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# Cooperative Photoredox- and Nickel-Catalyzed Alkylative Cyclization Reactions of Alkynes with 4-Alkyl-1,4-dihydropyridines

Yulin Zhang, Yoshiaki Tanabe, Shogo Kuriyama, and Yoshiaki Nishibayashi*

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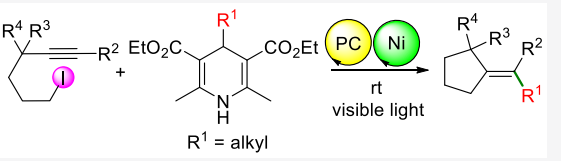
**ABSTRACT:** Cooperative photoredox- and nickel-catalyzed alkylative cyclization reactions of iodoalkynes with 4-alkyl-1,4-dihydropyridines as alkylation reagents under visible light irradiation have been achieved to afford the corresponding alkylated cyclopentylidenes in good to high yields. Introduction of substituents at the propargylic position of iodoalkynes has led to the stereoselective formation of *E*-isomers. The present reaction system provides a novel synthetic method for alkylative cyclization reactions of both terminal and internal alkynes with cooperative photoredox and nickel catalysis.



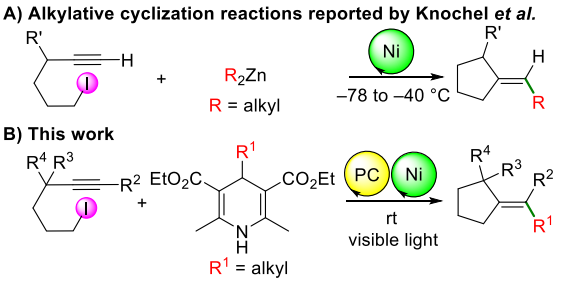



## INTRODUCTION

Recently, our group and others have demonstrated that 4-alkyl-1,4-dihydropyridines can be used as powerful alkylation reagents to offer a variety of alkylative reactions in photoredox-catalyzed molecular transformations,[1−13] providing an alternative to using classical, but highly reactive, organometallic alkylation reagents. The use of visible light excitement of a photoredox catalyst, followed by single-electron-transfer (SET) processes, leads to the generation of alkyl radicals from 4-alkyl-1,4-dihydropyridines,[1,2,14] enabling not only simple alkylation[3−5] but also alkylative reactions accompanied by other transformations such as cross-coupling reactions in the presence of additional catalysts.[6−13,15] In fact, we have recently succeeded in photoredox-catalyzed aromatic substitution reactions of cyanoarenes with 4-alkyl-1,4-dihydropyridines[3] and cooperative nickel- and photoredox-catalyzed cross-coupling reactions of aryl and alkenyl halides with 4-alkyl-1,4-dihydropyridines.[8,9]

In the course of our study to expand the utility of 4-alkyl-1,4-dihydropyridines toward alkylative reactions, we next planned to apply 4-alkyl-1,4-dihyropyridines to the alkylative cyclization reactions of haloalkynes.[16,17] Indeed, transition-metal-catalyzed alkylative cyclization reactions have been explored intensively to prepare the corresponding cyclic compounds valuable for both biological and pharmaceutical utilities.[18−20] As a selected example, Knochel and co-workers reported nickel-catalyzed alkylative cyclization reactions of 6-iodohex-1-ynes with alkyl zinc reagents to afford the corresponding alkylated cyclopentylidenes, where a lower temperature was required to suppress side reactions (Chart 1A).[16] Thus, we have applied 4-alkyl-1,4-dihydropyridines to the alkylative cyclization reactions of 6-iodohex-1-ynes in the presence of photoredox and nickel dual catalysts.[21] Here, we wish to report the cooperative photoredox- and nickel-catalyzed alkylative cyclization reactions of 6-iodohex-1-ynes with 4-alkyl-1,4-dihydropyridines employed as alkylation reagents at room temperature under the irradiation of visible light to afford the corresponding alkylated cyclopentylidenes. In addition, introduction of substituents at the propargylic position of 6-iodohex-1-ynes has led to the stereoselective formation of *E*-isomers (Chart 1B).

**Chart 1. Nickel-Catalyzed Alkylative Cyclization Reactions of Iodoalkynes with Alkylation Reagents**




## RESULTS AND DISCUSSION

We initially investigated the reaction of 6-iodohex-1-yne (**1a**) with 4-benzyl-3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine (**2a**) as typical substrates for the photoredox- and nickel-catalyzed alkylative cyclization reaction to afford (2-cyclopentylideneethyl)benzene (**3aa**) as the major product (Table 1). When the reaction of **1a** with 3 equiv of **2a** in THF was carried out in the presence of 2 mol % of *fac*-[Ir(ppy)$_3$] (ppy = 2-(2-pyridyl)phenyl), 10 mol % of anhydrous NiCl$_2$, 15

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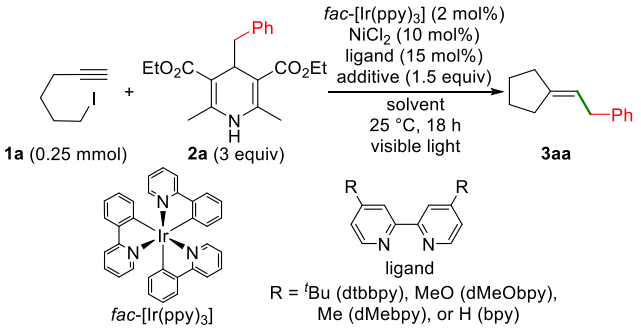
**Table 1. Photoredox- and Nickel-Catalyzed Alkylative Cyclization of 1a with 2a**[a]



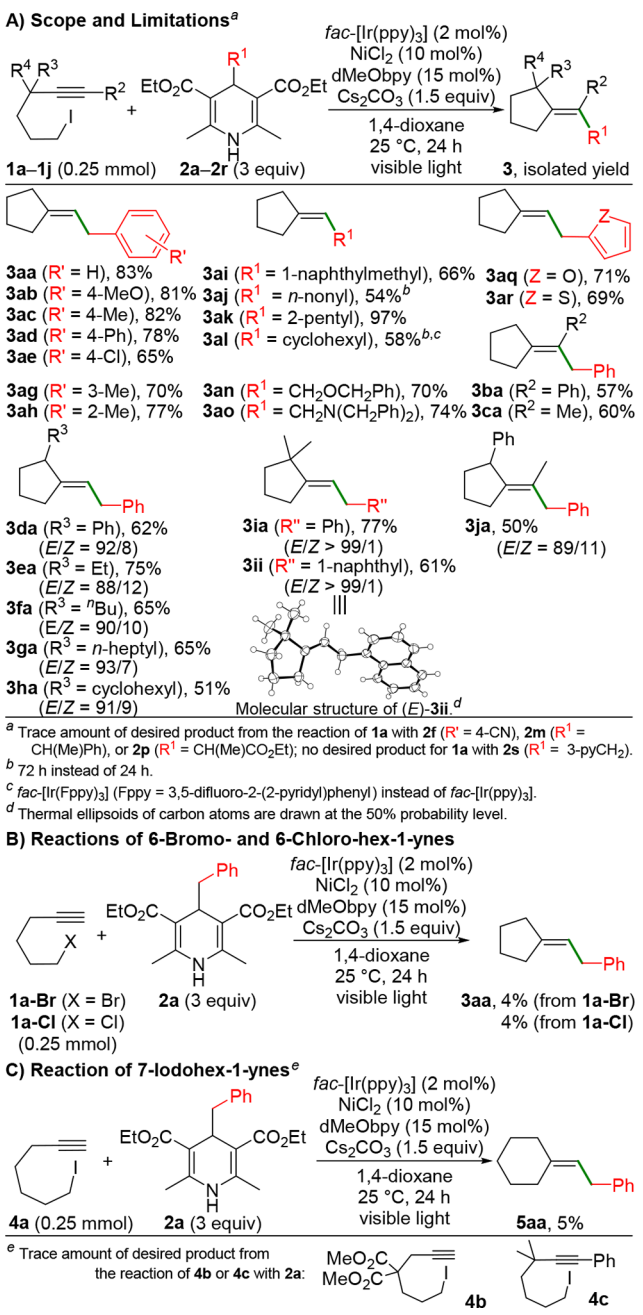

| entry | ligand | additive | solvent | yield (%)[b] |
|---|---|---|---|---|
| 1 | dtbbpy | $Cs_2CO_3$ | THF | 50 |
| 2 | dtbbpy | none | THF | 0[c] |
| 3 | dtbbpy | $K_2CO_3$ | THF | 40 |
| 4 | dtbbpy | NaOAc | THF | 32 |
| 5 | dtbbpy | $Cs_2CO_3$ | 1,4-dioxane | 69 |
| 6 | dtbbpy | $Cs_2CO_3$ | MeCN | 42 |
| 7 | dtbbpy | $Cs_2CO_3$ | DME | 35 |
| 8 | dtbbpy | $Cs_2CO_3$ | $Et_2O$ | 27 |
| 9 | none | $Cs_2CO_3$ | 1,4-dioxane | 0[c] |
| 10 | dMeObpy | $Cs_2CO_3$ | 1,4-dioxane | 75 |
| 11 | dMebpy | $Cs_2CO_3$ | 1,4-dioxane | 69 |
| 12 | bpy | $Cs_2CO_3$ | 1,4-dioxane | 56 |
| 13[d] | dMeObpy | $Cs_2CO_3$ | 1,4-dioxane | 0[c] |
| 14[e] | dMeObpy | $Cs_2CO_3$ | 1,4-dioxane | 0[c] |
| 15[f] | dMeObpy | $Cs_2CO_3$ | 1,4-dioxane | 0[c] |
| 16[g] | dMeObpy | $Cs_2CO_3$ | 1,4-dioxane | 83 |

[a]Reactions of **1a** (0.25 mmol) with **2a** (0.75 mmol) were carried out in the presence of fac-[Ir(ppy)$_3$] (0.005 mmol), anhydrous $NiCl_2$ (0.025 mmol), a ligand (0.0375 mmol), and an additive (0.375 mmol) in solvent (2.5 mL) with 12 W white LED illumination at 25 °C for 18 h. [b]Isolated yield. [c]Not detected by GC−MS. [d]In the absence of *fac*-[Ir(ppy)$_3$]. [e]In the absence of anhydrous $NiCl_2$. [f]In the absence of visible light. [g]24 h instead of 18 h.

mol % of 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy), and 1.5 equiv of $Cs_2CO_3$ as a photoredox catalyst, a cross-coupling catalyst, a coordination ligand for the nickel catalyst, and an additive, respectively, at 25 °C for 18 h under visible light illumination with a 12 W white light-emitting diode (LED), **3aa** was isolated in 50% yield (Table 1, entry 1). Here, addition of a base like $Cs_2CO_3$, well-known as an excellent and mild base to trap HI to promote cross-coupling reactions,[22] was necessary to produce **3aa** (Table 1, entry 2), whereas other bases like $K_2CO_3$ and NaOAc were found to be less effective to obtain **3aa** than $Cs_2CO_3$ (Table 1, entries 3 and 4). Solvent selection in catalysis was also examined to find out that use of 1,4-dioxane as a solvent instead of THF increased the yield of **3aa** up to 69% yield (Table 1, entry 5), while the use of other solvents such as acetonitrile, 1,2-dimethoxyethane (DME), and diethyl ether gave lower yields of **3aa**, respectively (Table 1, entries 6−8). Addition of a catalytic amount of a 2,2′-bipyridine derivative as a coordination ligand for nickel species was also found to be necessary for the formation of **3aa**, which was not obtained in the absence of dtbbpy (Table 1, entry 9). Further investigation on ligand selection for 2,2′-bipyridine derivatives revealed that use of 4,4′-dimethoxyl-2,2′-bipyridine (dMeObpy), where more electron-donating substituents were introduced onto the 4,4′-positions of the 2,2′-bipyridine skeleton, improved the yield of **3aa** up to 75% (Table 1, entry 10) compared to those found for using dtbbpy (Table 1, entry 5), 4,4′-dimethyl-2,2′-bipyridine (dMebpy) (Table 1, entry 11), or 2,2′-bipyridine (bpy) (Table 1, entry 12). When reactions were carried out in the absence of *fac*-[Ir(ppy)$_3$], anhydrous $NiCl_2$, or visible light irradiation, **3aa** was not obtained at all (Table 1, entries 13−15), demonstrating that both nickel and photoredox catalysts as well as visible light irradiation are all essential to promote the catalytic reaction. In addition, a longer reaction time (24 h) slightly improved the yield of **3a** in up to 83% yield (Table 1, entry 16).

With the optimized reaction conditions in hand, reactions of **1a** with various 4-alkyl-1,4-dihydropyridines (**2a**−**2s**) were next investigated (Scheme 1A). All the 4-benzyl-1,4-

**Scheme 1. Photodedox- and Nickel-Catalyzed Alkylative Cyclization Reactions**



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dihydropyridine derivatives, where either electron-donating or electron-withdrawing substituents (MeO: **2b**, Me: **2c**, Ph: **2d**, Cl: **2e**) were introduced at the 4-position of the benzene moiety, were successfully used as alkylation reagents to afford the corresponding alkylated cyclopentylidenes (**3aa**−**3ae**) in good to high yields, whereas only a trace amount of the corresponding desired product was obtained for the introduction of a cyano substituent at the same position (CN: **2f**) with most of **2f** transformed into *p*-tolunitrile as the major product. Introduction of a methyl group at the 3- or 2-position of the benzene moiety (3-Me: **2g**, 2-Me: **2h**) was also applicable to give the corresponding products (**3ag** and **3ah**) in good to high yields. Other 1,4-dihydropyridine derivatives with primary alkyl groups (1-naphthylmethyl: **2i**, *n*-nonyl: **2j**) or even with secondary alkyl groups (2-pentyl: **2ak**, cyclohexyl: **2l**) were also found to afford the corresponding alkylated cyclopentylidenes (**3ai**−**3al**) in good to high yields. The best yield (97%) was obtained for the isolation of (2-methylpentylidene)cyclopentane (**3ak**). On the other hand, the use of a bulkier secondary alkyl group such as CH(Me)Ph (**2m**) gave only a trace amount of the corresponding desired product. Alkylated cyclopentylidenes with ether or amine groups (**3an** and **3ao**) were also obtained in high yields from the corresponding 1,4-dihydropyridine derivatives (benzyloxymethyl: **2n**, *N*,*N*-dibenzylaminomethyl: **2o**), although introduction of an ester group was not successful (CH(Me)-$CO_2$Et: **2p**). It must be markworthy that the formation of the compounds with cyclopentylidene and heterocyclic units was achieved by using 4-methyl-1,4-dihydropyridine derivatives with heterocycle substituents (2-furyl: **2q**, 2-thienyl: **2r**) introduced to the methyl group to give the corresponding products (**3q** and **3r**) in high yields, whereas no desired product for the reaction of **1a** with a 3-pyridyl substituent (**2s**), mostly transformed into 3-methylpyridine.

In addition to **1a** containing a terminal alkyne moiety, conversion of internal iodoalkynes with methyl or phenyl groups introduced at the alkynyl group of 6-iodohex-1-yne (Me: **1b**, Ph: **1c**) were further investigated to react with **2a** to afford the corresponding alkylative cyclization products (**3ba**, **3ca**) in good yields (Scheme 1A). Thus, the present catalytic system is applicable to the internal alkynes, which was not achieved in the previous alkylative cyclization reactions using alkyl zinc reagents in the presence of nickel catalysts.[16]

Catalytic alkylative cyclization reactions of 6-iodohex-1-ynes containing one or two aryl or alkyl substituents introduced at the propargylic position with **2a** were further investigated (Scheme 1A). Indeed, treatment of (6-iodohex-1-yn-3-yl)-benzene (**1d**) with **2a** under the optimized reaction conditions afforded 2-(2-phenylcyclopentylidene)ethyl)benzene (**3da**) in 62% isolated yield as a mixture of *E*- and *Z*-isomers with the former as the major product (*E*/*Z* = 92/8). Introduction of one alkyl group such as ethyl (**1e**), *n*-butyl (**1f**), *n*-heptyl (**1g**), and cyclohexyl groups (**1h**) at the propargylic position in the starting iodohexynes also gave the corresponding desired products (**3ea**−**3ha**) in good yields with an excellent stereoselectivity (*E*/*Z* up to 93/7). Furthermore, the use of 6-iodo-3,3-dimethylhex-1-yne (**1i**), a terminal alkyne with two methyl groups introduced at the propargylic position, led to the formation of (2-(2,2-dimethylcyclopentylidene)ethyl)-benzene (**3ia**) in 77% yield almost selectively as an (*E*)-isomer (*E*/*Z* > 99/1). Similarly, reaction of **1i** with **2i** afforded 1-(2-(2,2-dimethylcyclopentylidene)ethyl)naphthalene (**3ii**) almost solely as an (*E*)-isomer (*E*/*Z* > 99/1), whose structure was determined by a single-crystal X-ray diffraction study (Scheme 1A).[23] The alkylative cyclization reaction of (7-iodohept-2-yn-4-yl)benzene (**1j**), an internal alkyne with one phenyl group introduced at the propargylic position, also proceeded to afford (2-(2-phenylcyclopentylidene)propyl)-benzene (**3ja**) as a mixture of two isomers with an *E*-stereoselectivity (*E*/*Z* = 89/11).

It must be noted that **3aa** was not obtained in a similar manner from the reaction of 6-bromohex-1-yne (**1a-Br**) or 6-chlorohex-1-yne (**1a-Cl**) instead of **1a** with **2a** under the typical reaction conditions, where **3aa** was obtained only in 4% yield (Scheme 1B). This result suggests that the existence of an iodide substituent as a leaving group is necessary for the dual catalytic system to proceed efficiently.[24]

Besides the alkylative cyclization reactions of 6-iodohex-1-ynes, the reaction of 7-iodohept-1-yne (**4a**) with **2a** was examined. Under the similar reaction conditions, the corresponding six-membered alkylative cyclization product (2-cyclohexylideneethyl)benzene (**5aa**) was obtained only in 5% yield (Scheme 1C). Expecting the Thorpe−Ingold effect,[25] introduction of substituents at the homopropargylic (**4b**) or propargylic position (**4c**) was also examined, but was in vain. Thus, the present catalytic alkylative cyclization reaction system is only effective for constructing a five-membered ring.

In order to obtain further mechanistic information, we next examined the reaction of **1a** with **2a** under the optimized reaction conditions but in the presence of 3 equiv of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical inhibitor. In fact, formation of the desired alkylative cyclization product **3aa** was perfectly inhibited. Instead, 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (**6a**),[26] the TEMPO-trapped benzyl adduct, was obtained in 69% yield. This experimental result demonstrates that the formation of a benzyl radical as a reactive intermediate is involved in the main catalytic reaction pathway (Figure 1A).[3,4,8,10,11,19,27]

Subsequently, Stern−Volmer analyses for emission quenching of *fac*-[Ir(ppy)$_3$] with **1** and **2a** were performed in 1,4-dioxane (Figure 1B). From the slopes obtained by the plot and the excited-state lifetime of *fac*-[Ir(ppy)$_3$] ($\tau$ = 1.90 $\mu$s),[28] the rate constants for the reduction of **1a** or **1d** and the oxidation of **2a** were determined to be at $k = (1.5 \pm 0.2) \times 10^7$ $M^{-1}$ $s^{-1}$ (**1a**), $k = (1.4 \pm 0.2) \times 10^7$ $M^{-1}$ $s^{-1}$ (**1d**), and $k = (7.3 \pm 0.7) \times 10^7$ $M^{-1}$ $s^{-1}$ (**2a**), respectively. This result indicates that reduction of **1** or oxidation of **2a** can occur *via* the SET process, where the oxidation of **2a** is 5 times as fast as the reduction of **1**. Additionally, the quantum yield of the typical reaction of **1a** with **2a** was measured to be $\Phi = 0.063 \pm 0.001$,[23] suggesting that the rate-determining step of the catalytic formation of **3aa** proceeds not *via* a radical chain process[29] but rather *via* sequential redox pathways, where alkyl radicals are mainly generated by the SET process between alkyl-1,4-dihydropyridines and an excited-state photoredox catalyst.[3,8,9,30,31] A light on/off experiment was further conducted for the reaction of **1a** with **2a** to afford **3aa** under the typical catalytic reaction conditions to present that the alkylative cyclization reaction perfectly ceased in the dark, which indicates that a chain propagation is not the main reaction pathway and that continuous irradiation of visible light is necessary for the reaction (Figure 1C).

On the other hand, formation of (2-(iodomethylene)-cyclopentyl)benzene (**7d**), a cyclic vinyl iodide, was observed spectroscopically as a reactive intermediate during the reaction of **1d** with **2a** to afford **3da** under the typical catalytic reaction


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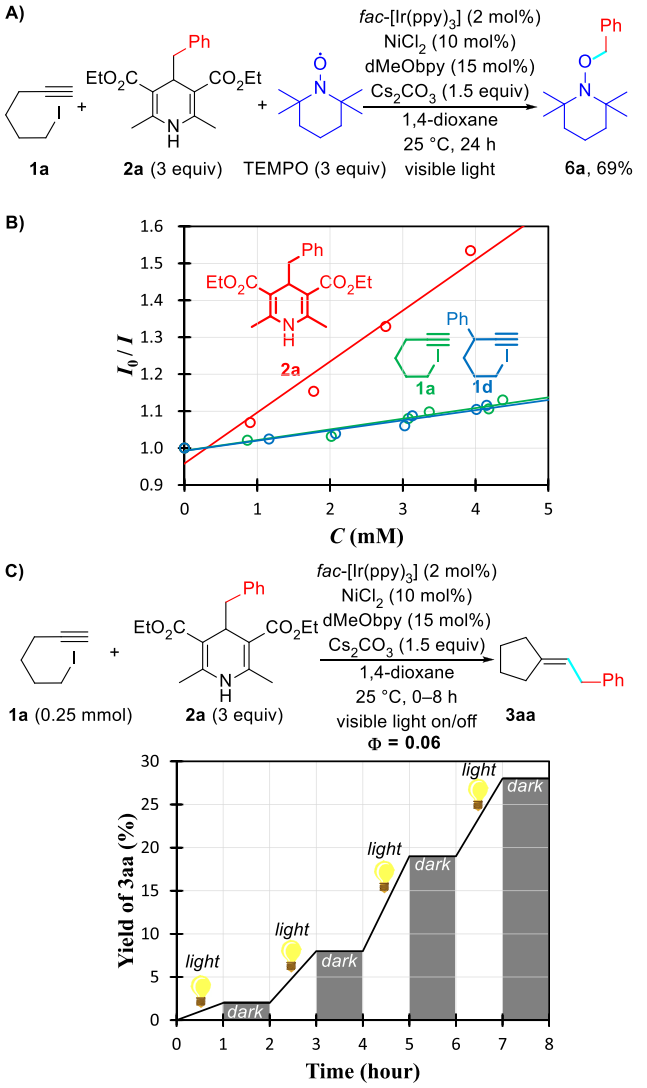


**Figure 1.** Mechanistic studies on the reactions of **1a** with **2a**. (A) Reaction in the presence of TEMPO. (B) Determination of quenching constants by Stern–Volmer plot for *fac*-[Ir(ppy)$_3$] with **1a**, **1d**, and **2a**. (C) Time profile of the reaction with and without visible light irradiation.

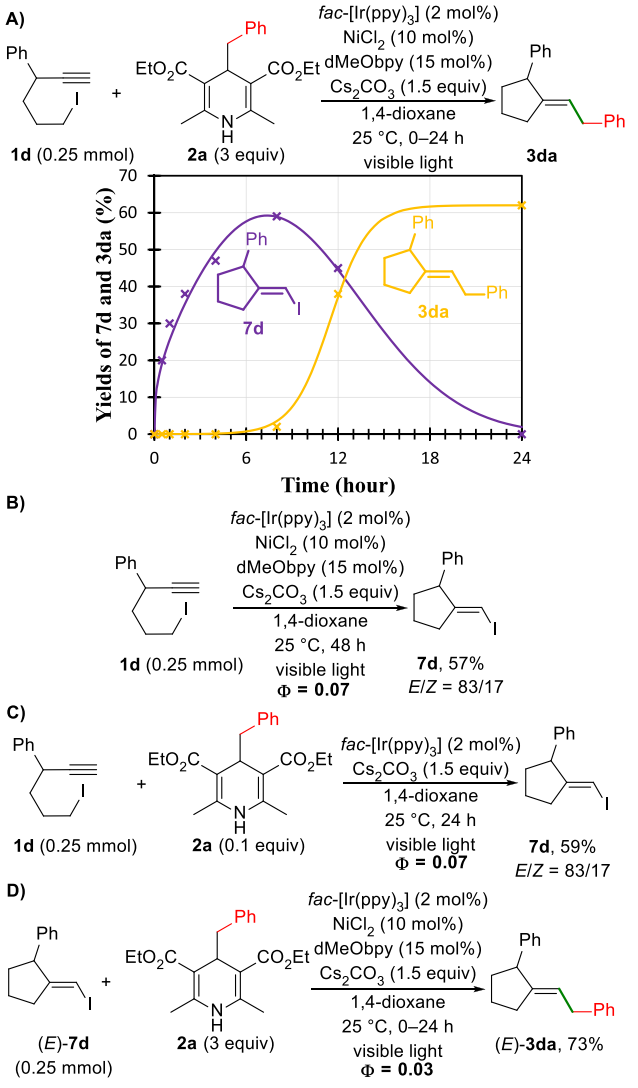


**Figure 2.** Formation of cyclopentylidene iodide as a reactive intermediate for the reactions of **1d** with **2a**. (A) Time profile of the reaction. (B) Reaction in the absence of **2a**. (C) Reaction in the presence of a catalytic amount of **2a** but in the absence of Ni catalysts. (D) Reaction of (*E*)-**7d** with **2a** to afford (*E*)-**3da** without *E*/*Z* isomerization.

conditions (Figure 2A). Indeed, **7d** was isolated as the major product in 57% yield with an *E*/*Z* ratio of 83/17 for the reaction of **1d** under the typical catalytic reaction conditions but in the absence of **2a** (Figure 2B) with the quantum yield found at $\Phi = 0.072 \pm 0.002$.[23] The control experiments exhibited that the conversion of **1d** into **7d** did not take place in the absence of any of *fac*-[Ir(ppy)$_3$], anhydrous $NiCl_2$, dMeObpy, $Cs_2CO_3$, or visible light irradiation, revealing that all these elements are required for the cyclization reaction to afford **7d**, when **2a** is not present. However, **7d** was also isolated as the major product in 59% yield with *E*/*Z* ratio of 83/17 without the formation of **3da** for the reaction of **1d** under the typical reaction conditions in the absence of anhydrous $NiCl_2$ and dMeObpy but in the presence of a catalytic amount of **2a** (0.1 equiv) (Figure 2C), clearly indicating that the cyclization reaction of **1d** into **7d** actually does not require nickel catalyst, when **2a** is present. It must be noted that Melchiorre and co-workers have recently demonstrated that 4-alkyl-1,4-dihydropyridines including **2a** have an ability to absorb visible light less than 420 nm in wavelength,[10,13] while almost no reaction occurred for the control experiment of Figure 2C in the absence of *fac*-[Ir(ppy)$_3$], confirming that **2a** does not work as an efficient photosensitizer and that the presence of *fac*-[Ir(ppy)$_3$] is necessary for visible-light-induced cyclization reactions. Cyclization reaction of 6-iodohex-1-ynes to afford cyclopentylidenes has been already known to be promoted by radical initiators,[32] and similar visible- or UV-light-induced cyclization reactions of 6-iodohex-1-ynes to afford cyclopentylidenes have been more recently reported by the groups of Martin[33] and Zhang,[34] where cyclization has been proposed to occur *via* the formation of a weak charge-transfer complex between an amine and alkyl iodide capable of forming an exciplex state under irradiation of blue light,[33] or *via* chain propagation pathways triggered by the abstraction of an iodine atom from alkyl iodide.[33,34] In the present reaction conditions, **2a** does not work to form an exciplex state,[35] thus a propagation pathway is more plausible for the formation of **7d**, although the low quantum yield at $\Phi = 0.067 \pm 0.003$ obtained under the reaction conditions similar


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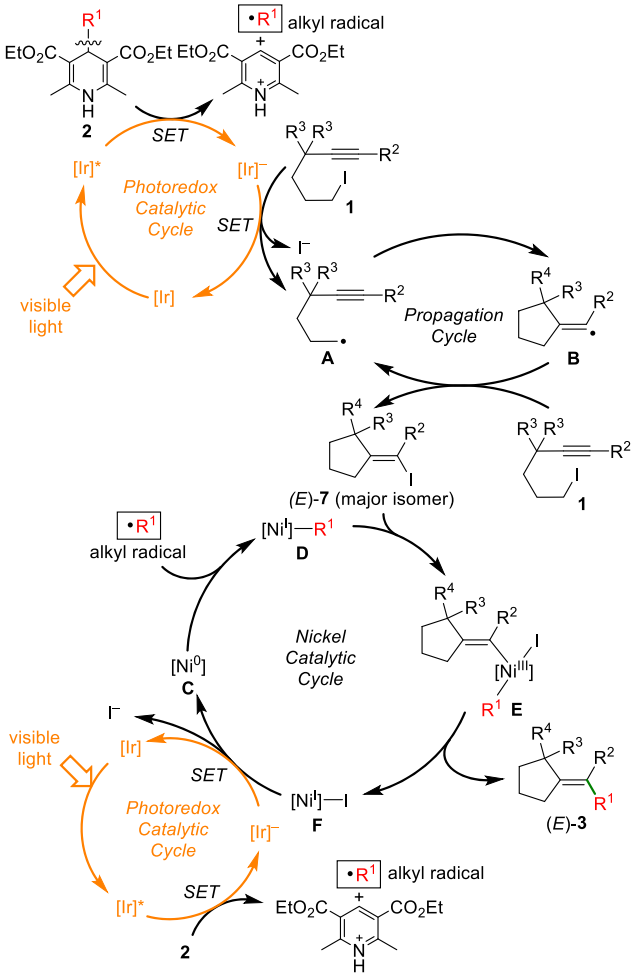
to Figure 2C[23] and the moderate quantum yield at Φ = 0.290 ± 0.003 obtained under the reaction conditions similar to Figure 2C but in the presence of 3 equiv of **2a**[23] have disclosed that the propagation is inhibited by any radicals formed *in situ* and that the reaction pathways of the initial cyclization reaction are rather complicated counting the contribution of nickel catalysis in the absence of **2a**,[23] which requires more deep mechanistic studies to clarify the roles of photoredox and nickel catalysts, and of 4-alkyl-dihydropyridines and 6-iodohex-1-ynes in catalysis. In all cases for the formation of **7d**, *E*/*Z* selectivity (83/17) is almost the same, which is thus likely controlled mainly by the steric hindrance of the substituent introduced to 6-iodohex-1-yne.

In order to confirm that vinyl iodide species like **7d** are the reactive intermediate of the present alkylative cyclization reactions, the reaction of isolated (*E*)-**7d** with **2a** under the similar catalytic conditions was further examined to elucidate that (*E*)-**3da** was obtained in 73% isolated yield as the sole stereoisomer (Figure 2D) with the low quantum yield observed at Φ = 0.028 ± 0.001. This result demonstrates that **7d** may be formed as a reactive intermediate. The photoredox- and nickel-catalyzed cross-coupling reaction of (*E*)-**7** with **2a** proceeds to afford (*E*)-**3da** without *E*/*Z* isomerization, which matches our previous report.[9]

A plausible reaction pathway for the cooperative photoredox- and nickel-catalyzed alkylative cyclization reactions can be drawn as shown in Scheme 2, consisting of two sequential reactions, *i.e.*, (1) cyclization reaction of **1** into **7** and (2) alkylation of **7** into **3**, both of which require the Ir photoredox catalyst. In the initial iridium photoredox cycle, excitation of the Ir(III) catalyst *fac*-[Ir(ppy)$_3$] ([Ir]) by the absorption of visible light occurs to give the excited state ([Ir]*). The subsequent SET processes between [Ir]* and other substrates including **1** or nickel species are possible, but the fastest SET process can occur between [Ir]* and **2** as suggested by the Stern−Volmer analysis (Figure 1B) to afford the reduced Ir(II) species ([Ir]$^-$) and a radical cationic 1,4-dihydropyridine, which is further converted to an alkyl radical (·R$^1$) and an aromatized pyridine derivative *via* C−C bond cleavage.[3,30] Here, [Ir]$^-$ is capable of abstracting iodide (I$^-$) from **1** to generate [Ir] and the hex-5-yn-1-yl radical (**A**), which is further cyclized into the cyclopentylidene radical (**B**).[33,34] **B** can be engaged in the iodine atom transfer with **1** to afford the radical **A** and the cyclopentylidene iodide **7**, where the (*E*)-isomer is rather preferentially formed. On the other hand, rather low quantum yields observed for the formation of **7** suggest that such propagation is inhibited by alkyl and other radicals formed *in situ*. It goes without saying that other reaction pathways including the cooperative photoredox- and nickel-catalyzed cyclization reaction pathway can also contribute to the formation of **7**,[23] which are not shown in Scheme 2 for clarity.

Subsequently to the formation of **7**, alkylation of **7** with the alkyl radical ·R$^1$ into **3** occurs by the cooperation of photoredox and nickel catalyst. In the nickel cycle, capture of the alkyl radical ·R$^1$ by an *in situ*-generated Ni(0) species (**C**) occurs to afford a Ni(I)−alkyl complex (**D**), where the oxidative addition of (*E*)-**7** occurs to give a Ni(III) (alkenyl)(alkyl) iodide complex (**E**), followed by the reductive elimination of the desired coupling product (*E*)-**3** along with the formation of a Ni(I) iodide complex (**F**). Finally, the nickel catalytic cycles are completed by a SET process between the reduced Ir(II) catalyst [Ir]$^-$ and the Ni(I) iodide complex **F**.

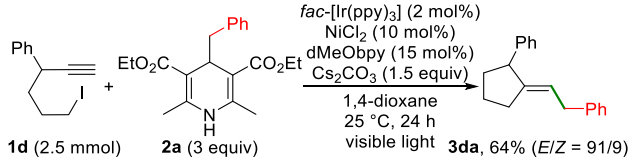
**Scheme 2. Plausible Reaction Pathway**




(*Z*)-**7** can also participate in the nickel-catalyzed transformation to afford (*Z*)-**3**, although (*E*)-**7** more preferentially adds the nickel catalyst to afford (*E*)-**3**, resulting in a slight increase in the ratio of (*E*)-**3** compared to that of (*E*)-**7** (83/17 to 92/8 in the case of **7d** and **3da**, respectively). The combination of two sequential reactions, *i.e.*, (1) cyclization reaction of **1** into **7** and (2) alkylation of **7** into **3**, can cause a long induction period for the conversion of **7d** into **3da** as it appears in Figure 2A, where the generated alkyl radical ·R$^1$ can be quenched in several ways.

Finally, a larger scale reaction of **1d** (2.5 mmol) with **2a** (7.5 mmol) was performed under the optimized reaction conditions to afford the alkylative cyclization product **3da** in 64% isolated yield as a mixture of *E*- and *Z*-isomers with an *E*/*Z* ratio of 91/9 (Scheme 3).

**Scheme 3. Large-Scale Preparation of 3da**





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## CONCLUSION

We have achieved the cooperative photoredox- and nickel-catalyzed alkylative cyclization reactions of 6-iodohex-1-ynes with 4-alkyl-1,4-dihydropyridines employed as alkylation reagents at room temperature under the irradiation of visible light to afford the corresponding alkylated cyclopentylidenes in good to high yields. In addition to terminal alkynes, internal alkynes can also be converted into the desired products, which were not achieved in the previously reported catalytic alkylative cyclization reactions with alkyl zinc reagents as alkylation reagents.[16] Introduction of substituents at the propargylic position of 6-iodohex-1-ynes has led to the stereoselective formation of *E*-isomers. We consider that the method described herein expands the usage of 4-alkyl-1,4-dihydropyridines as mild formal alkylation reagents in the combination of photoredox and transition metal catalysts to provide novel transformations of organic compounds under mild reaction conditions.

## EXPERIMENTAL SECTION

**General Information.** All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. **1a**,[36] **1a-Br**,[37] **1b**,[38] **1c**,[39] **1i**,[40] **2a**,[41] **2b**,[41] **2c**,[41] **2d**,[8] **2e**,[41] **2g**,[3] **2h**,[3] **2i**,[9] **2j**,[42] **2k**,[41] **2l**,[41] **2m**,[41] **2n**,[8] **2o**,[3] **2p**,[42] **2r**,[6] **2s**,[43] **4a**,[44] **4c**,[45] and **5aa**[46] were prepared according to the literature procedures. Other reagents including starting materials for the preparation of **1a−j**, **2a−s**, **4a−c**, **1a-Cl**, *fac*-[Ir(ppy)$_3$], *fac*-[Ir(Fppy)$_3$], anhydrous $NiCl_2$, ligands (bpy, dtbbpy, dMebpy, dMeObpy), bases, TEMPO, and solvents were obtained from commercial sources. Acetonitrile, diethyl ether, *n*-hexane, and THF were purified by passing through a purification system (Glass Contour) and were degassed before use. Other solvents were dried by general methods and degassed before use. Flash column chromatography was carried out on a Yamazen YFLC-AI-580 system. Gas chromatography−mass spectroscopy (GC−MS) was performed on a Shimadzu GCMS-QP2010 PLUS instrument. *E*/*Z* ratios were determined by quantitative measurements of GC−MS. X-ray analysis was performed by a Rigaku XtaLAB Synergy-S diffractometer. Photoluminescence spectra were measured on a Shimadzu RF-5300PC spectrophotometer. Melting points were measured by using a Stanford Research Systems OptiMelt MPA100. High-resolution FAB mass spectra were measured on a JEOL JMS-700 mass spectrometer. $^1$H NMR (400 MHz) and $^{13}$C{$^1$H} NMR (100 MHz) spectra were measured in $CDCl_3$ on a JEOL ECS-400 spectrometer with $\delta$ values calibrated by using residual peaks of $CHCl_3$ ($^1$H: 7.26) and $CDCl_3$ ($^{13}$C: 77.0), respectively.

**General Procedure for the Preparation of 6-Iodohex-1-yne Derivatives (1) (Taking (6-Iodohex-1-yn-3-yl)benzene (1d) as an Example).** In a 100 mL Schlenk flask were placed prop-2-yn-1-ylbenzene (2.32 g, 20.0 mmol) and THF (25 mL) at −78 °C by using a dry ice−methanol bath under $N_2$, where a hexane solution of $^n$BuLi (32 mL, 1.57 M, *ca.* 50 mmol) was added dropwise. The reaction mixture was gradually warmed to 30 °C by using an oil bath and was further stirred for 2 h. Then the reaction mixture was cooled back to −78 °C by using a dry ice−methanol bath, and 1-bromo-3-chloropropane (3.15 g, 20.0 mmol) was added dropwise. The reaction mixture was gradually warmed to 40 °C by using an oil bath and was further stirred for 2 h. The resultant mixture was quenched with a saturated aqueous solution of $NH_4Cl$ (40 mL), and the aqueous phase was extracted with $Et_2O$ (50 mL × 3). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was collected, and the solvent was removed under reduced pressure. The residue was further purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (6-chlorohex-1-yn-3-yl)benzene (**1d-Cl**) as a colorless oil (2.72 g, 14.1 mmol, 71% yield based on the amount of prop-2-yn-1-ylbenzene), which was directly used in the subsequent transformation to obtain (6-iodohex-1-yn-3-yl)benzene (**1d**) without further purification.

In a 100 mL Schlenk flask were placed **1d-Cl** (2.60 g, 13.5 mmol), NaI (10.1 g, 67.5 mmol), and acetone (40 mL) under $N_2$, and the reaction mixture was stirred and refluxed for 18 h by using an oil bath. Then, acetone was removed *in vacuo*, and the resultant mixture was diluted with 100 mL of *n*-hexane and was filtered. Solvent was removed from the collected filtrate under reduced pressure, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (6-iodohex-1-yn-3-yl)benzene (**1d**) as a colorless oil (3.64 g, 12.8 mmol, 95% yield based on the amount of **1d-Cl**, 64% yield based on the amount of prop-2-yn-1-ylbenzene). HRMS (FAB) *m*/*z* [M]$^+$ Calcd for $C_{12}H_{13}I$ 284.0062; Found: 284.0059. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.36−7.16 (m, 5H, CH of Ph), 3.62 (td, *J* = 6.0, 2.3 Hz, 1H, CHC≡), 3.12 (t, *J* = 6.8 Hz, 2H, $CH_2$I), 2.24 (d, *J* = 2.3 Hz, 1H, HC≡), 2.01−1.73 (m, 4H, $CH_2$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, $\delta$): 140.7 (*ipso*-C of Ph), 128.5, 127.2 (*o*- and *m*-CH of Ph), 126.9 (*p*-CH of Ph), 85.0 (C≡), 71.6 (HC≡), 38.7, 36.4, 30.8 (CH($CH_2$)$_2$), 6.2 ($CH_2$I).

*3-Ethyl-6-iodohex-1-yne (1e).* A colorless oil (283 mg, 1.20 mmol, 12% yield based on the amount of pent-1-yne (680 mg, 9.98 mmol)). HRMS (FAB) *m*/*z* [M]$^+$ Calcd for $C_8H_{13}I$ 236.0062; Found: 236.0054. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 3.19 (t of pseudo d, *J* = 4.8, 2.1 Hz, 2H, $CH_2$I), 2.31−2.22 (m, 1H, CHC≡), 2.10−1.97 (m, 1H, C$H_2$CH$_2$I), 2.05 (d, *J* = 2.4 Hz, 1H, HC≡), 1.96−1.84 (m, 1H, C$H_2$CH$_2$I), 1.62−1.39 (m, 4H, C$H_2$CHC$H_2$), 0.99 (t, *J* = 7.6 Hz, 3H, $CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, $\delta$): 86.8 (C≡), 69.8 (HC≡), 35.1, 32.2, 31.0, 27.9 ($CH_2$CH($CH_2$)$_2$), 11.6 ($CH_3$), 6.7 ($CH_2$I).

*4-Ethynyl-1-iodooctane (1f).* A colorless oil (451 mg, 1.71 mmol, 17% yield based on the amount of hept-1-yne (962 mg, 10.0 mmol)). HRMS (FAB) *m*/*z* [M]$^+$ Calcd for $C_{10}H_{17}I$ 264.0375; Found: 264.0383. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 3.20 (t of pseudo d, *J* = 6.9, 2.5 Hz, 2H, $CH_2$I), 2.38−2.28 (m, 1H, CHC≡), 2.14−1.98 (m, 1H, C$H_2$CH$_2$I), 2.05 (d, *J* = 2.2 Hz, 1H, HC≡), 1.97−1.84 (m, 1H, C$H_2$CH$_2$I), 1.64−1.22 (m, 8H, ($CH_2$)$_3$CHC$H_2$), 0.90 (t, *J* = 7.2 Hz, 3H, $CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, $\delta$): 87.1 (C≡), 69.7 (HC≡), 35.5, 34.6, 31.1, 30.5, 29.3, 22.5 (($CH_2$)$_3$CH($CH_2$)$_2$), 14.0 ($CH_3$), 6.7 ($CH_2$I).

*4-Ethynyl-1-iodoundecane (1g).* A colorless oil (334 mg, 1.09 mmol, 11% yield based on the amount of 1-bromo-3-chloropropane (1.57 g, 9.99 mmol)). HRMS (FAB) *m*/*z* [M]$^+$ Calcd for $C_{13}H_{23}I$ 306.0845; Found: 306.0840. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 3.20 (t of pseudo d, *J* = 7.0, 2.4 Hz, 2H, $CH_2$I), 2.37−2.28 (m, 1H, CHC≡), 2.12−1.98 (m, 1H, C$H_2$CH$_2$I), 2.04 (d, *J* = 2.4 Hz, 1H, HC≡), 1.97−1.84 (m, 1H, C$H_2$CH$_2$I), 1.63−1.20 (m, 14H, ($CH_2$)$_6$CHC$H_2$), 0.87 (t, *J* = 6.8 Hz, 3H, $CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, $\delta$): 87.1 (C≡), 69.7 (HC≡), 35.6, 34.9, 31.8, 31.1, 30.6, 29.4, 29.2, 27.2, 22.6 (($CH_2$)$_6$CH($CH_2$)$_2$), 14.1 ($CH_3$), 6.7 ($CH_2$I).

*(6-Iodohex-1-yn-3-yl)cyclohexane (1h).* A colorless oil (627 mg, 2.16 mmol, 28% yield based on the amount of 1-bromo-3-chloropropane (1.21 g, 7.69 mmol)). HRMS (FAB) *m*/*z* [M]$^+$ Calcd for $C_{12}H_{19}I$ 290.0532; Found: 290.0528. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 3.18 (t of pseudo d, *J* = 6.9, 1.5 Hz, 2H, $CH_2$I), 2.22−2.16 (m, 1H, CHC≡), 2.08−1.98 (m, 1H, CH of Cy), 2.03 (d, *J* = 2.4 Hz, 1H, HC≡), 1.91−1.44, 1.36−1.04 (both m, 8H and 6H, respectively, $CH_2$ of CyCH($CH_2$)$_2$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, $\delta$): 85.7 (C≡), 70.6 (HC≡), 40.9, 40.8, 36.7, 32.7, 31.3, 31.1, 29.0, 26.2, 26.1 (CyCH($CH_2$)$_2$), 6.8 ($CH_2$I).

**Preparation of (7-Iodohept-2-yn-4-yl)benzene (1j).** In a 100 mL Schlenk flask were placed prop-2-yn-1-ylbenzene (1.16 g, 10.0 mmol) and THF (14 mL) at −78 °C by using a dry ice−methanol bath under $N_2$, where a hexane solution of $^n$BuLi (16.1 mL, 1.57 mol/L, ca. 25 mmol) was added dropwise. The reaction mixture was gradually warmed to 30 °C by using an oil bath and was further stirred for 2 h. The reaction mixture was cooled back to −78 °C by using a dry ice−methanol bath, and 1-bromo-3-chloropropane (1.57 g, 10.0 mmol) was added dropwise. The reaction mixture was gradually warmed to 40 °C by using an oil bath and was further stirred for 2 h. Then, the reaction mixture was cooled to 0 °C by using an ice−water


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bath, and iodomethane (1.42 g, 10.0 mmol) was added dropwise. The reaction mixture was gradually warmed to 40 °C by using an oil bath and was further stirred for 2 h. The resultant mixture was quenched with a saturated solution of $NH_4Cl$ (40 mL), and the aqueous phase was extracted with $Et_2O$ (30 mL × 3). The combined organic layers were washed with brine (20 mL × 2), dried over $MgSO_4$, and filtered. The filtrate was collected, and the solvent was removed under reduced pressure. The residue was further purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (7-chlorohept-2-yn-4-yl)benzene (**1j-Cl**) as a colorless oil (924 mg, 0.447 mmol, 45% yield based on the amount of 1-bromo-3-chloropropane), which was directly used in the subsequent transformation to obtain (7-iodohept-2-yn-4-yl)benzene (**1j**) without further purification.

In a 100 mL Schlenk flask were placed **1j-Cl** (621 mg, 3.02 mmol), NaI (2.25 g, 15.0 mmol), and acetone (40 mL) under $N_2$, and the reaction was stirred and refluxed by using an oil bath for 18 h. Then, acetone was removed *in vacuo*, and the resultant mixture was diluted with 100 mL of *n*-hexane and was filtered. Solvent was removed from the collected filtrate under reduced pressure, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (7-iodohept-2-yn-4-yl)benzene (**1j**) as a colorless oil (608 mg, 2.04 mmol, 68% yield based on the amount of **1j-Cl**, 20% yield based on the amount of 1-bromo-3-chloropropane). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{13}H_{15}I$ 298.0219; Found 298.0207. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.38−7.30 (m, 4H, *o*-and *m*-CH of Ph), 7.24 (tt, *J* = 6.7, 2.1 Hz, 1H, *p*-CH of Ph), 3.62 (t of pseudo t, *J* = 8.3, 2.4 Hz, 1H, CHC≡), 3.20 (t, 2H, *J* = 6.8, $CH_2I$), 2.04−1.89 (m, 2H, $CH_2CH_3$), 1.88 (d, *J* = 2.8 Hz, 3H, $CH_3$), 1.88−1.74 (m, 2H, $CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 142.0 (*ipso*-C of Ph), 128.3, 127.2 (*o*- and *m*-CH of Ph), 126.6 (*p*-CH of Ph), 80.0, 78.9 (C≡C), 39.2, 36.7, 31.1 ($CH(CH_2)_2$), 6.5, 3.6 ($CH_2I$ and $CH_3$).

**General Procedure for the Preparation of Diethyl 4-Alkyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate Derivatives (1) (Taking Diethyl 4-(Furan-2-ylmethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2q) as an Example).** In a 50 mL Schlenk flask were placed 2-furanacetaldehyde (396 mg, 3.60 mmol), ethyl acetoacetate (938 mg, 7.20 mmol), and ethanol (20 mL) at room temperature under $N_2$, where an aqueous solution of 28 wt % $NH_3$ (1.1 mL, ca. 18 mmol) was added. The reaction mixture was stirred and refluxed for 18 h by using an oil bath, then was dried *in vacuo*. The residue was further purified by column chromatography ($SiO_2$) with a mixture of *n*-hexane/ethyl acetate (7:3) as an eluent to afford diethyl 4-(furan-2-ylmethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2q**) as a white solid (600 mg, 1.80 mmol, 50% yield based on the amount of 2-furanacetaldehyde). mp 106.0−107.3 °C. HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{18}H_{23}NO_5$ 333.1576; Found 333.1579. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.24 (dd, *J* = 1.8, 1.0 Hz, 1H, 5-CH of furyl), 6.19 (dd, *J* = 3.1, 1.8 Hz, 1H, 4-CH of furyl), 5.84 (d, *J* = 3.1 Hz, 1H, 3-CH of furyl), 5.69 (br, 1H, NH), 4.18 (t, *J* = 5.7 Hz, 1H, 4-CH of 1,4-dihydropyridine), 4.15−4.03 (m, 4H, $CH_3CH_2$), 2.59 (d, *J* = 5.7 Hz, 2H, $CH_2$ of furan-2-ylmethyl), 2.22 (s, 6H, 2-$CCH_3$ of 1,4-dihydropyridine) 1.25 (t, *J* = 7.0 Hz, 6H, $CH_3CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 167.6 ($CO_2$), 154.0 (2-C of furyl), 145.3 (2-C of 1,4-dihydropyridine), 140.8 (5-CH of furyl), 110.1, 106.8 (3-CH and 4-CH of furyl), 101.9 (3-C of 1,4-dihydropyridine), 59.7 ($CH_3CH_2$), 34.2, 33.9 (4-$CHCH_2$ of 1,4-dihydropyridine), 19.3 (2-$CCH_3$ of 1,4-dihydropyridine), 14.3 ($CH_3CH_2$).

*Diethyl 4-(4-Cyanobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2f**).* A white solid (371 mg, 1.01 mmol, 25% yield based on the amount of 4-(2-oxoethyl)benzonitrile (581 mg, 4.00 mmol)). mp 156.7−158.5 °C. HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{21}H_{24}N_2O_4$ 368.1736; Found: 368.1741. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.44, 7.10 (both d, *J* = 8.0 Hz, 2H each, $C_6H_4$), 5.74 (br, 1H, NH), 4.21 (t, *J* = 5.4 Hz, 1H, 4-CH of 1,4-dihydropyridine), 4.12−3.98 (m, 4H, $CH_3CH_2$), 2.62 (d, *J* = 5.4 Hz, 2H, $CH_2$ of 4-cyanobenzyl), 2.14 (s, 6H, 2-$CCH_3$ of 1,4-dihydropyridine) 1.21 (t, *J* = 7.2 Hz, 6H, $CH_3CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 167.5 ($CO_2$), 146.0 (*ipso*-C of $C_6H_4$), 145.4 (2-C of 1,4-dihydropyridine), 130.8, 130.7 (*o*- and *m*-CH of $C_6H_4$), 119.3 (CN), 109.2 (*p*-C of $C_6H_4$), 101.0 (3-C of 1,4-dihydropyridine), 59.6 ($CH_3CH_2$), 42.3 (4-$CHCH_2$ of 1,4-dihydropyridine), 35.4 (4-$CHCH_2$ of 1,4-dihydropyridine), 18.9 (2-$CCH_3$ of 1,4-dihydropyridine), 14.3 ($CH_3CH_2$).

**General Procedure for the Preparation of Alkylated Cyclopentylidenes (Taking (2-Cyclopentylideneethyl)benzene (3aa) as an Example).** In a 20 mL Schlenk flask were placed 6-iodohex-1-yne (**1a**) (50.1 mg. 0.241 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2a**) (260 mg, 0.756 mmol), *fac*-$[Ir(ppy)_3]$ (3.4 mg, 0.0052 mmol), anhydrous $NiCl_2$ (3.4 mg, 0.026 mmol), dMeObpy (8.0 mg, 0.037 mmol), and $Cs_2CO_3$ (122 mg, 0.375 mmol) under $N_2$, where 1,4-dioxane (2.5 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C and was illuminated from the bottom of the bath with an Aitech System TMN100×120−22WD 12 W white LED lamp (400−750 nm) at a distance of approximately 2 cm from the light source for 24 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (2-cyclopentylideneethyl)benzene (**3aa**) as a colorless oil (34.5 mg, 0.200 mmol, 83% yield based on the amount of **1a**). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{13}H_{16}$ 172.1252; Found: 172.1247. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.30 (t, *J* = 7.6 Hz, 2H, *m*-CH of Ph), 7.24−7.17 (m, 3H, *o*- and *p*-CH of Ph), 5.47 (tt, *J* = 7.2, 2.3 Hz, 1H, CH═), 3.35 (d, *J* = 7.2 Hz, 2H, $CH_2CH$═), 2.31 (pseudo q, *J* = 7.6 Hz, 4H, $\alpha$-$CH_2$ of cyclopentylidene), 1.73, 1.65 (both quint, *J* = 6.9 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 144.4 (*ipso*-C of cyclopentylidene), 141.8 (*ipso*-C of Ph), 128.3, 128.3 (*o*- and *m*-CH of Ph), 125.7 (*p*-CH of Ph), 118.6 (CH═), 35.9 ($CH_2CH$═), 33.6, 28.8 ($\alpha$-$CH_2$ of cyclopentylidene), 26.4, 26.3 ($\beta$-$CH_2$ of cyclopentylidene).

*1-(2-Cyclopentylideneethyl)-4-methoxylbenzene (**3ab**).* A colorless oil (39.4 mg, 0.195 mmol, 81% yield based on the amount of **1a** (50.3 mg, 0.242 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{14}H_{18}O$ 202.1358; Found: 202.1357. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.11, 6.84 (both dt, *J* = 8.8, 2.2 Hz, 2H each, $C_6H_4$), 5.44 (t of quint, *J* = 7.1, 2.1 Hz, 1H, CH═), 3.79 (s, 3H, $CH_3$), 3.28 (d, *J* = 7.1 Hz, 2H, $CH_2CH$═), 2.33−2.25 (m, 4H, $\alpha$-$CH_2$ of cyclopentylidene), 1.71, 1.64 (both quint, *J* = 6.7 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 157.7 (*p*-C of $C_6H_4$), 144.0 (*ipso*-C of cyclopentylidene), 133.9 (*ipso*-C of $C_6H_4$), 129.1 (*o*-C of $C_6H_4$), 119.0 (CH═), 113.7 (*m*-C of $C_6H_4$), 55.2 ($CH_3$), 35.0 ($CH_2CH$═), 33.6, 28.8 ($\alpha$-$CH_2$ of cyclopentylidene), 26.4, 26.3 ($\beta$-$CH_2$ of cyclopentylidene).

*1-(2-Cyclopentylideneethyl)-4-methylbenzene (**3ac**).* A colorless oil (36.8 mg, 0.198 mmol, 82% yield based on the amount of **1a** (50.1 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{14}H_{18}$ 186.1409; Found: 186.1400. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.17−7.06 (m, 4H, $C_6H_4$), 5.46 (t of quint, *J* = 7.1, 1.9 Hz, 1H, CH═), 3.31 (d, *J* = 7.1 Hz, 2H, $CH_2CH$═), 2.34 (s, 3H, $CH_3$), 2.34−2.26 (m, 4H, $\alpha$-$CH_2$ of cyclopentylidene), 1.72, 1.65 (both quint, *J* = 6.8 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 144.1 (*ipso*-C of cyclopentylidene), 138.7, 135.1 (*ipso*- and *p*-C of $C_6H_4$), 129.0, 128.1 (CH of $C_6H_4$), 118.9 (CH═), 35.5 ($CH_2CH$═), 33.6, 28.8 ($\alpha$-$CH_2$ of cyclopentylidene), 26.4, 26.3 ($\beta$-$CH_2$ of cyclopentylidene), 21.0 ($CH_3$).

*4-(2-Cyclopentylideneethyl)-1,1′-biphenyl (**3ad**).* A colorless oil (46.6 mg, 0.188 mmol, 78% yield based on the amount of **1a** (50.1 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{19}H_{20}$ 248.1565; Found: 248.1561. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.58 (dt, *J* = 7.8, 1.8 Hz, 2H, 2′- and 6′-CH of 1,1′-biphenyl), 7.53 (dt, *J* = 8.5, 1.8 Hz, 2H, 2- and 6-CH of 1,1′-biphenyl), 7.44 (tt, *J* = 7.8, 1.8 Hz, 2H, 3′- and 5′-CH of 1,1′-biphenyl), 7.33 (tt, *J* = 7.8, 1.8 Hz, 1H, 4′-CH of 1,1′-biphenyl), 7.28 (d, *J* = 8.5 Hz, 2H, 3- and 5-CH of 1,1′-biphenyl), 5.50 (t of quint, *J* = 7.2, 2.3 Hz, 1H, CH═), 3.39 (d, *J* = 7.2 Hz, 2H, $CH_2CH$═), 2.34, 2.32 (both t, *J* = 6.7 Hz, 2H each, $\alpha$-$CH_2$ of cyclopentylidene), 1.73, 1.66 (both quint, *J* = 6.7 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 144.6 (*ipso*-C of cyclopentylidene), 141.2, 140.9, 138.7 (1, 1′-, and 4-C of 1,1′-biphenyl), 128.7, 127.1, 127.0 (*o*- and *m*-CH of 1,1′-


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biphenyl with two resonances overlapping at δ 128.7), 126.9 (4′-CH of 1,1′-biphenyl), 118.5 (CH═), 35.6 ($CH_2CH$═), 33.7, 28.9 (α-$CH_2$ of cyclopentylidene), 26.5, 26.4 (β-$CH_2$ of cyclopentylidene).

*1-Chloro-4-(2-cyclopentylideneethyl)benzene (**3ae**).* A colorless oil (32.6 mg, 0.158 mmol, 65% yield based on the amount of **1a** (50.1 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{13}H_{15}Cl$ 206.0862; Found: 206.0863. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.24, 7.12 (both d, *J* = 7.8 Hz, 2H each, $C_6H_4$), 5.41 (t of quint, *J* = 7.4, 2.4 Hz, 1H, CH═), 3.30 (d, *J* = 7.4 Hz, 2H, $CH_2CH$═), 2.28 (t, *J* = 6.7 Hz, 4H, α-$CH_2$ of cyclopentylidene), 1.71, 1.64 (both quint, *J* = 6.7 Hz, 2H each, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 145.0 (*ipso*-C of cyclopentylidene), 140.2 (*ipso*-C of $C_6H_4$), 131.3 (*p*-C of $C_6H_4$), 129.6, 128.4 (CH of $C_6H_4$), 118.1 (CH═), 35.2 ($CH_2CH$═), 33.6, 28.8 (α-$CH_2$ of cyclopentylidene), 26.4, 26.3 (β-$CH_2$ of cyclopentylidene).

*1-(2-Cyclopentylideneethyl)-3-methylbenzene (**3ag**).* A colorless oil (31.7 mg, 0.170 mmol, 70% yield based on the amount of **1a** (50.3 mg, 0.242 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{14}H_{18}$ 186.1409; Found: 186.1411. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.18 (t, *J* = 7.6, 1H, 5-CH of $C_6H_4$), 7.03−6.98 (m, 3H, 1-, 4-, and 6-CH of $C_6H_4$), 5.45 (t of quint, *J* = 7.4, 2.3 Hz, 1H, CH═), 3.31 (d, *J* = 7.4 Hz, 2H, $CH_2CH$═), 2.34 (s, 3H, $CH_3$), 2.34−2.26 (m, 4H, α-$CH_2$ of cyclopentylidene), 1.72, 1.64 (both quint, *J* = 7.0 Hz, 2H each, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 144.2 (*ipso*-C of cyclopentylidene), 141.7, 137.9 (1- and 3-C of $C_6H_4$), 129.1, 128.2, 126.4, 125.3 (CH of $C_6H_4$), 118.8 (CH═), 35.9 ($CH_2CH$═), 33.6, 28.8 (α-$CH_2$ of cyclopentylidene), 26.4, 26.3 (β-$CH_2$ of cyclopentylidene), 21.4 ($CH_3$).

*1-(2-Cyclopentylideneethyl)-2-methylbenzene (**3ah**).* A white solid (54.1 mg, 0.186 mmol, 77% yield based on the amount of **1a** (52.2 mg, 0.242 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{14}H_{18}$ 186.1409; Found 186.1413. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.22−7.09 (m, 4H, $C_6H_4$), 5.40 (t of quint, *J* = 7.2, 2.4 Hz, 1H, CH═), 3.31 (d, *J* = 7.2 Hz, 2H, $CH_2CH$═), 2.32 (s, 3H, $CH_3$), 2.35−2.27 (m, 4H, α-$CH_2$ of cyclopentylidene), 1.73, 1.65 (both quint, *J* = 7.0 Hz, 2H each, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 144.2 (*ipso*-C of cyclopentylidene), 139.9, 136.1 (1- and 2-C of $C_6H_4$), 130.0, 128.6, 125.9, 125.9 (CH of $C_6H_4$), 117.9 (CH═), 33.7, 33.6, ($CH_2CH$═ and α-$CH_2$ of cyclopentylidene), 28.8 (α-$CH_2$ of cyclopentylidene), 26.4, 26.4 (β-$CH_2$ of cyclopentylidene), 19.5 ($CH_3$).

*1-(2-Cyclopentylideneethyl)naphthalene (**3ai**).* A colorless oil (35.6 mg, 0.160 mmol, 66% yield based on the amount of **1a** (50.3 mg, 0.242 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{17}H_{18}$ 222.1409; Found: 222.1402. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 8.05 (d, 1H, *J* = 8.0 Hz, 1H, 4-CH of 1-naphthyl), 7.86 (d, *J* = 7.6 Hz, 1H, 8-CH of 1-naphthyl), 7.73 (d, *J* = 7.6 Hz, 1H, 4-CH of 1-naphthyl), 7.56−7.46, 7.45−7.34 (both m, 2H each, 2-, 3-, 6-, and 7-CH of 1-naphthyl), 5.56 (t of quint, *J* = 6.5, 2.1 Hz, 1H, CH═), 3.78 (d, *J* = 6.5 Hz, 2H, $CH_2CH$═), 2.39, 2.30 (both br, 2H each, α-$CH_2$ of cyclopentylidene), 1.75, 1.65 (both quint, *J* = 6.7 Hz, 2H each, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 144.5 (*ipso*-C of cyclopentylidene), 137.8, 133.8, 132.0 (1-, 4a-, and 8a-C of 1-naphthyl), 128.6, 126.5, 125.7, 125.6, 125.5, 125.4, 124.1 (CH of 1-naphthyl), 118.3 (CH═), 33.7 (α-$CH_2$ of cyclopentylidene), 33.3 ($CH_2CH$═), 28.9 (α-$CH_2$ of cyclopentylidene), 26.5, 26.4 (β-$CH_2$ of cyclopentylidene).

*Decylidenecyclopentane (**3aj**).* A colorless oil (27.1 mg, 0.130 mmol, 54% yield based on the amount of **1a** (50.2 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{15}H_{28}$ 208.2191; Found 208.2183. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 5.23 (t, *J* = 6.9 Hz, 1H, CH═), 2.21, 2.16 (both t, *J* = 7.0 Hz, 2H each, α-$CH_2$ of cyclopentylidene), 1.94 (q, *J* = 6.9 Hz, 2H, $CH_2CH$═), 1.65, 1.58 (both quint, *J* = 7.0 Hz, 2H each, β-$CH_2$ of cyclopentylidene), 1.35−1.21 (m, 14H, $(CH_2)_7$), 0.88 (t, *J* = 6.6 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 142.9 (*ipso*-C of cyclopentylidene), 120.4 (CH═), 33.5 (α-$CH_2$ of cyclopentylidene), 31.9, 29.7, 29.7, 29.6, 29.4, 29.4 ($(CH_2)_7$ with two resonances overlapping at δ 29.6), 28.6 (α-$CH_2$ of cyclopentylidene), 26.5, 26.4 (β-$CH_2$ of cyclopentylidene), 22.7 ($CH_2CH_3$), 14.1 ($CH_3$).

*(2-Methylpentylidene)cyclopentane (**3ak**).* A colorless oil (35.7 mg, 0.234 mmol, 97% yield based on the amount of **1a** (50.2 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{11}H_{20}$ 152.1565; Found 152.1559. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 5.00 (d of quint, *J* = 9.2, 2.5 Hz, 1H, CH═), 2.25−2.13 (m, 5H, $CHCH_3$ and α-$CH_2$ of cyclopentylidene), 1.64, 1.58 (both quint, *J* = 7.0 Hz, 2H each, β-$CH_2$ of cyclopentylidene), 1.33−1.14 (m, 4H, $(CH_2)_2$), 0.90 (d, *J* = 6.8 Hz, 3H, $CH_3$), 0.86 (t, *J* = 7.0 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 141.2 (*ipso*-C of cyclopentylidene), 126.9 (CH═), 40.1 ($CH_2CHCH$═), 34.0 (α-$CH_2$ of cyclopentylidene), 33.5 (CHCH═), 28.5 (α-$CH_2$ of cyclopentylidene), 26.4, 26.4 (β-$CH_2$ of cyclopentylidene), 21.1, 20.6 ($CH_3CH$ and $CH_2CH_3$), 14.3 ($CH_3CH_2$).

*(Cyclopentylidenemethyl)cyclohexane (**3al**).* A colorless oil (23.0 mg, 0.140 mmol, 58% yield based on the amount of **1a** (50.2 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{12}H_{20}$ 164.1565; Found 164.1564. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 5.12−5.08 (m, 1H, CH═), 2.23−2.13 (m, 4H, α-$CH_2$ of cyclopentylidene), 2.08−1.95 (m, 1H, CH of Cy), 1.74−1.52, 1.32−1.08, 1.07−0.94 (all m, 8H, 4H, and 2H, respectively, $CH_2$ of Cy and β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 141.1 (*ipso*-C of cyclopentylidene), 126.4 (CH═), 38.7 (1-CH of Cy), 33.5 (α-$CH_2$ of cyclopentylidene), 33.2 (2- and 6-$CH_2$ of Cy), 28.4 (α-$CH_2$ of cyclopentylidene), 26.4, 26.3, 26.2 (4-$CH_2$ of Cy and β-$CH_2$ of cyclopentylidene), 26.2 (3- and 5-$CH_2$ of Cy).

*((2-Cyclopentylideneethoxy)methyl)benzene (**3an**).* A colorless oil (33.9 mg, 0.168 mmol, 70% yield based on the amount of **1a** (50.1 mg, 0.241 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{14}H_{18}O$ 202.1358; Found 202.1352. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.39−7.25 (m, 5H, CH of Ph), 5.52 (t of quint, *J* = 6.9, 2.3 Hz, 1H, CH═), 4.51 (s, 2H, $CH_2Ph$), 4.01 (d of quint, *J* = 6.9, 1.1 Hz, 2H, $CH_2CH$═), 2.30, 2.22 (both t, *J* = 6.8 Hz, 2H each, α-$CH_2$ of cyclopentylidene), 1.68, 1.62 (both quint, *J* = 6.8 Hz, 2H each, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 148.6 (*ipso*-C of cyclopentylidene), 138.6 (*ipso*-C of Ph), 128.3, 127.8 (*o*- and *m*-CH of Ph), 127.5 (*p*-CH of Ph), 116.4 (CH═), 72.0 ($OCH_2Ph$), 68.1 ($CH_2CH$═), 33.7, 28.8 (α-$CH_2$ of cyclopentylidene), 26.3, 26.0 (β-$CH_2$ of cyclopentylidene).

*N,N-Dibenzyl-2-cyclopentylideneethan-1-amine (**3ao**).* A white solid (54.1 mg, 0.186 mmol, 74% yield based on the amount of **1a** (52.2 mg, 0.251 mmol)). mp 176.8−178.0 °C (decomp.). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{21}H_{25}N$ 291.1987; Found 291.1985. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.70−7.66 (m, 4H, CH of Ph), 7.46−7.40 (m, 6H, CH of Ph), 5.65 (t of quint, *J* = 5.8, 2.2 Hz, 1H, CH═), 4.20−4.06 (m, 4H, $CH_2Ph$), 3.53−3.47 (m, 2H, $CH_2CH$═), 2.39−2.33, 1.99−1.93 (both m, 2H each, α-$CH_2$ of cyclopentylidene), 1.69−1.59 (m, 4H, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 155.7 (*ipso*-C of cyclopentylidene), 131.2, 129.3 (*o*- and *m*-CH of Ph) 129.8 (*p*-CH of Ph), 129.0 (*ipso*-C of Ph), 107.2 (CH═), 55.9 ($NCH_2Ph$), 50.7 ($CH_2CH$═), 34.3, 29.5 (α-$CH_2$ of cyclopentylidene), 26.0, 25.9 (β-$CH_2$ of cyclopentylidene).

*2-(2-Cyclopentylideneethyl)furan (**3aq**).* A colorless oil (29.1 mg, 0.179 mmol, 71% yield based on the amount of **1a** (52.2 mg, 0.251 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{11}H_{14}O$ 162.1045; Found 162.1041. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.31 (d, *J* = 1.4 Hz, 1H, 5-CH of furyl), 6.28 (dd, *J* = 3.2, 1.4 Hz, 1H, 4-CH of furyl), 5.98 (dd, *J* = 3.2, 0.9 Hz, 1H, 3-CH of furyl), 5.43 (t of quint, *J* = 7.2, 2.5 Hz, 1H, CH═), 3.33 (dd, *J* = 7.2, 0.9 Hz, 2H, $CH_2CH$═), 2.32−2.23 (m, 4H, α-$CH_2$ of cyclopentylidene), 1.74−1.58 (m, 4H, β-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ): 155.3, 145.8 (*ipso*-C of cyclopentylidene and 2-C of furyl), 140.9 (5-CH of furyl), 114.9, 110.1, 104.5 (3- and 4-CH of furyl and CH═), 33.6, 28.7, 28.5 ($CH_2CH$═ and α-$CH_2$ of cyclopentylidene), 26.4, 26.3 (β-$CH_2$ of cyclopentylidene).

*2-(2-Cyclopentylideneethyl)thiophene (**3ar**).* A colorless oil (30.8 mg, 0.173 mmol, 69% yield based on the amount of **1a** (52.2 mg, 0.251 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{11}H_{14}S$ 178.0816; Found 178.0814. $^1H$ NMR (400 MHz, $CDCl_3$, δ): 7.11 (dd, *J* = 4.9, 1.7 Hz, 1H, 5-CH of thienyl), 6.92 (dd, *J* = 4.9, 3.2 Hz, 1H, 4-CH of thienyl), 6.79 (dd, *J* = 3.2, 1.7 Hz, 1H, 3-CH of thienyl), 5.50 (t of


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quint, $J$ = 6.6, 2.2 Hz, 1H, CH═ ), 3.52 (d, $J$ = 6.6 Hz, 2H, $CH_2$CH═ ), 2.32−2.26 (m, 4H, $\alpha$-$CH_2$ of cyclopentylidene), 1.76−1.59 (m, 4H, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 145.2, 145.0 (*ipso*-C of cyclopentylidene and 2-C of thienyl), 126.7, 123.7, 123.0 (3-, 4- and 5-CH of thienyl), 118.0 (CH═ ), 33.6, 30.1, 28.7 ($CH_2$CH═ and $\alpha$-$CH_2$ of cyclopentylidene), 26.4, 26.3 ($\beta$-$CH_2$ of cyclopentylidene).

*(1-Cyclopentylideneethane-1,2-diyl)dibenzene (**3ba**).* A colorless oil (35.4 mg, 0.143 mmol, 57% yield based on the amount of **1b** (71.0 mg, 0.250 mmol)). HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{19}H_{20}$ 248.1565; Found 248.1561. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.26−7.09 (m, 10H, CH of Ph), 3.74 (s, 2H, $CH_2$C═), 2.47, 2.26 (both t, $J$ = 6.9 Hz, 2H each, $\alpha$-$CH_2$ of cyclopentylidene), 1.74, 1.62 (both quint, $J$ = 6.9 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 143.7, 142.6, 140.3 (*ipso*-C of cyclopentylidene and Ph), 129.9 (C═), 128.4, 128.3, 128.1, 127.8 (*o*- and *m*-CH of Ph), 125.8, 125.6 (*p*-CH of Ph), 41.1 ($CH_2$C═), 32.7, 31.2 ($\alpha$-$CH_2$ of cyclopentylidene), 27.1, 26.4 ($\beta$-$CH_2$ of cyclopentylidene).

*(2-Cyclopentylidenepropyl)benzene (**3ca**).* A colorless oil (28.1 mg, 0.151 mmol, 60% yield based on the amount of **1c** (55.6 mmol, 0.250 mmol)). HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{14}H_{18}$ 186.1409; Found 186.1411. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.33−7.25 (m, 2H, *m*-CH of Ph), 7.24−7.15 (m, 3H, *o*- and *p*-CH of Ph), 3.38 (s, 2H, $CH_2$C═), 2.38, 2.27 (both br, 2H each, $\alpha$-$CH_2$ of cyclopentylidene), 1.72, 1.71 (both quint, $J$ = 7.0 Hz, 2H each, $\beta$-$CH_2$ of cyclopentylidene), 1.59 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 140.9 (*ipso*-C of cyclopentylidene), 138.2 (*ipso*-C of Ph), 128.5, 128.2 (*o*- and *m*-CH of Ph), 125.6 (*p*-CH of Ph), 123.8 (C═), 41.5 ($CH_2$C═), 30.8, 30.8 ($\alpha$-$CH_2$ of cyclopentylidene), 27.1, 26.8 ($\beta$-$CH_2$ of cyclopentylidene), 18.9 ($CH_3$).

*(2-(2-Phenylcyclopentylidene)ethyl)benzene (**3da**).* A colorless oil (38.6 mg, 0.155 mmol, 62% yield based on the amount of **1d** (55.6 mmol, 0.250 mmol)) as a mixture of $E$ and $Z$ isomers ($E/Z$ = 92/8). (*E*)-**3da**: HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{19}H_{20}$ 248.1565; Found 248.1558. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.33−7.12 (m, 10H, CH of Ph), 5.13 (tq, $J$ = 7.8, 2.5 Hz, 1H, CH═ ), 3.59 (pseudo t, $J$ = 8.2 Hz, 1H, 2-CH of cyclopentylidene), 3.37 (d, $J$ = 7.8 Hz, 2H, $CH_2$CH═ ), 2.65−2.44 (m, 2H, 5-$CH_2$ of cyclopentylidene), 2.22−2.11, 2.01−1.89 (both m, 1H each, 3-$CH_2$ of cyclopentylidene), 1.83−1.65 (m, 2H, 4-$CH_2$ of cyclopentylidene). Relative NOE's observed at 2.0% for $\delta$ 3.37 and 2.55 (PhC$H_2$CH═ CC$H_2$) and at 1.7% for $\delta$ 5.13 and 3.59 (PhC$H_2$C*H*C═CC*H*Ph), respectively. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 147.9, 145.2, 141.4 (*ipso*-C of cyclopentylidene and Ph), 128.4, 128.3, 128.2, 128.2 (*o*- and *m*-CH of Ph), 125.9, 125.7 (*p*-CH of Ph), 121.4 (C═), 51.6 (2-CH of cyclopentylidene), 36.6 ($CH_2$CH═), 35.8 (5-$CH_2$ of cyclopentylidene), 29.7 (4-$CH_2$ of cyclopentylidene), 24.6 (3-$CH_2$ of cyclopentylidene). (*Z*)-**3da**: HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{19}H_{20}$ 248.1565; Found 248.1560. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.33−7.09 (m, 8H, CH of Ph), 6.94 (d, $J$ = 7.2 Hz, 2H, *o*-CH of Ph), 5.60 (tq, $J$ = 7.2, 1.9 Hz, 1H, CH═), 3.86 (pseudo t, $J$ = 7.0 Hz, 1H, 2-CH of cyclopentylidene), 3.12, 2.98 (both dd, $J$ = 15.5, 7.2 Hz, 1H each, $CH_2$CH═), 2.62−2.40 (m, 2H, 5-$CH_2$ of cyclopentylidene), 2.33−2.22 (m, 1H, 3-$CH_2$ of cyclopentylidene), 1.84−1.54 (m, 3H, 3- and 4-$CH_2$ of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 146.6, 146.1, 141.4 (*ipso*-C of cyclopentylidene and Ph), 128.4, 128.3, 128.2, 127.6 (*o*- and *m*-CH of Ph), 125.6, 125.6 (*p*-CH of Ph), 121.9 (C═), 47.1 (2-CH of cyclopentylidene), 38.3 ($CH_2$CH═), 35.6 (5-$CH_2$ of cyclopentylidene), 35.3 (4-$CH_2$ of cyclopentylidene), 25.1 (3-$CH_2$ of cyclopentylidene).

*(2-(2-Ethylcyclopentylidene)ethyl)benzene (**3ea**).* A colorless oil (37.6 mg, 0.188 mmol, 75% yield based on the amount of **1e** (59.1 mmol, 0.250 mmol)) as a mixture of $E$ and $Z$ isomers ($E/Z$ = 88/12). HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{15}H_{20}$ 200.1565; Found 200.1572. (*E*)-**3ea**: $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.32−7.28 (m, 2H, *m*-CH of Ph), 7.24−7.19 (m, 3H, *o*- and *p*-CH of Ph), 5.39 (tq, $J$ = 7.2, 2.4 Hz, 1H, CH═), 3.38 (d, $J$ = 7.2 Hz, 2H, $CH_2$CH═), 2.49−2.39 (m, 1H, 5-$CH_2$ of cyclopentylidene), 2.38−2.25 (m, 2H, 2-CH and 5-$CH_2$ of cyclopentylidene), 1.96−1.86, 1.85−1.73 (both m, 1H each, 3-$CH_2$ of cyclopentylidene), 1.72−1.53 (m, 2H, 4-$CH_2$ of cyclopentylidene), 1.35−1.20 (m, 2H, $CH_2CH_3$), 0.94 (t, $J$ = 7.4 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 147.9 (1-C of cyclopentylidene), 141.9 (*ipso*-C of Ph), 128.3, 128.3 (*o*- and *m*-CH of Ph), 125.6 (*p*-CH of Ph), 118.3 (CH═), 46.0 (2-CH of cyclopentylidene), 35.7 (5-$CH_2$ of cyclopentylidene), 32.3 ($CH_2$CH═), 29.5 (4-$CH_2$ of cyclopentylidene), 27.1 ($CH_2CH_3$), 24.1 (3-$CH_2$ of cyclopentylidene), 12.1 ($CH_3$). (*Z*)-**3ea** (overlapping peaks indistinctive from those of (*E*)-**3ea** not listed): $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 5.44 (tq, $J$ = 8.0, 1.9 Hz, 1H, CH═), 3.44 (dd, $J$ = 15.8, 8.0 Hz, 1H, $CH_2$CH═), 2.63 (br, 1H, 2-CH of cyclopentylidene), 0.95 (t, $J$ = 7.4 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 148.2 (1-C of cyclopentylidene), 128.1 (*o*- or *m*-CH of Ph), 125.7 (*p*-CH of Ph), 119.1 (CH═), 41.9 (2-CH of cyclopentylidene), 35.4 (5-$CH_2$ of cyclopentylidene), 33.4 ($CH_2$CH═), 31.4 (4-$CH_2$ of cyclopentylidene), 27.8 ($CH_2CH_3$), 24.0 (3-$CH_2$ of cyclopentylidene), 12.3 ($CH_3$).

*(2-(2-Butylcyclopentylidene)ethyl)benzene (**3fa**).* A colorless oil (37.1 mg, 0.162 mmol, 65% yield based on the amount of **1f** (66.0 mg, 0.250 mmol)) as a mixture of $E$ and $Z$ isomers ($E/Z$ = 90/10). HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{17}H_{24}$ 228.1878; Found 228.1882. (*E*)-**3fa**: $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.34−7.27 (m, 2H, *m*-CH of Ph), 7.24−7.16 (m, 3H, *o*- and *p*-CH of Ph), 5.38 (tq, $J$ = 7.0, 2.4 Hz, 1H, CH═), 3.37 (d, $J$ = 7.0 Hz, 2H, $CH_2$CH═), 2.49−2.38 (m, 1H, 5-$CH_2$ of cyclopentylidene), 2.38−2.20 (m, 2H, 2-CH and 5-$CH_2$ of cyclopentylidene), 1.95−1.85, 1.84−1.73 (both m, 1H each, 3-$CH_2$ of cyclopentylidene), 1.67−1.51 (m, 2H, 4-$CH_2$ of cyclopentylidene), 1.42−1.16 (m, 6H, $(CH_2)_3CH_3$), 0.91 (t, $J$ = 6.0 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 148.2 (1-C of cyclopentylidene), 141.9 (*ipso*-C of Ph), 128.3 (*o*- and *m*-CH of Ph), 125.6 (*p*-CH of Ph), 118.1 (CH═), 44.3 (2-CH of cyclopentylidene), 35.7 (5-$CH_2$ of cyclopentylidene), 34.2 (1-$CH_2$ of $^n$Bu), 32.8 ($CH_2$CH═), 30.1 (2-$CH_2$ of $^n$Bu), 29.4 (4-$CH_2$ of cyclopentylidene), 24.1 (3-$CH_2$ of cyclopentylidene), 23.0 (3-$CH_2$ of $^n$Bu), 14.2 ($CH_3$). (*Z*)-**3fa** (overlapping peaks indistinctive from those of (*E*)-**3fa** not listed): $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 5.40 (tq, $J$ = 7.6, 1.8 Hz, 1H, CH═), 3.34 (dd, $J$ = 15.6, 7.6 Hz, 1H, $CH_2$CH═), 2.68 (br, 1H, 2-CH of cyclopentylidene), 0.91 (t, $J$ = 7.4 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 148.4 (1-C of cyclopentylidene), 128.1 (*o*- or *m*-CH of Ph), 125.7 (*p*-CH of Ph), 118.9 (CH═), 40.2 (2-CH of cyclopentylidene), 35.4 (5-$CH_2$ of cyclopentylidene), 34.8 (1-$CH_2$ of $^n$Bu), 33.3 ($CH_2$CH═), 31.9 (2-$CH_2$ of $^n$Bu), 24.1 (3-$CH_2$ of cyclopentylidene), 22.8 (3-$CH_2$ of $^n$Bu).

*(2-(2-Heptylcyclopentylidene)ethyl)benzene (**3ga**).* A colorless oil (41.9 mg, 0.155 mmol, 65% yield based on the amount of **1g** (73.1 mg, 0.239 mmol)) as a mixture of $E$ and $Z$ isomers ($E/Z$ = 93/7). HRMS (FAB) $m/z$ $[M]^+$ Calcd for $C_{20}H_{30}$ 270.2348; Found 270.2338. (*E*)-**3ga**: $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.33−7.26 (m, 2H, *m*-CH of Ph), 7.24−7.16 (m, 3H, *o*- and *p*-CH of Ph), 5.38 (tq, $J$ = 6.8, 2.0 Hz, 1H, CH═), 3.37 (d, $J$ = 6.8 Hz, 2H, $CH_2$CH═), 2.48−2.38 (m, 1H, 5-$CH_2$ of cyclopentylidene), 2.38−2.26 (m, 2H, 2-CH and 5-$CH_2$ of cyclopentylidene), 1.95−1.86, 1.84−1.73 (both m, 1H each, 3-$CH_2$ of cyclopentylidene), 1.65−1.51 (m, 2H, 4-$CH_2$ of cyclopentylidene), 1.45−1.16 (m, 12H, $(CH_2)_6$), 0.90 (t, $J$ = 6.6 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 148.2 (1-C of cyclopentylidene), 141.9 (*ipso*-C of Ph), 128.3 (*o*- and *m*- CH of Ph, overlapping), 125.6 (*p*-CH of Ph), 118.1 (C═), 44.4 (2-CH of cyclopentylidene), 35.7 (5-$CH_2$ of cyclopentylidene), 34.5 (1-$CH_2$ of *n*-heptyl), 32.8 ($CH_2$CH═), 31.9 (5-$CH_2$ of *n*-heptyl), 29.9 (3-$CH_2$ of *n*-heptyl), 29.4 (4-$CH_2$ of *n*-heptyl and 4-$CH_2$ of cyclopentylidene, overlapping), 27.8 (2-$CH_2$ of *n*-heptyl), 24.1 (3-$CH_2$ of cyclopentylidene), 22.7 (6-$CH_2$ of *n*-heptyl), 14.1 ($CH_3$). (*Z*)-**3ga** (overlapping peaks indistinctive from those of (*E*)-**3ga** not listed): $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 5.40 (tq, $J$ = 7.6, 1.8 Hz, 1H, CH═), 3.34 (dd, $J$ = 15.6, 7.6 Hz, 1H, $CH_2$CH═), 2.68 (br, 1H, 2-CH of cyclopentylidene), 0.91 (t, $J$ = 7.4 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 148.5 (1-C of cyclopentylidene), 128.0 (*o*- or *m*-CH of Ph), 125.5 (*p*-CH of Ph), 118.9 (CH═), 40.2 (2-CH of cyclopentylidene), 35.4 (5-$CH_2$ of cyclopentylidene), 35.1 (1-$CH_2$ of *n*-heptyl), 33.4 ($CH_2$CH═), 29.8 (3-$CH_2$ of *n*-heptyl).


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*(2-(2-Cyclohexylcyclopentylidene)ethyl)benzene (**3ha**).* A colorless oil (33.0 mg, 0.130 mmol, 51% yield based on the amount of **1h** (73.5 mg, 0.253 mmol)) as a mixture of *E* and *Z* isomers (*E*/*Z* = 91/9). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{19}H_{26}$ 254.2035; Found 254.2035. (*E*)-**3ha**: $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.33−7.27 (m, 2H, *m*-CH of Ph), 7.24−7.16 (m, 3H, *o*- and *p*-CH of Ph), 5.36 (tq, *J* = 7.1, 2.4 Hz, 1H, CH═), 3.39 (d, *J* = 7.2 Hz, 2H, $CH_2CH$═), 2.49−2.39 (m, 1H, 5-$CH_2$ of cyclopentylidene), 2.34−2.26 (m, 1H, 2-CH of cyclopentylidene), 2.24−2.13 (m, 1H, 5-$CH_2$ of cyclopentylidene), 1.82−1.63, 1.61−1.42, 1.31−1.02 (all m, 7H, 3H, and 4H, respectively, CH and $CH_2$ of Cy, and 3- and 4-$CH_2$ of cyclopentylidene), 0.93 (qd, *J* = 11.9, 2.8 Hz, 1H, 3-CH of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 146.2 (1-C of cyclopentylidene), 141.9 (*ipso*-C of Ph), 128.3 (*o*- and *m*-CH of Ph, overlapping), 125.6 (*p*-CH of Ph), 118.7 (CH═), 50.0 (2-CH of cyclopentylidene), 40.3 (1-CH of Cy), 35.8 (5-$CH_2$ of cyclopentylidene), 32.4 ($CH_2CH$═), 29.8 (3-$CH_2$ of cyclopentylidene), 28.1 (2- and 6-$CH_2$ of Cy, overlapping), 27.0 (4-$CH_2$ of Cy), 26.8, 26.7 (3- and 5-$CH_2$ of Cy), 24.5 (4-$CH_2$ of cyclopentylidene). (*Z*)-**3ha** (overlapping peaks indistinctive from those of (*E*)-**3ha** not listed): $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 5.45 (tq, *J* = 7.3, 1.8 Hz, 1H, CH═), 3.46 (dd, *J* = 16.0, 7.3 Hz, 1H, $CH_2CH$═), 3.33 (dd, *J* = 15.8, 7.3 Hz, 1H, $CH_2CH$═), 2.69−2.55 (m, 1H, 2-CH of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 147.0 (1-C of cyclopentylidene), 128.1, 128.0 (*o*- and *m*- CH of Ph), 125.5 (*p*-CH of Ph), 119.8 (CH═), 45.8 (2-CH of cyclopentylidene), 41.4 (1-CH of Cy), 35.6 (5-$CH_2$ of cyclopentylidene), 34.4 (3-$CH_2$ of cyclopentylidene), 31.9 ($CH_2CH$═), 28.9, 28.0 (2- and 6-$CH_2$ of Cy), 26.9 (4-$CH_2$ of Cy), 26.7, 26.6 (3- and 5-$CH_2$ of Cy), 24.0 (4-$CH_2$ of cyclopentylidene).

*(E)-(2-(2,2-Dimethylcyclopentylidene)ethyl)benzene ((E)-**3ia**).* A colorless oil (39.0 mg, 0.195 mmol, 77% yield based on the amount of **1i** (59.9 mg, 0.254 mmol)). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{15}H_{20}$ 200.1565; Found 200.1564. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.31−7.24 (m, 2H, *m*-CH of Ph), 7.21−7.15 (m, 3H, *o*- and *p*-CH of Ph), 5.30 (tt, *J* = 7.2, 2.5 Hz, 1H, CH═), 3.33 (d, *J* = 7.2 Hz, 2H, $CH_2CH$═), 2.42 (tdt, *J* = 7.1, 2.5, 1.3 Hz, 2H, 3-$CH_2$ of cyclopentylidene), 1.70 (quint, *J* = 7.1 Hz, 2H, 4-$CH_2$ of cyclopentylidene), 1.53 (t, *J* = 7.1 Hz, 2H, 5-$CH_2$ of cyclopentylidene), 1.06 (s, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 152.9 (1-C of cyclopentylidene), 141.9 (*ipso*-C of Ph), 128.6 (*o*- and *m*-CH of Ph), 125.6 (*p*-CH of Ph), 116.7 (CH═), 42.2 (3-$CH_2$ of cyclopentylidene), 41.9 (2-C of cyclopentylidene), 35.5 ($CH_2CH$═), 29.3 (5-$CH_2$ of cyclopentylidene), 28.8 ($CH_3$), 22.3 (4-$CH_2$ of cyclopentylidene).

*(E)-1-(2-(2,2-Dimethylcyclopentylidene)ethyl)naphthalene ((E)-**3ii**).* A colorless oil (38.2 mg, 0.153 mmol, 61% yield based on the amount of **1i** (59.0 mmol, 0.250 mmol)). Colorless block crystals suitable for crystallographic study were further obtained by recrystallization from diethyl ether at −30 °C. HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{19}H_{22}$ 250.1722; Found 250.1724. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 8.02 (dd, *J* = 8.0, 1.6 Hz, 1H, 5-CH of 1-naphthyl), 7.86 (dd, *J* = 8.0, 1.6 Hz, 8-CH of 1-naphthyl), 7.72 (d, *J* = 7.5 Hz, 1H, 4-CH of 1-naphthyl), 7.51 (td, *J* = 8.0, 1.6 Hz, 1H, 6-CH of 1-naphthyl), 7.48 (td, *J* = 8.0, 1.6 Hz, 7-CH of 1-naphthyl), 7.40 (t, *J* = 7.5 Hz, 1H, 3-CH of 1-naphthyl) 7.33 (d, *J* = 7.5 Hz, 1H, 2-CH of 1-naphthyl), 5.38 (tt, *J* = 7.2, 2.6 Hz, 1H, CH═), 3.75 (d, *J* = 6.8 Hz, 2H, $CH_2CH$═), 2.50 (tdt, *J* = 7.2, 2.6, 1.3 Hz, 2H, 3-$CH_2$ of cyclopentylidene), 1.74 (quint, *J* = 7.2 Hz, 2H, 4-$CH_2$ of cyclopentylidene), 1.55 (t, *J* = 7.2 Hz, 2H, 5-$CH_2$ of cyclopentylidene), 1.07 (s, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 153.0 (1-C of cyclopentylidene), 137.8, 133.8, 132.1 (1-, 4a-, and 8a-C of 1-naphthyl), 128.6, 126.5, 125.6, 125.4, 125.3, 124.1 (CH of 1-naphthyl with two resonances overlapping at $\delta$ 125.6), 116.6 (CH═), 42.2 (3-$CH_2$ of cyclopentylidene), 42.1 (2-C of cyclopentylidene), 32.9 ($CH_2CH$═), 29.4 (5-$CH_2$ of cyclopentylidene), 28.8 ($CH_3$), 22.4 (4-$CH_2$ of cyclopentylidene).

*(2-(2-Phenylcyclopentylidene)propyl)benzene (**3ja**).* A colorless oil (32.8 mg, 0.125 mmol, 50% yield based on the amount of **1j** (75.0 mg, 0.251 mmol)) as a mixture of *E* and *Z* isomers (*E*/*Z* = 89/11). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{20}H_{22}$ 262.1722; Found 262.1723. (*E*)-**3ja**: $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 7.32−7.23 (m, 4H, *m*-CH of Ph), 7.23−7.11 (m, 6H, *o*- and *p*-CH of Ph), 3.87 (dd, *J* = 7.6, 2.4 Hz, 1H, 2-CH of cyclopentylidene), 3.44 (s, 2H, $CH_2CH$═), 2.58 (t, *J* = 6.4 Hz, 2H, 5-$CH_2$ of cyclopentylidene), 2.24−2.14, 1.80−1.64 (both m, 1H and 3H, respectively, 3- and 4-$CH_2$ of cyclopentylidene), 1.33 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 146.8, 140.7, 140.3 (*ipso*-C of cyclopentylidene and Ph), 128.5, 128.3, 128.2, 127.5 (*o*- and *m*-CH of Ph), 127.4 (C═), 125.7, 125.3 (*p*-CH of Ph), 48.3 (2-CH of cyclopentylidene), 41.8 ($CH_2CH$═), 37.9 (5-$CH_2$ of cyclopentylidene), 32.0 (4-$CH_2$ of cyclopentylidene), 24.6 (3-$CH_2$ of cyclopentylidene), 19.2 ($CH_3$). (*Z*)-**3ja** (overlapping peaks indistinctive from those of (*E*)-**3ga** not listed): $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 128.4 (*o*- or *m*-CH of Ph), 125.5 (*p*-CH of Ph), 36.7 (5-$CH_2$ of cyclopentylidene), 31.6 (4-$CH_2$ of cyclopentylidene), 22.6 (3-$CH_2$ of cyclopentylidene), 14.1 ($CH_3$).

**Preparation of Dimethyl 2-(3-Iodopropyl)-2-(prop-2-yn-1-yl)malonate (4b).** In a 50 mL Schlenk flask were placed a suspension of NaH, prepared from 461 mg of NaH (60% dispersion in mineral oil, 11.5 mmol) and 11 mL of THF at 0 °C by using an ice−water bath under $N_2$, where a THF solution (10 mL) of dimethyl propargylmalonate (1.70 g, 10.0 mmol) was added dropwise. The reaction mixture was gradually warmed to room temperature and was further stirred for 2 h. Then the reaction mixture was cooled back to 0 °C by using an ice−water bath, and 1-bromo-3-chloropropane (4.72 g, 30.0 mmol) was added dropwise. The reaction mixture was gradually warmed to room temperature and then was further refluxed for 24 h by using an oil bath. The resultant mixture was quenched with a saturated aqueous solution of $NH_4Cl$ (20 mL), and the aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine (30 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was collected, and the solvent was removed under reduced pressure. The residue was further purified by column chromatography ($SiO_2$) with a mixture of *n*-hexane/ethyl acetate (7:3) as an eluent to afford dimethyl 2-(3-chloropropyl)-2-(prop-2-yn-1-yl)malonate (**4b-Cl**) as a colorless oil (1.61 g, 6.54 mmol, 65% yield based on the amount of dimethyl propargylmalonate), which was directly used in the subsequent transformation to obtain 2-(3-iodopropyl)-2-(prop-2-yn-1-yl)-malonate (**4b**) without further purification.

In a 50 mL Schlenk flask were placed **4b-Cl** (1.61 g, 6.54 mmol), NaI (4.88 g, 32.6 mmol), and acetone (20 mL) under $N_2$, and the reaction mixture was stirred and refluxed for 22 h by using an oil bath. Then, acetone was removed *in vacuo*, and the resultant mixture was diluted with 20 mL of ethyl acetate and was filtered. Solvent was removed from the collected filtrate under reduced pressure, and the residue was purified by column chromatography ($SiO_2$) with a mixture of *n*-hexane/ethyl acetate (7:3) as an eluent to afford dimethyl 2-(3-iodopropyl)-2-(prop-2-yn-1-yl)malonate (**4b**) as a white waxy oil (1.72 g, 5.09 mmol, 78% yield based on the amount of **4b-Cl**, 65% yield based on the amount of dimethyl propargylmalonate). mp 266.5−268.1 °C (decomp.). HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{11}H_{15}IO_4$ 338.0015; Found: 338.0019. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$): 3.76 ($CO_2Me$), 3.17 (t, *J* = 7.0 Hz, 2H, $CH_2I$), 2.83 (d, *J* = 2.5 Hz, 2H, $CH_2C$≡), 2.19−2.13 (m, 2H, $CH_2CH_2CH_2I$), 2.03 (t, *J* = 2.5 Hz, 1H, HC≡), 1.81−1.71 (m, 2H, $CH_2CH_2I$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $\delta$): 170.3 ($CO_2$), 78.4 (C≡), 71.7 (HC≡), 56.3 ($C(CH_2)_3I$), 52.9 ($CH_3$), 33.2 ($CH_2(CH_2)_2I$), 28.3 ($CH_2CH_2I$), 23.2 ($CH_2C$≡), 5.2 ($CH_2I$).

**Preparation of (*E*)-(2-(Iodomethylene)cyclopentyl)benzene ((*E*)-7d).** *Method 1 (in the Absence of **2a**).* In a 20 mL Schlenk flask were placed **1d** (71.2 mg. 0.251 mmol), *fac*-$[Ir(ppy)_3]$ (3.4 mg, 0.0052 mmol), anhydrous $NiCl_2$ (3.4 mg, 0.026 mmol), dMeObpy (8.2 mg, 0.038 mmol), and $Cs_2CO_3$ (122 mg, 0.374 mmol) under $N_2$, where 1,4-dioxane (2.5 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C and was illuminated from the bottom of the bath with an Aitech System TMN100×120−22WD 12 W white LED lamp (400−750 nm) at a distance of approximately 2


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cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford ((2-(iodomethylene)-cyclopentyl)benzene (**7d**) as a colorless oil (40.6 mg, 0.143 mmol, 57% yield based on the amount of **1d**) as a mixture of *E* and *Z* isomers (*E*/*Z* = 83/17). Further purification by column chromatography ($SiO_2$) with *n*-hexane as an eluent gave (*E*)-((2-(iodomethylene)cyclopentyl)benzene) ((*E*)-**7d**) in a pure form (35.5 mg, 0.125 mmol, 50% yield based on the amount of **1d**).

*Method 2 (in the Presence of a Catalytic Amount of **2a** but in the Absence of $NiCl_2$/dMeObpy).* In a 20 mL Schlenk flask were placed **1d** (71.1 mg. 0.250 mmol), **2a** (8.7 mg, 0.025 mmol), *fac*-[$Ir(ppy)_3$] (3.4 mg, 0.0052 mmol), and $Cs_2CO_3$ (122 mg, 0.374 mmol) under $N_2$, where 1,4-dioxane (2.5 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C and was illuminated from the bottom of the bath with an Aitech System TMN100×120−22WD 12 W white LED lamp (400−750 nm) at a distance of approximately 2 cm from the light source for 24 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford ((2-(iodomethylene)cyclopentyl)benzene (**7d**) as a colorless oil (42.0 mg, 0.148 mmol, 59% yield based on the amount of **1d**) as a mixture of *E* and *Z* isomers (*E*/*Z* = 83/17). Further purification by column chromatography ($SiO_2$) with *n*-hexane as an eluent gave (*E*)-((2-(iodomethylene)cyclopentyl)benzene) ((*E*)-**7d**) in a pure form (33.4 mg, 0.118 mmol, 47% yield based on the amount of **1d**).

HRMS (FAB) *m*/*z* $[M]^+$ Calcd for $C_{12}H_{13}I$ 284.0062; Found: 284.0063. $^1H$ NMR (400 MHz, $CDCl_3$, *δ*): 7.35−7.28 (m, 2H, *m*-CH of Ph), 7.27−7.16 (m, 3H, *o*- and *p*-CH of Ph), 5.57 (pseudo quint, *J* = 2.4 Hz, 1H, CH═), 3.57 (t, *J* = 7.6 Hz, 1H, 2-CH of cyclopentylidene), 2.59−2.49, 2.48−2.36, 2.36−2.27, 2.00−1.84, 1.82−1.68 (all m, 1H, 1H, 1H, 2H, and 1H respectively, 3-, 4-, and 5-CH of cyclopentylidene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, *δ*): 159.4 (1-C of cyclopentylidene), 142.8 (*ipso*-C of Ph), 128.5, 128.2 (*o*- and *m*-CH of Ph), 126.5 (*p*-CH of Ph), 72.9 (CH═), 53.6 (2-CH of cyclopentylidene), 37.8, 37.6 (4- and 5-$CH_2$ of cyclopentylidene), 23.8 (3-$CH_2$ of cyclopentylidene).

**Preparation of (*E*)-3da by the Reaction of (*E*)-7d with 2a.** In a 20 mL Schlenk flask were placed (*E*)-**7d** (71.0 mg. 0.251 mmol), **2a** (257 mg, 0.751 mmol), *fac*-[$Ir(ppy)_3$] (3.4 mg, 0.0052 mmol), anhydrous $NiCl_2$ (3.5 mg, 0.027 mmol), dMeObpy (8.0 mg, 0.037 mmol), and $Cs_2CO_3$ (123 mg, 0.378 mmol) under $N_2$, where 1,4-dioxane (2.5 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C and was illuminated from the bottom of the bath with an Aitech System TMN100×120−22WD 12 W white LED lamp (400−750 nm) at a distance of approximately 2 cm from the light source for 24 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford (*E*)-**3da** as a colorless oil (45.3 mg, 0.182 mmol, 73% yield based on the amount of (*E*)-**7d**).

**Large-Scale Preparation of 3da.** In a 100 mL Schlenk flask were placed **1d** (710 mg. 2.50 mmol), **2a** (2.57 g, 7.49 mmol), *fac*-[$Ir(ppy)_3$] (32.0 mg, 0.0489 mmol), anhydrous $NiCl_2$ (34.2 mg, 0.264 mmol), dMeObpy (81.0 mg, 0.375 mmol), and $Cs_2CO_3$ (1.22 g, 3.74 mmol) under $N_2$, where 1,4-dioxane (25.1 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C and was illuminated from the bottom of the bath with an Aitech System TMN100×120−22WD 12 W white LED lamp (400−750 nm) at a distance of approximately 2 cm from the light source for 24 h. The volatiles were removed *in vacuo*, and the resultant mixture was extracted with dichloromethane *via* filtration. Solvent was removed from the collected filtrate under reduced pressure, and the residue was purified by column chromatography ($SiO_2$) with *n*-hexane as an eluent to afford **3da** as a colorless oil (397 mg, 1.60 mmol, 64% yield based on the amount of **1d**) as a mixture of *E* and *Z* isomers (*E*/*Z* = 91/9).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01018.

Experimental procedures and characterization data for new compounds (PDF)

### Accession Codes

CCDC 2061338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION


### Corresponding Author

**Yoshiaki Nishibayashi** − *Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan;* orcid.org/0000-0001-9739-9588; Email: ynishiba@g.ecc.u-tokyo.ac.jp

### Authors

**Yulin Zhang** − *Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

**Yoshiaki Tanabe** − *Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan;* orcid.org/0000-0001-5858-7834

**Shogo Kuriyama** − *Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c01018


### Notes

The authors declare no competing financial interest.

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