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Diels-Alder Reactions of 2-Oxazolidinone Dienes in Polar Solvents Using Catalysis or Non-conventional Energy Sources*

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Summary. The (*Z*)-*N*-substituted 4-methylene-5-propylidene-2-oxazolidinone dienes were prepared by a one-step synthesis, starting from 2,3-hexanedione and isocyanates. *Diels-Alder* cycloadditions of these dienes were carried out in the presence of the dienophiles methyl vinyl ketone, methyl propiolate, and a captodative olefin, under conditions such as solvents of high polarity, *Lewis* acid catalysis, and non-conventional energy sources. The reactions carried out either with mixtures of $H_2O/MeOH$ or under $BF_3 \cdot Et_2O$ catalysis yielded the highest regio- and stereoselectivities. The use of ionic liquids, microwaves, and ultrasound did not significantly increase the selectivity.

Keywords. Cycloadditions; Solvent effect; Ionic liquids; Microwaves; Ab initio calculations.

Introduction

The reactivity of 1,3-conjugated dienes in *Diels-Alder* cycloadditions depends on diverse factors, mainly associated with the electron demand of their substituents [1]. However, other factors such as conformational and geometrical effects [2–3], the 1,4-distance [1a], and steric hindrance [4] in the diene could accelerate or reduce the reaction rate and, consequently, modify the regio- and stereoselectivity of the process [5]. Although the structural features of the cycloaddends seem to be directly involved in controlling reactivity and selectivity, external variables can improve reactivity and selectivity, such as *Lewis* acid catalysis [1e, 6], highly polar and ionic liquid solvents [7], and non-conventional energy sources such as microwaves and ultrasound [8].

* Dedicated to Professor *Louis S. Hegedus* on the occasion of his 60th birthday

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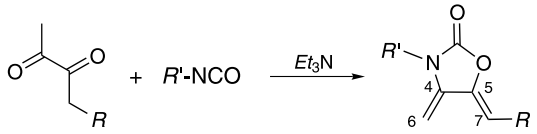


3a *R* = H
3b *R* = *Me*
3c *R* = *Et*

4

1 *R* = H
2 *R* = *Me*
5 *R* = *Et*

Scheme 1

We have developed a tandem methodology to prepare the novel *N*-substituted *exo*-2-oxazolidinone dienes **1** and **2** [9], which involves base-assisted condensation of α-diketones **3** and isocyanates **4** in the presence of a dehydrating agent (Scheme 1). The use of the unsymmetrical α-diketone **3b** under similar reaction conditions, furnished dienes **2** as a single regio- and stereoisomer [9b]. The selectivity was explained in terms of thermodynamic control in the formation of the enolate of **3b**. This methodology has been successfully applied to the synthesis of 1,4-dimethyl substituted dienes [10], and also of those analogues containing the dienic moiety in a six-membered ring [11]. Moreover, dienes **1** and **2** have shown to be useful synthons in the preparation of carbazoles [12], leading to the total synthesis of the natural alkaloid mukonine [13].

Herein, we describe the preparation of new *N*-substituted (*Z*)-4-methylene-5-propylidene-2-oxazolidines **5** with the aim of further extending the versatility of the method of preparation of these *exo*-heterocyclic dienes. Besides evaluating the effect of the ethyl substituent in *Diels-Alder* additions, we have also assessed the influence of solvent polarity, catalysis, and energy sources on the reactivity and selectivity of these reactions.

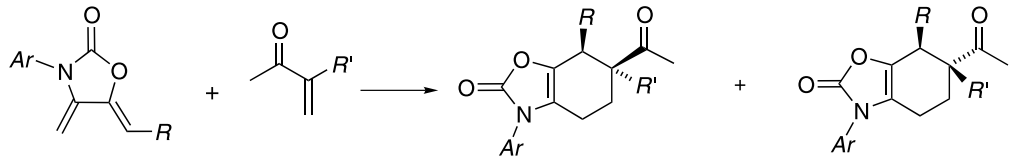
Results and Discussion

Table 1 summarizes the reaction conditions and yields for the preparation of dienes **5a**–**5h**. The optimum reaction conditions also corresponded to those applied to the

Table 1. Reaction conditions and yields in the preparation of diene **5**[a]

Entry	*R′*	Diene	Yield %[b]
1	*Ph*	**5a**	40
2	C_6H_4-4-Cl	**5b**	60
3	C_6H_4-3-Cl	**5c**	31
4	C_6H_4-2-Cl	**5d**	24
5	C_6H_4-4-*Me*	**5e**	60
6	C_6H_4-3-*Me*	**5f**	43
7	C_6H_4-2-*Me*	**5g**	20
8	C_6H_4-2-I	**5h**	traces

[a] Dioxane as solvent, with Et_3N (2.0 mol eq) as the base and Li_2CO_3 (1.2 mol eq) as additive at rt, except in entry 8 (25, 60, 100°C); the reaction time was 12 h; [b] After column chromatography and recrystallization; [c] Ref. [14]



5b *Ar* = C_6H_4*p*-Cl, *R* = *Et*
5c *Ar* = C_6H_4*m*-Cl, *R* = *Et*
2a *Ar* = *Ph*, *R* = *Me*
2c *Ar* = C_6H_4*m*-Cl, *R* = *Me*

6 *R*' = H
12 *R*' = *PNB*

7a *Ar* = C_6H_4*m*-Cl, *R* = *Et*, *R*' = H **8a**
7b *Ar* = C_6H_4*m*-Cl, *R* = *Me*, *R*' = H **8b**
13a *Ar* = C_6H_4*p*-Cl, *R* = *Et*, *R*' = *PNB* **14a**
13b *Ar* = *Ph*, *R* = *Me*, *R*' = *PNB* **14b**

Scheme 2

preparation of dienes **2** [9b]: 2,3-hexanedione (**3c**), Et_3N as the base, and Li_2CO_3 as the dehydrating agent, in dry dioxane, at room temperature, and a reaction time of 12 h give dienes **5** in fair yields [14]. The lowest yields obtained corresponded to the *ortho*-substituted isocyanates (Table 1, entries 4 and 7). For the *o*-iodoisocyanate **4h**, the reaction did not take place satisfactorily, even after heating to high temperature. The analysis of the crude showed the presence of starting materials and traces of diene **5h**. Since it is likely that the reaction outcome depends on the electron-donating effect of the substituent of the isocyanate [9], this low reactivity for **5h** could be associated with steric interactions of the *ortho*-substituent of **4h** at the cyclization step leading to the heterocycle [11].

As expected from the preparation of dienes **1** and **2**, the ^{1}H NMR analysis of the crude mixtures of dienes **5** did not give evidence of the presence of any other isomer, thereby, the reaction was highly regio- and stereoselective.

Thermal *Diels-Alder* addition of diene **5c** to methyl vinyl ketone (**6**) yielded a mixture of the *endo*/*exo* stereoisomeric adducts **7a**/**8a** (Scheme 2). As shown in Table 2, the reaction conditions were similar to those employed in the reaction with the methyl diene **2c** ($R' = C_6H_4$-*m*-Cl) [9b], indicating a comparable reactivity. However, the selectivity was significantly reduced, giving the *endo* isomer as the major one (Table 2, entries 1 and 2). These results suggest that the ethyl group attached to the diene frame might have an effect on controlling the approach of the cycloaddends at the *endo* transition state. Considering that this effect would have mainly steric and electronic components, it does not seem to affect the regioselectivity, since only the *ortho* isomer was observed. This is in contrast with dienes **1** which furnish a mixture of regioisomers *ortho*/*meta* in 8:2 ratio [9b].

In order to evaluate non-conventional energy sources on the reactivity and selectivity of this process, we investigated the use of microwaves (MW) at different temperatures (Table 2, entries 3–5) [8a]. It was found that the higher the temperature, the shorter the reaction time, maintaining, however, a quite similar *endo* selectivity. Nevertheless, the stereoselectivity was increased with respect to the thermal conditions (entry 1), with analogous yields.

The polarity of the solvent was modified as well, shifting to highly polar mixtures of *Me*OH/H_2O (Table 2, entries 6–8). Under these conditions, the reaction took place at lower temperatures (25°C) than those required for the reaction in xylene. Even though the reaction times increased, the *endo* stereoselectivity and the yields were largely increased as well. Upon varying the water proportion in the solvent mixture, the shorter reaction time and the best *endo* selectivity were found

Table 2. *Diels-Alder* cycloadditions of dienes **2a**, **2c**, **5b**, **5c**, and **5f** with olefins **6**, **9**, and **12**[a]

Entry	Diene	Olefin[b]	Energy source[c]	Catalyst	Solvent	T/°C	t/h	Products (ratio)	Yield/%[d]
1	**5c**	**6**	heat	–	*m*-xylene	120	1.5	**7a**:**8a** (72:28)	72
2	**2c**	**6**	heat	–	*m*-xylene	130	1.0	**7b**:**8b** (96:4)	90[e]
3	**5c**	**6**	MW	–	*m*-xylene	35	4.0	**7a**:**8a** (87:13)	81
4	**5c**	**6**	MW	–	*m*-xylene	60	1.0	**7a**:**8a** (88:12)	76
5	**5c**	**6**	MW	–	*m*-xylene	90	0.5	**7a**:**8a** (88:12)	75
6	**5c**	**6**	–	–	*Me*OH:H_2O (9:1)	25	12	**7a**:**8a** (94:6)	98
7	**5c**	**6**	–	–	*Me*OH:H_2O (1:1)	25	12	**7a**:**8a** (93:7)	97
8	**5c**	**6**	–	–	*Me*OH:H_2O (1:9)	25	72	**7a**:**8a** (91:9)	92
9	**5c**	**6**	)))	–	*Me*OH:H_2O (9:1)	50	12	**7a**:**8a** (92:8)	80
10	**5c**	**6**	MW	–	*Me*OH:H_2O (9:1)	35	2.0	**7a**:**8a** (92:8)	86
11	**5c**	**6**	MW	–	*m*-xylene:[*mpim*][Br] (27:1)	60	1.7	**7a**:**8a** (88:12)	78
12	**5c**	**6**	MW	–	*m*-xylene:[*mpim*][Br] (27:1)	90	1.2	**7a**:**8a** (87:13)	74
13	**5c**	**6**	MW	–	*m*-xylene:[*ppy*][Br] (27:1)	60	1.7	**7a**:**8a** (87:13)	76
14	**5c**	**6**	–	$AlCl_3$	CH_2Cl_2	−78	0.5	**7a**:**8a** (91:9)	86
15	**5c**	**6**	–	$BF_3 \cdot Et_2O$	CH_2Cl_2	−78	0.08	**7a**:**8a** (98:2)	96
16	**5c**	**9**	heat	–	*m*-xylene	120	8.0	**10a**:**11a** (85:15)	73
17	**5f**	**9**	heat	–	*m*-xylene	120	6.0	**10b**:**11b** (90:10)	84
18	**2a**	**9**	heat	–	*m*-xylene	130	1.0	**10c**:**11c** (93:7)	90[e]
19	**1a**	**9**	heat	–	*m*-xylene	120	6.0	**10d**:**11d** (6:4)	59[e]
20	**5c**	**9**	MW	–	*m*-xylene	60	8.5	**10a**:**11a** (88:12)	75
21	**5c**	**9**	–	–	*Me*OH:H_2O (9:1)	25	408	**10a**:**11a** (98:2)	96
22	**5c**	**9**	)))	–	*Me*OH:H_2O (9:1)	50	19.5	**10a**:**11a** (88:12)	77

(*continued*)

Table 2 (*continued*)

Entry	Diene	Olefin[b]	Energy source[c]	Catalyst	Solvent	T/°C	t/h	Products (ratio)	Yield/%[d]
23	**5c**	**9**	MW	–	*m*-xylene:[*ppy*][Br] (27:1)	60	6.5	**10a**:**11a** (85:15)	38[f]
24	**5b**	**12**	heat	–	*m*-xylene	120	8.0	**13a**:**14a** (86:14)	72
25	**2a**	**12**	heat	–	*m*-xylene	120	8.0	**13b**:**14b** (80:20)	70

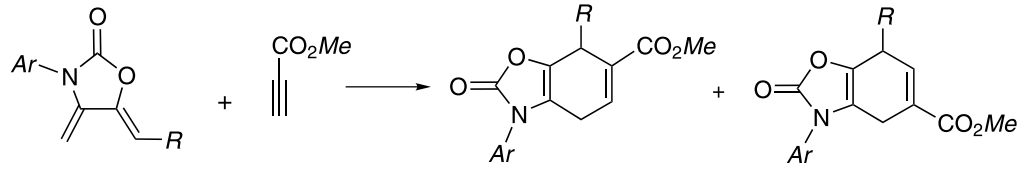
[a] All under N_2 atmosphere; thermal trials in the presence of 1–2% hydroquinone; [b] 2.0 mol equiv with olefins **6** and **9**, and 1.5 mol equiv with olefin **12**; [c] At 200 W for MW; [d] Corresponding to the isomeric mixtures after column chromatography; [e] See Ref. [9b]; [f] Starting material was recovered (37%)

for solvent mixtures containing up to 50% of water. The use of ultrasound and MW as energy sources with these polar solvents did not significantly change the *endo*/*exo* selectivity, although with the latter the reaction times were largely reduced (Table 2, entries 6, 9, and 10).

Recently, the use of ionic liquids has attracted widespread interest due to the enhancement of the reactivity and selectivity in a large number of reactions [7]. Two new ionic liquids were prepared, 3-methyl-1-*n*-pentyl-3*H*-imidazol-1-ium bromide ([*mpim*][Br]) and 1-*n*-pentylpyridinium bromide ([*ppy*][Br]), using *n*-pentyl bromide with 1-methylimidazole or pyridine under MW irradiation at normal pressure, which are more gentle conditions than those previously reported [7h]. They were employed as co-solvents, along with *m*-xylene under MW irradiation (Table 2, entries 11–13). However, there was no change with respect to those experiments carried out in neat *m*-xylene (entries 3–5).

The most relevant results were obtained when the reactions were carried out under *Lewis* acid catalysis at low temperature (Table 2, entries 14 and 15). Aluminum chloride in methylene chloride was very efficient, since the reaction took place in 30 min with high stereoselectivity. This result was improved even more by using $BF_3 \cdot Et_2O$ in methylene chloride, obtaining almost exclusively the *endo* isomer in high yield and in only 5 min.

The unsymmetrical dienophile methyl propiolate (**9**) was also evaluated under thermal conditions with dienes **5c** and **5f** (Scheme 3), providing **10a** as the major



5c *Ar* = C_6H_4*m*-Cl, *R* = *Et* **9**
5f *Ar* = C_6H_4*m*-*Me*, *R* = *Et*
2a *Ar* = *Ph*, *R* = *Me*
1a *Ar* = *Ph*, *R* = H

10a *Ar* = C_6H_4*m*-Cl, *R* = *Et* **11a**
10b *Ar* = C_6H_4*m*-*Me*, *R* = *Et* **11b**
10c *Ar* = *Ph*, *R* = *Me* **11c**
10d *Ar* = *Ph*, *R* = H **11d**

Scheme 3

regioisomer (Table 2, entries 16 and 17). Interestingly, both reactivity and regioselectivity were found to be higher in the case of the *m*-tolyl derivative **5f**. Moreover, the latter showed a regioselectivity quite similar to that obtained with the methyl diene **2a** [9b] (Table 2, entries 17 and 18), indicating that the presence of the ethyl group in dienes **5** seems to affect (steric effect) only slightly the orientation of the addition. However, the contribution of the electronic effect of this group to the regioselectivity control of these dienes is significant, since, unlike dienes **5**, almost no selectivity was observed with the unsubstituted dienes **1** (*e.g.* entry 19) [9b].

Unexpectedly, even though the reaction temperature was lower [1a], no significant increase in regioselectivity was observed for the reaction of diene **5c** neither when MW were applied, nor when a ionic liquid was added to the reaction mixture as a co-solvent (Table 2, entries 20 and 23). In contrast, the effect of a major change in the polarity of the solvent on the regioselectivity for this cycloaddition was clearly apparent. Thus, a high *ortho* regioselectivity was observed when the reaction between diene **5c** and **9** was carried out in a mixture of *Me*OH/H_2O (9:1) (Table 2, entry 21). The reaction time was shortened by using ultrasound in combination with this solvent mixture, although the regioselectivity decreased (entry 22).

Captodative olefin **12** (*PNB* = *p*-nitrobenzoyloxy) proved to be a highly reactive and selective dienophile in *Diels-Alder* cycloadditions, in spite of its highly hindered quaternary center [15]. This olefin exhibited good stereo- and regioselectivity with dienes **5b** and **2a** under thermal reaction conditions (Table 2, entries 24 and 25) since a single regioisomer was isolated, and high stereoisomeric ratios of **13**/**14** were recorded (Scheme 2). The comparable proportion of *endo*/*exo* adducts between these dienes would support a minimal contribution of steric factors in the control of the stereoselectivity of the additions, while an electronic effect might seem rather significant in determining the regioselectivity.

The structures of the major isomers were established by ^{1}H NMR experiments (COSY, HETCOR, and N*O*E) correlating the cyclohexene protons as previously described [9b]. For adduct **10b**, the assignment was confirmed by single-crystal X-ray diffraction (Fig. 1).

The relative reactivity and selectivity in the addition of dienes **5** to unsymmetrical dienophiles under thermal conditions with respect to unsubstituted dienes **1** [9b] confirms the expected higher reactivity and regioselectivity of dienes **5** due to the presence of the ethyl group [1c, 16]. Moreover, the methyl-substituted dienes **2**

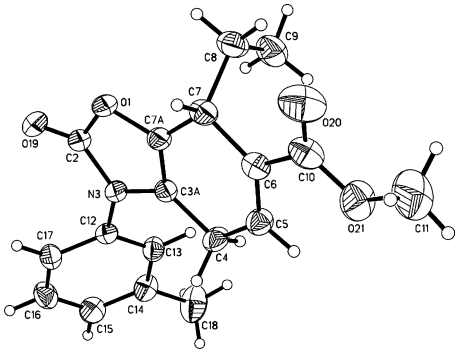


Fig. 1. X-Ray structure of **10b**

proved to be more regioselective and stereoselective than dienes **5** (Table 2). This may be associated to an enhancement of the steric effect by the ethyl group. Considering these facts, the comparable high stereoselectivity shown by dienes **2a** and **5b** in the cycloaddition with the captodative olefin **12** is difficult to explain, since a number of possible interactions at the transition state would modulate the stability of the major *endo*-adducts **13a** and **13b** obtained, most likely, by kinetic control. This *endo* preference at the transition state, displayed not only by olefin **12** but also by methyl vinyl ketone (**6**), seems to be associated with electronic effects rather than with steric control. This hypothesis is supported by the fact that in all the additions, the more crowded *ortho* regioisomer is obtained, regardless which substituent is in the diene or in the dienophile.

FMO theory has been successfully used to explain the regioselectivity of *Diels-Alder* cycloadditions of dienes **1** and **2** [9b]. Therefore, we have also used this model to correlate the energies and coefficients of the frontier molecular orbitals of dienes **5** with those of olefins **6**, **9**, and **12** [17]. Frontier orbitals of diene **5a** were calculated using the *ab initio* HF method. Geometries were optimized by the AM1 semiempirical method [18] and employed as the starting point for optimization, using the 3-21G and 6-31G* basis sets [19]. The orbital eigenvalues derived from these calculations are shown in Table 3, and compared with those previously calculated for the unsubstituted and methyl-substituted dienes **1a** and **2a** [9b]. The *normal electron demand* interaction [20], HOMO-diene/LUMO-dienophile, is largely preferred (1.8–3.1 eV) for all the additions. The energy value of the HOMO for diene **5a** is higher than those of dienes **1a** and **2a**, at both 3-21G and 6-31G* levels. As expected, the difference is more significant with respect to diene **1a**, whose dienic system does not have an electron-donor substituent. Consequently, dienes **5** should be more reactive and selective in [4 + 2] cycloadditions than dienes **1** and **2**.

Table 3. *Ab initio* RHF/3-21G, and 6-31G* frontier molecular orbitals of dienes **1a**, **2a**, and **5a**, and dienophiles **6**, **9**, and **12**

Compound	FMO	E/eV	
		3-21G	6-31G*
1a[a]	HOMO	−8.9855	−8.8342
1a[a]	LUMO	2.8161	2.9470
2a[a]	HOMO	−8.7227	−8.5804
2a[a]	LUMO	3.0093	3.1448
5a	HOMO	−8.7006	−8.5648
5a	LUMO	2.9957	3.1152
6[b]	HOMO	−10.5391	−10.4895
6[b]	LUMO	2.9002	2.9222
9[a]	HOMO	−11.6713	−11.4648
9[a]	LUMO	3.0719	3.2972
12[c]	HOMO	−11.0460	−11.0123
12[c]	LUMO	2.2417	2.4588

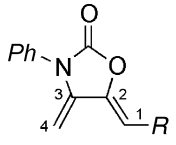
[a] See Ref. [9b]; [b] Of the most stable *s-cis* conformation, see Ref. [9b]; [c] Of the most stable nonplanar *s-trans* conformation, see Ref. [22]

We can see from Table 2 that, even though the HOMO of diene **5a** is less stable than that of diene **2a** (Table 3), the regioselectivity was slightly lower in the reaction of dienes **5c** and **5f** with olefin **9**, in comparison with diene **2a**. Nevertheless, the dienes **5** were, indeed, more reactive and regioselective than diene **1a** toward the same olefin.

The regiochemistry observed in the cycloadditions between dienes **5** and dienophiles **6**, **9**, and **12** [21] can be accounted for by the interactions of the appropriate largest orbital coefficients. In order to evaluate this, we calculated the relative magnitudes of the HOMO and LUMO coefficients at the 6-31G* level for the structurally most simple diene **5a** (Table 4). As expected from calculations of diene **2a** [9b], the coefficient at the diene terminus (C_4) is larger than that at carbon C-1 (C_1) in the HOMO. According to the coefficient differences ($\Delta C_i = C_4 - C_1$), whose values are identical for both dienes, **2a** and **5a**, one can predict no difference in regioselectivity. Possibly, a marginal difference in the steric contribution of the alkyl groups may explain the slightly better regiochemistry found for diene **2a** with respect to **5f** with olefin **9**. The same *ortho* regioselectivity can be predicted for dienes **2a** and **5b** with dienophile **12**, since the largest LUMO coefficient of this olefin is located at the unsubstituted carbon C-1 [22].

The *endo* stereoselectivity shown by the ethyl and methyl-substituted dienes **5c**, **5b**, and **2c** in the addition to dienophiles **6** and **12**, cannot be explained simply on the basis of steric or electrostatic effects [23]. The preferred quasi-orthogonal conformation of the *N*-phenyl or *N*-aryl ring of the dienes [9b] would preclude, in principle, the *endo* approach of the dienophile, unless a supplementary factor could stabilize it. Secondary orbital interactions (SOI) at the transition state (TS) have been traditionally invoked to account for the *endo* selectivity [20, 24]. Instead of

Table 4. *Ab initio* RHF/6-31G* coefficients (C_i) of the frontier molecular orbitals for dienes **2a** and **5a**, and dienophiles **6**, **9**, and **12**[a]



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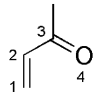
2a *R* = *Me*
5a *R* = *Et*



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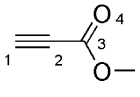

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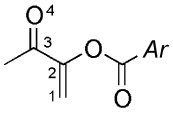

12 *Ar* = C_6H_4*p*-NO_2

Comp	HOMO					LUMO				
	C_1	C_2	C_3	C_4	ΔC_i[b]	C_1	C_2	C_3	C_4	ΔC_i[b]
1a[c]	0.259	0.176	−0.217	−0.334	0.075	−0.269	0.250	0.247	−0.262	0.019
2a	−0.268	−0.208	0.204	0.328	0.060	−0.286	0.235	0.254	−0.259	0.027
5a	−0.266	−0.207	0.203	0.326	0.060	0.281	−0.235	−0.249	0.256	0.025
6[c]	−0.346	−0.367	0.033	0.221	0.021	0.311	−0.207	−0.281	0.255	0.104
9[c]	−0.375	−0.394	0.034	0.192	0.019	0.289	−0.183	−0.339	0.279	0.106
12[c,d]	−0.359	−0.356	0.024	0.168	0.003	0.294	−0.239	−0.289	0.280	0.055

[a] These are the values of the $2p_z$ coefficients, the relative $2p_{z'}$ contributions and their ΔC_i are analogous; [b] $C_4 - C_1$ for the dienes and $C_1 - C_2$ for the dienophiles; [c] Ref. [10]; [d] Ref. [22]

these *classical* SOI, *Garcia et al.* observed, in particular for the *Lewis* acid-catalyzed *Diels-Alder* reaction, additional SOI for the energetically preferred *endo* TS, which are localized between the terminal carbon atom C-1 of the diene and the carbon atom of the carbonyl group, as a [4 + 3] or a three-center orbital interaction [25]. Moreover, recently, a bispericyclic transition state (BTS) leading to a merged [4 + 2] and [2 + 4] approach appears to rationalize the stabilizing interactions that favor the *endo* selectivity [26]. While for our addends *classical* SOI would imply a supplementary interaction between coefficients of carbon atoms C-2 of the diene and C-3 of the dienophile, a BTS would suggest a more favorable secondary interaction between the carbon atom C-3 of the diene and the oxygen atom O-4 of the dienophile [27]. The [4 + 3] approach would involve a three-center interaction between the carbon atom C-1 of the diene and the carbon atoms C-2 and C-3 of the olefin. Whatever the main secondary interaction is, the HOMO coefficients in carbons C-2 and C-3 of the diene, and the LUMO coefficients C_3 and C_4 in the dienophile (Table 4), are relatively large to take advantage of these probable *endo* stabilizing interactions. Calculation of the TSs for the processes herein described were undertaken, in order to obtain a further insight on the main interactions controlling the *endo* stereoselectivity, and they will be disclosed elsewhere.

Conclusions

We describe the synthesis of the ethyl substituted dienes **5c**–**5g** in moderate yields following the one-pot reaction between the α-diketone **3c** and the corresponding isocyanates **4**. The *Diels-Alder* additions of dienes **5** with the unsymmetric olefins **6** and **9** under thermal conditions proved to be highly regio- and stereoselective. In the case of dienophile **12**, dienes **5a** and **2a** also showed high stereo- and regioselectivity. The electron-releasing effect of the alkyl group in dienes **2** and **5** seems to be the cause for the increase in the reactivity and selectivity of these dienes with respect to dienes **1**, as suggested by FMO calculations. These calculations also explain the regioselectivity obtained in these cycloadditions. In contrast, steric hindrance of the bulkier substituent in dienes **5** does not seem to have a significant effect on the regio- and stereoselectivities. Microwave irradiation enhanced the stereo- and regioselectivity of the cycloadditions between diene **5c** and dienophiles **6** and **9** with respect to the thermal trials. However, the best improvement of both selectivities was reached by increasing the polarity of the solvent, by using mixtures of water/methanol, and by using *Lewis* acid catalysis.

Experimental

Melting points were determined with an Electrothermal capillary melting point apparatus. IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. ^{1}H (300 and 200 MHz) and ^{13}C (75.4 and 50 MHz) NMR spectra were recorded on Varian Mercury-300 and Mercury-200 instruments, in $CDCl_3$, *DMSO*-d_6, or acetone-d_6 as solvents and *TMS* as internal standard. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained, in electron impact (EI) (70 eV) mode, on Hewlett-Packard 5971A and Jeol JMS-AX 505 HA spectrometers. X-Ray data were collected on a Siemens P4 diffractometer. Microwave and ultrasound irradiations were carried out in a mono-mode microwave oven (600 W, 2.45 GHz) Mod. MIC-I from SEV (Mexico) [28], and with a Branson ultrasonic cleaner. Elemental analyses (C, H, N, S) were performed by M-H-W Laboratories (Phoenix, AZ); their results

were found to be in good agreement (±0.2%) with the calculated values. TLC analysis was carried out using E. Merck silica gel 60 F_{254} coated 0.25 plates visualizing by long- and short-wavelength UV lamp. Flash column chromatography was performed on 230–400 mesh silica gel (Natland Int.). All air moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. Dioxane and *m*-xylene were freshly distilled over Na, and CH_2Cl_2 over CaH_2, prior to use. Li_2CO_3 and molecular sieves were dried overnight at 120°C prior to use. Triethylamine was distilled over NaOH. All other reagents were used without further purification. Dienes **5a** and **5b** were prepared as reported [14].

General Procedure for the Synthesis (5Z)-N-Substituted-4-methylene-5-propylidene-2-oxazolidinones ***5c–5g***

A solution of 0.4 g of 2,3-hexanedione (**3c**) (3.5 mmol) in 1 cm^3 of dry dioxane was added dropwise to a magnetically stirred solution of 0.71 g of triethylamine (7.0 mmol) in 2 cm^3 of dry dioxane containing 0.31 g of anhydrous Li_2CO_3 (4.2 mmol) at rt under N_2 and the mixture was stirred for 30 min. A solution of the corresponding aryl isocyanate (5.2 mmol) in 2 cm^3 of dioxane was added dropwise and stirring was continued for 12 h at room temperature. The mixture was filtered and the solvent removed under vacuum. The residue was purified by column chromatography on silica gel impregnated with triethylamine (10%) in *n*-hexane (*n*-hexane:*Et*OA*c*, 9:1).

(5Z)-N-(3-Chlorophenyl)-4-methylene-5-propylidene-2-oxazolidinone (**5c**, $C_{13}H_{12}ClNO_2$)

From 0.79 g of **4c** 0.27 g (31%) of **5c** as colorless crystals; $R_f = 0.59$ (*n*-hexane:*Et*OA*c*, 9:1); mp 68–69°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1762$, 1691, 1637, 1479, 1391, 1293, 1042 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.14$ (t, $J = 7.5$ Hz, CH_3CH$_2$CH=), 2.32–2.45 (m, CH$_2$CH=), 4.26 (d, $J = 3.1$ Hz, H-6), 4.65 (d, $J = 3.1$ Hz, H-6), 5.43 (t, $J = 7.7$ Hz, H-7), 7.27 (dt, $J = 7.4$, 1.8 Hz, ArH), 7.37–7.47 (m, 3ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.7$ (*C*H$_3$CH$_2$CH=), 18.6 (CH$_3$*C*H$_2$CH=), 82.1 (C-6), 106.5 (C-7), 125.2 (ArH), 127.3 (ArH), 128.9 (ArH), 130.7 (ArH), 134.3 (Ar), 135.2 (Ar), 138.7 (C-4), 141.8 (C-5), 152.1 (C-2) ppm; MS (70 eV): $m/z(\%) = 251$ ($M^+ +$ 2, 6), 249 (M^+, 14), 190 (7), 154 (45), 152 (100), 125 (17), 111 (75), 90 (26), 75 (94), 55 (98).

(5Z)-N-(2-Chlorophenyl)-4-methylene-5-propylidene-2-oxazolidinone (**5d**, $C_{13}H_{12}ClNO_2$)

From 0.79 g of **4d** 0.21 g (24%) of **5d** as colorless crystals; $R_f = 0.60$ (*n*-hexane:*Et*OA*c*, 9:1); mp 73–74°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1764$, 1687, 1630, 1494, 1452, 1383, 1292, 1035 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.08$ (t, $J = 7.5$ Hz, CH_3CH$_2$CH=), 2.30–2.43 (m, CH$_2$CH=), 3.82 (d, $J = 3.1$ Hz, H-6), 4.56 (d, $J = 3.1$ Hz, H-6), 5.39 (t, $J = 7.7$ Hz, H-7), 7.30–7.50 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.4$ (*C*H$_3$CH$_2$CH=), 18.4 (CH$_3$*C*H$_2$CH=), 82.1 (C-6), 105.8 (C-7), 128.1 (ArH), 129.0 (Ar), 130.0 (ArH), 130.5 (2ArH), 133.6 (Ar), 138.2 (C-4), 141.9 (C-5), 151.8 (C-2) ppm; MS (70 eV): $m/z(\%) = 251$ ($M^+ + 2$, 2), 249 (M^+, 8), 190 (4), 154 (45), 152 (100), 125 (17), 111 (55), 90 (26), 75 (78), 55 (51).

(5Z)-4-Methylene-5-propylidene-N-(p-tolyl)-2-oxazolidinone (**5e**, $C_{14}H_{15}NO_2$)

From 0.69 g of **4e** 0.48 g (60%) of **5e** as colorless crystals; $R_f = 0.56$ (*n*-hexane:*Et*OA*c*, 9:1); mp 62–63°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1768$, 1497, 1400, 1290, 1040, 836 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.08$ (t, $J = 7.5$ Hz, CH_3CH$_2$CH=), 2.26–2.38 (m, CH$_2$CH=), 2.39 (s, *Me*Ar), 4.15 (d, $J = 2.7$ Hz, H-6), 4.56 (d, $J = 2.7$ Hz, H-6), 5.36 (t, $J = 7.7$ Hz, H-7), 7.22–7.43 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.6$ (*C*H$_3$CH$_2$CH=), 18.5 (CH$_3$*C*H$_2$CH=), 21.1 (CH$_3$Ar), 81.6 (C-6), 105.8 (C-7), 126.9 (2ArH), 130.1 (2ArH), 130.4 (Ar), 138.7 (C-4), 139.3 (Ar), 142.4 (C-5), 152.7 (C-2) ppm; MS (70 eV): $m/z(\%) = 229$ (M^+, 2), 132 (47), 91 (79), 69 (23), 65 (100), 55 (85).

(5Z)-4-Methylene-5-propylidene-N-(m-tolyl)-2-oxazolidinone (**5f**, $C_{14}H_{15}NO_2$)

From 0.69 g of **4f** 0.34 g (43%) of **5f** as colorless crystals; $R_f = 0.57$ (*n*-hexane:*Et*O*Ac*, 9:1); mp 58–59°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1767, 1691, 1637, 1495, 1397, 1293, 1037, 830\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.09$ (t, $J = 7.5$ Hz, CH_3CH$_2$CH=), 2.26–2.39 (m, CH$_2$CH=), 2.39 (s, *Me*Ar), 4.17 (d, $J = 2.9$ Hz, H-6), 4.58 (d, $J = 2.9$ Hz, H-6), 5.37 (t, $J = 7.7$ Hz, H-7), 7.10–7.16 (m, 2ArH), 7.21 (br d, $J = 7.6$ Hz, 1ArH), 7.36 (t, $J = 7.6$ Hz, 1ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.7$ (CH$_3$CH$_2$CH=), 18.5 (CH$_3$CH$_2$CH=), 21.2 (CH$_3$Ar), 81.7 (C-6), 105.9 (C-7), 124.0 (ArH), 127.6 (ArH), 129.4 (2ArH), 133.2 (Ar), 139.3 (C-4), 139.8 (Ar), 142.1 (C-5), 152.7 (C-2) ppm; MS (70 eV): $m/z(\%) = 229$ (M^+, 6), 184 (3), 170 (3), 132 (56), 104 (7), 91 (84), 77 (20), 65 (100).

(5Z)-4-Methylene-5-propylidene-N-(o-tolyl)-2-oxazolidinone (**5g**, $C_{14}H_{15}NO_2$)

From 0.69 g of **4g** 0.16 g (20%) of **5g** as colorless crystals; $R_f = 0.56$ (*n*-hexane:*Et*O*Ac*, 9:1); mp 69–70°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1767, 1495, 1391, 1032, 966, 759\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$ (t, $J = 7.5$ Hz, CH_3CH$_2$CH=), 2.29 (s, *Me*Ar), 2.30–2.45 (m, CH$_2$CH=), 3.89 (d, $J = 2.8$ Hz, H-6), 4.58 (d, $J = 2.8$ Hz, H-6), 5.42 (t, $J = 7.7$ Hz, H-7), 7.22–7.41 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.6$ (CH$_3$CH$_2$CH=), 17.3 (CH$_3$CH$_2$CH=), 18.5 (CH$_3$Ar), 81.8 (C-6), 106.1 (C-7), 127.3 (ArH), 128.4 (ArH), 129.6 (ArH), 131.3 (Ar), 131.4 (ArH), 139.0 (C-4), 139.8 (Ar), 142.1 (C-5), 152.5 (C-2) ppm; MS (70 eV): $m/z(\%) = 229$ (M^+, 10), 186 (10), 172 (11), 148 (29), 147 (17), 103 (17), 92 (42), 77 (74), 63 (100), 51 (68).

*General Procedure for the Diels-Alder Reactions of Dienophiles **6** and **9** with N-Aryl-4-methylene-5-propylidene-2-oxazolidinones **5c** and **5f***

Method A. A mixture of 0.4 mmol of **5**, 0.92 mmol of **6**, or 1.9 mmol of **9**, and 3 mg of hydroquinone in 0.4 cm^3 of dry *m*-xylene was placed in a threaded ACE glass pressure tube with a sealed Teflon screw cap under N_2 and in the dark. The mixture was stirred and heated at 120°C for 1.0–8.0 h (see Table 2). The mixture was filtered, the solvent removed under vacuum, and the residue purified by column chromatography on silica gel (*n*-hexane:*Et*O*Ac*, 4:1) to give the corresponding adducts **7a**/**8a** or **10a**–**10b**/**11a**–**11b**.

Method B. The same procedure as method A, with MW irradiation (200 W) at 60°C for 1.0–8.5 h (see Table 2), to give the corresponding adducts **7a**/**8a** or **10a**/**11a**.

Method C. The same procedure as method A, with a mixture of *Me*OH:H_2O (9:1) as the solvent, and allowing to react at room temperature for 12–408 h (see Table 2). The solvent was removed under vacuum, and the residue was extracted with 3×3 cm^3 of CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4), the solvent was evaporated under vacuum, and the residue was purified by column chromatography to give the corresponding adducts **7a**/**8a** or **10a**/**11a**.

Method D. The same procedure as method A, adding 0.028 g of [*mpim*][Br] (0.12 mmol) or 0.027 g of [*ppy*][Br] (0.12 mmol), and irradiating with MW (200 W) at 60°C for 1.7–6.5 h (see Table 2). The layers were separated, and the layer containing the ionic liquid was washed with 3×0.5 cm^3 of *m*-xylene. The extracts were combined, the solvent was evaporated under vacuum, and the residue was purified by column chromatography to give the corresponding adducts **7a**/**8a** or **10a**/**11a**.

Method E. To a solution of 0.1 g of **5c** (0.4 mmol) in 3 cm^3 of dry CH_2Cl_2 under N_2 at −78°C a solution of the *Lewis* acid ($AlCl_3$ or $BF_3 \cdot Et_2O$) (4.0 mmol) and 0.168 g of **6** (2.4 mmol) in 3 cm^3 of dry CH_2Cl_2 was slowly added. After being stirred at −78°C for 5–30 min (see Table 2), the reaction mixture was diluted with 20 cm^3 of CH_2Cl_2, washed with 2×5 cm^3 of aqueous 5% $NaHCO_3$, 2×10 cm^3 of aqueous 5% NH_4Cl, and finally the organic extract was dried (Na_2SO_4). The solvent was evaporated and the residue purified by column chromatography as described in method A, to give the corresponding adducts **7a**/**8a**.

Method F. The same procedure as method A, with ultrasound irradiation at 50°C for 12.0–19.5 h (see Table 2), to give the corresponding adducts **7a**/**8a** or **10a**/**11a**.

(6R,7R*)-6-Acetyl-N-(3-chlorophenyl)-7-ethyl-4,5,6,7-tetrahydrobenzoxazol-2-one* (**7a**, $C_{17}H_{18}ClNO_3$)

According to method B, and after reacting for 1 h, a mixture of **7a**:**8a** (88:12) was separated by column chromatography on silica gel (12 g, *n*-hexane:*Et*O*Ac*, 9:1), affording 0.092 g (72%) of **7a** as a white solid. $R_f = 0.26$ (*n*-hexane:*Et*O*Ac*, 7:3); mp 138–139°C (CH_2Cl_2:*n*-hexane, 1:1); IR (KBr): $\bar{\nu} = 1757$, 1706, 1588, 1482, 1381, 1184, 1162, 791, 752 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (t, $J = 7.5$ Hz, CH_3CH$_2$), 1.32–1.55 (m, CH$_3$CH_2), 1.85–2.10 (m, 2H-5), 2.24 (s, CH_3CO), 2.27–2.44 (m, 2H-4), 2.94 (ddd, $J = 11.6$, 5.1, 2.9 Hz, H-6), 3.00–3.10 (m, H-7), 7.24–7.42 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 12.3$ (*C*H$_3$CH$_2$), 19.3 (C-5), 20.0 (C-4), 23.5 (CH$_3$*C*H$_2$), 28.7 (*C*H$_3$CO), 35.4 (C-7), 51.0 (C-6), 120.6 (C-3a), 123.2 (ArH), 125.3 (ArH), 127.8 (ArH), 130.3 (ArH), 134.9 (Ar), 135.0 (Ar), 137.9 (C-7a), 154.0 (C-2), 207.9 (CH$_3$*C*O) ppm; MS (70 eV): $m/z(\%) = 319$ (M^+, 26), 290 (22), 276 (24), 248 (100), 232 (31), 168 (11), 151 (29), 111 (42), 95 (18), 75 (44), 55 (24).

6-Carbomethoxy-3-(3-chlorophenyl)-7-ethyl-4,7-dihydrobenzoxazol-2-one (**10a**, $C_{17}H_{16}ClNO_4$)

According to method A, and after heating for 8 h, a mixture of **10a**:**11a** (85:15) was separated by column chromatography on silica gel (12 g, *n*-hexane:*Et*O*Ac*, 95:5), affording 0.083 g (62%) of **10a** as a white solid. $R_f = 0.36$ (*n*-hexane:*Et*O*Ac*, 8:2); mp 119–120°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1761$, 1725, 1543, 1484, 1401, 1250, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ (t, $J = 7.4$ Hz, CH_3CH$_2$), 1.75–2.01 (m, CH$_3$CH_2), 3.16 (ddd, $J = 22.5$, 6.8, 4.4 Hz, H-4), 3.29 (ddd, $J = 22.5$, 7.0, 3.3 Hz, H-4), 3.81 (s, 3H, CO_2CH_3), 3.79–3.87 (m, H-7), 7.04–7.07 (m, H-5), 7.26–7.30 (m, ArH), 7.30–7.44 (m, 3ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 9.2$ (*C*H$_3$CH$_2$), 24.1 (CH$_3$*C*H$_2$), 24.4 (C-4), 34.3 (C-7), 52.1 (CO_2*C*H$_3$), 117.4 (C-3a), 123.1 (ArH), 125.2 (ArH), 128.0 (ArH), 130.5 (ArH), 131.5 (C-6), 134.1 (C-5), 134.8, 134.9, 135.8, 154.2 (C-2), 166.0 (*C*O$_2$CH$_3$) ppm; MS (70 eV): $m/z(\%) = 335$ (M^+, 32), 333 (M^+, 90), 306 (13), 304 (40), 274 (25), 272 (39), 260 (63), 245 (56), 230 (46), 201 (38), 180 (97), 167 (53), 166 (87), 153 (30), 133 (30), 111 (78), 91 (58), 77 (76), 59 (100).

6-Carbomethoxy-7-ethyl-3-(m-tolyl)-4,7-dihydrobenzoxazol-2-one (**10b**, $C_{18}H_{21}NO_4$)

According to method A, and after heating for 6 h, a mixture of **10b**:**11b** (90:10) was separated by column chromatography on silica gel (12 g, *n*-hexane:*Et*O*Ac*, 90:10), affording 0.08 g (64%) of **10b** as a white solid. $R_f = 0.28$ (*n*-hexane:*Et*O*Ac*, 7:3); mp 95–96°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1761$, 1718, 1597, 1491, 1407, 1271, 1220, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ (t, $J = 7.5$ Hz, CH_3CH$_2$), 1.76–2.05 (m, CH$_3$CH_2), 2.40 (s, CH_3Ar), 3.13 (ddd, $J = 22.5$, 6.9, 4.3 Hz, H-4), 3.24 (ddd, $J = 22.5$, 7.0, 3.2 Hz, H-4), 3.80 (s, CO_2CH_3), 3.83–3.95 (m, 1H, H-7), 7.05–7.12 (m, H-5), 7.10–7.42 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 10.1$ (*C*H$_3$CH$_2$), 21.3 (CH_3Ar), 23.9 (CH$_3$*C*H$_2$), 24.3 (C-4), 34.3 (C-7), 52.0 (CO_2*C*H$_3$), 117.8 (C-3a), 122.1 (ArH), 125.6 (ArH), 128.7 (ArH), 129.2 (ArH), 131.4 (C-6), 133.6 (Ar), 134.4 (C-5), 135.4, 139.6, 154.6 (C-2), 166.1 (*C*O$_2$CH$_3$) ppm; MS (70 eV): $m/z(\%) = 313$ (M^+, 62), 283 (48), 252 (69), 240 (40), 225 (40), 210 (26), 180 (72), 165 (20), 152 (10), 133 (30), 107 (28), 91 (100), 65 (88), 59 (68).

*General Procedure for the Diels-Alder Reaction of Dienophile **12** with **2a** and **5b***

A mixture of 5.0 mmol of diene, 0.61 g of **12** (2.6 mmol), and 3 mg of hydroquinone in 1 cm^3 of dry *m*-xylene was placed in a threaded ACE glass pressure tube with a sealed Teflon screw cap, under N_2 and

in the dark. The mixture was stirred and heated at 120°C for 8.0 h. The mixture was filtered, the solvent removed under vacuum, and the residue purified by column chromatography on silica gel (*n*-hexane:*Et*O*Ac*, 4:1) to give the corresponding adducts.

(6R,7R*)-6-Acetyl-3-(4-chlorophenyl)-7-ethyl-2-oxo-2,3,4,5,6,7-hexahydrobenzoxazol-6-yl 4-nitrobenzoate* (**13a**, $C_{24}H_{21}ClN_2O_7$)

Using the general procedure with 1.25 g of **5b** gave a mixture of **13a**:**14a** (86:14) which was separated and purified by column chromatography and recrystallization (CH_2Cl_2:*n*-hexane, 1:1), to yield 1.41 g (58%) of **13a** as a white solid. $R_f = 0.27$ (*n*-hexane:*Et*O*Ac*, 7:3); mp 149–150°C (CH_2Cl_2:*n*-hexane, 7:3); IR (KBr): $\bar{\nu} = 1766, 1725, 1528, 1497, 1282, 1092, 830, 743\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (t, $J = 7.4$ Hz, CH_3CH_2), 1.30–1.66 (m, CH_3CH_2), 2.00–2.20 (m, H-5), 2.25 (s, CH_3CO), 2.30–2.50 (m, 2H-4), 2.74–2.90 (m, H-5), 3.05 (dd, $J = 9.2$, 4.6 Hz, H-7), 7.20–7.44 (m, 4ArH), 8.12–8.37 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 11.9$ (CH_3CH_2), 17.4 (C-4), 22.4 (C-5), 24.0 (CH_3CH_2), 24.9 (CH_3CO), 41.9 (C-7), 87.8 (C-6), 119.9 (C-3a), 123.9 (ArH), 126.2 (ArH), 129.7 (ArH), 130.9 (ArH), 132.1 (Ar), 133.8 (Ar), 133.9 (C-7a), 135.8 (Ar), 151.2 (Ar), 154.7 (C-2), 163.6 ($ArCO_2$), 203.3 (CH_3CO) ppm; MS (70 eV): $m/z(\%) = 484$ (M^+, 2), 317 (100), 274 (55), 246 (31), 164 (6), 150 (23), 104 (18), 77 (16), 43 (78).

(6R,7R*)-6-Acetyl-7-methyl-2-oxo-3-phenyl-2,3,4,5,6,7-hexahydrobenzoxazol-6-yl 4-nitrobenzoate* (**13b**, $C_{23}H_{20}N_2O_7$)

Using the general procedure with 1.18 g of **2a** gave a mixture of **13b**:**14b** (80:20) which was separated and purified by column chromatography and recrystallization (CH_2Cl_2:*n*-hexane, 7:3), to yield 1.13 g (60%) of **13b** as a white solid. $R_f = 0.33$ (*n*-hexane:*Et*O*Ac*, 7:3); mp 145–146°C; IR (KBr): $\bar{\nu} = 1767, 1718, 1522, 1397, 1353, 1277, 1081, 715\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$ (d, $J = 7.0$ Hz, CH_3C-7), 2.20–2.45 (m, 2H-4, H-5), 2.25 (s, CH_3CO), 2.70–2.84 (m, H-5), 3.25 (br q, $J = 7.0$ Hz, H-7), 7.28–7.53 (m, 5PhH), 8.20–8.42 (m, 4ArH) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 14.9$ (CH_3C-7), 17.1 (C-4), 21.8 (C-5), 24.8 (CH_3CO), 34.9 (C-7), 88.0 (C-6), 119.4 (C-3a), 123.9 (ArH), 124.8 (PhH), 127.8 (PhH), 129.5 (PhH), 131.0 (ArH), 131.5 (Ph), 133.9 (C-7a), 135.8 (Ar), 151.1 (Ar), 154.3 (C-2), 163.7 ($ArCO_2$), 203.1 (CH_3CO) ppm; MS (70 eV): $m/z(\%) = 436$ (M^+, 6), 269 (100), 254 (31), 226 (96), 201 (14), 150 (70), 120 (13), 77 (15).

3-Methyl-1-n-pentyl-3H-imidazol-1-ium bromide ([mpim][Br])

A stirred mixture of 2.05 g of 1-methylimidazol (0.05 mol) and 4.53 g of 1-bromopentane (0.03 mol) was submitted to MW irradiation (100 W) at 80°C for 40 s. The mixture was washed with $2 \times 10\,cm^3$ of Et_2O and $2 \times 10\,cm^3$ of *Et*O*Ac*, and dried under vacuum at 80°C for 4 h, giving 5.7 g (98%) of [*mpim*][Br] as a colorless oily liquid. IR (CH_2Cl_2): $\bar{\nu} = 3079, 2955, 2864, 1628, 1569, 1462, 1168\,cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.68$ (t, $J = 6.6$ Hz, $CH_3(CH_2)_4N$), 1.00–1.25 (m, $4CH_3(CH_2)_4N$), 1.61–1.80 (m, $CH_3(CH_2)_4N$), 3.90 (s, CH_3N), 4.12 (t, $J = 7.3$ Hz, $CH_3(CH_2)_3CH_2N$), 7.37 (br s, 1imid-H), 7.49 (br s, 1imid-H), 9.90 (br s, 1imid-H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.5$ ($CH_3CH_2)_4N$), 21.6 ($CH_3(CH_2)_4N$), 27.8 ($CH_3(CH_2)_4N$), 29.5 ($CH_3(CH_2)_4N$), 36.2 (CH_3), 49.5 (CH_2N), 121.5 (imid-H), 123.1 (imid-H), 136.1 (imid-H); HRMS (FAB, M^+-Br) (*mNBA*): calcd for $C_9H_{17}N_2$ 153.1392, found 153.1386.

1-n-Pentylpyridinium bromide ([ppy][Br])

Following the method used for the preparation of [*mpim*][Br] 1.97 g of pyridine (0.025 mol), 4.53 g of 1-bromopentane (0.03 mol), and irradiating (100 W) at 100°C for 5 min gave 4.3 g (75%) of [*ppy*][Br]

as a colorless oily liquid. IR (CH_2Cl_2): $\bar{\nu} = 3046, 2956, 2932, 2864, 1632, 1488, 1171, 776, 684\,cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.73$ (t, $J = 6.6$ Hz, $CH_3(CH_2)_4N$), 1.12–1.32 (m, $4CH_3(CH_2)_4N$), 1.85–2.02 (m, $CH_3(CH_2)_4N$), 4.80 (t, $J = 7.3$ Hz, $CH_3(CH_2)_3CH_2N$), 8.07 (t, $J = 7.2$ Hz, 2pyr-H), 8.38–8.53 (m, 1pyr-H), 9.30 (d, $J = 6.2$ Hz, 2pyr-H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 13.7$ ($CH_3CH_2)_4N$, 21.9 ($CH_3(CH_2)_4N$), 27.8 ($CH_3(CH_2)_4N$), 31.4 ($CH_3(CH_2)_4N$), 61.6 (CH_2N), 128.1 (pyr-H), 144.4 (pyr-H), 144.9 (pyr-H) ppm; HRMS (FAB, M^+-Br) (*mNBA*): calcd for $C_{10}H_{16}N$ 150.1283, found 150.1276.

Single-Crystal X-ray Crystallography

A single-crystal of adduct **10b** was obtained by recrystallization from CH_2Cl_2:*n*-hexane (7:3) as white crystals. These were mounted in glass fibers. Crystallographic measurements were performed on a

Table 5. Crystallographic data of compound **10b**

Crystal	**10b**
Empirical formula	$C_{18}H_{19}NO_4$
Formula mass	313.34
Colour	white, prism
Crystal dimensions/mm	$0.44 \times 0.50 \times 0.56$
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a/Å	6.9818 (7)
b/Å	10.3225 (9)
c/Å	22.655 (2)
α/°	90
β/°	90.961 (8)
γ/°	90
Collection ranges	$-1 = h = 8$; $-1 = k = 12$; $-26 = l = 26$
Temperature/K	293 (2)
Volume/Å^3	1632.5 (3)
D_{calcd}/Mg m^{-3}	1.275
Radiation	Mo Kα ($\delta = 71073$ Å)
Absorption coeff. (μ)/mm^{-1}	0.090
Absorption correction	None
F (000)	664
θ range for data collection/°	1.80 to 25.00
Observed reflections	2091
Independent reflections	2873 ($R_{int} = 0.0157$)
Data/restraints/parameters	2835/0/211
Maximum shift/error	0.00
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.1066$
R indices (all data)	$R_1 = 0.0653$, $wR_2 = 0.1266$
Absolute structure parameter	N/a
Extinction coefficient	N/a
Largest fidd. peak and hole/e Å^{-3}	0.208 and −0.148

Siemens P4 diffractometer using Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å), and at room temperature. Three standard reflections were monitored periodically; they showed no change during data collection. Unit cell parameters were obtained from least-squares refinement of 26 reflections in the range $2 < 2\Theta < 20°$. Intensities were corrected for *Lorentz* and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates refined. Unit weights were used in the refinement. Structures were solved using the SHELXTL [29] program on a personal computer. Data for **10b** are summarized in Table 5. Further crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication number CCDC-232603. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-(0)1223-336 033 or e-mail: deposit@ccdc.cam.ac.uk].

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