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COMPARISON OF THIOL AND SELENOL ESTERS WITH OXY ESTERS IN SPECTROSCOPIC PROPERTIES

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COMPARISON OF THIOL AND SELENOL ESTERS WITH OXY ESTERS IN SPECTROSCOPIC PROPERTIES

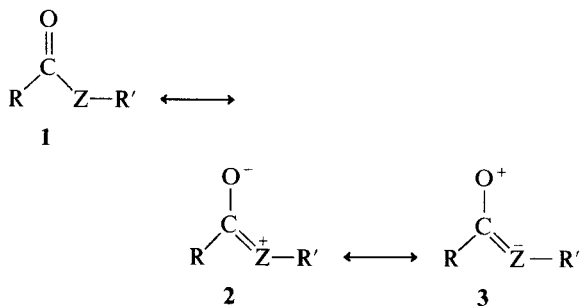
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The infrared and ^{13}C nmr spectra of the title compounds are reported in relation to the weights of the various resonance structures that describe the ester in question. The infrared spectra of thioesters show a somewhat reduced response to change in substituent in $\text{Ph}-\text{CO}-\text{S}(\text{O})-\text{Ar}$ than oxyesters, consistent with the view that sulfur does interact with carbonyl, but less so than oxygen. The ^{13}C shieldings for CO of thiol- and selenoesters are similar to ketones, and quite unlike oxyesters. These chemical shifts (corrected for anisotropy effects) lie in the reverse order than expected on the basis of electronegative effects, i.e. $0 < \text{S} < \text{Se}$. However, this order is consistent with the inhibition of charged resonance forms, (i.e. $\text{C}^+ - \text{O}^-$) for oxyesters, in agreement with infrared and chemical reactivity data. In thiol- and in oxyesters, reduced lone pair delocalization into the $\text{Ph}-\text{CO}-\text{S}(\text{O})-\text{Ar}$ ring is evident by ^{13}C shieldings, which suggests that both types of compounds have lone pairs delocalized into carbonyl. The response of the carbonyl ^{13}C to hydrogen bonding solvents is in disagreement with the supposed importance of resonance forms such as $\text{R}-\text{C}(\text{O}^+)-\text{S}^-\text{R}$.

The question of the resonance interaction between sulfur and carbonyl in thiol esters has received much commentary over the years.¹ Originally, Barnes, *et al.*, stated that resonance forms such as **2** were more important for thiol esters than for oxy esters, as evidenced by the low energy carbonyl infrared absorption for thiol esters.¹ Price, on the other hand, believes that the interaction between sulfur 3p orbitals and carbon 2p orbitals precludes strong resonance stabilization.² Baker and Harris consider resonance forms such as **2** as important, although less so than for oxy esters.³ In addition, due to the low basicity of the thiol ester carbonyl, as measured by the change in the ir frequency of external hydrogen bonding agents, Baker and Harris postulated the existence of a back donation of electron density from carbonyl to sulfur. Jencks accepted this point of view, and suggested resonance forms such as **3**.⁴ This view was also stated in a study of selenolesters by Renson and Draguet.⁵



In an intensive study of the ir spectra of thiol esters, Nyquist and Potts were reserved in judgement, although it was stated that neither the mass difference between sulfur and oxygen nor the difference in bond lengths were responsible for the higher frequency absorption of oxy esters.^{6,7} The importance of electronegativity of oxygen vs. sulfur was indicated, a view that we also share (*vide infra*).

On the other hand, Noe has shown that the rate of rotation about the C—S bond is slow in thiol acids, which is regarded as indicative of substantial resonance interaction.⁸ This view was accepted in a recent ^{13}C nmr study of thiol esters by Hall and Wemple.⁹

A prominent text in biological chemistry informs the reader "... oxygen esters are more stable than thiol esters in reactions at the acyl carbon as a result of greater stabilization of the ground state by resonance interaction of the sort": [cf. resonance structure **2**]. "Such interactions are largely absent in thiol esters, but important in oxygen esters..." The text goes on to discuss the stability of carbanions derived from thiol esters, and the chemical and biological importance of condensation reactions of these anions.¹⁰ The enhanced reactivity of the thiol esters in carbanion reactions has recently been successfully utilized in condensation reactions.¹¹

With regard to the statements in the biological chemistry text, thiol esters are undeniably higher

TABLE I
 ^{13}C NMR Chemical shifts for carbonyl, infrared carbonyl frequencies, and
 physical constant data for diarylthioester

		$p\text{--X--Ph--CO--S--Ph--Y}$ X substituent \rightarrow				
Y substituent \downarrow		NO ₂	Cl	H	CH ₃	OCH ₃
NO ₂	ir:	1686	1685	1684	1674 ^a	—
	nmr:	186.5	186.6	188.5	187.1	185.9
	mp:	145°	155°	125°	121°	144°
Cl	ir:	1682	1681	1678	1671	1668
	nmr:	187.9	188.1	189.2	188.7	187.9
	mp:	146°	138°	75°	119°	91°
H	ir:	1681	1677	1678	1671	1670
	nmr:	188.4	188.6	189.7	189.2	188.2
	mp:	160°	79°	56°	90°	91°
CH ₃	ir:	1678	1676	1676	1669	1667 ^b
	nmr:	188.8	189.0	190.1	189.7	188.7
	mp:	115°	111°	75°	124°	68°
$p\text{--X--Ph--CO--Se--Ph}$						
H	ir:	1692	1688	1686	1690	1688
	nmr:	192.1	191.8	—	192.3	190.9
	mp:	137°	83°	40°	93°	78°

^a More intense of split peaks at 1692, 1674 cm^{-1} is reported.

^b More intense of split peaks at 1670, 1667 cm^{-1} is reported.

energy than oxy esters.⁴ However, the bond dissociation energy of the C—O bond is over 13 kcal/mol greater than the C—S bond, which could more than account for the small difference in energy of thiol esters vs. oxy esters without recourse to resonance arguments.¹⁰ The putative higher reactivity of the thiol ester in fact depends upon reaction conditions. One important study showed that oxy esters and thiol esters were approximately equivalent in rate of alkaline hydrolysis, in aqueous solution.^{12,13} In acid catalyzed hydrolyses, the oxy esters were ca 20-fold more reactive. However, Bender and co-workers has shown that the carbonyl- ^{18}O exchange occurs in thiol esters under acidic conditions.¹⁴ The nucleofugicity (leaving group ability) of sulfur vs. oxygen species is an important factor.¹³ Other studies have shown that soft acids, such as mercuric ion, markedly accelerate the hydrolysis of thiol esters.¹⁵

In any case, reactivity data necessarily involve transition state energies vs. ground state energies. Spectroscopic data would appear to be the best mode of inquiry into the question of resonance interactions in the ground state. The purpose of the present study is to attempt to draw infrared, nmr, and chemical reactivity data into a consistent picture of the ground state electron distribution in thiol and selenol esters.

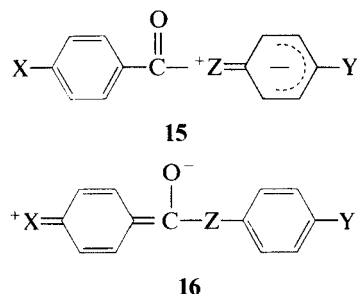
RESULTS

The carbonyl ^{13}C nmr resonances and the infrared carbonyl stretching absorptions are listed in Table I for a series of ring substituted diaryl thiol esters, and for analogous selenol esters. These data are in good agreement with the nmr results of Hall and Wemple⁹ and the infrared data of Renson and Draguet.⁵ Surprisingly little data were available on oxy esters directly comparable to the thiol esters of this study. Thus, limited data were obtained on oxy esters as well.

DISCUSSION

For rough comparison purposes, literature data on the effect of alkyl vs. aryl substitution in ketones, oxy esters, and thiol esters are shown in Scheme I.^{6,16} In ketones and in thiol esters, the introduction of an aryl group adjacent to carbonyl (i.e. **11** → **12**) leads to a strong decrease in $\bar{\nu}_{\text{CO}}$. The same effect occurs for oxy esters (**7** → **8**), but the change is much less. The indication is that electron delocalization is prominent in the ester group itself, and introduction of further possibilities for resonance with carbonyl (i.e. aryl substitution) has only a small effect.

In contrast, introduction of an aryl group next to the ester heteroatom leads to a large increase in $\tilde{\nu}_{\text{CO}}$ for the oxyester (**7** \rightarrow **9**), and also a substantial increase for the thiol ester (**11** \rightarrow **13**). Resonance structures such as **15** partially replace **2**, and thus carbonyl double bond character is enhanced, giving a larger $\tilde{\nu}_{\text{CO}}$. These data alone indicate that an interaction exists between $\text{Z}=\text{S}$ and carbonyl similar to $\text{Z}=\text{O}$.

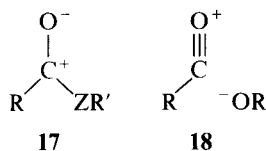


The effects of varying aromatic substituent X and Y are corroborative (cf. Table I). However, since X and Y only perturb the pi electron distribution, the effects are not as large as the alkyl vs. aryl substitution shown in Scheme I. For thiol esters, $\tilde{\nu}_{\text{CO}}$ increases by ca. 8 cm^{-1} for a change in Y from CH_3 to NO_2 . For oxy esters ($\text{X}=\text{H}$), the same change in Y leads to a 11 cm^{-1} change in $\tilde{\nu}_{\text{CO}}$. Electron withdrawing substituents Y enhance resonance structures such as **15** vs. **2** for both thiol esters and oxy esters. The data are rather similar to the effect of Y on diaryl amides, in which nitrogen has unquestioned ability to interact with carbonyl.¹⁷

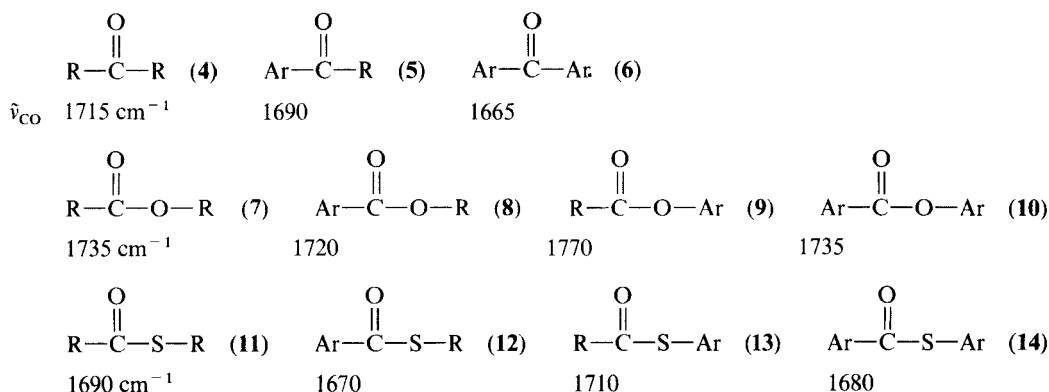
Electron donating substituents X decrease $\tilde{\nu}_{\text{CO}}$ due to a greater weight of forms such as **16**, and thus more carbonyl single bond character. For thiol

esters, the change in $\tilde{\nu}_{\text{CO}}$ is ca. 11 cm^{-1} ($\text{X}=\text{NO}_2 \rightarrow \text{CH}_3$), compared to ca. 13 cm^{-1} for similarly substituted acetophenones.¹⁹

The most substantive difference between oxy esters and thiol esters remains the high energy absorption for oxy esters (Scheme I).¹ A recurrent theme in the literature concerns the inhibition of singly bonded carbonyl structures such as **17**, by electronegative oxygen.^{1,5,9} The possibility of strengthening carbonyl by means of resonance forms such as **18** has also been considered.^{5,6}



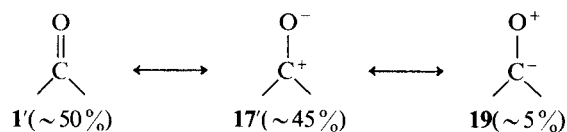
The ^{13}C nmr spectra of thiol and selenol esters vs. oxy esters present a similar picture. Thiol esters and selenol esters are rather similar to ketones in the ^{13}C chemical shift (ca. 190 ppm vs. 196 ppm), and quite unlike oxy esters (ca. 176 ppm).⁹ Stothers ascribes the anomalous high-field chemical shift of oxy esters to the lack of resonance forms such as **17**.²⁰ However, amides have a similar chemical shift to oxy esters, and there is no particular reason that **17** should be particularly unfavorable for amides. On the other hand, Maciel has analyzed the ^{13}C chemical shifts of a series of carbonyl compounds by a more complex methodology.^{21,22} Maciel corrects for the anisotropic, etc., effects of Z by subtracting the chemical shift of the sp^2 carbon in $\text{CH}_3\text{CZ}=\text{CZCH}_3$ from that of the carbonyl compound in question, $\text{R}-\text{CO}-\text{Z}$. The differences $[\delta_{\text{CO}} - \delta_{\text{C}=\text{C}}]$ were correlated with Taft's inductive substituent constants. The corrected chemical shifts *increased* as the electronegativity



Scheme I

of Z decreased, quite unlike the effect of Z on $^{13}\text{CH}_3\text{Z}$.

Theoretical calculations have indicated the following weights of carbonyl resonance forms:²³



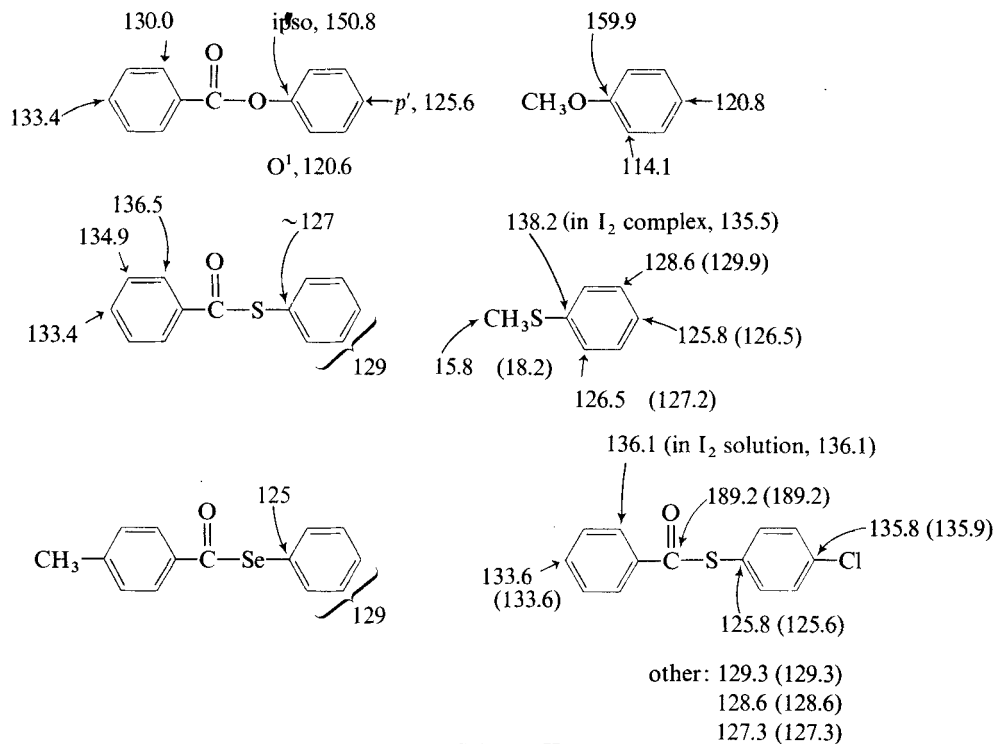
Maciel pointed out that depolarization of the carbonyl pi bond (essentially, elimination of **17**) would result in a 32 ppm upfield shift, which is indeed similar to the difference in chemical shift of ketones and oxy esters.

For the compounds of this study, the *ipso* aromatic carbons (bonded to Z) may be used as indicative of the anisotropic, etc., effects of Z (cf. Scheme II). The corrected carbonyl chemical shifts $[\delta_{\text{CO}} - \delta_{\text{ipso}}]$ line in the order: $Z = \text{Se}$ (66 ppm), S (64 ppm), and O (16 ppm), similar to Maciel's order: $\text{I} > \text{Br} > \text{Cl}$. The inverse order of chemical shifts based on expectations from electronegativity is consistent with Stothers' and Maciel's ideas based on the reduction of **17**, although the correction procedure is at best, approximate.

A recent review by Nelson and Williams has shown that charge density is but one of a group of mutually interactive effects on chemical shift of a given carbon.²⁴ Perhaps the most straightforward picture of a charge density effect occurs in the effect of a substituent on aromatic ^{13}C chemical shifts.²⁵ As seen in Scheme II, the chemical shifts of the p' carbons of oxy esters and thiol esters are indicative of a lesser degree of electron donation by $Z=\text{O}$ and S than in anisole or in methyl phenyl sulfide. The $Z=\text{O}$ or S lone pairs, thus, must be delocalized into carbonyl.

Electron-withdrawing substituents Y draw off the Z electron pairs, and thus indirectly affect ^{13}CO . In fact, a linear correlation is noted (Figure 1) between the Hammett σ constants for Y and δ_{CO} .

The question remains as to the importance, if any, of "wrong way" resonance forms such as **3**.^{3,4} The hydrogen-bonding tendencies of carbonyl may be studied by ^{13}C nmr, as well as by ir. In ketones, the response of carbonyl to progressively stronger hydrogen bonding solvents is a monotonic downfield shift (e.g. 14 ppm in pure trifluoroacetic acid, TFA).^{20,24} This downfield shift is due, most likely, to enhanced weights of resonance forms such as **17**, which impart stronger hydrogen bonding



Scheme II

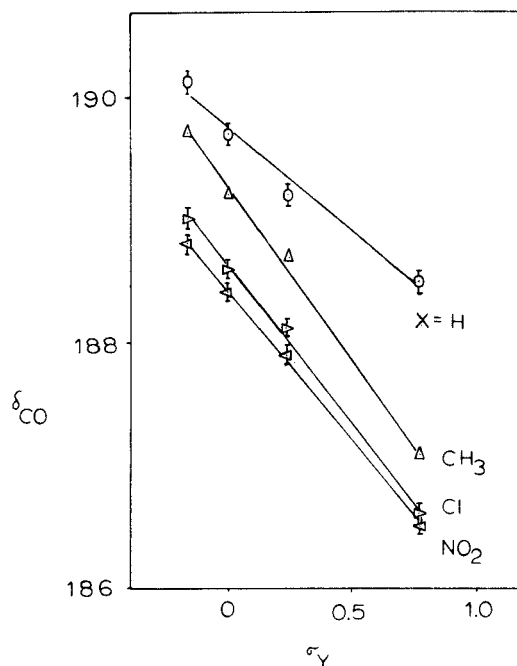


FIGURE 1 Plot of Hammett σ Values (Taft's revised values) vs. ^{13}C Chemical Shift of Carbonyl for Substrates of Different Substituent, X.

properties to carbonyl. Resonance forms such as **3** would reduce the negative charge density on oxygen and would inhibit hydrogen bonding. A random selection of oxy, thiol, and selenol esters was tested in trifluoroethanol and in TFA solutions. The data (Table II) indicate a *greater* downfield shift, and a *greater degree of hydrogen bonding* for thiol and selenol esters. It does not appear that **3** has a sufficiently large weight to inhibit hydrogen bonding. With regard to the ir work leading to the

postulate of **3**, other cases are now known in which $\tilde{\nu}_{\text{CH}}$ gave a false impression of the existence of hydrogen bonding.²⁶

On the other hand, the ability of sulfur to complex with iodine is reduced in the thiol ester, as indicated by the very close similarity of ^{13}C chemical shifts for the thiol ester (Scheme II) in the presence, and in the absence of iodine. The violet color of the iodine solution in the presence of this thiol ester was similar to the color in its absence, which is an indication of minor degrees of complexation.²⁷ In contrast, the chemical shifts of methyl phenyl sulfide in the presence of iodine, and also the color change (to reddish) were indicative of association.^{28,29} The strong implication is that the electron pair at sulfur in the thiol ester is less available for complexation, due to a combination of resonance and inductive effects. The selenol ester appeared to decompose in the presence of iodine.

In conclusion, the observation of a deshielded $^{13}\text{C}=\text{O}$ and the low energy ir stretch for carbonyl in thiol esters strongly suggest that dipolar resonance forms such as **17** are highly important compared to oxy esters. Scattered reports in the literature are in agreement.^{4-6,9,30} The effect of aromatic substituent on the nmr and ir properties of carbonyl are in agreement with the presence of resonance forms such as $\text{R}-\text{C}(\text{O}^-)=\text{Z}^+-\text{R}'$ for both types of esters, but indeed more so for oxy esters.^{6,10} The ^{13}C nmr work, in contrast to previous ir data,³ indicates that thiol esters are capable of strong hydrogen bonding, in disagreement with the presumed importance of forms such as $\text{R}-\text{C}(\text{O}^+)=\text{S}^--\text{R}'$. The high reactivity of thiol esters in condensation reactions is consistent with the high weight of the C^+-O^- form.

TABLE II
Carbonyl ^{13}C chemical shifts in hydrogen bonding solvents

Compound	CDCl_3	Solvent	
		$\text{CF}_3\text{CH}_2\text{OH}^a$	TFA ^a
$\text{Ph}-\text{CO}-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$	163.9	165.0	166.6
$\text{Ph}-\text{CO}-\text{S}-\text{C}_6\text{H}_4-\text{CH}_3$	189.2	191.6	196.0
$\text{CH}_3-\text{C}_6\text{H}_4-\text{CO}-\text{Se}-\text{Ph}$	192.3	195.2	~201

^a 83% CDCl_3 and 17% the indicated co-solvent (v/v).

EXPERIMENTAL

Preparation

The thiol esters were prepared essentially by the method of Vogel,³¹ either using commercial acid chlorides or acid chlorides prepared from the corresponding acids with thionyl chloride. For the compound, $X = Y = H$, 1 g (9.1 mmol) of thiophenol was placed in an Erlenmeyer flask with a slight molar excess of benzoyl chloride (ca. 1.3 g, ca. 9.3 mmol). Pyridine, (10 ml) was added with stirring and the resulting mixture was heated on a steam bath for 20 min. Then 5 ml of distilled water was added and the mixture was stirred with additional heating. The mixture was cooled in ice, and additional water added (ca. 50 ml), whereupon precipitation of the product usually occurred. The crude product was filtered, and recrystallized to purity from hot methanol (usually sacrificially in order to obtain very pure product) yields were thus low, ca. 50%. The purified product was air dried for a day, and further dried in an Abderhalden under vacuum in the presence of anhydrous calcium sulfate. The product was stored in a desiccator. The selenol esters were prepared by the method of Renson and Draguet.⁵ The melting points are listed in Table I with each compound. The ir, nmr ¹H and C were in complete agreement with anticipated structure and no impurities (extraneous peaks, etc.) were evidence, except for $X = OCH_3$, and $Y = NO_2$, where a minor impurity was evident.

Spectra

The infrared data were taken on a Beckman Acculab 4 using reagent grade methylene chloride as solvent in clear 1 mm sodium chloride cells. The solutions were approximately 0.002 g/ml. Several runs were made for each compound. The methylene chloride was distilled under nitrogen from P₂O₅ before use. Each compound was dried in an Abderhalden before spectral determination. The instrument was operated at its slowest speed using the high resolution slit width, and a four-fold horizontal expansion. A double calibration using polystyrene on either side of the carbonyl peak was used (1601.8 and 1444 cm⁻¹) and the carbonyl interpolated between these limits. For broad peaks, the average wavelength of the envelope is reported. Reproducibility is ± 2 cm⁻¹. In some cases, spectra were also run on a Perkin Elmer 621 instrument. Although greater resolution was obtained, this instrument has been the source of some difficulty in linearity on our hands. The infrared absorptions were similar on this instrument.

The ¹³C nmr spectra were obtained on a Varian XL-100 instrument operated at 5 KHz spectral width, using the maximum data points available, giving an expected error in line of position of ± 0.05 ppm. In order to obtain consistent data, a uniform concentration in CDCl₃ solvent was used, namely 0.000867 mole/3 ml solvent. The instrument collected 10 K of transients; a tipping angle of ca. 45° was used; the usual broadband decoupling at 6 watts power was used using a 1.5 KHz bandwidth using a low-field carrier frequency; a 2.5 K filter was used. The center line of the solvent pattern was used as the standard, taken as 76.9 ppm from the ultimate standard, TMS. Repetition of the spectra usually gave excellent agreement. For the runs in TFA or CF₃CH₂OH, however, internal TMS was used as standard (CDCl₃ was 77.2 ppm, in most cases).

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