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Synthesis of 2,3-Dihydrothiopyran-4-ones from 3-Oxo-1-pentene-4-ynes

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Summary. 3-Oxo-1-pentene-4-ynes were converted with sodium sulfide or hydrogensulfide to give 2,6-disubstituted 2,3-dihydrothiopyran-4-one derivatives. The starting materials were prepared in two steps from terminal alkynes and α,β-unsaturated aldehydes.

Keywords. Alkynes; Cyclizations; Enones; Heterocycles; Sulfur compounds.

Introduction

Successful drug development is dependent on the availability of heterocyclic building blocks with a specific substitution pattern. Of particular importance are compounds comprising aromatic and heteroaromatic side chains with the need for a broad variety of substituents. Moreover, in late stages of screening and optimization a scalable access to the intermediates is desirable. In the course of a search program with a background in medicinal chemistry we required 2,3-dihydrothiopyran-4-ones **2** with different aromatic substituents in the 2- and 6-positions (Scheme 1). Heterocycles of this type are known [1] and have been applied in organic synthesis related to electronic applications [2]. They have so far been accessed by oxidation of saturated tetrahydro-congeners **1** by halogenation-dehalogenation sequences with various chlorinating [3] and fluorinating reagents [4]. However, these oxidation reactions were reported to proceed without any significant regioselectivity, thus, only symmetrically substituted compounds **2** with $R = R'$ have been reported in the literature so far. Therefore, we envisioned ring closure of enynones **3** with sulfide in order to access our target structures **2** with $R \neq R'$. This concept was successfully applied in the literature in order to prepare tetrahydrothiopyran-4-ones **1** from divinylketones [5]. 4*H*-Thiopyran-4-ones have been similarly accessed

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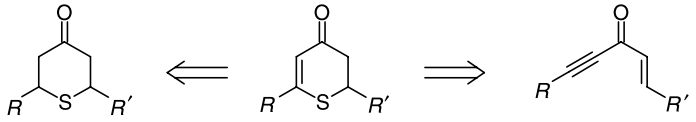


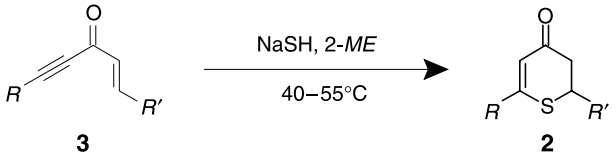
Scheme 1

before from dialkynylketones [6], however, analogous cyclization of alkynylvinylketones **3** has not been reported before.

Results and Discussion

Ring Closure with Sulfide

Model compound **3a** with $R = R' = Ph$ was first tested in order to evaluate reaction conditions for the ring closure by double thia-*Michael* reaction (Scheme 2). It turned out that the result of these conjugate additions was highly dependent on the solvent used. Two procedures have been identified to give satisfying results: method A applied an excess of $Na_2S \cdot 9H_2O$ as source of the nucleophile and a



Scheme 2

Table 1. Ring closure by double conjugate additions; Method A: $Na_2S \cdot 9H_2O$, *THF*/H_2O; Method B: $NaSH \cdot 1.2H_2O$, 2-*ME*

Starting material	*R*	*R′*	Method, *t*/h, *T*/°C	Yield/%
3a	*Ph*	*Ph*	A, 72, 23	94 (**2a**)
3b	3,4-(*Me*O)$_2$C$_6$H$_3$–	*Ph*	B, 2, 50; 14, 23	96 (**2b**)
3c	3-*Et*O-4-*Me*OC$_6$H$_3$–	*Ph*	B, 4, 40; 16, 23	92 (**2c**)
3d	2-CF$_3$C$_6$H$_4$–	*Ph*	B, 8, 40; 15, 23	84 (**2d**)
3e	2,4-F$_2$C$_6$H$_3$–	*Ph*	A, 5, 55; 3, 23	65 (**2e**)
			B, 3, 55;	43 (**2e**)
3f	2-thienyl	*Ph*	B, 18, 40	81 (**2f**)
3g	2-pyridyl	*Ph*	B, 2, 50	60 (**2g**)
3h	*t-Bu*	*Ph*	B, 16, 50	85 (**2h**)
3i	*TMS*, H[a]	*Ph*	A, 10, 55; 10, 23	34 (**2i**)
			B, 3, 60	70 (**2i**)
3j	3,4-(*Me*O)$_2$C$_6$H$_3$–	H	B, 2, 50; 14, 23	36 (**2j**)
3k	3-*Et*O-4-*Me*OC$_6$H$_3$–	H	B, 3, 50; 2, 23	16 (**2k**)
3l	2,4-F$_2$C$_6$H$_3$–	H	A, 3, 55	8 (**2l**)

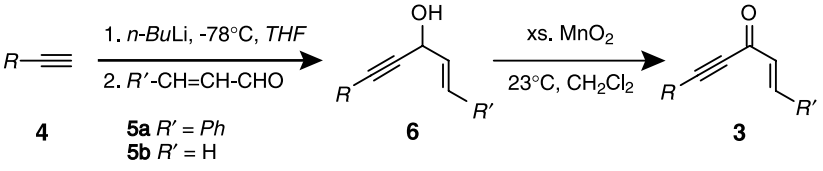
[a] The $R = TMS$ group in starting material **3i** is lost under reaction conditions, $R = H$ in product **2i**

mixture of *THF* and water (1:1) as solvent. Full conversion is achieved after 72 h at ambient temperature. Superior, however, is method B, which applied an excess of NaSH-hydrate as reagent. The solvent is 2-methoxyethanol (2-*ME*) in this case full conversion is achieved by stirring first for 4–16 h at 40–55°C, and then for a few hours at ambient temperature. After aqueous workup, the racemic products were purified by column chromatography (SiO_2). Results and reaction conditions for different starting materials are summarized in Table 1.

The yields of derivatives with $R' = Ph$ (**2a**–**2i**) range from satisfying (60% for **2g**) to excellent (96% for **2b**). For $R = Ph$ (**2a**) and electron rich aromatics (**2b** and **2c**) yields are reaching 90%. Substrates with electron deficient phenyl residues (**2d** and **2e**), electron rich (**2f**) and poor heteroaryl residues (**2g**) and aliphatic substituents (**2h**) gave yields from 60 to 85%. The $R = TMS$ group in starting material **3i** is lost under reaction conditions, presumably due to the strong nucleophilicity of sulfide. Product **2i** is unsubstituted in the 6-position ($R = H$). Yields for compounds **2j**–**2l** without a substituent in the 2-position are not satisfying at all (8–36%). This might actually originate from the low stability of the respective starting materials **3j**–**3l**, which decompose under reaction as well as ambient conditions (see below).

Synthesis of 3-Oxopentenynes

Enynones **3** (Scheme 3) were prepared starting from a series of terminal alkynes **4** by deprotonating them with one equivalent of *n-Bu*Li in *THF* and converting them further with cinnamaldehyde **5a** or acroleine **5b**. After aqueous workup and



Scheme 3

Table 2. Preparation of enynones **3** from alkynes **1** in two steps

Alkyne	Aldehyde	Yield alcohol %	Yield ketone %
4a, $R = Ph$	**5a**, $R' = Ph$	89 (**6a**)	96 (**3a**)
4b, $R = 3,4\text{-}(MeO)_2C_6H_3$–	**5a**, $R' = Ph$	90 (**6b**)	84 (**3b**)
4c, $R = 3\text{-}EtO\text{-}4\text{-}MeOC_6H_3$–	**5a**, $R' = Ph$	79 (**6c**)	99 (**3c**)
4d, $R = 2\text{-}CF_3C_6H_4$–	**5a**, $R' = Ph$	78 (**6d**)	99 (**3d**)
4e, $R = 2,4\text{-}F_2C_6H_3$–	**5a**, $R' = Ph$	66 (**6e**)	99 (**3e**)
4f, $R = 2$-thienyl	**5a**, $R' = Ph$	51 (**6f**)	99 (**3f**)
4g, $R = 2$-pyridyl	**5a**, $R' = Ph$	92 (**6g**)	75 (**3g**)
4h, $R = t\text{-}Bu$	**5a**, $R' = Ph$	85 (**6h**)	99 (**3h**)
4i, $R = TMS$	**5a**, $R' = Ph$	98 (**6i**)	97 (**3i**)
4b, $R = 3,4\text{-}(MeO)_2C_6H_3$–	**5b**, $R' = H$	71 (**6j**)	77 (**3j**)
4c, $R = 3\text{-}EtO\text{-}4\text{-}MeOC_6H_3$–	**5b**, $R' = H$	67 (**6k**)	62 (**3k**)
4e, $R = 2,4\text{-}F_2C_6H_3$–	**5b**, $R' = H$	71 (**6l**)	99 (**3l**)

chromatographic purification the racemic allylic alcohols **6** were obtained, which were subsequently oxidized with an excess (10–30 eq.) of MnO_2 at 23°C in CH_2Cl_2. The progress of this reaction was followed by TLC. After full conversion was achieved (5–30 min), manganese containing materials were simply removed by filtration to yield the double *Michael* acceptors **3**, which were in most cases analytically pure without further purification. Yields for both steps are generally very good, in some cases even quantitative (Table 2). Alcohols **6a**–**6i** and ketones **3a**–**3i** originating from cinnamaldehyde **5a** ($R' = Ph$) are exclusively obtained with the C–C double bond in *E*-configuration. Whereas vinylketones **3a**–**3i** with $R' = Ph$ show reasonable stability, their congeners **3j**–**3k** deriving from acroleine ($R' = H$) tend to decompose within an hour at ambient conditions and can not even be stored at lower temperatures and must therefore be further converted directly after filtration.

Experimental

General Methods

Procedures using *n-Bu*Li were performed in flame dried glassware and with absolute *THF* under an atmosphere of nitrogen. Acroleine (**5a**) was freshly distilled prior to use. MnO_2 (activated) was used as received from Fluka. *n-Bu*Li ($c = 1.6$ or $2.0\,M$ in pentane), $NaSH \cdot 1.2H_2O$ (72% NaSH, $M = 77.68\,g\,mol^{-1}$), and alkynes **4a**, **4d**, **4e**, **4g**, **4h**, **4i** were purchased from the Aldrich Chemical Company. Alkynes **4b** [7] and **4f** [8] were prepared from the corresponding aryl aldehydes according to literature procedures. Alkyne **4c** was prepared from 3-ethoxy-4-methoxybenzaldehyde (Aldrich) by adopting the procedure reported for **4b** [7]. Column chromatography was carried out using Merck SiO_2 60 with hexanes (*PE*, bp 40–60°C) and ethyl acetate (*EA*) as eluents. ^{1}H NMR spectra were recorded on a Bruker ARX 500 (500 MHz), Bruker ARX 300 (300 MHz), or a Bruker AC 250 (250 MHz). ^{13}C NMR spectra were recorded on a Bruker ARX 500 (125 MHz), a Bruker ARX 300 (75 MHz), or a Bruker AC 250 (62 MHz). Multiplicities were determined with DEPT experiments. Melting points were measured on a Büchi 510. Elemental analyses were carried out with a Analytik Jena Vario EL and their results agreed favourably with calculated values.

*General Procedure for the Synthesis of Alcohols **6***

A solution if *n-Bu*Li (1 eq.) was dropwise added under an atmosphere of N_2 and at −78°C to a solution of arylacetylene **4** (1 eq.) in abs. *THF* (*ca.* $2\,dm^3\,mol^{-1}$) and the resulting mixture was stirred for 90 min at −78°C. Then aldehyde **5** (1.1–1.5 eq.) was added and stirring at −78°C continued for 90 min. Saturated, aqueous NH_4Cl solution (*ca.* $5\,dm^3\,mol^{-1}$) was added, and the aqueous phase was extracted once with CH_2Cl_2 (*ca.* $5\,dm^3\,mol^{-1}$). The combined organic layers were dried ($MgSO_4$) and after filtration evaporated. The residue was chromatographed on SiO_2 (*PE*/*EA*) to give alcohols **6**.

(E)-3-Hydroxy-1,5-diphenyl-4-penten-1-yne (**6a**, $C_{17}H_{14}O$)

Alkyne **4a** (1.00 g, 9.79 mmol), *n-Bu*Li (7.35 cm^3, 11.8 mmol, $c = 1.6\,M$), and aldehyde **5a** (3.70 cm^3, 29.4 mmol) were converted according to the general procedure to yield the title compound **6a** (2.04 g, 89%) after chromatography (*PE*/*EA* = 5/1, $R_f = 0.26$) as a colorless solid, mp 65–67°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.13$ (d, $J = 4.8$ Hz, 1H), 5.29 (s, 1H), 6.38 (dd, $J = 15.8$, 6.1 Hz, 1H), 6.84 (d, $J = 15.7$ Hz, 1H), 7.25–7.49 (m, 10H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 63.37$ (CH), 86.38 (C), 87.96 (C), 122.35 (C), 126.78 (2CH), 128.01 (CH), 128.05 (CH), 128.27 (2CH), 128.55 (3CH), 131.71 (2CH), 131.95 (CH), 136.06 (C) ppm; IR (ATR): $\bar{\nu} = 3394$ (m), 3024 (m), 2232 (m), 1597 (m), 1489 (s), 1443 (m), 1398 (m), 1232 (m), 1092 (m), 1070 (m), 1028 (m), 1013 (s), 996 (s), 965 (s), 914 (m), 753 (s), 728 (m), 687 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 234 (73) [M$^+$], 215 (47), 204 (42), 157 (14), 129 (100), 115 (38), 104 (47), 102 (78), 91 (56), 77 (54).

(E)-1-(3,4-Dimethoxyphenyl)-3-hydroxy-5-phenyl-4-penten-1-yne (**6b**, $C_{19}H_{18}O_3$)
Alkyne **4b** (1.00 g, 6.17 mmol), *n-Bu*Li (3.1 cm^3, 6.2 mmol, $c = 2.0\,M$), and aldehyde **5a** (1.2 cm^3, 9.2 mmol) were converted according to the general procedure to yield the title compound **6b** (1.64 g, 90%) after chromatography ($PE/EA = 2/1$, $R_f = 0.26$) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.58$ (br, s, 1H), 3.85 (s, 3H), 3.87 (s, 3H), 5.27 (d, $J = 5.6$ Hz, 1H), 6.38 (dd, $J = 15.8$, 6.0 Hz, 1H), 6.78 (d, $J = 8.3$ Hz, 1H), 6.80 (d, $J = 15.9$ Hz, 1H), 6.98 (d, $J = 1.8$ Hz, 1H), 7.07 (dd, $J = 8.3$, 1.8 Hz, 1H), 7.25–7.44 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 55.87$ (OCH_3), 55.88 (OCH_3), 63.47 (CH), 86.38 (C), 86.59 (C), 110.94 (CH), 114.43 (CH), 114.55 (C), 125.08 (CH), 126.80 (2CH), 128.08 (CH), 128.32 (CH), 128.61 (2CH), 131.78 (CH), 136.15 (C), 148.57 (C), 149.67 (C) ppm; IR (ATR): $\bar{\nu} = 1513$ (s), 1265 (m), 1243 (m), 1023 (m) cm^{-1}; HR-MS (EI, 70 eV): m/z (%) = 294.1255 (100) [M^+], calcd 294.1256 (for $C_{19}H_{18}O_3$).

(E)-1-(3-Ethoxy-4-methoxyphenyl)-3-hydroxy-5-phenyl-4-penten-1-yne (**6c**, $C_{20}H_{20}O_3$)
Alkyne **4c** (500 mg, 2.84 mmol), *n-Bu*Li (1.5 cm^3, 3.0 mmol, $c = 2.0\,M$), and aldehyde **5a** (420 mg, 3.18 mmol) were converted according to the general procedure to yield the title compound **6c** (688 mg, 79%) after chromatography ($PE/EA = 2/1$, $R_f = 0.29$) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.45$ (t, $J = 7.0$ Hz, 3H), 2.35 (br, s, 1H), 3.87 (s, 3H), 4.07 (q, $J = 7.0$ Hz, 2H), 5.27 (dd, $J = 5.7$, 0.9 Hz, 1H), 6.38 (dd, $J = 15.8$, 6.0 Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 6.80 (br, d, $J = 16$ Hz, 1H), 6.97 (d, $J = 1.8$ Hz, 1H), 7.06 (dd, $J = 8.3$, 1.8 Hz, 1H), 7.24–7.28 (m, 1H), 7.30–7.34 (m, 2H), 7.40–7.43 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 14.72$ (CH_3), 55.91 (OCH_3), 63.51 (CH), 64.34 (OCH_2), 86.39 (C), 86.54 (C), 111.18 (CH), 114.45 (C), 115.74 (CH), 125.02 (CH), 126.81 (2CH), 128.09 (CH), 128.31 (CH), 128.61 (2CH), 131.83 (CH), 136.15 (C), 147.91 (C), 149.98 (C) ppm; IR (ATR): $\bar{\nu} = 1598$ (m), 1577 (m), 1510 (s), 1441 (m), 1416 (m), 1395 (m), 1319 (m), 1290 (m), 1261 (s), 1240 (s), 1198 (m), 1174 (m), 1136 (m), 1025 (s), 966 (m), 809 (m), 752 (m), 696 (m) cm^{-1}; HR-MS (EI, 70 eV): m/z (%) = 308.1413 (100) [M^+], calcd 308.1412 (for $C_{20}H_{20}O_3$).

(E)-3-Hydroxy-5-phenyl-1-(2-trifluoromethylphenyl)-4-penten-1-yne (**6d**, $C_{18}H_{13}F_3O$)
Alkyne **4d** (500 mg, 2.94 mmol), *n-Bu*Li (1.55 cm^3, 3.1 mmol, $c = 2.0\,M$), and aldehyde **5a** (430 mg, 3.25 mmol) were converted according to the general procedure to yield the title compound **6d** (690 mg, 78%) after chromatography ($PE/EA = 2/1$, $R_f = 0.49$) as a light yellow crystals, mp 79–80°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.15$ (d, $J = 3.4$ Hz, 1H), 5.30 (br, s, 1H), 6.39 (dd, $J = 15.8$, 5.7 Hz, 1H), 6.90 (dd, $J = 15.8$, 0.9 Hz, 1H), 7.23–7.36 (m, 3H), 7.38–7.54 (m, 4H), 7.60–7.70 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 63.43$ (s, CH), 82.52 (s, C), 93.43 (s, C), 120.67 (q, $^3J = 2.2$ Hz, C), 123.52 (q, $^1J = 273.5$ Hz, C), 125.88 (q, $^3J = 5.1$ Hz, CH), 126.88 (s, 2CH), 127.35 (s, CH), 128.19 (s, CH), 128.41 (s, CH), 128.64 (s, 2CH), 131.46 (s, CH), 131.66 (q, $^2J = 30.6$ Hz, C) 132.51 (s, CH), 134.16 (s, CH), 136.08 (s, C) ppm; IR (ATR): $\bar{\nu} = 3272$ (br, m), 1489 (m), 1449 (m), 1315 (s), 1265 (m), 1160 (s), 1107 (s), 1052 (m), 1010 (m), 965 (s), 906 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 302 (15) [M^+], 274 (7), 233 (100), 215 (12), 197 (26), 170 (26), 151 (10), 115 (9), 104 (18), 91 (15), 77 (9).

(E)-1-(2,4-Difluorophenyl)-3-hydroxy-5-phenyl-4-penten-1-yne (**6e**, $C_{17}H_{12}F_2O$)
Alkyne **4e** (500 mg, 3.62 mmol), *n-Bu*Li (1.8 cm^3, 3.6 mmol, $c = 2.0\,M$), and aldehyde **5a** (530 mg, 4.02 mmol) were converted according to the general procedure to yield the title compound **6e** (642 mg, 66%) after chromatography ($PE/EA = 2/1$, $R_f = 0.50$) as light yellow crystals, mp 64–66°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.82$ (br, s, 1H), 5.29 (d, $J = 5.6$ Hz, 1H), 6.36 (dd, $J = 15.8$, 6.0 Hz, 1H), 6.81 (t, $J = 8.2$ Hz, 1H), 6.83 (d, $J = 15.6$ Hz, 1H), 6.84 (d, $J = 1.9$ Hz, 1H), 7.21–7.45 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 63.41$ (s, CH), 78.88 (s, C), 93.03 (s, C), 104.31 (t, $^2J = 25.8$ Hz, CH), 107.40 (dd, $^2J = 15.9$ Hz, $^4J = 4.0$ Hz, C), 111.63 (dd, $^2J = 21.9$ Hz, $^4J = 3.8$ Hz, CH), 126.91 (s, 2CH), 127.62 (s, CH), 128.23 (s, CH), 128.67 (s, 2CH), 132.37 (s, CH), 134.53

(dd, $^3J = 9.7$ Hz, $^3J = 2.6$ Hz, CH), 136.05 (s, C), 162.91 (dd, $^1J = 252$ Hz, $^3J = 11.3$ Hz, C), 163.19 (dd, $^1J = 266$ Hz, $^3J = 10.9$ Hz, C) ppm; IR (ATR): $\bar{\nu} = 1502$ (m), 1424 (m), 1267 (m), 1217 (m), 1140 (m), 1101 (m), 1007 (m), 964 (m), 852 (m), 819 (m), 754 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 270 (100) [M^+], 251 (46), 220 (30), 193 (8), 165 (76), 151 (19), 138 (48), 127 (52), 104 (55), 91 (43), 77 (30).

(E)-3-Hydroxy-5-phenyl-1-(2-thienyl)-4-penten-1-yne (**6f**, $C_{15}H_{12}OS$)
Alkyne **4f** (345 mg, 3.19 mmol), *n-Bu*Li (1.6 cm^3, 3.2 mmol, $c = 2.0\,M$), and aldehyde **5a** (422 mg, 3.19 mmol) were converted according to the general procedure to yield the title compound **6f** (390 mg, 51%) after chromatography ($PE/EA = 2/1$, $R_f = 0.45$) as a light yellow crystals, mp 77–79°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.28$ (d, $J = 6.2$ Hz, 1H), 5.27 (dd, $J = 6.2$ Hz, $J = 0.9$ Hz, 1H), 6.35 (dd, $J = 15.8$, 6.1 Hz, 1H), 6.79 (d, $J = 15.8$ Hz, 1H), 6.97 (dd, $J = 5.1$, 3.8 Hz, 1H), 7.24–7.27 (m, 3H), 7.31–7.33 (m, 2H), 7.40–7.42 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 63.56$ (CH), 79.76 (C), 91.73 (C), 122.23 (C), 126.84 (2CH), 126.99 (CH), 127.56 (CH), 127.65 (CH), 128.17 (CH), 128.62 (2CH), 132.18 (CH), 132.53 (CH), 135.99 (C) ppm; IR (ATR): $\bar{\nu} = 1447$ (m), 1270 (m), 1187 (m), 1069 (m), 1002 (s), 962 (s), 835 (m), 752 (s), 690 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 240 (100) [M^+], 211 (79), 197 (17), 178 (43), 156 (19), 135 (72), 108 (83), 97 (32).

(E)-3-Hydroxy-5-phenyl-1-(2-pyridyl)-4-penten-1-yne (**6g**, $C_{16}H_{13}NO$)
Alkyne **4g** (500 mg, 4.85 mmol), *n-Bu*Li (2.4 cm^3, 4.8 mmol, $c = 2.0\,M$), and aldehyde **5a** (645 mg, 4.86 mmol) were converted according to the general procedure to yield the title compound **6g** (1.05 g, 92%) after chromatography ($PE/EA = 1/1$, $R_f = 0.25$) as a brown oil, which is crystallizing within a few hours, mp 81–84°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.30$ (br, s, 1H), 5.38 (dd, $J = 6.0$, 1.3 Hz, 1H), 6.40 (dd, $J = 15.8$, 6.0 Hz, 1H), 6.84 (dd, $J = 15.8$, 0.8 Hz, 1H), 7.20–7.35 (m, 4H), 7.36–7.48 (m, 3H), 7.64 (dt, $J = 1.8$, 7.8 Hz, 1H), 8.56 (ddd, $J = 4.9$, 1.7 Hz, 0.9 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 62.92$ (CH), 84.88 (C), 89.17 (C), 123.18 (CH), 126.84 (2CH), 127.34 (CH), 127.84 (CH), 128.01 (CH), 128.57 (2CH), 131.98 (CH), 136.22 (C), 136.44 (CH), 142.66 (C), 149.73 (CH) ppm; IR (ATR): $\bar{\nu} = 3186$ (br, m), 3057 (m), 1585 (s), 1563 (m), 1494 (m), 1465 (s), 1448 (m), 1429 (s), 1269 (m), 1027 (m), 966 (m), 778 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 235 (8) [M^+], 217 (11), 207 (100), 130 (34), 103 (32), 78 (26).

(E)-6,6-Dimethyl-3-hydroxy-1-phenyl-1-hepten-4-yne (**6h**, $C_{15}H_{18}O$)
Alkyne **4h** (0.950 g, 11.6 mmol), *n-Bu*Li (5.8 cm^3, 11.6 mmol, $c = 2.0\,M$), and aldehyde **5a** (1.55 g, 11.7 mmol) were converted according to the general procedure to yield the title compound **6h** (2.11 g, 85%) after chromatography ($PE/EA = 5/1$, $R_f = 0.31$) as a light yellow solid, mp 50–51°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.26$ (s, 9H), 2.00 (d, $J = 5.7$ Hz, 1H), 5.03 (td, $J = 5.3$, 0.8 Hz, 1H), 6.29 (dd, $J = 15.8$, 5.8 Hz, 1H), 6.74 (dd, $J = 15.8$, 1.0 Hz, 1H), 7.24–7.41 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 27.46$ (C), 30.94 ($3CH_3$), 63.08 (CH), 77.57 (C), 95.61 (C), 126.77 (2CH), 127.96 (CH), 128.57 (2CH), 128.92 (CH), 131.41 (CH), 136.28 (C) ppm; IR (ATR): $\bar{\nu} = 3349$ (br, m), 2969 (m), 1492 (m), 1449 (m), 1400 (br, m), 1363 (m), 1260 (m), 1204 (m), 1046 (s), 962 (vs), 867 (m), 751 (s), 693 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 214 (61) [M^+], 199 (97), 165 (24), 157 (39), 141 (15), 128 (27), 109 (54), 104 (100), 91 (66), 81 (32), 77 (39).

(E)-3-Hydroxy-1-phenyl-6-trimethylsilyl-1-penten-4-yne (**6i**, $C_{14}H_{18}OSi$)
Alkyne **4i** (1.09 g, 10.0 mmol), *n-Bu*Li (5.1 cm^3, 10.2 mmol, $c = 2.0\,M$), and aldehyde **5a** (1.35 g, 10.2 mmol) were converted according to the general procedure to yield the title compound **6i** (2.25 g, 98%) after chromatography ($PE/EA = 5/1$, $R_f = 0.41$) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.25$ (s, 9H), 2.15 (d, $J = 4.5$ Hz, 1H), 5.08 (br, t, $J = 4.4$ Hz, 1H), 6.32 (dd, $J = 15.8$, 5.9 Hz, 1H), 6.81 (d, $J = 15.8$ Hz, 1H), 7.29–7.32 (m, 1H), 7.35–7.38 (m, 2H), 7.44–7.45 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 0.00$ ($3CH_3$, TMS), 63.51 (CH), 91.51 (C), 104.37 (C), 126.97 (2CH), 128.01 (CH), 128.27 (CH), 128.76 (2CH), 132.22 (CH), 136.23 (C) ppm; IR (ATR): $\bar{\nu} = 3294$

(br, m), 2958 (m), 1448 (m), 1416 (br, m), 1250 (s), 1091 (m), 1068 (m), 1025 (s), 965 (s), 905 (m), 841 (vs) cm^{-1}; MS (EI, 70 eV): m/z (%) = 230 (38) [M^+], 197 (23), 139 (18), 125 (26), 105 (23), 104 (43), 91 (21).

1-(3,4-Dimethoxyphenyl)-3-hydroxy-4-penten-1-yne (**6j**, $C_{13}H_{14}O_3$)
Alkyne **4b** (1.00 g, 6.17 mmol), *n-Bu*Li (3.1 cm^3, 6.2 mmol, $c = 2.0\,M$), and aldehyde **5b** (520 mg, 9.26 mmol) were converted according to the general procedure to yield the title compound **6j** (950 mg, 71%) after chromatography ($PE/EA = 2{:}1$, $R_f = 0.29$) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.54$ (br, s, 1H), 3.86 (s, 3H), 3.87 (s, 3H), 5.10 (d, $J = 5.4$ Hz, 1H), 5.26 (dt, $J = 10.1$, 1.3 Hz, 1H), 5.52 (dt, $J = 17.0$, 1.3 Hz, 1H), 6.06 (ddd, $J = 17.0$, 10.1, 5.4 Hz, 1H), 6.78 (d, $J = 8.3$ Hz, 1H), 6.94 (d, $J = 1.8$ Hz, 1H), 7.05 (dd, $J = 8.3$, 1.8 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 55.87$ ($2OCH_3$), 63.65 (CH), 86.24 (C), 86.36 (C), 110.92 (CH), 114.39 (CH), 114.54 (C), 116.39 (CH_2), 125.04 (CH), 137.13 (CH), 148.53 (C), 149.62 (C) ppm; IR (ATR): $\bar{\nu} = 1514$ (m), 1266 (m), 1243 (m), 1023 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 218 (100) [M^+], 203 (21), 159 (12), 138 (14), 115 (15), 91 (10).

1-(3-Ethoxy-4-methoxyphenyl)-3-hydroxy-4-penten-1-yne (**6k**, $C_{14}H_{16}O_3$)
Alkyne **4k** (870 mg, 4.94 mmol), *n-Bu*Li (3.0 cm^3, 6.0 mmol, $c = 2.0\,M$), and aldehyde **5b** (350 mg, 6.24 mmol) were converted according to the general procedure to yield the title compound **6k** (770 mg, 67%) after chromatography ($PE/EA = 2/1$, $R_f = 0.36$) as a colorless solid, mp 53–55°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.45$ (t, $J = 7.1$ Hz, 3H), 2.28 (br, s, 1H), 3.87 (s, 3H), 4.07 (q, $J = 7.0$ Hz, 2H), 5.09 (br, s, 1H), 5.26 (d, $J = 10.1$ Hz, 1H), 5.52 (dd, $J = 17.0$, 0.8 Hz, 1H), 6.06 (ddd, $J = 17.0$, 10.1, 5.6 Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 6.95 (br, s, 1H), 7.03 (dd, $J = 8.2$, 0.9 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 14.72$ (CH_3), 55.92 (OCH_3), 63.70 (CH), 64.36 (CH_2), 86.20 (C), 86.39 (C), 111.20 (CH), 114.49 (C), 115.79 (CH), 116.40 (CH_2), 125.00 (CH), 137.15 (CH), 147.91 (C), 149.98 (C) ppm; IR (ATR): $\bar{\nu} = 3293$ (br, m), 2929 (m), 1598 (m), 1510 (s), 1439 (m), 1416 (m), 1393 (m), 1260 (m), 1241 (s), 1199 (m), 1174 (m), 1135 (s), 1021 (br, s), 935 (m), 894 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 232 (100) [M^+], 203 (13), 189 (16), 175 (13), 161 (13), 133 (17), 124 (9), 115 (24).

1-(2,4-Difluorophenyl)-3-hydroxy-4-penten-1-yne (**6l**, $C_{11}H_8F_2O$)
Alkyne **4l** (800 mg, 5.79 mmol), *n-Bu*Li (2.9 cm^3, 5.8 mmol, $c = 2.0\,M$), and aldehyde **5b** (360 mg, 6.42 mmol) were converted according to the general procedure to yield the title compound **6l** (798 mg, 71%) after chromatography ($PE/EA = 2/1$, $R_f = 0.47$) as a colorless solid, mp 30–32°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.11$ (br, s, 1H), 5.13 (d, $J = 5.2$ Hz, 1H), 5.29 (dt, $J = 10.1$, 1.1 Hz, 1H), 5.57 (dt, $J = 17.0$, 1.2 Hz, 1H), 6.07 (ddd, $J = 17.0$, 10.2, 5.3 Hz, 1H), 6.80–6.89 (m, 2H), 7.37–7.47 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 63.66$ (s, CH), 78.85 (s, C), 93.05 (s, C), 104.29 (t, $^2J = 24.9$ Hz, CH), 111.59 (dd, $^2J = 21.9$ Hz, $^4J = 3.7$ Hz, CH), 116.99 (s, CH_2), 134.46 (dd, $^3J = 9.9$ Hz, $^3J = 2.5$ Hz, CH), 136.46 (s, CH) ppm; resonances for carbon atoms C-1′, C-2′, and C-4′ are not observed due to poor signal-to-noise ratio; IR (ATR): $\bar{\nu} = 3317$ (br, m,), 1587 (m), 1500 (s), 1420 (m), 1289 (m), 1262 (s), 1217 (m), 1142 (m), 1095 (m), 1012 (br, m,), 962 (m), 932 (m), 847 (s), 810 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 194 (69) [M^+], 175 (16), 165 (100), 151 (64), 138 (32), 119 (54), 114 (60), 99 (15), 80 (22).

General Procedure for the Synthesis of Ketones ***3***
MnO_2 (up to 30 eq.) was added portionwise to a solution of alcohol **6** (1 eq.) in CH_2Cl_2 (10 $dm^3\,mol^{-1}$) at ambient temperature, until almost quantitative conversion was achieved (5–60 min). The progress of the reaction was monitored by TLC. If no starting material was left, the product started to decompose. The reaction mixture was filtered with vacuum through SiO_2 to separate MnO_2, the residue was washed several times with *EA*. The filtrate was concentrated under vacuum to give ketones **3** in analytically pure form in most cases. If necessary, the products **3** can be purified by chromatography on SiO_2

(*PE*/*EA*). Compounds with $R' = H$ are not stable, not even at low temperatures, and must be converted further directly after filtration and evaporation of the solvent.

(E)-1,5-Diphenyl-3-oxo-4-penten-1-yne (**3a**, $C_{17}H_{12}O$)
Alcohol **6a** (1.00 g, 4.27 mmol) and MnO_2 (4.30 g, 49.5 mmol) were converted according to the general procedure to yield ketone **3a** (952 mg, 96% without chromatography) as a yellow solid, mp 70–72°C. R_f (SiO_2, *PE*/*EA* = 5/1) = 0.39; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.88$ (d, $J = 16.1$ Hz, 1H), 7.41–7.50 (m, 6H), 7.59–7.67 (m, 4H), 7.92 (d, $J = 16.1$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 86.67$ (C), 91.56 (C), 120.28 (C), 128.61 (CH), 128.70 (2CH), 128.72 (2CH), 129.12 (2CH), 130.64 (CH), 131.18 (CH), 132.97 (2CH), 134.14 (C), 148.28 (CH), 178.22 (C=O) ppm; IR (ATR): $\bar{\nu} = 3061$ (m), 2212 (s), 2160 (m), 1626 (s), 1608 (s), 1595 (s), 1571 (s), 1488 (m), 1444 (m), 1311 (m), 1288 (m), 1173 (s), 971 (s), 873 (s), 757 (s), 689 (s), 672 (s), 579 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 232 (55) [M^+], 231 (100), 204 (22), 203 (41), 129 (40), 102 (30), 77 (14).

(E)-1-(3,4-Dimethoxyphenyl)-3-oxo-5-phenyl-4-penten-1-yne (**3b**, $C_{19}H_{16}O_3$)
Alcohol **6b** (500 mg, 1.70 mmol) and MnO_2 (3.20 g, 36.8 mmol) were converted according to the general procedure to yield ketone **3b** (415 mg, 84% after chromatography) as a yellow solid, mp 87–88°C. R_f (SiO_2, *PE*/*EA* = 2/1) = 0.38; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.92$ (s, 3H), 3.94 (s, 3H), 6.88 (d, $J = 16.3$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 7.14 (d, $J = 1.9$ Hz, 1H), 7.31 (dd, $J = 8.3$, 1.9 Hz, 1H), 7.42–7.47 (m, 3H), 7.59–7.63 (m, 2H), 7.89 (d, $J = 16.1$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 56.04$ (OCH_3), 56.08 (OCH_3), 86.39 (C), 92.67 (C), 111.09 (CH), 112.03 (C), 115.33 (CH), 127.28 (CH), 128.56 (2CH), 128.66 (CH), 129.08 (2CH), 131.09 (CH), 134.16 (C), 147.73 (CH), 148.87 (C), 151.57 (C), 178.18 (C=O) ppm; IR (ATR): $\bar{\nu} = 2184$ (m), 1737 (br, w), 1612 (m), 1589 (m), 1511 (m), 1457 (m), 1438 (m), 1228 (m), 1132 (m), 1017 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 292 (100) [M^+], 261 (13), 189 (17), 162 (24).

(E)-1-(3-Ethoxy-4-methoxyphenyl)-3-oxo-5-phenyl-4-penten-1-yne (**3c**, $C_{20}H_{18}O_3$)
Alcohol **6c** (500 mg, 1.62 mmol) and MnO_2 (3.2 g, 37 mmol) were converted according to the general procedure to yield ketone **3c** (495 mg, 99% without chromatography) as a yellow solid, mp 75–76°C. R_f (SiO_2, *PE*/*EA* = 2/1) = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.49$ (t, $J = 7.0$ Hz, 3H), 3.93 (s, 3H), 4.13 (q, $J = 7.0$ Hz, 2H), 6.87 (d, $J = 16.1$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 7.13 (d, $J = 1.8$ Hz, 1H), 7.29 (dd, $J = 8.3$, 1.8 Hz, 1H), 7.42–7.46 (m, 3H), 7.59–7.63 (m, 2H), 7.89 (d, $J = 16.0$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 14.70$ (CH_3), 56.03 (OCH_3), 64.55 (OCH_2), 86.34 (C), 92.84 (C), 111.31 (CH), 111.96 (C), 116.61 (CH), 127.18 (CH), 128.60 (CH), 128.66 (2CH), 129.08 (2CH), 131.06 (CH), 134.20 (C), 147.67 (CH), 148.22 (C), 151.88 (C), 178.19 (C=O) ppm; IR (ATR): $\bar{\nu} = 2181$ (vs), 1627 (s), 1591 (s), 1509 (vs), 1475 (m), 1441 (m), 1418 (m), 1308 (m), 1246 (vs), 1202 (m), 1181 (m), 1154 (m), 1132 (s), 1096 (s), 1041 (m), 1020 (s), 973 (m), 857 (m), 807 (m), 760 (s), 698 (m), 675 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 306 (100) [M^+], 235 (10), 176 (13), 148 (10).

(E)-3-Oxo-5-phenyl-1-(2-trifluoromethylphenyl)-4-penten-1-yne (**3d**, $C_{18}H_{11}F_3O$)
Alcohol **6d** (300 mg, 0.99 mmol) and MnO_2 (870 mg, 10.0 mmol) were converted according to the general procedure to yield ketone **3d** (294 mg, 99% without chromatography) as a yellow solid, mp 52–53°C. R_f (SiO_2, *PE*/*EA* = 2/1) = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.86$ (d, $J = 16.2$ Hz, 1H), 7.42–7.46 (m, 3H), 7.56–7.63 (m, 4H), 7.77 (d, $J = 7.3$ Hz, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 8.03 (d, $J = 16.1$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 86.04$ (s, C), 90.65 (s, C), 118.52 (q, $^3J = 1.8$ Hz, C), 123.40 (q, $^1J = 273.5$ Hz, CF_3), 126.22 (q, $^3J = 5.2$ Hz, CH), 128.49 (s, CH), 128.80 (s, 2CH), 129.14 (s, 2CH), 130.39 (s, CH), 131.36 (s, CH), 131.88 (s, CH), 132.43 (q, $^2J = 30.9$ Hz, C), 134.11 (s, C), 135.78 (s, CH), 149.85 (s, CH), 178.00 (s, C=O) ppm; IR (ATR): $\bar{\nu} = 2213$ (m), 1616 (s), 1595 (s), 1574 (m), 1487 (m), 1447 (m), 1318 (s), 1261 (s), 1154 (s), 1107 (s), 1054 (m), 969 (s), 758 (vs), 690 (m), 653 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%) = 300 (56) [M^+], 299 (67), 272 (18), 251 (47), 231 (100), 203 (25), 197 (18), 169 (28), 102 (14), 77 (10).

(E)-1-(2,4-Difluorophenyl)-3-oxo-5-phenyl-4-penten-1-yne (**3e**, $C_{17}H_{10}F_2O$)
Alcohol **6e** (450 mg, 1.66 mmol) and MnO_2 (2.9 g, 33 mmol) were converted according to the general procedure to yield ketone **3e** (440 mg, 99% without chromatography) as a yellow solid, mp 110–112°C. R_f (SiO_2, $PE/EA = 2/1$) = 0.55; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.86 (d, J = 16.1 Hz, 1H), 6.91–6.99 (m, 2H), 7.43–7.47 (m, 3H), 7.59–7.67 (m, 3H), 7.99 (d, J = 16.1 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 83.74 (s, C), 90.95 (t, ^3J = 2.4 Hz, C), 104.81 (dd, ^2J = 25.1 Hz, ^2J = 24.5 Hz, CH), 105.58 (dd, ^2J = 15.9 Hz, ^4J = 4.0 Hz, C), 112.35 (dd, ^2J = 22.5 Hz, ^4J = 5.9 Hz, CH), 128.34 (s, CH), 128.80 (s, 2CH), 129.12 (s, 2CH), 131.33 (s, CH), 134.03 (s, C), 135.84 (dd, ^3J = 10.0 Hz, ^3J = 1.7 Hz, CH), 149.33 (s, CH), 164.35 (d, ^1J = 256.7 Hz, C), 164.45 (d, ^1J = 256.7 Hz, C), 177.91 (s, C=O) ppm; IR (ATR): $\bar{\nu}$ = 2215 (m), 1632 (m), 1604 (m), 1496 (m), 1317 (m), 1267 (m), 1224 (m), 1174 (m), 1093 (m), 973 (m), 963 (m), 847 (m), 756 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 267 (100) [$M^+ - H$], 249 (55), 239 (59), 220 (17), 165 (45), 137 (14), 102 (33), 77 (21).

(E)-3-Oxo-5-phenyl-1-(2-thienyl)-4-penten-1-yne (**3f**, $C_{15}H_{10}OS$)
Alcohol **6f** (100 mg, 0.42 mmol) and MnO_2 (360 mg, 4.14 mmol) were converted according to the general procedure to yield ketone **3f** (99 mg, 99% without chromatography) as a yellow oil, which solidified after a few hours at 23°C, mp 69–72°C. R_f (SiO_2, $PE/EA = 2/1$) = 0.49; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.85 (d, J = 16.1 Hz, 1H), 7.10 (dd, J = 5.1, 3.7 Hz, 1H), 7.40–7.47 (m, 3H), 7.50 (dd, J = 5.1, 1.1 Hz, 1H), 7.54 (dd, J = 3.6, 1.1 Hz, 1H), 7.57–7.63 (m, 2H), 7.85 (d, J = 16.1 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 85.46 (C), 91.39 (C), 120.01 (C), 127.77 (CH), 128.26 (CH), 128.73 (2CH), 129.12 (2CH), 131.22 (CH), 131.38 (CH), 134.07 (C), 136.43 (CH), 148.03 (CH), 177.66 (C=O) ppm; IR (ATR): $\bar{\nu}$ = 2189 (vs), 1623 (vs), 1595 (s), 1449 (m), 1272 (m), 1222 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 238 (100) [M^+], 209 (34), 165 (17), 134 (28), 107 (23), 77 (17).

(E)-3-Oxo-5-phenyl-1-(2-pyridyl)-4-penten-1-yne (**3g**, $C_{16}H_{11}NO$)
Alcohol **6g** (400 mg, 1.70 mmol) and MnO_2 (3.00 g, 34.5 mmol) were converted according to the general procedure to yield ketone **3g** (298 mg, 75% after chromatography) as a brown oil, which solidified after a few hours at 23°C, mp 55–58°C. R_f (SiO_2, $PE/EA = 1/1$) = 0.41; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.89 (d, J = 16.1 Hz, 1H), 7.35–7.45 (m, 4H), 7.60–7.68 (m, 3H), 7.76 (dt, J = 7.7, 1.7 Hz, 1H), 8.00 (d, J = 16.1 Hz, 1H), 8.70 (dt, J = 4.7, 1.0 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 84.64 (C), 88.99 (C), 124.59 (CH), 128.21 (CH), 128.85 (3CH), 129.10 (2CH), 131.35 (CH), 133.97 (C), 136.47 (CH), 141.12 (C), 149.28 (CH), 150.54 (CH), 177.84 (C = O) ppm; IR (ATR): $\bar{\nu}$ = 2220 (m), 1627 (vs), 1577 (s), 1516 (s), 1460 (s), 1447 (m), 1426 (m), 1279 (s), 1183 (s), 1112 (m), 1083 (m), 972 (s), 867 (m), 778 (s), 761 (s), 697 (s), 676 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 233 (59) [M^+], 232 (92), 205 (41), 204 (100), 130 (21), 103 (12), 102 (19), 78 (19).

(E)-6,6-Dimethyl-3-oxo-1-phenyl-1-hepten-4-yne (**3h**, $C_{15}H_{16}O$)
Alcohol **6h** (400 mg, 1.87 mmol) and MnO_2 (2.2 g, 25 mmol) were converted according to the general procedure to yield ketone **3h** (392 mg, 99% without chromatography) as colorless crystals, mp 30–31°C. R_f (SiO_2, $PE/EA = 5/1$) = 0.42, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 9H), 6.77 (d, J = 16.0 Hz, 1H), 7.41–7.43 (m, 3H), 7.55–7.57 (m, 2H), 7.77 (d, J = 16.0 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 27.92 (C), 30.22 ($3CH_3$), 77.76 (C), 102.36 (C), 128.59 (2CH), 128.69 (CH), 129.03 (2CH), 130.98 (CH), 134.14 (C), 147.97 (CH), 178.74 (C=O) ppm; IR (ATR): $\bar{\nu}$ = 2968 (m), 2196 (br, m), 1620 (vs), 1449 (s), 1360 (m), 1275 (s), 1224 (s), 1197 (s), 976 (s), 950 (m), 878 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 212 (100) [M^+], 197 (80), 182 (20), 169 (44), 153 (24), 141 (29), 131 (27), 115 (16), 103 (29), 77 (23).

(E)-3-Oxo-1-phenyl-6-trimethylsilyl-1-penten-4-yne (**3i**, $C_{14}H_{16}OSi$)
Alcohol **6i** (500 mg, 2.17 mmol) and MnO_2 (2.5 g, 29 mmol) were converted according to the general procedure to yield ketone **3i** (480 mg, 97% without chromatography) as yellow oil. R_f (SiO_2,

PE/EA = 5/1) = 0.46; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.30 (s, 9H), 6.78 (d, J = 16.1 Hz, 1H), 7.40–7.47 (m, 3H), 7.53–7.59 (m, 2H), 7.84 (d, J = 16.1 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (62 MHz, $CDCl_3$): δ = −0.65 ($3CH_3$), 98.72 (C), 100.57 (C), 128.19 (CH), 128.69 (2CH), 129.05 (2CH), 131.21 (CH), 133.98 (C), 148.90 (CH), 177.99 (C=O) ppm; IR (ATR): $\bar{\nu}$ = 1626 (vs), 1598 (m), 1449 (m), 1236 (s), 1196 (s), 1122 (m), 976 (m), 869 (s), 845 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 228 (100) [M$^+$], 213 (43), 198 (12), 185 (42), 103 (13).

1-(3,4-Dimethoxyphenyl)-3-oxo-4-penten-1-yne (**3j**, $C_{13}H_{12}O_3$)
Alcohol **6j** (300 mg, 1.38 mmol) and MnO_2 (2.40 g, 27.6 mmol) were converted according to the general procedure to yield ketone **3j** (230 mg, 77% after chromatography) as a yellow oil. R_f (SiO_2, *PE/EA* = 2/1) = 0.40. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 3.93 (s, 3H), 6.22 (dd, J = 10.0, 1.2 Hz, 1H), 6.48 (dd, J = 17.4, 10.0 Hz, 1H), 6.66 (dd, J = 17.4, 1.2 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 7.09 (d, J = 1.9 Hz, 1H), 7.26 (dd, J = 8.3, 1.9 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (62 MHz, $CDCl_3$): δ = 56.01 (OCH_3), 56.03 (OCH_3), 85.56 (C), 93.25 (C), 111.09 (CH), 111.75 (C), 115.32 (CH), 127.43 (CH), 133.04 (CH_2), 138.02 (CH), 148.85 (C), 151.68 (C), 178.79 (C=O) ppm; IR (ATR): $\bar{\nu}$ = 2181 (s), 1735 (m), 1637 (s), 1593 (s), 1510 (s), 1461 (m), 1398 (m), 1248 (s), 1136 (m), 995 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 216 (100) [M$^+$], 189 (86), 173 (10), 145 (11).

1-(3-Ethoxy-4-methoxyphenyl)-3-oxo-4-penten-1-yne (**3k**, $C_{14}H_{14}O_3$)
Alcohol **6k** (480 mg, 2.07 mmol) and MnO_2 (5.4 g, 62 mmol) were converted according to the general procedure to yield ketone **3k** (295 mg, 62% after chromatography) as a yellow solid, mp 86–87°C. R_f (SiO_2, *PE/EA* = 2/1) = 0.42; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (t, J = 7.1 Hz, 3H), 3.91 (s, 3H), 4.10 (q, J = 7.1 Hz, 2H), 6.20 (dd, J = 10.1, 0.8 Hz, 1H), 6.48 (dd, J = 17.5, 10.4 Hz, 1H), 6.64 (dd, J = 16.7, 0.8 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 7.24 (dd, J = 8.4, 1.8 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 14.67 (CH_3), 56.02 (OCH_3), 64.54 (OCH_2), 85.54 (C), 93.42 (C), 111.33 (CH), 111.69 (C), 116.64 (CH), 127.32 (CH), 132.92 (CH_2), 138.05 (CH), 148.21 (C), 152.00 (C), 178.78 (C=O) ppm; IR (ATR): $\bar{\nu}$ = 2981 (m), 2186 (vs), 1636 (s), 1592 (s), 1575 (m), 1515 (vs), 1480 (m), 1397 (m), 1311 (m), 1251 (vs), 1165 (m), 1137 (s), 1018 (m), 1005 (m), 974 (m), 962 (m), 771 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 230 (100) [M$^+$], 203 (19), 175 (75), 159 (20), 131 (15).

1-(2,4-Difluorophenyl)-3-oxo-4-penten-1-yne (**3l**, $C_{11}H_6F_2O$)
Alcohol **6l** (400 mg, 2.06 mmol) and MnO_2 (2.7 g, 31 mmol) were converted according to the general procedure to yield ketone **3l** (394 mg, 99% without chromatography) as a yellow solid, mp 29–31°C. R_f (SiO_2, *PE/EA* = 2/1) = 0.56; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.28 (dd, J = 10.2, 0.8 Hz, 1H), 6.48 (dd, J = 17.3, 10.2 Hz, 1H) 6.72 (dd, J = 17.3, 0.8 Hz, 1H), 6.88–6.98 (m, 2H), 7.55–7.64 (m, 1H) ppm; ^{13}C{^{1}H} NMR (62 MHz, $CDCl_3$): δ = 77.24 (s, C), 84.18 (s, C), 104.79 (dd, ^2J = 26.7 Hz, ^2J = 24.1 Hz, CH), 105.29 (dd, ^2J = 19.3 Hz, ^4J = 4.5 Hz, C), 112.32 (dd, ^2J = 22.2 Hz, ^4J = 3.9 Hz, CH), 134.25 (s, CH_2), 135.87 (dd, ^3J = 10.2 Hz, ^3J = 1.9 Hz, CH), 137.82 (s, CH), 164.43 (d, ^1J = 261.4 Hz, C), 164.56 (d, ^1J = 255.9 Hz, C), 178.43 (s, C = O) ppm; IR (ATR): $\bar{\nu}$ = 2965 (m), 2203 (m), 1667 (s), 1607 (s), 1501 (s), 1427 (m), 1267 (m), 1223 (m), 1143 (s), 1094 (m), 966 (m), 848 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%) = 192 (45) [M$^+$], 165 (100), 137 (14).

2,3-Dihydro-2,6-diphenylthiopyran-4-one (**2a**, $C_{17}H_{14}OS$)
Method A: A mixture of ketone **3a** (470 mg, 2.02 mmol), $Na_2S \cdot 9H_2O$ (972 mg, 4.05 mmol), *THF* (9 cm^3), and H_2O (9 cm^3) was stirred for 72 h at 23°C. CH_2Cl_2 (25 cm^3) was added, and the mixture was further stirred for 17 h. The organic layer was separated. The aqueous phase was neutralized with saturated NH_4Cl solution (40 cm^3) and then extracted with CH_2Cl_2 (3×40 cm^3). The combined organic layers were washed with brine (50 cm^3) and dried ($MgSO_4$). After filtration, the solvent was stripped off and the residue purified by chromatography (SiO_2, *PE/EA* = 5/1, R_f = 0.44) to yield the title compound **2a** (507 mg, 94%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99 (dd, J = 16.4,

3.1 Hz, 1H), 3.15 (dd, $J = 16.4$, 14.1 Hz, 1H), 4.77 (dd, $J = 14.1$, 3.1 Hz, 1H), 6.58 (s, 1H), 7.35–7.49 (m, 8H), 7.64–7.66 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 44.31$ (CH_2), 46.72 (CH), 120.70 (CH), 127.18 (2CH), 127.59 (2CH), 128.62 (CH), 128.89 (2CH), 129.07 (2CH), 131.13 (CH), 136.93 (C), 137.85 (C), 160.37 (C), 195.00 (C=O) ppm; IR (ATR): $\bar{\nu} = 1646$ (vs), 1550 (s), 1318 (m), 1297 (m), 1266 (s), 856 (m), 762 (m), 725 (m), 695 (s), 633 (m) cm^{-1}; HR-MS (EI, 70 eV): m/z (%) = 266.0765 (81) [M^+], calcd 266.0759 (for $C_{17}H_{14}OS$).

General Procedure for the Ring Closure with NaSH (Method B)

A mixture of ketone **3** (1 eq.), $NaSH \cdot 1.2H_2O$ (3–5 eq.), and 2-*ME* (*ca.* 10 dm^3 mol^{-1}) was stirred for the time and at the temperature specified in Table 1. Saturated aqueous NH_4Cl solution (*ca.* 10 dm^3 mol^{-1}) was added and the mixture was extracted with *EA* (3×15 dm^3 mol^{-1}). The combined organic phases were dried ($MgSO_4$), filtered, and evaporated. The residue was chromatographed (SiO_2, *PE*/*EA*) to give dihydrothiopyranones **2**.

6-(3,4-Dimethoxyphenyl)-2,3-dihydro-2-phenylthiopyran-4-one (**2b**, $C_{19}H_{18}O_3S$)

Ketone **3b** (150 mg, 0.51 mmol), $NaSH \cdot 1.2H_2O$ (260 mg, 3.35 mmol), and 2-*ME* (15 cm^3) were converted for 2 h at 50°C and for 14 h at 23°C according to the general procedure (method B) to give dihydrothiopyranone **2b** (160 mg, 96%) after chromatography (SiO_2, $PE/EA = 2/1$, $R_f = 0.22$) as a brown solid, mp 89–92°C. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.98$ (dd, $J = 16.5$, 3.4 Hz, 1H), 3.15 (dd, $J = 16.5$, 13.8 Hz, 1H), 3.91 (s, 3H), 3.93 (s, 3H), 4.75 (dd, $J = 13.8$, 3.4 Hz, 1H), 6.57 (s, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 7.16 (d, $J = 2.2$ Hz, 1H), 7.32 (dd, $J = 8.4$, 2.2 Hz, 1H), 7.35–7.48 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 44.49$ (CH_2), 46.54 (CH), 55.99 (OCH_3), 56.04 (OCH_3), 109.86 (CH), 110.96 (CH), 119.32 (CH), 120.61 (CH), 127.68 (2CH), 128.66 (CH), 129.08 (2CH), 129.34 (C), 137.87 (C), 149.09 (C), 151.78 (C), 160.24 (C), 195.17 (C=O) ppm; IR (ATR): $\bar{\nu} = 1644$ (s), 1594 (m), 1546 (m), 1507 (s), 1458 (m), 1411 (m), 1257 (s), 1144 (s), 1022 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 326 (100) [M^+], 298 (10), 222 (28), 193 (48).

6-(3-Ethoxy-4-methoxyphenyl)-2,3-dihydro-2-phenylthiopyran-4-one (**2c**, $C_{20}H_{20}O_3S$)

Ketone **3c** (390 mg, 1.27 mmol), $NaSH \cdot 1.2H_2O$ (390 mg, 5.02 mmol), and 2-*ME* (25 cm^3) were converted for 4 h at 40°C and for 16 h at 23°C according to the general procedure (method B) to give dihydrothiopyranone **2c** (399 mg, 92%) after chromatography (SiO_2, $PE/EA = 2/1$, $R_f = 0.34$) as a yellow solid, mp 100–101°C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.48$ (t, $J = 6.9$ Hz, 3H), 2.98 (dd, $J = 16.5$, 3.1 Hz, 1H), 3.14 (dd, $J = 16.1$, 14.3 Hz, 1H), 3.91 (s, 3H), 4.13 (q, $J = 6.9$ Hz, 2H), 4.73 (dd, $J = 14.0$, 3.0 Hz, 1H), 6.55 (s, 1H), 6.89 (d, $J = 8.6$ Hz, 1H), 7.17 (d, $J = 2.2$ Hz, 1H), 7.30 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.36–7.46 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 14.71$ (CH_3), 44.51 (CH_2), 46.52 (CH), 56.06 (OCH_3), 64.50 (OCH_2), 111.17 (2CH), 119.24 (CH), 120.50 (CH), 127.66 (2CH), 128.62 (CH), 129.07 (2CH), 129.26 (C), 137.92 (C), 148.41 (C), 152.07 (C), 160.27 (C), 195.15 (C=O) ppm; IR (ATR): $\bar{\nu} = 1639$ (s), 1590 (m), 1546 (m), 1498 (m), 1260 (br, m), 1143 (m), 1021 (m), 871 (m), 797 (m), 719 (m), 695 (vs) cm^{-1}; MS (EI, 70 eV): m/z (%) = 340 (100) [M^+], 312 (12), 236 (30), 208 (41), 165 (21).

2,3-Dihydro-2-phenyl-6-(2-trifluoromethylphenyl)thiopyran-4-one (**2d**, $C_{18}H_{13}F_3OS$)

Ketone **3d** (160 mg, 0.53 mmol), $NaSH \cdot 1.2H_2O$ (220 mg, 2.83 mmol), and 2-*ME* (10 cm^3) were converted for 8 h at 40°C and for 15 h at 23°C according to the general procedure (method B) to give dihydrothiopyranone **2d** (149 mg, 84%) after chromatography (SiO_2, $PE/EA = 2/1$, $R_f = 0.55$) as a light brown oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.99$ (dd, $J = 16.4$, 3.1 Hz, 1H), 3.17 (dd, $J = 16.4$, 14.2 Hz, 1H) 4.83 (dd, $J = 14.2$, 3.0 Hz, 1H), 6.25 (s, 1H), 7.33–7.46 (m, 6H), 7.51 (t, $J = 7.7$, 1H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.72 (d, $J = 7.7$, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 43.93$ (s, CH_2), 47.98 (s, CH), 123.66 (q, $^1J = 274.1$ Hz, C), 124.80 (q, $^3J = 1.6$ Hz, C), 126.72 (q, $^3J = 5.3$ Hz, CH), 127.55 (s, 2CH), 127.91 (q, $^2J = 30.9$ Hz, C), 128.71 (s, CH), 129.09 (s, 2CH), 129.51 (s, CH), 130.26 (s, CH), 131.72 (s, CH), 135.85 (s, C), 137.51 (s, C), 157.96 (s, CH), 194.07 (s, C=O) ppm; IR

(ATR): $\bar{\nu} = 1655$ (s), 1565 (m), 1311 (s), 1287 (m), 1262 (m), 1167 (m), 1125 (s), 1107 (s), 1060 (m), 1033 (m), 764 (m) cm^{-1}; MS (CI, CH_4): m/z (%) = 335 (100) $[M + H^+]$, 306 (5), 257 (5), 230 (31), 211 (9), 202 (30), 176 (8), 131 (8), 104 (9).

6-(2,4-Difluorophenyl)-2,3-dihydro-2-phenylthiopyran-4-one (**2e**, $C_{17}H_{12}F_2OS$)
Method A: A mixture of ketone **3e** (100 mg, 0.37 mmol), $Na_2S \cdot 9\ H_2O$ (180 mg, 0.74 mmol), *THF* (3 cm^3), H_2O (3 cm^3), and *Ac*OH (0.5 cm^3) was stirred for 5 h at 55°C and for 3 h at 23°C. Water (10 cm^3) was added and the mixture was extracted with *EA* (2×15 cm^3). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was chromatographed (SiO_2, $PE/EA = 2/1$, $R_f = 0.56$) to give dihydrothiopyranone **2e** (74 mg, 65%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.99$ (dd, $J = 16.4$, 3.3 Hz, 1H), 3.18 (dd, $J = 16.4$, 13.9 Hz, 1H), 4.78 (dd, $J = 13.9$, 3.3 Hz, 1H), 6.48 (d, $J = 1.6$ Hz, 1H), 6.86–6.97 (m, 2H), 7.33–7.45 (m, 5H), 7.51–7.60 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 44.01$ (s, CH_2), 47.14 (s, CH), 105.07 (t, $^2J = 26.0$ Hz, CH), 111.90 (dd, $^2J = 21.6$ Hz, $^4J = 4.1$ Hz, CH), 121.42 (dd, $^3J = 13.4$ Hz, $^3J = 4.9$ Hz, C), 124.56 (d, $^4J = 5.1$ Hz, CH), 127.58 (s, 2CH), 128.75 (s, CH), 129.12 (s, 2CH), 131.21 (dd, $^3J = 9.9$ Hz, $^3J = 3.4$ Hz, CH), 137.46 (s, C), 153.01 (d, $^3J = 1.9$ Hz, C), 159.75 (dd, $^1J = 256$ Hz, $^3J = 12.4$ Hz, C), 163.92 (dd, $^1J = 254$ Hz, $^3J = 12.0$ Hz, C), 194.65 (s, C=O) ppm; IR (ATR): $\bar{\nu} = 1650$ (vs), 1608 (s), 1558 (m), 1496 (s), 1425 (m), 1264 (br, s), 1143 (s), 1100 (s), 975 (m), 850 (m), 733 (m), 698 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 302 (84) $[M^+]$, 274 (13), 225 (5), 198 (51), 170 (100), 126 (9), 104 (32).

2,3-Dihydro-2-phenyl-5-(2-thienyl)thiopyran-4-one (**2f**, $C_{15}H_{12}OS_2$)
Ketone **3f** (50 mg, 0.21 mmol), $NaSH \cdot 1.2H_2O$ (91 mg, 1.17 mmol), and 2-*ME* (3 cm^3) were converted for 18 h at 40°C according to the general procedure (method B) to give dihydrothiopyranone **2f** (45 mg, 81%) after chromatography (SiO_2, $PE/EA = 2/1$, $R_f = 0.44$) as a brown solid, mp 68–69°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.99$ (dd, $J = 16.6$, 3.4 Hz, 1H), 3.15 (dd, $J = 16.6$, 13.4 Hz, 1H), 4.76 (dd, $J = 13.5$, 3.4 Hz, 1H), 6.62 (s, 1H), 7.10 (dd, $J = 5.1$, 3.8 Hz, 1H), 7.35–7.45 (m, 5H), 7.48 (dd, $J = 5.1$, 1.1 Hz, 1H), 7.52 (dd, $J = 3.8$, 1.1 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 44.73$ (CH_2), 46.68 (CH), 118.51 (CH), 127.67 (2CH), 128.36 (CH), 128.41 (CH), 128.73 (CH), 129.13 (2CH), 129.81 (CH), 137.56 (C), 140.13 (C), 152.15 (C), 194.78 (C=O) ppm; IR (ATR): $\bar{\nu} = 1637$ (s), 1544 (s), 1495 (m), 1415 (m), 1354 (m), 1285 (m), 1259 (br, m), 1142 (m), 1049 (m), 823 (m), 696 (s) cm^{-1}; MS (CI, CH_4): m/z (%) = 273 (100) $[M + H^+]$, 244 (7), 168 (22), 140 (26).

2,3-Dihydro-2-phenyl-6-(2-pyridyl)thiopyran-4-one (**2g**, $C_{16}H_{13}NOS$)
Ketone **3g** (200 mg, 0.86 mmol), $NaSH \cdot 1.2H_2O$ (372 mg, 4.79 mmol), and 2-*ME* (20 cm^3) were converted for 2 h at 50°C according to the general procedure (method B) to give dihydrothiopyranone **2g** (139 mg, 60%) after chromatography (SiO_2, $PE/EA/NHEt_2 = 2/1/0.02$, $R_f = 0.27$) as a light yellow solid, mp 98–100°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.00$ (dd, $J = 16.4$, 3.5 Hz, 1H), 3.17 (dd, $J = 16.4$, 13.9 Hz, 1H), 4.72 (dd, $J = 13.9$, 3.5 Hz, 1H), 6.98 (s, 1H), 7.28–7.48 (m, 6H), 7.70–7.81 (m, 2H), 8.65–8.68 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 44.19$ (CH_2), 46.24 (CH), 120.71 (CH), 121.17 (CH), 125.13 (CH), 127.68 (2CH), 128.59 (CH), 129.02 (2CH), 137.00 (CH), 137.94 (C), 149.64 (CH), 153.48 (C), 158.99 (C), 195.56 (C=O) ppm; IR (ATR): $\bar{\nu} = 1636$ (vs), 1581 (w), 1548 (m), 1454 (s), 1436 (m), 1404 (m), 1316 (m), 1266 (m), 1251 (s), 1139 (m), 1089 (m), 992 (m), 860 (m), 783 (vs), 726 (s), 698 (s), 616 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 267 (26) $[M^+]$, 163 (38), 135 (20), 104 (14), 88 (100).

6-tert-Butyl-2,3-dihydro-2-phenylthiopyran-4-one (**2h**, $C_{15}H_{18}OS$)
Ketone **3h** (100 mg, 0.47 mmol), $NaSH \cdot 1.2H_2O$ (200 mg, 2.57 mmol), and 2-*ME* (6 cm^3) were converted for 16 h at 50°C according to the general procedure (method B) to give dihydrothiopyranone **2h** (98 mg, 85%) after chromatography (SiO_2, $PE/EA = 5/1$, $R_f = 0.30$) as an offensive smelling, light yellow solid, mp 62–63°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.26$ (s, 9H), 2.86 (dd, $J = 16.3$, 3.2 Hz, 1H), 3.00 (dd, $J = 16.4$, 14.5 Hz, 1H), 4.53 (dd, $J = 14.4$, 3.2 Hz, 1H), 6.28 (s, 1H), 7.34–7.41 (m, 5H)

ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 29.71$ ($3CH_3$), 38.76 (C), 44.06 (CH_2), 46.49 (CH), 119.04 (CH), 127.54 (2CH), 128.48 (CH), 128.97 (2CH), 138.19 (C), 174.43 (C), 195.81 (C=O) ppm; IR (ATR): $\bar{\nu} = 2958$ (br, m), 1639 (vs), 1550 (vs), 1496 (m), 1454 (m), 1404 (m), 1364 (m), 1315 (m), 1289 (s), 1269 (s), 1241 (s), 1201 (m), 1145 (m), 986 (m), 936 (m), 838 (m), 828 (m), 796 (s), 721 (s), 698 (vs), 618 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 246 (100) [M^+], 142 (21), 127 (56), 104 (13), 100 (16).

2,3-Dihydro-2-phenylthiopyran-4-one (**2i**, $C_{11}H_{10}OS$)
Ketone **3i** (108 mg, 0.47 mmol), $NaSH \cdot 1.2H_2O$ (227 mg, 2.92 mmol), and 2-*ME* (6 cm^3) were converted for 3 h at 60°C according to the general procedure (method B) to give dihydrothiopyranone **2i** (62 mg, 70%) after chromatography (SiO_2, *PE*/*EA* = 5/1, $R_f = 0.24$) as a light yellow solid, mp 49–50°C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.92$ (dd, $J = 16.3$, 3.1 Hz, 1H), 3.11 (dd, $J = 16.3$, 14.2 Hz, 1H), 4.69 (dd, $J = 14.2$, 3.1 Hz, 1H), 6.27 (d, $J = 10.2$ Hz, 1H), 7.32–7.42 (m, 5H), 7.49 (d, $J = 10.3$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 44.91$ (CH_2), 46.94 (CH), 123.48 (CH), 127.44 (2CH), 128.60 (CH), 129.03 (2CH), 137.80 (C), 146.26 (CH), 194.30 (C=O) ppm; IR (ATR): $\bar{\nu} = 1651$ (vs), 1547 (vs), 1489 (m), 1452 (m), 1400 (m), 1362 (m), 1350 (s), 1264 (s), 1250 (s), 1154 (m), 1134 (m), 1080 (m), 938 (m), 783 (s), 756 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 190 (69) [M^+], 104 (100), 86 (10), 78 (12), 77 (10).

6-(3,4-Dimethoxyphenyl)-2,3-dihydrothiopyran-4-one (**2j**, $C_{13}H_{14}O_3S$)
Ketone **3j** (120 mg, 0.56 mmol), $NaSH \cdot 1.2H_2O$ (260 mg, 3.35 mmol), and 2-*ME* (20 cm^3) were converted for 2 h at 50°C and for 14 h at 23°C according to the general procedure (method B) to give dihydrothiopyranone **2j** (50 mg, 36%) after chromatography (SiO_2, *PE*/*EA* = 2/1, $R_f = 0.19$) as a light yellow solid, mp 81–83°C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.74$–2.79 (m, 2H), 3.26–3.31 (m, 2H), 3.92 (s, 3H), 3.93 (s, 3H), 6.47 (s, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 7.14 (d, $J = 2.2$ Hz, 1H), 7.29 (dd, $J = 8.4$, 2.2 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 27.16$ (CH_2), 37.21 (CH_2), 55.99 (OCH_3), 56.05 (OCH_3), 109.86 (CH), 110.91 (CH), 119.59 (CH), 120.62 (CH), 129.84 (C), 149.05 (C), 151.71 (C), 160.51 (C), 194.87 (C=O) ppm; IR (ATR): $\bar{\nu} = 1633$ (s), 1591 (m), 1546 (m), 1513 (s), 1460 (m), 1335 (m), 1247 (s), 1168 (m), 1137 (s), 1016 (m), 805 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 250 (100) [M^+], 222 (69), 194 (86), 179 (48).

6-(3-Ethoxy-4-methoxyphenyl)-2,3-dihydrothiopyran-4-one (**2k**, $C_{14}H_{16}O_3S$)
Ketone **3k** (200 mg, 0.87 mmol), $NaSH \cdot 1.2H_2O$ (490 mg, 6.31 mmol), and 2-*ME* (20 cm^3) were converted for 3 h at 50°C and for 2 h at 23°C according to the general procedure (method B) to give dihydrothiopyranone **2k** (36 mg, 16%) after chromatography (SiO_2, *PE*/*EA* = 2/1, $R_f = 0.18$) as a light yellow solid, mp 82–85°C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.49$ (t, $J = 7.0$ Hz, 3H), 2.74–2.79 (m, 2H), 3.25–3.30 (m, 2H), 3.91 (s, 3H), 4.13 (q, $J = 7.0$ Hz, 2H), 6.45 (s, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 2.2$ Hz, 1H), 7.27 (dd, $J = 8.8$, 2.1 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 14.72$ (CH_3), 27.16 (CH_2), 37.21 (CH_2), 56.06 (OCH_3), 64.50 (OCH_2), 111.16 (CH), 111.24 (CH), 119.51 (CH), 120.52 (CH), 129.77 (C), 148.39 (C), 152.03 (C), 160.51 (C), 194.81 (C=O) ppm; IR (ATR): $\bar{\nu} = 1636$ (s), 1591 (m), 1540 (m), 1503 (s), 1441 (m), 1418 (m), 1394 (m), 1240 (s), 1139 (s), 1019 (s), 919 (m), 800 (m) cm^{-1}; MS (EI, 70 eV): m/z (%) = 264 (100) [M^+], 236 (51), 208 (75), 193 (11), 180 (17), 164 (31); HR-MS (EI, 70 eV): m/z (%) = 264.0821 (100) [M^+], calcd 264.0820 (for $C_{14}H_{16}O_3S$).

6-(2,4-Difluorophenyl)-2,3-dihydrothiopyran-4-one (**2l**, $C_{11}H_8F_2OS$)
Method A: A mixture of ketone **3l** (100 mg, 0.52 mmol), $Na_2S \cdot 9H_2O$ (250 mg, 1.04 mmol), *THF* (3 cm^3), H_2O (3 cm^3), and *Ac*OH (*ca.* 50 mg) were stirred for 3 h at 55°C. The mixture was then washed with water (10 cm^3). The aqueous phase was extracted with *EA* (2×20 cm^3). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was chromatographed (SiO_2, *PE*/*EA* = 2/1, $R_f = 0.40$) to yield the title compound **2l** (10 mg, 8%) as a light yellow oil. ^1H NMR

(500 MHz, $CDCl_3$): $\delta = 2.75$–2.84 (m, 2H), 3.28–3.36 (m, 2H), 6.38 (d, $J = 1.7$ Hz, 1H), 8.83–7.00 (m, 2H), 7.48–7.60 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): $\delta = 27.79$ (s, CH_2), 36.73 (s, CH_2), 105.03 (t, $^2J = 24.8$ Hz, CH), 111.75 (dd, $^2J = 21.5$ Hz, $^4J = 3.8$ Hz, CH), 124.85 (d, $^3J = 4.5$ Hz, CH), 131.25 (dd, $^3J = 9.9$ Hz, $^3J = 3.5$ Hz, CH), 194.14 (s, C=O) ppm; resonances for carbon atoms C-6, C-1′, C-2′, and C-4′ are not observed due to poor signal-to-noise ratio; IR (ATR): $\bar{\nu} = 2931$ (m), 1646 (s), 1613 (s), 1593 (s), 1497 (s), 1182 (s), 1141 (s), 1097 (s), 976 (s) 848 (s) cm^{-1}; MS (EI, 70 eV): m/z (%) = 226 (40) [M^+], 198 (28), 170 (100), 138 (9), 126 (8).

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