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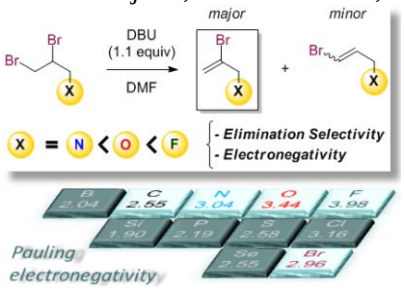

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DBU-Promoted regioselective HBr-elimination of vicinal dibromides: Effects of the adjacent oxygen and/or other heterofunctional groups

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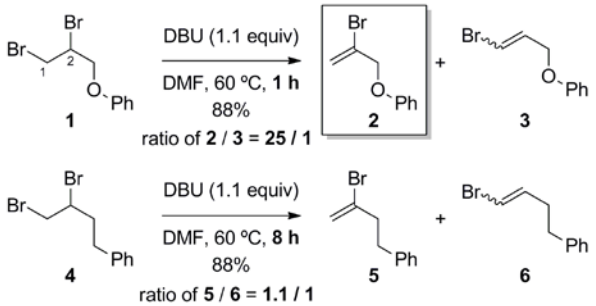
ABSTRACT

DBU-Promoted HBr-eliminations of a variety of vicinal dibromides having an adjacent heteroatom (F, O, or N) under mild basic conditions and relevant theoretical calculations were carried out. These HBr-eliminations proceeded more or less regioselectively, and all associated calculation results agreed with the experimental facts. This work suggests that the HBr-elimination selectivity is an effect of the electronegativity of the neighboring heteroatoms themselves rather than the electron-withdrawing effects of the entire heterofunctional group.

1. Introduction

2-Bromo-1-alkenes are extremely useful and versatile building blocks in organic synthesis. For example, they are used as substrates in preparing organometallic reagents such as vinyllithiums[1] and vinyl Grignard reagents,[2] coupling partners in a variety of transition-metal-catalyzed reactions, and precursors of alkynes,[3] α-halo ketones,[4] and heterocycles.[5]

In recent studies, Ohgiya, Nishiyama, et al. and we have explored the DBU-promoted regioselective HBr-elimination of vicinal dibromides having an adjacent *O*-functional group.[3g,6] A typical example is illustrated in Scheme 1, which shows that both the elimination reactivity and regioselectivity are affected by the presence or absence of the neighboring *O*-functional group in the substrate molecule. The reaction of dibromide **1** with 1.1 equiv of DBU for 1 h gave 2-bromo-1-alkene **2** in high yield (88%) with high selectivity (25/1). In contrast, the reaction of dibromide **4** for 8 h gave both 2-bromo-1-alkene **5** and 1-bromo-1-alkene **6** with almost no selectivity. Thus, the regioselective HBr-elimination of *O*-functionalized dibromides is an efficient and systematic way to synthesize 2-bromo-1-alkenes; it requires no expensive reagents, special laboratory equipments, or extra-dry conditions. For those reasons and the mild basic conditions, this synthetic method is very useful for natural product and its analogues syntheses[6a–d,7] and one-pot operation.[6f,6g] With regard to how the *O*-functional group affects the reaction, Nishiyama, et al. previously explained that the high regioselectivity was controlled by the acidity enhancement of the hydrogen at the C2 position caused by the inductive electron-withdrawing effects of the oxygen substituent (OR), in cooperation with the electron-withdrawing inductive effects of both the bromine atoms.[3g,6a] In this paper, we provide full details of the DBU-promoted regioselective HBr-elimination of vicinal dibromides having an adjacent oxygen and/or other hetero-functional group, and elucidate the mechanism of the selectivity arising.



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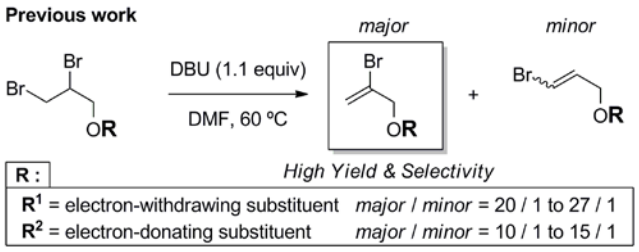
Scheme 1. Comparative experiments with and without the participation of a neighboring *O*-functional group.

2. Results and discussion

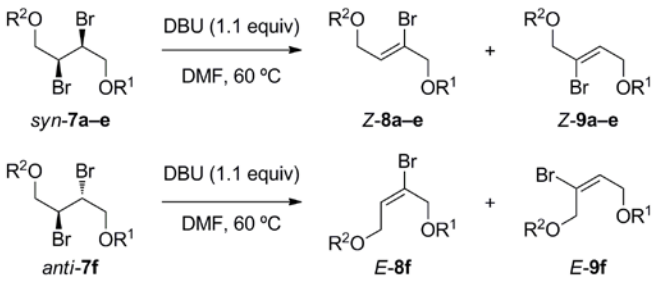
Ohgiya, Nishiyama, et al. described the significance of the neighboring *O*-functional group for appearance of the high selectivity through untiring research on the DBU-promoted HBr-elimination of vicinal dibromides having electron-withdrawing aryloxy- and acyloxy groups (OR^1)(Scheme 2).[3g,6a] Meanwhile, we also examined a wide variety of other *O*-functional groups including electron-donating benzyloxy- and silyloxy groups (OR^2) for their effect on the selectivity, and then realized the unique correlation that the elimination selectivity is obviously susceptible to the electronic effect of substituent (R) on the oxygen atom.[6e]



Scheme 2. DBU-Promoted regioselective HBr-elimination of vicinal dibromides.

Next, vicinal dibromides having both an electron-withdrawing *O*-functional group (OR^1) and an electron-donating *O*-functional group (OR^2) were tested to reveal the extent to which the relative difference between an electron-withdrawing substituent (R^1) and an electron-donating substituent (R^2) on each oxygen atom can induce the HBr-elimination regioselectivity (Table 1). The reaction of *syn*-dibromide **7a** having both a 4-nitrophenyl group (R^1) and a 4-methoxyphenyl group (R^2) with 1.1 equiv of DBU gave the vinyl bromide *Z*-**8a** and the regioisomer *Z*-**9a** with poor selectivity (1.6/1; entry 1). Because the effect of substituents at the *para* position of the phenyl group did not expressly affect the selectivity, both substituents (R^1 and R^2) were widely examined with a view to improving the regioselectivity of HBr-elimination. However, all observed regioselectivities were poorer than those required for general organic synthetic applications, although vinyl bromides **8** were always slightly predominant over both *syn*- and *anti*-dibromides **7** (entries 2–6), despite the difference in the types of atoms directly linked to oxygen (entries 4–6). These results imply that the elimination selectivity is more directly affected by the electronegativity of the oxygen atoms themselves rather than the electron-withdrawing effects of the substituents (R) on the oxygen atoms.

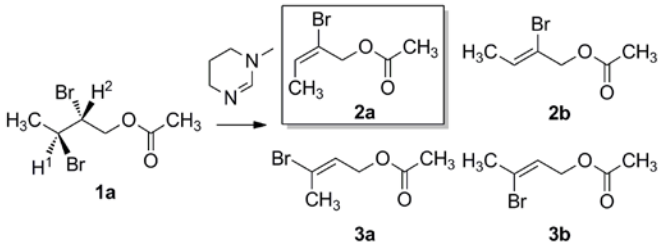
Table 1
DBU-Promoted elimination of vicinal dibromides having both an electron-withdrawing *O*-functional group (OR^1) and an electron-donating *O*-functional group (OR^2)



Entry	Dibromide **7**	Substituents R^1 and R^2	Time / h	**8** + **9** Yield / % [**8** / **9**][a]
1	*syn*-**7a**	R^1 = 4-$O_2NC_6H_4$ R^2 = 4-$MeOC_6H_4$	0.5	95 [1.6 / 1]
2	*syn*-**7b**	R^1 = Bz R^2 = Bn	2.0	71 [1.5 / 1][b]
3	*syn*-**7c**	R^1 = 4-$O_2NC_6H_4$ R^2 = Bn	5.5	92 [2.0 / 1]
4	*syn*-**7d**	R^1 = Bz R^2 = TIPS	1.2	91 [1.2 / 1][c]
5	*syn*-**7e**	R^1 = 4-$O_2NC_6H_4$ R^2 = TIPS	5.0	97 [1.6 / 1]
6	*anti*-**7f**	R^1 = Bz R^2 = TIPS	2.5	80 [1.6 /1]

[a]The ratio of **8** and **9** was determined by ^{1}H NMR. [b]Alkyne was obtained (13%). [c]Alkyne was obtained (6%).

We also carried out theoretical calculations.[8] For the DFT calculation using the B3LYP/6-31+G* method, **1a** was adopted as the representative of *anti*-vicinal dibromides having an adjacent acetoxy group, and 1-methyl-1,4,5,6-tetrahydropyrimidine as the DBU base (Scheme 3, Figure 1). **TS1** is the transition state that the DBU model coordinated on H^2, while **TS2** is the transition state that the base coordinated on H^1. In addition, the transition state **TS-a** is the *anti*-conformation (for H^2–Br(C^1)) of **1a**, and the transition state **TS-b** is the *gauche*-conformation of **1a**. **TS-I** and **TS-II** distinguish between directions of a base. For example, both **TS1-aI** and **TS1-aII** lead to the product **2a**, while both **TS2-bI** and **TS2-bII** lead to **3b**. All transition states show that **TS1** is more stable than **TS2**. The gas phase calculation indicates that the elimination reaction of a hydrogen atom H^2 together with a bromine atom at the C-1 position to produce **2a** (*via* **TS1-a**) or **2b** (*via* **TS1-b**) is more feasible than the elimination on the opposite side to produce **3a** (*via* **TS2-a**) or **3b** (*via* **TS2-b**). In addition, all transition states show that **TS-a** is more stable than **TS-b**; that is, this computational result indicates that the *anti*-conformation (**TS1-a** or **TS2-a**) is ready for the *trans* β-elimination to form the products **2a** or **3a**, whereas to form **2b** or **3b**, it must undergo *cis* β-elimination *via* the *gauche*-conformation (**TS1-b** or **TS2-b**). As for the directions of the DBU model (**TS-I** versus **TS-II**), the differences in the activation energies of **TS1-a**, **TS1-b**, and **TS2-b** were only 0.7, 1.0, and 0.3 kcal mol^{-1}, respectively. In contrast, the difference in the activation energies between **TS2-aI** and **TS2-aII** was relatively high (2.2 kcal mol^{-1}). As for the conformations of **1a**, the difference in the activation energies between **TS2-aI** and **TS2-bI** was also quite high (3.5 kcal mol^{-1}), although those of **TS1-I**, **TS1-II**, and **TS2-II** were 1.7, 2.0, and 1.6 kcal mol^{-1}, respectively. These calculations indicated that the estimate of the activation energy of **TS2-aI** was possibly lower than the actual value, because of the hydrogen bonding between the carbonyl oxygen atom and the base. Second order perturbation theory analysis of the Fock matrix in the NBO basis was then performed to evaluate the hydrogen bond. This calculation showed that the stabilization energy of **TS2-aI** associated with electron delocalization from the lone pair of the carbonyl oxygen atom to the base was 10.6 kcal mol^{-1}, whereas that of **TS1-aI** was only 4.5 kcal mol^{-1}. This result suggested that the activation energy of **TS2-aI** was overestimated by the stabilization energy of the hydrogen bonding between the carbonyl oxygen atom and the base. Nevertheless, the activation energy of **TS2-aI** was higher than that of **TS1-aI** by 0.7 kcal mol^{-1}. This fact underscores that the DBU-promoted HBr-elimination of **1a** proceeds to afford **2a** preferentially *via* **TS1-a** (Scheme 4).



Scheme 3. Model system of regioselective HBr-elimination of **1a**.

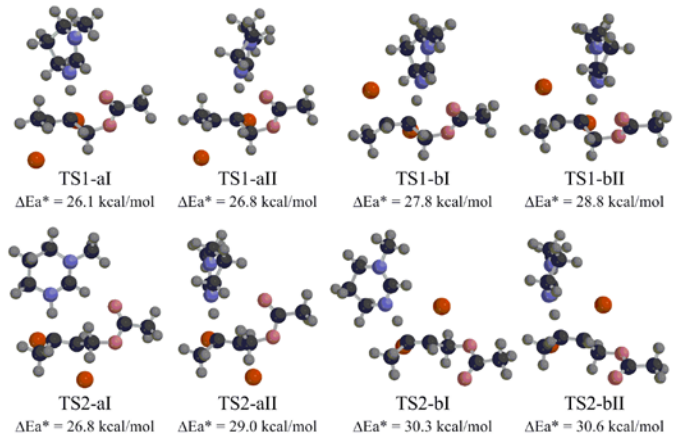
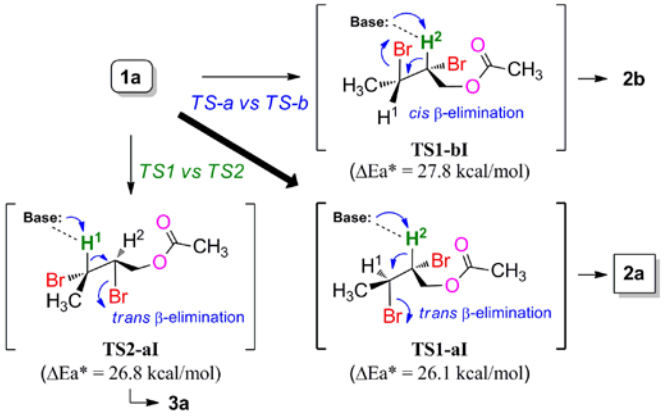
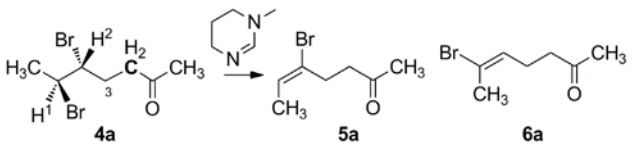


Figure 1. Transition states of proton abstraction from **1a** by DBU model optimized at B3LYP/6-31+G*



Scheme 4. Elimination mechanism based on the theoretical calculations.

For comparison, we also carried out theoretical calculations using the *anti*-vicinal dibromide **4a** without an oxygen atom at the C-3 position (Scheme 5, Figure 2). All transition states shown in Figure 2 are the *anti*-conformations. Both **TS1-aI** and **TS1-aII** lead to **5a**, and both **TS2-aI** and **TS2-aII** lead to **6a**. When **4a** reacts with 1-methyl-1,4,5,6-tetrahydropyrimidine, the estimated activation energy of the **TS2-aI** also seems to be lower than the actual value, as well as that of **1a**. For **4a**, the calculated result shows that **TS2** is relatively more stable than **TS1**. In conclusion, as explained above, DBU-promoted HBr-elimination is affected more by the neighboring electronic interaction than by the steric interaction, and all theoretical calculated results were practically coincident with the experimental facts.



Scheme 5. Model system of regioselective HBr-elimination of **4a**.

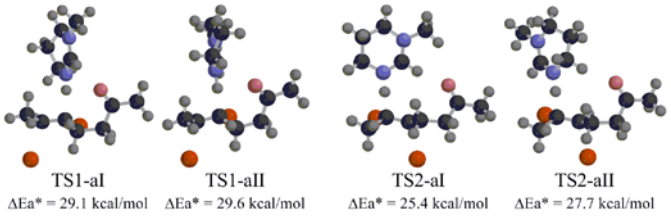
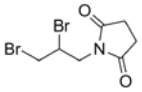
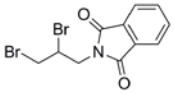
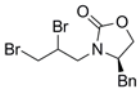


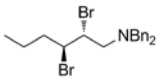
Figure 2. Transition states of proton abstraction from **4a** by DBU model optimized at B3LYP/6-31+G*

Based on these encouraging results, the DBU-promoted elimination of vicinal dibromides having an adjacent *N*-functional group was next considered,[6e] because the nitrogen atom is one of the important element for both organic and inorganic compounds, and also has a high electronegativity. However, all entries in Table 2 showed lower selectivities (3.6/1 to 1.2/1) than we had expected. It is not as easy to simply discuss the substrates having *N*-functional groups as the substrates having *O*-functional groups, because of the high nucleophilicity of the nitrogen atom. For example, De Kimpe et al. reported base-induced intramolecular cyclization of the substrates having *N*-alkyl amino groups and *N*-toluenesulfonyl (Ts) amino groups to afford the corresponding aziridines and/or azetidines.[9] They also reported the reaction of the vicinal dibromides having a *N*,*N*-bis(arylmethyl)amino group, such as **10b**, with KO*t*Bu in diethyl ether to afford the corresponding 2-bromo-1-alkenes *via* the intermediate 3-bromoazetidinium salt.[10] In other instances, *N*-benzoyl-1-substituted 1-amino-2,3-dibromopropane (**10**: R = H, R′ = Bz) was easily converted to the corresponding oxazoline through intramolecular cyclization.[11] Thus, all observed regioselectivities were poor compared with those for substrates bearing an *O*-functional group (see Scheme 2), although these results could simply be evaluated against the same standard.

Table 2
DBU-Promoted elimination of vicinal dibromides having an *N*-functional group

10 **11** **12**

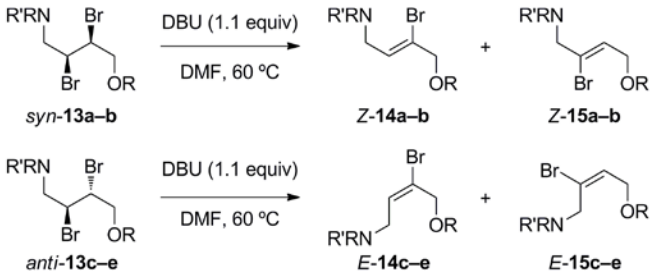
Entry	Dibromide **10**	Substituents R and R′	Time / h	**11** + **12** Yield / % [**11** / **12**][a]
1	**10a**	R = H R′ = Boc	2.0	89 [3.3 / 1]
2	**10b**	R = Bn R′ = Bn	3.0	79 [2.7 / 1]
3	**10c**	R = Ns[b] R′ = Bn	3.0	87 [3.5 / 1]
4	**10d**	R = Me R′ = Ts	2.0	99 [3.3 / 1]
5	**10e**		2.0	60 [1.6 / 1]
6	**10f**		2.0	84 [1.2 / 1]
7	**10g**		2.0	99 [3.6 / 1]

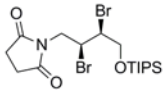
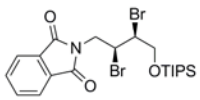
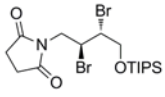
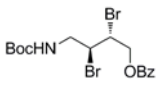
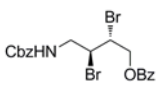
8	**10h**		8.0	91 [3.0 / 1]

[a]The ratio of **11** and **12** was determined by ^{1}H NMR. [b]Ns = 2-Nitrobenzenesulfonyl.

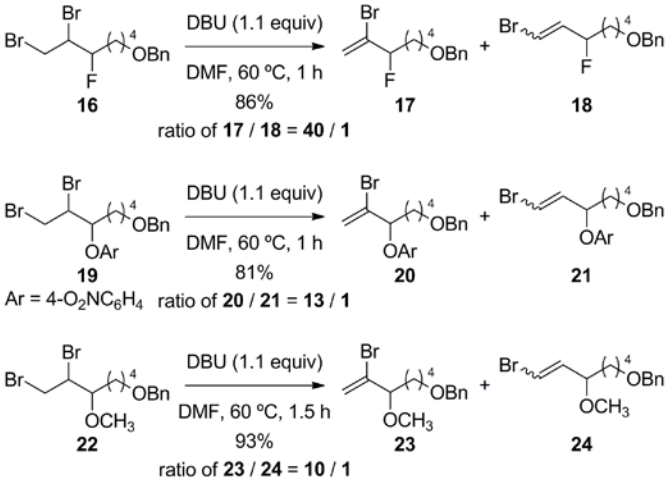
Next, vicinal dibromides having both an *O*-functional group and an *N*-functional group in their molecules were examined to reveal the extent to which the relative difference in electronegativity between the oxygen atom itself and the nitrogen atom itself can affect the HBr-elimination regioselectivity (Table 3). As expected, *syn*-dibromides **13a**–**b** gave the corresponding *Z*-vinyl bromides **14a**–**b** (entries 1–2), while *anti*-dibromides **13c**–**e** gave the corresponding *E*-vinyl bromides **14c**–**e** (entries 3–5), in high yields in both cases with excellent regio- and stereoselectivities. These results confirm the hypothesis that the elimination selectivity is subject to the electronegativity of the neighboring heteroatoms themselves rather than the electronic effects of the entire functional group. Moreover, we also examined the dibromide **16** having a neighboring fluorine, which is the most electronegative of the elements, for comparison with the oxygen-functionalized dibromides **19** and **22** (Scheme 6). As a result, the fluorinated vinyl bromide **17** was produced with remarkable regioselectivity (40/1), compared with those of the oxygenated **20** (13/1) and **23** (10/1). This elimination rule may, therefore, be applied to the effective synthesis of the fluorinated compounds, which is important for fluorine-containing biologically active agents such as pharmaceuticals and agrochemicals.[12]

Table 2
DBU-Promoted elimination of vicinal dibromides having both an *O*-functional group and an *N*-functional group



Entry	Dibromide **13**		Time / h	**14** + **15** Yield / % [**14** / **15**][a]
1	*syn*-**13a**		4.0	83 [18 / 1]
2	*syn*-**13b**		1.5	63 [18 / 1]
3	*anti*-**13c**		2.0	88 [23 / 1]
4	*anti*-**13d**		1.5	98 [8 / 1]
5	*anti*-**13e**		1.0	99 [11 / 1]

[a]The ratio of **14** and **15** was determined by ^{1}H NMR.



Scheme 6. DBU-Promoted elimination of vicinal dibromides having a fluorine and an *O*-functional group.

3. Conclusion

In summary, we have performed the DBU-promoted HBr-elimination of a variety of vicinal dibromides having an adjacent *O*-functional group, adjacent *O*-functional groups on both sides, an adjacent *N*-functional group, adjacent *O*- and *N*-functional groups on both sides, and an adjacent fluorine. All results suggest that the regioselectivity of the elimination is subject to the electronegativity of the neighboring heteroatoms themselves. Further efforts to expand the scope and application of this elimination rule are under way.

4. Experimental

4.1. General remarks

All melting points were determined on a Yanaco MP melting point apparatus and are uncorrected. Infrared spectra were recorded with a Horiba FT-710 spectrophotometer. ^{1}H and ^{13}C NMR spectral data were obtained with Bruker Avance 600, JEOL JNM-LA 500, or JEOL JNM-AL 300 instruments. Chemical shifts are quoted in ppm using tetramethylsilane (δ = 0 ppm) as the reference for ^{1}H NMR spectroscopy, and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Mass spectra were measured with a Bruker Daltonics microTOF-NR focus spectrometer. Column chromatography was carried out on silica gel (Kanto Chemical Co. or Merck Co. Ltd). All reactions were performed under an argon atmosphere. Bromoalkenes *Z*-**8c**/*Z*-**9c**, *Z*-**8e**/*Z*-**9e**, *E*-**8f**/*E*-**9f**, **11a**, **11b**/**12b**, *Z*-**14a**, and *E*-**14c** are known compounds and their analytical data have been reported.[13] In principle, the structures of bromoalkene isomers were determined without further separation, except for the several compounds which 2D NMR analysis was needed.

4.2. General procedure for the DBU-promoted elimination

A mixture of dibromoalkane (1.0 equiv) and DBU (1.1 equiv) in DMF (0.1 M) was stirred at 60 °C. The reaction was quenched with 1 M aq HCl or saturated aq NH_4Cl, and then the reaction mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by silica gel (Kanto Chemical Silica gel 60N, spherical, neutral, 63−210 μm) column chromatography or preparative TLC (Merck KGaA, PLC Silica gel $60F_{254}$, 0.5 mm) to afford the corresponding product.

*4.2.1. (Z)-2-Bromo-4-(4-methoxyphenoxy)-1-(4-nitrophenoxy)-2-butene (Z-**8a**).* 95% yield (colorless solid). M.p. 74.4−75.4 °C;

IR (KBr): 3047, 2900, 1511, 1342, 1234, 525 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 4.69 (dt, *J* = 5.4, 1.3 Hz, 2H), 4.79 (d, *J* = 1.4 Hz, 2H), 6.45 (tt, *J* = 5.4, 1.4 Hz, 1H), 6.82 (br s, 4H), 6.97 (d, *J* = 9.2 Hz, 2H), 8.20 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.3, 68.1, 72.8, 115.3 (x 2), 115.5 (x 2), 116.2 (x 2), 121.7, 126.6 (x 2), 129.7, 142.7, 152.6, 154.8, 163.1; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{16}BrNO_5Na$: 416.0104, found: 416.0103.

*4.2.2. (Z)-2-Bromo-1-(4-methoxyphenoxy)-4-(4-nitrophenoxy)-2-butene (Z-**9a**).* 95% yield (colorless solid). M.p. 52.0−53.2 °C; IR (KBr): 3047, 2900, 1511, 1342, 1234, 525 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.76 (s, 3H), 4.68 (d, *J* = 1.4 Hz, 2H), 4.82 (dt, *J* = 5.5, 1.4 Hz, 2H), 6.41 (tt, *J* = 5.5, 1.4 Hz, 1H), 6.81 (d, *J* = 9.4 Hz, 2H), 6.85 (d, *J* = 9.4 Hz, 2H), 6.93 (d, *J* = 9.4 Hz, 2H), 8.19 (d, *J* = 9.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.5, 68.5, 73.6, 115.50 (x 2), 115.54 (x 2), 117.1 (x 2), 125.7, 126.4, 126.8 (x 2), 142.6, 152.4, 155.4, 163.9; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{16}BrNO_5Na$: 416.0104, found: 416.0103.

*4.2.3. (Z)-2-Bromo-1-(benzoyloxy)-4-(benzyloxy)-2-butene (Z-**8b**) / (Z)-2-Bromo-4-(benzoyloxy)-1-(benzyloxy)-2-butene (Z-**9b**).* 71% yield (colorless oil as a mixture). IR (neat): 2939, 2854, 1265, 1095, 709 cm^{-1}; (*Z*-**8b**) ^1H NMR (500 MHz, $CDCl_3$): δ = 4.24 (d, *J* = 5.4 Hz, 2H), 4.54 (s, 2H), 4.99 (s, 2H), 6.38 (t, *J* = 5.4 Hz, 1H), 7.26−7.32 (m, 1H), 7.33−7.36 (m, 4H), 7.43−7.48 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 2H); (*Z*-**9b**) ^1H NMR (500 MHz, $CDCl_3$): δ = 4.21 (s, 2H), 4.57 (s, 2H), 5.01 (d, *J* = 6.0 Hz, 2H), 6.39 (t, *J* = 6.0 Hz, 1H), 7.26−7.31 (m, 1H), 7.33−7.36 (m, 4H), 7.43−7.45 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 63.8, 68.4, 69.1, 72.2, 72.8, 74.2, 121.6, 125.4, 126.6, 127.8 (x 2), 127.86 (x 2), 127.91, 128.1, 128.38 (x 2), 128.44 (x 2), 128.45 (x 2), 128.48 (x 2), 129.5, 129.7 (x 2), 129.79 (x 2), 129.83, 130.0, 133.1, 133.3, 137.4, 137.7, 165.6, 166.3; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{17}BrO_3Na$: 383.0253, found: 383.0253.

*4.2.4. (Z)-1-Benzoyloxy-2-bromo-4-triisopropylsiloxy-2-butene (Z-**8d**) / (Z)-4-Benzoyloxy-2-bromo-1-triisopropylsiloxy-2-butene (Z-**9d**).* 91% yield (colorless oil as a mixture). IR (neat): 2947, 2862, 1728, 1458, 1265 cm^{-1}; (*Z*-**8d**) ^1H NMR (500 MHz, $CDCl_3$): δ = 1.06−1.19 (m, 21H), 4.43 (d, *J* = 5.7 Hz, 2H), 4.99 (s, 2H), 6.47 (tt, *J* = 5.7, 1.5 Hz, 1H), 7.42−7.47 (m, 3H), 8.08 (d, *J* = 7.9 Hz, 2H); (*Z*-**9d**) ^1H NMR (500 MHz, $CDCl_3$): δ = 1.06−1.19 (m, 21H), 4.38 (d, *J* = 1.5 Hz, 2H), 5.01 (dt, *J* = 5.7, 1.3 Hz, 2H), 6.35 (t, *J* = 5.7 Hz, 1H), 7.54−7.59 (m, 3H), 8.05 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.90 (x 3), 11.94 (x 3), 17.89 (x 6), 17.91 (x 6), 63.2, 63.7, 67.8, 68.6, 118.6, 121.5, 128.3 (x 2), 128.4 (x 2), 129.56, 129.64 (x 2), 129.8 (x 2), 130.0, 133.0 (x 2), 133.2, 134.2, 165.7, 166.3; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{20}H_{31}BrO_3SiNa$: 449.1118, found: 449.1117.

*4.2.5. N-(tert-Butoxycarbonyl)-2-bromoallylamine (**11a**)[13] / N-(tert-Butoxycarbonyl)-3-bromoallylamine (**12a**).* 89% yield (colorless solid as a mixture). M.p. 51.2−52.9 °C; IR (KBr): 3317, 2978, 2924, 1689, 1535, 1288, 1257 cm^{-1}; (**11a**) ^1H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 9H), 3.96 (m, 2H), 4.89 (br s, 1H), 5.53 (m, 1H), 5.81 (d, *J* = 1.4 Hz, 1H); (**12a** as an *E*/*Z* mixture) ^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9H), 3.72−3.90 (m, 2H), 4.65 (m, 1H), 6.11−6.30 (m, 2H); (**11a**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (x 3), 48.6, 80.0, 117.0, 130.4, 155.3; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_8H_{14}BrNO_2Na$: 258.0100, found: 258.0102.

*4.2.6. N,N-Benzyl-(2-nitrobenzenesulfonyl)-2-bromoallylamine (**11c**) / N,N-Benzyl-(2-nitrobenzenesulfonyl)-3-bromoallylamine (**12c**).* 87% yield (colorless oil as a mixture). IR (neat): 3097, 3032, 2924, 1628, 1548, 1442, 1365, 1165, 926 cm^{-1}; (**11c**) ^1H NMR (500 MHz, $CDCl_3$): δ = 4.13 (s, 2H), 4.61 (s, 2H), 5.55 (d, *J* = 1.5 Hz, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 7.23−7.34 (m, 5H), 7.66−7.74 (m, 3H), 8.05 (d, *J* = 7.8 Hz, 1H); (**12c** as an *E*/*Z* mixture) ^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (d, *J* = 6.9 Hz, 0.8H), 4.03 (dd, *J* = 6.3, 1.4 Hz, 1.2H), 4.50 (s, 2H), 5.98 (m, 1H), 6.10 (d, *J* = 13.6 Hz, 0.4H), 6.20 (dt, *J* = 7.3, 1.4 Hz, 0.6H), 7.16−7.22 (m, 5H), 7.62−7.68 (m, 3H), 8.00 (d, *J* = 7.8 Hz, 1H); (**11c**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 50.7, 54.0, 120.4, 124.3, 127.0, 128.0, 128.2 (x 2), 128.7 (x 2), 131.2, 131.8, 133.7, 133.8, 134.7, 147.6; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{16}H_{15}BrN_2O_4SNa$: 432.9828, found: 432.9827.

*4.2.7. N,N-Methyl-(4-toluenesulfonyl)-2-bromoallylamine (**11d**) / N,N-Methyl-(4-toluenesulfonyl)-3-bromoallylamine (**12d**).* 99% yield (colorless solid as a mixture). M.p. 34.7−35.3 °C; IR (KBr): 2970, 1920, 1627, 1342, 917, 810 cm^{-1}; (**11d**) ^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 2.75 (s, 3H), 3.88 (s, 2H), 5.64 (m, 1H), 5.89 (m, 1H), 7.31−7.34 (m, 2H), 7.69−7.71 (m, 2H); (**12d** as an *E*/*Z* mixture) ^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 1.5H), 2.44 (s, 1.5H), 2.69 (s, 1.5H), 2.72 (s, 1.5H), 3.63 (d, *J* = 6.6 Hz, 1H), 3.84 (d, *J* = 6.3 Hz, 1H), 6.09 (m, 1H), 6.28 (d, *J* = 13.1 Hz, 0.5H), 6.36 (m, 0.5H), 7.34 (m, 2H), 7.65−7.68 (m, 2H); (**11d**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 34.6, 57.8, 119.2, 127.4 (x 2), 127.6, 129.8 (x 2), 134.8, 143.7; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{11}H_{14}BrNO_2SNa$: 325.9821, found: 325.9820.

*4.2.8. 1-(2-Bromoallyl)pyrrolidine-2,5-dione (**11e**) / 1-(3-Bromoallyl)pyrrolidine-2,5-dione (**12e**).* 60% yield (colorless oil as a mixture). IR (neat): 3610, 3471, 2938, 1766, 1704, 1635, 1411, 1334, 1164 cm^{-1}; (**11e**) ^1H NMR (300 MHz, $CDCl_3$): δ = 2.78 (s, 4H), 4.38 (s, 2H), 5.63 (m, 1H), 5.83 (m, 1H); (**12e** as an *E*/*Z* mixture) ^1H NMR (300 MHz, $CDCl_3$): δ = 2.73 (s, 3H), 2.74 (s, 1H), 4.07 (dd, *J* = 7.3, 1.1 Hz, 1.5H), 4.29 (dd, *J* = 6.1, 1.8 Hz, 0.5H), 6.13 (m, 0.25H), 6.20 (m, 0.75H), 6.37 (m, 0.25H), 6.46 (m, 0.75H); (**11e**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.1 (x 2), 45.9, 119.9, 125.3, 176.1 (x 2); HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_7H_8BrNO_2Na$: 239.9631, found: 239.9636.

*4.2.9. 2-(2-Bromoallyl)isoindoline-1,3-dione (**11f**) / 2-(3-Bromoallyl)isoindoline-1,3-dione (**12f**).* 84% yield (colorless solid as a mixture). M.p. 80.6−81.8 °C; IR (KBr): 3532, 3031, 2923, 1774, 1712, 1465, 1419, 1311 cm^{-1}; (**11f**) ^1H NMR (500 MHz, $CDCl_3$): δ = 4.55 (s, 2H), 5.63 (d, *J* = 2.1 Hz, 1H), 5.85 (d, *J* = 2.1 Hz, 1H), 7.75−7.77 (m, 2H), 7.81−7.91 (m, 2H); (**12f** as an *E*/*Z* mixture) ^1H NMR (500 MHz, $CDCl_3$): δ = 4.25 (d, *J* = 7.0 Hz, 1.2H), 4.47 (d, *J* = 6.1 Hz, 0.8H), 6.24 (m, 0.4H), 6.29 (m, 0.6H), 6.39 (dd, *J* = 7.2, 2.8 Hz, 0.4H), 6.48 (d, *J* = 13.2 Hz, 0.6H), 7.71−7.75 (m, 2H), 7.85−7.88 (m, 2H); (**11f**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 45.3, 110.9, 119.1, 123.6 (x 2), 134.1 (x 2), 134.3 (x 2), 167.3 (x 2); HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{11}H_8BrNO_2Na$: 287.9636, found: 287.9631.

*4.2.10. (R)-4-Benzyl-3-(2-bromoallyl)oxazolidin-2-one (**11g**).* 99% yield (yellow oil as a mixture). IR (neat): 3491, 3028, 2918, 1755, 1630, 1429, 1248 cm^{-1}; (**11g**) ^1H NMR (500 MHz, $CDCl_3$): δ = 2.71 (dd, *J* = 13.5, 7.7 Hz, 1H), 3.11 (dd, *J* = 13.5, 4.8 Hz, 1H), 3.80 (d, *J* = 15.9 Hz, 1H), 4.00−4.11 (m, 2H), 4.21−4.30 (m, 1H), 4.44 (d, *J* = 15.9 Hz, 1H), 5.65 (s, 1H), 5.72 (s, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.33 (dd, *J* = 7.3, 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.8, 50.4, 55.5, 67.2, 120.3, 127.3, 127.8, 128.98 (x 2), 129.04 (x 2), 135.4, 157.8; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{13}H_{14}BrNO_2Na$: 318.0100, found: 318.0098.

*4.2.11. (E)-N,N-Dibenzyl-2-bromo-2-hexenylamine (**11h**) / N,N-Dibenzyl-3-bromo-2-hexenylamine (**12h**).* 91% yield (colorless oil as a mixture). IR (neat): 3026, 2958, 2794, 1495, 1454, 1365, 1126 cm^{-1}; (**11h**) ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* =

7.3 Hz, 3H), 1.37 (tq, *J* = 7.3, 7.3 Hz, 2H), 2.03 (dt, *J* = 7.3, 7.3 Hz, 2H), 3.28 (s, 2H), 3.57 (s, 4H), 6.08 (t, *J* = 7.3 Hz, 1H), 7.20−7.37 (m, 6H), 7.44 (d, *J* = 7.7 Hz, 4H); (**12h** as a *E*/*Z* mixture) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.3 Hz, 3H), 1.51 (m, 2H), 2.30 (m, 2H), 3.04 (d, *J* = 7.2 Hz, 2H), 3.57 (s, 4H), 6.07 (m, 1H), 7.20−7.37 (m, 6H), 7.44 (m, 4H); (**11h**) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 22.4, 31.8, 55.8, 57.5 (x 2), 123.3, 126.9 (x 2), 128.2 (x 4), 128.9 (x 4), 136.4, 139.3 (x 2); HRMS-ESI: *m/z* $[M+H]^+$ calcd for $C_{20}H_{25}BrN$: 358.1165, found: 358.1165.

*4.2.12. (Z)-2-Bromo-4-phthalimidyl-1-triisopropylsiloxy-2-butene (Z-**14b**).* 63% yield (colorless solid). M.p. 34.2−35.1 °C; IR (KBr): 2946, 2892, 2861, 1720 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03−1.15 (m, 21H), 4.33 (s, 2H), 4.50 (d, *J* = 6.1 Hz, 2H), 6.26 (t, *J* = 6.1 Hz, 1H), 7.72 (m, 2H), 7.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.9 (x 3), 17.9 (x 6), 38.2, 67.7, 121.0, 123.3 (x 2), 128.8, 132.1 (x 2), 134.0 (x 2), 167.7 (x 2); HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{21}H_{30}BrNO_3SiNa$: 474.1071, found: 474.1070.

*4.2.13. (E)-1-Benzoyloxy-2-bromo-4-tert-butoxycarbonylamino-2-butene (E-**14d**).* 98% yield (colorless solid). M.p. 83.4−85.0 °C; IR (KBr): 3363, 3351, 2988, 2976, 1720, 1527, 1267 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (s, 9H), 3.95 (m, 2H), 4.91 (br s, 1H), 5.08 (s, 2H), 6.23 (t, *J* = 7.3 Hz, 1H), 7.46 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (x 3), 38.9, 63.9, 79.8, 121.1, 128.5 (x 2), 129.6, 129.8 (x 2), 133.3, 134.6, 155.5, 166.1; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{16}H_{20}BrNO_4Na$: 392.0468, found: 392.0470.

*4.2.14. (E)-1-Benzoyloxy-2-bromo-4-benzyloxycarbonylamino-2-butene (E-**14e**).* 99% yield (colorless solid). M.p. 83.0−84.5 °C; IR (KBr): 3297, 3062, 3031, 1719, 1686, 1540, 1257 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.02 (m, 2H), 5.08 (s, 2H), 5.11 (s, 2H), 5.21 (br s, 1H), 6.24 (t, *J* = 7.4 Hz, 1H), 7.29−7.37 (m, 5H), 7.45 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.4, 63.8, 66.9, 121.6, 128.1 (x 2), 128.2, 128.47 (x 2), 128.53 (x 2), 129.5, 129.9 (x 2), 133.4, 134.0, 136.2, 156.2, 166.2; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{19}H_{18}BrNO_4Na$: 426.0311, found: 426.0308.

*4.2.15. 1-Benzyloxy-6-bromo-5-fluoro-6-heptene (**17**).* 86% yield (colorless oil). IR (neat): 2939, 2862, 2360, 1628, 1450, 1365, 1203 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41−1.57 (m, 2H), 1.63−1.71 (m, 2H), 1.81−1.91 (m, 2H), 3.49 (t, *J* = 6.6 Hz, 2H), 4.50 (s, 2H), 4.85 (dt, *J* = 47.0, 6.2 Hz, 1H), 5.66 (s, 1H), 5.95 (s, 1H), 7.26−7.31 (m, 1H), 7.31−7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2 (d, *J* = 4.4 Hz), 29.3, 33.1 (d, *J* = 21.7 Hz), 70.0, 72.9, 94.3 (d, *J* = 178.7 Hz), 118.6 (d, *J* = 7.5 Hz), 127.5, 127.6 (x 2), 128.4 (x 2), 130.7 (d, *J* = 22.2 Hz), 138.5; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{14}H_{18}BrFONa$: 323.0416, found: 323.0417.

*4.2.16. 1-Benzyloxy-6-bromo-5-(4-nitrophenyloxy)-6-heptene (**20**).* 81% yield (colorless oil). IR (neat): 2925, 2854, 2360, 1728, 1589, 1516, 1338, 1250, 1107 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.49−1.63 (m, 2H), 1.63−1.72 (m, 2H), 1.89−2.02 (m, 2H), 3.50 (t, *J* = 6.1 Hz, 2H), 4.50 (s, 2H), 4.67 (dd, *J* = 7.3, 4.9 Hz, 1H), 5.66 (d, *J* = 2.4 Hz, 1H), 5.87 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 9.8 Hz, 2H), 7.25−7.36 (m, 5H), 8.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.0, 29.3, 33.6, 69.9, 73.0, 81.9, 115.8 (x 2), 118.8, 125.8 (x 2), 127.57, 127.62 (x 2), 128.4 (x 2), 131.1, 138.5, 142.0, 162.4; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}BrNO_4Na$: 442.0624, found: 442.0624.

*4.2.17. 1-Benzyloxy-6-bromo-5-methoxy-6-heptene (**23**).* 93% yield (colorless oil). IR (neat): 3019, 2941, 2863, 2326, 903 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35−1.51 (m, 2H), 1.59−1.68 (m, 4H), 3.28 (s, 3H), 3.47 (t, *J* = 6.2 Hz, 2H), 3.54 (m, 1H), 4.49 (s, 2H), 5.66 (s, 1H), 5.84 (d, *J* = 2.0 Hz, 1H), 7.25−7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.9, 29.5, 33.7, 56.5, 70.2, 72.9, 85.2, 118.8, 127.5, 127.6 (x 2), 128.3 (x 2), 135.1, 138.6; HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{15}H_{21}BrO_2Na$: 335.0617, found: 335.0620.

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