SUPPORTING INFORMATION

Alkynes as Masked Ylides: Gold Catalysed Intermolecular Reactions of Propargylic Carboxylates with Thioethers.

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General Experimental 2
Starting Materials 3
Products 5
References 10
NMR Comparison Tables 11
HPLC data (Scheme 5) 13
NMR Spectra 16
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 μ). 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). HPLC was performed on a Dionex Summit instrument: %ee determined by HPLC (Chiralpak AD column, 2-propanol : hexane = 5 : 95)
Starting Materials

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

Acylation Reaction: General Procedure (GP 1). The acylating reagent (1.2 eq.) is added to a solution of triethylamine (1.4 eq.) and propargylic alcohol (1 eq.) in dichloromethane (4 ml/mmol) at 0 °C under Ar. The reaction mixture is stirred 1-2 h and then treated with sat. NH₄Cl(aq), then with brine and extracted with ethyl acetate. Removal of solvent under reduced pressure affords a residue which is purified by flash chromatography in ethyl acetate/hexanes to afford the analytically pure propargylic carboxylates.

The following compounds were prepared by this method:

1-Phenylprop-2-ynyl benzoate
colourless crystals (4.66 mmol, 83% yield); ¹H-NMR (300 MHz, CDCl₃): δ = 8.08 (m, 2 H), 7.64-7.65 (m, 3 H), 7.47-7.39 (m, 5 H), 6.70 (d, J 2.2, 1 H), 2.70 (d, J 2.2, 1 H); ¹³C-NMR (75 MHz, CDCl₃): δ = 165.2, 136.5, 133.3, 129.8 (2 C), 129.5, 129.0, 128.7 (2 C), 128.3 (2 C), 127.6 (2 C), 80.2, 75.6, 65.8; IR (NaCl): ν = 3300, 1723, 1105, 1095, 739, 705; HR-MS (ES-TOF): m/z: calcd for C₁₆H₁₂O₂Na: 259.0735, found 259.0730 [M+Na].

1-Phenylprop-2-ynyl 2,2,2-trifluoroacetate
colourless oil (8.10 mmol, quant.); ¹H-NMR (300 MHz, CDCl₃): δ = 7.57 (m, 2 H), 7.44 (m, 3 H), 6.52 (d, J 2.3, 1 H), 2.82 (d, J 2.3, 1 H); ¹³C-NMR (75 MHz, CDCl₃): δ = 156.4 (q, J 43.1), 134.1, 130.0, 129.0 (2 C), 128.0 (2 C), 114.3 (q, J 285.8), 77.9, 77.7, 69.5; IR (NaCl): ν = 3300, 1789, 1372, 1226, 1172, 1147, 891, 760, 696; MS(EI) 228 (M⁺, 31%), 159 (5), 131 (22), 115 (100).

1-(2-bromophenyl)prop-2-ynyl acetate
n-BuLi (2.5 M solution in hexanes, 3.2 mL, 8.5 mmol) was added to a solution of ethynyltrimethylsilane (1.2 mL, 8.5 mmol) in anhydrous THF (20 mL) at -78 °C under Ar. The reaction was stirred at -78 °C for 20 min before the addition of the o-bromobenzaldehyde (0.7 mL, 6 mmol). The resulting mixture was allowed to warm to 0 °C and was stirred for 2 h. 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 (12 mmol) in methanol (20 mL). The mixture was stirred at RT until hydrolysis was complete. 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 desired propargylic carboxylate was prepared according to GP 1:

![Propargylic carboxylate](image_url)

colourless solid (1.29 g, 5.09 mmol, 85%); ¹H-NMR (300 MHz, CDCl₃): δ = 7.79 (dd, J 7.7 and 1.7, 1 H), 7.59 (dd, J 7.7 and 1.3, 1 H), 7.39 (ddd, J 7.7, 7.6 and 1.3, 1 H), 7.25 (ddd, J 7.7, 7.6 and 1.7, 1 H), 6.68 (d, J 2.3, 1 H), 2.67 (d, J 2.3, 1 H), 2.14 (s, 3 H); ¹³C-NMR (75 MHz, CDCl₃): δ = 169.3, 135.4, 133.1, 130.6, 129.5, 127.7, 123.3, 79.3, 75.8, 64.8, 20.7; IR (NaCl): ν = 3300, 1744, 1371, 1225, 1021, 739, 705; HR-MS (ES-TOF): m/z: calcd for C₁₁H₁₉O₂NaBr: 274.9684, found 274.9678 [M+Na].

All the thioether derivatives were prepared by alkylation of the corresponding thiol using a modified variant of the method reported by Ono.¹

Alkylation Reaction: General Procedure (GP 3).

To a mixture of thiol (9.8 mmol) and DBU (10.8 mmol) in toluene (30 mL) at 0 °C under Ar was slowly added allyl bromide (10.8 mmol). The reaction mixture was then stirred at RT for 1-3 h and was treated with aqueous NH₄Cl, then with brine and was extracted with ethyl acetate. The combined organic phases were dried over Na₂SO₄, filtered, and the solvent removed under reduce pressure to give the crude sulfide. The residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate) or by distillation to give the desired sulfide.

The following compounds were prepared by this method:

**Allyl phenylsulfide**
(Quant. yield). Spectroscopic data were identical to those reported in literature.²

**Allyl (p-tolyl)sulfide**
(Quant. yield). Spectroscopic data were identical to those reported in literature.³

**Allyl (4-methoxyphenyl)sulfide**
(95% yield). Spectroscopic data were identical to those reported in literature.⁴
Allyl (2-bromophenyl)sulfide

(82% yield). Spectroscopic data were identical to those reported in literature.⁵

Propargyl phenylsulfide

(Quant. yield). Spectroscopic data were identical to those reported in literature.⁶

Allyl(4-(trifluoromethyl)phenyl)sulfide

Colourless oil (quant. yield); ¹H-NMR (300 MHz, CDCl₃): δ = 7.51 (d, J 8.2, 2 H), 7.37 (d, J 8.2, 2 H), 5.88 (ddt, J 16.9, 10.0 and 6.7, 1 H), 5.24 (dq, J 16.9 and 1.3, 1 H), 5.15 (dq, J 10.0 and 1.1, 1 H), 3.62 (ddd, J 6.7, 1.3 and 1.1, 2 H); ¹³C-NMR (75 MHz, CDCl₃): δ = 141.6, 132.7, 130.8 (q, J 33), 128.0 (2 C), 127.4, 125.5 (2 C), 124.1 (q, J = 272 Hz), 118.3, 35.8; IR (NaCl): ν = 3086, 2982, 2919, 1607, 1402, 1328, 1165, 1124, 1096, 1064, 1014, 924, 824, 734; MS(EI) 218 (M⁺, 100%).

Allyl(4-bromophenyl)sulfide

The title compound was obtained according to the general procedure as a colourless oil (quant. yield); ¹H-NMR (300 MHz, CDCl₃): δ = 7.39 (d, J 8.3, 2 H), 7.20 (d, J 8.3, 2 H), 5.85 (m, 1 H), 5.10 (m, 2 H), 3.52 (d, J 6.8, 2 H); ¹³C-NMR (75 MHz, CDCl₃): δ = 135.0, 133.0, 131.6 (2 C), 131.2 (2 C), 119.9, 117.8, 37.0; IR (NaCl): ν = 3081, 3009, 2978, 2916, 1636, 1473, 1092, 1008, 920, 807, 734; MS(EI) 229 (M⁺, 100%).

Products

General Procedure for the Gold-Catalyzed Rearrangement-Coupling Reaction (Table 2)

AuCl (1.4 µmol, 5 mol%) was added to a solution of the propargylic carboxylate (0.29 mmol) and the thioether in 1,2-DCE (0.1 M). The resulting mixture was stirred at 70 °C under an atmosphere until the reaction was complete (GC/MS and TLC). The crude mixture was rapidly filtered under a plug of silica and the solvent was evaporated. The residue was either purified by flash chromatography (hexane/ethyl acetate, 95/5) to give the enol acetate derivative in analytically pure form, or the crude mixture was dissolved in MeOH (2 mL) and K₂CO₃ (2 eq) was added. The mixture was stirred at RT until hydrolysis was complete and 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 solvent, the residue was purified through silica gel flash chromatography (hexanes / ethyl acetate, 95/5) to yield the desired compounds.

The following compounds were prepared by this method:
(Z)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl acetate, 9a

Pale yellow oil; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.35$-$7.20$ (m, 10 H, H-Ar), $5.95$ (d, $J = 0.8$, 1 H, H-1), $5.71$ (ddt, $J = 17.0$, 10.2 and 6.8, 1 H, H-5), $5.07$ (ddt, $J = 17.0$, 1.5 and 1.5, 1 H, H-6a), $5.01$ (ddt, $J = 10.2$, 1.5 and 1.5, 1 H, H-6b), $3.67$ (t, $J = 7.6$, 1 H, H-3), $2.71$ (m, 1 H, H-4a), $2.55$ (m, 1 H, H-4b), $2.11$ (s, 3 H, H-20); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 167.7$ (C-19), 151.6 (C-2), 139.9 (C-13), 135.6 (C-5), 135.3 (C-7), 129.2 (2 C), 129.0 (2 C), 128.5 (2 C), 128.2 (2 C), 127.0, 126.6, 116.9 (C-6), 111.9 (C-1), 49.8 (C-3), 37.1 (C-4), 20.5 (C-20); IR (NaCl): $\nu = 3060$, 3027, 2978, 2921, 1759, 1582, 1479, 1440, 1368, 1194, 1134, 1024, 916, 742, 702, 692; HR-MS (ES-TOF): $m/z$: calcd for C$_{20}$H$_{20}$O$_2$NaS: 347.1082, found 347.1086 [M+Na].

(Z)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl pivalate, 9b

Colourless solid; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.35$-$7.20$ (m, 10 H, H-Ar), $5.96$ (s, 1 H, H-1), $5.71$ (m, 1 H, H-5), $5.02$ (m, 2 H, H-6), $3.70$ (t, $J = 7.5$, 1 H, H-3), $2.71$ (m, 1 H, H-4a), $2.54$ (m, 1 H, H-4b), $1.17$ (s, 9 H, H-21); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 175.4$ (C-19), 151.5 (C-2), 140.1 (C-13), 135.7 (C-5, C-7), 129.2 (2 C), 129.0 (2 C), 128.3 (4 C), 127.0, 126.5, 116.8 (C-6), 111.8 (C-1), 49.7 (C-3), 39.1 (C-20), 37.1 (C-4), 27.0 (C-21); IR (NaCl): $\nu = 3063$, 3029, 2976, 2933, 2872, 1746, 1479, 1115, 1026, 918, 739, 702; HR-MS (ES-TOF): $m/z$: calcd for C$_{23}$H$_{26}$O$_2$NaS: 389.1551, found 389.1548 [M+Na].

(Z)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl benzoate, 9c

Colourless solid; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 8.01$ (d, $J = 7.9$, 2 H, H-21, H-25), $7.58$ (t, $J = 7.4$, 1 H, H-23), $7.43$ (t, $J = 7.9$, 2 H, H-22, H-24), $7.33$-$7.19$ (m, 10 H, H-Ar), $6.05$ (s, 1 H, H-1), $5.77$ (m, 1 H, H-5), $5.08$ (dd, $J = 17.1$ and 1.3, 1 H, H-6a), $5.01$ (dd, $J = 10.2$ and 1.3, 1 H, H-6b), $3.82$ (t, $J = 7.5$, 1 H, H-3), $2.80$ (m, 1 H, H-4a), $2.63$ (m, 1 H, H-4b); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 163.5$ (C-19), 151.7 (C-2), 140.0 (C-13), 135.6 (C-5), 135.4 (C-7), 133.4, 130.1 (2 C), 129.1 (2 C), 129.1 (C-20), 129.0 (2 C), 128.5 (2 C), 128.4 (2 C), 128.2 (2 C), 127.0, 126.5, 116.9 (C-6), 112.3 (C-1), 50.0 (C-3), 37.1 (C-4); IR (NaCl):
ν = 3062, 3029, 2921, 2851, 1735, 1244, 1081, 1063, 705; HR-MS (ES-TOF): m/z: calcd for C_{25}H_{22}O_{2}NaS: 409.1238, found 409.1249 [M+Na].

(Z)-1-(4-Methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9d

Pale yellow oil; ¹H-NMR (300 MHz, CDCl₃): δ = 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); ¹³C-NMR (75 MHz, CDCl₃): δ = 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): ν = 3063, 3027, 3003, 2937, 2836, 1758, 1494, 1287, 1247, 1194, 1030, 703; HR-MS (ES-TOF): m/z: calcd for C_{21}H_{22}O_{3}NaS: 377.1187, found 377.1172 [M+Na].

(Z)-3-Phenyl-1-(p-tolylthio)hexa-1,5-dien-2-yl acetate, 9e

Pale yellow oil; ¹H-NMR (300 MHz, CDCl₃): δ = 7.32-7.22 (m, 7 H, H-Ar), 7.10 (d, J 8.1, 2 H, H-Ar), 5.91 (s, 1 H, H-1), 5.71 (m, 1 H, H-5), 5.00 (m, 2 H, H-6), 3.65 (t, J 7.6, 1 H, H-3), 2.69 (m, 1 H, H-4a), 2.53 (m, 1 H, H-4b), 2.31 (s, 3 H, H-13), 2.10 (s, 3 H, H-21); ¹³C-NMR (75 MHz, CDCl₃): δ = 167.8 (C-20), 150.7 (C-2), 140.0 (C-14), 136.8 (C-7), 129.7 (4 C), 128.4 (2 C), 128.2 (2 C), 127.0, 116.8 (C-6), 112.8 (C-1), 49.8 (C-3), 37.1 (C-4), 20.8 (C-13), 20.5 (C-21); IR (NaCl): ν = 3063, 3027, 2977, 2921, 2864, 1759, 1493, 1368, 1194, 1133, 1016, 806, 702; HR-MS (ES-TOF): m/z: calcd for C_{21}H_{22}O_{2}NaS: 361.1238, found 361.1247 [M+Na].

(Z)-3-(2-Bromophenyl)-1-(phenylthio)hexa-1,5-dien-2-yl acetate, 9i

Pale yellow oil; ¹H-NMR (300 MHz, CDCl₃): δ = 7.57 (d, J 8.1, 1 H, H-Ar), 7.37-7.26 (m, 7 H, H-Ar), 7.10 (m, 1 H, H-Ar), 6.05 (s, 1 H, H-1), 5.75 (m, 1 H, H-5), 5.07 (m, 1 H, H-6a), 5.02 (m, 1 H, H-6b), 4.31 (t, J 7.6, 1 H, H-3), 2.71 (m, 1 H, H-4a), 2.55 (m, 1 H, H-4b), 2.12 (s, 3 H, H-21); ¹³C-NMR (75 MHz, CDCl₃): δ = 167.6 (C-20), 150.0 (C-2), 139.1(C-13), 135.2 (C-7), 134.9 (C-5), 133.0, 129.2 (2 C), 129.0 (2 C), 128.8, 128.5, 127.6, 126.6, 125.4 (C-18), 117.2 (C-6),
112.7 (C-1), 48.0 (C-3), 36.6 (C-4), 20.5 (C-21); IR (NaCl): ν = 3060, 2922, 2851, 1761, 1479, 1469, 1368, 1191, 1136, 1024, 740, 690; HR-MS (ES-TOF): m/z: calcd for C_{20}H_{19}BrO_{2}NaS: 425.0187, found 425.0201 [M+Na].

**(Z)-3-(2-Bromophenyl)-1-(p-tolylthio)hexa-1,5-dien-2-yl acetate, 9j**

Pale yellow oil; ¹H-NMR (300 MHz, CDCl₃): δ = 7.56 (d, J 7.8, 1 H, H-Ar), 7.29 (m, 4 H, H-Ar), 7.09 (m, 3 H, H-Ar), 6.01 (s, 1 H, H-1), 5.74 (m, 1 H, H-5), 5.06 (m, 1 H, H-6a), 5.01 (m, 1 H, H-6b), 4.29 (t, J 7.4, 1 H, H-3), 2.68 (m, 1 H, H-4a), 2.55 (m, 1 H, H-4b), 2.33 (s, 3 H, H-13), 2.11 (s, 3 H, H-21); ¹³C-NMR (CDCl₃, 75 MHz): δ = 167.5 (C-20), 149.1 (C-2), 139.1 (C-14), 136.7 (C-10), 134.9 (C-5), 132.9, 131.4 (C-7), 129.7 (4 C), 128.7, 128.4, 127.5, 125.3 (C-19), 117.1 missing one C (C-6), 113.5 (C-1), 47.9 (C-3), 36.5 (C-4), 20.9 (C-13), 20.4 (C-21); IR (NaCl): ν = 3069, 2978, 2920, 1761, 1492, 1469, 1439, 1368, 1193, 1136, 1023, 806, 758, 734; HR-MS (ES-TOF): m/z: calcd for C_{21}H_{21}BrO_{2}NaS: 439.0343, found 439.0352 [M+Na].

**1-(4-Bromophenylthio)-3-phenylhex-5-en-2-one, 10f**

Pale yellow solid; ¹H-NMR (300 MHz, CDCl₃): δ = 7.34-7.26 (m, 5 H, H-Ar), 7.16 (m, 2 H-Ar), 7.05 (m, 2 H-Ar), 5.59 (m, 1 H, H-5), 4.99 (m, 1 H, H-6a), 4.91 (m, 1 H, H-6b), 4.04 (t, J 7.5, 1 H, H-3), 3.69 (d, J 15.5, 1 H, H-1a), 3.63 (d, J 15.5, 1 H, H-1b), 2.75 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b); ¹³C-NMR (75 MHz, CDCl₃): δ = 203.2 (C-2), 137.5 (C-13), 135.3 (C-5), 133.8 (C-7), 132.0 (2 C), 131.2 (2 C), 129.1 (2 C), 128.4 (2 C), 127.6, 120.7 (C-10), 117.0 (C-6), 56.4 (C-3), 42.9 (C-1), 36.5 (C-4); IR (NaCl): ν = 3056, 2893, 1709, 1474, 1092, 1007, 810, 738, 702; MS(EI) 362 (M⁺, 7%), 360 (M⁺, 7%), 203 (9), 201 (9), 172 (7), 131 (100).

**1-(2-Bromophenylthio)-3-phenylhex-5-en-2-one, 10g**

Pale yellow solid; ¹H-NMR (300 MHz, CDCl₃): δ = 7.51 (dd, J 7.8 and 1.3, 1 H, H-Ar), 7.32-7.16 (m, 5 H, H-Ar), 7.14-7.00 (m, 2 H, H-Ar), 5.58 (m, 1 H, H-5), 4.93 (dd, J 17.1 and 1.3, 1 H, H-6a), 4.89 (dd, J 10.1 and 1.3, 1 H, H-6b), 4.11 (t, J 7.5, 1 H, H-3), 3.69 (d, J 15.5, 1 H, H-1a), 3.63 (d, J 15.5, 1 H, H-1b), 2.75 (m, 1 H, H-4a), 2.44 (m, 1 H, H-4b); ¹³C-NMR (75 MHz, CDCl₃): δ = 203.4 (C-2), 137.5 (C-13), 135.9 (C-7), 135.2 (C-5), 133.0, 129.1, 129.0 (2 C),
128.4 (2 C), 127.8, 127.6, 127.4, 123.7 (C-12), 116.9 (C-6), 56.2 (C-3), 41.9 (C-1), 36.4 (C-4); IR (NaCl): ν = 3061, 3027, 2977, 2917, 1710, 1450, 1428, 1020, 746, 701; HR-MS (ES-TOF): m/z: calcd for C₁₈H₁₇BrNaOS: 383.0081, found 383.0092 [M+Na].

3-Phenyl-1-(4-(trifluoromethyl)phenylthio)hex-5-en-2-one, 10h

Pale yellow solid; ¹H-NMR (300 MHz, CDCl₃): δ = 7.42 (d, J 8.4, 2 H, H-Ar), 7.32-7.18 (m, 7 H, H-Ar), 5.58 (m, 1 H, H-5), 4.98 (dd, J 17.1 and 1.4, 1 H, H-6a), 4.92 (d, J 10.4, 1 H, H-6b), 4.06 (t, J 7.4, 1 H, H-3), 3.74 (d, J 15.8, 1 H, H-1a), 3.66 (d, J 15.8, 1 H, H-1b), 2.77 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b); ¹³C-NMR (75 MHz, CDCl₃): C-10 and C-13 are not observed δ = 203.0 (C-2), 140.2 (C-7), 137.4 (C-14), 135.1 (C-5), 129.1 (2 C), 128.3 (2 C), 127.9 (2 C), 127.7, 125.7 (q, J 2.7, 2 C), 117.0 (C-6), 56.5 (C-3), 41.8 (C-1), 36.5 (C-4); IR (NaCl): ν = 3065, 3029, 2923, 2852, 1712, 1606, 1328, 1167, 1125, 1096, 1064, 1013, 701; HR-MS (EI): m/z: calcd for C₁₉H₁₇F₃OS: 350.0952, found 350.0968.

1-(Allylthio)-3-phenylhex-5-en-2-one, 10k

Colourless oil; ¹H-NMR (300 MHz, CDCl₃): δ = 7.35-7.21 (m, 5 H, H-Ar), 5.67 (m, 2 H, H-5, H-8), 5.01 (m, 4 H, H-6, H-9), 4.08 (t, J 7.5, 1 H, H-3), 3.15 (d, J 14.8, 1 H, H-1a), 3.10 (d, J 14.8, 1 H, H-1b), 2.84 (ddd, J 16.8, 7.4 and 2.6, O=S=O), 2.79 (m, 1 H, H-4a), 2.47 (m, 1 H, H-4b); ¹³C-NMR (75 MHz, CDCl₃): δ = 203.7 (C-2), 137.9 (C-10), 135.5, 132.6, 128.9 (2 C), 128.3 (2 C), 127.4, 118.2, 116.7, 56.0 (C-3), 38.4 (C-1), 36.6 (C-4), 34.4 (C-7); IR (NaCl): ν = 3079, 3027, 2978, 2917, 1704, 1640, 1493, 1453, 992, 920, 753, 701; HR-MS (ES-TOF): m/z: calcd for C₁₅H₁₈NaOS: 269.0976, found 269.0968 [M+Na].

1-(Phenylthio)-3-phenylhex-5-yn-2-one, 16 / 1-phenyl-3-(phenylthio)hex-5-yn-2-one, 17 (Scheme 6)

Prepared using AuCl₃; Isolated as a 1 : 1.6 mixture of isomers 16 : 17; HPLC separation was performed using a Phenomenex SEMI-PREP Luna 10u C18 column, size 250 mm × 10 mm, acetonitrile / water = 70 : 30 (3 mL/min).

16-Colourless solid; ¹H-NMR (300 MHz, CDCl₃): δ = 7.33-7.16 (m, 10 H, H-Ar), 4.29 (t, J 7.4, 1 H, H-3), 3.65 (d, J = 15.2, 1 H, H-1a), 3.59 (d, J 15.2, 1 H, H-1b), 2.84 (ddd, J 16.8, 7.4 and 2.6,
1 H, H-4a), 2.54 (ddd, J 16.8, 7.4 and 2.6, 1 H, H-4b), 1.86 (t, J 2.6, 1 H, H-6); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 202.7$ (C-2), 136.7 (C-13), 134.5 (C-7), 129.9 (2 C), 129.1 (2 C), 129.0 (2 C), 128.3 (2 C), 128.0, 126.9, 81.7 (C-5), 69.8 (C-6), 55.0 (C-3), 42.9 (C-1), 22.0 (C-4); IR (NaCl): $\nu = 3289, 1708, 1482, 1454, 1086, 1069, 750, 670, 632$; HR-MS (ES-TOF): $m/z$: calcd for C$_{18}$H$_{16}$NaOS: 303.0820, found 303.0809 [M+Na$^+$].

17-Colourless oil; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.42$-7.18 (m, 10 H, H-Ar), 4.01 (d, J 15.4, 1 H, H-1a), 3.95 (d, J 15.4, 1 H, H-1b), 3.83 (dd, J 7.6 and 7.4, 1 H, H-3), 2.63 (ddd, J 17.2, 7.4 and 2.6, 1 H, H-4a), 2.48 (ddd, J 17.2, 7.6 and 2.6, 1 H, H-4b), 2.04 (t, J 2.6, 1 H, H-6); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 201.6$ (C-2), 134.5 (2 C), 133.6 (C-13), 130.6 (C-7), 129.6 (2 C), 129.2 (2 C), 129.1, 128.7 (2 C), 127.1, 80.7 (C-5), 70.7 (C-6), 53.8 (C-3), 47.5 (C-1), 20.2 (C-4); IR (NaCl): $\nu = 3291, 3061, 3029, 2976, 2933, 1712, 1496, 1439, 1341, 1091, 1025, 750, 693, 643$; HR-MS (ES-TOF): $m/z$: calcd for C$_{18}$H$_{16}$NaOS: 303.0820, found 303.0810 [M+Na$^+$].

(Z)-1-(4-Allyl-2,3-dihydrothiophen-2-yl)-2-phenylvinyl pivalate, 19 (Scheme 7)

Colourless solid; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 7.35$-7.20 (m, 5 H, H-Ar), 6.33 (br s, 1 H, H-6), 5.82 (m, 1 H, H-14), 5.74 (br s, 1 H, H-1), 5.10 (m, 2 H, H-15), 4.59 (dd, J 8.6 and 7.9, 1 H, H-4), 2.85 (m, 4 H, H-3, H-13), 1.25 (s, 9 H, H-18); $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 175.7$ (C-16), 147.9 (C-5), 135.1 (C-14), 133.9 (C-7), 133.4 (C-2), 128.5 (2 C), 128.1 (2 C), 127.4 (C-10), 117.9 (C-1), 116.9 (C-6), 116.6 (C-15), 51.7 (C-4), 41.9 (C-3), 39.1 (C-17), 36.0 (C-13), 27.1 (C-18); IR (NaCl): $\nu = 3057, 3027, 2976, 2933, 1745, 1480, 1112, 1030, 920, 739, 699$; HR-MS (ES-TOF): $m/z$: calcd for C$_{20}$H$_{24}$NaO$_2$S: 351.1395, found 351.1400 [M+Na$^+$].

References

## NMR Comparison Tables

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HPLC data (Scheme 5)

(R)-1-phenylprop-2-ynyl benzoate, (R)-6
(Z)-1-(4-methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9c [from (R)-6]

![Graph of HPLC analysis]

---

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(Z)-1-(4-methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9c [From racemic 6]
$^1$H-NMR (300 MHz, CDCl$_3$) of 9a
$^{13}$C-NMR (75 MHz, CDCl₃) of 9a
HSQC of 9a
HMBC of 9a
HMBC of 9a
HMBC of 9a
HMBC of 9a
HMBC of 9a
NOE of 9a
$^1$H-NMR (300 MHz, CDCl$_3$) of 9b
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9b
$^1$H-NMR (300 MHz, CDCl$_3$) of 9c
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9c
$^1$H-NMR (300 MHz, CDCl$_3$) of 9d
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9d
$^{1}$H-NMR (300 MHz, CDCl$_3$) of $^{9e}$
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9e
$^1$H-NMR (300 MHz, CDCl$_3$) of 10f

![NMR spectrum](image)
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 10f
$^1$H-NMR (300 MHz, CDCl$_3$) of 10g
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 10g
$^1$H-NMR (300 MHz, CDCl$_3$) of 10h
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 10h
$^1$H-NMR (300 MHz, CDCl$_3$) of 9i
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9i
$^1$H-NMR (300 MHz, CDCl$_3$) of 9j
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 9j
$^1$H-NMR (300 MHz, CDCl$_3$) of 10k
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HMBC of 16
HMBC of 16
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$^{13}$C-NMR (75 MHz, CDCl₃) of 17
HMBC of 17
HMBC of 17
HMBC of 17
$^1$H-NMR (300 MHz, CDCl$_3$) of 19
$^{13}$C-NMR (75 MHz, CDCl$_3$) of 19
HSQC of 19

Note: Assignment on the following spectra uses the numbering scheme as follows:
HSQC of 19
HSQC of 19
HMBC of 19
HMBC of 19
HMBC of 19
HMBC of 19
HMBC of 19
HMBC of 19
nOe of 19