Selected Paper

Intramolecular Substitution Reaction of Lithium Alkylidene Carbenoids. Regioselective Synthesis of Indenes

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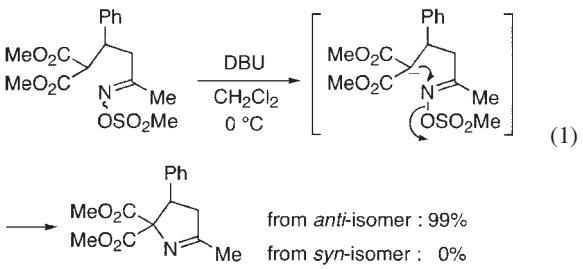
When 4,4-dibromo-3-alkenols are treated with butyllithium, an intramolecular substitution reaction with alkoxide moiety occurs at the lithium alkylidene carbenoid center to give dihydrofurans. The reaction mechanism of this intramolecular substitution reaction is studied by B3LYP density functional calculations with the 6-31+G(d) basis set, and the substitution is found to proceed in a concerted manner. This substitution reaction is applied to the regioselective preparation of indene derivatives. That is, treatment of 3-(*o*-bromophenyl)-1,1-dibromopropene derivatives **23** with butyllithium results in the formation of intramolecular substitution intermediates, 3-indenyllithiums **D**, which are trapped with electrophiles to afford substituted indenes regioselectively.

Recently we have reported the S_N2-type substitution reactions at sp^2 nitrogen of oxime derivatives.[1] For example, *anti* *O*-sulfonyloximes having an active methine group were converted to cyclic imines on treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), as shown in Eq. 1. Experimental investigations on the stereospecificity[1d,e] and a theoretical study[2] revealed that these reactions proceed via an unusual S_N2-type reaction at the sp^2 nitrogen of oximes.



(1)

Although an S_N2 reaction does not proceed at sp^2 atoms in general,[3] oxime derivatives readily suffer S_N2-type reactions at the sp^2 nitrogen of oximes. Accordingly, it was expected that S_N2 reaction would also occur at metal alkylidene carbenoids,[4] due to the structural similarity between oximes and metal alkylidene carbenoids, both of which have an electron pair (or negative charge) and a leaving group on the same atoms as depicted in Fig. 1.

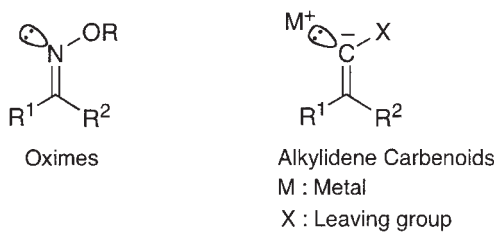
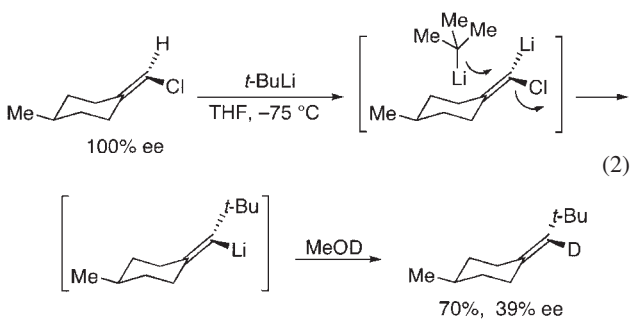


Fig. 1.

Actually there have been several examples of nucleophilic substitution of metal alkylidene carbenoids. In boron,[5a] zinc,[5b] aluminium,[6] chromium,[7] or zirconium[8] ate carbenoid complexes, the alkyl group on the metal migrates onto the carbenoid carbon with inversion of the configuration; this is known as 1,2-migration reaction of ate carbenoid complexes. Substitution reactions of lithium alkylidene carbenoids were also studied, and the inversion of the configuration was observed in the nucleophilic substitution at an optically active lithium alkylidene carbenoid carbon (Eq. 2),[9a,b] In addition, benzofurans were obtained from β,β-dichloro-*o*-hydroxy styrenes by treatment with alkyllithium at -100 °C (Eq. 3) by S_N2-type substitution.[9c] Although these results suggest the possibility of S_N2 reaction at sp^2 carbenoid carbon, other reaction mechanism should be taken into consideration. On the reaction of Eq. 2, due to the low inversion ratio (39% ee), insertion of carbene and/or electron transfer processes cannot be excluded as reaction pathways. In the latter case 6π-electrons cyclization and/or addition–elimination mechanism might be proposed as possible mechanisms.



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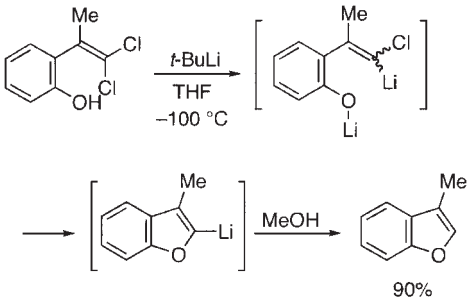
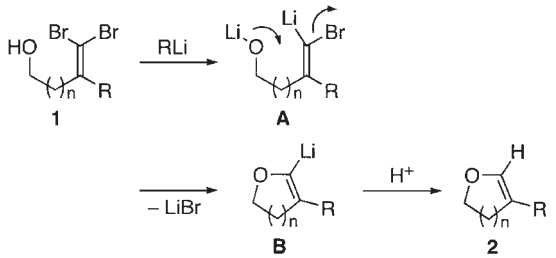


(3)

This article presents experimental and theoretical studies on the substitution reaction at lithium alkylidene carbenoid carbon and the application of this reaction to the regioselective preparation of indenes.

Results and Discussion

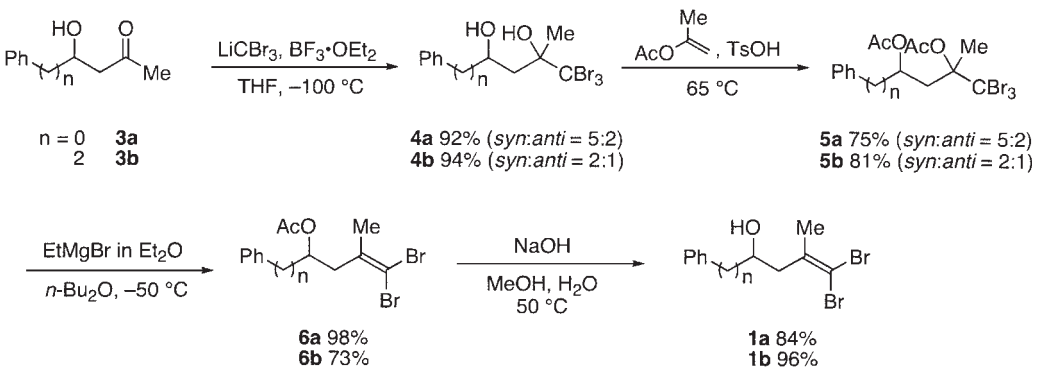
Intramolecular Reaction of Alkylidene Carbenoid with Alkoxide. *gem*-Dibromoalkenols **1** were chosen as model compounds to examine the substitution reaction of lithium carbenoids (Eq. 4). We supposed that alkylidene carbenoids **A** would be generated from **1** by treatment with alkyllithium via lithium–bromine exchange reaction.[10] A substitution reaction of the bromide with the intramolecular alkoxide moiety would occur at the carbenoid center of **A** to afford alkenyllithiums **B**, which would be finally protonated to give cyclic alkenyl ether **2**. Although this system is similar to the reaction of Eq. 3, non-conjugation with the methylene tether excludes the possibility of 6π-electrons cyclization for the formation of alkenyl ether **2**. Although we were afraid that only *E*-isomer of the intermediate **A** could participate in this reaction due to the stereospecificity of S_N2-type substitution, both (*E*)- and (*Z*)-lithium halogen alkylidene carbenoids are known to readily isomerize even at −85 °C.[11]



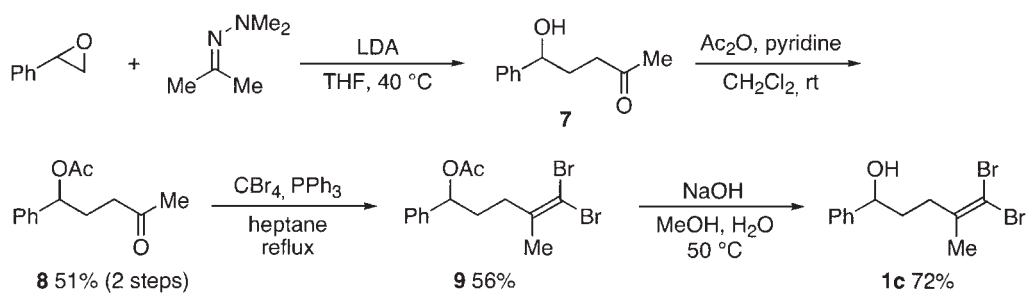
(4)

gem-Dibromoalkenols **1a**, **1b**, and **1c** were prepared by dibromomethylenation of the corresponding ketones, by applying either Normant's method[12] or Wittig-type dibromomethylenation[13] (Schemes 1 and 2).

Reaction of Dibromoalkenol 1a and Alkyllithium. 4,4-Dibromo-3-methyl-1-phenylbut-3-en-1-ol (**1a**) was treated with 3.3 molar amounts of *t*-butyllithium in tetrahydrofuran (THF) at −78 °C to generate carbenoid **A**. After 30 min at −78 °C, the reaction was quenched with MeOH to give the desired dihydrofuran **2a** in 26% yield along with 39% of (*E*)- and (*Z*)-monobromo alkenes **10a** in a 2:1 ratio (Table 1, entry 1). The formation of monobromoalkene **10a** shows that the cyclization of the carbenoid **A** did not complete at −78 °C because of the low nucleophilicity of the alkoxide moiety. To enhance the cyclization, the reaction was carried out at higher temper-

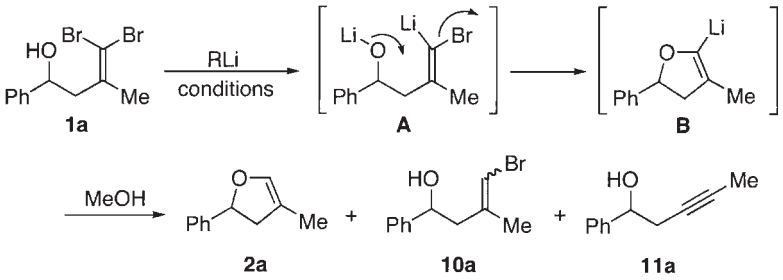


Scheme 1. Preparation of *gem*-dibromoalkenols **1a** and **1b**.



Scheme 2. Preparation of *gem*-dibromoalkenol **1c**.

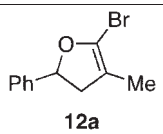
Table 1. Nucleophilic Substitution of Alkylidene Carbenoid



Entry	Solvent	RLi (equiv.)	Temp/°C	Time/min	Yield/%		
					2a	**10a**	**11a**
1	THF	*t*-BuLi (3.3)	−78	180	26	39	0
2	THF	*t*-BuLi (3.3)	−45	20	35	0	8
3[a,b]	toluene	*t*-BuLi (3.3)	−45	120	9	0	5
4	toluene	*t*-BuLi (3.3)	rt	6	42	0	15
5	toluene	*n*-BuLi (2.2)	rt	30	81	0	7

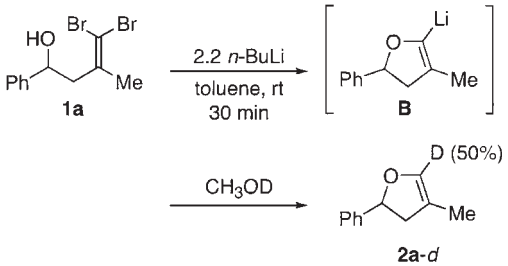
a) Starting material **1a** was recovered in 51%.

b) **12a** was obtained in 9% yield.



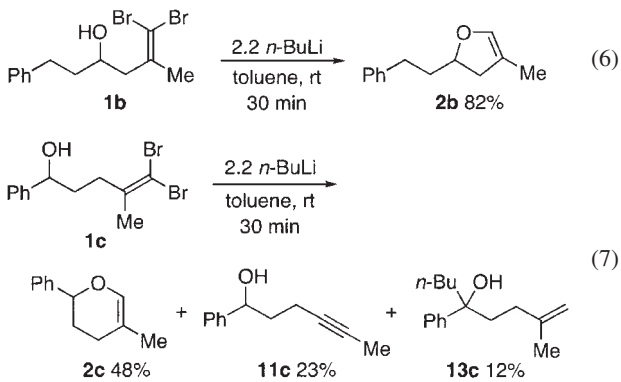
ature (−45 °C). The yield of **2a** was improved slightly but *t*-butyllithium was decomposed by the reaction with THF[14] (entry 2). In toluene at −45 °C, however, the lithiation of **1a** proceeded very slowly to recover 51% of the starting material **1a** with dihydrofuran **2a** and bromodihydrofuran **12a** in 18% total yield (entry 3). Bromodihydrofuran **12a** may be produced by lithium–bromine exchange between 2-lithiodihydrofuran **B** and **1a**. At room temperature **2a** was obtained in 42% yield (entry 4), and the yield was improved to 81% by using butyllithium instead of *t*-butyllithium (entry 5). A small amount of acetylene **11a** was detected as the consequence of 1,2-migration of alkylidene carbenoid **A**.[15] This means that the cyclization proceeds preferentially in the carbenoid **A** as compared with the well-known 1,2-migration of alkylidene carbenoids.

The formation of the cyclization intermediate, 5-lithio-2,3-dihydrofuran **B**, was confirmed by quenching the reaction with MeOD to give the deuterated **2a** (Eq. 5).



(5)

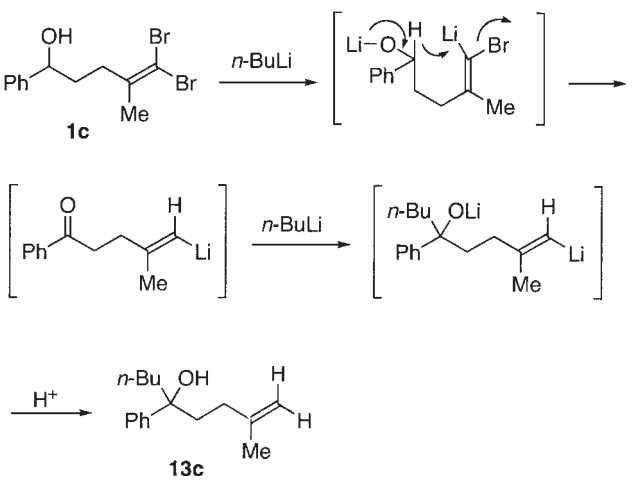
The cyclization of other dibromoalkenyl alcohols (**1b** and **1c**) was examined. Dihydrofuran formation from **1b** proceeded smoothly and dihydrofuran **2b** was obtained in 82% yield (Eq. 6). The 6-membered ring formation proceeded slower than that of the above 5-membered ring, dihydropyran **2c** was obtained from **1c** in 48% yield along with acetylene **11c** and alcohol **13c** (Eq. 7).



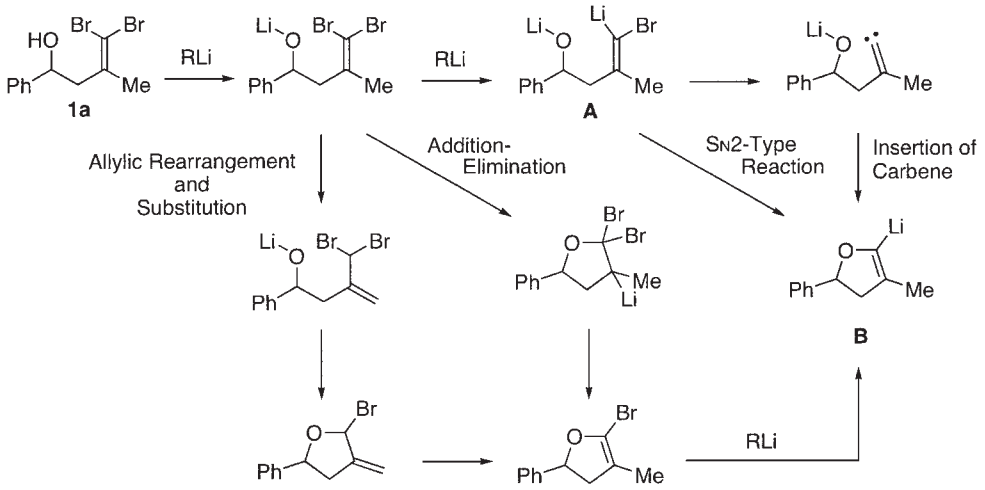
(6)

(7)

Alcohol **13c** was probably formed via the intramolecular hydride transfer as depicted in Scheme 3.[16]



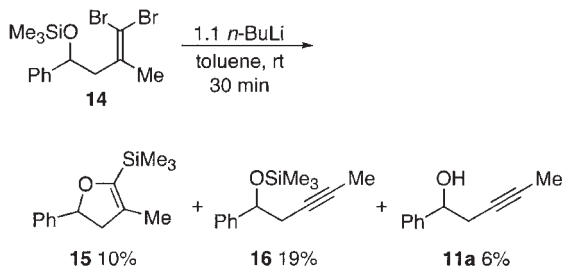
Scheme 3. Formation of alcohol **13c**.



Scheme 4. Four possible mechanisms.

At this stage, four possible mechanisms can be proposed for the cyclization: namely i) S_N2-type substitution, ii) insertion of carbene, iii) addition–elimination, and iv) allylic rearrangement and substitution reactions, as summarized in Scheme 4.

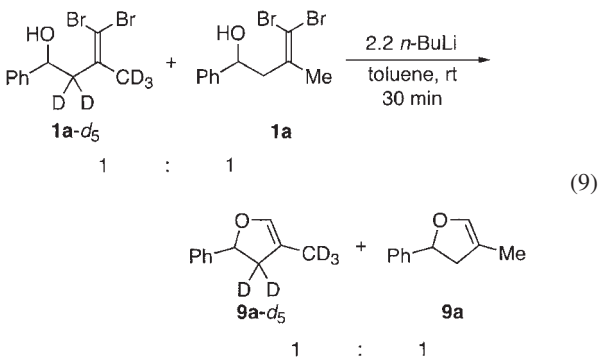
The alkylidene carbenes generated from 1-diazo-4-trimethylsiloxybut-1-ene derivatives readily undergo intramolecular insertion to the silicon–oxygen bond to give 5-trimethylsilyl-2,3-dihydrofurans in high yields.[17] When trimethylsiloxy dibromoalkene **14** was treated with slightly excess amounts of butyllithium under the same reaction conditions, dihydrofuran **15** was produced in only 10% yield, along with 25% yields of acetylenes **11a** and **16** (Eq. 8). Such results excluded the carbene insertion mechanism from being a major reaction pathway.



(8)

If the cyclization proceeds by the intramolecular addition of alkoxide to the dibromoalkene moiety and the successive elimination of bromide ion, bromodihydrofuran **12a** should be obtained from the lithium alkoxide of **1a**. When **1a** was treated with NaH or lithium diisopropylamide (LDA), however, none of the cyclized product was detected but the starting material **1a** was recovered after quenching with MeOH.

Allylic rearrangement and substitution by the reaction of the deuterated dibromoalkenol **1a**-d_5 (Eq. 9) were also improbable. When a mixture of deuterated **1a**-d_5 and non-deuterated **1a** was treated with butyllithium, no scramble of deuterium occurred, and only penta-deuterated 1,2-dihydrofuran **9a**-d_5 and no-deuterated **9a** were obtained. No scramble of deuterium was occurred.



(9)

Based on these results, the cyclization seems mostly to proceed by S_N2-type mechanism analogously to the substitution reactions of oxime derivatives. To confirm S_N2-type mechanism, one should check the stereospecificity of this cyclization and inversion of the configuration of the carbenoid center. It is, however, difficult to confirm experimentally which isomer participates in the cyclization, because *E* and *Z* isomerization of alkylidene carbenoids occurs even at low temperature as mentioned before.[11] We therefore have initiated a density functional theory (DFT) study of this reaction.

Theoretical Studies of the Lithium Alkylidene Carbenoids. To better understand these intramolecular substitution reactions of lithium alkylidene carbenoids, we have studied them computationally. All calculations were performed using the Gaussian 98 program.[18] Gibbs free energies are the values at 298.15 K and 1.00 atm obtained from the frequency calculations. The thermal energy corrections are not scaled.[19] Vibrational frequency calculations gave only one imaginary frequency for all transition structures and confirmed that those structures are authentic transition structures.

The lithium–bromine exchange reaction of dibromoalkenes with alkyllithium and the structures of the resulting lithium compounds were first studied (Eqs. 10, 11 and Fig. 2). The transition structure for the lithium–bromine exchange reaction of 1,1-dibromo-2-methylpropene **17** with methyllithium was located using density functional calculations with the B3LYP hybrid functional[20] and the 6-31+G(d) basis set. The attack

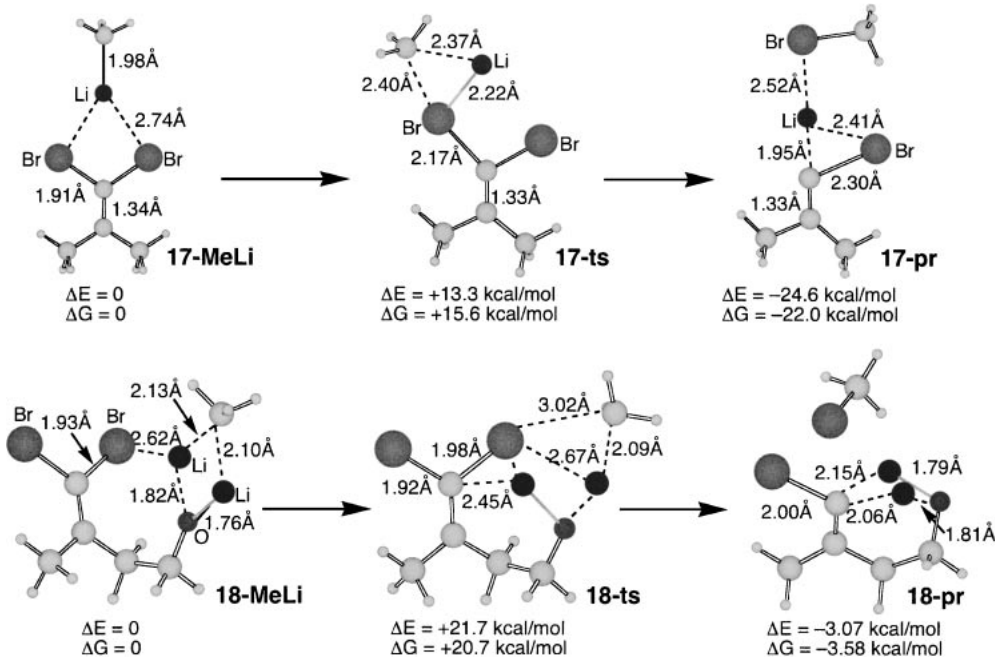
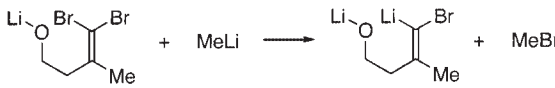


Fig. 2. Transition structures for the lithium–bromine exchange reaction [B3LYP/6-31+G(d)]. ΔE and ΔG are the differences in energy and the Gibbs free energy at 298.15 K, respectively.

by methyllithium on dibromoalkene initially involves the formation of a loose complex **17-MeLi** in which the incoming methyllithium is co-ordinated with two bromine atoms in the plane of the alkene. The activation free energy of the lithium–bromine exchange reaction is 15.6 kcal/mol. The reaction gives the bromolithioalkylidene carbenoid **17-pr**, where the sp^2 carbon contains both the positive metal (lithium) and the negative leaving group (bromine) and the C–Br bond is bridged by the lithium atom.

(10)



(11)

The C–Br bond in **17-pr** is 0.40 Å longer than that in **17** (1.90 Å) (B3LYP/6-31+G(d)). Furthermore, the structure of 1-bromo-1-lithio-2-methylpropene **19** in the presence of two dimethyl ether molecules was optimized (Fig. 3). The C–Br bond is 0.09 Å shorter than that in **17-pr**, while the Li–C and Li–Br distances are 0.04 and 0.11 Å longer than those of **17-pr**, respectively. In the presence of co-ordinating solvent, the C–Br bond is strengthened. These structures, **17-pr** and **19s** are consistent with both the ^{13}C NMR study[21] and the theoretical study[22] of the chlorolithioalkyl carbenoid (R_2CLiCl).

The lithium–bromine exchange reaction can also occur by the attack of the methyllithium having co-ordination to the O–Li part of the molecule **18**. The activation free energy for the lithium–bromine exchange reaction of **18** is 5 kcal/mol higher than that for **17** and the resulting lithium compound is the lithium cluster **18-pr**. Although the C–Br bond is not bridged by the lithium atom, it is still 0.10 Å longer than that in **18-MeLi**. The structure **18-pr** is rather similar to the crystal structure of 1-chloro-2,2-bis(4-chlorophenyl)-1-lithioethene in the presence of THF and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at −115 °C, where the lithium atom is solvated by TMEDA and THF.[23]

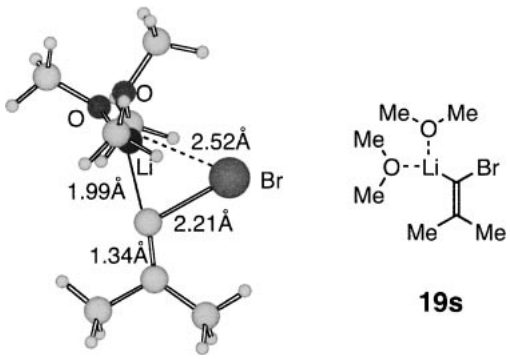


Fig. 3. The optimized structure of **19s** [B3LYP/6-31+G(d)].

Since either the lithium compounds are aggregated or the lithium atom is solvated in solution, the comparison of these lithium–bromine exchange processes is not straightforward. Judging from these results, we concluded that the intramolecular process for the lithium–bromine exchange reaction is not a particularly advantageous process compared to the intermolecular one. Therefore, we studied both types of the organolithium species **20**–**22** for the intramolecular substitution reaction of lithium alkylidene carbenoids (Scheme 5 and Fig. 4). The structures **20** and **21** are the two isomers where the C–Br bond is bridged by the lithium atom. The isomer **21** is

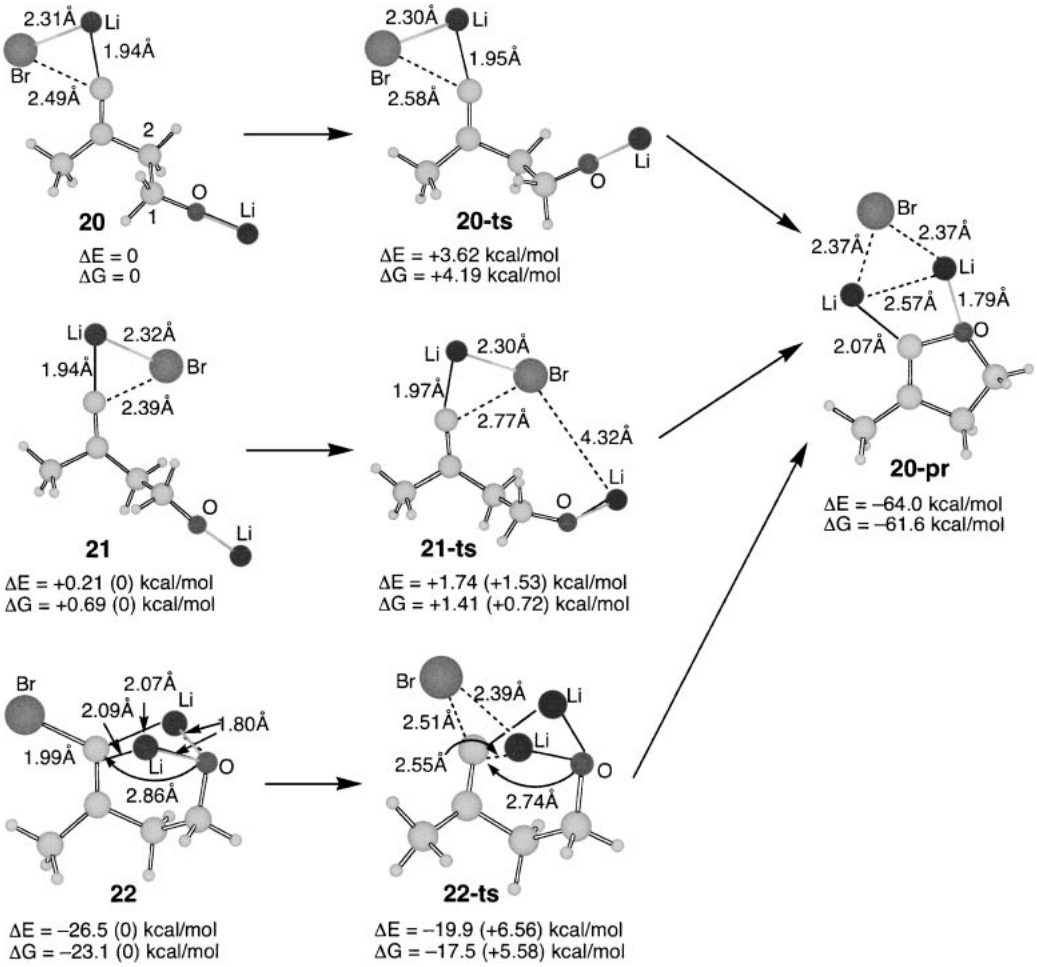
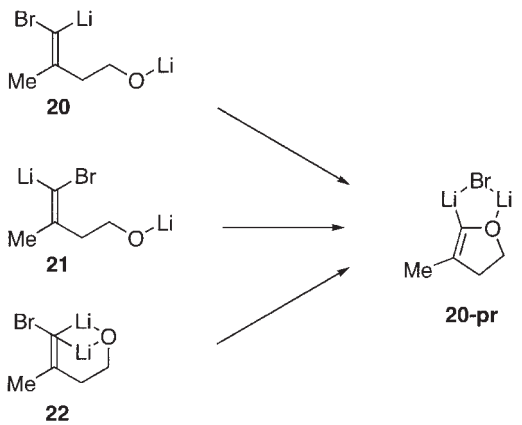


Fig. 4. Transition structures for the intramolecular substitution reaction of lithium alkylidene carbenoids [B3LYP/6-31+G(d)]. ΔE and ΔG are the differences in energy and the Gibbs free energy at 298.15 K, respectively.



Scheme 5.

0.69 kcal/mol higher than **20** in Gibbs free energy. The intramolecular substitution reactions of **20** and **21** require the activation energy of 4.19 and 0.72 kcal/mol, respectively, to give the dihydrofuran **20-pr**. Both the transition structures **20-ts** and **21-ts** are in essence the rotational ones around the C1–C2 bond. When the O–Li part is close enough to the Li–Br part of the molecule, they attract each other and the bromine atom separates completely apart from the alkylidene carbon. After that, the C–O bond forms to make the dihydrofuran **20-pr**. The lithium cluster compound **22** was obtained by removing methyl bromide from **18-pr** and optimizing the resulting structure. The existence of the lithium cluster structure makes **22** more stable than **20** by 23.1 kcal/mol. The cyclization reaction of **22** is also an easy process, it requires an activation energy of 5.58 kcal/mol. In the transition structure **22-ts**, the C–Br bond is almost broken (2.51 Å), while the C–O distance is only slightly shorter than that in **22** (2.74 Å vs 2.86 Å).

Although the activation energies of the cyclization of **20** and **21** are lower than that of **22**, **20** and **21** are more unstable than the cluster **22**. Accordingly, the cyclization mainly proceeds through cluster **22**. In all these mechanisms, the driving force of the reaction seems to be the Li–Br interaction rather than the O^- nucleophilic attack. However, the intramolecular substitution reaction of the lithium alkylidene carbenoid proceeds in a concerted manner.

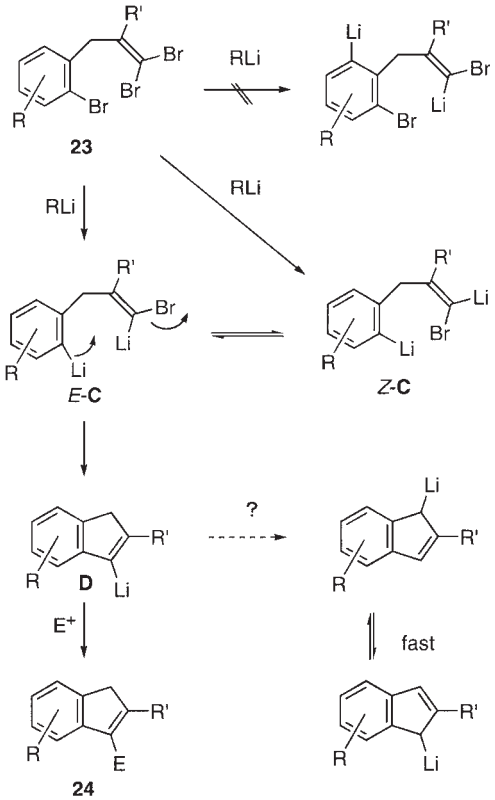
Reaction of Alkylidene Carbenoid with Intramolecular Carbanion Species. The substitution of lithium alkylidene carbenoids with intramolecular carbon nucleophiles was examined to explore a synthetic method for carbocycles. Firstly preparation of indene was examined from 3-(*o*-bromophen-

yl)-1,1-dibromopropenes **23** (Scheme 6). It was expected that dilithio compound **C** will be generated by lithium–bromine exchange reaction, and the successive intramolecular nucleophilic substitution would give 3-indenyllithium **D**. Alkenyllithium **D** thus formed would react with electrophiles to give poly-substituted indenes in a regioselective manner.

Dibromoalkenes **23a–d** were prepared by the reaction of the corresponding ketones with tribromomethyllithium[12] similarly to Scheme 1 (Normant's method), and 4-(*o*-bromophenyl)-1,1-dibromoalkenes **27a–d** were synthesized by Wittig-type reaction[13] (Table 2).

The reactions of **23a** with butyllithium under several reaction conditions are summarized in Table 3. No lithium–bromine exchange occurred at bromophenyl moiety in toluene and 78% of **23a** was recovered (entry 1). The reaction in THF at −78 °C afforded indene **28a** in 74% yield after being quenched with MeOH (entry 2). At a lower temperature (−90 °C), the yield of indene **28a** was increased to 85% (entry 3), whereas the yield of **28a** was lowered substantially at −105 °C (entry 4). It is noteworthy that dibromoalkene **23a** was recovered quantitatively when $BrCF_2CF_2Br$ was used as an electrophile instead of MeOH in the reaction at −105 °C, while the desired bromoindene **29a** was obtained in 83% yield at −90 °C (entries 5 and 6). These observations mean that dilithiation proceeded even at −105 °C,[10b] but little cyclization of lithium carbenoid **C** to alkenyllithium **D** occurred at −105 °C. For the cyclization, the reaction has to be carried out at −90 °C.

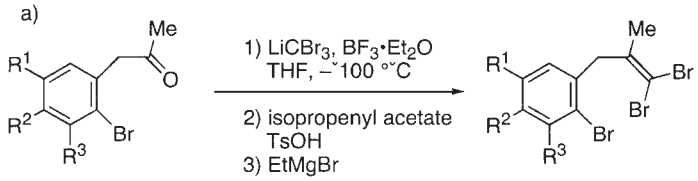
As previously mentioned, Topolski carried out the benzofuran formation by the intramolecular substitution of lithium alkylidene carbenoid with the phenoxide moiety at −100 °C



Scheme 6. Synthetic plan of indenes **24**.

Table 2. Preparation of **23** and **27**

a)

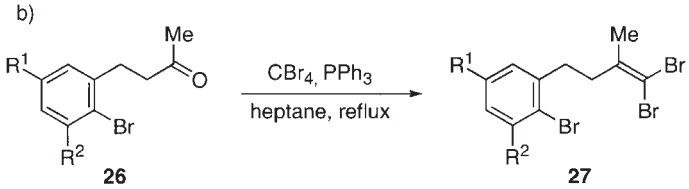


25 **23**

Entry	R^1	R^2	R^3	Yield*/%	
1	H	H	H	**23a**	76
2	MeO	H	H	**23b**	69
3	H	CF_3	H	**23c**	48
4	H	H	Me	**23d**	78

∗Total yield from **25** (3 steps).

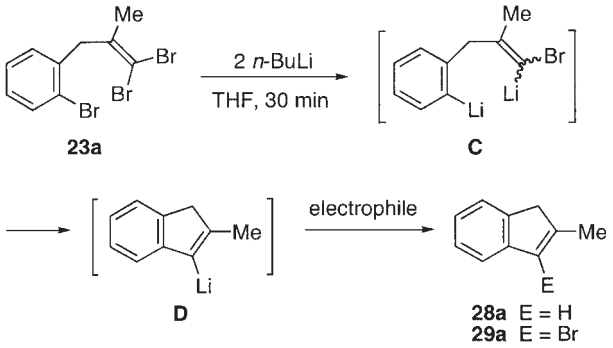
b)



26 **27**

Entry	R^1	R^2	Yield/%	
1	H	H	**27a**	74
2	MeO	H	**27b**	51
3	F	H	**27c**	53
4	H	Me	**27d**	73

Table 3. Nucleophilic Substitution with Aryllithium



Entry	Temp/°C	Electrophile	Yield/%		
			28a	**29a**	**23a**
1[a)]	−78	MeOH	0	—	78
2	−78	MeOH	74	—	0
3	−90	MeOH	85	—	0
4	−105	MeOH	45	—	0
5	−90	$BrCF_2CF_2Br$	0	83	0
6	−105	$BrCF_2CF_2Br$	0	0	quant.

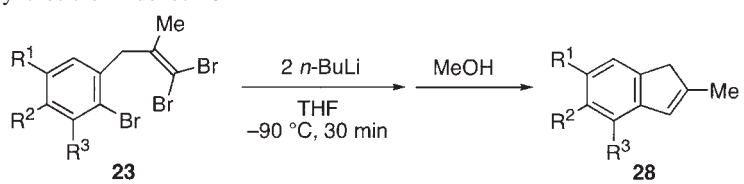
a) Toluene was used as a solvent instead of THF.

(Eq. 3). The cyclization of lithium carbenoids **C** with the intramolecular alkoxide and phenyl anion moieties had to be performed at higher temperature (rt and −90 °C, respectively), although the nucleophilicities of alkoxide and of phenyl anion are higher than that of phenoxide. These results imply that benzofuran formation would proceed mainly via 6π-electrons cyclization.

The preparation of indenes from various dibromoalkenes **23** is summarized in Table 4. Dibromoalkenes having methoxy- or trifluoromethyl-phenyl group were converted to indenes in good yields (entries 2 and 3). Furthermore, nucleophilic attack of sterically hindered ortho methylphenyl anion proceeded smoothly, but the expected **28d** and the double bond isomer **28d′** were obtained in a ratio of 5:1 in 86% total yield (entry 4). The formation of the regio isomer **28d′** occurred exceptionally only when the reaction was quenched with methanol, and no regioisomer was found in the reaction with other electrophiles (vide infra, Table 4). The regio isomer **28d′** was formed by the isomerization of resultant 3-indenyllithium to 1-indenyllithium by a sequential protonation and deprotonation with the product **28d** at the stage of quenching with MeOH. It is supposed that a more acidic proton source would depress the double bond isomerization by diminishing the formation of 1-indenyllithium. Actually, the ratio of **28d** and **28d′** changed to 12:1 by the use of 2 M HCl in ether as a proton source (entries 4 and 5). These phenomena indicate that the cyclization affords 3-indenyllithium[24] regioselectively and that little regio isomerization of the indenyl double bond occurs at −90 °C. This makes a keen contrast to 1-indenyllithium, which is likely to isomerize as allylic lithium species.

Since no double bond isomerization of 3-indenyllithium **D** was observed at −90 °C, regioselective preparation of polysubstituted indenes was examined by quenching 3-indenyllithium **D** with other electrophiles (Table 5). When the cyclized

Table 4. Synthesis of indenes **28**



Entry	**23**	R^1	R^2	R^3	Yield/%	
1	**23a**	H	H	H	**28a**	85
2	**23b**	MeO	H	H	**28b**	85
3	**23c**	H	CF_3	H	**28c**	86
4	**23d**	H	H	Me	**28d**	86[a)]
5[b)]	**23d**	H	H	Me	**28d**	86[c)]

a) Mixture of **28d**:**28d′** in a ratio of 5:1.
b) 2 M HCl in ether was used instead of MeOH.
c) Mixture of **28d**:**28d′** in a ratio of 12:1.

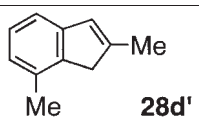
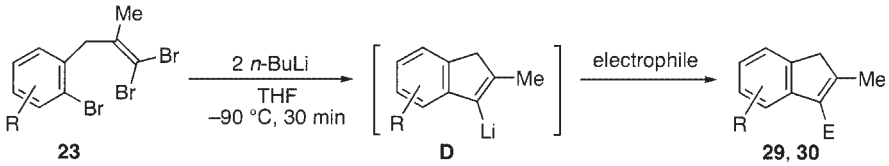
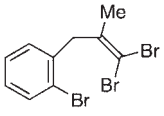
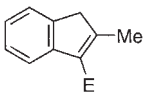
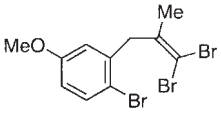
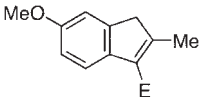
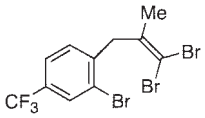
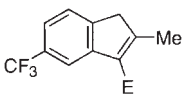
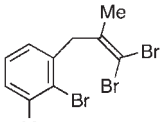
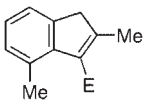


Table 5. Reactions of Intermediate **D** with Electrophiles



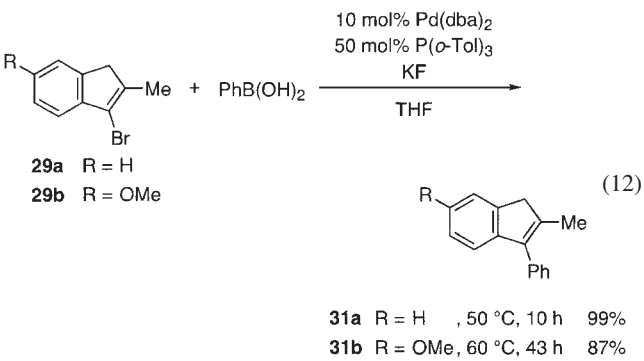
23 **D** **29, 30**

Entry	Substrate	Electrophile	Product	E	Yield/%	
1	 **23a**	$BrCF_2CF_2Br$		Br	**29a**	83
2		PhCHO		CH(OH)Ph	**30a**	84
3	 **23b**	$BrCF_2CF_2Br$		Br	**29b**	80
4		PhCHO		CH(OH)Ph	**30b**	87
5	 **23c**	$BrCF_2CF_2Br$		Br	**29c**	28
6		PhCHO		CH(OH)Ph	**30c**	49
7	 **23d**	$BrCF_2CF_2Br$		Br	**29d**	63
8		PhCHO		CH(OH)Ph	**30d**	87

intermediate **D** was treated with $BrCF_2CF_2Br$ at −90 °C, 3-bromoindene **29a** was obtained exclusively without forming 1-bromoindene (entry 1). By quenching with benzaldehyde, 3-substituted indene **30a** was also prepared regioselectively (entry 2). Substituted phenyl derivatives **23b–d** were also transformed to polysubstituted indenes **29** and **30** as shown in entries 3–8. 2-*o*-Anisyl-1,1-dibromoalkenes **23b** and *o*-tolylmethyldibromoalkenes **23d** gave indenes **29b**, **30b** and **29d**, **30d** in good yields, respectively (entries 3, 4, 7, and 8), while trifluoromethyl-substituted **23c** gave indenes **29c** and **30c** in moderate yields perhaps due to the lower nucleophilicity of indenyllithium **D**. Even sterically hindered 2,3,4-trisubstituted indenes **29d** and **30d** could be prepared exclusively from **23d** without forming 2,3,7-trisubstituted indenes (entries 5 and 6).

Indenes are known as precursors of indenyl ligands in various metal complexes such as Kaminsky-type catalysts.[25] Furthermore, an inhibitor of HIV protease has an indane skeleton, which was derived from an indene.[26] There are several methods to synthesize substituted indenes. Among them, two procedures are generally used to introduce a substituent onto the 5-membered ring of indenes: one is addition reaction to indanone followed by dehydroxylation,[27] and the other is metallation of indene followed by reaction with electrophiles.[28] Few examples, however, are reported for the regioselective preparation of polysubstituted indenes. For example, 1-indanones are not usually prepared regioselectively by Friedel–Crafts reactions, although the next addition reaction of nucleophiles to 1-indanones proceeds in a regioselective manner. The reaction of electrophiles with indenyllithiums is unreliable for the regioselective alkylation, because 1-indenyllithiums, which are generated by the deprotonation of indenes, can easily isomerize between two double bond isomers.

Synthesized 3-bromoindenes **29** were converted to 3-phenylindenes by Suzuki coupling[29] (Eq. 12). 3-Bromoindenes reacted with boronic acid by the palladium-catalyzed coupling to afford 3-phenylindenes in good yields.



29a R = H
29b R = OMe

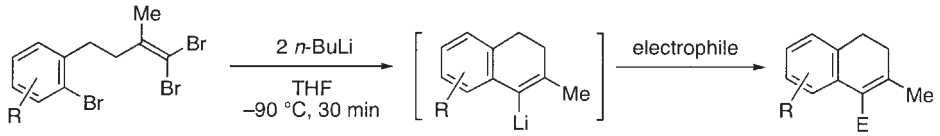
(12)

31a R = H , 50 °C, 10 h 99%
31b R = OMe, 60 °C, 43 h 87%

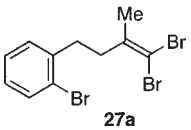
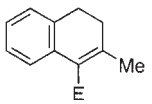
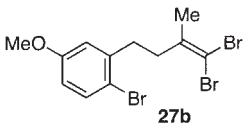
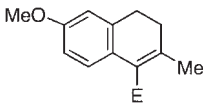
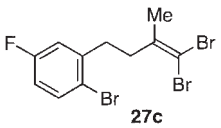
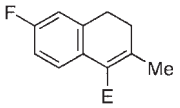
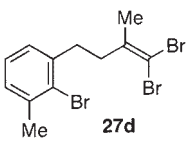
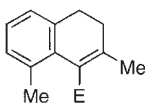
Along with indene formation, 4-substituted-1,2-dihydronaphthalene derivatives were also synthesized in good yields in a similar manner from 1,1-dibromo-4-(2-bromophenyl)but-1-enes **27** by the consecutive treatment of butyllithium and electrophile (Table 6). In this case, no regioisomerization of double bond was observed even in the reaction of *o*-methyl substituted bromophenyl derivative **27d** (entries 10–12).

In conclusion, 5 or 6-membered ring formation can be carried out by the intramolecular substitution reaction at lithium alkylidene carbenoid carbons which are generated by the treatment of *gem*-dibromoalkenes with alkyllithiums. Experimental and theoretical studies revealed that this reaction proceeds

Table 6. Preparation of dihydronaphthalenes **32–34**



27 **D** **32-34**

Entry	Substrate	Electrophile	Product	E	Yield/%	
1	 **27a**	MeOH		H	**32a**	76
2		$BrCF_2CF_2Br$		Br	**33a**	77
3		PhCHO		CH(OH)Ph	**34a**	77
4	 **27b**	MeOH		H	**32b**	64
5		$BrCF_2CF_2Br$		Br	**33b**	61
6		PhCHO		CH(OH)Ph	**34b**	58
7	 **27c**	MeOH		H	**32c**	81
8		$BrCF_2CF_2Br$		Br	**33c**	74
9		PhCHO		CH(OH)Ph	**34c**	76
10	 **27d**	MeOH		H	**32d**	49
11		$BrCF_2CF_2Br$		Br	**33d**	48
12		PhCHO		CH(OH)Ph	**34d**	45

in a concerted manner. Indenes are synthesized in good yields from 3-(*o*-bromophenyl)-1,1-dibromopropenes. Furthermore, the cyclized intermediates, 3-indenyllithiums, allow the regioselective introduction of electrophiles to be converted to polysubstituted indenes in a regioselective manner.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DRX 500 and a Bruker AVANCE 500 spectrometer in $CDCl_3$ solutions using $CHCl_3$ (for ^{1}H, $\delta = 7.24$) and $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-700P mass spectrometer [EI (ionization energy: 70 eV) or FAB]. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Toluene was distilled and dried over Molecular Sieves 4A. THF was purchased in anhydrous form from Kanto Chemical Co., Inc., and was dried over Molecular Sieves 4A. Preparative TLC was performed on a silica gel (Wakogel B-5F).

Preparation of Tribromomethyl Diol 4. The experimental procedure for the preparation of 4,4,4-tribromo-3-methyl-1-phenylbutane-1,3-diol (**4a**) is shown below as a typical example.

To an ice-cold solution of diisopropylamine (8.92 mL, 64 mmol) in THF (400 mL) was slowly added a solution of butyllithium in hexane (1.6 mol dm^{-3}, 37.4 mL, 58 mmol); the mixture was stirred at the same temperature for 30 min. This mixture then was cooled to -100 °C, and bromoform (5.10 mL, 58 mmol) was added, and the mixture was stirred at the same temperature for 25 min, followed by addition of 1-hydroxy-1-phenylbutan-3-one[30] (4.35 g, 27.0 mmol) in THF (20 mL), and consecutive addition of $BF_3 \cdot Et_2O$ (3.36 mL, 27 mmol). This mixture was stirred at the same temperature for 70 min. After the reaction was quenched with aq. sat. NH_4Cl, the mixture was extracted three times with ethyl acetate. The combined extracts was dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 4:1) to give 4,4,4-tribromo-3-methyl-1-phenylbutane-1,3-diol (**4a**) (10.2 g, 24.4 mmol, 92%).

4,4,4-Tribromo-3-methyl-1-phenylbutane-1,3-diol (4a): The *syn*(1*R**, 3*S**)/*anti*(1*R**, 3*R**) ratio was determined to be 5:2 by ^{1}H NMR analysis; the relative configurations were determined by measuring NOE of the acetonides **4a′** (prepared from diol **4a** with acetone dimethyl acetal in CH_2Cl_2 under the presence of a catalytic amount of *p*-$CH_3C_6H_4SO_3H$).

(1*R, 3*S**)-4,4,4-Tribromo-3-methyl-1-phenylbutane-1,3-diol (*syn*-4a):** White crystal; mp 87–88 °C (hexane); IR (KBr) 3207 (br), 1454, 1151, 1119, 729, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (3H, s), 2.28–2.32 (1H, m), 2.61 (1H, dd, $J = 10.7$, 14.7 Hz), 3.14 (1H, brs), 4.37 (1H, brs), 5.08 (1H, d, $J = 10.7$ Hz), 7.29–7.32 (1H, m), 7.36–7.41 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 44.2, 63.0, 72.3, 82.6, 125.7, 128.1, 128.8, 143.5; Anal. Found: C, 31.85; H, 3.10%. Calcd for $C_{11}H_{13}Br_3O_2$: C, 31.69; H, 3.14%.

(1*R, 3*R**)-4,4,4-Tribromo-3-methyl-1-phenylbutane-1,3-diol (*anti*-4a):** White crystal; mp 79 °C (hexane); IR (KBr) 3292 (br), 953, 764, 735, 712, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (3H, s), 2.37 (1H, brs), 2.43 (1H, dd, $J = 9.2$, 15.0 Hz), 2.56 (1H, dd, $J = 2.5$, 15.0 Hz), 3.27 (1H, brs), 5.25 (1H, dd, $J = 2.5$, 9.2 Hz), 7.27–7.30 (1H, m), 7.34–7.41 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.2, 44.9, 63.8, 71.9, 82.2, 125.7, 127.8, 128.7, 144.4; Anal. Found: C, 31.74; H, 3.12%. Calcd for $C_{11}H_{13}Br_3O_2$: C, 31.69; H, 3.14%.

(4*R, 6*S**)-2,2,4-Trimethyl-6-phenyl-4-tribromomethyl-1,3-dioxane (*syn*-4a′):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (3H, s), 1.60 (3H, s), 1.86 (3H, d, $J = 0.7$ Hz), 2.07 (1H, dd,

J = 2.4, 13.1 Hz), 2.23 (1H, ddq, J = 0.7, 11.6, 13.1 Hz), 4.99 (1H, dd, J = 2.4, 11.6 Hz), 7.29–7.32 (1H, m), 7.36–7.43 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.9, 24.2, 30.8, 38.2, 62.5, 68.6, 81.6, 101.2, 126.1, 128.0, 128.6, 141.3.

(4*R,6*R**)-2,2,4-Trimethyl-6-phenyl-4-tribromomethyl-1,3-dioxane (*anti*-4a′):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56 (3H, s), 1.61 (3H, s), 1.85 (3H, s), 2.04 (1H, dd, J = 10.6, 14.0 Hz), 2.65 (1H, dd, J = 5.4, 14.0 Hz), 5.04 (1H, dd, J = 5.4, 10.6 Hz), 7.27–7.30 (1H, m), 7.35–7.41 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.7, 27.3, 29.6, 41.3, 61.4, 69.7, 81.9, 102.5, 125.8, 127.8, 128.6, 141.4.

1,1,1-Tribromo-2-methyl-6-phenylhexane-2,4-diol (4b): The *syn*(2*R**, 4*R**)/*anti*(2*R**, 4*S**) ratio was determined to be 2:1 by ^{1}H NMR analysis, and relative configurations were determined by measuring NOE of the acetonides **4b′**.

(2*R, 4*R**)-1,1,1-Tribromo-2-methyl-6-phenylhexane-2,4-diol (*syn*-4b):** White crystal; mp 93 °C (hexane); IR (ZnSe) 3330 (br), 1120, 714, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (3H, s), 1.79–1.86 (1H, m), 1.88–1.95 (1H, m), 2.16 (1H, d, J = 14.4 Hz), 2.31 (1H, dd, J = 10.4, 14.4 Hz), 2.73 (1H, ddd, J = 6.7, 9.0, 14.1 Hz), 2.79 (1H, ddd, J = 6.3, 9.4, 14.1 Hz), 2.92 (1H, brs), 4.01–4.05 (1H, m), 4.16 (1H, brs), 7.17–7.21 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.9, 31.7, 39.7, 41.6, 63.5, 69.2, 82.8, 126.1, 128.4, 128.5, 141.4; Anal. Found: C, 35.10; H, 3.81%. Calcd for $C_{13}H_{17}Br_3O_2$: C, 35.09; H, 3.85%.

(2*R, 4*S**)-1,1,1-Tribromo-2-methyl-6-phenylhexane-2,4-diol (*anti*-4b):** White crystal; mp 114 °C (hexane); IR (ZnSe) 3423 (br), 3255 (br), 1111, 733, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (3H, s), 1.86–1.92 (3H, m), 2.11 (1H, dd, J = 8.9, 14.8 Hz), 2.38 (1H, dd, J = 2.4, 14.8 Hz), 2.71 (1H, ddd, J = 7.8, 8.0, 13.9 Hz), 2.80 (1H, ddd, J = 7.6, 7.8, 13.9 Hz), 4.13–4.19 (1H, m), 7.16–7.21 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.2, 32.0, 39.9, 42.9, 64.4, 69.1, 82.2, 126.0, 128.4, 128.5, 141.6; Anal. Found: C, 35.05; H, 3.78%. Calcd for $C_{13}H_{17}Br_3O_2$: C, 35.09; H, 3.85%.

(4*R, 6*S**)-2,2,4-Trimethyl-6-phenethyl-4-tribromomethyl-1,3-dioxane (*syn*-4b′):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (3H, s), 1.51 (3H, s), 1.67 (3H, s), 1.77–1.84 (2H, m), 1.90–1.98 (2H, m), 2.70 (1H, ddd, J = 8.1, 8.1, 14.0 Hz), 2.82 (1H, ddd, J = 5.3, 8.9, 14.0 Hz), 3.86 (1H, dddd, J = 2.4, 3.9, 8.3, 11.3 Hz), 7.17–7.20 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.9, 24.2, 30.8, 31.2, 36.2, 37.6, 63.0, 65.0, 81.5, 100.7, 125.9, 128.4, 128.5, 141.6.

(4*R, 6*R**)-2,2,4-Trimethyl-6-phenethyl-4-tribromomethyl-1,3-dioxane (*anti*-4b′):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (3H, s), 1.51 (3H, s), 1.71 (1H, dd, J = 9.9, 13.8 Hz), 1.78 (3H, s), 1.79–1.92 (2H, m), 2.33 (1H, dd, J = 5.6, 13.8 Hz), 2.64 (1H, ddd, J = 5.5, 9.5, 13.9 Hz), 2.81 (1H, ddd, J = 7.1, 9.1, 13.9 Hz), 3.88–3.94 (1H, m), 7.15–7.19 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.6, 27.0, 29.7, 31.5, 37.7, 38.9, 61.9, 66.9, 81.7, 102.0, 125.9, 128.4, 128.4, 141.7.

Preparation of Diacetate 5. The experimental procedure for the preparation of 2,4-diacetoxy-1,1,1-tribromo-2-methyl-4-phenylbutane (**5a**) is shown below as a typical example.

To a mixture of 4,4,4-tribromo-3-methyl-1-phenylbutane-1,3-diol (**4a**) (10.2 g, 24.4 mmol) and isopropenyl acetate (250 mL, 2.3 mol) was added $TsOH \cdot H_2O$ (32.6 g, 171 mmol) at once; then the mixture was heated to 65 °C for 9 h. After remove of isopropenyl acetate in vacuo, 200 mL of ethyl acetate was added, with subsequent addition of aq. K_2CO_3 to achieve neutrality. The mixture was extracted three times with ethyl acetate; then the combined mixture was washed with brine. The ethyl acetate solution was dried over anhydrous sodium sulfate, and ethyl acetate was removed in vacuo. The residue was purified by chromatography (silica gel, hexane:ethyl acetate = 9:1) to give 1,3-diacetoxy-4,4,4-tribromo-3-methyl-1-phenylbutane (**5a**) (9.14 g, 18.2 mmol, 75%).

2,4-Diacetoxy-1,1,1-tribromo-2-methyl-4-phenylbutane (5a): The diastereomer ratio was determined to be 5:2 by ^{1}H NMR analysis, and this ratio was same as **4a**, so we presumed that the major one was *syn* isomer.

(2*R, 4*R**)-2,4-Diacetoxy-1,1,1-tribromo-2-methyl-4-phenylbutane (*syn*-5a):** White needle; mp 77 °C (hexane); IR (KBr) 1751, 1738, 1234, 721, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.04 (3H, s), 2.05 (3H, s), 2.10 (3H, s), 2.59 (1H, dd, J = 3.6, 15.5 Hz), 3.06 (1H, dd, J = 9.1, 15.5 Hz), 6.19 (1H, dd, J = 3.6, 9.1 Hz), 7.26–7.29 (1H, m), 7.32–7.39 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 21.2, 22.4, 42.8, 56.4, 73.1, 89.1, 126.5, 128.2, 128.7, 140.7, 168.8, 169.7; Anal. Found: C, 36.12; H, 3.41%. Calcd for $C_{15}H_{17}Br_3O_4$: C, 35.96; H, 3.42%.

(2*R, 4*S**)-2,4-Diacetoxy-1,1,1-tribromo-2-methyl-4-phenylbutane (*anti*-5a):** White crystal; mp 90–92 °C (hexane); IR (KBr) 1741, 1722, 1250, 1232, 729 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (3H, s), 2.03 (3H, s), 2.05 (3H, s), 2.55 (1H, dd, J = 2.5, 16.0 Hz), 2.88 (1H, dd, J = 9.4, 16.0 Hz), 6.31 (1H, dd, J = 2.5, 9.4 Hz), 7.26–7.28 (1H, m), 7.32–7.35 (2H, m), 7.37–7.40 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 21.2, 22.0, 43.5, 56.9, 73.4, 89.0, 126.3, 128.1, 128.6, 140.8, 169.1, 169.8; Anal. Found: C, 36.24; H, 3.41%. Calcd for $C_{15}H_{17}Br_3O_4$: C, 35.96; H, 3.42%.

2,4-Diacetoxy-1,1,1-tribromo-2-methyl-6-phenylhexane (5b): The diastereomer ratio was determined to be 2:1 by ^{1}H NMR analysis, and this ratio was same as **4b**, so we presumed that the major one was *syn* isomer.

(2*R, 4*R**)-2,4-Diacetoxy-1,1,1-tribromo-2-methyl-6-phenylhexane (*syn*-5b):** Colorless oil; IR (neat) 3026, 1753, 1736, 1240, 715 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88–2.00, (2H, m), 2.01 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 2.41 (1H, dd, J = 2.7, 15.6 Hz), 2.64 (2H, t, J = 8.1 Hz), 2.75 (1H, dd, J = 8.5, 15.6 Hz), 5.37 (1H, dddd, J = 2.7, 6.1, 6.1, 8.5 Hz), 7.15–7.18 (3H, m), 7.24–7.27 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 21.2, 22.4, 31.4, 37.2, 40.5, 56.6, 71.0, 89.2, 126.0, 128.3, 128.5, 141.0, 168.8, 170.4; Anal. Found: C, 38.44; H, 3.98%. Calcd for $C_{17}H_{21}Br_3O_4$: C, 38.59; H, 4.00%.

(2*R, 4*S**)-2,4-Diacetoxy-1,1,1-tribromo-2-methyl-6-phenylhexane (*anti*-5b):** Colorless oil; IR (neat) 1739, 1736, 1367, 1228, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88–1.99 (2H, m), 1.93 (3H, s), 2.01 (3H, s), 2.08 (3H, s), 2.48 (1H, dd, J = 2.4, 15.9 Hz), 2.57 (1H, dd, J = 8.2, 15.9 Hz), 2.64 (2H, t, J = 8.2 Hz), 5.48 (1H, dddd, J = 2.4, 6.0, 6.1, 8.2 Hz), 7.14–7.17 (3H, m), 7.25–7.27 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.1, 21.2, 22.2, 31.4, 37.1, 41.2, 57.0, 71.3, 89.1, 125.9, 128.3, 128.4, 141.3, 169.0, 170.4; Anal. Found: C, 38.57; H, 4.03%. Calcd for $C_{17}H_{21}Br_3O_4$: C, 38.59; H, 4.00%.

Preparation of Dibromoalkenyl Acetate 6. The experimental procedure for the preparation of 4,4-dibromo-3-methyl-1-phenylbut-3-enyl acetate (**6a**) is shown below as a typical example.

To a dibutyl ether solution of 2,4-diacetoxy-1,1,1-tribromo-2-methyl-4-phenylbutane (**5a**) (8.54 g, 17.0 mmol) was added an ether solution of EtMgBr (3 mol dm^{-3}, 23 mL, 68 mmol) at −78 °C. The mixture was stirred at −50 °C for 2 h; then the reaction was quenched with aq. sat. NH_4Cl. The mixture was ex-

tracted three times with ethyl acetate; then the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give crude product of 4,4-dibromo-3-methyl-1-phenylbut-3-enyl acetate (**6a**) (6.01 g, 16.6 mmol, 98%). This crude product was used in the next reaction without further purification.

4,4-Dibromo-3-methyl-1-phenylbut-3-enyl Acetate (6a): Colorless oil; IR (ZnSe) 1738, 1225, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.85 (3H, s), 2.07 (3H, s), 2.61 (1H, dd, $J = 5.2$, 13.7 Hz), 2.96 (1H, dd, $J = 9.0$, 13.7 Hz), 5.95 (1H, dd, $J = 5.2$, 9.0 Hz), 7.27–7.36 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 23.6, 44.9, 73.5, 88.5, 126.3, 128.3, 128.6, 137.9, 139.7, 169.9; Anal. Found: C, 43.40; H, 3.84%. Calcd for $C_{13}H_{14}Br_2O_2$: C, 43.13; H, 3.90%.

4,4-Dibromo-3-methyl-1-phenethylbut-3-enyl Acetate (6b): Colorless oil; IR (neat) 1743, 1728, 1373, 1223, 812 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.82–1.97 (2H, m), 1.87 (3H, s), 2.03 (3H, s), 2.45 (1H, dd, $J = 5.1$, 13.6 Hz), 2.61 (1H, ddd, $J = 6.4$, 9.8, 13.9 Hz), 2.66 (1H, dd, $J = 8.0$, 13.6 Hz), 2.69 (1H, ddd, $J = 5.8$, 10.0, 13.9 Hz), 5.11 (1H, dddd, $J = 4.7$, 5.1, 8.0, 8.3 Hz), 7.15–7.19 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 23.3, 31.8, 35.7, 42.7, 71.4, 87.8, 126.0, 128.3, 128.5, 138.4, 141.2, 170.5; Anal. Found: C, 46.15; H, 4.64%. Calcd for $C_{15}H_{18}Br_2O_2$: C, 46.18; H, 4.65%.

Preparation of Dibromoalkenol 1a and 1b. The experimental procedure for the preparation of 4,4-dibromo-3-methyl-1-phenylbut-3-en-1-ol (**1a**) is shown below as a typical example.

To a solution of 4,4-dibromo-3-methyl-1-phenylbut-3-enyl acetate (**6a**) (5.76 g, 15.9 mmol) in a 1:1 mixture of MeOH and H_2O (120 mL) was added pellet NaOH (880 mg, 22 mmol); the mixture was stirred at 50 °C for 3 h under air. This was cooled to room temperature; then to the mixture was added sat. NH_4Cl, this combination was extracted four times with ethyl acetate, washed with brine, and dried over anhydrous magnesium sulfate. The ethyl acetate was removed in vacuo, and the residue was purified by chromatography (silica gel, hexane:ethyl acetate = 9:1) to afford 4,4-dibromo-3-methyl-1-phenylbut-3-en-1-ol (**1a**) (4.25 g, 13.3 mmol, 84%).

4,4-Dibromo-3-methyl-1-phenylbut-3-en-1-ol (1a): Colorless oil; IR (neat) 3394 (br), 1055, 814, 756, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.88 (3H, s), 1.91 (1H, brs), 2.59 (1H, dd, $J = 4.9$, 13.6 Hz), 2.80 (1H, dd, $J = 8.8$, 13.6 Hz), 4.92–4.95 (1H, m), 7.27–7.32 (1H, m), 7.33–7.37 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0, 47.5, 72.7, 87.6, 125.6, 127.9, 128.6, 139.3, 143.7; Anal. Found: C, 41.13; H, 3.73; Br, 50.00%. Calcd for $C_{11}H_{12}Br_2O$: C, 41.29; H, 3.78; Br, 49.94%.

6,6-Dibromo-5-methyl-1-phenylhex-5-en-3-ol (1b): Colorless oil; IR (neat) 3375 (br), 2918, 1495, 1452, 1047, 808, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.45 (1H, d, $J = 5.2$ Hz), 1.77–1.85 (2H, m), 1.91 (3H, s), 2.42 (1H, dd, $J = 4.4$, 13.6 Hz), 2.54 (1H, dd, $J = 8.6$, 13.6 Hz), 2.69 (1H, ddd, $J = 7.7$, 8.3, 13.8 Hz), 2.82 (1H, ddd, $J = 7.6$, 8.3, 13.8 Hz), 3.84–3.90 (1H, m), 7.16–7.20 (3H, m), 7.26–7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 32.0, 39.0, 45.8, 69.6, 87.2, 126.0, 128.4, 128.5, 139.4, 141.6; Anal. Found: C, 44.88; H, 4.61; Br, 46.10%. Calcd for $C_{13}H_{16}Br_2O$: C, 44.86; H, 4.63; Br, 45.91%.

5-Hydroxy-5-phenylpentan-2-one (7):[31] To an ice-cold solution of diisopropylamine (5.05 mL, 36 mmol) in THF (100 mL) was slowly added a solution of butyllithium in hexane (1.56 mol dm^{-3}, 20.2 mL, 32 mmol), and the mixture was stirred at the same temperature for 15 min. To the mixture was added the acetone *N*,*N*-dimethylhydrazone (3.02 g, 30 mmol), and this mixture was stirred at the same temperature for 1 h. Then styrene oxide (1.71 mL, 15 mmol) was added, and the mixture was stirred at 40 °C for 48 h. After cooling to room temperature, 2 M HCl was added to the mixture and this was stirred at room temperature for 5 h. The mixture was extracted twice with ethyl acetate, and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo to give crude 5-hydroxy-5-phenylpentan-2-one (**7**) (3.23 g). This product was used in the next acetylation reaction without further purification; Colorless oil; IR (neat) 3417 (br), 1712, 1452, 1360, 1028, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98–2.03 (2H, m), 2.12 (3H, s), 2.45 (1H, br), 2.53 (2H, t, $J = 7.0$ Hz), 4.70 (1H, t, $J = 6.2$ Hz), 7.24–7.39 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.9, 32.6, 39.8, 73.5, 125.7, 127.5, 128.5, 144.2, 209.2.

4-Oxo-1-phenylpentyl Acetate (8):[32] To an ice-cold solution of 5-hydroxy-5-phenylpentan-2-one (**7**) (3.23 g) and pyridine (8.10 mL, 100 mmol) in CH_2Cl_2 (50 mL) was added acetic anhydride (7.55 mL, 80 mmol), the mixture was stirred at room temperature for 20 h. To this mixture was added aqueous sat. NH_4Cl; this combination was extracted three times with chloroform, and then dried over anhydrous sodium sulfate. The chloroform was removed in vacuo; the residue was purified by chromatography (silica gel, hexane:ethyl acetate = 4:1) to give 4-oxo-1-phenylpentyl acetate (**8**) (1.69 g, 7.66 mmol, 51% for 2steps); Colorless oil; IR (neat) 1732, 1716, 1371, 1238, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.04 (3H, s), 2.08 (3H, s), 2.09–2.17 (2H, m), 2.35–2.45 (2H, m), 5.72 (1H, dd, $J = 6.0$, 7.6 Hz), 7.26–7.33 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 29.8, 30.1, 39.4, 75.0, 126.3, 128.0, 128.5, 140.0, 170.1, 207.2; Anal. Found: C, 70.71; H, 7.42%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

5,5-Dibromo-4-methyl-1-phenyl-4-pentenyl Acetate (9): A mixture of 4-oxo-1-phenylpentyl acetate (**8**) (1.14 g, 5.17 mmol), tetrabromomethane (5.11 g, 15.4 mmol), and triphenylphosphine (8.17 g, 31.1 mmol) in heptane (100 mL) was heated under reflux for 7 h. The heptane was removed in vacuo, and the residue was purified by chromatography twice (silica gel, hexane:ethyl acetate = 6:4, silica gel, hexane:ethyl acetate = 19:1) to give 5,5-dibromo-4-methyl-1-phenyl-4-pentenyl acetate (**9**) (1.09 g, 2.9 mmol, 56%); Colorless oil; IR (neat) 1743, 1732, 1373, 1234, 1022, 812, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.84 (3H, s), 1.91 (1H, dddd, $J = 5.7$, 5.9, 10.5, 13.6 Hz), 2.04 (1H, dddd, $J = 5.7$, 7.9, 10.1, 13.6 Hz), 2.07 (3H, s), 2.25 (1H, ddd, $J = 5.9$, 10.1, 13.3 Hz), 2.30 (1H, ddd, $J = 5.7$, 10.5, 13.3 Hz), 5.69 (1H, dd, $J = 5.7$, 7.9 Hz), 7.26–7.29 (1H, m), 7.30–7.36 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 22.7, 33.3, 34.4, 75.3, 85.7, 126.4, 128.1, 128.5, 140.0, 140.9, 170.2; Anal. Found: C, 44.73; H, 4.40%. Calcd for $C_{14}H_{16}Br_2O_2$: C, 44.71; H, 4.29%.

5,5-Dibromo-4-methyl-1-phenylpent-4-ene-1-ol (1c): To a solution of 5,5-dibromo-4-methyl-1-phenyl-4-pentenyl acetate (**9**) (1.09 g, 2.9 mmol) in 1:1 mixture of MeOH and H_2O (20 mL) was added 10 pellets of NaOH, and this mixture was stirred at 50 °C for 2 h under air. After neutralization by 1 M HCl, the mixture was extracted three times with ethyl acetate, and the combined organic layer was dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo. The crude product was purified by chromatography (silica gel, hexane:ethyl acetate = 9:1) to give 5,5-dibromo-4-methyl-1-phenylpent-4-ene-1-ol (**1c**) (670 mg, 2.1 mmol, 72%); White crystal; mp 57 °C (hexane); IR (KBr) 3248 (br), 1454, 1007, 820, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.83 (3H, s), 1.83–1.92 (3H, m), 2.33 (1H, ddd, $J = 6.3$, 10.1, 13.2 Hz), 2.39 (1H, ddd, $J = 5.5$, 10.4, 13.2 Hz), 4.66 (1H, dd, $J = 5.5$, 7.3 Hz), 7.25–7.30 (1H, m), 7.32–7.35

(4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 34.7, 35.9, 73.9, 85.3, 125.8, 127.8, 128.6, 141.6, 144.1; Anal. Found: C, 43.10; H, 4.16; Br, 47.90%. Calcd for $C_{12}H_{14}Br_2O$: C, 43.15; H, 4.22; Br, 47.84%.

Typical Procedure for the Nucleophilic Substitution Reaction of 1. (Table 1. entry 5): To a solution of 4,4-dibromo-3-methyl-1-phenylbut-3-ene-1-ol (**1a**) (123 mg, 0.38 mmol) in toluene (3.8 mL) was slowly added a hexane solution of butyllithium (1.56 mol dm^{-3}; 0.52 mL, 0.81 mmol). Next the mixture was stirred at room temperature for 30 min, then the mixture was quenched with MeOH. After addition of H_2O, the mixture was extracted three times with ether, and washed with brine, and the combined organic layer was dried over anhydrous magnesium sulfate. The ether was removed in vacuo; the crude product was purified by thin-layer chromatography to give 4-methyl-2-phenyl-2,3-dihydrofuran (**2a**) (50.4 mg, 0.31 mmol, 81%).

4-Methyl-2-phenyl-2,3-dihydrofuran (2a): Colorless oil; IR (neat) 2964, 1728, 1454, 1022, 997, 758, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66–1.67 (3H, m), 2.49–2.54 (1H, m), 2.94–3.00 (1H, m), 5.50 (1H, dd, J = 8.3, 10.6 Hz), 6.16 (1H, m), 7.25–7.29 (1H, m), 7.31–7.35 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 42.8, 82.5, 109.0, 125.5, 127.5, 128.5, 139.5, 143.5; Anal. Found: C, 82.30; H, 7.63%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

4-Methyl-2-phenethyl-2,3-dihydrofuran (2b): Colorless oil; IR (neat) 2929, 1454, 974, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (3H, ddd, J = 1.2, 1.3, 1.5 Hz), 1.82 (1H, dddd, J = 5.3, 6.4, 10.0, 13.6 Hz), 2.00 (1H, dddd, J = 5.6, 7.7, 9.8, 13.6 Hz), 2.19 (1H, dddq, J = 1.3, 2.0, 7.8, 14.8 Hz), 2.60 (1H, dddq, J = 1.2, 2.1, 10.0, 14.8 Hz), 2.67 (1H, ddd, J = 6.4, 9.8, 13.8 Hz), 2.75 (1H, ddd, J = 5.6, 10.0, 13.8 Hz), 4.51 (1H, dddd, J = 5.3, 7.7, 7.8, 10.0 Hz), 6.00 (1H, ddq, J = 1.5, 2.0, 2.1 Hz), 7.15–7.21 (3H, m), 7.25–7.28 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 31.8, 38.2, 39.8, 80.8, 109.1, 125.8, 128.4, 128.5, 139.1, 141.9; Anal. Found: C, 82.86; H, 8.37%. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%.

5-Methyl-2-phenyl-3,4-dihydro-2*H*-pyran (2c): Colorless oil; IR (neat) 3444(br), 2918, 1674, 1144, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59–1.60 (3H, m), 1.89–1.98 (2H, m), 2.02–2.06 (1H, m), 2.19–2.21 (1H, m), 4.70–4.73 (1H, m), 6.35 (1H, m), 7.26–7.29 (1H, m), 7.32–7.38 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.3, 25.9, 30.2, 76.4, 108.6, 125.9, 127.5, 128.3, 138.8, 142.1; Anal. Found: C, 82.60; H, 8.20%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

(*E*)-4-Bromo-3-methyl-1-phenylbut-3-en-1-ol (*E*-10a): Colorless oil; IR (neat) 3390 (br), 1051, 1024, 758, 723, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (3H, d, J = 1.5 Hz), 1.94 (1H, s), 2.50–2.54 (1H, m), 2.76–2.81 (1H, m), 4.93 (1H, dd, J = 5.0, 8.7 Hz), 6.01 (1H, m), 7.26–7.29 (1H, m), 7.33–7.36 (2H, m), 7.39–7.40 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.2, 44.1, 72.6, 103.3, 125.8, 127.8, 128.5, 138.7, 144.0; Anal. Found: C, 54.72; H, 5.49%. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.49%.

(*Z*)-4-Bromo-3-methyl-1-phenylbut-3-en-1-ol (*Z*-10a): Colorless oil; IR (neat) 3390 (br), 1053, 1028, 758, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (3H, d, J = 1.1 Hz), 1.93 (1H, s), 2.44–2.48 (1H, m), 2.51–2.56 (1H, m), 4.79–4.82 (1H, m), 6.00 (1H, m), 7.26–7.29 (1H, m), 7.32–7.35 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 48.2, 71.9, 104.3, 125.7, 127.8, 128.6, 138.3, 143.6.

1-Phenylpent-3-yn-1-ol (11a):[33] Colorless oil; IR (neat) 3423 (br), 2922, 1452, 1051, 756, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (3H, dd, J = 2.5, 2.5 Hz), 2.41 (1H, brs), 2.51–2.60 (2H, m), 4.79 (1H, dd, J = 4.8, 7.8 Hz), 7.25–7.29 (1H, m), 7.32–7.37 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.5, 30.0, 72.6, 75.2, 78.7, 125.7, 127.8, 128.4, 128.5, 142.9.

1-Phenylhex-4-yn-1-ol (11c):[34] Colorless oil; IR (neat) 3421 (br), 2922, 1452, 1061, 760, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (3H, dd, J = 2.5, 2.6 Hz), 1.81–1.88 (1H, m), 1.90–1.97 (1H, m), 2.12 (1H, brs), 2.14–2.22 (1H, m), 2.24–2.31 (1H, m), 4.83 (1H, dd, J = 5.0, 8.0 Hz), 7.25–7.29 (1H, m), 7.30–7.36 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 3.5, 15.5, 37.9, 73.5, 76.5, 78.4, 125.8, 127.6, 128.5, 144.2.

5-Bromo-4-methyl-2-phenyl-2,3-dihydrofuran (12a): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68 (3H, dd, J = 1.2, 1.2 Hz), 2.63 (1H, ddq, J = 1.2, 8.2, 14.7 Hz), 3.02 (1H, ddq, J = 1.2, 10.4, 14.7 Hz), 5.58 (1H, dd, J = 8.2, 10.4 Hz), 7.28–7.30 (1H, m), 7.33–7.37 (4H, m).

2-Methyl-5-phenylnon-1-en-5-ol (13c): Colorless oil; IR (neat) 3481 (br), 2956, 2935, 1446, 887, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (3H, t, J = 7.2 Hz), 0.98–1.03 (1H, m), 1.19–1.28 (3H, m), 1.67 (3H, s), 1.69–1.84 (4H, m), 1.91–2.03 (3H, m), 4.61 (1H, s), 4.65 (1H, s), 7.19–7.23 (1H, m), 7.31–7.37 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 23.0, 25.6, 31.8, 40.7, 43.1, 77.1, 109.8, 125.3, 126.3, 128.1, 146.1, 146.3.

1,1-Dibromo-2-methyl-4-phenyl-4-trimethylsiloxybut-1-ene (14): Colorless oil; IR (ZnSe) 1068, 837, 812, 748, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (9H, s), 1.83 (3H, s), 2.55 (1H, dd, J = 5.1, 13.2 Hz), 2.59 (1H, dd, J = 8.3, 13.2 Hz), 4.92 (1H, dd, J = 5.1, 8.3 Hz), 7.21–7.25 (1H, m), 7.28–7.33 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1, 25.0, 48.9, 73.1, 86.9, 125.6, 127.3, 128.2, 140.2, 144.5; Anal. Found: C, 43.08; H, 5.17%. Calcd for $C_{14}H_{20}Br_2OSi$: C, 42.87; H, 5.14%.

4-Methyl-2-phenyl-5-trimethylsilyl-2,3-dihydrofuran (15):[17] Colorless oil; IR (neat): 2956, 2925, 1250, 843, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.22 (9H, s), 1.71 (3H, dd, J = 1.3, 1.3 Hz), 2.49 (1H, ddq, J = 7.7, 15.5, 1.3 Hz), 3.05 (1H, ddq, J = 10.8, 15.5, 1.3 Hz), 5.40 (1H, dd, J = 7.7, 10.8 Hz), 7.26–7.32 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.3, 12.2, 46.1, 81.4, 119.9, 125.4, 127.1, 128.3, 144.8, 152.9.

Preparation of 3-Aryl-1,1-dibromo-1-alkenes 23. The experimental procedure for the preparation of 1,1-dibromo-3-(2-bromophenyl)-2-methylpropene (**23a**) is shown below as a typical example.

i) To an ice-cold solution of diisopropylamine (10.5 mL, 75 mmol) in THF was slowly added a hexane solution of butyllithium (1.6 mol dm^{-3}, 46 mL, 75 mmol); the mixture was stirred at the same temperature for 15 min. After cooling to −100 °C, to this solution was slowly added bromoform (6.50 mL, 74 mmol), and this mixture was stirred at the same temperature for 15 min, followed by slow addition of 1-(2-bromophenyl)propan-2-one (**25a**)[35] (10.5 g, 49 mmol) in THF and the successive addition of $BF_3 \cdot Et_2O$ (6.22 mL, 49 mmol). The mixture was stirred at the same temperature for 150 min. After the reaction was quenched with aq. sat. NH_4Cl, the mixture was extracted three times with ethyl acetate. The combined extracts was dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 97:3) to give 1,1,1-tribromo-3-(2-bromophenyl)-2-methylpropan-2-ol (16.3 g, 35 mmol, 71%).

1,1,1-Tribromo-3-(2-bromophenyl)-2-methylpropan-2-ol: White solid; mp 63 °C (hexane); IR (ZnSe) 3545, 1471, 1437, 1101, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (3H, s),

2.77 (1H, s), 3.58 (1H, d, $J = 13.9$ Hz), 3.72 (1H, d, $J = 13.9$ Hz), 7.14 (1H, ddd, $J = 1.7$, 7.4, 8.0 Hz), 7.28 (1H, ddd, $J = 1.2$, 7.4, 7.7 Hz), 7.43 (1H, dd, $J = 1.7$, 7.7 Hz), 7.57 (1H, dd, $J = 1.2$, 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 40.6, 63.6, 83.5, 126.1, 127.2, 128.7, 133.0, 133.0, 156.3; Anal. Found: C, 25.77; H, 2.18%. Calcd for $C_{10}H_{10}Br_4O$: C, 25.76; H, 2.16%.

ii) To a mixture of 1,1,1-tribromo-3-(2-bromophenyl)-2-methylpropan-2-ol (9.8 g, 21 mmol) and isopropenyl acetate (200 mL, 1.8 mol) was added $TsOH \cdot H_2O$ (32.6 g, 171 mmol) at once at 65 °C; then the mixture was stirred at the same temperature for 4 h. The isopropenyl acetate was removed in vacuo, then 200 mL of ethyl acetate was added; subsequent addition of aq. K_2CO_3 at 0 °C caused the mixture to become neutral. The mixture was extracted three times with ethyl acetate, and the combined mixture was washed with brine. The ethyl acetate solution was dried over anhydrous sodium sulfate, and ethyl acetate was removed in vacuo. The residue was purified by chromatography (silica gel, hexane:ethyl acetate = 97:3) to give 2,2,2-tribromo-1-(2-bromobenzyl)-1-methylethyl acetate (10.2 g, 20 mmol, 95%).

White solid; mp 74 °C (ethanol); IR (ZnSe) 1757, 1209, 1201, 1078, 1014 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (3H, s), 2.07 (3H, s), 3.66 (1H, d, $J = 13.9$ Hz), 3.77 (1H, d, $J = 13.9$ Hz), 7.13 (1H, ddd, $J = 1.7$, 7.3, 8.0 Hz), 7.26 (1H, ddd, $J = 1.1$, 7.3, 7.7 Hz), 7.31 (1H, dd, $J = 1.7$, 7.7 Hz), 7.56 (1H, dd, $J = 1.1$, 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 22.6, 41.9, 56.8, 91.5, 126.3, 127.2, 129.0, 132.5, 133.3, 135.7, 168.5; Anal. Found: C, 28.54; H, 2.47%. Calcd for $C_{12}H_{12}Br_4O_2$: C, 28.38; H, 2.38%.

iii) To a mechanically stirred dibutyl ether (210 mL) solution of 2,2,2-tribromo-1-(2-bromobenzyl)-1-methylethyl acetate (10.1 g, 20 mmol) was added EtMgBr in ether (3 mol dm^{-3}; 28 mL, 84 mmol) at −78 °C; this mixture was stirred at the same temperature for 2 h. The mixture was quenched with sat. NH_4Cl, extracted three times with ethyl acetate, and the combined organic layers were dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo, and the residue was purified by chromatography (silica gel, hexane) to give 1,1-dibromo-3-(2-bromophenyl)-2-methylpropene (**23a**) (6.6 g, 18 mmol, 88%).

1,1-Dibromo-3-(2-bromophenyl)-2-methylpropene (23a): Colorless oil; IR (ZnSe) 1466, 1437, 1028, 816, 798, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (3H, s), 3.76 (2H, s), 7.10 (1H, dd, $J = 7.6$, 7.8 Hz), 7.15 (1H, d, $J = 7.6$ Hz), 7.26 (1H, dd, $J = 7.6$ Hz), 7.55 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 43.5, 87.6, 124.9, 127.7, 128.3, 129.6, 132.9, 136.8, 139.7; Anal. Found: C, 32.66; H, 2.53%. Calcd for $C_{10}H_9Br_3$: C, 32.56; H, 2.46%.

1,1-Dibromo-3-(2-bromo-5-methoxyphenyl)-2-methylpropene (23b): White crystal; mp 55 °C (ethanol); IR (ZnSe) 1595, 1570, 1471, 1288, 1238, 1014, 804, 600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (3H, s), 3.71 (2H, s), 3.77 (3H, s), 6.66 (1H, dd, $J = 3.1$, 8.7 Hz), 6.71 (1H, d, $J = 3.0$ Hz), 7.43 (1H, d, $J = 8.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 43.6, 55.4, 87.6, 113.6, 115.2, 115.7, 133.4, 137.8, 139.7, 159.1; Anal. Found: C, 33.18; H, 2.79%. Calcd for $C_{11}H_{11}Br_3O$: C, 33.12; H, 2.78%.

1,1-Dibromo-3-(2-bromo-4-trifluoromethylphenyl)-2-methylpropene (23c): Colorless oil; IR (ZnSe) 1315, 1171, 1122, 1078, 1039, 825 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (3H, s), 3.79 (2H, s), 7.26 (1H, d, $J = 8.0$ Hz), 7.52 (1H, dd, $J = 0.9$, 8.0 Hz), 7.82 (1H, d, $J = 0.9$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 43.5, 88.7, 123.1 (q, $J_{CF} = 272$ Hz), 124.5 (q, $J_{CF} = 4$ Hz), 124.9, 129.7, 129.9 (q, $J_{CF} = 4$ Hz), 130.7 (q, $J_{CF} = 33$ Hz), 138.7, 140.9; Anal. Found: C, 30.40; H, 1.98%. Calcd for $C_{11}H_8Br_3F_3$: C, 30.24; H, 1.85%.

1,1-Dibromo-3-(2-bromo-3-methylphenyl)-2-methylpropene (23d): White crystal; mp 38 °C (ethanol); IR (ZnSe) 2949, 1458, 1446, 1437, 1026, 810 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (3H, s), 2.42 (3H, s), 3.78 (2H, s), 6.96 (1H, d, $J = 7.3$ Hz), 7.12 (1H, d, $J = 7.1$ Hz), 5.15 (1H, dd, $J = 7.1$, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 24.1, 44.3, 87.5, 126.9, 127.0, 127.5, 129.2, 137.1, 138.9, 139.9; Anal. Found: C, 34.68; H, 2.94%. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90%.

Preparation of Dibromoalkenes 27. The experimental procedure for the preparation of 1,1-dibromo-4-(2-bromophenyl)-2-methylbut-1-ene (**27a**) is shown below as a typical example.

A mixture of 4-(2-bromophenyl)-butan-2-one (**26a**) (1.14 g, 5.17 mmol), tetrabromomethane (5.11 g, 15.4 mmol), and triphenylphosphine (8.17 g, 31.1 mmol) in heptane (100 mL) was heated under reflux for 7 h. The heptane was removed in vacuo, and the residue was extracted with hexane. The hexane was removed in vacuo, and the residue was purified by chromatography (silica gel, hexane) to give 1,1-dibromo-4-(2-bromophenyl)-2-methylbut-1-ene (**27a**) (1.09 g, 2.9 mmol, 74%).

1,1-Dibromo-4-(2-bromophenyl)-2-methylbut-1-ene (27a): White crystal; mp 36 °C (ethanol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91 (3H, s), 2.53–2.56 (2H, m), 2.84–2.88 (2H, m), 7.05–7.08 (1H, m), 7.19–7.25 (2H, m), 7.51 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 33.4, 38.4, 86.1, 124.3, 127.6, 128.0, 130.5, 132.9, 140.0, 141.0; Anal. Found: C, 34.39; H, 2.90; Br, 62.27%. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90; Br, 62.60%.

1,1-Dibromo-4-(2-bromo-5-methoxyphenyl)-2-methylbut-1-ene (27b): White crystal; mp 32–34 °C (ethyl acetate); IR (KBr) 1473, 1240, 814, 808 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91 (3H, s), 2.52–2.55 (2H, m), 2.80–2.83 (2H, m), 3.77 (3H, s), 6.64 (1H, dd, $J = 3.0$, 8.7 Hz), 6.75 (1H, d, $J = 3.0$ Hz), 7.39 (1H, d, $J = 8.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 33.6, 38.4, 55.5, 86.1, 113.6, 114.8, 116.1, 133.3, 141.0, 141.0, 159.0; Anal. Found: C, 34.79; H, 3.07; Br, 58.21%. Calcd for $C_{12}H_{13}Br_3O$: C, 34.90; H, 3.17; Br, 58.05%.

1,1-Dibromo-4-(2-bromo-5-fluorophenyl)-2-methylbut-1-ene (27c): White crystal; mp 39–41 °C (ethyl acetate); IR (KBr) 1462, 1232, 1157, 1030, 814 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92 (3H, s), 2.52–2.55 (2H, m), 2.82–2.85 (2H, m), 6.81 (1H, ddd, $J = 3.0$, 5.4, 11.3 Hz), 6.94 (1H, dd, $J = 3.0$, 9.2 Hz), 7.46 (1H, dd, $J = 5.4$, 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 33.5, 38.1, 86.5, 115.2 (d, $J_{CF} = 22$ Hz), 117.3 (d, $J_{CF} = 22$ Hz), 118.4 (d, $J_{CF} = 2$ Hz), 133.9 (d, $J_{CF} = 8$ Hz), 140.5, 142.1 (d, $J_{CF} = 7$ Hz), 162.0 (d, $J_{CF} = 247$ Hz); Anal. Found: C, 33.04; H, 2.59; Br, 59.74; F, 4.48%. Calcd for $C_{11}H_{10}Br_3F$: C, 32.79; H, 2.50; Br, 59.50; F, 4.72%.

1,1-Dibromo-4-(2-bromo-3-methylphenyl)-2-methylbut-1-ene (27d): Colorless oil; IR (KBr) 1454, 1022, 814, 777, 764, 715 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92 (3H, s), 2.40 (3H, s), 2.53–2.56 (2H, m), 2.87–2.90 (2H, m), 7.04 (1H, dd, $J = 1.7$, 7.2 Hz), 7.08 (1H, dd, $J = 1.7$, 7.3 Hz), 7.12 (1H, dd, $J = 7.2$, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 24.0, 34.2, 38.5, 85.9, 127.0, 127.0, 127.8, 128.9, 138.7, 140.5, 141.2; Anal. Found: C, 36.43; H, 3.29%. Calcd for $C_{12}H_{13}Br_3$: C, 36.31; H, 3.30%.

Typical Procedure for the Nucleophilic Substitution Reaction of 23 and 27. (Methanol as an Electrophile). (Table 3. entry 3): To a THF (5 mL) solution of 1,1-dibromo-3-(2-bromophenyl)-2-methylpropene (**23a**) (184 mg, 0.50 mmol) was slowly added a hexane solution of butyllithium (1.61 mol dm^{-3}; 0.74 mL,

1.19 mmol) at −90 °C; this mixture was stirred for 30 min. The solution was quenched with methanol (2 mL), and aqueous sat. NH_4Cl was added; then the combination was extracted three times with ethyl acetate, and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo; the residue was purified by thin-layer chromatography (silica gel, hexane) to afford 2-methylindene (**28a**) (55.2 mg, 85%).

Typical Procedure for the Nucleophilic Substitution Reaction of 23 and 27. (Dibromoethane as an Electrophile). (Table 5. entry 1): To a THF (5 mL) solution of 1,1-dibromo-3-(2-bromophenyl)-2-methylpropene (**23a**) (187 mg, 0.51 mmol) was slowly added a hexane solution of butyllithium (1.63 mol dm^{-3}; 0.73 mL, 1.2 mmol) at −90 °C; this mixture was stirred for 30 min. To the solution was added 1,2-dibromotetrafluoroethane (0.60 mL, 5.0 mmol); stirring continued another 30 min at the same temperature. Then the solution was quenched with aqueous sat. NH_4Cl; this combination was extracted three times with ethyl acetate, and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo, the residue was purified by thin-layer chromatography (silica gel, hexane) to afford 3-bromo-2-methylindene (**29a**) (87.7 mg, 0.42 mmol, 83%).

Typical Procedure for the Nucleophilic Substitution Reaction of 23 and 27. (Benzaldehyde as an Electrophile). (Table 5. entry 4): To a THF (4 mL) solution of 1,1-dibromo-3-(2-bromo-5-methoxyphenyl)-2-methylpropene (**23b**) (159 mg, 0.40 mmol) was slowly added a hexane solution of butyllithium (1.61 mol dm^{-3}; 0.60 mL, 0.97 mmol) at −90 °C; this mixture was stirred for 30 min. To the solution was added a THF (2 mL) solution of benzaldehyde (208 mg, 2.0 mmol); stirring continued for another 1 h at the same temperature. The solution was quenched with aqueous sat. NH_4Cl; then this combination was extracted three times with ethyl acetate, and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo, and the residue was purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 8:2) to afford (6-methoxy-2-methyl-3-indenyl)phenylmethanol (**30b**) (92.7 mg, 0.35 mmol, 87%).

2-Methylindene (28a):[36] Colorless oil; IR (ZnSe): 1616, 1464, 1392, 750, 715, 810 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (3H, s), 3.29 (2H, d, $J = 0.7$ Hz), 6.48 (1H, t, $J = 0.7$ Hz), 7.07 (1H, ddd, $J = 1.3$, 7.3, 7.3 Hz), 7.21 (1H, ddd, $J = 0.4$, 7.0, 7.3 Hz), 7.25 (1H, dd, $J = 1.3$, 7.0 Hz), 7.36 (1H, dd, $J = 0.4$, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 42.6, 119.6, 123.2, 123.4, 126.1, 127.1, 143.3, 145.9, 146.0.

6-Methoxy-2-methylindene (28b): Colorless oil; IR (ZnSe): 1608, 1477, 1288, 1265, 1238, 1138, 1034, 852 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (3H, d, $J = 0.6$ Hz), 3.24 (2H, s), 3.79 (3H, s), 6.39 (1H, s), 6.76 (1H, dd, $J = 2.4$, 8.2 Hz), 6.97 (1H, d, $J = 2.4$ Hz), 7.11 (1H, d, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 42.7, 55.6, 110.3, 111.5, 119.7, 126.4, 139.0, 143.7, 145.1, 157.0; Anal. Found: C, 82.54; H, 7.79%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

2-Methyl-5-trifluoromethylindene (28c): Colorless oil; IR (ZnSe) 1435, 1319, 1281, 1153, 1111, 1057 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (3H, s), 3.32 (2H, s), 6.49–6.50 (1H, m), 7.33–7.34 (1H, m), 7.40–7.47 (2H, m); HRMS (EI$^+$) Found: m/z 199.0716. Calcd for $C_{11}H_9F_3$: $(M + H)^+$, 199.0735.

2,4-Dimethylindene (28d): Colorless oil; IR (ZnSe) 2958, 2925, 2910, 1728, 1448, 1437, 1284, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (3H, d, $J = 0.7$ Hz), 2.39 (3H, s), 3.29 (2H, s), 6.57 (1H, q, $J = 0.7$ Hz), 6.98–7.03 (2H, m), 7.19–7.21 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.9, 18.5, 42.9, 120.7, 123.5, 125.3, 127.2, 128.8, 143.1, 144.7, 145.5; HRMS (EI$^+$) Found: m/z 144.0944. Calcd for $C_{11}H_{12}$: M^+, 144.0939.

3-Bromo-2-methylindene (29a): White needle; mp 41 °C (2-propanol); IR (ZnSe) 1612, 1458, 1389, 1629, 935, 75 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (3H, s), 3.35 (2H, s), 7.17 (1H, ddd, $J = 3.5$, 4.9, 7.4 Hz), 7.30 (1H, dd, $J = 3.5$, 3.6 Hz), 7.30 (1H, ddd, $J = 0.6$, 4.9 Hz), 7.34 (1H, dd, $J = 0.6$, 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 42.2, 117.0, 119.3, 123.1, 125.0, 126.7, 140.6, 141.6, 144.0; Anal. Found: C, 57.18; H, 4.40%. Calcd for $C_{10}H_9Br$: C, 57.44; H, 4.34%.

3-Bromo-6-methoxy-2-methylindene (29b): White needle; mp 58 °C (2-propanol); IR (ZnSe) 1601, 1473, 1290, 1265, 1134, 1030, 825 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (3H, s), 3.31 (2H, s), 3.81 (3H, s), 6,84 (1H, dd, $J = 6.9$, 8.3 Hz), 6.94 (1H, d, $J = 6.9$ Hz), 7.17 (1H, d, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 42.2, 55.6, 110.2, 111.9, 116.4, 119.6, 137.2, 139.1, 142.3, 158.3; Anal. Found: C, 55.14; H, 4.55%. Calcd for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64%.

3-Bromo-2-methyl-5-trifluoromethylindene (29c): Colorless oil; IR (ZnSe) 1437, 1350, 1321, 1252, 1157, 1115, 1057, 960, 818 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (3H, s), 3.39 (2H, s), 7.41 (1H, d, $J = 8.0$ Hz), 7.44 (1H, dd, $J = 1.1$, 8.0 Hz), 7.53 (1H, d, $J = 1.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.6, 42.3, 116.2 (q, $J_{CF} = 4$ Hz), 116.4, 122.1 (q, $J_{CF} = 32$ Hz), 123.3, 127.2 (q, $J_{CF} = 134$ Hz), 129.5 (q, $J_{CF} = 32$ Hz), 143.8, 144.4, 144.8; HRMS (EI$^+$) Found: m/z 275.9744. Calcd for $C_{11}H_8BrF_3$: M^+, 275.9761.

3-Bromo-2,4-dimethylindene (29d): Colorless oil; IR (ZnSe) 2927, 1714, 1599, 1018, 933, 760, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11 (3H, s), 2.74 (3H, s), 3.28 (2H, s), 7.01 (1H, d, $J = 6.8$ Hz), 7.04 (1H, dd, $J = 6.8$, 6.8 Hz), 7.20 (1H, d, $J = 6.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 19.6, 42.0, 116.4, 121.3, 124.6 129.8, 130.5, 140.1, 141.4, 142.0; HRMS (FAB$^+$) Found: m/z 223.0121. Calcd for $C_{11}H_{11}Br$: $(M + H)^+$, 223.0122.

(2-Methyl-3-indenyl)phenylmethanol (30a): Colorless oil; IR (ZnSe) 3375, 1462, 1448, 1022, 760, 715, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (1H, d, $J = 3.2$ Hz), 2.22 (3H, s), 3.37 (2H, s), 6.07 (1H, d, $J = 3.2$ Hz), 7.06 (1H, ddd, $J = 1.2$, 7.3, 7.3 Hz), 7.10 (1H, ddd, $J = 0.5$, 7.3, 7.3 Hz), 7.22 (1H, tt, $J = 0.6$, 7.6), 7.26 (1H, dd, $J = 0.5$, 7.3 Hz), 7.31 (2H, dd, $J = 7.6$, 7.7 Hz), 7.35 (1H, dd, $J = 1.2$, 7.3 Hz), 7.47 (2H, dd, $J = 0.6$, 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 43.2, 69.5, 120.6, 123.3, 123.8, 125.8, 126.0, 127.1, 128.3, 138.0, 141.6, 142.2, 142.4, 143.8; HRMS (EI$^+$) Found: m/z 236.1197. Calcd for $C_{17}H_{16}O$: M^+, 236.1201.

(6-Methoxy-2-methyl-3-indenyl)phenylmethanol (30b): Colorless oil; IR (ZnSe) 3431, 1608, 1581, 1477, 1265, 1244, 1034, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (3H, s), 3.33 (2H, s), 3.75 (3H, s), 6.03 (1H, s), 6.65 (1H, dd, $J = 2.4$, 8.4 Hz), 6.94 (1H, d, $J = 2.4$ Hz), 7.13 (1H, d, $J = 8.4$ Hz), 7.22 (1H, t, $J = 7.5$ Hz), 7.30 (2H, dd, $J = 7.5$, 7.5 Hz), 7.45 (2H, d, $J = 7.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 43.1, 55.5, 69.5, 110.2, 111.2, 120.9, 125.7, 127.0, 128.3, 136.8, 137.5, 139.2, 142.3, 144.2, 157.1; HRMS (FAB$^+$) Found: m/z 289.1206. Calcd for $C_{18}H_{18}O_2$: $(M + Na)^+$, 289.1204.

(2-Methyl-6-trifluoromethyl-3-indenyl)phenylmethanol (30c): Colorless oil; IR (ZnSe) 3338, 1437, 1317, 1267, 1155, 1113, 1057, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (3H, s), 2.42 (1H, br), 3.37 (2H, s), 6.06 (1H, s), 7.25 (1H, t, $J = 7.2$ Hz), 7.33 (2H, dd, $J = 7.0$, 7.2 Hz), 7.34 (1H, d, $J = 7.5$ Hz), 7.40 (1H, d, $J = 7.5$ Hz), 7.45 (2H, d, $J = 7.0$ Hz), 7.61 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 43.1, 69.6, 117.4 (q, $J_{CF} = 4$ Hz), 120.8 (q, $J_{CF} = 4$ Hz), 123.2, 125.7, 124.7 (q, $J_{CF} =$

272 Hz), 127.4, 128.5, 128.5 (q, $J_{CF} = 32$ Hz), 137.7, 141.9, 143.1, 144.5, 146.0; HRMS (EI$^+$) Found: m/z 304.1096. Calcd for $C_{18}H_{15}F_3O_2$: M$^+$, 304.1075.

(2,4-Dimethyl-3-indenyl)phenylmethanol (30d): Colorless oil; IR (ZnSe) 3423, 1448, 1390, 1011, 1003, 762, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (3H, s), 2.18 (3H, s), 2.24 (1H,br), 3.39 (1H, d, $J = 23.0$ Hz), 3.45 (1H, d, $J = 23.0$ Hz), 6.31 (1H, s), 6.96 (1H, d, $J = 7.5$ Hz), 7.05 (1H, dd, $J = 7.2$, 7.5 Hz), 7.26 (1H, t, $J = 7.3$ Hz), 7.26 (1H, d, $J = 7.2$ Hz), 7.33 (2H, dd, $J = 7.3$, 7.7 Hz), 7.41 (2H, d, $J = 7.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 21.7, 43.6, 69.0, 120.9, 124.1, 126.0, 126.9, 128.3, 129.6, 130.4, 138.7, 142.5, 142.6, 143.2, 144.0; HRMS (EI$^+$) Found: m/z 250.1370. Calcd for $C_{18}H_{18}O$: M$^+$, 250.1358.

3-Methyl-1,2-dihydronaphthalene (32a):[37] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90 (3H, s), 2.21–2.25 (2H, m), 2.80 (2H, t, $J = 8.2$ Hz), 6.19–6.21 (1H, m), 6.94–6.95 (1H, m), 7.03–7.07 (2H, m), 7.09–7.13 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.5, 28.0, 28.8, 122.7, 125.1, 125.9, 126.3, 127.1, 134.0, 135.0, 138.2.

7-Methoxy-3-methyl-1,2-dihydronaphthalene (32b):[38] Colorless oil; IR (neat) 1608, 1498, 1252, 1153, 1039, 854 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (3H, m), 2.19 (2H, t, $J = 8.2$ Hz), 2.78 (2H, t, $J = 8.2$ Hz), 3.77 (3H, s), 6.15 (1H, m), 6.63–6.65 (2H, m), 6.87 (1H, d, $J = 7.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3, 28.5, 28.6, 55.2, 111.0, 113.5, 122.0, 125.9, 128.3, 135.4, 135.7, 158.0.

7-Fluoro-3-methyl-1,2-dihydronaphthalene (32c): Colorless oil; IR (ZnSe) 1491, 1265, 1230, 856, 561 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88 (3H, s), 2.20 (2H, t, $J = 8.2$ Hz), 6.16 (1H, d, $J = 1.2$ Hz), 6.75–6.80 (2H, m), 6.87 (1H, dd, $J = 5.7$, 9.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3, 28.2 (d, $J_{CF} = 2$ Hz), 28.3, 112.6 (d, $J_{CF} = 24$ Hz), 114.3 (d, $J_{CF} = 22$ Hz), 121.7, 126.1 (d, $J_{CF} = 8$ Hz), 131.1 (d, $J_{CF} = 3$ Hz), 136.3 (d, $J_{CF} = 7$ Hz), 137.2 (d, $J_{CF} = 2$ Hz), 161.2 (d, $J_{CF} = 244$ Hz); HRMS (EI$^+$) Found: m/z 162.0817. Calcd for $C_{11}H_{11}F$: M$^+$, 162.0845.

3,5-Dimethyl-1,2-dihydronaphthalene (32d): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (3H, d, $J = 1.2$ Hz), 2.18 (2H, t, $J = 8.1$ Hz), 2.28 (3H, s), 2.76 (2H, t, $J = 8.1$ Hz), 6.39 (1H, q, $J = 1.2$ Hz), 6.91–6.95 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.0, 24.0, 28.6, 28.7, 119.4, 125.0, 125.5, 128.2, 132.1, 133.0, 134.2, 138.5; HRMS (EI$^+$) Found: m/z 158.1074. Calcd for $C_{12}H_{14}$: M$^+$, 158.1096.

4-Bromo-3-methyl-1,2-dihydronaphthalene (33a): Colorless oil; IR (ZnSe) 1477, 1452, 1248, 937, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (3H, s), 2.39 (2H, t, $J = 7.9$ Hz), 2.80 (2H, t, $J = 7.9$ Hz), 7.06 (1H, d, $J = 7.3$ Hz), 7.10–7.13 (1H, m), 7.19–7.24 (1H, m), 7.58 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 27.9, 31.6, 118.2, 126.3, 126.6, 126.7, 127.0, 134.2, 135.3, 137.0; Anal. Found: C, 58.99; H, 5.15%. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97%.

4-Bromo-7-methoxy-3-methyl-1,2-dihydronaphthalene (33b): Colorless oil; IR (ZnSe) 1606, 1489, 1255, 1119, 1041, 592 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (3H, s), 2.35 (2H, t, $J = 7.9$ Hz), 2.76 (2H, t, $J = 7.9$ Hz), 3.78 (3H, s), 6.63 (1H, d, $J = 2.7$ Hz), 6.71 (1H, dd, $J = 2.7$, 8.6 Hz), 7.49 (1H, d, $J = 8.6$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.3, 28.3, 31.4, 55.3, 110.9, 113.0, 117.6, 127.5, 127.6, 134.1, 136.9, 158.8; HRMS (EI$^+$) Found: m/z 252.0133. Calcd for $C_{12}H_{13}BrO$: M$^+$, 252.0150.

4-Bromo-7-fluoro-3-methyl-1,2-dihydronaphthalene (33c): Colorless oil; IR (ZnSe) 1485, 1254, 862, 816, 584 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (3H, s), 2.37 (2H, t, $J = 8.0$ Hz), 2.77 (2H, t, $J = 8.0$ Hz), 6.78 (1H, dd, $J = 2.7$, 8.8 Hz), 6.86 (1H, ddd, $J = 2.7$, 8.6, 8.6 Hz), 7.53 (1H, dd, $J = 5.6$, 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.4, 28.0, 31.2, 112.9 (d, $J_{CF} = 21$ Hz), 113.8 (d, $J_{CF} = 22$ Hz), 117.1, 128.0 (d, $J_{CF} = 8$ Hz), 130.5 (d, $J_{CF} = 3$ Hz), 136.0 (d, $J_{CF} = 2$ Hz), 137.5 (d, $J_{CF} = 8$ Hz), 161.7 (d, $J_{CF} = 247$ Hz); Anal. Found: C, 54.90; H, 4.14%. Calcd for $C_{11}H_{18}BrF$: C, 54.80; H, 4.18%.

4-Bromo-3,5-dimethyl-1,2-dihydronaphthalene (33d): Colorless oil; IR (ZnSe) 1460, 893, 771 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (3H, s), 2.21–2.24 (2H, m), 2.57 (3H, s), 2.63–2.66 (2H, m), 6.96–7.00 (1H, m), 7.01–7.02 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 24.4, 29.8, 31.9, 114.8, 124.3, 126.7, 130.7, 134.0, 134.9, 138.8, 140.4; Anal. Found: C, 60.82; H, 5.65%. Calcd for $C_{12}H_{13}Br$: C, 60.78; H, 5.53%.

(2-Methyl-3,4-dihydronaphthalen-1-yl)phenylmethanol (34a): White solid; mp 97–98 °C (hexane); IR (neat) 3410 (br), 1633, 1012, 704 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (3H, s), 2.19–2.20 (1H, m), 2.29 (1H, ddd, $J = 6.7$, 6.9, 16.5 Hz), 2.40 (1H, ddd, $J = 6.4$, 11.3, 16.5), 2.71–2.83 (2H, m), 6.14 (1H, d, $J = 5.4$ Hz), 6.93–6.96 (1H, m), 7.00–7.03 (1H, m), 7.07 (1H, $J = 7.8$ Hz), 7.11 (1H, d, $J = 7.3$ Hz), 7.21–7.24 (1H, m), 7.30–7.34 (2H, m), 7.44–7.45 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 28.4, 31.4, 70.8, 124.6, 125.5, 125.9, 126.0, 126.7, 127.4, 128.4, 131.5, 133.2, 136.5, 137.6, 142.9; Anal. Found: C, 86.20; H, 7.29%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

(6-Methoxy-2-methyl-3,4-dihydronaphthalen-1-yl)phenylmethanol (34b): White solid; IR (ZnSe) 3460(br), 1606, 1496, 1252, 1039, 1030, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (3H, s), 2.14 (1H, d, $J = 5.4$ Hz), 2.26 (1H, ddd, $J = 6.6$, 6.7, 16.4 Hz), 2.38 (1H, ddd, $J = 6.5$, 11.7, 16.4 Hz), 2.70 (1H, ddd, $J = 6.5$, 6.7, 15.2 Hz), 2.77 (1H, ddd, $J = 6.6$, 11.7, 15.2 Hz), 3.71 (3H, s), 6.12 (1H, d, $J = 5.4$ Hz), 6.47 (1H, dd, $J = 2.8$, 8.6 Hz), 6.67 (1H, d, $J = 2.8$ Hz), 6.99 (1H, d, $J = 8.6$), 7.20–7.23 (1H, m), 7.29–7.33 (2H, m), 7.42–7.44 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 28.8, 31.2, 55.1, 70.7, 110.4, 113.7, 125.5, 125.9, 126.0, 126.6, 128.3, 130.9, 134.8, 138.4, 143.0, 157.5; HRMS (EI$^+$) Found: m/z 280.1493. Calcd for $C_{19}H_{20}O_2$: M$^+$, 280.1463.

(6-Fluoro-2-methyl-3,4-dihydronaphthalen-1-yl)phenylmethanol (34c): White solid; IR (ZnSe) 3384(br), 1493, 1244, 702, 565 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (3H, s), 2.13 (1H, d, $J = 4.0$ Hz), 2.29 (1H, ddd, $J = 6.7$, 7.1, 16.6 Hz), 2.38 (1H, ddd, $J = 6.6$, 10.7, 16.6 Hz), 2.71 (1H, ddd, $J = 6.6$, 7.1, 15.2 Hz), 2.77 (1H, ddd, $J = 6.7$, 10.7, 15.2 Hz), 6.14 (1H, d, $J = 4.0$ Hz), 6.61 (1H, ddd, $J = 2.8$, 8.7, 8.7 Hz), 6.79 (1H, dd, $J = 2.8$, 9.1 Hz), 7.07 (1H, dd, $J = 5.8$, 8.7 Hz), 7.20–7.24 (1H, m), 7.29–7.33 (2H, m), 7.40–7.42 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.3, 28.5, 31.0, 70.7, 112.3 (d, $J_{CF} = 21$ Hz), 114.3 (d, $J_{CF} = 21$ Hz), 125.4, 126.5 (d, $J_{CF} = 8$ Hz), 126.8, 128.4, 129.2 (d, $J_{CF} = 4$ Hz), 130.8, 136.5 (d, $J_{CF} = 2$ Hz), 139.1 (d, $J_{CF} = 7$ Hz), 142.6, 160.8 (d, $J_{CF} = 246$ Hz); HRMS (EI$^+$) Found: m/z 268.1279. Calcd for $C_{18}H_{17}FO$: M$^+$, 268.1263.

(2,8-Dimethyl-3,4-dihydronaphthalen-1-yl)phenylmethanol (34d): White solid; mp 113–114 °C (hexane); IR (ZnSe) 3438 (br), 2929, 1448, 773, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77 (3H, s), 2.02 (1H, ddd, $J = 5.4$, 6.3, 15.3 Hz), 2.14 (1H, ddd, $J = 5.5$, 11.3, 15.3 Hz), 2.20 (1H, brs), 2.42 (3H, s), 2.60 (1H, ddd, $J = 5.5$, 6.3, 14.8 Hz), 2.65 (1H, ddd, $J = 5.4$, 11.3, 14.8 Hz), 5.89 (1H, s), 7.01–7.04 (3H, m), 7.18–7.21 (1H, m),

7.27–7.30 (2H, m), 7.40–7.42 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 22.2, 30.0, 31.7, 72.3, 124.6, 125.6, 125.8, 126.3, 127.9, 130.5, 132.9, 134.6, 137.0, 138.4, 142.6, 144.4; HRMS (EI$^+$) Found: m/z 264.1523. Calcd for $C_{19}H_{20}O$: M^+, 264.1514.

Typical Procedure for the Suzuki Cross Coupling Reaction of 29. (Eq. 12): A THF (5 mL) solution of 3-bromo-2-methylindene (**29a**) (104 mg, 0.498 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (292 mg, 5.02 mmol), $Pd(dba)_2$ (28.3 mg, 0.0492 mmol), and (o-Tol)$_3$P (77.9 mg, 0.255 mmol) was heated at 50 °C for 10 h. Then the suspension was diluted with ether, filtrated through celite and concentrated in vacuo. Purification of the residue by thin-layer chromatography (silica gel, hexane:CH_2Cl_2 = 9:1) gave 2-methyl-3-phenylindene (**31a**) (102 mg, 0.494 mmol, 99%).

2-Methyl-3-phenylindene (31a):[39] White solid; IR (ZnSe) 3051, 3018, 2906, 1597, 1493, 1458, 1442 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (3H, s), 3.46 (2H, s), 7.14–7.48 (9H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 43.1, 119.3, 123.4, 124.0, 126.2, 127.0, 128.4, 129.1, 135.5, 138.7, 140.5, 142.4, 146.4.

6-Methoxy-2-methyl-3-phenylindene (31b): White plate; mp 85 °C (2-propanol); IR (ZnSe) 2935, 1606, 1475, 1261, 1032, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (3H, s), 3.41 (2H, s), 3.82 (3H, s), 6.78 (1H, dd, J = 2.4, 8.3 Hz), 7.04 (1H, d, J = 2.4 Hz), 7.11 (1H, d, J = 8.3 Hz), 7.32–7.46 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 43.0, 55.6, 110.3, 111.4, 119.4, 126.9, 128.4, 129.0, 135.7, 138.0, 138.2, 139.5, 144.1, 157.4; Anal. Found: C, 86.45; H, 6.94%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82%.

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