Synthesis of 3,4-dialkylsulfanyl- and 3,4,5-trialkylsulfanyl derivatives of bromobenzene and benzaldehyde

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Synthesis of 3,4-dialkylsulfanyl- and 3,4,5-trialkylsulfanyl derivatives of bromobenzene and benzaldehyde

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3,4-Dialkylsulfanyl- (1a[n], n = 8, 9, 11) and 3,4,5-trialkylsulfanyl bromobenzenes (1b[n], n = 6, 8, 10, 12) were prepared from 3,4-difluoro- and 3,4,5-trifluorobromobenzene, respectively, in 50–60% yields. The bromobenzenes 1[n] were converted to benzaldehydes 2[n] by lithium–halogen exchange followed by reaction with DMF.

Keywords: synthesis; nucleophilic aromatic substitution; alkyl aryl sulfides; substituted bromobenzenes; substituted benzaldehydes

1. Introduction

Alkylsulfanyl groups are used to modify molecular and bulk properties of organic materials that are based primarily on aromatic compounds. These substituents lower the ionization potential of the aromatic compounds, and sufficiently long chains increase solubility, lower melting points, or even induce liquid crystalline behavior. Good examples are derivatives of triphenylene (1) and phenanthrene (2), in which six hexylsulfanyl groups induce discotic columnar behavior and modify their electronic properties, so the materials exhibit relatively high hole mobility of photo-generated charges (3). Short alkylsulfanyl substituents are used in designing aromatics for charge-transfer salts (4), and C₆H₃S substituents modify electronic properties of a ligand for Ru²⁺ complex developed for solar cells (5). Six hexylsulfanyl groups have been used as substituents in highly fluorescent oligophenylenevinylene designed for detection of Ag⁺ ions (6). When the...
sulfur center is oxidized, the moderately electron-donating alkylsulfanyl group is transformed to a powerful electron-withdrawing alkylsulfonyl substituent that is particularly useful in designing of non-linear optical materials (7–9). We have envisioned di- and trialkylsulfanylphenyl groups as components of liquid crystalline 6-oxoverdazyls (10).

Polyalkylsulfanylphenyl groups are often introduced to more complexed molecular architectures by taking advantage of the bromo substituent that readily undergoes Pd-catalyzed coupling reactions (11) and lithium–halogen exchange (12). Reactions of the resulting aryllithium derivatives (4, 6, 9) give access to a variety of functional groups.

The preparation of the monoalkylsulfanyl bromobenzenes involves a straightforward alkylation of the readily available bromothiophenols (8, 9, 11). Alternatively, 1-alkylsulfanyl-4-bromobenzenes can be obtained by an Ullmann-type S-arylation of alkylmercaptans (13, 14), which exhibits high chemoselectivity for iodine (13, 15). Among polymercaptobromobenzenes, only 4-bromo-1,2-dimercaptobenzene is known (16), but its cumbersome preparation makes this route to 1-bromo-3,4-dialkylsulfanylbenzenes (1a[n]) impractical. Consequently, such compounds are scarce. Recently, a report (6) of 1-bromo-3,4,5-trihexylsulfanylbenzene (1b[6]), prepared from 1-bromo-3,4,5-trifluorobenzene, demonstrated a new route to poly(alkylsulfanyl)bromobenzenes. Although no experimental or analytical details were given, the reaction occurs in DMSO, and the net aromatic nucleophilic substitution process involves the SRN1 mechanism (17, 18). We have examined this reaction in detail and expanded it to other 1-bromo-3,4,5-trialkylsulfanylbenzenes (1b[n]) and also to 3,4-dialkylsulfanyl derivatives (1a[n]). Subsequently, these bromobenzenes were converted to the corresponding di- and trialkylsulfanylbenzaldehydes (2a[n] and 2b[n]), which belong to a class of practically unknown compounds (6, 19). Here we report general methods for preparation of a series of these compounds and their characterization.

2. Results and discussion

3,4-Dialkylsulfanyl- and 3,4,5-trialkylsulfanyl bromobenzenes (1[n]) were prepared by reacting 1-bromo-3,4-difluorobenzene and 1-bromo-3,4,5-trifluorobenzene, respectively, with appropriate sodium alkanethiolate in dry DMSO (Scheme 1). However, the efficient preparation of higher homologs, especially trisubstituted bromobenzenes (1b[n]), requires THF as a co-solvent (up to 30%) for a better dissolution of the highly aliphatic thiolates and the products. The initial reaction of the fluorobenzenes with the thiolate is exothermic, and for better control of the product formation, fluorobenzene was added at ambient temperature. Under these conditions, a 1:1 mixture of the desired product 1b[8] and a partially substituted intermediate (7.22 ppm, d, J = 6.1 Hz) was observed after 30 min by 1H NMR in a reaction of 1-bromo-3,4,5-trifluorobenzene and octanethiolate.

Subsequent heating of the reaction mixture led to the formation of bromides (1[n]) and products of bromine substitution (3[n]) as the sole products in proportions ranging from 10:1 to 10:5 for the longer members of the homologous series. The formation of the latter was demonstrated for two derivatives 3b[8] and 3b[12]. The by-products were easily identified in the 1H NMR spectra by the upfield-shifted aromatic signals. For instance, in 3b[n], the aromatic singlet is
Scheme 1. Reaction of polyfluorobromobenzenes with alkanethiolates.

moved by about 0.17 ppm relative to that in bromide 1b[n] (6.96 ppm). The observed exhaustive alkylsulfanylation of the bromofluorobenzenes cannot be avoided, but it can be minimized at lower temperatures. For instance, the ratio of 1b[8] to 3b[8] was 20:14, when the reaction mixture was heated at 100–105 °C, and 20:9 at 60 °C. The by-products 3[n] were separated from bromides 1[n] by chromatography as the more polar fraction. However, complete purification of bromobenzene 1[n] is often not necessary, since by-products 3[n] are inert in the lithiation process and are readily separated from aldehydes 2[n].

Scheme 2. Synthesis of benzaldehydes 2[n].

Benzaldehydes 2[n] were prepared in a routine way via lithium–halogen exchange of alkylsulfanyl bromobenzenes 1[n] with n-BuLi and subsequent reaction of the generated aryllithium with dry DMF at −78 °C (Scheme 2) (20). The resulting aldehydes were isolated by column chromatography as yellow oils or low melting solids in purities sufficient for subsequent transformations (10). Aldehyde 2b[6] was also obtained by formylation of aryllithium derived from 1b[6] with N-formylmorpholine (6).

Another protocol for the preparation of such benzaldehydes by nucleophilic substitution of the bromo and nitro groups in ethyl 3,5-dibromo-4-nitrobenzoate followed by reduction of the ester group was demonstrated for 2b[1] (19).

3. Conclusions

Polyfluorobromobenzenes are convenient starting materials for the preparation of polyalkylsulfanyl bromobenzenes in DMSO or DMSO/THF mixtures by the S_{RN1} mechanism. Although substitution of fluorine is faster than that of bromine in the starting material, the selectivity is low, and typically 3:1 mixtures of the desired bromide 1[n] and the exhaustively sulfanylated by-product 3[n] are formed, which requires chromatographic separation. The bromo derivatives 1[n] are convenient starting materials for other functional derivatives as demonstrated for aldehydes 2[n] and serve as key building blocks for advanced materials.
4. Experimental

Melting points are not corrected. NMR spectra were obtained at 400 or 600 MHz (1H) and 151 MHz (13C) in CDCl₃ and referenced to the solvent, unless otherwise specified. IR spectra were recorded using neat samples or KBr pellets.

4.1. 4,5-Dialkylsulfanyl- and 3,4,5-trialkylsulfanyl-1-bromobenzenes 1a[n] and 1b[n]:

general procedure

To a suspension of NaH (1.1 equiv. per mercaptane, 60% in oil) in dry DMSO (200 mL/25 mmol of 1-bromo-3,4-difluorobenzene, for the preparation of 1a[n], or 1-bromo-3,4,5-trifluorobenzene, for the preparation of 1b[n]), stoichiometric amounts of alkanethiol (2.0 or 3.0 equiv., respectively) were added slowly under Ar. For the preparation of tridecylsulfanyl and tridodecylsulfanyl derivatives 1b[10] and 1b[12], a mixture of DMSO and THF in a 5:2 ratio (280 mL/25 mmol of the substrate) was used to increase the solubility of the reactants and products.

The mixture was kept at ambient temperature by using a water bath, while adding the thiol. After 30 min, 1 equiv. of 1-bromo-3,4-difluorobenzene or 1-bromo-3,4,5-trifluorobenzene was added slowly at ambient temperature and the mixture was stirred at 60 °C overnight. The mixture was cooled, poured into water, organic products were extracted (hexanes), combined extracts dried (Na₂SO₄), and solvents evaporated. The oily viscous residue was passed through a silica gel plug (hexane) and then separated on a silica gel column. Initially, hexane was used to remove non-polar impurities (presumably partially substituted products), while a more polar eluent (hexanes/CH₂Cl₂, 8:1) gave the expected bromides 1a[n] or 1b[n] followed by tri- or tetrasulfanyl by-products 3a[n] or 3b[n]. The bromides were obtained in typical yields of 50–60% and purity >96%. Analytically pure samples were obtained by additional chromatography and/or recrystallization (hexane).

4.1.1. 1-Bromo-3,4-dioctylsulfanylbenzene (1a[8])

1H NMR (600 MHz, CDCl₃) δ 0.884 (t, J = 7.0 Hz, 3H), 0.879 (t, J = 7.0 Hz, 3H), 1.27–1.34 (m, 16H), 1.40–1.49 (m, 4H), 1.64 (quin., J = 7.1 Hz, 2H), 1.69 (quin., J = 7.1 Hz, 2H), 2.87 (t, J = 7.4 Hz, 2H), 2.90 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 8.3 Hz, 1H), 7.21 (dd, J₁ = 8.3 Hz, J₂ = 2.0 Hz, 1H), 7.31 (d, J = 2.1 Hz, 1H); 13C NMR (151 MHz, CDCl₃) δ 14.1, 22.6, 28.6, 28.86, 28.91, 29.00, 29.12, 29.13, 31.8, 33.2, 33.6, 119.9, 128.5, 130.0, 130.4, 135.5, 140.5. Anal. Calcd for C₂₂H₃₇BrS₂: C, 59.30; H, 8.37; S, 14.39. Found: C, 59.50; H, 8.43; S, 14.08.

4.1.2. 1-Bromo-3,4-dinonylsulfanylbenzene (1a[9])

1H NMR (600 MHz, CDCl₃) δ 0.884 (t, J = 7.0 Hz, 3H), 0.879 (t, J = 7.0 Hz, 3H), 1.27–1.34 (m, 16H), 1.40–1.49 (m, 4H), 1.64 (quin., J = 7.1 Hz, 2H), 1.69 (quin., J = 7.1 Hz, 2H), 2.87 (t, J = 7.4 Hz, 2H), 2.90 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 8.3 Hz, 1H), 7.21 (dd, J₁ = 8.3 Hz, J₂ = 2.0 Hz, 1H), 7.31 (d, J = 2.1 Hz, 1H); 13C NMR (151 MHz, CDCl₃) δ 14.1, 22.6, 28.6, 28.85, 28.89, 29.00, 29.12, 29.13, 31.8, 33.2, 33.6, 119.9, 128.5, 129.9, 130.4, 135.5, 140.5. Anal. Calcd for C₂₄H₄₁BrS₂: C, 60.86; H, 8.73; S, 13.54. Found: C, 61.01; H, 9.01; S, 13.27.

4.1.3. 1-Bromo-3,4-diundecylsulfanylbenzene (1a[11])

m.p. 37–38 °C; 1H NMR (600 MHz, CDCl₃) δ 0.88 (t, J = 7.0 Hz, 6H), 1.22–1.34 (m, 28H), 1.40–1.48 (m, 4H), 1.64 (quin., J = 7.1 Hz, 2H), 1.69 (quin., J = 7.1 Hz, 2H), 2.87 (t, J = 7.5 Hz, 2H),...
2.90 (t, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 1H), 7.21 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.0$ Hz, 1H), 7.32 (d, $J = 2.0$ Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 14.1, 22.7, 28.5, 28.8, 28.9, 28.9, 29.2, 29.3, 29.5, 29.5, 29.6, 29.6, 31.9, 33.2, 33.6, 119.9, 128.5, 130.0, 130.5, 135.5, 140.5. Anal. Calcd for C$_{28}$H$_{49}$BrS$_2$: C, 63.49; H, 9.32; S, 12.11. Found: C, 63.65; H, 9.46; S, 12.03.

4.1.4. 1-Bromo-3,4,5-trihexylsulfanylbenzene (1b[6]) (6)

m.p. 44–45 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 6.9$ Hz, 6H), 1.24–1.37 (m, 12H), 1.38–1.43 (m, 2H), 1.45–1.52 (m, 4H), 1.59 (quin., $J = 7.4$ Hz, 2H), 1.72 (quin., $J = 7.5$ Hz, 4H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.84 (t, $J = 7.2$ Hz, 4H), 6.96 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 22.5, 28.0, 28.9, 29.1, 29.2, 29.3, 29.5, 31.4, 32.3, 34.9, 122.5(CH), 123.9, 126.6, 148.5. Anal. Calcd for C$_{24}$H$_{41}$BrS$_3$: C, 57.00; H, 8.17. Found: C, 56.83; H, 8.16.

4.1.5. 1-Bromo-3,4,5-trioctylsulfanylbenzene (1b[8])

m.p. 32–35 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, $J = 6.9$ Hz, 3H), 0.89 (t, $J = 6.7$ Hz, 6H), 1.22–1.37 (m, 24H), 1.38–1.43 (m, 2H), 1.44–1.52 (m, 4H), 1.59 (quin., $J = 7.5$ Hz, 2H), 1.72 (quin., $J = 7.4$ Hz, 4H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.84 (t, $J = 7.3$ Hz, 4H), 6.96 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 28.0, 28.9, 29.1, 29.1, 29.2, 29.3, 29.4, 31.8, 32.3, 34.9, 122.5(CH), 123.9, 126.6, 148.5. Anal. Calcd for C$_{30}$H$_{53}$BrS$_3$: C, 61.09; H, 9.06. Found: C, 61.33; H, 9.00.

4.1.6. 1-Bromo-3,4,5-tridecylsulfanylbenzene (1b[10])

m.p. 52–53 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.86 (t, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 6H), 1.22–1.36 (m, 36H), 1.37–1.42 (m, 2H), 1.43–1.52 (m, 4H), 1.59 (quin., $J = 7.4$ Hz, 2H), 1.72 (quin., $J = 7.4$ Hz, 4H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.3$ Hz, 4H), 6.96 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.5, 28.0, 28.9, 29.1, 29.1, 29.2, 29.3, 29.4, 31.8, 31.9, 32.3, 34.9, 122.5(CH), 123.9, 126.6, 148.5. Anal. Calcd for C$_{36}$H$_{65}$BrS$_3$: C, 64.15; H, 9.72. Found: C, 64.12; H, 9.77.

4.1.7. 1-Bromo-3,4,5-tridodecylsulfanylbenzene (1b[12])

m.p. 63–64 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J = 6.9$ Hz, 9H), 1.22–1.37 (m, 48H), 1.38–1.43 (m, 2H), 1.44–1.52 (m, 4H), 1.59 (quin., $J = 7.7$ Hz, 2H), 1.72 (quin., $J = 7.4$ Hz, 4H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.4$ Hz, 4H), 6.96 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 22.7, 28.0, 28.9, 29.1; 29.1, 29.1, 29.1, 29.1, 29.4, 29.5, 29.5, 29.6, 31.8, 31.9, 32.3, 34.9, 122.5(CH), 123.9, 126.6, 148.5. Anal. Calcd for C$_{42}$H$_{77}$BrS$_3$: C, 66.54; H, 10.24. Found: C, 66.52; H, 10.38.

4.2. 3,4-Dialkylsulfanyl- and 3,4,5-trialkylsulfanylbenzaldehydes (2a[n] and 2b[n]):

**general procedure**

A solution of 1-bromo-3,4-dialkylsulfanylbenzene (1a[n]) or 1-bromo-3,4,5-trialkylsulfanylbenzene (1b[n]) (1.0 mmol) in dry THF (20 mL) was quickly cooled to −78 ºC and, before the starting material began to precipitate, n-BuLi (1.1 mmol) was added under Ar. The mixture was stirred at −78 ºC for 1 h and then warmed up to 0 ºC. After 1 h, the mixture was cooled to −78 ºC, and
rigorously dried DMF (1.5 mmol) was added. The mixture was stirred for 1 h, quenched with 5% HCl, organic products were extracted (Et₂O), extracts dried (Na₂SO₄), and solvents evaporated. The residue was passed through a silica gel plug (hexane/CH₂Cl₂, 2:1) and the resulting crude aldehyde was purified by column chromatography (hexane/CH₂Cl₂, 2:1) giving the expected product 2a[n] or 2b[n] as a yellowish oil or low melting solid in a typical yield of 60–80%.

4.2.1. 3,4-Dioctylsulfanylbenzaldehyde (2a[8])

1H NMR (600 MHz, CDCl₃) δ 0.875 (t, J = 6.9 Hz, 3H), 0.881 (t, J = 6.9 Hz, 3H), 1.22–1.37 (m, 16H), 1.42–1.51 (m, 4H), 1.68 (quin., J = 7.5 Hz, 2H), 1.75 (quin., J = 7.5 Hz, 2H), 2.98 (t, J = 7.3 Hz, 2H), 2.99 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.60 (dd, J₁ = 8.1 Hz, J₂ = 1.6 Hz, 1H), 7.74 (d, J = 1.6 Hz, 1H), 9.90 (s, 1H); 13C NMR (151 MHz, CDCl₃) δ 14.1, 22.6, 28.4, 28.8, 28.9, 29.05, 29.12, 29.13, 31.8, 31.9, 32.4, 33.5, 33.6, 125.1, 127.7, 129.0, 133.2, 136.3, 147.5, 191.0; IR (film, cm⁻¹) 1694 (C=O). Anal. Calcd for C₂₃H₃₈OS₂: C, 69.99; H, 9.70; S, 16.25. Found: C, 70.11; H, 9.85; S, 16.31.

4.2.2. 3,4,5-Trihexylsulfanylbenzaldehyde (2b[6]) (6)

1H NMR (400 MHz, CDCl₃) δ 0.87 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.1 Hz, 6H), 1.20–1.35 (m, 10H), 1.36–1.44 (m, 2H), 1.46–1.56 (m, 6H), 1.61 (quin., J = 7.4 Hz, 2H), 1.75 (quin., J = 7.5 Hz, 4H), 2.90 (t, J = 7.4 Hz, 2H), 2.94 (t, J = 7.4 Hz, 4H), 7.34 (s, 2H), 9.95 (s, 1H); IR (film, cm⁻¹) 1702 (C=O). HRMS Calcd for C₂₅H₄₃OS₃ (MH⁺): m/z 455.2471, found m/z 455.2476.

4.2.3. 3,4,5-Trioctylsulfanylbenzaldehyde (2b[8])

1H NMR (400 MHz, CDCl₃) δ 0.87 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 6H), 1.20–1.35 (m, 24H), 1.38–1.45 (m, 2H), 1.45–1.54 (m, 4H), 1.60 (quin., J = 7.4 Hz, 2H), 1.75 (quin., J = 7.5 Hz, 4H), 2.90 (t, J = 7.4 Hz, 2H), 2.94 (t, J = 7.4 Hz, 4H), 7.34 (s, 2H), 9.95 (s, 1H). HRMS Calcd for C₃₁H₅₅OS₃ (MH⁺): m/z 539.3410, found m/z 539.3435.

4.2.4. 3,4,5-Tridecylsulfanylbenzaldehyde (2b[10])

1H NMR (400 MHz, CDCl₃) δ 0.87 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 6.9 Hz, 6H), 1.22–1.37 (m, 36H), 1.38–1.44 (m, 2H), 1.45–1.54 (m, 4H), 1.60 (quin., J = 7.4 Hz, 2H), 1.75 (quin., J = 7.5 Hz, 4H), 2.90 (t, J = 7.4 Hz, 2H), 2.94 (t, J = 7.4 Hz, 4H), 7.34 (s, 2H), 9.95 (s, 1H). HRMS Calcd for C₃₇H₆₇OS₃ (MH⁺): m/z 623.4349, found m/z 623.4353.

4.2.5. 3,4,5-Tridodecylsulfanylbenzaldehyde (2b[12])

m.p. 46–48 °C; 1H NMR (500 MHz, CDCl₃) δ 0.88 (t, J = 6.8 Hz, 9H), 1.21–1.37 (m, 48H), 1.38–1.45 (m, 2H), 1.46–1.53 (m, 4H), 1.60 (quin., J = 7.5 Hz, 2H), 1.75 (quin., J = 7.5 Hz, 4H), 2.90 (t, J = 7.4 Hz, 2H), 2.94 (t, J = 7.4 Hz, 4H), 7.34 (s, 2H), 9.95 (s, 1H). HRMS Calcd for C₄₃H₇₉OS₃ (MH⁺): m/z 707.5288, found m/z 707.5305.

4.3. 1,3,4,5-Tetraoctylsulfanylbenzene (3b[8])

Isolated as a white solid by column chromatography as a more polar fraction during purification of 1b[8]: m.p. 37–38 °C; 1H NMR (400 MHz, CDCl₃) δ 0.84–0.92 (m, 12H), 1.20–1.35 (m, 32H),
1.36–1.52 (m, 8H), 1.61 (quin., \(J = 7.4\) Hz, 2H), 1.64–1.76 (m, 6H), 2.81 (t, \(J = 7.4\) Hz, 2H), 2.85 (t, \(J = 7.4\) Hz, 4H), 2.92 (t, \(J = 7.4\) Hz, 2H), 6.79 (s, 2H). HRMS Calcd for C\(_{38}\)H\(_{71}\)S\(_{4}\) (MH\(^+\)): \(m/z\) 655.4433, found \(m/z\) 655.4428.

4.4. \(\text{1,3,4,5-Tetradodecylsulfanylbenzene (3b[12])}\)

Isolated as a white solid by column chromatography as a more polar fraction during purification of 1b[12]: m.p. 59–60 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.7\) Hz, 12H), 1.22–1.34 (m, 64H), 1.35–1.51 (m, 8H), 1.61 (quin., \(J = 7.4\) Hz, 2H), 1.64–1.75 (m, 6H), 2.81 (t, \(J = 7.4\) Hz, 2H), 2.85 (t, \(J = 7.5\) Hz, 4H), 2.91 (t, \(J = 7.4\) Hz, 2H), 6.78 (s, 2H). HRMS Calcd for C\(_{54}\)H\(_{103}\)S\(_{4}\) (MH\(^+\)): \(m/z\) 879.6937, found \(m/z\) 879.6907.

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