Scandium-Catalyzed Propargylation of 1,3-Diketones with Propargyl Alcohols Bearing Sulfur or Selenium Functional Groups: Useful Transformation to Furans and Pyrans

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Received April 20, 2010; accepted June 7, 2010; published online June 8, 2010

Propargylations of 1,3-diketones using 3-sulfanyl and 3-selanylpropargyl alcohols 1 in $MeNO_2$–H_2O gave alkynyl ketones 2a—m, 2o—v and 6,7-dihydro-5*H*-cyclohexa[*b*]pyran-5-ones 3k—n. With some bases, the useful propargylated 1,3-diketones underwent intramolecular cyclization to give 6,7-dihydro-5*H*-benzofuran-4-ones 4a—i or 4,5,6,7-tetrahydrobenzofurans 5p, 6p—v.

Key words C–C bond formation; 1,3-diketone; furan; cyclization

Alkynyl and allenyl ketones have been widely used to form substituted furans and pyrans by methods such as acid-mediated[1—11] and metal-catalyzed[12—20] cyclizations. Because of the wide utility of these furans and pyrans as building blocks for natural products and pharmaceuticals,[21,22] extending the list of ketones starting materials known to be suitable for their creation is important. Useful examples of the synthesis of propargylated ketones exist,[23—26] but it is questionable whether the ketones obtained are indeed practical for the synthesis of furans and pyrans.[27—29] Recently, we developed a method for highly regioselective C–C bond formation using propargyl alcohols with nucleophiles catalyzed by scandium triflate in $MeNO_2$.[30,31] This unique reaction is achieved *via* the two-phase condition, and is effectively stabilized by α-sulfanyl and α-selanyl functional groups. During our on going study of catalytic reactions, we investigated in the formation of C–C bonds in propargyl alcohols with 1,3-diketones and their base-promoted transformations to heterocycles. In this article, we describe the formation of propargylated 1,3-diketones by Lewis-acid catalytic reactions, which easily yield furans and benzofurans under basic conditions.

Results and Discussion

First, we prepared the propargylated 1,3-diketones *via* our original method that uses sulfur-substituted propargyl alcohol **1a** with 1,3-diphenylpropanedione under the optimized conditions of 5 mol% scandium triflate, 10 mol% Bu_4NHSO_4, $MeNO_2$–H_2O (10 : 1). The reaction was completed within 10 min and the product was obtained as 2-benzoyl-3-(*p*-methoxyphenyl)-1-phenyl-5-(phenylsulfanyl)pent-4-yn-1-one (**2a**) in 77% yield. The structure of **2a** was determined from its spectral features, which consist of the acetylenic infrared absorption at 2189 cm^{-1} and a pair of doublets at 5.16 and 5.86 (J=10 Hz) in the ^{1}H-NMR spectra, and a molecular ion peak at m/z 476 ($C_{31}H_{24}O_3S$) in the mass spectrum. This result indicates that 1,3-diketone was added to the propargyl cation, not the allenic cation. We next investigated reactions of propargyl alcohols with other 1,3-diketones and similar analogs, and the results are shown in Table 1. The reaction of **1a** with 2,4-pentanedione gave the product **2b** in 47% yield (entry 2); however, the reaction of **1a** with ethyl acetoacetate gave rise to a complex mixture (entry 3). We also explored the reactions of the propargyl alcohols bearing a variety of aromatic groups at the α-position of the hydroxyl group, as shown in entries 4 and 5. In addition, we found that the selenium-substituted propargyl alcohols **1e—j** also gave the adducts **2e—j** in high yields (entries 6—11 of Table 1). However, the reactions of both 1,3-cyclohexanedione and cyclopentanedione gave 6,7-dihydro-5*H*-cyclohexa[*b*]pyran-5-one **3k**, **l** and the cyclopentane derivative **3n**, respectively, not the propanediones (entries 12, 13, 15 of Table 1).[32,33] The reaction of 2-methyl-1,3-hexanedione gave propargylated 1,3-propanedione **2m** (entry 14). The modes of this cyclization are reported to be fruitful because of the cycloalkanediones consumed.[32] We also examined the reactions of the similar propargyl alcohols with 1,3-cyclohexanedione, and found that most of the products were bicyclic pyrans **3k**, **l** and **3n** except for the reaction of 2,4,6-trimethylphenyl propargyl alcohol **1o**. These results indicate that stereoelectronic effects are very important in determining whether the reaction would give the normal adducts or the 6,7-dihydro-5*H*-benzofuran-4-ones, which are obtained by further proceeding to the intramolecular cyclization. In addition, Cadierno *et al.* reported that the production of furans *versus* pyrans is due to the size of the cyclic 1,3-diketone.[32] We further examined the reactions with 2-acetylcyclohexanone and -cyclopentanone, and found that, as shown in entries 17—23 of Table 1, the products are not 6,7-dihydro-5*H*-cyclohexa[*b*]pyran-5-ones but the normal adducts **2p—v**.

Because sulfanyl and selanylalkynyl groups are known to be good nucleophiles and electrophiles,[34—45] we attempted to reactions of propargylated 1,3-diketones with some bases and found that they undergo intramolecular cyclization using sodium methoxide. The results are shown in Table 2. The typical example, *p*-methoxyphenyl 1,3-diphenylpropanedione **2a**, with sodium methoxide gave furan **4a** *via* an anionic 5-exo-mode cyclization (entry 1 of Table 2).[46—48] From an analysis of its spectral features, we estimate the structure of **4a** to be 3-benzoyl-2-phenyl-5-(phenylsulfanylmethyl)furan. 3,4-Dimethoxyphenyl and benzodioxol-5-yl **2b—c** gave **4b—c** in high yields (entries 2, 3), and treatment of 1-(*p*-

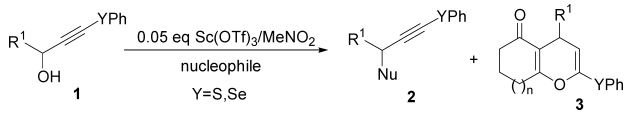

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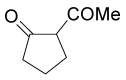
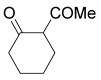
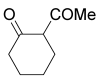
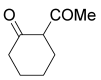
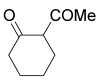
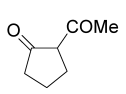
Table 1. Scandium-Catalyzed Propargylations of 1,3-Diketones

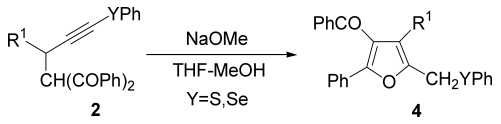
Run	Alcohol **1** R^1 (Y)	Nucleophile	Products (% yields)
1	*p*-$MeOC_6H_4$ (S)	$(PhCO)_2CH_2$	**2a** (77)
2		Ac_2CH_2	**2b** (47)
3		$AcCH_2CO_2Et$	—
4	Benzodioxol-5-yl (S)	$(PhCO)_2CH_2$	**2c** (quant.)
5	*p*-ClC_6H_4 (S)	$(PhCO)_2CH_2$	**2d** (71)
6	*p*-$MeOC_6H_4$ (Se)	$(PhCO)_2CH_2$	**2e** (71)
7	Benzodioxol-5-yl (Se)	$(PhCO)_2CH_2$	**2f** (80)
8	1-Naphthyl (Se)	$(PhCO)_2CH_2$	**2g** (82)
9	*p*-FC_6H_4 (Se)	$(PhCO)_2CH_2$	**2h** (83)
10	2-Thienyl (Se)	$(PhCO)_2CH_2$	**2i** (88)
11	2-Furyl (Se)	$(PhCO)_2CH_2$	**2j** (88)
12	*p*-$MeOC_6H_4$ (S)		**3k** (73)
13	1-Naphthyl (S)		**3l** (77)
14	*p*-$MeOC_6H_4$ (S)		**2m** (73)
15	*p*-$MeOC_6H_4$ (S)		**3n** (59)
16	2,4,6-$Me_3C_6H_2$ (S)		**2o** (99)
17	*p*-$MeOC_6H_4$ (S)		**2p** (95)[a]
18	*p*-$MeOC_6H_4$ (S)		**2q** (75)[b]
19	2-Thienyl (S)		**2r** (99)[c]
20	Benzodioxol-5-yl (S)		**2s** (75)[d]
21	Benzodioxol-5-yl (Se)		**2t** (72)
22	2-Thienyl (Se)		**2u** (64)
23	2-Thienyl (Se)		**2v** (70)

a—*d*) The diastereoisomer ratio is 46 : 54 (**2p**)/53 : 47 (**2q**)/57 : 43 (**2r**)/54 : 46 (**2s**)/55 : 45 (**2t**)/62 : 38 (**2u**)/54 : 46 (**2v**).

chlorophenyl)propargyl alcohols **2d** with sodium methoxide quantitatively transforms to the substituted furan **4d**. The reactions of the similar selenium-substituted alcohols **2e**—**i** also gave the phenylselanylmethylfurans **4e**—**i** (entries 5—9 of Table 2).

We further investigated the intramolecular cyclizations of the propargylated cycloalkanones **2** in some basic conditions

Table 2. Base-Promoted Cyclization of 1,3-Diketones to Furans



2 **4**

Run	Ketone **2** R^1 (Y)	Products (% yields)
1	*p*-$MeOC_6H_4$ (S)	**4a** (90)
2	3,4-$(MeO)_2C_6H_3$ (S)	**4b** (85)
3	3,4-$(OCH_2O)_2C_6H_3$ (S)	**4c** (93)
4	*p*-ClC_6H_4 (S)	**4d** (88)
5	*p*-$MeOC_6H_4$ (Se)	**4e** (93)
6	3,4-$(OCH_2O)_2C_6H_3$ (Se)	**4f** (80)
7	*p*-FC_6H_4 (Se)	**4g** (99)
8	2-Thienyl (Se)	**4h** (74)
9	2-Furyl (Se)	**4i** (quant.)

and the results are shown in Table 3. The acetyl cycloalkanones have two reactive sites in the molecules, one is the carbonyl of the acetyl group and the other is the carbonyl of cycloalkanone. The reaction of **2p** (Ar=*p*-$MeOC_6H_4$) using sodium methoxide in THF–MeOH gave the deacetylated product **5p** in 45% yield (entry 1 in Table 3). However, using other weak bases such as Bu_4NF, $CsCO_3$, K_2CO_3, and NaH provides 9-acetyl-3-(*p*-methoxyphenyl)-2-(phenyl-sulfanylmethyl)-4,5,6,7-tetrahydrobenzofuran (**6p**) in high yield, accompanied by furan **6p** (entries 2, 3). The reactions of the other acetyl cyclohexanones also provide the bicyclic compounds **6r**, **s** which easily converted to the corresponding 4,5,6,7-tetrahydrobenzofuran **7r** (Chart 1). Cyclopentanone derivatives **2q** and **2v** also provided the oxabicyclo-[3,3,0]octa-3,8-dienes in good yields. In summary, we have described a simple and convenient propargylation of 1,3-ketones from sulfur- and selenium-substituted propargyl alcohols with 1,3-diketones. The successive base-promoted intramolecular cyclization of the propargylated ketones gave a wide variety of furans and tetrahydrobenzofurans in high yields.

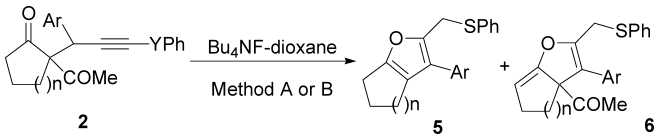
Experimental

Melting points were determined by a Yanagimoto micro-melting point apparatus and uncorrected. Elemental analyses were determined by using Micro Corder (MT-6) of J Science Lab. at the Life Science Research Center, Gifu University. ^{1}H- and ^{13}C-NMR spectra were determined on JEOL ECA-600 (600 MHz), ECA-500 (500 MHz) and ECA-400 (400 MHz) spectrometer. IR spectra were recorded with a JASCO FT-IR 460PLUS infrared spectrometer and are expressed in reciprocal centimeters. Electron ionization (EI) mass spectra (MS) were obtained using a JEOL MS-700 spectrometer with a direct-insertion probe at 70 eV. All high-resolution mass spectra were obtained using a JMSD300 JMA2000 on-line system.

Preparation of 1,3-Diphenyl-2-[1-(4-methoxyphenyl)-3-(phenylsulfanyl)prop-2-ynyl]propanedione (2a) To a solution of $MeNO_2$ (0.80 ml) and H_2O (0.08 ml) of 1-(*p*-methoxyphenyl)-3-(phenylsulfanyl)propargyl alcohol (**1a**) (50.0 mg, 0.18 mmol) was added 1,3-diphenylpropanedione (83 mg, 0.57 mmol), tetrabutylammonium hydrogensulfate (6.3 mg, 0.02 mmol), and scandium triflate (44 mg, 9.0 mmol). The reaction mixture was heated under reflux condition. The cooled mixture (50 ml) was poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1 : 5) to give 1,3-diphenyl-2-[1-(4-methoxyphenyl)-3-(phenylsulfanyl)prop-2-ynyl]propanedione (**2a**) (68 mg, 77%) as a yellow oil.

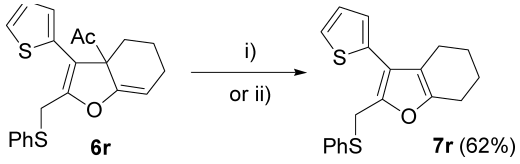
2a: IR (KBr, cm^{-1}) *v*: 1695, 1662, 1609, 1595, 1581, 1510, 1478, 1446, 1323, 1303, 1256, 1178, 1111, 1031, 985, 835, 764, 740, 687; ^{1}H-NMR

Table 3. Preparation of 4,5,6,7-Tetrahydrobenzofurans



Run	Ketones **1** Ar	Condition	Products **5** (% yield)	**6** (% yield)
1	*p*-MeOC$_6$H$_4$, *n*=2	NaOMe (5 eq), dioxane, reflux	**5p** (45)	
2		Bu$_4$NF (3 eq), DMF, reflux	**5p** (10)	**6p** (87)
3		DBU, dioxane, reflux		**6p** (71)
4	Benzodioxol-5-yl, *n*=2	DBU, dioxane, reflux		**6s** (quant.)
5	2-Thienyl, *n*=2	DBU, dioxane, reflux		**6r** (70)
6	*p*-MeOC$_6$H$_4$, *n*=1	DBU, dioxane, reflux		**6q** (76)
7	2-Thienyl, *n*=1	DBU, dioxane, reflux		**6v** (74)

Reagents: i) DBU/dioxane/reflux/10 min; ii) TsOH–H$_2$O/dioxane/reflux/10 min.



Reagents: i, DBU/dioxane/reflux/10 min, ii, TsOH-H$_2$O/dioxane/reflux/10 min

Chart 1. Conversion to Tetrahydrobenzofuran **7r**

(600 MHz, $CDCl_3$) δ: 3.69 (3H, s, OMe), 5.16 (1H, d, J=10 Hz, CH), 5.86 (1H, d, J=10 Hz, CH), 6.75 (2H, d, J=9 Hz, ArH), 7.09—7.13 (1H, m, ArH), 7.15 (5H, br s, ArH), 7.26—7.29 (2H, m, ArH), 7.37—7.44 (4H, m, ArH), 7.49—7.52 (1H, m, ArH), 7.73 (2H, d, J=9 Hz, ArH), 8.02 (2H, d, J=9 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.1 (d), 55.2 (q), 63.6 (d), 70.3 (s), 98.7 (s), 114.0 (d×2), 125.9 (d×2), 126.1 (d), 128.5 (d×2), 128.6 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×2), 129.5 (d×2), 130.2 (s), 132.7 (s), 133.7 (d), 136.3 (s), 136.6 (s), 158.9 (s), 192.7 (s), 193.1 (s); MS *m*/*z*: 476 (M^+), 371 (M^+-COPh). *Anal.* Calcd for $C_{31}H_{24}O_3S$: C, 77.16; H, 5.15. Found: C, 77.34; H, 5.19.

2-[1-(4-Methoxyphenyl)-3-(phenylsulfanyl)prop-2-ynyl]-2,4-pentanedione (**2b**): A yellow oil, IR (KBr, cm^{-1}) ν: 1732, 1702, 1609, 1583, 1511, 1478, 1442, 1357, 1304, 1178, 1152, 1033, 835, 741, 689; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.93 (3H, s, Me), 2.32 (3H, s, Me), 3.79 (3H, s, OMe), 4.20 (1H, d, J=11 Hz, CH), 4.64 (1H, d, J=11 Hz, CH), 6.86 (2H, d, J=8 Hz, ArH), 7.21 (2H, d, J=8 Hz, ArH), 7.26—7.36 (6H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 29.0 (q), 31.0 (q), 38.2 (d), 55.3 (q), 70.6 (s), 75.4 (d), 97.5 (s), 114.3 (d×2), 126.2 (d×2), 126.5 (d), 129.2 (d×2), 129.2 (d×2), 129.5 (s), 132.6 (s), 159.1 (s), 201.4 (s); MS *m*/*z*: 352 (M^+), 309 (M^+-COMe); high resolution mass Calcd for $C_{21}H_{20}O_3S$: 352.1128, Found *m*/*z* 352.1149.

1,3-Diphenyl-2-[1-(benzodioxol-5-yl)-3-(phenylsulfanyl)prop-2-ynyl]propanedione (**2c**): IR (KBr, cm^{-1}) ν: 3060, 2921, 1698, 1667, 1594, 1580, 1504, 1486, 1446, 1321, 1246, 1235, 1196, 1038, 932, 794, 741, 687; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.12 (1H, d, J=9 Hz, CH), 5.84 (2H, s, CH_2), 6.64 (1H, d, J=9 Hz, CH), 6.91 (1H, dd, J=9, 2 Hz, ArH), 6.99 (1H, d, J=2 Hz, ArH), 7.16—7.19 (5H, m, ArH), 7.24—7.32 (2H, m, ArH), 7.39—7.41 (2H, m, ArH), 7.43—7.46 (1H, m, ArH), 7.51—7.53 (1H, m, ArH), 7.76 (2H, dd, J=9, 1 Hz, ArH), 8.01 (2H, dd, J=8, 1 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.5 (d), 63.4 (d), 70.7 (s), 98.3 (s), 101.0 (t), 108.2 (d), 108.9 (d), 122.0 (d), 126.0 (d×2), 126.2 (d), 128.5 (d×2), 128.6 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×2), 131.9 (s), 132.6 (s), 133.5 (d), 133.6 (d), 136.3 (s), 136.5 (s), 146.9 (s), 147.7 (s), 192.5 (s), 193.0 (s); MS *m*/*z*: 490 (M^+), 385 (M^+-COPh), 381 (M^+-SPh). *Anal.* Calcd for $C_{31}H_{22}O_4S$: C, 75.96; H, 4.52. Found: C, 75.84; H, 4.59.

1,3-Diphenyl-2-[1-(4-chlorophenyl)-3-(phenylsulfanyl)prop-2-ynyl]propanedione (**2d**): mp 90—92 °C, IR (KBr, cm^{-1}) ν: 3061, 2361, 1695, 1667, 1595, 1580, 1541, 1489, 1447, 1407, 1321, 1267, 1198, 1179, 1091, 1016, 989, 835, 809, 762, 739, 710, 686; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.18 (1H, d, J=10 Hz, CH), 5.84 (1H, d, J=10 Hz, CH), 7.12—7.24 (6H, m, ArH), 7.29—7.31 (2H, m, ArH), 7.40—7.43 (5H, m, ArH), 7.44—7.47 (1H, m, ArH), 7.52—7.55 (1H, m, ArH), 7.74 (2H, d, J=8 Hz, ArH), 8.02 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.2 (d), 63.2 (d), 71.2 (s), 97.7 (s), 126.1 (d×2), 126.3 (d), 128.5 (d×2), 128.7 (d×2), 128.8 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×2), 129.9 (d×2), 132.4 (s), 133.4 (s), 133.7 (d), 133.7 (d), 136.1 (s), 136.4 (s), 136.9 (s), 192.3 (s), 192.8 (s); MS *m*/*z*: 480 (M^+), 375 (M^+-COPh), 371 (M^+-SPh). *Anal.* Calcd for $C_{30}H_{21}O_2ClS$: C, 74.91; H, 4.40. Found: C, 75.16; H, 4.61.

1,3-Diphenyl-2-[4-(methoxyphenyl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2e**): mp 92—94 °C, IR (KBr, cm^{-1}) ν: 3903, 3854, 3735, 3648, 3566, 2925, 2361, 1698, 1671, 1577, 1558, 1541, 1509, 1475, 1456, 1361, 1254, 1176, 1033, 835, 764, 738, 688; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.70 (3H, s, Me), 5.15 (1H, d, J=10 Hz, CH), 5.84 (1H, d, J=10 Hz, CH), 6.75 (2H, d, J=7 Hz, ArH), 7.14—7.15 (3H, m, ArH), 7.25—7.30 (4H, m, ArH), 7.37—7.44 (5H, m, ArH), 7.51—7.53 (1H, m, ArH), 7.73 (2H, d, J=8 Hz, ArH), 8.01 (2H, d, J=7 Hz ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.3 (d), 55.2 (q), 63.6 (d), 63.7 (s), 103.5 (s), 114.0 (d×2), 126.7 (d), 128.5 (d×2), 128.6 (d×2), 128.7 (s), 128.8 (d×4), 129.0 (d×2), 129.3 (d×2), 129.6 (d×2), 130.4 (s), 133.4 (d), 133.5 (d), 136.4 (s), 136.7 (s), 158.9 (s), 192.7 (s), 193.1 (s); MS *m*/*z*: 524 (M^+), 419 (M^+-COPh). High-resolution mass Calcd for $C_{31}H_{24}O_3Se$: 524.0890, Found *m*/*z*: 536.0870.

1,3-Diphenyl-2-[1-(benzodioxol-5-yl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2f**): IR (KBr, cm^{-1}) ν: 3058, 2891, 1697, 1666, 1595, 1578, 1503, 1485, 1446, 1321, 1246, 1234, 1196, 1181, 1102, 1038, 999, 933, 809, 794, 761, 736, 687, 633; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.12 (1H, dd, J=3, 9 Hz, CH), 5.85 (2H, d, J=9 Hz, CH_2), 6.63 (1H, d, J=8 Hz, CH), 6.91 (1H, d, J=8 Hz, ArH), 6.99 (1H, s, ArH), 7.13—7.14 (3H, m, ArH), 7.24—7.30 (5H, m, ArH), 7.38—7.44 (3H, m, ArH), 7.50—7.52 (1H, m, ArH), 7.76 (2H, d, J=8 Hz, ArH), 8.01 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.7 (d), 63.4 (d), 63.9 (s), 101.0 (t), 103.1 (s), 108.2 (d), 108.8 (d), 122.0 (d), 126.7 (d), 128.5 (d×2), 128.6 (d×2), 128.7 (d×3), 128.9 (d×2), 129.2 (d×2), 132.0 (s), 133.4 (d), 133.5 (d), 136.3 (s), 136.6 (s), 146.8 (s), 147.6 (s), 171.0 (s), 192.5 (s), 193.0 (s); MS *m*/*z*: 538 (M^+), 433 (M^+-COPh), 381 (M^+-SePh). High-resolution mass Calcd for $C_{31}H_{22}O_4Se$: 538.0683, Found *m*/*z*: 538.0642.

1,3-Diphenyl-2-[1-(1-naphthyl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2g**): A yellow oil, IR (KBr, cm^{-1}) ν: 3057, 2924, 1696, 1666, 1595, 1578, 1511, 1477, 1447, 1391, 1320, 1274, 1274, 1180, 1071, 999, 779, 734, 686; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.89 (1H, d, J=9 Hz, CHCOPh), 6.23 (1H, d, J=9 Hz, CH), 7.11—7.15 (5H, m, ArH), 7.16—7.29 (4H, m, ArH), 7.32—7.35 (1H, m, ArH), 7.37—7.40 (2H, m, ArH), 7.45—7.48 (1H, m, ArH), 7.51—7.53 (1H, m, ArH), 7.55—7.58 (1H, m, ArH), 7.60 (2H, d, J=8 Hz, ArH), 7.64 (1H, d, J=8 Hz, ArH), 7.77 (1H, d, J=8 Hz, ArH), 7.97 (2H, d, J=8 Hz, ArH), 8.45 (1H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 36.8 (d), 61.3 (d), 64.4 (s), 103.1 (s), 123.7 (d), 125.1 (d), 125.7 (d), 126.4 (d), 126.6 (d), 126.8 (d), 128.2 (d×2), 128.3 (d×2), 128.4 (d×2), 128.6 (d), 128.7 (d×3), 128.9 (d×2), 128.9 (d×2), 129.2 (d×2), 130.7 (s), 133.2 (s), 133.5 (s), 134.0 (s), 136.0 (s), 136.7 (s), 192.8 (s), 193.5 (s); MS *m*/*z*: 544 (M^+), 387 (M^+-SePh). *Anal.* Calcd for $C_{34}H_{24}O_2Se$: C, 75.13; H, 4.45. Found: C, 74.86; H, 4.49.

1,3-Diphenyl-2-[1-(4-fluorofhenyl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2h**): mp 85 °C, IR (KBr, cm^{-1}) ν: 3060, 2362, 1697,

1666, 1595, 1578, 1508, 1477, 1197, 1179, 1159, 1099, 1067, 1021, 985, 838, 763, 736, 687; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.18 (1H, d, J=10 Hz, CH), 5.84 (1H, dd, J=10, 5 Hz, CH), 6.88—6.91 (2H, m, ArH), 7.13—7.16 (3H, m, ArH), 7.24—7.30 (4H, m, ArH), 7.39—7.45 (5H, m, ArH), 7.51—7.54 (1H, m, ArH), 7.72 (2H, d, J=1 Hz, ArH), 8.01 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 39.3 (d), 63.4 (d), 64.3 (s), 102.9 (s), 115.4 (d), 115.5 (d), 126.8 (d), 128.5 (d×2), 128.7 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×2), 129.3 (d×2), 130.2 (d), 130.3 (d), 133.6 (d×2), 134.2 (s), 136.2 (s), 136.6 (s), 162.0 (d, J=248 Hz), 192.5 (s), 192.9 (s); MS m/z: 512 (M^+), 407 (M^+-COPh), 355 (M^+-SePh). *Anal.* Calcd for $C_{30}H_{21}O_2FSe$: C, 70.45; H, 4.14. Found: C, 70.66; H, 4.32.

1,3-Diphenyl-2-[1-(2-thienyl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2i**): A yellow oil, IR (KBr, cm^{-1}) ν: 3060, 2359, 1697, 1668, 1595, 1577, 1476, 1447, 1321, 1261, 1181, 1020, 983, 762, 735, 687; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.54 (1H, d, J=10 Hz, CH), 5.90 (1H, dd, J=1, 9 Hz, CH), 6.79 (1H, t, J=4 Hz, ArH), 6.99 (1H, d, J=3 Hz, ArH), 7.10 (1H, d, J=5 Hz, ArH), 7.16 (3H, m, ArH), 7.27—7.33 (3H, m, ArH), 7.37—7.40 (3H, m, ArH), 7.44—7.47 (1H, m, ArH), 7.50—7.53 (1H, m, ArH), 7.80 (2H, d, J=5 Hz, ArH), 8.00 (2H, dd, J=7, 1 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 35.2 (d), 63.6 (d), 64.6 (s), 102.1 (s), 124.9 (d), 126.7 (d), 126.9 (d), 128.3 (s), 128.5 (d×2), 128.7 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×4), 129.3 (d×2), 133.6 (d), 136.2 (s), 136.5 (s), 141.3 (s), 192.4 (s), 192.5 (s); MS m/z: 339 (M^+-SePh). *Anal.* Calcd for $C_{28}H_{20}O_2SSe$: C, 67.20; H, 4.23. Found: C, 67.13; H, 4.22.

1,3-Diphenyl-2-[1-(2-furyl)-3-(phenylselanyl)prop-2-ynyl]propanedione (**2j**): IR (KBr, cm^{-1}) ν: 3059, 2923, 2361, 1698, 1670, 1595, 1578, 1502, 1477, 1447, 1322, 1261, 1196, 1180, 1147, 1067, 1011, 918, 885, 789, 763, 736, 687; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.31 (1H, d, J=10 Hz, CH), 6.04 (1H, d, J=10 Hz, CH), 6.17 (1H, dd, J=1, 3 Hz, ArH), 6.22 (1H, d, J=3 Hz, ArH), 7.16—7.17 (5H, m, ArH), 7.18—7.29 (1H, m, ArH), 7.29—7.30 (1H, m, ArH), 7.35—7.37 (2H, m, ArH), 7.38—7.40 (2H, m, ArH), 7.48—7.53 (1H, m, ArH), 7.85 (2H, d, J=7 Hz, ArH), 7.98 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 33.8 (d), 59.9 (d), 63.9 (s), 100.1 (s), 108.2 (d), 110.6 (d), 126.8 (d), 128.5 (s), 128.6 (d×2), 128.7 (d×2), 128.8 (d×2), 128.9 (d×2), 129.0 (d×2), 129.3 (d×2), 133.5 (d), 133.6 (d), 135.9 (s), 136.4 (s), 142.1 (d), 150.1 (s), 192.4 (s), 192.6 (s); MS m/z: 407 (M^+-Ph), 479 (M^+-COPh). *Anal.* Calcd for $C_{28}H_{20}O_3Se$: C, 69.57; H, 4.17. Found: C, 66.15; H, 4.19.

2-[1-(4-Methoxyphenyl)-3-(phenylsulfanyl)prop-2-yn-1-yl]-1,3-cyclohexanedione (**3k**): mp 162 °C, IR (KBr, cm^{-1}) ν: 3059, 2996, 295, 2834, 1657, 1615, 1582, 1509, 1478, 1459, 1440, 1375, 1329, 1301, 1253, 1181, 1126, 1070, 1040, 999, 970, 916, 883, 863, 830, 744, 690, 629, 610; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.88—2.07 (2H, m, CH_2), 2.28—2.53 (4H, m, CH_2), 3.77 (3H, s, OMe), 4.41 (1H, d, J=5 Hz, CH), 5.72 (1H, d, J=5 Hz, CH), 6.81—6.84 (2H, m, ArH), 7.18—7.20 (2H, m, ArH), 7.24—7.25 (1H, m, ArH), 7.27—7.33 (2H, m, ArH), 7.39 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 20.6 (t), 27.4 (t), 35.9 (d), 37.0 (t), 55.2 (q), 113.6 (s), 113.9 (d×2), 116.9 (d), 127.3 (d), 129.0 (d×2), 129.1 (d×2), 129.6 (d×2), 132.8 (s), 136.5 (s), 142.3 (s), 158.4 (s), 166.8 (s), 197.2 (s); MS m/z: 364 (M^+), 257 ($M^+-C_6H_4Me$). *Anal.* Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.72; H, 5.58.

2-[1-(1-Naphthyl)-3-(phenylsulfanyl)prop-2-yn-1-yl]-1,3-cyclohexanedione (**3l**): IR (KBr, cm^{-1}) ν: 3057, 2925, 1658, 1616, 1582, 1509, 1479, 1439, 1382, 1333, 1273, 1243, 1188, 1167, 1130, 1070, 1043, 1024, 970, 917, 888, 852, 798, 778, 742, 689, 657, 630; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 2.03—2.06 (2H, m, CH_2), 2.31—2.41 (2H, m, CH_2), 2.48—2.53 (1H, m, CH_2), 2.59—2.64 (1H, m, CH_2), 5.29 (1H, d, J=4 Hz, CH), 5.90 (1H, d, J=4 Hz, CH), 7.21—7.34 (6H, m, ArH), 7.39—7.42 (1H, m, ArH), 7.46—7.49 (1H, m, ArH), 7.54—7.56 (1H, m, ArH), 7.71 (1H, d, J=8 Hz, ArH), 7.85 (1H, d, J=8 Hz, ArH), 8.29 (1H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 20.4 (t), 27.5 (t), 32.3 (d), 36.9 (t), 112.7 (s), 117.1 (d), 123.0 (d), 125.2 (d), 125.6 (d×2), 126.3 (d), 127.1 (d), 127.4 (d), 128.8 (d), 129.1 (d×2), 129.2 (d×2), 130.6 (s), 132.9 (s), 133.9 (s), 140.2 (s), 141.9 (s), 168.0 (s), 196.9 (s); MS m/z: 384 (M^+). *Anal.* Calcd for $C_{25}H_{20}O_2S$: C, 78.11; H, 5.24. Found: C, 78.06; H, 5.24.

2-[1-(4-Methoxyphenyl)-3-(phenylsulfanyl)prop-2-yn-1-yl]-2-methyl-1,3-cyclohexanedione (**2m**): A yellow oil, IR (KBr, cm^{-1}) ν: 2925, 1697, 1609, 1541, 1509, 1457, 1304, 1252, 1178, 1026, 837, 742, 690; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.32 (3H, s, Me), 1.48—1.76 (3H, m, CH_2), 2.41—2.62 (3H, m, CH_2), 3.78 (3H, s, Me), 4.50 (1H, s, CH), 6.80—6.82 (2H, d, J=9 Hz, ArH), 7.15 (2H, d, J=9 Hz, ArH), 7.20—7.25 (1H, m, ArH), 7.33—7.35 (2H, m, ArH), 7.46—7.48 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 16.8 (t), 19.6 (d), 39.3 (t), 39.5 (t), 45.0 (d), 55.2 (q), 67.9 (s), 71.3 (s), 96.8 (s), 113.7 (d×2), 126.3 (d×2), 126.4 (d), 128.2 (s), 129.2 (d×2), 130.3 (d×2), 133.0 (s), 159.2 (s), 208.9 (s), 209.3 (s); MS m/z: 378 (M^+), 269 (M^+-SPh). *Anal.* Calcd for $C_{23}H_{22}O_3S$: C, 72.41; H, 6.61. Found: C, 71.96; H, 6.55.

2-[1-(4-Methoxyphenyl)-3-(phenylsulfanyl)prop-2-yn-1-yl]-1,3-cyclopentanedione (**3n**): mp 149 °C, IR (KBr, cm^{-1}) ν: 3058, 2928, 2835, 2357, 1703, 1664, 1610, 1583, 1509, 1479, 1462, 1440, 1377, 1328, 1302, 1251, 1176, 1121, 1082, 1033, 997, 878, 862, 829, 743, 690, 613; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 2.35—2.44 (2H, m, CH_2), 2.55—2.66 (2H, m, CH_2), 3.77 (3H, s, OMe), 4.35 (1H, d, J=4 Hz, CH), 5.69 (1H, d, J=4 Hz, CH), 6.85 (2H, d, J=9 Hz, ArH), 7.17 (2H, d, J=9 Hz, ArH), 7.25—7.27 (1H, m, ArH), 7.28—7.35 (2H, m, ArH), 7.41—7.43 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 25.3 (t), 33.4 (t), 36.1 (d), 55.2 (q), 114.0 (d×2), 116.1 (d), 116.8 (s), 127.5 (d), 1289.0 (d×2), 129.2 (d×2), 129.7 (d×2), 132.3 (s), 134.4 (s), 144.4 (s), 158.6 (s), 178.8 (s), 202.5 (s); MS m/z: 350 (M^+), 241 (M^+-SPh). High-resolution mass Calcd for $C_{21}H_{18}O_3S$: 350.0977, Found m/z 350.0982.

2-[1-(2,4,6-Trimethylphenyl)-3-(phenylsulfanyl)prop-2-yn-1-yl]-1,3-cyclohexanedione (**2o**): IR (KBr, cm^{-1}) ν: 2950, 2923, 2357, 1726, 1662, 1636, 1583, 1479, 1455, 1439, 1384, 1219, 1199, 1177, 1156, 1137, 1116, 1085, 1053, 1024, 991, 907, 879, 852, 818, 741, 690, 621, 560; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 2.08 (3H, s, Me), 2.09—2.15 (2H, m, CH_2), 2.22 (3H, s, Me), 2.32—2.35 (2H, m, CH_2), 2.50 (3H, s, Me), 2.63—2.68 (2H, m, CH_2), 5.24 (1H, d, J=3 Hz, CH), 5.41 (1H, d, J=2 Hz, CH), 6.76 (1H, s, ArH), 6.86 (1H, s, ArH), 7.13—7.16 (1H, s, ArH), 7.23 (4H, d, J=4 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 19.1 (q), 20.8 (d), 21.4 (q×2), 21.6 (t), 23.3 (t), 36.9 (t), 44.0 (d), 95.1 (d), 126.2 (d), 128.3 (d×2), 128.9 (d×2), 129.2 (d), 130.9 (d), 132.2 (s), 135.9 (s), 136.5 (s), 136.6 (s), 137.1 (s), 159.9 (s), 173.3 (s), 193.3 (s); MS m/z: 376 (M^+), 267 (M^+-SPh). *Anal.* Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42. Found: C, 76.37; H, 6.56.

2-Acetyl-2-[1-(*p*-methoxyphenyl)-3-(phenylsulfanyl)-2-propyn-1-yl]cyclohexanone (**2p**): Yellow powders, mp 120—124 °C, IR (KBr, cm^{-1}) ν: 3224, 2939, 1720, 1699, 1551, 1478, 1441, 1254, 1178, 1033, 836, 741, 689; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.52—1.62 (2H, m, CH_2), 1.93 (3H, s, COMe), 1.94—1.98 (4H, m, CH_2), 2.13—2.18 (2H, m, CH_2), 2.52—2.57 (2H, m, CH_2), 3.77 (3H, s, OMe), 4.92 (1H, s, CH), 6.81 (2H, d, J=8 Hz, ArH), 7.18—7.26 (1H, m, ArH), 7.30—7.33 (2H, m, ArH), 7.38 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.4 (t), 25.9 (t), 27.3 (q), 29.9 (t), 42.0 (t), 42.5 (t), 55.2 (q), 697.0 (s), 72.0 (s), 98.5 (s), 113.3 (d×2), 126.0 (d×2), 126.2 (d), 127.6 (s), 129.1 (d×2), 130.1 (d×2), 133.3 (s), 159.2 (s), 204.4 (s), 206.8 (s); MS m/z: 392 (M^+), 349 (M^+-COMe). *Anal.* Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.44; H, 6.23.

Yellow powders, mp 87—91 °C, IR (KBr, cm^{-1}) ν: 2947, 1698, 1608, 1582, 1510, 1441, 1305, 1255, 1178, 1125, 1033, 836, 741, 539; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.34—1.47 (2H, m, CH_2), 1.67—1.85 (2H, m, CH_2), 2.04—2.14 (2H, m, CH), 2.24 (3H, s, COMe), 2.41—2.43 (1H, m, CH), 2.47—2.50 (1H, m, CH), 3.79 (3H, s, OMe), 5.14 (1H, s, CH), 6.82 (2H, d, J=8 Hz, ArH), 7.19—7.22 (1H, m, ArH), 7.31—7.38 (6H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.0 (t), 25.4 (t), 26.7 (q), 29.3 (t), 41.2 (d), 42.2 (t), 55.2 (q), 70.9 (s), 72.8 (s), 97.3 (s), 113.4 (d×2), 126.3 (d×2), 126.4 (d), 128.4 (s), 129.2 (d×2), 131.4 (d×2), 132.9 (s), 158.9 (s), 202.7 (s), 207.4 (s), MS m/z: 392 (M^+). *Anal.* Calcd $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.59; H, 6.18.

2-Acetyl-2-[1-(*p*-methoxyphenyl)-3-(phenylsulfanyl)-2-propyn-1-yl]cyclopentanone (**2q**): A yellow oil, IR (KBr, cm^{-1}) ν: 2959, 1739, 1705, 1609, 1582, 1512, 1478, 1442, 1357, 1304, 1255, 1179, 1137, 1033, 843, 741, 689, 555; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.67—1.69 (1H, m, CH), 1.72—2.02 (1H, m, CH), 2.17 (3H, COMe), 2.17—2.25 (1H, m, CH), 2.32—2.42 (2H, m, CH_2), 2.53—2.68 (1H, m, CH), 3.78 (3H, s, OMe), 4.90 (1H, s, CH), 6.82 (2H, d, J=8 Hz, ArH), 7.18—7.22 (3H, m, ArH), 7.30—7.35 (4H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 19.7 (t), 26.6 (q), 28.2 (t), 38.9 (t), 43.2 (d), 55.2 (q), 70.9 (s), 73.9 (s), 97.3 (s), 114.1 (d×2), 126.1 (d×2), 126.5 (d), 128.3 (s), 129.2 (d×2), 129.3 (d×2), 132.8 (s), 159.2 (s), 201.1 (s), 213.7 (s); MS m/z: 378 (M^+), 360 (M^+-H_2O), 335 (M^+-COMe). High resolution mass Calcd for $C_{23}H_{22}O_3S$: 378.1289, Found m/z: 378.1301.

Yellow powders, mp 63—64 °C, IR (KBr, cm^{-1}) ν: 2960, 1738, 1705, 1609, 1582, 1510, 1478, 1442, 1356, 1305, 1247, 1180, 1139, 1033, 969, 839, 741, 689; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.30—1.37 (1H, m, CH), 1.63—1.71 (2H, m, CH_2), 1.87—1.92 (1H, m, CH), 2.11—2.17 (1H, m, CH), 2.47 (3H, s, Me), 2.78—2.82 (1H, m, CH), 3.79 (3H, s, OMe), 5.01 (1H, s, CH), 6.84 (2H, d, J=9 Hz, ArH), 7.21—7.25 (1H, m, ArH), 7.27 (2H, d, J=9 Hz, ArH), 7.32—7.36 (4H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 19.2 (t), 25.8 (t), 25.9 (q), 39.5 (t), 42.6 (d), 55.2 (q), 71.3 (s), 74.2 (s), 96.5 (s), 113.8 (d×2), 126.3 (d×2), 126.6 (d), 127.7 (s), 129.2 (d×2), 130.5 (d×2), 132.6 (s), 159.2 (s), 201.1 (s), 213.6 (s); MS m/z: 378

(M^+), 360 (M^+-H_2O), 335 (M^+-COMe). *Anal.* Calcd for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86. Found: C, 72.98; H, 5.92.

2-Acetyl-2-[1-(2-thienyl)-3-(phenylsulfanyl)-2-propyn-1-yl]cyclohexanone (**2r**): Yellow prisms, mp 110—112 °C, IR (KBr, cm^{-1}) ν: 2941, 2865, 1699, 1582, 1478, 1440, 1353, 1261, 1177, 1124, 1086, 1024, 742, 690; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.58—1.64 (2H, m, CH_2), 1.87—1.94 (1H, m, CH), 1.96—1.99 (1H, m, CH), 2.05 (3H, s, COMe), 2.08—2.13 (1H, m, CH), 2.20—2.26 (1H, m, CH), 2.55—2.58 (1H, m, CH), 2.70—2.73 (1H, m, CH), 5.28 (1H, s, CH), 6.89—6.91 (2H, m, ArH), 7.19—7.23 (2H, m, ArH), 7.30—7.33 (2H, m, ArH), 7.39—7.40 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.4 (t), 26.1 (t), 27.0 (q), 30.8 (t), 38.4 (d), 41.9 (t), 70.7 (s), 72.1 (s), 97.2 (s), 125.6 (d), 126.1 (d×2), 126.3 (d), 126.5 (d), 127.2 (d), 129.1 (d×2), 132.8 (s), 138.2 (s), 203.8 (s), 206.8 (s); MS *m/z*: 325 (M^+-COMe). *Anal.* Calcd for $C_{21}H_{20}O_2S_2$: C, 68.45; H, 5.47. Found: C, 68.17; H, 5.43.

Yellow powders, mp 77—79 °C, IR (KBr, cm^{-1}) ν: 2944, 2870, 1702, 1581, 1478, 1440, 1358, 1287, 1228, 1176, 1124, 1089, 1023, 970, 851, 741, 707, 627, 525, 466; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.40—1.47 (2H, m, CH_2), 1.71—1.74 (1H, m, CH), 1.79—1.85 (1H, m, CH), 1.86—1.91 (1H, m, CH), 2.09—2.15 (1H, m, CH), 2.23 (3H, s, Me), 2.52—2.55 (2H, m, CH_2), 5.49 (1H, s, CH), 6.93 (1H, dd, J=4, 5 Hz, ArH), 7.09 (1H, d, J=4 Hz, ArH), 7.21—7.24 (2H, m, ArH), 7.33—7.36 (2H, m, ArH), 7.39 (2H, br d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.4 (t), 26.1 (t), 27.0 (q), 30.8 (t), 38.4 (d), 41.9 (t), 71.7 (s), 73.4 (s), 95.6 (s), 125.8 (d), 126.3 (d×2), 126.4 (d), 126.7 (d), 128.4 (d), 129.2 (d×2), 132.4 (s), 139.3 (s), 202.0 (s), 207.2 (s); MS *m/z*: 325 (M^+-COMe). *Anal.* Calcd for $C_{21}H_{20}O_2S_2$: C, 68.45; H, 5.47. Found: C, 68.30; H, 5.46.

2-Acetyl-2-[1-(benzodioxol-5-yl)-3-(phenylsulfanyl)-2-propyn-1-yl]cyclohexanone (**2s**): Colorless needles, mp 131—133 °C, IR (KBr, cm^{-1}) ν: 2941, 1699, 1504, 1489, 1442, 1362, 1248, 1220, 1038, 930, 741, 689; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.54—1.64 (2H, m, alkyl H), 1.85—1.88 (2H, m, alkyl H), 1.97 (3H, s, Me), 2.04—2.19 (2H, m, alkyl H), 2.55—2.57 (2H, m, alkyl H), 4.89 (1H, s, CH), 5.94 (2H, s, OCH_2O), 6.67 (1H, d, J=7 Hz, CH), 6.70 (1H, d, J=7 Hz, CH), 6.80 (1H, d, J=1 Hz, CH), 7.19—7.21 (1H, m, ArH), 7.31—7.33 (2H, m, ArH), 7.37—7.39 (2H, m, ArH); ^{13}C-NMR (600 MHz, $CDCl_3$) δ: 22.4 (t), 25.9 (t), 27.3 (q), 29.9 (t), 42.0 (t), 42.9 (d), 70.3 (s), 72.1 (s), 98.1 (s), 101.2 (t), 108.0 (d) 109.5 (d), 122.4 (d), 126.0 (d×2), 126.3 (d), 129.1 (d×2), 129.3 (s), 133.2 (s), 147.2 (s), 147.7 (s), 204.2 (s), 206.7 (s); MS *m/z*: 388 (M^+-H_2O), 363 (M^+-COMe). *Anal.* Calcd for $C_{24}H_{22}O_4S$: C, 70.91; H, 5.46. Found: C, 70.27; H, 5.42.

Pale yellow plates, IR (KBr, cm^{-1}) ν: 2944, 1698, 1582, 1503, 1488, 1442, 1360, 1248, 1236, 1173, 1125, 1039, 817, 705, 689; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.37—1,47 (2H, m, alkyl H), 1.62—1.79 (2H, m, alkyl H), 1.84—1.86 (1H, m, alkyl H), 2.04—2.14 (1H, m, alkyl H), 2.23 (3H, s, Me), 2.43—2.49 (2H, m, alkyl H), 5.13 (1H, s, CH), 5.94 (2H, d, J=3 Hz, OCH_2O), 6.73 (1H, d, J=8 Hz, CH), 6.90 (1H, dd, J=2, 8 Hz, CH), 6.96 (1H, d, J=1 Hz, CH), 7.20—7.22 (1H, m, ArH), 7.31—7.37 (4H, m, ArH); ^{13}C-NMR (600 MHz, $CDCl_3$) δ: 21.9 (t), 25.4 (t), 26.7 (q), 29.4 (t), 41.5 (d), 42.1 (t), 71.2 (s), 72.8 (s), 97.0 (s), 101.1 (t), 107.8 (d), 110.7 (d), 123.8 (d), 126.3 (d×2), 126.5 (d), 129.2 (d×2), 130.0 (s), 132.7 (s), 146.9 (s), 147.3 (s), 202.5 (s), 207.2 (s); MS *m/z*: 407 (M^+), 388 (M^+-H_2O), 363 (M^+-COMe). *Anal.* Calcd for $C_{24}H_{22}O_4S$: C, 70.91; H, 5.46. Found: C, 70.30; H, 5.35.

2-Acetyl-2-[1-(benzodioxol-5-yl)-3-(phenylselanyl)-2-propyn-1-yl]cyclohexanone (**2t**): mp 120—122 °C, IR (KBr, cm^{-1}) ν: 2942, 1721, 1699, 1577, 1503, 1488, 1441, 1361, 1249, 1124, 1038, 930, 814, 737, 689; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.53—1.67 (3H, m, alkyl H), 1.85—1.88 (1H, m, alkyl H), 1.96 (3H, s, Me), 2.10—2.20 (2H, m, alkyl H), 2.53—2.57 (2H, m, alkyl H), 4.90 (1H, s, CH), 5.94—5.97 (2H, s, CH_2), 6.65 (1H, dd, J=2, 8 Hz, ArH), 6,70 (1H, d, J=8 Hz, ArH), 6.80 (1H, d, J=2 Hz, ArH, CH), 7.22—7.32 (3H, m, ArH), 7.47—7.49 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.4 (t), 25.8 (t), 27.4 (q), 29.8 (t), 42.1 (t), 43.1 (d), 63.5 (s), 72.1 (s), 101.2 (t), 102.8 (s), 108.0 (d), 109.5 (d), 122.4 (d), 126.9 (d), 128.9 (d×2), 129.0 (s), 129.4 (d×2), 129.5 (s), 147.2 (s), 147.6 (s), 204.2 (s), 206.7 (s); MS *m/z*: 436 (M^+-H_2O), 411 (M^+-COMe). *Anal.* Calcd for $C_{24}H_{22}O_4Se$: C, 63.58; H, 4.89. Found: C, 63.23; H, 4.80.

Yellow plates, mp 112—116 °C, IR (KBr, cm^{-1}) ν: 2943, 1698, 1577, 1503, 1487, 1440, 1360, 1289, 1247, 1173, 1125, 1039, 932, 872, 816, 736, 688; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.38—1.44 (2H, m, alkyl H), 1.59 (1H, s, alkyl H), 1.70—1.85 (2H, m, alkyl H), 2.07—2.13 (1H, m, alkyl H), 2.22 (3H, s, Me), 2.42—2.48 (2H, m, alkyl H), 5.15 (1H, s, CH), 5.94 (2H, br s, CH_2), 6.72 (1H, d, J=8 Hz, ArH), 6.90 (1H, dd, J=2, 8 Hz, ArH), 6.95 (1H, d, J=2 Hz, ArH), 7.24—7.32 (3H, m, ArH), 7.47—7.48 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.0 (t), 25.4 (t), 26.7 (q), 29.2 (t), 41.7 (d), 42.1 (t), 64.3 (s), 72.9 (s), 101.1 (t), 107.7 (d), 110.8 (d), 123.8 (d), 127.1 (d), 128.6 (s), 129.2 (d×2), 129.5 (d×2), 130.2 (s), 146.9 (s), 147.3 (s), 202.5 (s), 207.3 (s); MS *m/z*: 436 (M^+-H_2O), 411 (M^+-COMe).

2-Acetyl-2-[3-(phenylselanyl)-1-(2-thienyl)-2-propyn-1-yl]cyclohexanone (**2u**): Yellow needles, mp 109—111 °C, IR (KBr, cm^{-1}) ν: 2948, 1698, 1577, 1476, 1439, 1360, 1179, 1125, 847, 737, 626; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.58—1.67 (2H, m, alkyl H), 1.86—1.88 (1H, m, alkyl H), 1.96—1.99 (1H, m, alkyl H), 2.04—2.13 (1H, m, alkyl H), 2.05 (3H, s, Me), 2.18—2.26 (1H, m, alkyl H), 2.55—2.57 (1H, m, alkyl H), 2.69—2.72 (1H, m, alkyl H), 5.29 (1H, s, CH), 6.89—6.91 (2H, m, ArH), 7.19 (1H, dd, J=1, 5 Hz, ArH), 7.23—7.26 (1H, m, ArH), 7.29—7.32 (2H, m, ArH), 7.50 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 22.5 (t), 26.1 (t), 27.0 (q), 30.9 (t), 38.6 (d), 42.0 (t), 64.1 (s), 72.2 (s), 101.9 (s), 125.6 (d), 126.5 (d), 127.0 (d), 127.2 (d), 128.8 (s), 129.0 (d×2), 129.4 (d×2), 138.4 (s), 203.9 (s), 206.9 (s); MS *m/z*: 398 (M^+-H_2O), 373 (M^+-COMe).

Yellow needles, mp 60—70 °C, IR (KBr, cm^{-1}) ν: 2942, 1698, 1577, 1477, 1439, 1357, 1286, 1221, 1176, 1125, 1021, 848, 756, 737, 707, 688; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.38—1.47 (2H, m, alkyl H), 1.70—1.73 (1H, m, alkyl H), 1.79—1.91 (2H, m, alkyl H), 2.08—2.17 (1H, m, alkyl H), 2.22 (3H, s, Me), 2.51—2.55 (2H, m, alkyl H), 5.49 (1H, s, CH), 6.92 (1H, dd, J=3, 5 Hz, ArH) 7.08 (1H, d, J=3 Hz, ArH), 7.19 (1H, dd, J=4, 5 Hz, ArH), 7.21—7.33 (3H, m, ArH), 7.48—7.50 (2H, m, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 22.1 (t), 25.3 (t), 26.2 (q), 28.5 (t), 38.0 (d), 42.0 (t), 65.0 (s), 73.4 (s), 99.9 (s), 125.7 (d), 126.3 (d), 127.2 (d), 128.4 (s+d), 129.3 (d×2), 129.5 (d×2), 139.3 (s), 202.0 (s), 207.2 (s); MS *m/z*: 398 (M^+-H_2O), 373 (M^+-COMe). *Anal.* Calcd for $C_{21}H_{20}O_2SSe$: C, 60.72; H, 4.85. Found: C, 60.28; H, 4.86.

2-Acetyl-2-[3-(phenylselanyl)-1-(2-thenyl)-2-propyn-1-yl]cyclopentanone (**2v**): Yellow powders, mp 70—72 °C, IR (KBr, cm^{-1}) ν: 2925, 1740, 1703, 1577, 1477, 1439, 1400, 1279, 1197, 1136, 1021, 737, 689, 442; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.75—1.85 (1H, m, alkyl H), 1.98—2.07 (1H, m, alkyl H), 2.19—2.28 (1H, m, alkyl H), 2.24 (3H, s, Me), 2.32—2.45 (2H, m, alkyl H), 2.69—2.73 (1H, m, alkyl H), 5.26 (1H, s, CH), 6.90 (1H, dd, J=3, 5 Hz, ArH), 6.92 (1H, d, J=3 Hz, ArH), 7.18—7.20 (1H, m, ArH), 7.23—7.27 (3H, m, ArH), 7.46—7.47 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 19.8 (t), 26.3 (q), 28.0 (t), 38.9 (t), 39.6 (d), 64.8 (s), 74.0 (s), 100.8 (s), 125.4 (d), 126.4 (d), 126.7 (d), 127.2 (d), 128.3 (s), 129.2 (d×2), 129.5 (d×2), 139.1 (s), 200.7 (s), 212.8 (s); MS *m/z*: 359 (M^+-COMe). *Anal.* Calcd for $C_{20}H_{18}O_2SeS$: C, 59.85; H, 4.52. Found: C, 59.16; H, 4.39.

Synthesis of 3-Benzoyl-4-(4-methoxyphenyl)-2-phenyl-5-(phenylsulfanylmethyl)furan (4a), Typical Procedure To a tetrahydrofuran (THF)–MeOH (2.0 ml, 1 : 1) solution of 1,3-diphenyl-2-[1-(4-methoxyphenyl)-3-(phenylsulfanyl)prop-2-ynyl]propanedione (**2a**) (0.10 g, 0.21 mmol) was added 5 M sodium methoxide (0.20 ml, 1.0 mmol) at room temperature. The reaction mixture was stirred for 5 min and poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1 : 20) to give **4a** (89 mg, 90%) as a yellow oil.

4a: IR (KBr, cm^{-1}) ν: 3058, 2932, 2835, 1659, 1596, 1579, 1560, 1510, 1485, 1446, 1386, 1327, 1290, 1249, 1177, 1030, 991, 902, 837, 766, 742, 691, 605; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.66 (3H, s, OMe), 4.17 (2H, s, CH_2), 6.69 (2H, d, J=9 Hz, ArH), 6.98 (2H, d, J=9 Hz, ArH), 7.12—7.26 (8H, m, ArH), 7.33—7.36 (1H, m, ArH), 7.39—7.40 (2H, m, ArH), 7.49—7.50 (2H, m, ArH), 7.73—7.75 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 30.6 (t), 55.0 (q), 113.7 (d×2), 121.6 (s), 123.3 (s), 125.5 (s), 125.8 (s), 126.2 (d×2), 127.2 (d), 128.2 (d×2), 128.3 (d×2), 128.8 (d×2), 129.4 (s), 129.7 (d×2), 130.2 (d×2), 131.8 (d×2), 133.2 (d), 134.7 (s), 137.2 (s), 146.4 (s), 151.5 (s), 158.7 (s), 193.4 (s); MS *m/z*: 476 (M^+), 371 (M^+-COPh), 367 (M^+-SPh). High-resolution mass Calcd for $C_{31}H_{24}O_3S$: 476.1446, Found *m/z*: 467.1772.

3-Benzoyl-4-(3,4-dimethoxyphenyl)-2-phenyl-5-(phenylsulfanylmethyl)furan (4b): IR (KBr, cm-1) ν: 3058, 2935, 2834, 1660, 1596, 1580, 1559, 1515, 1490, 1462, 1448, 1420, 1332, 1256, 1238, 1171, 1073, 1025, 904, 876, 809, 766, 740, 692; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.66 (3H, s, Me), 3.79 (3H, s, Me), 4.22 (2H, s, CH_2), 6.65 (1H, d, J=8 Hz, ArH), 6.67 (1H, s, ArH), 6.69 (1H, d, J=8 Hz, ArH), 7.24—7.29 (8H, m, ArH), 7.39—7.43 (3H, m, ArH), 7.51—7.52 (2H, m, ArH), 7.77 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 30.76 (t), 55.66 (q), 55.73 (q), 111.00 (d), 112.28 (d), 121.46 (d), 121.58 (s), 123.80 (s), 125.71 (s), 126.16 (d×2), 127.27 (d), 128.34 (d×2), 128.47 (d×2), 128.86 (d), 128.93 (d×2), 129.45 (s), 129.72 (d×2), 131.78 (d×2), 133.42 (d), 134.82 (s), 137.30 (s), 146.42 (s), 148.23 (s), 148.55 (s), 151.43 (s), 193.67 (s); MS *m/z*: 506 (M^+), 401

(M^+-COPh), 397 (M+-SPh). *Anal*. Calcd for $C_{32}H_{26}O_4S$: C, 75.87; H, 5.17. Found: C, 75.74; H, 5.12.

3-Benzoyl-4-(benzodioxol-5-yl)-2-phenyl-5-(phenylsulfanylmethyl)furan (**4c**): IR (KBr, cm^{-1}) *v*: 3058, 2892, 1661, 1596, 1580, 1559, 1488, 1444, 1394, 1339, 1320, 1239, 1175, 1129, 1101, 1072, 1039, 1001, 935, 906, 887, 810, 766, 743, 692; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.17 (2H, s, CH_2S), 5.85 (2H, s, OCH_2O), 6.49 (1H, d, J=1 Hz, ArH), 6.52 (1H, dd, J=2, 8 Hz, ArH), 6.61 (1H, d, J=8 Hz, ArH), 7.20—7.29 (8H, m, ArH), 7.39—7.42 (3H, m, ArH), 7.48—7.49 (2H, m, ArH), 7.73—7.75 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 30.7 (t), 101.0 (t), 108.3 (d), 109.5 (d), 121.5 (s), 122.8 (d), 124.8 (s), 125.6 (s), 126.3 (d×2), 127.4 (d), 128.3 (d×2), 128.4 (d×2), 128.4 (d), 128.9 (d×2), 129.4 (s), 129.7 (d×2), 132.1 (d×2), 133.3 (d), 134.6 (s), 137.2 (s), 146.7 (s), 146.9 (s), 147.4 (s), 151.6 (s), 193.3 (s); MS *m/z*: 489 (M^+-1), 386 (M^+-SPh). *Anal.* Calcd for $C_{31}H_{22}O_4S$: C, 75.96; H, 4.52. Found: C, 75.74; H, 4.57.

3-Benzoyl-4-(4-chlorophenyl)-2-phenyl-5-(phenylsulfanylmethyl)furan (**4d**): Yellow powders, mp 162 °C, IR (KBr, cm^{-1}) *v*: 3057, 2924, 1660, 1595, 1579, 1556, 1491, 1447, 1407, 1326, 1234, 1193, 1174, 1124, 1089, 1073, 1042, 1021, 996, 907, 869, 841, 770, 744, 712; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.14 (2H, s, CH_2S), 6.94 (2H, d, J=9 Hz, ArH), 7.12 (2H, d, J=9 Hz, ArH), 7.21—7.27 (8H, m, ArH), 7.37—7.48 (3H, m, ArH), 7.49—7.50 (2H, m, ArH), 7.73 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 30.8 (t), 121.2 (s), 124.8 (s), 126.3 (d×2), 127.6 (d), 128.3 (d×2), 128.4 (d×2), 128.5 (d×2), 128.6 (d), 129.0 (d×2), 129.2 (s), 129.6 (s), 129.7 (d×2), 130.3 (d×2), 132.3 (d×2), 133.3 (s), 133.4 (d), 134.3 (s), 137.0 (s), 147.0 (s), 152.0 (s), 192.9 (s); MS *m/z*: 480 (M^+), 375 (M^+-COPh), 371 (M^+-SPh). *Anal.* Calcd for $C_{30}H_{21}O_2ClS$: C, 74.91; H, 4.40. Found: C, 75.16; H, 4.61.

3-Benzoyl-4-(*p*-methoxyphenyl)-2-phenyl-5-(phenylselanylmethyl)furan (**4e**): IR (KBr, cm^{-1}) *v*: 3057, 2931, 2834, 1660, 1596, 1578, 1559, 1509, 1489, 1476, 1447, 1385, 1328, 1290, 1249, 1177, 1130, 1109, 1072, 1022, 990, 899, 832, 765, 739, 691; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.71 (3H, s, Me), 4.18 (2H, s, CH), 6.69 (2H, d, J=8 Hz, ArH), 6.96 (2H, d, J=8 Hz, ArH), 7.22—7.28 (8H, m, ArH), 7.37—7.40 (1H, m, ArH), 7.47—7.48 (2H, m, ArH), 7.56 (2H, d, J=7 Hz, ArH), 7.74 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 21.9 (t), 51.1 (q), 113.8 (d×2), 123.6 (s), 125.0 (s), 126.2 (d×2), 127.9 (d), 128.3 (d×2), 128.3 (d), 128.4 (d×2), 129.1 (d×2), 129.2 (s), 129.5 (s), 129.8 (d×2), 130.1 (d×2), 131.5 (d), 133.3 (d), 134.9 (d×2), 137.2 (s), 147.6 (s), 151.3 (s), 158.7 (s), 193.5 (s); MS *m/z*: 419 (M^+-COPh), 367 (M^+-SePh). *Anal.* Calcd for $C_{31}H_{24}O_3Se$: C, 71.13; H, 4.62. Found: C, 69.82; H, 4.72.

3-Benzoyl-4-(benzodioxol-5-yl)-2-phenyl-5-(phenylselanylmethyl)furan (**4f**): A yellow oil, IR (KBr, cm^{-1}) *v*: 3058, 2898, 1712, 1661, 1596, 1579, 1560, 1503, 1490, 1447, 1359, 1339, 1321, 1239, 1176, 1129, 1072, 1039, 999, 935, 904, 887, 810, 766, 739, 718, 692, 625; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.17 (2H, s, CH_2Se), 5.85 (2H, s, OCH_2O), 6.47 (1H, d, J=1 Hz, ArH), 6.50 (1H, dd, J=1, 8 Hz, ArH), 6.60 (1H, d, J=9 Hz, ArH), 7.21—7.29 (8H, m, ArH), 7.39—7.41 (1H, m, ArH), 7.46—7.47 (2H, m, ArH), 7.55—7.56 (2H, m, ArH), 7.72—7.74 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 21.8 (t), 100.9 (t), 108.2 (d), 109.4 (d), 121.7 (s), 122.7 (d), 125.0 (s×2), 126.2 (d×2), 127.9 (d), 128.3 (d), 128.4 (d×3), 129.0 (s), 129.1 (d×2), 129.4 (s), 129.7 (d×3), 133.3 (d), 135.0 (d×2), 137.2 (s), 146.8 (s), 147.4 (s), 147.8 (s), 151.3 (s), 193.3 (s); MS *m/z*: 461 (M^+-Ph). *Anal.* Calcd for $C_{31}H_{22}O_4Se$: C, 69.28; H, 4.13. Found: C, 69.43; H, 4.11.

3-Benzoyl-4-(4-fluorophenyl)-2-phenyl-5-(phenylselanylmethyl)furan (**4g**): mp 96 °C, IR (KBr, cm^{-1}) *v*: 3057, 2924, 2359, 1658, 1596, 1579, 1560, 1508, 1488, 1476, 1447, 1410, 1383, 1327, 1230, 1176, 1159, 1130, 1096, 1072, 1021, 993, 899, 835, 807, 766, 739, 691; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.14 (2H, s, CH_2Se), 6.81—6.84 (2H, m, ArH), 6.95—6.97 (2H, m, ArH), 7.20—7.30 (8H, m, ArH), 7.37—7.39 (1H, m, ArH), 7.47—7.54 (4H, m, ArH), 7.70—7.71 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 21.7 (t), 115.2 (d), 115.3 (d), 121.6 (s), 124.3 (s), 126.3 (d×2), 128.0 (d), 128.3 (d×2), 128.4 (d×2), 128.5 (d), 128.8 (s), 129.1 (d×2), 129.3 (s), 129.7 (d×2), 130.6 (d), 130.7 (d), 133.4 (d), 135.1 (d×2), 137.1 (s), 148.0 (s), 151.7 (s), 161.1 (s), 162.7 (s), 193.1 (s); MS *m/z*: 512 (M^+), 355 (M^+-SePh). *Anal.* Calcd for $C_{30}H_{21}O_2FSe$: C, 70.45; H, 4.14. Found: C, 70.17; H, 4.16.

3-Benzoyl-2-phenyl-5-(phenylselanylmethyl)-4-(2-thienyl)furan (**4h**): IR (KBr, cm^{-1}) *v*: 3057, 2923, 2852, 1661, 1596, 1579, 1561, 1490, 1476, 1447, 1384, 1348, 1316, 1231, 1175, 1129, 1071, 1020, 999, 943, 898, 849, 766, 735, 690; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.27—4.30 (2H, m, CH_2Se), 6.72 (1H, d, J=4 Hz, ArH), 6.81 (1H, dd, J=4, 5 Hz, ArH), 7.11—7.12 (1H, m, ArH), 7.20—7.29 (8H, m, ArH), 7.40—7.45 (3H, m, ArH), 7.59 (2H, d, J=6 Hz, ArH), 7.77 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 21.8 (t), 118.2 (s), 121.5 (s), 125.8 (d), 126.1 (d×2), 127.2 (d), 127.3 (d), 127.9 (d), 128.3 (d×2), 128.4 (d×2), 128.5 (d), 128.9 (s), 129.0 (d×2), 129.1 (s), 129.7 (d×2), 131.7 (s), 133.5 (d), 135.0 (d×2), 137.1 (s), 148.8 (s), 151.1 (s), 193.1 (s); MS *m/z*: 343 (M^+-SePh). *Anal.* Calcd for $C_{28}H_{20}O_2SSe$: C, 67.33; H, 4.04. Found: C, 67.48; H, 4.03.

3-Benzoyl-4-(2-furyl)-2-phenyl-5-(phenylselanylmethyl)furan (**4i**): IR (KBr, cm^{-1}) *v*: 3057, 2361, 1664, 1596, 1579, 1541, 1490, 1476, 1448, 1366, 1320, 1229, 1176, 1155, 1129, 1073, 1023, 999, 906, 809, 764, 736, 716, 690; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.41—4.44 (2H, m, CH_2Se), 6.05 (1H, d, J=3 Hz, ArH), 6.20 (1H, t, J=3 Hz, ArH), 7.18—7.26 (7H, m, ArH), 7.31—7.34 (2H, m, ArH), 7.40—7.48 (3H, m, ArH), 7.59—7.60 (2H, m, ArH), 7.83 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 22.7 (t), 108.1 (d), 111.0 (d), 115.2 (s), 119.4 (s), 126.1 (d×2), 127.9 (d), 128.4 (d×2), 128.5 (d×2), 128.9 (d×2), 129.0 (s), 129.1 (s), 129.5 (d), 129.4 (d), 129.7 (d×2), 133.6 (d), 134.9 (d), 137.1 (s), 141.7 (s), 145.5 (s), 148.3 (s), 151.1 (s), 193.2 (s); MS *m/z*: 483 (M^+), 327 (M^+-SePh). High-resolution mass Calcd for $C_{28}H_{20}O_3Se$: 484.0577, Found *m/z*: 484.0548.

Reaction of 2p with Bu_4NF in *N*,*N*-Dimethylformamide (DMF), Typical Procedure One molar tetrabutylammonium fluoride (0.38 ml, 0.38 mmol) was added to a DMF (0.50 ml) solution of **2p** (50 mg, 0.13 mmol) at room temperature. The reaction mixture was refluxed for 5 min and poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1 : 20) to give **6p** (43 mg, 87%) and **5p** (4 mg, 10%) as a yellow oil.

9-Acetyl-3-(*p*-methoxyphenyl)-2-(phenylsulfanylmethyl)-4,5,6,7-tetrahydrobenzofuran (**6p**): IR (KBr, cm^{-1}) *v*: 2936, 1703, 1607, 1513, 1440, 1354, 1286, 1247, 1180, 1102, 1086, 1035, 972, 741, 691, 607; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.22—1.28 (2H, m, alkyl H), 1.42—1.47 (1H, m, alkyl H), 1.60—1.64 (1H, m, alkyl H), 2.11 (3H, s, COMe), 2.15—2.18 (1H, m, alkyl H), 2.47—2.50 (1H, m, alkyl H), 3.73 (1H, d, J=14 Hz, SCH_2), 3.79 (1H, s, OMe), 3.87 (1H, d, J=14 Hz, SCH_2), 5.23 (1H, t, J=4 Hz, olefinic H), 6.79 (2H, d, J=9 Hz, ArH), 6.85 (2H, d, J=9 Hz, ArH), 7.21—7.23 (3H, m, ArH), 7.29—7.31 (2H, m, ArH); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 18.4 (t), 22.0 (t), 25.9 (q), 27.1 (t), 30.4 (t), 55.2 (q), 63.5 (s), 100.4 (d), 114.0 (d×2), 118.1 (s), 124.0 (s), 127.0 (d), 129.0 (d×2), 129.7 (d×2), 131.0 (d×2), 134.7 (s), 150.6 (s), 155.4 (s), 159.0 (s), 205.5 (s); MS *m/z*: 392 (M^+), 349 (M^+-COMe). High resolution mass Calcd for $C_{24}H_{24}O_3S$: 392.1446, Found *m/z*: 392.1381.

3-(*p*-Methoxyphenyl)-2-(phenylsulfanylmethyl)-4,5,6,7-tetrahydrobenzofuran (**5p**): A yellow oil, IR (KBr, cm^{-1}) *v*: 2932, 1760, 1607, 1511, 1440, 1289, 1250, 1177, 1034, 987, 837, 741, 419; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.70—1.73 (2H, m, alkyl H), 1.83—1.85 (2H, m, alkyl H), 2.37 (2H, t, J=6 Hz, alkyl H), 2.60 (2H, t, J=6 Hz, alkyl H), 3.82 (3H, s, Me), 4.17 (2H, s, CH_2), 6.90 (2H, d, J=8 Hz, ArH), 7.18—7.19 (3H, m, ArH), 7.22—7.24 (2H, m, ArH), 7.32—7.33 (2H, m, ArH); ^{13}C-NMR (600 MHz, $CDCl_3$) δ: 21.7 (t), 22.9 (t), 23.1 (t), 23.3 (t), 31.0 (t), 55.3 (t), 114.0 (d×2), 117.4 (s), 123.6 (s), 125.5 (s), 126.4 (d), 128.8 (d×2), 129.8 (d×2), 130.3 (d×2), 136.1 (s), 143.5 (s), 150.4 (s), 158.5 (s); MS *m/z*: 350 (M^+). High resolution mass Calcd for $C_{22}H_{22}O_2S$: 350.1340, Found *m/z* 350.1329.

9-Acetyl-3-(benzodioxol-5-yl)-2-(phenylsulfanylmethyl)-4,5,6,9-tetrahydrobenzofurane (**6s**): IR (KBr, cm^{-1}) *v*: 2936, 1703, 1504, 1489, 1439, 1354, 1245, 1146, 1088, 1039, 984, 935, 891, 869, 813, 741, 691, 616; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.21—1.29 (2H, m, alkyl H), 1.40—1.45 (1H, m, alkyl H), 1.65—1.69 (1H, m, alkyl H), 2.04—2.20 (1H, m, CH), 2.11 (3H, s, Me), 2.48 (2H, dt, J=3, 12 Hz, alkyl H), 3.72 (1H, d, J=14 Hz, CH_2), 3.84 (1H, d, J=14 Hz, CH_2), 5.24 (1H, t, J=3 Hz, olefinic H), 5.94 (2H, s, ArH), 6.36 (1H, d, J=8 Hz, OCH_2O), 6.69 (1H, d, J=8 Hz, OCH_2O), 7.22—7.26 (3H, m, ArH), 7.30—7.33 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 18.4 (t), 22.0 (t), 26.0 (q), 27.1 (t), 30.5 (t), 63.5 (s), 100.5 (d), 101.1 (t), 108.4 (d), 108.9 (d), 118.1 (s), 122.3 (d), 125.3 (s), 127.1 (d), 128.9 (d×2), 131.3 (d×2), 134.5 (s), 147.1 (s), 147.7 (s), 151.0 (s), 155.3 (s), 205.4 (s); MS *m/z*: 406 (M^+), 363 (M^+-COMe). High resolution mass Calcd for $C_{24}H_{22}O_4S$: 406.1239, Found *m/z*: 406.1132.

9-Acetyl-3-(2-thienyl)-2-(phenylsulfanylmethyl)-4,5,6,9-tetrahydrobenzofuran (**6r**): IR (KBr, cm^{-1}) *v*: 3422, 2932, 1712, 1635, 1582, 1480, 1439, 1355, 1300, 1247, 1147, 1087, 948, 848, 741, 691, 615; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.24—1.32 (1H, m, alkyl H), 1.45—1.53 (1H, m, alkyl H), 1.67—1.69 (1H, m, alkyl H), 2.06—2.10 (1H, m, alkyl H), 2.08 (3H, s, Me), 2.16—2.22 (1H, m, alkyl H), 2.72 (1H, dt, J=3, 12 Hz, alkyl H), 3.90 (1H, d, J=14 Hz, CH_2), 4.11 (1H, d, J=14 Hz, CH_2), 5.25 (1H, dd, J=3, 5 Hz, olefinic H), 6.76 (1H, dd, J=3, 1 Hz, ArH), 6.94—6.95 (1H, m, ArH), 7.19—7.26 (4H, m, ArH), 7.36—7.37 (2H, m, ArH); ^{13}C-NMR (150 MHz,

$CDCl_3$) δ: 18.3 (t), 21.8 (t), 25.8 (q), 27.1 (t), 30.6 (t), 63.1 (s), 101.0 (d), 112.6 (s), 125.0 (d), 126.0 (d), 127.1 (d), 127.3 (d), 128.9 (d×2), 131.1 (d×2), 132.8 (s), 134.5 (s), 151.8 (s), 154.8 (s), 204.8 (s); MS *m/z*: 368 (M^+), 325 (M^+-COMe). High resolution mass Calcd for $C_{21}H_{20}O_2S_2$: 368.0905, Found *m/z*: 368.0904.

5-Acetyl-4-(*p*-methoxyphenyl)-3-(phenylsulfanyl)-2-oxabicyclo[3,3,0]octa-3,8-diene (**6q**): IR (KBr, cm^{-1}) *v*: 2933, 1706, 1680, 1608, 1514, 1440, 1355, 1291, 1251, 1180, 1035, 950, 834, 741, 691; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.94—2.02 (1H, m, alkyl H), 2.07 (3H, s, COMe), 2.29—2.36 (1H, m, alkyl H), 2.52—2.58 (1H, m, alkyl H), 2.85 (1H, dd, *J*=5, 11 Hz, CH), 3.79 (3H, s, OMe), 3.91 (1H, d, *J*=14 Hz, CH_2), 4.02 (1H, d, *J*=14 Hz, CH_2), 5.07—5.08 (1H, m, CH), 6.82 (2H, d, *J*=8 Hz, ArH), 7.00 (2H, d, *J*=8 Hz, ArH), 7.20—7.27 (3H, m, ArH), 7.36—7.38 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 25.4 (q), 31.1 (t), 31.6 (t), 36.0 (t), 55.2 (q), 73.2 (s), 101.4 (s), 114.3 (d×2), 120.3 (s), 124.4 (s), 127.1 (d), 128.5 (d×2), 129.0 (d×2), 131.0 (d×2), 134.8 (s), 153.7 (s), 158.9 (s), 160.5 (s), 205.2 (s); MS *m/z*: 378 (M^+), 335 (M^+-COMe). High resolution mass Calcd for $C_{23}H_{22}O_3S$: 378.1289, Found: 378.1274.

5-Acetyl-4-(2-thienyl)-3-(phenylsulfanyl)-2-oxabicyclo[3,3,0]octa-3,8-diene (**6v**): IR (KBr, cm^{-1}) *v*: 2931, 1709, 1680, 1583, 1480, 1439, 1355, 1312, 1243, 1193, 1098, 1044, 943, 844, 744, 692; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 2.03—2.08 (1H, m, alkyl H), 2.04 (3H, s, Me), 2.34—2.38 (1H, m, alkyl H), 2.57—2.62 (1H, m, alkyl H), 2.96 (1H, dd, *J*=5, 11 Hz, alkyl H), 4.05 (1H, d, *J*=14 Hz, CH_2), 4.20 (1H, d, *J*=14 Hz, CH_2), 5.10—5.11 (1H, m, ArH), 6.78 (1H, t, *J*=3 Hz, ArH), 6.95 (1H, dd, *J*=3, 5 Hz, ArH), 7.21—7.28 (4H, m, ArH), 7.46 (2H, d, *J*=8 Hz, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 25.3 (q), 31.2 (t), 31.9 (t), 36.2 (t), 73.0 (s), 102.3 (d), 115.6 (s), 124.9 (d), 125.5 (d), 127.3 (d), 127.4 (d), 129.0 (d×2), 131.4 (d×2), 133.6 (s), 134.5 (s), 154.1 (s), 159.9 (s), 204.6 (s); MS *m/z*: 354 (M^+), 311 (M^+-COMe). High resolution mass Calcd for $C_{20}H_{18}O_2S_2$: 354.0748, Found *m/z* 354.0730.

Conversion of 9-Acetyl-3-(2-thienyl)-2-(phenylsulfanylmethyl)-4,5,6,7-tetrahydrobenzofuran (6r) to 3-(2-Thienyl)-2-(phenylsulfanylmethyl)-4,5,6,7-tetrahydrobenzofuran (7r) 1,8-Diazabicyclo[5.4.0]undec-7-ene (50 mg, 0.33 mmol) was added to a DMF (0.50 ml) solution of **6r** (40 mg, 0.11 mmol) at room temperature. The reaction mixture was stirred for 10 min and then poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–*n*-hexane (1 : 20) to give **7r** (28 mg, 70%) as a yellow oil.

7r: A yellow oil, IR (KBr, cm^{-1}) *v*: 3422, 2932, 1712, 1635, 1582, 1480, 1439, 1355, 1300, 1247, 1147, 1087, 948, 848, 741, 691, 615; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.24—1.32 (1H, m, alkyl H), 1.45—1.53 (1H, m, alkyl H), 1.67—1.69 (1H, m, alkyl H), 2.06—2.10 (1H, m, alkyl H), 2.08 (3H, s, Me), 2.16—2.22 (1H, m, alkyl H), 2.72 (1H, dt, *J*=3, 12 Hz, alkyl H), 3.90 (1H, d, *J*=14 Hz, CH_2), 4.11 (1H, d, *J*=14 Hz, CH_2), 5.25 (1H, dd, *J*=3, 5 Hz, olefinic H), 6.76 (1H, dd, *J*=3, 1 Hz, ArH), 6.94—6.95 (1H, m, ArH), 7.19—7.26 (4H, m, ArH), 7.36—7.37 (2H, m, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 18.3 (t), 21.8 (t), 25.8 (q), 27.1 (t), 30.6 (t), 63.1 (s), 101.0 (d), 112.6 (s), 125.0 (d), 126.0 (d), 127.1 (d), 127.3 (d), 128.9 (d×2), 131.1 (d×2), 132.8 (s), 134.5 (s), 151.8 (s), 154.8 (s), 204.8 (s); MS *m/z*: 368 (M^+), 325 (M^+-COMe). High resolution mass Calcd for $C_{21}H_{20}O_2S_2$: 368.0905, Found *m/z* 368.0904.

Conversion of 6r to 7r by *p*-Toluenesulfonic Acid *p*-Toluenesulfonic acid hydrate (44 mg, 0.23 mmol) was added a dioxane (0.50 ml) of **6r** (43 mg, 0.12 mmol) at room temperature. The mixture was refluxed for 10 min. The workup procedure gave **7r** (24 mg, 62%).

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