1,3-Dithiane-Derived Alkoxyamines as One-Carbon Radical Precursors

Antonio J. Herrera, Armido Studer*

Organisch Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstraße 40, 48149 Münster, Germany
Fax +49(251)8336523; E-mail: studer@uni-muenster.de

Received 15 February 2005

Dedicated to Prof. Dr. Bernd Giese

Abstract: A new method for the generation of C-2 centered radicals derived from 1,3-dithiane is presented. The radical precursors, 2-dialkylaminoxyl-1,3-dithianes, are readily prepared from 1,3-dithiane and stable nitroxides. Thermal reaction of 2-dialkylaminoxyl-1,3-dithianes with electron-deficient olefins affords carboaminoxylation products or oxidative addition products depending on the nitroxide used. The 2-dialkylaminoxyl-1,3-dithianes can also be used as initiators/regulators for the controlled living free radical polymerization of styrene.

Key words: radical chemistry, nitroxides, 1,3-dithianes, controlled radical polymerization, microwaves

1,3-Dithianes derived from aldehydes and ketones have become highly important in synthetic organic chemistry over the past 50 years.[1] Aldehyde derived dithianes are generally used as umpoled carbonyl groups in ionic chemistry.[2] The intrinsic electrophilic behavior of an aldehyde carbonyl carbon atom can be altered upon transformation into the corresponding 1,3-dithiane and subsequent lithiation. These lithiated 1,3-dithianes are nucleophilic acyl equivalents, which efficiently react with various electrophiles. Along with the umpolung, dithianes have found widespread application as protecting groups in organic synthesis.[3]

Acyl radicals are known to undergo fast decarbonylation.[4] Slow radical reactions using acyl radicals are therefore not possible. Dithiane chemistry may offer an answer to this problem. To our surprise, only a few reports on the use of 1,3-dithianes as one-carbon radical precursors have appeared in the literature to date. Byers showed that Se-substituted dithiane **1** (Figure 1) can be used in Se-group transfer chemistry.[5] Very recently, Zard reported on the use of xanthate **2** (Figure 1) as a C-radical precursor.[6] In addition, 1,3-dithiane-derived radicals have also been used in cyclization reactions.[7] All these studies showed that these C-radicals are nucleophilic and react efficiently only with activated electron-deficient olefins.

We have recently shown that alkoxyamines derived from persistent nitroxides can be used as C-radical precursors in cyclization and intermolecular addition reactions.[8] Thermal reversible C–O bond homolysis delivers efficiently C-radicals. These processes are controlled by the persistent radical effect (PRE).[9] Unfortunately, acyl radicals cannot be generated via this approach. For example, the activation energy for the C–O bond homolysis in alkoxyamine **3** (Figure 1) is 150.5 kJ/mol and therefore too high for clean thermal bond homolysis.[10] We assumed that 1,3-dithiane-derived alkoxyamines may offer a formal entry into long-lived acyl radicals using our methodology. Herein we present results on the use of alkoxyamines of type **4** (Figure 1) as one-carbon radical precursors in intermolecular addition reactions. Moreover, we show that these alkoxyamines can be applied as initiator/mediators for nitroxide-mediated styrene polymerization.[11]

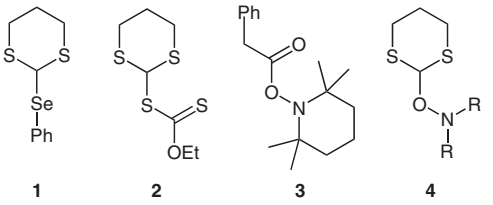
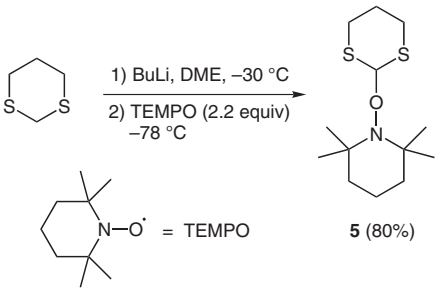


Figure 1 One-carbon radical precursors

TEMPO-derived dithiane **5** was readily prepared from 1,3-dithiane via lithiation and oxidation using TEMPO. In this reaction TEMPO acts as oxidant and as C-radical trapping reagent. Alkoxyamine **5** was isolated in 80% yield (Scheme 1).



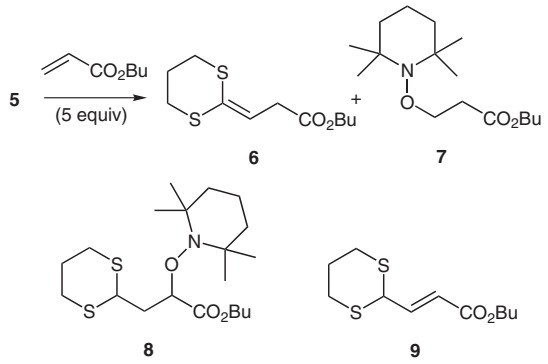
Scheme 1 Synthesis of alkoxyamine **5**

Radical additions were first studied using *n*-butyl acrylate as a radical acceptor. Reaction of **5** in DMF (0.07 M) with 5 equivalents of olefin at 135 °C for 18 hours provided a 1:1 mixture of dithiane **6** and TEMPO-adduct **7** in 16% combined yield (Scheme 2; Table 1, run 1). We found that alkoxyamine **5** is not perfectly stable under the applied conditions. Dithioketeneacetal **6** results from carboaminoxylation of *n*-butyl acrylate (→ **8**) with subsequent

SYNTHESIS 2005, No. 9, pp 1389–1396
Advanced online publication: 07.04.2005
DOI: 10.1055/s-2005-865288; Art ID: C00605SS

elimination[12] of TEMPOH to give **9**, which eventually isomerizes to **6**. The side product **7** is probably formed via TEMPO-radical addition onto *n*-butyl acrylate with subsequent reduction.[13] Reaction in $ClCH_2CH_2Cl$ at 120 °C afforded **6** as the sole product in 33% yield (run 2). Addition is even less efficient in toluene (run 3). In order to succeed, reaction in toluene was conducted at higher concentration.

Encouraged by our recent results on microwave induced alkoxyamine additions we decided to repeat the experiments under microwave conditions.[14,15] Reaction of **5** with *n*-butyl acrylate in DMF at 170 °C for 9 min provided **6** and **7** in 47% combined yield (run 4). Interestingly, running the experiment in the presence of Et_3N (1.5 equiv) under otherwise identical conditions yielded **6** as the sole product in 72% yield (run 5). Microwave experiments in *o*-$Cl_2C_6H_4$ and in DMSO were less efficient (runs 6 and 7). Therefore, the following experiments were conducted in DMF.



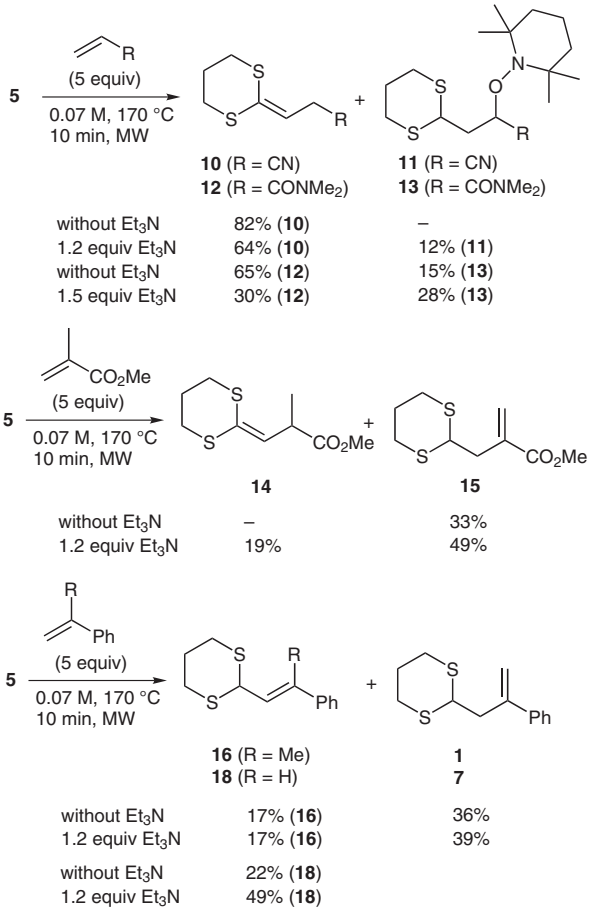
Scheme 2 Oxidative addition of **5** onto *n*-butyl acrylate

Table 1 Reaction of **5** with *n*-Butyl Acrylate under Different Conditions

Run	Temp (°C)	Time	c [M]	Solvent	**6** (%)	**7** (%)
1	130	18 h	0.07	DMF	8	8
2	120	38 h	0.07	$ClCH_2CH_2Cl$	33	–
3	120	21 h	1.00	toluene	12	21
4[a]	170	9 min	0.07	DMF	34	13
5[a]	170	8 min	0.07	DMF[b]	72	–
6[a]	180	8 min	0.07	DMSO[b]	39	10
7[a]	170	14 min	0.07	*o*-$Cl_2C_6H_4$	33	–

[a] Microwave-induced heating.
[b] Et_3N (1.5 equiv) was added.

Microwave-induced addition of **5** onto acrylonitrile provided the oxidative addition isomerization product **10** in a high yield (82%, Scheme 3). In the presence of Et_3N under otherwise identical conditions **10** was isolated in 64% along with 12% of carboaminoxylation product **11**. TEMPO-acrylonitrile adduct was formed in 12% yield. Obviously, Et_3N retards TEMPOH-elimination. Similar results were obtained for the reaction of **5** with *N*,*N*-dimethylacrylamide. In the amine-free experiment, **12** was obtained in 70% yield along with carboaminoxylation compound **13**. As above, the experiment conducted in the presence of Et_3N delivered more of the carboaminoxylation compound. Reaction of **5** with methyl methacrylate gave oxidative addition product **15** in moderate yield as the only regioisomer. In the presence of Et_3N, compound **15** was obtained in 49% yield. In addition, olefin **14** was formed in 19% yield. Hence, Et_3N influences the regioselectivity of the TEMPOH-elimination. Reaction with α-methyl styrene showed no amine effect. The regioisomers **16** and **17** were isolated in 53% or 56% combined yield (without or with Et_3N, respectively). Regioselective elimination was obtained for the carboaminoxylation/elimination reaction using styrene. Isomerization of the double bond was not observed. Styrene derivative **18** was isolated in 49% yield using Et_3N as an additive. The amine-free process provided **18** in lower yield (22%).

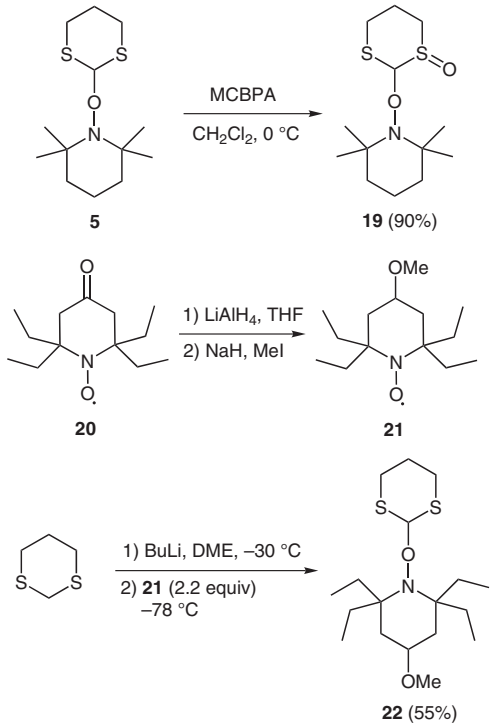


Scheme 3 Oxidative addition of **5** – variation of the olefin

As expected,[5,6] addition of **5** to electron rich olefins such as butyl vinyl ether or 1-octene did not work. Zard showed that oxidation of dithiane **2** to the corresponding mono sulfoxide can readily be accomplished. Moreover the oxidized xanthate delivers far more reactive one-carbon-

centered radicals than the parent dithiane **2**.[6] Therefore we prepared alkoxyamine **19** (Scheme 3). *m*-Chloroperbenzoic acid treatment of dithiane **5** afforded monosulfoxide **19** as a 5.8:1 mixture of diastereoisomers. The isomers were separated by chromatography. The relative configuration was not assigned. Unfortunately, both isomers of alkoxyamine **19** turned out to be highly unstable under the applied conditions. Attempted carboaminoxylation of *n*-butyl acrylate and 1-octene using **19** failed (both isomers were tested).

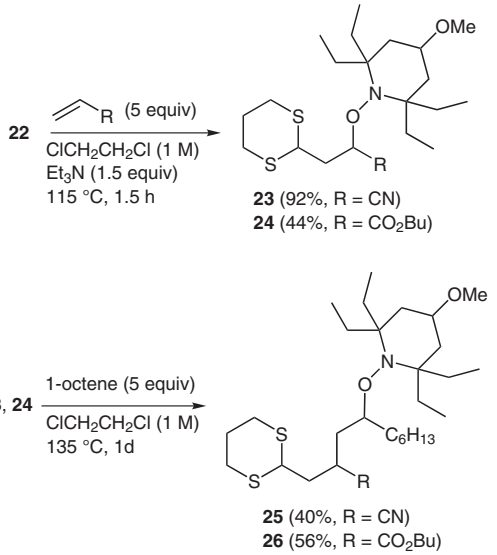
We have previously shown that the nitroxide structure heavily influences the outcome of nitroxide-mediated radical additions.[16] Based on these results we prepared alkoxyamine **22** from dithiane and nitroxide **21** (Scheme 4). Sterically highly hindered nitroxide **21** was readily prepared from known nitroxide **20**.[17]



Scheme 4 Synthesis of alkoxyamines **19** and **22**

Alkoxyamine **22** underwent highly efficient thermal addition onto acrylonitrile under conventional heating at 110 °C (Scheme 5). Product **23** was isolated in 92% yield. A lower yield was obtained for the addition of **22** to *n*-butyl acrylate (44%). Along with the desired carboaminoxylation product, telomers resulting from renewed addition of **24** onto *n*-butyl acrylate were observed (mainly containing 2 or 3 acrylate units). In order to decrease the propensity of telomer formation, reaction was repeated with 1.1 equivalent of acrylate (115 °C). Unfortunately, formation of telomers could not be completely suppressed. Carboaminoxylation product **24** was formed in 57% yield.

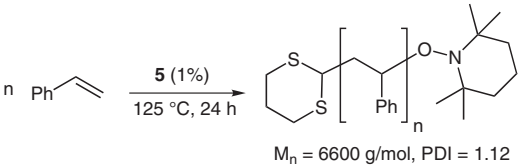
Guided by this unwanted side reaction we decided to study controlled carboaminoxylations using adducts **23** and **24**. To this end, alkoxyamines **23** and **24** were reacted



Scheme 5 Carboaminoxylations using alkoxyamines **22**

with 1-octene[16] to provide alkoxyamines **25** and **26** in good yields (**25**: 40%; **26**: 56%).

Moreover, we tested whether alkoxyamine **5** can be used as initiator/regulator for the controlled living radical polymerization of styrene.[11] Polymerization was conducted in a sealed tube using 1% of alkoxyamine initiator **5** at 125 °C and was stopped after 24 hours (neat styrene). The conversion (61%) was determined gravimetrically. The polydispersity index (PDI) and the molecular weight of the polymer were analyzed using SEC (M_n = 6600 g/mol, Scheme 6). The narrow PDI (1.12) obtained indicates that controlled polymerization of styrene occurred. Importantly, the 1,3-dithiane-modified polystyrene should readily be deprotonated using alkyl lithium bases. The corresponding polymeric Li-derivative can then be used to initiate an anionic polymerization. Hence, **5** can be regarded as radical and ionic polymerization initiator. Experiments along this line are under way.



Scheme 6 Polymerization of styrene using alkoxyamine **5**

Finally, we studied the kinetics of the C–O bond homolysis for alkoxyamines **5** and **22**. The kinetic experiments were conducted in the EPR cavity in *tert*-butylbenzene in the presence of oxygen at 403 K and 373 K for alkoxyamines **5** and **22**, respectively. Oxygen was used to scavenge the 3-dithianyl radical and the concentration of the released nitroxide was measured by EPR spectroscopy, as previously described.[18] The activation energies E_a were estimated from the experimentally determined rate

constants using the Arrhenius equation with $A = 2.4 \times 10^{14}$ s^{-1}.[19]

As expected, the sterically highly hindered alkoxyamine **22** shows a lower activation energy for C–O bond homolysis than TEMPO-derivative **5** (E_a[**5**] = 136.9 kJmol^{-1}, E_a[**22**] = 127.5 kJmol^{-1}). This is in agreement with the addition experiments where carboaminoxylation could be performed at 90 °C using the efficient alkoxyamine **22** (acrylonitrile, 10 h, 58%). For TEMPO-alkoxyamine **5**, however, reaction was successful only at higher temperatures (120 °C, see Table 1, runs 2 and 3). At 90 °C no addition product was observed using **5**.

In conclusion, we have show that readily prepared 1,3-dithiane derived alkoxyamines can be used as one-carbon radical precursors in radical addition reactions. The nucleophilic 1,3-dithane-2-yl radical reacts efficiently only with electron-deficient olefins. Depending on the nitroxide used, carboaminoxylation or oxidative addition of the alkoxyamine is obtained. Microwave induced heating can be applied to conduct these reactions in a short time. In addition, dithiane modified polystyrene with a narrow PDI can be prepared using **5** as alkoxyamine initiator/regulator.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX-400, ARX-300 or Varian inova-500 spectrometers. TLC as performed by using Merck silica gel coated aluminium 60 F_{254} plates; detection with UV or dipping into a solution of $KMnO_4$ (1.5 g in 400mL H_2O, 5 g $NaHCO_3$) or a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphomolybdic acid hydrate (25 g), concd H_2SO_4 (60 mL) and H_2O (940 mL). Flash column chromatography was performed using Merck silica gel 60 (40–63 μm) applying a pressure of about 0.4 bar. IR spectra were obtained as a thin film smeared onto NaCl plates on a Bruker IFS-28 spectrometer. Melting points were determined with a hot-stage apparatus. Mass spectra were recorded as ESI–MS on a waters-micromass Quattro LC or a Bruker MicroTof instrument. Elemental analyses were performed on an Elementar vario ELIII instrument. Solvents were purified by standard methods. Air and moisture sensitive compounds were handled under Ar using Schlenk techniques. Size Exclusion Chromatography (SEC) was carried out with THF as eluent at a flow rate of 1.0 mL/min at r.t. on a system consisting of a L6200A Intelligent Pump (Merck Hitachi), a set of two Plgel 5 μm MIXED-C columns (300 × 7.5 mm, Polymer Laboratories), and a RI-101 detector (Shodex). Data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) based upon calibration curves built upon polystyrene standards (Polymer Laboratories Polystyrene Medium MW Calibration Kit S-M-10) with peak molecular weights ranging from 500–3000000 g/mol. EPR spectra were recorder on a Bruker EMS 104 Analyzer. The nitroxide concentration was determined by double integration of the EPR spectra and calibration with a TEMPO solution in *tert*-butylbenzene (0.1 mM).

1-(1,3-Dithian-2-yloxy)-2,2,6,6-tetramethylpiperidine (5)

To a solution of 1,3-dithiane (2.845 g, 23.7 mmol) in anhyd dimethoxyethane (52 mL) was added dropwise a solution of *n*-BuLi (1.6 M in hexanes) (16.3 mL, 26.08 mmol) at –35 °C under an atmosphere of Ar and stirring was continued at –35 °C for 1 h. The mixture was cooled to –60 °C, TEMPO (7.817 g, 49.79 mmol) was added in one portion and the mixture turned orange. The reaction was slowly allowed to warm to 0 °C while the orange color changes to a pale yellow color. After 1.5 h the mixture was poured into sat. aq solution of NH_4Cl and extracted with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by crystallization from CH_2Cl_2–MeOH affording compound **5** (5.214 g, 18.96 mmol, 80%); crystalline solid; mp 80–81 °C.

IR (film): 3001, 2972, 2925, 2865, 1479, 1381, 1264, 1238, 961, 886, 799 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.63 (s, 1 H, CH), 3.22 (ddd, J_1 = J_2 = 6.9 Hz, J_3 = 13.9 Hz, 2 H, SCH_2), 2.68 (ddd, J_1 = J_2 = 4.8 Hz, J_3 = 13.8 Hz, 2 H, SCH_2), 2.08 (m, 2 H, SCH_2CH_2), 1.46 (br s, 6 H, $CCH_2CH_2CH_2$), 1.22 (br s, 12 H, 4 × CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 85.7 (CH), 60.5 (C), 40.3 (CH_2), 34.7 (CH_3), 26.0 (2 × CH_2), 25.2 (CH_2), 20.4 (CH_3), 17.0 (CH_2).

MS (ESI): *m*/*z* = 298 [M + Na]$^+$.

Anal. Calcd for $C_{13}H_{25}NOS_2$: C, 56.68; H, 9.15; N, 5.08. Found: C, 56.68; H, 8.97; N, 5.02.

Oxidative Addition Reaction; General Procedure (GP 1)

A solution of **5**, olefin and Et_3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. The reaction mixture was poured into an aq sat. solution of NH_4Cl, extracted with Et_2O (2 ×), dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.

Oxidative Addition Reaction ; General Procedure (GP 2)

A solution of **5**, olefin and Et_3N (in some cases) in degassed DMF (0.07 M) was sealed off under Ar. The mixture was flash heated at 170 °C in a microwave oven for 8–25 min. DMF and excess of olefin were removed in vacuo. The crude product was purified by flash chromatography on silica gel.

Butyl 3-(1,3-Dithian-2-ylidene)propanoate (6)[20]

According to GP1, compound **5** (156 mg, 0.567 mmol), *n*-butyl acrylate (363 mg, 2.836 mmol), Et_3N (86 mg, 0.85 mmol) in DMF (8 mL) were employed for 8 min. Flash chromatography (pentane–MTBE, 100:1) afforded **6** (100 mg, 0.406, 72%). Butyl 3-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanoate (**7**) was obtained as a side product if other conditions were applied (see text).

IR (film): 2599, 2931, 2872, 1738, 1463, 1422, 1274, 1062 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.05 (t, *J* = 7.0 Hz, 1 H, H_{vinyl}), 4.08 (t, *J* = 4.1 Hz, 2 H, OCH_2), 3.25 (d, *J* = 7.1 Hz, 2 H, $COCH_2$), 2.88 (t, *J* = 6.1 Hz, 2 H, SCH_2), 2.87 (t, *J* = 6.1 Hz, 2 H, SCH_2), 2.15 (m, 2 H, SCH_2CH_2), 1.61 (m, 2 H, OCH_2CH_2), 1.37 (m, 2 H, CH_3CH_2), 0.92 (t, *J* = 7.7 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9 (C), 130.5 (C), 123.7 (CH), 64.7 (CH_2), 34.8 (CH_2), 30.6 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 24.8 (CH_2), 19.1 (CH_2), 13.6 (CH_3).

MS (ESI): *m*/*z* = 269 [M + Na]$^+$.

Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36. Found: C, 53.13; H, 7.45.

Compound 7

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10 (t, *J* = 6.7 Hz, 2 H, OCH_2), 3.98 (t, *J* = 6.4 Hz, 2 H, $NOCH_2$), 2.49 (t, *J* = 6.4 Hz, 2 H, $COCH_2$), 1.61 (m, 2 H, OCH_2CH_2), 1.46 (m, 6 H, $CH_2CH_2CH_2$), 1.39 (m, 2 H, CH_3CH_2), 1.25 (br s, 6 H, CH_3), 1.11 (br s, 6 H, CH_3), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.8 (C), 72.6 (CH_2), 65.6 (CH_2), 60.7 (2 × C), 35.7 (CH_2), 34.7 (2 × CH_3), 32.4 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 25.7 (CH_2), 20.9 (2 × CH_3), 18.0 (CH_2), 14.6 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{31}NO_3$: 286.2377; found: 286.2365.

3-(1,3-Dithian-2-ylidene)propanenitrile (10)[20] and 3-(1,3-Dithian-2-yl)-2-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanenitrile (11)

Procedure A: According to GP 1, compound **5** (151 mg, 0.549 mmol), acrylonitrile (146 mg, 2.74 mmol) in DMF (7.8 mL) were employed for 10 min. Flash chromatography (pentane–Et_2O, 95:5) afforded a non-separable mixture (92 mg) of **10** and 3-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanenitrile (5.5:1) as determined by ^1H NMR spectroscopy: **10** (0.450 mmol, 82%).

Procedure B: According to GP 1, compound **5** (230 mg, 0.836 mmol), acrylonitrile (222 mg, 4.18 mmol), Et_3N (101 mg, 1.0 mmol) in DMF (12 mL) were employed for 10 min. Flash chromatography (pentane–Et_2O, 95:5) afforded **11** (33 mg, 0.1 mmol, 12%) and a non-separable mixture (137 mg) of **10** and 3-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanenitrile (2:1) as determined by ^1H NMR spectroscopy: **10** (0.535 mmol, 64%).

Compound 10

IR (film): 2975, 2916, 2248, 1678, 1580, 1420, 959 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.76 (t, *J* = 7.1 Hz, 1 H, H_{vinyl}), 3.27 (d, *J* = 7.1 Hz, 2 H, $NCCH_2$), 2.91 (m, 4 H, SCH_2), 2.17 (m, 2 H, SCH_2CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6 (C), 117.1 (C), 116.6 (CH), 29.3 (CH_2), 29.0 (CH_2), 24.2 (CH_2), 17.4 (CH_2).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_7H_9NS_2$: 194.0074; found: 194.0052.

Compound 11

IR (film): 2973, 2934, 2873, 1467, 1423, 1259, 1132 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.91 (t, *J* = 7.12 Hz, 1 H, OCH), 4.16 (t, *J* = 6.3 Hz, 1 H, SCH), 2.86 (m, 4 H, SCH_2), 2.33 (m, 2 H, $SCHCH_2$), 2.11 (m, 1 H, SCH_2CHH), 1.90 (m, 1 H, SCH_2CHH), 1.48 (m, 6 H, $NCH_2CH_2CH_2$), 1.31 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.5 (C), 65.9 (CH), 55.6 (C), 54.5 (C), 36.8 (CH), 34.7 (CH_2), 34.5 (CH_2), 33.0 (CH_2), 28.6 (CH_3), 28.5 (CH_3), 24.6 (CH_2), 24.5 (CH_2), 20.5 (CH_2), 15.2 (CH_3), 15.1 (CH_3), 11.7 (CH_2).

MS (ESI): *m*/*z* = 351 $[M + Na]^+$.

Anal. Calcd for $C_{16}H_{28}N_2OS_2$: C, 58.49; H, 8.59; N, 8.53. Found: C, 58.12; H, 8.66; N, 8.76.

3-[(2,2,6,6-Tetramethyl-1-piperidinyl)oxy]propanenitrile

^1H NMR (400 MHz, $CDCl_3$): δ = 3.93 (t, *J* = 6.3 Hz, 2 H, OCH_2), 2.52 (t, *J* = 6.3 Hz, 2 H, $NCCH_2$), 1.43 (m, 6 H, $CH_2CH_2CH_2$), 1.16 (s, 6 H, 2 × CH_3), 1.11 (s, 6 H, 2 × CH_3).

3-(1,3-Dithian-2-ylidene)-*N*,*N*-dimethylpropanamide (12) and 3-(1,3-Dithian-2-yl)-*N*,*N*-dimethyl-2-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]propanamide (13)

Procedure A: According to GP 2, compound **5** (158 mg, 0.57 mmol), *N*,*N*-dimethyl acrylamide (569 mg, 5.7 mmol) in DMF (8.1 mL) were employed for 5 min at 180 °C. Flash chromatography of the residue (pentane–acetone, 8:2) afforded **13** (32 mg, 0.085 mmol, 15%) and **12** (80 mg, 0.369 mmol, 65%).

Procedure B: According to GP 2, compound **5** (173 mg, 0.629 mmol), *N*,*N*-dimethyl acrylamide (623 mg, 6.29 mmol), Et_3N (95 mg, 0.943 mmol) in DMF (9 mL) were employed for 10 min. Flash chromatography of the residue (pentane–acetone, 8:2) afforded **13** (65 mg, 0.174 mmol, 28%) and **12** (40 mg, 0.184 mmol, 30%).

Compound 12

IR (film): 2927, 1644, 1502, 1400, 1141, 1056 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.13 (t, *J* = 6.9 Hz, 1 H, H_{vinyl}), 3.26 (d, *J* = 6.9 Hz, 2 H, $COCH_2$), 3.00 (s, 3 H, CH_3), 2.92 (s, 3 H, CH_3), 2.86 (m, 4 H, SCH_2), 2.14 (m, 2 H, SCH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C), 128.9 (C), 125.8 (CH), 37.3 (CH_3), 35.5 (CH_3), 34.4 (CH_2), 30.0 (CH_2), 29.5 (CH_2), 24.9 (CH_2).

MS (ESI): *m*/*z* = 218 $[M + H]^+$.

Anal. Calcd for $C_9H_{15}NOS_2$: C, 49.73; H, 6.96; N, 6.44. Found: C, 49.54; H, 7.16; N, 6.38.

Compound 13

IR (film): 2931, 1651, 1466, 1259, 1183, 1120, 909 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.86 (dd, J_1 = 10.7 Hz, J_2 = 4.1 Hz, 1 H, OCH), 3.84 (dd, J_1 = 10.9 Hz, J_2 = 4.3 Hz, 1 H, SCH), 3.24 (s, 3 H, NCH_3), 2.93 (s, 3 H, NCH_3), 2.80 (m, 4 H, SCH_2), 2.41 (m, 1 H, $SCHCH_2$), 2.20 (m, 1 H, $SCHCH_2$), 2.05 (m, 1 H, SCH_2CH_2), 1.85 (m, 1 H, SCH_2CH_2), 1.40 (m, 4 H, CCH_2), 1.28 (m, 2 H, CCH_2CH_2), 1.23 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5 (C), 77.2 (CH), 60.6 (C), 59.3 (C), 43.0 (CH), 40.4 (CH_2), 40.2 (CH_2), 37.8 (CH_3), 36.8 (CH_2), 35.8 (CH_3), 33.6 (CH_3), 32.4 (CH_3), 30.0 (CH_2), 29.7 (CH_2), 25.8 (CH_2), 20.2 (CH_3), 19.9 (CH_3), 16.9 (CH_2).

MS (ESI): *m*/*z* = 397 $[M + Na]^+$.

Anal. Calcd for $C_{18}H_{34}N_2O_2S_2$: C, 57.71; H, 9.15; N, 7.48. Found: C, 57.24; H, 8.98; N, 7.27.

Methyl 3-(1,3-Dithian-2-ylidene)-2-methylpropanoate (14), Methyl 2-(1,3-Dithian-2-ylmethyl)acrylate (15)

Procedure A: According to GP 2, compound **5** (151 mg, 0.549 mmol), methyl methacrylate (274 mg, 2.745 mmol) in DMF (7.8 mL) were employed for 5 min at 170 °C. Flash chromatography of the residue (pentane–Et_2O, 30:1) afforded **15** (40 mg, 0.183 mmol, 33%).

Procedure B: According to GP 2, compound **5** (156 mg, 0.67 mmol), methyl methacrylate (397 mg, 3.97 mmol), Et_3N (86 mg, 0.850 mmol) in DMF (7 mL) were employed for 20 min at 170 °C. Flash chromatography of the residue (pentane–Et_2O, 30:1) afforded **14** (23 mg, 0.105 mmol, 19%) and **15** (60 mg, 0.275 mmol, 49%).

Compound 14

IR (film): 2974, 2933, 1735, 1453, 1433, 1168, 1143 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.92 (d, *J* = 9.2 Hz, 1 H, H_{vinyl}), 3.67 (s, 3 H, OCH_3), 2.89 (m, 5 H, CH_3CH, SCH_2), 2.15 (m, 2 H, SCH_2CH_2), 1.24 (d, *J* = 7.1 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.2 (C), 130.6 (CH), 129.3 (C), 51.8 (CH), 39.9 (CH_3), 29.8 (CH_2), 29.1 (CH_2), 24.8 (CH_2), 17.4 (CH_3).

MS (ESI): *m*/*z* = 241 $[M + Na]^+$.

Anal. Calcd for $C_9H_{14}O_2S_2$: C, 49.51; H, 6.46. Found: C, 49.09; H, 6.61.

Compound 15

IR (film): 2993, 2949, 2901, 2829, 1721, 1630, 1437, 1199 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.27 (d, *J* = 1.2 Hz, 1 H, H_{vinyl}), 5.69 (d, *J* = 1.2 Hz, 1 H, H_{vinyl}), 4.25 (t, *J* = 7.6 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 2.83 (m, 4 H, SCH_2), 2.76 (d, *J* = 7.6 Hz, 2 H, CCH_2), 1.91 (m, 2 H, SCH_2CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7 (C), 135.7 (C), 128.2 (CH_2), 51.9 (CH), 45.3 (CH_3), 38.0 (CH_2), 29.9 (2 × CH_2), 25.7 (CH_2).

MS (ESI): *m*/*z* = 241 $[M + Na]^+$.

Anal. Calcd for $C_9H_{14}O_2S_2$: C, 49.51; H, 6.46. Found: C, 49.31; H, 6.59.

2-[(1*E*)-2-Phenyl-1-propenyl]-1,3-dithiane (16) and 2-(2-Phenyl-2-propenyl)-1,3-dithiane (17)

Procedure A: According to GP 1, compound **5** (150 mg, 0.545 mmol), styrene (515 mg, 4.36 mmol) in DMF (8 mL) were employed for 20 min at 170 °C. Flash chromatography of the residue (pentane–MTBE, 95:5) afforded **16** and **17** as a mixture (1:2.2) as determined by ^{1}H NMR spectroscopy (68 mg, 0.288 mmol, 53%).

Procedure B: According to GP 1, compound **5** (150 mg, 0.545 mmol), styrene (515 mg, 4.36 mmol), Et_3N (83 mg, 0.817 mmol) in DMF (8 mL) were employed for 20 min at 170 °C. Flash chromatography of the residue (pentane–MTBE, 95:5) afforded the isomers **16** and **17** as a mixture (1:2.2) as determined by ^{1}H NMR spectroscopy (72 mg, 0.305 mmol, 56%).

Compounds 16 and 17

IR (film): 3055, 3027, 2932, 2898, 2827, 1494, 1444, 763 cm^{-1}.

MS (ESI): m/z = 275 [M + Na]$^+$.

Anal. Calcd for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found: C, 65.89; H, 7.00.

Compound 16

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.47 (m, 5 H, H_{arom}), 5.76 (dq, J_1 = 9.78 Hz, J_2 = 1.43 Hz, 1 H, H_{vinyl}), 5.07 (d, J = 9.8 Hz, 1 H, SCH), 2.88 (m, 4 H, SCH_2), 2.21 (d, J = 1.43 Hz, 3 H, CH_3), 2.10 (m, 2 H, SCH_2CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1 (C), 128.2 (2 × CH), 127.5 (CH), 126.2 (2 × CH), 123.6 (CH), 44.8 (CH), 30.4 (2 × CH_2), 30.2 (CH_3), 24.9 (CH_2).

Compound 17

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.47 (m, 5 H, H_{arom}), 5.42 (s, 1 H, H_{vinyl}), 5.24 (s, 1 H, H_{vinyl}), 4.07 (t, J = 7.4 Hz, 1 H, SCH), 2.97 (d, J = 7.4 Hz, 2 H, CCH_2), 2.80 (m, 4 H, SCH_2), 1.88 (m, 2 H, SCH_2CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5 (C), 128.3 (2 × CH), 127.6 (CH), 125.9 (2 × CH), 115.7 (CH_2), 45.0 (CH), 41.4 (CH_2), 30.2 (2 × CH_2), 25.7 (CH_2).

2-(1-Styryl)-1,3-dithian (18)[20,21]

Procedure A: According to GP 1, compound **5** (160 mg, 0.582 mmol), styrene (484 mg, 4.65 mmol) in DMF (8 mL) were employed for 25 min at 170 °C. Flash chromatography of the residue (pentane–MTBE, 99:1) always afforded **18** (28 mg, 0.126 mmol, 22%) with a small amount of not identified side products.

Procedure B: According to GP 1, compound **5** (160 mg, 0.582 mmol), styrene (484 mg, 4.65 mmol), Et_3N (88 mg, 0.873 mmol) in DMF (8 mL) were employed for 25 min at 170 °C. Flash chromatography of the residue (pentane–MTBE, 99:1) always afforded **18** (63 mg, 0.284 mmol, 49%) with a small amount of non determined contaminants.

Compound 18

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.15 (m, 5 H, H_{arom}), 6.69 (d, J = 15.6, 1 H, CH_{vinyl}), 6.19 (dd, J_1 = 15.6 Hz, J_2 = 7.6 Hz, 1 H, CH_{vinyl}), 4.74 (d, J = 7.6 Hz, 1 H, SCH), 2.86 (m, 4 H, SCH_2), 2.05 (m, 1 H, SCH_2CH_2), 1.85 (m, 1 H, SCH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6 (C), 133.8 (CH), 128.9 (2 × CH), 128.5 (CH), 127.1 (2 × CH), 126 (CH), 48.0 (CH), 30.6 (2 × CH_2), 25.7 (CH_2).

2,2,6,6-Tetramethyl-1-[(1-oxido-1,3-dithian-2-yl)oxy]piperidine (19)

A solution of **5** (1.30 g, 4.745 mmol) in CH_2Cl_2 (9.5 mL) was cooled to 0 °C under a N_2 atmosphere. A solution of MCPBA (72%) (1.20 g, 5.03 mmol) in CH_2Cl_2 (11 mL) was slowly added. The resulting white suspension was stirred at 0 °C for another 60 min before allowing to warming to r.t. The mixture was then extracted with a sat. aq solution of $NaHCO_3$, brine, and dried over $MgSO_4$. The residue was purified by flash chromatography (pentane–acetone, 17:3) to afford the two regioisomers **19a** (182 mg, 0.625 mmol, 13%) and **19b** (1.058 g, 3.63 mmol, 77%) as solid compounds.

Compound 19a

IR (film): 3002, 2971, 2931, 2871, 1469, 1426, 1365, 1065, 879 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (s, 1 H, CH), 3.39 (dt, J_1 = 13.1 Hz, J_2 = 3.1 Hz, 1 H, $SOCH_2$), 2.80 (m, 2 H, SCH_2), 2.65 (m, 1 H, $SOCH_2$), 2.39 (m, 1 H, SCH_2CH_2), 1.68 (m, 1 H, SCH_2CH_2), 1.34 (br s, 6 H, $CCH_2CH_2CH_2$), 1.22 (br s, 12 H, 4 × CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 94.7 (C), 63.2 (2 × C), 46.3 (CH_2), 40.4 (2 × CH_2), 34.3 (2 × CH_3), 28.6 (CH_2), 24.4 (CH_2), 22.1 (2 × CH_3), 16.8 (CH_2).

MS (ESI): m/z = 314 [M + Na]$^+$.

Anal. Calcd for $C_{13}H_{25}NO_2S_2$: C, 53.57; H, 8.65; N, 4.81. Found: C, 53.21; H, 8.47; N, 4.60.

Compound 19b

IR (film): 2993, 2973, 2934, 1467, 1378, 1069, 1023, 954 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.53 (s, 1 H, CH), 3.02 (dt, J_1 = 13.2 Hz, J_2 = 2.6 Hz, 1 H, $SOCH_2$), 2.88 (dd, J_1 = 9.7 Hz, J_2 = 3.6 Hz, 2 H, SCH_2), 2.66 (m, 1 H, $SOCH_2$), 2.33 (dt, J_1 = 13.5 Hz, J_2 = 2.6 Hz, 1 H, SCH_2CH_2), 1.68 (m, 1 H, SCH_2CH_2), 1.49 (br s, 6 H, $CCH_2CH_2CH_2$), 1.21 (br s, 12 H, 4 × CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 96.2 (CH), 62.2(2 × C), 41.1 (CH_2), 40.4 (2 × CH_2), 36.4 (2 × CH_3), 23.2 (CH_2), 21.3 (2 × CH_3), 16.8 (CH_2), 14.0 (CH_2).

MS (ESI): m/z = 314 [M + Na]$^+$.

Anal. Calcd for $C_{13}H_{25}NO_2S_2$: C, 53.57; H, 8.65; N, 4.81. Found: C, 53.53; H, 8.48; N, 4.69.

2,2,6,6-Tetraethylpiperidin-4-methoxy-*N*-oxyl Radical (21)

$LiAlH_4$ (221 mg, 5.826 mmol) was added to a solution of **20**[17] (1.197 g, 5.296 mmol) in anhyd THF (15 mL) at r.t. and stirred for 30 min under an atmosphere of Ar. The excess of $LiAlH_4$ was destroyed by addition of small amounts of sat. aq solution of $NaSO_4$ under vigorous stirring, until the gray suspension turned white. The precipitate was removed by filtration and washed with MTBE. The organic mixture was washed with a 0.5 M aq HCl solution, dried over $MgSO_4$ and concentrated in vacuo. The resulting oil was dissolved in anhyd THF (8 mL) and was added slowly to a suspension of NaH (60% in oil) (318 mg, 7.944 mmol) in anhyd THF (8 ml) at r.t. under Ar. After 45 min of stirring, MeI (1.656 ml, 26.48 mmol) was added at r.t. and stirring was continued for another hour. The reaction mixture was poured into aq sat. NH_4Cl and extracted with Et_2O (3 ×). The combined organic layers were dried over $MgSO_4$ and the solvents were removed in vacuo. Purification by flash chromatography (pentane–MTBE, 95:5) afforded **21** (1.229 g, 5.078 mmol, 96%) as an orange oil.

Compound 21

EPR: g = 2.006; α_N = 14.25 G.

IR (film): 2966, 2881, 2819, 1463, 1382, 1099, 808 cm^{-1}.

MS (ESI): m/z = 265 [M + Na]$^+$.

Anal. Calcd for $C_{14}H_{28}NO_2$: C, 69.38; H, 11.64; N, 5.78. Found: C, 69.25; H, 11.77; N, 5.66.

1-(1,3-Dithian-2-yloxy)-2,2,6,6-tetraethyl-4-methoxypiperidine (22)

n-BuLi (1.6M) (0.625 ml, 1.0 mmol) was added to a solution of 1,3-dithiane (120 mg, 1.0 mmol) in anhyd dimethoxyethane (2.2 ml) at –35 °C under Ar. After 45 min of stirring, a solution of nitroxide **21** (484 mg, 2.0 mmol) in anhyd dimethoxyethane was added at –35 °C. The cooling bath was replaced by a water–ice cooling bath and stirring at 0 °C was continued for 1 h. The reaction mixture was then stirred at r.t. for 20 min, poured into a sat. aq solution of NH_4Cl and extracted (2 ×) with Et_2O. The combined organic layers were dried over $MgSO_4$. Flash chromatography (pentane–MTBE, 96:4) afforded **22** (197 mg, 0.545 mmol, 55%) and **21** (245 mg, 1.01 mmol) was recovered.

Compound 22

IR (film): 2961, 1463, 1377, 1098, 912 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.56 (s, 1 H, SCH), 3.36 (m, 1 H, MeOCH), 3.32 (s, 3 H, OCH_3), 3.25 (ddd, J_1 = 14.2 Hz, J_2 = 7.6 Hz, J_3 = 6.10 Hz, 2 H, SCH_2), 2.68 (ddd, J_1 = 13.6 Hz, J_2 = 4.5 Hz, J_3 = 4.3 Hz, 2 H, SCH_2), 1.82 (m, 2 H, SCH_2CH_2), 2.06 (m, 4 H, CH_2CH_3), 1.82 (m, 2 H, CCH_2), 1.74 (m, 2 H, CH_2CH_3), 1.45 (m, 2 H, CH_2CH_3), 1.28 (t, J = 11.4 Hz, 2 H, CCH_2), 0.92 (t, J = 7.2 Hz, 6 H, CH_3), 0.91 (t, J = 7.2 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.2 (CH), 71.0 (CH), 66.0 (C), 55.6 (CH_3), 36.1 (2 × CH_2), 30.4 (2 × CH_2), 27.7 (CH_2), 25.6 (2 × CH_2), 25.0 (CH_2), 10.0 (2 × CH_3), 8.1 (2 × CH_3).

MS (ESI): m/z = 384 $[M + Na]^+$.

Anal. Calcd for $C_{18}H_{35}NO_2S_2$: C, 59.79; H, 9.76; N, 3.87. Found: C, 59.99; H, 9.71; N, 3.71.

3-(1,3-Dithian-2-yl)-2-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl)oxy]propanenitrile (23)

A solution of **22** (35.5 mg, 0.098 mmol) and acrylonitrile (26 mg, 0.492 mmol) in degassed dichloroethane (0.13 mL, 0.75 M) was sealed off under Ar. The mixture was heated at 110 °C in an oil bath for 1.5 h and was then allowed to cool to r.t. The solvent and excess of acrylonitrile were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 9:1) to afford **23** (37 mg, 0.089 mmol, 92%).

Compound 23

IR (film): 2964, 2880, 2817, 1464, 1380, 1098, 906 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.7 (dd, J_1 = 9.7 Hz, J_2 = 5.6 Hz, 1 H, NCCH), 4.14 (dd, J_1 = 10.2 Hz, J_2 = 5.1 Hz, 1 H, SCH), 3.33 (m, 1 H, $MeOCH_3$), 3.30 (s, 3 H, OCH_3), 2.87 (m, 4 H, SCH_2), 2.38–2.19 (m, 2 H, SCH_2CH_2), 2.10 (m, 1 H, $SCHCH_2$), 1.94–1.19 (m, 13 H, $SCHCH_2$, $NCCH_2$), 0.98 (t, J = 7.1 Hz, 6 H, CH_3), 0.89 (t, J = 7.3, 3 H, CH_3), 0.87 (t, J = 7.6 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.6 (C), 70.7 (CH), 70.6 (CH), 66.4 (C), 65.8 (C), 55.7 (CH_3), 42.2 (CH), 38.6 (CH_2), 36.5 (CH_2), 36.3 (CH_2), 30.8 (2 × CH_2), 29.9 (CH_2), 29.5 (CH_2), 27.3 (2 × CH_2), 25.5 (CH_2), 15.1 (CH_3), 9.9 (CH_3), 8.6 (C3), 7.8 (CH_3).

MS (ESI): m/z = 437 $[M + Na]^+$.

Anal. Calcd for $C_{21}H_{38}N_2O_2S_2$: C, 60.83; H, 9.24; N, 6.76. Found: C, 60.68; H, 9.10; N, 6.47.

Butyl 3-(1,3-Dithian-2-yl)-2-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl)oxy]propanoate (24)

A solution of **22** (26 mg, 0.072 mmol) and *n*-butyl acrylate (10.1 mg, 0.079 mmol) in degassed dichloroethane (72 μL, 1 M) was sealed off under Ar. The mixture was heated at 115 °C in an oil bath for 9.5 h and was then allowed to cool to r.t. The solvent and excess of *n*-butyl acrylate were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford **24** (20 mg, 0.041 mmol, 57%).

Compound 24

IR (film): 2959, 2878, 2816, 1738, 1464, 1167, 1098, 990 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.42 (dd, J_1 = 10.0 Hz, J_2 = 4.3 Hz, 1 H, COCH), 4.11 (m, 2 H, OCH_2), 3.84 (dd, J_2 = 4.1 Hz, J_2 = 10.2 Hz, 1 H, SCH), 3.35 (m, 1 H, $MeOCH_3$), 3.31 (s, 3 H, OCH_3), 2.82 (m, 4 H, SCH_2), 2.29 (m, 1 H), 2.19–1.97 (m, 2 H), 1.91–1.20 (m, 17 H), 1.00 (t, J = 7.3 Hz, 3 H, CH_3), 0.94 (t, J = 7.4 Hz, 3 H, CH_3), 0.90–0.82 (m, 9 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (C), 80.8 (CH), 71.1 (CH), 66.1 (CH), 65.6 (C), 64.6 (CH_2), 55.7 (CH_3), 42.3 (CH), 38.9 (CH_2), 36.2 (CH_2), 36.1 (CH_2), 30.6 (CH_2), 30.4 (CH_2), 30.3 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 27.5 (CH_2), 27.2 (CH_2), 25.6 (CH_2), 19.2 (CH_2), 13.7 (2 × CH_3), 10.0 (CH_3), 8.1 (2 × CH_2).

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{25}H_{47}NO_4S_2$: 512.2844; found: 512.2831.

2-(1,3-Dithian-2-ylmethyl)-4-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl)oxy]decanenitrile (25)

A solution of **23** (20 mg, 0.048 mmol) and 1-octene (27 mg, 0.242 mmol) in degassed dichloroethane (48 μL, 1 M) was sealed off under Ar. The mixture was heated at 135 °C in an oil bath for 24 h and was then allowed to cool to r.t. The solvent and excess of 1-octene were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford **25** (10 mg, 0.019 mmol, 40%).

Compound 25 (Both Isomers)

IR (film): 2963, 2878, 2817, 2239, 1462, 1378, 1098 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.19 (m, 1 H, NOCH), 3.80 (m, 1 H, SCH), 3.37 (m, 1 H, MeOCH), 3.32 (s, 3 H, OCH_3), 2.92 (m, 1 H, CHCN), 2.86 (m, 4 H, SCH_2), 2.17–1.18 (m, 28 H), 0.97–0.78 (m, 15 H, 4 × CH_3, OCH_3).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 121.4 (C), 121.1 (C), 78.6 (CH), 78.4 (CH), 71.3 (CH), 65.8 (C), 65.7 (C), 55.5 (CH_3), 55.3 (CH_3), 44.4 (CH), 44.3 (CH), 38.3 (CH_2), 38.3 (CH_2), 37.2 (CH_2), 37.0 (CH_2), 36.8 (CH_2), 36.7 (CH_2), 35.4 (CH_2), 33.1 (CH_2), 32.3 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 30.9 (CH_2), 30.9 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 30.4 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.2 (CH), 25.8 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 25.3 (CH), 25.0 (CH_2), 22.6 (CH_2), 14.0 (CH_3), 10.2 (CH_3), 8.9 (CH_3), 8.7 (CH_3), 8.2 (CH_3), 7.6 (CH_3).

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{29}H_{54}N_2O_2S_2Na$: 549.3524; found: 549.3528.

Butyl 2-(1,3-Dithian-2-ylmethyl)-4-[(2,2,6,6-tetraethyl-4-methoxy-1-piperidinyl)oxy]decanoate (26)

A solution of **24** (13 mg, 0.0266 mmol) and 1-octene (15 mg, 0.133 mmol) in degassed dichloroethane (27 μL, 1 M) was sealed off under Ar. The mixture was heated at 135 °C in an oil bath for 24 h and was then allowed to cool to r.t. The solvent and excess of 1-octene were removed in vacuo. The residue was purified by flash chromatography (pentane–MTBE, 98:2) to afford **26** (9 mg, 0.015 mmol, 56%).

Compound 26 (Both Isomers)

IR (film): 2958, 2926, 2877, 1731, 1464, 1378, 1158, 1066 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.07 (m, 2 H, OCH_2, NOCH), 3.96 (dd, J = 8.4, 6.2 Hz, 2 H, OCH_2), 3.62 (m, 1 H, SCH), 3.36 (m, 1 H, MeOCH), 3.32 (s, 3 H, OCH_3), 2.86 (m, 1 H, COCH), 2.81 (m, 4 H, SCH_2), 2.16–1.17 (m, 32 H), 0.96–0.85 (m, 18 H, CH_3).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 175.4 (C), 175.2 (C), 79.2 (CH), 78.8 (CH), 71.4 (CH), 65.9 (C), 65.7 (C), 65.3 (C), 64.4 (CH), 64.4 (CH), 55.7 (CH_3), 45.1 (CH), 45.0 (CH), 39.8 (CH), 39.6 (CH), 38.3 (CH_2), 36.9 (CH_2), 36.8 (CH_2), 36.5 (CH_2), 36.0 (CH_2), 33.0 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 30.9 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 25.9 (CH_2), 25.9 (CH_2), 24.5 (CH_2), 22.6 (CH_3), 19.2 (CH_3), 14.1 (CH_3), 13.7 (CH_3), 10.5 (CH_3), 10.2 (CH_3), 8.8 (CH_3), 8.6 (CH_3), 8.2 (CH_3), 8.0 (CH_3).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{33}H_{64}NO_4S_2$: 602.4277; found: 602.4273.

Polymerization of Styrene with Alkoxyamine (5)

A Schlenk tube was charged with alkoxyamine initiator **5** (72 mg, 0.262 mmol) and styrene (3 mL, 26.21 mmol). The tube was subjected to three freeze-thaw cycles and sealed off under Ar. The polymerization was carried out under Ar at 125 °C for 24 h. The resulting mixture was cooled to r.t., dissolved in CH_2Cl_2, and poured into a glass dish, and the residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. The conversion was evaluated gravimetrically (1.667 g, 61%), the experimental number-average molecular weight ($M_{n,exp}$) = 6600 $gmol^{-1}$, and PDI = 1.12 were determined by SEC.

Acknowledgment

We thank the Alexander von Humboldt Foundation for financial support (stipend to A. J. H.). The Fonds der Chemischen Industrie is acknowledged for continuous support.

References

(1) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.
(2) Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357.
(3) Greene, T. W.; Wuts, P. G. M. *Protecting Groups in Organic Synthesis*, 3th ed.; Wiley: New York, **1999**.
(4) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991.
(5) Byers, J. H.; Whitehead, C. C.; Duff, M. E. *Tetrahedron Lett.* **1996**, *37*, 2743.
(6) de Greef, M.; Zard, S. Z. *Tetrahedron* **2004**, *60*, 7781.
(7) Nishida, A.; Kawahara, N.; Nishida, M.; Yonemitsu, O. *Tetrahedron* **1996**, *52*, 9713.
(8) Studer, A. *Chem. Soc. Rev.* **2004**, *33*, 267.
(9) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.
(10) Marque, S.; Fischer, H.; Baier, E.; Studer, A. *J. Org. Chem.* **2001**, *66*, 1146.
(11) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(12) Ananchenko, G. S.; Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3604.
(13) Connolly, T. J.; Scaiano, J. C. *Tetrahedron Lett.* **1997**, *38*, 1133.
(14) (a) Wetter, C.; Studer, A. *Chem. Commun.* **2004**, 174. (b) Teichert, A.; Jantos, K.; Harms, K.; Studer, A. *Org. Lett.* **2004**, *6*, 3477. (c) Review on microwave chemistry: Kappe, C. O. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250.
(15) The microwave experiments were conducted using professional laboratory microwave equipment. A MLS-Ethos 1600 Mikrowellen System (Milestone) was used for the present studies. The reactions were run in 40 mL MLS-reaction high-pressure vessels (up to 15 bars), which contain pressure control valves. An advanced temperature control system from MLS allowing direct contactless temperature monitoring was used. The microwave power is continuously and dynamically adjusted to follow the defined temperature profile.
(16) Molawi, K.; Schulte, T.; Siegenthaler, K. O.; Wetter, C.; Studer, A. *Chem.–Eur. J.* in press.
(17) Wetter, C.; Gierlich, J.; Knoop, C. A.; Müller, C.; Schulte, T.; Studer, A. *Chem.–Eur. J.* **2004**, *10*, 1156.
(18) (a) Schulte, T.; Studer, A. *Macromolecules* **2003**, *36*, 3078. (b) Wetter, C.; Gierlich, J.; Knoop, C. A.; Müller, C.; Schulte, T.; Studer, A. *Chem.–Eur. J.* **2004**, *10*, 1156.
(19) Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. *Macromolecules* **2000**, *33*, 4403.
(20) This compound decomposes in the absence of solvents, upon exposure to air.
(21) Jiang, B.; Chen, Z. *Tetrahedron: Asymmetry* **2001**, *12*, 2835.