Scheme 3. Reactions with aliphatic epoxides.

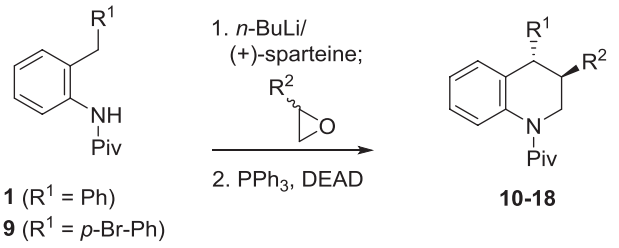
formation of (*S,S*)-amino alcohol **6** can be explained by the invertive electrophilic substitution of lithium intermediate (α*R*)-**2** and the backside approach to (*R*)-epoxide coordinated to the Li cation, as depicted in Scheme 2.

To expand the scope of this methodology to 3-alkyl substituted tetrahydroquinoline, we conducted electrophilic substitutions of **1** with methyloxirane and benzyloxirane as shown in Scheme 3. Lithiation of **1** in the presence of (+)-sparteine at −20 °C in MTBE, followed by the addition of methyloxirane at −78 °C, provided the corresponding amino alcohol **7** in 77% yield as a 60:40 mixture of two inseparable diastereomers with 82:18 and 80:20 er, respectively. In contrast to the reactions with aryl-substituted oxiranes, the substitution showed a different regioselectivity to attack the sterically favored position of oxirane. Under the same reaction conditions, the electrophilic substitution of benzyloxirane showed the same regioselectivity to afford amino alcohol **8** in 80% yield as a 52:48 mixture of two diastereomers with 90:10 and 66:34 er, respectively. No sign of any regioisomer was detected by NMR analysis. The reversal of regioselectivity means that in the aliphatic epoxides, the only governing factor would be the steric factor.[9]

Next, we initiated investigations into the reaction scope with various aryl-substituted oxiranes, as shown in Table 1. Lithiation of **1** in the presence of (+)-sparteine at −20 °C in MTBE, followed by the addition of 4-fluorophenyl oxirane at −78 °C, provided an amino alcohol as an 85:15 mixture of two inseparable diastereomers. Since the minor diastereomer did not provide the cyclized product, separation of the major diastereomer was not required. Therefore, the crude mixture of diastereomers was directly subjected to the Mitsunobu cyclodehydration condition, which afforded *trans*-tetrahydroquinoline **10** with 81:19 er in 63% overall yield (entry 1, Table 1). As shown in entries 2–5, the same procedure with 4-chlorophenyloxirane, 4-methylphenyl oxirane, 1-naphthyloxirane, and 2-naphthyloxirane provided 3,4-disubstituted tetrahydroquinolines **11–14** with a high level of asymmetric induction in 40–68% overall yields. With a practical procedure in hand, we examined the scope of the methodology with 2-(*p*-bromobenzyl)-*N*-pivaloylaniline **9**. Under identical reaction conditions, this simple two-step procedure is also efficient for the asymmetric preparation of 4-(*p*-bromophenyl)-substituted tetrahydroquinolines **15–18** with enantiomeric ratios ranging from 94:6 to 73:27 (entries 6–9).

In summary, we have developed a novel method for the asymmetric synthesis of *trans*-3,4-diaryl-substituted tetrahydroquinolines from ortho-substituted *N*-pivaloyl anilines. The enantioselective process includes (+)-sparteine-mediated stereoselective lithiation, kinetic resolution of epoxides in

Table 1. Asymmetric synthesis of tetrahydroquinolines **10–18**



1 (R^1 = Ph)
9 (R^1 = *p*-Br-Ph)

10-18

.

Entry	R^1	R^2	dr	Overall yield[a] (%)	er[b]
1	Ph	*p*-F-Ph	79:21	63 (**10**)	81:19
2	Ph	*p*-Cl-Ph	80:20	68 (**11**)	93:7
3	Ph	*p*-CH_3-Ph	75:25	67 (**12**)	87:13
4	Ph	1-Naph	82:18	68 (**13**)	96:4
5	Ph	2-Naph	73:27	40 (**14**)	88:12
6	*p*-Br-Ph	Ph	71:29	55 (**15**)	79:21
7	*p*-Br-Ph	1-Naph	75:25	51 (**16**)	94:6
8	*p*-Br-Ph	*p*-Cl-Ph	73:27	54 (**17**)	73:27
9	*p*-Br-Ph	2-Naph	74:26	45 (**18**)	77:23

[a] Isolated overall yields after two steps.
[b] The enantiomeric ratios were determined by chiral stationary phase high-performance liquid chromatography using racemic material as the standard.

substitution, and stereospecific Mitsunobu cyclization as the key reactions. The simple protocol can provide highly functionalized tetrahydroquinoline rings and would allow their further functionalization to access more complex target molecules.

Experimental

General Procedure for the Asymmetric Preparation of Tetrahydroquinolines 4 and 10–18. To a solution of *N*-pivaloylanilines **1** or **9** (0.5 mmol) and (+)-sparteine (258 mg, 2.2 equiv) in 3 mL of MTBE at −20 °C was added *n*-BuLi (0.7 mL, 1.6 M in hexane, 2.2 equiv). After the mixture was stirred at −20 °C for 1 h, an epoxide (2.5 equiv) was added at −78 °C. The mixture was stirred for 20 min at −78 °C and then quenched with excess methanol. The resulting mixture was dissolved in EtOAc, washed with saturated NH_4Cl, dried with $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by passing through a short silica gel column (EtOAc/hexanes solvents) to afford the amino alcohol as an inseparable mixture of two diastereomers. To a solution of the products in CH_3CN (2 mL) was added PBu_3 (2.5 equiv) and DEAD (2.5 equiv), and the mixture was stirred at room temperature for 6 h. After the solvent was removed *in vacuo*, chromatographic separation of the crude mixture on silica gel (EtOAc/hexanes solvents) afforded tetrahydroquinolines **4** and **10–18** in 68–40% overall yields.

***N*-Pivaloyl-(3*S*,4*S*)-3,4-diphenyltetrahydroquinoline (4).** A colorless oil, 121 mg, 66% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 1H), 7.29–6.90 (m, 13H), 4.38 (m, 1H), 4.28 (d, *J* = 10.0 Hz, 1H), 3.74 (dd, *J* = 13.2 and 10.8 Hz, 1H), 3.15 (m, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.9, 144.4, 141.5, 140.5, 133.0, 130.2, 128.8, 128.7, 128.3, 127.7, 127.2, 126.5, 125.9, 125.8, 124.8, 52.1, 51.8, 51.3, 40.2, 28.7; HRMS (FAB) calcd for $C_{26}H_{28}NO$ (M^+ + 1): 370.2173. Found 370.2171; CSP-HPLC (Chiralcel OD column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 87:13 er, 18.2 min (major), 21.6 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-3-(*p*-fluorophenyl)-4-phenyl tetrahydroquinoline (10).** A colorless oil, 122 mg, 63% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 1H), 7.54–6.89 (m, 12H), 4.34 (m, 1H), 4.20 (d, *J* = 9.6 Hz, 1H), 3.73 (dd, *J* = 13.2 and 10.8 Hz, 1H), 3.14 (m, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.9, 144.0, 140.4, 137.3, 135.1, 132.8, 130.1, 129.1, 129.0, 128.8, 128.4, 126.6, 126.0, 125.8, 124.9, 115.7, 115.5, 53.4, 52.4, 51.2, 50.9, 40.2, 28.7; HRMS (FAB) calcd for $C_{26}H_{27}FNO$ (M^+ + 1): 388.2077. Found 388.2077; CSP-HPLC (Chiralcel OD column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 81:19 er, 14.9 min (major), 18.9 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-3-(*p*-chlorohenyl)-4-phenyltetrahydroquinoline (11).** A colorless oil, 138 mg, 68% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 1H), 7.54–6.88 (m, 12H), 4.34 (m, 1H), 4.20 (d, *J* = 10.0 Hz, 1H), 3.73 (dd, *J* = 13.2 and 10.4 Hz, 1H), 3.12 (m, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.9, 143.8, 140.3, 140.0, 132.9, 132.7, 130.1, 129.0, 128.9, 128.8, 128.4, 126.6, 126.0, 125.8, 124.9, 52.2, 51.1, 51.0, 40.2, 28.7; HRMS (FAB) calcd for $C_{26}H_{27}ClNO$ (M^+ + 1): 404.1780. Found 404.1781; CSP-HPLC (Chiralcel OD column; 2% 2-propanol in hexane; 0.5 mL/min; 217 nm) 93:7 er, 14.1 min (major), 18.3 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-3-(*p*-methylphenyl)-4-phenyl tetrahydroquinoline (12).** A colorless oil, 129 mg, 67% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 1H), 7.19–6.90 (m, 12H), 4.37 (m, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 3.70 (dd, *J* = 13.2 and 10.8 Hz, 1H), 3.12 (m, 1H), 2.31 (s, 3H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.8, 144.5, 140.5, 138.5, 136.7, 133.1, 130.2, 129.4, 128.8, 128.3, 127.5, 126.4, 125.8, 124.8, 52.2, 51.5, 51.4, 40.1, 28.7, 21.1; HRMS (FAB) calcd for $C_{27}H_{30}NO$ (M^+ + 1): 384.2324. Found 384.2327; CSP-HPLC (Chiralpak AD-H column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 87:13 er, 19.7 min (minor), 21.2 min (major).

***N*-Pivaloyl-(3*S*,4*S*)-3-(1-naphtyl)-4-phenyltetrahydroquinoline (13).** A yellow oil, 143 mg, 68% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76–6.92 (m, 16H), 4.49 (m, 1H), 4.38 (m, 1H), 4.11 (m, 1H), 3.91 (m, 1H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.3, 144.7, 140.6, 130.2, 128.8, 128.5, 128.4, 127.6, 127.2, 126.4, 126.0, 125.9, 125.8, 125.6, 125.5, 125.0, 124.8, 52.2, 51.0, 44.5, 40.2, 28.7; HRMS (FAB) calcd for $C_{30}H_{30}NO$ (M^++1): 420.2327. Found 420.2325; CSP-HPLC (Chiralpak AD-H column; 2% 2-propanol in hexane; 0.5 mL/min; 217 nm) 96:4 er, 25.8 min (minor), 28.8 min (major).

***N*-Pivaloyl-(3*S*,4*S*)-3-(2-naphtyl)-4-phenyltetrahydro quinoline (14).** A pale yellow oil, 84 mg, 40% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57-6.90 (m, 16H), 4.48–4.40 (m, 2H), 3.84 (dd, J = 13.2 and 10.8 Hz, 1H), 3.32 (m, 1H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.9, 144.3, 140.6, 139.0, 133.5, 133.1, 132.6, 130.2, 128.8, 128.6, 128.4, 127.7, 127.6, 126.5, 126.4, 126.2, 125.9, 125.8, 125.7, 125.6, 125.5, 52.1, 52.0, 51.6, 40.2, 28.7; CSP-HPLC (Chiralcel OD column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 88:12 er, 23.6 min (major), 31.7 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-4-(*p*-bromophenyl)-3-phenyl tetrahydroquinoline (15).** A colorless oil, 123 mg, 55% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 1H), 7.31–6.76 (m, 12H), 4.39 (dd, J = 13.6 and 4.0 Hz, 1H), 4.26 (d, J = 9.6 Hz, 1H), 3.72 (dd, J = 13.2 and 11.2 Hz, 1H), 3.06 (m, 1H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.0, 143.4, 141.1, 140.5, 132.3, 131.5, 130.5, 130.0, 128.9, 127.6, 127.4, 126.1, 126.0, 124.9, 120.4, 51.8, 51.7, 51.3, 40.2, 28.7; CSP-HPLC (Chiralcel OD column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 79:21 er, 17.7 min (major), 25.7 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-4-(*p*-bromophenyl)-3-(1-naphtyl) tetrahydroquinoline (16).** A colorless oil, 127 mg, 51% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83–6.77 (m, 15H), 4.46(m, 1H), 4.36 (m, 1H), 4.05 (m, 1H), 3.86 (m, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.3, 143.7, 140.6, 133.7, 132.5, 131.5, 130.2, 130.1, 128.9, 128.5, 128.4, 127.7, 126.3, 126.2, 126.0, 125.7, 125.6, 125.0, 124.0, 122.1, 120.4, 51.9, 51.1, 44.3, 40.2, 28.7; CSP-HPLC (Chiralcel OD column; 2% 2-propanol in hexane; 0.5 mL/min; 217 nm) 94:6 er, 28.2 min (major), 38.4 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-4-(*p*-bromophenyl)-3-(*p*-chlorophenyl)tetrahydroquinoline (17).** A colorless oil, 130 mg, 54% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, 1H), 7.31–6.76 (m, 11H), 4.34 (dd, J = 13.2 and 3.6 Hz, 1H), 4.18 (d, J = 9.6 Hz, 1H), 3.71 (dd, J = 13.2 and 10.8 Hz, 1H), 3.05 (m, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.0, 142.9, 140.4, 139.6, 133.2, 132.0, 131.6, 130.5, 129.9, 129.1, 128.9, 126.3, 125.9, 125.0, 120.6, 51.7, 51.2, 51.0, 40.2, 28.7; CSP-HPLC (Chiralcel OD column; 1% 2-propanol in hexane; 0.5 mL/min; 217 nm) 73:27 er, 18.6 min (major), 26.6 min (minor).

***N*-Pivaloyl-(3*S*,4*S*)-4-(*p*-bromophenyl)-3-(2-naphtyl) tetrahydroquinoline (18).** A yellow oil, 112 mg, 45% overall yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82–6.76 (m, 15H), 4.46 (dd, J = 13.2 and 3.6 Hz, 1H), 4.38 (d, J = 10.0 Hz, 1H), 3.82 (dd, J = 13.2 and 11.2 Hz, 1H), 3.25 (m, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.8, 143.3, 140.5, 138.4, 133.4, 132.6, 132.4, 131.4, 130.4, 130.0, 128.7, 127.7, 127.6, 126.4, 126.3, 126.1, 125.9, 125.8, 125.4, 124.9, 120.4, 52.0, 51.6, 51.4, 40.1, 28.6; CSP-HPLC (Chiralcel OD column; 2% 2-propanol in hexane; 0.5 mL/min; 217 nm) 77:23 er, 18.0 min (major), 25.4 min (minor).

Acknowledgment. This work was supported by Konkuk University in 2014.

Supporting Information. Additional supporting information is available in the online version of this article.

References

1. (a) J. P. Michael, *Nat. Prod. Rep.* **2008**, *25*, 166; (b) C. J. Lovely, V. Badarinarayana, *Curr. Org. Chem.* **2008**, *12*, 1431; (c) R. T. Skerlj, G. J. Bridger, A. Kaller, E. J. McEachern, J. B. Crawford, Y. Zhou, B. Atsma, J. Langille, S. Nan, D. Veale, T. Wilson, C. Hartwig, S. Hatse, K. Princen, E. De Clercq, D. Schols, *J. Med. Chem.* **2010**, *53*, 3376.
2. V. Sridharan, P. A. Suryavanshi, J. C. Menèndez, *Chem. Rev.* **2011**, *111*, 7157.
3. (a) C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* **2012**, *134*, 8058; (b) M. M. Elenkov, L. Tang, A. Meetsma, B. Hauer, D. B. Janssen, *Org. Lett.* **2008**, *10*, 2417; (c) A. Gansäuer, C.-A. Fan, F. Keller, P. Karbaum, *Chem. Eur. J.* **2007**, *13*, 8084.
4. (a) Y. K. Ko, C. Im, J. Do, Y. S. Park, *Eur. J. Org. Chem.* **2014**, *2014*, 3460; (b) K. H. Kang, Y. Kim, C. Im, Y. S. Park, *Tetrahedron* **2013**, *69*, 2542; (c) K. H. Kang, J. Do, Y. S. Park, *J. Org. Chem.* **2012**, *77*, 808; (d) Y. S. Park, E. K. Yum, A. Basu, P. Beak, *Org. Lett.* **2006**, *8*, 2667; (e) Y. Kim, E.-k. Shin, P. Beak, Y. S. Park, *Synthesis* **2006**, 3805.
5. When the reaction of **1** was carried out in toluene, ether, or *n*-hexane, the asymmetric lithiation substitution reactions gave lower diastereoselectivities of 81:19, 84:16, and 83:17 dr, respectively. Among the solvents examined, *n*-hexane was found to give a slightly higher enantioselectivity (89:11 er of major diastereomer) than *t*-BuOMe and significant decrease in enantioselectivity was observed in the reactions in toluene (72:28 er) and ether (77:23 er).
6. The relative configuration of *trans*-**5** is assigned by comparison to the NMR of the authentic compound in the following literature. We assume the same stereochemical assignments for all tetrahydroquinolines **10–18**. b A. R. Katrizky, B. Rachwal, S. Rachwal, *J. Org. Chem.* **1995**, *60*, 7631.
7. The selectivity factor (s) was estimated using the equation, $s = k_R/k_S = \ln[(1 - C)(1 - ee)]/\ln[(1 - C)(1 + ee)]$, where ee is the enantiomeric excess of unconverted epoxide and the conversion (C) determined by ^{1}H NMR of reaction mixture. The selectivity (s = 7) is an average of three experiments, while conversion and er are for a specific case.
8. The (*S*)-configuration at benzylic position of **6** is consistent with the previously established results in the substitution of **1** with other electrophiles.[4]
9. (a) R.-H. Fan, X.-L. Hou, *J. Org. Chem.* **2003**, *68*, 726; (b) M. Tajbakhsh, R. Hosseinzadeh, P. Rezaee, H. Alinezhad, *J. Mex. Chem. Soc.* **2012**, *56*, 402; (c) A. T. Placzek, J. L. Donelson, R. Trivedi, R. A. Gibbs, S. K. De, *Tetrahedron Lett.* **2005**, *46*, 9029.

