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A Vanadium-Catalyzed Synthesis of Fully Substituted Pyrroles

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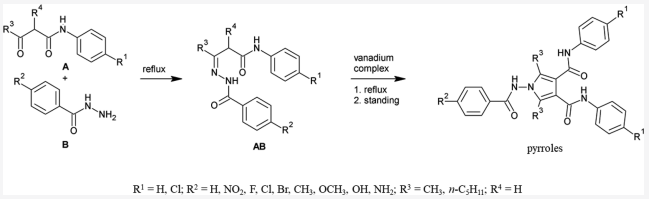
ABSTRACT: We present a straightforward, fast, inexpensive, and environmentally friendly synthesis of 1,2,3,4,5-pentasubstituted derivatives of pyrrole, which were produced in one-pot reactions of 3-oxoanilides with hydrazides of carboxylic acids, catalyzed by 10 mol % $VOSO_4 \cdot H_2O$. The reactions were carried out in ethanol in contact with air as the oxidant. The 19 pyrroles obtained were usually crystalline and did not require purification. The reaction tolerates various substituents in both substrates. All products were characterized by infrared, nuclear magnetic resonance, and ultraviolet−visible spectroscopy and elemental analysis. The molecular structures of the products and the intermediates were unambiguously determined by X-ray single-crystal analysis.



INTRODUCTION

Pyrroles make up one of the most important classes of heterocyclic compounds;[1] they exist in nature[2] (e.g., in heme, chlorophyll, and vitamin B_{12}) and have been found to be useful in materials science,[3] medicinal chemistry, drug discovery,[4] and organic synthesis.[5]

Classical methods for the preparation of polysubstituted pyrroles involve Knorr,[6] Paal−Knorr,[7] and Hantzsch syntheses.[8] The importance of pyrroles has resulted in the continuing development of new synthetic methods,[1] among them a variety of metal species catalysis strategies,[9] to fulfill today's requirements for organic syntheses: simplicity, diversity, readily available starting materials, possibility of automation, favorable economic factors, and little environmental influence.[10]

Although syntheses of functionalized pyrroles from 1,3-dicarbonyl compounds, catalyzed by transition metals, including In, Ru, and Ti, have been described in detail in the literature, they were two-, three-, or four-component reactions.[11] In our studies, we used the vanadium complexes that have proven to be effective catalysts.[12] We have developed the synthesis of the pyrrole ring in one step from only two substrates (a 3-oxoanilide and a hydrazide) on the pathway of vanadium-mediated oxidation followed by a ring closure. In contrast to a previous report,[13] we obtained the products as purely organic compounds, not metal complexes.

RESULTS AND DISCUSSION

During the research on vanadium complexes of Schiff bases, we found that **A1B1**, obtained *in situ* from acetoacetanilide **A1** (R^1 = H, R^3 = CH_3, and R^4 = H) and hydrazide of benzoic acid **B1** (R^2 = H), spontaneously cyclized under reaction conditions, giving unexpectedly a crystalline product, which turned out to be 1,2,3,4,5-pentasubstituted pyrrole **1** (Scheme 1). Having discovered a simple method of obtaining such compounds, we optimized the conditions of the reaction (Table 1).

We started our work by examining the reaction in ethanol in the presence of 1 equiv of $[VO(acac)_2]$. Under these conditions, pyrrole **1** was isolated in pure crystalline form but with an unsatisfactorily low yield (entry 1). When we decreased the amount of $[VO(acac)_2]$ to 10 mol %, we observed the formation of compound **C1** at first but on standing (528 h) **C1** completely transformed into **1** with a higher yield (entry 2). Using V_2O_4 and V_2O_5, lower yields were observed (entries 3 and 4, respectively). Next, the reactions of **A1** and **B1** in the presence of $VOSO_4 \cdot H_2O$ in a water/ethanol mixture (entries 5 and 6) and in ethanol (entries 7−9) were carried out, and the yields of **1** increased to 59% and 69%, respectively. We observed that the yield of **1** was independent of the amount of $VOSO_4 \cdot H_2O$ in the range of 10−100 mol %. We thus found that using 10 mol % $VOSO_4 \cdot H_2O$ in ethanol gave the best yields (entry 7). Finally, we carried out the synthesis out using isolated imine **A1B1** and $[VO(acac)_2]$ (entry 10) or $VOSO_4 \cdot H_2O$ (entry 11) as the vanadium complex. These reactions also gave product **1** with yields comparable to those of entries 1 and 9, respectively.

The reaction (see Table 1) was studied in an ethanol/water mixture or in ethanol. The reaction always proceeds in the presence of water; as both $VOSO_4$ and ethanol contain water, water is also liberated during the synthesis of the Schiff base. Under our conditions, the level of water, present in the system, was sufficient to ensure dissolution of $VOSO_4$ as a catalyst. As

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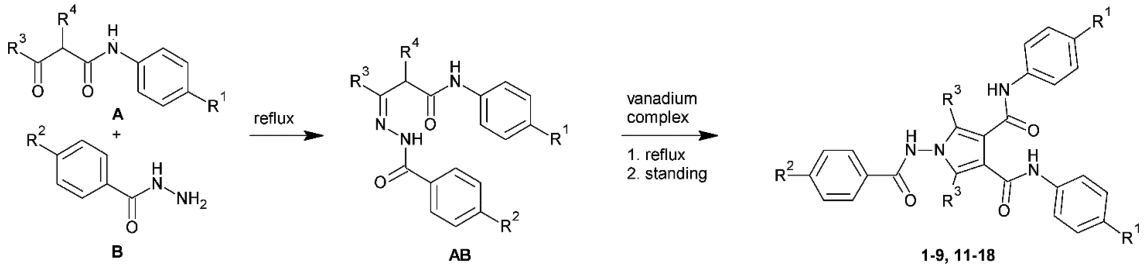
Scheme 1. Synthesis of Pyrroles 1−9 and 11−18 from Anilides A1−A3 and Hydrazides B1−B11[a]



[a]We also used 3-phenyl-1,2-oxazole-5-carbohydrazide **B10** and H_2NHNOC-$[CH_2]_4$-$CONHNH_2$ **B11** to obtain pyrroles **10** and **19**, respectively.

Table 1. Optimizing the Reaction Conditions Using A1 and B1 as Substrates

entry	catalyst (mmol)	solvent	time (min)	yield of pyrrole **1** (%)
1[a]	$[VO(acac)_2]$ (1.0)	EtOH	15 + 22	35
2[a]	$[VO(acac)_2]$ (0.1)	EtOH	15 + 22	46[b]
3[a]	V_2O_4 (4.0)	EtOH	15 + 15	7
4[a]	V_2O_5 (8.0)	EtOH	15 + 29	24
5[a]	$VOSO_4·H_2O$ (1.0)	EtOH/H_2O[c]	15 + 10	59
6[a]	$VOSO_4·H_2O$ (1.0)	EtOH/H_2O[c]	15 + 22	59
7[a]	$VOSO_4·H_2O$ (0.1)	EtOH	15 + 22	69
8[a]	$VOSO_4·H_2O$ (0.5)	EtOH	15 + 22	69
9[a]	$VOSO_4·H_2O$ (1.0)	EtOH	15 + 22	69
10[d]	$[VO(acac)_2]$ (1.0)	EtOH	0 + 32	37
11[d]	$VOSO_4·H_2O$ (1.0)	EtOH	0 + 32	62

[a]Reactions were carried out using **A1** (2.0 mmol) and **B1** (1.0 mmol). [b]Intermediate **C1** (R^1 = H, R^2 = H, and R^3 = CH_3), identified in Scheme 2, was formed first. [c]At a 4:1 (v/v) ratio. [d]Reactions were carried out using isolated imine **A1B1** (2.0 mmol).

Table 2. Scope and Limitations of Our Method

	3-oxoanilide **A**				hydrazide **B**						
entry	type	R^1	R^3	R^4	type	R^2	pyrrole	yield (%)	yield (g)	delay before collection (h)	mp (°C)
1	**A1**	H	CH_3	H	**B1**	H	**1**	69	0.3122	120	280.0−282.0
2	**A1**	H	CH_3	H	**B2**	4-NO_2	**2**	30	0.1520	648	280.5−282.5
3	**A1**	H	CH_3	H	**B3**	4-F	**3**	58	0.2729	288	260.0−262.0
4	**A1**	H	CH_3	H	**B4**	4-Cl	**4**	60	0.2922	240	265.0−267.0
5[a]	**A1**	H	CH_3	H	**B5**	4-Br	**5**	66	0.3507	240	253.5−255.5
6	**A1**	H	CH_3	H	**B6**	4-CH_3	**6**	69	0.3219	216	282.0−284.0
7	**A1**	H	CH_3	H	**B7**	4-OCH_3	**7**	48	0.2316	576	241.0−242.5
8	**A1**	H	CH_3	H	**B8**	4-OH	**8**	60	0.2811	240	311.0−313.0
9	**A1**	H	CH_3	H	**B9**	4-NH_2	**9**	43	0.2049	456	310.0−313.0
10[b]	**A1**	H	CH_3	H	**B10**	[c]	**10**	55	0.2858	192	247.5−249.5
11[a]	**A2**	4-Cl	CH_3	H	**B1**	H	**11**	52	0.2711	264	277.5−279.5
12[a]	**A2**	4-Cl	CH_3	H	**B3**	4-F	**12**	38	0.2114	408	273.0−275.0
13	**A2**	4-Cl	CH_3	H	**B4**	4-Cl	**13**	56	0.3163	288	295.0−297.0
14[a]	**A2**	4-Cl	CH_3	H	**B5**	4-Br	**14**	70	0.4202	240	300.0−302.0
15[a]	**A2**	4-Cl	CH_3	H	**B6**	4-CH_3	**15**	58	0.3105	240	275.0−277.0
16	**A3**	H	n-C_5H_{11}	H	**B1**	H	**16**	44	0.2485	192	295.5−297.0
17	**A3**	H	n-C_5H_{11}	H	**B4**	4-Cl	**17**	45	0.2696	45	280.5−282.5
18	**A3**	H	n-C_5H_{11}	H	**B9**	4-NH_2	**18**	15	0.0883	432	286.5−288.5
19[d]	**A1**	H	Me	H	**B11**	[e]	**19**	14	0.1155	144	317.5−319.5
20	**A4**	H	iC_3H_7	H	**B1**	H	–	46[f]			
21	**A5**	H	Me	Me	**B1**	H	–	–			

[a]With 100 mol % $VOSO_4·H_2O$. [b]With 25 mol % $VOSO_4·H_2O$. [c]With 3-phenyl-1,2-oxazole-5-carbohydrazide. [d]With 50 mol % $[VO(acac)_2]$. [e]With H_2NHNOC-$[CH_2]_4$-$CONHNH_2$. [f]Yield of **A4B1**.

the Schiff base is important for pyrrole formation, the results presented in Table 1 support the idea that pure ethanol, a stabilizing Schiff base, increases the reaction yield.

A small drawback of the procedure is the exceedingly long time required for the complete precipitation of the products; they were isolated after 120−648 h and after partial evaporation of the solvent. This time cannot be shortened by either prolonged refluxing of the reaction mixtures or chilling on standing. On the contrary, this stage needs no operations before the filtration of the products.

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Having optimized the reaction conditions, we examined the scope and limitations of this methodology (Table 2). While 4-F-, 4-Cl-, 4-Br-, 4-Me-, and 4-OH-substituted hydrazides in the reactions with acetoacetanilide gave the pyrroles in 58−69% yields (entries 3−6 and 8, respectively), 4-NO_2, 4-OMe, 4-NH_2, and 5-phenyl-1,2-oxazol-3-yl groups decreased the yields to 30−55% (entries 2, 7, 9, and 10, respectively). These results show that there is no clear connection between the electron-donating or electron-withdrawing character of the substituents in hydrazide **B** and the outcome of the reactions. On the contrary, introducing a 4-Cl substituent into the phenyl ring of acetoacetanilide only slightly influenced the yields of the products (entries 11 and 13−15, respectively) with respect to unsubstituted acetoacetanilide, with the disappointing exception of the reaction with 4-fluorobenzoic acid hydrazide (entry 12).

Replacing acetoacetanilide with 3-oxooctanoic acid anilide gave the corresponding pyrroles in noticeably lower yields of 15−45% (entries 16−18), and 4-methyl-3-oxopentanoic acid anilide gave no pyrrole product at all (entry 20). In this case, only the corresponding imine **A4B1** was formed. When we used 2-methyl-3-oxo-*N*-phenylbutanamide [$R^4 = CH_3$ (see Scheme 1)] instead of acetoacetanilide, we obtained neither pyrrole nor imine (entry 21). Finally, aliphatic adipic acid dihydrazide gave the product in only 14% yield (entry 19). Last but not least, the size of substituent R^3 seems to play a crucial role, as mentioned in the previous paragraph. The steric hindrance decreases the yield of the reaction in the following order: Me > *n*-pentyl > *i*Pr.

A great advantage of the reaction is obtaining pyrroles **1**−**19** in pure form after simply washing the product with small portions of ethanol. The results of EA (Table 3) showed deviations in the range 0.1−0.4% from calculated values. Only in the case of **6** and **C4** did the discrepancy reach 0.5%. In most cases, the experimental values are lower than the calculated ones, probably due to small amounts of water remaining in the products.

The mechanism of the reaction remains unclear. In the first step, 3-oxoacid anilide **A** and benzoic acid hydrazide **B** condense to give imine **AB** (see Scheme 1), which is supported by the fact that the isolated imine **A1B1** gave the same product as **A1** and **B1**, as mentioned above (Table 1, entries 7 and 11). The addition of the vanadium complex and the aerobic conditions are vital for the reaction to proceed as in the absence of the complex or under anaerobic conditions only imine **AB** could be isolated.

It is worth noting that in some cases an intermediate crystalline product **C** precipitates. It spontaneously transforms into the appropriate pyrrole on standing. The formation of intermediate **C** can be rationalized on the basis of an assumption that Schiff base **AB** is oxidized in the presence of the vanadium complex and air, to give the corresponding 2-oxo derivative, which condenses with another molecule of hydrazide **B** to give **C** (Scheme 2; also compare Scheme 1). A more detailed mechanistic proposal that includes the transformations of intermediate **C** to the final pyrrole has been suggested on the basis of the most probable Mannich/annulation pathway (Scheme 3).

The first step of pyrrole formation is the Mannich addition of acetoacetanilide to intermediate **C** followed by elimination of hydrazide R′-NH-NH_2. The long-term condensation of hydrazide R′-NH-NH_2 with the acetyl fragment of acetoacetanilide leads to the diimine intermediate, hydrazone D, that undergoes cyclization to the highly substituted pyrrole ring. The putative byproduct, nitrene R′-NH-N, reacts immediately with water giving the hydroxylamine derivative.

Table 3. Experimental and Calculated Compositions of the Compounds Examined in This Study

		composition [found (%) / calcd (%)]		
compound	formula	C	H	N
1	$C_{27}H_{24}N_4O_3$	71.6	5.2	12.5
		71.7	5.3	12.4
2	$C_{27}H_{23}N_5O_5{\cdot}0.5H_2O$	64.4	4.7	13.7
		64.0	4.8	13.8
3	$C_{27}H_{23}FN_4O_3$	68.8	5.1	11.6
		68.9	4.9	11.9
4	$C_{27}H_{23}ClN_4O_3$	66.4	4.7	11.4
		66.6	4.8	11.5
5	$C_{27}H_{23}BrN_4O_3$	60.7	4.4	10.2
		61.0	4.4	10.5
6	$C_{28}H_{26}N_4O_3$	71.6	5.7	11.8
		72.1	5.6	12.0
7	$C_{28}H_{26}N_4O_4$	69.6	5.5	11.6
		69.7	5.4	11.6
8	$C_{27}H_{24}N_4O_4$	68.8	5.2	11.7
		69.2	5.2	12.0
9	$C_{27}H_{25}N_5O_3{\cdot}0.5H_2O$	68.1	5.4	14.6
		68.1	5.5	14.7
10	$C_{30}H_{25}N_5O_4$	69.1	4.8	13.6
		69.4	4.8	13.5
11	$C_{27}H_{22}Cl_2N_4O_3$	62.3	4.3	10.7
		62.2	4.3	10.7
12	$C_{27}H_{21}Cl_2FN_4O_3{\cdot}2H_2O$	58.5	4.4	10.0
		58.3	4.5	10.1
13	$C_{27}H_{21}Cl_3N_4O_3{\cdot}0.5H_2O$	57.5	3.8	10.0
		57.4	3.9	9.9
14	$C_{27}H_{21}BrCl_2N_4O_3$	53.7	3.6	9.3
		54.0	3.5	9.3
15	$C_{28}H_{24}Cl_2N_4O_3$	62.4	4.5	10.4
		62.8	4.5	10.5

There have been known examples of complexes of Schiff bases with vanadium(IV), which bind molecular oxygen[14] and are then promising oxidation catalysts.[15] A number of important biological and industrial processes involve the metal-catalyzed oxidation of organic substrates, and for this purpose, the use of O_2 as the ultimate oxidant has obvious advantages in terms of cost and handling use.[16]

The molecular structures of **AB**, **C**, and final pyrroles **1**−**19** were unequivocally defined by X-ray crystallography, for example, intermediates **A1B4** (R^1 = H, R^2 = 4-Cl, $R^3 = CH_3$, and R^4 = H) and **C4** (R^1 = H, R^2 = 4-Cl, and $R^3 = CH_3$) and pyrrole **4** (R^1 = H, R^2 = 4-Cl, and $R^3 = CH_3$).[17] The structures of these compounds are presented in the Supporting Information. All new pyrroles were characterized by elemental and spectral analysis (^{1}H and ^{13}C NMR, IR, and UV−vis in the solid state).

Although the structures of **A1B4** and **C4** were confirmed by their crystal structures and their homogeneity, according to the elemental analysis, the NMR spectra of **A1B1**, **A1B4**, **C1**, and **C4** were complex to such an extent that we were unable to interpret them.

We think that there are two reasons for this complexity: (1) the existence of the compounds in several (probably at least three for each) tautomeric forms in solution and (2) the overlapping of nearly equivalent signals of aromatic rings,

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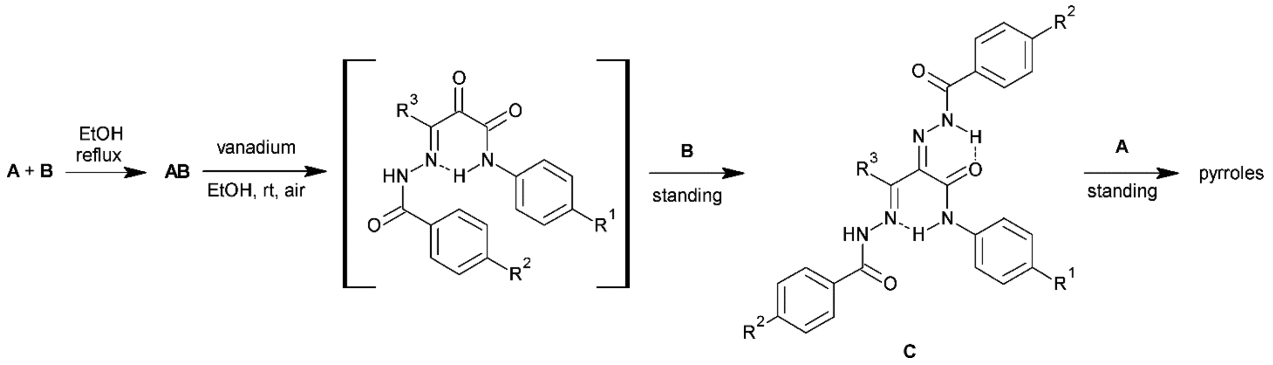
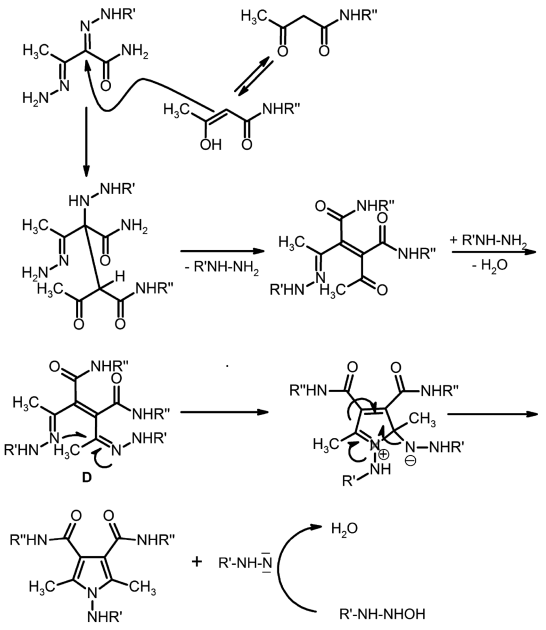
Scheme 2. Tentative Scheme for the Formation of Intermediates C



Scheme 3. Proposed Scheme of Pyrrole Formation



especially in the cases of **A1B1** and **C1**. Happily, IR allows one to trace the changes in the molecular structures on the reaction path: **AB** → **C** → pyrrole (Figure 1).

Contrary to the case for the intermediates, all signals in ^{1}H and ^{13}C spectra of all pyrroles **1**−**19** could be unequivocally assigned (with small exceptions in the spectra of **10** and **16**−**18**) without needing to record DEPT or correlation spectra, on the basis of only information taken from integration and chemical shifts of signals in the ^{1}H NMR spectra, aided by the intensities of the signals in the ^{13}C NMR spectra. The spectral analysis of the compounds is presented in the Experimental Section. Looking at the complete lists of signals in the NMR spectra of **1**−**19** (see the Experimental Section) allows one to notice changes in chemical shifts caused by various substituents, too. For example, the ^{13}C NMR spectra of pyrroles **1**−**19** include signals from C-7 (i.e., in position 2 of the pyrrole ring by IUPAC rules) in the range of 112.4−113.1 ppm, i.e., within only 0.7 ppm; C-6 atoms (position 3) absorb at 123.2−123.4 ppm when R^1 = H, and the shifts move to 126.9 ppm when R^2 = 4-Cl. C-1−C-5, C-8, and C-13 (see the Experimental Section for the assignment) remain nearly entirely insensitive to changes in the substituents. Generally, the molecules of pyrroles in this study can be divided into four nearly spectrally independent parts: the pyrrole ring, -R^3, -CONH-C_6H_4-R^1, and -NHCO-C_6H_4-R^2. These remarks also apply to ^{1}H NMR spectra.

In summary, the reaction apparently proceeds via at least two intermediates, which, in some cases, can be isolated. In spite of the fact that the molar ratio of **A** and **B** entities in the intermediates changes from 1:1 in **AB** to 1:2 in **C** to 2:1 in the final pyrroles **1**−**19**, the best yields were obtained for a 2:1 substrate ratio (see Table 1). Bearing in mind that the yields reached 70% in some cases, it seems that most of the molecules of **A** and **B** finally find their places in the pyrrole system.

CONCLUSIONS

In summary, we have developed an efficient and environmentally friendly methodology for the direct synthesis of 2,5-dialkyl-*N*,*N*-diaryl-1-[(arylcarbonyl)amino]-1*H*-pyrrole-3,4-dicarboxamides from simple and readily available derivatives of carboxylic acids, catalyzed by $VOSO_4 \cdot H_2O$. The reactions were carried out under mild conditions in the presence of air. The products were obtained usually in crystalline and pure form with yields of 14−70%. The reaction can be applied to a large number

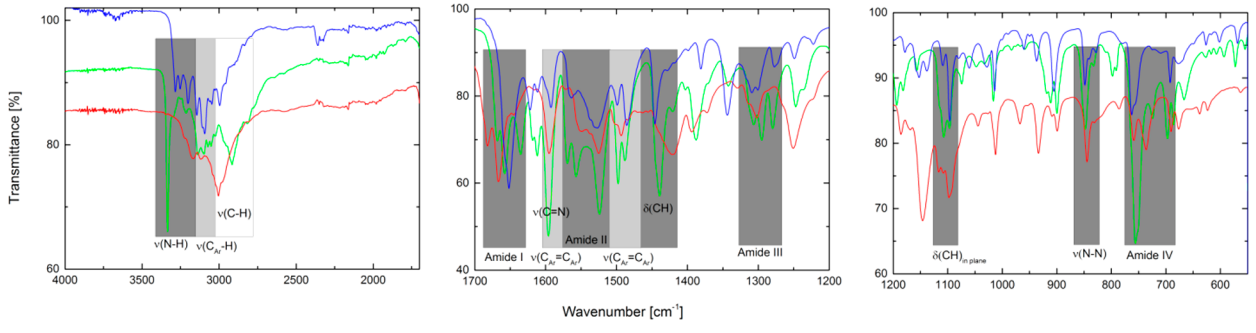


Figure 1. IR spectra of **A1B4**, **C4**, and **4** in the ranges of 4000−1700, 1700−1200, and 1200−550 cm^{-1}, respectively.

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of hydrazides, and the substituents in both starting 3-oxoanilides and hydrazides can be independently changed, which gives the possibility of obtaining a variety of the title pyrroles.

EXPERIMENTAL SECTION

General Methods. We used commercially available substrates purchased from Aldrich, Alfa Aesar, and Fluorochem without further purification with the exception of ethyl 3-oxooctanoate and ethyl 4-methyl-3-oxopentanoate, which were made according to the published procedure[18] and transformed into the corresponding anilides **A3** and **A4**.[19] 2-Methyl-3-oxo-*N*-phenylbutanamide was prepared by methylation of acetoacetanilide.[20]

Melting points were measured on an electrothermal IA9000 digital melting point apparatus and are uncorrected. Diffuse reflectance spectra were measured in $BaSO_4$ pellets with $BaSO_4$ as a reference using a Shimadzu UV-3600 apparatus equipped with an ISR-3100 attachment. Microanalyses of carbon, hydrogen, and nitrogen were performed using a Vario Micro Cube elemental analyzer. IR spectra were recorded on a Nicolet iS5 FT-IR (ATR) spectrophotometer with a diamond plate. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 600 or a Bruker Avance II 300 spectrometer. Chemical shifts are given in parts per million downfield from TMS. Coupling constants are given in hertz.

Single crystals suitable for X-ray diffraction of compounds **A1B4**, **C4**, and **4** were grown from ethanol. Diffraction data were collected on the Oxford Diffraction SuperNova four-circle diffractometer at 110 K, using the Mo (0.71069 Å) Kα radiation source and graphite monochromator. Cell refinement and data reduction were performed using the firmware.[21] The positions of all non-hydrogen atoms were determined by direct methods using *SIR-97*.[22] All non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares on F^2. Refinement and further calculations were carried out using *SHELXL-97*.[23]

Ethyl 4-Methyl-3-oxopentanoate. Yield: 48%. Colorless liquid. Bp: 92−97 °C/17 Torr (lit.,[24] 90−91 °C/16 Torr).

Ethyl 3-Oxooctanoate. Yield: 57%. Colorless liquid. Bp: 123−128 °C/17 Torr (lit.,[25] 124−125 °C/17 Torr).

*3-Oxo-N-phenyloctanamide (**A3**).* Yield: 40%. White needles (from petroleum ether, bp 60−90 °C). Mp: 82.5−84.0 °C (lit.,[26] 83−84 °C).

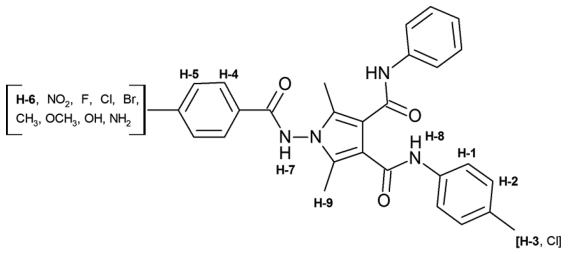
*4-Methyl-3-oxo-N-phenylpentanamide (**A4**).* Yield: 58%. Light rose oil.

General Procedure for the Synthesis of Pyrroles 1−19. 3-Oxoanilide **A** (2.0 mmol) and hydrazide **B** (1.0 mmol) in ethanol (30 mL) were refluxed (15 min) on the heating mantle. Then, $VOSO_4{\cdot}H_2O$ (0.1, 0.25, or 1 mmol) or $[VO(acac)_2]$ (0.5 mmol) (see Table 2) was added, and reflux was continued for 22 min. During the course of the reaction, the color of the mixture changed, after addition of the vanadium(IV) complex, to deep yellow and then to green, which indicated the optimal time of reflux. Next, the excess of the vanadium complex was filtered off and the reaction mixture was left to crystallize at room temperature. Upon standing at room temperature, the solution became dark brown or red and then, after all of the product had precipitated (beware that in some cases long light fibers of intermediate **C** were first formed), light yellow or brown.

After slow evaporation for 120−648 h (to $\sim^1/_3$ of the starting volume of the mixture), the precipitation of the product was completed, and the product was filtered off, washed several times with ethanol, and dried at room temperature. In some cases, the pyrroles crystallized with one or half of one molecule of water per molecule of the product.

Other methods of synthesis like microwave/ultrasonic waves were also used, but the problem was that the method described for the first time herein is the least expensive, as it does not require extra energy during reaction (standing). The yield of the reaction was also not higher. The formation of larger crystals of pyrrole, upon slow solvent evaporation, increases also the purity of the products.

The spectroscopic data for **1−19**, **A3**, **A1B1**, **A1B4**, **C1**, and **C4** (pyrroles and selected substrates and intermediates) are given below. The main imine forms of **A1B1** and **A1B4** exist in C_2D_6O solutions in equilibrium with two tautomeric enamine forms: geometric isomers *Z* and *E* (*cis* and *trans*). As a consequence, the NMR spectra of **A1B1** and **A1B4** show the presence of three different species. The poor solubility of **A1B1** and **A1B4** in C_2D_6O allowed us to analyze only the ^{1}H and ^{13}C signals assigned to the main imine forms and the ^{1}H signals assigned to the major enamine forms (*cis* isomers of **A1B1** and **A1B4**). According to the ^{1}H NMR data, we estimated isomer ratios for **A1B1** of 1:0.24:0.05 (imine:*cis*-enamine:*trans*-enamine) and for **A1B4** of 1:0.20:0.09 (imine:*cis*-enamine:*trans*-enamine). Intermediates **C1** and **C4** are very slightly soluble in deuterated solvents, so the NMR measurements were practically impossible.



1-9, 11-15

*2,5-Dimethyl-N-phenyl-1-[(phenylcarbonyl)amino)]-1H-pyrrole-3,4-dicarboxamide (**1**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{24}N_4O_3$: C, 71.7; H, 5.4; N, 12.4. Found: C, 71.6; H, 5.2; N, 12.5. λ_{max} ($BaSO_4$) (nm): 217, 251, 278. ν_{max} (cm^{-1}): 3338, 3288 (N−H); 3144, 3097, 3061, 3053, 3030 (C_{Ar}−H); 2954, 2928 (C−H); 1670, 1653, 1632 [amide I: ν(C═O)]; 1621; 1612; 1596 (C_{Ar}═C_{Ar}); 1579, 1568, 1556, 1521 [amide II: ν(C−N), δ(N−H)]; 1498, 1487 (C_{Ar}═C_{Ar}); 1437 δ(C−H); 1421; 1389; 1370; 1339, 1325; 1311, 1277, 1247 [amide III: ν(C−N), δ(N−H)]; 1193; 1177; 1155; 1113, 1102 δ(C−H)$_{in\ plane}$; 1075; 1045; 1024; 1001; 978; 958; 930; 917; 909 δ(pyrrole ring); 899; 893; 853, 845 ν(N−N); 832; 808; 796; 789; 751, 699, 689 [amide IV: δ(OCN)]; 662; 625; 618; 593; 571. ^{1}H NMR (C_2D_6OS, 300 MHz): δ 11.71 (s, 1H, H-7), 10.73 (s, 2H, H-8), 8.03 (dd, 2H, J = 8.3, 1.3, H-4), 7.71 (tt, 1H, J = 6.8, 1.3, H-6), 7.69 (dd, 4H, J = 8.5, 1.1, H-1), 7.61 (ddt, 2H, J = 8.1, 6.6, 1.5, H-5), 7.34 (ddt, 4H, J = 8.5, 7.4, 1.8, H-2), 7.08 (tt, 2H, J = 7.4, 1.0, H-3), 2.35 (s, 6H, H-9). ^{13}C{^{1}H} NMR (C_2D_6OS, 75 MHz): δ 165.9, 164.2, 139.0, 132.8, 132.7, 131.2, 128.7, 128.7, 127.6, 123.3, 119.6, 112.7, 10.4.

*1-[(4-Nitrobenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**2**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{24}N_5O_{5.5}$: C, 64.0; H, 4.8; N, 13.8. Found: C, 64.4; H, 4.7; N, 13.7. λ_{max} ($BaSO_4$) (nm): 204, 260, 279, 366. ν_{max} (cm^{-1}): 3235, 3208 (N−H); 3148, 3114, 3099, 3076, 3053, 3040 (C_{Ar}−H); 2994, 2951, 2920 (C−H); 1697, 1664 [amide I: ν(C═O)]; 1626; 1608; 1596 (C_{Ar}═C_{Ar}); 1566, 1559 1517 [amide II: ν(C−N), δ(N−H)]; 1496, 1482 (C_{Ar}═C_{Ar}); 1443 δ(C−H); 1406; 1375; 1351; 1328; 1315; 1303, 1273, 1254 [amide III: ν(C−N), δ(N−H)]; 1202; 1187; 1173; 1155; 1113, 1099, 1073 δ(C−H)$_{in\ plane}$; 1028; 1013; 971; 941; 926; 912; 895; 864, 856 [ν(N−N)]; 843; 795; 782; 749, 741, 726, 711, 689 [amide IV: δ(OCN)]; 668; 628; 620; 611. ^{1}H NMR (C_2D_6OS, 300 MHz): δ 12.06 (s, 1H, H-7), 10.70 (s, 2H, H-8), 8.44 (dt, 2H, J = 8.9, 2.2, H-5), 8.25 (dt, 2H, J = 8.9, 2.2, H-4), 7.67 (dd, 4H, J = 8.4, 0.8, H-1), 7.34 (ddt, 4H, J = 8.4, 7.5, 1.9, H-2), 7.08 (tt, 2H, J = 7.4, 1.1, H-3), 2.35 (s, 6H, H-9). ^{13}C{^{1}H} NMR (C_2D_6OS, 75 MHz): δ 164.6, 164.1, 149.8, 138.9, 136.7, 132.6, 129.3, 128.7, 123.9, 123.4, 119.6, 112.9, 10.3.

*1-[(4-Fluorobenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**3**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{23}FN_4O_3$: C, 68.9; H, 4.9; N, 11.9. Found: C, 68.8; H, 5.1; N, 11.6. λ_{max} ($BaSO_4$) (nm) 251, 281, 313; ν_{max} (cm^{-1}) 3341, 3293 (N−H); 3212; 3139, 3099, 3070, 3051, 3023 (C_{Ar}−H); 2955, 2926 (C−H); 1667, 1659, 1634 [amide I: ν(C═O)]; 1618; 1611; 1597 (C_{Ar}═C_{Ar}); 1569, 1557, 1521 [amide II: ν(C−N), δ(N−H)]; 1499, 1486 (C_{Ar}═C_{Ar}); 1438 [δ(C−H)]; 1423; 1391; 1371; 1342; 1309, 1279, 1242 [amide III: ν(C−N), δ(N−H)]; 1193; 1175; 1162; 1144; 1111, 1099 [δ(C−H)$_{in\ plane}$]; 1076; 1045; 1034; 1027; 1014; 1001; 977; 964; 960; 918; 910; 899; 853 [ν(N−N)]; 817; 795; 785; 752, 694 [amide IV: δ(OCN)]; 668; 624; 580; ^{1}H NMR (C_2D_6OS, 300 MHz) δ 11.73 (s, 1H, H-7), 10.70 (s, 2H, H-8), 8.09 [ddt, 2H, J = 8.9, 5.4 (H-4-F), 2.6,

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H-4], 7.68 (dd, 4H, J = 8.5, 1.0, H-1), 7.46 [ddt, 2H, J = 8.9, 8.9 (H-5-F), 2.6, H-5], 7.34 (ddt, 4H, J = 8.5, 7.4, 1.7, H-2), 7.07 (tt, 2H, J = 7.4, 1.0, H-3), 2.33 (s, 6H, H-9); $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz) δ 164.9, 164.1, 139.0, 132.8, 130.5 (d, J = 9.0), 128.7, 127.6 (d, J = 2.5), 119.6, 123.4, 115.8 (d, J = 22.0), 112.8, 10.4.

*1-[(4-Chlorobenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**4**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{23}ClN_4O_3$: C, 66.6; H, 4.8; N, 11.5. Found: C, 66.4; H, 4.7; N, 11.4. λ_{max} ($BaSO_4$) (nm): 213, 249, 279. ν_{max} (cm^{-1}): 3333, 3295 (N−H); 3214; 3139, 3096, 3073, 3051, 3024 (C_{Ar}−H); 2929, 2916, 2813 (C−H); 1668, 1658, 1635 [amide I: ν(C═O)]; 1618; 1612; 1596 (C_{Ar}═C_{Ar}); 1569, 1557, 1524 [amide II: ν(C−N), δ(N−H)]; 1498, 1488 (C_{Ar}═C_{Ar}); 1439 δ(C−H); 1403; 1387; 1342; 1306, 1295, 1279 [amide III: ν(C−N), δ(N−H)]; 1247; 1237; 1193; 1181; 1156; 1108, 1097 $\delta(C-H)_{in\ plane}$; 1074; 1047; 1032; 1016; 983; 976; 967; 959; 919; 911; 900; 848, 833 ν(N−N); 798; 791; 756, 751, 724, 697, 686 [amide IV: δ(OCN)]; 667; 627; 617; 606; 593; 572. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.79 (s, 1H, H-7), 10.71 (s, 2H, H-8), 8.04 (dt, 2H, J = 8.7, 2.2, H-4), 7.70 (dd, 2H, J = 8.7, 2.3, H-5), 7.68 (dd, 4H, J = 8.6, 1.0, H-1), 7.34 (ddt, 4H, J = 8.5, 7.4, 1.8, H-2), 7.07 (tt, 2H, J = 7.4, 1.0, H-3), 2.33 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.0, 164.1, 139.0, 137.6, 132.7, 129.9, 129.6, 128.9, 128.7, 123.4, 119.6, 112.8, 10.4.

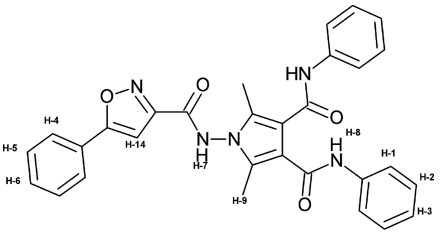
*1-[(4-Bromobenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**5**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{23}BrN_4O_3$: C, 61.0; H, 4.4; N, 10.5. Found: C, 60.7; H, 4.4; N, 10.2. λ_{max} ($BaSO_4$) (nm): 210, 256, 278. ν_{max} (cm^{-1}): 3333, 3296 (N−H); 3214; 3139, 3099, 3071, 3052, 3027 (C_{Ar}−H); 2930, 2917, 2808 (C−H); 1668, 1657, 1635 [amide I: ν(C═O)]; 1617; 1611; 1595 (C_{Ar}═C_{Ar}); 1568, 1556, 1524 [amide II: ν(C−N), δ(N−H)]; 1497, 1487 (C_{Ar}═C_{Ar}); 1439 δ(C−H); 1419; 1387; 1370; 1341; 1310, 1302, 1290, 1278 [amide III: ν(C−N), δ(N−H)]; 1246; 1234; 1193; 1181; 1156; 1114, 1107 $\delta(C-H)_{in\ plane}$; 1074; 1048; 1032; 1014; 984; 957; 927; 919; 911; 899; 853; 844, 833 ν(N−N); 797; 791; 755, 749, 719, 696, 685 [amide IV: δ(OCN)]; 667; 626; 616; 592. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.79 (s, 1H, H-7), 10.70 (s, 2H, H-8), 7.95 (dt, 2H, J = 8.6, 2.1, H-4), 7.84 (dt, 2H, J = 8.6, 2.1, H-5), 7.67 (dd, 4H, J = 8.6, 1.1, H-1), 7.34 (ddt, 4H, J = 8.6, 7.4, 1.8, H-2), 7.07 (tt, 2H, J = 7.4, 0.9, H-3), 2.33 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.1, 164.1, 139.0, 132.7, 131.8, 130.3, 129.7, 128.7, 126.5, 123.4, 119.6, 112.8, 10.4.

*1-[(4-Methylbenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**6**).* Light yellow, crystalline. Anal. Calcd for $C_{28}H_{26}N_4O_3$: C, 72.1; H, 5.6; N, 12.0. Found: C, 71.6; H, 5.7; N, 11.8. λ_{max} ($BaSO_4$) (nm): 204, 279, 257. ν_{max} (cm^{-1}): 3322, 3291 (N−H); 3226; 3143, 3109, 3094, 3075, 3053, 3040, 3028 (C_{Ar}−H); 2956, 2923 (C−H); 1666, 1651, 1637 [amide I: ν(C═O)]; 1618; 1612; 1597 (C_{Ar}═C_{Ar}); 1568, 1556, 1525 [amide II: ν(C−N), δ(N−H)]; 1498, 1485 (C_{Ar}═C_{Ar}); 1440 δ(C−H); 1422; 1389; 1370; 1340; 1310; 1302, 1286, 1279, 1248 [amide III: ν(C−N), δ(N−H)]; 1216; 1194; 1186; 1177; 1157; 1114, 1108, 1101 $\delta(C-H)_{in\ plane}$; 1074; 1046; 1038; 1031; 1020; 999; 979; 956; 928; 919, 909; 898; 855, 836 ν(N−N); 793; 781; 749, 712, 699, 685 [amide IV: δ(OCN)]; 669; 624; 581. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.62 (s, 1H, H-8), 10.71 (s, 2H, H-7), 7.92 (dd, 2H, J = 8.6, 0.7, H-4), 7.68 (dd, 4H, J = 8.6, 1.0, H-1), 7.41 (dd, 2H, J = 8.6, 0.7, H-5), 7.34 (ddt, 4H, J = 8.6, 7.4, 1.8, H-2), 7.07 (tt, 2H, J = 7.4, 1.2, H-3), 2.42 (s, 3H, CH_3), 2.33 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.8, 164.2, 142.9, 139.0, 132.9, 129.2, 128.7, 128.3, 127.7, 123.4, 119.6, 112.7, 21.0, 10.4.

*1-[(4-Methoxybenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**7**).* Light yellow, crystalline. Anal. Calcd for $C_{28}H_{26}N_4O_4$: C, 69.7; H, 5.4; N, 11.6. Found: C, 69.6; H, 5.5; N, 11.6. λ_{max} ($BaSO_4$) (nm): 204, 215, 259, 283, 320. ν_{max} (cm^{-1}): 3324, 3291 (N−H); 3224; 3140, 3095, 3068, 3054, 3040, 3021 (C_{Ar}−H); 2964, 2930, 2917, 2841 (C−H); 1668, 1652, 1635 [amide I: ν(C═O)]; 1608; 1597 (C_{Ar}═C_{Ar}); 1567, 1555, 1528 [amide II: ν(C−N), δ(N−H)]; 1510; 1498, 1459 (C_{Ar}═C_{Ar}); 1440 δ(C−H); 1420; 1388; 1369; 1335; 1323; 1313; 1292, 1265, 1249 [amide III: ν(C−N), δ(N−H)]; 1193; 1176; 1157; 1124; 1110, 1102 $\delta(C-H)_{in\ plane}$; 1074; 1034; 980; 971; 961; 949; 927; 913; 899; 852, 842 ν(N−N); 795; 779; 754, 748, 711, 699, 694, 686 [amide IV: δ(OCN)]; 637; 623; 581. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.54 (s, 1H, H-7), 10.72 (s, 2H, H-8), 8.00 (dt, 2H, J = 8.9, 2.4, H-4), 7.69 (dd, 4H, J = 8.5, 1.0, H-1), 7.34 (ddt, 4H, J = 8.5, 7.4, 1.9, H-2), 7.14 (tt, 2H, J = 8.9, 2.4, H-5), 7.08 (tt, 2H, J = 7.4, 1.1, H-3), 3.87 (s, 3H, OCH_3), 2.33 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.3, 164.2, 162.7, 139.0, 133.0, 129.7, 128.7, 123.3, 123.2, 119.6, 114.0, 112.6, 55.5, 10.4.

*1-[(4-Hydroxybenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**8**).* Cream, crystalline. Anal. Calcd for $C_{27}H_{24}N_4O_4$: C, 69.2; H, 5.2; N, 12.0. Found: C, 68.8; H, 5.2; N, 11.7. λ_{max} ($BaSO_4$) (nm): 204, 260, 279. ν_{max} (cm^{-1}): 3337 (O−H); 3305, 3229 (N−H); 3175, 3152, 3055, 3028, 3016 (C_{Ar}−H); 2969, 2932, 2918 (C−H); 1662, 1637, 1628 [amide I: ν(C═O); 1622; 1609; 1598 (C_{Ar}═C_{Ar}); 1586, 1568, 1553, 1526 [amide II: ν(C−N), δ(N−H); 1509; 1500, 1489 (C_{Ar}═C_{Ar}); 1442 δ(C−H); 1422; 1390; 1371; 1338; 1314; 1298, 1280, 1252 [amide III: ν(C−N), δ(N−H)]; 1236; 1218; 1195; 1176; 1155; 1117, 1100 $\delta(C-H)_{in\ plane}$; 1076; 1046; 1024; 1001; 982; 963; 930; 921; 915; 901; 850 ν(N−N); 820; 794; 785; 772; 754, 716, 695, 688 [amide IV: δ(OCN)]; 660; 624; 613; 583. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.42 (s, 1H, H-7), 10.72 (s, 2H, H-8), 10.31 (s, 1H, H-14), 7.90 (dt, 2H, J = 8.8, 2.4, H-4), 7.68 (dd, 4H, J = 8.6, 1.0, H-1), 7.34 (ddt, 4H, J = 8.4, 7.5, 1.8, H-2), 7.07 (tt, 2H, J = 7.4, 1.1, H-3), 6.94 (dt, 2H, J = 8.8, 2.4, H-5), 2.32 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.4, 164.2, 161.4, 139.0, 133.0, 129.8, 128.7, 123.4, 121.6, 119.6, 115.8, 112.6, 10.4.

*1-[(4-Aminobenzoyl)amino]-N,N′-diphenyl-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**9**).* Light yellow, crystalline. Anal. Calcd for $C_{27}H_{26}N_5O_{3.5}$: C, 68.1; H, 5.5; N, 14.7. Found: C, 68.1; H, 5.4; N, 14.6. λ_{max} ($BaSO_4$) (nm): 205, 213, 279, 293. ν_{max} (cm^{-1}): 3474, 3354 $\nu(NH_2)$; 3304, 3222 ν(N−H); 3149, 3060, 3048, 3022 ν(C_{Ar}−H); 2968, 2929 ν(C−H); 1658, 1642, 1629 [amide I: ν(C═O)]; 1602 ν(C_{Ar}═C_{Ar}); 1568, 1555, 1526 [amide II: ν(C−N), δ(N−H)]; 1510; 1498, 1490 ν(C_{Ar}═C_{Ar}); 1440 δ(C−H); 1422; 1391; 1370; 1340; 1313; 1286, 1279, 1251 [amide III: ν(C−N), δ(N−H)]; 1236; 1195; 1185; 1176; 1157; 1135; 1116, 1107 $\delta(C-H)_{in\ plane}$; 1075; 1047; 1030; 1000; 982; 973; 962; 949; 929; 919; 913; 899; 854, 841 ν(N−N); 828; 795; 788; 771, 762, 755, 751, 712, 697, 686 [amide IV: δ(OCN)]; 668; 660; 628; 620; 582. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.16 (s, 1H, H-7), 10.72 (s, 2H, H-8), 7.74 (d, 2H, J = 8.7, H-4), 7.68 (dd, 4H, J = 8.5, 1.0, H-1), 7.33 (ddt, 4H, J = 8.5, 7.4, 1.8, H-2), 7.07 (tt, 2H, J = 7.4, 1.1, H-3), 6.65 (d, 2H, J = 8.7, H-5), 5.93 (s, 2H, NH_2), 2.30 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.6, 164.3, 153.0, 139.0, 133.3, 129.4, 128.7, 123.3, 119.6, 117.1, 112.6, 112.4, 10.5.



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*1-[(5-Phenylisoxazol-3-yl)amino]-2,5-dimethyl-N-phenyl-1H-pyrrole-3,4-dicarboxamide (**10**).* Light yellow, crystalline. Anal. Calcd for $C_{30}H_{25}N_5O_4$: C, 69.4; H, 4.8; N, 13.5. Found: C, 69.1; H, 4.8; N, 13.6. λ_{max} ($BaSO_4$) (nm): 205, 214, 260, 280, 354. ν_{max} (cm^{-1}): 3466 (O−H); 3301, 3262 ν(N−H); 3214; 3180, 3129, 3076, 3058, 3037 (C_{Ar}−H); 2975, 2947, 2922 ν(C−H); 1726, 1646 [amide I: ν(C═O)]; 1619; 1610; 1595 ν(C_{Ar}═C_{Ar}); 1565, 1550 [amide II: ν(C−N), δ(N−H)]; 1498, 1486 ν(C_{Ar}═C_{Ar}); 1444 δ(C−H); 1421; 1399; 1386; 1372; 1338; 1316; 1280; 1258, 1234 [amide III: ν(C−N), δ(N−H)]; 1204; 1192; 1178; 1156; 1123, 1105 $\delta(C-H)_{in\ plane}$; 1095; 1077; 1070; 1049; 1041; 1033; 1025; 1003; 997; 977; 963; 947; 928; 916; 907; 901; 885; 855, 843 ν(N−N); 822; 796; 785; 765, 752, 689 [amide IV: δ(OCN)]; 676; 633; 616; 572. ^1H NMR (C_2D_6OS, 300 MHz): δ 12.37 (s, 1H, H-7), 10.71 (s, 2H, H-8), 7.69 (dd, 4H, J = 8.5, 0.9, H-1), 7.62 (s, 1H, H-14), 7.99−8.01 (2H, m), 7.56−7.61 (3H, m, H-17, H-18, H-

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19), 7.34 (ddt, 4H, J = 8.5, 7.5, 1.9, H-2), 7.08 (tt, 2H, J = 7.6, 1.1, H-3), 2.35 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 171.1, 164.0, 158.2, 157.3, 138.9, 132.4, 131.1, 129.3, 128.7, 125.9, 125.9, 123.4, 119.6, 113.0, 100.3, 100.3, 10.3, 10.3.

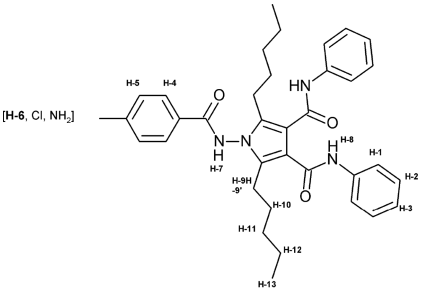
*1-[(Phenyl)amino]-N,N′-bis(4-chlorophenyl)-2,5-dimethyl-1H-pyrrole-3,4-dicarboxamide (**11**).* Light brown, crystalline. Anal. Calcd for $C_{27}H_{22}Cl_2N_4O_3$: C, 62.2; H, 4.3; N, 10.7. Found: C, 62.3; H, 4.3; N, 10.7. λ_{max} ($BaSO_4$) (nm): 214, 283, 303. ν_{max} (cm^{-1}): 3247, 3212 (N−H); 3190, 3110, 3065, 3053, 3032 (C_{Ar}−H); 2993, 2927 (C−H); 1697, 1632 [amide I: ν(C═O)]; 1602; 1589 (C_{Ar}═C_{Ar}); 1545, 1535, [amide II: ν(C−N), δ(N−H)]; 1515; 1489 (C_{Ar}═C_{Ar}); 1449 δ(C−H); 1424; 1409; 1402; 1391; 1379; 1330; 1306; 1291, 1272, 1249, 1243 [amide III: ν(C−N), δ(N−H)]; 1196, 1176; 1099, 1091, 1074 δ(C−H)$_{in\ plane}$; 1054; 1025; 1013; 992; 973; 956; 939; 931; 916; 898; 862, 849 ν(N−N); 823; 810; 786; 767; 749, 717; 690 [amide IV: δ(OCN)]; 647; 630; 596. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.72 (s, 1H, H-7), 10.75 (s, 2H, H-8), 8.02 (ddt, 2H, J = 8.3, 1.8, 1.3, H-4), 7.71 (d, 4H, J = 8.9, H-1), 7.67 (t, 1H, J = 1.4, H-6), 7.60 (ddt, 2H, J = 8.1, 6.6, 1.4, H-5), 7.39 (d, 4H, J = 8.9, H-2), 2.33 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.9, 164.1, 137.9, 133.0, 132.7, 131.2, 128.8, 128.6, 127.6, 126.9, 121.1, 112.7, 10.4.

*1-[(4-Fluorobenzoyl)amino]-N,N′-bis(4-chlorophenyl)-2,5-dimethyl-N-phenyl-1H-pyrrole-3,4-dicarboxamide Monohydrate (**12**).* Light brown, crystalline. Anal. Calcd for $C_{27}H_{25}Cl_2FN_4O_5$: C, 58.3; H, 4.5; N, 10.1. Found: C, 58.5; H, 4.4; N, 10.0. λ_{max} ($BaSO_4$) (nm): 211, 278, 321. ν_{max} (cm^{-1}): 3421 (O−H); 3339, 3306 (N−H); 3186; 3113, 3062, 3007 (C_{Ar}−H); 2973, 2927 (C−H); 1679, 1635 [amide I: ν(C═O)]; 1602; 1597 (C_{Ar}═C_{Ar}); 1574, 1550, 1520 [amide II: ν(C−N), δ(N−H)]; 1490 (C_{Ar}═C_{Ar}); 1456; 1447 δ(C−H), 1424; 1401; 1385; 1338; 1320; 1305, 1281; 1238, 1232 [amide III: ν(C−N), δ(N−H)]; 1193; 1174; 1158; 1095, 1091 δ(C−H)$_{in\ plane}$; 1047; 1011; 967; 952; 946; 930; 922; 898; 878; 864; 848; 836, 829 ν(N−N); 821; 795; 784; 769, 750, 710, 677 [amide IV: δ(OCN)]; 644; 625; 609; 600; 581. ^1H NMR (C_2D_6OS, 600 MHz): δ 11.74 (s, 1H, H-7), 10.73 (s, 2H, H-8), 8.09 [ddt, 2H, J = 8.9, 5.4 (H-4-F), 2.5, H-4], 7.70 (dt, 4H, J = 8.9, 2.5, H-1), 7.45 [ddt, 2H, J = 8.9, 8.9 (H-5-F), 2.5, H-5], 7.38 (dt, 4H, J = 8.9, 2.6, H-2), 2.32 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 150 MHz): δ 164.9, 164.3 (d, J = 160.3), 164.0, 137.9, 132.9, 130.5 (d, J = 9.3), 128.5, 127.6 (d, J = 2.1), 126.9, 121.1, 115.8 (d, J = 21.9), 112.7, 10.3.

*1-[(4-Chlorobenzoyl)amino]-N,N′-bis(4-chlorophenyl)-2,5-dimethyl-N-phenyl-1H-pyrrole-3,4-dicarboxamide Hemihydrate (**13**).* Light brown, crystalline. Anal. Calcd for $C_{27}H_{22}Cl_3N_4O_{3.5}$: C, 57.4; H, 3.9; N, 9.9. Found: C, 57.5; H, 3.8; N, 10.0. λ_{max} ($BaSO_4$) (nm): 216, 259, 282. ν_{max} (cm^{-1}): 3257 (N−H); 3192; 3123, 3094 (C_{Ar}−H); 2971, 2920 (C−H); 1667, 1662 [amide I: ν(C═O)]; 1608; 1593 (C_{Ar}═C_{Ar}); 1563, 1551 [amide II: ν(C−N), δ(N−H)]; 1506; 1491, 1482 (C_{Ar}═C_{Ar}); 1456; 1439 δ(C−H); 1408; 1398; 1383; 1378; 1363; 1325; 1299; 1293, 1273, 1251, 1243 [amide III: ν(C−N), δ(N−H)]; 1200; 1188; 1182; 1171; 1116 1095 δ(C−H)$_{in\ plane}$; 1044; 1012; 970; 951; 944; 931; 922; 906; 864; 848, 826 ν(N−N); 821; 804; 797; 786; 770; 764, 753, 728, 700 [amide IV: δ(OCN)]; 668; 627, 612. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.80 (s, 1H, H-7), 10.72 (s, 2H, H-8), 8.02 (dt, 2H, J = 8.7, 2.2, H-4), 7.70 (dt, 2H, J = 8.7, 2.2, H-5), 7.70 (dt, 4H, J = 8.9, 2.7, H-1), 7.38 (dt, 4H, J = 8.9, 2.7, H-2), 2.31 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.0, 164.0, 137.9, 137.6, 132.8, 129.9, 129.6, 128.9, 128.5, 126.9, 121.1, 112.7, 10.3.

*1-[(4-Bromobenzoyl)amino]-N,N′-bis(4-chlorophenyl)-2,5-dimethyl-N-phenyl-1H-pyrrole-3,4-dicarboxamide (**14**).* Light brown, crystalline. Anal. Calcd for $C_{27}H_{21}BrCl_2N_4O_3$: C, 54.0; H, 3.5; N, 9.3. Found: C, 53.7; H, 3.6; N, 9.3. λ_{max} ($BaSO_4$) (nm): 213, 280, 317. ν_{max} (cm^{-1}): 3247 (N−H); 3128, 3086, 3060, 3037 (C_{Ar}−H); 2975, 2920 (C−H); 1717, 1697, 1665, 1638 [amide I: ν(C═O)]; 1609; 1591 (C_{Ar}═C_{Ar}); 1562, 1550, 1511 [amide II: ν(C−N), δ(N−H)]; 1506; 1492, 1482 (C_{Ar}═C_{Ar}); 1456; 1435 δ(C−H); 1422; 1401; 1326, 1306, 1298, 1291, 1272, 1251, 1243 [amide III: ν(C−N), δ(N−H)]; 1199, 1189; 1178; 1111, 1095, 1070 δ(C−H)$_{in\ plane}$; 1046; 1012; 945; 929; 908; 896; 866; 840, 825, 821 ν(N−N); 808; 788; 766, 750, 713, 699 [amide IV: δ(OCN)]; 666; 648; 642; 628; 594. ^1H NMR (C_2D_6OS, 600 MHz): δ 11.81 (s, 1H, H-7), 10.73 (s, 2H, H-8), 7.95 (d, 2H, J = 8.8, H-4), 7.83 (d, 2H, J = 8.4, H-5), 7.70 (d, 4H, J = 8.8, H-1), 7.38 (d, 4H, J = 8.8, H-2), 2.31 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 150 MHz): δ 165.1, 164.0, 137.9, 132.8, 131.8, 130.2, 129.7, 128.5, 126.9, 126.5, 121.1, 112.7, 10.3.

*1-[(4-Methylbenzoyl)amino]-N,N′-bis(4-chlorophenyl)-2,5-dimethyl-N-phenyl-1H-pyrrole-3,4-dicarboxamide (**15**).* Light brown, crystalline. Anal. Calcd for $C_{28}H_{24}Cl_2N_4O_3$: C, 62.8; H, 4.5; N, 10.5. Found: C, 62.4; H, 4.5; N, 10.4. λ_{max} ($BaSO_4$) (nm): 220, 280, 311. ν_{max} (cm^{-1}): 3322, 3220 (N−H); 3125, 3083 (C_{Ar}−H); 2951, 2922 (C−H); 1671, 1651, 1639 [amide I: ν(C═O)]; 1612; 1592 (C_{Ar}═C_{Ar}); 1568, 1553, 1515 [amide II: ν(C−N), δ(N−H)]; 1491 (C_{Ar}═C_{Ar}); 1420; 1402; 1387; 1370; 1340; 1302, 1282, 1245, 1240 [amide III: ν(C−N), δ(N−H)]; 1194; 1181; 1094 δ(C−H)$_{in\ plane}$; 1039; 1015; 965; 947; 926; 917; 904; 860; 849, 835, 818 ν(N−N); 798; 780; 764, 745; 710, 680 [amide IV: δ(OCN)]; 647; 636; 614; 581. ^1H NMR (C_2D_6OS, 600 MHz): δ 11.63 (s, 1H, H-7), 10.75 (s, 2H, H-8), 7.92 (dd, 2H, J = 8.2, 1.6, H-4), 7.71 (dt, 4H, J = 8.9, 2.5, H-1), 7.41 (dd, 2H, J = 8.5, 0.6, H-5), 7.38 (dt, 4H, J = 8.9, 2.5, H-2), 2.41 (s, 3H, H-14), 2.32 (s, 6H, H-9). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 150 MHz): δ 165.8, 164.1, 142.9, 137.9, 133.0, 129.2, 128.5, 128.3, 127.7, 126.9, 121.1, 112.6, 21.0, 10.4.



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*1-[(Phenyl)amino]-N,N′-diphenyl-2,5-dipentyl-1H-pyrrole-3,4-dicarboxamide (**16**).* Light brown, crystalline. Anal. Calcd for $C_{35}H_{40}N_4O_3$: C, 74.4; H, 7.1; N, 9.9. Found: C, 74.3; H, 7.1; N, 9.9. λ_{max} ($BaSO_4$) (nm): 209, 280. ν_{max} (cm^{-1}): 3260, 3238 ν(N−H); 3133, 3060, 3040 ν(C_{Ar}−H); 2959, 2930, 2872, 2855 ν(C−H); 1667, 1633 [amide I: ν(C═O)]; 1598 ν(C_{Ar}═C_{Ar}); 1562, 1538 [amide II: ν(C−N), δ(N−H)]; 1499, 1488 ν(C_{Ar}═C_{Ar}); 1466; 1439 δ(C−H); 1380; 1323, 1304, 1288, 1254 [amide III: ν(C−N), δ(N−H)]; 1216; 1206; 1178; 1156; 1117, 1103 δ(C−H)$_{in\ plane}$; 1073; 1028; 1001; 969; 937; 915; 897; 870; 841 ν(N−N); 801; 772; 749, 690 [amide IV: δ(OCN)]; 631; 614; 579. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.66 (s, 1H, H-7), 10.53 (s, 2H, H-8), 7.96 (ddt, 2H, J = 8.2, 1.6, 1.3, H-4), 7.70 (tt, 1H, J = 7.4, 1.8, H-6), 7.65 (dd, 4H, J = 7.5, 1.2, H-1), 7.61 (tt, 2H, J = 7.0, 1.5, H-5), 7.32 (ddt, 4H, J = 8.4, 7.5, 1.8, H-2), 7.06 (tt, 2H, J = 7.4, 0.9, H-3), 2.80 (ddd, 2H, J = 14.6, 9.4, 6.2, H-9′), 2.62 (ddd, 2H, J = 14.6, 9.4, 6.2, H-9), 1.38−1.63 (m, 4H, H-10), 1.11−1.33 (m, 8H, H-11, H-12), 0.75 (t, 6H, H-13). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 166.2, 164.2, 139.0, 136.3, 132.5, 131.5, 128.8, 128.6, 127.4, 123.3, 119.5, 113.0, 30.9, 28.2, 24.0, 21.4, 13.5.

*1-[(4-Chlorobenzoyl)amino]-N,N′-diphenyl-2,5-dipentyl-1H-pyrrole-3,4-dicarboxamide (**17**).* Light brown, crystalline. Anal. Calcd for $C_{35}H_{39}ClN_4O_3$: C, 70.2; H, 6.6; N, 9.4. Found: C, 70.2; H, 6.6; N, 9.2. λ_{max} ($BaSO_4$) (nm): 205, 246, 278. ν_{max} (cm^{-1}): 3260, 3243 ν(N−H); 3133, 3056, 3039 ν(C_{Ar}−H); 2955, 2928, 2870, 2853 ν(C−H); 1666, 1634 [amide I: ν(C═O)]; 1597 ν(C_{Ar}═C_{Ar}); 1562, 1540 [amide II: ν(C−N), δ(N−H)]; 1499, 1486 ν(C_{Ar}═C_{Ar}); 1466; 1439 δ(C−H); 1380; 1324, 1300, 1277, 1254 [amide III: ν(C−N), δ(N−H)]; 1215; 1206; 1178; 1155; 1112, 1096 δ(C−H)$_{in\ plane}$; 1074; 1029; 1016; 984; 966; 935; 915; 898; 844 ν(N−N); 800; 749, 690 [amide IV: δ(OCN)]; 666; 621; 614; 579. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.75 (s, 1H, H-7), 10.54 (s, 2H, H-8), 7.99 (dt, 2H, J = 8.6, 2.2, H-4), 7.71 (dt, 2H, J = 8.6, 2.2, H-5), 7.65 (dd, 4H, J = 8.5, 0.9, H-1), 7.32 (ddt, 4H, J = 8.5, 7.4, 1.8, H-2), 7.06 (tt, 2H, J = 7.4, 1.0, H-3), 2.79 (ddd, 2H, J = 14.1, 9.4, 6.3, H-9′), 2.61 (ddd, 2H, J = 14.4, 9.5, 6.1, H-9), 1.40−1.61 (m, 4H, H-10), 1.11−1.25 (m, 8H, H-11, H-12), 0.74 (t, 6H, J = 7.1, H-13).

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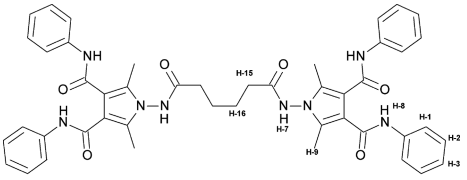
$^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.2, 164.1, 139.0, 137.5, 136.2, 130.1, 129.4, 129.0, 128.6, 123.3, 119.5, 113.1, 30.8, 28.2, 24.0, 21.5, 13.6.

*1-[(4-Aminobenzoyl)amino]-N,N′-diphenyl-2,5-dipentyl-1H-pyrrole-3,4-dicarboxamide Hemihydrate (**18**).* Light brown, crystalline. Anal. Calcd for $C_{35}H_{42}N_5O_{3.5}$: C, 71.4; H, 7.2; N, 11.9. Found: C, 71.4; H, 7.1; N, 11.7. λ_{max} ($BaSO_4$) (nm): 205, 285, 434. ν_{max} (cm^{-1}): 3487, 3390 $\nu(NH_2)$; 3254, 3232 ν(N−H); 3131, 3056, 3040 $\nu(C_{Ar}$−H); 2959, 2926, 2870, 2855 ν(C−H); 1652, 1621 [amide I: ν(C═O)]; 1596 $\nu(C_{Ar}$═$C_{Ar})$; 1561, 1538 [amide II: ν(C−N), δ(N−H)]; 1499 $\nu(C_{Ar}$═$C_{Ar})$; 1466; 1439 δ(C−H); 1381; 1311, 1289, 1254 [amide III: ν(C−N), δ(N−H)]; 1215; 1206; 1184; 1155; 1132; 1116, 1103 $\delta(C-H)_{in\ plane}$; 1073; 1029; 99; 983; 965; 943; 935; 916; 898; 872; 837 ν(N−N); 798; 750, 692 [amide IV: δ(OCN)]; 627; 602. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.09 (s, 1H, H-7), 10.54 (s, 2H, H-8), 7.70 (d, 2H, J = 8.7, H-4), 7.65 (dd, 4H, J = 8.5, 1.0, H-1), 7.32 (ddt, 4H, J = 8.5, 7.3, 1.7, H-2), 7.06 (tt, 2H, J = 7.4, 1.1, H-3), 6.65 (d, 2H, J = 8.7, H-5), 5.91 (s, 2H, NH_2), 2.77 (ddd, 2H, J = 14.1, 9.5, 6.2, H-9′), 2.57 (ddd, 2H, J = 14.2, 9.5, 5.9, H-9), 1.37−1.62 (m, 4H, H-10), 1.10−1.34 (m, 8H, H-11, H-12), 0.75 (t, 6H, J = 7.0, H-13). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 165.8, 164.3, 152.9, 139.1, 136.7, 129.3, 128.6, 123.2, 119.4, 117.4, 112.6, 112.6, 30.9, 28.2, 24.1, 21.4, 13.6.



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*1-({6-[1-(Hexanoylamino)-2,5-dimethyl-N,N′-diphenyl-1H-pyrrolo-3,4-dicarboxamido]-6-oxohexanoyl}amino)-2,5-dimethyl-N,N′-diphenyl-1H-pyrrole-3,4-dicarboxamide Monohydrate (**19**).* Light brown, crystalline. Anal. Calcd for $C_{46}H_{48}N_8O_7$: C, 67.0; H, 5.9; N, 13.6. Found: C, 66.9; H, 5.8; N, 13.6. λ_{max} ($BaSO_4$) (nm): 216, 259, 283, 306. ν_{max} (cm^{-1}): 3289, 3265 (N−H); 3145, 3096, 3060, 3040 (C_{Ar}−H); 2959, 2938, 2898, 2876 (C−H); 1679, 1666 [amide I: ν(C═O)]; 1610; 1595 (C_{Ar}═C_{Ar}); 1566, 1521 [amide II: ν(C−N), δ(N−H)]; 1500 (C_{Ar}═C_{Ar}); 1444 δ(C−H); 1412; 1377; 1363; 1331, 1311; 1255 [amide III: ν(C−N), δ(N−H)]; 1204; 1186; 1156; 1133, 1116, 1104 $\delta(C-H)_{in\ plane}$; 1076; 1048; 1027; 967; 936; 921; 893; 862; 830 ν(N−N); 790; 763, 747, 688 [amide IV: δ(OCN)]; 631; 568. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.13 (s, 2H, H-7), 10.67 (s, 4H, H-8), 7.66 (dd, 8H, J = 8.5, 0.9, H-1), 7.33 (ddt, 8H, J = 8.5, 7.4, 1.9, H-2), 7.08 (tt, 4H, J = 7.4, 1.0, H-3), 2.47 (t, 4H, J = 6.0, H-15), 2.28 (s, 12H, H-9), 1.75 (t, 4H, J = 6.0, H-16). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 171.5, 164.2, 139.0, 132.5, 128.7, 123.3, 119.5, 112.6, 32.7, 24.5, 10.3.

*3-Oxo-N-phenyloctanamide (**A3**).* White, crystalline. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.1; H, 8.2; N, 6.0. Found: C, 71.7; H, 8.2; N, 6.0. ν_{max} (cm^{-1}): 3287, 3254 (N−H); 3196, 3137, 3080, 3066, 3046, 3022 (C_{Ar}−H); 2951, 2931, 2898, 2869 (C−H); 1721, 1713, 1658 [amide I: ν(C═O)]; 1620; 1605; 1599 (C_{Ar}═C_{Ar}); 1557, 1550 [amide II: ν(C−N), δ(N−H)]; 1500, 1485 (C_{Ar}═C_{Ar}); 1467; 1445 δ(C−H); 1413; 1374; 1347; 1328; 1321; 1311; 1301; 1266, 1240, 1233 [amide III: ν(C−N), δ(N−H)]; 1202; 1176; 1170; 1160; 1155; 1124; 1074; 1063; 1040; 1029; 1007; 1001; 986; 962; 903; 884; 841; 754, 740, 716, 692 [amide IV: δ(OCN)]; 666; 591. ^1H NMR (C_2D_6OS, 300 MHz): δ 9.16 (s, 1H, H-4), 7.54 (dd, 2H, J = 8.4, 0.9, H-1), 7.32 (ddt, 2H, J = 8.4, 7.5, 1.8, H-2), 7.11 (tt, 1H, J = 7.5, 0.9, H-3), 3.55 (s, 2H, H-5), 2.57 (t, 2H, J = 7.4, H-6), 1.62 (quintet, 2H, J = 7.4, H-7), 1.26−1.36 (m, 4H, H-8, H-9), 0.90 (t, 3H, J = 7.1, H-10). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 207.8, 163.5, 137.5, 128.9, 124.5, 120.1, 49.0, 44.1, 31.1, 23.0, 22.3, 13.8.

*(3E)-N-Phenyl-3-[2-(phenylcarbonyl)hydrazinylidene]-butanamide (**A1B1**).* White, crystalline. Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.1; H, 5.8; N, 14.2. Found: C, 69.3; H, 5.8; N, 14.2. ν_{max} (cm^{-1}): 3282, 3249 (N−H); 3198, 3140, 3091, 3049, 3029 (C_{Ar}−H); 2997, 2952, 2935, 2913, 2880, 2831 (C−H); 1659 [amide I: ν(C═O)]; 1649 ν(C═N); 1622; 1611; 1597 (C_{Ar}═C_{Ar}); 157, 1561, 1522 [amide II: ν(C−N), δ(N−H)]; 1491 (C_{Ar}═C_{Ar}); 1447 δ(C−H); 1421; 1379; 1346; 1311, 1303, 1289, 1273, 1256 [amide III: ν(C−N), δ(N−H)]; 1225; 1178; 1157; 1149; 1141; 1096, 1079, 1071, 1062 $\delta(C-H)_{in\ plane}$; 1031; 1026; 1002; 996; 973; 963; 935, 924; 906; 844, 830 ν(N−N); 800; 767, 715, 695, 688 [amide IV: δ(OCN)]; 666; 646; 617; 600; 569. Imine form. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.39 (br s, 1H), 10.37 (br s, 1H), 7.87 (d, 2H, J = 7.0), 7.59 (d, 2H, J = 7.5), 7.53 (t, 1H, J = 5.5), 7.51 (t, 2H, J = 5.6), 7.33 (t, 2H, J = 7.5), 7.09 (t, 1H, J = 7.4), 3.61 (s, 2H), 2.11 (s, 3H). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 167.1, 166.7, 138.3, 133.6, 131.4, 128.7, 128.4, 128.3, 127.4, 123.8, 119.5, 46.3, 24.0. Enamine form, isomer "*Z*". ^1H NMR (C_2D_6OS, 300 MHz): δ 10.33 (s, 1H), 9.25 (s, 1H), 8.26 (s, 1H), 7.96 (d, 2H, J = 6.8), 7.5 (m, 3H), 7.28 (t, 2H, J = 7.9), 7.19 (t, 2H, J = 7.5), 6.88 (t, 1H, J = 7.3), 5.08 (s, 1H), 2.29 (s, 3H).

*(3E)-3-{2-[(4-Chlorophenyl)carbonyl]hydrazinylidene}-N-phenylbutanamide (**A1B4**).* White, crystalline. Anal. Calcd for $C_{17}H_{16}ClN_3O_2$: C, 61.9; H, 4.9; N, 12.7. Found: C, 61.7; H, 4.9; N, 12.7. ν_{max} (cm^{-1}): 3283, 3252 (N−H); 3201, 3145, 3108, 3093, 3046, 3025 (C_{Ar}−H); 2996, 2956, 2900, 2883, 2835 (C−H); 1656 [amide I: ν(C═O)]; 1652 ν(C═N); 1622; 1611; 1592 (C_{Ar}═C_{Ar}); 1564, 1558; 1538, 1527 [amide II: ν(C−N), δ(N−H)]; 1499, 1485 (C_{Ar}═C_{Ar}); 1446 δ(C−H); 1428; 1381; 1344; 1318; 1309, 1300, 1277, 1272, 1249 [amide III: ν(C−N), δ(N−H)]; 1222; 1178; 1158; 1152; 1138; 1109, 1096, 1080 $\delta(C-H)_{in\ plane}$; 1060; 1027; 1014; 1000; 989; 967; 961; 950; 937; 906; 848, 840, 828 ν(N−N); 780; 763, 756, 725, 692 [amide IV: δ(OCN)]; 677; 626; 602; 569. Imine form. ^1H NMR (C_2D_6OS, 300 MHz): δ 11.42 (br s, 1H), 10.36 (br s, 1H), 7.88 (d, 2H, J = 6.0), 7.61 (d, 2H, J = 8.5), 7.58 (m, 2H), 7.33 (t, 1H, J = 5.6), 7.30 (m, 1H), 7.06 (m, 1H), 3.62 (s, 2H), 2.11 (s, 3H). $^{13}C\{^1H\}$ NMR (C_2D_6OS, 75 MHz): δ 167.0, 166.6, 138.9, 129.6, 129.3, 128.7, 128.6, 128.5, 128.3, 123,2, 119.0, 46.3, 24.0. Enamine form, isomer "*Z*". ^1H NMR (C_2D_6OS, 300 MHz): δ 10.66 (s, 1H), 10.22 (br s, 1H), 8.28 (s, 1H), 7.97 (d, 2H, J = 8.6), 7.5 (m, 4H), 7.19 (t, 2H, J = 7.5), 6.89 (t, 1H, J = 7.3), 5.08 (s, 1H), 2.29 (s, 3H).

*(2E,3Z)-2,3-Bis[2-(phenylcarbonyl)hydrazinylidene]-N-phenylbutanamide (**C1**).* White, crystalline. ν_{max} (cm^{-1}): 3236 (N−H); 3149, 3108, 3041, 3025 (C_{Ar}−H); 3003, 2978, 2907 (C−H); 1669 [amide I: ν(C═O)]; 1650 ν(C═N); 1619; 1596 (C_{Ar}═C_{Ar}); 1582, 1547, 1528 [amide II: ν(C−N), δ(N−H)]; 1501, 1488 (C_{Ar}═C_{Ar}); 1456; 1423; 1334; 1332; 1322; 1309, 1302, 1247, 1224 [amide III: ν(C−N), δ(N−H)]; 1193; 1163; 1139, 1110 $\delta(C-H)_{in\ plane}$; 1073; 1045; 1025; 1000; 970; 935; 909; 896; 854, 842, 822, 809 ν(N−N); 798; 779; 754, 701, 690 [amide IV: δ(OCN)]; 666; 626.

*(2E,3Z)-2,3-Bis{2-[(4-chlorophenyl)carbonyl]hydrazinylidene}-N-phenylbutanamide (**C4**).* White, crystalline. Anal. Calcd for $C_{24}H_{19}Cl_2N_5O_3$: C, 58.1; H, 3.9; N, 14.1. Found: C, 58.6; H, 4.0; N, 13.9. ν_{max} (cm^{-1}): 3225 (N−H), 3169, 3115, 3041, 3024 (C_{Ar}−H), 3003, 2978 (C−H), 1682 [amide I: ν(C═O)]; 1667, 1645 ν(C═N); 1617; 1595 (C_{Ar}═C_{Ar}); 1572, 1550, 1538, 1525 [amide II: ν(C−N), δ(N−H)]; 1502; 1493; 1484; 1471; 1464; 1455; 1420; 1394; 1372; 1329; 1314, 1302, 1250, 1222 [amide III: ν(C−N), δ(N−H)]; 1185; 1170; 1146; 1116; 1108; 1098; 1093; 1080; 1044, 1012 $\delta(C-H)_{in\ plane}$; 967; 933; 910; 899; 845, 830 ν(N−N); 785; 758; 736; 691 [amide IV: δ(OCN)]; 677, 638; 624; 563.

Single-Crystal X-ray Data for Compounds A1B4, C4, and 4. Crystal structure data for **A1B4**: $C_{17}H_{16}ClN_3O_2$, M = 329.78, monoclinic, a = 12.821(5) Å, b = 10.891(5) Å, c = 12.841(5) Å, V = 1621.8(12) Å^3, T = 113(2) K, space group $P2_1/c$, Z = 4, 19921 reflections measured, 3349 unique (R_{int} = 0.0368). The final $wR(F2)$ was 0.0820 (all data). Crystallographic data (including structure factors) for **A1B4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 950456.

Crystal structure data for **C4**: $C_{24}H_{19}Cl_2N_5O_3$, M = 496.34, triclinic, a = 9.113(5) Å, b = 11.090(5) Å, c = 11.922(5) Å, V = 1106.2(9) Å^3, T = 110(2) K, space group $P\bar{1}$, Z = 2, 14276 reflections measured, 4576 unique (R_{int} = 0.0378). The final $wR(F2)$ was 0.0981 (all data). Crystallographic data (including structure factors) for **C4** have been

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deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 950454.

Crystal structure data for **4**: $C_{27}H_{23}ClN_4O_3$, M = 486.94, triclinic, a = 7.257(5) Å, b = 12.602(5) Å, c = 13.243(5) Å, V = 1146.5(10) Å^3, T = 110(2) K, space group $P\bar{1}$, Z = 2, 15045 reflections measured, 4744 unique (R_{int} = 0.0203). The final $wR(F2)$ was 0.0893 (all data). Crystallographic data (including structure factors) for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 950455.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02451.

^{1}H NMR, ^{13}C NMR, and IR spectra of final compounds **1**−**19** and selected substrates and intermediates; lists of NMR signal shifts for **1**−**19**; and structures of **A1B4**, **C4**, and **4** (PDF)

Accession Codes

CCDC 950454−950456 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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