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Synthesis and Diels–Alder Cycloadditions of *exo*-Imidazolidin-2-one Dienes

Rafael Bautista,[†] Pablo Bernal,[†,‡] Rafael Herrera,[§] Blanca M. Santoyo,[†] J. Miguel Lazcano-Seres,[‡] Francisco Delgado,[†] and Joaquín Tamariz*[,†]

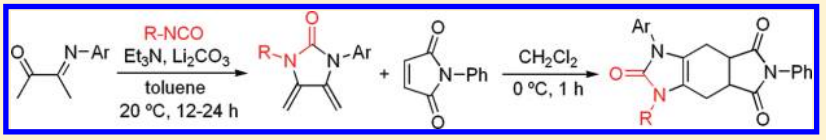
[†]Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Prol. Carpio y Plan de Ayala, S/N, 11340 México, D. F. Mexico

[‡]Departamento de Investigación y Desarrollo, Signa, S.A. de C.V., Av. Industria Automotriz No. 301, Zona Industrial Toluca, 50200, Toluca, Estado de México, Mexico

[§]Instituto de Investigaciones Quimicobiológicas, Universidad Michoacana de San Nicolas de Hidalgo, Edif. B-1, Ciudad Universitaria, Francisco J. Mujica S/N, 58066 Morelia, Michoacán, Mexico

Supporting Information

ABSTRACT:



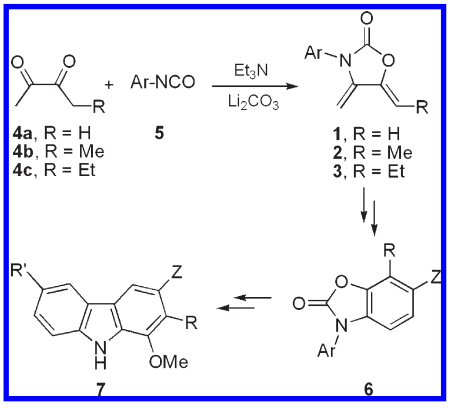
An efficient and versatile synthesis of novel *exo*-imidazolidin-2-one dienes is described. This involves the base-assisted condensation/cyclization cascade reaction of the monoimino derivatives of diacetyl with a series of isocyanates. This methodology enables preparation of symmetrical dienes, as long as the substrates have the same N substituent. Moreover, use of different N-substituted starting materials leads to formation of nonsymmetrical dienes. The reactivity of these dienes was evaluated in Diels–Alder reactions, showing a high reactivity.

INTRODUCTION

Conjugated dienes represent a privileged molecular system for evaluating the stereospecificity, endo/exo stereoselectivity, regioselectivity, and π-facial control, among other properties, in Diels–Alder cycloaddition.[1] Owing to the seminal importance of this process from a theoretical point of view,[2] as well as to its potential in synthesis,[3] a diversity of dienes have been designed, including outer-ring *o*-carbodimethylenes.[4] In particular, there has been considerable interest in the preparation and study of the reactivity of *exo*-heterocyclic dienes,[4c,5] because the heteroatoms enhance their reactivity in Diels–Alder reactions, and by this means, heteroatomic substituents can be readily and selectively introduced to the cyclohexene frame.

Previously, we described the regio- and stereoselective synthesis of novel *N*-substituted *exo*-2-oxazolidinone dienes **1**–**3**[6] through a cascade reaction that involves a base-assisted condensation of α-diketones **4** and isocyanates **5** in the presence of a dehydrating agent (Scheme 1). This methodology was successfully applied to the synthesis of 1,4-disubstituted dienes[7] and heterocycle-fused *endo*-cyclohexenic dienes.[8] These dienes proved to be highly regioselective in Diels–Alder additions to monosubstituted dienophiles with electron-withdrawing groups,[6] whose corresponding adducts were useful templates for preparing 2-(3*H*)-benzoxazolones **6**[9] and for developing a general approach for preparation of the carbazole scaffold **7**.[10] This approach was applied in the total synthesis of natural carbazoles.[11] Moreover, dienes **1**–**3** have also been efficient substrates for the synthesis of

Scheme 1. Synthesis of *exo*-2-Oxazolidinone Dienes and Their Conversion into Carbazoles



η^4:π^2-diene iridium(I) complexes, which react with alkynylphosphines and aldehydes to yield rearranged η^2:σ^2-iridium(III) complexes,[12] and for the synthesis of $Fe(CO)_3$ complexes and to study their reactivity toward alkyllithium addition reactions for preparation of conjugated enamido–enol $Fe(CO)_3$ complexes.[13] These dienes were also converted into new polycyclic oxazol-2-

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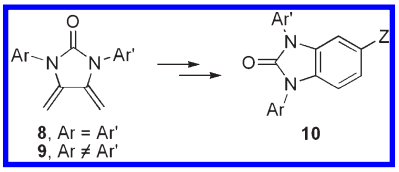
Scheme 2. *exo*-Imidazolidin-2-one Dienes as Precursors of Benzimidazol-2-ones



one derivatives by a cascade [4 + 2] cycloaddition/cyclopentannulation/1,5-sigmatropic rearrangement process with Fischer (arylalkynyl)(alkoxy)carbenes.[14]

Owing to the relevance of the *exo*-heterocyclic dienes and to our ongoing studies toward preparation of new heterocyclic systems and with the aim of determining the scope of the cascade reaction applied in the preparation of dienes **1**−**3**, the synthesis of novel *exo*-imidazolidin-2-one dienes **8** and **9** was undertaken and the results are herein disclosed. In principle, they could be valuable synthons in the preparation of vicinal diamino compounds[15] and of pharmacologically active benzimidazol-2-ones **10** (Scheme 2).[16]

RESULTS AND DISCUSSION

The first attempt to synthesize dienes **8** was designed on the basis of two approaches: (a) the mechanism of formation of dienes **1**[6−8] and (b) the simple concept of disconnection, i.e., that the heterocycle may be built through a condensation reaction between diacetyl (**4a**) and *N*,*N*-diphenylurea (**11a**) (Scheme 3). Actually, preliminary results for the synthesis of diene **1a**, using a not strictly dry solvent (dioxane), showed variable yields of diene **8a**, presumably by hydrolysis of the isocyanate to give the respective urea. Consequently, a series of ureas were submitted to react with **4a**. However, for most of cases, the desired dienes **8** were either not detected in the crude mixtures or they were isolated in very low yield (<15%).

Although these preliminary results were unsuccessful, we were able to standardize a method of synthesis of dienes **8** by condensing diacetyl (**4a**) with isocyanates **5a**−**d**. Thus, upon applying similar conditions (Et_3N, Li_2CO_3, 20 °C, 24 h) to the preparation of dienes **1** (Scheme 1), though without drying solvent and reagents, and by using toluene as the solvent, a series of dienes **8a**−**d** was obtained in low to moderate yields as stable powders (Table 1). The structure of these novel compounds was established by spectrometric analyses. The ^{1}H NMR spectra show, unlike dienes **1** where the chemical shifts of the four vinyl protons are different,[6b] only two doublets (J = 2.1−2.7 Hz) with chemical shifts ranging from 4.26 to 4.41 ppm for the *out* protons H-6a and H-7a and from 4.77 to 4.87 ppm for the *in* protons H-6b and H-7b. These chemical shifts are comparable to those found for the signals of the vinyl protons of the enamide moiety of dienes **1**.[6b] Also, similar chemical shifts were observed from the ^{13}C NMR signals corresponding to the latter (84.7−85.2 ppm), to carbons C-6 and C-7 (82.6−83.8 ppm) of dienes **8**, and to carbons C-4 and C-5 (ca. 140 ppm). Unexpectedly, the chemical shift (ca. 153 ppm) for carbon C-2 of dienes **8** was also close to that of dienes **1**, in spite of the presence of different heteroatoms bonded to the carbonyl group.[17] Signal assignment of the pairs *out* protons, H-6a/H-7a, and *in* protons, H-6b/H-7b, was carried out by NOE experiments. Thus, for diene **8a**, when the aromatic protons were irradiated, an enhancement was observed in the shielded doublet attributed to the *out* protons H-6a/H-7a. On the other hand, when the signal of the *out* protons H-6a/H-7a was irradiated, an enhancement was found in both signals of the doublet attributed to the *in* protons H-6b/H-7b as well as in the signals of the multiplet attributed to the aromatic protons.

Scheme 3. Synthesis of *exo*-Imidazolidin-2-one Dienes from Ureas

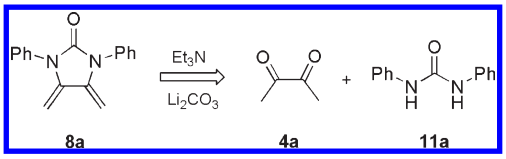
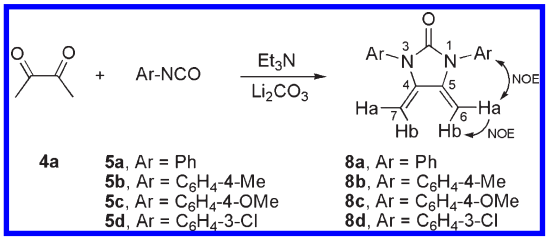


Table 1. Yields of Dienes 8a−8d, Obtained by Condensation of α-Diacetyl (4a) and Isocyanates 5a−d,[a] and ^{1}H and ^{13}C NMR Data for Selected Nuclei[b]



entry	5 (Ar)	8 (%)[c]	δ (Ha)	δ (Hb)	δ (C-2)	δ (C-4)[d]	δ (C-6)[e]
1	**5a** (C_6H_5)	**8a** (25)	4.37	4.82	153.5	140.0	82.9
2	**5b** (C_6H_4-4-Me)	**8b** (35)	4.30	4.78	153.7	140.3	82.6
3	**5c** (C_6H_4-4-OMe)	**8c** (36)	4.26	4.77	154.0	140.6	82.6
4	**5d** (C_6H_4-3-Cl)	**8d** (50)	4.41	4.87	152.8	139.3	83.8

[a] Reaction conditions: **5** (2.5 mol equiv), Et_3N (2.5 mol equiv), Li_2CO_3 (10 mol equiv), and toluene (30 mL) at 20 °C for 24 h. [b] In $CDCl_3$ as the solvent and TMS as the internal standard. [c] After column chromatography and recrystallization. [d] By molecular symmetry, this value also corresponds to C-5. [e] By molecular symmetry, this value also corresponds to C-7.

Since dienes **8a**−**d** could not be obtained by condensation of ureas **11** with **4a**, the method described in Table 1 would rule out the idea of in situ formation of ureas as reaction intermediates. Therefore, it was considered that in situ formation of other reactive species, such as bis-imines **13**, enamines **14**, and/or monoimines **15**, possibly takes place through this process via previous formation of the anilines by decomposition of the isocyanates in the presence of moist solvents. In order to test this hypothesis in regard to the first species, bis-imines **13a**,**b** were prepared in high yields by treatment of **4a** with an excess of anilines **12a**,**b** in MeOH as the solvent under mild conditions (Scheme 4). Then, the former were reacted with phenylisocyanate (**5a**) under the same reaction conditions as those used in Table 1. However, no dienes **8a** and **8e** were detected in the crude mixture. Even more, reaction of **13a** with *N*,*N*-diphenylurea (**11a**) was also assayed without obtaining the expected product.

For the preparation of enamines **14a**,**b**, α-diketones **4a**,**b** were treated with aniline (**12a**) in the presence of Lewis ($AlCl_3$) or Brønsted (*p*-TsOH, AcOH) acids (Scheme 5). Yet, in the case of **4a**, only the corresponding imine **15a** was obtained, while with **4b** a mixture of the novel enamine **14b** and imine **15b**[18] was isolated in low yield. The yield of **14b** was slightly improved (35%) by stirring the reaction mixture and using *p*-TsOH as the catalyst (12 h) in the presence of MeOH as the solvent. The (*Z*)

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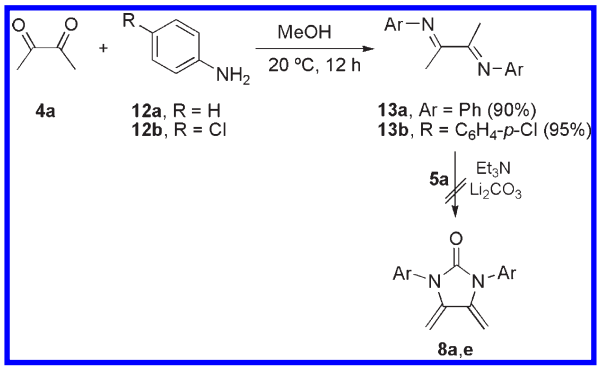
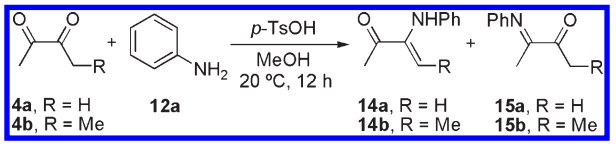
Scheme 4. Failed Synthesis of Dienes from Bis-imines



Scheme 5. Preparation of Enamines 14a,b and Imines 15a,b

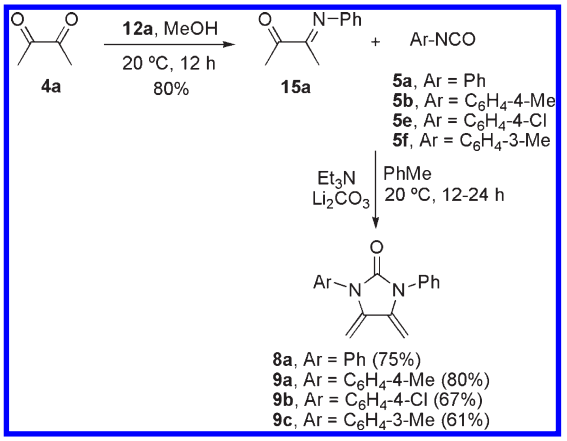


configuration of **14b** was established by NOE experiments, since there was even greater enhancement of the signal attributed to the phenyl group by irradiating the vinylic methyl group.[19] The fact that the procedure failed to yield enamine **14a** supports the results previously reported in which evidence was given of the difficulty in preparing enamines from primary amines and methyl ketones.[20] Although enamine **14b** already possesses the enamine moiety of dienes **8**, reaction with isocyanate **5a** in the presence of the (Et_3N) and dehydrating additive (Li_2CO_3) was unable to furnish the desired product, even by irradiation with MW.

Finally, we tested the in situ generation of monoimines **15** as intermediates involved in formation of dienes **8a**−**d**. Thus, α-iminoketone **15a** was prepared in good yield by following the same mild conditions (20 °C, 12 h) as those used for bis-imines **13** with α-diketone **4a** but with only 1.2 mol equiv of aniline (**12a**) (Scheme 6). Surprisingly and in contrast with the previous processes, reaction of **15a** with isocyanate **5a** efficiently produced the desired symmetric diene **8a** in good yield. This methodology was also efficient for affording the novel unsymmetrical imidazolidin-2-one dienes **9a**−**c** in fairly good yields, starting from isocyanates **5b** and **5e,f** (Scheme 6). Unlike with the reactions of Table 1, where moist reagents and solvents were used, in this method the conditions were strictly anhydrous. When numerous dehydrating agents were tested ($MgSO_4$, Na_2SO_4, K_2CO_3, molecular sieves, etc.) in order to preserve these conditions, Li_2CO_3 provided the best yields, thus proving itself to be the most efficient. Although these dienes are not particularly light sensitive in the solid state, the solution-medium process must be performed in the dark to avoid radical-promoted polymerization. Actually, dienes **8** and **9** are stable solids at room temperature for several days (some additional slight spots are detected by tlc) and can be kept refrigerated (4 °C) for months. However, they are not very stable in solution, suffering polymerization at room temperature in a few hours, for example, when in EtOAc or CH_2Cl_2 as solvents.

Therefore, this methodology gives evidence not only that imines are the most probable intermediates in formation of these

Scheme 6. Synthesis of Dienes 8a and 9a−c via α-Iminoketone 15a



dienes but also that this is the most efficient approach for obtaining such interesting and novel exo-heterocyclic dienes.

It is noteworthy that the ^{1}H NMR spectrum of nonsymmetrical diene **9a** displays only slightly different chemical shifts ($\Delta\delta$ = 0.03 ppm) for the signals (doublet, J = 2.4 Hz) of the *out* protons H-6a and H-7a as well as ($\Delta\delta$ = 0.01 ppm) for the signals (doublet, J = 2.4 Hz) of the *in* protons H-6b and H-7b of the diene moiety. These data suggest that the effects that can induce the chemical shifts of these protons, e.g., the electron-donating effect of the two nonequivalent nitrogen atoms (the enamidic effect) and the shielding effect of the aryl rings, are almost identical on the terminal carbons C-6 and C-7. Actually, the electron density on the nitrogen atom is probably nearly unperturbed by the π-electron density of the aryl ring, owing to the fact that the latter should be almost orthogonal to the plane of the heterocycle (see the calculated geometry of dienes **8a** and **9a**, Figure 1), as shown by X-ray diffraction analysis of dienes **1**−**3**.[6−8] The signal discrimination between protons H-6a and H-6b as well as between protons H-7a and H-7b was carried out by NOE experiments. An enhancement in the shielded signal attributed to the *out* protons H-6a/H-7a was observed when the aromatic protons were irradiated, indicating their spatial proximity. It is likely that the enamidic effect along with the well-known anisotropic effect of the rigid dienic system are governing the different chemical shifts between the *in* and the *out* protons, as suggested for dienes **1** and **2**.[6b] In contrast, attribution of the signals by NOE was impossible in relation to the *out* protons H-6a and H-7a as well as for the *in* protons H-6b and H-7b of diene **9a** due to the extremely small $\Delta\delta$. However, for diene **9d** (see below) the doublet signals for each proton are separated sufficiently to make this attribution.

Preparation of the series of symmetrical dienes **8b**−**e** with *N*,*N*′-diaryl substituents was attained when the α-iminoketones **15c**−**f** were submitted to addition of the corresponding isocyanates **5b**−**e**, leading to the desired dienes in good yields (Scheme 7). α-Iminoketones **15c**−**f** were obtained under similar conditions to those used for **15a** in fairly good yields by condensing diacetyl (**4a**) with the respective anilines **12b**−**e**.

Further combination between α-iminoketones and arylisocyanates could be the pathway for the synthesis of other series of nonsymmetrical dienes. For example, when the reaction is carried out between α-iminoketones **15c** and **15g** with arylisocyanates **5d** and **5e**, dienes **9d**−**f** were satisfactorily prepared

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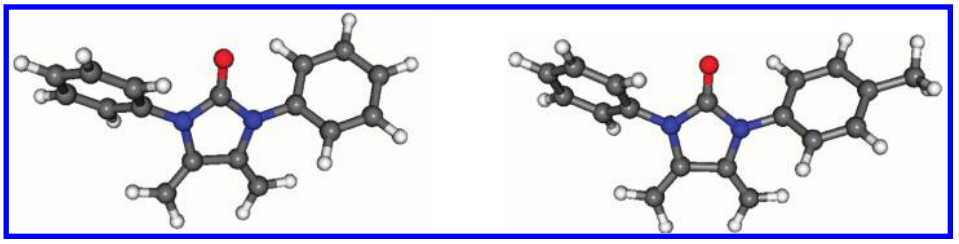
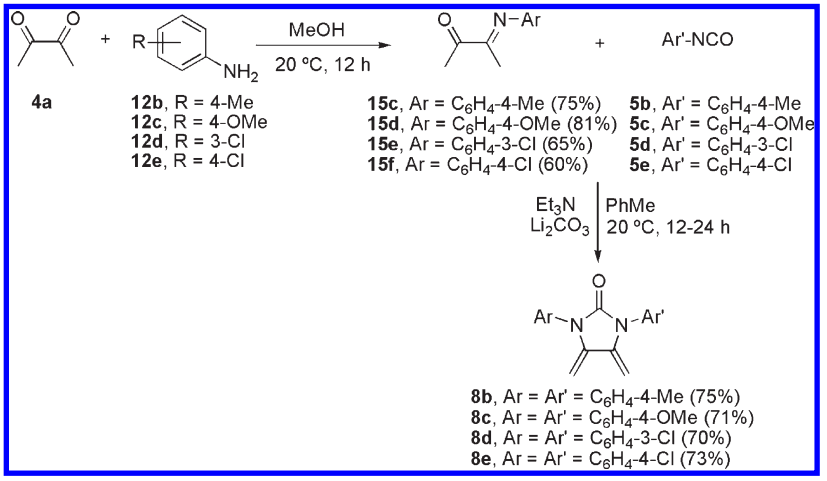
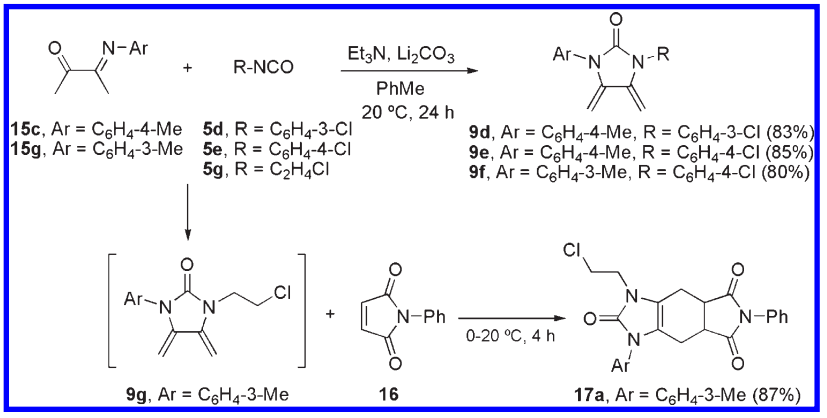


Figure 1. Geometry of Dienes **8a** and **9a** Fully Optimized by the B3LYP/6-31G** Calculation Method.

Scheme 7. Synthesis of Symmetric Dienes 8b−e



Scheme 8. Preparation of Nonsymmetrical Dienes 9d−g



(Scheme 8). In contrast, use of alkylisocyanates such as **5g** provided the corresponding diene **9g**, which was detected by ^{1}H NMR of the crude mixtures yet it was unstable to the isolation conditions, suffering rapid polymerization. Diene **9g** was trapped in situ by adding *N*-phenylmaleimide (**16**) at 0−20 °C to efficiently furnish the corresponding adduct **17a**.

Interestingly, these results would support the idea that the chemical stability of dienes **8** and **9** seems to be associated with the *N*-aryl groups, since the *N*-alkyl *N*-aryl diene **9g** was less stable. However, the carbonyl group of the heterocycle would also contribute to this stability, because the diene moiety is more structurally related to an enamidic than an enaminic moiety. The latter should be much more reactive than the former with different eletrophilic species, such as protons, which can promote their decomposition or polymerization.[20b]

The reactivity of these dienes was evaluated in the Diels−Alder cycloaddition of diene **8a** with methyl vinyl ketone (**18a**). Under catalyst-free conditions, in CH_2Cl_2 as the solvent and at room temperature, the reaction did not occur. When the temperature was increased to 60−80 °C, a low-yield conversion and decomposition of the diene were observed. However, under Lewis acid catalysis the expected adduct **19a** was afforded in high yield (Scheme 9). Interestingly, the reaction took place at a low temperature for 25 min, supporting the idea that these dienes must be more reactive than oxazolidin-2-one dienes **1**−**3** due to the presence of two strong electron-releasing nitrogen atoms attached to the diene.

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Scheme 9. Diels–Alder Additions of Dienes 8a and 9b, and Synthesis of Benzimidazol-2-ones 10a,b

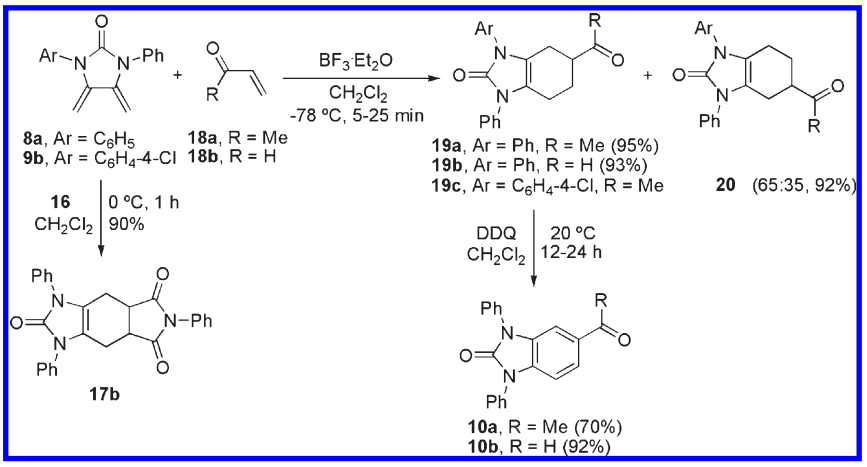
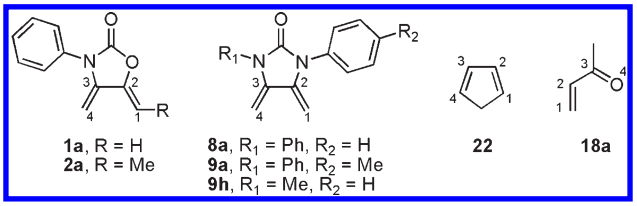


Table 2. Ab Initio RHF/6-31G Calculations of Energies (eV) and Coefficients (C_i) of the Frontier Molecular Orbitals for Dienes 1a, 2a, 8a, 9a, 9h, and 22 and Dienophile 18a[a]**



	HOMO						LUMO					
compd[b]	E (eV)	C_1	C_2	C_3	C_4	ΔC_i[c]	E (eV)	C_1	C_2	C_3	C_4	ΔC_i[c]
1a[d]	−8.8051	0.246	0.164	−0.209	−0.326	0.080	2.9065	0.263	−0.245	−0.245	0.258	−0.005
2a[d]	−8.5610	−0.257	−0.199	0.198	0.320	0.063	3.1035	0.274	−0.222	−0.245	0.248	−0.026
8a	−7.9496	0.250	0.135	−0.135	−0.250	0.000	2.8602	0.244	−0.232	−0.232	0.244	0.000
9a	−7.8805	−0.247	−0.131	0.126	0.238	−0.009	2.8975	0.243	−0.231	−0.234	0.245	0.002
9h	−8.1050	−0.290	−0.171	0.170	0.304	−0.014	3.0640	0.260	−0.244	−0.249	0.258	−0.002
22	−8.1874	−0.317	−0.233	0.233	0.317	0.000	3.7519	0.286	−0.206	−0.206	0.286	0.000
18a[d]	−10.4868	0.346	0.366	−0.039	−0.221	−0.020	2.9217	0.311	−0.208	−0.280	0.254	0.103

[a] These are the values of the p_z coefficients; the relative p_z' contributions and their ΔC_i are analogous. [b] For the most stable planar *s-cis* conformation for olefin **18a**. [c] Carbon 4 − carbon 1 for the dienes; carbon 1 − carbon 2 for the dienophile. [d] Reference 6b.

Further evidence of the enhanced reactivity of dienes **8** or **9** is the fact that diene **1a** (Ar = Ph) reacts with *N*-phenylmaleimide (**16**) at 180 °C for 1 h[6b] while diene **8a** undergoes cycloaddition to **16** at 0 °C for 1 h to give adduct **17b** (Scheme 9).

Similarly, reaction of diene **8a** with acrolein (**18b**), under analogous conditions of catalysis and low temperature (−78 °C) for 5 min, gave rise to adduct **19b** in 93% yield. In contrast, when the same reaction was carried out at room temperature, only a tar residue was isolated.

Reaction between the nonsymmetrical diene **9b** with **18a** under similar conditions to those used for diene **8a** afforded an inseparable mixture of adducts **19c**/**20** in a modest regioselectivity (not assigned) (Scheme 9). As evidenced by the ^{1}H NMR chemical shift data of the protons of the diene moiety (vide supra), this low regioselectivity is probably due to the fact that the substituents in the aromatic rings attached to the nitrogen atoms do not display a significant electronic effect to induce a differentiable perturbation on the diene terminal carbon atoms.

With the aim of exploring a preliminary synthetic application of these molecules, adducts **19a**,**b** were converted into the aromatic derivatives benzo[*d*]imidazol-2-ones **10a**,**b** by a DDQ-promoted oxidation (Scheme 9), providing the products as stable white powders in good yield.

Frontier molecular orbital (FMO) theory was used to rationalize the reactivity and regioselectivity of the new dienes **8** and **9** in the Diels–Alder cycloaddition, in comparison to dienes **1a** and **2a**. The geometries of the latter as well that of dienophile **18a** have been previously calculated,[6b] while the geometries of dienes **8a** and **9a** were calculated and optimized using the B3LYP/6-31G**[21] method without any symmetry constraints. These geometries were employed for single-point calculation of energies and coefficients of the FMOs by using the RHF/6-31G** basis set.[22] As expected, like dienes **1** and **2**, the aryl rings of dienes **8a** and **9a** adopt a preferential noncoplanar conformation with respect to the plane of the heterocycle and that of the exocyclic diene as well (Figure 1). This conformation inhibits the

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conjugation of the electron lone pairs of the nitrogen atoms with the aryl rings. Therefore, as aforementioned, this would support the hypothesis that no relevant π-electronic effects of the aryl substituents, but instead only their weak inductive effects,[23] should be transmitted onto the dienic moiety.

By using the same basis set, the energies of the FMOs were calculated for both kinds of dienes and for cyclopentadiene (**22**), the latter for the purpose of comparison with a well-known reactive diene. The energy gaps for the possible interactions were measured (Table 2), showing that the interaction between $HOMO_{diene}-LUMO_{dienophile}$ (normal electronic demand) is more favorable with respect to the $LUMO_{diene}-HOMO_{dienophile}$ interaction (inverse electronic demand).

As expected, the presence of two nitrogen atoms attached to the dienic moiety in dienes **8a** and **9a** results in a greater energy of the HOMO, compared to the HOMO energy of diene **1** and even to the HOMO energies of the methyl substituted diene **2** or diene **22**. Hence, the reactivity of dienes **8a** and **9a** should be higher than the other ones. This is in agreement with the experimental results in the particular case of dienes **1** and **8a**, compared to the cycloadditions to dienophile **16**.

The low regioselectivity observed in the cycloaddition of **9b** with **18a** to yield the mixture of **19c**/**20** (Scheme 9) can be explained on the basis of the coefficient differences for the $HOMO_{diene}-LUMO_{dienophile}$ interactions for the analogue diene **9a** (Table 2). Indeed, if the FMO coefficients of the diene termini C1 and C4 are almost equal ($\Delta C_i = 0.009$, Table 2), only a nonregioselective interaction with the coefficients of the dienophile **18a** can be expected. It seems that even for the more differentiated diene **9h** the regioselectivity should not be significantly increased, since the calculated coefficients do not show a large difference between the diene termini C1 and C4 ($\Delta C_i = 0.014$, Table 2). Nevertheless, taking into account the behavior between dienes **1** and **2**,[6b] the regioselectivity of dienes **8** or **9** may be largely improved by attaching electron-donating groups, such as a methyl group, in one of the diene termini.

CONCLUSION

In summary, we developed an efficient method to prepare the novel symmetric *exo*-2-imidazolidinone dienes **8a**−**e**. Unsymmetrical dienes **9a**−**f** and in situ formation of **9g** were also made available by this methodology. The mechanistic study provided strong evidence that the key intermediate in heterocyclic ring formation corresponded to an α-ketoimino derivative, **15**. The synthetic potential of these dienes was demonstrated, since diene **8a** can easily undergo Diels−Alder cycloaddition to give the corresponding adducts, which in turn can be transformed into the synthetically attractive heterocycle benzimidazol by aromatization. Further studies of the preparation of a wide spectrum of substituted dienes and their use in the synthesis of a variety of heterocycles are currently under active investigation.

EXPERIMENTAL SECTION

General. Melting points (uncorrected) were determined with a capillary melting point apparatus. ^{1}H (300 or 500 MHz) and ^{13}C (75.4 or 125 MHz) NMR spectra were recorded with TMS as an internal standard. Assignment of the NMR signals was made by HMQC and HMBC 2D methods. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained in the electron impact (EI) (70 eV) mode. Analytical thin-layer chromatography was carried out using silica gel coated 0.25 plates, visualized by a long- and short-wavelength UV lamp. Flash column chromatography was performed over silica gel (230−400 mesh). All air moisture-sensitive reactions were carried out under nitrogen using oven-dried glassware. MeOH and toluene were freshly distilled over sodium and methylene chloride over calcium hydride prior to use. Acetone was dried by distillation after treatment with 4 Å molecular sieves. Li_2CO_3 was dried overnight at 200 °C prior to use. Triethylamine was freshly distilled from NaOH. All other reagents were used without further purification.

(*E*,*E*)-*N*,*N*′-(Butane-2,3-diylidene)dianiline (13a). A mixture of **4a** (0.98 g, 11.4 mmol) and **12a** (1.42 g, 15.3 mmol) in MeOH (100 mL) was stirred at room temperature under N_2 atmosphere for 12 h. The solid was filtered, washed with MeOH (3 × 15 mL), and dried under vacuum to give 2.42 g (90%) of **13a** as a yellow solid; R_f 0.73 (hexane/EtOAc, 4:1); mp 135−136 °C [Lit.[24] 138−139 °C]. IR (KBr) 1633, 1480, 1445, 1355, 1207, 1116, 1071, 809, 762, 695 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 6H, CH_3), 6.75−6.85 (m, 4H, H-2, H-2′), 7.08−7.16 (m, 2H, H-4, H-4′), 7.32−7.43 (m, 4H, H-3, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.4 (CH_3C=N), 118.7 (C-2, C-2′), 123.8 (C-4, C-4′), 128.9 (C-3, C-3′), 150.9 (C-1, C-1′), 168.3 (CH_3C=N). HRMS (EI) m/z [M$^+$] calcd for $C_{16}H_{16}N_2$: 236.1314. Found: 236.1316.

(*E*,*E*)-*N*,*N*′-(Butane-2,3-diylidene)bis(4-chloroaniline) (13b). Following the procedure for **13a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12b** (1.45 g, 11.4 mmol) in MeOH (100 mL) gave 3.30 g (95%) of **13b** as a yellow powder; R_f 0.77 (hexane/EtOAc, 4:1); mp 175−176 °C [Lit.[25] 176−177 °C]. IR (KBr) 1629, 1480, 1425, 1363, 1205, 1123, 1087, 845 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 6H, CH_3), 6.68−6.76 (m, 4H, H-2, H-2′), 7.28−7.38 (m, 4H, H-3, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.4 (CH_3C=N), 120.2 (C-2, C-2′), 129.1 (C-3, C-3′), 129.3 (C-4, C-4′), 149.2 (C-1, C-1′), 168.7 (CH_3C=N). HRMS (EI) m/z [M$^+$] calcd for $C_{16}H_{14}N_2Cl_2$: 304.0534. Found: 304.0541.

(*Z*)-3-(Phenylamino)pent-3-en-2-one (14b). A mixture of **4b** (0.95 g, 9.5 mmol) and *p*-TsOH (0.36 g, 2.1 mmol) in MeOH (150 mL) was stirred at room temperature under N_2 atmosphere for 0.5 h. Then, **12a** (0.44 g, 4.7 mmol) was added, and the mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum, and the residue was purified by column chromatography over silica gel (10 g/g of crude, hexane/EtOAc, 98:2) to give 0.58 g (35%) of **14b** as a pale yellow oil; R_f 0.55 (hexane/EtOAc, 4:1). IR (film) 1717, 1631, 1495, 1412, 1256, 840, 759 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (d, J = 7.2 Hz, 3H, H-5), 2.40 (s, 3H, CH_3CO), 6.06 (br s, 1H, NH), 6.35 (q, J = 7.2 Hz, 1H, H-4), 6.63−6.71 (m, 2H, H-2′), 6.79−6.87 (m, 1H, H-4′), 7.17−7.25 (m, 2H, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.3 (C-5), 24.8 (C-1), 116.4 (C-2′), 119.8 (C-4′), 124.9 (C-4), 128.8 (C-3′), 139.0 (C-3), 143.7 (C-1′), 196.5 (C-2). MS (70 eV) m/z 175 (M$^+$, 13), 132 (100), 103 (9), 77 (94), 51 (45). HRMS (EI) m/z [M$^+$] calcd for $C_{11}H_{13}NO$: 175.0997. Found: 175.0998.

General Method for the Preparation of α-Ketoimines 15a−g. *(E)-3-(Phenylimino)butan-2-one (**15a**).* A mixture of **4a** (0.98 g, 11.4 mmol) and **12a** (1.12 g, 11.4 mmol) in MeOH (150 mL) was stirred at room temperature under N_2 atmosphere for 12 h. The solvent was removed under vacuum, and the residue was purified by column chromatography over silica gel (10 g/g crude, hexane/EtOAc, 98:2) to give 1.46 g (80%) of **15a** as a pale yellow oil;[26] R_f 0.65 (hexane/EtOAc, 4:1). IR (film) 1700, 1593, 1485, 1355, 1117, 762, 695 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, H-4), 2.52 (s, 3H, H-1), 6.72−6.83 (m, 2H, H-2′), 7.10−7.19 (m, 1H, H-4′), 7.33−7.42 (m, 2H, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.0 (C-4), 24.6 (C-1), 118.6 (C-2′), 124.7 (C-4′), 129.0 (C-3′), 149.4 (C-1′), 165.9 (C-3), 180.0 (C-2). HRMS (EI) m/z [M$^+$] calcd for $C_{10}H_{11}NO$: 161.0841. Found: 161.0838.

*(E)-2-(Phenylimino)pentan-3-one (**15b**).* Following the procedure for **15a**, a mixture of **4b** (0.95 g, 9.5 mmol) and **12a** (0.88 g, 9.5 mmol) in MeOH (150 mL) gave 1.41 g (85%) of **15b** as a pale yellow oil;[27] R_f 0.63

(hexane/EtOAc, 4:1). IR (film) 1701, 1647, 1593, 1485, 1354, 1216, 1093, 782, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J = 7.3 Hz, 3H, H-5), 1.95 (s, 3H, H-1), 3.00 (q, J = 7.3 Hz, 2H, H-4), 6.75 (d, J = 7.8 Hz, 2H, H-2′), 7.11 (t, J = 6.9 Hz, 1H, H-4′), 7.34 (t, J = 7.7 Hz, 2H, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 7.7 (C-5), 14.0 (C-4), 29.6 (C-1), 118.4 (C-2′), 124.4 (C-4′), 128.8 (C-3′), 149.4 (C-1′), 165.4 (C-2), 202.5 (C-3). MS (70 eV) m/z 175 (M^+, 12), 118 (100), 77 (78), 51 (34). HRMS (EI) m/z [M^+] calcd for $C_{11}H_{13}NO$: 175.0997. Found: 175.0994.

*(E)-3-(4-Tolylimino)butan-2-one (**15c**).* Following the procedure for **15a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12b** (1.22 g, 11.4 mmol) in MeOH (150 mL) gave 1.49 g (75%) of **15c** as a pale yellow oil;[26] R_f 0.61 (hexane/EtOAc, 4:1). IR (film) 2922, 1700, 1638, 1504, 1425, 1356, 1221, 1116, 840, 826, 750, 599 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.97 (s, 3H, H-4), 2.35 (s, 3H, CH_3Ar), 2.51 (s, 3H, H-1), 6.68−6.70 (m, 2H, H-2′), 7.16−7.19 (m, 1H, H-3′). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (C-4), 20.9 (CH_3Ar), 24.6 (C-1), 118.9 (C-2′), 129.5 (C-3′), 134.4 (C-4′), 146.8 (C-1′), 165.7 (C-3), 200.6 (C-2). MS (70 eV) m/z 175 (M^+, 28), 158 (9), 133 (12), 132 (100), 91 (41), 89 (5), 65 (8). HRMS (EI) m/z [M^+] calcd for $C_{11}H_{13}NO$: 175.0997. Found: 175.0998.

*(E)-3-(4-Methoxyphenylimino)butan-2-one (**15d**).* Following the procedure for **15a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12c** (1.40 g, 11.4 mmol) in MeOH (150 mL) gave 1.77 g (81%) of **15d** as a pale yellow oil;[26] R_f 0.60 (hexane/EtOAc, 4:1). IR (film) 1698, 1603, 1503, 1355, 1244, 1115, 1034, 842, 748 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3H, H-4), 2.49 (s, 3H, H-1), 3.79 (s, 3H, OMe), 6.76−6.81 (m, 2H, H-3′), 6.88−6.93 (m, 2H, H-2′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.7 (C-4), 24.4 (C-1), 55.1 (OMe), 113.9 (C-3′), 121.0 (C-2′), 142.0 (C-1′), 157.0 (C-4′), 165.0 (C-3), 200.4 (C-2). MS (70 eV) m/z 191 (M^+, 12), 148 (100), 105 (13), 92 (52), 77 (12), 64 (26). HRMS (EI) m/z [M^+] calcd for $C_{11}H_{13}NO_2$: 191.0946. Found: 191.0956.

*(E)-3-(3-Chlorophenylimino)butan-2-one (**15e**).* Following the procedure for **15a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12d** (1.46 g, 11.4 mmol) in MeOH (150 mL) gave 1.45 g (65%) of **15e** as a pale yellow oil;[28] R_f 0.75 (hexane/EtOAc, 4:1). IR (film) 1703, 1648, 1590, 1468, 1357, 1118, 865, 790, 682, 627 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, H-4), 2.50 (s, 3H, H-1), 6.65 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H, H-6′), 6.79 (t, J = 2.0 Hz, 1H, H-2′), 7.12 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H, H-4′), 7.30 (t, J = 8.0 Hz, 1H, H-5′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.0 (C-4), 24.4 (C-1), 116.7 (C-6′), 118.7 (C-2′), 124.5 (C-4′), 130.2 (C-5′), 134.7 (C-3′), 150.7 (C-1′), 166.7 (C-3), 199.8 (C-2). MS (70 eV) m/z 195 (M^+, 5), 152 (100), 111 (42), 85 (4), 75 (19), 51 (4). HRMS (EI) m/z [M^+] calcd for $C_{10}H_{10}ClNO$: 195.0451. Found: 195.0451.

*(E)-3-(4-Chlorophenylimino)butan-2-one (**15f**).* Following the procedure for **15a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12e** (1.46 g, 11.4 mmol) in MeOH (150 mL) gave 1.33 g (60%) of **15f** as a pale yellow oil;[29] R_f 0.59 (hexane/EtOAc, 4:1). IR (film) 2965, 1702, 1638, 1492, 1359, 1311, 1118, 844, 826, 651 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, H-4), 2.50 (s, 3H, H-1), 6.65−6.74 (m, 2H, H-2′), 7.32−7.39 (m, 1H, H-3′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.0 (C-4), 24.5 (C-1), 120.2 (C-2′), 124.7 (C-4′), 129.0 (C-3′), 149.1 (C-1′), 166.5 (C-3), 200.1 (C-2). MS (70 eV) m/z 195 (M^+, 3), 154 (31), 152 (100), 111 (89), 75 (93). HRMS (EI) m/z [M^+] calcd for $C_{10}H_{10}ClNO$: 195.0451. Found: 195.0452.

(E)-3-(3-Tolylimino)butan-2-one (15g). Following the procedure for **15a**, a mixture of **4a** (0.98 g, 11.4 mmol) and **12f** (1.22 g, 11.4 mmol) in MeOH (150 mL) gave 1.34 g (84%) of **15g** as a pale yellow oil;[28] R_f 0.75 (hexane/EtOAc, 4:1). IR (film) 1702, 1645, 1600, 1583, 1482, 1422, 1356, 1117, 936, 898, 795, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H, H-4), 2.34 (s, 3H, CH_3Ar), 2.49 (s, 3H, H-1), 6.53−6.59 (m, 2H, H-2′, H-6′), 6.94 (dd, J = 7.5, 0.6 Hz, 1H, H-4′), 7.23 (t, J = 7.5 Hz, 1H, H-5′). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.7 (C-4), 21.2 (CH_3Ar), 24.3 (C-1), 115.4 (C-6′), 119.1 (C-2′), 125.2 (C-4′), 128.7 (C-5′), 138.7 (C-3′), 149.4 (C-1′), 165.6 (C-3), 200.2 (C-2). MS (70 eV) m/z 175 (M^+, 5), 132 (100), 91 (77), 89 (26), 65 (64), 51 (12). HRMS (EI) m/z [M^+] calcd for $C_{11}H_{13}NO$: 175.0997. Found: 175.0995.

4,5-Dimethylene-1,3-diphenylimidazolidin-2-one (8a). *Method A.* A mixture of **4a** (0.49 g, 5.7 mmol), Et_3N (1.44 g, 14.3 mmol), and Li_2CO_3 (4.20 g, 56.8 mmol) in toluene (30 mL) was stirred at 20 °C under N_2 for 1.5 h in the dark. Then, **5a** (1.69 g, 14.2 mmol) in toluene (30 mL) was added dropwise, and the mixture was stirred at room temperature for 24 h. The mixture was filtered over Celite and washed with CH_2Cl_2 (2 × 20 mL). The solvent was removed under vacuum, and the crude was purified by column chromatography over silica gel (10 g/g of crude, hexane/EtOAc, 95:5) to give **8a** (0.37 g, 25%) as a white solid.

Method B. Following method A, a mixture of **15a** (0.300 g, 1.86 mmol), Et_3N (0.570 g, 5.60 mmol), Li_2CO_3 (1.00 g, 13.5 mmol), and **5a** (0.560 g, 4.71 mmol) in anhydrous toluene (75 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8a** (0.37 g, 75%) as a white solid. R_f 0.61 (hexane/EtOAc, 8:2); mp 75−76 °C. IR (film) 1712, 1600, 1541, 1499, 1447, 1403, 1315, 1228, 1068, 756, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, J = 2.4 Hz, 2H, H-6a, H-7a), 4.82 (d, J = 2.4 Hz, 2H, H-6b, H-7b), 7.34−7.45 (m, 6H, ArH), 7.46−7.53 (m, 4H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 82.9 (C-6, C-7), 127.5 (ArH), 127.9 (ArH), 129.4 (ArH), 134.2 (Ar), 140.0 (C-4, C-5), 153.5 (C-2). MS (70 eV) m/z 262 (M^+, 69), 249 (100), 191 (24), 128 (12), 115 (18), 76 (12), 69 (18). HRMS (FAB) m/z [$M + 1$]$^+$ calcd for $C_{17}H_{15}N_2O$: 263.1184. Found: 263.1180.

4,5-Dimethylene-1,3-bis(4-tolyl)imidazolidin-2-one (8b). *Method A.* Following method A for preparation of **8a**, a mixture of **4a** (0.25 g, 2.9 mmol), Et_3N (0.71 g, 7.0 mmol), Li_2CO_3 (2.00 g, 27.0 mmol), and **5b** (0.940 g, 7.07 mmol) in toluene (30 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8b** (0.30 g, 35%) as a white solid.

Method B. Following method B for preparation of **8a**, a mixture of **15c** (0.250 g, 1.43 mmol), Et_3N (0.360 g, 3.57 mmol), Li_2CO_3 (1.00 g, 13.5 mmol), and **5b** (0.570 g, 4.29 mmol) in anhydrous toluene (70 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8b** (0.31 g, 75%) as a white solid. R_f 0.58 (hexane/EtOAc, 8:2); mp 119−120 °C. IR (KBr) 1732, 1629, 1512, 1403, 1376, 1258, 1170, 845, 813 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 6H, CH_3Ar), 4.30 (d, J = 2.3 Hz, 2H, H-6a, H-7a), 4.78 (d, J = 2.3 Hz, 2H, H-6b, H-7b), 7.27 (s, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.2 (CH_3Ar), 82.6 (C-6, C-7), 127.4 (ArH), 130.0 (ArH), 131.6 (Ar), 137.8 (Ar), 140.3 (C-4, C-5), 153.7 (C-2). HRMS (EI) m/z [M^+] calcd for $C_{19}H_{18}N_2O$: 290.1419. Found: 290.1412.

1,3-bis(4-Methoxyphenyl)-4,5-dimethyleneimidazolidin-2-one (8c). *Method A.* Following method A for preparation of **8a**, a mixture of **4a** (0.24 g, 2.8 mmol), Et_3N (0.71 g, 7.0 mmol), Li_2CO_3 (2.50 g, 33.8 mmol), and **5c** (1.06 g, 7.1 mmol) in toluene (30 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8c** (0.32 g, 36%) as a pale yellow solid.

Method B. Following method B for preparation of **8a**, a mixture of **15d** (0.250 g, 1.31 mmol), Et_3N (0.330 g, 3.27 mmol), Li_2CO_3 (0.96 g, 13.0 mmol), and **5c** (0.580 g, 3.89 mmol) in anhydrous toluene (65 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8c** (0.30 g, 71%) as a pale yellow solid. R_f 0.57 (hexane/EtOAc, 8:2); mp 160−161 °C. IR (KBr) 1726, 1623, 1512, 1410, 1300, 1253, 1169, 844, 825 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 6H, OCH_3), 4.26 (d, J = 2.1 Hz, 2H, H-6a, H-7a), 4.77 (d, J = 2.1 Hz, 2H, H-6b, H-7b), 6.95−7.02 (m, 4H, ArH), 7.25−7.33 (m, 4H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 55.4 (OMe), 82.6 (C-6, C-7), 114.7 (ArH), 126.8 (Ar), 128.9 (ArH), 140.6 (C-4, C-5), 154.0 (C-2), 159.0 (Ar). HRMS (EI) m/z [M^+] calcd for $C_{19}H_{18}N_2O_3$: 322.1318. Found: 322.1330.

1,3-Bis(3-chlorophenyl)-4,5-dimethyleneimidazolidin-2-one (8d). *Method A.* Following method A for preparation of **8a**, a mixture of **4a** (0.24 g, 2.8 mmol), Et_3N (0.71 g, 7.0 mmol), Li_2CO_3 (2.50 g, 33.8 mmol), and **5d** (1.07 g, 7.0 mmol) in toluene (30 mL) was stirred at

room temperature under N_2 for 24 h in the dark to give **8d** (0.46 g, 50%) as a white solid.

Method B. Following method B for preparation of **8a**, a mixture of **15e** (0.250 g, 1.28 mmol), Et_3N (0.320 g, 3.17 mmol), Li_2CO_3 (0.95 g, 12.8 mmol), and **5d** (0.590 g, 3.84 mmol) in anhydrous toluene (30 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8d** (0.30 g, 70%) as a white solid. R_f 0.61 (hexane/EtOAc, 8:2); mp 137−138 °C. IR (KBr) 1719, 1635, 1590, 1481, 1436, 1407, 1253, 1212, 1132, 851, 790 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.41 (d, J = 2.7 Hz, 2H, H-6a, H-7a), 4.87 (d, J = 2.7 Hz, 2H, H-6b, H-7b), 7.29−7.46 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 83.8 (C-6, C-7), 125.7 (C-13, C-13′), 127.8 (C-9, C-9′), 128.3 (C-11, C-11′), 130.4 (C-12, C-12′), 135.0 (C-8, C-8′), 135.2 (C-10, C-10′), 139.3 (C-4, C-5), 152.8 (C-2). MS (70 eV) m/z 332 (M^+ + 1, 100), 331 (M^+, 74), 298 (28), 297 (41), 262 (12), 116 (13). HRMS (EI) m/z [M^+] calcd for $C_{17}H_{12}N_2OCl_2$: 330.0327. Found: 330.0364.

1,3-Bis(4-chlorophenyl)-4,5-dimethyleneimidazolidin-2-one (8e). Following method B for preparation of **8a**, a mixture of **15f** (0.250 g, 1.28 mmol), Et_3N (0.320 g, 3.17 mmol), Li_2CO_3 (0.95 g, 12.8 mmol), and **5e** (0.490 g, 3.19 mmol) in anhydrous toluene (30 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **8e** (0.31 g, 73%) as a white solid. R_f 0.56 (hexane/EtOAc, 8:2); mp 162−163 °C. IR (KBr) 1713, 1632, 1498, 1397, 1257, 1132, 1094, 837, 815, 656 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.36 (d, J = 2.5 Hz, 2H, H-6a, H-7a), 4.84 (d, J = 2.5 Hz, 2H, H-6b, H-7b), 7.32−7.37 (m, 4H, ArH), 7.44−7.49 (m, 4H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.4 (C-6, C-7), 128.8 (C-9, C-9′), 129.7 (C-10, C-10′), 132.6 (Ar), 133.8 (Ar), 139.5 (C-4, C-5), 153.1 (C-2). MS (70 eV) m/z 331 (M^+, 100), 329 (45), 297 (26), 295 (78), 294 (20), 260 (17), 232 (12), 205 (12), 178 (10), 115 (17), 75 (18). Anal. Calcd for $C_{17}H_{12}Cl_2N_2O$: C, 61.65; H, 3.65; N, 8.46. Found: C, 61.61; H, 3.73; N, 8.16.

4,5-Dimethylene-1-phenyl-3-(4-tolyl)imidazolidin-2-one (9a). Following method B for preparation of **8a**, a mixture of **15a** (1.000 g, 6.21 mmol), Et_3N (2.150 g, 21.29 mmol), Li_2CO_3 (4.59 g, 62.1 mmol), and **5b** (2.480 g, 18.65 mmol) in anhydrous toluene (200 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9a** (1.38 g, 80%) as a white solid. R_f 0.42 (hexane/EtOAc, 8:2); mp 144−145 °C. IR (KBr) 1717, 1632, 1517, 1413, 1256, 1130, 850, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3Ar), 4.32 (d, J = 2.4 Hz, 1H, H-6a or H-7a), 4.35 (d, J = 2.4 Hz, 1H, H-7a or H-6a), 4.80 (t, J = 2.4 Hz, 2H, H-6b, H-7b), 7.28 (s, 4H, ArH), 7.32−7.52 (m, 5H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.2 (CH_3Ar), 82.7 (C-6, C-7), 127.3 (ArH), 127.5 (ArH), 127.8 (ArH), 129.3 (ArH), 129.4 (Ar), 130.0 (ArH), 131.4 (Ar), 134.2 (Ar), 137.8 (ArH), 140.0 (C-5), 140.1 (C-4), 153.6 (C-2). MS (70 eV): m/z 276 (M^+, 89), 275 (89), 261 (76), 179 (100), 151 (81), 133 (45), 120 (28), 107 (82), 91 (28), 77 (40). HRMS (EI) m/z [M^+] calcd for $C_{18}H_{16}N_2O$: 276.1263. Found: 276.1264.

1-(4-Chlorophenyl)-4,5-dimethylene-3-phenylimidazolidin-2-one (9b). Following method B for preparation of **8a**, a mixture of **15a** (0.200 g, 1.24 mmol), Et_3N (0.380 g, 3.76 mmol), Li_2CO_3 (0.92 g, 12.4 mmol), and **5e** (0.480 g, 3.13 mmol) in anhydrous toluene (40 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9b** (0.25 g, 67%) as a white solid. R_f 0.63 (hexane/EtOAc, 8:2); mp 150−151 °C. IR (KBr) 1717, 1631, 1595, 1495, 1412, 1256, 1213, 1130, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.36 (d, J = 2.7 Hz, 1H, H-6a or H-7a), 4.37 (d, J = 2.7 Hz, 1H, H-7a or H-6a), 4.83 (d, J = 2.7 Hz, 1H, H-6b or H-7b), 4.84 (d, J = 2.7 Hz, 1H, H-7b or H-6b), 7.35−7.55 (m, 9H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 83.0 (C-6), 83.3 (C-7), 127.5 (ArH), 128.0 (ArH), 128.8 (Ar), 129.5 (ArH), 129.7 (Ar), 134.0 (Ar, ArH), 139.7 (C-4) 139.8 (C- 5), 152.8 (C-2). MS (70 eV): m/z 297 (M^+ + 1, 40), 296 (M^+, 70), 295 (94), 285 (89), 279 (23), 189 (14), 138 (27), 118 (70), 105 (100), 90 (27). HRMS (EI) m/z [M^+] calcd for $C_{17}H_{13}ClN_2O$: 296.0716. Found: 296.0736.

4,5-Dimethylene-1-phenyl-3-(3-tolyl)imidazolidin-2-one (9c). Following method B for preparation of **8a**, a mixture of **15a** (0.220 g, 1.37 mmol), Et_3N (0.420 g, 4.16 mmol), Li_2CO_3 (1.01 g, 13.7 mol), and **5f** (0.460 g, 3.46 mmol) in anhydrous toluene (40 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9c** (0.24 g, 61%) as a white solid. R_f 0.60 (hexane/EtOAc, 8:2); mp 111−112 °C. IR (KBr) 1719, 1632, 1492, 1406, 1263, 1231, 1181, 849, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3Ar), 4.34 (d, J = 3.1 Hz, 1H, H-6a or H-7a), 4.35 (d, J = 3.1 Hz, 1H, H-7a or H-6a), 4.80 (d, J = 2.4 Hz, 2H, H-6b, H-7b), 7.14−7.50 (m, 9H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.3 (CH_3Ar), 82.8 (C-6), 82.9 (C-7), 124.5 (ArH), 127.5 (ArH), 127.8 (ArH), 128.2 (ArH), 128.8 (ArH), 129.2 (ArH), 129.4 (ArH), 134.1 (Ar), 134.3 (Ar), 139.4 (Ar), 140.0 (C-4 or C-5), 140.1 (C-5 or C-4), 153.6 (C-2). HRMS (FAB) m/z [M + 1]$^+$ calcd for $C_{18}H_{17}N_2O$: 277.1341. Found: 277.1341.

1-(3-Chlorophenyl)-4,5-dimethylene-3-(4-tolyl)imidazolidin-2-one (9d). Following method B for preparation of **8a**, a mixture of **15c** (1.00 g, 5.7 mmol), Et_3N (1.44 g, 14.3 mmol), Li_2CO_3 (4.22 g, 0.057 mol), and **5d** (2.61 g, 17.1 mmol) in anhydrous toluene (200 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9d** (1.47 g, 83%) as a white solid. R_f 0.47 (hexane/EtOAc, 8:2); mp 136−137 °C. IR (KBr) 1717, 1632, 1517, 1484, 1409, 1255, 1212, 1131, 853, 820, 786 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3Ar), 4.33 (d, J = 2.5 Hz, 1H, H-7a), 4.39 (d, J = 2.5 Hz, 1H, H-6a), 4.81 (d, J = 2.5 Hz, 2H, H-7b), 4.84 (d, J = 2.5 Hz, 2H, H-6b), 7.24−7.30 (m, 4H, ArH), 7.30−7.35 (m, 2H, ArH), 7.40 (t, J = 8.0 Hz, 1H, ArH), 7.44 (t, J = 8.0 Hz, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3Ar), 83.1 (C-6 or C-7), 83.2 (C-7 or C-6), 125.7 (ArH), 127.3 (ArH), 127.8 (ArH), 128.0 (ArH), 130.1 (ArH), 130.3 (ArH), 131.3 (Ar), 134.8 (Ar), 135.5 (Ar), 138.1 (Ar), 139.6 (C-4 or C-5), 140.0 (C-5 or C-4), 153.3 (C-2). MS (70 eV): m/z 310 (M^+, 39), 297 (19), 140 (59), 133 (59), 105 (39), 81 (99), 77 (100). HRMS (EI) m/z [M^+] calcd for $C_{18}H_{15}ClN_2O$: 310.0873. Found: 310.0873.

1-(4-Chlorophenyl)-4,5-dimethylene-3-(4-tolyl)imidazolidin-2-one (9e). Following method B for preparation of **8a**, a mixture of **15c** (1.00 g, 5.7 mmol), Et_3N (1.44 g, 14.3 mmol), Li_2CO_3 (4.22 g, 0.057 mol), and **5e** (2.61 g, 17.1 mmol) in anhydrous toluene (200 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9e** (1.51 g, 85%) as a white solid. R_f 0.47 (hexane/EtOAc, 8:2); mp 135−136 °C. IR (KBr) 1717, 1632, 1496, 1413, 1091, 966, 817 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3Ar), 4.32 (d, J = 2.5 Hz, 1H, H-7a), 4.34 (d, J = 3.0 Hz, 1H, H-6a), 4.80 (d, J = 2.5 Hz, 1H, H-7b), 4.82 (d, J = 3.0 Hz, 2H, H-6b), 7.23−7.31 (m, 4H, ArH), 7.33−7.38 (m, 2H, ArH), 7.43−7.47 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3Ar), 82.9 (C-7), 83.2 (C-6), 127.5 (ArH), 128.8 (ArH), 129.5 (ArH), 129.7 (ArH), 132.8 (Ar), 133.6 (Ar), 134.1 (Ar), 138.1 (Ar), 139.7 (C-4 or C-5), 139.9 (C-5 or C-4), 153.3 (C-2). MS (70 eV) m/z 310 (M^+, 25), 309 (100), 259 (13), 205 (13), 99 (12), 91 (38), 77 (45). HRMS (EI) m/z [M^+] calcd for $C_{18}H_{15}ClN_2O$: 310.0873. Found: 310.0874.

1-(4-Chlorophenyl)-4,5-dimethylene-3-(3-tolyl)imidazolidin-2-one (9f). Following method B for preparation of **8a**, a mixture of **15g** (1.00 g, 5.7 mmol), Et_3N (1.44 g, 14.3 mmol), Li_2CO_3 (4.22 g, 0.057 mol), and **5e** (2.61 g, 17.1 mmol) in anhydrous toluene (200 mL) was stirred at room temperature under N_2 for 24 h in the dark to give **9f** (1.40 g, 80%) as a white solid. R_f 0.45 (hexane/EtOAc, 8:2); mp 145−146 °C. IR (KBr) 1717, 1631, 1494, 1409, 1262, 1179, 1131, 1089, 856, 836, 791 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3Ar), 4.35 (d, J = 2.5 Hz, 2H, H-6a, H-7a), 4.81 (d, J = 2.5 Hz, 1H, H-6b or H-7b), 4.82 (d, J = 2.5 Hz, 1H, H-7b or H-6b), 7.16−7.21 (m, 3H, ArH), 7.32−7.38 (m, 3H, ArH), 7.43−7.47 (m, 2H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (CH_3Ar), 82.9 (C-6 or C-7), 83.3 (C-7 or C-6), 124.5 (ArH), 128.2 (ArH), 128.8 (2ArH), 128.9 (ArH), 129.2 (ArH), 129.6 (2ArH), 132.6 (Ar), 133.5 (Ar), 133.9 (Ar), 139.5 (Ar), 139.7 (C-4 or C-5), 140.0

(C-5 or C-4), 153.3 (C-2). MS (70 eV): m/z 310 (M^+, 20), 300 (27), 282 (49), 267 (60), 256 (75), 236 (35), 168 (27), 128 (20), 117 (100), 104 (41), 76 (40). HRMS (EI) m/z [M^+] calcd for $C_{18}H_{15}ClN_2O$: 310.0873. Found: 310.0872.

1-(2-Chloroethyl)-6-phenyl-3-(3-tolyl)-4,4a,7a,8-tetrahydroimidazo[4,5-*f*]isoindole-2,5,7(1*H*,3*H*,6*H*)-trione (17a). A mixture of **15g** (0.300 g, 1.71 mmol), Et_3N (0.430 g, 4.26 mmol), Li_2CO_3 (1.27 g, 0.017 mol), and **5g** (0.450 g, 9.51 mmol) in anhydrous toluene (60 mL) was stirred at room temperature under N_2 for 24 h in the dark. The mixture was filtered over Celite, washing with CH_2Cl_2 (2 × 5 mL), and cooled to 0 °C. Then, **16** (0.330 g, 1.91 mmol) was added, stirring to the same temperature under N_2 for 1 h and to 20 °C for 3 h. The mixture was diluted with CH_2Cl_2 (15 mL) and poured into H_2O (10 mL). The organic layer was washed with a 5% aqueous solution of $NaHCO_3$ (2 × 5 mL) with a 5% aqueous solution of NH_4Cl (2 × 15 mL) and dried (Na_2SO_4). The solvent was removed under vacuum, and the crude was purified by column chromatography over silica gel (20 g, hexane/EtOAc, 8:2) to give **17a** (0.65 g, 87%) as a white solid. R_f 0.15 (hexane/EtOAc, 1:1); mp 74−75 °C. IR (KBr) 1710, 1603, 1495, 1436, 1384, 1243, 1173, 747, 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 2.76 (ddm, J = 16.5, 8.0 Hz, 1H, H-4 or H-8), 2.95 (ddm, J = 16.5, 8.5 Hz, 1H, H-4 or H-8), 3.04 (dm, J = 16.5 Hz, 1H, H-4 or H-8), 3.18 (dm, J = 16.5 Hz, 1H, H-4 or H-8), 3.46 (td, J = 8.5, 3.0 Hz, 1H, H-4a or H-7a), 3.53 (td, J = 8.5, 3.0 Hz, 1H, H-7a or H-4a), 3.78 (m, 2H, CH_2N), 3.97 (t, J = 6.0 Hz, 2H, CH_2Cl), 7.05−7.48 (m, 9H, Ar−H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5 (CH_2), 19.7 (CH_2), 21.3 (CH_3), 38.5 (CH), 38.8 (CH), 42.4 (CH_2N), 43.3 (CH_2Cl), 114.2 (C-3a or C-8a), 115.4 (C-8a or C-3a), 123.1 (ArH), 126.2 (ArH), 126.8 (ArH), 128.3 (ArH), 128.8 (ArH), 129.1 (ArH), 129.2 (ArH), 131.7 (Ar), 134.1 (Ar), 139.4 (Ar), 152.6 (C-2), 177.7 (CO), 177.8 (CO). MS (70 eV) m/z 436 (M^+, 4), 279 (18), 251 (56), 223 (79), 208 (89), 182 (90), 181 (95), 180 (100), 167 (98), 146 (50), 91 (98), 77 (35), 65 (30). HRMS (EI) m/z [M^+] calcd for $C_{24}H_{22}ClN_3O_3$: 435.1350. Found: 435.1350.

1,3,6-Triphenyl-4,4a,7a,8-tetrahydroimidazo[4,5-*f*]isoindole-2,5,7(1*H*,3*H*,6*H*)-trione (17b). A mixture of **8a** (0.050 g, 0.19 mmol) and **16** (0.036 g, 0.20 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at 0 °C under N_2 for 1 h. The mixture was diluted with CH_2Cl_2 (15 mL) and poured into H_2O (10 mL). The organic layer was washed with a 5% aqueous solution of $NaHCO_3$ (2 × 5 mL) with a 5% aqueous solution of NH_4Cl (2 × 15 mL) and dried (Na_2SO_4). The solvent was removed under vacuum, and the crude was purified by column chromatography over silica gel (20 g, hexane/EtOAc, 8:2) to give **17b** (0.075 g, 90%) as a white solid. R_f 0.20 (hexane/EtOAc, 7:3); mp 128−129 °C. IR (KBr) 1709, 1672, 1597, 1498, 1411, 1379, 1194, 759, 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.83 (dm, J = 16.0 Hz, 2H, H-4, H-8), 3.12 (d, J = 16.0 Hz, 2H, H-4, H-8), 3.46−3.55 (m, 2H, H-3a, H-8a), 7.25−7.54 (m, 10H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.1 (C-4, C-8), 38.8 (C-4a, C-7a), 115.3 (C-3a, C-8a), 126.2 (ArH), 127.5 (ArH), 128.8 (ArH), 129.3 (ArH), 129.4 (ArH), 131.7 (Ar), 134.4 (Ar), 152.2 (C-2), 177.8 (C-5, C-7). HRMS (EI) m/z [M^+] calcd for $C_{27}H_{21}N_3O_3$: 435.1583. Found: 435.1582.

5-Acetyl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (19a). A mixture of **8a** (0.060 g, 0.23 mmol) and **18a** (0.050 g, 0.71 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at −78 °C under N_2, and $BF_3 \cdot Et_2O$ (0.0065 g, 0.046 mmol) was added dropwise. The mixture was stirred for 25 min, diluted with CH_2Cl_2 (15 mL), and poured into H_2O (10 mL). The organic layer was washed with a 5% aqueous solution of $NaHCO_3$ (2 × 5 mL) and a 5% aqueous solution of NH_4Cl (2 × 15 mL) and dried (Na_2SO_4). The solvent was removed under vacuum, and the crude was purified by column chromatography over silica gel (20 g, hexane/EtOAc, 8:2) to give **19a** (0.072 g, 95%) as a white solid. R_f 0.17 (hexane/EtOAc, 7:3); mp 110−112 °C. IR (KBr) 2920, 1712, 1532, 1520, 1332, 1251, 1212, 1171, 841, 815, 760, 751 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.73−1.85 (m, 1H, H-6), 2.12−2.24 (m, 1H, H-6), 2.21 (s, 3H, CH_3CO), 2.36−2.53 (m, 3H, H-4, 2H-7), 2.60−2.72 (m, 1H, H-4), 2.76−2.84 (m, 1H, H-5), 7.28−7.49 (m, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 22.9, 24.8, 28.2, 47.3, 116.1, 117.0, 126.1 (ArH), 126.2 (ArH), 127.0 (ArH), 127.1 (ArH), 129.0 (ArH), 129.1 (ArH), 134.8 (Ar), 135.0 (Ar), 152.1 (C-2), 209.3 ($COCH_3$). MS (70 eV) m/z 332 (M^+, 1), 265 (6), 237 (100), 223 (14), 195 (20), 159 (18), 133 (10), 109 (13), 91 (10). HRMS (EI) m/z [M^+] calcd for $C_{21}H_{20}N_2O_2$: 332.1525. Found: 332.1524.

5-Formyl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (19b). Following the method for preparation of **19a**, a mixture of **8a** (0.100 g, 0.38 mmol), **18b** (0.064 g, 1.14 mmol), and $BF_3 \cdot Et_2O$ (0.010 g, 0.07 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at −78 °C under N_2 for 5 min to give **19b** (0.113 g, 93%) as a pale yellow oil. R_f 0.15 (hexane/EtOAc, 7:3). IR (film) 2929, 1702, 1663, 1597, 1498, 1406, 1265, 759, 734, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.80−1.96 (m, 1H, H-6), 2.15−2.26 (m, 1H, H-6), 2.40−2.48 (m, 2H, H-7), 2.55 (dm, J = 15.6 Hz, 1H, H-4), 2.62−2.80 (m, 2H, H-4, H-5), 7.26−7.49 (m, 10H, ArH), 9.71 (s, 1H, CHO). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 19.9 (C-7), 20.8 (C-4), 22.1 (C-6), 46.0 (C-5), 115.7 (C-7a), 117.3 (C-3a), 126.1 (ArH), 126.2 (ArH), 127.1 (ArH), 127.2 (ArH), 129.0 (ArH), 129.1 (ArH), 134.7 (Ar), 134.8 (Ar), 152.0 (C-2), 202.3 (CHO). MS (70 eV) m/z 318 (M^+, 63), 290 (15), 287 (19), 261 (28), 249 (100), 170 (10), 130 (6), 105 (13), 77 (14). HRMS (EI) m/z [M^+] calcd for $C_{20}H_{18}N_2O_2$: 318.1368. Found: 318.1366.

5-Acetyl-1,3-diphenyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (10a). A mixture of **19a** (0.070 g, 0.21 mmol) and DDQ (0.095 g, 0.42 mmol) in anhydrous CH_2Cl_2 (15 mL) was stirred at 20 °C under N_2 for 24 h. The mixture was filtered through column chromatography packed with Celite (3 g) on top of silica gel (5 g) (CH_2Cl_2). The solvent was removed under vacuum, and the crude was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 95:5) to give **10a** (0.048 g, 70%) as a white solid. R_f 0.48 (hexane/EtOAc, 7:3); mp 170−171 °C. IR (KBr) 1718, 1675, 1587, 1496, 1448, 1389, 1255, 743, 695, 654 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 3H, CH_3CO), 7.16 (dd, J = 8.0, 0.5 Hz, 1H, H-7), 7.43−7.49 (m, 2H, Ph-H), 7.50−7.62 (m, 8H, Ph-H), 7.75 (dd, J = 2.0, 0.5 Hz, 1H, H-4), 7.77 (dd, J = 8.0, 2.0 Hz, 1H, H-6). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5 ($COCH_3$), 108.2 (C-7), 108.6 (C-4), 124.0 (C-6), 126.1 (ArH), 126.2 (ArH), 128.2 (ArH), 128.3 (ArH), 129.7 (ArH), 129.8 (ArH), 129.9 (Ar), 131.9 (Ar), 133.4 (C-5), 133.8 (C-3a or C-7a), 133.9 (C-7a or C-3a), 152.6 (C-2), 196.8 ($COCH_3$). MS (70 eV) m/z 328 (M^+, 46), 313 (66), 285 (26), 256 (38), 179 (38), 166 (32), 154 (20), 77 (100), 51 (33). HRMS (EI) m/z [M^+] calcd for $C_{21}H_{16}N_2O_2$: 328.1212. Found: 328.1232.

5-Formyl-1,3-diphenyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (10b). Following the method for preparation of **10a**, a mixture of **19b** (0.100 g, 0.31 mmol) and DDQ (0.149 g, 0.66 mmol) in anhydrous CH_2Cl_2 (15 mL) was stirred at 20 °C under N_2 for 12 h to give **10b** (0.091 g, 92%) as a pale yellow solid. R_f 0.35 (hexane/EtOAc, 7:3); mp 186−187 °C. IR (KBr) 1726, 1689, 1593, 1498, 1466, 1393, 1254, 1175, 759, 694 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 1H, H-7), 7.45−7.51 (m, 2H, Ph-H), 7.56−7.62 (m, 8H, Ph-H), 7.65 (dd, J = 8.0, 1.5 Hz, 1H, H-6), 7.67 (br s, 1H, H-4), 9.92 (s, 1H, CHO). ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.4 (C-4), 108.7 (C-7), 126.1 (ArH), 126.2 (ArH), 126.8 (C-6), 128.3 (ArH), 128.5 (ArH), 129.7 (ArH), 129.8 (ArH), 130.3 (Ar), 131.4 (C-5), 133.71 (Ar or C-7a), 133.75 (Ar or C-3a), 134.7 (Ar), 152.5 (C-2), 191.0 (CHO). HRMS (EI) m/z [M^+] calcd for $C_{20}H_{14}N_2O_2$: 314.1055. Found: 314.1057.

5-Acetyl-1-(4-chlorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (19c) and 6-Acetyl-1-(4-chlorophenyl)-3-phenyl-4,5,6,7-tetrahydro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (20). Following the method for preparation

of **19a**, a mixture of **9b** (0.100 g, 0.34 mmol), **18a** (0.07 g, 1.0 mmol), and $BF_3 \cdot Et_2O$ (0.0095 g, 0.067 mmol) in anhydrous CH_2Cl_2 (20 mL), stirring at −78 °C for 5 min, gave a mixture of **19c**/**20** (65:35) (0.113 g, 92%) as a white solid. R_f 0.18 (hexane/EtOAc, 7:3); mp 105−110 °C. IR (KBr) 2928, 1706, 1688, 1597, 1495, 1402, 1168, 1091, 1013, 837, 767, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 1.77−1.86 (m, 1H, H-6), 2.19−2.24 (m, 1H, H-6), 2.22 (s, 3H, CH_3CO), 2.39−2.55 (m, 3H, H-4, 2H-7), 2.62−2.69 (m, 1H, H-4), 2.79−2.85 (m, 1H, H-5), 7.31−7.47 (m, 9H, ArH). Signals attributed to the minor isomer **20**: 2.21 (s, CH_3CO). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 22.9, 24.8, 28.1, 47.3, 115.8, 116.7, 126.2 (ArH), 127.3 (ArH), 127.4 (ArH), 129.1 (ArH), 129.3 (ArH), 132.8 (Ar), 133.5 (Ar), 134.9 (Ar), 152.0 (C-2), 209.0 ($COCH_3$). Signals attributed to the minor isomer **20**: 20.8, 28.2, 47.2, 116.6, 117.4, 126.3 (ArH), 127.2 (ArH), 129.3 (ArH), 132.7 (Ar), 133.6 (Ar), 134.7 (Ar), 209.1 ($COCH_3$). MS (70 eV): *m*/*z* 367 (M^+, 11), 348 (15), 322 (34), 291 (45), 286 (86), 257 (43), 232 (24), 208 (43), 166 (50), 131 (49), 115 (80), 103 (61), 77 (100). HRMS (EI) *m*/*z* [M^+] calcd for $C_{21}H_{19}N_2O_2Cl$: 366.1135. Found: 366.1133.

Theoretical Calculations. The ab initio HF/6-31G(d,p) and DFT B3LYP/6-31G(d,p) calculations were carried out using Gaussian 03[30] (PC-Linux). Geometries were calculated at the B3LYP/6-31G(d,p) level, and these were employed as the starting point for optimizations at the same level. The energies and coefficients of the frontier molecular orbitals were obtained at single point from the HF/6-31G(d,p) level.

■ ASSOCIATED CONTENT

Supporting Information. Appendix 1, Copies of the ^1H NMR and ^{13}C NMR spectra of all new compounds; Appendix 2, Cartesian coordinates (B3LYP/6-31G**), energies, and lowest vibrational frequencies (RHF/6-31G**) of the optimized geometries of dienes **8a**, **9a**, **9h**, as well as cyclopentadiene (**22**). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +5255-5729-6300/46211. E-mail: jtamariz@woodward.encb.ipn.mx; jtamarizm@gmail.com

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