

Stereoselective Michael Addition and Michael-aldol Tandem Reaction of Diorganyl Diselenides or Disulfides with Conjugated Alkynones Mediated by Samarium Diiodide[†]

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Stereoselective Michael addition and Michael-aldol tandem reaction of diorganyl diselenides and disulfides with conjugated alkynones mediated by samarium diiodide were studied. The reaction temperature was critical for the stereoselectivity. β -Organylselenoalkenones or β -organylthioalkenones and γ -organylselenoallylic alcohols or γ -organylthioallylic alcohols were prepared in good yields.

Keywords Michael addition, Michael-aldol tandem reaction, diorganyl diselenide or disulfide, conjugated alkynone, samarium diiodide

Introduction

Michael addition is one of the classical organic reactions which have played important roles in organic synthesis.¹ The tandem reaction has been of great interest for organic synthesis because it offers a convenient and economical method to prepare desired organic molecules.² The Michael-aldol tandem reaction attracted much attention in organic synthesis.³

The synthesis of multifunctional alkenes is an important goal in organic chemistry and is still being actively explored because of the fact that many biologically active compounds have the structure of substituted alkenes.⁴ Diorganyl diselenides and disulfides are useful difunctional group reagents which have been applied widely for the synthesis of various organic sulfides and selenides.⁵ Vinyl selenides have been widely used as building blocks in organic chemistry.⁶ Kamimura reported the stereoselective thio-Michael/aldol tandem reaction to α,β -conjugated esters⁷ and the magnesium cation-induced *anti*-aldol selective tandem Michael/aldol reaction.⁸ It is doubtless that Kamimura's results are wonderful and of introductory meaning for our investigation. Next Huang *et al.*^{9,10} found the stereoselective Michael/aldol tandem reaction of phenylselenomagnesium bromide with acetylenic sulfones and aldehydes. However, to the best of our knowledge, there are no reports on the synthesis of functionalized alkenes from S—S or Se—Se difunctional reagent with al-

kyones. Conjugated alkynones are known as electrophiles,¹¹ whereas selenolate or thionate and their analogues are good nucleophiles for Michael addition. Herein we wish to report our results of the stereoselective Michael addition and Michael-aldol tandem reactions of diorganyl diselenides or disulfides with conjugated alkynones mediated by samarium diiodide.

Results and discussion

The Michael addition reaction was carried out by adding diorganyl diselenides or disulfides to SmI₂ in THF and the mixture was stirred continuously for 2 h at 60 °C. The conjugated alkynone was added and the reaction mixture was cooled down and reacted at room temperature for 1 h. Then 0.1 mol/L HCl was added. The 1,4-addition products, **2** (*Z*) and **3** (*E*) were obtained in good yields after chromatography on silica gel (Scheme 1).

The reductive cleavage of RSeSeR followed by Michael-addition to α,β -unsaturated ketones has been reported,^{5g} however, such an addition to conjugated alkynone (or alkynal) was not studied yet. It was reported that the nucleophilic addition of the electron-deficient carbon-carbon triple bond may result in some stereoselectivity, because the repulsion of the electron pairs on the sulfur (selenium) atom and the electron pairs of the carbanion makes the (*E*) intermediate **4** kinetically un-

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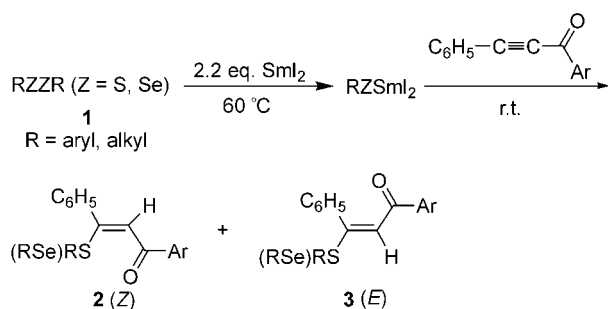
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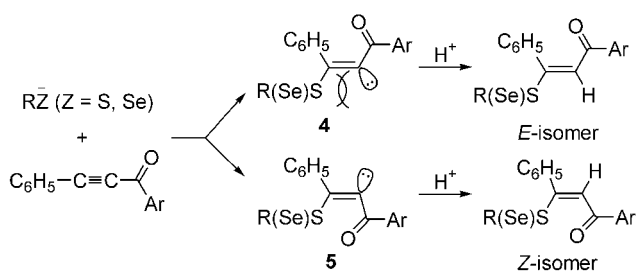
[†] Dedicated to Professor Chengye Yuan on the occasion of his 80th birthday.

stable, while in (*Z*) intermediate **5** the two relevant electron pairs are far away from each other¹² (Scheme 2). But the reaction has no obvious stereoselectivity at room temperature. We proposed that the *Z*-isomers should be formed initially during the reaction, and they isomerize to the thermally stable *E*-isomers in the presence of acid at room temperature.¹³ As a result the products are the mixture of *Z*-isomers and *E*-isomers.

Scheme 1



Scheme 2

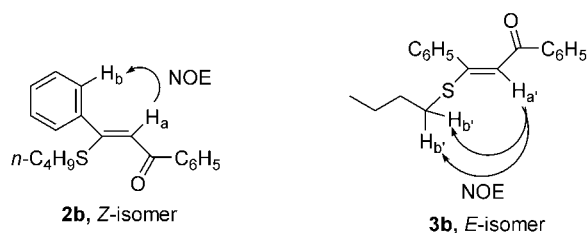


For differently substituted substrates the results are summarized in Table 1.

The configuration of *cis/trans* isomers (**2-Z** and **3-E**) could be confirmed by ¹H-¹H 2D NOESY spectrum. For example, the strong NOE correlation of the H_a-H_b in compound **2b** and the H_a-H_b' in compound **3b** was observed (Scheme 3).

To improve reaction stereoselectivity, the influence of solvent and temperature on the stereoselectivity was explored. It was found that change of solvents could not

Scheme 3



enhance the reaction stereoselectivity. But the stereoselectivity was influenced by reaction temperature remarkably. The experiment indicated that the stereoselectivity of Michael addition reaction was elevated at $-28\text{ }^\circ\text{C}$. Decreasing reaction temperature can help to increase reaction stereoselectivity.

In the course of our further experiment the three-component Michael-aldol tandem reactions of diorganyl diselenides or disulfides with α,β -conjugated alkyones mediated by samarium diiodide were studied.¹⁴ When alkyne and aldehyde or ketone were added to the solution of RZSmI₂ (Z=S, Se) in THF at room temperature based on Scheme 1 and stirred for 1 h, the adducts **4** and **5** were formed in 72%–92% total yields (Scheme 4). The results of Michael-aldol tandem reaction indicated that the reaction stereoselectivity was enhanced. The results of reaction were shown in Table 2.

The configuration of *cis/trans* isomers (**4** and **5**) could be confirmed by ¹H-¹H 2D NOESY spectrum. For example, the strong NOE correlation of the H_a-H_b in

Scheme 4

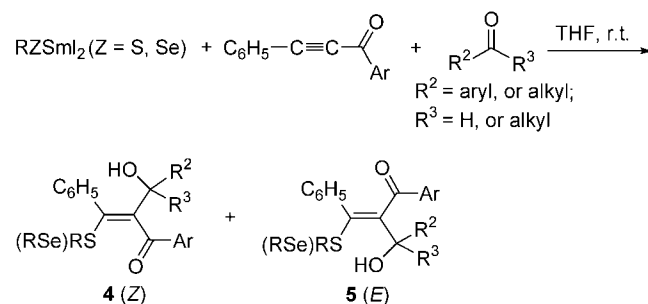


Table 1 The results of Michael addition promoted by samarium diiodide

Entry	(RZ) ₂ (Z=S, Se)	Ar	Reaction time/h (r.t.)	Reaction time/h ($-28\text{ }^\circ\text{C}$)	Product	Yield ^a /% (r.t.)	Yield ^a /% ($-28\text{ }^\circ\text{C}$)	2 : 3 (Z/E) ^b (r.t.)	2 : 3 (Z/E) ^b ($-28\text{ }^\circ\text{C}$)
1	(<i>n</i> -C ₄ H ₉ S) ₂	<i>p</i> -CH ₃ C ₆ H ₄	1	4	2a, 3a	88	89	54/46	82/18
2	(<i>n</i> -C ₄ H ₉ S) ₂	C ₆ H ₅	1	4	2b, 3b	90	93	52/48	85/15
3	(C ₆ H ₅ Se) ₂	<i>p</i> -CH ₃ OC ₆ H ₄	1.5	5	2c, 3c	85	82	58/42	77/23
4	(C ₆ H ₅ Se) ₂	2,6-Cl ₂ C ₆ H ₃	0.5	2	2d, 3d	95	95	61/39	92/8
5	(C ₆ H ₅ Se) ₂	<i>p</i> -CH ₃ C ₆ H ₄	1	4	2e, 3e	92	91	55/45	85/15
6	(<i>p</i> -ClC ₆ H ₄ S) ₂	C ₆ H ₅	1	4	2f, 3f	83	82	57/43	86/14
7	(<i>p</i> -ClC ₆ H ₄ S) ₂	<i>p</i> -ClC ₆ H ₄	1	4	2g, 3g	84	87	51/49	84/16
8	(C ₆ H ₅ S) ₂	2,6-Cl ₂ C ₆ H ₃	0.5	2	2h, 3h	88	90	55/45	90/10
9	(C ₆ H ₅ S) ₂	C ₆ H ₅	1	4	2i, 3i	86	88	51/49	75/25

^a Isolated total yield of product based on **1**. ^b Determined by isolated yield.

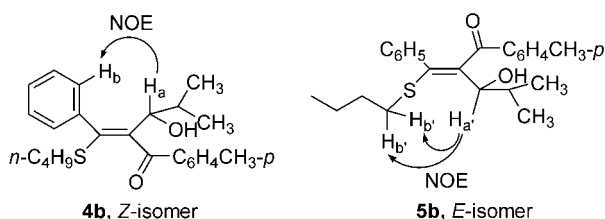
Table 2 The results of Michael-aldol tandem reaction

Entry	(RZ) ₂ (Z=S, Se)	Ar	R ² , R ³	Product	Yield ^a /% (r.t.)	Yield ^a /% (-28 °C)	4 : 5 (Z/E) ^b (r.t.)	4 : 5 (Z/E) ^b (-28 °C)
1	(<i>n</i> -C ₄ H ₉ S) ₂	<i>p</i> -CH ₃ C ₆ H ₄	<i>n</i> -Pr, H	4a , 5a	88	86	59/41	92/8
2	(<i>n</i> -C ₄ H ₉ S) ₂	<i>p</i> -CH ₃ C ₆ H ₄	<i>i</i> -Pr, H	4b , 5b	86	84	62/38	94/6
3	(<i>n</i> -C ₄ H ₉ S) ₂	Ph	<i>p</i> -NO ₂ C ₆ H ₄ , H	4c , 5c	92	91	100/0	100/0
4	(<i>n</i> -C ₄ H ₉ Se) ₂	Ph	<i>p</i> -NO ₂ C ₆ H ₄ , H	4d , 5d	96	95	100/0	100/0
5	(<i>p</i> -ClC ₆ H ₄ S) ₂	C ₆ H ₅	<i>n</i> -Pr, H	4e , 5e	83	80	55/45	88/12
6	(PhS) ₂	C ₆ H ₅	<i>i</i> -Pr, H	4f , 5f	85	82	61/39	95/5
7	(PhSe) ₂	<i>p</i> -CH ₃ C ₆ H ₄	<i>n</i> -Pr, H	4g , 5g	86	83	64/36	90/10
8	(PhSe) ₂	<i>p</i> -CH ₃ C ₆ H ₄	<i>i</i> -Pr, H	4h , 5h	87	84	63/37	95/5
9	(PhSe) ₂	2,6-Cl ₂ C ₆ H ₃	<i>n</i> -Pr, H	4i , 5i	72	72	62/38	96/4
10	(<i>n</i> -C ₄ H ₉ S) ₂	Ph	cyclopentanone	—	0	0	—	—
11	(<i>n</i> -C ₄ H ₉ S) ₂	Ph	acetone	—	0	0	—	—

^a Isolated total yield of product based on **1**. ^b Determined by isolated yield.

compound **4b** and the H_a-H_b' in compound **5b** was observed (Scheme 5).

Scheme 5



The stereoselectivity of Michael-aldol tandem reaction was remarkably influenced by reaction temperature. At -28 °C Michael-aldol tandem reaction showed high stereoselectivity.

In conclusion, Michael and Michael-aldol tandem reactions of diorganyl diselenides and disulfides with α,β -conjugated alkynones mediated by samarium diiodide have been studied. β -Organylselenoalkenones or β -organylthioalkenones and β -organylselenoallylic alcohols or β -organylthioallylic alcohols were conveniently prepared in good yield. The reaction stereoselectivity can be enhanced by decreasing reaction temperature. Further studies on the application of the reaction are now underway in our laboratory.

Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were determined on an X-4 micro melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AC-400 instrument as CDCl₃ solutions using TMS as internal standard. IR spectra were recorded using KBr disks with a Bruker Vector-22 infrared spectrometer. Elemental analyses were performed on an EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources,

without further purification before use.

General procedure for the Michael addition (**2a**, **3a**—**2i**, **3i**)

The reaction was carried out by adding diorganyl diselenides or disulfides to SmI₂ (1.1 mmol) in THF and the mixture was stirred continuously for 2 h at 60 °C. The alkynone was added and reacted at room temperature or -28 °C. Then 0.1 mol/L HCl was added. The reaction mixture was extracted with diethyl ether (3 × 20 mL), and the mixed organic layer was washed with saturated Na₂S₂O₃ solution (10 mL) and water (10 mL), and dried over anhydrous Na₂SO₄. After the solvent was removed by evaporation under reduced pressure, the crude product was purified by preparative TLC on silica gel (eluent: cyclohexane/ethyl acetate = 18 : 1). The 1,4-addition products **2** (Z) and **3** (E) were obtained in good yields.

(Z)-3-Butylthio-1-(4-methylphenyl)-3-phenylpropenone (2a): Yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ : 8.17 (d, *J*=8.2 Hz, 2H), 7.70 (d, *J*=8.2 Hz, 2H), 7.45—7.20 (m, 5H), 7.05 (s, 1H), 2.40 (s, 3H), 2.38 (t, *J*=6.4 Hz, 2H), 1.46 (t, *J*=7.2 Hz, 2H), 1.44—1.24 (m, 2H), 0.76 (t, *J*=3.6 Hz, 3H); IR (KBr) ν : 3057, 2959, 2929, 2872, 1636, 1605, 1533, 1488, 1248, 1178, 1031, 1013, 813, 760, 702 cm⁻¹; MS (70 eV) *m/z* (%): 312 (M⁺+2, 5.15), 311 (M⁺+1, 21.52), 310 (M⁺, 11.91), 293 (4.14), 277 (3.62), 255 (6.23), 254 (18.51), 253 (97.39), 221 (2.39), 219 (2.50), 210 (2.12), 178 (2.21), 134 (2.14), 121 (6.09), 120 (9.83), 119 (100.00), 91 (50.25), 77 (5.59), 65 (22.88). Anal. calcd for C₂₀H₂₂OS: C 77.37, H 7.14; found C 77.43, H 7.25.

(E)-3-Butylthio-1-(4-methylphenyl)-3-phenylpropenone (3a): Yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ : 7.91 (d, *J*=8.2 Hz, 2H), 7.52 (d, *J*=8.2 Hz, 2H), 7.43—7.18 (m, 5H), 6.74 (s, 1H), 2.76 (t, *J*=6.4 Hz, 2H), 2.47 (s, 3H), 1.54 (t, *J*=7.2 Hz, 2H), 1.52—1.33 (m, 2H), 0.96 (t, *J*=3.6 Hz, 3H); IR (KBr) ν : 3059, 2956, 2930, 2872, 1637, 1605, 1532, 1487, 1245, 1180, 1030, 1013, 795, 767, 699 cm⁻¹; MS (70

eV) m/z (%): 312 ($M^+ + 2$, 7.65), 311 ($M^+ + 1$, 18.22), 310 (M^+ , 13.45), 293 (4.77), 277 (4.12), 255 (6.88), 254 (14.55), 253 (88.97), 221 (1.48), 219 (2.57), 210 (3.66), 178 (2.27), 134 (3.21), 121 (6.88), 120 (7.24), 119 (100.00), 91 (52.25), 77 (6.67), 65 (24.76). Anal. calcd for $C_{20}H_{22}OS$: C 77.37, H 7.14; found C 77.51, H 7.01.

(Z)-3-Butylthio-1,3-diphenyl-propenone (2b): Yellow oil; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.80 (d, $J=8.1$ Hz, 2H), 7.51—7.32 (m, 8H), 7.07 (s, 1H), 2.43 (t, $J=6.6$ Hz, 2H), 1.25—1.27 (m, 2H), 1.43—1.45 (m, 2H), 0.77 (t, $J=3.8$ Hz, 3H); IR (KBr) ν : 3057, 2958, 2929, 2871, 1633, 1597, 1577, 1530, 1486, 1244, 1074, 1043, 955, 761, 700, 669 cm^{-1} ; MS (70 eV) m/z (%): 298 ($M^+ + 2$, 4.13), 297 ($M^+ + 1$, 18.96), 296 (13.93), 295 (4.90), 279 (4.80), 263 (4.08), 241 (7.56), 240 (19.96), 239 (100.00), 223 (2.62), 207 (2.31), 179 (2.26), 178 (4.14), 177 (3.12), 176 (2.11), 134 (2.29), 121 (5.97), 109 (2.35), 106 (7.42), 105 (91.66), 103 (3.84), 102 (5.30), 91 (5.60), 77 (54.23). Anal. calcd for $C_{19}H_{20}OS$: C 76.98, H 6.80; found C 77.06, H 6.69.

(E)-3-Butylthio-1,3-diphenyl-propenone (3b): Yellow oil; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.81 (d, $J=8.1$ Hz, 2H), 7.34—7.12 (m, 8H), 6.68 (s, 1H), 2.78 (t, $J=6.6$ Hz, 2H), 1.62—1.64 (m, 2H), 1.47—1.45 (m, 2H), 0.96 (t, $J=3.8$ Hz, 2H); IR (KBr) ν : 3057, 2958, 2930, 2872, 1635, 1597, 1574, 1533, 1487, 1244, 1075, 1042, 957, 763, 701, 669 cm^{-1} ; MS (70 eV) m/z (%): 298 ($M^+ + 2$, 4.89), 297 ($M^+ + 1$, 14.90), 296 (16.88), 295 (3.43), 279 (8.44), 263 (4.48), 241 (7.11), 240 (23.26), 239 (100.00), 223 (1.62), 207 (2.12), 179 (2.23), 178 (4.13), 177 (3.73), 176 (2.85), 134 (2.86), 121 (6.73), 109 (2.31), 106 (9.21), 105 (78.67), 103 (3.81), 102 (5.35), 91 (16.60), 77 (48.67). Anal. calcd for $C_{19}H_{20}OS$: C 76.98, H 6.80; found C 76.88, H 6.91.

(Z)-3-Phenyl-3-phenylseleno-1-(4-methoxyphenyl)-propenone (2c): Yellow solid; m.p. 114—116 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.96 (d, $J=8.4$ Hz, 2H), 7.53 (s, 1H), 7.33—7.25 (m, 3H), 7.11—7.09 (m, 6H), 7.07—7.00 (m, 3H), 3.84 (s, 3H); IR (KBr) ν : 3050, 1631, 1570, 1472, 1434, 1294, 1153, 1063, 1019, 995, 733, 686 cm^{-1} ; MS (70 eV) m/z (%): 393 (M^+ , 2.20), 316 (2.90), 313 (2.50), 312 (8.57), 311 (3.68), 310 (5.43), 239 (2.42), 237 (7.50), 235 (8.49), 234 (11.65), 233 (8.14), 232 (7.90), 157 (36.62), 155 (21.40), 154 (24.73), 153 (11.57), 149 (0.86), 117 (7.73), 105 (4.03), 139 (1.23), 91 (3.70), 77 (100.00), 51 (47.62). Anal. calcd for $C_{22}H_{18}O_2Se$: C 67.00, H 4.85; found C 67.13, H 4.82.

(E)-3-Phenyl-3-phenylseleno-1-(4-methoxyphenyl)-propenone (3c): Yellow solid; m.p. 118—120 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.75 (d, $J=8.4$ Hz, 2H), 6.91 (s, 1H), 7.23—7.21 (m, 3H), 7.10—7.08 (m, 6H), 7.00—6.92 (m, 3H), 3.83 (s, 3H); IR (KBr) ν : 3051, 1633, 1574, 1471, 1438, 1159, 1066, 1021, 998, 737, 690 cm^{-1} ; MS (70 eV) m/z (%): 393 (M^+ , 4.21), 316 (1.31), 313 (5.25), 312 (7.46), 311 (3.11), 310 (4.45), 239 (2.78), 237 (10.01), 235 (9.59), 234 (17.66), 233 (8.78), 232 (7.96), 157 (41.98), 155 (26.44), 154 (21.76), 153 (13.11), 149 (1.86), 117 (7.73), 105 (2.13), 139

(9.97), 91 (3.77), 77 (100.00), 51 (58.54). Anal. calcd for $C_{22}H_{18}O_2Se$: C 67.00, H 4.85; found C 67.09, H 4.72.

(Z)-3-Phenyl-3-phenylseleno-1-(2,6-dichlorophenyl)-propenone (2d): Yellow solid; m.p. 128—129 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.38—7.27 (m, 5H), 7.09—7.04 (m, 8H), 6.99 (s, 1H); IR (KBr) ν : 3442, 3044, 1628, 1586, 1559, 1531, 1512, 1480, 1429, 1315, 1230, 1110, 944, 790, 765, 738, 633 cm^{-1} ; MS (70 eV) m/z (%): 434 ($M^+ + 2$, 2.13), 433 ($M^+ + 1$, 1.01), 432 (M^+ , 3.21), 430 (1.46), 400 (2.54), 399 (10.09), 398 (6.06), 397 (24.77), 396 (4.73), 395 (12.06), 394 (4.81), 393 (4.23), 357 (2.37), 355 (3.73), 353 (1.97), 277 (1.10), 275 (1.62), 259 (1.13), 179 (1.89), 178 (4.45), 177 (11.93), 176 (8.04), 175 (62.86), 174 (10.62), 173 (100.00), 157 (8.42), 155 (4.27), 154 (2.15), 149 (2.93), 147 (16.01), 146 (2.66), 145 (24.88), 111 (5.55), 110 (3.22), 109 (14.77), 105 (14.44), 102 (10.78), 77 (31.64). Anal. calcd for $C_{21}H_{14}Cl_2OSe$: C 58.35, H 3.26; found C 58.24, H 3.41.

(E)-3-Phenyl-3-phenylseleno-1-(2,6-dichlorophenyl)-propenone (3d): Yellow solid; m.p. 128—129 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.27—7.15 (m, 5H), 6.97—6.92 (m, 8H), 6.65 (s, 1H); IR (KBr) ν : 3442, 3045, 1626, 1588, 1562, 1537, 1515, 1477, 1432, 1314, 1233, 1114, 940, 788, 765, 738, 632 cm^{-1} ; MS (70 eV) m/z (%): 434 ($M^+ + 2$, 3.01), 433 ($M^+ + 1$, 1.61), 432 (M^+ , 3.88), 430 (1.65), 400 (2.98), 399 (11.19), 398 (6.76), 397 (28.79), 396 (6.72), 395 (14.66), 394 (4.54), 393 (4.85), 357 (3.05), 355 (4.77), 353 (2.54), 277 (1.81), 275 (1.31), 259 (1.01), 179 (1.64), 178 (4.31), 177 (14.92), 176 (8.84), 175 (68.87), 174 (12.43), 173 (100.00), 157 (10.42), 155 (4.55), 154 (2.82), 149 (3.64), 147 (13.31), 146 (2.98), 145 (23.84), 111 (5.75), 110 (3.82), 109 (14.51), 105 (15.43), 102 (11.38), 77 (33.33). Anal. calcd for $C_{21}H_{14}Cl_2OSe$: C 58.35, H 3.26; found C 58.30, H 3.11.

(Z)-3-Phenyl-3-phenylseleno-1-(4-methylphenyl)-propenone (2e): Yellow solid; m.p. 108—110 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 8.01 (d, $J=8.3$ Hz, 2H), 7.57 (s, 1H), 7.31—7.27 (m, 4H), 7.12—7.10 (m, 6H), 7.09—7.00 (m, 2H), 2.44 (s, 3H); IR (KBr) ν : 3416, 3056, 1623, 1607, 1567, 1485, 1437, 1332, 1239, 1206, 1179, 944, 818, 767, 741, 698, 636 cm^{-1} ; MS (70 eV) m/z (%): 379 ($M^+ + 2$, 2.18), 378 ($M^+ + 1$, 7.08), 377 (M^+ , 1.84), 376 ($M^+ - 1$, 3.92), 375 (1.84), 374 (1.48), 301 (6.44), 259 (0.66), 221 (1.34), 178 (1.34), 157 (2.96), 119 (100.00), 105 (2.83), 91 (39.05), 77 (8.97), 65 (18.42). Anal. calcd for $C_{22}H_{18}OSe$: C 70.02, H 4.80; found C 69.96, H 4.97.

(E)-3-Phenyl-3-phenylseleno-1-(4-methylphenyl)-propenone (3e): Yellow solid; m.p. 114—116 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 8.21 (d, $J=8.3$ Hz, 2H), 7.77 (s, 1H), 7.521—7.49 (m, 4H), 7.22—7.19 (m, 6H), 7.12—7.03 (m, 2H), 2.43 (s, 3H); IR (KBr) ν : 3414, 3058, 1627, 1600, 1566, 1481, 1433, 1319, 1244, 1205, 1177, 938, 819, 769, 747, 696, 634 cm^{-1} ; MS (70 eV) m/z (%): 379 ($M^+ + 2$, 2.68), 378 ($M^+ + 1$, 7.78), 377 (M^+ , 2.55), 376 ($M^+ - 1$, 3.76), 375 (1.33), 374 (1.45),

301 (6.79), 259 (0.76), 221 (1.38), 178 (1.35), 157 (2.91), 119 (100.00), 105 (2.44), 91 (40.87), 77 (8.67), 65 (19.32). Anal. calcd for $C_{22}H_{18}OSe$: C 70.02, H 4.80; found C 70.21, H 4.75.

(Z)-1,3-Diphenyl-3-(4-chlorophenylthio)-propenone (2f): Yellow solid; m.p. 152—153 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 8.07—8.05 (m, 2H), 7.57—7.55 (m, 4H), 7.23—7.12 (m, 6H), 7.06—7.03 (m, 2H), 7.25 (s, 1H); IR (KBr) ν : 3424, 3060, 1632, 1595, 1575, 1524, 1474, 1442, 1241, 1095, 1041, 1014, 954, 822, 779, 766, 704, 666 cm^{-1} ; MS (70 eV) m/z (%): 353 (1.48), 352 ($M^+ + 2$, 4.31), 351 ($M^+ + 1$, 5.93), 350 (M^+ , 9.18), 349 (3.41), 273 (1.04), 247 (1.98), 246 (1.43), 245 (5.46), 244 (1.65), 239 (2.96), 210 (3.28), 178 (1.49), 165 (1.49), 143 (2.53), 121 (2.06), 108 (6.27), 106 (8.85), 105 (100.00), 77 (38.56). Anal. calcd for $C_{21}H_{15}ClOS$: C 71.88, H 4.30; found C 71.69, H 4.28.

(E)-1,3-Diphenyl-3-(4-chlorophenylthio)-propenone (3f): Yellow solid; m.p. 147—149 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.95—7.93 (m, 2H), 7.35—7.32 (m, 4H), 7.22—7.12 (m, 6H), 6.94—6.88 (m, 2H), 7.28 (s, 1H); IR (KBr) ν : 3426, 3058, 1633, 1595, 1576, 1522, 1473, 1441, 1244, 1099, 1042, 1012, 952, 820, 783, 755, 696, 668 cm^{-1} ; MS (70 eV) m/z (%): 353 (1.66), 352 ($M^+ + 2$, 4.88), 351 ($M^+ + 1$, 6.28), 350 (M^+ , 8.87), 349 (3.95), 273 (1.24), 247 (2.56), 246 (1.77), 245 (6.01), 244 (1.97), 239 (3.33), 210 (3.64), 178 (1.24), 165 (1.33), 143 (3.41), 121 (2.21), 108 (6.54), 106 (9.87), 105 (100.00), 77 (39.52). Anal. calcd for $C_{21}H_{15}ClOS$: C 71.88, H 4.30; found C 71.86, H 4.41.

(Z)-3-Phenyl-1-(4-chlorophenyl)-3-(4-chlorophenylthio)-propenone (2g): Yellow solid; m.p. 164—166 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 8.32 (d, $J=8.2$ Hz, 2H), 7.85 (d, $J=8.1$ Hz, 2H), 7.60—7.71 (m, 9H), 7.12 (s, 1H); IR (KBr) ν : 3406, 1645, 1587, 1487, 1474, 1400, 1283, 1091, 1027, 847, 754, 691 cm^{-1} ; MS (70 eV) m/z (%): 386 ($M^+ + 2$, 5.41), 385 ($M^+ + 1$, 4.44), 384 (M^+ , 7.45), 383 (3.87), 273 (3.30), 247 (5.06), 246 (3.08), 245 (14.34), 244 (3.22), 243 (5.68), 242 (8.70), 241 (16.99), 240 (18.01), 214 (11.95), 213 (6.49), 212 (34.25), 210 (7.35), 176 (12.03), 141 (34.78), 140 (9.13), 139 (100.00), 129 (54.13), 113 (15.15), 112 (5.55), 111 (43.87), 109 (6.33), 108 (14.34), 105 (6.23), 77 (9.11). Anal. calcd for $C_{21}H_{14}Cl_2OS$: C 65.46, H 3.66; found C 65.55, H 3.74.

(E)-3-Phenyl-1-(4-chlorophenyl)-3-(4-chlorophenylthio)-propenone (3g): Yellow solid; m.p. 173—175 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 8.14 (d, $J=8.2$ Hz, 2H), 7.73 (d, $J=8.1$ Hz, 2H), 7.47—7.60 (m, 9H), 7.01 (s, 1H); IR (KBr) ν : 3406, 1643, 1589, 1486, 1477, 1401, 1285, 1092, 1030, 849, 756, 693 cm^{-1} ; MS (70 eV) m/z (%): 386 ($M^+ + 2$, 3.23), 385 ($M^+ + 1$, 4.87), 384 (M^+ , 5.55), 383 (4.01), 273 (3.34), 247 (5.91), 246 (3.43), 245 (16.77), 244 (3.34), 243 (5.88), 242 (8.73), 241 (16.22), 240 (18.45), 214 (13.57), 213 (5.87), 212 (33.27), 210 (7.99), 176 (12.43), 141 (36.70), 140 (10.67), 139 (100.00), 129 (58.94), 113 (18.45), 112 (6.26), 111 (47.87), 109 (6.95), 108 (11.33), 105 (6.66), 77 (13.07). Anal. calcd for $C_{21}H_{14}Cl_2OS$: C 65.46, H

3.66; found C 65.41, H 3.63.

(Z)-3-Phenyl-1-(2,6-dichlorophenyl)-3-phenylthio-propenone (2h): Yellow solid; m.p. 109—110 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.63—6.87 (m, 13H), 6.67 (s, 1H); IR (KBr) ν : 3415, 3055, 1646, 1574, 1559, 1537, 1480, 1429, 1235, 1205, 1105, 1027, 952, 769, 750, 689 cm^{-1} ; MS (70 eV) m/z (%): 388 (3.92), 387 (8.80), 386 ($M^+ + 2$, 13.82), 385 ($M^+ + 1$, 17.57), 384 (M^+ , 17.96), 383 (9.25), 351 (8.62), 349 (21.11), 307 (6.69), 247 (3.00), 239 (8.09), 212 (13.44), 211 (68.18), 210 (17.95), 178 (10.36), 177 (13.53), 176 (10.60), 175 (63.45), 174 (11.65), 173 (100.00), 165 (5.65), 147 (18.19), 145 (27.95), 110 (10.03), 109 (47.27), 105 (5.49), 102 (13.21), 77 (24.43). Anal. calcd for $C_{21}H_{14}Cl_2OS$: C 65.46, H 3.66; found C 65.52, H 3.79.

(E)-3-Phenyl-1-(2,6-dichlorophenyl)-3-phenylthio-propenone (3h): Yellow solid; m.p. 116—118 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.59—6.82 (m, 13H), 6.68 (s, 1H) cm^{-1} ; IR (KBr) ν : 3414, 3056, 1645, 1575, 1561, 1536, 1481, 1427, 1232, 1200, 1109, 1030, 955, 769, 751, 688 cm^{-1} ; MS (70 eV) m/z (%): 388 (3.33), 387 (8.23), 386 ($M^+ + 2$, 14.01), 385 ($M^+ + 1$, 18.23), 384 (M^+ , 17.77), 383 (10.12), 351 (9.01), 349 (21.99), 307 (9.23), 247 (3.43), 239 (8.78), 212 (12.67), 211 (69.28), 210 (19.87), 178 (12.34), 177 (13.55), 176 (10.69), 175 (64.47), 174 (12.01), 173 (100.00), 165 (5.88), 147 (18.28), 145 (28.87), 110 (12.77), 109 (47.95), 105 (4.87), 102 (11.21), 77 (28.44). Anal. calcd for $C_{21}H_{14}Cl_2OS$: C 65.46, H 3.66; found C 65.56, H 3.70.

(Z)-1,3-Diphenyl-3-phenylthio-propenone (2i): Yellow solid; m.p. 100—102 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.62 (d, $J=8.0$ Hz, 2H), 7.28—7.05 (m, 10H), 6.82—6.40 (m, 3H), 6.38 (s, 1H); IR (KBr) ν : 3415, 3057, 1632, 1595, 1576, 1527, 1479, 1439, 1244, 1210, 1042, 1021, 953, 780, 764, 746, 706, 687 cm^{-1} ; MS (70 eV) m/z (%): 318 ($M^+ + 2$, 2.48), 317 ($M^+ + 1$, 9.45), 316 (M^+ , 12.61), 315 (6.03), 299 (1.67), 240 (1.41), 239 (7.64), 212 (5.42), 211 (31.44), 210 (8.13), 179 (1.23), 178 (4.32), 165 (1.67), 152 (1.11), 121 (2.22), 109 (8.22), 106 (8.35), 105 (100.00), 102 (3.55), 77 (61.64), 51 (23.51). Anal. calcd for $C_{21}H_{16}OS$: C 79.71, H 7.45; found C 79.69, H 7.58.

(E)-1,3-Diphenyl-3-phenylthio-propenone (3i): Yellow solid; m.p. 106—108 °C; 1H NMR ($CDCl_3$, 400 MHz) δ : 7.54 (d, $J=8.0$ Hz, 2H), 7.22—7.02 (m, 10H), 6.80—6.40 (m, 3H), 6.33 (s, 1H); IR (KBr) ν : 3415, 3055, 1633, 1596, 1577, 1526, 1477, 1440, 1245, 1212, 1043, 1024, 955, 781, 766, 747, 710, 688 cm^{-1} ; MS (70 eV) m/z (%): 318 ($M^+ + 2$, 2.44), 317 ($M^+ + 1$, 10.11), 316 (M^+ , 13.66), 315 (6.73), 299 (1.44), 240 (1.45), 239 (7.67), 212 (5.32), 211 (33.45), 210 (8.98), 179 (1.22), 178 (4.76), 165 (2.45), 152 (2.01), 121 (2.02), 109 (8.88), 106 (8.01), 105 (100.00), 102 (3.21), 77 (68.68), 51 (22.55). Anal. calcd for $C_{21}H_{16}OS$: C 79.71, H 7.45; found C 79.54, H 7.31.

General procedure for the Michael-aldol tandem reaction (4a, 5a—4i, 5i)

The reaction was carried out by adding diorganyl

diselenides or diorganyl disulfides to SmI_2 (1.1 mmol) in THF and the mixture was stirred continuously for 2 h at 60 °C. The alkyne and aldehyde were added and reacted at room temperature or -28 °C. After the reaction checked by TLC was completed, 0.1 mol/L HCl was added. The reaction mixture was extracted with diethyl ether (3×20 mL), and the mixed organic layer was washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL) and water (10 mL), and dried over anhydrous Na_2SO_4 . After the solvent was removed by evaporation under reduced pressure, the crude product was purified by preparative TLC on silica gel (eluent: cyclohexane/ethyl acetate = 8 : 1). The Michael-aldol tandem reaction products **4** (*Z*) and **5** (*E*) were obtained in good yields.

(Z)-3-Hydroxy-1-(4-methylphenyl)-2-(1-butylthio-1-phenylmethylene)hexan-1-one (4a): Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48 (d, $J=8.2$ Hz, 2H), 7.21 (d, $J=8.0$ Hz, 2H), 7.07–6.95 (m, 5H), 5.23 (s, 1H), 3.62 (s, 1H), 2.30 (t, $J=4.8$ Hz, 2H), 2.24 (s, 3H), 1.64–1.60 (m, 4H), 1.43–1.40 (m, 2H), 1.27–1.24 (m, 2H), 0.96 (t, $J=3.8$ Hz, 3H), 0.78 (t, $J=3.8$ Hz, 3H); IR (KBr) ν : 3416, 3057, 2958, 2929, 2871, 1655, 1604, 1572, 1488, 1443, 1383, 1271, 1178, 1028, 841, 787, 700, 592 cm^{-1} ; MS (70 eV) m/z (%): 381 (M^+-1 , 0.11), 367 (2.68), 366 (9.74), 365 (M^+-17 , 36.30), 339 (8.78), 325 (10.66), 293 (25.87), 247 (9.37), 221 (9.46), 201 (3.88), 181 (6.95), 131 (5.28), 129 (16.34), 121 (7.12), 120 (10.16), 119 (100.00), 105 (5.98), 91 (56.41), 77 (7.96), 71 (15.11), 65 (17.99), 57 (13.37), 55 (11.26). Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}$: C 75.35, H 7.90; found C 75.42, H 7.65.

(E)-3-Hydroxy-1-(4-methylphenyl)-2-(1-butylthio-1-phenylmethylene)hexan-1-one (5a): Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.80 (d, $J=8.2$ Hz, 2H), 7.50–7.28 (m, 7H), 5.24 (s, 1H), 3.64 (s, 1H), 2.45 (s, 3H), 2.11 (t, $J=4.8$ Hz, 2H), 1.63–1.01 (m, 4H), 1.05–0.97 (m, 4H), 0.77 (t, $J=4.4$ Hz, 3H), 0.66 (t, $J=4.4$ Hz, 3H); IR (KBr) ν : 3454, 3057, 2958, 2930, 2871, 1655, 1604, 1571, 1488, 1444, 1408, 1380, 1313, 1272, 1251, 1179, 1079, 1028, 841, 745, 700, 650, 602 cm^{-1} ; MS (70 eV) m/z (%): 381 (M^+-1 , 2.80), 367 (2.96), 366 (9.97), 365 (M^+-17 , 36.26), 339 (8.73), 325 (9.44), 293 (28.18), 247 (7.18), 221 (15.65), 201 (2.83), 181 (4.02), 131 (3.66), 129 (16.44), 121 (5.13), 120 (9.56), 119 (100.00), 105 (6.50), 91 (50.41), 77 (7.11), 71 (8.31), 65 (17.35), 57 (23.46), 55 (10.45). Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}$: C 75.35, H 7.90; found C 75.45, H 7.87.

(Z)-3-Hydroxy-4-methyl-1-(4-methylphenyl)-2-(1-butylthio-1-phenylmethylene)pentan-1-one (4b): Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.45 (d, $J=8.4$ Hz, 2H), 7.28–7.22 (m, 2H), 7.07–6.93 (m, 5H), 4.97 (s, 1H), 4.22 (s, 1H), 2.32 (s, 3H), 2.26 (t, $J=5.2$ Hz, 2H), 1.83–1.81 (m, 1H), 1.60–1.39 (m, 2H), 1.28–1.21 (m, 2H), 1.03 (d, $J=16.0$ Hz, 6H), 0.76 (t, $J=3.6$ Hz, 3H); IR (KBr) ν : 3450, 3057, 2958, 2929, 2871, 1655, 1604, 1569, 1487, 1465, 1444, 1408, 1380, 1312, 1261, 1251, 1179, 1079, 1030, 836, 746, 700, 648, 600 cm^{-1} ; MS (70 eV) m/z (%): 382 (M^+ , 0.70), 381

(M^+-1 , 2.22), 367 (8.44), 366 (26.86), 365 (M^+-17 , 100.00), 339 (20.65), 325 (1.68), 311 (5.45), 293 (4.55), 253 (9.74), 247 (15.08), 221 (4.67), 191 (2.59), 181 (1.44), 157 (2.89), 131 (4.08), 129 (12.58), 121 (5.40), 120 (8.16), 119 (86.85), 105 (3.54), 91 (48.55), 77 (5.78), 71 (2.61), 65 (16.05), 57 (9.67), 55 (5.65). Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}$: C 75.35, H 7.90; found C 75.43, H 7.79.

(E)-3-Hydroxy-4-methyl-1-(4-methylphenyl)-2-(1-butylthio-1-phenylmethylene)pentan-1-one (5b): Yellow oil; ^1H NMR (CDCl_3 , 400 MHz) δ : 8.05 (d, $J=8.4$ Hz, 2H), 7.50–7.28 (m, 7H), 4.96 (s, 1H), 3.98 (s, 1H), 2.45 (s, 3H), 2.10 (t, $J=5.2$ Hz, 2H), 1.64–1.55 (m, 1H), 1.44–1.28 (m, 2H), 1.19–1.17 (m, 2H), 0.92 (d, $J=16.0$ Hz, 6H), 0.66 (t, $J=3.6$ Hz, 3H) cm^{-1} ; IR (KBr) ν : 3416, 3056, 2957, 2926, 2870, 1658, 1604, 1572, 1487, 1465, 1443, 1408, 1382, 1312, 1294, 1263, 1178, 1074, 1030, 836, 746, 591 cm^{-1} ; MS (70 eV) m/z (%): 381 (M^+-1 , 1.66), 367 (0.95), 366 (2.31), 365 (M^+-17 , 8.53), 339 (11.49), 307 (2.19), 295 (2.92), 293 (2.24), 253 (7.23), 247 (5.96), 221 (4.25), 205 (16.32), 191 (2.87), 157 (1.05), 131 (2.29), 129 (10.02), 121 (6.73), 120 (9.81), 119 (100.00), 105 (7.79), 91 (51.66), 77 (9.35), 71 (5.89), 65 (20.15), 57 (20.70), 55 (14.61). Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}$: C 75.35, H 7.90; found C 75.21, H 7.95.

(Z)-3-Butylthio-2-[hydroxy(4-nitrophenylmethyl)]-1,3-diphenyl-2-propen-1-one (4c): White solid; m.p. 70–72 °C; ^1H NMR (CDCl_3 , 400 MHz) δ : 8.42 (d, $J=8.4$ Hz, 1H), 8.13–8.03 (m, 3H), 7.77 (d, $J=8.3$ Hz, 2H), 7.55–7.37 (m, 8H), 5.63 (s, 1H), 4.12 (s, 1H), 2.14 (t, $J=5.2$ Hz, 2H), 1.31–1.27 (m, 2H), 1.06–1.04 (m, 2H), 0.70 (t, $J=3.8$ Hz, 3H); IR (KBr) ν : 3422, 3060, 2957, 2928, 2870, 1653, 1597, 1520, 1447, 1346, 1316, 1265, 1050, 954, 813, 746, 700, 565 cm^{-1} ; MS (70 eV) m/z (%): 431 (4.21), 430 (M^+-17 , 13.89), 390 (4.39), 359 (5.07), 358 (20.64), 342 (1.29), 280 (2.69), 252 (1.21), 239 (2.31), 236 (2.56), 208 (1.45), 207 (6.71), 206 (1.60), 178 (4.17), 167 (15.78), 152 (2.17), 151 (3.48), 150 (7.92), 134 (1.45), 130 (1.58), 129 (14.30), 121 (6.66), 106 (9.78), 105 (100.00), 91 (1.48), 77 (55.13). Anal. calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4\text{S}$: C 69.77, H 5.63, N 3.12; found C 69.75, H 5.48, N 3.24.

(Z)-3-Butylseleno-2-[hydroxy(4-nitrophenylmethyl)]-1,3-diphenyl-2-propen-1-one (4d): Light yellow solid; m.p. 124–126 °C; ^1H NMR (CDCl_3 , 400 MHz) δ : 8.04 (d, $J=8.1$ Hz, 2H), 7.79 (d, $J=8.0$ Hz, 2H), 7.59–7.26 (m, 10H), 5.61 (s, 1H), 4.10 (s, 1H), 2.14 (t, $J=5.2$ Hz, 2H), 1.21–1.17 (m, 2H), 1.10–0.99 (m, 2H), 0.67 (t, $J=3.8$ Hz, 3H); IR (KBr) ν : 3451, 3060, 2955, 2927, 2868, 1649, 1596, 1511, 1449, 1345, 1235, 1047, 955, 812, 769, 701, 689, 570 cm^{-1} ; MS (70 eV) m/z (%): 478 (M^+-17 , 2.29), 476 (1.27), 440 (1.18), 439 (1.50), 438 (5.68), 436 (3.22), 359 (5.51), 358 (21.39), 340 (1.03), 280 (3.68), 236 (2.75), 207 (7.04), 206 (1.86), 189 (1.38), 179 (2.24), 178 (5.37), 167 (16.24), 152 (2.81), 151 (3.28), 150 (6.44), 134 (0.58), 130 (2.35), 129 (21.24), 106 (10.74), 105 (100.00), 91 (0.98), 77 (61.99). Anal. calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4\text{Se}$: C

63.15, H 5.09, N 2.83; found C 63.22, H 5.07, N 2.96.

(Z)-3-Hydroxy-1-phenyl-2-[phenyl(4-chlorophenylthiomethylene)]hexan-1-one (4e): Light yellow solid; m.p. 45—47 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 7.60 (d, *J*=8.1 Hz, 2H), 7.31—7.04 (m, 9H), 6.88—6.81 (m, 3H), 5.38 (s, 1H), 3.56 (s, 1H), 1.74—1.61 (m, 2H), 1.24—1.21 (m, 2H), 1.00 (t, *J*=3.8 Hz, 3H); IR (KBr) *v*: 3443, 3058, 2958, 2930, 2871, 1658, 1595, 1578, 1475, 1477, 1389, 1315, 1272, 1274, 1092, 1012, 817, 747, 730, 699, 689 cm⁻¹; MS (70 eV) *m/z* (%): 424 (0.18), 422 (M⁺, 0.42), 407 (2.86), 406 (2.29), 405 (M⁺—17, 7.61), 381 (2.70), 379 (7.01), 351 (2.74), 317 (2.68), 280 (5.37), 279 (24.81), 235 (6.87), 208 (2.49), 207 (9.15), 179 (1.06), 178 (2.06), 167 (8.95), 157 (2.04), 144 (3.00), 143 (2.85), 131 (4.00), 130 (2.19), 129 (15.90), 115 (4.84), 109 (2.95), 108 (5.52), 106 (8.60), 105 (100.00), 91 (2.99), 77 (66.45). Anal. calcd for C₂₅H₂₃ClO₂S: C 70.99, H 5.48; found C 71.12, H 5.35.

(E)-3-Hydroxy-1-phenyl-2-[phenyl(4-chlorophenylthiomethylene)]hexan-1-one (5e): Light yellow solid; m.p. 42—44 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 8.14 (d, *J*=8.1 Hz, 2H), 7.63—7.54 (m, 3H), 7.38—7.27 (m, 5H), 7.00 (d, *J*=8.1 Hz, 2H), 6.88 (d, *J*=8.1 Hz, 2H), 5.39 (s, 1H), 3.58 (s, 1H), 1.72—1.60 (m, 2H), 0.97—0.95 (m, 2H), 0.79 (t, *J*=3.8 Hz, 3H); IR (KBr) *v*: 3441, 3059, 2959, 2871, 1655, 1596, 1475, 1447, 1384, 1314, 1271, 1273, 1095, 1012, 950, 818, 779, 755, 699 cm⁻¹; MS (70 eV) *m/z* (%): 424 (0.17), 422 (M⁺, 0.37), 407 (3.72), 406 (2.96), 405 (M⁺—17, 9.48), 381 (2.77), 379 (6.65), 351 (2.48), 317 (2.57), 280 (5.30), 279 (24.40), 235 (7.06), 208 (2.31), 207 (9.18), 179 (0.98), 178 (2.65), 167 (8.53), 157 (2.08), 144 (2.91), 143 (2.55), 131 (3.84), 130 (2.21), 129 (17.82), 115 (4.33), 109 (2.39), 108 (5.40), 106 (8.77), 105 (100.00), 91 (2.87), 77 (60.85). Anal. calcd for C₂₅H₂₃ClO₂S: C 70.99, H 5.48; found C 70.97, H 5.24.

(Z)-3-Hydroxy-4-methyl-1-phenyl-2-(phenylphenylthiomethylene)pentan-1-one (4f): Light yellow solid; m.p. 45—46 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 8.04 (d, *J*=8.1 Hz, 2H), 7.57—7.48 (m, 3H), 7.24—7.05 (m, 10H), 5.10 (t, *J*=8.4 Hz, 1H), 4.12 (d, *J*=8.4 Hz, 1H), 1.098—1.91 (m, 1H), 1.10 (d, *J*=6.8 Hz, 6H); IR (KBr) *v*: 3415, 3058, 2958, 2868, 1637, 1617, 1468, 1446, 1257, 1024, 745, 689, 624 cm⁻¹; MS (70 eV) *m/z* (%): 387 (M⁺—1, 0.40), 372 (21.45), 371 (M⁺—17, 75.67), 345 (33.46), 267 (3.61), 235 (11.64), 105 (100.00), 77 (64.08). Anal. calcd for C₂₅H₂₄O₂S: C 77.28, H 6.22; found C 77.31, H 6.41.

(E)-3-Hydroxy-4-methyl-1-phenyl-2-(phenylphenylthiomethylene)pentan-1-one (5f): Light yellow solid; m.p. 41—43 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 8.26 (d, *J*=8.1 Hz, 2H), 7.55—7.47 (m, 3H), 7.23—7.04 (m, 10H), 5.18 (t, *J*=8.4 Hz, 1H), 4.11 (d, *J*=8.4 Hz, 1H), 1.10—1.90 (m, 1H), 1.11 (d, *J*=6.8 Hz, 6H); IR (KBr) *v*: 3455, 3060, 2959, 2867, 1640, 1611, 1466, 1449, 1255, 1028, 747, 688, 624 cm⁻¹; MS (70 eV) *m/z* (%): 387 (M⁺—1, 0.55), 372 (23.68), 371 (M⁺—17, 76.66), 345 (35.40), 267 (4.75), 235 (11.87), 105

(100.00), 77 (65.28). Anal. calcd for C₂₅H₂₄O₂S: C 77.28, H 6.22; found C 77.15, H 6.24.

(Z)-3-Hydroxy-1-(4-methylphenyl)-2-(phenylphenylselenomethylene)hexan-1-one (4g): Yellow solid; m.p. 62—64 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 7.56 (d, *J*=8.2 Hz, 2H), 7.28 (d, *J*=8.2 Hz, 2H), 7.08—6.77 (m, 10H), 4.90 (s, 1H), 3.99 (s, 1H), 2.24 (s, 3H), 1.66—1.62 (m, 2H), 1.13—1.06 (m, 2H), 0.85 (t, *J*=3.8 Hz, 3H); IR (KBr) *v*: 3422, 3055, 2957, 2868, 1654, 1631, 1603, 1576, 1475, 1439, 1384, 1310, 1259, 1178, 1151, 1021, 736, 690, 592 cm⁻¹; MS (70 eV) *m/z* (%): 449 (M⁺, 0.51), 432 (M⁺—17, 1.28), 433 (4.98), 431 (2.83), 408 (2.19), 407 (8.10), 405 (5.22), 404 (2.17), 403 (2.18), 293 (2.25), 291 (1.56), 275 (2.00), 250 (4.66), 249 (16.49), 222 (2.78), 221 (9.81), 191 (1.27), 189 (1.32), 157 (5.30), 129 (17.57), 120 (9.32), 119 (100.00), 115 (2.32), 105 (5.18), 91 (47.54), 77 (11.07). Anal. calcd for C₂₆H₂₆O₂Se: C 69.48, H 5.83; found C 69.59, H 5.72.

(E)-3-Hydroxy-1-(4-methylphenyl)-2-(phenylphenylselenomethylene)hexan-1-one (5g): Yellow solid; m.p. 73—75 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 7.85 (d, *J*=8.2 Hz, 2H), 7.48 (d, *J*=8.2 Hz, 2H), 7.27—6.95 (m, 10H), 4.92 (s, 1H), 4.01 (s, 1H), 2.26 (s, 3H), 1.65—1.63 (m, 2H), 1.11—1.07 (m, 2H), 0.90 (t, *J*=3.8 Hz, 3H); IR (KBr) *v*: 3423, 3055, 2958, 2867, 1654, 1632, 1603, 1577, 1474, 1440, 1385, 1312, 1260, 1179, 1150, 1022, 738, 690, 593 cm⁻¹; MS (70 eV) *m/z* (%): 449 (M⁺, 0.55), 432 (M⁺—17, 1.31), 433 (4.76), 431 (2.75), 408 (2.22), 407 (8.12), 405 (5.25), 404 (2.11), 403 (2.20), 293 (2.43), 291 (1.88), 275 (2.06), 250 (4.87), 249 (16.34), 222 (2.95), 221 (10.21), 191 (1.55), 189 (1.66), 157 (5.45), 129 (17.87), 120 (9.66), 119 (100.00), 115 (2.77), 105 (5.24), 91 (48.65), 77 (13.86). Anal. calcd for C₂₆H₂₆O₂Se: C 69.48, H 5.83; found C 69.46, H 5.93.

(Z)-3-Hydroxy-4-methyl-1-(4-methylphenyl)-2-(phenylphenylselenomethylene)pentan-1-one (4h): Yellow solid; m.p. 54—55 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 8.07 (d, *J*=8.0 Hz, 2H), 7.56 (d, *J*=8.0 Hz, 2H), 7.36—6.99 (m, 7H), 6.83—6.82 (m, 3H), 5.20 (s, 1H), 4.41 (s, 1H), 2.26 (s, 3H), 1.15—1.07 (m, 1H), 0.86 (d, *J*=7.4 Hz, 6H); IR (KBr) *v*: 3442, 3056, 2957, 2870, 1653, 1603, 1475, 1439, 1311, 1271, 1178, 1151, 1065, 957, 834, 737, 691 cm⁻¹; MS (70 eV) *m/z* (%): 449 (M⁺, 0.32), 448 (0.33), 435 (3.56), 434 (4.72), 433 (16.78), 432 (M⁺—17, 3.44), 431 (9.11), 430 (4.02), 408 (2.93), 407 (10.15), 405 (6.07), 404 (2.47), 403 (2.14), 293 (2.96), 275 (3.69), 250 (4.73), 249 (17.69), 222 (2.46), 221 (7.71), 191 (1.31), 189 (1.18), 157 (6.65), 129 (16.13), 120 (9.14), 119 (100.00), 115 (2.69), 105 (3.86), 91 (57.57), 77 (13.05). Anal. calcd for C₂₆H₂₆O₂Se: C 69.48, H 5.83; found C 69.33, H 5.95.

(E)-3-Hydroxy-4-methyl-1-(4-methylphenyl)-2-(phenylphenylselenomethylene)pentan-1-one (5h): Yellow solid; m.p. 46—48 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 8.12 (d, *J*=8.0 Hz, 2H), 7.61 (d, *J*=8.0 Hz, 2H), 7.41—7.03 (m, 7H), 6.88—6.87 (m, 3H), 5.21 (s, 1H), 4.42 (s, 1H), 2.47 (s, 3H), 1.13—1.07 (m, 1H),

0.88 (d, $J=7.4$ Hz, 6H); IR (KBr) ν : 3443, 3056, 2958, 2922, 2868, 1632, 1603, 1439, 1384, 1311, 1260, 1177, 1149, 1021, 738, 691 cm^{-1} ; MS (70 eV) m/z (%): 449 (M^+ , 0.33), 448 (0.64), 435 (0.91), 434 (1.24), 433 (4.29), 432 (M^+-17 , 1.03), 431 (2.25), 430 (1.20), 408 (0.41), 407 (1.61), 405 (0.94), 404 (0.44), 403 (0.39), 294 (3.37), 293 (15.21), 275 (5.32), 250 (1.51), 249 (5.07), 222 (3.32), 221 (15.51), 191 (1.28), 189 (1.09), 157 (9.02), 129 (19.75), 120 (9.35), 119 (100.00), 115 (5.91), 105 (3.80), 91 (51.07), 77 (10.74). Anal. calcd for $\text{C}_{26}\text{H}_{26}\text{O}_2\text{Se}$: C 69.48, H 5.83; found C 69.37, H 5.71.

(Z)-3-Hydroxy-1-(2,6-dichlorophenyl)-2-(phenylphenylselenomethylene)hexan-1-one (4i): Yellow solid; m.p. 48—50 °C; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.28—6.64 (m, 13H), 5.14 (s, 1H), 4.40 (s, 1H), 1.68—1.65 (m, 2H), 1.16—1.10 (m, 2H), 0.93 (t, $J=4.0$ Hz, 3H); IR (KBr) ν : 3424, 3057, 2957, 2929, 2870, 1623, 1559, 1475, 1429, 1475, 1429, 1273, 1252, 1194, 1157, 1114, 1091, 1070, 1022, 799, 779, 740, 720, 691 cm^{-1} ; MS (70 eV) m/z (%): 465 (2.14), 463 (6.82), 462 (2.96), 461 (M^+-43 , 11.03), 349 (9.54), 347 (15.59), 277 (15.09), 275 (21.60), 177 (12.97), 176 (10.65), 175 (63.82), 174 (12.19), 173 (100.00), 157 (13.55), 155 (7.68), 147 (15.37), 145 (23.57), 131 (9.07), 129 (21.81), 115 (11.31), 111 (8.00), 109 (12.68), 105 (18.01), 77 (47.38). Anal. calcd for $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{O}_2\text{Se}$: C 59.54, H 4.39; found C 59.66, H 4.37.

(E)-3-Hydroxy-1-(2,6-dichlorophenyl)-2-(phenylphenylselenomethylene)hexan-1-one (5i): Yellow solid; m.p. 61—63 °C; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.48—6.86 (m, 13H), 5.20 (s, 1H), 4.44 (s, 1H), 1.66—1.61 (m, 2H), 1.13—1.10 (m, 2H), 0.90 (t, $J=4.0$ Hz, 3H); IR (KBr) ν : 3423, 3058, 2957, 2929, 2871, 1622, 1560, 1474, 1430, 1475, 1427, 1274, 1255, 1193, 1156, 1114, 1091, 1071, 1022, 800, 779, 742, 721, 691 cm^{-1} ; MS (70 eV) m/z (%): 465 (2.33), 463 (6.55), 462 (2.78), 461 (M^+-43 , 11.25), 349 (9.55), 347 (15.54), 277 (15.11), 275 (21.66), 177 (12.86), 176 (10.64), 175 (63.45), 174 (12.97), 173 (100.00), 157 (13.20), 155 (7.41), 147 (15.25), 145 (23.22), 131 (9.37), 129 (21.53), 115 (11.33), 111 (8.26), 109 (12.71), 105 (18.86), 77 (48.37). Anal. calcd for $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{O}_2\text{Se}$: C 59.54, H 4.39; found C 59.61, H 4.21.

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