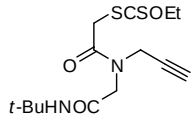
General procedure for the synthesis of Ugi adducts:

To a 1 M solution of aldehyde (1 mmol) in methanol were added successively 1 equiv. of amine, 1 equiv. of chloroacetic acid and 1 equiv. of isocyanide. The resulting mixture was stirred at room temperature until completion of starting materials (TLC). Then, potassium *O*-ethylxanthogenate was added and the reaction mixture was stirred at room temperature for 2-3 h. After extraction, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography on silica gel.

Typical procedure for the alkyne-xanthates cyclizations under reductive conditions:

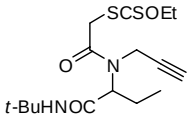
To a degassed solution of the appropriate alkyne-xanthate adduct (generally 0.3-0.5 mmol) in isopropanol (0.02 M) heated at reflux under argon was added lauroyl peroxide (1 equiv.). When starting material was totally consumed, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. This crude reaction mixture was purified by flash column chromatography on silica gel, using diethyl ether or ethyl acetate/petroleum ether.

Dithiocarbonic acid *S*-{[(*tert*-butylcarbamoyl-methyl)-prop-2-ynyl-carbamoyl]-methyl} ester *O*-ethyl ester 1a



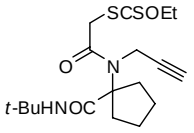
General procedure for this Ugi adduct, using formaldehyde (as a 40% aqu. solution). Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 20:80) gave **1a** as a 1:1.5 mixture of two rotamers as a yellow oil.
Yield 72% (rt, 16h).
R_f 0.3 (80:20 diethyl ether / petroleum ether).
Major rotamer :
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.95 (br s, 1H, N*H*), 4.68 (q, 2H, *J* = 7.1 Hz, OC*H*$_2$CH$_3$), 4.36 (d, 2H, *J* = 2.2 Hz, H-1), 4.19 (s, 2H, H-3), 4.06 (s, 2H, H-4), 2.43 (t, 1H, *J* = 2.2 Hz, H-2), 1.44 (t, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$), 1.29 (s, 9H, C(C*H*$_3$)$_3$).
Mixture of rotamers :
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 214.46 (*C*=S), [167.92, 167.88 (*C*=O)], 168.60 (*C*=O), 74.47 (CH), 73.92 (Cq), 71.41 (O*C*H$_2$CH$_3$), 52.54 (CH$_2$), 52.33 (CH$_2$), 51.91 (*C*(CH$_3$)$_3$), 39.42 (CH$_2$), 39.02 (CH$_2$), 29.09 (C(*C*H$_3$)$_3$), 14.21 (OCH$_2$*C*H$_3$).
MS (DI, CI NH$_3$) *m/z* 331 (M+H$^+$).
HRMS Calcd. 330.1072, Found 330.1080.

Dithiocarbonic acid *S*-{[(1-*tert*-butylcarbamoyl-propyl)-prop-2-ynyl-carbamoyl]-methyl} ester *O*-ethyl ester 1b



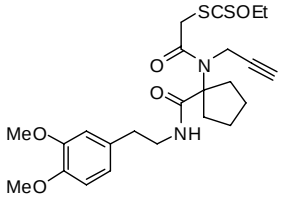
General procedure for this Ugi adduct. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 30:70) gave **1b** as a yellow oil.
Yield 70% (rt, 16h).
R_f 0.3 (70:30 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.98 (br s, 1H, N*H*), 4.82 (t, 1H, *J* = 8.1 Hz), 4.65 (q, 2H, *J* = 7.1 Hz, OC*H*$_2$CH$_3$), 4.31 (d, 1H, *J* = 16.1 Hz), 4.30 (dd, 2H, *J* = 2.4, 9.0 Hz), 4.11 (d, 1H, *J* = 16.1 Hz), 2.38 (t, 1H, *J* = 2.4 Hz), 1.98-1.95 (m, 1H), 1.76-1.74 (m, 1H), 1.38 (t, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$), 1.32 (s, 9H), 0.91 (t, 3H, *J* = 7.4 Hz).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 214.58 (*C*=S), 169.43 (*C*=O), 168.70 (*C*=O), 79.37 (*C*H), 73.74 (Cq), 70.83 (O*C*H$_2$CH$_3$), 59.98 (CH), 52.01 (Cq), 39.54 (CH$_2$), 35.05 (CH$_2$), 29.02 (Cq), 21.90 (CH$_2$), 14.18 (OCH$_2$*C*H$_3$), 11.07 (CH$_3$).
MS (DI, CI NH$_3$) *m/z* 359 (M+H$^+$).
I.R. (thin film) 3267, 2964, 1645, 1382, 1187, 1086 cm^{-1}.
HRMS Calcd. 358.1385, Found 358.1380.

Dithiocarbonic acid *S*-{[(1-*tert*-butylcarbamoyl-cyclopentyl)-prop-2-ynyl-carbamoyl]-methyl} ester *O*-ethyl ester 1c



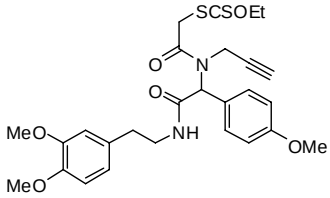
Ugi reaction under microwaves :
Propargylamine (1 mmol), cyclopentanone (1 equiv.), chloroacetic acid (1 equiv.), *tert*butylisocyanide (1 equiv.) and methanol (1 mL) were introduced together in the reactor of the microwave apparatus. The reaction mixture, mechanically stirred, was irradiated under an incident power of 50W for 5 min, with a maximum temperature controlled to 50 °C. The reaction mixture was then cooled, potassium *O* ethylxanthogenate (1 equiv.) was added and the reaction mixture was stirred at room temperature for 2 h. After extraction, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography (silica gel ; petroleum ether/diethyl ether, 50:50) to afford **1c** as a white solid.
Yield 99%
mp 107-108 °C (cyclohexane).
R$_f$ 0.3 (50:50 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.38 (br s, 1H, N*H*), 4.68 (q, 2H, *J* = 7.1 Hz, OC*H*$_2$CH$_3$), 4.30 (br s, 2H), 4.18 (br s, 2H), 2.56-2.54 (m, 2H), 2.47 (br s, 1H), 2.02-2.00 (m, 2H), 1.75-1.70 (m, 4H), 1.43 (t, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$), 1.30 (s, 9H).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 213.84 (*C*=S), 168.90 (*C*=O), 168.80 (*C*=O), 73.77 (CH), 71.20 (O*C*H$_2$CH$_3$), 70.59 (Cq), 57.56 (Cq), 51.52 (*C*(CH$_3$)$_3$), 40.74 (CH$_2$), 36.32 (CH$_2$), 36.18 (CH$_2$), 28.91 (C(*C*H$_3$)$_3$), 24.06 (CH$_2$), 14.22 (OCH$_2$*C*H$_3$).
MS (DI, CI NH$_3$) *m/z* 385 (M+H$^+$).
I.R. (thin film) 3310, 2885, 1658, 1193 cm^{-1}.

Dithiocarbonic acid *S*-[({1-[2-(3,4-dimethoxy-phenyl)-ethylcarbamoyl]-cyclopentyl}-prop-2-ynyl-carbamoyl)-methyl] ester *O*-ethyl ester 1d



Ugi reaction under microwaves : Same procedure as **1c.**
Purification by flash column chromatography (silica gel ; petroleum ether-diethyl ether, 20:80) gave **1d** as a yellow oil.
Yield 50%
R$_f$ 0.3 (80:20 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.79 (d, 1H, *J* = 7.8 Hz), 6.73-6.71 (m, 2H), 6.49 (br t, 1H, *J* = 5.4 Hz, N*H*), 4.63 (q, 2H, *J* = 7.1 Hz, OC*H*$_2$CH$_3$), 4.21 (br s, 2H), 4.10 (br s, 2H), 3.87 (s, 3H, OC*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 3.49-3.44 (m, 2H), 2.72 (t, 2H, *J* = 6.8 Hz), 2.54-2.51 (m, 2H), 2.32 (br s, 1H), 2.00 (br s, 2H), 1.44 (br s, 4H), 1.40 (t, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 214.42 (*C*=S), 173.37 (*C*=O), 168.43 (*C*=O), 149.27 (Cq), 147.91 (Cq), 132.00 (Cq), 121.15 (CH), 112.32 (CH), 111.56 (CH), 79.70 (Cq), 74.27 (CH), 71.10 (O*C*H$_2$CH$_3$), 64.59 (Cq), 56.34 (O*C*H$_3$), 56.30 (O*C*H$_3$), 41.23 (CH$_2$), 40.85 (CH$_2$), 36.42 (CH$_2$), 36.39 (CH$_2$), 35.53 (CH$_2$), 24.02 (CH$_2$), 14.21 (OCH$_2$*C*H$_3$).
MS (DI, CI NH$_3$) *m/z* 493 (M+H$^+$).
I.R. (thin film) 3295, 2898, 1675, 1187, 1063 cm^{-1}.

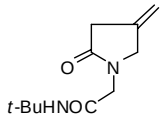
Dithiocarbonic acid *S*-({[[2-(2,3-dimethoxy-phenyl)-ethylcarbamoyl]-(4-methoxy-phenyl)-methyl]-prop-2-ynyl-carbamoyl}-methyl) ester *O*-ethyl ester 1e



General procedure for this Ugi adduct. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 10:90) gave **1e** as a yellow oil.
Yield 40% (rt, 16h).
R$_f$ 0.3 (90:10 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.24 (d, 2H, *J* = 8.4 Hz, Har), 6.87 (d, 2H, *J* = 8.4 Hz), 6.79-6.70 (m, 3H), 6.36 (br t, 1H, *J* = 5.1 Hz, N*H*), 6.16 (s, 1H), 4.64 (q, 2H, *J* = 7.1 Hz, OC*H*$_2$CH$_3$), 4.26- 4.12 (m,

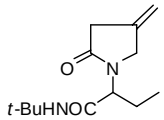
4H), 3.85 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 3.60-3.56 (m, 1H), 3.49-3.46 (m, 1H), 2.77 (t, 2H, *J* = 6.9 Hz), 2.14 (t, 1H, *J* = 2.2 Hz), 1.38 (t, 3H, *J* = 7.1 Hz, OCH$_2$C*H*$_3$).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 214.03 (*C*=S), 169.54 (*C*=O), 168.36 (*C*=O), 160.17 (Cq), 149.30 (Cq), 147.98 (Cq), 131.66 (Cq), 131.16 (CH), 126.43 (CH), 121.15 (CH), 114.56 (CH), 112.35 (CH), 111.63 (CH), 79.32 (CH), 73.04 (Cq), 71.05 (O*C*H$_2$CH$_3$), 61.31 (CH), 56.29 (O*C*H$_3$), 56.22 (O*C*H$_3$), 55.71 (O*C*H$_3$), 41.32 (CH$_2$), 39.93 (CH$_2$), 35.81 (CH$_2$), 35.68 (CH$_2$), 14.18 (OCH$_2$*C*H$_3$).
MS (DI, CI NH$_3$) *m/z* 545 (M+H$^+$).
I.R. (thin film) 3289, 2956, 1656, 1634, 1390, 1275, 1054 cm^{-1}.
HRMS Calcd. 544.1702, Found 544.1707.

N-tert-Butyl-2-(4-methylene-2-oxo-pyrrolidin-1-yl)-acetamide 2a



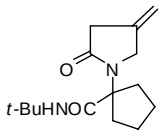
General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1a**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 30:70) gave **2a** as a yellow oil.
Yield 68% (16h).
R$_f$ 0.2 (70:30 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.86 (br s, 1H, N*H*), 5.15 (pent., 2H, *J* = 2.5 Hz), 4.16-4.14 (m, 2H), 3.85 (s, 2H), 3.19-3.18 (m, 2H), 1.38 (s, 9H, C(C*H*$_3$)$_3$).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 174.04 (*C*=O), 167.32 (*C*=O), 136.60 (Cq), 110.26 (CH$_2$), 54.36 (CH$_2$), 51.93 (*C*(CH$_3$)$_3$), 48.00 (CH$_2$), 37.34 (CH$_2$), 29.10 (C(*C*H$_3$)$_3$).
MS (DI, CI NH$_3$) *m/z* 211 (M+H$^+$).
HRMS Calcd. 210.1368, Found 210.1362.

N-tert-Butyl-2-(4-methylene-2-oxo-pyrrolidin-1-yl)-butyramide 2b



General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1b**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 30:70) gave **2b** as a yellow oil.
Yield 88% (16h).
R$_f$ 0.3 (80:20 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.88 (br s, 1H, N*H*), 5.13 (pent., 2H, *J* = 2.4 Hz), 4.39 (t, 1H, *J* = 7.5 Hz), 4.14 (dd, 1H, *J* = 2.4, 14.2 Hz), 4.02 (dd, 1H, *J* = 2.4, 14.2 Hz), 3.20-3.18 (m, 2H), 1.96-1.93 (m, 1H), 1.70-1.68 (m, 1H), 1.29 (s, 9H), 0.92 (t, 3H, *J* = 7.4 Hz).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 173.95 (*C*=O), 169.26 (*C*=O), 136.92 (Cq), 110.05 (CH$_2$), 57.44 (CH), 51.81 (*C*(CH$_3$)$_3$), 49.92 (CH$_2$), 37.97 (CH$_2$), 29.10 (C(*C*H$_3$)$_3$), 21.54 (CH$_2$), 11.89 (CH$_3$).
MS (DI, CI NH$_3$) *m/z* 239 (M+H$^+$).
I.R. (thin film) 2945, 1678, 1543, 1456, 1230, 1012 cm^{-1}.
HRMS Calcd. 238.1681, Found 238.1678.

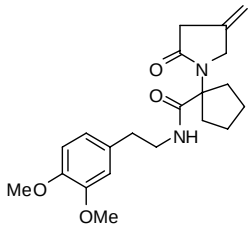
1-(4-Methylene-2-oxo-pyrrolidin-1-yl)-cyclopentanecarboxylic acid *tert*-butylamide 2c



Alkyne-xanthate cyclization under microwaves :
A stirred solution of xanthate 1c (0,04 mmol) and dilauroyl peroxide (1 equiv.) in isopropanol (2 ml) was irradiated under an incident power of 50W for 20 min, with a maximum temperature programmed at 90 °C. The reaction mixture was then cooled, concentrated and purified by flash column chromatography (silica gel ; petroleum ether-diethyl ether, 20:80) to afford **2c** as a yellow oil.
Yield 61%
R$_f$ 0.2 (80:20 diethyl ether / petroleum ether).

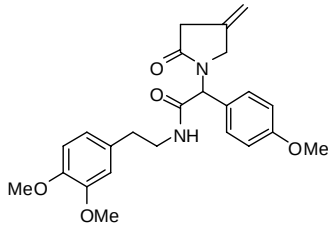
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.86 (br s, 1H, N*H*), 5.09 (pent., 2H, *J* = 2.4 Hz), 4.13 (t, 2H, *J* = 2.4 Hz), 3.18 (t, 2H, *J* = 2.4 Hz), 2.50-2.43 (m, 2H), 2.10-2.03 (m, 2H), 1.72-1.69 (m, 4H), 1.33 (s, 9H).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 173.45 (*C*=O), 168.32 (*C*=O), 136.89 (Cq), 109.75 (CH_2), 57.46 (Cq), 53.19 (CH_2), 51.37 ($C(CH_3)_3$), 39.13 (CH_2), 35.21 (CH_2), 29.07 ($C(CH_3)_3$), 23.00 (CH_2).
MS (DI, CI NH$_3$) *m/z* 265 ($M+H^+$).
HRMS Calcd. 264.1838, Found 264.1843.

1-(4-Methylene-2-oxo-pyrrolidin-1-yl)-cyclopentanecarboxylic acid [2-(3,4-dimethoxyphenyl)-ethyl]-amide 2d.



Alkyne-xanthate cyclization under microwaves : Same procedure as **2c.**
Purification by flash column chromatography (silica gel ; petroleum ether-diethyl ether, 10:90) gave **2d** as a yellow oil.
Yield 77%.
R$_f$ 0.2 (90:10 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.97 (br t, 1H, *J* = 5.1 Hz, N*H*), 6.80-6.75 (m, 3H), 5.05 (pent., 2H, *J* = 2.5 Hz), 4.02 (br s, 2H), 3.87 (s, 3H, OC*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 3.51 (ddd, 2H, *J* = 5.1, 7.1, 12.9 Hz), 3.06 (br s, 2H), 2.77 (t, 2H, *J* = 7.1 Hz), 2.45-2.43 (m, 2H), 2.06-2.03 (m, 2H), 1.69-1.65 (m, 4H).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 174.85 (*C*=O), 173.14 (*C*=O), 149.23 (Cq), 147.87 (Cq), 136.76 (Cq), 131.79 (Cq), 120.93 (CH), 112.18 (CH), 111.48 (CH), 109.72 (CH_2), 70.57 (Cq), 56.26 (O*C*H$_3$), 56.24 (O*C*H$_3$), 53.09 (CH_2), 40.95 (CH_2), 38.92 (CH_2), 35.52 (CH_2), 35.35 (CH_2), 23.11 (CH_2).
MS (DI, CI NH$_3$) *m/z* 373 ($M+H^+$).
HRMS Calcd. 372.2049, Found 372.2055.

***N*-[2-(3,4-Dimethoxy-phenyl)-ethyl]-2-(4-methoxy-phenyl)-2-(4-methylene-2-oxopyrrolidin-1-yl) acetamide 2e**

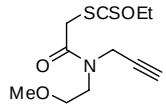


General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1e**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 10:90) gave **2e** as a yellow oil.
Yield 60% (16h).
R$_f$ 0.3 (90:10 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.22 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 6.78 (d, 1H, *J* = 8.7 Hz), 6.70-6.68 (m, 2H), 5.82 (br t, 1H, *J* = 6.3 Hz, N*H*), 5.79 (s, 1H), 5.06 (pent., 1H, *J* = 2.2 Hz), 4.99 (pent., 1H, *J* = 2.3 Hz), 4.32 (br d, 1H, *J* = 13.9 Hz), 3.87 (s, 3H, OC*H*$_3$), 3.83 (s, 6H, OC*H*$_3$), 3.65-3.56 (m, 2H), 3.49 (dt, 1H, *J* = 6.3, 12.9 Hz), 3.22 (ddd, 1H, *J* = 2.2, 2.3, 14.3 Hz), 3.13 (ddd, 1H, *J* = 2.2, 2.3, 21.3 Hz), 2.76 (t, 2H, *J* = 7.1 Hz).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 173.51 (*C*=O), 169.44 (*C*=O), 160.18 (Cq), 149.38 (Cq), 148.06 (Cq), 137.08 (Cq), 131.39 (Cq), 130.86 (CH_2), 126.36 (Cq), 121.03 (CH), 114.68 (CH), 112.19 (CH), 111.65 (CH), 109.66 (CH), 58.41 (CH), 56.29 (O*C*H$_3$), 56.20 (O*C*H$_3$), 55.73 (O*C*H$_3$), 50.96 (CH_2), 41.22 (CH_2), 37.92 (CH_2), 35.57 (CH_2).
MS (DI, CI NH$_3$) *m/z* 425 ($M+H^+$).
I.R. (thin film) 2865, 1663, 1578, 1125, 1026 cm^{-1}.
HRMS Calcd. 424.1998, Found 424.2003.

General procedure for the synthesis of alkyne-xanthate adducts (1f, 1g, 1h, 1i):

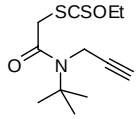
To a solution of starting amine (5 equiv.) in dichloromethane (0.5 M) was added the bromoalkyne (1 equiv.) dropwise with stirring at room temperature for 3h. To the mixture obtained after filtration and evaporation of the residual amine and solvent, were added dichloromethane (0.5 M) and ethyldiisopropyl-amine (1 equiv.). To this solution was then added dropwise chloroacetyl chloride (1 equiv) at 0°C for 2h. After extraction (H_2O/dichloromethane) and evaporation of the solvent, the product was dissolved in ethanol (1 M) and potassium *O*-ethylxanthogenate (1 equiv.) was added, this reaction mixture was then stirred at room temperature for 4 h. After extraction and removal of the solvent under reduced pressure, the starting xanthates were purified by flash column chromatography (silica gel ; petroleum ether/diethyl ether).

Dithiocarbonic acid *O*-ethyl ester *S*-{[(2-methoxy-ethyl)-prop-2-ynyl-carbamoyl]-methyl} ester 1f.



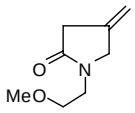
General procedure for the formation of this alkyne-xanthate adduct, obtained as a yellow oil, as a 1:1.6 mixture of two rotamers.
Yield 57% (over the 3 steps)
R_f 0.3 (70:30 diethyl ether / petroleum ether).
Major rotamer :
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.66 (q, 2H, *J* = 7.1 Hz, OCH_2CH_3), 4.33 (d, 2H, *J* = 2.4 Hz), 4.24 (s, 2H), 3.77 (t, 2H, *J* = 5.4 Hz), 3.63 (t, 2H, *J* = 5.4 Hz), 3.38 (s, 3H, OCH_3), 2.25 (t, 1H, *J* = 2.4 Hz), 1.44 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3).
Mixture of rotamers :
^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 214.38 (*C*=S), 167.43 (*C*=O), 82.93 (Cq), 72.82 (CH), 71.58 (CH_2), 70.82 (OCH_2CH_3), 59.50 (CH_2), 58.85 (CH_2), 47.56 (CH_2), 47.12 (CH_2), 39.79 (CH_2), 39.72 (CH_2), 35.66 (CH_2), 14.12 (OCH_2CH_3).
MS (DI, CI NH_3) *m/z* 276 ($M+H^+$).

Dithiocarbonic acid *S*-[(*tert*-butyl-prop-2-ynyl-carbamoyl)-methyl] ester *O*-ethyl ester 1g.



General procedure for the formation of this alkyne-xanthate adduct, obtained as a yellow solid.
Yield 55% (over the 3 steps)
R_f 0.3 (80:20 diethyl ether / petroleum ether).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.66 (q, 2H, *J* = 7.1 Hz, OCH_2CH_3), 4.25 (s, 2H), 4.19 (d, 2H, *J* = 2.4 Hz), 2.37 (t, 1H, *J* = 2.4 Hz), 1.52 (s, 9H), 1.44 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3).
^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 214.40 (*C*=S), 167.32 (*C*=O), 80.43 (Cq), 73.22 (CH), 70.78 (OCH_2CH_3), 59.28 ($C(CH_3)_3$), 42.89 (CH_2), 35.46 (CH_2), 28.98 ($C(CH_3)_3$), 14.22 (OCH_2CH_3).
MS (DI, CI NH_3) *m/z* 274 ($M+H^+$).

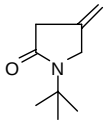
1-(2-Methoxy-ethyl)-4-methylene-pyrrolidin-2-one 2f



General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1f**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 60:40) gave **2f** as a yellow oil.
Yield 45% (4h).
R_f 0.3 (60:40 diethyl ether / petroleum ether).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.15 (pent., 2H, *J* = 2.3 Hz), 4.16-4.12 (m, 2H), 3.57-3.53 (m, 4H), 3.37 (s, 3H, OCH_3), 3.16-3.12 (m, 2H).

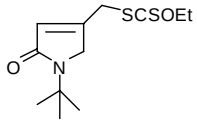
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 173.32 (*C*=O), 137.71 (Cq), 109.39 (CH_2), 71.29 (CH_2), 59.15 (OCH_3), 54.60 (CH_2), 42.63 (CH_2), 37.77 (CH_2).
MS (DI, CI NH$_3$) *m/z* 156 ($M+H^+$).
I.R. (thin film) 2935, 1586, 1176, 1043 cm^{-1}.
HRMS calcd for $C_8H_{13}NO_2$: 155.0946, found: 155.0941.

1-*tert*-Butyl-4-methylene-pyrrolidin-2-one 2g.



General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1g**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 50:50) gave **2g** as a yellow oil.
Yield 45% (4h).
R$_f$ 0.4 (60:40 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.03 (pent., 2H, *J* = 2.5 Hz), 4.12-4.10 (m, 2H), 3.13-3.11 (m, 2H), 1.43 (s, 9H).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 173.40 (*C*=O), 137.87 (Cq), 108.83 (CH_2), 54.51 ($C(CH_3)_3$), 52.04 (CH_2), 39.79 (CH_2), 28.08 ($C(CH_3)_3$).
MS (DI, CI NH$_3$) *m/z* 154 ($M+H^+$).
I.R. (thin film) 2942, 1654, 1234, 1056 cm^{-1}.
HRMS calcd for $C_9H_{15}NO$: 153.1154, found: 153.1148.

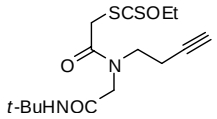
Dithiocarbonic acid *S*-(1-*tert*-butyl-5-oxo-2,5-dihydro-1*H*-pyrrol-3-ylmethyl) ester *O*-ethyl ester 3g.



General procedure for this alkyne-xanthate cyclization under reductive conditions, using adduct **1g**. Purification by flash column chromatography (silica gel; petroleum ether-diethyl ether, 50:50) gave **3g** (yellow oil), as a side product obtained with **2g**.
Yield 8% (4h).
R$_f$ 0.2 (90:10 diethyl ether / petroleum ether).
^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.02 (s, 1H), 4.68 (q, 2H, *J* = 7.1 Hz, OCH_2CH_3), 4.10 (s, 2H), 4.02 (s, 2H, H-3), 1.43 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3), 1.30 (s, 9H).
^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 213.18 (*C*=S), 171.59 (*C*=O), 151.83 (Cq), 127.52 (CH), 71.19 (OCH_2CH_3), 54.42 ($C(CH_3)_3$), 52.72 (CH_2), 34.74 (CH_2), 28.81 ($C(CH_3)_3$), 14.21 (OCH_2CH_3).
MS (DI, CI NH$_3$) *m/z* 274 ($M+H^+$).
I.R. (thin film) 3034, 2935, 1664, 1175, 1049 cm^{-1}.

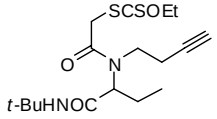
General procedure for the formation of xanthates 1j,1k,1l.
A solution of the 1-azido-but-4-yne (185 mg, 2 mmol) in ether (6 mL) was cooled at 0 °C. Then triphenyl phosphine (765.35 mg, 3 mmol) was added to the solution and stirred at room temperature overnight. Solvent was removed under reduced pressure and the residue was dissolved in methanol anhydrous (9 mL). The aldehyde (2.1 mmol) was added and the reaction mixture stirred for 1 hour. Then chloroacetic acid monohydrate (2 mmol) and *t*-butyl isocyanide (2 mmol) was added to the reaction mixture and stirred for 48 hours. Potassium ethyl xanthogenate (2.3 mmol) was added to the reaction mixture and stirred for 1 hour. Methanol was removed under reduced pressure. The crude residue was purified by flash column chromatography.

_S_-2-(But-3-ynyl(2-(tert-butylamino)-2-oxoethyl)amino)-2-oxoethyl-O-ethyl carbonodithioate 1j.



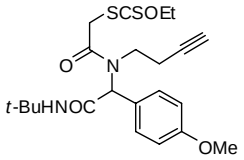
General procedure with formaldehyde. Purification by flash column chromatography (6:4 hexane/EtOAc) to give **1j** (45%) as a pale yellow solid:
mp 82-83 °C.
R$_f$ 0.3 (60:40 hexane / ethyl acetate).
^{1}**HNMR** (300 MHz, $CDCl_3$) δ (ppm) 6.20 (bs, 1H), 4.65 (q, J=7.2 Hz, 2H), 4.25 (s, 2H), 3.95 (s, 2H), 3.74 (t, J=6.6 Hz, 2H), 2.61 (td, J=2.7 Hz, J=6.6 Hz, 2H), 2.09 (t, J=2.7 Hz, 1H), 1.43 (t, J=7.2 Hz, 3H), 1.32 (s, 9H). Rotamer (3:1) 5.95, 4.13, 4.03, 3.58, 2.49, 2.02, 1.39.
^{13}**CNMR** (75.4 MHz, $CDCl_3$) δ (ppm) 213.88 (*C*=S), 167.33 (*C*=O), 166.52 (*C*=O), 81.46 (*C*≡C), 71.58 (O*C*H_2), 70.76 (H*C*≡C), 52.52 (*C*H_2N), 51.25 (*C*(CH_3)$_3$), 48.41(*C*H_2N), 38.81 (*C*H_2S), 28.66 (C(*C*H_3)$_3$), 18.64 (*C*H_2), 13.70 (*C*H_3).
IR γ (cm^{-1}) 640.33 (C=C-H), 1050.59 (C-O-C), 1225.41 (C=S), 1393.48, 1364.83, 1451.74 (C-H), 1647.2 (C=O), 2970.86, 2932.91 (C-H), 3307.5 (N-H).
HRMS (FAB+) calcd for $C_{15}H_{25}N_2O_3S_2$: [M+1] 345.1307, found: 345.1308.

_S_-2-(But-3-ynyl(1-(tert-butylamino)-1-oxobutan-2-yl)amino)-2-oxoethyl-_O_-ethyl carbonodithioate 1k.



General procedure with propionaldehyde. Purification by flash column chromatography (8:2 hexane/EtOAc) to give **1k** (60%) as a yellow oil:
R$_f$ 0.5 (70:30 hexane / ethyl acetate).
^{1}**HNMR** (300 MHz, $CDCl_3$) δ (ppm) 6.30 (bs, 1H), 4.65 (q, J=7.2 Hz, 2H), 4.59 (t, J=8.1 Hz, 1H), 4.31 (d, J=15.6, 1H), 4.23 (d, J=15.6, 1H), 3.76-3.55 (m, 2H), 2.59 (td, J=7.5 Hz, J= 2.7 Hz, 2H), 2.05-1.93 (m, 1H), 1.75-1.60 (m, 1H), 2.07 (t, J=2.7 Hz, 1H), 1.43 (t, J=7.2 Hz, 3H), 1.31 (s, 9H), 0.89 (t, J=7.5 Hz, 3H).
^{13}**CNMR** (75.4 MHz, $CDCl_3$) δ (ppm) 213.81 (*C*=S), 169.66 (*C*=O), 168.67 (*C*=O), 80.70 (*C*≡C), 71.51 (O*C*H_2), 70.72 (H*C*≡C), 60.41(*C*HN), 51.17 (*C*(CH_3)$_3$), 43.70 (*C*H_2N), 39.67 (*C*H_2S), 28.52 (*C*(CH_3)$_3$), 21.03 (*C*H_2), 19.62 (*C*H_2), 13.76 (*C*H_3), 10.57 (*C*H_3).
IR γ (cm^{-1}) 642.6, 1113.3, 1226.2, 1390.1, 1412, 1455, 1676.8, 1642.6, 2934.2, 2969.4, 3307.8.
HRMS (FAB+) calcd for $C_{17}H_{28}N_2O_3S_2$: [M+1] 372.1541, found: 372.1541.

_S_-2-(But-3-ynyl(2-(*tert*-butylamino)-1-(4-methoxyphenyl)-2-oxoethyl)amino)-2-oxoethyl _O_-ethyl carbonodithioate 1l.

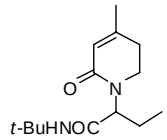


General procedure with *p*-methoxybenzaldehyde. Purification by flash column chromatography (7:3 hexane/EtOAc) to give **1l** (50%) as a yellow solid:
mp 108-109 °C.
R$_f$ 0.4 (60:40 hexane / ethyl acetate).
^{1}**HNMR** (300 MHz, $CDCl_3$) δ (ppm) 7.33 (d, J=8.7 Hz, 2H), 6.90 (d, J=8.4 Hz, 2H), 5.81 (s, 1H), 5.64 (bs, 1H), 4.65 (q, J=7.2 Hz, 2H), 4.26 (s, 2H), 3.82 (s, 3H), 3.73-3.55 (m, 2H), 2.31-2.16 (m, 2H), 1.97 (s, 1H), 1.42 (t, J=7.2 Hz, 3H), 1.33 (s, 9H).
^{13}**CNMR** (75.4 MHz, $CDCl_3$) δ (ppm) 213.75 (*C*=S), 168.61 (*C*=O), 167.77 (*C*=O), 159.88 (O-*C*=C), 130.86 (H*C*=C), 125.56 (*C*=C), 114.39 (H*C*=C), 80.76 (*C*≡C), 70.82 (O*C*H_2), 70.51(HC≡*C*), 62.17 (*C*HN), 55.28 (*C*H_3O), 51.62 (*C*(CH_3)$_3$), 44.86 (*C*H_2N), 39.66 (*C*H_2S), 28.58 (C(*C*H_3)$_3$), 19.65 (*C*H_2), 13.75 (*C*H_3).
IR γ (cm^{-1}) 640.1, 1049.3, 1226.3, 1249.4, 1364.2, 1394.9, 1417.5, 1454, 1513.1, 1644.2, 1681.3, 2933. 4, 2969.4, 3071.3, 3304.1.

HRMS (FAB+) calcd for $C_{22}H_{31}N_2O_4S_2$: [M+1] 451.1725, found: 451.1726.

Synthesis of pyrazinone 4k.
A deaerated solution xanthate **1k** (1 mmol) in isopropanol (3 mL) was heated at reflux while dilauroyl peroxide (1.2 mmol) was added portionwise (0.12 mmol/h). After completion (10h), the solution was cooled and the isopropanol evaporated under reduced pressure. The residue was purified by flash chromatography (8:2 hexane/EtOAc) to give **4k** (58%) as a yellow oil.

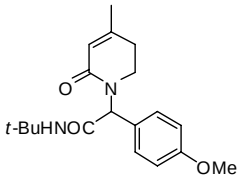
***N*-*tert*-Butyl-2-(4-methyl-2-oxo-5,6-dihydropyridin-1(2*H*)-yl)butanamide 4k.**



R$_f$ 0.2 (70:30 hexane / ethyl acetate).
^{1}HNMR (300 MHz, $CDCl_3$) δ (ppm) 5.99 (bs, 1H), 5.77 (dd, J=2.7 Hz, 1.5 Hz 1H), 4.81 (dd, J=8.7 Hz, 6.9 Hz, 1H), 3.35 (t, J=7.2 Hz, 2H), 2.30-2.24 (m, 2H), 1.92 (s, 3H), 1.71-1.58 (m, 2H), 1.31 (s, 9H), 0.88 (t, J=7.2 Hz, 3H).
^{13}CNMR (75.4 MHz, $CDCl_3$) δ (ppm) 169.97 (*C*=O), 165.87 (*C*=O), 151.76 (*C*=C), 120.43 (C=*C*), 57.18 (*C*HN), 51.09 (*C*$(CH_3)_3$), 40.19 (*C*H_2N), 29.59 (*C*H_2), 28.68 (C(*C*$H_3)_3$), 22.73 (*C*H_2), 20.40 (*C*H_3), 10.62 (*C*H_3).
IR γ (cm^{-1}) 858.1, 1364.3, 1438.5, 1453.8, 1547.7, 1612.1, 1666.9, 2933.3, 2968.0, 3312.6.
HRMS (FAB+) calcd for $C_{14}H_{24}N_2O_2$: [M+1] 253.1916, found: 253.1911.

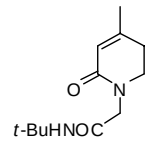
General procedure for the preparation of piperazinones 4l and 4j.
A deaerated solution of the corresponding xanthate (1 mmol) in isopropanol (3 mL) was heated at reflux, and 1.2 mmol of dilauroyl peroxide was added portionwise (0.12 mmol/h). After completion (10h), 0.1 mmol of DBU was added to the solution and heated at reflux by 3 h. After that the solution was cooled and the isopropanol evaporated under reduced pressure. The residue was purified by a silica gel column chromatography.

***N*-*tert*-Butyl-2-(4-methoxyphenyl)-2-(4-methyl-2-oxo-5,6-dihydropyridin-1(2*H*)-yl)acetamide 4l.**



This residue was purified by flash chromatography (6:4 hexane/EtOAc) to give **4l** (30%) as a pale yellow solid:
mp 157-158 °C.
R$_f$ 0.2 (50:50 hexane / ethyl acetate).
^{1}HNMR (300 MHz, $CDCl_3$) δ (ppm) 7.29 (d, J=9 Hz, 2H), 6.88 (d, J=8.4 Hz, 2H), 6.14 (s, 1H), 5.76 (dd, J=3 Hz, 1.5 Hz, 1H), 5.63 (bs, 1H), 3.81 (s, 3H), 3.64-3.55 (m, 1H), 3.04-2.95 (m, 1H), 2.37-2.26 (m, 1H), 2.16-2.04 (m, 1H), 1.84 (s, 3H), 1.36 (s, 9H).
^{13}CNMR (75.4 MHz, $CDCl_3$) δ (ppm) 169.15 (*C*=O), 165.51 (*C*=O), 159.41 (O-*C*=C), 151.96 (C=*C*), 130.32 (H*C*=C), 127.75 (C=*C*), 120.36 (C=*C*), 114.07 (HC=*C*), 58.82 (*C*HN), 55.28 (*C*H_3O), 51.61 (*C*$(CH_3)_3$), 41.98 (*C*H_2N), 29.80 (*C*H_2), 28.71 (C(*C*$H_3)_3$), 22.72 (*C*H_3).
IR γ (cm^{-1}) 653.4, 809.5, 1034.8, 1173.2, 1250.3, 1329.6, 1443, 1470.3, 1510, 1552, 1609.4, 1664.7, 2931.2, 2959.9, 3070.2, 3279.63.
HRMS (FAB+) calcd for $C_{19}H_{26}N_2O_3$: [M+1] 331.2022, found: 331.2025.

_N_-_tert_-Butyl-2-(4-methyl-2-oxo-5,6-dihydropyridin-1(2_H_)-yl)acetamide 4j.



This residue was purified by flash chromatography (EtOAc) to give the mixture (40%) as a pale yellow solid

mp 139-140 °C.

R_f 0.1 (50:50 hexane / ethyl acetate).

^{1}HNMR (300 MHz, $CDCl_3$) δ (ppm) 5.76 (dd, J= 2.7 Hz, 1.5 Hz, 1H), 3.92 (s, 2H), 3.51 (t, J=7.2 Hz, 2H), 2.35 (t, J=7.2 Hz, 2H), 1.93 (m, 3H), 1.33 (s, 9H).

^{13}CNMR (75 MHz, $CDCl_3$) δ (ppm) 168.39 (*C*=O), 165.80 (*C*=O), 152.33 (*C*=C), 120.00 (C=*C*), 52.27 (*C*H_2N), 51.19 (*C*$(CH_3)_3$), 46.68 (CH_2N), 29.47 (CH_2), 28.69 (*C*$(CH_3)_3$), 22.84 (*C*H_3).

IR γ (cm^{-1}) 688.1, 856.2, 1362.9, 1452.2, 1485.9, 1556.3, 1613.4, 1667.5, 2928.4, 2969.6, 3074.1, 3308.7.

HRMS (FAB+) calcd for $C_{12}H_{20}N_2O_2$: [M+1] 225.1603 found: 225.1600.