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Allylation

Silver-Catalyzed Allylation of Ketones and Intramolecular Cyclization through Carbene Intermediates from Cyclopropenes Under Ambient Conditions

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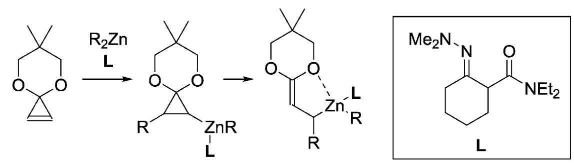
Abstract: Tandem C–C bond formation was achieved through silver-catalyzed ring-opening of cyclopropenes via carbene intermediates. The reaction of cyclopropenes in the presence of a silver catalyst gave indene derivatives under ambient conditions. In contrast, the insertion of organozinc reagents to silver carbene or allylic cation intermediates afforded allylmetal intermediates for the tandem allylation of carbonyl compounds.

Introduction

The allylation reaction is one of the most important and popular methods for C–C bond formation.[1] The resulting homoallylic alcohol products can be used as intermediates for the synthesis of natural products.[2] The allylation reaction with allyl halides mediated by a low valence metal, such as Mg, Zn, and In, has become a practical method for the alkylation of carbonyl compounds.[3] In particular, Zn-mediated addition reactions are some of the most effective methods for chemo- and stereoselective C–C bond formation.[4] Allylzinc reagents show higher nucleophilicity toward carbonyl compounds than other alkylzinc intermediates due to the formation of a six-membered transition state. However, there are several limitations for the generation of allylzinc reagents, which require unstable allyl halide derivatives. Therefore, further studies on the generation of allylmetal intermediates are necessary. Previously, Oshima and co-workers reported the metal-mediated or -catalyzed retro-allylation of homoallylic alcohols with the generation of allylmetal intermediates.[5] The subsequent allylation reaction of aldehydes gave various homoallylic alcohols in one-pot. In 2005, Tamaru and co-workers reported the Pd-catalyzed allylation reaction of imines using allylic alcohol as an allyl source.[6] Further efficient methods for the generation of nucleophilic allylation reagents bearing a variety of functional groups or substituents are needed.

We previously reported a C–C bond cleavage and formation sequence using cyclopropenes to form allylzinc intermediates, the nucleophilic attack of which gives various hydrazines, homoallylic alcohols, and amines (Scheme 1).[7] In these reports,



Scheme 1. Previous working hypothesis.

the initial step is thought to be the carbozincation of cyclopropenes, as Richey and co-workers reported the sequential carbometalation and ring-opening of cyclopropenes using organoaluminum reagents for the generation of allylaluminum intermediates.[8] However, our studies on the Cu-catalyzed carbometalation of cyclopropenes to give cyclopropylzinc intermediates for the sequential ring-opening of cyclopropyl metal intermediates were unsuccessful after extensive screening of the reaction conditions.[9] Recently, the generation of carbene complexes from cyclopropenes has been reported; gold carbene complexes from cyclopropenes typically react with various nucleophiles.[10–12] Furthermore, Fischer-type carbene complexes gave various cyclic products via the nucleophilic attack of lithium and sodium enolates.[13] In this context, the insertion of a carbene intermediate derived from a cyclopropene into a dialkylzinc seems to be an alternative approach for the generation of allylzinc intermediates.

Our alternative proposal for the allylation reaction using cyclopropenes and organozinc reagents includes metal carbene

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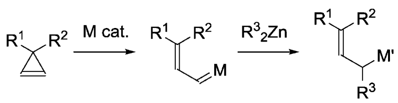


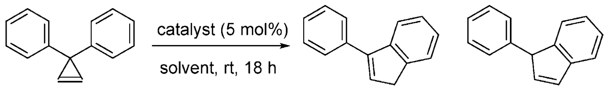
Scheme 2. Alternative approach to allylation using cyclopropenes.

intermediates (Scheme 2). The allylmetal intermediate would be obtained via the intramolecular shift of an alkyl group derived from an organozinc reagent. In this reaction, generation of a carbene intermediate is considered to be a key step. Therefore, the screening of transition metal catalysts to generate carbene intermediates from cyclopropenes was carried out.

Results and Discussion

The screening of effective catalysts for the generation of carbene intermediates, which took part in the intramolecular cyclization to give indene derivatives, was performed (Table 1).

Table 1. Screening of catalysts for indene.



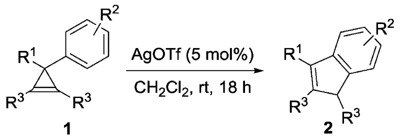
1a **2a** **2a'**

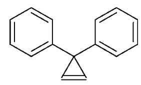
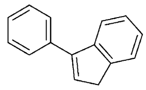
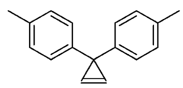
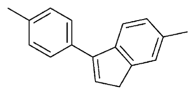
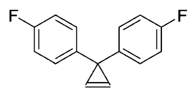
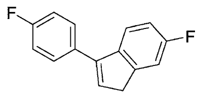
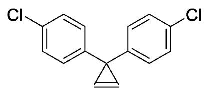
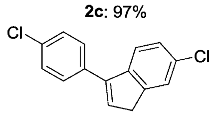
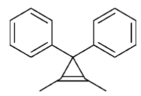
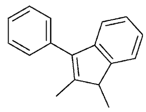
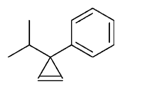
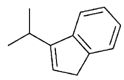
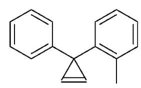
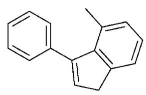
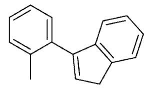
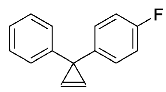
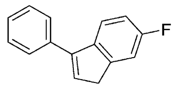
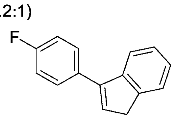
Entry	Catalyst	Solvent	**2a/2a'** Yield [%]
1	**AgOTf**	**CH_2Cl_2**	**96/–**
2	**AgOAc**	**CH_2Cl_2**	**95/–**
3	$AgNO_3$	CH_2Cl_2	92/–
4	AgF	CH_2Cl_2	93/–
5	Ag_2CO_3	CH_2Cl_2	15/–
6	Ag_2O	CH_2Cl_2	nr
7	$[Au(PPh_3)Cl]$	CH_2Cl_2	nr
8	$[Au(PPh_3)Cl]$ (5 mol%) AgOTf (5 mol%)	CH_2Cl_2	7/14
9	ZnI_2	CH_2Cl_2	71/–
10	CuI	CH_2Cl_2	84/–
11	$[RhCl(cod)]_2$	CH_2Cl_2	93/–
12	AgOTf	toluene	62/–
13	AgOTf	THF	73/–

The synthesis of indenes using cyclopropenes has been reported in the presence of cationic Au or Pd catalysts.[14] In contrast, the generation of carbene or allylic cation intermediates in the presence of a Ag catalyst was already known; thus, we focused on the use of silver salts in the present tandem allylation reaction using cyclopropenes.[15,16] The effective silver catalysts were confirmed for the indene syntheses via carbene or allylic cation intermediates derived from cyclopropenes. The reaction of cyclopropene **1a** in the presence of a Ag catalyst, such as AgOTf, AgOAc, $AgNO_3$, and AgF, gave the indene product **2a** in high yield even at room temperature (Table 1, entries 1–4). However, when Ag_2CO_3 was used, product **2a** was obtained in lower yield (Table 1, entry 5). Indene was not formed in the presence of Ag_2O as a catalyst (Table 1, entry 6). The use of $[Au(PPh_3)Cl]$ catalyst did not give the desired product at all (Table 1, entry 7). The in situ-generated $[Au(PPh_3)OTf]$ catalyst gave the desired product in low yield as a mixture of regioisomers (Table 1, entry 8). Other catalysts, such as Zn, Cu, and Rh gave good results (Table 1, entries 9–11). The screening of solvents showed that CH_2Cl_2 is the most suitable medium for the present reaction (Table 1, entries 12 and 13).

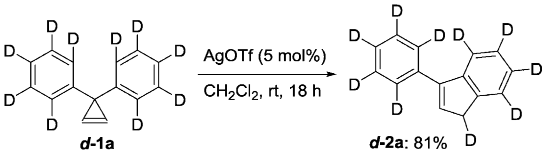
Under the optimized reaction conditions, the scope of cyclopropenes was investigated (Table 2). Various 3,3-diaryl cyclopropenes **1a**, **1b**, **1c**, and **1d** gave the indene products **2a**, **2b**, **2c**, and **2d** in high yields, respectively (Table 2, entries 1–4). 1,2-Disubstitued cyclopropene **1e** could be used in the present reaction (Table 2, entry 5). When 3,3-alkyl,aryl cyclopropene **1f** was used, the desired product **2f** was also obtained in good yield (Table 2, entry 6). The unsymmetrical 3,3-diaryl cyclopropenes **1g** and **1h** gave a mixture of products (Table 2, entries 7 and 8). In these cases, selectivity was not observed.

Table 2. Synthesis of various indenes.

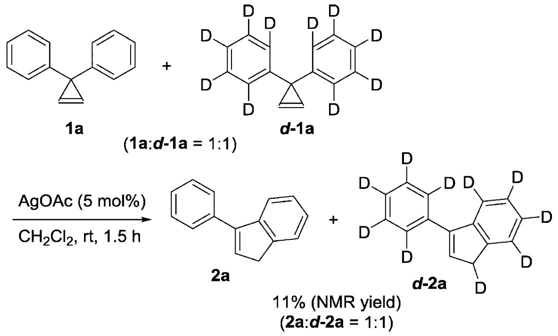


Entry	Cyclopropene	Product: Yield [%]
1	 **1a**	 **2a**: 96%
2	 **1b**	 **2b**: 92%
3	 **1c**	 **2c**: 97%
4	 **1d**	 **2d**: 96%
5	 **1e**	 **2e**: 95%
6	 **1f**	 **2f**: 63%
7	 **1g**	 **2g**  **2g'** 97% (**2g**/**2g'** = 3.2:1)
8	 **1h**	 **2h**  **2h'** 96% (**2h**:**2h'** = 1:1)

The synthesis of indenes was carried out using deuterated cyclopropene ***d*-1 a**. The indene product ***d*-2 a** was obtained in good yield from cyclopropene ***d*-1 a** [Eq. (1)]. When a mixture of **1 a** and ***d*-1 a** was used, a mixture of **2 a** and ***d*-2 a** was obtained in the same ratio after the reaction had proceeded halfway [Eq. (2)]. These results suggested that C–H bond cleavage might not be the rate-determining step in the present reaction. Therefore, a Friedel–Crafts-type reaction could occur to give the indene product.



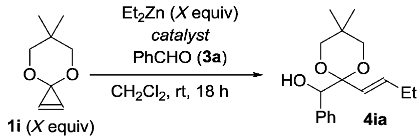
(1)



(2)

The silver-catalyzed generation of carbene intermediates from cyclopropenes under ambient conditions prompted us to further investigate the generation of allylmetal intermediates via the insertion of organometallic reagents into carbene intermediates for the tandem allylation reaction of carbonyl compounds. Accordingly, optimization of the reaction conditions for the allylation of aldehydes was carried out using Ag catalysts (Table 3). The cyclopropene **1 i** was chosen as a model substrate for the present allylation reaction; in our previous report, the allylation reaction proceeded smoothly when cyclopropene **1 i** bearing an acetal moiety was used.[7] When the allylation reaction was performed without any catalyst, the desired product **4 ia** was obtained in low yield as a mixture of unidentified by-products; the Zn-mediated generation of a carbenoid intermediate or a simple carbozincation/ring-opening sequence might take place (Table 3, entry 1). When AgOTf was used, the product **4 ia** was obtained in moderate yields (Table 3, entries 2 and 3). The yields did not increase in the presence of a Au catalyst (Table 3, entries 4 and 5). These results suggested that a Ag catalyst is essential for the present allylation reaction. Therefore, screening of Ag catalysts was carried out (Table 3, entries 6–11). The use of AgOAc as a catalyst gave the desired product **4 ia** in 54 % yield. When the amount of **1 i** and Et_2Zn was increased, **4 ia** was obtained in 91 % yield (Table 3, entry 8); the previous method gave a comparable result with the use of excess **1 i** and Et_2Zn.[7b] On the other hand, ZnI_2 showed low catalytic activity compared with a Ag catalyst (Table 3, entries 12 and 13).[17,18]

Table 3. Optimization for tandem allylation.



Entry	*X* [equiv]	Catalyst	Yield [%]
1	1.1	–	< 24
2	1.1	AgOTf (5 mol %)	40
3[a]	1.1	AgOTf (5 mol %)	31
4	1.1	$[Au(PPh_3)Cl]$ (5 mol %) + AgOTf (5 mol %)	43
5	1.1	$[Au(PPh_3)Cl]$ (5 mol %)	35
6	1.1	AgOAc (5 mol %)	54
7	2.0	AgOAc (5 mol %)	74
8	**3.0**	**AgOAc (5 mol %)**	**91**
9	1.1	Ag_2CO_3 (5 mol %)	51
10	1.1	$AgNO_3$ (5 mol %)	33
11	1.1	$AgSbF_6$ (5 mol %)	nd
12	1.1	ZnI_2 (20 mol %)	22
13	1.1	ZnI_2 (100 mol %)	38

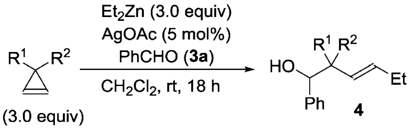
[a] Toluene was used as a solvent.

We expected that the present catalyst system might be suitable for the reaction using simple non-functionalized cyclopropenes instead of **1 i** bearing an acetal moiety, although the previous conditions gave poor results (Table 4). To our delight, the cyclopropene **1 j** gave the homoallylic alcohol **4 ja** in 77 % yield as a diastereomeric mixture (Table 4, entry 1). The reaction of cyclopropene **1 k** also gave the desired product **4 ka**, however, **1 f** bearing a bulky group did not give the corresponding product **4 fa** (Table 4, entries 2 and 3). The cyclopropene **1 l** bearing a 1-naphthyl group gave the product **4 la** in lower yield due to steric hindrance (Table 4, entry 4). The cyclopropene **1 a** also gave the product **4 aa** in good yield (Table 4, entry 5); however, cyclopropene **1 b** did not give the desired product (Table 4, entry 6). The cyclopropenes **1 c** and **1 d** bearing electron-withdrawing groups gave the desired products **4 ca** and **4 da**, respectively, in moderate yields (Table 4, entries 7 and 8). However, with cyclopropene **1 m**, the corresponding product was not obtained at all (Table 4, entry 9).

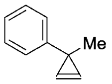
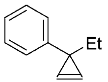
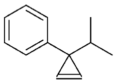
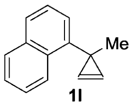
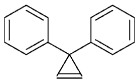
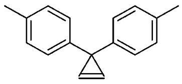
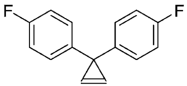
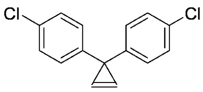
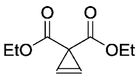
The scope of the reaction using ketones as an electrophile was examined under the present catalyst system (Table 5). The reaction of cyclopropene **1 j** and ketones **3 b**, **3 c**, **3 d**, **3 e**, and **3 f** gave the homoallylic alcohols **4 jb**, **4 jc**, **4 jd**, **4 je**, and **4 jf**, respectively, in good yields (Table 5, entries 1–5). The dioxanone **3 g** could be used in the present reaction to give the densely functionalized product **4 jg** (Table 5, entry 6). When 3-pentanone **3 h** was used, a mixture of **4 jh** and regioisomer **5 jh** was obtained (Table 5, entry 7). Furthermore, the bulky ketones **3 i**, **3 j**, and **3 k** gave the products **5 ji**, **5 jj**, and **5 jk**, respectively (Table 5, entries 8–10).[19] Steric hindrance might inhibit the creation of consecutive quaternary centers.

The generation of products **5** suggested that the present reaction includes the isomerization of allylmetal intermediates (Scheme 3). Namely, the nucleophilic attack of allylmetal intermediates **I** derived from cyclopropenes **1** to ketones could take place to give the products **4**. However, bulky ketones inhibit the nucleophilic attack of allylmetal intermediates **I** due

Table 4. Scope of cyclopropenes.

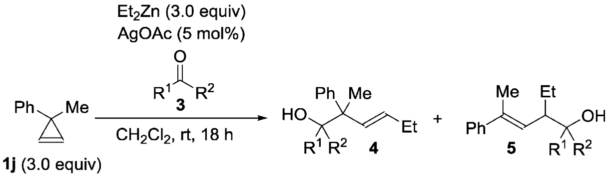


1 (3.0 equiv)

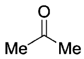
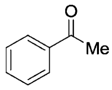
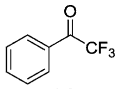
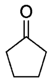
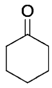
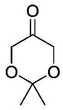
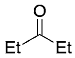
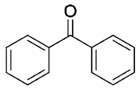
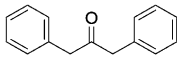
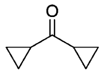
Entry	Cyclopropene	Yield [%]
1	 **1j**	77 (**4ja**)[a]
2	 **1k**	63 (**4ka**)[b]
3	 **1f**	trace
4	 **1l**	32 (**4la**)[c]
5	 **1a**	56 (**4aa**)
6	 **1b**	nd[d]
7	 **1c**	33 (**4ca**)
8	 **1d**	48 (**4da**)
9	 **1m**	nd

[a] d.r. = 1.4:1. [b] d.r. = 4:1. [c] d.r. = 5:3. [d] Indene product **2b** was observed.

Table 5. Scope of ketones.



1j (3.0 equiv)

Entry	Ketone	Yield [%]
1	 **3b**	67 (**4jb**)
2	 **3c**	83 (**4jc**)[a]
3	 **3d**	51 (**4jd**)[b]
4	 **3e**	86 (**4je**)
5	 **3f**	88 (**4jf**)
6	 **3g**	78 (**4jg**)
7	 **3h**	38 (**4jh**), 21 (**5jh**)
8	 **3i**	55 (**5ji**)
9	 **3j**	58 (**5jj**)
10	 **3k**	27 (**5jk**)

[a] d.r. = 2:1. [b] d.r. = 10:9.

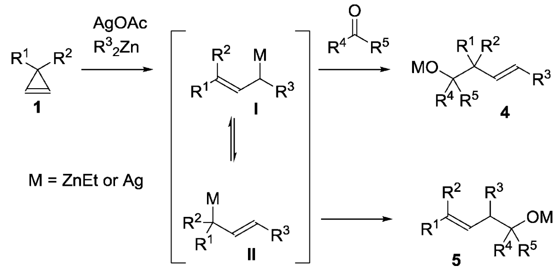
to the steric hindrance. Therefore, the isomerization of allylmetal intermediates **I** to allylmetal intermediate **II** would occur, followed by the allylation to bulky ketones to give the regioisomers **5**.

The rationale for the high stereoselectivity of the olefinic geometry seems to be the formation of the six-membered transition states: **TS-I** or **TS-III**; a larger substituent, such as Et or Ph, should be placed at the equatorial positions (Figure 1). A bulky substituent at the axial positions gives unfavorable **TS-II** or **TS-IV** due to steric hindrance.

When an unsymmetrical ketone, such as acetophenone **3c**, was used, the product **4jc** was obtained as a diastereomeric mixture, as shown in Table 5. In this case, the allylation reaction might proceed via **TS-V**, **VI**, **VII**, and **VIII** (Figure 2). A diastereomeric mixture **4jc-A** and **4jc-B** was obtained due to the steric repulsion between Me and Ph at the axial or equatorial positions.

When cyclopropene **1i** was used for the addition to acetophenone **3c**, the corresponding product **6ic** was obtained in low yield after deprotection of the acetal moiety [Eq. (3)]. This result suggested that an intramolecular coordination of the acetal moiety on a metal-center might stabilize the allylmetal intermediates. Therefore, the allylmetal intermediates derived from **1j** showed higher reactivity in the addition to ketones (Figure 3).

In preliminary experiments, other electrophiles were examined for the development of tandem reactions using allylmetal intermediates via cyclopropenes. The allylation reaction using benzoylchloride as an electrophile gave the ketone product **7**



Scheme 3. Generation of regioisomer **5**.

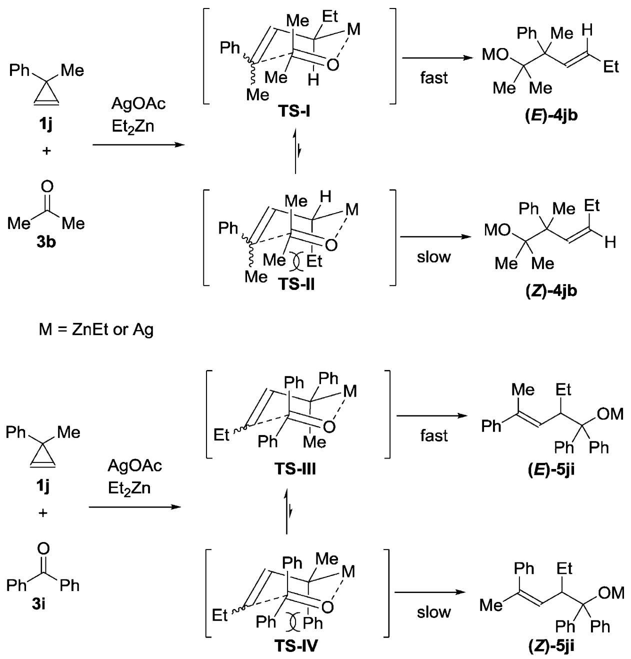


Figure 1. *E*-selectivity of products.

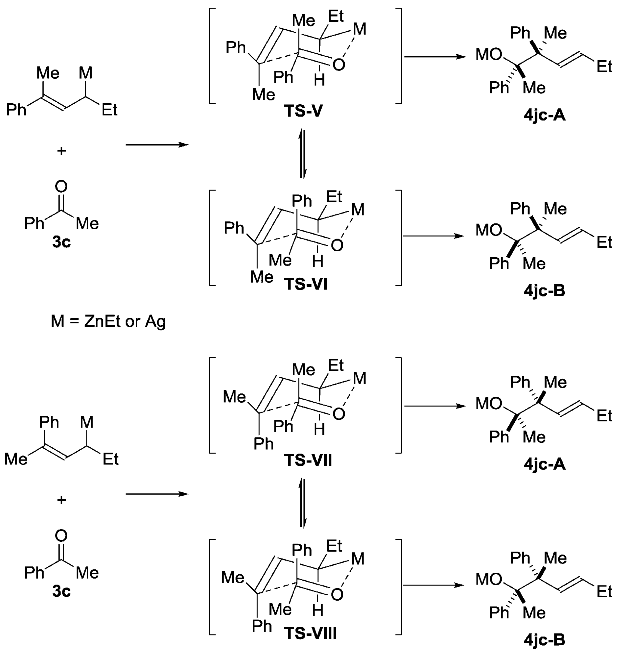
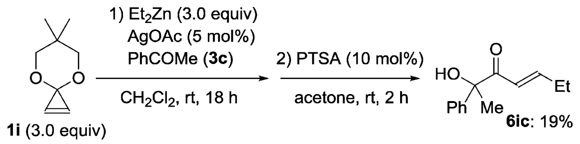


Figure 2. Transition state model for diastereoselectivity.



(3)

in moderate yield [Eq. (4)]. On the other hand, when benzeneacetonitrile was used, a trace amount of the ketone product **8** was observed, but could not be isolated [Eq. (5)].

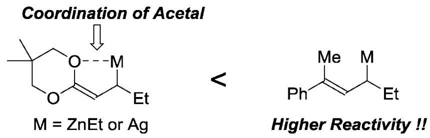
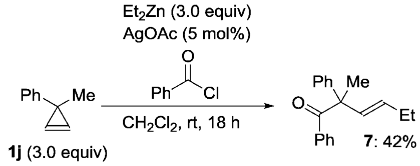
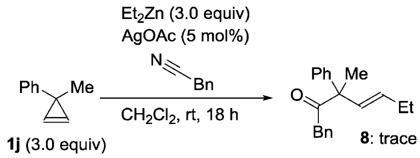


Figure 3. Reactivity of allylmetal intermediates.



(4)



(5)

A proposed mechanism for the present reaction is shown in Figure 4. The vinylcarbenoid **A-1** is generated from cyclopropene **1** in the presence of a Ag catalyst. There are several reports for the generation of a silver–carbene complexes derived from cyclopropenes; the allylic cation intermediates **A-2** and/or **A-3** seem to be other candidates for the active intermediates in the present reaction.[15,20] When AgOTf is used, the Friedel–Crafts-type reaction occurs to give the indene product **2** via intermediate **B**. In the allylation reaction, allylmetal interme-

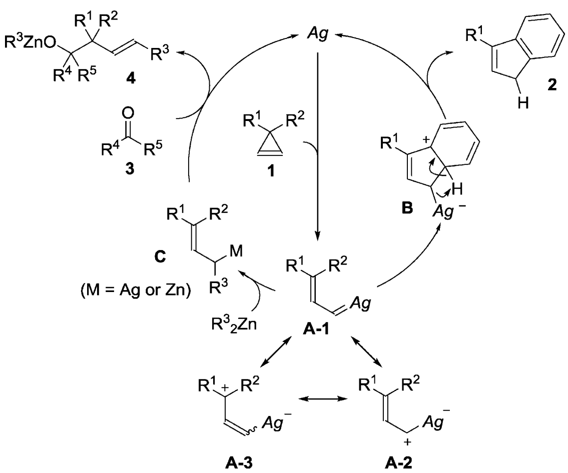


Figure 4. Proposed mechanism.

diate **C** is generated with an organozinc reagent. The allylation reaction of carbonyl compounds proceeded to give the desired product **4**. In the present reaction, only nucleophilic attack of an allylmetal intermediate proceeded chemoselectively without the addition of organozinc reagent R^3_2Zn. We currently cannot exclude the presence of allylsilver intermediates for the allylation of carbonyl compounds.

Conclusions

A Ag-catalyzed tandem allylation reaction and Friedel–Crafts-type reaction for the synthesis of indenes have been developed. These reactions involve the generation of a vinyl carbenoid or cationic intermediates from cyclopropenes in the presence of a Ag catalyst. The addition of organozinc reagents gave allylmetal intermediates, which in turn gave homoallylic alcohols via an allylation reaction. The present results for the generation of carbene intermediates under ambient conditions may be useful for the further development of tandem reactions including an asymmetric version using a variety of nucleophiles.

Experimental Section

General Method: ^{1}H NMR was recorded on a 400 MHz NMR spectrometer (JEOL ECS 400). Chemical shifts δ are reported in ppm using TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J) and integration. ^{13}C NMR spectra were recorded on at 100 MHz. The chemical shifts were determined in the δ-scale relative to $CDCl_3$ (δ = 77.0 ppm). The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. HRMS (APCI or ESI, positive) was measured with a TOF mass spectrometer. All of the melting points were measured with a micro melting point apparatus. All solvents were distilled and stored over drying agents.

General Procedure (Preparation of 2b)

To a suspension of AgOTf (3.9 mg, 0.015 mmol) in CH_2Cl_2 (1.5 mL), cyclopropene **1b** (66.0 mg, 0.3 mmol) was added at room temperature. The reaction mixture was stirred for 18 h and was quenched with sat. NH_4Cl. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (*n*-hexane) to afford **2b** (60.7 mg, 0.27 mmol) in 92% yield. In a similar manner, indene derivatives **2a**,[14b] **2c**, **2d**, **2e**, **2f**, **2g**, **2g′**, **2h**, **2h′**, and ***d*-2a** were obtained.

6-Methyl-3-(*p*-tolyl)-1*H*-indene (**2b**) was obtained as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 2.34 (s, 3H), 3.37 (d, J = 1.8 Hz, 2H), 6.39 (t, J = 1.8 Hz, 1H), 7.04–7.06 (m, 1H), 7.15–7.18 (m, 2H), 7.26 (s, 1H), 7.38–7.43 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.4, 37.9, 120.0, 125.0, 126.8, 127.5, 129.2, 129.4, 133.4, 134.4, 137.2, 141.4, 144.8, 145.1 ppm; IR (neat): $\tilde{\nu}$ = 3440, 3022, 2918, 1655, 1609, 1570, 1508, 1475, 1449, 1390, 1183, 1109, 1037, 970, 941, 867, 825, 770 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{17}H_{16}$ 220.1252 [M^+]; found: 220.1250.

6-Fluoro-3-(4-fluorophenyl)-1*H*-indene (**2c**) (66.3 mg, 0.29 mmol) was obtained in 97% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (d, J = 1.8 Hz, 2H), 6.41 (t, J = 1.8 Hz, 1H), 6.91–6.96 (m, 1H), 7.02–7.08 (m, 2H), 7.13–7.16 (m, 1H), 7.32–7.36 (m, 1H), 7.42–7.47 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1, 111.7 (d, J = 22.9 Hz), 113.1 (d, J = 22.9 Hz), 115.5 (d, J = 21.0 Hz), 120.6 (d, J = 9.5 Hz), 129.2 (d, J = 7.6 Hz), 130.3, 131.9, 139.7, 143.5, 146.7 (d, J = 8.8 Hz), 161.5 (d, J = 242 Hz), 162.4 ppm (d, J = 245 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −118.34, −114.19 ppm; IR (neat): $\tilde{\nu}$ = 3066, 2887, 1613, 1581, 1506, 1475, 1409, 1390, 1236, 1157, 1141, 1124, 1095, 950, 924, 841, 812, 776, 761 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{15}H_{10}F_2$ 228.0751 [M^+]; found: 228.0748.

6-Chloro-3-(4-chlorophenyl)-1*H*-indene (**2d**) (74.8 mg, 0.28 mmol) was obtained in 96% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (d, J = 2.3 Hz, 2H), 6.48 (t, J = 2.3 Hz, 1H), 7.20–7.22 (m, 1H), 7.32–7.35 (m, 3H), 7.39–7.42 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.0, 120.8, 124.5, 126.4, 128.8 (2 carbons overlapped), 131.2, 131.5, 133.6, 134.0, 142.0, 143.5, 146.3 ppm; IR (neat): $\tilde{\nu}$ = 3065, 2884, 1654, 1600, 1564, 1488, 1459, 1418, 1388, 1187, 1143, 1090, 1068, 1014, 973, 939, 872, 835, 776, 752, 685 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{15}H_{10}Cl_2$ 260.0160 [M^+]; found: 260.1059.

1,2-Dimethyl-3-phenyl-1*H*-indene (**2e**) (62.6 mg, 0.28 mmol) was obtained in 95% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, J = 7.8 Hz, 3H), 1.98 (s, 3H), 3.29 (q, J = 7.8 Hz, 1H), 7.07–7.16 (m, 3H), 7.25–7.29 (m, 1H), 7.32–7.40 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 15.8, 47.4, 119.2, 122.5, 124.1, 126.3, 126.9, 128.3, 129.2, 135.5, 137.1, 144.9, 145.6, 148.2 ppm; IR (neat): $\tilde{\nu}$ = 3018, 2964, 2927, 2868, 1597, 1493, 1463, 1442, 1158, 1074, 1023, 934, 772, 701, 658 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{17}H_{16}$ 220.1252 [M^+]; found: 220.1250.

3-Isopropyl-1*H*-indene (**2f**) (29.8 mg, 0.18 mmol) was obtained in 63% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, J = 6.9 Hz, 6H), 2.83–2.90 (m, 1H), 3.24 (s, 2H), 6.12 (s, 1H), 7.10–7.13 (m, 1H), 7.20–7.24 (m, 1H), 7.32–7.34 (m, 1H), 7.37–7.39 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 26.9, 37.5, 119.3, 123.8, 124.3, 125.3, 125.8, 144.8, 145.0, 151.0 ppm; IR (neat): $\tilde{\nu}$ = 3067, 3017, 2961, 2871, 1605, 1457, 1395, 1381, 1158, 1110, 1015, 968, 915, 766, 720 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{12}H_{15}$ 159.1174 [$M+H^+$]; found: 159.1173.

A mixture of 4-methyl-3-phenyl-1*H*-indene (**2g**) and 3-(*o*-Tolyl)-1*H*-indene (**2g′**) (45.6 mg, 0.22 mmol) was obtained in 97% yield in a 3:1 ratio as a colorless oil; for **2g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 3.38 (d, J = 1.8 Hz, 2H), 6.28 (t, J = 1.8 Hz, 1H), 6.93–6.95 (m, 1H), 7.04–7.08 (m, 1H), 7.13–7.32 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 38.0, 121.7, 124.9, 127.0, 127.8, 128.9, 129.0, 131.5, 132.6, 139.2, 142.4, 144.8, 146.9 ppm; for **2g′**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 3.46 (d, J = 1.8 Hz, 2H), 6.35 (t, J = 1.8 Hz, 1H), 7.04–7.08 (m, 1H), 7.13–7.32 (m, 6H), 7.45–7.47 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 38.4, 120.5, 123.8, 124.7, 125.6, 126.1, 127.5, 129.4, 130.2, 131.6, 135.7, 136.4, 143.9, 145.0, 145.2 ppm; IR (neat): $\tilde{\nu}$ = 3422, 3058, 2923, 1654, 1594, 1542, 1509, 1490, 1457, 1389, 765, 701 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{16}H_{14}$ 206.1096 [M^+]; found: 206.1093.

A mixture of 3-(4-fluorophenyl)-1*H*-indene (**2h**) and 6-fluoro-3-phenyl-1*H*-indene (**2h′**) (60.4 mg, 0.28 mmol) was obtained in 96% yield in a 1:1 ratio as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40–3.43 (m, 2H), 6.45–6.47 (m, 1H), 6.85–7.51 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.1, 111.7 (d, J = 22.9 Hz), 113.1 (d, J = 22.9 Hz), 115.5 (d, J = 21.0 Hz), 120.1, 120.8 (d, J = 8.6 Hz), 124.1, 124.9, 126.2, 127.6, 127.7, 128.6, 129.3 (d, J = 7.6 Hz), 130.3, 130.9, 132.1, 135.8, 139.9, 143.8, 144.2, 144.5, 144.7, 146.8 (d, J = 8.6 Hz), 161.5 (d, J = 241 Hz), 162.3 ppm (d, J = 246 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −118.56, −114.50 ppm; IR (neat): $\tilde{\nu}$ = 3064, 2884, 2768, 1890, 1655, 1613, 1596, 1505, 1475, 1445, 1390, 1274, 1234, 1157, 1141, 1123, 1095, 1081, 1024, 972, 948, 922, 841, 814, 765, 720 cm^{-1}; HRMS (APCI) *m/z* calcd. $C_{15}H_{11}F$ 210.0845 [M^+]; found: 210.0843.

3-(Phenyl-d_5)-1*H*-indene-1,4,5,6,7-d_5 (***d*-2 a**) (49.0 mg, 0.24 mmol) was obtained in 81% yield as a colorless oil; H NMR (400 MHz, $CDCl_3$): δ=3.43 (d, J=2.3 Hz, 1H), 6.50 ppm (d, J=2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=37.8 (t, J=19.1 Hz), 119.9 (t, J=24.8 Hz), 123.7 (t, J=24.8 Hz), 124.3 (t, J=23.8 Hz), 125.6 (t, J=23.8 Hz), 127.0 (t, J=23.8 Hz), 127.4 (t, J=23.8 Hz), 128.0 (t, J=23.8 Hz), 130.9, 136.0, 143.9, 144.6, 145.2 ppm; IR (neat): $\tilde{\nu}$=2923, 2275, 1654, 1560, 1375, 1247, 1017, 927, 853, 821, 769, 731 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{15}H_3D_{10}$ 203.1645 [M+H$^+$]; found: 203.1643.

General Procedure (Preparation of 4 aa)

To a suspension of AgOAc (2.5 mg, 0.015 mmol) in CH_2Cl_2 (1.5 mL), cyclopropene **1 a** (173.0 mg, 0.9 mmol), Et_2Zn (0.9 mL, 1.0 M in toluene), and benzaldehyde (31.8 μL, 0.3 mmol) were added at room temperature. The reaction mixture was stirred for 18 h and was quenched with a sat. NH_4Cl. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layer was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane/AcOEt=20:1) to afford **4 aa** (55.0 mg, 0.16 mmol) in 56% yield.

(*E*)-1,2,2-Triphenylhex-3-en-1-ol (**4 aa**) was obtained as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.93 (t, J=7.3 Hz, 3H), 2.02–2.09 (m, 2H), 2.40 (br, 1H), 5.08 (dt, J=16.0, 6.0 Hz, 1H), 5.47 (s, 1H), 5.99 (d, J=16.0 Hz, 1H), 6.70–6.72 (m, 2H), 6.99–7.32 ppm (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.6, 26.0, 59.6, 77.9, 126.2, 126.3, 127.0, 127.2, 127.4, 127.7, 128.3, 129.2, 130.6, 131.1, 137.6, 140.7, 143.8, 145.1 ppm; IR (neat): $\tilde{\nu}$=3547, 3057, 3030, 2961, 2929, 1654, 1599, 1494, 1444, 1379, 1186, 1083, 1042, 910, 732, 700 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{24}H_{24}NaO$ 351.1725 [M+Na$^+$]; found: 351.1731.

(*E*)-2,2-Bis(4-fluorophenyl)-1-phenylhex-3-en-1-ol (**4 ca**) (36.0 mg, 0.09 mmol) was obtained in 33% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.92 (t, J=7.3 Hz, 3H), 1.97–2.10 (m, 2H), 2.28 (d, J=6.0 Hz, 1H), 5.03 (dt, J=15.6, 6.4 Hz, 1H), 5.37 (d, J=6.0 Hz, 1H), 5.91 (d, J=15.6 Hz, 1H), 6.69–6.71 (m, 2H), 6.80–6.98 (m, 6H), 7.03–7.13 (m, 3H), 7.21–7.26 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.6, 26.0, 58.5, 78.2, 114.2 (d, J=21.0 Hz), 114.5 (d, J=21.0 Hz), 127.2, 127.5, 128.2, 130.8 (d, J=7.6 Hz), 131.2, 132.1 (d, J=7.6 Hz), 137.7, 139.3, 140.4, 140.8, 161.2 (d, J=244 Hz), 161.5 ppm (d, J=244 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−116.44, −116.31 ppm; IR (neat): $\tilde{\nu}$=3448, 3032, 2962, 2927, 1603, 1508, 1455, 1232, 1162, 1108, 1044, 911, 835, 764, 734, 703 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{24}H_{22}F_2NaO$ 387.1536 [M+Na$^+$]; found: 387.1535.

(*E*)-2,2-Bis(4-chlorophenyl)-1-phenylhex-3-en-1-ol (**4 da**) (56.8 mg, 0.14 mmol) was obtained in 48% yield as a white solid, M.p.=112–113 °C (from AcOEt/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91 (t, J=7.8 Hz, 3H), 2.00–2.07 (m, 2H), 2.26 (br, 1H), 5.03 (dt, J=15.6, 6.4 Hz, 1H), 5.36 (s, 1H), 5.87 (d, J=15.6 Hz, 1H), 6.70–6.72 (m, 2H), 6.91–6.94 (m, 2H), 7.04–7.21 ppm (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.5, 26.0, 58.7, 78.0, 127.3, 127.5, 127.6, 127.9, 128.2, 130.7, 130.8, 131.9, 132.1, 132.4, 137.9, 140.2, 141.9, 143.4 ppm; IR (neat): $\tilde{\nu}$=3448, 2961, 1658, 1654, 1560, 1542, 1508, 1490, 1457, 1398, 1260, 1093, 1012, 801, 701 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{24}H_{22}Cl_2NaO$ 419.0945 [M+Na$^+$]; found: 419.0941.

(*E*)-2-Ethyl-1,2-diphenylhex-3-en-1-ol (**4 ka**) (54.8 mg, 0.18 mmol) was obtained in 63% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (major): δ=0.51 (t, J=7.8 Hz, 3H), 0.95 (t, J=7.8 Hz, 3H), 1.50–1.66 (m, 2H), 1.91 (d, J=3.2 Hz, 1H), 2.05–2.18 (m, 2H), 5.05 (d, J=3.2 Hz, 1H), 5.25 (dt, J=15.6, 6.4 Hz, 1H), 5.80 (d, J=15.6 Hz, 1H), 7.01–7.34 ppm (m, 10H); (minor): δ=0.66 (t, J=7.3 Hz, 3H), 1.00 (t, J=7.4 Hz, 3H), 1.73–1.90 (m, 2H), 2.05–2.18 (m, 3H), 4.85 (d, J=5.5 Hz, 1H), 5.57 (d, J=16.0 Hz, 1H), 5.67 (dt, J=16.0, 6.0 Hz, 1H), 6.69–6.71 (m, 2H), 7.01–7.34 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=8.8, 13.7, 14.0, 26.3, 27.9, 28.0, 53.7, 53.9, 80.1, 80.3, 126.2, 127.0, 127.1, 127.4, 127.5, 128.0, 128.2, 128.4, 128.5, 129.3, 131.0, 134.1, 134.3, 140.5, 140.6, 141.1, 143.1 ppm; IR (neat): $\tilde{\nu}$=3453, 3086, 3058, 3029, 2964, 2932, 2857, 1946, 1654, 1600, 1493, 1453, 1378, 1188, 1083, 1042, 988, 914, 756, 701, 670 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{20}H_{24}NaO$ 303.1723 [M+Na$^+$]; found: 303.1723.

(*E*)-2-Methyl-2-(naphthalen-1-yl)-1-phenylhex-3-en-1-ol (**4 la**) (30.1 mg, 0.09 mmol) was obtained in 32% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (major): δ=0.87 (t, J=7.3 Hz, 3H), 1.38 (s, 3H), 1.97–2.05 (m, 2H), 2.26 (d, J=4.6 Hz, 1H), 5.16 (dt, J=15.6, 6.9 Hz, 1H), 5.61 (d, J=4.6 Hz, 1H), 5.87 (d, J=15.6 Hz, 1H), 6.78–6.79 (m, 2H), 7.01–7.10 (m, 2H), 7.23–7.44 (m, 5H), 7.66–7.68 (m, 1H), 7.78–7.82 (m, 1H), 8.33–8.35 ppm (m, 1H); ^{1}H NMR (400 MHz, $CDCl_3$) (minor): δ=0.72 (t, J=7.3 Hz, 3H), 1.46 (s, 3H), 1.78–1.86 (m, 2H), 4.96 (dt, J=16.0, 6.4 Hz, 1H), 5.54 (d, J=2.3 Hz, 1H), 5.77 (d, J=16.0 Hz, 1H), 6.78–6.79 (m, 2H), 7.01–7.10 (m, 2H), 7.23–7.44 (m, 5H), 7.61–7.62 (m, 1H), 7.74–7.76 (m, 1H), 8.41–8.43 ppm (m, 1H), OH proton was not observed clearly; ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.5, 13.6, 23.1, 23.9, 25.9, 26.0, 50.4, 51.1, 77.2, 77.8, 124.2, 124.3, 124.6, 124.9, 125.0, 126.0, 127.0, 127.1, 127.3, 127.4, 127.5, 127.6, 128.1, 128.5, 128.6, 129.3, 129.4, 130.9, 131.5, 132.9, 134.0, 134.3, 134.4, 135.0, 135.3, 140.5, 140.6, 141.3 ppm; IR (neat): $\tilde{\nu}$=3448, 3029, 2961, 2929, 1654, 1600, 1508, 1492, 1452, 1396, 1374, 1186, 1023, 975, 939, 909, 799, 778, 758, 734, 704 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{23}H_{24}NaO$ 339.1725 [M+Na$^+$]; found: 339.1728.

(*E*)-2,3-Dimethyl-3-phenylhept-4-en-2-ol (**4 jb**) (44.0 mg, 0.20 mmol) was obtained in 67% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.94 (t, J=7.3 Hz, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 1.30 (br, 1H), 1.45 (s, 3H), 2.02–2.10 (m, 2H), 5.49 (dt, J=15.6, 6.4 Hz, 1H), 6.24 (d, J=15.6 Hz, 1H), 7.11–7.15 (m, 1H), 7.19–7.25 (m, 2H), 7.38–7.41 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 20.9, 25.9, 26.1, 26.3, 50.3, 74.7, 126.0, 127.6, 128.5, 131.8, 134.1, 145.7 ppm; IR (neat): $\tilde{\nu}$=3473, 2966, 2931, 1654, 1598, 1541, 1495, 1458, 1371, 1113, 1028, 985, 952, 871, 755, 702 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{15}H_{22}NaO$ 241.1568 [M+Na$^+$]; found: 241.1564.

(*E*)-3-Methyl-2,3-diphenylhept-4-en-2-ol (**4 jc**) (69.5 mg, 0.24 mmol) was obtained in 83% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (major): δ=0.90 (t, J=7.4 Hz, 3H), 1.37 (s, 3H), 1.45 (s, 3H), 1.89 (s, 1H), 1.97–2.08 (m, 2H), 5.40 (dt, J=15.6, 6.4 Hz, 1H), 6.30 (d, J=15.6 Hz, 1H), 7.00–7.20 ppm (m, 10H); (minor): δ=0.92 (t, J=7.8 Hz, 3H), 1.35 (s, 3H), 1.49 (s, 3H), 1.86 (s, 1H), 1.97–2.08 (m, 2H), 5.40 (dt, J=15.6, 6.4 Hz, 1H), 6.30 (d, J=15.6 Hz, 1H), 7.00–7.20 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.8, 20.9, 21.1, 25.8, 26.1, 26.2, 26.3, 50.8, 78.2, 78.4, 126.2, 126.4, 126.5, 126.6, 126.7, 127.1, 127.2, 127.26, 127.30, 128.8, 132.1, 132.2, 133.3, 133.5, 144.5, 144.7, 144.8, 144.9 ppm; IR (neat): $\tilde{\nu}$=3567, 3089, 3056, 2961, 1654, 1599, 1493, 1444, 1372, 1170, 1069, 1027, 986, 906, 759, 701 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd. $C_{20}H_{24}NaO$ 303.1725 [M+Na$^+$]; found: 303.1727.

(*E*)-1,1,1-Trifluoro-3-methyl-2,3-diphenylhept-4-en-2-ol (**4 jd**) (54.9 mg, 0.15 mmol) was obtained in 51% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (major): δ=0.94 (t, J=7.3 Hz, 3H), 1.38 (s, 3H), 2.00–2.11 (m, 2H), 2.64 (s, 1H), 5.39 (dt, J=15.6, 6.4 Hz, 1H), 6.54 (d, J=15.6 Hz, 1H), 7.13–7.34 ppm (m, 10H); (minor): δ=0.91 (t, J=7.8 Hz, 3H), 1.47 (s, 3H), 2.00–2.11 (m, 2H), 2.81 (s, 1H), 5.52 (dt, J=15.6, 6.4 Hz, 1H), 6.35 (d, J=15.6 Hz, 1H), 7.13–

7.34 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.01, 13.5, 21.5, 21.8, 26.1, 26.2, 49.9, 50.0, 81.3 (q, J = 25.7 Hz), 81.5 (q, J = 25.7 Hz), 126.9, 127.0, 127.1, 127.2, 127.4, 127.5, 127.6, 128.1, 128.2, 128.8, 129.0, 131.4, 131.9, 133.0, 133.5, 136.0, 136.3, 142.2, 142.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −67.5, −67.0 ppm; IR (neat): $\tilde{\nu}$ = 3552, 3059, 2963, 1955, 1654, 1600, 1496, 1446, 1377, 1260, 1153, 1062, 1030, 911, 794, 725, 701, 669 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{20}H_{21}F_3NaO$ 357.1442 [M+Na$^+$]; found: 357.1445.

(*E*)-1-(2-Phenylhex-3-en-2-yl)cyclopentanol (**4je**) (62.7 mg, 0.25 mmol) was obtained in 86% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.4 Hz, 3H), 1.06 (br, 1H), 1.23–1.27 (m, 1H), 1.32–1.37 (m, 1H), 1.42–1.52 (m, 2H), 1.46 (s, 3H) 1.62–1.83 (m, 4H), 2.01–2.08 (m, 2H), 5.50 (dt, J = 16.0, 6.4 Hz, 1H), 6.10 (d, J = 16.0 Hz, 1H), 7.11–7.15 (m, 1H), 7.19–7.24 (m, 2H), 7.40–7.42 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 21.7, 24.0, 24.1, 26.3, 35.8, 36.3, 49.7, 87.0, 126.0, 127.6, 128.4, 132.2, 134.3, 146.0 ppm; IR (neat): $\tilde{\nu}$ = 3461, 2960, 2870, 1654, 1597, 1542, 1495, 1443, 1374, 1196, 1095, 1000, 906, 758, 701 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{17}H_{24}NaO$ 267.1725 [M+Na$^+$]; found: 267.1718.

(*E*)-1-(2-Phenylhex-3-en-2-yl)cyclohexanol (**4jf**) (68.0 mg, 0.26 mmol) was obtained in 88% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–1.01 (m, 5H), 1.27–1.42 (m, 8H), 1.43 (s, 3H), 1.51 (br, 1H), 2.02–2.09 (m, 2H), 5.46 (dt, J = 16.0, 6.4 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 7.10–7.14 (m, 1H), 7.19–7.23 (m, 2H), 7.34–7.37 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.3, 21.8, 21.9, 25.6, 26.4, 31.9 (2 carbons overlapped), 50.6, 75.0, 125.8, 127.4, 128.8, 131.7, 134.1, 145.7 ppm; IR (neat): $\tilde{\nu}$ = 3567, 2932, 2857, 1685, 1597, 1493, 1444, 1375, 1258, 1127, 1027, 967, 925, 843, 790, 710 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{18}H_{26}NaO$ 281.1881 [M+Na$^+$]; found: 281.1886.

(*E*)-2,2-Dimethyl-5-(2-phenylhex-3-en-2-yl)-1,3-dioxan-5-ol (**4jg**) (71.8 mg, 0.23 mmol) was obtained in 78% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.3 Hz, 3H), 1.27 (s, 3H), 1.30 (s, 3H), 1.45 (s, 3H), 2.04–2.12 (m, 2H), 3.09 (s, 1H), 3.27–3.35 (m, 2H), 3.85 (d, J = 11.9 Hz, 1H), 3.93 (d, J = 11.9 Hz, 1H), 5.52 (dt, J = 16.0, 6.4 Hz, 1H), 6.11 (d, J = 16.0 Hz, 1H), 7.10–7.15 (m, 1H), 7.18–7.22 (m, 2H), 7.41–7.44 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 18.3, 20.4, 26.1, 28.5, 46.8, 65.7, 66.0, 70.6, 97.9, 126.3, 127.5, 128.4, 132.1, 132.5, 144.2 ppm; IR (neat): $\tilde{\nu}$ = 3482, 3090, 3055, 2987, 2874, 1654, 1599, 1494, 1445, 1372, 1255, 1226, 1201, 1154, 1087, 1054, 1031, 991, 931, 834, 810, 759, 733, 701 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{18}H_{26}NaO_3$ 313.1780 [M+Na$^+$]; found: 313.1784.

(*E*)-3-Ethyl-4-methyl-4-phenyloct-5-en-3-ol (**4jh**) (28.2 mg, 0.11 mmol) was obtained in 38% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72 (t, J = 7.8 Hz, 3H), 0.75 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H), 1.32–1.44 (m, 2H), 1.45 (s, 3H), 1.47–1.61 (m, 3H), 2.00–2.08 (m, 2H), 5.43 (dt, J = 15.6, 6.9 Hz, 1H), 6.25 (d, J = 15.6 Hz, 1H), 7.10–7.14 (m, 1H), 7.19–7.23 (m, 2H), 7.38–7.41 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1, 9.2, 13.9, 21.2, 26.3, 27.7, 27.8, 51.4, 77.2, 125.9, 127.5, 128.6, 130.9, 134.9, 146.5 ppm; IR (neat): $\tilde{\nu}$ = 3586, 2963, 1654, 1597, 1542, 1491, 1458, 1376, 1260, 1121, 1028, 960, 761, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{17}H_{26}NaO$ 269.1881 [M+Na$^+$]; found: 269.1877.

(*E*)-3,4-Diethyl-6-phenylhept-5-en-3-ol (**5jh**) (15.3 mg, 0.06 mmol) was obtained in 21% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.85 (m, 9H), 1.17–1.27 (m, 2H), 1.44–1.47 (m, 3H), 1.54–1.65 (m, 2H), 2.01 (s, 3H), 2.42–2.48 (m, 1H), 5.59 (d, J = 10.5 Hz, 1H), 7.15–7.19 (m, 1H), 7.23–7.27 (m, 2H), 7.33–7.35 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.6, 7.8, 12.7, 16.7, 22.4, 28.6, 28.8, 47.5, 76.8, 125.8, 126.8, 128.2, 129.1, 137.6, 144.0 ppm; IR (neat): $\tilde{\nu}$ = 3586, 2965, 1654, 1560, 1542, 1508, 1491, 1458, 1379, 948, 756, 696 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{17}H_{26}NaO$ 269.1881 [M+Na$^+$]; found: 269.1876.

(*E*)-2-Ethyl-1,1,4-triphenylpent-3-en-1-ol (**5ji**) (56.5 mg, 0.16 mmol) was obtained in 55% yield as a white solid; M.p. = 104–105 °C (from AcOEt/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.4 Hz, 3H), 1.19–1.29 (m, 1H), 1.57–1.66 (m, 1H), 1.87 (s, 3H), 3.32–3.38 (m, 1H), 5.52 (d, J = 10.6 Hz, 1H), 7.02–7.19 (m, 9H), 7.25–7.34 (m, 5H), 7.46–7.48 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 16.9, 23.7, 48.9, 81.0, 125.8, 125.9, 126.2, 126.4, 126.6, 126.7, 127.7, 128.0, 128.1, 128.2, 137.4, 144.3, 146.3, 146.5 ppm; IR (neat): $\tilde{\nu}$ = 3567, 3056, 2961, 2870, 1654, 1598, 1542, 1491, 1446, 1377, 1158, 1031, 877, 757, 698 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{25}H_{26}NaO$ 365.1881 [M+Na$^+$]; found: 365.1884.

(*E*)-2-Benzyl-3-ethyl-1,5-diphenylhex-4-en-2-ol (**5jj**) (65.8 mg, 0.17 mmol) was obtained in 58% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (t, J = 7.3 Hz, 3H), 1.29–1.41 (m, 1H), 1.64 (s, 3H), 1.70 (br, 1H), 1.77–1.88 (m, 1H), 2.28–2.34 (m, 1H), 2.78–2.87 (m, 4H), 5.45 (d, J = 10.6 Hz, 1H), 7.15–7.24 ppm (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 16.6, 23.7, 43.1, 43.8, 48.0, 76.9, 125.8, 126.2, 126.3, 126.9, 127.9, 128.0, 128.1, 128.2, 130.8, 130.9, 137.7, 137.8, 139.8, 143.7 ppm; IR (neat): $\tilde{\nu}$ = 3548, 3082, 3059, 3026, 2959, 2871, 1945, 1878, 1803, 1601, 1493, 1453, 1378, 1181, 1155, 1125, 1081, 1030, 940, 925, 873, 782, 755, 699 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{27}H_{30}NaO$ 393.2194 [M+Na$^+$]; found: 393.2196.

(*E*)-1,1-Dicyclopropyl-2-ethyl-4-phenylpent-3-en-1-ol (**5jk**) (21.9 mg, 0.08 mmol) was obtained in 27% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18–0.47 (m, 8H), 0.73–0.79 (m, 1H), 0.82 (t, J = 7.8 Hz, 3H), 0.94–1.01 (m, 2H), 1.32–1.43 (m, 1H), 1.85–1.94 (m, 1H), 2.02 (s, 3H), 2.52–2.58 (m, 1H), 5.69 (d, J = 10.6 Hz, 1H), 7.15–7.17 (m, 1H), 7.23–7.28 (m, 2H), 7.32–7.35 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.69, 0.37, 1.00, 1.64, 12.8, 16.0, 16.6, 17.5, 23.1, 53.3, 72.6, 125.7, 126.7, 128.2, 129.8, 137.7, 144.0 ppm; IR (neat): $\tilde{\nu}$ = 3586, 3006, 2961, 2928, 2870, 1654, 1560, 1542, 1509, 1491, 1458, 1379, 1261, 1020, 911, 799, 758, 696 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{19}H_{26}NaO$ 293.1881 [M+Na$^+$]; found: 293.1878.

(*E*)-2-Hydroxy-2-phenylhept-4-en-3-one (**6ic**) (11.6 mg, 0.05 mmol) was obtained in 19% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.3 Hz, 3H), 1.70 (s, 3H), 2.06–2.14 (m, 2H), 4.71 (s, 1H), 6.11 (d, J = 15.1 Hz, 1H), 7.05 (dt, J = 15.1, 6.9 Hz, 1H), 7.21–7.38 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1, 24.0, 25.8, 78.6, 121.7, 126.3, 128.0, 128.6, 141.4, 152.5, 199.6 ppm; IR (neat): $\tilde{\nu}$ = 3447, 2970, 2933, 1685, 1624, 1492, 1447, 1367, 1287, 1220, 1139, 1067, 1007, 978, 914, 861, 760, 699 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{13}H_{16}NaO_2$ 227.1048 [M+Na$^+$]; found: 227.1052.

(*E*)-2-Methyl-1,2-diphenylhex-3-en-1-one (**7**) (33.1 mg, 0.12 mmol) was obtained in 42% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3H), 1.56 (s, 3H), 1.97–2.05 (m, 2H), 5.55 (dt, J = 15.6, 6.4 Hz, 1H), 5.87 (d, J = 15.6 Hz, 1H), 7.12–7.30 (m, 8H), 7.46–7.48 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 26.1, 27.2, 57.6, 126.4, 126.7, 127.8, 128.9, 130.1, 131.5, 131.7, 134.6, 136.2, 145.4, 201.1 ppm; IR (neat): $\tilde{\nu}$ = 3024, 2964, 2931, 1678, 1596, 1577, 1491, 1446, 1371, 1232, 1181, 1076, 1027, 972, 909, 853, 763, 700 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{19}H_{20}NaO$ 287.1412 [M+Na$^+$]; found: 287.1421.

Synthesis of Substrate

Cyclopropenes were synthesized from ketones in 4 steps.[20]

1-Methyl-2-(1-phenylcycloprop-2-en-1-yl)benzene (**1g**) (185 mg, 0.9 mmol) was obtained in 6% yield (4 steps) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 6.88–6.91 (m, 2H), 7.03–7.21 (m, 7H), 7.45 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4, 30.8, 113.6, 125.1, 126.3, 126.6 (2 carbons overlapped), 127.8, 129.1, 130.4, 137.2, 144.1, 148.1 ppm; IR (neat): $\tilde{\nu}=3567$, 2923, 1638, 1598, 1542, 1509, 1490, 1445, 1136, 902, 749, 728, 698 cm^{-1}; HRMS (APCI) m/z calcd. $C_{16}H_{14}$ 206.1096 [M^+]; found: 206.1094.

1-Fluoro-4-(1-phenylcycloprop-2-en-1-yl)benzene (**1h**) (506 mg, 2.4 mmol) was obtained in 32% yield (4 steps) as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.99$–7.06 (m, 2H), 7.18–7.28 (m, 5H), 7.33–7.37 (m, 2H), 7.52 (s, 1H), 7.53 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.2$, 113.3, 114.8 (d, $J=21.0$ Hz), 125.8, 127.9, 128.1, 129.5 (d, $J=7.6$ Hz), 142.7, 146.9, 161.1 ppm (d, $J=243$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-117.23$ ppm; IR (neat): $\tilde{\nu}=3100$, 3056, 3023, 2926, 1892, 1640, 1599, 1507, 1491, 1445, 1224, 1157, 1094, 1074, 1014, 992, 900, 854, 810, 754, 700, 671 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{15}H_{12}F$ 211.0923 [$M+H^+$]; found: 211.0921.

1,1′-(cycloprop-2-ene-1,1-diyl)bis(benzene-2,3,4,5,6-d_5) (***d*-1a**) (933 mg, 4.6 mmol) was obtained in 46% yield (4 steps) as a colorless oil; H NMR (400 MHz, $CDCl_3$): $\delta=7.55$ ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.6$, 113.2, 125.2 (t, $J=24.8$ Hz), 127.5 (t, $J=23.8$ Hz), 127.6 (t, $J=22.9$ Hz), 146.9 ppm; IR (neat): $\tilde{\nu}=3134$, 3098, 2926, 2273, 1640, 1566, 1437, 1369, 1281, 1206, 1063, 991, 901, 862, 823, 751 cm^{-1}; HRMS (ESI-TOF) m/z calcd. $C_{15}H_3D_{10}$ 203.1645 [$M+H^+$]; found: 203.1641.

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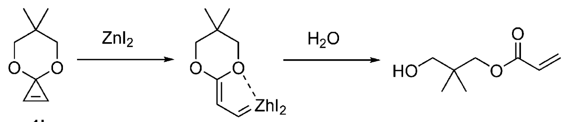

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