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# Photodriven Transfer Hydrogenation of Olefins

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*Dedicated to the memory of Professor Carlos F. Barbas III*

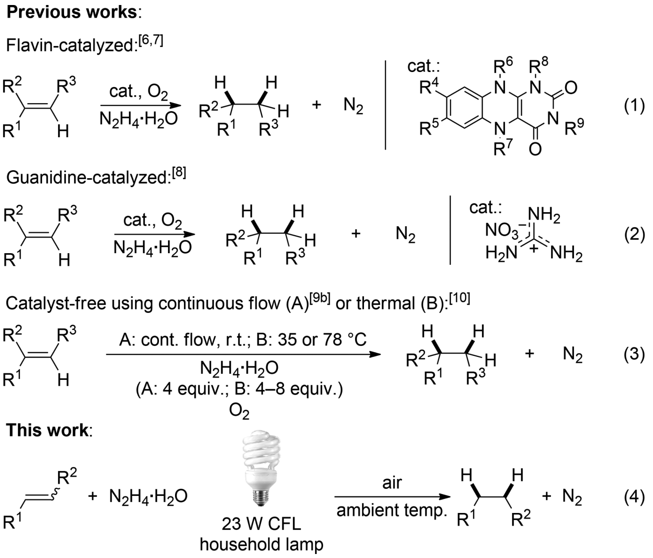
**Keywords:** Diimides / Hydrazine / Reduction / Hydrogen transfer / Alkenes

An improved practical method for the photodriven diimide reduction of olefins was investigated. This catalyst-free procedure proceeds at ambient temperature, utilizes air as oxidant and a lower hydrazine loading, and produces inert nitrogen gas as the sole byproduct. Several functional groups were tolerated, and in some cases, the reaction was chemoselective. Challenging substrates such as cinnamate ester derivatives and *trans*-stilbene were reduced in excellent yields. The small amount of UVA rays emitted from a household compact fluorescent light bulb was proposed to enable the *cis*/*trans* isomerization of the diimide and to promote the loss of hydrogen from the diimide.

## Introduction

The hydrogenation of olefins is one of the most important organic transformations. Traditional methods rely on heterogeneous[1] and homogeneous[2] transition-metal catalysts. There are concerns on issues such as chemoselectivity (cleavage of benzyl group) and alkene migration. On the other hand, metal-free transfer hydrogenation by using diimide, which is generated in situ from hydrazine, offers complementary reactivity.[3] The history of this reaction can be traced back a century ago when it was first discovered by Hanuš in 1905.[4a] However, its synthetic applications remained relatively unexplored until the 1960s. Several groups independently established the important role of diimide and expanded its utility in organic synthesis.[4b–4e]

Diimide reduction is one of the greener transfer-hydrogenation reactions. Hydrazine has a high hydrogen content (12.5%). It is cheap and abundantly available (0.142 USD per gram, Sigma–Aldrich). The reaction's only byproduct is gaseous $N_2$. Owing to these advantages, there has been renewed interest in the development of new catalytic systems for the diimide reduction reaction in recent years. Imada, Naota, and co-workers employed synthetic flavins as catalysts for the oxidation of hydrazine [Equation (1)].[5,6] Subsequently, several other groups also contributed to this area.[7]



Prabhu's group disclosed a guanidinium salt catalyzed system [Equation (2)].[8] They proposed that diimide was activated by the catalyst through double hydrogen bonding. Recently, the Jamison and Kappe groups developed continuous-flow technologies for the reduction of olefins through hydrogen transfer from diimide.[9] In particular, Kappe and co-workers used hydrazine for their technology [Equation (3), conditions A].[9b] A couple of teams found that if both the reaction temperature and the amount of hydrazine were increased, the reduction also proceeded smoothly without any catalyst [Equation (3), conditions B].[10] However, the substrate scope was narrower than that of the catalytic examples. Other miscellaneous catalysts have also been explored.[11]

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Noncatalytic processes often require long reaction times, high temperature, and an oxygen atmosphere. A large excess amount of hydrazine is also needed because of disproportionation and decomposition of diimide to $N_2$. Although there are many reports on increasing the rate of hydrazine oxidation, few describe improvements in the efficiency of the diimide hydrogenation step.[8] Diimide is generated as an equal mixture of both *cis* and *trans* isomers (Figure 1). They undergo slow interconversion, as the *trans* isomer is more stable than the *cis* isomer by approximately 8 kcal mol$^{-1}$.[3] However, experimental observations indicate that the *cis* isomer is the reactive species.[4b–4e]

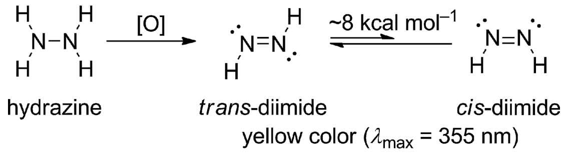
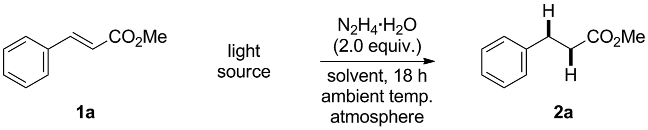


Figure 1. Physical properties of *trans*- and *cis*-diimide.

The photoisomerization of diimide is well studied.[12,13] The maximum absorption for *trans*-diimide is 355 nm.[13c] We hypothesize that the rate of isomerization will increase under photoirradiation. Photocatalysis has already been utilized in synthetic organic chemistry.[14,15] Currently, this area is under intense development.[16,17] Herein, we disclose the transfer hydrogenation of olefins accelerated by the isomerization of diimide with irradiation from household compact fluorescent light (CFL) bulbs [Equation (4)].

Table 1. Reaction optimization.[a,b]



| Entry | Light source | Atmosphere | Yield [%] |
|---|---|---|---|
| 1 | 23 W 6500 K CFL | air | 72 |
| 2 | 23 W 6500 K CFL | $O_2$ | 86 |
| 3 | 23 W 6500 K CFL | Ar | 9 |
| 4 | 23 W 6500 K CFL | air | 91[c,d] |
| 5 | 23 W 2700 K CFL | air | 93[c,d] |
| 6 | — | air | 24[c] |
| 7 | — | air | 44[c,e] |
| 8 | blue LEDs (460–490 nm) | air | 59[c] |
| 9 | green LEDs (520–550 nm) | air | 48[c] |
| 10 | 4 W UVA (365 nm) | air | 91[c,d] |

[a] Unless otherwise noted, the reactions were performed with methyl cinnamate (**1a**, 0.12 mmol) and $N_2H_4 \cdot H_2O$ (2.0 equiv.) in solvent (1.0 mL) at ambient temperature under irradiation of a light source under a specific atmosphere for 18 h. [b] Yield was determined by analysis of the unpurified reaction mixture by $^1H$ NMR spectroscopy by using $MeNO_2$ as an internal standard. [c] $N_2H_4 \cdot H_2O$ (2.5 equiv.) was used. [d] Reaction temperature peaked at 35 °C. [e] Reaction was conducted at 35 °C. See the Supporting Information for details.

## Results and Discussion

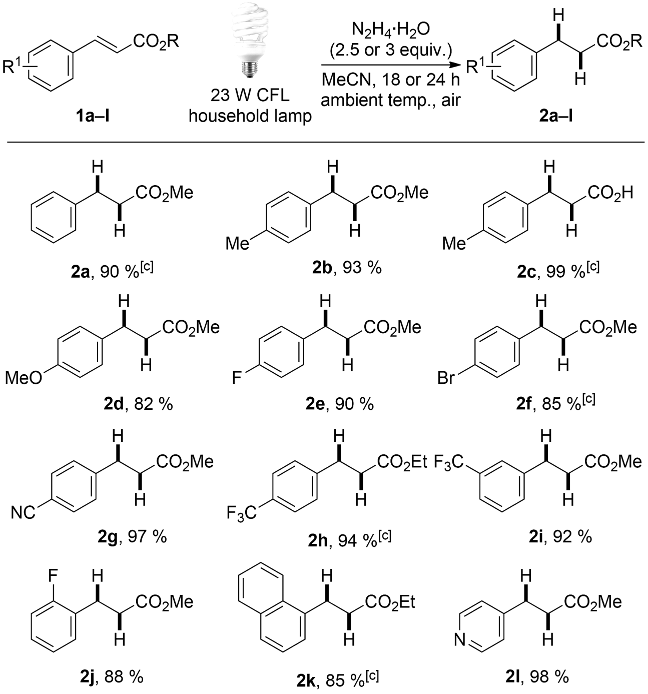
The noncatalytic diimide reduction of cinnamate esters is still not efficient.[6b,8,10a,11d] Therefore, we commenced our studies on the transfer hydrogenation of methyl cinnamate (**1a**) with hydrazine under household CFL irradiation (Table 1). A quick screening of solvents revealed that MeCN was most favorable (Table 1, Entry 1; Table S1). The reaction yield was enhanced under an $O_2$ atmosphere with irradiation of 6500 K CFL (Table 1, Entry 2) as well as 2700 K CFL (Table S2, Entry 3). The reaction slowed down if argon was used (Table 1, Entry 3). It is likely that dioxygen from air is responsible for the oxidation of hydrazine to diimide. By increasing the amount of $N_2H_4$ (from 2 to 2.5 equiv.), an optimal yield was obtained (Table 1, Entry 4). Both 6500 and 2700 K CFL emit the majority of light in the visible region with a small amount of UVB (280–315 nm), UVA (315–400 nm), and infrared (>700 nm) radiation. They could be used interchangeably, but the latter was chosen (Table 1, Entry 5).

The reaction slowed down significantly in the absence of light (Table 1, Entry 6). The heating effect of the lamp was also investigated. The reaction temperatures under both 6500 and 2700 K CFL irradiation were measured and were found to reach a maximum of 35 °C (Table 1, Entries 4 and 5). If the same reaction was heated to 35 °C in the dark, the yield remained low. This proved that light was essential (Table 1, Entry 7). Using light-emitting diodes (LEDs) with specific ranges of wavelengths such as blue (460–490 nm) and green (520–550 nm) with no UV emission led to lower yields (Table 1, Entries 8 and 9). However, irradiation with a longer-wavelength 4 W UV lamp (365 nm) led again to an enhancement in the yield (Table 1, Entry 10).

Under these optimized conditions, an array of synthetically useful cinnamate derivatives **1a**–**l** were tested (Table 2). Generally, the photostimulated transfer hydrogenation of cinnamate esters afforded saturated esters **2a**–**l** in excellent yields. However, the reaction yield was low (20%) if the aromatic ring was replaced by an aliphatic straight chain such as an *n*-butyl group. This indicated that steric and electronic effects of the olefin were important factors in the diimide reduction, although this was not unique to our system. Dimethyl maleate and maleimides were also tested, but they gave significant amounts of the corresponding cyclic hydrazides. Cinnamaldehyde and chalcone gave the desired reduced products along with imine, diimine, and pyrazole side products.[10b]

Another important class of olefins is the styrene derivatives, which are electronically neutral relative to cinnamate ester derivatives. Many noncatalytic examples in the literature reported modest yields for the diimide reduction of

Table 2. Scope of cinnamate ester derivatives.[a,b]

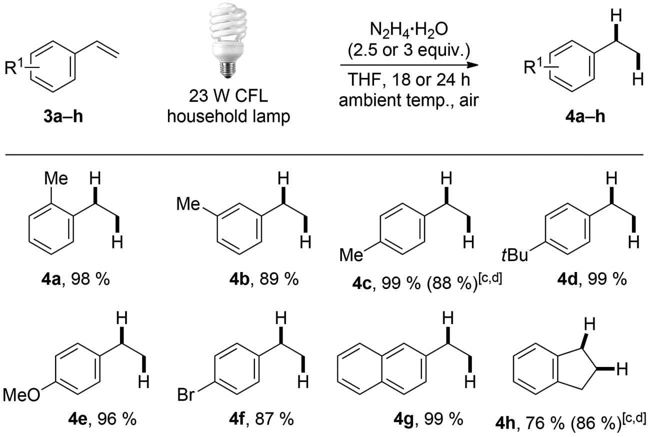


[a] Unless otherwise noted, the reactions were conducted with **1** (0.12 mmol) and $N_2H_4{\cdot}H_2O$ (2.0 equiv.) in MeCN (1.0 mL) under irradiation with a 23 W CFL for 12 h; then, $N_2H_4{\cdot}H_2O$ (1.0 equiv.) was added, and the mixture was stirred for 12 h. [b] Yield of isolated product. [c] $N_2H_4{\cdot}H_2O$ (2.5 equiv.), 18 h. See the Supporting Information for details.

styrene derivatives in air.[8,10] A diversity of styrene derivatives was examined (Table 3). The optimized solvent was THF (Table S5). Gratifyingly, the styrene reduction reaction was also accelerated by light to full consumption of the starting material at ambient temperature in air (see the Supporting Information for details). Bulky substrates such as 2-substituted styrene **3a** gave the desired product in excellent yield. This method was also applicable to cyclic styrene **3h**, although the internal double bond was sterically hindered.

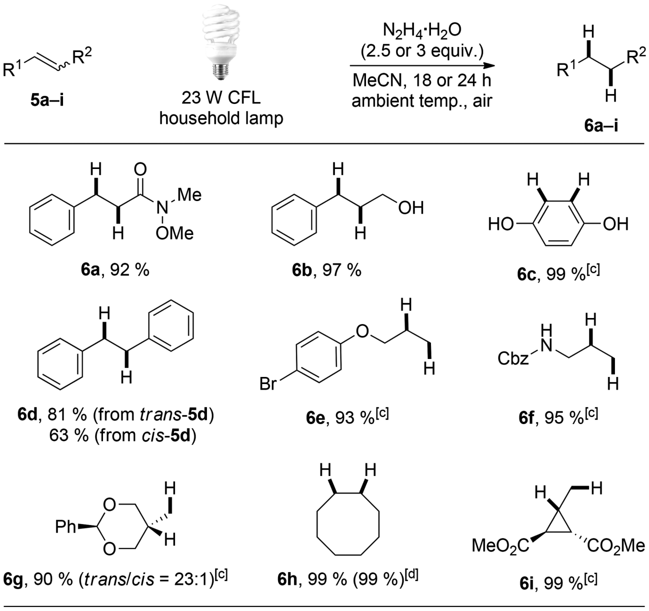
We then explored a wide range of olefins as well as the functional-group tolerance under our reaction conditions (Table 4). Generally, other than cinnamate esters, amide **5a** and alcohol **5b** were compatible with our reaction conditions. These are also sterically more demanding substrates containing internal double bonds.[8] Quinone **5c** was successfully reduced to hydroquinone **6c**. Stilbene *trans*-**5d** has remained a problematic substrate requiring harsh conditions for the diimide reduction.[7a,8,11d] However, under our optimized conditions, it was reduced smoothly in good yields. It also gave a better yield than its *cis* counterpart, which is well known in the literature.[3a] Substrates **5e** and **5f** containing allylic heteroatom groups reacted smoothly to give saturated products in excellent yields. Notably, the benzyloxycarbonyl (Cbz) group in amine **6f** remained intact.

Table 3. Scope of the styrene derivatives.[a,b]



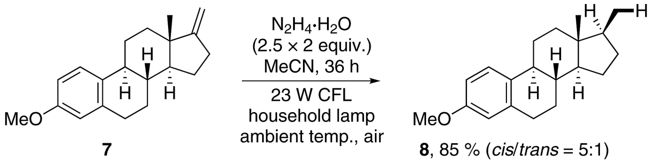
[a] Unless otherwise noted, the reactions were performed with styrene **3** (0.12 mmol) and $N_2H_4{\cdot}H_2O$ (2.5 equiv.) in THF (1.0 mL) under irradiation with a 23 W CFL for 18 h. [b] Yield of isolated product. [c] $N_2H_4{\cdot}H_2O$ (2 equiv.), 12 h; then $N_2H_4{\cdot}H_2O$ (1 equiv.), 12 h. [d] As a result of the volatility of the product, the yield was determined by $^1$H NMR spectroscopy; total recovered materials (starting material and product; some were evaporated off during concentration) in parentheses.

Table 4. Diverse range of unsaturated substrates.[a,b]



[a] Unless otherwise noted, the reactions were conducted with olefin **5** (0.12 mmol) and $N_2H_4{\cdot}H_2O$ (2.0 equiv.) in MeCN (1.0 mL) under irradiation of a 23 W CFL for 12 h; then $N_2H_4{\cdot}H_2O$ (1.0 equiv.) was added, and the mixture was stirred for 12 h. [b] Yield of isolated product. [c] $N_2H_4{\cdot}H_2O$ (2.5 equiv.), 18 h. [d] As a result of the volatility of the product, the yield was determined by $^1$H NMR spectroscopy; total recovered materials (starting material and product; some were evaporated off during concentration) in parentheses.

For dioxane **6g**, diimide reduction occurred with excellent *trans* selectivity, in accord with the literature.[18] The selectivity was attributed to the anisotropy effect induced by the oxygen atoms, as previously proposed. An isolated olefin was also an effective substrate, as demonstrated by **6h**. The observed *cis* selectivity is similar to that obtained in traditional Pd/C reductions or in iron-catalyzed reductive couplings with the use of silanes.[19] The alkyne analogue of **5e** was also tested, but the reduction did not stop at the alkene stage; as such, a mixture of the alkene and the fully saturated product was obtained. Unlike Lindlar's catalyst, this reaction was not chemoselective towards alkene formation. The alkyne analogue of **5e** was fully reduced to the saturated alkane if hydrazine (4 equiv.) was used. Last but not least, sterically encumbered estrone derivative **8** bearing two vicinal all-carbon quaternary centers was isolated in 85% yield with a diastereomeric ratio of 5:1 in favor of the *cis* isomer (Scheme 1).

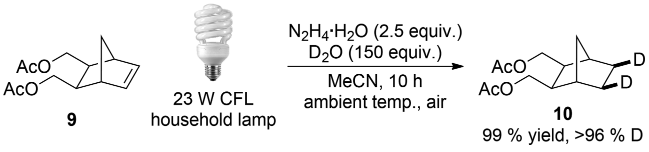


Scheme 1. Photodriven diimide reduction of estrone derivative **7**.

Ester of Feist's acid **6i** contained a sensitive cyclopropyl group that survived the reaction. From this result, we could exclude any radical mechanism for the photodriven diimide reduction reaction. To gain further insight into the mechanism, preliminary kinetic studies were conducted (see Figure S2). The $k_{obs}$ for the photodriven and nonlight (control) reactions were $1.62 \times 10^{-4}$ and $4.45 \times 10^{-5}$ $M^{-1}s^{-1}$, respectively. The overall order of the reaction is two.

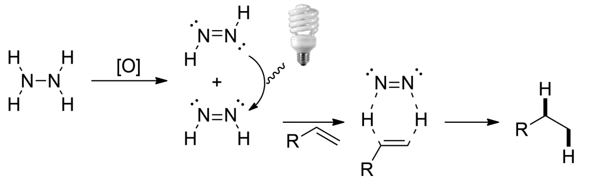
The half-life of diimide in the gas phase at room temperature is several minutes.[3c] Therefore, it is likely that a small amount of diimide is present in the solution at any given time. The photochemistry of diimide in the gas phase was studied at wavelengths of 310–405 nm. Theoretical studies predicted the stepwise loss of hydrogen in the photolysis of *cis*-diimide.[3c,20] We observed that the yield was also improved under irradiation with a long-wavelength 4 W UV lamp (365 nm; Table 1, Entry 10), even achieving an 80% yield under 8 h (Table S4, Entry 12) compared to a 37% yield for irradiation under a CFL (Figure S2).

We also determined the stereochemistry of the photoinduced diimide reduction of a disubstituted alkyne, diphenylacetylene, which is a challenging substrate.[10b] Upon treatment of this substrate with $N_2H_4·H_2O$ (4 equiv.) under 4 W UVA irradiation in air for 64 h, *cis*-stilbene and bibenzyl were obtained in 18 and 25% yield, respectively. No *trans*-stilbene was observed. Hence, the reduction might proceed through a concerted mechanism involving a *cis*-diimide intermediate.[10b] 1,2-Deuteration of olefin **9** was performed, and the reduction proceeded in a *cis* fashion in 99% yield under an air atmosphere over 10 h (Scheme 2).[6] The relative stereochemistry was determined by comparison with the literature data,[6a,6c] and this result reaffirmed the *cis* selectivity of the photoinduced diimide reduction process. Notably, the isolation of deuterated hydrazine, which is explosive, could be avoided. It was generated in situ simply by prestirring $N_2H_4·H_2O$ in a mixture of MeCN and $D_2O$. Similarly, the reaction proceeded with 95% yield under 4 W UVA irradiation under an air atmosphere in 10 h.



Scheme 2. Selective *cis*-1,2-deuteration of olefin **9**.

From these experimental observations, a plausible mechanism is that the minute amount of UVA emitted from the household CFL at a distance of 2 cm is sufficient to induce the *cis*/*trans* isomerization[12,13] of the small amount of diimide present in the solution (Scheme 3). Then, reduction of the olefin proceeds with *cis*-diimide through a six-membered transition state. At this stage, we also cannot rule out the possibility that the UVA irradiation promotes the stepwise loss of hydrogen from diimide and thus accelerates the reduction step.[3c,20] More in-depth studies will be needed to elucidate the reaction mechanism.



Scheme 3. Plausible mechanism by photoinduced isomerization of diimide.

## Conclusions

We developed an efficient method that utilizes a photodriven strategy for the diimide reduction of olefins at ambient temperature. Currently, many noncatalytic processes use pure oxygen as the oxidant, which is not safe for large-scale applications. Our new protocol is operationally easy and obviates the need for pure oxygen gas. Among the noncatalytic processes, the amount of hydrazine is also reduced, which makes this reaction less hazardous, more practical, and cost-effective. This reaction tolerates several functional groups and is chemoselective in some cases. We also overcame several challenging substrates that contain internal double bonds, including cinnamate derivatives and *trans*-stilbene. We proposed that the reaction proceeds through irradiation of diimide with a small amount of UVA from a household CFL. This causes *cis*/*trans* isomerization of diimide and promotes the loss of hydrogen from diimide. Further development of continuous-flow technology can potentially lead to large-scale applications. Mechanistic studies are currently underway in our laboratory.

## Experimental Section

### General Procedure for the Photodriven Transfer Hydrogenation of Olefins

**Method A:** A 15 cm × 2 cm, 47 mL Pyrex tube with a polytetrafluoroethylene (PTFE) lined screw cap equipped with a magnetic stir bar was charged with olefin **1** or **5** (0.12 mmol, 1.0 equiv.) and $N_2H_4\cdot H_2O$ (12 µL, 0.24 mmol, 2.0 equiv.). ***CAUTION: Hydrazine is an extremely toxic chemical and should be handled in a well-maintained fume hood!*** MeCN (HPLC grade, 1.0 mL) was used to wash down the solids on the sides of the wall. The tube was then capped and placed approximately 2 cm from the light source (23 W 2700 K CFL). After stirring for 12 h, $N_2H_4\cdot H_2O$ (6.0 µL, 0.12 mmol, 1.0 equiv.) was added, and the mixture was kept for another 12 h. Then, the crude mixture was filtered through a short pad of silica gel. EtOAc (3× 2 mL) was used for washing. The filtrate was concentrated in vacuo, and the resulting residue was purified by column chromatography or preparative TLC (hexanes/EtOAc). This method can be used for olefins **1b**, **1d**, **1e**, **1g**, **1i**, **1j**, **5a**, **5b**, **5d**, and **5h**.

**Method B:** A 15 cm × 2 cm, 47 mL Pyrex tube with a PTFE-lined screw cap equipped with a magnetic stir bar was charged with olefin **1**, **5**, or **7** (0.12 mmol, 1.0 equiv.) and $N_2H_4\cdot H_2O$ (15 µL, 0.30 mmol, 2.5 equiv.). ***CAUTION: Hydrazine is an extremely toxic chemical and should be handled in a well-maintained fume hood!*** MeCN (HPLC grade, 1.0 mL) was used to wash down the solids on the sides of the wall. The tube was then capped and placed approximately 2 cm from the light source (23 W 2700 K CFL). After stirring for 12 h, the crude mixture was filtered through a short pad of silica gel. EtOAc (3× 2 mL) was used for washing. The filtrate was concentrated in vacuo, and the resulting residue was purified by column chromatography or preparative TLC (hexanes/EtOAc). This method can be used for olefins **1a**, **1c**, **1f**, **1h**, **1k**, **5c**, **5e**–**g**, **5i**, and **7**.

**Method C:** A 15 cm × 2 cm, 47 mL Pyrex tube with a PTFE-lined screw cap equipped with a magnetic stir bar was charged with styrene **3** (0.12 mmol, 1.0 equiv.) and $N_2H_4\cdot H_2O$ (12 µL, 0.24 mmol, 2.0 equiv.). ***CAUTION: Hydrazine is an extremely toxic chemical and should be handled in a well maintained fume hood!*** THF (HPLC grade, 1.0 mL) was used to wash down the solids on the sides of the wall. The tube was then capped and placed approximately 2 cm from the light source (23 W 6500 K CFL). After stirring for 12 h, $N_2H_4\cdot H_2O$ (6.0 µL, 0.12 mmol, 1.0 equiv.) was added, and the mixture was kept for another 12 h. Then, the crude mixture was filtered through a short pad of silica gel. $Et_2O$ (3× 2 mL) was used for washing. The filtrate was concentrated in vacuo, and the resulting residue was used for $^1H$ NMR spectroscopy analysis. This method can be used for olefins **3c** and **3h**.

**Method D:** A 15 cm × 2 cm, 47 mL Pyrex tube with a PTFE-lined screw cap equipped with a magnetic stir bar was charged with styrene **3** (0.12 mmol, 1.0 equiv.) and $N_2H_4\cdot H_2O$ (15 µL, 0.30 mmol, 2.5 equiv.). ***CAUTION: Hydrazine is an extremely toxic chemical and should be handled in a well maintained fume hood!*** THF (HPLC grade, 1.0 mL) was used to wash down the solids on the sides of the wall. The tube was then capped and placed approximately 2 cm from the light source (23 W 6500 K CFL). After stirring for 18 h, the crude mixture was filtered through a short pad of silica gel. $Et_2O$ (3× 2 mL) was used for washing. The filtrate was concentrated in vacuo, and the resulting residue was purified by column chromatography or preparative TLC (hexanes/EtOAc). This method can be used for olefins **3a**, **3b**, and **3d**–**g**.

**Supporting Information** (see footnote on the first page of this article): Experimental details and copies of the$^1$H NMR and $^{13}$C NMR spectra.

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