Novel Synthesis of Alkenes via Triethylborane-Induced Free-Radical Reactions of Alkyl Iodides and β-Nitrostyrenes

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Reactions of (*E*)-β-nitrostyrenes **1** and triethylborane **2** or tricyclohexylborane **4** in THF solution at room temperature in the presence of oxygen in the air as radical initiator generate high yields of *trans*-alkenes (*E*)-**3** or (*E*)-**5**. Medium to high yields of different (*E*)-alkenes (*E*)-**5**, **7**, **10**, **12**, and **14** also can be prepared when **1** reacts with different radicals, prepared from secondary alkyl iodides **6** and **8** or tertiary alkyl iodides **9**, **11**, and **13**, in the presence of **2** and air as radical initiator. The generation of the only product (*E*)-alkenes can be explained by the generation of the benzylic radical **A** and/or **B** as the intermediate only and the mechanism is similar to Scheme 1. Both (*E*)- and (*Z*)-**16a**−**c** are generated when (*E*)- and (*Z*)-**15a**−**c** are used to react with adamantyl radical under similar conditions. Only (*Z*)-**16d** was observed when either (*E*)- or (*Z*)-**15d** was used to react with adamantyl radical. The generation of the (*E*)- and/or (*Z*)-alkenes can be explained by the free rotation of the **A** and/or **B** to generate **A′** and/or **B′** and vice versa, and the mechanism is proposed to be a free-radical reaction via NO_2/alkyl substitution and is shown as Scheme 2.

Introduction

Nitro olefins are useful intermediates in organic synthesis and are important structural units that can be used as starting materials for many classes of compounds.[1] Reactions of β-nitrostyrenes with organometallic reagents such as dialkylzinc[2a] or organozinc halides,[2b,c] *t*-BuHgX/KI,[3] organomanganese,[4] trialkylgallium,[5] trialkylaluminum or dialkylaluminum chloride,[6] and Grignard reagents,[7] respectively, generate alkenes and/or nitroalkanes or halooximes have been reported. Our previous study found that medium to high yields of alkenes can be generated when (*E*)-β-nitrostyrenes **1** react with triethylborane in THF solution under refluxing condition in the presence of a trace of oxygen in the nitrogen or by photolysis in the presence of *tert*-butyl peroxide as radical initiator.[8] All these results indicate that β-nitrostyrenes can react with different organometallic reagents to generate nitroalkanes or alkenes under different conditions and workup procedures and the reaction mechanism is proposed to be a free-radical and/or an ionic reaction.[1−8] In this paper, we wish to report an improved and effective method, based on our previous study,[8] to synthesize different alkenes by reaction of β-nitrostyrenes with different radicals that were prepared from alkyl iodides and triethylborane in the presence of oxygen in the air as radical initiator.

Results and Discussion

At room temperature, (*E*)-β-nitrostyrenes **1** reacted with triethylborane **2** or tricyclohexylborane **4** in THF solution in the presence of oxygen in the air to generate 87−100% of 1-aryl-1-butene **3** or 79−98% of 1-aryl-2-cyclohexylethene **5** within 5−10 min (eq 1 and Table 1). All spectral data indicate that the alkenes have (*E*) configuration (J_{trans} = 16.0 Hz for vinyl hydrogen) after the mixture were purified by flash column chromatography and the spectral data of the known products are also consistent with literature report.[2,8] Compared to our previous study to stimulate the reaction by refluxing or by photolysis the solution,[8] the reaction condition of this method is mild and easy to follow and the reaction rate is also accelerated dramatically by the presence of the oxygen in the air so that the reaction time can be reduced from few hours to only 5−10 min. The mechanism is also proposed to be a free-radical reaction proceeding through an addition and elimination reaction to generate (*E*)-alkenes that are similar to our previous report.[8]

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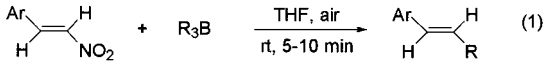


(*E*)-**1** **2** or **4** (*E*)-**3** or **5**

1

a: Ar = Ph
b: Ar = 4-MeOC$_6$H$_4$
c: Ar = 4-ClC$_6$H$_4$
d: Ar = 2-thienyl
e: Ar = 2-furyl
f: Ar = 3-(*N*-phenyl)indolyl

2. R = Et

4. R = *c*-C$_6$H$_{11}$

3

a: Ar = Ph, R = Et
b: Ar = 4-MeOC$_6$H$_4$, R = Et
c: Ar = 4-ClC$_6$H$_4$, R = Et
d: Ar = 2-thienyl, R = Et
e: Ar = 2-furyl, R = Et
f: Ar = 3-(*N*-phenyl)indolyl, R = Et

5

a: Ar = Ph, R = *c*-C$_6$H$_{11}$
b: Ar = 4-MeOC$_6$H$_4$, R = *c*-C$_6$H$_{11}$
c: Ar = 4-ClC$_6$H$_4$, R = *c*-C$_6$H$_{11}$
d: Ar = 2-thienyl, R = *c*-C$_6$H$_{11}$
e: Ar = 2-furyl, R = *c*-C$_6$H$_{11}$
f: Ar = 3-(*N*-phenyl)indolyl, R = *c*-C$_6$H$_{11}$

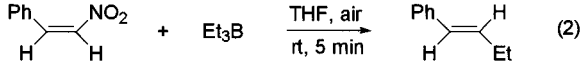
Table 1. Reaction of *trans*-β-Nitrostyrenes 1 (1 Equiv) with R$_3$B 2 or 4 (3 Equiv) in THF under an Air Atmosphere at Room Temperature

entry	**1**	R$_3$B	product	yield (%)[a]
1	**1a**	2	**3a**	96
2	**1b**	2	**3b**	100
3	**1b**	2	**3b**	tr[b]
4	**1b**	2	**3b**	96[c]
5	**1c**	2	**3c**	89
6	**1d**	2	**3d**	98
7	**1e**	2	**3e**	87
8	**1f**	2	**3f**	99
9	**1a**	4	**5a**	79
10	**1b**	4	**5b**	97
11	**1c**	4	**5c**	85
12	**1d**	4	**5d**	90
13	**1e**	4	**5e**	98
14	**1f**	4	**5f**	92

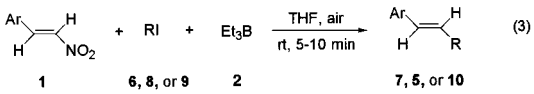
[a] Isolated yields. [b] 50 mol % galvinoxyl was added and 92% unreacted **1b** was recovered. [c] Pure oxygen was used.

Other evidence to prove the free-radical reaction is that the reaction is retarded or inhibited by the addition of galvinoxyl, an efficient scavenger for free radicals.[9] After addition of 50 mol % galvinoxyl under similar conditions, only a trace of **3b** was observed and 92% unreacted **1b** was recovered (Table 1, entry 3). Oxygen is not only known to be a free-radical initiator but also is known to be a radical scavenger. When the reaction was conducted in pure oxygen, 96% **3b** (Table 1, entry 4) was obtained, which is lower than with the use of air (100%) under similar procedures (Table 1, entry 2). These results indicate that the use of air is good enough for these reactions.

It has been reported that both (*E*)- and (*Z*)-**1a** react with diethylzinc to give the (*E*)-**3a** only.[2a] In addition to (*E*)-**1a**, (*Z*)-**1a** was also used to react with **2** under similar conditions as described above (eq 2). As expected, 90% yield of the same product (*E*)-**3a** was also isolated, and this result is actually consistent with literature report.[2a]



(*Z*)-**1a** **2** (*E*)-**3a**



1 **6, 8,** or **9** **2** **7, 5,** or **10**

6. R = *i*-Pr
8. R = *c*-C$_6$H$_{11}$
9. R = *t*-Bu

7

a: Ar = Ph, R = *i*-Pr
b: Ar = 4-MeOC$_6$H$_4$, R = *i*-Pr
c: Ar = 4-ClC$_6$H$_4$, R = *i*-Pr
d: Ar = 2-thienyl, R = *i*-Pr
e: Ar = 2-furyl, R = *i*-Pr
f: Ar = 3-(*N*-phenyl)indolyl, R = *i*-Pr

10

a: Ar = Ph, R = *t*-Bu
b: Ar = 4-MeOC$_6$H$_4$, R = *t*-Bu
c: Ar = 4-ClC$_6$H$_4$, R = *t*-Bu
d: Ar = 2-thienyl, R = *t*-Bu
e: Ar = 2-furyl, R = *t*-Bu
f: Ar = 3-(*N*-phenyl)indolyl, R = *t*-Bu

Table 2. Reaction of *trans*-β-Nitrostyrenes 1 (1 Equiv) with RI (Excess) and Et$_3$B (3 Equiv) in THF in the Presence of Oxygen under an Air Atmosphere

entry	**1**	RI (equiv)	product (yield %)[a]
1	**1a**	6 (12)	**7a** (85)
2	**1b**	6 (12)	**7b** (97)
3	**1b**	6 (12)	**7b** (100)[b]
4	**1b**	6 (12)	**7b** (38)[c]
5	**1b**	6 (12)	**7b** (64)[d]
6	**1c**	6 (12)	**7c** (98)
7	**1d**	6 (12)	**7d** (100)
8	**1e**	6 (20)	**7e** (100)
9	**1f**	6 (20)	**7f** (92)
10	**1a**	8 (12)	**5a** (79)[e]
11	**1b**	8 (12)	**5b** (97)[e]
12	**1c**	8 (12)	**5c** (97)[e]
13	**1d**	8 (12)	**5d** (94)[e]
14	**1e**	8 (12)	**5e** (77)[e]
15	**1f**	8 (12)	**5f** (57)[e]
16	**1a**	9 (6)	**10a** (72)
17	**1b**	9 (6)	**10b** (67)
18	**1c**	9 (6)	**10c** (75)
19	**1d**	9 (6)	**10d** (77)
20	**1e**	9 (6)	**10e** (75)
21	**1f**	9 (6)	**10f** (57)

[a] Isolated yields. [b] Pure oxygen was used. [c] One equivalent of Et$_3$B was used and 62% unreacted **1b** was recovered. [d] Two equivalents of Et$_3$B was used and 36% unreacted **1b** was recovered. [e] NMR yields.

Triethylborane not only can be served as one of the methods for the generation of radical species but also can be used as an effective radical initiator to generate different radicals by reaction of triethylborane with alkyl iodides under mild conditions.[10,11] On the basis of these reports, we apply this methodology to β-nitrostyrenes by using triethylborane and air as the free radical initiator to induce alkyl iodide to generate different radicals. As expected, good to excellent yields of alkenes (*E*)-**7**, **5**, or **10** were generated within 5−10 min when **1** (1 equiv) and excess alkyl iodides such as isopropyl iodide **6**, cyclohexyl iodide **8**, or *tert*-butyl iodide **9** (6−20 equiv) were put in the THF solution and then **2** (3 equiv) was added into the THF solution slowly by syringe at room temperature under similar conditions (eq 3 and Table 2).

It has been found that 3 equiv of triethylborane **2** is necessary to generate enough ethyl radical as radical

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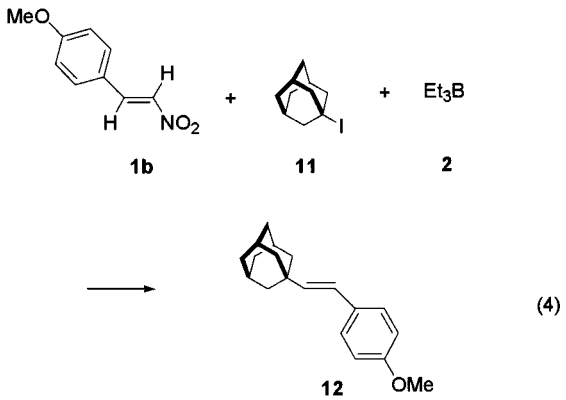
initiator to undergo further reactions. When 1 equiv of **2** was used, only 38% **7b** and 62% unreacted **1b** were found in the crude NMR analysis (Table 2, entry 4). Similarly, only 64% **7b** and 36% unreacted **1b** were found when 2 equiv of **2** was used (Table 2, entry 5). Similar to eq 2, 76% of **10a** was also isolated when (*Z*)-**1a** reacted with **9** and **2** under similar conditions, and this result is also good enough to prove that both (*E*)-**1a** and (*Z*)-**1a** can react with the same radical to generate the same product *trans*-alkene.

Compared to Table 1 and our previous study,[8] we found that the same or similar alkenes also could be prepared easily just by adding alkyl iodides to the reaction mixture under similar conditions. The condition of this improved method is not only mild and convenient but this method also can be used to synthesize high yield of alkenes with three components in a one-pot reaction at room temperature. For example, 57−77% (*E*)-**10a**−**f** (Table 2, entries 16−21) were generated when **1** reacted with **9** and **2** as described above. In addition to (*E*)-**10a**−**f**, 78% of the same product (*E*)-3,3-dimethyl-1-(4-methylphenyl)-1-butene that has been reported in our previous report[8] also was isolated when (*E*)-2-(4-methylphenyl)-1-nitroethene reacted with **9** and **2** in THF solution in the presence of the oxygen in the air but only 50% yield was observed when the same starting material reacted with *B*-*tert*-butyl-9-BBN in THF solution under refluxing condition in the presence of a trace of oxygen in the nitrogen.[8]

It has been reported that different alkyl radicals including 1-adamantyl radical and aryl radical can be generated by the reduction of alkyl or aryl halides with (ethylenediamine)chromium(II) complexes in dry dimethylformamide.[12] The palladium-catalyzed reaction of 1-bromoadamantane with styrene and donor-substituted styrenes give the corresponding Heck-type coupling product (*E*)-1-adamantyl-2-arylethene in 15−41% also has been reported by Bräse et al.[13] Similarly, Yamataka and co-workers also have reported that both (*Z*)- and (*E*)-1-adamantyl-2-arylethene mixture had been prepared from the Wittig reaction of substituted benzaldehydes with (1-adamantylmethylidene)triphenylphosphorane.[14] According to these reports and eq 3, it might be possible to prepare similar products by reaction of **1** with 1-iodoadamantane **11** under similar conditions. As expected, when **1b** (1 equiv) reacted with **11** (6 equiv) and **2** (3 equiv) in the presence of the oxygen within 5−10 min, the only product is (*E*)-1-adamantyl-2-(4-methoxyphenyl)-ethene **12** and the yield is 100% when the crude mixture was analyzed by the proton NMR (eq 4). This result indicates that the same adamantyl radical actually could



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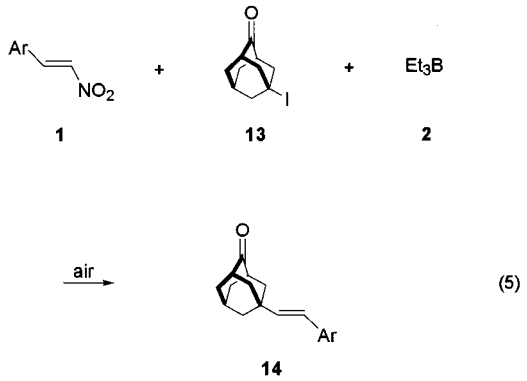

(5)

Table 3. Preparation of 14 by Reaction of 1 (1 Equiv), 13 (6 Equiv), and 2 (3 Equiv) in the Presence of Oxygen

entry	1	14	yield[a] (%)
1	**1a**	**14a**	71
2	**1b**	**14b**	60
3	**1c**	**14c**	99
4	**1d**	**14d**	86
5	**1e**	**14e**	82
6	**1f**	**14f**	100

[a] Isolated yields.

be generated by using **11**, **2**, and air at room temperature.[13,14]

5-Substituted-2-adamantanones and their derivatives are useful and interesting compounds for the study of diastereoselectivities in the reactions of sterically unbiased ketones.[15] Many 5-substituted-2-adamantanones with different withdrawing and donor groups such as CN, $COOCH_3$, CF_3, F, Cl, Br, I, OH, NMe_2, OCH_3, $OCOCH_3$, CH_3, *t*-Bu, $SiMe_3$, and $SnMe_3$ have been prepared.[15] On the basis of eq 4, compounds **1** were also used to react with 5-iodoadamantan-2-one **13** and **2** to yield 60−100% of (*E*)-1-(4-oxoadamantyl)-2-arylethene (*E*)-**14** under similar conditions (eq 5 and Table 3). The generation of **14** indicates that not only the alkyl radicals but the γ-keto radical also could be produced by this useful methodology.

Steric hindrance is one of the effects to affect reactions and always plays an important role in determining of the intermediate and final product stability. After observation substrate **1**, we then focus our study on the reactions of steric hindered α-alkyl-β-nitrostyrenes such as (*E*)-**15** and (*Z*)-**15**, prepared from the substitution of the α-hydrogen of the β-nitrostyrenes **1** by different alkyl groups,[16] with **11** and **2** as described above (eq 6 and Table 4).

Surprisingly, not only (*E*)-**16a** but also (*Z*)-**16a** was generated when either (*E*)-**15a** or (*Z*)-**15a** reacted with **11** and **2** under similar conditions, and the total yields were 74% and 90%, respectively. The gas chromatography analysis of the crude mixture found that the ratio of (*E*)-**16a** to (*Z*)-**16a** approximately equal to 96:4 or 92:8

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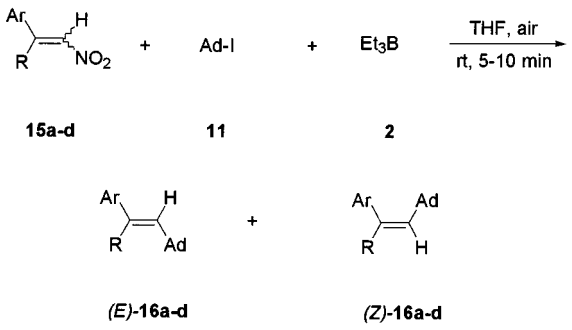


a: Ar = 3,4-$(MeO)_2C_6H_3$, R = C_2H_5

b: Ar = 4-$MeOC_6H_4$, R = *c*-C_5H_9

c: Ar = 4-$MeOC_6H_4$, R = *c*-C_6H_{11}

d: Ar = 4-$MeOC_6H_4$, R = *t*-C_4H_9

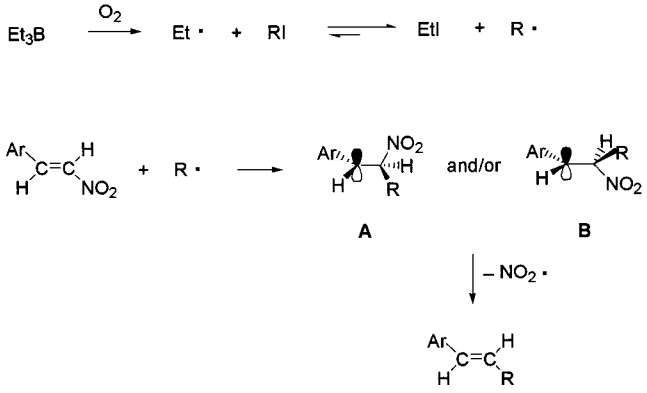
Table 4. Preparation of 16 by Reaction of 15 (1 Equiv), 11 (6 Equiv), and 2 (3 Equiv) in the Presence of Oxygen

entry	15	16	yield[a] (%)	*E*/*Z*[b]
1	(*E*)-**15a**	**16a**	74	96:4
2	(*Z*)-**15a**	**16a**	90	92:8
3	(*E*)-**15b**	**16b**	59	32:68
4	(*Z*)-**15b**	**16b**	50	37:63
5	(*E*)-**15c**	**16c**	73	18:82
6	(*Z*)-**15c**	**16c**	63	13:87
7	(*E*)-**15d**	**16d**	35	<1:99[c]
8	(*Z*)-**15d**	**16d**	32	<1:99[c]

[a] Isolated yields. [b] GC ratio. [c] (*E*)-Product was not detected in GCMS.

when (*E*)-**15a** or (*Z*)-**15a** was used (Table 4, entries 1 and 2). The stereochemistry of (*E*)- and (*Z*)-**16a** can be assigned by the NOE difference spectrum. Thus, only the NOE enhancement of the aryl hydrogen was observed when the vinyl hydrogen of (*E*)-**16a** was irradiated and only the NOE enhancement of the ethyl hydrogen was observed when the vinyl hydrogen of (*Z*)-**16a** was irradiated. Under similar conditions, both (*E*)-**16b** and (*Z*)-**16b** were observed in 59% or 50% yields when (*E*)-**15b** or (*Z*)-**15b** was used to react with **11** and **2**. The ratio of (*E*)-**16b** to (*Z*)-**16b** approximately equal to 32:68 when (*E*)-**15b** was used and approximately equal to 37:63 when (*Z*)-**15b** was used (Table 4, entries 3 and 4). The stereochemistry of (*E*)- and (*Z*)-**16b** was also assigned by the NOE difference spectrum. Similar to (*E*)- and (*Z*)-**16a**, only the NOE enhancement of the aryl hydrogen was observed when the vinyl hydrogen of (*E*)-**16b** was irradiated and only the NOE enhancement of the tertiary hydrogen of the cyclopentyl group was observed when the vinyl hydrogen of (*Z*)-**16b** was irradiated. After observation of substrates **15a-b**, **15c-d** were also checked as described above. The results for **15c** were similar to **15b**. The yields of (*E*)-**16c** and (*Z*)-**16c** were 73% and 63%, and the ratio of (*E*)-**16c** to (*Z*)-**16c** was approximately equal to 18:82 or 13:87 when (*E*)-**15c** or (*Z*)-**15c** was used (Table 4, entries 5 and 6). We were surprised to find that only 35% or 32% of (*Z*)-**16d** and some other products were observed when the crude mixture was analyzed by the NMR or GC/MS when (*E*)-**15d** or (*Z*)-**15d** was used to react with adamantyl radical as described above (Table 4, entries 7 and 8). The stereochemistry of (*Z*)-**16d** also can be assigned by the NOE difference spectrum. Thus, NOE enhancement of the *tert*-butyl hydrogen was observed when the vinyl hydrogen was irradiated and vice versa.

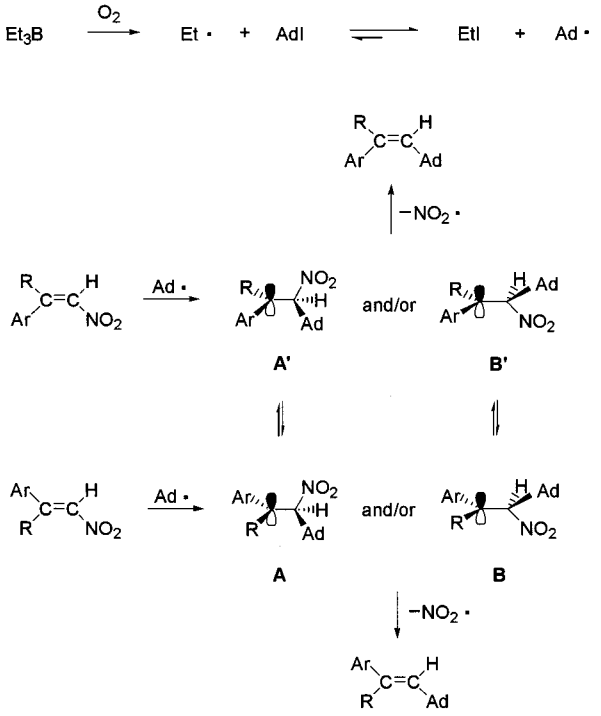
Scheme 1



According to literature reports[2,6,8] and eqs 1−6, we can conclude that the addition of the alkyl or adamantyl radical to (*E*)-*β*-nitrostyrenes **1** generates benzylic radical **A** and/or **B** and to (*Z*)-*β*-nitrostyrenes **1** generates benzylic radical **A′** and/or **B′**. The free rotation of the single bond of **A** and/or **B** generate **A′** and/or **B′** and vice versa. When R is the hydrogen, **A** and/or **B** is the only intermediate to undergo elimination to yield (*E*)-alkene due to the product stability of (*E*)-alkene is much more stable than (*Z*)-alkene in energy. The reaction mechanism is also proposed to proceed through an addition and elimination reaction, which is similar to Scheme 1. However, both (*E*)-alkene and (*Z*)-alkene were generated when R was the alkyl group (**15a**−**d**) and the approaching radical is adamantyl radical. A possible explanation is that the steric hindrance between the adamantyl and the alkyl group or the adamantyl and the aryl group becomes more crowded so that this effect becomes more important in the determination of the stability of the final product. When R is the ethyl group (**15a**), the product (*E*)-**16a** is still more stable than (*Z*)-**16a** in energy so that only a portion of the intermediate **A** and/or **B** converts into **A′** and/or **B′** when (*E*)-**15a** was used and most of the **A′** and/or **B′** convert into **A** and/or **B** very fast before undergoing elimination when (*Z*)-**15a** was used (Scheme 2). However, when R is the cyclopentyl or cyclohexyl, the steric hindrance between the cyclopentyl or cyclohexyl and the adamantyl group is increased dramatically and this effect can affect the product stability so that (*Z*)-**16b**−**c** are much more stable than (*E*)-**16b**−**c** and become to be the major products. These results indicate that **A′** and/or **B′** is the major intermediate and **A** and/or **B** is the minor intermediate during the reaction no matter if (*E*)- or (*Z*)-**15b**−**c** was used. When R is the *tert*-butyl group, (*Z*)-**16d** is the only product to be isolated when (*E*)-**15d** or (*Z*)-**15d** was used. These interesting results indicate that only **A′** and/or **B′** was generated during reaction even though **A** and/or **B** also could be generated at the beginning and this reactive intermediate can rotate to generate **A′** and/or **B′** very fast due to the large steric hindrance between *tert*-butyl and adamantyl group when (*E*)-**15d** was used.

In conclusion, we have developed an improved and easy method for the synthesis of different (*E*)-alkenes by reaction of (*E*)- or (*Z*)-*β*-nitrostyrenes with different radicals, prepared from trialkylborane or alkyl iodide and triethylborane, in the presence of the oxygen in the air at room temperature. When α-alkyl-*β*-nitrostyrenes were

Scheme 2



used, (*E*)- and/or (*Z*)-alkenes can be generated under similar conditions. The generation of the different alkenes can be explained by the generation of the different intermediates during reaction and the different stability of the final product in energy. The application of this method would broaden the scope of utility of organoborane reagents in organic synthesis.

Experimental Section

General Methods. All reactions were performed in flame- or oven-dried glassware under a positive pressure of air. Analytical thin-layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography by use of E. Merck silica gel 60 (230−400 mesh). MS or HRMS were measured on JEOL JMS-D300 or JEOL JMS-HX110 spectrometers. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200. All NMR data were obtained in $CDCl_3$ solution, and chemical shifts (δ) are given in ppm relative to TMS.

Materials. (*E*)-*β*-Nitrostyrenes **1a**−**f**, triethylborane **2**, 2-iodopropane **6**, cyclohexyl iodide **8**, 2-iodo-2-methylpropane **9**, and 1-iodoadamantane **11** were purchased from Aldrich Chemical Co., and other commercially available reagents were used without further purification. Starting material (*Z*)-*β*-nitrostyrene **1a**,[17] tricyclohexylborane **4**,[18] 5-iodoadamantan-2-one **13**,[19] and (*E*)- and (*Z*)-**15a**−**d**[16] were prepared according to the literature procedures. Products (*E*)-**3a**,[2,8,20] (*E*)-**3b**,[20e,21] (*E*)-**3c**,[21b] (*E*)-**3d**,[21a] (*E*)-**3e**,[8] (*E*)-**5a**,[8,22] (*E*)-**5b**,[23] (*E*)-**5e**,[24] (*E*)-**7a**,[20f,25] (*E*)-**7b**,[25a] (*E*)-**10a**,[25c,26] and (*E*)-**10b**[22b,26a] are all consistent with the literature reports.

(*Z*)-*β*-Nitrostyrene ((*Z*)-1a).[17] This compound was prepared according to literature procedures: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54−7.37 (m, 5H), 6.98 (d, J = 9.6 Hz, 1H), 6.79 (d, J = 9.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.76, 133.85, 130.71, 130.51, 129.91, 128.59; MS *m*/*z* (relative intensity) 149 (M^+, 58), 132 (19), 119 (6), 102 (77), 91 (62), 77 (100), 66 (19), 51 (39).

Typical Experimental Procedures for the Synthesis of Alkenes 3 or 5 from the Reaction of (*E*)-*β*-Nitrostyrenes 1 and Triethylborane 2 or Tricyclohexylborane 4 in THF Solution in the Presence of the Oxygen in the Air (Equation 1 and Table 1). In a Pyrex test tube with a magnetic stirrer were placed *trans*-*β*-nitrostyrene **1a** (1 mmol) and triethylborane **2** (3 mmol, 1.0 M in THF solution) in 8 mL of THF, and the solution was bubbled with the air that filled in the balloon. After 5−10 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 96% of (*E*)-**3a**. The spectral data are all consistent with literature report.[2,8,20] All the experimental results are shown in Table 1, and the spectral data of other alkenes are shown as following.

(*E*)-1-(4-Chlorophenyl)-1-butene ((*E*)-3c):[21b] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23 (s, 4H), 6.31 (d, J = 15.6 Hz, 1H), 6.21 (dt, J = 15.6, 5.8 Hz, 1H), 2.21 (dq, J = 7.4, 5.8 Hz, 2H), 1.08 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.51, 133.36, 132.32, 128.60, 127.72, 127.14, 25.92, 13.40; MS *m*/*z* (relative intensity) 168 ($(M + 2)^+$, 23), 166 (M^+, 69), 153 (25), 151 (73), 131 (100), 115 (77), 91 (21), 75 (13), 63 (13), 51 (11); HRMS calcd for $C_{10}H_{11}{}^{37}Cl$ 168.0520, found 168.0519; calcd for $C_{10}H_{11}{}^{35}Cl$ 166.0552, found 166.0549.

(*E*)-1-(*N*-Phenyl-3-indolyl)-1-butene ((*E*)-3f). This compound is very unstable after isolation and decomposes at room temperature: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.93−7.88 (m, 1H), 7.57−7.20 (m, 9H), 6.61 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 16.0, 6.4 Hz, 1H), 2.34−2.22 (m, 1H), 1.14 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.57, 136.61, 130.60, 129.60, 127.25, 126.42, 125.61, 124.31, 122.70, 120.61, 120.56, 120.26, 116.33, 110.62, 26.58, 14.01; MS *m*/*z* (relative intensity) 247 (M^+, 98), 232 (100), 217 (15), 206 (21), 193 (10), 180 (5), 165 (4), 154 (7), 128 (15), 115 (9), 104 (20), 77(17).

(*E*)-1-Cyclohexyl-2-(4-methoxyphenyl)ethene ((*E*)-5b):[23] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (dt, J = 8.4, 2.2 Hz, 2H), 6.82 (dt, J = 8.4, 2.2 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 6.02 (dd, J = 16.0, 6.8 Hz, 1H), 3.78 (s, 3H), 2.13−2.04 (m, 1H), 1.80−1.60 (m, 5H), 1.43−1.20 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.69, 134.82, 130.97, 127.02, 126.60, 113.93, 55.21, 41.04, 33.03, 26.13, 26.01; MS *m*/*z* (relative intensity) 216 (M^+, 50), 173 (33), 159 (28), 144 (11), 134 (100), 128 (11), 121 (48), 115 (21), 108 (21), 91 (22), 77 (10), 65 (8), 51 (5); HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1521.

(*E*)-1-Cyclohexyl-2-(4-chlorophenyl)ethene ((*E*)-5c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (s, 4H), 6.29 (d, J = 16.2 Hz,

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1H), 6.12 (dd, J = 16.2, 6.4 Hz, 1H), 2.23−2.04 (m, 1H), 1.83−1.60 (m, 5H), 1.44−1.03 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.69, 134.82, 130.97, 127.02, 126.60, 113.93, 41.04, 33.03, 26.13, 26.01; MS m/z (relative intensity) 222 ($(M + 2)^+$, 5), 220 (M^+, 15), 177 (6), 163 (4), 151 (6), 140 (33), 138 (100), 129 (23), 115 (16), 103 (8), 95 (13), 77 (8), 67 (11), 51 (6); HRMS calcd for $C_{14}H_{16}{}^{37}Cl$ 221.0911, found 221.0919; calcd for $C_{10}H_{11}{}^{35}Cl$ 219.0941, found 219.0940.

(*E*)-1-Cyclohexyl-2-(2-thienyl)ethene ((*E*)-5d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.06 (d, J = 4.8 Hz, 1H), 6.93 (dd, J = 4.8, 2.8 Hz, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.50 (d, J = 15.8 Hz, 1H), 6.10 (d, J = 15.8, 6.8 Hz, 1H), 2.20−1.96 (m, 1H), 1.86−1.60 (m, 5H), 1.44−1.02 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.50, 136.84, 127.21, 124.20, 122.97, 120.67, 40.86, 32.74, 26.07, 25.92; MS m/z (relative intensity) 192 (M^+, 20), 149 (8), 135 (17), 123 (9), 115 (10), 110 (100), 97 (16), 91 (10), 79 (8), 65 (5), 53 (3); HRMS calcd for $C_{12}H_{16}S$ 192.0973, found 192.0974.

(*E*)-1-Cyclohexyl-2-(2-furyl)ethene ((*E*)-5e):[24] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31−7.27 (m, 1H), 6.33 (dd, J = 3.4, 1.8 Hz, 1H), 6.17−6.10 (m, 3H), 2.18−1.98 (m, 1H), 1.86−1.60 (m, 5H), 1.44−1.02 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.65, 141.15, 135.82, 116.16, 111.09, 105.98, 40.74, 32.73, 26.07, 25.92; MS m/z (relative intensity) 176 (M^+, 18), 133 (5), 120 (4), 107 (5), 94 (100), 79 (11), 65 (7), 55 (8); HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1199.

(*E*)-1-Cyclohexyl-2-(*N*-phenyl-3-indolyl)ethene ((*E*)-5f). This compound is very unstable after isolation and decomposes at room temperature: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.93−7.87 (m, 1H), 7.59−7.36 (m, 9H), 6.57 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 16.0, 7.0 Hz, 1H), 2.30−2.06 (m, 1H), 1.96−1.60 (m, 5H), 1.46−1.16 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.62, 136.64, 134.99, 129.62, 127.27, 126.43, 125.63, 124.34, 122.70, 120.53, 120.26, 118.95, 116.37, 110.64, 41.65, 33.26, 26.17, 26.07; MS m/z (relative intensity) 301 (M^+, 100), 258 (40), 244 (66), 230 (10), 219 (19), 206 (40), 193 (67), 180 (10), 167 (11), 128 (7), 115 (10), 104 (5), 77(10).

Typical Experimental Procedures for the Synthesis of 3a from the Reaction of (*Z*)-*β*-Nitrostyrene 1a and Triethylborane 2 in THF Solution in the Presence of the Oxygen in the Air (Equation 2). In a Pyrex test tube with a magnetic stirrer were placed (*Z*)-*β*-nitrostyrene **1a** (1 mmol) and triethylborane **2** (3 mmol, 1.0 M in THF solution) in 8 mL of THF, and the solution was bubbled with the air that filled the balloon. After 5 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 90% of (*E*)-**3a**. The spectral data are all consistent with literature reports.[2,8,20]

Typical Experimental Procedures for the Synthesis of Alkenes 7, 5, or 10 from the Reaction of *trans*-*β*-Nitrostyrenes 1, Alkyl Iodides 6, 8, or 9, and Triethylborane 2 in THF Solution in the Presence of the Oxygen in the Air (Equation 3 and Table 2). In a Pyrex test tube with a magnetic stirrer were placed *trans*-*β*-nitrostyrene **1a** (1 mmol) and 2-iodopropane **6** (20 mmol) in 8 mL of THF, the solution was bubbled with the air that filled the balloon, and then triethylborane **2** (3 mmol, 1.0 M in THF solution) was slowly added into the solution by syringe. After 5−10 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 85% of (*E*)-**7a**. All the experimental results are shown in Table 2.

(*E*)-3-Methyl-1-phenyl-1-butene ((*E*)-7a):[20f,25] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37−7.10 (m, 5H), 6.34 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 6.4 Hz, 1H), 2.45 (oct, J = 6.4 Hz, 1H), 1.08 (d, J = 6.4 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.07, 132.68, 128.51, 126.92, 126.80, 126.02, 31.45, 22.37; MS m/z (relative intensity) 146 (M^+, 32), 131 (100), 115 (19), 103 (7), 91 (50), 77 (11), 65 (7), 51 (11).

(*E*)-3-Methyl-1-(4-methoxyphenyl)-1-butene ((*E*)-7b):[25a] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (dt, J = 8.8, 2.0 Hz, 2H), 6.82 (dt, J = 8.8, 2.0 Hz, 2H), 6.29 (d, J = 16.0 Hz, 1H), 6.04 (dd, J = 16.0, 6.4 Hz, 1H), 3.78 (s, 3H), 2.43 (dsept, J = 6.4, 6.8 Hz, 1H), 1.08 (d, J = 6.8 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.75, 136.00, 130.88, 127.07, 126.25, 113.96, 55.21, 31.38, 22.47; MS m/z (relative intensity) 176 (37), 161 (100), 146 (14), 131 (10), 121 (15), 115 (14), 103 (7), 91 (28), 77 (12), 63 (8), 51 (9); HRMS calcd for $C_{12}H_{16}O$ 176.1200, found 176.1201.

(*E*)-3-Methyl-1-(4-chlorophenyl)-1-butene ((*E*)-7c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (s, 4H), 6.29 (d, J = 16.2 Hz, 1H), 6.04 (dd, J = 16.2, 6.2 Hz, 1H), 2.43 (oct, J = 6.8 Hz, 1H), 1.08 (d, J = 6.8 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.75, 136.54, 132.32, 128.62, 127.22, 125.78, 31.44, 22.26; MS m/z (relative intensity) 182 ($(M + 2)^+$, 11), 180 (M^+, 34), 167 (33), 165 (100), 145 (50), 130 (66), 125 (35), 115 (29), 101 (12), 89 (14), 75 (18), 63 (17), 51 (18); HRMS calcd for $C_{11}H_{13}{}^{35}Cl$ 180.0694, found 180.0706.

(*E*)-3-Methyl-1-(2-thienyl)-1-butene ((*E*)-7d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.07 (d, J = 4.8 Hz, 1H), 6.93 (dd, J = 4.8, 2.8 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.10 (dd, J = 15.8, 6.8 Hz, 1H), 2.41 (oct, J = 6.8 Hz, 1H), 1.08 (d, J = 6.6 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.38., 138.02, 127.24, 124.26, 123.05, 120.33, 31.27, 22.20; MS m/z (relative intensity) 153 [$(M + 2)^+$, 8], 152 [$(M + 1)^+$, 61], 137 (100), 123 (6), 109 (7), 103 (14), 97 (39), 91 (14), 84 (3), 77 (10); HRMS calcd for $C_9H_{11}S$ 151.0582, found 151.0578.

(*E*)-1-(2-Furyl)-3-methyl-1-butene ((*E*)-7e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (d, J = 1.8 Hz, 1H), 6.34 (dd, J = 3.2, 1.8 Hz, 1H), 6.17−6.09 (m, 3H), 2.56−2.30 (m, 1H), 1.06 (d, J = 6.6 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.56, 141.22, 137.07, 115.84, 111.11, 106.02, 31.14, 22.18; MS m/z (relative intensity) 136 (M^+, 68), 121 (100), 107 (8), 103 (11), 91 (50), 81 (15), 77 (45); HRMS calcd for $C_9H_{12}O$ 136.0888, found 136.0880.

(*E*)-3-Methyl-1-(*N*-phenyl-3-indolyl)-1-butene ((*E*)-7f). This compound is very unstable after isolation and decomposes at room temperature: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.93−7.88 (m, 1H), 7.55−7.19 (m, 9H), 6.57 (d, J = 16.0 Hz, 1H), 6.24 (dd, J = 16.0, 6.8 Hz, 1H), 2.60−2.46 (m, 1H), 1.49 (d, J = 6.8 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.57, 136.63, 136.10, 129.60, 127.25, 126.42, 125.66, 124.31, 122.70, 120.54, 120.26, 118.60, 116.25, 110.62, 31.97, 22.73; MS m/z (relative intensity) 261 (M^+, 60), 246 (100), 234 (22), 222 (32), 215 (10), 206 (14), 193 (12), 180 (5), 167 (9), 152 (4), 139 (3), 128 (8), 115 (8), 104 (8), 77(10).

(*E*)-3,3-Dimethyl-1-phenyl-1-butene ((*E*)-10a):[25c,26] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39−7.13 (m, 5H), 6.35 (d, J = 16.2 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.91, 138.11, 128.51, 126.78, 126.07, 124.63, 33.27, 29.54; MS m/z (relative intensity) 160 (M^+, 64), 145 (100), 128 (31), 117 (56), 105 (20), 91 (50), 77 (17), 65 (10).

(*E*)-3,3-Dimethyl-1-(4-methoxyphenyl)-1-butene ((*E*)-10b):[22b,26a] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (dt, J = 8.8, 2.4 Hz, 2H), 6.84 (dt, J = 8.8, 2.4 Hz, 2H), 6.26 (d, J = 16.4 Hz, 1H), 6.11 (d, J = 16.4 Hz, 1H), 3.80 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.67, 139.78, 130.88, 127.07, 123.94, 113.91, 55.14, 33.11, 29.60; MS m/z (relative intensity) 190 (M^+, 64), 175 (100), 160 (27), 145 (15), 128 (14), 121 (28), 115 (22), 91 (20), 77 (10), 65 (6).

(*E*)-3,3-Dimethyl-1-(4-chlorophenyl)-1-butene ((*E*)-10c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.23 (s, 2H), 1.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.62, 136.67, 132.32, 128.62, 127.30, 123.58, 33.34, 29.47; MS m/z (relative intensity) 196 ($(M + 2)^+$, 16), 194 (M^+, 49), 181 (41), 179 (100), 159 (15), 151 (20), 144 (41), 128 (38), 115 (25), 101 (9), 89 (8), 75 (8), 63 (7), 57 (3); HRMS calcd for $C_{14}H_{16}{}^{37}Cl$ 196.0833, found 196.0853; calcd for $C_{10}H_{11}{}^{35}Cl$ 194.0862, found 194.0869.

(*E*)-3,3-Dimethyl-1-(2-thienyl)-1-butene ((*E*)-10d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.07 (d, J = 4.8 Hz, 1H), 6.93 (dd, J = 4.8, 2.8 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.10 (d, J = 15.8 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.55, 141.86, 127.24, 124.31, 123.02, 118.30, 33.34, 29.44; MS m/z (relative intensity) 166 (M^+, 51), 151 (100), 135 (8), 123 (10), 117 (16), 105 (8), 97 (23), 77 (7); HRMS calcd for $C_{10}H_{14}S$ 166.0816, found 166.0813.

(*E*)-1-(2-Furyl)-3,3-dimethyl-1-butene ((*E*)-10e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (dd, J = 2.0, 0.4 Hz, 1H), 6.34 (dd, J = 3.2, 2.0 Hz, 1H), 6.24 (d, J = 16.2 Hz, 1H), 6.14 (dd, J = 3.2, 0.4 Hz, 1H), 6.12 (d, J = 16.2 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.68, 141.19, 140.92, 113.84,

111.14, 106.12, 33.15, 29.41; MS *m*/*z* (relative intensity) 150 (M^+, 46), 135 (100), 117 (14), 107 (24), 91 (39), 79 (25), 55 (17); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1044.

(*E*)-3,3-Dimethyl-1-(*N*-phenyl-3-indolyl)-1-butene ((*E*)-10f). This compound is very unstable after isolation and decomposes at room temperature: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.94−7.89 (m, 1H), 7.55−7.19 (m, 9H), 6.54 (d, J = 16.2 Hz, 1H), 6.33 (d, J = 16.2 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.00, 139.59, 136.64, 129.59, 127.28, 126.40, 125.61, 124.29, 122.68, 120.51, 120.21, 116.27, 110.62, 33.46, 29.77; MS *m*/*z* (relative intensity) 275 (M^+, 43), 260 (100), 244 (18), 230 (11), 217 (8), 204 (6), 193 (5), 180 (2), 167 (5), 128 (4), 115 (7), 104 (3), 77(6).

Typical Experimental Procedures for the Synthesis of 12 from the Reaction of 1b, Iodoadamantane 11, and Triethylborane 2 in THF Solution in the Presence of Oxygen (Equation 4). In a Pyrex test tube with a magnetic stirrer were placed **1b** (1 mmol) and iodoadamantane **11** (6 mmol) in 8 mL of THF, the solution was bubbled with air that filled the balloon, and then triethylborane **2** (3 mmol, 1.0 M in THF solution) was slowly added into the solution by syringe. After 10 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 100% of (*E*)-**12**.

(*E*)-1-Adamantyl-2-(4-methoxyphenyl)ethene ((*E*)-12): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (dt, J = 8.4, 1.0 Hz, 2H), 6.82 (dt, J = 8.4, 1.0 Hz, 2H), 6.19 (d, J = 16.2 Hz, 1H), 5.96 (d, J = 16.2 Hz, 1H), 3.78 (s, 3H), 2.01 (br s, 3H), 1.79−1.62 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.64, 140.18, 131.03, 127.04, 123.82, 113.90, 55.24, 42.29, 36.84, 34.96, 28.45; MS *m*/*z* (relative intensity) 268 (M^+, 100), 211 (37), 159 (14), 121 (24), 91 (18), 77 (10); HRMS calcd for $C_{19}H_{24}O$ 268.1827, found 268.1861.

Typical Experimental Procedures for the Synthesis of 14 from the Reaction of (*E*)-*β*-Nitrostyrenes 1 and 5-Iodo-2-adamantanone 13 in THF Solution in the Presence of Triethylborane 2 and Air (Equation 5 and Table 3). In a Pyrex test tube with a magnetic stirrer were placed **1a** (1 mmol) and 5-iodo-2-adamantanone **13** (6 mmol) in 8 mL of THF, the solution was bubbled with the air that filled the balloon, and then triethylborane **2** (3 mmol, 1.0 M in THF solution) was slowly added into the solution by syringe. After 5−10 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 71% of **14a**. All the experimental results are shown in Table 3.

(*E*)-1-(4-Oxoadamantyl)-2-phenylethene ((*E*)-14a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39−7.16 (m, 5H), 6.30 (d, J = 16.2 Hz, 1H), 6.09 (d, J = 16.2 Hz, 1H), 2.61 (br s, 2H), 2.21 (br s, 1H), 2.04−1.93 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.96, 138.25, 137.42, 128.56, 127.22, 126.29, 126.08, 46.28, 43.26, 41.00, 38.51, 34.93, 27.63; MS *m*/*z* (relative intensity) 252 (M^+, 100), 194 (13), 181 (62), 167 (21), 153 (10), 141 (24), 128 (20), 115 (18), 103 (9), 91 (28), 77 (11); HRMS calcd for $C_{18}H_{20}O$ 252.1514, found 252.1513.

(*E*)-1-(4-Oxoadamantyl)-2-(4-methoxyphenyl)ethene ((*E*)-14b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (dt, J = 8.8, 2.2 Hz, 2H), 6.84 (dt, J = 8.8, 2.2 Hz, 2H), 6.24 (d, J = 16.2 Hz, 1H), 5.95 (d, J = 16.2 Hz, 1H), 3.78 (s, 3H), 2.59 (br s, 2H), 2.19 (br s, 1H), 2.06−1.88 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$)δ 217.93, 158.90, 136.07, 130.07, 127.08, 125.52, 113.89, 55.09, 46.22, 43.27, 41.00, 38.42, 34.70, 27.55; MS *m*/*z* (relative intensity) 282 (M^+, 100), 211 (27), 197 (6), 181 (7), 171 (9), 159 (8), 141 (7), 128 (8), 121 (20), 91 (13), 77 (7); HRMS calcd for $C_{19}H_{22}O_2$ 282.1620, found 282.1616.

(*E*)-1-(4-Oxoadamantyl)-2-(4-chlorophenyl)ethene ((*E*)-14c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (s, 4H), 6.26 (d, J = 16.2 Hz, 1H), 6.06 (d, J = 16.2 Hz, 1H), 2.62 (br s, 2H), 2.22 (br s, 1H), 2.06−1.88 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.78, 138.92, 135.94, 132.79, 127.68, 127.31, 125.20, 46.22, 43.19, 40.92, 38.49, 35.00, 27.60; MS *m*/*z* (relative intensity) 288 ($(M + 2)^+$, 37), 286 (M^+, 100), 230 (4), 228 (12), 217 (18), 215 (47), 179 (18), 165 (18), 153 (10), 141 (14), 125 (17), 115 (13), 103 (6), 91 (11), 77 (10); HRMS calcd for $C_{18}H_{19}O^{37}Cl$ 288.1095, found 288.1107; calcd for $C_{18}H_{19}O^{35}Cl$ 286.1124, found 286.1126.

(*E*)-1-(4-Oxoadamantyl)-2-(2-thienyl)ethene ((*E*)-14d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11 (d, J = 5.0 Hz, 1H), 6.96−6.89 (m, 2H), 6.44 (d, J = 16.2 Hz, 1H), 5.95 (d, J = 16.2 Hz, 1H), 2.60 (br s, 2H), 2.20 (br s, 1H), 2.05−1.88 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.81, 142.74, 137.98, 127.33, 125.01, 123.56, 119.85, 46.20, 43.12, 40.89, 38.46, 34.96, 27.57; MS *m*/*z* (relative intensity) 258 (M^+, 100), 187 (48), 153 (21), 135 (14), 115 (9), 97 (17), 77 (8); HRMS calcd for $C_{16}H_{18}OS$ 258.1078, found 258.1079.

(*E*)-1-(4-Oxoadamantyl)-2-(2-furyl)ethene ((*E*)-14e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (dd, J = 2.0, 0.8 Hz, 1H), 6.36 (dd, J = 3.2, 2.0 Hz, 1H), 6.19−6.09 (m, 3H), 2.60 (br s, 2H), 2.22 (br s, 1H), 2.05−1.86 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 217.89, 152.92, 141.51, 136.90, 115.16, 112.21, 107.04, 46.17, 43.08, 40.81, 38.43, 34.75, 27.54; MS *m*/*z* (relative intensity) 242 (M^+, 100), 171 (24), 143 (21), 128 (17), 115 (12), 91 (17), 77 (11); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1310.

(*E*)-1-(4-Oxoadamantyl)-2-(*N*-phenyl-3-indolyl)ethene ((*E*)-14f). This compound is very unstable after isolation and decomposes at room temperature: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90−7.80 (m, 1H), 7.55−7.17 (m, 9H), 6.52 (d, J = 16.4 Hz, 1H), 6.15 (d, J = 16.4 Hz, 1H), 2.61 (br s, 2H), 2.20 (br s, 1H), 2.02−1.85 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 218.13, 139.38, 136.66, 136.14, 129.60, 127.01, 126.55, 126.04, 124.29, 122.81, 120.65, 120.04, 118.09, 115.72, 110.70, 46.37, 43.52, 41.23, 38.54, 35.06, 27.71; MS *m*/*z* (relative intensity) 367 (M^+, 100), 296 (37), 256 (23), 243 (9), 232 (8), 218 (10), 206 (9), 193 (7), 180 (7), 165 (5), 115 (5), 91 (6), 77(8).

Typical Experimental Procedures for the Synthesis of (*E*)-16 or (*Z*)-16 from the Reaction of (*E*)-15 or (*Z*)-15 and Iodoadamantane 11 in THF Solution in the Presence of Triethylborane 2 and Oxygen (Equation 6 and Table 4). In a Pyrex test tube with a magnetic stirrer were placed (*E*)-**15a** (0.93 mmol) and 5-iodo-2-adamantane **11** (6 mmol) in 8 mL of THF, the solution was bubbled with the air that filled the balloon, and then triethylborane **2** (3 mmol, 1.0 M in THF solution) was slowly added into the solution by syringe. After 5−10 min, the solvent was evaporated and the oily residue was purified by flash column chromatography by using hexane to obtain 74% of (*E*)-**16a** and (*Z*)-**16a**. The ratio of (*E*)-**16a** to (*Z*)-**16a** was approximately equal to 96:4 when the crude mixture was analyzed by the gas chromatography. Similar procedures were repeated as described above when (*Z*)-**15a** was used to obtain the same product in 90% yield and the ratio of (*E*)-**16a** to (*Z*)-**16a** approximately equal to 92:8 by GC analysis.

(*E*)-2-Cyclopentyl-2-(4-methoxyphenyl)-1-nitroethene ((*E*)-15b). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16 (dt, J = 8.8, 2.2 Hz, 2H), 6.95 (s, 1H), 6.89 (dt, J = 8.8, 2.2 Hz, 2H), 4.01−3.74 (m, 1H), 3.82 (s, 3H), 2.02−1.90 (m, 2H), 1.71−1.40 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 160.13, 157.63, 136.82, 129.22, 128.45, 113.70, 55.20, 41.03, 31.17, 25.34; MS *m*/*z* (relative intensity) 247 (M^+, 18), 216 (12), 201 (100), 185 (5), 173 (18), 159 (39), 147 (29), 133 (71), 121 (66), 115 (23), 103 (7), 91 (23), 77 (22); HRMS calcd for $C_{14}H_{17}NO_3$ 247.1209, found 247.1202.

(*Z*)-2-Cyclopentyl-2-(4-methoxyphenyl)-1-nitroethene ((*Z*)-15b). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.07 (dt, J = 8.8, 2.2 Hz, 2H), 7.02 (s, 1H), 6.91 (dt, J = 8.8, 2.2 Hz, 2H), 3.95 (s, 3H), 2.89−2.73 (m, 1H), 1.88−1.35 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.66, 155.38, 134.15, 128.54, 113.81, 113.70, 55.15, 47.37, 31.00, 24.40; MS *m*/*z* (relative intensity) 247 (M^+, 66), 230 (8), 213 (15), 203 (24), 186 (14), 175 (45), 159 (41), 147 (30), 135 (33), 128 (27), 121 (100), 115 (43), 108 (13), 91 (32), 77 (29); HRMS calcd for $C_{14}H_{17}NO_3$ 247.1209, found 247.1208.

(*E*)-2-Cyclohexyl-2-(4-methoxyphenyl)-1-nitroethene ((*E*)-15c). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16 (dt, J = 8.8, 2.2 Hz, 2H), 6.90 (dt, J = 8.8, 2.2 Hz, 2H), 6.87 (s, 1H), 3.83 (s, 3H), 3.70−3.50 (m, 1H), 1.79−1.06 (m, 10H); ^{13}C

NMR (50 MHz, $CDCl_3$) δ 160.00, 158.64, 136.14, 129.07, 128.53, 113.57, 55.15, 40.07, 30.80, 26.02, 25.58; MS *m*/*z* (relative intensity) 261 (M^+, 17), 215 (100), 199 (5), 185 (6), 173 (27), 159 (30), 147 (29), 133 (81), 121 (82), 115 (25), 107 (13), 91 (21), 77 (15); HRMS calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1370.

(*Z*)-2-Cyclohexyl-2-(4-methoxyphenyl)-1-nitroethene ((*Z*)-15c). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.05 (dt, J = 8.8, 2.2 Hz, 2H), 6.95 (s, 1H), 6.90 (dt, J = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 2.36−2.25 (m, 1H), 1.83−1.14 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.70, 156.73, 134.61, 128.31, 128.12, 113.77, 55.11, 45.61, 31.24, 26.11, 25.69; MS *m*/*z* (relative intensity) 261 (M^+, 54), 217 (25), 199 (13), 189 (12), 173 (17), 160 (25), 147 (33), 135 (43), 121 (100), 115 (31), 108 (11), 91 (23), 77 (20); HRMS calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1365.

(*E*)-2-*tert*-Butyl-2-(4-methoxyphenyl)-1-nitroethene ((*E*)-15d). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.09 (dt, J = 8.8, 2.2 Hz, 2H), 6.87 (dt, J = 8.8, 2.2 Hz, 2H), 6.58 (s, 1H), 3.82 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.32, 153.59, 136.00, 130.71, 129.18, 113.35, 55.20, 36.46, 29.15; MS *m*/*z* (relative intensity) 235 (M^+, 100), 220 (5), 203 (4), 189 (7), 174 (13), 159 (23), 147 (19), 132 (67), 121 (18), 115 (27), 103 (10), 91 (20), 77 (16), 57 (85); HRMS calcd for $C_{13}H_{15}NO_3$ 235.1208, found 235.1207.

(*Z*)-2-*tert*-Butyl-2-(4-methoxyphenyl)-1-nitroethene ((*Z*)-15d). This compound was prepared according to the literature procedures:[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.97 (dt, J = 8.8, 2.2 Hz, 2H), 6.90 (dt, J = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.22, 159.13, 135.70, 128.77, 126.75, 113.40, 55.12, 36.75, 28.50; MS *m*/*z* (relative intensity) 235 (M^+, 98), 220 (3), 203 (4), 189 (6), 174 (11), 159 (16), 147 (17), 132 (63), 121 (18), 115 (20), 103 (9), 89 (24), 77 (16), 57 (100); HRMS calcd for $C_{13}H_{15}NO_3$ 235.1208, found 235.1210.

(*E*)-1-Adamantyl-2-(3,4-dimethoxyphenyl)-1-butene ((*E*)-16a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.87−6.76 (m, 3H), 5.26 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.63 (q, J = 7.4 Hz, 2H), 1.99 (br s, 4H), 1.88−1.71 (m, 11H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.46, 147.78, 141.25, 138.33, 137.90, 119.00, 110.80, 110.41, 55.73, 43.00, 36.73, 35.08, 28.74, 28.48, 23.81, 13.75; MS *m*/*z* (relative intensity) 326 (M^+, 54), 311 (29), 295 (41), 201 (41), 135 (20), 91 (16), 79 (17); HRMS calcd for $C_{22}H_{30}O_2$ 326.2245, found 326.2244.

(*Z*)-1-Adamantyl-2-(3,4-dimethoxyphenyl)-1-butene ((*Z*)-16a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.79 (d, J = 8.4 Hz, 1H), 6.65−6.61 (m, 2H), 5.13 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.14 (q, J = 7.4 Hz, 2H), 1.80 (br s, 3H), 1.62−1.46 (m, 12H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.93, 147.31, 140.04, 136.69, 135.50, 121.20, 112.66, 110.18, 55.85, 55.70, 43.35, 36.69, 35.43, 35.37, 28.56, 13.19; MS *m*/*z* (relative intensity) 326 (M^+, 100), 311 (10), 295 (40), 201 (42), 135 (38), 91 (17), 79 (17); HRMS calcd for $C_{22}H_{30}O_2$ 326.2245, found 326.2254.

(*E*)-1-Adamantyl-2-cyclopentyl-2-(4-methoxyphenyl)ethene ((*E*)-16b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.02 (dt, J = 8.8, 2.2 Hz, 2H), 6.78 (dt, J = 8.8, 2.2 Hz, 2H), 5.01 (s, 1H), 3.79 (s, 3H), 3.34−3.21 (m, 1H), 1.98 (br s, 3H), 1.86−1.28 (m, 20H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.88, 143.26, 141.06, 136.83, 130.54, 112.64, 55.14, 43.44, 42.04, 36.87, 34.96, 31.50, 28.94, 25.01; MS *m*/*z* (relative intensity) 336 (M^+, 52), 267 (27), 201 (40), 187 (17), 171 (26), 159 (10), 147 (7), 135 (100), 121 (23), 107 (8), 93 (15), 79 (18); HRMS calcd for $C_{24}H_{32}O$ 336.2453, found 336.2453.

(*Z*)-1-Adamantyl-2-cyclopentyl-2-(4-methoxyphenyl)ethene ((*Z*)-16b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94 (dt, J = 8.8, 2.2 Hz, 2H), 6.79 (dt, J = 8.8, 2.2 Hz, 2H), 5.18 (s, 1H), 3.81 (s, 3H), 2.53−2.36 (m, 1H), 1.78 (br s, 3H), 1.78−1.21 (m, 20H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.93, 140.86, 136.81, 134.05, 130.82, 112.43, 55.08, 51.21, 43.49, 36.72, 35.38, 31.41, 28.62, 24.40; MS *m*/*z* (relative intensity) 336 (M^+, 54), 267 (29), 201 (41), 187 (20), 171 (27), 159 (10), 147 (7), 135 (100), 121 (22), 107 (8), 93 (16), 79 (17); HRMS calcd for $C_{24}H_{32}O$ 336.2453, found 336.2456.

(*E*)-1-Adamantyl-2-cyclohexyl-2-(4-methoxyphenyl)ethene ((*E*)-16c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00 (dt, J = 8.8, 2.2 Hz, 2H), 6.78 (dt, J = 8.8, 2.2 Hz, 2H), 4.90 (s, 1H), 3.79 (s, 3H), 2.98−2.78 (m, 1H), 2.06−0.83 (m, 25H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.85, 146.40, 139.63, 137.07, 130.33, 112.52, 55.14, 43.38, 41.01, 36.89, 34.93, 32.08, 28.82, 26.67, 25.90; MS *m*/*z* (relative intensity) 350 (M^+, 73), 267 (35), 215 (64), 201 (27), 185 (4), 171 (22), 159 (9), 147 (10), 135 (100), 121 (24), 107 (9), 93 (16), 79 (17); HRMS calcd for $C_{25}H_{34}O$ 350.2610, found 350.2606.

(*Z*)-1-Adamantyl-2-cyclohexyl-2-(4-methoxyphenyl)ethene ((*Z*)-16c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.93 (dt, J = 8.8, 2.2 Hz, 2H), 6.79 (dt, J = 8.8, 2.2 Hz, 2H), 5.12 (s, 1H), 3.82 (s, 3H), 2.02−1.83 (m, 1H), 1.83−0.90 (m, 25H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.90, 143.64, 136.69, 134.05, 130.73, 112.28, 55.06, 49.05, 43.45, 36.69, 35.28, 32.36, 28.59, 26.67, 26.07; MS *m*/*z* (relative intensity) 350 (M^+, 88), 267 (44), 215 (75), 201 (33), 185 (5), 171 (27), 159 (11), 147 (11), 135 (100), 121 (28), 107 (11), 93 (18), 79 (20); HRMS calcd for $C_{25}H_{34}O$ 350.2610, found 350.2611.

(*Z*)-1-Adamantyl-2-*tert*-butyl-2-(4-methoxyphenyl)-ethene ((*Z*)-16d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92 (dt, J = 8.8, 2.2 Hz, 2H), 6.78 (dt, J = 8.8, 2.2 Hz, 2H), 5.23 (s, 1H), 3.82 (s, 3H), 1.82−1.70 (m, 3H), 1.70−1.323 (m, 12H), 0.99 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.94, 146.28, 135.03, 132.99, 131.86, 111.93, 55.09, 43.35, 36.72, 36.38, 35.28, 30.00, 28.65; MS *m*/*z* (relative intensity) 324 (M^+, 32), 267 (100), 211 (3), 171 (9), 159 (6), 147 (10), 135 (79), 121 (11), 107 (8), 93 (12), 79 (13); HRMS calcd for $C_{23}H_{32}O$ 324.2453, found 324.2452.

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Supporting Information Available: ^{1}H and ^{13}C spectra of compounds (*Z*)-**1a**, (*E*)-**3c**, (*E*)-**3f**, (*E*)-**5b**−**f**, (*E*)-**7a**−**f**, (*E*)-**10a**−**f**, (***E***)-**12**, (*E*)-**14a**−**f**, (*E*)- and (*Z*)-**15a**−**d**, (*E*)- and (*Z*)-**16a**−**c**, and (*Z*)-**16d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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