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A Cationic Driven Tandem Ring-Enlargement-Annulation Reaction for the Rapid Assembly of the *cis*-Fused Bicyclo[3.2.0]heptane Framework

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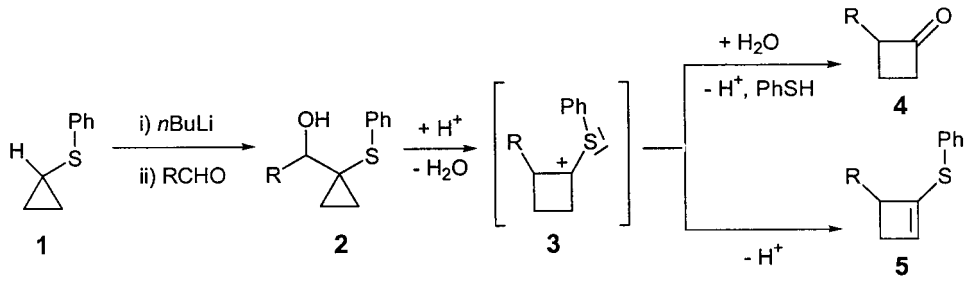
Abstract—The first intramolecular interception of a thionium cation generated through a cyclopropylcarbinyl-cyclobutyl ring expansion with an in situ formed enol is reported. © 2000 Published by Elsevier Science Ltd.

Introduction

The interplay between the release of ring strain and the directional power of 1-donor-substituents in cyclopropyl carbinyl cations generated from oxaspiropentanes or 1-donor-substituted cyclopropylcarbinols has made cyclopropylcarbinyl-cyclobutyl ring enlargement reactions to a powerful method for the construction of four-membered rings.[1] Readily available 1-donor-substituted cyclopropylcarbinols rearrange with ease under acid catalysis and are important precursors for the synthesis of cyclobutanones. They have found wide use in the synthesis of natural products[2] and recent progress of asymmetric versions[3] guarantee future applications.

Particularly the ambivalent aptitude of sulfur[4] to stabilise adjacent anionic as well as cationic centres has proved to be beneficial for the development of cyclopropyl phenyl sulfides as reagents for the four membered ring synthesis.[1,5] Cyclopropyl phenyl sulfide (**1**) is selectively deprotonated with *n*-butyllithium and adds to carbonyl compounds to give the β-hydroxy sulfide **2**, that thereupon may rearrange under acid catalysis in wet benzene to cyclobutanone **4** or under anhydrous reaction conditions to cyclobutenyl phenyl sulfide **5** (Scheme 1).

The driving force for the ring expansion of **2** to **4** and **5**, respectively, is attributed to the directional power of the sulfur atom and its aptitude to stabilise the adjacent cationic centre in the α-thiocarbocation (thionium ion) intermediate **3**. However, although α-thiocarbocations—more generally associated with, and obtained in the Pummerer reaction[6]—are considered as versatile reactive intermediates for carbon-carbon bond forming processes, the reaction of the α-thiocarbocation **3** with nucleophiles other than water has not been described yet.[7] We report here the first intramolecular interception of a thionium ion generated via a ring enlargement process related to the formation of **3** with a nucleophilic carbon species.



Scheme 1.

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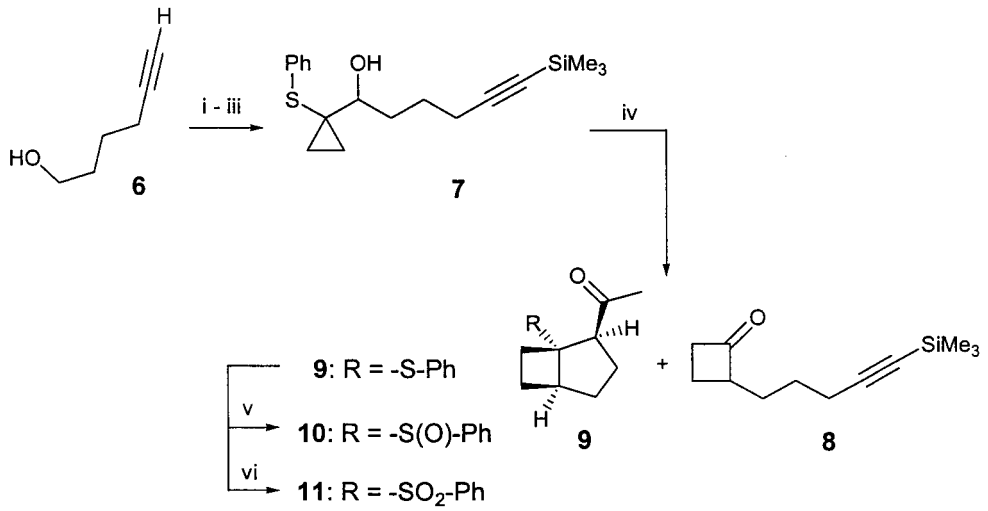


Scheme 2. *Reagents and conditions:* (i) *n*-BuLi (2 equiv.), THF, −78 to −20°C, then Me_3SiCl (2.5 equiv.), −78 to 20°C, then HOAc/H_2O, (96%); (ii) $(COCl)_2$, DMSO, CH_2Cl_2, −78°C, (65%); (iii) **1** (1.2 equiv.), *n*-BuLi, THF, 0°C, then addition to the aldehyde, −78°C, THF, (45%); (iv) TsOH·H_2O (1 equiv.), wet benzene, 70–80°C, **8** (10–26%), **9** (20–32%); (v) *m*CPBA (1 equiv.), CH_2Cl_2, −15°C, (76%); (vi) *m*CPBA (2 equiv.), −15°C, (96%).

Results and Discussion

At the outset of our studies we intended the synthesis of the cyclobutanone **8** through the acid catalysed ring expansion of alcohol **7**, which was smoothly obtained from 5-hexyn-1-ol (**6**) as outlined in Scheme 2. Surprisingly, acidification of **7** with *p*-toluenesulfonic acid in refluxing wet benzene gave besides the anticipated cyclobutanone **8** also the unexpected bicyclo[3.2.0]heptane **9** as a single diastereomer. The ring enlargement products were received as a mixture difficult to separate by simple chromatographic means in variable yields ranging from 10 to 26% for **8** and from 20 to 32% for **9**, respectively.[8]

However, the sulfoxides **10** (mixture of diastereomers) were obtained analytically pure after oxidation of **9** with *m*-CPBA followed by chromatography on silica gel. A procedure that also allowed the isolation of **8** effectively. Furthermore treatment of the received reaction mixture with an excess of *m*-CPBA permitted the isolation of the sulfone **11** in high yields after crystallisation from $CHCl_3$/pentane (colourless plates, mp 95°C).

The structural assignment of **11** having a *cis*-fused bicyclo[3.2.0]heptane framework with an *endo*-oriented acetyl group at C-2 was unambiguously revealed by the X-ray crystal structure analysis (Fig. 1)[9] and 2D NMR spectroscopy (Table 1).

The S atom is tetrahedrally bonded to two C and O atoms with tetrahedral angles ranging from 107.18(8) to 108.01(8)° with exception of the O–S–O angle which is 118.14(9)°. The five-membered ring shows an envelop conformation (dihedral angle between least squares plane

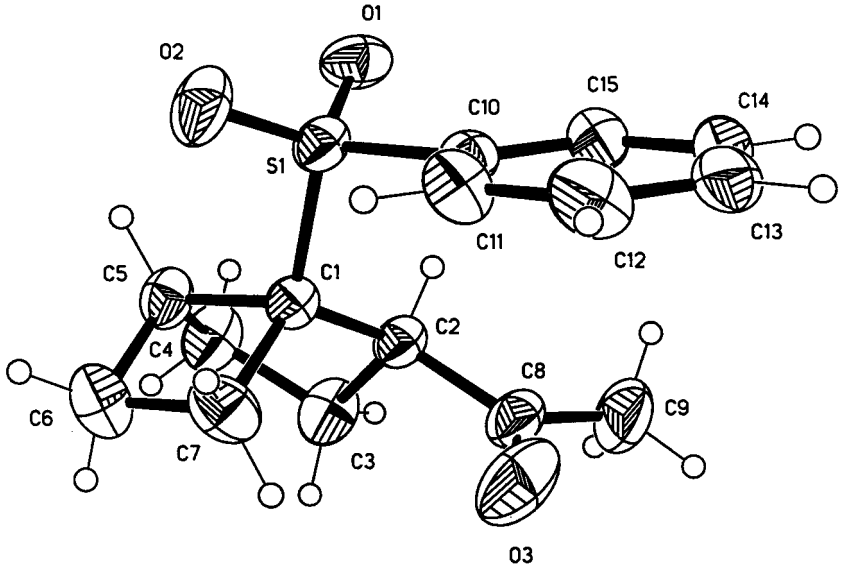


Figure 1. Molecular structure of **11**. Selected bond lengths [Å] and angles [°]: C1–C2 1.534(2), C1–C5 1.575(2), C1–C7 1.551(2), C2–C3 1.550(3), C3–C4 1.528(3), C4–C5 1.522(3), C5–C6 1.530(3), C6–C7 1.528(3); C2–C1–C5 106.13(12), C2–C1–C7 119.29(14), C7–C1–C5 89.22(14), C1–C2–C3 103.01(14), C2–C3–C4 103.3(2), C3–C4–C5 104.7(2), C4–C5–C1 105.70(14), C1–C5–C6 89.05(14), C5–C6–C7 91.7(2), C6–C7–C1 90.02(14).

Table 1. NMR data of compound **11** (spectra recorded in $CDCl_3$. Assignment based on H,H-COSY, C,H-COSY and DEPT spectra)

Position number	δ^1H (mult.)	J (Hz)	δ^{13}C	DEPT
1	–	–	73.2	s
2	3.38 (dd)	11.5, 6.8	53.7	d
3	2.15 (m), 2.3 (m)	–	30.5	t
4	1.63 (m)[a]	–	30.9	t
5	3.35 (m)	–	43.1	d
6	1.50 (m), 2.05 (m)	–	20.7	t
7	2.30 (m), 2.50 (m)	–	20.9	t
8	–	–	207.1	s
9	2.11 (s)	–	31.2	q
10	–	–	136.9	s
11	7.92 (dd)	8.2, 1.7	129.3	d
12	7.57 (dd)	8.2, 7.4	129.1	d
13	7.67 (tt)	7.4, 1.7	133.8	d

[a] Overlapping signals.

C2/C3/C4 and C1/C2/C4/C5 of 40.3°). The four-membered ring is planar and making a dihedral angle of 60.6° with the best least squares plane through C1/C2/C4/C5 of the five membered ring. All bond parameters are in good agreement with the structure of 2,5-dimethyl-1-(phenylsulfonyl)bicyclo[3.2.0]heptane-2,3-diol, published by Zuckerman-Schpector and Monteiro.[10]

The formation of the product **9** may be best explained by a tandem reaction[11] sequence implying as final step the intramolecular addition of an in situ formed enol as carbon nucleophile to the α-thiocarbocation generated during the anticipated cyclopropylcarbinyl-cyclobutyl ring expansion. Indeed the formation of an enol and likewise a ketone moiety via the hydration of the acetylene unit of **7** followed by a desilylation step seems to be likely under the reaction conditions employed.

Further support for the suggested tandem reaction sequence was gained from the acid catalysed ring-enlargement-annulation reaction of ketone **13** (Scheme 3). The latter was obtained from **7** by desilylation to **12** followed by the careful hydration of the acetylene unit with mercury(II) acetate and *p*-toluenesulfonic acid monohydrate in THF at 80°C. Under these conditions a rearrangement of the cyclopropylcarbinol moiety was not observed.

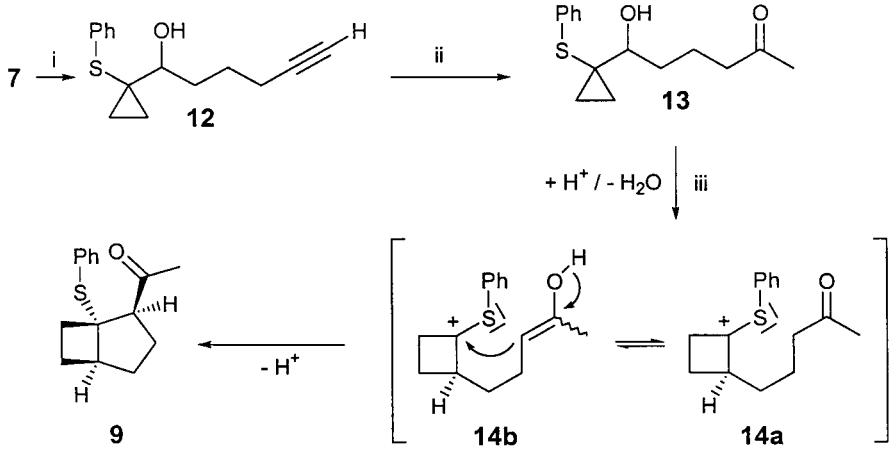
Gratifyingly, when ketone **13** was subjected to the reaction condition operable for the rearrangement of **7** to **8** and **9** ($TsOH{\cdot}H_2O$, wet benzene, 70–80°C) the annulative ring enlargement product **9** was now obtained in 89% yield.[11] Importantly, this conversion was accomplished with complete diastereoselectivity, establishing three contiguous stereocenters in a single step. The fact that **9** was received as a single product and no cyclobutanone formation was observed indicated that the intramolecular reaction of the enol unit in **14b** with the α-thiocarbocation—generated through the ring expansion process starting with the protonation of **13**—must have been orders of magnitude faster than the competitive hydrolysis of the α-thiocarbocation in **14a/14b**.

In conclusion we have found a novel diastereoselective tandem ring-enlargement–annulation reaction sequence that is mediated by the strong directional power of the phenylthio group and its aptitude to stabilise an adjacent cationic centre sufficiently for further annulative carbon–carbon bond forming processes. If this novel tandem reaction is suitable for the rapid assembly of more functionalised *cis*-fused bicyclo[3.2.0]-frameworks as found in natural products like kelsoene[12] and poduran,[13] has to be determined in future applications.

Experimental

General procedures

Reactions requiring anhydrous conditions were performed using flame-dried glassware and conducted under an atmosphere of nitrogen. Anhydrous solvents were prepared in accordance with standard protocols. Compounds were purified by chromatography on silica gel 60 (63–230 mesh). Melting points were measured on a Büchi melting-point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer 16PC. Spectra were recorded as thin films or in KBr pellets.



Scheme 3. *Reagents and conditions*: (i) K_2CO_3, MeOH, 20°C (77%); (ii) $TsOH{\cdot}H_2O$ (1 equiv.), $Hg(OAc)_2$ (0.3 equiv.), THF, 80°C (62%); (iii) $TsOH{\cdot}H_2O$ (1 equiv.), benzene, 70–80°C (89%).

NMR spectra were recorded in $CDCl_3$ as solvent on Bruker AMX 400 and Bruker AC 200 spectrometers with either TMS or solvent as internal reference; *J*-values are given in Hz with an accuracy of ±0.2. Assignments were supported by DEPT spectra and in the case of **11** by 2D NMR experiments. Elemental analyses were carried out on a Perkin–Elmer EA 240 elemental analyser and on a Perkin–Elmer 2400 CHN elemental analyser. Mass spectra were recorded under EI conditions on a Finnigan MAT 90 spectrometer.

6-(Trimethylsilyl)-5-hexyn-1-ol. 5-Hexyn-1-ol (**6**) (20 g, 0.2 mol) was added to a solution of *n*-BuLi (294 mL, 1.5 M solution in hexane) in THF (400 mL) at −78°C. The solution was allowed to warm to −20°C and was stirred for 30 min. After addition of Me_3SiCl (54 g, 0.5 mol) at −78°C the mixture was allowed to warm to room temperature during 4 h. Then 5% acetic acid (480 mL) was added and the mixture was stirred vigorously for 1 h at room temperature, concentrated and extracted with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. The diethyl ether solution was concentrated in vacuo and was purified via vacuum distillation to afford 6-(trimethylsilyl)-5-hexyn-1-ol (32.6 g, 96%) as a colourless oil, bp: 80–90°C/0.1 mmHg; IR (film): ν 3345, 2957, 2900, 2868, 2174, 1457, 1452, 1436, 1430, 1046 cm^{-1}; ^1H NMR (400 MHz): δ=3.65 (2H, t, *J*=6.1 Hz), 2.26 (2H, t, *J*=6.9 Hz), 2.21 (1H, s, OH), 1.59–1.67 (4H, m), 0.14 (9H, s,); ^{13}C NMR (100 MHz): δ=107.1 (s), 84.7 (s), 62.1 (t), 31.6 (t), 24.8 (t), 19.5 (t), 0.04 (q); MS, *m/z* (%): 170 (M^+,1), 169 (2), 168 (2), 167 (12), 153 (3), 125 (5), 111 (9), 96 (12), 75 (100), 73 (40), 59 (11).

6-(Trimethylsilyl)-5-hexyn-1-al. DMSO (8.4 mL, 119.4 mmol) was added to a solution of oxalyl chloride (5.2 mL, 59.5 mmol) in CH_2Cl_2 (200 mL) at −78°C. After 3 min 6-(trimethylsilyl)-5-hexyn-1-ol (8.46 g, 49.5 mmol) was added followed after 15 min by NEt_3 (34.5 mL, 247.4 mmol). The mixture was stirred for 15 min at −78°C and allowed to warm to room temperature. CH_2Cl_2 (200 mL) was added and the reaction mixture was washed with 1 M HCl (100 mL), saturated sodium bicarbonate solution, brine and dried with $MgSO_4$. The resulting solution was concentrated in vacuo and was purified via vacuum distillation to afford 6-(trimethylsilyl)-5-hexyn-1-al (5.44 g, 65%) as a colourless oil, bp: 65–70°C/0.1 mmHg; IR (film): ν 2957, 2174, 1738, 1455, 1435 cm^{-1}; ^1H NMR (400 MHz): δ=9.81 (1H, s), 2.59 (2H, td, *J*=7.1 Hz, *J*=1.0 Hz), 2.30 (2H, t, *J*=7.1 Hz), 1.85 (2H, quint, *J*=7.1 Hz), 0.15 (9H, s); ^{13}C NMR (100 MHz): δ=201.8 (d), 105.8 (s), 85.7 (s), 42.5 (t), 21.1 (t), 19.1 (t), −0.05 (q); MS, *m/z* (%): 169 (M^+, 3), 153 (46), 140 (5), 125 (9), 97 (75), 75 (100), 73 (52).

6-(Trimethylsilyl)-1-(1′-phenylthiocyclopropyl)hex-5-yn-1-ol (7). *n*-BuLi (33 mL, 1.5 M solution in hexane) was added to a stirred solution of cyclopropyl phenyl sulfide (**1**) (7 mL, 0.05 mol) in THF (40 mL) at 0°C. The resulting solution was stirred for 90 min at 0°C and transferred by syringe into a solution of 6-(trimethylsilyl)-5-hexyn-1-al (6.72 g, 0.04 mmol) in THF (40 mL) at −78°C. After the addition was completed the mixture was warmed to room temperature during 30 min, and was kept at room temperature for additional 30 min. Afterwards, brine and diethyl ether were added. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the crude product was purified by column chromatography on silica gel (diethyl ether/hexanes=2:8 (v/v)) to afford **7** (5.81 g, 45%) as a colourless oil. IR (film): ν 3432, 3060, 2957, 2174, 1584, 1480, 1439, 760, 739 cm^{-1}; ^1H NMR (400 MHz): δ=7.46 (2H, d), 7.26 (2H, t), 7.17 (1H, t), 3.25–3.35 (1H, m), 2.21 (2H, t, *J*=6.9 Hz), 1.95 (1H, s, OH), 1.75–1.85 (1H, m), 1.50–1.75 (3H, m), 0.95–1.10 (4H, m), 0.14 (9H, s); ^{13}C NMR (100 MHz): δ=136.3 (s), 129.0 (d), 128.6 (d), 125.9 (d), 107.0 (s), 84.8 (s), 75.6 (d), 33.8 (t), 31.3 (s), 24.9 (t), 19.5 (t), 14.0 (t), 13.9 (t), 0.07 (q); MS, *m/z* (%): 318 (M^+, 14), 285 (2), 272 (4), 149 (25), 91 (23), 75 (37), 73 (100), 45 (5).

2-[5′-(Trimethylsilyl)pent-4′-ynyl]cyclobutanone (8) and bicyclo[3.2.0]*trans*-1-phenylthio-2-aceto-heptane (9). A stirred solution of **7** (2.70 g, 8.48 mmol) and *p*-toluenesulfonic acid monohydrate (1.61 g, 8.46 mmol) in benzene (40 mL) was heated for 2 h under reflux. After cooling to room temperature, saturated sodium bicarbonate solution (40 mL) was added and the organic layer was separated. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with brine and dried with $MgSO_4$. The crude product was purified by column chromatography on silica gel (diethyl ether/hexanes=1:19 (v/v)) to afford a mixture (869 mg) of **9** (2.71 mmol, 32%) and **8** (0.93 mmol, 11%).

2-[5′-(Trimethylsilyl)pent-4′-ynyl]cyclobutanone (8) and bicyclo[3.2.0]*trans*-1-phenylsulfinyl-2-aceto-heptane (10). To the mixture of **8** and **9** in CH_2Cl_2 (40 mL) was added *m*CPBA (576 mg, 3.34 mmol) at −15°C over a period of 3 h. The resulting reaction mixture was washed with saturated sodium bicarbonate solution (30 mL) and brine (30 mL), dried with $MgSO_4$ and evaporated. The obtained residue was chromatographed on silica gel (diethyl ether/hexanes=gradient from 1:19 to 1:1 (v/v)) to afford **8** (172 mm, 86%) as a colourless liquid (bp: 95–105°C/0.1 mmHg) and **10** (541 mg, 76%) as a mixture of diastereomers. **8**: IR (film): ν 2957, 2863, 2173, 1779, 1457 cm^{-1}; ^1H NMR (400 MHz): δ=3.25–3.4 (1H, m), 2.8–3.1 (2H, m), 2.1–2.4 (3H, m), 1.5–1.9 (5H, m), 0.14 (9H, s); ^{13}C NMR (100 MHz): δ=211.7 (s), 106.6 (s), 84.8 (s), 59.9 (d), 44.4 (t), 28.6 (t), 26.0 (t), 19.6 (t), 16.8 (t), 0.0 (q); MS, *m/z* (%): 209 (M^+, 27), 193 (64), 180 (40), 165 (25), 137 (20), 123 (16), 109 (33), 97 (22), 83 (23), 75 (87), 73 (100), 59 (34); Anal. Calcd. for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 68.82; H, 9.71. **10**: ^1H NMR (400 MHz): δ=7.48–7.76 (10H, m), 3.34 (1H, dd, *J*=11.7 Hz, *J*=6.6 Hz), 3.27–3.34 (1H, m), 3.02 (1H, dd, *J*=11.7 Hz, *J*=6.6 Hz), 2.95–3.03 (1H, m), 2.56–2.63 (1H, m), 2.04–2.42 (6H, m), 2.20 (3H, s), 1.90 (3H, s), 1.50–1.60 (4H, m), 1.25–1.41 (2H, m); ^{13}C NMR (100 MHz): δ=207.3, 140.6, 131.3, 131.1, 128.6, 125.5, 124.8, 70.4, 69.9, 53.9, 51.7, 40.8, 39.7, 31.0, 30.6, 30.54, 30.49, 29.7, 29.0, 21.1, 20.91, 20.88, 20.78; Anal. Calcd. for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.39; H, 6.90.

2-[5′-(Trimethylsilyl)pent-4′-ynyl]cyclobutanone (8) and bicyclo[3.2.0]*trans*-1-phenylsulfonyl-2-aceto-heptane (11). To a solution of 547 mg of a mixture of **8** (1.64 mmol) and

9 (0.82 mmol) in CH_2Cl_2 (20 mL) was added *m*CPBA (512 mg, 2.98 mmol) at −15°C. The crude product crystallised overnight and was washed several times with diethyl ether/hexanes=1:19 (v/v). Chromatography on silica gel with diethyl ether/hexanes (gradient from 1:19 to 1:1 (v/v)) afforded **8** (150 mg, 44%) and **11** (220 mg, 96%). Spectroscopic data of **11**: colourless crystals, mp 95°C (from $CHCl_3$–pentane); IR (film): ν 3003, 2951, 2860, 1713, 1443, 1365, 1144, 763, 721 cm^{-1}; ^1H NMR (400 MHz): δ=7.92 (2H, dd, J=8.2 Hz, J=1.7 Hz), 7.67 (1H, tt, J=7.4 Hz, J=1.7 Hz), 7.57 (2H, dd, J=8.2 Hz, J=7.4 Hz), 3.38 (1H, dd, J=11.5 Hz, J=6.8 Hz), 3.35 (1H, m), 2.66 (1H, m), 2.50 (1H, m), 2.30 (1H, m), 2.15 (1H, m), 2.11 (3H, s), 2.05 (1H, m), 1.63 (2H, m), 1.50 (1H, m); ^{13}C NMR (100 MHz): δ=207.1 (s), 136.9 (s), 133.8 (d), 129.3 (d), 129.1 (d), 73.2 (s), 53.7 (d), 43.1 (d), 31.2 (q), 30.9 (t), 30.5 (t), 20.9 (t), 20.7 (t); MS, *m*/*z* (%) 278 (M^+, 2), 259 (1), 137 (34), 93 (46), 77 (21), 43 (100); Anal. Calcd. for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.72; H, 6.46.

1-(1′-Phenylthiocyclopropyl)hex-5-yn-1-ol (12). Potassium carbonate (0.32 g, 2.32 mmol) was added to a stirred solution of **7** (1.52 g, 4.77 mmol) in methanol (26 mL) at 20°C. After 24 h another portion of potassium carbonate (0.16 g, 1.16 mmol) was added. After 24 h the reaction mixture was purified by column chromatography on silica gel (diethyl ether/hexanes=2:8 (v/v)) to afford **12** (0.91 g, 77%) as colourless oil. IR (film): ν 3424, 3297, 3075, 3059, 3004, 2948, 2866, 2115, 1583, 1479, 1455, 1439, 1384, 1328, 1304, 1247, 1156, 1088, 1072, 1025, 968, 740, 692, 637 cm^{-1}; MS, *m*/*z* (%): 246 (M^+, 39), 179 (13), 161 (24), 149 (81), 135 (29), 117 (91), 110 (52), 91 (71), 77 (34), 69 (34), 41 (100), 39 (46); Anal. Calcd. for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 72.73; H, 7.27.

6-Hydroxy-6-(1-phenylthiocyclopropyl)-hexan-2-one (13). A stirred solution of **12** (162 mg, 0.656 mmol), *p*-toluenesulfonic acid monohydrate (130 mg, 0.68 mmol) and mercury(II) acetate (60 mg, 0.19 mmol) in THF (20 mL) was heated for 1 h under reflux. After cooling to room temperature the mixture was partitioned between diethyl ether (20 mL) und saturated sodium bicarbonate solution (15 mL). The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried with $MgSO_4$ and purified by column chromatography on silica gel (diethyl ether/hexanes=3:7 (v/v)) to afford **13** (108 mg, 62%) as colourless oil. ^1H NMR (200 MHz): δ=7.45 (2H, d), 7.11–7.29 (3H, m), 3.32 (1H, d), 2.42 (2H, t, J=6.5 Hz), 2.20 (1H, br s, OH), 2.10 (s, 3H), 1.43–1.79 (4H, m), 0.91–1.09 (4H, m); ^{13}C NMR (50 MHz): δ=209.1 (s), 136.3 (s), 129.1 (d) 128.7 (d) 126.0 (d), 75.7 (d), 43.3 (t), 34.4 (t), 31.1 (s), 29.8 (q), 20.2 (t), 13.9 (t) 13.6 (t); MS, *m*/*z* (%): 264 (M^+, 15), 246 (9), 188 (31), 178 (100), 150 (26), 115 (41), 97 (23), 77 (13), 71 (30), 43 (65).

Bicyclo[3.2.0]*trans*-1-phenylthio-2-aceto-heptane (9). A stirred solution of **13** (48 mg, 0.181 mmol) and *p*-toluenesulfonic acid monohydrate (40 mg, 0.21 mmol) in benzene (10 mL) was heated for 45 min under reflux. After cooling to room temperature, saturated sodium bicarbonate solution (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with brine and dried with $MgSO_4$ to afford **9** (40 mg, 89%). An analytical pure sample was obtained after column chromatography on silica using diethyl ether/hexanes=1:9 (v/v) as eluent. IR (film): ν 3058, 2955, 2857, 1704, 1583, 1474, 1438, 1360, 1300, 1274, 1245, 1211, 1185, 1161, 1129, 1068, 1025, 948, 902, 749, 695 cm^{-1}; ^1H NMR (200 MHz): δ=7.52 (2H, d), 7.31–7.39 (3H, m), 2.98–3.04 (1H, m), 2.87 (1H, dd, J=11.7 Hz, J=6.6 Hz), 1.96–2.45 (5H, m), 2.27 (3H, s), 1.75–1.89 (1H, m), 1.38–1.59 (2H, m); ^{13}C NMR (50 MHz): δ=208.5 (s), 134.9 (d), 133.3 (s), 128.9 (d), 128.4 (d), 58.7 (d), 58.4 (s), 47.9 (d), 31.9 (q), 30.4 (t), 27.3 (t), 26.4 (t), 20.8 (t); MS, *m*/*z* (%): 246 (M^+, 45), 218 (73), 203 (32), 137 (17), 110 (66), 109 (35), 93 (27), 91 (22), 77 (21), 65 (11), 43 (100); Anal. Calcd. for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C 72.92; H, 7.17.

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8. Yields were determined by NMR data from the mixture of **8** and **9**.

9. Crystal data for **11**: $C_{15}H_{18}O_3S$, M=278.35, T=293(2) K, triclinic, space group $P\bar{1}$, a=8.374(2), b=8.469(2), c=10.889(2) Å,

α=100.39(3)°, β=99.88(3)°, γ=106.01(3)°, V=709.8(2) Å^3, Z=2, D_c=1.302 g cm^{-3}, μ=0.229 mm^{-1}, reflections collected=5479, independent reflections=2537 (R_{int}=0.0250), reflections with $I \geq 2\sigma(I) = 2280$, final R indices $[I > 2\sigma(I)]$: $R1$=0.0411, **wR**2=0.1095, final $R1$=0.0459, $wR2$=0.1147 for all data. The crystal structure of **11** was solved by direct methods, SHELXS-86 (Sheldrick, G. M., University of Göttingen, 1990), and refined by full-matrix least squares method on F^2 using SHELXL-93 (Sheldrick, G. M., University of Göttingen, 1993). Data were corrected for Lorentz and polarisation effects but not for absorption. All hydrogen atoms were included on calculated positions with isotropic thermal parameters 20% larger than the atom to which they were attached. The nonhydrogen atoms were refined anisotropically. Crystallographic data of **11** were deposited with the Cambridge Crystallographic Data Centre. CCDC reference number: 144016.

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