# Preparation and Application of Odorless 1,3-Propanedithiol Reagents

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**2-Dodecyl-1,3-propanedithiol (2a) was prepared without a malodorous procedure as an odorless reagent that was usable in place of 1,3-propanedithiol (1) in organic reactions, *e.g.*, in the reduction of azides and protection of carbonyl groups. The 1,3-dithioacetals obtained in the latter reaction were effectively reduced to methylene with Raney nickel and reconverted to the original carbonyl compounds by hydrolysis with *N*-bromosuccinimide in aqueous 2-butanone. In addition, the anion of 1,3-dithiane prepared from 2a and formaldehyde could be utilized as a synthetic equivalent of an anionic carbonyl carbon.**

**Key words** 2-dodecyl-1,3-propanedithiol; odorless 1,3-propanedithiol; dithioacetal; odorless 1,3-dithiane

We have reported the preparation and application of odorless organosulfur reagents that can be used in place of ethanethiol, benzenethiol, phenylmethanethiol, and dimethyl sulfide in organic synthesis.[1—5] The strategy for reducing malodorousness is based on the increase in their molecular weights to raise boiling points and suppress volatilities. For example, dodecanethiol is completely odorless although decanethiol still smells faintly and ethanethiol, as is well known, creates a stench.

1,3-Propanedithiol (**1**) as well as the other organosulfuric reagents mentioned above is an indispensable chemical especially in the protection of carbonyl groups, reduction of carbonyl groups to methylene *via* dithioacetal, and reduction of azides. Polymer-supported 1,3-dithiol[6—8] and ketene dithioacetal derivatives[9—11] were already reported to be odorless 1,3-dithiols, although the preparation of these reagents still requires odorous chemicals such as carbon disulfide and thioacetate. We here report a useful procedure in which neither odorous reagents nor a malodorous work-up are required to prepare odorless 1,3-propanedithiol and 1,3-dithiane derivatives with a long alkyl chain at the C-2 position, and their reactivity in several organic reactions as a part of our study on odorless organosulfuric reagents.

## Results and Discussion

In spite of being a known compound, 2-dodecyl-1,3-propanedithiol (**2a**) was not prepared by the method reported in the literature accompanied by the generation of thioacetate[12,13] but by modifying Shon *et al.*'s method[14] to avoid generating malodorous odors during the reaction. The reaction of dodecyl bromide and diethyl malonate in the presence of sodium ethoxide giving diethyl 2-dodecylmalonate (**3a**) was followed by reduction with lithium aluminum hydride to afford 2-dodecyl-1,3-propanediol (**4a**). Thus the 1,3-diols (**4a**) were derived to give mesylate (**5a**), which was treated with thiourea and successively hydrolyzed with sodium hydroxide. The obtained substance must be reduced once with sodium borohydride to afford **2a** in pure form due to the formation of disulfides (**6a**) by air oxidation during hydrolysis. 2-Decyl-1,3-propanedithiol (**2b**) was prepared in the same way from **3b** *via* **4b**, and **5b** (Chart 1). As expected, **2a** that was reported to form chelates with Au or $^{99m}$Tc was not malodorous,[14,15] while **2b** smelled faintly. Next, the reactivity of **2a** in several organic reactions was compared with that of **1**.

In general, reactions with 1,3-propanedithiol (**1**) proceed much faster than those with alkane thiols in the reaction requiring two equivalents of mercapto groups, since intramolecular nucleophilic attack by the second mercapto group of **1** causes less decrease in the activated entropy in the transition state than the corresponding intermolecular reactions. This could explain why the reduction of azides or dithioacetalization of carbonyl groups proceed more quickly when using **1** than when using alkane thiols. Thus diphenylmethyl azide (**7**)[16] and *p*-bromophenyl azide (**8**) were respectively reduced with **2a** to amines (**9**, **10**) initially. The reaction proceeded in

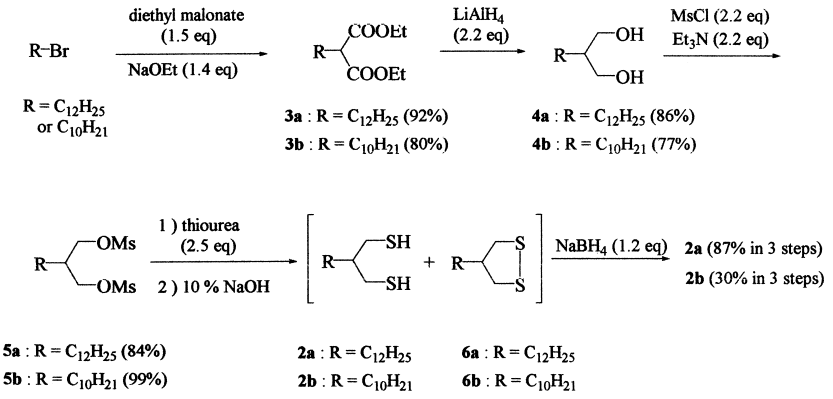


Chart 1. Synthesis of 2-Alkyl-1,3-propanedithiols

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excellent yields accompanied by a mixture of **2a** and **6a**, which was reusable after the reduction with sodium borohydride (Chart 2).

Next, 1,3-dithiol (**2a**) was applied in the reduction of the carbonyl group in ketones to the methylene group *via* dithioacetals. The formation of dithioacetals (**11**—**13**) from carbonyl compounds (**14**—**16**) proceeded in excellent yields using the conventional method (Table 1), and the reduction of **11**—**13** with Raney nickel gave satisfactory results (Table 2). The dithioacetals (**11**—**13**) were obtained as a mixture of *cis*- and *trans*-isomers, of which the ratio was dependent on the structures of ketones. Among them, only compound **12** could be separated on HPLC .

Moreover, hydrolysis of dithioacetals (**17**, **18**) with *N*-bromosuccinimide (NBS)[17] in aqueous 2-butanone gave the original ketones in good yields, while hydrolysis with methyl iodide,[18,19] phenyl iodine(III)bis(trifluoroacetate),[20] and Dess–Martin periodate[21] did not give good results (Table 3).

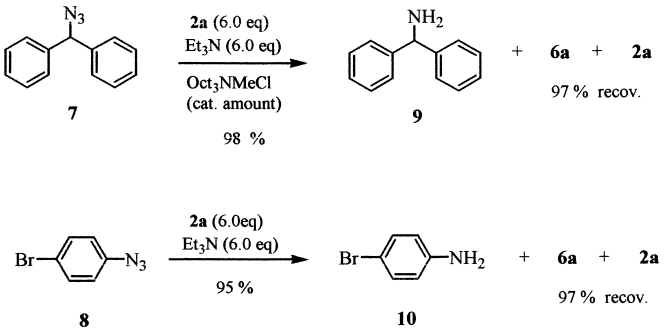
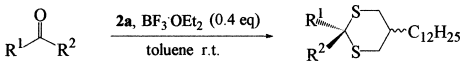


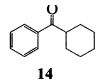
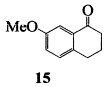
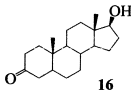

Chart 2. Reduction of Azides into Amines with **2a**

We attempted to use 5-dodecyl-1,3-dithiane (**19**), which can be easily prepared from **2a** and paraformaldehyde in the presence of *p*-toluenesulfonic acid in refluxed benzene, as a precursor of a carbonyl anion equivalent. First, the proton at the C-2 position of **19** was abstracted with *n*-butyllithium to afford the odorless 1,3-dithiane anion. The reaction of the anion with *n*-dodecyl iodide gave *trans*-2,5-didodecyl-1,3-dithiane (**20**) in excellent yield.[22] Deprotonation of 2-substituted 5-dodecyl-1,3-dithianes (**21**, **22**) and successive alkylation with *n*-dodecyl iodide yielded *trans*-2,5-didodecyl-1,3-dithiane derivatives (**23**, **24**), of which the yield was dependent on the bulkiness of the substituent at the C-2 position (Table 4). The *trans*-configuration of **20**, **23**, and **24** was affected by the thermodynamically favorable orientation of the equatorial anion stabilized by the gauche effect,[23] formation of a lithium complex,[24] and $n_c \rightarrow s^*_{s\text{-}c}$ interaction,[25] and other factors reported in the literature.[26—28]

In conclusion, 2-dodecyl-1,3-propanedithiol (**2a**), a useful odorless substitute for 1,3-propanedithiol (**1**) in organic reactions, was prepared without using a malodorous procedure *via* a synthetic route using thiourea as the sulfur source. It was possible to utilize 5-dodecyl-1,3-dithiane (**19**) prepared from **2a** and formaldehyde as an odorless dithiane substitute, *e.g.*, abstraction of the proton at C-2 with *n*-butyllithium or *s*-butyllithium provided a useful synthetic equivalent of anionic carbonyl carbon. It is noteworthy that there are no malodorous procedures either in the preparation of **2a** and **19** or dur-

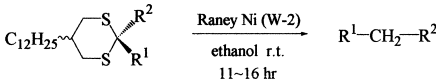
Table 1. Dithioacetalization of Carbonyl Compounds with **2a**




| Entry | Ketones | **2a** (eq) | Time (h) | Product | Yield (%) | Diastereomer ratio[a] |
|---|---|---|---|---|---|---|
| 1 |  **14** | 1.2 | 22 | **11** | 99 | 3 : 1 |
| 2 |  **15** | 1.2 | 24 | **12** | 89 | 4 : 1 |
| 3 |  **16** | 1.2 | 24 | **13** | 98 | —[b] |

*a*) The ratio was determined by $^1$H-NMR on the basis of the integral value of the signals assigned to the protons at C-4 and C-6 on the dithiane rings. *b*) The ratio could not be determined.

Table 2. Reduction of Dithioacetals (**11**—**13**) with Raney Nickel



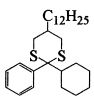
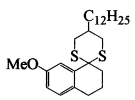
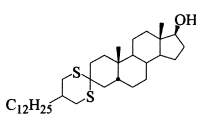
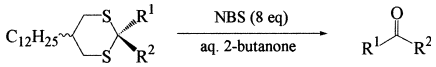

| Entry | 1 | 2 | 3 |
|---|---|---|---|
| Dithioacetals |  **11** |  **12** |  **13** |
| Yield (%) | 78 | 93 | 91 |

Table 3. Hydrolysis of Dithioacetals (**17**, **18**) with NBS



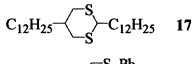
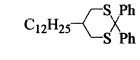
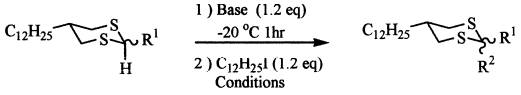
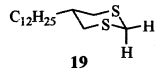
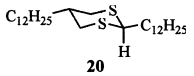
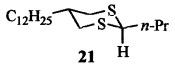
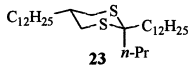
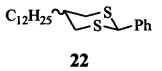
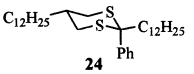

| Entry | Dithioacetals | | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  | **17** | $C_{12}H_{25}$–CHO | 87 |
| 2 |  | **18** |  | 98 |

Table 4. Substitution of Odorless Dithiane (**19**) and Its Derivatives




| Entry | Substrate | Base | Conditions | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 |  **19** | *n*-BuLi | −20 °C to r.t. 14 h |  **20** | 95 |
| 2 |  **21** | *n*-BuLi | 0 °C to r.t. 10 h |  **23** | 73 |
| 3 |  **22** *trans* : *cis* = 7 : 3 | *s*-BuLi | −20 °C to r.t. 28 h |  **24** | 96 |

The stereochemistry of **20**, **21**, **23**, **24** was supported by $^{1}$H–$^{1}$H COSY and NOESY spectra.

ing the work-up of the reactions mentioned above.

## Experimental

**General** Infrared (IR) spectra were recorded on a Shimadzu FTIR-8300 diffraction-grating infrared spectrophotometer and $^{1}$H-NMR spectra were obtained on a JEOL JNM-AL300, Varian XL-300, or Varian Unity INOVA-400 spectrometer with tetramethylsilane as an internal standard. $^{13}$C-NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer with $CDCl_3$ as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC-mate mass spectrometer. Wako gel C-200 (silica gel) (100—200 mesh, Wako) was used for open column chromatography. Flash column chromatography was performed using Silica Gel 60N (Kanto Chemical Co., Inc.) as a solid support in the immobile phase. Kieselgel 60 F-254 plates (Merck) were used for thin-layer chromatography (TLC). Preparative TLC (PTLC) was conducted with Kieselgel 60 F-254 plates (0.25 mm, Merck) or Silica gel 60 F-254 plates (0.5 mm, Merck). Unless purification with silica gel gave a sufficiently pure compound, the compounds were further treated with recycling HPLC (JAI LC-908) on a GPC column (JAIGEL 1H and 2H). When possible, diastereomeric mixtures were also separated with recycling HPLC (JAI LC-908) on a silica gel column (Kusano Si-10) after the purification mentioned above.

**Diethyl 2-Dodecylmalonate (3a)** Sodium ethoxide (19.1 g, 281 mmol) in ethanol (120 ml) was added to a solution of diethyl malonate (48.2 g, 301 mmol) and *n*-dodecyl bromide (50.0 g, 201 mmol) in THF (200 ml) at 0 °C and refluxed for 4 h. After the reaction, the reaction mixture was neutralized with HCl 1 M, condensed *in vacuo*, and extracted with ethyl acetate. The organic layer was successively washed with an aqueous solution of sodium thiosulfate and brine, dried over sodium sulfate, and evaporated. The residue was purified by distillation to afford **3a** (60.4 g, 92%). Colorless oil: bp. 160 °C (3.5 mmHg). $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=7 Hz), 1.27 (6H, t, $J$=7.2 Hz), 1.34—1.20 (20H, m), 1.88 (2H, q, $J$=7.2 Hz), 3.31 (1H, t, $J$=7.6 Hz), 4.20 (4H, q, $J$=7.2 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.06, 14.09, 22.66, 27.30, 28.72, 29.19, 29.30, 29.32, 29.5, 29.6, 29.61, 29.63, 31.2, 52.1, 61.2, 169.9. IR ($CHCl_3$) cm$^{-1}$: 2928, 2855, 1724, 1466, 1371, 1300, 1238, 1178, 1030. HR-MS *m/z*: 328.2613 [Calcd for $C_{19}H_{36}O_4$ ($M^+$): 328.2614]. MS (70 eV) *m/z*: 328 ($M^+$) 283, 173, 160, 133.

**2-Dodecyl-1,3-propanediol (4a)** A solution of 2-diethyl dodecylmalonate (**4a**) (59.0 g, 180 mmol) in THF (150 ml) was added to a suspension of $LiAlH_4$ (15.0 g, 395 mmol) in THF (100 ml) at 0 °C, and the mixture was stirred for 1.5 h at room temperature. After the reaction, water (15 ml), 15% aqueous solution of sodium hydroxide (30 ml), and water (15 ml) were successively added to the reaction mixture, which was filtered through Hyflo Super-Cel. The filtrate was condensed *in vacuo*, and the residue was purified by recrystallization from ethyl acetate to afford 2-dodecyl-1,3-propanediol (**4a**) (37.7 g, 86%). Colorless needles (ethyl acetate): mp 67—68 °C. $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=6.8 Hz), 1.39—1.19 (22H, m), 1.83—1.72 (1H, m), 2.13 (2H, s), 3.66 (2H, d, B part of AB, $J_{AB}$=10.5 Hz, $J$=7.5 Hz), 3.83 (2H, d, A part of AB, $J_{AB}$=10.5 Hz, $J$=3.8 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.3, 22.9, 27.4, 27.9, 29.5, 29.7, 29.82, 29.84, 29.85, 29.86, 30.1, 32.1, 42.2, 67.1. IR ($CHCl_3$) cm$^{-1}$: 3628, 3447, 3034, 3018, 3009, 2928, 2855, 1468, 1423, 1379, 1352, 1238, 1267, 1198, 1022, 960. HR-MS *m/z*: 245.2480 [Calcd for $C_{15}H_{33}O_2$ ($M^+$+1): 245.2476]. MS (CI) *m/z*: 245 ($M^+$+1), 227, 208, 196, 168, 153, 139, 125. *Anal.* Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20. Found: C, 73.95, H, 13.22.

**2-Dodecyl-1,3-propanediol Dimethanesulfonate (5a)** Methanesulfonyl chloride (38.8 g, 339 mmol) and triethylamine (34.3 g, 339 mmol) were added to a suspension of 2-dodecyl-1,3-propanediol (**4a**) (37.7 g, 154 mmol) in ethyl acetate (650 ml) at 0 °C, and the mixture was stirred for 24 h. After the reaction, the reaction mixture was washed with water, dried over sodium sulfate, and evaporated. The residue was purified by recrystallization from ethyl acetate to afford 2-dodecyl-1,3-propanediol dimethanesulfonate (**5a**) (51.8 g, 84%). Colorless needles (ethyl acetate): mp 63—64 °C. $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=7.2 Hz), 1.48—1.18 (22H, m), 2.23—2.09 (1H, m), 3.05 (6H, s), 4.20 (2H, d, B part of AB, $J_{AB}$=10.1 Hz, $J$=6.8 Hz), 4.29 (2H, d, A part of AB, $J_{AB}$=10.1 Hz, $J$=4.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 26.6, 27.0, 29.32, 29.37, 29.49, 29.52, 29.58, 29.61, 29.63, 31.9, 37.3, 38.2, 68.2. IR ($CHCl_3$) cm$^{-1}$: 3036, 2928, 2855, 1468, 1362, 1344, 1265, 1231, 1209, 1176. HR-MS *m/z*: 400.1954 [Calcd for $C_{17}H_{36}O_6S_2$ ($M^+$): 400.1953]. MS (CI) *m/z*: 400 ($M^+$), 304, 208, 193, 180, 166, 152. *Anal.* Calcd for $C_{17}H_{36}O_6S_2$: C, 50.97; H, 9.06. Found: C, 50.86, H, 8.88.

**2-Dodecyl-1,3-propanedithiol (2a)** Thiourea (24.5 g, 322 mmol) was added to a suspension of 2-dodecyl-1,3-propanediol dimethanesulfonate (**5a**) (51.6 g, 129 mmol) in 2-propanol (589 ml), and the mixture was refluxed for 24 h. After the reaction mixture was cooled to room temperature, a 10% aqueous solution of sodium hydroxide (124 ml) was added, and the mixture was refluxed for another 24 h. The reaction was quenched by adding hydrochloric acid 1 M until the pH value reached 1. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford a mixture of 2-dodecyl-1,3-propanedithiol (**2a**) and 4-dodecyl-1,2-dithiorane (**6a**) (31.5 g). To a solution of the mixture in THF and methanol (1 : 1, 380 ml), $NaBH_4$ (5.21 g, 138 mmol) was added at 0 °C, and the mixture was stirred for 2 h. After the reaction, the reaction mixture was acidified to pH 1 with hydrochloric acid 6 M and extracted with *n*-hexane. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford 2-dodecyl-1,3-propanedithol (**2a**) (31.0 g, 87%). Colorless oil: $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=6.4 Hz), 1.20 (2H, t, $J$=8.0 Hz), 1.35—1.18 (20H, m), 1.39 (2H, q, $J$=7 Hz), 1.73—1.63 (1H, m), 2.76—2.59 (4H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 26.7, 26.9, 29.3, 29.54, 29.60, 29.63, 29.66, 29.71, 31.4, 31.9, 42.6. IR ($CHCl_3$) cm$^{-1}$: 3030, 3020, 3009, 2928, 2855, 1466, 1425, 1377, 1342, 1279, 1227, 1207. HR-MS *m/z*: 276.1943 [Calcd for $C_{15}H_{32}S_2$ ($M^+$): 276.1945]. MS (70 eV) *m/z*: 278 ($M^+$+2), 276 ($M^+$), 274.

**Diphenylmethyl Azide (7)**[16] Sodium azide (109.7 mg 1.69 mmol) was

added to a solution of benzhydryl chloride (114.0 mg, 0.562 mmol) in DMF (1 ml), and the reaction mixture was stirred for 4 h at room temperature. After the reaction, the reaction mixture was poured into ice water and extracted with diethyl ether. The organic layer was successively washed with water and brine, dried over magnesium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford diphenylmethyl azide (**7**) (28.0 mg, 24%).

Colorless oil: $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 5.71 (1H, s) 7.43—7.25 (10H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 68.5, 126.5, 127.4, 128.0, 128.5, 128.7. IR ($CHCl_3$) cm$^{-1}$: 3034, 2102, 1603, 1495, 1454. HR-MS *m/z*: 209.0955 [Calcd for $C_{13}H_{11}N_3$ ($M^+$): 209.0953]. MS (70 eV) *m/z*: 209 ($M^+$), 180, 167, 152.

**1-Azido-4-bromobenzene (8)** A solution of 4-bromoaniline (166.1 mg, 0.966 mmol) in hydrochloric acid 6 M (1.0 ml) was added to an aqueous solution (1.2 ml) of sodium nitrite (100 mg, 1.45 mmol) at 0 °C and the mixture was stirred for 1 h. Then, an aqueous solution (2 ml) of sodium azide (251.1 mg, 3.86 mmol) and diethyl ether (4 ml) was added to the solution, and the reaction mixture was stirred for another 2 h at room temperature. After the reaction, water was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was washed with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford 1-azido-4-bromobenzene (**8**) (133 mg, 69%). $^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$: 7.14—7.04 (2H, m), 7.63—7.54 (2H, m). $^{13}$C-NMR (50 MHz, DMSO-$d_6$) $\delta$: 117.1, 121.4, 132.8, 139.0. IR ($CHCl_3$) cm$^{-1}$: 3032, 3022, 2124, 2093, 1883, 1655, 1585, 1482, 1294, 1273, 1128, 1072, 1011. HR-MS *m/z*: 196.9586 [Calcd for $C_6H_4BrN_3$ ($M^+$): 196.9588]. MS (70 eV) *m/z*: 199 ($M^+$+2), 197 ($M^+$), 171, 169.

**1,1-Diphenylmethyl Amine (9)** 2-Dodecyl-1,3-propanedithiol (**2a**) (142.7 mg, 0.516 mmol) was added to a solution of diphenylmethyl azide (**7**) (18.0 mg, 0.0860 mmol), triethylamine (52.2 mg, 0.516 mmol), and trioctylmethylammonium chloride (1 drop) in methanol (1.5 ml) and stirred. 1,1-Diphenylmethylamine (**9**) (15.4 mg, 98%) was finally obtained, and distillation of the residue gave a mixture of **2a** and **6a** (138.3 mg, 97% recovery).

**4-Bromoaniline (10)** 2-Dodecyl-1,3-propanedithiol (**2a**) (393.3 mg, 1.422 mmol) was added to a solution of 1-azido-4-bromobenzene (**8**) (47.0 mg, 0.237 mmol) and triethylamine (143.8 mg, 1.422 mmol) in methanol (2 ml) and stirred. 4-Bromoaniline (**10**) (38.6 mg, 95%) was finally obtained, and distillation of the residue gave a mixture of **2a** and **6a** (373.7 mg, 95% recovery).

**2-Cyclohexyl-5-dodecyl-2-phenyl-1,3-dithiane (11)** Cyclohexyl phenyl ketone (**14**) (79.9 mg, 0.424 mmol) and boron trifluoride diethylether complex (24.0 mg, 0.170 mmol) were added to a solution of **2a** (140.8 mg, 0.509 mmol) in toluene at 0 °C, and the reaction mixture was stirred at room temperature. After the reaction, saturated aqueous solution of sodium bicarbonate was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford 2-cyclohexyl-5-dodecyl-2-phenyl-1,3-dithiane (**11**) (188 mg, 99%). Colorless oil: a mixture of *cis*- and *trans*-isomers. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.34—0.84 (31H, m), 1.74—1.62 (2H, m), 1.90—1.76 (2H, m), 2.06—1.92 (2H, m), 2.62—2.54 (1.6H, m), 2.31—2.22 (1.6 H, m), 2.51—2.45 (0.4H, m), 2.81—2.77 (0.4H, m), 7.27—7.25 (1H, m), 7.39—7.35 (2H, m), 7.93—7.90 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 26.2, 26.3, 26.6, 27.9, 28.2, 29.3, 29.4, 29.5, 29.6, 32.2, 32.9, 33.2, 36.3, 36.4, 50.2, 64.8, 126.5, 127.8, 128.0, 130.3. IR ($CHCl_3$) cm$^{-1}$: 2928, 2855, 1600, 1215, 1204. HR-MS *m/z*: 446.3048 [Calcd for $C_{28}H_{46}S_2$ ($M^+$): 446.3041]. MS (70 eV) *m/z*: 446 ($M^+$), 363, 273, 204, 171.

**Spiro[5-dodecyl-1,3-dithiane-2,1′(2*H*)-7′-methoxy-3′,4′-dihydronaphtalene] (12)** 7-Methoxy-1-tetralone (**15**) (117.2 mg, 0.666 mmol) and boron trifluoride diethylether complex (37.8 mg, 0.226 mmol) were added to a solution of **2a** (220.7 mg, 0.798 mmol) in toluene at 0 °C, and the reaction mixture was stirred at room temperature. After the reaction, a saturated aqueous solution of sodium bicarbonate was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane : ethyl acetate=40 : 1) to afford spiro[5-dodecyl-1,3-dithiane-2,1′(2*H*)-7′-methoxy-3′,4′-dihydronaphtalene] (**12**) (256.7 mg, 89%). Further separation of the diastereoisomers was achieved with HPLC equipped with Kusano Si-10 (*n*-hexane : ethyl acetate=20 : 1).

Major Isomer: Colorless oil, $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=7.2 Hz), 1.20—1.52 (22H, m), 1.90—2.25 (3H, m), 2.60—2.58 (2H, m), 2.65 (2H, dd, B part of AB, $J_{AB}$=14.6 Hz, $J$=3.2 Hz), 2.74 (2H, t, $J$=6.4 Hz), 2.86 (2H, dd, A part of AB, $J_{AB}$=14.6 Hz, $J$=11.6 Hz), 3.81 (3H, s), 6.75 (1H, dd, $J$=8.4, 2.8 Hz, aromatic), 6.96 (1H, d, $J$=8.4 Hz, aromatic), 7.54 (1H, d, $J$=2.4 Hz, aromatic). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 20.3, 22.7, 26.4, 29.2, 29.3, 29.53, 29.59, 29.63, 29.65, 29.67, 31.9, 33.6, 35.9, 36.0, 36.7, 52.4, 55.4, 113.8, 115.2, 128.0, 129.8, 129.9, 157.8. IR ($CHCl_3$) cm$^{-1}$: 2928, 2855, 1609, 1501, 1466, 1317, 1238. HR-MS *m/z*: 434.2676 [Calcd for $C_{26}H_{42}OS_2$ ($M^+$): 434.2677]. MS (70 eV) *m/z*: 434 ($M^+$), 401, 273, 192, 159, 144.

Minor Isomer: Colorless oil, $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=6.4 Hz), 1.18—1.42 (20H, m), 1.86—1.78 (1H, m), 1.88—2.00 (4H, m), 2.57—2.58 (2H, m), 2.58 (2H, dd, B part of AB, $J_{AB}$=14.2 Hz, $J$=2.8 Hz), 2.73 (2H, t, $J$=6.4 Hz), 3.37 (2H, dd, A part of AB, $J_{AB}$=14.2 Hz, $J$=2.8 Hz), 3.82 (3H, s), 6.75 (1H, dd, $J$=8.4, 2.8 Hz, aromatic), 6.96 (1H, d, $J$=8.4 Hz, aromatic), 7.59 (1H, d, $J$=2.8 Hz, aromatic). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 20.2, 22.7, 27.2, 28.1, 29.2, 29.36, 29.66, 29.7, 29.9, 31.9, 32.6, 36.0, 52.4, 55.3, 114.3, 114.8, 129.6, 129.8, 139.4, 157.8. IR ($CHCl_3$) cm$^{-1}$: 3686, 2928, 2855, 1609, 1499, 1466, 1317, 1238. HR-MS *m/z*: 434.2676 [Calcd for $C_{26}H_{42}OS_2$ ($M^+$): 434.2677]. MS (70 eV) *m/z*: 434 ($M^+$), 401, 273, 192, 159.

**(5*S*)-4,5-Dihydrotestosterone Cyclic 2-Dodecyl-1,3-propanediyl Dithioacetal (13)** (5*S*)-4,5-Dihydrotestosterone (**16**) (90.5 mg, 0.312 mmol) and boron trifluoride diethylether complex (17.7 mg, 0.125 mmol) were added to a solution of **2a** (103.4 mg, 0.374 mmol) in toluene at 0 °C, and the reaction mixture was stirred at room temperature. After the reaction, a saturated aqueous solution of sodium bicarbonate was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane : ethyl acetate=20 : 1 and then 2 : 1) to afford (5*S*)-4,5-dihydrotestosterone cyclic 2-dodecyl-1,3-propanediyl dithioacetal (**13**) (167.0 mg, 98%). Amorphous powder: a mixture of *cis*- and *trans*-isomers; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.719 (3H, s), 0.881 (3H, t, $J$=6.4 Hz), 0.97 (3H, s), 0.95—1.12 (1H, m), 1.15—1.92 (42H, m), 1.95—2.26 (3H, m), 2.46—2.80 (4H, m), 3.63 (1H, t, $J$=8.4Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 11.1, 14.1, 20.5, 22.7, 23.3, 23.5, 25.8, 26.48, 26.51, 29.33, 29.52, 29.58, 29.62, 29.64, 30.6, 31.3, 31.7, 31.9, 32.8, 35.4, 35.5, 35.7, 35.9, 36.8, 38.4, 39.0, 40.2, 43.0, 50.9, 51.0, 81.9. IR ($CHCl_3$) cm$^{-1}$: 3609, 3454, 2928, 2855, 1603, 1468, 1447, 1412, 1379, 1358, 1342, 1312, 1269, 1236, 1205, 1198, 1171, 1157, 1136, 1119, 1094, 1069, 1051, 1032, 1009. HR-MS *m/z*: 548.4091 [Calcd for $C_{34}H_{60}OS_2$ ($M^+$): 548.4085]. MS (70 eV), *m/z* 548 ($M^+$), 515, 313, 291, 274, 255, 239, 213, 201, 173.

**Reduction of 2-Cyclohexyl-5-dodecyl-2-phenyl-1,3-dithiane (11)** A suspension of Raney nickel (W-2) (6.0 ml) was added to 2-cyclohexyl-5-dodecyl-2-phenyl-1,3-dithiane (**11**) (147.9 mg, 0.312 mmol), and the mixture was stirred at room temperature for 15 h. After the reaction, the mixture was filtered through celite, and the filtrate was condensed *in vacuo*. The residue was purified on silica gel preparative TLC (*n*-hexane) to afford benzylcyclohexane (45.2 mg, 78%), which was identified by the comparison of the $^1$H-NMR spectrum with the data reported in the literature.[29]

**Reduction of Spiro[5-dodecyl-1,3-dithiane-2,1′(2*H*)-7′-methoxy-3′,4′-dihydronaphtalene] (12)** A suspension of Raney nickel (W-2) (6.0 ml) was added to spiro[5-dodecyl-1,3-dithiane-2,1′(2*H*)-7′-methoxy-3′,4′-dihydronaphtalene] (**12**) (102.0 mg, 0.235 mmol), and the mixture was stirred at room temperature for 16 h. After the reaction, the mixture was filtered through celite, and the filtrate was condensed *in vacuo*. The residue was purified on silica gel column chromatography (*n*-hexane : ethyl acetate=80 : 1 and then ethyl acetate) to afford 7-methoxy-3,4-dihydronaphtalene (35.6 mg, 93%), which was identified by the comparison of the $^1$H-NMR spectrum with the data reported in the literature.[30]

**Reduction of (5*S*)-4,5-Dihydrotestosterone Cyclic 2-Dodecyl-1,3-propanediyl Dithioacetal (13)** A suspension of Raney nickel (W-2) (6.0 ml) was added to (5*S*)-4,5-dihydrotestosterone cyclic 2-dodecyl-1,3-propanediyl dithioacetal (**13**) (56.0 mg, 0.102 mmol), and the mixture was stirred at room temperature for 11 h. After the reaction, the mixture was filtered through celite, and the filtrate was condensed *in vacuo*. The residue was purified on silica gel column chromatography (*n*-hexane and then $CHCl_3$ : MeOH=10 : 1) to afford (5*S*)-3-deoxy-4,5-dihydrotestosterone (25.6 mg, 91%), which was identified by the comparison of the $^1$H-NMR spectrum with the data reported in the literature.[31]

**Hydrolysis of 2,5-Didodecyl-1,3-dithiane (17)** A solution of 2,5-didodecyl-1,3-dithiane (**17**) (200 mg, 0.409 mmol) in 2-butanone (80 ml) was added to an aqueous 97% 2-butanone (20 ml) solution of NBS (582.8 mg, 3.27 mmol) at 0 °C, and the reaction mixture was stirred for 20 min at room temperature. After the reaction, a saturated aqueous solution of sodium

bisulfite (40 ml) was added to the reaction mixture, and the mixture was stirred another 20 min. The reaction mixture was extracted with chloroform, and the aqueous layer was extracted with *n*-hexane after the pH value was adjusted to 11. The organic layer was washed with brine, dried over sodium sulfate, and evaporated to afford tridecanal (75.6 mg, 87%).

**Hydrolysis of 5-Dodecyl-2,2-diphenyl-1,3-dithiane (18)** A solution of 5-dodecyl-2,2-diphenyl-1,3-dithiane (**18**) (50 mg, 0.113 mmol) in 2-butanone (20 ml) was added to an aqueous 97% 2-butanone (5 ml) solution of NBS (161 mg, 0.907 mmol) at 0 °C, and the reaction mixture was stirred for 20 min at room temperature. After the reaction, a saturated aqueous solution of sodium bisulfite (40 ml) was added to the reaction mixture, and the mixture was stirred another 20 min. The reaction mixture was extracted with chloroform, and the aqueous layer was extracted with *n*-hexane after the pH value was adjusted to 11. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane : ethyl acetate=20 : 1) to afford benzophenone (20.1 mg, 98%).

**5-Dodecyl-1,3-dithiane (19)** Paraformaldehyde (10.97 g) and *p*-toluenesulfonic acid monohydrate (0.695 g, 3.65 mmol) were added to a solution of **2a** (10.1 g, 36.5 mmol) in benzene (82 ml), and the mixture was refluxed for 2 h. After the reaction, the reaction mixture was filtered. The filtrate was partitioned between ethyl acetate and water, and the organic layer was successively washed with saturated aqueous solution of sodium bicarbonate, water, and brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane : ethyl acetate=10 : 1) to afford 5-dodecyl-1,3-dithiane (**19**) (10.0 g, 95%). Colorless needles (*n*-hexane): mp 41—42 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=6.8 Hz), 1.16—1.48 (22H, m), 1.81—1.92 (1H, m), 2.54 (2H, dd, B part of ABX, $J_{AB}$=14.5 Hz, $J$=9.9 Hz), 2.78 (2H, ddd, A part of ABX, $J_{AB}$=14.5 Hz, $J$=2.7 Hz, 1.6 Hz), 3.51 (1H, dt, B part of AB, $J_{AB}$=13.9 Hz, 1.6 Hz), 3.90 (1H, d, A part of AB, $J_{AB}$=13.9 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 29.26, 29.34, 29.5, 29.58, 29.63, 29.7, 31.7, 31.9, 35,3, 35.8, 36.0. IR ($CHCl_3$) cm$^{-1}$: 2988, 2930, 2855, 2361, 2343, 2332, 1466, 1427, 1410, 1389, 1288, 1236, 1221, 1198, 1186, 1165; HR-MS *m*/*z*: 288.1946 [Calcd for $C_{16}H_{32}S_2$ ($M^+$): 288.1945]. MS (70 eV) *m*/*z*: 288 ($M^+$), 207, 149. *Anal.* Calcd for $C_{16}H_{32}S_2$: C, 66.60; H, 11.18. Found: C, 66.78; H, 10.97.

***trans*-2,5-Didodecyl-1,3-dithiane (20)** *n*-BuLi (35.3 mg, 0.546 mmol) was added to a solution of 5-dodecyl-1,3-dithiane (**19**) (131.3 mg, 0.456 mmol) in THF (2 ml) at −20 °C, the mixture was stirred for 1 h, and then *n*-dodecyl iodide (161.7 mg, 0.546 mmol) was slowly added to the reaction mixture. After stirring for 14 h at room temperature, a saturated aqueous solution of ammonium chloride was added to the mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford *trans*-2,5-didodecyl-1,3-dithiane (**20**) (210.5 mg, 95%). Colorless needles (*n*-hexane): mp 73.0—74.0 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (6H, t, $J$=7 Hz), 1.12—1.36 (40H, m), 1.45—1.55 (2H, m), 1.68—1.83 (3H, m), 2.54 (2H, dd, B part of AB, $J_{AB}$=14.3 Hz, $J$=11.2 Hz), 2.76 (2H, dd, A part of AB, $J_{AB}$=14.3 Hz, $J$=2.8 Hz), 4.00 (1H, t, $J$=6.8 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 26.4, 26.8, 29.3, 29.6, 31.9, 34.8, 36.4, 36.6, 47.8. IR ($CHCl_3$) cm$^{-1}$: 2922, 2855, 1425, 1377, 1377, 1300. HR-MS *m*/*z*: 456.3821 [Calcd for $C_{28}H_{56}S_2$ ($M^+$): 456.3823]. *Anal.* Calcd for $C_{28}H_{56}S_2$: C, 73.61; H, 12.35. Found: C, 73.73; H, 12.29.

***trans*-2-Propyl-5-dodecyl-1,3-dithiane (21)** *n*-BuLi (30.5 mg, 0.472 mmol) was added to a solution of 5-dodecyl-1,3-dithiane (**19**) (113.5 mg, 0,393 mmol) in THF (2 ml) at −20 °C, the mixture was stirred for 1 h, and then *n*-propyl iodide (80.2 mg, 0.472 mmol) was slowly added to the reaction mixture. After stirring for 24 h at room temperature, a saturated aqueous solution of ammonium chloride was added to the mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford *trans*-2-propyl-5-didodecyl-1,3-dithiane (**21**) (111.8 mg, 86%). Colorless needles (*n*-hexane): mp 72—74 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, $J$=7.2 Hz), 0.93 (3H, t, $J$=7.6 Hz), 1.18—1.40 (22H, m), 1.52 (2H, quint, $J$=7.5 Hz), 1.73 (2H, quint. $J$=7.9 Hz), 1.70—1.82 (1H, m), 2.54 (2H, dd, A part of AB, $J_{AB}$=14.4 Hz, $J$=11.0 Hz), 2.76 (2H, dd, B part of AB, $J_{AB}$=14.4 Hz, $J$=2.7 Hz), 4.02 (1H, t, $J$=6.8 Hz). $^{13}$C-NMR ($CDCl_3$) $\delta$: 13.7, 14.1, 20.1, 22.7, 26.4, 29.3, 29.51, 29.58, 29.63, 29.65, 31.9, 36.3, 26.61, 36.64, 36.8, 47.5. IR ($CHCl_3$) cm$^{-1}$: 3686, 2958, 2928, 2885, 2359, 1601, 1242. HR-MS *m*/*z*: 330.2414 [Calcd for $C_{19}H_{38}S_2$ ($M^+$): 330.2415]. MS (70 eV) *m*/*z*: 330 ($M^+$), 287. *Anal.* Calcd for $C_{19}H_{38}S_2$: C, 69.02; H, 11.58. Found: C, 68.99; H, 11.86.

**2-Phenyl-5-dodecyl-1,3-dithiane (22)** Benzaldehyde (20.0 mg, 0.188 mmol) and $BF_3 \cdot Et_2O$ (10.7 mg, 0.075 mmol) were added to a solution of **2a** (62.5 mg, 0.226 mmol) in toluene (1.0 ml), and the mixture was stirred at room temperature. After stirring for 17 h, the mixture was poured into a saturated aqueous solution of sodium bicarbonate and extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride, dried over anhydrous sodium sulfate, and condensed *in vacuo*. The residue was purified on preparative TLC on silica gel to afford **22** as a mixture of *cis*- and *trans*-isomers. Amorphous powder. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (3H, t, J=6.8 Hz), 1.20—1.96 (23H, m), 2.70—2.80 (2H, m), 2.86 (1.4H, dd, $J$=14.3, 2.9 Hz), 3.21 (0.6H, dd, $J$=13.6, 1.2 Hz), 5.09 (0.3H, s), 5.12 (0.7H, s), 7.25—7.37 (3H, m), 7.45—7.54 (2H, m). $^{13}$C-NMR ($CDCl_3$) $\delta$: 14.1, 22.7, 26.9, 28.9, 29.3, 29.52, 29.58, 29.6, 29.8, 31.9, 35.7, 36.2, 36.6, 37.7, 51.5, 127.7, 127.9, 128.2, 128.4, 128.6, 128.7. IR ($CHCl_3$) cm$^{-1}$: 3001, 2986, 2959, 2855, 1497, 1466, 1452. HR-MS *m*/*z*: 364.2250 [Calcd for $C_{22}H_{36}S_2$ ($M^+$): 364.2258]. MS (70 eV) *m*/*z*: 364 ($M^+$), 279, 273, 167, 149.

***trans*-2,5-Didodecyl-2-propyl-1,3-dithiane (23)** *n*-BuLi (54.0 mg, 0.835 mmol) was added to a solution of *trans*-2-propyl-5-didodecyl-1,3-dithiane (**21**) (138.1 mg, 0.418 mmol) in THF (2 ml) at 0 °C, and the mixture was stirred for 1 h. Then *n*-decyl iodide (495.0 mg, 1.671 mmol) was slowly added to the reaction mixture. After stirring for 10 h at room temperature, a saturated aqueous solution of ammonium chloride was added to the mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford *trans*-didodecyl-2,5-propyl-1,3-dithiane (**23**) (151.2 mg, 73%). Colorless needles (*n*-hexane): mp 48.0—49.0 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (6H, t, $J$=7.2 Hz), 0.95 (3H, t, $J$=7.2 Hz), 1.18—1.48 (44H, m), 1.63—1.82 (3H, m), 1.86—1.98 (2H, m), 2.62 (2H, d, B part of AB, $J_{AB}$=14.3 Hz, $J$=9.6 Hz), 2.67 (2H, d, A part of AB, $J_{AB}$=14.3 Hz, $J$=4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 14.2, 18.0, 22.7, 23.7, 26.5, 29.34, 29.42, 29.54, 29.58, 29.63, 29.66, 29.9, 31.5, 31.9, 35.2, 35.3, 38.6, 39.6, 53.2. IR ($CHCl_3$) cm$^{-1}$: 2957, 2932, 2855, 1466, 1411, 1379, 1354, 1303, 1244, 1225, 1205, 1121, 1103. HR-MS *m*/*z*: 498.4290 [Calcd for $C_{31}H_{62}S_2$ ($M^+$): 498.4293]. MS (70 eV) *m*/*z* : 498 ($M^+$), 455, 329, 273, 255. *Anal.* Calcd for $C_{31}H_{62}S_2$: C, 74.62; H, 12.52. Found: C, 74.79; H, 12.72.

***trans*-2,5-Didodecyl-2-phenyl-1,3-dithiane (24)** *s*-BuLi (16.1 mg, 0.249 mmol) was added to a solution of 5-dodecyl-2-phenyl-1,3-dithiane (**22**) (75.5 mg, 0.207 mmol) in THF (1.5 ml) at −20 °C, the mixture was stirred for 1 h, and then *n*-dodecyl iodide (161.7 mg, 0.249 mmol) was slowly added to the reaction mixture. After stirring for 28 h at room temperature, a saturated aqueous solution of ammonium chloride was added to the mixture, which was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified on silica gel column chromatography (*n*-hexane) to afford *trans*-2,5-didodecyl-2-phenyl-1,3-dithiane (**24**) (105.6 mg, 96%). Colorless needles (*n*-hexane): $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.88 (6H, t, $J$=7 Hz), 1.34—1.08 (42H, m), 1.89—1.92 (1H, m), 1.92—2.00 (2H, m), 2.33 (2H, dd, B part of AB, $J_{AB}$=14.4 Hz, $J$=11.4 Hz), 2.58 (2H, dd, A part of AB, $J_{AB}$=14.4 Hz, $J$=2.9 Hz), 7.28—7.22 (1H, tt, $J$=6, 1.2 Hz), 7.40—7.34 (2H, m), 7.94—7.88 (2H, m). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 22.7, 24.0, 26.4, 29.2, 29.3, 29.46, 29.48, 29.55, 29.60, 29.63, 31.9, 33.2, 36.0, 36.3, 45.2, 59.2, 126.7, 128.28, 128.33, 128.9, 142.0. IR ($CHCl_3$) cm$^{-1}$: 3684, 3032, 2926, 2855, 1601, 1466, 1443, 1234, 1200. HR-MS *m*/*z*: 532.2434 [Calcd for $C_{34}H_{60}S_2$ ($M^+$): 532.4136]. MS (70 eV) *m*/*z*: 532 ($M^+$), 363, 289, 274, 257. *Anal.* Calcd for $C_{34}H_{60}S_2$: C, 76.62; H, 11.35. Found: C, 76.64, H, 11.32.

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