Clean and Economic Synthesis of Alkanesulfonyl Chlorides from *S*-Alkyl Isothiourea Salts via Bleach Oxidative Chlorosulfonation

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Abstract: A simple procedure for clean and economic synthesis of alkanesulfonyl chlorides via bleach-mediated oxidative chlorosulfonation of *S*-alkyl isothiourea salts is disclosed. This procedure is environment- and worker-friendly with the advantages of readily accessible materials and reagents, simple and safe operations, easy purification without chromatography, and affords high yields of up to 99%.

Key words: bleach, sulfonyl chloride, *S*-alkyl isothiourea, chlorosulfonation, oxidation

Sulfonyl chlorides are an extraordinarily important class of compounds that have been widely used as synthetic intermediates and building blocks in both synthetic and medicinal chemistry.[1] As a result, many methods have been developed for their syntheses.[1,2] Among the starting materials involved, *S*-alkyl isothiourea salts are considered as easily accessible, inexpensive, and green. They can be converted into the corresponding sulfonyl chlorides via the oxidative chlorosulfonation. Chlorine gas,[3a,b] H_2O_2–HCl,[3c,d] $KMnO_4$/HCl,[3e] HCl-treated silica gel and PhIO,[3f,g] and $NaClO_3$/HCl[3i] have been applied in the oxidative chlorosulfonation. Recently, we successfully realized the oxidative chlorosulfonation of *S*-alkyl isothiourea salts into the corresponding sulfonyl chlorides with *N*-chlorosuccinimide[3h] and $NaClO_2$[3j] as the oxidative chlorinating reagents under acidic conditions. In the *N*-chlorosuccinimide method, organic by-product succinimide is generated three times the amount of sulfonyl chlorides. Although it can be converted to *N*-chlorosuccinimide with sodium hypochlorite in acetic acid, it interferes with the purification of desired products in some cases. To overcome the drawbacks, the best way is to use the inorganic, clean, and atom-economic reagents, among which $NaClO_2$ is a choice. After analyzing its oxidative chlorosulfonation mechanism, we rationalized that NaClO should be another clean and atom-economic reagent for the oxidative chlorosulfonation of *S*-alkyl isothiourea salts. Thus, we turned to the ubiquitous household chemical bleach, which was reported to mediate oxidative chlorosulfonation of odious starting materials, heteroaryl thiols, alkyl thiols, and disulfides, into the corresponding sulfonyl chlorides.[4]

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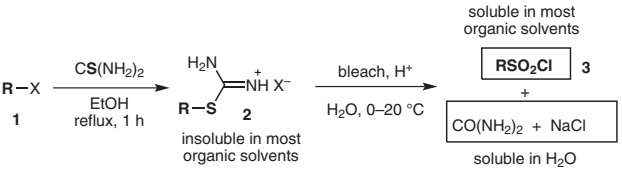
Bleach has been widely applied in bleaching, disinfection, and water treatment. In synthetic chemistry, it is commonly used in chlorination[5] and oxidation.[6] Among the many chlorinating and oxidizing reagents, it is regarded as one of the most environment-friendly and atom-economic reagents, according to the reagent guide developed by Dunn and co-workers.[7] Thus, it has the potential to replace other unsatisfactory chlorinating and oxidizing reagents in synthetic chemistry, and presents simple and green procedures. Based on these facts, we planned the direct oxidative chlorosulfonation of *S*-alkyl isothiourea salts, which are readily accessible from the reaction of corresponding alkyl halides or mesylates and thiourea. This procedure is supported by the fact that *S*-alkyl isothiourea salts and sulfonyl chlorides have distinctly different solubilities in most organic solvents, and the by-products urea and sodium salts are well soluble in water (Scheme 1). Therefore, the products can be easily isolated and purified by extraction with suitable organic solvents. In continuation of our work on simple and green syntheses of sulfonic acid derivatives, especially sulfonyl chlorides, herein, we present the bleach-mediated oxidative chlorosulfonation of *S*-alkyl isothiourea salts to synthesize alkanesulfonyl chlorides.

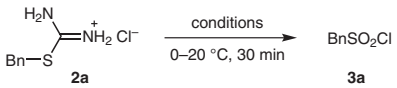


Scheme 1 Synthesis and purification of alkanesulfonyl chlorides from *S*-alkyl isothiourea salts via NaClO oxidative chlorosulfonation

The reaction optimization commenced with the treatment of *S*-benzyl isothiouronium chloride (**2a**) as an example with bleach and hydrochloric acid (Table 1, entries 1–3). The results suggest that, to add the accurate amount of the bleach, it should better be titrated prior to use for both the bench-stored bleach and the freshly manufactured sample to afford good results. For the highest yield, the oxidative chlorosulfonation of **2a** was carried out with 30 mL of freshly manufactured 5% bleach and 2 mL of 6 M H_2SO_4.

During the optimization, we found that the starting material **2a** did not completely dissolve in water; thus, when the product **3a** was generated, it was contaminated with trace amount of **2a**. As a result, purification of **3a** by direct

Table 1 Optimization of Reaction Conditions[a]



2a 3a

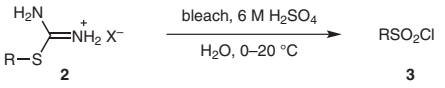
Entry	Conditions	Yield (%)
1[b]	10% bleach (30 mL), 2 M HCl (10 mL)	39
2[c]	5% bleach (30 mL), 3 M HCl (10 mL)	65
3[d]	5% bleach (30 mL), concd HCl (2 mL)	88
4[d]	5% bleach (30 mL), 6 M H_2SO_4 (2 mL)	93

[a] Reactions conducted on a 5 mmol scale.
[b] The bleach was 1 year and 4 months old. A series of optimizations using different volumes up to 30 mL of bleach and different concentrations of HCl gave poor results.
[c] Freshly purchased bleach was used, but the sample was 6 months old.
[d] Freshly purchased bleach manufactured within 2 months was used.

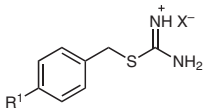
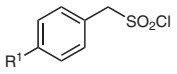
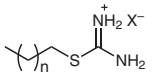
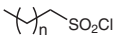
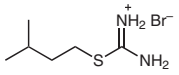
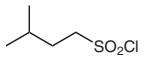
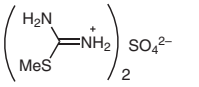
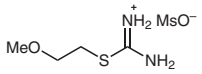
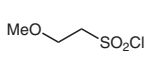
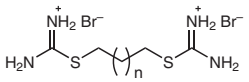
filtration upon completion of the reaction seemed to be not so satisfactory; consequently, further purification such as recrystallization is required. This problem was also encountered by Sprague and co-workers who employed chlorine gas to mediate the oxidative chlorosulfonation of isothiourea salts. To solve this problem and to get the highly pure product by simple purification, we decided to add diethyl ether to the reaction vessel. When **3a** was generated, it would be extracted immediately into the ethereal phase, leaving **2a** as a suspension in the aqueous phase to react with NaClO. As expected, **3a** was easily separated in high purity by partition of the ethereal phase, which could be isolated by the usual workup procedure. Moreover, the extraction of **3a** into diethyl ether minimized its hydrolysis, and thus gave a good 93% yield after the usual workup (see experimental).

With this simple procedure in hand, we decided to synthesize various significantly important sulfonyl chlorides. Phenylmethanesulfonyl chloride and its phenyl-modified congeners have been extensively used as sulfene precursors in mechanistic studies,[8] and as building blocks for the antibacterial medicines and enzyme inhibitors.[9] These privileged structures became our preferred synthetic targets. To our delight, the substituted phenylmethanesulfonyl chlorides were obtained in good (Table 2, entries 5, 6) to excellent yields (entries 2–4), regardless of the electron-donating or electron-withdrawing substituents. The relatively low yield (85%) of 4-nitrophenylmethanesulfonyl chloride is attributed to its high reactivity to water, while that of 4-tolylmethanesulfonyl chloride (87%) to its intrinsic property to decompose because of the electron-donating methyl group. The alkanesulfonyl chlorides, especially those with long chains, are widely applied in the production of fine chemicals such as detergents and dyes.[10] In synthetic chemistry, they also have powerful functions, which have been exemplified by the asymmetric synthesis of β-sultones[1d] and β-sultams[1e] as reported by

Table 2 Synthesis of Diverse Important Sulfonyl Chlorides[a]



2 3

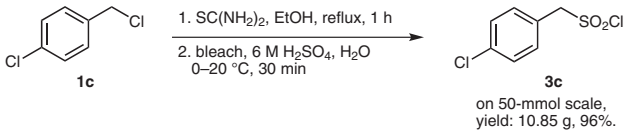
Entry	Substrate	2	Product	3	Yield (%)
					
1	R^1 = H, X = Cl	**2a**	R^1 = H	**3a**	93
2	R^1 = F, X = Cl	**2b**	R^1 = F	**3b**	99
3	R^1 = Cl, X = Cl	**2c**	R^1 = Cl	**3c**	99
4	R^1 = CN, X = Cl	**2d**	R^1 = CN	**3d**	99
5	R^1 = NO_2, X = Br	**2e**	R^1 = NO_2	**3e**	85
6	R^1 = Me, X = Cl	**2f**	R^1 = Me	**3f**	87
					
7	n = 2, X = Br	**2g**	n = 2	**3g**	98
8	n = 4, X = Br	**2h**	n = 4	**3h**	93
9	n = 6, X = Br	**2i**	n = 6	**3i**	96
10	n = 10, X = Br	**2j**	n = 10	**3j**	97
11	n = 14, X = Br	**2k**	n = 14	**3k**	98
12		**2l**		**3l**	80
13[b]		**2m**	$MeSO_2Cl$	**3m**	71
14		**2n**		**3n**	94
					
15[c]	n = 1	**2o**	n = 1	**3o**	60
16[c]	n = 2	**2p**	n = 2	**3p**	83

[a] Reactions conducted in a 5 mmol scale. For entries 1−4, 6, and 14, 30 mL of 5% bleach (4 equiv) was used; for entries 5 and 7−12, 37.5 mL of 5% bleach (5 equiv) was used.
[b] Conditions: 6 M H_2SO_4 (4 mL) and 5% bleach (60 mL, 8 equiv).
[c] Conditions: 6 M H_2SO_4 (4 mL) and 5% bleach (75 mL, 10 equiv).

Peters and co-workers. Satisfactory results in synthesizing these compounds were realized. The alkanesulfonyl chlorides, whether having branched or straight chains, were synthesized in good to excellent yields, regardless of the chain lengths (entries 7–12). Additionally, methanesulfonyl chloride (**3m**) was also synthesized in 71% yield from

S-methyl isothiouronium sulfate (**2m**), which was prepared from the inexpensive dimethyl sulfate and thiourea (entry 13). Not only the isothiouronium halides and sulfonates, but also the mesylates are suitable substrates for this method (entry 14), delivering the desired product **3n** in an excellent 94% yield. This example extends the sources of isothiourea salts from alkyl halides to compounds with other good leaving groups. Next, we tried to use our simple procedure to synthesize alkanedisulfonyl dichlorides, which were usually synthesized by chlorination of the corresponding disodium alkanedisulfonates and purified through a tedious sequence.[11] Presumably due to the difficult accesses to these compounds, their applications are very limited.[12] In contrast, by our method, propane-1,3-disulfonyl dichloride (**3o**) and butane-1,4-disulfonyl dichloride (**3p**) were readily obtained in moderate 60% and good 83% yield, respectively (entries 15 and 16). It can be predicted that alkanedisulfonyl dichlorides with longer chains are also accessible by this method.

In an attempt to extend the current method to a large-scale preparation, *p*-chlorophenylmethanesulfonyl chloride was smoothly synthesized in 96% yield after simple purification on a 50 mmol scale (Scheme 2).

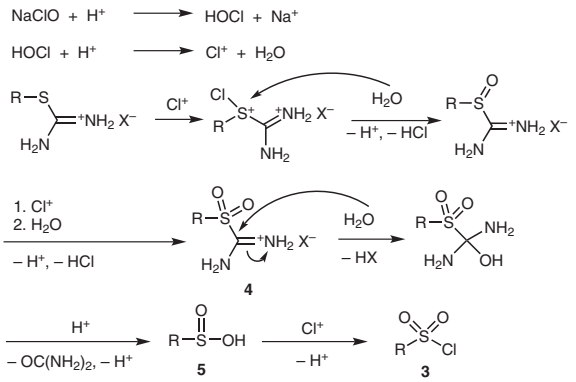


Scheme 2 Large-scale synthesis of sulfonyl chlorides

The reaction of hypochlorite and hydrochloric acid can give rise to chlorinium ion (Cl^+) and chlorine gas. Both chlorinium ion and chlorine gas can convert *S*-alkyl isothiourea salts into the corresponding sulfonyl chlorides. However, the reaction of hypochlorite and sulfuric acid can generate chlorinium ion only, revealing that the chlorinium ion is the key oxidant and shows higher reactivity than chlorine gas in the oxidative chlorosulfonation.

The oxidative chlorosulfonation mechanism, similar to that of NCS/HCl method,[3h] is proposed and depicted in Scheme 3. In the presence of aqueous acidic solution, hypochlorite is converted into chlorinium ion. The *S*-alkyl isothiourea salt is oxidized into the corresponding alkylsulfonyl methanimidamide salt **4** via two consecutive chlorinium ion oxidation steps. Through a sequence of attack by water, leaving of X^- anion, proton transfer, and leaving of protonated urea, **4** gives rise to the corresponding sulfinic acid **5**, which subsequently undergoes a further oxidation to produce the corresponding sulfonyl chloride **3**.

In conclusion, a simple procedure for clean and economic synthesis of alkanesulfonyl chlorides via bleach-mediated oxidative chlorosulfonation of *S*-alkyl isothiourea salts is described. The materials and reagents involved are readily accessible, rendering this method the versatility in synthesizing structurally diverse alkanesulfonyl chlorides and



Scheme 3 Proposed mechanism for the bleach oxidative chlorosulfonation of *S*-alkyl isothiourea salts

alkanedisulfonyl chlorides. Additionally, this method is environment- and worker-friendly, simple, and safe to operate. Easy purification of the products without chromatography affords high yields of up to 99%. All these advantages make this procedure a good choice for the synthesis of structurally diverse alkanesulfonyl chlorides and alkanedisulfonyl chlorides.

All starting materials, solvents, and reagents were used directly as received, without further purification. Petroleum ether (PE) used refers to the fraction boiling in the 60–90 °C range. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer with TMS as an internal standard in $CDCl_3$ solution.

Sulfonyl Chlorides 3a–h,m–p; General Procedure

The appropriate alkyl halide (or mesylate) (5 mmol) and thiourea (0.381 g, 5 mmol) were refluxed in EtOH (5 mL) for 1 h. After removal of the solvent in vacuum and washing with Et_2O (3 × 5 mL), the corresponding *S*-alkyl isothiourea salt was obtained as a white solid or sticky oil in an almost quantitative yield. Without purification, the product was transferred into a three-necked round-bottomed flask equipped with a thermometer and an addition funnel in an ice-bath. Then, 6 M H_2SO_4 (2 mL), followed by Et_2O (30 mL) were added. To the resultant vigorously stirred mixture was added dropwise 5% bleach (for alkyl chlorides and mesylates, 30 mL; for alkyl bromides, 37.5 mL) by keeping the inner temperature 0–20 °C (for the preparation of alkanedisulfonyl dichlorides, 0.762 g, 10 mmol thiourea, 4 mL of 6 M H_2SO_4, 50 mL of Et_2O, and 75 mL of 5% bleach were used). After the addition, the mixture was stirred for another 30 min. The mixture was partitioned in a separatory funnel, and the ethereal phase was washed with brine (25 mL), dried (Na_2SO_4), and evaporated in vacuum to afford the desired product. The oily products were extracted with $CHCl_3$ (3 × 2.5 mL) and evaporated to remove the by-product, bromine. If necessary, the products can be dissolved in minimal PE–EtOAc (5:1) and filtered through a column of silica gel (h = 5 cm) with PE–EtOAc (5:1) as eluent to remove the impurities (Table 2).

Sulfonyl Chlorides 3i–l; General Procedure

The corresponding *S*-alkyl isothiourea salt was prepared as described above and was transferred to 6 M H_2SO_4 (2 mL) kept in a three-necked round-bottomed flask equipped with a thermometer and an addition funnel at r.t. To the resultant vigorously stirred mixture was added dropwise 5% bleach (45 mL) by keeping the inner temperature less than 40 °C. After 1 h, the mixture was cooled to r.t. and Et_2O (30 mL) was added. The same workup as described above afforded the desired product in each case (Table 2).

All the sulfonyl chlorides synthesized are known compounds. Their ^{1}H NMR spectra and melting points of the solid products are identical with those reported.

Phenylmethanesulfonyl Chloride (3a)
Yield: 0.886 g (93%); colorless crystals; mp 92–94 °C (Lit.[2i] mp 91–93 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 5 H), 4.83 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.4, 130.3, 129.2, 126.1, 70.9.

(4-Fluorophenyl)methanesulfonyl Chloride (3b)
Yield: 1.066 g (99%); colorless crystals; mp 68–69 °C (Lit.[3f] mp 66–67 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.13 (m, 4 H), 4.84 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.85 (d, $J_{C,F}$ = 251.2 Hz), 133.34 (d, $J_{C,F}$ = 8.8 Hz), 122.1 (d, $J_{C,F}$ = 3.4 Hz), 116.40 (d, $J_{C,F}$ = 22.1 Hz), 69.94.

(4-Chlorophenyl)methanesulfonyl Chloride (3c)
Yield: 1.114 g (99%) on a 5 mmol scale and 10.85 g (96%) on a 50 mmol scale; colorless crystals; mp 96–97 °C (Lit.[2i] mp 92–93 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 4 H), 4.83 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.8, 132.6, 129.5, 124.6, 70.0.

(4-Cyanophenyl)methanesulfonyl Chloride (3d)
Yield: 1.090 g (99%); colorless crystals; mp 102–103 °C (Lit.[13] mp 102–103 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.62 (m, 4 H), 4.91 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.9, 132.1, 131.1, 117.8, 114.4, 69.8.

(4-Nitrophenyl)methanesulfonyl Chloride (3e)
Yield: 1.001 g (85%); colorless crystals; mp 88–89 °C (Lit.[2i] mp 92–93 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.7 Hz, 2 H), 7.70 (d, J = 8.7 Hz, 2 H), 4.96 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.0, 133.2, 132.6, 124.3, 73.2.

***p*-Tolylmethanesulfonyl Chloride (3f)**
Yield: 0.899 g (87%); colorless crystals; mp 80–81 °C (Lit.[3f] mp 84–85 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 4 H), 4.83 (s, 2 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.6, 131.2, 129.9, 123.0, 70.8, 21.3.

Butane-1-sulfonyl Chloride (3g)[3h]
Yield: 0.768 g (98%); yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89–3.65 (m, 2 H), 2.10–1.97 (m, 2 H), 1.61–1.50 (m, 2 H), 1.01 (t, J = 7.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.2, 26.2, 20.9, 13.3.

Hexane-1-sulfonyl Chloride (3h)[3h]
Yield: 0.855 g (93%); yellowish oil

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76–3.65 (m, 2 H), 2.08–1.98 (m, 2 H), 1.50–1.35 (m, 6 H), 0.91 (t, J = 6.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.5, 31.0, 27.2, 24.2, 22.2, 13.8.

Octane-1-sulfonyl Chloride (3i)[3h]
Yield: 0.958 g (96%); yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76–3.64 (m, 2 H), 2.08–1.98 (m, 2 H), 1.53–1.46 (m, 2 H), 1.33–1.29 (m, 8 H), 0.85 (t, J = 6.8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.5, 31.6, 28.8, 27.3, 24.6, 22.5, 14.0.

Dodecane-1-sulfonyl Chloride (3j)
Yield: 1.304 g (97%); white solid; mp 40–41 °C (Lit.[3b] 42–43 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88–3.72 (m, 2 H), 2.14–1.98 (m, 2 H), 1.56–1.46 (m, 2 H), 1.37–1.27 (m, 16 H), 0.88 (t, J = 6.7 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.5, 31.9, 29.55, 29.53, 29.4, 29.3, 29.1, 28.9, 27.6, 24.3, 22.7, 14.1.

Hexadecane-1-sulfonyl Chloride (3k)
Yield: 1.628 g (98%); white solid; mp 50–52 °C (Lit.[3f] 51–52 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75–3.51 (m, 2 H), 2.06–2.02 (m, 2 H), 1.49–1.26 (m, 26 H), 0.88 (t, J = 6.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.5, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 28.9, 27.6, 24.3, 22.7, 14.1.

3-Methylbutane-1-sulfonyl Chloride (3l)[3h]
Yield: 0.680 g (80%); yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76–3.65 (m, 2 H), 1.96–1.88 (m, 2 H), 1.84–1.74 (m, 1 H), 0.99 (d, J = 6.4 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 64.0, 32.5, 26.9, 22.0, 21.9.

Methanesulfonyl Chloride (3m)[3h]
Yield: 0.808 g (71%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 52.5.

2-Methoxyethanesulfonyl Chloride (3n)[3h]
Yield: 0.746 g (94%); yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97–3.94 (m, 4 H), 3.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.8, 64.9, 59.1.

Propane-1,3-disulfonyl Dichloride (3o)
Yield: 0.718 g (60%); white solid; mp 46–48 °C (Lit.[14] mp 46.5–47.0 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.04–3.94 (m, 4 H), 2.80–2.67 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 49.5, 19.7.

Butane-1,4-disulfonyl Dichloride (3p)
Yield: 1.000 g (83%); colorless crystals; mp 90–91 °C (Lit.[3f] mp 89–90 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85–3.75 (m, 4 H), 2.32–2.27 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 64.0, 22.5.

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