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Electrophilic Addition of Allylic Carbocations to 2-Cyclopropylidene-2-arylethanols: A Strategy to 3-Oxabicyclo[3.2.0]heptanes

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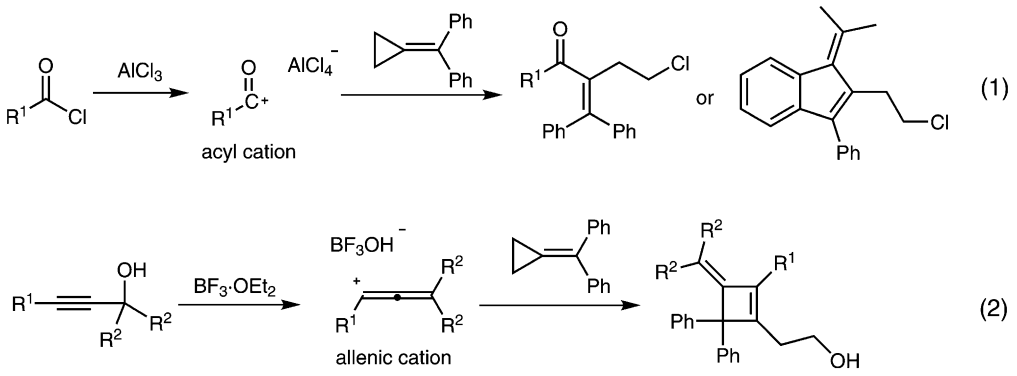
Abstract: We have developed an electrophilic addition of allylic carbocations to 2-cyclopropylidene-2-arylethanols constructing carbon-carbon bonds with excellent regio- and stereoselectivities. The reaction affords 3-oxabicyclo[3.2.0]heptanes in moderate to good yields *via* the electrophilic addition/ring-opening/vinyl group shift/intramolecular cyclization sequence.

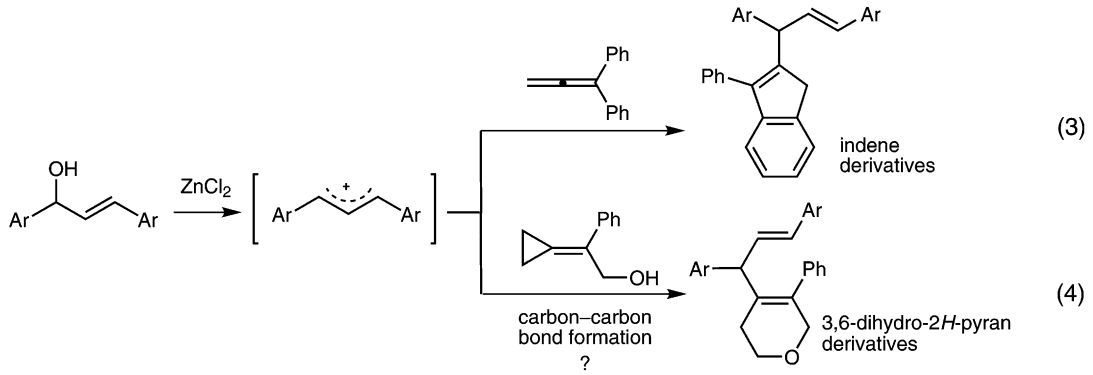
Keywords: C–C bond formation; 2-cyclopropylidene-2-arylethanols; electrophilic addition; 3-oxabicyclo[3.2.0]heptanes; vinyl group shift

Introduction

The electrophilic addition of methylenecyclopropanes (MCPs)[1] is rather attractive since the possible ring-opening may lead to the construction of interesting and complex structures of synthetic or pharmaceutical importance.[2] During the last decades, the direct electrophilic additions of MCPs have been widely investigated, employing a variety of electrophiles, such as H^+,[2a–d] X^+,[2e,f] $ArSe^+$,[2g–i] and ArS^+.[2h] Particularly, the introduction of suitable carbocations as the electrophile has attracted much attention due to the efficiency of carbon-carbon bond formation and the potential utility of the products. In 2007, the electrophilic addition of acyl carbocation to MCPs was successfully realized in our laboratory [Scheme 1, Eq. (1)].[3] Later, Shi's group employed propargylic/allenic carbocation as the electrophile [Scheme 1, Eq. (2)].[4] However, the electrophilic addition of MCPs utilizing allylic carbocations as electrophiles has not been documented well due to the difficulties in the introduction of carbocations with proper reactivity and the control of chemoselectivity. Recently, the electrophilic reaction of allylic carbocation and allenes affording



Scheme 1. Previous work on the electrophilic additions of acyl and propargylic/allenic carbocations with MCPs.



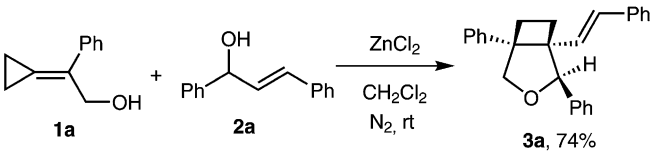
Scheme 2. The electrophilic addition of allylic carbocation.

indene derivatives has been also reported [Scheme 2, Eq. (3)].[5] Since allylic carbocation intermediates could be easily formed *via* the treatment of 1,3-diarylprop-2-en-1-ols with Lewis acid, we were interested in whether the allylic carbocation could be introduced as the electrophile to react with MCPs.

Based on this knowledge, we envisioned that if a hydroxy group is equipped as an intramolecular nucleophile, a cyclic product may be generated *via* an electrophilic addition/ring-opening/intramolecular nucleophilic cyclization sequence [Scheme 2, Eq. (4)]. Herein, we wish to report the $ZnCl_2$-promoted electrophilic addition of 1,3-diarylprop-2-en-1-ols to 2-cyclopropylidene-2-arylethanols to furnish 3-oxabicyclo-[3.2.0]heptane derivatives.

Results and Discussion

Initially, the reaction was carried out utilizing 2-cyclopropylidene-2-phenylethanol **1a**, 1,3-diphenyl-prop-2-en-1-ol **2a** and $ZnCl_2$ in CH_2Cl_2 at room temperature. Interestingly, the reaction did not form the preconceived 3,6-dihydro-2*H*-pyran derivative [Scheme 2, Eq. (4)].[6] Instead, an unexpected new product **3a** was obtained (Scheme 3). The structure of **3a** was determined by the X-ray diffraction analysis, namely (1*S**,2*R**,5*R**,*E*)-2,5-diphenyl-1-styryl-3-oxabicyclo-[3.2.0]heptane (Figure 1).[7] Apparently, the 1,3-diphenylallyl group from **2a** no longer existed in the product, being transformed to the phenyl group and the styryl group. The reaction showed excellent stereoselectivity, giving the product **3a** with the cyclobutane



Scheme 3. The trial reaction for the electrophilic addition of **1a** and **2a** in the presence of $ZnCl_2$.

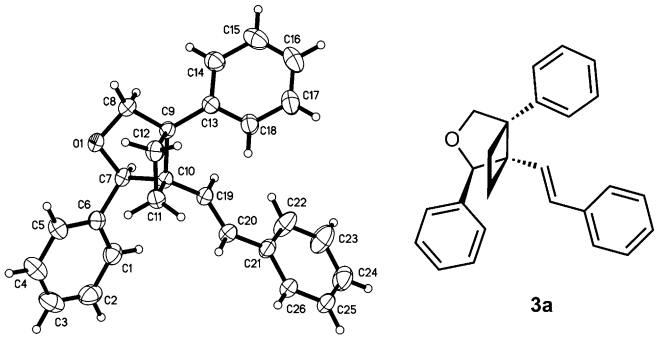


Figure 1. ORTEP representation of one enantiomer of **3a**.

and the phenyl group (from **2a**) on the same side of the tetrahydrofuran ring.

The cyclobutane[8] and tetrahydrofuran[9] units are prominent structural features of many bioactive natural products and pharmaceutical molecules. Moreover, the structural skeleton of **3a**, 3-oxabicyclo-[3.2.0]heptane, has been proved to be active scaffold in novel bicyclic nucleosides **A**–**E** with anti-HIV activity (Figure 2).[10] Synthetic methods have been developed to approach 3-oxabicyclo[3.2.0]heptane deriva-

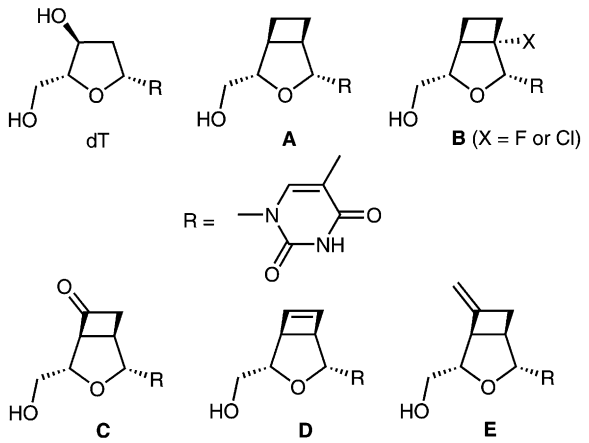
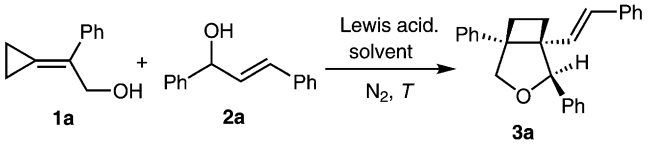


Figure 2. Anti-HIV agent dT and the novel class of nucleosides **A**–**E** built on a 3-oxabicyclo[3.2.0]heptane scaffold.

Table 1. Optimization of the conditions for the electrophilic addition reaction of 2-cyclopropylidene-2-phenylethanol **1a** and 1,3-diphenylprop-2-en-1-ol **2a**.[a]



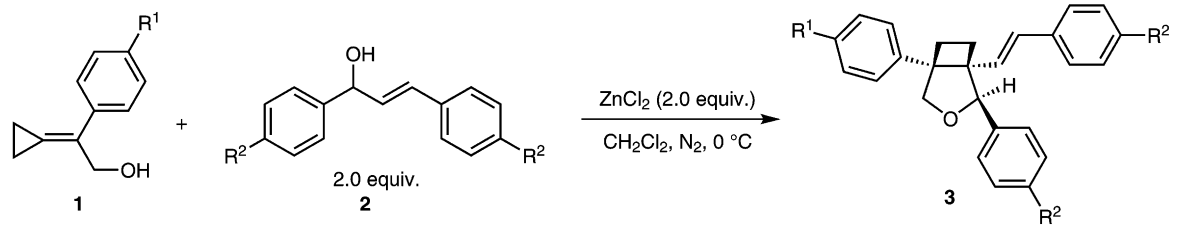
Entry	Solvent	Temperature [°C]	Lewis Acid	Time [h]	Yield of **3a** [%][b]
1	DCM	r.t.	$ZnCl_2$	5	74
2	DCM	r.t.	$FeCl_3{\cdot}6H_2O$	10.5	0
3	DCM	r.t.	$FeCl_3$	24	trace
4	DCM	r.t.	$ZrCl_4$	2.5	21
5	toluene	r.t.	$ZnCl_2$	2.5	67
6	THF	r.t.	$ZnCl_2$	12.2	26
7	$CHCl_3$	r.t.	$ZnCl_2$	6.2	36
8	DCE	r.t.	$ZnCl_2$	1	69
9	DCM	0	$ZnCl_2$	6.7	79
10	DCM	−40	$ZnCl_2$	9.3	71
11[c]	DCM	0	$ZnCl_2$	2.5	86

[a] Unless otherwise specified, the reactions were conducted using 0.3 mmol of **1a**, 0.3 mmol of **2a**, and 0.3 mmol of Lewis acid in 3 mL of solvent under a nitrogen atmosphere in a Schlenk tube.
[b] Isolated yield.
[c] The reaction was conducted utilizing 0.3 mmol of **1a**, 0.6 mmol of **2a**, and 0.6 mmol of $ZnCl_2$.

tives *via* the [2+2]photocycloaddition or the Pd-catalyzed [2+2]cycloaddition of olefins.[11] However, in most of the known procedures, the irradiation with high energy UV light, the employment of transition metal catalyst, and the unsatisfactory stereoselectivity are inevitable disadvantages. Therefore, an efficient strategy to synthesize 3-oxabicyclo[3.2.0]heptane analogues is still of significant importance. Thus, we tried to optimize the conditions of this electrophilic addition (Table 1). Several Lewis acids were tested first. $FeCl_3{\cdot}6H_2O$ and $FeCl_3$ barely gave any product **3a** (Table 1, entries 2 and 3) and $ZrCl_4$ resulted in a very low yield (21%, Table 1, entry 4). The solvent effect was also examined (Table 1, entries 5–8). It is demonstrated that the reaction can also proceed smoothly in toluene and 1,2-dichloroethane, yielding **3a** in moderate yields (Table 1, entries 5 and 8). Reactions conducted in THF or $CHCl_3$ gave **3a** in merely 26% and 36% yields, respectively (Table 1, entries 6 and 7). Dichloromethane was an even better choice. When the reaction was carried out at 0 °C, the yield of **3a** was raised to 79% (Table 1, entry 9). However, the reaction did not yield **3a** in higher yield when the reaction temperature was −40 °C (71%, Table 1, entry 10). By utilizing 2.0 equiv. of **2a** and $ZnCl_2$, the yield of **3a** could be further improved to 86% (Table 1, entry 11).

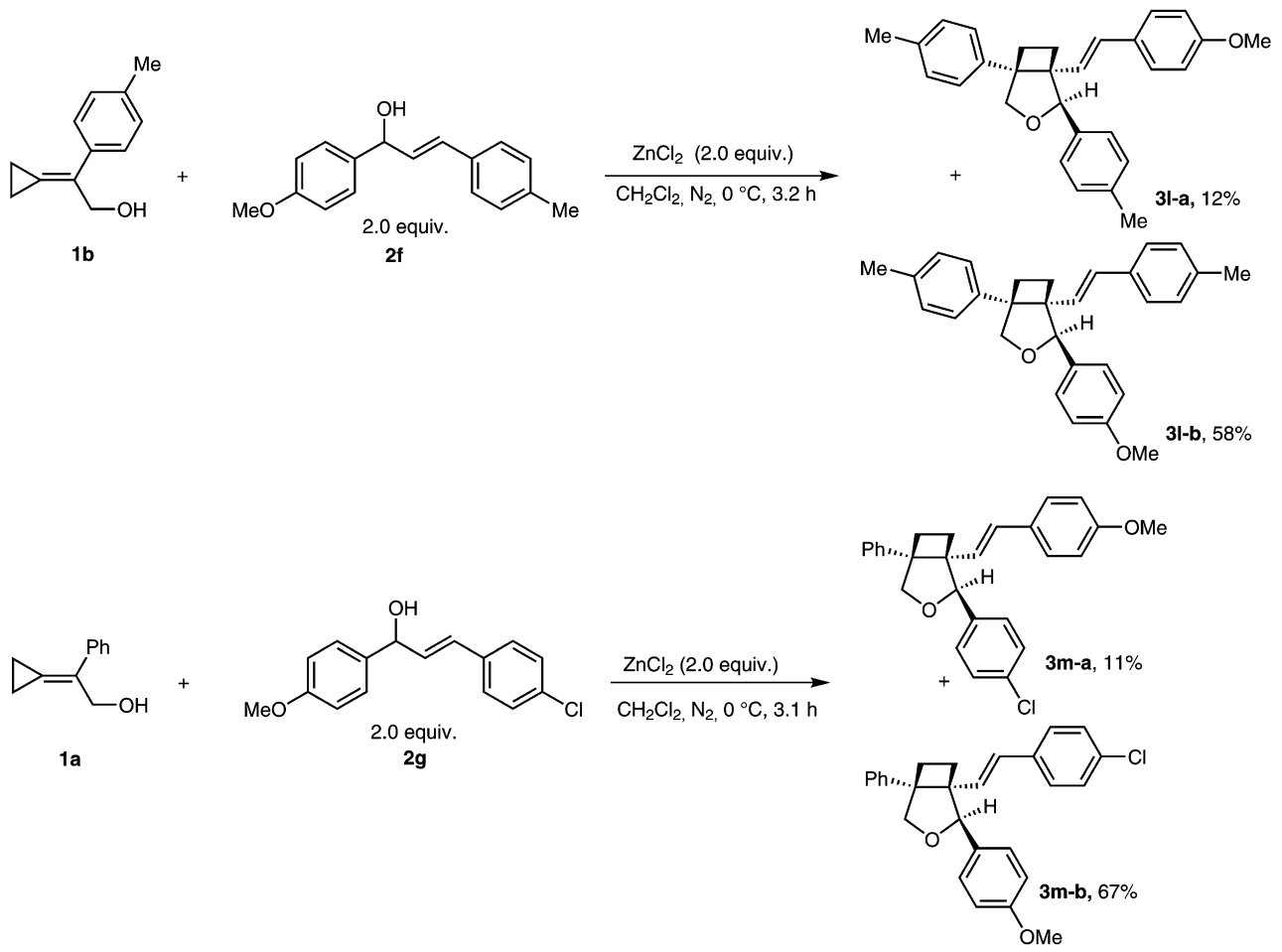
With the optimal conditions in hand, we explored the scope of this electrophilic addition of a series of 1,3-diarylprop-2-en-1-ols **2** with 2-cyclopropylidene-2-arylethanols **1** to synthesize 3-oxabicyclo-[3.2.0]heptanes **3** (Table 2). It is demonstrated that

Table 2. Reactions of 2-cyclopropylidene-2-arylethanols **1** with 1,3-diarylprop-2-en-1-ols **2** for the synthesis of 3-oxabicyclo-[3.2.0]heptane derivatives **3**.[a]



Entry	**1** (R^1)	**2** (R^2)	Time [h]	Yield of **3** [%][b]
1	**1a** (R^1=H)	**2a** (R^2=H)	2.5	86 (**3a**)
2	**1a**	**2b** (R^2=Cl)	3	71 (**3b**)
3	**1a**	**2c** (R^2=Br)	2.9	73 (**3c**)
4	**1a**	**2d** (R^2=Me)	2.8	61 (**3d**)
5	**1a**	**2e** (R^2=OMe)	3	63 (**3e**)
6	**1b** (R^1=Me)	**2a** (R^2=H)	4.3	77 (**3f**)
7	**1b**	**2c** (R^2=Br)	5.1	75 (**3g**)
8	**1b**	**2e** (R^2=OMe)	3.7	49 (**3h**)
9	**1c** (R^1=OMe)	**2a** (R^2=H)	2.3	64 (**3i**)
10	**1d** (R^1=Cl)	**2a** (R^2=H)	2.6	65 (**3j**)
11	**1d**	**2c** (R^2=Br)	2.5	77 (**3k**)

[a] The reactions were conducted using 0.3 mmol of **1**, 0.6 mmol of **2**, and 0.6 mmol of $ZnCl_2$ in 3 mL of CH_2Cl_2 under nitrogen atmosphere in a Schlenk tube.
[b] Isolated yield of **3** based on **1**.



Scheme 4. Reactions of **1a** or **1b** with non-symmetrical 1,3-diarylprop-2-en-1-ols **2f** and **2g**.

both 1,3-diarylprop-2-en-1-ols **2b** and **2c** bearing electron-deficient aryl rings could be employed smoothly to yield products **3b** and **3c** in 71% and 73% yields, respectively (Table 2, entries 2 and 3). When an aryl ring with an electron-donating group Me or OMe was introduced, i.e., **2d** or **2e**, products **3d** and **3e** were generated in relatively lower yields (61% and 63%, Table 2, entries 4 and 5). Moreover, 2-cyclopropylidene-2-arylethanols **1b**, **1c** and **1d** with substituents Me, OMe and Cl on the aryl ring were also applied successfully and gave corresponding products **3f–k** in moderate to good yields (Table 2, entries 6–11).

Furthermore, when 1,3-diarylprop-2-en-1-ol **2f** with two differently substituted aryl rings was employed to react with **1b**, two regioisomers **3l-a** and **3l-b** were isolated in 12% and 58% yields (Scheme 4). Similarly, the reaction of **1a** and non-symmetrical **2g** gave the regioisomers **3m-a** and **3m-b** in 11% and 67% yields, respectively. The relative configurations of major isomer **3l-b** and **3m-b** were determined by the NOESY study (Figure 3).

Interestingly, when **2h** equipped with a strong electron-withdrawing group, NO_2, and a strong electron-donating group, OMe, was employed, the reaction

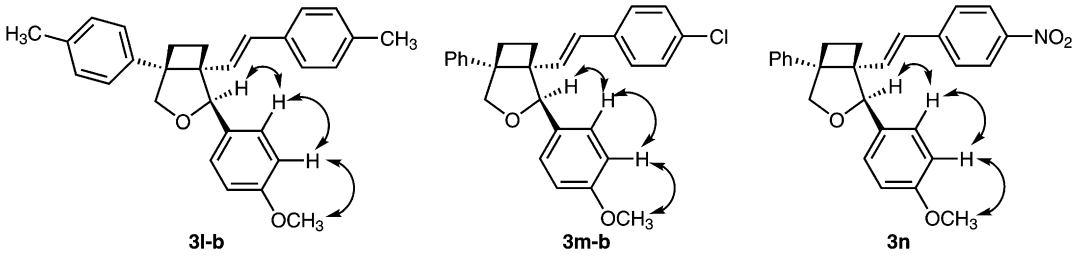
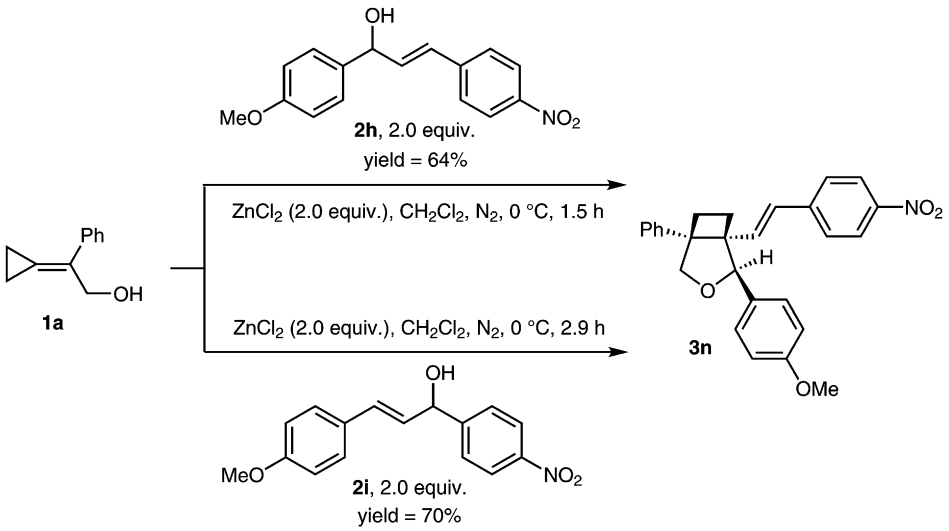


Figure 3. NOESY studies of **3l-b**, **3m-b**, and **3n**.

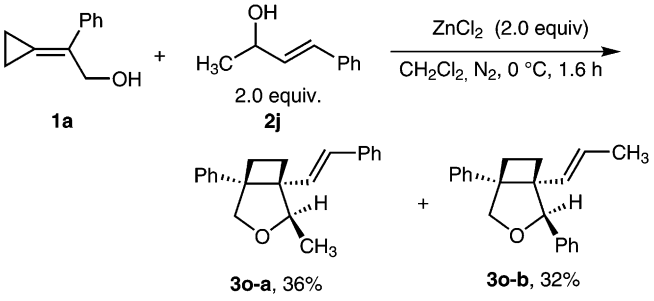


Scheme 5. Reactions of **1a** with isomeric non-symmetrical 1,3-diarylprop-2-en-1-ols **2h** and **2i**.

showed excellent regioselectivity, giving isomer **3n** in 64% yield as the sole product (Scheme 5). The reaction with isomeric non-symmetrical 1,3-diarylprop-2-en-1-ol **2i** also gave the same product **3n** as the only product in 70% yield, which indicates that **2h** and **2i** give the same allylic carbocation intermediate with the electron-rich aryl group stabilizing the carbocationic center.

Furthermore, (*E*)-4-phenylbut-3-en-2-ol **2j** with an alkyl group and a phenyl group could also be employed to react with **1a**, affording two regioisomers **3o-a** and **3o-b** in 36% and 32% yields, respectively (Scheme 6). The structures of the isomers **3o-a** and **3o-b** were established by the analysis of the ^{1}H NMR spectrum.

Equipped with two allylic groups sharing the same CH(OH) unit, (1*E*,4*E*)-1,5-diarylpenta-1,4-dien-3-ols **4** may also act as a precursor of an allylic carbocation and undergo a similar electrophilic addition reaction with 2-cyclopropylidene-2-arylethanols **1**. With this notion in mind, we tested the reaction of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-ol **4a** and 2-cyclo-propylidene-2-phenylethanol **1a** under the optimized reaction conditions (Table 3, entry 1). The reaction proceeded



Scheme 6. Reaction of **1a** with **2j**.

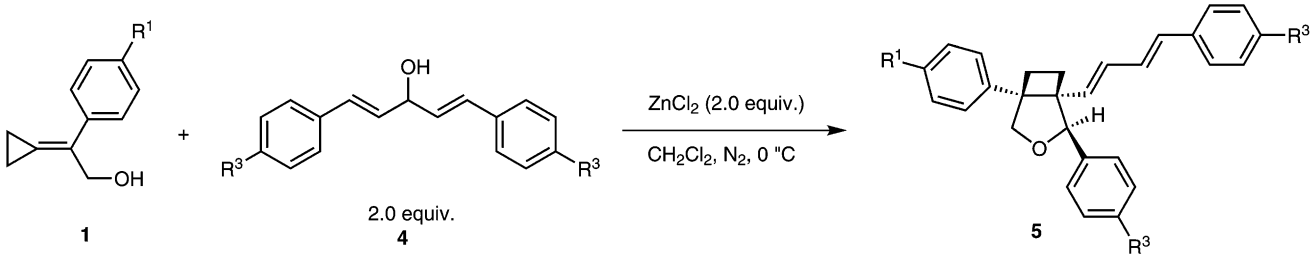
successfully, and the product **5a** bearing a conjugated 1,3-dienyl group, namely, (1*S**,2*R**,5*R**)-2,5-diphenyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-3-oxabicyclo-[3.2.0]heptane, was isolated in 62% yield (Table 3, entry 1). (1*E*,4*E*)-1,5-Diarylpenta-1,4-dien-3-ols **4b** and **4c** with a *p*-Me or *p*-Cl substituent could be employed smoothly, affording corresponding products **5b** and **5c** in 51% and 59% yields, respectively (Table 3, entries 2 and 3). Also, the reactions of 2-cyclopropylidene-2-*p*-tolylethanol **1b** with **4a** and **4d** yielded **5d** and **5e** in moderate yields (Table 3, entries 4 and 5).

Moreover, the reaction of (*E*)-1,3-diphenylprop-2-enyl amine **6** with **1b** under the optimal conditions led to an unidentified mixture (Scheme 7).

To shed light on the possible mechanism, some control experiments were conducted. By employing 2.0 or 4.0 equiv. of HCl (solution in anhydrous CH_2Cl_2), the reaction of **1d** with **2a** afforded product **3j** in 19% and 22% yields, respectively, indicating that $ZnCl_2$ is vital in the reaction (compare Scheme 8 with Table 2, entry 10).

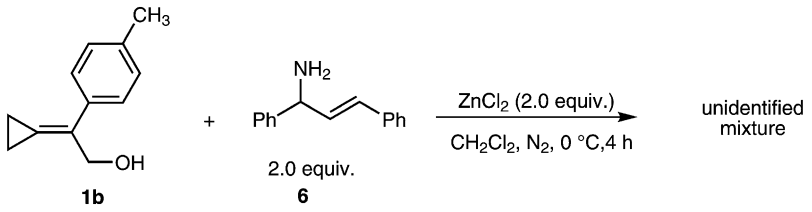
Based on these experimental facts, a plausible mechanism for this reaction is proposed (Scheme 9). Allylic carbocation intermediate **A** would be formed *via* the interaction of $ZnCl_2$ with the allylic alcohol **2**. Electrophilic addition of the *in-situ* generated cation **A** with the C=C bond on the C-1 position of the MCP **1** affords the cation intermediate **B**. Notably, when the two aryl rings of the allylic alcohol **2** are differently substituted, the electrophilic addition could occur on both C-1 and C-3 atoms of carbocation **A**, and the electrophilic addition on the carbon atom near the relatively electron-rich aryl group is favored (Scheme 4 and Scheme 5). The cyclobutane intermediate **C** is formed *via* the ring-opening 1,2-carbon shift process. The observation of the highly stereoselective formation of product **3** may suggest that the

Table 3. Reactions of 2-cyclopropylidene-2-arylethanols **1** with (1*E*,4*E*)-1,5-diarylpenta-1,4-dien-3-ols **4** for the synthesis of 3-oxabicyclo[3.2.0]heptane derivatives **5**.[a]

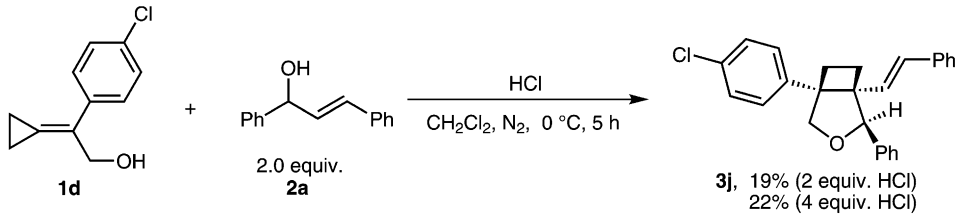


Entry	**1** (R^1)	**4** (R^3)	Time [h]	Yield of **5** [%][b]
1	**1a** (R^1 = H)	**4a** (R^3 = H)	3.8	62 (**5a**)
2	**1a**	**4b** (R^3 = Me	4.8	51 (**5b**)
3	**1a**	**4c** (R^3 = Cl)	3	59 (**5c**)
4	**1b** (R^1 = Me)	**4a** (R^3 = H)	4.8	53 (**5d**)
5	**1b**	**4d** (R^3 = Br)	4.3	57 (**5e**)

[a] The reactions were conducted using 0.3 mmol of **1**, 0.6 mmol of **4**, and 0.6 mmol of $ZnCl_2$ in 3 mL of CH_2Cl_2 under nitrogen atmosphere in a Schlenk tube.
[b] Isolated yield of **5** based on **1**.



Scheme 7. Reaction of **1b** with (*E*)-1,3-diphenylprop-2-enylamine **6**.

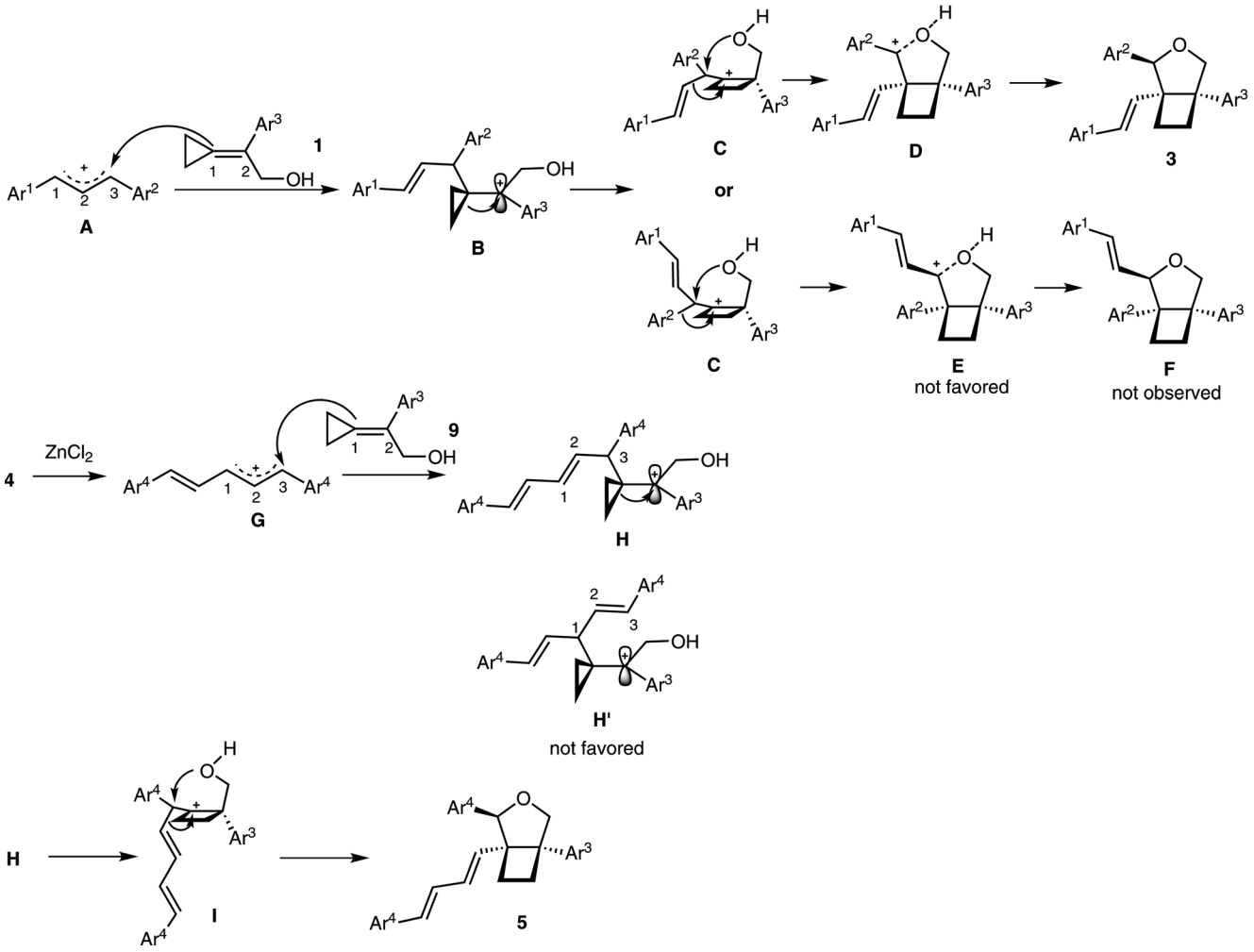


Scheme 8. Experiment with HCl replacing $ZnCl_2$.

subsequent vinyl migration/intramolecular cyclization process occurs in a concerted manner. The transient intermediate **D** bearing the benzylic carbocation is more stable than **E** with the allylic carbocation,[12] which may explain the exclusive migration of vinyl group forming **3**, not **F**. The *cis*-orientation of the vinyl group and the Ar^3 is determined by the rigid bicyclic skeleton while the *trans*-orientation of that and the Ar^2 may be explained by avoiding the steric interaction of these two groups. Similarly, (1*E*,4*E*)-1,5-diarylpenta-1,4-dien-3-ol **4** affords cation **G** in the presence of $ZnCl_2$. The electrophilic addition occurs on the C-3 position with perfect regioselectivity due to the higher stability of intermediate **H** as compared to **H′**.[13] Subsequent ring-opening/vinyl group shift/intramolecular cyclization sequence affords product **5** bearing the conjugated 1,3-dienyl group.

Conclusions

In conclusion, we have disclosed the first electrophilic addition of allylic carbocation with MCPs. 3-Oxabicyclo[3.2.0]heptanes, the skeleton of novel nucleosides, have been constructed in moderate to good yields. In contrast to the conventional synthetic methods, this electrophilic reaction strategy showed excellent regio- and stereoselectivities. In addition, the uti-



Scheme 9. Proposed mechanism.

lization of high energy UV light and transition metal catalysts was avoided, affording the desirable products in an economical and environmentally friendly manner. Due to the high efficiency of the carbon-carbon bond formation, the excellent selectivity of the reaction and the potential utility of the products, this methodology may be of high interest for organic and pharmaceutical chemistry.

Experimental Section

Materials

All reactions were conducted under an N_2 atmosphere and in oven-dried glassware. Anhydrous solvents were distilled before use: THF and toluene were distilled from sodium benzophenone; CH_2Cl_2, $CHCl_3$ and $ClCH_2CH_2Cl$ were distilled from P_2O_5. Petroleum ether refers to the fraction with boiling point in the range 60–90 °C. 2-Cyclopropylidene-2-arylethanols **1**,[14] (*E*)-1,3-diphenyl-prop-2-en-1-ols **2a**–**i**,[15b–i] (*E*)-4-phenylbut-3-en-2-ol **2j**,[15a,j] (1*E*,4*E*)-1,5-diarylpenta-1,4-dien-3-ols **4**[16] and (*E*)-1,3-diphenylprop-2-en-1-amine **6**[17] were prepared according to the known procedures. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. ^{1}H NMR experiments of compounds **3f**, **3h**, **3i**, **3j**, **3k**, **3l-a**, **3o-a**, **5c** and **5e** were measured with tetramethylsilane (0 ppm) in C_6D_6 or the signal of residual benzene (7.16 ppm) as the internal reference. Other ^{1}H NMR experiments were measured with tetramethylsilane (0 ppm) in $CDCl_3$ or the signal of residual chloroform (7.26 ppm) as the internal reference. ^{13}C NMR experiments were measured in relative to the signal of residual chloroform (77.0 ppm) in $CDCl_3$.

Typical Experimental Procedure for 1[14a]

To a stirred suspension of NaH (2.0 g, 51 mmol) in anhydrous THF (50 mL) was added cyclopropyltriphenylphosphonium bromide (20.3 g, 53 mmol) at room temperature. After being stirred for 10 h at 65 °C, a solution of 2-(*tert*-butyldiphenylsilyloxy)-1-arylethanone (22.3 mmol) in THF (10 mL) was added, followed by stirring for 3 h at the same temperature. Then the resulting mixture was quenched with water (50 mL) and extracted with Et_2O (40 mL × 3). The combined extracts were washed with brine and dried over

Na_2SO_4. Filtration, evaporation, and purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded cyclopropylideneethyl silyl ether. To a stirred solution of the silyl ether (0.5 mmol) in THF (10 mL) was added a 1 M solution of Bu_4NF in THF (1.0 mL, 1.0 mmol). After being stirred for 3 h at room temperature, the resulting mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with brine. The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **1**.

2-Cyclopropylidene-2-phenylethanol (1a):[6,14b,c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.0 Hz, 2H, Ar-H), 7.33 (t, J = 7.5 Hz, 2H, Ar-H), 7.22 (t, J = 7.5 Hz, 1H, Ar-H), 4.66 (s, 2H, CH_2), 2.75 (brs, 1H, OH), 1.52–1.26 (m, 2H, CH_2), 1.25–1.14 (m, 2H, CH_2).

2-Cyclopropylidene-2-*p*-tolylethanol (1b):[6,14b,c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.6 Hz, 2H, Ar-H), 7.16 (t, J = 7.6 Hz, 2H, Ar-H), 4.66 (s, 2H, CH_2), 2.34 (s, 3H, CH_3), 1.93 (brs, 1H, OH), 1.44–1.36 (m, 2H, CH_2), 1.25–1.18 (m, 2H, CH_2).

2-Cyclopropylidene-2-(4-methoxyphenyl)ethanol (1c):[6,14c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.0 Hz, 2H, Ar-H), 6.86 (d, J = 8.4 Hz, 2H, Ar-H), 4.63 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 2.01 (brs, 1H, OH), 1.43–1.33 (m, 2H, CH_2), 1.24–1.10 (m, 2H, CH_2).

2-(4-Chlorophenyl)-2-cyclopropylideneethanol (1d):[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2H, Ar-H), 7.32 (d, J = 8.4 Hz, 2H, Ar-H), 4.69 (s, 2H, CH_2), 1.88 (brs, 1H, OH), 1.55–1.38 (m, 2H, CH_2), 1.27–1.18 (m, 2H, CH_2).

Typical Experimental Procedure for 2 and 4[15a]

To a solution of (*E*)-1,3-diarylprop-2-en-1-one (or (1*E*,4*E*)-1,5-diarylpenta-1,4-dien-3-one) (5 mmol) in 15 mL of CH_3OH was added $NaBH_4$ (209 mg, 5.5 mmol). The reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, water was added to quench the reaction. CH_3OH was removed under reduced pressure, and the residue was extracted with Et_2O (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **2** (or **4**).

(*E*)-1,3-Diphenylprop-2-en-1-ol (2a):[15b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.16 (m, 10H, Ar-H), 6.70 (d, J = 16.0 Hz, 1H, CH=), 6.39 (dd, J = 6.6, 15.8 Hz, 1H, CH=), 5.39 (d, J = 6.4 Hz, 1H, PhCH), 2.04 (brs, 1H, OH).

(*E*)-1,3-Bis(4-chlorophenyl)prop-2-en-1-ol (2b):[15c,d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.15 (m, 8H, Ar-H), 6.60 (d, J = 15.6 Hz, 1H, CH=), 6.28 (dd, J = 6.4, 16.0 Hz, 1H, CH=), 5.33 (d, J = 6.4 Hz, 1H, ArCH), 2.20 (brs, 1H, OH).

(*E*)-1,3-Bis(4-bromophenyl)prop-2-en-1-ol (2c):[15d,e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.8 Hz, 2H, Ar-H), 7.38 (d, J = 8.4 Hz, 2H, Ar-H), 7.22 (d, J = 8.0 Hz, 2H, Ar-H), 7.15 (d, J = 8.4 Hz, 2H, Ar-H), 6.51 (d, J = 16.0 Hz, 1H, CH=), 6.23 (dd, J = 6.2, 15.8 Hz, 1H, CH=), 5.23 (d, J = 6.0 Hz, 1H, ArCH), 2.85 (brs, 1H, OH).

(*E*)-1,3-Di-*p*-tolylprop-2-en-1-ol (2d):[15d,f] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.04 (m, 8H, Ar-H), 6.64 (d, J = 16.0 Hz, 1H, CH=), 6.32 (dd, J = 6.4, 15.6 Hz, 1H, CH=), 5.33 (d, J = 6.4 Hz, 1H, ArCH), 2.35 (brs, 7H, CH_3×2+ OH).

(*E*)-1,3-Bis(4-methoxyphenyl)prop-2-en-1-ol (2e):[15g] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.13 (m, 4H, Ar-H), 6.93–6.70 (m, 4H, Ar-H), 6.52 (d, J = 16.0 Hz, 1H, CH=), 6.19 (dd, J = 6.6, 15.8 Hz, 1H, CH=), 5.23 (d, J = 6.0 Hz, 1H, ArCH), 3.73 (s, 6H, OCH_3×2), 3.04 (brs, 1H, OH).

(*E*)-1-(4-Methoxyphenyl)-3-*p*-tolylprop-2-en-1-ol (2f):[15g] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.20 (m, 4H, Ar-H), 7.10 (d, J = 7.6 Hz, 2H, Ar-H), 6.88 (d, J = 8.4 Hz, 2H, Ar-H), 6.61 (d, J = 16.0 Hz, 1H, CH=), 6.31 (dd, J = 6.2, 15.8 Hz, 1H, CH=), 5.30 (d, J = 6.0 Hz, 1H, ArCH), 3.79 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3), 2.15 (brs, 1H, OH).

(*E*)-3-(4-Chlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-ol (2g):[15g] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.18 (m, 6H, Ar-H), 6.81 (d, J = 8.4 Hz, 2H, Ar-H), 6.52 (d, J = 15.6 Hz, 1H, CH=), 6.13 (dd, J = 7.0, 15.8 Hz, 1H, CH=), 5.25 (d, J = 6.8 Hz, 1H, ArCH), 3.76 (s, 3H, OCH_3), 2.78 (brs, 1H, OH).

(*E*)-1-(4-Methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-ol (2h):[15h] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.0 Hz, 2H, Ar-H), 7.46 (d, J = 8.4 Hz, 2H, Ar-H), 7.32 (d, J = 8.4 Hz, 2H, Ar-H), 6.89 (d, J = 8.8 Hz, 2H, Ar-H), 6.73 (d, J = 16.4 Hz, 1H, CH=), 6.53 (dd, J = 5.4, 15.8 Hz, 1H, CH=), 5.35 (d, J = 4.8 Hz, 1H, ArCH), 3.79 (s, 3H, OCH_3), 2.58 (brs, 1H, OH).

(*E*)-3-(4-Methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-ol (2i):[15h,i] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26–8.00 (m, 2H, Ar-H), 7.54 (d, J = 8.4 Hz, 2H, Ar-H), 7.26 (d, J = 8.8 Hz, 2H, Ar-H), 6.81 (d, J = 8.8 Hz, 2H, Ar-H), 6.59 (d, J = 16.0 Hz, 1H, CH=), 6.11 (dd, J = 7.0, 15.8 Hz, 1H, CH=), 5.40 (d, J = 6.8 Hz, 1H, ArCH), 3.76 (s, 3H, OCH_3), 3.50 (brs, 1H, OH).

(*E*)-4-Phenylbut-3-en-2-ol (2j):[15a,j] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.12 (m, 5H, Ar-H), 6.53 (d, J = 15.6 Hz, 1H, CH=), 6.23 (dd, J = 6.6, 15.8 Hz, 1H, CH=), 4.50–4.40 (m, 1H, CH), 2.29 (brs, 1H, OH), 1.34 (d, J = 6.0 Hz, 3H, CH_3).

(1*E*,4*E*)-1,5-Diphenylpenta-1,4-dien-3-ol (4a):[16a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.16 (m, 10H, Ar-H), 6.67 (d, J = 16.0 Hz, 2H, CH=×2), 6.31 (dd, J = 6.2, 15.8 Hz, 2H, CH=×2), 5.04–4.95 (m, 1H, CH), 1.90 (brs, 1H, OH).

(1*E*,4*E*)-1,5-Di-*p*-tolylpenta-1,4-dien-3-ol (4b):[16a,b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.0 Hz, 4H, Ar-H), 7.12 (d, J = 7.6 Hz, 4H, Ar-H), 6.62 (d, J = 16.4 Hz, 2H, CH= × 2), 6.26 (dd, J = 6.4, 16.0 Hz, 2H, CH= × 2), 5.00–4.90 (m, 1H, CH), 2.33 (s, 6H, CH_3×2), 1.86 (brs, 1H, OH).

(1*E*,4*E*)-1,5-Bis(4-chlorophenyl)penta-1,4-dien-3-ol (4c):[13a,16a,b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 8H, Ar-H), 6.56 (d, J = 16.0 Hz, 2H, CH= 2), 6.22 (dd, J = 6.6, 15.8 Hz, 2H, CH=×2), 4.96–4.89 (m, 1H, CH), 2.02 (brs, 1H, OH).

(1*E*,4*E*)-1,5-Bis(4-bromophenyl)penta-1,4-dien-3-ol (4d):[16a,b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.6 Hz, 4H, Ar-H), 7.24 (d, J = 8.4 Hz, 4H, Ar-H), 6.59 (d, J = 16.0 Hz, 2H, CH= × 2), 6.27 (dd, J = 6.2, 16.2 Hz, 2H, CH= × 2), 4.99–4.92 (m, 1H, CH), 2.05 (brs, 1H, OH).

Typical Experimental Procedure for the Synthesis of 6[17]

To a solution of (*E*)-1,3-diphenylallyl acetate (760 mg, 3.0 mmol) in aqueous NH_3/1,4-dioxane (1/2 v/v, 75 mL) was added $Pd(PPh_3)_4$ (350 mg, 0.3 mmol). After stirring for 18 h at room temperature, the reaction mixture was diluted with a saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2 and the combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by preparative TLC on silica gel (eluent: petroleum ether/*i*-$PrNH_2$ = 19/1) to afford **6**.

(*E*)-1,3-Diphenylprop-2-en-1-amine (6):[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.11 (m, 10H, Ar-H), 6.58 (d, J = 16.0 Hz, 1H, CH=), 6.35 (dd, J = 6.6, 15.8 Hz, 1H, CH=), 4.68 (d, J = 6.0 Hz, 1H, PhCH), 1.73 (brs, 2H, NH_2).

Typical Experimental Procedures for 3 and 5

Under a nitrogen atmosphere, anhydrous $ZnCl_2$ (0.6 mmol) was added to a Schlenk tube. A solution of **1** (0.3 mmol) and **2** (or **4**) (0.6 mmol) in 3 mL of CH_2Cl_2 was then added at 0 °C. The reaction mixture was stirred at 0 °C and the reaction was monitored by TLC. When the reaction was complete, the mixture was eluted with 10 mL of CH_2Cl_2 and filtered through a short column of silica gel (eluent: CH_2Cl_2 10 mL × 3). The organic phase was concentrated under reduced pressure and purified by chromatography on silica gel to afford 3-oxabicyclo[3.2.0]heptane derivatives **3** (or **5**).

Spectroscopic Data of the Products 3 and 5

(1*S,2*R**,5*R**,*E*)-2,5-Diphenyl-1-styryl-3-oxabicyclo-[3.2.0]heptane (3a):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2a** (126 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3a** (eluent: petroleum ether/ethyl acetate = 100/1) as a solid; yield: 91 mg (86%); mp 120.0–120.5 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 7.2 Hz, 2H, Ar-H), 7.36–7.10 (m, 13H, Ar-H), 6.21 (d, J = 16.0 Hz, 1H, CH=), 6.14 (d, J = 16.0 Hz, 1H, CH=), 4.98 (s, 1H, OCH), 4.30 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.23 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 2.53–2.42 (m, 1H, one proton of CH_2), 2.32–2.20 (m, 1H, one proton of CH_2), 2.08–1.95 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 137.4, 137.3, 131.3, 131.1, 128.4, 128.1, 127.8, 127.4, 127.20, 127.18, 126.5, 126.3, 126.1, 87.8, 79.6, 59.7, 58.9, 27.4, 20.5; IR (neat) ν (cm^{-1}) 3026, 2941, 2854, 1720, 1600, 1495, 1448, 1177, 1058, 1025; MS (EI, 70 ev) m/z (%) 352 (M^+, 90.0), 91 (100); HR-MS (EI): m/z = 352.1830, calcd. for $C_{26}H_{24}O$ (M^+): 352.1827.

(1*S,2*R**,5*R**,*E*)-2-(4-Chlorophenyl)-1-(4-chlorostyryl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3b):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2b** (168 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3b** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 90 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.17 (m, 11H, Ar-H), 7.08 (d, J = 8.4 Hz, 2H, Ar-H), 6.15 (d, J = 16.0 Hz, 1H, CH=), 6.08 (d, J = 16.0 Hz, 1H, CH=), 4.91 (s, 1H, OCH), 4.30 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.23 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 2.54–2.43 (m, 1H, one proton of CH_2), 2.31–2.19 (m, 1H, one proton of CH_2), 2.03–1.90 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 135.74, 135.70, 133.1, 130.0, 131.7, 130.2, 128.7, 128.2, 128.0, 127.8, 127.4, 127.3, 126.5, 87.2, 79.6, 59.7, 59.0, 27.4, 20.4; IR (neat): ν = 3025, 2955, 2862, 1715, 1600, 1492, 1452, 1073, 1027 cm^{-1}; MS (EI, 70 eV): m/z (%) = 424 [M^+(^{37,37}Cl), 6.32], 422 [M^+(^{37,35}Cl), 28.79], 420 [M^+(^{35,35}Cl), 40.46], 139 (100); HR-MS (EI): m/z = 420.1042, calcd. for $C_{26}H_{22}{}^{35,35}Cl_2O$ (M^+): 420.1048.

(1*S,2*R**,5*R**,*E*)-2-(4-Bromophenyl)-1-(4-bromostyryl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3c):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2c** (222 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3c** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 112 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.0 Hz, 2H, Ar-H), 7.40–7.15 (m, 9H, Ar-H), 7.02 (d, J = 8.0 Hz, 2H, Ar-H), 6.16 (d, J = 16.0 Hz, 1H, CH=), 6.07 (d, J = 16.4 Hz, 1H, CH=), 4.89 (s, 1H, OCH), 4.31 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 4.23 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.54–2.43 (m, 1H, one proton of CH_2), 2.31–2.19 (m, 1H, one proton of CH_2), 2.05–1.88 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 136.2, 136.1, 131.8, 131.6, 130.9, 130.3, 128.2, 128.1, 127.6, 127.3, 126.5, 121.3, 121.1, 87.1, 79.5, 59.6, 58.9, 27.4, 20.3; IR (neat): ν = 3027, 2947, 2856, 1722, 1594, 1487, 1448, 1068, 1009 cm^{-1}; MS (EI, 70 eV): m/z (%) = 508 [M^+(^{79,79}Br), 21.95], 510 [M^+(^{79,81}Br), 43.17], 512 [M^+(^{81,81}Br), 22.70], 117 (100); HR-MS (EI): m/z = 508.0033, calcd. for $C_{26}H_{22}{}^{79,79}Br_2O$ (M^+): 508.0037.

(1*S,2*R**,5*R**,*E*)-1-(4-Methylstyryl)-5-phenyl-2-*p*-tolyl-3-oxabicyclo[3.2.0]heptane (3d):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2d** (143 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3d** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 70 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.23 (m, 5H, Ar-H), 7.22–7.00 (m, 8H, Ar-H), 6.16 (d, J = 16.0 Hz, 1H, CH=), 6.11 (d, J = 16.0 Hz, 1H, CH=), 4.94 (s, 1H, OCH), 4.29 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.21 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.52–2.40 (m, 1H, one proton of CH_2), 2.36–2.18 (m, 7H, CH_3 × 2 and one proton of CH_2), 2.10–1.92 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 137.0, 136.7, 134.7, 134.2, 130.8, 130.3, 129.1, 128.5, 128.1, 127.4, 126.4, 126.2, 126.0, 87.8, 79.6, 59.6, 58.7, 27.5, 21.14, 21.11, 20.4; IR (neat): ν = 3024, 2924, 2862, 1716, 1608, 1512, 1448, 1178, 1061, 1020 cm^{-1}; MS (EI, 70 eV): m/z (%) = 380 (M^+, 16.91), 119 (100); HR-MS (EI): m/z = 380.2148, calcd. for $C_{28}H_{28}O$ (M^+): 380.2140.

(1*S,2*R**,5*R**,*E*)-2-(4-Methoxyphenyl)-1-(4-methoxystyryl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3e):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2e** (162 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3e** (eluent: petroleum ether/ethyl acetate = 60/1) as an oil; yield: 78 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 6H, Ar-H), 7.22–7.15 (m, 1H, Ar-H), 7.11 (d, J = 8.8 Hz, 2H, Ar-H), 6.85 (d, J = 8.8 Hz, 2H, Ar-H), 6.78 (d, J = 9.2 Hz, 2H, Ar-H), 6.09 (d, J = 16.0 Hz, 1H, CH=), 6.04 (d, J = 16.0 Hz, 1H, CH=), 4.92 (s, 1H, OCH), 4.28 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.20 (d, J = 10.0 Hz, 1H, one proton of OCH_2), 3.78 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 2.53–2.40 (m, 1H, one proton of CH_2), 2.30–2.19 (m, 1H, one proton of CH_2), 2.10–1.93 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 158.8, 141.6, 130.4, 130.3, 129.5, 129.2, 128.1, 127.7, 127.5, 127.2, 126.2, 113.9,

113.2, 87.6, 79.7, 59.6, 58.7, 55.2, 55.1, 27.5, 20.5; IR (neat): ν = 3024, 2930, 2852, 1714, 1607, 1511, 1460, 1174, 1033 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 352 (M^+, 4.0), 199 (100); HR-MS (EI): *m/z* = 412.2032, calcd. for $C_{28}H_{28}O_3$ (M^+): 412.2038.

(1*S,2*R**,5*R**,*E*)-2-Phenyl-1-styryl-5-*p*-tolyl-3-oxabicyclo-[3.2.0]heptane (3f):** The reaction of anhydrous $ZnCl_2$ (85 mg, 0.6 mmol), **1b** (52 mg, 0.3 mmol), and **2a** (126 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3f** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 85 mg (77%). ^1H NMR (400 MHz, C_6D_6): δ = 7.58 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.23–7.15 (m, 2H, Ar-H), 7.15–6.90 (m, 10H, Ar-H), 6.19 (d, *J* = 16.0 Hz, 1H, CH=), 6.11 (d, *J* = 16.0 Hz, 1H, CH=), 4.90 (s, 1H, OCH), 4.16 (d, *J* = 9.6 Hz, 1H, one proton of OCH_2), 4.13 (d, *J* = 9.2 Hz, 1H, one proton of OCH_2), 2.36–2.24 (m, 1H, one proton of CH_2), 2.21–2.04 (m, 5H, CH_3 and CH_2), 1.98–1.85 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 137.5, 137.3, 135.8, 131.4, 131.0, 128.9, 128.4, 127.8, 127.3, 127.2, 127.1, 126.5, 126.2, 87.8, 79.7, 59.5, 58.6, 27.5, 21.0, 20.4; IR (neat): ν = 3026, 2943, 2855, 1721, 1601, 1494, 1449, 1059, 1026 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 366 (M^+, 27.29), 105 (100); HR-MS (EI): *m/z* = 366.1989, calcd. for $C_{27}H_{26}O$ (M^+): 366.1984.

(1*S,2*R**,5*R**,*E*)-2-(4-Bromophenyl)-1-(4-bromostyryl)-5-*p*-tolyl-3-oxabicyclo[3.2.0]heptane (3g):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1b** (52 mg, 0.3 mmol), and **2c** (223 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3g** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 118 mg (75%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.34 (m, 4H, Ar-H), 7.30–7.10 (m, 6H, Ar-H), 7.04 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.18 (d, *J* = 16.0 Hz, 1H, CH=), 6.06 (d, *J* = 16.0 Hz, 1H, CH=), 4.87 (s, 1H, OCH), 4.27 (d, *J* = 9.2 Hz, 1H, one proton of OCH_2), 4.19 (d, *J* = 9.2 Hz, 1H, one proton of OCH_2), 2.54–2.10 (m, 5H, CH_3 and CH_2), 2.03–1.86 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 136.2, 136.1, 136.0, 131.9, 131.6, 130.9, 130.1, 128.9, 128.1, 127.6, 127.2, 121.2, 121.0, 87.1, 79.6, 59.5, 58.6, 27.5, 21.0, 20.3; IR (neat): ν = 3025, 2943, 2856, 1721, 1590, 1486, 1449, 1067, 1009 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 526 [M^+-($^{81,81}Br$), 16.72], 524 [M^+($^{79,81}Br$), 31.35], 522 [M^+($^{79,79}Br$), 15.95], 131 (100); HR-MS (EI): *m/z* = 522.0197, calcd. for $C_{27}H_{24}{}^{79,79}Br_2O$ (M^+): 522.0194.

(1*S,2*R**,5*R**,*E*)-2-(4-Methoxyphenyl)-1-(4-methoxystyryl)-5-*p*-tolyl-3-oxabicyclo[3.2.0]heptane (3h):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1b** (52 mg, 0.3 mmol), and **2e** (163 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3h** (eluent: petroleum ether/ethyl acetate = 60/1) as an oil; yield: 63 mg (49%). ^1H NMR (400 MHz, C_6D_6): δ = 7.55 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.13 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.06 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.02 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.67 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.17 (d, *J* = 16.4 Hz, 1H, CH=), 6.11 (d, *J* = 16.0 Hz, 1H, CH=), 4.94 (s, 1H, OCH), 4.21 (d, *J* = 9.2 Hz, 1H, one proton of OCH_2), 4.17 (d, *J* = 8.8 Hz, 1H, one proton of OCH_2), 3.29 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 2.41–2.30 (m, 1H, one proton of CH_2), 2.27–2.15 (m, 2H, CH_2), 2.11 (s, 3H, CH_3), 2.05–1.92 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 158.7, 138.5, 135.6, 130.33, 130.25, 129.5, 129.2, 128.8, 127.6, 127.3, 127.2, 113.8, 113.1, 87.6, 79.7, 59.4, 58.3, 55.2, 55.1, 27.5, 20.9, 20.4; IR (neat): ν = 3025, 2933, 2836, 1714, 1608, 1510, 1460, 1174, 1059, 1032 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 426 (M^+, 19.1), 135 (100); HR-MS (EI): *m/z* = 426.2199, calcd. for $C_{29}H_{30}O_3$ (M^+): 426.2195.

(1*S,2*R**,5*R**,*E*)-5-(4-Methoxyphenyl)-2-phenyl-1-styryl-3-oxabicyclo[3.2.0]heptane (3i):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1c** (57 mg, 0.3 mmol), and **2a** (125 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3i** (eluent: petroleum ether/ethyl acetate = 70/1) as an oil; yield: 73 mg (64%). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.34–7.15 (m, 10H, Ar-H), 6.87 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.20 (d, *J* = 16.2 Hz, 1H, CH=), 6.15 (d, *J* = 16.2 Hz, 1H, CH=), 4.95 (s, 1H, OCH), 4.26 (d, *J* = 9.0 Hz, 1H, one proton of OCH_2), 4.20 (d, *J* = 9.6 Hz, 1H, one proton of OCH_2), 3.77 (s, 3H, OCH_3), 2.48–2.38 (m, 1H, one proton of CH_2), 2.28–2.19 (m, 1H, one proton of CH_2), 2.05–1.93 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 137.45, 137.36, 133.3, 131.5, 131.1, 128.5, 128.4, 127.8, 127.2, 126.5, 126.1, 113.5, 87.8, 79.5, 59.4, 58.3, 55.2, 27.6, 20.4; IR (neat): ν = 3024, 2933, 2852, 1700, 1609, 1513, 1453, 1181, 1059, 1031 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 382 (M^+, 4.0), 84 (100); HR-MS (EI): *m/z* = 382.1933, calcd. for $C_{27}H_{26}O_2$ (M^+): 382.1933.

(1*S,2*R**,5*R**,*E*)-5-(4-Chlorophenyl)-2-phenyl-1-styryl-3-oxabicyclo[3.2.0]heptane (3j):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1d** (59 mg, 0.3 mmol), and **2a** (125 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3j** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 75 mg (65%). ^1H NMR (500 MHz, C_6D_6): δ = 7.55 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.21–7.17 (m, 2H, Ar-H), 7.13–6.92 (m, 8H, Ar-H), 6.80 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.07 (d, *J* = 16.5 Hz, 1H, CH=), 5.99 (d, *J* = 16.5 Hz, 1H, CH=), 4.80 (s, 1H, OCH), 4.02 (d, *J* = 9.5 Hz, 1H, one proton of OCH_2), 3.90 (d, *J* = 9.5 Hz, 1H, one proton of OCH_2), 2.10–1.99 (m, 3H, one proton of CH_2 and CH_2), 1.86–1.73 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.9, 137.1, 137.0, 132.0, 131.5, 130.7, 128.7, 128.5, 128.2, 127.8, 127.34, 127.26, 126.4, 126.1, 87.7, 79.2, 59.6, 58.3, 27.5, 20.4; IR (neat): ν = 3029, 2937, 2855, 1728, 1600, 1464, 1448, 1095, 1061, 1013 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 388 [M^+(^{37}Cl), 3.36], 386 [M^+(^{35}Cl), 8.53], 105 (100); HR-MS (EI): *m/z* = 386.1437, calcd. for $C_{26}H_{23}{}^{35}ClO$ (M^+): 386.1437.

(1*S,2*R**,5*R**,*E*)-2-(4-Bromophenyl)-1-(4-bromostyryl)-5-(4-chlorophenyl)-3-oxabicyclo[3.2.0]heptane (3k):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1d** (59 mg, 0.3 mmol), and **2c** (199 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3k** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 126 mg (77%). ^1H NMR (400 MHz, C_6D_6): δ = 7.29 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.16–7.09 (m, 6H, Ar-H), 6.75 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.61 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.79 (d, *J* = 16.0 Hz, 1H, CH=), 5.74 (d, *J* = 16.0 Hz, 1H, CH=), 4.54 (s, 1H, OCH), 3.95 (d, *J* = 9.6 Hz, 1H, one proton of OCH_2), 3.84 (d, *J* = 9.2 Hz, 1H, one proton of OCH_2), 2.08–1.92 (m, 2H, CH_2), 1.88–1.78 (m, 1H, one proton of CH_2), 1.74–1.64 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 136.0, 135.8, 132.3, 131.7, 131.2, 131.0, 130.7, 128.7, 128.4, 128.0, 127.6, 121.4, 121.3, 87.1, 79.2, 59.6, 58.4, 27.5, 20.3; IR (neat): ν = 3026, 2953, 2855, 1717, 1589, 1488, 1178, 1067, 1008 cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 548 [M^+($^{37}Cl^{81,81}Br$), 4.49], 546 [M^+($^{37}Cl^{79,81}Br$, $^{35}Cl^{81,81}Br$), 22.32], 544 [M^+($^{37}Cl^{79,79}Br$, $^{35}Cl^{79,81}Br$), 31.42], 542 [M^+($^{35}Cl^{79,79}Br$), 14.51], 183 (100); HR-MS (EI): *m/z* = 541.9646, calcd. for $C_{26}H_{21}{}^{79,79}Br_2{}^{35}ClO$ (M^+): 541.9648.

(1*S,2*R**,5*R**,*E*)-1-(4-Methoxystyryl)-2,5-di-*p*-tolyl-3-oxabicyclo[3.2.0]heptane (3l-a) and (1*S**,2*R**,5*R**,*E*)-2-(4-methoxyphenyl)-1-(4-methylstyryl)-5-*p*-tolyl-3-oxa-bicyclo-[3.2.0]heptane (3l-b):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1b** (52 mg, 0.3 mmol), and **2f** (154 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3l-a** (yield: 15 mg, 12%) and **3l-b** (yield: 72 mg, 58%) (eluent: petroleum ether/ethyl acetate = 90/1).

3l-a: Oil; ^{1}H NMR (600 MHz, C_6D_6): δ = 7.56 (d, J = 7.8 Hz, 2H, Ar-H), 7.12 (d, J = 7.8 Hz, 2H, Ar-H), 7.09–6.95 (m, 6H, Ar-H), 6.66 (d, J = 8.4 Hz, 2H, Ar-H), 6.15 (d, J = 16.2 Hz, 1H, CH=), 6.10 (d, J = 16.2 Hz, 1H, CH=), 4.95 (s, 1H, OCH), 4.20 (d, J = 9.0 Hz, 1H, one proton of OCH_2), 4.17 (d, J = 9.0 Hz, 1H, one proton of OCH_2), 3.25 (s, 3H, OCH_3), 2.40–2.30 (m, 1H, one proton of CH_2), 2.24–2.16 (m, 2H, CH_2) 2.13–2.07 (m, 6H, $CH_3 \times 2$), 2.02–1.90 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 138.5, 136.6, 135.7, 134.4, 130.4, 130.2, 129.2, 128.8, 128.4, 127.32, 127.25, 126.4, 113.8, 87.8, 79.7, 59.4, 58.4, 55.2, 27.5, 21.1, 21.0, 20.4; IR (neat): ν = 3025, 2950, 2857, 1607, 1512, 1458, 1177, 1061, 1036 cm^{-1}; MS (EI, 70 eV): m/z (%) = 410 (M^+, 5.31), 49 (100); HR-MS (EI): m/z = 410.2250, calcd. for $C_{29}H_{30}O_2$ (M^+): 410.2246.

3l-b: Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.8 Hz, 2H, Ar-H), 7.20 (d, J = 8.0 Hz, 2H, Ar-H), 7.16–7.01 (m, 6H, Ar-H), 6.84 (d, J = 8.4 Hz, 2H, Ar-H), 6.17 (d, J = 16.0 Hz, 1H, CH=), 6.10 (d, J = 16.0 Hz, 1H, CH=), 4.91 (s, 1H, OCH), 4.26 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 4.18 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 3.78 (s, 3H, OCH_3), 2.50–2.38 (m, 1H, one proton of CH_2), 2.35–2.18 (m, 7H, $CH_3 \times 2$ and one proton of CH_2), 2.07–1.93 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 138.4, 136.9, 135.7, 134.7, 130.7, 130.4, 129.4, 129.1, 128.8, 127.6, 127.3, 126.1, 113.1, 87.6, 79.7, 59.4, 58.4, 55.1, 27.6, 21.1, 20.9, 20.4; IR (neat): ν = 3025, 2931, 2856, 1611, 1512, 1458, 1176, 1061, 1035 cm^{-1}; MS (EI, 70 eV): m/z (%) = 410 (M^+, 46.72), 135 (100); HR-MS (EI): m/z = 410.2244, calcd. for $C_{29}H_{30}O_2$ (M^+): 410.2246.

(1*S,2*R**,5*R**,*E*)-2-(4-Chlorophenyl)-1-(4-methoxystyryl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3m-a) and (1*S**,2*R**,5*R**,*E*)-1-(4-chlorostyryl)-2-(4-methoxyphenyl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3m-b):** The reaction of anhydrous $ZnCl_2$ (85 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2g** (165 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3m-a** (yield: 14 mg, 11%) and **3m-b** (84 mg, 67%) (eluent: petroleum ether/ethyl acetate = 100/1).

3m-a: Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 8H, Ar-H), 7.24–7.17 (m, 1H, Ar-H), 7.12 (d, J = 8.4 Hz, 2H, Ar-H), 6.79 (d, J = 8.4 Hz, 2H, Ar-H), 6.09 (d, J = 16.4 Hz, 1H, CH=), 6.03 (d, J = 16.0 Hz, 1H, CH=), 4.91 (s, 1H, OCH), 4.30 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 4.23 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 3.78 (s, 3H, OCH_3), 2.52–2.42 (m, 1H, one proton of CH_2), 2.29–2.19 (m, 1H, one proton of CH_2), 2.04–1.88 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 141.3, 136.0, 133.0, 130.8, 130.1, 128.7, 128.2, 127.9, 127.8, 127.4, 127.3, 126.3, 114.0, 87.3, 79.7, 59.7, 58.7, 55.3, 27.4, 20.4; IR (neat): ν = 3024, 2935, 2855, 1713, 1607, 1492, 1456, 1171, 1094, 1031 cm^{-1}; MS (EI, 70 eV): m/z (%) = 418 [M^+(^{37}Cl), 3.32], 416 [M^+(^{35}Cl), 8.96], 135 (100); HR-MS (EI): m/z = 416.1552, calcd. for $C_{27}H_{25}{}^{35}ClO_2$ (M^+): 416.1543.

3m-b: Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 6H, Ar-H), 7.25–7.15 (m, 3H, Ar-H), 7.08 (d, J = 8.4 Hz, 2H, Ar-H), 6.85 (d, J = 8.0 Hz, 2H, Ar-H), 6.17 (d, J = 16.0 Hz, 1H, CH=), 6.08 (d, J = 16.0 Hz, 1H, CH=), 4.92 (s, 1H, OCH), 4.29 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.21 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 3.78 (s, 3H, OCH_3), 2.54–2.43 (m, 1H, one proton of CH_2), 2.34–2.19 (m, 1H, one proton of CH_2), 2.11–1.92 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 141.3, 135.9, 132.8, 132.2, 129.9, 129.2, 128.6, 128.2, 127.6, 127.4, 127.3, 126.3, 113.3, 87.5, 79.6, 59.6, 58.9, 55.2, 27.4, 20.5; IR (neat): ν = 3025, 2929, 2855, 1713, 1605, 1492, 1455, 1172, 1092, 1032 cm^{-1}; MS (EI, 70 eV): m/z (%) = 418 [M^+(^{37}Cl), 1.0], 416 [M^+(^{35}Cl), 3.0], 135 (100); HR-MS (EI): m/z = 416.1548, calcd. for $C_{27}H_{25}{}^{35}ClO_2$ (M^+): 416.1543.

(1*S,2*R**,5*R**,*E*)-2-(4-Methoxyphenyl)-1-(4-nitrostyryl)-5-phenyl-3-oxabicyclo[3.2.0]heptane (3n):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2h** (172 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3n** (eluent: petroleum ether/ethyl acetate = 60/1) as an oil; yield: 82 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.8 Hz, 2H, Ar-H), 7.38–7.18 (m, 9H, Ar-H), 6.87 (d, J = 8.4 Hz, 2H, Ar-H), 6.39 (d, J = 16.4 Hz, 1H, CH=), 6.19 (d, J = 16.0 Hz, 1H, CH=), 4.96 (s, 1H, OCH), 4.31 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.24 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 3.79 (s, 3H, OCH_3), 2.58–2.47 (m, 1H, one proton of CH_2), 2.34–2.24 (m, 1H, one proton of CH_2), 2.16–2.07 (m, 1H, one proton of CH_2), 2.06–1.94 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 146.7, 143.8, 140.9, 136.8, 129.2, 129.0, 128.3, 127.6, 127.3, 126.53, 126.50, 123.9, 113.4, 87.4, 79.6, 59.9, 59.5, 55.2, 27.3, 20.6; IR (neat): ν = 3025, 2936, 2851, 1715, 1598, 1514, 1448, 1342, 1178, 1109, 1034 cm^{-1}; MS (EI, 70 eV): m/z (%) = 427 (M^+, 22.37), 133 (100); HR-MS (EI): m/z = 427.1786, calcd. for $C_{27}H_{25}O_4$ (M^+): 427.1784.

Alternatively, the reaction of anhydrous $ZnCl_2$ (83 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2i** (171 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3n** (eluent: petroleum ether/ethyl acetate = 60/1) as an oil; yield: 90 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.8 Hz, 2H, Ar-H), 7.37–7.17 (m, 9H, Ar-H), 6.87 (d, J = 8.4 Hz, 2H, Ar-H), 6.39 (d, J = 16.0 Hz, 1H, CH=), 6.19 (d, J = 16.0 Hz, 1H, CH=), 4.96 (s, 1H, OCH), 4.31 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 4.24 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 3.79 (s, 3H, OCH_3), 2.59–2.47 (m, 1H, one proton of CH_2), 2.34–2.23 (m, 1H, one proton of CH_2), 2.17–2.06 (m, 1H, one proton of CH_2), 2.06–1.94 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 146.6, 143.7, 140.9, 136.8, 129.2, 128.9, 128.3, 127.6, 127.3, 126.5, 123.9, 113.3, 87.4, 79.5, 59.9, 59.4, 55.2, 27.3, 20.5; IR (neat): ν = 3025, 2932, 2852, 1724, 1596, 1514, 1447, 1342, 1177, 1109, 1033 cm^{-1}; MS (EI, 70 eV): m/z (%) = 427 (M^+, 21.52), 133 (100); HR-MS (EI): m/z = 427.1782, calcd. for $C_{27}H_{25}O_4$ (M^+): 427.1784.

(1*S,2*R**,5*R**,*E*)-2-Methyl-5-phenyl-1-styryl-3-oxabicyclo-[3.2.0]heptane (3o-a) and (1*S**,2*R**,5*R**,*E*)-2,5-diphenyl-1-(prop-1-enyl)-3-oxabicyclo[3.2.0]heptane (3o-b):** The reaction of anhydrous $ZnCl_2$ (84 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **2j** (90 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **3o-a** (yield: 31 mg, 36%) and **3o-b** (yield: 28 mg, 32%) (eluent: petroleum ether/ethyl acetate = 100/1).

3o-a: Oil; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.14–6.95 (m, 10H, Ar-H), 6.24 (d, J = 16.8 Hz, 1H, CH=), 6.02 (d, J = 16.0 Hz, 1H, CH=), 4.03 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 3.93–3.84 (m, 2H, OCH and one proton of OCH_2), 2.43–2.26 (m, 2H, CH_2), 2.10–2.01 (m, 1H, one proton of CH_2), 1.97–1.87 (m, 1H, one proton of CH_2), 1.26 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 137.4, 131.2, 129.8, 128.4, 128.1, 127.3, 127.1, 126.1, 126.0, 82.0, 81.0, 59.0, 58.2, 27.3, 20.3, 13.2; IR (neat): ν = 3026, 2930, 2853, 1600, 1495, 1448, 1380, 1086, 1053 cm^{-1}; MS (EI, 70 eV): m/z (%) = 290 (M^+, 32.43), 129 (100); HR-MS (EI): m/z = 290.1674, calcd. for $C_{21}H_{22}O$ (M^+): 290.1671.

3o-b: Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.15 (m, 10H, Ar-H), 5.46 (d, J = 15.2 Hz, 1H, CH=), 5.31–5.19 (m, 1H, CH=), 4.85 (s, 1H, OCH), 4.25 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.13 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.50–2.36 (m, 1H, one proton of CH_2), 2.24–2.14 (m, 1H, one proton of CH_2), 1.96–1.76 (m, 2H, CH_2), 1.61 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 137.6, 131.7, 127.9, 127.7, 127.6, 127.1, 126.5, 126.0, 87.8, 79.9, 59.3, 58.0, 27.1, 20.3, 18.2; IR (neat): ν = 3027, 2934, 2855, 1601, 1495, 1449, 1376, 1060, 1026 cm^{-1}; MS (EI, 70 eV): m/z (%) = 290 (M^+, 30.86), 91 (100); HR-MS (EI): m/z = 290.1667, calcd. for $C_{21}H_{22}O$ (M^+): 290.1671.

(1*S,2*R**,5*R**)-2,5-Diphenyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-3-oxabicyclo[3.2.0]heptane (5a):**[18] The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **4a** (144 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **5a** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 70 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.15 (m, 15H, Ar-H), 6.71 (dd, J = 15.4, 10.6 Hz, 1H, CH=), 6.38 (d, J = 15.6 Hz, 1H, CH=), 6.01 (dd, J = 15.6, 10.4 Hz, 1H, CH=), 5.82 (d, J = 15.2 Hz, 1H, CH=), 4.93 (s, 1H, OCH), 4.28 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.19 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.52–2.42 (m, 1H, CH), 2.30–2.19 (m, 1H, CH), 2.07–1.87 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 137.3, 137.2, 135.2, 131.9, 131.3, 128.9, 128.5, 128.2, 127.8, 127.44, 127.35, 127.2, 126.5, 126.3, 126.2, 87.8, 79.8, 60.0, 59.1, 27.3, 20.5; IR (neat): ν = 3026, 2924, 2853, 1720, 1600, 1494, 1449, 1177, 1061, 1026 cm^{-1}; MS (EI, 70 eV): m/z (%) = 378 (M^+, 45.99), 105 (100); HR-MS (EI): m/z = 378.1980, calcd. for $C_{28}H_{26}O$ (M^+): 378.1984.

(1*S,2*R**,5*R**)-5-Phenyl-2-*p*-tolyl-1-[(1*E*,3*E*)-4-*p*-tolylbuta-1,3-dienyl]-3-oxabicyclo[3.2.0]heptane (5b):** The reaction of anhydrous $ZnCl_2$ (82 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **4b** (158 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **5b** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 62 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.18 (m, 9H, Ar-H), 7.17–7.02 (m, 4H, Ar-H), 6.66 (dd, J = 16.0, 10.2 Hz, 1H, CH=), 6.34 (d, J = 15.6 Hz, 1H, CH=), 5.99 (dd, J = 15.2, 10.0 Hz, 1H, CH=), 5.78 (d, J = 15.2 Hz, 1H, CH=), 4.90 (s, 1H, OCH), 4.27 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.17 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.51–2.40 (m, 1H, one proton of CH_2), 2.40–2.15 (m, 7H, CH_3×2 and one proton of CH_2), 2.06–1.86 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 137.2, 136.8, 134.6, 134.5, 134.3, 131.9, 131.1, 129.3, 128.5, 128.1, 128.0, 127.5, 126.4, 126.2, 126.1, 87.8, 79.8, 59.9, 58.9, 27.4, 21.2, 21.1, 20.5; IR (neat): ν = 3023, 2922, 2854, 1723, 1604, 1511, 1448, 1182, 1062, 1021 cm^{-1}; MS (EI, 70 eV): m/z (%) = 406 (M^+, 6.85), 105 (100); HR-MS (EI): m/z = 406.2295, calcd. for $C_{30}H_{30}O$ (M^+): 406.2297.

(1*S,2*R**,5*R**)-2-(4-Chlorophenyl)-1-[(1*E*,3*E*)-4-(4-chlorophenyl)buta-1,3-dienyl]-5-phenyl-3-oxabicyclo[3.2.0]heptane (5c):** The reaction of anhydrous $ZnCl_2$ (81 mg, 0.6 mmol), **1a** (48 mg, 0.3 mmol), and **4c** (182 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **5c** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 79 mg (59%). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.30 (d, J = 8.4 Hz, 2H, Ar-H), 7.23–7.16 (m, 4H, Ar-H), 7.12–7.01 (m, 5H, Ar-H), 6.78 (d, J = 8.8 Hz, 2H, Ar-H), 6.37 (dd, J = 15.8, 10.2 Hz, 1H, CH=), 5.98 (d, J = 15.2 Hz, 1H, CH=), 5.80 (dd, J = 15.4, 10.6 Hz, 1H, CH=), 5.58 (d, J = 15.2 Hz, 1H, CH=), 4.68 (s, 1H, OCH), 4.08 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 4.04 (d, J = 9.6 Hz, 1H, one proton of OCH_2), 2.34–2.21 (m, 1H, one proton of CH_2), 2.11–2.00 (m, 1H, one proton of CH_2), 1.99–1.88 (m, 1H, one proton of CH), 1.83–1.72 (m, 1H, one proton of CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 135.8, 135.7, 135.4, 133.1, 132.9, 131.9, 130.2, 129.2, 128.7, 128.2, 128.0, 127.8, 127.4, 126.4, 87.2, 79.9, 60.0, 59.1, 27.3, 20.4; IR (neat): ν = 3027, 2937, 2857, 1720, 1598, 1491, 1448, 1091, 1062, 1013 cm^{-1}; MS (EI, 70 eV): m/z (%) = 450 [M^+(^{35,35}Cl), 2.10], 448 [M^+(^{35,37}Cl), 10.97], 446 [M^+(^{35,35}Cl), 15.50], 139 (100); HR-MS (EI): m/z = 446.1202, calcd. for $C_{28}H_{24}{}^{35,35}Cl_2O$ (M^+): 446.1204.

(1*S,2*R**,5*R**)-2-Phenyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-5-*p*-tolyl-3-oxabicyclo[3.2.0]heptane (5d):** The reaction of anhydrous $ZnCl_2$ (84 mg, 0.6 mmol), **1b** (52 mg, 0.3 mmol), and **4a** (142 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **5d** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 62 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.10 (m, 14H, Ar-H), 6.71 (dd, J = 15.2, 10.0 Hz, 1H, CH=), 6.37 (d, J = 16.0 Hz, 1H, CH=), 6.00 (dd, J = 15.4, 10.2 Hz, 1H, CH=), 5.82 (d, J = 15.2 Hz, 1H, CH=), 4.91 (s, 1H, OCH), 4.25 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 4.17 (d, J = 9.2 Hz, 1H, one proton of OCH_2), 2.49–2.39 (m, 1H, one proton of CH_2), 2.32 (s, 3H, CH_3), 2.27–2.15 (m, 1H, one proton of CH_2), 2.04–1.86 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 137.4, 137.2, 135.7, 135.4, 131.8, 131.1, 128.9, 128.8, 128.5, 127.8, 127.3, 127.2, 126.4, 126.2, 87.7, 79.8, 59.8, 58.8, 27.4, 21.0, 20.5; IR (neat): ν = 3026, 2940, 2857, 1718, 1600, 1493, 1450, 1059, 1026 cm^{-1}; MS (EI, 70 eV): m/z (%) = 392 (M^+, 7.7), 51 (100); HR-MS (EI): m/z = 392.2134, calcd. for $C_{29}H_{28}O$ (M^+): 392.2140.

(1*S,2*R**,5*R**)-2-(4-Bromophenyl)-1-[(1*E*,3*E*)-4-(4-bromophenyl)buta-1,3-dienyl]-5-*p*-tolyl-3-oxabicyclo [3.2.0]heptane (5e):** The reaction of anhydrous $ZnCl_2$ (84 mg, 0.6 mmol), **1b** (53 mg, 0.3 mmol), and **4d** (235 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) afforded **5e** (eluent: petroleum ether/ethyl acetate = 100/1) as an oil; yield: 94 mg (57%). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 (d, J = 8.0 Hz, 2H, Ar-H), 7.24 (d, J = 8.0 Hz, 2H, Ar-H), 7.22–7.16 (m, 2H, Ar-H), 7.10–7.00 (m, 4H, Ar-H), 6.70 (d, J = 8.0 Hz, 2H, Ar-H), 6.39 (dd, J = 15.6, 10.4 Hz, 1H, CH=), 5.96 (d, J = 16.0 Hz, 1H, CH=), 5.81 (dd, J = 15.4, 10.6 Hz, 1H, CH=), 5.61 (d, J = 15.2 Hz, 1H, CH=), 4.67 (s, 1H, OCH), 4.14–4.03 (m, 2H, OCH_2), 2.41–2.24 (m, 1H, one proton of CH_2), 2.20–2.00 (m, 4H, CH_3 and one proton of CH_2), 2.00–1.88 (m, 1H, one proton of CH_2), 1.85–1.71 (m, 1H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 136.3, 136.1, 135.9, 135.7, 131.7, 131.6, 130.9, 130.1, 129.4, 128.9, 128.1, 127.7, 127.2,

121.2, 121.0, 87.1, 79.8, 59.8, 58.8, 27.4, 21.0, 20.3; IR (neat): $\nu = 3026, 2942, 2857, 1720, 1589, 1485, 1400, 1066, 1008\ cm^{-1}$; MS (EI, 70 eV): m/z (%) = 552 [M^+(^{81,81}Br), 23.21], 550 [M^+ (^{79,81}Br), 43.42], 548 [M^+ (^{79,79}Br), 22.05], 131 (100); HR-MS (EI): m/z = 548.0350, calcd. for $C_{29}H_{26}{}^{79,79}Br_2O$ (M^+): 548.0350.

Reaction of 1b with (*E*)-1,3-Diphenylprop-2-enyl amine 6

Under a nitrogen atmosphere, anhydrous $ZnCl_2$ (0.6 mmol) was added to a Schlenk tube. A solution of **1b** (0.3 mmol) and **6** (0.6 mmol) in 3 mL of CH_2Cl_2 was then added at 0 °C. The reaction mixture was stirred at 0 °C. When the reaction was complete as monitored by TLC, the mixture was eluted with 10 mL of CH_2Cl_2 and filtered through a short column of silica gel (eluent: CH_2Cl_2 10 mL × 3). The organic phase was concentrated under reduced pressure and the crude product was analyzed by ^{1}H NMR measurement.

Control Experiments with HCl Replacing $ZnCl_2$

Under s nitrogen atmosphere, a solution of **1d** (0.3 mmol) and **2a** (0.6 mmol) in 2 mL of CH_2Cl_2 was added to a Schlenk tube. A CH_2Cl_2 solution of HCl (0.2956 M), prepared by bubbling HCl (gas) into anhydrous CH_2Cl_2, was then added at 0 °C. The reaction mixture was stirred at 0 °C. When the reaction was complete as monitored by TLC, the mixture was eluted with 10 mL of CH_2Cl_2 and filtered through a short column of silica gel (eluent: CH_2Cl_2 10 mL × 3). The organic phase was concentrated under reduced pressure and the crude product was analyzed by ^{1}H NMR measurement.

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[7] Crystal data for compound **3a**: $C_{26}H_{24}O$, MW = 352.45, monoclinic, space group $P21/n$, final R indices [$I > 2\sigma(I)$], $R1 = 0.0406$, $wR2 = 0.0809$, R indices (all data) $R1 = 0.1025$, $wR2 = 0.0908$, $a = 10.6062(5)$ Å, $b = 9.3855(4)$ Å, $c = 20.1820(10)$ Å, $\alpha = 90°$, $\beta = 96.479(4)°$, $\gamma = 90°$, $V = 1996.18(17)$ Å^3, $T = 293(2)$ K, $Z = 4$, reflections collected/unique: 9615/3649 ($R_{int} = 0.0398$), number of observations [$> 2\sigma(I)$] 1709, parameters: 244. CCDC 892249 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[18] A NOESY study of **5a** was conducted. As demonstrated in the NOESY spectrum (mixing time: 600 ms), strong interactions of H^5 and H^2, H^1 and H^2 were found. Weak interaction of H^1 and H^3 was also observed. NOESY study (mixing time: 300 ms) was then conducted. Strong interactions of H^5 and H^2, H^1 and H^2 could still be observed; however, the interaction of H^1 and H^3 was not shown, indicating that the spatial distance between H^1 and H^3 was farther than that beween H^1 and H^2. These observations all support the stereochemistry of **5a**. For the spectrum of this NOESY study, please see the Supporting Information.