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Iridium-catalyzed enantioselective allylation of sodium 2-aminobenzenethiolate: an access to chiral benzo-fused *N*,*S*-heterocycles

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ABSTRACT

The use of sodium 2-aminobenzenethiolate in the enantioselective iridium catalyzed allylic substitution with a range of methyl allyl carbonates allows the concise synthesis of the branch-type products with both excellent regio- and enantioselectivities, which are functionalized *N*,*S*-containing allylic intermediates for the formation of chiral benzo-fused *N*,*S*-heterocycles.

1. Introduction

Analogs of both antiarrhythmic KT-362[1] and Dazolicine[1c] (Fig. 1) are of great importance with regards to benzo-fused *N*,*S*-heterocycle with interesting biological activities.[2] Construction of the carbon–sulfur bond by means of the asymmetrical transition metal-catalyzed allylic substitution is less studied,[3] however, use of sulfur nucleophile in the enantioselective palladium-catalyzed allylic alkylation was described.[4] Few sulfur nucleophiles, such as 4-chloro-thiophenol, 2-mercaptopyridine and 2-mercaptopyrimidine are effective for the palladium catalyst system but more basic sulfur nucleophiles fail to undergo this reaction.[4a,4c] Iridium-catalyzed enantioselective allylation has become one of the powerful methods for the synthesis of chiral compounds.[5] Recent progress in chiral carbon–sulfur bond formation catalyzed via iridium complex has been made by the group of Hartwig,[6] You,[7] and us.[8] To date, the utilization of sodium 2-aminobenzenethiolate in the iridium-catalyzed allylation has not been explored, in which an *ortho* substituent group may lead to the detrimental *ortho* substituent effect on the stereoselectivity. In connect of our efforts aimed at forming carbon–sulfur bond, we have discovered that different types of sulfur nucleophiles have a strong influence on regio- and enantioselectivity of the iridium-catalyzed allylation.[7] We envision that the asymmetrical allylic substitution of sodium 2-aminobenzenethiolate could provide useful *N*,*S*-containing intermediates for the preparation of chiral benzo-fused *N*,*S*-heterocycles.

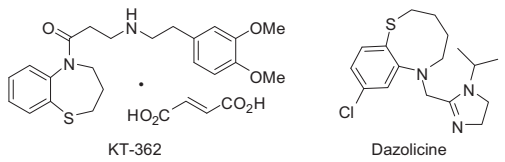

Fig. 1. The chemical structures of both KT-365 and Dazolicine.

Herein we report the enantioselective iridium-catalyzed allylic substitution of sodium 2-aminobenzenethiolate with structurally diverse allylic carbonates. This study presents the first example for the preparation of *N*,*S*-containing allyl branch-type products in good yields with both excellent regio- and enantioselectivities.

2. Results and discussion

Our first attempt involved a model reaction of (*E*)-cinnamyl methyl carbonate (**2a**) with sodium 2-aminobenzenethiolate (**3a**), which has two different nucleophilic positions, *N* or *S*. This reaction was performed under our previous optimized conditions[8a] and a mixture of the branched product **4a** and linear product **5a** in a ratio of 65/35 was obtained. To our delight, 96% ee of **4a** was

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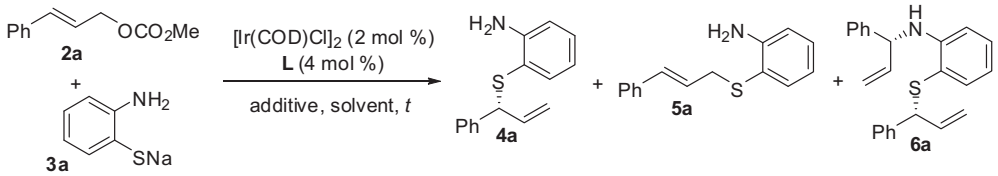
achieved; a trace amount of the amination product **6a** was also observed (Table 1, entry 1). In contrast, this reaction without the use of CsF also gave similar results (Table 1, entry 1 vs entry 2).

regioselectivity, albeit with 86% ee (Table 1, entry 13). The iridium complex derived from ligand **L4** resulted in somewhat improved results compared with **L2** (Table 1, entry 13 vs entry 14). The remaining

Table 1
Optimization of the enantioselective Ir-catalyzed allylic substitution of sodium 2-aminobenzenethiolate with (*E*)-cinnamyl methyl carbonate[a]



Entry	L	Solvent	Base	**2a**/**3**	Temp [°C]	Yield[b] [%]	**4a**/**5a**/**6a**[c]	ee[d] [%]
1	**L3**	DCM	CsF	2.5/1	25	58	65/35/Trace	96
2	**L3**	DCM	—	2.5/1	25	59	70/30/trace	98
3	**L3**	DCM	DABCO	2.5/1	25	39	70/30/-	95
4	**L3**	DCM	Cs_2CO_3	2.5/1	25	66	72/23/5	98
5	**L3**	DCM	KOAc	2.5/1	25	83	96/4/trace	96
6	**L3**	DCM	KOAc	1.5/1	25	30	58/42/-	96
7	**L3**	DCM	KOAc	2.5/1	0	trace[e]	—	—
8	**L3**	DCM	KOAc	2.5/1	Reflux	41	79/21/trace	96
9	**L3**	THF	KOAc	2.5/1	25	Trace[e]	—	—
10	**L3**	Toluene	KOAc	2.5/1	25	Trace[e]	—	—
11	**L3**	CH_3CN	KOAc	2.5/1	25	Trace[e]	—	—
12	**L1**	DCM	KOAc	2.5/1	25	Trace[e]	—	—
13	**L2**	DCM	KOAc	2.5/1	25	20	31/69/-	86
14	**L4**	DCM	KOAc	2.5/1	25	54	75/25/trace	95
15	**L5**	DCM	KOAc	2.5/1	25	Trace[e]	—	—
16	**L6**	DCM	KOAc	2.5/1	25	Trace[e]	—	—

[a] Reaction conditions: 2 mol % of $[Ir(COD)Cl]_2$, 4 mol % of **L**, and 5.0 equiv of additive.
[b] Isolated yields of **4a**.
[c] Determined by ^1H NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis.
[e] Monitored by TLC.

As is commonly seen in the iridium-catalyzed allylic substitution of sulfur compounds,[6–8] the nature of bases has a dramatic influence on efficiency, regio-, and enantioselectivity. Thus, a range of bases including DABCO,[9] Cs_2CO_3, and KOAc was probed. Use of DABCO gave the poor regioselectivities (Table 1, entry 3). When Cs_2CO_3 was used, it led to the slight improvement of the yield and regioselectivity; the formation of **6a** was observed as well (Table 1, entry 4). Interestingly, employing KOAc gave rise to the branched product **4a** in the highest yield (83%) with both excellent regio- and enantioselectivity (96/4 and 96% ee, Table 1, entry 5). Probably, KOAc may prevent the coordination of **3a** to Ir-complex in the course of the reaction.[10] Variation of **2a**/**3a** ratio and change of the reaction temperature both have a drastic effect on the results of this reaction (Table 1, entries 5–8). Solvent screen revealed that DCM is the optimum solvent for this allylation, whereas other solvents (e.g., THF, toluene, and CH_3CN) gave poor outcomes (Table 1, entries 5, 9–11). In order to evaluate how the structural variation of ligands influences efficiency, regio-, and enantioselectivity, a range of phosphoramidite ligands including **L1**,[11] **L2**,[12] **L3**,[13] **L4**,[11] **L5**,[14] and **L6**[15] was screened (Fig. 2). The reaction with ligand **L2** led to the branched product **4a** in the poor yield and

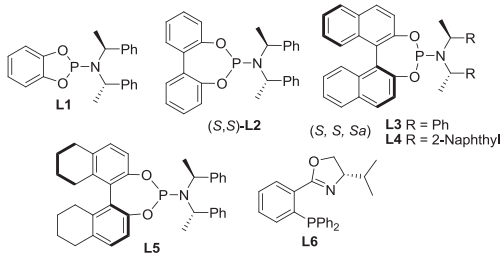


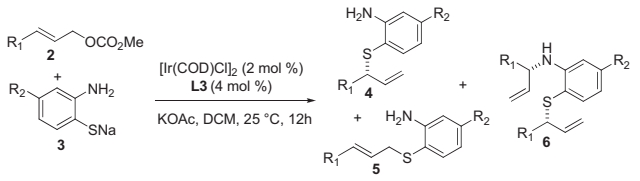
Fig. 2. Chiral ligands **L1**–**L6** evaluated for the titled allylic substitution.

ligand **L1**, **L5**, and **L6** are ineffective for this reaction (Table 1, entries 12, 15, and 16).

Having established the optimized reaction conditions, the generality and scope of the enantioselective iridium-catalyzed allylation of sodium 2-aminobenzenethiolate with a range of methyl allylic carbonates were further examined. All aromatic methyl allylic substrates **2a**–**2f** with either electron-donating group (e.g., 3-CH_3O, 4-CH_3O, and 4-CH_3) or electron-withdrawing group (e.g., 4-Cl, 4-Br, and 3-CF_3) on the phenyl ring gave the branch-type products **4a**–**4g** in good to high isolated yields (58–84%) with both excellent regioselectivities (90/10–94/6) and enantioselectivities (93–97% ee, Table 2, entries 1–7). The detrimental *ortho* substituent effect of sodium 2-aminobenzenethiolate on the regioselectivity is in agreement with results obtained by the transition metal-catalyzed allylic substitution reaction.[16] To our surprise, 8% yield of the diallylation product **6b** was also obtained when methyl allylic carbonate **2b**, with a *meta*-methoxyl group on the phenyl ring, was used as a substrate (Table 2, entry 2). It should be noted that the aliphatic allylic substrates **2h**–**2k** resulted in the allylation product **4h**–**4k** and **4n** in moderate to good yields (54–76%) with excellent regioselectivities (90/10–98/2) and enantioselectivities (81–96% ee), except for **2h**–**2k**, which led to **4h**–**4k** and **4n** along with a trace amount of the inseparable **5h**–**5k**, and **5n**, respectively (Table 2, entries 8–11). The different nucleophile, such as sodium 2-amino-4-chlorobenzenethiolate **3b** was employed to react with allylic carbonates **2a**, **2f**, and **2i**, respectively (Table 2, entries 12–14); they gave the corresponding **4l**, **4m**, and **4n** in good yields (52–58%) and good to high regioselectivities (85/15–90/10) with the high level of regioselectivities (89–94% ee).

The X-ray crystal structure analysis of **4f** (Fig. 3, see the Supplementary data for details) generated from **2f** in the enantiopure form revealed its absolute configuration as *R*.

Table 2
Ir-catalyzed enantioselective allylic alkylation of sodium 2-aminobenzenethiolate with a range of methyl allylic carbonates[a]



Entry	R_1	R_2	Yield[b] of **4** [%]	**4**/**5**/**6**[c]	ee[d] [%]
1	Ph	H	**4a**, 83	96/4/trace	96
2	3-MeOC_6H_4	H	**4b**, 74	84/8/8	96
3	4-MeOC_6H_4	H	**4c**, 70	90/10/trace	96
4	4-MeC_6H_4	H	**4d**, 67	93/7/trace	96
5	4-ClC_6H_4	H	**4e**, 58	94/6/trace	97
6	4-BrC_6H_4	H	**4f**, 67	94/6/trace	93
7	3-$CF_3C_6H_4$	H	**4g**, 75	94/6/trace	97
8	$BnCH_2$	H	**4h**, 84[f]	90/10/trace[e]	94
9	*n*-Pr	H	**4i**, 75[f]	96/4/trace[e]	94
10	Et	H	**4j**, 76[f]	97/3trace[e]	81
11	Me	H	**4k**, 54	98/2/trace[e]	94
12	Ph	Cl	**4l**, 58	86/14/trace	94
13	4-BrC_6H_4	Cl	**4m**, 52	85/15/trace	93
14	*n*-Pr	Cl	**4n**, 56[f]	90/10/trace	89

[a] Reaction conditions: 2 mol % of $[Ir(COD)Cl]_2$, 4 mol % of **L3**, and 5.0 equiv of KOAc.
[b] Isolated yields.
[c] Determined by ^1H NMR of the crude reaction mixture.
[d] Determined by chiral HPLC analysis.
[e] Determined by GC–MS.
[f] The yield of **4**+**5**.

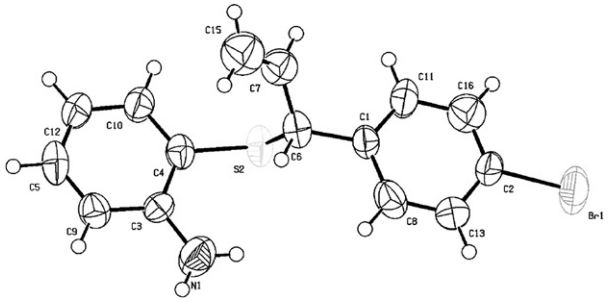
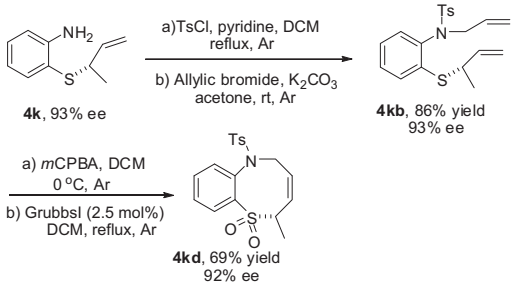


Fig. 3. X-ray structure of (*R*)-**4f**.

As an exemplification of the employment of this methodology, an enantioenriched eight-membered benzo-fused *N*,*S*-heterocycle was prepared by the following synthetic sequence (Scheme 1). The enantioenriched **4kb**, which was produced by the protection of the branched product **4k** and the alkylation with allylic bromide, was oxidized with *m*CPBA, followed via the ring-closing metathesis (RCM) in the presence of Grubbs' first-generation catalyst (2.5 mol %) to furnish the enantioenriched benzo-fused *N*,*S*-heterocycle **4kd**[17] in 62% yield of two steps with 92% ee.



Scheme 1. Synthesis of the enantioenriched benzo-fused *N*,*S*-heterocycle **4kd** from the enantioenriched allyl product **4k**.

3. Conclusions

We have developed a highly efficient iridium-catalyzed allylation of sodium 2-aminobenzenethiolate with a range of methyl allylic carbonates, which provided *N*,*S*-containing branch-type allylic products with both excellent regio- and enantioselectivities. Using this method, an enantioenriched benzo-fused *N*,*S*-heterocycle was synthesized in high yield with excellent ee value.

4. Experimental section

4.1. General procedure for the synthesis of sodium 2-aminobenzenethiolate 3a

NaH (9.6 mmol, 1.2 equiv, 80% in liquid paraffin) was added in THF (15 mL) at 0 °C, into which 2-aminothiophenol (8.0 mmol, 1.0 equiv) was added dropwise. This reaction was performed about 2 h at 0 °C, and then the solvent was evaporated. The residual was washed with petroleum ether and ether, respectively. Sodium 2-aminobenzenethiolate **3a** was obtained as pale gray powder. Sodiun 2-amino-4-chlorobenenethiolate **3b** was prepared according to this method.

4.2. General procedure for iridium-catalyzed allylation of sodium 2-aminobenzenethiolate

$[Ir(COD)Cl]_2$ (0.0040 mmol, 2.0 mol %), phosphoramidite ligand **L3** [*O*,*O*′-(*S*)-(1,1′-dinaphthyl-2,2′-diyl)-*N*,*N*′-di-(*S*,*S*)[phenylethylphospho-ramidite] (0.0080 mmol, 4.0 mol %) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate 2 (0.50 mmol, 2.5 equiv), sodium 2-aminobenzenethiolate 3 (0.20 mmol), potassium acetate (1.0 mmol, 5.0 equiv), and dichloromethylene (2.0 mL) were added. The reaction mixture was stirred at room temperature overnight. The crude residue was purified by flash column chromatography to give the desired products **4**.

*4.2.1. (R)-2-(1-Phenylallylthio)aniline (**4a**).* Yield 83% (38.9 mg); a white solid; mp 68–70 °C; $[\alpha]_D^{20}$ −24.8 (*c* 1.0, $CHCl_3$). The enantiomeric excess of the product is determined by HPLC analysis (214 nm, 25 °C) t_R=7.16 min (minor); 7.82 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 96%; ^1H NMR (400 MHz, $CDCl_3$) 7.35–7.26 (m, 4H, Ar), 7.24–7.21 (m, 2H, Ar), 7.10 (dd, *J*=8.0, 7.2 Hz, 1H, Ar), 6.70 (d, *J*=8.0 Hz, 1H, Ar), 6.61 (dd, *J*=7.6, 7.2 Hz, 1H, Ar), 6.13 (ddd, *J*=16.8, 9.6, 8.8 Hz, 1H, =CH), 5.00 (d, *J*=10.0 Hz, 1H, =CH), 4.90 (d, *J*=16.8 Hz, 1H, =CH), 4.62 (d, *J*=8.4 Hz, 1H, CH), 4.55–4.16 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 140.4, 137.6, 137.3, 130.4, 128.5, 127.7, 127.3, 118.2, 116.9, 116.2, 114.8, 55.9 ppm; IR (KBr, cm^{-1}) 3461, 3359, 3061, 3018, 1747, 1604, 1479, 1449, 1412, 1311, 1265, 1159, 981, 922, 741, 716; HRMS (EI) calcd for $C_{15}H_{15}NS$ 241.0925; found 241.0930.

*4.2.2. (R)-2-(1-(3-Methoxyphenyl)allylthio)aniline (**4b**).* Yield 74% (38.8 mg); a pale yellow thick oil; $[\alpha]_D^{20}$ −29.2 (*c* 0.8, $CHCl_3$); The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=9.89 min (minor); 12.46 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 96%; ^1H NMR (400 MHz, $CDCl_3$) 7.26–7.19 (m, 2H), 7.10 (ddd, *J*=8.0, 6.4, 1.6 Hz, 1H, Ar), 6.91 (d, *J*=7.6 Hz, 1H, Ar), 6.85–6.82 (m, 1H, Ar), 6.78 (dd, *J*=8.4, 2.0 Hz, 1H, Ar), 6.70 (dd, *J*=8.0, 0.8 Hz, 1H, Ar), 6.62 (ddd, *J*=7.2, 6.4, 1.2 Hz, 1H, Ar), 6.12 (ddd, *J*=16.8, 10.0, 8.4 Hz, 1H, =CH), 5.01 (d, *J*=10.0 Hz, 1H, =CH), 4.91 (d, *J*=16.8 Hz, 1H, =CH), 4.58 (d, *J*=8.4 Hz, 1H, CH), 4.55–4.05 (m, 2H,

NH_2), 3.76 (s, 3H, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) 159.6, 149.0, 141.9, 137.6, 137.2, 130.4, 129.5, 120.0, 118.2, 116.8, 116.1, 114.8, 113.3, 112.9, 55.9, 55.2 ppm; IR (KBr, cm^{-1}) 3456, 3362, 3061, 3004, 2924, 2833, 2360, 1605, 1584, 1477, 1435, 1309, 1263, 1156, 1046, 920, 750, 694; HRMS (EI) calcd for $C_{16}H_{17}NOS$ 271.1031; found 271.1032.

*4.2.3. (R)-2-(1-(4-Methoxyphenyl)allylthio)aniline (**4c**).* Yield 70% (37.4 mg); a white solid; mp 86–87 °C; $[\alpha]_D^{20}$ −39.2 (*c* 0.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=9.71 min (minor); 11.59 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 98%; ^1H NMR (400 MHz, $CDCl_3$) 7.25–7.20 (m, 3H, Ar), 7.10 (ddd, *J*=7.6, 6.4, 1.2 Hz, 1H, Ar), 6.86–6.82 (m, 2H, Ar), 6.70 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.62 (ddd, *J*=7.6, 6.4, 1.2 Hz, 1H, Ar), 6.11 (ddd, *J*=16.8,10.0, 8.4 Hz, 1H, =CH), 4.99 (d, *J*=10.0 Hz, 1H, =CH), 4.88 (d, *J*=16.8 Hz, 1H, =CH), 4.60 (d, *J*=8.4 Hz, 1H, CH), 4.39–4.27 (m, 2H, NH_2), 3.79 (s, 3H, OMe) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 158.8, 149.0, 137.6, 137.5, 132.4, 130.3, 128.8, 118.2, 117.1, 115.8, 114.8, 113.9, 55.34, 55.26 ppm; IR (KBr, cm^{-1}) 3467, 3365, 3083, 2987, 2954, 2913, 2833, 1600, 1510, 1477, 1447, 1303, 1241, 1178, 1035, 908, 834, 748; HRMS (EI) calcd for $C_{16}H_{17}NOS$ 271.1031; found 271.1033.

*4.2.4. (R)-2-(1-p-Tolylallylthio)aniline (**4d**).* Yield 67% (28.3 mg); a white solid; mp 81–83 °C; $[\alpha]_D^{20}$ −27.0 (*c* 0.9, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=10.20 min (minor); 12.94 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 96%; ^1H NMR (400 MHz, $CDCl_3$) 7.26–7.19 (m, 3H, Ar), 7.14–7.07 (m, 3H, Ar), 6.70 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.62 (ddd, *J*=7.6, 7.2, 1.2 Hz, 1H, Ar), 6.11 (ddd, *J*=16.8, 10.0, 8.4 Hz, 1H, =CH), 4.97 (d, *J*=10.0 Hz, 1H, =CH), 4.86 (d, *J*=16.8 Hz, 1H, =CH), 4.58 (d, *J*=8.4 Hz, 1H, CH), 4.43–4.24 (m, 2H, NH_2), 2.32 (s, 3H, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 137.6, 137.5, 137.3, 137.0, 130.2, 129.2, 127.6, 118.2, 117.1, 115.8, 114.8, 55.9, 21.1 ppm; IR (KBr, cm^{-1}) 3457, 3357, 2917, 2358, 1602, 1509, 1478, 1447, 1310, 1255, 1019, 923, 822, 740; HRMS (EI) calcd for $C_{16}H_{17}NS$ 255.1082; found 255.1083.

*4.2.5. (R)-2-(1-(4-Chlorophenyl)allylthio)aniline (**4e**).* Yield 58% (27.2 mg); a pale gray solid; mp 80–82 °C; $[\alpha]_D^{20}$ −83.7 (*c* 0.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=7.39 min (minor); 7.90 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 97%; ^1H NMR (400 MHz, $CDCl_3$) 7.27–7.20 (m, 4H, Ar), 7.17 (dd, *J*=7.6, 1.2 Hz, 1H, Ar), 7.11 (dd, *J*=8.0, 7.6 Hz, 1H, Ar), 6.70 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.61 (ddd, *J*=7.6, 7.6, 1.2 Hz, 1H, Ar), 6.09 (ddd, *J*=17.2, 10.0, 8.8 Hz, 1H, =CH), 5.05 (d, *J*=10.0 Hz, 1H, =CH), 4.95 (d, *J*=16.8 Hz, 1H, =CH), 4.60 (d, *J*=8.4 Hz, 1H, CH), 4.33 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 139.0, 137.6, 136.82, 133.0, 130.5, 129.1, 128.6, 118.3, 116.6, 116.4, 114.9, 55.0 ppm; IR (KBr, cm^{-1}) 3661, 3469, 3365, 2922, 2851, 1600, 1477, 1447, 1400, 1306, 1254, 1159, 1091, 922, 827, 750, 515; HRMS (EI): calcd for $C_{15}H_{14}ClNS$ 275.0535; found 275.0532.

*4.2.6. (R)-2-(1-(4-Bromophenyl)allylthio)aniline (**4f**).* Yield 67% (44.3 mg); a white solid; mp 93–95 °C; $[\alpha]_D^{20}$ −40.0 (*c* 0.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=8.96 min (minor); 9.85 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 93%; ^1H NMR (400 MHz, $CDCl_3$) 7.41 (d, *J*=8.4 Hz, 2H, Ar), 7.19–7.14 (m, 3H, Ar), 7.12 (ddd, *J*=8.0, 7.6, 1.2 Hz, 1H, Ar), 6.71 (d, *J*=8.0 Hz, 1H, Ar), 6.61 (ddd, *J*=7.6, 7.6, 0.8 Hz, 1H, Ar), 6.08 (ddd, *J*=16.8, 10.0, 8.4 Hz, 1H, =CH), 5.05 (d, *J*=10.0 Hz, 1H, =CH), 4.94 (d, *J*=16.8 Hz, 1H, =CH), 4.59 (d, *J*=8.4 Hz, 1H, CH), 4.55–3.83 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 139.5, 137.6, 137.7, 131.6, 130.5, 129.5, 121.1, 118.4, 116.7, 116.4, 114.9, 55.0 ppm; IR (KBr, cm^{-1}) 3470, 3366, 1599, 1477, 1448, 1384, 1303, 1162, 922, 826, 750, 509; HRMS (EI): calcd for $C_{15}H_{14}BrNS$ 319.0030; found 319.0028.

*4.2.7. (R)-2-(1-(3-(Trifluoromethyl)phenyl)allylthio)aniline (**4g**).* Yield 75% (50.8 mg); a colorless oil; $[\alpha]_D^{20}$ −130.9 (*c* 1.2, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=7.65 min (minor); 7.97 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 97%; ^1H NMR (400 MHz, $CDCl_3$) 7.49–7.45 (m, 3H, Ar), 7.41–7.37 (m, 1H, Ar), 7.15–7.08 (m, 2H, Ar), 6.70 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.59 (ddd, *J*=7.6, 6.4, 1.2 Hz, 1H), 6.13 (ddd, *J*=16.8, 10.0, 8.4 Hz, 1H, =CH), 5.10 (d, *J*=10.0 Hz, 1H, =CH), 5.01 (d, *J*=16.8 Hz, 1H, =CH), 4.69 (d, *J*=8.4 Hz, 1H, =CH), 4.32 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.1, 141.5, 137.6, 136.4, 131.2 (q, *J*=1.4 Hz), 130.7 (q, *J*=32.1 Hz), 130.68, 128.9, 124.6 (q, *J*=3.6 Hz), 124.1 (q, *J*=3.6 Hz), 124.0 (q, *J*=270.5 Hz), 118.3, 117.1, 116.0, 114.9, 55.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) −62.6 ppm; IR (KBr, cm^{-1}) 3458, 3357, 3059, 2916, 2846, 1602, 1475, 1446, 1330, 1249, 1163, 1122, 1072, 918, 804, 748, 702; HRMS (EI): calcd for $C_{16}H_{15}F_3NS$ $[M+H]^+$ 310.0877; found 310.0872.

*4.2.8. (S)-2-(5-Phenylpent-1-en-3-ylthio)aniline (**4h**).* Yield 84% (47.8 mg, **4h** together with a small amount of the linear product **5h**, which cannot be separated by flash column chromatography); a colorless oil; $[\alpha]_D^{20}$ −16.8 (*c* 0.9, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=6.88 min (minor); 8.96 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 93%; ^1H NMR (400 MHz, $CDCl_3$) 7.30–7.25 (m, 3H, Ar), 7.20–7.16 (m, 3H, Ar), 7.10 (dd, *J*=8.0, 6.4, 1.6 Hz, 1H, Ar), 6.70 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.64 (dd, *J*=8.4, 7.2 Hz, 1H, Ar), 5.70 (ddd, *J*=16.8, 9.6, 7.2 Hz, 1H, =CH), 4.93 (dd, *J*=10.0, 0.4 Hz, 1H, =CH), 4.77 (d, *J*=17.2 Hz, 1H, =CH), 4.36–4.24 (m, 2H, NH_2), 3.44 (dt, *J*=8.4, 6.0 Hz, 1H, CH), 2.80–2.68 (m, 2H, CH_2), 2.07–1.88 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 141.4, 138.4, 137.6, 130.0, 128.40, 128.37, 125.9, 118.2, 116.4, 116.0, 114.8, 51.4, 35.8, 33.3 ppm; IR (KBr, cm^{-1}) 3467, 3368, 3062, 3026, 2926, 2855, 1747, 1605, 1496, 1478, 1440, 1384, 1266, 971, 942, 792, 748, 699; HRMS (EI) calcd for $C_{17}H_{19}NS$ 269.1238; found 269.1235.

*4.2.9. (S)-2-(Hex-1-en-3-ylthio)aniline (**4i**).* Yield 75% (29.3 mg, **4i** containing a trace amount of the linear product **5i**, which cannot be separated by flash column chromatography), a colorless oil; $[\alpha]_D^{20}$ −28.6 (*c* 0.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=19.69 min (major); 27.74 min (minor) [Daicel CHIRALCEL OJ-H (0.46 cm×25 cm); hexane/2-propanol, 98/2, 1.0 mL/min] to be 94%; ^1H NMR (400 MHz, $CDCl_3$) 7.30 (dd, *J*=8.0, 1.6 Hz, 1H, Ar), 7.11 (ddd, *J*=7.2, 6.4, 1.6 Hz, 1H, Ar), 6.71 (dd, *J*=8.0, 1.2 Hz, 1H, Ar), 6.66 (ddd, *J*=7.2, 6.0, 1.2 Hz, 1H, Ar), 5.64 (ddd, *J*=16.8, 9.6, 7.2 Hz, 1H, =CH), 4.87 (dd, *J*=10.0, 1.2 Hz, 1H, =CH), 4.72 (ddd, *J*=16.8, 1.6, 1.2 Hz, 1H, =CH), 4.41–4.28 (m, 2H, NH_2), 3.43 (dt, *J*=8.8, 5.6 Hz, 1H, CH), 1.68–1.56 (m, 2H, CH_2), 1.49–1.38 (m, 2H, CH_2), 0.91 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 138.8, 137.6, 130.0, 118.1, 116.8, 115.4, 114.7, 52.0, 36.4, 20.5, 13.8 ppm. IR (KBr, cm^{-1}) 3462, 3364, 3065, 2957, 2929, 2871, 2360, 2342, 1605, 1559, 1477, 1384, 1157, 913, 747; HRMS (EI): calcd for $C_{12}H_{17}NS$ 207.1082; found 207.1080.

*4.2.10. (S)-2-(Pent-1-en-3-ylthio)aniline(**4j**).* Yield 76% (32.8 mg, **4j** along with a trace amount of the linear product **5j**, which cannot be separated by flash column chromatography); a colorless oil; $[\alpha]_D^{20}$ −27.7 (*c* 0.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=11.12 min (minor); 12.51 min (major) [Daicel CHIRALCEL OD-H (0.46 cm×25 cm); hexane/2-propanol, 98/2, 0.7 mL/min] to be 81%; ^1H NMR (400 MHz, $CDCl_3$) 7.31 (d, *J*=7.6 Hz, 1H, Ar), 7.11 (ddd, *J*=8.0, 6.8,

1.2 Hz, 1H, Ar), 6.72 (d, *J*=8.0 Hz, 1H, Ar), 6.66 (dd, *J*=7.6, 7.2 Hz, 1H, Ar), 5.65 (ddd, *J*=16.8, 9.6, 7.2 Hz, 1H, =CH), 4.91 (d, *J*=10.0 Hz, 1H, =CH), 4.77 (d, *J*=16.8 Hz, 1H, =CH), 4.44–4.28 (m, 2H, NH_2), 3.39–3.29 (m, 1H, CH), 1.78–1.58 (m, 2H, CH_2), 0.99 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 138.5, 137.6, 130.0, 118.2, 116.8, 115.7, 114.7, 53.9, 27.5, 11.8 ppm; IR (KBr, cm^{-1}) 3650, 2962, 2361, 2344, 1541, 1508, 1384, 1260, 1093, 1021, 800, 746; HRMS (ESI) calcd for $C_{11}H_{16}NS[M+H]^+$ 194.1003; found 194.1001.

*4.2.11. (S)-2-(But-3-en-2-ylthio)aniline (**4k**).* Yield 54% (20.8 mg); a colorless oil; $[\alpha]_D^{20}$ −33.8 (*c* 0.4, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=11.83 min (minor); 12.44 min (major) [Daicel CHIRALCEL OJ-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 94%; ^1H NMR (400 MHz, $CDCl_3$) 7.33 (d, *J*=7.6 Hz, 1H, Ar), 7.12 (dd, *J*=7.6, 7.2 Hz, 1H, Ar), 6.72 (d, *J*=8.0 Hz, 1H, Ar), 6.67 (dd, *J*=7.6, 7.2 Hz, 1H, Ar), 5.79 (ddd, *J*=16.8, 9.6, 9.2 Hz, 1H, =CH), 4.90 (d, *J*=10.0 Hz, 1H, =CH), 4.84 (d, *J*=17.2 Hz, 1H, =CH), 4.48–4.24 (m, 2H, NH_2), 3.61 (dd, *J*=7.2, 6.8 Hz, 1H, CH), 1.35 (d, *J*=6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 139.8, 137.6, 130.1, 118.2, 116.8, 114.8, 114.5, 46.2, 20.1 ppm; IR (KBr, cm^{-1}) 3459, 3362, 3063, 2963, 2933, 1605, 1477, 1446, 1384, 1306, 1023, 916, 748, 711; HRMS (EI) calcd for $C_{10}H_{13}NS$ 179.0769; found 179.0771.

*4.2.12. (R)-5-Chloro-2-(1-phenylallylthio)aniline (**4l**).* Yield 58% (37.6 mg); a white solid; mp 66–67 °C; $[\alpha]_D^{20}$ −131.9 (*c* 1.8, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=8.42 min (major); 9.07 min (minor) [Daicel CHIRALCEL OD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 94%; ^1H NMR (400 MHz, $CDCl_3$) 7.30–7.27 (m, 4H, Ar), 7.26–7.21 (m, 1H, Ar), 7.10 (d, *J*=8.4 Hz, 1H, Ar), 6.68 (d, *J*=2.4 Hz, 1H, Ar), 6.57 (dd, *J*=8.0, 2.0 Hz, 1H, Ar), 6.10(ddd, *J*=17.2, 10.0, 8.4 Hz, 1H, =CH), 5.02 (d, *J*=10.0 Hz, 1H, =CH), 4.92 (d, *J*=16.8 Hz, 1H, =CH), 4.56 (d, *J*=8.8 Hz, 1H, CH), 4.39 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.9, 140.0, 138.6, 136.9, 136.0, 128.6, 127.7, 127.4, 118.2, 116.5, 115.1, 114.3, 56.1 ppm; IR (KBr, cm^{-1}) 3460, 3357, 2912, 1593, 1548, 1471, 1411, 1253, 1068, 908, 844, 781, 723, 696; HRMS (ESI): calcd for $C_{15}H_{15}ClNS$ $[M+H]^+$ 276.0614; found 276.0682.

*4.2.13. (R)-2-(1-(4-Bromophenyl)allylthio)-5-chloroaniline (**4m**).* Yield 52% (38.8 mg); a white solid; mp 91–92 °C; $[\alpha]_D^{20}$ −141.8 (*c* 1.5, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=10.40 min (minor); 10.76 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 0.7 mL/min] to be 93%; ^1H NMR (400 MHz, $CDCl_3$) 7.43–7.40 (m, 2H, Ar), 7.16–7.12 (m, 2H, Ar), 7.06 (d, *J*=8.4 Hz, 1H, Ar), 6.69 (d, *J*=2.0 Hz, 1H, Ar), 6.57 (dd, *J*=8.0, 2.0 Hz, 1H, Ar), 6.05(ddd, *J*=17.2, 10.0, 8.0 Hz, 1H, =CH), 5.06 (d, *J*=10.0 Hz, 1H, =CH), 4.95 (d, *J*=16.8 Hz, 1H, =CH), 4.53 (d, *J*=8.4 Hz, 1H, CH), 4.39 (m, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.9, 139.2, 138.6, 136.4, 136.2, 131.6, 129.4, 121.3, 118.3, 117.0, 114.6, 114.4, 55.2 ppm; IR (KBr, cm^{-1}) 3471, 3363, 2958, 2918, 2848, 1597, 1548, 1467, 1413, 1398, 1253, 1089, 1070, 1008, 921, 825, 788, 750; HRMS (EI): calcd for $C_{15}H_{13}BrClNS$ 352.9641; found 352.9641.

*4.2.14. (S)-5-Chloro-2-(hex-1-en-3-ylthio)aniline (**4n**).* Yield 56% (29.5 mg, **4 n** containing a trace amount of the linear product **5n**, which cannot be separated by flash column chromatography); a colorless oil; $[\alpha]_D^{20}$ −18.1 (c 1.3, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=7.27 min (major); 7.67 min (minor) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 98/2, 1.0 mL/min] to be 89%; ^1H NMR (400 MHz, $CDCl_3$) 7.20 (d, *J*=8.0 Hz, 1H, Ar), 6.80 (d, *J*=2.4 Hz, 1H, Ar), 6.62 (dd, *J*=8.0, 2.4 Hz, 1H, Ar), 5.60 (ddd, *J*=17.2, 9.6, 7.2 Hz, 1H, =CH), 4.88 (dd, *J*=10.0, 1.2 Hz, 1H, =CH), 4.71 (d, *J*=16.8 Hz, 1H, =CH), 4.42 (m, 2H, NH_2), 3.37 (dt, *J*=8.8, 6.0 Hz, 1H, CH), 1.70–1.52 (m, 2H, CH_2), 1.48–1.37 (m, 2H, CH_2), 0.91 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 149.9, 138.7, 138.4, 135.6, 118.1, 115.7, 115.2, 114.2, 52.3, 36.3, 20.5, 13.7 ppm; IR (KBr, cm^{-1}) 3462, 3381, 2954, 2922, 2862, 1597, 1471, 1411, 1245, 1085, 902, 840, 792; HRMS (ESI): calcd for $C_{12}H_{17}ClNS$ $[M+H]^+$ 242.0770; found 242.0772.

*4.2.15. N-((S)-1-Phenylallyl)-2-((R)-1-phenylallylthio)aniline (**6a**).* A colorless oil; ^1H NMR (400 MHz, $CDCl_3$) 7.38–7.22 (m, 11H, Ar), 7.09 (dd, *J*=8.0, 8.0 Hz, 1H, Ar), 6.55 (dd, *J*=8.0, 8.0 Hz, 1H, Ar), 6.50 (d, *J*=8.0 Hz, 1H, Ar), 6.21–5.97 (m, 2H, =CH), 5.65–5.56 (m, 1H, CH), 5.29–5.16 (m, 2H, =CH, NH), 5.00 (d, *J*=8.0 Hz, 1H, =CH), 4.95–4.90 (m, 1H, CH), 4.87 (d, *J*=16.0 Hz, 1H, =CH), 4.59 (d, *J*=8.0 Hz, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 148.6, 141.6, 140.3, 139.0, 137.6, 137.2, 130.5, 128.7, 128.5, 127.7, 127.44, 127.36, 127.0, 116.8, 116.2, 115.8, 111.4, 60.6, 56.5 ppm. HRMS (ESI) calcd for $C_{24}H_{24}NS$ $[M+H]^+$ 358.1629; found 358.1630.

4.3. General procedure for the synthesis of compound (4kd)[2a–d]

(*S*)-2-(But-3-en-2-ylthio)aniline **4k** (34.5 mg, 0.2 mmol) was added to a solution of CH_2Cl_2 (6.0 mL) containing pyridine (0.2 mL), and then toluenesulfonyl chloride (88.9 mg, 0.47 mmol) was added at room temperature. The reaction mixture was then heated at reflux for 12 h. The solvent was evaporated and the residue was purified by column chromatography (PE/EA=15/1) to afford **4ka** as a colorless thick oil (60.6 mg, 94% yield). Allyl bromide (162.0 mg, 1.3 mmol) and K_2CO_3 (151.0 mg, 1.1 mmol) were added to a solution of (*S*)-*N*-(2-(but-3-en-2-ylthio)phenyl)-4-methyl-benzenesulfonamide **4ka** (60.0 mg, 0.18 mmol) in acetone (5 mL), and the reaction mixture was then stirred at room temperature for 24 h. The base was removed by filtration and the solvent was removed under reduced pressure, then the residue was purified by column chromatography (PE/EA=10/1) to produce **4kb** as a colorless thick oil (60.9 mg, 91% yield). The compound **4kb** was oxidized by *m*CPBA (2.5 equiv) at room temperature under argon in dry DCM. After completion, the reaction mixture was then poured into a saturated solution of Na_2CO_3 (15 mL) and extracted with additional DCM (15 mL). The organic extracts were washed with brine (15 mL), dried over Na_2SO_4, filtered, and evaporated to give a thick yellow oil (**4kc**). After simple workout, dissolving the Grubbs' first generation catalyst (G1) (2.3 mg, 0.0028 mmol, 3.3 mol %) in dry DCM (2 mL) under argon, and a solution of sulfane **4kc** in dry DCM (3 mL) was added in. The reaction mixture was heated at reflux under argon for 12 h. The reaction mixture was evaporated and the residue was purified by column chromatography (PE/EA=1/1) to afford **4kd** as a white solid (29.4 mg, two steps 69% yields).

*4.3.1. (S)-N-(2-(But-3-en-2-ylthio)phenyl)-4 methylbenzenesulfonamide (**4ka**).* Yield 94% (60.0 mg); a colorless thick oil; $[\alpha]_D^{20}$ −124.5 (*c* 0.4, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=36.32 min (minor); 38.43 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 98/2, 0.7 mL/min] to be 98%; ^1H NMR (400 MHz, $CDCl_3$) 8.01–7.93 (m, 1H, Ar), 7.70 (d, *J*=8.4 Hz, 2H, Ar), 7.64 (dd, *J*=8.4, 1.2 Hz, 1H, Ar), 7.35 (dd, *J*=8.0, 1.6 Hz, 1H, Ar), 7.29–7.25 (m, 1H, Ar), 7.22 (d, *J*=8.0 Hz, 2H, Ar), 6.98(ddd, *J*=7.6, 7.6, 1.2 Hz, 1H, Ar), 5.61 (ddd, *J*=17.2, 10.0, 8.8 Hz, 1H, =CH), 4.79 (d, *J*=10.0 Hz, 1H, =CH), 4.59 (d, *J*=17.2 Hz, 1H, =CH), 3.28–3.17 (m, 1H, NH), 2.36 (s, 3H, CH_3), 1.28 (d, *J*=6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 144.0, 139.5, 138.6, 137.3, 136.3, 130.2, 129.6, 127.2, 124.1, 122.7, 118.8, 115.6, 48.4, 21.5, 19.9 ppm; IR (KBr, cm^{-1}) 3258, 2966, 2923, 1589, 1476, 1448, 1386,

1336, 1273, 1164, 1091, 916, 813, 756, 706, 664, 564; HRMS (ESI) calcd for $C_{17}H_{19}NO_2S_2Na$ $[M+Na]^+$ 356.0755; found 356.0749.

*4.3.2. (S)-N-Allyl-N-(2-(but-3-en-2-ylthio)phenyl)-4-methylbenzenesulfon-amide (**4kb**).* Yield 91% (60.9 mg); a colorless thick oil; $[\alpha]_D^{20}$ −84.9 (*c* 0.6, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=10.48 min (minor); 11.20 min (major) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 93%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.67 (d, *J*=8.0 Hz, 2H, Ar), 7.34 (d, *J*=8.0 Hz, 1H, Ar), 7.27 (d, *J*=8.0 Hz, 2H, Ar), 7.25–7.20 (m, 1H, Ar), 7.05 (dd, *J*=8.0, 7.2 Hz, 1H, Ar), 6.92–6.80 (m, 1H, Ar), 5.92–5.64 (m, 2H, =CH), 5.24–4.87 (m, 4H, =CH), 4.24–4.08 (m, 2H, CH_2), 3.93–3.83 (m, 1H, CH), 2.43 (s, 3H, CH_3), 1.45–1.36 (m, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 143.3, 136.8, 132.8, 130.4, 130.2, 129.3, 128.4, 128.1, 128.0, 125.6, 125.4, 118.9, 115.5, 114.7, 54.0, 44.3, 21.5, 20.0 ppm; IR (KBr, cm^{-1}) 3080, 2970, 2923, 1597, 1467, 1384, 1304, 1219, 1163, 1091, 1057, 991, 923, 864, 815, 726, 662, 577, 548; HRMS (ESI) calcd for $C_{20}H_{23}NO_2S_2Na$ $[M+Na]^+$ 396.1068; found 396.1062.

*4.3.3. 5,6-Dihydro-2H-1,6-benzothiazocine-1,1-dioxide (**4kd**).* Yield 93% (29.4 mg); a white solid; mp 169–171 °C; $[\alpha]_D^{20}$ −65.8 (*c* 0.7, $CHCl_3$). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 °C) t_R=42.46 min (major); 45.19 min (minor) [Daicel CHIRALPAK AD-H (0.46 cm×25 cm); hexane/2-propanol, 90/10, 1.0 mL/min] to be 93%; ^{1}H NMR (400 MHz, $CDCl_3$) 8.14–8.08 (m, 1H, Ar), 7.89 (d, *J*=8.4 Hz, 2H, Ar), 7.60–7.53 (m, 2H, Ar), 7.40 (d, *J*=8.0 Hz, 2H, Ar), 7.14–7.08 (m, 1H, Ar), 5.55–5.42 (m, 2H, =CH), 4.83 (dq, *J*=15.6, 6.8 Hz, 1H, CH), 4.62 (d, *J*=15.6 Hz, 1H, CH), 3.68 (dd, *J*=15.6, 5.6 Hz, 1H, CH), 2.49 (s, 3H, CH_3), 1.59 (d, *J*=6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 144.9, 140.3, 135.2, 134.8, 134.0, 130.7, 130.1, 130.0, 129.7, 128.7, 128.2, 128.0, 59.5, 50.1, 21.6, 11.7 ppm; IR (KBr, cm^{-1}) 3064, 2923, 1596, 1477, 1444, 1353, 1306, 1219, 1164, 1142, 1091, 1062, 1010, 963, 872, 818, 802, 769, 730, 713, 679, 660, 637, 548; HRMS (ESI) calcd for $C_{18}H_{19}NO_4S_2Na$ $[M+Na]^+$ 400.0653; found 400.0648.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.09.010.

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