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One-Pot Five-Component Synthesis of Spirocyclopenta[*b*]chromene Derivatives and Their Acid-Catalyzed Rearrangement

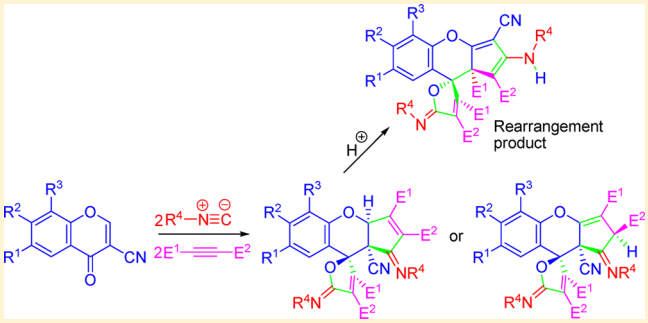
Michael A. Terzidis,[†] Tryfon Zarganes-Tzitzikas,[†] Constantinos Tsimenidis,[†] Julia Stephanidou-Stephanatou,*[,†] Constantinos A. Tsoleridis,*[,†] and George E. Kostakis[‡]

[†]Department of Chemistry, Laboratory of Organic Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Macedonia, Greece

[‡]Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Supporting Information

ABSTRACT: The reaction of the zwitterionic intermediate, generated in situ from either *tert*-butylisocyanide or cyclohexylisocyanide and acetylenedicarboxylates, with 3-cyanochromones is described, whereupon spirochromenofuran derivatives **5** or **6** were obtained in good yields. The subsequent acid-catalyzed rearrangement of the isolated 2-imino-spirochromenofurans **5** to 2-amino-spirochromenofurans **7** has also been studied. Rational mechanistic schemes for the formation of compounds **5**, **6**, and **7** are proposed. The structure elucidation of the products was accomplished by 1D and 2D NMR experiments and confirmed by X-ray crystallographic analysis. Full assignment of all ^{1}H and ^{13}C NMR chemical shifts has been unambiguously achieved with the aid of DFT/GIAO calculations.



INTRODUCTION

In addition to forming the basic nucleus of an entire class of natural products, i.e., flavones,[1] the chromone moiety is also part of pharmacophores of various biologically active molecules[2,3] including anticancer agents such as psorospermin and pluramycin A[4,5] (Figure 1). Concerning 3-cyano-4-benzopyrones, the introduction of an electron-withdrawing group at the 3-position of the chromone system changes crucially the reactivity of the pyrone ring and provides a broad synthetic potential in organic[6] and in medicinal[7] chemisty. As a result, 3-cyano-4-benzopyrones are important intermediates not only in the synthesis of therapeutically useful antiallergic drugs such as amlexanox[7a] but also in the synthesis of benzopyranopyridines with anti-inflammatory activity.[7b] They are also reported as useful dienophiles in [4+2] cycloaddition reactions and in the construction of the tricyclic ring of arisugacin A, which is a selective inhibitor of acetylcholine esterase.[7c]

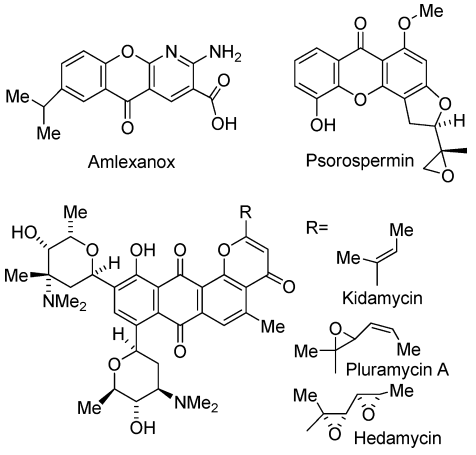


Figure 1. Structures of amlexanox, psorospermin, and pluramycin family natural products.

In vew of the synthetic potential of cyanochromones and the well-known fact that the rich and fascinating chemistry that stems from multicomponent reactions (MCRs) provides a powerful tool toward the one-pot synthesis of diverse and complex compounds on the one hand and small and "drug-like" heterocycles on the other hand,[8] we sought to establish new multicomponent reactions involving chromones. Since MCRs involving isocyanides are by far the more versatile reactions in terms of scaffolds and number of accessible compounds,[9] recently we initiated a study in trapping the zwitterionic intermediates, derived from acetylenecarboxylates and isocyanides, with 3-cyanochromones whereupon, instead of the expected fused cyclopentadienochromone derivatives, novel spirobenzofuranocyclopentadienes were isolated[10] as the only reaction products in very good yields. In the present work, we wish to report our extended investigations in this field, since by

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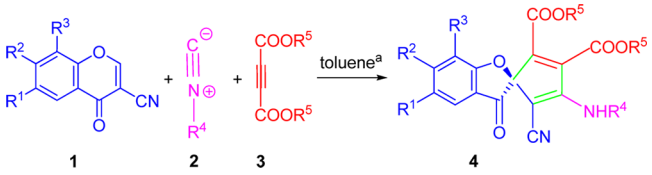
using isocyanides and acetylenedicarboxylates with 3-cyanochromones in a 3:3:1 molar ratio novel spirochromenofuran derivatives with structures related to rhodamine and fluorescein chemosensors[11] were isolated in good yields.

At this point it is also worth mentioning that spirocyclic systems constitute a very interesting class of compounds.[12] Among them spiroheterocycles represent an important part of natural products characterized by their highly pronounced biological activities,[12] mainly due to the unalterable configuration of their reactive sites to the corresponding key positions of the substrate peptides. Spiro derivatives from the keto group of various chromanones have been patented for their inhibitory effect on sodium-dependent glucose cotransporter (SGLT).[13a] Moreover, it was found that some spirohydantoin derivatives of 8-aza-4-chromanone have excellent biological activity as aldose reductase inhibitors.[13b]

RESULTS AND DISCUSSION

As already mentioned, some time ago we studied the reaction of 3-cyanochromones with isocyanides and acetylenedicarboxylates in a 1:1.2:1.2 molar ratio, whereupon spirobenzofuranocyclopentadienes **4** were isolated as the only reaction products in very good yields (60−70%, Scheme 1).[10]

Scheme 1. Synthesis of Spiro Derivatives 4

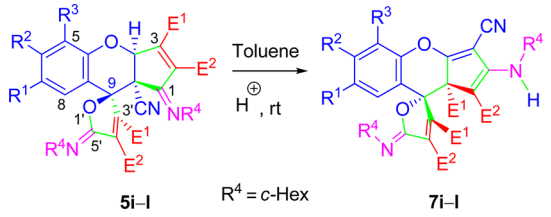


[a]In the case of R^4 = *t*-Bu at reflux for 3 h; in the case of R^4 = *c*-Hex at rt for 24 h.

In the present work, we wish to report our extended investigations, whereupon through a five-component one-pot synthesis by using isocyanides and acetylenedicarboxylates with 3-cyanochromones in a 3:3:1 molar ratio the novel spirochromenofuran derivatives **5** or **6** were isolated in good yields (60−80%, Scheme 2). The isolation of these spiroderivatives is unexpected, since as it is well-known that the chromone system bearing an electron-withdrawing group in the 3-position (i.e., CHO, CN) reacts preferably from the C-2 carbon,[14] providing a useful route to the preparation of a variety of rearranged products and new heterocyclic systems, whereas reaction from the chromone-4-carbonyl is not observed. In fact, to our knowledge, this is the first example of a reaction observed in the chromone-4-carbonyl leading through a multicomponent reaction to formation of spiro derivatives.

The isolated spirochromenofuran derivatives **5** and **6** are quite stable in the solid state and in solution in the absence of acids. However, in the case of the cyclohexyl-substituted derivatives **5i−5l,n**, even at room temperature in the $CDCl_3$ solution in the NMR tube, quantitative transformation to the corresponding derivatives **7i−7l,n** occurred due to acid traces present in $CDCl_3$ (Scheme 3). This transformation was

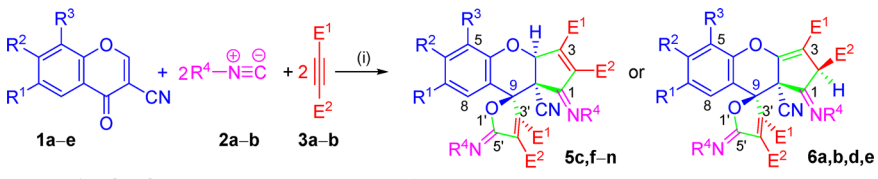
Scheme 3. Transformation of Cyclohexyl-Substituted Spirochromenofurans 5 to Spirochromenofuranes 7



accelerated by addition of a catalytic amount of acid (*p*-TSA (2% mol) in toluene). To the contrary, the *tert*-butyl-substituted derivatives **5a,b,c,e,h** appeared to be stable, and no transformation was observed even in the presence of a catalytic amount of *p*-TSA.

Mechanistically, for the formation of the spiro derivatives **5** (Scheme 4) it is conceivable that the zwitterionic intermediate **8**, initially formed by the 1:1 interaction between the isocyanide and DMAD, attacks preferentially the C-2 chromone carbon leading to intermediate **9**. If we suppose that the attack of **8** occurs from the upper side of the chromone ring leading to the energetically activated intermediate **9**, in the next step, the second molecule of **8**, being in excess, would attack the chromone-4-carbonyl preferentially from the opposite site of the chromone ring, in respect to the previously inserted zwitterionic species (intermediate **10**), favored due to reduced van der Waals interactions, leading thus to **5**. This sequence can explain the *cis* configuration at the junction of the cyclopentene with the pyran ring and the *trans* orientation of CN group in respect to the oxygen of the spirofuran ring. Subsequently, in the case of some *tert*-butyl-substituted derivatives (Table 1) the transformation of **5** to **6** can be rationalized on the basis of leading to more stabilized structures by [1,3] hydride shift. Thus, for the nonsubstituted chromone the transformation of **5a** to **6a** is calculated to gain in energy 7.57 kcal/mol (DFT, Table 2). On the other hand, the 6-chloro-substituted derivative **5c** is stable enough and does not isomerize to the corresponding **6c**.

Scheme 2. Reaction of 3-Cyanochromones with Isocyanides and Acetylenedicarboxylates



	R^1	R^2	R^3
1a	H	H	H
1b	Me	H	H
1c	Cl	H	H
1d	Me	Me	H
1e	Cl	H	Cl

	R^4
2a	*t*-Bu
2b	*c*-Hex

	E^1	E^2
3a	COOMe	COOMe
3b	COOEt	COOEt
3c	COOMe	H

(i) Toluene, 40 °C, 12 h

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Scheme 4. Mechanistic Rationalization for the Formation of Compounds 5, 6, and 7

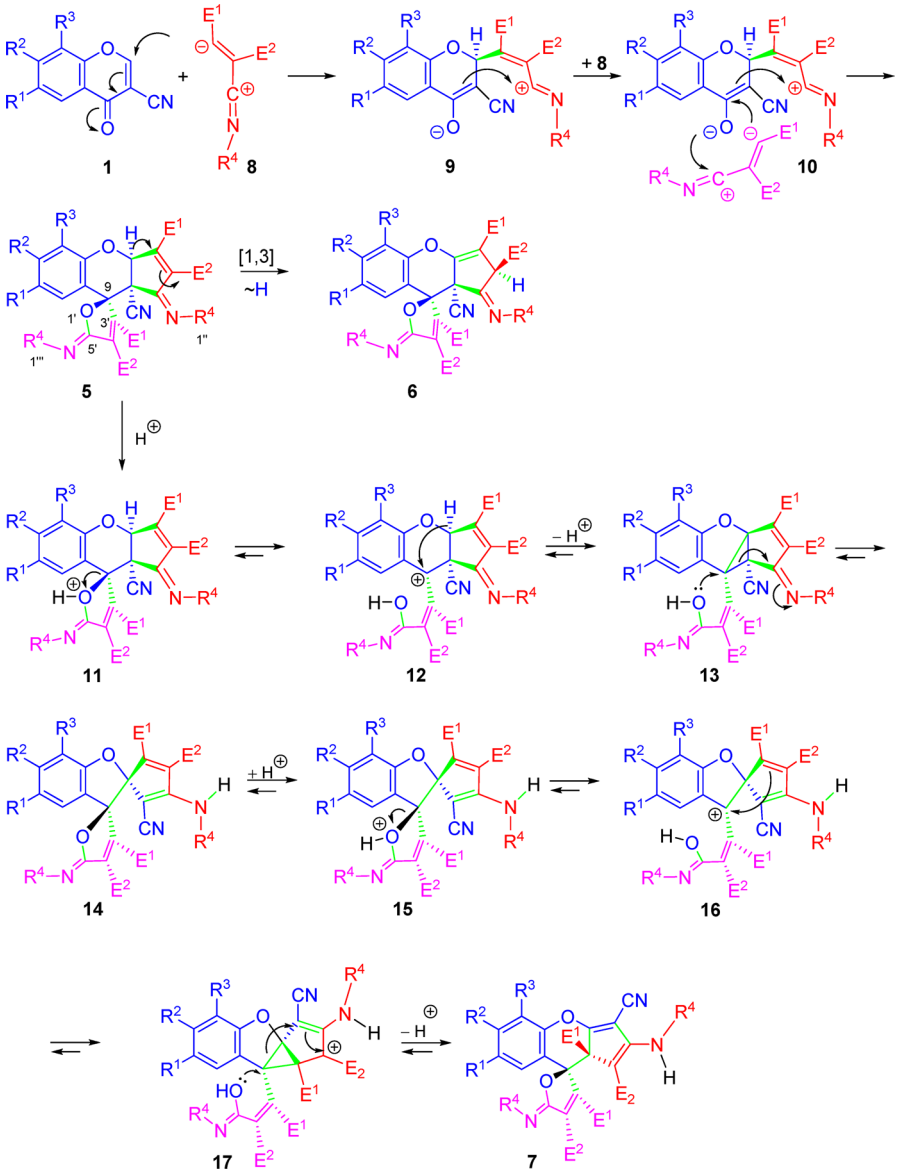

Table 1. Reaction of 3-Cyanochromones with Isocyanides and Acetylenedicarboxylates or Propiolates

entry	1	R^1	R^2	R^3	2	R^4	3	E^1, E^2	product 5	product 6	product 7
1	**1a**	H	H	H	**2a**	*t*-Bu	**3a**	CO_2Me		**a** (79)	
2	**1b**	Me	H	H	**2a**	*t*-Bu	**3a**	CO_2Me		**b** (82)	
3	**1c**	Cl	H	H	**2a**	*t*-Bu	**3a**	CO_2Me	**c** (88)		
4	**1d**	Me	Me	H	**2a**	*t*-Bu	**3a**	CO_2Me		**d** (85)	
5	**1e**	Cl	H	Cl	**2a**	*t*-Bu	**3a**	CO_2Me		**e** (63)	
6	**1a**	H	H	H	**2a**	*t*-Bu	**3b**	CO_2Et	**f** (63)		
7	**1b**	Me	H	H	**2a**	*t*-Bu	**3b**	CO_2Et	**g** (69)		
8	**1c**	Cl	H	H	**2a**	*t*-Bu	**3b**	CO_2Et	**h** (79)		
9	**1a**	H	H	H	**2b**	*c*-Hex	**3a**	CO_2Me	**i** (77)		**i** (92)
10	**1b**	Me	H	H	**2b**	*c*-Hex	**3a**	CO_2Me	**j** (79)		**j** (91)
11	**1c**	Cl	H	H	**2b**	*c*-Hex	**3a**	CO_2Me	**k** (65)		**k** (72)
12	**1d**	Me	Me	H	**2b**	*c*-Hex	**3a**	CO_2Me	**l** (71)		**l** (71)
13	**1e**	Cl	H	Cl	**2b**	*c*-Hex	**3a**	CO_2Me	**m** (63)		
14	**1a**	H	H	H	**2b**	*c*-Hex	**3b**	CO_2Et	**n** (89)		**n** (90)
15	**1a**	H	H	H	**2a**	*t*-Bu	**3c**	CO_2Me, H	**o** (80)		

The acid-promoted transformation of **5** to **7**, according to the mechanism depicted in Scheme 4, most probably begins by protonation of the furan oxygen (intermediate **11**), since this oxygen was calculated to have more negative charge than the

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Table 2. Total Energies[a] for Some Representative Compounds

compound	E_{total}	ΔE^b 6 − 5	ΔE^b 7 − 5	ΔE^b 7 − 6
5a	−2156.276829			
6a	−2156.288896	−7.57		
7a	−2156.316066		−24.62	−17.05
5i	−2311.058216			
6i	−2311.063513	−3.32		
7i	−2311.079552		−13.39	−10.06

[a]Calculated by DFT (B3LYP/6-31G(d)). E_{total} is the sum of electronic and zero-point energy correction (in hartrees). [b]The stabilization energy resulting from the corresponding transformation (in kcal/mol).

exocyclic imine nitrogen (−0.550 e versus −0.477 e for compound **5i**) followed by fission of the C9−O1′ bond (intermediate **12**). By a mechanism analogous to the one discussed in our previous work[10] concerning the formation of the spiroderivatives **4**, intermediate **13** can be formed. This intermediate is unstable due to the cyclopropane bis-fused ring and by subsequent bond fission and protonation on the exocyclic nitrogen leads to **14** having a structure analogous to that of compounds **4**. Further protonation to **15** and C−O bond fission lead to carbocation **16**, which can be transformed to give **17** by attack of the double bond between the ester groups to the carbocationic center. Finally, after proton abstraction and bond rearrangement the isolated product **7** with the given stereochemistry can be obtained. To our knowledge, no analogous acid-catalyzed spontaneous transformation of cyclopentene ring derivatives has been reported in the literature.

In Table 2 the total energies (E_{total}) for the corresponding compounds (unsubstituted in the chromone moiety) bearing a *tert*-butyl (**5a**, **6a**, **7a**) or a cyclohexyl (**5i**, **6i**, **7i**) substituent in the isocyanide moiety are presented. From a comparison, it can be concluded that the transformation of **5a** to **6a** can stabilize the system by 7.57 kcal/mol, whereas the corresponding transformation of the cyclohexyl derivatives **5i** to **6i** offers only about half that amount of stabilization 3.32 kcal/mol. This small amount of energy seems not enough to force the reaction to proceed. On the other hand, the acid-promoted transformation of **5a** to **7a** and **5i** to **7i** is calculated to have an energy gain of 24.62 and 13.39 kcal/mol, respectively. However, experimentally this transformation of **6** to **7** was not observed in the case of the *tert*-butyl derivatives. This fact could be attributed mainly to the higher protection of the possible protonation center, due to the stiffness and symmetry of the *tert*-butyl group compared to that of the cyclohexyl moiety.

Structure Assignments of the New Compounds. The assigned molecular structures of the new compounds **5**, **6**, and **7** were based on rigorous spectroscopic analysis including IR, NMR (^{1}H, ^{13}C, COSY, NOESY, HETCOR and COLOC), MS, and elemental analysis data and confirmed by X-ray crystallographic analysis.

In Figure 2, some diagnostic COLOC correlations of protons with carbons via ^2J and ^3J coupling constants for compounds **5j** and **7j** are depicted.

A typical ^{1}H NMR spectrum of the spiro derivative **5j** contains a characteristic sequence of three aromatic protons, four singlets for the protons of the four carbomethoxy groups, and two characteristic sequences for the two cyclohexyl moieties. Very characteristic are the two one- proton multiplets

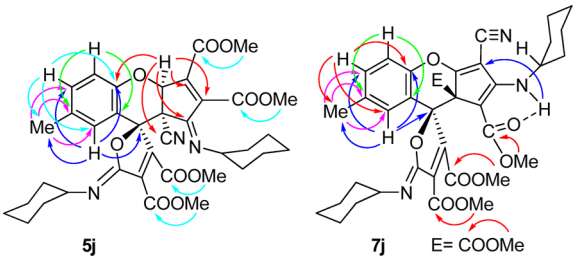

Figure 2. Some diagnostic COLOC correlations between protons and carbons (via $^2J_{C-H}$ and $^3J_{C-H}$) in compounds **5j** and **7j**.

at δ 3.24−3.34 and δ 3.55−3.65 corresponding to the two 1-cyclohexylimino protons, in addition to the singlet for the 3a proton at δ 5.80. This particular proton is of high diagnostic value since it shows COLOC correlations with the carbons at 153.5 (C-1), at 144.0 (C-2), at 138.3 (C-3), at 150.3 ppm (C-4a), and at 116.8 ppm (CN) (Figure 2). These COLOC correlations reveal that the pyran ring can adopt in solution interconverting chair and boat conformations, so that it can be possible for the 3a-H proton to be in the favored "almost coplanar" configuration with the above-mentioned carbons. Moreover, the ^{13}C NMR spectrum contains a characteristic set of signals of a tris-substituted phenyl moiety, the chromone carbonyl signal being replaced by a quaternary C_{sp3} carbon at 87.0 ppm (C-9). The identification of the C-9 carbon is confirmed by its COLOC correlation with the 8-H proton, which is also correlating with the C-4a carbon. In the IR spectrum a quite intensive peak at 2221 cm^{-1} easily identifies the presence of CN group.

The rearranged product **7j** also contains the characteristic sequence of three aromatic protons, four singlets for the protons of the four carbomethoxy groups, and two characteristic sequences for the two cyclohexyl moieties. Very characteristic are the two one-proton multiplets at δ 3.20−3.32 and δ 3.52−3.62 (the 1-cyclohexylamino proton being shifted to lower field) corresponding to the two 1-cyclohexylamino protons, in addition to the doublet for the NH proton at δ 8.90, which has replaced the 3a-H proton at δ 5.80 and shows COLOC correlations with the carbon at 87.1 ppm (C-3). Moreover, the ^{13}C NMR spectrum contains a characteristic set of signals of a tris-substituted phenyl moiety, the chromone carbonyl signal being replaced by a quaternary C_{sp3} carbon at 89.0 ppm (C-9). The identification of the C-9 carbon is also confirmed by its COLOC correlation with the 8-proton, which is also correlating with the C-4a. In the IR spectrum a quite intensive peak at 2222 cm^{-1} is in accordance with the presence of the CN group. The final structure of compounds **7** could not be fully resolved by NMR due to the lack of protons in the cyclopentane ring, which could be of help by means of C−H correlations. Therefore, X-ray crystal analysis was used to investigate this unpredictable product structure.

In Figure 3 the crystal structures of compounds **5c**, **6a**, and **7i** are depicted.[15] In **5c** the *cis* fusion of the cyclopentene with the chromone ring forms a torsion angle between the two rings of about 60−90° depending on the position of spirocyclic moiety on C-9, upward or downward of the chromone ring plane. The structure of **6a** is more planar, since it contains a double bond in the junction of the two rings, while compound **7i** is almost planar, showing thus the higher stability with less van der Waals interactions. In accordance with X-ray analysis data, by comparing the chemical shifts of C-9 for compounds **5j** (87.0 ppm) and **7j** (89.0 ppm) it can again be concluded that in **5j**

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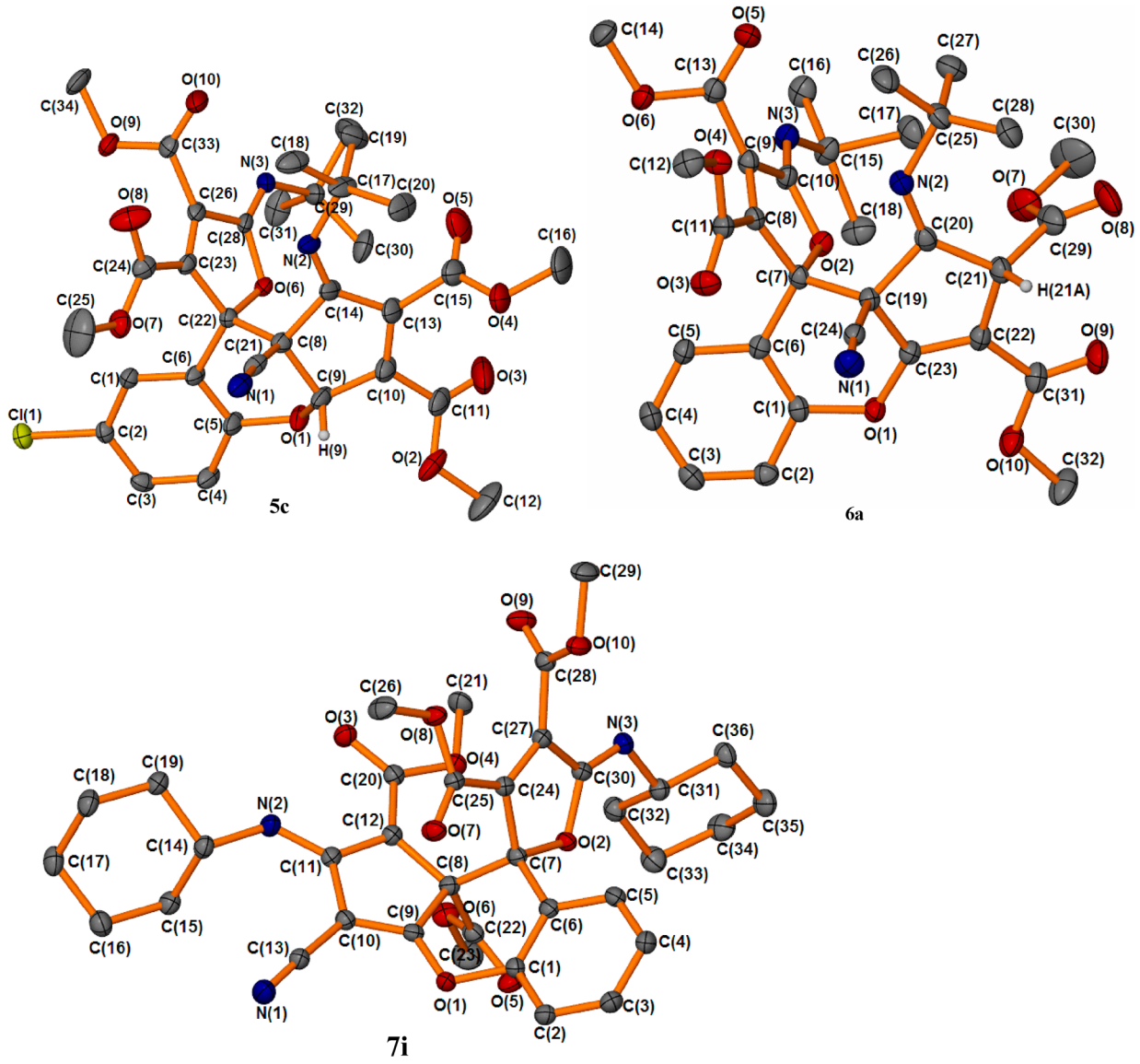

Figure 3. ORTEP diagram of the molecular structure of compounds **5c**, **6a**, and **7i** as determined by single-crystal XRD (atoms ellipsoid probability 30%). Methyl and aromatic H-atoms as well as N(2)-H in **7i** are omitted for clarity.

there are more stereochemical interactions moving the resonance of this carbon to higher magnetic field. On the other hand, the existence of six distinct carbon signals for each cyclohexane ring reveals that in solution there is no free rotation of the cyclohexane ring around the N–*c*-Hex bond to provide symmetry to the cyclohexane rings.

Theoretical Calculations. For the calculation of the relative stability of isomers **5**, **6**, and **7** theoretical calculations were carried out at the B3LYP level of density functional theory (DFT). In addition, in order to achieve a reliable assignment of the quaternary carbon signals of the cyclopentane and of the furan ring, the above-mentioned theoretically calculated structures were used for the calculation of the isotropic magnetic shieldings with the DFT/GIAO.[16−19] The geometries of the selected compounds **5c**, **6a**, and **7i** have been optimized, and the isotropic nuclear magnetic shielding constants (IMS) were calculated by using the 6-31G(d) basis set (Table 3). The theoretical chemical shifts are presented as ΔIMS differences relatively to TMS shielding calculated at the same theoretical level. The assignment of quaternary carbons mentioned above can be based on these theoretical chemical shifts, since most of them have very good coincidence with the experimental values.

CONCLUSIONS

The present work demonstrates the versatility of chromones in bringing about one-pot synthetic procedures, the outcome of the reaction depending in the studied reactions on the molar ratio of the reactants. Thus, from the reaction of isocyanides and acetylenedicarboxylates with 3-cyanochromones in a 1.2:1.2:1 molar ratio, spirobenzofuranocyclopentadienes **4** were isolated[10] as the only reaction products, whereas when the molar ratio was changed to 3:3:1, novel spirochromenofuran derivatives **5** or **6** were isolated in good yields (60−80%) involving also the highly unexpected reaction of the chromone-4-carbonyl for the formation of spiro heterocycles.

Moreover, in the case of the cyclohexyl-substituted derivatives **5i−l,n** a spontaneous quantitative transformation to the corresponding spirochromenofuran derivatives **7i−l,n** took place which constitutes a previously unreported transformation of cyclopentene ring derivatives. The *tert*-butyl-

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Table 3. Calculated Isotropic Magnetic Shieldings Relative to TMS[a] (ΔIMS) in Comparison with the Observed Chemical Shifts for Carbon and Proton Nuclei of Selected Compounds

	compound								
	5c			**6a**			**7i**		
atom	IMS	ΔIMS[b]	**expt**	IMS	ΔIMS	**expt**	IMS	ΔIMS	**expt**
1	40.6	149.1	**152.9**	42.7	147.0	**151.2**	104.0	85.7	**85.9**
2	50.5	141.2	**141.0**	135.0	54.7	**51.6**	36.3	153.4	**155.0**
3	48.5	141.2	**139.1**	80.4	109.3	**109.5**	104.4	85.3	**87.7**
3a	112.1	77.6	**79.5**	40.7	149.0	**152.7**	19.0	170.7	**173.8**
4a	46.7	143.0	**148.9**	44.6	145.1	**148.1**	42.1	147.6	**151.6**
8a	67.6	122.1	**126.1**	73.3	116.4	**120.9**	73.1	116.6	**120.2**
9	101.7	88.0	**87.6**	101.2	88.5	**86.8**	97.7	92.0	**89.1**
9a	130.3	59.4	**57.5**	133.5	56.2	**54.3**	127.7	62.0	**60.6**
3′	33.3	156.4	**148.0**	53.4	136.3	**138.8**	51.2	138.5	**142.1**
4′	63.6	126.1	**140.5**	51.0	138.7	**142.1**	54.6	135.1	**136.5**
5′	49.4	140.3	**149.8**	48.2	141.5	**149.1**	39.7	150.0	**158.6**
1″[c]	128.8	60.9	**59.0**	129.6	60.1	**58.2**	134.1	55.6	**52.3**
1‴	133.1	56.6	**55.3**	131.9	57.8	**55.4**	129.8	59.9	**57.2**
CN	84.1	105.6	**117.5**	85.6	104.1	**114.7**	84.3	105.4	**112.3**
2-H				27.74	4.44	**4.58**			
3a-H	26.57	5.61	**5.80**						
N-H							22.88	9.11	**8.88**

[a]Isotropic magnetic shieldings for TMS calculated by B3LYP/6-31G(d) method: for ^{1}H IMS_{TMS} = 32.18; for ^{13}C IMS_{TMS} = 189.7 ppm. [b]Relative ΔIMS = $IMS_{TMS} - IMS_X$ for magnetic nuclei X. [c]1″ refers to carbon substituted on 1-N and 1‴ refers to carbon substituted on 5′-N. For atom numbering see Scheme 3.

substituted derivatives **5c,f,g,h** appeared to be stable in the presence of acids. In addition, in all studied reactions our initial goal, namely, the isolation of products with an intact chromone moiety, was achieved. The described reactions present an example of the multidisciplinary way the chromones react and give an answer to the question why this moiety appears in so many important biological systems and procedures used in nature.

EXPERIMENTAL SECTION

General. Column chromatography was carried out using silica gel (70−230 mesh), and TLC was performed using precoated silica gel glass plates 0.25 mm containing fluorescent indicator UV_{254} using a 3:1 mixture of petroleum ether−ethyl acetate. Petroleum ether refers to the fraction boiling between 60 and 80 °C. NMR spectra were recorded at room temperature at 300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively, using $CDCl_3$ as solvent. Chemical shifts are expressed in δ values (ppm) relative to TMS as internal standard for ^{1}H and relative to TMS (0.00 ppm) or to $CDCl_3$ (77.05 ppm) for ^{13}C NMR spectra. Coupling constants ^nJ are reported in Hz. IR spectra were recorded on a FTIR spectrometer in the form of KBr disks, except in the case of **5n** and **5o**, and are reported in wave numbers (cm^{-1}). Mass spectra were obtained with the LC-ESI method at 1.65 eV ionization potential and are reported as *m*/*z* (relative intensity to the base peak).

Moreover, the complete assignment of ^{1}H and ^{13}C NMR signals was possible using 1D and 2D experiments [^{1}H, ^{13}C, COSY, NOESY, HETCOR (or HMQC) and COLOC (or HMBC)] using the standard commercial pulse programs. For DFT optimizations the AM1 geometry was used as input, and total energy calculations have been performed with the 6-31G(d) basis set by using the restricted B3LYP functional as implemented in the Gaussian 2004 package.[15]

General Experimental Procedure. *Reaction of 3-Cyanochromones with Acetylenecarboxylates and Isocyanides.* To a stirred solution of 3-cyanochromone **1** (1.0 mmol) and the appropriate acetylenedicarboxylate (3.0 mmol) in toluene (20 mL) was added *tert*-butylisocyanide (0.297 g, 3.0 mmol) or cyclohexylisocyanide (0.327 g, 3.0 mmol) via a syringe, and the reaction mixture was stirred at 40 °C until chromone **1** was consumed completely (followed by TLC, approximately 12 h). The solvent was removed in vacuo, and the residue was subjected to chromatography on silica gel using petroleum ether/AcOEt (7:1) as eluent, slowly increasing the polarity up to 4:1 to give products **5** or **6**.

*Tetramethyl (1Z,2R,5′Z,9S,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-2,9a-dihydro-1H,5′H-spiro[cyclopenta[b]-chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**6a**).* Yellowish crystals; 0.491 g (79%); mp 206−208 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9 H, 5′-C(CH_3)$_3$), 1.28 (s, 9 H, 1-C(CH_3)$_3$), 3.70 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 4.58 (s, 1 H, 2-H), 7.13−7.21 (m, 2 H, 5,7-H), 7.34 (d, *J* = 8.2 Hz, 1 H, 8-H), 7.44−7.51 (m, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 28.7 (1-C(CH_3)$_3$), 29.8 (5′-C(CH_3)$_3$), 51.5 (C-2), 52.1 (OCH_3), 52.2 (OCH_3), 52.76 (OCH_3), 52.81 (OCH_3), 54.3 (C-9a), 55.4 (C-1″), 58.2 (C-1‴), 86.8 (C-9), 109.5 (C-3), 114.7 (CN), 117.9 (C-5), 120.9 (C-8a), 124.5 (C-7), 127.3 (C-8), 132.1 (C-6), 138.6 (C-3′), 142.1 (C-4′), 148.1 (C-4a), 149.1 (C-5′), 151.2 (C-1), 152.7 (C-3a), 160.7 (C═O), 161.9 (C═O), 162.4 (C═O), 168.5 (2-C═O); IR (KBr) 2252, 1736, 1716 cm^{-1}; LC−MS (ESI, 1.65 eV) *m*/*z* 644 [100, $(M + Na)^+$]. Anal. Calcd for $C_{32}H_{35}N_3O_{10}$ (621.63): C, 61.83; H, 5.68; N, 6.76. Found: C, 62.00; H, 5.71; N 6.84.

*Tetramethyl (1E,2R,5′Z,9S,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-7-methyl-2,9a-dihydro-1H,5′H-spiro[cyclopenta-[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**6b**).* Yellowish crystals; 0.521 g (82%); mp 188−190 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9 H,

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5′-C(CH_3)$_3$), 1.27 (s, 9 H, 1-C(CH_3)$_3$), 2.34 (s, 3 H, 7-CH_3), 3.69 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 4.57 (s, 1 H, 2-H), 6.92 (d, J = 1.5 Hz, 1 H, 8-H), 7.22 (d, J = 8.5 Hz, 1 H, 5-H), 7.27 (dd, J = 8.5, 1.5 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 20.9 (7-CH_3), 28.7 (1-C(CH_3)$_3$), 29.9 (5′-C(CH_3)$_3$), 51.6 (C-2), 52.1 (OCH_3), 52.2 (OCH_3), 52.76 (OCH_3), 52.83 (OCH_3), 54.6 (C-9a), 55.5 (C-1‴), 58.2 (C-1″), 87.0 (C-9), 108.9 (C-3), 114.8 (CN), 117.6 (C-5), 120.6 (C-8a), 127.2 (C-8), 132.7 (C-6), 134.4 (C-7), 138.6 (C-3′), 142.1 (C-4′), 148.2 (C-4a), 149.25 (C-5′), 149.32 (C-1), 153.2 (C-3a), 160.8 (C═O), 162.0 (C═O), 162.6 (C═O), 168.6 (2-C═O); IR (KBr) 2250, 1743, 1708 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 658 [100, (M + Na)$^+$]. Anal. Calcd for $C_{33}H_{37}N_3O_{10}$ (635.66): C, 62.35; H, 5.87; N, 6.61. Found: C, 62.23; H, 5.78; N 6.74.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-1,5′-Bis(tert-butylimino)-7-chloro-9a-cyano-3a,9a-dihydro-1H,5′H-spiro[cyclopenta-[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5c**).* Yellowish crystals; 0.577 g (88%); mp 145−147 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9 H, 5′-C(CH_3)$_3$), 1.30 (s, 9 H, 1-C(CH_3)$_3$), 3.83 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 5.73 (s, 1 H, 3a-H), 7.04 (d, J = 8.6 Hz, 1 H, 5-H), 7.26 (d, J = 2.5 Hz, 1 H, 8-H), 7.34 (dd, J = 8.6, 2.5 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 29.8 (1-C(CH_3)$_3$), 30.3 (5′-C(CH_3)$_3$), 52.7 (OCH_3), 52.8 (OCH_3), 52.9 (OCH_3), 53.1 (OCH_3), 55.3 (C-1‴), 57.5 (C-9a), 59.0 (C-1″), 79.5 (C-3a), 87.6 (C-9), 117.6 (CN), 119.7 (C-5), 126.1 (C-8a), 127.6 (C-8), 128.4 (C-7), 131.7 (C-6), 139.1 (C-3), 140.5 (C-4′), 141.7 (C-2), 147.9 (C-3′), 148.9 (C-4a), 149.8 (C-5′), 152.9 (C-1), 161.3 (C═O), 161.5 (C═O), 162.2 (C═O), 164.1 (C═O); IR (KBr) 2250, 1745, 1736 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 678/680 [79, (M + Na)$^+$], 656/658 [100, (M + H)$^+$]. Anal. Calcd for $C_{32}H_{34}ClN_3O_{10}$ (656.08): C, 58.58; H, 5.22; N, 6.40. Found: C, 58.49; H, 5.21; N 6.34.

*Tetramethyl (1E,2R,5′Z,9S,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-6,7-dimethyl-2,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**6d**).* Yellowish crystals; 0.552 g (85%); mp 165−167 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9 H, 5′-C(CH_3)$_3$), 1.27 (s, 9 H, 1-C(CH_3)$_3$), 2.22 (s, 3 H, 6-CH_3), 2.29 (s, 3 H, 7-CH_3), 3.69 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 4.56 (s, 1 H, C(3a)), 6.86 (s, 1 H, 8-H), 7.13 (s, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 19.2 (6-CH_3), 19.9 (7-CH_3), 28.7 (1-C(CH_3)$_3$), 30.0 (5′-C(CH_3)$_3$), 51.6 (C-2), 52.1 (OCH_3), 52.2 (OCH_3), 52.7 (OCH_3), 52.8 (OCH_3), 54.7 (C-9a), 55.4 (5′-*C*(CH_3)$_3$), 58.1 (1-*C*(CH_3)$_3$), 87.0 (C-9), 108.9 (C-3), 115.0 (CN), 117.9 (C-8a), 118.7 (C-5), 127.6 (C-8), 133.1 (C-7), 138.9 (C-3′), 141.4 (C-6), 141.9 (C-4′), 148.4 (C-4a), 149.28 (C-5′), 149.33 (C-1), 153.4 (C-3a), 160.9 (C═O), 162.1 (C═O), 162.7 (C═O), 168.7 (C═O); IR (KBr) 2245, 1743, 1730 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 672 [100, (M + Na)$^+$], 650 [79, (M + H)$^+$]. Anal. Calcd for $C_{34}H_{39}N_3O_{10}$ (649.69): C, 62.86; H, 6.05; N, 6.47. Found: C, 62.75; H, 5.96; N 6.54.

*Tetramethyl (1E,2R,5′Z,9S,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-5,7-dichloro-2,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**6e**).* Yellowish crystals; 0.491 g (63%); mp 189−191 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 9 H, 5′-C(CH_3)$_3$), 1.28 (s, 9 H, 1-C(CH_3)$_3$), 3.71 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 4.58 (s, 1 H, 3a-H), 7.06 (d, J = 2.1 Hz, 1 H, 8-H), 7.56 (d, J = 2.1 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 28.6 (1-C(*C*H_3)$_3$), 29.9 (5′-C(*C*H_3)$_3$), 51.6 (C-2), 52.4 (OCH_3), 52.5 (OCH_3), 52.88 (OCH_3), 52.93 (OCH_3), 53.7 (C-9a), 55.8 (1‴-C(CH_3)$_3$), 58.4 (1″-C(CH_3)$_3$), 86.1 (C-9), 111.5 (C-3), 114.1 (CN), 123.5 (C-5), 124.0 (C-8a), 125.7 (C-8), 129.6 (C-7), 132.6 (C-6), 137.8 (C-3′), 142.3 (C-4′), 145.9 (C-4a), 147.1 (C-5′), 148.5 (C-1), 150.9 (C-3a), 160.5 (C═O), 161.5 (C═O), 162.1 (C═O), 168.2 (C═O); IR (KBr) 2255, 1743, 1698 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 712/714/716 [79, (M + Na)$^+$], 690/692/694 [100, (M + H)$^+$]. Anal. Calcd for $C_{32}H_{33}Cl_2N_3O_{10}$ (690.52): C, 55.66; H, 4.82; N, 6.09. Found: C, 55.72; H, 4.78; N 6.04.

*Tetraethyl (1Z,3aR,5′Z,9R,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-3a,9a-dihydro-1H,5′H-spiro[cyclopenta[b]-chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5f**).* Yellow crystals; 0.427 g (63%); mp 105−107 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9 H, 5′-C(CH_3)$_3$), 1.28−1.42 (m, 12 H, 4 × CH_2CH_3), 1.32 (s, 9 H, 1-C(CH_3)$_3$), 4.25−4.48 (m, 8 H, 4 × CH_2CH_3), 5.77 (s, 1 H, 3a-H), 7.03−7.12 (m, 2 H, 5-H, 7-H), 7.30 (dd, J = 8.0, 1.5 Hz, 1 H, 8-H), 7.37 (dd, J = 8.0 Hz, 1.5, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.5 (Me), 13.6 (Me), 13.9 (Me), 13.9 (Me), 29.7 (1- C(CH_3)$_3$), 30.3 (5′-C(CH_3)$_3$), 54.9 (5′-*C*(CH_3)$_3$), 57.5 (C-9a), 58.5 (1-*C*(CH_3)$_3$), 61.8 (OCH_2), 62.0 (OCH_2), 62.2 (OCH_2), 62.3 (OCH_2), 79.3 (C-3a), 88.1 (C-9), 117.8 (CN), 118.0 (C-5), 123.0 (C-7), 124.6 (C-8a), 127.6 (C-8), 131.5 (C-6), 138.6 (C-3), 140.6 (C-4′), 140.7 (C-2), 148.5 (C-3′), 149.5 (C-4a), 150.2 (C-5′), 154.2 (C-1), 160.9 (C═O), 161.4 (C═O), 161.8 (C═O), 163.7 (C═O); IR (KBr) 2230, 1735, 1688 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 677 (100, M$^+$). Anal. Calcd for $C_{36}H_{43}N_3O_{10}$ (677.74): C, 63.80; H, 6.39; N, 6.20. Found: C, 63.70; H, 6.31; N 6.14.

*Tetraethyl (1Z,3aR,5′Z,9R,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-7-methyl-3a,9a-dihydro-1H,5′H-spiro[cyclopenta-[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5g**).* Yellowish crystals; 0.477 g (69%); mp 133−135 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9 H, 5′-C(CH_3)$_3$), 1.30 (t, J = 7.2 Hz, 6 H, 2 × CH_2CH_3), 1.32 (s, 9 H, 1-C(CH_3)$_3$), 1.38 (t, J = 7.2 Hz, 6 H, 2 × CH_2CH_3), 2.30 (s, 3 H, 7-CH_3), 4.30−4.50 (m, 8 H, 4 × CH_2CH_3), 5.71 (s, 1 H, 3a-H), 6.94 (d, J = 8.2 Hz, 1 H, 5-H), 7.05 (d, J = 1.9 Hz, 1 H, 8-H), 7.14 (dd, J = 8.2, 1.9 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (Me), 13.8 (Me), 14.1 (Me), 14.1 (Me),) 21.0 (7-CH_3), 29.9 (1-C(CH_3)$_3$), 30.5 (5′-C(CH_3)$_3$), 55.0 (C-1‴), 57.9 (C-9a), 58.7 (C-1″), 62.0 (OCH_2), 62.1 (OCH_2), 62.3 (OCH_2), 62.4 (OCH_2), 79.6 (C-3a), 88.4 (C-9), 117.8 (C-5), 118.1 (CN), 124.5 (C-8a), 128.1 (C-8), 132.0 (C-7), 132.7 (C-6), 139.0 (C-3), 140.8 (C-4′), 140.9 (C-2), 148.3 (C-3′), 149.8 (C-4a), 150.5 (C-5′), 152.2 (C-1), 161.1 (C═O), 161.7 (C═O), 162.0 (C═O), 164.0 (C═O); IR (KBr) 2223, 1746, 1732 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 692 [100, (M + H)$^+$]. Anal. Calcd for $C_{37}H_{45}N_3O_{10}$ (691.77): C, 64.24; H, 6.56; N, 6.07. Found: C, 64.20; H, 6.61; N 6.14.

*Tetraethyl (1Z,3aR,5′Z,9R,9aS)-1,5′-Bis(tert-butylimino)-7-chloro-9a-cyano-3a,9a-dihydro-1H,5′H-spiro[cyclopenta[b]-chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5h**).* Yellowish crystals; 0.562 g (79%); mp 137−139 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09(s, 9 H, 5′-C(CH_3)$_3$), 1.32 (s, 9 H, 1-C(CH_3)$_3$), 1.33−1.42 (m, 12 H, 4 × CH_2CH_3), 4.23−4.47 (m, 8 H, 4 × CH_2CH_3), 5.71 (s, 1 H, 3a-H), 6.94 (d, J = 8.2 Hz, 1 H, 5-H), 7.05 (d, J = 1.9 Hz, 1 H, 8-H), 7.14 (dd, J = 8.2, 1.9 Hz, 2 H, 6-H); ^{13}C NMR (75 MHz,

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$CDCl_3$) δ (ppm) 13.7 (Me), 13.8 (Me), 14.06 (Me), 14.10 (Me), 29.9 (1-C(CH_3)$_3$), 30.4 (5′-C(CH_3)$_3$), 55.0 (C-1″), 57.9 (C-9a), 58.9 (C-1‴), 62.1 (OCH_2), 62.3 (OCH_2), 62.4 (OCH_2), 62.5 (OCH_2), 79.7 (C-3a), 87.6 (C-9), 117.7 (CN), 119.6 (C-5), 126.3 (C-8a), 127.8 (C-8),128.3 (C-7), 131.5 (C-6), 138.9 (C-3), 140.0 (C-4′), 141.1 (C-2), 148.3 (C-3′), 149.1 (C-4a), 150.0 (C-5′), 153.0 (C-1), 160.8 (C═O), 161.3 (C═O), 161.8 (C═O), 163.8 (C═O); IR (KBr)2225, 1745, 1731 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 711/713 [100, $(M + H)^+$]. Anal. Calcd for $C_{36}H_{42}ClN_3O_{10}$ (712.19): C, 60.71; H, 5.94; N, 5.90. Found: C, 60.80; H, 5.91; N 5.83.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-9a-Cyano-1,5′-bis-(cyclohexylimino)-3a,9a-dihydro-1H,5′H-spiro[cyclopenta-[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5i**).* Yellow crystals; 0.562 g (77%); mp 180−182 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.43 (m, 10 H, H_{ax}), 1.45−1.65 (m, 6 H, 3″,3‴, 4″,4‴5″,5‴-H_{eq}), 1.70−1.85 (m, 4 H, 2″,2‴,6″,6‴H_{eq}), 3.22−3.36 (m, 1 H, 1‴-H), 3.53−3.67 (m, 1 H, 1″-H), 3.84 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 5.84 (s, 1 H, 3a-H), 7.02 (dd, J = 8.1, 1.1 Hz, 1 H, 5-H), 7.12 (ddd, J = 7.6, 7.6, 1.1 Hz, 1 H, 7-H), 7.27 (dd, J = 7.6, 1.6 Hz, 1 H, 8-H), 7.38 (ddd, J = 8.1, 7.6, 1.6 Hz, 1 H, 7-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.0 and 24.3 (C-3‴, C-5‴), 24.8 (C-3″, C-5″), 25.3 (C-4‴), 25.7 (C-4″), 33.0 and 33.4 (C-2″, C-6″), 33.6 (C-2‴, C-6‴), 52.9 (OCH_3), 53.0 (OCH_3), 53.08 (OCH_3), 53.14 (OCH_3), 55.5 (C-9a), 56.7 (C-1″), 62.5 (C-1‴), 79.9 (C-3a), 86.9 (C-9), 116.7 (CN), 118.7 (C-5), 123.5 (C-8a), 123.9 (C-7), 126.7 (C-8), 131.7 (C-6), 135.6 (C-4′), 138.3 (C-3), 143.9 (C-2), 145.6 (C-3′), 151.7 (C-4a), 152.6 (C-5′), 153.4 (C-1), 160.8 (C═O), 161.8 (2 × C═O), 164.2 (C═O); IR (KBr) 2209, 1748 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 674 [100, $(M + H)^+$]. Anal. Calcd for $C_{36}H_{39}N_3O_{10}$ (673.71): C, 64.18; H, 5.83; N, 6.24. Found: C, 64.05; H, 5.91; N 6.14.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-9a-Cyano-1,5′-bis-(cyclohexylimino)-7-methyl-3a,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5j**).* Yellowish crystals; 0.543 g (79%); mp 131−133 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.40 (m, 10 H, H_{ax}), 1.50−1.70 (m, 6 H, 2″,2‴, 4″,4‴,6″,6‴-H_{eq}), 1.70−1.90 (m, 4 H, 3″,3‴,5″,5″-H_{eq}), 2.31 (s, 3 H), 3.24−3.34 (m, 1 H, 1‴-H_{eq}), 3.55−3.65 (m, 1 H, 1″-H_{eq}), 3.84 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 5.80 (s, 1 H, 3a-H), 6.90 (d, J = 8.2 Hz, 1 H, 5-H), 7.02 (d, J = 1.5 Hz, 1 H, 8-H), 7.16 (dd, J = 8.2, 1.5 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.1 (CH_3), 24.0 and 24.3 (C-3″, C-5″), 24.8 and 24.9 (C-3‴, C-5‴), 25.3 (C-4″), 25.7 (C-4‴), 33.1 and 33.3 (C-2″, C-6″), 33.6 (C-2‴, C-6‴), 52.9 (OCH_3), 53.0 (OCH_3), 53.07 (OCH_3), 53.11 (OCH_3), 55.6 (C-9a), 56.7 (C-1″), 62.5 (C-1‴), 79.9 (C-3a), 87.0 (C-9), 116.8 (C≡N), 118.4 (C-5), 123.1 (C-8a), 126.9 (C-8), 132.3 (C-6), 133.6 (C-7), 135.2 (C-4′), 138.3 (C-3), 144.0 (C-2), 145.9 (C-3′), 150.3 (C-4a), 151.8 (C-5′), 153.5 (C-1), 160.9 (C═O), 161.8 (C═O), 161.9 (C═O), 164.3 (C═O); IR (KBr) 2221, 1743 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 688 [100, $(M + H)^+$]. Anal. Calcd for $C_{37}H_{41}N_3O_{10}$ (687.74): C, 64.62; H, 6.01; N, 6.11. Found: C, 64.48; H, 5.91; N 6.14.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-7-Chloro-9a-cyano-1,5′-bis(cyclohexylimino)-3a,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5k**).* Yield 65%; yellow solid; mp 121−123 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.45 (m, 10 H, H_{ax}), 1.50−1.66 (m, 6 H, 2″,2‴, 4″,4‴,6″,6‴-H_{eq}), 1.68−1.88 (m, 4 H, 3″,3‴,5″,5″-H_{eq}), 3.25−3.38 (m, 1 H, 1‴-H_{eq}), 3.50−3.60 (m, 1 H, 1″-H_{eq}), 3.85 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 5.82 (s, 1 H, 3a-H), 6.99 (d, J = 8.6 Hz, 1 H, 5-H), 7.24 (d, J = 2.4 Hz, 1 H, 8-H), 7.35 (dd, J = 8.6, 2.4 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 23.9 and 24.2 (C-3″, C-5″), 24.7 (C-3‴, C-5‴), 25.3 (C-4″), 25.6 (C-4‴), 33.0 and 33.3 (C-2″, C-6″), 33.5 and 33.6 (C-2‴, C-6‴), 53.0 (2 × OCH_3), 53.1 (OCH_3), 53.2 (OCH_3), 55.2 (C-1‴), 56.8 (C-9a), 62.6 (C-1″), 80.1 (C-3a), 86.4 (C-9), 116.4 (C≡N), 120.1 (C-5), 125.0 (C-8a), 126.9 (C-8), 128.9 (C-7), 131.8 (C-6), 136.4 (C-3′), 138.3 (C-3), 143.8 (C-2), 144.3 (C-4′), 151.2 (C-5′), 151.3 (C-4a), 153.1 (C-1), 160.7 (C═O), 161.5 (C═O), 161.7 (C═O), 164.1 (C═O); IR (KBr) 2251, 1740 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 730/732 [100, $(M + Na)^+$], 708/710 [45, $(M + H)^+$]. Anal. Calcd for $C_{36}H_{38}ClN_3O_{10}$ (708.15): C, 61.06; H, 5.41; N, 5.93. Found: C, 61.18; H, 5.31; N 6.04.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-9a-Cyano-1,5′-bis-(cyclohexylimino)-6,7-dimethyl-3a,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5l**).* Yield 71%; yellow crystals; mp 178−180 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.50 (m, 10 H, H_{ax}), 1.52−1.68 (m, 6 H, 2″,2‴, 4″,4‴,6″,6‴-H_{eq}), 1.68−2.00 (m, 4 H, 3″,3‴,5″,5″-H_{eq}), 2.20 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 3.24−3.34 (m, 1 H, 1‴-H_{eq}), 3.55−3.65 (m, 1 H, 1″-H_{eq}), 3.84 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 5.78 (s, 1 H, 3a-H), 6.81 (s, 1 H, 5-H), 6.95 (s, 1 H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 19.2 (CH_3), 19.7 (CH_3), 23.9 and 24.1 (C-3″, C-5″), 24.7 (C-3‴, C-5‴), 25.2 (C-4″), 25.6 (C-4‴), 32.9 and 33.2 (C-2″, C-6″), 33.4 and 33.5 (C-2‴, C-6‴), 52.6 (OCH_3), 52.7 (OCH_3), 52.86 (OCH_3), 52.90 (OCH_3), 55.5 (C-1‴), 56.5 (C-9a), 62.2 (C-1″), 79.8 (C-3a), 86.8 (C-9), 116.4 (C≡N), 119.2 (C-5), 120.2 (C-8a), 127.2 (C-8), 131.9 (C-7), 135.8 (C-3′), 138.0 (C-3), 140.6 (C-6), 144.2 (C-2), 145.2 (C-4′), 150.5 (C-4a), 151.9 (C-5′), 153.5 (C-1), 160.9 (C═O), 161.6 (C═O), 161.8 (C═O), 164.2 (C═O); IR (KBr) 2217, 1739 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 702 [100, $(M + H)^+$]. Anal. Calcd for $C_{38}H_{43}N_3O_{10}$ (701.76): C, 65.04; H, 6.18; N, 5.99. Found: C, 65.28; H, 6.31; N 5.80.

*Tetramethyl (1Z,3aR,5′Z,9R,9aS)-5,7-Dichloro-9a-cyano-1,5′-bis(cyclohexylimino)-3a,9a-dihydro-1H,5′H-spiro-[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5m**).* Yield 63%; yellow solid; mp 160−162 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.50 (m, 10 H, H_{ax}), 1.52−1.70 (m, 6 H, 2″,2‴, 4″,4‴,6″,6‴-H_{eq}), 1.70−1.88 (m, 4 H, 3″,3‴,5″,5″-H_{eq}), 3.24−3.36 (m, 1 H, 1‴-H_{eq}), 3.58−3.69 (m, 1 H, 1″-H_{eq}), 3.85 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 5.89 (s, 1 H, 3a-H), 7.15 (d, J = 2.3 Hz, 1 H, 8-H), 7.44 (d, J = 2.3 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.0 and 24.2 (C-3″, C-5″), 24.66 and 24.74 (C-3‴, C-5‴), 25.3 (C-4″), 25.6 (C-4‴), 33.16 and 33.24 (C-2″, C-6″), 33.5 and 33.6 (C-2‴, C-6‴), 53.1 (OCH_3), 53.21 (2 × OCH_3), 53.24 (OCH_3), 55.1 (C-1‴), 56.8 (C-9a), 62.7 (C-1″), 80.5 (C-3a), 86.1 (C-9), 116.0 (C≡N), 125.0 (C-8a), 125.1 (C-8), 126.5 (C-5), 129.3 (C-7), 131.8 (C-6), 134.9 (C-3′), 138.9 (C-3), 143.0 (C-2), 145.5 (C-4′), 147.1 (C-4a), 150.8 (C-5′), 152.9 (C-1), 160.4 (C═O), 161.4 (C═O), 161.7 (C═O), 163.9 (C═O); IR (KBr) 2251, 1765, 1741 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 764/766/768 [70, $(M + Na)^+$], 742/744/746 [100, $(M + H)^+$].

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Anal. Calcd for $C_{36}H_{37}Cl_2N_3O_{10}$ (742.60): C, 58.23; H, 5.02; N, 5.66. Found: C, 58.18; H, 5.11; N 5.74.

*Tetraethyl (1Z,3aR,5′Z,9R,9aS)-9a-Cyano-1,5′-bis(cyclohexylimino)-3a,9a-dihydro-1H,5′H-spiro[cyclopenta[b]chromene-9,2′-furan]-2,3,3′,4′-tetracarboxylate (**5n**).* Yellowish oil; 0.650 g (89%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.92 (m, 32 H, 4 × CH_3, H_{ax}, H_{eq}), 3.32−3.45 (m, 1 H, 1‴-H), 3.55−3.67 (m, 1 H, 1″-H), 4.10−4.44 (m, 8 H, 4 × CH_2), 5.84 (s, 1 H, 3a-H), 7.00 (dd, J = 8.0, 1.0 Hz, 1 H, 5-H), 7.10 (ddd, J = 7.9, 7.5, 1.0 Hz, 1 H, 7-H), 7.30 (dd, J = 7.9, 1.6 Hz, 1 H, 8-H), 7.33 (ddd, J = 8.0, 7.5, 1.6 Hz, 1 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.6 (2 × CH_3), 13.8 (CH_3), 13.9 (CH_3), 23.9 and 24.1 (C-3‴, C-5‴), 24.6 (C-3″, C-5″), 25.3 (C-4‴), 25.7 (C-4″), 33.0 and 33.3 (C-2″, C-6″), 33.49 and 33.53 (C-2‴, C-6‴), 55.4 (C-1‴), 55.8 (C-9a), 61.8 (OCH_2), 62.0 (OCH_2), 62.1 (2 × OCH_2), 62.5 (C-1″), 80.1 (C-3a), 86.9 (C-9), 116.7 (C≡N), 118.5 (C-5), 123.6 (C-7), 123.7 (C-8a), 126.8 (C-8), 131.4 (C-6), 135.6 (C-3′), 138.0 (C-3), 144.1 (C-2), 145.0 (C-4′), 151.7 (C-4a), 152.7 (C-5′), 153.7 (C-1), 160.3 (C═O), 161.3 (2 × C═O), 163.6 (C═O); IR (KBr) 2212, 1745 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 730 [100, (M + H)$^+$]. Anal. Calcd for $C_{40}H_{47}N_3O_{10}$ (729.82): C, 65.83; H, 6.49; N, 5.76. Found: C, 65.95; H, 6.58; N 5.65.

*Dimethyl (1E,3aR,5′Z,9R,9aS)-1,5′-Bis(tert-butylimino)-9a-cyano-3a,9a-dihydro-1H,5′H-spiro[cyclopenta[b]chromene-9,2′-furan]-3,3′-dicarboxylate (**5o**).* Yellowish oil; 0.650 g (89%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 9 H, 3 × CH_3), 1.36 (s, 9 H, 3 × CH_3), 3.77 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 5.98 (s, 1 H, 3a-H), 6.16 (br s, 1 H), 6.82 (dd, J = 8.0, 1.1 Hz, 1 H, 5-H), 7.04 (s, 1 H), 7.20 (ddd, J = 8.0, 7.5, 1.1 Hz, 1 H, 7-H), 7.45 (ddd, J = 8.0, 7.5, 1.8 Hz, 1 H, 6-H), 7.96 (dd, J = 8.0, 1.8 Hz, 1 H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 28.6 (1-C(CH_3)$_3$), 30.3 (5′-C(CH_3)$_3$), 50.9 (C-3a), 52.8 (OCH_3), 52.9 (OCH_3), 54.8 (C-9a), 55.0 (1-C(CH_3)$_3$), 58.6 (5′-C(CH_3)$_3$), 81.9 (C-3a), 108.9 (C-4′), 115.0 (CN), 117.8 (C-8a), 118.7 (C-5), 127.6 (C-8), 133.1 (C-7), 138.9 (C-3), 141.4 (C-6), 141.7 (C-2), 148.4 (C-3′), 149.3 (C-4a), 149.2 (C-1), 153.3 (C-5′), 160.9 (C═O), 162.1 (C═O), 162.7 (C═O), 168.7 (C═O); IR (KBr) 2213, 1752 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 506 [100, (M + H)$^+$]. Anal. Calcd for $C_{28}H_{31}N_3O_6$ (505.56): C, 66.52; H, 6.18; N, 8.31. Found: C, 66.75; H, 6.41; N 8.55.

Acid-Catalyzed Conversion of 5 to 7. To a stirred solution of compound **5** (1.0 mmol) in toluene (20 mL) was added a small amount (0.02 mmol) of p-TSA, and the mixture was stirred at rt to 40 °C until **5** was consumed completely (followed by TLC, approximately 12 h). The solvent was removed in vacuo, and the residue was subjected to chromatography on silica gel using petroleum ether/AcOEt (7:1) as eluent, slowly increasing the polarity up to 4:1 to give products **7**. Only cyclohexyl derivatives were transformed under these experimental conditions.

*Tetramethyl 9a-Cyano-1′-cyclohexyl-1-(cyclohexylimino)-5′-oxo-1′, 5′-dihydro-9aH-spiro[cyclopenta[b]chromene-9,2′-pyrrole]-2,3,3′,4′-tetracarboxylate (**7i**).* Yield 92%; yellow crystals; 0.620 g (92%); mp 195−197 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17−1.54 (m, 10 H, H_{ax}), 1.56−1.68 (m, 2 H, 4″,4‴-H_{eq}), 1.68−2.07 (m, 8 H, 2″,2‴,3″,3‴,5″,5‴,6″,6‴-H_{eq}), 3.51−3.56 (m, 1 H, 1‴-H masked under methoxy-group signals), 3.56 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.95−4.07 (m, 1 H, 1″-H), 7.09 (dd, J = 7.7, 1.6 Hz, 1 H, 8-H), 7.21 (ddd, J = 7.7, 7.4, 1.2 Hz, 1 H, 7-H), 7.26 (dd, J = 7.7, 1.2 Hz, 1 H, 5-H), 7.42 (ddd, J = 7.7, 7.4, 1.6 Hz, 1 H, 6-H), 8.88 (d, J = 8.7 Hz, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.0 and 24.2 (C-3‴, C-5‴), 24.95 and 25.00 (C-3″, C-5″), 25.1 (C-4‴), 25.7 (C-4″), 32.9 and 33.2 (C-2″, C-6″), 34.0 and 35.1 (C-2‴, C-6‴), 51.0 (OCH_3), 52.3 (C-1″), 52.5 (OCH_3), 53.0 (OCH_3), 53.5 (OCH_3), 57.2 (C-1‴), 60.6 (C-9a), 85.9 (C-1), 87.7 (C-3), 89.1 (C-9), 112.3 (CN), 116.4 (C-5), 120.2 (C-8a), 125.3 (C-7), 126.1 (C-8), 131.0 (C-6), 136.5 (C-3′), 142.1 (C-4′), 151.6 (C-4a), 155.0 (C-2), 158.6 (C-5′), 160.2 (C═O), 161.8 (C═O), 165.0 (C═O), 166.9 (C═O), 173.8 (C-3a); IR (KBr) 2223, 1753, 1723 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 696 [100, (M + Na)$^+$], 674 [12, (M + H)$^+$]. Anal. Calcd for $C_{36}H_{39}N_3O_{10}$ (673.71): C, 64.18; H, 5.83; N, 6.24. Found: C, 64.25; H, 5.71; N 6.18.

*Tetramethyl 9a-Cyano-1′-cyclohexyl-1-(cyclohexylimino)-7-methyl-5′-oxo-1′,5′-dihydro-9aH-spiro[cyclopenta[b]chromene-9,2′-pyrrole]-2,3,3′,4′-tetracarboxylate (**7j**).* Yellowish crystals; 0.626 g (91%); mp 190−192 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17−1.55 (m, 10 H, H_{ax}), 1.56−1.68 (m, 2 H, 4″,4‴-H_{eq}), 1.68−2.06 (m, 8 H, 2″,2‴,3″,3‴,5″,5‴,6″,6‴-H_{eq}), 2.32 (s, 3 H, CH_3), 3.51−3.56 (m, 1 H, 1‴-H masked under methoxy-group signals), 3.56 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.95−4.08 (m, 1 H, 1″-H), 6.83 (d, J = 1.8 Hz, 1 H, 8-H), 7.12 (d, J = 8.3 Hz, 1 H, 5-H), 7.19 (dd, J = 8.3, 1.8 Hz, 1 H, 6-H), 8.91 (br d, J = 7.7 Hz, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.0 (CH_3), 24.0 and 24.3 (C-3‴, C-5‴), 25.0 (C-3″, C-5″), 25.1 (C-4‴), 25.7 (C-4″), 33.0 and 33.2 (C-2″, C-6″), 34.0 and 35.1 (C-2‴, C-6‴), 51.0 (OCH_3), 52.3 (C-1‴), 52.6 (OCH_3), 53.1 (OCH_3), 53.6 (OCH_3), 57.1 (C-1″), 60.8 (C-9a), 85.3 (C-1), 87.1 (C-3), 89.0 (C-9), 112.2 (CN), 116.2 (C-5), 119.4 (8a), 126.2 (C-8), 131.8 (C-6), 135.0 (C-7), 136.3 (C-3′), 142.2 (C-4′), 149.6 (C-4a), 155.2 (C-2), 158.6 (C-5′), 160.2 (C═O), 161.9 (C═O), 165.1 (C═O), 166.9 (C═O), 174.1 (C-3a); IR (KBr) 2222, 1756, 1727 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 688 [100, (M + H)$^+$]. Anal. Calcd for $C_{37}H_{41}N_3O_{10}$ (687.74): C, 64.62; H, 6.01; N, 6.11. Found: C, 64.73; H, 5.94; N 5.99.

*Tetramethyl 7-Chloro-9a-cyano-1′-cyclohexyl-1-(cyclohexylimino)-5′-oxo-1′,5′-dihydro-9aH-spiro[cyclopenta[b]chromene-9,2′-pyrrole]-2,3,3′,4′-tetracarboxylate (**7k**).* Yellowish crystals; 0.510 g (72%); mp 179−181 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ δ 1.15−1.55 (m, 10 H, H_{ax}), 1.56−1.68 (m, 2 H, 4″-H_{eq},4‴-H_{eq}), 1.69−1.90 (m, 4 H, 3″,3‴,5″,5‴-H_{eq}), 1.92−2.05 (m, 4 H, 2″,2‴,6″,6‴-H_{eq}), 3.51−3.65 (m, 1 H, 1‴-H masked under methoxy-group signals), 3.58 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.95−4.10 (m, 1 H, 1″-H), 7.02 (d, J = 2.4 Hz, 1 H, 8-H), 7.19 (d, J = 8.7 Hz, 1 H, 5-H), 7.37 (dd, J = 8.7, 2.4 Hz, 1 H, 6-H), 8.90 (br d, J = 8.0 Hz, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 24.0 and 24.2 (C-3‴, C-5‴), 24.9 (C-3″, C-5″), 25.2 (C-4‴), 25.8 (C-4″), 33.1 and 33.3 (C-2″, C-6″), 34.1 and 35.1 (C-2‴, C-6‴), 51.1 (OCH_3), 52.4 (C-1″), 52.7 (OCH_3), 53.1 (OCH_3), 53.7 (OCH_3), 57.3 (C-1‴), 60.4 (C-9a), 85.5 (C-1), 88.3 (C-3), 88.6 (C-9), 112.1 (CN), 117.8 (C-5), 122.1 (C-8a), 126.2 (C-8), 130.4 (C-7), 131.1 (C-6), 136.6 (C-3′), 141.8 (C-4′), 150.2 (C-4a), 154.6 (C-2), 158.4 (C-5′), 160.2 (C═O), 161.5 (C═O), 164.9 (C═O), 166.8 (C═O), 173.1 (C-3a); IR (KBr) 2223, 1759, 1724 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 708/710 [100, (M + H)$^+$]. Anal. Calcd for $C_{36}H_{38}ClN_3O_{10}$ (708.15): C, 61.06; H, 5.41; N, 5.93. Found: C, 61.13; H, 5.36; N 6.00.

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*Tetramethyl 9a-Cyano-1′-cyclohexyl-1-(cyclohexylimino)-6,7-dimethyl-5′-oxo-1′,5′-dihydro-9aH-spiro[cyclopenta[b]-chromene-9,2′-pyrrole]-2,3,3′,4′-tetracarboxylate (**7l**).* Yellow crystals; 0.498 g (71%); mp 201−203 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17−1.55 (m, 10 H, H_{ax}), 1.56−1.70 (m, 2 H, 4″-H_{eq},4‴-H_{eq}), 1.71−2.05 (m, 8 H, 2″,2‴,3″,3‴,5″,5‴,6″,6‴-H_{eq}), 2.21 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 3.50−3.60 (m, 1 H, 1‴-H masked under methoxy-group signals), 3.56 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.96−4.08 (m, 1 H, 1″-H), 6.77 (s, 1 H, 8-H), 7.03 (s, 1 H, 5-H), 8.89 (d, J = 8.8 Hz, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 19.4 (CH_3), 19.7 (CH_3), 24.0 and 24.2 (C-3‴,C-5‴), 24.96 and 24.98 (C-3″,C-5″), 25.2 (C-4‴), 25.8 (C-4″), 33.1 and 33.2 (C-2″,C-6″), 34.2 and 35.1 (C-2‴,C-6‴), 51.0 (OCH_3), 52.3 (C-1″), 52.4 (OCH_3), 53.0 (OCH_3), 53.5 (OCH_3), 57.1 (C-1‴), 60.7 (C-9a), 85.7 (C-1), 87.2 (C-3), 89.2 (C-9), 112.4 (CN), 116.8 (C-8a), 117.2 (C-5), 126.6 (C-8), 133.8 (C-7), 136.3 (C-3′), 140.3 (C-6), 142.3 (C-4′), 149.7 (C-4a), 155.2 (C-2), 158.7 (C-5′) 160.3 (C═O), 161.9 (C═O), 165.2 (C═O), 167.0 (C═O), 174.4 (C-3a); IR (KBr) 2251, 1740 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 724 [100, (M + Na)$^+$]. Anal. Calcd for $C_{38}H_{43}N_3O_{10}$ (701.76): C, 65.04; H, 6.18; N, 5.99. Found: C, 65.12; H, 6.26; N 6.14.

*Tetraethyl 9a-Cyano-1′-cyclohexyl-1-(cyclohexylimino)-5′-oxo-1′,5′dihydro-9aH-spiro[cyclopenta[b]chromene-9,2′-pyrrole]-2,3,3′,4′-tetracarboxylate (**7n**).* Yellowish crystals; 0.657 g (90%); mp 195−197 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J = 7.1 Hz, 3 H, CH_3), 1.11 (t, J = 7.1 Hz, 3 H, CH_3), 1.22 (t, J = 7.1 Hz, 3 H, CH_3), 1.32 (t, J = 7.1 Hz, 3 H, CH_3), 1.10−1.50 (m, 10 H, H_{ax}), 1.52−1.68 (m, 2 H, 4″,4‴-H_{eq}), 1.70−2.07 (m, 8H, 2″,2‴, 3″,3‴,5″,5‴,6″,6‴-H_{eq}), 3.48−3.60 (m, 1 H, 1‴-H), 3.85−4.15 (m, 6 H, 3 × OCH_2), 4.25−4.52 (m, 3 H, 1″-H, OCH_2), 7.09 (dd, J = 7.7, 1.5 Hz, 1 H, 8-H), 7.17 (ddd, J = 7.7, 7.4, 1.2 Hz, 1 H, 7-H), 7.21 (dd, J = 8.2, 1.2 Hz, 1 H, 5-H), 7.38 (ddd, J = 8.2, 7.4, 1.5 Hz, 1 H, 6-H), 8.87 (br d, J = 7.5 Hz, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.71 (CH_3), 13.74 (CH_3), 14.0 (CH_3), 15.0 (CH_3), 24.1 and 24.3 (C-3‴, C-5‴), 24.8 and 25.0 (C-3″, C-5″), 25.2 (C-4‴), 25.8 (C-4″), 32.9 and 33.6 (C-2″, C-6″), 34.4 and 35.0 (C-2‴, C-6‴), 52.3 (C-1″), 56.9 (C-1‴), 59.5 (OCH_2), 60.7 (C-9a), 61.9 (OCH_2), 62.1 (OCH_2), 62.8 (OCH_2), 86.5 (C-1), 87.8 (C-3), 89.2 (C-9), 112.5 (CN), 116.2 (C-5), 121.0 (C-8a), 125.1 (C-7), 126.0 (C-8), 130.7 (C-6), 136.1 (C-3′), 142.5 (C-4′), 151.8 (C-4a), 155.3 (C-2), 158.5 (C-5′), 160.0 (2 × C═O), 161.5 (C═O), 164.2 (C═O), 173.8 (C-3a); IR (KBr) 2230, 1753, 1723 cm^{-1}; LC−MS (ESI, 1.65 eV) m/z 752 [100, (M + Na)$^+$], 730 [12, (M + H)$^+$]. Anal. Calcd for $C_{40}H_{47}N_3O_{10}$ (729.82): C, 65.83; H, 6.49; N, 5.76. Found: C, 65.79; H, 6.58; N 5.68.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra for all novel compounds. Optimized geometries (in Cartesian coordinates) for compounds **5a**, **5c**, **5i**, **6a**, **6i**, **7a**, and **7i**. Crystallographic data, bond lengths, bond angles, and structure refinement for compounds **5c**, **6a**, and **7i**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ioulia@chem.auth.gr; tsolerid@chem.auth.gr.

Notes

The authors declare no competing financial interest.

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