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## Structural Assignment of Stilbenethiols and Chalconethiols and Differentiation of Their Isomeric Derivatives by Means of $^1\text{H}$ - and $^{13}\text{C}$ -NMR Spectroscopy

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**Abstract:** The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of some substituted stilbenes and chalcones were assigned unambiguously on the basis of a combination of homo- (COSY) and heteronuclear (HETCOR) two-dimensional methods, the chemical shifts, as well as spin-coupling constants. The  $A_{ik}$  empirical parameters of the  $-\text{O}-\text{C}(\text{S})-\text{N}(\text{CH}_3)_2$ ,  $-\text{S}-\text{C}(\text{O})-\text{N}(\text{CH}_3)_2$ , and  $-\text{SH}$  group were calculated to help predict the chemical shifts of substituted stilbenes, 4'-nitrostilbenes, and chalcones. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra have been shown to be able to differentiate between the isomers of *O*-stilbenyl (**4**, **5**) and *S*-stilbenyl *N,N*-dimethylthiocarbamates (**7**, **8**) as well as *O*-chalconyl (**6**) and *S*-chalconyl *N,N*-dimethylthiocarbamates (**9**).

**Keywords:** Chalcone,  $^{13}\text{C}$ -NMR, correlation techniques (COSY, HETCOR), coupling constant,  $^1\text{H}$ -NMR, stilbene

### INTRODUCTION

Stilbene, chalcone, and their derivatives make an important group of organic compounds. It has been established that many chalcones show antimicrobial,<sup>[1]</sup> antiinflammatory,<sup>[2]</sup> antiviral,<sup>[3]</sup> as well as biological<sup>[4]</sup> activities. Natural hydroxystilbenes exhibit a broad spectrum of antimicrobial and anticonvulsant activity.<sup>[5–9]</sup>

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A few reports on  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR investigation of some stilbene<sup>[9–14]</sup> and chalcone<sup>[15–19]</sup> derivatives have been published, but no data and detailed discussion of stilbenethiols and chalconethiols have been provided. In this work, a complete  $^1\text{H}$  and  $^{13}\text{C}$  signals assignment for chalcones and stilbenes was achieved using  $^1\text{H}$ – $^{13}\text{C}$  correlation experiments, with the chemical shifts and spin-coupling constants determined from  $^1\text{H}$ -NMR spectra. The Correlation Spectroscopy (COSY) experiment was used in order to obtain structural information via the spin connectivities revealed by the cross-peaks. The initial correlation between  $^1\text{H}$  and  $^{13}\text{C}$  data was confirmed using the Heteronuclear Correlation (HETCOR) experiment, which allowed unambiguous assignment of the  $^{13}\text{C}$ -NMR spectra.

*O*-stilbenyl and *O*-chalconyl *N,N*-dimethylthiocarbamates (**4–6**), *S*-stilbenyl and *S*-chalconyl *N,N*-dimethylthiocarbamates (**7–9**), as well as 4-stilbenethiols (**1**, **2**) and 4-chalconethiol (**3**) used in the current study were synthesized by the method of Newman and Karnes.<sup>[20,21]</sup>

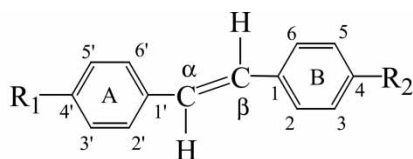
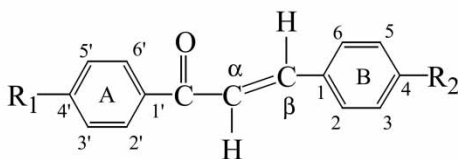
## EXPERIMENTAL

All 1D and 2D NMR spectra were recorded at room temperature on a Varian Mercury 300 MHz Spectrometer operating at 75.462 MHz for  $^{13}\text{C}$  and 300.071 MHz for  $^1\text{H}$ . The spectra were measured in  $(\text{CD}_3)_2\text{CO}$  for **1**, **2**, **4**, **5**, **7**, and **8** and  $\text{CDCl}_3$  for **3**, **6**, and **9** ( $\sim 10$  mg of the sample were dissolved in 0.5 mL of the solvent and transferred into 5-mm NMR tube) with TMS (tetramethylsilane) as an internal standard.

The  $^1\text{H}$ -NMR spectra were recorded with spectral width 9 kHz, acquisition time 3.5 s, pulse width 6.0  $\mu\text{s}$ , and double precision acquisition. The  $^{13}\text{C}$ -NMR spectra were recorded with spectral width 23 kHz, acquisition time 1.5 s, recycle delay 1.0 s, and pulse width 8.0  $\mu\text{s}$ . The homonuclear  $^1\text{H}$ – $^1\text{H}$  shift correlated two-dimensional diagrams were obtained on a Varian Gemini 300 spectrometer using the COSY pulse sequence. The spectral width was 3.05 kHz, a relaxation delay of 1 s, number of increments in  $t_1$  256, and number of scans 16. The heteronuclear 2D  $^1\text{H}$ – $^{13}\text{C}$  chemical shift correlation experiments were carried out using HETCOR spectra. The spectra were acquired with 2048 data points in the  $F_2$  dimension and 256 increments in the  $F_1$  dimension. Increments were obtained using 128 scans and a relaxation delay of 1 s. The spectral width was 15 kHz in the  $F_2$  and 3.2 kHz in the  $F_1$  dimension.

## RESULTS AND DISCUSSION

The structures and numbering schemes for **1–9** are given in Fig. 1, and the data are collected in Tables 1–3. The  $^1\text{H}$ -NMR spectra of compounds **4–6** show two singlets (3.33–3.46 ppm) assigned to the protons of the dimethylamino group in *O*-aryl *N,N*-dimethylthiocarbamates, while the  $^1\text{H}$ -NMR

**1, 2, 4, 5, 7, 8****3, 6, 9**

Compd.	R <sub>1</sub>	R <sub>2</sub>
<b>1</b>	H	SH
<b>2</b>	NO <sub>2</sub>	SH
<b>3</b>	H	SH
<b>4</b>	H	O-C(S)-N(CH <sub>3</sub> ) <sub>2</sub>
<b>5</b>	NO <sub>2</sub>	O-C(S)-N(CH <sub>3</sub> ) <sub>2</sub>
<b>6</b>	H	O-C(S)-N(CH <sub>3</sub> ) <sub>2</sub>
<b>7</b>	H	S-C(O)-N(CH <sub>3</sub> ) <sub>2</sub>
<b>8</b>	NO <sub>2</sub>	S-C(O)-N(CH <sub>3</sub> ) <sub>2</sub>
<b>9</b>	H	S-C(O)-N(CH <sub>3</sub> ) <sub>2</sub>

**Figure 1.** The structures and numbering of carbons of **1–9**.

spectra of the *S*-aryl analogues (**7–9**) reveal a single broad peak assigned to the same type protons, shifted upfield to  $\sim 3.05$  ppm. The carbon signals corresponding to the N-(CH<sub>3</sub>)<sub>2</sub> group occur at  $\sim 38.7$  ppm and  $\sim 43.2$  ppm for **4–6** and at  $\sim 36.9$  ppm for **7–9**, respectively.

Thanks to the lone electron pair, the nitrogen atom plays an important role in the molecules with inhibited internal rotation. If a single-bond C–N gains the character of partly double bond (e.g., as a result of strong electronegativity of oxygen atoms), then the inhibition of the rotation is expected, leading to the appearance of a greater number of signal groups (two groups of signals assigned to the methyl groups). This effect is observed for compounds **4–6**. The rotation is a consequence of the lower attractive force of the sulfur atom acting on the lone electron pair of the nitrogen atom.

**Table 1.** <sup>1</sup>H-NMR chemical shifts (δ, ppm) and coupling constants (J, Hz) of **1–9**

Compound	δ (ppm) J (Hz)						N-(CH <sub>3</sub> ) <sub>2</sub>
	H-α d, 1H	H-β d, 1H	H-2',6' d, 2H	H-3',5' t, 2H	H-2,6 d, 2H	H-3,5 d, 2H	
<b>1</b> <sup>a</sup>	7.20 s, 2H		7.49 (8.4)	7.36	7.58 (8.5)	7.31 (8.5)	—
<b>2</b> <sup>a</sup>	7.39 (16.5)	7.50 (16.5)	7.86 (8.8)	8.24 d, 2H (8.8)	7.59 (8.5)	7.36 (8.5)	—
<b>3</b> <sup>b</sup>	7.48 (15.6)	7.75 (15.6)	8.01 (8.2)	7.50 (7.4)	7.50 (8.5)	7.28 (8.5)	—
<b>4</b> <sup>a</sup>	7.22 s, 1H	7.26 s, 1H	7.60 (8.0)	7.38	7.62 (8.6)	7.07 (8.6)	3.37 s, 3H 3.41 s, 3H
<b>5</b> <sup>a</sup>	7.40 (16.5)	7.56 (16.5)	7.88 (8.8)	8.25 d, 2H (8.8)	7.71 (8.6)	7.12 (8.6)	3.38 s, 3H 3.42 s, 3H
<b>6</b> <sup>b</sup>	7.49 (15.6)	7.81 (15.6)	8.02 (8.2)	7.51 (7.4)	7.68 (8.5)	7.13 (8.5)	3.33 s, 3H 3.46 s, 3H
<b>7</b> <sup>a</sup>	7.29 s, 2H		7.46 (8.5)	7.37	7.62 (8.2)	7.30 (8.6)	3.02 s, 6H
<b>8</b> <sup>a</sup>	7.48 (16.5)	7.57 (16.5)	7.90 (8.5)	8.26 d, 2H (8.5)	7.70 (8.2)	7.51 (8.2)	3.05 s, 6H
<b>9</b> <sup>b</sup>	7.54 (15.6)	7.79 (15.6)	8.01 (8.2)	7.50 (7.1)	7.64 (8.5)	7.54 (8.5)	3.06 s, 6H

<sup>a</sup>Spectra determined in (CD<sub>3</sub>)<sub>2</sub>CO.

<sup>b</sup>Spectra determined in CDCl<sub>3</sub>.

Table 2. <sup>13</sup>C-NMR chemical shifts (δ, ppm) of 1–9

Carbon	1 <sup>a</sup>	2 <sup>a</sup>	3 <sup>b</sup>	4 <sup>a</sup>	5 <sup>a</sup>	6 <sup>b</sup>	7 <sup>a</sup>	8 <sup>a</sup>	9 <sup>b</sup>
1	135.5	133.5	131.9	135.6	134.8	132.6	129.0	130.4	131.4
2,6	127.9	128.7	128.9	127.6	128.4	129.3	127.5	127.9	128.5
3,5	129.4	129.7	127.9	123.9	124.1	123.4	136.6	136.4	135.7
4	131.8	130.8	138.0	154.4	155.2	155.5	138.9	137.8	137.9
α	128.3	126.6	121.3	128.4	127.0	122.2	128.5	128.2	122.8
β	128.9	133.0	143.9	129.2	133.1	143.7	130.6	133.0	143.6
1'	138.2	145.2	134.8	138.1	144.9	138.1	138.1	144.6	135.3
2',6'	127.2	128.0	128.3	127.1	127.8	128.4	127.5	128.0	128.3
3',5'	129.8	124.8	128.5	129.3	124.6	128.6	129.5	124.6	128.5
4'	128.6	147.5	132.7	128.2	147.4	132.7	128.6	147.6	132.7
C=O <sup>c</sup>	—	—	190.2	—	—	190.3	—	—	190.1
C=O <sup>d</sup>	—	—	—	—	—	—	165.9	165.5	165.9
C=S	—	—	—	187.9	187.7	187.2	—	—	—
N(CH <sub>3</sub> ) <sub>2</sub>	—	—	—	43.2	43.3	43.2	36.8	36.9	36.9
				38.7	38.8	38.7			

<sup>a</sup>Spectra determined in (CD<sub>3</sub>)<sub>2</sub>CO.

<sup>b</sup>Spectra determined in CDCl<sub>3</sub>.

<sup>c</sup>The carbon atom of the ketone group.

<sup>d</sup>The carbon atom of the carbamate.

Table 3. Empirical parameters for the calculation of chemical shifts of *p*-styrylbenzene A, *p*-(4'-nitrostyryl)benzene B, and *p*-benzoiloethylenebenzene C, calculated by Eq. (1)

R <sub>i</sub> (i = 4)	A <sub>44</sub>	A <sub>43</sub>	A <sub>42</sub>	A <sub>41</sub>
SH A	+3.77	+0.24	+0.94	−2.49
SH B	+1.49	+0.24	+0.82	−3.82
SH C	+7.51	−1.02	+0.49	−2.96
O–C(S)–N(CH <sub>3</sub> ) <sub>2</sub> A	+26.32	−5.31	+0.63	−2.36
O–C(S)–N(CH <sub>3</sub> ) <sub>2</sub> B	+25.88	−5.39	+0.52	−2.52
O–C(S)–N(CH <sub>3</sub> ) <sub>2</sub> C	+24.98	−5.52	+0.81	−2.33
S–C(O)–N(CH <sub>3</sub> ) <sub>2</sub> A	+10.86	+7.40	+0.51	−8.91
S–C(O)–N(CH <sub>3</sub> ) <sub>2</sub> B	+8.51	+6.90	+0.07	−6.94
S–C(O)–N(CH <sub>3</sub> ) <sub>2</sub> C	+7.36	+6.75	+0.03	−3.55

Constant terms C<sub>k</sub>: A, C-1 137.95, C-2,6 127.00, C-3,5 129.17, C-4 128.07<sup>[14]</sup>, B, C-1 137.29, C-2,6 127.84, C-3,5 129.48, C-4 129.31 (Measured chemical shifts (δ, ppm) of (E)-4'-nitrostilbene in (CD<sub>3</sub>)<sub>2</sub>CO: C-1 137.29, C-2,6 127.84, C-3,5 129.48, C-4 129.31, C-α 127.02, C-β 133.93, C-1' 144.87, C-2',6' 127.76, C-3',5' 124.59, C-4' 147.52.); C, C-1 134.90, C-2,6 128.45, C-3,5 128.94, C-4 130.51.<sup>[15]</sup>

The superposition of the signals assigned to the methyl groups in compounds **7–9** is a result of the methyl group rotation around the single C–N bond, leading to the averaging of the groups interactions with the remaining part of the molecule.

To differentiate the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of ring A from those of ring B of the compounds **1–9**, two-dimensional COSY and HETCOR techniques were employed.

In the  $^{13}\text{C}$ -NMR spectrum of substituted stilbenes **1**, **4**, and **7**, the differences in the chemical shifts of some carbons are very small (six signals in the region 127–129 ppm were observed). It is interesting that in the  $^1\text{H}$ -NMR spectra of **1** and **7**, the chemical shifts at the ethylenic protons H- $\alpha$  and H- $\beta$  give only one signal as observed in the spectra of **1** and **7** as a singlet at 7.29 and 7.20 ppm, respectively. The one-bond coupling between the signals at 128.4 and 129.2 for **4**, 128.5 and 130.6 for **7**, as well as 128.3 and 128.9 ppm for **1** with the  $^1\text{H}$ -NMR signals at 7.22 and 7.26 ppm for **4**, 7.29 for **7**, and 7.20 ppm for **1** allows the assignment of these signals to C- $\alpha$  and C- $\beta$  carbons and differentiated these signals from those corresponding to C-4'.

A change from SH to S–C(O)–N(CH<sub>3</sub>)<sub>2</sub> was found to exert a greater shielding influence on the C-4, C-3,5, and C-1 carbons than on the C-2,6 carbons of the stilbene moiety. Thus, C-1 in **7** was shielded (ca. 6.4 ppm), whereas C-4 and C-3,5 were deshielded (ca. 7.1 ppm) relative to 4-stilbenethiol (**1**). In the case of 4-*O*-stilbene *N,N*-dimethylthiocarbamate (**4**), a change from OH to O–C(S)–N(CH<sub>3</sub>)<sub>2</sub> affected the carbons C-1 and C-3,5 and shifted these signals to downfield, whereas those of C-4 and C-2,6 were shielded (ca. 3.7 and 1.1 ppm) relative to 4-hydroxystilbene.<sup>[10]</sup>

The two sets of well-separated doublets (H-3,5 and H-2,6) for **4** from the benzene rings substituted by *N,N*-dimethyl-*O*-thiocarbamate moved both closer and downfield after the rearrangement to *N,N*-dimethyl-*S*-thiocarbamate in **7**.

The doublet at  $\sim 7.6$  ppm (2H) in the  $^1\text{H}$ -NMR spectrum due to H-2,6 correlates with the signal at 127.6 (**4**), 127.5 (**7**), and 127.9 ppm (**1**) in the  $^{13}\text{C}$ -NMR spectrum. This proton signal is also coupled in the HH-COSY spectrum to H-3,5 at 7.07 (**4**), 7.30 (**7**), and 7.31 ppm (**1**), respectively.

For all compounds **2**, **5**, and **8**, the  $^1\text{H}$  resonances were well resolved and could be assigned on the basis of the magnitude of their splitting, their chemical shifts, and literature data.<sup>[13]</sup> For these compounds, the  $^1\text{H}$ -NMR spectra exhibits a strong doublet at 7.86 ppm (**2**), 7.88 ppm (**5**), or 7.90 ppm (**8**) ascribed to the H-2',6' protons. The HETCOR experiment exhibited cross-peaks between H-2',6' and the signals at 128.0 ppm (**2**), 127.8 ppm (**5**), or 128.0 ppm (**8**). Therefore, the latter was attributed to C-2',6'. From our NMR study, it is seen that the  $^1\text{H}$  doublet at  $\sim 8.25$  ppm for **2**, **5**, and **8** correlates with the  $^{13}\text{C}$  signals at  $\sim 124.6$  ppm and belongs to H-3',5' protons. In 4'-nitro-4-*O*-stilbenyl *N,N*-dimethylthiocarbamate (**5**), a change from OH to O–C(S)–N(CH<sub>3</sub>)<sub>2</sub> affected differently the carbons of ring B. Thus, the signals assigned to C-1 and C-3,5 in **5** were deshielded

(ca. 5.3 ppm and 7.7 ppm) relative to 4'-nitro-4-hydroxystilbene. In **8**, a change from SH to S-C(O)-N(CH<sub>3</sub>)<sub>2</sub> shifted the C-1 resonance upfield (ca. 3.1 ppm) as well as those of C-3,5 and C-4 downfield (ca. 6.7 and 7.0 ppm), respectively, relative to 4'-nitro-4-stilbenethiol (**2**).

In the <sup>1</sup>H-NMR spectrum of **2**, the signals of H-3,5 and H-α overlapped at δ 7.36–7.39 ppm, and the resulting peak showed correlations to those of the two groups in the CH-COSY spectra, with <sup>13</sup>C chemical shifts of 129.7 and 126.6 ppm, respectively.

As can be seen from the HETCOR results, the <sup>1</sup>H signal at 7.75–7.81 ppm assigned to the Hβ protons correlates with the <sup>13</sup>C signals at 143.6–143.8 ppm in the spectra of **3**, **6**, and **9** supporting the assignment of the Cβ carbons of 4-substituted chalcone. Analysis of the values of coupling constants of *cis*- and *trans*-ethylenic bond hydrogens and J values (Hα, Hβ) from Table 1 shows that all investigated compounds have *E*-configurations as expected. The chemical shifts of H-α (7.48–7.54 ppm) and C-α (121.3–122.8 ppm) in the series of chalcone derivatives are at higher field than those of H-β (7.75–7.81 ppm) and C-β (143.6–143.9 ppm). This is caused by the polarization of the C=C double bond by the carbonyl group. The assignment of the carbonyl group (Ph-CO-CH=CH-Ph) was unambiguous in all compounds, as the signal of this group appeared as a single band in the lowest field (~190 ppm).

Chemical shift assigned to the carbons C-2',6', C-3',5', and C-4' of the phenyl group in compounds **3**, **6**, and **9** are in the same range. The correlation between the pair of signals at ~128.3 ppm and ~128.5 ppm with the <sup>1</sup>H signals at 8.01 ppm and 7.50 ppm allows the assignment of these signals to C-2',6' and C-3',5' in the series of 4-substituted chalcone, respectively. The signal at ~132.7 ppm in the <sup>13</sup>C-NMR spectrum of **3**, **6**, and **9** correlates with the <sup>1</sup>H triplet at 7.59 ppm and can be assigned to C-4'. The <sup>1</sup>H-NMR spectrum of chalconethiol **3** exhibits a strong doublet at 7.28 ppm (2H) ascribed to the H-3,5 protons. The CH-HETCOR experiment exhibited cross-peaks between H-3,5 and the signal at 127.9 ppm (C-3,5). In **9**, a change from SH to S-C(O)-N(CH<sub>3</sub>)<sub>2</sub> led to a downfield shift of the C-3,5 resonance (ca. 7.8 ppm) relative to **3**. However, when the OH group was changed by O-C(S)-N(CH<sub>3</sub>)<sub>2</sub> group, the C-1 and C-3,5 resonance shifted downfield (ca. 4.8 and 7.4 ppm), whereas C-4 and C-2,6 resonances shifted upfield (ca. 2.5 and 1.2 ppm) relative to 4-hydroxychalcone (Measured chemical shifts (δ, ppm) of (*E*)-4-hydroxychalcone in CD<sub>3</sub>Cl: C-1 127.75, C-2,6 130.49, C-3,5 115.99, C-4 157.98, C-α 119.82, C-β 144.83, C-1' 138.42, C-2',6' 128.45, C-3',5' 128.59, C-4' 132.65).

The <sup>1</sup>H-NMR spectra of **1–3** show additional singlets at 4.36, 4.49, and 3.59 ppm, respectively, assigned to the -SH proton.

The information derived from the <sup>13</sup>C-NMR spectra of **4–9** (Table 2) can be used for differentiation of isomers. The presence in the <sup>13</sup>C-NMR spectra of **4–6** of the carbon signals in the region ~155 ppm (C-4) and ~187 ppm (C=S) allows differentiation of isomeric *O*-stilbenyl and *O*-chalconyl *N,N*-dimethylthiocarbamates **4–6** from *S*-stilbenyl and *S*-chalconyl



*N,N*-dimethylthiocarbamates **7–9**. In the  $^{13}\text{C}$ -NMR spectra of **7–9**, the presence of the signals of the carbons of  $\text{C}=\text{O}$  and  $\text{N}(\text{CH}_3)_2$  groups in the region  $\sim 166$  ppm and  $\sim 36$  ppm, respectively, indicates the *N,N*-dimethyl-*S*-thiocarbamates.

A comparison of the position of the signal of the H-3,5 and  $\text{N}(\text{CH}_3)_2$  protons in the  $^1\text{H}$ -NMR spectra of **4–9** allows a differentiation of isomeric *O*-stilbenyl or *O*-chalconyl *N,N*-dimethylthiocarbamates **4–6** and *S*-stilbenyl or *S*-chalconyl *N,N*-dimethylthiocarbamates **7–9**:

**4** (*O*-stilbenyl): 7.07 ppm (H-3,5); 3.37 and 3.41 ppm  $\text{N}(\text{CH}_3)_2$

**7** (*S*-stilbenyl): 7.30 ppm (H-3,5); 3.02 ppm  $\text{N}(\text{CH}_3)_2$

**5** (4'-nitro-*O*-stilbenyl): 7.12 ppm (H-3,5); 3.38 and 3.42 ppm  $\text{N}(\text{CH}_3)_2$

**8** (4'-nitro-*S*-stilbenyl): 7.51 ppm (H-3,5); 3.05 ppm  $\text{N}(\text{CH}_3)_2$

**6** (*O*-chalconyl): 7.13 ppm (H-3,5); 3.33 and 3.46 ppm  $\text{N}(\text{CH}_3)_2$

**9** (*S*-chalconyl): 7.54 ppm (H-3,5); 3.06 ppm  $\text{N}(\text{CH}_3)_2$

The substituent constants were calculated by using the following equation:

$$\delta_{Ck} = C_k + \sum A_{ik}(R_i) \quad (1)$$

where  $\delta_{Ck}$  is the observed chemical shift at the *k* position,  $C_k$  is the chemical shift at the *k* position of the unsubstituted chalcone or stilbene, and  $A_{ik}$  is the substituent constant at the *k* position induced by the *i* substituent.

The  $A_{ik}$  empirical parameters of the  $-\text{SH}$ ,  $-\text{O}-\text{C}(\text{S})-\text{N}(\text{CH}_3)_2$ , and  $-\text{S}-\text{C}(\text{O})-\text{N}(\text{CH}_3)_2$  groups for prediction of the chemical shifts of substituted stilbene, 4'-nitrostilbene, and chalcone are given in Table 3. They were calculated for stilbene/**1**, **4**, and **7**, 4'-nitrostilbene/**2**, **5**, and **8**, or chalcone/**3**, **6**, and **9** pairs.

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