SUPPORTING INFORMATION

A reactivity switch in the gold-catalysed coupling of allylsulfides with propargylic carboxylates

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General Experimental 2
Starting Materials 2
Products 4
General Experimental

All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na), Et₂O (Na), CH₂Cl₂ (P₄O₁₀), Et₃N (CaH₂), toluene (Na). Anhydrous ClCH₂CH₂Cl was purchased from Aldrich.

Flash chromatography: Fluorochem silica gel 60 (40-63 u). IR: Perkin–Elmer Paragon 1600 FTIR spectrometer spectrometer, wavenumbers (ν) in cm⁻¹. MS and HRMS (EI): VG-ZabSpec, MS and HRMS (ES): Micromass LCT. Melting points: Kofler hot stage. Elemental analyses: Carlo Erba EA1110. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. NMR: Spectra were recorded on Bruker AC300, AV300 and Bruker AV400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δC = 77.0 ppm; residual CHCl₃ in CDCl₃: δH = 7.26 ppm; CD₂Cl₂: δC = 53.8 ppm; residual CH₂Cl₂ in CD₂Cl₂: δH = 5.32 ppm). Where indicated, the signal assignments in the NMR spectra are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: PENDANT, DEPT 45, DEPT 135; Gradient COSY 90; Gradient HSQC for ¹J(C,H) = 145 Hz; Gradient HMBC for correlations via ²J(C,H).

Starting Materials

All the propargylic carboxylate derivatives were prepared using the following standard procedure from the propargylic alcohol.

1-(4-Acetoxyphenyl)prop-2-ynyl acetate, 1e

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\[\text{AcO} \quad \text{O} \quad \text{O} \quad \text{AcO}\]

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\[\text{AcO} \quad \text{O} \quad \text{O} \quad \text{AcO}\]
The combined organic phases were washed with brine, dried over Na₂SO₄ and filtered. After evaporation of the filtrate, the residue was treated with K₂CO₃ (12 mmol) in methanol (20 mL). The mixture was stirred at RT until complete consumption of the alkynylsilane was observed. The reaction mixture was quenched with aqueous NH₄Cl and extracted with diethyl ether. The combined organic phases were washed with brine, dried over Na₂SO₄ and filtered. After evaporation of the filtrate, the residue was treated with K₂CO₃ (12 mmol) in methanol (20 mL). The mixture was stirred at RT until complete consumption of the alkynylsilane was observed. The reaction mixture was quenched with aqueous NH₄Cl, and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na₂SO₄ and filtered. After evaporation of the filtrate, the residue was treated with K₂CO₃ (3.3 mmol) in methanol (20 mL) and stirred at RT for 1 h. The combined organic phases were washed with brine, dried over Na₂SO₄ and filtered. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 9/1) to give the ketal propargylic carboxylate 1-(5-Acetylfuran-2-yl)prop-2-ynyl pivalate, 1f.
(561 mg, 60%). The ketal (505 mg, 1.73 mmol) was hydrolysed with aqueous 2.4 N HCl (3 mL) in MeOH (10 mL) at 0°C for 1 h. The reaction mixture was quenched with aqueous NaHCO₃, and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na₂SO₄ and filtered. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 9/1) to give the desired propargylic carboxylate as a colourless solid (402 mg, 94%); ¹H-NMR (300 MHz, CDCl₃): δ = 7.14 (d, J 3.5, 1 H), 6.68 (dd, J 3.5 and 0.6, 1 H), 6.49 (d, J 2.3, 1 H), 2.63 (d, J 2.3, 1H), 2.48 (s, 3 H), 1.23 (s, 9H); ¹³C-NMR (75 MHz, CDCl₃): δ = 186.8, 176.6, 153.1, 152.8, 117.3, 111.8, 76.6, 75.3, 58.2, 38.8, 26.9, 26.0; IR (NaCl): ν =3450, 3239, 3120, 2981, 2935, 1735, 1666, 1521, 1298, 1131, 1027; HR-MS (ES-TOF): m/z: calcd for C₁₄H₁₆O₄Na: 271.0946, found 271.0941 [M+Na].

*All thioether derivatives were prepared by alkylation of the corresponding thiol using a modified variant of the method reported by Ono.*

**Products**

**General Procedure for the AuCl-Catalyzed Rearrangement-Coupling Reaction**

Gold catalyst (AuCl, AuCl₃ or AuBr₃) (1.4 µmol, 5 mol%) was added to a solution of the propargylic carboxylate (0.29 mmol) and the thioether (1.1 eq) in 1,2-DCE (0.1 M). The resulting mixture was stirred at 70 °C under Ar atmosphere until the reaction was complete (GC/MS and TLC). The crude mixture was rapidly filtered under a plug of silica and the solvents were evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate, 95/5) to give the desired enol acetate derivative in analytically pure form.

The following compounds were prepared by this method:

**(Z)-1-(Benzyllthio)-3-(phenyl)hexa-1,5-dien-2-yl acetate, 3ab**

Pale yellow oil; ¹H-NMR (300 MHz, CDCl₃): δ = 7.31-7.20 (m, 8 H, H-Ar), 7.11 (m, 2 H, H-Ar), 5.61 (m, 1 H, H-5), 5.59 (d, J 0.9, 1 H, H-1), 4.96 (m, 1 H, H-6a), 4.91 (m, 1 H, H-6b), 3.80 (s, 2 H, H-7), 3.55 (dd, J 8.1 and 6.8, 1 H, H-3), 2.60 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b), 2.05 (s, 3 H, H-21); ¹³C-NMR (75 MHz, CDCl₃): δ = 167.6 (C-20), 149.5 (C-2), 140.0 (C-14), 137.3 (C-8), 135.6 (C-5), 128.8 (2 C), 128.5 (2 C), 128.3 (2 C), 128.2
IR (NaCl): $\nu = 3443, 3062, 3028, 1755, 1640, 1494, 1453, 1368, 1195, 1131, 701$; HR-MS (ES-TOF): $m/z$: calcd for $C_{21}H_{22}O_2NaS$: 361.1238, found 361.1240 [$M+Na$].

**(Z)-1-(4-Methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 3ae**

Pale yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): 
$\delta = 7.32-7.21$ (m, 7 H, H-Ar), 6.84 (m, 2 H, H-Ar), 5.85 (s, 1 H, H-1), 5.69 (m, 1 H, H-5), 5.00 (m, 2 H, H-6), 3.79 (s, 3 H, H-13), 3.62 (t, $J = 7.7$, 1 H, H-3), 2.67 (m, 1 H, H-4a), 2.52 (m, 1 H, H-4b), 2.10 (s, 3 H, H-21);

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 167.8$ (C-20), 159.1 (C-10), 149.7 (C-2), 140.0 (C-14), 135.6 (C-5), 132.2 (2 C), 128.4 (2 C), 128.2 (2 C), 127.0, 125.4 (C-7), 116.8 (C-6), 114.7 (2 C), 113.9 (C-1), 55.3 (C-13), 49.7 (C-3), 37.1 (C-4), 20.5 (C-21); IR (NaCl): $\nu = 3063, 3027, 3003, 2937, 2836, 1758, 1494, 1283, 1247, 1194, 1149, 1030, 703$; HR-MS (ES-TOF): $m/z$: calcd for $C_{21}H_{22}O_2NaS$: 377.1187, found 377.1172 [$M+Na$]; $C_{21}H_{22}O_2S$: calcd C 71.16, H 6.26, S 9.05, found C 71.3, H 6.10.

**(Z)-1-(4-Methoxyphenylthio)-3-[(4-acetoxyphenyl)hexa-1,5-dien-2-yl acetate, 3ea**

Pale yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): 
$\delta = 7.31$ (d, $J = 8.9$, 2 H, H-Ar), 7.22 (d, $J = 8.5$, 2 H, H-Ar), 7.04 (d, $J = 8.5$, 2 H, H-Ar), 6.84 (d, $J = 8.9$, 2 H, H-Ar), 5.86 (d, $J = 1.0$, 1 H, H-1), 5.69 (m, 1 H, H-5), 5.02 (m, 1 H, H-6a), 4.98 (m, 1 H, H-6b), 3.79 (s, 3 H, H-13), 3.63 (t, $J = 7.5$, 1 H, H-3), 2.67 (m, 1 H, H-4a), 2.47 (m, 1 H, H-4b), 2.29 (s, 3 H, H-23), 2.11 (s, 3 H, H-21);

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 169.3$ (C-22), 167.8 (C-20), 159.2 (C-10), 149.5, 149.2, 137.6 (C-14), 135.4 (C-5), 132.3 (2 C), 129.0 (2 C), 125.2 (C-7), 121.4 (2 C), 116.9 (C-6), 114.7 (2 C), 114.2 (C-1), 55.3 (C-13), 49.1 (C-3), 37.2 (C-4), 21.1 (C-23), 20.5 (C-21); IR (NaCl): $\nu = 3068, 3003, 2938, 2837, 1759, 1494, 1369, 1287, 1247, 1198, 1018, 912$; HR-MS (ES-TOF): $m/z$: calcd for $C_{23}H_{24}O_5NaS$: 435.1242, found 435.1239 [$M+Na$].
(Z)-3-(5-Acetylfuran-2-yl)-1-(phenylthio)hexa-1,5-dien-2-yl pivalate, 3fa

Pale brown oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.36-7.22 (m, 5 H, H-Ar, H-16), 7.11 (d, $J$ 3.5, 1 H, H-15), 6.31 (d, $J$ 3.5, 1 H, H-17), 6.02 (d, $J$ 0.7, 1 H, H-1), 5.77 (m, 1 H, H-5), 5.11 (m, 1 H, H-6a), 5.06 (m, 1 H, H-6b), 3.86 (t, $J$ 7.6, 1 H, H-3), 2.67 (m, 2 H, H-4), 2.45 (s, 3H, H-18), 1.26 (s, 9 H, H-21); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 186.2 (C-17), 175.1 (C-19), 158.3 (C-13), 152.1 (C-14), 147.1 (C-2), 135.0 (C-7), 134.4 (C-5), 129.5 (2 C), 129.0 (2 C), 126.8 (1 C), 118.3 (C-15), 117.7 (C-6), 113.7 (C-1), 109.8 (C-16), 44.3 (C-3), 39.2 (C-20), 35.0 (C-4), 27.1 (C-21), 25.9 (C-18); IR (NaCl): $\nu$ = 3340, 3075, 2975, 2932, 2872, 1751, 1676, 1510, 1479, 1108, 1026, 739; HR-MS (ES-TOF): $m/z$: calcd for C$_{23}$H$_{26}$O$_4$NaS: 421.1450, found 421.1460 [M+Na$^+$].

(Z)-1-(Benzylthio)-3-(phenyl)hexa-1,5-dien-2-yl pivalate, 3gb

Pale yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.31-7.20 (m, 8 H, H-Ar), 7.11 (m, 2 H, H Ar), 5.61 (m, 1 H, H-5), 5.59 (d, $J$ 0.9, 1 H, H-1), 4.96 (m, 1 H, H-6a), 4.91 (m, 1 H, H-6b), 3.80 (s, 2 H, H-7), 3.58 (dd, $J$ 8.3 and 6.8, 1 H, H-3), 2.58 (m, 1 H, H-4a), 2.42 (m, 1 H, H-4b), 1.15 (s, 9 H, H-22); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 175.3 (C-20), 149.6 (C-2), 140.1 (C-14), 137.5 (C-8), 135.7 (C-5), 128.9 (2 C), 128.5 (2 C), 128.3 (2 C), 128.2 (2 C), 127.2 (1 C), 126.8 (1 C), 116.6 (C-6), 111.8 (C-1), 49.4 (C-3), 39.0 (C-21), 37.6 (C-7), 37.0 (C-4), 27.0 (C-22); IR (NaCl): $\nu$ = 3438, 3062, 3028, 2974, 2930, 2870, 1744, 1494, 1478, 1453, 1119, 700; HR-MS (ES-TOF): $m/z$: calcd for C$_{24}$H$_{28}$O$_2$NaS: 403.1708, found 403.1712 [M+Na$^+$].
**Z**-1-Methylthio-3-phenylhexa-1,5-dien-2-yl pivalate, 3gd

Pale yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.31$ 7.17 (m, 5 H, H-Ar), 5.66 (m, 1 H, H-5), 5.59 (d, $J$ 0.9, 1H, H-1), 5.01 (m, 1 H, H-6a), 4.95 (m, 1 H, H-6b), 3.60 (dd, $J$ 8.8 and 6.5, 1 H, H-3), 2.67 (m, 1 H, H-4a), 2.47 (m, 1 H, H-4b), 2.23 (s, 3 H, H-7), 1.16 (s, 9 H, H-16); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 175.3$ (C-14), 148.2 (C-2), 140.2 (C-8), 135.8 (C-5), 128.4 (2 C), 128.3 (2 C), 126.8 (1 C), 116.6 (C-6), 114.8 (C-1), 49.4 (C-3), 39.1 (C-15), 37.1 (C-4), 27.0 (C-16), 16.8 (C-7); IR (NaCl): $\nu = 3062$, 3027, 2975, 2923, 2870, 1744, 1478, 1120, 700; HR-MS (ES-TOF): $m/z$: calcd for C$_{18}$H$_{24}$O$_2$NaS: 327.1395, found 327.1389 [M+Na].

**(E)**-1-(5-Acetylfuran-2-yl)-3-(benzylthio)hexa-1,5-dien-2-yl pivalate, E-6fb

Pale brown oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.11$ (m, 6 H, H-Ar, H-16), 6.33 (d, $J$ 3.6, 1 H, H-17), 6.22 (s, 1 H, H-1), 5.80 (m, 1 H, H-5), 5.10 (m, 1 H, H-6a), 5.02 (m, 1 H, H-6b), 4.45 (dd, $J$ 8.7 and 7.6, 1 H, H-3), 3.75 (d, $J$ 13.8, 1 H, H-7a), 3.67 (d, $J$ 13.8, 1 H, H-7b), 2.48 (m, 2 H, H-4), 2.14 (s, 3 H, H-19), 1.35 (s, 9 H, H-22); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 186.4$ (C-18), 176.5 (C-20), 152.0 (C-14), 151.9 (C-15), 149.3 (C-2), 138.0 (C-8), 134.4 (C-5), 128.6 (2 C), 128.2 (2 C), 126.7 (1 C), 117.7 (C-16), 117.4 (C-6), 113.0 (C-17), 110.6 (C-1), 44.3 (C-3), 39.5 (C-21), 36.3 (C-4), 35.6 (C-7), 27.3 (C-22), 25.9 (C-19); IR (NaCl): $\nu = 3443$, 3062, 3028, 2975, 2931, 2872, 1753, 1674, 1495, 1480, 1272, 1204, 1105, 1030, 917, 732, 702; HR-MS (ES-TOF): $m/z$: calcd for C$_{24}$H$_{28}$O$_4$NaS: 435.1606, found 435.1616 [M+Na].

(E)-1-(5-Acetylfuran-2-yl)-3-(allylthio)hexa-1,5-dien-2-yl pivalate, E-6fc

Pale brown oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.16$ (d, $J$ 3.6, 1 H, H-12), 6.40 (d, $J$ 3.6, 1 H, H-13), 6.21 (s, 1 H, H-1), 5.87 (m, 1 H, H-5), 5.72 (m, 1 H, H-8), 5.15 (m, 1 H, H-6a), 5.07 (m, 1 H, H-6b), 4.85 (m, 1 H, H-9a), 4.76 (m, 1 H, H-9b), 4.55 (m, 1 H, H-10a), 4.43 (m, 1 H, H-10b), 3.89 (s, 1 H, H-16); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 184.0$ (C-18), 176.3 (C-20), 152.0 (C-14), 151.9 (C-15), 149.3 (C-2), 138.0 (C-8), 134.4 (C-5), 128.6 (2 C), 128.2 (2 C), 126.7 (1 C), 117.7 (C-16), 117.4 (C-6), 113.0 (C-17), 110.6 (C-1), 44.3 (C-3), 39.5 (C-21), 36.3 (C-4), 35.6 (C-7), 27.3 (C-22), 25.9 (C-19); IR (NaCl): $\nu = 3443$, 3062, 3028, 2975, 2931, 2872, 1753, 1674, 1495, 1480, 1272, 1204, 1105, 1030, 917, 732, 702; HR-MS (ES-TOF): $m/z$: calcd for C$_{24}$H$_{28}$O$_4$NaS: 435.1606, found 435.1616 [M+Na].
4.58 (dd, J 8.5 and 6.8, 1 H, H-3), 3.18 (m, 1 H, H-7a), 3.08 (m, 1 H, H-7b), 2.49 (m, 2 H, H-4), 2.46 (s, 3H, H-15), 1.33 (s, 9H, H-18); $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 186.0 (C-14), 176.3 (C-16), 152.6 (C-10), 151.8 (C-11), 149.8 (C-2), 134.5 (C-5 or C-8), 134.4 (C-5 or C-8), 118.3 (C-12), 117.5 (C-6 or C-9), 117.0 (C-6 or C-9), 112.8 (C-13), 110.2 (C-1), 44.4 (C-3), 39.5 (C-17), 36.5 (C-4), 34.5 (C-7), 27.2 (C-18), 26.1 (C-15); IR (NaCl): ν =3452, 3078, 2976, 2929, 2871, 1754, 1675, 1496, 1480, 1102, 1030, 925; HR-MS (ES-TOF): m/z: calcd for C$_{20}$H$_{26}$O$_4$NaS: 385.1450, found 385.1453 [M+Na].

**{(E)}-1-(5-Acetylfuran-2-y)-3-(methylthio)hexa-1,5-dien-2-yl pivalate, E-6fd**

Pale brown oil; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 7.16 (d, J 3.6, 1 H, H-10), 6.39 (d, J 3.6, 1 H, H-11), 6.20 (s, 1 H, H-1), 5.85 (m, 1 H, H-5), 5.15 (m, 1 H, H-6a), 5.07 (m, 1 H, H-6b), 4.54 (dd, J 8.5 and 6.8, 1 H, H-3), 2.48 (m, 2 H, H-4), 2.47 (s, 3H, H-13), 2.09 (s, 3 H, H-7), 1.32 (s, 9 H, H-16); $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 185.8 (C-12), 176.4 (C-14), 152.8 (C-8), 151.7 (C-9), 149.4 (C-2), 134.5 (C-5), 118.5 (C-10), 117.4 (C-6), 112.7 (C-11), 110.2 (C-1), 46.8 (C-3), 39.5 (C-15), 36.1 (C-4), 27.2 (C-18), 26.0 (C-13), 14.8 (C-7); IR (NaCl): ν =3485, 2975, 2921, 2871, 1754, 1674, 1495, 1480, 1296, 1271, 1204, 1103, 1030; HR-MS (ES-TOF): m/z: calcd for C$_{18}$H$_{24}$O$_4$NaS: 359.1293, found 359.1295 [M+Na].

**{(Z)}-1-(5-Acetylfuran-2-y)-3-(methylthio)hexa-1,5-dien-2-yl pivalate, Z-6fd**

Pale brown oil; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 7.13 (d, J 3.6, 1 H, H-10), 6.42 (d, J 3.6, 1 H, H-11), 6.25 (s, 1 H, H-1), 5.85 (m, 1 H, H-5), 5.14 (m, 1 H, H-6a), 5.10 (m, 1 H, H-6b), 3.35 (t, J 7.3, 1 H, H-3), 2.54 (m, 2 H, H-4), 2.43 (s, 3H, H-13), 2.08 (s, 3 H, H-7), 1.39 (s, 9 H, H-16); $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 185.7 (C-12), 175.4 (C-14), 153.2 (C-8), 151.1 (C-9), 149.1 (C-2), 134.4 (C-5), 119.4 (C-10), 117.6 (C-6), 111.6 (C-1), 107.6 (C-11), 51.0 (C-3), 39.4 (C-15), 36.5 (C-4), 27.2 (C-18), 25.9 (C-13), 14.1 (C-7); IR (NaCl): ν =3478, 2974, 2921, 2872, 1754, 1673, 1494, 1297, 1270, 1104, 1030; HR-MS (ES-TOF): m/z: calcd for C$_{18}$H$_{24}$O$_4$NaS: 359.1293, found 359.1288 [M+Na].
(E)-3-Methylthio-1-phenylhexa-1,5-dien-2-yl pivalate, E-6gd

Ple yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta =$ 7.33-7.22 (m, 5 H, H-Ar), 6.47 (s, 1 H, H-1), 5.89 (m, 1H, H-5), 5.15 (m, 1 H, H-6a), 5.11 (m, 1 H, H-6b), 3.91 (dd, $J$ 8.7 and 6.7, 1 H, H-3), 2.51 (m, 1 H, H-4a), 2.36 (m, 1 H, H-4b), 1.94 (s, 3 H, H-7), 1.33 (s, 9 H, H-16);

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta =$ 176.8 (C-14), 146.4 (C-2), 134.9 (C-5), 134.5 (C-8), 128.9 (2 C), 128.4 (2 C), 127.2 (1 C), 122.2 (C-1), 117.4 (C-6), 45.6 (C-3), 39.4 (C-15), 36.4 (C-4), 27.3 (C-16), 14.7 (C-7); IR (NaCl): $\nu =$ 3078, 3024, 2975, 2917, 2870, 1752, 1479, 1114, 699; HR-MS (ES-TOF): $m/z$: calcd for C$_{18}$H$_{24}$O$_2$NaS: 327.1395, found 327.1390 [M+Na].

(Z)-3-Methylthio-1-phenylhexa-1,5-dien-2-yl pivalate, Z-6gd

Ple yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta =$ 7.35-7.20 (m, 5 H, H-Ar), 6.22 (s, 1 H, H-1), 5.88 (m, 1H, H-5), 5.16 (m, 1 H, H-6a), 5.10 (m, 1 H, H-6b), 3.37 (t, $J$ 7.2, 1 H, H-3), 2.60 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b), 2.12 (s, 3 H, H-7), 1.26 (s, 9 H, H-16);

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta =$ 175.4 (C-14), 146.0 (C-2), 135.0 (C-5), 134.1 (C-8), 128.5 (2 C), 128.2 (2 C), 127.3 (1 C), 118.4 (C-1), 117.2 (C-6), 50.9 (C-3), 39.1 (C-15), 36.8 (C-4), 27.2 (C-16), 14.0 (C-7); IR (NaCl): $\nu =$ 3469, 3078, 3027, 2975, 2918, 2871, 1746, 1107, 699; HR-MS (ES TOF): $m/z$: calcd for C$_{18}$H$_{24}$O$_2$NaS: 327.1395, found 327.1402 [M+Na].

(Z)-3,3-Dimethyl-1-(phenylthio)hexa-1,5-dien-2-yl acetate, A-3a

Ple yellow oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta =$ 7.33-7.17 (m, 5 H, H-Ar), 5.88 (s, 1 H, H-1), 5.79 (m, 1 H, H-5), 5.06 (m, 1 H, H-6a), 5.02 (m, 1 H, H-6b), 2.21 (s, 3 H, H-14), 2.16 (d, 2 H, H-4), 1.08 (s, 6 H, H-15);

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta =$ 167.7 (C-13), 156.1 (C-2), 135.7 (C-7), 134.5 (C-5), 129.1 (2 C), 129.0 (2 C), 126.5 (C-10), 117.7 (C-6), 109.4 (C-1), 44.5 (C-4), 40.1 (C-3), 25.4 (C-15), 20.6 (C-14); IR (NaCl): $\nu =$ 3073, 2968, 2925, 1763, 1191, 1064, 741, 690; HR-MS (ES-TOF) : $m/z$: calcd for C$_{18}$H$_{20}$NaO$_2$S : 299.1082, found 299.1086 [M+Na].