# A Simple and Practical Synthetic Protocol for Acetalisation, Thioacetalisation and Transthioacetalisation of Carbonyl Compounds under Solvent-Free Conditions

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*Dedicated to Professor G. Mehta on the occasion of his 60th birthday*

**Keywords:** Protecting groups / Carbonyl compounds / Acetals / Dithioacetals / Solvent-free reactions

A wide variety of carbonyl compounds can be converted smoothly to the corresponding acetals on treatment with alcohols or diols and triethyl orthoformate in the presence of a catalytic amount of (bromodimethyl)sulfonium bromide at room temperature. Similarly, various carbonyl compounds can be transformed into the corresponding dithioacetals on reaction with thiol or dithiols at room temperature by employing the same catalyst without any solvent. Moreover, O,O-acetals can also be converted into the corresponding dithioacetals under identical conditions. Some of the major advantages are mild reaction conditions, a high degree of efficiency, compatibilty with other protecting groups and the lack of solvents, particularly for thioacetalisation. In addition, no brominations occur at the double bond or α to the keto position or even in the aromatic ring under these experimental conditions.


## Introduction

The protection of a carbonyl functionality as an acetal[1] or 1,3-dithiane[2] is a very common practice in multi-step organic syntheses. Protection of carbonyl groups as dithioacetals, in particular, is an even more important transformation than to the corresponding acetals due to their higher stability under both acidic and basic reaction conditions. In addition, they also often serve as masked acyl anion equivalents[3] or masked methylene functions[4] in carbon−carbon bond-forming reactions. Moreover, various 1,3-dithiane derivatives play an important role as valuable building blocks in natural product synthesis; this has been reviewed very recently.[5] For example, 2-styryl-1,3-dithiane (**27**) and the 1,3-dithiane derivative **31** have been used recently as key starting materials for the synthesis of kurzilactone[6a] and bicyclic acetals, a precursor present in several polyfunctionalised 1,7-dioxaspiro[5.5]undecane spiroacetal systems,[6b] respectively. Although numerous methods have been developed both for the acetalisation[1] and dithioacetalisation[2] of carbonyl compounds over the years, there is still a need to find better alternatives that work efficiently under mild conditions. Some of the recently employed reagents that can catalyse acetalisation in the presence of trialkyl orthoformates as water scavenger are Amberlyst-15,[7a] $ZrCl_4$,[7b] DDQ,[7c] NBS,[7d] $Sc(NTf_2)_3$,[7e] and TBATB.[7f] Unfortunately, many of these procedures have some drawbacks such as longer reaction times, the need for excess reagents, harsh reaction conditions and the use of expensive reagents. Similarly, some new catalytic procedures have recently been developed for thioacetalisation using LiBr,[8] $LiBF_4$,[9] $InCl_3$,[10] molecular $I_2$,[11] NBS,[12] $Sn(OTf)_3$[13] and $NiCl_2$.[14] Unfortunately, some of these methods also require long reaction times, provide low yields, require a stoichiometric amount of catalyst, involve expensive reagents, require an inert atmosphere for the reaction,[8−12] fail to protect deactivated aromatic substrates[13] and ketonic compounds,[14] or require solvent in order to carry out the transformations. In light of the gradual changes in current working practices to provide greener and more environmentally friendly alternatives,[15] there is a need for a solvent-free and catalytically efficient alternative for the acetalisation and thioacetalisation of carbonyl compounds, which might work under mild and cheaper reaction conditions. As part of our ongoing research project to develop new synthetic methodologies, particularly for the protection and deprotection of carbonyl compounds as oxathioacetals and dithioacetals,[16] we envisioned that (bromodimethyl)sulfonium bromide, which can generate HBr in the reaction medium on reaction with alcohol,[17a] might be a useful catalyst for the protection of carbonyl compounds as acetals and dithioacetals. Previously, (bromodimethyl)sulfonium bromide has been utilised for

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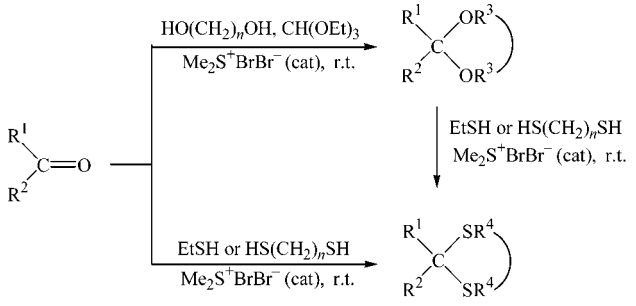
the conversion of alcohols to the corresponding alkyl bromides,[17a] enones to their α-bromoenones,[17b] oxidation of thiols to disulfides[17c] and deprotection of dithioacetals to the corresponding carbonyl compounds.[17d] However, the versatility of this reagent has not been well studied. Very recently, we have demonstrated the utility of this reagent for tetrahydropyranylation/depyranylation of alcohols and phenols.[18] Here we wish to report for the first time a simple and practical synthetic protocol for acetalisation, thioacetalisation and transthioacetalisation using (bromodimethyl)sulfonium bromide as a new catalyst under solvent-free conditions (Scheme 1).




$R^1$ = aryl/alkyl; $R^2$ = H/alkyl; $R^3$ = Me, $-(CH_2)_n-$, $n$ = 2, 3

$R^1$ = aryl/alkyl; $R^2$ = H/alkyl/aryl; $R^4$ = Et, $-(CH_2)_n-$, $n$ = 2, 3

Scheme 1

## Results and Discussion

(Bromodimethyl)sulfonium bromide was prepared by following a literature procedure.[17d] As per our expectation, a mixture of benzaldehyde (5 mmol), 1,2-ethanediol [A] (6 mmol) and triethyl orthoformate (6 mmol) in the presence of (bromodimethyl)sulfonium bromide (0.05 mmol) at room temperature was converted smoothly to the desired 2-phenyl-1,3-dioxolane (**1**) in 82% yield. Similarly, a mixture of benzaldehyde (5 mmol), 1,3-propanediol [B] (6 mmol) and triethyl orthoformate (6 mmol) provided the corresponding 2-phenyl-1,3-dioxane (**2**) in 78% yield at room temperature with a catalytic amount of (bromodimethyl)-sulfonium bromide. Likewise, 4-methoxybenzaldehyde was transformed into the 1,3-dioxane derivative **3** under identical reaction conditions. Subsequently, various aromatic aldehydes such as 4-chlorobenzaldehyde and 4-nitrobenzaldehyde were converted into the corresponding 1,3-dioxolane derivatives **4** and **5** in good yields, on treatment with 1,2-ethanediol in the presence of triethyl orthoformate (which acts as water scavenger) and a catalytic amount of (bromodimethyl)sulfonium bromide at room temperature. By following the above reaction procedure, a wide variety of aldehydes such as phenylacetaldehyde, 4-(*tert*-butyldimethylsilyloxy)benzaldehyde, 4-(allyloxy)benzaldehyde, cinnamaldehyde and the highly acid-sensitive substrate 2-furaldehyde were efficiently transformed into the corresponding 1,3-dioxolanes derivatives **7**, **8**, **9** and **10**, respectively, in fairly good yields. It is noteworthy to mention that the conversion can be achieved without affecting other protecting groups such as allyl and TBS ethers. We have noticed that highly deactivated aromatic aldehydes and acid-sensitive substrates can also be protected to the corresponding acetals in very good yields. Cetylaldehyde does not react with ethylene glycol under the above conditions, but it could be converted smoothly to the corresponding acyclic acetal **11** on treatment with dry methanol under identical conditions.

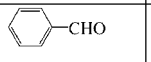
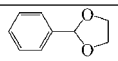
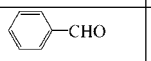
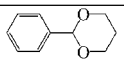
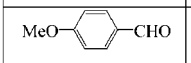
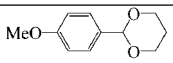
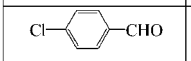
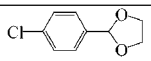
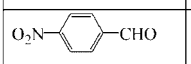
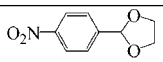
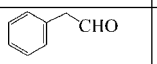
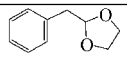
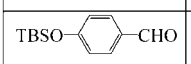
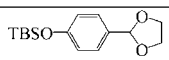
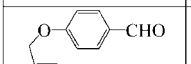
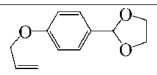
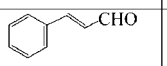
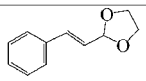
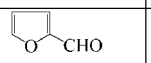
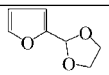
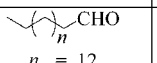
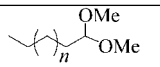
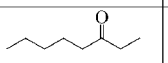
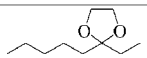
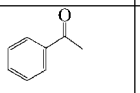
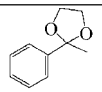
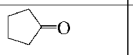
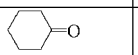
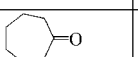
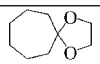
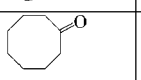
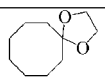
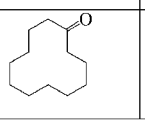
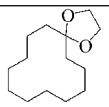
Next, we switched our attention to the protection of various ketonic compounds under identical reaction conditions. By extending our protocol, various 1,3-dioxolane derivatives **12**, **13**, **14**, **15**, **16**, **17** and **18** were prepared from the respective ketones 3-octanone, acetophenone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone and cyclododecanone. The results are summarised in the Table 1 and the products were fully characterised by IR and $^1$H NMR spectroscopy and elemental analysis. The $^1$H NMR spectroscopic data of the compounds **1**, **2**, **9**, **10**, **13**, **14**, **15**, and **16** were also compared with those of the reported compounds in the literature.[19] The results shown in Table 1 clearly indicate the scope and generality of the reaction with respect to various carbonyl compounds. It is also important to highlight that no brominations occur α to the keto positions.

We then turned our attention to whether the same catalyst can be used for thioacetalisation. When a mixture of benzaldehyde (1 mmol) and 1,3-propanedithiol (1.1 mmol) was treated with a catalytic amount of (bromodimethyl)sulfonium bromide (0.05 mmol) without any solvent at room temperature, it was smoothly transformed into the corresponding 2-phenyl-1,3-dithiane (**19**) in very good yield. Compound **19** was characterised by IR, $^1$H NMR and $^{13}$C NMR spectroscopy and elemental analysis. This result encouraged us to investigate further the usefulness of the catalyst. In a similar manner, 4-chlorobenzaldehyde was converted into the corresponding 1,3-dithiane derivative of 4-chlorobenzaldehyde **20** under identical reaction conditions. Likewise, various aromatic aldehydes were converted easily and chemoselectively into the corresponding acyclic or cyclic dithioacetals **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28** and **29**, on treatment with thiol or dithiol in the presence of the same catalyst in solvent-free mode without affecting the other protecting groups such as benzoyl, allyl, cyclohexenyl and TBS ether. These results are summarised in Table 2.

Next we converted phenylacetaldehyde, furfural, heptanal and 5-(*tert*-butyldiphenylsilyloxy)pentanal into the corresponding dithioacetals **30**, **31, 32** and **33**, respectively, under identical reaction conditions depending upon the 1,2-dithiol or 1,3-dithiol used. Moreover, various dithioacetals derivatives **34**−**42** were obtained in very good yields from the corresponding ketones and diketones by employing the same catalyst under solvent-free conditions. Remarkably, by using our protocol both aliphatic and aromatic aldehydes, and various ketones can be transformed easily into the corresponding dithioacetals without non-aqueous work up. All the results are summarised in Table 2. All the products were

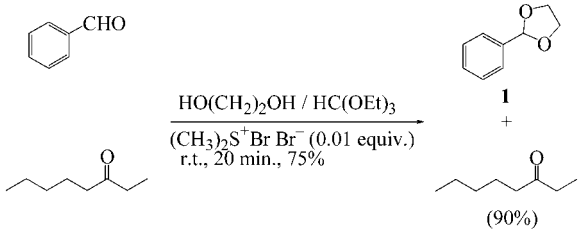
Table 1. Protection of carbonyl compounds to the corresponding acetals by employing 0.01 equiv. of (bromodimethyl)sulfonium bromide as catalyst

| Substrate | Diol or alcohol used[a] | Time min/ [h] | Product[b] | Yield[c] % | Product number[d] |
|---|---|---|---|---|---|
|  | A | 20 |  | 82 | **1**[19a] |
|  | B | 30 |  | 78 | **2**[19b] |
|  | B | 10 |  | 80 | **3** |
|  | A | 20 |  | 75 | **4** |
|  | A | 35 |  | 90 | **5** |
|  | A | 25 |  | 65 | **6** |
|  | A | 30 |  | 72 | **7** |
|  | A | 30 |  | 75 | **8** |
|  | A | 12 |  | 65 | **9**[19c] |
|  | A | 5 |  | 68 | **10**[19c] |
|  $n = 12$ | C | 10 |  $n = 12$ | 75 | **11** |
|  | A | [1] |  | 80 | **12** |
|  | A | 10 |  | 83 | **13**[19d] |
|  | A | 20 |  | 81 | **14**[19d] |
|  | A | 15 |  | 77 | **15** |
|  | A | 50 |  | 68 | **16**[19d] |
|  | A | 20 |  | 87 | **17** |
|  | A | [2] |  | 88 | **18** |

[a] Diol used: A = $HOCH_2CH_2OH$, B = $HOCH_2CH_2CH_2OH$, C = MeOH. [b] Products were characterised by IR, $^1H$ NMR and $^{13}C$ NMR spectroscopy and elemental analysis. [c] Isolated yield. [d] $^1H$ NMR spectroscopic data of the products were compared with the reported literature data.

characterised by recording their IR, $^1H$ NMR and $^{13}C$ NMR spectra and elemental analysis. The NMR spectroscopic data of the compounds as well as melting points of compounds **20**, **23**, **24**, **27**, **35**, **36** and **42** were compared with the reported data.[12,20] It is important to mention that no brominations occur at the double bond, at the α-position of the ketone or even in the highly electron-rich aromatic ring. It is pertinent to mention that a highly acid-sensitive substrate, furfural, can be easily protected under identical conditions at a much faster rate and in much higher yield than reported recently.[11] These results clearly demonstrate the efficiency and generalisation of the procedure. It is worthwhile to mention that thioacetalisation can be carried out with larger amounts of the carbonyl compounds. For example, when a mixture of 4-methoxybenzaldehyde (1.36 g, 10 mmol) and 1,2-ethanedithiol (0.84 mL, 10 mmol) was treated with (bromodimethyl)sulfonium bromide (0.111 g, 0.5 mmol), it was smoothly converted within 3 min into the corresponding 1,3-dithiolane derivative of 4-methoxybenzaldehyde **43**. The product was obtained by recrystallisation without column chromatography in 93% yield (1.98 g), and was characterised by its melting point, and IR and NMR spectra. The capability of (bromodimethyl)sulfonium bromide to promote thioacetalisation on a large scale was also investigated to establish the potential scope of the procedure. To this end, 4-methoxybenzaldehyde (13.6 g, 100 mmol), 1,2-ethanedithiol (8.4 mL, 100 mmol) and (bromodimethyl)sulfonium bromide (1.1 g, 5 mmol) were mixed together at room temperature affording complete conversion in 2−3 min. The pure protected compound was obtained in 95% yield after recrystallisation.

Interestingly, this procedure can be applied for the chemoselective acetalisation of an aldehyde group in the presence of a ketone. For example, when an equimolar mixture of benzaldehyde and 3-octanone, triethyl orthoformate and 1,2-ethanediol was allowed to react in the presence of a catalytic amount of (bromodimethyl)sulfonium bromide only the 1,3-dioxolane derivative of benzaldehyde was obtained in 75% yield with 90% recovery of the 3-octanone (Scheme 2).



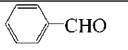
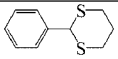
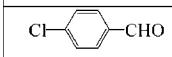
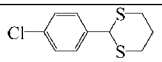
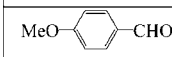
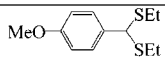
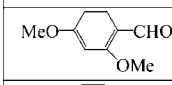
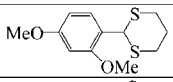
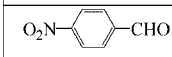
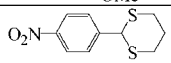
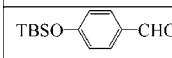
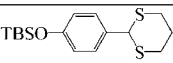
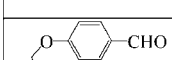
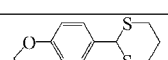
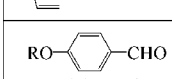
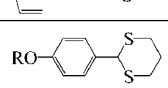
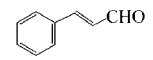
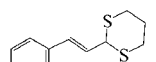
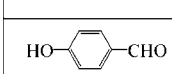
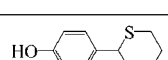
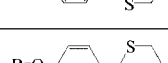
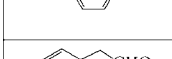
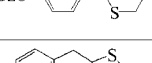

Scheme 2

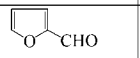
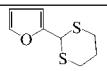
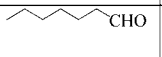
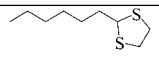
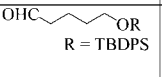
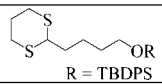
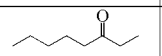
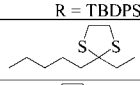
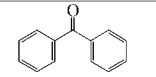
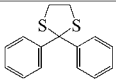
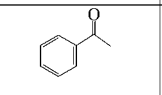
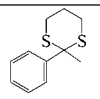
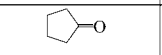
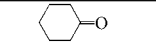
Furthermore, the aldehyde group of the keto aldehyde **44** was chemoselectively protected to the corresponding dithioacetals **45** in the presence of 0.05 equivalents of the same catalyst in 90% yield under solvent-free conditions, as shown in Scheme 3.

Moreover, we have also noticed that the catalyst is equally efficient for the transthioacetalisation of O,O-acetals and O,O-ketals, as represented in Scheme 4.

The formation of acetals and dithioacetals from the carbonyl compounds can be explained as follows. The (bromo-

Table 2. Protection of various carbonyl compounds to the corresponding dithioacetals using (bromodimethyl)sulfonium bromide as catalyst

| Substrate | Thiol or dithiol used[a] | Time min/ [h] | Product[b] | Yield[c] % | Product number[h] |
|---|---|---|---|---|---|
|  | A | 15 |  | 90[d] | **19** |
|  | A | 35 |  | 82[d] | **20**[12] |
|  | B | 25 |  | 86[d] | **21** |
|  | A | 10 |  | 96[d] | **22** |
|  | A | 35 |  | 70[d] | **23**[20a] |
|  | A | 10 |  | 89[d] | **24**[14] |
|  | A | 25 |  | 95[d] | **25** |
|  | A | 25 |  | 91[d] | **26** |
|  | A | 12 |  | 94[d] | **27**[20b] |
|  | A | 10 |  | 95[d] | **28** |
|  | A | 30 |  | 94[d] | **29** |
|  | C | 15 |  | 84[d] | **30** |

| Substrate | Thiol or dithiol used[a] | Time min/ [h] | Product[b] | Yield[c] % | Product number[h] |
|---|---|---|---|---|---|
|  | A | 5 |  | 98[d] | **31** |
|  | C | 7 |  | 65[d] | **32** |
|  | A | 10 |  | 73[d] | **33** |
|  | C | 8 |  | 87[e] | **34** |
|  | C | [12] |  | 83[c] | **35**[20a] |
|  | A | 30 |  | 88[e] | **36**[20a] |
|  | C | 4 |  | 90[e] | **37** |
|  | A | 7 |  | 93[c] | **38** |
|  | C | 6 |  | 83[c] | **39** |
|  | C | 12 |  | 90[c] | **40** |
|  | C | 50 |  | 92[f] | **41** |
|  | C | 60 |  | 89[f] | **42**[20b] |
|  | C | 3 |  | 95[g] | **43** |

[a] Thiol or dithiol used: A = $HSCH_2CH_2CH_2SH$, B = EtSH, C = $HSCH_2CH_2SH$. [b] Products were characterised by IR, $^1H$ NMR and $^{13}C$ NMR spectroscopy and elemental analysis. [c] Isolated yield. [d] The reaction was carried out with 0.05 equivalents of catalyst. [e] The reaction was carried out with 0.15 equivalents of catalyst. [f] The reaction was carried out with 0.30 equivalents of catalyst. [g] The reaction was carried out on a 100 mmol scale. [h] $^1H$ NMR spectroscopic data of the products were compared with the reported literature data.




Scheme 3




Scheme 4

dimethyl)sulfonium bromide catalyst, on reaction with the diol, thiol or dithiol, gives HBr in the reaction medium, which is the actual catalyst for the acetalisation or thioacetalisation. We have also found that the pH of the reaction mixture drops to about 2−3 while carrying out the reaction.

## Conclusion

In conclusion, various carbonyl compounds were efficiently converted into the corresponding acetals at room temperature using triethyl orthoformate as a water scavenger, and (bromodimethyl)sulfonium bromide as a new and efficient catalyst. We have also demonstrated that both acyclic and cyclic dithioacetals can be prepared in very high yields from the corresponding carbonyl compounds using the same catalyst under solvent-free reaction conditions.

This methodology can also be applied on a large scale without the need for solvents or chromatographic separation. In addition, this methodology can be applied for the chemoselective protection of an aldehyde group by acetalisation or thioacetalisation in the presence of a ketone. It is noteworthy that no bromination takes place under these experimental conditions and the reaction can be performed in the presence of other protecting groups without affecting them. Transthioacetalisation is also possible by using the same catalyst.

## Experimental Section

Melting points were recorded with a Büchi B-545 melting point apparatus and are uncorrected. IR spectra were recorded in KBr or neat with a Nicolet Impact 410 spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded with a Bruker 200, Bruker 300 or Jeol 400 MHz spectrometer in $CDCl_3$ using TMS as internal reference. Elemental analyses were carried out with a Perkin−Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyser. Column chromatographic separations were done on SRL silica gel (60−120 mesh).

**General Procedure for Acetalisation:** A catalytic amount of (bromodimethyl)sulfonium bromide (0.011 g, 0.05 mmol) was added to a mixture of the appropriate carbonyl compound (5 mmol), triethyl orthoformate (1 mL, 6 mmol) and 1,2-ethanediol (0.350 mL, 6 mmol) or 1,3-propanediol (0.420 mL, 6 mmol) at room temperature and the mixture stirred until the starting material had disappeared, as monitored by TLC. After completion of the reaction, it was neutralised with $NaHCO_3$ solution and extracted with $CH_2Cl_2$ (2 × 25 mL), washed with water (2 × 15 mL) and dried with anhydrous $Na_2SO_4$. The organic extract was concentrated on a rotary evaporator and the crude residue was finally purified by alumina column chromatography or by distillation under reduced pressure to obtain the desired protected compound.

**2-[4′-Methoxyphenyl]-1,3-dioxane (3):** 0.780 g, 80%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2965, 2842, 1603, 1521, 1465, 1429, 1393, 1321, 1250, 1163, 1106, 1035, 988 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.81 (m, 1 H, $OCH_2CH_aH_bCH_2O$), 2.21 (m, 1 H, $OCH_2CH_aH_bCH_2O$), 3.59 (s, 3 H, $OCH_3$), 3.80 (m, 4 H, 2 × $OCH_2$), 5.20 (s, 1 H, ArCH), 6.84 (d, $J$ = 8.7 Hz, 2 H, ArH), 7.41 (d, $J$ = 8.7 Hz, 2 H, ArH) ppm. $C_{11}H_{14}O_3$ (194.23): calcd. C 68.02, H 7.26; found C 68.19, H 7.16.

**2-[4′-Chlorophenyl]-1,3-dioxolane (4):** 0.690 g, 75%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2975, 2930, 2883, 1603, 1490, 1444, 1403, 1342, 1209, 1116, 1096, 1060, 1014, 922, 846, 809 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.08 (m, 4 H, $OCH_2$), 5.80 (s, 1 H, ArCH), 7.23 (d, $J$ = 8.6 Hz, 2 H, ArH), 7.44 (d, $J$ = 8.4 Hz, 2 H, ArH) ppm. $C_9H_9ClO_2$ (184.62): calcd. C 58.55, H 4.91; found C 58.73, H 4.85.

**2-[4′-Nitrophenyl]-1,3-dioxolane (5):** 0.880 g, 90%. Light yellow solid. IR (KBr): $\tilde{\nu}$ = 2986, 2935, 2883, 1609, 1532, 1347, 1209, 1107, 1055, 1020, 856 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.10 (m, 4 H, 2 × $OCH_2$), 5.90 (s, 1 H, ArCH), 7.66 (d, $J$ = 8.4 Hz, 2 H, ArH), 8.24 (d, $J$ = 8.4 Hz, 2 H, ArH) ppm. $C_9H_9NO_4$ (195.17): calcd. C 55.39, H 4.65, N 7.18; found C 55.28, H 4.59, N 7.01.

**2-[Benzyl]-1,3-dioxolane (6):** 0.530 g, 65%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2981, 2930, 2884, 1609, 1496, 1460, 1378, 1352, 1214, 1132, 1061, 1015 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.94 (d, $J$ = 5.7 Hz, 2 H, $CHCH_2$), 3.40−3.50 (m, 2 H, $OCH_2$), 3.57−3.73 (m, 2 H, $OCH_2$), 4.64 (t, $J$ = 5.7 Hz, 1 H, CH), 7.23 (m, 5 H, ArH) ppm. $C_{10}H_{12}O_2$ (164.20): calcd. C 73.15, H 7.37; found C 73.30, H 7.22.

**2-[4′-(*tert*-Butyldimethylsilyloxy)phenyl]-1,3-dioxolane (7):** 1.0 g, 72%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2986, 2935, 2883, 1609, 1532, 1347, 1209, 1107, 1055, 1020, 856 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.16 [s, 6 H, $Si(CH_3)_2$], 0.92 [s, 9 H, $SiC(CH_3)_3$], 3.84 (m, 4 H, 2 × $OCH_2$), 5.36 (s, 1 H, ArCH), 6.82 (d, $J$ = 8.5 Hz, 2 H, ArH), 7.31 (d, $J$ = 8.5 Hz, 2 H, ArH) ppm. $C_{15}H_{24}O_3Si$ (280.44): calcd. C 64.24, H 8.63; found C 64.53, H 8.56.

**2-[4′-Allyloxyphenyl]-1,3-dioxolane (8):** 0.770 g, 75%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2970, 2883, 1655, 1613, 1555, 1373, 1306, 1244, 1091, 1050, 1029, 994, 927, 835 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.93 (m, 4 H, 2 × $OCH_2$), 4.50 (m, 2 H, $CH_2OAr$), 5.24 (dd, $J$ = 1.4, $J$ = 10.5 Hz, 1 H, $CH_2$=C), 5.29 (dd, $J$ = 1.5, $J$ = 17.3 Hz, 1 H, $CH_2$=C), 5.89 (s, 1 H, OCHO), 6.04 (m, 1 H, CH=C), 6.85 (d, $J$ = 8.7 Hz, 2 H, ArH), 7.35 (d, $J$ = 8.6 Hz, 2 H, ArH) ppm. $C_{12}H_{14}O_3$ (206.24): calcd. C 69.89, H 6.84; found C 69.74, H 6.76.

**Cetylaldehyde Dimethyl Acetal (11):** 1.070 g, 75%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 2924, 2852, 1464, 1383, 1126, 1055 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $J$ = 6.5 Hz, 3 H, $CH_3$), 1.18−1.25 (br. s, 26 H, $CH_2$), 1.55−1.60 (m, 2 H, $CHCH_2$), 3.30 (s, 6 H, 2 × $OCH_3$), 4.35 (t, $J$ = 5.7 Hz, 1 H, CH) ppm. $C_{18}H_{38}O_2$ (286.50): calcd. C 75.46, H 13.37; found C 75.18, H 13.48.

**2-Ethyl-2-pentyl-1,3-dioxolane (12):** 0.690 g, 80%. Colourless liquid. IR (neat): $\tilde{\nu}$ = 3068, 3037, 2975, 2935, 2889, 1470, 1372, 1214, 1176, 1050, 989, 753 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, $J$ = 6.8 Hz, 3 H , $CH_3$), 0.93 (t, $J$ = 6.8 Hz, 3 H, $CH_3$), 1.20−1.40 (m, 6 H, $CH_2$), 1.55−1.65 (m, 4 H, $CH_2$), 3.91−3.96 (m, 4 H, 2 × $OCH_2$) ppm. $C_{10}H_{20}O_2$ (172.27): calcd. C 69.73, H 11.70; found C 69.91, H 11.62.

**1,4-Dioxaspiro[4.7]dodecane (17):** 0.740 g, 87%. Colourless gummy liquid. IR (neat): $\tilde{\nu}$ = 2924, 2873, 1470, 1444, 1378, 1244, 1152, 1111, 1050, 968 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.30−1.42 (m, 10 H, $CH_2$), 1.50−1.64 (m, 4 H, $CH_2$), 3.91 (s, 4 H, 2 × $OCH_2$) ppm. $C_{10}H_{18}O_2$ (170.25): calcd. C 70.55, H 10.66; found C 70.36, H 10.54.

**1,4-Dioxaspiro[4.11]hexadecane (18):** 0.990 g, 88%. Low melting solid. IR (neat): $\tilde{\nu}$ = 2929, 2847, 1470, 1444, 1332, 1224, 1122, 1086, 1055, 1015, 953 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.30−1.42 (m, 18 H, $CH_2$), 1.50−1.64 (m, 4 H, $CH_2$), 3.91 (s, 4 H, 2 × $OCH_2$) ppm. $C_{14}H_{26}O_2$ (226.36): calcd. C 74.29, H 11.58; found C 74.01, H 11.65.

**General Procedure for Thioacetalisation:** A catalytic amount of (bromodimethyl)sulfonium bromide (as indicated in Table 2) was added to a mixture of the carbonyl compound (1 mmol) and thiol (2.2 mmol) or dithiol (1.1 mmol) and the mixture stirred at room temperature. After completion of the reaction, it was neutralised with two drops of saturated $NaHCO_3$ solution. Then, the reaction mixture was passed directly through a silica gel column without aqueous work up to get the desired dithioacetal. In the case of a large-scale reaction (10−100 mmol), the product can be obtained by direct recrystallisation instead of chromatographic separation if the product is solid.

**2-Phenyl-1,3-dithiane (19):** 0.176 g, 90%. White solid; m.p. 74 °C; $SiO_2$-TLC (hexane/EtOAc, 19:1), $R_f$ = 0.94. IR (KBr): $\tilde{\nu}$ = 3037,

2940, 2894, 2827, 1593, 1491, 1429, 1281, 1183, 1066, 912, 728, 697 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.85−1.96 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.09−2.16 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.85−2.90 (m, 2 H, $SCH_2$), 2.99−3.07 (m, 2 H, $SCH_2$), 5.16 (S, 1 H, ArCH), 7.24−7.35 (m, 3 H, ArH), 7.45−7.47 (m, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 24.96, 31.95 (2 C), 51.34, 127.61 (2 C), 128.29, 128.59 (2 C), 138.99 ppm. $C_{10}H_{12}S_2$ (196.34): calcd. C 61.17, H 6.16, S 32.66; found C 61.95, H 6.14, S 32.49.

**4′-Methoxyphenyl Diethyl Dithioacetal (21):** 0.208 g, 86%. White solid; m.p. 43 °C; $SiO_2$-TLC (hexane/EtOAc, 19:1), $R_f$ = 0.94. IR (KBr): ṽ = 2965, 2928, 1609, 1510, 1447, 1301, 1261, 1174, 1106, 1025 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, $J$ = 7.3 Hz, 6 H, 2 × $SCH_2CH_3$), 2.46−2.63 (m, 4 H, 2 × $SCH_2CH_3$), 3.80 (s, 3 H, $OCH_3$), 4.91 (s, 1 H, ArCH), 6.85 (d, $J$ = 8.6 Hz, 2 H, ArH), 7.37 (d, $J$ = 8.5 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.24 (2 C), 26.15 (2 C), 51.69, 55.22, 113.75 (2 C), 128.77 (2 C), 132.37, 159.00 ppm. $C_{12}H_{18}OS_2$ (242.41): calcd. C 59.46, H 7.48, S 26.46; found C 59.65, H 7.59, S 26.22.

**2-[2′,4′-Dimethoxyphenyl]-1,3-dithiane (22):** 0.246 g, 96%. White solid; m.p. 103 °C; $SiO_2$-TLC (hexane/EtOAc, 9:1), $R_f$ = 0.83. IR (KBr): ṽ = 2996, 2939, 2893, 2837, 1618, 1505, 1454, 1424, 1326, 1290, 1116, 1039, 992 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.85−1.92 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.12−2.17 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.84−2.90 (m, 2 H, $SCH_2$), 3.05−3.16 (m, 2 H, $SCH_2$), 3.78 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 5.61 (S, 1 H, ArCH), 6.42 (d, $J$ = 2.4 Hz, 1 H, ArH), 6.48 (dd, $J$ = 2.4, $J$ = 8.5 Hz, 1 H, ArH), 7.48 (d, $J$ = 8.5 Hz, 1 H, ArH) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 25.20, 32.41 (2 C), 43.10, 55.30, 55.60, 98.50, 104.70, 119.80, 129.70, 156.40, 160.60 ppm. $C_{12}H_{16}O_2S_2$ (256.39): calcd. C 56.22, H 6.29, S 25.01; found C 56.01, H 6.36, S 25.14.

**2-[4′-Allyloxyphenyl]-1,3-dithiane (25):** 0.239 g, 95%. White solid; m.p. 81 °C; $SiO_2$-TLC (hexane/EtOAc, 99:1), $R_f$ = 0.66. IR (KBr): ṽ = 2914, 1603, 1506, 1429, 1245, 1183, 1015, 779 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.84−1.97 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.11−2.17 (m, 1 H, $SCH_2CH_aH_b$ $CH_2S$), 2.86−2.91 (m, 2 H, $SCH_2$), 3.00−3.14 (m, 2 H, $SCH_2$), 4.50−4.52 (m, 2 H, $OCH_2CH$=$CH_2$), 5.13 (s, 1 H, ArCH), 5.27 (dd, $J$ = 3.0, $J$ = 10.6 Hz, 1 H, $OCH_2CH$=$CH_aH_b$), 5.39 (dd, $J$ = 3.2, $J$ = 17.1 Hz, 1 H, $OCH_2CH$=$CH_aH_b$), 5.98−6.08 (m, 1 H, $OCH_2CH$=$CH_aH_b$), 6.87 (d, $J$ = 8.8 Hz, 2 H, ArH), 7.38 (d, $J$ = 8.8 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 24.97, 32.10 (2 C), 50.66, 68.81, 114.86 (2 C), 118.26, 128.86 (2 C), 131.34, 133.03, 158.49 ppm. $C_{13}H_{16}OS_2$ (252.40): calcd. C 61.86, H 6.39, S 25.41; found C 61.69, H 6.32, S 25.18.

**2-[4′-(Cyclohexenyloxy)phenyl]-1,3-dithiane (26):** 0.266 g, 91%. White solid; m.p. 103−104 °C; $SiO_2$-TLC (hexane/ /EtOAc, 99:1), $R_f$ = 0.45. IR (KBr): ṽ = 2933, 1605, 1509, 1242, 1168 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.57−1.65 (m, 2 H, $CH_2$), 1.76−1.89 (m, 2 H, $CH_2$), 1.91−2.03 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.05−2.18 (m, 3 H, $SCH_2CH_aH_b$ $CH_2S$ and $CH_2$), 2.84−2.92 (m, 2 H, $SCH_2$), 3.01−3.15 (m, 2 H, $SCH_2$), 3.54−3.55(m, 1 H, CH=CHCHO), 5.10 (s, 1 H, ArCH), 5.81 (dd, $J$ = 2.0, $J$ = 10.0 Hz, 1 H, CH=CHCHO), 6.03−6.08 (m, 1 H, $CH_2CH$=CHCHO), 6.87 (d, $J$ = 8.8 Hz, 2 H, ArH), 7.37 (d, $J$ = 8.8 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 21.37, 24.93, 25.04, 29.80, 32.24 (2 C), 38.08, 50.94, 116.38, 126.87, 128.95, 129.36, 131.00, 131.18 (2 C), 154.14 ppm. $C_{16}H_{20}OS_2$ (292.47): calcd. C 65.71, H 6.89, S 21.93; found C 65.52, H 6.81, S 21.79.

**2-[4′-Hydroxyphenyl]-1,3-dithiane (28):** 0.201 g, 95%; m.p. 158 °C; $SiO_2$-TLC (hexane/EtOAc, 9:1), $R_f$ = 0.36. IR (KBr): ṽ = 3370, 2940, 2894, 2807, 1609, 1516, 1450, 1363, 1250, 1173, 1112, 851, 774 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.85−1.96 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.12−2.19 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.86−2.92 (m, 2 H, $SCH_2$), 3.01−3.08 (m, 2 H, $SCH_2$), 5.12 (S, 1 H, ArCH), 6.77 (d, $J$ = 8.2 Hz, 2 H, ArH), 7.31 (d, $J$ = 8.3 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 25.06, 32.18 (2 C), 50.74, 115.58 (2 C), 129.18 (2 C), 131.45, 155.61 ppm. $C_{10}H_{12}OS_2$ (212.34): calcd. C 56.56, H 5.70, S 32.20; found C 56.34, H 5.63, S 32.01.

**2-[4′-(Benzoyloxy)phenyl]-1,3-dithiane (29):** 0.297 g, 94%; m.p. 163−164 °C; $SiO_2$-TLC (hexane/EtOAc, 9:1), $R_f$ = 0.36. IR (KBr): ṽ = 3068, 2955, 2894, 1731, 1593, 1506, 1424, 1265, 1204, 1168, 1071, 1020, 886, 769, 707 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.88−1.98 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.15−2.18 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.89−2.93 (m, 2 H, $SCH_2$), 3.03−3.09 (m, 2 H, $SCH_2$), 5.20 (S, 1 H, ArCH), 7.20 (d, $J$ = 8.8 Hz, 2 H, ArH), 7.51 (m, 2 H, ArH), 7.53 (d, $J$ = 8.5 Hz, 2 H, ArH), 7.63 (m, 1 H, ArH), 8.18 (m, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 25.04, 32.03 (2 C), 50.72, 121.95 (2 C), 128.57 (2 C), 129.03 (2 C), 129.43, 130.17 (2 C), 133.64, 136.74, 150.80, 164.95 ppm. $C_{17}H_{16}O_2S_2$ (316.44): calcd. C 64.53, H 5.10, S 20.27; found C 64.35, H 5.03, S 20.01.

**2-Benzyl-1,3-dithiolane (30):** 0.165 g, 84%. Colourless liquid; $SiO_2$-TLC (hexane/EtOAc, 9:1), $R_f$ = 0.36. IR (neat): ṽ = 3037, 2925, 2843, 1598, 1501, 1424, 1286, 1132, 1030, 846, 738 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 3.04 (d, $J$ = 7.1 Hz, 2 H, $PhCH_2$), 3.08−3.21 (m, 4 H, 2 × $SCH_2$), 4.66 (t, $J$ = 7.1 Hz, 1 H, $PhCH_2CH$), 7.16−7.26 (m, 5 H, ArH) ppm. $C_{10}H_{12}S_2$ (196.34): calcd. C 61.17, H 6.16, S 32.66; found C 61.31, H 6.10, S 32.43.

**2-Furfuryl-1,3-dithiane (31):** 0.182 g, 98%. Pale yellow liquid; $SiO_2$-TLC (hexane/EtOAc, 19:1), $R_f$ = 0.63. IR (neat): ṽ = 2899, 1495, 1424, 1275, 1163, 1014, 748 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.92−2.01 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.08- 2.16 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.88−2.93 (m, 4 H, 2 × $SCH_2$), 5.20 (s, 1 H, SCHS), 6.32 (dd, $J$ = 2.0, $J$ = 3.2 Hz, 1 H, H-4), 6.37 (d, $J$ = 3.1 Hz, 1 H, H-3), 7.34 (d, $J$ = 1.9 Hz, 1 H, H-5) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 25.22, 30.24 (2 C), 41.99, 107.83, 110.56, 142.27, 151.66 ppm. $C_8H_{10}OS_2$ (186.30): calcd. C 51.58, H 5.41, S 34.42; found C 51.39, H 5.33, S 34.23.

**2-Hexyl-1,3-dithiolane (32):** 0.123 g, 65%. Colourless liquid; $SiO_2$-TLC (hexane/EtOAc, 99:1), $R_f$ = 0.4. IR (neat): ṽ = 2960, 2929, 2852, 1465, 1429, 1383, 1275, 1102, 979, 855, 728 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, $J$ = 6.6 Hz, 3 H, $CH_3$), 1.25−1.42 (m, 8 H, $CH_2$), 1.76−1.82 (m, 2 H, $CH_2CHS$), 3.14−3.25 (m, 4 H, 2 × $SCH_2$), 4.44 (t, $J$ = 7.08 Hz, 1 H, SCHS) ppm. $C_9H_{18}S_2$ (190.37): calcd. C 56.78, H 9.53, S 33.69; found C 56.49, H 9.46, S 33.51.

**2-[4′-(*tert*-Butyldiphenylsilyloxy)butane]-1,3-dithiane (33):** 0.314 g, 73%. Colourless liquid; $SiO_2$-TLC (hexane/EtOAc, 95:5), $R_f$ = 0.70. IR (neat): ṽ = 3068, 2935, 2863, 1588, 1434, 1260, 1107, 835, 748, 707. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.57−1.59 (m, 2 H, $CH_2$), 1.75−1.79 (m, 3 H, $CH_2$ and $SCH_2CH_aH_bCH_2S$), 1.83−1.93 (m, 1 H, $SCH_2CH_aH_bCH_2S$), 2.58−2.69 (m, 4 H, $SCH_2$ and $CH_2$), 2.71−2.83 (m, 2 H, $SCH_2$), 3.65 (t, $J$ = 5.8 Hz, 2 H, $OCH_2$), 4.00 (t, $J$ = 7.1 Hz, 1 H, CH), 7.34−7.42 (m, 5 H, ArH), 7.64−7.67 (m, 5 H, ArH) ppm. $C_{24}H_{34}OS_2Si$ (430.75): calcd. C 66.92, H 7.96, S 14.89; found C 66.78, H 7.84, S 15.02.

**2-Ethyl-2-pentyl-1,3-dithiolane (34):** 0.177 g, 87%. Colourless liquid; $SiO_2$-TLC (hexane/EtOAc, 19:1), $R_f$ = 0.83. IR (neat): ṽ =

2960, 2930, 2853, 1465, 1373, 1276, 1148, 984, 892, 851, 810, 733, 692 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, $J$ = 7.0 Hz, 3 H, $CH_3$), 0.99 (t, $J$ = 7.30 Hz, 3 H, $CH_3$), 1.21−1.31 (m, 4 H, $CH_2$), 1.38−1.46 (m, 2 H, $CH_2$), 1.84−1.93 (m, 4 H, $CH_2$), 3.21 (br. s, 4 H, $SCH_2$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 11.16, 14.01, 22.53, 26.58, 31.95, 36.12, 39.37 (2 C), 42.88, 72.41 ppm. $C_{10}H_{20}S_2$ (204.40): calcd. C 58.76, H 9.86, S 31.38; found C 58.54, H 9.79, S 31.09.

**1,4-Dithiaspiro[4.4]nonane (37):** 0.144 g, 90%. Colourless liquid; $SiO_2$-TLC (hexane), $R_f$ = 0.92. IR (neat): ṽ = 2960, 2924, 2878, 1449, 1275, 1168, 1101, 978, 851, 692 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.74−1.77 (m, 4 H, $CH_2$), 2.07−2.14 (m, 4 H, $CH_2$), 3.30 (s, 4 H, 2 × $SCH_2$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 24.48 (2 C), 39.37 (2 C), 43.92 (2 C), 70.86 ppm. $C_7H_{12}S_2$ (160.30): calcd. C 52.45, H 7.55, S 40.00; found C 52.12, H 7.50, S 39.85.

**1,4-Dithiaspiro[5.5]decane (38):** 0.175 g, 93%. Colourless Liquid; $SiO_2$-TLC (hexane/ethyl acetate, 99:1); $R_f$ = 0.75. IR (neat): ṽ = 2930, 2853, 1440, 1265, 1127, 1015, 907, 861, 764 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.43−1.49 (m, 2 H, $CH_2$), 1.60−1.67 (m, 4 H, $CH_2$), 1.96−2.02 (m, 6 H, $SCH_2CH_2CH_2S$ and 2 × $CH_2$), 2.79−2.83 (m, 4 H, 2 × $SCH_2$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 21.97 (2 C), 25.79 (2 C), 25.87, 26.12, 37.86 (2 C), 50.32 ppm. $C_9H_{16}S_2$ (188.36): calcd. C 57.39, H 8.56, S 34.05; found C 57.14, H 8.50, S 34.23.

**1,4-Dithiaspiro[4.6]undecane (39):** 0.156 g, 83%. White solid; m.p. 56 °C; $SiO_2$-TLC (hexane); $R_f$ = 0.75. IR (KBr): ṽ = 2919, 2842, 1460, 1424, 1275, 1244, 1234, 1152, 1101, 963, 846, 692 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.57 (m, 8 H, $CH_2$), 2.17−2.19 (m, 4 H, $CH_2$), 3.26 (s, 4 H, $SCH_2$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 25.62 (2 C), 28.55 (2 C), 38.84 (2 C), 46.11 (2 C), 71.88 ppm. $C_9H_{16}S_2$ (188.36): calcd. C 57.39, H 8.56, S 34.05; found C 57.18, H 8.48, S 33.87.

**1,4-Dithiaspiro[4.11]hexadecane (40):** 0.232 g, 90%. White solid; m.p. 88 °C; $SiO_2$-TLC (hexane); $R_f$ = 0.81. IR (KBr): ṽ = 2955, 2858, 1470, 1440, 1045, 799, 738, 687 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.18−1.51 (m, 18 H, $CH_2$), 1.95 (dd, $J$ = 7.6, $J$ = 8.3 Hz, 4 H, $CH_2$), 3.22 (s, 4 H, $SCH_2$) ppm. $C_{14}H_{26}S_2$ (258.49): calcd. C 65.05, H 10.14, S 24.81; found C 65.30, H 10.06, S 24.63.

**1,3-Dithiolanes 41 of *cis*-Bicyclo[3.3.0]octane-3,7-dione:** 0.266 g, 92%. White solid; m.p. 176−177 °C; $SiO_2$-TLC (hexane); $R_f$ = 0.62. IR (KBr): ṽ = 2957, 2920, 2843, 1426, 1275, 1210, 974 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.05 (dd, $J$ = 7.1, $J$ = 13.2 Hz, 4 H, $CH_2$), 2.37−2.40 (dd, $J$ = 7.1, $J$ = 13.2 Hz, 4 H, $CH_2$), 2.79−2.87 (m, 2 H, $CH_2$), 3.26−3.34 (m, 8 H, $SCH_2$) ppm. $C_{12}H_{18}S_4$ (290.54): calcd. C 49.61, H 6.24, S 44.15; found C 49.43, H 6.18, S, 44.10.

**2-[4′-Methoxyphenyl]-1,3-dithiolane (43):** 20.14 g, 95%. White solid; m.p. 65 °C; $SiO_2$-TLC (hexane/EtOAc, 95:5), $R_f$ = 0.88. IR (KBr): ṽ = 1608, 1520, 1256, 1180, 1028 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 3.28−3.35 (m, 2 H, $SCH_2$), 3.44−3.51 (m, 2 H, $SCH_2$), 3.77 (s, 3 H, $OCH_3$), 5.62 (S, 1 H, ArCH), 6.83 (d, $J$ = 8.56 Hz, 2 H, ArH), 7.44 (d, $J$ = 8.76 Hz, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 40.02 (2 C), 55.19, 55.94, 113.74 (2 C), 129.04 (2 C), 131.69, 159.25 ppm. $C_{10}H_{12}OS_2$ (212.33): calcd. C 56.57, H 5.70, S 30.20; found C 56.70, H 5.58, S 30.35.

**Keto Aldehyde 44:** Colourless liquid. IR (neat): ṽ = 2930, 2853, 1726, 1685, 1598, 1450, 1409, 1363, 1276, 1214, 1178, 1076, 1009, 753 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.26−1.33 (m, 6 H, $CH_2$), 1.69−177 (m, 2 H, $CH_2$), 2.42 (ddd, 2 H, $J$ = 2.0, $J$ = 7.6 Hz, $PhCOCH_2$), 2.96 (t, $J$ = 7.3 Hz, 2 H, $CH_2CHO$), 7.46 (t, $J$ = 7.6 Hz, 2 H, ArH), 7.54−7.57 (m, 1 H, ArH), 7.95 (d, $J$ = 8.6 Hz, 2 H, ArH), 9.76 (s, 1 H, CHO) ppm. $C_{14}H_{18}O_2$ (218.29): calcd. C 77.03, H 8.31; found C 77.23, H 8.25.

**Keto Dithioacetal 45:** 0.265 g, 90%. Colourless liquid. IR (neat): ṽ = 2930, 2853, 1685, 1598, 1450, 1368, 1276, 1209, 1102, 1086, 1035, 974, 758 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.18−1.30 (m, 8 H, $CH_2$), 1.63−177 (m, 2 H, $CH_2$), 2.77−2.83 (m, 2 H, $PhCOCH_2$), 2.87−2.94 (m, 2 H, $SCH_2$), 3.11−3.21 (m, 2 H, $SCH_2$), 4.40 (t, $J$ = 7.0 Hz, 1 H, $CH_2CHS$), 7.39 (t, $J$ = 7.6 Hz, 2 H, ArH), 7.48 (t, $J$ = 7.3 Hz, 1 H, ArH), 7.89 (d, $J$ = 7.3 Hz, 2 H, ArH) ppm. $C_{16}H_{22}OS_2$ (294.48): calcd. C 65.26, H 7.53, S 21.78; found C 65.01, H 7.45, S 21.58.

**General Procedure for Transthioacetalisation:** A catalytic amount of (bromodimethyl)sulfonium bromide (as indicated in Scheme 4) was added to a mixture of O,O-acetal or O,O-ketal (1 mmol) and dithiol (1.1 mmol) and the mixture stirred at room temperature. After completion of the reaction, it was neutralised by addition of two drops of saturated $NaHCO_3$ solution. Then, the reaction mixture was purified through a silica gel column to get the required dithioacetal.

**2-[4′-Nitrophenyl]-1,3-dithiolane (46):** 0.204 g, 90%; yellow low melting solid; $SiO_2$-TLC (hexane/EtOAc, 9:1), $R_f$ = 0.85. IR (neat): ṽ = 2930, 2853, 1603, 1521, 1424, 1352, 1317, 1291, 1245, 1112, 1015, 984, 876, 830, 784 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.37−3.43 (m, 2 H, $SCH_2$), 3.45−3.55 (m, 2 H, $SCH_2$), 5.65 (s, 1 H, ArCH), 7.66 (d, $J$ = 8.6 Hz, 2 H, ArH), 8.17 (d, $J$ = 8.7 Hz, 2 H, ArH) ppm. $C_9H_9NO_2S_2$ (227.31): calcd. C 47.56, H, 3.99, N 6.16, S 28.21; found C 47.29, H 3.95, N 6.01, S 28.01.

**2-Methyl-2-phenyl-1,3-dithiolane (47):** 0.176 g, 90%; gummy liquid; $SiO_2$-TLC (hexane/EtOAc, 9.9:0.1), $R_f$ = 0.9. IR (neat): ṽ = 2971, 2935, 1598, 1491, 1445, 1276, 1071, 1030, 774, 702 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, $CH_3$), 3.31−3.47 (m, 4 H, 2 × $SCH_2$), 7.19−7.23 (m, 1 H, ArH), 7.28−7.32 (m, 2 H, ArH); 7.72−7.75 (m, 2 H, ArH) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 33.81, 40.22 (2 C), 68.52, 126.68 (2 C), 126.99, 127.90 (2 C), 145.82 ppm. $C_{10}H_{12}S_2$ (196.34): calcd. C 61.17, H 6.16, S 32.66; found C 61.01, H 6.09, S 32.43.

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