¹⁷O NMR Spectra of Vinyl Ethers

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The ¹⁷O NMR spectra of 58 α , β -unsaturated (vinyl) ethers were recorded in CDCl₃ solution. The dependence of the chemical shift on the number and position of alkyl substituents in the vinyl moiety and on the nature and bulkiness of the alkoxy group was explored. The oxygen chemical shifts proved to be sufficiently sensitive to structural factors to make ¹⁷O NMR spectroscopy a useful tool in the investigation of the electronic and spatial structures of vinyl ethers.

KEY WORDS NMR ¹⁷O NMR Vinyl ethers

INTRODUCTION

During the past two decades, the structures and thermodynamic stabilities of vinyl ethers have been studied extensively in our laboratory by several techniques including chemical equilibration,¹ dipole moment measurements² and ¹³C NMR spectroscopy.³ The interesting properties of vinyl ethers arise from the direct linkage between an O atom and the C=C bond, which, under favourable spatial orientation of these units, leads to effective p- π conjugation in the vinyloxy system:

 $-0-C=C\leftrightarrow -\overset{+}{O}=C-\overset{-}{C}$

In addition to being a function of stereochemistry, the strength of this conjugation, and accordingly the charge distribution in the vinyloxy moiety, depend also on the nature, number and position of substituents attached to the -O-C=C system. ¹⁷O NMR chemical shifts are known⁴ to be sensitive to π electron density; thus the structure-dependent charge concentration on the O atom makes vinyl ethers an interesting research subject by this spectroscopic technique. In the chemical literature, the number of papers dealing with this topic and the number of vinyl ethers investigated therein are scanty.⁴⁻⁸ In this paper, the ¹⁷O NMR chemical shifts of 58 vinyl ethers of type (1) are reported, and the relationship between structure and chemical shift is explored.



RESULTS AND DISCUSSION

The experimental data are summarized in Table 1. The effect of structure on chemical shift will be analysed in

CCC 0749-1581/94/060353-05 © 1994 by John Wiley & Sons, Ltd. terms of substituent effects, which are defined here as follows. The term SCS(R) (SCS = substituent induced chemical shift) describes the difference in ¹⁷O NMR chemical shift between an alkyl vinyl ether and the corresponding methyl vinyl ether, i.e. the effect of the alkoxy group, with the MeO group as a standard. The remaining three substituent effects, SCS(R_n), denote the change in ¹⁷O NMR chemical shift occurring on replacement of a hydrogen atom of the vinyl group with the substituent in question. If several substituents are present in the vinyl group, the substituent effect of a given group is defined similarly, i.e. the chemical shift of the corresponding compound with a hydrogen atom in place of the substituent concerned.

Effect of the alkoxy group in alkyl vinyl and alkyl propenyl ethers

Table 1 includes chemical shift values for 10 alkyl vinyl ethers, together with those for allyl vinyl and 2-chloroethyl vinyl ethers. The shift values for Me, Et, n-Pr, i-Bu, i-Pr and t-Bu vinyl ethers, as reported by Kalabin et al.⁷ for the neat compounds, are generally slightly (3 ppm or less) higher than those found here in CDCl₃ solution. In this series the increasing bulkiness of the alkyl group leads to stereochemical changes in the orientation of the alkoxy group: methyl vinyl ether, like other alkyl vinyl ethers with a primary alkyl group, exists mainly as a planar s-cis conformer, whereas the bulky tert-butyl and tert-amyl vinyl ethers are likely to prefer a slightly non-planar gauche form:⁹



The remaining vinyl ethers with a secondary alkyl group exist as a roughly equimolar mixture of two conformers, probably similar in structure to those mentioned above. Owing to the presence of several rotamers, the observed changes in the chemical shift for

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Compound	R	R,	R2	R ₃	Shift	SCS(R)	SCS(R1)	SCS(R ₂)	SCS(R3)
1	Me	н	н	H	57		_		
2	Et	Н	н	н	85	28	—		
3	n-Pr	н	н	н	81	24	<u> </u>		
4	Aliyi	н	н	н	77	20	_		—
5	i-Bu	н	н	н	80	23			
6	Me ₃ CCH ₂	н	н	н	79	22	—		
7	CICH,CH,	н	н	н	75	18			
8	í-Pr	н	н	н	106	49			
9	Et ₂ CH	н	н	н	97	40	—		_
10	(<i>i</i> -Pr)₂CH	н	н	н	90	33			<u> </u>
11	t-Bu	н	н	н	114	57			
12	t-Am	н	н	н	109	52			
13	Me	Me	н	н	68	_	11		
14	Et	Me	н	н	98	30	13		_
15	Me	Et	н	н	65	—	8		
16	Me	n-Pr	н	н	67		10		
17	Me	i-Bu	н	н	66		9		
18	Me	Me ₃ CCH ₂	н	н	70		13		
19	Me	MeOCH ₂ CH ₃	н	н	(-20)* 66	_	9		
20	Me	i-Pr	н	н	60		3		
21	Me	Et ₂ CH	н	н	61		4		
22	Me	cvclo-Pr	. H	н	59		2		
23	Me	cvclo-Hx	н	н	64		7		_
24	Me	t-Bu	Н	н	62		5		
25	Me	Н	Me	н	44	_		-13	
26	Me	н	Et	н	45		_	-12	
27	Me	Н	i-Pr	н	40			-17	_
28	Me	H	t-Bu	н	38			-19	
29	Me	н	н	Me	35				-22
30	Me	н	н	Ft	37		_		-20
31	Me	н	й	i-Pr	34	_			-23
32	Me	н	н	<i>t</i> -Ru	38		_		-19
33	Me	н	Me	Me	28			7	-16
34	Ft	н	Me	Me	<u>-0</u> 60	32		-7	-13
35	Me	н	Ft	Ft	30	_	_	-7	-15
36	Me	н	(CH_))	26				
37	Me	Me	Me	′5 H	59	_	15	-9	
38	Me	Me	Ft	н	59		14	-9	
39	Me	Me	MeOCH.	н	(-12)*68	_	_	ő	_
40	Me	Me	<i>i</i> -Pr	н	57		17	-11	
41	Me	Ft	Me	н	55		11	-10	
42	Me	i-Pr	Me	н	47		3	-13	
43	Me	i-Pr	i-Pr	н	45		5	-15	
44	Me	Me		Me	36	_	1		-32
45	Me	Ft	н	Me	28	_	-7		-37
46	Me	i. Pr	н	Me	20		-11		_36
47	Me	<i>i</i> -Pr	н	i. Pr	25		-9		_25
48	Me	Me	Me	Me	32		Д	4	-27
49	Me	Me	Ft	Ft	34		4	-	-25
50	Me	Me	(CH)	\	31				20
51	Me	Ft	Me	/5 Mo	24		-4	-4	-31
52	Me	i_Ru	Mo	Mo	24 26		-3		-31
52	Ft	,- ου μ	Me		20	20	- 3		
54	در ز_D،	ח ע .	Mo	п	73	23 17		_15	
55	1-F1 + D	ה נו	IALG	n L	31	+/ E0	_	-15	
50	(-DU E+	n U	IVIE	n Ma	103	09 22	—	-11	
50	СL ; D-	n u	n L		0/	32	_		-18
58	1-51 t_Rii	л Ц	л Ц	MA	104	60	_		-10
00	t-DU	п	n	ING	104	03	_		-10
^a Signal of	the MeOCH ₂ gi	roup.							

 Table 1. ¹⁷O NMR chemical shifts (CDCl₃ solution) for some vinyl ethers of type 1, relative to water, together with the various substituent effects as defined in the text

different alkoxy groups may in part be due to varying strengths of conjugation in the different conformers.

be comparable to that in alkyl vinyl ethers. This view is confirmed by the present data: for R = Et, *i*-Pr and *t*-Bu, the values of SCS(R) are 28, 49 and 57 ppm for alkyl vinyl ethers and 29, 47 and 59 ppm for alkyl (*E*)-

In alkyl (*E*)-propenyl ethers ($R_1 = R_3 = H$, $R_2 = Me$), the effect of the alkoxy group on $\delta(^{17}O)$ is likely to

propenyl ethers. On the other hand, the values of SCS(R) in alkyl (Z)-propenyl ethers (32, 56 and 69 ppm for $\mathbf{R} = \mathbf{E}t$, *i*-Pr and *t*-Bu, respectively) deviate significantly from those for the E isomers. In the (Z)-propenyl ethers, the s-cis structure is effectively hindered by the Me group *cis* to the O atom, and all these compounds are likely to assume essentially similar spatial structures, probably not far from the planar s-trans form.³ Against this background it is of interest to note the values of the respective substituent effects in related saturated ethers: 30, 51 and 61 ppm for alkyl methyl ethers, and 29, 51 and 63 ppm for alkyl ethyl ethers.⁵ In magnitude, these effects are intermediate to those found in the geometrical isomers of alkyl propenyl ethers. Apparently, the observed differences in the values of SCS(R) between the saturated and unsaturated ethers may be explained as follows.

Previous ¹³C NMR studies of alkyl (Z)-propenyl ethers have shown that the strength of $p-\pi$ conjugation in these compounds, as monitored by the chemical shift of the β -carbon of the vinyl group, is promoted by increasing increasing electron-releasing power (increasing bulkiness) of the alkyl group.³ Accordingly, the differences in SCS(R) between these unsaturated ethers and the related saturated ethers might be expected to increase in this sequence, in line with observation. Of course, the same inductive effect is operative in the Eisomers also, but for bulky alkyl groups the increase in inductive effect is more than counterbalanced by the enhanced contribution of the non-s-cis conformer(s), which may not be equally favourable for conjugation. Hence the reduced conjugation in bulky alkyl (E)-propenyl ethers, relative to the strength of conjugation in methyl (E)-propenyl ether (25), leads to substituent effects which are smaller than those found in the saturated ethers.

Substituent effects SCS(R_n)

Let us now consider the effects of substituents attached to the vinyl moiety. In alkyl (E)-propenyl ethers ($\mathbf{R}_1 =$ $R_3 = H, R_2 = Me$) the values of SCS(R_2) (-13, -13, -15 and -11 ppm for R = Me, Et, *i*-Pr, and *t*-Bu, respectively) are essentially equal, independent of the bulkiness of the alkoxy group. The marked values of $SCS(R_2)$ suggest a considerable decrease in p- π conjugation in the vinyloxy system, due to the electronreleasing inductive effect of the Me group, which tends to polarize the C=C bond in a direction opposite to that caused by the alkoxy group. The decrease in conjugation, with an accompanying weakening of molecular stability, has been observed previously in thermodynamic studies of isomeric vinyl ethers: the double-bond stabilizing ability of a single Me group on the β -carbon of the vinyl group is only ca 4 kJ mol⁻¹, some 7 kJ mol⁻¹ less than the corresponding value in ordinary alkenes.¹⁰ Further, the data in Table 1 show that the presence of a bulkier (more electropositive) alkyl group on C- β gives rise to an even higher inhibitive effect on p- π conjugation; cf. the substituent effects of -17 and -19 ppm for the *i*-Pr and *t*-Bu groups, respectively.

On the other hand, in alkyl (Z)-propenyl ethers $(R_1 = R_2 = H, R_3 = Me)$ the values of $SCS(R_3)$ are

markedly affected by the size of the alkoxy group, varying from -22 ppm for R = Me to -10 ppm for R = t-Bu. This, of course, is mainly a result of rotational isomerism in the reference compounds, alkyl vinyl ethers, as explained above. It is noteworthy that if the reference compound and the compound under inspection assume similar spatial structures (which is likely to be the case for R = t-Bu, SCS(R_3) is equal to SCS(R_2) in the respective E isomer.

Once the strength of $p-\pi$ conjugation in alkyl vinyl ethers has been reduced by the presence of a single alkyl substituent on the β -carbon, the introduction of an additional alkyl group on the same carbon causes a further decrease in conjugation, as revealed by the substituent effects SCS(R₂) and SCS(R₃) for compounds 33-35. However, these effects are 6-7 ppm smaller than those in the respective monosubstituted compounds, which means that the decrease in conjugation due to the second alkyl group is less marked than that caused by the first. This finding is also in line with previous thermodynamic results: the double-bond stabilizing ability of the second Me group on the β -carbon of the vinyl group is significantly higher than that of the first Me group, amounting to about 8 kJ mol⁻¹.¹⁰

The previous discussion of substituent effects is concerned with compounds without a substituent in the α position of the vinyl group. In the presence of such a substituent, the effect SCS(R₂) in α,β -dialkyl-substituted vinyl ethers appears to be a few ppm smaller than that in compounds without the α -substituent. Apparently, in these compounds the group R_2 is unable to oppose as efficiently as in the previous compounds the combined electron-releasing effect of the alkoxy and alkyl groups attached to C- α . On the other hand, in the Z isomers of α,β -dialkyl-substituted vinyl ethers the values of $SCS(R_3)$ are exceptionally large, about -35 ppm, revealing an essential inhibition of $p-\pi$ conjugation in the -O - C = C system. The reduced conjugation points to a dominance of non-planar conformers of the alkoxy group in these compounds. This phenomenon, also observed previously by ¹³C NMR spectroscopy,¹¹ is in agreement with the unexpectedly low thermodynamic stability of the Z isomers of α,β -dialkyl-substituted vinyl ethers.¹² (On the basis of MM2 calculations it has been claimed,13 contrary to conclusive experimental evidence,^{11,12} that it is the E isomer which has the lower thermodynamic stability.)

An interesting (and perplexing) case is compound 39, with an MeOCH₂ group attached to C- β . As suggested above, the values of SCS(R₂) appear to be determined by the magnitude of the inductive effect of the group R₂. Since the values of Taft's substituent constant σ^* for an H atom and an MeOCH₂ group are essentially equal (0.49 and 0.52, respectively),¹⁴ the value of SCS(R₂) for the MeOCH₂ moiety might be expected to be negligible, which indeed is the case. Thus it could be inferred that the strength of p- π conjugation in 39 corresponds to that in 2-methoxypropene (13), suggesting a high thermodynamic stability of 39, relative to the isomeric compound 19. However, none of the expected enhanced stability of 39 was found experimentally.¹⁵

In α,β,β -trialkyl-substituted vinyl ethers the values of SCS(R₃) are lower than in α,β -dialkyl-substituted compounds, which is understandable since in the reference

compounds, $(E)-\alpha,\beta$ -dialkyl-substituted vinyl ethers, the strength of conjugation has already been diminished by the group \mathbb{R}_2 . It is also noteworthy that $SCS(\mathbb{R}_2)$ is only -4 ppm in these α,β,β -trialkyl-substituted vinyl ethers; the small but non-zero values of the substituent effect suggest that in the reference compounds, $(Z)-\alpha,\beta$ -dialkyl-substituted vinyl ethers, $p-\pi$ conjugation is essentially but not entirely absent.

Let us now consider the values of substituent effects for alkyl groups in the α -position of the vinyl group. In monosubstituted compounds ($R_1 = alkyl$; $R_2 = R_3 =$ H), the value of $SCS(R_1)$ is 11 ppm for a Me group, about 9 ppm for all primary groups and about 3 ppm for secondary groups except cyclohexyl (7 ppm). Further, the value of $SCS(R_1)$ for a t-Bu group, 5 ppm, is comparable to that of a secondary alkyl group. On the other hand, if there is an Me group on the β -carbon in position R₂, the values of SCS(R₁), viz. 15, 11 and 3 ppm for Me, Et and i-Pr groups, respectively, are on average higher than those (11, 8 and 3 ppm) in the respective α -monosubstituted compounds. This is understandable when viewed against the polarization present in the reference compounds: the -O-C=Csystem of unsubstituted alkyl vinyl ethers is more polarized, and hence less prone to further polarization by the α -alkyl group, than that of the β -methyl-substituted vinyl ethers.

In the Z isomers of α -alkyl- β -methyl disubstituted vinyl ethers the values of SCS(R₁) are 1, -7 and -10 ppm for alkyl = Me, Et and *i*-Pr, respectively. The low values of SCS(R₁) point to a marked decrease in conjugation, which shows that the α -substituent forces the MeO group to assume a significantly more non-planar conformation than it has in the reference compounds, alkyl (Z)-propenyl ethers. Moreover, the low values of SCS(R₁) for Et and *i*-Pr groups, relative to that for a Me group, show that the increased non-planarity of the MeO-C=C system, due to the α -substituent, is more significant for bulky alkyl groups, as demonstrated earlier by ¹³C NMR spectroscopy.¹¹

Naturally, the same effect that was found in the previous compounds works also in α -alkyl- β , β -dimethylsubstituted vinyl ethers: the SCS(R₁) values for Me, Et and *i*-Bu groups (4, -4 and -3 ppm, respectively) are significantly lower than those for the corresponding mono- α -alkyl-substituted compounds.

In summary, the above data and discussion show that ¹⁷O NMR spectroscopy is a valuable tool in the investigation of the electronic and spatial structures of vinyl ethers.

EXPERIMENTAL

Materials

Compounds 1, 2, 5, 7 and 13 were commercial products and were used as received. The preparation of compounds 4, 26, 27, 30 and 31 has been described in Ref. 16, that of 15–17, 37, 38, 40, 41, 44 and 45 in Ref. 10, that of 42, 46 and 51 in Ref. 12, that of 18, 43, 47 and 52 in Ref. 17, that of 20 and 48 in Ref. 18, that of 25, 29 and 53–58 in Ref. 19, that of 22, 23 and 50 in Ref. 20, that of 19 and 39 in Ref. 15, that of 24 in Ref. 21, that of 33 and 35 in Ref. 23. Compounds 3, 6 and 9–11 were synthesized from ethyl vinyl ether

and the respective alcohols by transetherification following the procedure of Watanabe and Conlon.²⁴ The remaining compounds listed below were synthesized from the appropriate carbonyl compounds (aldehydes or ketones), $HC(OR)_3$, and ROH (where R = Me, or Et) with *p*-TsOH as catalyst, with or without isolation of the intermediate acetals (see e.g. Ref. 18).

Compound 3. B.p. 65°C; ¹H NMR 6.45 (dd, 1H), 4.14 (d, J = 14.6, 1H), 3.94 (d, J = 6.8, 1H), 3.62 (tr, J = 6.4, 2H), 1.68 (m, 2H), 0.95 (tr, J = 7.3, 3H); ¹³C NMR, 151.9 (C- α), 86.0 (C- β), 69.5 (OCH₂), 22.3 (C- CH_2 -C), 10.3 (CH₃).

Compound 6. B.p. 99-101 °C/766 Torr; ¹H NMR, 6.51 (dd, 1H), 4.14 (dd, J = 14.2 and 1.8, 1H), 3.93 (dd, J = 6.8 and 1.8, 1H), 3.32 (s, 1H), 0.95 (s, 9H); ¹³C NMR, 152.6 (C- α), 85.7 (C- β), 78.1 (OCH₂), 31.7 (C-C-C), 26.6 (CH₃).

Compound 9. B.p. 85 °C; ¹H NMR, 6.33 (dd, 1H), 4.26 (d, J = 14.2, 1H), 3.94 (d, J = 6.6, 1H), 3.59 (m, 1H), 1.57 (m, 4H), 0.91 (tr, J = 7.5, 6H); ¹³C NMR, 151.8 (C- α), 87.5 (C- β), 82.8 (OCH), 26.5 (CH₂), 9.6 (CH₃).

Compound 10. B.p. $101-102 \,^{\circ}$ C; ¹H NMR, 6.28 (dd, 1H), 4.26 (d, J = 13.7, 1H), 3.82 (d, J = 6.3, 1H), 3.11 (tr, J = 5.9, 1H), 1.8–1.9 (m, 2H), 0.90 (d, J = 6.5, 6H), 0.91 (d, J = 6.5, 6H); ¹³C NMR, 155.2 (C- α), 86.1 (C- β), 92.3 (OCH), 30.5 (2 C--C-C), 20.0 (CH₃), 17.6 (CH₃).

Compound 11. B.p. 74 °C (lit.²⁵ 75 °C); ¹H NMR, 6.44 (dd, 1H), 4.37 (d, J = 13.4, 1H), 4.00 (d, J = 6.2, 1H), 1.22 (s, 9H); ¹³C NMR, 146.3 (C- α), 90.3 (C- β), 73.3 (OCC), 25.9 (CH₃).

Compound 14. B.p. 56-57 °C (acetal 36-39 °C/45 Torr, 61%); ¹H NMR, 3.82 (d, J = 5.4, 2H), 3.71 (q, J = 7.0, 2H), 1.82 (s, 3H), 1.30 (tr, J = 7.1, 3H); ¹³C NMR, 159.9 (C- α), 81.1 (C- β), 62.7 (OCH₂), 21.2 (CC=C), 14.6 (OCC).

Compound 21. B.p. 60–62 °C, 92% of this isomer, the remainder being compound 49 (acetal 50–52 °C/11 Torr, yield 63%); ¹H NMR 3.89 (s, 1H), 3.82 (d, J = 1.8, 1H), 3.51 (s), 1.83 (m, 1H), 1.42 (m, 4H), 0.84 (tr, J = 7.5, 6H); ¹³C NMR, 165.4 (C- α), 81.0 (C- β), 54.3 (CH₃O), 49.2 (O–C–C), 25.8 (C–C–C), 24.2 (C–C–C), 11.9 (CH₃).

Compound 28. B.p. 90-92 °C (acetal 58-59 °C/40 Torr, 61%); ¹H NMR, 6.23 (d, J = 12.7, 1H), 4.82 (d, 1H), 3.48 (s, 3H), 1.02 (s, 1H); ¹³C NMR, 144.9 (C- α), 117.0 (C- β), 55.9 (CH₃O), 30.7 (CH₃), 30.0 (C--C-C).

Compound 32. See **28.** ¹H NMR, 5.66 (d, J = 6.8, 1H), 4.21 (d, 1H), 3.53 (s, 3H), 1.10 (s, 1H); ¹³C NMR, 144.5 (C- α), 115.3 (C- β), 59.6 (CH₃O), 30.7 (CH₃), the signal of the quaternary carbon was not found, probably being hidden by the former signal.

Compound 34. B.p. 91-92 °C/741 Torr (acetal 58-59 °C/45 Torr, yield 90%); ¹H NMR, 5.72 (m, 1H), 3.63 (q, 2H), 1.54 (s, 3H), 1.48 (s, 3H), 1.16 (tr, J = 7.1, 3H); ¹³C NMR, 139.9 (C- α), 110.2 (C- β), 67.0 (C--O), 19.5 (CH₃), 15.2 (CH₃), 14.4 (CH₃).

Compound 36. B.p. $53-54 \,^{\circ}C/13$ Torr (acetal $65-67 \,^{\circ}C/13$ Torr); ¹H NMR, 5.73 (m, 1H), 3.51 (s, 3H), 2.17 (m, 2H), 1.93 (m, 2H), 1.50 (m, 6H). ¹³C NMR, 138.8 (C-a), 118.1 (C- β), 30.4 (=C--C), 28.3 (=C--C), 27.0 (C--C--C), 26.8 (C--C--C), 25.3 (C--C--C).

Compound 49. See **21.** ¹H NMR, 3.46 (s, 3H), 2.09 (q, J = 7.5, 2H), 1.95 (q, J = 7.5, 2H), 1.78 (s, 3H), 0.94 (tr, J = 7.5, 6H); ¹³C NMR, 145.3 (C- α), 124.3 (C- β), 56.2 (CH₃O), 23.4 (=C-C-C), 21.3 (=C-C-C), 13.7 (CH₃), 13.4 (CH₃), 13.2 (CH₃).

NMR spectra

The ¹H, ¹³C, and ¹⁷O NMR were recorded at 21 °C in $CDCl_3$ solution on a Jeol GX-400 NMR spectrometer operating at frequencies of 399.8, 100.5 and 54.2 MHz, respectively. A solvent-to-solute volume ratio of 2:1 was used to obtain the ¹⁷O NMR spectra, with pulse width 20 µs, pulse delay 75 ms, 8K data points, acquisi-

tion time 50 ms, and repetition time 75 ms. The halfheight widths were in the range 120-340 Hz, generally increasing with increasing molecular mass of the compound concerned. Peak positions were referenced against external water (reproducibility 1-2 ppm) or, in most cases, against 1,4-dioxane (10 vol.-%) as internal standard. In the latter case, the shift values, measured from the internal standard, were converted to the water scale by applying a correction term of -1.3 ppm, corresponding to a measured difference between the chemical shifts of 1,4-dioxane and external water, i.e. $\delta_{water} =$ $\delta_{1,4-\text{dioxane}} - 1.3$ ppm. (The dioxane signal was found 1.3 ppm upfield from that of water; the shift difference given is the average of a large number of independent determinations.) The overall accuracy of the shift values given in Table 1 is likely to be 1-2 ppm. The ¹H NMR and ¹³C NMR chemical shifts are given relative to internal TMS.

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