

Direct Oxidation of Methyl Ethers to Carbonyl Compounds with a Combination of Nitrogen Dioxide and Water in the Presence or Absence of Ozone

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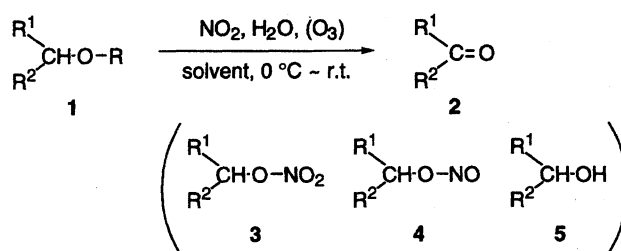
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A combination of nitrogen dioxide and water has been found to provide a new agent for the transformation of various alkyl methyl ethers **1** (R = Me) to carbonyl compounds **2** under mild conditions. The oxidation can be achieved successfully in dichloromethane, but hexafluoro-2-propanol was found to be most satisfactory as the solvent. The reaction was generally clean, and simple evaporation gave the expected oxidation product **2** in moderate to good yield. In the presence of ozone, but without water, the similar oxidation was observed only after prolonged reaction time, suggesting that some initial minor reaction with a strong oxidant, possible nitrogen trioxide, afforded an acidic promoter, which then worked as a catalyst similar to that involved in the reaction with a nitrogen dioxide and water system.

During our continuing efforts for exploring the usage of a novel nitration methodology based on nitrogen dioxide and ozone (the *kyodai*-nitration),¹⁾ we have found that this procedure can be modified for the oxidation of some secondary ethers to the corresponding ketones when nitrogen dioxide is used in an excess. Furthermore, we found the oxidation of the ethers can be successfully accomplished with nitrogen dioxide alone, if a small amount of water was added to the reaction system. In this paper, we first describe a facile oxidative cleavage of aliphatic ethers to carbonyl compounds with nitrogen dioxide in the presence of ozone, and then go into a similar oxidation in the absence of ozone, but with added water.

The nitrogen dioxide and ozone system provides an effective and useful nitration methodology for a wide variety of aromatic compounds, and the reaction has recently been established to proceed via the electron transfer process involving nitrogen trioxide generated in situ, when a substrate is oxidizable.²⁾ With some alkyl aromatic compounds, however, the oxidation of benzylic position occurred concurrently with nuclear nitration to give benzyl nitrate as a by-product.³⁾ Based on this observation, the synthetic potential of the oxidation by this reagent system has now been examined. Among a variety of aromatic and aliphatic substrates examined, secondary alkyl ethers **1** were found to be efficiently oxidized to give the corresponding ketones **2** in moderate to good yields (Scheme 1). The oxidative cleavage of alkyl ethers to carbonyl compounds may be a useful functional group transformation in organic synthesis, but it is generally difficult to effect as compared with those of benzyl, silyl, and stannyl ethers.

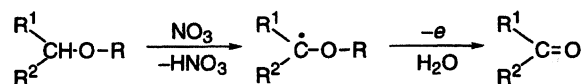
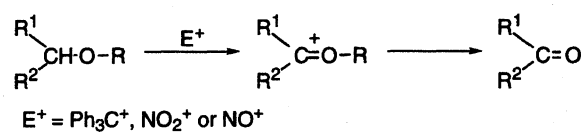
Several methods are known to oxidize alkyl ethers directly to ketones. However, they are not free from some disadvantages. Oxidations of alkyl ethers with chromic acid/ace-



Scheme 1.

tic acid,⁴⁾ cerium(IV) sulfate in acetic acid,⁵⁾ and silver(II) oxide⁶⁾ are usually carried out under highly acidic conditions, which are incompatible with acid-sensitive groups. Silica gel supported metal nitrates such as $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ have been used for the oxidative cleavage of alkyl and benzyl ethers;⁷⁾ however many technical problems arise from the insoluble nature of these reagents. Uranium hexafluoride⁸⁾ and cerium(IV) ammonium nitrate coupled with sodium bromate⁹⁾ have also been reported in the literature.

Electrophilic reagent such as trityl tetrafluoroborate¹⁰⁾ has been introduced by Barton for the oxidation of several ethers via the hydride ion abstraction mechanism (Scheme 2). This salt is somewhat difficult to prepare, but can oxidize cleanly *t*-butyl, trityl, and benzyl ethers to carbonyl compounds. Ox-



Scheme 2.

ides of nitrogen are also used to cleave ethers oxidatively via the hydride transfer mechanism. Thus Olah and Ho have reported the oxidation of alkyl methyl ethers with nitronium tetrafluoroborate in dichloromethane.¹¹ They have also used nitrosonium salt for the oxidative cleavage of trialkylstannyl and trialkylsilyl ethers.¹² Nitrogen trioxide generated by anodic oxidation of nitrate has been reported to oxidize ethers, where the reaction is assumed to begin with the hydrogen abstraction.¹³ These procedures sometimes lead to the ring cleavage, depending on the structure of a substrate used. For example, nitrosonium and nitrosyl compounds are known to act as the nitrosation agent for cyclic ketones to form the α -hydroxyimino derivatives, which eventually lead to open-chain products in the presence of acid.^{11,14}

We have found that this type of oxidation was successfully achieved for a variety of secondary alkyl ethers **1** with nitrogen dioxide in dichloromethane in the presence of added water. The reaction was generally clean; simple evaporation of the reaction mixture gave the oxidation product **2** in good to moderate yield, sometimes along with small amounts of nitrate **3**, nitrite **4**, or alcohol **5**. In the presence of ozone, however, the reaction became somewhat sluggish and a similar oxidation was observed only after prolonged reaction time. We herein report the details of these reactions to reveal its synthetic applicability.

Results and Discussion

In dichloromethane at 0 °C, secondary alkyl methyl ethers **1** (R=Me) readily reacted with nitrogen dioxide and ozonized oxygen to give the corresponding ketones **2** in moderate to good yields, along with a minor amount of nitrate **3** (Scheme 1). In some cases, the corresponding nitrite **4** and/or alcohol **5** also accompanied the reaction. In order to improve the yield of ketones, the effect of several additives was in-

vestigated using cyclohexyl methyl ether **1a** as a common substrate; the results obtained are shown in Table 1. In the presence of fuming nitric acid (1.0 mol amt.), the reaction was accelerated and completed within 1.0 h, the yield of ketone **2a** being increased up to 70%. Methanesulfonic acid and anhydrous aluminum chloride also promoted the reaction, but the yield of the ketone was not so good and ring-opened by-products were often formed. With silver nitrate added, no noticeable effect was observed; this may be attributed to the insolubility of silver salt in dichloromethane. Interestingly enough, water was found to be most effective as a catalyst for the production of ketones.

Oxidation of cyclohexyl methyl ether **1a** was compared in several different solvents in order to find the optimum conditions for the formation of ketone. In dichloromethane, the conversion was relatively slow and the yield of nitrate was higher than that of ketone at the 1 h stage (which corresponded to the feeding of 2 mol amt. of ozone). The reaction showed an induction period and began to be accelerated after 1 h, reaching completion in 1.5 h. In a more polar solvent such as acetonitrile or nitromethane, the rate of the reaction was increased, but the total yield of products **2** and **3** became lower. In nonpolar solvents such as carbon tetrachloride and hexane, the reaction was very slow, which suggests that the oxidative cleavage reaction is likely to proceed via an ionic process in the present system. The control reaction of cyclohexyl nitrate **3a** under the similar conditions showed no significant conversion of the nitrate.

The reaction was also examined for various types of alkyl and silyl cyclohexyl ethers (Table 2). Cyclohexyl ethyl ether reacted under similar conditions to give cyclohexanone in 50% yield, cyclohexyl nitrate being obtained as an additional product in 40% yield. The reaction of cyclohexyl *t*-butyl ether with nitrogen dioxide and ozone (2 mol amt.)

Table 1. Oxidation of Cyclohexyl Methyl Ether (**1a**) with Nitrogen Dioxide in the Presence of Ozone under Various Conditions^{a)}

Solvent	Additive (mol amt.)	Conversion (%)	Yield of products (%) ^{b)} 2a : 3a
CH ₂ Cl ₂	None	23	2 : 21
	None	96 ^{c)}	66 : 23
	None	99 ^{d)}	2 : 67
	None	75 ^{e)}	29 : 4
	fum-HNO ₃ (1.0)	100 ^{f)}	70 : 11
	MeSO ₃ H (1.0)	100 ^{f)}	52 : 0
	AlCl ₃ (1.0)	100 ^{f)}	43 : 0
	AgNO ₃ (1.0)	23	2 : 17
	H ₂ O (0.5)	95	88 : 5
MeCN	None	96	12 : 3
MeNO ₂	None	100	57 : 3
ClCH ₂ CH ₂ Cl	None	12	3 : 8
CHCl ₃	None	6	3 : 3
CCl ₄	None	7	3 : 4
Hexane	None	10	4 : 6

a) Unless otherwise stated, all reactions were carried out for solutions of ether **1a** (5 mmol) and nitrogen dioxide (2.5 mL) in a given solvent (20 mL). Ozonized oxygen was introduced for 1 h at a rate of 10 mmol h⁻¹ at 0 °C. b) Product distributions were determined by GLC, at a low injection-port temperature (150 °C). c) Reaction time was 2 h. d) Reaction was carried out at -20 °C for 2 h. e) Reaction was carried out at -78 °C for 2 h. f) Reaction time was 0.5 h.

Table 2. Oxidation of a Variety of Ethers (1) with Nitrogen Dioxide in the Presence of Ozone^{a)}

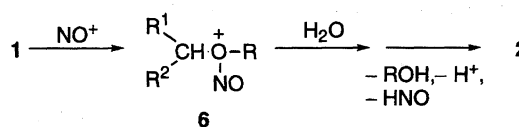
R ¹ CHR ²	R	Time (h)	Yield of products (%) ^{b)} 2 : 3
Cyclopentyl	Me	3	46 : 12
Cyclohexyl	Me	3	82 : 6
	Et	3	51 : 40
	<i>t</i> -Bu	2	0 : 99
	<i>t</i> -BuMe ₂ Si	3	19 : 79
	PhCH ₂	1	20 : 80
	<i>p</i> -NO ₂ -C ₆ H ₄ CH ₂	5	43 : 37
Cyclododecyl	Me	3	93 : 1
2-Octyl	Me	3	10 : 73

a) All reactions were carried out for dichloromethane solutions (50 mL) of a given substrate (10 mmol) and nitrogen dioxide. Ozone was introduced at a rate of 10 mmol h⁻¹ at 0 °C. b) Product distributions were determined by GLC, at a low injection-port temperature (150 °C).

completed within 2 h, giving the corresponding nitrate exclusively in 99% yield. This trend in the cleavage of the ether linkage suggests a possible involvement of an oxonium intermediate. *t*-Butyldimethylsilyl ether is one of the most popular ways for the protection of alcohols. This ether reacted with nitrogen dioxide and ozone to give cyclohexanone in 19% yield, while the nitrate was a major product (79% yield). Benzyl ether linkage is also commonly used as the protecting group for polyols and carbohydrates owing to its comparatively high stability toward acids and bases. Benzyl cyclohexyl ether was smoothly oxidized with the present system to give benzaldehyde in almost quantitative yield. In this case, the formation of cyclohexyl nitrate and benzaldehyde occurred concurrently. 4-Nitrobenzyl cyclohexyl ether was similarly cleaved to give the corresponding ketone and nitrate, though the reaction was slower. Other secondary alkyl ethers, which included cyclopentyl, cyclododecyl, and 2-octyl ethers, were also cleaved oxidatively, as shown in Table 2. 3-Decyl methyl ether similarly reacted to afford the corresponding ketone and nitrate. In every case, the ketonic product was easily separated from the accompanying nitrate by silica-gel column chromatography. Compared with the previously reported methods for the oxidation of ethers, the reaction with nitrogen dioxide and ozone is more attractive because of its simpler operation, good yield of products, economy, and mild reaction conditions.

In the presence of small amounts of added water, the re-

action can proceed without ozone (Table 3). This oxidation is unique enough to require both water and nitrogen dioxide. Control experiments using fuming nitric acid revealed that this reagent does not oxidize the ethers to carbonyl compounds at all under our reaction conditions. In the presence of oxygen, the reaction proceeded faster than those under air and under an argon atmosphere. We have investigated this reaction using cyclododecyl methyl ether as a common substrate in various solvents (Table 4). The oxidation occurred most efficiently in hexafluoro-2-propanol, which may be taken to reflect the increased stability of a possible oxonium intermediate,¹⁵⁾ but the actual mechanism of the reaction is not clear at present. One possible explanation for this novel type of oxidation may be depicted as shown in Scheme 3. The reaction of nitrogen dioxide and water produces both nitric and nitrous acids, which are in equilibrium with the nitrosonium ion. An attack of the nitrosonium ion on the ether oxygen occurs to form the oxonium ion intermediate **6**, followed by a nucleophilic attack of water or some oxide species, eventually leading to the corresponding ketone. The reaction profile against time shows that the nitrate was

Table 3. Oxidation of Cyclohexyl Methyl Ether (1a) with Nitrogen Dioxide and Water under Various Conditions^{a)}

Reaction conditions	Time	Conversion	Yield of 2a
	h	%	%
NO ₂ , 1.0 mL; r.t.; under Ar	3	0	—
NO ₂ , 0.5 mL; H ₂ O, 0.02 mL; r.t.; under Ar	3	92	58
NO ₂ , 0.5 mL; H ₂ O, 0.10 mL; r.t.; under Ar	5	48	38
NO ₂ , 0.5 mL; H ₂ O, 0.18 mL; r.t.; under Ar	5	30	26
NO ₂ , 0.5 mL; H ₂ O, 0.02 mL; r.t.; under Air	2	86	75
NO ₂ , 0.5 mL; H ₂ O, 0.02 mL; r.t.; under O ₂	1	93	86
Fuming HNO ₃ , 1.0 mol amt.; r.t.; under Ar	12	0	—

a) All reactions were carried out for dichloromethane solutions (5 mL) of substrate **1a** (1 mmol) and nitrogen dioxide/water.

Table 4. Oxidation of Cyclododecyl Methyl Ether (**1b**) with Nitrogen Dioxide and Water in Various Solvents^{a)}

Solvent	Additive (amount added, mL)	Conversion %	Yield of products (%) ^{b)}
			2b : 3b : 5b
CH ₂ Cl ₂	None	25 ^{c)}	25 : 0 : 0
	H ₂ O (0.05)	44	26 : 0 : 0
	H ₂ O (0.10)	23	15 : 0 : 0
	H ₂ O (0.5)	6	0 : 0 : 6
	AcOH (0.10)	27	15 : 0 : 12
EtNO ₂	H ₂ O (0.10)	39	3 : 0 : 0
CCl ₄	H ₂ O (0.10)	3	0 : 0 : 1
AcOEt	H ₂ O (0.10)	2	0 : 0 : 1
CF ₃ CH ₂ OH	H ₂ O (0.10)	87	32 : 6 : 1
CF ₃ CHOHCF ₃	H ₂ O (0.10)	100	70 : 0 : 0

a) All reactions were carried out for given solutions (5 mL) of substrate **1b** (1 mmol) and nitrogen dioxide (0.1 mL)/water overnight (12 to 15 h) at room temperature under air, unless otherwise indicated. b) Product distributions were determined by GLC, at a low injection-port temperature (150 °C). c) Stood for 2 d.

formed at initial stage of the reaction and the formation of ketone began after a lapse of time (Fig. 1). The initially formed nitrate did not increase much after all. A similar trend was observed for the reaction of ethers with nitrogen dioxide and ozone, which, however, occurred only after a prolonged induction period (Fig. 2). The role of added water could be a good nucleophile. Hence, if water was not present, the nucleophile should be sought for a nitrate or an unknown compound formed from some side reaction, which would have rendered the yield of ketone somewhat lower in the latter type of oxidation.

Conclusion

Secondary alkyl methyl ethers can be oxidized smoothly with nitrogen dioxide and ozone in dichloromethane at 0 °C to give corresponding ketones in good yield, showing the strong oxidizing ability of this coupled reagent system. In the presence of a small amount of water, the oxidation was accelerated and the yield of ketones was considerably in-

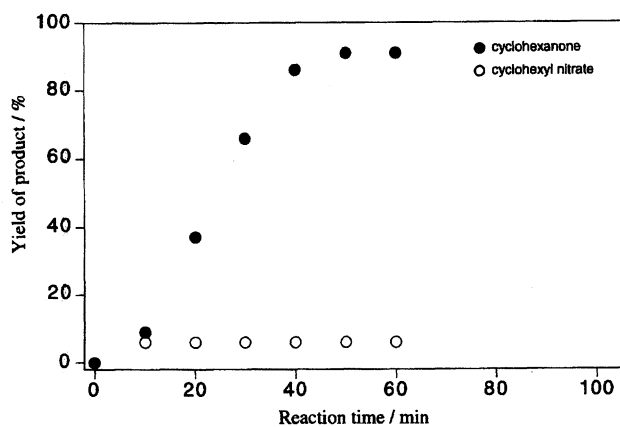


Fig. 1. Oxidation of cyclohexyl methyl ether with nitrogen dioxide in the presence of water. Reaction was carried out for 5 mmol of substrate in dichloromethane (20 mL) at 0 °C in the presence of 1 mol amt. of water.

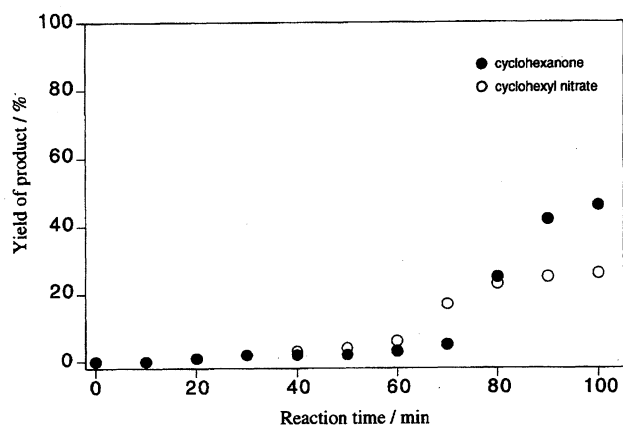


Fig. 2. Oxidation of cyclohexyl methyl ether with nitrogen dioxide in the presence of ozone. Reaction was carried out for 5 mmol of substrate in dichloromethane (20 mL) at 0 °C. Ozone was introduced at a rate of 10 mmol h⁻¹.

creased, even if ozone was omitted. The water-promoted oxidation of ethers with nitrogen dioxide proceeded faster in hexafluoro-2-propanol than in dichloromethane. This new type of oxidation, which features simple operation, economy, and mild reaction conditions, may find use in the direct transformation of some alkyl ethers into the corresponding alkyl ketones. The reaction mechanism has been interpreted in terms of the electrophilic attack of nitronium ion on the ether oxygen, followed by the nucleophilic reaction with a water molecule.

Experimental

General. General experimental details are described in previous papers.²⁾ CI mass spectra were recorded on a Shimadzu QP5000 (CI gas = isobutane) spectrometer. Methyl and ethyl ethers,¹⁶⁾ *t*-butyl ether,¹⁷⁾ *t*-butyldimethylsilyl ether,¹⁸⁾ benzyl ether,¹⁶⁾ and *p*-nitrobenzyl ether¹⁹⁾ were prepared from the corresponding alcohols, according to the literature procedures. Cyclododecane was recrystallized from ethanol and used as an internal standard for GLC analyses. Nitrogen dioxide (99% pure) was purchased from Sumitomo Seika Co., Ltd. in a cylinder. An apparatus (Nippon

Ozone Co., Ltd., type ON-1-2) was used for the generation of ozone. The machine produced ozone at a rate of 10 mmol h^{-1} with an oxygen flow of 10 L h^{-1} under an applied voltage of 80 V. All products are known and identified by direct comparison of $^1\text{H NMR}$, IR and GC-MS spectra.

Oxidation of Ethers with Nitrogen Dioxide and Ozone. Typical Procedure. Cyclohexyl methyl ether (0.57 g, 5.0 mmol) was dissolved in a freshly distilled dichloromethane (20 mL) containing nitrogen dioxide (3 mL), and the solution was placed in a two necked flask fitted with a gas inlet tube and a vent which permitted a waste gas to escape. The mixture was stirred vigorously at 0°C , while the ozonized oxygen was slowly introduced from an inlet tube. After a lapse of an appropriate time, the reaction was quenched by addition of ice-cooled water. The organic phase was separated, extracted with dichloromethane, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a mixture of products as an oily residue, which was separated into each component on a silica gel column. Yield of products and conversion rate were determined by GLC using cyclododecane as an internal standard at a low injection-port temperature (150°C).

Oxidation of Ethers with a Combination of Nitrogen Dioxide and Water. General Procedure. To a solution of an ether (1 mmol) in dry hexafluoro-2-propanol (5 mL) containing water (0.1 mL), nitrogen dioxide (0.1 mL) was added with a glass syringe in the dark at room temperature. After an appropriate time, the reaction mixture was evaporated and the residue was analyzed. If necessary, a crude mixture of products was chromatographed on silica gel. The progress of the reaction as well as the relative variation of each product were monitored by GLC at a low injection-port temperature (150°C).

***t*-Butyl Cyclohexyl Ether:** Colorless oil; IR (NaCl) 1199, 1076 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 1.1\text{--}1.3$ (13H, m), 1.5–1.6 (2H, m), 1.7–1.8 (4H, m), 3.2–3.4 (1H, m); MS(Cl) m/z 157 ($\text{M}^+ + 1$); 100, 141 (50), 99 (47).

***t*-Butyldimethylsilyl Cyclohexyl Ether:** Colorless oil; IR (NaCl) 1253, 1097, 837 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 0.05$ (6H, s), 0.89 (9H, s), 1.2–1.4 (6H, m), 1.7–1.8 (4H, m), 3.6–3.8 (1H, m); MS(Cl) m/z 215 ($\text{M}^+ + 1$); 86, 214 (44), 199 (83), 157 (100).

Cyclohexyl Nitrate: Colorless oil; IR (NaCl) 1630, 1280, 870 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 1.3\text{--}1.6$ (6H, m), 1.7–1.8 (2H, m), 1.9–2.0 (2H, m), 4.9–5.0 (1H, m); MS(EI) m/z 83 ($\text{M}^+ - 46$); 24, 55 (100), 43 (81).

Cyclododecyl Nitrate: White crystals, mp $35\text{--}36^\circ\text{C}$ (from hexane); IR (NaCl) 1620, 1280, 860 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 1.3\text{--}1.4$ (18H, m), 1.6–1.8 (4H, m), 5.1–5.2 (1H, M); MS(EI) m/z 183 ($\text{M}^+ - 46$); 100, 167 (33), 113 (35), 85 (82).

4-*t*-Butylcyclohexyl Nitrate: Colorless oil; IR 1630, 1280, 870 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 0.87$ (9H, s), 0.9–1.5 (5H, m), 1.8–1.9 (2H, m), 2.1–2.2 (2H, m), 4.7–4.9 (1H, m); MS(EI) m/z 154 ($\text{M}^+ - 47$); 2, 139 (6), 67 (100).

Cycloheptyl Nitrate: Colorless oil; IR 1622, 1277, 868 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 1.48\text{--}1.80$ (10H, m), 1.85–2.06 (2H, m), 5.08–5.16 (1H, m); MS(Cl) m/z 113 ($\text{M}^+ - 46$); 32, 97 (100).

2-Octyl Nitrate: Colorless oil; IR 1620, 1280, 870 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 0.8\text{--}0.9$ (3H, m), 1.3–1.4 (11H, m), 1.5–1.7 (2H, m), 5.0–5.1 (1H, m); MS(EI) m/z 113 ($\text{M}^+ - 62$); 3, 90 (100), 85 (31).

3-Decyl Nitrate: Colorless oil; IR 1626, 1277, 868 cm^{-1} ; $^1\text{H NMR}$ (200 MHz) $\delta = 0.8\text{--}0.9$ (6H, m), 1.2–1.3 (10H, m), 1.6–1.7 (4H, m), 4.9–5.1 (1H, m); MS(Cl) m/z 220 ($\text{M}^+ + 1$); 1, 157 (100), 141 (65).

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