# Radical Allylation, Vinylation, Alkynylation, and Phenylation Reactions of α-Halo Carbonyl Compounds with Organoboron, Organogallium, and Organoindium Reagents

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**Abstract:** Allylic gallium and indium reagents are found to mediate radical allylation reactions of α-iodo or α-bromo carbonyl compounds. Treatment of benzyl bromoacetate with allylgallium, prepared from allylmagnesium chloride and gallium trichloride, in the presence of triethylborane provided benzyl 4-pentenoate in excellent yield. Addition of water as a co-solvent improved the yields of allylated products. Allylic indium reagents are also useful and can replace the gallium reagents. A diallylborane reagent can allylate an α-iodo ester in good yield. Alkenylation reactions of α-halo carbonyl compounds with alkenylindium proceeded via a radical process in the presence of triethylborane. Unactivated alkene moieties and styryl groups were introduced by this method. The carbon-carbon double bond geometry of the alkenylindiums was retained during the alkenylation. Preparation of an alkenylindium via a hydroindation of 1-alkyne and subsequent radical alkenylation established an efficient one-pot strategy. Radical alkynylations and phenylations with organoindium reagents are disclosed herein.

**Keywords:** allylation, vinylation, radical reaction, gallium, indium

Radical reactions often allow the conversion of polyfunctional compounds that may suffer under the more drastic ionic reactions.[1] The majority of modern radical reactions are based on tin reagents, such as tributyltin hydride, allyltributyltin or tributylvinyltin, as chain carriers. However, organotin compounds are toxic[2] as well as difficult to remove completely from the desired reaction products. Various attempts have therefore been made to overcome these problems and, furthermore, to pursue a higher reactivity. For radical reduction reactions, silanes,[3] germanes,[4] other metal hydride compounds[5] and phosphorous compounds,[6] such as hypophosphorous acid, are found to be good alternatives to tributyltin hydride and are widely used in organic synthesis.[7] On the other hand, the development of new allylating and vinylating reagents for radical processes is still premature and deserves further exploitation. Herein, we report the development of such reagents based on group 13 metals.

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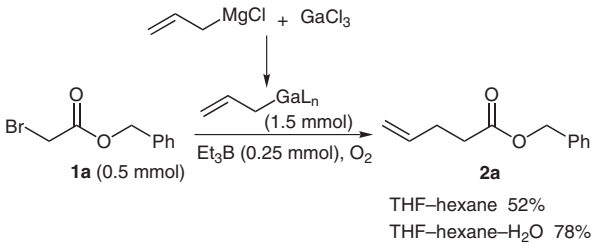
## Radical Allylation of α-Halo Carbonyl Compounds with Allylgallium Reagents[8]

Radical allylation reactions with allylstannanes represent a mild and efficient method to install allyl groups into organic molecules.[9,10] However, tin-based methods have serious drawbacks in the synthesis of organic compounds of biological interest due to the inherent toxicity of organotin derivatives and the difficulty of complete removal of residual tin compounds. Allylsilanes[11] and allyl sulfones[12] are efficient surrogates, and are being actively investigated.[13] Herein we show that radical allylation proceeds smoothly with allylgallium reagents.[14]

Allylmagnesium chloride (1.5 mmol) was added to a mixed THF (2 mL) and hexane (1.5 mL) solution of $GaCl_3$ (1.5 mmol) under argon to prepare an allylgallium reagent. Benzyl bromoacetate (**1a**; 0.5 mmol) and triethylborane (1.0 M hexane solution, 0.25 mL, 0.25 mmol)[15] were added to the solution, and air (10 mL) was introduced to the reaction flask by syringe. After the mixture was stirred for two hours, extractive workup was followed by silica gel column purification to afford benzyl 4-pentenoate (**2a**) in 52% yield (Scheme 1).




**Scheme 1**

The reaction with the allylgallium reagent did not proceed at all in the absence of $Et_3B$. An azo initiator, V-70 [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)],[16] was also effective to afford **2a** in 48% yield after 14 hours at 25 °C. Additionally, radical scavengers such as galvinoxyl and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) inhibited the reaction. A radical reaction mechanism is therefore suggested for the allylation. Although the yield was moderate, the result encouraged us to modify the reaction conditions. Consequently, we found that addition of water as a co-solvent to the reaction mixture improved the yield of

**2a**. Water (1 mL) was added to a THF (2 mL) and hexane (1.5 mL) solution of the allylgallium reagent prior to the addition of benzyl bromoacetate, $Et_3B$, and air. After two hours at 25 °C, **2a** was obtained in 78% yield. Allylgallium species, like allylindium reagents,[17] proved to be somewhat stable in aqueous media and to act as radical allylating reagents. A gallium reagent prepared from gallium trichloride and two or three equivalents of allyl Grignard reagent produced **2a** in much lower yield.

While the allylgallium resisted immediate hydrolysis, it gradually decomposed in the presence of water. The addition of benzyl bromoacetate, triethylborane, and air to the allylgallium species, which was treated with 1 mL of water for three hours prior to the radical reaction, furnished **2a** in only 39% yield. Exposure of the allylgallium reagent to water for 14 hours before addition of **1a** resulted in complete recovery of **1a**.

The origin of the favorable solvent effect might be due to the highly polar nature of water.[18] The high polarity of wa-

## Biographical Sketches

**Kazuaki Takami** was born in Ishikawa, Japan, in 1977. He graduated from Kyoto University in 2000, where he is pursuing his Ph.D. under the direction of Professor Koichiro Oshima. He has been a Research Fellow of the Japan Society for the Promotion of Science (JSPS) since 2004. His research activity focuses on the development of synthetic reactions with organoindium compounds.

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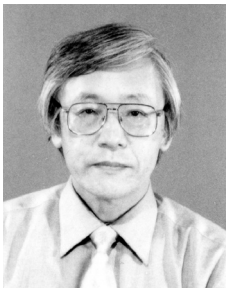
**Hideki Yorimitsu** was born in Kochi, Japan, in 1975. He obtained his B.S. in 1997 and his Ph.D. in 2002 from Kyoto University under the supervision of Professor Koichiro Oshima. He served as a JSPS postdoctoral fellow, working with Professor Eiichi Nakamura at the University of Tokyo, from 2002 to 2003. He has been an Assistant Professor at Kyoto University since 2003. His research interests are the development of new organic reactions by using radical intermediates, and synthesis of new ligands applicable to organic reactions, biological science, and materials science.



**Koichiro Oshima** was born in Hyogo, Japan, in 1947. He received his B.S. and Ph.D. degrees from Kyoto University in 1970 and 1975 under the guidance of Professor Hitosi Nozaki. He spent two and a half years as a postdoctoral fellow with Professor Barry Sharpless at MIT from 1975 to 1977, and became an Assistant Professor at Kyoto University in 1977. He was promoted to Lecturer in 1984, Associate Professor in 1986, and Professor in 1993. His current research interests include the development of new synthetic methods via radical reactions and organometallic reagents.

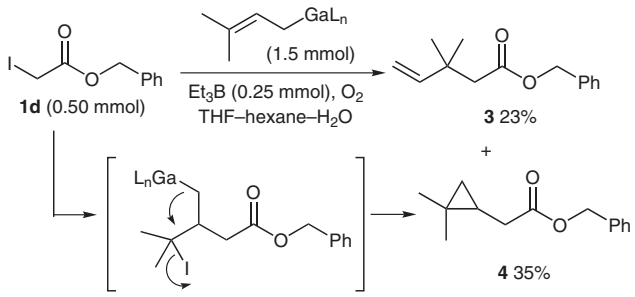
ter causes a reduction in the volume of an hydrophobic organic molecule, thus enhancing the radical addition step.[18a] Moreover, water molecules could act as a Lewis acid and activate the iodo ester and the corresponding radical through coordination of the carbonyl group to a proton of $H_2O$.[18c] It is also probable that the structure of the allylgallium species could change and that water could increase the reactivity of allylgallium. Allylgallium dichloride is likely to transform into allylgallium hydroxide that is possibly more reactive for radical allylation.[19]

Various combinations of α-halo carbonyl compounds and allylic gallium reagents were examined (Table 1). The more reactive α-iodo carbonyl compounds gave better results than their bromo analogs. 2-Halopropanoates or 2-halopropanamides also reacted with the allylgallium reagent to yield 2-methyl-4-pentenoate or 2-methyl-4-pentenamide (entries 2, 3, and 5). In contrast, 2-bromo-2-methylpropanoate did not give the anticipated product, and the starting material was recovered unchanged, probably due to the steric hindrance around the carbon-centered radical. Interestingly, allylation was effective for substrates with a terminal carbon-carbon double bond (entries 9 and 10). An electron-deficient (alkoxycarbonyl)methyl radical reacted faster with the highly electron-rich alkene moiety of the allylgallium species than with the olefinic parts of the substrate and of the product. Furthermore, **1k**, prepared from butyroin, was selectively allylated to give 4-pentenoate **2k** in excellent yield (entry 11). Allylation of the ketone moiety was not observed.[20]

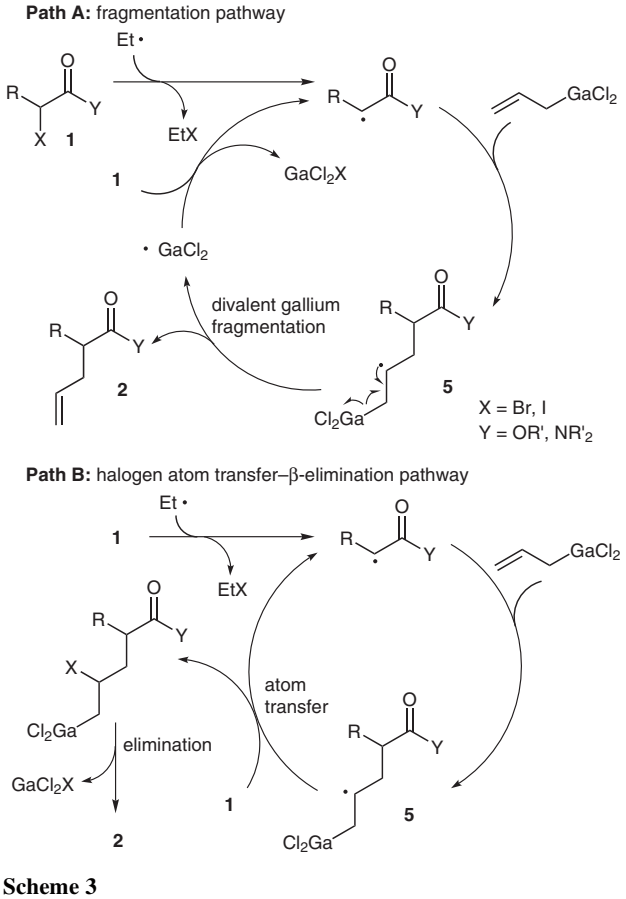
2-Butenylgallium, not 1-methyl-2-propenylgallium, was also available by simply mixing $GaCl_3$ and a Grignard reagent prepared from 1-chloro-2-butene and magnesium, whereas synthesis of 2-butenylstannane is somewhat troublesome.[21] We confirmed that the reaction of $GaCl_3$ with crotylmagnesium chloride gives 2-butenylgallium as an *E*/*Z* isomeric mixture by the following NMR experiments. In the $^1$H NMR, the vinylic proton signals of 2-butenyltributylstannane appeared at 5.4–5.7 (1 H) and 5.9–6.1 (1 H) ppm in THF, whereas those of 1-methyl-2-propenyltributylstannane were detected at 5.0–5.2 (2 H) and 6.4–6.6 (1 H) ppm. In the $^{13}$C NMR of 2-butenylstannane, we detected two sets of two singlets at 118, 130 ppm (for the major isomer) and 120, 131 ppm (for the minor isomer). The $^{13}$C NMR spectrum of 1-methyl-2-propenylstannane showed two singlets at 106 and 145 ppm. The NMR analysis of the mixture of $GaCl_3$ and crotylmagnesium chloride in anhydrous THF showed vinylic proton signals at 5.15–5.40 (1 H, multiplet) and 5.60–5.78 (1 H, multiplet) ppm. Furthermore, two sets of two singlets were observed at 119.6, 130.9 ppm (for the major isomer) and 117.7, 130.0 ppm (for the minor isomer) in the $^{13}$C NMR analysis. Upon addition of water, very little change was observed and signals appeared at 5.22–5.38 (1 H, multiplet), 5.63–5.74 (1 H, multiplet) ppm in the $^1$H NMR and at 120.7, 130.2 ppm (for the major isomer) and 118.7, 129.3 ppm (for the minor isomer) in the $^{13}$C NMR. These signals became smaller during continued analysis of the aqueous sample over ten hours. Based on comparison of the signals of the gallium species with those of stannanes, the 2-butenyl form of the gallium reagent is evident. With the crotylgallium reagent, 3-methyl-4-pentenoates were obtained in high yields without contamination by 4-hexenoates (Table 1, entries 12–16).

Methallylation of α-halo carbonyl compounds with 2-methyl-2-propenylgallium was disappointing (ca. 10% yield in the case of **1a**). The starting materials were mostly recovered. Allylation of 1-iododododecane or 2-iododododecane did not occur under the reaction conditions.

The reaction of **1d** with prenylgallium reagent afforded 3,3-dimethyl-4-pentenoate **3** in spite of the steric effect of the dimethyl groups in the gallium reagent (Scheme 2). In this case, the allylation product was contaminated with cyclopropane **4**. Bond formation at the less substituted

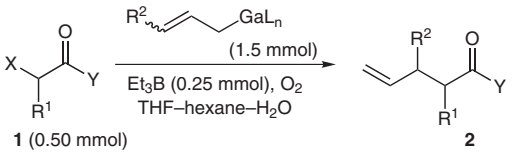


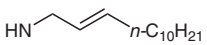
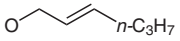
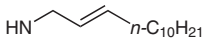

**Scheme 2**




**Scheme 3**

**Table 1** Radical Allylation of α-Halo Carbonyl Compounds with Allylgallium Species




| Entry | 1 | X | Y | $R^1$ | $R^2$ | Time (h) | | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | Br | $OCH_2Ph$ | H | H | 2 | **2a:** | 78 |
| 2 | **1b** | Br | $OCH_2Ph$ | Me | H | 2 | **2b:** | 63 |
| 3 | **1c** | Br | $NMe_2$ | Me | H | 2 | **2c:** | 64 |
| 4 | **1d** | I | $OCH_2Ph$ | H | H | 0.5 | **2a:** | 89 |
| 5 | **1e** | I | $OCH_2Ph$ | Me | H | 0.5 | **2b:** | 81 |
| 6 | **1f** | I |  | H | H | 1 | **2f:** | 87 |
| 7 | **1g** | I |  | H | H | 0.5 | **2g:** | 95 |
| 8 | **1h** | I | $O(CH_2)_6Cl$ | H | H | 1 | **2h:** | 85 |
| 9 | **1i** | I | $O(CH_2)_2OCH_2CH{=}CH_2$ | H | H | 0.5 | **2i:** | 64 |
| 10 | **1j** | I | $OCH(Ph)CH_2CH{=}CH_2$ | H | H | 2 | **2j:** | 71 |
| 11 | **1k** | I | $OCH(n\text{-}C_3H_7)CO(n\text{-}C_3H_7)$ | H | H | 1 | **2k:** | 84 |
| 12 | **1d** | I | $OCH_2Ph$ | H | Me | 0.5 | **2a′:** | 70 |
| 13 | **1f** | I |  | H | Me | 2 | **2f′:** | 85 |
| 14 | **1h** | I | $O(CH_2)_6Cl$ | H | Me | 1 | **2h′:** | 46 |
| 15 | **1a** | Br | $OCH_2Ph$ | H | Me | 2 | **2a′:** | 50 |
| 16 | **1c** | Br | $NMe_2$ | Me | Me | 7 | **2c′:** | 65[a] |

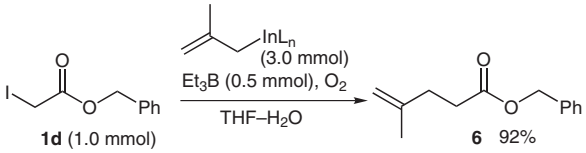
[a] Diastereomeric ratio = 2:1.

carbon yields the 3-iodoalkylgallium via atom-transfer addition; the organogallium intermediate then undergoes intramolecular cyclization to form the cyclopropane ring.[22]

The reaction mechanism of the allylation, especially the fate of the γ-gallylalkyl radical intermediate **5**, is not clear. Scheme 3 illustrates two plausible mechanisms, in the absence of water for clarity, which involve: (1) elimination of divalent gallium radical from **5** (Path A); or (2) halogen atom abstraction of **5** from α-halo carbonyl compound **1** (Path B). The former mechanism is proposed in the reaction with allylstannane[10] and the latter in that of allylsilane.[11]

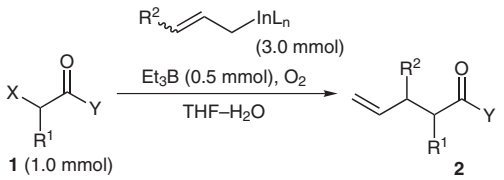
## Radical Allylation of α-Halo Carbonyl Compounds with Allylindium Reagents

Based on recent research reports on divalent indium compounds and their capacity as radical mediators in radical chain reactions,[23,24] it is feasible that allylindium reagents would also work. As anticipated, radical allylation proceeded with allylic indium reagents prepared in a similar manner. The results are summarized in Table 2. The reagents were prepared from indium trichloride and Grignard reagents in THF. Addition of water also accelerated the radical reaction. It is worth noting that methallylation with methallylindium reagent afforded the corresponding product in excellent yield (Scheme 4), whereas methallylgallium failed to yield the product. Surprisingly, use of indium trichloride tetrahydrate instead of anhydrous indium trichloride as a precursor of the allylindium reagent led to a comparable result (Scheme 5). The transmetallation generating an allylindium reagent is faster than the reaction of allyl Grignard reagent with water of hydration.



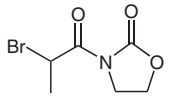

**Scheme 4**

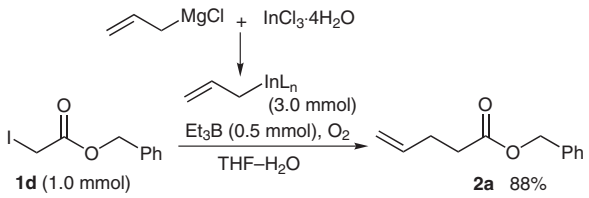
**Table 2** Allylation with Allylindium Reagents




| Entry | 1 | $R^2$ | 2 | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | **1a** | H | **2a** | 3.5 | 62 (25) |
| 2 | **1b** | H | **2b** | 3.5 | 65 (14) |
| 3 | **1d** | H | **2a** | 0.5 | 89 (64) |
| 4 | **1f** | H | **2f** | 0.5 | 90 |
| 5 | **1l**[b] | H | **2l** | 3.0 | 88 |
| 6 | **1d** | Me | **2a′** | 0.5 | 87 |

[a] Yields in parentheses were obtained in the absence of water.
[b] **1l** :



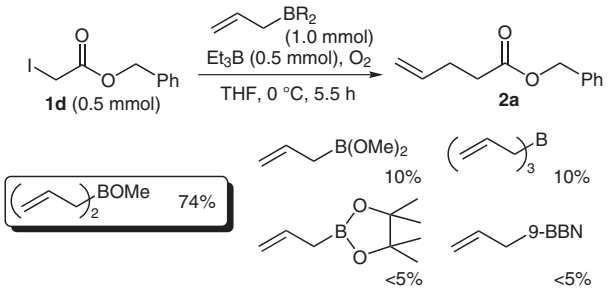




**Scheme 5**

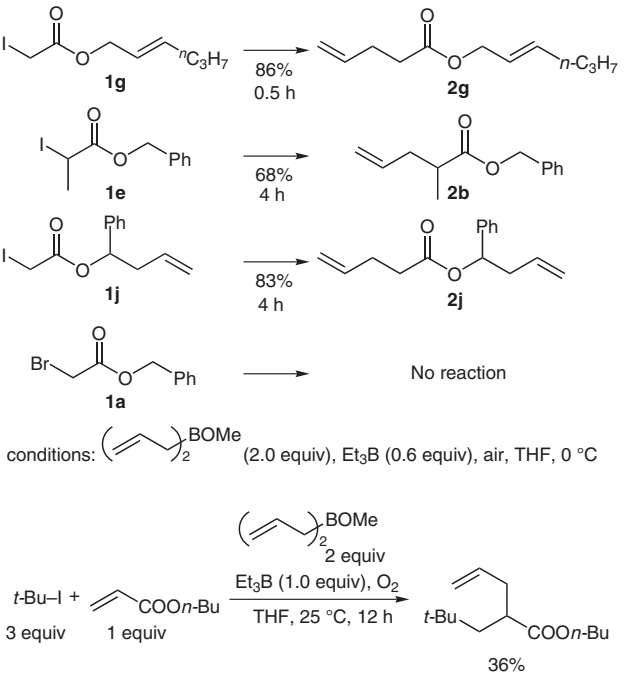
## Radical Allylation of α-Halo Carbonyl Compounds with Diallylborane Reagents

An allylborane reagent, prepared from trimethoxyborane and two equivalents of allylmagnesium chloride, was effective for the radical allylation of **1d** (Scheme 6). Other allylborane reagents failed to yield **2a**. For instance, treatment of **1d** with 9-allyl-9-borabicyclo[3.3.1]nonane (allyl-9-BBN) mainly led to allylation of the carbonyl group, and to a reduction that produced benzyl acetate. The reaction with allyldimethoxyborane yielded a considerable amount of benzyl acetate (20%) in addition to **2a** (10%). Diallylmethoxyborane was less reactive than the allylgallium and allylindium reagents. Allylation of an α-bromo ester with the allylborane reagent did not take place (Scheme 7). An intermolecular radical addition–allylation sequence in the reaction of *tert*-butyl iodide, diallylmethoxyborane and butyl acrylate can rationalize the radical mechanism.

Attempts to use allylaluminum reagents failed. Allylaluminum reagents are so reactive that carbonyl groups did not survive under the reaction conditions.



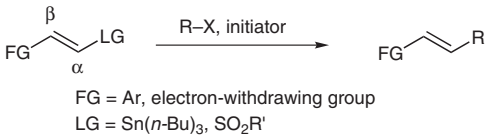

**Scheme 6**




**Scheme 7**

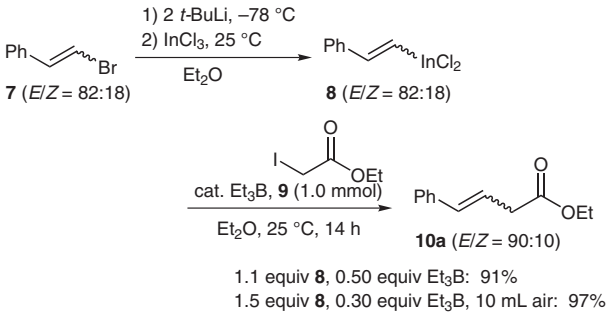
## Radical Vinylation of α-Halo Carbonyl Compounds with Vinylindium Reagents[25]

Alkenylation reactions of organic halides by 1-alkenylstannanes,[26] 1-alkenyl sulfones[27] or 1-alkenylmercury compounds[28] via a free radical process[1,9b] provide an efficient method for the installation of a 1-alkenyl moiety. However, activation of the carbon-carbon double bond with the aid of an electron-withdrawing group or an aryl group at the alkenyl β-carbon is essential to perform these reactions (Scheme 8). In addition, vigorous conditions are necessary to carry out these reactions successfully. Radical vinylation hence deserves further exploitation.




**Scheme 8**

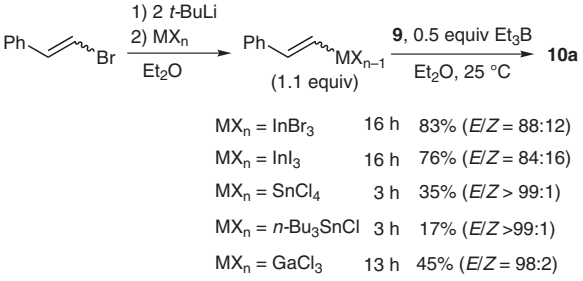
At first, we examined radical alkenylation of ethyl iodoacetate (**9**) with β-styrylindium dichloride (**8**) (Scheme 9). The indium reagent was prepared in situ via transmetalation of indium trichloride with β-styryllithium in diethyl ether. β-Styryllithium was prepared from β-bromostyrene (**7**, *E*/*Z* = 82:18) and two equivalents of *tert*-butyllithium. The stereochemistry of alkenylindium **8** was determined by iodolysis. Treatment of **9** with a small excess of **8** (1.1 equivalents) and triethylborane (0.50 equivalent) as a radical initiator at ambient temperature afforded alkenylation product **10a** in 91% yield. In contrast to the allylation with allylic gallium reagents, the addition of water as a co-solvent showed no significant effect. When a higher yield was required, an increased amount of **8** and injection of air into the reaction flask were particularly effective. For instance, combined use of **8** (1.5 equivalents), triethylborane (0.30 equivalent), and air (10 mL) improved the yield to 97%.



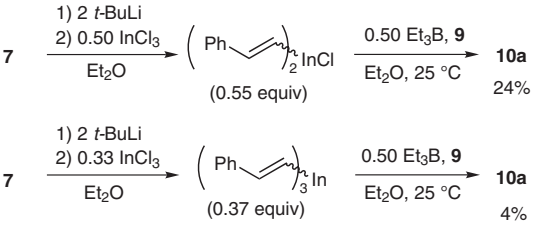

**Scheme 9**

β-Styrylindium prepared from β-styryl Grignard reagent and indium trichloride in THF resulted in a lower yield of **10a**.[29] Both indium tribromide and indium triiodide could replace indium trichloride, but the reactions were somewhat inferior to that with indium trichloride (Scheme 10: $InBr_3$, 83%; $InI_3$, 76%). To our surprise, tin-based reagents, prepared from tin chlorides such as $SnCl_4$ and *n*-$Bu_3SnCl$, were much less effective. A styrylgallium reagent also failed to attain a high yield (45%). We also attempted to apply distyrylindium chloride and tristyrylindium to this radical alkenylation reaction; however, both of these were unsuccessful (Scheme 11).

This alkenylation reaction did not proceed in the absence of triethylborane, as depicted in Scheme 12. Addition of TEMPO thoroughly prevented the reaction. Furthermore, nonafluorobutyl iodide, wherein nucleophilic substitution is difficult, was alkenylated by this method.[30] These results strongly suggest that the reaction proceeds via a radical chain mechanism as illustrated in Scheme 13.

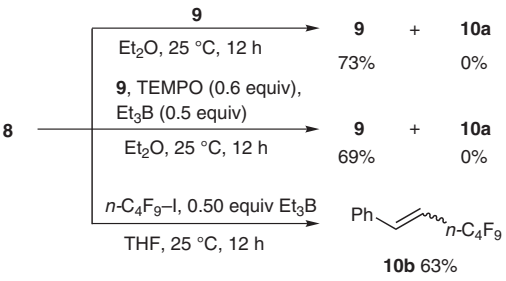



**Scheme 10**



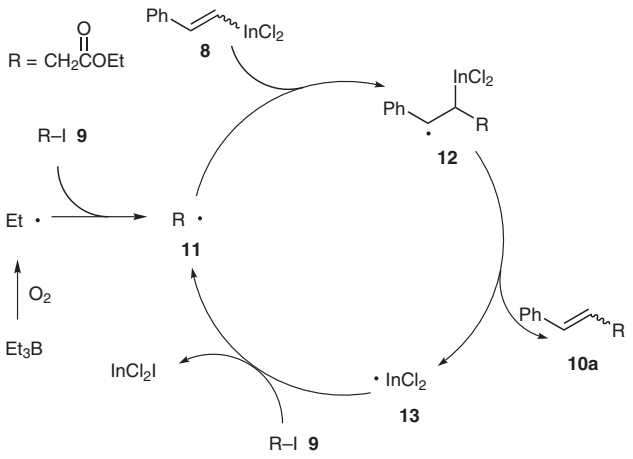

**Scheme 11**

Ethoxycarbonylmethyl radical (**11**), generated from **9**, adds to the carbon atom that is attached to the indium atom. The elimination of dichloroindium radical (**13**) from **12** affords alkenylated product **10a**, and the released indium radical abstracts iodine from substrate **9** to regenerate radical **11**. As opposed to the discussion regarding Scheme 3, the retention of configuration of the alkene moiety eliminates the possibility of a halogen atom transfer–β-elimination process wherein loss of stereochemistry would take place (vide infra).




**Scheme 12**

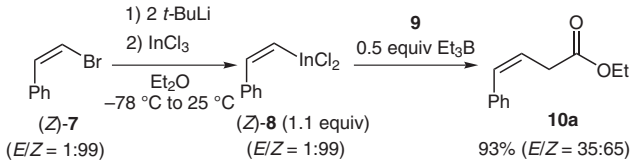
To broaden the scope of the present method, we applied this system to a variety of α-halo carbonyl compounds (Table 3). Styrylation of α-alkylated α-iodo esters took place smoothly (entries 1 and 2). In contrast, α,α-dialkylated α-iodo ester did not undergo the alkenylation at all. The reaction can be applied not only to α-iodo esters but also to α-iodo amides (entries 3 and 4). α-Iodo ketones can also be employed, though the β,γ-unsaturated ketone generated at the initial stage of the reaction isomerized to 1,4-diphenyl-2-buten-1-one (**14**) during the reaction (entry 5). Unfortunately, alkenylation of α-bromo ester afforded **10a** in only 50% yield under the same reaction conditions (entry 6). Employing a catalytic amount of V-70 as a rad-




**Scheme 13**

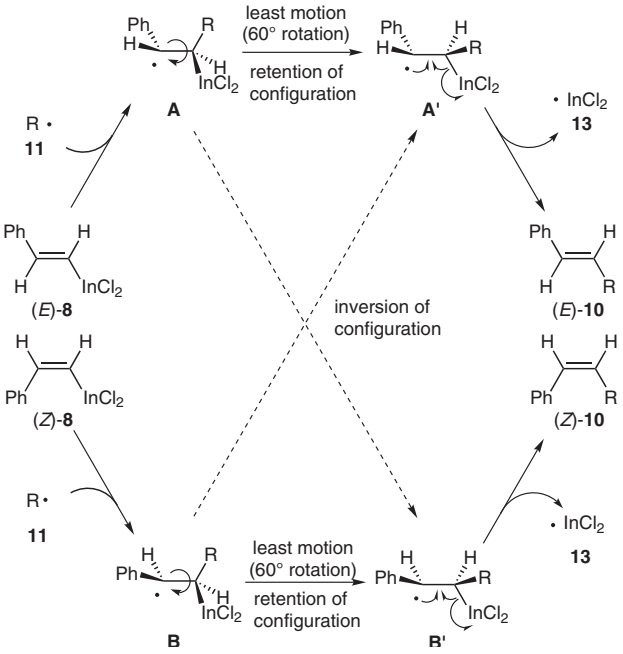
ical initiator instead of triethylborane also yielded **10a** in moderate yield (entry 7). This result eliminates the possibility of an $S_N2$ alkenylation of the α-halo carbonyl compound with an alkenylmetal reagent, and supports the radical chain mechanism which we proposed in Scheme 13. Use of a two-fold excess of the styrylindium reagent provided sufficient improvement in yield (entry 8). Under these modified conditions, various α-bromo carbonyl compounds can be styrylated in good to high yields (entries 9–11). On the other hand, styrylation of α-chloro carbonyl compounds was very sluggish (entries 12 and 13).

When the reaction was performed with (*Z*)-enriched styrylindium dichloride [(*Z*)-**8**], the thermodynamically disfavored (*Z*)-alkenylated product was mainly obtained (Scheme 14). The stereochemistry of styrylindium (*Z*)-**8** generated in situ was determined by deuteration and iodination. To explain this moderate stereospecificity, we propose a mechanism shown in Scheme 15. The intermediates **A** and **B**, which are generated at the first step, liberate dichloroindium radical (**13**) to generate alkenylation products **10**. Because of the great elimination ability of dichloroindium radical **13**,[31,32] we are tempted to assume that this indium radical elimination is fast enough to proceed via a least motion process.

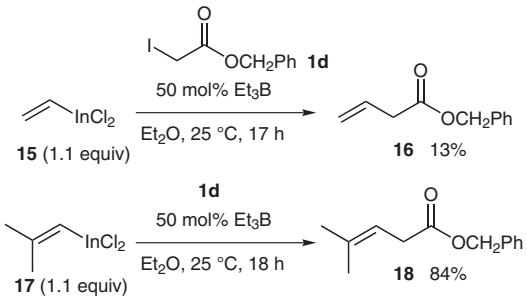



**Scheme 14**

Next, we employed unactivated alkenylindiums to this reaction system (Scheme 16). Unfortunately, it was difficult to achieve vinylation with unsubstituted vinylindium dichloride (**15**). However, 2,2-dimethyl substitution dramatically improved the reactivity of the alkenylindium dichloride to yield **18**.




**Scheme 15**



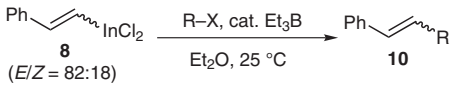

**Scheme 16**

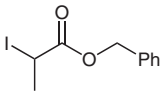
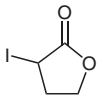
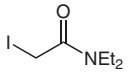
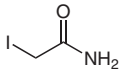
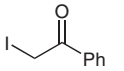
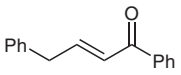
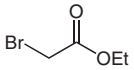
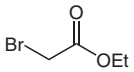
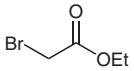
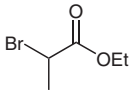
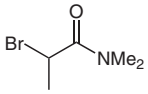
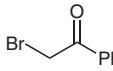
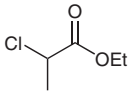
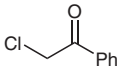
As observed in the styrylations, the reaction starting with (*E*)-iodo alkene **19** retained the alkene geometry to give **21** in good yield (Scheme 17). The reaction with (*Z*)-alkenylindium **23** yielded predominantly the thermodynamically less stable (*Z*)-alkenylation product **24**. The stereochemistry of alkenylindiums **20** and **23** was determined by iodolysis and deuteriolysis.

Alkenylindium **26a**, prepared from the corresponding iodide **25a**, effected alkenylation of **9** to provide **27a**, predominantly as the *E* form (Scheme 18). The reaction with **26b** also afforded the expected product **27b** with complete retention of configuration.

In a previous report, we disclosed a stereoselective preparation of alkenylindiums via a hydroindation reaction.[23] Accordingly, we attempted to construct a one-pot hydroindation–alkenylation sequence. Upon alkenylation reaction with alkenylindium reagents prepared via the hydroindation reaction, only unsatisfactory results were obtained. After extensive modifications, we successfully combined the two reactions by using DMSO as a co-solvent (Scheme 19). The stereospecificity of the alkenylation reaction was largely retained in this one-pot system.

**Table 3** Radical Styrylation of Various α-Halo Carbonyl Compounds[a]

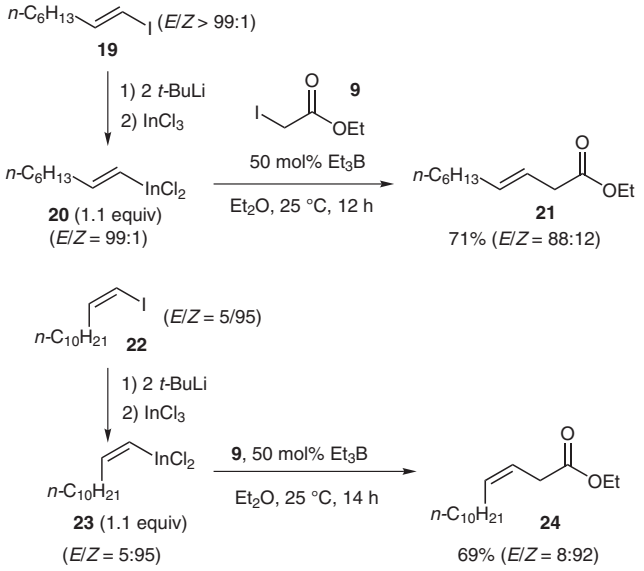



| Entry | **8** (mmol) | R–X | **10** | Yield (%) | *E*/*Z* |
|---|---|---|---|---|---|
| 1 | 1.1 |  | **10c** | 93 | 90:10 |
| 2 | 1.1 |  | **10d** | 99 | 86:14 |
| 3 | 1.1 |  | **10e** | 85 | 94:6 |
| 4 | 1.1 |  | **10f** | 91 | 88:12 |
| 5 | 1.1 |  |  **14**[c] | 71 | 93:7 |
| 6 | 1.1 |  | **10a** | 50 | 95:5 |
| 7[b] | 1.1 |  | **10a** | 62 | 95:5 |
| 8 | 2.0 |  | **10a** | 88 | 97:3 |
| 9 | 2.0 |  | **10g** | 86 | 95:5 |
| 10 | 2.0 |  | **10h** | 57 | 95:5 |
| 11 | 2.0 |  | **14**[c] | 71 | 93:7 |
| 12 | 2.0 |  | **10g** | 4 | n.d. |
| 13 | 2.0 |  | **14**[c] | 28 | 95:5 |

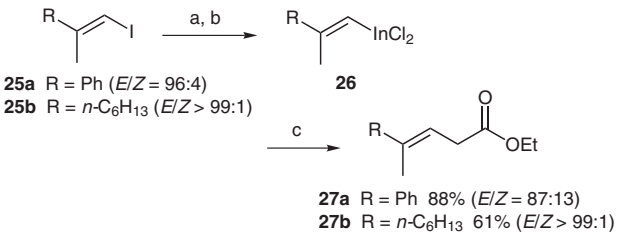
[a] All reactions were performed with R–X (1.0 mmol) and triethylborane (0.50 mmol).
[b] The reaction was performed with 10 mol% of V-70 in place of triethylborane at 45 °C (bath temperature).
[c] The expected product **10** was not observed at all, but 1,4-diphenyl-2-buten-1-one (**14**) was obtained.

## Radical Alkynylation of α-Iodo Ester with Alkynylindium Reagents

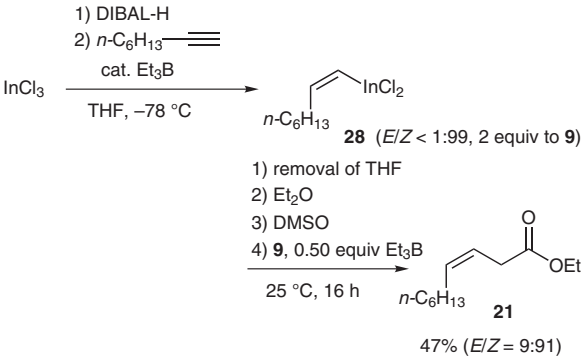
Radical alkynylation reactions with alkynylgallium have been reported.[33,34] Alkynylindium dichloride similarly serves as an alkynylation agent (Scheme 20).[35] An ethereal solution of lithium phenylacetylide (**29**) was added to $InCl_3$ to prepare phenylethynylindium dichloride. Ethyl iodoacetate (**9**) and 0.10 equivalent of V-70 were added sequentially. The resulting mixture was stirred for two hours at reflux. Extractive workup, followed by silica gel column purification, provided ethyl 4-phenyl-3-butynoate




**Scheme 17**

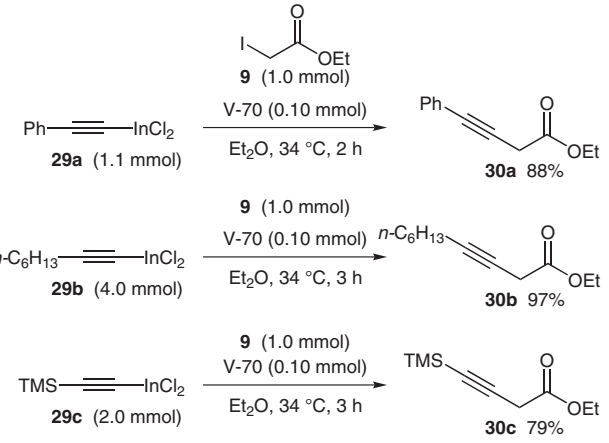



**Scheme 18** *Reagents:* (a) *t*-BuLi (2 equiv); (b) $InCl_3$; (c) **9**, 50 mol% $Et_3B$.




**Scheme 19**

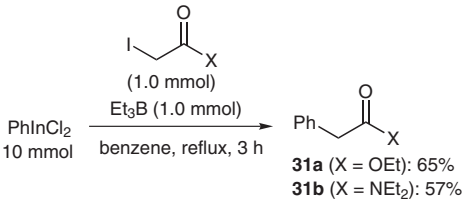
(**30a**) in 88% yield. Alkynylations with **29b** and **29c** were also facile. The reaction of **9** with **29a**, for three hours without radical initiator, afforded **30a** (6%) and recovered **9** (64%). TEMPO (0.10 equivalent) completely suppressed the reaction (66% recovery of **9**).




**Scheme 20**

## Radical Phenylation of α-Iodo Ester with Phenylindium Reagent

Phenylation via a radical chain process is quite challenging. Taking advantage of the high reactivity of organoindium reagents, we examined the intermolecular radical phenylation reaction with phenylindium dichloride. The phenylation was indeed successful, and treatment of ethyl iodoacetate with ten equivalents of phenylindium chloride in the presence of triethylborane in refluxing benzene afforded ethyl phenylacetate (**31a**) in good yield (Scheme 21). The large excess of reagent was essential to attain the high yield. For instance, use of two equivalents of the reagent gave **31a** in only 16% yield. α-Halo amide also underwent the phenylation. Triethylborane was indispensable in these reactions to obtain **31**. The mechanism can involve either a radical addition–indium-centered radical elimination sequence or single electron transfer from the electron-rich phenylindium species to the electron-deficient carbon-centered radical.




**Scheme 21**

## Conclusion

Allylgallium and allylindium reagents are found to be effective for the radical allylation of α-iodo or α-bromo carbonyl compounds in place of allylstannane. The addition of water as a co-solvent improved the yields of allylated products. The presented allylic metal reagents are readily prepared, and this allylation avoids the use of tin reagents that require prior preparation of the reagent and special treatment for its removal. Radical alkenylation of α-halo

carbonyl compounds with alkenylindiums provided a facile introduction of unactivated alkene moieties to α-halo carbonyl compounds via a radical process, which was difficult to carry out by previous radical alkenylation methods. During this alkenylation reaction, the stereochemistry of alkenylindiums was essentially retained. A combination of the alkenylation reaction with the hydroindation of alkynes highlights the significance of this radical alkenylation reaction. Alkynylindiums effected radical alkynylations of α-halo carbonyl compounds under mild conditions. The indium-based reaction allows for an intermolecular radical phenylation. These organoindium and organogallium reagents, which are readily prepared, highly reactive, and easily removable, can replace tin reagents for radical reactions of α-halo carbonyl compounds.

$^1$H NMR (300 MHz) and $^{13}$C NMR (75.3 MHz) spectra were taken on Varian GEMINI 300 and Mercury 300 spectrometers. $^1$H NMR and $^{13}$C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates coated with a 0.25-mm layer of Merck Silica gel 60$F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Benzene was dried over slices of sodium. $GaCl_3$ was purchased from Aldrich and was diluted in a glove box under argon to prepare 1.0 M hexane solution. Anhydrous $InCl_3$ was purchased from Aldrich Chemicals and was thoroughly dried in a reaction flask under reduced pressure (0.5 torr) by heating with a hair drier for 2 min before use. Neat $Et_3B$ and DIBAL-H were obtained from Aldrich and were diluted with dry hexane to prepare 1.0 M solutions. *t*-BuLi was purchased from Kanto Chemical Inc. as a pentane solution and stored in a refrigerator.

All reactions were performed in a reaction flask connected with a toy balloon that was filled out with argon. Oxygen molecules, which are indispensable for causing an initiation reaction with $Et_3B$, penetrate the balloon moderately.

Compounds **1** were commercially available or readily prepared from chloroacetyl chloride and the corresponding alcohol or amine. Treatment in $CH_2Cl_2$ in the presence of pyridine followed by NaI/acetone gave compounds **1** in more than 70% overall yields.

### Allylation with Allylgallium in Aqueous THF (Table 1, Entry 4); Typical Procedure

THF (2 mL) was mixed with a hexane solution of $GaCl_3$ (1.0 M, 1.5 mL, 1.5 mmol) under argon. Allylmagnesium chloride (1.0 M THF solution, 1.5 mL, 1.5 mmol) was added dropwise to the solution of $GaCl_3$ at 25 °C to give a white suspension. The suspension was stirred for 20 min at 25 °C, and then $H_2O$ (1 mL) was added to the suspension. The whole mixture turned clear although it was heterogeneous. A solution of benzyl iodoacetate (**1d**; 0.14 g, 0.50 mmol) in THF (2 mL), $Et_3B$ (1.0 M hexane solution, 0.25 mL, 0.25 mmol), and air (10 mL) were then successively added. After being vigorously stirred for 0.5 h, the mixture was poured into 1 M HCl solution, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over $Na_2SO_4$ and was concentrated in vacuo. Purification of the residual oil by silica gel column chromatography provided benzyl 4-pentenoate (**2a**; 85 mg, 0.45 mmol) in 89% yield.

### NMR Analysis of the Crotylgallium Reagents

Under an atmosphere of argon, a hexane solution of $GaCl_3$ (1.0 M, 1.0 mL, 1.0 mmol) was placed in a 20-mL reaction flask. THF (2 mL) was added. Crotylmagnesium chloride in THF (1.0 M, 1.0 mL, 1.0 mmol) was then added at ambient temperature. The mixture was stirred for 10 min. The solvent was removed in vacuo to obtain a white solid. THF-$d_8$ (2 mL) was added to the solid to give a white suspension. A part of the supernatant of the suspension (0.7 mL) was taken for NMR analysis under argon. The NMR analysis revealed vinylic proton signals at 5.15–5.40 (1 H, multiplet) and 5.60–5.78 ppm (1 H, multiplet). Two sets of two singlets were observed at 119.6, 130.9 (for major isomer) and 117.7, 130.0 ppm (for minor isomer) in the $^{13}$C NMR analysis. $H_2O$ (0.5 mL) was then added to the remaining solution of gallium reagent in the reaction flask; 20 min after the addition of $H_2O$, 0.7 mL of the upper layer of the suspension was again transferred to an NMR tube under inert atmosphere. Signals appeared at 5.22–5.38 (1 H, multiplet), 5.63–5.74 ppm (1 H, multiplet) in the $^1$H NMR and at 120.7, 130.2 (for major isomer) and 118.7, 129.3 ppm (for minor isomer) in the $^{13}$C NMR. These signals became smaller during continued measurements of the aqueous sample over 10 h.

### Allylation with Allylindium in Aqueous THF (Table 2, Entry 3); Typical Procedure

Dried $InCl_3$ (663 mg, 3.0 mmol) was dissolved in THF (2 mL) under argon. Allylmagnesium chloride (1.0 M THF solution, 3.0 mL, 3.0 mmol) was added dropwise to the solution at 25 °C to give a clear solution. The resulting solution was then stirred for 20 min at 25 °C. $H_2O$ (1 mL) was added to the solution to make the solution cloudy. A solution of benzyl iodoacetate (**1d**; 0.28 g, 1.0 mmol) in THF (2 mL), $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol), and air (10 mL) were then added successively. After being vigorously stirred for 30 min, the mixture was poured into 1 M HCl solution, and the product was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over $Na_2SO_4$ and was concentrated in vacuo. Purification of the residual oil on silica gel furnished benzyl 4-pentenoate (**2a**; 0.17 g, 0.89 mmol) in 89% yield.

### Allylation with Allylborane in THF (Scheme 6)

Under an argon atmosphere, trimethoxyborane (0.11 mL, 1.0 mmol) and THF (3 mL) were placed in a 20-mL reaction flask. Allylmagnesium chloride (0.92 M THF solution, 2.2 mL, 2.0 mmol) was added dropwise to the solution at 0 °C. The mixture was then stirred for 20 min at 25 °C. A solution of benzyl iodoacetate (**1d**; 0.14 g, 0.50 mmol) in THF (2 mL), $Et_3B$ (1.0 M hexane solution, 0.30 mL, 0.30 mmol), and air (10 mL) were then added successively at 0 °C. After being vigorously stirred for 2 h, $Et_3B$ (0.20 mmol) was added again and the mixture was stirred for an additional 3.5 h. The reaction was quenched with 1 M HCl (5 mL). Extractive work-up with EtOAc (3 × 20 mL) followed by silica gel column purification provided benzyl 4-pentenoate (**2a**; 70 mg, 0.37 mmol) in 74% yield.

9-Allyl-9-borabicyclo[3.3.1]nonane was prepared in situ from 9-bromo-9-borabicyclo[3.3.1]nonane and allylmagnesium chloride. Allylpinacolatoborane was prepared from isopropoxypinacolatoborane and the Grignard reagent.

### Radical Alkenylation of α-Halo Carbonyl Compounds with Alkenylindium Reagent (Scheme 9); General Procedure

A pentane solution of *t*-BuLi (1.5 M, 1.5 mL, 2.2 mmol) was added to a solution of β-bromostyrene (**7**; 211 mg, 1.15 mmol) in dry $Et_2O$ (6 mL) at –78 °C. The solution was immediately warmed to 25 °C. Stirring at the same temperature for 30 min changed the color to clear reddish yellow. Then, this solution was added to a stirred white suspension of $InCl_3$ (243 mg, 1.1 mmol) in dry $Et_2O$ (4 mL)

that was prepared beforehand in another reaction flask. After 30 min at 25 °C, ethyl iodoacetate (**9**; 214 mg, 1.0 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol) were added successively and the resulting mixture was stirred vigorously for 14 h. The reaction was quenched with 1.0 M HCl (10 mL) and extracted with hexane–EtOAc (10:1; 3 × 10 mL). The organic extracts were dried over $Na_2SO_4$ and concentrated in vacuo. Purification by silica gel using hexane–EtOAc (10:1) as eluant afforded ethyl 4-phenyl-3-butenoate (**10a**, *E*/*Z* = 90:10; 173 mg, 0.91 mmol) as a colorless oil.

**Radical Alkenylation with Alkenylindium: An Increased Amount of Styrylindium and Injection of Air (Scheme 9)**

According to the procedure mentioned above, β-styrylindium dichloride was prepared from β-bromostyrene (**7**; 284 mg, 1.55 mmol), *t*-BuLi (1.5 M pentane solution, 2.0 mL, 3.0 mmol) and dried $InCl_3$ (332 mg, 1.5 mmol) in $Et_2O$ (12 mL). At 25 °C, ethyl iodoacetate (**9**; 214 mg, 1.0 mmol), $Et_3B$ (1.0 M hexane solution, 0.30 mL, 0.30 mmol) and air (10 mL) were syringed into the reaction flask. The resulting mixture was stirred vigorously for 15 h. Extractive workup and purification as above gave ethyl 4-phenyl-3-butenoate (**10a**, *E*/*Z* = 90:10; 185 mg, 0.97 mmol).

**Radical Styrylation with β-Styrylstannane (Scheme 10)**

β-Styryllithium (1.1 mmol), prepared according to the above-mentioned method, was dropped into to $SnCl_4$ (287 mg, 1.1 mmol) at 25 °C. To the solution, ethyl iodoacetate (**9**; 214 mg, 1.0 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol) were added successively at 25 °C. After 12 h, the reaction was quenched with 1.0 M HCl (10 mL). The organic layer was extracted with hexane–EtOAc (10:1; 3 × 10 mL), dried over $Na_2SO_4$ and concentrated in vacuo. Silica gel column purification provided ethyl (*E*)-4-phenyl-3-butenoate (**10a**; 65 mg, 0.35 mmol).

**Radical Styrylation with β-Styrylgallium Dichloride (Scheme 10)**

An ethereal solution of β-styryllithium (1.1 mmol) prepared as above was dropped to $GaCl_3$ (1.0 M hexane solution, 1.1 mL, 1.1 mmol) at 25 °C. After 30 min, ethyl iodoacetate (**9**, 214 mg, 1.0 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol) were added and the reaction mixture was stirred for 13 h at the same temperature. The resulting mixture was hydrolyzed with 1.0 M HCl and was subjected to standard extraction and purification. As a consequence, the product 4-phenyl-3-butenoate (**10a**, *E*/*Z* = 98:2; 86 mg, 0.45 mmol) was obtained and starting ethyl iodoacetate (**9**; 1.5 mg, 0.070 mmol) was recovered.

**Reaction in the Presence of TEMPO (Scheme 12)**

β-Styrylindium dichloride (**8**) was prepared with β-bromostyrene (**7**; 211 mg, 1.15 mmol), *t*-BuLi (1.5 M pentane solution, 1.5 mL, 2.2 mmol) and dry $InCl_3$ (243 mg, 1.1 mmol) in $Et_2O$ (10 mL) as mentioned above. To the solution, TEMPO (94 mg, 0.60 mmol), ethyl iodoacetate (**9**; 241 mg, 1.0 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol) were sequentially added at 25 °C. After being stirred for 12 h, the resulting mixture was quenched with 1 M HCl (10 mL). Extraction with hexane–EtOAc (10:1, 3 × 10 mL) followed by silica gel column purification resulted in recovery of ethyl iodoacetate (**9**, 148 mg, 0.69 mmol). None of the desired product **10a** was obtained.

**Alkenyl Halide Starting Materials**

According to literature procedures, (*Z*)-β-bromostyrene [(*Z*)-**7**],[36] (*E*)-1-iodo-1-octene (**19**),[37] (*Z*)-1-iodo-1-dodecene (**22**),[23a] (*E*)-1-iodo-2-phenyl-1-propene (**25a**)[38] and (*E*)-1-iodo-2-methyl-1-octene (**25b**)[38] were prepared. The stereochemistry of these compounds was determined by comparison of $^1H$ NMR spectral data with the literature.

**Iodolysis of Alkenylindiums; General Procedure**

Preparation of styrylindium dichloride was carried out with β-bromostyrene (**7**, *E*/*Z* = 1:99; 183 mg, 1.0 mmol), *t*-BuLi (1.5 M pentane solution, 1.3 mL, 2.0 mmol) and dry $InCl_3$ (221 mg, 1.0 mmol) in $Et_2O$ (10 mL) according to the aforementioned method. After addition of $I_2$ (254 mg, 1.0 mmol) at 25 °C, the mixture was stirred for 30 min. To the resulting mixture, 1 M HCl (10 mL) and saturated sodium hydrogen sulfite (1.0 mL) were sequentially added. Extraction with hexane (3 × 10 mL) followed by silica gel column chromatography provided iodostyrene (*E*/*Z* = 1:99; 228 mg, 0.99 mmol).

**Hydroindation Followed by Radical Alkenylation (Scheme 19)**

To a solution of dry $InCl_3$ (454 mg, 2.05 mmol) in THF (8.0 mL), DIBAL-H (1.0 M hexane solution, 2.0 mL, 2.0 mmol) was added at –78 °C and the solution was stirred for 30 min. After addition of 1-octyne (231 mg, 2.1 mmol) and $Et_3B$ (1.0 M hexane solution, 0.40 mL, 0.40 mmol), the resulting mixture was stirred for 3 h at the same temperature. The solvent and volatile components were then removed under reduced pressure. $Et_2O$ (5.0 mL), DMSO (1.0 mL), ethyl iodoacetate (**9**; 214 mg, 1.0 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol) were added successively at ambient temperature. After being stirred for 16 h, the reaction was quenched with 1.0 M HCl (10 mL). The organic layer was extracted with hexane–EtOAc (10:1; 3 × 10 mL) was dried over $Na_2SO_4$ and concentrated in vacuo. Silica gel column purification provided ethyl 3-decenoate (**21**, *E*/*Z* = 9:91; 93 mg, 0.47 mmol).

**Radical Alkynylation of Ethyl Iodoacetate with Alkynylindium Reagents (Scheme 20)**

In $Et_2O$ (3.0 mL) at 25 °C, dried $InCl_3$ (243 mg, 1.1 mmol) was treated with 2-phenylethynyllithium [prepared from ethynylbenzene (112 mg, 1.1 mmol) and *n*-BuLi (1.6 M hexane solution, 0.69 mL, 1.1 mmol) in $Et_2O$ (3 mL) at 0 °C] and the resulting mixture was stirred for 30 min. After addition of ethyl iodoacetate (**9**; 214 mg, 1.0 mmol) and V-70 (31 mg, 0.10 mmol), the reaction mixture was stirred at reflux for 2 h. Quenching with 1.0 M HCl (10 mL) and processing as above afforded ethyl 4-phenyl-3-butynoate (**30a**; 166 mg, 0.88 mmol) as well as starting ethyl iodoacetate (**9**; 8.6 mg, 0.040 mmol).

**Radical Phenylation of Ethyl Iodoacetate with Phenylindium Dichloride (Scheme 21)**

Dry $InCl_3$ (1.11 g, 5.0 mmol) was treated with phenyllithium (1.0 M $Et_2O$–cyclohexane solution, 5.0 mL, 5.0 mmol) in $Et_2O$ (5 mL) at 25 °C. The solvent was exchanged to benzene (10 mL) by removal of $Et_2O$ under reduced pressure. After addition of ethyl iodoacetate (**9**; 107 mg, 0.50 mmol) and $Et_3B$ (1.0 M hexane solution, 0.50 mL, 0.50 mmol), the reaction mixture was refluxed in a preheated bath (90 °C) for 3 h. Aqueous workup followed by silica gel column purification furnished ethyl 2-phenylacetate (**31**; 54 mg, 0.33 mmol).

**Characterization Data**

Compounds **3**,[39] **10a**,[40] **10b**,[41] **10e**,[42] **10f**,[43] **10g**,[44] **14**,[45] **16**,[46] and **27a**[47] can be found in the literature.

***N*-[(*E*)-2-Tridecenyl]iodoacetamide (1f)**

Yield: 72%; off-white powder.

IR (nujol): 3450, 3082, 2964, 1728, 1641, 1416, 1279, 1246, 1175, 1115, 1063, 1020, 995, 972, 916, 829 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.90–6.14 (br s, 1 H), 5.64 (dt, *J* = 15.3, 6.6 Hz, 1 H), 5.41 (dt, *J* = 15.3, 6.6 Hz, 1 H), 3.81 (t, *J* = 6.0 Hz, 2 H), 3.68 (s, 2 H), 2.00 (dt, *J* = 6.9, 6.6 Hz, 2 H), 1.15–1.40 (m, 16 H), 0.85 (t, *J* = 6.6 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = –0.53, 14.00, 22.58, 28.97, 29.07, 29.24, 29.38, 29.51, 29.52, 31.82, 32.15, 42.30, 124.64, 134.75, 166.41.

Anal. Calcd for $C_{15}H_{28}INO$: C, 49.32; H, 7.73%. Found: C, 49.61; H, 7.69%.

**6-Chlorohexyl Iodoacetate (1h)**
Yield: 73%; colorless oil.

IR (neat): 3049, 2937, 2860, 1732, 1462, 1416, 1383, 1267, 1140, 1092, 1047, 986, 893, 837, 729, 650 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 4.11 (t, *J* = 6.6 Hz, 2 H), 3.66 (s, 2 H), 3.51 (t, *J* = 6.6 Hz, 2 H), 1.49–1.81 (m, 4 H), 1.32–1.48 (m, 4 H).

$^{13}C$ NMR ($CDCl_3$): δ = –5.57, 24.98, 26.31, 28.08, 32.28, 44.83, 65.88, 169.02.

Anal. Calcd for $C_8H_{14}ClIO_2$: C, 31.55; H, 4.63%. Found: C, 31.47; H, 4.60%.

**1-Phenyl-3-butenyl Iodoacetate (1j)**
Yield: 84%; colorless oil.

IR (neat): 3445, 3064, 3034, 2977, 2941, 1732, 1643, 1495, 1454, 1416, 1265, 1203, 1088, 1029, 980, 922, 762, 700 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 7.25–7.37 (m, 5 H), 5.61–5.81 (m, 2 H), 5.05–5.12 (m, 2 H), 3.68 (s, 2 H), 2.52–2.72 (m, 2 H).

$^{13}C$ NMR ($CDCl_3$): δ = –5.32, 40.40, 76.88, 118.56, 126.63, 128.30, 128.56, 132.89, 139.27, 167.97.

Anal. Calcd for $C_{12}H_{13}IO_2$: C, 45.59; H, 4.03%. Found: C, 45.29; H, 4.14%.

**2-Oxo-1-propylpentyl Iodoacetate (1k)**
Yield: 70%; colorless oil.

IR (neat): 3051, 2963, 2936, 2876, 1740, 1732, 1464, 1416, 1381, 1265, 1100, 1090, 1018, 970, 935, 891, 743 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 4.96 (dd, *J* = 7.8, 4.8 Hz, 1 H), 3.75 (d, *J* = 9.9 Hz, 1 H), 3.69 (d, *J* = 9.9 Hz, 1 H), 2.28–2.50 (m, 2 H), 1.50–1.78 (m, 4 H), 1.31–1.46 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = –6.48, 13.43, 13.44, 16.38, 18.30, 32.17, 40.37, 79.51, 168.42, 206.89.

HRMS: *m/z* calcd for $C_{10}H_{17}IO_3$: 312.0222; found: 312.0215.

**2,*N*,*N*-Trimethyl-4-pentenamide (2c)**
Colorless oil.

IR (neat): 3470, 3076, 2972, 2934, 1643, 1495, 1462, 1398, 1373, 1135, 1259, 1167, 1101, 1059, 997, 914, 739 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.67–5.82 (m, 1 H), 5.03 (d, *J* = 16.8 Hz, 1 H), 4.98 (d, *J* = 11.1 Hz, 1 H), 3.03 (s, 3 H), 2.93 (s, 3 H), 2.71–2.79 (m, 1 H), 2.35–2.45 (m, 1 H), 2.04–2.14 (m, 1 H), 1.09 (d, *J* = 6.9 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 16.93, 35.50, 35.61, 37.16, 38.04, 116.49, 136.32, 176.19.

HRMS: *m/z* calcd for $C_8H_{15}NO$: 141.1154; found: 141.1147.

***N*-[(*E*)-2-Tridecenyl]-4-pentenamide (2f)**
White solid.

IR (nujol): 3287, 3080, 1634, 1558, 1310, 1261, 1229, 964, 910, 802 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.74–5.88 (m, 1 H), 5.58 (dt, *J* = 15.0, 6.9 Hz, 1 H), 5.35–5.45 (m, 2 H), 5.05 (d, *J* = 17.1 Hz, 1 H), 4.99 (d, *J* = 10.2 Hz, 1 H), 3.79 (t, *J* = 6.0 Hz, 2 H), 2.34–2.44 (m, 2 H), 2.15–2.27 (m, 2 H), 1.94–2.01 (m, 2 H), 1.20–1.38 (m, 16 H), 0.85 (t, *J* = 6.9 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 14.11, 22.67, 29.11, 29.16, 29.33, 29.47, 29.59, 29.60, 29.61, 31.89, 32.21, 35.91, 41.45, 115.55, 125.50, 134.03, 137.10, 171.84.

HRMS: *m/z* calcd for $C_{18}H_{33}NO$: 279.2562; found: 279.2567.

**(*E*)-2-Hexenyl 4-Pentenoate (2g)**
Colorless oil.

IR (neat): 3080, 2980, 2932, 2874, 1760, 1737, 1674, 1641, 1447, 1421, 1379, 1350, 1238, 1169, 1101, 1024, 972, 916, 827, 784, 739, 700 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.68–5.86 (m, 2 H), 5.53 (dt, *J* = 15.3, 6.6 Hz, 1 H), 5.03 (d, *J* = 17.1 Hz, 1 H), 4.97 (d, *J* = 10.2 Hz, 1 H), 4.49 (d, *J* = 6.6 Hz, 2 H), 2.30–2.42 (m, 4 H), 2.00 (dt, *J* = 6.9, 6.9 Hz, 2 H), 1.28–1.44 (m, 2 H), 0.87 (t, *J* = 7.2 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 13.47, 21.90, 28.75, 33.46, 34.19, 65.16, 115.49, 124.01, 136.43, 136.77, 172.97.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%. Found: C, 72.29; H, 10.16%.

**6-Chlorohexyl 4-Pentenoate (2h)**
Colorless oil.

IR (neat): 3080, 2937, 2862, 1738, 1641, 1447, 1390, 1352, 1256, 1175, 1105, 997, 916, 731, 650 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.72–5.87 (m, 1 H), 4.94–5.08 (m, 2 H), 4.05 (t, *J* = 6.6 Hz, 2 H), 3.51 (t, *J* = 6.6 Hz, 2 H), 2.29–2.42 (m, 4 H), 1.70–1.80 (m, 2 H), 1.56–1.66 (m, 2 H), 1.29–1.49 (m, 4 H).

$^{13}C$ NMR ($CDCl_3$): δ = 25.15, 26.36, 28.36, 28.77, 32.32, 33.44, 44.83, 64.20, 115.49, 136.78, 173.26.

Anal. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76%. Found: C, 60.12; H, 8.84%.

**3-Oxa-5-hexenyl 4-Pentenoate (2i)**
Colorless oil.

IR (neat): 3080, 2932, 2862, 1738, 1641, 1421, 1346, 1254, 1177, 1119, 1060, 997, 920, 860, 787 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.73–5.95 (m, 2 H), 5.26 (d, *J* = 17.1 Hz, 1 H), 5.18 (d, *J* = 10.5 Hz, 1 H), 5.03 (d, *J* = 17.1 Hz, 1 H), 4.97 (d, *J* = 10.2 Hz, 1 H), 4.21 (t, *J* = 4.8 Hz, 2 H), 4.00 (d, *J* = 8.7 Hz, 2 H), 3.61 (t, *J* = 4.8 Hz, 2 H), 2.30–2.46 (m, 4 H).

$^{13}C$ NMR ($CDCl_3$): δ = 28.71, 33.33, 63.51, 67.87, 72.08, 115.55, 117.42, 134.48, 136.72, 173.18.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%. Found: C, 65.47; H, 8.95%.

**1-Phenyl-3-butenyl 4-Pentenoate (2j)**
Colorless oil.

IR (neat): 3078, 3034, 2930, 2858, 1738, 1643, 1605, 1587, 1495, 1418, 1373, 1240, 1167, 1115, 1028, 997, 918, 856, 787, 760, 700 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 7.24–7.36 (m, 5 H), 5.61–5.86 (m, 3 H), 4.94–5.10 (m, 4 H), 2.30–2.44 (m, 4 H), 2.45–2.69 (m, 2 H).

$^{13}C$ NMR ($CDCl_3$): δ = 28.74, 33.63, 40.70, 75.06, 115.52, 118.07, 126.60, 127.99, 128.47, 133.42, 136.72, 140.20, 172.34.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%. Found: C, 78.10; H, 8.02%.

**2-Oxo-1-propylpentyl 4-Pentenoate (2k)**
Colorless oil.

IR (neat): 3080, 2963, 2936, 2876, 1740, 1732, 1641, 1466, 1418, 1379, 1248, 1171, 1115, 1067, 1026, 999, 966, 916, 843, 789, 743, 700 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.74–5.89 (m, 1 H), 4.95–5.09 (m, 3 H), 2.28–2.51 (m, 6 H), 1.52–1.71 (m, 4 H), 1.30–1.45 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 13.53, 13.54, 16.49, 18.49, 28.63, 32.32, 33.14, 40.42, 78.19, 115.68, 136.56, 172.82, 207.68.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80%. Found: C, 69.11; H, 10.08%.

**Benzyl 3-Methyl-4-pentenoate (2a′)**
Colorless oil.

IR (neat): 3069, 3034, 2963, 2932, 2874, 1738, 1641, 1499, 1456, 1418, 1379, 1352, 1171, 1103, 997, 916, 739, 698 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 7.26–7.37 (m, 5 H), 5.75 (ddd, *J* = 7.2, 10.5, 17.1 Hz, 1 H), 5.10 (s, 2 H), 4.98 (d, *J* = 17.1 Hz, 1 H), 4.93 (d, *J* = 10.5 Hz, 1 H), 2.64–2.74 (m, 1 H), 2.26–2.44 (m, 2 H), 1.03 (d, *J* = 6.9 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 19.60, 34.35, 41.20, 66.11, 113.48, 128.27, 128.33, 128.60, 136.09, 142.47, 172.49.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%. Found: C, 76.23; H, 8.02%.

**2,3,*N*,*N*-Tetramethyl-4-pentenamide (2c′)**
2:1 mixture of diastereomers; colorless oil.

IR (neat): 3377, 3078, 2970, 2934, 2875, 1628, 1504, 1462, 1421, 1404, 1373, 1259, 1128, 1060, 1001, 968, 916, 827, 781, 750 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.55–5.80 (m, 1 H), 4.89–5.07 (m, 2 H), 3.06 (s, 0.67 × 3 H), 3.02 (s, 0.33 × 3 H), 2.97 (s, 0.67 × 3 H), 2.94 (s, 0.33 × 3 H), 2.36–2.66 (m, 2 H), 1.07 (d, *J* = 6.6 Hz, 0.33 × 3 H), 1.03 (d, *J* = 6.6 Hz, 0.67 × 3 H), 1.00 (d, *J* = 6.6 Hz, 0.33 × 3 H), 0.93 (d, *J* = 6.6 Hz, 0.67 × 3 H).

$^{13}C$ NMR ($CDCl_3$): For major isomer: δ = 15.78, 18.84, 35.68, 37.49, 40.66, 41.68, 115.05, 141.72, 176.58; for minor isomer, δ = 14.29, 15.98, 35.67, 37.47, 40.11, 40.67, 113.88, 142.18, 176.61.

HRMS: *m/z* calcd for $C_9H_{17}NO$: 155.1310; found: 155.1308.

***N*-[(*E*)-2-Tridecenyl]-3-methyl-4-pentenamide (2f′)**
White solid.

IR (nujol): 3285, 3080, 2681, 1643, 1551, 1310, 1250, 1207, 993, 966, 912 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.75 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 5.58 (dt, *J* = 15.3, 6.6 Hz, 1 H), 5.34–5.50 (m, 2 H), 5.01 (d, *J* = 17.1 Hz, 1 H), 4.94 (d, *J* = 10.2 Hz, 1 H), 3.78 (t, *J* = 6.0 Hz, 2 H), 2.62–2.72 (m, 1 H), 2.04–2.23 (m, 2 H), 1.97 (dt, *J* = 6.6, 6.6 Hz, 2 H), 1.20–1.38 (m, 16 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 0.85 (t, *J* = 6.9 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 13.98, 19.53, 22.56, 29.02, 29.05, 29.23, 29.37, 29.50, 29.51, 31.80, 32.11, 34.67, 41.34, 43.80, 113.50, 125.63, 134.04, 142.95, 171.53.

HRMS: *m/z* calcd for $C_{19}H_{35}NO$: 293.2719; found: 293.2718.

**6-Chlorohexyl 3-Methyl-4-pentenoate (2h′)**
Colorless oil.

IR (neat): 3080, 2935, 2862, 1737, 1641, 1456, 1417, 1354, 1252, 1177, 1090, 1049, 995, 916, 880, 731 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 5.74 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 4.99 (d, *J* = 17.1 Hz, 1 H), 4.92 (d, *J* = 10.2 Hz, 1 H), 4.04 (t, *J* = 6.6 Hz, 2 H), 3.50 (t, *J* = 6.6 Hz, 2 H), 2.58–2.74 (m, 1 H), 2.18–2.36 (m, 2 H), 1.70–1.80 (m, 2 H), 1.55–1.66 (m, 2 H), 1.28–1.49 (m, 4 H), 1.02 (d, *J* = 6.9 Hz, 3 H).

$^{13}C$ NMR ($CDCl_3$): δ = 19.59, 25.16, 26.36, 28.39, 32.34, 34.33, 41.25, 44.81, 64.09, 113.33, 142.57, 172.68.

Anal. Calcd for $C_{12}H_{21}ClO_2$: C, 61.93; H, 9.09%. Found: C, 61.92; H, 9.32%.

**Benzyl (2,2-Dimethylcyclopropyl)acetate (4)**
Colorless oil.

IR (neat): 3065, 3034, 2949, 2870, 2737, 1738, 1647, 1499, 1456, 1418, 1377, 1327, 1250, 1165, 1120, 1094, 1051, 1005, 918, 866, 748, 698 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 7.26–7.38 (m, 5 H), 5.12 (s, 2 H), 2.35 (d, *J* = 7.2 Hz, 2 H), 1.03 (s, 3 H), 1.00 (s, 3 H), 0.82–0.90 (m, 1 H), 0.49 (dd, *J* = 4.8, 7.8 Hz, 1 H), 0.01 (dd, *J* = 4.8, 4.8 Hz, 1 H).

$^{13}C$ NMR ($CDCl_3$): δ = 15.24, 19.36, 19.78, 19.89, 26.88, 34.85, 66.07, 128.18, 128.20, 128.59, 136.26, 173.67.

HRMS: *m/z* calcd for $C_{14}H_{18}O_2$: 218.1307; found: 218.1315.

**Benzyl 4-Methyl-4-pentenoate (6)**
Colorless oil.

IR (neat): 2936, 1738, 1649, 1456, 1153, 891, 737, 698 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.73 (s, 3 H), 2.35 (t, *J* = 7.5 Hz, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 4.68 (s, 1 H), 4.74 (s, 1 H), 5.12 (s, 2 H), 7.31–7.38 (m, 5 H).

$^{13}C$ NMR ($CDCl_3$): δ = 22.46, 32.53, 32.61, 60.20, 110.40, 128.17, 128.19, 128.50, 135.96, 143.96, 173.07.

HRMS: *m/z* calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1152.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%. Found: C, 76.29; H, 8.07%.

**Benzyl 2-Methyl-4-phenyl-3-butenoate (10c)**
*E*/*Z* = 90:10; colorless oil.

IR (neat): 3030, 2934, 1732, 1600, 1497, 1165, 964, 746, 694 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.31 (d, *J* = 7.2 Hz, 0.10 × 3 H), 1.38 (d, *J* = 7.2 Hz, 0.90 × 3 H), 3.37 (dq, *J* = 7.8, 7.8 Hz, 1 H), 5.15 (s, 2 H), 5.71 (dd, *J* = 7.8, 11.7 Hz, 0.10 H), 6.29 (dd, *J* = 7.8, 15.9 Hz, 0.90 H), 6.48 (d, *J* = 15.9 Hz, 0.90 H), 6.56 (d, *J* = 11.7 Hz, 0.10 H), 7.19–7.39 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): For major isomer: δ = 17.37, 43.10, 66.26, 126.08, 127.29, 127.79, 127.92, 128.29 (2C), 128.33, 131.04, 135.77, 136.57, 173.87.

HRMS: *m/z* calcd for $C_{18}H_{18}O_2$: 266.1307; found: 266.1320.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. Found: C, 80.95; H, 7.00%.

**2-[(*E*)-2-Phenylethenyl]-4-butanolide [(*E*)-10d]**
Pale-yellow powder.

IR (nujol): 2932, 2858, 1747, 1261, 1180, 1032 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.23–2.37 (m, 1 H), 2.51 (m, 1 H), 3.38–3.48 (m, 1 H), 4.30 (ddd, *J* = 6.6, 9.0, 9.0 Hz, 1 H), 4.44 (ddd, *J* = 3.3, 9.0, 9.0 Hz, 1 H), 6.26 (dd, *J* = 6.3, 15.9 Hz, 1 H), 6.58 (d, *J* = 15.9 Hz, 1 H), 7.20–7.40 (m, 5 H).

$^{13}C$ NMR ($CDCl_3$): δ = 29.23, 42.45, 66.67, 123.80, 126.30, 127.82, 128.49, 133.30, 136.13, 176.99.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. Found: C, 76.27; H, 6.47%.

**2-[(*Z*)-2-Phenylethenyl]-4-butanolide [(*Z*)-10d]**
Pale-yellow powder.

IR (nujol): 2926, 1755, 1600, 1448, 1377, 1159, 1020, 970, 952, 750, 694 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.11–2.24 (m, 1 H), 2.39–2.49 (m, 1 H), 3.74 (ddd, *J* = 9.3, 9.3, 9.3 Hz, 1 H), 4.22 (m, 1 H), 4.38–4.46 (m, 1 H), 5.58 (dd, *J* = 9.3, 11.1 Hz, 1 H), 6.82 (d, *J* = 11.1 Hz, 1 H), 7.26–7.42 (m, 5 H).

$^{13}$C NMR ($CDCl_3$): δ = 30.78, 39.45, 66.60, 126.02, 127.52, 128.33, 128.40, 134.29, 136.01, 177.56.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. Found: C, 76.17; H, 6.50%.

**2,*N*,*N*-Trimethyl-4-phenyl-3-butenamide (10h)**
*E*/*Z* = 95:5; pale-yellow oil.

IR (neat): 2932, 1634, 1495, 1375, 1138, 1059, 965 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.32 (d, *J* = 6.9 Hz, 0.95 × 3 H), 1.34 (d, *J* = 6.9 Hz, 0.05 × 3 H), 2.98 (br s, 3 H), 3.08 (br s, 3 H), 3.55 (dq, *J* = 8.1, 6.9 Hz, 1 H), 5.73 (dd, *J* = 8.1, 11.1 Hz, 0.05 H), 6.28 (dd, *J* = 8.1, 15.9 Hz, 0.95 H), 6.42 (d, *J* = 15.9 Hz, 0.95 H), 6.53 (d, *J* = 11.1 Hz, 0.05 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.36 (d, *J* = 7.5 Hz, 2 H).

$^{13}$C NMR ($CDCl_3$): δ = 18.31, 35.75, 37.10, 40.22, 125.96, 127.18, 128.28, 129.94, 130.25, 136.67, 173.49.

HRMS: *m*/*z* calcd for $C_{13}H_{17}NO$: 203.1311; found: 203.1320.

**Benzyl 4-Methyl-3-pentenoate (18)**
Colorless oil.

IR (neat): 3034, 2930, 1738, 1456, 1377, 1312, 1153, 737, 696 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.63 (s, 3 H), 1.75 (s, 3 H), 3.09 (d, *J* = 7.2 Hz, 2 H), 5.12 (s, 2 H), 5.33 (t, *J* = 7.2 Hz, 1 H), 7.31–7.41 (m, 5 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.97, 25.61, 33.75, 66.17, 115.55, 127.94 (2C), 128.31, 135.41, 135.83, 171.91.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%. Found: C, 76.17; H, 7.80%.

**Ethyl 3-Decenoate (21)**
*E*/*Z* = 88:12; colorless oil.

IR (neat): 2928, 2856, 1740, 1466, 1369, 1250, 1159, 1032, 968 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.22–1.45 (m, 11 H), 2.03 (dt, *J* = 6.9, 5.4 Hz, 2 H), 3.02 (d, *J* = 5.4 Hz, 0.88 × 2 H), 3.08 (d, *J* = 5.4 Hz, 0.12 × 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 5.46–5.61 (m, 2 H).

$^{13}$C NMR ($CDCl_3$): For major isomer: δ = 14.13, 14.25, 22.66, 28.84, 29.16, 31.74, 32.51, 38.19, 60.44, 121.40, 134.65, 171.99.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%. Found: C, 72.74; H, 11.27%.

**Ethyl 3-Tetradecenoate (24)**
*E*/*Z* = 8:92; colorless oil.

IR (neat): 2926, 2855, 1742, 1466, 1367, 1323, 1252, 1163, 1036 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.22–1.40 (m, 19 H), 2.03 (q, *J* = 6.6 Hz, 2 H), 3.01 (d, *J* = 5.7 Hz, 0.08 × 2 H), 3.08 (d, *J* = 5.7 Hz, 0.92 × 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 5.49–5.63 (m, 2 H).

$^{13}$C NMR ($CDCl_3$): For major isomer: δ = 14.22, 14.30, 22.77, 27.49, 29.32, 29.41 (2C), 29.59, 29.69 (2C), 31.98, 33.10, 60.58, 120.68, 133.38, 171.89.

Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89%. Found: C, 75.24; H, 12.19%.

**Ethyl (*E*)-4-Methyl-3-decenoate (27b)**
Colorless oil.

IR (neat): 2930, 2858, 1740, 1466, 1369, 1315, 1258, 1159, 1034 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.24–1.33 (m, 6 H), 1.34–1.45 (m, 2 H), 1.62 (s, 3 H), 2.02 (t, *J* = 7.2 Hz, 2 H), 3.03 (d, *J* = 6.9 Hz, 2 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 5.31 (t, *J* = 6.9 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$): δ = 14.20, 14.32, 16.33, 22.71, 27.78, 28.98, 31.81, 33.85, 39.57, 60.41, 115.37, 139.14, 172.24.

HRMS: *m*/*z* calcd for $C_{13}H_{24}O_2$: 212.1777; found: 212.1778.

**Ethyl 4-Phenyl-3-butynoate (30a)**
Colorless oil.

IR (neat): 2984, 1746, 1599, 1491, 1369, 1263, 1185, 1034, 758, 692, 530 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.31 (t, *J* = 7.2 Hz, 3 H), 3.50 (s, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 7.26–7.34 (m, 3 H), 7.42–7.48 (m, 2 H).

$^{13}$C NMR ($CDCl_3$): δ = 14.26, 26.85, 61.66, 81.17, 83.38, 122.84, 128.02, 128.05, 131.59, 167.99.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. Found: C, 76.30; H, 6.46%.

**Ethyl 3-Decynoate (30b)**
Colorless oil.

IR (neat): 2930, 1755, 1456, 1377, 1153, 1020, 970, 748, 694 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3 H), 1.23–1.35 (m, 7 H), 1.38 (quint, *J* = 6.9 Hz, 2 H), 1.50 (quint, *J* = 6.9 Hz, 2 H), 2.19 (tt, *J* = 2.4, 6.9 Hz, 2 H), 3.24 (t, *J* = 2.4 Hz, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H).

$^{13}$C NMR ($CDCl_3$): δ = 14.13, 14.19, 18.84, 22.62, 26.17, 28.57, 28.71, 31.40, 61.38, 71.39, 83.83, 168.81.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. Found: C, 73.21; H, 10.53%.

**Ethyl 4-Trimethylsilyl-3-butynoate (30c)**
Colorless oil.

IR (neat): 2963, 2903, 2187, 1747, 1369, 1252, 1165, 1051, 845, 762, 700, 644 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.18 (s, 9 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 3.31 (s, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H).

$^{13}$C NMR ($CDCl_3$): δ = –0.03, 14.14, 27.22, 61.57, 88.30, 97.41, 167.77.

Anal. Calcd for $C_9H_{16}SiO_2$: C, 58.65; H, 8.75%. Found: C, 58.55; H, 8.81%.

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