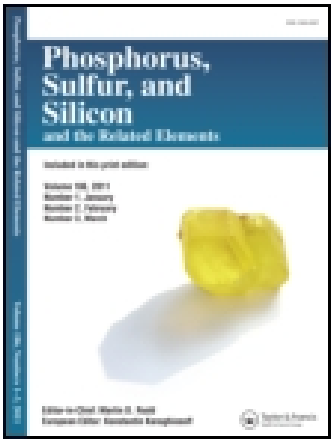

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An Efficient Method for Thioacetalization of Carbonyl Compounds in the Presence of a Catalytic Amount of Benzyltriphenylphosphonium Tribromide Under Solvent-Free Conditions

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A variety of carbonyl compounds have been successfully converted to the corresponding thioacetal derivatives in good to excellent yields on the reaction of carbonyl compounds with 1,2-ethanedithiole, 1,3-propanedithiol, and ethanethiol in the presence of catalytic amount of benzyltriphenylphosphonium tribromide under solvent-free conditions. Some of the major advantages of this method are mild reaction conditions, high efficiency, and compatibility with other reported methods. In addition, no bromination occurs at the double bond, or α to the keto position, or even in the aromatic ring under these experimental conditions.

Keywords Aldehydes; solvent free; thioacetalization; tribromide

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INTRODUCTION

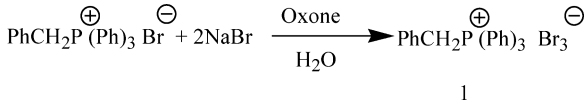
One of the major challenging problems during multistep syntheses is protection of carbonyl functional groups from nucleophilic attack until its electrophilic nature is exploited. For this reason, the protection of carbonyl groups is essential for organic chemists. Among carbonyl protecting groups, dithioacetals constitute an important class of compounds as acyl anion equivalents[1] or masked methylene functions in carbon-carbon bond forming reactions. On the other hand, these substrates are versatile[2] due to their straightforward preparation and also to their stability under basic or mildly acidic conditions. Different methods have been reported for protection of carbonyl compounds,[3–16] but many of these procedures are associated with certain limitations such as low yields, harsh reaction conditions, longer reaction times, and expensive reagents. Therefore milder, simpler, and more efficient alternatives are still desirable for protection of carbonyl compounds.

Organic Ammonium Tribromides (OATB)[17] are extremely useful reagents in organic synthesis particularly for deprotection of dithioacetals,[18] natural product synthesis,[19] deprotection of tButyldimethylsillyl ether (TBDMS)[20] and protection/deprotection of terahydropyran (THP) ethers.[21] Several tribromides have been reported;[22] however, their preparation mostly involves using bromine, which in most cases causes an environmental problem.

RESULTS AND DISCUSSION

In the course of our studies on reaction under solvent-free conditions and developing a new method for transformation of organic functional groups,[23–25] here we introduce a new and environmentally benign method for the synthesis of Benzyltriphenylphosphonium Tribromide (BTPTB) 1 and application of this reagent as a mild and efficient catalyst for protection of the carbonyl functional group.

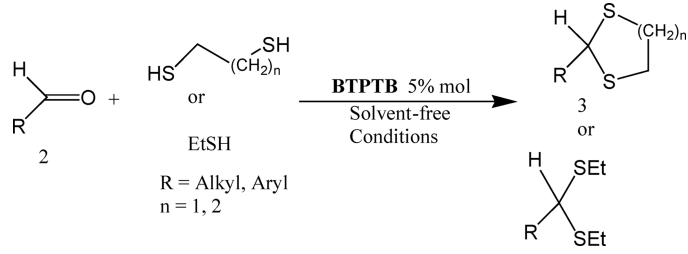
Reagent **1** has been synthesized by dropwise addition of a solution of inexpensive and commercially available Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$) to a solution of benzyltriphenylphosphonium bromide and NaBr in water at r.t. to afford a yellow precipitate in quantitative yields that showed an intense electronic absorbtion at 279 nm typical of tribromide (Scheme 1).[18] Reagent **1** is a very stable compound and can be stored at bench for months without losing its activity. This reagent also is a highly chemoselective catalyst for the conversion of aldehydes in the presence of ketones to the corresponding dithioacetals under solvent-free conditions.



1

SCHEME 1

Initially we tried the protection of aldehydes **2** to the corresponding dithioacetals **3** by 1,2-ethanedithiol, 1,3-propanedithiol, and ethanethiol in a mortar in the presence of 5 mol % of BTPTB at r.t. under solvent-free conditions. This reaction gave dithioacetal derivatives in a 90–98% yield after 3–7 min. The reaction was tried using a wide variety of aldehydes containing electron-withdrawing and electron-donating substituents. The protection of heteroaromatic and α, β-unsaturated aldehydes also were carried out under similar reaction conditions. (Scheme 2, Table I) The reaction proceeded efficiently for aldehydes at ambient temperature in essentially mild and almost neutral conditions. This has been further substantiated by protecting an acid-sensitive substrate such as furfural as its dithioacetals derivative in an almost quantitative yield without the formation of any side products. In addition, no bromination occurred at the double bond, or α to the keto position, or even in the aromatic ring under these experimental conditions.



SCHEME 2

The thioacetalization of ketone **4** with 1,2-ethanedithiol under solvent-free conditions was carried out in the presence of 5 mol% of BTPTB to afford product 5 (Scheme 3). As shown in Table II, in comparison to aldehydes, the reaction times for protection of ketones are longer (1–2 h).

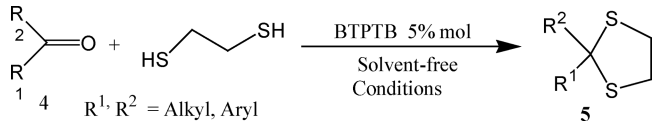
Moreover, this procedure is highly chemoselective, providing selective protection of an aldehyde in the presence of a ketone. Treatment of an equimolar mixture of benzaldehyde and acetophenone in the presence of 1,2-ethanedithiol and a catalytic amount of BTPTB (5 mol%) under solvent-free conditions produced only 1,2-dithiolane derivative of

TABLE I Thioacetalization of Aldehyde 2 with Thiols under Solvent-Free Conditions[a]

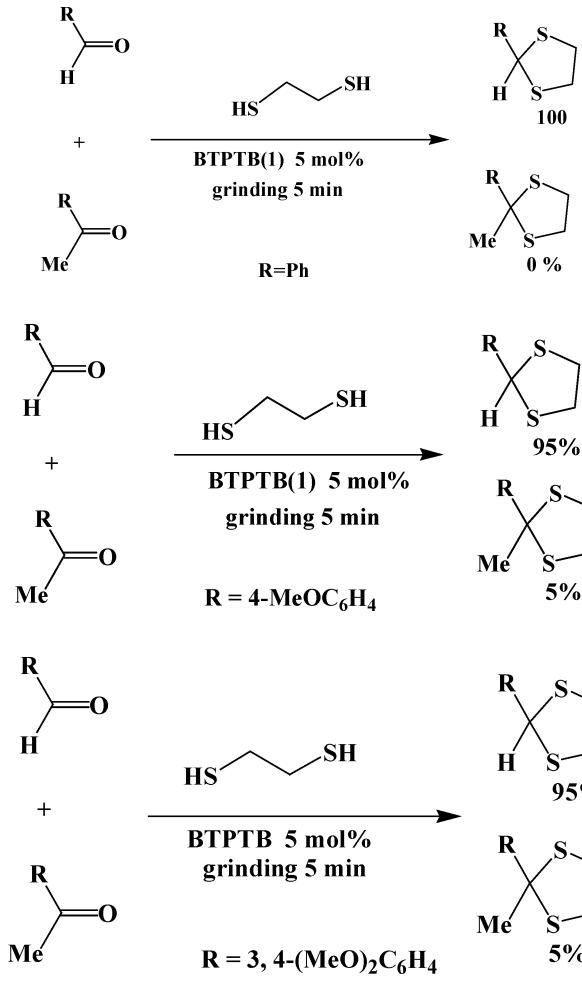
Substrate	R	Protecting Groups	Time (min)	Yield[b] (%)
2a	Ph	$HS(CH_2)_3SH$	5	97
2b	Ph	$HS(CH_2)_2SH$	7	95
2c	4-$(NO_2)C_6H_4$	SEt	7	95
2d	4-$(Cl)C_6H_4$	$HS(CH_2)_2SH$	5	90
2e	4-$(MeO)C_6H_4$	SEt	5	90
2f	4 $(Me_2N)C_6H_4$	SEt	3	90
2g	2-$(MeO)C_6H_4$	$HS(CH_2)_2SH$	7	98
2h	3-$(MeO)C_6H_4$	$HS(CH_2)_2SH$	3	98
2i	4-$(TBSO)C_6H_4$	$HS(CH_2)_3SH$	4	98
2j	4-$(AllylO)C_6H_4$	$HS(CH_2)_3SH$	3	97
2k	4-$(Cyclohexyl)C_6H_4$	$HS(CH_2)_3SH$	4	98
2l	4$(BzO)C_6H_3$	$HS(CH_2)_3SH$	4	98
2m	$PhCH_2$	$HS(CH_2)_3SH$	3	95
2n	4-$(OH)C_6H_4$	$HS(CH_2)_3SH$	3	93
2o	2-Furyl	$HS(CH_2)_3SH$	3	98
2p	4-$(O_2N)C_6H_4$	$HS(CH_2)_2SH$	3	90
2q	PhCH═CH	$HS(CH_2)_3SH$	4	90
2r	n-C_6H_{13}	$HS(CH_2)_2SH$	6	90
2s	TBDPSO-n-C4H8	$HS(CH_2)_3SH$	5	94
2t	4-$(MeO)C_6H_4$	$HS(CH_2)_2SH$	4	98
2u	4-$(Me)C_6H_4$	$HS(CH_2)_2SH$	3	97
2v	4-$(OH)C_6H_4$	$HS(CH_2)_2SH$	4	98
2w	4-(OH)-2-$(MeO)C_6H_4$	$HS(CH_2)_2SH$	5	94
2x	4 $(Me_2N)C_6H_4$	$HS(CH_2)_2SH$	7	91
2y	3-Formyl-hexane	$HS(CH_2)_2SH$	6	94
2z	2,5-$(MeO)_2C_6H_3$	$HS(CH_2)_3SH$	5	92

[a]Confirmed by TLC, GC, IR, ^1H, ^{13}C NMR, and CHN analysis.
[b]Yield of isolated pure product after purification.

benzaldehyde, while the acetophenone was completely recovered back; this competitive reaction illustrates the chemoselectivity of the present method (Eq. (1), Scheme 4). The other competition reactions are shown in Eqs. (1)–(3).



SCHEME 3



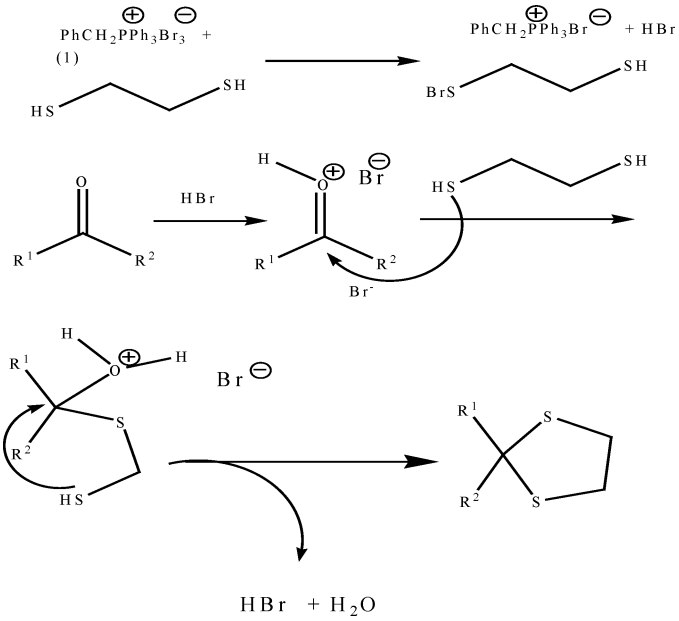
The possible mechanism is shown in Scheme 4; initially BTPTB reacted with 1,2-ethandithiol to generate HBr as a catalyst, and HBr activated as the carbonyl group for further reaction with dithiol to formal hemithioacetal-type intermediate, which by losing an H_2O molecule afforded the corresponding dithioacetal derivatives and HBr (Scheme 4).

Another noteworthy aspect of this procedure is that BTPTB is recyclable. To recover BTPTB, after completing the reaction and isolating the product by ether, the residue was dissolved in water and treated with a new batch of Oxone® and NaBr to produce the catalyst again. This method therefore is also important from the point of view of green chemistry.

TABLE II Thioacetalization of Ketone 4 with 1,2-Ethanedithiol under Solvent-Free Conditions at r.t.[a]

Subtrate	R^1	R^2	Time (h)	Yield (%)[b]
4a	Ph	Me	1.5	98
4b	4-(Me)C_6H_4	Me	1.7	93
4c	4-(Me)C_6H_4	Ph	1.3	93
4d	4-(OH)C_6H_4	Me	1.5	98
4e	4-(Cl)C_6H_4	Me	1.5	95
4f	$C_6H_4CH_2$	Me	1.5	97
4g	Ph	Ph	1.5	91
4h	4-(Br)C_6H_4	Me	2.0	94
4i	$-(CH_2)_4-$		2.0	91
4j	n-Pen	Et	2.0	94
4k	$-(CH_2)_6-$		1.5	96
4l	$-(CH_2)_5-$		2.0	93
4m	$CH_3(CH_2)_4$	Me	1.5	96
4n	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	1.5	97

[a]Confirmed by TLC, GC, IR, ^1H, ^{13}C NMR, and CHN analysis.
[b]Yield of isolated pure product after purification.



SCHEME 4

In summary, we report here an efficient method for protection of aldehydes and ketones with thiols to form the corresponding dithioacetals under solvent-free conditions. This procedure is an efficient method for protection of aliphatic and aromatic ketones and aldehydes since the yields of the products are high and the reaction times are low. The catlyst is stable and may be kept in laboratory for months without loss of activity, which is reproducible and easy to handle.

EXPERIMENTAL

General

All yields refer to isolated products after purification. All of the products were characterized by comparison of their spectral (IR, ^{1}H NMR, TLC, and GC) and physical data (melting or boiling points) with those of authentic samples.[3–17,26–30] All ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ relative to TMS as an internal standard. All ^{13}CNMR spectra were recorded at 75 MHz in $CDCl_3$ relative to TMS as an internal standard. All of the reactions were carried out in a mortar in a hood with strong ventilation.

Procedure for the Preparation of BTPTB

To a solution of BTPTB (0.01 mol, 3.88 g) and sodium bromide (0.023 mol, 2.37 g) in water (100 mL) was add dropwise a solution of Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$) (0.022 mol, 13.65 g) in water (20 mL) under stirring at r.t. until a yellow precipitate was formed. After stirring for 30 min, the mixture was filtered and washed with water (3×30 mL). The filter cake was dried and recrystallized from $CHCl_3$ to afford BTPTB as yellow crystals (4.15 g, 70% yield), m.p.: 136–137°C. IR (**KBr**) υ: 3050 (m), 2950 (s), 1580 (s), 1115 (s), 900 (m) cm^{-1}H NMR: $\delta = 7.22$–7.98 (m, 20H) 4.90 (d, J = 18 Hz, 2H), UV (CH_2Cl_2) λ_{max}: 279 nm. Anal calcd. for $C_{25}H_{22}Br_3P$: C, 50.84%; H, 3.72%. Founder C, 50.74%; H, 3.60%.

Thioacetalization Under Solvent-Free Conditions

In a mortar, a mixture of 1,2-ethanedithiol, 1,3-propanedithiol, or ethanethiol (14 mmol), and BTPTB (0.5 mmol 0.3 g) was added to aldehyde or ketone (10 mmol). The reaction mixture was ground by pestle at r.t. under solvent-free conditions. After disappearance of the starting material (monitored by TLC), the mixture was extracted with diethyl ether (2×20 mL) and filtered. The filtrate was evaporated under reduced pressure, and the resulting crude material was purified by

column chromatography (EtOAc:n-hexane) to afford pure dithioacetal (Tables I and II).

2-Phenyl-1,3-dithiane (3a)

White solid; m.p. 74°C; IR (KBr): 3037, 2940, 2894, 2827, 1593, 1491, 1429, 1281, 1183, 1066, 912, 728, 697 cm^{-1}. ^1H NMR: $\delta = 1.85–1.96$ (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 (125 MHz, $CDCl_3$): $\delta = 24.96$, 31.95 (2 C), 51.34, 127.61 (2 C), 128.29, 128.59 (2 C), 138.99 ppm. Anal calcd. for $C_{10}H_{12}S_2$ (196.34): C, 61.17; H, 6.16; S, 32.66%. Found: C, 61.95, H, 6.14; S, 32.49%.

2-Phenyl 1,3-dithiolane (3b)

IR (neat): 3429, 3060, 3026, 2922, 1690, 1661, 1600, 1494, 1451, 1422, 1276 cm^{-1}. ^1H NMR: $\delta = 3.23–3.46$ (m, 4 H), 5.61 (s, 1 H), 7.19–7.30 (m, 3 H), 7.49 (d, J = 7.10Hz, 2 H). ^{13}C NMR: $\delta = 40.81$ (2 CH_2), 56.82, 128.52, 128.56, 129.02, 140.94.

3-Nitrobenzaldehyde Diethyldithioacetal (3c)

Light yellow oil. ^1H NMR. $\delta = 8.28$ (br d, $J = 1.5$ Hz, 1 H), 8.12 (br dd, $J = 8.0$, 1.5 Hz, 1 H), 7.80 (br dd, $J = 8.0$, 1.5Hz, 1 H), 7.52 (t, $J = 8.0$ Hz, 1 H), 4.92 (s, 1 H), 2.58–2.46 (m, 4 H), 1.22 (t, $J = 7.0$ Hz, 6 H). EIMS: $m/z = 257$ (M^+), 196, 168, 121. Anal. calcd. for $C_{11}H_{15}NO_2S_2$: C, 51.36; H, 7.55; N, 5.45; Found: C, 51.55; H, 7.72; N, 5.38.

2-(4-Chlorophenyl) 1,3-dithiolane (3d)

IR (neat): 3006, 2903, 1486, 1404, 1085, 1012, 754 cm^{-1}. ^1H NMR: $\delta =$ 3.20–3.70 (m, 4 H), 5.58 (s, 1 H), 7.31 (d, J = 8.4Hz, 2 H), 7.41 (d, J = 8.4Hz, 2 H). ^{13}C NMR: $\delta = 40.27$ (2 CH_2), 55.44, 128.57, 129.30, 133.61, 139.02.

4′-Methoxyb Diethenzaldehyde Diethyldithioacetal (3e)

White solid; m.p. 43°C; IR (KBr): 2965, 2928, 1609, 1510, 1447, 1301, 1261, 1174, 1106, 1025 cm^{-1}. ^1H NMR: $\delta = 1.22$ (t, J = 7.3Hz, 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: $\delta = 14.24$ (2 C), 26.15 (2 C), 51.69, 55.22, 113.75

(2 C), 128.77 (2 C), 132.37, 159.00 ppm. Anal. calcd. for $C_{12}H_{18}OS_2$ (242.41): C, 59.46; H, 7.48; S, 26.46%. Found: C, 59.60; H, 7.50; S, 26.20%.

4-N,N-*Dimethylbenzaldehyde Diethyldithioacetal (3f)*

Light yellow oil. ^{1}H NMR: $\delta = 7.30$ (d, $J = 8.0$ Hz, 2 H), 6.68 (d, $J = 8.0$ Hz, 2 H), 4.86 (s, 1 H), 2.98 (s, 6 H), 2.62–2.43 (m, 4 H), 1.16 (t, $J = 7.0$ Hz, 6 H). EIMS: $m/z = 255$ (M^+), 240, 194, 179, 120. Anal. calcd. for $C_{13}H_{21}NS_2$: C, 61.18; H, 8.24; N, 5.49%. Found: C, 61.32; H, 8.17; N, 5.33%.

2-(2-Methoxyphenyl) 1,3-dithiolane (3g)

IR (neat): 3038, 2999, 2923, 2833, 1597, 1488, 1464, 1434, 1316, 1263, 1149, 1047, 862, 779, 749, 693 cm^{-1}. ^{1}H NMR: $\delta = 3.10$–3.45 (m, 4 H), 3.73 (s, 3 H), 5.58 (s, 1 H), 6.76 (d, $J = 7.32$ Hz, 1 H), 7.05–7.21 (m, 3 H). ^{13}C NMR: $\delta = 40.04$ (2 CH_2), 55.08, 56.04, 113.34 (2 C), 120.14, 129.32, 141.91, 159.45.

2-(2-Methoxyphenyl) 1,3-dithiolane (3h)

IR (neat): 3068, 2921, 2777, 1609, 1500, 1487, 1443, 1370, 1249, 1183, 1096, 1038, 927, 866, 750 cm^{-1}. ^{1}H NMR: $\delta = 3.25$–3.53 (m, 4 H), 5.60 (s, 1 H), 5.94 (s, 2 H), 6.69 (d, $J = 8$ Hz, 1 H), 6.91–6.95 (dd, $J = 8$, 1.7Hz, 1 H), 7.10 (d, $J = 1.7$ Hz, 1 H). ^{13}C NMR: $\delta = 40.24$ (2 CH_2), 56.35, 101.20, 107.73, 108.32, 121.35, 133.88, 147.46, 147.85.

2-(4-tert-Butyldimethylsilyloxyphenyl)-1,3-dithiane (3i)

^{1}H NMR: $\delta = 0.19$ (s, 6 H), 0.97 (s, 9 H), 3.26–3.35 (m, 2 H), 3.40–3.66 (m, 2 H), 6.76 (d, J = 8.5Hz, 2 H), 7.38 (d, J = 8.5Hz, 2 H). ^{13}C: $\delta = -4.2$, 19.5, 27.6, 40.5, 57.3, 120.8, 131.7, 134.5, 156.3. MS: m/z = 313 ($M + H^+$), Anal calcd. for $C_{15}H_{24}OS_2Si$: C, 57.64; H, 7.74%. Found: C, 57.60; H, 7.70%.

2-(4′-Allyloxyphenyl)-1,3-dithiane (3j)

White solid; m.p. 81°C; IR (KBr): 2914, 1603, 1506, 1429, 1245, 1183, 1015, 779 cm^{-1}. ^{1}H NMR: $\delta = 1.84$–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: $\delta = 24.97$, 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. Anal. calcd. for

$C_{13}H_{16}OS_2$ (252.40): C, 61.86; H, 6.39; S, 25.41%. Found: C, 61.60; H, 6.30; S, 25.20%.

2-(4′-(Cyclohexenyloxy)phenyl)-1,3-dithiane (3k)

White solid; m.p. 103–104°C; IR (KBr): 2933, 1605, 1509, 1242, 1168 cm^{-1}. ^1H NMR: $\delta = 1.57–1.65$ (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: $\delta = 21.37$, 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. Anal. calcd. for. $C_{16}H_{20}OS_2$ (292.47): C, 65.71; H, 6.89; S, 21.93; Found: C, 65.52; H, 6.81; S, 21.79%.

2-(4′-(Benzoyloxy)phenyl)-1,3-dithiane (3l)

M.p. 163–164°C; IR (KBr): 3068, 2955, 2894, 1731, 1593, 1506, 1424, 1265, 1204, 1168, 1071, 1020, 886, 769, 707 cm^{-1}. ^1H NMR: $\delta = 1.88–1.98$ (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: $\delta = 25.04$, 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. Anal. calcd. for $C_{17}H_{16}O_2S_2$ (316.44): C, 64.53; H, 5.10; S, 20.27%. Found: C, 64.40; H, 5.00; S, 20.00%.

2-Benzyl-1,3-dithiane (3m)

Colorless liquid; IR (neat): 3037, 2925, 2843, 1598, 1501, 1424, 1286, 1132, 1030, 846, 738 cm^{-1}. ^1H NMR: $\delta = 3.04$ (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. Anal. calcd. for $C_{10}H_{12}S_2$ (196.34): C, 61.17; H, 6.16; S, 32.66%. Found: C, 61.30; H, 6.10; S, 32.40%.

2-(4′-Hydroxyphenyl)-1,3-dithiane (3n)

M.p. 158°C; IR (KBr): 3370, 2940, 2894, 2807, 1609, 1516, 1450, 1363, 1250, 1173, 1112, 851, 774 cm^{-1}. ^1H NMR: $\delta = 1.85–1.96$ (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: $\delta = 25.06$, 32.18 (2 C), 50.74, 115.58 (2 C), 129.18 (2 C), 131.45, 155.61

ppm. Anal. calcd. for $C_{10}H_{12}OS_2$ (212.34): C 56.56, H 5.70, S 32.20%. Found: C, 56.30; H, 5.60; S, 32.00%.

2-Furfuryl-1,3-dithiane (3o)

Pale yellow liquid; IR (neat): 2899, 1495, 1424, 1275, 1163, 1014, 748 cm^{-1}. ^1H NMR: $\delta = 1.92–2.01$ (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: $\delta = 25.22$, 30.24 (2 C), 41.99, 107.83, 110.56, 142.27, 151.66 ppm. Anal. calcd. for $C_8H_{10}OS_2$ (186.30): C, 51.58; H, 5.41; S, 34.42%. Found: C, 51.40; H, 5.30; S 34.20%.

2-(4′-Nitrophenyl)-1,3-dithiolane (3p)

Yellow low melting solid; IR (neat): 2930, 2853, 1603, 1521, 1424, 1352, 1317, 1291, 1245, 1112, 1015, 984, 876, 830, 784 cm^{-1}. ^1H NMR: $\delta = 3.37–3.43$ (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. Anal. calcd. for $C_9H_9NO_2S_2$ (227.31): C, 47.56; H, 3.99; N, 6.16; S, 28.21%. Found: C, 47.30; H, 3.90; N, 6.00; S, 28.00%.

2-Styrenyl-1,3-dithiane (3q)

IR (neat): 3083, 3057, 3028, 2963, 2924, 1599, 1576, 1497, 1447, 1434, 1421, 968, 763, 687 cm^{-1}. ^1H NMR: $\delta = 3.24–3.37$ (m, 4 H), 5.21 (d, $J = 9.1$ Hz, 1 H), 6.16–6.25 (dd, $J = 9.1$, 15.5 Hz, 1 H), 6.49 (d, $J = 15.5$ Hz, 1 H), 7.22–7.38 (m, 5 H). ^{13}C NMR: $\delta = 39.59$ (2 CH_2), 54.47, 126.60, 127.81, 128.53, 129.02, 130.14, 136.04.

2-Hexyl-1,3-dithiane (3r)

Colorless liquid; IR (neat): 2960, 2929, 2852, 1465, 1429, 1383, 1275, 1102, 979, 855, 728 cm^{-1}. ^1H NMR: $\delta = 0.85$ (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. Anal. calcd. for $C_9H_{18}S_2$ (190.37): C, 56.78; H, 9.53; S, 33.69%. Found: C, 56.50; H, 9.50; S, 33.50%.

2-(4′-(tert-Butyldiphenylsilyloxy)butyl)-1,3-dithiane (3s)

Colorless liquid; IR (neat): 3068, 2935, 2863, 1588, 1434, 1260, 1107, 835, 748, 707. ^1H NMR: $\delta = 1.04$ (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. Anal.

calcd. for $C_{24}H_{34}OS_2Si$ (430.75): C, 66.92; H, 7.96; S, 14.89%. Found: C, 66.80; H, 7.80; S, 15.00%.

2-(4-Methoxyphenyl)-1,3-dithiolane (3t)

White solid; m.p. 65°C; IR (KBr): 1608, 1520, 1256, 1180, 1028 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): = 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, $CDCl_3$): $\delta = 40.02$ (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): Anal. calcd. for C, 56.57; H, 5.70; S, 30.20%; Found: C, 56.70; H, 5.58; S, 30.35%.

2-(4′-Methylphenyl)-1,3-dithiolane (3u)

IR (neat): 3004, 1510, 1437, 1411, 1277, 1177, 1165, 830, 777 cm^{-1}. ^1H NMR: $\delta = 2.32$ (s, 3 H), 3.29–3.52 (m, 4 H), 5.62 (s, 1 H), 7.10 (d, $J = 6.5$ Hz, 2 H), 7.40 (d, $J = 6.5$ Hz, 2 H). ^{13}C NMR: $\delta = 21.11$, 40.20 (2 CH_2), 56.12, 127.80, 129.15, 137.10, 137.84.

2-(4′-hydroxyphenyl)-1,3-dithiolane (3v)

IR (neat): 3188 (br), 2919, 1595, 1509, 1448, 1237, 1173, 838 cm^{-1}. ^1H NMR: $\delta = 3.30$–3.51 (m, 4 H), 5.00 (s, 1 H), 5.62 (s, 1 H), 6.73–6.79 (m, 2 H), 7.37–7.43 (m, 2 H). ^{13}C NMR: 40.20 (2 CH_2), 56.01, 115.31, 129.41, 131.99, 155.31.

2-(4′-hydroxy-3-methoxyphenyl)-1,3-dithiolane (3w)

IR (thin film): 3434 (br), 2996, 2918, 1607, 1596, 1509, 1464, 1449, 1427, 1266, 1227, 1145, 1118, 1026 cm^{-1}. ^1H NMR: $\delta = 3.29$–3.53 (m, 4 H), 3.88 (s, 3 H), 5.69 (s, 1 H), 6.81 (d, $J = 8.1$ Hz, 1 H), 6.90–7.00 (dd, $J = 8.1$, 1.69Hz, 1 H), 7.09 (s, 1 H). ^{13}C NMR: $\delta = 40.14$ (2 CH_2), 55.91, 56.69, 110.26, 113.97, 121.07, 131.22, 145.54, 146.47.

2-(4′-*N,N*-dimethylphenyl)-1,3-dithiolane (3x)

IR (neat): 757, 824, 949, 1069, 1171, 1230, 1247, 1359, 1443, 1482, 1523, 1609, 2807, 2904, 3054 cm^{-1}. ^1H NMR: $\delta = 2.95$ (s, 6 H), 3.32–3.36 (m, 2 H), 3.48–3.54 (m, 2 H), 5.65 (s, 1 H), 6.81 (d, $J = 6.8$ Hz, 2 H), 7.42 (d, $J = 6.8$ Hz, 2 H). ^{13}C NMR: $\delta = 40.09$ (2 CH_3), 40.80 (2 CH_2), 56.40, 112.60, 125.90, 128.77, 149.88.

2-(3-Formyl)-1,3-dithiolane (3y)

IR (neat): 2955, 2926, 2854, 1735, 1465, 1377, 1275, 851, 725 cm^{-1}. ^1H NMR: $\delta = 0.87$ (t, $J = 7.2$ Hz, 3 H), 1.1–1.47 (m, 8 H), 1.79 (br s, 2 H), 3.18 (br s, 4 H), 4.35–4.45 (m, 1 H). ^{13}C NMR: $\delta = 14.07$, 22.57, 28.89, 29.10, 31.47, 38.34 (2 CH_2), 39.41, 53.81.

2-(2′,4′-Dimethoxyphenyl)-1,3-dithiane (3z)

White solid; m.p. 103°C; IR (KBr): 2996, 2939, 2893, 2837, 1618, 1505, 1454, 1424, 1326, 1290, 1116, 1039, 992 cm^{-1}. ^1H NMR: = 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 = 2.4Hz, 1 H, ArH), 6.48 (dd, J = 2.4, J = 8.5Hz, 1 H, ArH), 7.48 (d, J = 8.5Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): = 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. $C_{12}H_{16}O_2S_2$.

2-Methyl-2-phenyl-1,3-dithiolane (5a)

Gummy liquid; IR (neat): 2971, 2935, 1598, 1491, 1445, 1276, 1071, 1030, 774, 702 cm^{-1}. ^1H NMR: = 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: = 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): Anal. calcd. for C, 61.17; H, 6.16; S, 32.66%; Found: C, 61.01; H, 6.09; S, 32.43%.

2-Methyl-2-p-Tolyl-1,3-dithiolane (5b)

IR (neat): 731, 819, 1018, 1072, 1126, 1185, 1275, 1371, 1443, 1508, 1610, 1654, 2861, 2921, 2965, 3022 cm^{-1}. ^1H NMR: $\delta = 2.14$ (s, 3 H), 2.32 (s, 3 H), 3.30–3.52 (m, 4 H), 7.11 (d, $J = 8$ Hz, 2 H), 7.63 (d, $J = 8$ Hz, 2 H). ^{13}C NMR: $\delta = 20.89$, 33.87, 40.29 (2 CH_2), 68.39, 126.67, 128.64, 136.74, 142.87.

2-Phenyl-2-p-Tolyl-1,3-dithiolane (5c)

IR (thin film): 696, 741, 1032, 1186, 1275, 1443, 1506, 1594, 2874, 2921, 3022, 3056 cm^{-1}. ^1H NMR: $\delta = 2.31$ (s, 3 H), 3.39 (m, 4 H), 7.08 (d, $J = 8.1$ Hz, 2 H), 7.23–7.27 (m, 3 H), 7.48 (d, $J = 8$ Hz, 2 H), 7.60 (m, 2 H). ^{13}C NMR: $\delta = 20.96$, 40.12 (2 CH_2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.77.

2-Methyl-2-(4-hydoxyphenyl)-1,3-dithiolane (5d)

IR (neat): 687, 738, 831, 844, 1074, 1180, 1230, 1273, 1375, 1442, 1508, 1596, 1608, 2876, 2929, 2969, 3225 (br) cm^{-1}. ^1H NMR: $\delta = 2.13$ (s, 3 H), 3.35–3.51 (m, 4 H), 5.60 (br s, 1 H), 6.75 (d, J = 7.7 Hz, 2 H), 7.63 (d, J = 7.7 Hz, 2 H). ^{13}C NMR: $\delta = 33.91, 40.35$ (2 CH_2), 68.22, 114.71, 128.33, 137.73, 154.64.

2-Methyl-2-(4-chlorophenyl)-1,3-dithiolane (5e)

IR (neat): 734, 830, 1011, 1069, 1093, 1275, 1372, 1396, 1422, 1444, 1489, 1570, 1591, 2860, 2922, 2966, 3059 cm^{-1}. ^1H NMR: $\delta = 2.1$ (s, 3 H), 3.30–3.45 (m, 4 H), 7.26 (d, $J = 6.4$ Hz, 2 H), 7.68 (d, $J = 6.4$ Hz, 2 H). ^{13}C NMR: $\delta = 33.46, 40.31$ (2 CH_2), 67.82, 127.87, 128.24, 132.70, 144.55.

2-Benzyl-2-methyl-[1,3]dithiolane (5f)

B.p. 129–130/1.5°C. IR (neat): 3083, 3060, 3027, 2959, 2919, 2856, 1602, 1494, 1452, 1372, 1276, 1083, 752, 698 cm^{-1}. ^1H NMR: $\delta = 1.71$ (s, 3 H), 3.00–3.32 (m, 6 H), 7.15–7.36 (m, 5 H). ^{13}C NMR: d = 31.78, 39.72 (2 CH2), 51.41, 66.59, 126.68, 127.66, 130.69, 137.74.

2,2-Diphenyl-[1,3]dithiolane (5g)

M.p. 105–106°C. IR (thin film): 696, 741, 1032, 1186, 1275, 1443, 1506, 1594, 2874, 2921, 3022, 3056 cm^{-1}. ^1H NMR: $\delta = 3.39$ (m, 4 H), 7.08 (d, $J = 8.1$ Hz, 4 H), 7.23–7.27 (m, 6 H). ^{13}C NMR: $\delta = 40.12$ (2 CH_2), 127.10, 127.73, 127.97, 128.17, 128.64, 136.95, 141.47, 144.7

2-Methyl-2-(4-bromophenyl)-1,3-dithiolane (5h)

IR (neat): 731, 827, 1007, 1077, 1275, 1391, 1486, 1583, 2858, 2922, 2965, 3061 cm^{-1}. ^1H NMR: $\delta = 2.07$ (s, 3 H), 3.30–3.45 (m, 4 H), 7.38 (d, $J = 6.8$ Hz, 2 H), 7.60 (d, $J = 6.8$ Hz, 2 H). ^{13}C NMR: $\delta = 34.10, 41.01$ (2 CH_2), 68.50, 114.03, 129.60, 131.50, 145.76.

1,4-Dithiaspiro(4.4)nonane (5i)

Colorless liquid; IR (neat): 2960, 2924, 2878, 1449, 1275, 1168, 1101, 978, 851, 692 cm^{-1}. ^1H NMR: $\delta = 1.74$–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: $\delta = 24.48$ (2 C),

39.37 (2 C), 43.92 (2 C), 70.86 ppm. $C_7H_{12}S_2$ (160.30): Anal. calcd. for C, 52.45; H, 7.55; S, 40.00%; Found: C, 52.12; H, 7.50; S, 39.85%.

2-Ethyl-2-pentyl-1,3-dithiolane (5j)

Colorless liquid; IR (neat): 2960, 2930, 2853, 1465, 1373, 1276, 1148, 984, 892, 851, 810, 733, 692 cm^{-1}. ^1H NMR: $\delta = 0.85$ (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, $CDCl_3$): = 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): Anal. calcd. for C, 58.76; H, 9.86; S, 31.38%; Found: C, 58.54; H, 9.79; S, 31.09.

1,4-Dithiaspiro(4.6)undecane (5k)

White solid; m.p. 56°C; SiO_2-TLC (hexane). IR (KBr): 2919, 2842, 1460, 1424, 1275, 1244, 1234, 1152, 1101, 963, 846, 692 cm^{-1}. ^1H NMR: $\delta =$ 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: $\delta = 25.62$ (2 C), 28.55 (2 C), 38.84 (2 C), 46.11 (2 C), 71.88 ppm. $C_9H_{16}S_2$ (188.36): Anal. calcd. for C, 57.39; H, 8.56; S, 34.05; Found: C, 57.18; H, 8.48; S, 33.87%.

1,4-Dithiaspiro(5.5)decane (5l)

Colorless liquid; IR (neat): 2930, 2853, 1440, 1265, 1127, 1015, 907, 861, 764 cm^{-1}. ^1H NMR: $\delta = 1.43$–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: $\delta = 21.97$ (2 C), 25.79 (2 C), 25.87, 26.12, 37.86 (2 C), 50.32 ppm. $C_9H_{16}S_2$ (188.36): Anal. calcd. for C, 57.39; H, 8.56; S, 34.05%; Found: C, 57.14; H, 8.50; S, 34.23%.

2-Butyl-2-methyl-1,3-dithiolane (5m)

IR (neat): 686, 733, 852, 972, 1056, 1139, 1276, 1374, 1448, 2859, 2927, 2957 cm^{-1}. ^1H NMR: $\delta = 0.92$ (t, $J = 7.1$ Hz, 3 H), 1.30–1.38 (m, 2 H), 1.43–1.54 (m, 2 H), 1.75 (s, 3 H), 1.90–1.95 (m, 2 H), 3.30 (m, 4 H). ^{13}C NMR: $\delta = 14.00$, 22.90, 29.50, 32.30, 40.00 (2 CH_2), 45.80, 66.80.

2, 2-Dipropyl-1,3-dithiolane (5n)

IR (neat): 2961, 2873, 1707, 1459, 1380, 1275 cm^{-1}. ^1H NMR: $\delta = 0.90$ (t, $J = 7.3$ Hz, 6 H), 1.35–1.63 (m, 4 H), 2.73–2.76 (m, 1 H), 3.13–3.23

(m, 4 H), 4.63 (d, $J = 6.2$ Hz, 1 H). ^{13}C NMR: $\delta = 10.91$ (2 CH_3), 23.94 (2 CH_2), 28.72, 38.42 (2 CH_2), 58.22.

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