

Selected Paper

Stereospecific C–S Bond Formation from Chiral Tertiary Alcohols by Quinone-Mediated Oxidation–Reduction Condensation Using Alkyl Diphenylphosphinites and Its Application to the Synthesis of a Chiral Tertiary Thiol

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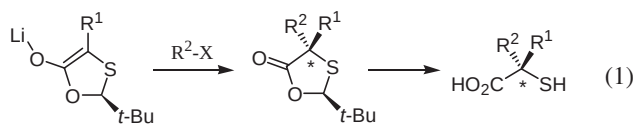
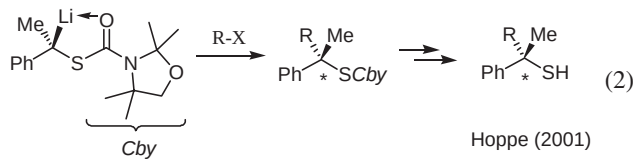
Oxidation–reduction condensation between 2-sulfanyl-1,3-benzothiazole (Btz-SH) and the alkyl diphenylphosphinites **1**, prepared from tertiary alcohols, proceeded smoothly in the presence of 2,6-di-*t*-butyl-1,4-benzoquinone (DBBQ) and the corresponding *S*-alkylated products **2** were afforded in good yields. The stereo-inverted chiral Btz sulfides **2** were also produced stereospecifically by this condensation that used **1** derived from chiral tertiary alcohols. Subsequent removal of the Btz groups of **2** with *t*-BuLi or $LiAlH_4$ provided a new synthetic route to chiral tertiary thiols and the structurally-related dialkyl sulfides.

A bimolecular nucleophilic substitution (S_N2) reaction that uses chiral alkylating agents is a simple and particularly-effective tool for the stereospecific preparation of chiral molecules in synthetic organic chemistry.[1] Chiral secondary thiols and the corresponding sulfides have been synthesized from the corresponding chiral secondary alcohols on treatment with weakly acidic sulfur nucleophiles such as arenethiols and thioacetic acids in the presence of triphenylphosphine and diethyl azodicarboxylate[2,3] or with tributylphosphine and diaryl disulfides,[4] both of which were developed previously by Mitsunobu et al. or Hata et al. based on the concept of "oxidation–reduction condensation."[5] However, it has generally been known that sterically-hindered tertiary alcohols do not give the corresponding sulfides by the above condensation reactions because the starting alcohols are recovered or the undesired olefins are produced exclusively by the elimination reactions.[1a,6] Therefore, the synthesis of chiral building blocks possessing sulfur-containing quaternary carbons has long been carried out by employing asymmetric *C*-alkylation methodologies (see Eqs. 1 and 2).



(1)

Kellogg (1987)



(2)

Hoppe (2001)

Kellogg et al. reported the synthesis of chiral tertiary thiols from chiral α-sulfanylcarboxylic acids by using Seebach's "self-regeneration of stereocenters" method[7] of using 2-*t*-butyl-1,3-oxathiolanones,[8] which was recently applied to the asymmetric synthesis of (5*R*)-thiolactomycin.[9] Hoppe et al. also described the synthesis of chiral tertiary benzylic (or allylic) thiols from the corresponding chiral secondary thiols by asymmetric *C*-alkylation of the configurationally-stable α-sulfanylbenzyl- (or α-sulfanylallyl-) lithium intermediates.[10]

Recently, it has been reported from our laboratory that the synthesis of stereo-inverted *t*-alkyl carboxylates from chiral tertiary alcohols and carboxylic acids was carried out successfully via a new-type of oxidation–reduction condensation using a combination of *t*-alkyl diphenylphosphinites and 1,4-benzoquinone derivatives such as 2,6-dimethyl-1,4-benzoquinone (DMBQ).[5a,11] This method was then successfully applied to the preparation of alkyl–aryl or alkyl–alkyl ethers,[12] alkyl–aryl sulfides,[13] alkane sulfonamides or imides,[14] alkyl cyanides[15] or isocyanides,[16] and 3,3-disubstituted propionic acid derivatives.[17]

In this article, we would like to report a successful application of the above condensation protocols to the stereospecific formation of sulfur-containing quaternary stereogenic centers from chiral tertiary alcohols and 2-sulfanyl-1,3-benzothiazole (Btz-SH). In this reaction, a new combination of alkyl diphenylphosphinite **1** and 2,6-di-*t*-butyl-1,4-benzoquinone (DBBQ) was chosen, which furnished the Btz sulfides **2** with high levels of stereo-inversion together with 3,5-di-*t*-butyl-4-hydroxyphenyl diphenylphosphinate via the intermediates **A** and **B** (see Scheme 1). A chiral tertiary thiol and the corresponding dialkyl sulfides were obtained from the chiral tertiary

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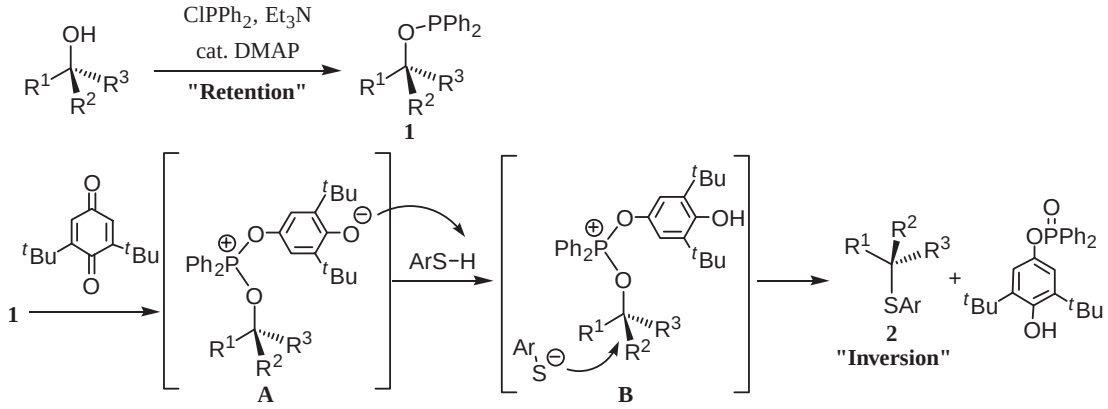
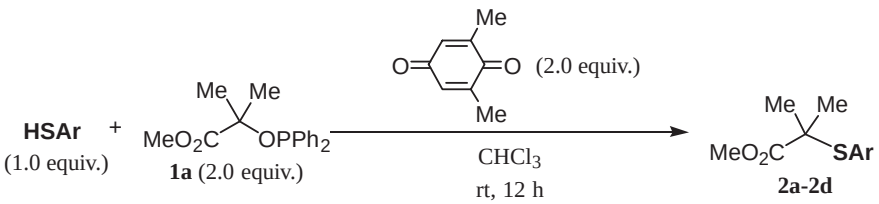
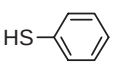
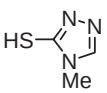
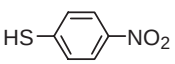
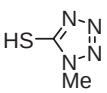
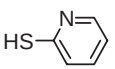
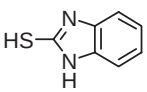
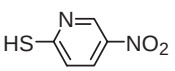
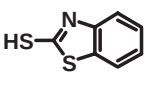
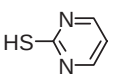
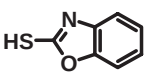
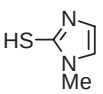


Scheme 1. *S*-Alkylation of arenethiols with the phosphinite **1** and DBBQ.

Table 1. *S*-Alkylation of Various Aromatic Thiols and Thioacetic Acid with **1a** and DMBQ[a)]



Entry	Nucleophile	Yield/%[b)]	Product	Entry	Nucleophile	Yield/%[b)]	Product
1		ND[c)]	—	7		ND[c)]	—
2		15 (89)[d)]	**2a**	8		ND[c)]	—
3		ND[c)]	—	9		ND[c)]	—
4		12 (96)[d)]	**2b**	**10**		**84**	**2c**
5		ND[c)]	—	**11**		**84**	**2d**
6		ND[c)]	—	12		ND[c)]	—

a) The reactions were carried out by using **1a** (1.0 mmol), arenethiol (0.5 mmol), and DMBQ (1.0 mmol) in $CHCl_3$ (0.5 mL) at rt for 12 h. b) Based on the amount of Btz-SH. c) Not detected. d) DBBQ was used instead of DMBQ.

alcohols after removal of the Btz groups of **2**, a part of which has already been reported.[18]

Results and Discussion

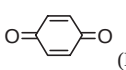
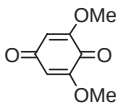
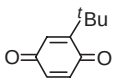
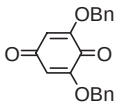
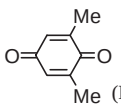
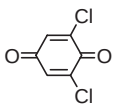
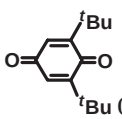
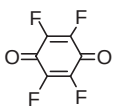
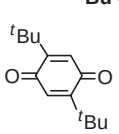
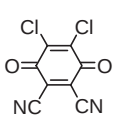
Preparation of Alkyl Diphenylphosphinites from Tertiary Alcohols. In this study, all the alkyl diphenylphosphinites **1a**–**1z** were prepared from the corresponding tertiary alcohols on treatment with chlorodiphenylphosphine ($ClPPh_2$) in the presence of triethylamine (Et_3N) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) according to the reported procedure.[18,19] The isolated yields of the phosphinites **1** were generally high (see Tables 3 and 4) except for the case of terpinen-4-ol, which afforded **1o** in 55% yield (Table 4, Entry 6). The addition of DMAP to the reaction mixture is crucial for increasing the reaction rate since conversion of tertiary alcohols was not observed in the absence of DMAP. The usefulness of the present conditions is obvious if compared to the previously-reported harsh reaction conditions that used butyllithium as a base[11,20] and gave **1l** in only 8% yield.

Oxidation–Reduction Condensation between Achiral Tertiary Alcohols and Btz-SH. With sufficient amounts of phosphinites in hand, the nucleophilicities of various arene-

thiols and thioacetic acid were first investigated in the oxidation–reduction condensation in order to find the most reactive nucleophiles (Table 1). The phosphinite **1a** having an α-carboxylic ester group was chosen as a model on the consideration that it is one of the most suitable substrates for the nucleophilic substitution.[1a] When benzenethiol (pK_a 7.78 in EtOH–H_2O,[21a] 10.3 in DMSO[21b]) or 2-sulfanylpyridine was treated with **1a** and DMBQ, the desired *S*-alkylated products were not afforded in spite of their sufficient acidities. Based on the consideration of the effect of pK_a values of nucleophiles in this type of condensation,[14,22] more acidic nucleophiles such as 4-nitrobenzenethiol (pK_a 5.11 in EtOH–H_2O,[21] 5.5 in DMSO[21b]) and 5-nitro-2-sulfanylpyridine were then tried. However, the yields of the desired products **2a** and **2b** were poor (Table 1, Entries 1–4). A survey of various sulfur nucleophiles revealed that Btz-SH (pK_a 7.00 in EtOH–H_2O[21a]) and 2-sulfanyl-1,3-benzoxazole (Box-SH; pK_a 7.30 in EtOH–H_2O[21a]) were the reagents of choice because they showed notably-high reactivities to furnish the desired *S*-alkylated products **2c** and **2d** in high yields (84% yields, respectively; Table 1, Entries 10 and 11). It is noteworthy that there was no clear correlation between yields and pK_a values of sulfur nucleophiles probably due to the steric factor of the bulky *t*-alkyl group of **1a**.

Next, the reactivities of various 1,4-benzoquinone derivatives were examined in the condensation of the phosphinite **1a** with Btz-SH (see Table 2). As postulated from our previous reports,[11,12,14a] the condensation reaction using unsubstituted 1,4-benzoquinone gave the *S*-alkylated product **2c** in a lower yield compared to that of DMBQ (Table 2, Entry 1). The yield

Table 2. Screening of Various 1,4-Benzoquinone Derivatives in the Condensation of **1a** with Btz-SH[a)]

Entry	Oxidant	Yield /%[b)]	Entry	Oxidant	Yield /%[b)]
1	 (BQ)	34	6		91
2		51	7		91
3	 (DMBQ)	84	8		6
4	 **(DBBQ)**	**quant.**	9		ND[c)]
5		ND[c)]	10		ND[c)]

a) The reactions were carried out by using **1a** (1.0 mmol), Btz-SH (0.5 mmol), and an oxidant (1.0 mmol) in $CHCl_3$ (0.5 mL) at rt for 12 h. b) Based on the amount of Btz-SH. c) Not detected.

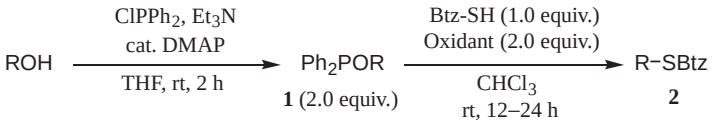
of **2c** increased in the order of 2,6-di-*t*-butyl-1,4-benzoquinone (DBBQ) > 2,6-dimethoxy-1,4-benzoquinone > DMBQ > 2-*t*-butyl-1,4-benzoquinone > 1,4-benzoquinone (Table 2, Entries 1–7). The use of the 2,5-di-*t*-butyl derivative did not give **2c** at all (Table 2, Entry 5). These results clearly indicate that the introduction of bulky substituents at 2- and 6-positions of 1,4-benzoquinone is essential for this reaction.[14a,23] The use of DBBQ also improved the yields of **2a** and **2b** up to 89 and 96% as shown in Table 1, Entries 2 and 4. While such electron-rich quinone derivatives having alkyl, methoxy, or benzyloxy functionality successfully gave **2c**, electron-poor quinones such as 2,6-dichloro-1,4-benzoquinone, tetrafluoro-1,4-benzoquinone,[12] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone caused intensely-exothermic reactions and complicated mixtures resulted (Table 2, Entries 8–10).

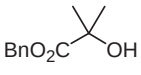
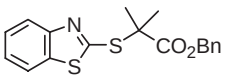
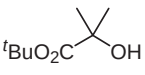
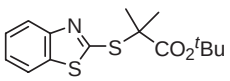
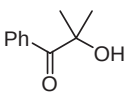
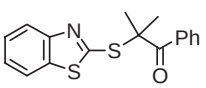
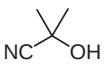
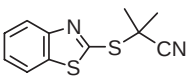
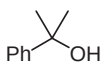
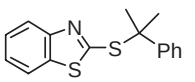
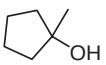
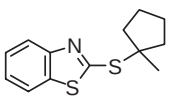
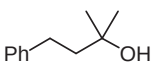
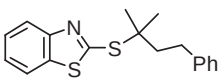
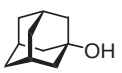
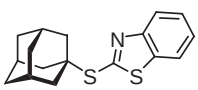
Since suitable nucleophiles and oxidants were shown, condensation of various achiral tertiary alcohols was next tried to investigate its scope (see Table 3). The reactions employing the phosphinites **1b–1d** and **1f** having an α-ester, -ketone, or -phenyl group proceeded most effectively in the presence of DBBQ to afford the *S*-alkylated products **2e–2h** in high yields (Table 3, Entries 1–3 and 5). In the reactions with the non-reactive aliphatic phosphinites **1g–1i**, either DMBQ or DBBQ showed almost similar efficiencies and the desired products **2i–2k** were obtained in moderate-to-good yields (Table 3, Entries 6–8).[24] As an exception, the phosphinite **1e** derived from the corresponding cyanohydrin was found to be quite stable under the above conditions, presumably because the reducing ability of the phosphinite was weakened by the strongly electron-withdrawing property of the α-cyano group (Table 3, Entry 4).

Oxidation–Reduction Condensation between Chiral Tertiary Alcohols and Btz-SH. Taking the above results into consideration, the possibility of stereo-inversion of chiral tertiary alcohols was further investigated as depicted in Table 4. Thus, different types of chiral tertiary alcohols were prepared, transformed into the corresponding diphenylphosphinites **1j–1n**, and subjected to the subsequent *S*-alkylation using Btz-SH and DBBQ. The reactions with the phosphinites **1j–1l** bearing the α-ester groups yielded the inverted *t*-alkyl Btz sulfides **2l–2n** in good yields, and their ee values were completely maintained during the condensation (>99–97% inversion; Table 4, Entries 1–3). Similarly, the aliphatic phosphinite **1m** gave the Btz sulfide **2o** in 67% ee and 97% inversion from the corresponding tertiary alcohol (69% ee), though the yield diminished due to the competitive E2 reaction (Table 4, Entry 4). The reaction with the phosphinite **1o** derived from (*R*)-terpinen-4-ol did not afford alkylated products, probably because the isopropyl group located in the neighboring position interfered with the attack of the thiolate anion (Table 4, Entry 6).

To perform stereo-inversion with the benzylic phosphinite **1n** derived from (*S*)-2-phenyl-2-butanol was more challenging because the benzylic cation was expected to be generated more easily (see Table 4, Entry 5 and Table 5). Screening of various oxidants such as benzoquinones, alkyl azides, and disulfide revealed that the oxidants influenced the inversion ratio significantly (Table 5, Entries 1–6) and that the condensed product **2p** obtained was of enhanced optical purity when DBBQ was employed at room temperature (86% ee, 89% inversion;

Table 3. Condensation of Achiral *tert*-Alcohols with Btz-SH[a)]



Entry	Alcohol	Phosphinite (% yield)	Product		Yield of **2**/%[b)]		
					1,4-Benzoquinone	DBBQ	DMBQ
1		**1b** (98)		**2e**	26	78	87
2		**1c** (99)		**2f**	—	66	90
3		**1d** (94)		**2g**	<17	22	67
4		**1e** (quant.)		—	—	NR[c)]	NR[c)]
5		**1f** (99)		**2h**	53	78	90
6		**1g** (98)		**2i**	30	48	53
7		**1h** (98)		**2j**	—	35	34
8		**1i** (98)		**2k**	—	65	59

a) The condensation reactions were carried out by using **1** (1.0 mmol), Btz-SH (0.5 mmol), and an oxidant (1.0 mmol) in $CHCl_3$ (0.5 mL) at rt for 12–24 h. b) Based on the amount of Btz-SH. c) No reaction.

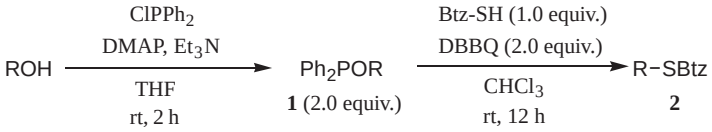
Table 5, Entry 6). Also, it was unexpectedly found that even the 2,6-substituents on 1,4-benzoquinone affected the inversion ratio (see the results with DMBQ or DBOBQ shown in Table 5, Entries 4 and 5). In addition, the use of (trimethylsilyl)methyl azide[14b] gave **2p** in the highest level of stereoinversion (85% ee, 88% inversion), albeit the yield was modest (Table 5, Entry 1). The optical yield was further improved at the lower reaction temperatures (Table 5, Entries 6–10) and **2p** was obtained in 91% ee (94% inversion) at $-10\,^{\circ}C$ (Table 5, Entry 10), while it dropped to 79% ee (81% inversion) at $60\,^{\circ}C$ (Table 5, Entry 7).

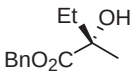
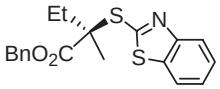
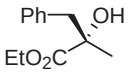
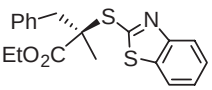
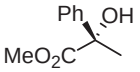
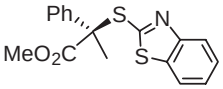
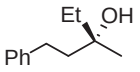
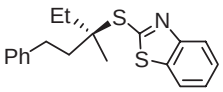
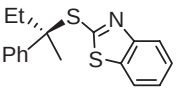
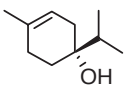
The direct synthesis of **2p** from (*S*)-2-phenyl-2-butanol was also tried by using the known combination of trialkylphosphine and BtzSSBtz as shown in Scheme 2. However, the adduct **2p** was not obtained when a combination of Ph_3P and BtzSSBtz was used. Alternatively, it was found that the use of Me_3P as a reducing agent gave **2p** in a single step from the alcohol, although the ee and yield were unsatisfying (78% ee, 24% yield).

The condensation of (*R*)-linalool (90% ee), a chiral allylic tertiary alcohol, with Btz-SH was also tried (see Scheme 3). Since the corresponding allylic diphenylphosphinite decomposes gradually at room temperature because of the known [2,3] sigmatropic rearrangement,[25] it should be used as soon as possible after preparation. As a result, the reactions with (*R*)-linalool afforded both S_N2 and S_N2' products, namely **2q** and **2r**, in 59% total yield as an inseparable mixture. ^1H and ^{13}C NMR spectra and chiral HPLC analysis of the mixture indicated the desired *t*-alkyl sulfide (*S*)-**2q** to be obtained in 15% yield with almost complete inversion (89% ee, 99% inversion). The attack of a thiolate anion occurred preferentially on the less hindered side of the substrate to afford (*E*)- and (*Z*)-**2q′** as the major products in 44% yield ($E/Z = 79/21$).

Synthesis of Tertiary Thiols and Alkyl *t*-Alkyl Sulfides from Btz Sulfides and Determination of Absolute Configurations. With the *t*-alkyl Btz sulfides **2** in hand, deprotection of the Btz groups was next tried so as to provide a new route to tertiary thiols and the related dialkyl sulfides from tertiary alcohols (see Table 6). Since Katritzky et al. reported a convenient method for the removal of Btz groups from primary or secondary alkyl Btz sulfides by using *t*-butyllithium (*t*-BuLi),[26] the protocol was then applied to the above tertiary ones (see Table 6). Thus, the treatment of the Btz sulfides **2h** and **2j** with *t*-BuLi (1.0 equiv) in anhydrous THF generated the corresponding lithium thiolate in situ along with the formation of 2-*t*-butyl-1,3-benzothiazole (**4**). The subsequent trapping of

Table 4. Condensation of Chiral *tert*-Alcohols with Btz-SH[a)]



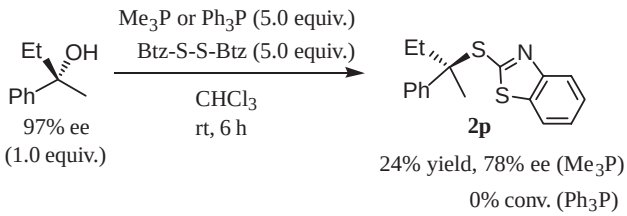
Entry	Alcohol	Phosphinite (% yield)	Product (% yield[b)])		%Ee (Config.) Alcohol	%Ee (Config.) Product	Inversion[c)] /%
1		**1j** (97)		**2l** (73)	>99 (*S*)	>99 (*R*)	>99
2		**1k** (quant.)		**2m** (61)	78 (*S*)	76 (*R*)	97
3		**1l** (99)		**2n** (73)	>99 (*S*)	99 (*R*)	99
4		**1m** (96)		**2o** (26)	69 (*S*)	67 (*R*)	97
5[d)]		**1n** (96)		**2p** (75)	97 (*S*)	91 (*S*)	94
6		**1o** (55)	ND		72 (*R*)	—	—

a) The condensation reactions were carried out by using **1** (1.0 mmol), Btz-SH (0.5 mmol), and DBBQ (1.0 mmol) in $CHCl_3$ (0.5 mL) at rt for 12 h. b) Based on the amount of Btz-SH. c) Inversion (%) was defined as % ee of **2**/% ee of the starting alcohol. d) The condensation of **1n** was carried out at −10 °C for 60 h (see Table 5).

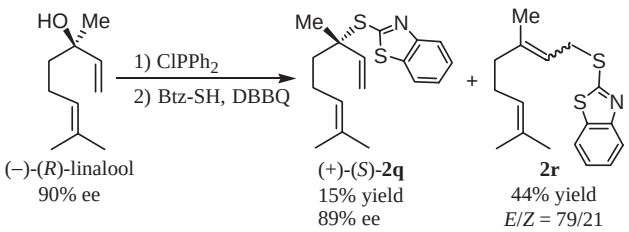
Table 5. Effects of Oxidants and Temperatures on the Condensation of **1n** with Btz-SH (Synthesis of **2p**)[a)]

Entry	Oxidant	Temp /°C	Time /h	Yield[b)] /%	Ee /%	Inversion[c)] /%
1	$(Me_3Si)CH_2N_3$	rt	12	55	85	88
2	*p*-MeO-C_6H_4-N_3	rt	12	72	79	81
3[d)]	Btz-S-S-Btz	rt	12	38	72	75
4	DMBQ	rt	6	74	65	67
5	DBOBQ[e)]	rt	12	79	64	66
6	**DMBQ**	**rt**	**12**	**76**	**86**	**89**
7	DMBQ	60	2	68	79	81
8	DMBQ	40	4	69	82	84
9	DMBQ	0	36	75	89	92
10	**DMBQ**	**−10**	**60**	**75**	**91**	**94**

a) The reactions were carried out by using **1n** (97% ee; 2.0 equiv), Btz-SH (1.0 equiv), and an oxidant (2.0 equiv) in $CHCl_3$. b) Based on the amount of Btz-SH. c) Inversion (%) was defined as % ee of **2**/% ee of the starting alcohol. d) The reaction was carried out by using equimolar amounts of **1n** and BtzSSBtz in $CHCl_3$ in the absence of BtzSH. e) DBOBQ: 2,6-di(benzyloxy)-1,4-benzoquinone.



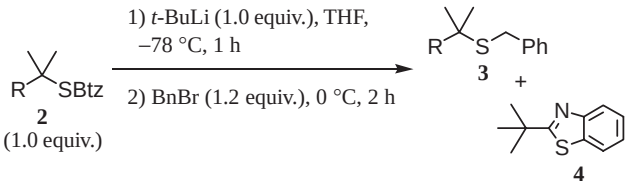
Scheme 2. Direct *S*-alkylation with benzylic *tert*-alcohol.



Scheme 3. Reagents and conditions; 1) linalool (2.0 equiv), $ClPPh_2$ (2.2 equiv), Et_3N (2.4 equiv), DMAP (0.6 equiv), THF, rt, 2 h; 2) Btz-SH (1.0 equiv), DBBQ (2.0 equiv), $CHCl_3$, 0 °C, 9 h. Yields were calculated based on the amount of Btz-SH.

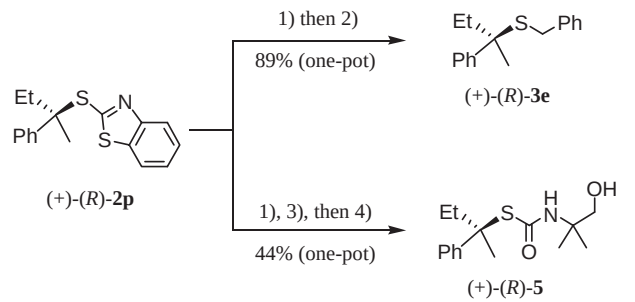
the thiolate with benzyl bromide afforded the *t*-alkyl benzyl sulfides **3a** and **3b** in high yields (Table 6, Entries 1 and 2). Although the reaction with the benzyl ester **2e** resulted in a complicated mixture, the *t*-butyl ester **2f** and acid **2s** afforded the desired products **3c** and **3d** in moderate-to-good yields (Table 6, Entries 3–5). In a similar fashion, the one-pot deprotection/*S*-alkylation procedure with the chiral sulfide (*R*)-**2p** provided the corresponding benzyl sulfide (*R*)-**3e** in 89% yield without any loss of optical purity, which was confirmed by

Table 6. One-Pot Synthesis of Unsymmetirical Dialkyl Sulfides[a)]

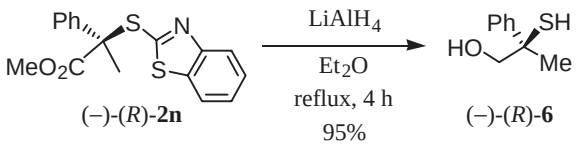


Entry	Substrate R		Yield/%	Product
1	Ph	**2h**	93	**3a**
2	$(CH_2)_2Ph$	**2j**	92	**3b**
3	CO_2Bn	**2e**	messy	—
4	CO_2t-Bu	**2f**	45	**3c**
5[b)]	CO_2H	**2s**	79	**3d**

a) The reactions were carried out by using **2** (1.0 equiv), *t*-BuLi (a 1.48 M solution in pentane; 1.0 equiv), and BnBr (1.2 equiv) in THF. b) 2.0 equiv of *t*-BuLi was used.



Scheme 4. Reagents and conditions; 1) *t*-BuLi, THF, −78 °C, 1 h; 2) BnBr, 0 °C, 1 h; 3) triphosgene, −78 to 0 °C, 1 h; 4) 2-amino-2-methylpropanol, 0 °C, 0.5 h.



Scheme 5. Synthesis of the chiral tertiary thiol **6**.

HPLC analysis (see Scheme 4). The absolute stereochemistry of **2p** was then determined to be (*R*) by chemical correlation; that is, the known carbonate (+)-(*R*)-**5** was prepared in 44% yield (one-pot from **2p**) and its optical rotation, $[\alpha]_D^{22}$ +21.8 (*c* 0.77, CH_2Cl_2), was consistent with the literature value of its enantiomer (−)-(*S*)-**5**.[10a] The conversion of the sulfide **2n** into the corresponding tertiary thiol **6** was also carried out successfully by the reductive cleavage of the Btz group (Scheme 5). Treatment of (*R*)-**2n** with $LiAlH_4$ (4.0 equiv) in refluxing Et_2O for 4 h furnished the desired chiral tertiary thiol (−)-(*R*)-**6** in 95% yield, whose optical rotation, $[\alpha]_D^{23}$ −32.6 (*c* 0.41, CH_2Cl_2), was also in good agreement with the reported value with respect to sign and absolute value.[10a] To the best of our knowledge, this is the first example of the stereospecific synthesis of an inverted chiral tertiary thiol from a chiral tertiary alcohol via S_N2 displacement. The stereospecificity of these transformations unambiguously indicates that the absolute configurations of the other chiral compounds **2l**, **2m**, **2o**, and **2q** are enantiomeric of the starting chiral alcohols.

Conclusion

In conclusion, the oxidation–reduction condensation using the phosphinites **1**, Btz-SH, and DBBQ is an effective method for the stereospecific formation of carbon–sulfur bonds from tertiary alcohols. Characteristic points of the present method are featured as follows: (1) The preparation of **1** from bulky tertiary alcohols and $ClPPh_2$ is carried out under the mild conditions of using Et_3N and a catalytic amount of DMAP at rt, (2) commercially available Btz-SH (or Box-SH) as the odorless sulfur nucleophile and DBBQ as the oxidant are used, and (3) the stereospecific synthesis of chiral molecules having sulfur-containing quaternary centers is achieved via the inversion of chiral tertiary alcohols (>99–94% inversion). The yields of the Btz sulfides **2** were affected by the α-substitents of alcohols such as α-ester, -ketone, and -phenyl groups while aliphatic or crowded substrates such as **1m** or **1o** were not particularly reactive (Tables 3 and 4). In the case of the chiral benzylic substrate **1n**, the extent of erosion in optical purity can be mitigated by the use of DBBQ at low temperatures (Table 5). Finally, the removal of Btz groups of **2** with *t*-BuLi or $LiAlH_4$ provides chiral tertiary thiols and their derivatives without loss of enantiomeric purities.

Experimental

General. All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and remain uncorrected. Infrared (IR) spectra were recorded on a HORIBA FT-300 or a SensIR Technologies Travel*IR*™ spectrometer. ^1H NMR spectra were recorded on a JEOL JNM-EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ = 77.0 ppm). Carbon–^{31}P coupling constants are reported when possible. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700T or a Thermo Electron Finnigan TSQ Quantum Ultra AM mass spectrometer. Elemental analysis was performed on a vario EL III analyzer. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. All reactions were carried out under an argon atmosphere in dried glassware, unless otherwise noted. 2,6-Di(benzyloxy)-1,4-benzoquinone[27] was prepared according to the reported procedure and the other 1,4-benzoquinone derivatives were purchased from Tokyo Kasei Kogyo and used without further purification. *p*-Methoxyphenyl azide[28] was prepared according to the reported procedure. Arenethiols, achiral tertiary alcohols, $ClPPh_2$, Ph_3P, DMAP, Et_3N, and (trimethylsilyl)methyl azide were purchased from Tokyo Kasei Kogyo (TCI). Me_3P and BtzSSBtz (99% grade) were purchased from Aldrich. Dehydrated solvents (THF and $CHCl_3$), $LiAlH_4$, and *t*-BuLi in pentane were purchased from Kanto Chemical Co., Inc. Activated alumina (ca. 300 mesh) was purchased from Wako Pure Chemical Industries, Ltd.

Procedures for the Preparation of Chiral Tertiary Alcohols. (*R*)-Terpinen-4-ol and (*R*)-linalool were purchased from ACROS Organics and Fluka Chemika, respectively. (*S*)-Ethyl α-methyl-β-phenyllactate (Table 4, Entry 2) was prepared from commercially available (*S*)-β-phenyllactic acid (Tokyo Kasei Kogyo) according to the reported procedure.[7a,29] (*S*)-3-Methyl-5-phenyl-3-pentanol (Table 4, Entry 4) and (*S*)-2-phenyl-2-butanol (Table 4, Entry 5) were prepared according to Walsh's procedure.[11c,30]

(*S*)-Benzyl 2-Hydroxy-2-methylbutyrate (Table 4, Entry 1):[1a] To a suspension of (*S*)-2-hydroxy-2-methylbutyric acid[31] (>99% ee; 958 mg, 8.11 mmol) and K_2CO_3 (1.68 g, 12.2 mmol) in 30 mL of anhydrous acetonitrile was added benzyl bromide (1.45 mL, 12.2 mmol) at rt. The mixture was stirred for 36 h at rt, diluted with EtOAc, and then filtered through a celite bed. After concentration of the filtrate, the residue was purified by a silica-gel column (hexane/EtOAc = 19/1) to give the title product as a colorless oil (1.62 g, 96%). $[\alpha]_D^{19}$ −4.9 (*c* 1.35, $CHCl_3$); IR (neat, cm^{-1}) 1727, 1230, 1168, 1144, 748, 696; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42–7.29 (m, 5H), 5.20 (s, 2H), 3.13 (s, 1H), 1.88–1.59 (m, 2H), 1.41 (s, 3H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 176.9, 135.3, 128.5, 128.4, 128.0, 75.0, 67.4, 33.1, 25.7, 8.0; HRMS (FAB^+) Calcd for $C_{12}H_{17}O_3$: $[M+H]^+$ 209.1178. Found: *m*/*z* 209.1181.

(*S*)-Methyl α-Phenyllactate (Table 4, Entry 3):[32] (*S*)-α-Phenyllactic acid (>99% ee) was prepared from the commercially available racemate according to Corey's procedure for the preparation of the (*R*)-enantiomer.[33] To a suspension of (*S*)-α-phenyllactic acid (3.38 g, 20.3 mmol) and K_2CO_3 (4.22 g, 30.5 mmol) in 40 mL of anhydrous acetonitrile was added methyl iodide (1.90 mL, 30.5 mmol) at rt, then the mixture was warmed to 40 °C. After 6 h, the mixture was cooled to rt, diluted with EtOAc, and then filtered through a celite bed. After concentration of the filtrate, the residue was purified by a silica-gel column (hexane/EtOAc = 5/1) to give the title product as a colorless oil (2.15 g, 57%). $[\alpha]_D^{23}$ +59.2 (*c* 0.68, $CHCl_3$); IR (ATR, cm^{-1}) 1727, 1250, 1144, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.58–7.48 (m, 2H), 7.39–7.23 (m, 3H), 3.88 (brs, 1H), 3.75 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 175.8, 142.5, 128.2, 127.6, 125.0, 75.7, 53.2, 26.7.

General Procedure for the Preparation of Alkyl Diphenylphosphinites. To a solution of an alcohol (10.0 mmol), DMAP (367 mg, 3.0 mmol), and Et_3N (1.66 mL, 12.0 mmol) in 20 mL of anhydrous THF was added $ClPPh_2$ (1.97 mL, 11.0 mmol) at rt. After having been stirred for 2 h at rt, the white slurry was concentrated in vacuo. The residue was diluted with a mixed solution of hexane–EtOAc (v/v = 8/1; ca. 100 mL), filtered through a pad of alumina–celite on a buchner funnel (ϕ 40 mm disc diagram; the thickness of the alumina layer was ca. 10 mm) and the filtered cake was then washed with additional hexane–EtOAc (v/v = 8/1; ca. 100 mL). After concentration, the corresponding phosphinite was obtained as an analytically pure form and was stored under dry argon in a refrigerator (<10 °C). For ^{1}H and ^{13}C NMR spectra of the phosphinites, $CDCl_3$ stabilized with a silver foil (containing 0.03 vol % TMS; purchased from Merck) was used as the solvent.

Methyl 2-[(Diphenylphosphino)oxy]-2-methylpropionate (1a): White solid; mp 61–63 °C; IR (KBr, cm^{-1}) 1738, 1139, 970, 746, 693; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57–7.45 (m, 4H), 7.40–7.25 (m, 6H), 3.66 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.7 (d, J = 1 Hz), 142.5 (d, J = 15 Hz), 130.0 (d, J = 22 Hz), 128.8, 128.0 (d, J = 7 Hz), 79.1 (d, J = 15 Hz), 52.1, 27.0 (d, J = 9 Hz); HRMS (EI) Calcd for $C_{17}H_{19}O_3P$: $[M]^+$ 302.1072. Found: *m*/*z* 302.1045.

Benzyl 2-[(Diphenylphosphino)oxy]-2-methylpropionate (1b): Colorless oil; IR (neat, cm^{-1}) 1740, 1136, 742, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54–7.42 (m, 4H), 7.40–7.19 (m, 11H), 5.11 (s, 2H), 1.62 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.0, 142.4 (d, J = 15 Hz), 135.4, 130.3, 129.9, 128.8, 128.1, 128.0 (×2), 79.2 (d, J = 15 Hz), 66.9, 27.0 (d, J = 10 Hz); HRMS (EI) Calcd for $C_{23}H_{23}O_3P$: $[M]^+$ 378.1385. Found: *m*/*z* 378.1352.

***t*-Butyl 2-[(Diphenylphosphino)oxy]-2-methylpropionate (1c):** White solid; mp 56–58 °C; IR (KBr, cm^{-1}) 1727, 1143; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60–7.46 (m, 4H), 7.40–7.24 (m, 6H), 1.56 (s, 6H), 1.35 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.3 (d, J = 1 Hz), 143.0 (d, J = 16 Hz), 130.0 (d, J = 23 Hz), 128.7, 128.0 (d, J = 7 Hz), 81.5, 79.6 (d, J = 15 Hz), 27.9, 27.0 (d, J = 9 Hz); HRMS ($APCI^+$) Calcd for $C_{20}H_{26}O_3P$: $[M+H]^+$ 345.1620. Found: *m*/*z* 345.1615.

2-[(Diphenylphosphino)oxy]-2-methylpropiophenone (1d): White solid; mp 71–72 °C; IR (KBr, cm^{-1}) 1676, 1161, 950, 695; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.45–7.10 (m, 13H), 1.72 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.2, 141.7 (d, J = 15 Hz), 132.1, 130.7, 130.3, 130.2, 129.1, 128.1, 128.0, 127.6, 84.8 (d, J = 13 Hz), 27.4 (d, J = 10 Hz); HRMS (EI) Calcd for $C_{22}H_{21}O_2P$: $[M]^+$ 348.1279. Found: *m*/*z* 348.1268.

2-[(Diphenylphosphino)oxy]-2-methylpropionitrile (1e): Colorless oil; IR (ATR, cm^{-1}) 1434, 1154, 969, 898, 742, 693; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53–7.32 (m, 10H), 1.73 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 140.5 (d, J = 15 Hz), 130.5 (d, J = 22 Hz), 129.6, 128.3 (d, J = 7 Hz), 121.0 (d, J = 2 Hz), 71.6 (d, J = 20 Hz), 29.0 (d, J = 8 Hz); HRMS ($APCI^+$) Calcd for $C_{16}H_{17}NOP$: $[M+H]^+$ 270.1048. Found: *m*/*z* 270.1055.

1-Methyl-1-phenylethyl Diphenylphosphinite (1f): White solid; mp 87–88 °C; IR (KBr, cm^{-1}) 948, 694; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56–7.41 (m, 6H), 7.37–7.18 (m, 9H), 1.73 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.3 (d, J = 3 Hz), 143.2 (d, J = 16 Hz), 130.1 (d, J = 22 Hz), 128.7, 128.1, 128.0, 126.8, 125.3, 79.5 (d, J = 14 Hz), 30.4 (d, J = 10 Hz); HRMS ($APCI^+$) calcd for $C_{21}H_{22}OP$: $[M+H]^+$ 321.1404. Found: *m*/*z* 321.1410.

1-Methylcyclopentyl Diphenylphosphinite (1g): White solid; mp 42–43 °C; IR (KBr, cm^{-1}) 915, 693; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53–7.14 (m, 10H), 2.19–1.97 (m, 2H), 1.80–1.34 (m, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.6 (d, J = 16 Hz), 129.9 (d, J = 22 Hz), 128.6, 128.0 (d, J = 7 Hz), 87.8 (d, J = 12 Hz), 40.3 (d, J = 8 Hz), 26.6 (d, J = 11 Hz), 23.9; HRMS ($APCI^+$) calcd for $C_{18}H_{22}OP$: $[M+H]^+$ 285.1404. Found: *m*/*z* 285.1467.

1,1-Dimethyl-3-phenylpropyl Diphenylphosphinite (1h): Colorless oil; IR (ATR, cm^{-1}) 911, 693; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62–7.45 (m, 4H), 7.33–7.00 (m, 11H), 2.70–2.60 (m, 2H), 2.02–1.92 (m, 2H), 1.40 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.6 (d, J = 16 Hz), 142.3, 130.1, 129.7, 128.6, 128.2, 128.1, 128.0, 125.5, 78.4 (d, J = 12 Hz), 45.1 (d, J = 6 Hz), 30.7, 28.1 (d, J = 10 Hz); HRMS (EI) Calcd for $C_{23}H_{25}OP$: $[M]^+$ 348.1643. Found: *m*/*z* 348.1638.

1-Adamantyl Diphenylphosphinite (1i): White solid; mp 66–68 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.42 (m, 4H), 7.38–7.21 (m, 6H), 2.21–2.09 (m, 3H), 2.04–1.91 (m, 6H), 1.69–1.54 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.7 (d, J = 17 Hz), 129.9 (d, J = 22 Hz), 128.5, 128.0 (d, J = 7 Hz), 75.7 (d, J = 11 Hz), 44.2 (d, J = 8 Hz), 36.2, 31.1; HRMS ($APCI^+$) Calcd for $C_{22}H_{26}OP$: $[M+H]^+$ 337.1717. Found: *m*/*z* 337.1714.

(*S*)-Benzyl 2-[(Diphenylphosphino)oxy]-2-methylbutyrate (1j): Colorless oil; $[\alpha]_D^{26}$ −27.8 (*c* 1.20, $CHCl_3$); IR (neat, cm^{-1}) 1739, 1130, 743; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.58–7.44 (m, 4H), 7.38–7.18 (m, 11H), 5.20–5.04 (m, 2H), 2.07–1.86 (m,

2H), 1.58 (d, $J = 5.8$ Hz, 3H), 0.91 (q, $J = 7.3$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.7, 143.3, 143.0, 142.6, 142.4, 135.4, 130.3, 130.1, 130.0, 129.8, 128.9, 128.6, 128.3, 128.1, 128.0 (×3), 127.9, 127.8, 82.2 (d, $J = 13$ Hz), 66.8, 33.6 (d, $J = 6$ Hz), 24.2 (d, $J = 12$ Hz), 8.4; HRMS (APCI$^+$) Calcd for $C_{24}H_{26}O_3P$: $[M + H]^+$ 393.1620. Found: m/z 393.1605.

(*S*)-Ethyl 2-[(Diphenylphosphino)oxy]-2-methyl-3-phenylpropionate (1k): Colorless oil; $[\alpha]_D^{24}$ −11.8 (*c* 1.14, $CHCl_3$); IR (neat, cm^{-1}) 1738, 1103, 742, 698; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.50–7.18 (m, 15H), 4.07 (q, $J = 7.1$ Hz, 2H), 3.24 (d, $J = 13.5$ Hz, 1H), 3.15 (d, $J = 13.5$ Hz, 1H), 1.57 (s, 3H), 1.03 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.4, 143.4, 143.1, 142.4, 142.2, 135.7, 130.7, 130.5, 130.1, 130.0, 129.7, 128.9, 128.4, 128.1, 128.0, 127.7 (×2), 126.7, 82.1 (d, $J = 13$ Hz), 61.2, 46.9 (d, $J = 4$ Hz), 24.2 (d, $J = 13$ Hz), 13.9; HRMS (APCI$^+$) Calcd for $C_{24}H_{26}O_3P$: $[M + H]^+$ 393.1620. Found: m/z 393.1607.

(*S*)-Methyl 2-[(Diphenylphosphino)oxy]-2-phenylpropionate (1l): Colorless oil; $[\alpha]_D^{22}$ −5.9 (*c* 1.33, $CHCl_3$); IR (ATR, cm^{-1}) 1742, 1227, 1125, 1103, 692; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.61–7.48 (m, 6H), 7.39–7.24 (m, 9H), 3.63 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.2, 142.6, 142.4, 142.2, 142.0, 141.7, 141.7, 130.6, 130.4, 130.3, 130.1, 129.1, 128.8, 128.2 (×2), 128.1 (×2), 128.0, 127.9, 125.4, 82.8 (d, $J = 16$ Hz), 52.4, 26.5 (d, $J = 12$ Hz); HRMS (EI) Calcd for $C_{22}H_{21}O_3P$: $[M]^+$ 364.1228. Found: m/z 364.1215.

(*S*)-1-Ethyl-1-methyl-3-phenylpropyl Diphenylphosphinite (1m): Colorless oil; $[\alpha]_D^{19}$ +3.5 (*c* 1.01, $CHCl_3$); IR (ATR, cm^{-1}) 908, 739, 693; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60–7.46 (m, 4H), 7.40–7.00 (m, 11H), 2.63–2.54 (m, 2H), 2.04–1.90 (m, 2H), 1.80 (q, $J = 7.4$ Hz, 2H), 1.38 (s, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.9, 143.8, 143.6 (×2), 142.5, 130.2, 130.1, 129.8 (×2), 128.6 (×2), 128.2, 128.1, 128.0, 125.5, 81.0 (d, $J = 10$ Hz), 42.2 (d, $J = 7$ Hz), 33.2 (d, $J = 7$ Hz), 30.4, 25.3 (d, $J = 11$ Hz), 8.7; HRMS (APCI$^+$) Calcd for $C_{24}H_{28}OP$: $[M + H]^+$ 363.1878. Found: m/z 363.1877.

(*S*)-1-Methyl-1-phenylpropyl Diphenylphosphinite (1n): White solid; mp 83–85 °C; $[\alpha]_D^{22}$ −6.40 (*c* 1.09, $CHCl_3$); IR (KBr, cm^{-1}) 916, 694; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.63–7.16 (m, 15H), 2.22–1.89 (m, 2H), 1.70 (s, 3H), 0.70 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 145.8 (×2), 143.7, 143.4, 143.2, 130.4, 130.3, 130.0 (×2), 128.7, 128.6, 128.1 (×2), 128.0 (×2), 127.9, 126.7, 125.8 (×2), 82.6 (d, $J = 13$ Hz), 36.6 (d, $J = 6$ Hz), 27.2 (d, $J = 13$ Hz), 8.8; HRMS (FAB$^+$) Calcd for $C_{22}H_{24}OP$: $[M + H]^+$ 335.1565. Found: m/z 335.1555.

(*R*)-1-Isopropyl-4-methyl-3-cyclohexenyl Diphenylphosphinite (1o): Colorless crystal; 63–65 °C; $[\alpha]_D^{16}$ −8.1 (*c* 0.75, $CHCl_3$); IR (ATR, cm^{-1}) 1433, 922, 902, 744, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54–7.40 (m, 4H), 7.34–7.18 (m, 6H), 5.26 (brs, 1H), 2.50–2.35 (m, 1H), 2.25–1.45 (m, 9H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.82 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 144.1, 143.9, 133.8, 131.1, 130.7, 129.5, 129.2, 128.8, 128.1, 127.9, 127.8 (×2), 127.7, 118.5, 81.1 (d, $J = 9$ Hz), 35.8 (d, $J = 5$ Hz), 32.5 (d, $J = 11$ Hz), 30.0 (d, $J = 8$ Hz), 28.0, 23.1, 17.7, 17.2; HRMS (APCI$^+$) Calcd for $C_{22}H_{28}OP$: $[M + H]^+$ 339.1878. Found: m/z 339.1863.

General Procedure for Condensation of Alkyl Diphenylphosphinites with Btz-SH. To a suspension of the diphenylphosphinite **1** (1.0 mmol) and Btz-SH (83.6 mg, 0.5 mmol) in 0.5 mL of $CHCl_3$ was added DBBQ (220 mg, 1.0 mmol) at rt. Btz-SH gradually dissolved as the reaction proceeded. After 12–24 h, the formation of **2** together with 3,5-di-*t*-butyl-4-hydroxyphenyl diphenylphosphinate was confirmed by TLC monitoring and the crude product was directly purified by preparative TLC on silica-gel (haxane/EtOAc, 90/10 or 95/5) to afford the desired Btz sulfide **2**.

3,5-Di-*t*-butyl-4-hydroxyphenyl Diphenylphosphinate (Scheme 1): White solid; mp 170–171 °C; IR (ATR, cm^{-1}) 3221, 2950, 1590, 1428, 1218, 1176, 1130, 1109, 985, 970, 860, 730, 693, 547, 527; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94–7.87 (m, 4H), 7.53–7.46 (m, 6H), 6.85 (s, 2H), 5.00 (s, 1H), 1.30 (s, 18H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 150.3, 143.0 (d, $J = 8$ Hz), 136.8, 132.3, 132.1, 132.1, 131.8, 131.6, 130.2, 128.4, 128.2, 117.3, 117.2, 34.3, 30.0; HRMS (APCI$^+$) Calcd for $C_{26}H_{32}O_3P$: $[M + H]^+$ 423.2089. Found: m/z 423.2083.

Methyl 2-Methyl-2-[(4-nitrophenyl)sulfanyl]propionate (2a): Colorless oil; IR (ATR, cm^{-1}) 1727, 1516, 1341, 1266, 1152, 1121, 851; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.16 (ddd, $J = 2.1, 2.5, 8.9$ Hz, 2H), 7.57 (ddd, $J = 2.1, 2.5, 8.9$ Hz, 2H), 3.71 (s, 3H), 1.56 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 147.5, 140.8, 135.1, 123.3, 52.5, 51.5, 25.9; HRMS (FAB$^+$) Calcd for $C_{11}H_{14}NO_4S$: $[M + H]^+$ 256.0644. Found: m/z 256.0652.

Methyl 2-Methyl-2-[(5-nitropyridin-2-yl)sulfanyl]propionate (2b): Colorless oil; IR (ATR, cm^{-1}) 1731, 1585, 1566, 1511, 1339, 1264, 1099, 854, 750; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.17 (d, $J = 2.7$ Hz, 1H), 8.23 (dd, $J = 2.7, 8.7$ Hz, 1H), 7.26 (d, $J = 8.7$ Hz, 1H), 3.71 (s, 3H), 1.72 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.0, 166.0, 144.3, 140.9, 130.3, 121.2, 52.8, 51.6, 26.1; HRMS (FAB$^+$) Calcd for $C_{10}H_{13}N_2O_4S$: $[M + H]^+$ 257.0596. Found: m/z 257.0582.

Methyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylpropionate (2c): Colorless oil; IR (neat, cm^{-1}) 1737, 1459, 1429, 1267, 1157, 1126, 989; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.2$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.50–7.22 (m, 2H), 3.74 (s, 3H), 1.74 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.5, 161.0, 153.0, 136.1, 125.9, 124.8, 122.3, 120.8, 53.8, 52.8, 26.3; HRMS (FAB$^+$) Calcd for $C_{12}H_{14}NO_2S_2$: $[M + H]^+$ 268.0466. Found: m/z 268.0479.

Methyl 2-[(1,3-Benzoxazol-2-yl)sulfanyl]-2-methylpropionate (2d): IR (ATR, cm^{-1}) 1736, 1503, 1452, 1118, 1091, 743; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.64–7.54 (m, 1H), 7.46–7.36 (m, 1H), 7.30–7.17 (m, 2H), 3.71 (s, 3H), 1.76 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.1, 161.2, 151.3, 141.5, 124.3, 124.1, 119.0, 109.8, 53.0, 52.9, 26.5; HRMS (FAB$^+$) Calcd for $C_{12}H_{14}NO_3S$: $[M + H]^+$ 252.0694. Found: m/z 252.0693.

Benzyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylpropionate (2e): Colorless oil; IR (neat, cm^{-1}) 1734, 1459, 1428, 1260, 1155, 989; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.1$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.44–7.18 (m, 7H), 5.17 (s, 2H), 1.78 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.9, 161.8, 153.1, 136.1, 135.4, 128.2, 127.9, 127.8, 125.9, 124.8, 122.4, 120.8, 67.4, 54.0, 26.4; HRMS (FAB$^+$) Calcd for $C_{18}H_{18}NO_2S_2$: $[M + H]^+$ 344.0779. Found: m/z 344.0792.

***t*-Butyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylpropionate (2f):** White solid; mp 40–42 °C; IR (KBr, cm^{-1}) 1728, 1458, 1425, 1272, 1151, 991; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.90 (d, $J = 7.9$ Hz, 1H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.48–7.22 (m, 2H), 1.73 (s, 6H), 1.42 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.9, 162.4, 153.1, 136.1, 125.8, 124.6, 122.1, 120.8, 81.6, 54.7, 27.7, 26.5; HRMS (FAB$^+$) Calcd for $C_{15}H_{20}NO_2S_2$: $[M + H]^+$ 310.0935. Found: m/z 310.0954.

2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylpropiophenone (2g): White solid; mp 41–42 °C; IR (neat, cm^{-1}) 1678, 1455, 1252, 984; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.10 (d, $J = 7.7$ Hz,

2H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.68 (d, $J = 7.9$ Hz, 1H), 7.52–7.21 (m, 5H), 1.85 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 200.3, 161.1, 152.9, 136.5, 136.1, 131.6, 128.9, 127.7, 125.9, 124.8, 122.3, 120.8, 58.0, 27.3; HRMS (FAB$^+$) Calcd for $C_{17}H_{16}NOS_2$: $[M + H]^+$ 314.0673. Found: m/z 314.0681.

2-[(1-Methyl-1-phenylethyl)sulfanyl]-1,3-benzothiazole (2h): Colorless oil; IR (neat, cm^{-1}) 1421, 983, 760; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.1$ Hz, 1H), 7.72–7.57 (m, 3H), 7.47–7.11 (m, 5H), 1.96 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.3, 152.8, 144.7, 136.4, 128.2, 127.2, 126.7, 125.8, 124.7, 122.5, 120.7, 54.8, 30.3; HRMS (FAB$^+$) Calcd for $C_{16}H_{16}NS_2$: $[M + H]^+$ 286.0724. Found: m/z 286.0722.

2-[(1-Methylcyclopentyl)sulfanyl]-1,3-benzothiazole (2i): Colorless oil; IR (neat, cm^{-1}) 1427, 984, 758; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.2$ Hz, 1H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.51–7.24 (m, 2H), 2.26–2.08 (m, 2H), 1.98–1.63 (m, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.4, 153.4, 135.9, 125.8, 124.5, 122.2, 120.7, 60.0, 40.9, 28.8, 24.3; HRMS (FAB$^+$) Calcd for $C_{13}H_{16}NS_2$: $[M + H]^+$ 250.0724. Found: m/z 250.0725.

2-[(1,1-Dimethyl-3-phenylpropyl)sulfanyl]-1,3-benzothiazole (2j): Colorless oil; IR (neat, cm^{-1}) 1456, 1423, 983, 754; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.1$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.48–7.00 (m, 7H), 2.91–2.77 (m, 2H), 2.22–2.08 (m, 2H), 1.61 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.9, 153.6, 141.9, 136.2, 128.3 ($\times$2), 125.9, 125.7, 124.8, 122.5, 120.8, 54.2, 44.4, 31.6, 29.0; HRMS (FAB$^+$) Calcd for $C_{18}H_{20}NS_2$: $[M + H]^+$ 314.1037. Found: m/z 314.1034.

2-[(1-Adamantyl)sulfanyl]-1,3-benzothiazole (2k): White solid; mp 73–74 °C; IR (neat, cm^{-1}) 2904, 1450, 1414, 1300, 1035, 982, 756; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.01 (d, $J = 7.9$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.50–7.32 (m, 2H), 2.20–2.05 (m, 9H), 1.75–1.66 (m, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 161.6, 153.5, 136.8, 125.9, 124.8, 122.7, 120.7, 53.0, 43.5, 36.1, 30.3; HRMS (FAB$^+$) Calcd for $C_{17}H_{20}NS_2$: $[M + H]^+$ 302.1037. Found: m/z 302.1043.

(*R*)-Benzyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylbutyrate (2l): Colorless oil; >99% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): $t_R = 54.9$ min (*S*), 60.4 min (*R*); $[\alpha]_D^{19}$ +19.4 (*c* 1.15, $CHCl_3$); IR (neat, cm^{-1}) 1731, 1458, 1233, 1147, 989; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, $J = 7.9$ Hz, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.44–7.17 (m, 7H), 5.18 (s, 2H), 2.25–1.94 (m, 2H), 1.76 (s, 3H), 1.00 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.3, 161.6, 153.0, 136.1, 135.3, 128.1, 127.8 ($\times$2), 125.8, 124.7, 122.3, 120.7, 67.3, 58.8, 31.6, 23.0, 9.2; HRMS (FAB$^+$) Calcd for $C_{19}H_{20}NO_2S_2$: $[M + H]^+$ 358.0935. Found: m/z 358.0923.

(*R*)-Ethyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methyl-3-phenylpropionate (2m): Colorless oil; 76% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 400/1, flow rate = 1.0 mL min^{-1}): $t_R = 33.4$ min (*R*), 34.0 min (*S*); $[\alpha]_D^{15}$ +21.4 (*c* 0.67, $CHCl_3$); IR (neat, cm^{-1}) 1730, 1457, 1241, 1200, 1098, 989; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93 (dd, $J = 0.7$, 8.1 Hz, 1H), 7.78 (dd, $J = 0.7$, 7.9 Hz, 1H), 7.48–7.14 (m, 7H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.51 (d, $J = 13.5$ Hz, 1H), 3.35 (d, $J = 13.5$ Hz, 1H), 1.68 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.0, 161.7, 153.1, 136.1, 135.4, 130.4, 127.9, 127.0, 125.9, 124.8, 122.3, 120.8, 61.8, 58.8, 43.9, 23.3, 14.0; HRMS (FAB$^+$) Calcd for $C_{19}H_{20}NO_2S_2$: $[M + H]^+$ 358.0935. Found: m/z 358.0917.

(*R*)-Methyl 2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-phenylpropionate (2n): Colorless solid; mp 48–49 °C; 99% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 400/1, flow rate = 1.0 mL min^{-1}): $t_R = 28.5$ min (*S*), 31.8 min (*R*); $[\alpha]_D^{20}$ −90.0 (*c* 0.85, $CHCl_3$); IR (KBr, cm^{-1}) 1729, 1454, 1422, 1236, 984; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.1$ Hz, 1H), 7.75–7.53 (m, 3H), 7.47–7.20 (m, 5H), 3.76 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.9, 162.4, 152.7, 138.5, 135.9, 128.5, 128.3, 126.7, 125.8, 124.7, 122.2, 120.8, 61.5, 53.2, 25.6; HRMS (FAB$^+$) Calcd for $C_{17}H_{16}NO_2S_2$: $[M + H]^+$ 330.0622. Found: m/z 330.0632.

(*R*)-2-[(1-Ethyl-1-methyl-3-phenylpropyl)sulfanyl]-1,3-benzothiazole (2o): Colorless oil; 67% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): $t_R = 21.3$ min (*R*), $t_R = 27.1$ min (*S*); $[\alpha]_D^{17}$ +10.5 (*c* 0.59, $CHCl_3$); IR (ATR, cm^{-1}) 1453, 1423, 970, 754, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 7.9$ Hz, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.48–7.10 (m, 7H), 2.92–2.71 (m, 2H), 2.22–1.80 (m, 4H), 1.54 (s, 3H), 1.06 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.8, 153.6, 142.1, 136.2, 128.3 ($\times$2), 125.9, 125.7, 124.8, 122.4, 120.8, 58.5, 41.8, 32.9, 31.2, 25.7, 9.0; HRMS (FAB$^+$) Calcd for $C_{19}H_{22}NS_2$: $[M + H]^+$ 328.1194. Found: m/z 328.1185.

(*R*)-2-[(1-Methyl-1-phenylpropyl)sulfanyl]-1,3-benzothiazole (2p): Colorless oil; 86% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): $t_R = 23.7$ min (*S*), 31.6 min (*R*); $[\alpha]_D^{21}$ +127.9 (*c* 1.14, $CHCl_3$); IR (neat, cm^{-1}) 1453, 1420, 981, 756; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.78–7.53 (m, 3H), 7.51–7.21 (m, 5H), 2.38–2.15 (m, 2H), 1.97 (s, 3H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.1, 152.6, 143.0, 136.3, 128.1, 127.2, 127.0, 125.7, 124.6, 122.4, 120.6, 58.9, 35.7, 25.4, 9.2; HRMS (FAB$^+$) Calcd for $C_{17}H_{18}NS_2$: $[M + H]^+$ 300.0881. Found: m/z 300.0900.

(*S*)-2-[(1,5-Dimethyl-1-vinyl-4-hexenyl)sulfanyl]-1,3-benzothiazole (2q), 2-[(3,7-Dimethyl-2,6-octadienyl)sulfanyl]-1,3-benzothiazole (2r). To a solution of (*R*)-linalool (90% ee; 309 mg, 2.0 mmol), DMAP (73.3 mg, 0.6 mmol), and Et_3N (0.33 mL, 2.4 mmol) in 4.0 mL of anhydrous THF was added $ClPPh_2$ (0.40 mL, 2.2 mmol) at rt. After 2 h at rt, the mixture was concentrated in vacuo, diluted in hexane/EtOAc (20 mL, v/v = 8/1) and then filtered through a pad of celite and alumina. The filtrate was concentrated and dried in vacuo at rt for 1 h to give the corresponding crude phosphinite (582 mg, ca. 86%) as a colorless oil. The residue was dissolved in 1.0 mL of chloroform, and Btz-SH (167 mg, 1.0 mmol) and DBBQ (441 mg, 2.0 mmol) were added at 0 °C. The mixture was allowed to react at 0 °C for 9 h. The crude product was purified by preparative TLC (hexane/EtOAc = 95/5) to give a mixture of **2q** and **2r** (179 mg, 59% based on Btz-SH) as a pale-yellow oil. HPLC analysis of the mixture using a DAICEL CHIRALCEL OD-H column showed that **2q** was formed in 15% yield and 89% ee along with **2r** (44% yield, $E/Z = 79/21$). Analytical samples were partially separated by HPLC using a CHIRALCEL OD column. (*S*)-**2q**: Colorless oil; $[\alpha]_D^{23}$ +18.8 (*c* 0.72, $CHCl_3$); The ee value was determined by chiral HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): $t_R = 16.1$ min (*S*), 18.0 min (*R*); IR (ATR, cm^{-1}) 1453, 1425, 980, 756; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 7.2$ Hz, 1H), 7.48–7.31 (m, 2H), 6.10 (dd, $J = 10.7$, 17.3 Hz, 1H), 5.18–5.03

(m, 3H), 2.25–1.78 (m, 4H), 1.68 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.3, 153.1, 142.0, 136.7, 132.2, 125.9, 124.9, 123.3, 122.7, 120.8, 114.7, 57.4, 40.7, 25.8, 24.1, 23.5, 17.8; HRMS (FAB$^+$) Calcd for $C_{17}H_{22}NS_2$: $[M + H]^+$ 304.1194. Found: m/z 304.1184. (*E*)-**2r**: Colorless oil; HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): t_R = 80.4 min; IR (ATR, cm^{-1}) 1456, 1426, 992, 754, 725; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.46–7.24 (m, 2H), 5.42 (t, J = 6.6 Hz, 1H), 5.10–5.00 (m, 1H), 4.01 (d, J = 7.7 Hz, 2H), 2.15–1.98 (m, 4H), 1.77 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.0, 153.1, 141.9, 135.2, 131.7, 125.9, 124.0, 123.6, 121.3, 120.8, 117.4, 39.6, 31.9, 26.4, 25.7, 17.8, 16.4; HRMS (FAB$^+$) Calcd for $C_{17}H_{22}NS_2$: $[M + H]^+$ 304.1194. Found: m/z 304.1209. (*Z*)-**2r**: Colorless oil; HPLC analysis (DAICEL CHIRALCEL OD-H column, hexane/*i*-PrOH = 900/1, flow rate = 1.0 mL min^{-1}): t_R = 53.1 min; IR (ATR, cm^{-1}) 1458, 1427, 994, 755, 726; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.46–7.24 (m, 2H), 5.44 (t, J = 7.9 Hz, 1H), 5.18–5.08 (m, 1H), 4.01 (d, J = 7.9 Hz, 2H), 2.23–2.04 (m, 4H), 1.77 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.0, 153.1, 142.0, 135.1, 132.2, 125.9, 124.0, 123.6, 121.3, 120.8, 118.1, 32.1, 31.7, 26.6, 25.8, 23.6, 17.8; HRMS (FAB$^+$) Calcd for $C_{17}H_{22}NS_2$: $[M + H]^+$ 304.1194. Found: m/z 304.1209.

2-[(1,3-Benzothiazol-2-yl)sulfanyl]-2-methylpropionic Acid (2s). To a solution of **2d** (910 mg, 2.65 mmol) in THF (7.7 mL) and MeOH (3.8 mL) was added 2 M aq NaOH (1.99 mL, 3.98 mmol) at rt. The mixture was stirred overnight. The solution was acidified with 1 M aq HCl, extracted with EtOAc (×3), and then dried over Na_2SO_4. After evaporation, the residue was purified by a silica-gel column ($CHCl_3$/MeOH = 98/2) and recrystallized (hexane/EtOAc) to give the title compound as white solids (565 mg, 84%). mp 148–149 °C; IR (ATR, cm^{-1}) 2864 (br), 1712, 1496 (br), 1453, 1407, 1314, 1253, 1240, 1158, 1118, 998, 758; ^{1}H NMR (270 MHz, $CDCl_3$) δ 12.59 (brs, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.58–7.35 (m, 2H), 1.77 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.9, 165.6, 151.0, 134.7, 126.8, 125.5, 121.4, 121.2, 54.2, 25.8; Anal. Calcd for $C_{11}H_{11}NO_2S_2$: C, 52.15; H, 4.38; N, 5.53; S, 25.31%. Found: C, 51.96; H, 4.35; N, 5.44; S, 25.25%.

A Typical Procedure for the Deprotection of Btz Groups with *t*-BuLi: Synthesis of Benzyl 1-Methyl-1-phenylethyl Sulfide (3a).[34] To a solution of the sulfide **2h** (250 mg, 0.876 mmol) in 4.4 mL of anhydrous THF was added *t*-BuLi (1.48 M solution in pentane; 0.592 mL, 0.876 mmol) at −78 °C. After stirring for 1 h at the same temperature, benzyl bromide (0.125 mL, 1.05 mmol) was added. The solution was allowed to warm up to 0 °C and then stirred for an additional 2 h. The mixture was partitioned with Et_2O and water. The organic layer was separated, dried over Na_2SO_4, filtered, and then concentrated. The crude product was purified by preparative TLC (hexane/EtOAc = 98/2) to give **3a** (198 mg, 93%) as a colorless oil. IR (neat, cm^{-1}) 1448, 704; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 2H), 7.41–7.08 (m, 8H), 3.39 (s, 2H), 1.71 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.1, 137.9, 128.8, 128.2, 128.0, 126.6, 126.5, 126.4, 48.5, 34.5, 30.3.

Benzyl 1,1-Dimethyl-3-phenylpropyl Sulfide (3b):[34] Colorless oil; IR (neat, cm^{-1}) 1456, 705; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45–7.01 (m, 10H), 3.78–3.63 (m, 2H), 2.82–2.60 (m, 2H), 1.90–1.70 (m, 2H), 1.35 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 142.2, 138.2, 128.8, 128.3, 128.2 (×2), 126.6, 125.5, 46.1, 44.3, 32.9, 31.4, 28.9.

***t*-Butyl 2-(Benzylsulfanyl)-2-methylpropionate (3c):** Colorless oil; IR (neat, cm^{-1}) 1720, 1277, 1149; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.35–7.10 (m, 5H), 3.85 (s, 2H), 1.49 (s, 15H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.7, 137.1, 128.9, 128.3, 126.9, 80.9, 48.5, 34.6, 27.9, 25.6; HRMS (FAB$^+$) Calcd for $C_{15}H_{23}O_2S$: $[M + H]^+$ 267.1419. Found: m/z 267.1406.

2-(Benzylsulfanyl)-2-methylpropionic Acid (3d): White solid; mp 148–149 °C; IR (ATR, cm^{-1}) 2970 (br), 1680, 1284, 1168, 1129, 708; ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.14 (brs, 1H), 7.32–7.13 (m, 5H), 3.86 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 180.8, 137.0, 129.0, 128.4, 126.9, 48.5, 34.8, 25.8; HRMS (FAB$^+$) Calcd for $C_{11}H_{15}O_2S$: $[M + H]^+$ 211.0793. Found: m/z 211.0805.

2-*t*-Butyl-1,3-benzothiazole (4):[26] Colorless oil; IR (ATR, cm^{-1}) 2963, 1512, 1438, 1248, 1044, 1007, 757, 728; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.07–7.95 (m, 1H), 7.79 (m, 1H), 7.52–7.26 (m, 2H), 1.51 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 181.6, 153.0, 134.8, 125.6, 124.4, 122.5, 121.3, 38.3, 30.8.

(*R*)-Benzyl 1-Methyl-1-phenylpropyl Sulfide (3e): Colorless oil; 86% ee; The ee value was determined by chiral HPLC analysis (DAICEL CHIRALPAK AS-H column, hexane, flow rate = 0.1 mL min^{-1}): t_R = 54.0 min (*S*), t_R = 57.2 min (*R*); $[\alpha]_D^{21}$ +53.7 (*c* 0.97, $CHCl_3$); IR (neat, cm^{-1}) 1496, 1452, 703; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.42–7.07 (m, 8H), 3.46 (d, J = 12.0 Hz, 1H), 3.27 (d, J = 12.0 Hz, 1H), 2.16–1.81 (m, 2H), 1.72 (s, 3H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 144.6, 138.0, 128.8, 128.2, 128.0, 127.1, 126.6, 126.3, 52.8, 35.4, 33.9, 25.5, 9.2; HRMS (FAB$^+$) Calcd for $C_{17}H_{21}S$: $[M + H]^+$ 257.1364. Found: m/z 257.1371.

(*R*)-*S*-1-Methyl-1-phenylpropyl *N*-(2-Hydroxy-1,1-dimethylethyl)thiocarbamate (5).[10a] At −78 °C, to a solution of (*R*)-**2p** (37% ee; 119 mg, 0.397 mmol) in 3 mL of anhydrous THF was added *t*-BuLi (1.48 M in pentane; 0.268 mL, 0.397 mmol). After 1 h, triphosgene (47.1 mg, 0.159 mmol) in 1 mL of THF was added and the mixture was stirred at −78 °C for 30 min, then at 0 °C for an additional 30 min. 2-Amino-2-methylpropanol (0.143 mL, 1.50 mmol) was then added to the mixture, which was stirred at 0 °C for 30 min. The reaction was worked up with water, extracted with ethyl acetate (×2), and the combined organic layer was dried over Na_2SO_4. After concentration, the crude product was purified by preparative TLC (hexane/EtOAc = 3/1) to give **5** (49.6 mg, 44%, 37% ee) as a colorless oil. The ee value was determined by chiral HPLC analysis (DAICEL CHIRALPAK AD-H column, hexane/*i*-PrOH = 50/1, flow rate = 1.0 mL min^{-1}): t_R = 45.7 min (*S*), t_R = 47.8 min (*R*). **5**: $[\alpha]_D^{22}$ +21.8 (*c* 0.77, CH_2Cl_2), lit.[10a] $[\alpha]_D^{19}$ −48.1 (*c* 0.56, CH_2Cl_2) for the (*S*)-enantiomer (97% ee); IR (ATR, cm^{-1}) 1652, 1490, 1446, 1205, 1056, 857, 733, 697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 2H), 7.40–7.19 (m, 3H), 5.24 (brs, 1H), 3.50–3.30 (m, 3H), 2.22–2.01 (m, 2H), 1.94 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 0.79 (t, J = 7.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.5, 143.8, 128.1, 127.0, 126.8, 69.8, 57.2, 56.6, 35.5, 25.3, 24.4, 24.2, 9.0; HRMS (FAB$^+$) Calcd for $C_{15}H_{24}NO_2S$: $[M + H]^+$ 282.1528. Found: m/z 282.1538.

(*R*)-2-Phenyl-2-sulfanyl-1-propanol (6).[10a] To a mixture of $LiAlH_4$ (66.4 mg, 1.75 mmol) in 13.0 mL of anhydrous Et_2O was added **2n** (150 mg, 0.437 mmol) in anhydrous Et_2O (5.0 mL) at rt, and the mixture was then refluxed for 4 h. After having been cooled to rt, the mixture was carefully poured into 1 M aq HCl, extracted with Et_2O (×2), dried over Na_2SO_4, and concentrated. The crude product was purified by preparative TLC (hexane/EtOAc = 3/1) to give **6** (70.2 mg, 95%) as a colorless oil. **6**:

99% ee concluded from the substrate **2n**; $[\alpha]_D^{23}$ −32.6 (*c* 0.41, CH_2Cl_2); lit.[10a] $[\alpha]_D^{20}$ −31.8 (*c* 0.36, CH_2Cl_2, ≥99% ee of the (*R*)-enantiomer); IR (neat, cm^{-1}) 3402, 2560, 696; ^1H NMR (270 MHz, $CDCl_3$) δ 7.58–7.44 (m, 2H), 7.40–7.17 (m, 3H), 3.80 (s, 2H), 2.37 (brs, 1H), 2.11 (s, 1H), 1.74 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.5, 128.3, 127.1, 126.2, 72.8, 51.7, 28.0; HRMS (EI) Calcd for $C_9H_{12}OS$: $[M]^+$ 168.0609. Found: *m*/*z* 168.0603.

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