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Expanding the scope of Et_3B/O_2-mediated coupling reactions of O,Te-acetal

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ABSTRACT

Et_3B/O_2-mediated radical coupling reactions of O,Te-acetal **2** were explored using diverse electrophilic double bonds. Ethyl radical derived from Et_3B under air cleaved the C–Te bond of **2** to generate α-alkoxy bridgehead radical **I**, which reacted with cycloalkenones, cycloalkylidenemalononitriles, allyl halides, and imines at or below ambient temperature. These intermolecular reactions from O,Te-acetal **2** were mild and versatile, and were superior to those of O,Se-acetal **1** in terms of efficiency and substrate scope. A total of 14 new and nine improved coupling reactions are described, all of which realized the installation of the functionalized carbon units at the sterically hindered bridgehead position of trioxaadamantane.

1. Introduction

Radical-based C–C bond formations are powerful reactions for assembling multiple-substituted carboskeletons, and have been employed for the total syntheses of natural products.[1] Carbon radical species are highly reactive, yet electronically neutral, so they are suitable for installation of sterically congested tri- and tetra-substituted carbon centers without affecting polar functional groups. In addition, because of their complementary nature, sequential use of radical and ionic processes offers great potential for streamlining the construction of structurally complex organic molecules.

Our recent efforts have been directed toward the development of radical-based coupling strategies for the synthesis of highly oxygenated natural products. We have been particularly interested in the effective utilization of α-alkoxy bridgehead radicals as the key intermediates.[2,3] The advantageous features of α-alkoxy bridgehead radicals include enhanced reactivity, minimized steric hindrance, and the stereochemically predestined structure of the radical-generating carbon center. In this context, the intermolecular reaction between O,Se-acetal **1** and cyclopentenone **3a** was developed to connect the contiguous tri- and tetrasubstituted carbon centers of oxygenated carbocycle **7a** (Scheme 1A).[2a] The radical at the α-alkoxy bridgehead position of the trioxaadamantane structure was formed by slow addition of *n*-Bu_3SnH and V-40 into the refluxing toluene solution of **1**. The generated nucleophilic radical **I** added to the electron-deficient double bond of **3a** to form the second radical intermediate **II**, which was then hydrogenated by *n*-Bu_3SnH to afford **7a** and the stannyl radical. The α-alkoxy bridgehead radical strategy has been further applied to the total syntheses of complex natural terpenoids.[4]

Despite its efficiency for the intermolecular formation of hindered bonds, transformation of O,Se-acetal **1** to **7a** has several drawbacks. First, tedious chromatography is required to remove excess tin residue from the products.[5] Second, unwanted reactions originating from the use of *n*-Bu_3SnH at elevated temperatures competes to decrease the yield of the desired product (e.g., addition of the stannyl radical to unsaturated bonds,[6] or premature reduction of the radical intermediates).[7] To improve the synthetic utility of the bridgehead radical couplings, milder conditions without use of the tin reagent are highly desirable.[8]

To realize mild tin-free coupling, O,Te-acetal **2** was designed as a more reactive radical precursor,[9,10] and the combination of Et_3B and O_2 was selected as a more versatile set of reagents (Scheme 1A).[11] In this alternative scenario, Et_3B would play three key roles: radical initiation, reaction acceleration, and radical termination. Namely, Et_3B, under an O_2 atmosphere, would eject an ethyl radical, which would homolytically cleave the C–Te bond of O,Te-acetal **2** to generate α-alkoxy bridgehead radical **I**.[12] The smaller bond dissociation energy (BDE) of the C–Te bond compared to that of the C–Se bond should help facilitate the radical exchange

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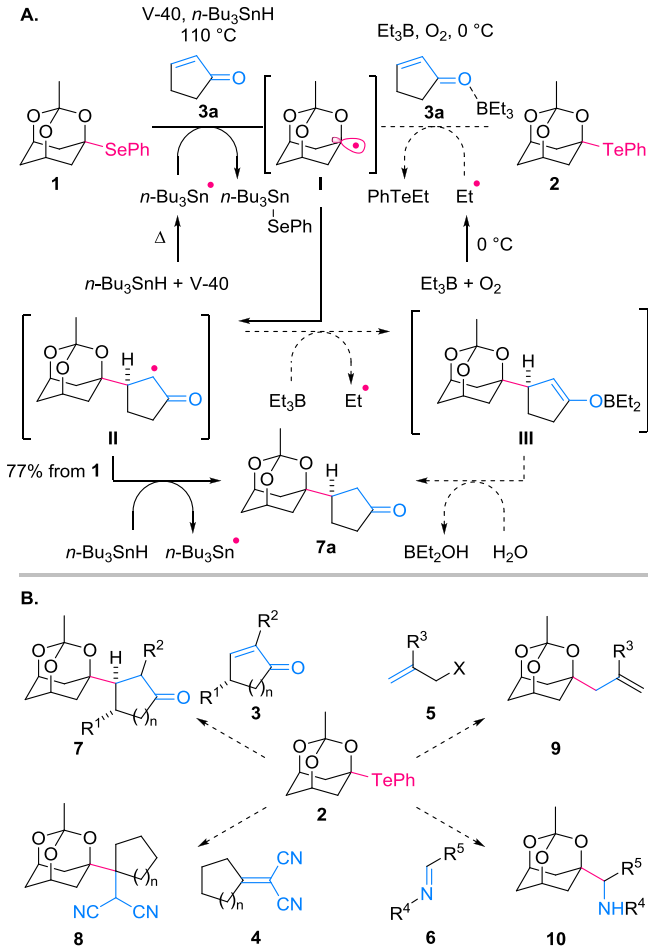


Scheme 1. (**A**) Coupling reactions of α-alkoxy bridgehead radical intermediate **I** derived from O,Se-acetal **1** or O,Te-acetal **2**. (**B**) Radical acceptors (**3**–**6**) used for coupling reactions of O,Te-acetal **2**. V-40=1,1′-azobis(cyclohexanecarbonitrile).

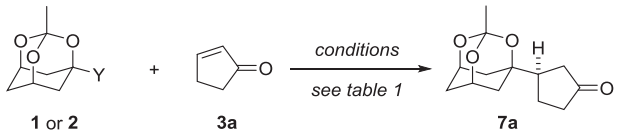
reaction from ethyl radical to **I**.[13] Et_3B also would function as a Lewis acid toward the C=O bond of **3a**, thereby decreasing the LUMO energy level of the conjugated C=C double bond.[14] Accordingly, addition of **I** to Et_3B-activated **3a** would be accelerated, and the resulting α-carbonyl radical **II** would in turn be captured by Et_3B to generate the boron enolate intermediate **III**. As the radical reaction would be terminated by Et_3B, this reaction system does not require excess amount of hydrogen donor, and thus direct hydrogenation of **I** would be prevented. Finally, hydrolysis of **III** would afford the desired adduct **7a**. In this report, the scope of Et_3B/O_2-mediated coupling reactions of O,Te-acetal **2** was explored in detail. O,Te-acetal **2** was consistently superior in reactivity to O,Se-acetal **1**, and was demonstrated to serve as an excellent precursor of α-alkoxy bridgehead radical **I** for intermolecular reactions with the four structurally distinct acceptors (**3**, **4**, **5** and **6**), even at or below ambient temperature (Scheme 1B).

2. Results and discussion

2.1. Comparison of reactivity of O,Te-acetal 2 and O,Se-acetal 1

First, the applicability of O,Te-acetal **2** to the reagent system of Et_3B and O_2 below ambient temperature was validated (Table 1). Upon treatment of a mixture of **2** and cyclopentenone **3a** (3 equiv) with Et_3B (3 equiv) under air in CH_2Cl_2 (0.1 M) at 0 °C (entry 1), the radical coupling reaction smoothly proceeded to incorporate the

Table 1
Investigation of the reactivity of **1** and **2**



Entry	Radical donor	Conditions	Yield (%)
1[a]	**2**: Y=TePh	Et_3B, O_2, CH_2Cl_2, 0 °C	88
2[b]	**1**: Y=SePh	V-40, n-Bu_3SnH, toluene, 110 °C	77
3[a]	**1**: Y=SePh	Et_3B, O_2, CH_2Cl_2, 0 °C	0[d]
4[c]	**1**: Y=SePh	Et_3B, O_2, n-Bu_3SnH, toluene, 0 °C	12[e]

[a] Reaction conditions: **1** or **2** (1 equiv), **3a** (3 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.1 M), 0 °C, 15 min.
[b] Reaction conditions: **1** (1 equiv), **3a** (5 equiv), V-40 (0.6 equiv), n-Bu_3SnH (6 equiv), refluxing toluene (0.02 M). V-40 (0.2 equiv) and n-Bu_3SnH were added by syringe pump over 3 h, and the reaction mixture was stirred for additional 1 h (Ref. 2a).
[c] Reaction conditions: **1** (1 equiv), **3a** (5 equiv), Et_3B (0.6 equiv), n-Bu_3SnH (6 equiv), toluene (0.02 M), 0 °C. Et_3B (0.2 equiv) and n-Bu_3SnH were added by syringe pump over 3 h, and the reaction mixture was stirred for additional 1 h.
[d] **1** was recovered in 97% yield.
[e] **1** was recovered in 47% yield.

five-membered ring at the bridgehead position of the trioxaadamantane structure.[9a] Thus, generation of the α-alkoxy bridgehead radical intermediate **I** and its coupling reaction both occurred at 0 °C to furnish the adduct **7a**. The yield of the adduct **7a** (88%) in entry 1 was higher than that of **7a** (77%) in entry 2, where O,Se-acetal **1** was subjected to the previous conditions [**3a** (5 equiv), n-Bu_3SnH (6 equiv) and V-40 (0.6 equiv) in refluxing toluene (0.02 M)]. O,Se-acetal **1** was completely inert under tin-free conditions at 0 °C (recovery of **1**, 97%, entry 3). Even when n-Bu_3SnH was introduced to a mixture of **2** and Et_3B under air at 0 °C to produce the stannyl radical,[15] the efficiency of the reaction improved only slightly, affording **7a** in 12% yield (entry 4). These data together clarified the greater reactivity of **2** as the radical precursor, and the benefit of milder conditions using **2**, Et_3B, and O_2 for the coupling efficiency.

2.2. Coupling reactions of O,Te-acetal 2 with cycloalkenone or cycloalkylidenemalononitrile derivatives

The reaction outcomes of O,Te-acetal **2** and O,Se-acetal **1** were accessed further by using the four cycloalkenones (**3b**–**e**, Table 2). In doing so, **2** and **1** were separately submitted to their optimized conditions (Et_3B and O_2 in CH_2Cl_2 at 0 °C for **2**, n-Bu_3SnH, and V-40 in toluene at 110 °C for **1**). Cyclohexenone **3b**, cycloheptenone **3c**, and cyclooctenone **3d** all participated in the coupling reaction with O,Te-acetal **2** by the action of Et_3B and O_2, giving rise to **7b**, **7c**, and **7d** in 80, 78, and 87% yields, respectively (entries 1–3). Irrespective of the ring size of the radical acceptor, the products **7b**, **7c**, and **7d** were formed in higher yields from **2** than from **1**. Remarkably, the yield of **7c** with the seven-membered ketone was tripled by switching the radical precursor **1** with **2** (entry 2), accentuating the advantageous feature of the mild reaction system. The Et_3B/O_2-promoted intermolecular addition of O,Te-acetal **2** to chiral cyclopentenone **3e** proceeded from the opposite face of the bulky α-oriented OTBS group, providing **7e** as a single isomer (72%, entry 4). The yield of **7e** from **2** was again higher than that from **1**.

Next, the 5-, 6-, 7- and 8-membered malononitriles **4a**–**d** were utilized as acceptors, along with **2** or **1** as the precursor of the α-alkoxy bridgehead radical (Table 3). Coupling reactions using O,Te-acetal **2** with cycloalkylidenemalononitriles **4a**–**d** with Et_3B and O_2 at 0 °C linked the two functionalized carbocycles, producing the adducts **8a**–**d** in 58, 88, 87, and 33% yields, respectively (entries 1–4). Significantly, the extremely hindered bond between the

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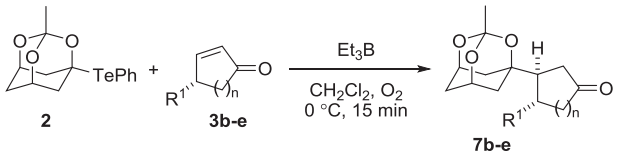
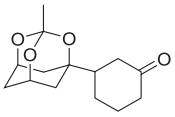
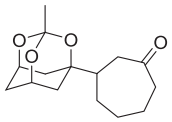
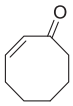
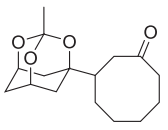
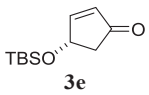
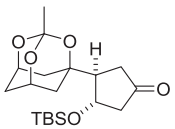
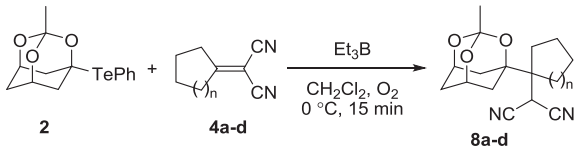
Table 2
Coupling reactions between **2** and cycloalkenones **3b**–**e**[a]

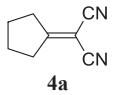
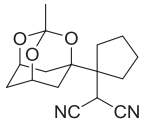
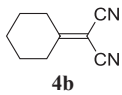
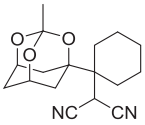
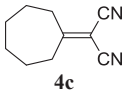
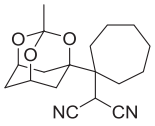
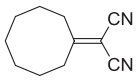
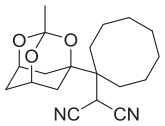


Entry	Radical acceptor	Product	Yield[b] (%)
1	 **3b**	 **7b**	80 (56)
2	 **3c**	 **7c**	78 (26)
3	 **3d**	 **7d**	87 (45)
4	 **3e**	 **7e**	72 (65)

[a] Reaction conditions: **2** (1 equiv), **3b**–**e** (3 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.1 M), 0 °C, 15 min.
[b] Yields in parentheses represent results of coupling of O,Se-acetal **1** (1 equiv) and **3** (5 equiv) by using V-40 (0.6 equiv) and *n*-Bu_3SnH (6 equiv) in refluxing toluene (0.02 M) (Ref. 2a).

Table 3
Coupling reactions between **2** and cycloalkylidenemalononitriles **4a**–**d**[a]



Entry	Radical acceptor	Product	Yield[b] (%)
1	 **4a**	 **8a**	58 (54)
2	 **4b**	 **8b**	88 (72)
3	 **4c**	 **8c**	87 (57)
4	 **4d**	 **8d**	33[c] (27)

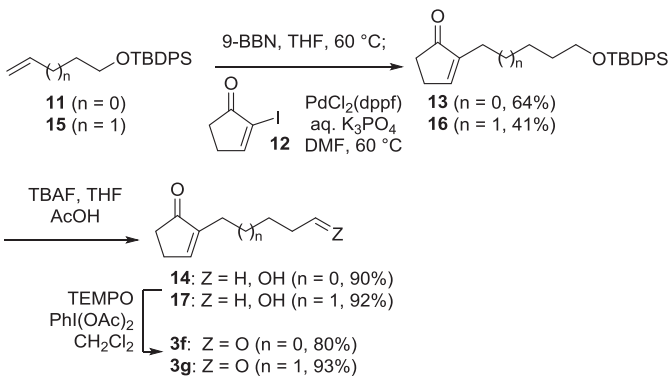
[a] Reaction conditions: **2** (1 equiv), **4a**–**d** (3 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.1 M), 0 °C, 15 min.
[b] Yields in parentheses represent results of coupling of O,Se-acetal **1** (1 equiv) and **4** (5 equiv) by using V-40 (0.6 equiv) and *n*-Bu_3SnH (6 equiv) in refluxing toluene (0.02 M) (Ref. 2a).
[c] Yield was determined by ^1H NMR analysis.

tetrasubstituted and quaternary carbons was formed through intermolecular radical addition to the electron-withdrawing tetrasubstituted olefin of **4a**–**d**. Although O,Se-acetal **1** was used as the starting material for the preparation of **8a**–**d** by means of *n*-Bu_3SnH and V-40, the yields were generally lower. Consequently, single-step construction of the two contiguous tetrasubstituted carbons at 0 °C from O,Te-acetal **2** corroborated the power of the present radical coupling strategy.

2.3. Radical-polar crossover reaction between O,Te-acetal 2 and 3f or 3g

The Et_3B/O_2-mediated coupling reactions of O,Te-acetal **2** were shown to be a robust method for introduction of carbocycles at the sterically congested bridgehead position of the trioxaadamantane (Tables 1–3). To further increase molecular complexity in a single step, we planned to utilize the boron enolate intermediate **III** for the intramolecular aldol reaction with the aldehyde (Scheme 1A). Namely, cycloalkenones **3f** and **3g** were designed to contain the aldehyde within the molecules (Scheme 2). The boron enolate intermediate generated from **3f** or **3g** would participate in the aldol reaction, prior to its protonation, to produce spiro-fused ring system.[9,16]

Compounds **3f** and **3g** were synthesized in three steps from **11** and **15**, respectively (Scheme 2). Hydroboration of the terminal alkene of **11**/**15** was followed by Suzuki–Miyaura coupling[17] with **12** using catalytic $PdCl_2$(dppf) and K_3PO_4 to provide the coupling product **13**/**16**. The OTBDPS group of the elongated carbon chain of **13**/**16** was deprotected with TBAF to afford the primary alcohol **14**/**17**, which was then oxidized to the corresponding aldehyde **3f**/**3g** by applying TEMPO as a catalyst and $PhI(OAc)_2$ as a co-oxidant.[18]



Scheme 2. Synthesis of radical acceptors **3f** and **3g**. 9-BBN=9-borabicyclo[3.3.1]nonane, dppf=1,1′-bis(diphenylphosphino)ferrocene, TBAF=tetra-*n*-butylammonium fluoride, TEMPO=2,2,6,6-tetramethylpiperidine 1-oxyl.

Upon treatment of **3f** and **3g** with **2** and Et_3B under air at 0 °C, O,Te-acetal **2** indeed reacted with the trisubstituted olefin of **3f** and **3g** to produce **7f** and **7g** bearing the 5/5- and 5/6-membered spiro-

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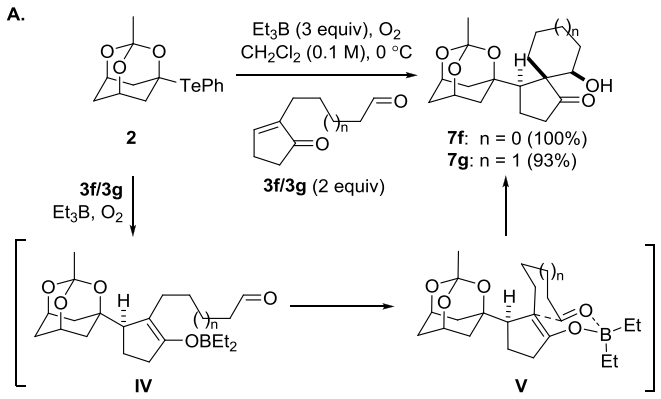
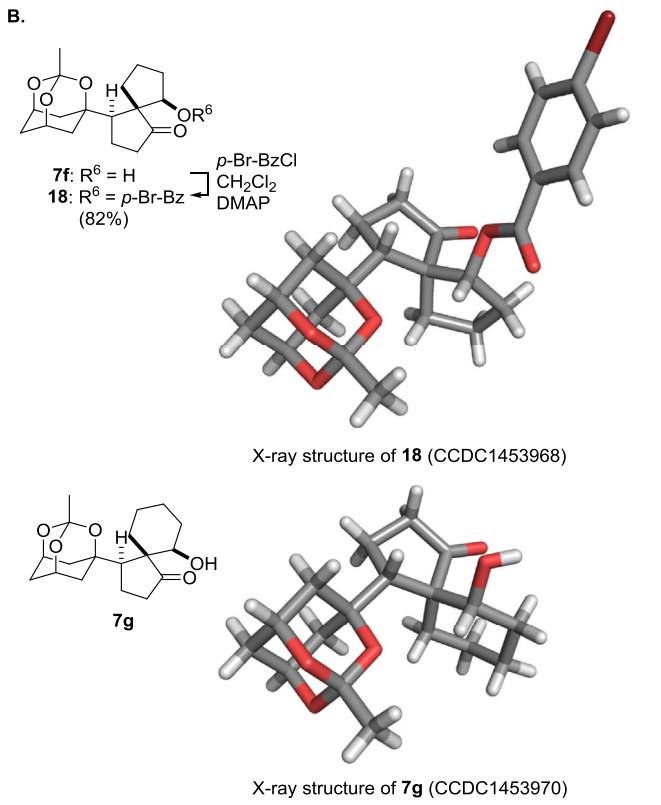
fused rings, respectively, as a single stereoisomer (Scheme 3A). Compound **7f** was derivatized to *p*-bromobenzoate **18**, and the structures of **18** and **7g** were determined by X-ray crystallographic analysis, thereby establishing their stereochemistries (Scheme 3B).[19] Thus, a single operation integrated the relative stereochemistry of the two tertiary, one quaternary, and bridgehead tetrasubstituted carbon centers. These reaction outcomes can be explained by a radical-polar crossover mechanism. After generation of bridgehead radical **I** from **2**, **I** adds to the tri-substituted olefin of **3f**/**3g**, subsequently transforming to boron enolate **IV** by reaction with Et_3B. Then, the boron atom fixes the most sterically favorable 5/6-membered transition state **V**. The new C–C bond stereoselectively forms from **V** through an intramolecular aldol reaction to furnish **7f**/**7g**.[20] It is noteworthy that the aldehyde group of **3f**/**3g** served as acceptor for the polar addition, but not for the radical addition,[21] showing the high chemoselectivity of the present reaction.



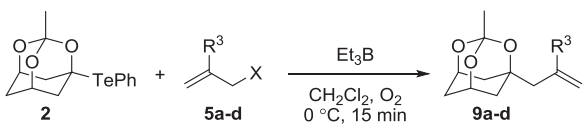


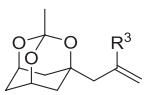
Scheme 3. (**A**) Synthesis of the spiro-fused ring system **7f**/**7g** from O,Te-acetal **2** via the radical-polar crossover reaction. (**B**) The structure confirmation of **7f** and **7g** by the X-ray crystallographic analyses of **18** and **7g**. DMAP=*N*,*N*-dimethyl-4-aminopyridine.

2.4. Coupling reactions of O,Te-acetal 2 with allyl halide or imine derivatives

Because of the high reactivity and chemoselectivity of the present reaction system, we presumed that the scope of the radical acceptors could be expanded from the electrophilic olefins in Tables 1–3 to the allyl halide and imine derivatives in Tables 4 and 5. The five allyl halide derivatives **5a**–**d** (Table 4) are problematic substrates for the radical reactions in general, because the carbon-halogen bonds are potentially reactive under the conditions, and the double bonds are less polarized in comparison to the carbonyl conjugated olefins.[22] In fact, the coupling reaction between O,Se-acetal **1** and 2,3-dichloroprop-1-ene **5a** using *n*-Bu_3SnH and V-40 at 110 °C afforded **9a** only in 12% yield (entry 1), presumably due to direct hydrogenation of the allylic chloride of **5a** with *n*-Bu_3SnH. In contrast, treatment of O,Te-acetal **2** and **5a** with Et_3B and O_2 at 0 °C led to formation of **9a** in 79% yield through an S_H2' reaction (entry 2). Consequently, ethyl radical derived from Et_3B chemoselectively activated the C–Te bond of **2** without cleaving the allylic C–Cl bond of **5a** or the vinylic C–Cl bonds of **5a** and **9a**.[23] While reaction between **2** and allyl chloride **5ba** proceeded smoothly to give **9b** in 65% yield (entry 3), **2** added to 2-bromo-3-chloroprop-1-ene **5c** (71%) with retention of the vinylic C–Br bond (entry 4). The two allylic bromides **5bb** and **5d** were submitted to the Et_3B/O_2 conditions to produce the monosubstituted olefin **9b** (57%, entry 5) and the disubstituted olefin **9d** (61%, entry 6), respectively. These results indicated that even scission of the weak allylic C–Br bond was not the major pathway. Therefore, Et_3B/O_2-mediated radical conditions effectively distinguished the C–Te bond from the C–Cl/C–Br bond.

Table 4
Coupling reactions between **2** with allyl halides **5a**–**d**[a]

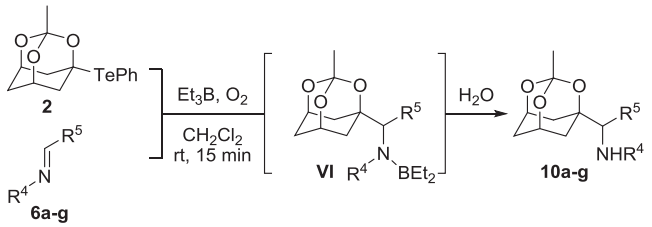


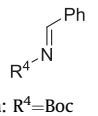
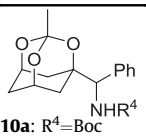
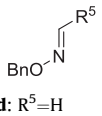
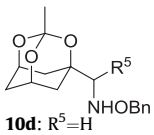
Entry	Radical acceptor	Product	Yield (%)
			
1[b]	**5a**: R^3=Cl	**9a**: R^3=Cl	12
2	**5a**: R^3=Cl	**9a**: R^3=Cl	79
3	**5ba**: R^3=H	**9b**: R^3=H	65
4	**5c**: R^3=Br	**9c**: R^3=Br	71
			
5	**5bb**: R^3=H	**9b**: R^3=H	57
6	**5d**: R^3=Me	**9d**: R^3=Me	61

[a] Reaction conditions: **2** (1 equiv), **5a**–**d** (5 equiv), Et_3B (5 equiv), CH_2Cl_2 (0.1 M), 0 °C, 15 min.
[b] Reaction conditions: **1** (1 equiv), **5c** (5 equiv), V-40 (0.6 equiv), *n*-Bu_3SnH (6 equiv), refluxing toluene (0.02 M). V-40 (0.2 equiv) and *n*-Bu_3SnH were added by syringe pump over 3 h, and the reaction mixture was stirred for additional 1 h.

Finally, the seven imine derivatives **6a**–**g** were used as the radical acceptors (Table 5). Entry 1 represents the negative control experiment, in which O,Se-acetal **1** and Boc-protected imine **6a** were treated with *n*-Bu_3SnH and V-40 at 110 °C. As a result, reduction of the C=N double bond of **6a** occurred to give the corresponding Boc-protected amine without formation of **10a**, suggesting the inadequateness of the stannyl radical-promoted

Table 5
Coupling reactions between **2** and imines **6a**–**g**[a]



Entry	Radical acceptor	Product	Yield (%)
			
1[b]	**6a**: R^4=Boc	**10a**: R^4=Boc	0
2	**6a**: R^4=Boc	**10a**: R^4=Boc	93
3	**6b**: R^4=Ts	**10b**: R^4=Ts	76
4	**6c**: R^4=Ph	**10c**: R^4=Ph	60
			
5	**6d**: R^5=H	**10d**: R^5=H	93
6	**6e**: R^5=Ph	**10e**: R^5=Ph	70
7	**6f**: R^5=*i*-Bu	**10f**: R^5=*i*-Bu	38
8	**6g**: R^5=CO_2Et	**10g**: R^5=CO_2Et	89

[a] Reaction conditions: **2** (1 equiv), **6a**–**g** (3 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.1 M), room temperature, 15 min.

[b] Reaction conditions: **1** (1 equiv), **6a** (5 equiv), V-40 (0.6 equiv), *n*-Bu_3SnH (6 equiv), refluxing toluene (0.02 M). V-40 (0.2 equiv) and *n*-Bu_3SnH were added by syringe pump over 3 h, and the reaction mixture was stirred for additional 1 h. O,Se-acetal **1** was recovered in 28% yield, and the Boc-protected benzyl amine was obtained in 63% yield based on **6a**.

conditions. On the other hand, when the mixture of O,Te-acetal **2** and the same imine **6a** was treated with Et_3B under air at room temperature, **10a** was obtained in 93% yield (entry 2). In this reaction, coordination of BEt_3 to the C=N double bond of **6a** and subsequent conversion of the unstable amidyl radical to the boron amide by BEt_3 would have favorable effects on the facile coupling.[24] *N*-Ts imine **6b** and *N*-Ph imine **6c** reacted with O,Te-acetal **2** in the presence of Et_3B and O_2, leading to **10b** (76%, entry 3) and **10c** (60%, entry 4). Benzyloxyimine **6d** was transformed to **10d** in 93% yield under the same conditions (entry 5).[25] The three benzyloxyimines **6e**, **6f**, and **6g** also served as acceptors, and their reactions led to formation of benzyl amine **10e** (70%, entry 6), aliphatic amine **10f** (38%, entry 7), and amino acid derivative **10g** (89%, entry 8). Single-step preparation of the functionalized amine motif demonstrated here would have further application to the efficient synthesis of structurally related pharmaceuticals and natural products.

3. Conclusions

In summary, we successfully expanded the scope of the radical acceptors for the Et_3B/O_2-mediated coupling reactions of O,Te-acetal **2**. Compared to the previous method using O,Se-acetal **1**, *n*-Bu_3SnH, and V-40 at 110 °C, the present tin-free reaction system significantly improved efficiency and chemoselectivity. Key features include facile conversion of **2** to the α-alkoxy bridgehead radical below ambient temperature, and the multiple roles of Et_3B as radical initiator, Lewis acid and radical terminator. A variety of cycloalkenones, cycloalkylidenemalononitriles, allyl halides and imines participated in the couplings to allow efficient attachment of carbocycles, allyl groups, and amino-substituted alkyl groups to the sterically cumbersome bridgehead position of the trioxaadamantane. In addition, the boron enolate intermediate formed after addition of the bridgehead radical to the cyclopentenones was intramolecularly attacked on the aldehyde moiety to stereoselectively generate the spiro-fused bicycles in a single operation. Because of the high efficiency in connecting the hindered carbon atoms and the high tolerance of the various polar and reactive functional groups, the present method will serve as a pivotal transformation for simplifying schemes for total synthesis of structurally complex natural products. Further application of the present coupling method to natural product synthesis is currently underway in this laboratory.

4. Experimental section

4.1. General

All radical reactions using Et_3B were carried out under air. The other reactions sensitive to air or moisture were carried out under argon atmosphere in dry solvents, unless otherwise noted. CH_2Cl_2, THF and toluene were purified by Glass Contour solvent dispensing system (Nikko Hansen & Co., Ltd., Japan). All other reagents were used as supplied. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F_{254} pre-coated plates (0.25 mm). Preparative thin-layer chromatography (PTLC) was performed using Merck silica gel 60 F_{254} pre-coated plates (0.5 mm). Flash column chromatography was performed using 40–50 μm Silica Gel 60N (Kanto Chemical Co., Inc., Japan). Melting points were measured on Yanaco MP-J3 micro melting point apparatus, and are uncorrected. Infrared (IR) spectra were recorded on JASCO FT/IR-4100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JNM-ECX-500 or JNM-ECS-400 spectrometer. Chemical shifts were reported in ppm on the δ scale relative to $CHCl_3$ (δ=7.26 for ^1H NMR), $CDCl_3$ (δ=77.0 for ^{13}C NMR), CD_3OD (δ=49.0 for ^{13}C NMR) as internal references. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet; br, broaden peak. High resolution mass spectra were measured on JEOL JMS-T100LP instrument (ESI or DART).

4.2. General procedure A: synthesis of compound 7a from O,Te-acetal 2 [CAS: 1326319-34-9]

Et_3B (1.03 M in hexane, 0.37 mL, 0.38 mmol) was added to a solution of O,Te-acetal **2**[9a] (46.1 mg, 0.128 mmol) and cyclopentenone **3a** (32 μL, 0.38 mmol) in CH_2Cl_2 (1.3 mL) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, and was then directly subjected to flash column chromatography on silica gel (10 g, hexane/EtOAc 1/1) to afford **7a** (26.9 mg, 0.113 mmol) in 88% yield. The analytical data of **7a** were identical to those reported previously.[2a]

4.3. Synthesis of compound 7a from O,Se-acetal 1

Et_3B (0.99 M in hexane, 43 μL, 0.042 mmol) was added to a solution of O,Se-acetal **1**[2a] (33.0 mg, 0.106 mmol) and cyclopentenone **3a** (46 μL, 0.53 mmol) in toluene (2.0 mL) at 0 °C. Two other solutions of *n*-Bu_3SnH (176 μL, 0.636 mmol) in toluene (1.0 mL) and Et_3B (0.99 M in hexane, 21 μL, 0.021 mmol) in toluene (1.0 mL) were simultaneously added to the above mixture at 0 °C via syringe pumps over 3 h. After additional 1 h at 0 °C, the reaction mixture was concentrated. The residue was purified by flash chromatography [a column consecutively packed with silica gel 4 g and 10% (w/w) KF contained silica gel 1 g, hexane/EtOAc 5/1 to 3/1] to afford **7a** (3.0 mg, 0.013 mmol) and the unreacted **1** (15.5 mg, 0.498 mmol) in 12% and 47% yields, respectively.

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4.4. Compound 7b [CAS: 1326319-35-0]

According to the general procedure A, **7b** (18.2 mg, 0.0721 mmol) was synthesized in 80% yield from O,Te-acetal **2** (32.4 mg, 0.0900 mmol) and cyclohexenone **3b** (26 μL, 0.27 mmol) by using Et_3B (1.03 M in hexane, 0.26 mL, 0.27 mmol) in CH_2Cl_2 (0.90 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 1/1). The analytical data of **7b** were identical to those reported previously.[2a]

4.5. Compound 7c [CAS: 1326319-36-1]

According to the general procedure A, **7c** (20.3 mg, 0.0762 mmol) was synthesized in 78% yield from O,Te-acetal **2** (35.1 mg, 0.0975 mmol) and cycloheptenone **3c** (32.0 mg, 0.290 mmol) by using Et_3B (1.03 M in hexane, 0.28 mL, 0.29 mmol) in CH_2Cl_2 (0.98 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). The analytical data of **7c** were identical to those reported previously.[2a]

4.6. Compound 7d [CAS: 1326319-37-2]

According to the general procedure A, **7d** (26.4 mg, 0.0942 mmol) was synthesized in 87% yield from O,Te-acetal **2** (38.8 mg, 0.108 mmol) and cyclooctenone **3d** (40.0 mg, 0.322 mmol) by using Et_3B (1.03 M in hexane, 0.31 mL, 0.32 mmol) in CH_2Cl_2 (1.1 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). The analytical data of **7d** were identical to those reported previously.[2a]

4.7. Compound 7e [CAS: 1326319-38-3]

According to the general procedure A, **7e** (26.2 mg, 0.0711 mmol) was synthesized in 72% yield from O,Te-acetal **2** (35.5 mg, 0.0986 mmol) and 4-(*tert*-butyldimethylsilyloxy)-2-cyclopentenone **3e**[26] (63.0 mg, 0.297 mmol) by using Et_3B (1.03 M in hexane, 0.29 mL, 0.30 mmol) in CH_2Cl_2 (0.99 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 3/1). The analytical data of **7e** were identical to those reported previously.[2a]

4.8. Compound 8a [CAS: 1326319-42-9]

According to the general procedure A, **8a** (16.6 mg, 0.0576 mmol) was synthesized in 58% yield from O,Te-acetal **2** (35.7 mg, 0.0992 mmol) and cyclopentylidenemalononitrile **4a** (39.0 mg, 0.295 mmol) by using Et_3B (1.03 M in hexane, 0.29 mL, 0.30 mmol) in CH_2Cl_2 (0.99 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). The analytical data of **8a** were identical to those reported previously.[2a]

4.9. Compound 8b [CAS: 1326319-43-0]

According to the general procedure A, **8b** (26.0 mg, 0.0860 mmol) was synthesized in 88% yield from O,Te-acetal **2** (35.1 mg, 0.0975 mmol) and cyclohexylidenemalononitrile **4b** (43.0 mg, 0.294 mmol) by using Et_3B (1.03 M in hexane, 0.28 mL, 0.29 mmol) in CH_2Cl_2 (0.98 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). The analytical data of **8b** were identical to those reported previously.[2a]

4.10. Compound 8c [CAS: 1326319-44-1]

According to the general procedure A, **8c** (26.0 mg, 0.0822 mmol) was synthesized in 87% yield from O,Te-acetal **2** (34.2 mg, 0.0950 mmol) and cycloheptylidenemalononitrile **4c**[27] (46.0 mg, 0.287 mmol) by using Et_3B (1.03 M in hexane, 0.28 mL, 0.29 mmol) in CH_2Cl_2 (0.95 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). The analytical data of **8c** were identical to those reported previously.[2a]

4.11. Compound 8d [CAS: 1326319-45-2]

According to the general procedure A, **8d** (16.7 mg) containing impurity was synthesized from O,Te-acetal **2** (35.0 mg, 0.0973 mmol) and cyclooctylidenemalononitrile **4d**[27] (51.0 mg, 0.293 mmol) by using Et_3B (1.03 M in hexane, 0.28 mL, 0.29 mmol) in CH_2Cl_2 (0.97 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1). Because of inseparable impurity, the yield was calculated to be 33% (0.0321 mmol) based on the ^1H NMR analysis using anisole as an internal standard. The ^1H NMR data of **8d** was identical to those reported previously.[2a]

4.12. Aldehyde 3f

9-BBN (0.5 M THF solution, 8.5 mL, 4.3 mmol) was added to a solution of 4-[(*tert*-butyldiphenylsilyl)oxy]-1-butene **11** (1.20 g, 3.86 mmol) in THF (8.5 mL) at 0 °C, and resultant mixture was stirred at 60 °C for 4 h. The above reaction mixture and 3 M aqueous K_3PO_4 (3.2 mL, 9.6 mmol) were successively added to a solution of 2-iodo-2-cyclopentene-1-one **12**[28] (800 mg, 3.85 mmol) and $PdCl_2$(dppf) (281 mg, 0.344 mmol) in DMF (8.5 mL) at room temperature. After being stirred at 60 °C for 2 h, the reaction mixture was cooled to room temperature. Then, H_2O (20 mL) was added. The resultant mixture was extracted with EtOAc (20 mL x3), and the combined organic layers were washed with H_2O (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (40 g, hexane/EtOAc 4/1) to afford enone **13** (961 mg, 2.45 mmol) in 64% yield: colorless oil; IR (film) 3069, 3048, 2931, 2859, 1704, 1631, 1589, 1468, 1428, 1388, 1361, 1301, 1254, 1192, 1108, 1002 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (9H, s, *t*-Bu), 1.53–1.62 (4H, m, $CH_2CH_2CH_2OTBDPS$), 2.16 (2H, m, C(=O)CCH_2), 2.39 (2H, m, C(=O)CH_2), 2.55 (2H, ddd, J=9.2, 4.6, 1.7 Hz, C(=O)CH_2CH_2), 3.67 (2H, t, J=6.3 Hz, $CH_2OTBDPS$), 7.27 (1H, m, C(=O)CC*H*), 7.35–7.44 (6H, m, aromatic), 7.66 (4H, dd, J=8.0, 1.8 Hz, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 23.9, 24.5, 26.4, 26.8 (3C), 32.2, 34.6, 63.6, 127.6 (4C), 129.5 (2C), 134.0 (2C), 135.5 (4C), 146.3, 157.3, 210.0; HRMS (ESI) calcd for $C_{25}H_{32}NaO_2Si$ $[M+Na]^+$ 415.2064, found 415.2072.

TBAF (1 M in THF, 1.1 mL, 1.1 mmol) was added to a solution of enone **13** (144 mg, 0.367 mmol) and AcOH (0.11 mL, 1.8 mmol) in THF (1.8 mL) at room temperature. The reaction mixture was stirred at room temperature for 22 h, and then saturated aqueous NH_4Cl (10 mL) was added. The resultant mixture was extracted with $CHCl_3$ (10 mL x2), and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 1/4) to afford alcohol **14** (50.9 mg, 0.330 mmol) in 90% yield: colorless oil; IR (film) 3413, 2933, 2865, 1688, 1629, 1441, 1355, 1254, 1204, 1056, 1004 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.47–1.58 (4H, m, $CH_2CH_2CH_2OH$), 2.15 (2H, m, C(=O)CCH_2), 2.35 (2H, m, C(=O)CH_2), 2.42–2.58 (3H, m, C(=O)CH_2CH_2, O*H*), 3.60 (2H, t, J=6.3 Hz, CH_2OH), 7.30 (1H, m, C(=O)CC*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.9, 24.3, 26.4, 32.2, 34.5, 62.2, 146.0, 157.9, 210.3; HRMS (ESI) calcd for $C_9H_{14}NaO_2$ $[M+Na]^+$ 177.0886, found 177.0879.

$PhI(OAc)_2$ (467 mg, 1.45 mmol) and TEMPO (19.0 mg, 0.122 mmol) were successively added to a solution of alcohol **14** (187 mg, 1.21 mmol) in CH_2Cl_2 (2.4 mL) at room temperature. The reaction mixture was stirred at room temperature for 18 h, and was then concentrated. The residue was purified by flash column

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chromatography on silica gel (15 g, hexane/EtOAc 1/1) to afford aldehyde **3f** (147 mg, 0.966 mmol) in 80% yield: colorless oil; IR (film) 2926, 2846, 2727, 1696, 1631, 1442, 1403, 1357, 1297, 1254, 1202, 1169, 1088, 1051, 1002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.79 (2H, dt, J=15.1, 7.8 Hz, CH_2CH$_2$CHO), 2.17 (2H, m, C(=O)CCH_2), 2.37 (2H, m, C(=O)CH_2), 2.43 (2H, td, J=7.3, 1.8 Hz, CH_2CHO), 2.55 (2H, ddd, J=9.2, 4.6, 2.3 Hz, C(=O)CH$_2$CH_2), 7.33 (1H, m, C(=O)CCH), 9.73 (1H, t, J=1.4 Hz, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 24.1, 26.4, 34.4, 43.3, 145.3, 158.1, 202.0, 209.7; HRMS (ESI) calcd for $C_9H_{12}NaO_2$ $[M+Na]^+$ 175.0730, found 175.0723.

4.13. Aldehyde 3g

According to the synthetic protocol of **13**, enone **16** (635 mg, 1.56 mmol) was synthesized from **12** (800 mg, 3.85 mmol) and 5-[(*tert*-butyldiphenylsilyl)oxy]-1-penten **15**[29] (1.25 g, 3.85 mmol) in 41% yield by using 9-BBN (8.5 mL of a 0.5 M solution in THF, 4.3 mmol), THF (8.5 mL), $PdCl_2$(dppf) (281 mg, 0.344 mmol) and DMF (8.5 mL). The residue was purified by flash column chromatography on silica gel (30 g, hexane/EtOAc 10/1): colorless oil; IR (film) 3065, 3048, 2931, 2859, 2361, 1703, 1631, 1466, 1432, 1386, 1355, 1297, 1251, 1193, 1106, 1002 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (9H, s, *t*-Bu), 1.34–1.52 (4H, m, CH_2CH_2CH$_2$CH$_2$OTBDPS), 1.58 (2H, dt, J=14.6, 6.9 Hz, CH_2CH$_2$OTBDPS), 2.17 (2H, m, C(=O)CCH_2), 2.39 (2H, m, C(=O)CH_2), 2.54 (2H, ddd, J=9.2, 4.6, 2.3 Hz, C(=O)CH$_2$CH_2), 3.66 (2H, t, J=6.4 Hz, CH_2OTBDPS), 7.27 (1H, m, C(=O)CCH), 7.35–7.45 (6H, m, aromatic), 7.67 (4H, dd, J=8.2, 1.8 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 24.7, 25.6, 26.4, 26.8 (3C), 27.4, 32.3, 34.6, 63.8, 127.5 (4C), 129.5 (2C), 134.1 (2C), 135.5 (4C), 146.3, 157.3, 210.0; HRMS (ESI) calcd for $C_{26}H_{34}NaO_2Si$ $[M+Na]^+$ 429.2220, found 429.2222.

According to the synthetic protocol of **14**, alcohol **17** (242 mg, 1.44 mmol) was synthesized from enone **16** (635 mg, 1.56 mmol) in 92% yield by using TBAF (1 M in THF, 4.7 mL, 4.7 mmol) in AcOH (0.45 mL, 7.8 mmol) and THF (7.8 mL). The residue was purified by flash column chromatography on silica gel (30 g, hexane/EtOAc 1/4): colorless oil; IR (film) 3402, 2930, 2861, 1691, 1630, 1441, 1407, 1350, 1301, 1249, 1203, 1148, 1053, 1004 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (2H, m, CH_2CH$_2$CH$_2$OH), 1.38–1.56 (4H, m, CH_2CH$_2$CH_2CH$_2$OH), 2.11 (2H, m, C(=O)CCH_2), 2.26–2.36 (3H, m, C(=O)CH_2, OH), 2.50 (2H, ddd, J=9.2, 4.6, 2.3 Hz, C(=O)CH$_2$CH_2), 3.55 (2H, t, J=6.9 Hz, CH_2OH), 7.26 (1H, m, C(=O)CCH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 25.4, 26.3, 27.4, 32.3, 34.5, 62.4, 146.1, 157.7, 210.2; HRMS (ESI) calcd for $C_{10}H_{16}NaO_2$ $[M+Na]^+$ 191.1043, found 191.1033.

According to the synthetic protocol of **3f**, aldehyde **3g** (188 mg, 1.13 mmol) was synthesized from alcohol **17** (203 mg, 1.21 mmol) in 93% yield by using $PhI(OAc)_2$ (467 mg, 1.45 mmol), TEMPO (19.0 mg, 0.122 mmol) in CH_2Cl_2 (6.1 mL). The residue was purified by flash column chromatography on silica gel (15 g, hexane/EtOAc 1/1): colorless oil; IR (film) 2929, 2862, 2725, 1721, 1697, 1631, 1442, 1407, 1390, 1351, 1298, 1252, 1200, 1160, 1092, 1045, 1003 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (2H, m, CH_2CH$_2$CH$_2$CHO), 1.62 (2H, dt, J=15.6, 7.8 Hz, CH_2CH$_2$CHO), 2.18 (2H, m, C(=O)CCH_2), 2.37 (2H, m, C(=O)CH_2), 2.44 (2H, td, J=7.3, 1.8 Hz, CH_2CHO), 2.54 (2H, ddd, J=9.2, 4.6, 1.8 Hz, C(=O)CH$_2$CH_2), 7.30 (1H, m, C(=O)CCH), 9.74 (1H, t, J=1.8 Hz, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.4, 26.3, 27.1, 34.4, 43.4, 145.6, 157.6, 202.3, 209.8; HRMS (ESI) calcd for $C_{10}H_{14}NaO_2$ $[M+Na]^+$ 189.0886, found 189.0885.

4.14. Compound 7f

According to the general procedure A, **7f** (16.1 mg, 0.0522 mmol) was synthesized in 100% yield from O,Te-acetal **2** (18.8 mg, 0.0522 mmol) and 4-(5-oxocyclopent-1-en-1-yl)butanal **3f** (16.0 mg, 0.105 mmol) by using Et_3B (1.03 M hexane solution, 0.15 mL, 0.16 mmol) in CH_2Cl_2 (0.52 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 1/3): colorless oil; IR (film) 3449, 3003, 2952, 2872, 2360, 2340, 1728, 1447, 1395, 1324, 1298, 1226, 1150, 1129, 1073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (3H, s, CCH_3), 1.52 (1H, dd, J=12.8, 1.4 Hz, COCH_{ax}H$_{eq}$CHO), 1.60 (1H, dt, J=12.8, 1.8 Hz, CHOCH_{ax}H$_{eq}$CHO), 1.64–1.95 (6H, m, COCH_{ax}H$_{eq}$CHO, C(=O)CH$_2$CH_AH$_B$, CH(OH)CH_AH$_B$, CH(OH)CH$_2$CH_2, CH(OH)CH$_2$CH$_2$CH_AH$_B$), 1.99–2.26 (3H, m, C(=O)CH_AH$_B$, C(=O)CH$_2$CH$_A$$H_B$, CH(OH)CH$_A$$H_B$), 2.26–2.40 (4H, m, C(=O)CH$_A$$H_B$, C(=O)CC$H$, CH(OH)CH$_2CH_2CH_A$$H_B$, COCH$_{ax}$$H_{eq}$CHO), 2.42–2.57 (2H, m, COCH$_{ax}$$H_{eq}$CHO, CHOCH$_{ax}$$H_{eq}$CHO), 4.28 (1H, t, J=7.3 Hz, CH(OH)), 4.38–4.46 (2H, m, CH$_2$CHOCH$_2$ x2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.4, 26.1, 28.9, 32.5, 33.9, 34.6, 37.4, 37.5, 51.2, 62.6, 68.0, 68.2, 74.6, 81.0, 110.0, 222.2; HRMS (ESI) calcd for $C_{17}H_{24}NaO_5$ $[M+Na]^+$ 331.1516, found 331.1517.

4.15. Compound 7g

According to the general procedure A, **7g** (30.1 mg, 0.0934 mmol) was synthesized in 93% yield from O,Te-acetal **2** (36.0 mg, 0.100 mmol) and **3g** (33.0 mg, 0.199 mmol) by using Et_3B (1.03 M hexane solution, 0.29 mL, 0.30 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 1/3): colorless prism; mp 173–174 °C; IR (film) 3449, 2948, 2863, 1727, 1448, 1394, 1394, 1324, 1298, 1154, 1129, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (1H, m, CH(OH)CH$_2$CH_AH$_B$), 1.40–1.52 (2H, m, CH(OH)CH$_2$CH$_2$CH_2), 1.43 (3H, s, CCH_3), 1.54–1.64 (2H, m, COCH_{ax}H$_{eq}$CHO x2), 1.69 (1H, m, CH(OH)CH$_2$CH$_2$CH$_2$CH_AH$_B$), 1.73–1.86 (3H, m, CHOCH_{ax}H$_{eq}$CHO, CH(OH)CH_AH$_B$, CH(OH)CH$_2$CH$_A$$H_B$), 1.86–2.02 (3H, m, C(=O)CH$_2$CH_2, CH(OH)CH$_2$CH$_2$CH$_2$CH$_A$$H_B$), 2.02–2.24 (2H, m, C(=O)CH_AH$_B$, CH(OH)CH$_A$$H_B$), 2.37 (1H, m, C(=O)CH$_A$$H_B$), 2.45–2.62 (3H, m, COCH$_{ax}$$H_{eq}$CHO x2, CHOCH$_{ax}$$H_{eq}$CHO), 2.67 (1H, dd, J=11.0, 8.2 Hz, C(=O)CH$_2$CH$_2$CH), 3.99 (1H, dd, J=11.4, 5.5 Hz, CH(OH)), 4.41 (2H, m, CH$_2$CHOCH$_2$ x2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 20.3, 24.3, 26.1, 27.0, 31.3, 32.5, 35.2, 37.6, 37.9, 48.6, 57.5, 68.2, 68.3, 72.7, 74.9, 110.1, 220.8; HRMS (ESI) calcd for $C_{18}H_{26}NaO_5$ $[M+Na]^+$ 345.1672, found 345.1664.

4.16. *p*-Bromobenzoyl ester 18

p-Bromobenzoyl chloride (*p*-Br-BzCl, 22.0 mg, 0.100 mmol) was added to a solution of alcohol **7f** (27.5 mg, 0.0892 mmol) and DMAP (13.0 mg, 0.106 mmol) in CH_2Cl_2 (0.89 mL) at room temperature. The reaction mixture was stirred at room temperature for 12 h, and then was directly subjected to flash column chromatography on silica gel (10 g, hexane/EtOAc 1/1) to afford *p*-bromobenzoyl ester **18** (35.7 mg, 0.0727 mmol) in 82% yield: colorless prism; mp 158.0–159.0 °C; IR (film) 2952, 2360, 2341, 1732, 1716, 1590, 1395, 1272, 1128, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, s, CCH_3), 1.49 (1H, dd, J=12.8, 1.4 Hz, COCH_{ax}H$_{eq}$CHO), 1.60 (1H, m, CHOCH_{ax}H$_{eq}$CHO), 1.80–2.11 (7H, m), 2.17–2.36 (5H, m), 2.37–2.48 (2H, m), 2.53 (1H, m, CHOCH$_{ax}$$H_{eq}$CHO), 4.38–4.46 (2H, m, CH$_2$CHOCH$_2$ x2), 5.45 (1H, dd, J=6.4, 6.0 Hz, CHOC(=O)Ar), 7.56 (2H, m, aromatic), 7.79 (2H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.5, 26.0, 28.6, 30.0, 32.5, 34.3, 37.0, 37.6, 51.4, 61.1, 67.9, 68.2, 74.6, 83.0, 110.0, 128.2, 129.0, 131.0, 131.8, 165.5, 218.3; HRMS (ESI) calcd for $C_{24}H_{27}BrNaO_6$ $[M+Na]^+$ 513.0883, found 513.0891.

4.17. Synthesis of olefin 9a from O,Se-acetal 1 and 5a

A solution of O,Se-acetal **1** (33.0 mg, 0.106 mmol), 2,3-dichloroprop-1-ene **5a** (50 μL, 0.53 mmol) and V-40 (10.4 mg, 0.0424 mmol) in toluene (2.0 mL) was degassed by freeze-thaw procedure (×3). The mixture was heated to 110 °C. Then, another degassed solution of *n*-Bu_3SnH (176 μL, 0.636 mmol) and V-40 (5.2 mg, 0.021 mmol) in toluene (2.0 mL) by freeze-thaw procedure (×3) was added via a syringe pump over 3 h. After additional 1 h at

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110 °C, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography [a column consecutively packed with silica gel 4 g and 10% (w/w) KF contained silica gel 1 g, hexane/EtOAc 20/1 to 10/1] to give the crude **9a** (15.0 mg). The crude was further purified by PTLC (hexane/EtOAc 5/1×2) to afford **9a** (3.0 mg, 0.013 mmol) in 12% yield.

4.18. Synthesis of olefin 9a from O,Te-acetal 2 and 5a

According to the general procedure A, **9a** (18.5 mg, 0.0802 mmol) was synthesized in 79% yield from O,Te-acetal **2** (36.6 mg, 0.102 mmol) and 2,3-dichloroprop-1-ene **5a** (47 μL, 0.51 mmol) by using Et_3B (1.03 M hexane solution, 0.49 mL, 0.51 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1): colorless oil; IR (film) 3009, 2971, 2947, 2930, 2851, 1632, 1444, 1395, 1325, 1298, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, s, CCH_3), 1.57 (1H, dt, J=12.8, 1.8 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.80 (2H, d, J=13.3 Hz, COC$H_{ax}H_{eq}$CHO x2), 2.27 (2H, m, COC$H_{ax}H_{eq}$CHO x2), 2.47–2.55 (3H, m, CHOC$H_{ax}H_{eq}$CHO, CH_2C(Cl)=CH_2), 4.42 (2H, m, CH_2CHOCH_2 x2), 5.25 (1H, s, CH_2C(Cl)=CH_AH_B), 5.35 (1H, d, J=0.9 Hz, CH_2C(Cl)=CH_AH_B); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 32.1, 36.4 (2C), 51.0, 68.1 (2C), 72.3, 110.4, 117.2, 135.8; HRMS (DART) calcd for $C_{11}H_{16}ClO_3$ $[M+H]^+$ 231.0782, found 231.0785.

4.19. Synthesis of olefin 9b from O,Te-acetal 2 and 5ba

According to the general procedure A, **9b** (12.0 mg, 0.0611 mmol) was synthesized in 65% yield from O,Te-acetal **2** (33.7 mg, 0.0936 mmol) and allyl chloride **5ba** (38 μL, 0.47 mmol) by using Et_3B (1.03 M hexane solution, 0.45 mL, 0.47 mmol) in CH_2Cl_2 (0.94 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1): colorless oil; IR (film) 3077, 3008, 2953, 2929, 2850, 1445, 1395, 1325, 1297, 1160, 1127 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (3H, s, CCH_3), 1.54 (1H, d, J=13.3 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.59 (2H, d, J=13.3 Hz, COC$H_{ax}H_{eq}$CHO x2), 2.16–2.25 (4H, m, COC$H_{ax}H_{eq}$CHO x2, CH_2CH=CH_2), 2.51 (1H, m, CHOC$H_{ax}H_{eq}$CHO), 4.40 (2H, br s, CH_2CHOCH_2 x2), 5.07–5.16 (2H, m, CH_2CH=CH_2), 5.81 (1H, ddt, J=17.8, 10.5, 7.3 Hz, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 32.3, 36.4 (2C), 46.3, 68.1 (2C), 72.5, 110.3, 118.8, 131.8; HRMS (DART) calcd for $C_{11}H_{17}O_3$ $[M+H]^+$ 197.1172, found 197.1180.

4.20. Olefin 9c

According to the general procedure A, **9c** (20.0 mg, 0.0727 mmol) was synthesized in 71% yield from O,Te-acetal **2** (37.1 mg, 0.103 mmol) and 2-bromo-3-chloroprop-1-ene **5c** (49 μL, 0.52 mmol) by using Et_3B (1.03 M hexane solution, 0.50 mL, 0.52 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 10/1): colorless oil; IR (film) 3007, 2953, 2929, 2846, 2359, 1626, 1394, 1324, 1298, 1160, 1147, 1126 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, s, CCH_3), 1.57 (1H, dt, J=13.3, 1.8 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.81 (2H, d, J=12.8 Hz, COC$H_{ax}H_{eq}$CHO x2), 2.28 (2H, dt, J=13.3, 2.3 Hz, COC$H_{ax}H_{eq}$CHO x2), 2.52 (1H, dtt, J=13.3, 4.6, 2.3 Hz, CHOC$H_{ax}H_{eq}$CHO), 2.67 (2H, s, CH_2C(Br)=CH_2), 4.42 (2H, m, CH_2CHOCH_2 x2), 5.62 (1H, d, J=1.4 Hz, CH_2C(Br)=CH_AH_B), 5.71 (1H, d, J=0.9 Hz, CH_2C(Br)=CH_AH_B); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 32.1, 36.4 (2C), 52.8, 68.1 (2C), 72.5, 110.4, 122.0, 125.5; HRMS (DART) calcd for $C_{11}H_{16}BrO_3$ $[M+H]^+$ 275.0277, 277.0257, found 275.0286, 277.0267.

4.21. Synthesis of olefin 9b from O,Te-acetal 2 and 5bb

According to the general procedure A, **9b** (10.5 mg, 0.0535 mmol) was synthesized in 57% yield from O,Te-acetal **2** (34.0 mg, 0.0945 mmol) and allyl bromide **5bb** (41 μL, 0.47 mmol) by using Et_3B (1.03 M hexane solution, 0.46 mL, 0.47 mmol) in CH_2Cl_2 (0.94 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1).

4.22. Olefin 9d

According to the general procedure A, **9d** (13.1 mg, 0.0623 mmol) was synthesized in 61% yield from O,Te-acetal **2** (36.7 mg, 0.102 mmol) and 3-bromo-2-methylprop-1-ene **5d** (51 μL, 0.51 mmol) by using Et_3B (1.03 M hexane solution, 0.50 mL, 0.51 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 10/1): colorless oil; IR (film) 3073, 3007, 2951, 2851, 1645, 1445, 1394, 1324, 1297, 1125 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, s, CCH_3), 1.55 (1H, dt, J=13.3, 1.8 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.56 (2H, d, J=13.3 Hz, COC$H_{ax}H_{eq}$CHO x2), 1.81 (3H, s, CH$_2$C(CH_3)=CH$_2$), 2.18 (2H, s, CH_2C(CH$_3$)=CH$_2$), 2.25 (2H, m, COCH$_{ax}H_{eq}$CHO x2), 2.51 (1H, dtt, J=12.8, 4.6, 2.3 Hz, CHOCH$_{ax}H_{eq}$CHO), 4.40 (2H, m, CH$_2$CHOCH$_2$ x2), 4.70 (1H, m, CH$_2$C(CH$_3$)=CH_AH_B), 4.89 (1H, m, CH$_2$C(CH$_3$)=CH_AH_B); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.6, 26.2, 32.4, 36.6 (2C), 49.7, 68.2 (2C), 72.8, 110.2, 115.0, 140.9; HRMS (DART) calcd for $C_{12}H_{19}O_3$ $[M+H]^+$ 211.1329, found 211.1338.

4.23. The reaction of O,Se-acetal 1 and 6a

A solution of O,Se-acetal **1** (33.0 mg, 0.106 mmol), *tert*-butyl(-phenylmethylene)carbamate **6a** (109 mg, 0.530 mmol) and V-40 (10.4 mg, 0.0424 mmol) in toluene (2.0 mL) was degassed by freeze-thaw procedure (×3). The mixture was heated to 110 °C. Then another degassed solution of *n*-Bu_3SnH (176 μL, 0.636 mmol) and V-40 (5.2 mg, 0.021 mmol) in toluene (2.0 mL) by freeze-thaw procedure (×3) was added via a syringe pump over 3 h. After additional 1 h at 110 °C, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography [a column consecutively packed with silica gel 4 g and 10% (w/w) KF contained silica gel 1 g, hexane/EtOAc 20/1 to 5/1] to afford the unreacted O,Se-acetal **1** (9.3 mg, 0.030 mmol) in 28% yield and *tert*-butyl benzylcarbamate (69.0 mg, 0.336 mmol) in 63% yield based on **6a**.

4.24. General procedure B: carbamate 10a

Et_3B (1.03 M hexane solution, 0.31 mL, 0.32 mmol) was added to a solution of O,Te-acetal **2** (38.3 mg, 0.106 mmol) and *tert*-butyl(-phenylmethylene)carbamate **6a** (65.0 mg, 0.317 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. The reaction mixture was stirring for 15 min, and then saturated aqueous $NaHCO_3$ (10 mL) was added. The resultant solution was extracted with EtOAc (5 mL x2), and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 3/1) to afford **10a** (35.5 mg, 0.0982 mmol) in 93% yield: colorless oil; IR (film) 3451, 3354, 2969, 1710, 1495, 1394, 1367, 1324, 1297, 1246, 1167, 1129 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34–1.48 (13H, m, *t*-Bu, CCH_3, COC$H_{ax}H_{eq}$CHO), 1.50–1.65 (2H, m, COC$H_{ax}H_{eq}$CHO, CHOC$H_{ax}H_{eq}$CHO), 1.85 (1H, d, J=12.4 Hz, COCH$_{ax}H_{eq}$CHO), 2.48 (1H, dtt, J=13.3, 3.6, 1.8 Hz, CHOCH$_{ax}H_{eq}$CHO), 2.60 (1H, dtt, J=13.3, 2.3, 2.3 Hz, COCH$_{ax}H_{eq}$CHO), 4.27 (1H, m, CH$_2$CHOCH$_2$), 4.34–4.49 (2H, m, CH$_2$CHOCH$_2$, PhCH), 5.53 (1H, br d, J=5.9 Hz, NH), 7.24–7.34 (5H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, 40 °C) δ 26.0, 28.2, 28.3 (3C), 32.3, 34.1, 34.7, 67.7, 68.1, 74.3, 79.6, 110.6, 127.5, 128.1

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(2C), 128.5 (2C), 138.4, 155.7; HRMS (ESI) calcd for $C_{20}H_{27}NNaO_5$ $[M+Na]^+$ 384.1781, found 384.1783.

4.25. Sulfonamide 10b

According to the general procedure B, **10b** (32.5 mg, 0.0782 mmol) was synthesized in 76% yield from O,Te-acetal **2** (37.0 mg, 0.103 mmol) and *N*-benzylidene-*p*-toluenesulfonamide **6b** (80.0 mg, 0.308 mmol) by using Et_3B (1.03 M hexane solution, 0.30 mL, 0.31 mmol) in CH_2Cl_2 (1.0 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1 to 2/1): colorless solid; mp 177–179 °C; IR (film) 3279, 2954, 1451, 1397, 1324, 1299, 1160, 1128, 1091, 1059 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (1H, dd, J=13.3, 1.8 Hz, COC$H_{ax}H_{eq}$CHO), 1.41 (3H, s, CCH_3), 1.42–1.48 (2H, m, COC$H_{ax}H_{eq}$CHO, CHOC$H_{ax}H_{eq}$CHO), 1.93 (1H, dtt, J=12.8, 1.8, 1.8 Hz, COCH$_{ax}H_{eq}$CHO), 2.32 (3H, s, ArCH_3), 2.44 (1H, dtt, J=13.3, 3.6, 1.8 Hz, CHOCH$_{ax}H_{eq}$CHO), 2.58 (1H, dtt, J=13.3, 2.3, 2.3 Hz, COCH$_{ax}H_{eq}$CHO), 4.06 (1H, d, J=6.9 Hz, PhCH), 4.27 (1H, m, CH_2CHOCH_2), 4.39 (1H, m, CH_2CHOCH_2), 5.53 (1H, d, J=6.4 Hz, NH), 7.00–7.06 (4H, m, aromatic), 7.08–7.19 (3H, m, aromatic), 7.39–7.44 (2H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 25.9, 32.1, 33.0, 34.6, 64.9, 67.6, 67.9, 74.4, 110.6, 127.0 (2C), 127.7, 127.9 (2C), 128.6 (2C), 129.1 (2C), 135.4, 137.1, 142.9; HRMS (ESI) calcd for $C_{22}H_{25}NNaO_5S$ $[M+Na]^+$ 438.1346, found 438.1330.

4.26. Aniline 10c

According to the general procedure B, **10c** (21.0 mg, 0.0622 mmol) was synthesized in 60% yield from O,Te-acetal **2** (37.4 mg, 0.104 mmol) and *N*-benzylideneaniline **6c**[30] (94.0 mg, 0.519 mmol) by using Et_3B (1.03 M hexane solution, 0.51 mL, 0.52 mmol) in CH_2Cl_2 (1.0 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1): colorless oil; IR (film) 3390, 3053, 3008, 2956, 2931, 2850, 1602, 1503, 1395, 1320, 1298, 1146, 1127 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (1H, dd, J=13.3, 1.4 Hz, COC$H_{ax}H_{eq}$CHO), 1.46 (1H, d, J=13.3 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.51 (3H, s, CCH_3), 1.55 (1H, dd, J=12.8, 1.4 Hz, COC$H_{ax}H_{eq}$CHO), 2.36 (1H, m, COCH$_{ax}H_{eq}$CHO), 2.43–2.57 (2H, m, COCH$_{ax}H_{eq}$CHO, CHOCH$_{ax}H_{eq}$CHO), 4.13 (1H, s, PhCH), 4.37 (1H, m, CH_2CHOCH_2), 4.42 (1H, m, CH_2CHOCH_2), 6.53 (2H, d, J=7.8 Hz, aromatic), 6.66 (1H, t, J=7.3 Hz, aromatic), 7.06 (2H, t, J=7.3 Hz, aromatic), 7.24–7.44 (5H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 32.36, 32.39, 35.4, 66.2, 68.0, 68.1, 74.7, 110.7, 114.2 (2C), 117.8, 127.7, 128.3 (2C), 128.6 (2C), 128.9 (2C), 138.0, 147.6; HRMS (ESI) calcd for $C_{21}H_{23}NNaO_3$ $[M+Na]^+$ 360.1570, found 360.1562.

4.27. *O*-Benzylhydroxylamine 10d

According to the general procedure B, **10d** (25.7 mg, 0.0882 mmol) was synthesized in 93% yield from O,Te-acetal **2** (34.0 mg, 0.0944 mmol) and formaldehyde *O*-benzyloxime **6d**[31] (38.0 mg, 0.281 mmol) by using Et_3B (1.03 M hexane solution, 0.28 mL, 0.28 mmol) in CH_2Cl_2 (0.94 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 2/1): colorless oil; IR (film) 3276, 2950, 2929, 2854, 1395, 1323, 1298, 1165, 1149, 1127 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (3H, s, CCH_3), 1.57 (1H, dt, J=13.2, 1.8 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.61 (2H, d, J=13.2 Hz, COC$H_{ax}H_{eq}$CHO x2), 2.35 (2H, m, COCH$_{ax}H_{eq}$CHO x2), 2.51 (1H, dtt, J=13.2, 4.6, 2.3 Hz, CHOCH$_{ax}H_{eq}$CHO), 2.92 (2H, s, NHCH_2), 4.39 (2H, br s, CH_2CHOCH_2 x2), 4.69 (2H, s, PhCH_2), 7.27–7.37 (5H, m, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 32.4, 35.5 (2C), 60.8, 68.0 (2C), 72.4, 75.9, 110.3, 127.8, 128.3 (2C), 128.4 (2C), 137.8; HRMS (ESI) calcd for $C_{16}H_{21}NNaO_4$ $[M+Na]^+$ 314.1363, found 314.1359.

4.28. *O*-Benzylhydroxylamine 10e

According to the general procedure B, **10e** (25.5 mg, 0.0694 mmol) was synthesized in 70% yield from O,Te-acetal **2** (35.7 mg, 0.0991 mmol) and benzaldehyde *O*-benzyloxime **6e**[32] (63.0 mg, 0.298 mmol) by using Et_3B (1.03 M hexane solution, 0.29 mL, 0.30 mmol) in CH_2Cl_2 (1.0 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 4/1): colorless oil; IR (film) 3267, 3061, 3029, 2952, 2864, 1453, 1395, 1323, 1298, 1145, 1127 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (1H, dd, J=13.2, 1.8 Hz, COC$H_{ax}H_{eq}$CHO), 1.37 (1H, dt, J=13.2, 1.7 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.457 (1H, m, COC$H_{ax}H_{eq}$CHO), 1.459 (3H, s, CCH_3), 2.24 (1H, m, COCH$_{ax}H_{eq}$CHO), 2.41 (1H, dtt, J=13.2, 3.6, 1.8 Hz, CHOCH$_{ax}H_{eq}$CHO), 2.47 (1H, m, COCH$_{ax}H_{eq}$CHO), 4.03 (1H, s, PhCH), 4.28–4.35 (2H, m, CH_2CHOCH_2 x2), 4.54 (1H, d, J=11.5 Hz, PhCH_AH_B), 4.58 (1H, d, J=11.5 Hz, PhCH_AH_B), 6.48 (1H, s, NH), 7.13–7.18 (2H, m, aromatic), 7.22–7.29 (3H, m, aromatic), 7.30–7.38 (3H, m, aromatic), 7.42–7.47 (2H, m, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 31.2, 32.3, 35.5, 67.97, 68.0, 72.7, 74.4, 76.7, 110.4, 127.6, 127.8, 127.9 (2C), 128.2 (2C), 128.5 (2C), 129.1 (2C), 137.1, 137.7; HRMS (ESI) calcd for $C_{22}H_{25}NNaO_4$ $[M+Na]^+$ 390.1676, found 390.1681.

4.29. *O*-Benzylhydroxylamine 10f

According to the general procedure B, **10f** (12.8 mg, 0.0363 mmol) was synthesized in 38% yield from O,Te-acetal **2** (34.3 mg, 0.0953 mmol) and 3-methylbutanal *O*-benzyloxime **6f**[33] (55.0 mg, 0.288 mmol) by using Et_3B (1.03 M hexane solution, 0.28 mL, 0.29 mmol) in CH_2Cl_2 (0.95 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 5/1): colorless oil; IR (film) 2952, 2867, 1453, 1394, 1365, 1323, 1298, 1129 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.91 (3H, d, J=6.9 Hz, CHCH_3), 0.95 (3H, d, J=6.9 Hz, CHCH_3), 1.21 (1H, ddd, J=16.6, 9.8, 2.9 Hz, NHCHCH_AH_B), 1.42 (3H, s, CCH_3), 1.44 (1H, m, NHCHCH_AH_B), 1.56 (1H, dt, J=13.2, 1.7 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.66–1.73 (2H, m, COC$H_{ax}H_{eq}$CHO x2), 1.84 (1H, m, $(CH_3)_2CH$), 2.17 (1H, m, COCH$_{ax}H_{eq}$CHO), 2.43 (1H, m, COCH$_{ax}H_{eq}$CHO), 2.45 (1H, m, CHOCH$_{ax}H_{eq}$CHO), 2.74 (1H, dd, J=9.7, 2.3 Hz, NHCH), 4.35–4.43 (2H, m, CH_2CHOCH_2 x2), 4.66 (1H, d, J=11.5 Hz, PhCH_AH_B), 4.70 (1H, d, J=11.5 Hz, PhCH_AH_B), 6.06 (1H, br s, NH), 7.27–7.37 (5H, m, aromatic); ^{13}C NMR (100 MHz, CD_3OD) δ 22.1, 24.3, 26.46, 26.52, 33.4, 35.1, 35.3, 36.2, 66.9, 69.8, 69.9, 76.2, 77.0, 111.6, 128.8, 129.3 (2C), 129.5 (2C), 139.3; HRMS (ESI) calcd for $C_{20}H_{29}NNaO_4$ $[M+Na]^+$ 370.1989, found 370.1999.

4.30. *O*-Benzylhydroxylamine 10g

According to the general procedure B, **10g** (34.3 mg, 0.0944 mmol) was synthesized in 89% yield from O,Te-acetal **2** (38.3 mg, 0.106 mmol) and *O*-benzyl-protected ethyl glyoxylate oxime **6g**[34] (66.0 mg, 0.318 mmol) by using Et_3B (1.03 M hexane solution, 0.31 mL, 0.32 mmol) in CH_2Cl_2 (1.1 mL). The residue was purified by flash column chromatography on silica gel (10 g, hexane/EtOAc 3/1): colorless solid; mp 79–81 °C; IR (film) 3266, 2955, 1731, 1453, 1396, 1325, 1299, 1230, 1201, 1191, 1164, 1128 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, J=6.9 Hz, $CO_2CH_2CH_3$), 1.38 (3H, s, CCH_3), 1.41 (1H, dd, J=12.8, 0.9 Hz, COC$H_{ax}H_{eq}$CHO), 1.53 (1H, d, J=12.8 Hz, CHOC$H_{ax}H_{eq}$CHO), 1.75 (1H, dd, J=13.3, 0.9 Hz, COC$H_{ax}H_{eq}$CHO), 2.23 (1H, m, CHOCH$_{ax}H_{eq}$CHO), 2.48 (2H, m, COCH$_{ax}H_{eq}$CHO x2), 3.49 (1H, s, NHCH), 4.27 (2H, m, $CO_2CH_2CH_3$), 4.33–4.38 (2H, m, CH_2CHOCH_2 x2), 4.66 (1H, d, J=11.9 Hz, PhCH_AH_B), 4.69 (1H, d, J=11.9 Hz, PhCH_AH_B), 7.26–7.37 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 25.9, 32.2, 33.4, 34.8, 61.1, 67.8, 68.0, 70.8, 72.8, 76.1,

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110.4, 127.8, 128.2 (2C), 128.6 (2C), 137.6, 170.8; HRMS (ESI) calcd for $C_{19}H_{25}NNaO_6$ $[M+Na]^+$ 386.1580, found 386.1563.

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Supplementary data

Supplementary data (the NMR spectra of newly synthesized compounds) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.04.023.

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