CO_2-induced amidobromination of olefins with bromamine-T†

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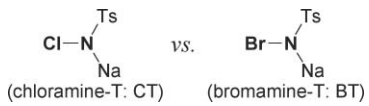
The carbon dioxide (CO_2)-induced amidobromination of olefins with bromamine-T is described. The method can be used in reactions with a wide range of olefins, both aromatic and aliphatic, as well as electron-rich and deficient olefins, leading to the regioselective formation of amidobrominated compounds.

Introduction

Vicinal haloamine derivatives are valuable synthetic intermediates for use in constructing a variety of functional materials and biologically active compounds.[1] The direct functionalization of carbon–carbon double bonds with amine and halogen groups is a significant approach to useful building blocks for organic synthesis.[2] Among the halogens, the bromine atom is a versatile substituent that can be used in organic transformations. In this context, since the amidobromination of olefins constitutes a significant and potentially useful transformation, many systems employing brominated amide derivatives,[3] combinations of amides (sulfonamides or carboxamides) and *N*-bromosuccinimides (NBS)[4] or *N*-bromo-*N*-sodio-*p*-toluenesulfonamide (bromamine-T)[5] have been developed.

In our continuing efforts to develop new methods for the synthesis of N-heterocycles, we previously reported on the utility of nitrogen–halogen bonds bearing electron-withdrawing groups on the nitrogen.[6] As a representative reagent containing a N–Cl bond, *N*-chloro-*N*-sodio-*p*-toluenesulfonamide (chloramine-T: CT) was utilized in various transformations, and a unique CO_2-induced vicinal amidochlorination was reported.[7] This amidochlorination could lead to the development of a metal-free process for this type of synthesis. However, the functionalization of olefins using CT was restricted to relatively electron-rich olefins.

From these points of view, we report herein on the use of bromamine-T (BT) in the CO_2-induced amidobromination of olefins. BT showed a different regioselectivity in amidohalogenation reactions, compared with that of CT, and could function successfully in the amidobromination of not only aromatic and aliphatic olefins, but also electron-rich and deficient olefins (Scheme 1). Although BT is not commercially available, it can be readily prepared from chloramine-T, Br_2, and aqueous NaOH.[8]



(chloramine-T: CT) (bromamine-T: BT)

Scheme 1

Results and discussion

As described in our previous report,[7] the nitrogen–chlorine bond of CT regioselectively added to the carbon–carbon double bond of styrene under an atmosphere of carbon dioxide to give exclusively α-chlorinated compound **2a** (X = Cl) (Table 1, entries 1–3). When BT was employed in the reaction instead of CT, α-brominated compound **2a** (X = Br) was obtained selectively under an atmospheric pressure of CO_2 (entry 4). When the pressure of CO_2 was increased, the reverse regioselectivity was observed, giving β-brominated compound **1a** (X = Br) in good yields (entries 5–8). Although the reason for this phenomenon is unclear (*vide infra*), it is interesting to note that regioselectivity is dependent on the specific halogen species in the haloamine salt.

p-Substituted styrene derivatives were subjected to the amidobromination, in an attempt to determine the active species for the reaction. The reaction of *p*-nitrostyrene with BT under CO_2 afforded predominantly the α-brominated sulfonamide **2b**, but the regioselectivity was the reverse of that observed for styrene (Table 2, entry 1). Electron-donating groups at the *para*-position of styrene induced the selective formation of β-brominated compounds (**1c–e**) and the reaction was complete in less time (entries 2–4). These results suggest that the reaction proceeds through a cationic active species, such as a cyclic bromonium intermediate.

The amidobromination reaction was applied to disubstituted aromatic and aliphatic olefins, and an enol ether (Table 3). When *trans*-β-methylstyrene was treated with BT under 30 atm of CO_2, the α-brominated product **3** was stereo- and regioselectively obtained as the sole product in good yield. Although a β-brominated amide was mainly produced in the case of styrene, in the presence of a β-substituent attached in a *trans* orientation, the regioselectivity was reversed (entry 1). BT added to indene to give the β-brominated amide **4** with the same regioselectivity that was observed for styrene (entry 2). Terminal, internal and cyclic aliphatic olefins were also converted to amidobrominated compounds (entries 3–6). It is especially noteworthy that the stereospecific addition of BT to *trans*- and *cis*-3-hexene suggests that a cyclic cationic intermediate is likely involved in the reaction. An electron-rich olefin, butyl vinyl ether, was found to be a good substrate for the reaction, resulting in the formation of the expected terminal bromide **9** in good yield (entry 7).

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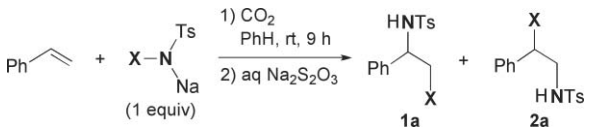
† Electronic supplementary information (ESI) available: NMR spectra and mass spectrometry results. See DOI: 10.1039/b923253m

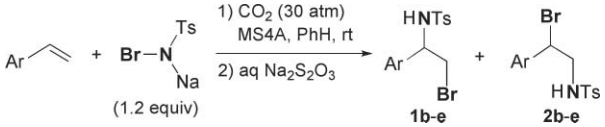
Table 1 Amidohalogenation of styrene under CO_2 (CT *vs.* BT)



Entry	X	CO_2 (atm)	Yield (%)	**1a** : **2a**
1	Cl	1	9	0 : 100
2[a]	Cl	10	80	0 : 100
3[a]	Cl	30	63	0 : 100
4	Br	1	46	15 : 85
5	Br	10	72	75 : 25
6	Br	30	73	97 : 3
7[b]	Br	30	81	95 : 5
8[c]	Br	30	80	97 : 3

[a] Reaction time: 6 h. [b] Reaction time: 24 h. [c] Addition of MS4A, reaction time: 3 h.

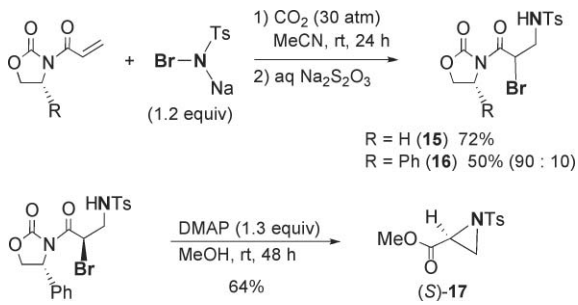
Table 2 Addition of BT to styrene derivatives under CO_2



Entry	Ar	Time/h	Yield (%)	**1** : **2**
1	4-$NO_2C_6H_4$	12	88 (**1b** + **2b**)	15 : 85
2	4-ClC_6H_4	4.5	88 (**1c** + **2c**)	84 : 16
3	4-MeC_6H_4	3	86 (**1d**)	100 : 0
4	4-$MeOC_6H_4$	1	90 (**1e**)	100 : 0

Although the reaction of CT with electron-deficient olefins in the presence of CO_2 did not proceed at all, BT was found to react with olefins (Table 4). All the reactions proceeded under an atmospheric pressure of CO_2. Even though the use of one equivalent of BT yielded the desired products, the use of two equivalents resulted in improved yields. In the case of the amidobromination of chalcone, the position β to carbonyl group was regioselectively brominated (entry 1). The amidobromination of electron-deficient olefins conjugated with aromatic rings has been extensively investigated,[2–5] but no examples of the amidohalogenation of terminal electron-deficient olefins have been reported.[9] Using the present method, the addition reaction proceeded, giving α-brominated compounds (entries 2–5). Among these, the amidobromination of an α,β-unsaturated amide proceeded with relatively good product yield (entry 5).

This result (Table 4, entry 5) prompted us to investigate diastereoselective amidobromination of an olefin bearing a chiral auxiliary (Evans' oxazolidinone) (Scheme 2). A 2-acryloyloxazolidinone without a stereocentre was first employed in the reaction. The desired amidobromination proceeded, even under an atmospheric pressure of CO_2, but the efficiency of the reaction was greatly improved when a CO_2 pressure of 30 atm was used. A phenyl-substituted chiral olefin also reacted, affording the α-bromo-β-amino product in good diastereoselectivity. The diastereomers were readily separated and the major isomer was treated with 4-di(methylamino)pyridine (DMAP) in MeOH,

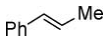
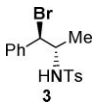
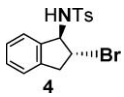
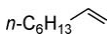
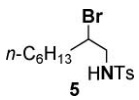
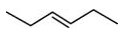
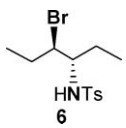
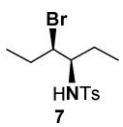
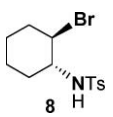
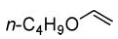
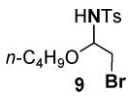


Scheme 2

leading to the formation of the enantiopure (*S*)-aziridine **17**. The purity of aziridine **17** was confirmed by chiral HPLC analysis[10] and *S* configuration was determined by optical rotation measurements, which were in agreement with previously reported data.[11] This chiral aziridine should be a good precursor of amino acid derivatives through a ring-opening reaction.[12] From the absolute configuration of aziridine **17**, the stereocenter, α to the carbonyl group, in the major diastereomer of **16** would be predicted to have an *R* configuration.

Since the present reaction proceeded under an atmosphere of CO_2, the reaction of BT with CO_2 was monitored by ^1H NMR (Fig. 1). Signals corresponding to the tosyl group were shifted downfield by the addition of CO_2, indicating that CO_2 is inserted into the to N–Na bond of BT.

Table 3 Addition of BT to olefins under CO_2[a]

Entry	Olefin	Adduct	Yield (%)
1[b]		 **3**	84
2[b]		 **4**	62
3		 **5**	45[c]
4[d]		 **6**	53
5		 **7**	60
6		 **8**	51
7[e]		 **9**	83

[a] Reaction conditions: olefin (0.5 mmol), BT (0.6 mmol), CO_2 (30 atm), MS4A (180 mg), PhH (1.5 mL), rt, 3 h. [b] 9 h, without MS4A. [c] Regioisomer ratio: 84 : 16 (major isomer is depicted). [d] 9 h. [e] Olefin (0.5 mmol), BT (0.3 mmol), THF (1.5 cm^3).

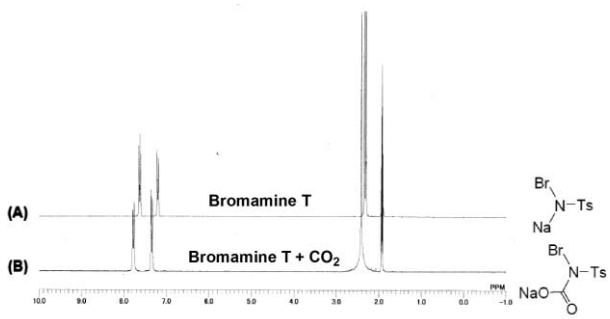
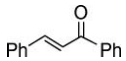
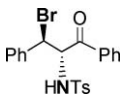
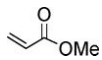
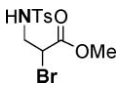
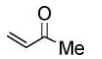
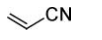
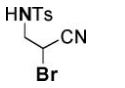
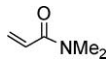


Fig. 1 ^{1}H NMR spectra of BT (**A**) and BT with CO_2 (**B**).

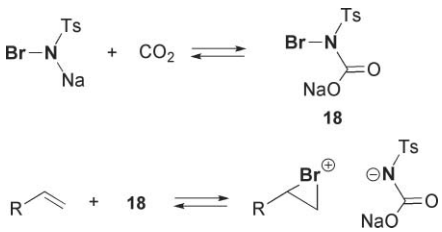
We conclude that the active species **18** induces a cyclic bromonium intermediate on reaction with an olefin, as shown in Scheme 3. This conclusion is supported by the results shown in Table 2.

The case of CT would also be predicted to proceed *via* the same pathway, because the measurement of ^{1}H NMR of CT with CO_2 showed the same results as that of BT. The results in Table 1 can be explained as follows. The pressure of CO_2 affects the regioselectivity in the reaction of BT with styrene, but the reaction of CT led to the production of an α-chlorinated sulfonamide regardless of the pressure. In the case of CT, nitrogen nucleophiles (carbamate anion or CT) would attack the less hindered carbon of the cyclic chloronium intermediate. An increase of CO_2 pressure might increase the polarity of solvent, which would polarize the benzylic carbon–Br bond in contrast to that of the C–Cl bond. This phenomena would induce the formation of the β-brominated sulfonamide (Scheme 4).

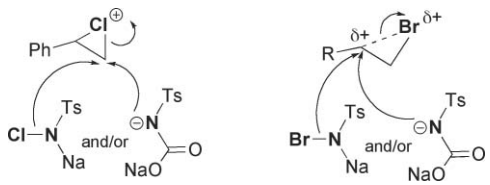
Table 4 Addition of BT to electron-deficient olefins under CO_2[a]

Entry	Olefin	Adduct	Yield (%)
1			53 (**10**)
2			48 (**11**)
3			41 (**12**)
4			24 (**13**)
5			61 (**14**)

[a] Reaction conditions: olefin (0.3 mmol), BT (0.6 mmol), CO_2 (1 atm), MeCN (1.5 cm^3), rt, 24 h.



Scheme 3



Scheme 4

Conclusions

In summary, the use of a unique combination of BT and CO_2 permitted the successful amidobromination of various olefins. When BT is used, the regioselectivity of the reaction is different from that with CT in the amidohalogenation of some olefins.

The use of CT under CO_2 does not lead to the desired addition reaction in the case of terminal electron-deficient olefins, but the present method using BT readily gave amidobrominated products. The method provides a clear demonstration of producing an enantiopure aziridine *via* diastereoselective amidobromination.

Experimental

General

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained on a JASCO FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter using a 10 cm microcell at ambient temperature. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Co.). Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness) (Merck Co.). Compounds were visualized by UV light or treatment with an ethanolic solution of phosphomolybdic acid followed by heating. Since the minor regioisomers **2a**, **2b** and **2c** could not be isolated in pure form, the structures were determined from selected spectral data, mainly ^{1}H NMR and mass measurements, in a form of a mixture with the corresponding major regioisomers.

Experimental procedure

Recrystallized chloramine-T·3H_2O (9 g) was dissolved in water (130 cm^3) and liquid bromine (2 cm^3) was added dropwise from a burette with constant stirring of the solution. The golden yellow precipitate of dibromamine-T was thoroughly washed with water, filtered under suction and dried in a vacuum desiccator for 24 h to give dibromamine-T (10.3 g, 98%). Dibromamine-T (10.3 g) was dissolved, in small lots at a time and with stirring, in an aqueous solution of sodium hydroxide (4.32 g) in water (20 cm^3), and the solution was cooled in ice. Pale yellow crystals of bromamine-T separated out. They were filtered off under suction, washed quickly with the minimum quantity of water and dried over phosphorus pentoxide, to give bromamine-T·1.5H_2O (7.2 g, 75%).

Typical procedure for the amidobromination of styrene derivatives and aliphatic olefins with chloramine-T under CO_2: a magnetic stirring bar, bromamine-T (180 mg, 0.6 mmol), MS4A (180 mg), *p*-methoxystyrene (134 mg, 0.5 mmol), and benzene (1.5 cm^3) were placed in a 50 cm^3 stainless steel autoclave lined with a glass liner. The autoclave was closed, purged three times with carbon dioxide, pressurized with 30 atm of CO_2 and then stirred at room temperature for 1 h. After discharging the excess CO_2, aqueous $Na_2S_2O_3$ (0.5 M, 5 cm^3) was added to the reaction mixture. The solution was then extracted with CH_2Cl_2 (20 cm^3 × 5). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **1e** (173 mg, 90%).

Typical procedure for the amidobromination of elecron-deficient olefins with chloramine-T under CO_2: methyl acrylate (86 mg, 0.3 mmol) was added to a suspension of bromamine-T (108 mg, 0.6 mmol) in MeCN (10 cm^3) at room temperature under an atmosphere of CO_2. After stirring for 24 h, aqueous $Na_2S_2O_3$ (0.5 M, 5 cm^3) was added to the reaction mixture and the solution was extracted with CH_2Cl_2 (20 cm^3 × 5). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **11** (48 mg, 48%).

Spectroscopic data

Bromamine-T·1.5 H_2O[8]. Pale yellow crystal; mp. 202–205 °C; ^{1}H NMR (270 MHz, CD_3CN) δ 2.35 (s, 3H), 7.21 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz); ^{13}C NMR (68 MHz, CD_3CN) δ 21.3, 128.1, 129.3, 140.8, 142.9; Anal. Calcd for $C_7H_{10}BrNNaO_{3.5}S$: C, 28.11; H, 3.37; N, 4.68. Found: C, 28.08; H, 3.26; N, 4.71.

2-Bromo-1-phenyl-1-(*p*-toluenesulfonamido)ethane (1a)[4a]. Colorless solid (136 mg, 77%); mp. 167–169 °C; IR (KBr, ν_{max}/cm^{-1} 3259, 1313, 1161; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.54-3.65 (m, 2H), 4.56 (td, 1H, J = 5.9, 5.9 Hz), 5.13 (br d, 1H, J = 5.9 Hz, D_2O exchangeable), 7.10-7.26 (m, 7H), 7.63 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.7, 36.3, 57.5, 127.0, 128.0, 128.6, 129.4, 134.0, 136.0, 136.5, 143.6; MS (CI, isobutane): *m*/*z* (relative intensity, %) 354 ([M + H]$^+$, 99), 356 ([M + 2 + H]$^+$, 100), 274 ([M-Br]$^+$, 65); HRMS (CI): *m*/*z* Calcd for $C_{15}H_{17}BrNO_2S$ (M + H) 354.0163, found 354.0169; Anal. Calc. for $C_{15}H_{16}BrNO_2S$: C, 50.9; H, 4.6; N, 3.95. Found: C, 50.6; H, 4.2; N, 3.95.

1a and 1-bromo-1-phenyl-2-(*p*-toluenesulfonamido)ethane (2a)[4a]. Obtained as an inseparable mixture: colorless solid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.40 (s, 3H, 1a), 2.45 (s, 3H, 2a), 3.48-3.66 (m, 4H, 2H of 1a and 2 H of 2a), 4.57 (td, 1H, J = 5.9, 5.9 Hz, 1a), 4.69 (br t, 1H, J = 7.3 Hz, D_2O exchangeable, 2a), 4.90 (dd, 1H, J = 7.4, 7.4 Hz, 2a), 5.14 (br d, 1H, J = 6.5 Hz, D_2O exchangeable, 1a), 7.10-7.13 (m, 2H, 1a), 7.19-7.34 (m, 12H, 5H of 1a and 7H of 2a), 7.62 (d, 2H, J = 8.4 Hz, 1a), 7.73 (d, 2H, J = 8.4 Hz, 2a); ^{13}C NMR (68 MHz, $CDCl_3$) (1a + 2a) δ 21.5, 21.6, 36.6, 50.0, 52.6, 58.1, 126.6, 126.9, 127.0, 127.5, 128.1, 128.5, 128.8, 129.0, 129.4, 129.7, 136.7, 137.5, 138.0, 143.4, 143.7; MS (CI, isobutane): *m*/*z* (relative intensity, %) 1a: 354 ([M + H]$^+$, 96), 356 ([M + 2 + H]$^+$, 100), 274 ([M − Br]$^+$, 48) 2a: 354 ([M + H]$^+$, 19), 356 ([M + 2 + H]$^+$, 22), 274 ([M − Br]$^+$, 100).

2-Bromo-1-(4-nitrophenyl)-1-(*p*-toluenesulfonamido)ethane (1b) and 1-bromo-1-(4-nitrophenyl)-2-(*p*-toluenesulfonamido)ethane (2b). Obtained as an inseparable mixture: brown oil (176 mg, 88%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (s, 3H, 1b), 2.45 (s, 3H, 2b), 3.52-3.60 (m, 4H, 2H of 1b and 2H of 2b), 4.57 (td, 1H, J = 5.7, 5.7 Hz, 1b), 4.94 (br t, 1H, J = 7.0 Hz, D_2O exchangeable, 2b), 5.01 (dd, 1H, J = 7.2, 7.2 Hz, 2b), 5.38 (br d, 1H, J = 7.0 Hz, D_2O exchangeable, 1b), 7.21-7.37 (m, 6H, 4H of 1b and 2H of 2b), 7.49 (d, 2H, J = 8.9 Hz, 2b), 7.62 (d, 2H, J = 8.4 Hz, 1b), 7.70 (d, 2H, J = 8.4 Hz, 2b), 8.11 (d, 2H, J = 8.4 Hz, 1b), 8.17 (d, 2H, J = 8.4 Hz, 2b); ^{13}C NMR (68 MHz, $CDCl_3$) (1b + 2b) δ 21.6, 21.6, 35.9, 49.7, 49.9, 57.2, 123.6, 123.9, 126.8, 127.0, 127.7, 128.8, 129.6, 129.8, 136.3, 136.4, 144.0, 144.1, 144.7, 145.1, 147.4, 147.7; MS (CI, isobutane): *m*/*z* (relative intensity, %) 1b: 399

([M + H]$^+$, 30), 401 ([M + 2 + H]$^+$, 37), 319 ([M − Br]$^+$, 25) 2b: 399 ([M + H]$^+$, 75), 401 ([M + 2 + H]$^+$, 89), 319 ([M − Br]$^+$, 100).

2-Bromo-1-(4-chlorophenyl)-1-(*p*-toluenesulfonamido)ethane (1c)[4b]. Colorless solid (123 mg, 76%); mp. 147–148 °C; IR (KBr, ν_{max}/cm^{-1} 3240, 1321, 1166; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.54 (d, 2H, J = 5.9 Hz), 4.56 (td, 1H, J = 5.9, 6.2 Hz), 5.11 (br d, J = 6.2 Hz, 1H, D_2O exchangeable), 7.06 (d, 2H, J = 8.1 Hz), 7.20-7.26 (m, 4H), 7.61 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.7, 36.3, 57.5, 127.0, 128.0, 128.6, 129.4, 134.0, 136.0, 136.5, 143.6; MS (CI, isobutane): *m/z* (relative intensity, %) 388 ([M + H]$^+$, 72), 390 ([M + 2 + H]$^+$, 100), 308 ([M − Br]$^+$, 73); HRMS (CI, isobutane): *m/z* Calc. for $C_{15}H_{16}BrClNO_2S$ (M + H) 387.9975, Found 387.9765; Anal. Calc. for $C_{15}H_{15}BrClNO_2S$: C, 46.35; H, 3.9; N, 3.6. Found: C, 46.1; H, 3.8; N, 3.6.

1c and 1-bromo-1-(4-chlorophenyl)-2-(*p*-toluenesulfonamido)-ethane (2c)[4b]. Obtained as an inseparable mixture: colorless solid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (s, 3H, 1c), 2.45 (s, 3H, 2c), 3.50-3.57 (m, 4H, 2H of 1c and 2H of 2c), 4.56 (td, 1H, J = 5.9, 5.9 Hz, 1c), 4.87-4.92 (m, 2H, 2c) 5.33 (br d, 1H, J = 6.48, 1c), 7.06 (m, 4H, 2H of 1c and 2H of 2c), 7.18-7.59 (m, 8H, 4H of 1c and 4H of 2c), 7.61 (d, 2H, J = 8.4 Hz, 1c), 7.71 (d, 2H, J = 8.6 Hz, 2c); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 36.4, 50.0, 51.5, 57.4, 126.9, 127.1, 128.0, 128.7, 128.9, 129.0, 129.5, 129.8, 134.1, 134.8, 136.0, 136.6, 136.7, 143.7, 143.8; MS (CI, isobutane): *m/z* (relative intensity, %) 1c: 388 ([M + H]$^+$, 72), 390 ([M + 2 + H]$^+$, 100), 308 ([M − Br]$^+$, 32).

2-Bromo-1-(4-methylphenyl)-1-(*p*-toluenesulfonamido)ethane (1d). Colorless solid (145 mg, 86%); mp. 142–143 °C; IR (KBr, ν_{max}/cm^{-1} 3242, 1321, 1167; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.41 (s, 3H), 3.54-3.63 (m, 2H), 4.48-4.53 (m, 1H), 5.09 (br d, 1H, J = 4.3 Hz, D_2O exchangeable), 7.00 (d, 2H, J = 8.4 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.7, 36.8, 57.8, 126.4, 127.1, 129.2, 129.3, 134.4, 136.6, 138.0, 143.4; MS (CI, isobutane): *m/z* (relative intensity, %) 368 ([M + H]$^+$, 64), 370 ([M + 2 + H]$^+$, 66), 288 ([M − Br]$^+$, 73); HRMS (CI, isobutane): *m/z* Calc. for $C_{16}H_{19}BrNO_2S$ (M + H) 368.0321, Found 368.0327; Anal. Calc. for $C_{16}H_{18}BrNO_2S$: C, 52.2; H, 4.9; N, 3.8. Found: C, 51.8; H, 4.6; N, 3.9.

2-Bromo-1-(4-methoxyphenyl)-1-(*p*-toluenesulfonamido)ethane (1e). White solid (173 mg, 90%); mp. 124–126 °C; IR (KBr, ν_{max}/cm^{-1} 3273, 1325, 1252, 1165; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.52-3.61 (m, 2H), 3.77 (s, 3H), 4.50 (td, 1H, J = 6.0, 6.0 Hz), 5.12 (br d, 1H, J = 4.1 Hz, D_2O exchangeable), 6.76 (d, 2H, J = 8.8 Hz), 7.03 (d, 2H, J = 8.8 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 36.7, 55.2, 57.8, 113.8, 127.0, 127.7, 129.3, 129.5, 136.7, 143.2, 159.1; MS (FAB, NBA and NaI): *m/z* (relative intensity, %) 406 ([M + Na]$^+$, 98), 408 ([M + 2 + Na]$^+$, 100), 326 ([M − Br + Na]$^+$, 32); HRMS (CI, isobutane): *m/z* Calc. for $C_{16}H_{19}BrNO_2S$ (M) 383.0191, Found 383.0199; Anal. Calc. for $C_{16}H_{18}BrNO_3S$: C, 50.00; H, 4.72; N, 3.65. Found: C, 49.91; H, 4.61; N, 3.62.

(±)-*trans*-1-Bromo-1-phenyl-2-(*p*-toluenesulfonamido)propane (3)[4a]. Colorless oil (84%); mp. 123–124 °C; IR (KBr, ν_{max}/cm^{-1} 3274, 1331, 1161; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.10 (d, 3H, J = 5.4 Hz), 2.42 (s, 3H), 3.54-3.62 (m, 1H), 4.99 (br d, 1H, J = 8.9 Hz), 5.06 (d, 1H, J = 3.8 Hz), 7.25-7.31 (m, 7H), 7.72 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.1, 21.6, 55.1, 61.7, 126.9, 128.1, 128.2, 128.3, 129.7, 137.5, 137.6, 143.5; MS (CI, isobutane): *m/z* (relative intensity, %) 368 ([M + H]$^+$, 25), 370 ([M + 2 + H]$^+$, 26), 288 ([M − Br]$^+$, 100); HRMS (CI, isobutane): *m/z* Calc. for $C_{16}H_{19}BrNO_2S$ (M+H) 368.0320, Found 368.0314.

(±)-*trans*-2-Bromo-1-(*p*-toluenesulfonamido)indane (4)[4a]. Colorless solid (113 mg, 62%); dec. 169–170 °C; IR (KBr, ν_{max}/cm^{-1} 3249, 1331, 1153; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.15-3.23 (dd, 1H, J = 16.7, 5.4 Hz), 3.54-3.62 (dd, 1H, J = 16.6, 6.8 Hz), 4.32 (q, 1H, J = 5.7 Hz), 4.80 (d, 1H, J = 7.8 Hz), 4.86-4.94 (m, 1H), 7.09 (d, 1H, J = 8.1 Hz), 7.14-7.37 (m, 5H), 7.85 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.7, 41.1, 51.8, 67.1, 124.5, 124.8, 127.3, 127.8, 129.2, 129.7, 137.1, 139.1, 140.1, 143.8; MS (CI, isobutane): *m/z* (relative intensity, %) 366 ([M + H]$^+$, 96), 368 ([M + 2 + H]$^+$, 100), 286 ([M − Br]$^+$, 49); HRMS (CI, isobutane): *m/z* Calc. for $C_{16}H_{17}BrNO_2S$ (M + H) 366.0163, Found 366.0158.

2-Bromo-1-(*p*-toluenesulfonamido)octane (major regioisomer of 5). Colorless oil (68 mg, 38%); IR (neat, cm^{-1}) 3440, 1328, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 6.6 Hz), 1.24-1.46 (m, 8H), 1.76 (dt, 2H, J = 7.8, 7.8 Hz), 2.44 (s, 3H), 3.11-3.21 (m, 1H), 3.33-3.42 (m, 1H), 3.92-4.02 (m, 1H), 4.87 (br t, 1H, J = 7.3 Hz, D_2O exchangeable), 7.32 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 21.6, 22.6, 27.3, 28.5, 31.6, 36.1, 49.6, 55.7, 126.9, 129.7, 136.7, 143.6; MS (CI, isobutane): *m/z* (relative intensity,%) 362 ([M + H]$^+$, 95), 364 ([M + 2 + H]$^+$, 100), 282 ([M − Br]$^+$, 69); HRMS (CI, isobutane): *m/z* Calc. for $C_{15}H_{25}BrNO_2S$ (M + H) 362.0791, Found 362.0783; Anal. Calc. for $C_{15}H_{24}BrNO_2S$: C, 49.75; H, 6.7; N, 3.9. Found: C, 49.7; H, 6.5; N, 4.0.

1-Bromo-2-(*p*-toluenesulfonamido)octane (minor regioisomer of 5)[13]. Colorless oil (13 mg, 7%); IR (neat, ν_{max}/cm^{-1} 3440, 1329, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, 3 H, J = 6.9 Hz), 1.14-1.25 (m, 8 H), 1.44-1.52 (m, 2 H), 2.44 (s, 3 H), 3.29-3.43 (m, 3 H), 4.65 (br d, 1H, J = 8.4 Hz, D_2O exchangeable), 7.31 (d, 2 H, J = 8.4 Hz), 7.76 (d, 2 H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 21.6, 22.5, 25.3, 28.7, 31.6, 33.5, 38.4, 53.1, 126.9, 129.6, 137.6, 143.5; MS (CI, isobutane): *m/z* (relative intensity, %) 362 ([M + H]$^+$, 98), 364 ([M + 2 + H]$^+$, 100), 282 ([M − Br]$^+$, 45); HRMS (CI, isobutane): *m/z* Calc. for $C_{15}H_{25}BrNO_2S$ (M + H) 362.0791, Found 362.0786.

3-Bromo-4-(*p*-toluenesulfonamido)hexane (6). Colorless solid (89 mg, 53%); dec. 114–115 °C; IR (KBr, ν_{max}/cm^{-1} 3273, 1325, 1171; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, 3H, J = 7.4 Hz), 0.95 (t, 3H, J = 7.2 Hz), 1.41-1.58 (m, 2H), 1.71-1.80 (m, 2H), 2.44 (s, 3H), 3.13-3.19 (m, 1H), 3.81-3.85 (m, 1H), 4.71 (br d, 1H, J = 6.5 Hz, D_2O exchangeable), 7.31 (d, 2H, J = 8.2 Hz), 7.76 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.3, 12.9, 21.7, 23.2, 29.4, 59.0, 65.2, 126.8, 129.5, 137.9, 143.3; MS (CI, isobutane): *m/z* (relative intensity, %) 334 ([M + H]$^+$, 96), 336 ([M + 2 + H]$^+$, 100), 254 ([M − Br]$^+$, 33); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{21}BrNO_2S$ (M + H) 334.0477, found 334.0485; Anal. Calc. for $C_{13}H_{20}BrNO_2S$: C, 46.7; H, 6.0; N, 4.2. Found: C, 46.4; H, 5.9; N, 4.2.

3-Bromo-4-(*p*-toluenesulfonamido)hexane (7). Colorless solid (100 mg, 60%); dec. 99–101 °C; IR (KBr, ν_{max}/cm^{-1} 3261, 1331, 1163; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, 3H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.2 Hz), 1.38-1.49 (m, 1H), 1.53-1.66 (m, 1H), 1.70-1.87 (m, 2H), 2.43 (s, 3H), 3.24-3.30 (m, 1H), 3.97-4.01 (m, 1H), 4.58 (br d, 1H, J = 6.5 Hz, D_2O exchangeable), 7.30 (d, 2H, J = 8.2 Hz), 7.76 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 12.8, 21.7, 27.9, 29.3, 36.5, 58.9, 62.5, 126.7, 129.5, 138.3, 143.2; MS (CI, isobutane): m/z (relative intensity, %) 334 ([M + H]$^+$, 99), 336 ([M + 2 + H]$^+$, 100), 254 ([M − Br]$^+$, 35); HRMS (CI, isobutane): m/z Calc. for $C_{13}H_{21}BrNO_2S$ (M + H) 334.0477, Found 334.0475; Anal. Calc. for $C_{13}H_{20}BrNO_2S$: C, 46.7; H, 6.0; N, 4.2. Found: C, 46.45; H, 5.7; N, 4.2.

(±)-*trans*-2-Bromo-1-(*p*-toluenesulfonamide)cyclohexane (8)[4a]. Colorless solid (85 mg, 51%); mp. 65–66 °C; IR (KBr, ν_{max}/cm^{-1} 3245, 1380, 1188; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.26 (m, 3H), 1.65-1.86 (m, 3H), 2.05-2.27 (m, 2H), 2.43 (s, 3H), 3.11-3.21 (m, 1H), 3.80-3.89 (m, 1H), 4.89 (br d, 1H, J = 5.1 Hz), 7.31 (d, 2H, J = 8.4 Hz), 7.78 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 23.5, 25.5, 33.0, 35.9, 55.1, 58.7, 127.2, 129.4, 136.7, 143.3; MS (CI, isobutane): m/z (relative intensity, %) 332 ([M + H]$^+$, 100), 334 ([M + 2 + H]$^+$, 99), 252 ([M − Br]$^+$, 37); HRMS (EI): m/z Calc. for $C_{13}H_{18}BrNO_2S$ (M) 331.0242, Found 331.0240.

2-Bromo-2-*n*-butoxy-1-(*p*-toluenesulfonamido)ethane (9). Colorless oil (87 mg, 83%); IR (neat, ν_{max}/cm^{-1} 3277, 1335, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3H), 1.18-1.31 (m, 2H), 1.37-1.47 (m, 2H), 2.43 (s, 3H), 3.23-3.53 (m, 4H), 4.73 (ddd, 1 H, J = 9.7, 4.3, 3.5 Hz), 5.22 (br d, 1H, J = 9.5 Hz, D_2O exchangeable), 7.31 (d, 2H, J = 8.4 Hz), 7.77 (d, 2H, J = 8.4); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.9, 19.2, 21.6, 31.2, 35.1, 68.3, 82.2, 126.7, 129.6, 137.9, 143.7; MS (FAB): m/z (relative intensity, %) 350 ([M + H]$^+$, 4), 352 ([M + 2 + H]$^+$, 4), 276 ([M − ^{n}BuO]$^+$, 61), 278 ([M + 2 − ^{n}BuO]$^+$, 62); HRMS (FAB): m/z Calc. for $C_{13}H_{21}BrNO_2S$ (M + H) 350.0426, Found 350.0418; Anal. Calc. for $C_{13}H_{20}BrNO_3S$: C, 44.6; H, 5.8; N, 4.0. Found: C, 44.6; H, 5.6; N, 3.9.

(±)-*trans*-3-Phenyl-3-Bromo-2-(*p*-toluenesulfonamido)propiophenone (10)[4a]. Colorless solid (73 mg, 53%); mp. 123–124 °C; IR (KBr, ν_{max}/cm^{-1} 3426, 1681, 1340, 1161; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.26 (s, 3H), 5.11 (d, 1H, J = 7.0 Hz), 5.48-5.50 (m, 2H), 7.00 (d, 2H, J = 7.8 Hz), 7.25-7.60 (m, 10H), 7.77 (d, 2H, J = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 51.6, 60.9, 127.0, 128.4, 128.5, 128.6, 128.7, 128.9, 129.3, 134.1, 134.9, 136.2, 136.4, 143.5; MS (CI): m/z (relative intensity, %) 458 ([M + H]$^+$, 57), 460 ([M + 2 + H]$^+$, 58), 378 ([M − Br]$^+$, 100); HRMS (CI): m/z Calc. for $C_{22}H_{21}BrNO_3S$ (M + H) 458.0426, Found 458.0419.

Methyl 2-bromo-3-(*p*-toluenesulfonamido)propanoate (11)[14]. Colorless oil (48 mg, 48%); IR (neat, ν_{max}/cm^{-1} 3291, 1741, 1331, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3 H), 3.34-3.57 (m, 2 H), 3.78 (s, 3 H), 4.36 (dd, 1 H, J = 8.2, 6.1 Hz), 5.29 (br t, 1H, D_2O exchangeable), 7.33 (d, 2 H, J = 8.4 Hz), 7.74 (d, 2 H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 41.7, 45.8, 53.4, 126.9, 129.8, 136.5, 143.8, 168.9; MS (CI, isobutane): m/z (relative intensity, %) 336 ([M + H]$^+$, 95), 338 ([M + 2 + H]$^+$, 100), 256 ([M − Br]$^+$, 16); HRMS (CI, isobutane): m/z Calc. for $C_{11}H_{15}BrNO_4S$ (M + H) 335.9905, Found 335.9917; Anal. Calc. for $C_{11}H_{14}BrNO_4S$: C, 39.3; H, 4.2; N, 4.2. Found: C, 39.15; H, 4.0; N, 4.1.

2-Bromo-3-oxo-1-(*p*-toluenesulfonamido)butane (12)[14]. Colorless oil (39 mg, 41%); IR (neat, ν_{max}/cm^{-1} 3290, 1716, 1329, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.44 (s, 3 H), 3.29-3.51 (m, 2H), 4.45 (dd, 1H, J = 5.7, 5.4 H), 5.12 (br t, 1H, J = 6.5 Hz, D_2O exchangeable), 7.33 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 27.7, 44.6, 48.6, 126.9, 129.8, 136.5, 143.8, 201.1; MS (CI, isobutane): m/z (relative intensity, %) 320 ([M + H]$^+$, 97), 322 ([M + 2 + H]$^+$, 100), 242 ([M − Br]$^+$, 48); HRMS (CI, isobutane): m/z Calc. for $C_{11}H_{15}BrNO_3S$ (M + H) 319.9956, Found 319.9965; Anal. Calc. for $C_{11}H_{14}BrNO_4S$: C, 41.3; H, 4.4; N, 4.4. Found: C, 41.2; H, 4.2; N, 4.3.

2-Bromo-2-cyano-1-(*p*-toluenesulfonamido)butane (13)[14]. Colorless crystal (22 mg, 24%); mp. 117–119 °C; IR (KBr, ν_{max}/cm^{-1} 3317, 2254, 1336, 1155; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.41-3.60 (m, 2H), 4.44 (dd, 1H, J = 7.2, 7.2 Hz), 5.50 (br t, 1H, J = 6.5 Hz, D_2O exchangeable), 7.35 (d, 2H, J = 8.4 Hz), 7.77 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.7, 26.5, 47.0, 115.5, 126.9, 130.0, 136.1, 144.4; MS (CI, isobutane): m/z (relative intensity, %) 303 ([M + H]$^+$, 98), 305 ([M + 2 + H]$^+$, 100), 225 ([M − Br]$^+$, 31); HRMS (CI, isobutane): m/z Calc. for $C_{10}H_{12}BrN_2O_2S$ (M + H) 302.9803, Found 302.9796; Anal. Calc. for $C_{10}H_{11}BrN_2O_2S$: C, 39.6; H, 3.7; N, 9.2. Found: C, 39.8; H, 3.5; N, 9.0.

2-Bromo-*N*,*N*-dimethyl-3-(*p*-toluenesulfonamido)propanamide (14)[14]. Colorless oil (64 mg, 61%); IR (neat, ν_{max}/cm^{-1} 3228, 1647, 1331, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.98 (s, 3H), 3.05 (s, 3H), 3.38-3.59 (m, 2H), 4.52 (dd, 1H, J = 9.2, 5.1 Hz), 5.23 (br t, 1H, J = 5.1 Hz, D_2O exchangeable), 7.32 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 36.2, 37.5, 39.6, 45.9, 126.8, 129.7, 136.8, 143.5, 167.1; MS (CI, isobutane): m/z (relative intensity, %) 349 ([M + H]$^+$, 96), 351 ([M + 2 + H]$^+$, 100), 269 ([M − Br]$^+$, 31); HRMS (CI, isobutane): m/z Calc. for $C_{12}H_{18}BrN_2O_3S$ (M + H) 349.0222, Found 349.0233.

3-[{1-Bromo-2-(*p*-toluenesulfonamido)ethyl}carbonyl]-2-oxazolidinone (15). Colorless solid (84 mg, 72%); dec. 132–133 °C; IR (KBr, ν_{max}/cm^{-1} 3250, 1765, 1701, 1336, 1157; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.45-3.66 (m, 2H), 3.97-4.12 (m, 2H), 4.47 (t, 2H, J = 8.1 Hz), 5.11 (br t, 1H, J = 6.8 Hz, D_2O exchangeable), 5.41 (dd, 1H, J = 8.6, 5.4 Hz), 7.33 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 39.9, 42.6, 45.0, 62.2, 126.8, 129.7, 136.4, 143.7, 152.7, 167.6; MS (CI, isobutane): m/z (relative intensity, %) 391 ([M + H]$^+$, 41), 393 ([M + 2 + H]$^+$, 43), 311 ([M − Br]$^+$, 100); HRMS (CI, isobutane): m/z Calc. for $C_{13}H_{16}BrN_2O_5S$ (M + H) 390.9964, Found 390.9968. Anal. Calc. for $C_{11}H_{14}BrNO_4S$: C, 39.9; H, 3.9; N, 7.2. Found: C, 39.8; H, 3.7; N, 7.1.

3-[{(1*R*)-1-Bromo-2-(*p*-toluenesulfonamido)ethyl}carbonyl]-4-phenyl-(4*R*)-2-oxazolidinone (major diastereoisomer of 16). White solid (63 mg, 45%); dec. 181–183 °C; IR (KBr, ν_{max}/cm^{-1} 3305, 1767, 1705, 1335, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.38-3.56 (m, 2H), 4.28 (dd, 1H, J = 8.9, 4.6 Hz), 4.76 (dd, 1H, J = 8.9, 8.9 Hz), 5.06 (br t, 1H, J = 6.8 Hz, D_2O exchangeable), 5.41 (dd, 1H, J = 8.9, 4.6 Hz), 5.63 (dd, 1H, J = 8.4, 5.9 Hz), 7.29-7.40 (m, 7H), 7.72 (d, 2H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 40.4, 44.8, 57.6, 70.1, 125.4, 126.7, 128.8, 129.1, 129.7, 136.4, 137.4, 143.7, 152.0, 167.0; MS (CI, isobutane):

m/z (relative intensity, %) 467 ([M + H]$^+$, 30), 469 ([M + 2 + H]$^+$, 32), 387 ([M − Br]$^+$, 100); HRMS (CI, isobutane): *m/z* Calc. for $C_{19}H_{20}BrN_2O_5S$ (M + H) 467.0277, Found 467.0274; Anal. Calc. for $C_{19}H_{19}BrNO_2S$: C, 48.8; H, 4.1; N, 6.0. Found: C, 49.0; H, 4.0; N, 5.9.

3-[{(1*S*)-1-Bromo-2-(*p*-toluenesulfonamido)ethyl}carbonyl]-4-phenyl-(4*R*)-2-oxazolidinone (minor diastereoisomer of 16). Colorless oil (7 mg, 5%); IR (neat, ν_{max}/cm^{-1} 3305, 1767, 1707, 1334, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 3.38-3.56 (m, 2 H), 4.25 (dd, 1 H, J = 8.6, 3.5 Hz), 4.76 (dd, 1H, J = 8.6, 8.6 Hz), 4.76 (br, 1H, D_2O exchangeable), 5.39 (dd, 1H, J = 8.6, 3.5 Hz), 5.62 (dd, 1H, J = 8.0, 5.8 Hz), 7.26-7.44 (m, 7H), 7.67 (d, 2H, J = 8.1); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 40.1, 45.0, 58.0, 70.1, 125.5, 126.7, 128.9, 129.2, 129.7, 136.4, 137.8, 143.7, 152.0, 167.4; MS (CI, isobutane): *m/z* (relative intensity, %) 467 ([M + H]$^+$, 21), 469 ([M + 2 + H]$^+$, 23), 387 ([M − Br]$^+$, 100); HRMS (CI, isobutane): *m/z* Calc. for $C_{19}H_{20}BrN_2O_5S$ (M + H) 467.0277, Found 467.0279.

(2*S*)-Methyl *N*-*p*-toluenesulfonylaziridine-2-carboxylate (17)[11]. Brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.46 (s, 3 H), 2.56 (d, 1H, J = 4.1 Hz), 2.77 (d, 1H, J = 4.1 Hz), 3.38-3.59 (dd, 2H, J = 7.0, 4.1 Hz), 3.74 (s, 3H), 7.34-7.37 (d, 2H), 7.84 (d, 2 H, J = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.9, 32.2, 35.8, 53.1, 128.2, 128.9, 133.9, 145.3, 167.3; $[\alpha]_D^{23}$ −20.4 (*c* 0.764, in $CHCl_3$); HPLC (Daicel Chiralcel IA, hexane–2-propanol, 95 : 5, 0.5 mL min^{-1}, 254 nm), t_S = 35.5 min (for racemic **17**, t_R = 34.8 min, t_S = 35.7 min.)

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