




Article

# A Complete $^1\text{H}$ and $^{13}\text{C}$ NMR Data Assignment for Three 3-[Substituted methylene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-ones

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**Abstract:** A combination of 1D and 2D NMR techniques, including HMQC, HSQC,  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC, was used to provide completely assigned  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for the structures of three 3-[substituted methylene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-ones—3-[(4-methoxyphenyl)methylene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, 3-[(4-fluorophenyl)methylene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one and 3-[(thiophen-3-yl)methylene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one. The heteronuclear coupling constants  $^1\text{J}_{\text{CF}}$  and  $^3\text{J}_{\text{HF}}$  were correspondingly determined. Additionally, IR and Raman spectral data were provided in support of the assigned structures.

**Keywords:** 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one; 3-[(4-methoxyphenyl)methylene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one; 3-[(4-fluorophenyl)methylene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one; 3-[(thiophen-3-yl)methylene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one; NMR



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## 1. Introduction

It is often very unlikely to find fully assigned NMR spectral data for the structures of novel or rare organic compounds. For their structure determination, many NMR spectroscopic techniques and computer programmes for NMR spectrum interpretation have been developed throughout the years. Combining 1D and 2D NMR experiments is a spectroscopic approach that has been proven to be the most informative for the connectivity of carbons and protons in complex organic structures, especially for the ones that are not very well studied. In addition, interpretive NMR library search programmes [1,2] and online web-based NMR reference databases [3,4] have been created to assist with solving complicated structure determination problems. The work of such software tools relies either on importing  $^1\text{H}$  and/or  $^{13}\text{C}$  NMR spectral data (e.g.,  $^1\text{H}$  or  $^{13}\text{C}$  chemical shifts, multiplicity, signal intensity,  $^1\text{H}$ - $^{13}\text{C}$  correlations) into the programme, which is subsequently used for structure or substructure searches in a given database, or, reversely, on the importation of a correct tentative structure for 1D ( $^1\text{H}$  or  $^{13}\text{C}$  NMR, DEPT 135) and 2D NMR (HSQC, COSY, HMBC) spectrum prediction. Thus, the structure determination can be eased to a given degree as the human errors in NMR spectrum interpretation can also be significantly decreased. Therefore, improvements in the existing NMR reference databases and the development of new ones rely on the efforts of NMR experts to provide fully and accurately assigned NMR data for the structures of interest.

1,8-Naphthalic anhydride has been demonstrated to possess a significant potential for organic synthesis. Previously, it was described that 1,8-naphthalic anhydride was used as a precursor for the synthesis of various derivatives that could find applications

predominantly as thymidylate synthase (TS) inhibitors [5–7] or even as luminescent-active sulphur-containing organic compounds [8]. The current work confirmed once again the applicability of 1,8-naphthalic anhydride as an efficient organic reagent used for the synthesis of three naphthopyranones with structures similar to that of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one.

3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one was first obtained by O. Aly et al. following the condensation of phenylacetic acid with naphthalic anhydride in the presence of sodium acetate [9,10]. Later, O. Aly and W. Awad were the first to describe the synthesis of several derivatives of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one based on the condensation of para- or ortho-substituted phenylacetic acids with naphthalic anhydride [11]. Recently, 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one was also used as a precursor for the synthesis of various organic compounds through Friedel–Crafts acylation [12]. However, the corresponding structures of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one and its derivatives reported in the works of O. Aly and W. Awad were not supported by a sufficient amount of spectral data, which put the identity of the synthesized compounds under question. It was not until 2011 when a complete  $^1\text{H}$  and  $^{13}\text{C}$  NMR data assignment was presented for the first time for the structure of 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one [13]. In this case, a new procedure was developed to obtain 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one, with a higher yield compared to the previously reported yields [10]. Correspondingly, 3-phenylmethylene-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one was mentioned to serve as a basic compound for synthesizing a number of derivatives [13]. For example, two derivative compounds were recently suggested to be obtained—3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Figure 1a, Va) and 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Figure 1b, Vb). In addition, 3-(2-thienylmethylene)-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-ones were previously synthesized by Stoyanov et al. after the condensation of 1,8-naphthalic anhydride and 6-bromo-1,8-naphthalic anhydride with 2-thienylacetic acid [14]. Subsequently, 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Figure 1c, Vc) was proposed to be obtained after the condensation of 1,8-naphthalic anhydride with 3-thienylacetic acid in the presence of anhydrous sodium acetate. To the best of our knowledge, there are almost no existing spectral data that could support the structures of Va, Vb and Vc. Only for the structure of 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one can a scarce amount of IR spectral data, based on the assignment of the carbonyl stretching frequency, be found [11]. Therefore, the main aim of this work was the verification of the structures of the synthesized compounds Va, Vb and Vc by using a combination of 1D ( $^1\text{H}$  and  $^{13}\text{C}$ , DEPT 135) and 2D NMR experiments (HMQC, HSQC,  $^1\text{H}$ - $^1\text{H}$  COSY, HMBC). As a result, the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were completely assigned for the three structures, which were additionally supported by IR and Raman spectral data.

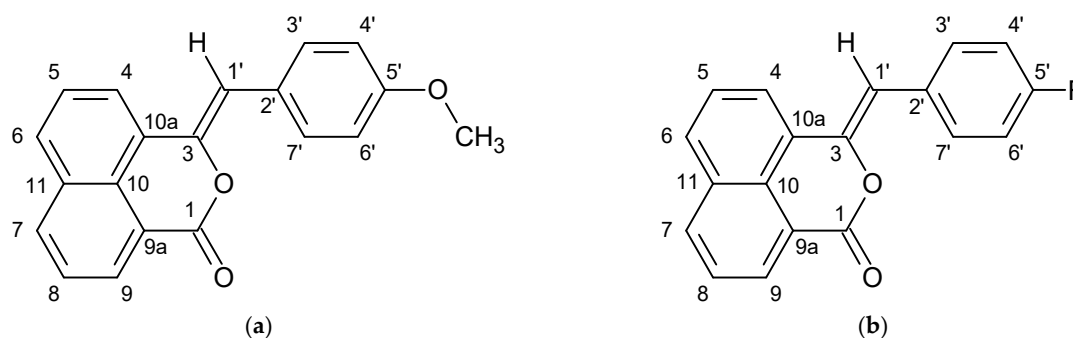
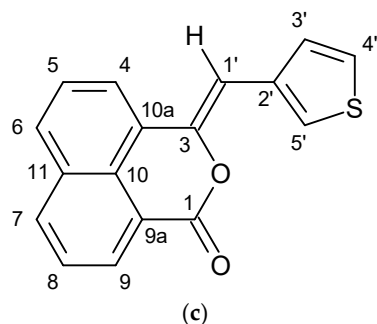


Figure 1. Cont.

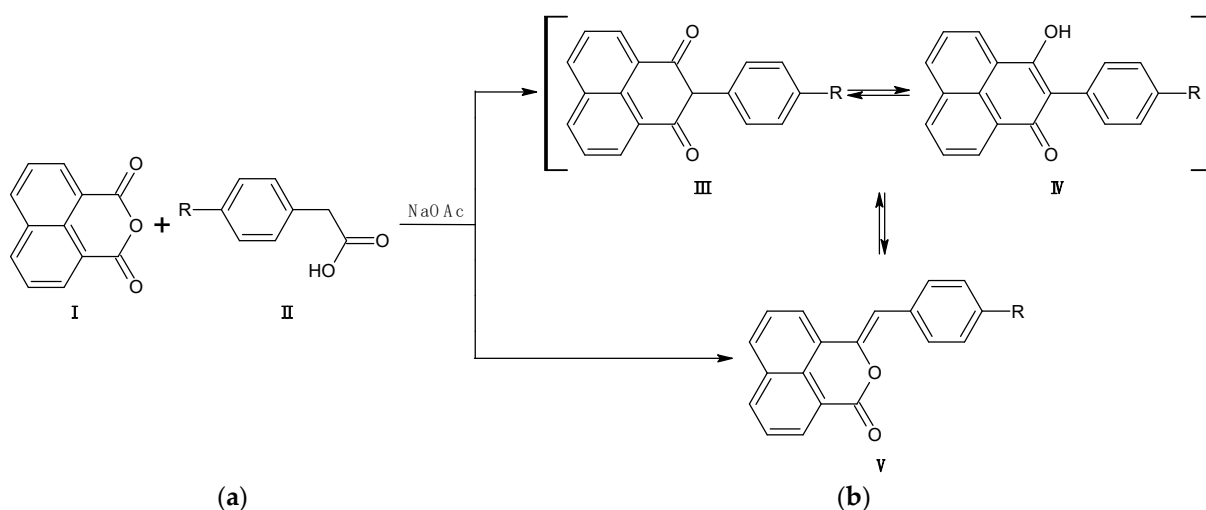


**Figure 1.** The structures of the studied compounds with their respective names. (a) 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Va). (b) 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Vb). (c) 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Vc).

## 2. Experimental

### 2.1. Synthesis of 3-[(4-Methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one and 3-[(4-Fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one

3-[(4-substitutedphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-ones were synthesized as per the previously published methods by Marinov and Stoyanov [15] and Penchev et al. [13]. According to Figure 2, 0.04 mol (7.93 g) of 1,8-naphthalic anhydride (I), 0.12 mol of the corresponding 4-substituted phenylacetic acid (4-methoxyphenylacetic acid, IIa/4-fluorophenylacetic acid, IIb) and 0.06 mol (4.8 g) of anhydrous sodium acetate were mixed and heated at a temperature of 230–240 °C for 3 h. The mixture was cooled to room temperature as 500 mL of a 3% aqueous ammonia was added afterwards to the achieved product, which was subsequently vacuum-filtered. The filtrate contained the soluble compounds III (2-(4-methoxyphenyl)-1*H*-phenalene-1,3(2*H*)-dione, IIIa/2-(4-fluorophenyl)-1*H*-phenalene-1,3(2*H*)-dione, IIIb) and IV (3-hydroxy-2-(4-methoxyphenyl)-1*H*-phenalen-1-one, IVa/2-(4-fluorophenyl)-3-hydroxy-1*H*-phenalen-1-one, IVb), which are not the subject of this study. The insoluble part of the mixture was washed with water until a neutral reaction has been obtained, then dried and extracted in a Soxhlet apparatus with petroleum ether. After complete evaporation of the solvent, the resulting product (3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, Va/3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, Vb) was recrystallized from ethanol.



**Figure 2.** Synthesis of 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Va) and 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one (Vb). (a) R = OMe, (b) R = F.

A total of 7.93 g (0.04 mol) of 1,8-naphthalic anhydride, 17.04 g (0.12 mol) of 3-thienylacetic acid and 4.80 g (0.06 mol) of anhydrous sodium acetate were heated in an argon atmosphere at a temperature 190–200 °C for two hours. The reaction mixture was cooled to room temperature, then 50 mL of ethanol was added to it, followed by a one-hour reflux and subsequent filtration of the mixture. A Soxhlet extraction with petroleum ether was applied for the obtained solid residue, leading to the compound Vc, which underwent subsequent recrystallization with ethanol.

3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one (Va):

Yield: 29%; M. p.: 168–169 °C;  $R_f^a = 0.61$ ,  $R_f^b = 0.83$

Eluent systems: (a) ethyl acetate/petroleum ether = 1:2; (b) chloroform/acetone = 9:1.

3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one (Vb):

Yield: 29%; M. p.: 171–172 °C;  $R_f^a = 0.65$ ,  $R_f^b = 0.86$

Eluent systems: (a) ethyl acetate/petroleum ether = 1:2; (b) chloroform/acetone = 9:1.

3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one (Vc):

Yield: 45%; M. p.: 166–167 °C;  $R_f^a = 0.51$ ,  $R_f^b = 0.80$

Eluent systems: (a) ethyl acetate/petroleum ether = 1:2; (b) chloroform/acetone = 9:1.

## 2.2. Instrumentation and Spectral Measurements

A VERTEX 70 FT-IR (Bruker Optics, Billerica, MA, USA) spectrometer was used for the registration of the IR spectra in KBr pellets with a resolution of 2 cm<sup>-1</sup> and 25 scans within the range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>.

The Raman spectra (stirred crystals placed in aluminium discs) were recorded in the range from 4000 cm<sup>-1</sup> to 50 cm<sup>-1</sup> on RAM II (Bruker Optics) with a resolution of 2 cm<sup>-1</sup> and 25 scans. The applied power of the focused laser beam of a Nd:YAG laser (1064 nm) was 100 mW, 40 mW and 10 mW for **Va**, **Vb** and **Vc**, respectively.

A Bruker Avance II + 600 MHz NMR spectrometer (Bruker Optics, Billerica, MA, USA) working at the frequencies of 600.130 MHz (<sup>1</sup>H) and 150.903 MHz (<sup>13</sup>C) was utilized for registering all NMR spectra. TMS was applied as an internal standard, whereas DMSO-d<sub>6</sub> was used as a solvent. The temperature during the NMR measurements was 293.0 K. The units for the chemical shifts and coupling constants were, correspondingly, ppm and Hertz. The registration of the NMR spectra was performed by using the standard Bruker pulse. The <sup>1</sup>H NMR spectra were acquired with a spectral width of 9615.4 Hz, digitized with 65,536 points, giving a spectral resolution of 0.15 Hz/point. The <sup>13</sup>C NMR spectra were acquired with a spectral width of 36,057.7 Hz, digitized with 65,536 points, giving a spectral resolution of 0.55 Hz/point.

### 2.2.1. IR and Raman Spectral Data for 3-[(4-Methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one

**IR spectral bands (cm<sup>-1</sup>):** 3436, 3058 (ν(C-H), arom.), 2838 (ν(-OCH<sub>3</sub>)), 2809, 1726 (ν(C=O)), 1626 (ν(C=C)), 1605 (ν(C=C), arom.), 1513 (ν(C=C), arom.), 1432, 1403, 1335, 1285, 1260, 1248, 1189, 1173, 1148, 1084, 1067, 1029, 849, 833, 811, 768 (γ(C-H), arom.), 644, 549, 531, 509.

**Raman spectral bands (cm<sup>-1</sup>):** 3067 (ν(C-H), arom.), 1728 (ν(C=O)), 1627 (ν(C=C)), 1604 (ν(C=C), arom.), 1583, 1509 (ν(C=C), arom.), 1441, 1403, 1370, 1338, 1327, 1306, 1248, 1218, 1187, 1174, 1125, 933, 703 (γ(C-H), arom.), 600, 532, 456, 415, 71.

### 2.2.2. IR and Raman Spectral Data for 3-[(4-Fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one

**IR spectral bands (cm<sup>-1</sup>):** 3056 (ν(C-H), arom.), 1747 (ν(C=O)), 1630 (ν(C=C)), 1620, 1599 (ν(C=C), arom.), 1585, 1514, 1506 (ν(C=C), arom.), 1466 (ν(C=C), arom.), 1437, 1415, 1401, 1354, 1340, 1321, 1296, 1248, 1229, 1186, 1178, 1162, 1140, 1119, 1084, 1063, 1032, 1015, 938, 928, 870, 849, 833, 799, 771, 765 (γ(C-H), arom.), 722, 711 (γ(C-H), arom.), 642, 605, 545, 536, 518, 502, 461, 434, 406.

**Raman spectral bands ( $\text{cm}^{-1}$ ):** 3069 ( $\nu(\text{C-H})$ , arom.), 1736 ( $\nu(\text{C=O})$ ), 1630 ( $\nu(\text{C=C})$ ), 1600 ( $\nu(\text{C=C})$ , arom.), 1583, 1507 ( $\nu(\text{C=C})$ , arom.), 1468 ( $\nu(\text{C=C})$ , arom.), 1437, 1403, 1368, 1341, 1321, 1298, 1279, 1248, 1226, 1210, 1188, 1163, 1148, 1121, 1086, 1066, 1033, 1017, 932, 871, 850, 776, 703 ( $\gamma(\text{C-H})$ , arom.), 597, 546, 520, 462, 452, 407, 334, 236, 218, 58.

### 2.2.3. IR and Raman Spectral Data for 3-[(Thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one

**IR spectral bands, ( $\text{cm}^{-1}$ ):** 3458, 3141, 3096 ( $\nu(\text{C-H})$ , arom.), 3061 ( $\nu(\text{C-H})$ , arom.), 1776, 1740 ( $\nu(\text{C=O})$ ), 1627 ( $\nu(\text{C=C})$ ), 1578, 1516 ( $\nu(\text{C=C})$ , arom.), 1464 ( $\nu(\text{C=C})$ , arom.), 1400, 1385, 1350, 1328, 1291, 1269, 1241, 1212, 1180, 1158, 1150, 1140, 1116, 1083, 1070, 1028, 987, 970, 950, 907, 891, 874, 855, 844, 831, 798, 784, 765, 727, 716, 680, 648, 634, 582, 516, 464, 452, 432, 415.

**Raman spectral bands, ( $\text{cm}^{-1}$ ):** 3100 ( $\nu(\text{C-H})$ , arom.), 3064 ( $\nu(\text{C-H})$ , arom.), 3006 ( $\nu(\text{C-H})$ , arom.), 1736 ( $\nu(\text{C=O})$ ), 1627 ( $\nu(\text{C=C})$ ), 1598 ( $\nu(\text{C=C})$ , arom.), 1580, 1518, 1508 ( $\nu(\text{C=C})$ , arom.), 1466 ( $\nu(\text{C=C})$ , arom.), 1437, 1411, 1390, 1375, 1351, 1293, 1282, 1249, 1214, 1179, 1164, 1117, 1085, 1068, 971, 952, 908, 839, 798, 692, 682, 640, 598, 541, 470, 453, 414, 332.

## 3. Results and Discussion

### 3.1. Discussion of Structure Verification of Va Presented in Table 1

The molecular formula of 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one is  $\text{C}_{20}\text{H}_{14}\text{O}_3$ . The structure of the compound (Va) with atom numbering, used for the signal assignments, is presented on Figure 1a. Its  $^{13}\text{C}$  NMR spectrum showed 18 signals (atoms 3' and 7', as well as 4' and 6', are chemically equivalent), while nine peaks were found in the DEPT 135 spectrum for the CH groups. The significantly higher intensity of the resonances at  $\delta_{\text{C}}$  131.17 ppm and  $\delta_{\text{C}}$  114.13 ppm compared to the intensities of the other peaks in the  $^{13}\text{C}$  NMR spectrum indicated that the signals at  $\delta_{\text{C}}$  131.17 ppm and  $\delta_{\text{C}}$  114.13 ppm correspond to the carbons, C-3'/7' and C-4'/6'. The  $^{13}\text{C}$  NMR signal with the highest chemical shift,  $\delta_{\text{C}}$  159.80 ppm, was assigned to the carbonyl carbon ( $\text{C}^1=\text{O}$ ), while the peak at the lowest chemical shift,  $\delta_{\text{C}}$  55.18 ppm, was for the carbon in the methoxy group ( $-\text{OCH}_3$ ). The signal at  $\delta_{\text{C}}$  144.61 ppm was assigned to the olefin carbon, C-3. The described assignments were confirmed by the 2D NMR spectra (see the Discussion below).

The  $^1\text{H}$  NMR spectrum showed two singlets at  $\delta_{\text{H}}$  6.98 ppm and  $\delta_{\text{H}}$  3.80 ppm with an area of 1.01 and 2.73, respectively. Additionally, the HMQC correlations ( $\delta_{\text{H}}$  6.98 ppm– $\delta_{\text{C}}$  108.19 ppm) and ( $\delta_{\text{H}}$  3.80 ppm– $\delta_{\text{C}}$  55.18 ppm), as well as the HMBC correlation ( $\delta_{\text{H}}$  3.80 ppm– $\delta_{\text{C}}$  158.75 ppm), were found. Consequently, the signals at  $\delta_{\text{H}}$  3.80 ppm and  $\delta_{\text{C}}$  55.18 ppm were assigned to the protons and the carbon in the methoxy group ( $-\text{OCH}_3$ ) while the signal at  $\delta_{\text{C}}$  158.75 ppm was for the carbon C-5'. Also, one weak HMBC correlation was found between the signals at  $\delta_{\text{H}}$  6.98 ppm and  $\delta_{\text{C}}$  159.80 ppm. Thus, the signals with the chemical shifts  $\delta_{\text{H}}$  6.98 ppm and  $\delta_{\text{C}}$  108.19 ppm were assigned correspondingly to H-1' and C-1'.

The resonances of the benzenoid protons, H-3'/7' and H-4'/6', formed a deceptively simple AA'XX' spectrum, as each of the AA' and XX' parts consisted of only six lines. For this reason, the chemical shifts and coupling constants of the signals of the protons H-3'/7' and H-4'/6' were determined by simulating the AA' and XX' halves of the AA'XX' spectrum using the "Spin Simulation" tool from the MestreNova software (version 6.0.2-5475). The following set of parameters, ( $\delta_{\text{H}}$  7.03 ppm for H-4'/6' (AA' part);  $\delta_{\text{H}}$  7.89 ppm for H-3'/7' (XX' part);  $J^4_{\text{AA}'} = 3.8$  Hz,  $J^4_{\text{XX}'} = 3.0$  Hz,  $J^3_{\text{AX}} = J^3_{\text{A}'\text{X}'} = 7.8$  Hz,  $J^5_{\text{AX}'} = J^5_{\text{A}'\text{X}} = 0.45$  Hz), presented in Table 1, was used to achieve the best possible similarity between the simulated and real AA'XX' spectra. Strong COSY correlations were found between the signals of the protons from each of the following pairs: (H-3' and H-4'; H-6' and H-7'). Also, there were weak COSY correlations between the signals of the proton H-1' and the pair of protons H-3' and H-7'. The strong HMBC correlations of the signals of the protons H-1' and H-3'/7' with the signals of the carbons C-3'/7' and C-1' confirmed the assignment of the signals at  $\delta_{\text{H}}$  7.03 ppm and  $\delta_{\text{H}}$  7.89 ppm to the protons H-4'/6' and H-3'/7'.

**Table 1.** H and  $^{13}\text{C}$  NMR data assignment for Va [600.130 MHz ( $^1\text{H}$ ) and 150.903 MHz ( $^{13}\text{C}$ )]<sup>a</sup>.

Atom	$\delta$ ( $^{13}\text{C}$ ), ppm	DEPT <sup>b</sup>	$\delta$ ( $^1\text{H}$ ), ppm	Multiplicity (J, Hz)	$^1\text{H}$ - $^1\text{H}$ COSY <sup>b</sup>	HMBC <sup>b</sup>
1(C=O)	159.80	C				
3	144.61	C				
4	121.57	CH	8.26	dd (7.6; 0.5)	5, 6 <sup>d</sup>	3, 10, 11 <sup>c</sup>
5	127.42	CH	7.70	t (7.9)	4, 6	4 <sup>c</sup> , 10 <sup>d</sup> , 10a, 11
6	127.74	CH	8.03	d (8.1)	4 <sup>d</sup> , 5	4, 7, 10, 10a <sup>c</sup> , 11 <sup>c</sup>
7	134.35	CH	8.31	dd (8.3; 0.8)	8	9, 9a <sup>d</sup> , 10a <sup>d</sup> , 10, 11 <sup>d</sup>
8	126.85	CH	7.75	dd (8.2; 7.3)	7, 9	9 <sup>c</sup> , 9a, 11
9	128.99	CH	8.29	dd (7.2; 1.1)	8	1, 7, 10
9a	119.21	C				
10	127.47	C				
10a	124.08	C				
11	132.11	C				
1'	108.19	CH	6.98	s	3'/7' <sup>c</sup>	1 <sup>c</sup> , 2' <sup>c</sup> , 3, 10a, 3'/7'
2'	126.79	C				
3'	131.17	CH	7.89	m	1' <sup>c</sup> , 4'	1', 2' <sup>d</sup> , 4' <sup>c</sup> , 5', 7'
4'	114.13	CH	7.03	m	3'	2', 5', 6', 7' <sup>d</sup>
5'	158.75	C				
6'	114.13	CH	7.03	m	7'	2', 3' <sup>d</sup> , 4', 5'
7'	131.17	CH	7.89	m	1' <sup>c</sup> , 6'	1', 2' <sup>d</sup> , 3', 5', 6' <sup>c</sup>
OCH <sub>3</sub>	55.18	C	3.80	s		5'

<sup>a</sup> The solvent used is DMSO- $d_6$  (solvent reference:  $^1\text{H}$   $\delta_{\text{ref}}$  2.50 ppm,  $^{13}\text{C}$   $\delta_{\text{ref}}$  39.51 ppm). COSY, HMQC and HMBC spectra assisted the corresponding assignments. <sup>b</sup> Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum;  $^1\text{H}$ - $^1\text{H}$  COSY, proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long-range  $^1\text{H}$ - $^{13}\text{C}$  Heteronuclear Multiple Bond Correlation experiment. <sup>c</sup> Weak correlations. <sup>d</sup> Extremely weak correlations.

Two strong COSY correlations of the signal at  $\delta_{\text{H}}$  7.75 ppm with the signals at  $\delta_{\text{H}}$  8.29 ppm and  $\delta_{\text{H}}$  8.31 ppm were found. Due to the strong HMBC correlation between the signals at  $\delta_{\text{H}}$  8.29 ppm and  $\delta_{\text{C}}$  159.80 ppm (C-1), the signal at  $\delta_{\text{H}}$  8.29 ppm was assigned to the proton H-9, while the signals at  $\delta_{\text{H}}$  7.75 ppm and  $\delta_{\text{H}}$  8.31 ppm were assigned to the protons H-8 and H-7, respectively. In addition, two strong COSY correlations were found between the signal at  $\delta_{\text{H}}$  7.70 ppm and the signals at  $\delta_{\text{H}}$  8.03 ppm and  $\delta_{\text{H}}$  8.26 ppm, as there was an extremely weak COSY correlation between the signals at  $\delta_{\text{H}}$  8.03 ppm and  $\delta_{\text{H}}$  8.26 ppm. Because the signal at  $\delta_{\text{H}}$  8.26 ppm showed a strong HMBC correlation with the peak at  $\delta_{\text{C}}$  144.61 ppm (C-3), the signal at  $\delta_{\text{H}}$  8.26 was assigned to the proton H-4, while the signals with the chemical shifts  $\delta_{\text{H}}$  8.03 ppm and  $\delta_{\text{H}}$  7.70 ppm were correspondingly assigned to the protons, H-6 and H-5. The six assignments of the protons H-4, H-5, H-6, H-7, H-8 and H-9 were additionally supported by the coupling constants and the multiplet structure of the signals.

Due to the fact that only meta (vicinal) couplings ( $^3J_{\text{CH}}$ ) can usually be resolved in benzene rings [16], the following strong HMBC correlations were found: for the naphthalene moiety—H<sub>4</sub>-C<sub>3</sub>, H<sub>4</sub>-C<sub>10</sub>, H<sub>5</sub>-C<sub>10a</sub>, H<sub>5</sub>-C<sub>11</sub>, H<sub>6</sub>-C<sub>4</sub>, H<sub>6</sub>-C<sub>7</sub>, H<sub>6</sub>-C<sub>10</sub>, H<sub>7</sub>-C<sub>9</sub>, H<sub>7</sub>-C<sub>10</sub>, H<sub>8</sub>-C<sub>9a</sub>, H<sub>8</sub>-C<sub>11</sub>, H<sub>9</sub>-C<sub>1</sub>, H<sub>9</sub>-C<sub>7</sub>, H<sub>9</sub>-C<sub>10</sub>; and for the benzene ring—H<sub>3'/7'</sub>-C<sub>5'</sub>, H<sub>3'/7'</sub>-C<sub>7'</sub>, H<sub>7'</sub>-C<sub>3'</sub>, H<sub>4'/6'</sub>-C<sub>2'</sub>, H<sub>4'/6'</sub>-C<sub>6'</sub>, H<sub>6'</sub>-C<sub>4'</sub>, H<sub>4'/6'</sub>-C<sub>5'</sub>. Also, a weak and an extremely weak HMBC correlation were found for the signal at  $\delta_{\text{C}}$  126.79 ppm with the signal at  $\delta_{\text{H}}$  6.98 ppm and at  $\delta_{\text{H}}$  7.89 ppm. Therefore, the signal at  $\delta_{\text{C}}$  126.79 ppm was assigned to the carbon C-2'.



This conclusion was supported by the strong HMBC correlations of the protons H-4' and H-6' with the carbon C-2'. Additionally, the strong HMBC correlations ( $\delta_{\text{H}} 6.98 \text{ ppm} - \delta_{\text{C}} 144.61 \text{ ppm}$ ) and ( $\delta_{\text{H}} 6.98 \text{ ppm} - \delta_{\text{C}} 124.08 \text{ ppm}$ ) confirmed that the signals at  $\delta_{\text{C}} 144.61 \text{ ppm}$  and  $\delta_{\text{C}} 124.08 \text{ ppm}$  were for the carbons C-3 and C-10a, respectively. The assignments of the four quaternary carbons in the naphthalene moiety, C-9a, C-10, C-10a and C-11, were based on the described strong meta (vicinal) HMBC correlations and supported also by the strong HMBC correlation between H-1' and C-10a.

### 3.2. Discussion of Structure Verification of Vb Presented in Table 2

The molecular formula of 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one is  $\text{C}_{19}\text{H}_{11}\text{O}_2\text{F}$ . The structure of the compound (Vb) with a numbering of its atoms, used only for the signal assignments, is presented in Figure 1b. In comparison with the previous structure, the substituent at the para position in the benzene ring connected with the carbon C-5' is fluorine. Probably due to the higher electronegativity of F than O in the methoxy group, the chemical shifts of the signals of the carbons C-3'/7', C-4'/6' and C-5' were increased as a result of the stronger deshielding effect of F. It was found that F could double the signals of the carbons C-2', C-3'/7', C-4'/6' and C-5', as there are two peaks for each of these carbons in the  $^{13}\text{C}$  NMR spectrum. Meanwhile, the signal of the carbon C-3 was split, appearing almost as a doublet, most likely due to the influence of F. Therefore, the chemical shifts of the carbons C-3, C-2', C-3'/7', C-4'/6' and C-5' are presented in Table 2 as averages from two values.

**Table 2.** H and  $^{13}\text{C}$  NMR data assignment for Vb [600.130 MHz ( $^1\text{H}$ ) and 150.903 MHz ( $^{13}\text{C}$ )]<sup>a</sup>.

Atom	$\delta$ ( $^{13}\text{C}$ ), ppm	DEPT <sup>b</sup>	$\delta$ ( $^1\text{H}$ ), ppm	Multiplicity (J, Hz)	$^1\text{H}-^1\text{H}$ COSY <sup>b</sup>	HMBC <sup>b</sup>
1(C=O)	159.61	C				
3	145.93 <sup>c</sup>	C				
4	122.18	CH	8.33	dd (7.5; 0.5)	5, 6 <sup>d</sup>	3, 6
5	127.42	CH	7.73	t (7.9)	4, 6	10a, 11
6	128.36	CH	8.08	d (8.1)	4 <sup>d</sup> , 5	4, 7, 10, 11 <sup>d</sup>
7	134.49	CH	8.35	dd (8.3; 0.8)	8	9, 9a <sup>e</sup> , 11 <sup>d</sup>
8	126.91	CH	7.77	dd (8.2; 7.2)	7, 9	9 <sup>e</sup> , 9a, 11
9	129.29	CH	8.34	dd (7.2; 1.1)	8	1, 7
9a	119.09	C				
10	127.52	C				
10a	123.68	C				
11	132.05	C				
1'	107.03	CH	7.06	s	3'/7' <sup>d</sup>	1, 3, 4 <sup>e</sup> , 10a, 3'/7'
2'	130.78 <sup>c</sup>	C				
3'	131.60 <sup>c</sup>	CH	7.96	m	1' <sup>d</sup> , 4'	1', 5', 7'
4'	115.57 <sup>c</sup>	CH	7.30	m	3'	2', 5', 6'
5'	161.25 <sup>c</sup>	C				
6'	115.57 <sup>c</sup>	CH	7.30	m	7'	2', 4', 5'
7'	131.60 <sup>c</sup>	CH	7.96	m	1' <sup>d</sup> , 6'	1', 3', 5'

<sup>a</sup> The solvent used is DMSO- $d_6$  (solvent reference:  $^1\text{H}$   $\delta_{\text{ref}}$  2.50 ppm,  $^{13}\text{C}$   $\delta_{\text{ref}}$  39.51 ppm). COSY, HMQC and HMBC spectra assisted the corresponding assignments. <sup>b</sup> Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum;  $^1\text{H}-^1\text{H}$  COSY, proton–proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long-range  $^1\text{H}-^{13}\text{C}$  Heteronuclear Multiple Bond Correlation experiment. <sup>c</sup> Average from two values. <sup>d</sup> Weak correlations. <sup>e</sup> Extremely weak correlations.

The  $^{13}\text{C}$  NMR signal with the highest chemical shift,  $\delta_{\text{C}}$  161.25 ppm, was assigned for the carbon C-5', whereas the signals with the chemical shifts  $\delta_{\text{C}}$  131.60 ppm and  $\delta_{\text{C}}$  115.57 ppm from the  $^{13}\text{C}$  NMR spectrum were assigned to the carbons C-3'/7' and C-4'/6', respectively. In addition, the coupling constants ( $^n\text{J}_{\text{CF}}$ ) in the benzene ring supported the corresponding assignments (Table 3).

**Table 3.** Carbon–fluorine coupling constants,  $^n\text{J}_{\text{CF}}$ .

Coupling Constants ( $^n\text{J}_{\text{CF}}$ )	Values, Hz
$^1\text{J}_{\text{CF}}$	246.1
$^2\text{J}_{\text{CF}}$	21.4
$^3\text{J}_{\text{CF}}$	8.0
$^4\text{J}_{\text{CF}}$	3.2

It was found that the  $\text{J}_{\text{CF}}$  constants correlated well with those reported in the literature for some fluorobenzenes and fluoronaphthalenes [17,18]. The signal at  $\delta_{\text{C}}$  159.61 ppm was for the carbonyl carbon C-1, while the one with the lowest chemical shift,  $\delta_{\text{C}}$  107.03 ppm, was assigned to the olefin carbon C-1'. Meanwhile, the peak at  $\delta_{\text{C}}$  145.93 ppm corresponded to the other olefin carbon, C-3. The described assignments were confirmed by the 2D NMR spectra (see the discussion below).

The fluorine and proton nuclei in the benzene ring form a five-spin AA'MM'X system, leading to the registration of deceptively simple spectra for the AA' and MM' parts. Analogously to the previous case, the “Spin Simulation” tool from the MestreNova software was used to simulate the spectra for the AA' and MM' parts of the AA'MM'X system in order to determine the chemical shifts and coupling constants of the signals of the protons and fluorine. Correspondingly, the following set of parameters, ( $\delta_{\text{H}}$  7.96 ppm for H-3'/7' (AA' part);  $\delta_{\text{H}}$  7.30 ppm for H-4'/6' (MM' part);  $\delta_{\text{F}}$  −59 254.16 ppm (X part);  $\text{J}^3_{\text{MX}} = \text{J}^3_{\text{M'X}} = 11.0$  Hz,  $\text{J}^4_{\text{AX}} = \text{J}^4_{\text{A'X}} = 7.5$  Hz,  $\text{J}^4_{\text{AA'}} = \text{J}^4_{\text{MM'}} = 3.25$  Hz,  $\text{J}^3_{\text{AM}} = \text{J}^3_{\text{A'M'}} = 10.5$  Hz,  $\text{J}^5_{\text{AM}} = \text{J}^5_{\text{A'M}} = 0.35$  Hz), presented in Table 2, was used to achieve the most similar appearance of the simulated spectra to the real ones obtained for the AA' and MM' parts of the AA'MM'X system. A strong COSY correlation was found between the signals of the protons from each of the following pairs: H-3' and H-4', as well as H-6' and H-7'. The assignment of the singlet at  $\delta_{\text{H}}$  7.06 ppm to the proton H-1' was confirmed by the weak COSY correlations of the signal of H-1' with the ones of the protons H-3' and H-7'. The strong HMBC correlations of the signal of H-1' with the one of H-3'/7', corresponding with the signals of C-3'/7' and C-1', supported the assignment of the signals at  $\delta_{\text{H}}$  7.96 ppm and  $\delta_{\text{H}}$  7.30 ppm to the protons H-3'/7' and H-4'/6'.

Two strong COSY correlations of the signal at  $\delta_{\text{H}}$  7.77 ppm with the signals at  $\delta_{\text{H}}$  8.34 ppm and  $\delta_{\text{H}}$  8.35 ppm were found. Due to its strong HMBC correlation, ( $\delta_{\text{H}}$  8.34 ppm– $\delta_{\text{C}}$  159.61 ppm), the signal with the chemical shift  $\delta_{\text{H}}$  8.34 ppm was assigned to the proton H-9, while the signals at  $\delta_{\text{H}}$  7.77 ppm and  $\delta_{\text{H}}$  8.35 ppm were correspondingly assigned to the protons H-8 and H-7. Additionally, strong COSY correlations of the signal at  $\delta_{\text{H}}$  7.73 ppm with the signals at  $\delta_{\text{H}}$  8.08 ppm and  $\delta_{\text{H}}$  8.33 ppm were found, and there was also one weak COSY correlation between the signals at  $\delta_{\text{H}}$  8.08 ppm and  $\delta_{\text{H}}$  8.33 ppm. Furthermore, the signal at  $\delta_{\text{H}}$  8.33 ppm showed a strong HMBC correlation with a peak at  $\delta_{\text{C}}$  145.93 ppm; thus, the signal at  $\delta_{\text{H}}$  8.33 ppm was assigned to the proton H-4, while the signals at  $\delta_{\text{H}}$  8.08 ppm and  $\delta_{\text{H}}$  7.73 ppm were for H-6 and H-5, respectively. The assignments of the chemical shifts of the signals for the protons H-4, H-5, H-6, H-7, H-8 and H-9 were additionally confirmed from the coupling constants and the multiplet structure of the proton signals.

As was previously mentioned, only the meta (vicinal) couplings ( $^3\text{J}_{\text{CH}}$ ) can be usually resolved into benzene rings [16]. In this case, the following strong HMBC correlations were found: for the naphthalene moiety—H4-C3, H4-C6, H5-C10a, H5-C11, H6-C4, H6-



C<sub>7</sub>, H<sub>6</sub>-C<sub>10</sub>, H<sub>7</sub>-C<sub>9</sub>, H<sub>8</sub>-C<sub>9a</sub>, H<sub>8</sub>-C<sub>11</sub>, H<sub>9</sub>-C<sub>1</sub>, H<sub>9</sub>-C<sub>7</sub>; and for the benzene ring—H<sub>3'/7'</sub>-C<sub>5'</sub>, H<sub>3'</sub>-C<sub>7'</sub>, H<sub>7'</sub>-C<sub>3'</sub>, H<sub>4'/6'</sub>-C<sub>2'</sub>, H<sub>4'</sub>-C<sub>6'</sub>, H<sub>6'</sub>-C<sub>4'</sub>, H<sub>4'/6'</sub>-C<sub>5'</sub>. The signals at  $\delta_{\text{H}}$  7.06 ppm and  $\delta_{\text{H}}$  8.33 ppm showed strong HMBC correlations, with the peak at  $\delta_{\text{C}}$  145.93 ppm, confirming the hypothesis that the signal at  $\delta_{\text{C}}$  145.93 ppm corresponded to the olefin carbon C-3 next to the oxygen. Additionally, the strong HMBC correlations ( $\delta_{\text{H}}$  7.06 ppm– $\delta_{\text{C}}$  145.93 ppm) and ( $\delta_{\text{H}}$  7.06 ppm– $\delta_{\text{C}}$  123.68 ppm) confirmed that the signals at  $\delta_{\text{C}}$  145.93 ppm and  $\delta_{\text{C}}$  123.68 ppm were for the carbons C-3 and C-10a, respectively. The assignments of the four quaternary carbons in the naphthalene moiety, C-9a, C-10, C-10a and C-11, were based on the described strong meta (vicinal) HMBC correlations, and they were supported also by the strong HMBC correlation between H-1' and C-10a.

### 3.3. Discussion of Structure Verification of Vc Presented in Table 4

The molecular formula of 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one is C<sub>17</sub>H<sub>10</sub>O<sub>2</sub>S. The structure of the compound (Vc) with the numbering of its atoms, used only for the signal assignments, is presented on Figure 1c. The major structural difference between 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one and 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one is the replacement of the *p*-substituted benzene ring bonded to the methylidene group with thiophene in the structure of the last compound. Therefore, there are no substantial differences between the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts and the coupling constants (*J*<sub>HH</sub>) of the signals found for the 1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one moiety in the three compounds (Table 4). Significant changes were observed only for the chemical shifts of the signals of the proton H-1' ( $\delta_{\text{H}}$  7.18 ppm) and carbon C-1' ( $\delta_{\text{C}}$  103.35 ppm) in the case of the 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one. However, the most interesting part about the structure verification of 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one was the assignment of the signals of the thiophene protons. The <sup>1</sup>H NMR spectrum showed that two of the thiophene protons have signals with the same chemical shift ( $\delta_{\text{H}}$  7.66 ppm), while all three of the thiophene protons form an ABX system that produced a complex second-order spectrum. For this reason, to correctly assign the signals of the thiophene protons, the ABX spectrum was simulated by using the “Spin Simulation” tool from the MestreNova software. The best possible similarity between the simulated and real ABX spectra was achieved by accepting the following inserted values for the chemical shifts and coupling constants of the signals of the thiophene protons:  $\delta_{\text{H}}$  7.92 ppm for H-3' (<sup>3</sup>*J*<sub>HH</sub> = 2.8 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz), as well as  $\delta_{\text{H}}$  7.655 ppm and  $\delta_{\text{H}}$  7.664 ppm for H-4' (<sup>4</sup>*J*<sub>HH</sub> = 4.8 Hz, <sup>3</sup>*J*<sub>HH</sub> = 2.8 Hz) and H-5' (<sup>4</sup>*J*<sub>HH</sub> = 4.8 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.3 Hz). Additionally, the simulation was supported by the following weak COSY and HMBC correlations: ( $\delta_{\text{H}}$  7.664 ppm– $\delta_{\text{H}}$  7.18 ppm), ( $\delta_{\text{H}}$  7.92 ppm– $\delta_{\text{H}}$  7.18 ppm), ( $\delta_{\text{H}}$  7.664 ppm– $\delta_{\text{C}}$  103.35 ppm) and ( $\delta_{\text{H}}$  7.92 ppm– $\delta_{\text{C}}$  103.35 ppm). The assignments of the signals of the thiophene carbons were supported by the HMQC correlations (7.92 ppm–125.64 ppm), (7.655 ppm–128.90 ppm) and (7.664 ppm–126.27 ppm).

**Table 4.** <sup>1</sup>H and <sup>13</sup>C NMR data assignment for Vc [600.130 MHz (<sup>1</sup>H) and 150.903 MHz (<sup>13</sup>C)]<sup>a</sup>.

Atom	$\delta$ ( <sup>13</sup> C), ppm	DEPT <sup>b</sup>	$\delta$ ( <sup>1</sup> H), ppm	Multiplicity (J, Hz)	<sup>1</sup> H- <sup>1</sup> H COSY <sup>b</sup>	HMBC <sup>b</sup>
1(C=O)	159.75	C				
3	144.95	C				
4	121.62	CH	8.26	dd (7.5; 0.5)	5, 6 <sup>c</sup> , 1' <sup>c</sup>	3, 5, 6, 9a <sup>d</sup> , 11 <sup>d</sup>
5	127.48	CH	7.72	t (7.8)	4, 6	10a, 11

Table 4. Cont.

Atom	$\delta$ ( $^{13}\text{C}$ ), ppm	DEPT <sup>b</sup>	$\delta$ ( $^1\text{H}$ ), ppm	Multiplicity (J, Hz)	$^1\text{H}$ - $^1\text{H}$ COSY <sup>b</sup>	HMBC <sup>b</sup>
6	128.05	CH	8.07	d (8.1)	4 <sup>c</sup> , 5, 7 <sup>d</sup>	4, 7, 10, 11 <sup>c</sup>
7	134.44	CH	8.34	dd (8.3; 0.8)	6 <sup>d</sup> , 8	9, 9a <sup>d</sup> , 11 <sup>c</sup>
8	126.95	CH	7.78	dd (8.2; 7.2)	7, 9	9 <sup>c</sup> , 9a, 11
9	129.20	CH	8.32	dd (7.2; 1.1)	8	1, 7, 10
9a	119.23	C				
10	127.51	C				
10a	123.69	C				
11	132.11	C				
1'	103.35	CH	7.18	s	4 <sup>c</sup> , 3' <sup>c</sup> , 5' <sup>d</sup>	1, 3, 10a, 2' <sup>d</sup> , 3', 4', 5'
2'	135.07	C				
3'	125.64	CH	7.92	m	1' <sup>c</sup> , 4'	1' <sup>d</sup> , 2' <sup>c</sup> , 4' <sup>c</sup> , 5' <sup>c</sup>
4'	128.90	CH	7.655	m	3'	2', 3', 5'
5'	126.27	CH	7.664	m	1' <sup>d</sup>	1' <sup>d</sup> , 2', 3', 4' <sup>c</sup>

<sup>a</sup> The solvent used is DMSO- $d_6$  (solvent reference:  $^1\text{H}$   $\delta_{\text{ref}}$  2.50 ppm,  $^{13}\text{C}$   $\delta_{\text{ref}}$  39.51 ppm). COSY, HMQC and HMBC spectra assisted the corresponding assignments. <sup>b</sup> Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum;  $^1\text{H}$ - $^1\text{H}$  COSY, proton–proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long-range  $^1\text{H}$ - $^{13}\text{C}$  Heteronuclear Multiple Bond Correlation experiment. <sup>c</sup> Weak correlations. <sup>d</sup> Extremely weak correlations.

#### 4. Shift Predictions with NMRShiftDB Database

As is shown in the literature, the chemical shift prediction based on hierarchically ordered spherical environment (HOSE) coding is better than using quantum chemistry [19,20]. Also, HOSE predictions are way faster than quantum chemistry calculations [21]. The NMRShiftDB database provides an option for  $^{13}\text{C}$  NMR chemical shift prediction based on HOSE codes [3,4,22]. The HOSE code predictions for  $^{13}\text{C}$  NMR chemical shifts utilize canonical linear string descriptions of a maximum size of six spheres that can describe the spherical environment for each carbon in every structure available in the NMRShiftDB database. The resulting HOSE codes are stored in look-up tables along with their assigned chemical shift values. Performing a shift prediction for a structure that is not available in the NMRShiftDB database involves generating HOSE codes for it, which are subsequently searched in previously generated tables in the database. For each code describing the structure, there are hits with differing shifts presented in a look-up table. Finally, an average shift value accompanied by some statistics is obtained for a given HOSE code. In this case, rough predictions for the  $^{13}\text{C}$  chemical shifts are presented for the three structures by using the NMRShiftDB database (Table 5).

For each structure, the predicted  $^{13}\text{C}$  chemical shifts for the range of atoms from C-1 to C-10a remained almost the same, with the exception of the predicted shift of the C-8 atom in 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, where a slight change was observed. Although there are some differences between the shifts predicted for the carbons in the naphthalene moiety that is present in all structures (C-3, C-4, C-7, C-10a) and the measured shifts, there is still a good agreement between the experimental and predicted values. Excluding the difference between the predicted and measured shift for C-1' in 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, the predicted shifts for the carbons in the substituents which are bound to C-1' in all three structures correlate well with the experimental ones.

Table 5. Comparison of the experimental and predicted  $^{13}\text{C}$  chemical shifts with HOSE code.

3-[(4-Methoxyphenyl)methylidene]- 1 <i>H</i> ,3 <i>H</i> -naphtho[1,8- <i>cd</i> ]-pyran-1-one			3-[(4-Fluorophenyl)methylidene]- 1 <i>H</i> ,3 <i>H</i> -naphtho[1,8- <i>cd</i> ]-pyran-1-one			3-[(Thiophen-3-yl)methylidene]-1 <i>H</i> ,3 <i>H</i> - naphtho[1,8- <i>cd</i> ]-pyran-1-one		
Atom	$\delta$ ( $^{13}\text{C}$ ), exp <sup>a</sup> (ppm)	$\delta$ ( $^{13}\text{C}$ ), pred <sup>b</sup> (ppm)	Atom	$\delta$ ( $^{13}\text{C}$ ), exp <sup>a</sup> (ppm)	$\delta$ ( $^{13}\text{C}$ ), pred <sup>b</sup> (ppm)	Atom	$\delta$ ( $^{13}\text{C}$ ), exp <sup>a</sup> (ppm)	$\delta$ ( $^{13}\text{C}$ ), pred <sup>b</sup> (ppm)
1(C=O)	159.80	162.84	1(C=O)	159.61	162.84	1(C=O)	159.75	162.84
3	144.61	160.76	3	145.93	160.76	3	144.95	160.76
4	121.57	127.92	4	122.18	127.92	4	121.62	127.92
5	127.42	126.39	5	127.42	126.39	5	127.48	126.39
6	127.74	127.50	6	128.36	127.50	6	128.05	127.50
7	134.35	127.41	7	134.49	127.41	7	134.44	127.41
8	126.85	127.48	8	126.91	127.67	8	126.95	127.48
9	128.99	132.43	9	129.29	132.43	9	129.20	132.43
9a	119.21	118.89	9a	119.09	118.89	9a	119.23	118.89
10	127.47	128.55	10	127.52	128.55	10	127.51	128.55
10a	124.08	130.42	10a	123.68	130.42	10a	123.69	130.42
11	132.11	130.65	11	132.05	130.65	11	132.11	130.65
1'	108.19	107.15	1'	107.03	107.15	1'	103.35	111.12
2'	126.79	130.38	2'	130.78	130.38	2'	135.07	135.70
3'	131.17	132.80	3'	131.60	133.40	3'	125.64	128.00
4'	114.13	114.57	4'	115.57	116.80	4'	128.90	128.60
5'	158.75	160.80	5'	161.25	162.50	5'	126.27	130.20
6'	114.13	114.57	6'	115.57	116.80			
7'	131.17	132.80	7'	131.60	133.40			
OCH <sub>3</sub>	55.18	55.33						

<sup>a</sup> Experimental. <sup>b</sup> Predicted.

## 5. Conclusions

Completely assigned NMR data were presented for the structures of 3-[(4-methoxyphenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one, 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one and 3-[(thiophen-3-yl)methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-one. The methylidene substituents in the corresponding structures produced complex  $^1\text{H}$  NMR spectra requiring computer-assisted simulations to be performed in order to assign the chemical shifts and coupling constants of the signals of the protons in the *p*-substituted benzene rings and thiophene. The proposed structures were additionally verified with the  $^{13}\text{C}$  NMR predictions provided by the NMRShiftDB database. A future perspective would be the synthesis of other 3-[substituted methylidene]-1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1-ones and their structure verification by means of 1D and 2D NMR techniques.

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