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Preparation of Azobenzenealkanethiols for Self-Assembled Monolayers with Photoswitchable Properties

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A series of azobenzenealkanethiol compounds with the structure *p*-$RC_6H_4N{=}NC_6H_4(CH_2)_nSH$ ($n = 3, 4$) was synthesized using a divergent strategy with the two anilines $H_2NC_6H_4(CH_2)_nSAc$ as central compounds. This strategy provides fast access to a broad variety of the respective azobenzenethiols without (note!) an oxygen atom in the alkyl chain, thus permitting the self-assembly of these compounds onto gold in a predictable conformation, also taking advantage of the previously found odd–even effect in aromatic–aliphatic hybrid systems. Initial experiments indicate that all of these molecules indeed form dense monolayers, in which the orientation of the azobenzene unit is determined by the number of methylene groups in the aliphatic part of the molecules.

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Introduction

Self-assembled monolayers (SAMs), in particular of thiols on gold, are useful tools for the adjustment of surface properties.[1–3] Although most systems used, for example, in material science or biochemistry have to be viewed as static in their properties, a number of applications, such as data storage, require surfaces that are temporally and locally switchable.

Azobenzenes are probably the best-known photoswitchable moieties[4–8] and therefore have been intensively studied in connection with SAMs, e.g. for optical information storage, optoelectronics, non-linear optics,[4,9,10] and even for the photochemical switching of biochemical interactions.[11–15] The reversible switching between the thermodynamically more stable *trans*- (360 nm) and the *cis*-configuration (450 nm)[16–19] causes not only the change in optical properties, but also a change in the orientation of the head group,[20] and therefore, depending on the R group, also a change in the surface dipole moment (Fig. 1).[5,21]

This change of dipole moment can be determined as a variation of the surface potential in well-ordered SAMs.[21–24]

As 4-hydroxyazobenzenes are easily accessible via azo-coupling,[25] almost exclusively alkoxy-azobenzene derivatives have been attached to surfaces.[26,27] The problem with oxygen atoms within these chains is that owing to steric and electronic effects of the non-binding electron pairs (lone pairs) of the oxygen atom, distortions from the all-*trans* conformation occur (Scheme 1).

Another factor known to significantly influence the orientation of the head groups in monolayers is the number (odd or even) of methylene groups: owing to the binding angle at the carbon atom (104°) and a preferred dihedral angle of 180° within *n*-alkane chains, the orientation of the head group of an aryl-terminated alkanethiol is predictable for monolayers on gold and silver substrates, because the binding angles at the sulfur atoms at these substrates are fixed.[28–33] This parity effect also determines the structure and the structural quality within these monolayers. If azobenzenes are introduced as aryl head groups, we expect to observe a similarly predictable orientation for both the *cis*- and the *trans*-configuration as shown in Fig. 2.

As different applications might require different head groups, we were looking to develop a strategy that would permit efficient access to this class of substances. This can be achieved by a divergent strategy with the node compound being as close to the final products as possible. We decided to use two node compounds to obtain entry to the two classes of compounds with three (**1b**) and four methylene groups (**1a**), respectively (Scheme 2). These compounds should consist of the carbon backbone and carry the sulfur atom as well, although in protected form. The azobenzene unit should be formed from an amino group already present in the node compounds by reaction with a variety of nitroso benzenes.[18,34–40] The late introduction of the azobenzene group is also advantageous regarding the handling of the compounds, because azobenzenes are often sensitive to elevated temperatures, light, and many reagents.

After deprotection, the different azobenzene thiols should be used for monolayer formation, followed by a first characterization of the completeness of layer formation and the properties of the newly formed surfaces.

Results and Discussion

Synthetic Route

As the central compounds should already carry the sulfur atom necessary for binding to the gold substrate, and nitroso compounds readily react with free thiol groups, forming a variety of non-specific products,[41–45] we had to protect the thiol group. Thioesters are popular protective groups for this purpose because both the introduction and the removal of the acyl group proceed cleanly and with high yields. However, amino compounds are frequently used to achieve this deprotection,[46–50] so we needed to make sure that the free amino group in our desired node

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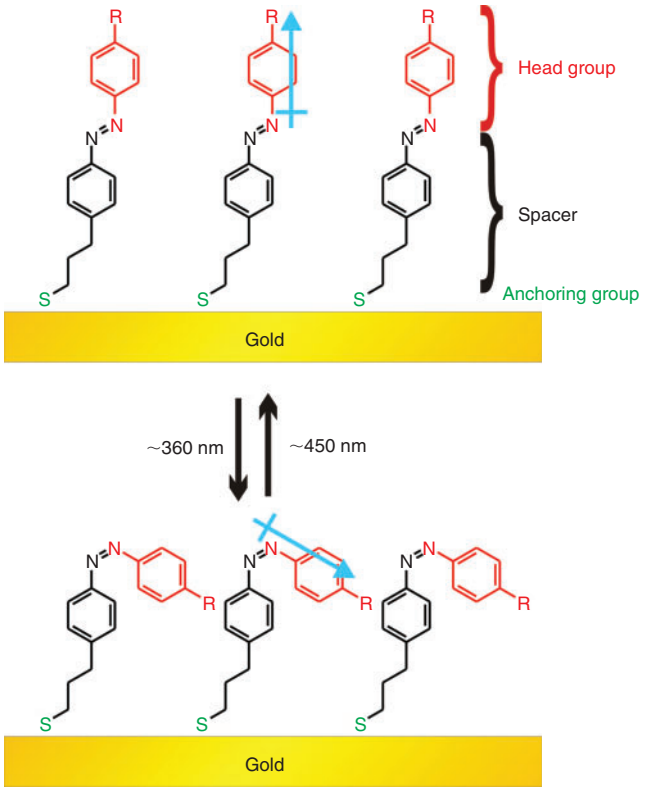


Fig. 1. Basic principle of a photoswitchable azobenzene-terminated self-assembled monolayer on gold: if the molecules carry a suitable head group R, the effective surface dipole moment can be changed (blue arrow).

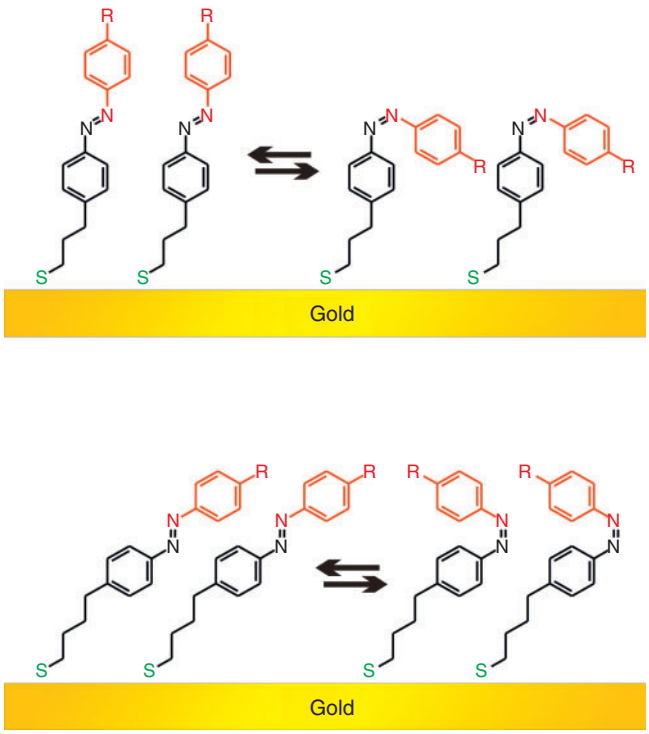
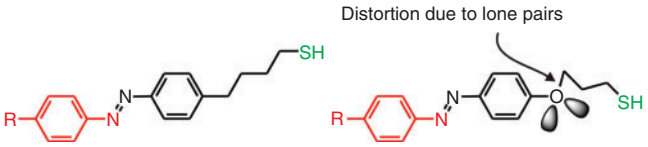


Fig. 2. The orientation of the molecules, and thus their exact switching behaviour, should depend on the parity of the number (odd-even) of methylene groups in the alkane chain.



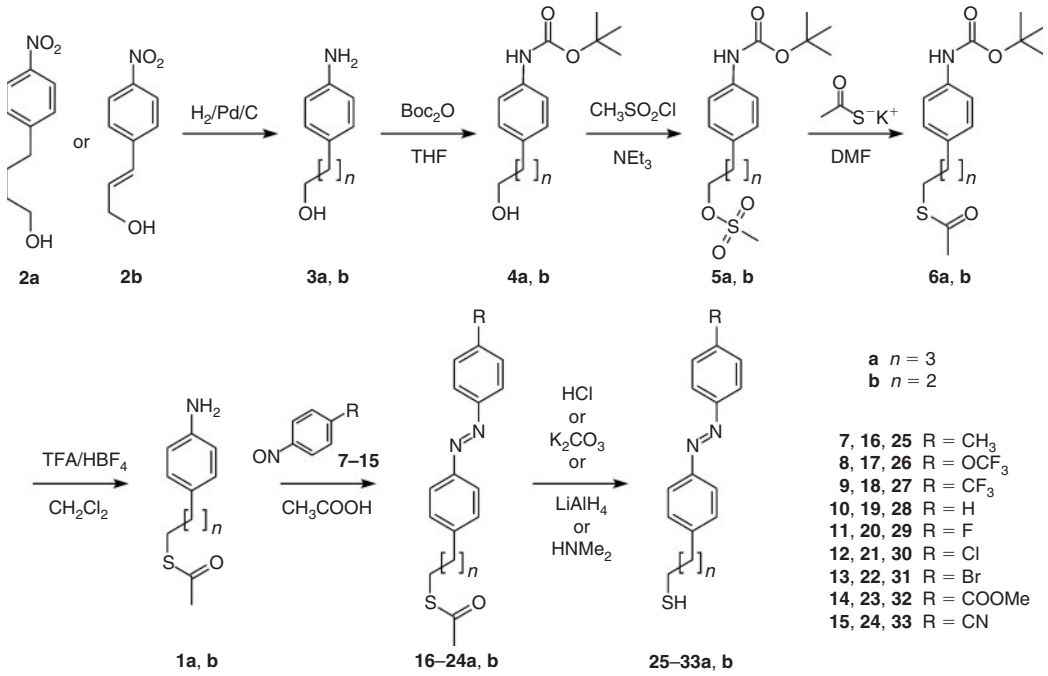
Scheme 1. Most azobenzene thiols published until now contain an oxygen atom between the alkyl chain and the azobenzene unit (right). This oxygen atom results in bond distortion, whereas a heteroatom-free alkyl chain can adopt an all-*trans* conformation.

compounds would not interfere with the protection chemistry. Our assumption that anilines are too weakly basic to achieve the deprotection of aliphatic thioesters was supported by initial experiments, in which we treated dodecanethioacetate with equimolar amounts of *p*-toluidine in THF for a prolonged time. NMR and TLC proved that no reaction between these compounds takes place, thus suggesting the compatibility of these two functionalities in one molecule. As the coupling reaction between nitroso benzenes and anilines is best performed in acetic acid,[34–40] the compatibility of the aliphatic thioester and the aniline was also tested in this solvent without and with addition of 4-methylnitrosobenzene: the thioester was not altered in either case and the formation of the azobenzene proceeded cleanly both at room temperature and when heated to reflux.

With these positive results, we were confident enough to pursue the synthesis of the two node compounds **1a**, **b**. The synthesis of both could be achieved from the respective ω-(4-nitrophenyl)alcohols **2a**, **b**, which themselves had to be obtained by different routes. While 3-(4-nitrophenyl)propenol **2b** was obtained by the reduction of *trans*-4-nitrocinnamaldehyde,[51] the ω-(4-nitrophenyl)butanol **2a** was synthesized in a two-step manner from 4-phenylbutyric acid via nitration[52] and reduction with borane.[53]

Both compounds were converted to the ω-(4-aminophenyl) alkanols **3a**, **b** by catalytic hydrogenation.[53] Because these amino compounds are light-, oxygen-, and temperature-sensitive, and to permit the subsequent chemistry for the attachment of the sulfur atom, the amino groups were protected as *tert*-butoxycarbamates (BOC) using di-*tert*-butyl dicarbonate in THF at 80°C, generating compounds **4a**, **b**.[54] The introduction of the sulfur atom took place in a two-step reaction. First, the alcohol functions were converted quantitatively to the mesylates **5a**, **b**, which were obtained as crystalline solids; **5b** yielded crystals suitable for X-ray diffraction.[55] The mesylates were transformed to the respective thioacetates **6a**, **b** by means of potassium thioacetate. Because reactions involving thioacetate almost always result in a variety of coloured side-products with different polarity, the purification of these compounds required careful investigation. Although **6a** and **6b** are crystalline compounds, neither recrystallization nor sublimation under reduced pressure yielded pure products. After screening a wide variety of conditions, we found that apparently only chromatography on silica gel with a mixture of toluene and dichloromethane (sometimes twice) was able to solve the purification problems. These two compounds were then used as stock materials because at −20°C, they were stable for a prolonged time.

The deprotection of these compounds to obtain the node compounds **1a**, **b** turned out to be surprisingly difficult. Although in general the BOC group can efficiently be removed using trifluoroacetic acid (TFA), for example in methylene chloride, in this case TFA alone was not enough. After several attempts, a mixture



Scheme 2. Synthetic route to the library of azobenzenealkanethiols with three and four methylene groups in the alkyl chain. The central building blocks are the thioacetates **1a** and **1b**, from which the final thiols could be obtained in two steps.

of TFA and HBF_4 turned out to be suitable, but the optimal reaction times and temperatures needed to be adjusted every time by following the reaction with, for example, TLC.

The amines **1a** and **1b** obtained this way turned out to be quite sensitive to light and air and therefore could not be purified by chromatography. Instead, they were directly reacted with the nitrosobenzenes **7**–**15** to yield the different azobenzenealkane thioacetate species **16a**, **b**–**24a**, **b**.[40] The required nitrosobenzenes **7**–**15** could be obtained in good to very good yields by the oxidation of the respective anilines with hydrogen peroxide in the presence of a catalytic amount of ammonium molybdate tetrahydrate.[56] To remove side-products (in particular the nitro compound), chromatography on silica was performed. Owing to the high volatility of the nitrosobenzenes, it is highly advised to use pentane for this purification step. In most cases, the purification of these compounds could be skipped and the products **7**–**15** used directly. The side-products were then eliminated after the coupling step by chromatography.

Presumably because both coupling partners (amines **1a**, **b**, and the nitrosobenzenes **7**–**15**) had to be used as crude materials, a number of impurities showed up after the coupling step, the removal of which turned out to be tedious. Because the molecules **16a**, **b**–**24a**, **b** are very sensitive to elevated temperatures, recrystallization and sublimation were not suitable for purification, although some of the compounds (in particular **24a** and **b**) showed a strong tendency to crystallize in the chromatography column. Only in the case of compounds **24a**, **b** could this behaviour be exploited for purification by vapour crystallization, although this had to be repeated several times.

The choice of the best reagent for the deprotection of the thiol group depended on the head-group substituent. Certain reagents such as dimethylamine or the frequently used $LiAlH_4$ were suitable in some cases, but often resulted in too many side-products. For the deprotection of most of the thioacetates, the best choice turned out to be either HCl/MeOH or K_2CO_3/MeOH, depending on the head group. Nevertheless, both systems also showed their problems: while the acidic system sometimes did not yield 100% conversion, the alkaline system often resulted in too many side-products. A striking example is the partial solvolysis (under alkaline conditions!) of the cyano group in **24a** or **b** that resulted in the formation of small amounts of **23a**, **b**, which could not be separated from the final products.

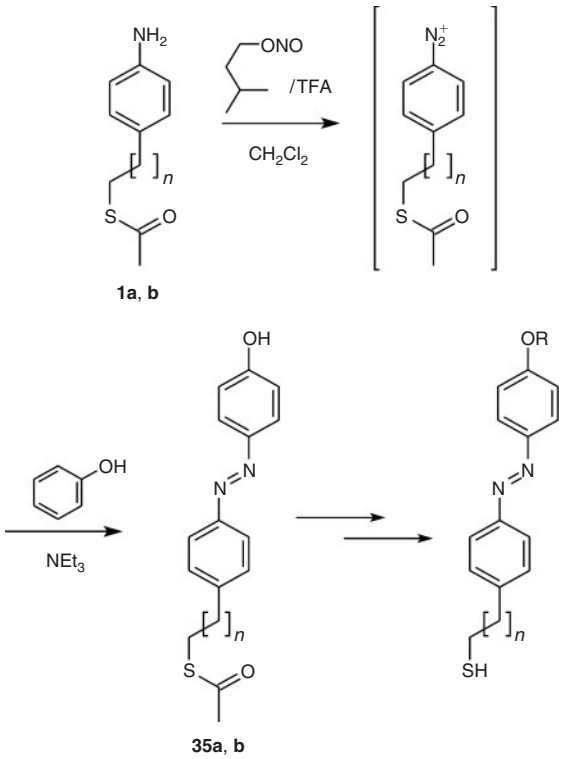
In general, the compounds **23a**, **b** and **24a**, **b** turned out to be the most problematic because, even under acidic conditions and exclusion of air, the deprotection of the SAc group resulted in the formation of significant amounts of disulfides (in some cases, complete conversion took place). In contrast to this, thiol **32b** was obtained during chromatography of thioester **23b** on Al_2O_3.

As with the thioacetates, some of the thiols also had the tendency to crystallize on the column during chromatography, thus hampering their purification. As a result, many of the compounds had to be chromatographed several times.

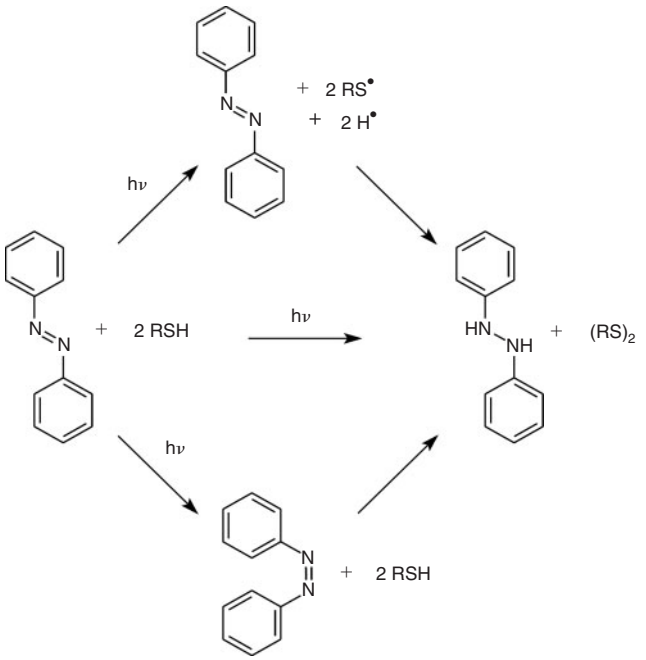
Nevertheless, with the exception of compounds **30b** and **33b**, which were obtained either mainly or exclusively as disulfides, all azobenzene thiols could finally be attained in very good purity.

Attempts at the Synthesis of Alkoxy-Terminated Azobenzene Thiols

Although a broad variety of substituted azobenzene thiols could be attained by the nitrosobenzene–aniline coupling reaction, the electron-rich alkoxy azobenzenes were not accessible in this manner. This already started with surprising difficulties during the oxidation of 4-methoxyaniline (*p*-anisidine) to the respective nitrosobenzene **34**, which could only be obtained in low yield (~30%). Furthermore, this nitroso compound did not react with the amines **1a**, **b** to yield the azobenzenes, presumably owing to a too-high electron density at the nitroso group.



Scheme 3. Attempted access route to the alkoxy derivatives via an azo-coupling reaction. **35a** was obtained in a too small yield to make this route feasible.



Scheme 4. The observed light-induced reaction and two proposed pathways.

We therefore decided to attempt to access this class of compounds by the aforementioned azo-coupling with phenol, followed by the etherification of the hydroxy group (Scheme 3).

For this, the amines **1a**, **b** were converted to the respective diazonium compounds under anhydrous conditions (to avoid the hydrolysis of the thioacetate) and reacted with phenol.

First results on the synthesis of 4-[4-((4-hydroxyphenyl) diazenyl)phenyl]butylethanethioate **35a** showed that the desired product could only be obtained in a limited yield (<30%) and its purification turned out to be tedious. As the alkoxy derivatives were not crucial for our investigations of surface-bound molecular switches, we decided to shift the synthesis of these compounds to the future.

Light Sensitivity

During our experiments, we often were surprised that NMR spectra of seemingly pure thiols (as determined for example by TLC) showed extra peaks, in particular in the aromatic range. The impurities causing these signals could not be removed by repeated chromatography and – even worse – became sometimes stronger after purification. A careful evaluation resulted in the observation that the disulfide content of the samples correlated well with the amount of 'impurities' in the aromatic range and that these two effects roughly correlated with the waiting time in the NMR queue, suggesting a decomposition reaction either mediated by the acidity of the solvent ($CDCl_3$ releases small amounts of DCl over time) or by daylight. The substitution of $CDCl_3$ by C_6D_6 reduced the effect, but did not completely suppress it, hinting at the minor role of acid traces. As the interaction of light with azobenzenes usually at most results in isomerization at the –N=N– double bond but not in further reactions, we suspected that the presence of free thiol groups changed the situation. This assumption was confirmed by experiments, in which NMR spectra of an equimolar mixture of non-substituted azobenzene (Ph–N=N–Ph) with dodecanethiol ($C_{12}H_{25}SH$) were recorded after different time-spans. Only the samples exposed to light showed similar signals to the ones mentioned before. With these simpler molecules, it was also possible to identify the reaction products: obviously a light-driven redox reaction occurs with the transfer of hydrogen atoms, resulting in the formation of hydrazobenzene and dodecyldisulfide, as indicated by the appearance of signals at δ 7.16 and 6.84 (hydrazobenzene) and 2.68 (disulfide). The brutto reaction shown in Scheme 4 (centre) turned out to be compatible with all the observations.

Two possible pathways for this reaction exist. The first is the light-induced, homolytic cleavage of the S–H bond with formation of hydrogen and sulfyl radicals, with the first being scavenged by the azobenzene, while the latter dimerizes. It is also imaginable that the azobenzene is switched into the *cis*-form, which is then the better oxidant,[57,58] thus consuming the thiol.

Within the current project, the consequence of this observation was that all spectra of the thiols were then recorded in C_6D_6 as solvent, using brown NMR tubes. These measures completely eliminated this undesired reaction.

Initial Monolayer Characterization

For further studies, it is important to show that the molecules indeed form dense monolayers on gold. A suitable characterization method is ellipsometry, which permits the determination of the thickness of very thin layers. As the molecules contain both, aliphatic and aromatic parts, an intermediate refractive index of 1.50 (at $\lambda = 632$ nm) was assumed for all molecules. The data shown in Table 1 indeed speak for the formation of dense monolayers in which the molecules adopt a tilt angle of ~20–30° with respect to the surface normal. This tilting has been found in many systems.[59–62] A peculiarity is the systematically higher

Table 1. Layer thickness and wetting properties (advancing contact angle of water) of the respective self-assembled monolayers on gold

Head group	No. of CH_2 groups	Compound	Layer thickness [Å]	Contact angle [°]
CH_3	4	**25a**	18.3 ± 0.5	96 ± 2
	3	**25b**	19.6 ± 1.2	98 ± 2
OCF_3	4	**26a**	17.8 ± 0.3	100 ± 1
	3	**26b**	18.7 ± 1.3	110 ± 0.5
CF_3	4	**27a**	16.5 ± 0.2	95 ± 1
	3	**27b**	18.7 ± 0.1	98 ± 0.5
H	4	**28a**	16.3 ± 0.6	83 ± 1
	3	**28b**	17.8 ± 0.6	86 ± 1
F	4	**29a**	16.0 ± 0.8	92 ± 0.5
	3	**29b**	18.1 ± 0.6	93 ± 0.5
Cl	4	**30a**	15.8 ± 0.8	87 ± 1
	3	**30b**	20.2 ± 1.3	94 ± 0.5
Br	4	**31a**	18.4 ± 0.4	85 ± 2
	3	**31b**	21.8 ± 0.9	90 ± 0.5
COOMe	4	**32a**	21.0 ± 0.4	61 ± 2
	3	**32b**	21.1 ± 0.8	62 ± 2
CN	4	**33a**	19.1 ± 1.0	55 ± 1
	3	**33b**	18.3 ± 0.5	56 ± 2

thickness of the thiols bearing a propylene chain (three CH_2 groups, derivatives **25**–**33b**) compared with the ones with the longer butylene chain (four CH_2 groups, derivatives **25**–**33a**). While this thickness decrease of ~2 Å seems to be in contradiction with the additional methylene unit, it is fully consistent with previous results in the araliphatic series, as mentioned in the Introduction.[28–33]

Alkane chains with an even number of methylene units force the stiff aromatic part into a higher tilt angle, thus rendering these layers effectively thinner (Fig. 2). The only exceptions are the layers of **33a** and **33b**, where, in the latter case not the thiol, but the respective disulfide was used for the layer formation. Although, according to the literature, this change should not have any influence on the final monolayers, in this case a clear reversal of the trend is visible.

A very sensitive tool for the outermost chemistry of monolayers is the contact angle of liquids. The typical sensitivities for the respective head groups could be found with water droplets: the ester and the cyano group turned out to be the most hydrophilic, while the fluorine-terminated monolayers were the most hydrophobic. On top of this general trend, it can be seen that the contact angles for the shorter-chained derivatives **25**–**33b** were in all cases higher than the ones measured for the layers of the $(CH_2)_4$ derivatives **25**–**33a**, hinting again at layers in which the surface dipole moments are almost perpendicularly oriented to the surfaces.

All these results suggest the formation of very dense and highly ordered monolayers, at least of the *trans*-azobenzene thiols.

Conclusions

In conclusion, we were able to develop a divergent route to a family of azobenzene alkanethiols with different alkyl chain lengths and a variety of head groups, with a central building block for each alkyl series. The attachment of the head groups is based on an N–N-coupling forming the desired azobenzene units. Owing to the different chemical behaviour of the head groups, a portfolio of deprotection reactions had to be used, with an optimal one for each thiol.

In contrast to previous studies, no oxygen atoms were used as linkers between the azobenzene unit and the alkane chain. While this made the development of a new synthetic strategy necessary, the monolayers formed by these thiols behaved quite predictably and in accord with previously studied aromatic–aliphatic hybrid systems, in particular regarding the odd–even effect imposed by the configuration of the alkane chain.

These works provide a solid basis for the study of the photoresponse of these systems. In the next steps, we are planning to investigate the structure of the systems before and after irradiation with different wavelength using several microscopic and spectroscopic methods.

Experimental

Substrates

Phenylbutyric acid was purchased from Acros Organics. *p*-Toluidine was obtained from Merck whereas 4-bromoaniline, 4-fluoroaniline, and 4-aminobenzonitrile were obtained from Aldrich. 4-Aminobenzotrifluoride and 4-(trifluoromethoxy) aniline were purchased from Apollo Scientific, and 4-chloroaniline and methyl 4-aminobenzoate were obtained from Alfa Aesar. Commercially available thioacetic acid (Merck) was distilled and kept under N_2.

NMR Measurements

^1H, ^{19}F, and ^{13}C NMR spectra were obtained on Avance 300 or DRX 400 Bruker spectrometers. Furthermore, some ^1H and ^{13}C NMR spectra were recorded on a DRX 500 Bruker spectrometer. IR spectra were carried out on a Bruker IFS 88 spectrometer. Mass spectra were recorded on Finnigan MAT TSQ 700 or MAT 95S spectrometers. Elemental analyses were recorded on an EA 1108 CHNS-O from Carlo Erba Instruments in the chemistry department at the University of Hamburg. Melting points were determined on a Dr Tottoli apparatus (Büchi) and are uncorrected.

Monolayers

For ellipsometry, 200 nm of gold with chromium as adhesion promoter were deposited onto (100) silicon wafers (used as delivered, Wacker Siltronic AG).

The Au substrates were prepared by first evaporating 5 nm of titanium and subsequently 100 nm of gold onto Si(100) wafers in a recipient with a residual gas pressure of 10^{-5} Pa. The adsorption of the organothiolate monolayers was carried out by immersing the substrates into ethanolic solutions of the thiols for 24 h. In the case of azobenzene alkanethiols, 1 mM solutions were used.

Contact Angle

Contact angle measurements (sessile drop method) were performed using a Multiskop (Optrel GBR, Germany). The water droplets images were captured with a charge-coupled device camera before the included software calculated their shape and the respective contact angles. In all cases, the advancing angle was determined.

Ellipsometry

The thicknesses of the films were determined using an ellipsometer SE 400 (Sentech Instruments GmbH) under an incidence angle of 70° at a wavelength of 633 nm. The substrates were cleaned using a hydrogen plasma before determination of the substrate parameters Δ and Ψ.[63] For the organic layers, a refractive index of $n = 1.50$ was assumed.

Preparation of tert-*Butyl 4-(4-Hydroxybutyl) phenylcarbamate* ***4a****; Typical Procedure*

4-(*p*-Aminophenyl)butanol **3a** (14.8 g, 89 mmol) was dissolved in THF (150 mL). To the solution, di-*tert*-butyldicarbonate (23.3 g, 107 mmol) was added. The mixture was heated to 80°C under nitrogen for 24 h. The solvent was removed under vacuum and the residue extracted with dichloromethane and water. The organic phase was evaporated to dryness. A small amount of the product (1.0 g) was purified by chromatography on silica gel using light petroleum/ethyl acetate 7:3 → 3:7 as eluent for analysis.

Yield: 26.3 g (99 mmol, 111%, contaminated by di-*tert*-butyl-dicarbonate), yellow-beige solid. Mp 74–76°C (Found: C 67.90, H 8.74, N 5.24. Calc. for $C_{15}H_{23}NO_3$: C 67.90, H 8.74, N 5.28%.) ν_{max}(KBr)/cm^{-1} 3360, 3358, 2984 (ν_{-CH3}), 2937 (ν_{-CH2}), 2860 (ν_{-CH2}), 1809 (ν_{C-O}), 1758 ($\nu_{C=O}$), 1695 (ν_{-HNCO-}), 1615 (ν_{C-Car}), 1593 (ν_{C-Car}), 1520 (δ_{-NH}, $\nu_{N-C=O}$), 1462 (δ_{-CH2}, δ_{-CH3}), 1412, 1316, 1240, 1162, 1057, 825 (δ_{C-Har}). δ_H (400 MHz, $CDCl_3$) 7.25 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.10 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.61 (s, 1H, N*H*), 3.62 (t, $^3J_{HH}$ 6.4, 2H, $CH_2CH_2CH_2CH_2OH$), 2.57 (t, $^3J_{HH}$ 7.4, 2H, $CH_2CH_2CH_2CH_2OH$), 2.01 (s, 1H, $CH_2CH_2CH_2CH_2OH$), 1.68–1.52 (m, 4H, $CH_2CH_2CH_2CH_2OH$), 1.50 (s, 9H, NHCOOC(CH_3)$_3$). δ_C (100 MHz, $CDCl_3$) 152.94 (NH*C*OOC(CH_3)$_3$), 136.99 (C_4), 135.99 (C_1), 128.73 (C_3), 118.69 (C_2), 80.24 (NHCOO*C*(CH_3)$_3$), 62.60 ($CH_2CH_2CH_2CH_2OH$), 34.82 ($CH_2CH_2CH_2CH_2OH$), 32.10 ($CH_2CH_2CH_2CH_2OH$), 28.28 ($CH_2CH_2CH_2CH_2OH$), 27.52 (NHCOOC(CH_3)$_3$). *m/z* (EI) 265 (24%, M^+), 209 (100%, $M^+ - C_4H_8$), 150 (38%, $C_{10}H_{14}O$), 132 (10%), 106 (62%, $C_6H_6N_2$ or $C_7H_8N^+$), 57 (85%, $C_4H_9^+$).

tert-*Butyl 4-(3-Hydroxypropyl)phenylcarbamate* ***4b***

Yield: 24.0 g (95.6 mmol, 101%, contaminated by di-*tert*-butyl-dicarbonate), yellow-brown oil (Found: C 65.43, H 8.43, N 4.98. Calc. for $C_{14}H_{21}NO_3$: C 66.91, H 8.42, N 5.57%.) ν_{max}(KBr)/cm^{-1} 3350, 3321, 2977 (ν_{-CH3}), 2935 (ν_{-CH2}), 2858 (ν_{-CH2}), 1700 (ν_{-HNCO-}), 1597 (ν_{C-Car}), 1526 (δ_{-NH}, $\nu_{N-C=O}$), 1454 (δ_{-CH2}, δ_{-CH3}), 1412 (δ_{-CH2}, δ_{-CH3}), 1316, 1245, 1163, 1056, 832 (δ_{C-Har}). δ_H (500 MHz, $CDCl_3$) 7.26 (d, $^3J_{HH}$ 8.1, 2H, H_2), 7.10 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.49 (s, 1H, N*H*), 3.65 (t, $^3J_{HH}$ 6.4, 2H, $CH_2CH_2CH_2OH$), 2.65 (t, $^3J_{HH}$ 7.7, 2H, $CH_2CH_2CH_2OH$), 1.89–1.81 (m, 2H, $CH_2CH_2CH_2OH$), 1.51 (s, 9H, NHCOOC(CH_3)$_3$). δ_C (125 MHz, $CDCl_3$) 152.90 (NH*C*OOC(CH_3)$_3$), 136.51 (C_4), 136.17 (C_1), 128.84 (C_3), 118.82 (C_2), 80.35 (NHCOO*C*(CH_3)$_3$), 62.14 ($CH_2CH_2CH_2$OH), 34.24 ($CH_2CH_2CH_2OH$), 31.32 ($CH_2CH_2CH_2OH$), 28.33 (NHCOOC(CH_3)$_3$). *m/z* (EI) 251 (11%, M^+), 195 (43%, $M^+ - C_4H_8$), 177 (14%), 151 (31%, $C_9H_{13}NO$), 132 (20%), 106 (100%, $C_6H_6N_2$ or $C_7H_8N^+$), 57 (46%, $C_4H_9^+$), 41 (25%, $C_3H_5^+$).

*4-[4-(*tert-*Butoxycarbonylamino)phenyl]butyl Methanesulfonate* ***5a****; Typical Procedure*

To a solution of *tert*-butyl 4-(4-hydroxybutyl)phenylcarbamate **4a** (25.2 g, 95 mmol) in dry dichloromethane (220 mL) was added triethylamine (21 mL) before the mixture was cooled down to −20°C. Then methanesulfonyl chloride was added. The solution was kept at −30°C for a couple of minutes. Then the mixture was stirred for 20 minutes without cooling. The solution was washed with water (2 × 100 mL). The organic phase was evaporated under vacuum. A small amount (6.3 g) was purified by chromatography on silica gel using dichloromethane/diethyl ether (1% → 5%) as eluent to yield 4-[4-(*tert*-butoxycarbonylamino)phenyl]butylmethanesulfonate **5a** as a white solid (6 g) for further analysis.

Yield: 32.1 g (93 mmol, 99%), light brown solid. Mp 52–54°C (Found: C 55.70, H 7.29, N 4.07, S 8.94. Calc. for $C_{16}H_{25}NO_5S$: C 55.96, H 7.34, N 4.08, S 9.34%.) ν_{max}(KBr)/cm^{-1} 3370 (ν_{N-H}), 2979 (ν_{-CH3}), 2937 (ν_{-CH2}), 2868 (ν_{-CH2}), 1703 ($\nu_{C=O}$), 1593 (ν_{C-Car}), 1528 (δ_{-HNCO-}), 1467 (δ_{-CH2}, δ_{-CH3}), 1352, 1171, 825 (δ_{C-Har}). δ_H (400 MHz, $CDCl_3$) 7.27 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.07 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.52 (s, 1H, N*H*), 4.21 (t, $^3J_{HH}$ 6.2, 2H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 2.97 (s, 3H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 2.59 (t, $^3J_{HH}$ 7.2, 2H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 1.78–1.60 (m, 4H, $CH_2CH_2CH_2CH_2OSO_2CH_3$), 1.50 (s, 9H, NHCOOC($CH_3$)$_3$). δ_C (100 MHz, $CDCl_3$) 152.90 (NH*C*OOC(CH_3)$_3$), 136.37 (C_4), 136.21 (C_1), 128.84 (C_3), 118.82 (C_2), 80.38 (NHCOO*C*(CH_3)$_3$), 69.88 ($CH_2CH_2CH_2CH_2OSO_2CH_3$), 37.36 ($CH_2CH_2CH_2CH_2OSO_2CH_3$), 34.44 ($CH_2CH_2CH_2CH_2OSO_2CH_3$), 28.52 ($CH_2CH_2CH_2CH_2OSO_2CH_3$), 28.35 (NHCOOC($CH_3$)$_3$), 27.21 ($CH_2CH_2CH_2CH_2OSO_2CH_3$). *m/z* (EI) 343 (12%, M^+), 287 (42%, $M^+ - C_4H_8$), 243 (32%, $C_{11}H_{17}NO_3S$), 163 (21%), 132 (15%), 106 (100%, $C_6H_6N_2$ or $C_7H_8N^+$), 79 (10%, $CH_3SO_2^+$), 57 (72%, $C_4H_9^+$).

*3-[4-(*tert-*Butoxycarbonylamino)phenyl]propyl Methanesulfonate* ***5b***

Yield: 61.9 g (188 mmol, 99%), colourless solid. Mp 79–81°C (Found: C 54.69, H 7.15, N 4.19, S 9.89. Calc. for $C_{15}H_{23}NO_5S$: C 54.69, H 7.04, N 4.25, S 9.73%.) ν_{max}(KBr)/cm^{-1} 3381 (ν_{N-H}), 2983 (ν_{-CH3}), 2939 (ν_{-CH2}), 1702 ($\nu_{C=O}$), 1593 (ν_{C-Car}), 1524 (δ_{-HNCO-}), 1460 (δ_{-CH2}, δ_{-CH3}), 1358, 1158, 838 (δ_{C-Har}). δ_H (500 MHz, $CDCl_3$) 7.28 (d, $^3J_{HH}$ 8.1, 2H, H_2), 7.10 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.44 (s, 1H, N*H*), 4.20 (t, $^3J_{HH}$ 6.3, 2H, $CH_2CH_2CH_2OSO_2CH_3$),

2.98 (s, 3H, $CH_2CH_2CH_2OSO_2CH_3$), 2.70 (t, $^3J_{HH}$ 7.5, 2H, $CH_2CH_2CH_2OSO_2CH_3$), 2.30–1.90 (m, 2H, $CH_2CH_2CH_2OSO_2CH_3$), 1.51 (s, 9H, $NHCOOC(CH_3)_3$). δ_C (125 MHz, $CDCl_3$) 152.81 ($NHCOOC(CH_3)_3$), 136.60 (C_4), 134.89 (C_1), 128.91 (C_3), 118.88 (C_2), 80.47 ($NHCOOC(CH_3)_3$), 69.07 ($CH_2CH_2CH_2OSO_2CH_3$), 37.35 ($CH_2CH_2CH_2OSO_2CH_3$), 30.80 ($CH_2CH_2CH_2OSO_2CH_3$), 30.69 ($CH_2CH_2CH_2OSO_2CH_3$), 28.33 ($NHCOOC(CH_3)_3$). *m/z* (EI) 329 (7%, M^+), 273 (32%, $M^+ - C_4H_8$), 229 (67%, $C_{10}H_{15}NO_3S$), 132 (41%), 106 (100%, $C_6H_6N_2$ or $C_7H_8N^+$), 79 (12%, $CH_3SO_2^+$), 57 (63%, $C_4H_9^+$), 44 (98%), 39 (76%), 28 (33%).

*4-[4-(*tert*-Butoxycarbonylamino)phenyl]butylethanethioate* ***6a****; Typical Procedure*

To a solution of potassium-*tert*-butanolate (17.1 g, 152 mmol) in DMF (250 mL), thioacetic acid (23.7 g, 305 mmol) was added. Then 4-[4-(*tert*-butoxycarbonylamino)phenyl]butylmethanesulfonate **5a** (26.1 g, 76 mmol) in DMF (150 mL) was added. The mixture was stirred at room temperature for 2 days. DMF and thioacetic acid were removed under vacuum. The residue was dissolved in water and extracted with dichloromethane. The organic phase was evaporated under vacuum (32.2 g). For purification, the residue was stirred in water for 15 min. The product was isolated by decantation (this was repeated twice). The residue was further purified by chromatography on silica gel using dichloromethane/light petroleum 3:7 → 7:3, only dichloromethane (from the beginning on 1% diethyl ether), dichloromethane/diethyl ether (1% → 10%) as eluent to yield 4-[4-(*tert*-butoxycarbonylamino)phenyl]butylethanethioate **6a** as a brown solid.

Yield: 20.4 g (63 mmol, 83%), auburn solid. Mp 52–54°C (Found: C 62.78, H 7.82, N 4.29, S 10.33. Calc. for $C_{17}H_{25}NO_3S$: C 63.13, H 7.79, N 4.33, S 9.91%.) ν_{max}(KBr)/cm^{-1} 3362 (ν_{N-H}), 2976 (ν_{-CH3}), 2931 (ν_{-CH2}), 2858 (ν_{-CH2}), 1729 ($\nu_{C=O}$), 1668 (ν_{-HNCO-}), 1593 (ν_{C-Car}), 1526 (δ_{-HNCO-}), 1455 (δ_{-CH2}, δ_{-CH3}), 1230, 1157, 833 (δ_{C-Har}). δ_H (400 MHz, $CDCl_3$) 7.25 (d, $^3J_{HH}$ 8.5, 2H, H_2), 7.08 (d, $^3J_{HH}$ 8.5, 2H, H_3), 6.44 (s, 1H, N*H*), 2.87 (t, $^3J_{HH}$ 6.9, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.55 (t, $^3J_{HH}$ 7.1, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.31 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.67–1.55 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.51 (s, 9H, $NHCOOC(CH_3)_3$). δ_C (100 MHz, $CDCl_3$) 195.91 ($CH_2CH_2CH_2CH_2SCOCH_3$), 152.84 ($NHCOOC(CH_3)_3$), 136.64 (C_4), 136.08 (C_1), 128.73 (C_3), 118.64 (C_2), 80.21 ($NHCOOC(CH_3)_3$), 34.55 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.55 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.46 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.93 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.83 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.28 ($NHCOOC(CH_3)_3$). *m/z* (EI) 323 (32%, M^+), 267 (22%, $M^+ - C_4H_8$), 223 (83%, $C_{12}H_{17}NOS$), 132 (10%), 106 (100%, $C_6H_6N_2$ or $C_7H_8N^+$), 57 (99%, $C_4H_9^+$), 43 (52%, $C_2H_3O^+$ or $C_3H_7^+$).

*3-[4-(*tert*-Butoxycarbonylamino)phenyl] propylethanethioate* ***6b***

Yield: 55.6 g (179 mmol, 99%), red brown solid. Mp 65–67°C (Found: C 62.21, H 7.57, N 4.49, S 10.03. Calc. for $C_{16}H_{23}NO_3S$: C 62.11, H 7.49, N 4.53, S 10.36%.) ν_{max}(KBr)/cm^{-1} 3377 (ν_{N-H}), 2972 (ν_{-CH3}), 2928 (ν_{-CH2}), 1695 ($\nu_{C=O}$), 1690 (ν_{-HNCO-}), 1590 (ν_{C-Car}), 1521 (δ_{-HNCO-}), 1453 (δ_{-CH2}, δ_{-CH3}), 1235, 1158, 829 (δ_{C-Har}). δ_H (500 MHz, $CDCl_3$) 7.26 (d, $^3J_{HH}$ 8.0, 2H, H_2), 7.08 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.44 (s, 1H, N*H*), 2.86 (t, $^3J_{HH}$ 7.3, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.63 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.33 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.90–1.80 (m, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.51 (s, 9H, $NHCOOC(CH_3)_3$). δ_C (125 MHz, $CDCl_3$) 195.86 ($CH_2CH_2CH_2SCOCH_3$), 152.83 ($NHCOOC(CH_3)_3$), 136.28 (C_4), 135.79 (C_1), 128.88 (C_3), 118.73 (C_2), 80.37 ($NHCOOC(CH_3)_3$), 34.08 ($CH_2CH_2CH_2SCOCH_3$), 31.13 ($CH_2CH_2CH_2SCOCH_3$), 30.63 ($CH_2CH_2CH_2SCOCH_3$), 28.45 ($CH_2CH_2CH_2SCOCH_3$), 28.31 ($NHCOOC(CH_3)_3$). *m/z* (EI) 309 (10%, M^+), 253 (43%, $M^+ - C_4H_8$), 209 (41%, $C_{11}H_{15}NOS$), 132 (10%), 106 (100%, $C_6H_6N_2$ or $C_7H_8N^+$), 57 (81%, $C_4H_9^+$), 43 (64%, $C_2H_3O^+$ or $C_3H_7^+$).

Removal of the tert*-Butoxycarbonyl Function; 4-(4-Aminophenyl)butylethanethioate* ***1a****; Typical Procedure*

To a solution of 4-[4-(*tert*-butoxycarbonylamino)phenyl]butyl ethanethioate **6a** (7.5 g, 23.0 mmol) in dichloromethane (60 mL) was added trifluoroacetic acid (3.2 mL, 46.6 mmol). The mixture was stirred at 35°C for 24 h until HBF_4 (2.3 mL, 17.9 mmol) dissolved in diethyl ether was added. The mixture was stirred for 48 h at room temperature and another 24 h at 35°C. The acid was quenched by adding saturated $NaHCO_3$ solution. The organic phase was separated and the solvent was removed under vacuum to yield 2.1 g of compound **1a**.

Yield: 2.1 g (9.4 mmol, 96%), light brown solid. Mp 67–69°C ν_{max}(KBr)/cm^{-1} 3399 (ν_{NH2}), 3317 (ν_{NH2}), 2955 (ν_{-CH3}), 2929 (ν_{-CH2}), 2856 (ν_{-CH2}), 1614 ($\nu_{C=O}$), 1515, 1481 (δ_{-NH2}, δ_{-NH3}), 1472 (δ_{-NH2}, δ_{-NH3}), 1440 (δ_{-CH2}, δ_{-CH3}), 1256, 1049, 822 (δ_{C-Har}). δ_H (400 MHz, $CDCl_3$) 6.97 (d, $^3J_{HH}$ 8.3, 2H, H_3), 6.68 (d, $^3J_{HH}$ 8.3, 2H, H_2), 3.96 (s, 2H, NH_2), 2.88 (t, $^3J_{HH}$ 7.0, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.52 (t, $^3J_{HH}$ 7.2, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.32 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.72–1.52 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$). δ_C (100 MHz, $CDCl_3$) 195.94 ($CH_2CH_2CH_2CH_2SCOCH_3$), 142.96 (C_1), 132.93 (C_4), 129.15 (C_3), 115.79 (C_2), 34.45 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.72 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.59 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.99 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.94 ($CH_2CH_2CH_2CH_2SCOCH_3$).

3-(4-Aminophenyl)propylethanethioate ***1b***

Yield: 2.5 g (12 mmol, 100%), light-brown oil. δ_H (400 MHz, $CDCl_3$) 6.96 (d, $^3J_{HH}$ 8.2, 2H, H_3), 6.62 (d, $^3J_{HH}$ 8.3, 2H, H_2), 3.56 (s, 2H, NH_2), 2.87 (t, $^3J_{HH}$ 7.3, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.58 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.33 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.89–1.78 (m, 2H, $CH_2CH_2CH_2SCOCH_3$). δ_C (100 MHz, $CDCl_3$) 195.91 ($CH_2CH_2CH_2SCOCH_3$), 144.38 (C_1), 131.14 (C_4), 129.21 (C_3), 115.25 (C_2), 33.94 ($CH_2CH_2CH_2SCOCH_3$), 31.33 ($CH_2CH_2CH_2SCOCH_3$), 30.64 ($CH_2CH_2CH_2SCOCH_3$), 28.57 ($CH_2CH_2CH_2SCOCH_3$).

4-[4-((4-Hydroxyphenyl)diazenyl)phenyl] butylethanethioate ***35a***

To a solution of 4-(4-aminophenyl)butylethanethioate **1a** (1.2 g, 5.0 mmol) in dry dichloromethane (40 mL) was added trifluoroacetic acid (0.9 g, 8.1 mmol) before the mixture was cooled to −30°C. Then, isoamylnitrite was added (0.9 g, 8.0 mmol). The solution was stirred at −20°C for 45 min until the addition of phenol (1.7 g, 18.0 mmol) followed and the stirring was continued for another 20 min. While keeping the temperature at −20°C, the mixture was quenched by addition of triethylamine (6 mL).

After a few minutes, the solution was acidified using a small amount of hydrochloric acid and the addition of ammonium chloride solution followed. The organic phase was washed with water and dried under vacuum. The residue was purified by chromatography on silica gel first using dichloromethane/methanol (1 and 2%), for the second chromatography using light petroleum/diethyl ether (1:1) as eluent to yield 4-[4-((4-hydroxyphenyl)diazenyl)phenyl]butylethanethioate **35a** as an orange-brown viscous semi-solid compound.

Yield: 0.45 g (1.4 mmol, 27%), orange-brown viscous semi-solid compound (Found: C 64.64, H 6.28, N 8.22, S 11.15. Calc. for $C_{18}H_{20}N_2O_2S$: C 65.83, H 6.14, N 8.53, S 9.76%.) ν_{max}(KBr)/cm^{-1} 3347 (ν_{OH}), 2926 (ν_{-CH3}, ν_{-CH2}), 2855 (ν_{-CH2}), 1687 ($\nu_{C=O}$), 1664, 1589 (ν_{C-Car}), 1504, 1461 (δ_{-CH2}, δ_{-CH3}), 1437, 1411, 1273, 1227, 1139, 844 (δ_{C-Har}). δ_H (400 MHz, $CDCl_3$) 7.88 (d, $^3J_{HH}$ 8.8, 2H, H_2), 7.81 (d, $^3J_{HH}$ 8.3, 2H, $H_{2'}$), 7.28 (d, $^3J_{HH}$ 8.3, 2H, H_3), 6.96 (d, $^3J_{HH}$ 8.8, 2H, $H_{3'}$), 2.91 (t, $^3J_{HH}$ 7.1, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.69 (t, $^3J_{HH}$ 7.5, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.34 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.80–1.69 (m, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.69–1.57 (m, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$). δ_C (100 MHz, $CDCl_3$) 196.61 ($CH_2CH_2CH_2CH_2SCOCH_3$), 159.11 ($C_{4'}$), 150.45 (C_1), 146.60 ($C_{1'}$), 145.05 (C_4), 129.09 (C_3), 125.25 ($C_{2'}$), 122.57 (C_2), 115.99 ($C_{3'}$), 35.20 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.63 ($CH_2CH_2CH_2CH_2SCOCH_3$), 30.22 ($CH_2CH_2CH_2CH_2SCOCH_3$), 29.04 ($CH_2CH_2CH_2CH_2SCOCH_3$), 28.91 ($CH_2CH_2CH_2CH_2SCOCH_3$). *m/z* (EI) 328 (73%, M^+), 149 (11%, $C_{10}H_{15}N$), 123 (29%), 121 (61%, $C_6H_5N_2O^+$), 107 (44%, $C_7H_9N^+$), 93 (100%, C_6H_7N), 65 (22%), 43 (42%, $C_2H_3O^+$ or $C_3H_7^+$).

*Deprotection of Azobenzenealkanethioate using LiAlH$_4$; 4-[4-(*p*-Tolyldiazenyl)phenyl]butanethiol **25a**; Typical Procedure*

To a stirred suspension of lithium aluminium hydride (0.4 g, 10.8 mmol) in dry THF (20 mL), a solution of 4-[4-(*p*-tolyldiazenyl)phenyl]butylethanethioate **16a** (1.16 g, 3.6 mmol) in dry THF (30 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature. Then, acidification with hydrochloric acid (1 M, 15 mL) was followed by removal of the solvent under reduced pressure. The residue was extracted three times with dichloromethane. The solvent was removed under vacuum and the residue was purified by chromatography on silica gel using dichloromethane/light petroleum 1:4 → 7:3, as eluent to yield 4-[4-(*p*-tolyldiazenyl)phenyl]butanethiol **25a** as an orange solid.

Yield: 0.8 g (2.8 mmol, 78%), orange solid. Mp 66–68°C (Found: C 71.67, H 7.07, N 9.87, S 11.04. Calc. for $C_{17}H_{20}N_2S$: C 71.79, H 7.09, N 9.85, S 11.27%.) ν_{max}(KBr)/cm^{-1} 3021 (ν_{C-Har}), 2925 (ν_{-CH3}, ν_{-CH2}), 2852 (ν_{-CH2}), 1600 (ν_{C-Car}), 1579 (ν_{C-Car}), 1497, 1445 (δ_{-CH2}, δ_{-CH3}), 1414, 1153, 823 (δ_{C-Har}). δ_H (300 MHz, C_6D_6) 8.07 (d, $^3J_{HH}$ 8.2, 2H, H_2), 8.04 (d, $^3J_{HH}$ 7.7, 2H, $H_{2'}$), 7.01 (d, $^3J_{HH}$ 8.5, 2H, H_3), 7.00 (d, $^3J_{HH}$ 8.1, 2H, $H_{3'}$), 2.27 (t, $^3J_{HH}$ 7.4, 2H, $CH_2CH_2CH_2CH_2SH$), 2.10 (q, $^3J_{HH}$ 7.2, 2H, $CH_2CH_2CH_2CH_2SH$), 2.03 (s, 3H, CH_3ar), 1.43–1.15 (m, 4H, $CH_2CH_2CH_2CH_2SH$), 1.05 (t, $^3J_{HH}$ 7.9, 1H, $CH_2CH_2CH_2CH_2SH$). δ_C (75 MHz, C_6D_6) 151.81 (C_1), 151.55 ($C_{1'}$), 145.59 (C_4), 141.32 ($C_{4'}$), 130.01 (C_3), 129.32 ($C_{3'}$), 123.39 ($C_{2'}$), 123.33 (C_2), 35.33 ($CH_2CH_2CH_2CH_2SH$), 33.72 ($CH_2CH_2CH_2CH_2SH$), 29.92 ($CH_2CH_2CH_2CH_2SH$), 24.40 ($CH_2CH_2CH_2CH_2SH$), 21.26 (CH_3ar). *m/z* (EI) 284 (75%, M^+), 165 (32%, $C_{10}H_{13}S^+$), 123 (38%), 91 (100%, $C_7H_7^+$), 65 (15%).

*Deprotection of Azobenzenealkanethioate using MeOH/HCl; 4-[4-((4-Trifluoromethoxyphenyl)diazenyl) phenyl]butanethiol **26a**; Typical Procedure*

To a solution of 4-[4-((4-trifluoromethoxyphenyl)diazenyl) phenyl]butylethanethioate **17a** (1.2 g, 3.4 mmol) in dry methanol (60 mL) was added degassed hydrochloric acid (25%, 2.5 mL). The mixture was refluxed for 24 h under a nitrogen atmosphere (reaction status monitored by TLC). The solvent was removed under vacuum and the residue was dissolved in dichloromethane, washed with water and dried under vacuum. The residue was purified by chromatography on silica gel using light petroleum/diethyl ether (1%) as eluent to yield 4-[4-((4-trifluoromethoxyphenyl)diazenyl)phenyl]butanethiol **26a** as an orange solid.

Yield: 0.7 g (2.0 mmol, 58% yield), orange solid. Mp 28–30°C (Found: C 57.88, H 4.92, N 7.86, S 9.08. Calc. for $C_{17}H_{17}F_3N_2OS$: C 57.62, H 4.84, N 7.90, S 9.05%.) ν_{max}(KBr)/cm^{-1} 2930 (ν_{-CH3}, ν_{-CH2}), 2854 (ν_{-CH2}), 1594 (ν_{C-Car}), 1496, 1460 (δ_{-CH2}, δ_{-CH3}), 1417, 1273, 1170, 860 (δ_{C-Har}). δ_H (500 MHz, C_6D_6) 7.99 (d, $^3J_{HH}$ 8.6, 2H, H_2), 7.77 (d, $^3J_{HH}$ 8.9, 2H, $H_{2'}$), 7.02 (d, $^3J_{HH}$ 8.3, 2H, H_3), 6.90 (d, $^3J_{HH}$ 8.2, 2H, $H_{3'}$), 2.28 (t, $^3J_{HH}$ 7.5, 2H, $CH_2CH_2CH_2CH_2SH$), 2.11 (q, $^3J_{HH}$ 7.3, 2H, $CH_2CH_2CH_2CH_2SH$), 1.44–1.32 (m, 2H, $CH_2CH_2CH_2CH_2SH$), 1.32–1.22 (m, 2H, $CH_2CH_2CH_2CH_2SH$), 1.04 (t, $^3J_{HH}$ 7.8, 1H, $CH_2CH_2CH_2CH_2SH$). δ_C (125 MHz, C_6D_6) 151.47 (C_1), 151.31 ($C_{1'}$), 150.87 (d, $^3J_{CF}$ 1.5, F–$C_{4'}$), 146.48 (C_4), 129.42 (C_3), 124.60 ($C_{2'}$), 123.54 (C_2), 121.51 ($C_{3'}$), 121.06 (q, $^1J_{CF}$ 257.6, CF_3), 35.35 ($CH_2CH_2CH_2CH_2SH$), 33.65 ($CH_2CH_2CH_2CH_2SH$), 29.87 ($CH_2CH_2CH_2CH_2SH$), 24.36 ($CH_2CH_2CH_2CH_2SH$). δ_F (300 MHz, C_6D_6) −57.48. *m/z* (EI) 354 (69%, M^+), 189 (28%, $C_6H_4F_3N_2O^+$), 165 (55%, $C_{10}H_{13}S^+$), 161 (98%, $C_7H_4F_3O^+$), 123 (100%), 95 (77%).

*Methyl 4-[4-(4-Mercaptobutyl)phenyl]diazenyl Benzoate **32a***

The product was purified by chromatography using toluene/dichloromethane (1%) as eluent.

Yield: 0.3 g (0.9 mmol, 70%), orange solid. Mp 78–80°C (Found: C 65.82, H 6.26, N 8.45, S 9.57. Calc. for $C_{18}H_{20}N_2O_2S$: C 65.83, H 6.14, N 8.53, S 9.76%.) ν_{max}(KBr)/cm^{-1} 2930 (ν_{-CH3}, ν_{-CH2}), 2856 (ν_{-CH2}), 1716 ($\nu_{C=O,COOCH3}$), 1601 (ν_{C-Car}), 1496, 1447 (δ_{-CH2}, δ_{-CH3}), 1432, 1281, 1221, 1192, 1141, 1113, 862 (δ_{C-Har}). δ_H (500 MHz, C_6D_6) 8.15 (d, $^3J_{HH}$ 8.7, 2H, $H_{3'}$), 7.97 (d, $^3J_{HH}$ 8.3, 2H, $H_{2'}$), 7.91 (d, $^3J_{HH}$ 8.7, 2H, H_2), 7.01 (d, $^3J_{HH}$ 8.4, 2H, H_3), 3.50 (s, 3H, $COOCH_3$), 2.28 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2CH_2SH$), 2.12 (q, $^3J_{HH}$ 7.3, 2H, $CH_2CH_2CH_2CH_2SH$), 1.43–1.32 (m, 2H, $CH_2CH_2CH_2CH_2SH$), 1.32–1.22 (m, 2H, $CH_2CH_2CH_2CH_2SH$), 1.08 (t, $^3J_{HH}$ 7.8, 1H, $CH_2CH_2CH_2CH_2SH$). δ_C (125 MHz, C_6D_6) 166.06 ($COOCH3$), 155.57 ($C_{1'}$), 151.57 (C_1), 146.77 (C_4), 132.29 ($C_{4'}$), 130.92 ($C_{3'}$), 129.40 (C_3), 123.72 ($C_{2'}$), 122.98 (C_2), 51.75 ($COOCH_3$), 35.37 ($CH_2CH_2CH_2CH_2SH$), 33.69 ($CH_2CH_2CH_2CH_2SH$), 29.83 ($CH_2CH_2CH_2CH_2SH$), 24.38 ($CH_2CH_2CH_2CH_2SH$). *m/z* (EI) 328 (68%, M^+), 165 (81%, $C_{10}H_{13}S^+$), 135 (50%, $C_8H_7O_2$), 123 (100%), 106 (20%, $C_6H_6N_2$ or $C_7H_8N^+$).

4-[4-(4-Mercaptobutyl)phenyl]diazenyl Benzonitrile ***33a***

Yield: 0.6 g (2.0 mmol, 60%), orange solid. Mp 92–94°C (Found: 68.47, H 5.81, N 13.91, 10.74. Calc. for $C_{17}H_{17}N_3S$: C 69.12, H 5.80, N 14.22, S 10.85%.) ν_{max}(KBr)/cm^{-1} 3042 ($\nu_{C–Har}$), 2932 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2853 ($\nu_{–CH2}$), 2226 ($\nu_{–CN}$), 1599 ($\nu_{C–Car}$), 1491, 1454 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1413, 1303, 1221, 1156, 854 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.94 (d, $^3J_{HH}$ 8.4, 2H, $H_{2'}$), 7.56 (d, $^3J_{HH}$ 8.6, 2H, H_2), 7.02 (d, $^3J_{HH}$ 8.3, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ 8.3, 2H, H_3), 2.27 (t, $^3J_{HH}$ 7.4, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$SH), 2.11 (q, $^3J_{HH}$ 7.2, 2H, CH$_2$CH$_2$CH$_2$C*H*$_2$SH), 1.45–1.18 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$SH), 1.06 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$S*H*). δ_C (75 MHz, C_6D_6) 154.49 ($C_{1'}$), 151.37 (C_1), 147.38 (C_4), 133.10 ($C_{3'}$), 129.50 (C_3), 123.77 ($C_{2'}$), 123.21 (C_2), 118.44 (*C*N), 114.31 ($C_{4'}$), 35.38 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.62 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.78 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.34 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). *m/z* (EI) 295 (49%, M$^+$), 181 (27%, $C_{12}H_9N_2^+$), 165 (58%, $C_{10}H_{14}S^+$), 123 (100%), 118 (56%, $C_7H_6N_2$), 106 (93%, $C_6H_6N_2$ or $C_7H_8N^+$), 102 (46%, $C_7H_5N^+$), 91 (34%, $C_7H_7^+$), 77 (15%, $C_6H_5^+$).

4-[4-(3-Mercaptopropyl)phenyl]diazenyl Benzonitrile ***33b***

Only the disulfide could be isolated. The product was purified by vapour crystallization using chloroform as the solvent and pentane as the non-solvent.

Yield: 0.5 g (0.9 mmol, 47%), orange solid. Mp 126–128°C (Found: 68.53, H 5.07, N 15.00, 11.09. Calc. for $C_{16}H_{15}N_3S$: C 68.30, H 5.37, N 14.93, S 11.40%.) ν_{max}(KBr)/cm^{-1} 3033 ($\nu_{C–Har}$), 2928 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2852 ($\nu_{–CH2}$), 2234 ($\nu_{–CN}$), 1600 ($\nu_{C–Car}$), 1493, 1454 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1413, 1288, 1222, 1156, 1109, 851 ($\delta_{C–Har}$). δ_H (400 MHz, C_6D_6) 7.92 (d, $^3J_{HH}$ 8.3, 2H, $H_{2'}$), 7.55 (d, $^3J_{HH}$ 8.6, 2H, H_2), 7.00 (d, $^3J_{HH}$ 8.5, 4H, $H_{3',3}$), 2.42 (q, $^3J_{HH}$ 7.3, 4H, C*H*$_2$CH$_2$C*H*$_2$S), 1.88–1.75 (m, 2H, CH$_2$C*H*$_2$CH$_2$S). δ_C (100 MHz, C_6D_6) 154.41 ($C_{1'}$), 151.47 (C_1), 146.38 (C_4), 133.11 ($C_{3'}$), 129.59 (C_3), 123.83 ($C_{2'}$), 123.20 (C_2), 118.37 (*C*N), 114.47 ($C_{4'}$), 38.02 (CH$_2$CH$_2$*C*H$_2$S), 34.35 (*C*H$_2$CH$_2$CH$_2$S), 30.44 (CH$_2$*C*H$_2$CH$_2$S). *m/z* (EI) 281 (67%, M$^+$), 151 (100%, $C_9H_{11}S^+$), 123 (24%), 118 (28%, $C_7H_6N_2$), 102 (83%, $C_7H_5N^+$), 91 (25%, $C_7H_7^+$).

4-[4-(Phenyldiazenyl)phenyl]butanethiol ***28a***

The mixture was refluxed for 1.5 h and stirred at room temperature for another 1.5 h before the solvent was removed. The product was purified by chromatography on silica gel using dichloromethane/light petroleum 1:4 → 1:3 → 1:1 → 3:1 (+0.5% diethyl ether) as eluent.

Yield: 0.7 g (2.6 mmol, 86%), orange liquid (Found: C 71.11, H 6.73, N 10.36, S 11.99. Calc. for $C_{16}H_{18}N_2S$: C 71.07, H 6.71, N 10.36, S 11.86%.) ν_{max}(KBr)/cm^{-1} 2935 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2853 ($\nu_{–CH2}$), 2226, 1599 ($\nu_{C–Car}$), 1501, 1490, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1413, 1303, 1156, 1140, 854 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 8.09–8.00 (m, 4H, $H_{2',2}$), 7.24–7.15 (m, 2H, $H_{3'}$), 7.13–7.05 (m, 1H, $H_{4'}$), 7.00 (d, $^3J_{HH}$ 8.5, 2H, H_3), 2.26 (t, $^3J_{HH}$ 7.4, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$SH), 2.10 (q, $^3J_{HH}$ 7.2, 2H, CH$_2$CH$_2$CH$_2$C*H*$_2$SH), 1.43–1.18 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$SH), 1.05 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$S*H*). δ_C (75 MHz, C_6D_6) 153.33 ($C_{1'}$), 151.69 (C_1), 145.91 (C_4), 130.93 ($C_{4'}$), 129.33 ($C_{3'}$), 129.29 (C_3), 123.48 ($C_{2'}$), 123.25 (C_2), 35.33 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.69 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.89 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.39 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). *m/z* (EI) 270 (47%, M$^+$), 165 (41%, $C_{10}H_{13}S^+$), 123 (78%), 106 (44%, $C_6H_6N_2$ or $C_7H_8N^+$), 77 (100%, $C_6H_5^+$).

4-[4-((4-Fluorophenyl)diazenyl)phenyl]butanethiol ***29a***

Yield: 1.0 g (3.5 mmol, 87%), orange solid. Mp 42–44°C (Found: C 66.70, H 6.14, N 9.69, S 11.41. Calc. for $C_{16}H_{17}FN_2S$: C 66.64, H 5.94, N 9.71, S 11.12%.) ν_{max}(KBr)/cm^{-1} 2931 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2855 ($\nu_{–CH2}$), 1592 ($\nu_{C–Car}$), 1494, 1460 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1417, 1227, 1150, 1136, 1089, 847 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.98 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.88–7.77 (m, 2H, $H_{2'}$), 7.01 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.84–6.71 (m, 2H, $H_{3'}$), 2.78 (t, $^3J_{HH}$ 7.4, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$SH), 2.11 (q, $^3J_{HH}$ 7.1, 2H, CH$_2$CH$_2$CH$_2$C*H*$_2$SH), 1.44–1.19 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$SH), 1.06 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$S*H*). δ_C (75 MHz, C_6D_6) 164.55 (d, $^1J_{CF}$ 251.3, $C_{4'}$), 151.47 (C_1), 149.69 (d, $^4J_{CF}$ 2.9, $C_{1'}$), 146.01 (C_4), 129.35 (C_3), 125.13 (d, $^3J_{CF}$ 8.8, $C_{2'}$), 123.41 (C_2), 116.14 (d, $^2J_{CF}$ 22.8, $C_{3'}$), 35.34 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.69 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.89 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.38 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). δ_F (300 MHz, C_6D_6) −109.47. *m/z* (EI) 288 (55%, M$^+$), 165 (37%, $C_{10}H_{13}S^+$), 123 (100%, $C_6H_4FN_2^+$), 111 (37%, C_6H_6FN), 95 (82%, $C_6H_4F^+$), 91 (21%, $C_7H_7^+$), 77 (18%, $C_6H_5^+$).

3-[4-((4-Fluorophenyl)diazenyl)phenyl]propanethiol ***29b***

Yield: 0.6 g (2.2 mmol, 69%), orange solid. Mp 43–45°C (Found: C 65.70, H 5.70, N 10.11, S 11.73. Calc. for $C_{15}H_{15}FN_2S$: C 65.67, H 5.51, N 10.21, S 11.69%.) ν_{max}(KBr)/cm^{-1} 3026 ($\nu_{C–Har}$), 2935 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2853 ($\nu_{–CH2}$), 1590 ($\nu_{C–Car}$), 1492, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1415, 1225, 1150, 1136, 1090, 844 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.96 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.88–7.78 (m, 2H, $H_{2'}$), 6.98 (d, $^3J_{HH}$ 8.5, 2H, H_3), 6.84–6.72 (m, 2H, $H_{3'}$), 2.35 (t, $^3J_{HH}$ 7.6, 2H, C*H*$_2$CH$_2$CH$_2$SH), 2.08 (q, $^3J_{HH}$ 7.4, 2H, CH$_2$CH$_2$C*H*$_2$SH), 1.59–1.45 (m, 2H, CH$_2$C*H*$_2$CH$_2$SH), 1.05 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$S*H*). δ_C (75 MHz, C_6D_6) 164.57 (d, $^1J_{CF}$ 251.4, $C_{4'}$), 151.53 (C_1), 149.69 (d, $^4J_{CF}$ 3.1, $C_{1'}$), 145.21 (C_4), 129.42 (C_3), 125.14 (d, $^3J_{CF}$ 8.9, $C_{2'}$), 123.43 (C_2), 116.15 (d, $^2J_{CF}$ 22.8, $C_{3'}$), 35.33 (CH$_2$*C*H$_2$CH$_2$SH), 34.29 (*C*H$_2$CH$_2$CH$_2$SH), 23.93 (CH$_2$CH$_2$*C*H$_2$SH). δ_F (300 MHz, C_6D_6) −109.40. *m/z* (EI) 274 (100%, M$^+$), 151 (74%, $C_9H_{11}S^+$), 123 (37%, $C_6H_4FN_2^+$), 95 (83%, $C_6H_4F^+$), 91 (17%, $C_7H_7^+$).

Deprotection of Azobenzenealkanethioate using Dimethylamine; 4-[4-((4-Trifluoromethylphenyl)diazenyl) phenyl]butanethiol ***27a****; Typical Procedure*

To a solution of 4-[4-((4-trifluoromethylphenyl)diazenyl) phenyl]butylethanethioate **18a** (0.6 g, 1.58 mmol) in dry ethanol (30 mL) was added dimethylamine (0.2 g, 4.6 mmol). The solution was stirred at room temperature for 3 days. The solvent was removed under vacuum and the residue extracted with dichloromethane and water. The organic phase was evaporated to dryness to yield 4-[4-((4-trifluoromethylphenyl)diazenyl)phenyl]butanethiol **27** as an orange solid. The crude product was used without further purification.

Yield: 0.5 g (1.57 mmol, 99%), orange solid. Mp 37–39°C (Found: C 60.28, H 5.37, N 8.26, S 9.45. Calc. for $C_{17}H_{17}F_3N_2S$: C 60.34, H 5.06, N 8.28, S 9.48%.) ν_{max}(KBr)/cm^{-1} 2931 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2859 ($\nu_{–CH2}$), 1610 ($\nu_{C–Car}$), 1503, 1461 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1410, 1321, 1162, 1127, 1103, 849 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.98 (d, $^3J_{HH}$ 8.4, 2H, $H_{2'}$), 7.77 (d,

$^3J_{HH}$ 8.5, 2H, H_2), 7.36 (d, $^3J_{HH}$ 8.5, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ 8.3, 2H, H_3), 2.27 (t, $^3J_{HH}$ 7.4, 2H, CH_2CH$_2$CH$_2$CH$_2$SH), 2.11 (q, $^3J_{HH}$ 7.2, 2H, CH$_2$CH$_2$CH$_2$CH_2SH), 1.42–1.20 (m, 4H, CH$_2$CH_2CH_2CH$_2$SH), 1.05 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$SH). δ_C (75 MHz, C_6D_6) 154.85 ($C_{1'}$), 151.45 (C_1), 146.99 (C_4), 129.46 (d, $^3J_{CF}$ 2.2, F–$C_{4'}$), 126.47 (C_3), 126.46 (q, $^3J_{CF}$ 3.7, $C_{3'}$), 124.64 (q, $^1J_{CF}$ 272.3, CF_3), 123.75 ($C_{2'}$), 123.25 (C_2), 35.37 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.65 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.82 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.35 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). δ_F (300 MHz, C_6D_6) –62.10. *m/z* (EI) 338 (76%, M^+), 165 (89%, $C_{10}H_{13}S^+$), 145 (96%, $C_7H_5F_3^+$), 123 (100%), 91 (21%, $C_7H_7^+$).

4-[4-((4-Chlorophenyl)diazenyl)phenyl]butanethiol ***30a***

The residue was purified by chromatography on silica gel using dichloromethane/light petroleum 1:4 → 7:3, followed by only dichloromethane as eluent.

Yield: 0.7 g (2.4 mmol, 72%), orange solid. Mp 74–76°C (Found: C 62.86, H 5.85, N 9.14, S 10.78. Calc. for $C_{16}H_{17}ClN_2S$: C 63.04, H 5.62, N 9.19, S 10.52%.) ν_{max}(KBr)/cm^{-1} 3023 ($\nu_{C–Har}$), 2929 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2852 ($\nu_{–CH2}$), 1574 ($\nu_{C–Car}$), 1480, 1452 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1413, 1150, 1098, 1083, 842 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.99 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.75 (d, $^3J_{HH}$ 8.8, 2H, $H_{2'}$), 7.10 (d, $^3J_{HH}$ 8.8, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ 8.5, 2H, H_3), 2.27 (t, $^3J_{HH}$ 6.9, 2H, CH_2CH$_2$CH$_2$CH$_2$SH), 2.10 (q, $^3J_{HH}$ 7.2, 2H, CH$_2$CH$_2$CH$_2$CH_2SH), 1.44–1.18 (m, 4H, CH$_2$CH_2CH_2CH$_2$SH), 1.05 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$SH). δ_C (75 MHz, C_6D_6) 151.51 ($C_{1'}$), 151.45 (C_1), 146.30 (C_4), 136.87 ($C_{4'}$), 129.55 ($C_{3'}$), 129.38 (C_3), 124.42 ($C_{2'}$), 123.52 (C_2) 35.35 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.66 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.86 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.37 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). *m/z* (EI) 304 (84%, M^+), 165 (86%, $C_{10}H_{13}S^+$), 139 (29%, $C_6H_4ClN_2^+$), 123 (100%), 107 (100%, $C_7H_9N^+$), 90 (28%, $C_4H_{10}S$).

3-[4-((4-Chlorophenyl)diazenyl)phenyl]propanethiol ***30b***

We obtained a mixture of thiol and disulfide. The purification is similar to compound **30a**.

Yield of disulfide: 0.4 g (0.7 mmol, 31%), orange solid. Mp 123–126°C

Yield of thiol: 0.3 g (1.0 mmol, 46%), orange solid. Mp 74–76°C (Found for thiol: C 62.05, H 5.42, N 9.57, S 10.91. Calc. for $C_{15}H_{15}ClN_2S$: C 61.95, H 5.20, N 9.63, S 11.03%.) ν_{max}(KBr)/cm^{-1} 3025 ($\nu_{C–Har}$), 2931 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2855 ($\nu_{–CH2}$), 1574 ($\nu_{C–Car}$), 1479, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1413, 1296, 1217, 1149, 1103, 1083, 840 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.96 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.75 (d, $^3J_{HH}$ 8.8, 2H, $H_{2'}$), 7.10 (d, $^3J_{HH}$ 8.8, 2H, $H_{3'}$), 6.97 (d, $^3J_{HH}$ 8.4, 2H, H_3), 2.35 (t, $^3J_{HH}$ 7.6, 2H, CH_2CH$_2$CH$_2$SH), 2.07 (q, $^3J_{HH}$ 7.4, 2H, CH$_2$CH$_2$CH_2SH), 1.59–1.44 (m, 2H, CH$_2$CH_2CH$_2$SH), 1.03 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$SH). δ_C (75 MHz, C_6D_6) 151.56 ($C_{1'}$), 151.53 (C_1), 145.50 (C_4), 136.92 ($C_{4'}$), 129.56 ($C_{3'}$), 129.46 (C_3), 124.42 ($C_{2'}$), 123.55 (C_2) 35.30 (CH$_2$*C*H$_2$CH$_2$SH), 34.30 (*C*H$_2$CH$_2$CH$_2$SH), 23.91 (CH$_2$CH$_2$*C*H$_2$SH). *m/z* (EI) 290 (78%, M^+), 151 (50%, $C_9H_{11}S^+$), 139 (15%, $C_6H_4ClN_2^+$), 123 (15%), 111 (57%), 91 (16%, $C_6H_4Cl^+$).

4-[4-((4-Bromophenyl)diazenyl)phenyl]butanethiol ***31a***

Purification is the same as for compound **30a**.

Yield: 0.6 g (1.7 mmol, 56%), orange solid. Mp 86–88°C (Found: C 55.04, H 5.19, N 8.01, S 8.85. Calc. for $C_{16}H_{17}BrN_2S$: 55.02, H 4.91, N 8.02, S 9.81.) ν_{max}(KBr)/cm^{-1} 3043 ($\nu_{C–Har}$), 2930 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2854 ($\nu_{–CH2}$), 1571 ($\nu_{C–Car}$), 1476, 1456 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1396, 1155, 1096, 1063, 1005, 837 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.96 (d, $^3J_{HH}$ 8.3, 2H, H_2), 7.66 (d, $^3J_{HH}$ 8.7, 2H, $H_{2'}$), 7.27 (d, $^3J_{HH}$ 8.7, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ 8.3, 2H, H_3), 2.27 (t, $^3J_{HH}$ 7.4, 2H, CH_2CH$_2$CH$_2$CH$_2$SH), 2.11 (q, $^3J_{HH}$ 7.2, 2H, CH$_2$CH$_2$CH$_2$CH_2SH), 1.43–1.18 (m, 4H, CH$_2$CH_2CH_2CH$_2$SH), 1.06 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$CH$_2$SH). δ_C (75 MHz, C_6D_6) 151.83 ($C_{1'}$), 151.45 (C_1), 146.34 (C_4), 132.54 ($C_{3'}$), 129.37 (C_3), 125.37 ($C_{4'}$), 124.63 ($C_{2'}$), 123.53 (C_2), 35.36 (*C*H$_2$CH$_2$CH$_2$CH$_2$SH), 33.67 (CH$_2$CH$_2$*C*H$_2$CH$_2$SH), 29.84 (CH$_2$*C*H$_2$CH$_2$CH$_2$SH), 24.39 (CH$_2$CH$_2$CH$_2$*C*H$_2$SH). *m/z* (EI) 350 (100%, M^+), 348 (96%, M^+), 165 (63%, $C_{10}H_{13}S^+$), 155 (52%, C_6H_5Br), 123 (66%), 90 (21%, $C_4H_{10}S$).

*Deprotection of Azobenzenealkanethioate using MeOH/K_2CO_3; 3-[4-(*p*-Tolyldiazenyl)phenyl] propanethiol* ***25b****; Typical Procedure*

To a solution of 3-[4-(*p*-tolyldiazenyl)phenyl]propyl ethanethioate **16b** (0.9 g, 2.9 mmol) in dry methanol (80 mL) was added degassed K_2CO_3 (3.4 g, 25 mmol). The mixture was stirred for 1.5 h until degassed hydrochloric acid (25%, 7 mL) was added and the solvent removed under vacuum. The residue was dissolved in dichloromethane, washed with water and dried under vacuum. The product was purified by chromatography on silica gel using dichloromethane/light petroleum (1/9 → 1/4) and diethyl ether (1%) as eluent to yield 3-(4-(*p*-tolyldiazenyl)phenyl)propanethiol **25b**.

Yield: 0.7 g (2.4 mmol, 84%), orange solid. Mp 57–59°C (Found: C 71.09, H 6.84, N 10.31, S 11.84. Calc. for $C_{16}H_{18}N_2S$: C 71.07, H 6.71, N 10.36, S 11.86%.) ν_{max}(KBr)/cm^{-1} 3023 ($\nu_{C–Har}$), 2923 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2854 ($\nu_{–CH2}$), 1599 ($\nu_{C–Car}$), 1579 ($\nu_{C–Car}$), 1496, 1437, 1415, 1153, 823 ($\delta_{C–Har}$). δ_H (400 MHz, C_6D_6) 8.03 (d, $^3J_{HH}$ 8.0, 4H, $H_{2,2'}$), 7.01 (d, $^3J_{HH}$ 8.3, 2H, H_3), 6.98 (d, $^3J_{HH}$ 8.4, 2H, $H_{3'}$), 2.35 (t, $^3J_{HH}$ 7.6, 2H, CH_2CH$_2$CH$_2$SH), 2.08 (q, $^3J_{HH}$ 7.4, 2H, CH$_2$CH$_2$CH_2SH), 2.04 (s, 3H, CH_3ar), 1.59–1.43 (m, 2H, CH$_2$CH_2CH$_2$SH), 1.05 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$SH). δ_C (100 MHz, C_6D_6) 151.79 (C_1), 151.49 ($C_{1'}$), 144.79 (C_4), 141.39 ($C_{4'}$), 130.09 ($C_{3'}$), 129.39 (C_3), 123.42 ($C_{2'}$), 123.34 (C_2), 35.39 (CH$_2$*C*H$_2$CH$_2$SH), 34.28 (*C*H$_2$CH$_2$CH$_2$SH), 23.95 (CH$_2$CH$_2$*C*H$_2$SH), 21.28 (*C*H$_3$ar). *m/z* (EI) 270 (81%, M^+), 151 (50%, $C_9H_{11}S^+$), 119 (28%, $C_7H_7N_2^+$), 107 (31%, $C_7H_9N^+$), 91 (100%, $C_7H_7^+$).

3-[4-((4-Trifluoromethoxyphenyl)diazenyl)phenyl] propanethiol ***26b***

Yield: 0.7 g (2.1 mmol, 81%), orange solid. Mp 44–46°C (Found C 56.41, H 4.78, N 8.06, S 9.43. Calc. for $C_{16}H_{15}F_3N_2OS$: C 56.46, H 4.44, N 8.23, S 9.42%.) ν_{max}(KBr)/cm^{-1} 3025 ($\nu_{C–Har}$), 2935 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2860 ($\nu_{–CH2}$), 1603 ($\nu_{C–Car}$), 1593 ($\nu_{C–Car}$), 1494, 1458 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1417, 1245, 1201, 1167, 1100, 837 ($\delta_{C–Har}$). δ_H (500 MHz, C_6D_6) 7.96 (d, $^3J_{HH}$ 8.3, 2H, H_2), 7.77 (d, $^3J_{HH}$ 8.9, 2H, $H_{2'}$), 6.97 (d, $^3J_{HH}$ 8.4, 2H, H_3), 6.90 (d, $^3J_{HH}$ 8.2, 2H, $H_{3'}$), 2.35 (t, $^3J_{HH}$ 7.6, 2H, CH_2CH$_2$CH$_2$SH), 2.07 (q, $^3J_{HH}$ 7.4, 2H, CH$_2$CH$_2$CH_2SH), 1.57–1.48 (m, 2H, CH$_2$CH_2CH$_2$SH), 1.04 (t, $^3J_{HH}$ 7.9, 1H, CH$_2$CH$_2$CH$_2$SH). δ_C (125 MHz, C_6D_6) 151.48 (C_1), 151.27 ($C_{1'}$), 150.88 (d, $^3J_{CF}$ 1.5, F–$C_{4'}$), 145.69 (C_4), 129.49 (C_3), 124.61 ($C_{2'}$), 123.62 (C_2), 121.52 ($C_{3'}$), 121.05 (q, $^1J_{CF}$ 257.7, CF_3), 35.32 (CH$_2$*C*H$_2$CH$_2$SH), 34.28 (*C*H$_2$CH$_2$CH$_2$SH),

23.91 ($CH_2CH_2CH_2SH$). δ_F (300 MHz, C_6D_6) −57.49. *m/z* (EI) 340 (100%, M^+), 189 (18%, $C_6H_4F_3N_2O^+$), 161 (77%, $C_7H_4F_3O^+$), 151 (98%, $M^+ - C_6H_4F_3N_2O^+$), 123 (24%,), 117 (35%,), 91 (21%, $C_7H_7^+$).

3-[4-((4-Trifluoromethylphenyl)diazenyl)phenyl] propanethiol ***27b***

Yield: 0.7 g (2.2 mmol, 81%), orange solid. Mp 50–52°C (Found: C 59.41, H 4.90, N 8.58, S 9.94. Calc. for $C_{16}H_{15}F_3N_2S$: C 59.25, H 4.66, N 8.64, S 9.89%.) ν_{max}(KBr)/cm^{-1} 3055 ($\nu_{C–Har}$), 2936 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2855 ($\nu_{–CH2}$), 1602 ($\nu_{C–Car}$), 1503, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1409, 1315, 1160, 1120, 1100, 849 ($\delta_{C–Har}$). δ_H (400 MHz, C_6D_6) 7.93 (d, $^3J_{HH}$ 8.3, 2H, $H_{2'}$), 7.77 (d, $^3J_{HH}$ 8.2, 2H, H_2), 7.37 (d, $^3J_{HH}$ 8.4, 2H, $H_{3'}$), 6.98 (d, $^3J_{HH}$ 8.2, 2H, H_3), 2.37 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SH$), 2.09 (q, $^3J_{HH}$ 7.3, 2H, $CH_2CH_2CH_2SH$), 1.59–1.49 (m, 2H, $CH_2CH_2CH_2SH$), 1.06 (t, $^3J_{HH}$ 7.9, 1H, $CH_2CH_2CH_2SH$). δ_C (100 MHz, C_6D_6) 154.82 ($C_{1'}$), 151.43 (C_1), 146.20 (C_4), 132.04 (q, $^2J_{CF}$ 32.3, F–$C_{4'}$), 129.49 (C_3), 126.46 (q, $^3J_{CF}$ 3.7, $C_{3'}$), 124.62 (q, $^1J_{CF}$ 272.3, CF_3), 123.75 ($C_{2'}$), 123.26 (C_2), 35.27 ($CH_2CH_2CH_2SH$), 34.31 ($CH_2CH_2CH_2SH$), 23.92 ($CH_2CH_2CH_2SH$). δ_F (300 MHz, C_6D_6) −62.12. *m/z* (EI) 324 (77%, M^+), 151 (100%, $C_9H_{11}S^+$), 145 (59%, $C_7H_5F_3^+$), 123 (20%), 91 (23%, $C_7H_7^+$).

3-[4-(Phenyldiazenyl)phenyl]propanethiol ***28b***

Yield: 0.6 g (2.3 mmol, 69%), orange liquid (Found: C 69.89, H 6.34, N 10.83, S 12.38. Calc. for $C_{15}H_{16}N_2S$: C 70.27, H 6.29, N 10.93, S 12.51%.) ν_{max}(KBr)/cm^{-1} 3064 ($\nu_{C–Har}$), 2928 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2857 ($\nu_{–CH2}$), 2570 ($\nu_{S–H}$), 2543 ($\nu_{S–H}$), 1599 ($\nu_{C–Car}$), 1497, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1441 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1294, 1221, 1151, 1102, 849 ($\delta_{C–Har}$). δ_H (400 MHz, C_6D_6) 8.05 (d, $^3J_{HH}$ 7.5, 2H, $H_{2'}$), 8.00 (d, $^3J_{HH}$ 8.3, 2H, H_2), 7.19 (t, $^3J_{HH}$ 7.6, 2H, $H_{3'}$), 7.09 (t, $^3J_{HH}$ 7.3, 1H, $H_{4'}$), 6.97 (d, $^3J_{HH}$ 8.3, 2H, H_3), 2.35 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SH$), 2.07 (q, $^3J_{HH}$ 7.4, 2H, $CH_2CH_2CH_2SH$), 1.58–1.46 (m, 2 H, $CH_2CH_2CH_2SH$), 1.04 (t, $^3J_{HH}$ 7.9, 1H, $CH_2CH_2CH_2SH$). δ_C (100 MHz, C_6D_6) 153.31 ($C_{1'}$), 151.73 (C_1), 145.10 (C_4), 130.96 ($C_{4'}$), 129.39 ($C_{3'}$), 129.29 (C_3), 123.51 ($C_{2'}$), 123.25 (C_2), 35.34 ($CH_2CH_2CH_2SH$), 34.28 ($CH_2CH_2CH_2SH$), 23.92 ($CH_2CH_2CH_2SH$). *m/z* (EI) 256 (98%, M^+), 222 (20%, $M^+ - SH_2$), 179 (28%, $C_9H_{11}N_2S^+$), 151 (100%, $C_9H_{11}S^+$), 123 (20%), 105 (24%, $C_6H_5N_2^+$), 91 (23%, $C_7H_7^+$), 77 (75%, $C_6H_5^+$), 49 (30%).

3-[4-((4-Bromophenyl)diazenyl)phenyl]propanethiol ***31b***

Yield: 0.7 g (2.1 mmol, 78%), orange solid. Mp 89–91°C (Found: C 53.71, H 4.69, N 8.38, S 9.52. Calc. for $C_{15}H_{15}BrN_2S$: C 53.74, H 4.51, N 8.36, S 9.56%.) ν_{max}(KBr)/cm^{-1} 3025 ($\nu_{C–Har}$), 2932 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2856 ($\nu_{–CH2}$), 1570 ($\nu_{C–Car}$), 1476, 1455 ($\delta_{–CH2}$, $\delta_{–CH3}$), 1394, 1295, 1218, 1150, 1100, 1064, 1002, 837 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 7.95 (d, $^3J_{HH}$ 8.4, 2H, H_2), 7.67 (d, $^3J_{HH}$ 8.8, 2H, $H_{2'}$), 7.27 (d, $^3J_{HH}$ 8.8, 2H, $H_{3'}$), 6.96 (d, $^3J_{HH}$ 8.5, 2H, H_3), 2.34 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SH$), 2.07 (q, $^3J_{HH}$ 7.4, 2H, $CH_2CH_2CH_2SH$), 1.54–1.43 (m, 2H, $CH_2CH_2CH_2SH$), 1.04 (t, $^3J_{HH}$ 7.9, 1H, $CH_2CH_2CH_2SH$). δ_C (75 MHz, C_6D_6) 151.85 ($C_{1'}$), 151.54 (C_1), 145.54 (C_4), 132.56 ($C_{3'}$), 129.45 (C_3), 125.42 ($C_{4'}$), 124.62 ($C_{2'}$), 123.56 (C_2) 35.28 ($CH_2CH_2CH_2SH$), 34.30 ($CH_2CH_2CH_2SH$), 23.92 ($CH_2CH_2CH_2SH$). *m/z* (EI) 336 (55%, M^+), 334 (50%, M^+), 171 (29%, C_6H_6BrN), 167 (33%, $C_9H_{13}NS$), 155 (29%, C_6H_5Br), 151 (100%, $C_9H_{11}S^+$), 123 (18%), 106 (75%, $C_6H_6N_2$ or $C_7H_8N^+$), 91 (18%, $C_7H_7^+$).

Methyl 4-[4-(3-Mercaptopropyl)phenyl]diazenyl Benzoate ***32b****; Separated while Purifying Compound* ***23b***

Yield: 0.2 g (1.0 mmol), orange solid. Mp 87–89°C (Found: C 64.99, H 5.93, N 8.75, S 10.04. Calc. for $C_{17}H_{18}N_2O_2S$: C 64.94, H 5.77, N 8.91, S 10.20%.) ν_{max}(KBr)/cm^{-1} 2934 ($\nu_{–CH3}$, $\nu_{–CH2}$), 2859 ($\nu_{–CH2}$), 1719 ($\nu_{C=O,COOCH3}$), 1601 ($\nu_{C–Car}$), 1497, 1436, 1407, 1279 ($\nu_{C–O,COOCH3}$), 1193, 1145, 1109, 865 ($\delta_{C–Har}$). δ_H (300 MHz, C_6D_6) 8.16 (d, $^3J_{HH}$ 8.7, 2H, $H_{3'}$), 7.97 (d, $^3J_{HH}$ 8.4, 2H, $H_{2'}$), 7.92 (d, $^3J_{HH}$ 8.7, 2H, H_2), 6.97 (d, $^3J_{HH}$ 8.4, 2H, H_3), 3.48 (s, 3H, $COOCH_3$), 2.35 (t, $^3J_{HH}$ 7.6, 2H, $CH_2CH_2CH_2SH$), 2.08 (q, $^3J_{HH}$ 7.4, 2H, $CH_2CH_2CH_2SH$), 1.59–1.43 (m, 2H, $CH_2CH_2CH_2SH$), 1.05 (t, $^3J_{HH}$ 7.9, 1H, $CH_2CH_2CH_2SH$). δ_C (75 MHz, C_6D_6) 166.06 ($COOCH3$), 155.59 ($C_{1'}$), 151.65 (C_1), 145.95 (C_4), 132.36 ($C_{4'}$), 130.94 ($C_{3'}$), 129.47 (C_3), 123.75 ($C_{2'}$), 122.98 (C_2), 51.72 ($COOCH_3$), 35.27 ($CH_2CH_2CH_2SH$), 34.32 ($CH_2CH_2CH_2SH$), 23.92 ($CH_2CH_2CH_2SH$). *m/z* (EI) 314 (74%, M^+), 179 (10%, $C_9H_{11}N_2S^+$), 151 (100%, $C_8H_9NO_2$), 135 (50%, $C_8H_7O_2^+$), 123 (15%), 91 (13%, $C_7H_7^+$).

Accessory Publication

The synthesis and characterization of the compounds **7**–**15**, **16**–**24a**, **b**, and **34** are available on the Journal's website.

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