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Asymmetric Synthesis of Bicyclic Nitrocyclopropanes from Primary Nitro Compounds and Stereoselective Formation of Tetrahydro-2*H*-cyclopenta[*b*]furans via Ring Expansion/Cyclization Reaction

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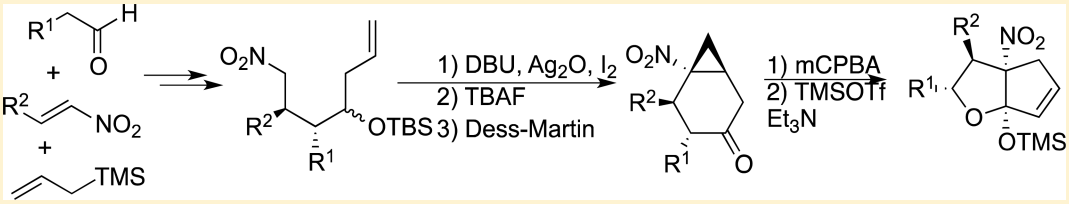
Supporting Information



ABSTRACT: Optically active bicyclic nitrocyclopropanes are readily prepared from primary chiral nitro compounds, prepared by the conjugate addition of propionaldehyde to a nitro alkene in the presence of proline-derived organocatalysts. The one-step cyclopropanation took place smoothly in a highly stereoselective manner regardless of the stereogenic center adjacent to the allylic unit. Although the allylation reaction catalyzed by $BF_3{\cdot}OEt_2$ provides a mixture of two possible diastereomers, subsequent oxidation of the alcoholic carbon after the formation of nitrocyclopropanes gave diastereomerically pure single products. As a result, separation of the diastereomers during the reaction sequence is unnecessary. Baeyer–Villiger oxidation of the bicyclic nitrocyclopropane ketones followed by enolization resulted in stereoselective formation of a novel cyclopenta[*b*]furan ring in good yield via ring expansion followed by transannular nucleophilic cyclization.

INTRODUCTION

Cyclopropanes are recognized as an important unit in natural and biologically active compounds, and the formation of cyclopropanes has been of interest in organic synthesis.[1] Cyclopropanation by diazo compounds using organometallic catalysts,[2] Simmons–Smith-type reactions,[3] conjugate addition–substitution reactions,[4] and the Kulinkovic reaction[5] are representative methods for the formation of cyclopropanes. Nitrocyclopropanes[6] are regarded as precursors to aminocyclopropane,[7] a unit observed among many biologically active compounds where the nitro group is potentially converted to amino group by reductive treatment.[8] For example, the preparation of nitrocyclopropanes has been explored by Charrett and co-workers using an α-nitroester by oxidative generation of carbene intermediate.[9] Asymmetric cyclopropanation by Michael-induced ring closure reactions using bromonitromethane was also reported.[10] Recently, we found that the oxidative treatment of primary nitro compounds readily provided nitrocyclopropanes in a stereoselective manner.[11] This method provided a useful preparation of bicyclic nitrocyclopropanes in which the nitro group is located at the bridge-head position. These compounds are expected to be precursors to bicyclic amino cyclopropanes[12] that include bioactive products.[13] Preparation of optically active nitrocyclopropanes is regarded as important to access such compounds. Optically active primary nitro compounds that have an aldehyde unit can be prepared by conjugate addition of aliphatic aldehydes to nitroalkenes, and the addition reaction is modified in an enantioselective manner using a chiral organocatalyst.[14] Following allylation would afford the precursors of the cyclopropanation. To the best of our knowledge, there has been no report to prepare such bicyclic nitrocyclopropanes in an enantioselective form. In this paper, we report a useful preparation of optically active bicyclic nitrocyclopropanes from primary chiral nitro compounds in a multistep sequence. We also report that subsequent Baeyer–Villiger oxidation of the bicyclic nitrocyclopropanes followed by enolization with $TMSOTf/Et_3N$ resulted in the novel formation of tetrahydro-2*H*-cyclopenta[*b*]furans in a highly stereoselective manner. This transformation is regarded to proceed through a ring cleavage/expansion reaction of the cyclopropane moiety followed by a novel nucleophilic transannular cyclization[15] by the nitronate anion to the lactone carbonyl function.

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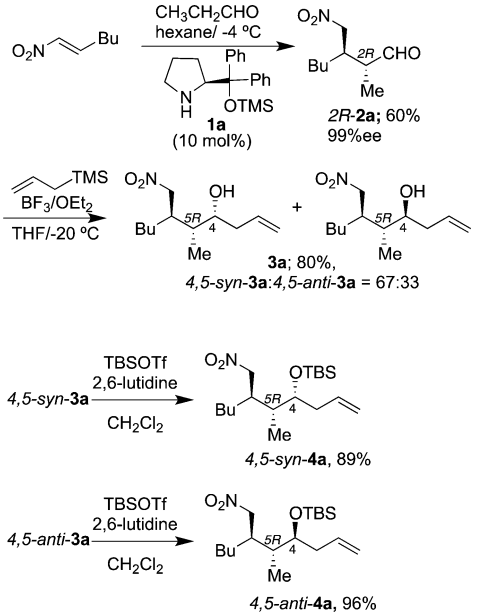
RESULTS AND DISCUSSION

The starting material for the synthesis of nitrocyclopropane **5a** was nitro aldehyde **2a**, prepared by asymmetric conjugate addition to a nitro alkene catalyzed by an L-proline-derived organocatalyst **1a**, giving 2*R*-**2a** in 99% ee (Scheme 1).[14]

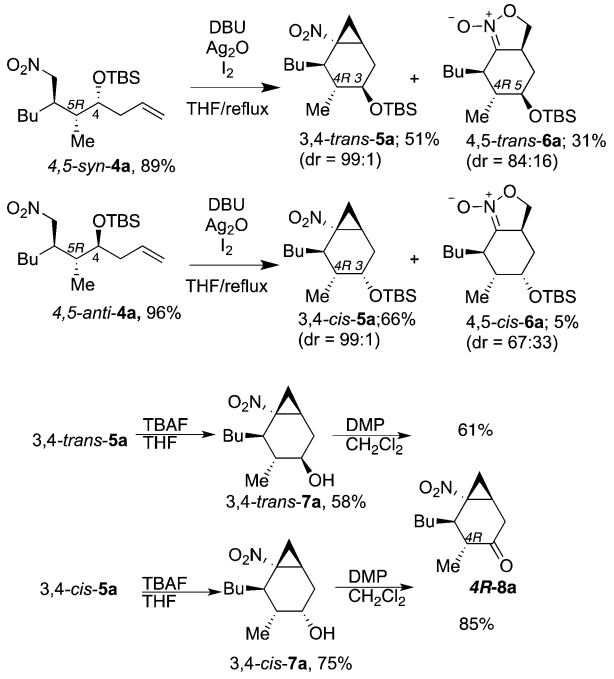
Scheme 1



Treatment of compound **2a** with allyltrimethylsilane in the presence of $BF_3{\cdot}OEt_2$ resulted in the smooth formation of the allylated product **3a** in 81% yield. Unfortunately, stereoselectivity of the allylation was not high, and the two possible diastereomers 4,5-*syn*-**3a** and 4,5-*anti*-**3a** were formed in an approximate 2:1 ratio. The separation of the two diastereomers was achieved by usual column chromatographic purification, and each of the diastereomers was protected by the TBS group to give 4,5-*syn*-**4a** and 4,5-*anti*-**4a**.

Cyclopropanation of **4a** was examined under oxidative conditions; thus, 4,5-*syn*-**4a** was treated with DBU and Ag_2O in the presence of I_2 under refluxing THF conditions. Compound 4,5-*syn*-**4a** was consumed within 1 h, and the two products, cyclopropanes **5a** and isoxazoline-*N*-oxide **6a**, were obtained in 51% and 31% yields, respectively. Both products contained single isomers, and the formation of **5a** and **6a** occurred in a stereoselective manner. The same treatment of 4,5-*anti*-**4a** resulted in the formation of **5a** in 66% yield, but the formation of **6a** occurred in only 5% yield. Compounds **5a** and **6a** formed here were different diastereomers of **5a** and **6a** that were obtained from 4,5-*syn*-**4a**, respectively. Fortunately, compound **5a** derived from 4,5-*anti*-**4a** gave a good crystal for X-ray analysis, which clearly indicated 3,4-*cis*-configuration in **5a** as shown in Scheme 2.[16] To determine the stereochemistry of **5a** derived from 4,5-*syn*-**4a**, the following experiments were performed. The TBS group in *trans*- and *cis*-**5a** was removed by treatment with TBAF in THF, and the corresponding alcohols *trans*- and *cis*-**7a** were obtained in 58% and 75%, respectively. Exposure of each of **7a** to Dess−Martin periodinane led to the conversion to ketone **8a** in 61% and 85%, respectively. Compound **8a** obtained from the two isomers of **7a** showed identical NMR spectra. These data clearly suggest that the difference of configuration between the

Scheme 2



two isomers of **5a** was only the configuration at C3 position, and configurations at the other stereogenic centers were the same. Thus, 3,4-*trans*-**5a** was produced from the reaction of 4,5-*syn*-**4a**.

These results clearly suggest that the stereoselectivity of cyclopropanation depends on the configuration at the C6 position of precursor **4a**, which offers the key steric bias to determine the stereoselectivity of the cyclopropanation reaction. Consequently, the configuration of C4 in **4a** has no effect on the stereoselectivity. Based on these results, the present cyclopropanation progresses in a similar mechanism as that of the previous reaction,[11a,b] and we suggest a proposed mechanism shown in Scheme 3. Thus, treatment of the primary nitro group with base and Ag_2O gives an α-nitro radical that undergoes radical cyclization to attack the terminal alkenyl unit. During cyclization, two chair conformations **A** and **B** are possible. However, conformation **A** should be more preferable than **B** because of the steric congestion caused by the axial conformation of both butyl and methyl groups. The radical intermediate **A** undergoes cyclization to give radical **C**, which should be trapped by molecular iodine to give **E**. Then intermediate **E** undergoes intramolecular S_N2 reaction to form nitrocyclopropane 1*S*-**5a** in a stereoselective manner.

Subsequently, we examined the generality of the reaction scheme for the preparation of chiral cyclohexanone-fused nitrocyclopropane of type **8**. Starting materials **2** were prepared by a literature method.[14] The reaction catalyzed by L-proline-derived amine **1a** and D-proline-derived amine **1b** selectively provided 2*R*-**2** and 2*S*-**12** (*ent*-**2**) products, respectively. The enantiomeric excesses of the products were 99%. Although the allylation of **2** and **12** provided the two diastereoisomers of **3** and **13**, the stereogenic center at the hydroxyl group will disappear with the oxidation of **7** and **17**(*ent*-**7**). Therefore, the separation of the diastereomers for the overall conversion is unnecessary. The results are summarized in Tables 1 and 2.

As expected the five-step sequence from chiral nitroaldehyde **2** and **12** (*ent*-**2**) provided chiral cyclohexanone-fused nitro-

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Scheme 3

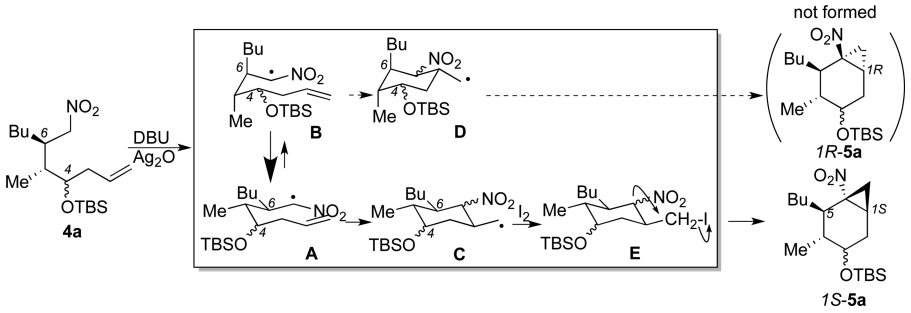
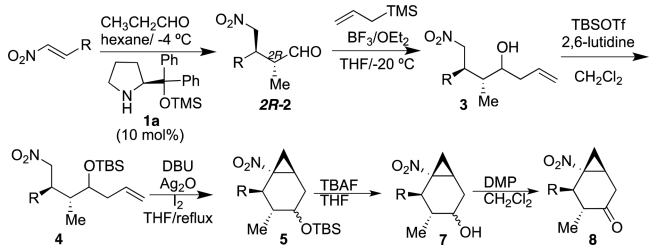


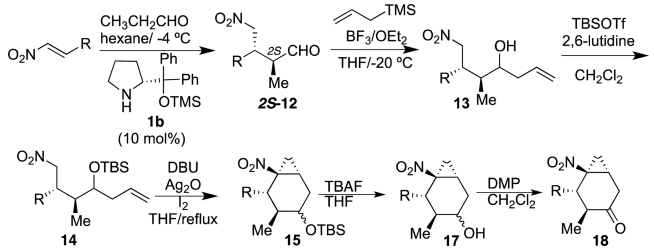
Table 1. Preparation of Cyclohexanone-Fused Nitrocyclopropane 8



entry	R	3; yield (%)[a]	3; ds ratio	4; yield (%)[a]	5; yield (%)[a]	7; yield (%)[a]	8; yield (%)[a]	8; ee (%)[b]
1	Bu	**3a**; 80	67/33	**4a**; 96	**5a**; 74	**7a**; 70	**8a**; 91	99
2	Pr	**3b**; 89	68/32	**4b**; 88	**5b**; 70	**7b**; 89	**8b**; 98	99
3	C_5H_{11}	**3c**; 84	68/32	**4c**; 88	**5c**; 66	**7c**; 79	**8c**; 65	99
4	*i*Pr	**3d**; 89	79/21	**4d** 95	**5d**; 62	**7d**; 79	**8d**; 91	98
5	Et	**3e**; 59	71/29	**4e**; 92	**5e**; 59	**7g**; 95	**8f**; 87	96

[a]Isolated yields. [b]Determined by HPLC analyses using Chiral-Pak IC, YMC CHIRAL Amylose-SA, and YMC Chiral Cellulose-C.

Table 2. Preparation of cyclohexanone-fused nitrocyclopropane 18 (*ent*-8)



entry	R	13; yield (%)[a]	13; ds ratio	14; yield (%)[a]	15; yield (%)[a]	17; yield (%)[a]	18; yield (%)[a]	18; ee (%)[b]
1	Bu	**13a**; 80	73/27	**14a**; 95	**15a**; 63	**17a**; 90	**18a**; 88	98
2	Pr	**13b**; 71	73/27	**14b**; 85	**15b**; 66	**17b**; 90	**18b**; 83	99
3	C_5H_{11}	**13c**; 73	88/12	**14c**; 94	**15c**; 60	**17c**; 75	**18c**; 79	99
4	*i*Pr	**13d**; 84	79/21	**14d**; 93	**15d**; 64	**17d**; 73	**18d**; 84	99
5	Et	**13e**; 67	71/29	**14e**; 97	**15e**; 79	**17e**; 82	**18e**; 86	98
6	*c*-C_6H_{11}	**13f**; 59	89/11	**14f**; 97	**15f**; 68	**17f**; 79	**18e**; 75	99

[a]Isolated yields. [b]Determined by HPLC analyses using Chiral-Pak IC, YMC CHIRAL Amylose-SA, and YMC Chiral Cellulose-C.

cyclopropane **8** and **18** (*ent*-**8**) as a single isomer in good yield. The diastereomeric ratios of **3** were from 67/33 to 89/11 ratios. For example, 3*R*-**2a** underwent allylation upon treatment with allyltrimetylsilane in the presence of $BF_3{\cdot}OEt_2$ to give **3a** in 80% yield in 67:33 diastereomeric mixture. Compound **3a** was subjected to protection of the OH group without separation of the diastereomers. Compound **4a** was prepared in 96% yield, and the diastereomeric ratio did not change. The cyclopropanation of **4a** progressed smoothly by treatment with DBU, Ag_2O, and I_2, and the desired **5a** was isolated as a diastereomeric mixture. The ratio of **5a** was revealed to be 63:37. The ratio only changed slightly, likely due to the difference of the reactivity of the two diastereomers of **4a** toward the cyclopropanation. Following removal of the TBS group and oxidation by Dess−Martin periodinane, we obtained **8a** in good yield as a single isomer. The enantiomeric excess of **8a** was determined by chiral HPLC analyses and was estimated to be 99% ee. Thus, no racemization took place during the five steps of the synthetic sequence. Compound **8** has several functional groups and is a potentially useful synthetic building block. In addition, both enantiomers can be prepared by the choice in the enantiomer of the chiral catalyst. Therefore, this

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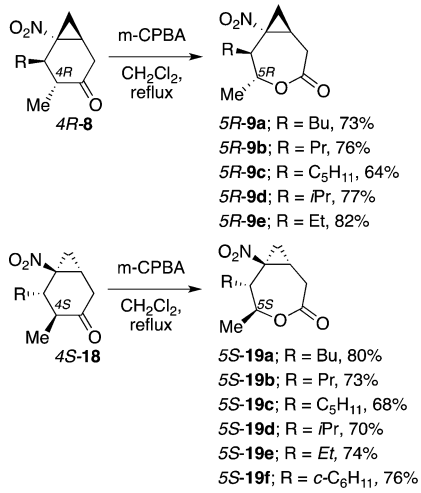
synthetic sequence will provide a useful method for nitrocyclopropane synthesis.

To enhance the present synthetic sequence, we attempted to cleave the carbocyclic ring by Baeyer–Villiger oxidation (Scheme 4). Exposure of compound **8** or **18** to mCPBA

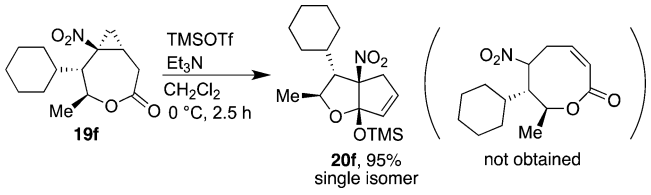
Scheme 4



under refluxing CH_2Cl_2 conditions resulted in the selective introduction of an oxygen atom into the carbocyclic ring, and corresponding lactone **9** or **19**, respectively, was obtained in good yields. The oxidation exclusively progressed on the C4 side of **8** or **18**, and single isomers of **9** or **19** were obtained in all cases.

To achieve ring opening/expansion via ketene acetal formation from the bicyclic lactones, we treated compound **19f** with TMSOTf/Et_3N at −30 °C and obtained product **20f** in good yield. However, isolated compound **20f** did not show any carbonyl carbon peaks in the ^{13}C NMR spectrum as well as did not show carbonyl stretching bands in the IR spectra. Conversely, a new carbon peak appeared around 110 ppm in the ^{13}C NMR spectrum, indicating the presence of an acetal carbon in compound **20f**. Fortunately, compound **20f** gave a good crystal suitable for X-ray crystallographic analysis.[17] To our surprise, the obtained structure was not an eight-membered lactone as we expected but was a tetrahydro-2*H*-cyclopenta[*b*]furan (Scheme 5). Note that the product **20f** contained a diastereomerically single compound. Thus, the reaction progressed in a very stereoselective manner.

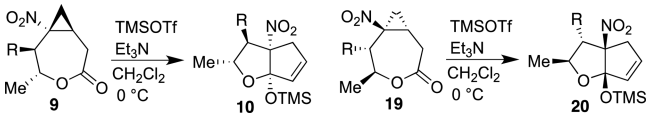
Scheme 5



To check the generality of the conversion, we exposed a variety of bicyclic lactones **9** and **19** to these reaction conditions. The results are summarized in Table 3.

The reaction progressed smoothly within several hours, and tetrahydro-2*H*-cyclopenta[*b*]furans were obtained in good yields. The products always contained only a single isomer,

Table 3. Conversion of 9 or 19 to Tetrahydro-2H-cyclopenta[*b*]furan 10 or 20



entry	substrate	R	time (h)	yield (%)[a]
1	**9a**	Bu	3	**10a**; 87
2	**9b**	Pr	1.5	**10b**; 48
3	**9c**	C_5H_{11}	1.5	**10c**; 93
4	**9e**	Et	1.5	**10e**; 86
5	**19a**	Bu	2.5	**20a**; 93
6	**19b**	Pr	1.5	**20b**; 77
7	**19c**	C_5H_{11}	1	**20c**; 98
8	**19d**	*i*Pr	4.5	**20d**; 74
9	**19e**	Et	2	**20e**; 86

[a]Isolated yields.

and no diastereoieomers were observed. Thus, the diastereoselectivity of the reaction was very high. The TMS ether moiety of the products was very stable, and no decomposition on silica gel chromatography was observed.

We assume a reaction mechanism shown in Scheme 6. Exposure of lactone **19** to TMSOTf resulted in the conversion to ketene acetal **A**, which undergoes a ring opening/expansion reaction to give zwitter ionic eight-membered lactone **B**. Because the lactone carbonyl group in **B** is activated and should be located close to the nitronate anionic part, nucleophilic ring closure gives compound **20**. Lactone intermediate **B** has two types of conformations, **C** and **D**, for the formation of the bicyclic system. Conformation **D** should be less favored due to the steric hindrance between the methyl group and hydrogen in the β-position of unsaturated system, caused by transannular effect. As a result, ring closure progressed through the conformation **C** to exclusively give diastereomer **20**. This is the first example of nucleophilic cyclization of lactone carbonyl by a nitronate anion, although a few examples of similar cyclization by a heteroatom nucleophile were reported.[18] The cyclopenta[*b*]furan structure is regarded as potentially useful in organic synthesis,[19] and we are now investigating new uses of these compounds in organic synthesis.[20]

In conclusion, we have successfully developed a chiral modification of one-step cyclopropanation of primary nitro compounds. Oxidative cyclopropanation using DBU, Ag_2O, and I_2, and related synthetic processes did not affect the chiral centers introduced during the chiral Michael addition reaction catalyzed by organocatalysts. Desired bicyclic nitrocyclopropanes are isolated as a single isomer, although allylation reaction gave the two diastereomers in approximately 2:1 to 8:1 ratios. The obtained bicyclic nitrocyclopropanes are converted to tetrahydro-2*H*-cyclopenta[*b*]furans via a Baeyer–Villiger reaction followed by a ring expansion/transannular cyclization reaction. The present procedure provides a useful preparation of optically active nitrocyclopropanes and nitro cyclopenta[*b*]-furans that are regarded as potentially useful synthetic building blocks in organic synthesis.

EXPERIMENTAL SECTION

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)dec-1-en-4-ol (3a). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (0.7 mL, 5.57 mmol) was added to a solution of allyltrimethylsilane (0.88 mL, 5.47 mmol) and compound **2a** (0.6812 g, 3.64 mmol) in CH_2Cl_2 (3 mL) at −20 °C, and the

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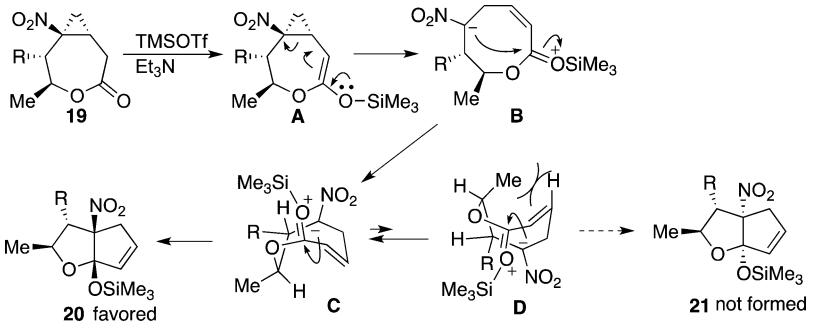
Scheme 6



reaction mixture was stirred at the same temperature for 14 h. Aqueous $NaHCO_3$ (30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 30:1 to 7:1) to give **3a** in 80% yield (0.6612 g, 2.89 mmol). Further careful separation by flash chromatography provided diastereomerically pure *syn*-**3a** (0.3012 g) and *anti*-**3a** (0.1720 g).

syn-3a. Colorless oil; $[\alpha]_D$ −21.4 ($CHCl_3$, *c* 1.04); ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (dddd, *J* = 16.7, 10.4, 8.2, 6.2 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.52 (dd, *J* = 12.6, 5.7 Hz, 1H), 4.41 (dd, *J* = 12.6, 7.8 Hz, 1H), 3.75−3.66 (m, 1H), 2.35−2.14 (m, 3H), 1.76−1.66 (m, 1H), 1.55−1.44 (m, 2H), 1.37−1.20 (m, 5H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 119.1, 78.3, 70.1, 41.5, 40.5, 37.6, 29.2, 28.9, 22.8, 14.0, 10.7; HRMS (ESI-TOF): calcd for $C_{12}H_{23}NNaO_3$, 252.1576 [M + Na^+], found 252.1574.

anti-3a. Colorless oil; $[\alpha]_D$ +30.4 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 5.86−5.74 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 5.17 (d, *J* = 17.3 Hz, 1H), 4.43 (dd, *J* = 11.9, 5.4 Hz, 1H), 4.33 (dd, *J* = 11.9, 9.5 Hz, 1H), 3.50−3.41 (m, 1H), 2.77 (dtt, *J* = 9.2, 5.8, 2.9 Hz, 1H), 2.44 (dddt, *J* = 11.5, 5.7, 2.5, 1.2 Hz, 1H), 2.10−2.00 (m, 1H), 1.60 (d, *J* = 4.7 Hz, 1H), 1.56−1.49 (m, 2H), 1.41−1.22 (m, 4H), 1.17−1.04 (m, 1H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 119.6, 78.4, 71.5, 39.9, 39.3, 37.9, 29.7, 26.5, 22.9, 14.1, 11.2; HRMS (ESI-TOF): calcd for $C_{12}H_{23}NNaO_3$, 252.1576 [M + Na^+], found 252.1569.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)non-1-en-4-ol (3b). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.2 mL, 9.5 mmol) was added to a solution of allyltrimethylsilane (1.5 mL, 9.3 mmol) and compound **2b** (1.0582 g, 6.11 mmol) in CH_2Cl_2 (12 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 12 h. Aqueous NH_4Cl-$NaHCO_3$ buffer solution (2:1 v/v, 30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 to 5:1) to give **3b** in 71% yield (0.9367 g, 4.35 mmol).

Colorless oil; $[\alpha]_D$ −17.6 ($CHCl_3$, *c* 1.00 for *syn*-**3b**), +20.5 ($CHCl_3$, *c* 1.00 for *anti*-**3b**); ^1H NMR (500 MHz, $CDCl_3$) δ 5.86−5.70 (m, 1H), 5.22−5.11 (m, 2H), 4.52 (ddd, *J* = 12.6, 5.7, 0.6 Hz, 1H for *syn*-**3b**), 4.42 (dd, *J* = 7.0, 5.9 Hz, 1H for *anti*-**3b**), 4.39 (dd, *J* = 12.3, 8.0 Hz, 1H for *syn*-**3b**), 4.32 (ddd, *J* = 12.0, 9.4, 0.6 Hz, 1H for *anti*-**3b**), 3.70 (dt, *J* = 8.1, 3.9 Hz, 1H for *syn*-**3b**), 3.45 (td, *J* = 8.7, 2.9 Hz, 1H for *anti*-**3b**), 2.79 (tdt, *J* = 9.2, 5.8, 3.1 Hz, 1H for *anti*-**3b**), 2.44 (dddt, *J* = 13.8, 6.0, 2.8, 1.4 Hz, 1H for *anti*-**3b**), 2.37−2.13 (m, 3H for *syn*-**3b**), 2.12−1.98 (m, 1H for *anti*-**3b**), 1.75−1.66 (m, 1H for *syn*-**3b**), 1.65−1.26 (m, 5H), 1.09 (dtd, *J* = 13.4, 10.0, 4.9 Hz, 1H for *anti*-**3b**), 0.98 (dd, *J* = 7.0, 0.6 Hz, 3H for *syn*-**3b**), 0.93 (t, *J* = 7.0 Hz, 3H for *anti*-**3b**), 0.90 (d, *J* = 7.0 Hz, 3H for *syn*-**3b**), 0.84 (dd, *J* = 7.0, 0.6 Hz, 3H for *anti*-**3b**); ^{13}C NMR (126 MHz, $CDCl_3$) for *anti*-**3b**: δ 134.3, 119.6, 78.4, 71.4, 39.9, 39.3, 37.7, 28.9, 20.7, 14.3, 11.1; for *syn*-**3b**: δ 134.6, 119.1, 78.3, 70.1, 41.3, 40.6, 37.6, 31.4, 20.2, 14.2, 10.8; HRMS (ESI-TOF): calcd for $C_{11}H_{22}NO_3$, 216.1600 [M + H^+], found 216.1593.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)undec-1-en-4-ol (3c). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.1 mL, 8.7 mmol) was added to a solution of allyltrimethylsilane (1.5 mL, 9.3 mmol) and compound **2c** (1.2454 g, 6.19 mmol) in CH_2Cl_2 (8 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 5 h. Aqueous NH_4Cl-$NaHCO_3$ buffer solution (2:1 v/v, 30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 to 5:1) to give **3c** in 73% yield (1.1019 g, 4.53 mmol).

Colorless oil; $[\alpha]_D$ −16.3 ($CHCl_3$, *c* 1.00 for *syn*-**3c**), +34.0 ($CHCl_3$, *c* 1.07 for *anti*-**3c**); ^1H NMR (500 MHz, $CDCl_3$) δ 5.86−5.71 (m, 1H), 5.22−5.11 (m, 2H), 4.52 (dd, *J* = 12.6, 5.7 Hz, 1H for *syn*-**3c**), 4.43 (dd, *J* = 10.4, 5.6 Hz, 1H for *anti*-**3c**), 4.39 (dd, *J* = 14.0, 11.5 Hz, 1H for *syn*-**3c**), 4.32 (dd, *J* = 11.9, 9.5 Hz, 1H for *anti*-**3c**), 3.70 (dq, *J* = 7.9, 3.8 Hz, 1H for *syn*-**3c**), 3.49−3.40 (m, 1H for *anti*--**3c**), 2.82−2.71 (m, 1H for *anti*-**3c**), 2.48−2.39 (m, 1H for *anti*-**3c**), 2.35−2.13 (m, 3H for *syn*-**3c**), 2.05 (dt, *J* = 14.0, 8.5 Hz, 1H for *anti*-**3c**), 1.76−1.66 (m, 1H for *syn*-**3c**), 1.62−1.19 (m, 9H), 1.17−1.04 (m, 1H for *anti*-**3c**), 0.98 (d, *J* = 7.0 Hz, 3H for *syn*-**3c**), 0.87 (t, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H for *anti*-**3c**); ^{13}C NMR (126 MHz, $CDCl_3$) for *anti*-**3c** δ 134.3, 119.6, 78.4, 71.5, 39.9, 39.3, 37.9, 32.0, 27.3, 26.7, 22.6, 14.1, 11.1; for *syn*-**3c**: δ 134.6, 119.1, 78.3, 70.1, 41.5, 40.6, 37.6, 31.9, 29.1, 26.7, 22.6, 14.1, 10.7; HRMS (ESI-TOF): calcd for $C_{13}H_{25}NNaO_3$, 266.1732 [M + Na^+], found 266.1732.

(5*R*,6*R*)-5,7-Dimethyl-6-(nitromethyl)oct-1-en-4-ol (3d). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (0.41 mL, 3.26 mmol) was added to a solution of allyltrimethylsilane (0.56 mL, 3.5 mmol) and compound **2d** (0.4065 g, 2.35 mmol) in CH_2Cl_2 (10 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 19 h. Aqueous $NaHCO_3$ solution (20 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 8:1 to 5:1) to give **3d** in 58% yield (0.2982 g, 1.36 mmol).

Colorless oil; $[\alpha]_D$ −15.8 ($CHCl_3$, *c* 1.04); ^1H NMR (500 MHz, $CDCl_3$) δ 5.82−5.70 (m, 1H), 5.22−5.11 (m, 2H), 4.60 (dd, *J* = 13.8, 4.4 Hz, 1H for *syn*-**3d**), 4.46−4.40 (m, 1H), 4.39 (dd, *J* = 14.3, 7.0 Hz, 1H for *anti*-**3e**), 3.76−3.72 (m, 1H for *syn*-**3d**), 3.51 (d, *J* = 8.8 Hz, 1H for *anti*-**3d**), 2.47 (t, *J* = 5.8 Hz, 1H for *anti*-**3d**), 2.41 (dd, *J* = 14.3, 5.9 Hz, 1H for *anti*-**3d**), 2.28−2.16 (m, 3H for *syn*-**3d**), 2.11−1.97 (m, 1H for *anti*-**3d**), 1.97−1.85 (m, *J* = 6.8 Hz, 1H), 1.81 (p, *J* = 7.0 Hz, 1H), 1.50 (d, *J* = 3.6 Hz, 1H), 1.04 (d, *J* = 7.1 Hz, 3H for *anti*-**3d**), 1.00 (d, *J* = 7.1 Hz, 3H for *syn*-**3d**), 0.97 (d, *J* = 6.8 Hz, 3H for *syn*-**3d**), 0.95 (d, *J* = 7.0 Hz, 3H for *anti*-**3d**), 0.88 (d, *J* = 6.9 Hz, 3H for *syn*-**3d**), 0.85 (d, *J* = 7.0 Hz, 3H for *anti*-**3d**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**3d**: 134.5, 119.5, 76.1, 71.8, 44.3, 39.9, 39.4, 27.1, 22.6, 18.5, 13.2; for *syn*-**3d**: 134.7, 118.9, 76.4, 70.0, 47.1, 40.6, 37.2, 29.0, 21.3, 18.9, 11.7;

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HRMS (ESI-TOF): calcd for $C_{11}H_{21}NNaO_3$, 238.1419 [M + Na^+], found 238.1413.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)oct-1-en-4-ol (3e). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.95 mL, 16.1 mmol) was added to a solution of allyltrimethylsilane (2.6 mL,16.4 mmol) and compound **2e** (1.7292 g, 10.86 mmol) in CH_2Cl_2 (17 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 19 h. Aqueous $NaHCO_3$ solution (20 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 25:1 to 10:1) to give **3e** in 59% yield (1.2859 g, 6.39 mmol).

Pale yellow oil; $[\alpha]_D$ −5.83 ($CHCl_3$, *c* 1.17); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83−5.71 (m, 1H), 5.22−5.12 (m, 2H), 4.54 (dd, *J* = 12.8, 5.8 Hz, 1H for *syn*-**3e**), 4.46 (dd, *J* = 11.8, 5.4 Hz, 1H for *anti*-**3e**), 4.42 (dd, *J* = 12.2, 7.7 Hz, 1H for *syn*-**3e**), 4.33 (dd, *J* = 11.6, 9.0 Hz, 1H for *anti*-**3e**), 3.74−3.68 (m, 1H for *syn*-**3e**), 3.49−3.43 (m, 3H for *anti*-**3e**), 2.72−2.63 (m, 3H for *anti*-**3e**), 2.44 (dd, *J* = 14.7, 5.7 Hz, 3H for *anti*-**3e**), 2.29−2.15 (m, 3H for *syn*-**3e**), 2.07 (dt, *J* = 13.5, 9.0 Hz, 3H for *anti*-**3e**), 1.75−1.71 (m, 1H for *syn*-**3e**), 1.60 (d, *J* = 4.5 Hz, 4H), 1.59−1.50 (m, 2H for *anti*-**3e**), 1.46 (d, *J* = 3.7 Hz, 1H for *syn*-**3e**), 1.41 (dt, *J* = 14.5, 7.3 Hz, 2H for *syn*-**3e**), 1.21−1.10 (m, 1H for *anti*-**3e**), 0.98 (d, *J* = 7.0 Hz, 3H for *syn*-**3e**), 0.95 (t, *J* = 7.7 Hz, 3H for *anti*-**3e**), 0.93 (t, *J* = 7.4 Hz, 3H for *syn*-**3e**), 0.85 (d, *J* = 7.0 Hz, 3H for *anti*-**3e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**3e**: 134.4, 119.5, 78.1, 71.6, 39.9, 39.7, 39.3, 19.7, 12.0, 11.2; for *syn*-**3e**: 134.7, 119.0, 78.0, 70.2, 43.1, 40.5, 37.2, 22.0, 11.4, 10.7; HRMS (ESI-TOF): calcd for $C_{10}H_{19}NNaO_3$, 224.1263 [M + Na^+], found 224.1257.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)dec-1-en-4-ol (13a). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.3 mL, 10.5 mmol) was added to a solution of allyltrimethylsilane (1.8 mL, 11.2 mmol) and compound **12a** (1.3734 g, 7.33 mmol) in CH_2Cl_2 (14 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 19 h. Aqueous NH_4Cl-$NaHCO_3$ buffer solution (2:1 v/v, 30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 to 5:1) to give **13a** in 76% yield (1.2811g, 5.59 mmol). Further chromatographic treatment gave diastereomerically pure isomer of *syn*-**13a** and *anti*-**13a**.

*syn-**13a**.* Colorless oil; $[\alpha]_D$ +19.9 ($CHCl_3$, *c* 1.00); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (dq, *J* = 17.3, 8.4 Hz, 1H), 5.07−5.00 (m, 2H), 4.44 (ddd, *J* = 12.9, 5.8, 4.0 Hz, 1H), 4.31 (ddd, *J* = 11.3, 7.2, 3.2 Hz, 1H), 3.66−3.59 (m, 1H), 2.25−2.07 (m, 3H), 2.04−1.96 (m, 1H), 1.40 (q, *J* = 7.0 Hz, 1H), 1.21 (m, 6H), 0.88 (d, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.7, 118.3, 78.3, 70.2, 41.3, 40.4, 37.4, 29.0, 28.8, 22.7, 13.9, 10.6; HRMS (ESI-TOF): calcd for $C_{12}H_{23}NNaO_3$, 252.1576 [M + Na^+], found 252.1581.

*anti-**13a**.* Colorless oil; $[\alpha]_D$ −29.5 ($CHCl_3$, *c* 1.01); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (dt, *J* = 16.7, 8.4 Hz, 1H), 5.31−5.22 (m, 2H), 4.51 (dd, *J* = 11.7, 5.5 Hz, 1H), 4.41 (dd, *J* = 11.9, 9.6 Hz, 1H), 3.54 (d, *J* = 17.8 Hz, 1H), 2.85 (dtd, *J* = 9.5, 6.2, 2.9 Hz, 1H), 2.53 (dd, *J* = 14.6, 5.6 Hz, 1H), 2.14 (dt, *J* = 14.5, 9.3 Hz, 1H), 1.69 (d, *J* = 5.1 Hz, 1H), 1.66−1.58 (m, 1H), 1.49−1.30 (m, 5H), 1.20 (dt, *J* = 14.7, 7.4 Hz, 1H), 0.98 (t, *J* = 6.1 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 119.6, 78.5, 71.6, 40.0, 39.4, 38.0, 29.8, 26.6, 23.0, 14.1, 11.3; HRMS (ESI-TOF): calcd for $C_{12}H_{23}NNaO_3$, 252.1576 [M + Na^+], found 252.1577.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)non-1-en-4-ol (13b). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.0 mL, 8.1 mmol) was added to a solution of allyltrimethylsilane (1.3 mL, 8.1 mmol) and compound **12b** (0.9300g, 5.37 mmol) in CH_2Cl_2 (8 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 24 h. Aqueous NH_4Cl-$NaHCO_3$ buffer solution (2:1 v/v, 30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 20:1 to 5:1) to give **13b** in 71% yield (0.8122g, 43.77 mmol). Further chromatographic treatment gave diastereomerically pure isomer of *syn*-**13b** and *anti*-**13b**.

*syn-**13b**.* Colorless oil; $[\alpha]_D$ +17.5 ($CHCl_3$, *c* 1.01); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (td, *J* = 16.8, 8.0 Hz, 1H), 5.19−5.11 (m, 2H), 4.52 (dd, *J* = 12.5, 6.2 Hz, 1H), 4.41 (dd, *J* = 12.3, 7.6 Hz, 1H), 3.74−3.68 (m, 1H), 2.36−2.28 (m, 1H), 2.28−2.14 (m, 2H), 1.71 (dd, *J* = 6.8, 3.6 Hz, 1H), 1.64−1.44 (m, 3H), 1.38−1.22 (m, 2H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 119.0, 78.3, 70.1, 41.3, 40.5, 37.6, 31.4, 20.2, 14.2, 10.7; HRMS (ESI-TOF): calcd for $C_{11}H_{21}NNaO_3$, 238.1419 [M + Na^+], found 238.1426.

*anti-**13b**.* Colorless oil; $[\alpha]_D$ −29.8 ($CHCl_3$, *c* 0.98); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86−5.74 (m, 1H), 5.22−5.14 (m, 2H), 4.42 (dd, *J* = 11.3, 5.7 Hz, 1H), 4.33 (dd, *J* = 11.3, 9.1 Hz, 1H), 3.45 (td, *J* = 8.2, 3.4 Hz, 1H), 2.79 (dtd, *J* = 9.4, 6.0, 2.7 Hz, 1H), 2.48−2.40 (m, 1H), 2.04 (dt, *J* = 13.9, 8.6 Hz, 1H), 1.56−1.45 (m, 2H), 1.45−1.28 (m, 4H), 1.15−1.05 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 119.5, 78.5, 71.5, 39.9, 39.4, 37.7, 29.0, 20.7, 14.3, 11.2; HRMS (ESI-TOF): calcd for $C_{11}H_{21}NNaO_3$, 238.1419 [M + Na^+], found 238.1426.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)undec-1-en-4-ol (13c). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.6 mL, 13 mmol) was added to a solution of allyltrimethylsilane (2.2 mL, 14 mmol) and compound **12c** (1.8216 g, 9.05 mmol) in CH_2Cl_2 (15 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 5 h. Aqueous NH_4Cl-$NaHCO_3$ buffer solution (2:1 v/v, 30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 to 5:1) to give **13c** in 73% yield (1.6158g, 6.64 mmol).

Colorless oil; $[\alpha]_D$ +5.14 ($CHCl_3$, *c* 1.05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85−5.70 (m, 1H), 5.20−5.10 (m, 2H), 4.51 (dd, *J* = 12.6, 5.8 Hz, 1H for *syn*-**13c**), 4.40 (d, *J* = 7.4 Hz, 1H for *anti*-**13c**), 4.39 (dd, *J* = 12.6, 7.6 Hz, 1H for *syn*-**13c**), 4.31 (t, *J* = 10.6 Hz, 1H for *anti*-**13c**), 3.73−3.66 (m, 1H for *syn*-**13c**), 3.44 (t, *J* = 8.7 Hz, 1H for *anti*-**13c**), 2.75 (q, *J* = 8.4 Hz, 1H for *anti*-**13c**), 2.42 (dd, *J* = 14.6, 5.7 Hz, 1H for *anti*-**13c**), 2.33−2.14 (m, 2H for *syn*-**13c**), 2.09−1.99 (m, 1H for *anti*-**13c**), 1.73−1.66 (m, 1H for *syn*-**13c**), 1.55−1.43 (m, 2H), 1.36−1.10 (m, 8H), 0.96 (d, *J* = 7.3 Hz, 3H for *syn*-**13c**), 0.86 (t, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H for *anti*-**13c**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**13c**; 134.3, 119.4, 78.4, 71.5, 39.9, 39.3, 37.9, 32.0, 27.2, 26.7, 22.6, 14.1, 11.1; for *syn*-**13c**; 134.6, 119.0, 78.3, 70.1, 41.5, 40.5, 37.5, 31.9, 29.1, 26.6, 22.6, 14.1, 10.7; HRMS (ESI-TOF): calcd for $C_{13}H_{25}NNaO_3$, 266.1732 [M + Na^+], found 266.1735.

(5*S*,6*S*)-5,7-Dimethyl-6-(nitromethyl)oct-1-en-4-ol (13d). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.3 mL, 10 mmol) was added to a solution of allyltrimethylsilane (1.5 mL, 9.3 mmol) and compound **12d** (1.0902g, 6.29 mmol) in CH_2Cl_2 (10 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 5 h. Aqueous $NaHCO_3$ solution (20 mL) was added to the reaction mixture and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 12:1 to 5:1) to give **13d** in 83% yield (1.1279g, 5.24 mmol).

Colorless oil; $[\alpha]_D$ +20.1 ($CHCl_3$, *c* 0.63); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84−5.69 (m, 1H), 5.22−5.10 (m, 2H), 4.60 (ddd, *J* = 14.2, 4.4, 1.6 Hz, 1H for *syn*-**13d**), 4.42 (ddd, *J* = 8.2, 6.4, 1.6 Hz, 1H), 4.38 (ddd, *J* = 15.1, 6.6, 1.5 Hz, 1H for *anti*-**13d**), 3.78−3.69 (m, 1H for *syn*-**13d**), 3.57−3.48 (m, 1H for *anti*-**13d**), 2.52−2.37 (m, 2H for *anti*-**13d**), 2.28−2.16 (m, 3H for *syn*-**13d**), 2.14−1.97 (m, 1H for *anti*-**13d**), 1.96−1.86 (m, 1H), 1.85−1.77 (m, 1H), 1.50 (d, *J* = 3.9 Hz, 1H), 1.03 (dd, *J* = 8.7, 1.5 Hz, 3H for *anti*-**13d**), 1.00 (dd, *J* = 7.0, 1.6 Hz, 3H for *syn*-**13d**), 0.97 (dd, *J* = 6.8, 1.5 Hz, 3H for *syn*-**13d**), 0.94

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J. Org. Chem. 2016, 81, 4664−4681

(dd, J = 7.0, 1.6 Hz, 3H for *anti*-**13d**), 0.87 (dd, J = 6.9, 1.6 Hz, 3H for *syn*-**13d**), 0.85 (dd, J = 6.9, 1.6 Hz, 3H for *anti*-**13d**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**13d**: 134.5, 119.5, 76.1, 71.8, 44.3, 39.9, 39.4, 27.1, 22.6, 18.5, 13.2; *syn*-**13d**: 134.7, 118.9, 76.4, 70.0, 47.1, 40.6, 37.2, 29.0, 21.3, 18.9, 11.7; HRMS (ESI-TOF): calcd for $C_{11}H_{22}NO_3$, 216.1600 [M + H^+], found 216.1599.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)oct-1-en-4-ol (13e). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.74 mL, 13.8 mmol) was added to a solution of allyltrimethylsilane (2.35 mL, 14.8 mmol) and compound **12e** (1.5703g, 9.86 mmol) in CH_2Cl_2 (13 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 48 h. Aqueous $NaHCO_3$ solution (30 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 12:1 to 5:1) to give **13e** in 67% yield (1.337, 6.64 mmol).

Colorless oil; $[\alpha]_D$ +5.84 ($CHCl_3$, c 0.98); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (tq, J = 16.3, 8.1 Hz, 1H), 5.19−5.10 (m, 2H), 4.52 (dd, J = 12.6, 5.6 Hz, 1H for *syn*-**13e**), 4.45 (dd, J = 13.8, 5.5 Hz, 1H for *anti*-**13e**), 4.40 (dd, J = 12.9, 7.9 Hz, 1H for *syn*-**13e**), 4.32 (t, J = 11.5, 9.7 Hz, 1H for *anti*-**13e**), 3.73−3.66 (m, 1H for *syn*-**13e**), 3.45 (t, J = 8.9 Hz, 1H for *anti*-**13e**), 2.70−2.62 (m, 1H for *anti*-**13e**), 2.42 (dd, J = 14.7, 5.2 Hz, 1H for *anti*-**13e**), 2.26−2.13 (m, 3H for *syn*-**13e**), 2.09−2.00 (m, 1H for *anti*-**13e**), 1.73−1.69 (m, 1H for *syn*-**13e**), 1.66−1.47 (m, 3H), 1.45−1.31 (m, 1H for *syn*-**13e**), 1.19−1.07 (m, 1H for *anti*-**13e**), 0.96 (d, J = 7.0 Hz, 3H for *syn*-**13e**), 0.92 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H for *syn*-**13e**), 0.83 (d, J = 7.2 Hz, 3H for *syn*-**13e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**13e**; 134.3, 119.4, 78.1, 71.6, 39.9, 39.7, 39.3, 19.7, 12.0, 11.2; for *syn*-**13e**; 134.6, 119.0, 78.1, 71.6, 43.1, 40.5, 37.2, 22.0, 11.4, 10.8; HRMS (ESI-TOF): calcd for $C_{10}H_{19}NNaO_3$, 224.1263 [M + Na^+], found 224.1269.

(5*S*,6*S*)-6-Cyclohexyl-5-methyl-7-nitrohept-1-en-4-ol (13f). Under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (1.1 mL, 8.7 mmol) was added to a solution of allyltrimethylsilane (1.45 mL, 9.12 mmol) and compound **12f** (1.2872 g, 6.04 mmol) in CH_2Cl_2 (12 mL) at −20 °C, and the reaction mixture was stirred at the same temperature for 24 h. Aqueous $NaHCO_3$ solution (20 mL) was added to the reaction mixture, and organic phase was separated. Aqueous phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 30:1 to 10:1) to give **13f** in 59% yield (0.9043 g, 3.54 mmol). Further chromatographic treatment gave diastereomerically pure isomer of *syn*-**13f**.

Pale yellow oil; $[\alpha]_D$ +19.3 ($CHCl_3$, c 0.86); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85−5.69 (m, 1H), 5.25−5.06 (m, 2H), 4.59 (dd, J = 14.2, 4.2 Hz, 1H for *syn*-**13f**), 4.46 (d, J = 5.1 Hz, 1H for *anti*-**13f**), 4.45−4.39 (m, 1H), 3.71 (t, J = 4.0 Hz, 1H for *syn*-**13f**), 3.51 (t, J = 8.5 Hz, 1H for *anti*-**13f**), 2.55−2.44 (m, 1H for *anti*-**13f**), 2.42 (dd, J = 15.4, 6.3 Hz, 1H for *anti*-**13f**), 2.27−2.15 (m, 3H for *syn*-**13f**), 2.03 (m, 1H for *anti*-**13f**), 1.93−1.42 (m, 7H), 1.35−1.02 (m, 5H), 1.00 (d, J = 7.0 Hz, 3H for *syn*-**13f**), 0.93 (d, J = 7.2 Hz, 3H for *anti*-**13f**), 0.91−0.78 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**13f**: 134.5, 119.5, 76.7, 71.8, 44.0, 39.7, 39.5, 37.5, 33.0, 29.4, 26.9, 26.5, 26.4, 13.3; for *syn*-**13f**: 134.7, 118.9, 76.5, 70.0, 46.6, 40.7, 39.3, 36.6, 31.5, 29.5, 26.6, 26.5, 26.4, 11.8; HRMS (ESI-TOF): calcd for $C_{14}H_{25}NNaO_3$, 278.1732 [M + Na^+], found 278.1724.

(4*R*,5*R*,6*R*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-decene (*syn*-4a). Under nitrogen atmosphere, TBSOTf (0.34 mL, 1.48 mmol) and 2,6-lutidine (0.17 mL, 1.54 mmol) were added to a solution of compound *syn*-**3a** (0.2934 g, 1.28 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 40 h. Water (20 mL) was added, and the organic layer was separated. Water phase was extracted with CH_2Cl_2 (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 v/v) to give *syn*-**4a** in 89% yield (0.3905 g, 1.14 mmol).

Colorless oil; $[\alpha]_D$ −8.0 ($CHCl_3$, c 1.10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.07 (d, J = 17.2 Hz, 1H), 5.04 (d, J = 10.6 Hz, 1H), 4.50 (dd, J = 12.2, 6.1 Hz, 1H), 4.32 (dd, J = 12.2, 7.7 Hz, 1H), 3.73 (td, J = 6.2, 4.0 Hz, 1H), 2.27 (t, J = 10.3 Hz, 2H), 1.70 (qdd, J = 7.0, 5.4, 4.0 Hz, 1H), 1.42 (dddd, J = 10.8, 5.9, 5.2, 2.8 Hz, 1H), 1.35−1.20 (m, 6H), 0.90 (d, J = 6.9 Hz, 3H), 0.88 (s, 9H), 0.88 (t, J = 7.3 Hz, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 117.6, 78.4, 73.3, 39.9, 39.4, 37.1, 28.6, 28.2, 26.0 (3C), 22.9, 18.2, 14.1, 11.2, −3.7, −4.3; HRMS (ESI-TOF): calcd for $C_{18}H_{37}NNaO_3Si$, 366.2440 [M + Na^+], found 366.2432.

(4*S*,5*R*,6*R*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-decene (*anti*-4a). Under nitrogen atmosphere, TBSOTf (0.20 mL, 0.87 mmol) and 2,6-lutidine (0.10 mL, 0.87 mmol) were added to a solution of compound anti-**3a** (0.1612 g, 0.703 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 40 h. Water (20 mL) was added, and the organic layer was separated. Water phase was extracted with CH_2Cl_2 (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1) to give *anti*-**4a** in 96% yield (0.2318 g, 0.675 mmol).

Colorless oil; $[\alpha]_D$ +45.8 ($CHCl_3$, c 1.16); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (dddd, J = 17.8, 9.6, 7.9, 6.2 Hz, 1H), 5.09−5.01 (m, 2H), 4.38 (ddd, J = 11.8, 5.2, 0.9 Hz, 1H), 4.27 (ddd, J = 11.7, 9.0, 0.9 Hz, 1H), 3.63 (td, J = 6.1, 4.5 Hz, 1H), 2.58 (dtt, J = 9.3, 5.4, 2.4 Hz, 1H), 2.30 (dt, J = 14.4, 6.3 Hz, 1H), 2.23 (dddt, J = 14.5, 7.9, 4.5, 1.0 Hz, 1H), 1.67−1.56 (m, 2H), 1.37−1.22 (m, 4H), 1.12−1.00 (m, 1H), 0.92−0.87 (m, 3H), 0.90 (s, 9H), 0.81 (dd, J = 6.9, 0.9 Hz, 3H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 117.5, 78.6, 73.8, 38.9, 37.9, 37.7, 29.6, 26.9, 25.9 (3C), 23.2, 18.1, 14.1, 11.1, −3.9, −4.8; HRMS (ESI-TOF): calcd for $C_{18}H_{37}NNaO_3Si$, 366.2440 [M + Na^+], found 366.2445.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)-oxy-1-nonene (4b). Under nitrogen atmosphere, TBSOTf (1.6 mL, 6.97 mmol) and 2,6-lutidine (0.9 mL, 7.78 mmol) were added to a solution of compound **3b** (1.3542 g, 6.29 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 26 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 40:1 v/v) to give **4b** in 88% yield (1.8351 g, 5.57 mmol).

Pale yellow oil; $[\alpha]_D$ −4.76 ($CHCl_3$, c 0.59); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83−5.65 (m, 1H), 5.11−5.00 (m, 2H), 4.50 (ddd, J = 12.2, 6.1, 1.0 Hz, 1H for *syn*-**4b**), 4.37 (ddd, J = 11.8, 5.2, 1.1 Hz, 1H for *anti*-**4b**), 4.32 (ddd, J = 12.2, 7.7, 1.0 Hz, 1H for *syn*-**4b**), 4.26 (ddd, J = 11.8, 9.1, 1.1 Hz, 1H for *anti*-**4b**), 3.73 (tdd, J = 6.2, 4.5, 1.0 Hz, 1H for *syn*-**4b**), 3.63 (td, J = 5.4, 5.0 Hz, 1H for *anti*-**4b**), 2.65−2.55 (m, 1H for *anti*-**4b**), 2.35−2.20 (m, 3H for *syn*-**4b** and 2H for *anti*-**4b**), 1.74−1.64 (m, 1H for *syn*-**4b**), 1.65−1.51 (m, 1H for *anti*-**4b**), 1.45−1.18 (m, 4H for *syn*-**4b** and 3H for *anti*-**4b**), 1.10−0.98 (m, 1H for *anti*-**4b**), 0.96−0.79 (m, 15H), 0.07 (s, 3H for *syn*-**4b**), 0.06 (s, 3H for *anti*-**4b**), 0.06 (s, 3H for *syn*-**4b**), 0.04 (d, J = 1.0 Hz, 3H for *anti*-**4b**), ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**4b**; 134.0, 117.5, 78.6, 73.7, 38.9, 37.8, 37.5, 29.3, 25.9 (3C), 20.7, 18.1, 14.5, 11.1, −3.9, −4.8; for *syn*-**4b**; 134.3, 117.5, 78.4, 73.3, 39.8, 39.4, 37.1, 30.7, 26.0 (3C), 19.7, 18.2, 14.3, 11.2, −3.7, −4.3; HRMS (ESI-TOF): calcd for $C_{17}H_{35}NNaO_3Si$, 352.2284 [M + Na^+], found 352.2290.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)-oxy-1-undecene (4c). Under nitrogen atmosphere, TBSOTf (1.15 mL, 5.01 mmol) and 2,6-lutidine (0.63 mL, 5.45 mmol) were added to a solution of compound **3c** (1.1019 g, 4.53 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 26 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by

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J. Org. Chem. 2016, 81, 4664−4681

flash chromatography (silica gel/hexane, then hexane-EtOAc 40:1 v/v) to give **4c** in 88% yield (1.4276 g, 3.99 mmol).

Colorless oil; $[\alpha]_D$ +9.97 ($CHCl_3$, *c* 1.04); ^1H NMR (500 MHz, $CDCl_3$) δ 5.77−5.64 (m, 1H), 5.10−4.99 (m, 2H), 4.49 (ddd, *J* = 12.0, 9.7, 6.0 Hz, 1H for *syn*-**4c**), 4.32 (m, 1H for *syn*-**4c** and 2H for *anti*-**4c**), 3.72 (dq, *J* = 9.8, 6.0 Hz, 1H for *syn*-**4c**), 3.66−3.58 (m, 1H for *anti*-**4c**), 2.57 (ddt, *J* = 8.8, 6.0, 3.1 Hz, 1H for *anti*-**4c**), 2.34−2.18 (m, 3H for *syn*-**4c** and 2H for *anti*-**4c**), 1.73−1.64 (m, 1H for *syn*-**4c**), 1.65−1.52 (m, 1H for *anti*-**4c**), 1.47−1.18 (m, 8H for *syn*-**4c** and 7H for *anti*-**4c**), 1.14−0.97 (m, 1H for *anti*-**4c**), 0.93−0.73 (m, 15H), 0.09−0.03 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**4c**; 134.0, 117.5, 78.5, 73.7, 38.9, 37.9, 37.7, 32.3, 28.5, 27.1, 26.2 (3C), 22.6, 18.1, 14.1, 11.1, −3.9, −4.8; for *syn*-**4c**; 134.3, 117.6, 78.4, 73.3, 39.9, 39.4, 37.1, 32.0, 28.5, 27.1, 26.0 (3C), 22.6, 18.2, 14.1, 11.2, −3.7, −4.3; HRMS (ESI-TOF): calcd for $C_{19}H_{39}NNaO_3Si$, 380.2597 [M + Na^+], found 380.2596.

(5*R*,6*R*)-5,7-Dimethyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-octene (4d). Under nitrogen atmosphere, TBSOTf (0.82 mL, 3.57 mmol) and 2,6-lutidine (0.45 mL, 3.87 mmol) were added to a solution of compound **3d** (0.6958 g, 3.23 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 19 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 10:1 v/v) to give **4d** in 95% yield (1.0082 g, 3.06 mmol).

Pale yellow oil; $[\alpha]_D$ +3.75 ($CHCl_3$, *c* 1.07); ^1H NMR (500 MHz, $CDCl_3$) δ 5.80−5.63 (m, 1H), 5.11−4.98 (m, 2H), 4.63 (ddt, *J* = 13.8, 4.1, 1.1 Hz, 1H for *syn*-**4d**), 4.37 (ddd, *J* = 13.6, 4.4, 1.3 Hz, 1H for *anti*-**4d**), 4.31 (ddd, *J* = 13.2, 6.9, 1.7 Hz, 1H for *syn*-**4d**), 4.27 (ddd, *J* = 12.8, 6.9, 2.1 Hz, 1H for *anti*-**4d**), 3.78 (tdd, *J* = 6.1, 3.2, 1.6 Hz, 1H for *syn*-**4d**), 3.68 (q, *J* = 4.8 Hz, 1H for *anti*-**4d**), 2.37−2.10 (m, 3H), 1.92−1.63 (m, 2H), 0.91 (m, 18H), 0.07 (s, 3H for *syn*-**4d**), 0.06 (s, 3H for *syn*-**4d**), 0.04 (s, 6H for *anti*-**4d**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**4d**; 135.0, 117.2, 76.1, 73.9, 43.5, 40.0, 37.7, 26.7, 25.9 (3C), 22.4, 18.2, 18.1, 12.2, −4.0, −4.5; for *syn*-**4d**; 134.6, 117.6, 76.2, 73.3, 45.7, 39.7, 36.7, 28.5, 26.0 (3C), 21.3, 18.2, 17.5, 12.3, −4.0, −4.5; HRMS (ESI-TOF): calcd for $C_{17}H_{36}NO_3Si$, 330.2464 [M + H^+], found 330.2452.

(5*R*,6*R*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-octene (4e). Under nitrogen atmosphere, TBSOTf (1.6 mL, 6.97 mmol) and 2,6-lutidine (0.9 mL, 7.78 mmol) were added to a solution of compound **3e** (1.2575 g, 6.25 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 33 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 30:1 v/v) to give **4e** in 92% yield (1.8124 g, 5.74 mmol). Further chromatographic separation gave diastereomerically pure *syn*-**4e**.

Colorless oil; $[\alpha]_D$ +7.04 ($CHCl_3$, *c* 1.03); ^1H NMR (500 MHz, $CDCl_3$) δ 5.70 (dq, *J* = 16.9, 7.7 Hz, 1H), 5.09−5.00 (m, 2H), 4.51 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.31 (dd, *J* = 12.7, 8.3 Hz, 1H), 3.73 (dt, *J* = 11.4, 5.4 Hz, 1H), 2.32−2.17 (m, 3H), 1.73−1.67 (m, 1H), 1.47 (dp, *J* = 15.5, 8.3 Hz, 1H), 1.32 (dp, *J* = 14.8, 7.4 Hz, 1H), 0.91−0.85 (m, 6H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 117.5, 77.9, 73.5, 41.2, 39.3, 36.8, 26.0 (3C), 21.2, 18.1, 11.2, 10.6, −3.8, −4.3; HRMS (ESI-TOF): calcd for $C_{16}H_{34}NO_3Si$, 316.2308 [M + H^+], found 316.2299.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-decene (14a). Under nitrogen atmosphere, TBSOTf (1.4 mL, 6.10 mmol) and 2,6-lutidine (0.8 mL, 6.91 mmol) were added to a solution of compound **13a** (1.2738 g, 5.55 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 32 h. $NaHCO_3$ aq (20 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 30:1 v/v) to give **14a** in 95% yield (1.8118 g, 5.27 mmol).

Colorless oil; $[\alpha]_D$ −37.0 ($CHCl_3$, *c* 1.07); ^1H NMR (500 MHz, $CDCl_3$) δ 5.82−5.65 (m, 1H), 5.11−5.01 (m, 2H), 4.50 (ddd, *J* = 12.2, 6.0, 1.1 Hz, 1H for *syn*-**14a**), 4.38 (ddd, *J* = 11.8, 5.2, 1.1 Hz, 1H for *anti*-**14a**), 4.32 (ddd, *J* = 12.2, 7.8, 1.1 Hz, 1H for *syn*-**14a**), 4.27 (ddd, *J* = 11.9, 9.0, 1.1 Hz, 1H for *anti*-**14a**), 3.73 (tdd, *J* = 6.3, 4.6, 1.1 Hz, 1H for *syn*-**14a**), 3.63 (dt, *J* = 6.4, 5.8 Hz, 1H for *anti*-**14a**), 2.63−2.53 (m, 1H for *anti*-**14a**), 2.35−2.21 (m, 3H for *syn*-**14a** and 2H for *anti*-**14a**), 1.75−1.65 (m, 1H for *syn*-**14a**), 1.66−1.56 (m, 1H for *anti*-**14a**), 1.48−1.36 (m, 1H for *syn*-**14a**), 1.36−1.20 (m, 5H), 1.12−1.00 (m, 1H for *anti*-**14a**), 0.95−0.84 (m, 15H for *syn*-**14a** and 12H for *anti*-**14a**), 0.82 (dd, *J* = 7.0, 1.1 Hz, 3H for *anti*-**14a**), 0.07 (s, 3H for *syn*-**14a**), 0.06 (s, 3H), 0.04 (s, 3H for *anti*-**14a**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**14a**; 134.0, 117.5, 78.6, 73.7, 38.9, 37.9, 37.7, 29.6, 26.9, 25.9 (3C), 23.2, 18.1, 14.1, 11.1, −3.9, −4.8; for *syn*-**14a**; 134.4, 117.6, 78.4, 73.3, 39.9, 39.4, 37.1, 28.6, 28.2, 26.0 (3C), 22.9, 18.2, 14.1, 11.2, −3.7, −4.3; HRMS (ESI-TOF): calcd for $C_{18}H_{38}NO_3Si$, 344.2621 [M + H^+], found 344.2626.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-nonene (14b). Under nitrogen atmosphere, TBSOTf (0.95 mL, 4.1 mmol) and 2,6-lutidine (0.52 mL, 4.5 mmol) were added to a solution of compound **13b** (0.8122 g, 3.77 mmol) in CH_2Cl_2 (7.5 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 24 h. $NaHCO_3$ aq (20 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 20:1 v/v) to give **14b** in 88% yield (1.0911 g, 3.31 mmol).

Colorless oil; $[\alpha]_D$ +1.01 ($CHCl_3$, *c* 0.99); ^1H NMR (500 MHz, $CDCl_3$) δ 5.83−5.63 (m, 1H), 5.11−5.01 (m, 2H), 4.49 (ddd, *J* = 12.1, 6.1, 1.3 Hz, 1H for *syn*-**14b**), 4.37 (ddd, *J* = 11.7, 5.2, 1.3 Hz, 1H for *anti*-**14b**), 4.32 (ddd, *J* = 12.3, 7.7, 1.3 Hz, 1H for *syn*-**14b**), 4.26 (ddd, *J* = 11.9, 8.9, 1.3 Hz, 1H for *anti*-**14b**), 3.77−3.69 (m, 1H for *syn*-**14b**), 3.64 (td, *J* = 6.1, 5.3 Hz, 1H for *anti*-**14b**), 2.64−2.54 (m, 1H for *anti*-**14b**), 2.35−2.18 (m, 3H for *syn*-**14b** and 2H for *anti*-**14b**), 1.69 (tdd, *J* = 6.8, 3.7, 1.7 Hz, 1H for *syn*-**14b**), 1.66−1.57 (m, 1H for *anti*-**14b**), 1.44−1.19 (m, 4H for *syn*-**14b** and 3H for *anti*-**14b**), 1.11−1.00 (m, 1H for *anti*-**14b**), 0.97−0.77 (m, 15H), 0.08−0.04 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *syn*-**14b**; 134.3, 117.6, 78.4, 73.4, 39.8, 39.4, 37.1, 30.7, 26.0 (3C), 19.7, 18.2, 14.3, 11.1, −3.7, −4.3; for *anti*-**14b**; 134.0, 117.5, 78.6, 73.8, 39.0, 37.9, 37.5, 29.4, 25.9 (3C), 20.7, 18.1, 14.5, 11.1, −3.9, −4.8; HRMS (ESI-TOF): calcd for $C_{17}H_{35}NNaO_3Si$, 352.2284 [M + Na^+], found 352.2288.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-undecene (14c). Under nitrogen atmosphere, TBSOTf (1.7 mL, 7.7 mmol) and 2,6-lutidine (1.0 mL, 8.7 mmol) were added to a solution of compound **13c** (1.3298 g, 5.46 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 192 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 30:1 v/v) to give **14c** in 94% yield (1.8312g, 5.12 mmol).

Colorless oil; $[\alpha]_D$ −13.7 ($CHCl_3$, *c* 1.21); ^1H NMR (500 MHz, $CDCl_3$) δ 5.82−5.67 (m, 1H), 5.11−5.01 (m, 2H), 4.50 (dd, *J* = 12.2, 6.1 Hz, 1H for *syn*-**14c**), 4.38 (dd, *J* = 11.9, 5.5 Hz, 1H for *anti*-**14c**), 4.32 (dd, *J* = 12.0, 7.5 Hz, 1H for *syn*-**14c**), 4.27 (dd, *J* = 11.7, 9.3 Hz, 1H for *anti*-**14c**), 3.74 (td, *J* = 5.9, 4.0 Hz, 1H for *syn*-**14c**), 3.63 (td, *J* = 6.2, 4.5 Hz, 1H for *anti*-**14c**), 2.62−2.54 (m, 1H for *anti*-**14c**), 2.34−2.20 (m, 3H for *syn*-**14c** and 2H for *anti*-**14c**), 1.74−1.67 (m, 1H for *syn*-**14c**), 1.66−1.55 (m, 1H for *anti*-**14c**), 1.47−1.37 (m, 1H for *syn*-**14c**), 1.33−1.20 (m 7H), 1.12−1.00 (m, 4H for *anti*-**14c**), 0.91 (d, *J* = 6.4 Hz, 3H for *syn*-**14c**), 0.90 (s, 9H for *anti*-**14c**), 0.89 (s, 9H for *syn*-**14c**), 0.90−0.86 (m, 3H), 0.82 (d, *J* = 6.9 Hz, 3H for *anti*-**14c**), 0.08 (s, 3H for *syn*-**14c**), 0.07 (s, 3H for *syn*-**14c**), 0.07 (s, 3H for *anti*-**14c**), 0.05 (s, 3H for *anti*-**14c**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**14c**; 133.8, 117.2, 78.3, 73.5, 38.7, 37.6, 37.5, 32.0, 31.4, 26.9, 25.7

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J. Org. Chem. 2016, 81, 4664−4681

(3C), 22.5, 17.9, 14.0, 10.8, −4.2, −5.0; for *syn*-**14c**; 134.1, 117.3, 78.1, 73.1, 39.7, 39.2, 36.8, 31.8, 28.2, 25.9 (3C), 25.7, 22.3, 17.9, 13.8, 10.9, −4.0, −4.5; HRMS (ESI-TOF): calcd for $C_{19}H_{40}NO_3Si$, 358.2777 [M + H^+], found 358.2786.

(5*S*,6*S*)-5,7-Dimethyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)oxy-1-octene (14d). Under nitrogen atmosphere, TBSOTf (1.1 mL, 4.7 mmol) and 2,6-lutidine (0.70 mL, 6.1 mmol) were added to a solution of compound **13d** (0.9196 g, 4.27 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 24 h. $NaHCO_3$ aq (20 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 60:1 v/v) to give **14d** in 93% yield (1.3006 g, 3.95 mmol).

Colorless oil; $[\alpha]_D$ +1.16 ($CHCl_3$, *c* 0.95); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77−5.63 (m, 1H), 5.11−4.99 (m, 2H), 4.62 (dd, *J* = 13.3, 5.9 Hz, 1H for *syn*-**14d**), 4.36 (dd, *J* = 12.4, 5.4 Hz, 1H for *anti*-**14d**), 4.32 (dd, *J* = 13.9, 7.2 Hz, 1H for *syn*-**14d**), 4.24−4.17 (m, 1H for *anti*-**14d**), 3.78 (t, *J* = 6.6 Hz, 1H for *syn*-**14d**), 3.68 (dd, *J* = 10.2, 5.5 Hz, 1H for *anti*-**14d**), 2.38−2.12 (m, 3H), 1.92−1.61 (m, 2H), 1.05−0.77 (m, 18H), 0.07 (s, 3H for *syn*-**14d**), 0.06 (s, 3H for *syn*-**14d**), 0.05 (s, 6H for *anti*-**14d**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**14d**: 135.0, 117.2, 76.1, 73.9, 43.5, 40.0, 37.7, 26.7, 25.9 (3C), 22.4, 17.5, 14.2, 12.2, −4.0, −4.5; for *syn*-**14d**: 134.6, 117.6, 76.2, 73.3, 45.7, 39.7, 36.7, 28.5, 26.0 (3C), 21.3, 18.2, 18.2, 12.3, −3.7, −4.2; HRMS (ESI-TOF): calcd for $C_{17}H_{35}NNaO_3Si$, 352.2284 [M + Na^+], found 352.2285.

(5*S*,6*S*)-5-Methyl-6-(nitromethyl)-4-(*tert*-butyldimethylsilyl)-oxy-1-octene (14e). Under nitrogen atmosphere, TBSOTf (1.61 mL, 7.01 mmol) and 2,6-lutidine (0.88 mL, 7.60 mmol) were added to a solution of compound **13e** (1.2789 g, 6.35 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 33 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 20:1 v/v) to give **14e** in 97% yield (1.9392 g, 6.15 mmol).

Colorless oil; $[\alpha]_D$ −5.79 ($CHCl_3$, *c* 1.03); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83−5.65 (m, 1H), 5.10−5.01 (m, 2H), 4.53 (dd, *J* = 12.2, 5.9 Hz, 1H for *syn*-**14e**), 4.39 (dd, *J* = 11.8, 5.1 Hz, 1H for *anti*-**14e**), 4.33 (dd, *J* = 12.2, 8.3 Hz, 1H for *syn*-**14e**), 4.27 (dd, *J* = 11.4, 8.7 Hz, 1H for *anti*-**14e**), 3.73 (td, *J* = 6.3, 3.8 Hz, 1H for *syn*-**14e**), 3.65−3.60 (m, 1H for *anti*-**14e**), 2.55−2.48 (m, 1H for *anti*-**14e**), 2.33−2.19 (m, 3H for *syn*-**14e** and 2H for *anti*-**14e**), 1.70 (dq, *J* = 11.7, 6.1 Hz, 1H for *syn*-**14e**), 1.62 (qd, *J* = 7.8, 3.0 Hz, 1H for *anti*-**14e**), 1.48 (qd, *J* = 13.5, 6.0 Hz, 1H for *syn*-**14e**), 1.33 (dp, *J* = 14.5, 7.3 Hz, 1H), 1.16−1.06 (m, 1H for *anti*-**14e**), 0.95 (t, *J* = 7.4 Hz, 3H for *anti*-**14e**), 0.91 (t, *J* = 4.8 Hz, 3H for *syn*-**14e**), 0.89 (s, 9H for *anti*-**14e**), 0.89 (d, *J* = 7.5 Hz, 3H for *syn*-**14e**), 0.88 (s, 9H for *syn*-**14e**), 0.80 (d, *J* = 7.0 Hz, 3H for *anti*-**14e**), 0.07 (s, 3H for *syn*-**14e**), 0.06 (s, 3H for *anti*-**14e**), 0.06 (s, 3H for *syn*-**14e**), 0.04 (s, 3H for *anti*-**14e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *anti*-**14e**; 134.0, 117.5, 78.1, 73.5, 39.1, 38.8, 37.9, 25.9 (3C), 19.8, 18.1, 11.7, 11.0, −3.9, −4.8; for *syn*-**14e**; 134.4, 117.6, 78.0, 73.5, 41.2, 39.3, 36.8, 26.0 (3C), 21.2, 18.2, 11.3, 10.7, −3.8, −4.3; HRMS (ESI-TOF): calcd for $C_{16}H_{34}NO_3Si$, 316.2308 [M + H^+], found 316.2305.

(5*S*,6*S*)-6-Cyclohexyl-5-methyl-7-nitro-4-(*tert*-butyldimethylsilyl)oxy-1-heptene (14f). Under nitrogen atmosphere, TBSOTf (1.29 mL, 5.62 mmol) and 2,6-lutidine (0.84 mL, 7.25 mmol) were added to a solution of compound **13f** (0.8955 g, 3.51 mmol) in CH_2Cl_2 (7 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 137 h. $NaHCO_3$ aq (30 mL) was added, and the organic layer was separated. Water phase was extracted with EtOAc (20 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporator, and residue was purified by flash chromatography (silica gel/hexane, then hexane-EtOAc 10:1 v/v) to give **14f** in 97% yield (1.2577 g, 3.40 mmol). Further chromatographic separation gave diastereomerically pure *syn*-**14f**.

Colorless oil; $[\alpha]_D$ +0.45 ($CHCl_3$, *c* 0.89); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75−5.63 (m, 1H), 5.10−4.99 (m, 2H), 4.62 (dd, *J* = 13.6, 4.1 Hz, 1H), 4.34 (dd, *J* = 13.6, 7.1 Hz, 1H), 3.76 (td, *J* = 8.0, 2.5 Hz, 1H), 2.30−2.15 (m, 3H), 1.80 (td, *J* = 7.7, 2.9 Hz, 1H), 1.77−1.70 (m, 3H), 1.68−1.57 (m, 3H), 1.47 (s, 1H), 1.14 (m, 4H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ *anti*-**14f**; 134.8, 117.3, 76.8, 74.2, 43.3, 39.3, 38.0, 37.2, 32.8, 28.6, 26.9, 26.6, 26.4, 26.0 (3C), 14.2, 12.6, −4.0, −4.5; *syn*-**14f**; 134.6, 117.6, 76.5, 73.3, 45.2, 39.7, 38.9, 36.1, 31.7, 28.7, 26.8, 26.6, 26.4, 26.0 (3C), 18.2, 12.3, −3.7, −4.2; HRMS (ESI-TOF): calcd for $C_{20}H_{39}NNaO_3Si$, 392.2597 [M + Na^+], found 392.2593.

(1*S*,3*R*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-butyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (3,4-*trans*-5a). Under nitrogen atmosphere, DBU (0.10 mL, 0.67 mmol), Ag_2O (0.2178 g, 0.940 mmol), and iodine (0.2341 g, 0.922 mmol) were added in this order to a solution of *syn*-**4a** (0.1616 g, 0.470 mmol) in dry THF (10 mL) at room temperature. The reaction mixture was stirred for 3 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 50:1 then 4:1 v/v) to give 3,4-*trans*-**5a** in 51% yield (0.0821 g, 0.240 mmol) along with 4,5-*trans*-**6a** in 31% yield (0.050 g, 0.146 mmol). Compound **5a** was isolated as diastereomerically pure single isomers and the ratio was >99/1.

Colorless oil; $[\alpha]_D$ −53.3 ($CHCl_3$, *c* 0.73); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (td, *J* = 7.7, 5.2 Hz, 1H), 2.95 (tdd, *J* = 7.3, 5.1, 1.3 Hz, 1H), 2.21 (ddd, *J* = 13.7, 8.2, 5.2 Hz, 1H), 2.10 (ddd, *J* = 11.0, 5.4, 1.2 Hz, 1H), 1.95 (dtd, *J* = 10.6, 8.0, 2.3 Hz, 1H), 1.62 (ddt, *J* = 13.6, 10.2, 4.7 Hz, 1H), 1.51−1.43 (m, 1H), 1.37−1.22 (m, 6H), 1.19 (dd, *J* = 7.8, 5.4 Hz, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.87 (s, 9H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.03 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 72.0, 67.7, 38.8, 33.7, 31.0, 29.1, 25.9, 25.4 (3C), 23.2, 20.6, 18.1, 17.3, 14.1, 0.1, −4.5, −4.8; IR ($CHCl_3$) ν 1533, 1340 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{18}H_{36}NO_3Si$, 342.2464 [M + H^+], found 342.2456.

(3a*S*,5*R*,6*R*,7*R*)-7-Butyl-5-((*tert*-butyldimethylsilyl)oxy)-6-methyl-3,3a,4,5,6,7- hexahydrobenzo[*c*]isoxazol-*N*-oxide (4,5-*trans*-6a). Colorless oil; $[\alpha]_D$ −60.0 ($CHCl_3$, *c* 0.90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (t, *J* = 8.5 Hz, 1H), 3.95 (t, *J* = 8.1 Hz, 1H), 3.82 (s, 1H), 3.78−3.70 (m, 1H), 2.58 (t, *J* = 8.0 Hz, 1H), 2.11−1.97 (m, 1H), 1.92−1.84 (m, 1H), 1.69 (t, *J* = 12.5 Hz, 1H), 1.41−1.33 (m, 2H), 1.35−1.21 (m, 4H), 0.90 (d, *J* = 7.5 Hz, 3H), 0.87 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.04 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 118.3, 72.5, 69.4, 40.3, 39.8, 36.9, 34.5, 33.3, 30.4, 25.8 (3C), 22.8, 19.3, 18.0, 14.1, −4.8, −5.0; IR (neat) ν 1643 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{18}H_{36}NO_3Si$, 342.2464 [M + H^+], found 342.2456.

(1*S*,3*S*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-butyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (3,4-*cis*-5a). Under nitrogen atmosphere, DBU (0.08 mL, 0.62 mmol), Ag_2O (0.1880 g, 0.811 mmol), and iodine (0.1910 g, 0.753 mmol) were added in this order to a solution of *anti*-**4a** (0.1313 g, 0.382 mmol) in dry THF (7.5 mL) at room temperature. The reaction mixture was stirred for 2 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 50:1 then 5:1 v/v) to give 3,4-*cis*-**5a** in 66% yield (0.0866 g, 0.254 mmol) along with 4,5-*cis*-**6a** in 5% yield (0.0056 g, 0.02 mmol). Compound **5a** was isolated as diastereomerically pure single isomers and the ratio was >99/1.

White solid; mp 47−48 °C; $[\alpha]_D$ + 14.7 ($CHCl_3$, *c* 0.58) ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (ddt, *J* = 5.0, 3.2, 1.5 Hz, 1H), 3.22−3.13 (m, 1H), 2.18−2.12 (m, 1H), 2.09 (ddd, *J* = 12.6, 8.3, 5.4 Hz, 1H), 1.99 (dtd, *J* = 10.9, 8.2, 2.5 Hz, 1H), 1.60−1.53 (m, 1H), 1.46 (dt, *J* = 14.0, 3.0 Hz, 1H), 1.35−1.18 (m, 6H), 1.07 (dtd, *J* = 7.4, 6.0, 1.8 Hz, 1H), 1.02 (d, *J* = 6.0 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 68.9, 68.1, 38.0, 35.3, 32.9, 31.7, 29.1, 25.8 (3C), 23.3, 20.6, 18.0, 16.5, 14.2, 1.1, −4.5, −4.8; IR ($CHCl_3$) ν 1531, 1338 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{18}H_{35}NNaO_3Si$, 364.2284 [M + Na^+], found 364.2279.

(3a*S*,5*S*,6*R*,7*R*)-7-Butyl-5-((*tert*-butyldimethylsilyl)oxy)-6-methyl-3,3a,4,5,6,7-hexahydrobenzo[*c*]isoxazol-*N*-oxide (4,5-*cis*-6a). Colorless oil; $[\alpha]_D$ −7.0 ($CHCl_3$, *c* 0.19); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (t, *J* = 8.1 Hz, 1H), 3.97 (p, *J* = 7.8 Hz, 1H), 3.87

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(dd, J = 16.8, 8.7 Hz, 1H), 3.69−3.59 (m, 1H), 2.59−2.45 (m, 1H), 1.99 (dd, J = 12.7, 5.1 Hz, 1H), 1.68 (m, 1H), 1.53 (t, J = 12.2 Hz, 1H), 1.44−1.18 (m, 6H), 0.99 (d, J = 6.7 Hz, 3H), 0.91 (t, J = 6.3 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 118.3, 72.5, 69.4, 40.3, 39.8, 36.9, 34.5, 33.3, 30.4, 25.9 (3C), 22.8, 19.3, 18.0, 14.1, −4.8, −5.0; IR (neat) ν 1645, 1253 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{18}H_{36}NO_3Si$, 342.2464 [M + H$^+$], found 342.2465.

(1*S*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-propyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (5b). Under nitrogen atmosphere, DBU (0.65 mL, 4.48 mmol), Ag_2O (1.7132 g, 7.41 mmol), and iodine (1.7452 g, 9.22 mmol) were added in this order to a solution of **4b** (1.1746 g, 6.90 mmol) in dry THF (55 mL) at room temperature. The reaction mixture was stirred for 2.5 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 5:1 v/v) to give **5b** in 70% yield (0.821 g, 2.53 mmol).

Colorless oil; $[\alpha]_D$ −38.6 ($CHCl_3$, c 1.19); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (ddd, J = 5.4, 3.6, 1.8 Hz, 1H for 3,4-*cis*-**5b**), 3.47−3.38 (m, 1H for 3,4-*trans*-**5b**), 3.18 (dq, J = 8.1, 4.4, 3.9 Hz, 1H for 3,4-*cis*-**5b**), 2.96 (dddd, J = 7.7, 6.7, 5.3, 3.5 Hz, 1H for 3,4-*trans*-**5b**), 2.31−2.04 (m, 2H), 2.04−1.89 (m, 1H), 1.70−1.50 (m, 1H), 1.49−1.38 (m, 1H), 1.37−1.14 (m, 5H), 1.04−0.93 (m, 3H), 0.91−0.83 (m, 12H), 0.06−0.01 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for 3,4-*cis*- **5b**; 68.9, 68.1, 38.0, 35.6, 31.7, 26.0, 25.9 (3C), 25.8, 20.6, 20.2, 18.1, 16.5, 14.7, −4.5, −4.8; for 3,4-*trans*-**5b**; 71.9, 67.8, 38.7, 36.2, 31.2, 25.8, 25.7, 25.4, 20.6, 20.2, 18.0, 17.3, 14.6, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{17}H_{33}NNaO_3Si$, 350.2127 [M + Na$^+$], found 350.2123.

(1*S*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-pentyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (5c). Under nitrogen atmosphere, DBU (0.72 mL, 4.81 mmol), Ag_2O (1.9104 g, 8.24 mmol), and iodine (1.9624 g, 7.33 mmol) were added in this order to a solution of **4c** (1.4342 g, 4.03 mmol) in dry THF (60 mL) at room temperature. The reaction mixture was stirred for 6 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 60:1 then 5:1 v/v) to give **5c** in 66% yield (0.9425 g, 2.65 mmol).

Colorless oil; $[\alpha]_D$ −17.5 ($CHCl_3$, c 1.05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.55−3.51 (m, 1H for 3,4-*cis*-**5c**), 3.42 (td, J = 7.0, 5.2 Hz, 1H for 3,4-*trans*-**5c**), 3.16 (dt, J = 11.9, 7.0 Hz, 1H for 3,4-*cis*-**5c**), 2.93 (q, J = 6.4 Hz, 1H for 3,4-*trans*-**5c**), 2.35−1.87 (m, 3H), 1.74−1.38 (m, 2H), 1.34−1.14 (m, 8H), 1.14−1.03 (m, 1H), 1.01 (d, J = 6.1 Hz, 3H for 3,4-*cis*-**5c**), 0.97 (d, J = 6.6 Hz, 3H for 3,4-*trans*-**5c**), 0.90−0.86 (m, 3H), 0.85 (s, 9H for 3,4-*cis*-**5c**), 0.84 (s, 9H for 3,4-*trans*-**5c**), 0.02 (s, 6H for 3,4-*trans*-**5c**), 0.01 (s, 3H for 3,4-*cis*-**5c**), −0.00 (s, 3H for 3,4-*cis*-**5c**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for 3,4-*cis*-**5c**; 68.9, 68.0, 38.0, 35.4, 33.2, 32.5, 31.7, 26.6, 25.7 (3C), 25.7, 22.7, 20.5, 18.0, 16.4, 14.2, −4.6, −4.9; for 3,4-*trans*-**5c**; 71.9, 67.6, 38.8, 33.9, 32.4, 31.7, 31.0, 26.6, 25.9 (3C), 25.2, 22.6, 20.4, 18.1, 17.3, 14.1, −4.5, −4.9; HRMS (ESI-TOF): calcd for $C_{19}H_{38}NO_3Si$, 356.2621 [M + H$^+$], found 356.2621.

(1*S*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-isopropyl-4-methyl-6-nitrobicyclo- [4.1.0]heptane (5d). Under nitrogen atmosphere, DBU (0.90 mL, 6.0 mmol), Ag_2O (2.4549 g, 10.5 mmol), and iodine (2.4777 g, 9.76 mmol) were added in this order to a solution of **4d** (1.616 g, 4.93 mmol) in dry THF (60 mL) at room temperature. The reaction mixture was stirred for 3 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 3:1 v/v) to give **5d** in 69% yield (1.1190 g, 3.42 mmol).

Colorless oil; $[\alpha]_D$ −82.4 ($CHCl_3$, c 0.70); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (q, J = 4.2 Hz, 1H for *trans*-**5d**), 3.53−3.47 (m, 1H for *cis*-**5d**), 3.06 (dd, J = 9.1, 2.5 Hz, 1H for *cis*-**5d**), 2.86 (dd, J = 9.8, 3.2 Hz, 1H for *trans*-**5d**), 2.20−1.85 (m, 5H), 1.77−1.46 (m, 2H), 1.02 (d, J = 6.9 Hz, 3H for *cis*-**5d**), 0.99 (d, J = 7.1 Hz, 3H for *trans*-**5d**), 0.97 (d, J = 6.9 Hz, 3H for *cis*-**5d**), 0.93 (d, J = 6.9 Hz, 3H for *trans*-**5d**), 0.88−0.84 (m, 3H), 0.86 (s, 9H for *cis*-**5d**), 0.85 (s, 9H for *trans*-**5d**), 0.03 (s, 3H for *trans*-**5d**), 0.01 (s, 3H for *trans*-**5d**), 0.01 (s, 3H for *cis*-**5d**), 0.00 (s, 3H for *cis*-**5d**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**5d**; 71.8, 66.4, 43.9, 33.7, 31.2, 26.4, 26.1, 25.8 (3C), 20.9, 20.8, 20.0, 19.1, 18.0, −4.9, −5.0; for *cis*-**5d**; 66.6, 66.2, 44.8, 34.5, 29.9, 26.0, 25.9, 25.8 (3C), 21.1, 20.9, 19.6, 19.1, 18.1, −4.7, −4.8; HRMS (ESI-TOF): calcd for $C_{17}H_{34}NO_3Si$, 328.2308 [M + H$^+$], found 328.2300.

(1*S*,4*R*,5*R*,6*R*)-3-(*tert*-Butyldimethylsilyl)oxy-5-ethyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (5e). Under nitrogen atmosphere, DBU (0.96 mL, 6.4 mmol), Ag_2O (1.0649 g, 4.61 mmol), and iodine (1.156 g, 4.57 mmol) were added in this order to a solution of **4e** (0.6321 g, 2.01 mmol) in dry THF (30 mL) at room temperature. The reaction mixture was stirred for 2 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 6:1 v/v) to give **5e** in 59% yield (0.3725 g, 1.19 mmol).

Colorless oil; $[\alpha]_D$ −46.2 ($CHCl_3$, c 1.60); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.55 (ddd, J = 5.2, 3.3, 1.7 Hz, 1H for *cis*-**5e**), 3.43 (td, J = 8.0, 5.2 Hz, 1H for *trans*-**5e**), 3.16 (qd, J = 8.7, 3.7 Hz, 1H for *cis*-**5e**), 2.91 (td, J = 7.5, 4.9 Hz, 1H for *trans*-**5e**), 2.30−2.04 (m, 2H), 2.04−1.84 (m, 1H), 1.78−1.59 (m, 1H), 1.58−1.41 (m, 2H), 1.37−1.05 (m, 2H), 1.03 (d, J = 6.6 Hz, 3H for *cis*-**5e**), 1.00 (d, J = 6.8 Hz, 3H for *trans*-**5e**), 0.94−0.89 (m, 4H), 0.87 (s, 9H for *trans*-**5e**), 0.86 (s, 9H for *cis*-**5e**), 0.13 to −0.01 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *cis*-**5e**; 69.0, 67.7, 37.7, 36.3, 31.9, 26.2, 25.9 (3C), 25.5, 25.4, 18.1, 16.5, 11.3, −4.5, −4.8; for *trans*-**5e**: 72.0, 67.4, 40.0, 38.6, 31.5, 26.2, 25.9 (3C), 25.7, 25.0, 20.5, 17.0, 11.3, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{16}H_{31}NNaO_3Si$, 336.1971 [M + Na$^+$], found 336.1969.

(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-butyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15a). Under nitrogen atmosphere, DBU (1 mL, 6.69 mmol), Ag_2O (1.6016 g, 6.91 mmol), and iodine (1.7640 g, 6.95 mmol) were added in this order to a solution of **14a** (1.0957 g, 3.189 mmol) in dry THF (60 mL) at room temperature. The reaction mixture was stirred for 3.5 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 10:1 v/v) to give **15a** in 63% yield (0.6899 g, 2.02 mmol).

Pale yellow oil; $[\alpha]_D$ +38.5 ($CHCl_3$, c 0.81) ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (ddt, J = 5.6, 3.6, 1.8 Hz, 1H for 3,4-*trans*-**15a**), 3.43 (tdd, J = 7.4, 5.0, 1.9 Hz, 1H for 3,4-*cis*-**15a**), 3.17 (dt, J = 7.8, 5.9 Hz, 1H for 3,4-*cis*-**15a**), 2.95 (dtt, J = 9.4, 6.8, 1.6 Hz, 1H for 3,4-*trans*-**15a**), 2.32−1.90 (m, 3H), 1.68−1.38 (m, 4H), 1.36−1.16 (m, 5H), 1.01 (d, J = 6.8 Hz, 3H for 3,4-*cis*-**15a**), 0.98 (dd, J = 6.8, 2.0 Hz, 3H for 3,4-*trans*-**15a**), 0.89−0.84 (m, 12H), 0.05−0.00 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**15a**; 76.9, 71.9, 67.7, 38.8, 33.6, 31.1, 29.1, 25.9 (3C), 25.4, 23.2, 20.6, 18.0, 17.3, 14.1, 0.2, −4.5, −4.8; for *cis*-**15a**; 68.8, 68.1, 38.0, 35.3, 32.9, 31.7, 29.1, 25.8 (3C), 23.3, 20.6, 18.0, 17.3, 16.5, 1.4, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{18}H_{35}NNaO_3Si$, 364.2284 [M + Na$^+$], found 364.2283.

(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-propyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15b). Under nitrogen atmosphere, DBU (1 mL, 6.69 mmol), Ag_2O (1.9010 g, 8.23 mmol), and iodine (2.0591 g, 6.95 mmol) were added in this order to a solution of **14b** (1.3268 g, 8.14 mmol) in dry THF (80 mL) at room temperature. The reaction mixture was stirred for 2.5 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 10:1 v/v) to give **15b** in 64% yield (0.8427 g, 2.57 mmol).

Pale yellow oil; $[\alpha]_D$ +46.4 ($CHCl_3$, c 1.03); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58−3.51 (m, 1H for 3,4-*cis*-**15b**), 3.43 (tdd, J = 7.7, 5.1, 1.2 Hz, 1H for 3,4-*trans*-**15b**), 3.23−3.09 (m, 1H for 3,4-*trans*-**15b**), 3.00−2.91 (m, 1H for 3,4-*cis*-**15b**), 2.33−1.91 (m, 3H), 1.67−1.15 (m, 7H), 1.02 (d, J = 5.9 Hz, 3H for 3,4-*cis*-**15b**), 0.98 (dd, J = 6.8, 1.2 Hz, 3H for 3,4-*trans*-**15b**), 0.92−0.85 (m, 12H), 0.05−0.00 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**15b**; 71.9, 67.7, 38.8, 33.6, 31.1, 29.1, 25.9 (3C), 25.4, 23.2, 20.6, 18.1, 17.3, 14.1, −4.5, −4.8; for *cis*-**15b**; 68.8, 68.1, 38.0, 35.3, 32.9, 31.7, 29.1, 25.7 (3C), 23.3, 20.6, 18.0, 16.5, 14.1, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{17}H_{34}NO_3Si$, 328.2308 [M + H$^+$], found 328.2300.

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(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-pentyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15c). Under nitrogen atmosphere, DBU (0.79 mL, 5.29 mmol), Ag_2O (1.8765 g, 8.12 mmol), and iodine (2.2173 g, 8.76 mmol) were added in this order to a solution of **14c** (1.2474 g, 3.49 mmol) in dry THF (45 mL) at room temperature. The reaction mixture was stirred for 1 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 10:1 v/v) to give **15c** in 60% yield (0.7495 g, 2.11 mmol).

Pale yellow oil; $[\alpha]_D$ +28.9 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.56−3.52 (m, 1H for 3,4-*cis*-**15c**), 3.42 (q, *J* = 7.0 Hz, 1H for 3,4-*trans*-**15c**), 3.21−3.13 (m, 1H for 3,4-*cis*-**15c**), 2.94 (q, *J* = 6.8 Hz, 1H for 3,4-*trans*-**15c**), 2.25−1.89 (m, 3H), 1.64−1.51 (m, 1H), 1.50−1.40 (m, 1H), 1.37−1.20 (m, 8H), 1.21−1.06 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H for 3,4-*cis*-**15c**), 0.97 (d, *J* = 6.8 Hz, 3H for 3,4-*trans*-**15c**), 0.86 (s, 9H for 3,4-*trans*-**15c**), 0.89−0.84 (m, 3H), 0.85 (s, 9H for 3,4-*cis*-**15c**), 0.03 (s, 6H for 3,4-*trans*-**15c**), 0.02 (s, 3H for 3,4-*cis*-**15c**), 0.00 (s, 3H for 3,4-*cis*-**15c**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for 3,4-*cis*-**15c**; 68.8, 68.0, 38.0, 35.4, 33.2, 32.5, 31.7, 26.6, 25.8, 25.7 (3C), 22.7, 20.5, 18.0, 16.5, 14.2, −4.5, −4.8; for 3,4-*trans*-**15c**; 71.9, 67.7, 38.8, 33.9, 32.4, 31.7, 31.0, 26.6, 25.9 (3C), 25.3, 22.6, 20.5, 18.1, 17.3, 14.1, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{19}H_{38}NO_3Si$, 356.2621 [M + H^+], found 356.2613.

(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-isopropyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15d). Under nitrogen atmosphere, DBU (0.84 mL, 5.62 mmol), Ag_2O (2.0701 g, 8.96 mmol), and iodine (2.3073 g, 8.94 mmol) were added in this order to a solution of **14d** (1.3144 g, 3.99 mmol) in dry THF (50 mL) at room temperature. The reaction mixture was stirred for 1 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 5:1 v/v) to give **15d** in 64% yield (0.8306 g, 2.53 mmol). Further purification provided single isomer of *trans*-**15d**.

Pale yellow oil oil; $[\alpha]_D$ +83.6 ($CHCl_3$, *c* 0.41); ^1H NMR (500 MHz, $CDCl_3$) δ 3.65 (q, *J* = 3.6 Hz, 1H), 2.86 (d, *J* = 9.8 Hz, 1H), 2.15 (dd, *J* = 11.1, 5.1 Hz, 1H), 2.05 (ddd, *J* = 15.3, 6.9, 4.1 Hz, 1H), 2.00−1.87 (m, 3H), 1.66 (dd, *J* = 14.6, 3.5 Hz, 1H), 1.51 (dd, *J* = 8.6, 5.6 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.8, 66.4, 43.9, 33.7, 31.2, 26.4, 26.1, 25.8 (3C), 20.9, 20.8, 20.0, 19.1, 18.0, −4.9, −5.0; HRMS (ESI-TOF): calcd for $C_{17}H_{34}NO_3Si$, 328.2308 [M + H^+], found 328.2310.

(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-ethyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15e). Under nitrogen atmosphere, DBU (0.89 mL, 5.96 mmol), Ag_2O (2.1483 g, 9.30 mmol), and iodine (2.3540 g, 9.30 mmol) were added in this order to a solution of **14e** (1.1850 g, 3.756 mmol) in dry THF (45 mL) at room temperature. The reaction mixture was stirred for 1 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 5:1 v/v) to give **15e** in 79% yield (0.9371 g, 2.98 mmol).

Colorless oil; $[\alpha]_D$ +38.0 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.54 (ddd, *J* = 5.1, 3.4, 1.4 Hz, 1H for 3,4-*trans*-**15e**), 3.41 (td, *J* = 7.9, 5.3 Hz, 1H for 3,4-*cis*-**15e**), 3.14 (td, *J* = 7.8, 4.2 Hz, 1H for 3,4-*cis*-**15e**), 2.89 (dd, *J* = 6.8, 4.7 Hz, 1H for 3,4-*trans*-**15e**), 2.27−1.82 (m, 3H), 1.77−1.58 (m, 1H), 1.56−1.39 (m, 1H), 1.36−1.20 (m, 2H), 1.20−1.04 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 3H for 3,4-*cis*-**15e**), 0.98 (d, *J* = 6.6 Hz, 3H for 3,4-*trans*-**15e**), 0.89 (t, *J* = 7.8 Hz, 3H), 0.86 (s, 9 H for 3,4-*cis*-**15e**), 0.85 (s, 9H for 3,4-*trans*-**15e**), 0.03 (s, 6H for 3,4-*cis*-**15e**), 0.02 (s, 3H for 3,4-*trans*-**15e**), 0.00 (s, 3H for 3,4-*trans*-**15e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for 3,4-*cis*-**15c**; 69.0, 67.7, 38.5, 36.2, 31.9, 25.7 (3C), 25.4, 25.1, 22.8, 18.0, 16.5, 11.3, −4.5, −4.8; for *trans*-**15e**; 72.0, 67.4, 40.0, 37.7, 31.5, 26.1, 25.9 (3C), 25.5, 20.6, 18.1, 17.0, 11.3, −4.5, −4.8; HRMS (ESI-TOF): calcd for $C_{16}H_{32}NO_3Si$, 314.2151 [M + H^+], found 314.2159.

(1*R*,4*S*,5*S*,6*S*)-3-(*tert*-Butyldimethylsilyl)oxy-5-cyclohexyl-4-methyl-6-nitrobicyclo-[4.1.0]heptane (15f). Under nitrogen atmosphere, DBU (0.71 mL, 4.76 mmol), Ag_2O (1.7687 g, 7.66 mmol), and iodine (1.9384 g, 7.66 mmol) were added in this order to a solution of **14f** (1.2553 g, 3.396 mmol) in dry THF (50 mL) at room temperature. The reaction mixture was stirred for 4 h at the same temperature and then filtered. Solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane-EtOAc 30:1 then 3:1 v/v) to give **15f** in 68% yield (0.8486 g, 2.3 mmol). Further purification provided single isomer of *trans*-**15f**.

Pale yellow oil; $[\alpha]_D$ +53.6 ($CHCl_3$, *c* 1.10); ^1H NMR (500 MHz, $CDCl_3$) δ 3.64 (dd, *J* = 5.5, 4.8 Hz, 1H), 2.91 (d, *J* = 9.7 Hz, 1H), 2.15 (dd, *J* = 11.3, 5.0 Hz, 1H), 2.07−2.00 (m, 1H), 1.99−1.91 (m, 1H), 1.76−1.70 (m, 1H), 1.70−1.56 (m, 1H), 1.15 (m, 11H), 0.98 (dd, *J* = 13.4, 7.6 Hz, 1H), 0.91 (d, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.7, 66.8, 43.5, 39.7, 33.5, 31.5, 31.0, 28.3, 28.1, 26.6, 26.5, 26.3, 25.9, 25.8 (3C), 19.8, 18.1, −4.7, −4.8; HRMS (ESI-TOF): calcd for $C_{20}H_{37}NNaO_3Si$, 390.2440 [M + Na^+], found 390.2448.

(1*S*,3*R*,4*R*,5*R*,6*R*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (3,4-*trans*-7a). TBAF (1.0 M in THF, 1.4 mL, 1.4 mmol) was added to a solution of 3,4-*trans*-**5a** (72.1 mg, 0.212 mmol) in THF (1 mL), and the reaction mixture was stirred at room temperature for 12 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 6:1 v/v) to give 3,4-*trans*-**7a** in 58% yield (28.2 mg, 0.124 mmol).

Colorless oil; $[\alpha]_D$ −101.1 ($CHCl_3$, *c* 0.63); ^1H NMR (500 MHz, $CDCl_3$) δ 3.42 (q, *J* = 7.8 Hz, 1H), 2.91 (td, *J* = 7.3, 4.7 Hz, 1H), 2.40 (ddd, *J* = 13.8, 9.4, 5.5 Hz, 1H), 2.21 (dd, *J* = 11.2, 5.9 Hz, 1H), 1.94 (dtd, *J* = 9.3, 8.6, 2.9 Hz, 1H), 1.71−1.62 (m, 1H), 1.53−1.45 (m, 1H), 1.46−1.33 (m, 1H), 1.33−1.22 (m, 6H), 1.09 (s, 3H), 1.04 (td, *J* = 7.4, 6.1 Hz, 1H), 0.87 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.5, 67.9, 39.5, 39.3, 33.2, 32.4, 29.0, 25.3, 23.3, 20.8, 16.0, 14.1; HRMS (ESI-TOF): calcd for $C_{12}H_{21}NNaO_3$, 250.1419 [M + Na^+], found 250.1408.

(1*S*,3*S*,4*R*,5*R*,6*R*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (3,4-*cis*-7a). TBAF (1.0 M in THF, 1.0 mL, 1.0 mmol) was added to a solution of 3,4-*cis*-**5a** (69.6 mg, 0.204 mmol) in THF (1.5 mL), and the reaction mixture was stirred at room temperature for 14 h. $NaHCO_3$ aq (30 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 50 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 7:1 v/v) to give 3,4-*cis*-**7a** in 75% yield (35.0 mg, 0.154 mmol).

Colorless oil; $[\alpha]_D$ −32.3 ($CHCl_3$, *c* 1.07); ^1H NMR (500 MHz, $CDCl_3$) δ 3.62 (dt, *J* = 5.7, 2.9 Hz, 1H), 3.19 (td, *J* = 6.9, 4.8 Hz, 1H), 2.18−2.04 (m, 3H), 1.66 (dd, *J* = 12.3, 4.9 Hz, 1H), 1.58−1.50 (m, 2H), 1.36−1.24 (m, 6H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 6.5 Hz, 3H), 0.85−0.82 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 67.9, 67.8, 37.2, 35.8, 33.0, 30.2, 29.2, 25.6, 23.2, 19.9, 15.5, 14.1; HRMS (ESI-TOF): calcd for $C_{12}H_{21}NNaO_3$, 250.1419 [M + Na^+], found 250.1404.

(1*S*,4*R*,5*R*,6*R*)-5-Propyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (7b). TBAF (1.0 M in THF, 3 mL, 3 mmol) was added to a solution of **5b** (0.1997 g, 0.61 mmol) in THF (1.5 mL), and the reaction mixture was stirred at room temperature for 100 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 10:1 v/v) to give **7b** in 89% yield (0.1158 g, 0.543 mmol).

Pale yellow oil; $[\alpha]_D$ −64.7 ($CHCl_3$, *c* 1.05); ^1H NMR (500 MHz, $CDCl_3$) δ 3.64−3.60 (m, 1H for 3,4-*cis*-**7b**), 3.43 (q, *J* = 8.3 Hz, 1H for 3,4-*trans*-**7b**), 3.20 (q, *J* = 6.8 Hz, 1H for 3,4-*cis*-**7b**), 2.93 (q, *J* = 7.4 Hz, 1H for 3,4-*trans*-**7b**), 2.41 (ddd, *J* = 14.1, 9.0, 5.6 Hz, 1H for 3,4-*trans*-**7b**), 2.21 (dd, *J* = 11.0, 5.8 Hz, 1H for 3,4-*trans*-**7b**), 2.18−2.05 (m, 3H for 3,4-*cis*-**7b**), 1.94 (qd, *J* = 10.5, 2.8 Hz, 1H for 3,4-*trans*-**7b**), 1.70−1.60 (m, 1H), 1.55 (s, 1H), 1.47−1.23 (m, 5H), 1.13−1.06 (m, 3H), 1.06−1.00 (m, 1H for 3,4-*trans*-**7b**), 0.92 (t, *J* = 6.7 Hz, 3H for

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J. Org. Chem. 2016, 81, 4664−4681

3,4-*cis*-**7b**), 0.89 (t, J = 6.9 Hz, 3H for 3,4-*trans*-**7b**), 0.87−0.81 (m, 1H for 3,4-*cis*-**7b**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for 3,4-*trans*-**7b**; 71.3, 68.0, 39.4, 39.3, 35.8, 32.4, 25.5, 20.7, 20.1, 16.0, 14.6; for 3,4-*cis*-**7b**; 68.1, 67.8, 37.1, 35.6, 35.6, 30.1, 25.8, 20.3, 20.0, 15.4, 14.5; HRMS (ESI-TOF): calcd for $C_{11}H_{19}NNaO_3$, 236.1263 [M + Na^+], found 236.1271.

(1*S*,4*R*,5*R*,6*R*)-5-Pentyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (7c). TBAF (1.0 M in THF, 1.4 mL, 1.4 mmol) was added to a solution of **5c** (0.6339 g, 1.78 mmol) in THF (3 mL), and the reaction mixture was stirred at room temperature for 92 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 15:1 then 10:1 v/v) to give **7c** in 79% yield (0.3395 g, 1.41 mmol).

Pale yellow oil; $[\alpha]_D$ −42.0 ($CHCl_3$, c 1.07); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.60 (ddd, J = 6.5, 4.2, 2.0 Hz, 1H for *cis*-**7c**), 3.40 (td, J = 9.2, 5.7 Hz, 1H for *trans*-**7c**), 3.21−3.13 (m, 1H for *cis*-**7c**), 2.90 (dddd, J = 8.6, 7.2, 4.3, 1.3 Hz, 1H for *trans*-**7c**), 2.39 (dddd, J = 14.8, 9.1, 5.6, 1.1 Hz, 1H for *tran*-**7c**), 2.26−2.16 (m, 1H for *trans*-**7c**), 2.17−2.05 (m, 3H for *cis*-**7c**), 1.92 (dddd, J = 10.8, 9.2, 7.8, 2.7 Hz, 1H for *trans*-**7c**), 1.72−1.47 (m, 2H), 1.46−1.11 (m, 9H), 1.13−1.00 (m, 4H), 0.85 (t, J = 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**7c**; 71.4, 67.9, 39.5, 37.1, 33.4, 32.4, 32.3, 26.7, 25.3, 22.6, 20.7, 16.0, 14.1; for *cis*-**7c**; 68.0, 67.8, 39.4, 35.8, 33.3, 32.4, 30.1, 26.5, 25.6, 22.6, 19.9, 15.4, 14.1; HRMS (ESI-TOF): calcd for $C_{13}H_{23}NNaO_3$, 264.1576 [M + Na^+], found 264.1569.

(1*S*,4*R*,5*R*,6*R*)-5-Isopropyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (7d). TBAF (1.0 M in THF, 6 mL, 6 mmol) was added to a solution of **5d** (1.0455 g, 3.19 mmol) in THF (5 mL), and the reaction mixture was stirred at room temperature for 12 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 15:1 then 10:1 v/v) to give **7d** in 79% yield (0.5073 g, 2.38 mmol). Further chromatographic treatment gave diastereomerically pure *trans*-**7d**.

White solid; mp 73−73.8 °C; $[\alpha]_D$ −99.9 ($CHCl_3$, c 1.36); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.70−3.65 (m, 1H), 2.90 (dd, J = 8.6, 4.4 Hz, 1H), 2.24 (dd, J = 11.3, 5.4 Hz, 1H), 2.19 (ddd, J = 14.4, 7.2, 4.9 Hz, 1H), 1.97−1.86 (m, 2H), 1.80 (q, J = 6.2 Hz, 1H), 1.62 (dd, J = 14.7, 5.4 Hz, 1H), 1.39 (dd, J = 7.7, 5.6 Hz, 1H), 1.30 (d, J = 3.3 Hz, 1H), 1.01 (d, J = 6.8 Hz, 6H), 0.91 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.5, 66.5, 43.9, 34.7, 31.3, 28.2, 25.2, 20.8, 20.8, 20.5, 18.2; HRMS (ESI-TOF): calcd for $C_{11}H_{19}NNaO_3$, 236.1263 [M + Na^+], found 236.1277.

(1*S*,4*R*,5*R*,6*R*)-5-Ethyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-ol (7e). TBAF (1.0 M in THF, 1.36 mL, 1.36 mmol) was added to a solution of **5e** (0.1807 g, 0.5754 mmol) in THF (1.2 mL), and the reaction mixture was stirred at room temperature for 22 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 15:1 then 10:1 v/v) to give **7e** in 79% yield (0.1094 g, 0.549 mmol).

Pale yellow oil; $[\alpha]_D$ −67.8 ($CHCl_3$, c 0.57); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.56 (ddd, J = 6.1, 4.0, 2.2 Hz, 1H for *cis*-**7e**), 3.41−3.33 (m, 1H for *trans*-**7e**), 3.08 (td, J = 7.6, 4.9 Hz, 1H for *cis*-**7e**), 2.82 (td, J = 7.4, 3.8 Hz, 1H for *trans*-**7e**), 2.40−2.31 (m, 1H for *trans*-**7e**), 2.17 (ddd, J = 11.0, 5.5, 1.5 Hz, 1H for *trans*-**7e**), 2.14−1.97 (m, 3H for *cis*-**7e**), 1.87 (dtd, J = 10.8, 8.6, 2.7 Hz, 1H for *trans*-**7e**), 1.72 (dqd, J = 15.0, 7.6, 4.3 Hz, 1H for *trans*-**7e**), 1.66−1.54 (m, 1H), 1.54−1.36 (m, 1H for *cis*-**7e** and 2H for *trans*-**7e**), 1.31 (tt, J = 10.2, 3.2 Hz, 2H for *trans*-**7e**), 1.23 (td, J = 7.2, 2.3 Hz, 2H for *cis*-**7e**), 1.06−1.01 (m, 3H), 0.99 (dd, J = 7.9, 5.8 Hz, 1H for *trans*-**7e**), 0.89 (d, J = 7.7 Hz, 3H for *cis*-**7e**), 0.85 (t, J = 7.5 Hz, 3H for *trans*-**7e**), 0.79 (dd, J = 7.7, 5.7 Hz, 1H for *cis*-**7e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *cis*-**7e**: 67.5, 67.4, 36.8, 36.8, 30.4, 25.7, 25.2, 19.9, 15.5, 11.4; for *trans*-**7e**; 71.4, 68.0, 40.3, 39.1, 32.5, 25.7, 24.9, 20.7, 15.8, 11.1; HRMS (ESI-TOF): calcd for $C_{10}H_{17}NNaO_3$, 222.1106 [M + Na^+], found 222.1108.

(1*R*,4*S*,5*S*,6*S*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-ol (17a). TBAF (1.0 M in THF, 5.8 mL, 5.8 mmol) was added to a solution of **15a** (0.4792 g, 1.403 mmol) in THF (3 mL), and the reaction mixture was stirred at room temperature for 120 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 50 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 10:1 v/v) to give **17a** in 90% yield (0.2869 g, 1.26 mmol).

Pale yellow oil; $[\alpha]_D$ +64.4 ($CHCl_3$, c 1.37); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64−3.58 (m, 1H for *cis*-**17a**), 3.42 (q, J = 8.5, 7.9 Hz, 1H for *trans*-**17a**), 3.18 (q, J = 6.6 Hz, 1H for *cis*-**17a**), 2.91 (q, J = 7.1 Hz, 1H for *trans*-**17a**), 2.40 (dt, J = 14.6, 7.4 Hz, 1H for *trans*-**17a**), 2.21 (dd, J = 11.0, 6.0 Hz, 1H for *trans*-**17a**), 2.18−2.04 (m, 3H for *cis*-**17a**), 1.94 (q, J = 9.3 Hz, 1H for *trans*-**17a**), 1.88−1.63 (m, 1H), 1.56 (s, 1H), 1.47−1.19 (m, 7H), 1.13−1.06 (m, 3H), 1.04 (t, J = 7.3 Hz, 1H for *trans*-**17a**), 0.88 (t, J = 6.7 Hz, 3H for *trans*-**17a**), 0.86 (t, J = 5.0 Hz, 3H for *cis*-**17a**), 0.85−0.82 (m, 1H for *cis*-**17a**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**17a**; 71.5, 67.9, 39.5, 39.3, 33.2, 32.4, 29.0, 25.2, 23.3, 20.7, 16.0, 14.1; for *cis*-**17a**; 67.9, 67.8, 37.2, 35.8, 33.0, 30.2, 29.2, 25.6, 23.2, 19.8, 15.4, 14.1; HRMS (ESI-TOF): calcd for $C_{12}H_{21}NNaO_3$, 250.1419 [M + Na^+], found 250.1418.

(1*R*,4*S*,5*S*,6*S*)-5-Propyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (17b). TBAF (1.0 M in THF, 1 mL, 1 mmol) was added to a solution of **15b** (0.1578 g, 0.4635 mmol) in THF (1 mL), and the reaction mixture was stirred at room temperature for 93 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 20:1 then 10:1 v/v) to give **17b** in 90% yield (0.0886 g, 0.4154 mmol).

Colorless oil; $[\alpha]_D$ +35.9 ($CHCl_3$, c 1.37); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63−3.58 (m, 1H for 3,4-*cis*-**17b**), 3.41 (q, J = 8.4 Hz, 1H for 3,4-*trans*-**17b**), 3.18 (dd, J = 13.8, 6.8 Hz, 1H for 3,4-*cis*-**17b**), 2.95−2.87 (m, 1H for 3,4-*trans*-**17b**), 2.39 (dt, J = 14.8, 7.4 Hz, 1H for 3,4-*trans*-**17b**), 2.20 (t, J = 10.6, 4.8 Hz, 1H for 3,4-*trans*-**17b**), 2.16−2.04 (m, 3H for 3,4-*cis*-**17b**), 1.93 (q, J = 9.2 Hz, 1H for 3,4-*trans*-**17b**), 1.69−1.59 (m, 1H), 1.60−1.44 (m, 1H), 1.43−1.22 (m, 5H), 1.11−1.05 (m, 3H), 1.03 (t, J = 7.1 Hz, 1H for 3,4-*trans*-**17b**), 0.90 (t, J = 7.2 Hz, 3H for 3,4-*cis*-**17b**), 0.87 (t, J = 6.8 Hz, 3,4-*trans*-**17b**), 0.86−0.80 (m, 1H for 3,4-*cis*-**17b**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**17b**; 71.4, 67.9, 39.5, 39.3, 35.8, 32.4, 25.3, 20.7, 20.1, 16.0, 14.7; for *cis*-**17b**; 68.0, 67.8, 37.2, 35.7, 35.6, 30.2, 25.6, 20.3, 19.9, 15.5, 14.6; HRMS (ESI-TOF): calcd for $C_{11}H_{19}NNaO_3$, 236.1263 [M + Na^+], found 236.1262.

(1*R*,4*S*,5*S*,6*S*)-5-Pentyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (17c). TBAF (1.0 M in THF, 3.6 mL, 3.6 mmol) was added to a solution of **15c** (0.7343 g, 2.065 mmol) in THF (3 mL), and the reaction mixture was stirred at room temperature for 50 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 8:1 v/v) to give **17c** in 75% yield (0.1365 g, 1.546 mmol).

Pale yellow oil; $[\alpha]_D$ +61.6 ($CHCl_3$, c 1.12); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (ddt, J = 6.4, 5.0, 2.1 Hz, 1H for *cis*-**17c**), 3.46−3.38 (m, 1H for *trans*-**17c**), 3.19 (dq, J = 7.2, 4.7 Hz, 1H for *cis*-**17c**), 2.92 (ddt, J = 8.4, 7.0, 2.7 Hz, 1H for *trans*-**17c**), 2.45−2.35 (m, 1H for *trans*-**17c**), 2.21 (ddt, J = 10.9, 5.8, 1.5 Hz, 1H for *trans*-**17c**), 2.17−2.06 (m, 3H for *cis*-**17c**), 1.94 (dtdd, J = 11.9, 9.1, 2.8, 1.3 Hz, 1H for *trans*-**17c**), 1.73−1.58 (m, 1H), 1.58−1.49 (m, 1H), 1.47−1.16 (m, 9H), 1.14−1.00 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**17c**; 71.4, 67.9, 39.4, 39.4, 33.4, 32.4, 32.4, 26.5, 25.3, 22.6, 20.8, 16.0, 14.2; for *cis*-**17c**; 67.9, 67.8, 37.1, 35.8, 33.3,

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32.3, 30.1, 26.7, 25.7, 22.6, 19.9, 15.5, 14.2; HRMS (ESI-TOF): calcd for $C_{13}H_{23}NNaO_3$, 264.1576 [M + Na^+], found 264.1573.

(1*R*,4*S*,5*S*,6*S*)-5-Isopropyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (17d). TBAF (1.0 M in THF, 1.5 mL, 1.5 mmol) was added to a solution of **15d** (0.2835 g, 0.8656 mmol) in THF (1.5 mL), and the reaction mixture was stirred at room temperature for 48 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 10:1 then 3:1 v/v) to give **17d** in 73% yield (0.1365 g, 0.641 mmol). Further chromatographic treatment gave diastereomerically pure *trans*-**17d**.

White solid; mp 73.1−73.6 °C; $[\alpha]_D$ +99.6 ($CHCl_3$, *c* 0.90); ^1H NMR (500 MHz, $CDCl_3$) δ 3.61 (dq, *J* = 5.8, 5.4 Hz, 1H), 2.85 (dt, *J* = 8.2, 4.1 Hz, 1H), 2.23−2.11 (m, 2H), 1.96−1.79 (m, 3H), 1.82−1.70 (m, 1H), 1.65−1.51 (m, 1H), 1.41−1.32 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 6H), 0.87 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.5, 66.5, 43.9, 34.7, 31.3, 28.1, 25.2, 20.8, 20.8, 20.5, 18.2; HRMS (ESI-TOF): calcd for $C_{11}H_{19}NNaO_3$, 236.1263 [M + Na^+], found 236.1270.

(1R,4S,5S,6S)-5-Ethyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-ol (17e). TBAF (1.0 M in THF, 3 mL, 3 mmol) was added to a solution of **15e** (0.4924 g, 1.57 mmol) in THF (3 mL), and the reaction mixture was stirred at room temperature for 77 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 15:1 then 10:1 v/v) to give **17e** in 82% yield (0.2578 g, 1.294 mmol).

Pale yellow oil; $[\alpha]_D$ +68.1 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.51 (ddd, *J* = 6.3, 4.0, 2.0 Hz, 1H for *cis*-**17e**), 3.30 (td, *J* = 9.0, 5.5 Hz, 1H for *trans*-**17e**), 3.03 (td, *J* = 7.6, 5.1 Hz, 1H for *cis*-**17e**), 2.77 (td, *J* = 7.7, 4.0 Hz, 1H *trans*-**17e**), 2.54−2.38 (m, 1H), 2.31 (ddd, *J* = 14.2, 9.1, 5.7 Hz, 1H *trans*-**17e**), 2.13 (dd, *J* = 10.9, 5.8 Hz, 1H *trans*-**17e**), 2.10−1.93 (m, 3H for *cis*-**17e**), 1.88−1.78 (m, 1H *trans*-**17e**), 1.75−1.63 (m, 1H *trans*-**17e**), 1.63−1.54 (m, 1H), 1.45−1.16 (m, 2H *trans*-**17e** and 3H *cis*-**17e**), 1.08−0.92 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H for *cis*-**17e**), 0.83 (t, *J* = 8.2 Hz, 3H *trans*-**17e**); ^{13}C NMR (126 MHz, $CDCl_3$) δ for *trans*-**17e**; 71.1, 67.6, 40.3, 38.9, 36.7, 32.5, 25.6, 20.8, 15.7, 11.1; for *cis*-**17e**; 67.6, 67.5, 40.3, 38.9, 36.7, 30.1, 25.2, 20.0, 15.4, 11.4; HRMS (ESI-TOF): calcd for $C_{10}H_{17}NNaO_3$, 222.1106 [M + Na^+], found 222.1114.

(1*R*,4*S*,5*S*,6*S*)-5-Ethyl-4-cyclohexyl-6-nitrobicyclo[4.1.0]-heptan-3-ol (17f). TBAF (1.0 M in THF, 6.3 mL, 6.3 mmol) was added to a solution of **15f** (0.8368 g, 2.28 mmol) in THF (4.5 mL), and the reaction mixture was stirred at room temperature for 240 h. $NaHCO_3$ aq (20 mL) was added, and THF was removed in vacuo. Resulting aqueous solution was extracted with EtOAc (2 × 30 mL), and combined organic phase was dried over Na_2SO_4. After filtration, solvent was removed, and residue was subjected to flash chromatography (silica gel/hexane-EtOAc 15:1 then 10:1 v/v) to give **17f** in 79% yield (0.4533 g, 1.79 mmol). Further chromatographic treatment gave diastereomerically pure *trans*-**17f**.

Pale yellow oil; $[\alpha]_D$ +78.8 ($CHCl_3$, *c* 0.38); ^1H NMR (500 MHz, $CDCl_3$) δ 3.63 (q, *J* = 5.7 Hz, 1H), 2.92 (dd, *J* = 8.0, 5.1 Hz, 1H), 2.24 (dt, *J* = 8.6, 4.2 Hz, 1H), 2.20 (t, *J* = 9.2, 6.9 Hz, 1H), 1.95−1.83 (m, 2H), 1.83−1.49 (m, 9H), 1.36 (dd, *J* = 8.1, 5.6 Hz, 1H), 1.25−1.10 (m, 4H), 1.01 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 71.5, 66.5, 43.2, 41.4, 34.0, 31.3, 30.9, 28.6, 26.8, 26.7, 26.6, 25.2, 20.6, 18.1; HRMS (ESI-TOF): calcd for $C_{14}H_{23}NNaO_3$, 276.1576 [M + Na^+], found 276.1584.

(1*S*,4*R*,5*R*,6*R*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (8a) from 3,4-*trans*-7a. A solution of 3,4-*trans*-**7a** (0.0190 g, 0.084 mmol) and Dess−Martin periodinane (0.050 g, 0.118 mmol) in CH_2Cl_2 (0.2 mL) was stirred at room temperature for 12 h. The reaction mixture was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 10:1 then 6:1 v/v) to give **8a** in 61% yield (0.0116 g, 0.051 mmol).

(1*S*,4*R*,5*R*,6*R*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (8a) from 3,4-*cis*-7a. A solution of 3,4-*cis*-**7a** (0.0150 g, 0.066 mmol) and Dess−Martin periodinane (0.0322 g, 0.076 mmol) in CH_2Cl_2 (0.2 mL) was stirred at room temperature for 2 h. The reaction mixture was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 10:1 then 5:1 v/v) to give **8a** in 85% yield (0.0127 g, 0.0564 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 32.0 min (minor); t_R 39.7 min (major) [CHIRALPAK IC (0.46 cm × 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ −147.0 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.36 (dt, *J* = 7.4, 6.0 Hz, 1H), 2.88 (dd, *J* = 17.7, 6.9 Hz, 1H), 2.43 (d, *J* = 17.7 Hz, 1H), 2.39−2.26 (m, 2H), 2.10 (dt, *J* = 13.9, 6.9 Hz, 1H), 1.57−1.47 (m, 1H), 1.45−1.24 (m, 5H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.15 (t, *J* = 6.5, 5.5 Hz, 1H), 0.88 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 66.2, 45.6, 40.3, 36.2, 32.5, 28.1, 25.3, 22.9, 19.6, 15.1, 14.0; IR (neat) ν 1714, 1531, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{12}H_{19}NNaO_3$, 248.1263 [M + Na^+], found 248.1268.

(1*S*,4*R*,5*R*,6*R*)-5-Propyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-one (8b). A solution of **7b** (0.3402 g, 1.595 mmol) and Dess−Martin periodinane (1.352 g, 3.188 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 93 h. Precipitate was removed by filtration and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **8b** in 98% yield (0.3313 g, 1.57 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 17.3 min (major); t_R 18.7 min (minor) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ −146.9 ($CHCl_3$, *c* 1.20); ^1H NMR (500 MHz, $CDCl_3$) δ 3.38 (q, *J* = 6.2 Hz, 1H), 2.88 (dd, *J* = 17.7, 6.7 Hz, 1H), 2.42 (d, *J* = 17.6 Hz, 1H), 2.39−2.28 (m, 2H), 2.10 (p, *J* = 7.0 Hz, 1H), 1.55−1.31 (m, 4H), 1.23 (dd, *J* = 6.8, 0.6 Hz, 3H), 1.15 (t, *J* = 6.2 Hz, 1H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 66.2, 45.6, 40.2, 36.1, 35.1, 25.3, 19.6, 19.3, 15.1, 14.3; IR (neat) ν 1714, 1533, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_3$, 212.1287 [M + H^+], found 212.1290.

(1*S*,4*R*,5*R*,6*R*)-5-Pentyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-one (8c). A solution of **7c** (0.3632 g, 1.505 mmol) and Dess−Martin periodinane (1.4089 g, 3.322 mmol) in CH_2Cl_2 (4 mL) was stirred at room temperature for 22 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 8:1) to give **8c** in 65% yield (0.2352 g, 0.9828 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 13.3 min (minor); t_R 15.1 min (major) [YMC Chiral Cellulose-C (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ −138.0 ($CHCl_3$, *c* 0.92); ^1H NMR (500 MHz, $CDCl_3$) δ 3.34 (q, *J* = 5.5 Hz, 1H), 2.87 (dd, *J* = 17.7, 6.7 Hz, 1H), 2.40 (d, *J* = 17.6 Hz, 1H), 2.37−2.24 (m, 2H), 2.09 (p, *J* = 7.0 Hz, 1H), 1.55−1.44 (m, 1H), 1.43−1.23 (m, 7H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.14 (dd, *J* = 6.8, 5.7 Hz, 1H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 66.2, 45.6, 40.3, 36.1, 32.8, 32.0, 25.7, 25.3, 22.6, 19.6, 15.1, 14.1; IR (neat) ν 1714, 1533, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{22}NO_3$, 240.1600 [M + H^+], found 240.1599.

(1*S*,4*R*,5*R*,6*R*)-5-Isopropyl-4-methyl-6-nitrobicyclo[4.1.0]-heptan-3-one (8d). A solution of **7d** (0.1359 g, 0.637 mmol) and Dess−Martin periodinane (1.5397 g, 1.27 mmol) in CH_2Cl_2 (1.3 mL) was stirred at room temperature for 7 days. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **8d** in 91% yield (0.1222 g, 0.577 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 13.4 min (major); t_R 17.2 min (minor) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 98% ee. $[\alpha]_D$ −153.6 ($CHCl_3$, *c* 0.49); ^1H NMR (500 MHz, $CDCl_3$) δ 3.34 (dd, *J* = 10.0, 3.1 Hz, 1H), 2.91 (ddd, *J* = 16.9, 7.7, 0.8 Hz, 1H), 2.59 (dtd, *J* = 10.8, 7.7, 1.5 Hz, 1H), 2.50 (qd, *J* = 7.0, 3.1 Hz, 1H), 2.36 (dd, *J* = 10.8, 6.5 Hz, 1H), 2.29 (d, *J* = 17.0

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J. Org. Chem. 2016, 81, 4664−4681

Hz, 1H), 1.35 (dtd, J = 13.2, 6.6, 3.4 Hz, 1H), 1.30 (d, J = 7.1 Hz, 3H), 1.02 (t, J = 6.6 Hz, 1H), 1.00 (d, J = 6.5 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7, 65.3, 48.4, 43.9, 35.1, 30.8, 27.6, 21.6, 20.9, 20.2, 17.5; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_3$, 212.1287 [M + H^+], found 212.1271.

(1*S*,4*R*,5*R*,6*R*)-5-Ethyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (8e). A solution of **7e** (0.3778 g, 1.9 mmol) and Dess−Martin periodinane (1.600 g, 3.772 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 72 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 8:1) to give **8e** in 87% yield (0.3241 g, 1.64 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 20.9 min (major); t_R 24.5 min (minor) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 96% ee. $[\alpha]_D$ −179.0 ($CHCl_3$, *c* 1.11); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.16 (dt, J = 8.1, 5.7 Hz, 1H), 2.79 (dd, J = 17.7, 6.7 Hz, 1H), 2.34 (d, J = 17.8 Hz, 1H), 2.27−2.12 (m, 2H), 2.00 (qdd, J = 7.8, 5.4, 2.1 Hz, 1H), 1.55 (dqd, J = 14.9, 7.5, 5.2 Hz, 1H), 1.39 (dqd, J = 14.9, 7.5, 6.0 Hz, 1H), 1.14 (dd, J = 6.9, 5.8 Hz, 1H), 1.09 (d, J = 6.9 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 65.9, 44.7, 40.9, 36.2, 24.8, 24.7, 19.1, 14.4, 10.0; IR (neat) ν 1712, 1531, 1348 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{10}H_{15}NNaO_3$, 220.0950 [M + Na^+], found 220.0963.

(1*R*,4*S*,5*S*,6*S*)-5-Butyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18a). A solution of **17a** (0.2729 g, 1.201 mmol) and Dess−Martin periodinane (1.3828 g, 3.26 mmol) in CH_2Cl_2 (13 mL) was stirred at room temperature for 16 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 20:1) to give **18a** in 88% yield (0.2383 g, 1.06 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 37.6 min (minor); t_R 31.5 min (major) [CHIRALPAK IC (0.46 cm × 25 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 98% ee. $[\alpha]_D$ +128.3 ($CHCl_3$, *c* 1.10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (dt, J = 7.3, 5.9 Hz, 1H), 2.88 (dd, J = 17.5, 6.8 Hz, 1H), 2.42 (dt, J = 17.6, 1.4 Hz, 1H), 2.38−2.27 (m, 2H), 2.10 (p, J = 6.9 Hz, 1H), 1.57−1.24 (m, 6H), 1.22 (d, J = 6.9 Hz, 3H), 1.15 (ddd, J = 7.4, 5.7, 1.4 Hz, 1H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5, 66.2, 45.6, 40.3, 36.1, 32.5, 28.1, 25.3, 22.9, 19.5, 15.1, 14.0; IR (neat) ν 1678, 1533 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{12}H_{19}NNaO_3$, 248.1263 [M + Na^+], found 248.1276.

(1*R*,4*S*,5*S*,6*S*)-5-Propyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18b). A solution of **17b** (0.1678 g, 0.7868 mmol) and Dess−Martin periodinane (0.7451 g, 1.76 mmol) in CH_2Cl_2 (9 mL) was stirred at room temperature for 24 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **18b** in 83% yield (0.1375 g, 0.651 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 18.9 min (minor); t_R 19.3 min (major) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ +152.2 ($CHCl_3$, *c* 1.10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (q, J = 5.7 Hz, 1H), 2.89 (ddd, J = 17.7, 7.0, 2.6 Hz, 1H), 2.42 (d, J = 17.7 Hz, 1H), 2.39−2.27 (m, 2H), 2.10 (p, J = 6.7 Hz, 1H), 1.54−1.30 (m, 4H), 1.22 (dd, J = 7.0, 2.3 Hz, 3H), 1.15 (ddd, J = 6.9, 5.7, 2.3 Hz, 1H), 0.90 (t, J = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5, 66.2, 45.6, 40.2, 36.1, 35.1, 25.3, 19.5, 19.3, 15.1, 14.3; IR (neat) ν 1712, 1531, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_3$, 212.1287 [M + H^+], found 212.1286.

(1*R*,4*S*,5*S*,6*S*)-5-Pentyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18c). A solution of **17c** (0.2641 g, 1.09 mmol) and Dess−Martin periodinane (0.9212 g, 2.172 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 72 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **8c** in 79% yield (2.079 g, 0.869 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 13.5 min (major); t_R 14.8 min (minor) [YMC Chiral Cellulose-C (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ +136.0 ($CHCl_3$, *c* 1.05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (ddd, J = 7.1, 5.9, 4.9 Hz, 1H), 2.87 (dd, J = 18.7, 6.9 Hz, 1H), 2.42 (d, J = 18.0 Hz, 1H), 2.39−2.27 (m, 2H), 2.10 (p, J = 6.9 Hz, 1H), 1.55−1.44 (m, 1H), 1.46−1.24 (m, 5H), 1.22 (d, J = 6.9 Hz, 3H), 1.15 (dd, J = 6.8, 5.7 Hz, 1H), 0.85 (t, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 66.2, 45.6, 40.3, 36.1, 32.8, 32.0, 25.7, 25.3, 22.6, 19.6, 15.1, 14.1; IR (neat) ν 1713, 1533, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{21}NNaO_3$, 262.1419 [M + Na^+], found 262.1416.

(1*R*,4*S*,5*S*,6*S*)-5-Isopropyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18d). A solution of **17d** (0.2151 g, 1.01 mmol) and Dess−Martin periodinane (0.8610 g, 2.03 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 70 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **18d** in 84% yield (0.178 g, 0.8426 mmol).

White solid; mp 36−37 °C. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 14.0 min (minor); t_R 17.8 min (major) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ +143.9 ($CHCl_3$, *c* 0.98); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.22 (tt, J = 8.6, 3.6 Hz, 1H), 2.82 (dt, J = 15.1, 7.1 Hz, 1H), 2.53−2.43 (m, 1H), 2.43−2.33 (m, 1H), 2.27−2.12 (m, 2H), 1.32−1.22 (m, 1H), 1.19 (d, J = 6.8 Hz, 3H), 0.94 (t, J = 6.6 Hz, 1H), 0.89 (d, J = 5.7 Hz, 3H), 0.84 (d, J = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 65.3, 48.2, 43.8, 35.1, 30.7, 27.5, 21.5, 20.8, 20.1, 17.3; IR (neat) ν 1714, 1533, 1342 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_3$, 212.1287 [M + H^+], found 212.1280.

(1*R*,4*S*,5*S*,6*S*)-5-Ethyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18e). A solution of **17e** (0.1064 g, 0.534 mmol) and Dess−Martin periodinane (0.4832 g, 1.14 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 66 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **18e** in 86% yield (0.0906 g, 0.459 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 20.9 min (minor); t_R 23.9 min (major) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 98% ee. $[\alpha]_D$ +174.2 ($CHCl_3$, *c* 1.03); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (dt, J = 8.3, 6.7 Hz, 1H), 2.88 (dd, J = 17.8, 6.6 Hz, 1H), 2.45 (d, J = 17.8 Hz, 1H), 2.40−2.24 (m, 2H), 2.10 (p, J = 7.2 Hz, 1H), 1.71−1.59 (m, 1H), 1.55−1.42 (m, 1H), 1.22 (dd, J = 6.9, 2.0 Hz, 3H), 1.18 (td, J = 6.5, 1.6 Hz, 1H), 0.94 (td, J = 7.5, 2.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 65.9, 44.9, 41.1, 36.3, 25.1, 24.7, 19.2, 14.7, 10.2; IR (neat) ν 1712, 1529, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{10}H_{15}NNaO_3$, 220.0950 [M + Na^+], found 220.0951.

(1*R*,4*S*,5*S*,6*S*)-5-Cyclohexyl-4-methyl-6-nitrobicyclo[4.1.0]heptan-3-one (18f). A solution of **17f** (0.2995 g, 1.18 mmol) and Dess−Martin periodinane (1.0052 g, 2.37 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 92 h. Precipitate was removed by filtration, and the fitrate was concentrated. The residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1) to give **8f** in 75% yield (0.2237 g, 0.89 mmol).

Pale yellow oil. The enantiomeric purity was determined by HPLC analysis (237 nm, 40 °C) t_R 13.7 min (minor); t_R 16.7 min (major) [YMC CHIRAL Amylose-SA (0.46 cm × 25 cm) hexane/*i*-PrOH, 98/2, 0.70 mL/min] as 99% ee. $[\alpha]_D$ +128.3 ($CHCl_3$, *c* 1.10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43−3.37 (m, 1H), 2.90 (dd, J = 17.0, 7.7 Hz, 1H), 2.61−2.49 (m, 2H), 2.34 (dd, J = 10.8, 6.5 Hz, 1H), 2.28 (d, J = 16.9 Hz, 1H), 1.89 (ddd, J = 10.6, 4.9, 2.8 Hz, 1H), 1.80−1.61 (m, 4H), 1.29 (d, J = 7.1 Hz, 3H), 1.22−1.08 (m, 3H), 1.08−0.92 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 65.1, 47.2, 43.0, 40.3, 35.3, 31.1, 30.4, 27.6, 26.3, 26.2, 26.2, 21.6, 17.5; IR (neat) ν 1714, 1533, 1342 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{14}H_{21}NNaO_3$, 274.1419 [M + Na^+], found 274.1422.

(1*S*,5*R*,6*S*,7*R*)-6-Butyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]octan-3-one (9a). A solution of **8a** (0.4166 g, 1.85 mmol) and mCPBA (0.5148 g, 80%, 1.83 mmol) in CH_2Cl_2 (2 mL) was heated to

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J. Org. Chem. 2016, 81, 4664−4681

refluxing temperature for 15 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **9a** in 73% yield (0.326 g, 1.35 mmol).

White solid; mp 90−91 °C; $[\alpha]_D$ +92.2 ($CHCl_3$, *c* 1.10); ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (dq, *J* = 6.0, 10.4 Hz, 1H), 3.53 (dddd, *J* = 1.0, 4.7, 8.4, 10.3 Hz, 1H), 3.09 (dd, *J* = 8.4, 14.7 Hz, 1H), 2.49 (dd, *J* = 8.2, 14.8 Hz, 1H), 2.40 (ddt, *J* = 0.9, 6.3, 10.6 Hz, 1H), 2.32 (dq, *J* = 8.4, 10.6 Hz, 1H), 1.66−1.55 (m, 1H), 1.48 (d, *J* = 6.2 Hz, 3H), 1.40−1.16 (m, 5H), 1.05 (dd, *J* = 6.4, 7.7 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 75.2, 68.8, 41.3, 32.5, 31.7, 28.7, 25.5, 23.2, 20.4, 20.2, 13.9; IR ($CHCl_3$) ν 1747, 1537, 1344 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{12}H_{19}NNaO_4$, 264.1212 [M + Na^+], found 264.1212.

(1*S*,5*R*,6*S*,7*R*)-6-Propyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (9b). A solution of **8b** (0.2107 g, 0.997 mmol) and mCPBA (0.2714 g, 80%, 0.969 mmol) in CH_2Cl_2 (2 mL) was heated to refluxing temperature for 23 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **9b** in 76% yield (0.172 g, 0.75 mmol).

White solid; mp 86−87 °C; $[\alpha]_D$ +80.9 ($CHCl_3$, *c* 1.08); ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (dq, *J* = 10.8, 6.2 Hz, 1H), 3.44 (td, *J* = 9.3, 4.6 Hz, 1H), 2.97 (dd, *J* = 14.7, 8.4 Hz, 1H), 2.50 (dd, *J* = 14.7, 8.8 Hz, 1H), 2.33 (dd, *J* = 10.7, 6.3 Hz, 1H), 2.22 (dq, *J* = 10.6, 8.4 Hz, 1H), 1.48 (ddt, *J* = 13.5, 11.2, 5.0 Hz, 1H), 1.40 (d, *J* = 6.1 Hz, 3H), 1.37−1.10 (m, 3H), 1.06 (dd, *J* = 8.0, 6.4 Hz, 1H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 75.0, 69.0, 41.3, 34.0, 32.3, 25.7, 20.2, 20.1, 19.9, 14.5; IR ($CHCl_3$) ν 1743, 1533, 1344 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_4$, 228.1236 [M + H^+], found 228.1216.

(1*S*,5*R*,6*S*,7*R*)-6-Pentyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (9c). A solution of **8c** (0.2066 g, 0.8633 mmol) and mCPBA (0.244 g, 80%, 0.871 mmol) in CH_2Cl_2 (2 mL) was heated to refluxing temperature for 24 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **9c** in 64% yield (0.1408 g, 0.552 mmol).

White solid; mp 88−89 °C; $[\alpha]_D$ +86.7 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (dq, *J* = 11.9, 6.2 Hz, 1H), 3.44 (td, *J* = 9.4, 4.8 Hz, 1H), 2.98 (dd, *J* = 14.7, 8.4 Hz, 1H), 2.50 (dd, *J* = 14.7, 8.7 Hz, 1H), 2.33 (dd, *J* = 10.6, 6.3 Hz, 1H), 2.23 (dq, *J* = 10.6, 8.4 Hz, 1H), 1.56−1.45 (m, 1H), 1.40 (d, *J* = 6.1 Hz, 3H), 1.35−1.08 (m, 7H), 1.06 (dd, *J* = 8.0, 6.3 Hz, 1H), 0.81 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 75.1, 68.9, 41.4, 32.4, 32.2, 31.8, 26.2, 25.7, 22.4, 20.3, 20.2, 14.0; IR ($CHCl_3$) ν 1747, 1535, 1344 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{21}NNaO_4$, 278.1368 [M + Na^+], found 278.1372.

(1*S*,5*R*,6*S*,7*R*)-6-Isopropyl-5-methyl-7-nitro-4-oxabicyclo-[5.1.0]octan-3-one (9d). A solution of **8d** (0.0092 g, 0.044 mmol) and mCPBA (0.0320 g, 80%, 0.114 mmol) in CH_2Cl_2 (1.2 mL) was heated to refluxing temperature for 18 h. The reaction mixture was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 4:1 then 2:1) to give **9d** in 77% yield (0.0077 g, 0.034 mmol).

White solid; mp 133.0−134.0 °C; $[\alpha]_D$ +31.9 ($CHCl_3$, *c* 0.29); ^1H NMR (500 MHz, $CDCl_3$) δ 4.19 (dt, *J* = 14.2, 6.4 Hz, 1H), 3.54 (dd, *J* = 9.5, 5.3 Hz, 1H), 3.09 (dd, *J* = 14.9, 7.7 Hz, 1H), 2.62−2.54 (m, 2H), 2.05 (dq, *J* = 15.4, 8.7, 7.7 Hz, 1H), 2.02−1.92 (m, 1H), 1.54 (d, *J* = 6.3 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 74.3, 67.4, 45.1, 33.2, 30.0, 23.4, 20.2, 20.1, 19.5, 18.7; HRMS (ESI-TOF): calcd for $C_{11}H_{17}NNaO_4$ 250.1055 [M + Na^+], found 250.1045.

(1*S*,5*R*,6*S*,7*R*)-6-Ethyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (9e). A solution of **8e** (0.2851 g, 1.446 mmol) and mCPBA (0.4597 g, 80%, 1.641 mmol) in CH_2Cl_2 (3 mL) was heated to refluxing temperature for 27 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **9e** in 82% yield (0.2523 g, 1.183 mmol).

White solid; mp 105−106 °C; $[\alpha]_D$ +73.8 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (dq, *J* = 12.0, 6.1 Hz, 1H), 3.31 (td, *J* = 9.8, 4.7 Hz, 1H), 2.89 (dd, *J* = 14.8, 8.5 Hz, 1H), 2.49 (dd, *J* = 14.7, 8.8 Hz, 1H), 2.27 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.14 (dq, *J* = 10.6, 8.5 Hz, 1H), 1.57 (ddt, *J* = 14.7, 12.2, 7.4 Hz, 1H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.14 (ddt, *J* = 16.6, 14.8, 7.5 Hz, 1H), 1.07 (dd, *J* = 8.1, 6.4 Hz, 1H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 74.9, 68.6, 42.3, 36.0, 25.7, 24.3, 20.1, 20.0, 11.0; IR ($CHCl_3$) ν 1745, 1539, 1342 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{10}H_{15}NNaO_4$, 236.0899 [M + Na^+], found 236.0900.

(1*R*,5*S*,6*R*,7*S*)-6-Butyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (19a). A solution of **18a** (0.483 g, 2.14 mmol) and mCPBA (0.6992 g, 80%, 2.50 mmol) in CH_2Cl_2 (3.5 mL) was heated to refluxing temperature for 26 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **19a** in 80% yield (0.4135 g, 1.714 mmol).

White solid; mp 90−91 °C; $[\alpha]_D$ −83.1 ($CHCl_3$, *c* 1.08); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (dq, *J* = 12.0, 6.1 Hz, 1H), 3.43 (td, *J* = 7.6, 4.2 Hz, 1H), 2.99 (dd, *J* = 14.7, 8.3 Hz, 1H), 2.50 (dd, *J* = 14.7, 8.8 Hz, 1H), 2.33 (dd, *J* = 10.5, 5.8 Hz, 1H), 2.22 (dq, *J* = 10.8, 8.5 Hz, 1H), 1.58−1.44 (m, 1H), 1.42 (d, *J* = 6.2 Hz, 3H), 1.35−1.10 (m, 5H), 1.07 (t, *J* = 7.1 Hz, 1H), 0.83 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 75.0, 69.0, 41.3, 32.4, 31.5, 28.7, 25.7, 23.1, 20.3, 20.2, 13.9; IR ($CHCl_3$) ν 1745, 1535, 1346 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{12}H_{19}NNaO_4$, 264.1212 [M + Na^+], found 264.1191.

(1*R*,5*S*,6*R*,7*S*)-6-Propyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (19b). A solution of **18b** (0.1527 g, 0.7228 mmol) and mCPBA (0.2029 g, 80%, 0.7246 mmol) in CH_2Cl_2 (2 mL) was heated to refluxing temperature for 26 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **9b** in 73% yield (0.1196 g, 0.526 mmol).

White solid; mp 105−106 °C; $[\alpha]_D$ −88.0 ($CHCl_3$, *c* 1.03); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (dq, *J* = 10.3, 6.1 Hz, 1H), 3.48 (dddd, *J* = 9.7, 8.8, 4.4, 2.0 Hz, 1H), 3.02 (dd, *J* = 14.7, 8.4 Hz, 1H), 2.49 (dd, *J* = 14.6, 8.7 Hz, 1H), 2.36 (ddd, *J* = 10.6, 6.4, 1.0 Hz, 1H), 2.26 (dq, *J* = 10.6, 8.4 Hz, 1H), 1.58−1.47 (m, 1H), 1.43 (d, *J* = 6.1 Hz, 3H), 1.42−1.11 (m, 3H), 1.06 (dd, *J* = 8.0, 6.3 Hz, 1H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 75.1, 68.9, 41.3, 34.1, 32.4, 25.6, 20.3, 20.2, 19.9, 14.5; IR ($CHCl_3$) ν 1546, 1356 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{18}NO_4$, 228.1236 [M + H^+], found 228.1242.

(1*R*,5*S*,6*R*,7*S*)-6-Pentyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (19c). A solution of **18c** (0.1729 g, 0.722 mmol) and mCPBA (0.1944 g, 80%, 0.694 mmol) in CH_2Cl_2 (1.5 mL) was heated to refluxing temperature for 24 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **19c** in 68% yield (0.1265 g, 0.495 mmol).

White solid; mp 91−92 °C; $[\alpha]_D$ −72.8 ($CHCl_3$, *c* 1.11); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (pd, *J* = 6.0, 1.9 Hz, 1H), 3.42 (dtt, *J* = 9.8, 6.6, 2.9 Hz, 1H), 2.96 (ddd, *J* = 14.6, 8.4, 2.2 Hz, 1H), 2.49 (ddd, *J* = 14.7, 8.7, 2.1 Hz, 1H), 2.32 (dd, *J* = 10.8, 6.5 Hz, 1H), 2.21 (p, *J* = 9.0 Hz, 1H), 1.54−1.44 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 3H), 1.33−1.09 (m, 7H), 1.05 (t, *J* = 6.1 Hz, 1H), 0.80 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 75.0, 69.0, 41.4, 32.3, 32.2, 31.8, 26.2, 25.8,

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J. Org. Chem. 2016, 81, 4664−4681

22.4, 20.3, 20.2, 14.0; IR ($CHCl_3$) ν 1745, 1535, 1344 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{21}NNaO_4$, 278.1368 [M + Na^+], found 278.1362.

(1*R*,5*S*,6*R*,7*S*)-6-Isopropyl-5-methyl-7-nitro-4-oxabicyclo-[5.1.0]octan-3-one (19d). A solution of **18d** (0.122 g, 0.577 mmol) and mCPBA (0.1636 g, 80%, 0.584 mmol) in CH_2Cl_2 (1.2 mL) was heated to refluxing temperature for 22 h. The reaction mixture was washed with an aqueous solution of $Na_2S_3O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 2:1) to give **19d** in 70% yield (0.0914 g, 0.402 mmol).

White solid; mp 133−134 °C; $[\alpha]_D$ −25.3 ($CHCl_3$, *c* 1.15); ^1H NMR (500 MHz, $CDCl_3$) δ 4.14 (dq, *J* = 9.7, 6.2 Hz, 1H), 3.44 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.95 (dd, *J* = 14.9, 8.1 Hz, 1H), 2.55 (dd, *J* = 14.9, 8.4 Hz, 1H), 2.50 (dd, *J* = 10.9, 6.4 Hz, 1H), 2.00 (dddd, *J* = 14.4, 11.3, 7.2, 5.7 Hz, 1H), 1.95−1.79 (m, 1H), 1.44 (d, *J* = 6.1 Hz, 3H), 1.28 (t, *J* = 8.1, 6.8 Hz, 1H), 0.89 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 74.3, 67.4, 45.0, 32.7, 29.9, 23.4, 20.1, 20.0, 19.4, 18.4; IR ($CHCl_3$) ν 1743, 1531, 1338 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{11}H_{17}NNaO_4$ 250.1055 [M + Na^+], found 250.1059.

(1*R*,5*S*,6*R*,7*S*)-6-Ethyl-5-methyl-7-nitro-4-oxabicyclo[5.1.0]-octan-3-one (19e). A solution of **18e** (0.1865 g, 0.946 mmol) and mCPBA (0.3071 g, 80%, 1.097 mmol) in CH_2Cl_2 (2.5 mL) was heated to refluxing temperature for 21 h. The reaction mixture was washed with an aqueous solution of $Na_2S_3O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 10:1) to give **19e** in 74% yield (0.1489 g, 0.6983 mmol).

White solid; mp 105−106 °C; $[\alpha]_D$ −81.7 ($CHCl_3$, *c* 1.43); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (dq, *J* = 11.9, 6.2 Hz, 1H), 3.40−3.28 (m, 1H), 3.00−2.85 (m, 1H), 2.49 (dd, *J* = 14.8, 8.9 Hz, 1H), 2.35−2.24 (m, 1H), 2.24−2.11 (m, 1H), 1.66−1.54 (m, 1H), 1.39−1.30 (m, 3H), 1.24−1.10 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 1H), 0.89−0.79 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 74.9, 68.6, 42.3, 32.2, 25.6, 24.4, 20.1, 20.0, 11.0; HRMS (ESI-TOF): calcd for $C_{10}H_{15}NNaO_4$, 236.0899 [M + Na^+], found 236.0898.

(1*R*,5*S*,6*R*,7*S*)-6-Cyclohexyl-5-methyl-7-nitro-4-oxabicyclo-[5.1.0]octan-3-one (19f). A solution of **18f** (0.1836 g, 0.730 mmol) and mCPBA (0.2007 g, 80%, 0.717 mmol) in CH_2Cl_2 (1.5 mL) was heated to refluxing temperature for 20 h. The reaction mixture was washed with an aqueous solution of $Na_2S_3O_3$ and $NaHCO_3$ (1:4, 20 mL) and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 3:1) to give **19f** in 76% yield (0.149 g, 0.5574 mmol).

White solid; mp 182−183 °C; $[\alpha]_D$ −29.0 ($CHCl_3$, *c* 1.09); ^1H NMR (500 MHz, $CDCl_3$) δ 4.22 (dq, *J* = 9.3, 6.3 Hz, 1H), 3.53 (ddd, *J* = 9.3, 5.4, 1.0 Hz, 1H), 3.09 (dd, *J* = 14.9, 7.7 Hz, 1H), 2.61 (ddd, *J* = 10.6, 6.9, 0.8 Hz, 1H), 2.57 (dd, *J* = 15.1, 7.8 Hz, 1H), 1.95 (dq, *J* = 10.7, 8.0 Hz, 1H), 1.80−1.62 (m, 6H), 1.59 (d, *J* = 11.4 Hz, 1H), 1.54 (d, *J* = 6.3 Hz, 3H), 1.26 (ddd, *J* = 8.5, 7.0, 3.9 Hz, 1H), 1.24−1.11 (m, 3H), 1.06 (ddd, *J* = 23.7, 12.1, 3.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 73.9, 67.6, 45.1, 41.0, 33.0, 30.5, 28.7, 26.9, 26.8, 26.3, 23.6, 20.2, 19.7; IR ($CHCl_3$) ν 1747, 1533, 1344 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{14}H_{21}NNaO_4$, 290.1368 [M + Na^+], found 290.1366.

(2*R*,3*S*,3a*S*,6a*S*)-3-Butyl-2-methyl-3a-nitro-6a-trimethylsily-loxy-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (10a). TMSOTf (0.16 mL, 0.884 mmol) and Et_3N (0.18 mL, 1.291 mmol) were added in this order to a solution of **9a** (0.1761 g, 0.7298 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **10a** in 87% yield (0.1983 g, 0.6326 mmol).

Pale yellow oil; $[\alpha]_D$ +43.5 ($CHCl_3$, *c* 1.19); ^1H NMR (500 MHz, $CDCl_3$) δ 5.95 (dt, *J* = 5.4, 2.4 Hz, 1H), 5.50 (dt, *J* = 5.8, 2.3 Hz, 1H), 3.41 (dt, *J* = 18.5, 2.4 Hz, 1H), 3.30 (dq, *J* = 10.4, 6.0 Hz, 1H), 3.09 (td, *J* = 10.1, 4.9 Hz, 1H), 2.58 (dt, *J* = 18.5, 2.4 Hz, 1H), 1.42 (ddt, *J* = 13.3, 11.5, 4.4 Hz, 1H), 1.33 (d, *J* = 6.0 Hz, 3H), 1.31−1.00 (m, 5H), 0.84 (t, *J* = 7.1 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.6, 130.5, 116.8, 102.2, 76.8, 50.6, 35.2, 29.3, 27.0, 23.0, 18.4, 13.8, 1.5 (3C); IR (neat) ν 1536, 1356, 1249, 1205 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{15}H_{27}NNaO_4Si$, 336.1607 [M + Na^+], found 336.1610.

(2*R*,3*S*,3a*S*,6a*S*)-3-Propyl-2-methyl-3a-nitro-6a-trimethylsily-loxy-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (10b). TMSOTf (0.13 mL, 0.718 mmol) and Et_3N (0.15 mL, 1.076 mmol) were added in this order to a solution of **9b** (0.136 g, 0.598 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **10b** in 48% yield (0.0856 g, 0.286 mmol).

Pale yellow oil; $[\alpha]_D$ +36.4 ($CHCl_3$, *c* 1.00); ^1H NMR (500 MHz, $CDCl_3$) δ 5.97 (dt, *J* = 5.9, 2.5 Hz, 1H), 5.53 (dt, *J* = 5.9, 2.3 Hz, 1H), 3.42 (dt, *J* = 19.2, 2.8 Hz, 1H), 3.32 (dq, *J* = 10.5, 6.0 Hz, 1H), 3.12 (td, *J* = 10.0, 4.9 Hz, 1H), 2.59 (dt, *J* = 18.5, 2.4 Hz, 1H), 1.45−1.36 (m, 1H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.32−1.20 (m, 1H), 1.20−1.08 (m, 2H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.6, 116.8, 102.2, 76.8, 50.5, 35.3, 29.6, 20.6, 18.4, 14.5, 1.5 (3C); IR (neat) ν 1545, 1358, 1249, 1205 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{14}H_{26}NO_4Si$, 300.1631 [M + H^+], found 300.1631.

(2*R*,3*S*,3a*S*,6a*S*)-3-Pentyl-2-methyl-3a-nitro-6a-trimethylsily-loxy-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (10c). TMSOTf (0.045 mL, 0.249 mmol) and Et_3N (0.055 mL, 0.395 mmol) were added in this order to a solution of **9c** (0.0520 g, 0.2 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 10:1 v/v) to give **10c** in 93% yield (0.062 g, 0.189 mmol).

Colorless oil. $[\alpha]_D$ +38.6 ($CHCl_3$, *c* 2.06); ^1H NMR (500 MHz, $CDCl_3$) δ 5.98 (dt, *J* = 5.8, 2.4 Hz, 1H), 5.53 (dt, *J* = 5.9, 2.3 Hz, 1H), 3.43 (dt, *J* = 19.3, 1.7 Hz, 1H), 3.31 (dq, *J* = 10.3, 6.0 Hz, 1H), 3.11 (td, *J* = 10.2, 4.9 Hz, 1H), 2.59 (dt, *J* = 18.5, 2.4 Hz, 1H), 1.46−1.37 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.32−1.03 (m, 7H), 0.85 (t, *J* = 6.2 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.6, 116.8, 102.2, 76.8, 50.6, 35.2, 32.2, 27.3, 26.9, 22.4, 18.4, 14.1, 1.6 (3C); IR (neat) ν 1547, 1356, 1249, 1208 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{16}H_{29}NNaO_4Si$, 350.1764 [M + Na^+], found 350.1780.

(2*R*,3*S*,3a*S*,6a*S*)-3-Ethyl-2-methyl-3a-nitro-6a-trimethylsily-loxy-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (10e). TMSOTf (0.22 mL, 1.216 mmol) and Et_3N (0.25 mL, 1.794 mmol) were added in this order to a solution of **9e** (0.2166 g, 1.016 mmol) in CH_2Cl_2 (3 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 15:1 v/v) to give **10e** in 86% yield (0.2489 g, 0.8712 mmol).

White solid; mp 43−44 °C; $[\alpha]_D$ +49.4 ($CHCl_3$, *c* 1.20); ^1H NMR (500 MHz, $CDCl_3$) δ 5.95 (dt, *J* = 5.6, 2.5 Hz, 1H), 5.50 (dt, *J* = 5.8, 2.3 Hz, 1H), 3.41 (dt, *J* = 18.4, 2.2 Hz, 1H), 3.30 (dq, *J* = 10.3, 5.9 Hz, 1H), 3.04 (td, *J* = 10.4, 5.0 Hz, 1H), 2.58 (dt, *J* = 18.6, 2.5 Hz, 1H), 1.51 (dqd, *J* = 14.9, 7.5, 4.9 Hz, 1H), 1.32 (d, *J* = 6.1 Hz, 3H), 1.17 (ddq, *J* = 14.6, 10.2, 7.4 Hz, 1H), 0.82 (t, *J* = 7.5 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.5, 116.8, 101.9, 76.6, 51.9, 35.0, 20.1, 18.3, 11.5, 1.4 (3C); IR ($CHCl_3$) ν 1545, 1348, 1249, 1205 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{23}NNaO_4Si$, 308.1294 [M + Na^+], found 308.1288.

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(2*S*,3*R*,3a*R*,6a*R*)-3-Butyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20a). TMSOTf (0.16 mL, 0.884 mmol) and Et_3N (0.18 mL, 1.291 mmol) were added in this order to a solution of **19a** (0.1730 g, 0.717 mmol) in CH_2Cl_2 (2 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 2.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **20a** in 93% yield (0.2091 g, 0.6671 mmol).

Colorless oil; $[\alpha]_D$ −54.1 ($CHCl_3$, *c* 1.10); ^1H NMR (500 MHz, $CDCl_3$) δ 5.95 (dt, *J* = 5.1, 2.4 Hz, 1H), 5.50 (dt, *J* = 5.8, 2.3 Hz, 1H), 3.41 (dt, *J* = 18.9, 2.6 Hz, 1H), 3.30 (dq, *J* = 11.0, 5.7 Hz, 1H), 3.09 (td, *J* = 10.2, 4.9 Hz, 1H), 2.58 (dt, *J* = 18.6, 2.3 Hz, 1H), 1.47−1.36 (m, 1H), 1.32 (d, *J* = 6.1 Hz, 3H), 1.30−1.19 (m, 3H), 1.19−1.09 (m, 1H), 1.09−0.98 (m, 1H), 0.83 (t, *J* = 7.1 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.5, 116.8, 102.1, 76.7, 50.6, 35.1, 29.2, 26.9, 22.9, 18.3, 13.7, 1.4 (3C); IR (neat) ν 1546, 1356, 1249, 1204 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{15}H_{27}NNaO_4Si$, 336.1607 [M + Na^+], found 336.1605.

(2*S*,3*R*,3a*R*,6a*R*)-3-Propyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20b). TMSOTf (0.048 mL, 0.2652 mmol) and Et_3N (0.055 mL, 0.397 mmol) were added in this order to a solution of **19b** (0.0458 g, 0.2015 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **20b** in 77% yield (0.0464 g, 0.1549 mmol).

Colorless oil; $[\alpha]_D$ −34.2 ($CHCl_3$, *c* 1.49); ^1H NMR (500 MHz, $CDCl_3$) δ 5.83 (q, *J* = 5.2, 2.5 Hz, 1H), 5.40 (dt, *J* = 6.0, 2.4 Hz, 1H), 3.29 (dt, *J* = 18.9, 2.6 Hz, 1H), 3.18 (dq, *J* = 10.2, 5.9 Hz, 1H), 2.99 (td, *J* = 9.8, 4.9 Hz, 1H), 2.46 (dt, *J* = 18.8, 2.4 Hz, 1H), 1.31−1.23 (m, 1H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.17−1.12 (m, 1H), 1.06−1.01 (m, 1H), 1.01−0.95 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.7, 116.9, 102.3, 76.9, 50.5, 35.3, 29.6, 20.6, 18.4, 14.5, 1.5 (3C); HRMS (ESI-TOF): calcd for $C_{14}H_{26}NO_4Si$, 300.1631 [M + H^+], found 300.1629.

(2*S*,3*R*,3a*R*,6a*R*)-3-Pentyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20c). TMSOTf (0.05 mL, 0.276 mmol) and Et_3N (0.06 mL, 0.430 mmol) were added in this order to a solution of **19c** (0.0515 g, 0.2017 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 1 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 10:1 then 3:1 v/v) to give **20c** in 98% yield (0.0650 g, 0.198 mmol).

Colorless oil; $[\alpha]_D$ −38.0 ($CHCl_3$, *c* 1.34); ^1H NMR (500 MHz, $CDCl_3$) δ 5.97 (d, *J* = 5.8 Hz, 1H), 5.52 (d, *J* = 5.8 Hz, 1H), 3.43 (d, *J* = 18.2 Hz, 1H), 3.31 (dq, *J* = 11.8, 5.9 Hz, 1H), 3.15−3.06 (m, 1H), 2.59 (d, *J* = 18.8 Hz, 1H), 1.44−1.40 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.30−1.01 (m, 7H), 0.84 (t, *J* = 6.5 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.6, 116.8, 102.2, 76.8, 50.6, 35.2, 32.2, 27.3, 26.9, 22.4, 18.4, 14.0, 1.6 (3C); IR (neat) ν 1547, 1356, 1250, 1208 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{16}H_{29}NNaO_4Si$, 350.1764 [M + Na^+], found 350.1760.

(2*S*,3*R*,3a*R*,6a*R*)-3-Isopropyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20d). TMSOTf (0.08 mL, 0.442 mmol) and Et_3N (0.088 mL, 0.631 mmol) were added in this order to a solution of **19d** (0.0799 g, 0.3516 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 4.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (20 mL × 5). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **20d** in 74% yield (0.0783 g, 0.261 mmol).

White solid; mp 85−86 °C; $[\alpha]_D$ −32.8 ($CHCl_3$, *c* 1.27); ^1H NMR (500 MHz, $CDCl_3$) δ 5.98−5.93 (m, 1H), 5.55−5.50 (m, 1H), 3.58−3.46 (m, 2H), 2.98−2.89 (m, 1H), 2.68 (d, *J* = 18.3 Hz, 1H), 1.65−1.54 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.5, 130.7, 115.7, 103.4, 76.9, 56.9, 36.2, 27.4, 21.9, 21.8, 21.1, 1.5 (3C); IR (neat) ν 1549, 1348, 1249, 1205 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{14}H_{26}NO_4Si$, 300.1631 [M + H^+], found 300.1627.

(2*S*,3*R*,3a*R*,6a*R*)-3-Ethyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20e). TMSOTf (0.065 mL, 0.360 mmol) and Et_3N (0.073 mL, 0.506 mmol) were added in this order to a solution of **19e** (0.0616 g, 0.289 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 2 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 3). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 15:1 v/v) to give **20e** in 86% yield (0.071 g, 0.249 mmol).

Pale yellow oil; $[\alpha]_D$ −31.2 ($CHCl_3$, *c* 1.36); ^1H NMR (500 MHz, $CDCl_3$) δ 5.97 (dt, *J* = 5.5, 2.5 Hz, 1H), 5.53 (dt, *J* = 6.2, 2.3 Hz, 1H), 3.44 (dt, *J* = 18.6, 2.3 Hz, 1H), 3.32 (dq, *J* = 11.8, 6.0 Hz, 1H), 3.07 (td, *J* = 10.3, 5.0 Hz, 1H), 2.59 (dt, *J* = 18.5, 2.4 Hz, 1H), 1.58−1.46 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.19 (tdd, *J* = 14.7, 10.1, 7.3 Hz, 1H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.6, 116.8, 102.0, 76.8, 52.0, 35.1, 20.2, 18.4, 11.7, 1.6 (3C); IR ($CHCl_3$) ν 1547, 1346, 1249, 1207 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{13}H_{23}NNaO_4Si$, 308.1294 [M + Na^+], found 308.1286.

(2*S*,3*R*,3a*R*,6a*R*)-3-Cyclohexyl-2-methyl-3a-nitro-6a-trimethylsilyloxy-3,3a,4,6a-tetrahydro-*2H*-cyclopenta[*b*]furan (20f). TMSOTf (0.22 mL, 1.22 mmol) and Et_3N (0.25 mL, 1.794 mmol) were added in this order to a solution of **19f** (0.2655 g, 0.993 mmol) in CH_2Cl_2 (3.5 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 2.5 h. NH_4Cl aq (5 mL) was added to the reaction mixture, and water phase was extracted with EtOAc (30 mL × 5). The organic phase was combined and dried over Na_2SO_4. After filtration, organic solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel/hexane then hexane-EtOAc 5:1 v/v) to give **20f** in 95% yield (0.2779 g, 0.9436 mmol).

White solid; mp 83−84 °C; $[\alpha]_D$ −61.0 ($CHCl_3$, *c* 1.24); ^1H NMR (500 MHz, $CDCl_3$) δ 5.96 (dt, *J* = 6.1, 2.3 Hz, 1H), 5.53 (dt, *J* = 5.9, 2.4 Hz, 1H), 3.57 (dq, *J* = 10.0, 5.8 Hz, 1H), 3.51 (dt, *J* = 18.5, 2.4 Hz, 1H), 2.98 (t, *J* = 9.6 Hz, 1H), 2.69 (dt, *J* = 18.5, 1.5 Hz, 1H), 1.85 (d, *J* = 12.5 Hz, 1H), 1.78−1.57 (m, 3H), 1.44 (d, *J* = 5.9 Hz, 3H), 1.40−0.95 (m, 7H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.5, 130.7, 115.7, 103.4, 76.7, 56.1, 37.4, 36.3, 31.8, 31.7, 26.4, 26.3, 26.0, 21.6, 1.5 (3C); IR (neat) ν 1548, 1373, 1250, 1205 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{17}H_{29}NNaO_4Si$ 362.1764 [M + Na^+], found 362.1760.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00566.

NMR data for compounds **3**−**10** and **13**−**20**, and HPCC charts for compounds **8** and **18** (PDF)

Crystallographic data for 3,4-*cis*-**5a** (CIF)

Crystallographic data for 3,4-*cis*-**20f** (CIF)

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Notes

The authors declare no competing financial interest.

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