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Structural and mechanistic studies of the base-induced Sommelet–Hauser rearrangement of *N*-α-branched benzylic azetidine-2-carboxylic acid-derived ammonium salts

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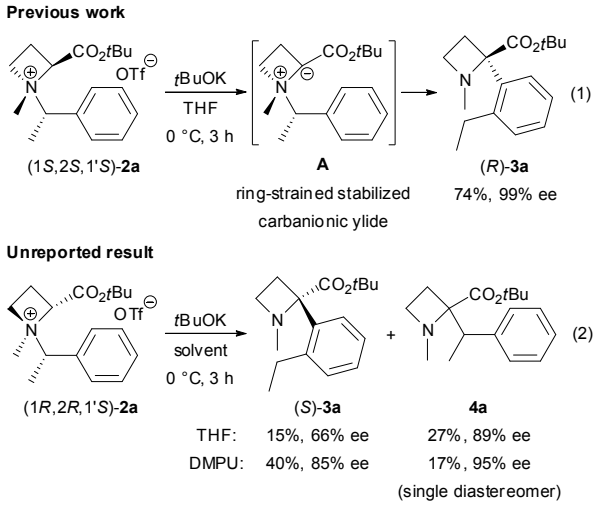
The base-induced Sommelet–Hauser rearrangement of *N*-α-branched benzylic azetidine-2-carboxylic acid ester-derived ammonium salts to obtain α-arylazetidine-2-carboxylic acid esters was investigated. The substrates, two diastereomeric salts (1*S*,2*S*,1′*S*)- and (1*R*,2*R*,1′*S*)-**2**, showed different reactivities. The rearrangement of (1*S*,2*S*,1′*S*)-**2a** proceeded with a perfect N-to-C chirality transfer to provide (*R*)-**3a** in 74% yield with 99% ee. However, the rerrangement of (1*R*,2*R*,1′*S*)-**2a** under the same conditions afforded (*S*)-**3a** in only 15% yield with a lower 66% ee, along with the competitive [1,2] Stevens rearrangement product **4a**. Structural and mechanistic studies of this rearrangement were carried out to clarify the exact reason. Our results expand the scope and limitations of the Sommelet–Hauser rearrangement and provide unique synthetic access to α-aryl amino acid derivatives.

Introduction

Azetidine-2-carboxylic acid derivatives are interesting compounds because of their unique and valuable characters. The ring-strained four-membered nitrogen-containing heterocycle is reactive for nucleophilic ring-opening reactions while still being sufficiently stable to serve as a building block for synthetic transformations leading to nitrogen-containing compounds.[1] Thus, the development of an efficient synthetic method for functionalized azetidine-2-carboxylic acid derivatives has been studied.

Recently, we reported the base-induced Sommelet–Hauser (S–H) rearrangement[2-6] of *N*-benzylic azetidine-2-carboxylic acid ester-derived ammonium salts to produce α-arylazetidine-2-carboxylic acid esters without a competitive [1,2] Stevens rearrangement.[7,8] For example, the S–H rearrangement of (1*S*,2*S*,1′*S*)-**2a**[9] proceeded with a perfect N-to-C chirality transfer[10] to provide (*R*)-**3a** in 74% yield with 99% ee (Scheme 1, eqn (1)). The ring-strain of the four-membered *N*-heterocycle, as in (1*S*,2*S*,1′*S*)-**2a**, enables the efficient generation of the desired carbanionic ylide intermediate **A**.[11,12] Because the undesired ammonium enolate form is unstabilized by the formation of a ring-strained sp^2 α-carbon. Thereby, the rate of the carbanionic [2,3] sigmatropic rearrangement leading to (*R*)-**3a** is enhanced.

Scheme 1 Difference in reactivity between (1*S*,2*S*,1′*S*)- and (1*R*,2*R*,1′*S*)-**2a** in base-induced S–H rearrangement



On the other hand, when the reaction of the other diastereomer (1*R*,2*R*,1′*S*)-**2a** was carried out under the same conditions, the corresponding (*S*)-**3a** was obtained in only 15% yield with a lower 66% ee, along with one diastereomer of the competitive [1,2] Stevens rearrangement product **4a**[13] in 27% yield with 89% ee (eqn (2)). Even when the reaction was carried out at a lower temperature (–40 °C, 3 h), the ratio of **3a**/**4a** (S–H vs. [1,2]) was not improved (**3a**: 2% yield, **4a**: 13% yield). The use of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) as the solvent improved the yield and ee

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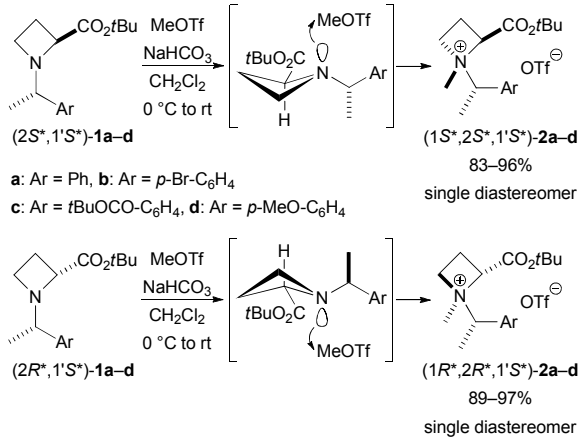
of (*S*)-**3a** to 40% and 85%, respectively, but the formation of the undesired **4a** could not be inhibited. The rate-enhancement effect of the S–H rearrangement by the ring-strain proposed in our previous work (eqn (1)) was not observed upon changing the diastereomeric salt (1*S*,2*S*,1′*S*)-**2a** into (1*R*,2*R*,1′*S*)-**2a**. We started to investigate the base-induced S–H rearrangement of *N*-α-branched benzylic azetidine-2-carboxylic acid ester-derived ammonium salts **2** to clarify the exact reason and define the scope and limitations.

Results and discussion

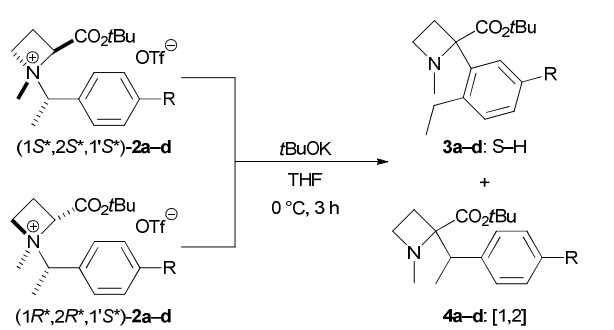
We prepared the racemic *N*-α-methylbenzylic ammonium triflates (1*S**,2*S**,1′*S**)- and (1*R**,2*R**,1′*S**)-**2a–d** as substrates by the *N*-quaternization of the precursor amines **1a–d**[14] with methyl triflate (Scheme 2).[15] The salts **2** were obtained in diastereomerically pure form because the adjacent 2- and *N*-substituents, as in **1**, are in an equatorial position to avoid steric repulsion and the axial lone pair of the nitrogen atom reacts with methyl triflate.[16]

Scheme 2 Diastereoselective *N*-quaternization of (2*S**,1′*S**)- and (2*R**,1′*S**)-**1**



First, the reactions of (1*S**,2*S**,1′*S**)-**2a–d** that would be the preferred diastereomers for the S–H rearrangement depicted in Scheme 1 were investigated (Table 1, entries 1–4). A reaction of *N*-α-methylbenzyl derivative (1*S**,2*S**,1′*S**)-**2a** gave almost the same result as the chiral substrate (entry 1). The desired S–H product **3a** was obtained in 80% yield with no detectable amount of the [1,2] Stevens product **4a**. Similarly, the reactions of the *para*-bromo and *tert*-butoxycarbonyl derivatives, (1*S**,2*S**,1′*S**)-**1b** and **1c**, afforded only **3b** and **3c** in approximately 80% yields (entries 2–3), respectively. When the migrating group was substituted by an electron-donating group (EDG) such as *para*-methoxy (entry 4), the yield of **3d** was decreased to 61% with the formation of two diastereomers **4d1** and **4d2** in a 12% combined yield (8/2 dr, separable by silica gel column chromatography, R_f: **4d1** > **4d2**). A deactivation effect of an EDG on the *N*-benzylic migrating group in the S–H rearrangement was observed, similar to our previous results.[5e,5g]

Table 1 Base-induced S–H rearrangement of (1*S**,2*S**,1′*S**)- and (1*R**,2*R**,1′*S**)-**2**



entry	diastereomer	R		**3** (%)[a]	**4**[b] (%)[a]
1	(1*S**,2*S**,1′*S**)	H	**a**	80	0
2	(1*S**,2*S**,1′*S**)	Br	**b**	83	0
3[c]	(1*S**,2*S**,1′*S**)	CO_2tBu	**c**	81	0
4	(1*S**,2*S**,1′*S**)	OMe	**d**	61	12[d]
5	(1*R**,2*R**,1′*S**)	H	**a**	24	23[e]
6	(1*R**,2*R**,1′*S**)	Br	**b**	63	13[e]
7[f]	(1*R**,2*R**,1′*S**)	CO_2tBu	**c**	57	11[e]
8	(1*R**,2*R**,1′*S**)	OMe	**d**	5[g]	37[h]

[a] Isolated yield unless otherwise noted. [b] The stereochemistry of compounds **4** was not determined. [c] The Hoffmann eliminated product, *tert*-butyl 4-vinylbenzoate (**6**) was formed in 3% yield, determined by ^{1}H NMR analysis of the crude product using mesitylene as an internal standard. [d] Two diastereomers **4d1** and **4d2** (8/2 dr) were obtained. [e] One diastereomer was isolated. [f] The Hoffmann eliminated product **6** was isolated in 20% yield. [g] Determined by ^{1}H NMR analysis of the crude product using mesitylene as an internal standard. [h] Two diastereomers **4d1** and **4d2** (3/7 dr) were obtained.

Next, we examined the reactions of other diastereomers, (1*R**,2*R**,1′*S**)-**2a–d** (Entries 5–8), which would be disfavoured for the S–H rearrangement depicted in Scheme 1. A reaction of (1*R**,2*R**,1′*S**)-**2a** produced a similar result to the chiral substrate to give **3a** in only 24% yield along with one diastereomer of **4a** in 23% yield (entry 5). When the migrating group was substituted by a *para*-bromo or *tert*-butoxycarbonyl, the yields of **3** were improved to moderate levels (entries 6–7, **3b**: 63% yield, **3c**: 57% yield) by the rate-enhancement effect of the S–H rearrangement by an electron-withdrawing group (EWG) on the *N*-benzylic migrating group.[5e,5g] As the side product, one diastereomer of undesired **4** was obtained (**4b**: 13% yield, **4c**: 11% yield). Additionally, a Hoffmann elimination giving **5** and **6** (Scheme 3) was observed in the reaction of (1*R**,2*R**,1′*S**)-**2c** (entry 7), and the styryl derivative **6** was isolated in 20% yield. Upon the use of the *para*-methoxy derivative (1*R**,2*R**,1′*S**)-**2d** as the substrate, the yield of **3d** was minimized to 5% (entry 8). An undesired [1,2] Stevens rearrangement proceeded and mainly provided the two diastereomers **4d1** and **4d2** in a 37% combined yield (3/7 dr).

We applied this S–H rearrangement to the synthesis of an α-benzo-fused ring substituted azetidine-2-carboxylic ester **3e** (Scheme 4), and the results clarified the difference of reactivity between the (1*S*,2*S*,1′*S*)- and (1*R*,2*R*,1′*S*)-**2** diastereomers. The stereoselective *N*-quaternization of *N*-(indan-1-yl)amine

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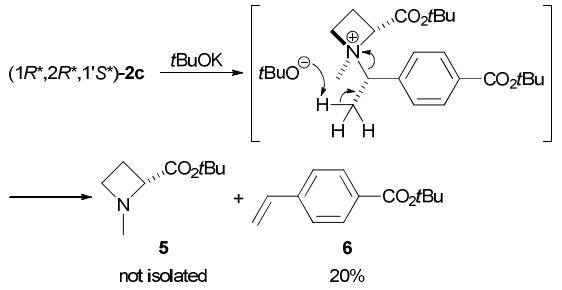
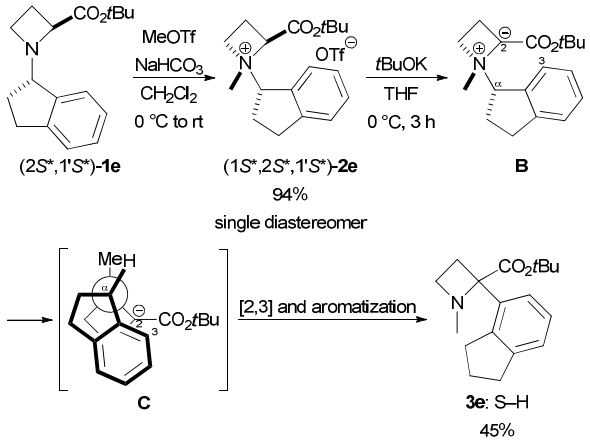
(2*S**,1′*S**)-**1e** followed by the rearrangement of the resulting salt (1*S**,2*S**,1′*S**)-**2e** provided the target **3e** in 45% yield. The TLC analysis of the crude product showed some side products that might cause a lower yield of **3e**, but the undesired [1,2] Stevens product was not obtained. This reaction would proceed via the formation of the ylide **B**, the conformer **C**, [2,3] sigmatropic rearrangement and aromatization. In the [2,3] rearrangement step, the steric repulsion between the indane and azetidine moieties may inhibit the C_2–C_3 bond formation and decrease the yield of **3e**.

Scheme 3 Hoffman elimination to **5** and **6** from (1*R**,2*R**,1′*S**)-**2c**

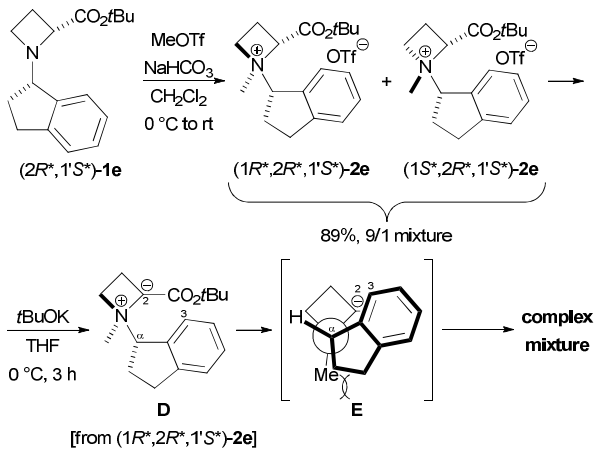


Scheme 4 Base-induced S–H rearrangement of (1*S**,2*S**,1′*S**)-**2e** via conformer **C**



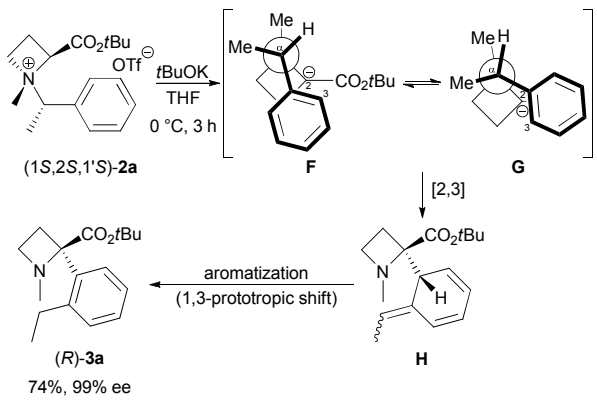
On the other hand, the *N*-quaternization of (2*R**,1′*S**)-**1e** gave a 9/1 mixture of (1*R**,2*R**,1′*S**)-**2e**[17] and (1*S**,2*R**,1′*S**)-**2e** that was not separable by silica gel column chromatography (Scheme 5). The rearrangement of the 9/1 mixture failed completely and gave a complicated mixture (dark purple). The possible conformer **E**, derived from (1*R**,2*R**,1′*S**)-**2e** and the corresponding ylide **D**, would be quite unfavourable for the [2,3] rearrangement because of the methylene-methyl eclipsed-like conformation. Although the exact reason for the formation of side products from **2e** is unclear at present, the Hoffman elimination from **2e** might proceed to give indene, which provides various side products under basic conditions.

Scheme 5 Base-induced S–H rearrangement of (1*R**,2*R**,1′*S**)-**1e** via eclipsed-like conformer **E**.



These results in hand, we proposed a reason for the lower yield in the S–H rearrangement of (1*R*,2*R*,1′*S*)-**2a** into (*S*)-**3a** involving the lack of ee (Scheme 1, eqn (2)). First, the ylide generated from (1*S*,2*S*,1′*S*)-**2a**, which is the desired diastereomer for the S–H rearrangement, enables the formation of the two conformers **F** and **G** (Scheme 6). **F** is similar to that of **C** described in Scheme 4. **G** is in an eclipsed-like conformation, but the repulsions arising from the hydrogen-methyl and methyl-azetidinyl methylene eclipsing would be small. The [2,3] rearrangement from both **F** and **G** provides a dearomatized intermediate **H** followed by a 1,3-prototropic shift in the presence of *t*BuOK and *t*BuOH to give aromatized (*R*)-**3a** in 74% with 99% ee (THF).

Scheme 6 Proposed mechanism for the S–H rearrangement of (1*S*,1*S*,1′*S*)-**2a**



The other diastereomer (1*R*,2*R*,1′*S*)-**2a** forms two conformers **I** and **J** (Scheme 7). The [2,3] rearrangement from **I** proceeds with a high degree of N-to-C chirality transfer to provide (*S*)-**3a** with higher ee. **J** is similar to that of **E** described in Scheme 5. The methyl-methyl eclipsed-like conformation

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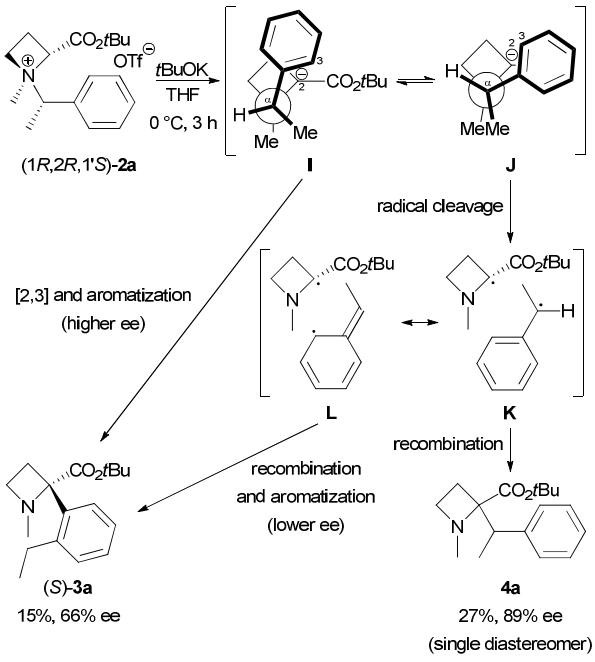
inhibits the [2,3] rearrangement, and a radical cleavage of the N–C bond might occur to generate a radical pair intermediate **K**. The intermediate **K** provides the [1,2] Stevens rearrangement product **4a** with an N-to-C chirality transfer by recombination.[10,13] The radical, as in the intermediate **K**, is delocalized by the phenyl ring to form other radical pair intermediates such as **L**.[18] The radical recombination of **L** followed by aromatization would afford (*S*)-**3a** with a lower degree of N-to-C chirality transfer. The use of DMPU as the solvent would improve the reactivity of the carbanionic ylide, and the rate of the [2,3] rearrangement from **I** is enhanced to afford (*S*)-**3a** in better yield and ee (40% yield, 85% ee).

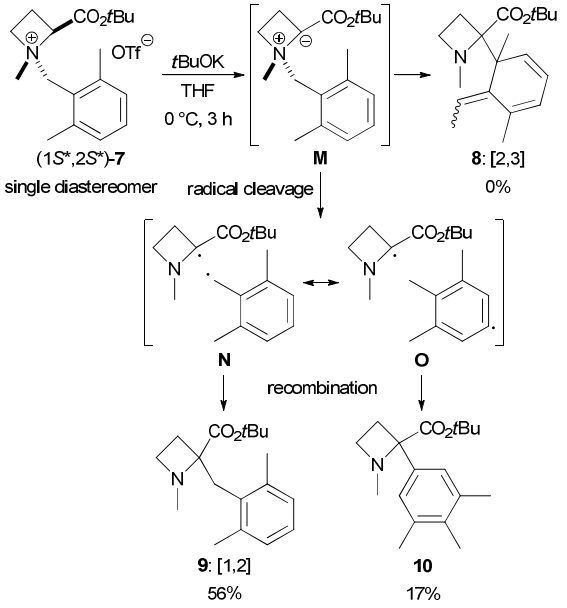
Scheme 7 Proposed mechanism for the S–H rearrangement of (1*R*,1*R*,1′*S*)-**2a**



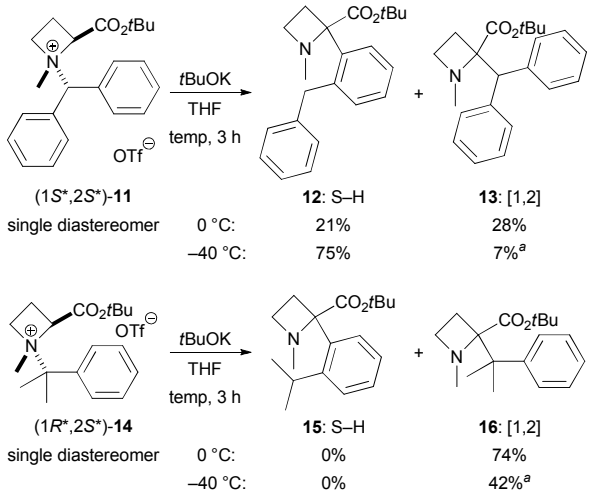
To support our proposed mechanism described in Scheme 7, we prepared the 2,6-dimethylbenzyl ammonium salt (1*S**,2*S**)-**7**[19] and carried out the rearrangement (Scheme 8). The isolated products were the [1,2] Stevens rearrangement product **9** (56% yield) and the α-(3,4,5-trimethylphenyl) derivative **10** (17% yield). The ylide **M** generated from (1*S**,2*S**)-**7** did not give the [2,3] rearrangement product **8** due to the steric repulsion arising from the two *ortho*-methyl substituents.[20] The radical cleavage of **M** generated the radical pair intermediates **N** and **O**, followed by recombination that would provide **9** and **10**, respectively. This result proved our proposed reaction pathway from the intermediate **L** into (*S*)-**3a**.

Finally, we examined the base-induced S–H rearrangement of other types of *N*-α-branched benzylic ammonium salts to define the substrate scope and limitations (Scheme 9). When a rearrangement of *N*-diphenylmethyl derivative (1*S**,2*S**)-**11**[19] was carried out at 0 °C, the corresponding S–H (**12**) and [1,2] (**13**) rearrangement products were obtained without selectivity (**12**: 21% yield, **13**: 28% yield). In this case, a lower reaction temperature (–40 °C) improved the ratio of **12**/**13**, and the desired **12** was obtained in 75% yield. The S–H rearrangement from the *N*-α,α-dimethylbenzyl salt (1*R**,2*S**)-**14**[19] into **15** did not proceed. The [1,2] rearrangeed **16** was obtained as the only identifiable product.

Scheme 8 Formation of α-(3,4,5-trimethylphenyl) derivative **10** via ylide formation, radical cleavage, delocalization and recombination.



Scheme 9 Base-induced rearrangement of *N*-α-branched benzylic ammonium salts (1*S**,2*S**)-**11** and (1*R**,2*S**)-**14**.



[a] Determined by ^{1}H NMR analysis of the crude product using mesitylene as an internal standard.

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Conclusions

In conclusion, we demonstrated the base-induced Sommelet–Hauser (S–H) rearrangement of two diastereomeric salts of *N*-α-branched benzylic azetidine-2-carboxylic acid ester-derived ammonium salts **2**. The two diastereomeric salts **2** showed different reactivities. One diastereomer provided the desired S–H rearrangement product, α-arylazetidine-2-carboxylic acid esters **3**, in good yield with excellent ee, but the other did not. Our experimental studies on this rearrangement clarified the reason for the difference and the reaction mechanisms.

The S–H rearrangement still has structural limitations in that it requires the product to have an *o*-substituted aryl component. Our studies would expand the scope and limitations of this rearrangement and provide unique synthetic access to α-aryl amino acid derivatives. Further studies are in progress in our group to demonstrate the synthetic utility of the S–H rearrangement.

Experimental

General

Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum GX FT-IR. ^{1}H and ^{13}C NMR spectra were measured on a Varian or a Bruker 400 MHz spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz). The splitting patterns are denoted as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad peak. High-resolution mass spectra were measured on a Thermo Fisher Scientific LC/FT-MS spectrometer. Specific rotations were recorded on a JASCO polarimeter P–1010. Normal phase HPLC analyses were performed using a JASCO HPLC pump PU-2080 or PU-2089, and a UV/VIS detector UV-2075. Reversed phase HPLC analyses were performed using a Shimazu HPLC pump LC-20AT and a UV/VIS detector SPD-20A. Reactions involving air- or moisture-sensitive compounds were conducted in appropriate round-bottomed flasks with a magnetic stirring bars under an argon atmosphere. Tetrahydrofuran (THF) was purchased from KANTO Chemical Co., Inc., Japan as an anhydrous solvent. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was purchased from Wako Pure Chemical Industries, Ltd., Japan and dried over molecular sieves 4Å. A 1.0 M potassium *tert*-butoxide (*t*BuOK) solution in THF were purchased from Tokyo Chemical Industry (TCI) Co., Ltd., Japan. For thin layer chromatography (TLC) analysis throughout this work, Merck TLC plates (silica gel 60 F_{254}) was used. The products were purified by preparative column chromatography on silica gel (silica gel 60N, spherical neutral, KANTO Chemical Co., Inc., Japan).

Representative procedure for preparation of (1*S*,2*S*,1´*S*)-2-(*tert*-butoxycarbonyl)-1-methyl-1-(1´-phenylethyl)azetidin-1-ium trifluoromethanesulfonate [(1*S*,2*S*,1´*S*)-2a]

A mixture of (2*S*,1´*S*)-*tert*-butyl 1-(1´-phenylethyl)azetidine-2-carboxylate [(2*S*,1´*S*)-**1a**] (447 mg, 1.71 mmol) and $NaHCO_3$ (0.43 g, 5.1 mmol) in CH_2Cl_2 (8.6 mL) was treated with MeOTf (387 μL, 3.42 mmol) at 0 °C and stirred for 1 h at room temperature. The resulting mixture was evaporated to ca. 1/2 to 1/3 volume and purified by chromatography on silica gel (CH_2Cl_2/MeOH = 15/1 to 7/1 as the eluent) to obtain (1*S*,2*S*,1´*S*)-**2a** (635 mg, 87% yield) as a colourless gum. $[\alpha]^{22}_{589}$ –26.2 (*c* 1.0 in EtOH); IR (KBr) ν_{max}/cm^{-1} 3059, 2983, 1736, 1630, 1499, 1459, 1421, 1397, 1372, 1274, 1258, 1225, 1156, 1031, 993, 971, 934, 881, 839, 773, 756, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (2H, m, Ph), 7.50-7.42 (3H, m, Ph), 5.59 (1H, dd, *J* = 9.8, 9.8 Hz, 2-H), 5.28 (1H, q, *J* = 7.0 Hz, 1´-H), 4.90 (1H, ddd, *J* = 10.0, 10.0, 9.7 Hz, 4-H), 3.29 (1H, ddd, *J* = 9.7, 9.7, 3.4 Hz, 4-H), 3.01 (3H, s, NCH_3), 2.96-2.75 (2H, m, 3-H), 1.75 (3H, d, *J* = 7.0 Hz, 1´-CH_3), 1.54 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 131.0, 130.8, 130.0, 129.4, 120.7 (q, *J* = 318 Hz), 86.0, 72.9, 71.3, 61.4, 39.6, 27.8, 17.9, 14.0; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2$ [M–OTf]$^+$ 276.1958, found 276.1948.

(1*R*,2*R*,1´*S*)-2-(*tert*-Butoxycarbonyl)-1-methyl-1-(1´-phenylethyl)azetidin-1-ium trifluoromethanesulfonate [(1*R*,2*R*,1´*S*)-2a]

Prepared in 91% yield from (2*R*,1´*S*)-*tert*-butyl 1-(1´-phenylethyl)azetidine-2-carboxylate [(2*R*,1´*S*)-**1a**]; colourless gum; $[\alpha]^{22}_{589}$ +23.9 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3053, 2983, 2935, 1732, 1497, 1459, 1423, 1397, 1371, 1351, 1259, 1224, 1155, 1101, 1030, 987, 935, 881, 836, 775, 756, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (2H, m, Ph), 7.51-7.42 (3H, m, Ph), 5.58 (1H, dd, *J* = 9.6, 9.6 Hz, 2-H), 5.25 (1H, q, *J* = 7.0 Hz, 1´-H), 4.83 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz, 4-H), 4.04 (1H, ddd, *J* = 9.6, 9.6, 3.8 Hz, 4-H), 3.15 (3H, s, NCH_3), 2.98-2.75 (2H, m, 3-H), 1.68 (3H, d, *J* = 7.0 Hz, 1´-CH_3), 1.18 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 131.5, 130.7, 130.1, 129.4, 120.7 (q, *J* = 318 Hz), 84.9, 72.9, 69.9, 62.6, 39.3, 27.4, 18.1, 13.5; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2$ [M–OTf]$^+$ 276.1958, found 276.1949.

(1*S,2*S**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-methyl-1-(1´-phenylethyl)azetidin-1-ium trifluoromethanesulfonate [(1*S**,2*S**,1´*S**)-2a]**

Prepared in 83% yield from (2*S**,1´*S**)-**1a**; white solid; mp 146–147 °C; IR (KBr) ν_{max}/cm^{-1} 3053, 2991, 1742, 1500, 1462, 1423, 1390, 1371, 1261, 1225, 1155, 1104, 1071, 1058, 1031, 1015, 992, 968, 932, 871, 840, 776, 757, 709.

(1*R,2*R**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-methyl-1-(1´-phenylethyl)azetidin-1-ium trifluoromethanesulfonate [(1*R**,2*R**,1´*S**)-2a]**

Prepared in 96% yield from (2*R**,1´*S**)-**1a**; colourless gum.

(1*S,2*S**,1´*S**)-1-(1´-(4´´-Bromophenyl)ethyl)-2-(*tert*-butoxycarbonyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*S**,2*S**,1´*S**)-2b]**

Prepared in 95% yield from (2*S**,1´*S**)-**1b**; colourless gum; IR (KBr) ν_{max}/cm^{-1} 2984, 1738, 1593, 1491, 1466, 1421, 1398, 1373, 1259, 1224, 1154, 1079, 1030, 1010, 934, 879, 833, 784, 756, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (2H, d, *J* = 8.4 Hz, ArH), 7.49 (2H, d, *J* = 8.4 Hz, ArH), 5.58 (1H, dd, *J* = 9.8, 9.8 Hz, 2-H), 5.30 (1H, q, *J* = 7.0 Hz, 1´-H), 4.89 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz, 4-H), 3.30 (1H, ddd, *J* = 9.6, 9.6, 2.6 Hz, 4-H), 3.01 (3H, s, NCH_3), 2.97-2.75 (2H, m, 3-H), 1.74 (3H, d, *J* = 7.0 Hz, 1´-CH_3), 1.54 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 132.7, 131.7, 130.0, 125.5, 120.7 (q, *J* = 318 Hz), 86.2, 72.1, 71.6, 61.5,

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39.5, 27.8, 17.9, 14.0; HRMS (ESI): calcd. for $C_{17}H_{25}BrNO_2$ [M–OTf]$^+$ 354.1063, found 354.1056.

(1*R,2*R**,1´*S**)-1-(1´-(4´´-Bromophenyl)ethyl)-2-(*tert*-butoxycarbonyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*R**,2*R**,1´*S**)-2b]**

Prepared in 89% yield from (2*R**,1´*S**)-**1b**; colourless gum; IR (film) ν_{max}/cm^{-1} 2983, 1733, 1593, 1491, 1460, 1421, 1397, 1370, 1258, 1225, 1155, 1077, 1030, 1010, 990, 934, 880, 831, 786, 757, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (2H, d, *J* = 8.4 Hz, ArH), 7.52 (2H, d, *J* = 8.4 Hz, ArH), 5.56 (1H, dd, *J* = 10.0, 9.4 Hz, 2-H), 5.24 (1H, q, *J* = 7.0 Hz, 1´-H), 4.76 (1H, ddd, *J* = 9.8, 9.8, 9.4 Hz, 4-H), 4.06 (1H, ddd, *J* = 9.8, 9.8, 3.2 Hz, 4-H), 3.13 (3H, s, NCH_3), 2.91 (1H, dddd, *J* = 11.9, 10.0, 9.8, 9.8 Hz, 3-H), 2.79 (1H, dddd, *J* = 11.9, 9.4, 9.4, 3.2 Hz, 3-H), 1.66 (3H, d, *J* = 7.0 Hz, 1´-CH_3), 1.21 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 132.4, 131.7, 130.5, 125.3, 120.7 (q, *J* = 319 Hz), 85.2, 72.1, 70.2, 62.8, 39.1, 27.4, 17.8, 13.3; HRMS (ESI): calcd. for $C_{17}H_{25}BrNO_2$ [M–OTf]$^+$ 354.1063, found 354.1056.

(1*S,2*S**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(1´-(4´´-(*tert*-butoxycarbonyl)phenyl)ethyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*S**,2*S**,1´*S**)-2c]**

Prepared in 94% yield from (2*S**,1´*S**)-**1c**; colourless amorphous; IR (KBr) ν_{max}/cm^{-1} 2981, 2935, 1739, 1715, 1613, 1460, 1426, 1396, 1371, 1276, 1258, 1224, 1159, 1120, 1064, 1030, 994, 970, 933, 870, 840, 778, 756, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (2H, ddd, *J* = 8.6, 2.0, 2.0 Hz, ArH), 7.66 (2H, ddd, *J* = 8.6, 2.0, 2.0 Hz, ArH), 5.66 (1H, dd, *J* = 9.6, 9.6 Hz, 2-H), 5.42 (1H, q, *J* = 7.2 Hz, 1´-H), 4.99 (1H, ddd, *J* = 10.3, 9.6, 9.6 Hz, 4-H), 3.27 (1H, ddd, *J* = 10.3, 6.9, 5.0 Hz, 4-H), 3.01 (3H, s, NCH_3), 2.94-2.81 (2H, m, 3-H), 1.78 (3H, d, *J* = 7.2 Hz, 1´-CH_3), 1.59 (9H, s, *t*Bu), 1.54 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 163.7, 135.0, 134.3, 130.3, 130.0, 120.7 (q, *J* = 318 Hz), 86.2, 81.8, 72.2, 71.6, 61.7, 39.7, 28.1, 27.8, 18.1, 14.0; HRMS (ESI): calcd. for $C_{22}H_{34}NO_4$ [M–OTf]$^+$ 376.2482, found 376.2465.

(1*R,2*R**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(1´-(4´´-(*tert*-butoxycarbonyl)phenyl)ethyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*R**,2*R**,1´*S**)-2c]**

Prepared in 94% yield from (2*R**,1´*S**)-**1c**; colourless gum; IR (KBr) ν_{max}/cm^{-1} 2982, 2937, 1731, 1716, 1614, 1578, 1459, 1426, 1396, 1371, 1257, 1225, 1160, 1122, 1080, 1065, 1031, 990, 934, 882, 866, 846, 778, 755, 715; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, d, *J* = 8.4 Hz, ArH), 7.67 (2H, d, *J* = 8.4 Hz, ArH), 5.61 (1H, dd, *J* = 9.6, 9.6 Hz, 2-H), 5.34 (1H, q, *J* = 6.8 Hz, 1´-H), 4.85 (1H, ddd, *J* = 10.0, 9.6, 9.6 Hz, 4-H), 4.07 (1H, ddd, *J* = 9.6, 9.6, 3.6 Hz, 4-H), 3.16 (3H, s, NCH_3), 2.99-2.76 (2H, m, 3-H), 1.71 (3H, d, *J* = 6.8 Hz, 1´-CH_3), 1.59 (9H, s, *t*Bu), 1.18 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.0, 135.5, 134.2, 130.2, 130.0, 120.7 (q, *J* = 318 Hz), 85.2, 81.7, 72.3, 70.2, 62.9, 39.4, 28.0, 27.4, 18.1, 13.4; HRMS (ESI): calcd. for $C_{22}H_{34}NO_4$ [M–OTf]$^+$ 376.2482, found 376.2468.

(1*S,2*S**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(1´-(4´´-methoxyphenyl)ethyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*S**,2*S**,1´*S**)-2d]**

Prepared in 96% yield from (2*S**,1´*S**)-**1d**; colourless gum; IR (KBr) ν_{max}/cm^{-1} 2984, 1738, 1611, 1519, 1464, 1397, 1372, 1257, 1224, 1156, 1030, 871, 839; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (2H, d, *J* = 8.6 Hz, ArH), 6.95 (2H, d, *J* = 8.6 Hz, ArH), 5.50 (1H, dd, *J* = 9.6, 9.2 Hz, 2-H), 5.18 (1H, q, *J* = 6.8 Hz, 1´-H), 4.78 (1H, ddd, *J* = 9.8, 9.6, 9.4 Hz, 4-H), 3.82 (3H, s, OCH_3), 3.29 (1H, dd, *J* = 9.8, 9.4 Hz, 4-H), 3.01 (3H, s, NCH_3), 2.92 (1H, dddd, *J* = 9.8, 9.8, 9.8, 9.6 Hz, 3-H), 2.74 (1H, ddd, *J* = 9.8, 9.6, 9.2 Hz, 3-H), 1.72 (3H, d, *J* = 6.8 Hz, 1´-CH_3), 1.54 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.0, 131.2, 122.7, 120.5 (q, *J* = 319 Hz), 114.4, 85.7, 72.5, 70.9, 60.8, 55.1, 39.2, 27.5, 17.4, 13.9; HRMS (ESI): calcd. for $C_{18}H_{28}NO_3$ [M–OTf]$^+$ 306.2064, found 306.2052.

(1*R,2*R**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(1´-(4´´-methoxyphenyl)ethyl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*R**,2*R**,1´*S**)-2d]**

Prepared in 97% yield from (2*R**,1´*S**)-**1d**; colourless gum; IR (film) ν_{max}/cm^{-1} 2983, 2939, 2842, 1732, 1611, 1584, 1518, 1462, 1396, 1370, 1257, 1225, 1156, 1064, 1031, 989, 921, 876, 839, 785, 755, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, d, *J* = 8.8 Hz, ArH), 6.95 (2H, d, *J* = 8.8 Hz, ArH), 5.53 (1H, dd, *J* = 9.8, 9.4 Hz, 2-H), 5.17 (1H, q, *J* = 6.8 Hz, 1´-H), 4.72 (1H, ddd, *J* = 10.0, 9.8, 9.4 Hz, 4-H), 4.05 (1H, ddd, *J* = 9.8, 9.8, 3.0 Hz, 4-H), 3.81 (3H, s, OCH_3), 3.13 (3H, s, NCH_3), 2.90 (1H, dddd, *J* = 11.9, 10.0, 9.8, 9.8 Hz, 3-H), 2.77 (1H, dddd, *J* = 11.9, 9.4, 9.4, 3.0 Hz, 3-H), 1.65 (3H, d, *J* = 6.8 Hz, 1´-CH_3), 1.20 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.0, 131.2, 123.2, 120.6 (q, *J* = 319 Hz), 114.3, 84.6, 72.5, 69.6, 62.0, 55.1, 38.9, 27.2, 17.5, 13.3; HRMS (ESI): calcd. for $C_{18}H_{28}NO_3$ [M–OTf]$^+$ 306.2064, found 306.2057.

(1*S,2*S**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(2´,3´-dihydro-1´*H*-inden-1´-yl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*S**,2*S**,1´*S**)-2e]**

Prepared in 94% yield from (2*S**,1´*S**)-**1e**; white solid; mp 126–127 °C; IR (KBr) ν_{max}/cm^{-1} 3054, 2989, 2947, 2862, 1742, 1462, 1420, 1396, 1373, 1342, 1265, 1225, 1160, 1048, 1030, 1004, 975, 934, 910, 889, 860, 834, 805, 760, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (1H, d, *J* = 7.5 Hz, ArH), 7.42 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz, ArH), 7.35 (1H, d, *J* = 7.5 Hz, ArH), 7.29 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz, ArH), 5.68 (1H, d, *J* = 9.0 Hz, 1´-H), 5.65 (1H, dd, *J* = 9.6, 9.6 Hz, 2-H), 5.09 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz, 4-H), 3.85 (1H, ddd, *J* = 9.6, 9.6, 3.6 Hz, 4-H), 3.17-2.83 (4H, m, 3-H and 3´-H), 2.80-2.68 (1H, m, 2´-H), 2.74 (3H, s, NCH_3), 2.50 (1H, dddd, *J* = 15.8, 9.0, 9.0, 9.0 Hz, 2´-H), 1.52 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 146.2, 133.6, 131.2, 127.9, 125.92, 125.91, 120.7 (q, *J* = 319 Hz), 86.0, 79.4, 71.4, 62.7, 39.4, 30.9, 27.8, 25.8, 18.8; HRMS (ESI): calcd. for $C_{18}H_{26}NO_2$ [M–OTf]$^+$ 288.1958, found 288.1952.

(1*R,2*R**,1´*S**)-2-(*tert*-Butoxycarbonyl)-1-(2´,3´-dihydro-1´*H*-inden-1´-yl)-1-methylazetidin-1-ium trifluoromethanesulfonate [(1*R**,2*R**,1´*S**)-2e]**

Prepared in 89% yield from (2*R**,1´*S**)-**1e**. ^{1}H NMR analysis showed a 9/1 mixture of (1*R**,2*R**,1´*S**) and (1*S**,2*R**,1´*S**) diastereomers; colourless gum; IR (film) ν_{max}/cm^{-1} 2981, 1734, 1463, 1396, 1371, 1356, 1259, 1224, 1154, 1052, 1030, 1004, 978, 935, 903, 860, 834, 759, 724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (0.9H, d, *J* = 7.6 Hz, $ArH_{(1R^*,2R^*,1'S^*)}$), 7.48-7.39 (0.1H, m, $ArH_{(1S^*,2R^*,1'S^*)}$), 7.42 (0.9H, ddd, *J* = 7.6, 7.6, 1.0 Hz,

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$ArH_{(1R^*,2R^*,1'S^*)}$), 7.38 (0.1H, d, J = 7.6 Hz, $ArH_{(1S^*,2R^*,1'S^*)}$), 7.33 (1H, d, J = 7.6 Hz, ArH), 7.26 (1H, dd, J = 7.6, 7.6 Hz, ArH), 5.67 (0.9H, dd, J = 7.6, 7.6 Hz, 2-$H_{(1R^*,2R^*,1'S^*)}$), 5.63 (0.9H, d, J = 8.4 Hz, 1′-$H_{(1R^*,2R^*,1'S^*)}$), 5.57 (0.1H, d, J = 8.4 Hz, 1′-$H_{(1S^*,2R^*,1'S^*)}$), 5.03 (0.1H, ddd, J = 9.2, 4.0, 2.0 Hz, 2-$H_{(1S^*,2R^*,1'S^*)}$), 4.95 (0.1H, ddd, J = 10.0, 10.0, 9.6 Hz, 4-$H_{(1S^*,2R^*,1'S^*)}$), 4.75 (0.9H, ddd, J = 10.0, 10.0, 10.0 Hz, 4-$H_{(1R^*,2R^*,1'S^*)}$), 4.22 (0.9H, ddd, J = 10.0, 10.0, 4.4 Hz, 4-$H_{(1R^*,2R^*,1'S^*)}$), 4.14 (0.1H, dddd, J = 9.6, 9.6, 4.0, 2.0 Hz, 4-$H_{(1S^*,2R^*,1'S^*)}$), 3.32 (0.1H, dddd, J = 12.4, 9.6, 9.6, 9.6 Hz, 3-$H_{(1S^*,2R^*,1'S^*)}$), 3.24-3.01 (1.1H, m), 3.01-2.74 (3.1H, m), 2.86 (2.7H, s, NCH_3 $_{(1R^*,2R^*,1'S^*)}$), 2.64-2.45 (1H, m, 2′-H), 2.34 (0.9H, ddd, J = 8.4, 7.6, 7.6 Hz, 2′-$H_{(1R^*,2R^*,1'S^*)}$), 2.30-2.21 (0.1H, m, 2′-$H_{(1S^*,2R^*,1'S^*)}$), 1.58 (0.9H, s, tBu$_{(1S^*,2R^*,1'S^*)}$), 1.41 (8.1H, s, tBu$_{(1R^*,2R^*,1'S^*)}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ [assigned only (1*R**,2*R**,1′*S**)] 163.5, 146.6, 133.2, 131.2, 127.6, 127.1, 125.5, 120.7 (q, J = 319 Hz), 85.6, 79.4, 71.2, 62.6, 40.1, 30.8, 27.7, 26.4, 18.2; HRMS (ESI): calcd. for $C_{18}H_{26}NO_2$ $[M–OTf]^+$ 288.1958, found 288.1948.

Representative procedure for base-induced rearrangement of (1*R*,2*R*,1′*S*)-2a

A solution of (1*R*,2*R*,1′*S*)-**2a** (225 mg, 0.529 mmol) in THF (4.8 mL) was treated with a 1 M solution of *t*BuOK in THF (0.63 mL, 0.63 mmol) at 0 °C under an argon atmosphere and stirred for 3 h at the same temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined extracts were washed with saturated aqueous $NaHCO_3$ followed by brine, dried over Na_2SO_4, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 to 5/1 as the eluent, R_f: **3a** > **4a**) afforded (*S*)-**3a** (21.2 mg, 15% yield) as a colourless oil and **4a** (39.4 mg, 27% yield) as a colourless oil.

(*R*)-*tert*-Butyl 2-(2-ethylphenyl)-1-methylazetidine-2-carboxylate (*R*)-3a[7]

Colourless oil; $[\alpha]^{23}_{589}$ +159.9 (*c* 1.0 in EtOH); 99% ee [determined by HPLC analysis: Daicel Chiralcel OD-RH column (15 cm), H_2O/MeCN = 30/70 as the eluent, flow rate = 0.50 mL/min, t_R = 8.6 min for (*R*)-**3a** (99.5%) and 9.6 min for (*S*)-**3a** (0.5%)]; IR (film) ν_{max}/cm^{-1} 3065, 2971, 2931, 2852, 2782, 1714, 1481, 1454, 1391, 1367, 1253, 1196, 1164, 1121, 1086, 1045, 1029, 975, 952, 908, 845, 822, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (1H, m, ArH), 7.23-7.14 (3H, m, ArH), 3.48 (1H, ddd, J = 8.5, 6.0, 2.4 Hz, 4-H), 3.34 (1H, ddd, J = 8.9, 8.2, 6.0 Hz, 4-H), 2.93 (1H, ddd, J = 10.5, 8.2, 2.4 Hz, 3-H), 2.49 (3H, s, NCH_3), 2.355 (1H, q, J = 7.4 Hz, CH_2CH$_3$), 2.351 (1H, q, J = 7.4 Hz, CH_2CH$_3$), 2.19 (1H, ddd, J = 10.5, 8.9, 8.5 Hz, 3-H), 1.42 (9H, s, *t*Bu), 1.19 (3H, dd, J = 7.4, 7.4 Hz, CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 142.0, 139.3, 127.6, 126.7, 125.4, 125.1, 81.6, 75.7, 52.2, 39.9, 29.8, 28.1, 24.3, 14.5; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2$ $[M+H]^+$ 276.1958, found 276.1949.

(*S*)-*tert*-Butyl 2-(2-ethylphenyl)-1-methylazetidine-2-carboxylate (*S*)-3a

Colourless oil; $[\alpha]^{23}_{589}$ –108.8 (*c* 1.0 in EtOH); 66% ee [determined by HPLC analysis: Daicel Chiralcel OD-RH column (15 cm), H_2O/MeCN = 40/60 as the eluent, flow rate = 0.50 mL/min, t_R = 13.4 min for (*R*)-**3a** (16.9%) and 15.0 min for (*S*)-**3a** (83.1%)].

(*rac*)-*tert*-Butyl 2-(2-ethylphenyl)-1-methylazetidine-2-carboxylate 3a

Colourless crystals; mp 40–42 °C; IR (KBr) ν_{max}/cm^{-1} 3066, 3010, 2974, 2934, 2875, 2840, 2778, 1710, 1480, 1453, 1389, 1366, 1287, 1252, 1235, 1207, 1197, 1167, 1126, 1087, 1033, 973, 957, 946, 906, 844, 822, 795, 765, 743.

***tert*-Butyl 1-methyl-2-(1'-phenylethyl)azetidine-2-carboxylate 4a**

Colourless oil; $[\alpha]^{22}_{589}$ –34.2 (*c* 1.0 in EtOH); 89% ee [determined by HPLC analysis: Daicel Chiralcel OJ-H column (25 cm), *n*-hexane/*i*PrOH = 95/5 as the eluent, flow rate = 0.50 mL/min, t_R = 9.0 min (94.3%) and 11.8 min (5.7%)]; IR (film) ν_{max}/cm^{-1} 3060, 3027, 2973, 2931, 2878, 2832, 2779, 1717, 1495, 1475, 1451, 1391, 1367, 1282, 1247, 1214, 1168, 1120, 1085, 1043, 1029, 981, 948, 910, 847, 828, 789, 770, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (2H, m, Ph), 7.24-7.18 (3H, m, Ph), 3.29 (1H, q, J = 7.2 Hz, 1'-H), 3.12 (1H, ddd, J = 8.3, 5.9, 2.6 Hz, 4-H), 2.90 (1H, ddd, J = 8.8, 8.3, 5.9 Hz, 4-H), 2.36 (1H, ddd, J = 10.4, 8.3, 2.6 Hz, 3-H), 2.33 (3H, s, NCH_3), 2.04 (1H, ddd, J = 10.4, 8.8, 8.3 Hz, 3-H), 1.48 (9H, s, *t*Bu), 1.30 (3H, d, J = 7.2 Hz, 1'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 142.0, 129.0, 127.6, 126.3, 81.4, 76.8, 51.4, 45.3, 40.0, 28.3, 25.0, 14.2; HRMS (ESI): calcd. for $C_{17}H_{26}NO_2$ $[M+H]^+$ 276.1958, found 276.1953.

(*rac*)-*tert*-Butyl 1-methyl-2-(1'-phenylethyl)azetidine-2-carboxylate 4a

Colourless oil.

***tert*-Butyl 2-(5-bromo-2-ethylphenyl)-1-methylazetidine-2-carboxylate 3b**

Colourless crystals; mp 72–74 °C; IR (KBr) ν_{max}/cm^{-1} 3065, 3015, 2967, 2931, 2859, 2786, 1713, 1590, 1561, 1477, 1458, 1390, 1365, 1250, 1209, 1195, 1161, 1122, 1084, 1054, 974, 956, 944, 914, 892, 841, 832, 789, 768, 748; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, J = 2.2 Hz, ArH), 7.32 (1H, dd, J = 8.2, 2.2 Hz, ArH), 7.04 (1H, d, J = 8.2 Hz, ArH), 3.47 (1H, ddd, J = 8.6, 6.0, 2.4 Hz, 4-H), 3.33 (1H, ddd, J = 8.6, 8.4, 6.0 Hz, 4-H), 2.91 (1H, ddd, J = 10.3, 8.4, 2.4 Hz, 3-H), 2.46 (3H, s, NCH_3), 2.29 (2H, q, J = 7.6 Hz, CH_2CH$_3$), 2.14 (1H, ddd, J = 10.3, 8.6, 8.6 Hz, 3-H), 1.43 (9H ,s, *t*Bu), 1.17 (3H, t, J = 7.6 Hz, CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 144.2, 138.4, 129.7, 129.4, 128.3, 119.5, 81.9, 75.1, 52.0, 39.6, 29.6, 28.1, 23.9, 14.3; HRMS (ESI): calcd. for $C_{17}H_{25}BrNO_2$ $[M+H]^+$ 354.1063, found 354.1055.

***tert*-Butyl 2-(1'-(4-bromophenyl)ethyl)-1-methylazetidine-2-carboxylate 4b**

Colourless oil; IR (film) ν_{max}/cm^{-1} 2973, 2931, 2833, 2781, 1716, 1590, 1488, 1457, 1403, 1392, 1367, 1247, 1213, 1166, 1121, 1087, 1076, 1043, 1010, 974, 948, 911, 847, 822, 788, 766, 722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, ddd, J = 8.4, 2.2, 2.2 Hz, ArH), 7.09 (2H, ddd, J = 8.4, 2.2, 2.2 Hz, ArH), 3.24 (1H, q, J = 7.2 Hz, 1'-H), 3.08 (1H, ddd, J = 8.4, 6.0, 2.4 Hz, 4-H), 2.90 (1H, ddd, J = 8.6, 8.4, 6.0 Hz, 4-H), 2.32 (1H, ddd, J = 10.6, 8.4, 2.4 Hz, 3-H), 2.30 (3H, s, NCH_3), 1.93 (1H, ddd, J = 10.6, 8.6, 8.4 Hz, 3-H), 1.50 (9H, s, *t*Bu), 1.24 (3H, d, J = 7.2 Hz, 1'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 141.1, 130.9, 130.6, 120.2, 81.6, 76.6, 51.4, 44.1, 39.7, 28.3, 24.0, 14.0; HRMS (ESI): calcd. for $C_{17}H_{25}BrNO_2$ $[M+H]^+$ 354.1063, found 354.1051.

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tert-Butyl 2-(5-(_tert_-butoxycarbonyl)-2-ethylphenyl)-1-methylazetidine-2-carboxylate 3c

Colourless oil; IR (film) ν_{max}/cm^{-1} 2974, 2932, 2856, 2784, 1712, 1609, 1574, 1475, 1457, 1414, 1392, 1367, 1307, 1247, 1164, 1127, 1086, 1059, 981, 948, 917, 882, 845, 822, 789, 766, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (1H, d, J = 1.7 Hz, ArH), 7.82 (1H, dd, J = 8.1, 1.7 Hz, ArH), 7.21 (1H, d, J = 8.1 Hz, ArH), 3.49 (1H, ddd, J = 8.5, 6.0, 2.4 Hz, 4-H), 3.36 (1H, ddd, J = 8.6, 8.2, 6.0 Hz, 4-H), 2.92 (1H, ddd, J = 10.3, 8.2, 2.4 Hz, 3-H), 2.51 (3H, s, NCH_3), 2.39 (2H, q, J = 7.4 Hz, CH_2CH_3), 2.15 (1H, ddd, J = 10.3, 8.6, 8.5 Hz, 3-H), 1.59 (9H, s, _t_Bu), 1.42 (9H, s, _t_Bu), 1.20 (3H, t, J = 7.4 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 166.1, 144.5, 142.2, 129.2, 127.8, 127.7, 126.6, 81.8, 80.4, 75.3, 52.1, 39.6, 29.7, 28.2, 28.1, 24.5, 14.3; HRMS (ESI): calcd. for $C_{22}H_{34}NO_4$ $[M+H]^+$ 376.2482, found 376.2474.

tert-Butyl 2-(1'-(4''-(_tert_-butoxycarbonyl)phenyl)ethyl)-1-methylazetidine-2-carboxylate 4c

Colourless oil; IR (film) ν_{max}/cm^{-1} 2975, 2932, 2834, 2781, 1712, 1609, 1574, 1476, 1457, 1414, 1392, 1367, 1293, 1249, 1213, 1166, 1115, 1087, 1045, 1018, 975, 948, 911, 848, 779, 734, 711; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, ddd, J = 8.2, 1.6, 1.6 Hz, ArH), 7.27 (2H, ddd, J = 8.2, 1.6, 1.6 Hz, ArH), 3.34 (1H, q, J = 7.2 Hz, 1'-H), 3.06 (1H, ddd, J = 8.4, 6.0, 2.6 Hz, 4-H), 2.90 (1H, ddd, J = 8.6, 8.2, 6.0 Hz, 4-H), 2.33 (1H, ddd, J = 10.4, 8.2, 2.6 Hz, 3-H), 2.31 (3H, s, NCH_3), 1.96 (1H, ddd, J = 10.4, 8.6, 8.4 Hz, 3-H), 1.59 (9H, s, _t_Bu), 1.51 (9H, s, _t_Bu), 1.27 (3H, d, J = 7.2 Hz, 1'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 165.9, 147.2, 130.0, 129.1, 128.6, 81.6, 80.7, 76.7, 51.4, 44.6, 39.7, 28.3, 28.2, 24.0, 14.0; HRMS (ESI): calcd. for $C_{22}H_{34}NO_4$ $[M+H]^+$ 376.2482, found 376.2474.

tert-Butyl 4-vinylbenzoate 6[21]

Colourless oil; IR (film) ν_{max}/cm^{-1} 3089, 2977, 2930, 1711, 1629, 1608, 1567, 1474, 1456, 1402, 1392, 1368, 1311, 1293, 1255, 1166, 1118, 1107, 1015, 989, 915, 861, 850, 783, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (2H, ddd, J = 8.4, 1.8, 1.8 Hz, ArH), 7.44 (2H, ddd, J = 8.4, 1.8, 1.8 Hz, ArH), 6.75 (1H, dd, J = 17.6, 11.2 Hz, C_H_=CH_2), 5.85 (1H, dd, J = 17.6, 0.6 Hz, CH=C_H_$_2$), 5.36 (1H, dd, J = 11.2, 0.6 Hz, CH=C_H_$_2$), 1.59 (9H, s, _t_Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 141.4, 136.1, 131.1, 129.7, 125.9, 116.1, 80.9, 28.2.

Representative procedure for base-induced rearrangement of (1_S_*,2_S_*,1'_S_*)-2d

A solution of (1_S_*,2_S_*,1'_S_*)-**2d** (146 mg, 0.321 mmol) in THF (2.9 mL) was treated with a 1 M solution of _t_BuOK in THF (0.39 mL, 0.39 mmol) at 0 °C under an argon atmosphere and stirred for 3 h at the same temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined extracts were washed with saturated aqueous $NaHCO_3$ followed by brine, dried over Na_2SO_4, and concentrated. First, ^{1}H NMR analysis of the crude material using mesitylene as an internal standard determined the yield of **3d** (73% yield), **4d1** (10% yield) and **4d2** (3% yield). Purification of the crude material by chromatography on silica gel (_n_-hexane/EtOAc = 7/1 to 3/1 as the eluent, R_f: **3d** > **4d1** > **4d2**) gave **3d** (60.2 mg, 61% yield) as a colourless oil and **4d1** (8.5 mg, 9% yield) as a colourless oil. The pure **4d2** could not be obtained because of inseparable impurities.

Representative procedure for base-induced rearrangement of (1_R_*,2_R_*,1'_S_*)-2d

The reaction was performed by the same procedure depicted above using (1_R_*,2_R_*,1'_S_*)-**2d** (123 mg, 0.270 mmol), THF (2.4 mL), a 1 M solution of _t_BuOK in THF (0.32 mL, 0.32 mmol). ^{1}H NMR analysis of the crude material using mesitylene as an internal standard determined the yield of **3d** (5% yield), **4d1** (10% yield) and **4d2** (33% yield). Purification of the crude material by chromatography on silica gel (_n_-hexane/EtOAc = 7/1 to 3/1 as the eluent, R_f: **3d** > **4d1** > **4d2**) gave **4d2** (22.4 mg, 27% yield) as colourless crystals. The product **3d** was not isolated because of small amount. The pure **4d1** could not be obtained because of inseparable impurities.

tert-Butyl 2-(2-ethyl-5-methoxyphenyl)-1-methylazetidine-2-carboxylate 3d

Colourless oil; IR (film) ν_{max}/cm^{-1} 2969, 2932, 2853, 2834, 2782, 1714, 1609, 1578, 1496, 1464, 1424, 1391, 1367, 1253, 1216, 1160, 1120, 1086, 1044, 978, 948, 931, 863, 844, 812, 773, 751, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (1H, d, J = 3.1 Hz, ArH), 7.08 (1H, d, J = 8.3 Hz, ArH), 6.75 (1H, dd, J = 8.3, 3.1 Hz, ArH), 3.82 (3H, s, OCH_3), 3.46 (1H, ddd, J = 8.6, 6.0, 2.6 Hz, 4-H), 3.32 (1H, ddd, J = 8.8, 8.0, 6.0 Hz, 4-H), 2.91 (1H, ddd, J = 10.5, 8.0, 2.6 Hz, 3-H), 2.47 (3H, s, NCH_3), 2.29 (2H, q, J = 7.6 Hz, C_H_$_2$CH$_3$), 2.17 (1H, ddd, J = 10.5, 8.8, 8.6 Hz, 3-H), 1.43 (9H, s, _t_Bu), 1.16 (3H, t, J = 7.6 Hz, CH_2C_H_$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 157.4, 143.2, 131.4, 128.5, 111.6, 111.2, 81.5, 75.4, 55.0, 51.9, 39.6, 29.6, 28.0, 23.4, 14.6; HRMS (ESI): calcd. for $C_{18}H_{28}NO_3$ $[M+H]^+$ 306.2064, found 306.2054.

tert-Butyl 2-(1'-(4''-methoxyphenyl)ethyl)-1-methylazetidine-2-carboxylate 4d1

Colourless oil; IR (film) ν_{max}/cm^{-1} 2973, 2931, 2834, 2779, 1715, 1612, 1582, 1512, 1457, 1391, 1367, 1274, 1246, 1215, 1177, 1129, 1094, 1063, 1039, 974, 948, 927, 913, 832, 787, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (2H, ddd, J = 8.6, 2.6, 2.6 Hz, ArH), 6.78 (2H, ddd, J = 8.6, 2.6, 2.6 Hz, ArH), 3.76 (3H, s, OCH_3), 3.33 (1H, ddd, J = 7.5, 6.0, 3.6 Hz, 4-H), 3.07 (1H, q, J = 7.2 Hz, 1'-H), 3.02 (1H, ddd, J = 8.4, 8.4, 6.0 Hz, 4-H), 2.45-2.34 (2H, m, 3-H), 2.27 (3H, s, NCH_3), 1.37 (3H, d, J = 7.2 Hz, 1'-CH_3), 1.28 (9H, s, _t_Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 157.9, 136.0, 129.0, 113.4, 80.9, 77.2, 55.2, 52.0, 42.4, 39.2, 28.0, 22.5, 17.6; HRMS (ESI): calcd. for $C_{18}H_{28}NO_3$ $[M+H]^+$ 306.2064, found 306.2053.

tert-Butyl 2-(1'-(4''-methoxyphenyl)ethyl)-1-methylazetidine-2-carboxylate 4d2

Colourless crystals; mp 52–57 °C; IR (KBr) ν_{max}/cm^{-1} 2998, 2972, 2956, 2913, 2842, 2787, 1709, 1613, 1581, 1512, 1476, 1460, 1437, 1391, 1366, 1341, 1304, 1282, 1248, 1212, 1197, 1179, 1149, 1131, 1096, 1062, 1035, 1004, 980, 943, 911, 845, 822, 787, 751, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (2H, ddd, J = 8.6, 2.6, 2.6 Hz, ArH), 6.83 (2H, ddd, J = 8.6, 2.6, 2.6 Hz, ArH), 3.79 (3H, s, OCH_3), 3.23 (1H, q, J = 7.2 Hz, 1'-H), 3.13 (1H, ddd, J = 8.4, 6.2, 2.4 Hz, 4-H), 2.90 (1H, ddd, J = 8.4, 8.2, 6.2 Hz, 4-H), 2.34 (1H, ddd, J = 10.5, 8.2, 2.4 Hz, 3-H), 2.33 (3H, s, NCH_3),

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2.01 (1H, ddd, *J* = 10.5, 8.4, 8.4 Hz, 3-H), 1.49 (9H, s, *t*Bu), 1.27 (3H, d, *J* = 7.2 Hz, 1'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 158.0, 134.0, 129.9, 113.0, 81.3, 76.9, 55.1, 51.4, 44.4, 40.0, 28.3, 24.8, 14.4; HRMS (ESI): calcd. for $C_{18}H_{28}NO_3$ $[M+H]^+$ 306.2064, found 306.2056.

***tert*-Butyl 2-(2,3-dihydro-1*H*-inden-4-yl)-1-methylazetidine-2-carboxylate 3e**

Yellow oil; IR (film) ν_{max}/cm^{-1} 3059, 2964, 2932, 2844, 1780, 1716, 1592, 1472, 1447, 1391, 1367, 1286, 1252, 1200, 1163, 1123, 1086, 1063, 1014, 950, 915, 845, 819, 779, 744, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, dd, *J* = 7.6 Hz, ArH), 7.16 (1H, dd, *J* = 7.6, 7.0 Hz, ArH), 7.11 (1H, d, *J* = 7.0 Hz, ArH), 3.47 (1H, ddd, *J* = 8.4, 6.2, 2.4 Hz, 4-H), 3.30 (1H, ddd, *J* = 8.9, 8.2, 6.2 Hz, 4-H), 2.90 (1H, ddd, *J* = 10.5, 8.2, 2.4 Hz, 3-H), 2.87 (2H, t, *J* = 7.4 Hz, indenyl-CH_2), 2.67-2.51 (2H, m, indenyl-CH_2), 2.50 (3H, s, NCH_3), 2.15 (1H, ddd, *J* = 10.5, 8.9, 8.4 Hz, 3-H), 2.09-1.92 (2H, m, indenyl-CH_2), 1.42 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 144.1, 140.1, 139.3, 126.0, 122.7, 122.1, 81.4, 75.4, 52.2, 40.1, 32.5, 31.0, 28.7, 28.1, 25.3; HRMS (ESI): calcd. for $C_{18}H_{26}NO_2$ $[M+H]^+$ 288.1958, found 288.1957.

***tert*-Butyl 2-(2,6-dimethylbenzyl)-1-methylazetidine-2-carboxylate 9**

Colourless oil; IR (film) ν_{max}/cm^{-1} 3066, 3005, 2971, 2928, 2854, 2780, 1716, 1586, 1474, 1391, 1367, 1328, 1251, 1213, 1166, 1118, 1083, 1056, 1032, 999, 949, 903, 846, 814, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.97 (3H, m, ArH), 3.07 (1H, d, *J* = 14.8 Hz, CH_2Ar), 3.07-2.98 (2H, m, 4-H), 2.86 (1H, d, *J* = 14.8 Hz, CH_2Ar), 2.35 (3H, s, NCH_3), 2.32-2.21 (1H, m, 3-H), 2.28 (6H, s, ArCH_3), 1.87 (1H, ddd, *J* = 10.0, 8.6, 8.6 Hz, 3-H), 1.47 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 138.0, 135.4, 127.8, 126.0, 81.0, 74.1, 51.8, 38.1, 34.1, 28.2, 26.1, 21.0; HRMS (ESI): calcd. for $C_{18}H_{28}NO_2$ $[M+H]^+$ 290.2115, found 290.2104.

***tert*-Butyl 1-methyl-2-(3,4,5-trimethylphenyl)azetidine-2-carboxylate 10**

Colourless crystals; mp 54–57 °C; IR (KBr) ν_{max}/cm^{-1} 2973, 2929, 2841, 2782, 1712, 1607, 1578, 1486, 1454, 1413, 1391, 1366, 1312, 1268, 1254, 1197, 1169, 1123, 1084, 1036, 1016, 993, 947, 931, 874, 845, 810, 766, 746, 715; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (2H, s, ArH), 3.33-3.23 (2H, m, 4-H), 2.81 (1H, ddd, *J* = 10.9, 7.3, 5.6 Hz, 3-H), 2.47-2.34 (1H, m, 3-H), 2.30 (3H, s, NCH_3), 2.28 (6H, s, 3,5-ArCH_3), 2.15 (3H, s, 4-ArCH_3), 1.47 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 137.6, 136.1, 133.9, 124.8, 81.2, 74.5, 51.3, 39.6, 29.3, 28.1, 20.8, 15.2; HRMS (ESI): calcd. for $C_{18}H_{28}NO_2$ $[M+H]^+$ 290.2115, found 290.2106.

Representative procedure for base-induced rearrangement of (1*S,2*S**)-11**

A solution of (1*S**,2*S**)-**11** (102 mg, 0.209 mmol) in THF (1.9 mL) was treated with a 1 M solution of *t*BuOK in THF (0.25 mL, 0.25 mmol) at –40 °C under an argon atmosphere and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous NH_4Cl and the mixture was extracted with EtOAc. The combined extracts were washed with saturated aqueous $NaHCO_3$ followed by brine, dried over Na_2SO_4, and concentrated. ^{1}H NMR analysis of the crude material using mesitylene as an internal standard determined the yield of **12** (85% yield) and **13** (7% yield). Purification of the crude material by chromatography on silica gel (*n*-hexane/EtOAc = 15/1 to 7/1 as the eluent) gave **12** (52.8 mg, 75% yield) as colourless crystals.

***tert*-Butyl 2-(2-benzylphenyl)-1-methylazetidine-2-carboxylate 12**

Colourless crystals; mp 50–52 °C; IR (KBr) ν_{max}/cm^{-1} 3061, 3025, 2972, 2934, 2856, 2782, 1715, 1599, 1495, 1479, 1452, 1391, 1364, 1253, 1236, 1196, 1161, 1124, 1085, 1038, 975, 953, 906, 844, 818, 767, 753, 741, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, *J* = 7.8, 1.4 Hz, ArH), 7.30-7.17 (4H, m, ArH), 7.16-7.07 (3H, m, ArH), 6.86 (1H, ddd, *J* = 7.6, 1.4, 0.6 Hz, ArH), 3.73 (2H, s, CH_2Ph), 3.47 (1H, ddd, *J* = 8.5, 6.2, 2.4 Hz, 4-H), 3.33 (1H, ddd, *J* = 8.8, 8.1, 6.2 Hz, 4-H), 2.89 (1H, ddd, *J* = 10.4, 8.1, 2.4 Hz, 3-H), 2.51 (3H, s, NCH_3), 2.17 (1H, ddd, *J* = 10.4, 8.8, 8.5 Hz, 3-H), 1.44 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 142.5, 140.3, 136.3, 129.8, 129.4, 128.3, 126.7, 126.0, 125.9, 125.4, 81.9, 75.7, 52.2, 39.9, 37.6, 29.8, 28.2; HRMS (ESI): calcd. for $C_{22}H_{28}NO_2$ $[M+H]^+$ 338.2115, found 338.2111.

***tert*-Butyl 2-benzhydryl-1-methylazetidine-2-carboxylate 13**

Colourless crystals; mp 80–82 °C; IR (KBr) ν_{max}/cm^{-1} 3087, 3064, 3026, 3001, 2966, 2930, 2825, 2776, 1711, 1497, 1472, 1449, 1392, 1370, 1280, 1269, 1250, 1217, 1168, 1153, 1118, 1086, 1031, 989, 949, 848, 760, 739, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (4H, m, Ph), 7.22-7.15 (4H, m, Ph), 7.12 (1H, ddd, *J* = 6.8, 1.6, 1.6 Hz, Ph), 4.33 (1H, s, C*H*Ph$_2$), 3.06-2.97 (2H, m, 4-H), 2.61 (1H, ddd, *J* = 10.2, 5.2, 5.2 Hz, 3-H), 2.35 (3H, s, NCH_3), 2.13 (1H, ddd, *J* = 10.2, 8.6, 8.6 Hz, 3-H), 1.16 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.7, 141.0, 130.9, 128.9, 128.2, 127.3, 126.2, 126.1, 81.1, 76.8, 54.8, 52.6, 38.5, 27.7, 23.4; HRMS (ESI): calcd. for $C_{22}H_{28}NO_2$ $[M+H]^+$ 338.2115, found 338.2111.

***tert*-Butyl 1-methyl-2-(2'-phenylpropan-2'-yl)azetidine-2-carboxylate 16**

Colourless oil; IR (film) ν_{max}/cm^{-1} 3089, 3057, 2977, 2929, 2834, 2783, 1713, 1600, 1496, 1476, 1444, 1391, 1366, 1273, 1247, 1217, 1151, 1122, 1084, 1063, 1031, 976, 952, 908, 848, 822, 780, 760, 734, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (4H, m, Ph), 7.15 (1H, tt, *J* = 6.8, 1.4 Hz, Ph), 3.32 (1H, ddd, *J* = 8.6, 6.3, 3.0 Hz, 4-H), 2.87 (1H, ddd, *J* = 8.8, 8.6, 6.3 Hz, 4-H), 2.58 (1H, ddd, *J* = 10.8, 8.6, 3.0 Hz, 3-H), 2.47 (1H, ddd, *J* = 10.8, 8.8, 8.6 Hz, 3-H), 2.32 (3H, s, NCH_3), 1.51 (3H, s, 2'-CH_3); 1.41 (3H, s, 2'-CH_3), 1.18 (9H ,s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 147.6, 127.6, 126.8, 125.7, 81.0, 79.7, 51.8, 43.2, 42.3, 27.85, 27.80, 24.4, 22.7; HRMS (ESI): calcd. for $C_{18}H_{28}NO_2$ $[M+H]^+$ 290.2115, found 290.2111.

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13 The stereochemistry of the [1,2] Stevens rearrangement products **4** was not determined, but they can be predicted. Because the [1,2] Stevens rearrangement mainly proceeds via a radical pair intermediate with the retention of configuration. See ref. 4b, 4h and 4i. Thereby, **4a** was obtained in 89% ee. Other related examples: see ref. 10b, 10c, 10e and 10h.
14 Diastereomers (2*S**,1'*S**)- and (2*R**,1'*S**)-**1** were easily separable by silica gel column chromatography. The stereochemistry of (2*S*,1'*S*)- and (2*R*,1'*S*)-**1a** was assigned in our previous work, see ref. 7. The stereochemistry of **1b–e** was assigned by analogy. Examples of chromatographic separation of other analogs of **1**, see: (a) S.-h. Ma, D. H. Yoon, H.-J. Ha and W. K. Lee, *Tetrahedron Lett.*, 2007, **48**, 269; (b) F. Couty, G. Evano, M. Vargas-Sanchez and G. Bouzas, *J. Org. Chem.*, 2005, **70**, 9028.
15 Sodium hydrogen carbonate was added as a scavenger of triflic acid, which may cause the decomposition of the *tert*-butyl ester.
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17 The relative stereochemistry of (1*R**,2*R**,1'*S**)-**2e** was determined by the single-crystal X-ray diffraction of the tetraphenylborate salt [(1*R**,2*R**,1'*S**)-**2e-BPh$_4$**] prepared by ion exchange. CCDC-1553029 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the CCDC via www.ccdc.cam.ac.uk/data_request/cif. Experimental details: see the ESI.
18 Previously, it was reported that this type of intermediate would be generated in an ylide rearrangement under aprotic conditions: S. Okazaki, N. Shirai and Y. Sato, *J. Org. Chem.*, 1990, **55**, 334; see also, ref. 4i.
19 The stereochemistry was tentatively determined by analogy with our previous work, see ref. 7.
20 Previous examples of isolation of dearomatized product from *N*-benzylic ammonium ylide: see ref. 2g, 2h and 2i.

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21 T. Tanako, K. Hiramatsu, Y. Kobayashi and H. Ohno, *Tetrahedron*, 2005, **61**, 6726.

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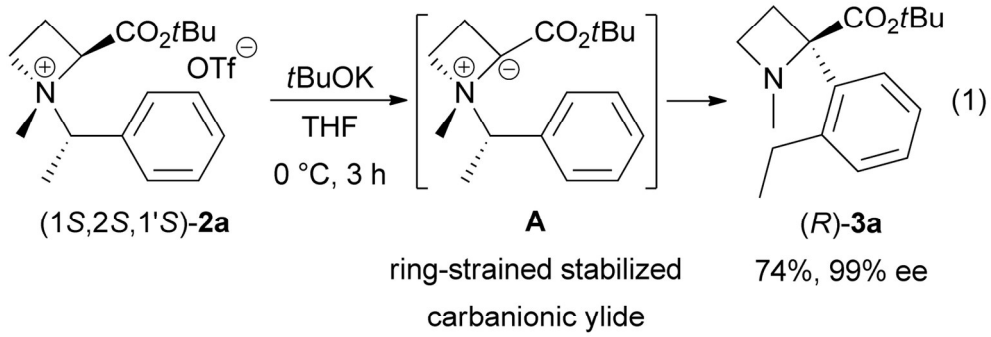
Previous work

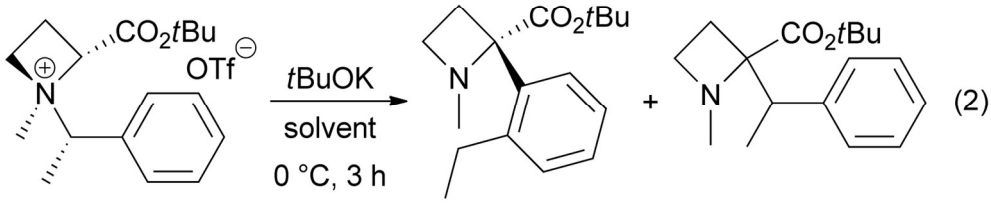


(1*S*,2*S*,1'*S*)-**2a** **A** (*R*)-**3a**

ring-strained stabilized carbanionic ylide

74%, 99% ee

Unreported result



(1*R*,2*R*,1'*S*)-**2a** (*S*)-**3a** **4a**

THF:	15%, 66% ee	27%, 89% ee
DMPU:	40%, 85% ee	17%, 95% ee
		(single diastereomer)

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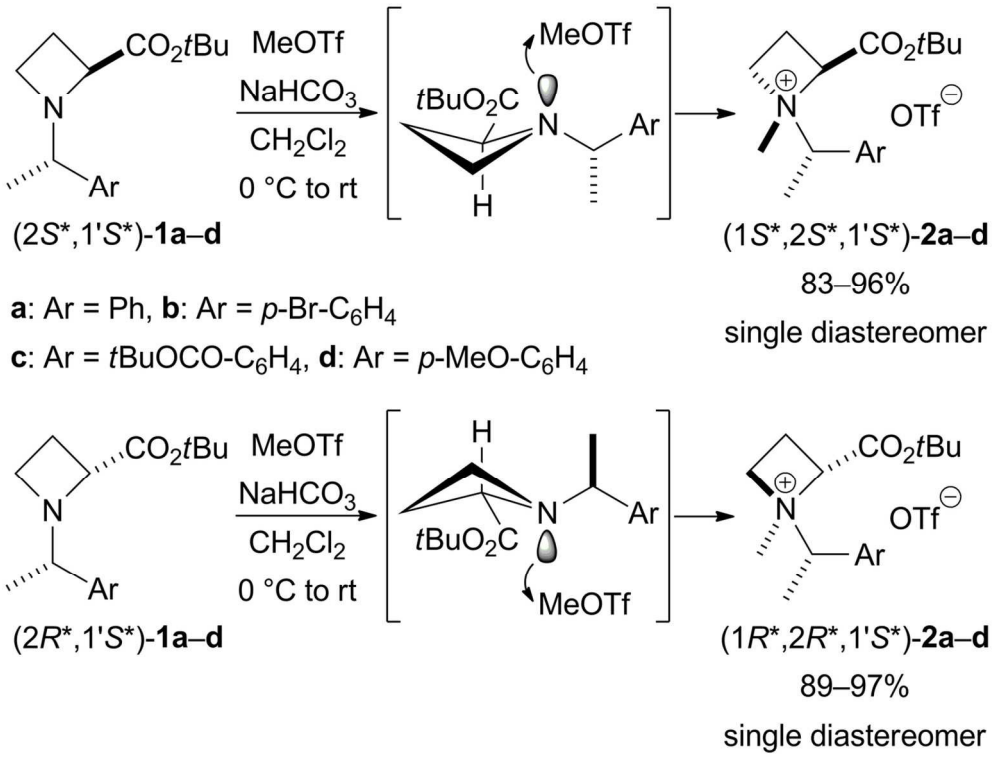

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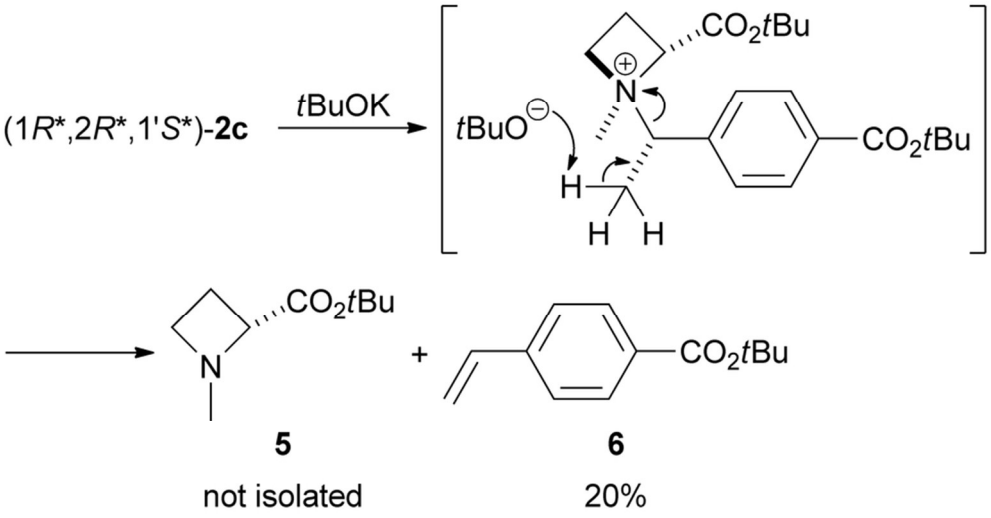

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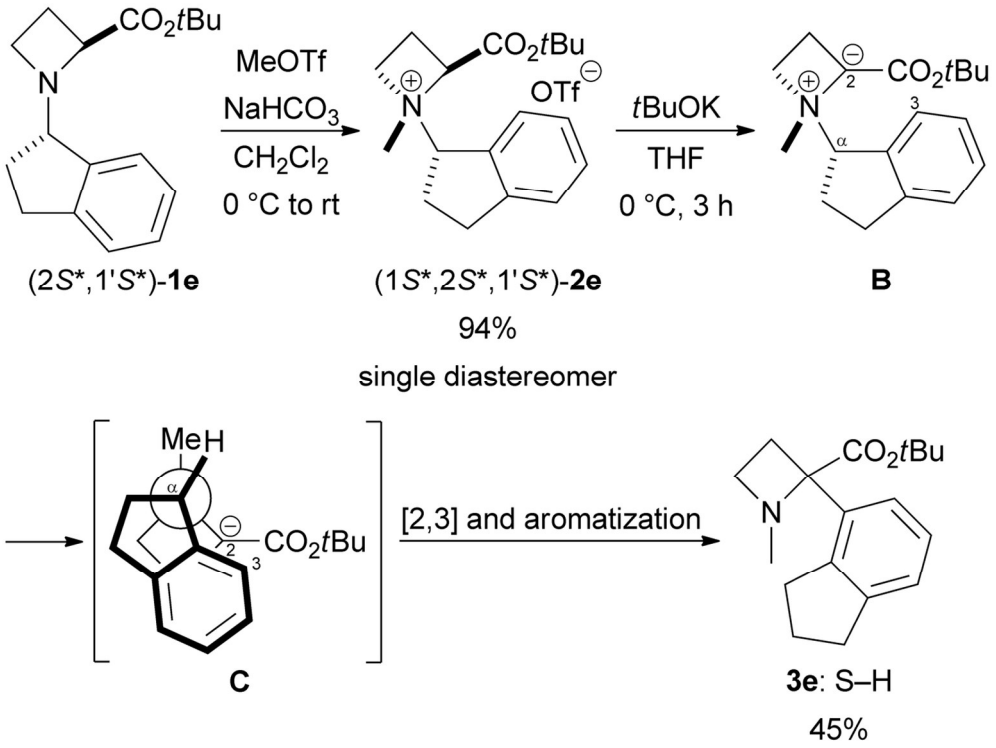

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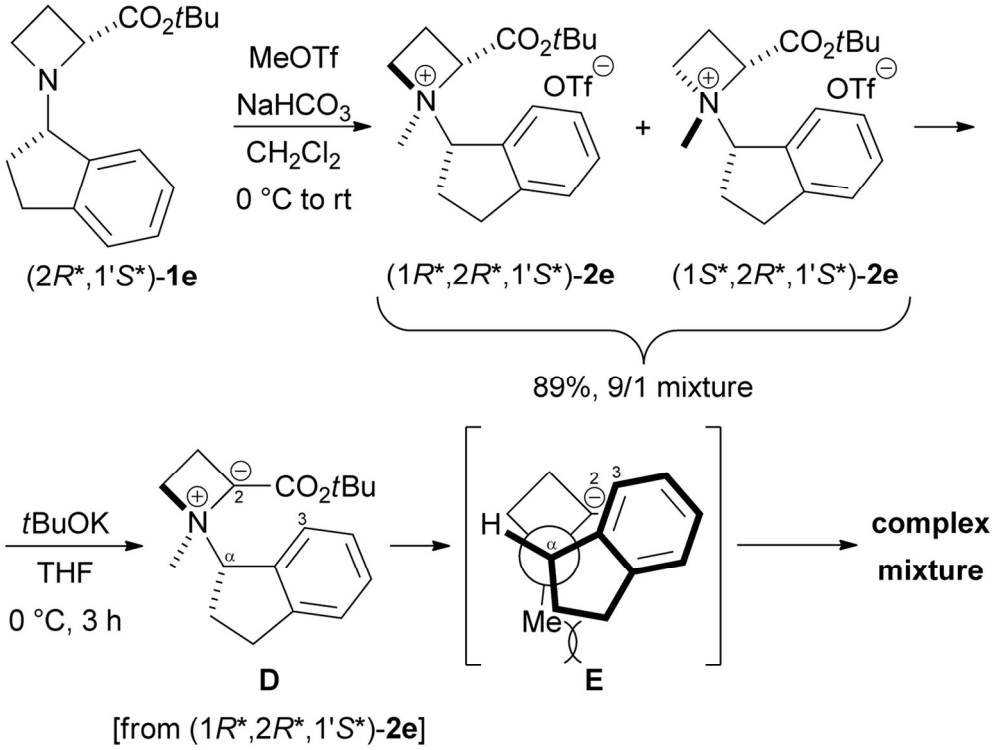

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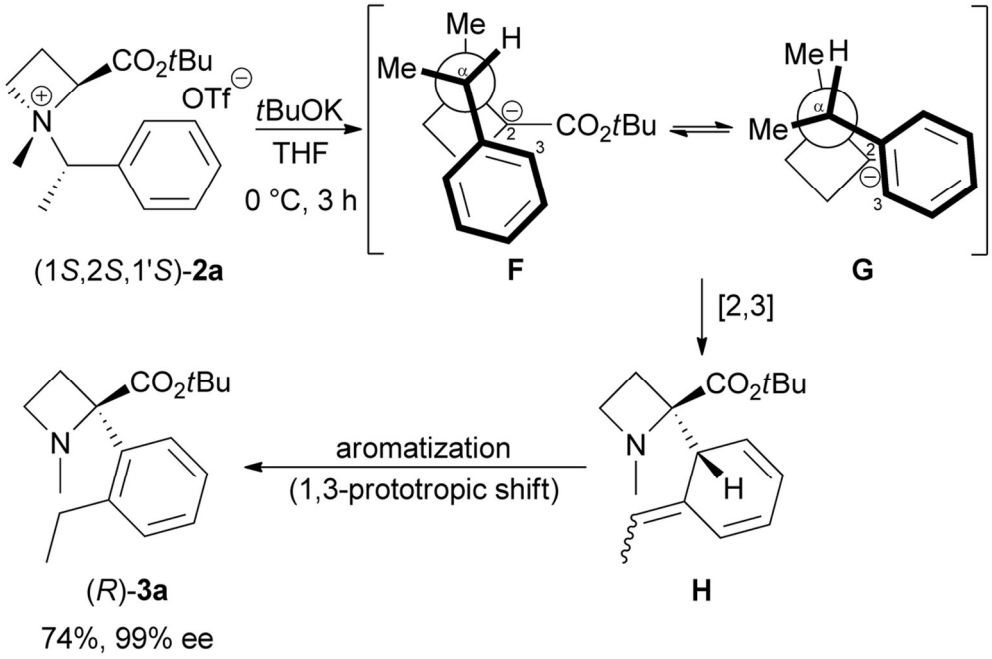

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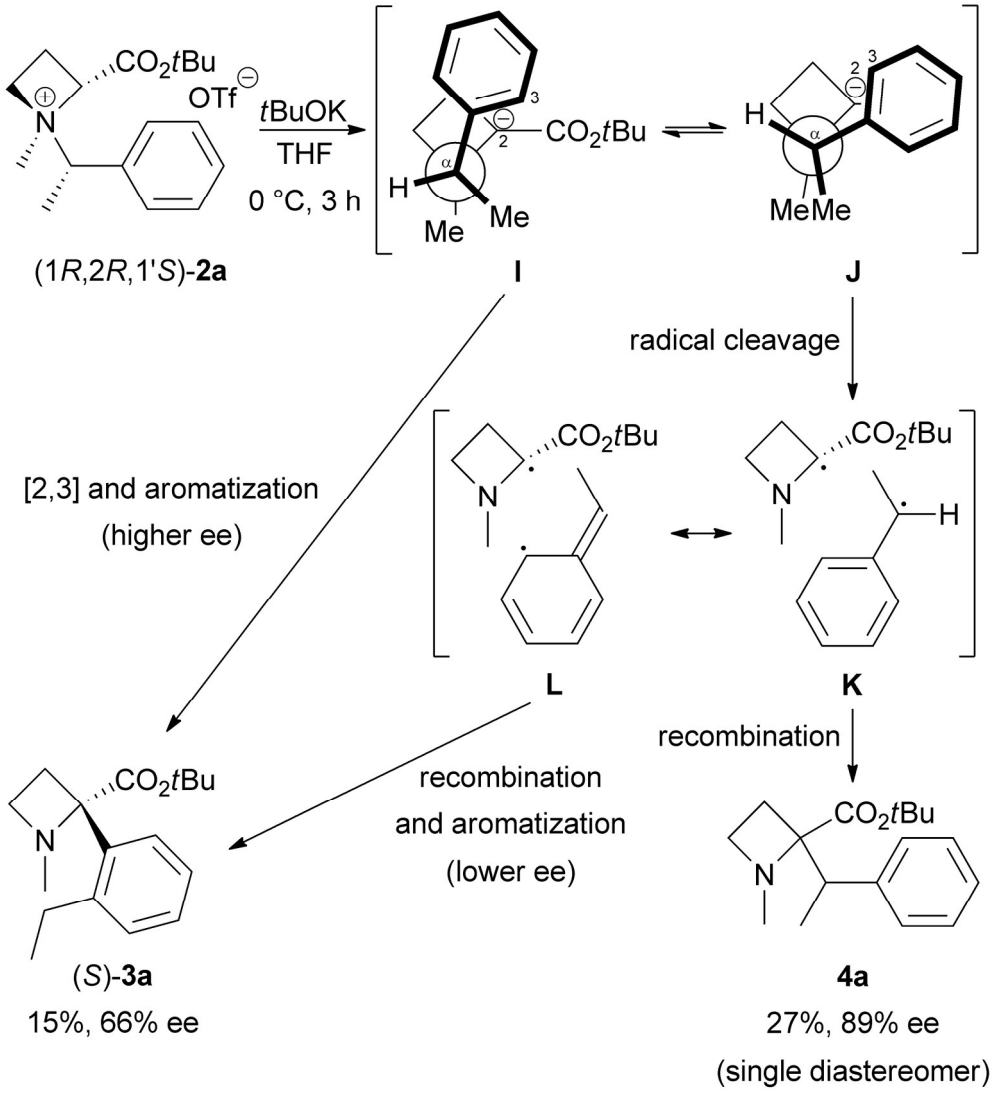

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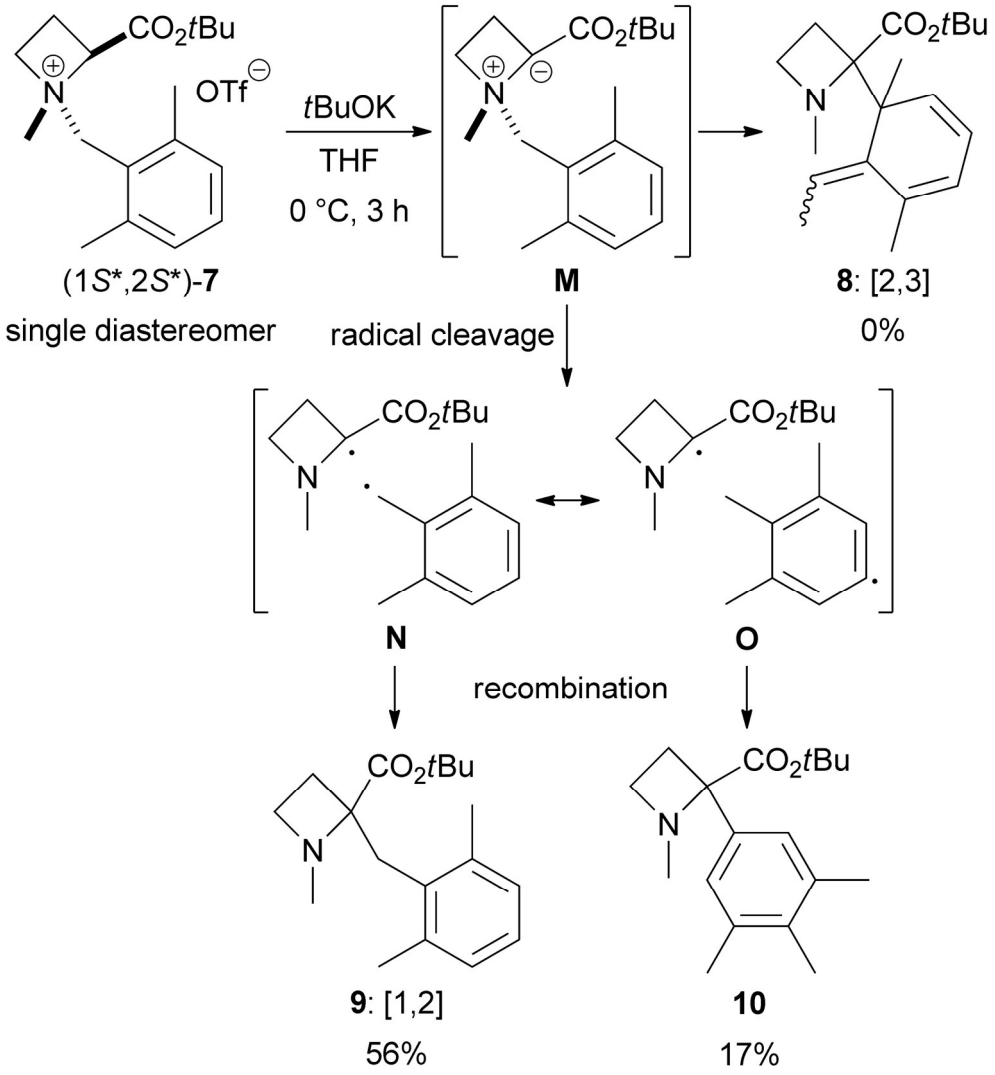

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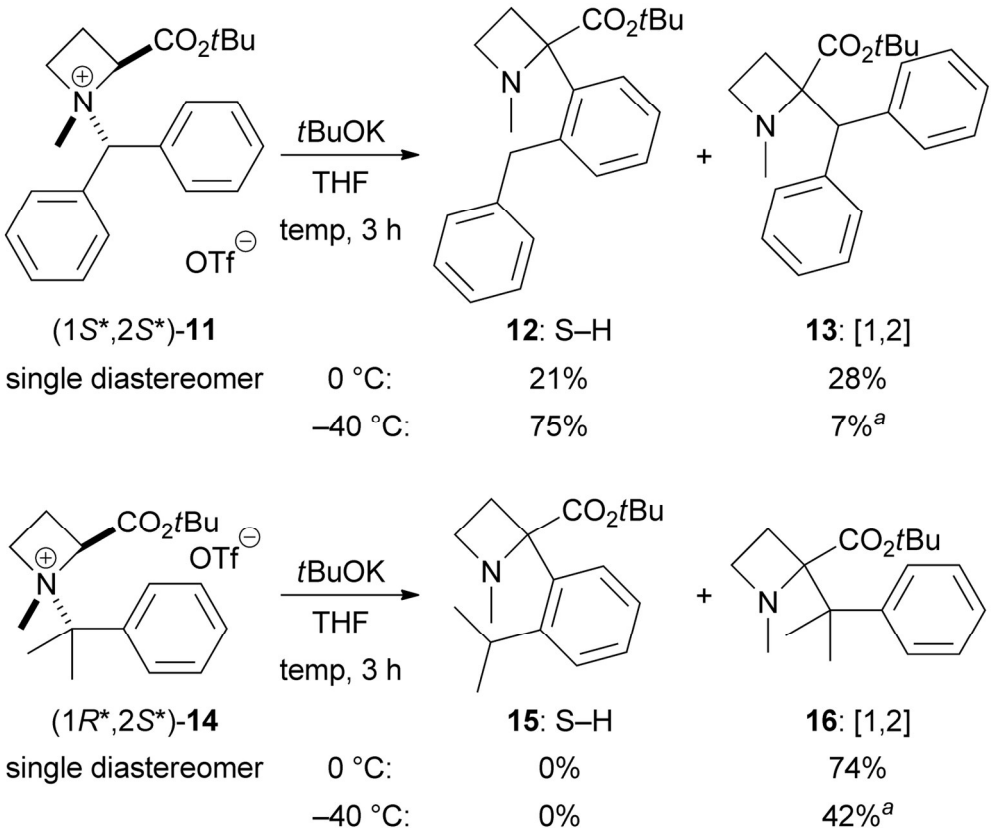

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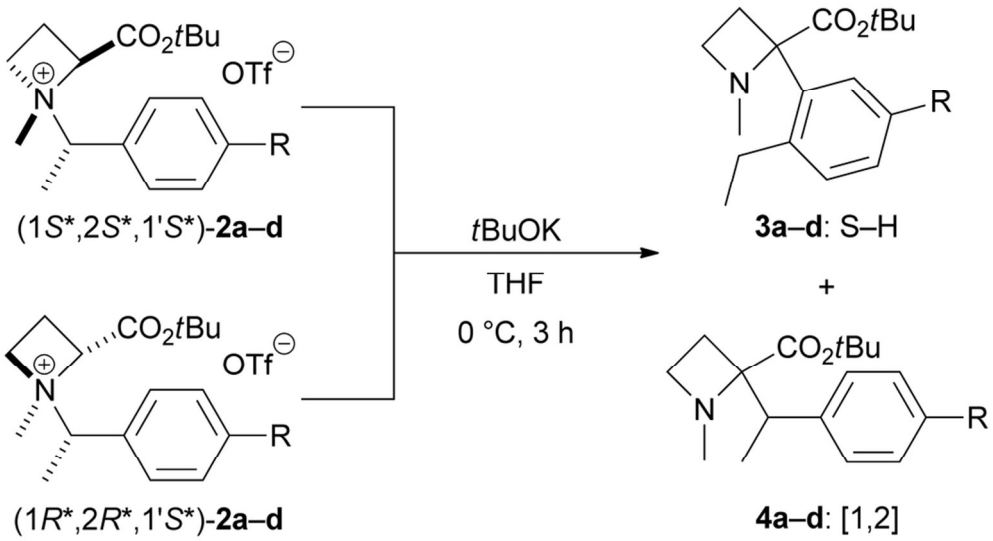

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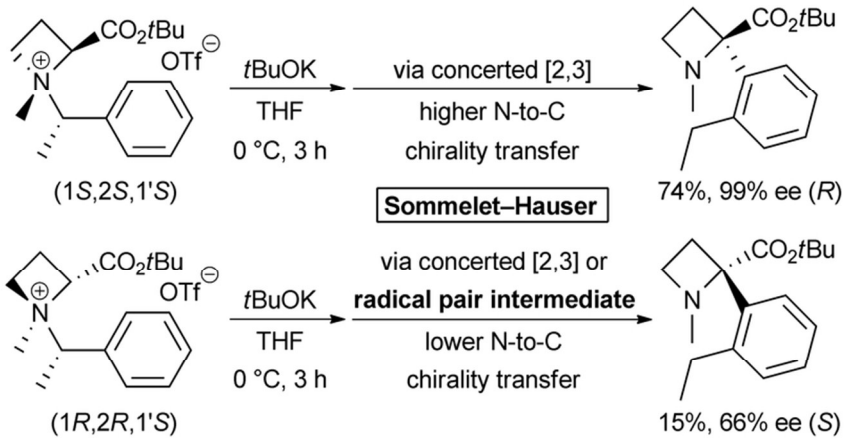
The base-induced Sommelet–Hauser rearrangement of *N*-α-branched benzylic azetidine-2-carboxylic acid ester-derived ammonium salts was demonstrated.



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