

Studies on the Nuclear Magnetic Resonance Spectra of (*E*)-1-Aryl-3-(2- and 3-thienyl)-2-propenones and Unique Observation of 4J and 5J Coupling in Their ^1H - ^1H COSY

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^1H and ^{13}C NMR spectra of series of (*E*)-1-aryl-(2- and 3-thienyl)-2-propenones, that are aldol condensation products between 2- and 3-thiophenecarbaldehydes and *m*- and *p*-substituted acetophenones, were examined to make complete assignments of the chemical shifts. Long range couplings, 4J and 5J , are observed in the ^1H - ^1H COSY of both 2- and 3-thienyl compounds, which makes the elucidation of the conformation in solution possible. In contrast, the 2-furyl analogue shows the long range coupling phenomena, but the 3-furyl and phenyl analogues do not show similar phenomena.

Key Words: ^1H and ^{13}C NMR, Thiophene, Furan, Enone, Conformation in solution

Introduction

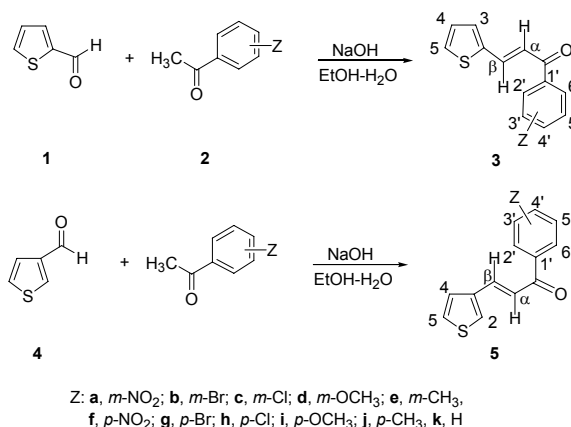
Thiophene is considered to have the closest physico-chemical properties to benzene among the five-membered heteroaromatic compounds. For example, the electronegativity of S atom is 2.5, which is same as that of carbon atom. Therefore, it seems reasonable to state that thiophene is the closest compound to benzene. When the ^1H chemical shift difference between the α - and β -Hs of the monoheteroaromatic aromatic compounds are compared, thiophene ($\Delta\delta = 0.24$) is the smallest among thiophene, furan ($\Delta\delta = 1.08$) and pyrrole ($\Delta\delta = 0.57$).¹ The difference in ^{13}C chemical shifts of the α - and β -Cs also shows a similar trend: thiophene 1.5 ppm; furan 33.1 ppm, and pyrrole 10.3 ppm.²

However, the physico-chemical properties originated by the presence of functional groups on either α - or β -position show quite different behaviors. For example, 2-thiophenecarbaldehyde (**1**) shows the $^{13}\text{C}=\text{O}$ signal at 182.93 ppm whereas that of the 3-isomer (**4**) appears at 184.88 ppm.³ Considering the $^{13}\text{C}=\text{O}$ signal of benzaldehyde that appears at 192.0 ppm, one can say that the electronic effect of 3-thienyl group is closer to that of phenyl group than the 2-thienyl group is.

In the course of our extensive studies on the aromaticities of the five-membered monoheterocyclic compounds we examined the NMR spectra of the positional isomers of (*E*)-1-aryl-3-thienyl-2-propenones (**3** and **5**) to find out that the chemical shifts are correlated with the Hammett σ values of the substituents in the aryl group.⁴ As we extended the studies to explore the effect of the heteroatom on the chemical shifts and the coupling constants, we found quite remarkable coupling behaviors of the protons in solution of CDCl_3 . Especially, the long range couplings are observed in the ^1H - ^1H COSY of the thiophene compound whereas the furan analogues do not show such phenomena. We now report the spectroscopic characteristics of these compounds.

Results and Discussion

(*E*)-1-Aryl-3-thienyl-2-propenones (**3** and **5**) were prepared by the aldol condensations of 2- and 3-thiophenecarbaldehyde (**1** and **4**), respectively, with *m*- and *p*-substituted acetophenones (**2**) in the presence of NaOH in ethanol-water solution.⁵ The yields were generally good (60 - 90%).



All products were purified by recrystallization from ethanol to analytical purity, which is essential for spectroscopic analysis. The NMR spectra of **3** and **5** were obtained in 0.1 M CDCl_3 solutions. Assignments were made with the aid of ^1H - ^1H COSY and ^1H - ^{13}C HETCOR spectroscopy. The chemical shift values are listed in Tables 1-5.

The ^{13}C chemical shift values for **3** were reported in literature for the compounds having *p*-substituents (**3f**, **3h**, **3i**, **3j** and **3k**), which were recorded at 25.05 MHz.⁶ However, we found that the reported assignments for the several peaks are inaccurate based on our data obtained at 100 MHz and assigned with aids of ^1H - ^{13}C HETCOR spectra.

In order to rationalize the coupling behaviors of the thiophene

Table 1. ^1H Chemical Shift Values (δ) of **3** in 0.1 *M*- CDCl_3

	3-H	4-H	5-H	α -H	β -H	2'-H	3'-H	4'-H	5'-H	6'-H
a	7.43	7.13	7.50	7.32	8.03	8.82		8.43	7.72	8.34
b	7.38	7.10	7.45	7.25	7.95	8.12		7.70	7.38	7.92
c	7.38	7.10	7.45	7.26	7.96	7.97		7.55	7.44	7.87
d^a	7.36	7.09	7.42	7.31	7.94	7.53		7.13	7.41	7.58
e^a	7.36	7.09	7.42	7.32	7.93	7.81		7.39	7.39	7.79
f	7.42	7.13	7.50	7.28	7.99	8.13	8.35		8.35	8.13
g	7.37	7.10	7.44	7.27	7.95	7.87	7.64		7.64	7.87
h	7.37	7.10	7.44	7.28	7.95	7.95	7.47		7.47	7.95
i^a	7.35	7.08	7.40	7.35	7.93	8.02	6.98		6.98	8.02
j^a	7.35	7.08	7.41	7.33	7.93	7.92	7.30		7.30	7.92
k	7.36	7.09	7.42	7.34	7.95	8.01	7.50	7.58	7.50	8.01
Ave	7.37 ^b	7.10 ^c	7.44 ^d	7.30 ^e	7.95 ^f					

^aMethyl signal, δ : **3d**, 3.88; **3e**, 2.44; **3i**, 3.89; **3j**, 2.43. ^b $J = 3.5$ and 0.8 Hz. ^c $J = 0.8$ and 5.0 Hz. ^d $J = 3.5$ and 5.0 Hz. ^e $J = 15.6$ Hz. ^f $J = 15.8$ Hz.

compounds (**3** and **5**), we reexamined the assignments of the chemical shifts. The assignments of the proton chemical shift values of the 3-, 4- and 5-Hs of the thiophene ring in **3** are quite straight-forward by consideration of the coupling constants. Unsubstituted thiophene shows the signals corresponding to the 2- and 5-Hs in downfield (δ 7.20) and the 3- and 4-Hs in

upfield (δ 6.96).⁷ The coupling constants are noticeably large: $J_{2,3} = 4.8$ Hz, $J_{2,4} = 1.0$ Hz, $J_{2,5} = 2.8$ Hz, and $J_{3,4} = 3.5$ Hz, compared to other heterocyclic analogues such as furan and pyrrole.⁸

Satonaka reported the chemical shift values and coupling constants for ten 2- and 3-substituted (H, OCH_3 , CH_3 , Cl, Br, I,

Table 2. ^{13}C Chemical Shift Values (ppm) of **3** in 0.1 *M*- CDCl_3

	C=O	2-C	3-C	4-C	5-C	α -C	β -C
a	187.34	139.82	133.10	128.58	129.87	119.17	138.99
b	188.34	140.11	132.52	128.44	129.27	120.02	137.99
c	188.45	140.10	132.52	128.44	129.26	120.04	137.98
d^d	189.58	140.36	132.07	128.33	128.82	120.79	137.21
e^a	190.05	140.43	131.95	128.31	128.69	120.97	137.00
f	188.26	139.82	133.16	128.61	129.90	119.77	139.01
g	188.67	140.17	132.41	128.42	129.12	120.06	137.73
h	188.47	140.18	132.37	128.41	129.07	120.11	137.66
i^a	188.07	140.55	131.74	128.27	128.41	120.61	136.40
j^a	189.34	140.49	131.85	128.29	128.57	120.82	136.76
k	189.90	140.38	132.06	128.34	128.79	120.78	137.21
Ave	188.77	140.22	132.34	128.40	129.07	120.28	137.63

^aMethyl signal, ppm: **3d**, 55.46; **3e**, 21.39; **3i**, 55.47; **3j**, 21.66.

Table 4. ^{13}C Chemical Shift Values (ppm) of **5** in 0.1 *M*- CDCl_3

	C=O	2-C	3-C	4-C	5-C	α -C	β -C
a	188.19	129.87	137.69	125.17	127.39	120.29	140.00
b	189.23	129.74	137.92	125.17	127.18	121.10	139.03
c	189.36	129.70	137.93	125.17	127.18	121.16	139.02
d^d	190.46	129.15	138.16	125.21	127.03	121.85	138.25
e^a	190.95	129.05	138.19	125.21	126.99	121.97	138.06
f	189.22	130.42	137.68	125.10	127.42	121.00	140.04
g	189.56	129.56	137.97	125.13	127.15	121.14	138.75
h	189.40	129.50	137.99	125.15	127.14	121.21	138.75
i^a	188.89	128.72	138.30	125.20	126.92	121.58	137.40
j^a	190.22	128.88	138.26	125.22	126.96	121.84	137.81
k	190.78	129.16	138.14	125.18	127.04	121.80	138.25
Ave	189.66	129.43	138.02	125.17	127.13	121.36	138.69

^aMethyl signal, ppm: **5d**, 55.47; **5e**, 21.38; **5i**, 55.46; **5j**, 21.65

Table 3. ^1H Chemical Shift Values (δ) of **5** in 0.1 *M*- CDCl_3

	2-H	4-H	5-H	α -H	β -H	2'-H	3'-H	4'-H	5'-H	6'-H
a	7.67	7.44	7.39	7.32	7.86	8.81		8.44	7.72	8.34
b	7.64	7.43	7.39	7.27	7.81	8.11		7.70	7.38	7.91
c	7.64	7.43	7.39	7.28	7.82	7.96		7.55	7.44	7.87
d^d	7.61	7.42	7.38	7.32	7.80	7.53		7.13	7.41	7.58
e^a	7.60	7.43	7.37	7.34	7.79	7.81		7.39	7.39	7.79
f	7.68	7.44	7.41	7.29	7.83	8.12	8.35		8.35	8.12
g	7.62	7.42	7.38	7.28	7.80	7.86	7.64		7.64	7.86
h	7.62	7.42	7.38	7.29	7.80	7.94	7.47		7.47	7.94
i^a	7.59	7.42	7.37	7.36	7.79	8.02	6.98		6.98	8.02
j^a	7.59	7.42	7.37	7.35	7.79	7.92	7.30		7.30	7.92
k	7.61	7.43	7.38	7.35	7.80	8.00	7.50	7.58	7.50	8.00
Ave	7.62 ^b	7.43 ^c	7.38 ^d	7.31 ^e	7.81 ^f					

^aMethyl signal, δ : **5d**, 3.88; **5e**, 2.40; **5i**, 3.89; **5j**, 2.43. ^b $J = 2.8$ and 0.8 Hz. ^c $J = 0.8$ and 5.0 Hz. ^d $J = 2.8$ and 5.0 Hz. ^e $J = 15.5$ Hz. ^f $J = 15.6$ Hz.

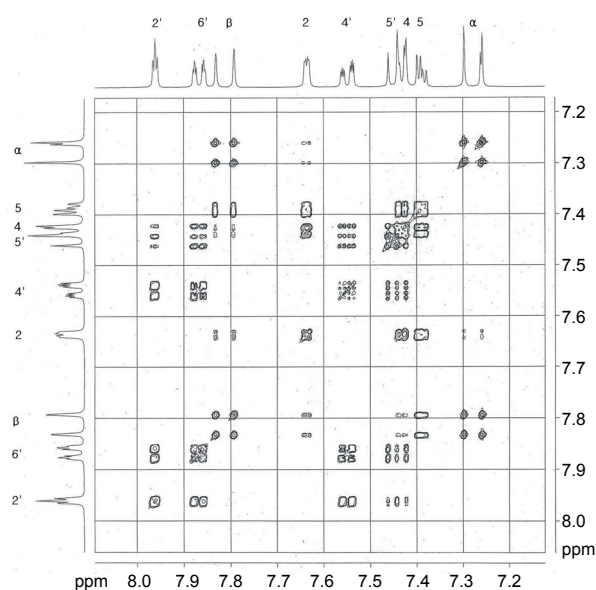
Table 5. ^{13}C Chemical Shift Values (ppm) of Carbon Atoms in Benzene Ring of **3** and **5** in 0.1 M- CDCl_3

	1'-C	2'-C	3'-C	4'-C	5'-C	6'-C
3a	139.42	123.15	148.39	126.99	129.87	133.97
5a	139.51	123.16	148.35	126.96	130.44	134.02
3b	139.90	131.37	122.95	135.56	130.18	126.87
5b	140.01	131.40	122.91	135.50	130.17	126.89
3c	139.68	128.43	134.89	132.64	129.26	126.42
5c	139.82	128.48	134.88	132.59	129.92	126.45
3d	139.49	112.74	159.86	119.25	129.55	120.93
5d	139.63	112.80	159.87	119.18	129.53	120.95
3e	138.44	128.91	138.14	133.54	128.45	125.58
5e	138.25	128.93	138.41	133.48	128.42	125.60
3f	142.94	129.29	123.84	150.01	123.84	129.29
5f	143.10	129.31	123.82	149.99	123.82	129.31
3g	136.80	131.90	129.90	127.85	139.90	131.90
5g	136.92	131.88	129.93	127.77	129.93	131.88
3h	136.39	129.79	128.91	139.16	128.91	129.79
5h	136.51	129.82	128.90	139.10	128.90	129.82
3i	130.69	130.97	128.41	163.39	128.41	130.97
5i	131.09	130.70	113.79	163.34	113.79	130.70
3j	135.52	129.30	128.52	143.59	128.52	129.30
5j	135.65	129.29	128.56	144.52	128.56	129.29
3k	138.10	128.61	128.38	132.75	128.38	128.61
5k	138.21	128.58	128.41	132.69	128.41	128.58

CHO, COCH₃, COOCH₃, and NO₂) thiophenes.⁹ For 2-substituted thiophenes the reported coupling constants are: $J_{4,5} = 4.90 - 5.60$ Hz, $J_{3,5} = 1.05 - 1.60$ Hz, and $J_{3,4} = 3.50 - 4.00$ Hz. Similarly, the coupling constants for 3-substituted thiophenes are: $J_{2,4} = 1.05 - 1.40$ Hz, $J_{2,5} = 2.85 - 3.35$ Hz, and $J_{4,5} = 4.95 - 5.30$ Hz. Although the coupling constants were observed in the similar ranges for both 2- and 3-substituted thiophenes regardless of the electronic nature of the substituents, the chemical shifts of the protons in the thiophene ring showed quite contrasts. When the electron-donating groups such as OCH₃ and CH₃ are at the 2-position, the order of the appearance from the upfield was 3-H < 5-H < 4-H. With Cl, Br, and I at the 2-position the order was 4-H < 3-H < 5-H. But the order changed to 4-H < 5-H < 3-H in the cases of CHO, COCH₃, COOCH₃, and NO₂.

On the other hand, the orders of the appearance of the proton signals in the 3-thiophene series are quite different: 2-H < 4-H < 5-H with OCH₃ and CH₃; 4-H < 2-H < 5-H with the halogens; and 5-H < 4-H < 2-H with CHO, COCH₃, COOCH₃, and NO₂. Katritzky, *et al.* reported a similar trend for 2- and 3-nitrothiophenes.¹⁰

The observed average coupling constants of the protons in the thiophene ring of **3** are $J_{3,4} = 3.5$ Hz, $J_{4,5} = 5.0$ Hz, and $J_{3,5} = 0.8$ Hz, as shown in Table 1. These values along with the chemical shift values (averaged values: 3-H = δ 7.37, 4-H = δ 7.10, and 5-H = δ 7.44) readily make the assignment possible. It is conceivable that the substituent at 2-position may cause similar effect on the chemical shift values of the 4-H and 5-H because both of them are four bonds apart from the 2-substituent. The chemical shift difference of the 5-H between unsubstituted thiophene and **3** is 0.24 (= 7.44 - 7.20) and that of the 4-H is 0.14

**Figure 1.** ^1H - ^1H COSY spectrum of **5c**.

(= 7.10 - 6.96), which may be considered reasonably close.

Similar consideration may be applied for the assignments of **5**. The ^1H NMR spectra of **5** show three doublet of doublets approximately at δ 7.38 ($J = 5.0, 2.8$ Hz), 7.43 ($J = 5.0, 0.87$ Hz), and 7.62 ($J = 2.8, 0.8$ Hz), as shown in Table 3. Although the chemical shifts of the protons in the substituted thiophene may be varied by the nature of the substituents, the coupling constants do not vary much. Therefore, the assignments can be made for the 2-H (δ 7.62), 4-H (δ 7.43), and 5-H (δ 7.38). Furthermore, the observed values may indicate a set of coupling constants which are $J_{2,4} = 0.8$ Hz, $J_{2,5} = 2.8$ Hz, and $J_{4,5} = 5.0$ Hz. These values are comparable with the literature values.⁹

It is reasonable to assume that the effects by the substituent at the 3-position should be close on the chemical shifts of the 2-H and 4-H because both of them are three bonds apart from the 3-substituent. The calculated differences in chemical shift values between **5** and unsubstituted thiophene are pretty close: 0.42 (= 7.62 - 7.20) ppm for the 2-H at δ 7.62 and 0.47 (= 7.43 - 6.96) ppm for the 4-H at δ 7.43. The signal corresponding to the 5-H (δ 7.38) of **5** is shifted 0.18 (= 7.38 - 7.20) ppm down field, which is approximately the value corresponding to the effect of the meta substituent in benzene ring.

However, the assignments are based on the assumption that the 3-substituent which is an enone is an electron-withdrawing group like the carbonyl derivatives listed in the literature.⁹ In addition, the difference of the averaged values of $\delta_{4\text{-H}}$ and $\delta_{5\text{-H}}$ is only 0.05 ppm. In the cases of 2-substituted thiophenes **3** the effect of the enones are compatible with the halogen substituents. This is a quite striking observation that the electronic effect of the enone varies depending on the position on the thiophene ring.

In order to understand the origin of such variation of the effects, we examined the ^1H - ^1H COSY spectrum of **5**. Figure 1 is the COSY spectrum of **5c** as an example. The spectrum of **5c** was chosen because the peaks were well separated compared to those of other compounds.

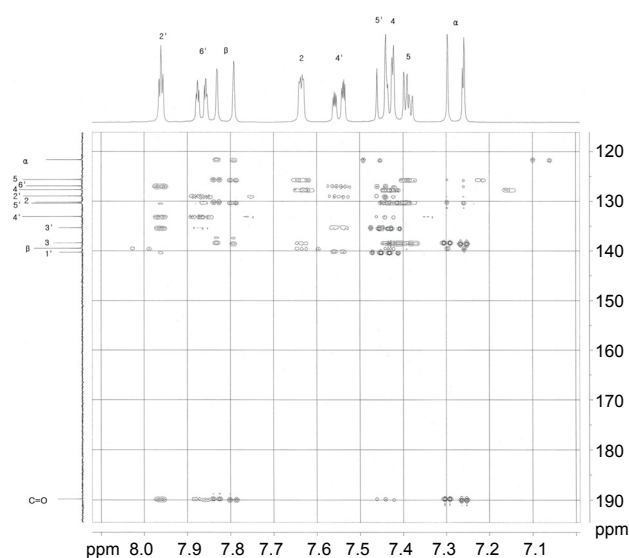


Figure 2. HMBC spectrum of **5c**.

The spectrum clearly shows a strong coupling between the signals at δ 7.39 (5-H) and the signals at δ 7.82 which correspond to the β -H. Figure 1 also shows the weakest coupling between the β -H and the peaks at δ 7.43 (4-H) and modest coupling between the β -H and the peaks at δ 7.64 (2-H). It is also noticeable that the α -H at δ 7.28 couples only with the peaks at δ 7.64 (2-H) in addition to the coupling with the β -H. One would suspect that the signals at δ 7.39 might correspond to either the 4-H or 2-H because it is a four-bond coupling (4J). But, as discussed above, the signals at δ 7.39 are assigned to 5-H by consideration of the coupling constants. This means that a five-bond coupling (5J) is observed more strongly than a four-bond coupling (4J) between the β -H and 4-H (or 2-H). Estimation of the long range coupling constants was possible by peak-picking the shoulders in the expanded spectra, although the values were only approximation. The estimated values are: $^5J_{\alpha,2} = 0.8$, $^4J_{\beta,2} = 1.2$, $^4J_{\beta,4} = 0.5$, and $^5J_{\beta,5} = 1.5$ Hz.

Such ambiguities could be cleared by the HMBC spectroscopy which gives useful information about the connectivity. Figure 2 shows the HMBC spectrum of **5c**.

The β -H signals at δ 7.82 clearly couple with ^{13}C signals at 121.16 (α -C), 125.17, 129.70 (2-C), and 137.93 (3-C) ppm. On the other hand, the α -H signals at δ 7.28 clearly show coupling with the signals at 129.70, 137.93, and 139.02 (β -C) ppm as well as a very weak coupling with the peak at 125.17 ppm. Because the distance from the β -H to 4-C is closer than to 5-C, the signal at 125.17 ppm that couples with both β - and α -H should correspond to 4-C. Such assignment leads to the assignment for the signal at 127.18 ppm to 5-C.

Once the assignment for ^1H and ^{13}C were made, the correctness of such assignment was confirmed by ^1H - ^{13}C HETCOR spectroscopy, as shown in Figure 3. Clearly, the appearance of the 4- and 5-H is opposite to that of 4- and 5-C.

The coupling phenomena also seem to give decisive information on the conformation of the double bonds in **5** in CDCl_3 solution. There are four possible conformations for **5** such as **I-IV**.

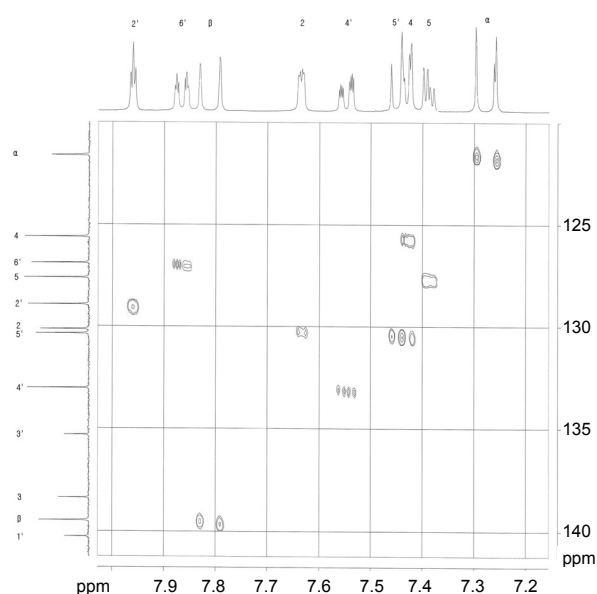
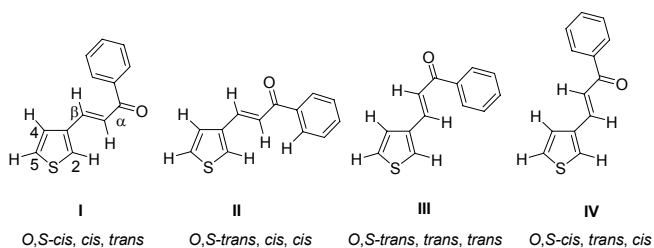


Figure 3. ^1H - ^{13}C HETCOR spectrum of **5c**.



The β -H and 4-H are in a same side in the conformations **I** and **II**, and a ω -coupling (4J) is likely, which is the observed case. Both conformations should show a coupling between the 2-H and α -H because they are in a same side and apart by five bonds (5J). Such coupling is also observed, in addition to the 5J between the β -H and 5-H, as shown in Figure 1.

Conformations like **III** and **IV** should show a strong coupling between the β -H and 2-H and a weak coupling between the α -H and 4-H. It can be said that the former coupling is observed, but the latter is not. Therefore, the conformations **III** and **IV** are ruled out. Between **I** and **II**, the more likely conformation should be **I**. If it is **II**, a coupling (5J) between the α -H and 2'-H (or 6'-H) should be observed because they are in the same side and separated by five bonds. Figure 1 shows that the α -H couples only with the 2-H, in addition to the coupling with the β -H.

The most favorable conformation of **3** seems to be **V** which is similar to that of **5**. The ^1H - ^1H COSY spectrum of **3c** is shown in Figure 4.

The β -H shows a coupling with the 3-H (4J). Although they are a four-bond coupling, the intensity seems to be a little weaker than those in the case of **5**. This may be because they are in the opposite side. The coupling between the β -H and 5-H (5J) is observed as well as that between the α -H and 3-H. The latter is 5J and the two protons are in the same side. Because there is no coupling observed between the α -H and 2'-H, the conformation **VI** is ruled out. The long-range coupling constants for **3c**

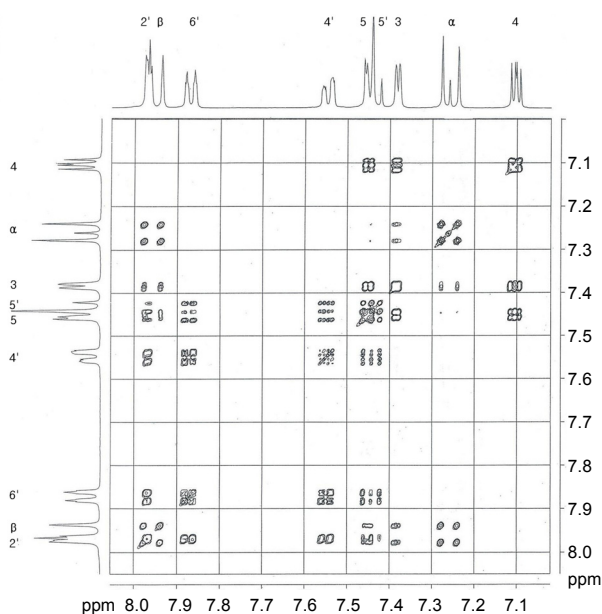


Figure 4. ^1H - ^1H COSY spectrum of **3c**.

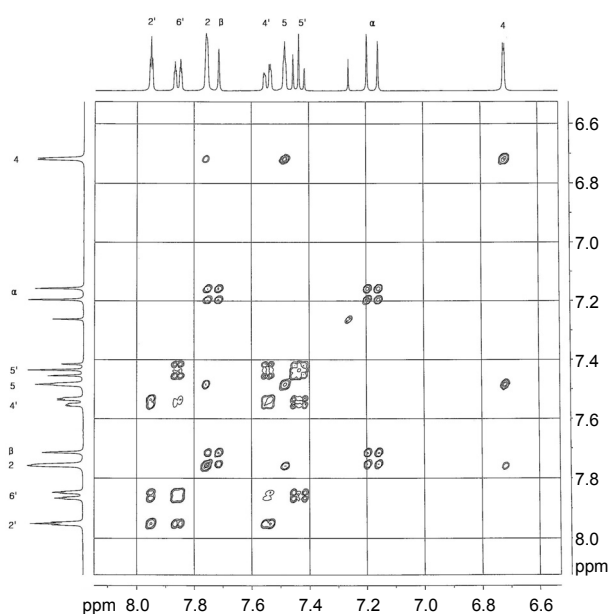
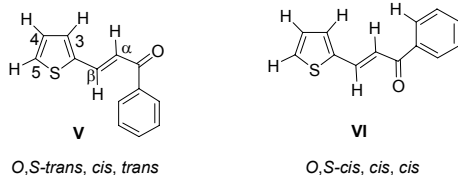
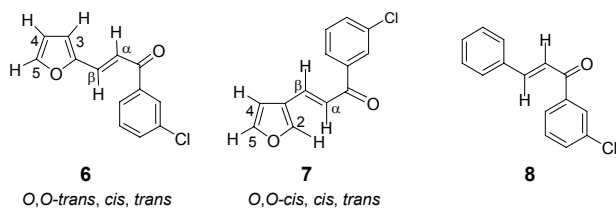


Figure 5. ^1H - ^1H COSY spectrum of **7**.

were estimated by the similar method for **5c**, and the values are: $^4J_{\alpha,3} = 1.0$, $^4J_{\beta,3} = 1.2$, and $^5J_{\beta,5} = 0.5$ Hz.



Because the conformations of the enones are same (*cis*, *trans*) for **3** and **5**, the conformation of S and O atoms of **3** and **5** becomes different: *O,S-cis* for **3** and *O,S-trans* for **5**. In order to confirm if the strong long range coupling (5J) between the 5-H and β -H of **3** may be the result of the S atom in the series, we prepared the furan analogues **6** and **7** from 2- and 3-furan-carbaldehyde (furfural) and *m*-chloroacetophenone, respectively, by the similar aldol reactions so that a direct comparison is possible. The phenyl analogue **8** was also prepared similarly.



As shown in Figure 5, there is no long range coupling, 4J or 5J , observed in the ^1H - ^1H COSY of the 3-furyl compound **7**. The phenyl analogue also does not show any long range coupling phenomena (spectrum is not shown).

On the other hand, 3-H (δ 6.76) of the 2-furyl compound **6** showed a modest coupling with the α -H (δ 7.39) and a weak coupling with the β -H (δ 7.61), as shown in Figure 6. The former coupling corresponds to 5J and the latter corresponds to 4J .

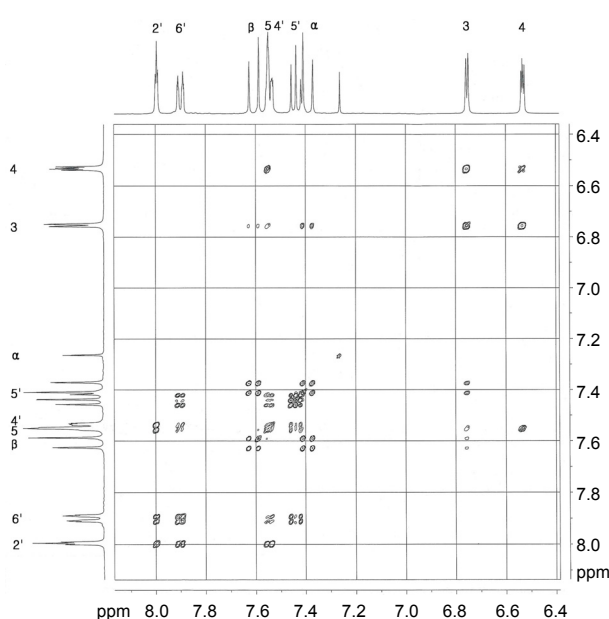
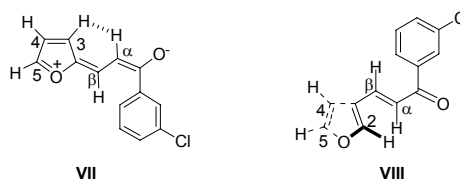


Figure 6. ^1H - ^1H COSY spectrum of **6**.

Again, it is quite remarkable that the 5J is stronger than 4J . The observation may be the result of the conformation like **VII**.



The 3-H and α -H are in close distance composing a six-membered ring so that the spin of one proton gives strong influence to the other, although they are separated by five bonds. On the

Table 6. Influence of the Carbonyl Group on the Chemical Shift Values (δ) of α - and β -H^a

	α -H, obs ($\Delta \delta$)	β -H, obs ($\Delta \delta$)		α -H, obs ($\Delta \delta$)	β -H, obs ($\Delta \delta$)
3c	7.26 (0.59)	7.96 (0.42)	6	7.39 (0.72)	7.62 (0.08)
5c	7.28 (0.61)	7.82 (0.28)	7	7.18 (0.51)	7.73 (0.19)

^aThe calculated values for 1,3-diphenyl-2-propenone (**8**) are: α -H: δ 6.67; β -H: δ 7.54.¹¹

other hand, the 3-H and β -H lie in the opposite direction and the spin-spin coupling may not be effective, although the protons are separated by four bonds.

No long range coupling observed in **7** may be an indication of the ineffective conjugation of the furan ring and the enone moiety, as illustrated in **VIII**.

Although we have no definite evidence that the C α -C β and C-O double bonds are *s-trans*, the fact that the influence of the carbonyl group on the value of the chemical shift of the α -H is greater than that of the β -H may be an indication of such conformation, as shown in Table 6.

Experimental

NMR Spectra. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for ¹H and 100 MHz for ¹³C and were referenced to tetramethylsilane. The solutions were 0.10 M in CDCl₃. Each solution was prepared in a 1 mL cylindrical volumetric flask by weighing the compound into the flask and filling with solvent containing 1%-TMS. A portion (0.6 mL) of the solution was transferred into a 5 mm NMR tube and the spectrum was obtained at 20 °C. The chemical shift values are listed in Tables 1-5. COSY spectra were recorded in magnitude mode using spectral widths of

4112 Hz and acquisition times of 125 μ sec in t_2 with 512 t_1 increments and one order of zero filling. Recycle delay time of 1.5 sec were applied between each of 16 transients recorded per t_1 increment. Pseudo-echo weighting was applied in both time domains prior to Fourier transformation. HETCOR spectra were obtained with polarization transfer and refocusing delays optimized for ¹J_{CH} = 145 Hz; 2048 transients were recorded for each of 512 t_1 increments with a recycle delay time of 1.5 sec.

Compounds. Starting materials **1**, **2**, and **4** are all commercial compounds and were used as delivered. 2- and 3-furfural were distilled prior to use. The aldol condensation products **3**, **5**, **6**, **7**, and **8** were prepared by following literature procedures.^{4,5}

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