**Synthesis of polysubstituted 3,4-dihydro-2H-thiopyrans by regioselective annulation of 3,3-disubstituted allylic alcohols with a β-oxodithioester**

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**Supporting Information**

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**General Information:** Melting points of all the compounds were recorded on Veego programmable melting point apparatus and are uncorrected. IR spectra were recorded on a PerkineElmer FT-IR 240-C spectrophotometer using KBr optics. $^1$H NMR spectra were recorded on Bruker AV 300 MHz in CDCl$_3$ using TMS as internal standard. Electron Spray Ionization (ESI) and high-resolution spectra were recorded on QSTARXL hybrid MS/MS system (Applied Biosystems, USA) under electrospray ionization. All the reactions were monitored by thin layer chromatography (TLC) on precoated silica gel 60 F254 (mesh); spots were visualized with UV light. Merck silica gel (60-120 mesh) was used for column chromatography.

**Crystal data for compound 3o:** $C_{15}H_{17}ClO_1S_2$, $M = 312.86$, crystal size, 0.40 x 0.20 x 0.10 mm$^3$, triclinic, space group P$_{\text{Error!}}$ (No. 2), $a = 5.8350(4)$, $b = 8.6412(6)$, $c = 15.4578(10)$ Å, $\alpha = 85.662(1)$, $\beta = 83.585(1)$, $\gamma = 86.652(1)^{\circ}$, $V = 771.32(9)$ Å$^3$, $Z = 2$, $D_c = 1.347$ g/cm$^3$, $F_{000} = 328$, CCD area detector, MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 293(2)$K, $2\theta_{\text{max}} = 50^{\circ}$, 7421 reflections collected, 2701 unique ($R_{\text{int}} = 0.014$), Final $GooF = 1.07$, $R1 = 0.0376$, $wR2 = 0.1066$, $R$ indices based on 2701 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 175 parameters, $\mu = 0.508$ mm$^{-1}$, minimum and maximum residual density = -0.23 and 0.33 e/Å$^3$, respectively. 

CCDC 1561129 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Data collection and Structure solution:** X-ray data for BD31 compound were collected at room temperature using the Bruker Smart Apex CCD diffractometer with graphite monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$Å) with $\omega$-scan method.$^1$ Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5082 reflections. Integration and scaling of intensity data were accomplished using SAINT program.$^1$ The structure was solved by Direct Methods.
using SHELXS97 and refinement was carried out by full-matrix least-squares technique using SHELXL97,2,3 Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$ for methyl atoms.


Typical procedure for synthesis of substituted dihydrothiopyran 3a: In a 50 ml round bottom flask, 2-cyclopentylideneethanol 1a (320 mg, 2.85 mmol), methyl 3-oxo-3-phenylpropanedithioate 2a (500 mg, 2.38 mmol) and dichloromethane (5 ml) were taken and to this mixture, BF$_3$.OEt$_2$ (0.06 ml, 0.4 mmol) was added with a syringe and stirred at room temperature for 3 hours. After completion of reaction (monitored by TLC), the crude reaction mixture was diluted with chloroform (20 ml) and washed with water (20 ml) followed by brine. Then the organic layer was dried over Na$_2$SO$_4$ and solvent was evaporated under vacuum. The residue was purified by column chromatography (silica gel 60-120 mesh) to obtain (7-(methylthio)-6-thiaspiro[4.5]dec-7-en-8-yl)(phenyl)methanone 3a as a yellow liquid (0.60 g, 83%) and its characterization data is as follows:

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.83$ (d, $J = 7.17$ Hz, 2H), 7.53 (t, $J = 7.17$, 7.47 Hz, 1H), 7.45 (t, $J = 7.63$, 7.32 Hz, 2H), 2.56 (t, $J = 6.41$, 6.56 Hz, 2H), 2.15 (s, 3H), 1.98-1.89 (m, 6H), 1.79-1.73 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 197.2$, 137.4, 133.7, 132.8, 132.6, 128.8, 128.4, 55.6, 40.0, 34.2, 27.5, 24.2, 17.6; IR (thin film): $\nu$ 3059, 2952, 2868, 1660,
1264, 704 cm\(^{-1}\); MS (ESI) 305 (M+H). ESI-HRMS obtained for C\(_{17}H_{21}OS_2\) (M+H) = 305.1023 (calculated: 305.1028).

Characterization data obtained for compounds substituted dihydrothiopyran 3a-3q:

(7-(methylthio)-6-thiaspiro[4.5]dec-7-en-8-yl)(phenyl)methanone (3a): Yield 83% (0.60 g), yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.83\) (d, \(J = 7.17\) Hz, 2H), 7.53 (t, \(J = 7.17, 7.47\) Hz, 1H), 7.45 (t, \(J = 7.63, 7.32\) Hz, 2H), 2.56 (t, \(J = 6.41, 6.56\) Hz, 2H), 2.15 (s, 3H), 1.98-1.89 (m, 6H), 1.79-1.73 (m, 4H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 197.2, 137.4, 133.7, 132.8, 132.6, 128.8, 128.4, 55.6, 40.0, 34.2, 27.5, 24.2, 17.6\); IR (thin film): \(\nu = 3059, 2952, 2868, 1661, 1264, 704\) cm\(^{-1}\); MS (ESI) 305 (M+H). ESI-HRMS obtained for C\(_{17}H_{21}OS_2\) (M+H) = 305.1023 (calculated: 305.1028).

(4-chlorophenyl)(7-(methylthio)-6-thiaspiro[4.5]dec-7-en-8-yl)methanone (3b): Yield 80% (0.55 g), yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.76\) (d, \(J = 8.54\) Hz, 2H), 7.43 (d, \(J = 8.39\) Hz, 2H), 2.59 (t, \(J = 6.41, 6.56\) Hz, 2H), 2.17 (s, 3H), 1.98-1.89 (m, 6H), 1.78-1.73 (m, 4H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 195.9, 138.9, 136.0, 134.0, 132.9, 130.2, 128.8, 55.7, 40.1, 34.2, 27.5, 24.2, 17.6\); IR (thin film): \(\nu = 3058, 2954, 2866, 1661, 1264, 706\) cm\(^{-1}\); MS (ESI) 339 (M+H). ESI-HRMS obtained for C\(_{17}H_{20}ClOS_2\) (M+H) = 339.0561 (calculated: 339.0568).
(4-ethylphenyl)(7-(methylthio)-6-thiaspiro[4.5]dec-7-en-8-yl)methanone (3c): Yield 82% (0.57 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.78 (d, $J = 8.19$ Hz, 2H), 7.29 (d, $J = 8.19$ Hz, 2H), 2.74-2.68 (q, $J = 7.58$, 7.58 Hz, 2H), 2.58 (t, $J = 6.48$, 6.60 Hz, 2H), 2.17 (s, 3H), 2.00-1.89 (m, 6H), 1.78-1.72 (m, 4H), 1.26 (t, $J = 7.70$, 7.58 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 197.1, 149.8, 134.8, 134.3, 131.2, 129.2, 128.0, 55.5, 40.1, 34.3, 28.9, 27.6, 24.2, 17.8, 15.0; IR (thin film): ν 2959, 2869, 1659, 1603, 1265, 1176 cm$^{-1}$; MS (ESI) 333 (M+H). ESI-HRMS obtained for C$_{19}$H$_{25}$O$_2$S$_2$ (M+H) = 333.1387 (calculated: 333.1341).

(4-methoxyphenyl)(7-(methylthio)-6-thiaspiro[4.5]dec-7-en-8-yl)methanone (3d): Yield 77% (0.53 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.85 (d, $J = 9.04$ Hz, 2H), 6.95 (d, $J = 8.92$ Hz, 2H), 3.87 (s, 3H), 2.57 (t, $J = 6.48$, 6.72 Hz, 2H), 2.18 (s, 3H), 1.99-1.88 (m, 6H), 1.78-1.71 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 196.3, 163.4, 134.6, 131.4, 130.1, 129.9, 113.8, 55.5, 55.4, 40.1, 34.3, 27.6, 24.3, 17.9; IR (thin film): ν 3059, 2955, 2866, 1666, 1264, 703 cm$^{-1}$; MS (ESI) 335 (M+H). ESI-HRMS obtained for C$_{19}$H$_{22}$O$_2$S$_2$ (M+H) = 335.1129 (calculated: 335.1134).

(6-(methylthio)-2,2-diphenyl-3,4-dihydro-2H-thiopyran-5-
yl)(phenyl)methanone (3e): Yield 83% (0.80 g), pale yellow solid, mp 114-116 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.57\) (d, \(J = 7.01\) Hz, 2H), 7.49-7.43 (m, 5H), 7.38-7.33 (m, 6H), 7.29 (t, \(J = 7.32, 7.32\) Hz, 2H), 2.87 (t, \(J = 6.40, 6.25\) Hz, 2H), 2.35 (t, \(J = 6.25, 6.40\) Hz, 2H), 2.25 (s, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 197.1, 143.7, 137.3, 135.5, 132.7, 131.6, 128.8, 128.5, 128.3, 127.7, 127.3, 59.2, 33.7, 27.0, 17.3\); IR (KBr): \(\nu = 3447, 3059, 2925, 1661, 1442, 1263, 700\) cm\(^{-1}\); MS (ESI) 403 (M+H). ESI-HRMS obtained for C\(_{25}\)H\(_{23}\)O\(_2\)S\(_2\) (M+H) = 403.1239 (calculated: 403.1184).

![Structure of 3f](image)

(4-chlorophenyl)(6-(methylthio)-2,2-diphenyl-3,4-dihydro-2H-thiopyran-5-yl)methanone (3f): Yield 84% (0.75 g), pale yellow solid, mp 137-139 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.48-7.43\) (m, 6H), 7.37 (t, \(J = 7.32, 7.48\) Hz, 4H), 7.31-7.29 (m, 4H), 2.88 (t, \(J = 6.40, 6.40\) Hz, 2H), 2.35 (t, \(J = 6.40, 6.40\) Hz, 2H), 2.26 (s, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 195.9, 143.5, 139.0, 135.7, 134.8, 132.4, 130.2, 128.6, 127.7, 127.4, 59.3, 33.7, 27.0, 17.2\); IR (KBr): \(\nu = 3447, 3058, 2953, 1662, 1444, 1266, 702\) cm\(^{-1}\); MS (ESI) 437 (M+H). ESI-HRMS obtained for C\(_{25}\)H\(_{22}\)OC\(_{2}\)S\(_2\) (M+H) = 437.0721 (calculated: 437.0726).

![Structure of 3g](image)

(4-ethylphenyl)(6-(methylthio)-2,2-diphenyl-3,4-dihydro-2H-thiopyran-5-yl)methanone (3g): Yield 81% (0.73 g), pale yellow solid, mp 118-120 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.53\) (d, \(J = 8.24\) Hz, 2H), 7.44 (d, \(J = 7.32\) Hz, 4H), 7.37 (t, \(J = 7.32, 7.93\) Hz, 4H), 7.30 (t, \(J = 6.10, 7.17\) Hz, 2H), 7.17 (d, \(J = 8.24\) Hz, 2H), 2.88 (t, \(J = 2H), 2.25 (s, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 197.1, 143.7, 137.3, 135.5, 132.7, 131.6, 128.8, 128.5, 128.3, 127.7, 127.3, 59.2, 33.7, 27.0, 17.3\); IR (KBr): \(\nu = 3447, 3059, 2925, 1661, 1442, 1263, 700\) cm\(^{-1}\); MS (ESI) 437 (M+H). ESI-HRMS obtained for C\(_{25}\)H\(_{22}\)OC\(_{2}\)S\(_2\) (M+H) = 437.0721 (calculated: 437.0726).
6.40, 6.40 Hz, 2H), 2.69-2.65 (q, \( J = 7.47, 7.62 \) Hz, 2H), 2.33 (t, \( J = 6.25, 6.40 \) Hz, 2H), 2.27 (s, 3H), 1.24 (t, \( J = 7.62, 7.62 \) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 193.9, 144.2, 139.5, 138.2, 136.7, 136.0, 135.7, 132.5, 130.2, 129.0, 128.8, 128.7, 128.5, 128.1, 127.0, 126.6, 47.4, 27.1, 18.2; IR (KBr): \( \nu = 3444, 3055, 2953, 1663, 1441, 1265, 703 \) cm\(^{-1}\); MS (ESI) 449 (M+H). MS (ESI) 431 (M+H). ESI-HRMS obtained for C\(_{27}\)H\(_{27}\)OS\(_2\) (M+H) = 431.1485 (calculated: 431.1497).

(2-(methylthio)-1-thiaspiro[5.5]undec-2-en-3-yl)(phenyl)methanone (3h): Yield 79% (0.60 g), yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.82 (d, \( J = 7.01 \) Hz, 2H), 7.54 (t, \( J = 7.32, 7.47 \) Hz, 1H), 7.45 (t, \( J = 7.62, 7.32 \) Hz, 2H), 2.55 (t, \( J = 6.56, 6.56 \) Hz, 2H), 2.19 (s, 3H), 1.95-1.91 (m, 4H), 1.73-1.62 (m, 6H), 1.56-1.50 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 197.2, 137.5, 133.8, 132.6, 128.9, 128.5, 49.8, 37.4, 35.0, 25.9, 25.7, 22.0, 17.9; IR (thin film): \( \nu = 3059, 2926, 2854, 1660, 1446, 1264, 703 \) cm\(^{-1}\); MS (ESI) 319 (M+H). ESI-HRMS obtained for C\(_{18}\)H\(_{23}\)OS\(_2\) (M+H) = 319.11813 (calculated: 319.1184).

(4-chlorophenyl)(2-(methylthio)-1-thiaspiro[5.5]undec-2-en-3-yl)methanone (3i): Yield 80% (0.58 g), yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.74 (d, \( J = 8.55 \) Hz, 2H), 7.42 (d, \( J = 8.55 \) Hz, 2H), 2.53 (t, \( J = 6.48, 6.60 \) Hz, 2H), 2.19 (s, 3H), 1.93-1.89 (m, 4H), 1.71-1.61 (m, 6H), 1.56-1.49 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 195.9, 138.9, 136.0, 133.4, 133.0, 130.2, 128.8, 50.0, 37.4, 35.0, 25.9, 25.6, 22.0, 17.9; IR
(thin film): $\nu$ 3060, 2927, 2857, 1662, 1265, 702 cm$^{-1}$; MS (ESI) 353 (M+H). ESI-HRMS obtained for C$_{18}$H$_{22}$ClOS$_2$ (M+H) = 353.0791 (calculated: 353.0795).

(4-ethylphenyl)(2-(methylthio)-1-thiaspiro[5.5]undec-2-en-3-yl)methanone (3j): Yield 72% (0.52 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.77 (d, $J$ = 8.24 Hz, 2H), 7.29 (d, $J$ = 8.24 Hz, 2H), 2.73-2.69 (q, $J$ = 7.47, 7.63 Hz, 2H), 2.52 (t, $J$ = 6.56, 6.56 Hz, 2H), 2.20 (s, 3H), 1.95-1.90 (m, 4H), 1.72-1.60 (m, 6H), 1.55-1.50 (m, 2H), 1.26 (t, $J$ = 7.62, 7.62 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 197.1, 149.8, 134.8, 134.4, 130.5, 129.2, 128.1, 49.7, 37.4, 35.0, 28.9, 25.9, 25.7, 22.0, 18.0, 15.1; IR (thin film): $\nu$ 3058, 2922, 2855, 1661, 1443, 1262, 700 cm$^{-1}$; MS (ESI) 347 (M+H). ESI-HRMS obtained for C$_{20}$H$_{27}$OS$_2$ (M+H) = 347.1494 (calculated: 347.1497).

(2-methyl-6-(methylthio)-2-phenyl-3,4-dihydro-2H-thiopyran-5-yl)(phenyl)methanone (3k): Yield 75% (0.60 g), pale yellow solid, mp 82-84 $^\circ$C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.65-7.60 (m, 4H), 7.49 (t, $J$ = 7.32, 7.47 Hz, 1H), 7.42 (t, $J$ = 7.47, 7.93 Hz, 2H), 7.38-7.30 (m, 3H), 2.64-2.58 (m, 1H), 2.55-2.50 (m, 1H), 2.36-2.29 (m, 1H), 2.25-2.21 (m, 1H), 2.21 (s, 3H), 1.77 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 197.3, 144.4, 137.2, 134.7, 132.7, 131.4, 128.8, 128.6, 128.4, 127.2, 126.4, 51.8, 35.7, 29.4, 27.0, 17.4; IR (KBr): $\nu$ 3447, 3052, 2958, 2923, 1665, 1444, 1235, 702 cm$^{-1}$; MS (ESI) 341 (M+H). ESI-HRMS obtained for C$_{20}$H$_{21}$OS$_2$ (M+H) = 341.1024 (calculated: 341.1028).
(4-chlorophenyl)(2-methyl-6-(methylthio)-2-phenyl-3,4-
dihydro-2H-thiopyran-5-yl)methanone (3l): Yield 72% (0.55 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.62 (d, $J$ = 7.33 Hz, 2H), 7.49 (d, $J$ = 8.55 Hz, 2H), 7.40 (t, $J$ = 7.33, 8.06 Hz, 2H), 7.31 (t, $J$ = 7.82, 8.43 Hz, 3H), 2.63-2.50 (m, 2H), 2.32-2.21 (m, 2H), 2.19 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 195.8, 144.2, 138.8, 135.6, 134.0, 132.1, 130.0, 128.6, 128.5, 127.1, 126.3, 51.8, 35.6, 29.4, 26.9, 17.1; IR (thin film): $\nu$ 3448, 3055, 2960, 2923, 1667, 1443, 1234, 701 cm$^{-1}$; MS (ESI) 375 (M+H). ESI-HRMS obtained for C$_{20}$H$_{20}$ClOS$_2$ (M+H) = 375.0640 (calculated: 375.0638).

(4-ethylphenyl)(2-methyl-6-(methylthio)-2-phenyl-3,4-
dihydro-2H-thiopyran-5-yl)methanone (3m): Yield 70% (0.54 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.63 (d, $J$ = 7.33 Hz, 2H), 7.56 (d, $J$ = 8.19 Hz, 2H), 7.41 (t, $J$ = 7.33, 7.94 Hz, 2H), 7.31 (t, $J$ = 7.21, 7.33 Hz, 1H), 7.18 (d, $J$ = 8.19 Hz, 2H), 2.70-2.64 (q, $J$ = 7.70, 7.58 Hz, 2H), 2.59-2.49 (m, 2H), 2.34-2.23 (m, 2H), 2.21 (s, 3H), 1.76 (s, 3H), 1.23 (t, $J$ = 7.58, 7.58 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 187.0, 145.6, 137.4, 137.0, 134.6, 133.5, 133.4, 132.8, 129.3, 128.9, 128.7, 128.4, 127.6, 127.3, 126.7, 126.6, 57.7, 18.6; IR (thin film): $\nu$ 3448, 2965, 2923, 1667, 1443, 1234, 701 cm$^{-1}$; MS (ESI) 369 (M+H). ESI-HRMS obtained for C$_{22}$H$_{25}$OS$_2$ (M+H) = 369.1341 (calculated: 369.1341).
(2,2-dimethyl-6-(methylthio)-3,4-dihydro-2H-thiopyran-5-yl)(phenyl)methanone (3n): Yield 68 % (0.48 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.77$ (d, $J = 6.96$ Hz, 2H), 7.47 (t, $J = 7.21$, 7.45 Hz, 1H), 7.39 (t, $J = 7.58$, 7.21 Hz, 2H), 2.51 (t, $J = 6.60$, 6.48 Hz, 2H), 2.09 (s, 3H), 1.78 (t, $J = 6.60$, 6.60 Hz, 2H), 1.37 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 197.2$, 137.4, 133.2, 132.7, 132.2, 128.9, 128.5, 44.7, 35.9, 29.0, 26.7, 17.7; IR (thin film): $\nu$ 3449, 2962, 2923, 1658, 1262, 1109, 801 cm$^{-1}$; MS (ESI) 279 (M+H). ESI-HRMS obtained for C$_{15}$H$_{19}$OS$_2$ (M+H) = 279.0910 (calculated: 279.0871).

(4-chlorophenyl)(2,2-dimethyl-6-(methylthio)-3,4-dihydro-2H-thiopyran-5-yl)methanone (3o): Yield 70 % (0.45 g), pale yellow solid, mp 97-99 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.69$ (d, $J = 8.55$ Hz, 2H), 7.35 (d, $J = 8.55$, 7.45 Hz, 2H), 2.50 (t, $J = 6.60$, 6.48 Hz, 2H), 2.10 (s, 3H), 1.78 (t, $J = 6.48$, 6.60 Hz, 2H), 1.36 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 195.9$, 139.0, 136.0, 133.3, 132.4, 130.2, 128.8, 44.8, 35.9, 29.0, 26.7, 17.6; IR (thin film): $\nu$ 3450, 2966, 2922, 1659, 1263, 1109, 803 cm$^{-1}$; MS (ESI) 313 (M+H). ESI-HRMS obtained for C$_{15}$H$_{18}$OClS$_2$ (M+H) = 313.0477 (calculated: 313.0482).
(2,2-dimethyl-6-(methylthio)-3,4-dihydro-2H-thiopyran-5-yl)(4-ethylphenyl)methanone (3p): Yield 75% (0.48 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 7.78 (d, $J = 8.19$ Hz, 2H), 7.29 (d, $J = 8.19$ Hz, 2H), 2.74-2.68 (q, $J = 7.58$, 7.58 Hz, 2H), 2.56 (t, $J = 6.60$, 6.48 Hz, 2H), 2.18 (s, 3H), 1.85 (t, $J = 6.60$, 6.60 Hz, 2H), 1.44 (s, 6H), 1.26 (t, $J = 7.70$, 7.58 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 197.1, 149.8, 134.8, 133.8, 130.5, 129.2, 128.0, 44.6, 35.9, 29.0, 28.9, 26.7, 17.8, 15.0; IR (thin film): $\nu$ 3451, 2965, 2921, 1661, 1261, 1109, 804 cm$^{-1}$; MS (ESI) 307 (M+H). ESI-HRMS obtained for C$_{17}$H$_{23}$OS$_2$ (M+H) = 307.1180 (calculated: 307.1184).

(2,2-dimethyl-6-(methylthio)-3,4-dihydro-2H-thiopyran-5-yl)(4-methoxyphenyl)methanone (3q): Yield 68% (0.44 g), yellow liquid; $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 7.85 (d, $J = 8.85$ Hz, 2H), 6.95 (d, $J = 9.00$ Hz, 2H), 3.87 (s, 3H), 2.56 (t, $J = 6.56$, 6.56 Hz, 2H), 2.19 (s, 3H), 1.85 (t, $J = 6.56$, 6.56 Hz, 2H), 1.43 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 196.3, 163.5, 134.0, 131.4, 129.9, 129.5, 113.8, 55.4, 44.6, 35.9, 29.0, 26.8, 17.9; IR (thin film): $\nu$ 3449, 2965, 2921, 1655, 1266, 1111, 807 cm$^{-1}$; MS (ESI) 309 (M+H). ESI-HRMS obtained for C$_{16}$H$_{21}$O$_2$S$_2$ (M+H) = 309.0974 (calculated: 309.0977).
$^1$H NMR CDCl$_3$, 300 MHz

$^{13}$C NMR CDCl$_3$, 75 MHz
$^1$H NMR CDCl$_3$, 300 MHz

$^1$C NMR CDCl$_3$, 75 MHz