Pergamon

Tetrahedron 57 (2001) 6703–6711

TETRAHEDRON

Stereoselective aldol reaction of α-seleno carbonyl compounds: preparation of (*Z*)-α,β-unsaturated carbonyl compounds

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Received 27 April 2001; accepted 30 May 2001

Abstract—The aldol reaction of the titanium enolates of α-seleno esters in the presence of Ph_3P or Ph_3PO gave the products with high stereoselectivity favoring the *syn* isomers. Reaction of α-seleno ketones with $TiCl_4$ in the presence of 2 equiv. of Et_3N, and subsequently with aldehydes, gave the aldol products with high *syn* selectivity. The stereoselectivity in the aldol reaction of 3-pentanone also increased by using an excess amount of Et_3N. The aldol products thus obtained from the α-seleno carbonyl compounds could be stereospecifically converted to (*Z*)-α,β-unsaturated carbonyl compounds by treatment with pyridine. (*Z*)-Alkylidenecyclopentanones were exclusively formed by treatment of the *syn*-aldol products with Et_3N in the dark.

1. Introduction

The stereoselective formation of α,β-unsaturated carbonyl compounds is one of the most important reactions to be developed. The Wittig, the Horner–Wadsworth–Emmons and the Peterson reactions have served as the most powerful methodology for the formation of α,β-unsaturated carbonyl compounds. Recently, several attempts for the preparation of *Z*-olefins using the Horner–Wadsworth–Emmons reaction[1] and the Peterson olefination[2] have been reported. However, these *Z*-selective methods are not applicable to all the derivatives, e.g., the Horner–Wadsworth–Emmons reaction with aliphatic aldehydes often gives products with low stereoselectivity, although the reaction with aromatic aldehydes gives products with high *Z*-stereoselectivity. The β-hydroxy-α-silyl compounds stereospecifically form the double bond through either *syn*- or *anti*-elimination,[3] but the reaction of carbanions derived from α-silyl carbonyl compounds with aldehydes or ketones generally affords a mixture of *syn*- and *anti*-β-hydroxysilanes with low selectivity.[4] The diastereomerically pure β-hydroxysilanes are obtainable by several other methods such as reduction of α-silyl ketones[5] or nucleophilic ring-opening reaction of the diastereomerically pure α-silyl epoxides,[6] but these methods would not be applicable to the preparation of (*Z*)-α,β-unsaturated carbonyl compounds. In general, it is difficult to prepare titanium enolates from nonactivated esters.[7] On the other hand, we have succeeded in the preparation of the enolates by introducing the phenylseleno group at α position, to the carbonyl group and preliminarily communicated the stereoselective aldol reaction of the α-seleno enolates derived from the α-phenylseleno esters.[8] We now report, in detail, the highly stereoselective reaction of the titanium enolates starting from α-seleno carbonyl compounds with various aldehydes. We also report the highly (*Z*)-selective formation of the α,β-unsaturated carbonyl compounds from the aldol products.

2. Results and discussion

2.1. Stereoselective aldol reaction of α-seleno carbonyl compounds

First, we examined the reaction of the titanium enolates of the α-seleno esters **1a**,**b** with aldehydes. The results are summarized in Table 1.

A CH_2Cl_2 solution of methyl 2-(phenylseleno)acetate (**1a**) was treated with 1.1 equiv. of $TiCl_4$ and 1.1 equiv. of ethyldiisopropylamine at −78°C.[9] After 1 h, 1.1 equiv. of benzaldehyde was added to the reaction mixture to give the product **2a** in 96% yield in a *syn*/*anti* ratio of 80:20 (entry 1). The stereoselectivity of the reaction increased by use of 2.0 equiv. of Et_3N as a base (entry 2). When phosphorus reagents were added to the reaction mixture, the stereoselectivity was also improved (entries 3–6). Especially, triphenylphosphine oxide showed significantly high stereoselectivity (entry 6). Reaction of **1a** with various aldehydes, such as *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, 3-phenylpropionaldehyde, (*E*)-cinnamaldehyde and hexanal, proceeded with high stereoselectivity in the presence of triphenylphosphine oxide (entries 7–11). Furthermore, the reaction of ethyl 2-(phenylseleno)propio-

Keywords: aldol reactions; olefination; selenium and compounds; titanium and compounds.

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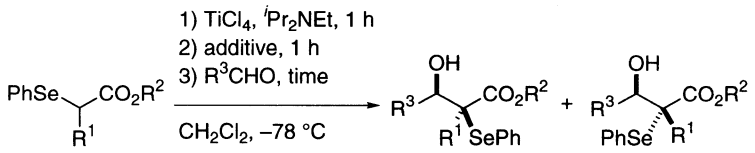
0040–4020/01/$ - see front matter
PII: S0040-4020(01)00606-8

Table 1. The $TiCl_4$-mediated aldol reaction of the α-seleno esters **1a**,**b** with aldehydes under various conditions



1a: R^1 = H, R^2 = Me
1b: R^1 = Me, R^2 = Et

syn-**2** *anti*-**2**

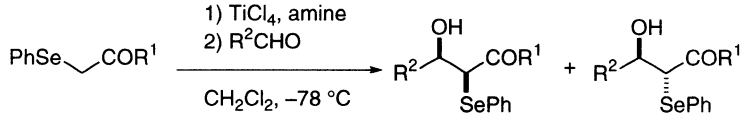
Entry	Ester		Aldehyde	Additive	Product	Time (h)	Yield (%)	Ratio, *syn*/*anti*
	R^1	R^2	R^3					
1	H	Me	Ph	–	**2a**	3	97	80:20[a]
2[b]	H	Me	Ph	–	**2a**	2	82	95:5
3	H	Me	Ph	Ph_3P	**2a**	2	85	95:5[a]
4	H	Me	Ph	Bu_3P	**2a**	4	98	90:10[a]
5	H	Me	Ph	$(Ph_2PCH_2)_2$	**2a**	1	62	91:9[a]
6	H	Me	Ph	Ph_3PO	**2a**	2	92	97:3[a]
7	H	Me	*p*-ClC_6H_4	Ph_3PO	**2b**	2	85	95:5[c]
8	H	Me	*p*-$MeOC_6H_4$	Ph_3PO	**2c**	2.5	83	>98:2[a]
9	H	Me	$PhCH_2CH_2$	Ph_3PO	**2d**	2	92	88:12[c]
10	H	Me	(*E*)-PhCH=CH	Ph_3PO	**2e**	5	81	>98:2[c]
11	H	Me	*n*-C_5H_{11}	Ph_3PO	**2f**	1	83	95:5[c]
12	Me	Et	Ph	Ph_3P	**2g**	2.5	93	>98:2[a]
13	Me	Et	^{i}Pr	Ph_3P	**2h**	2	92	>98:2[a]

[a] Diastereomer ratio was determined by the ^{1}H NMR analysis.
[b] Et_3N (2.0 equiv.) was used.
[c] Diastereomer ratio was determined by the HPLC analysis.

nate (**1b**) with benzaldehyde or isobutyraldehyde in the presence of triphenylphosphine afforded the products **2g**,**h** with complete stereoselectivity (entries 12 and 13). The aldol reaction of the α-seleno ketones **3** was also examined, but triphenylphosphine and triphenylphosphine oxide could not be used in this reaction, because these phosphorus compounds eliminated the phenylseleno group from the substrate.[10] Instead, amine bases such as triethylamine or ethyldiisopropylamine were found to be significantly effective for increasing the stereoselectivity. The results are summarized in Table 2.

The reaction of 1-(phenylseleno)propanone **3a** with benzaldehyde and $TiCl_4$ was carried out in the presence of 1.1 equiv. of triethylamine or ethyldiisopropylamine giving **4a** with moderate stereoselectivity (entries 1 and 3). Stereoselectivity was significantly improved, when 2.2 equiv. of Et_3N was used (entry 2). An excess amount of Et_3N seems to

Table 2. The $TiCl_4$-mediated aldol reaction of the α-seleno ketones **3a**–**c** with aldehydes under various conditions

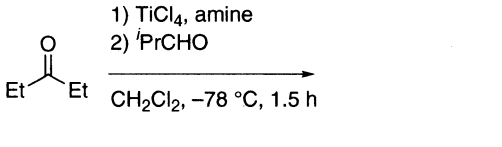


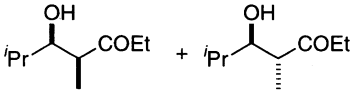
3a-c

syn-**4** *anti*-**4**

3a: R^1 = Me
3b: R^1 = Et
3c: R^1 = ^{i}Pr

Entry	Ketone, R^1	Aldehyde, R^2	Amine (equiv.)	Product	Yield (%)	Ratio, *syn*/*anti*
1	Me	Ph	Et_3N (1.1)	**4a**	91	85:15
2	Me	Ph	Et_3N (2.2)	**4a**	91	>98:2
3	Me	Ph	$^iPr_2NEt$ (1.1)	**4a**	93	87:13
4	Me	Ph	$^iPr_2NEt$ (2.2)	**4a**	87	94:6
5	Me	^{i}Pr	Et_3N (2.2)	**4b**	75	>98:2
6	Me	PhCH=CH	Et_3N (2.2)	**4c**	74	96:4
7	Me	$PhCH_2CH_2$	Et_3N (2.2)	**4d**	94	93:7
8	Me	*n*-$C_6H_{13}C{\equiv}C$	Et_3N (2.2)	**4e**	97	94:6
9	Et	Ph	Et_3N (2.2)	**4f**	71	>98:2
10	^{i}Pr	$PhCH_2CH_2$	Et_3N (2.2)	**4g**	92	>98:2





syn *anti*

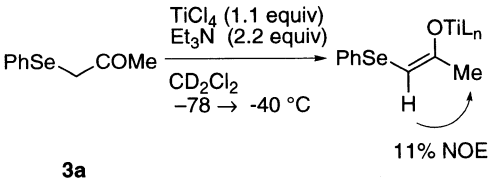
Et_3N (equiv)	yield (%)	ratio *syn* : *anti*
1.1	84	92 : 8
2.2	79	98 : 2

Scheme 1.

be more effective than $^{i}Pr_2NEt$. Reaction of **3a** with various aldehydes using 2.2 equiv. of Et_3N gave the products **4b–e** with high stereoselectivity (entries 5–8). Reaction of the ethyl ketone **3b** and the isopropyl ketone **3c** also afforded the products **4f,g** with high stereoselectivity (entries 9 and 10). The relative stereochemistry of the aldol products **2** and **4** was determined by the coupling constants between the hydrogens α and β to the carbonyl group in the ^1H NMR spectra, where the *anti* isomers showed larger $J_{\alpha\beta}$ values than those of the *syn*-isomers.[11]

We found that the striking effect of Et_3N on stereoselectivity was not limited to the aldol reaction of phenylseleno ketones. Significant increase of the stereoselectivity was obtained in the aldol reaction of 3-pentanone with isobutyraldehyde in the presence of 1.1 equiv. of $TiCl_4$ and 2.2 equiv. of Et_3N as shown in Scheme 1.

These results should be noted, because the reaction of the titanium enolate of 3-pentanone with isobutyraldehyde without an amine as a base has been reported to give the product with low stereoselectivity (*syn*/*anti*=68:32).[12] We also showed the efficiency of triphenylphosphine or triphenylphosphine oxide in the reaction of the α-seleno esters with aldehydes. Triphenylphosphine has been reported to improve the stereoselectivity in the Mukaiyama aldol reaction of silylketeneacetals using $TiCl_4$.[13] $TiCl_4$ is known to form a 1:1 or a 1:2 complex with triphenylphosphine oxide.[14] Since the aldol reaction of the α-seleno ketones **3** with 2 equiv. of the base occurred only at α position to the seleno group, an excess base would not work as a deprotonating base, but would coordinate titanium to improve the stereoselectivity.[15]



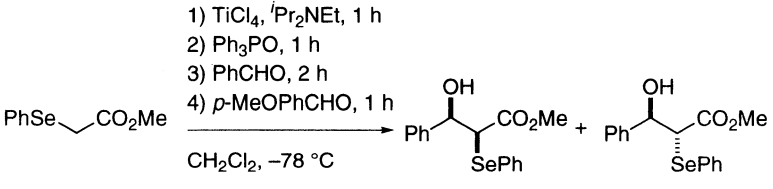
3a

Figure 1. The titanium enolate of **3a**.

We have confirmed that no retro-aldol reaction of the product **2a** occurs during the reaction as follows. The titanium enolate prepared from **1a** was treated with benzaldehyde at −78°C and the mixture was stirred for 2 h. Then *p*-methoxybenzaldehyde was added (Scheme 2).

The product consisted of a 97:3 mixture of *syn*-**2a** and *anti*-**2a** formed from benzaldehyde, but the aldol product derived from *p*-methoxybenzaldehyde was not observed. This fact indicates that no retro-aldol reaction would occur through the course of the reaction, i.e., the stereoselective outcome in the reaction of **1a** should be kinetically controlled. In order to obtain more information on the reaction mechanism, we confirmed the geometry of the titanium enolate of **3a** by the ^1H NMR spectrum (Fig. 1).

The ^1H NMR spectrum at −40°C of the titanium enolate, derived from **3a** by treatment with 1.1 equiv. of $TiCl_4$ and 2.2 equiv. of Et_3N in CD_2Cl_2 at −78°C, showed the vinyl proton at 5.48 ppm as a single isomer. In addition, a significant nuclear Overhauser effect (11%) between the vinyl and the methyl protons showed the *Z*-geometry of the titanium enolate. The *Z*-enolate was probably formed through the interaction between titanium and selenium. In general, the aldol reaction of titanium enolates with aldehydes affords the *syn*-isomers with moderate to high selectivity.[16,17] It has been reported that the aldol reaction of the *Z*-titanium enolate formed from the α-benzyloxy carbonyl compounds exclusively gives the *anti* isomers through a transition state involving chelation of titanium with the carbonyl and the benzyloxy oxygens.[18] However, the reaction of α-silyloxyl ketones preferentially affords the *syn*-isomer due to the weaker interaction of titanium with oxygen of the silyloxy group in comparison with that of the benzyloxy group. Furthermore, (*Z*)-titanium enolates of α-thio esters give the products with *syn*-selectivity.[19] Thus, it is likely that the reaction of the titanium enolates of the α-selenocarbonyl compounds **1** and **3** with aldehydes proceeds through a



1a *syn*-**2a** *anti*-**2a**

90%
97 : 3

Scheme 2.

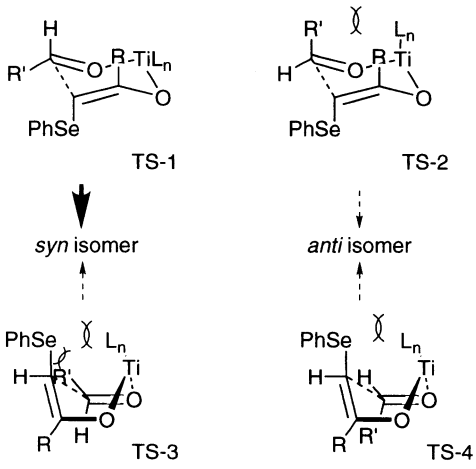


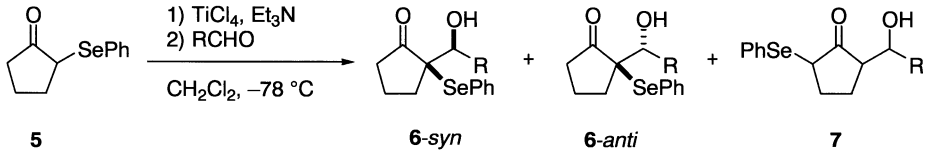
Figure 2. Assumed transition states of reaction of titanium enolates derived from α-seleno carbonyl compounds and aldehydes.

cyclic transition state[11a,20] without the interaction of titanium and selenium. Four transition states derived from the *Z*-enolate are shown in Fig. 2. The chair-like transition states (TS-1 and 2) would be more stable than the boat-like cyclic transition states (TS-3 and 4), and TS-1 would be more stable than TS-2 by the 1,3-*diaxial* repulsion between the ligand and the alkyl group in the aldehyde, giving the *syn*-isomer.

We next examined the reaction of the α-selenocyclopentanone **5**. The results are summarized in Scheme 3. When the reaction was carried out using 1.1 equiv. of $TiCl_4$ and Et_3N each, the aldol product **6** was formed with low stereoselectivity and, in addition, the PhSe-migrated aldol product **7** was obtained. The reaction was carried out using less than one equivalent each of $TiCl_4$ and Et_3N to give the aldol products **6a**,**b** with high stereoselectivity without formation of **7**.

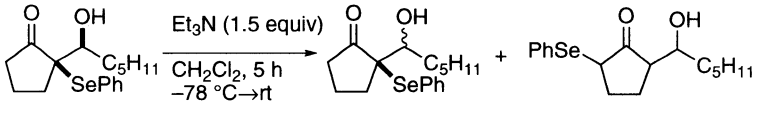
When *syn*-**6a** was treated with 1.5 equiv. of Et_3N in CH_2Cl_2, a diastereomeric mixture of **6a** and the phenylseleno group-migrated product **7** were obtained (Scheme 4). The partial epimerization of *syn*-**6a** to *anti*-**6a** was observed during the above treatment, which occurred apparently by the migration of the phenylseleno group.

The compound **7** was formed by migration of the phenylseleno group via enolization of **6** with an excess amount of Et_3N. This is in accord with the results, reported by Liotta and co-workers, that migration of the seleno group to the α′-position is caused by treatment of α-(phenylseleno)cycloalkanones with 0.5 equiv. of LDA.[21] Interestingly, treatment of a diastereomeric mixture of the isolated **7** with Et_3N (1.5 equiv.) afforded the remigrated product *anti*-**6a** as a single diastereomer besides **7** (Scheme 5). Formation of *anti*-**6a** by the seleno migration apparently lowers the stereoselectivity in the aldol reaction of **5** (Scheme 3).



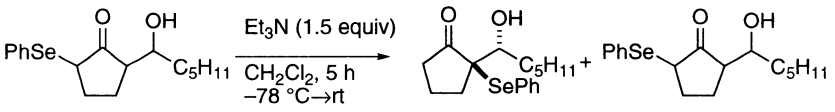
	$TiCl_4$, Et_3N (equiv)	**6**: yield (%)	*syn* : *anti*	**7**: yield (%)
5a: R = *n*-C_5H_{11}	1.1	42	74 : 26	44
5a: R = *n*-C_5H_{11}	0.8	78	98 : 2	-
5b: R = TMS-C C-	0.95	63	98 : 2	-

Scheme 3.



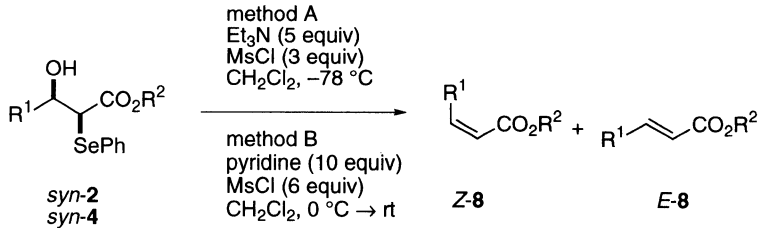
syn-**6a**	:	*anti*-**6a**	:	**7**
86	:	5	:	9

Scheme 4.



Scheme 5.

Table 3. Preparation of the α,β-unsaturated carbonyl compounds **8** from the aldol products *syn*-**2** and *syn*-**4**



Entry		R^1	R^2	Amine	Time (h)	Product	Yield (%)	Z/E[a]
1	**2a**	Ph	OMe	Et_3N	1.5	**8a**	82	>98:2
2	**2a**	Ph	OMe	Pyridine	2	**8a**	79	93:7
3	**2b**	*p*-$MeOC_6H_4$	OMe	Et_3N	4	**8b**	88	21:79
4	**2b**	*p*-$MeOC_6H_4$	OMe	Pyridine	3.5	**8b**	95	81:19
5	**2c**	*p*-ClC_6H_4	OMe	Et_3N	3	**8c**	41	10:90
6	**2c**	*p*-ClC_6H_4	OMe	Pyridine	3	**8c**	95	80:20
7	**2d**	(*E*)-PhCH=CH	OMe	Et_3N	5	**8d**	54	2:>98
8	**2d**	(*E*)-PhCH=CH	OMe	Pyridine	2	**8d**	69	90:10
9	**2e**	$PhCH_2CH_2$	OMe	Pyridine	1.5	**8e**	86	>98:2
10	**2f**	*n*-C_5H_{11}	OMe	Pyridine	4	**8f**	83	>98:2
11	**4e**	$C_6H_{13}C\equiv C$	Me	Pyridine	2	**8g**	88	96:4
12	**4g**	$PhCH_2CH_2$	^{i}Pr	Pyridine	2.5	**8h**	82	93:7

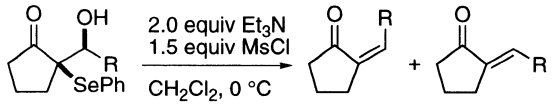
[a] The *Z*/*E* ratio was determined by the ^1H NMR spectral analysis.

Thus, the reaction of **5** using 0.8 equiv. or 0.95 equiv. each of $TiCl_4$ and Et_3N suppressed the seleno migration of the once-formed *syn*-**6a**, giving **6a**,**b** with high stereoselectivity.

2.2. Preparation of the (*Z*)-α,β-unsaturated carbonyl compounds from the aldol products

The stereospecific conversion of the obtained *syn* aldol products **2** and **4** to (*Z*)-α,β-unsaturated carbonyl compounds **8** was achieved by treatment with methanesulfonyl chloride (MsCl) and a base (Table 3).

The *syn* aldol products **2** were treated under the conditions either in the presence of 5 equiv. of Et_3N and 3 equiv. of MsCl at −78°C or in the presence of 10 equiv. of pyridine and 5 equiv. of MsCl at from 0°C to rt. The *Z*/*E* ratio of the α,β-unsaturated esters varied depending on the amine used. The α-seleno-β-hydroxy ester **2a** (R^1=Ph) exclusively gave the *Z*-isomer by treatment with Et_3N (entry 1). In other cases examined, Et_3N generally gave the *E*-isomers predominantly, where **2d** (R^1=PhCH=CH) exclusively gave the *E*-isomer (entry 7). On the other hand, pyridine predominantly gave the *Z*-isomers. Especially, the aldol products **2e** and **f** produced from phenylpropionaldehyde and hexanal, respectively, gave the *Z*-isomers exclusively (entries 9 and 10). The *Z*-isomer was apparently formed via the *anti*-elimination of the phenylseleno and the mesyloxy groups through an episelenonium ion intermediate.[22] Predominant formation of the *E*-isomer in the reaction of *syn*-**2** with Et_3N can be ascribed to the isomerization of the *syn*-isomer into the *anti*-isomer through the retro-aldol reaction. Indeed, formation of *anti*-**2** during the reaction of *syn*-**2** in the presence of Et_3N was confirmed by the TLC analysis of the reaction mixture. The geometry of the obtained olefins **8** was determined by the coupling constant values in their ^1H NMR spectra. The elimination reaction of the α-selenocyclopentanones *syn*-**6** was carried out with MsCl and Et_3N. When the reaction was carried out without taking special care, the product **9** was formed with high *E*-selectivity (Scheme 6).



R	reaction conditions	yield (%)	Z : E
n-C_5H_{11}	without cover	89	2 : >98
n-C_5H_{11}	in the dark	93	>98 : 2
TMS-C≡C	in the dark	88	>98 : 2

Scheme 6.

We found that (*Z*)-**9** was extremely sensitive to light and readily isomerized to *E*-**9** by exposure even to the fluorescent light.[23] Indeed, the *Z*-products **9a**,**b** were exclusively formed, when the reaction of *syn*-**6a**,**b** with MsCl and Et_3N was carried out in the dark or in a round-bottom flask wrapped with aluminum foil. We further confirmed that *Z*-**9a** completely isomerized to *E*-**9a** by exposure to sunlight for 2 min.

3. Conclusion

We have reported the highly stereoselective reaction of titanium enolates derived from α-seleno carbonyl compounds with various aldehydes, demonstrating the effect of bases on the stereoselectivity. We also showed the highly stereospecific formation of the (*Z*)-α,β-unsaturated carbonyl

compounds by treatment of the *syn*-aldol products with methanesulfonyl chloride and amines.

4. Experimental

All reactions were performed in oven- and flame-dried glassware under a positive pressure of argon. Air- and moisture sensitive reagents and solvents were transferred via syringe or cannula, and were introduced into the reaction vessels though a rubber septum. CH_2Cl_2 was distilled from calcium hydride. All the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60f-254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on a column packed with Fuji Silysia silica gel BW-200. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra for solutions in $CDCl_3$ were recorded on a Varian Gemini-200. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane or $CHCl_3$, and *J* values are given in Hz. Infrared spectra were recorded on a JASCO A-102 spectrometer. Mass spectra (eV) were recorded on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin–Elmer-240. Optical rotations were measured on a JASCO DIP-4 polarimeter operating at λ=589 nm corresponding to the sodium D line, in the indicated solvent and concentration in grams of solute per 100 cm^3. HPLC analyses were performed on a JASCO TRI ROTOR IV using 4.6×250 mm COSMOSIL packed column.

4.1. Representative procedure for the reaction of α-seleno esters with aldehydes

4.1.1. Methyl 3-hydroxy-3-phenyl-2-(phenylseleno)propionate (2a). To a solution of methyl 2-(phenylseleno)acetate (97 mg, 0.43 mmol) in CH_2Cl_2 (2.1 mL) was added $TiCl_4$ (0.051 mL, 0.49 mmol) and ^{i}Pr$_2$NEt (0.082 mL, 0.47 mmol) at −78°C and the mixture was stirred for 1 h. A solution of triphenylphosphine oxide (130 mg, 0.47 mmol) in CH_2Cl_2 (1.0 mL) was added to the reaction mixture. After stirring for 1 h, benzaldehyde (0.048 mL, 0.47 mmol) was added, and the mixture was stirred for 30 min. Saturated aq. NH_4Cl (2 mL) was then added, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 15 g, hexane/ethyl acetate=85:15) to give *syn*-**2a** (130 mg, 92%). The *syn*/*anti* ratio was determined to be 97:3 by the ^{1}H NMR analysis of the crude product. *syn*-**2a**: ^{1}H NMR δ 3.48 (d, 1H, *J*=2.0 Hz), 3.55 (s, 3H), 3.86 (d, 1H, *J*=6.6 Hz), 5.07 (dd, 1H, *J*=2.0, 6.6 Hz), 7.20–7.54 (m, 10H); IR (neat) 3470, 3050, 2950, 1715, 1570, 1490, 1470, 1430, 1320, 1255, 1190, 1165, 1130, 1055, 1040, 1020, 905, 735, 690 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_3Se$: C, 57.32; H, 4.81. Found: C, 57.21; H, 4.75. *anti*-**2a**: ^{1}H NMR δ 3.29 (d, 1H, *J*=6.4 Hz), 3.65 (s, 3H), 3.90 (d, 1H, *J*=7.6 Hz), 5.12 (dd, 1H, *J*=6.4, 7.6 Hz), 7.14–7.54 (m, 10H); IR (neat) 3440, 3040, 2940, 1715, 1570, 1470, 1425, 1260, 1190, 1020, 910, 760, 735, 690 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_3Se$: C, 57.32; H, 4.81. Found: C, 57.45; H, 4.97.

4.1.2. Methyl 3-(4-chlorophenyl)-3-hydroxy-2-(phenylseleno)propionate (2b). *syn*-**2b**: ^{1}H NMR δ 3.55 (s, 1H), 3.57 (s, 3H), 3.78 (d, 1H, *J*=6.6 Hz), 5.03 (d, 1H, *J*=6.6 Hz), 7.21–7.52 (m, 9H); IR (neat) 3460, 2950, 1710, 1570, 1480, 1430, 1250, 1080, 1010, 830, 730, 690 cm^{-1}. Anal. calcd for $C_{16}H_{15}ClO_3Se$: C, 51.98; H, 4.09. Found: C, 52.20; H, 4.13.

4.1.3. Methyl 3-hydroxy-3-(4-methoxyphenyl)-2-(phenylseleno)propionate (2c). *syn*-**2c**: ^{1}H NMR δ 3.36 (s, 1H), 3.53 (s, 3H), 3.80 (s, 3H), 3.84 (d, 1H, *J*=7.1 Hz), 4.99 (d, 1H, *J*=7.1 Hz), 6.86–7.53 (m, 9H); IR (neat) 3470, 3000, 2930, 1720, 1600, 1510, 1430, 1250, 1170, 1020, 830, 735 cm^{-1}. Anal. calcd for $C_{17}H_{18}O_4Se$: C, 55.90; H, 4.97. Found: C, 55.67; H, 4.93.

4.1.4. Methyl 3-hydroxy-5-phenyl-2-(phenylseleno)pentanoate (2d). *syn*-**2d**: ^{1}H NMR δ 1.90–2.00 (m, 2H), 2.70–2.80 (m, 2H), 3.25–3.30 (br, 1H), 3.61 (d, 1H, *J*=4.9 Hz), 3.65 (s, 3H), 3.90–4.00 (m, 1H), 7.25–7.61 (m, 10H); IR (neat) 3500, 3000, 1710, 1570, 1430, 1240, 1190, 1060, 1010, 730, 685 cm^{-1}. Anal. calcd for $C_{18}H_{20}O_3Se$: C, 59.51; H, 5.55. Found: C, 59.59; H, 5.47.

4.1.5. Methyl 3-hydroxy-5-phenyl-2-(phenylseleno)pentenoate (2e). *syn*-**2e**: ^{1}H NMR δ 3.22 (d, 1H, *J*=2.8 Hz), 3.65 (s, 3H), 3.78 (d, 1H, *J*=6.3 Hz), 4.60–4.70 (m, 1H), 6.25 (dd, 1H, *J*=6.3, 15.9 Hz), 6.71 (d, 1H, *J*=15.9 Hz), 7.22–7.67 (m, 10H); IR (neat) 3430, 3020, 1705, 1570, 1425, 1270, 1190, 1020, 960, 730, 680 cm^{-1}. Anal. calcd for $C_{18}H_{18}O_3Se$: C, 59.84; H, 5.02. Found: C, 59.80; H, 5.06.

4.1.6. Methyl 3-hydroxy-2-(phenylseleno)hexanoate (2f). *syn*-**2f**: ^{1}H NMR δ 0.82–1.83 (m, 11H), 3.19 (d, 1H, *J*=2.4 Hz), 3.63 (d, 1H, *J*=5.0 Hz), 3.67 (s, 3H), 3.90–4.00 (m, 1H), 7.26–7.68 (m, 5H); IR (neat) 3480, 3010, 1705, 1570, 1430, 1260, 1115, 1015, 830, 680 cm^{-1}. Anal. calcd for $C_{15}H_{22}O_3Se$: C, 54.71; H, 6.73. Found: C, 54.76; H, 6.78.

4.1.7. Ethyl 3-hydroxy-2-methyl-3-phenyl-2-(phenylseleno)propionate (2g). *syn*-**2g**: ^{1}H NMR δ 1.14 (t, 3H, *J*=7.0 Hz), 1.34 (s, 3H), 3.53 (d, 1H, *J*=2.0 Hz), 4.03 (q, 2H, *J*=7.0 Hz), 5.19 (d, 1H, *J*=2.0 Hz), 7.26–7.54 (m, 8H), 7.62–7.76 (m, 2H); ^{13}C NMR δ 13.8, 17.3, 57.9, 61.1, 74.8, 126.7, 127.8, 128.0, 128.9, 129.5, 138.0, 138.1, 172.6; IR (neat) 3470, 3050, 3030, 2980, 2930, 1710, 1595, 1570, 1470, 1445, 1435, 1375, 1285, 1240, 1170, 1150, 1100, 1080, 1040, 1020, 915, 860, 740, 690 cm^{-1}. Anal. calcd for $C_{18}H_{20}O_3Se$: C, 59.51; H, 5.55. Found: C, 59.78; H, 5.63.

4.1.8. Ethyl 3-hydroxy-2,4-dimethyl-2-(phenylseleno)-pentanoate (2h). *syn*-**2g**: ^{1}H NMR δ 0.80 (d, 3H, *J*=6.8 Hz), 0.94 (d, 3H, *J*=6.8 Hz), 1.10 (t, 3H, *J*=7.2 Hz), 1.48 (s, 3H), 1.70–1.80 (m, 1H), 2.81 (br, 1H), 3.78 (d, 1H, *J*=6.6 Hz), 3.93 (q, 2H, *J*=7.2 Hz), 7.04–7.68 (m, 5H); IR (neat) 3480, 3050, 2950, 2800, 1700, 1465, 1445, 1435, 1370, 1295, 1240, 1160, 1120, 1090, 1025, 960, 940, 860, 740, 685 cm^{-1}. Anal. calcd for $C_{15}H_{22}O_3Se$: C, 54.71; H, 6.73. Found: C, 54.60; H, 6.82.

4.2. Representative procedure for the reaction of α-seleno ketones with aldehydes

4.2.1. 4-Hydroxy-4-phenyl-3-(phenylseleno)butan-2-one (4a). To a solution of 1-(phenylseleno)propan-2-one (**3a**) (45 mg, 0.21 mmol) in CH_2Cl_2 (1.1 mL) was added $TiCl_4$ (0.025 mL, 0.23 mmol) and Et_3N (0.064 mL, 0.46 mmol) at −78°C and the mixture was stirred for 1 h. Benzaldehyde (0.024 mL, 0.23 mmol) was then added to the reaction mixture. After stirring for 3 h, saturated aq. NH_4Cl (3 mL) was added and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave an oil which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate=85:15) to give *syn*-**4a** (61 mg, 91%). The *syn*/*anti* ratio was determined to be >98:2 by the ^1H NMR analysis of the crude product. *syn*-**4a**: ^1H NMR δ 2.21 (s, 3H), 3.84 (d, 1H, J=5.2 Hz), 5.18 (m, 2H, J=6.6 Hz), 7.21–7.52 (m, 10H); IR (KBr) 3450, 3010, 1650, 1370, 1260, 1210, 1100, 1040, 950, 740 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_2Se$: C, 60.19; H, 5.05. Found: C, 60.30; H, 4.92.

4.2.2. 4-Hydroxy-5-methyl-3-(phenylseleno)hexan-2-one (4b). *syn*-**4b**: ^1H NMR δ 0.93 (d, 3H, J=6.7 Hz), 1.03 (d, 3H, J=6.6 Hz), 2.04 (m, 1H), 2.23 (s, 3H), 3.28 (br, 1H), 3.65 (dd, 1H, J=4.6, 7.0 Hz), 3.86 (s, 1H, J=4.6 Hz), 7.26–7.40 (m, 3H), 7.58–7.69 (m, 2H); IR (KBr) 3420, 300, 1620, 1550, 1205, 1050, 1010 cm^{-1}. Anal. calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.88; H, 6.21.

4.2.3. (*E*)-4-Hydroxy-6-phenyl-3-(phenylseleno)-5-hexen-2-one (4c). *syn*-**4c**: ^1H NMR δ 2.28 (s, 3H), 3.32 (d, 1H, J=2.5 Hz), 3.79 (d, 1H, J=5.5 Hz), 4.71 (m, 1H), 6.28 (dd, 1H, J=6.1, 15.9 Hz), 6.73 (d, 1H, J=15.9 Hz), 7.17–7.68 (m, 10H); IR (KBr) 3450, 3010, 2905, 2850, 1665, 1570, 1475, 1430, 1395, 1350, 1305, 1295, 1260, 1205, 1170, 1110, 1090, 1060, 1020, 995, 960, 740, 685 cm^{-1}. Anal. calcd for $C_{18}H_{18}O_2Se$: C, 62.61; H, 5.25. Found: C, 62.60; H, 5.25. *anti*-**4c**: ^1H NMR δ 2.34 (s, 3H), 2.92 (d, 1H, J=6.3 Hz), 3.79 (d, 1H, J=7.9 Hz), 4.68 (m, 1H), 6.38 (dd, 1H, J=6.4, 16.0 Hz), 6.69 (d, 1H, J=16.0 Hz), 7.12–7.64 (m, 10H); IR (KBr) 3450, 3010, 2905, 2850, 1665, 1570, 1475, 1430, 1395, 1350, 1305, 1295, 1260, 1205, 1170, 1110, 1090, 1060, 1020, 995, 960, 740, 685 cm^{-1}.

4.2.4. 4-Hydroxy-4-phenyl-3-(phenylseleno)butan-2-one (4d). *syn*-**4d**: ^1H NMR δ 1.80–1.90 (m, 1H), 2.10–2.15 (m, 1H), 2.19 (s, 3H), 2.70 (ddd, 1H, J=7.1, 9.1, 13.8 Hz), 2.89 (ddd, 1H, J=5.2, 9.6, 13.8 Hz), 3.30 (br, 1H), 3.65 (d, 1H, J=4.4 Hz), 3.95–4.05 (m, 1H), 7.11–7.41 (m, 8H), 7.55–7.67 (m, 2H); IR (neat) 3465, 3030, 2920, 2850, 1675, 1595, 1575, 1490, 1475, 1445, 1435, 1350, 1290, 1170, 1060, 1020, 995, 960, 910, 735, 690 cm^{-1}. Anal. calcd for $C_{18}H_{20}O_2Se$: C, 62.25; H, 5.80. Found: C, 62.48; H, 5.66.

4.2.5. 4-Hydroxy-3-(phenylseleno)-5-dodecyn-2-one (4e). *syn*-**4e**: ^1H NMR δ 0.87 (t, 3H, J=6.6 Hz), 1.15–1.60 (m, 8H), 2.22 (dt, 2H, J=1.9, 6.9 Hz), 3.09 (d, 1H, J=3.8 Hz), 3.87 (d, 1H, J=5.6 Hz), 4.75–4.85 (m, 1H), 7.25–7.75 (m, 5H); IR (neat) 3400, 2930, 2850, 2220, 1680, 1570, 1430, 1350, 1240, 1040, 730, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 352 (M^+-1, 12), 214 (100), 157 (32). Anal. calcd for $C_{18}H_{24}O_2Se$: C, 61.53; H, 6.88. Found: C, 61.76; H, 7.00.

4.2.6. 1-Hydroxy-1-phenyl-2-(phenylseleno)pentan-2-one (4f). *syn*-**4f**: ^1H NMR δ 0.97 (t, 3H, J=7.3 Hz), 2.23 (dq, 1H, J=7.3, 17.5 Hz), 2.68 (dq, 1H, J=7.3, 17.5 Hz), 3.64 (br, 1H), 3.84 (d, 1H, J=5.5 Hz), 5.15 (d, 1H, J=5.5 Hz), 7.16–7.47 (m, 10H); IR (neat) 3430, 3020, 2980, 2940, 2900, 1670, 1570, 1490, 1445, 1370, 1340, 1290, 1255, 1195, 1125, 1105, 1085, 1065, 1035, 980, 50, 730, 690, 670 cm^{-1}. Anal. calcd for $C_{17}H_{18}O_2Se$: C, 61.26; H, 5.44. Found: C, 61.50; H, 5.53.

4.2.7. 5-Hydroxy-2-methyl-7-phenyl-4-(phenylseleno)-heptan-3-one (4g). *syn*-**4g**: ^1H NMR δ 1.00 (d, 3H, J=7.1 Hz), 1.11 (d, 3H, J=6.7 Hz), 1.72–2.27 (m, 2H), 2.58–3.03 (m, 3H), 3.39 (br, 1H), 3.76 (d, 1H, J=5.0 Hz), 3.95–4.00 (m, 1H), 7.12–7.64 (m, 10H); IR (neat) 3480, 3050, 2950, 1680, 1440, 1380, 1290, 1060, 910, 740, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 376 (M^+-1, 36), 242 (72), 157 (19), 91 (100). Anal. calcd for $C_{20}H_{24}O_2Se$: C, 64.00; H, 6.44. Found: C, 63.75; H, 6.45.

4.2.8. 2-(1-Hydroxyhexyl)-2-(phenylseleno)cyclopentanone (6a). *syn*-**6a**: ^1H NMR δ 0.85–0.90 (m, 3H), 1.10–1.70 (m, 8H), 1.80–2.70 (m, 6H), 3.27 (br, 1H), 3.68 (dd, 1H, J=1.9, 9.8 Hz), 7.20–7.70 (m, 5H); IR (KBr) 3450, 2930, 2850, 1710, 1570, 1430, 1300, 1260, 1140, 1060, 1020, 740, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 340 (M^+-1, 26), 240 (100), 157 (40), 77 (18), 55 (28). Anal. calcd for $C_{17}H_{24}O_2Se$: C, 60.17; H, 7.13. Found: C, 59.89; H, 7.15. *anti*-**6a**: ^1H NMR δ 0.85–0.90 (m, 3H), 1.18–1.70 (m, 8H), 1.80–2.45 (m, 5H), 2.60–2.80 (m, 1H), 3.70–3.80 (m, 1H), 7.20–7.50 (m, 5H).

4.2.9. 5-(1-Hydroxyhexyl)-2-(phenylseleno)cyclopentanone (7a). ^1H NMR δ 0.85–0.90 (m, 3H), 1.15–1.65 (m, 8H), 1.70–1.90 (m, 2H), 2.00–2.20 (m, 3H), 2.30–2.50 (m, 1H), 3.69 (t, 1H, J=8.6 Hz), 3.82 (br, 1H), 7.22–7.65 (m, 5H); IR (KBr) 3450, 3050, 2930, 2850, 1710, 1570, 1430, 1300, 1060, 740, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 340 (M^+-1, 28), 240 (100).

4.2.10. 2-(1-Hydroxy-3-trimethylsilylpropynyl)-2-(phenylseleno)cyclopentanone (7b). *syn*-**7b**: ^1H NMR δ 0.14 (s, 9H), 1.90–2.73 (m, 6H), 2.86 (d, 1H, J=2.9 Hz), 4.52 (d, 1H, J=2.9 Hz), 7.25–7.68 (m, 5H); IR (KBr) 3400, 2960, 2180, 1705, 1405, 1245, 1160, 1070, 995, 840, 740, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 366 (M^+-1, 0.2), 240 (100). Anal. calcd for $C_{17}H_{22}O_2SeSi$: C, 55.88; H, 6.07. Found: C, 55.91; H, 6.04.

4.3. Representative procedure for the preparation of α,β-unsaturated esters

4.3.1. Methyl 3-(*p*-methoxyphenyl)prop-2-enoate (8b). To a solution of methyl 3-(4-chlorophenyl)-3-hydroxy-2-(phenylseleno)propionate (*syn*-**2b**) (84 mg, 0.23 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of CH_3SO_2Cl (0.11 mL, 1.42 mmol) in CH_2Cl_2 and pyridine (0.19 mL, 2.30 mmol) at 0°C. After stirring for 3 h, H_2O (2 mL) was added and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried

over Na_2SO_4, and concentrated under reduced pressure to leave an oil which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate=97:3) to give *Z*-**8b** (34 mg, 77%) and *E*-**8b** (8 mg, 18%). The *Z*/*E* ratio was determined to be 81:19 by the ^{1}H NMR analysis. *Z*-**8b**: ^{1}H NMR δ 3.73 (s, 3H), 3.83 (s, 3H), 5.83 (d, 1H, *J*=12.7 Hz), 6.88 (d, 1H, *J*=12.7 Hz), 6.88 (d, 2H, *J*=8.8 Hz), 7.69 (d, 2H, *J*=8.8 Hz); IR (neat) 2950, 1710, 1595, 1510, 1430, 1250, 1160, 1303, 840 cm^{-1}. Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.62; H, 6.41. *E*-**10b**: ^{1}H NMR δ 3.79 (s, 3H), 3.84 (s, 3H), 6.30 (d, 1H, *J*=15.9 Hz), 6.80–7.70 (m, 6H).

4.3.2. Methyl cinnamate (8a). *Z*-**8a**: ^{1}H NMR δ 3.71 (s, 3H), 5.95 (d, 1H, *J*=12.6 Hz), 6.96 (d, 1H, *J*=12.6 Hz), 7.17–7.47 (m, 5H); IR (neat) 2950, 1710, 1630, 1430, 1270, 1160, 1070, 1010, 820, 760, 690 cm^{-1}. Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.96; H, 6.31. *E*-**8a**: ^{1}H NMR δ 3.81 (s, 3H), 6.44 (d, 1H, *J*=15.9 Hz), 7.10–7.75 (m, 6H).

4.3.3. Methyl 3-(*p*-chlorophenyl)prop-2-enoate (8c). *Z*-**8c**: ^{1}H NMR δ 3.72 (s, 3H), 5.96 (d, 1H, *J*=12.6 Hz), 6.89 (d, 1H, *J*=12.6 Hz), 7.25–7.73 (m, 4H); IR (neat) 2950, 1715, 1630, 1590, 1490, 1440, 1270, 1200, 1170, 1090, 1015, 850 cm^{-1}. Anal. calcd for $C_{10}H_9ClO_2$: C, 61.08; H, 4.61. Found: C, 61.25; H, 4.44. *E*-**8c**: ^{1}H NMR δ 3.81 (s, 3H), 6.40 (d, 1H, *J*=15.9 Hz), 7.35 (d, 2H, *J*=8.6 Hz), 7.45 (d, 1H, *J*=8.6 Hz), 7.64 (d, 1H, *J*=15.9 Hz).

4.3.4. Methyl 5-phenylpenta-2,4-dienoate (8d). (2*Z*,4*E*)-**8d**: ^{1}H NMR δ 3.77 (s, 3H), 5.74 (d, 1H, *J*=11.4 Hz), 6.68–6.91 (m, 2H), 7.27–7.56 (m, 5H), 8.14 (dd, 1H, *J*=11.4, 15.6 Hz); IR (neat) 3030, 2950, 1705, 1620, 1430, 1230, 1170, 1130, 1000, 750, 690 cm^{-1}. Anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.27; H, 6.73. (2*E*,4*E*)-**8d**: ^{1}H NMR δ 3.77 (s, 3H), 6.01 (d, 1H, *J*=15.9 Hz), 6.80–7.00 (m, 2H), 7.28–7.52 (m, 6H).

4.3.5. Methyl 5-phenylpent-2-enoate (8e). *Z*-**8e**: ^{1}H NMR δ 2.70–2.80 (m, 2H), 2.90–3.00 (m, 2H), 3.70 (s, 3H), 5.78 (d, 1H, *J*=11.5 Hz), 6.20–6.30 (m, 1H), 7.15–7.34 (m, 5H); IR (neat) 3010, 2920, 1710, 1630, 1430, 1190, 1170, 100, 810, 690 cm^{-1}. Anal. calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.75; H, 7.43.

4.3.6. Methyl oct-2-enoate (8f). *Z*-**8f**: ^{1}H NMR δ 0.82–1.52 (m, 9H), 2.64 (dt, 2H, *J*=7.0, 7.3 Hz), 3.71 (s, 3H), 5.76 (d, 1H, *J*=11.5 Hz), 5.76 (dt, 1H, *J*=7.3, 11.4 Hz); IR (neat) 2930, 1720, 1640, 1435, 1405, 1200, 1170, 820, 780 730 cm^{-1}. Anal. calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.02; H, 10.51.

4.3.7. Dodec-3-en-5-yn-2-one (8g). *Z*-**8g**: ^{1}H NMR δ 0.89 (t, 3H, *J*=6.6 Hz), 1.25–1.70 (m, 8H), 2.44 (dt, 2H, *J*=1.6, 7.1 Hz), 2.49 (s, 3H), 2.70–2.80 (m, 2H), 6.10–6.25 (m, 2H); IR (neat) 2920, 2850, 2300, 2200, 1660, 1580, 1450, 1410, 1350, 1260, 1200, 1170, 1020 cm^{-1}. Anal. calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.25. *E*-**8g**: ^{1}H NMR δ 0.87 (t, 3H, *J*=6.5 Hz), 1.25–1.70 (m, 8H), 2.30–2.50 (m, 2H), 2.48 (s, 3H), 2.70–2.80 (m, 2H), 6.45–6.55 (m, 1H), 6.60–6.70 (m, 1H).

4.3.8. 2-Methyl-7-phenylhept-4-en-3-one (8h). *Z*-**8h**: ^{1}H NMR δ 1.07 (d, 6H, *J*=7.0 Hz), 2.59 (hep, 1H, *J*=7.0 Hz), 2.70–2.80 (m, 2H), 2.90–3.00 (m, 2H), 6.04–6.25 (m, 2H), 7.15–7.35 (m, 5H); ^{13}C NMR δ 18.0, 30.8, 35.1, 41.4, 125.9, 128.3, 128.5, 141.3, 147.5, 205.3; IR (neat) 2950, 1680, 1610, 1450, 1050, 740, 690 cm^{-1}; EIMS *m*/*z* (rel. intensity) 202 (M^+-1, 67), 159 (100), 91 (100). Anal. calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 9.10.

4.3.9. 2-Hexylidencyclopentanone (9). *Z*-**9**: ^{1}H NMR δ 0.80–0.90 (m, 3H), 1.19–1.50 (m, 6H), 1.88 (tt, 2H, *J*=7.5, 7.5 Hz), 2.25–2.35 (m, 2H), 2.54–2.72 (m, 2H), 5.96 (tt, 1H, *J*=2.0, 7.5 Hz); IR (neat) 2930, 2860, 1710, 1635, 1435, 1360, 1270, 1170, 1110, 1025, 860, 830 cm^{-1}. Anal. calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.58; H, 10.80. *E*-**9**: ^{1}H NMR δ 0.80–0.90 (m, 3H), 1.19–1.55 (m, 6H), 1.93 (tt, 2H, *J*=7.4, 7.4 Hz), 2.14 (dt, 2H, *J*=7.2, 7.5 Hz), 2.33 (t, 2H, *J*=7.4 Hz), 2.58 (dt, 1H, *J*=2.6, 7.4 Hz), 6.55 (tt, 1H, *J*=2.6, 7.5 Hz).

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