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Ceric ammonium nitrate (CAN) as a green and highly efficient promoter for the 1,4-addition of thiols and benzeneselenol to α,β-unsaturated ketones

Cheng-Ming Chu, Shijay Gao, M. N. V. Sastry, Chun-Wei Kuo, Chaowei Lu, Ju-Tsung Liu and Ching-Fa Yao*

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei 116, Taiwan, ROC

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Abstract—A mild and efficient process for the 1,4-addition of thiols and benzeneselenols to various α,β-unsaturated ketones using a catalytic amount of CAN with excellent product yields is described. This inexpensive, nontoxic, and readily available catalytic ceric(IV) ammonium nitrate system efficiently catalyzes conjugate addition reactions between thiol derivatives and various α,β-unsaturated ketones under solvent-free conditions. A plausible mechanism for the role of CAN, both as a promoter in free radical chain addition reactions as well as a catalyst for the conjugate addition process is proposed.

1. Introduction

The base catalyzed 1,4-addition of thiols to α,β-unsaturated carbonyl compounds to form carbon–sulfur bonds constitutes a key reaction in various biosynthetic processes as well as in organic synthesis.[1,2] The 1,4-addition of mercaptans can be catalyzed by strong bases such as alkali metal alkoxides, hydroxides,[3] and amines.[4] Alternatively, the use of Lewis acids such as $Hf(OTf)_3$,[5a] $InBr_3$,[5b] $Bi(NO_3)_3$,[5c] $Bi(OTf)_3$,[5d] $InCl_3$,[5e] $Cu(BF_4)_2$,[5f] and $Zn(ClO_4)_2\cdot 6H_2O$[5g] has been investigated. However, the use of either strongly acidic or basic conditions typically leads to the formation of undesirable side products owing to side reactions, such as polymerization, self-condensation, and rearrangements.[6] Chakraborti et al. recently reported on the 1,4-conjugate addition of thiols to α,β-unsaturated carbonyl compounds in water at room temperature, without any metal catalyst leading to the facile and highly efficient synthesis of α-sulfido carbonyl compounds. However, there has been no straightforward synthesis of these uncomplicated enones and methyl acrylate leading to the preparation of typical enones (e.g., chalcone, *trans*-4-phenyl-3-buten-2-one, etc.), which cannot react in water even under forcible conditions.[7] In addition, these reactions are well documented in the literature with several heterogeneous systems such as zeolites and others.[8]

It also has been reported that the addition of a thiol, including aryl and alkyl thiols, to different alkenes can complete very fast under different conditions.[9] Evidence for a free radical chain reaction mechanism is based on the fact that the reaction rate is accelerated or initiated by the addition of free radical initiators or the presence of an excess of oxygen or under conditions of photolysis. Although the addition of oxidant-initiated mercaptans to various olefins is one of the most straightforward methods for generating monoadducts, undesired β-hydroxy sulfides or diadducts are generated in the synthesis of multifunctional compound in some cases.[9a–c] However, only few of these reactions have the radical character of an alkene with a different substituted group and examples of the addition of thiols to α,β-unsaturated ketones or reactions involving oxidation addition are scarce or have not been reported.

Among the electron transfer oxidizing agents, ceric(IV) ammonium nitrate is a convenient and widely used reagent for affecting a wide array of synthetic transformations due to its many advantages such as solubility in organic solvents, low toxicity, high reactivity, and ease of handling. A preliminary report on the use of Ce(IV) salts for the preparation of carbon-centered radicals dates back to the pioneering work of Heiba and Dessau in 1971.[10] Nair et al. developed a facile CAN-mediated protocol for the thiocyanation and selenocyanation of olefins, which led to different products under different conditions.[11] In recent years, several synthetic transformations involving both C–C as well as C–X (X=hetero atom) bond-forming reactions facilitated by

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* Corresponding author. Tel.: +886 2 29350749; fax: +886 2 29324249; e-mail: cheyaocf@scc.ntnu.edu.tw

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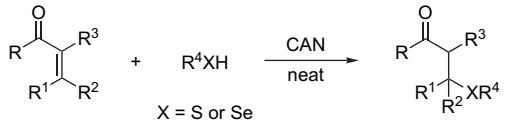
catalytic amounts of CAN have been reported.[12] In a continuation of our ongoing investigations of radical-mediated mechanistic pathways, we were prompted to explore the CAN-mediated conjugate addition of thiol and benzeneselenol compounds to α,β-unsaturated ketones and to explore the mechanism of CAN-mediated reactions. Herein, we wish to report on the simple and efficient 1,4-addition of thiols and benzeneselenols to α,β-unsaturated ketones mediated by CAN and a plausible mechanism for the reaction (Scheme 1).



1 **2, 4** **3, 5**

1a: R + R^1 = -$(CH_2)_3$- , R^2 = R^3 = H
1b: R + R^1 = -$(CH_2)_2$- , R^2 = R^3 = H
1c: R = Me, R^1 = R^2 = R^3 = H
1d: R = Me, R^2 = Ph, R^1 = R^3 = H
1e: R = Ph, R^2 = Ph, R^1 = R^3 = H
1f: R = Ph, R^1 = R^2 = Me, R^3 = H
1g: R = Me, R^2 + R^3 = -$(CH_2)_4$- , R^1 = H
1h: R = CH_2=$CHCH_2O$, R^1 = R^2 = R^3 = H
1i: R = CH_2=$CHC(CH_3)_2O$, R^1 = R^2 = R^3 = H

2a: R^4 = Ph
2b: R^4 = *c*-C_6H_{11}
2c: R^4 = $C_6H_5CH_2$
2d: R^4 = C_3H_7
2e: R^4 = CH_2=$CHCH_2$

Scheme 1.

2. Results and discussion

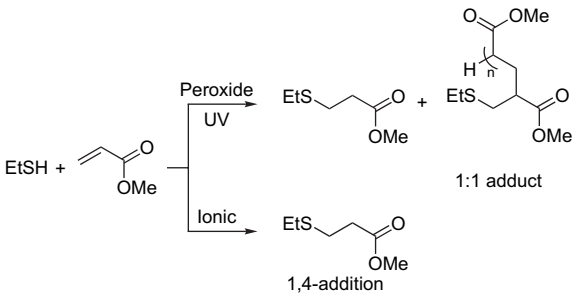
2.1. CAN promotes thiol addition

Several blank reactions were conducted at this stage between **1d** and 1.1 equiv of thiophenol **2a** at different temperatures under different atmospheres. Under these conditions, the yield of **3da** was negligible, demonstrating that the rate of the uncatalyzed reaction is unfavorable for 1,4-addition (Table 1). No significant change in the reaction mixture was observed, when it was conducted under different atmospheres such as Ar, air, and O_2. It was also observed that the reaction proceeded, to a small extent, under photolytic conditions even in different atmospheres. An identical reaction conducted in the presence of a free radical initiator such as AIBN and illuminating the system with an ultraviolet light resulted in the formation of the 1,4-conjugate addition product **3da** in 20% yield (entry 5). The same reaction under both thermal and photochemical conditions (90 °C) afforded the conjugate addition product only in good yield, without the 1:1 adduct being detected by ^{1}H NMR and GC–MS. However, the literature revealed that the radical addition of thiols to α,β-unsaturated esters and nitriles involves the formation of both the 1,4-conjugate addition product along with the 1:1 adduct with the RS group attached to the β-carbon atom (Scheme 2).[9] This clearly demonstrates the difference between conjugate addition reactions of thiols with α,β-unsaturated enones and α,β-unsaturated esters and nitriles.

Table 1. The 1,4-addition of thiophenol **2a** to enone **1d** under solvent-free condition at different temperatures

Entry	Additive (mol %)	Condition[a]	Time	**1d**[b] (%)	**3da**[b] (%)
1	—	Ar, 25 °C	3 h	99	tr
2	—	Air, 25 °C	3 h	98	2
3	—	O_2, 25 °C	3 h	96	4
4	—	Ar, 25 °C, *hν*[c]	3 h	96	4
5	AIBN (5)	Ar, 25 °C, *hν*[c]	3 h	80	20
6	—	Ar, 35 °C	3 h	84	12
7	—	Ar, 35 °C	8 h	82	18
8	—	Ar, 50 °C	3 h	87	13
9	—	Ar, 50 °C	16 h	71	29
10	—	Ar, 50 °C, *hν*[c]	3 h	79	21
11	AIBN (5)	Ar, 50 °C, *hν*[c]	3 h	56	44
12	Galvinoxyl (10)[d]	Ar, 50 °C, *hν*[c]	4 h	99	tr
13	—	Air, 50 °C	3 h	85	13
14	—	O_2, 50 °C	3 h	64	17
15	—	Ar, 90 °C	3 h	59	41
16	AIBN (5)	Ar, 90 °C	3 h	38	62

[a] Conditions: enone **1d** (2.0 mmol) and **2a** (2.2 mmol) were mixed together under different atmospheres at different temperatures.
[b] Yields were determined by ^{1}H NMR and GC.
[c] The photochemical reactions were performed using a 275 W general electric sunlamp at about a 20 cm distance.
[d] Reaction was carried out in 0.5 mL of $CHCl_3$.



Scheme 2.

These investigations prompted us to consider the use of CAN as a catalyst for the conjugate addition of thiophenol **2a** with enones. Thus in the presence of 5 mol % CAN under solvent-free conditions, the reaction of thiophenol **2a** with cyclohexenone **1a** proceeded smoothly within 10 min to afford the conjugate addition products exclusively and in quantitative yields (Fig. 1). Analogously, a decrease in the amount of CAN led to the partial recovery of the starting material, even when the reaction time was prolonged. A further series of experiments revealed that the optimal molar ratio of enone, thiol, and CAN was 1:1.1:0.05. The yield of product was not improved when 5 or 10 mol % CAN was used as a promoter, suggesting that 5 mol % of CAN is appropriate for the reaction.

We subsequently examined the effect of solvent on the catalytic activity of CAN during the reaction of **1d** with **2a**

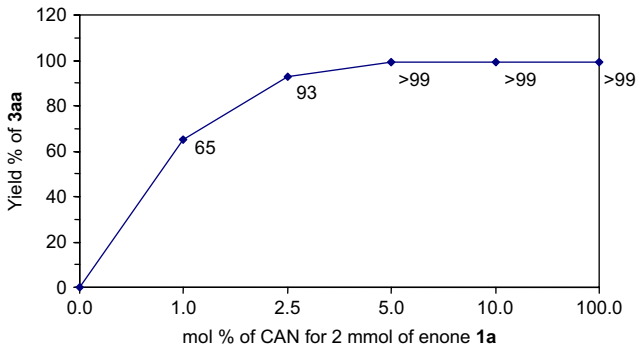
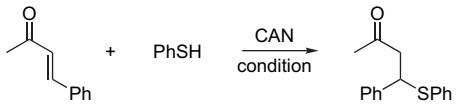


Figure 1.

Table 2. Reaction of **1d** with **2a** in various solvents under the catalytic influence of CAN



1d **2a** **3da**

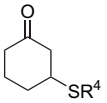
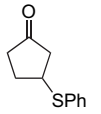
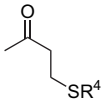
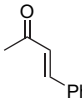
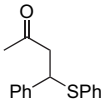
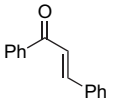
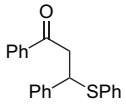
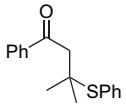
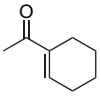
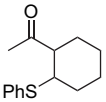
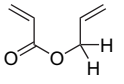
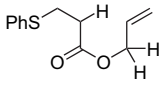
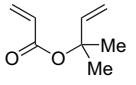
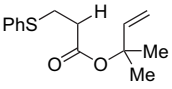
Entry	CAN (mol %)	Solvent	Condition[a]	**3da**[b] (%)	Recovered **1d**[b] (%)
1	5	CH_2Cl_2	Air, rt, 3 h	47	53
2	5	CH_3CN	Air, rt, 3 h	71	29
3	5	CH_3COCH_3	Air, rt, 3 h	57	43
4	5	$C_2H_5OC_2H_5$	Air, rt, 3 h	61	39
5	5	C_6H_6	Air, rt, 3 h	47	53
6	5	CH_3OH	Air, rt, 3 h	68	25
7	5	—	Ar, rt, 1 h	86	14
8	5	—	Air, rt, 1 h	80	20
9	5	—	O_2, rt, 1 h	56	18
10	5	—	Ar, 50 °C, 1 h	99	—
11	5	—	Air, 50 °C, 1 h	94	6
12	5	—	O_2, 50 °C, 0.5 h	86	10
13	10	—	Ar, 50 °C, 1 h	92	9
14	10	—	Air, 50 °C, 1 h	81	19
15	10	—	O_2, 50 °C, 0.5 h	82	18

[a] All reactions were performed using 2 mmol of **1d** and 2.2 mmol of **2a** in 2 mL of degassed solvent under different atmospheres.
[b] Yields were determined by ^{1}H NMR.

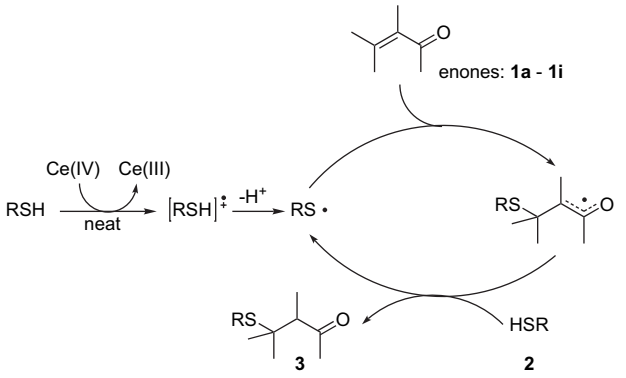
(Table 2). The type of solvent had little effect and almost all of the solvents tested afforded the product in moderate to high yields. Good product yields were obtained in polar solvents whereas only moderate yields were obtained when benzene and dichloromethane were used. The reduced catalytic activity is most probably due to the poor solubility of CAN in these solvents. Moreover, the reaction was promoted under an atmosphere of argon, compared to an O_2 or air atmosphere at ambient temperature (entries 7–15). However, at elevated temperature (50 °C) the yield of the addition product (**3da**) was practically quantitative and only a slight difference was observed in terms of both yield and reaction rate either in an Ar or an air atmosphere (entries 10 and 11). On the other hand, no substance containing two or more molecules of 1:1 adduct was detected, except when the addition was carried out in an O_2 atmosphere, in which some of enone **1d** underwent reduction to produce a ketone and the transformation to a sulfonate by itself (Table 1, entry 14 and Table 2, entry 9).[13d]

To demonstrate the versatility of CAN-promoted 1,4-addition reactions, a variety of enones **1a–g** were reacted with both aliphatic and aromatic thiols **2a–e** in the presence of CAN, giving good to practically quantitative yields of the racemic product as confirmed by HPLC analysis (Table 3).[14] The product also could be easily isolated by simple purification by flash column chromatography. It is noteworthy that the highly steric cyclohexanethiol **2b** and the unstable allyl mercaptan **2e** also afforded the 1,4-adduct in 95% and 99% yield, respectively, after isolation (entries 2 and 5). In other cases, steric effects were observed when bulkier enones were used, and in such reactions, more driving conditions were required. Both an increase in the reaction temperature as well as the amount of CAN were needed in cases of sterically bulkier substrates such as **1d–g** (entries 13–16). It is noteworthy that no byproducts resulting from 1,2-additions or bis-additions were observed by ^{1}H NMR and GC. Moreover, the reactions are clean, high yielding, and sometimes quantitative. Compared to conventional methods, enhanced reaction rates, improved yields, and excellent 1,4-selectivity are the main features of these CAN catalyzed reactions. The CAN-mediated generation of a radical by single electron transfer has also been investigated.[13,16d] Indeed, we also observed the exclusive formation of disulfides, when thiols were treated with 1 equiv of CAN. Based on our investigations, we propose a plausible mechanism for this reaction (Scheme 3).

Table 3. Cerium(IV) ammonium nitrate (CAN) promoted 1,4-addition of thiols to enones[a]

Entry	**1**	**2**	Temp (°C)/ time	Product **3**		Yield[b] (%)
1		**2a**	rt/10 min		**3aa**	98
2		**2b**	rt/1 h		**3ab**	95
3		**2c**	rt/40 min		**3ac**	98
4		**2d**	rt/40 min		**3ad**	95
5		**2e**	rt/20 min		**3ae**	99
6		**2a**	rt/20 min		**3ba**	98
7		**2a**	rt/40 min		**3ca**	99
8		**2b**	rt/20 min		**3cb**	96
9		**2c**	rt/40 min		**3cc**	98
10		**2d**	rt/20 min		**3cd**	86
11		**2e**	rt/20 min		**3ce**	90
12		**2a**	rt/3 h		**3da**	86
13		**2a**	50/1 h			90
14[c,d]		**2a**	50/30 min		**3ea**	80
15[d]		**2a**	50/4 h		**3fa**	82
16[d]		**2a**	50/4 h		**3ga**	86[e]
17		**2a**	0/2 h		**3ha**	14[f]
18		**2a**	50/30 min			98[g]
19		**2a**	50/2 h		**3ia**	60

[a] All reactions were performed using 1 equiv (2 mmol) of enone **1** and 1.1 equiv (2.2 mmol) of mercaptan **2** in the presence of 5 mol % of CAN under solvent-free condition in air atmosphere.
[b] Isolated yields.
[c] Reaction was carried out in 1 mL of CH_3CN.
[d] Compound **2a** (2 equiv, 4 mmol) and 10 mol % of CAN were used.
[e] The two diastereomers formed in 98:2 (*trans*:*cis*) and were separated by column chromatography.
[f] Eight percent of 1:1 adduct product **3ha′** and 40% of di-addition **3ha″** were isolated.
[g] Trace of 1:1 adduct product **3ha′** was isolated.



Scheme 3. Plausible mechanism for the role of CAN as a promoter of free radical chain reactions of 1,4-addition.

During the reaction, CAN converts the thiol to a thiyl radical cation, and subsequently to a thiyl radical from the fragmentation of the radical cation. This thiyl radical then undergoes a radical chain addition to the enone to form the final 1,4-addition product. Furthermore, another mechanistic rationale for this reaction is based on the oxidizing nature of CAN. The use of a strong oxidizing catalyst such as CAN could easily form a strong coordinate bond with the carbonyl oxygen of the α,β-unsaturated ketone, which in turn, would increase the electrophilicity of the β-carbon thus permitting the conjugate addition reaction to proceed under mild conditions in a short time.

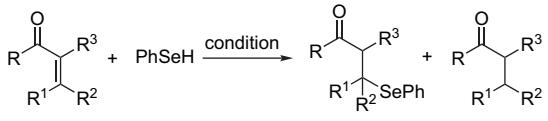
Encouraged by these results, we examined the scope of CAN as a catalyst for the 1,4-addition of thiols to diene esters such as **1h–i** (Table 3, entries 17–19). As expected, the reaction proceeded smoothly in the case of **1h** at 50 °C to afford the 1,4-addition product in excellent yield with only a trace of dimerized product. Conversely, only a moderate yield was obtained when a sterically hindered substrate such as **1i** was used, with undetectable amounts of 1:1 adduct. The lower yield of **1i** (60% isolated yield) may be explained on the basis of the lower electrophilicity of the vinyl ester **1i**, which has a poor reactivity, as well as the steric hindrance associated with the *gem*-dimethyl allyl group, which would hinder the nucleophilic thiyl addition to the electrophilic β-carbon. In fact a γ-lactone product resulting from exocyclization was not observed, as anticipated during the reaction of a thiol with a sterically hindered *gem*-dialkyl ester[15] such as acrylic acid 1,1-dimethyl-allyl ester **1i**. Presumably, the rate at which the radical intermediate traps the hydrogen from thiophenol is much faster than the rate of cyclization of the same radical.[16] Furthermore, regioselectivity is an important criterion for the addition to occur exclusively on the conjugated double bond. Most probably, the RS radical is an electrophilic species and the reverse might be expected, since the conjugated double bond is more electron poor. It is also significant that a 1:1 adduct with an RS group on the β-carbon atom of **3ha′** was observed along with the normal 1,4-adducts **3ha** and **3ha″** when the reaction involved heating or the use of a sunlamp, which is due to CAN-promoted free radical chain reactions.[9]

2.2. CAN promotes benzeneselenol addition

During the past decade, many efforts have been directed toward the synthesis of stable organoselenium compounds that could be used as antioxidants, enzyme inhibitors, antitumor, and anti-infective agents, cytokine inducers, and immuno modulators.[17] Furthermore, the biochemical role of selenium in mammals was clearly established by the discovery that it is a component of the active site of the antioxidant enzyme glutathione peroxidase (GPx).[18] Increased interest in the use of organoselenium compounds in biochemistry has generated a growing demand for their synthesis as well as their pharmacological activity.

We further examined the addition of benzeneselenols to α,β-unsaturated ketones (Table 4). In an initial experiment, a blank reaction was run with benzeneselenol **4** and enones **1a–g** in the absence of CAN at 0 °C or room temperature. Surprisingly, the reaction afforded the β-seleno adduct **5** in poor to moderate yields along with detectable amounts of the reduction product **6**. The results for chalcone **1e** were also examined in the addition reactions using ethanol without the aid of a catalyst.[19] In addition to 1,4-addition products, saturated ketones were produced as competitive products depending on the nature of the substrate, which was identified by GC–MS and compared with authentic standards.[20] It is noteworthy that reactions using complicated enones **1d–f** resulted in the formation of the reduced product as the major component and the 1,4-addition product as a minor component. The reason for the formation of the reduced product may be due to simple hydrogenation via a free radical intermediate in the presence of the less acidic hydrogen of benzeneselenol and the more electrophilic enone. This is most probably due to the fact that the photolysis of selenols yields hydrogen radicals H.[20a] This is probably due to competitive addition and reduction in the presence of the less steric of β-carbon. Therefore, inferior results are obtained for a β-carbon containing a bulky substituent (entries 4–6 and 10–13).

Table 4. Comparison of the results of the CAN-promoted conjugate addition of benzeneselenol **4** to α,β-unsaturated ketones



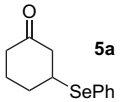
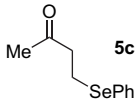
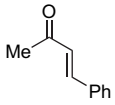
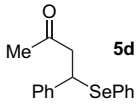
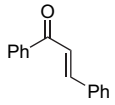
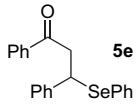
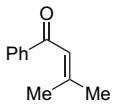
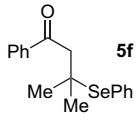
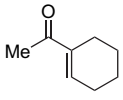
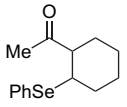
Entry	1	CAN (mol %)	Condition[a]	5[b] (%)	6[b] (%)
1	**1a**	—	Air, 0 °C, 10 min	**5a** (94)	**6a** (tr)
2	**1c**	—	Air, 0 °C, 20 min	**5c** (95)	**6c** (tr)
3[c]	**1d**	—	Ar, rt, 24 h	**5d** (40)	**6d** (32)
4	**1d**	—	Air, rt, 24 h	**5d** (20)	**6d** (42)
5[c]	**1d**	—	Air, rt, 24 h	**5d** (10)	**6d** (42)
6[c]	**1d**	—	O_2, rt, 24 h	**5d** (7)	**6d** (39)
7	**1d**	2	Ar, rt, 5 min	**5d** (>99)	**6d** (—)
8	**1d**	2	Air, rt, 5 min	**5d** (>99)	**6d** (—)
9	**1d**	2	O_2, rt, 5 min	**5d** (>99)	**6d** (—)
10[d]	**1e**	—	Air, rt, 24 h	**5e** (13)	**6e** (17)
11[e]	**1e**	—	Air, rt, 20 min	**5e** (44)	**6e** (12)
12	**1f**	—	Air, rt, 24 h	**5f** (17)	**6f** (45)
13[e]	**1f**	—	Air, rt, 40 min	**5f** (6)	**6f** (44)
14	**1g**	—	Air, rt, 24 h	**5g** (75)	**6g** (tr)

[a] All chemicals and glassware were degassed thoroughly using argon prior to use and the reactions were carried out by using 2 mmol of **1d** and 3 mmol of **4** under different conditions.
[b] Yields were determined by ^{1}H NMR.
[c] Phenylselenol **4** (2.2 mmol, 1.1 equiv) was used.
[d] Reaction was carried out in 1 mL of CH_3CN.
[e] Reaction was carried out in 1.7 mL of EtOH.

As indicated in entries 7–9, various types of atmospheres, including oxygen, air and argon, were investigated for the reaction of **1d** with **4** in the presence of CAN. The procedure is very simple, and it should be noted that CAN is able to promote these reactions under different atmospheres. This is probably due to the strong oxidizing nature of CAN. However, the reaction is efficient under different atmospheres. When the reaction was carried out under an atmosphere of O_2, no significant change in the reaction, compared with that for an Ar atmosphere. This may be due to the fact that the reaction, when run in an atmosphere of O_2 is inhibited and the reactant is oxidized to diphenyl-diselane from benzeneselenol.[21] Indeed; diphenyl diselenide was detected in this reaction.

Under optimized reaction conditions, the 1,4-addition of various α,β-unsaturated ketones with benzeneselenol was investigated and the results are summarized in Table 5. We attempted a variety of reactions between benzeneselenol **4** and enones **1** with catalytic amounts of CAN (2–5 mol %), which afforded various β-seleno adducts in excellent yields. It is noteworthy that reduction products were predominantly formed in the absence of CAN with these substrates. No apparent significant steric effect of β-site substituents was observed (Table 5, entries 3–5). To apply this method, diene esters **1h–i** were reacted with benzeneselenol in the presence of CAN under similar conditions. Unfortunately, the reactions did not proceed and only unreacted starting materials were recovered.

Table 5. Cerium(IV) ammonium nitrate (CAN)-catalyzed 1,4-addition of benzeneselenol **4** to various enones **1a–g**[a]

Entry	1	CAN (mol %)	Temp (°C)/ time	5	Yield[b] (%)
1		2	0/5 min	 **5a**	98
2		2	0/5 min	 **5c**	99
3		2	rt/5 min	 **5d**	98
4[c]		5	rt/10 min	 **5e**	99
5		5	rt/15 min	 **5f**	98
6[d]		5	rt/40 min		47[e]
7		5	rt/10 min	 **5g**	98

[a] All Reactions were carried out using 1 equiv (2 mmol) of enone **1** and 1.5 equiv (3 mmol) of benzeneselenol **4** in the presence of 2–5 mol % of CAN under solvent-free condition in air atmosphere.
[b] Isolated yields.
[c] Reaction was carried out in 1 mL of CH_3CN.
[d] Reaction was carried out in 1.7 mL of EtOH.
[e] Twenty nine percent of unreacted **1f** and 17% of reduction product ketone were isolated.

3. Conclusion

In summary, we successfully developed a general synthetic protocol for the mild and efficient 1,4-addition of thiols and selenophenols to various α,β-unsaturated ketones using a catalytic amount of CAN. The reaction is simple, convenient and can be applied to a wide variety of substrates with excellent product yields under solvent-free conditions. We also examined various parameters such as solvent, temperature, and additives to achieve maximum yields of 1,4-addition products. A plausible mechanism is proposed for the role of CAN, both as a promoter in free radical chain addition reactions as well as a catalyst in the conjugate addition process. This inexpensive catalyst not only offers advantages such as high catalytic activity, operational simplicity, and the broadest substrate scope with excellent product yields but also stands as an alternative to conventional methods, which involve the use of expensive, noxious, and/or air-sensitive catalysts. We are currently in the process of expanding the scope of these reactions and to elucidate more aspects regarding the reaction mechanism.

4. Experimental section

4.1. General methods

All reactions were performed in oven-dried glassware and some reactions were carried out under a positive pressure of argon when the reactions were sensitive to moisture or oxygen. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography based E. Merck silica gel 60 (230–400 mesh). GC was measured by a SHIMADZU GC-14B instrument. MS or HRMS were measured using a JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 or Bruker Avance EX 400 FT NMR.

4.2. Typical experimental procedure for the 1,4-addition of thiophenol 2a to cyclohexenone 1a in the presence of ceric(IV) ammonium nitrate (CAN) to generate 3-phenylthiocyclohexanone (3aa)[22]

In a 10 mL round bottom flask were first added cyclohexenone **1a** (0.198 g, 2 mmol) and thiophenol **2a** (0.249 g, 2.2 mmol). The mixture was thoroughly degassed using vacuum and argon purge cycles, and ceric ammonium nitrate (CAN) (0.0548 g, 0.1 mmol) was then added under a dry air atmosphere, which was passed through $CaCl_2$. The mixture was stirred at room temperature for 10 min. After completion of the reaction (monitored by TLC and GC), the crude product was purified by flash column chromatography (ethyl acetate–hexanes 1:20) to give the pure product **3aa** in 98% (0.404 g) isolated yield as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.429 (dt, J=8.0, 1.6 Hz,

2H), 7.34–7.21 (m, 3H), 3.47–3.39 (m, 1H), 2.68 (dd, J=14.4, 4.4 Hz, 1H), 2.41–2.29 (m, 3H), 2.16–2.12 (m, 2H), 1.76–1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.90, 133.41, 133.19, 129.24, 127.97, 47.95, 46.30, 41.05, 31.43, 24.22; m/z (relative intensity) 206 (M^+, 60), 110 (100), 109 (42), 97 (57), 96 (30), 84 (18), 77 (19), 69 (100), 68 (85), 66 (34), 65 (34), 55 (38). HRMS calcd for $C_{12}H_{14}OS$ 206.0760, found 206.0770.

4.2.1. 3-Cyclohexylsulfanyl-cyclohexanone (3ab).[23] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12–3.07 (m, 1H), 2.75–2.62 (m, 2H), 2.38–2.22 (m, 3H), 2.15–2.04 (m, 2H), 1.94–1.82 (m, 2H), 1.78–1.52 (m, 5H), 1.34–1.13 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.12, 48.95, 42.48, 41.22, 41.05, 34.09, 34.04, 32.29, 26.14, 26.11, 25.85, 24.48; m/z (relative intensity) 212 (M^+, 35), 116 (22), 115 (52), 114 (27), 97 (75), 96 (79), 83 (43), 82 (48), 81 (29), 69 (50), 68 (70), 67 (85), 55 (100). HRMS calcd for $C_{12}H_{20}OS$ 212.1229, found 212.1252. Anal. Calcd for $C_{12}H_{20}OS$: C, 67.87; H, 9.49; S, 15.10. Found: C, 67.87; H, 9.09; S, 14.84.

4.2.2. 3-Benzylthiocyclohexanone (3ac). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.21 (m, 5H), 3.76 (dd, J=15.2, 13.6 Hz, 2H), 2.96–2.89 (m, 1H), 2.69 (dd, J=14.4, 4.4 Hz, 1H), 2.41–2.30 (m, 3H), 2.11–2.07 (m, 2H), 1.75–1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.86, 138.08, 128.91, 128.79, 127.33, 48.00, 42.15, 41.12, 35.12, 31.49, 24.30; m/z (relative intensity) 220 (M^+, 5), 124 (15), 123 (15), 97 (29), 96 (13), 91 (100), 77 (10), 69 (12), 68 (35), 65 (20), 55 (10). HRMS calcd for $C_{13}H_{16}OS$ 220.0916, found 220.0920.

4.2.3. 3-*n*-Propylthio-1-cyclohexanone (3ad).[24] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15–3.00 (m, 1H), 2.72 (d, J=14.1 Hz, 1H), 2.53 (dt, J=7.4, 2.5 Hz, 2H), 2.42–2.30 (m, 3H), 2.20–2.13 (m, 2H), 1.75–1.70 (m, 2H), 1.70–1.55 (m, 2H), 0.99 (dt, J=7.4, 2.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.90, 48.32, 42.80, 41.01, 32.62, 31.74, 24.30, 23.12, 13.57; m/z (relative intensity) 172 (M^+, 60), 119 (8), 115 (20), 110 (14), 98 (23), 97 (100), 96 (81), 76 (18), 74 (19), 69 (100), 68 (86), 67 (30), 55 (62). HRMS calcd for $C_9H_{16}OS$ 172.0916, found 172.0926.

4.2.4. 3-Allylsulfanyl-cyclohexanone (3ae). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80–5.67 (m, 1H), 5.15–5.00 (m, 2H), 3.15 (d, J=7.0 Hz, 2H), 3.05–2.95 (m, 1H), 2.65 (d, J=14.2 Hz, 1H), 2.36–2.26 (m, 3H), 2.13–2.02 (m, 2H), 1.74–1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.76, 134.33, 117.25, 47.97, 41.53, 41.01, 33.64, 31.42, 24.25; m/z (relative intensity) 170 (M^+, 51), 129 (18), 98 (18), 114 (27), 97 (100), 96 (30), 69 (86), 68 (57), 67 (35), 55 (54). HRMS calcd for $C_9H_{14}OS$ 170.0760, found 170.0769. Anal. Calcd for $C_9H_{14}OS$: C, 63.48; H, 8.29; S, 18.83. Found: C, 63.03; H, 8.13; S, 18.94.

4.2.5. 3-(Phenylthio)cyclopentanone (3ba).[25] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, J=7.7, 1.6 Hz, 2H), 7.34–7.22 (m, 3H), 3.92–3.84 (m, 1H), 2.55 (dd, J=18.4, 7.2 Hz, 2H), 2.52–2.40 (m, 1H), 2.37–2.15 (m, 3H), 2.05–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.27, 134.31, 131.94, 129.15, 127.42, 45.25, 43.38, 36.78, 29.36; m/z (relative intensity) 192 (M^+, 36), 110 (23), 109 (44), 83 (24), 77 (10), 69 (10), 68 (57), 65 (23), 55 (100). HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0610.

4.2.6. 4-Phenylsulfanyl-butan-2-one (3ca).[26] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 4H), 7.18 (tt, J=7.2, 1.3 Hz, 1H), 3.12 (t, J=7.2 Hz, 2H), 2.74 (t, J=7.2 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.70, 135.81, 129.62, 129.13, 126.42, 43.17, 30.20, 27.56; m/z (relative intensity) 180 (M^+, 5), 179 (8), 178 (65), 163 (100), 135 (45), 134 (12), 110 (20), 109 (55), 101 (20), 91 (45), 77 (15), 69 (16), 65 (27). HRMS calcd for $C_{10}H_{12}OS$ 180.0609, found 180.0422.

4.2.7. 4-Cyclohexylsulfanyl-butan-2-one (3cb).[23] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78–2.69 (m, 4H), 2.64–2.60 (m, 1H), 2.17 (s, 3H), 2.02–1.90 (m, 2H), 1.82–1.71 (m, 2H), 1.65–1.58 (m, 1H), 1.38–1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.00, 44.05, 43.84, 33.63, 30.11, 26.09, 25.83, 23.84; m/z (relative intensity) 186 (M^+, 48), 116 (17), 115 (68), 114 (38), 83 (40), 82 (33), 81 (42), 71 (56), 67 (70), 55 (100). HRMS calcd for $C_{10}H_{18}OS$ 168.1073, found 168.1083. Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74; S, 17.21. Found: C, 64.17; H, 9.77; S, 17.06.

4.2.8. 4-Benzylsulfanyl-butan-2-one (3cc). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.19 (m, 5H), 3.69 (s, 2H), 2.65–2.58 (m, 4H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.60, 138.25, 128.78, 128.48, 127.00, 43.25, 36.61, 29.92, 25.17; m/z (relative intensity) 194 (M^+, 17), 160 (5), 124 (14), 123 (18), 92 (12), 91 (100), 77 (7), 65 (21), 63 (7), 55 (10). HRMS calcd for $C_{11}H_{14}OS$ 194.0760, found 194.0773.

4.2.9. 4-Propylsulfanyl-butan-2-one (3cd).[27] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75–2.71 (m, 4H), 2.50 (t, J=7.2 Hz, 2H), 2.17 (s, 3H), 1.61 (sext, J=7.2 Hz, 2H), 0.98 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.95, 43.80, 34.48, 30.11, 25.77, 22.91, 13.48; m/z (relative intensity) 146 (M^+, 100), 117 (10), 104 (5), 103 (30), 83 (40), 89 (7), 71 (45), 61 (20), 55 (3). HRMS calcd for $C_7H_{14}OS$ 146.0760, found 146.0772.

4.2.10. 4-Allylmercapto-butan-2-one (3ce). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84–5.73 (m, 1H), 5.15–5.08 (m, 2H), 3.15 (d, J=7.2 Hz, 2H), 2.75–2.65 (m, 4H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.78, 134.27, 117.16, 43.44, 35.08, 30.08, 24.46; m/z (relative intensity) 144 (M^+, 100), 103 (35), 101 (8), 85 (12), 74 (13), 73 (27), 71 (20), 59 (5), 55 (5). HRMS calcd for $C_7H_{12}OS$ 144.0603, found 144.0613.

4.2.11. 4-Phenyl-4-phenylsulfanyl-butan-2-one (3da).[23,28] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 6H), 7.24–7.16 (m, 4H), 4.70 (dd, J=7.8, 6.8 Hz, 1H), 3.08 (dd, J=14.0, 7.8 Hz, 1H), 3.02 (dd, J=14.0, 6.8 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.64, 141.24, 134.25, 133.08, 129.02, 128.67, 127.89, 127.80, 127.61, 49.71, 48.26, 30.87; m/z (relative intensity) 256 (M^+, 71), 148 (11), 147 (99), 135 (9), 111 (11), 109 (100), 105 (14), 104 (41), 103 (41), 91 (18), 77 (44), 65 (37), 51 (23). HRMS calcd for $C_{16}H_{16}OS$ 256.0922, found 256.0915.

4.2.12. 1,3-Diphenyl-3-phenylsulfanyl-propan-1-one (3ea).[29] White solid; mp 118–119 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=8.56 Hz, 2H), 7.49 (t, J=7.3 Hz, 1H), 7.37 (t, J=7.8 Hz, 2H), 7.35–7.27 (m, 4H), 7.25–7.13 (m, 6H), 4.96 (dd, J=8.0, 6.1 Hz, 1H), 3.65 (dd, J=17.0, 8.0 Hz, 1H), 3.56 (dd, J=17.0, 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.08, 141.36, 136.87, 134.42, 133.37, 132.87, 128.99, 128.74, 128.59, 128.19, 127.95, 127.66, 127.50, 48.38, 44.85; *m/z* (relative intensity) 319 (M+1, 21), 318 (M^+, 85), 209 (67), 207 (11), 110 (18), 109 (78), 106 (80), 105 (100), 104 (46), 103 (47), 78 (49), 77 (97), 65 (30), 51 (51). HRMS calcd for $C_{21}H_{18}OS$ 318.1078, found 318.1072.

4.2.13. 3-Phenylthio-3-methyl-butyrophenone (3fa).[29] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J=8.8 Hz, 2H), 7.58–7.52 (m, 3H), 7.45–7.32 (m, 5H), 3.22 (s, 2H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.31, 138.19, 137.98, 133.20, 131.75, 129.33, 128.88, 128.76, 128.31, 49.12, 48.00, 28.57; *m/z* (relative intensity) 270 (M^+, 11), 161 (30), 110 (10), 109 (14), 106 (12), 105 (100), 77 (47), 65 (7), 51 (11). HRMS calcd for $C_{17}H_{18}OS$ 270.1078, found 270.1084.

4.2.14. *trans*-1-(2-Phenylsulfanyl-cyclohexyl)-ethanone (3ga). *Major product*: white solid; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J=8.2 Hz, 2H), 7.28 (t, J=6.9 Hz, 2H), 7.20 (tt, J=6.9, 1.1 Hz, 1H), 3.80–3.77 (dt, J=7.6, 3.8 Hz, 1H), 2.73–2.68 (dt, J=10.2, 4.0 Hz, 1H), 2.16 (s, 3H), 2.06–1.99 (m, 1H), 1.88–1.68 (m, 5H), 1.53–1.30 (m, 1H), 1.33–1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.07, 135.93, 131.95, 129.16, 127.15, 54.16, 49.05, 31.59, 28.35, 24.58, 24.11, 21.52; *m/z* (relative intensity) 234 (M^+, 77), 125 (18), 110 (100), 109 (20), 81 (26), 79 (10), 77 (10), 65 (11). HRMS calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1072. Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.57; H, 7.61; S, 13.94.

4.2.15. *cis*-1-(2-Phenylsulfanyl-cyclohexyl)-ethanone (3ga). *Minor product*: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J=8.2 Hz, 2H), 7.30–7.20 (m, 3H), 3.19 (td, J=11.0, 3.8 Hz, 1H), 2.53 (dt, J=11.0, 3.6 Hz, 1H), 2.22 (s, 3H), 2.11–2.06 (m, 1H), 1.92–1.87 (m, 1H), 1.75–1.67 (m, 2H), 1.43–1.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.62, 133.91, 133.13, 128.88, 127.45, 55.95, 47.82, 33.56, 29.99, 29.70, 25.88, 24.84.

4.2.16. 3-Phenylsulfanyl-propionic acid allyl ester (3ha). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, J=8.0, 1.6 Hz, 2H), 7.31–7.18 (m, 3H), 5.95–5.85 (m, 1H), 5.33–5.21 (m, 2H), 4.59 (d, J=5.8 Hz, 2H), 3.17 (t, J=7.4 Hz, 2H), 2.65 (t, J=7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.52, 135.34, 132.13, 130.32, 129.19, 126.75, 118.58, 65.54, 34.54, 29.21; *m/z* (relative intensity) 222 (M^+, 80), 165 (30), 163 (30), 139 (40), 137 (50), 135 (55), 123 (45), 110 (55), 109 (100), 77 (38), 69 (53), 65 (44), 55 (58). HRMS calcd for $C_{12}H_{14}O_2S$ 222.0709, found 222.0717.

4.2.17. Diallyl 2-(phenylthiomethyl)pentanedioate (3ha′). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, J=7.6, 1.4 Hz, 2H), 7.31–7.21 (m, 3H), 5.93–5.83 (m, 2H), 5.35–5.21 (m, 4H), 4.58 (m, J=6.0 Hz, 4H), 3.25 (dd, J=13.4, 8.0 Hz, 1H), 3.05 (dd, J=13.4, 6.1 Hz, 1H), 2.70 (m, 1H), 2.37 (m, 2H); 2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.57, 172.44, 135.53, 132.26, 132.13, 130.59, 129.24, 126.91, 118.77, 118.57, 65.69, 65.46, 44.95, 36.25, 31.79, 26.78; *m/z* (relative intensity) 334 (M^+, 5), 332 (10), 222 (25), 150 (20), 149 (30), 135 (30), 123 (30), 117 (40), 110 (100), 110 (100), 109 (50), 77 (30), 69 (32), 66 (32), 55 (51). HRMS calcd for $C_{18}H_{22}O_4S$ 334.1239, found 334.0889.

4.2.18. 1-(2-Phenylsulfanyl-cyclohexyl)-ethanone (3ia). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dt, J=7.4, 1.5 Hz, 2H), 7.31–7.17 (m, 3H), 6.10 (dd, J=17.44, 10.84 Hz, 1H), 5.19 (dd, J=17.48, 10.92 Hz, 2H), 3.13 (dd, J=7.52, 7.36 Hz, 2H), 2.56 (dd, J=7.36, 7.52 Hz, 2H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.80, 142.55, 135.67, 130.20, 129.18, 126.64, 113.01, 81.49, 35.55, 29.34, 26.64; *m/z* (relative intensity) 250 (M^+, 17), 182 (100), 181 (40), 163 (15), 137 (25), 135 (20), 123 (90), 110 (47), 109 (58), 77 (20), 69 (64), 65 (34), 55 (20), 53 (25). HRMS calcd for $C_{14}H_{18}O_2S$ 250.1022, found 222.1033.

4.2.19. 3-Phenyl selenocyclohexanone (5a).[30] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, J=7.4, 1.8 Hz, 2H), 7.36–7.26 (m, 3H), 3.52–3.44 (m, 1H), 2.68 (ddd, J=14.4, 4.4, 2.0 Hz, 1H), 2.49 (dd, J=14.3, 11 Hz, 1H), 2.41–2.07 (m, 4H), 1.86–1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.98, 135.88, 129.35, 128.38, 127.68, 48.93, 41.04, 40.42, 32.28, 25.42; *m/z* (relative intensity) 254 (M^+, 30), 158 (45), 157 (30), 156 (25), 155 (20), 154 (15), 117 (10), 97 (65), 96 (25), 78 (100), 77 (60), 69 (80), 68 (85), 55 (33), 51 (41). HRMS calcd for $C_{12}H_{14}OSe$ 254.0204, found 204.0201. Anal. Calcd for $C_{12}H_{14}OSe$: C, 56.92; H, 5.57. Found: C, 56.69; H, 5.36.

4.2.20. 4-(Benzoseleno)-butan-2-one (5c).[31] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, J=7.7, 1.8 Hz, 2H), 7.28–7.23 (m, 3H), 3.05 (t, J=7.2 Hz, 2H), 2.84 (t, J=7.2 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.15, 132.98, 129.84, 129.28, 127.25, 44.22, 30.12, 20.61; *m/z* (relative intensity) 228 (M^+, 48), 226 (23), 185 (20), 178 (30), 158 (34), 157 (53), 155 (30), 149 (17), 91 (37), 79 (28), 78 (100), 77 (100), 69 (37), 68 (27), 67 (28), 57 (38), 55 (86), 51 (64). HRMS calcd for $C_{10}H_{12}OSe$ 228.0048, found 228.0051. Anal. Calcd for $C_{10}H_{12}OSe$: C, 52.87; H, 5.32. Found: C, 52.87; H, 5.07.

4.2.21. 4-Phenyl-4-phenylselenyl-butan-2-one (5d).[32] White solid; mp 53–54 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, J=8, 1.4 Hz, 2H), 7.30–7.15 (m, 8H), 4.79 (dd, J=8.6, 6.4 Hz, 1H), 3.26 (dd, J=17.1, 8.6 Hz, 1H), 3.10 (dd, J=17.1, 6.4 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.02, 141.61, 135.94, 129.12, 129.04, 128.61, 128.38, 127.73, 127.36, 49.74, 41.84, 30.67; *m/z* (relative intensity) 304 (M^+, 5), 302 (3), 234 (3), 158 (32), 157 (25), 156 (17), 147 (35), 146 (51), 145 (50), 131 (84), 104 (17), 103 (100), 102 (16), 78 (75), 77 (96), 76 (16), 51 (59). HRMS calcd for $C_{16}H_{16}OSe$ 304.0361, found 304.0369. Anal. Calcd for $C_{16}H_{16}OSe$: C, 63.37; H, 5.32. Found: C, 63.32; H, 5.11.

4.2.22. 1,3-Diphenyl-3-phenylselenyl-propan-1-one (5e).[19] White solid; mp 120–121 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, J=7.9, 1.4 Hz, 2H), 7.52 (tt, J=7.4,

1.2 Hz, 1H), 7.43–7.37 (m, 4H), 7.28–7.13 (m, 8H), 5.03 (dd, J=8.4, 6.0 Hz, 1H), 3.85 (dd, J=17.3, 8.5 Hz, 1H), 3.66 (dd, J=17.3, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.51, 141.80, 136.90, 135.88, 133.41, 129.27, 129.15, 128.80, 128.59, 128.33, 128.23, 127.84, 127.31, 44.91, 42.29. Anal. Calcd for $C_{21}H_{18}OSe$: C, 69.04; H, 4.97. Found: C, 68.87; H, 4.64.

4.2.23. 3-Methyl-1-phenyl-3-phenylselenyl-butan-1-one (5f). Pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, J=7.2, 1.4 Hz, 2H), δ 7.68 (dt, J=7.9, 1.4 Hz, 2H), δ 7.56–7.30 (m, 6H), 3.34 (s, 2H), 1.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.37, 138.62, 138.08, 133.21, 129.04, 128.99, 128.76, 128.28, 127.89, 50.38, 44.29, 29.80; m/z (relative intensity) 318 (M^+, 2), 243 (5), 161 (7), 160 (20), 159 (28), 145 (25), 131 (7), 117 (8), 105 (100), 83 (15), 78 (17), 77 (63), 55 (13), 51 (28). HRMS calcd for $C_{17}H_{18}OSe$ 318.0517, found 318.0527. Anal. Calcd for $C_{17}H_{18}OSe$: C, 63.37; H, 5.32. Found: C, 62.59; H, 5.36.

4.2.24. 1-(2-Phenylselenyl-cyclohexyl)-ethanone (5g). White solid; mp 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), δ 7.28–7.23 (m, 3H), 3.77–3.75 (m, 1H), 2.76–2.73 (m, 1H), 2.11 (s, 3H), 2.13–1.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.14, 134.41, 130.66, 129.24, 127.63, 54.90, 46.74, 33.02, 28.15, 25.30, 24.43, 22.90; m/z (relative intensity) 282 (M^+, 60), 280 (30), 158 (85), 157 (38), 156 (46), 155 (30), 154 (25), 125 (45), 124 (30), 109 (43), 81 (98), 79 (60), 78 (100), 77 (76), 53 (32), 51 (43). HRMS calcd for $C_{14}H_{18}OSe$ 282.0517, found 282.0521. Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 59.85; H, 6.39.

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Supplementary data

The ^{1}H and ^{13}C NMR spectra for all compounds are available. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.12.018.

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