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Electrophile-Induced C−C Bond Activation of Vinylcyclopropanes for the Synthesis of *Z*-Alkylidenetetrahydrofurans

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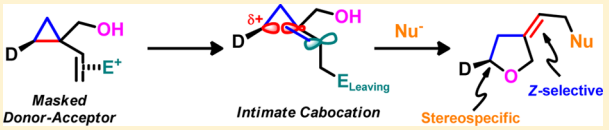
Supporting Information

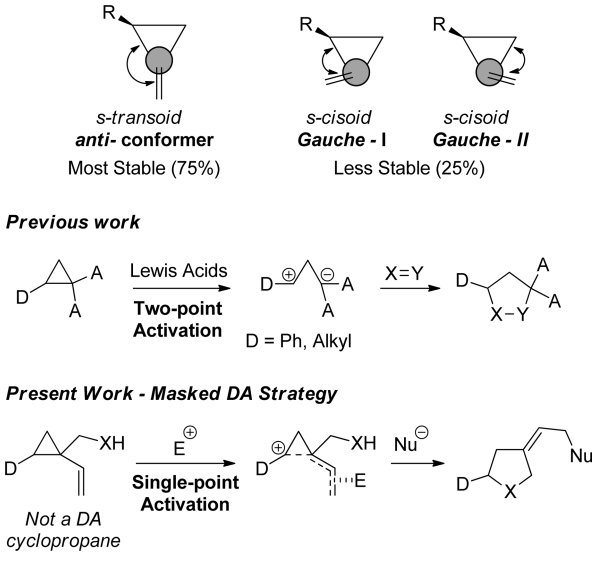
ABSTRACT: We present a detailed study on the behavior of vinylcyclopropanes as masked donor−acceptor system toward the stereoselective synthesis of *Z*-alkylidenetetrahydrofurans. Results of bromenium catalyzed indirect activation of C−C bond of vinylcyclopropanes and concomitant cyclization to alkylidenetetrahydrofuran and other heterocycles have been discussed. The stereoselective formation of the *Z*-isomer is strongly controlled by the extent of destabilization of one of the gauche conformers of the vinylcyclopropane. The ring-opening/cyclization step was found to be stereospecific as in the case of DA cyclopropanes. The activation of the C−C bond leads to a tight-carbocation intermediate, which is evident from the complete retention of the stereochemistry. The retention of configuration has been established by a necessary control experiment that rules out the possibility of a double inversion pathway. The present results serve as direct stereochemical evidence in support of a tight ion-pair intermediate versus the controversial S_N2 pathway. A 2D potential energy scan has been carried out at B3LYP/6-31G(d) level theory to obtain the relative energies of the conformers. The *Z*-selectivity observed has been explained on the basis of the relative population of the conformers and modeling the intermediate and transition state involved in the reaction at M06−2x/6-31+G(d) level. Energy profile for the cyclization step was modeled considering various possible pathways through which cyclization can happen. The methodology has been successfully demonstrated on vinylcyclobutanes as well.



INTRODUCTION

Vinylcyclopropanes (VCPs) have stimulated much interest as essential intermediates in target-oriented synthesis of complex molecular skeletons due to their diverse reactivity patterns and the cascade type transformations.[1−6] The quest to understand the reactivity pattern and the mechanism involved[7] led to the development of a variety of cycloaddition reactions mediated by thermal, photochemical activation and by a variety of transition metal complexes.[8−32] Wender and co-workers explored a number of cycloaddition reactions of VCPs and recently reported the [5 + 2]-cycloaddition reaction between VCPs and acetylenes mediated by a rhodium-dnCOT catalyst.[33] A more recent report by Plietker et al. on the reactivity of diactivated, electron-deficient VCPs with nucleophilic iron complex is noteworthy,[34] while the radical mediated ring-opening of unactivated VCPs with a stoichiometric amount of $Fe(CO)_5$ was reported by Taber et al. earlier.[35] The nucleophilic ring-opening of diactivated vinylcyclopropanes has also been dealt with in great detail.[36−38] In contrast, the electrophilic ring-opening of VCPs and stereochemical outcome of the reaction mediated by Lewis, Brønsted acids and with halogens[39−44] are not well addressed.[45−49] This is probably due to the lack of selectivity over the formation of isomeric mixtures and challenges faced in stereocontrol of the reaction. The *anti*-conformer of the VCP is the most favorable conformer and constitutes about 75% of the stable conformers in liquid and gaseous state (Scheme 1).[50,51] In the *anti*-conformation, the substituents on the cyclopropane have very little steric influence on the reactivity of the double bond leading to poor facial selectivity, and therefore, controlling the stereochemical outcome of the reaction becomes a major challenge.

Scheme 1. Masked Donor−Acceptor Strategy by Single-Point Activation



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In recent years, our group has been actively involved in studying the reactivity of VCPs and VCBs (vinylcyclobutanes) under transition metal-free, electrophilic conditions directed toward the synthesis of chiral bicyclic amidines.[52,53] In the present work, we have employed the concept of indirect activation of C−C bond of VCPs and VCBs developed by our group using catalytically generated electrophilic bromine for the synthesis of alkylidenetetrahydrofurans.

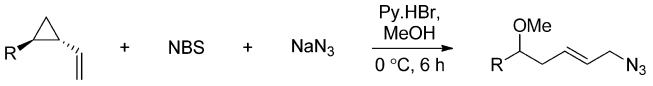
Functionalized tetrahydrofuran derivatives are key skeletal building blocks in numerous natural products. New strategies for the synthesis of functionalized tetrahydrofurans are developed to meet the challenges in the synthesis of these natural products.[54−60] In a number of cases, donor−acceptor (DA) cyclopropane diesters have been utilized elegantly as key precursors for [3 + 2]-cycloaddition reaction mediated by Lewis acids for the synthesis of substituted tetrahydrofurans.[16,32,61−74] Among the Lewis acid-catalyzed ring-opening of phenyl- or alkyl-substituted DA systems, presence of a *gem*-carboxylate group has been shown to be crucial for two-point activation, without which the reaction would not occur.[75] Herein, we introduce vinylcyclopropanes as masked-donor acceptor systems where the ring-opening can be triggered by single point activation (Scheme 1).

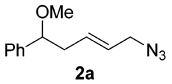
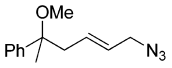
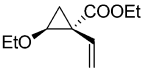
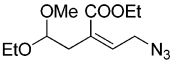
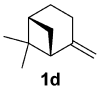
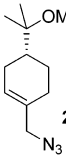
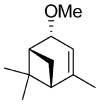
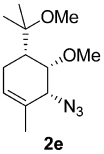
RESULTS AND DISCUSSION

From our earlier work, it was anticipated that treatment of VCPs and VCBs with electrophiles would trigger the ring-opening process. We decided to study the reactivity of vinylcyclopropanes with simple electrophilic bromine source like *N*-bromosuccinimde (NBS) under solvolytic conditions in MeOH in order to ascertain the possibility of ring-opening. For our preliminary studies we explored the reactivity of VCP **1a**[76] with NBS (1 equiv) in MeOH at 0 °C, NaN_3 (1.5 equiv) and pyridinium bromide (0.1 equiv) at rt. The reaction led to the formation of the corresponding azide **2a** as the only product in good yield. Similarly, VCPs (**1b** and **1c**)[77−79] bearing substituents of varying electron-donating ability when subjected to the above reaction conditions yielded the corresponding products (**2b** and **2c**), respectively, in good yields. The reaction was further extended to VCB **1d** (*β*-pinene) and **1e** (*O*-methylverbenol). Under similar reaction conditions, **1d** and **1e** underwent solvolytic ring-opening reaction to give **2d** (67%) and **2e** (60%), respectively (Table 1).

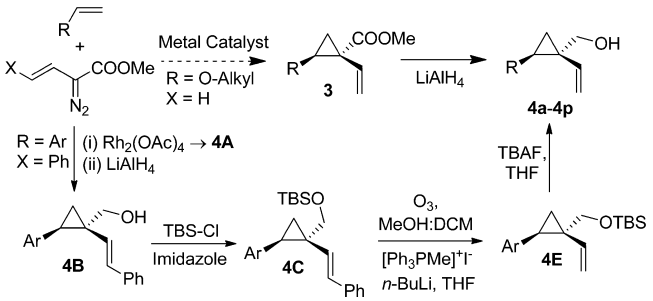
We envisioned that the introduction of a suitable nucleophile at an appropriate position in the substrate can yield a variety of interesting heterocycles. To begin with, the required ethoxy-substituted VCP **4a** was synthesized from the corresponding VCP ester **3** following Davies' cyclopropanation with vinyldiazoesters (Scheme 2).[78,80] Since, the cyclopropanation with vinyldiazoacetate is limited to alkoxy-substituted olefins, the synthesis of other hydroxymethyl VCPs were carried out using styryldiazoacetates under similar conditions to get styrylcyclopropane ester **4A**. The ester **4A** was converted to the desired hydroxymethylVCPs (**4b−4j**, **4l−4p**) by reduction-ozonolysis/Wittig reaction sequence. VCP **4a**, when treated with NBS, pyridinium bromide (catalyst) and NaN_3 in CH_2Cl_2 at 0 °C, yielded the desired alkylidenetetrahydrofuran **7** in 57% yield along with a mixture of other products. When the reaction was carried out in a more polar solvent like acetonitrile, the reaction furnished the desired product **7** without appreciable improvement in the yield (60%) (Scheme 3). We then decided to employ the conditions developed earlier in our group for the ring-opening of VCPs

Table 1. Reactivity of VCPs and VCBs with NBS and NaN_3

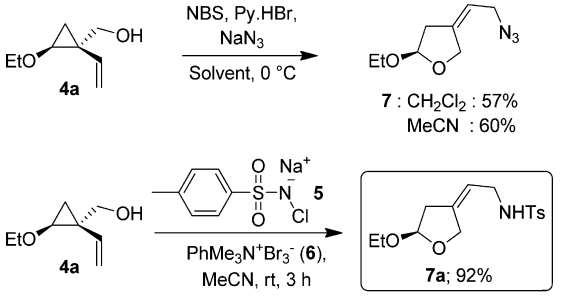


Entry	Substrate	Product	Yield
1	 **1a**	 **2a**	68%
2	 **1b**	 **2b**	71%
3	 **1c**	 **2c**	71%
4	 **1d**	 **2d**	67%
5	 **1e**	 **2e**	60%

Scheme 2. General Scheme for the Synthesis of HydroxymethylVCPs



Scheme 3. Comparison of Reactivity between NBS and Catalytically Generated Br^+ Species



and VCBs, involving catalytically generated electrophilic bromine.[52,53]

Accordingly, VCP **4a** was treated with chloramine-T **5** (1.1 equiv) and PTAB **6** (10 mol %) in acetonitrile at room temperature (3 h). The reaction resulted in the successful formation of the desired *Z*-alkylidenetetrahydrofuran **7a** in excellent yield (92%) and with high stereoselectivity (Scheme 3). The configuration

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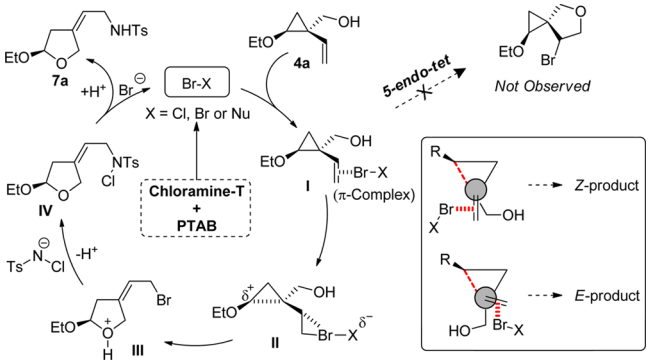
across the double bond was determined by 2D-NMR experiments (see the Supporting Information)

A plausible mechanism has been proposed for the formation of **7a** on the basis of our earlier studies on the reactivity of vinylcyclopropanes.[52,53] Treatment of chloramine-T with PTAB (catalyst) resulted in the in situ generation of an interhalogen compound like BrCl (in catalytic amounts), which during the course of its addition across the double bond of **4a** forms a π-complex **I** (Scheme 4). The formation of the π-complex

Scheme 4. Proposed Mechanistic Pathway for the Formation of 7a from VCP 4a

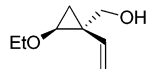
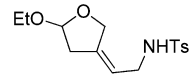
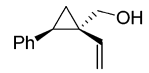
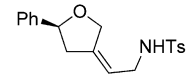
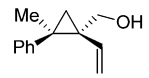
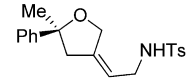
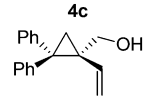
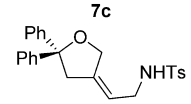
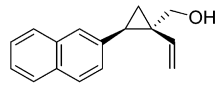
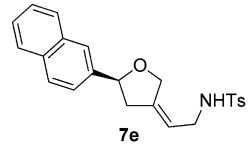
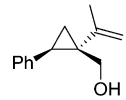
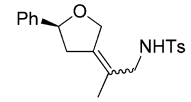
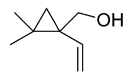
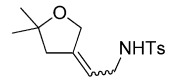
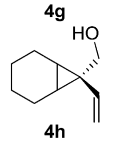
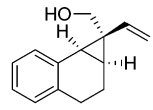
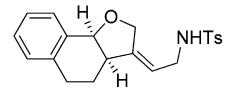
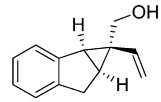
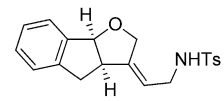
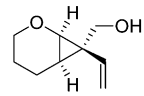
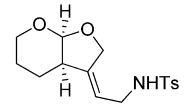


indirectly activates the C−C σ-bond of the cyclopropane (as C−C σ-orbital overlaps with the π^*-orbital), thereby triggering the ring-opening (**II**). The hydroxyl group (nucleophile) placed at the appropriate position traps the incipient carbocation facilitating the cyclization to form *Z*-alkylidenetetrahydrofuran derivative **III**. The bromide in **III** is then displaced by chloramine-T, and expulsion of chlorine results in the formation of amino alkylidenetetrahydrofuran **7a** regenerating BrCl back into the catalytic cycle (Scheme 4). The *5-endotet* cyclization of **I** to a spirocyclopropane product was not observed. The origin of *Z*-selectivity is due to the facile ring-opening through the *anti*-conformer of VCP **4a**.

This result encouraged us to study various aspects of the reaction like substrate scope, stereoselectivity in different stages of the reaction and extend it as a general route to alkylidenetetrahydrofurans from hydroxymethyl substituted VCPs. The methodology was then extended to a variety of phenyl and naphthyl substituted VCPs **4b**−**4e** (Table 2). In all the cases, VCPs were completely converted to the corresponding *Z*-alkylidenetetrahydrofurans **7b**−**7e**, respectively, in excellent yields (81−90%) with >95% diastereoselectivity across the double bond, though the steric environment for both *E*- and *Z*-isomer is similar around the double bond. The structure of **7d** was unambiguously confirmed by X-ray crystallography.[81] Introduction of a methyl group at the β-carbon of the double bond (**4f**) resulted in complete loss in the selectivity resulting in a 1:1 mixture of *E*- and *Z*-isomers of **7f** (entry 6, Table 2). This is due to the drastic destabilization of the *anti*-conformer where the methyl and the phenyl group experience a repulsive steric interaction. The *gauche-I* and *gauche-II* conformers become relatively stable because of the minimized steric crowding that leads to a mixture of *E*- and *Z*-isomers, respectively.

VCP **4g** bearing *gem*-dimethyl group undergoes ring-opening smoothly under standard reaction conditions to give the expected product **7g** as a mixture of *E*- and *Z*-isomers (28:72) in 90% yield. The cyclohexane fused VCP **4h** under the same reaction conditions led to an intraceable mixture of compounds.

Table 2. Reaction of VCPs Leading to Alkylidenetetrahydrofurans[a]

Entry	Reactant	Time (h)	Product	Yield
1	 **4a**	3	 **7a**	92%
2	 **4b**	4	 **7b**	88%
3	 **4c**	4	 **7c**	90%
4	 **4d**	4	 **7d**	81%
5	 **4e**	4	 **7e**	84%
6	 **4f**	4	 **7f**	82% (55:45)
7	 **4g**	4	 **7g**	90% (72:28)
8	 **4h**		Mixture of Products	
9	 **4i**	4	 **7i**	87%
10	 **4j**	4	 **7j**	91%
11	 **4k**	3	 **7k**	87%

[a]Reaction conditions: VCP (1 mmol), chloramine-T (1.1 mmol), PTAB (0.1 mmol), MeCN (5 mL), rt. Yield is of the isolated product.

The methodology was then extended to the synthesis of more complex polycyclic alkylidenetetrahydrofuran skeletons to demonstrate its generality. The 1,2-dihydronaphthalene derived VCP **4i**, when treated with chloramine-T and PTAB in acetonitrile, successfully yielded the 6,6,5-tricyclic alkylidenetetrahydrofuran **7i** in 87% yield. Similarly, indene derived VCP **4j** was also converted to the 6,5,5-fused alkylidenetetrahydrofuran **7j** efficiently in 91% yield. Then, we decided to employ the present methodology on dihydropyran derived VCP **4k** for the synthesis of fused furopyran skeleton, which are in general synthetically attractive. To our delight, VCP **4k** also reacted

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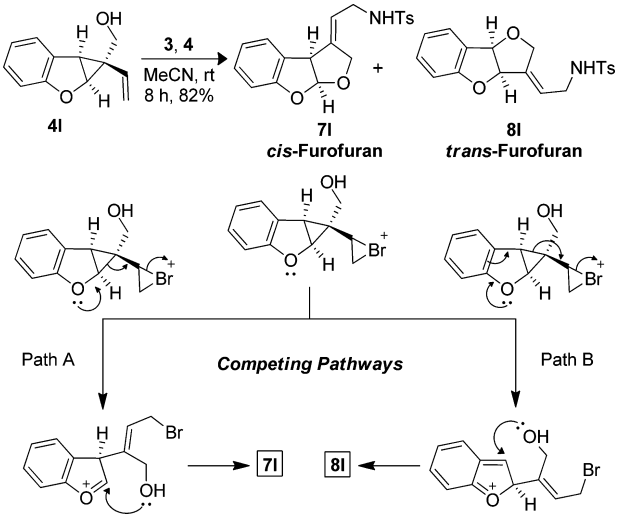
under the standard reaction condition to furnish the desired alkylidene *cis*-furopyran **7k** in 87% yield (Table 2).

This result prompted us to apply the present protocol to the synthesis of fused furotetrahydrofurans as well. Because of the synthetic challenges involved in the synthesis of dihydrotetrahydrofuran derived VCP, where a competing Cope product is obtained as the major product, we utilized the benzotetrahydrofuran derived VCP **4l**, which was obtained from the corresponding VCP ester.[82] Under the usual reaction conditions, the VCP **4l** underwent ring-opening and cyclization but led to a regioisomeric mixture of *cis*-fused furotetrahydrofuran **7l** and *trans*-fused furotetrahydrofuran **8l** derivatives (1:1, conv: 82%). The product distribution can be rationalized by the comparable stability of the incipient carbocation. The formation of bromonium ion triggers the ring-opening by two pathways, involving (i) the activation of C-2 position with the assistance of oxygen directly through an oxycarbenium species (Path A, Scheme 5)

Scheme 5. *cis*- and *trans*-Furotetrahydrofurans from Benzotetrahydrofuran Derived VCP, 4l



and (ii) the activation of C-3 position with the assistance of oxygen involving the π-electrons of the phenyl-ring through an oxycarbenium species (Path B, Scheme 5).

Next, we were interested in studying the diastereoselectivity of the cyclization step. For this, we chose **4m**, bearing a secondary alcohol in its diastereomerically pure form. Reaction of **4m** with chloramine-T and PTAB in acetonitrile at rt resulted in the formation of *Z*-alkylidenetetrahydrofuran **7m** in 87% yield and with excellent diastereoselectivity (*dr*: >95%). From 2D-NMR experiments, it was found that the attack of the hydroxyl group occurred from the same face as that of the C−C bond undergoing cleavage with retention of configuration at the phenyl-attached carbon center (Scheme 6). The retention of configuration was further confirmed by designing a VCP substrate (**4n**) bearing a spectator methyl group as a chirality marker. The reaction of **4n** under standard reaction conditions resulted in the formation of **7n** with complete retention of configuration (*dr*: >95:5). The stereochemical assignment correlated well with the results obtained from the ROESY experiment. The excellent diastereoselectivity with complete retention of configuration observed in the case of **4m** and **4n** strongly supports the existence of a tight-carbocation intermediate. Earlier reports on the solvolysis reaction of diactivated donor−acceptor cyclopropanes by Cram[83−85] and recent reports by Johnson[16,66,69] and Waser[70,73,75] on the Lewis acid mediated ring-opening of donor−acceptor (DA) cyclopropanes bearing dicarboxylate groups have shown the prevalence of a tight-carbocation−carbanion pair. The DA cyclopropane ring-opening has always resulted in inversion at the C-2 center (phenyl attached center), where the approach of the nucleophile occurred from the rear end of the tight ion-pair or epimerization (in the absence of a nucleophile). The formation of the inversion product has raised questions as to whether the reaction follows a conventional S_N2 pathway or the intermediacy of an ion-pair.[66] To date there is no direct stereochemical evidence to rule out the S_N2 pathway. In the present work, it has been shown that the product formation takes place with complete retention due to the directed approach of the nucleophile. Our work provides a direct proof for the existence of a tight-carbocation intermediate.

Subsequently, we were interested to study the reactivity of spiro-VCP lactols as nucleophiles for the construction of *cis*-furotetrahydrofuran skeleton in a diastereoselective fashion. To begin with, we synthesized the spiro-cyclopropane following Doyle's procedure (Scheme 6).[86] The lactone was subsequently reduced to the corresponding lactol using DIBAL-H/toluene to yield the spiro-VCP lactols **4o** and **4o′** as a mixture of (α- and β-hydroxy) diastereomers (1:1). The mixture of lactols was subjected to the standard reaction conditions with chloramine-T (rt, 8 h) until the disappearance of the starting material. The reaction resulted in the formation of the desired *cis*-fused furopyran **7o** and **8o** as a diastereomeric mixture (2.3:1) at -NHTs center (Scheme 6). The relative stereochemistry was determined with the help of 2D-NMR spectroscopy (COSY, HSQC, and ROESY (see the Supporting Information)). Surprisingly, the α-isomer alone was converted to the desired *cis*-furotetrahydrofuran **7o** and **8o**, whereas the β-diastereomer of the lactol **4o′** did not undergo cyclization, and it led to an intraceable mixture of compounds. The failed reactivity of β-diastereomer **4o′** in addition to the high diastereoselectivity observed in the cyclization step of α-diastereomer with retention of configuration establishes the existence of a tight-carbocation intermediate. The diastereomers **7o** and **8o** were formed because of the lack of facial selectivity in the bromination step. In the case of substituted VCP **4p**, the reaction resulted in the expected product **7p** successfully but with poor diastereoselectivity. Though the cyclization step is stereospecific, the initial bromination does not proceed with any appreciable facial selectivity.

The reaction was extended to study the reactivity of vinylcyclobutanes under similar conditions. Since the syntheses of vinylcyclobutanes are quite challenging, we decided to demonstrate the methodology on dimethyl substituted vinylcyclobutanes derived from (±)-α-pinene[87] and pinonic acid. The reactivity of vinylcyclobutanes was explored with various oxygen and nitrogen nucleophiles to effect cyclization leading to various five membered heterocycles (Table 3). Under the reaction conditions (chloramine-T, **5** (1.1 equiv); PTAB, **6** (10 mol %); MeCN; 4 h, rt) compounds **9a−c** were converted to the desired tetrahydrofurans (**10a−c**) in good yields but with poor facial selectivity, leading to a mixture of *E*- and *Z*-isomers (1:1) (Table 3).

On the basis of our observations on the reactivity of VCPs (Scheme 4), a mechanism has been proposed for the formation of **10a** from vinylcyclobutane **9a** (Scheme 7). Br−X formed in situ reacts with VCB **9a** to form VCB-π-complex. The π-complex undergoes spontaneous ring-opening/cyclization to tetrahydrofuran skeleton **V**. Intermediate **V** reacts with chloramine-T to

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Scheme 6. Diastereoselective Cyclization and Evidence for a Tight-Carbocation Intermediate

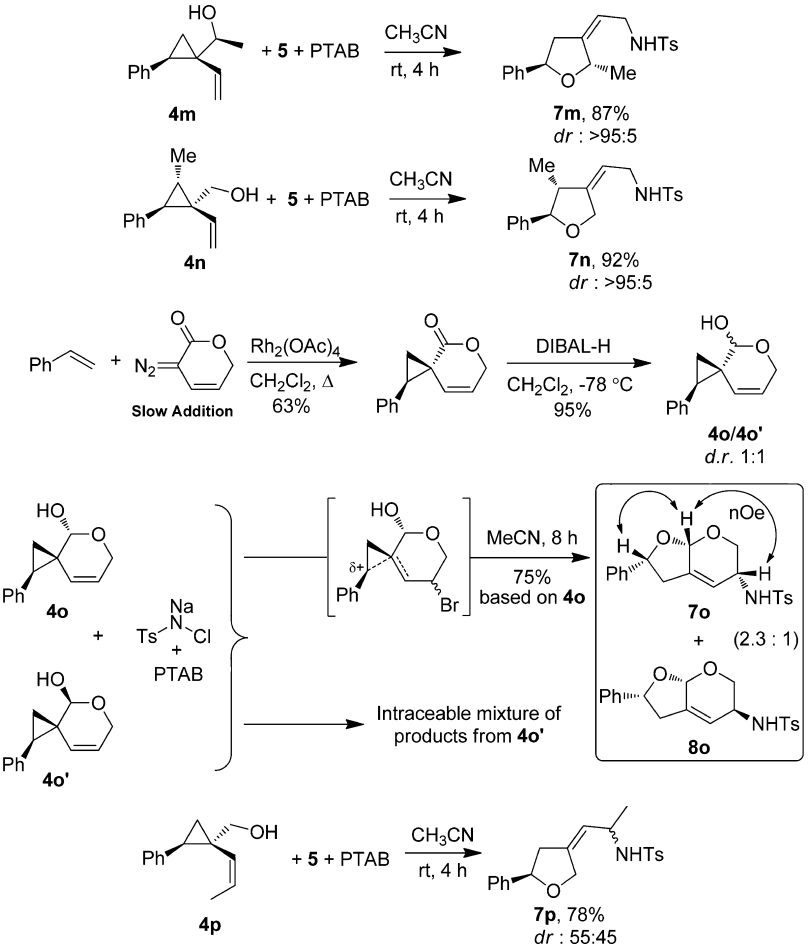
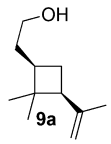
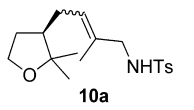
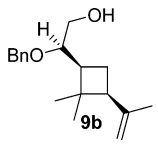
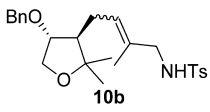
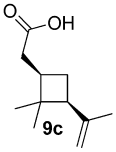
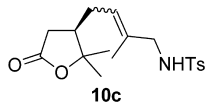
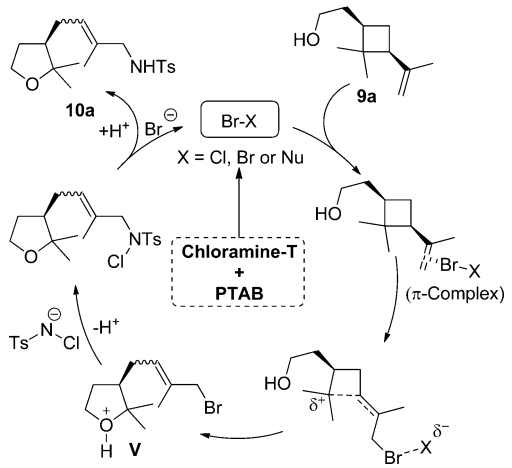


Table 3. Reactivity of Vinylcyclobutanes under Similar Reaction Conditions[a]

Entry	Reactant	Time (h)	Product	Yield
1		3		75%
2		4		76%
3		4		70%

[a]Reaction conditions: VCP (1 mmol), chloramine-T (1.1 mmol), PTAB (0.1 mmol), MeCN (5 mL), rt. Yield is of the isolated product.

Scheme 7. Proposed Mechanism for the Formation of 10a from VCB 9a



form **10a** and Br−X, which further propagates the catalytic cycle as in the case of VCPs.

***E*- and *Z*-Selectivity in the Product Formation: Computational Studies.** In order to understand the *Z*-selectivity in the product formation and to quantify the existence of a tight-carbocation, the potential energy surfaces of hydroxymethyl VCPs were mapped by varying the torsion angle of the vinyl group with respect to the cyclopropane C−C bond ($\Phi_{(C1-C3-C4-C5)}$), Scheme 8. The geometrical aspects of the unsubstituted VCPs have already been extensively studied employing gas-phase spectroscopic techniques, solution phase NMR studies, and a variety of theoretical methods as well.[88−99] However, the conformational analysis of substituted VCPs and information on the effect of substituents on the conformers are limited in the

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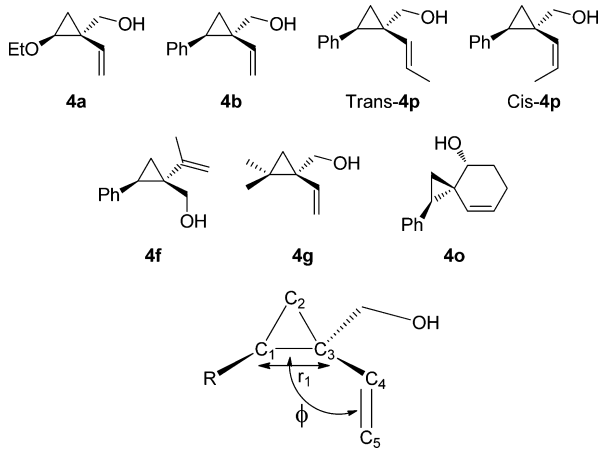
Scheme 8. VCPs Considered for Quantum Chemical Calculations



literature. Hence, we mapped the 2-D potential energy surface for a variety of VCPs that are employed in the present work (viz., **4a**, **4b**, **4f** and **4g**) at B3LYP/6-31G(d) level of theory. The overlay plot has been presented in Figure 1. The PES plots

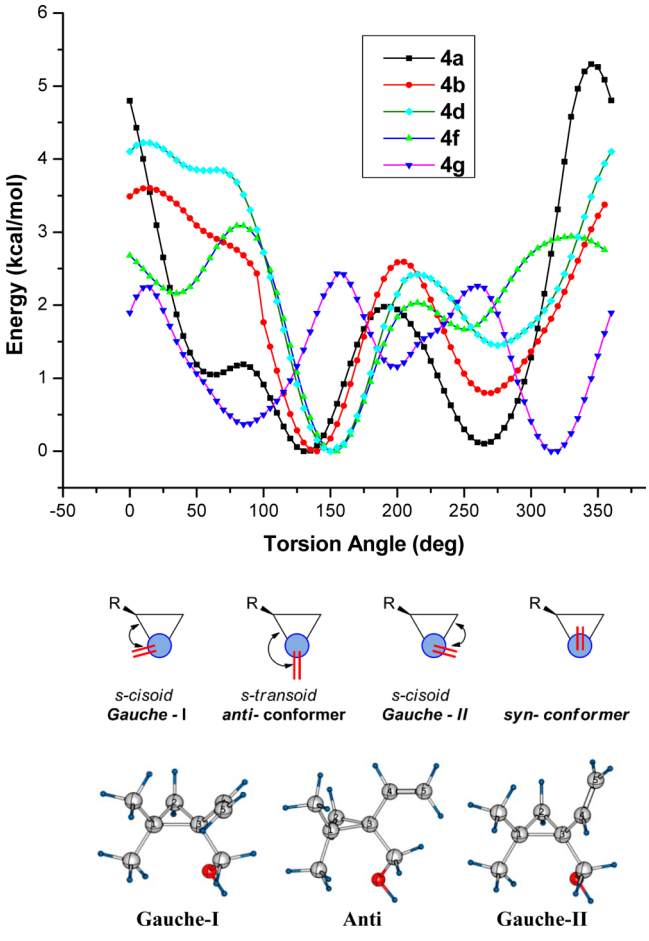


Figure 1. Overlay plot of PES for **4a**, **4b**, **4d**, **4f** and **4g**.

confirmed the existence of three minimum energy conformers (viz., *anti*, *gauche-I*, and *-II*), out of which *gauche-I* was found to be the least stable conformer in most of the cases (except for **4f**). The relative energies of the conformers obtained from the 2D-PES were used in the Boltzmann distribution equation to obtain the relative population of the three rotamers at 298.15 K.

Using the values of the dihedral angles from the plots as an initial guess, the geometry of each rotamer was optimized at M06−2X/6-31+G(d) level of theory. The harmonic frequencies and the thermodynamic parameters were also calculated at the same level of theory at 298.15 K. Our predictions show that at room temperature, hydroxymethyl VCPs **4a** and **4b** exist predominantly in the *anti*-conformation, whereas VCP **4g** exists both in the *anti* and *gauche-II* conformation in almost equal ratio. The reason for predominance of the *anti*-conformer is due to the minimized steric crowding, in addition to the stabilization gained through interaction between the C−C σ-bonds of the cyclopropane ring and π-bond of the vinyl group. The *anti*-conformer is benefitted by maximum overlap between the vinyl group and both C1−C3 and C2−C3 σ-bonds. However, this dual stabilization is absent in *gauche* conformations (entry 3 and 4; Table 4). An attempt has been made to quantify the orbital interaction energies between the vinyl group and the σ-bond of the cyclopropane for each conformer using NBO analysis. The orbital interaction energies and significant bond parameters are presented in Table 4.

Unlike other VCPs, **4f** predominantly exists in gauche conformation, and the *anti*-conformer was found to be the least stable among the three minimum energy conformers. The behavior is similar to 2-cyclopropylpropene (CPP) system, which has been studied earlier. A report on the conformational analysis of CPP system showed the *anti*-conformer to be the most stable conformer, contradicting our present results.[100] This could possibly be due to the steric repulsion experienced by the methyl group with the geminal hydroxymethyl group.

To summarize, among the hydroxymethyl VCPs studied, the population of *gauche-II* conformer is quite dominant in the case of **4f** and **4g**. Our experimental results (entry 6 and 7 of Table 2) show that compound **4f** and **4g** exhibit poor *E*-/*Z*-selectivity under the standard reaction conditions, whereas in other cases excellent *Z*-selectivity is observed. Correlating our experimental and computational results, we speculate that the loss of selectivity could be due to the increasing population of *gauche-II* conformer. In order to thoroughly understand the reason behind the loss in selectivity, we decided to study the intricate details of the mechanism, the nature of π-complex of *anti*- and *gauche-II* conformers and the respective transition states and intermediates. Since the population of *gauche-I* conformer is much less, it can be safely ignored.

The bond parameters and heat of complexation of VCP **4a**, **4b**, **4g** and **4o** with Br−Cl for *anti*- and *gauche-II* conformers on both the faces of the vinyl group have been calculated (Table 5). For VCP **4f**, the major conformers, *gauche-I* and *gauche-II* have been considered for the study. The $\Delta\Delta H$ of **4b**, **4g** and **4o**···Br−Cl in the *anti*-conformation are in the range of 1−1.5 kcal/mol. From the $\Delta\Delta H$ value of the *anti*-conformer, the *Re*-face complexation of the vinyl group is favored over *Si*-face, but the difference in ΔH between the faces is not strikingly large, suggesting that the steric bulk of the substituents on the cyclopropane ring has no major effect on the complexation. In the *gauche-II* conformation, profound facial differentiation of the vinyl group was observed because of the steric effect of substitutents on the cyclopropane ring. The $\Delta\Delta H$ values of **4a**, **4b** and **4g**···**Br−Cl** suggests that the *Si*-face complexation is strongly disfavored by 2 to >4 kcal/mol and the dihedral angle ($\Phi_{(C3-C4-C5-Br)}$) deviates as much as 30° from the usual (90 ± 10°) because of the strong steric repulsion offered by the substituents on the ring. The *Si*-face complex in

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Table 4. Bond Parameters and Orbital Interaction Energies of the Rotamers of VCPs[a]

	4a			4b			4f			4g		
VCP	A	G-I	G-II	A	G-I	G-II	A	G-I	G-II	A	G-I	G-II
r_1 (Å)[b]	1.505	1.496	1.497	1.521	1.519	1.521	1.528	1.514	1.523	1.533	1.518	1.523
Φ (deg)[b]	151.5	39.7	248.6	146.2	50.1	263.9	−159.1	−45.6	88.2	128.4	59.4	264.3
E_{rel}[b]	0	2.04	1.43	0	1.88	1.11	1.25	0	0.02	0	0.80	0.03
$NBO_{E(C1-C3)}$	3.46	–	1.73	4.10	–	3.30	3.17	–	4.35	4.17	–	3.30
$NBO_{E(C2-C3)}$	4.70	2.21	–	4.31	1.02	–	4.11	1.76	–	3.25	0.81	–
ratio (%)[b]	92	2.5	5.5	80	<1	20	8	60	32	50	8	42

[a]A = anti; G-I = gauche-I; G-II = gauche-II. [b]r_1 = bond distance of C1−C3; Φ = dihedral angle between C1−C3 and C4−C5; E_{rel} = relative energies of the conformers; ratio = relative population using Boltzmann distribution equation.

Table 5. Thermochemical and Bond Parameters of VCP···BrCl Complex

		bond distances (Å) and angles (deg)			facial selectivity in π-complex			
VCP···BrCl π-complex		$d_{(C=C\cdots Br)}$ *Si*; *Re*	$\angle_{(C4-C5-Br)}$ *Si*; *Re*	$\Phi_{(C3-C4-C5-Br)}$ *Si*; *Re*	$\Delta H_{(Si)}$	$\Delta H_{(Re)}$	$\Delta\Delta H_{(Si-Re)}$	$\Delta\Delta G_{(Si-Re)}$
4a	*Anti*	2.79; 2.80	78.8; 84.6	−89.7; 89.1	−14.9	−14.8	−0.1	−0.6
	Gauche-II	2.95; 2.81	88.3; 75.1	96.6; −89.7	−12.5	−14.2	1.6	1.1
4b	*Anti*	2.80; 2.81	77.2; 77.7	89.7; −89.3	−13.2	−14.7	1.5	1.4
	Gauche-II	–; 2.80	–; 76.6	–; −88.3	nd	−13.3	na	na
4f	*Gauche-I*	2.75; 2.79	81.3;79.8	−96.5; 100.3	−19.7	−15.1	−4.7	0.9
	Gauche-II	2.73; 2.77	79.0; 80.3	95.6; −100.2	−14.7	−15.2	0.5	1.0
4g	*Anti*	2.82; 2.85	74.4; 81.7	89.1; −77.4	−12.9	−14.0	1.1	0.0
	Gauche-II	2.99; 2.88	75.4; 78.7	121.1; −78.3	−9.6	−12.6	3.0	3.0
4o	*Anti*	2.76; 2.84	77.0; 72.0	101.1; −102.2	−14.3	−15.3	1.0	0.5

gauche-II conformation is less likely to form, and therefore, only the *Re*-complex of *gauche-II* and the *anti*-conformer were considered for our further studies. The ***Re*-4o···Br−Cl** complex showed an interesting $Br^{\delta+}\cdots Ph_{\pi}$ interaction with the centroid to bromine distance of 3.39 Å (Figure 2).

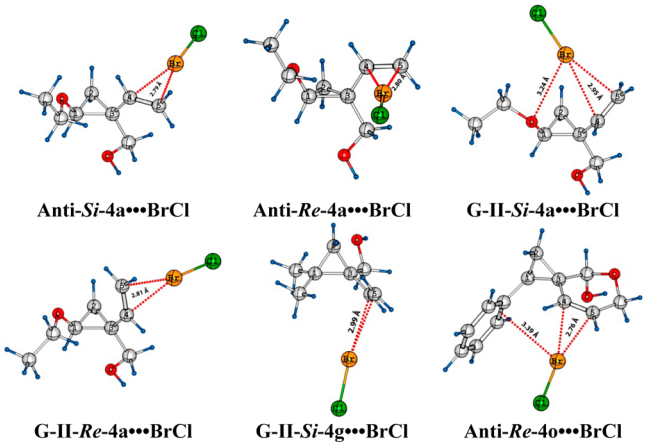

Figure 2. Energy minimized structure of VCP···BrCl complex.

The transition states involved in the ring-opening at C1−C3 from the corresponding π-complexes were then modeled. To begin with, the transition states for the ring-opening were modeled for the *Si* and *Re*-face complexes of VCP **4a** in its *anti*-conformation. The guess transition state for the ring-opening of **4a···Br−Cl** complex was obtained by scanning the interatomic distance between bromine and the vinyl group. The geometry of *Si*-face transition state, shown in Figure 3, was found to be stabilized by a cooperative hydrogen bonding network between the hydroxyl group and the chloride ion that is leaving. The elongation of the concerned cyclopropane C−C bond (C1−C3) was up to 1.58 Å, with the free energy of activation being

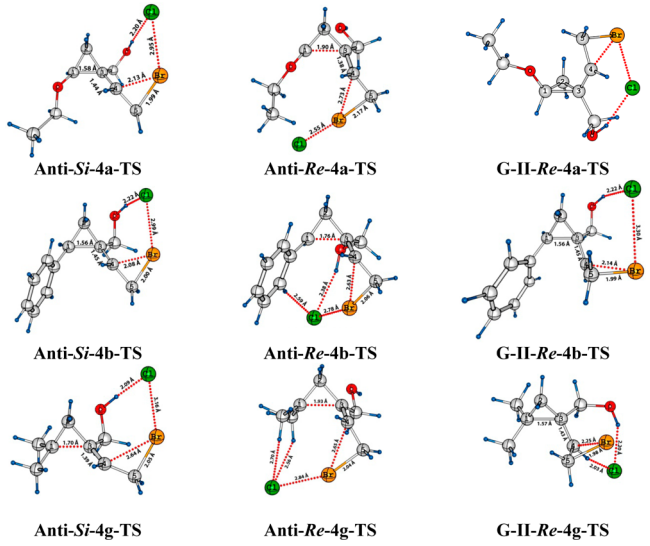

Figure 3. Ring-opening transition states of VCPs.

$\Delta G^{\ddagger}_{Si}$ = 25 kcal/mol (Table 6). The bromine atom was oriented almost symmetrically across the vinyl group. On the other hand, the *Re*-face attack of Br−Cl triggered the C−C bond cleavage to a great extent (1.90 Å) with $\Delta G^{\ddagger}_{Si}$ = 14.9 kcal/mol. Concurrently, appreciable shortening of C3−C4 bond was also observed in both *Si*- and *Re*-face transition states.

According to the Curtin−Hammett principle, if two conformers of a reactant yield two different products that are not easily interconvertible, then the product ratios are controlled by the free energies of the transition states and are independent of the population of conformers of the reactant. To explain the formation of a mixture of products in the case of **4g**, where the *anti*- and the *gauche-II* conformers are in the ratio 54:46, we compared the ring-opening transition states. Our studies show that the ring-opening transition states of ethoxy and phenyl

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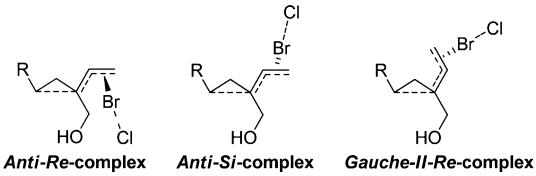
Table 6. Thermochemical and Bond Parameters of Transition State of VCP Ring-Opening



	ring-opening TS anti conformer			ring-opening TS gauche conformer		d_{C1-C3} (Å) anti	
VCP	$\Delta G^{\ddagger}_{(Si)}$	$\Delta G^{\ddagger}_{(Re)}$	$\Delta\Delta G^{\ddagger}$	$\Delta G^{\ddagger}_{(Re)}$	$\Delta\Delta G^{\ddagger}_{Re\ (gauche-anti)}$	$d_{(Si)}$	$d_{(Re)}$
4a	24.69	14.86	9.83	22.45	7.59	1.58	1.90
4b	24.16	22.43	1.73	27.96	5.56	1.56	1.76
T-4p[a]	21.39	22.01	−0.62	−[b]	−[b]	1.55	1.77
C-4p[a]	19.44	18.72	0.72	23.91	5.19	1.56	1.74
4o	27.75	8.31	19.44	n.a.[c]	n.a.[c]	1.56	2.30
4g	**23.76**	**21.05**	**2.71**	**17.44**	**-3.61**	**1.70**	**1.93**

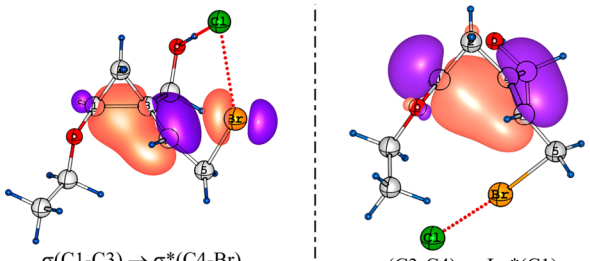
[a]**T-4p**: *trans*-4p. **C-4p**: *cis*-**4p**. [b]Experimental data not available to compare. [c]n.a. = not applicable.

substituted VCP **4a**,**b** resulting from *gauche-II* conformation are disfavored by at least ∼7.5 and ∼5.6 kcal/mol, respectively, when compared with the *anti*-conformer. This large difference in the free energy results in excellent *Z*-selectivity. On the other hand, it is reverse in the case of the ring-opening of dimethyl substituted VCP **4g**. The ring-opening resulting from *gauche-II* conformer is favored by ∼3.6 kcal/mol over *anti*-conformer. Hence, **4g** shows very poor selectivity at 298 K.

NBO and full population analysis of the transition state geometry revealed the orbital interactions involved. The HOMO and the LUMO diagrams are presented in Table 7. The *Si*-face

Table 7. NBO Interactions at the Ring-Opening Transition State of 4a

Transition State	NBO Interactions	Energy (kcal/mol)
Anti-*Si*-4a-TS	σ(C1-C3) → σ*(C4-Br)	15.2
	σ(C4-Br) → σ*(C5-Br)	27.6
	σ(C5-Br) → σ*(C4-Br)	12.5
	Lp (O6) → σ*(C1-C3)	16.5
	Lp (Cl) → σ*(O-H)	22.5
	Lp (Cl) → σ*(C5-Br)	12.9
Anti-*Re*-4a-TS	σ(C2-C3) → Lp*(C1)	54.6
	π(C3-C4) → Lp*(C1)	136.1
	σ(C5-Br) → σ*(C3-C4)	25.9
	Lp (O6) → Lp* (C1)	106.9
	Lp (Cl) → σ*(C5-Br)	64.1



σ(C1-C3) → σ*(C4-Br)
Anti-*Si*-4a-TS

π(C3-C4) → Lp*(C1)
Anti-*Re*-4a-TS

ring-opening transition state involves an overlap between the C1−C3 σ-orbital and C4−Br σ*-orbital. Similarly, the lone pair of the OEt group interacts with the σ*-orbital of C1−C3 bond facilitating the ring cleavage. The *Re*-face transition state is a late transition state favored over *Si*-face by 10 kcal/mol in free energy scale, where most of the ring-opening to a tight-carbocation has already taken place. NBO analysis predicted low electron occupancy of 0.71 in the p-orbital of carbon C3 and bears a natural charge of +0.33 C. Moreover, the Walsh-type σ-orbital between C1−C3 of the starting cyclopropane has been transformed to a simple p-orbital in the transition state with 96% p-character. This p-orbital stabilized by the lone-pair of -OEt group interacts strongly with the newly formed π-orbital of C3−C4 resulting in a tight-carbocation. Other significant orbital interactions and the corresponding energies obtained from NBO analysis are presented in Table 7. In the case of less electron-donating substituents like phenyl or *gem*-dimethyl groups, a similar trend was observed as in OEt substituted VCP, where the extent of ring-opening in *Si*-face transition state is less (∼1.55 Å) than the *Re*-face transition state (>1.70 Å). Interestingly, the *Re*-transition state of **4o** is unusually stabilized ($\Delta\Delta G^{\ddagger}$= 8.3 kcal/mol), which is probably due to the added ring strain of being a spirocyclopropane by nature. The thermodynamic parameters of the transition states are presented in Table 7.

Energy minimization of the transition state geometry to the immediate minimum leads to the tight-carbocation intermediate similar to the proposed intermediate in the mechanistic discussion (Scheme 4). On careful observation of the geometries of the tight-carbocation intermediates of VCPs **4a**, **4b**, **4p**, **4g** and **4o** (Figure 4), the configuration across the double bond solely depends on

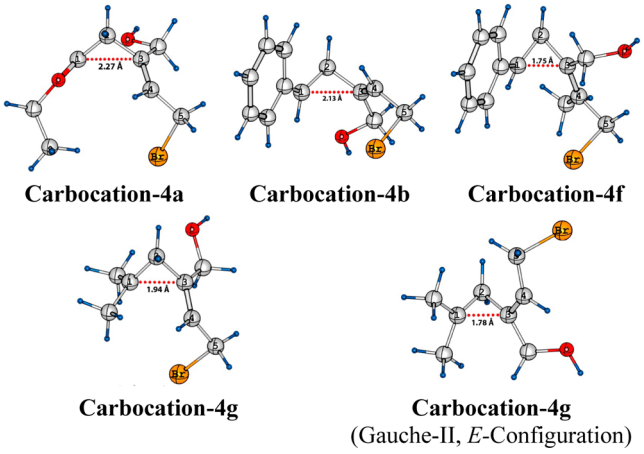


Figure 4. Tight carbocation intermediates.

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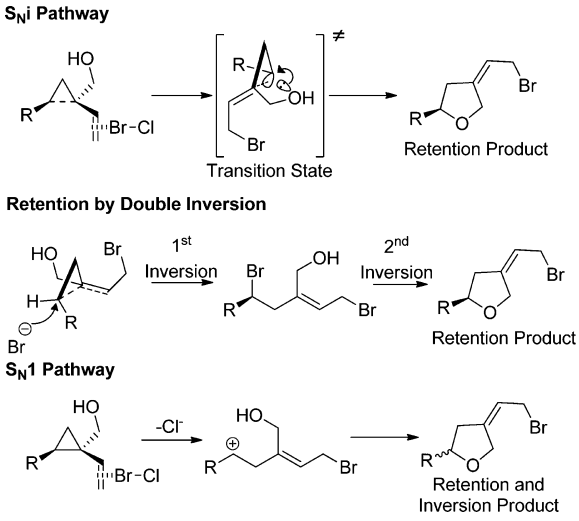
whether the conformer is *anti* or *gauche-II*. Our calculation predicts that the *anti*-conformer always leads to *Z*-product and the *gauche-II* conformer always leads to *E*-product independent of the face of attack of Br−Cl. These results directly corroborate our speculation that increase in the population of *gauche-II* is responsible for the mixture of *E*- and *Z*-products in the case of **4g** and **4f**. For the sake of curiosity, we carried out optimization of the *gauche-I* tight intermediate to study the configuration across the double bond. The resultant configuration across the double bond was found to be *Z*- across C3−C4, which is the reverse of *gauche-II* as expected.

Tight Carbocation and Retention of Configuration during Cyclization. To justify our speculation that a tight-carbocation intermediate is responsible for retention of configuration, the energy profiles of the possible pathways leading to the desired product need to be compared. We propose three possible pathways for the cyclization to happen from the tight-carbocation intermediate: (1) internal nucleophilic substitution (S_Ni) pathway, (2) nucleophilic double displacement pathway, and (3) S_N1 pathway by complete cleavage of C1−C3 bond

Out of the three possible pathways, S_Ni and double displacement pathway can lead to the product with retention of configuration, whereas S_N1 pathway will lead to a mixture of products.

The S_Ni pathway involves the attack of the hydroxyl group on to the tight-carbocation at C1 from the same face as that of the C1−C3 bond as the approach of the nucleophile is directed because of the short-chain length leading to retention of configuration at C1 center (Scheme 9). In the double displacement pathway, an external nucleophile that can act as a good leaving group as well gets involved in a nucleophile assisted ring-opening at C1, followed by the second attack by the hydroxyl group resulting in the desired product. Even in this case the configuration at C1 center is retained, since both the steps are stereospecific in nature. However, in the case of S_N1 pathway, the reaction follows a "barrier-free two-step" process, involving a complete cleavage C1−C3 bond to enable a free rotation of C1−C2 σ-bond, resulting in the formation of a free-carbocation at the C1 center, which can be energy demanding. The energy of the free-carbocation was calculated by freezing the torsion angles C1−C2−C3−C4 at 180° and H−C1−C2−C3 at 0° of the intermediate.

Scheme 9. Plausible Pathways for Cyclization



The transition state energies for cyclization through various pathways have been modeled (Figure 5), and the thermodynamic parameters are compared in Table 8 and Figure 6. The present level of theory predicts the lowest energy barrier for the

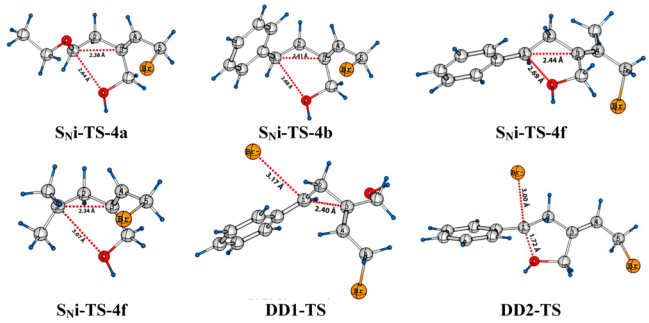


Figure 5. Transition states for S_Ni and double displacement pathways.

Table 8. Thermochemical Parameters for the Cyclization Transition State

	S_Ni vs S_N1		
ring-opened intermediate	$\Delta G^{\ddagger}$ (S_Ni)	ΔG (S_N1)	$d_{(C1-O)}$ Å
4a	0.6	6.3	2.64
4b	2.2	16.6	2.68
4f	3.5	10.9	2.69
4g	3.6	13.9	3.07

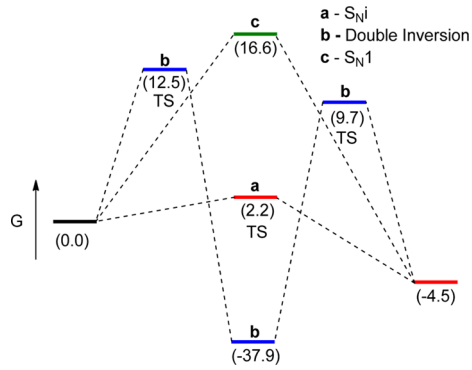


Figure 6. Comparison of energy profiles of various cyclization pathways for **4b**.

S_Ni pathway (0.5−3.5 kcal/mol). In the case of double-displacement pathway, the attack of bromide on C1 center of the tight-carbocation is of the order of 12.5 kcal/mol, which is at least 3-fold higher than the S_Ni pathway. Formation of free carbocation through S_N1 pathway is far more energy demanding than the other two processes. Our models show that the reaction could proceed through an S_Ni pathway preferentially and the cyclization step is stereospecific.

CONCLUSION

In conclusion, a highly diastereoselective one-step protocol for the synthesis of *Z*-alkylidenetetrahydrofurans from a variety of vinylcyclopropanes has been demonstrated. The present work provides direct stereochemical evidence for the existence of a tight ion-pair in the Lewis acid mediated ring-opening of donor−acceptor cyclopropanes. As in the case of DA cyclopropanes, the ring-opening/cyclization process is observed to be stereospecific.

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A plausible mechanism has been presented explaining the *Z*-selectivity observed during the product formation. Since the *anti*-conformer is naturally an s-transiod conformer, the attack of Br−Cl on either face of the double bond (*Si*/*Re*-face) would result in the product with *Z*-geometry. With the *gauche-II* conformer being an s-cisoid conformer in relation to the C1−C3 bond, the attack of Br−Cl on the double bond will lead to the other stereoisomer (*E*-isomer). The methodology has been applied successfully for the construction of polycyclic tetrahydrofuran derivatives bearing multiple chiral centers. The interesting reactivity of benzofuran derived VCP leading to *cis*-furotetrahydrofuran and *trans*-furotetrahydrofuran has been explained. In the case of substituted VCPs, though excellent diastereoselectivity has been observed in the cyclization, our efforts to realize the facial discrimination of the vinyl group during the initial bromination were unsuccessful. A thorough insight into the mechanism of ring-opening/cyclization and the stereocontrol observed has been explained with the help of quantum chemical calculations. The methodology has been extended to vinylcyclobutanes as well.

EXPERIMENTAL SECTION

General Information. All solvents for routine isolation of products and chromatography were reagent grade and redistilled. Acetonitrile and DCM used for the reaction were dried under reflux over CaH_2 and stored over 3 Å molecular sieves. Flash chromatography was performed using silica gel (230−400 mesh) with hexanes and ethyl acetate as eluent. All reactions were monitored by thin-layer chromatography on 0.25 mm silica plates (F-254) visualizing with UV light and developed using phosphomolybdate or vanillin solution. ^{1}H, ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer and are described as chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz (Hz), and number of protons. HRMS were measured with electrospray ionization (ESI) and quadrupolar mass analyzer.

Computational Methods. All calculations were performed using density functional theory (DFT) with the help of Gaussian 09 program.[101] The natural bonding orbital (NBO) interactions have been studied using NBO3.1 program. The potential energy surface (PES) was mapped for hydroxymethyl VCPs by performing a relaxed scan along the torsion angle of cyclopropane C−C bond and the vinyl group at B3LYP/6-31G* level of theory.[102,103] The geometries of all the stationary states were optimized using hybrid meta-generalized gradient approximation (meta-GGA) functional using M06−2X developed by Truhlar and Zhao, which has been widely implemented in modeling intermediates, and transition states involved in organic reactions.[104] The thermochemical parameters of the vinylcyclopropane−BrCl complexes were calculated using split-valence double-ζ M06−2X/6-31+G(d) level at 298.15 K. Harmonic frequencies were calculated at the same level of theory to characterize the intermediates and transition states. The transition states for the ring-opening reaction were also modeled at M06−2X/6-31+G(d) level. The guess geometries of the transition states were obtained by scanning through the bond distances of the atoms involved in the reaction site. All the geometry optimizations that were carried out were fully optimized to the minimum other than the free carbocations modeled in Table 8.

Procedure for NBS Mediated Solvolysis Reaction. To a stirred solution of VCP (0.5 mmol, 1 equiv) in MeOH (3 mL) at 0 °C was added NBS (0.55 mmol, 1.1 equiv). After the addition, the reaction mixture was allowed to warm to room temperature, and solid NaN_3 (0.75 mmol, 1.5 equiv) was added followed by a catalytic amount of pyridinium bromide (0.05 mmol, 0.1 equiv). The progress of the reaction was monitored by TLC. After complete consumption of the starting material, the reaction mixture was concentrated in vacuo. The residue was then washed with water and extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product provided the corresponding azide in its pure form (**2a**−**2e**).

(*E*)-5-Azido-1-methoxy-1-phenylpent-3-ene (2a). According to the general procedure for NBS mediated reaction, **2a** was formed in 68% yield (0.043 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.042 g of **1a**:[75] R_f = 0.4 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 3030, 2983, 2933, 2824, 2101, 1452, 1240, 1103, 971, 759, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.39−7.26 (m, 5H), 5.77−5.67 (m, 1H), 5.59−5.49 (m, 1H), 4.16 (dd, *J* = 5.7 Hz, 7.3 Hz, 1H), 3.68 (d, *J* = 3.6 Hz, 1H), 3.22−3.20 (m, 1H), 3.22 (s, 3H), 2.66−2.51 (m, 1H), 2.48−2.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.3, 132.6, 128.4, 127.7, 126.6, 125.3, 83.5, 56.8, 52.7, 40.9; HRMS *m*/*z* calcd for $C_{12}H_{15}N_3O$ [M + Na$^+$] 240.1113, found 240.1122.

(*E*)-5-Azido-1-methoxy-1-methyl-1-phenylpent-3-ene (2b). According to the general procedure for NBS mediated reaction, **2b** was formed in 71% yield (0.028 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.027 g of **1b**:[76,77] R_f = 0.4 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 3034, 2980, 2936, 2826, 2097, 1446, 1072, 975, 763, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.36−7.33 (m, 4H), 7.28−7.25 (m, 1H), 5.63−5.58 (m, 1H), 5.54−5.49 (m, 1H), 3.66 (d, *J* = 6.4 Hz, 2H), 3.08 (s, 3H), 2.54 (ddd, *J* = 6.4 Hz, 17.6 Hz, 24.0 Hz, 2H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.3, 132.0, 128.2, 127.0, 126.2, 126.2, 78.5, 52.7, 50.6, 45.8, 22.6; HRMS *m*/*z* calcd for $C_{13}H_{17}N_3O$ [M + Na$^+$] 254.1269, found 254.1261.

(*Z*)-Ethyl 4-azido-2-(2-ethoxy-2-methoxyethyl)but-2-enoate (2c). According to the general procedure for NBS mediated reaction, **2c** was formed in 65% yield (0.035 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.039 g of **1c**:[78] R_f = 0.4 (hexanes/EtOAc, 8:2); IR (neat) $\bar{\nu}$ 3030, 2983, 2933,2824, 2102, 1452, 1252, 1080, 968, 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 6.85 (dd, *J* = 6.4 Hz, 6.4 Hz, 1H), 4.45 (dd, *J* = 5.6 Hz, 1H), 4.23 (dd, *J* = 7.2 Hz, 14.6 Hz, 2H), 4.07 (ddd, *J* = 7.2 Hz, 14.4 Hz, 16.8 Hz, 2H), 3.70−3.65 (m, 1H), 3.52−3.48 (m, 1H), 3.35 (s, 3H), 2.64 (d, *J* = 13.6 Hz, 2H), 1.32 (t, *J* = 5.2 Hz, 3H), 1.19 (t, *J* = 5.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.8, 137.4, 130.5, 03.4, 63.1, 61.0, 54.4, 49.6, 32.2, 15.1, 14.1; HRMS *m*/*z* calcd for $C_{11}H_{19}N_3O_4$ [M + Na$^+$] 280.1273, found 280.1274.

(*S*)-1-(Azidomethyl)-4-(2-methoxypropan-2-yl)cyclohex-1-ene (2d). According to the general procedure for NBS mediated reaction, **2d** was formed in 67% yield (0.043 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.042 g of **1d**: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 2971, 2936, 2100, 1457, 1257, 1077, 897 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.74−5.73 (m, 1H), 3.65 (dd, *J* = 24 Hz, 27.6 Hz, 2H), 3.19 (s, 3H), 2.11−2.07 (m, 3H), 1.96−1.85 (m, 2H), 1.81−1.86 (m, 1H), 1.25−1.16 (m, 1H), 1.12 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 132.4, 126.8, 76.5, 57.4, 48.8, 41.6, 27.7, 26.6, 23.5, 22.2, 21.9; HRMS *m*/*z* calcd for $C_{11}H_{19}N_3O$ [M + Na$^+$] 232.1426, found 232.1426.

(4*S*,5*S*,6*R*)-6-Azido-5-methoxy-4-(2-methoxypropan-2-yl)-1-methylcyclohex-1-ene (2e). According to the general procedure for NBS mediated reaction, **2e** was formed in 60% yield (0.036 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.042 g of **1e**: R_f = 0.3 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 2974, 2936, 2825,2099, 1450, 1255, 1090, 880 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.86 (dd, *J* = 1.5 Hz, 3.3 Hz, 1H), 3.69−3.83 (m, 2H), 3.37 (s, 3H), 2.98 (s, 3H), 2.01−1.93 (m, 1H), 1.84−1.81 (m, 5H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 128.3, 127.5, 78.2, 75.9, 61.1, 57.3, 48.6, 40.3, 23.9, 23.0, 22.9, 21.8; HRMS *m*/*z* calcd for $C_{12}H_{21}N_3O_2$ [M + Na$^+$] 262.1531, found 262.1525.

General Procedure for Reduction with $LiAlH_4$ (Procedure A). To a stirred suspension of $LiAlH_4$ (0.114 g, 3 mmol, 1 equiv) in THF (5 mL) at 0 °C was added dropwise a solution of the vinylcyclopropane ester (3 mmol, 1 equiv) in THF (2 mL). After the reaction mixture was warmed to room temperature while stirring for 3 h, it was quenched by the addition of EtOAc at 0 °C, followed by the treatment of sat. citric acid solution. The mixture was extracted with EtOAc (2 × 20 mL), and the organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product provided the alcohol in its pure form.

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((1*S,2*S**)-2-Ethoxy-1-vinylcyclopropyl)methanol (4a).** According to the general procedure A, **4a** was formed in 92% yield (0.071 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.042 g of **3**: R_f = 0.5 (hexanes/EtOAc, 8:2); nature, liquid; yield, 92%; IR (neat) $\overline{\nu}$ 3398, 2946, 2839, 1640, 1037, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 5.75 (dd, J = 11.2 Hz, 18.0 Hz, 1H), 5.25 (d, J = 17.6 Hz, 1H), 5.17 (d, J = 11.2 Hz, 1H), 3.56−3.48 (m, 4H), 3.33 (dd, J = 4.0 Hz, 6.0 Hz, 1H), 2.48 (s, 1H), 1.18 (t, J = 6.8 Hz, 3H), 0.99−0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.2, 113.3, 66.4, 65.3, 62.6, 30.5, 18.1, 14.9; HRMS m/z calcd for $C_8H_{14}O_2$ [M + Na^+] 165.0891, found 165.0891.

(*Z*)-4-(2-Azidoethylidene)-2-ethoxytetrahydrofuran (7). According to the general procedure for NBS mediated reaction, **7** was formed in 60% yield (0.042 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.054 g of **4a**: R_f = 0.6 (hexanes/EtOAc, 9:1); IR (neat) $\overline{\nu}$ 2971, 2976, 2931, 2868, 2109, 1098, 1050, 1031, 929, 878 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 5.54−5.47 (m, 1H), 5.28 (dd, J = 6.4 Hz, 26.5 Hz, 1H), 4.46−4.42 (m, 2H), 3.81−3.69 (m, 3H), 3.69−3.43 (m, 1H), 2.81−2.54 (m, 2H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.3, 113.9, 102.8, 69.0, 66.6, 49.5, 36.3, 15.2; HRMS m/z calcd for $C_8H_{13}N_3O_2$ [M + Na^+] 206.0905, found 206.0905.

General Procedure for the Conversion of VCPs to *Z*-Alkylidenetetrahydrofurans (Procedure B). To a stirred solution of VCP (0.5 mmol, 1 equiv) in MeCN (3 mL) at rt was added solid chloramine-T (0.155 g, 1.1 mmol, 1.1 equiv) and phenyltrimethylammonium tribromide (PTAB, 0.019 g, 0.1 mmol, 0.1 equiv). The reaction was monitored by TLC. After complete conversion of the starting material and the intermediate bromide, the reaction mixture was concentrated in vacuo and then washed with water (10 mL) and extracted with DCM (2 × 10 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product afforded the alkylidene furan in its pure form.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2-ethoxytetrahydrofuran (7a).** According to the general procedure A, **7a** was formed in 92% yield (0.023 g) as a liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.012 g of **4a**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\overline{\nu}$ 3270, 2931, 2864, 1326, 1159, 1092, 815, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.74 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.26−5.21 (m, 1H), 5.15 (d, J = 6.4 Hz, 1H), 4.58 (t, J = 5.7 Hz, 1H), 4.30 (s, 2H), 3.74−3.69 (m, 1H), 3.50−3.41 (m, 3H), 2.63−2.57 (m, 1H), 2.44−2.40 (m, 1H), 2.44 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.5, 129.7, 127.2, 126.5, 115.3, 102.7, 66.4, 62.6, 42.3, 39.3, 21.5, 15.1; HRMS m/z calcd for $C_{15}H_{21}NO_4S$ [M + Na^+] 334.1089, found 334.1093.

General Procedure for TBS-Protection (Procedure C). To a stirred solution of alcohol **A** (1 mmol, 1 equiv) in DMF (6 mL) was added solid imidazole (0.136 g, 2 mmol, 2 equiv) at rt. The reaction mixture was cooled to 0 °C, and TBS-Cl (0.180 g, 1.2 mmol, 1.2 equiv) was added. The reaction was monitored by TLC. After complete conversion of the starting material, the reaction mixture was washed with water (20 mL) and extracted with ether (2 × 20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product afforded the TBS-protected alcohol **B** in its pure form.

General Procedure for Ozonolysis Followed by the Wittig Reaction (Procedure D). (a) To a stirred solution of TBS-protected alcohol **B** (1 mmol, 1 equiv) in DCM:MeOH (4:1, 5 mL) was added a pinch of solid $NaHCO_3$. The reaction mixture was cooled to −78 °C, and ozone/oxygen mixture was bubbled until the blue color persists. Then oxygen was bubbled for additional 5 min to remove excess dissolved ozone. The mixture was quenched by adding dimethyl sulfide (1 mL) when cold. The reaction mixture was concentrated followed by filtering through short silica column and gave a crude mixture of aldehyde **C**. The crude mixture was carried over further without characterization. (b) To a stirred supension of triphenylmethylphosphonium iodide (2.5 mmol, 2.0 equiv) in THF (3 mL) at 0 °C was added dropwise a 1.6 M solution of *n*-BuLi in THF (2 mmol, 1.5 equiv), and the solution turned orange. The formed ylide was stirred for 15 min and added to a cold solution of the crude aldehyde (1 mmol, 1 equiv) obtained after ozonolysis in THF (3 mL). The reaction was monitored using TLC. After complete consumption of the aldehyde, the reaction was quenched with water and extracted with Et_2O (2 × 15 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product furnished the corresponding alkene **D**.

General Procedure for TBS-Deprotection (Procedure E). To a stirred solution of alkene D (1 mmol, 1 equiv) in THF (6 mL) was added a 1 M solution of TBAF (1.5 mL, 1.5 mmol, 1.5 equiv) in THF at 0 °C. The reaction was monitored by TLC. After complete conversion of the starting material, the reaction mixture was washed with water (20 mL) and extracted with DCM (2 × 20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product afforded the desired VCP methanol in its pure form.

(1*R,2*R**)-Methyl 2-phenyl-1-vinylcyclopropanecarboxylate (4bB): Procedure D.** The VCP ester **4bB** was prepared from the corresponding phenyl sustituted VCP ester[78] through an ozonolysis−Wittig sequence. According to the general procedure D, **4bB** was formed in 76% yield (0.080 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.145 g of the corresponding ester: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\overline{\nu}$ 3027, 2952, 1723, 1436, 1269, 1146, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.28−7.19 (m, 3H), 7.11−7.08 (m, 2H), 5.82 (dd, J = 10.8 Hz, 17.4 Hz, 1H), 5.08−4.93 (m, 2H), 3.75 (s, 3H), 2.97 (dd, J = 7.5 Hz, 9 Hz, 1H), 1.90−1.85 (m, 1H), 1.71 (dd, J = 5.1 Hz, 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.6, 135.9, 132.1, 129.8, 129.3, 128.4, 127.3, 118.1, 52.9, 35.1, 34.2, 17.7; HRMS m/z calcd for $C_{13}H_{14}O_2$ [M + Na^+] 225.0891, found 225.0888.

((1*R,2*R**)-2-Phenyl-1-vinylcyclopropyl)methanol (4b): Procedure A.** According to the general procedure A, **4b** was formed in 95% yield (0.065 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.080 g of **4bB**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\overline{\nu}$ 3398, 3020, 2928, 1472, 716, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.30−7.25 (m, 2H), 7.20−7.15 (m, 3H), 5.32−5.13 (m, 2H), 5.04−5.01 (m, 1H), 3.81 (d, J = 11.1 Hz, 1H), 3.70 (d, J = 11.4 Hz, 1H), 2.34 (dd, J = 6.6 Hz, 8.4 Hz, 1H), 1.64 (s, 1H), 1.31−1.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 138.2, 137.9, 129.6, 128.5, 126.7, 115.4, 68.7, 33.0, 29.4, 16.6; HRMS m/z calcd for $C_{12}H_{14}O$ [M + Na^+] 197.0942, found 197.0945.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2-phenyltetrahydrofuran (7b): Procedure B.** According to the general procedure B, **7b** was formed in 88% yield (0.113 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.065 g of **4b**: R_f = 0.5 (hexanes/EtOAc, 6:4); IR (neat) $\overline{\nu}$ 3277, 2921, 2853, 1598, 1451, 1325, 1157, 1043, 700, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.75 (d, J = 8.4 Hz, 2H), 7.34−7.29 (m, 7H), 5.30−5.23 (m, 1H), 4.85 (dd, J = 6.3 Hz, 12 Hz, 1H), 4.56−4.48 (m, 2H), 4.32−4.26 (m, 1H), 3.50 (dd, J = 0.3 Hz, 8 Hz, 2H), 2.86 (ddd, J = 0.9 Hz, 6.4 Hz, 15.6 Hz, 1H), 2.5−2.43 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.3, 144.1, 141.6, 137.3, 130.2, 128.9, 128.2, 127.7, 126.3, 115.4, 80.9, 69.0, 425.5, 41.5, 22.0; HRMS m/z calcd for $C_{19}H_{21}NO_3S$ [M + Na^+] 366.1104, found 366.1107.

((1*R,2*R**)-2-Methyl-2-phenyl-1-((*E*)-styryl)cyclopropyl)methanol (4cA): Procedure A.** According to the general procedure A, **4cA** was formed in 87% yield (0.112 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.150 g of corresponding ester: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\overline{\nu}$ 3387, 3013, 2928, 2953, 1512, 1463, 770, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.28−7.05 (m, 8H), 7.00 (d, J = 7.6 Hz, 2H), 6.45 (d, J = 16.4 Hz, 1H), 5.43 (d, J = 16.4 Hz, 1H), 4.17 (d, J = 12 Hz, 1H), 3.92 (d, J = 12 Hz, 1H), 1.76 (s, 1H), 1.56 (s, 3H), 1.43 (d, J = 9.2 Hz, 1H), 1.05 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.1, 136.7, 132.3, 128.3, 127.4, 127.3, 126.5, 125.8, 125.3, 124.8, 63.9, 33.2, 24.3, 23.0; HRMS m/z calcd for $C_{19}H_{20}O$ [M + Na^+] 287.1412, found 287.1403.

***O*-*tert*-Butyldimethylsilyl-((1*R**,2*R**)-2-methyl-2-phenyl-1-((*E*)-styryl)cyclopropyl)methanol (4cB): Procedure C.** According to the general procedure C, **4cB** was formed in 90% yield (0.145 g) as a gummy liquid after flash column chromatography using silica gel

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(hexanes/EtOAc, 9:1) from 0.112 g of **4ca**: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.21−7.20 (m, 4H), 7.12−7.09 (m, 3H), 7.01 (m, 1H), 6.95 (d, J = 7.2 Hz, 2H), 6.36 (d, J = 16 Hz, 1H), 5.46 (d, J = 16 Hz, 1H), 4.22 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 1.51 (s, 3H), 1.33 (d, J = 4.8 Hz, 1H), 0.94 (s, 9H), 0.92−0.84 (m, 1H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.4, 138.9, 135.1, 130.0, 128.9, 128.7, 127.5, 126.9, 126.5, 126.2, 66.0, 34.4, 34.1, 26.5, 25.5, 24.9, 18.8, −4.8; HRMS m/z calcd for $C_{25}H_{34}OSi$ [M + Na^+] 401.2277, found 401.2259.

***O*-*tert*-Butyldimethylsilyl-((1*R**,2*R**)-2-methyl-2-phenyl-1-vinylcyclopropyl)methanol (4cD): Procedure D.** According to the general procedure D, **4cD** was formed in 73% yield (0.085 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.145 g of **4cB**: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.28−7.14 (m, 5H), 5.17 (dd, J = 10.4 Hz, 17.3 Hz, 1H), 4.94 (dd, J = 1.6 Hz, 17.3 Hz, 1H), 4.74 (dd, J = 1.6 Hz, 10.8 Hz, 1H), 4.15 (d, J = 10.8 Hz, 1H), 3.64 (d, J = 10.8 Hz, 1H), 1.50 (s, 3H), 1.28 (d, J = 5.2 Hz, 1H), 0.95 (s, 9H), 0.86 (d, J = 5.2 Hz, 1H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.9, 141.3, 129.3, 128.0, 125.8, 111.6, 65.2, 33.9, 33.1, 25.9, 24.1, 23.6, 18.2, −5.5; HRMS m/z calcd for $C_{19}H_{30}OSi$ [M + Na^+] 325.1964, found 325.1959.

((1*R,2*R**)-2-Methyl-2-phenyl-1-vinylcyclopropyl)methanol (4c): Procedure E.** According to the general procedure E, **4c** was formed in 92% yield (0.048 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.085 g of **4cD**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3398, 3020, 2928, 1472, 716, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.21−7.20 (m, 2H), 7.19−7.17 (m, 3H), 5.09 (d, J = 4.4 Hz, 2H), 4.88 (dd, J = 1.3 Hz, 4.4 Hz, 1H), 4.10 (d, J = 9.6 Hz, 1H), 3.88 (d, J = 9.6 Hz, 1H), 1.77 (s, 1H), 1.55 (s, 3H), 1.36 (d, J = 4 Hz, 1 H), 0.99 (d, J = 4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.1, 140.6, 129.2, 128.2, 127.5, 126.1, 112.4, 64.4, 34.5, 33.6, 24.4, 23.8, 20.6; HRMS m/z calcd for $C_{13}H_{16}O$ [M + Na^+] 211.1099, found 211.1094.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2-methyl-2-phenyltetrahydrofuran (7c): Procedure B.** According to the general procedure B, **7c** was formed in 90% yield (0.083 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.048 g of **4c**: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3285, 2927, 2839, 1449, 1333, 1162, 1043, 771, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (d, J = 8 Hz, 2H), 7.34−7.23 (m, 7H), 5.18 (bs, 1H), 4.64 (t, J = 7.2 Hz, 1H), 4.32 (dd, J = 16 Hz, 44 Hz, 2H), 3.40 (d, J = 5 Hz, 2H), 2.73 (dd, J = 16 Hz, 44 Hz, 2H), 2.41 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.5, 144.0, 137.3, 130.2, 128.9, 127.6, 127.3, 126.1, 125.2, 115.4, 84.7, 67.7, 46.2, 42.4, 29.5, 22.0; HRMS m/z calcd for $C_{20}H_{23}NO_3S$ [M + Na^+] 380.1296, found 380.1293.

(*R,*E*)-(2,2-Diphenyl-1-styrylcyclopropyl)methanol (4dA): Procedure A.** According to the general procedure A, **4dA** was formed in 88% yield (0.136 g) as a colorless solid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.175 g of the corresponding ester: R_f = 0.4 (hexanes/EtOAc, 8:2); mp 92 °C; IR (neat) $\bar{\nu}$ 3393, 3057, 3024, 2927, 1493, 1020, 748, 706, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.40−7.36 (m, 4H), 7.19−7.04 (m, 11H), 6.55 (d, J = 15.2 Hz, 1H), 3.68 (d, J = 11.7 Hz, 1H), 3.43 (d, J = 11.7 Hz, 1H), 1.99 (s, 1H), 1.73−1.71 (m, 1H), 1.56 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.6, 142.4, 137.4, 132.1, 130.1, 128.9, 128.4, 128.2, 128.0, 126.7, 126.4, 126.2, 125.7, 65.2, 44.1, 34.7, 23.7; HRMS m/z calcd for $C_{24}H_{22}O$ [M + Na^+] 349.1568, found 349.1564.

(*R,*E*)-*O*-*tert*-Butyldimethylsilyl(2,2-diphenyl-1-styrylcyclopropyl)methane (4dB): Procedure C.** According to the general procedure C, **4dB** was formed in 93% yield (0.171 g) as a gummy liquid after flash column chromatography using silica gel (hexanes) from 0.136 g of **4dA**: R_f = 0.5 (hexanes); IR (neat) $\bar{\nu}$ 2953, 2928, 2856, 1493, 1255, 1079, 836, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.46 (d, J = 9.2 Hz, 2H), 7.40 (d, J = 33.6 Hz, 2H), 7.24−6.96 (m, 11H), 6.48 (d, J = 21.6 Hz, 1H), 5.82 (d, J = 21.6 Hz, 1H), 3.80 (d, J = 14.0 Hz, 1H), 3.23 (d, J = 14.0 Hz, 1H), 1.53 (dd, J = 6.8 Hz, 11.6 Hz, 2H), 0.86 (s, 9H), 0.29 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.0, 144.6, 139.9, 134.5, 132.0, 131.5, 130.1, 129.8, 128.2, 127.9, 127.4, 67.4, 46.3, 36.4, 28.6, 27.7, 24.9, 20.0, −3.9, −4.0; HRMS m/z calcd for $C_{30}H_{36}OSi$ [M + Na^+] 463.2433, found 463.2434.

(*R)-1-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2,2-diphenylcyclopropanecarbaldehyde (4dC): Procedure D.** R_f = 0.5 (hexanes/EtOAc, 19:1); nature, crude; ^{1}H NMR (400 MHz, $CDCl_3$) 9.07 (s, 1H), 7.54 (d, J = 1.6 Hz, 2H), 7.52 (d, J = 1.2 Hz, 2H), 7.45−7.28 (m, 4H), 7.24−7.21 (m, 2H), 3.82 (d, J = 10.8 Hz, 1H), 3.73 (d, J = 10.8 Hz, 1H), 2.17 (d, J = 5.2 Hz, 1H), 2.01 (d, J = 5.2 Hz, 1H), 0.90 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 200.3, 141.1, 140.9, 129.6, 129.3, 128.7, 128.4, 127.1, 127.0, 60.4, 46.6, 43.4, 25.9, 21.3, 18.2, −5.66.

(*R)-*O*-*tert*-Butyldimethylsilyl-(2,2-diphenyl-1-vinylcyclopropyl)methanol (4dD).** According to the general procedure D, **4dD** was formed in 78% yield (0.110 g) as a gummy liquid after flash column chromatography using silica gel (hexanes) from 0.171 g of **4dB**: R_f = 0.5 (hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) 7.69−7.66 (m, 2H), 7.54−7.51 (m, 2H), 7.40−7.33 (m, 4*H*), 7.29−7.23 (m, 2H), 5.75 (dd, J = 10.8 Hz, 19.4 Hz, 1H), 5.20 (dd, J = 1.5 Hz, 17.4 Hz, 1H), 5.07 (dd, J = 1.5 Hz, 10.8 Hz, 1H), 3.90 (d, J = 10.4 Hz, 1H), 3.90 (d, J = 10.4 Hz, 1H), 3.39 (d, J = 10.4 Hz, 1H), 1.68 (d, J = 5.1 Hz, 1H), 1.05 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.3, 143.1, 139.7, 130.2, 129.8, 128.1, 126.2, 126.0, 113.3, 65.7, 44.2, 35.1, 25.9, 21.8, 18.3, −5.7, −5.8; HRMS m/z calcd for $C_{24}H_{32}OSi$ [M + Na^+] 387.2120, found 387.2127.

(*R)-(2,2-Diphenyl-1-vinylcyclopropyl)methanol (4d): Procedure E.** According to the general procedure E, **4d** was formed in 93% yield (0.070 g) as a gummy liquid after flash column chromatography using silica gel (hexanes) from 0.110 g of **4dB**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3381, 3056, 3024, 2921, 1447, 1154, 1033, 706, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.45 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.26−7.21 (m, 4H), 7.16−7.11 (m, 2H), 5.45 (dd, J = 1.2 Hz, 10.8 Hz, 1H), 5.19 (dd, J = 1.2 Hz, 17.6 Hz, 1H), 5.06 (dd, J = 1.2 Hz, 10.8 Hz, 1H), 3.70 (d, J = 11.6 Hz, 1H), 3.47 (d, J = 12 Hz, 1H), 1.72 (d, J = 5.2 Hz, 1H), 1.51 (d, J = 5.2 Hz, 1H), 1.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.7, 142.6, 139.6, 130.2, 129.2, 128.6, 128.2, 126.6, 126.4, 113.9, 65.2, 43.8, 35.4, 23.1; HRMS m/z calcd for $C_{18}H_{18}O$ [M + Na^+] 273.1255, found 273.1257.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2,2′-diphenyltetrahydrofuran (7d): Procedure B.** According to the general procedure E, **4d** was formed in 81% yield (0.095 g) as a gummy liquid after flash column chromatography using silica gel (hexanes) from 0.070 g of **4d**: R_f = 0.5 (hexanes/EtOAc, 6:4); nature, colorless solid; mp 148−152 °C; yield, 81%; IR (neat) $\bar{\nu}$ 3276, 2952, 2928, 2830, 1337, 1161, 1043, 770, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.72 (d, J = 8.4 Hz, 2H), 7.43−7.24 (m, 12H), 5.31−5.29 (m, 1H), 4.52 (dd, J = 6.0 Hz, 1H), 4.39−4.38 (m, 2H), 3.44 (dd, J = 10.0 Hz, 11.2 Hz, 2H), 3.21 (d, J = 1.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.6, 143.5, 143.3, 136.8, 129.7, 128.3, 128.2, 127.1, 127.0, 125.8, 125.7, 114.8, 87.5, 67.1, 45.3, 41.9, 21.5; HRMS m/z calcd for $C_{25}H_{25}NO_3S$ [M + Na^+] 442.1453, found 442.1417.

(1*R,2*R**)-Methyl 2-(naphthalen-2-yl)-1-((*E*)-styryl)-cyclopropanecarboxylate (4e′).** To a stirred solution of 2-vinylnaphthalene (5 mL) in DCM (15 mL) under argon atmosphere was added solid $Rh_2(OAc)_4$ (0.026 g, 0.059 mmol, 0.01 equiv) at rt. The mixture was vigorously stirred and refluxed. To the refluxing mixture styryldiazoacetate solution (1.2 g, 5.9 mmol, 1 equiv) in 60 mL of DCM was added dropwise through a dropping funnel for 2 h. The reaction was monitored by TLC. After an additional 1 h reflux, the reaction was cooled to rt and filtered through a thin pad of Celite. The solvent was evaporated in vacuo, and the residue was further purified by column chromatography using silica gel (hexanes/EtOAc, 8:2) to afford **4e′** as a liquid in 68% yield (1.2 g): R_f = 0.5 (hexanes/EtOAc, 8:2); IR (neat) $\bar{\nu}$ 3026, 2950, 1721, 1249, 1141, 964, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.74−7.67 (m, 3H), 7.60 (s, 1H), 7.40−7.38 (m, 2H), 7.24 (dd, J = 1.2 Hz, 6.8 Hz, 1H), 7.14−7.07 (m, 5H), 6.41 (d, J = 12.8 Hz, 1H), 6.15 (d, J = 12.8 Hz, 1H), 3.77 (s, 3H), 3.15 (dd, J = 12 Hz, 1H), 2.10 (dd, J = 4.0 Hz, 7.2 Hz, 1H), 1.94 (dd, J = 4.4 Hz, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 174.1, 136.9, 133.3, 133.2, 133.1, 132.4, 128.3, 127.8, 127.5, 127.5, 127.3, 126.2, 126.0, 125.6, 52.4, 35.1, 33.5, 18.9; HRMS m/z calcd for $C_{23}H_{20}O_2$ [M + Na^+] 351.1361, found 351.1365.

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((1*R,2*R**)-2-Naphthyl-1-((*E*)-styryl)cyclopropyl)methanol (4eA): Procedure A.** According to the general procedure A, **4eA** was formed in 83% yield (0.169 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.230 g of **4e′**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\overline{\nu}$ 3379, 3056, 3025, 2923, 2870, 1600, 1028, 817, 749, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.78−7.70 (m, 4H), 7.64 (s, 1H), 7.43−7.39 (m, 3H), 7.31 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H), 7.13−7.07 (m, 3H), 6.58 (d, *J* = 16.4 Hz, 1H), 5.68 (d, *J* = 16.4 Hz, 1H), 3.88 (d, *J* = 11.2 Hz, 1H), 3.83 (d, *J* = 11.2 Hz, 1H), 2.54 (dd, *J* = 8.4 Hz, 8.4 Hz, 1H), 1.84 (s, 1H), 1.49 (dd, *J* = 5.6 Hz, 5.6 Hz, 1H), 1.39 (dd, *J* = 4.0 Hz, 8.4 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) 137.2, 135.4, 133.3, 132.1, 130.3, 129.5, 128.3, 128.1, 127.7, 127.6, 127.5, 127.4, 127.2, 126.8, 126.0, 125.8, 125.3, 68.6, 32.4, 29.6, 17.2; HRMS *m*/*z* calcd for $C_{22}H_{20}O$ [M + Na^+] 323.1412, found 323.1418.

***O*-*tert*-Butyldimethylsilyl-((1*R**,2*R**)-2-naphthyl-1-((*E*)-styryl)cyclopropyl)methanol (4eB): Procedure C.** According to the general procedure C, **4eB** was formed in 96% yield (0.239 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.169 g of **4eA**: R_f = 0.8 (hexanes/EtOAc, 9:1); nature, liquid; yield, 96%; IR (neat) $\overline{\nu}$ 2955, 2929, 2857, 1252, 1094, 836, 774, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.79−7.71 (m, 3H), 7.65 (s, 1H), 7.46−7.40 (m, 2H), 7.34 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.16−7.05 (m, 4H), 6.49 (d, *J* = 16 Hz, 1H), 5.72 (d, *J* = 16 Hz, 1H), 4.02 (d, *J* = 10 Hz, 1H), 3.86 (d, *J* = 10 Hz, 1H), 2.62 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 1.84 (s, 1H), 1.45−1.42 (m, 2H), 0.98 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.7, 136.5, 133.4, 132.1, 130.7, 129.5, 128.3, 128.0, 127.6, 127.5, 127.4, 127.1, 126.6, 125.8, 125.7, 125.1, 66.7, 31.6, 28.2, 26.0, 18.3, 16.3, −5.2; HRMS *m*/*z* calcd for $C_{28}H_{34}OSi$ [M + Na^+] 437.2277, found 437.2272.

(1*R,2*R**)-1-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-(naphthalen-2-yl)cyclopropane carbaldehyde (4eC): Procedure D.** R_f = 0.7 (hexanes/EtOAc, 9:1); nature, crude; IR (neat) $\overline{\nu}$ 2954, 2928, 2856, 1700, 1100, 837, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.71 (s, 1H), 7.79−7.74 (m, 4H), 7.48−7.44 (m, 2H), 7.40 (dd, *J* = 1.6 Hz, 4.4 Hz, 1H), 4.18 (d, *J* = 9.8 Hz, 1H), 3.97 (d, *J* = 9.8 Hz, 1H), 3.07 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 2.04 (dd, *J* = 5.2 Hz, 7.2 Hz, 1H), 1.73 (dd, *J* = 5.2 Hz, 8.4 Hz, 1H), 0.93 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.7, 136.5, 133.4, 132.1, 130.7, 129.5, 128.3, 128.0, 127.6, 127.4, 127.1, 126.6, 125.8, 125.1, 66.7, 31.6, 28.2, 26.0, 18.3, 16.3, −5.2; HRMS *m*/*z* calcd for $C_{21}H_{28}O_2Si$ [M + Na^+] 363.1756, found 363.1754.

***O*-*tert*-Butyldimethylsilyl-((1*R**,2*R**)-2-naphthyl-1-vinylcyclopropyl)methanol (4eD).** According to the general procedure D, **4eB** was formed in 96% yield (0.078 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.100 g of **4eC**: R_f = 0.6 (hexanes/EtOAc, 9:1); nature, liquid; yield, 81%; IR (neat) $\overline{\nu}$ 2954, 2929, 2856, 1684, 1527, 1095, 836, 775, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.77 (t, *J* = 8.0 Hz, 3H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.45−7.39 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 5.33−5.27 (m, 1H), 5.00 (d, *J* = 17.6 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 3.93 (d, *J* = 10.4 Hz, 1H), 3.77 (d, *J* = 10.4, 1H), 2.55 (dd, *J* = 7.6 Hz, 1H), 1.32 (d, *J* = 7.6 Hz, 1H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.2, 136.5, 133.3, 132.0, 128.2, 127.6, 127.5, 127.3, 126.9, 125.8, 113.9, 66.3, 31.7, 27.7, 25.9, 18.3, 15.0, −5.3, −5.31; HRMS *m*/*z* calcd for $C_{22}H_{30}OSi$ [M + Na^+] 361.1964, found 361.1963.

((1*R,2*R**)-2-Naphthyl-1-vinylcyclopropyl)methanol (4e): Procedure E.** According to the general procedure E, **4e** was formed in 90% yield (0.047 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.078 g of **4eC**: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\overline{\nu}$ 3381, 3056, 3024, 2921, 1447, 1154, 1033, 706, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.80−7.73 (m, 4H), 7.59 (s, 1H), 7.47−7.40 (m, 2H), 5.32−5.16 (m, 2H), 4.98 (dd, *J* = 3.6 Hz, 10.0 Hz, 1H), 3.85 (d, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = 7.2 Hz, 1H), 2.50 (dd, *J* = 7.2 Hz, 8.0 Hz, 1H), 1.57 (s, 1H), 1.43 (dd, *J* = 5.6 Hz, 1H), 1.32 (dd, *J* = 5.2 Hz, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 135.4, 133.3, 133.1, 128.1, 128.0, 127.6, 127.5, 127.0, 126.0, 125.4, 114.9, 68.2, 32.7, 29.2, 16.3; HRMS *m*/*z* calcd for $C_{16}H_{16}O$ [M + Na^+] 247.1099, found 247.1090.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2-naphthyltetrahydrofuran (7e): Procedure B.** According to the general procedure B, **7e** was formed in 84% yield (0.068 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.078 g of **4e**: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, gummy; yield, 84%; IR (neat) $\overline{\nu}$ 3273, 2948, 2928, 1346, 1160, 1042, 771, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.84−7.74 (m, 6H), 7.49−7.40 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.31−5.28 (m, 1H), 5.03 (dd, *J* = 6.4 Hz, 12.4 Hz, 1H), 4.57 (d, *J* = 13.6 Hz, 1H), 4.36 (d, *J* = 13.6 Hz, 1H), 3.52 (dd, *J* = 6.0 Hz, 6.0 Hz, 2H), 2.91 (dd, *J* = 6.4 Hz, 16.0 Hz, 1H), 2.56 (dd, *J* = 8.8 Hz, 16.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.8, 143.6, 138.6, 137.0, 133.2, 133.0, 129.7, 128.3, 127.9, 127.7, 127.2, 126.2, 125.9, 124.6, 123.8, 115.0, 80.5, 68.6, 42.1, 41.0, 21.5; HRMS *m*/*z* calcd for $C_{23}H_{23}NO_3S$ [M + Na^+] 416.1296, found 416.1294.

(1*R,2*R**)-Ethyl 2-phenyl-1-(propen-2-yl)-cyclopropanecarboxylate (4fB): Procedure D(b).** VCP ester **4fB** was prepared from the corresponding cyclopropane keto-ester reported in the literature.[105,106] According to the general procedure D(b), **4fB** was formed in 82% yield (0.122 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.150 g of keto-ester: R_f = 0.5 (hexanes/EtOAc, 9:1); nature, liquid; yield, 82%; IR (neat) 3242, 2952, 2917, 1330, 1253, 799, 677 cm^{-1}; ^1HNMR (400 MHz, $CDCl_3$) 7.25−7.16 (m, 5H), 5.07 (s, 1H), 5.02 (s, 1H), 3.84−3.73 (m, 2H), 2.67 (dd, *J* = 8.0 Hz, 1H), 2.68 (dd, *J* = 4.8 Hz, 6.4 Hz, 1H), 1.98 (s, 3H), 1.31 (dd, *J* = 4.8 Hz, 9.2 Hz, 1H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.4, 144.2, 136.7, 129.1, 127.8, 126.5, 114.1, 60.4, 38.7, 31.8, 21.9, 18.3, 13.7; HRMS *m*/*z* calcd for $C_{15}H_{18}O_2$ [M + Na^+] 253.1204, found 253.1202.

General Procedure for Reduction of Esters with $LiBH_4$: Procedure F. To a stirred solution of the ester (3 mmol, 1 equiv) in THF (5 mL) at rt was added $LiBH_4$ (6 mmol, 2 equiv) and MeOH (0.2 mL). After stirring for 5 min, the reaction mixture was refluxed for 1 h approximately until complete consumption of the starting material (monitored by TLC). The reaction was quenched with saturated NH_4Cl, the mixture was extracted with EtOAc (2 × 20 mL), and the organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product provided the alcohol in its pure form.

((1*R,2*R**)-2-Phenyl-1-(propen-2-yl)cyclopropyl)methanol (4f): Procedure F.** According to the general procedure F, **4f** was formed in 75% yield (0.074 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.122 g of **4fB**: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) 3242,2952, 2917, 1330, 1253, 799, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.31−7.10 (m, 5H), 5.05 (s, 1H), 5.02 (s, 1H), 3.39 (d, *J* = 12 Hz, 1H), 3.34 (d, *J* = 12 Hz, 1H), 2.34 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 1.91 (s, 3H), 1.19 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.0, 137.9, 129.0, 128.3, 126.3, 113.5, 63.9, 35.7, 28.5, 20.5, 14.7; HRMS *m*/*z* calcd for $C_{13}H_{16}O$ [M + Na^+] 211.1099, found 211.1098.

(*S,*Z*/*E*)-4-(2-(*N*-*p*-Toluenesulfonamido)propylidene)-2-phenyltetrahydrofuran (7f): Procedure B.** According to the general procedure B, **7f** was formed in 82% yield (0.116 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.074 g of **4f**: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) 3242, 2952, 2917, 1330, 1253, 799, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.74 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.35−7.26 (m, 9H), 4.89 (m, 1H), 4.54−4.46 (m, 2H), 4.26 (dd, *J* = 14.4 Hz, 1H), 3.61−3.45 (m, 2H), 2.85−2.74 (m, 1H), 2.42 (s, 1.5 H), 2.36−2.29 (m, 1H), 1.56 (s, 1.5H), 1.48 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.5, 141.1, 138.0, 136.8, 129.6, 129.6, 128.4, 127.7, 127.1, 125.8, 120.3, 120.2, 81.2, 80.8, 70.2, 69.3, 47.2, 46.4, 39.2, 38.2, 21.5, 17.5, 16.6; HRMS *m*/*z* calcd for $C_{20}H_{23}NO_3S$ [M + Na^+] 380.1296, found 380.1302.

(1-((*tert*-Butyldimethylsilyl)oxymethyl)-2,2-dimethylcyclopropyl)methanol (4gA): Procedure C. According to the general procedure F, **7f** was formed in 82% yield (0.116 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.074 g of diol: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, liquid; yield, 85%; ^1H NMR (**400** MHz, $CDCl_3$) 3.97 (dd, *J* = 12 Hz, 12 Hz, 2H), 3.61 (d, *J* = 10.4 Hz, 1H), 3.52 (dd, *J* = 8.0 Hz, 10.8 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 1H), 1.25 (s, 3H), 1.18 (s, 3H), 0.90

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(s, 9H), 0.34 (d, J = 4.8 Hz, 1H), 0.26 (d, J = 4.8 Hz, 1H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 69.0, 68.4, 31.3, 25.8, 22.7, 22.4, 22.1, 20.9, 18.0, −5.6, −5.7; HRMS m/z calcd for $C_{13}H_{28}O_2Si$ [M + Na^+] 267.1756, found 267.1755.

(2,2-Dimethyl-1-vinylcyclopropyl)methanol (4g). To a stirred solution of cyclopropane **4gA** (1 mmol, 1 equiv) in DCM (6 mL) was added DMP (1.1 mmol, 1.1 equiv) at 0 °C. The reaction was monitored by TLC. After complete conversion of the starting material, the excess DMP present is quenched by the treatment of 20% aq. solution of $Na_2S_2O_3$ (5 mL). The mixture was washed with $NaHCO_3$ solution (20 mL) and extracted with DCM (2 × 20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. The crude product was carried over to the next step following procedure D(b) without further purification. According to the general procedure D, **4g** was formed in 67% yield (0.043 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.116 g of **4gA**: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, liquid; yield, 67% (over 3 Steps); IR (neat) 3411, 3004, 2932, 1443, 1157, 682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 5.86 (dd, J = 10.8 Hz, 17.2 Hz, 1H), 5.18−5.12 (m, 2H), 3.70 (s, 2H), 1.67 (s, 1H), 1.20 (s, 3H), 1.05 (s, 3H), 0.65 (d, J = 4.8 Hz, 1H), 0.53 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.1, 115.5, 65.9, 34.2, 24.2, 22.6, 22.4, 21.6; HRMS m/z calcd for $C_8H_{14}O$ [M + Na^+] 149.0942, found 149.0942.

(*Z*/*E*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2,2′-dimethyltetrahydrofuran (7g): Procedure B. According to the general procedure B, **7g** was formed in 90% yield (0.079 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.043 g of **4g**: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) 3312, 2934, 2923, 1337, 1246, 671 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.75 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 5.28−5.25 (m, 0.4H), 5.25−5.20 (m, 1H), 5.01 (dd, J = 5.6 Hz, 5.6 Hz, 0.4H), 4.89 (dd, J = 5.6 Hz, 5.6 Hz, 1H), 4.31 (s, 0.8H), 4.24 (s, 2H), 3.46−3.43 (m, 2.8H), 3.29 (d, J = 8.8 Hz, 0.8H), 2.63 (d, J = 12.6 Hz, 0.4H), 2.43 (s, 3H), 2.43 (s, 1.6H), 2.33 (d, J = 12.6 Hz, 0.4H), 2.27 (s, 2H), 1.85 (s, 0.8H), 1.34 (s, 1.3H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.8, 143.5, 142.7, 136.8, 129.7, 127.1, 116.1, 114.9, 81.6, 80.3, 67.7, 66.7, 45.2, 42.2, 41.9, 41.8, 39.3, 26.4, 23.7, 21.5; HRMS m/z calcd for $C_{15}H_{21}NO_3S$ [M + Na^+] 318.1140, found 318.1146.

(1*R,6*S**,7*S*)-7-(((*tert*-Butyldimethylsilyl)oxy)methyl)bicyclo[4.1.0]heptane-7-carbaldehyde (4hC): Procedure D.** R_f = 0.5 (hexanes/EtOAc, 20:1); nature, liquid; yield, 87%; IR (neat) $\bar{\nu}$ 2932, 2858, 1393, 1470, 1255, 1088, 853, 837, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 9.71 (s, 1H), 3.75 (s, 2H), 2.01−1.94 (m, 2H), 1.81−1.76 (m, 2H), 1.69−1.62 (m, 2H), 0.83 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 203.2, 63.3, 40.6, 25.8, 24.5, 21.9, 19.0, 18.2, −5.50.

***tert*-Butyldimethylsilyl(((1*R**,6*S**,7*R*)-7-vinylbicyclo[4.1.0]heptan-7-yl)methanol (4hD).** According to the general procedure D, **4hD** was formed in 80% yield (0.079 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.043 g of the ester: R_f = 0.5 (hexanes); IR (neat) $\bar{\nu}$ 3392, 3021, 2924, 1643, 1600, 1494, 1445, 1024, 749, 705 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) 5.76 (dd, J = 11.2 Hz, 17.1 Hz, 1H), 5.26 (dd, J = 0.9 Hz, 4.5 Hz, 1H), 5.21 (dd, J = 2.4 Hz, 7.5 Hz, 1H), 3.50 (s, 2H), 1.86−1.80 (m, 2H), 1.50−1.43 (m, 2H), 1.22−1.16 (m, 4H), 1.03−1.01 (m, 2H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 135.9, 117.4, 69.4, 29.6, 26.0, 22.0, 19.4, 18.4, 17.8, −5.3; HRMS m/z calcd for $C_{16}H_{30}OSi$ [M + Na^+] 289.1964, found 289.1964.

((1*R,6*S**,7*R*)-7-Vinylbicyclo[4.1.0]heptan-7-yl)methanol (4h): Procedure E.** According to the general procedure E, **4h** was formed in 95% yield (0.065 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.079 g of the **4hD**: R_f = 0.25 (hexanes/EtOAc, 8:2); nature, liquid; yield, 95%; IR (neat) $\bar{\nu}$ 3392, 3021, 2924, 1643, 1600, 1494, 1445, 1024, 749, 705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.79 (dd, J = 11.1 Hz, 17.8 Hz, 1H), 5.38−5.31 (m, 2H), 3.44 (s, 2H), 1.92−1.85 (m, 2H), 1.71 (s, 1H), 1.54−1.47 (m,2H), 1.30−1.15 (m,4H), 1.08−0.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 135.1, 117.8, 70.6, 31.0, 21.8, 19.3; HRMS m/z calcd for $C_{10}H_{16}O$ [M + Na^+] 175.1099, found 175.1098.

((1*R,1a*S**,7b*S**)-1-((*E*)-Styryl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalen-1-yl)methanol (4iA): Procedure A.** According to the general procedure A, **4iA** was formed in 78% yield (0.182 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.257 g of the corresponding ester: R_f = 0.5 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3379, 3056, 3025, 2923, 2870, 1600, 1028, 817, 749, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.36−7.00 (m, 9H), 6.43 (d, J = 16.5 Hz, 1H), 5.82 (d, J = 16.5, 1H), 3.85 (d, J = 11.4 Hz, 1H), 3.71 (dd, J = 6.6 Hz, 1H), 2.64 (dd, J = 6.0 Hz, 6.0 Hz, 1H), 2.50−2.39 (m, 2H), 2.24 (d, J = 9.0 Hz, 1H), 2.01−1.94 (m, 2H), 1.69−1.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.4, 136.0, 134.3, 132.6, 129.9, 128.3, 128.1, 127.1, 126.1, 126.0, 125.8, 70.0, 61.9, 36.3, 35.9, 27.7, 25.9, 23.8, 18.7. HRMS m/z calcd for $C_{20}H_{20}O$ [M + Na^+] 299.1412, found 299.1411.

(1*S,1a*S**,7b*S**)-1-(((*tert*-Butyldimethylsilyl)oxy)methyl)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalene-1-carbaldehyde (4iC): Procedure D.** R_f = 0.5 (hexanes/EtOAc, 9:1); nature, liquid; ^{1}H NMR (400 MHz, $CDCl_3$) 8.91 (s, 1H), 7.19−7.16 (m, 1H), 7.10−7.00 (m, 3H), 3.99 (d, J = 10.8 Hz, 1H), 3.70 (d, J = 10.8 Hz, 1H), 2.89−2.80 (m, 1H), 2.63 (d, J = 8.1 Hz, 1H), 2.47−2.38 (m, 1H), 2.20−2.01 (m, 3H), 0.82 (S, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 203.0, 136.7, 131.9, 129.9, 128.4, 126.8, 126.6, 62.3, 43.4, 28.3, 27.4, 26.2, 25.9, 18.9, 18.2.

***O*-*tert*-Butyldimethylsilyl(((1*R**,1a*S**,7b*S**)-1-vinyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalen-1-yl)methanol (4iD).** According to the general procedure D, **4iD** was formed in 73% yield (0.118 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.257 g of **4iA**: R_f = 0.8 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.16−7.12 (m, 1H), 7.07−7.00 (m, 2H), 6.99−6.93 (m, 1H), 5.33 (dd, J = 10.8 Hz, 17.4 Hz, 1H), 4.95 (dd, J = 1.4 Hz, 23. Four Hz, 1H), 4.90 (dd, J = 1.80 Hz, 16.5 Hz, 1H), 3.62 (dd, J = 9.9 Hz, 12.3 Hz, 2H), 2.66−2.56 (m, 1H), 2.47−2.37 (m, 1H), 2.09 (d, J = 8.7 Hz, 1H), 1.98−176 (m, 2H), 1.68−1.59 (m, 1H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.8, 135.6, 135.1, 129.9, 128.2, 125.9, 125.4, 116.8, 68.0, 35.2, 28.0, 25.9, 23.9, 22.0, 18.9, 18.3, −5.3; HRMS m/z calcd for $C_{20}H_{30}OSi$ [M + Na^+] 337.1964, found 337.1964.

((1*R,1a*S**,7b*S**)-1-Vinyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[a]naphthalen-1-yl)methanol (4i): Procedure E.** According to the general procedure E, **4i** was formed in 95% yield (0.071 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.118 g of **4iD**: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, liquid; yield, 95%; IR (neat) $\bar{\nu}$ 3381, 3054, 3034, 2928, 1157, 1038, 718, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.26 (d, J = 6.9 Hz, 1H), 7.17−7.03 (m, 3H), 5.41 (dd, J = 8.1 Hz, 18.0 Hz, 1H), 5.19−5.08 (m, 2H), 3.83 (d, J = 10.8 Hz, 1H), 3.43 (dd, J = 6.1 Hz, 10.8 Hz, 1H), 2.76−2.66 (m, 1H), 2.55−2.45 (m, 1H), 2.18 (d, J = 8.7 Hz, 1H), 2.08−1.86 (m, 2H), 1.70−1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.6, 134.7, 134.2, 13.0, 128.2, 126.0, 128.8, 117.5, 69.5, 36.4, 27.9, 25.6, 23.3, 18.8; HRMS m/z calcd for $C_{14}H_{16}O$ [M + Na^+] 223.1099, found 223.1094.

(*Z*)-3-*N*-*p*-Toluenesulfonamidoethylidene(3a*R,9b*S**)-2,3,3a,4,5,9b-hexahydronaphtho[1,2-b]furan (7i): Procedure B.** According to the general procedure E, **4i** was formed in 87% yield (0.113 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.071 g of **7i**: R_f = 0.3 (hexanes/EtOAc, 7:3); nature, gummy; yield, 87%; IR (neat) $\bar{\nu}$ 3284, 2926, 2855, 1598, 1326, 1158, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.74 (d, J = 8.4 Hz, 2H), 7.41−7.38 (m, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.23−7.20 (m, 2H), 7.12−7.09 (m, 1H), 5.35−5.30 (m, 1H), 4.77 (d, J = 6.0 Hz, 1H), 4.62 (dd, J = 6.0 Hz, 1H), 4.29 (dd, J = 13.2 Hz, 23.7 Hz, 2H), 3.57−3.44 (m, 2H), 2.79−2.58 (m, 2H), 2.43 (s, 3H), 1.79−1.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.4, 143.6, 137.6, 130.0, 129.7, 128.4, 127.9, 127.2, 126.5, 126.4, 115.1, 67.7, 43.0, 42.1, 28.0, 26.0, 21.5; HRMS m/z calcd for $C_{21}H_{23}NO_3S$ [M + Na^+] 392.1296, found 392.1294.

((1*R,1a*S**,6a*S**)-1-((*E*)-Styryl)-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1-yl)methanol (4jA): Procedure A.** According to the general procedure A, **4jA** was formed in 87% yield (0.196 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.250 g of the corresponding ester: R_f = 0.5 (hexanes/EtOAc, 8:2); IR (neat) $\bar{\nu}$ 3362, 3023, 2909, 1474, 1019, 964, 747, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.29 (d, J = 6.8 Hz, 1H), 7.18−7.02 (m, 8H),

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6.57 (d, J = 16.4 Hz, 1H), 5.46 (d, J = 16.4 Hz, 1H), 3.80 (d, J = 11.6 Hz, 1H), 3.61 (d, J = 11.6 Hz, 1H), 3.17 (dd, J = 11.2 Hz, 17.6 Hz, 1H), 2.87 (d, J = 17.6 Hz, 1H), 2.75 (d, J = 6.0 Hz, 1H), 2.07 (dd, J = 6.8 Hz, 6.8 Hz, 1H) 1.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.9, 141.6, 137.3, 133.0, 128.3, 127.0, 126.2, 126.1, 125.7, 124.9, 124.5, 124.2, 68.3, 36.7, 33.8, 32.2, 28.6; HRMS m/z calcd for $C_{19}H_{18}O$ [M + Na^+] 285.1255, found 285.1258.

***O*-*tert*-Butyldimethylsilyl((1*R**,1a*S**,6a*S**)-1-((*E*)-styryl)-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1-yl)methanol (4jB): Procedure C.** According to the general procedure C, **4jB** was formed in 90% yield (0.253 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.196 g of **4jA**: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 2954, 2429, 2856, 1466, 1255, 1099, 836, 775, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 (d, J = 7.2 Hz, 1H), 7.25−7.14 (m, 6H), 7.10 (d, J = 7.2 Hz, 2H), 6.57 (d, J = 8.4 Hz, 1H), 5.56 (d, J = 8.4 Hz, 1H), 3.93 (d, J = 10.4 Hz, 1H), 3.84 (d, J = 10.4 Hz, 1H), 3.25 (dd, J = 6.8 Hz, 10.8 Hz, 1H), 2.94 (d, J = 17.6 Hz, 1H), 2.82 (d, J = 6.4 Hz, 1H), 2.22 (dd, J = 6.8 Hz, 6.8 Hz, 1H), 1.00 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.3, 142.5, 137.9, 132.7, 128.3, 126.7, 126.1, 125.9, 125.8, 125.6, 124.4, 124.2, 67.3, 35.6, 32.7, 32.5, 27.8, 25.9, 18.3, −5.24, −5.26; HRMS m/z calcd for $C_{25}H_{32}OSi$ [M + Na^+] 399.2120, found 399.2117.

***O*-*tert*-Butyldimethylsilyl((1*R**,1a*S**,6a*S**)-1-vinyl-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1-yl)methanol (4jD): Procedure D.** According to the general procedure C, **4jD** was formed in 75% yield (0.090 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.150 g of **4jB**: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.28 (d, J = 6.8 Hz, 1H), 7.15−7.12 (m, 3H), 5.14 (d, J = 6.4 Hz, 2H), 5.05−5.03 (m, 1H), 3.78 (dd, J = 6.4 Hz, 6.4 Hz, 2H), 3.16 (dd, J = 7.2 Hz, 14.4 Hz, 1H), 2.86 (d, J = 17.6 Hz, 1H), 2.73 (d, J = 6.4 Hz, 1H), 2.11 (dd, J = 6.8 Hz, 6.8 Hz, 1H), 0.95 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.6, 142.8, 133.8, 126.1, 125.7, 124.5, 124.1, 117.5, 66.7, 35.4, 62.8, 62.4, 27.3, 26.0, 18.4, −5.23; HRMS m/z calcd for $C_{19}H_{28}OSi$ [M + Na^+] 323.1807, found 323.1808.

((1*R)-1-Vinyl-1,1a,6,6a-tetrahydrocyclopropa[a]inden-1-yl)-methanol (4j): Procedure E.** According to the general procedure C, **4j** was formed in 95% yield (0.052 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.090 g of **4jD**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.27−7.25 (m, 1H), 7.14−7.09 (m, 3H), 5.28−5.20 (m, 1H), 5.12−5.04 (m, 2H), 3.74 (d, J = 11.2 Hz, 1H), 3.56 (d, J = 11.2 Hz, 1H), 3.17 (dd, J = 7.2 Hz, 17.6 Hz, 1H), 2.84 (d, J = 17.6 Hz, 1H), 2.70 (d, J = 6.4 Hz, 1H), 2.03 (dd, J = 6.8 Hz, 1H), 1.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.2, 141.8, 133.1, 126.3, 126.1, 124.7, 124.3, 118.2, 67.9, 36.5, 34.1, 32.2, 28.3; HRMS m/z calcd for $C_{13}H_{14}O$ [M + Na^+] 209.0942, found 209.0937.

(*Z*)-3-(*N*-*p*-Toluenesulfonamidoethylidene)-(3a*R,8b*S**)-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-b]furan (7j): Procedure B.** According to the general procedure B, **7j** was formed in 91% yield (0.090 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.052 g of **4j**: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, gummy; yield, 91%; IR (neat) $\bar{\nu}$ 3244, 2921, 2832, 1578, 1322, 1253, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 6.8 Hz, 1H), 7.28−7.21 (m, 4H), 7.15 (d, J = 7.2 Hz, 1H), 5.56 (d, J = 6.8 Hz, 1H), 5.35−5.31 (m, 1H), 4.66 (dd, J = 6.0 Hz, 6.4 Hz, 1H), 4.33 (d, J = 13.6 Hz, 1H), 3.96 (d, J = 13.6 Hz, 1H), 3.49−3.67 (m, 3H), 3.22 (dd, J = 8.4 Hz, 16.4 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.9, 143.5, 142.4, 141.1, 136.7, 129.7, 128.8, 127.1, 127.0, 125.3, 124.8, 115.9, 87.4,68.0, 46.4, 42.2, 38.3, 21.5; HRMS m/z calcd for $C_{20}H_{21}NO_3S$ [M + Na^+] 378.1140, found 378.1142.

((1*R,6*R**,7*S**)-7-Vinyl-2-oxabicyclo[4.1.0]heptan-7-yl)-methanol (4k): Procedure A.** According to the general procedure A, **7j** was formed in 91% yield (0.071 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.100 g of the corresponding ester: R_f = 0.5 (hexanes/EtOAc, 7:3); nature, liquid; yield, 85%; IR (neat) $\bar{\nu}$ 3405, 2944, 2859, 1632, 1038, 862 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.90 (dd, J = 14.1 Hz, 18.0 Hz, 1H), 5.42 (dd, J = 1.8 Hz, 10.2 Hz, 1H), 5.36 (dd, J = 1.8 Hz, 3.0 Hz, 1H), 3.68 (dt, J = 3.3 Hz, 11.4 Hz, 1H), 3.58 (d, J = 4.2 Hz, 1H), 3.55 (s, 1H), 3.35−3.27 (m, 2H), 2.03−1.86 (m, 1H), 1.81−1.73 (m, 2H), 1.50−1.41 (m, 2H), 1.08 (ddd, J = 0.6 Hz, 8.1 Hz, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 133.4, 117.4, 67.0, 64.4, 58.9, 32.0, 22.3, 18.7, 15.8; HRMS m/z calcd for $C_9H_{14}O_2$ [M + Na^+] 177.0891, found 177.0887.

(*Z*)-3-(*N*-*p*-Toluenesulfonamidoethylidene)-(3a*R,7a*S**)-tetrahydro-2*H*-furo[2,3-b]pyran (7k): Procedure B.** According to the general procedure B, **7k** was formed in 85% yield (0.127 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.071 g of **4k**: R_f = 0.5 (hexanes/EtOAc, 6:4); IR (neat) $\bar{\nu}$ 3270, 2931, 2864, 1326, 1159, 1092, 815, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.75 (D, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.23−5.16 (m, 1H), 5.80 (d, J = 3.9 Hz, 1H), 4.88 (t, J = 5.7 Hz, 1H), 4.47 (d, J = 13.5 Hz, 1H), 4.35 (d, J = 13.5 Hz, 1H), 3.83−3.78 (m, 1H), 3.53−3.47 (m, 2H), 3.40 (td, J = 1.8 Hz, 11.4 Hz, 1H), 2.56−2.55 (m, 1H), 2.43 (s, 3H), 1.88−1.81 (m, 2H), 1.56−1.36 (m, 1H), 1.27−1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.6, 142.2, 136.8, 129.7, 127.1, 114.8, 101.1, 68.5, 64.5, 42.2, 41.9, 22.3, 21.5, 20.2; HRMS m/z calcd for $C_{16}H_{21}NO_4S$ [M + Na^+] 346.1089, found 346.1096.

((1*R,1a*S**,6b*R**)-1-((*E*)-Styryl)-1a,6b-dihydro-1*H*-cyclopropa[b]benzofuran-1-yl)methanol (4lA): Procedure A.** According to the general procedure A, **4lA** was formed in 87% yield (0.157 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.200 g of the corresponding ester: R_f = 0.5 (hexanes/EtOAc, 6:4); IR (neat) $\bar{\nu}$ 3367, 2924, 1475, 1463, 1226, 1016, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.23 (d, J = 9.6 Hz, 2H), 7.11−6.97 (m, 5H), 6.78 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 7.2 Hz, 1H), 6.55 (d, J = 16.5 Hz, 1H), 5.47 (d, J = 16.5 Hz, 1H), 4.72 (d, J = 5.4 Hz, 1H), 3.58 (dd, J = 11.7 Hz, 18.9 Hz, 2H), 2.87 (d, J = 5.4 Hz, 1H), 2.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.3, 137.5, 135.1, 128.9, 128.3, 127.9, 127.0, 126.5, 125.4, 122.0, 121.5, 110.0, 70.1, 66.0, 32.7, 26.8; HRMS m/z calcd for $C_{18}H_{16}O_2$ [M + Na^+] 287.1048, found 287.1040.

***O*-*tert*-Butyldimethylsilyl((1*R**,1a*S**,6b*R**)-1-((*E*)-styryl)-1a,6b-dihydro-1*H*-cyclopropa[b]benzofuran-1-yl)methanol (4lB): Procedure C.** According to the general procedure C, **4lB** was formed in 87% yield (0.195 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.157 g of **4lA**: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 2954, 2929, 2857, 2886, 1475, 1463, 1226, 1096, 836, 747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.26−7.24 (d, J = 7.5 Hz, 2H), 7.13−7.08 (m, 6H), 6.82−6.74 (t, J = 7.5 Hz, 2H), 6.67 (d, J = 7.5 Hz, 1H), 5.56 (d, J = 16.2 Hz, 1H), 3.87 (d, J = 3.2 Hz, 1H), 3.77 (d, J = 3.2 Hz, 1H), 2.98 (d, J = 5.4 Hz, 1H), 0.83 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 160.9, 137.4, 134.0, 128.2, 127.4, 127.2, 125.8, 124.7, 122.3, 120.7, 109.3, 69.4, 64.9, 31.2, 25.7, 24.8, 18.2, −5.1; HRMS m/z calcd for $C_{24}H_{30}O_2Si$ [M + Na^+] 401.1913, found 401.1914.

***tert*-Butyldimethylsilyl((1*R**,1a*S**,6b*R**)-1-vinyl-1a,6b-dihydro-1*H*-cyclopropa[b]benzofuran-1-yl)methanol (4lD): Procedure D.** According to the general procedure D, **4lD** was formed in 76% yield (0.118 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.195 g of **4lB**: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) 7.24−7.18 (m, 1H), 7.03−7.00 (m, 1H), 6.81−6.76 (m, 1H), 6.71−6.68 (m, 1H), 5.12−5.09 (m, 2H), 4.98 (d, J = 4.5 Hz, 1H), 4.95 (d, J = 3.9 Hz, 1H), 3.79 (d, J = 11.2 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H), 2.09 (d, J = 4.5 Hz, 1H), 0.83 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.1, 132.0, 128.4, 127.3, 127.2, 124.7, 120.6, 118.8, 109.2, 69.4, 64.2, 30.9, 25.8, 24.6, 18.2, −5.45; HRMS m/z calcd for $C_{18}H_{26}O_2Si$ [M + Na^+] 325.1600, found 325.1594.

((1*R,1a*S**,6b*R**)-1-Vinyl-1a,6b-dihydro-1*H*-cyclopropa[b]-benzofuran-1-yl)methanol (4l): Procedure E.** According to the general procedure E, **4l** was formed in 90% yield (0.066 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.118 g of **4lD**: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) 3367, 2924, 1475, 1463, 1226, 1016, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.29 (d, J = 7.2 Hz, 2H), 7.15−7.09 (m, 1H), 6.91−6.86 (m, 1H), 6.83−6.78 (m, 1H), 5.36−5.12 (m, 3H), 4.79 (d, J = 5,4 Hz, 1H), 3.64 (dd, J = 11.4 Hz, 15.6 Hz, 2H), 2.94 (d, J = 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 160.9, 129.8, 128.2, 127.4, 124.8, 120.9,

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119.8, 109.4, 69.4, 65.0, 31.7, 26.4; HRMS m/z calcd for $C_{12}H_{12}O_2$ [M + Na^+] 211.0735, found 211.0734.

(*Z*)-3-(*N*-*p*-Toluenesulfonamidoethylidene)-2,3,3a,8b-tetrahydrofuro[3,2-b]benzofuran (7l): Procedure B. According to the general procedure E, **7l** was formed in 43% yield (0.054 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.118 g of **4l**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.72 (d, J = 8.4 Hz, 2H), 7.33−7.26 (m, 3H), 7.17 (dd, J = 7.6 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 5.6 Hz, 1H), 5.58 (dd, J = 6.4 Hz, 6.4 Hz, 1H), 4.56 (dd, J = 6.0 Hz, 6.0 Hz, 1H), 4.46 (d, J = 12.8 Hz, 1H), 4.21 (d, J = 5.6 Hz, 1H), 4.14 (d, J = 13.2 Hz, 1H), 3.53−3.48 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.7, 143.6, 129.8, 129.7, 129.2, 127.2, 126.4, 124.1, 121.4, 117.0, 110.6, 109.8, 67.3, 51.4, 42.1, 21.5; HRMS m/z calcd for $C_{19}H_{19}NO_4S$ [M + Na^+] 380.0932, found 380.0930.

(*Z*)-3-(*N*-*p*-Toluenesulfonamidoethylidene)-2,3,3a,8a-tetrahydrofuro[2,3-b]benzofuran (8l): Procedure B. According to the general procedure E, **8l** was formed in 38% yield (0.047 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.118 g of **4l**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.27−7.24 (m, 1H), 6.94 (dd, J = 7.2 Hz, 7.2 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 5.79 (dd, J = 6.8 Hz, 6.8 Hz, 1H), 5.66 (d, J = 6.0 Hz, 1H), 5.26 (d, J = 6.4 Hz, 1H), 4.62 (dd, J = 6.0 Hz, 6.0 Hz, 1H), 4.37 (d, J = 13.2 Hz, 1H), 4.03 (d, J = 13.2 Hz, 1H), 3.59 (dd, J = 6.8 Hz, 6.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 160.1, 143.7, 142.0, 136.7, 130.9, 129.8, 127.2, 126.1, 125.3, 122.9, 121.3, 110.1, 86.5, 82.7, 66.0, 42.2, 21.5; HRMS m/z calcd for $C_{19}H_{19}NO_4S$ [M + Na^+] 380.0932, found 380.0932.

(1*R,2*R**)-Ethyl 1-(*S*)-1-*tert*-butyldimethylsilyloxyethyl-2-phenylcyclopropane carboxylate (4mA).** According to the general procedure C, **4mA** was formed in 91% yield (0.337 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.228 g of ester: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.15- 7.12 (m, 4H), 7.09−7.05 (m, 1H), 4.36 (dd, J = 6.0 Hz, 12.0 Hz, 1H), 3.69−3.59 (m, 2H), 2.47 (dd, J = 8.8 Hz, 8.8 Hz, 1H), 1.69 (dd, J = 4.4 Hz, 7.6 Hz, 1H), 1.47 (dd, J = 4.4 Hz, 8.8 Hz, 1H), 1.35 (d, J = 6.0 Hz, 3H), 0.82 (s, 9H), 0.67 (t, J = 7.2 Hz, 3H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.4, 137.7, 129.1, 127.6, 126.1, 65.9, 59.7, 37.8, 27.2, 25.7, 22.7, 18.0, 15.3, 13.5, −4.55, −5.00; HRMS m/z calcd for $C_{20}H_{32}O_3Si$ [M + Na^+] 371.2018, found 371.2010.

((1*S,2*R**)-1-((*S**)-1-((*tert*-Butyldimethylsilyl)oxy)ethyl)-2-phenylcyclopropyl)methanol (4mB): Procedure A.** According to the general procedure A, **4mB** was formed in 81% yield (0.233 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.337 g of ester: R_f = 0.5 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.30- 7.18 (m, 5H), 4.11 (d, J = 7.2 Hz, 1H), 3.46 (dd, J = 6.4 Hz, 12.8 1H), 3.28−3.26 (b, 1H), 3.13 (d, J = 12.0 Hz, 1H), 2.36 (dd, J = 6.4 Hz, 1H), 1.38 (d, J = 6.4 Hz, 3H), 0.96(s, 9H), 0.93(dd, J = 5.6 Hz, 9.6 Hz, 1H), 0.84 (dd, J = 5.6 Hz, 8.4 Hz, 1H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.9, 129.0, 128.3, 126.3, 75.3, 63.1, 33.1, 28.5, 25.3, 20.2, 12.1, −4.9, −5.1; HRMS m/z calcd for $C_{18}H_{30}O_2Si$ [M + Na^+] 329.1913, found 329.1910.

1-*tert*-Butyldimethylsilyloxyethyl((*R)-1-((1*R**,2*R**)-2-phenyl-1-vinylcyclopropane (4mD) .** To a stirred solution of cyclopropane **4mB** (1 mmol, 1 equiv) in DCM (6 mL) was added DMP (1.1 mmol, 1.1 equiv) at 0 °C. The reaction was monitored by TLC. After complete conversion of the starting material, the excess DMP present is quenched by the treatment of 20% aq. solution of $Na_2S_2O_3$ (5 mL). The mixture was washed with $NaHCO_3$ solution (20 mL) and extracted with DCM (2 × 20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. The crude product was carried over to the next step following procedure D(b) without further purification. R_f = 0.5 (hexanes/EtOAc, 9:1); nature, liquid; ^{1}H NMR (400 MHz, $CDCl_3$) 7.52−7.48 (m, 2H), 7.43−7.41 (m, 3H), 6.78 (dd, J = 10.8 Hz, 17.6 Hz, 1H), 5.23 (m, 2H), 3.49 (q, J = 6.4 Hz, 1H), 2.40 (dd, J = 7.6 Hz, 1H), 1.61 (dd, J = 5.2 Hz, 8.4 Hz, 1H), 1.42 (d, J = 6.4 Hz, 3H), 1.21−1.16 (m, 1H), 1.04 (s, 9H), 0.0 (s, 3H), −0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.6, 137.9, 129.1, 127.9, 126.0, 117.0, 68.1, 36.8, 34.3, 25.9, 22.3, 17.9, 13.2, −4.0, −5.9; HRMS m/z calcd for $C_{19}H_{30}OSi$ [M + Na^+] 325.1964, found 325.1964.

(*R)-1-((1*R**,2*R**)-2-Phenyl-1-vinylcyclopropyl)ethanol (4m): Procedure E.** According to the general procedure E, **4m** was formed in 72% yield (0.103 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.233 g of **4mB**: R_f = 0.5 (hexanes/EtOAc, 9:1); IR (neat) $\bar{\nu}$ 3315, 2957, 1457, 1026, 678 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.96−7.83 (m, 5H), 7.07 (dd, J = 10.0 Hz, 17.2 Hz, 1H), 5.77−5.69 (m, 2H), 3.78 (q, J = 8 Hz, 1H), 2.90 (dd, J = 8.0 Hz, 1H), 1.92 (dd, J = 5.6 Hz, 8.4 Hz, 1H), 1.88 (s, 1H), 1.79 (d, J = 6.8 Hz, 3H), 1.73 (dd, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.9, 137.6, 128.7, 128.5, 126.5, 113.5, 69.2, 35.7, 32.5, 25.9, 19.9, 14.0; HRMS m/z calcd for $C_{13}H_{16}O$ [M + Na^+] 211.1099, found 211.1120.

(*S,*Z*)-4-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-2-methyl-5-phenyltetrahydrofuran (7m): Procedure B.** According to the general procedure B, **7m** was formed in 87% yield (0.085 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.050 g of **4m**: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3286, 2934, 2812, 1333, 1143, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.73 (d, J = 6.4 Hz, 2H), 7.34−7.24 (m, 7H), 5.13−5.09 (t, J = 5.6 Hz, 1H), 4.72 (dd, J = 4.4 Hz, 1H), 4.58 (dd, J = 4.8 Hz, 9.6 Hz, 1H), 3.58 (dd, J = 6.0 Hz, 11.2 Hz, 2H), 3.54 (dd, J = 5.4 Hz, 10.8 Hz, 1H), 2.88 (dd, J = 5.6 Hz, 12.8 Hz, 1H), 2.46−2.41 (m, 1H), 2.41 (s, 3H), 1.21 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.2, 143.5, 142.0, 137.0, 129.7, 128.4, 127.5, 127.1, 125.7, 125.6, 114.6, 78.2, 42.6, 37.2, 21.5, 20.6; HRMS m/z calcd for $C_{20}H_{23}NO_3S$ [M + Na^+] 380.1296, found 380.1296.

((1*S,2*S**,3*R**)-2-Methyl-3-phenyl-1-((*E*)-styryl)cyclopropyl)-methanol (4nA): Procedure A.** According to the general procedure A, **4nA** was formed in 87% yield (0.085 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.100 g of ester: R_f = 0.4 (hexanes/EtOAc, 7:3); IR (neat) $\bar{\nu}$ 3347, 2952, 1513, 1445, 1134, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.26−7.12 (m, 10H), 6.59 (d, J = 16.4 Hz, 1H), 5.64 (d, J = 16.4 Hz, 1H), 4.13 (d, J = 11.2 Hz, 1H), 3.80 (d, J = 11.2 Hz, 1H), 2.06 (d, J = 6.4 Hz, 1H), 1.73 (dd, J = 6.4 Hz, 12.8 Hz, 1H), 1.65 (s, 1H), 1.42 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.1, 137.4, 131.3, 130.0, 128.7, 128.4,128.0, 126.9, 126.1, 125.8, 64.9, 37.4, 36.6, 24.9, 13.7; HRMS m/z calcd for $C_{19}H_{20}O$ [M + Na^+] 287.1412, found 287.1409.

***O*-*tert*-Butyldimethylsilyl-((1*S**,2*S**,3*R**)-2-methyl-3-phenyl-1-((*E*)-styryl)cyclopropyl)methanol (4nB): Procedure C.** According to the general procedure C, **4nB** was formed in 90% yield (0.109 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.085 g of **4nA**: R_f = 0.8 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.10−6.96 (m, 10H), 6.42 (d, J = 16.4 Hz, 1H), 5.52 (d, J = 16.4 Hz, 1H), 4.00 (d, J = 10.8 Hz, 1H), 3.68 (d, J = 10.8 Hz, 1H), 1.95 (d, J = 6.4 Hz, 1H), 1.59−1.53 (m, 1H), 1.27 (d, J = 6.4 Hz, 3H), 0.83 (s, 9H), 0.0 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.9, 138.2, 132.5, 129.2, 129.0, 128.4, 128.0, 127.9, 127.6, 126.6, 125.9, 125.8, 65.3, 37.0, 35.9, 26.0, 24.9, 18.4, 13.8, −5.2, −5.3; HRMS m/z calcd for $C_{25}H_{34}OSi$ [M + Na^+] 401.2277, found 401.2279.

***O*-*tert*-Butyldimethylsilyl((1*S**,2*S**,3*R**)-2-methyl-3-phenyl-1-vinylcyclopropyl)methanol (4nD): Procedure E.** According to the general procedure E, **4nD** was formed in 72% yield (0.063 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.109 g of **4nB**: R_f = 0.8 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.26−7.22 (m, 2H), 7.16−7.11 (m, 3H), 5.22 (dd, J = 10.8 Hz, 17.6 Hz, 1H), 5.09 (dd, J = 2.0 Hz, 17.6 Hz, 1H), 4.90 (dd, J = 1.6 Hz, 10.8 Hz, 1H), 4.02 (d, J = 10.4 Hz, 1H), 3.74 (d, J = 10.4 Hz, 1H), 2.01 (d, J = 2.4 Hz, 1H), 1.62−1.56 (m, 1H), 1.34 (d, J = 6.4 Hz, 3H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.7, 138.8, 128.9, 127.8, 125.7, 113.3, 64.4, 36.4, 36.0, 25.9, 23.6, 18.3, 13.5, −5.4, −5.5; HRMS m/z calcd for $C_{19}H_{30}OSi$ [M + Na^+] 325.1964, found 325.1969.

((1*S,2*S**,3*R**)-2-Methyl-3-phenyl-1-vinylcyclopropyl)-methanol (4n): Procedure F.** According to the general procedure A, **4n** was formed in 95% yield (0.037 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 7:3) from 0.063 g of **4nD**: R_f = 0.4 (hexanes/EtOAc, 7:3); nature, liquid; yield,

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95%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.27−7.23 (m, 2H), 7.18−7.11 (m, 3H), 5.21 (m, 2H), 5.02 (dd, J = 4.4 Hz, 8.4 Hz, 1H), 4.06 (d, J = 12 Hz, 1H), 3.73 (d, J = 12 Hz, 1H), 2.00 (d, J = 6.4 Hz, 1H), 1.67−1.61 (m, 2H), 1.37 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.0, 138.0, 128.8, 128.0, 126.0, 114.4, 64.4, 36.9, 36.8, 23.9, 13.6; HRMS m/z calcd for $C_{13}H_{16}O$ [M + Na^+] 211.1099, found 211.1102.

(*S,*Z*)-3-(2-(*N*-*p*-Toluenesulfonamido)ethylidene)-4-methyl-5-phenyltetrahydrofuran (7n): Procedure B.** According to the general procedure A, **7n** was formed in 92% yield (0.065 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.037 g of **4n**: R_f = 0.4 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, J = 8.0 Hz, 2H), 7.37−7.28 (m, 7H), 5.11−5.07 (m, 1H), 4.74 (dd, J = 5.6 Hz, 5.6 Hz, 1H), 4.57 (d, J = 14.0 Hz, 1H), 4.33 (d, J = 14.0 Hz, 1H), 4.14 (d, J = 5.6 Hz, 1H), 3.52 (dd, J = 6.4 Hz, 6.4 Hz, 2H), 2.43 (s, 3H), 2.43−2.38 (m, 1H), 0.94 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.5, 143.5, 140.0, 137.0, 129.7, 128.4, 128.0, 127.2, 126.4, 126.1, 113.8, 87.8, 68.6, 46.4, 41.7, 21.5, 13.4; HRMS m/z calcd for $C_{20}H_{23}NO_3S$ [M + Na^+] 380.1296, found 380.1298.

Procedure for the Conversion of Lactone to Lactol. To a solution of lactone (0.1 g, 0.5 mmol, 1 equiv) in DCM (3 mL) cooled to −78 °C was added a solution of DIBAL-H/toluene (20% solution, 0.55 mmol, 1.1 equiv) dropwise for 10 min. The reaction was monitored by TLC. After complete consumption of the starting material (1 h approx.), the reaction was quenched with an aqueous solution of sodium potassium tartarate at −78 °C. The reaction mixture was extracted with DCM (2 × 10 mL), and the organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography using silica gel (hexanes/EtOAc, 8:2) of the crude product afforded the lactol in its pure form in 95% yield (0.096 g).

(1*R,3*R**)-1-Phenyl-5-oxaspiro[2.5]oct-7-en-4-ol (4o/4o′).** R_f = 0.4 (hexanes/EtOAc, 8:2); ^{1}H NMR (400 MHz, $CDCl_3$) 7.29−7.19 (m, 10H), 5.69 (d, J = 2.0 Hz, 1H), 5.67 (d, J = 2.0 Hz, 1H), 4.97−4.84 (m, 4H), 4.44 (dd, J = 1.2 Hz, 16.4 Hz, 2H), 4.25 (dd, J = 1.6 Hz, 16.4 Hz, 2H), 3.91 (d, J = 5.2 Hz, 1H), 3.87 (d, J 5.2 Hz, 1H), 2.65 (dd, J = 7.6 Hz, 1H), 2.41 (dd, J = 7.6 Hz, 8.0 Hz, 1H), 1.55 (dd, J = 5.6 Hz, 8.8 Hz, 1H), 1.31 (dd, J = 5.6 Hz, 8.8 Hz, 1H), 1.22−1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.7, 137.5, 129.0, 129.0, 128.1, 126.2, 126.2, 125.8, 125.6, 125.2, 125.0, 96.2, 96.1, 61.2, 61.2, 29.2, 28.9, 28.8, 25.9, 17.0, 14.4; HRMS m/z calcd for $C_{13}H_{14}O_2$ [M + Na^+] 225.0891, found 225.0891.

5-(*N*-*p*-Toluenesulfonamido)(2*R,5*R**,7a*S**)-2-phenyl-3,5,6,7a-tetrahydro-2*H*-furo[2,3-b]pyran (7o) and 5-(*N*-*p*-Toluenesulfonamido)(2*R**,5*S**,7a*S**)-2-phenyl-3,5,6,7a-tetrahydro-2*H*-furo[2,3-b]pyran (8o): Procedure B.** R_f = 0.4 (hexanes/EtOAc, 8:2); nature, gummy mixture; yield, 0.018 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.78 (d, J = 8.0 Hz, 1.5H), 7.72−7.70 (d, J = 8.4 Hz, 0.6H), 7.36−7.26 (m, 9.3H), 5.54 (d, J = 2.4 Hz, 1 H), 5.35−5.25 (m, 2H), 5.14 (dd, J = 5.2 Hz, 10.4 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.71 (d, J = 9.6 Hz, 0.4H), 3.87−3.71 (m, 4.1 H), 3.18−3.03 (m, 0.4H), 2.83 (dd, J = 5.2 Hz, 14 Hz, 1H), 2.59−2.52 (m, 1H), 2.45−2.42 (m, 1H), 2.44 (s, 3H), 2.42 (s, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.8, 142.4, 140.7, 138.1, 130.0, 128.6, 128.4, 128.1, 127.7, 127.0, 125.8, 125.4, 120.0, 119.4, 100.1, 99.8, 81.5, 79.3, 66.9, 66.7, 47.2, 47.2, 39.5, 37.8, 21.6; HRMS m/z calcd for $C_{20}H_{21}NO_4S$ [M + Na^+] 394.1089, found 394.1088.

***O*-*tert*-Butyldimethylsilyl((1*R**,2*R**)-2-phenyl-1-((*Z*)-prop-1-en-1-yl)cyclopropyl)methanol (4pA).** To a stirred supension of triphenylethylphosphonium iodide (2.5 mmol, 2.0 equiv) in THF (3 mL) at 0 °C was added dropwise a 1.6 M solution of *n*-BuLi in THF (2 mmol, 1.5 equiv), and the solution turned orange. The formed ylide was stirred for 15 min and added to a cold solution of the crude aldehyde **4bC** (290 mg, 1 mmol, 1 equiv) obtained after ozonolysis in THF (3 mL). The reaction was monitored using TLC. After complete consumption of the aldehyde, the reaction was quenched with water and extracted with Et_2O (2 × 15 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. Flash chromatography of the crude product furnished the corresponding alkene in 67% yield (0.202 g): R_f = 0.8(hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.31−7.27 (m, 3H), 7.17−7.13 (m, 2H), 5.66−5.59 (m, 1H), 5.19 (d, J = 8.8 Hz, 1H), 3.70 (dd, J = 10.4 Hz, 17.6 Hz, 1H), 2.25 (dd, J = 6.0 Hz, 8.4 Hz, 1H), 1.94 (d, J = 6.4 Hz, 1H), 1.70 (d, J = 8.8 Hz, 3H), 1.43 (dd, J = 4.8 Hz, 8.8 Hz, 1H), 1.09 (dd, J = 5.6 Hz, 5.6 Hz, 1H), 0.99 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.6, 130.8, 128.5, 127.9, 125.3, 68.0, 29.3, 26.0, 24.8, 18.4, 16.1, 14.3, −5.3, −5.3; HRMS m/z calcd for $C_{19}H_{30}OSi$ [M + Na^+] 325.1964, found 325.1961.

((1*R,2*R**)-2-Phenyl-1-((*Z*)-prop-1-en-1-yl)cyclopropyl)-methanol (4p): Procedure E.** According to the general procedure E, **4p** was formed in 93% yield (0.058 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.100 g of **4pA**: R_f = 0.5(hexanes/EtOAc, 8:2); ^{1}H NMR (400 MHz,$CDCl_3$) 7.25−7.21 (m, 2H), 7.16−7.12 (m, 1H), 7.07 (d, J = 8.0 Hz, 2H), 5.69−5.61 (m, 1H), 5.17−5.14 (d, J = 10.8 Hz, 1H), 3.62 (d, J = 11.2 Hz, 1H), 3.54 (d, J = 11.2 Hz, 1H), 2.10 (d, J = 6.0 Hz, 8.4 Hz, 1H), 1.90 (s, 1H), 1.67 (d, J = 6.8 Hz, 3H), 1.31 (dd, J = 4.8 Hz, 8.4 Hz, 1H), 1.16−1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.7, 131.8, 128.0, 127.7, 127.0, 125.6, 70.0, 29.9, 26.3, 17.4, 14.3; HRMS m/z calcd for $C_{13}H_{16}O$ [M + Na^+] 211.1099, found 211.1095.

(*S,*Z*)-3-((*S**)-2-(*N*-*p*-Toluenesulfonamido)propylidene)-4-methyl-5-phenyltetrahydrofuran (7p): Procedure B.** According to the general procedure B, **7p** was formed in 78% yield (0.085 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.100 g of **4p**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, J = 8.0 Hz, 1.8 Hz), 7.70 (d, J = 8.0 Hz, 2H), 7.36−7.28 (m, 10 H), 7.21 (d, J = 8.0 Hz, 2H), 5.05 (m, 0.8 H), 4.98 (m, 1H), 4.83 (dd, J = 8.0 Hz, 8.4 Hz, 1H), 4.71 (dd, J = 6.0 Hz, 9.2 Hz, 0.8H), 4.67 (d, J = 10.4 Hz, 0.8 H), 4.62 (d, J = 6.4 Hz, 1H), 4.45 (dd, J = 13.4 Hz, 1.8H), 4.24−4.23 (m, 1H), 4.21−4.19 (m, 1H), 3.89−3.77 (m, 1.8H), 2.74 (ddd, J = 1 Hz, 6.4 Hz, 12.6 Hz, 1H), 2.60 (ddd, J = 1 Hz, 6.4 Hz, 12.6 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.25−2.19 (m, 1H), 1.19 (d, J = 6.4 Hz, 3H), 1.17 (d, J = 6.4 Hz, 2.5H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.2, 141.4, 141.2, 141.1, 140.9, 138.0, 137.9, 129.5, 128.4, 127.7, 127.6, 127.3, 127.2, 125.8, 125.8, 121.5, 121.2, 80.3, 80.3, 68.5, 68.3, 49.4, 49.3, 41.0, 40.9, 22.1, 22.1, 21.5, 21.4; HRMS m/z calcd for $C_{20}H_{23}NO_3S$ [M + Na^+] 380.1296, found 380.1295.

(*R)-*N*-(*p*-Toluenesulfonamido)-(2,2-dimethyltetrahydrofuran-3-yl)-2-methylbut-2-ene (10a): Procedure B.** According to the general procedure B, **10a** was formed in 75% yield (0.060 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.030 g of **9a**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.77−7.73 (m, 3.5H), 7.32−7.29 (m, 3.5H), 5.28−5.25 (m, 1.75H), 4.61 (dd, J = 6.0 Hz, 6.0 Hz, 0.6H), 4.48 (dd, J = 5.6 Hz, 5.6 Hz, 1H), 3.81−3.68 (m, 3.5H), 3.52 (d, J = 5.6 Hz, 2H), 3.46 (d, J = 5.6 Hz, 2H), 2.43 (s, 5.8H), 2.04−1.91 (m, 3.9H), 1.86−1.65 (m, 8.5H), 1.57−1.44 (m, 4.6H), 1.20 (s, 1.8H), 1.15 (s, 3H), 0.99 (s, 1.8H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.5, 143.3, 136.6, 131.0, 130.5, 129.6, 128.8, 127.1, 127.0, 81.3, 81.2, 64.7, 64.6, 50.9, 48.5, 48.3, 44.0, 31.8, 31.8, 28.5, 28.5, 27.6, 27.5, 22.0, 21.9, 21.7, 21.5, 14.4; HRMS m/z calcd for $C_{18}H_{27}NO_3S$ [M + Na^+] 360.1609, found 360.1606.

(*R)-2-(Benzyloxy)-2-((1*S**,3*R**)-3-(1-hydroxyethyl)-2,2-dimethylcyclobutyl)ethanol 9bA.** According to the general procedure A, **10a** was formed in 75% yield (0.113 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 4:6): R_f = 0.5 (hexanes/EtOAc, 5:5); nature, liquid; yield, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.37−7.26 (m, 5H), 4.60−4.58 (s, 2H), 3.74−3.63 (m, 2H), 3.48−3.36 (m, 2H), 2.04−1.94 (m, 2H), 1.92−1.75 (b, 2H), 1.75−1.61 (m, 2H), 1.12−1.10 (s, 3H), 1.05−1.04 (s, 5H), 1.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.5, 138.4, 128.4, 127.7, 127.6, 81.0, 80.9, 72.5, 72.3, 69.0, 68.9, 63.7, 50.1, 49.9, 42.8, 42.4, 39.5, 39.3, 31.5, 30.7, 25.5, 24.8, 22.6, 21.2, 16.7, 16.6; HRMS m/z calcd for $C_{17}H_{26}O_3$ [M + Na^+] 301.1780, found 301.1782.

1-((1*R,3*S**)-3-((*R**)-1-(Benzyloxy)-2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2,2-dimethylcyclobutyl)ethanol (9bB).** According to the general procedure C, **9bB** was formed in 75% yield (0.115 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 3:7) from 0.113 g of **9bA**: R_f = 0.3 (hexanes/EtOAc, 5:5); nature, liquid; yield, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.25−7.18 (m, 5H), 4.70 (d, J = 11.6 Hz, 1H), 4.47 (d, J = 11.6 Hz, 1H), 3.64−3.57 (m, 1H), 3.55−3.44 (m, 2H), 3.33−3.28 (m, 1H), 1.90−1.77 (m, 2H), 1.63−1.56 (m, 1H), 1.21 (dd, J = 10 Hz, 20 Hz,

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1H), 1.03 (s, 3H), 0.97 (s, 3H), 0.97 (d, J = 6.4 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.3, 128.2, 127.7, 127.3, 80.9, 72.9, 69.2, 65.9, 49.8, 42.6, 39.3, 31.7, 25.9, 23.8, 21.2, 18.3, 17.0, −5.4, −5.4; HRMS m/z calcd for $C_{23}H_{40}O_3Si$ [M + Na^+] 415.2644, found 415.2642.

1-((1*R,3*S**)-3-((*R*)-1-(Benzyloxy)-2-((*tert*-butyldimethylsilyl)-oxy)ethyl)-2,2-dimethylcyclobutyl)ethanone 9bC.** To a stirred solution of cyclopropane **9bB** (0.3 mmol, 1 equiv) in DCM (6 mL) was added DMP (0.137 g, 1.1 mmol, 1.1 equiv) at 0 °C. The reaction was monitored by TLC. After complete conversion of the starting material, the excess DMP present was quenched by the treatment of 20% aq. solution of $Na_2S_2O_3$ (5 mL). The mixture was washed with $NaHCO_3$ solution (20 mL) and extracted with DCM (2 × 20 mL). The organic layer was dried over anhyd. Na_2SO_4 and concentrated in vacuo. The crude product was carried over to the next step following procedure D(b) without further purification. **9bC** was formed in 87% yield (0.100 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2): R_f = 0.5 (hexanes/EtOAc, 9:1); nature, liquid; yield, 87%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.35−7.25 (m, 5H), 4.76 (d, J = 11.2 Hz, 1H), 4.55 (d, J = 11.2 Hz, 1H), 3.58 (dd, J = 3.6 Hz, 10.8 Hz, 1H), 3.53 (dd, J = 3.6 Hz, 10.8 Hz, 1H), 3.40−3.35 (m, 1H), 2.79 (dd, J = 7.2 Hz, 10.0 Hz, 1H), 2.16 (dd, J = 10.4 Hz, 21.1 Hz, 1H), 2.10−2.04 (m, 1H), 2.04 (s, 3H), 1.96−1.89 (m, 1H), 1.28 (s, 3H), 0.91 (s, 9H), 0.91 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 208.6, 139.4, 128.8, 128.3, 128.0, 81.1, 73.7, 66.1, 54.3, 43.4, 43.3, 31.2, 30.7, 26.4, 21.5, 18.8, 18.1, −4.8, −4.9; HRMS m/z calcd for $C_{23}H_{38}O_3Si$ [M + Na^+] 413.2488, found 413.2480.

2-((1*R,3*S**)-3-((*R**)-1-(Benzyloxy)-2-((*tert*-butyldimethylsilyl)-oxy)ethyl)-2,2-dimethylcyclobutyl)propene (9bD): Procedure D(b).** According to the general procedure D(b), **9bD** was formed in 80% yield (0.081 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.100 g of **9bC**: R_f = 0.8 (hexanes/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) 7.34−7.30 (m, 5H), 4.80−4.77 (m, 2H), 4.58−4.55 (m, 2H), 3.63−5.52 (m, 2H), 3.39−3.35 (m, 1H), 2.33- 2.28 (m, 1H), 2.00−1.92 (m, 2H), 1.71−1.67 (m, 1H), 1.68 (s, 3H), 1.14 (s, 3H), 0.92 (s, 9H), 0.79 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.2, 139.3, 133.8, 128.6, 128.5, 127.8, 127.3, 109.4, 81.1, 73.0, 66.0, 48.8, 42.7, 41.0, 31.0, 25.9, 23.9, 23.0, 18.3, 16.6, −5.4, −5.4; HRMS m/z calcd for $C_{24}H_{40}O_2Si$ [M + Na^+] 411.2695, found 411.2691.

2-((1*R,3*S**)-3-((*R**)-1-(Benzyloxy)-2-hydroxyethyl)-2,2-dimethylcyclobutyl)propene 9b.** According to the general procedure E, **9b** was formed in 92% yield (0.052 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 9:1) from 0.081 g of **9bD**: R_f = 0.8 (hexanes/EtOAc, 9:1); nature, liquid; yield, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) 7.35−7.25 (m, 5H), 4.82 (s, 1H), 4.62−4.58 (s, 3H), 3.70−3.66 (m, 1H), 3.45−3.35 (m, 2H), 2.38−2.34 (s, 1H), 2.08−2.00 (s, 3H), 1.85−1.77 (m, 1H), 1.65 (s, 3H), 1.16 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.0, 138.5, 128.4, 127.7, 109.6, 81.2, 72.5, 63.8, 49.2, 42.5, 41.2, 30.9, 24.8, 23.0, 16.4; HRMS m/z calcd for $C_{18}H_{26}O_2$ [M + Na^+] 297.1830, found 297.1829.

(*R)-*N*-(*p*-Toluenesulfonamido)-4-benzyloxy-(2,2-dimethyltetrahydrofuran-3-yl)-2-methylbut-2-ene (10b).** According to the general procedure B, **9b** was formed in 76% yield (0.064 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.052 g of **9b**: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.73−7.71 (m, 2H), 7.34−7.26 (m, 8H), 5.33−5.31 (m, 1H), 4.48−4.33 (m, 3H), 3.97−3.90 (m, 1H), 3.90−3.73 (m, 2H), 3.50−3.39 (m, 2H), 2.42 (s, 1.5H), 2.41 (s, 1.5H), 2.07−2.03 (m, 1H), 1.97−1.84 (m, 2H), 1.66 (s, 1H), 1.64 (s, 1.5H), 1.57 (s, 1.5H), 1.27 (s, 1H), 1.24 (s, 1.5 H), 1.04 (s, 1H), 0.96 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.4, 143.3, 138.0, 137.9, 137.0, 136.6, 131.2, 130.7, 129.6, 128.4, 128.3, 127.7, 127.6, 127.1, 127.0, 126.7, 84.9, 84.5, 81.9, 81.9, 71.9, 71.7, 69.5, 69.4,53.9, 53.7, 51.0, 43.4, 28.3, 28.1, 27.4, 27.1, 25.5, 22.3, 21.8, 21.4, 14.4; HRMS m/z calcd for $C_{25}H_{33}NO_4S$ [M + Na^+] 466.2028, found 466.2025.

(*S)-*N*-(4-(2,2-Dimethyl-5-oxotetrahydrofuran-3-yl)-3-methylbut-2-en-1-yl)-*p*-toluenesulfonamide (10c).** According to the general procedure B, **10c** was formed in 70% yield (0.068 g) as a gummy liquid after flash column chromatography using silica gel (hexanes/EtOAc, 8:2) from 0.050 g: R_f = 0.5 (hexanes/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) 7.77−7.73 (m, 1.6H), 7.33−7.31 (m, 2H), 5.24−5.10 (m, 1.6H), 3.51−3.44 (m, 2H), 2.57−2.52 (m, 0.9H), 2.43 (s, 2.7H), 2.25−2.09 (m, 2H), 1.66 (s, 1.4 H), 1.59 (s, 1.6H), 1.40 (s, 1H), 1.39 (s, 1.4H), 1.25 (s, 1H), 1.20 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.6, 175.5, 143.5, 143.4, 137.0, 136.7, 132.8, 132.4, 129.7, 127.1, 127.0, 126.4, 124.4, 86.4, 50.5, 45.5, 45.2, 43.2, 34.8, 34.7, 27.8, 27.6, 27.4, 21.8, 21.8, 21.5, 14.5, 14.1; HRMS m/z calcd for $C_{18}H_{25}NO_4S$ [M + Na^+] 374.1402, found 374.1401.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds, crystal data (CIF) for **7d**, and Cartesian coordinates from the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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