Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 64 (2008) 2642–2650
www.elsevier.com/locate/tet

Radical reactions initiated by the photochemical cleavage of carbon–indium bonds of organoindium compounds

Tsunehisa Hirashita*, Ayumi Hayashi, Makoto Tsuji, Jiro Tanaka, Shuki Araki

Omohi College, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Received 15 November 2007; received in revised form 21 December 2007; accepted 2 January 2008
Available online 6 January 2008

Abstract

Intra- and intermolecular reactions of carbon-centered radicals generated by photolysis of organoindium compounds were examined. The photolysis of vinylindium compounds and indium acetylides provided vinyl and alkynyl radicals, respectively, which were trapped with ethyl iodoacetate giving the corresponding β,γ-unsaturated esters. Allylic indium compounds, prepared from 8-bromo- or 8-iodooct-1,6-dienes and powdered indium metal, underwent an intramolecular radical cyclization to afford the 5-*exo-trig* product.

1. Introduction

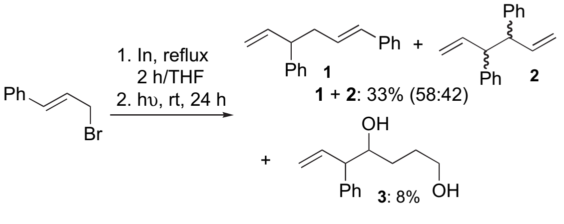
Organoindium compounds have hitherto been developed as mild nucleophilic reagents in organic synthesis.[1] Addition to carbonyl compounds and imines is a typical reaction of allylindium reagents, giving the corresponding homoallylic alcohols and amines, respectively. Alkynes,[2] allenes,[3] and cyclopropenes[4] also undergo allylindation to afford allylated products, where a suitably introduced hydroxy group exerts significant effects on both acceleration and stereoselectivity of the allylation. However, an addition to carbon–carbon double bonds without a proper activation, such as substitution by electron-withdrawing groups[5] or introduction of a hydroxy group adjacent to the double bond,[6] has not been attained owing to the low nucleophilicity of organoindium compounds. Recently, indium-mediated radical reactions have been reported, involving single electron transfer (SET) reactions caused by metallic indium or reactions of organoindium reagents with organic radicals.[7] Although photolysis of organoindium compounds leading to organic radicals is documented for porphyrin–indium complexes,[8] photochemical synthetic reactions dealing with organoindium compounds remains unexplored. Here we report a generation of organic radicals by a photolytic cleavage of carbon–indium bonds in organoindium compounds and subsequent intra- and intermolecular additions to carbon–carbon double bonds.[9]

2. Results and discussion

2.1. Photochemical intermolecular reaction of organoindium compounds

2.1.1. Allylic and benzylindium

Cinnamylindium sesquibromide, prepared from cinnamyl bromide and indium, was irradiated with a high-pressure mercury lamp (100 W, Pyrex filter) in THF, leading to a formation of dimers **1** and **2** as the major products (Eq. 1). A small amount of diol **3** (8%), which was coupled with THF, was also isolated. Similarly, the irradiation of benzylindium sesquiiodide gave 1,2-diphenylethane (**4**) in 64% yield (Eq. 2).



(1)

---

* Corresponding author. Tel./fax: +81 52 735 5206.
E-mail address: hirasita@nitech.ac.jp (T. Hirashita).

0040-4020/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.01.013

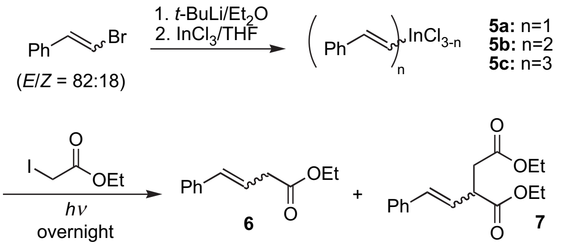
$$\mathrm{PhCH_2I} \xrightarrow[\text{2. h}\nu\text{, rt, 20 h}]{\text{1. In, rt, 2 h/DMF}} \underset{\mathbf{4}\text{: 64\%}}{\mathrm{PhCH_2CH_2Ph}} \qquad (2)$$

2.1.2. Vinylindium

We turned our attention on reactions of vinyl radicals generated from a homolytic cleavage of vinylindium compounds by irradiation. Styrylindium was a choice of vinylindium compounds. Lithiation of β-bromostyrene with *t*-BuLi at −78 °C followed by an addition of $InCl_3$ gave styrylindium **5a–c** depending on the amount of $InCl_3$.[7g]

The photochemical reaction of **5a** with ethyl iodoacetate at the stoichiometric molar ratio gave **6** in 56% yield with *E*/*Z* ratio 86:14 (Table 1, entry 1). The yield of **6** was decreased by shortening the irradiation time (entries 2 and 3). These facts imply that the cleavage of the C–In bond by irradiation is the rate-determining step for this reaction, although the radical chain mechanism cannot be excluded. The Et_3B/O_2-induced radical reaction of stylylindium dichloride with ethyl iodoacetate has been reported,[7f] where the geometry of stylyl bromide (*E*/*Z*=1:99) was retained during the lithiation–transmetallation process; however, the radical reaction of ethyl iodoacetate gave **6** in 93% yield as a mixture of geometric isomers (*E*/*Z*=35:65). These results indicate that the partial isomerization (approximately 30%) occurred through the radical chain process. We performed the photo-induced reaction of **5a** using *Z*-enriched stylyl bromide (*E*/*Z*=8:92), which resulted in a formation of **6** in 83% yield with *E*/*Z* ratio 56:44 (entry 4). The formation of *E*-enriched **6** from *Z*-enriched **5a**, even though there is a possibility that the isomerization of *Z* to *E* occurs under the irradiation conditions, can be rationalized by assuming that the reaction proceeds via stylyl radical. The reaction of **5b** gave **6** in lower yield along with compound **7**, which is derived from the reaction of an enolate generated from **6** with ethyl iodoacetate. Stylylindium **5c** brought a further erosion of the yields (entries 7 and 8). Although the precise mechanism underlying the radical reactions remains unclear at this stage, large decreases in the yields with increasing the number of the organic groups on the indium atom were also observed in the radical reactions of organoindium compounds initiated by Et_3B.[7g]

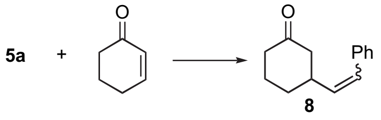
Table 1
Photochemical reaction of styrylindium compounds **5a–c** with ethyl iodoacetate[a]



Entry	5	5/ICH_2CO_2Et	Yield (%)	
			6 (*E*/*Z*)[b]	**7** (*E*/*Z*)[b]
1	**5a**	1:1	56 (86:14)	0
2	**5a**	2:1	68 (85:15)	0
3[c]	**5a**	2:1	39 (91:9)	0
4	**5a**[d]	2:1	83 (56:44)	0
5	**5b**	1:1	32 (86:14)	12 (97:3)
6	**5b**	2:1	29 (100:0)	19 (92:8)
7	**5c**	1:1	18 (87:13)	0
8	**5c**	2:1	Complex mixture	

[a] Styrylindium compounds and ethyl iodoacetate were irradiated overnight.
[b] Determined by ^1H NMR.
[c] Irradiation time was 2.5 h.
[d] Derived from β-bromostyrene (*E*/*Z*=8:92).

Table 2
Photochemical reaction of styrylindium **5a** with 2-cyclohexenone[a]



Entry	Conditions	Yield (%) (*E*/*Z*)[b]
1	rt, CH_3CN	No reaction
2	Reflux, THF	No reaction
3	*hν*, THF	25 (43:57)
4	*hν*, CH_3CN	35 (37:63)

[a] All reactions were performed overnight with styrylindium (2.0 mmol) and 2-cyclohexenone (1.0 mmol).
[b] Determined by ^1H NMR.

Next, photochemical reactions of styrylindium **5a** with 2-cyclohexenone were examined. The dark reaction of **5a** with 2-cyclohexenone at room temperature or under reflux in THF yielded no coupling product (Table 2, entries 1 and 2), while under the irradiation conditions, the adduct **8** was obtained in 25% yield (entry 3). The reaction in acetonitrile gave better results (entry 4). These facts clearly show that the cleavage of the C_{sp^2}–In bond occurred not by pyrolysis but photolysis. In contrast to the reaction of ethyl iodoacetate, the major geometry of **8** was *Z*. To confirm the isomerization of *E*-**8** to *Z*-**8** during the irradiation, **8** (*E*/*Z*=63:37) was irradiated in acetonitrile for 15 h, which gave *Z*-enriched **8** (*E*/*Z*=33:67) quantitatively.

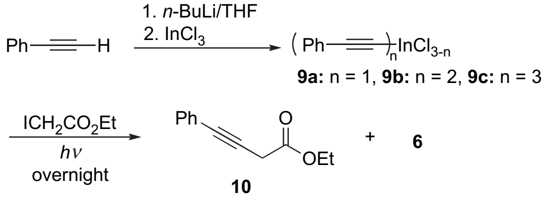
2.1.3. Indium acetylide

Photochemical cleavage of a C_{sp}–In bond was examined with (phenylethynyl)indium **9a–c**. Lithiation of phenylacetylene with *n*-BuLi, followed by transmetallation with $InCl_3$ gave a series of (phenylethynyl)indium compounds **9a–c** according to the amount of $InCl_3$ employed. The solution of **9** was irradiated in the presence of ethyl iodoacetate at room temperature. The results are summarized in Table 3. (Phenylethynyl)indium dichloride **9a** gave a coupling product **10** in 52% yield and a small amount of **6** (Table 3, entry 1). A better yield was obtained by increasing the amount of **9a** (entry 2). Diorganoindium **9b** afforded **10** in 31% yield along with **6** (entry 3). When the ratio of **9b** was increased or triorganoindium **9c** was employed, the reactions gave complicated mixtures (entries 4–6).

2.2. Photochemical intramolecular reaction of organoindium compounds

The difficulty observed in the intermolecular radical attack toward a C–C double bond prompted us to examine the

Table 3
Photochemical reaction of indium acetylide **9a–c** with ethyl iodoacetate[a]



Entry	9	9:ICH$_2$CO$_2$Et	Yield (%)	
			10	**6**
1	**9a**	2:1	52	2
2	**9a**	3:1	73	0
3	**9b**	1:1	31	11[b]
4	**9b**	2:1	Complex mixture	
5	**9c**	1:1	Complex mixture	
6	**9c**	2:1	Complex mixture	

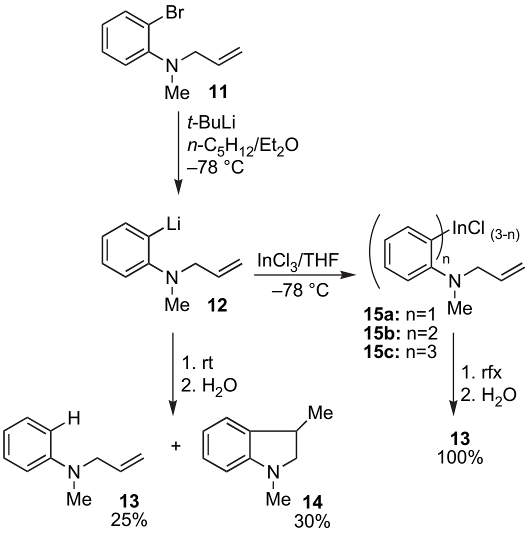
[a] Alkynylindium compounds and ethyl iodoacetate were irradiated overnight.

[b] E/Z=22:78.

photo-induced intramolecular cyclizations of organoindium compounds.

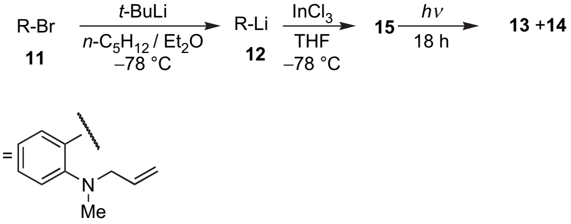
2.2.1. Arylindium

Phenyllithium **12** was prepared from phenyl bromide **11** with *t*-BuLi at −78 °C. When the solution of **12** was allowed to warm to room temperature, the debrominated product **13** and the cyclization product **14** were obtained in low yields (Scheme 1). The addition of InCl$_3$ to **12** afforded a series of phenylindium **15a–c** depending on the amount of InCl$_3$. The solution of **15b** was heated under reflux conditions to give **13** quantitatively, showing that the transmetallation of **12** to **15** occurred completely and phenylindium **15b** is thermally stable even under the reflux conditions. Next, the photo-induced reactions of **15a–c** were performed and the results are shown in Table 4. The irradiation of **15a** afforded the 5-*exo* product **14** in 30% yield along with **13** in 15% yield (Table 4, entry 1). The cyclization of **15b** occurred efficiently to give better yields (entry 2). Triarylindium **15c** yielded **14** selectively in a modest yield (entry 3). These results clearly show that the photo-induced cleavage of C$_{sp^2}$–In bond occurs by the irradiation.



Scheme 1.

Table 4
Photochemical cyclization of **15a–c**



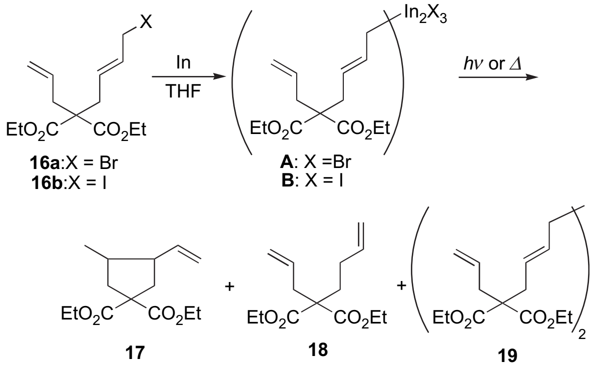
Entry	15	Yield[a] (%)	
		13	**14**
1	RInCl$_2$ **15a**	15	30
2	R$_2$InCl **15b**	6	66
3	R$_3$In **15c**	0	38

[a] Based on R.

2.2.2. Allylindium

Diene **16a** and indium were refluxed in THF for 3 h giving allylic indium **A**, which was then irradiated in THF to afford the 5-*exo*-cyclization product **17** in 51% yield (Table 5, entry 1). The corresponding 6-*endo*-cyclization product was not obtained. In order to estimate the amount of **17** formed via a pyrolytic course, the allylic indium compound **A** was quenched with 1 M HCl prior to the irradiation, leading to the corresponding protonated product **18** in 11% yield together with a small amount of **17** (3%) (entry 2). These results indicate that the present cyclization is induced by the photolysis of **A** and the thermal decomposition is negligible.

Table 5
Intramolecular cyclization of allylindium compounds **A** and **B**



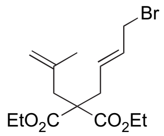
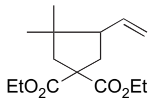
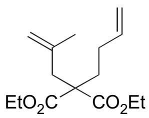
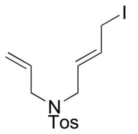
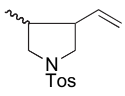
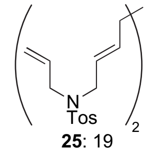
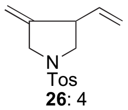
Entry	16	Conditions	Products and yield (cis/trans)
1	**16a**	Reflux, 3 h→*hν*, rt, 36 h	**17**: 51% (85:15)
2	**16a**	Reflux, 4 h	**17**: 3%, **18**: 11%
3	**16b**	rt, 2 h→*hν*, rt, 24 h	**17**: 34% (93:7), **19**: 24%
4	**16b**	rt, 2 h	**18**: 18%, **19**: 10%
5[a]	**16a**	rt, 2 h→*hν*, rt, 20 h	**17**: 16% (57:43), **19**: 61%

[a] With LiI.

The protonolysis of allylindium compounds generally proceeds selectively at the γ-position to give the corresponding protonated products in good yields.[10] The low yield of the protonolysis product **18** in entry 2 may be attributed to the significant decomposition–polymerization of **A** under the refluxing conditions. Therefore, the allylic indium compound was next prepared at room temperature by changing the bromide **16a** to the more reactive iodide **16b**. The disappearance of metallic indium was observed by mixing **16b** at room temperature for 2 h, and the resulting solution was irradiated for 24 h to produce **17** in 34% yield together with the dimer **19** in 24% yield (entry 3). Quenching **B** by 1 M HCl furnished the protonolysis product **18** in 18% yield and the dimer **19** in 10% yield (entry 4). The reaction of allylic indium derived from **16a** in the presence of LiI at room temperature gave rise to the dimer **19** predominantly (61% yield) and **17** was obtained only in 16% yield (entry 5). These results suggest that allylindium compound **B** derived from **16b** has a tendency to undergo the dimerization, which make it difficult to use **B** in the intramolecular cyclization.

Next, similar dienes **20** and **23** were subjected to the photochemical intramolecular cyclization reaction. The results are summarized in Table 6. Diene **20**, in which a methyl group was introduced at the reactive site, also gave the corresponding cyclization product **21** in moderate yield along with the protonolysis product **22** (entry 1, Table 6). In the case of tosyl amide **23**, the 5-*exo*-cyclization product **24** was formed in 42% yield along with the dimer **25** in 19% yield (entry 2). The allylic indium compound prepared with InI in place of In gave **24** in 32% yield with a small amount of the dehydrogenated product **26** (entry 3). The reactions of dienes bearing a stylyl group **27** and linked by an ether bond **28** gave complicated mixtures and no cyclization product was found.

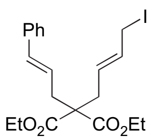
Table 6
Photochemical reaction of allylic indium compounds derived from **20** and **23**[a]

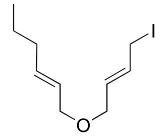
Entry	Substrate	*t* (h)	Product and yield (%)	
1	 **20**	23	 **21**:33	 **22**: 6
2	 **23**	20	 **24**:42 (51:49)[b]	 **25**: 19
3[c]	**23**	22	**24**:32 (63:37)[b]	 **26**: 4

[a] Allylindium compounds, prepared from diene **20** or **23** in THF at reflux, were irradiated in THF (30 mL).

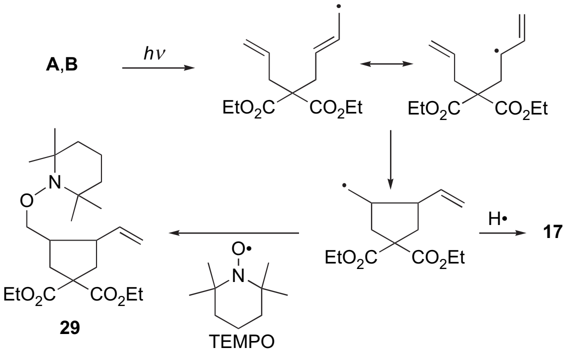
[b] Diastereomeric ratio in the crude product.

[c] InI was used instead of In.


27


28

The most plausible mechanism is depicted in Scheme 2; the irradiation of **A** or **B** causes a homolytic cleavage of the In–C bond and the resulting radical attacks the carbon–carbon double bond intramolecularly in a 5-*exo-trig* fashion leading to the cyclopentylmethyl radical, which abstracts hydrogen from the solvent THF to produce **17**. The presence of the radical intermediate was confirmed by an experiment using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO):[11] the photolysis of allylic indium **A** in the presence of TEMPO gave adduct **29** in 17% yield.



Scheme 2. Possible mechanism for the photochemical radical cyclization.

3. Summary

The photochemical reactions of organoindium compounds were found to generate the corresponding carbon-centered radicals, which can be used for the radical reaction with the intra- and intermolecular ways. Alkenyl- and alkynylindium compounds underwent the intermolecular reactions with ethyl α-iodoacetate to afford the corresponding β,γ-unsaturated esters. Similar to the success with the reactions of monoalkenyl- and monoalkynylindium reagents initiated by Et_3B, the use of alkenyl- and alkynylindium dichlorides is essential for high levels of yield in the photo-induced reactions. Aryl- and allylindium reagents bearing a carbon–carbon double bond underwent the intramolecular addition to give the corresponding five-membered ring products. The present photochemical process using organoindium compounds obviates the need for additional reagents to initiate the reaction, but also provides an alternative precursor to the radical reactions in place of conventional organotin compounds.

4. Experimental section

4.1. General

IR spectra were recorded on a JASCO IRA-102 spectrophotometer. ^1H NMR spectra were obtained for solutions in $CDCl_3$ on a Varian Mercury 200 spectrometer (200 MHz) or a Varian Gemini 300 spectrometer (300 MHz) with Me_4Si as internal standard; *J*-values are given in hertz. ^{13}C NMR spectra were measured for solutions in $CDCl_3$ with a Varian Gemini 200 spectrometer (50 MHz). Mass spectra were measured on a Hitachi M-2000 spectrometer at 70 eV. Elemental analyses were done with Perkin–Elmer 2400II. For photochemical reactions, a Riko Kagaku Sangyo UVL-100HA apparatus was used. Photolyses were carried out under an argon atmosphere using a 100 W high-pressure mercury lamp with a Pyrex filter. Indium powder (99.99%) was obtained from Aldrich and use as received. $InCl_3$ (99.999%) was purchased from Aldrich and dried by heating with a heat gun in vacuo before use. THF and ether were dried with $LiAlH_4$ before use.

4.2. Intermolecular reaction

4.2.1. Photochemical reaction of cinnamylindium sesquibromide (Eq. 1)

A mixture of powdered metallic indium (0.26 g, 2.3 mmol) and cinnamyl bromide (0.33 mL, 2.3 mmol) in THF (2 mL) was refluxed for 2 h. The resulting cinnamyl sesquibromide was diluted by THF (80 mL) and irradiated for 24 h. The reaction was quenched with water (2 mL) and the solvent was removed under reduced pressure. The product was extracted with ether and the extracts were washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–CH_2Cl_2=1:1) to give fractions consisting of 3,6-diphenylhexa-1,5-diene[12] (**1**) (37 mg, 15%), a mixture of **1** and 3,4-diphenylhexa-1,5-diene[12] (**2**) (24 mg, 10%, **1**/**2**=45:55), **2** (25 mg, 10%), and 5-phenylhept-6-en-1,4-diol[13] (**3**) (40 mg, 8%).

4.2.2. Photochemical reaction of benzylindium sesquiiodide (Eq. 2)

A mixture of powdered metallic indium (92 mg, 0.80 mmol) and benzyl iodide (0.17 g, 0.80 mmol) in DMF (1 mL) was stirred at room temperature for 2 h. The resulting benzylindium sesquiiodide was diluted with THF (80 mL) and then irradiated for 20 h. The reaction was quenched with water and the solvent was removed under reduced pressure. The product was extracted with ether, washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane) to give 1,2-diphenylethane[14] (**4**) (47 mg, 64%).

4.2.3. Photochemical reaction of styrylindium **5a** (Table 1, entry 1)

To a solution of β-bromostyrene (128 μL, 1.0 mmol) in Et_2O (2 mL), *t*-BuLi (*n*-pentane solution, 1.6 mol/L, 1.25 mL, 2.0 mmol) was added at −78 °C and the reaction mixture was kept for 1 h. The reaction mixture was treated with a solution of $InCl_3$ (221 mg, 1.0 mmol) in THF (5 mL) at −78 °C and the mixture was stirred for 1 h. The resulting styrylindium was diluted with THF (1.5 mL) and irradiated in the presence of ethyl iodoacetate (118 μL, 1.0 mmol) at room temperature overnight. The reaction was quenched with water (5 mL). The products were extracted with ether, washed with water and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a crude product (142 mg), which was purified by chromatography on silica gel (hexane–AcOEt=80:1 to AcOEt) to afford ethyl 4-phenyl-3-butenoate[7f] (**6**) (106 mg, 56%, *E*/*Z*=86:14).

4.2.4. Photochemical reaction of (Z)-styrylindium (Table 1, entry 4)

β-Bromostyrene[15] (*E*/*Z*=8:92, 183 mg, 1.0 mmol) used in place of β-bromostyrene (*E*/*Z*=82:18) gave a crude product (151 mg), which was purified by chromatography on silica gel (hexane–AcOEt=80:1 to AcOEt) to give **6** (79 mg, 83%, *E*/*Z*=56:44).

4.2.5. Photochemical reaction of styrylindium **5b** (Table 1, entry 6)

To a solution of β-bromostyrene (256 μL, 4.0 mmol) in Et_2O (2 mL), *t*-BuLi (*n*-pentane solution, 1.6 M, 5.0 mL, 8.0 mmol) was added at −78 °C, and the reaction mixture was kept for 1 h. The resulting styryllithium was treated with a solution of $InCl_3$ (442 mg, 2.0 mmol) in THF (5 mL) at −78 °C and the mixture was stirred for 1 h. The resulting styrylindium was diluted with THF (1.5 mL) and irradiated in the presence of ethyl iodoacetate (118 μL, 1.0 mmol) at room temperature overnight. The reaction was quenched with water (5 mL). The products were extracted with ether, washed with water and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a crude product (142 mg), which was purified by chromatography on silica gel (hexane–AcOEt=80:1 to AcOEt) to afford (*E*)-**6** (56 mg, 29%) and diethyl 2-styryl-1,4-butanedioate (**7**) (26 mg, 19%, *E*/*Z*=92:8).

*4.2.5.1. Diethyl 2-styryl-1,4-butanedioate (**7**).* ^1H NMR (200 MHz, $CDCl_3$) δ 1.24 (t, *J*=6.1 Hz, 3H, CH_3), 1.27 (t, *J*=8.0 Hz, 3H, CH_3), 2.61 (dd, *J*=6.1, 16.4 Hz, 1H, one of CH_2CO_2), 2.94 (dd, *J*=8.7, 16.4 Hz, 1H, the other of CH_2CO_2), 3.65 (ddt, *J*=0.8, 8.3, 10.3 Hz, 1H, CH), 4.05–4.24 (m, 4H, $CO_2CH_2CH_3$), 6.17 (dd, *J*=8.3, 15.8 Hz, 1H, =CH), 6.54 (d, *J*=15.8 Hz, 1H, PhCH=), 7.10–7.40 (m, 5H, aromatic H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4, 36.6, 45.1, 60.7, 61.1, 125.3, 126.2, 127.6, 128.3, 132.7, 136.2, 170.9, 172.3; IR (neat, cm^{-1}) 3349, 2981, 2872, 1950, 1881, 1732, 1599, 1463, 1159, 1095, 1028, 967, 859, 747, 649; MS (EI) *m*/*z* 276 (M^+); HRMS calcd for $C_{16}H_{20}O_4$ (M^+): 276.1362, found: 276.1381.

4.2.6. Photochemical reaction of styrylindium **5a** with 2-cyclohexenone (Table 2, entry 4)

To a solution of β-bromostyrene (256 μL, 4.0 mmol) in Et_2O (2 mL), *t*-BuLi (*n*-pentane solution, 1.6 M, 5.0 mL, 8.0 mmol) was added at −78 °C, and the reaction mixture was kept for 1 h. The resulting styryllithium was treated with a solution of $InCl_3$ (442 mg, 2.0 mmol) in THF (5 mL) at −78 °C and the mixture was stirred for 1 h. The resulting styrylindium was diluted with CH_3CN (10 mL) and irradiated in the presence of 2-cyclohexenone (97 μL, 1.0 mmol) at room temperature overnight. The reaction was quenched with 1 M HCl (5 mL). The products were extracted with ether and washed with water and brine, and dried over Na_2SO_4 to give a crude product (320 mg), which was purified by chromatography on silica gel (hexane–AcOEt=80:1 to AcOEt) to afford **8**[16,17] (70 mg, 35%, *E*/*Z*=37:63).

4.2.7. Photochemical reaction of 2-phenylethynylindium **9a** with ethyl iodoacetate (Table 3, entry 1)

To a solution of phenylacetylene (110 μL, 1.0 mmol) in THF (2 mL), *n*-BuLi (*n*-hexane solution 1.6 M, 0.70 mL, 1.1 mmol) was added at −78 °C and the reaction mixture was stirred for 1 h. A solution of $InCl_3$ (221 mg, 1.0 mmol) in THF (5 mL) was added to the lithium acetylide at −78 °C and the mixture was kept for another 1 h. The resulting solution was diluted with THF (3 mL) and irradiated in the presence of ethyl iodoacetate (60 μL, 0.50 mmol) at room temperature overnight. The reaction was quenched with water (5 mL), and the products were extracted with ether. The organic layer was washed with water and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure giving a crude product (98 mg), which was purified by chromatography on silica gel (hexane–AcOEt) to afford a mixture of ethyl 4-phenyl-3-butenoate (**6**) and ethyl 4-phenyl-3-butynoate[7g] (**10**) (10 mg, **6**: 2%, **10**: 9% the ratio was determined by ^{1}H NMR) and **10** (40 mg, 43%).

4.2.8. Photochemical reaction of 2-phenylethynylindium **9b** (Table 3, entry 3)

To a solution of phenylacetylene (110 μL, 1.0 mmol) in THF (2 mL), *n*-butyllithium (*n*-hexane, 1.6 M, 0.70 mL, 1.1 mmol) was added at −78 °C and the mixture was kept for 1 h at this temperature. A solution of $InCl_3$ (110 mg, 0.50 mmol) in THF (5 mL) was added to the lithium acetylide at −78 °C and the mixture was kept for another 1 h at this temperature. The resulting solution was diluted with THF (3 mL) and irradiated in the presence of ethyl iodoacetate (60 μL, 0.50 mmol) at room temperature overnight. The reaction was quenched with water (5 mL) and the products were extracted with ether. The organic layer was washed with water and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure giving a crude product (108 mg), which was purified by chromatography on silica gel (hexane–AcOEt) to afford a mixture of **6** and **10** (39 mg, **6**: 11%, *E*/*Z*=22:78 and **10**: 31%). The ratios were determined by ^{1}H NMR.

4.3. Intramolecular reaction

4.3.1. Photochemical reaction of dichloroindioaniline **15a** (Table 4, entry 1)

t-BuLi (*n*-pentane solution, 1.6 mol/L, 0.70 mL, 1.1 mmol) was added to a solution of 2-bromo-*N*-allyl-*N*-methylaniline[18] (**11**) (113 mg, 0.50 mmol) in *n*-pentane–ether (v/v=9:1, 1.5 mL) at −78 °C and the mixture was stirred for 1 h at this temperature. To the resulting mixture, a solution of $InCl_3$ (110 mg, 0.50 mmol) in THF (5 mL) was added and the reaction mixture was kept for another 1 h at −78 °C. The mixture was diluted with THF (30 mL) and irradiated at room temperature overnight. The reaction was quenched with water and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (elution with hexane then AcOEt) to give a mixture of *N*-allyl-*N*-methylaniline[19] (**13**) and 2,3-dihyrdo-1,3-dimethylindoline[20] (**14**) (18 mg, **14**: 5%, **13**: 15% determined by ^{1}H NMR) and **14** (15 mg, 25%).

4.3.2. Synthesis of allylic bromide **16a**

To a mixture of NaH (60% oil suspension, 0.48 g, 12 mmol) in THF (20 mL), diethyl allylmalonate (2.0 mL, 10 mmol) was added at 0 °C and the mixture was stirred at room temperature for 1 h. 1,4-Dibromobut-2-ene (3.2 g, 15 mmol) was added and refluxed for 3 h. The reaction was quenched with water and the product was extracted with ether, and the extracts were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution with hexane–EtOAc=20:1) to give **16a** (1.6 g, 47%).

*4.3.2.1. Diethyl 2-allyl-2-[4-bromo-2-butenyl]-1,3-propanedioate (**16a**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, *J*=7.1 Hz, 6H, CH_3), 2.64 (d, *J*=6.5 Hz, 4H, CH_2), 3.90 (d, *J*=7.1 Hz, 2H, CH_2Br), 4.19 (q, *J*=7.1 Hz, 4H, CH_2CH_3), 5.12 (d, *J*=11 Hz, 1H, cis $=CH_2$), 5.13 (d, *J*=15 Hz, 1H, trans $=CH_2$), 5.53–5.85 (m, 3H, CH=); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.8, 32.9, 35.6, 37.6, 57.7, 61.8, 119.7, 129.8, 130.8, 132.2, 170.5; IR (neat, cm^{-1}) 3030, 1740, 1450, 1380, 1290, 1210, 1160, 1100, 1040, 980, 930, 860. Anal. Calcd for $C_{14}H_{21}BrO_4$: C, 50.46; H, 6.35. Found: C, 50.45; H, 6.62.

4.3.3. Synthesis of allylic iodide **16b**

To a mixture of NaI (0.23 g, 1.5 mmol) in acetone (1 mL), bromide **16a** (0.33 g, 1.0 mmol) was added at room temperature and the mixture was stirred for 5 h. The reaction was quenched with 1 M HCl and the product was extracted with ether. The extracts were successively washed with aqueous Na_2SO_3, water, and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give **16b** (0.37 g, 96%).

*4.3.3.1. Diethyl 2-allyl-2-[4-iodo-2-butenyl]-1,3-propanedioate (**16b**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, *J*=7.2 Hz, 6H, CH_3), 2.59–2.65 (m, 4H, CH_2), 3.83 (d, *J*=7.8 Hz, 2H, CH_2I), 4.20 (q, *J*=7.2 Hz, H, CH_2CH_3), 5.11 (d, *J*=11 Hz, 1H, cis $=CH_2$), 5.13 (d, *J*=17 Hz, 1H, trans $=CH_2$), 5.48–5.89 (m, 3H, CH=); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.4, 14.3, 35.1, 37.1, 57.3, 61.4, 119.2, 127.9, 131.8, 131.9, 170.1; IR (neat, cm^{-1}) 3050, 3000, 1730, 1640, 1440, 1390, 1370, 1280, 1250, 1210, 1150, 1110, 1060, 1030, 970, 920, 860. Anal. Calcd for $C_{14}H_{21}IO_4$: C, 44.22; H, 5.57. Found: C, 44.30; H, 5.78.

*4.3.4. Photochemical reaction of allylic indium compound derived from **16a** (Table 5, entry 1)*

A mixture of powdered metallic indium (46 mg, 0.40 mmol) and 8-bromo-4,4-diethoxycarbonyloct-1,6-diene (**16a**) (0.20 g, 0.60 mmol) in THF (4 mL) was refluxed for 3 h. The resulting allylic indium reagent was diluted with THF (90 mL) and then irradiated for 36 h. The reaction was quenched with 1 M HCl and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=20:1) to give **17** (77 mg, 51%, cis/trans=85:15). The cis/trans ratio was determined by the comparison with the reported data of 1-methyl-2-vinylcyclopentane:[21] δ 0.86 (d, J=7.2 Hz, 3H, Me, cis) and 0.99 (d, J=5.9 Hz, 3H, Me, trans), and dimethyl 3-methyl-4-vinylcyclopentane-1,1-dicarboxylate:[21] δ 0.87 (d, J=7.0 Hz, 3H, Me, cis) and 0.98 (d, J=6.3 Hz, 3H, Me, trans).

*4.3.4.1. Diethyl 3-methyl-4-vinyl-1,1-cyclopentanedicarboxylate[22] (**17**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (d, J=6.9 Hz, 3H, cis CH_3), 0.97 (d, J=6.1 Hz, 3H, trans CH_3), 1.25 (t, J=7.1 Hz, 6H, CH_3), 1.90–2.75 (m, 6H), 4.19 (q, J=7.1 Hz, 4H, CH_2CH_3), 4.98–5.05 (m, 2H, $=CH_2$), 5.75 (ddd, J=18, 9.6, 8.2 Hz, 1H, CH=); IR (neat, cm^{-1}) 3100, 3000, 1730, 1640, 1460, 1440, 1380, 1365, 1290, 1250, 1180, 1145, 1100, 1050, 1030, 1000, 920, 860.

*4.3.5. Reaction of the allylic indium compound derived from **16a** (Table 5, entry 2)*

A mixture of powdered metallic indium (23 mg, 0.20 mmol) and **16a** (0.10 g, 0.30 mmol) in THF (2 mL) was refluxed for 4 h. The reaction was quenched with 1 M HCl and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=20:1) to give a fraction consisting of **17** and diethyl 2-allyl-2-(3-butenyl)-1,3-propanedioate[23](**18**). The individual yield (**17**: 3%, **18**: 11%) was determined on the basis of ^{1}H NMR data (**17**/**18**=23:77).

*4.3.6. Photochemical reaction of the allylic indium compound derived from **16b** (Table 5, entry 3)*

A mixture of powdered metallic indium (15 mg, 0.10 mmol) and **16b** (76 mg, 0.20 mmol) in THF (1 mL) was stirred at room temperature for 2 h. The resulting allylic indium reagent was diluted with THF (30 mL), and the solution was irradiated for 22 h. The reaction was quenched with water (10 mL), and the product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=40:1) to give **17** (17 mg, 34%, cis/trans=93:7) and dimer **19** (25 mg, 24%).

*4.3.6.1. Tetraethyl 1,6,10,15-hexadecatetraene-4,4,13,13-tetracarboxylate (**19**).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, J=7.2 Hz, 12H, CH_3), 1.92–2.10 (m, 4H,), 2.57–2.66 (m, 6H), 4.19 (q, J=7.2 Hz, 8H, CH_2CH_3), 4.95–5.72 (m, 10H, $CH=CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 32.5, 35.4, 36.6, 57.3, 61.0, 118.6, 123.6, 132.1, 134.1, 170.3; IR (neat, cm^{-1}) 3000, 2950, 1730, 1640, 1440, 1360, 1280, 1210, 1140, 1100, 1040, 970, 920, 860, 800. Anal. Calcd for $C_{28}H_{42}O_8$: C, 66.38; H, 8.36. Found: C, 66.48; H, 8.62.

*4.3.7. Reaction of the allylic indium compound derived from **16b** (Table 5, entry 4)*

A mixture of powdered metallic indium (52 mg, 0.45 mmol) and **16b** (0.17 mg, 0.45 mmol) in THF (2 mL) was stirred at room temperature for 2 h. The reaction was quenched with water (5 mL) and the solvent was removed under reduced pressure. The reaction was quenched with 1 M HCl and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=40:1) to give **18** (21 mg, 18%) and dimer **19** (11 mg, 10%).

*4.3.8. Photochemical reaction of allylic indium compound derived from **16a** in the presence of LiI (Table 5, entry 5)*

A mixture of powdered metallic indium (35 mg, 0.30 mmol), LiI (60 mg, 0.45 mmol), and **16a** (0.15 g, 0.45 mmol) in THF (2 mL) was refluxed for 2 h. The resulting allylic indium reagent was diluted with THF (50 mL) and irradiated for 20 h. The reaction was quenched with 1 M HCl (4 mL) and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=40:1) to give **17** (18 mg, 16%, cis/trans=57:43) and dimer **19** (70 mg, 61%).

*4.3.9. Synthesis of diene **20***

To a mixture of NaH (60% oil suspension, 0.20 g, 5 mmol) in THF (10 mL), diethyl methallylmalonate (1.0 g, 4.7 mmol) was added at 0 °C and the mixture was stirred at room temperature for 1 h. 1,4-Dibromobut-2-ene (2.0 g, 9.4 mmol) was added and the mixture was refluxed overnight. The reaction was quenched with 1 M HCl and the product was extracted with ether, and the extracts were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution with hexane–EtOAc=40:1) to give **20** (0.58 g, 35%).

*4.3.9.1. Diethyl 2-(4-bromo-2-butenyl)-2-(2-methyl-2-propenyl)-1,3-propanedioate (**20**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, J=7.2 Hz, 6H, CH_3), 1.66 (s, 3H, CH_3), 2.66 (d, J=6.0 Hz, 2H, CH_2), 2.70 (s, 2H, CH_2), 3.90 (d, J=6.6 Hz, 2H, CH_2Br), 4.19 (q, J=7.2 Hz, 4H, CH_2CH_3), 4.76 (s, 1H, CH_2=), 4.88 (s, 1H, CH_2=), 5.57–5.84 (m, 2H, CH=); IR (neat, cm^{-1}) 3475, 3100, 3000, 1730, 1640, 1440, 1360, 1270, 1240, 1200, 1150, 1090, 1060, 1030, 970, 900, 860, 730. Anal. Calcd for $C_{15}H_{23}BrO_4$: C, 51.88; H, 6.68. Found: C, 52.04; H, 6.56.

4.3.10. *Photochemical reaction of allylic indium compound derived from **20** (Table 6, entry 1)*

A mixture of powdered metallic indium (35 mg, 0.30 mmol) and diene **20** (0.16 g, 0.45 mmol) in THF (2 mL) was refluxed for 2 h. The resulting allylic indium reagent was diluted with THF (30 mL) and then irradiated for 23 h. The reaction was quenched with 1 M HCl and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=20:1) to give a mixture of **21** and **22** (47 mg). The yields (**21**: 33%, **22**: 6%) were determined by ^1H NMR.

4.3.10.1. *Diethyl 3,3-dimethyl-4-vinylcyclopentane-1,1-dicarboxylate (**21**).* ^1H NMR (200 MHz, $CDCl_3$) δ 0.78 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.25 (t, J=7.2 Hz, 6H, CH_3), 2.17–2.43 (m, 5H), 4.18 (q, J=7.2 Hz, 4H, CH_2), 4.98–5.08 (m, 2H, $=CH_2$), 5.60–5.78 (m, 1H, $=CH$). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.81; H, 8.63.

4.3.10.2. *Diethyl 2-(3-butenyl)-2-(2-methyl-2-propenyl)-1,3-propanedioate[24] (**22**).* ^1H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, J=7.2 Hz, 6H, CH_3), 1.95–1.99 (m, 4H, CH_2), 2.73 (s, 3H, CH_3), 4.18 (q, J=7.2 Hz, 4H, CH_2), 4.74 (s, 1H, $CH_2=$), 4.86 (s, 1H $CH_2=$), 4.95 (d, J=9.2 Hz, 1H, cis $CH_2=$), 5.02 (d, J=19 Hz, 1H, trans $CH_2=$), 5.69–5.90 (m, 1H, $=CH$); IR (neat, cm^{-1}) 3100, 3000, 1730, 1640, 1440, 1360, 1300, 1260, 1240, 1200, 1180, 1100, 1030, 910, 860.

4.3.11. *Synthesis of diene **23***

To a mixture of NaH (60% oil suspension, 0.26 g, 6.5 mmol) in DMF (50 mL), *N*-allyl-4-methylbenzenesulfonamide[25] (2.0 g, 10 mmol) was added at room temperature and stirred for 2 h. 1,4-Dibromobut-2-ene (6.4 g, 30 mmol) was added and the reaction mixture was stirred at room temperature for 23 h. The reaction was quenched with 1 M HCl and the product was extracted with ether, and the extracts were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (elution with hexane–EtOAc=40:1) to give *N*-allyl-*N*-(4-bromo-2-butenyl)-4-methylbenzenesulfonamide (0.90 g, 27%). This bromide (0.89 g, 2.7 mmol) was treated with NaI (0.81 g, 5.4 mmol) in acetone (10 mL) at room temperature for 3 h. The product was extracted with ether and washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give *N*-allyl-*N*-(4-iodo-2-butenyl)-4-methylbenzenesulfonamide (**23**) (0.86 g, 82%).

4.3.11.1. *N-Allyl-N-(4-bromo-2-butenyl)-4-methylbenzenesulfonamide*. ^1H NMR (200 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.80 (d, J=6.2 Hz, 4H, CH_2N), 3.87 (d, J=7.4 Hz, 2H, CH_2Br), 5.11–5.20 (m, 2H, $CH_2=$), 5.50–5.86 (m, 3H, $CH=$), 7.26–7.32 (m, 2H, Ph), 7.66–7.71 (m, 2H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) 21.7, 31.6, 47.8, 49.8, 119.2, 126.9, 129.4, 129.5, 130.2, 132.2, 136.8, 143.1; IR (neat, cm^{-1}) 2950, 1640, 1600, 1490, 1440, 1340, 1300, 1290, 1250, 1210, 1160, 1100, 1040, 970, 940, 910, 820, 760, 710, 660.

4.3.11.2. *N-Allyl-N-(4-iodo-2-butenyl)-4-methylbenzenesulfonamide (**23**).* ^1H NMR (200 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.77–3.89 (m, 6H, CH_2), 5.15 (d, J=11 Hz, 1H, cis $CH_2=$), 5.17 (d, J=17 Hz, 1H, trans $CH_2=$), 5.42–5.89 (m, 3H, $CH=$), 7.26–7.32 (m, 2H, Ph), 7.66–7.71 (m, 2H, Ph); IR (neat, cm^{-1}) 2950, 1640, 1600, 1500, 1440, 1340, 1300, 1290, 1250, 1150, 1120, 1090, 1020, 960, 930, 910, 820, 750, 700, 640. Anal. Calcd for $C_{14}H_{18}INO_2S$: C, 42.98; H, 4.64; N, 3.58. Found: C, 43.37; H, 4.78; N, 3.51.

4.3.12. *Photochemical reaction of allylic indium compound derived from **23** (Table 6, entry 2)*

A mixture of powdered metallic indium (31 mg, 0.27 mmol) and diene **23** (0.16 g, 0.40 mmol) in THF (1 mL) was stirred at room temperature for 2 h. The resulting allylic indium reagent was diluted with THF (30 mL) and then irradiated for 20 h. The reaction was quenched with 1 M HCl and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=20:1) to give 3-methyl-4-vinyl-1-(4-methylbenzenesulfonyl)pyrrolidine[26] (**24**) (45 mg, d.r.=55:45) and dimer **25** (20 mg, 19%).

4.3.12.1. *3-Methyl-4-vinyl-1-(4-methylbenzenesulfonyl)pyrrolidine[26] (**24**).* ^1H NMR (200 MHz, $CDCl_3$) δ 0.76 (d, J=6.8 Hz, 3H, cis or trans CH_3), 0.90 (d, J=6.6 Hz, 3H, trans or cis CH_3), 2.14–2.27 (m, 1H), 2.59–2.72 (m, 1H), 2.96 (dd, J=9.8, 6.0 Hz, 1H, CH), 3.18 (dd, J=9.8, 6.0 Hz, 1H, CH), 3.36–3.60 (m, 2H), 4.97 (d, J=10 Hz, 1H, cis $CH_2=$), 4.98 (d, J=17 Hz, 1H, trans $CH_2=$), 5.49 (ddd, J=17, 10, 8.2 Hz, 1H, $CH=$), 7.33 (m, 2H, Ph), 7.72 (m, 2H, Ph); IR (neat, cm^{-1}) 3050, 2950, 2900, 2850, 1640, 1590, 1490, 1470, 1450, 1420, 1380, 1340, 1300, 1280, 1160, 1090, 1040, 1010, 910, 810, 800, 730, 700, 650.

4.3.12.2. *Dimer **25***. ^1H NMR (200 MHz, $CDCl_3$) δ 1.96–2.04 (m, 1H, CH), 2.42 (s, 3H, CH_3), 3.70–3.79 (m, 4H, CH_2), 4.92–5.69 (m, 5H), 7.26–7.32 (m, 2H, Ph), 7.69–7.75 (m, 2H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1, 32.1, 49.1, 49.6, 119.0, 125.0, 127.4, 129.8, 133.0, 134.8, 137.6, 143.3.

4.3.12.3. *3-Methylene-4-vinyl-1-(4-methylbenzenesulfonyl)pyrrolidine[27] (**26**).* ^1H NMR (200 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 2.75–2.90 (m, 1H), 3.13–3.35 (m, 1H), 3.49–3.78 (m, 2H), 3.94–4.13 (m, 1H), 4.83–5.14 (m, 4H, $CH_2=$), 5.40–5.59 (m, 1H, $CH=$), 7.29–7.38 (m, 2H, Ph), 7.65–7.78 (m, 2H, Ph).

4.3.13. Photochemical reaction of allylindium A in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (Scheme 2)

A mixture of powdered indium (35 mg, 0.30 mmol) and **16a** (0.15 g, 0.45 mmol) in THF (2 mL) was refluxed for 2 h. The resulting allylic indium reagent was diluted with THF (80 mL) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (0.14 g, 0.90 mmol) was added. The solution was irradiated at room temperature for 22 h. The reaction was quenched with water (5 mL) and the solvent was removed under reduced pressure. The product was extracted with ether and washed with water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (elution with hexane–EtOAc=80:1) to give **29** (31 mg, 17%).

*4.3.13.1. Diethyl 3-[[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]-methyl] 4-vinyl-1,1-cyclopentanedicarboxylate (**29**).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05–1.10 (m, 12H, CH_3), 1.25 (t, J=7.2 Hz, 6H, CH_3), 1.35–1.60 (m, 6H, CH_2), 2.11–2.21 (m, 2H), 2.27–2.55 (m, 3H), 2.71–2.85 (m, 1H), 3.52–3.98 (m, 2H, OCH_2), 4.19 and 4.20 (each q, J=7.1 Hz, total 4H, CH_2CH_3), 4.95–5.07 (m, 2H, $=CH_2$), 5.79 (ddd, J=17.0, 10.1, 8.3 Hz, 1H, CH=); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 17.1, 20.0, 33.0, 36.8, 39.0, 39.6, 42.0, 45.1, 59.2, 59.7, 61.3, 115.3, 138.1, 172.4, 172.7; IR (neat, cm^{-1}) 2980, 2940, 1730, 1450, 1360, 1300, 1250, 1180, 1130, 1100, 1040, 1000, 910, 860, 800, 710. Anal. Calcd for $C_{23}H_{39}NO_5$: C, 67.45; H, 9.60; N, 3.42. Found: C, 67.42; H, 9.68; N, 3.30.

References and notes

1. (a) Cintas, P. *Synlett* **1995**, 1087–1096; (b) Marshall, J. A. *Chemtracts: Org. Chem.* **1997**, *10*, 481–496; (c) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149–11176; (d) Araki, S.; Hirashita, T. *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 323–386.
2. (a) Araki, S.; Imai, A.; Shimizu, K.; Butsugan, Y. *Tetrahedron Lett.* **1992**, *33*, 2581–2582; (b) Araki, S.; Imai, A.; Shimizu, K.; Yamada, M.; Mori, A.; Butsugan, Y. *J. Org. Chem.* **1995**, *60*, 1841–1847.
3. Araki, S.; Usui, H.; Kato, M.; Butsugan, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4699–4700.
4. (a) Araki, S.; Nakano, H.; Subburaj, K.; Hirashita, T.; Shibutani, K.; Yamamura, H.; Kawai, M.; Butsugan, Y. *Tetrahedron Lett.* **1998**, *39*, 6327–6330; (b) Araki, S.; Shiraki, F.; Tanaka, T.; Nakano, H.; Subburaj, K.; Hirashita, T.; Yamamura, H.; Kawai, M. *Chem.—Eur. J.* **2001**, *7*, 2784–2790.
5. Araki, S.; Horie, T.; Kato, M.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 2331–2334.
6. Araki, S.; Kamei, T.; Igarashi, Y.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 7999–8002.
7. (a) Miyabe, H.; Naito, T. *Org. Biomol. Chem.* **2004**, *2*, 1267–1270; (b) Miyabe, H.; Ueda, M.; Nishimura, A.; Naito, T. *Tetrahedron* **2004**, *60*, 4227–4235; (c) Yanada, R.; Koh, Y.; Nishimori, N.; Matsumura, A.; Obika, S.; Mitsuya, H.; Fujii, N.; Takemoto, Y. *J. Org. Chem.* **2004**, *69*, 2417–2422; (d) Yanada, R.; Obika, S.; Nishimori, N.; Yamauchi, M.; Takemoto, Y. *Tetrahedron Lett.* **2004**, *45*, 2331–2334; (e) Takami, K.; Mikami, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2003**, *59*, 6627–6635; (f) Takami, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4555–4558; (g) Takami, K.; Usugi, S.; Yorimitsu, H.; Oshima, K. *Synthesis* **2005**, 824–839.
8. Yamaji, M.; Hama, Y.; Arai, S.; Hoshino, M. *Inorg. Chem.* **1987**, *26*, 4375–4378.
9. Preliminary communication: Hirashita, T.; Tanaka, J.; Hayashi, A.; Araki, S. *Tetrahedron Lett.* **2005**, *46*, 289–292.
10. Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S.-J.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538–2542.
11. Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4992.
12. (a) Pasto, D. J.; L'Hermine, G. *Tetrahedron* **1993**, *49*, 3259–3272; (b) Nishino, T.; Watanabe, T.; Okada, M.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 966–969.
13. Nishikawa, T.; Shinokubo, H.; Ohshima, K. *Tetrahedron* **2003**, *59*, 9661–9668.
14. Soundararajan, N.; Platz, M. S. *Tetrahedron Lett.* **1987**, *28*, 2813–2816.
15. Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron Lett.* **2001**, *42*, 3893–3896.
16. Tucci, F.; Chieffi, A.; Comasseto, J. *J. Org. Chem.* **1996**, *61*, 4975–4989.
17. Oi, S.; Moro, M.; Ito, H.; Honma, Y.; Miyano, S.; Inoue, Y. *Tetrahedron* **2002**, *58*, 91–97.
18. Sisko, J.; Weinreb, S. M. *Synth. Commun.* **1988**, *18*, 1035–1041.
19. Beholz, G. L.; Stille, R. J. *J. Org. Chem.* **1993**, *58*, 5095–5100.
20. Kurono, N.; Honda, E.; Komatsu, F.; Orito, K.; Yokuda, M. *Tetrahedron* **2004**, *60*, 1791–1801.
21. Lennom, P.; Rosenblum, M. *J. Am. Chem. Soc.* **1983**, *105*, 1233–1241.
22. Kim, S.; Cho, J. R. *Synlett* **1992**, 629–630.
23. Bein, S.; Ovadia, D. *J. Chem. Soc., Perkin Trans. 1* **1974**, 333–336.
24. Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95–96.
25. Miyama, O.; Ozawa, Y.; Ninomiya, I.; Naito, T. *Tetrahedron* **2000**, *56*, 6199–6207.
26. Oppolzer, W.; Schröder, F. *Tetrahedron Lett.* **1994**, *35*, 7939–7942.
27. Oppolzer, W.; Fürstner, A. *Helv. Chim. Acta* **1993**, *76*, 2329–2337.