DOI: 10.1002/chem.201602377

Catalytic Antioxidants

Alkyltelluro Substitution Improves the Radical-Trapping Capacity of Aromatic Amines

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Abstract: The synthesis of a variety of aromatic amines carrying an *ortho*-alkyltelluro group is described. The new antioxidants quenched lipidperoxyl radicals much more efficiently than α-tocopherol and were regenerable by aqueous-phase *N*-acetylcysteine in a two-phase peroxidation system. The inhibition time for diaryl amine **9b** was four-fold longer than recorded with α-tocopherol. Thiol consumption in the aqueous phase was found to correlate inversely to the inhibition time and the availability of thiol is the limiting factor for the duration of antioxidant protection. The proposed mechanism for quenching of peroxyl radicals involves O-atom transfer from peroxyl to Te followed by H-atom transfer from amine to alkoxyl radical in a solvent cage.

Introduction

Autoxidation is an undesired, stepwise, free-radical reaction whereby organic compounds R–H are oxidatively converted to the corresponding hydroperoxides, ROOH [Eq. (1)]. The most successful way to inhibit or at least slow down the process has been to add small amounts of a radical trapping antioxidant,

$$\mathrm{R{-}H} + \mathrm{O_2} \rightarrow \mathrm{R{-}OOH} \quad (1)$$

$$\mathrm{R{-}OO^{\bullet}} + \mathrm{A{-}H} \xrightarrow{k_{inh}} \mathrm{R{-}OOH} + \mathrm{A^{\bullet}} \quad (2)$$

$$\mathrm{R{-}OO^{\bullet}} + \mathrm{R{-}H} \xrightarrow{k\mathrm{prop}} \mathrm{R{-}OOH} + \mathrm{R^{\bullet}} \quad (3)$$

A–H, which could transfer a hydrogen atom to peroxyl radicals considerably faster [$k_{inh}=10^5$–$10^6\,\mathrm{M^{-1}\,s^{-1}}$; Eq. (2)] than the hydrocarbon R–H itself [$k_{prop}=$ up to $10^2\,\mathrm{M^{-1}\,s^{-1}}$; Eq. (3)] and which gives rise to a relatively unreactive radical, $\mathrm{A^{\bullet}}$.

Among chain-breaking antioxidants found in biological systems or used for the stabilization of man-made materials and products, phenols and aromatic amines clearly predominate. Evolution gave us α-tocopherol (**1**) which has become a benchmark ($k_{inh}=3.2\times10^6\,\mathrm{M^{-1}\,s^{-1}}$)[1] for a reactive phenolic antioxidant and 60 years of industrial and academic experimentation provided us with the 4,4′-dialkyldiphenylamines **2** ($k_{inh}=1.8\times10^5\,\mathrm{M^{-1}\,s^{-1}}$),[2] which are one of the favorite additives to oils, fuels and other petroleum products. Since the 1960s, considerable efforts have been invested to improve the radical-trapping activity of phenolic compounds.

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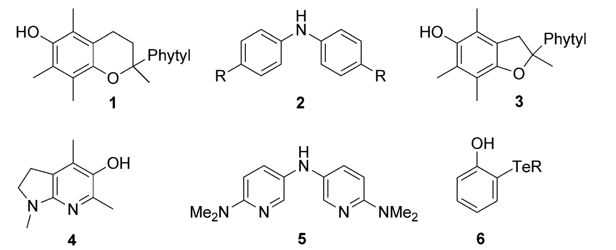
Supporting information and ORCID from the author for this article are available on the WWW under http://dx.doi.org/10.1002/chem.201602377.

Early on,[3] electron-donating substituents such as methoxyls or methyls that could stabilize the developing phenoxyl radical were found to lower the O–H bond dissociation enthalpy and increase reactivity towards peroxyl radicals. It was also realized that the orientation of the lone pairs of an oxygen substituent relative to the aromatic plane was critical for the stabilizing effect. For example, this overlap is better in the ring-contracted tocopherol **3** than in the parent **1** and the rate constant for quenching of peroxyl radicals increases by a factor of almost two.[4]



The 21st century has seen more dramatic improvements in the reactivities of radical trapping antioxidants.[5,6] In 2003 Pratt, Valgimigli and Porter published a seminal paper describing the excellent radical trapping activity of 3-pyridinols carrying strongly electron-donating substituents.[7] By substitution of CH for N in the aromatic part of a phenol, the O–H bond could be weakened by *para*-substitution with a strongly electron-donating dimethylamino group while the ionization potential of the antioxidant did not drop below the critical point where a direct reaction with dioxygen becomes a problem. 3-Pyridinol **4**—the most reactive compound of this kind—was an impressive 88-times more reactive towards peroxyl radicals than α-tocopherol. More vitamin E-like compounds of this type, which were about 15-times more reactive than the parent, were also prepared.[8,9]

Not unexpectedly, the principles for maximizing the radical trapping activity of phenols holds also for diaryl amine antioxidants.[2] Thus, the di-3-pyridyl amine **5** was 200-times more reactive towards peroxyl radicals than the industrial standard diaryl amine **2** ($R=C_8H_{17}$).

We have found another way to improve the performance of phenolic antioxidants.[10] Incorporation of an alkyltelluro group next to the OH in phenol (compound **6**) was found to increase the rate constant for quenching of peroxyl radicals by about four orders of magnitude. Thus, compounds of this type are about ten-fold more reactive than α-tocopherol. To account for the high reactivities, we have proposed a rather unconventional mechanism involving oxygen transfer from peroxyl radical to tellurium, followed by H-atom transfer, in a solvent cage, from phenol to the resulting alkoxyl radical.[11] Interestingly, in a two-phase system designed to model a biological membrane, water-soluble co-antioxidants contained in the aqueous layer could regenerate the organotellurium antioxidant in the lipid phase and allow for a catalytic mode of chain-breaking activity.

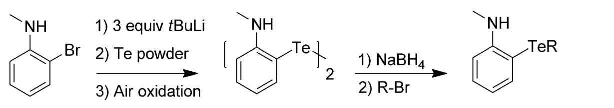
In the following we describe our attempts to improve the radical-trapping activity of aromatic amine antioxidants by alkyltelluro substitution. Since the valency of nitrogen is higher than that of oxygen, the opportunities for structural variations are richer in aromatic amines than in phenolic compounds. Novel antioxidants prepared were evaluated both for their reactivity towards lipidperoxyl radicals and their regenerability in the two-phase system.

Results and Discussion

Synthesis

Only a few alkyltelluro substituted arylamines are known in the literature and their preparation is often rather lengthy.[12,13] We thought that *t*BuLi-induced lithium-halogen exchange in a bromoaniline derivative, followed by addition of a dialkyl ditelluride as an electrophile would provide the corresponding alkyltelluro-functionalized aniline in a one-pot reaction. However, all attempts to lithiate 2-bromoaniline and treat it with a dialkyl ditelluride resulted in the formation of rather complex mixtures from which the desired product could never be isolated in pure form.

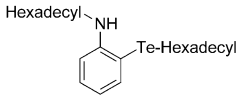
We also tried to use elemental tellurium as an electrophile. After oxidation of the resulting lithium arene tellurolate to a ditelluride, borohydride reduction and alkylation would provide the desired alkyltelluro functionalized aniline. Although this sequence of reactions returned only small amounts of the desired product when 2-bromoaniline was used as a starting material, it was useful for the preparation of the corresponding *N*-alkylated products **7** [Eq. (4)].



(4)

7a R = Butyl (76%)
7b R = Octyl (63%)
7c R = Hexadecyl (47%)

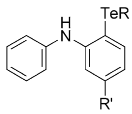
Thus, alkyltelluro groups could be introduced in fair yields into the *ortho*-position of *N*-methylaniline.



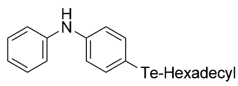
8 (51%)

In a similar fashion, *N*-hexadecyl-2-bromoaniline provided lipophilic compound **8** in 51% yield. As exemplified by compounds **9**, the procedure also provided convenient access to diarylamines carrying *ortho*-alkyltelluro substituents. It would seem that the protocol described in Equation (4) could be simplified by addition of the appropriate alkyl halide to the in situ prepared solution of the lithium arenetellurolate formed before oxidation. However, whenever this was tried, a difficult-to-separate, complex mixture of products was obtained.

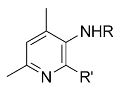
Our previous work[11] with alkyltelluro phenols suggested that the radical trapping activity as well as the regenerability was better if the two functional groups were oriented *ortho* rather than *para* to each other. For comparison, using the methodology shown in Equation (4), we synthesized diphenylamine **10**, carrying a *para*-hexadecyltelluro group.



9a R = Butyl, R'=H (50%)
9b R = Hexadecyl, R'=H (63%)
9c R = Hexadecyl, R'=OMe (59%)



10 (26%)

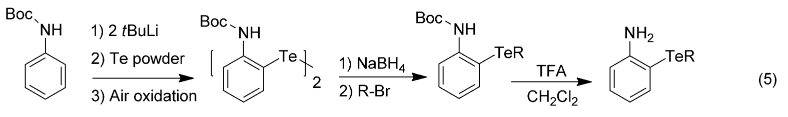


11a R = H, R' = Br
11b R = Methyl, R' = Br (88%)
11c R = H, R' = Te-Octyl (22%)
11d R = Me, R' = Te-Octyl (32%)

Curious to see if the radical trapping activity of 3-aminopyridines could be improved, we prepared 3-amino-2-bromo-4,6-dimethylpyridine (**11a**)[10b] and subjected it to alkyltelluro functionalization as described in Equation (4). Telluride **11c** was isolated in modest yield. The corresponding *N*-methylated compound **11d** was obtained from **11b** in a similar fashion.

We also explored *ortho*-lithiation[14] for the introduction of alkyltelluro groups [Eq. (5)]. Thus, Boc-protected aniline was dilithiated with *t*BuLi and allowed to react with elemental tellurium. After air-oxidation, the crude ditelluride obtained was reduced with sodium borohydride and the arenetellurolate formed was allowed to react with butyl bromide to provide **12a** in 37% yield. Deprotection to give **13a** occurred by stirring in methylene chloride containing trifluoroacetic acid (TFA). The corresponding hexadecyltelluro derivative **13b** was similarly prepared from **12b**.

Following a literature procedure,[15] Boc-protected tetrahydroquinoline was *peri*-lithiated with *sec*-BuLi. Addition of dibutyl- and dihexadecyl ditelluride afforded compounds **14a** and **14b**, respectively, in 57 and 33% isolated yield after deprotection with TFA.



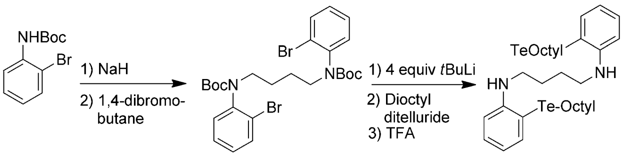
(5)

12a R = Butyl (37%)
12b R = Hexadecyl (29%)
13a R = Butyl (95%)
13b R = Hexadecyl (55%)

14a R = Butyl (57%)
14b R = Hexadecyl (33%)
15 (31%)

Alkyl aryl amines offer a possibility to install the alkyltelluro moiety also into the alkyl part of the molecule. Compound **15** appeared as an interesting target. Separated from the nitrogen by a three-carbon spacer, the alkyltelluro group would still be able to interact intramolecularly with the arylamine moiety. Compound **15** was prepared in 31 % yield by dilithiation of *N*-(2-bromobenzyl)aniline, followed by reaction with dibutyl ditelluride.

Previously, in the case of phenolic antioxidants, we observed that compounds carrying two alkyltelluro groups showed considerably better regenerability than their monofunctionalized counterparts.[10e] Towards this end, it was envisaged to connect two molecules of an aromatic amine antioxidant via a linker attached to the nitrogen atoms. A suitable starting material **16** was obtained by allowing Boc-protected 2-bromoaniline to react with 1,4-dibromobutane [Eq. (6)]. The desired compound **17** was then obtained in one pot after lithiation, reaction with dioctyl ditelluride and TFA-deprotection.



(6)

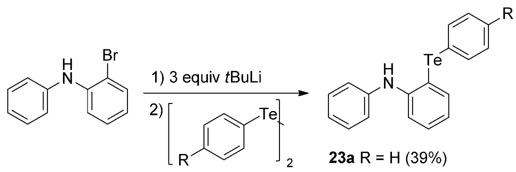
16 (55%)
17 (38%)

We also thought it would be interesting to try to introduce another alkyltelluro group into the aniline part of antioxidant **15**. However, all attempts to access the desired compound **20** by dilithiation of the corresponding dibromo compound failed. A reductive amination approach turned out to be more rewarding [Eq. (7)]. The diethyl acetal of 2-bromobenzaldehyde was a suitable starting material. First, butyltelluro (**18a**) and hexadecyltelluro (**18b**) groups were introduced using the chemistry described in Equation (4).

The acetals were then hydrolyzed and the resulting aldehydes **19** condensed with anilines **13** (**19a** with **13a** and **19b** with **13b**) to give the bis-functionalized amines **20a** and **20b** in low yield after reduction with sodium cyanoborohydride. 2,2′-Dibromodiphenylamine (**21**) was converted in one pot to the corresponding bis-alkyltelluro derivative **22** by using the chemistry described in Equation (4) (5 equiv of *t*BuLi).

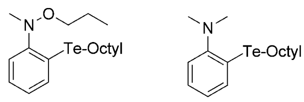
21
22 R = Te-Hexadecyl (15%)

In order to study the influence of electronic effects on antioxidant activity, diphenylamines **23a–c** were synthesized by lithiation of 2-bromodiphenylamine, followed by addition of the corresponding diaryl ditellurides.

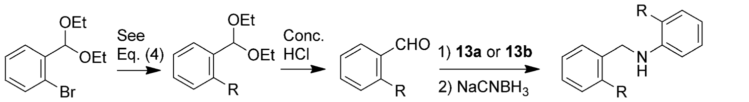


23a R = H (39%)
23b R = OMe (42%)
23c R = CF_3 (46%)

For reference purposes, octyltelluro-substituted *N*-alkoxy-*N*-methylaniline (**24**) and *N*,*N*-dimethylaniline (**25**) were prepared from the corresponding bromo derivatives by lithiation followed by reaction with electrophilic tellurium species.



24 (63%)
25 (88%)



(7)

18a R=Te-Butyl
18b R=Te-Hexadecyl (59%)
19a R=Te-Butyl
19b R=Te-Hexadecyl (98%)
20a R=Te-Butyl (18%)
20b R=Te-Hexadecyl (41%)

Evaluation

The radical trapping capacity as well as the regenerability of novel aromatic amine antioxidants were evaluated in a primitive (lipid phase/aqueous phase) model of a biological membrane as previously described.[10] Briefly, autoxidation of linoleic acid in air was initiated by radicals formed during decomposition of 2,2′-azobis(2,4-dimethylvaleronitrile) (AMVN) at 42 °C in chlorobenzene (lipid phase). The aqueous phase contained *N*-acetylcysteine (NAC), a thiol co-antioxidant capable of regenerating the lipid-soluble antioxidant and thus extending the inhibition time, T_{inh} (the time during which the antioxidant could efficiently inhibit peroxidation) beyond the value recorded in a control experiment with pure water. The progress of peroxidation was monitored by HPLC with UV detection of conjugated diene formed. Good radical trapping antioxidants (such as α-tocopherol) keep formation of conjugated diene at a minimum as long as they last (the inhibited rate of peroxidation, R_{inh}, is low), but then it increases markedly (Figure 1).

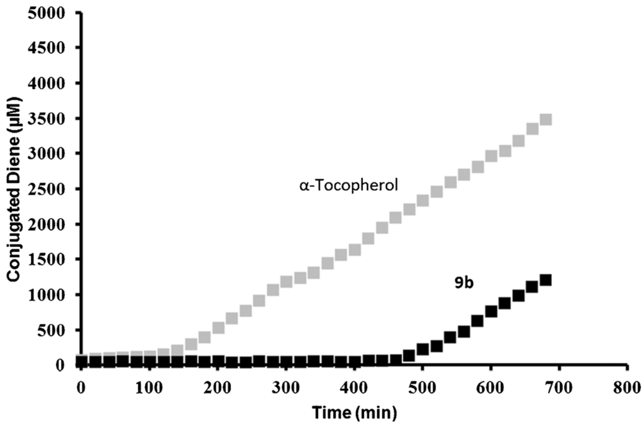


Figure 1. Peroxidation traces (linoleic acid hydroperoxide concentration vs. time) recorded using compound **9b** and α-tocopherol as antioxidants in the chlorobenzene layer in the presence of NAC (1 mM) in the aqueous phase.

α-Tocopherol was used as a benchmark in the two-phase model. It can quench two peroxyl radicals before it is all consumed and the rate of linoleic acid peroxidation increases rapidly. Control experiments with and without NAC in the aqueous phase produced essentially identical peroxidation traces (R_{inh} = 25–28 μM h^{-1} and T_{inh} = 97–109 min; Table 1). Thus, α-tocopherol is not regenerable under the conditions of our two-phase assay. In the absence of NAC, no inhibited phase of peroxidation could be distinguished for the alkyltelluro-substituted aromatic amines and relatively high inhibited rates of peroxidation were observed (R_{inh} = 198–544 μM h^{-1}; Table 1). This is probably because the organotellurium catalyst has been oxidized by the residual amounts of linoleic acid hydroperoxide that is always present in commercial samples of linoleic acid. On the contrary, primary and secondary amines carrying alkyltelluro groups effectively inhibited lipid peroxidation (R_{inh} = 2–9 μM h^{-1}) in the presence of NAC, a compound known to readily reduce tetravalent organotelluriums to the divalent state. Also, inhibition times were extended and were often much longer than recorded for α-tocopherol. This seems to indicate that the organotellurium antioxidants are continuously regenerated by NAC. Alkyltelluro anilines **13** were among the least regenerable compounds (Table 1) and T_{inh} values were shorter than recorded for the corresponding alkyltelluro phenols **6**.[10e] The inhibition times for *N*-alkylated alkyltelluro anilines (**7a**–**c**, **8** and **14a**–**b**) were clearly longer (148–342 min). However, the best results were obtained with diphenylamines **9**. Whereas the butyltelluro compound **9a** inhibited peroxidation for 237 min, the t_{inh} for the hexadecyltelluro analogue **9b** was almost two-fold longer (461 min). Peroxidation traces for **9b** and α-tocopherol are shown in Figure 1.

For compounds **7**–**9** and **14** there is a trend in which regenerability increases as the compounds become more lipophilic. The reasons for this are not clear. The long alkyl chains could somehow improve regeneration by facilitating communication between the aqueous and chlorobenzene layers in the two-phase system. Alternatively, they could serve to stabilize the solvent cage in the proposed mechanism (vide infra).

The *ortho*-substituted alkyltelluro phenols previously tested[11] showed much better regenerability than their corresponding *para*-substituted analogues. In line with these results, *para*-substituted diphenyamine **10** (T_{inh} = 152 min) could not match **9b** when it comes to inhibition time in the presence of

Table 1. Inhibited rates of conjugated diene formation (R_{inh}) and inhibition times (T_{inh}) in the presence and absence of NAC (1 mM) in the two-phase system.

Antioxidant (40 μM)	With NAC R_{inh}[a] [μM h^{-1}]	With NAC T_{inh}[b] [min]	Without NAC R_{inh}[a] [μM h^{-1}]	Without NAC T_{inh}[b] [min]
7a	5±1	204±5	393	0
7b	5±1	218±7	449	0
7c	3±1	219±4	434	0
8	7±2	300±6	544	0
9a	2±1	237±1	401	0
9b	2±1	461±10	393	0
9c	2±1	444±6	356	0
10	6±1	152±2	290	0
11c	6±2	95±5	466	0
11d	4±0	106±0	532	0
13a	4±1	87±7	533	0
13b	4±2	137±10	444	0
14a	4±1	148±1	385	0
14b	2±1	342±4	235	0
15	4±1	132±2	247	0
17	9±3	159±11	460	0
20a	8±3	135±11	254	0
20b	3±1	147±4	269	0
22	3±0	420±7	243	0
23a	7±1	34±9	348	0
23b	7±3	410±11	441	0
23c	44±7	279±6	311	0
24	27±5	134±8	198	0
25	90±4	54±5	470	0
α-tocopherol	25±1	97±5	28±2	109±2

[a] Rate of peroxidation during the inhibited phase (uninhibited rate ca. 479 μM h^{-1}). Errors correspond to ±SD for triplicates. [b] Inhibited phase of peroxidation. Reactions were monitored for 680 min. Errors correspond to ±SD for triplicates.

NAC. It was also a slightly poorer quencher of peroxyl radicals. 3-Pyridinols carrying alkyltelluro groups in position 2 have recently been shown to act as regenerable and efficient radical-trapping agents.[10a,b] It was therefore disappointing to find that the corresponding 3-aminopyridine derivative **11 c** and its *N*-methyl analogue **11 d** inhibited peroxidation for only about 100 min.

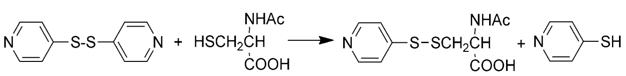
N-Benzyl aniline **15** is the only compound where the alkyltelluro group is placed in the alkyl rather than the aryl part of the molecule. Gratifyingly, peroxyl radicals were efficiently quenched (R_{inh} = 4 μM h^{-1}). However, as noted with some of the other anilines, the antioxidant protection did not last for long (T_{inh} = 132 min).

Based on the results with alkyltelluro phenols,[10e] one would think that aniline antioxidants carrying more than one alkyltelluro group would show better regenerability than their mono-substituted counterparts. However, based on the results with compounds **17**, **20** and **22** it is not worthwhile to introduce a second alkyltelluro group. Although the compounds carrying two alkyltelluro groups were tested at the same concentration (40 μM) as the mono-functionalized antioxidants, regenerability was often poorer (**22** vs. **9 b** and **17** vs. **7 b**) for the more complex compound.

In diphenylamines **23** the electron density at tellurium is varied in a systematic way. As shown in Table 1, there is a trend that electron-withdrawing substituents cause a reduction in the inhibition time (**23 b** > **23 a** > **23 c**). Furthermore, compound **23 c** carrying a 4-CF_3-C_6H_4Te-group was considerably less reactive (R_{inh} = 44 μM h^{-1}) towards peroxyl radicals than the other two. Replacement of a *para*-hydrogen for a methoxy group in the aryl part of the diphenylamine (compound **9 c** vs. **9 b**) only influenced the antioxidative properties marginally.

Compounds **24** and **25** represent anilines lacking an N–H bond. None of them could inhibit peroxidation for long in the presence of NAC and both of them (R_{inh} = 27 and 90 μM h^{-1}, respectively) were poor radical-trapping agents. It may be that these compounds quench peroxyl radicals by electron transfer, followed by disproportionation of the resulting, labile, Te^{III} species.

The two-phase system for assessment of reactivity and regenerability of novel antioxidants relies on analysis of conjugated diene formed in the organic phase. Only rarely,[10b] have we tried to study what is going on in the aqueous phase. What we have seen is that NAC is oxidized to the corresponding disulfide. In order to follow the thiol consumption more carefully during a peroxidation experiment, the aqueous phase was sampled every 30 min and allowed to react with bis-4-pyridyl disulfide (Aldrithiol-4™). The concentration of pyridine-4-thiol formed in the substitution reaction with NAC [Eq. (8)] was then determined spectrophotometrically at 324 nm.



(8)

A control experiment with nothing but NAC in the two-phase system (Table 2) showed a slow consumption of the thiol (27 μM h^{-1}). This did not increase much when AMVN and linoleic acid (37 μM h^{-1}) were added and α-tocopherol (33 μM h^{-1}) as an antioxidant. Probably, since the uncatalyzed reaction of NAC with alkylhydroperoxides is slow, the thiol consumption does not reflect the amount of hydroperoxide present in the chlorobenzene layer.

Table 2. NAC consumption in the aqueous phase during a two-phase peroxidation experiment.

Antioxidant (40 μM)	Rate of NAC-consumption [μM h^{-1}][a]
7 b	222 ± 18
9 b	146 ± 13
9 c	150 ± 14
10	321 ± 22
11 d	736 ± 18
13 b	458 ± 27
14 b	274 ± 10
15	586 ± 21
17	305 ± 14
20 b	415 ± 18
22	187 ± 8
23 a	160 ± 5
23 b	126 ± 10
23 c	188 ± 8
24	500 ± 16
25	538 ± 26
α-tocopherol	33 ± 4
NAC + linoleic acid + AMVN	37 ± 8
NAC	27 ± 5

[a] Errors correspond to ± SD for triplicates.

In support of this hypothesis, addition of telluride **25** after 140 min to the ongoing peroxidation caused a notable increase in the consumption of NAC (Figure 2). The telluride is known to catalyze (via telluroxide formation) the thiol-induced reduction of hydroperoxides. Thiol consumption was also recorded with most of the aromatic amine antioxidants (Table 2). Although their reactivity towards peroxyl radicals were very similar (as judged from the R_{inh} values in Table 1), NAC consumption varied a lot and was often much higher than recorded with α-tocopherol. Overall, the inhibition time recorded was inversely related to the thiol consumption. Thus, diaryla-

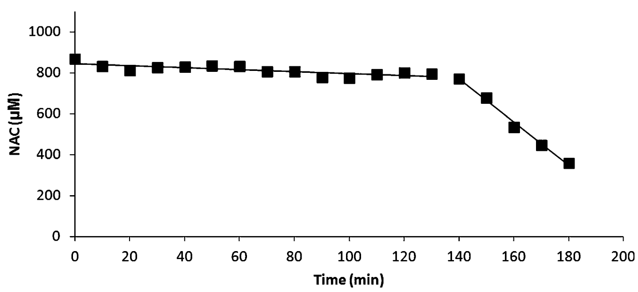


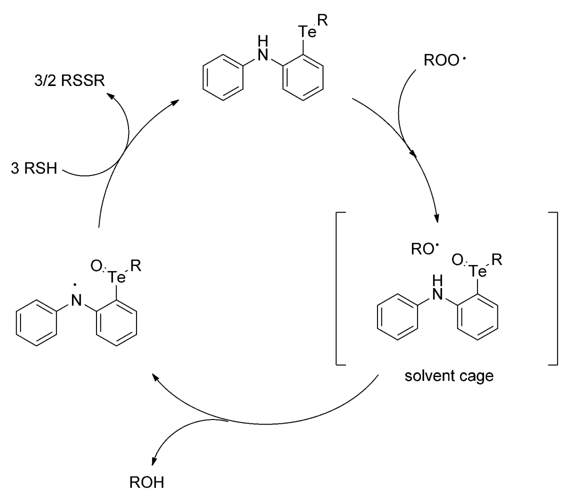
Figure 2. NAC concentration versus time during a normal peroxidation experiment with α-tocopherol (40 μM) as an antioxidant. After 140 min, telluride **25** (40 μM) was added.

mines **9b**, **9c** and **23b** showed the longest T_{inh} values (> 400 min) and the slowest rates of thiol consumption (≤ 150 μM h^{-1}). The fastest rates of thiol consumption were recorded with aminopyridine **11d** (736 μM h^{-1}) and benzyl phenyl amine **15** (586 μM h^{-1}). Both of them offered antioxidant protection for only slightly more than 100 min. Reference compounds **24** and **25**, both lacking N–H groups, caused a rapid consumption of thiol (500 and 538 μM h^{-1}, respectively) but were unable to inhibit oxidation for long. The *para*-disubstituted diphenylamine **10** consumed thiol at a more than two-fold higher rate than the corresponding *ortho*-disubstituted analogue **9b**.

Mechanism

In our previous work with alkyltelluro phenols[11] we proposed an unconventional antioxidant mechanism involving oxygen-atom transfer from peroxyl radicals to tellurium, followed by H-atom transfer from phenol to the resulting alkoxyl radical in a solvent cage. We believe that a similar mechanism is operative with alkyltelluro anilines (Scheme 1). After transfer of oxygen, the resulting alkoxyl radical can abstract a hydrogen atom from the amine. Regeneration of the antioxidant from the telluroxide/aminyl radical is brought about by the thiol and is accompanied by disulfide formation. Whereas the thiol-induced reduction of telluroxide to telluride is well documented in the literature,[16] the reduction of an aminyl radical to amine has little precedence. We speculate that proton-coupled electron transfer (PCET) could be involved, facilitated by the large chalcogen.

Why is it then that certain antioxidants can delay peroxidation for more than 400 min with a minimal consumption of aqueous-phase thiol whereas others offer protection for less than 100 min with an up to six-fold higher rate of thiol oxidation? We feel that the key to success for the long-lasting antioxidants is efficient quenching of alkoxyl radicals within the solvent cage and facile reduction of the aminyl radical. Alkoxyl radicals that diffuse out of the cage are reactive enough to



Scheme 1. Proposed mechanism for quenching of peroxyl radicals.

start new chains and for every oxygen-transfer event two equivalents of thiol are used up to reduce telluroxide to telluride. Under such conditions the thiol in the aqueous phase will be rapidly consumed, catalyst will be converted to its oxidized inactive form and peroxidation will increase to the uninhibited rate. Inefficient quenching of alkoxyl radicals in the solvent cage by *para*-substituted alkyltelluro diphenylamine **10** may be the reason for its shorter T_{inh} and higher rate of thiol consumption than the corresponding *ortho*-substituted compound **9b**. Obviously, if hydrogen bonding to NH is important in the solvent cage, the close (*ortho*) arrangement of amine and alkyltelluro groups is better than the distant (*para*).

Diarylaminyl radicals have for long been known to react with peroxyl radicals to form nitroxides. After combination with an alkyl radical, an alkoxyamine will result.[17,18] At elevated temperature homolytic cleavage of the N–O bond occurs, accompanied by reactions which allow for regeneration of the diarylamine antioxidant.[18] Curious to see if an alkoxyamine is likely to be formed under the conditions of our two-phase assay, we synthesized and tested compound **24**. The poor performance of the compound in comparison with the corresponding aniline **7b** brings us to conclude that alkoxyamines are not likely to be involved in the chemistry responsible for the antioxidant activity of aromatic amines carrying alkyltelluro groups.

Conclusions

The synthesis of a variety of alkyltelluro-substituted aromatic amines has enabled the study of their radical trapping activity and regenerability by thiols in a two-phase lipid peroxidation system. We found that introduction of alkyltelluro groups into the aromatic amine scaffold causes a substantial (ca. 100-fold) increase in the reactivity towards lipidperoxyl radicals. Also, regeneration of the aromatic amine antioxidant by thiol co-antioxidants is greatly facilitated. To account for the remarkable antioxidative properties of the organochalcogen compounds we propose an unconventional mechanism involving transfer of an oxygen atom from peroxyl to tellurium, followed by hydrogen abstraction by the resulting alkoxyl radical. Overall, an alcohol rather than a hydroperoxide is the final product of peroxidation. Conventional chain-breaking antioxidants formally transfer a hydrogen atom to peroxyl radicals and drag them out of the autoxidation chain reaction. However, the resulting hydroperoxide needs to be dealt with (reduced) in a separate step by some preventive antioxidant. Our novel antioxidants are, at the same time, chain-breaking and peroxide-decomposing and would therefore be properly described as "multifunctional". Aromatic amines are privileged when it comes to stabilization of many types of petroleum-derived products. One of the merits of these antioxidants is their capacity to trap multiple radicals per molecule of amine.[19] However, the catalytic mechanism is only operative at elevated temperatures (typically 160 °C). Aromatic amines carrying an alkyltelluro group are regenerable by thiols at considerably lower temperatures. In this respect they are complementary to the industrially used diarylamine antioxidants. We feel that this facile regenerability may be taken advantage of for the development of novel antioxidants for petroleum products that are not exposed to elevated temperatures during their service life (fuels, certain oils and greases). Regeneration of tellurium-based antioxidants in homogeneous phase by lipid soluble thiols has been previously demonstrated.[10b]

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on 300 MHz (^{1}H: 300 MHz; ^{13}C: 75 MHz), 400 MHz (^{1}H: 399.97 MHz; ^{13}C: 100.58 MHz) and 500 MHz (^{1}H: 499.93 MHz; ^{13}C: 125.70 MHz) spectrometers, using the residual solvent peaks of $CDCl_3$ (^{1}H: $\delta = 7.26$ ppm; ^{13}C: $\delta = 77.0$ ppm) as an indirect reference to TMS. ^{125}Te NMR spectra were recorded on a 400 MHz spectrometer (^{125}Te: 126.19 MHz) using Ph_2Te_2 ($\delta = 423$ ppm) as external standard. ^{19}F NMR spectra were recorded on a 400 MHz spectrometer (^{19}F: 376 MHz) using $CFCl_3$ ($\delta = 0.0$ ppm) as external standard. The melting points are uncorrected. Flash column chromatography was performed using silica gel (0.04–0.06 mm). Tetrahydrofuran was dried in a solvent purification system by passing it through an activated alumina column. Dibutyl ditelluride,[20] dioctyl ditelluride,[21] dihexadecyl ditelluride,[22] 2-bromodiphenylamine,[23] diphenyl ditelluride,[24] bis(4-methoxyphenyl) ditelluride,[25] bis(4-trifluoromethylphenyl) ditelluride,[26] *N*-(2-bromophenyl)-*N*-methyl-*O*-propylhydroxylamine,[27] *N*-Boc-2-bromoaniline,[28] *N*-2-bromobenzyl aniline,[29] **11 a**,[10a] **18 a**,[24] and **19 a**[30] were prepared according to literature procedures.

General procedure: introduction of alkyltelluro groups into anilines by lithiation

To a solution of the proper bromoaniline derivate (1.0 equiv) in anhydrous THF (10 mL) at −78 °C under nitrogen, *tert*-butyl lithium (1.7 M, 3.0–5.0 equiv) was added. The solution was stirred for 2 h at −78 °C prior to the addition of freshly ground tellurium powder (1.0–4.0 equiv). After being stirred for 2 h at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (10 mL) and extracted with diethyl ether (20 mL × 3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was dissolved in ethanol (25 mL) followed by addition of sodium borohydride (5.0 equiv) at ambient temperature under nitrogen. After being stirred for 15 min, the corresponding alkylbromide (1.0 equiv) was added and the solution was allowed to stir overnight. After addition of water (20 mL) and extraction with diethyl ether (25 mL x 3), the organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound.

2-(Butyltelluro)-*N*-methylaniline (7 a): 2-Bromo-*N*-methylaniline (186 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromobutane (0.1 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (222 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (dd, $J = 1.6$, 7.6 Hz, 1 H), 7.29 (m, 1 H), 6.63 (dd, $J = 0.8$, 8.0 Hz, 1 H), 6.56 (m, 1 H), 4.84 (s, 1 H), 2.90 (s, 3 H), 2.76 (t, $J = 7.6$ Hz, 2 H), 1.72 (m, 2 H), 1.40 (m, 2 H), 0.91 ppm (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.5$, 142.7, 130.7, 117.5, 108.3, 99.7, 33.7, 31.1, 24.8, 13.3, 7.9 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 278$ ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{11}H_{17}NTeH$ $[M+H]^+$: 294.0496. Found: 294.0496.

***N*-Methyl-2-(octyltelluro)aniline (7 b)**: 2-Bromo-*N*-methylaniline (186 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromooctane (0.2 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (219 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.79$ (dd, $J = 1.6$, 7.2 Hz, 1 H), 7.29 (m, 1 H), 6.62 (d, $J = 8.0$ Hz, 1 H), 6.56 (m, 1 H), 4.83 (s, 1 H), 2.90 (s, 3 H), 2.76 (t, $J = 8.0$ Hz, 2 H), 1.74 (m, 2 H), 1.28–1.38 (several peaks, 10 H), 0.91 ppm (t, $J = 6.8$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.5$, 142.7, 130.7, 117.5, 108.4, 99.8, 31.8 (2C), 31.7, 31.1, 29.2, 28.9, 22.6, 14.1, 8.4 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 278$ ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{15}H_{25}NTeH$ $[M+H]^+$: 350.1123. Found: 350.1123.

2-(Hexadecyltelluro)-*N*-methylaniline (7 c): 2-Bromo-*N*-methylaniline (186 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromohexadecane (0.3 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (215 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (dd, $J = 1.6$, 7.2 Hz, 1 H), 7.26 (m, 1 H), 6.58 (d, $J = 8.4$ Hz, 1 H), 6.52 (m, 1 H), 4.81 (s, 1 H), 2.87 (s, 3 H), 2.73 (t, $J = 7.2$ Hz, 2 H), 1.71 (m, 2 H), 1.24–1.35 (several peaks, 26 H), 0.89 ppm (t, $J = 6.8$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.5$, 142.7, 130.7, 117.5, 108.3, 99.8, 31.9, 31.8, 31.7, 31.1, 29.7 (2C), 29.6 (3C), 29.5, 29.4, 28.9, 22.7, 14.1, 8.3 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 277$ ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{23}H_{41}NTeH$ $[M+H]^+$: 462.2374. Found: 462.2374.

2-Bromo-*N*-hexadecylaniline: To a solution of 2-bromoaniline (860 mg, 5 mmol) in anhydrous THF (15 mL) at −78 °C under nitrogen was added *n*-butyl lithium (1.6 M, 3.1 mL, 5 mmol). After being stirred for 1 h at −78 °C, 1-bromohexadecane (1.53 mL, 5 mmol) was added and the solution was allowed to stir at ambient temperature overnight. The solution was quenched with saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL × 3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound as a white solid (1.17 g, 59%). M.p. 35–37 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.51$ (dd, $J = 0.8$, 6.4 Hz, 1 H), 7.26 (m, 1 H), 6.71 (d, $J = 6.8$ Hz, 1 H), 6.64 (m, 1 H), 4.38 (s, 1 H), 3.23 (t, $J = 5.6$ Hz, 2 H), 1.76 (m, 2 H), 1.41–1.57 (several peaks, 26 H), 1.04 ppm (t, $J = 5.6$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.0$, 132.2, 128.3, 117.2, 111.0, 109.5, 43.8, 32.0, 29.8, 29.7 (3C), 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{22}H_{38}BrN$ $[M]^+$: 395.2188. Found: 395.2194.

***N*-Hexadecyl-2-(hexadecyltelluro)aniline (8)**: 2-Bromo-*N*-hexadecylaniline (397 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromohexadecane (0.3 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow solid (343 mg, 51%). M.p. 41–44 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (dd, $J = 1.2$, 6.0 Hz, 1 H), 7.23 (m, 1 H), 6.58 (dd, $J = 1.2$, 8.1 Hz, 1 H), 6.50 (m, 1 H), 4.80 (s, 1 H), 3.14 (t, $J = 6.6$ Hz, 2 H), 2.73 (t, $J = 7.5$ Hz, 2 H), 1.62–1.74 (several peaks, 4 H), 1.27–1.45 (several peaks, 52 H), 0.86–0.91 ppm (several peaks, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.7$, 142.9, 130.7, 117.3, 108.9, 99.9, 44.3, 31.9, 31.8 (2C), 29.7 (2C), 29.6, 29.5, 29.4 (2C), 29.3, 28.9, 27.3, 22.7, 14.1, 8.3 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 278$ ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{38}H_{72}NTe$ $[M+H]^+$: 672.4725. Found: 672.4727.

2-Bromo-5-methoxydiphenylamine: To a solution of 2-bromo-5-methoxyaniline (1.8 g, 8.9 mmol) in DMSO (16 mL) were added cyclohex-2-en-1-one (1.1 mL, 12.1 mmol), iodine (1.3 g, 4.4 mmol) and *p*-toluensulfonic acid (167 mg, 1.0 mmol) at room temperature under nitrogen. After being stirred at 90 °C for 3 h, the reaction was quenched by addition of sodium thiosulfate (100 mL 20% aq.) and extracted by dichloromethane (100 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound as a pale yellow oil (562 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.8 Hz, 1 H), 7.35 (m, 2 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 7.08 (dd, *J* = 7.6 Hz, 1 H), 6.84 (d, *J* = 2.8 Hz, 1 H), 6.35 (dd, *J* = 2.8, 8.8 Hz, 1 H), 6.10 (s, 1 H), 3.74 ppm (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 142.2, 141.3, 133.0, 129.4, 122.9, 120.6, 106.4, 102.8, 101.5, 55.4 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{13}H_{12}BrNO$ [*M*]$^+$: 277.0102. Found: 277.0105.

2-(Butyltelluro)diphenylamine (9 a): 2-Bromodiphenylamine (248 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromobutane (0.1 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (176 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.24–7.35 (several peaks, 3 H), 7.27 (m, 1 H), 7.15 (m, 2 H), 7.03 (m, 1 H), 6.80 (m, 1 H), 6.48 (s, 1 H), 2.83 (t, *J* = 7.6 Hz, 2 H), 1.77 (m, 2 H), 1.40 (m, 2 H), 0.91 ppm (t, *J* = 7.2, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 143.1, 141.6, 129.7, 129.3, 121.6, 121.4, 118.8, 115.4, 105.2, 33.6, 24.9, 13.3, 8.5 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 314 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{16}H_{19}NTe$ [*M*]$^+$: 355.0580. Found: 355.0586.

2-(Hexadecyltelluro)diphenylamine (9 b): 2-Bromodiphenylamine (248 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromohexadecane (0.3 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a pale yellow solid (326 mg, 63%). M.p. 49–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.28–7.32 (several peaks, 3 H), 7.23 (m, 1 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.98 (dd, *J* = 7.6 Hz, 1 H), 6.76 (m, 1 H), 6.45 (s, 1 H), 2.79 (t, *J* = 7.6 Hz, 2 H), 1.74 (m, 2 H), 1.23–1.35 (several peaks, 26 H), 0.91 ppm (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 143.1, 141.8, 129.8, 129.3, 121.6, 121.4, 118.8, 115.4, 105.2, 31.9, 31.8, 31.6, 29.7, 29.6 (3C), 29.5, 29.4, 28.9, 22.7, 14.1, 8.9 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 313 ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{28}H_{43}NTeH$ [*M*+H]$^+$: 524.2530. Found: 524.2539.

2-(Hexadecyltelluro)-5-methoxydiphenylamine (9 c): 2-Bromo-5-methoxy-diphenylamine (300 mg, 1.1 mmol), *tert*-butyl lithium (1.7 M, 1.9 mL, 3.2 mmol), freshly ground tellurium powder (137 mg, 1.1 mmol), sodium borohydride (204 mg, 5.4 mmol) and 1-bromohexadecane (0.33 mL, 1.1 mmol) were reacted according to the general procedure to give the title compound as a pale yellow solid (354 mg, 59%). M.p. 39–40 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1 H), 7.35 (m, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.04 (dd, *J* = 7.2 Hz, 1 H), 6.90 (d, *J* = 2.4 Hz, 1 H), 6.73 (s, 1 H), 6.36 (dd, *J* = 2.4, 8.4 Hz, 1 H), 3.78 (s, 3 H), 2.74 (t, *J* = 8.0 Hz, 2 H), 1.74 (m, 2 H), 1.26–1.37 (several peaks, 26 H), 0.95 ppm (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 161.8, 147.9, 144.0, 142.5, 129.3, 122.0, 119.7, 106.6, 100.1, 93.9, 55.0, 31.9, 31.7, 31.5, 29.7, 29.6 (4C), 29.5, 29.3, 28.8, 22.7, 14.1, 9.2 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 278 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{29}H_{45}NOTe$ [*M*]$^+$: 553.2563. Found: 553.2559.

4-(Hexadecyltelluro)diphenylamine (10): 4-Bromodiphenylamine (248 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromohexadecane (0.3 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a pale yellow solid (133 mg, 26%). M.p. 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 2.4, 10.8 Hz, 2 H), 7.29 (m, 2 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 6.97 (dd, *J* = 7.2 Hz, 1 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 5.72 (s, 1 H), 2.85 (t, *J* = 7.6 Hz, 2 H), 1.79 (m, 2 H), 1.28–1.39 (several peaks, 26 H), 0.91 ppm (t, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 142.3, 140.6, 129.3, 121.6, 118.5, 117.9, 100.4, 31.9 (2C), 31.8, 29.7, 29.6 (2C), 29.5, 29.3, 28.9, 22.7, 14.1, 9.1 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 495 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{28}H_{43}NTe$ [*M*]$^+$: 523.2458. Found: 523.2472.

3-Amino-2-bromo-*N*,4,6-trimethylpyridine (11 b): To a solution of 3-amino-2-bromo-4,6-dimethylpyridine (1.2 g, 6 mmol) in anhydrous THF (30 mL) at −78 °C under nitrogen, *n*-butyl lithium (1.6 M, 3.8 mL, 6 mmol) was added. After being stirred for 1 h, iodomethane was added and the reaction was allowed to stir overnight at ambient temperature. The solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (25 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 95:5) to give the title compound as a yellow oil (1.14 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81 (s, 1 H), 3.50 (s, 1 H), 2.74 (s, 3 H), 2.37 (s, 3 H), 2.29 ppm (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3, 141.3, 140.3, 136.4, 125.6, 34.9, 22.9, 18.9 ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_8H_{11}BrN_2H$ [*M*+H]$^+$: 215.0178. Found: 215.0176.

3-Amino-4,6-dimethyl-2-(octyltelluro)pyridine (11 c): 3-Amino-2-bromo-4,6-dimethylpyridine (1.29 g, 6.0 mmol), *tert*-butyl lithium (1.7 M, 14 mL, 24.0 mmol), freshly ground tellurium powder (767 mg, 6.0 mmol), sodium borohydride (1.13 g, 30.0 mmol) and 1-bromooctane (1.1 mL, 6.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (487 mg, 22%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.63 (s, 1 H), 3.74 (s, 2 H), 3.06 (t, *J* = 7.7 Hz, 2 H), 2.36 (s, 3 H), 2.08 (s, 3 H), 1.81 (m, 2 H), 1.22–1.36 (several peaks, 10 H), 0.85 ppm (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.5, 142.0, 128.9, 127.0, 123.3, 32.0, 31.9, 31.7, 29.1, 28.8, 23.2, 22.5, 17.8, 14.0, 10.3 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 387 ppm. HRMS (TOF MS ES$^+$) *m/z* calcd for $C_{15}H_{26}N_2TeH$ [*M*+H]$^+$: 365.1232. Found: 365.1229.

3-Amino-*N*,4,6-trimethyl-2-(octyltelluro)pyridine (11 d): To a solution of **11 b** (180 mg, 0.8 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7, 1.4 mL, 2.4 mmol). After being stirred for 2 h, freshly ground tellurium powder (102 mg, 0.8 mmol) was added and the reaction mixture was allowed to stir overnight at ambient temperature. The solution was quenched with saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was dissolved in ethanol (40 mL) followed by addition of sodium borohydride (151 mg, 4 mmol) at ambient temperature under nitrogen. After being stirred for 15 min, 1-bromoctane (0.14 mL, 0.8 mmol) was added and the solution was allowed to stir overnight. After addition of water (20 mL) and extraction with diethyl ether (25 mL×3), the organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 95:5) to give the title compound as a pale yellow oil (96 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (s, 1 H), 3.06 (t, *J* = 7.6 Hz, 2 H), 2.90 (s, 1 H), 2.74 (s, 3 H), 2.42 (s, 3 H), 2.22 (s, 3 H), 1.86 (m, 2 H), 1.26–1.42 (several peaks, 10 H), 0.87 ppm (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8, 144.5, 140.3, 138.6, 122.8, 35.7, 32.3, 31.9, 31.8, 29.2, 29.0, 23.5, 22.6, 17.5, 14.1, 9.5 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ =

444 ppm. HRMS (TOF MS ES$^+$) m/z calcd for $C_{16}H_{28}N_2TeH$ $[M+H]^+$: 379.1388. Found: 379.1389.

***N*-Boc-2-(butyltelluro)aniline (12 a)**: To a solution of *N*-Boc-aniline (1.16 g, 6.0 mmol) in anhydrous THF (10 mL) at −40 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 7.76 mL, 13.2 mmol). The solution was stirred for 2 h at −40 °C prior to the addition of freshly ground tellurium powder (842 mg, 6.6 mmol). After being stirred for 2 h at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was dissolved in ethanol (25 mL) and sodium borohydride (684 mg, 18 mmol) was added at ambient temperature under nitrogen. After being stirred for 15 min, 1-bromobutane (0.66 mL, 6.0 mmol) was added and the solution was allowed to stir overnight. The reaction was quenched with water (20 mL) and extracted with diethyl ether (25 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 99:1) to give the title compound as a yellow oil (827 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.4 Hz, 1 H), 7.85 (dd, J = 1.2, 7.6 Hz, 1 H), 7.50 (s, 1 H), 7.33 (m, 1 H), 6.85 (m,1 H), 2.76 (t, J = 7.2 Hz, 1 H), 1.70 (m, 2 H), 1.54 (s, 9 H), 1.37 (m, 2 H), 0.89 ppm (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 142.1, 141.6, 130.3, 123.6, 118.3, 104.3, 80.4, 33.5, 28.3, 24.8, 13.3, 9.4 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 317 ppm. HRMS (TOF MS ES$^+$) m/z calcd for $C_{15}H_{23}NO_2TeNa$ $[M+Na]^+$: 402.0684. Found: 402.0684.

***N*-Boc-2-(hexadecyltelluro)aniline (12 b)**: To a solution of *N*-Boc-aniline (1.16 g, 6.0 mmol) in anhydrous THF (10 mL) at −40 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 7.76 mL, 13.2 mmol). The solution was stirred for 2 h at −40 °C prior to the addition of freshly ground tellurium powder (842 mg, 6.6 mmol). After being stirred for 2 h at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was dissolved in ethanol (25 mL) and sodium borohydride (684 mg, 18 mmol) was added at ambient temperature under nitrogen. After being stirred for 15 min, 1-bromohexadecane (1.83 mL, 6.0 mmol) was added and the solution was allowed to stir overnight. The reaction was quenched with water (20 mL) and extracted with diethyl ether (25 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a yellow oil (935 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.6 Hz, 1 H), 7.85 (dd, J = 1.6, 8.0 Hz, 1H), 7.50 (s, 1 H), 7.33 (m, 1 H), 6.85 (m, 1 H), 2.75 (t, J = 8.0 Hz, 2 H), 1.71 (m, 2 H), 1.54 (s, 9 H), 1.24–1.35 (several peaks, 26 H), 0.88 ppm (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 142.2, 141.6, 130.3, 123.6, 118.4, 104.3, 80.5, 31.9, 31.8, 31.5, 29.7, 29.6 (3C), 29.5, 29.3, 28.9, 28.3, 22.7, 22.3, 14.1, 14.0, 9.9 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 316 ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{27}H_{47}NOTe$ $[M]^+$: 547.2669. Found: 547.2660.

2-(Butyltelluro)aniline (13 a): To a solution of **12 a** (400 mg, 1.1 mmol) in dichloromethane (8.5 mL) was added trifluoroacetic acid (0.45 mL, 5.0 mmol) under nitrogen. After being stirred for 3 h, the solution was quenched with a saturated sodium hydrogen carbonate solution (30 mL) and extracted with dichloromethane (30 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 95:5) to give the title compound as a yellow oil (290 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (dd, J = 1.2, 7.6 Hz, 1 H), 7.16 (m, 1 H), 6.78 (dd, J = 0.8, 7.6 Hz, 1 H), 6.57 (m, 1 H), 4.22, (s, 2 H), 2.78 (t, J = 8.0 Hz, 2 H), 1.72 (m, 2 H), 1.36 (m, 2 H), 0.88 ppm (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 142.5, 130.5, 119.0, 113.3, 99.0, 33.8, 24.9, 13.3, 7.9 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 301 ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{10}H_{15}NTe$ $[M]^+$:279.0267. Found: 279.0270.

2-(Hexadecyltelluro)aniline (13 b): To a solution of **12 b** (900 mg, 1.65 mmol) in dichloromethane (14 mL) was added trifluoroacetic acid (0.98 mL, 12.8 mmol) under nitrogen. After being stirred for 6 h, the solution was quenched with sodium hydrogen carbonate (30 mL) and extracted with dichloromethane (30 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 95:5) to give the title compound as yellow crystals (403 mg, 55%). M.p. 35–38 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, J = 1.6, 7.6 Hz, 1 H), 7.16 (m, 1 H), 6.78 (dd, J = 1.2, 8.0 Hz, 1 H), 6.58 (m, 1 H), 4.30 (s, 2 H), 2.79 (t, J = 7.6 Hz, 2 H), 1.75 (m, 2 H), 1.26–1.37 (m, 26 H), 0.91 ppm (t, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 142.5, 130.4, 119.0, 113.2, 99.0, 31.9, 31.8, 31.7, 29.7, 29.6 (3C), 29.5, 29.3, 28.9, 22.7, 14.1, 8.2 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 301 ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{22}H_{39}NTe$ $[M]^+$: 447.2145. Found: 447.2152.

***N*-Boc-1,2,3,4-tetrahydroquinoline**: To a solution of *N*-1,2,3,4-tetrahydroquinoline (2.0 g, 15.0 mmol) in anhydrous THF (60 mL) was added sodium hydride (60% w.t., 660 mg, 16.5 mmol) under nitrogen. After reflux for 90 min, di-*tert*-butyl dicarbonate (3.9 g, 17.9 mmol) was added and the reaction mixture was allowed to reflux for 2 days. The reaction was quenched with water (60 mL) and extracted with diethyl ether (30 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 95:5) to give the title compound as a light yellow oil (2.94 g, 84%). The ^{1}H and ^{13}C spectra were in accord with the literature.[31]

8-(Butyltelluro)-1,2,3,4-tetrahydroquinoline (14 a): To a solution of *N*-Boc-1,2,3,4-tetrahydroquinoline (466 mg, 2.0 mmol) and tetramethylethylenediamine (0.35 mL, 2.4 mmol) in anhydrous diethyl ether (10 mL) was added *sec*-butyl lithium (1.4 M, 1.7 mL, 2.4 mmol) at −78 °C under nitrogen. After being stirred for 2 h at −78 °C, dibutyl ditelluride (884 mg, 2.4 mmol) was added and the solution was allowed to stir at ambient temperature overnight. The solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was filtered through a short plug (pentane/ethyl acetate = 100:0 to 97.5:2.5) to remove the unreacted dibutyl ditelluride. The evaporated crude product was dissolved in dichloromethane (10 mL) and trifluoroacetic acid (0.57 mL, 7.5 mmol) was added under nitrogen. After being stirred for 30 min, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with dichloromethane (10 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound as a yellow oil (363 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (m, 1 H), 6.96 (dd, J = 0.8, 7.6 Hz, 1 H), 6.45 (t, J = 7.6 Hz, 1 H), 4.90 (s, 1 H), 3.40 (dt, J = 2.4, 5.6 Hz, 2 H), 2.75–2.79 (several peaks, 4 H), 1.94 (m, 2 H), 1.75 (m, 2 H), 1.41 (m, 2 H), 0.92 ppm (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 140.2, 130.6, 120.3, 117.0, 98.7, 42.5, 33.8, 27.8, 24.9, 22.1, 13.3, 7.7 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 270$ ppm. HRMS (TOF MS ES$^+$) m/z calcd for $C_{13}H_{19}NTeH$ $[M+H]^+$: 320.0653. Found: 320.0651.

8-(Hexadecyltelluro)-1,2,3,4-tetrahydroquinoline (14b): To a solution of *N*-Boc-1,2,3,4-tetrahydroquinoline (466 mg, 2.0 mmol) and tetramethylethylenediamine (0.35 mL, 2.4 mmol) in anhydrous diethyl ether (10 mL) was added *sec*-butyl lithium (1.4 M, 1.7 mL, 2.4 mmol) at −78 °C under nitrogen. After being stirred for 2 h at −78 °C, dihexadecyl ditelluride (1.69 g, 2.4 mmol) was added and the solution was allowed to stir at ambient temperature overnight. The solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was filtered through a short plug (pentane/ethyl acetate = 100:0 to 97.5:2.5) to remove the unreacted dihexadecyl ditelluride. The evaporated crude product was dissolved in dichloromethane (10 mL) and trifluoroacetic acid (0.57 mL, 7.5 mmol) was added under nitrogen. After being stirred for 30 min, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with dichloromethane (10 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound as a yellow oil (320 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (m, 1H), 6.92 (dd, $J = 1.6$, 7.6 Hz, 1H), 6.42 (t, $J = 7.6$ Hz, 1H), 4.86 (s, 1H), 3.37 (t, $J = 5.2$ Hz, 2H), 2.71–2.76 (several peaks, 4H), 1.92 (m, 2H), 1.72 (m, 2H), 1.22–1.35 (several peaks, 26H), 0.89 ppm (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.3$, 140.3, 130.7, 120.3, 117.0, 98.7, 42.6, 31.9, 31.8, 31.7, 29.7 (2C), 29.6 (2C), 29.5, 29.3, 28.9, 27.9, 22.7, 22.2, 14.1, 8.2 ppm. ^{125}Te NMR ($CDCl_3$): $\delta = 269$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{25}H_{43}NTe$ $[M]^+$: 487.2458. Found: 487.2456.

***N*-(2-(Butyltelluro)benzyl)aniline (15)**: To a solution of *N*-(2-bromobenzyl)aniline (262 mg, 1 mmol) in anhydrous THF (15 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 1.76 mL, 3.0 mmol). After being stirred for 2 h at −78 °C, dibutyl ditelluride (368 mg, 1.0 mmol) was added and the solution was allowed to stir at ambient temperature overnight. The solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 97.5:2.5) to give the title compound as yellow oil (114 mg, 31%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.73$ (dd, $J = 1.5$, 7.5 Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.15–7.28 (several peaks, 4H), 6.79 (m, 1H), 6.71 (dd, $J = 1.0$, 9.0 Hz, 2H), 4.39 (d, $J = 5.0$ Hz, 2H), 3.90 (t, $J = 5.0$ Hz, 1H), 2.91 (t, $J = 9.0$ Hz, 2H), 1.83 (m, 2H), 1.47 (m, 2H), 0.98 ppm (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 147.5$, 142.4, 136.5, 129.1, 128.3, 128.0, 127.2, 118.0, 116.7, 113.2, 52.4, 33.5, 25.2, 13.4, 7.9 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 408$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{17}H_{21}NTe$ $[M]^+$: 369.0736. Found: 369.0743.

***N*^{1},*N*^{4}-Di-*tert*-butyloxycarbonyl-*N*^{1},*N*^{4}-bis(2-bromophenyl)butane-1,4-diamine (16)**: To a solution of *N*-Boc-2-bromoaniline (2.36 g, 8.67 mmol) in anhydrous THF (60 mL), sodium hydride (60% wt., 586 mg, 24.5 mmol) was added at 0 °C under nitrogen. The solution was stirred for 1 h at room temperature before the addition of 1,4-dibromobutane (0.52 mL, 4.33 mmol) at 0 °C. After being heated at reflux for 38 h, the solution was quenched with water (30 mL) and extracted with diethyl ether (40 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 95:5) as eluent to give the title compound as a yellow oil (1.42 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (s, 2H), 7.12–7.27 (several peaks, 6H), 3.69 (m, 2H), 3.35 (m, 2H), 1.27–1.56 ppm (several peaks, 22H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.9$, 141 (2C), 133.3 (rotamer), 132.9, 130.6 (rotamer), 130.1, 128.5 (rotamer), 128.2, 128.0 (rotamer), 127.7, 123.7, 80.3 (rotamer), 79.8 (rotamer), 79.7, 49.7 (rotamer), 48.8, 28.2 (rotamer), 27.9, 26.0 (rotamer), 25.6 ppm. HRMS (TOF MS ES$^+$) m/z calcd for $C_{26}H_{35}Br_2N_2O_4$ $[M+H]^+$: 599.0943. Found: 599.0940.

***N*^{1},*N*^{4}-Bis[2-(octyltelluro)phenyl]butane-1,4-diamine (17)**: To a solution of **16** (724 mg, 1.2 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen, *tert*-butyl lithium (1.7 M, 2.4 mL, 4.8 mmol) was added. The solution was stirred for 3 h at −78 °C before the addition of dioctyl ditelluride (1.41 g, 2.4 mmol). After being stirred overnight at room temperature, the solution was quenched with a saturated ammonium chloride solution (30 mL) and extracted with diethyl ether (40 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified on a short silica plug using pentane/ethyl acetate (100:0 to 95:5) as eluent to remove the unreacted dioctyl ditelluride. To the evaporated crude product dissolved in dichloromethane (5 mL) was added trifluoroacetic acid (0.82 mL, 10.8 mmol) under nitrogen. After being stirred for 4 h, another portion of trifluoroacetic acid (0.82 mL, 10.8 mmol) was added and the reaction was allowed to stir for 2 h. The reaction was quenched with a saturated sodium hydrogen carbonate solution (10 mL) and extracted with dichloromethane (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 97.5:2.5) as eluent to give the title compound as a yellow oil (327 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$ (dd, $J = 1.6$, 7.6 Hz, 2H), 7.29 (m, 2H), 6.65 (dd, $J = 0.8$, 8.4 Hz, 2H), 6.58 (m, 2H), 4.90 (s, 2H), 3.27 (t, $J = 5.6$ Hz, 4H), 2.78 (t, $J = 8.0$ Hz, 4H), 1.87 (m, 4H), 1.77 (m, 4H), 1.31–1.41 (several peaks, 20H), 0.95 ppm (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.4$, 142.8, 130.6, 117.5, 108.8, 100.1, 44.0, 31.7(2C), 29.1, 28.8, 26.9, 22.6, 14.0, 8.3 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 279$ ppm. HRMS (TOF MS ES$^+$) m/z calcd for $C_{32}H_{53}BN_2Te_2$ $[M+H]^+$:725.2328. Found: 725.2333.

2-(Diethoxymethyl)phenyl hexadecyl telluride (18b): To a solution of 1-bromo-2-(diethoxymethyl)benzene (777 mg, 3.0 mmol) in anhydrous THF (20 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 3.5 mL, 6.0 mmol). The solution was stirred for 2 h at −78 °C prior to the addition of freshly ground tellurium powder (383 mg, 3.0 mmol). After being stirred for 2 h at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was dissolved in ethanol (25 mL) followed by addition of sodium borohydride (342 mg, 9.0 mmol) at ambient temperature under nitrogen. After being stirred for 15 min, 1-bromohexadecane (0.9 mL, 3.0 mmol) was added and the solution was allowed to stir overnight. The reaction was quenched with water (20 mL) and extracted with diethyl ether (25 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a yellow oil (935 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.63$ (dd, $J = 1.2$, 8.0 Hz, 1H), 7.58 (dd, $J = 1.2$, 8.0 Hz, 1H), 7.23 (m, 1H), 7.15 (m, 1H), 5.45 (s, 1H), 3.58 (m, 4H), 2.83 (t, $J = 7.6$ Hz, 2H), 1.80 (m, 2H), 1.23–1.38 (several peaks, 32H), 0.88 ppm (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 141.6$, 135.6, 128.7, 126.8, 126.5, 115.8, 103.4, 61.3, 32.2, 31.9, 31.4, 29.7 (2C), 29.6 (2C), 29.5, 29.4, 29.0, 22.7, 15.3, 14.1, 8.2 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 411 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{27}H_{48}O_2Te$ [*M*]$^+$: 534.2717. Found: 534.2706.

2-(Hexadecyltelluro)benzaldehyde (19b): To **18b** (880 mg, 1.65 mmol) in a round-bottom flask was added concentrated HCl (0.68 mL). After being stirred for 15 min at room temperature, the solution was quenched with a saturated sodium hydrogen carbonate solution (10 mL) and extracted with diethyl ether (10 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduce pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a yellow powder (739 mg, 98%). M.p. 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.14 (s, 1H), 7.82 (dd, *J* = 1.6, 6.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.37–7.41 (several peaks, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 1.84 (m, 2H), 1.26–1.48 (several peaks, 26H), 0.8 ppm (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 136.9, 136.7, 133.4, 132.7, 125.5, 123.2, 32.4, 31.9, 30.2, 29.6 (3C), 29.5, 29.3, 29.0, 22.6, 14.1, 6.7 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 560 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{23}H_{38}OTe$ [*M*]$^+$: 460.1985. Found: 460.1984.

2-(Butyltelluro)-*N*-[2-(butyltelluro)benzyl]aniline (20a): To a solution of 2-(butyltelluro)benzaldehyde (224 mg, 0.77 mmol) and *N*-Boc-2-(butyltelluro)aniline (235 mg, 0.85 mmol) in methanol (5 mL) was added a zinc chloride solution (0.5 M in THF, 1.7 mL, 0.85 mmol) under nitrogen. After being stirred for 1 h, sodium cyanoborohydride (54 mg, 0.85 mmol) was added and the solution was allowed to stir overnight. The reaction was quenched with water (10 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a yellow oil (76 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.19–7.25 (several peaks, 2H), 7.13 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.56 (m, 1H), 5.12 (s, 1H), 4.40 (s, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.79 (m, 2H), 1.70 (m, 2H), 1.31–1.46 (several peaks, 4H), 0.85–0.94 ppm (several peaks, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 142.9, 142.4, 136.9, 130.6, 128.1, 128.0, 127.4, 118.3, 116.3, 109.7, 100.5, 52.9, 33.8, 33.6, 25.2, 24.9, 13.4 (2C), 8.60, 8.21 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 403, 284 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{21}H_{29}NTe_2$ [*M*]$^+$: 555.0425. Found: 555.0408.

2-(Hexadecyltelluro)-*N*-2-(hexadecyltelluro)benzyl]aniline (20b): To a solution of **19b** (352 mg, 0.77 mmol) and **14b** (380 mg, 0.85 mmol) in methanol (5 mL) was added zinc chloride solution (0.5 M in THF, 2 mL, 1.0 mmol) under nitrogen. After being stirred for 1 h, sodium cyanoborohydride (54 mg, 0.85 mmol) was added and the solution was allowed to stir overnight. The reaction was quenched with water (10 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate = 98:2) to give the title compound as a yellow solid (280 mg, 41%). M.p. 49–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.70 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.36 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.18–7.25 (several peaks, 2H), 7.12 (m, 1H), 6.63 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.56 (m, 1H), 5.11 (t, *J* = 5.6 Hz, 1H), 4.40 (d, *J* = 5.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.80 (m, 2H), 1.75 (m, 2H), 1.28–1.45 (several peaks, 52H), 0.90 ppm (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 142.9, 142.4, 136.9, 130.6, 128.1, 128.0, 127.4, 118.3, 116.4, 109.7, 100.5, 52.9, 32.2, 31.9 (2C), 31.7, 31.5, 29.7 (2C), 29.6, 29.5, 29.4, 29.0, 28.9, 22.7, 14.1, 8.9, 8.5 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 404, 284 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{45}H_{77}NTe_2$ [*M*]$^+$: 891.4181. Found: 891.4160.

2,2′-Dibromodiphenylamine (21): To a solution of 2-bromoaniline (1.7 g, 10 mmol) in DMSO (20 mL) were added 2-bromocyclohex-2-en-1-one (2.3 g, 13.2 mmol), iodine (1.3 g, 5 mmol) and *p*-toluensulfonic acid (188 mg, 1.1 mmol) at room temperature under nitrogen. After being stirred at 90 °C, overnight, the reaction was quenched with sodium thiosulfate (100 mL 20% aq.) and extracted with dichloromethane (100 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 99:1) as eluent to give the title compound as a pale yellow oil (1.3 g, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 1.0, 8.0 Hz, 2H), 7.30 (dd, *J* = 1.5, 8.5 Hz, 2H), 7.20 (m, 2H), 6.85 (m, 2H), 6.45 ppm (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 133.2, 128.1, 122.5, 117.9, 114.2 ppm. The ^{1}H NMR data were in accord with reported data in the literature.[32]

2,2′-Di(hexadecyltelluro)diphenylamine (22): Compound **20** (327 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 2.9 mL, 5.0 mmol), freshly ground tellurium powder (508 mg, 4.0 mmol), sodium borohydride (380 mg, 10 mmol) and 1-bromohexadecane (0.6 mL, 2.0 mmol) were reacted according to the general procedure to give the title compound as a pale yellow solid (267 mg, 15%). M.p. 66–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 1.2, 7.8 Hz, 2H), 7.20 (m, 2H), 7.13 (dd, *J* = 1.5, 8.1 Hz, 2H), 6.92 (s, 1H), 6.79 (m, 2H), 2.82 (t, *J* = 7.5 Hz, 4H), 1.74 (m, 4H), 1.22–1.33 (several peaks, 54H), 0.88 ppm (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.3, 140.8, 129.4, 122.3, 117.0, 106.9, 32.0, 31.9, 31.6, 29.7 (2C), 29.6, 29.5, 29.4, 28.9, 22.7, 14.1, 8.6 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 337 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{44}H_{75}NTe_2$ [*M*]$^+$: 877.4024. Found: 877.3997.

2-(Phenyltelluro)diphenylamine (23a): To a solution of 2-bromodiphenylamine (247 mg, 1.0 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol). The solution was stirred for 1 h at −78 °C prior to the addition of diphenyl ditelluride (409 mg, 1.0 mmol). After being stirred, overnight, at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 97.5:2.5) as eluent to give the title compound as a red oil (147 mg, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.65 (m, 2H), 7.19–7.31 (several peaks, 7H), 6.95–7.01 (several peaks, 3H), 6.81 (m, 1H), 6.23 ppm (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 143.0, 140.9, 137.0, 130.2, 129.6, 129.3, 127.8, 122.2, 121.8, 119.1, 116.7, 114.1, 108.7 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): δ = 552 ppm. HRMS (TOF MS EI$^+$) *m/z* calcd for $C_{18}H_{15}NTe$ [*M*]$^+$: 375.0267. Found: 375.0257.

2-(4-Methoxyphenyltelluro)diphenylamine (23b): To a solution of 2-bromodiphenylamine (247 mg, 1.0 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 1.8 mL, 10.0 mmol). The solution was stirred for 2 h at −78 °C prior to the addition of bis(4-methoxyphenyl)ditelluride (469 mg, 1.0 mmol). After being stirred, overnight, at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL×3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 97.5:2.5) as eluent to give the title compound as a pale yellow solid (168 mg, 42%). M.p. 57–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–

7.65 (several peaks, 2H), 7.56 (dd, $J = 1.2$, 8.0 Hz, 1H), 7.16–7.25 (several peaks, 4H), 6.90–6.94 (several peaks, 3H), 6.75–6.79 (several peaks, 3H), 6.03 (s, 1H), 3.78 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.0$, 145.1, 143.4, 140.3, 139.1, 129.4, 129.3, 122.9, 121.4, 118.4, 118.0, 115.7, 111.1, 102.6, 55.2 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 554$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{19}H_{17}NOTe$ $[M]^+$: 405.0372. Found: 405.0360.

2-(4-Trifluoromethylphenyl)diphenylamine (23 c): To a solution of 2-bromodiphenylamine (247 mg, 1.0 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen was added *tert*-butyl lithium (1.7 M, 1.8 mL, 3.0 mmol). The solution was stirred for 2 h at −78 °C prior to the addition of bis(4-trifluoromethylphenyl)ditelluride (545 mg, 1.0 mmol). After being stirred, overnight, at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL × 3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 97.5:2.5) as eluent to give the title compound as a red solid (201 mg, 46%). M.p. 76–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.86$ (m, 1H), 7.64 (dd, $J = 0.8$, 8.4 Hz, 2H), 7.42 (dd, $J = 0.8$, 8.4 Hz, 2H), 7.28–7.35 (several peaks, 4H), 7.02–7.06 (several peaks, 3H), 6.91 (m, 1H), 6.34 ppm (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 146.3$, 142.5, 142.1, 135.7, 131.0, 129.6 (q, $J_{CF} = 32$ Hz), 129.3, 125.9 (q, $J_{CF} = 4$ Hz), 124.0 (q, $J_{CF} = 270$ Hz), 122.3, 122.1, 120.3, 119.5, 116.3, 107.0 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 551$ ppm. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -63$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{19}H_{14}F_3NTe$ $[M]^+$: 443.0141. Found: 443.0138.

***N*-Methyl-*N*-2-(ocyltelluro)phenyl-*O*-propylhydroxylamine (24)**: To a solution of *N*-(2-bromophenyl)-*N*-methyl-*O*-propylhydroxylamine (355 g, 1.5 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen was added *n*-butyl lithium (1.6 M, 1.1 mL, 1.74 mmol). The solution was stirred for 1.5 h at −78 °C prior to the addition of dioctyl ditelluride (698 mg, 1.5 mmol). After being stirred, overnight, at ambient temperature, the solution was quenched with a saturated ammonium chloride solution (20 mL) and extracted with diethyl ether (20 mL × 3). The organic layer was dried over magnesium sulfate, filtered and evaporated under reduced pressure. The mixture was purified by flash column chromatography (pentane/ethyl acetate = 98:2) as eluent to give the title compound as pale a yellow oil (255 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.46$ (dd, $J = 1.2$, 7.6 Hz, 1H), 7.28 (dd, $J = 1.2$, 7.2 Hz, 1H), 7.23 (m, 1H), 7.10 (m, 1H), 3.62 (t, $J = 6.4$ Hz, 2H), 2.90 (s, 3H), 2.80 (t, $J = 7.6$ Hz, 2H), 1.86 (m, 2H), 1.60 (m, 2H), 1.30–1.47 (several peaks, 10H), 0.87–0.92 ppm (several peaks, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.9$, 131.1, 127.4, 127.1, 121.1, 114.4, 74.2, 47.2, 32.4, 31.8, 31.1, 29.1, 29.0, 22.6, 21.9, 14.0, 10.5, 5.1 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 395$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{18}H_{31}NOTe$ $[M]^+$: 407.1468. Found: 407.1463.

***N*,*N*-Dimethyl-2-(octyltelluro)aniline (25)**: 2-Bromo-*N*,*N*-dimethylaniline (200 mg, 1.0 mmol), *tert*-butyl lithium (1.7 M, 1.2 mL, 2.0 mmol), freshly ground tellurium powder (128 mg, 1.0 mmol), sodium borohydride (190 mg, 5.0 mmol) and 1-bromooctane (0.2 mL, 1.0 mmol) were reacted according to the general procedure to give the title compound as a yellow oil (317 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.32$ (d, $J = 7.5$ Hz, 1H), 7.19 (m, 1H), 7.13 (dd, $J = 1.0$, 8.0 Hz, 1H), 7.05 (m, 1H), 2.76 (t, $J = 7.5$ Hz, 2H), 2.69 (s, 6H), 1.86 (m, 2H), 1.29–1.47 (several peaks, 10H), 0.90 ppm (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 155.1$, 131.8, 126.8, 126.2, 120.6, 118.3, 45.4, 32.5, 31.8, 31.2, 29.1, 29.0, 22.6, 14.1, 4.8 ppm. ^{125}Te NMR (126 MHz, $CDCl_3$): $\delta = 398$ ppm. HRMS (TOF MS EI$^+$) m/z calcd for $C_{16}H_{27}NTe$ $[M]^+$: 363.1206. Found: 363.1212.

HPLC peroxidation assay

The experimental setup for recording inhibited rates of peroxidation (R_{inh}) and inhibition times (T_{inh}) during azo-initiated peroxidation of linoleic acid in a two-phase chlorobenzene-water system has been recently described.[33] The values of R_{inh} and T_{inh} reported in the presence of NAC are means ± SD based on triplicates. As R_{inh} and T_{inh} values show slight variations depending on the amount of linoleic acid hydroperoxide which is always present in commercial samples as an impurity, and increases upon storage, the procedure is standardized in the following way. To a newly received sample of linoleic acid was added small amounts of peroxidized linoleic acid from an older bottle until the concentration, as assessed by UV spectroscopy of conjugated diene at 234 nm, was about 175 µM.

NAC consumption assay

The concentration of NAC in the aqueous phase of the two-phase system during ongoing peroxidation was determined by using the assay of Means,[34] with slight modifications. Every 30 min during the first 3 h of peroxidation, 20 µL of the aqueous phase was withdrawn by syringe and injected into a UV cuvette containing 1 mL of a 0.25 M solution of Aldrithiol-4 in water/DMF (49:1). The concentration of pyridin-4-thiol was determined spectrophotometrically at 324 nm in comparison with a standard curve. The rate of NAC consumption was calculated by least-square methods from time/concentration plots.

Acknowledgements

The Swedish Research Council (grant 621-2011-4006) is gratefully acknowledged. We also thank the COST-action CM1201 (Biomimetic Radical Chemistry) for financial support.

Keywords: antioxidants · amines · chain-breaking activity · organotellurium · regenerable

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Received: May 18, 2016
Published online on ■■ ■■, 0000

FULL PAPER

Catalytic Antioxidants

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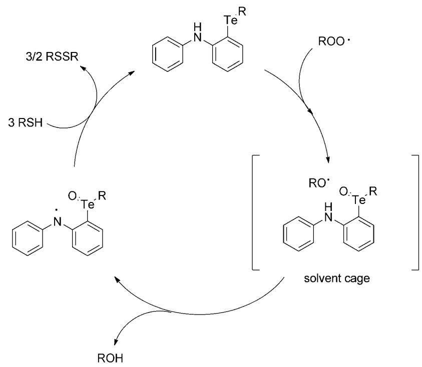
Alkyltelluro Substitution Improves the Radical-Trapping Capacity of Aromatic Amines



Te time: Aromatic amines carrying alkyltelluro groups quench lipidperoxyl radicals more efficiently than α-tocopherol in chlorobenzene and are regenerable by aqueous-phase *N*-acetylcysteine. According to the proposed mechanism (see scheme), the compounds are multifunctional in the sense that they, at the same time, are both chain-breaking and hydroperoxide decomposing.