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β-Arylthio-α-chloroalkyl Ethers − Novel 1,1-Bis-electrophiles for Geminal Alkylation

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A novel protocol for geminal alkylation is suggested based upon the consecutive generation of two cationoid intermediates from the easily prepared adducts of arylsulfenyl chlorides and vinyl ethers.

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Introduction

The availability of diverse and reliable methods for performing a sequence of alkylation reactions leading to the introduction of two different substituents at the same carbon atom is of obvious importance for organic synthesis.

Most commonly this goal could be achieved by using various types of synthetic equivalents of 1,1-bis-nucleophilic synthons. The list of compounds which could be used in this role includes such classical reagents as malonic and acetoacetic esters,[1a] nitromethane[1b] and various types of thioacetals.[1c] Ample experimental evidence attests to the versatility and preparative usefulness of the general protocol based upon a sequential one-pot 1,1-bis-alkylation of the carbanionic species derived from these types of precursors.[2]

There is much less data referring to the alternative option based upon the sequential alkylation of a 1,1-bis-electrophilic center with two different carbon nucleophiles (Nu_C). Cahiez et al. employed various acyl chlorides as synthetic equivalents of 1,1-electrophilic synthons in an efficient one-pot preparation of unsymmetrical tertiary alcohols which involves consecutive treatment of these electrophiles first with organomanganese and then with organomagnesium (or lithium) compounds.[3] Mayr and Gorath described the formation of the products of 1,1-geminal allylation in the $BHal_3$-initiated reaction of aromatic aldehydes or acetals with allylsilanes which was shown to proceed via the sequential generation of cationoid species at the benzylic carbon atom.[4] A similar use of aromatic aldehydes as 1,1-bis-electrophiles was described recently by Shiina et al. who have shown that a series of 4,4-diarylbut-1-enes could be prepared by the successive allylation of aromatic aldehydes with allylsilanes or stannanes followed by Friedel–Crafts alkylation in the presence of $HfCl_4$ or $Cl_2Si(OTf)_2$ as Lewis acid.[5] An entirely different and synthetically promising protocol for the sequential one-pot introduction of two different carbon nucleophiles at the same carbon atom was elaborated by Suga et al.[6] As was shown in these studies, methyl 2,2-bis(trimethylsilyl)pyrrolidine-1-carboxylate could be employed as a convenient precursor for the stepwise electrochemical generation of *N*-acyliminium ions in a controllable way that secured a highly selective substitution of both silyl groups with two different nucleophiles.

The ArS group is known to anchimerically facilitate the substitution of a nucleofuge at the β-position as a result of the stabilization of the developing carbocationic center via the formation of a episulfonium ion (ESI) type intermediate.[7] Once formed these intermediates exhibit rather high electrophilic activity and their reaction with a number of carbon nucleophiles (Nu_C), like silicon- or tin-capped π donors, is well-documented as a useful preparative method (see below). Hence one might have suggested that placing two leaving groups (LGs) at the β-position to an ArS group, as shown in the fragment **1**, would provide an opportunity for employing the latter as an equivalent of geminal bis-electrophilic synthon **1′** provided effective control could be executed over the selectivity of the consecutive reactions, as shown in Scheme 1.

Here we wish to report the results of our study attesting to the validity of this concept and its potential for the elaboration of a new methodology of controlled geminal bis-alkylation.

β-Arylthio-α-chloroalkyl ethers of the general formula **2** (Scheme 2) were chosen as promising candidates for the role of synthetic equivalents to the synthon **1′**, both because of the obvious difference in the nucleofugacity of the Cl and MeO groups and their easy availability through the Ad_E reaction of ArSCl to vinyl ethers.[8]

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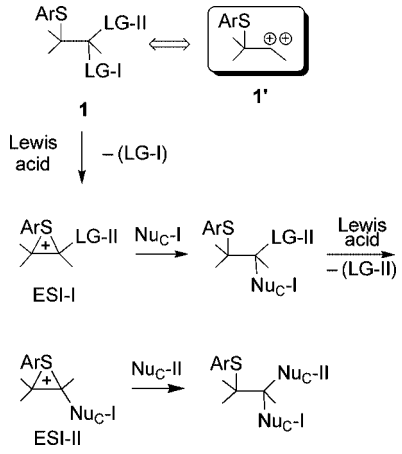
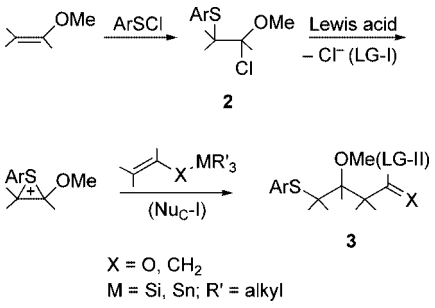


Scheme 1.



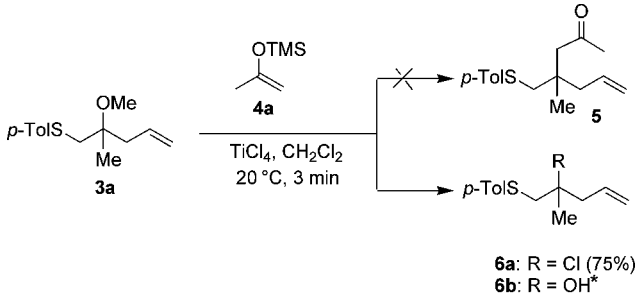
Scheme 2.

Earlier studies revealed that the interaction of adducts **2** with a Lewis acid leads to the generation of a cationoid intermediate of ESI-I type which can be effectively used as the electrophile in C–C bond-forming reactions with a wide range of carbon nucleophiles (Nu_C) such as vinyl silyl ethers and ketene acetals, allylsilanes or stannanes resulting in the formation of the corresponding adducts **3** in good-to-excellent yields (Scheme 2).[9] Regardless of the structure of the substrate and the nature of the Lewis acid, in all cases the formation of the electrophilic ESI-I involved the selective removal of chlorine (LG-I) due to the better nucleofugacity of this group and the enhanced stabilization of the intermediate ESI-I by the methoxy substituent at the developing cationoid center.

While the presence of the β-methoxyalkyl arylthio fragment in adducts **3** makes them potentially useful precursors for the Lewis acid induced generation of the next cationoid intermediate (ESI-II, Scheme 1), the viability of such a transformation is far from self-evident in view of the rather poor nucleofugacity of the methoxy group. In fact, previous literature data pertinent to the ability of the methoxy group to serve as a nucleofuge in related transformations are rather scarce and refer exclusively to intramolecular cyclization reactions initiated by the generation of ESI-like intermediates from substrates bearing appropriately positioned double bond(s).[10a,10b]

Results and Discussion

In order to evaluate the ease of generation of ESI-II intermediates, the interaction of adduct **3a**[11] with trimethylsilyl enolate **4a** in the presence of Lewis acids within the temperature range of –78 and 20 °C was studied as a model reaction. Initially $TiCl_4$ was employed as the Lewis acid and it was found that no reaction occurred at low temperatures (TLC monitoring data). However, an increase in temperature up to 20 °C resulted in fast and complete conversion of the adduct **3a**. However, instead of the expected alkylation product **5**, the Cl adduct **6a** (evidently as a result of the substitution of MeO by Cl) was exclusively formed (Scheme 3).



Scheme 3. *__6b__ was obtained upon hydrolysis of **6a** on silica gel (see Exp. Sect.).

The clean formation of the adduct **6a** prompted us to study its potential as an alternative precursor for the desired transformation. It turned out that Lewis acids like $TiCl_4$, BF_3, TMSOTf, BF_3 + TMSOTf, or $AgSbF_6$ could not promote the reaction of **6a** (formed in situ from **3a**) with **4a**. No reaction occurred at low temperatures and complex mixtures of unidentified products were formed at ambient temperatures. However, the use of Et_2AlCl resulted in the formation of the target product **5**, albeit in a rather modest yield.

This Lewis acid was shown to be useful for promoting the reactions of in situ formed chloro adduct **6a** with a number of other carbon nucleophiles such as silyl enolates **4b**,**c** and silyl ketene acetal **4d**, giving the expected alkylation products **7**–**9** in moderate yields (see procedure A, Expt. Sect.) (Scheme 4).

Further studies revealed that use of the stronger Lewis acid Et_2AlCl·TMSOTf[12,13] allowed us to perform the direct reaction of the methoxy adduct **3a** with a series of carbon nucleophiles thus bypassing the necessity to obtain the above-mentioned chloro adduct **6a**. As is shown in Scheme 5, under these conditions the alkylation of siloxyalkenes **4c**,**d** as well as methallylsilane **4e** furnishes the corresponding adducts **8**–**10** in satisfactory-to-good yields (see procedure B, Expt. Sect.). Finally, we have also demonstrated the possibility of preparing the adduct **8** starting from 2-methoxypropene by a one-pot sequence of three Ad_E reactions, as is also shown in Scheme 5 (see procedure C, Expt. Sect.).

The possibility of extending the scope of the above-shown transformations was also studied for [α-chloro-α-

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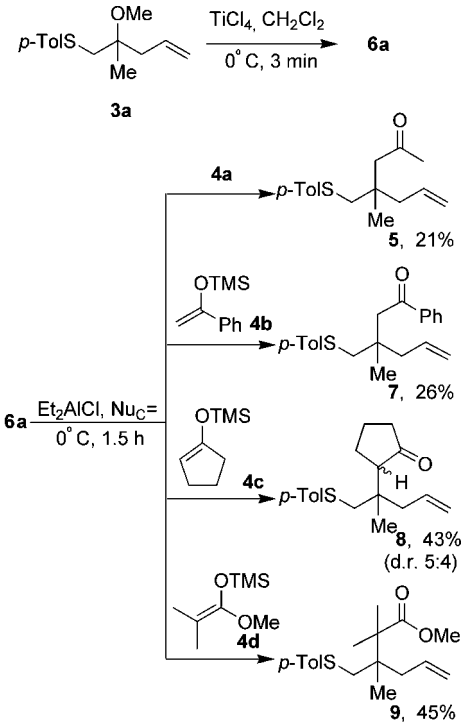
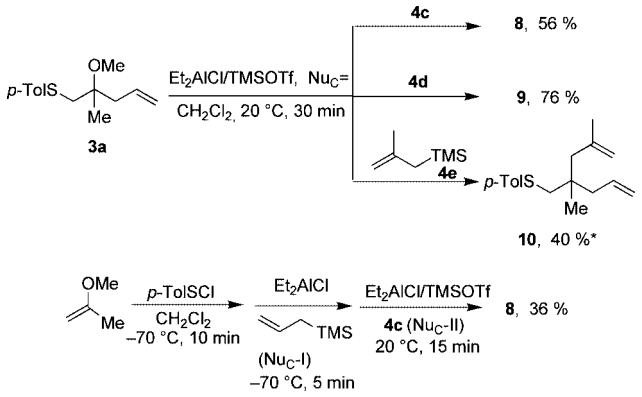


Scheme 4.



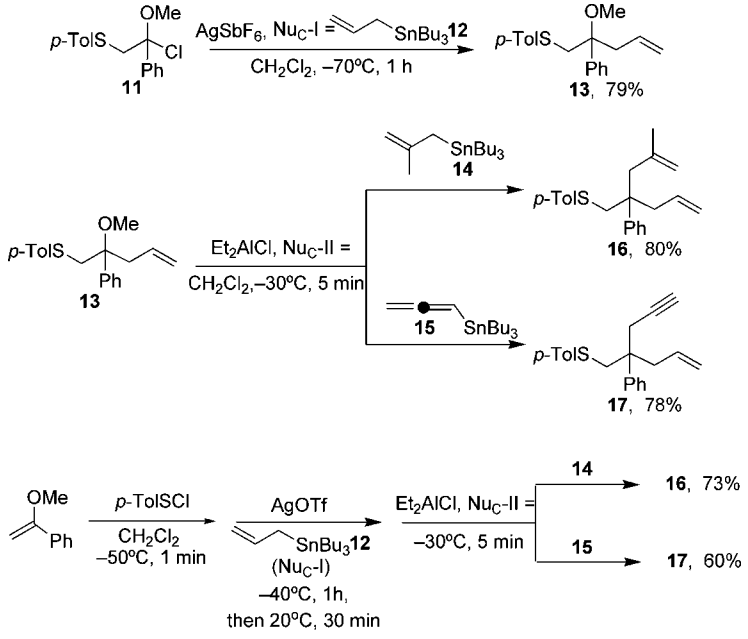
Scheme 5. *An inseparable mixture of **10** and *p*-TolSCH$_2$C(CH$_3$)=CH$_2$ (20% of the total, NMR spectroscopic data) was formed.[14]

methoxy-β-(*p*-tolylthio)ethyl]benzene (**11**), readily prepared from α-methoxystyrene and *p*-TolSCl.[15] No data were available concerning the Lewis acid initiated reactions of **11** with π donors. After some preliminary experimentation it was found that the interaction of **11** with allylstannane **12** proceeds smoothly under the action of $AgSbF_6$ at –50 °C to furnish the corresponding adduct **13** in a good yield.

The nucleofugacity of the methoxy group in the adduct **13** should clearly be higher than that in the adduct **3**. Therefore it was not surprising to find that Et_2AlCl was sufficiently active as the Lewis acid in the reaction of **13** with methallylstannane **14** or allenylstannane **15**, employed as Nu$_C$-II, to give the expected adducts **16** or **17** in good yields (Scheme 6) (see procedure D, Expt. Sect.). We also found that the consecutive transformation of α-methoxystyrene first to the adduct **11**, then to the product **13** and finally to the 1,1-bis-alkylation products **16** or **17** could be carried out as a one-pot sequence with a good overall yield (see procedure E, Expt. Sect.).

It is to be emphasized that in the latter sequence as well as in the one-pot preparation of adduct **8** (Scheme 5) the initially formed adducts of *p*-TolSCl and the respective vinyl ethers act as the precursors of 1,1-bifunctional electrophiles following the mechanism which was tentatively outlined in Scheme 1.

The functionalities present in the adducts **5**, **7**–**10**, **16** and **17** suggest quite a number of options for their further use



Scheme 6.

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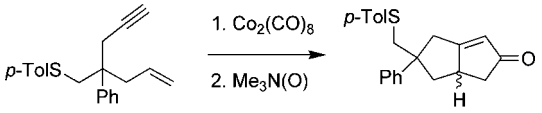
as substrates in various intramolecular cyclization reactions, such as the carbonyl-ene reaction, electrophilic cyclization of 1,5-dienes or intramolecular Pauson–Khand cyclization reaction.

In order to illustrate the usefulness of the described synthetic protocol, the feasibility of the Pauson–Khand transformation[16] was studied for the 1,6-enyne **17** (Scheme 7). It was found that treatment of **17** with $Co_2(CO)_8$ and then trimethylamine *N*-oxide led to the formation of the expected bicyclo[3.3.0]octenone **18** in a satisfactory yield (nonoptimized). Note that this product was eventually prepared from three simple precursors in only two separate steps in 40% overall yield.



17 **18** 66% (d.r. 1:1)

Scheme 7.

Conclusions

The results shown above provide "proof-of-principle" evidence for controlled geminal alkylation as a novel protocol for the easy assembly of polyfunctional substrates from simple starting compounds. Further studies aimed at optimizing the reaction conditions and broadening the preparative scope of the disclosed reaction sequence are most certainly warranted.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on a 200, 250, 300 or 500 MHz instrument at 22 °C unless otherwise noted. The chemical shifts (δ) are measured in ppm relative to internal $CHCl_3$ (δ = 7.26 ppm for ^1H) or $CDCl_3$ (δ = 77 ppm for ^{13}C). All reactions, unless otherwise noted, were conducted under argon. Liquid reagents were transferred to reaction flasks through a rubber septum using a hypodermic syringe.

Materials: Unless otherwise noted, materials were obtained from commercial suppliers and reagent grade materials were used without further purification. CH_2Cl_2 was freshly distilled over CaH_2 prior to use. THF was commercially available and used as received. *p*TolSCl was prepared following a previously described procedure.[17] Analytical TLC was performed on precoated silica gel 60 F_{254}. Column chromatography was performed on silica gel 60–120 μ.

Procedure A: Titanium tetrachloride (0.1 mmol, 19 mg in 0.12 mL of CH_2Cl_2) was added to a cold solution (0 °C) of **3a** (46 mg, 0.2 mmol) in dry CH_2Cl_2 (2 mL). The reaction mixture turned yellow. After 3 min TLC monitoring (ethyl acetate/hexane, 10:1) showed complete conversion of **3a** (R_f = 0.38) into chloride **6a** (R_f = 0.55). Corresponding silyl enolate (0.8 mmol) was added followed by Et_2AlCl (0.6 mmol, 0.33 mL of a 1.8 M solution in toluene). After 1.5 h the reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and solvents were removed in vacuo. The resulting oil was subjected to column chromatography (ethyl acetate/hexane, gradient 0:100 to 1:60) or preparative TLC (ethyl acetate/hexane, 1:20). The R_f (ethyl acetate/hexane, 10:1) value, the method of purification, yield and physical data for each product (**5**, **7**–**9**) are given below.

Procedure B: TMSOTf (0.4 mL, 2.2 mmol) was added to a cold (0 °C) solution of Et_2AlCl (2.2 mmol, 1.2 mL of a 1.8 M solution in toluene) in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 5 min. A solution of **3a** (101 mg, 0.43 mmol) and silyl enolate (0.86 mmol) in CH_2Cl_2 (5 mL) was added, the cooling bath removed and the reaction mixture stirred at room temp. until (ca. 30 min) TLC monitoring (ethyl acetate/hexane, 10:1) showed complete consumption of **3a** (R_f = 0.38). The reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and solvents were removed in vacuo. The resulting oil was subjected to column chromatography (ethyl acetate/hexane, gradient 0:100 to 1:60, unless otherwise mentioned) or preparative TLC (ethyl acetate/hexane, 1:20). The R_f (ethyl acetate/hexane, 10:1) value, method and conditions of purification, yield and physical data for the products **8**–**10** are given below.

Procedure C: 2-Methoxypropene (63 mg, 0.88 mmol) was added dropwise to a cold (–70 °C) orange solution of *p*-TolSCl (126 mg, 0.79 mmol) in dry CH_2Cl_2 (3 mL). After 10 min the reaction mixture turned colourless. Allyltrimethylsilane (94 mg, 0.82 mmol) and Et_2AlCl (1.0 mmol, 0.55 mL of a 1.8 M solution in toluene) were added and in 5 min TLC monitoring (ethyl acetate/hexane, 10:1) showed complete formation of **3a** (R_f = 0.38). (Trimethylsiloxy) cyclopentene (**4c**) (475 mg, 3.1 mmol) followed by Et_2AlCl (3.8 mmol, 2.13 mL of a 1.8 M solution in toluene) and TMSOTf (0.7 mL, 3.8 mmol) were added and the reaction mixture was stirred at room temp. for 15 min until TLC monitoring (ethyl acetate/hexane, 10:1) showed complete consumption of **3a** and formation of **8** (R_f = 0.22). The reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and solvents were removed in vacuo. The residue was purified by column chromatography (ethyl acetate/hexane, 0:100 to 1:40) to give 82 mg (36%) of **8** (*dr* = 1:1).

Procedure D: Et_2AlCl (0.79 mmol, 0.44 mL of a 1.8 M solution in toluene) was added to a cold solution (–30 °C) of **13** (130 mg, 0.44 mmol) and **14** or **15** (0.48 mmol) in dry CH_2Cl_2 (5 mL). The resulting mixture was stirred for 5 min until TLC monitoring (for **14**: ethyl acetate/hexane, 10:1, **13** R_f = 0.38; for **15**: toluene, **13** R_f = 0.73) showed complete consumption of **13**. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, solvents were removed in vacuo and the residue was purified by column chromatography (ethyl acetate/hexane, 0:100 to 1:50) to give the product **16** or **17**. The physical data for **16** and **17** are given below.

Procedure E: α-Methoxystyrene (45 mg, 0.33 mmol) was added dropwise to a cold orange (–50 °C) solution of *p*-TolSCl (53 mg, 0.33 mmol) in dry CH_2Cl_2 (3 mL). After 1 min the reaction mixture turned colourless. Allyltributylstannane (**12**) (122 mg, 0.37 mmol) and AgOTf (103 mg, 0.4 mmol) were added and the resulting mixture was stirred at –40 °C for 1 h until TLC monitoring (toluene) showed complete formation of **13**. The cooling bath was removed and stirring was continued at room temp. for 30 min (to make an excess of allyltributylstannane react with AgOTf) followed by cooling to –30 °C and addition of **14** or **15** (0.43 mmol) and Et_2AlCl

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(1 mmol, 0.56 mL of a 1 M solution in toluene). The resulting mixture was stirred for 5 min until TLC monitoring (for **14**: ethyl acetate/hexane, 10:1, **13** R_f = 0.38; for **15**: toluene, **13** R_f = 0.73) showed complete consumption of **13**. The reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, the solvent was removed in vacuo and the residue was purified by column chromatography to give the product **16** or **17**. The physical data for **16** and **17** are given below.

4-Methyl-4-(*p*-tolylsulfanylmethyl)hept-6-en-2-one (5): Procedure A: yield 21% (11.0 mg); purification: column chromatography; R_f = 0.29. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.30–7.27 (d, 2 H, Ar), 7.10–7.07 (d, 2 H, Ar), 5.85–5.68 (m, 1 H, CH_2=*CH*CH_2), 5.11–5.04 (m, 2 H, *CH_2*=CH), 3.14 (d, J = 12 Hz, 1 H, CH_aS), 3.07 (d, J = 12 Hz, 1 H, CH_bS), 2.52 (s, 2 H, CH_2C=O), 2.36–2.17 (m, 2 H, CH_2=CH*CH_2*), 2.32 (s, 3 H, *CH_3*–Ar), 2.04 (s, 3 H, CH_3–C=O), 1.10 (s, 3 H, CH_3–C_q) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ = 207.8, 135.9, 133.9, 133.6, 130.1, 129.6, 118.4, 49.6, 44.5, 43.4, 37.7, 31.7, 24.4, 20.9 ppm. $C_{16}H_{22}OS$ (262.41): C 73.23, H 8.45, S 12.22; found C 73.25, H 8.56, S 12.00.

3-Methyl-1-phenyl-3-(*p*-tolylsulfanylmethyl)hex-5-en-1-one (7): Procedure A: yield 26% (16.9 mg); purification: preparative TLC; R_f = 0.42. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.03–7.01 (m, 9 H, Ar), 5.90–5.73 (m, 1 H, CH_2=*CH*CH_2), 5.12–5.06 (m, 2 H, *CH_2*=CH), 3.26, (d, J = 15 Hz, 1 H, CH_aS), 3.17 (d, J = 15 Hz, 1 H, CH_bS), 3.06 (s, 2 H, CH_2C=O), 2.48–2.33 (m, 2 H, CH_2=CH*CH_2*), 2.27 (s, 3 H, *CH_3*–Ar), 1.17 (s, 3 H, CH_3–C) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ = 199.3, 138.3, 136.1, 134.1, 132.8, 130.5, 129.6, 128.7, 128.0, 125.7, 118.7 ppm. $C_{21}H_{24}OS$ (324.48): C 77.73, H 7.46, S 9.88; found C 77.95, H 7.78, S 9.51.

2-[1-Methyl-1-(*p*-tolylsulfanylmethyl)but-3-enyl]cyclopentanone (8): Procedure A: yield 43% (24.8 mg); purification: preparative TLC; procedure B: yield 56% (69.5 mg); purification: column chromatography; one-pot procedure C: yield 36%; purification: column chromatography; R_f = 0.22; NMR spectroscopic data are given for a mixture of diastereomers (4:5). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32–7.08 (m, 4 H, Ar), 5.88–5.70 (m, 1 H, CH_2=*CH*CH_2), 5.14–5.08 (m, 2 H, *CH_2*=CH), 3.28 (s, 2 H, CH_2S), 3.22 (d, J = 12 Hz, 1 H, CH_aS), 2.92 (d, J = 12 Hz, 1 H, CH_bS), 2.58–1.62 (m, 9 H, CH_2=CH*CH_2*, *CH_2*CH_2*CH_2*CH*C=O), 2.33 (s, 3 H, *CH_3*–Ar), 1.04, 1.02 (2 s, 3 H, CH_3–C_q) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ = 219.8, 219.7, 135.9, 135.7, 134.1, 133.7, 130.1, 129.9, 129.6, 118.5, 118.4, 54.2, 43.9, 42.9, 41.6, 40.7, 40.3, 39.8, 39.6, 25.9, 21.7, 20.9, 20.1 ppm. $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found C 74.66, H 8.33, S 10.80.

Methyl 2,2,3-Trimethyl-3-(*p*-tolylsulfanylmethyl)hex-5-enoate (9): Procedure A: yield 45% (27.6 mg); purification: preparative TLC; procedure B: yield 76% (100.2 mg); purification: column chromatography; R_f = 0.67. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.07 (m, 4 H, Ar), 5.93–5.77 (m, 1 H, CH_2=*CH*CH_2), 5.11–5.03 (m, 2 H, *CH_2*=CH), 3.66 (s, 3 H, OCH_3), 3.13 (d, J = 12 Hz, 1 H, CH_aS), 3.12 (d, J = 12 Hz, 1 H, CH_bS), 2.44–2.32 (m, 2 H, CH_2=CH*CH_2*), 2.32 (s, 3 H, *CH_3*–Ar), 1.26 [s, 6 H, C-$(CH_3)_2$], 1.05 (s, 3 H, CH_3–C_q) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ = 177.2, 136.0, 135.4, 134.8, 130.0, 129.7, 117.9, 51.6, 51.6, 49.1, 22.4, 22.2, 21.3, 21.1 ppm. $C_{18}H_{26}O_2S$ (306.46): C 70.54, H 8.55, S 10.46; found C 70.22, H 8.45, S 10.19.

1-(2-Allyl-2,4-dimethylpent-4-enylsulfanyl)-4-methylbenzene (10): Procedure B: yield 40% (60.0 mg of a mixture of products); purification: column chromatography (hexane); adduct **10** could not be separated from ca. 50 mol.% of *p*-TolSCH_2C(Me)=CH_2 (evaluated from the integration of the ^{1}H NMR spectrum); R_f = 0.55. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32–7.08 (m, 4 H, Ar), 5.93–5.26 (m, 1 H, CH_2=*CH*CH_2), 5.18–5.06 (m, 2 H, *CH_2*=CH), 4.93, 4.79 (2 s, 2 H, CH_3–C=*CH_2*), 2.93 (s, 2 H, CH_2S), 2.35 (s, 3 H, *CH_3*–Ar), 2.30–2.10 (m, 2 H, *CH_2*–C=CH_2), 1.84 (s, 3 H, CH_3–C=C), 1.03 (s, 3 H, CH_3–C_q) ppm. GC-MS: m/z = 260 $[M]^+$.

1-(2-Chloro-2-methoxy-2-phenylethylsulfanyl)-4-methylbenzene (11). NMR-Monitored Preparation: α-Methoxystyrene (23 mg, 0.17 mmol) was added to a cold (–50 °C) orange solution of *p*-TolSCl (26 mg, 0.17 mmol) in dry CD_2Cl_2 (1 mL). After 1 min the reaction mixture turned colourless. A syringe cooled in dry ice was used to transfer 0.5 mL of the prepared solution to a NMR tube closed with a septum and placed in a bath at –78 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 203°K): δ = 7.60–7.06 (m, 9 H, Ar), 3.92 (d, J = 3 Hz, 1 H, CH_aS), 3.78 (d, J = 3 Hz, 1 H, CH_bS), 3.43 (s, 3 H, OCH_3), 2.28 (s, 3 H, *CH_3*–Ar) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 140.8, 137.9, 132.3, 11.6, 130.5, 129.7, 129.1, 127.6, 111.0, 54.2, 49.4, 21.8 ppm. The instability of the adduct **11** precluded its isolation and it was used, prepared in situ, as described above.

1-[(2-Methoxy-2-phenyl-4-pentenyl)sulfanyl]-4-methylbenzene (13): α-Methoxystyrene (317 mg, 2 mmol) was added dropwise to a cold (–50 °C) orange solution of *p*-TolSCl (317 mg, 2 mmol) in dry CH_2Cl_2 (5 mL). After 1 min the reaction mixture turned colourless. The temperature was lowered to –70 °C and allyltributylstannane (**12**) (795 mg, 2.4 mmol) followed by $AgSbF_6$ (756 mg, 2.2 mmol in 1 mL of CH_2Cl_2) were added. The resulting mixture was stirred for 1 h (TLC monitoring, ethyl acetate/hexane, 1:10, showed complete formation of **13**, R_f = 0.38), quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, the solvent removed in vacuo and the residue purified by chromatography (ethyl acetate/hexane, 0:100 to 1:60) to give 466 mg (79%) of **13**. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41–7.05 (m, 9 H, Ar), 5.70–5.54 (m, 1 H, CH_2=*CH*CH_2), 5.14–5.06 (m, 2 H, *CH_2*=CH), 3.50 (d, J = 12.5 Hz, 1 H, CH_aS), 3.47 (d, J = 12.5 Hz, 1 H, CH_bS), 3.17 (s, 3 H, OCH_3), 2.97–2.77 (m, 2 H, *CH_2*–C=CH_2), 2.33 (s, 3 H, *CH_3*–Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.2, 13.1, 133.3, 132.9, 130.6, 129.6, 129.4, 128.2, 127.4, 126.7, 118.7, 80.6, 50.5, 42.5, 40.9, 21.0 ppm. $C_{19}H_{22}OS$ (298.44): C 76.46, H 7.43, S 10.74; found C 76.35, H 7.79, S 10.76.

2-Allyl-4-methyl-2-phenylpent-4-enyl 4-Methylphenyl Sulfide (16): Procedure D: yield 80% (113.5 mg); procedure E: yield 73% (77.7 mg); R_f = 0.35 (ethyl acetate/hexane, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.07 (m, 9 H, Ar), 5.70–5.56 (m, 1 H, CH_2=*CH*CH_2), 5.30–5.02 (m, 2 H, *CH_2*=CH), 4.79 (s, 1 H, CH_3–C=*CH_a*), 4.69 (s, 1 H, CH_3–C=*CH_a*), 3.40 (s, 2 H, CH_2S), 2.74 (d, J = 7 Hz, 2 H, *CH_2*–C=CH_2), 2.64 (d, J = 15 Hz, 1 H, *CH_a*–C=CH_2), 2.53 (d, J = 15 Hz, 1 H, *CH_b*–C=CH_2), 2.34 (s, 3 H, *CH_3*–Ar), 1.24 (s, 3 H, CH_3–C=C) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 142.2, 135.9, 134.0, 130.3, 129.6, 128.1, 126.8, 126.2, 118.6, 115.1, 47.0, 44.8, 43.2, 41.5, 24.7, 21.1 ppm. $C_{22}H_{26}S$ (322.51): C 81.93, H 8.13, S 9.94; found C 81.59, H 8.26; S 9.96.

1-Methyl-4-(2-phenyl-2-prop-2-ynylpent-4-enylsulfanyl)benzene (17): Procedure D: yield 78% (105.2 mg); procedure E: yield 60% (60.7 mg); R_f = 0.88 (toluene). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41–7.06 (m, 9 H, Ar), 5.57–5.43 (m, 1 H, CH_2=*CH*CH_2), 5.17–5.03 (m, 2 H, *CH_2*=CH), 3.48 (s, 2 H, CH_2S), 2.92 (dd, J_1 = 17, J_2 = 3 Hz, 1 H, CH_a–C≡C), 2.82 (dd, J_1 = 17, J_2 = 3 Hz, 1 H, CH_b–C≡C), 2.74–2.70 (m, 2 H, CH_2=CH*CH_2*), 2.33 (s, 3 H, *CH_3*–Ar), 2.02 (dd, J_1 = J_2 = 3 Hz, 1 H, C≡CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 136.1, 133.5, 133.4, 130.8, 129.5, 128.2, 126.5, 118.6, 81.2, 71.3, 45.1, 44.9, 42.8, 26.4, 21.1 ppm. $C_{21}H_{22}S$ (306.46): C 82.30, H 7.24, S 10.46; found C 81.92, H 7.22, S 10.48.

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5-[(4-Methylphenyl)sulfanylmethyl]-5-phenyl-3a,4,5,6-tetrahydro-2(3*H*)-pentalenone (18): A solution of **17** (200 mg, 0.65 mmol) and $Co_2(CO)_8$ (220 mg, 0.78 mmol) in THF (10 mL) was stirred at room temp. for 1 h until CO liberation stopped and the solution turned cherry-red. TLC monitoring (ethyl acetate/hexane, 1:10) showed complete consumption of **17** (R_f = 0.38) and the formation of a brown-coloured complex (R_f = 0.75). $Me_3NO{\cdot}H_2O$ (360 mg, 3.9 mmol) was added and the reaction mixture stirred for an additional 16 h. TLC monitoring showed complete consumption of the complex and formation of **18** (R_f = 0.17). The reaction mixture was filtered through a plug of silica gel (4 cm) using diethyl ether as eluent. Solvents were removed in vacuo and the residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:10 to 1:5) to give 143 mg (66%) of **18** (inseparable mixture of diastereomers, *dr* = 1:1). NMR spectroscopic data is given for the mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.00 (m, 9 H, Ar), 5.95, 5.92 (2 s, 1 H, =CH–C=O), 3.47–3.04 (m, 4 H, CH_2S, CH_2C=O), 2.87–2.60 (m, 3 H, CH_2–C=C, CH–C=C), 2.39 (s, 3 H, *CH*$_3$–Ar), 2.14–2.18, 1.76–1.70 (br. d, m, 2 H, Ph–C–*CH*$_2$–CH) ppm. ^{13}C (125 MHz, $CDCl_3$): δ = 210.0, 209.7, 188.1, 146.8, 145.7, 136.3, 133.2, 130.3, 129.6, 128.5, 128.3, 126.7, 126.6, 126.5, 126.3, 125.3, 125.3, 53.4, 53.2, 49.7, 49.5, 44.7, 44.5, 42.8, 42.6, 42.5, 42.2, 40.5, 39.6, 21.0 ppm. $C_{22}H_{22}OS$ (334.47): C 79.00, H 6.63, S 9.59; found C 79.15, H 6.57, S 9.94.

1-(2-Chloro-2-methylpent-4-enylsulfanyl)-4-methylbenzene (6a): Titanium tetrachloride (0.22 mmol, 42 mg in 0.24 mL of CH_2Cl_2) was added to a cold solution (0 °C) of **3a** (100 mg, 0.42 mmol) in dry CH_2Cl_2 (4 mL). The reaction mixture turned yellow. In 3 min TLC monitoring (ethyl acetate/hexane, 10:1) showed complete conversion of **3a** (R_f = 0.38) into **6a** (R_f = 0.55). The reaction mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered through a plug of Celite and the solvent was removed in vacuo. The residue was dissolved in hexane (30 mL) and filtered through a plug of silica gel (3 mm). Evaporation of hexane in vacuo gave 83 mg (75%) of **6a**. Chloride **6a** reacts with AgOTf in DCM to give a precipitate of AgCl. Subjection of **6a** to column chromatography (ethyl acetate/hexane, 1:10) partly converts **6a** into the corresponding alcohol **6b** probably due to hydrolysis on silica gel. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.35–7.09 (m, 4 H, Ar), 5.99–5.80 (m, 1 H, CH_2=*CH*CH_2), 5.19–5.10 (m, 2 H, *CH*$_2$=CH), 3.35 (s, 2 H, CH_2S), 2.66–2.61 (m, 2 H, *CH*$_2$–C=CH_2), 2.33 (s, 3 H, *CH*$_3$–Ar), 1.61 (s, 3 H, CH_3–C–Cl) ppm.

2-Methyl-1-(*p*-tolylsulfanyl)pent-4-en-2-ol (6b): R_f = 0.1 (ethyl acetate/hexane, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.10 (m, 4 H, Ar), 5.90–5.71 (m, 1 H, CH_2=*CH*CH_2), 5.17–5.08 (m, 2 H, *CH*$_2$=CH), 3.12 (d, *J* = 12 Hz, 1 H, CH_2S), 3.05 (d, *J* = 12 Hz, 1 H, CH_2S), 2.43–2.27 (m, 2 H, *CH*$_2$–C=CH_2), 2.33 (s, 3 H, *CH*$_3$–Ar), 1.27 (s, 3 H, CH_3–C–OH) ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3560 cm^{-1}.

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