An Improved and Easy Method for the Preparation of 2,2-Disubstituted 1-Nitroalkenes

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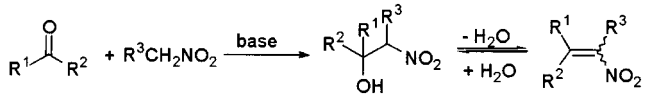
Reactions of ketones **1**, nitromethane **2**, and catalytic amount of piperidine **3** in the presence of mercaptan **6** generate *β*-nitroalkyl sulfides **7**−**9**. At 0 °C and by the use of dichloromethane as solvent, *β*-nitroalkyl sulfides **7**−**9** can be oxidized by *m*-chloroperoxybenzoic acid (*m*-CPBA) **10** to generate *β*-nitroalkyl sulfoxides **11**−**13** and undergo elimination in carbon tetrachloride solution to produce medium to high yield of 2,2-disubstituted 1-nitroalkenes **5**. The irreversibility of the synthetic mechanism not only can overcome the reversibility of the Henry reaction in the synthesis of 2,2-disubstituted 1-nitroalkenes **5** but also can generate the major products "*exo*-nitro olefins" **5c**−**e** when cyclic ketones **1c**−**e** were used. Under similar conditions, medium to high yield of 5-substituted-2-nitromethyl-2-phenylthioadamantane **17** also can be prepared from the reaction of 5-substituted-2-adamantanones **15**, nitromethane **2**, piperidine **3**, thiophenol **6a**. The intermediate **17** can be oxidized by *m*-CPBA **10** in dichloromethane solution and then undergo elimination at room temperature or can be dissolved in solvent, coated on silica gel, and then heated at 90−100 °C to generate 5-substituted-2-nitromethyleneadamantane **16**.

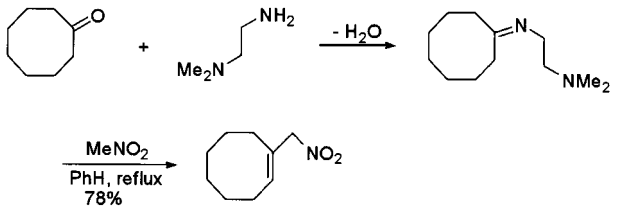
Introduction

Nitro olefins are useful intermediates in organic synthesis and are important structural units which can be used as starting materials for many classes of compounds including bioactive compounds.[1] Generally, nitroalkenes are prepared by nitro-aldol approach of the nitroalkanes with a carbonyl compound, followed by dehydration of the 2-nitro alcohols (Scheme 1).[2] Unfortunately, the Henry reaction is impractical for the preparation of 2,2-disubstituted 1-nitroalkenes due to the reversibility of the reaction when ketones are used.[3] Tamura et al. have utilized *N*,*N*-dimethylethylenediamine to drive the condensation of ketones with nitroalkanes, but the major products are *β*,*γ*-unsaturated tautomers (Scheme 2).[3c] It has been reported by Loubinoux and co-workers that di- and trisubstituted α-nitroalkenes can be prepared from the treatment of tertiary *β*-nitro alcohols with acetic anhydride and followed by potassium methoxide or *tert*-butoxide (Scheme 3).[4] Knochel and co-workers have described the preparation of 2,2-disubstituted 1-nitroalkenes from the addition/elimination of copper−zinc organometallic reagents to nitroalkenes substituted with leaving groups at the *β*-position (Scheme 4).[5] In 1981, Sakakibara et al. have reported the synthesis of 1-nitroalkenes from nitroalkanes utilizing selenium chemistry (Scheme 5).[6] It was in 1993 Denmark and Marcin

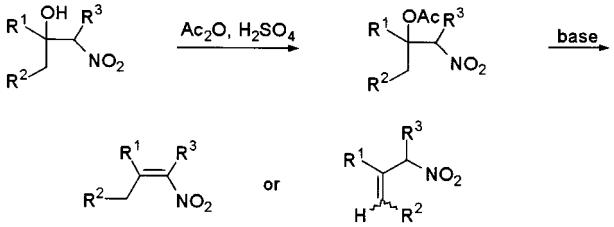
Scheme 1



Scheme 2



Scheme 3



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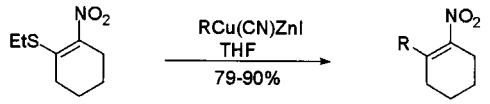
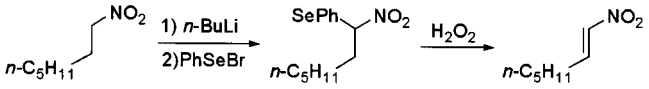
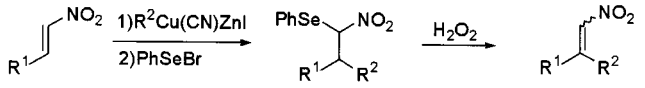
Scheme 4



Scheme 5



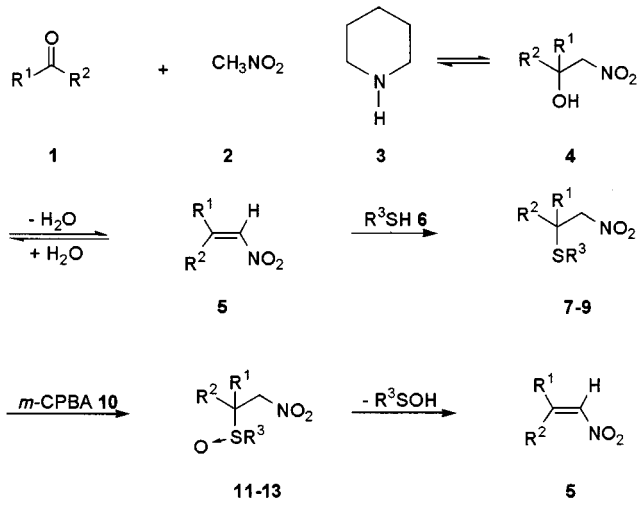
Scheme 6



had reported a synthesis of 2,2-disubstituted 1-nitroalkenes by combining Knochel's and Sakakibara's work, involving the conjugate addition of copper−zinc reagents to 1-nitroalkenes, followed by phenylselenation and oxidative elimination (Scheme 6).[7]

It has been reported that sulfoxides and sulfones with a β-hydrogen undergo elimination on treatment with an alkoxide.[8] Sulfoxides also undergo elimination on pyrolysis at about 80 °C, and the reaction is proposed to proceed through Ei mechanism with syn elimination.[9] Sulfoxides have been used as intermediates for the conversion of ketones, aldehydes, and carboxylic esters to their α,β-unsaturated derivatives.[10] The preparation of *tert*-benzylthionitroalkanes from the mixture of ketones, nitromethane, and benzyl mercaptan in benzene in the presence of piperidine also has been reported.[11] On the basis of above observation,[9−11] we developed an improved method by the use of ketones **1**, nitromethane **2**, piperidine **3**, mercaptan **6**, and *m*-chloroperoxybenzoic acid (*m*-CPBA) **10**, which is an amalgamation of Carroll's and Trost's work, involving the nitro-aldol addition to generate the intermediate tertiary β-nitro alcohols **4**, dehydration of **4** to form nitroalkenes **5** (reversible), conjugate addition of the mercaptan **6** to **5** to yield β-nitro sulfides **7**−**9**, oxidation of **7**−**9** with *m*-CPBA **10** to form β-nitro sulfoxides **11**−**13**, and finally undergo β-elimination to obtain 2,2-disubstituted 1-nitroalkenes **5** (Scheme 7).

Scheme 7



1, 4, 5

a. $R^1 = R^2 = CH_3$

b. $R^1 = CH_3$, $R^2 = C_2H_5$

c. $R^1 + R^2 = (CH_2)_4$

d. $R^1 + R^2 = (CH_2)_5$

e. $R^1 + R^2 = (CH_2)_6$

6

a. $R^3 = Ph$

b. $R^3 = PhCH_2$

c. $R^3 = CH_2CH{=}CH_2$

7, 11

a. $R^1 = R^2 = CH_3$, $R^3 = Ph$

b. $R^1 = CH_3$, $R^2 = C_2H_5$, $R^3 = Ph$

c. $R^1 + R^2 = (CH_2)_4$, $R^3 = Ph$

d. $R^1 + R^2 = (CH_2)_5$, $R_3 = Ph$

e. $R^1 + R^2 = (CH_2)_6$, $R_3 = Ph$

8, 12

a. $R^1 = R^2 = CH_3$, $R^3 = PhCH_2$

b. $R^1 = CH_3$, $R^2 = C_2H_5$, $R^3 = PhCH_2$

c. $R^1 + R^2 = (CH_2)_4$, $R^3 = PhCH_2$

d. $R^1 + R^2 = (CH_2)_5$, $R_3 = PhCH_2$

e. $R^1 + R^2 = (CH_2)_6$, $R_3 = PhCH_2$

9, 13

a. $R^1 = R^2 = CH_3$, $R^3 = CH_2CH{=}CH_2$

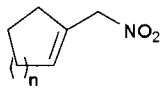
b. $R^1 = CH_3$, $R^2 = C_2H_5$, $R^3 = CH_2CH{=}CH_2$

c. $R^1 + R^2 = (CH_2)_4$, $R^3 = CH_2CH{=}CH_2$

d. $R^1 + R^2 = (CH_2)_5$, $R_3 = CH_2CH{=}CH_2$

e. $R^1 + R^2 = (CH_2)_6$, $R_3 = CH_2CH{=}CH_2$

14



a. n = 1

b. n = 2

c. n = 3

Results and Discussion

It has been reported by Eckstein et al. that cycloheptanone **1e** reacts with nitromethane **2** to give 14% of *endo*-nitro olefin 1-cycloheptenylnitromethane **14c** after 18 days at 45−50 °C in the presence of piperidine **3** as catalyst. This method was also improved by treating **1e** with nitromethane **2**, piperidine **3**, and using benzene as solvent, and the solution was heated on a steam bath to remove water to give about 60% of **14c**.[12a,b] Similarly, the preparation of 1-cyclohexenylnitromethane **14b** by heating 1-nitromethyl-1-hydroxycyclohexane with piperidine also has been reported by the same group.[12c,d] The isomerization of 2-nitro-2-nonene into the mixture of 2-nitro-2-nonene and 2-nitro-3-nonene under the catalysis of *N*,*N*-dimethylethylenediamine in refluxing benzene

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Table 1. The Preparation of β-Nitroalkyl Sulfides 7−9 from the Reaction of Ketone 1, Nitromethane 2, Piperidine 3, and Mercaptan 6

entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	**6** (equiv)	time (h)[a]	**7−9**	yield (%)[b]
1	**1a** (3.2)	1.0	0.6	**6a** (3.6)	60[c]	**7a**	84
2	**1b** (1.2)	1.0	0.5	**6a** (1.2)	23	**7b**	95
3	**1c** (1.0)	4.0	0.6	**6a** (2.4)	61	**7c**	100
4	**1d** (1.2)	1.0	0.6	**6a** (3.6)	60[c]	**7d**	84
5	**1e** (1.1)	1.0	0.2	**6a** (1.3)	70	**7e**	NR
6	**1a** (1.0)	1.0	0.35	**6b** (1.0)	12−15	**8a**	87−100[d]
7	**1b** (1.0)	1.0	0.35	**6b** (1.0)	12−15	**8b**	87−100[d]
8	**1c** (1.0)	1.0	0.35	**6b** (1.0)	12−15	**8c**	87−100[d]
9	**1d** (1.0)	1.0	0.35	**6b** (1.0)	12−15	**8d**	87−100[d]
10	**1e** (1.0)	1.0	0.35	**6b** (1.0)	12−15	**8e**	87−100[d]
11	**1a** (1.0)	1.0	0.1	**6c** (0.9)	8[c]	**9a**	77[e]
12	**1b** (1.0)	1.0	0.2	**6c** (1.1)	17	**9b**	94
13	**1c** (1.1)	1.0	0.2	**6c** (1.3)	78	**9c**	76
14	**1d** (1.0)	1.0	0.1	**6c** (0.9)	8[c]	**9d**	76[e]
15	**1e** (1.1)	1.0	0.2	**6c** (1.1)	67	**9e**	22[f]

[a] Benzene was used as solvent with a Dean−Stark trap to remove water. [b] Isolated yield. [c] The reaction was performed in solvent-free at 80 °C. [d] Reference 11. [e] Reference 16. [f] 55% of **14c** was also isolated.

for 24 h and the mechanism has been proposed in the literature.[3c] According to these reports,[3c,7,12−15] it seems to be impossible to prepare **5c−e** directly by the use of cyclic ketones and nitromethane in the presence of base. To prepare pure *exo*-nitroolefins, it might be possible to trap the product *exo*-nitro olefins by using suitable reagent to prevent the transformation of *exo*-nitro olefins into *endo*-nitro olefins. On the basis of literature reports,[11,16,17] we added mercaptan as trapping reagent with a Dean−Stark trap to remove water to obtain the intermediate β-nitroalkyl sulfides **7−9**. Although literature had reported that benzyl mercaptan[11] or allyl mercaptan[16] can be used to prepare β-nitroalkyl sulfides, we speculated that the choice of trapping reagent mercaptan **6** might be critical for successful reactions with different ketones **1**. To find the most suitable mercaptan, condensation of ketones **1** with nitromethane **2** and different mercaptan **6** in the presence of a catalytic amount of piperidine **3** in refluxing benzene with a Dean−Stark trap to remove water by azeotropic distillation or just performed in solvent-free condition were studied (Scheme 1 and Table 1).

To ketones **1a−d**, mercaptan **6a**, **6b**, and **6c** all can trap the nitroalkenes **5** to generate medium to high yield of β-nitroalkyl sulfides **7−9**. When acetone **1a** was used, the reaction was just performed in solvent-free condition due to the low boiling point of **1a** (entries 1 and 11). No expected product **7e** was observed when **1e** was used to react with **2**, **3**, and thiophenol **6a** under similar conditions (entry 5). Only **6b** can trap **5e** successfully to generate high yield of **8e** when **1e** was used (entry 10), and this result is also consistent with literature report.[11] We are surprised to find that not only 22% of **9e** but also 55% of **14c** was isolated when allyl mercaptan **6c** was used. The NMR analysis of the crude mixture at different stage also found that both **9e** and **14c** increased gradually and this result indicates that some product **5e** had already been converted into **14c** before it was trapped by allyl mercaptan **6c**.

Table 2. The Preparation of 2,2-Disubstituted-1-nitroalkene 5 from β-Nitroalkyl Sulfides 7−9

entry	**7−9**	**10** (equiv)	CH_2Cl_2 time (h)	CCl_4 time (h)	**5**	yield (%)[a]
1	**7a**	1.0	0.5	6.0	**5a**	67
2	**7b**	1.0	1.0	3.0	**5b**	78[b]
3	**7c**	1.0	1.0	2.0	**5c**	67
4	**7d**	1.0	1.5	1.0	**5d**	100
5	**8a**	1.0	1.0	4.5	**5a**	100
6	**8b**	1.0	0.5	2.0	**5b**	87[b]
7	**8c**	1.1	0.25	3.0	**5c**	97
8	**8d**	1.0	0.5	2.0	**5d**	100
9	**8e**	1.0	1.0	2.5	**5e**	54
10	**9a**	1.15	0.5	5.0	**5a**	82
11	**9b**	1.0	0.5	4.5	**5b**	90[b]
12	**9c**	1.1	1.0	1.0	**5c**	100
13	**9d**	1.15	0.5	5.0	**5d**	78
14	**9e**	1.0	1.0	2.0	**5e**	78

[a] Isolated yield. [b] $E + Z$ isomers.

After purified by chromatography, β-nitroalkyl sulfides **7−9** were oxidized with 1.0−1.15 equiv of *m*-CPBA **10** in CH_2Cl_2 solution, and the solution was stirred for 0.25−1 h at room temperature. When the reaction was complete, the solvent CH_2Cl_2 was removed by distillation to obtain the crude product β-nitroalkyl sulfoxides **11−13 (11a**, **12a**, and **13a** were purified by chromatography). Carbon tetrachloride was added to the mixture, and the solution was refluxed for 1−6 h to obtain the final product **5** (Table 2). Only trace of **5** were generated if the elimination reaction was also performed in CH_2Cl_2 because the temperature is too low for **11−13** to undergo elimination reaction.[9]

The NMR and GC analysis of the crude product indicated only the *exo*-nitro olefins **5c−e** were generated, and none of *endo*-nitro olefins **14a−c** were detected. Only traces of **14a−c** could be found after chromatography purification, and this result indicates that **5c−e** actually isomerize to **14a−c** during column purification. Compared to literature report,[3c] we found this improved and easy method is good enough to prepare medium to high yields of *exo*-nitro olefins **5c−e**. When intermediates **11−13** undergo Ei elimination, the generation of the *exo*-nitro olefins **5c−e** but not the *endo*-nitro olefins **14a−c** is due to the thermodynamic driving force of the conjugation of the olefin with the nitro group in the *exo* product.

It was in 1983 that Barton et al. had reported 2-nitromethyleneadamantane **16a** can be prepared from the

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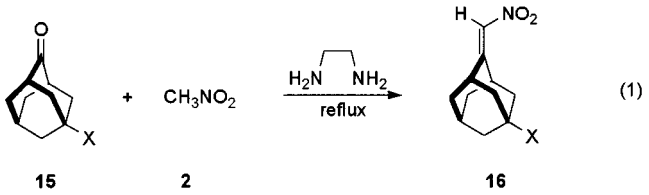
Table 3. The Preparation of 5-Substituted 2-Nitromethyleneadamantane 16 According to Barton's Methodology



(1)

15 **2** **16**

15, 16

a. X = H **d**. X = Cl
b. X = Ph **e**. X = Br
c. X = F **f**. X = I

entry	15	16	reflux 3 h yield (%)	reflux 24 h yield (%)[b]
1	**15a**	**16a**	65	86
2	**15b**	**16b**	84	89
3	**15c**	**16c**	60	72
4	**15d**	**16d**	62	83
5	**15e**	**16e**	56	80
6	**15f**	**16f**	74	79

[a] Isolated yield. [b] NMR yield.

reaction of 2-adamantanone **15a** and nitromethane **2** in the presence of ethylenediamine as catalyst under refluxing condition (eq 1).[18] According to literature procedures, our study found compound **16** actually can be synthesized by this useful methodology but some of unreacted 5-substituted 2-adamantanone **15** were always recovered even the solution was refluxed for 24 h (Table 3).

To improve these reactions, **15** were used to react with nitromethane **2**, thiophenol **6a**, and piperidine **3** in refluxing benzene, and the system was also equipped with a Dean−Stark trap to remove water as described above. To obtain higher yields of 5-substituted- 2-nitromethyl-2-phenylthioadamantane **17**, equal amounts of **2**, **6a**, and **3** were added to the solution at different stages, and the solution was refluxed for 36−98 h. After evaporation of the solvent, medium to high yields of **17** were isolated by column chromatography (eq 2 and Table 4). Conversion of **15a** to **16a** requires a significantly longer reaction time than does the conversion of **1c** to **5c**, presumably due to the greatly increased steric hindrance of the ketone in **15a**.

When **17a**−**e** were treated with *m*-CPBA **10** in CH_2Cl_2 solution and were stirred for 1−2 h at room temperature, high yields of **16a**−**e** were isolated. In contrast to the conversion of **7**−**9** to **5** as summarized in Table 2, a one-pot reaction done in CH_2Cl_2 solution was sufficient to convert **17** to **16** with the exception of **17f** which gave only a trace amount of **16f** as shown in eq 3 and Table 5.

During the purification of the intermediate **17** by column chromatography, we found trace of **16** always were isolated, and this result indicated that **17** possibly also can undergo elimination on the silica gel surface. To prove this assumption, **17** was dissolved in a little amount of dichloromethane or ethyl acetate, and then the solution was coated on silica gel. After heating the silica gel at 90−100 °C for 1−6 h, medium to high yield of **16** were formed (eq 4 and Table 6). From substance **17f**, 95% of **16f** was isolated, and the result was much better than the former result which was described above (eq 3).

In conclusion, we have developed an improved and easy method for the synthesis of 2,2-disubstituted 1-nitroalkenes. We have demonstrated the utility of this method to synthesize of *exo*-nitro olefins **5c**−**e** as the major products which are not easy to be prepared according to literature procedures. Similarly, 5-substituted-2-nitromethyleneadamantane **16** are also can be synthesized by this method or can be prepared by heating **17** with silica gel at 90−100 °C. The application of these nitroalkenes for cycloaddition has been studied and will be reported in the future.

Experimental Section

General. All reactions were performed in flame- or oven-dried glassware under a positive pressure of nitrogen. Benzene and CH_2Cl_2 were distilled from calcium hydride. CCl_4 was distilled from P_2O_5. 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 by JEOL JMS-D300 or JEOL JMS−HX110 spectrometer. ^1H 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) were given in ppm relative to TMS. Elemental analysis was performed on a Perkin-Elmer 2400 instrument. All melting points were determined with MEL-TEMPII apparatus and were uncorrected.

Materials. Ketones **1a**−**e**, nitromethane **2**, piperidine **3**, mercaptan **6a**−**c**, *m*-chloroperoxybenzoic acid **10**, and 2-adamantanone **15a** were purchased from Aldrich Chemical Co and other commercially available reagents were used without further purification. Starting material **15b**,[19,20a] **15c**,[19,20] **15d**,[19,20a] **15e**,[19,20a,21,22] and **15f**[19,23] were prepared according to the literature procedures.

Typical Experimental Procedures for the Synthesis of the β-Nitroalkyl Sulfides 7−9 from the Reaction of Ketones 1, Nitromethane 2, and Mercaptan 6 in the Presence of Piperidine 3 as Catalyst and Benzene as Solvent (Table 1). In a 100 mL round-bottomed flask fitted with a Dean−Stark trap were placed the ethyl methyl ketone **1b** (36 mmol), nitromethane **2** (30 mmol), piperidine **3** (15 mmol), and thiophenol **6a** (36 mmol) in 50 mL of benzene, and the solution was refluxed for 23 h. After the solution was cooled, the solution was washed with ice cold dilute hydrochloric acid solution, washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The purification of the mixture was carried out by flash column chromatography by using hexanes−ethyl acetate (200:1) to obtain 95% of **7b**. Not only 22% of **9e** but also 55% of **14c** was isolated when ketone **1e** was used to react with allyl mercaptan **6c** under similar conditions.

Typical Experimental Procedures for the Synthesis of the β-Nitroalkyl Sulfides 7a, 7d, and 9e from the Reaction of Ketone 1a or 1d, Nitromethane 2, and Mercaptan 6a or 6c in the Presence of Piperidine 3 under Solvent-Free Conditions (Table 1). A stirred mix-

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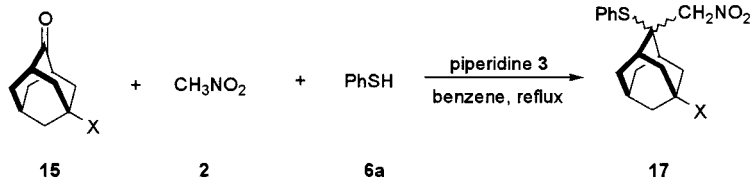
Table 4. The Preparation of 17 from 15, Nitromethane 2, Piperidine 3, and Thiophenol 6a



(2)

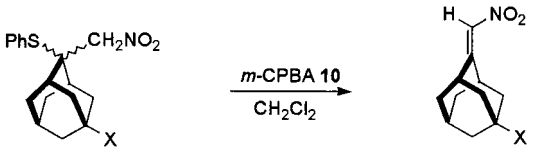
15 **2** **6a** **17**

15,17 a. X = H b. X = Ph c. X = F d. X = Cl e. X = Br f. X = I

entry	**15**	**2** (equiv)	**3** (equiv)	**6a** (equiv)	time(h)[a]	**17**	yield(%)[b]
1	**15a**	16	6	8	36	**17a**	100
2	**15b**	32	3	16	86	**17b**	100
3	**15c**	40	4	20	98	**17c**	87
4	**15d**	32	2	16	62	**17d**	65
5	**15e**	32	4	16	50	**17e**	86
6	**15f**	32	5	19	87	**17f**	100

[a] Benzene was used as solvent with a Dean−Stark trap to remove water. [b] Isolated yield.

Table 5. The Preparation of 16 by Treating 17 with m-CPBA 10



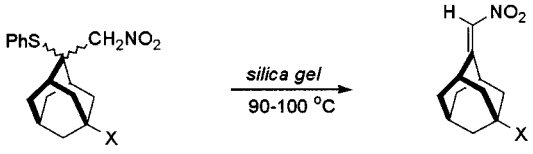
(3)

17 **16**

entry	**17**	time(h)	**16**	yield(%)[a]
1	**17a**	1.5	**16a**	97
2	**17b**	1.0	**16b**	96
3	**17c**	1.0	**16c**	96
4	**17d**	1.0	**16d**	100
5	**17e**	1.0	**16e**	100
6	**17f**	2.0	**16f**	tr

[a] Isolated yield.

Table 6. The Preparation of 16 by Heating 17 with Silica Gel at 90−100 °C



(4)

17 **16**

entry	**17**	time(h)	**16**	yield(%)[a]
1	**17a**	6	**16a**	89
2	**17b**	1	**16b**	70
3	**17c**	1	**16c**	87
4	**17d**	1	**16d**	79
5	**17e**	6	**16e**	67
6	**17f**	1	**16f**	95

[a] Isolated yield.

ture of nitromethane **2** (10 mmol), piperidine **3** (3 mmol), and thiophenol **6a** (18 mmol) was treated with acetone **1a** (16 mmol). Heat evolved, and the mixture was heated at 80 °C (oil bath) for 8 h. After the solution was cooled, additional acetone **1a** (16 mmol), piperidine **3** (3 mmol), and thiophenol **6a** (18 mmol) were added into the reaction mixture, and the solution was heated for another 30 h at 80 °C. Dichloromethane was added, and the resulting solution was washed with ice cold dilute hydrochloric acid solution, washed with brine, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the oily residue containing **7a** was purified by flash column chromatography by using hexanes−ethyl acetate (200:1) to obtain 84% of **7a**.

1-Nitro-2-methyl-2-phenylthiopropane (7a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60−7.35 (m, 5H), 4.42 (s, 2H), 1.44 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 130.0, 129.7, 129.2, 84.9, 46.5, 26.3. MS *m*/*z* (relative intensity) 211 (M^+, 8), 165 (31), 110 (100). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.84; H, 6.20; N, 6.63. Found: C, 57.09; H, 6.29; N, 6.62.

1-Nitro-2-methyl-2-phenylthiobutane (7b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58∼7.27 (m, 5H), 4.50 (d, J = 11.0 Hz, 1H), 4.40 (d, J = 11.0 Hz, 1H), 1.70 (m, 2H), 1.34 (m, 3H), 1.14 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.9, 129.9, 129.5, 129.2, 83.3, 50.9, 30.4, 23.6, 8.4. MS *m*/*z* (relative intensity) 225 (M^+, 7), 179 (13), 110 (100). HRMS calcd for $C_{11}H_{15}N_2S$ (M^+) 225.0823, found 225.0804.

1-Nitromethyl-1-phenylthiocyclopentane (7c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.62−7.54 (m, 2H), 7.44−7.32 (m, 3H), 4.49 (s, 2H), 2.10−1.66 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.4, 130.8, 129.7, 129.2, 82.2, 58.1, 36.0, 23.5. HRMS calcd for $C_{12}H_{15}NO_2S$ (M^+) 237.0823, found 237.0818. Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.59; H, 6.49; N, 5.75.

1-Nitromethyl-1-phenylthiocyclohexane (7d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.63−7.55 (m, 2H), 7.46−7.29 (m, 3H), 4.41 (s, 2H), 2.05−1.17 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 129.8, 129.5, 129.2, 84.1, 51.8, 33.1, 25.3, 21.6. MS *m*/*z* (relative intensity) 251 (M^+, 38), 205 (16), 110 (100). HRMS calcd for $C_{13}H_{17}NO_2S$ (M^+) 251.0980, found 251.0984. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.58. Found: C, 62.05; H, 6.82; N, 5.70.

2-Benzylthio-2-nitromethylpropane (8a):[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37−7.23 (m, 5H), 4.43 (s, 2H), 3.81 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.1, 129.0, 128.8, 127.5, 85.0, 44.4, 33.5, 26.4. MS *m*/*z* (relative intensity) 225 (M^+, 0.5), 123 (4.5), 91 (100). HRMS calcd for $C_{11}H_{15}NO_2S$ (M^+) 225.0824, found 225.0822. Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22. Found: C, 58.56; H, 6.83; N, 6.42.

2-Benzylthio-2-nitromethylbutane (8b):[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36−7.31 (m, 5H), 4.51 (d, J = 11 Hz, 1H), 4.44 (d, J = 11 Hz, 1H), 3.37 (d, J = 12.1 Hz, 1H), 3.70 (d, J = 12.1 Hz, 1H), 1.78 (q, J = 7.2 Hz, 2H), 1.44 (s, 3H), 1.05 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.9, 129.0, 128.7, 127.4, 83.5, 48.6, 32.8, 30.5, 23.5, 8.2. MS *m*/*z* (relative intensity) 339 (M^+, 45), 193 (100), 179 (45). HRMS calcd for $C_{12}H_{17}NO_2S$ (M^+) 239.0980, found 239.0982.

1-Benzylthio-1-nitromethylcyclopentane (8c):[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.37−7.19 (m, 5H), 4.55 (s, 2H), 3.76 (s, 2H), 1.97−1.65 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.7, 128.8, 128.3, 126.9, 82.1, 54.9, 36.3, 33.6, 23.4. MS *m*/*z* (relative

intensity) 251 (M^+, 9), 205 (17), 203(78), 124 (15), 123 (71), 91 (100). HRMS calcd for $C_{13}H_{17}NO_2S$ (M^+) 251.0980, found 251.0981. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.58. Found: C, 62.22; H, 6.85; N, 5.82.

1-Benzylthio-1-nitromethylcyclohexane (8d):[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35−7.16 (m, 5H), 4.46 (s, 2H), 3.65 (s, 2H), 1.85−1.12 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.8, 129.0, 128.5, 127.2, 84.5, 49.4, 33.2, 31.9, 25.1, 21.2. MS *m/z* (relative intensity) 265 (M^+, 0.5), 219 (1.5), 91 (100). HRMS calcd for $C_{14}H_{19}NO_2S$ (M^+) 265.1137, found 265.1138. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.35; H, 7.48; N, 5.37.

1-Benzylthio-1-nitromethylcycloheptane (8e):[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39−7.19 (m, 5H), 4.47 (s, 2H), 3.74 (s, 2H), 2.09−1.38 (m, 12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.9, 129.1, 128.7, 127.3, 84.5, 52.4, 36.6, 33.0, 29.6, 22.5. MS *m/z* (relative intensity) 279 (M^+, 170), 233 (20), 123 (27), 91 (100). HRMS calcd for $C_{15}H_{21}NO_2S$ (M^+) 279.1293, found 279.1290.

2-Allylthio-2-methyl-1-nitropropane (9a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.95−5.74 (ddt, J = 17.1, 10.0, 7.0 Hz, 1H), 5.29−5.18 (dq, J = 17.1, 1.4 Hz, 1H), 5.18−5.10 (dq, J = 10.0, 1.2 Hz, 1H), 4.52 (s, 2H) 3.29−3.24 (dt, J = 6.8, 1.2 Hz, 2H), 1.48 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.1, 117.7, 84.8, 43.9, 31.9, 26.2. MS *m/z* (relative intensity) 175 (M^+, 6), 129 (22), 73 (100). HRMS calcd for $C_7H_{13}NO_2S$ (M^+) 175.0667, found 175.0670.

2-Allylthio-2-methyl-1-nitrobutane (9b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.94−5.73 (ddt, J = 17.0, 10.7 Hz, 1H), 5.29−5.19 (dq, J = 17.0, 1.4 Hz, 1H), 5.16−5.08 (dq, J = 10.0, 1.2 Hz, 1H), 4.57 (d, J = 11.4 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 3.23−3.18 (dt, J = 7, 1.2 Hz, 2H), 1.73 (q, J = 7 Hz, 2H), 1.42 (s, 3H), 1.05 (t, J = 7.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.1, 117.9, 83.4, 48.3, 31.4, 30.4, 23.4, 8.1. MS *m/z* (relative intensity) 189 (M^+, 9), 143 (24), 87 (100). HRMS calcd for $C_8H_{15}NO_2S$ (M^+) 189.0824, found 189.0821.

1-Allylthio-1-nitromethylcyclopentane (9c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.96−5.75 (ddt, J = 17.1, 9.8, 7 Hz, 1H), 5.27−5.16 (dq, J = 17.0, 1.2 Hz, 2H), 5.14−5.10 (dq, J = 9.9, 1.2 Hz, 1H), 4.60 (s, 2H), 3.21 (dt, J = 7, 1.4 Hz, 2H), 1.97−1.63 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.1, 117.4, 82.4, 54.8, 36.4, 32.5, 23.5. MS *m/z* (relative intensity) 201 (M^+, 60), 155 (100), 128 (40). HRMS calcd for $C_{11}H_{19}NO_2S$ (M^+) 201.0823, found 201.0826.

1-Allylthio-1-nitromethylcyclohexane (9d):[16] ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.85 (ddt, J = 17, 9.8, 7 Hz, 1H), 5.23 (dq, J = 16.9, 1.4 Hz, 1H), 5.12 (dq, J = 9.9, 1 Hz, 1H), 4.54 (s, 2H), 3.15 (dt, J = 7, 1.4 Hz, 2H), 1.55−1.87 (m, 9H), 1.26 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.0, 117.8, 84.7, 49.3, 33.3, 30.9, 25.2, 21.4. MS *m/z* (relative intensity) 215 (M^+, 60), 95 (M^+, 100).

1-Allylthio-1-nitromethylcycloheptane (9e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.95−5.74 (ddt, J = 17.1, 9.8, 7.0 Hz, 1H), 5.22 (dq, J = 16.9, 1.6 Hz, 1H), 5.11 (dq, J = 9.9, 1.2 Hz, 1H), 4.51 (s, 2H), 3.20 (dt, J = 7, 1.2 Hz, 2H), 2.06−1.44 (m, 12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.1, 117.8, 84.6, 52.1, 36.7, 31.6, 29.5, 22.5. MS *m/z* (relative intensity) 229 (M^+, 56), 183 (100), 156 (53). HRMS calcd for $C_{11}H_{19}NO_2S$ (M^+) 229.1137, found 229.1138.

Typical Experimental Procedures for the Synthesis of Nitroalkenes 5 from the Oxidation of *β*-Nitroalkyl Sulfides 7−9 with *m*-CPBA 10 in CH_2Cl_2 Solution and Followed by Elimination in Refluxing CCl_4 (Table 2). At 0 °C, 8 mmol of **7d** and 8 mmol *m*-CPBA of **10** were dissolved in 50 mL of CH_2Cl_2 and stirred for few minutes at the same temperature. The temperature was raised to room temperature, and the solution was stirred for 1.5 h. After the reaction was complete by checking with TLC plate, CH_2Cl_2 was distilled to obtain crude product **11**−**13** (**11a**, **12a**, and **13a** were purifed by chromatography). To the crude mixture was then added 50 mL of CCl_4, and it was refluxed for 1 h. After the solution was cooled, the solution was washed with brine, extracted by dichloromethane solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The purification of the mixture was carried out by flash column chromatography by using hexanes−ethyl acetate (400:1) to obtain 100% of **5d**.

(2-Methyl-1-nitro-propane-2-sulfinyl)benzene (11a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.65−7.55 (m, 5H), 4.74 (d, J = 11.2 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 1.43 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.9, 132.3, 129.1, 126.3, 76.4, 57.7, 19.5, 18.8. MS *m/z* (relative intensity) 227 (M^+, tr), 125 (100). HRMS calcd for $C_{10}H_{13}NO_3S$ (M^+) 227.0616, found 227.0614.

(2-Methyl-1-nitropropane-2-sulfinylmethyl)benzene (12a): Colorless solid and the melting point is 46−48 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40−7.31 (m, 5H), 4.74 (d, J = 11.4 Hz, 1H), 4.55 (d, J = 11.4 Hz, 1H), 3.93 (d, J = 12.8 Hz, 1H), 3.71 (d, J = 31.2 Hz, 1H) 1.48 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 130.4, 130.1, 129.0, 128.5, 79.8, 55.9, 52.9, 19.6, 18.4. MS *m/z* (relative intensity) 241 (M^+, 3), 129 (11), 123 (100), 91(73). HRMS calcd for $C_{11}H_{15}NO_3S$ (M^+) 241.0773, found 241.0778. Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80. Found: C, 54.86; H, 6.18; N, 5.68.

3-(2-Methyl-1-nitropropane-2-sulfinyl)propene (13a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.07−5.86 (m, 1H), 5.51 (s, 1H), 5.44 (dd, J = 6.2, 1 Hz, 1H), 4.76 (d, J = 11.2 Hz, 1H), 4.58 (d, J = 11.2 Hz, 1H), 3.377 (dd, J = 10, 12.8 Hz, 1H), 3.376 (dd, J = 17.3, 12.8 Hz, 1H) 1.45 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.5, 123.8, 79.8, 55.9, 50.8, 19.8, 18.3. MS *m/z* (relative intensity) 191 (M^+, tr), 73 (56), 41 (100). HRMS calcd for $C_7H_{13}NO_3S$ (M^+) 191.0616, found 191.0626.

2-Methyl-1-nitro-1-propene (5a): ^{1}H NMR (200 MHz,-$CDCl_3$) δ 6.98 (m, 1H), 2.27 (d, J = 1.4 Hz, 3H), 1.96 (d, J = 1.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.9, 135.2, 24.1, 19.9. MS *m/z* (relative intensity) 101 (M^+, 10), 84 (100), 67 (2). HRMS calcd for $C_4H_8NO_2$ (M^+) 102.0555, found 102.0560.

***(E)*-2-Methyl-1-nitro-1-butene (5b):**[11] ^{1}H NMR (200 MHz,-$CDCl_3$) δ 6.98−6.96 (m, 1H), 2.31−2.18 (m, 2H), 2.26−2.24 (m, 3H), 1.14 (t, J = 7.6 Hz, 3H) ^{13}C NMR (50 MHz, CDCl3) δ 154.8, 134.8, 31.2, 18.5, 11.6. MS *m/z* (relative intensity) 115 (M^+, 16), 98 (100), 81 (14), 72 (19). HRMS calcd for $C_5H_9NO_2$ (M^+) 115.0633, found 115.0635.

***(Z)*-2-Methyl-1-nitro-1-butene (5b):**[11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92−6.88 (m, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.23 (t, J = 10.6 Hz, 3H), 1.93 (d, J = 1.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.1, 134.3, 26.0, 21.4, 11.4. MS *m/z* (relative intensity) 115 (M^+, 16), 98 (100), 81 (14), 72 (19). HRMS calcd for $C_5H_9NO_2$ (M^+) 115.0633, found 115.0635.

Nitromethylenecyclopentane (5c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17−7.10 (m, 1H), 3.06−2.93 (m, 2H), 2.59−2.47 (m, 2H), 1.91−1.67 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.7, 132.2, 33.9, 33.3, 25.9, 25.4. MS *m/z* (relative intensity) 127 (M^+, 2), 111 (11), 81 (68), 79 (100). HRMS calcd for $C_6H_9NO_2$ (M^+) 127.0633, found 127.0615.

Nitromethylenecyclohexane (5d):[4,11] ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94−6.89 (m, 1H), 2.89−2.83 (m, 2H), 2.24−2.18 (m, 2H), 1.77−1.59 (m, 6H),^{13}C NMR (50 MHz, $CDCl_3$) δ 155.8, 132.4, 34.4, 28.9, 28.2, 27.3, 25.8. MS *m/z* (relative intensity) 141 (M^+, 3), 109 (15), 95 (3), 81 (100). HRMS calcd for C_7H_{11}-NO_2 (M^+) 141.0790, found 141.0788.

Nitromethylenecycloheptane (5e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.99 (s, 1H), 3.00−2.92 (m, 2H), 2.42−2.35 (m, 2H), 1.85−1.50 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 160.2, 134.8, 35.4, 32.1, 29.5, 28.8, 27.9, 25.5. MS *m/z* (relative intensity) 155 (M^+, 4), 139 (64), 109 (11), 91 (100). HRMS calcd for C_8H_{13}-NO_2(M^+) 155.0946, found 155.0937.

1-Nitromethylcycloheptene (14c):[3c] ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.05 (t, J = 6.2 Hz, 1H), 4.82 (s, 2H), 2.29−2.16 (m, 4H), 1.82−1.60 (m, 2H), 1.59−1.48 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.3, 134.4, 84.2, 31.8, 31.1, 28.4, 26.1, 26.0. MS *m/z* (relative intensity) 155 (M^+, tr), 109 (100), 93 (8). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.24; H, 8.30; N, 8.72.

Typical Experimental Procedures for the Synthesis of Nitroalkenes 16a−f from Reactions of Ketone 15a−f and Nitromethane 2 in the Presence of Ethylenediamine According to Barton's Methodology (Table 3).[18a] Nitromethane **2** (15 mL), 2-adamantanone **15a** (500 mg), and ethylenediamine (20 mg) were placed in a 25 mL round-bottomed flask, and the solution was refluxed for 3 (or 24) h under an nitrogen atmosphere. After the solvent was evapo-

rated in vacuo, the residue was purified by flash column chromatography by using hexanes−ethyl acetate (400:1) to obtain 65% (or 86%) of **16a**.

2-Nitromethyleneadamantane (16a):[18a] Pale yellow solid and the melting point is 81−82 °C (literature 78−81 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.96 (s, 1H), 4.08 (s, 1H), 2.46 (s, 1H), 2.12−1.81 (m, 12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.3, 128.7, 39.7, 38.6, 37.8, 36.1, 31.8, 27.3. MS *m*/*z* (relative intensity) 193 (M^+, 1), 77 (100). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.09; H, 7.88; N, 7.53.

5-Phenyl-2-nitromethyleneadamantane (16b): Colorless solid and the melting point is 98.5−99.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40−7.15 (m, 5H), 7.00 (s, 1H), 4.23 (s, 1H), 2.63 (s, 1H), 2.32−1.86 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.9, 148.4, 129.2, 128.4, 126.2, 124.7, 44.9, 43.8, 41.9, 39.2, 38.3, 35.9, 32.2, 28.3. MS *m*/*z* (relative intensity) 269 (M^+, 4), 91 (100), 77 (25). HRMS calcd for $C_{17}H_{19}NO_2$ (M^+) 269.1416, found 269.1415.

5-Fluoro-2-nitromethyleneadamantane (16c): Pale yellow solid and the melting point is 89−91 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.93 (s, 1H), 4.28 (s, 1H), 2.73 (s, 1H), 2.41 (s, 1H), 2.30−1.65 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.8 (d, J = 2.3 Hz), 130.0, 90.4 (d, J = 185.1 Hz), 43.1 (d, J = 19.7 Hz), 42.2 (d, J = 19.0 Hz), 41.5 (d, J = 18.2 Hz), 39.7 (d, J = 9.85 Hz), 38.5 (d, J = 2.3 Hz), 37.4 (d, J = 2.25 Hz), 33.6 (d, J = 9.9 Hz), 30.8 (d, J = 9.85 Hz). MS *m*/*z* (relative intensity) 211 (M^+, tr), 91 (100). Anal. Calcd for $C_{11}H_{14}NO_2F$: C, 62.55; H, 6.68; N, 6.63. Found: C, 62.44; H, 6.81; N, 6.49.

5-Chloro-2-nitromethyleneadamantane (16d): Colorless solid and the melting point is 74−75 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.95 (s, 1H), 4.20 (s, 1H), 2.66 (s, 1H), 2.42−1.76 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.7, 129.7, 64.9, 47.9, 47.0, 46.0, 39.7, 37.8, 36.7, 33.9, 30.5. MS *m*/*z* (relative intensity) 229 (tr), 227 (M^+, tr), 91 (100). HRMS calcd for $C_{11}H_{13}NO^{37}Cl$ 212.0645, found 212.0651. HRMS calcd for $C_{11}H_{13}NO^{35}Cl$ 210.0681, found 210.0677. Anal. Calcd for $C_{11}H_{14}NO_2Cl$: C, 58.03; H, 6.20; N, 6.15. Found: C, 58.23; H, 6.29; N, 6.11.

5-Bromo-2-nitromethyleneadamantane (16e): Colorless solid and the melting point is 69.5−70.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.93 (s, 1H), 4.18 (s, 1H), 2.68−2.39 (m, 7H), 2.24 (s, 1H), 2.12−1.82 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.7, 130.1, 60.6, 49.8, 48.8, 47.7, 40.7, 38.0, 36.9, 35.0, 31.5. MS *m*/*z* (relative intensity) 273 (1), 271 (M^+, 1), 91 (100). Anal. Calcd for $C_{11}H_{14}NO_2Br$: C, 48.55; H, 5.19; N, 5.15. Found: C, 48.52; H, 5.07; N, 4.82.

5-Iodo-2-nitromethyleneadamantane (16f): Pale yellow solid and the melting point is 52−54 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.92 (s, 1H), 4.05 (s, 1H), 3.10−2.62 (m, 6H), 2.48 (s, 1H), 2.25−1.85 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.9, 130.2, 53.0, 52.0, 50.6, 42.4, 41.2, 37.9, 36.7, 35.7, 31.7. MS *m*/*z* (relative intensity) 319 (M^+, tr), 73 (100). Anal. Calcd for $C_{11}H_{14}NO_2I$: C, 41.40; H, 4.42; N, 4.39. Found: C, 41.47; H, 4.27; N, 4.35.

Typical Experimental Procedures for the Synthesis of 5-Substituted-2-nitromethyl-2-phenylthioadamantane 17 from Reactions of Ketones 15, Nitromethane 2, and Thiophenol 6a in the Presence of Piperidine 3 in Refluxing Benzene (Table 4). In a 100 mL round-bottomed flask fitted with a Dean−Stark trap were placed the 2-adamantanone **15a** (2.0 mmol), nitromethane **2** (8.0 mmol), piperidine **3** (3.0 mmol), and thiophenol **6a** (4.0 mmol) in 50 mL of benzene, the solution was refluxed for 7 h, and then additional amounts **2** (8.0 mmol), **3** (3.0 mmol), and **6a** (4.0 mmol) were added to the solution. Similar procedures were repeated, and the total amounts were as follows: nitromethane **2** (32.0 mmol), piperidine **3** (12.0 mmol), thiophenol **6a** (16.0 mmol). After the solution was refluxed 36 h, the solution was cooled and then poured into ice cold dilute hydrochloric acid solution, washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The purification of the mixture was carried out by flash column chromatography by using hexanes−ethyl acetate (200:1) to obtain 100% of **17a**.

2-Nitromethyl-2-phenylthioadamantane (17a): Colorless solid and the melting point is 103−105 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73−7.63 (m, 2H), 7.44−7.30 (m, 3H), 4.70 (s, 2H), 2.80 (d, J = 10.8 Hz, 2H), 2.09−1.89 (m, 6H), 1.87−1.62 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 129.5, 129.4, 128.9, 78.7, 58.6, 38.7, 33.2, 32.9, 27.4, 26.9. MS *m*/*z* (relative intensity) 303 (M^+, 7), 110 (100). HRMS calcd for $C_{17}H_{21}NO_2S$ (M^+) 303.1294, found 303.1292. Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62. Found: C, 66.92; H, 6.96; N, 4.65.

***(Z)*-2-Nitromethyl-5-phenyl-2-phenylthioadamantane [(*Z*)-17b]:** Colorless solid and the melting point is 171.5−173.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75−7.65 (m, 2H), 7.49−7.30 (m, 7H), 7.28−7.18 (m, 1H), 4.76 (s, 2H), 3.02 (d, J = 12.8 Hz, 2H), 2.25−1.72 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.5, 137.5, 129.5, 129.2, 129.0, 128.3, 126.0, 124.9, 78.6, 57.7, 44.1, 38.4, 35.9, 33.7, 32.4, 27.6. MS *m*/*z* (relative intensity) 302 [(M − C_6H_5)$^+$, tr], 270 [(M − C_6H_5S)$^+$, tr], 218 (100). Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.86; H, 6.68; N, 3.93.

***(E)*-2-Nitromethyl-5-phenyl-2-phenylthioadamantane [(*E*)-17b]:** Colorless solid and the melting point is 99−101 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.77−7.70 (m, 2H), 7.44−7.29 (m, 7H), 7.25−7.16 (m, 1H), 4.72 (s, 2H), 2.89 (d, J = 10.6 Hz, 2H), 2.30−1.90 (m, 9H), 1.72 (d, J = 13.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.1, 137.6, 129.6, 129.1, 128.4, 126.2, 124.7, 78.7, 57.8, 45.0, 38.5, 35.7, 33.8, 32.2, 28.2. MS *m*/*z* (relative intensity) 269 [(M − C_6H_5SH)$^+$, 2], 91 (100). HRMS calcd for $C_{23}H_{24}S$ (M^+) 332.1616, found 332.1591.

***(Z)*-5-Fluoro-2-nitromethyl-2-phenylthioadamantane [(*Z*)-17c]:** Colorless solid and the melting point is 138−139 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75−7.63 (m, 2H), 7.48−7.31 (m, 3H), 4.66 (s, 2H), 2.97 (s, 2H), 2.40−2.15 (m, 3H), 2.09−1.58 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.4, 129.8, 129.2, 128.6, 91.5 (d, J = 183.6 Hz), 78.3 (d, J = 0.15 Hz), 56.5 (d, J = 2.3 Hz), 43.5 (d, J = 18.2 Hz), 37.7 (d, J = 19.7 Hz), 36.4 (d, J = 10.6 Hz), 31.5 (d, J = 1.5 Hz), 29.8 (d, J = 9.9 Hz). MS *m*/*z* (relative intensity) 321 (M^+, tr), 110 (100). Anal. Calcd for $C_{17}H_{20}NO_2SF$: C, 63.53; H, 6.27; N, 4.36. Found: C, 63.73; H, 6.40; N, 4.22.

***(E)*-5-Fluoro-2-nitromethyl-2-phenylthioadamantane [(*E*)-17c]:** Colorless solid and the melting point is 136−137 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76−7.64 (m, 2H), 7.49−7.31 (m, 3H), 4.69 (s, 2H), 2.75 (d, J = 12.6 Hz, 2H), 2.41 (s, 1H), 2.32−2.08 (m, 4H), 2.03−1.81 (m, 4H), 1.58 (d, J = 13.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) *d* 137.5, 129.8, 129.2, 129.1, 91.1 (d, J = 184.4 Hz), 78.4, 56.6, 43.7 (d, J = 16.7 Hz), 38.0 (d, J = 19.0 Hz), 36.3 (d, J = 9.85 Hz), 31.3 (d, J = 1.5 Hz), 30.5 (d, J = 9.85 Hz). MS *m*/*z* (relative intensity) 321 (M^+, tr), 110 (100). Anal. Calcd for $C_{17}H_{20}NO_2SF$: C, 63.53; H, 6.27; N, 4.36. Found: C, 63.77; H, 6.36; N, 4.38.

***(Z)*-5-Chloro-2-nitromethyl-2-phenylthioadamantane [(*Z*)-17d]:** Colorless solid and the melting point is 137−139 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76−7.66 (m, 2H), 7.49−7.32 (m, 3H), 4.67 (s, 2H), 3.22 (d, J = 12.4 Hz, 2H), 2.32−1.65 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.6, 129.8, 129.3, 128.6, 78.3, 66.4, 56.4, 48.6, 42.6, 36.4, 31.4, 30.0. MS *m*/*z* (relative intensity) 339 (1), 337 (M^+, 3), 110 (100). HRMS calcd for $C_{17}H_{20}NO_2S^{35}Cl$ (M^+) 337.0903, found 337.0867. Anal. Calcd for $C_{17}H_{20}NO_2SCl$: C, 60.43; H, 5.97; N, 4.15. Found: C, 60.18; H, 5.82; N, 4.05.

***(E)*-5-Chloro-2-nitromethyl-2-phenylthioadamantane [(*E*)-17d]:** Colorless solid and the melting point is 129−131 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75−7.63 (m, 2H), 7.49−7.32 (m, 3H), 4.70 (s, 2H), 2.78 (d, J = 11.6 Hz, 2H), 2.48−2.24 (m, 3H), 2.24−2.08 (m, 6H), 1.64 (d, J = 13.2 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 129.8, 129.2, 128.9, 78.3, 65.7, 56.5, 48.7, 42.9, 36.3, 31.1, 30.6. MS *m*/*z* (relative intensity) 339 (2), 337 (M^+, 6), 110 (93), 91 (100). HRMS calcd for $C_{17}H_{20}NO_2S^{37}Cl$ (M^+) 339.0800, found 339.0837. HRMS calcd for $C_{17}H_{20}NO_2S^{35}Cl$ (M^+) 337.0903, found 337.0883. Anal. Calcd for $C_{17}H_{20}NO_2SCl$: C, 60.43; H, 5.97; N, 4.15. Found: C, 60.39; H, 5.93; N, 4.08.

***(Z)*-5-Bromo-2-nitromethyl-2-phenylthioadamantane [(*Z*)-17e]:** Colorless solid and the melting point is 117.5−119 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.81−7.62 (m, 2H), 7.56−7.32 (m, 3H), 4.65 (s, 2H), 3.40 (d, J = 12.2 Hz, 2H), 2.48−1.94 (m, 9H), 1.79 (d, J = 13.6 Hz, 2H). ^{13}C NMR (50 MHz,

$CDCl_3$) δ 137.5, 129.8, 129.2, 128.5, 78.3, 62.9, 56.3, 50.0, 43.9, 37.0, 31.3, 30.7. MS *m*/*z* (relative intensity) 383 (2), 381 (M^+, 2), 110 (100). Anal. Calcd for $C_{17}H_{20}NO_2SBr$: C, 53.41; H, 5.27; N, 3.66. Found: C, 53.64; H, 5.22; N, 3.75.

(*E*)-5-Bromo-2-nitromethyl-2-phenylthioadamantane [(*E*)-17e]: Colorless solid and the melting point is 117−118.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74−7.61 (m, 2H), 7.49−7.31 (m, 3H), 4.71 (s, 2H), 2.82 (d, J = 13.0 Hz, 2H), 2.61 (d, J = 13.6 Hz, 2H), 2.50−2.28 (m, 5H), 2.11 (s, 2H), 1.68 (d, J = 13.4 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 129.8, 129.2, 128.8, 78.4, 61.8, 56.5, 50.2, 44.3, 37.1, 31.4, 31.1. MS *m*/*z* (relative intensity) 383 (1), 381 (M^+, 1), 110 (100). Anal. Calcd for $C_{17}H_{20}NO_2SBr$: C, 53.41; H, 5.27; N, 3.66. Found: C, 53.38; H, 5.32; N, 3.83.

***(Z)*-5-Iodo-2-nitromethyl-2-phenylthioadamantane [(*Z*)-17f]:** Colorless solid and the melting point is 134.5−135.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74−7.61 (m, 2H), 7.49−7.31 (m, 3H), 4.62 (s, 2H), 3.62 (d, J = 12.4 Hz, 2H), 2.61 (s, 2H), 2.49 (d, J = 12.4 Hz, 2H), 2.24−1.76 (m, 7H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.4, 129.8, 129.2, 128.4, 78.3, 56.4, 53.1, 46.9, 45.3, 37.3, 31.3, 31.1. MS *m*/*z* (relative intensity) 429 (M^+, tr), 110 (100). Anal. Calcd for $C_{17}H_{20}NO_2SI$: C, 47.56; H, 4.70; N, 3.26. Found: C, 47.34; H, 4.54; N, 3.05.

***(E)*-5-Iodo-2-nitromethyl-2-phenylthioadamantane [(*E*)-17f]:** Colorless solid and the melting point is 129.5−130.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71−7.59 (m, 2H), 7.47−7.30 (m, 3H), 4.72 (s, 2H), 3.00−2.48 (m, 8H), 2.09 (s, 1H), 1.96 (s, 2H), 1.75 (d, J = 13.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.5, 129.8, 129.2, 128.7, 78.4, 56.6, 53.3, 47.3, 44.0, 37.5, 31.8, 31.1. MS *m*/*z* (relative intensity) 429 (M^+, tr), 123 (100). Anal. Calcd for $C_{17}H_{20}NO_2SI$: C, 47.56; H, 4.70; N, 3.26. Found: C, 47.83; H, 4.52; N, 2.93.

Typical Experimental Procedures for the One-Pot Synthesis of 5-Substituted-2-nitromethyleneadamantane 16a−f from the Oxidation of 5-Substituted-2-nitromethyl-2-phenylthioadamantane 17 with *m*-CPBA 10 and Followed by Elimination in CH_2Cl_2 Solution (Table 5). At 0 °C, 0.5 mmol of **17a** and 0.75 mmol *m*-CPBA **10** were dissolved in 50 mL of CH_2Cl_2 and stirred for few minutes at the same temperature. The temperature was then raised to room temperature, and the solution was stirred for 1.5 h. After the reaction was complete by checking with TLC plate, the solution was washed with brine, extracted by dichloromethane solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The purification of the mixture was carried out by flash column chromatography by using hexane to obtain 97% of **17a**.

Typical Experimental Procedures for the Synthesis of 5-Substituted-2-nitromethyleneadamantane 16a−f from the Reaction of 5-Substituted-2-nitromethyl-2-phenylthioadamantane 17 with Silica Gel (Table 6). At room temperature, 0.5 mmol of **17a** was dissolved in small amount of methylene chloride or ethyl acetate and 3.03 g of silica gel was added to the solution and the mixture was stirred vigorously for few minutes at the same temperature. The temperature was then raised to 90−100 °C and stirred for 6 h. After the reaction was complete, the mixture was washed with ethyl acetate to obtain 89% of crude product **16a**. If necessary, **16a** was purified by flash column chromatography by using hexane as described above.

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Supporting Information Available: ^{1}H and ^{13}C spectra of compounds **5a−e**, **7a−d**, **8a−e**, **9a−c, 9f**, **11a**, **12a**, **13a**, **14c**, **16a−f**, **17a−f**. This material is available free of charge via Internet http://pubs.acs.org.

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