One-Step Synthesis and Highly Regio- and Stereoselective Diels−Alder Cycloadditions of Novel *exo*-2-Oxazolidinone Dienes

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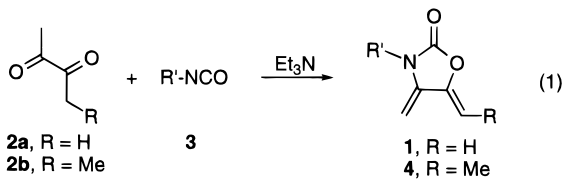
An improved synthesis of *exo*-heterocyclic dienes like *N*-substituted 4,5-dimethylene 2-oxazolidinones **1**, by a one-step method from diacetyl and isocyanates, was described. This highly convergent synthetic strategy has been successfully used for the preparation of novel (*Z*)-5-ethylidene-4-methylene analogs **4** in fair yields. Both dienes **1** and **4** undergo efficient addition of symmetric dienophiles in thermal Diels−Alder reactions, inasmuch as they react stereo- and regioselectively with the unsymmetric olefins methyl vinyl ketone (MVK) and methyl propiolate. This regioselectivity was greatly improved by using Lewis acid catalysts ($TiCl_4$, $AlCl_3$). The nitrogen atom of the 2-oxazolidinone ring seems to control the orientation of the dienophile approach. These results have been rationalized in terms of the frontier molecular orbital theory by *ab initio* calculations. For dienes **4**, addition of MVK gave the *endo* isomer as the major product. Dimerization of dienes **4** was also highly regio-, chemo-, and stereoselective, giving only isomer **17**. This reaction furnished a second product, which corresponded to dienes **18** obtained by the [1,5] sigmatropic rearrangement of **4**. The structure of the dienes and main products was established by NMR experiments and X-ray diffraction analysis.

Exocyclic dienes have attracted special attention due to their high reactivity in cycloaddition reactions and because of their synthetic potential.[1] Particularly, the preparation and study of *exo*-heterocyclic dienes have been the subject of numerous investigations.[2] Recently, we described a one-pot synthesis of the novel *N*-substituted 4,5-dimethylene 2-oxazolidinones **1** from diacetyl (**2a**) and the corresponding isocyanate **3** (eq 1).[3] Dienes **1** proved to be, for the most part, stable, and they undergo



2a, R = H
2b, R = Me

3

1, R = H
4, R = Me

Diels−Alder cycloadditions in good yields. This preliminary work has now been extended to the preparation of the substituted analogs **4**, in order to evaluate the general applicability and selectivity of our methodology. We have also studied the reactivity and selectivity of these dienes in Diels−Alder cycloadditions.

Herein, we report full details of the optimized method for the preparation of dienes **1** and the highly selective synthesis of new unsymmetric dienes **4** through the same methodology, but with 2,3-pentanedione (**2b**) as starting material. The behavior of both dienes **1** and **4** in Diels−Alder cycloadditions with symmetric and unsymmetric dienophiles is also presented. We disclose MO calculations as well, which rationalize the regioselectivity observed in these processes.

Results

Table 1 summarizes reaction conditions and yields for the preparation of dienes **1a**−**h**. For the *N*-arylated derivatives, it was found that the optimum reaction conditions corresponded to a reaction time of 24 h, with reaction mixtures diluted to a concentration of about 0.1 g/mL in dry dioxane. In addition, the stirring time of the mixture of **2a**, Et_3N, and Li_2CO_3 at room temperature was also extended in order to increase the concentration of the enolate of **2a**. Even though dienes **1** were prepared in fair yields, these were even better than those usually obtained by multistep synthetic approaches for similar *exo*-heterocyclic dienes.[2] The reaction was likely dependent on the substituent of the isocyanate, because aryl isocyanates with electron-withdrawing groups on the *N*-benzene ring, such as the nitro, gave no reaction.

Dienes **4a**−**j** were prepared under similar conditions using 2,3-pentanedione (**2b**) as the starting α-diketone. The reaction time was shorter (12 h) for these compounds, and the yields were comparable to those of dienes **1**, with the exception of derivatives **4g**−**j**. The low yields ob-

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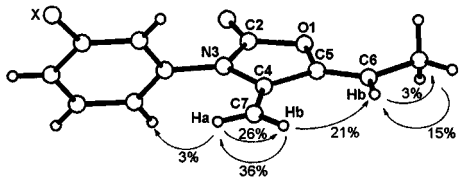
Table 1. Improved Reaction Conditions and Yields in the Preparation of Dienes 1 and 4[a]

entry	R′	diene	yield (%)[b]	mp (°C)
1	Ph	**1a**	54	75−76
2	C_6H_4-*p*-Cl	**1b**	70	106−107
3	C_6H_4-*m*-Cl	**1c**	40	57-dec
4	C_6H_4-*o*-Me	**1d**	45	oil
5	C_6H_4-*p*-Me	**1e**	45	79−80
6	C_6H_4-*m*-Me	**1f**	40	54−55
7	C_6H_4-*o*-Br	**1g**	60	88−89
8	$(CH_2)_2Cl$	**1h**	69	oil
9	Ph	**4a**	53	83−84
10	C_6H_4-*p*-Cl	**4b**	54	78−79
11	C_6H_4-*m*-Cl	**4c**	47	82−83
12	C_6H_4-*p*-Me	**4d**	40	92−93
13	C_6H_4-*m*-Me	**4e**	42	80−81
14	C_6H_4-*m*-MeO	**4f**	38	83−84
15	C_6H_4-*o*-Cl	**4g**	27	79−80
16	C_6H_4-*o*-Br	**4h**	18	78−79
17	C_6H_4-*o*-Me	**4i**	23	81−82
18	$(CH_2)_2Cl$	**4j**	26	oil

[a] Dioxane as the solvent, with Et_3N (1.5 mol equiv for dienes **1** and 2.0 mol equiv for dienes **4**) as the base and Li_2CO_3 (1.2 mol eq) as the additive at rt, except in entry 8 (60 °C). The reaction time was 24 h for dienes **1**, except diene **1h** (4 h), and 12 h for dienes **4**. [b] After column chromatography and recrystallization.



4a, X = H
4c, X = Cl

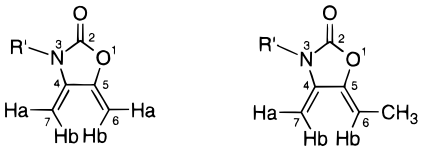
Figure 1. Structure of diene **4c** and NOEs observed upon irradiation of protons in diene **4a**. The figure was constructed from the X-ray crystallographic data of **4c**.

tained for some of the latter could be associated with steric interactions between the *ortho*-substituent of the aryl isocyanate and the more crowded diketone **2b**. It is noteworthy that ^{1}H NMR analysis of the crude mixtures did not give evidence of the presence of any other isomer. Therefore, the reaction was highly regio- and stereoselective.

Diene **4c** was isolated as colorless crystals (acetone/hexane, 9:1) and its structure was unambiguously established by X-ray diffraction analysis.[4] It can be observed that the aromatic ring is almost perpendicular to the diene plane, with the oxazolidinone ring being planar due to the sp^2 configuration of the nitrogen (Figure 1). ^{1}H NMR spectra of dienes **4** showed chemical shifts for the vinylic protons similar to those in dienes **1**, along with the H_6 signal at low-field as a quartet (Table 2). The most shielded proton corresponded to H_{7a}. The assignment was done by NOE experiments, indicating that the methyl group was located on methylene C_6, vicinal to the oxygen, and with *Z* configuration, as shown by the X-ray structure.

In dienes **1**, the most shielded proton also corresponded to H_{7a}, with H_{6b} being at the lowest field. A shielding magnetic effect of the aryl ring on the spatial region of

Table 2. ^{1}H NMR Data of the Vinylic Protons of Dienes 1a−h and 4a−j



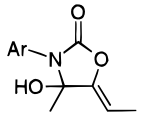
1 **4**

	δ (ppm)			
diene	H-6a[a] or CH_3[b]	H-6b	H-7a[c]	H-7b[c]
1a	4.93	4.98[a]	4.35	4.76
1b	4.93	4.99[a]	4.35	4.78
1c	4.95	5.00[a]	4.40	4.80
1d	4.94	4.98[a]	4.01	4.72
1e	4.90	4.95[a]	4.30	4.72
1f	4.92	4.97[a]	4.34	4.75
1g	4.96	5.00[a]	4.01	4.76
1h	4.89	4.95[a]	4.42	4.79
4a	1.86	5.42[d]	4.18	4.58
4b	1.86	5.43[d]	4.17	4.59
4c	1.86	5.43[d]	4.21	4.61
4d	1.85	5.40[d]	4.15	4.55
4e	1.86	5.40[d]	4.16	4.56
4f	1.86	5.43[d]	4.22	4.58
4g	1.87	5.43[d]	3.85	4.57
4h	1.90	5.44[d]	3.82	4.59
4i	1.86	5.41[d]	3.83	4.53
4j	1.82	5.39[d]	4.23	4.61

[a] As a doublet, *ca.* J = 3.6 Hz. [b] As a doublet, *ca.* J = 7.3 Hz. [c] As doublets, *ca.* J = 3.0 Hz. [d] As a quartet, *ca.* J = 7.3 Hz.

H_{7a},[5] as expected from the almost orthogonal position of the aryl ring plane with respect to the *bis*-methylene plane (Figure 1), could account for the diamagnetic shift of this proton. However, this factor should be discarded, because a similar chemical shift pattern for the dienic protons was observed for the *N*-alkyl derivative **1h**. It could be argued[6] that there is a common electron-releasing effect from the nitrogen atom lone-pair, present in all the dienes as an enamide system. The signal assignment was done by NOE experiments (Figure 1).

Interestingly, in the preparation of *N*-tolyl derivatives **4d** and **4e**, 5-ethylidene-4-hydroxy-4-methyl-2-oxazolidinones **5a** and **5b** were also isolated, respectively, in low yields. The structure of these compounds suggests that they may be involved as the last precursors in the mechanism of formation of dienes **4** by dehydration (vide infra).



5a, Ar = *p*-tolyl
5b, Ar = *m*-tolyl

The thermal Diels−Alder reaction of dienes **1a** and **4a** with the symmetrical dienophile dimethyl acetylenedicarboxylate (**6**) (Scheme 1) provided the corresponding adducts **7** and **8** (Table 3, entries 1 and 4). The reaction of *N*-phenylmaleimide (**9**) with dienes **1a** and **1b** also took place readily at 180 °C to give adducts **10a** and **10b**, respectively.

As illustrated in Scheme 2, the cycloadditions of dienes **1a**, **1b**, **4a**, **4c**, and **4d** with unsymmetrical olefins such

(4) The authors have deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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Scheme 1

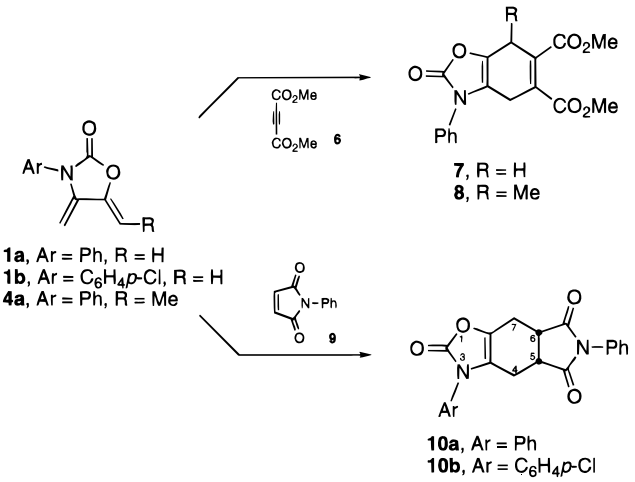


Table 3. Diels−Alder Cycloadditions of Dienes 1a, 1b, and 4a with Symmetric Olefins 6 and 9[a]

entry	diene	olefin[b]	*T* (°C)	*t* (h)	product	yield (%)[c]
1	**1a**	**6**	180	1.0	**7**	56
2	**1a**	**9**	180	1.0	**10a**	75
3	**1b**	**9**	180	1.0	**10b**	79
4	**4a**	**6**	130	1.0	**8**	85

[a] All under N_2 atmosphere. Thermal trials in the presence of 1−2% hydroquinone. [b] 3.0 mol equiv with dienes **1a** and **1b**, and 2.0 mol equiv with diene **4a**. [c] Corresponding to the major isomer after column chromatography and recrystallization.

as methyl vinyl ketone (**11**) and methyl propiolate (**12**) were carried out either thermally or catalytically to provide the corresponding adducts with significant selectivity (Table 4). Thus, thermal (180 °C) cycloaddition of **1a** to **11** furnished a 4:1 ratio of regioisomers **13a**/**14a**. The use of catalysts such as $TiCl_4$ and $AlCl_3$ at low temperature and shorter reaction times improved this selectivity (entries 2 and 3). $BF_3{\cdot}Et_2O$ was in all cases the least efficient catalyst. Analogous results were obtained in the reaction with **12** (entries 5−11), regioisomer **15a** being the major product. As expected,[7] by decreasing the reaction temperature, the regioselectivity was much higher (entries 5−8). In order to evaluate the effect of the substituent in the aromatic ring on the selectivity, diene **1b** was added under similar conditions to dienophiles **11** and **12**, showing no difference with respect to diene **1a** (entries 12−19).

Substituted dienes **4a**, **4c**, and **4d** proved to be much more selective, since the thermal (130 °C) cycloaddition of these compounds with **11** stereoselectively furnished isomers *endo*/*exo* **13c**/**13d**, **13e**/**13f**, and **13g**/**13h**, respectively, in high yields (Table 4, entries 20, 22, and 24). None of the corresponding regioisomers **14c**−**h** were detected by ^{1}H NMR in the crude mixtures. Comparable selectivities were exhibited by the thermal reaction with **12** (entries 21 and 23), to give regioisomers **15** as the major products. No significant effect can then be attributed to the functional group in the aromatic ring, suggesting an absence or a very small electronic perturbation of the latter on the nitrogen, which could cause a change in the polarization of the diene orbitals. This inhibition of the electronic effects of the substituted benzene ring could be rationalized by the fact that the aryl ring is in an almost orthogonal conformation with respect to the *exo*-diene plane, as shown by the X-ray structure of diene **4c**.

The structures of the major isomers were established by ^{1}H NMR spectroscopy. In the case of isomers **13** and **15**, double irradiation, COSY, and NOE experiments were carried out in order to correlate the cyclohexene protons. For example, for **13c** the signals of two vicinal CH and methylene groups were observed (Figure 2). The coupling constants for proton $H_{5\beta}$ (**13a**, J = 13.8, 10.6, 9.3, and 5.8 Hz; **13c**, J = 14.0, 12.1, 10.2, and 6.4 Hz) suggest that the conformational equilibrium of the half-chair is shifted toward maintaining the equatorial position of the acetyl group on carbon C_6 (Figure 3). For isomers **13c**, **13e**, and **13g**, the methyl group on carbon C_7 would be in a pseudoaxial position. In cycloadducts **15**, the carboxymethyl group was also readily located by NOE experiments, as shown in Figure 2, because an enhancement of the signals of vinylic and aromatic protons was observed when the bis-allylic protons C_4 were irradiated.

This assignment was confirmed by single-crystal X-ray diffraction of adduct **13c**,[4] which could be recrystallized from mixtures of acetone/hexane to give colorless crystals. The cyclohexene ring exhibits a half-chair conformation with the acetyl and methyl groups in the equatorial and pseudo-axial positions, respectively, as anticipated by ^{1}H NMR spectroscopy (Figure 3). The axial conformation of H_6 gives rise to a spatial proximity to the *syn* $H_{4\alpha}$, in agreement with the NOE effect displayed when the former is irradiated.

In contrast with the dimerization of diene **1a**, in which a mixture of all possible adducts was obtained,[3] the thermal (xylene, 120 °C, 10 h) dimerization of dienes **4a** and **4c** turned out to be highly regio-, chemo-, and stereoselective, inasmuch as it afforded only the corresponding isomeric dimers **17a** and **17b**, as determined from ^{1}H NMR of the crude reaction mixtures (Scheme 3). The structures of dimers **17** were established by double irradiation and NOE experiments as depicted in Figure 4. The enhancement observed in the signals attributed to protons $H_{7\alpha}$ and $H_{5\alpha}$, when the vinylic proton H_{13} was irradiated, indicates their spatial proximity. Consequently, the methyl group C_8 and proton $H_{4\beta}$ are expected to have an interaction with the *N*-phenyl protons in the spiro oxazolidinone ring in C_6. Indeed, these enhancements were observed, supporting the relative configuration shown, which supposes a preferential *exo* transition state, with respect to the dienophilic π system, in this process.

Interestingly, besides dimers **17a** and **17b**, a second product was present in the crude reaction mixtures. This product was isolated and characterized, proving to be dienes **18a** and **18b**, respectively. Scheme 3 shows the dimer **17**/diene **18** ratios and yields obtained for the thermal treatment of dienes **4a** and **4c**. Considering the conditions of the reaction, these products were probably formed by a [1,5] sigmatropic rearrangement of the protons attached to the methyl group. In order to determine a possible equilibrium between the isomeric species **4** and **18**, they were separately heated to 120 °C, at high dilution in order to minimize the dimerization. Thus, diene **4a** was totally converted to **18a**, but the latter remained unchanged. This suggests the higher stability of isomer **18a** with the *endo*-cyclic half-dienic moiety, in comparison with the *exo*-cyclic diene system of **4a**. The *s-trans* conformation of dienes **18** was established by NOE experiments.

(7) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

Scheme 2

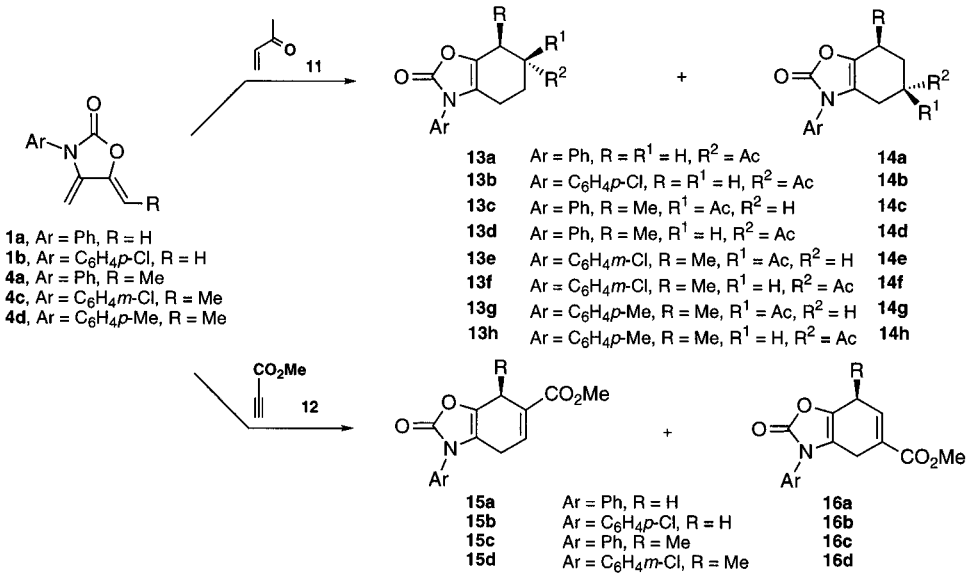
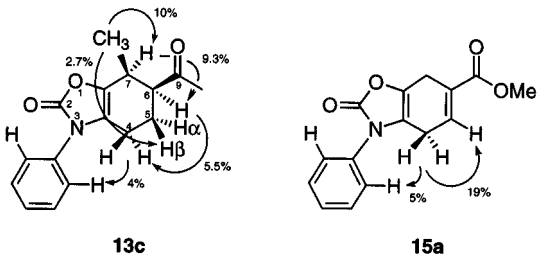


Table 4. Diels–Alder Cycloadditions of Dienes 1a, 1b, 4a, 4c, and 4d with Olefins 11 and 12[a]

entry	diene	olefin[b]	solvent	catalyst[c]	*T* (°C)	*t* (h)	products (ratio)	yield[d] (%)
1	**1a**	**11**	xylene		180	1.0	**13a**/**14a** (8:2)	63
2	**1a**	**11**	CH_2Cl_2	$TiCl_4$	−78	0.5	**13a**/**14a** (95:5)	70
3	**1a**	**11**	CH_2Cl_2	$AlCl_3$	−78	0.5	**13a**/**14a** (9:1)	68
4	**1a**	**11**	CH_2Cl_2	$BF_3{\cdot}Et_2O$	−78	0.5	**13a**/**14a** (8:2)	60
5	**1a**	**12**	xylene		180	1.0	**15a**/**16a** (1:1)	47[e]
6	**1a**	**12**	xylene		160	1.0	**15a**/**16a** (6:4)	44[e]
7	**1a**	**12**	xylene		120	6.0	**15a**/**16a** (6:4)	59[e]
8	**1a**	**12**	xylene		60	18.0	**15a**/**16a** (7:3)	60[e]
9	**1a**	**12**	CH_2Cl_2	$TiCl_4$	−78	0.5	**15a**/**16a** (92:8)	68
10	**1a**	**12**	CH_2Cl_2	$AlCl_3$	−78	0.5	**15a**/**16a** (89:11)	61
11	**1a**	**12**	CH_2Cl_2	$BF_3{\cdot}Et_2O$	−78	0.5	**15a**/**16a** (57:43)	58
12	**1b**	**11**	xylene		180	1.0	**13b**/**14b** (8:2)	46
13	**1b**	**11**	CH_2Cl_2	$TiCl_4$	−78	0.5	**13b**/**14b** (95:5)	72
14	**1b**	**11**	CH_2Cl_2	$AlCl_3$	−78	0.5	**13b**/**14b** (9:1)	65
15	**1b**	**11**	CH_2Cl_2	$BF_3{\cdot}Et_2O$	−78	0.5	**13b**/**14b** (7:3)	64
16	**1b**	**12**	xylene		180	1.0	**15b**/**16b** (1:1)	40[e]
17	**1b**	**12**	CH_2Cl_2	$TiCl_4$	−78	0.5	**15b**/**16b** (9:1)	72
18	**1b**	**12**	CH_2Cl_2	$AlCl_3$	−78	0.5	**15b**/**16b** (9:1)	53
19	**1b**	**12**	CH_2Cl_2	$BF_3{\cdot}Et_2O$	−78	0.5	**15b**/**16b** (6:4)	57[e]
20	**4a**	**11**	xylene		130	1.0	**13c**/**13d** (96:4)	90
21	**4a**	**12**	xylene		130	1.0	**15c**/**16c** (93:7)	90
22	**4c**	**11**	xylene		130	1.0	**13e**/**13f** (96:4)	91
23	**4c**	**12**	xylene		130	1.0	**15d**/**16d** (92:8)	92
24	**4d**	**11**	xylene		130	1.0	**13g**/**13h** (9:1)	88

[a] All under N_2 atmosphere. Thermal trials in the presence of 1−2% hydroquinone. [b] 3.0 mol equiv with dienes **1a** and **1b**, and 2.0 mol equiv with dienes **4a**, **4c**, and **4d**. [c] 5.0 mol equiv. [d] Corresponding to the major isomer after column chromatography and recrystallization. [e] Of the pure isomeric mixture.



13c **15a**

Figure 2. NOE percentages shown in compounds **13c** and **15a**.

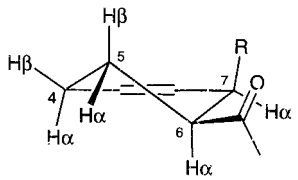
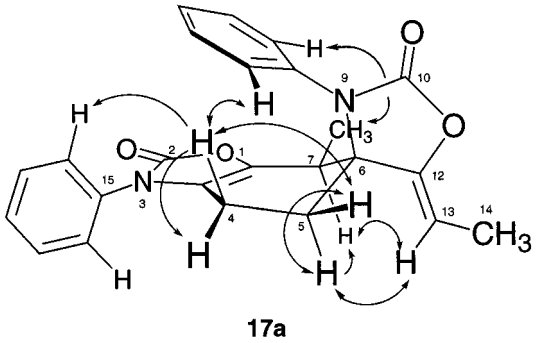


Figure 3. Half-chair conformation of cyclohexene moiety of adducts **13a** (R = H) and **13c** (R = Me).

Discussion

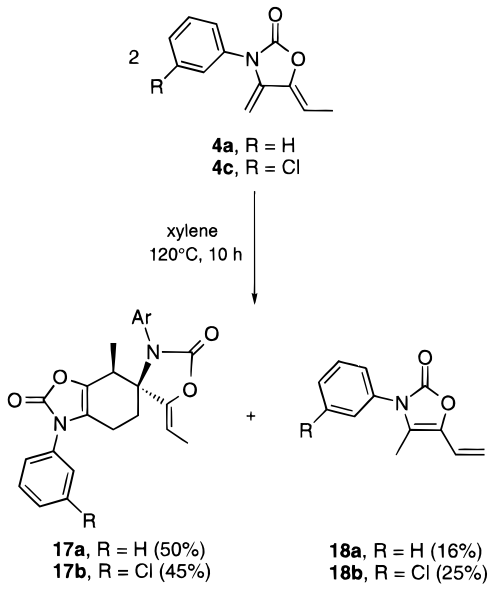
The one-pot reaction method for the preparation of dienes **1a**–**h** was improved by modifying some reaction parameters. This method also proved to be applicable to the synthesis of novel substituted dienes **4a**–**j**, as the formation of these compounds was highly selective. Considering these results, one can propose a reaction mechanism for this synthetic pathway (Scheme 4). In the case of dienes **4**, the thermodynamically more stable enolate **19b**, with respect to **20b** and **21**, adds to the isocyanate to give intermediate **22b**. The ring closure would give rise to oxazolidinone **23b** by addition of the carbamide to the carbonyl group. Protonation and dehydration of this intermediate would provide the desired dienes **4**, probably via precursors **5** and **25b**. The



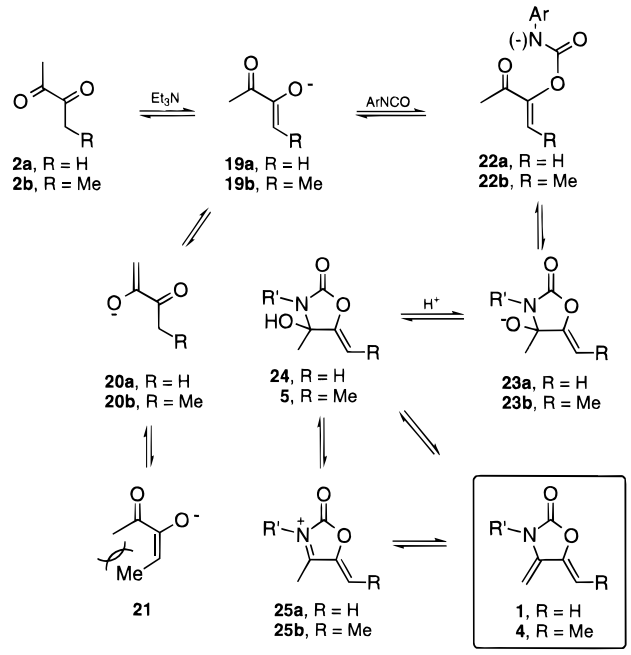
17a

Figure 4. NOEs observed upon irradiation of protons in compound **17a**.

Scheme 3



Scheme 4



isolation of 4-hydroxy-2-oxazolidinones **5a** and **5b** would support this mechanism. The dehydration step would be favored by the presence of drying agents, such as Li_2CO_3 or $MgSO_4$. In fact, the yield of the reaction dramatically decreases in the absence of these additives.[3] A similar mechanism could be postulated for the formation of dienes **1** (Scheme 4).

The cyclization step seems to be the rate-determining one. Considering that this process would depend on the nucleophilicity of the carbamide anion **22**, one might expect that electron-withdrawing groups in the *N*-aryl ring restrain the addition to the carbonyl group. Indeed, the reaction with nitroaryl isocyanates and diacetyl (**2a**) failed to give the corresponding dienes.[3]

The stereoselectivity in the formation of dienes **4** would depend on the stability of the primarily formed enolate **19b**, this being even more stable than the *E* enolate **21**. This is probably due to repulsive van der Waals interactions generated between the vinylic methyl and the acetyl groups.

It was also possible to assess the relative reactivity and selectivity in the addition of dienes **1** and **4** to symmetrical and unsymmetrical dienophiles under both thermal and Lewis acid conditions. Thus, the temperature used in the reaction between diene **4a** and olefin **6** was lower than that used in the reaction with the unsubstituted diene **1a**, obtaining similar yields within the same reaction time. This confirms the expected higher reactivity of diene **4a** due to the presence of the methyl group.[8]

Moreover, substituted dienes **4a** and **4c** proved to be much more regioselective than dienes **1**, since the thermal cycloaddition of the former compounds with **11** stereoselectively furnished the *endo*/*exo* isomers **13c**/**13d** and **13e**/**13f** in high yields (Table 4). An analogous comparison can be made with the regioselectivities exhibited with olefin **12** (Table 4). The enhancement of the regioselectivity shown by dienes **4** could also be a consequence of the polarization of the π system toward the C_7 terminus, due to the electron-donating effect of the methyl group on C_6. Bond distances in the X-ray structure of **4c** (Figure 1) would reveal this polarization and the delocalization of the lone-pair of the heteroatoms of the 2-oxazolidinone ring through the dienic π system. The shortening of the $C_5{=}C_6$ (1.28(1) Å) double bond in comparison with $C_4{=}C_7$ (1.34(1) Å) suggests a larger electron-donating effect of the lone-pair of the nitrogen atom with respect to that of the oxygen. In addition, the shortness of the $O_1{-}C_2$ (1.329(9) Å; average length, 1.350 Å[9]) bond reflects electronic delocalization of the lone-pair of the oxygen O_1 toward the carbonyl group rather than the dienic moiety. The above would be further supported by an $O_1{-}C_5$ (1.419(8) Å, average length: 1.354 Å[9]) bond longer than expected, as indeed is shown by the crystal structure.

No significant effect on the regioselectivity could be detected by changing the functional group in the *N*-aromatic ring (Table 4), suggesting the absence of or a very small electronic perturbation of the latter on the nitrogen atom, which would polarize the diene orbitals differently. This could be explained by the fact that the aryl ring molecular π orbitals cannot efficiently overlap the nitrogen lone-pair, because they are almost orthogonal, as shown by X-ray structure of diene **4c** (Figure 1).

The high stereoselectivity displayed by the additions of dienes **4** to **11**, giving as major isomers **13c**, **13e**, and **13g**, indicates an *endo* preference at the transition state

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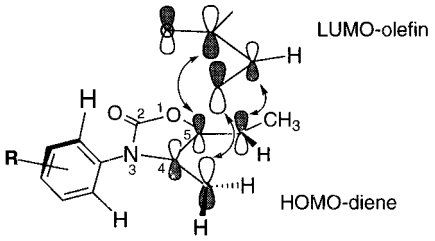

Figure 5. Possible Diels−Alder transition state for the *endo* cycloaddition between dienes **4** and dienophile **11**, showing the secondary orbital interaction between C_5 and C=O.

Table 5. *Ab initio* RHF/3-21G, 6-31G*, and 6-31G Frontier Molecular Orbitals of Dienes 1a and 4a and Olefins 11 and 12**

		3-21G	6-31G*	6-31G**
compound	FMO	*E* (eV)	*E* (eV)	*E* (eV)
1a	HOMO	−8.9855	−8.8342	−8.8051
1a	LUMO	2.8161	2.9470	2.9065
4a	HOMO	−8.7227	−8.5804	−8.5610
4a	LUMO	3.0093	3.1448	3.1035
11[a]	HOMO	−10.5391	−10.4895	−10.4868
11[a]	LUMO	2.9002	2.9222	2.9217
12[b]	HOMO	−11.6713	−11.4648	−11.4621
12	LUMO	3.0719	3.2972	3.2891

[a] Of the most stable *s-cis* conformation. [b] For levels 6-31G* and 6-31G**, the gaps for dienophile **12** were calculated with the NHOMO, since its HOMO does not have any p_z contribution.

(Figure 5). The dienophile seems not to be perturbed by the position of the aryl ring out of the plane of the exocyclic diene. The *endo* preference also suggests a minimal contribution from possible electrostatic repulsions between the lone-pairs of the heteroatoms, i.e., oxygen and nitrogen, and the π electrons of the acetyl group.[10]

The regioselectivity cannot be explained simply on the basis of the steric effect exerted by the *N*-aryl ring of the diene component. Therefore, this could be correlated instead to the energies and coefficients of the frontier molecular orbitals.[11] Frontier molecular orbitals (FMO) of dienes **1a** and **4a** and methyl vinyl ketone (**11**) and methyl propiolate (**12**) were calculated using an *ab initio* RHF procedure. Geometries were fully optimized by the AM1 semiempirical method[12] and employed as the starting point for optimization, using 3-21G, 6-31G*, and 6-31G** basis sets.[13] The energy levels derived from these calculations are summarized in Table 5. The energies for both HOMO and LUMO of dienes **1a** and **4a** are lower at the 3-21G level with respect to the other two levels, 6-31G** providing the less stable HOMO set; however, in the case of LUMOs, the 6-31G* level yielded the highest energies. A similar trend is shown by the FMOs of olefins **11** and **12**. From the energy diagrams (only 6-31G** is illustrated, Figure 6) it appears that the *normal electron demand* interaction,[14] HOMO-diene/LUMO-dienophile, is largely preferred (1.47−2.88 eV) (Table 6). The higher reactivity shown by diene **4a** in comparison with **1a** could account for a more energetic HOMO of the former with respect to the latter by 0.244 eV. Figure 6 would also explain the origin of the larger regioselectivity found for **11** with both dienes, since the energy gap of HOMO-diene/LUMO-**11** is smaller than that of HOMO-diene/LUMO-**12** (0.367 eV) due to the more stable LUMO of **11**.

Table 7 lists the relative magnitudes for the HOMO and LUMO coefficients calculated at the 6-31G** level. On the basis of coefficient differences for the proper frontier orbital interaction between diene and dienophile, regioselectivity could then be estimated. It can be observed that the relative magnitude of the coefficient of the diene terminus C_4 is bigger than that of carbon C_1 in the HOMO of both dienes **1a** and **4a**. This polarization of the π-system could be caused by the lower electronegativity and higher releasing capacity of the lone-pair nitrogen atom, as compared with the oxygen atom of the heterocycle. A significant coefficient on the nitrogen atom in the HOMO would support this preferential contribution. Therefore, in order to rationalize the presence of adducts **13** and **15** as the major regioisomers when the addition takes place with olefins **11** and **12**, respectively, the main interactions to be expected are those between carbon C_4 of dienes **1a** and **4a** with carbon C_1 of dienophiles **11** and **12**. This was confirmed by the RHF calculations, assuming that the largest FMO coefficients will become bonded preferentially at the transition state.[11,14] The largest LUMO coefficients of the dienophiles are located on the unsubstituted carbon C_1 (Table 7), as depicted in Figure 7. Similar predictions were deduced from the calculations at the 3-21G and 6-31G* levels.

Our calculations also show large coefficients on the diene internal carbons C_4 and C_5. Particularly, the C_4 coefficient could participate in stabilizing the *endo* transition state by secondary orbital interactions,[15] with the large coefficients in the carbonyl group of the dienophile (Figure 5).[16]

The self-addition of dienes **4**, which yielded only one of the eight possible adducts, could be controlled by steric effects.[17] The interaction between the diene and the methyl group of the C_5=C_6 double bond of the dienophile would prevent addition to this substituted terminus. The preferential cycloaddition to the methylene on C_4 would be restrained in the orientation of the cycloaddends, yielding the *meta* regioisomer (position of the methyl group relative to the spiro quaternary carbon), because of the possible destabilizing interactions between the

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(13) RHF/3-21G and 6-31G* calculations were performed using MacSpartan,[13a] and at the 6-31G** level with Gaussian 94.[13b] (a) MacSpartan, v 1.0, Wave Function Inc., 18401 Von Karman, Suite 370, Irvine, CA 92715. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Reploge, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

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Table 6. Energy Gaps (eV) of Frontier Orbitals for Dienes 1a and 4a and Dienophiles 11 and 12

		11[a]			12[a]		
method	diene	HOMO−LUMO	LUMO−HOMO	diff	HOMO−LUMO	LUMO−HOMO	diff
6-31G** [b]	**1a**	11.727	13.393	1.666	12.094	14.368	2.274
6-31G** [b]	**4a**	11.483	13.590	2.107	11.850	14.565	2.715
6-31G* [b]	**1a**	11.756	13.436	1.680	12.131	14.412	2.281
6-31G* [b]	**4a**	11.502	13.634	2.132	11.877	14.610	2.733
3-21G	**1a**	11.885	13.355	1.470	12.057	14.487	2.430
3-21G	**4a**	11.623	13.548	1.925	11.795	14.680	2.885

[a] HOMO-diene/LUMO-dienophile and LUMO-diene/HOMO-dienophile. [b] The gaps for dienophile **12** were calculated with the NHOMO, since its HOMO does not have any p_z contribution.

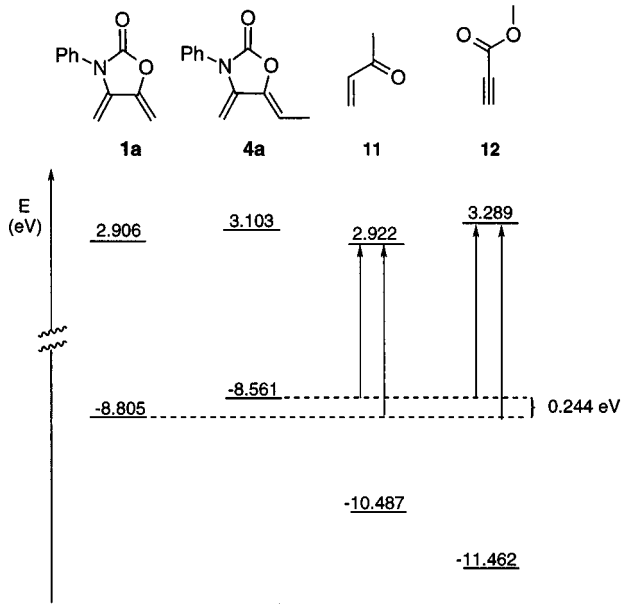

Figure 6. *Ab initio* RHF/6-31G** frontier molecular orbital interactions for the Diels−Alder reaction between dienes **1a** and **4a** and olefins **11** and **12**.

N-phenyl ring of the diene and the bulky substituents of the dienophile.

The enhancement of the regioselectivity of the additions of **1a** to olefins **11** and **12** by the presence of Lewis acids has been explained as a consequence of complexation of the dienophile with the Lewis acid.[18] This interaction stabilizes the LUMO and increases the relative magnitude of the eigenvector coefficient on the unsubstituted terminus of the olefin, leading to a stronger perturbation and, consequently, to an increase in both reactivity and selectivity.[8a,11]

Conclusion

In summary, the one-pot reaction between α-diketones and the corresponding isocyanates, used originally for preparing dienes **1**, proved to be a versatile and efficient methodology to obtain methyl-substituted dienes **4a**−**j**, in moderate yields. The geometry and position of the methyl group on the exocyclic diene was completely controlled in the process. Dienes **4** proved to be highly regio- and stereoselective in Diels−Alder additions with unsymmetric olefins **11** and **12** under thermal conditions. In the case of dienes **1**, the use of Lewis acids drastically improved the regioselectivity with the same dienophiles. The methyl group in dienes **4** appears to be the reason for the increase in the reactivity and selectivity of these dienes with respect to dienes **1**. The highly selective dimerization of dienes **4** would be controlled by steric hindrance. The FMO model, using *ab initio* calculations, seems to interpret the regioselectivity obtained in our Diels−Alder cycloadditions. Isomerization of dienes **4** to dienes **18** *via* a [1,5] sigmatropic rearrangement would be controlled by the greater thermodynamic stability of the latter.

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Experimental Section

General. All air and moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. Dioxane and xylene were freshly distilled from sodium. Li_2CO_3 was dried overnight at 100 °C before using. Triethylamine was freshly distilled from NaOH. Further analytical procedures were described elsewhere.[19]

General Procedure for the Preparation of *N*-Aryl-4,5-Dimethylene-2-oxazolidinones (1a−g). A solution of 2,3-butanedione (**2a**) (3.0 g, 34 mmol) in dry dioxane (10 mL) and triethylamine (5.29 g, 52 mmol) were added dropwise to a magnetically stirred solution of dioxane (10 mL) containing anhydrous Li_2CO_3 (2.5 g, 34 mmol) at rt under N_2 atmosphere, and the mixture was stirred for 30 min. Then, a solution of the corresponding aryl isocyanate (52 mmol) in dioxane (10 mL) was added over a period of 30 min and stirring was continued for 12 h at rt. The mixture was filtered and the solvent removed under vacuo. The residue was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 95:5) to give dienes **1a**−**g**.

4,5-Dimethylene-*N*-phenyl-2-oxazolidinone (1a). Using the general procedure with 6.23 g of phenyl isocyanate (**3a**) gave 3.52 g (54%) of **1a** as colorless crystals (CH_2Cl_2/hexane, 1:3): R_f 0.63 (hexane/EtOAc, 8:2); mp 75−76 °C; IR (KBr) 1745, 1510, 1400, 1310 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.35 (d, J = 3.0 Hz, 1H), 4.76 (d, J = 3.0 Hz, 1H), 4.93 (d, J = 3.5 Hz, 1H) 4.98 (d, J = 3.5 Hz, 1H), 7.35−7.55 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.2 (C-7), 87.5 (C-6), 127.5 (C-9), 129.3 (C-11), 130.3 (C-10), 133.6 (C-8), 139.4 (C-4), 149.4 (C-5), 152.9 (C-2); MS (70 eV) 187 (M^+, 45), 143 (87), 117 (49), 104 (51), 91 (22), 77 (100), 51 (52). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.57; H, 4.84; N, 7.48. Found: C, 70.39; H, 4.87; N, 7.33.

***N*-(*p*-Chlorophenyl)-4,5-dimethylene-2-oxazolidinone (1b).** Using the general procedure with 7.98 g of *p*-chlorophenyl isocyanate (**3b**) gave 5.4 g (70%) of **1b** as colorless crystals (CH_2Cl_2/hexane, 1:1): R_f 0.68 (hexane/EtOAc, 8:2); mp 106−107 °C; IR (KBr) 1750, 1700, 1490, 1400, 1300 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.35 (d, J = 3.2 Hz, 1H), 4.78 (d, J = 3.2 Hz, 1H), 4.93 (d, J = 3.6 Hz, 1H), 4.99 (d, J = 3.6 Hz, 1H), 7.27−740 (m, 2H), 7.40−7.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.7 (C-7), 87.3 (C-6), 128.2, 130.0, 131.5, 134.6, 138.5, 148.6, 152.1; MS (70 eV) 221 (M^+, 100), 186 (19), 177 (7), 151 (34), 142 (83), 137 (84), 111 (49), 102 (21), 75 (73), 51 (9). Anal. Calcd for $C_{11}H_8ClNO_2$: C, 59.61; H, 3.64. Found: C, 59.57; H, 3.77.

General Procedure for the Preparation of (5*Z*)-*N*-Substituted-5-ethylidene-4-methylene-2-oxazolidino-

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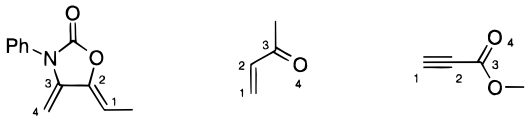
Table 7. *Ab Initio* RHF/6-31G Calculations of Coefficients (C_i) of the Frontier Molecular Orbitals for Dienes 1a and 4a and Dienophiles 11 and 12[a]**



1a, R = H
4a, R = Me

11

12

	HOMO							LUMO						
compound	C_1	C_2	C_3	C_4	C_N	C_O	ΔC_i[b]	C_1	C_2	C_3	C_4	C_N	C_O	ΔC_i[b]
1a	0.246	0.164	−0.209	−0.326	−0.242	0.139	0.080	0.263	−0.245	−0.245	0.258	0.068	0.058	0.005
4a	−0.257	−0.199	0.198	0.320	−0.216	0.150	0.063	0.274	−0.222	−0.245	0.248	0.066	0.050	0.026
11	0.346	0.366	−0.039	−0.221			−0.020	0.311	−0.208	−0.280	0.254			0.103
12[c]	0.374	0.394	−0.034	−0.192			−0.020	0.289	−0.184	−0.338	0.278			0.105

[a] These are the values of the $2p_z$ coefficients; the relative $3p_z$ contributions and their ΔC_i are analogous. [b] Carbon 4−carbon 1 for the dienes and carbon 1−carbon 2 for the olefins. [c] These values are for the NHOMO; the HOMO does not have any p_z contribution.

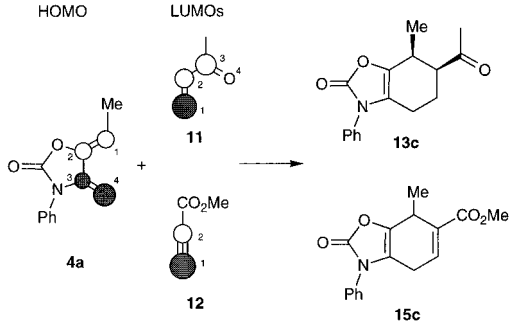


Figure 7. *Ab initio* RHF/6-31G** frontier molecular orbital interactions for the Diels−Alder reaction between diene **4a** and olefins **11** and **12**.

nes (4a−j). A solution of 2,3-pentanedione (**2b**) (0.35 g, 3.5 mmol) in dry dioxane (1 mL) was added dropwise to a magnetically stirred solution of triethylamine (0.71 g, 7.0 mmol) in dioxane (2 mL) containing anhydrous Li_2CO_3 (0.31 g, 4.2 mmol) at rt under N_2 atmosphere, and the mixture was stirred for 30 min. Then, a solution of the corresponding aryl isocyanate (5.2 mmol) in dioxane (2 mL) was added over a period of 30 min and stirring was continued for 12 h at rt. The mixture was filtered and solvent removed under vacuo. The residue was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 9:1) to give dienes **4a−j**.

(5*Z*)-5-Ethylidene-4-methylene-*N*-phenyl-2-oxazolidinone (4a). Using the general procedure with phenyl isocyanate (**3a**) (0.62 g) gave 0.55 g (53%) of **4a** as colorless crystals (CH_2Cl_2/hexane, 1:1): R_f 0.5 (hexane/EtOAc, 9:1); mp 83−84 °C; IR (KBr) 1770, 1690, 1480, 1390 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (dt, J = 7.3, 0.7 Hz, 3H, CH_3C=), 4.18 (d, J = 2.9 Hz, 1H, H-7a), 4.58 (d, J = 2.9 Hz, 1H, H-7b), 5.42 (q, J = 7.3 Hz, 1H, H-6b), 7.33−7.53 (m, 5H, PhH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 (q, J = 129.0 Hz, C-8), 81.6 (t, J = 164.5 Hz, C-7), 99.0 (dq, J = 158.8, 7.4 Hz, C-6), 127.1 (ddd, J = 162.9, 7.5, 4.9 Hz, C-10), 128.7 (dt, J = 161.7, 7.5 Hz, C-12), 129.7 (dd, J = 162.7, 7.8 Hz, C-11), 133.4 (t, J = 8.7 Hz, C-9), 139.4 (br s, C-4), 143.3 (m, C-5), 152.7 (s, C-2); MS (70 eV) 201 (M^+, 4), 156 (4), 118 (41), 104 (13), 91 (9), 77 (93), 55 (26), 51 (100). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.50; N, 6.96. Found: C, 71.55; H, 5.64; N, 6.84.

(5*Z*)-*N*-(*p*-Chlorophenyl)-5-ethylidene-4-methylene-2-oxazolidinone (4b). Using the general procedure with *p*-chlorophenyl isocyanate (**3b**) (0.79 g) gave 0.65 g (54%) of **4b** as colorless crystals (CH_2Cl_2/hexane, 1:1): R_f 0.45 (hexane/EtOAc, 9:1); mp 78−79 °C; IR (KBr) 1780, 1700, 1500, 1390 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (dt, J = 7.3, 0.7 Hz, 3H), 4.17 (d, J = 3.1 Hz, 1H), 4.59 (d, J = 3.1 Hz, 1H), 5.43 (q, J = 7.3 Hz, 1H), 7.25−7.32 (m, 2H), 7.42−7.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 (q, J = 128.8 Hz, C-8), 81.7 (t, J = 164.7 Hz, C-7), 99.5 (dq, J = 159.1, 7.3 Hz, C-6), 128.0 (dd, J = 165.2, 5.7 Hz, C-10), 130.2 (dd, J = 168.3, 5.3 Hz, C-11), 131.7 (m, C-9), 134.6 (m, C-12), 138.9 (br s, C-4), 143.0 (m, C-5), 152.5 (s, C-2); MS (70 eV) 237 (M^+ + 2, 33), 235 (M^+, 100), 220 (2), 190 (9), 152 (90), 138 (39), 129 (17), 111 (38), 75 (31). Anal. Calcd for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.27; N, 5.94. Found: C, 60.90; H, 4.16; N, 5.79.

(5*Z*)-*N*-(*m*-Chlorophenyl)-5-ethylidene-4-methylene-2-oxazolidinone (4c). Using the general procedure with *m*-chlorophenyl isocyanate (**3c**) (0.79 g) gave 0.57 g (47%) of **4c** as colorless crystals (CH_2Cl_2/hexane, 1:1); R_f 0.45 (hexane/EtOAc, 9:1); mp 82−83 °C; IR (KBr) 1780, 1700, 1510, 1400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (d, J = 7.3 Hz, 3H), 4.21 (d, J = 3.1 Hz, 1H), 4.61 (d, J = 3.1 Hz, 1H), 5.43 (q, J = 7.3 Hz, 1H), 7.26 (dt, J = 7.4, 1.8 Hz, 1H), 7.37−7.48 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4, 81.9, 99.6, 125.3, 127.4, 128.9, 130.7, 134.5, 135.3, 138.8, 143.0, 152.4; MS (70 eV) 237 (M^+ + 2, 33), 235 (M^+, 100), 191 (5), 190 (13), 154 (37), 152 (91), 138 (12), 129 (11), 111 (41), 75 (31). Anal. Calcd for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.27; N, 5.94. Found: C, 61.38; H, 4.55; N, 6.11.

(5*Z*)-5-Ethylidene-4-methylene-*N*-*p*-tolyl-2-oxazolidinone (4d). Using the general procedure with *p*-tolyl isocyanate (**3e**) (0.69 g) gave a mixture of **4d**/**5a**, which after purification yielded 0.44 g (40%) of **4d** as colorless crystals (CH_2Cl_2/hexane, 1:1) and 0.17 g (14%) of **5a** as colorless crystals (CH_2Cl_2/hexane, 1:1). **4d**: R_f 0.5 (hexane/EtOAc, 9:1); mp 92−93 °C; IR (KBr) 1780, 1690, 1510, 1400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, J = 7.3 Hz, 3H), 2.39 (s, 3H), 4.15 (d, J = 2.9 Hz, 1H), 4.55 (d, J = 2.9 Hz, 1H), 5.40 (q, J = 7.3 Hz, 1H), 7.18−7.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4, 21.2, 81.5, 98.9, 126.9, 130.3, 130.6, 138.8, 139.5, 143.3, 152.9; MS (70 eV) 215 (M^+, 90), 200 (9), 170 (80, 132 (100), 91 (46), 65 (28). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.08; N, 6.50. Found: C, 72.54; H, 6.20; N, 6.45. **5a**: R_f 0.4 (hexane/EtOAc, 4:1); mp 104−105 °C; IR (KBr) 3320, 1770, 1710, 1520, 1390 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H), 1.75 (d, J = 7.0 Hz, 3H), 2.37 (s, 3 H), 3.08 (s, 1H), 5.10 (q, J = 7.0 Hz, 1H), 7.21−7.34 (m, 4H); ^{13}H NMR (75 MHz, $CDCl_3$) δ 9.9, 21.1, 25.4, 87.8, 99.6, 127.0, 129.0, 131.0, 137.0, 150.9, 152.9. Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.13; H, 6.60; N, 5.96.

General Procedures for the Diels−Alder Reaction of Dienophiles Dimethyl Acetylenedicarboxylate (6), *N*-Phenylmaleimide (9), Methyl Vinyl Ketone (11), and Methyl Propiolate (12) with *N*-Aryl-4,5-dimethylene-2-oxazolidinones 1a and 1b. Method A. A mixture of diene **1** (0.8 mmol), dienophile (2.4 mmol), and hydroquinone (0.003 g) in dry xylene (3 mL) was placed in a sealed tube under N_2 atmosphere and heated at 180 °C for 1 h. The solvent was removed under vacuo and the residue purified by column chromatography (hexane/EtOAc, 4:1) to give the corresponding adducts.

Method B. To a solution of the diene (0.8 mmol) in dry CH_2Cl_2 (3 mL) under N_2 atmosphere at −78 °C was added the Lewis acid ($AlCl_3$, $TiCl_4$, or $BF_3{\cdot}Et_2O$) (4.0 mmol) and dienophile (2.4 mmol) in dry CH_2Cl_2 (3 mL). After being stirred at

−78 °C for 30 min, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous 5% $NaHCO_3$ (2 × 5 mL) and aqueous 5% NH_4Cl (2 × 10 mL), and finally the organic extract was dried (Na_2SO_4). The solvent was evaporated and the residue purified as above.

6-Acetyl-*N*-phenyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13a). Method A. Reaction of **1a** (0.15 g) with methyl vinyl ketone (**11**) (0.17 g) gave a mixture of **13a**/**14a** (4:1) as a pale yellow powder, which was purified and recrystallized from acetone/hexane, 9:1, to yield 0.13 g (63%) of major isomer **13a** as colorless needles: R_f 0.44 (hexane/EtOAc, 6:4); mp 111−112 °C; IR (KBr) 1750, 1700, 1500, 1400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.79 (dddd, J = 13.8, 10.6, 9.3, 5.8 Hz, 1H), 2.12−2.21 (m, 1H), 2.26 (s, 3H), 2.36−2.51 (m, 2H), 2.67−2.72 (m, 2H), 2.85−2.93 (m, 1H), 7.30−7.40 (m, 3H), 7.40−7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 22.8, 24.2, 28.1, 46.7, 120.4, 125.0, 127.6, 129.4, 133.8, 133.9, 154.4, 208.3; MS (70 eV) 257 (M^+, 21), 242 (4), 214 (4), 186 (8), 170 (38), 158 (46), 143 (44), 130 (35), 117 (47), 104 (18), 91 (9), 77 (100), 51 (36). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.16; H, 6.01; N, 5.33.

Method B. Reaction of **1a** (0.15 g) with **11** (0.17 g) in the presence of $AlCl_3$ (0.53 g) gave a mixture of **13a**/**14a** (9:1) and purification by column chromatography and recrystallization from toluene gave 0.14 g (68%) of **13a**.

Reaction of **1a** (0.15 g) with **11** (0.17 g) in the presence of $BF_3{\cdot}Et_2O$ (0.57 g) gave a mixture of **13a**/**14a** (8:2), and purification as above gave 0.124 g (60%) of **13a**.

Reaction of **1a** (0.15 g) with **11** (0.17 g) in the presence of $TiCl_4$ (0.76 g) gave a mixture of **13a**/**14a** (95:5), which was purified and recrystallized from toluene to yield 0.144 g (70%) of **13a** as colorless needles.

6-Acetyl-*N*-(*p*-chlorophenyl)-4,5,6,7-tetrahydrobenzoxazol-2-one (13b). Method A. Reaction of **1b** (0.18 g) with **11** (0.17 g) gave a mixture of **13b**/**14b** (8:2) as a pale yellow powder, which was purified and recrystallized from acetone/hexane (9:1) to yield 0.109 g (46%) of **13b**: R_f 0.41 (hexane/EtOAc, 6:4); mp 106−107 °C; IR (KBr) 1762, 1695, 1496 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.74−1.89 (m, 1H), 2.14−2.25 (m, 1H), 2.29 (s, 3H), 2.34−2.48 (m, 2H), 2.67−2.74 (m, 2H), 2.85−2.94 (m, 1H), 7.29−7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 22.8, 24.1, 28.1, 46.6, 120.1, 126.2, 129.6, 132.5, 133.3, 134.1, 154.1, 207.8. Anal. Calcd for $C_{15}H_{14}ClNO_3$: C, 61.76; H, 4.84; N, 4.80. Found: C, 61.90; H, 4.77; N, 4.67.

Method B. Reaction of **1b** (0.18 g) with **11** (0.17 g) in the presence of $AlCl_3$ (0.53 g) gave a mixture of **13b**/**14b** (9:1), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.154 g (65%) of **13b**.

Reaction of **1b** (0.18 g) with **11** (0.17 g) in the presence of $BF_3{\cdot}Et_2O$ (0.57 g) gave a mixture of **13b**/**14b** (7:3), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.152 (64%) of **13b**.

Reaction of **1b** (0.18 g) with **11** (0.17 g) in the presence of $TiCl_4$ (0.76 g) gave a mixture of **13b**/**14b** (95:5), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.171 g (72%) of **13b**.

6-(Carboxymethyl)-*N*-phenyl-4,7-dihydrobenzoxazol-2-one (15a). Method A. Reaction of **1a** (0.15 g) with methyl propiolate (**12**) (0.202 g) gave a mixture of **15a**/**16a** (1:1), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.102 g (47%) of **15a**/**16a** (1:1).

Method B. Reaction of **1a** (0.15 g) with **12** (0.202 g) in the presence of $AlCl_3$ (0.53 g) gave a mixture of **15a**/**16a** (89:11), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.132 g (61%) of **15a**.

Reaction of **1a** (0.15 g) with **12** (0.202 g) in the presence of $BF_3{\cdot}Et_2O$ (0.57 g) gave a mixture of **15a**/**16a** (57:43), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.126 (58%) of **15a**/**16a** (6:4).

Reaction of **1a** (0.15 g) with **12** (0.202 g) in the presence of $TiCl_4$ (0.76 g) gave a mixture of **15a**/**16a** (92:8), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.147 (68%) of **15a** as colorless needles: R_f 0.38 (hexane/EtOAc, 1:1); mp 175−176 °C; IR (KBr) 1750, 1700, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.20−3.27 (m, 2H), 3.40−3.47 (m, 2H), 3.82 (s, 3H), 7.02−7.08 (m, 1H), 7.31−7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 24.7, 52.8, 117.8, 125.8, 128.2, 128.5, 130.1, 133.3, 134.0, 134.4, 155.1, 166.7; MS (70 eV) 271 (M^+, 100), 256 (3), 212 (9), 167 (4), 77 (82), 59 (29), 51 (71). Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83. Found: C, 66.53; H, 4.78.

6-(Carboxymethyl)-*N*-(*p*-chlorophenyl)-4,7-dihydrobenzoxazol-2-one (15b). Method A. Reaction of **1b** (0.18 g) with **12** (0.202 g) gave a mixture of **15b**/**16b** (1:1), which was purified to yield 0.099 g (40%) of **15b**/**16b** (1:1).

Method B. Reaction of **1b** (0.18 g) with **12** (0.202 g) in the presence of $AlCl_3$ (0.53 g) gave a mixture of **15b**/**16b** (9:1), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.11 g (53%) of **15b**.

Reaction of **1b** (0.18 g) with **12** (0.202 g) in the presence of $BF_3{\cdot}Et_2O$ (0.57 g) gave a mixture of **15b**/**16b** (6:4), which was purified to yield 0.118 g (57%) of **15b**/**16b** (6:4).

Reaction of **1b** (0.015 g) with **12** (0.202 g) in the presence of $TiCl_4$ (0.75 g) gave a mixture of **15b**/**16b** (9:1), which was purified and recrystallized from acetone/hexane (9:1) to yield 0.149 g (72%) of **15b** as colorless crystals: R_f 0.34 (hexane/EtOAc, 1:1); mp 192−194 °C; IR (KBr) 1750, 1710, 1500, 1290 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.19−3.27 (m, 2H), 3.40−3.47 (m, 2H), 3.82 (s, 3H), 7.03−7.07 (m, 1H), 7.29−7.33 (m, 2H), 7.43−7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 24.6, 52.8, 117.4, 127.0, 128.2, 130.3, 133.0, 133.6, 134.1, 134.3, 154.8, 166.6; MS (70 eV) 305 (M^+, 31), 303 (100), 272 (32), 228 (3), 200 (3), 171 (3), 111 (5), 75 (15), 63 (19). Anal. Calcd for $C_{15}H_{12}ClNO_4$: C, 58.93; H, 3.96; N, 4.58. Found: C, 59.00; H, 4.07; N, 4.70.

5,6-Bis(carboxymethyl)-*N*-phenyl-4,7-dihydrobenzoxazol-2-one (7). Method A. Reaction of **1a** (0.15 g) with dimethyl acetylenedicarboxylate (**6**) (0.34 g) gave a pale yellow powder, which was recrystallized from acetone/hexane (9:1) to yield 0.148 g (56%) of **7** as colorless crystals: R_f 0.4 (hexane/EtOAc, 6:4); mp 149−150 °C; IR (KBr) 1740, 1700, 1450, 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.34−3.42 (m, 2H), 3.51−3.56 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 7.30−7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 52.7, 52.8, 116.9, 125.3, 128.2, 129.7, 130.6, 131.6, 131.8, 133.5, 154.3, 166.8, 167.2; MS (70 eV) 327 (M^+ − 2, 86), 296 (100), 281 (8), 237 (4), 77 (38), 51 (26). Anal. Calcd for $C_{17}H_{15}NO_6$: C, 62.00; H, 4.59; N, 4.25. Found: C, 61.91; H, 4.60; N, 4.18.

3*N*,9*N*-Diphenyl-3,4,5,6,7,8,9,10-octahydro-2*H*-pyrrolo[3,4-*f*]benzoxazole-2,8,10-trione (10a).[20] **Method A.** Reaction of **1a** (0.15 g) with *N*-phenylmaleimide (**9**) (0.415 g) gave a pale yellow powder, which was recrystallized from toluene to yield 0.216 g (75%) of **10a** as colorless crystals: R_f 0.4 (hexane/EtOAc, 6:4); mp 156−158 °C; IR (KBr) 1750, 1700, 1600, 1500, 1390, 1170 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (ddt, J = 17.2, 8.4, 2.4 Hz, 1H), 3.01 (ddt, J = 17.2, 3.5, 1.9 Hz, 1H), 3.06−3.11 (m, 2H), 3.49 (ddd, J = 8.7, 8.4, 3.5 Hz, 1H), 3.58 (dt, J = 8.7, 6.5 Hz, 1H), 7.25−7.52 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 20.0, 37.8, 37.9, 118.4, 125.4, 126.1, 128.2, 128.9, 129.2, 129.6, 131.5, 131.9, 133.3, 154.1, 176.9, 177.0. Anal. Calcd for $C_{21}H_{16}N_2O_4$: C, 69.99; H, 4.48; N, 7.77. Found: C, 69.78; H, 4.61; N, 7.62.

3*N*-(*p*-Chlorophenyl)-9*N*-phenyl-3,4,5,6,7,8,9,10-octahydro-2*H*-pyrrolo[3,4-*f*]benzoxazole-2,8,10-trione (10b). Method A. Reaction of **1b** (0.18 g) with **9** (0.415 g) gave a pale yellow powder, which was recrystallized from acetone/hexane (9:1) to yield 0.253 g (79%) of **10b** as colorless crystals: R_f 0.34 (hexane/EtOAc, 1:1); mp 237−238 °C; IR (KBr) 1763, 1708, 1500, 1390 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.82 (ddt, J = 16.9, 8.3, 2.3 Hz, 1H), 2.99 (ddt, J = 16.9, 3.2, 1.8 Hz, 1H), 3.08 (m, 2H), 3.49 (ddd, J = 8.7, 8.3, 3.2 Hz, 1H), 3.58 (dt, J = 8.6, 6.5 Hz, 1H), 7.30 (m, 4H), 7.40−7.55 (m, 6H). Anal. Calcd for $C_{21}H_{15}ClN_2O_4$: C, 63.89, H, 3.83, N, 7.09. Found: C, 63.67; H, 3.98; N, 6.83.

General Procedure for the Diels−Alder Reaction of Dienophiles Methyl Vinyl Ketone (11), Methyl Propiolate (12), and Dimethyl Acetylenedicarboxylate (6) with Dienes 4. A mixture of diene **4** (0.8 mmol), dienophile (1.6 mmol), and hydroquinone (0.002 g) in dry xylene (3 mL) was

(20) See Scheme 1 for the numbering scheme used.

placed in a sealed tube under N_2 atmosphere and heated at 130 °C for 1 h. The solvent was removed under vacuo and the residue purified by column chromatography (hexane/EtOAc, 4:1) to give the corresponding adducts.

(6*R,7*R**)-6-Acetyl-7-methyl-*N*-phenyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13c) and (6*R**,7*S**)-6-Acetyl-7-methyl-*N*-phenyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13d).** Using the general procedure with **4a** (0.16 g) and methyl vinyl ketone (**11**) (0.11 g) gave a mixture of **13c**/**13d** (96:4), which was purified and recrystallized from acetone/hexane (1:1) as colorless crystals to yield 0.19 g (90%) of **13c**: R_f 0.45 (hexane/EtOAc, 7:3); mp 132−133 °C; IR (KBr) 1760, 1700, 1500, 1390 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (d, J = 6.8 Hz, 3H), 1.84 (dddd, J = 14.0, 12.1, 10.2, 6.4 Hz, 1H), 1.98 (dddd, J = 14.0, 5.2, 2.8, 2.5 Hz, 1H), 2.23 (s, 3H), 2.28−2.39 (m, 2H), 2.96 (ddd, J = 12.1, 5.4, 2.8 Hz, 1H), 3.21−3.28 (m, 1H), 7.32−7.48 (m, 5H). Signals attributed to minor isomer **13d**: 0.86 (d, J = 6.8 Hz), 2.22 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 18.6, 19.9, 28.3, 28.7, 50.9, 120.5, 125.0, 127.6, 129.4, 133.8, 137.9, 154.4, 208.0; MS (70 eV) 271 (M$^+$, 70), 256 (4), 228 (11), 214 (14), 201 (100), 184 (10), 156 (7), 118 (10), 104 (4), 77 (17). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.31; N, 5.16. Found: C, 70.82; H, 6.14; N, 5.10.

(6*R,7*R**)-6-Acetyl-*N*-(*m*-chlorophenyl)-7-methyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13e) and (6*R**,7*S**)-6-Acetyl-*N*-(*m*-chlorophenyl)-7-methyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13f).** Using the general procedure with **4c** (0.204 g) and **11** (0.11 g) gave a mixture of **13e**/**13f** (96:4), which was purified and crystallized from acetone/hexane (1:1) to yield 0.236 (91%) of **13e** as colorless crystals: R_f 0.4 (hexane/EtOAc, 7:3); mp 143−144 °C; IR (KBr) 1760, 1710, 1480 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (d, J = 6.8 Hz, 3H), 1.85 (dddd, J = 14.0, 12.1, 10.2, 6.4 Hz, 1H), 2.00 (dddd, J = 14.0, 5.2, 2.7, 2.5 Hz, 1H), 2.23 (s, 3H), 2.28−2.41 (m, 2H), 2.96 (ddd, J = 12.1, 5.3, 2.7 Hz, 1H), 3.20−3.31 (m, 1H), 7.26 (ddd, J = 7.8, 2.22, 1.3 Hz, 1H), 7.32 (ddd, J = 7.5, 2.0, 1.3 Hz, 1H), 7.36−7.41 (m, 2H). Signals attributed to minor isomer **13f**: 0.83 (d, J = 6.8 Hz), 2.21 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 18.7, 20.3, 28.3, 28.7, 50.9, 120.2, 123.1, 125.2, 127.8, 130.4, 135.0, 135.1, 138.4, 154.0, 207.7; MS (70 eV) 307 (M$^+$ + 2, 33), 305 (M$^+$, 92), 290 (24), 262 (59), 248 (43), 235 (86), 218 (100), 152 (36), 111 (53), 75 (33), 43 (86). Anal. Calcd for $C_{16}H_{16}ClNO_3$: C, 62.85; H, 5.26; N, 4.58. Found: C, 63.08; H, 5.49; N, 4.62.

(6*R,7*R**)-6-Acetyl-7-methyl-*N*-*p*-tolyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13g) and (6*R**,7*S**)-6-Acetyl-7-methyl-*N*-*p*-tolyl-4,5,6,7-tetrahydrobenzoxazol-2-one (13h).** Using the general procedure with **4d** (0.17 g) and **11** (0.11 g) gave a mixture of **13g**/**13h** (9:1), which was purified and recrystallized from acetone/hexane (1:1) to yield 0.198 g (88%) of **13g** as colorless crystals: R_f 0.45 (hexane/EtOAc, 7:3); mp 140−141 °C; IR (KBr) 1760, 1700, 1510, 1390 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (d, J = 6.8 Hz, 3H), 1.83 (dddd, J = 13.9, 12.0, 9.9, 6.7 Hz, 1H), 1.96 (dddd, J = 13.9, 5.3, 2.9, 2.5 Hz, 1H), 2.22 (s, 3H), 2.25−2.33 (m, 2H), 2.37 (s, 3H), 2.95 (ddd, J = 12.0, 5.3, 2.9 Hz, 1H), 3.24 (m, 1H), 7.18−7.27 (m, 4H). Signals attributed to minor isomer **13h**: 0.85 (d, J = 6.8 Hz), 2.23 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 18.8, 19.9, 21.0, 28.4, 28.6, 51.1, 120.7, 125.1, 130.0, 131.4, 137.8, 137.9, 154.6, 207.7; MS (70 eV) 285 (M$^+$, 75), 270 (7), 242 (16), 228 (20), 215 (100), 198 (29), 132 (33), 91 (31), 43 (17). Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.70; N, 4.90. Found: C, 71.45; H, 6.49; N, 4.78.

6-Carbomethoxy-7-methyl-*N*-phenyl-4,7-dihydrobenzoxazol-2-one (15c) and 5-Carbomethoxy-7-methyl-*N*-phenyl-4,7-dihydrobenzoxazol-2-one (16c). Using the general procedure with **4a** (0.16 g) and methyl propiolate (**12**) (0.134 g) gave a mixture of **15c**/**16c** (93:7), which was purified and recrystallized from acetone/hexane (1:1) to yield 0.204 g (90%) of **15c** as colorless crystals: R_f 0.40 (hexane/EtOAc, 7:3); mp 180−181 °C; IR (KBr) 1760, 1720, 1700, 1500, 1250 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.4 (d, J = 6.7 Hz, 3H), 3.15 (ddd, J = 22.5, 7.1, 4.1 Hz, 1H), 3.26 (ddd, J = 22.5, 7.1, 3.3 Hz, 1H), 3.73−3.78 (m, 1H), 3.81 (s, 3H), 6.97 (m, 1H), 7.34−7.50 (m, 5H). Signals attributed to minor isomer **16c**: 1.33 (d, J = 6.7 Hz), 3.76 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 24.0, 28.8, 52.0, 116.3, 125.2, 127.9, 129.6, 132.9, 133.5, 133.9, 137.3, 154.5, 166.1; MS (70 eV) 285 (M$^+$, 100), 270 (36), 254 (11), 238 (24), 226 (57), 211 (54), 167 (21), 107 (26), 77 (40), 59 (23). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.90. Found: C, 67.32; H, 5.12; N, 4.87.

6-Carbomethoxy-*N*-(*m*-chlorophenyl)-7-methyl-4,7-dihydrobenzoxazol-2-one (15d) and 5-Carbomethoxy-*N*-(*m*-chlorophenyl)-7-methyl-4,7-dihydrobenzoxazol-2-one (16d). Using the general procedure with **4c** (0.204 g) and **12** (0.134 g) gave a mixture of **15d**/**16d** (92:8), which was purified and recrystallized from acetone/hexane (1:1) to yield 0.25 g (92%) of **15d** as colorless crystals: R_f 0.4 (hexane/EtOAc, 7:3); mp 145−146 °C; IR (KBr) 1760, 1730, 1710, 1480, 1250 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (d, J = 6.7 Hz, 3H), 3.17 (ddd, J = 22.4, 7.1, 4.2 Hz, 1H), 3.28 (ddd, J = 22.4, 7.0, 3.3 Hz, 1H), 3.70−3.80 (m, 1H), 3.81 (s, 3H), 6.98 (ddd, J = 4.2, 3.3, 1.2 Hz, 1H), 7.28 (ddd, J = 7.7, 1.8, 1.5 Hz, 1H), 7.35 (ddd, J = 8.1, 1.8, 1.5 Hz, 1H), 7.38−7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 24.1, 28.8, 52.0, 115.9, 123.2, 125.3, 128.0, 130.5, 132.6, 133.5, 135.1, 135.2, 137.7, 154.1, 165.9; MS (70 eV) 321 (M$^+$ + 2, 33), 319 (M$^+$, 100), 304 (33), 272 (22), 235 (6), 260 (59), 245 (44), 166 (15), 109 (32), 107 (37), 75 (24), 59 (59). Anal. Calcd for $C_{16}H_{14}ClNO_4$: C, 60.10; H, 4.41; N, 4.38. Found: C, 60.23; H, 4.60; N, 4.35.

5,6-Dicarbomethoxy-7-methyl-*N*-phenyl-4,7-dihydrobenzoxazol-2-one (8). Using the general procedure with **4a** (0.16 g) and dimethyl acetylenedicarboxylate (**6**) (0.23 g) gave 0.23 g (85%) of **8** as colorless crystals (acetone/hexane, 1:1): R_f 0.40 (hexane/EtOAc, 7:3); mp 175−176 °C; IR (KBr) 1770, 1720, 1410, 1270 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (d, J = 7.0 Hz, 3H), 3.23 (dd, J = 21.7, 7.8 Hz, 1H), 3.46 (dd, J = 21.7, 8.0 Hz, 1H), 3.76 (s, 3H), 3.77−3.84 (m, 1H), 3.85 (s, 3H), 7.34−7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.6, 24.4, 31.1, 52.6, 116.3, 125.3, 127.4, 128.2, 129.7, 133.6, 134.7, 140.4, 154.3, 166.3, 167.5; MS (70 eV) 343 (M$^+$, 27), 312 (7), 284 (74), 252 (100), 225 (55), 180 (31), 121 (26), 77 (47), 59 (38). Anal. Calcd for $C_{18}H_{17}NO_6$: C, 62.98; H, 4.99; N, 4.08. Found: C, 62.79; H, 5.06; N, 4.12.

General Procedure for the Dimerization and Isomerization of Dienes 4a and 4c. A solution of diene **4a** or **4c** (0.5 mmol) in dry xylene (2 mL) was placed in a sealed tube under N_2 atmosphere and heated at 120 °C for 10 h. The solvent was removed under vacuo and the residue purified by column chromatography.

Dimerization and Isomerization of Diene 4a. Using the general procedure with diene **4a** (0.10 g), the reaction gave three products: unreacted **4a** (0.02 g, 20%), dimer **17a** (0.05 g, 50%) as a colorless amorphous solid ($CHCl_3$/hexane), and 4-methyl-*N*-phenyl-5-vinyl-1,3-oxazolin-2-one (**18a**) (0.16 g, 16%) as colorless crystals (acetone/hexane). **17a**: R_f 0.4 (hexane/EtOAc, 4:1); mp 243−244 °C; IR (KBr) 1790, 1750, 1700, 1500, 1250 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38−1.52 (m, 1H), 1.53 (d, J = 7.1 Hz, 3H), 1.80 (d, J = 6.9 Hz, 3H), 1.98 (ddd, J = 17.0, 7.6, 2.6 Hz, 1H), 2.11 (ddd, J = 14.5, 10.7, 7.7 Hz, 1H), 2.38 (dd, J = 14.5, 6.5 Hz, 1H), 3.04−3.08 (m, 1H), 4.70 (q, J = 6.9 Hz, 1H), 6.78−6.82 (m, 2H), 7.22−7.39 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.1, 10.2, 18.3, 34.2, 40.0, 67.4, 97.2, 119.7, 125.2, 127.9, 128.8, 129.3, 129.4, 133.2, 134.1, 134.2, 136.4, 150.9, 154.3; MS (70 eV) 402 (M$^+$, 6), 215 (13), 201 (100), 156 (7), 118 (18), 91 (5), 77 (14), 51 (4). Anal. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.44; H, 5.30; N, 6.84. **18a**: R_f 0.4 (hexane/EtOAc, 9:1); mp 90−91 °C; IR (KBr) 1750, 1500, 1380 cm^{-1}; ^{1}NMR (300 MHz, $CDCl_3$) δ 1.97 (s, 3H), 5.19 (dm, J = 11.3 Hz, 1H), 5.58 (dm, J = 17.5 Hz, 1H), 6.33 (dd, J = 17.5, 11.3 Hz, 1H), 7.26−7.51 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.9, 112.5, 119.8, 120.6, 127.0, 128.6, 129.6, 133.4, 134.8, 152.8; MS (70 eV) 201 (M$^+$, 6), 118 (23), 77 (36), 64 (7), 53 (14), 51 (100). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.53; H, 5.65; N, 6.99.

Dimerization and Isomerization of Diene 4c. Using the general procedure with diene **4c** (0.117 g), the reaction gave three products: unreacted **4c** (0.03 g, 26%), dimer **17b** (0.053 g, 45%) as colorless crystals (CH_2Cl_2/hexane), and 4-methyl-*N*-(*m*-chlorophenyl)-5-vinyl-1,3-oxazolin-2-one (**18b**): (0.029 g, 25%) as colorless crystals (CH_2Cl_2/hexane). **17b**: R_f 0.37 (hexane/EtOAc, 4:1); mp 288−289 °C; IR (KBr) 1780, 1750,

1710, 1480, 1240 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37−1.50 (m, 1H), 1.51 (d, J = 7.1 Hz, 3H), 1.80 (d, J = 6.9 Hz, 3H), 2.05−2.21 (m, 2H), 2.34−2.44 (m, 1H), 3.03−3.12 (m, 1H), 4.72 (q, J = 6.9 Hz, 1H), 6.81−6.88 (m, 2H), 7.16 (ddd, J = 7.9, 2.1, 1.2 Hz, 1H), 7.23−7.33 (m, 4H), 7.39 (ddd, J = 8.1, 1.9, 1.2 Hz, 1H). Anal. Calcd for $C_{24}H_{20}Cl_2N_2O_4$: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.34; H, 4.40; N, 5.95. **18b**: R_f 0.4 (hexane/EtOAc, 9:1); mp 136−137 °C; IR (KBr) 1740, 1480, 1380 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 3H), 5.21 (dm, J = 11.3 Hz, 1H), 5.59 (dm, J = 17.3 Hz, 1H), 6.32 (dd, J = 17.3, 11.3 Hz, 1H), 7.22 (dt, J = 6.9, 2.1 Hz, 1H), 7.26−7.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.9, 113.0, 119.7, 120.1, 125.1, 127.2, 128.9, 130.5, 134.6, 135.1, 135.2, 153.4. MS (70 eV) 235 (M^+, 11), 152 (37), 111 (38), 75 (89), 63 (44), 55 (96), 51 (100). Anal. Calcd for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.30; H, 4.40; N, 5.85.

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Supporting Information Available: Crystallographic acquisition data and ORTEP structures of **4c** and **13c**, relative magnitudes of the FMO coefficients calculated for **1a**, **4a**, **11**, and **12** at 3-21G, 6-31G*, and 6-31G** levels, and details of the preparation of dienes **1c**−**h**, **4e**−**j**, and **5b**, along with complete spectroscopic data of these products (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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