Assignment of Quaternary Carbons via Two-Bond Heteronuclear Selective NOE Difference, a Useful Structure Elucidation Aid

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Very low power irradiation of suitable narrow peaks in the proton frequency range generated NOE enhancement in neighbouring quaternary carbons, positioned two bonds from the irradiated protons. Subsequent FID acquisition under normal broad band decoupling yielded the NOE-containing FID, which, after subtraction of the unperturbed broad band decoupled FID (devoid of NOE), gave the final NOE difference FID to which only the carbons undergoing NOE enhancement had contributed. Fourier transformation of the latter gave the NOE difference spectrum, usually a one- or two-peak spectrum. This technique proved particularly useful for polysubstituted aromatic rings.

INTRODUCTION

One of the most powerful tools for structure elucidation by NMR is the nuclear Overhauser effect (NOE). The well known $^{1}H\{^{1}H\}$NOE has been widely used in configurational and conformational studies.[1] Unselective $^{13}C\{^{1}H\}$NOE has also been frequently employed,[2] although its usual determination technique (gated broad band decoupling) restricts its use mainly to protonated carbons. More recently, a technique for the measurement of selective $^{13}C\{^{1}H\}$NOE has been described[3] and applied to the structural elucidation of several natural products, including sesquiterpenes,[4] cephalosporins[5] and other antibiotics,[6] as well as for some synthetic compounds.[7,8] This technique, which yields NOE enhancement factors, η, for carbons close to a given proton, requires very low-power coherent irradiation of this proton, collection of the coupled (or selectively decoupled) ^{13}C FID and final use of integration to measure multiplet areas in the resulting fully coupled carbon spectrum.[3] Its application is, therefore, heavily dependent on the absence of strongly overlapping multiplets in the region of interest of the coupled carbon spectrum. Also essential is the use of high sample concentrations (20%) and long accumulation times in wide (10 mm) sample tubes, in order to obtain meaningful integrations.

Recently, difference spectroscopic methods have been described in which heteronuclear NOE is found on quaternary carbons, using intermediate power for selective proton decoupling and NOE generation.[8,9] In the peptide field, the hydrogen bonds of valinomycin have been established by a difference spectroscopic method which can yield NOE enhancement factors for hydrogen-bonded carbonyl carbons on weak irradiation of the hydrogen bonding amide proton.[10]

This paper describes an alternative technique for the *detection* of two-bond, selective $^{13}C\{^{1}H\}$NOE, which operates, using 5 mm tubes in the usual concentration range under broad band decoupling conditions in the difference spectroscopic mode, by direct acquisition of the NOE information only, and which was used successfully for the unambiguous assignment of two quite close ($\Delta\nu = 2$ Hz) quaternary carbons.

EXPERIMENTAL

FT ^{13}C NMR spectra were recorded at 20.15 MHz on a Bruker WP-80-SY spectrometer, at 35 °C, using a switchable $^{1}H/^{13}C$ dual probe (5 mm tubes), with quadrature detection, and using a spectral width of 4800 Hz for 16K data points (8K for each detector). Proton noise decoupled spectra were obtained under broad band decoupling conditions (2 W). Two-bond, selective heteronuclear NOE difference spectra were obtained under Aspect 2000 computer control, using the microprogram shown in Scheme 1. This micro-

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 1  ZE
 2  FL FQLIST
 3  IF FQLIST
 4  D1 O2 S1 CW
 5  D2 O2 S2 BB DO
 6  GO = 4 DO
 7  NM
 8  LO TO 2 TIMES 2
 9  RF FQLIST.ØØ1
1Ø  LO TO 2 TIMES C
11  EXIT
```

Scheme 1. Microprogram used for two-bond, selective heteronuclear NOE generation and detection.

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program performed sequentially the following operations:

(i) Selective NOE generation (step 4 of microprogram). Very low power coherent selective irradiation at the chosen proton frequency (on resonance) for a time D1 long enough to generate NOE on quaternary carbons. Decoupler power S1 = 35–45 L (γB_2 = 8–2.5 Hz). Irradiation time D1 = 10–20 s.
(ii) Decoupler switching (step 5 of microprogram). The decoupler O2 frequency is moved to the centre of the ^{1}H region, its power S2 is increased to approximately 2W and its mode is changed to broadband (BB) decoupling, although gated off (decoupler out, DO). Satisfactory settings were D2 = 1 ms (as short as possible for decoupler switching without loss of NOE enhancement) and decoupler power S2 = 7H (approximately 2 W), for good broad band decoupling.
(iii) FID acquisition (with selective NOE) under normal broad band decoupling conditions (step 6 of microprogram).
(iv) FID acquisition (without NOE). Repetition of steps (i)–(iii) with a different setting (off resonance) of the decoupler frequency in step (i).
(v) Differential FID acquisition (step 7 of microprogram). Subtraction of the FID obtained in (iv) (without NOE) from that obtained in (iii) (with NOE).
(vi) Time averaging. Repetition of the entire sequence (i)–(v) for an overnight accumulation period in order to obtain good signal-to-noise ratio.

Fourier transformation of this NOE difference FID yielded the NOE difference spectrum, showing only peaks undergoing NOE enhancement during step (i).

^{1}H NMR spectra were obtained in the FT mode, at 80 MHz, using the same instrument and probe, to determine decoupler positions. Chemical shifts for both ^{1}H and ^{13}C are given in ppm downfield from internal TMS. Some samples lacking TMS were referenced to suitable solvent peaks, as indicated in the corresponding tables.

Samples

Piperazinium 2-hydroxy-5-(4-methylbenzenesulphonyloxy)benzenesulphonate(**1**) was provided by Dr J. Frigola of Laboratorios del Doctor Esteve, Barcelona, Spain.

2,2′-Dihydroxy-4,4′-di-*n*-octyloxy-α,α′-dimethylbenzalazine(**2**) and 2,2′-dihydroxy-4,4′-di-*n*-octyloxy-α-methylbenzalazine(**3**) were provided by Dr J. L. Serrano, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Zaragoza, Zaragoza, Spain.

N-Methyl-2-methoxy-5-nitroaniline(**5**) and 2-(1-morpholinyl)-5-nitroanisole(**6**) were prepared by Mr J. Cervelló in our laboratories, and will be fully reported elsewhere.[11]

6-Chlorobenzoxazolone(**8**) was prepared by chlorination of benzoxazolone(**7**), as described by Eckstein and Zukowski.[12]

2,5-Dihydro-7-hydroxydibenzofuran-2,5-dione(**10**) was provided by Professor J. M. Saá, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Mallorca, Palma de Mallorca, Majorca, Spain.

RESULTS AND DISCUSSION

Piperazinium 2-hydroxy-5-(4-methylbenzenesulphonyloxy)benzenesulphonate(**1**) is a commercial hypolipaemic agent, known commercially as sultosylic acid (piperazine salt). Its chemical synthesis (addition of bisulphite to *p*-benzoquinone, followed by monotosylation) is not unambiguous, since structure **1′** could not be excluded (Fig. 1). The ^{1}H NMR spectrum of **1** in DMSO-d_6 is given in Table 1, and its ^{13}C NMR spectrum is given (with assignments) in Table 2. On weak irradiation of the methyl singlet at δ_H = 2.37, a selective two-bond heteronuclear NOE difference experiment resulted in a one-peak ^{13}C NMR spectrum, at δ_C = 145.6, which was therefore assigned to C-4′. On the other hand, weak irradiation of the narrow doublet appearing at δ_H = 7.21 (H-6) resulted in an NOE difference spectrum showing signals at δ_C = 140.4 (C-5) and 131.4 (C-1). Note the close proximity of the latter signal to that of C-1′ (δ_C 131.6) (see Fig. 2), which showed no NOE enhancement. Final confirmation of structure **1**, rather than **1′**, was obtained by coherent selective decoupling of the broad singlet corresponding to H-3 plus H-4 (δ_H = 6.78) at a low decoupler power setting. Under these conditions, the remaining coupled aromatic proton H-6 showed residual couplings to C-5 [^2J(C-5, H-6) = 3.1 Hz] and to C-2 [^3J(C-2, H-6) = 5.2 Hz], these residual couplings having been measured on the selectively decoupled ^{13}C NMR spectrum. Since for benzene systems $J_{ortho} < J_{meta}$,[13a] this result is only compatible with constitution **1** if the tosyloxy-bearing carbon (C-5) absorbs at δ 140.4 and the hydroxylated carbon (C-2) absorbs

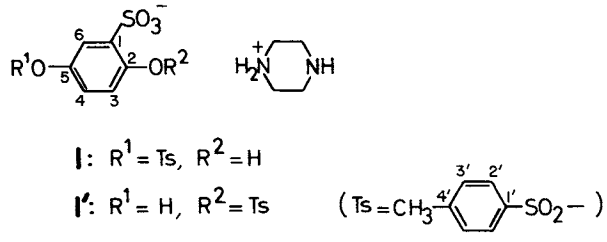


Figure 1. The possible structures of sultosylic acid (piperazine salt).

Table 1. 80 MHz ^{1}H NMR spectrum of 1 in DMSO-d_6

Proton	δ (ppm)	m	J (Hz)	Int.
H-2′+H-6′	7.72	d	8.4	2H
H-3′+H-5′	7.42	d	8.4	2H
H-6	7.21	dd	2.2 and 1.1	1H
X—H[a]	6.94	bd	—	4H
H-3+H-4	6.78	m	—	2H
CH_2	2.92	s	—	8H
CH_3	2.37	s	—	3H

[a] This broad signal, due to the exchangeable protons (OH, SO_3H, NH), moved to δ = 4.66 ppm on addition of methanol-d_4.

Table 2. 20 MHz ^{13}C NMR spectrum of 1 in DMSO-d_6[a]

	Carbon atom											
	1	2	3	4	5	6	1′	2′	3′	4′	CH_2	CH_3
δ (ppm)	131.4[b]	152.2	117.5[c]	124.5[c]	140.4[b]	120.5[c]	131.6	128.0[c]	130.1[c]	145.6[b]	43.1	21.0

[a] Internal reference: central peak of DMSO-d_6 at δ 39.5 ppm.
[b] Assignment confirmed by two-bond, selective heteronuclear NOE (see text).
[c] Assignment confirmed by selective decoupling of the corresponding proton.

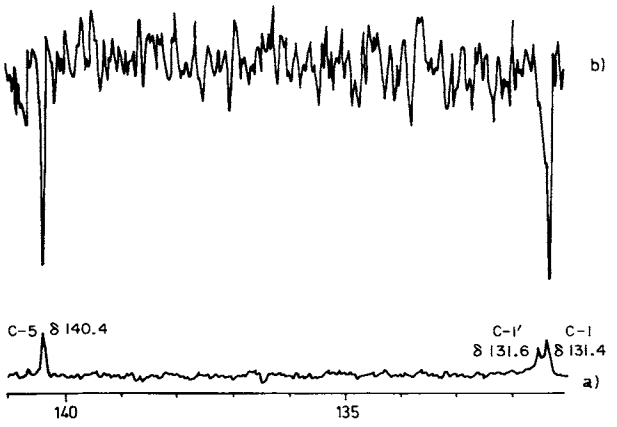
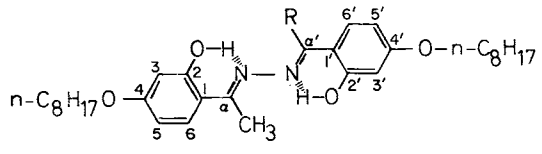


Figure 2. Partial 20 MHz ^{13}C NMR spectra of **1** in DMSO-d_6: (a) normal spectrum (broad band proton decoupling); (b) two-bond, selective heteronuclear ^{13}C{^{1}H} NOE difference spectrum, irradiation at $\delta_H = 7.21$ (H-6). The NOE difference spectrum has been plotted upside down in order to distinguish clearly which peak (δ 131.6 or 131.4) is due to C-1.



2: R = CH_3

3: R = H

Figure 3. Structures, numbering and hydrogen bonds of benzalazines **2** and **3**.

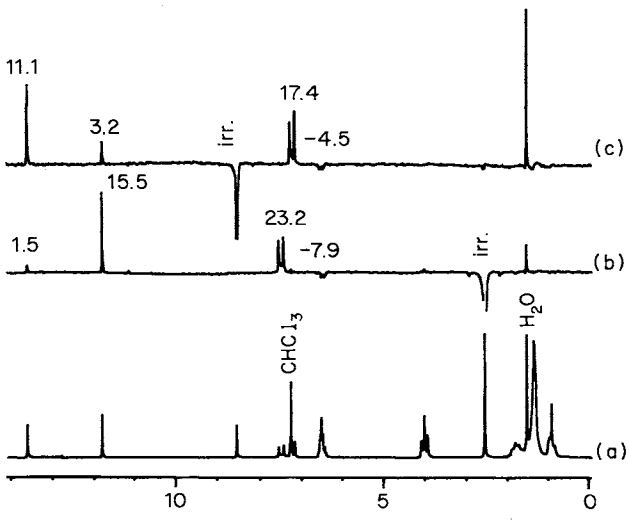


Figure 4. 80 MHz ^{1}H NMR spectrum of benzalazine **3**; (10 mM, 2.5 mg in 0.5 ml) in $CDCl_3$: (a) normal spectrum; (b) homonuclear NOE difference spectrum, irradiation at $\delta_H = 2.53$ (C-α—CH_3); (c) homonuclear NOE difference spectrum, irradiation at $\delta_H = 8.54$ (H-α′). Figures above the peaks show percentage NOE enhancements.

downfield at δ = 152.2. This result would also be compatible with constitution **1′**, but in this case the hydroxylated carbon (now C-5) should absorb at δ 140.4, i.e. *upfield* from the tosyloxy-bearing C-2 at δ 152.2. The known shifts for oxygen-bearing carbons in phenol (155.1)[13b] and phenyl methanesulphonate (149.4)[13c] demonstrate that on formation of a sulphonyl ester there is a sizeable upfield shift for the quaternary carbon of phenol. Thus, **1** fulfils this requirement while **1′** does not. Further, the hydroxylated carbon of hydroquinone absorbs at δ 151.5,[13b] close to the δ 152.2 shift shown by C-2 in **1**. These facts rule out constitution **1′**.

Benzalazine **2** is known to display very strong intramolecular hydrogen bonds (see Fig. 3) which increase its mesogenic properties,[14] while benzalazine **3** is expected to behave similarly. The ^{1}H NMR spectrum of **2** has been described previously,[14] and its most interesting feature is the appearance of a chelated hydroxyl proton singlet at $\delta_H = 13.76$ (10 mM solution in $CDCl_3$). The ^{1}H NMR spectrum of **3** (10 mM, $CDCl_3$) is shown in Fig. 4a, and Figs 4b and 4c show the results of two homonuclear ^{1}H{^{1}H} NOE difference experiments. The NOE enhancements shown in Fig. 4 allowed the assignments shown in Table 3. The ^{13}C NMR spectra of **2** and **3** are given in Table 4. The difficult problem of assigning the C-2 (C-2′) signals for compound **3**, so close to those of C-4 (C-4′) in its spectrum, could be solved by means of a pair of two-bond selective heteronuclear NOE difference experiments, in which irradiation at each chelated hydroxyl proton yielded NOE enhancement at the corresponding aromatic hydroxyl-bearing carbon (Fig. 5). Moreover, when a similar experiment was performed on benzalazine **2** by irradiation at $\delta_H = 13.76$, NOE enhancements were observed for both C-2 and C-α (Fig. 6), thus showing that the great strength of the intramolecular hydrogen bond[14] effectively places the C-α carbon at a distance of two bonds from the chelated hydroxyl proton.

Table 3. 80 MHz ^{1}H NMR spectrum of 3 (excluding the octyl groups) in $CDCl_3$[a]

Proton	δ (ppm)	m	J (Hz)	Int.
C-2—OH	13.60	s		1H
C-2′—OH	11.80	s		1H
H-3+H-5+ H-3′+H-5′	6.4–6.6	m		4H
H-6	7.49	d	9.50	1H
H-6′	7.23	d	9.25	1H
C-α—CH_3	2.53	s		3H
H-α′	8.54	s		1H

[a] Internal reference: $CHCl_3$ peak at δ 7.25 ppm.

Table 4. 20 MHz ^{13}C NMR spectra of 2 and 3 in $CDCl_3$[a]

Excluding octyl groups			Octyl groups		
	δ (ppm)			δ (ppm)	
Carbon	Cpd. 2	Cpd. 3	Carbon	Cpd. 2	Cpd. 3
1	112.7	112.5	1	68.3	68.3
1′	—	111.5	1′	—	68.4
2	162.9[b]	162.8[b]	2, 2′	29.3[c]	29.3[c]
2′	—	161.9[b]	3, 3′	26.0	26.0
3	102.2	102.3	4, 4′	29.2[c]	29.2[c]
3′	—	101.8	5, 5′	29.2[c]	29.2[c]
4	163.0[d]	163.0[d]	6, 6′	31.8	31.8
4′	—	163.6[d]	7, 7′	22.6	22.6
5	107.3	107.2	8, 8′	14.0[e]	14.0[e]
5′	—	107.9			
6	130.0	130.1			
6′	—	133.4			
α	166.7[b]	168.3			
α′	—	161.4			
α-CH_3	14.6[f]	14.4[e]			

[a] Internal reference: central peak of $CDCl_3$ at δ 77.0 ppm.
[b] Assignment confirmed by two-bond, selective heteronuclear NOE.
[c] These assignments can be interchanged.
[d] Assignment complementary to footnote b, and made by exclusion.
[e] Assignment confirmed by comparison of two single-frequency off-resonance decoupled spectra obtained with proton irradiation at $\delta_H = 0$ and at $\delta_H = 10$ ppm.
[f] Assignment confirmed by selective decoupling of the corresponding proton.

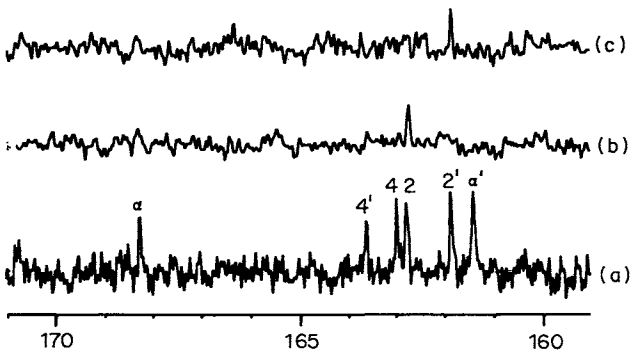


Figure 5. Partial 20 MHz ^{13}C NMR spectra of **3** in $CDCl_3$: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$NOE difference spectrum, irradiation at $\delta_H = 13.60$ (C-2—OH); (c) same as (b), but irradiation at $\delta_H = 11.80$ (C-2′—OH).

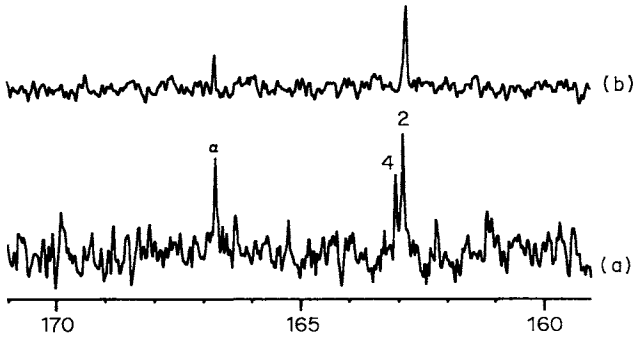
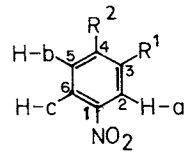


Figure 6. Partial 20 MHz ^{13}C NMR spectra of **2** in $CDCl_3$: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$ NOE difference spectrum, irradiation at $\delta_H = 13.76$ (C-2—OH).



4: $R^1 = R^2 = OCH_3$
5: $R^1 = NHCH_3$, $R^2 = OCH_3$
6: $R^1 = OCH_3$, $R^2 = N\square O$

Figure 7. Structures and numbering of 4-nitroveratrole(**4**) and its photosubstitution products **5** and **6**.

It has been found in our laboratories[11] that UV irradiation of 4-nitroveratrole(**4**) with amines leads to photosubstitution of either methoxyl group, depending on the nature of the amine. The complete study will be fully reported elsewhere,[11] but the use of two-bond, heteronuclear, selective NOE difference spectroscopy for product identification is reported here. Thus, reaction of **4** with methylamine under UV irradiation yielded **5**, while reaction of **4** with morpholine under identical conditions gave **6** (Fig. 7). The ^{13}C NMR spectra of **5** and **6** are given in Table 5. To confirm the constitution of these two compounds, selective heteronuclear NOE difference experiments were performed, in both cases by irradiation of the less coupled aromatic proton H-a. The results are shown in Figs 8 and 9. Clearly, these results confirm constitution **5**, since no NOE was detected on the most deshielded carbon (bearing the methoxy group). However, the results of an equivalent experiment performed on **6** were not so clear-cut, since in this case the signal of H-c was very close to the irradiated proton H-a, $\Delta\nu_{H\text{-}a\text{-}H\text{-}c} = 8$ Hz). Nevertheless, a significant NOE enhancement was exhibited by the most deshielded carbon (bearing the methoxyl), thereby confirming constitution **6**.

Chlorination of benzoxazolone(**7**) has been reported[12] to yield 6-chlorobenzoxazolone(**8**), although direct evidence to exclude the alternative 5-chlorobenzoxazolone(**9**) was lacking (Fig. 10). The assigned ^{1}H NMR spectrum of **8** is given in Table 6, and the ^{13}C NMR spectra of **7** and **8** are given in Table 7. Fig. 11 shows a two-bond, heteronuclear NOE difference spectrum of **8**, in which selective irradiation at $\delta_H = 7.18$ generated NOE enhancement on the peaks appearing at $\delta_C = 128.5$ (C-6, the chlorine-bearing carbon) and at $\delta_C = 145.7$ (the most deshielded quaternary carbon of the benzene ring, undoubtedly the oxygen-bearing carbon), thereby ruling out constitution **9**.

A last example will show the usefulness of selective heteronuclear NOE difference spectroscopy in the identification of unexpected products. It has been shown that oxidation of 4-phenoxyphenol by Fremy's salt, $\cdot ON(SO_3K)_2$, gives 2-(2-hydroxyphenyl)-*p*-benzoquinone.[15] However, when this reaction was performed in the heterophase and in the presence of sunlight (or under UV irradiation), a new product accumulated which was more highly oxidized than the expected hydroxyphenylquinone.[16] The complete characterization of this new product as 2,5-dihydro-7-hydroxydibenzofuran-2,5-dione(**10**) (Fig. 12), as well as its mechanism of formation, will be fully reported elsewhere,[16] but the use of two-bond, selective heteronuclear NOE difference spectroscopy for its identification will be reported here. This over-oxidized

Table 5. 20 MHz ^{13}C NMR spectra of nitrobenzenes 5 and 6 in $CDCl_3$

Compound	Carbon number[a] 1	2	3	4	5	6	OCH_3	$NHCH_3$	OCH_2	NCH_2
5	142.6[b]	102.9[c]	139.6[b]	151.6	107.7[c]	112.8[c]	55.9	29.8	—	—
6	142.3	106.9[c]	151.4[b]	147.2	116.4[c]	117.8[c]	56.0	—	66.8	50.4

[a] See Fig. 7 for numbering.
[b] Assignment confirmed by two-bond, selective heteronuclear NOE difference (see text).
[c] Assignment confirmed by selective decoupling of the corresponding proton.

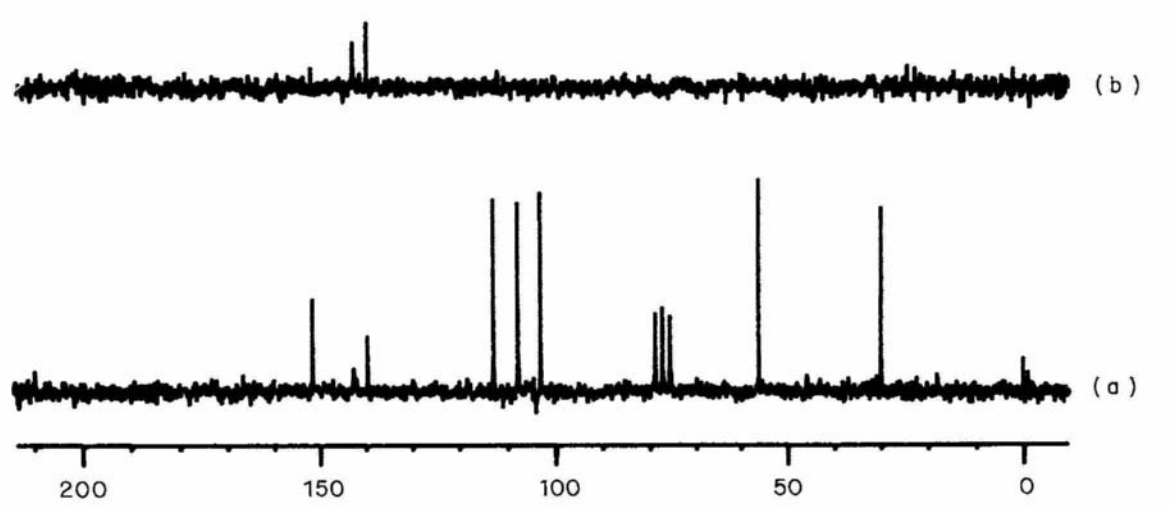


Figure 8. 20 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$ NOE difference spectrum, irradiation at $\delta_H = 7.35$ (H-a, Fig. 7).

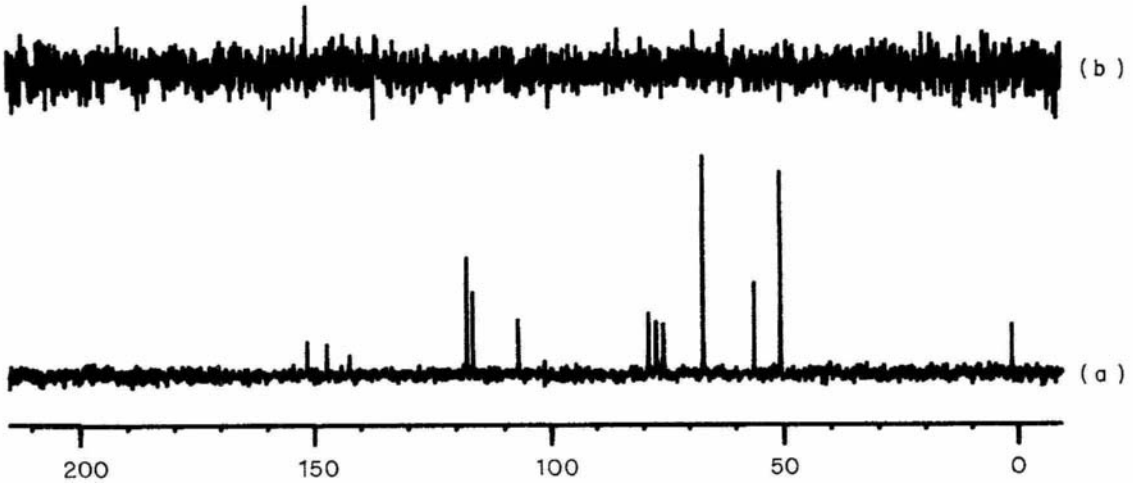
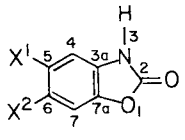


Figure 9. 20 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$ NOE difference spectrum, irradiation at $\delta_H = 7.80$ (H-a, Fig. 7).



7: $X^1 = X^2 = H$
8: $X^1 = H$; $X^2 = Cl$
9: $X^1 = Cl$; $X^2 = H$

Figure 10. Structures and numbering of benzoxazolone(**7**) and its conceivable chlorination products **8** and **9**.

Table 6. 80 MHz ^{1}H NMR spectrum of 8 in methanol-d_4

Proton	δ (ppm)	m	J (Hz)
H-3	4.76	bd	
H-4	6.95	dd	J(H-4, H-5) = 8.2; J(H-4, H-7) = 0.7
H-5	7.08	dd	J(H-5, H-7) = 1.8
H-7	7.18	dd	

Table 7. 20 MHz ^{13}C NMR spectra of benzoxazolones 7[a] and 8[b]

Compound	Carbon number						
	2	3a	4[c]	5	6	7[c]	7a
7	154.8	130.5	109.9	123.6	121.7	109.3	143.6
8	[d]	130.5	111.5	125.0	128.5	111.4	145.7

[a] In methanol-d_4–DMSO-d_6 mixture.
[b] In methanol-d_4.
[c] These assignments can be interchanged.
[d] No peak was observed for this very slowly relaxing carbon under the usual FID recording conditions.

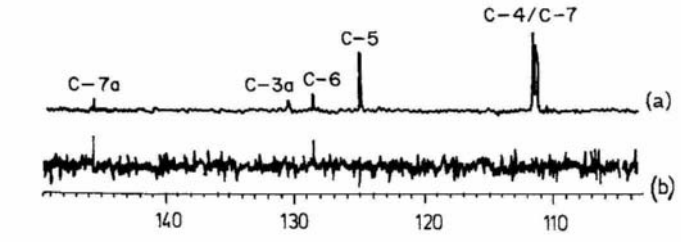
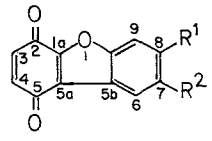


Figure 11. Partial 20 MHz ^{13}C NMR spectra of **8** in CD_3OD: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$ NOE difference spectrum, irradiation at $\delta_H = 7.18$ (H-7).



10: $R^1 = H$; $R^2 = OH$
11: $R^1 = OH$; $R^2 = H$

Figure 12. Structures and numbering of two possible oxidation products of 4-phenoxyphenol.

Table 8. 80 MHz ^{1}H NMR spectrum of 10 in DMSO-d_6

Proton (s)	δ (ppm)	m	J (Hz)
H-3+H-4	6.80	s	
H-6	7.27	dd	J(H-6, H-8) = 2.6; J(H-6, H-9) = 0.6
H-8	7.00	dd	J(H-8, H-9) = 9.0
H-9	7.60	dd	

product showed spectra compatible with either constitution **10** or **11**. Its ^{1}H NMR spectrum is given in Table 8, while its ^{13}C NMR spectrum is given in Table 9. The result of a selective heteronuclear NOE difference experiment, carried out by irradiation of the narrow double doublet appearing at $\delta_H = 7.27$, is shown in Fig. 13. In this experiment, NOE was exhibited by the quaternary carbons appearing at δ 149.4 and 122.4. This result could not be accommodated by structure **11**, in which *both* carbons undergoing NOE

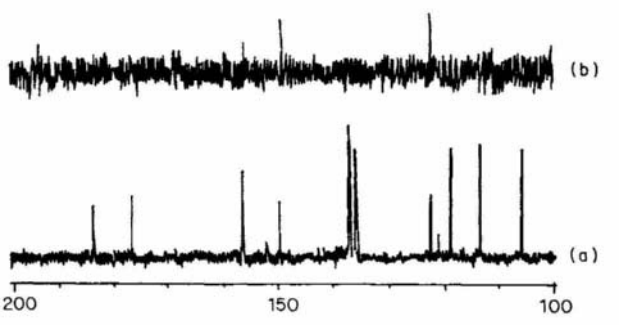


Figure 13. Partial 20 MHz ^{13}C NMR spectrum of **10** in DMSO-d_6: (a) normal broad band proton decoupling; (b) two-bond, selective heteronuclear $^{13}C\{^1H\}$NOE difference spectrum, irradiation at $\delta_H = 7.27$ (H-6).

enhancement bear an oxygen substituent, and therefore should both appear around 150 δ_C. Thus, structure **10**, was confirmed for this compound.

CONCLUSION

The preceding examples show the usefulness of two-bond, selective heteronuclear $^{13}C\{^1H\}$NOE difference spectroscopy for structure elucidation and for the assignment of quaternary carbons in the ^{13}C NMR spectrum, particularly when two conditions are met, namely (i) the proton to be irradiated should appear as a narrow signal in the ^{1}H NMR spectrum (or as a well separated first order multiplet) and (ii) the carbons undergoing selective NOE enhancement should be quaternary carbons positioned two bonds from the irradiated proton, and their T_1 relaxation times should not be too long.

It is noticeable that no NOE enhancements were detected beyond two bonds by the present method. It is possible that rigid molecules would be a better probe for testing the scope of the method.

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Table 9. 20 MHz ^{13}C NMR spectrum of 10 in DMSO-d_6

	Carbon atom											
	1a	2	3	4	5	5a	5b	6	7	8	9	9a
δ (ppm)	155.9	176.4	136.8[a,b]	135.6[a,b]	183.6	121.0	122.4[c]	105.7[b]	149.4[c]	118.7[b]	113.3[b]	151.8

[a] This pair of assignments can be interchanged.
[b] Assignment confirmed by selective decoupling of the corresponding proton.
[c] Assignment confirmed by two-bond, selective heteronuclear NOE (see text).

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