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Synthesis and structural studies of novel fused seven-membered carbocycles derived from

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exo-2-oxazolidinone dienes through (4 + 3) cycloadditions Patricia Alcázar^a, Indira Cruz^a, Carlos González-Romero^a, Erick Cuevas-Yañez^b, Eduardo Díaz^c, Joaquín

Tamariz^d, Hugo A. Jiménez-Vázquez^d, David Corona-Becerril^b, Rubén A. Toscano^c, and Aydeé Fuentes-Benítes^a.*

^a Facultad de Química, Universidad Autónoma del Estado de México, Paseo Tollocan y Colón, 50000, Toluca, Estado de México, México.

^b Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM. Carretera Toluca-Atlacomulco, Km. 14.5, Toluca, 50200, Estado de México, México.

^c Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, C.U. Coyoacán, 04510 México, D.F., México. ^d Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Prol. Carpio y Plan de Ayala S/N, 11340, México, D.F. México.





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Synthesis and structural studies of novel fused seven-membered carbocycles derived from *exo*-2-oxazolidinone dienes through (4 + 3) cycloadditions

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^a Facultad de Química, Universidad Autónoma del Estado de México, Paseo Tollocan y Colón, 50120, Toluca, Estado de México, México.

^b Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM. Carretera Toluca-Atlacomulco, Km. 14.5, Toluca, 50200, Estado de México, México. ^c Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, C.U. Coyoacán, 04510 México, D.F., México.

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

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A series of novel, fused seven-membered rings was obtained from (4 + 3) cycloadditions of diverse *exo*-2-oxazolidinone dienes and an oxyallyl cation. 2D-NMR studies (COSY, NOESY, HMBC and HSQC) showed that the fused carbocycles were obtained as *endo/exo* diastereoisomeric mixtures. The structure of the predominant *exo* diastereoisomer was unambiguously established for one of the analogues by X-ray crystallography. It is noteworthy that for the *N*-benzyl diene, a highly *exo* stereoselective cycloaddition took place to afford a single isomer.

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1. Introduction

Seven-membered carbocyclic rings represent an essential moiety in the structure of many natural products and of several compounds that display important medical and therapeutic activities (e.g., some anticarcinogenics¹⁻² and antivirals).³⁻⁴ One efficient and frequently used synthetic strategy for the formation of seven-membered rings is the (4 + 3) cycloaddition approach with a reaction that involves allyl or oxyallyl cations and 1,3-dienes as starting materials.⁵⁻⁹ From the point of view of the number of electrons involved in this process, a [4 + 2] cycloaddition (4 electrons from the diene and 2 electrons from the allyl ion) is electronically homologous to the Diels-Alder reaction.

The synthesis of exocyclic dienes derived from *N*-substituted 2-oxazolidinones has been previously described.¹⁰⁻¹¹ They have been extensively studied in Diels-Alder reactions¹²⁻¹³ and used as starting materials in a novel synthetic approach to the carbazole core, which has allowed for the total synthesis of naturally occurring alkaloids.¹⁴ These *exo*-heterocyclic dienes have been prepared through a highly convergent and regioselective methodology, which involves the use of either symmetrical or non symmetrical α -diketones and isocyanates to generate the corresponding dienes linked to the 2-oxazolidinone ring (Scheme 1).¹¹ It has also been established that alkyl groups attached to the



Scheme 1. Synthesis of exocyclic dienes of N-aryl-2-oxazolidinones.

exocyclic methylene carbons of the diene system increase the regioselectivity in thermal and Lewis-acid catalyzed Diels-Alder cycloadditions, under conditions of normal electron demand.¹⁵

Despite the versatility of these exocyclic dienes in Diels-Alder cycloadditions, few reactions have been studied that take advantage of the reactivity potential of these systems.¹⁶ Therefore, we have undertaken the evaluation of these dienes in (4 + 3) cycloadditions, focusing on the preparation of novel seven-membered rings fused to 2-oxazolidinones. A summary of our recent success in this area is described herein.

2. Results and Discussion

The synthesis of the *exo*-2-oxazolidinone dienes 1-5 was carried out from the corresponding 1,2-diketones and aryl isocyanates in the presence of triethylamine and lithium carbonate, in accordance with the previously reported method (Scheme 2).¹⁰⁻¹³



Scheme 2. Synthesis of exo-2-oxazolidinone dienes 1-5



Scheme 3. Formation of carbocycle 8 from diene 2 and dibromoketone 6.



Scheme 4. Synthesis of the *exo/endo* diastereoisomeric mixtures of carbocycles **9a/9b–12a/12b** from *exo-*2-oxazolidinone dienes 1 and 3–5.

In a model reaction, the exo-2-oxazolidinone diene 2 reacted with the oxyallyl cation 7a, which was generated in situ from 2,4dibromopentan-3-one (6), to yield the bicyclic-fused compound 8 as the single product (Scheme 3). The NMR analysis of this structure revealed the anti relative configuration of the methyl groups at the C-7 and C-8 centers of the cycloheptanone moiety. This suggests that the cycloaddition between 2 and 7a essentially took place through the *exo* transition state to stereoselectively attain cycloadduct 8, which implies that the oxyallyl cation 7a adopted the W conformation along the entire reaction pathway. Considering this restriction and assuming a concerted process, the reaction can occur through endo or exo transition states, leading in each case to a distinct stereochemical relationship between the methyl groups at the C-5, C-7, and C-8 positions of the adducts. Accordingly, the endo approach leads to an all syn configuration of the methyl groups, while the exo geometry results in the anti configuration of the C-8 methyl group with respect to the other two.

The behavior of this successful diastereoselective reaction encouraged us to explore the scope of the process. Thus, the *exo*-2-oxazolidinone dienes 1 and 3–5 were treated with dibromo ketone 6, providing mixtures of the corresponding adducts 9a/9b-12a/12b (Scheme 4). After purification of these mixtures by column chromatography, the heterocyclic-fused sevenmembered carbocycles were isolated and identified as diastereoisomeric pairs, which were characterized through a detailed analysis of their ¹H NMR spectra. In addition, the structure of adduct 10a was established by X-ray crystallography (*vide infra*).

These reactions took place with low *exo/endo* stereoselectivity, giving an almost 1:1 ratio of the sevenmembered carbocyclic mixtures 9a/9b, 10a/10b, 11a/11b and 12a/12b. According to the structure of these products, the reaction proceeded through a concerted cycloaddition between the locked *s-cis* conformation of the diene and the *W* conformation of the oxyallyl cation 7a (Scheme 5).⁵ Unlike the case of diene 2 in which the *exo* adduct 8 was obtained as the single product, these reactions were not stereoselective. This fact can be tentatively explained by the steric hindrance, which would be produced by the rotation of the *N*-benzyl group of the diene, thus making the *endo* approach of the oxyallyl cation more difficult. Table 1 displays the most relevant proton chemical



Scheme 5. *Endo/exo* transition states for the cycloaddition of dienes 1-5 and oxyallyl cations 7a-b leading to isomers 8, 9a/9b, 10a/10b, 11a/11b and 12a/12b

shifts of compounds 8 and 10a.

We selected the pair of isomers **10a/10b** for a detailed ¹H NMR structural analysis. Since the ¹H spectrum of this mixture in CDCl₃ turned out to be very complex, with many overlapping signals, we selected C_6D_6 as solvent and used homonuclear decoupling experiments to overcome the interpretation problems. Under these conditions we were able to make a suitable assignment of the signals of compound **10a** and to identify it as the major isomer in the 55:45 *exo/endo* mixture. The ¹H NMR and ¹³C NMR chemical shifts for **8**, **9a**, **9b**, **10a**, **10b**, **11a**, **11b**, **12a**, and **12b** are summarized in Tables 2 and 3.

The ¹H NMR signals of the **10a/10b** mixture displayed overlapping signals for the key protons (H-5, H-7 and H-8) of both structures (Figure 1, (a)), which led to the collapse of the multiplets of the AB pattern expected for methines H-7 and H-8 ($\delta = 2.55$ and 2.51, respectively). However, through selective irradiations on the Me-10 and Me-11 doublets ($\delta = 0.92$ and 0.91, respectively), we were able to discern the coupling constant (J = 5.0 Hz) for methines H-7 and H-8 of **10b** (Figure 1, (b)). This simple experiment combined with the Karplus¹⁸ approach enabled us to estimate a *ca*. 60° dihedral angle between protons H-7 and H-8, which is consistent with the *syn* configuration of the methyl groups Me-10 and Me-11.

When the selected irradiations on the doublets for the methyl groups Me-10 and Me-11 ($\delta = 1.06$ and 0.96, respectively) of isomer **10a** were carried out, it was observed that the H-7 and H-8 methines also displayed an AB pattern with a vicinal coupling constant ${}^{3}J = 9.0$ Hz (Figure 1, (c) and (d)). This suggests that the dihedral angle for these protons should be *ca.* 180°, with the consequent *anti* configuration of Me-10 and Me-11.

We were able to assign the signals for H-5 in both isomers through decouplin experiments (Figure 1 (e)). We also carried out the conformational analysis of **10a** and **10b**, at the M06- $2X/6-31+G(d,p)^{19}$ level of Density Functional Theory considering the effect of the dielectric constant of benzene, according to the PCM²⁰ formalism. The lowest-energy conformers located for each isomer are shown in Figure 2, along with the corresponding dihedral angles between H-7 and H-8. Note that these angles correspond closely with the values there is a syn relationship between protons H-5 and H-7 in both expected from the NMR spectrum and the Karplus equation. isomers 10a and 10b. Moreover, protons H-7 and H-8 have an

The COSY spectrum of the 10a/10b mixture was interpreted in order to obtain all proton-proton correlations of the isomeric mixture. The methines at $\delta = 2.55$ and 2.51 (H-7 and H-8 of **10b**) correlate only with the overlapped doublets for methyls Me-10

Table 1. Proposal for the preferential conformations adopted by compounds 8 and 10a, derived from the ¹H NMR chemical shifts (δ) and ${}^{3}J_{\text{H-H}}$ coupling constants for 8.

Me 10 7 H	Ph Ph O N O 1 O I	$Me_{10} \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{3} N \xrightarrow{CI} O_{1}$			
Protons	8 δ ppm (CDCl ₃)	10a δ ppm (CDCl ₃)	$\Delta\delta$ ppm		
H_{4b}	2.84	2.80	- 0.04		
H_{4a}	2.14	2.12	- 0.02		
H_5	2.77	2.85	+0.08		
H_7	H ₇ 2.79		+0.09		
H_8	2.46	2.54	+0.09		
	Coupling constant	ts for 8 (in Hertz)			
Couple	ed protons	Coupling constants (Hz)			
H ₄	a - H _{4b}	${}^{2}J = -16.0$			
Н	4a - H5	$^{3}J = 6.5$			
Н	_{4a} - H ₈	${}^{5}J = 1.0$			
Н	_{4b} - H ₅	$^{3}J = 5.5$			
H	_{4b} - H ₈	${}^{5}J = 2.0$			
Н	5 - H9	${}^{3}J = 7$	7.0		
Н	7 - H ₈	$^{3}J = 10.0$			
Н	10 - H7	${}^{3}J = 7$	7.0		
H	8 - H11	$^{3}J = 7.0$			

and Me-11 at $\delta = 0.92$ and 0.91, respectively (Figure 3). Likewise, the overlapped signals (at $\delta = 2.25$ and 2.28) for methines H-7 and H-8, respectively, of derivative 10a correlate with the cross peaks for methyls Me-10 (0.96 ppm) and Me-11 (1.06 ppm). The H-5 methine at $\delta = 2.15$ ppm correlates with the cross peaks for the Me-9 methyl of **10b** at $\delta = 0.80$ and the Me-9 methyl of 10a ($\delta = 0.80$), and with the cross peaks of the H-4 methylene protons at $\delta = 2.09$, 1.93 and 1.58 for both compounds.

Furthermore, the NOESY spectrum of the mixture of molecules 10a and 10b (Figure 4) showed the vicinal correlation of the H-7 and H-8 methines (at $\delta = 2.55$ and 2.51, respectively) with the Me-10 and Me-11 methyl groups (at $\delta = 0.92$ and 0.91, respectively). These signals correspond to isomer 10b.

The most important dipolar correlation was observed between the diagonal peaks for methine H-7 ($\delta = 2.55$) and two cross peaks, those for the H-5 methine ($\delta = 2.15$) and one of the protons of the H-4 methylene. This suggests a long range spatial correlation (NOE) between the H-7 and H-5 methines of 10b. A dipolar correlation was also shown between H-7 ($\delta = 2.25$) and H-5 (δ = 2.11) of isomer 10a, detected from the cross peaks. Regarding the H-7 methine of 10a, the expected vicinal correlation with the Me-10 methyl protons ($\delta = 0.96$) was also observed, as was the dipolar correlation with the Me-11 methyl group ($\delta = 1.06$). The latter suggests the spatial proximity (syn relationship) between the H-7 methine and Me-11, which was not observed for isomer 10b. The H-8 methine ($\delta = 2.28$) for isomer **10a** displayed a dipolar correlation with the Me-10 methyl ($\delta =$ 0.96) and a vicinal correlation with the Me-11 methyl ($\delta = 1.06$). The aforementioned observations allowed us to establish that *anti* relationship in **10a** and a *syn* relationship in **10b**.

Additional information obtained from the NOESY spectrum established a relationship between the diagonal peaks and cross peaks for H-7/H-8 (δ = 2.25 and 2.28, respectively) of **10a** with H-7/H-8 (δ = 2.55 and 2.51, respectively) of **10b**. On the other hand, the absence of EXSY cross peaks between both pairs of H-7/H-8 methines of 10b with H-7/H-8 methines of 10a enabled us to rule out the possibility that **10a** and **10b** may be conformers. To further explore this consideration, we recorded ¹H NMR spectra for 10a and 10b using perdeutero-acetone as solvent at different temperatures (from 25° to -80°C). None of the compounds displayed relevant changes in the chemical shift of the proton signals of both molecules within this temperature range.

Having unambiguously assigned the Me-9, Me-10, and Me-11 protons, as well as the remaining H-5, H-7 and H-8 methine protons, and the H-4 methylene protons of the seven-membered ring moiety of **10a** and **10b**, we aimed to assign the ¹³C NMR signals using HSQC and HMBC spectra. For example, C-6 correlated $({}^{3}J_{C-H})$ with the Me-9 and Me-10 methyl protons, as well as with the H-4 methylene and the H-8 methine. The ${}^{3}J_{C-H}$ also showed that the quaternary C-8a carbon correlated with the H-4 methylene as well as with the Me-11 and H-7 protons, while the ${}^{2}J_{C-H}$ demonstrated that this carbon correlated with H-8. The 3 J_{C-H} showed that the C-3a carbon correlated with the H-5 and H-8 methine protons, while the ${}^{2}J_{C-H}$ demonstrated that this carbon correlated with H-4. The remaining carbons of the phenyl ring, attached to the nitrogen atom in the five-membered ring, were assigned in a similar way for each compound (Table 4).

After obtaining suitable crystals for 10a from the mixture of 10a/10b, the corresponding X-ray crystallographic analysis confirmed the proposed exo configuration of this isomer (Figures 5 and 6, Tables 5 and 6). Figure 5 shows the asymmetric unit within the P-1 triclinic unit cell, which contains a pair of enantiomeric structures (Z = 4) of **10a** (5S, 7R, 8R and 25R, 27S, 28S), half a molecule of benzene (solvent), and one disordered molecule of dichloromethane.

The enantiomeric structures correspond to slightly different variations of the same seven-membered ring conformation, particularly with respect to the orientation of the phenyl ring. This was confirmed by the overlapping of both geometries. Moreover, the solid state conformation is essentially the same as that found in the theoretical conformational analysis mentioned previously (see Figure 2). The heterocyclic five-membered ring and the phenyl ring are essentially planar. The angle between their normals is $66.15(5)^{\circ}$ and $67.1(5)^{\circ}$ for the molecules with the 5S and 25R configuration, respectively. The Cremer & Pople puckering parameters²¹ [Molecule 5S: $q_2 = 0.897(10)$, $q_3 =$ 0.349(10), Q = 0.963(10) Å, $\Phi_2 = 18.8$ (6)°, $\Phi_3 = 287.5$ (16)°. Molecule 25*R*: $q_2 = 0.873(11)$, $q_3 = 0.333(11)$, Q = 0.934(11) Å, $\Phi_2 = 197.5(7)^\circ, \Phi_3 = 109.9(18)^\circ$ suggest a boat conformation² (Figure 5) for the seven-membered ring with a synclinal relationship [Torsion angles: molecule 5S, 59.7° and 85.1°; molecule 25R: -58.9° and -87.2°] between the methyl substituents at C-5, C-7 and C-8 (C-25, C-27 and C-28 for the second molecule). Relevant dihedral angles for structure 5S are: H(7)-C(7)-C(8)-H(8), -180°; H(4B)-C(4)-C(5)-H(5), 74°; H(4A)-C(4)-C(5)-H(5), -44°; H(5)-C(5)-C(7)-H(7), 57.6°. For molecule 25*R*: H(27)-C(27)-C(28)-H(28), 179.0°; H(24A)-C(24)-C(25)-H(25), -74°; H(24B)-C(24)-C(25)-H(25), 45°; H(25)-C(25)-C(27)-H(27), 57.6°.

Because an NMR pattern similar to that already described was observed for diastereoisomers 9a/9b, 11a/11b and 12a/12b, we assume that the structural features of these epimeric pairs are analogous to those determined for 10a/10b.

Finally, we theoretically addressed the issue of the lack of stereoselectivity in the cycloaddition of the oxyallyl species 7a-b with the exocyclic diene. In a first approximation we assumed

that acetonitrile has a dielectric constant high enough to allow for the dissociation of the Na⁺ ion and the oxyallyl zwitterion. Thus we located the endo and exo transition states (TS) for the cycloaddition of zwitterion 7b to diene 1, which led to the formation of 9a and 9b at the M06-2X/6-31+G(d,p)/PCM level of DFT theory in acetonitrile (stationary points are shown in Figure 7).

Table 2. ¹H NMR chemical shifts of compounds 8, 9a, 9b, 10a, 10b, 11a, 11b, 12a, and 12b.

A нь 8, Ar = Bn, R = H **9a**, Ar = C₆H₅, R = H **10a**, Ar = Cl-p-C₆H₄, R = H **11a**, Ar = CH₃O-p-C₆H₄, R = H **12a**, Ar = $CH_3O-p-C_6H_4$, R = CH_3



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9b, Ar = C₆H₅, R = H 10b, Ar = Cl-p-C₆H₄, R = H 11b, Ar = CH₃O-p-C₆H₄, R = H 12b, Ar = CH₃O-p-C₆H₄, R = CH₃

Proton	8 (ppm)	9a (ppm)	9b (ppm)	10a (ppm)	10b (ppm)	11a (ppm)	11b (ppm)	12a (ppm)	12b (ppm)
H-4a	2.84	2.25	2.95	2.09	1.93	2.82	2.62	2.75	2.4 <mark>4</mark>
H-4b	2.14	1.70	1.70	1.58	1.58	2.07	2.07	2.10	2.10
Н-5	2.77	2.16	2.19	2.11	2.15	2.89	2.84	2.87	2.94
H-7	2.79	2.32	2.63	2.25	2.55	2.89	3.26	3.01	3.08
H-8	2.45	2.32	2.56	2.28	2.51	2.52	3.03	2.56	2.90
Н-9	0.92	0.81	0.79	0.80	0.80	1.09	1.08	1.08	1.09
H-10	1.14	0.97	0.93	0.96	0.92	1.12	1.15	1.18	1.17
H-11	1.34	1.08	0.93	1.06	0.93	1.38	1.10	1.79, 1.97	1.33, 1.71
CH ₃					<u> </u>			0.96	0.99
CH ₂ (Bn)	4.71(Ha); 4.76 (Hb)				Y				
CH ₃ O						3.83	3.83	3.84	3.84
ortho	7.22	7.05	6.92	6.59	6.68	7.18	7.18	7.18	7.18
meta	7.35	7.04	7.04	6.95	6.98	6.9 <mark>9</mark>	6.99	6.98	6.99
para	7.30	6.99	6.97						

Table 3. ¹³C NMR chemical shifts of compounds 8, 9a, 9b, 10a, 10b, 11a, 11b, 12a, and 12b.

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8, Ar = Bn, R = H 9a, Ar = C ₆ H ₅ , R = H	9b , Ar =
10a , Ar = Cl- <i>p</i> -C ₆ H ₄ , R = H	10b , Ar =



11a, Ar = CH_3O -*p*- C_6H_4 , R = H **12a**, Ar = CH_3O -*p*- C_6H_4 , R = CH_3

9b, $Ar = C_6H_5$, R = H**10b**, $Ar = CI-p-C_6H_4$, R = H**11b**, $Ar = CH_3O-p-C_6H_4$, R = H**12b**, $Ar = CH_3O-p-C_6H_4$, $R = CH_3$

Carbon	8 (ppm)	9a (ppm)	9b (ppm)	10a (ppm)	10b (ppm)	11a (ppm)	11b (ppm)	12a (ppm)	12b (ppm)
C-2	155.7	153.6	153.7	153.2	153.3	154. <mark>3</mark>	154. <mark>4</mark>	154.4	154.3
C-3a	120.1	120.9	119.6	120.4	119.2	121. <mark>2</mark>	120. <mark>2</mark>	122.5	120.4
C-4	26.7	26.8	27.3	26.8	27.2	26.5	27. <mark>2</mark>	26.7	28.1
C-5	45.4	45.6	45.0	45.4	44.8	45. <mark>7</mark>	45.0	45.1	44.1
C-6	213.6	212.2	211.8	211.9	211.4	213. <mark>2</mark>	213. <mark>8</mark>	213.6	213.4
C-7	50.0	48.3	46.7	48.3	46.7	48.1	46. <mark>8</mark>	45.1	48.7
C-8	36.3	36.6	34.0	36.5	33. <mark>9</mark>	36. <mark>5</mark>	33.8	41.9	40.2
C-8a	136.0	137.7	139.2	137.9	139.3	137.5	139.0	136.4	139.2
C-9	15.6	15.8	16.0	15.8	16.0	15.7	13. <mark>3</mark>	15.8	16.3
C-10	14.6	14.8	13.3	<mark>14.8</mark>	<mark>13.3</mark>	16.0	13. <mark>4</mark>	14.9	13.3
C-11	19.7	18.2	13.4	<mark>18.2</mark>	13.3	18. <mark>2</mark>	14.5	24.2	21.6

CH ₃			AC	CEPTEI	D MANU	SCRIPT		9.3	12.4
CH ₂ (Bn)	45.8								
CH ₃ O						55.4	55.4	55.5	55.5
C_{ipso}	<mark>136.3</mark>	134.3	134.2	134. <mark>2</mark>	134.0	1 <mark>25</mark> .7	125.7	125.7	125.7
Cortho	127.4	127.5	127.8	128.9	128.3	128.8	<mark>128.7</mark>	128.8	128.6
C _{meta}	129.3	129.5	129.5	129.7	128.6	114.8	114.8	114.8	114.8
Cpara	129.4	128.3	128.3	132.6	132.7	159.7	159. <mark>8</mark>	159.7	159.7



Figure 1. ¹H NMR (500 MHz, C_6D_6) of the 10a/10b mixture. (a) Normal spectrum of 10a and 10b. Expansion ranges δ 2.60–2.10 and δ 2.18–1.88. (b) Irradiation at 0.92 ppm. (c) Irradiation at 1.06 ppm. (d) Irradiation at 0.96 ppm. (e) Irradiation at 0.80 ppm.



 $\label{eq:Figure 2. H-7/H-8} \textit{ dihedral angles for the M06-2X/6-31+G(d,p) lowest-energy conformers of 10a~(179.7^\circ) and 10b~(-55.2^\circ). \end{tabular}$





Figure 4. NOESY (500 MHz, C₆D₆) of the 10a/10b mixture.

Table 4. ${}^{2}J_{C:H}$ and ${}^{3}J_{C:H}$ relationships derived from HMBC for compounds **10a** and **10b**





		10a		100	
 Carbon 10a	δC	Interaction with proton	Carbon 10b	δC	Interaction with proton
C-2	153.2		C-2	153.3	
C-4	26.8	0.82 (Me-9), 2.11 (H-5)	C-4	27.2	0.81 (Me-9), 2.15 (H-5)
C-5	45.4	0.82 (Me-9), 2.08 (H-4a)	C-5	44.8	1.92 (H-4a)
C-6	211.8	0.82 (Me-9), 0.96 (Me-10), 1.56 (H-4b), 2.08 (H-4a), 2.11 (H-5), 2.25 (H-7), 2.28 (H-8)	C-6	211.4	0.81 (Me-9), 0.91 (Me-10), 1.56 (H-4B), 1.92 (H-4a), 2.15 (H-5), 2.51 (H-8), 2.55 (H-7)
C-7	48.3	0.96 (Me-10), 1.06, (Me-11), 2.28 (H-8)	C-7	46.7	0.92 (Me-11), 2.51 (H-8)
C-8	36.5	0.96 (Me-10), 1.06, (Me-11), 2.25 (H-7)	C-8	33.9	0.92 (Me-11), 2.55 (H-7)
C-8a	137.9	1.06, (Me-11), 1.56 (H-4b), 2.08 (H-4a), 2.25 (H-7), 2.28 (H-8)	C-8a	139.3	0.92 (Me-11), 1.56 (H-4b), 1.92 (H-4a), 2.51 (H-8), 2.55 (H-7)
C-3a	120.4	1.56 (H-4b), 2.08 (H-4a), 2.28 (H-8)	C-3a	119.2	1.56 (H-4b), 1.92 (H-4a), 2.51 (H-8)
C-9	15.8	1.56 (H-4b), 2.11 (H-5)	C-9	16.08	1.56 (H-4b), 1.92 (H-4a)
C-10	14.7	2.25 (H-7)	C-10	13.3	2.51 (H-8), 2.55 (H-7)

8	Tetrahedron								
		AC	CEPTED	MANU	SCRIPT				
C-11	10.6	2.28 (H-8)	C-11	13.3	2.51 (H-8), 2.55 (H-7)				
C-12	134.2	6.59 (H-16), 6.94 (H-17)	C-12	134.0	6.68 (H-16), 6.98 (H-17)				
C-13,17	128.9	6.59 (H-16)	C-13,17	128.6	6.98 (H-16)				
C-14,16	129.6	6.94 (H-17)	C-14,16	129.6	6.68 (H-17)				
C-15	132.5	6.59 (H-16)	C-15	132.7	6.98 (H-16)				

Table 5. Crystal data for compound 10a^a

Crystal data	
Empirical Formula	$C_{18.75}H_{20}C_{1.25}NO_3$
Formula Weight	351.67
Crystal color	Colorless needle
Crystal system	Triclinic
Space group	P -1
a, À	$7.822(2) \alpha = 100.384(4)^{\circ}$
b, Å	$13.453(3) \beta = 90.104(4)^{\circ}$
c, Å	$19.602(5) \gamma = 101.064(4)^{\circ}$
Volume, Å ³	1989.9(8)
Z	4
Density (calcd.),g/cm ³	1.174
Absorption coefficient, (mm ⁻¹)	0.240
F(000)	739
Crystal Size (mm)	0.356 x 0.302 x 0.072
Data collection	
Temperature, K	298(2)
Radiation, λ (Å)	0.71073
$\theta \min, \max,^{\circ}$	1.72, 25.42
Index ranges	$-9 \le h \le 9, -16 \le k \le 15, 0 \le l \le 23$
Reflections Collected	7288
Independent reflections	7293 ($R_{int} = 0.1189$)
Observed reflects	R1 = 0.1609, wR2 = 0.2948
$[I > 2.0\sigma(1)]$	
Refinement	
Data-to-parameter ratio	7293 / 407 / 449
R, wR2	R1 = 0.2323, wR2 = 0.3282
G.O.F.	1.230
Largest diff. peak,hole ,e Å ⁻³	0.370, -0.253

⁴ Deposition number of Cambridge Crystallographic Data Centre: CCDC 984027

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Table 6. Selected bond distances (Å) and angles (°) for $10a$.				
Bond	Distance (Å)			
Cl(1)-C(14)	1.744(10)			
O(2)-C(2)	1.202(10)			
O(3)-C(6)	1.198(11)			
O(1)-C(2)	1.375(11)			
O(1)-C(9)	1.401(10)			
C(2)-N(3)	1.357(11)			
N(3)-C(10)	1.401(10)			
N(3)-C(11)	1.437(11)			
C(4)-C(10)	1.509(11)			
C(4)-C(5)	1.539(12)			
C(5)-C(17)	1.517(13)			
C(5)-C(6)	1.519(14)			
C(6)-C(7)	1.558(14)			
C(7)-C(18)	1.510(13)			
C(7)-C(8)	1.571(13)			
C(8)-C(9)	1.494(12)			
C(8)-C(19)	1.514(14)			
C(9)-C(10)	1.312(11)			
C(11)-C(16)	1.375(12)			
C(11)-C(12)	1.388(12)			
C(12)-C(13)	1.385(13)			
C(13)-C(14)	1.361(14)			
C(14)-C(15)	1.384(13)			
C(15)-C(16)	1.370(12)			
Cl(2)-C(34)	1.760(10)			
O(22)-C(22)	1.207(10)			
O(23)-C(26)	1.203(13)			
O(21)-C(22)	1.339(10)			
Bond	Angle (°)			
C(2)-O(1)-C(9)	107.7(7)			
O(2)-C(2)-N(3)	130.3(10)			
O(2)-C(2)-O(1)	123.5(9)			
N(3)-C(2)-O(1)	106.3(7)			
C(2)-N(3)-C(10)	109.7(7)			
C(2)-N(3)-C(11)	122.5(7)			
C(10)-N(3)-C(11)	127.8(7)			
C(10)-C(4)-C(5)	111.5(7)			
C(17)-C(5)-C(6)	109.8(8)			
C(17)-C(5)-C(4)	111.3(8)			







Figure 6. Crystal-lattice of the X-ray structure of compound 10a



Figure 7. Transition states for the cycloadditions of oxyallyl zwitterion **7a** and cation **7b** to **1**, obtained at the M06-2X/6-31+G(d,p)/PCM (acetonitrile) level of theory. The smaller bold numbers correspond to internuclear distances (Å). The first set of numbers in the lower section of the figures correspond to $\Delta\Delta H^{t}$ in kcal/mol and the numbers in parentheses to $\Delta\Delta G^{t}$ (25 °C, 1 atm). See text.

The most interesting feature of these TS is the fact that they occur rather early in the reaction coordinate. Whereas the shortest internuclear distances for the interacting atoms are found for the endo TS, for the exo TS both distances are slightly longer than 3.0 Å. In both cases the shortest C-C distance is found for the interaction of the exocyclic methylene with the zwitterion, as expected from the combined polarization effects of the nitrogen atom and methyl group in the diene. It is also of interest to note that the endo TS seems to have an additional C-H--O interaction (2.650 Å) between the oxygen of the zwitterion and one of the ortho hydrogen atoms of the phenyl ring. This interaction should contribute to the stability of the structure by making it tighter. The analysis of the energetics of the process reveals that in terms of energy contents (electronic energies, ZPE-corrected energies, or enthalpy-corrected energies) the endo TS is indeed more stable than the exo by ~2 kcal/mol (Figure 7). We would have expected a relatively high endo stereoselectivity, something that was not observed experimentally.

However, from the consideration of entropy effects, which can be calculated from the difference in free energies between both TS ($\Delta\Delta G^{t}$), a very slight predominance of the *exo* TS can be appreciated. This becomes more important as the temperature raises ($\Delta\Delta G^{t} = 0.1$ kcal/mol at 298 K, with a 53:47 *exo/endo* ratio; $\Delta\Delta G^{t} = 0.33$ kcal/mol at 328 K, the temperature at which the experimental reaction was carried out, with a 63:37 *exo/endo* ratio). The effect of the solvent polarity is not really important in terms of the energetics of the reaction, evidenced by the fact that the results obtained in the gas phase were rather similar to those already described. So, it is the higher entropy of the *exo* TS (a looser interaction) that leads to the loss of stereoselectivity. According to our calculations, at r.t. the *exo* TS is 8.1 e.u. higher in entropy than the tighter *endo* stationary point at the level of theory employed. We also located the TS for the cycloaddition between the oxyallyl cation **7b** and **1** (Figure 7), considering that complexation with an ion such as Na⁺ stabilizes the open oxyallyl species with respect to the corresponding cyclopropanone.^{25,26} Furthermore, complexation is expected to yield a more electrophilic cationic species,^{26,27} favoring the cycloaddition to an electron-rich diene such as **1**. The corresponding transition states located under the same conditions as before are also shown in Figure 7.

It can be seen that the complexed TS are very similar to those obtained for the neutral system. In the *endo* TS the Na⁺ ion is interacting with all three oxygen atoms of the complex, giving a more compact TS. In this case the *ortho* hydrogen is farther away from the oxyallyl oxygen (2.892 Å), as expected when considering that the interaction with the sodium cation was stronger. The complexed *exo* TS is slightly more compact than in the neutral reaction but it is less stable relative to the *endo* geometry by some 3.5 kcal/mol, when taking only enthalpy-corrected energies are taken into account. As aforementioned, the higher entropy of the *exo* TS decreases the energy difference as temperature rises. At 328 K the free energy-corrected difference amounts to 0.79 kcal/mol, still favoring the *endo* approach. Our theoretical results agree quite well with the experimental observations.

3. Conclusions

In conclusion, the heterocyclic-fused seven-membered rings **9–12** were obtained when *exo*-2-oxazolidinone dienes **1** and **3–5** reacted with the oxyallyl species **7**, to afford diastereoisomeric mixtures whose structures were established by NMR and X-ray techniques. This work indicates that either the oxyallyl ion **7a** or the sodium complex **7b** was added to the dienes in a *W* conformation through concerted *endo/exo* transition states. Despite the fact that the *endo* TS has more stabilizing interactions and is more stable when only $\Delta H^{\hat{t}}$ is considered, the higher

latter TS (in terms of ΔG^{t}) and to a 1:1 stereoisomeric kinetic mixture of adducts. In this mixture, the *endo* product is only slightly predominant and this predominance is expected to decrease as the temperature rises. In contrast to the behavior of dienes 1 and 3–5, diene 2 reacted with 7 through a highly stereoselective (4 + 3) cycloaddition to provide the *exo* isomer 8 as the single product. It is likely that in this case the C-H···O⁻ or O···Na⁺ interactions mentioned previously are nonexistent and that the steric interactions of the rotating benzyl group make the *endo* approach more energetic, leading to the selective formation of the *exo* adduct.

The synthetic versatility of the oxazolin-2-one moiety, which can be readily functionalized²⁸ or broken to be transformed to alkaloids,¹⁴ grants carbocyclic seven-membered natural compounds 8–12 structural characteristics that make them useful intermediates for the synthesis of natural products^{6,29} and pharmacologically active agents.³⁰ We are currently exploring methods for the synthesis of the five-membered heterocyclic framework in analogues of naturally occurring sesquiterpenes that possess the bicyclo[5.3.0]decane system.³¹ In such analogues, the seven-membered ring would be maintained and endowed with similar substituents (Figure 8). Among these sesquiterpenes, the skeletons of guaiane, ³² nor-guaiane, daucane³³ and lactarane may serve as carbocyclic targets in the reference parent compounds used to prepare or synthetically approach their five-membered heterocyclic ring analogues through (4+3) cycloadditions.31



Figure 8. Natural skeletons of sesquiterpene to be used as the reference compounds for the preparation of their five-membered heterocyclic ring analogues such as adducts 8-12, through (4+3) cycloadditions.

4. Experimental Section

Melting points were determined with an Electrothermal capillary melting point apparatus and they are uncorrected. ¹H and ¹³C NMR spectra were recorded using a Varian 500 and Bruker Advance Ultrashield 300, and the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). The mass spectra were recorded on a JEOL JMS-SX102A spectrometer in the EI mode, at 70 eV and 200 °C via direct inlet probe. Only the molecular and parent ions (m/z) are reported. IR spectra were recorded on a Nicolet Avatar 360 FT-IR-ESP instrument. For the X-ray diffraction studies, crystals of compound **10a** were obtained by slow evaporation of a diluted CH₂Cl₂/benzene solution, and the reflections were acquired with a Bruker diffractometer. 2,4-Dibromopentan-3-one (**6**) was prepared according to the procedure described by Hoffmann.³⁴

Synthesis of *exo-2-oxazolidinone dienes. General Procedure.* Lithium carbonate (9.00 g, 176.5 mmol) was placed in a flask and dried at 300 °C for 24 h. Toluene (10 mL), 2,3-pentanedione (2.00 g, 20 mmol), and anhydrous triethylamine

from light and stirred for 30 min. The appropriate aryl isocyanate (30 mmol) dissolved in anhydrous toluene (5 mL) was added drop by drop (for 20 min) into the reaction mixture and stirred at room temperature for 18 h. The mixture was filtered through Celite and extracted with CH_2Cl_2 (3 × 15 mL). The organic extracts were combined, dried over Na_2SO_4 , and the solvent was removed under vacuum. The final product was purified by column chromatography (SiO₂ with 10% triethylamine, hexane/AcOEt, 95:5) to afford the corresponding *exo*-2-oxazolidinone diene.

11

5-Ethylidene-4-methylene-3-phenyloxazolidin-2-one (1). Yellow solid, 1.2 g (30%), m.p. 82-84 °C (lit.^{11a,11b} 83-84 °C). ¹H NMR (300 MHz, CDCl₃) δ : 1.86 (d, J = 7.3 Hz, 3H, H-8), 4.18 (d, J = 2.9 Hz, 1H, H-6a), 4.58 (d, J = 2.9 Hz, 1H, H-6b), 5.42 (q, J = 7.3 Hz, 1H, H-7), 7.31-7.52 (m, 5H, PhH). ¹³C NMR (75 MHz, CDCl₃) δ : 10.4 (C-8), 81.6 (C-6), 99.0 (C-7), 127.1 (C-10), 128.5 (C-12), 129.5 (C-11), 133.0 (C-9), 139.0 (C-4), 143.0 (C-5), 152.6 (C-2).

3-Benzyl-5-ethylidene-4-methyleneoxazolidin-2-one (2). Yellow solid, 1.3 g (40%), m.p. 78-80 °C (lit.^{11b,11c} 80 °C). ¹H NMR (300 MHz, CDCl₃) δ : 1.79 (d, J = 7.2 Hz, 3H, H-8), 4.08 (d, J = 2.7 Hz, 1H, H-6a), 4.48 (d, J = 2.7 Hz, 1H, H-6b), 4.70 (s, 2H, H-9), 5.31 (q, J = 7.2 Hz, 1H, H-7), 7.12-7.47 (m, 5H, Ar). ¹³C NMR (75 MHz, CDCl₃) δ : 10.4 (C-8), 45.1 (C-9), 81.2 (C-6), 99.3 (C-7), 128.0 (C-11), 128.7 (C-13), 129.6 (C-12), 134.9 (C-10), 137.8 (C-4), 143.2 (C-5), 154.0 (C-2).

3-(4-Chlorophenyl)-5-ethylidene-4-methyleneoxazolidin-2one (3). White solid, 1.8 g (40%), m.p. 79-80 °C (lit.^{11a,11b} 78-79 °C). ¹H NMR (300 MHz, CDCl₃) δ : 1.86 (d, *J* = 7.5 Hz, 3H, H-8), 4.18 (d, *J* = 3.0 Hz, 1H, H-6a), 4.60 (d, *J* = 3.0 Hz, 1H, H-6b), 5.43 (q, *J* = 7.5 Hz, 1H, H-7), 7.27-7.34 (m, 2H, H-10), 7.44-7.50 (m, 2H, H-11). ¹³C NMR (75 MHz, CDCl₃) δ : 10.4 (C-8), 81.7 (C-6), 99.5 (C-7), 128.3 (C-10), 129.9 (C-11), 131.6 (C-9), 134.4 (C-12), 138.7 (C-4), 142.9 (C-5), 152.4 (C-2).

5-Ethylidene-3-(4-methoxyphenyl)-4-methyleneoxazolidin-2-one (4). Yellow solid, 2.06 g (64%), m.p. 76-78 °C (lit.^{11b,11c} 78-79 °C). ¹H NMR (300 MHz, CDCl₃) δ : 1.86 (d, *J* = 7.5 Hz, 3H, H-8), 3.83 (s, 3H, CH₃O), 4.11 (d, *J* = 3.0 Hz, 1H, H-6a), 4.54 (d, *J* = 3.0 Hz, 1H, H-6b), 5.40 (q, *J* = 7.5 Hz, 1H, H-7), 6.9-7.0 (m, 2H, H-10), 7.23-7.25 (m, 2H, H-11). ¹³C NMR (75 MHz, CDCl₃) δ : 10.5 (C-8), 55.7 (C-13), 81.6 (C-6), 99.2 (C-7), 115.1 (C-11), 125.8 (C-10), 128.6 (C-9), 139.8 (C-4), 143.4 (C-5), 153.2 (C-2), 159.8 (C-12).

3-(4-Methoxyphenyl)-4-methylene-5-propylideneoxazolidin-2-one (5).³⁵ Use of the general procedure with 2.0 g of 2,3hexanedione and 3.9 g of *p*-methoxyphenyl isocyanate gave 1.67 g (39%) of **5** as a white solid. M.p. 76-78 °C (lit.^{11c} 76-78 °C). ¹H NMR (300 MHz, CDCl₃) δ : 1.09 (t, *J* = 7.5 Hz, 3H, H-9), 2.32 (q, *J* = 7.5 Hz, 2H, H-8), 3.84 (s, 3H, OCH₃), 4.12 (d, *J* = 2.7 Hz, 1H, H-6a), 4.56 (d, *J* = 2.7 Hz, 1H, H-6b), 5.37 (t, *J* = 7.5 Hz, 1H, H-7), 6.96-7.04 (m, 2H, H-12), 7.21-7.29 (m, 2H, H-11). ¹³C NMR (75 MHz, CDCl₃) δ : 13.7 (C-9), 18.5 (C-8), 55.9 (OCH₃), 81.6 (C-6), 106.0 (C-7), 114.9 (C-12), 125.6 (C-10), 128.4 (C-11), 139.7 (C-4), 142.1 (C-5), 153.0 (C-2), 159.5 (C-13).

Synthesis of 3-Benzyl- and 3-Aryl-5,7,8-trimethyl-4,5,7,8tetrahydro-3*H*-cyclohepta[*d*]oxazole-2,6-diones 8-12. General Procedure. The corresponding *exo*-2-oxazolidinone diene (2.12 mmol) was added to a suspension of freshly activated copper³⁶ (0.872 g, 13.72 mmol) and dry NaI (3.74 g, 24.9 mmol) in dry acetonitrile (8.7 mL, 6.86 g, 167.07 mmol). The resulting mixture was stirred under a nitrogen atmosphere and 2,4-dibromopentan-3-one **6** (0.58 mL, 4.2 mmol) was added. The reaction mixture was stirred at 55 °C under a nitrogen atmosphere for 20 h. The solvent was removed under vacuum and the solid was poured into cold water (10 mL) and cold CH_2Cl_2 (10 mL). The insoluble copper salts were filtered and the organic phase was separated at 0 °C. The aqueous phase was extracted with cold CH_2Cl_2 (6 × 5 mL). The organic extracts were combined, washed with a 25% aqueous solution of NH₄Cl (10 mL), then with cold distilled water (3 x 10 mL), and dried over Na₂SO₄. The solvent was removed under vacuum. The final product was purified by column chromatography (SiO₂, hexane/AcOEt, 8:2) to afford the corresponding cycloheptaoxazole-2,6-dione.

(7R*,8R*,5S*)-3-Benzyl-5,7,8-trimethyl-4,5,7,8-tetrahydro-

3H-cyclohepta[d]oxazole-2,6-dione (8). Use of the general procedure, with 0.50 g of 2, 0.88 g of copper, 3.8 g of sodium iodide and 1.12 g of 6 in 10.2 mL of acetonitrile, gave 0.505 g (73%) of 8 as a reddish oil. R_f 0.45 (hexane/EtOAc, 7:3). IR (KBr) 2979 (-CH₃), 2860 (-CH₂-), 1750 (C=O). ¹H NMR (500 MHz, CDCl₃) δ : 0.92 (d, J = 7.0 Hz, 3H, H-9), 1.14 (d, J = 7.0Hz, 3H, H-10), 1.34 (d, J = 7.0 Hz, 3H, H-11), 2.14 (ddd, J = -15.5, 6.5, 1.0 Hz , 1H, H-4b), 2.45 (m, 1H, H-8), 2.77 (m, 1H, H-5), 2.79 (m, 1H, H-7), 2.84 (ddd, J = -15.5, 5.5, 2.0 Hz, 1H, H-4a), 4.71 (d, J = -16.0 Hz, 1H, Ar-CH_a), 4.76 (d, J = -16.0 Hz, 1H, Ar-CH_b), 7.22 (d, J = 8.0 Hz, 2H, H_{ortho}), 7.30 (t, J = 1Hz, 1H, H_{para}), 7.35 (t, J = 8.0, 1.0, 2H, H_{meta}). ¹³C NMR (125 MHz, CDCl₃) **δ:** 14.6 (C-10), 15.6 (C-9), 19.7 (C-11), 26.7 (C-4), 36.3 (C-8), 45.4 (C-5), 45.8 (C-ArCH₂), 50.0 (C-7), 120.1 (C-3a), 127.4 (C_{ortho}), 129.3 (C_{meta}), 129.4 (C_{para}), 136.0 (C-8a), 136.3 (C_{ipso}) , 155.7 (C-2), 213.6 (C-6). MS $C_{18}H_{21}NO_3$ [EI⁺] m/z (%): 299 (M⁺), 284 (7), 266 (9), 208 (11), 125 (22), 65 (59), 43 (58), 41 (76). HRMS (EI) m/z [M⁺] calcd for C₁₈H₂₁NO₃: 299.1521. Found: 299.1524.

Mixture of adducts 9a/9b. Use of the general procedure, with 0.50 g of 1, 1.02 g of copper, 4.3 g of sodium iodide in 10.2 mL of acetonitrile and 1.21 g of 6, gave 0.498 g (72%) of 9a/9b as a reddish solid. R_f 0.43 (hexane/EtOAc, 6:4); m.p. 78-80 °C (CH₂Cl₂-hexane). IR (KBr) 2970 (-CH₃), 2934 (-CH₂-), 1741 (-NCO₂-), 1699 (C=O), 1396 (C=C) cm⁻¹. Signals assigned to adduct **9a**: ¹H NMR (500 MHz, C_6D_6) **5**: 0.81 (d, J = 7.0 Hz, H-9), 0.97 (d, J = 6.0 Hz, 3H, H-10), 1.08 (d, J = 6.5 Hz, 3H, H-11), 1.70 (dd, J = -16.0, 6.5 Hz, 1H, H-4b), 2.16 (m, 2H), 2.25 (dd, J = -16.0, 4.0, 3.5 Hz, 1H, H-4a), 2.32 (m, 1H, H-7), 2.32 (m, 1H, H-8), 6.99 (t, J = 7.0 Hz, 1H, H_{para}), 7.04 (t, J = 7.0, 2H, H_{meta}), 7.05 (d, J = 7.0 Hz, 2H, H_{ortho}). ¹³C NMR (125 MHz, C₆D₆) δ : 14.8 (C-10), 15.8 (C-9), 18.2 (C-11), 26.8 (C-4), 36.6 (C-8), 45.6 (C-5), 48.3 (C-7), 120.9 (C-3a), 127.5 (2C_{ortho}), 129.5 (2C C_{meta}), 128.3 (C_{para}), 134.3 (C_{ipso}), 137.7 (C-8a), 153.6 (C-2), 212.2 (C-6). Signals assigned to adduct **9b**: ¹H NMR (500 MHz, C_6D_6) δ : 0.79 (d, J = 7.0 Hz, 3H, H-9), 0.93 (d, J = 6.5 Hz, 3H, H-10), 0.93 (d, J = 6 Hz, 3H, H-11), 1.70 (dd, J = -16.0, 6.5 Hz, 1H, H-4b), 2.19 (m, 1H, H-5), 2.95 (dd, J = -16.0, 4.0, 3.0 Hz, 1H, H-4a), 2.56 (m, 1H, H-8), 2.63 (m, 1H, H-7), 6.92 (d, J = 8.0 Hz, 2H, H_{ortho}), 6.97 (t, J = 8.0, 1.0 Hz, 1H, H_{para}), 7.04 (t, J = 8.0 Hz, 2H, H_{meta}). ¹³C-NMR (C₆D₆, 125 MHz) δ: 13.3 (C-10), 13.4 (C-11), 16.0 (C-9), 27.3 (C-4), 34.0 (C-8), 45.0 (C-5), 46.7 (C-7), 119.6 (C-3a), 127.8 (2Cortho), 128.3 (Cpara), 129.5 (2Cmeta), 134.2 (C_{ipso}), 139.2 (C-8a), 153.7 (C-2), 211.8 (C-6) ppm. MS $C_{17}H_{19}NO_3$ [EI⁺] m/z (%): 285 (M⁺), 270 (20), 252 (17), 240 (9), 228 (60), 214 (49), 198 (30), 77 (50). HRMS (EI) m/z [M⁺] calcd for C₁₇H₁₉NO₃: 285.1365. Found: 285.1359.

Mixture of adducts 10a/10b. Use of the general procedure, with 0.50 g of **3**, 0.872 g of copper, 3.74 g of sodium iodide in 8.7 mL

of acetonitrile and 1.0 g of 6, gave 0.648 g (76%) of 10a/10b as a white powder. R_f 0.38 (hexane/EtOAc, 7:3); m.p. 76-78 °C (CH₂Cl₂-hexane); IR (KBr) 2981 (CH₃), 2869 (-CH₂-), 1739 (-NCO₂-), 1702 (C=O) cm⁻¹. Signals assigned to adduct **10a**: ¹H NMR (500 MHz, C_6D_6) δ : 0.80 (d, J = 7.0 Hz, 3H, H-9), 0.96 (d, J = 6.0 Hz, 3H, H-10), 1.06 (d, J = 6.5 Hz, 3H, H-11), 1.58 (m, 1H, H-4b), 2.09 (ddd, J = -16.0, 5.0, 1.5 Hz, 1H, H-4a), 2.11 (m, 1H, H-5), 2.25 (m, 1H, H-7), 2.28 (m, 1H, H-8), 6.59 (dd, J = 9.0, 1.0 Hz, 2H, H_{ortho}), 6.95 (dd, J = 9.0, 1.0 Hz, 2H, H_{meta}). ¹³C NMR (125 MHz, C₆D₆) δ: 14.8 (C-10), 15.8 (C-9), 18.2 (C-11), 26.8 (C-4), 36.5 (C-8), 45.4 (C-5), 48.3 (C-7), 120.4 (C-3a), 128.9 (Cortho), 129.7 (Cmeta), 132.6 (Cpara), 134.2 (Cipso), 137.9 (C-8a), 153.2 (C-2), 211.9 (C-6). Signals assigned to adduct 10b: ¹H NMR (500 MHz, C_6D_6) δ : 0.80 (d, J = 7.0 Hz, 3H, H-9), 0.92 (d, J = 6.0 Hz, 3H, H-10), 0.93 (d, J = 6.5 Hz, 3H, H-11), 1.58 (m, 1H, H-4b), 1.93 (ddd, J = -16.0, 5.0, 1.5 Hz, 1H, H-4a), 2.15 (m, 1H, H-5), 2.51 (m, 1H, H-8), 2.55 (m, 1H, H-7), 6.68 (dd, J = 9.0, 1.0 Hz, 2H, H_{ortho}), 6.98 (dd, J = 9.0, 1.0 Hz, 2H, H_{meta}). ¹³C NMR (125 MHz, C₆D₆) δ: 13.3 (C-11), 13.3 (C-10), 16.0 (C-9), 27.2 (C-4), 33.9 (C-8), 44.8 (C-5), 46.7(C-7), 119.2 (C-3a), 128.3 (C_{ortho}) , 128.6 (C_{meta}) , 132.7 (C_{para}) , 134.0 (C_{ipso}) , 139.3 (C-8a), 153.3 (C-2), 211.4 (C-6). MS C₁₇H₁₈ClNO₃ [EI⁺] m/z (%): 319 (M⁺), 304 (12), 286 (17), 260 (15), 204 (12), 168 (100), 167 (85), 151 (22), 137 (20). HRMS (EI) m/z [M⁺] calcd for C₁₇H₁₈ClNO₃: 319.0975. Found: 319.0972.

Mixture of adducts 11a/11b. Use of the general procedure, with 0.50 g of 4, 0.825 g of copper, 3.6 g of sodium iodide in 8.5 mL of acetonitrile and 1.05 g of 6, gave 0.513 g (75%) of 11a/11b as a yellow oil. R_f 0.42 (hexane-EtOAc, 6:4). IR (KBr) 2950 (-CH₃), 2890 (-CH₂-), 1780 (-NCO₂-), 1710 (C=O), 1399 (C=C), 1280 (Ar-O), 2296 (CH₃O) cm⁻¹. Signals assigned to adduct **11a**: ¹H NMR (500 MHz, CDCl₃) δ : 1.09 (d, J = 6.5 Hz, 3H, H-9), 1.12 (d, J = 6.5 Hz, 3H, H-10), 1.38 (d, J = 6.5 Hz, 3H, H-11), 2.07(ddd, J = -16.0, 5.0, 1.5 Hz, 1H, H-4b), 2.52 (m, 1H, H-8), 2.82(m, 1H, H-4a), 2.89 (m, 1H, H-5), 2.89 (m, 1H, H-7), 3.83 (s, 3H, OCH₃), 6.99 (dd, J = 9.0, 1.0 Hz, 2H, H_{meta}), 7.18 (dd, J = 9.0, 1.0 Hz, 2H, H_{ortho}). ¹³C NMR (125 MHz, CDCl₃) δ: 15.7 (C-9), 16.0 (C-10), 18.2 (C-11), 26.5 (C-4), 36.5 (C-8), 45.7 (C-5), 48.1 (C-7), 55.4 (CH₃O), 114.8 (C_{meta}), 121.2 (C-3a), 125.7 (C_{ipso}), 128.8 (Cortho), 137.5 (C-8a), 154.3 (C-2), 159.7 (Cpara), 213.2 (C-6). Signals assigned to adduct **11b**: ¹H-NMR (500 MHz, CDCl₃) δ: 1.08 (d, J = 6.5 Hz, 3H, H-9), 1.10 (d, J = 6.5 Hz, 3H, H-11), 1.15 (d, J = 6.5 Hz, 3H, H-10), 2.07 (m, 1H, H-4b), 2.62 (ddd, J = -16.0, 5.0, 1.5 Hz, 1H, H-4a), 2.84 (m, 1H, H-5), 3.03 (m, 1H, H-8), 3.26 (dq, J = 6.5, 4.5 Hz, 1H, H-7), 3.83 (s, 3H, CH₃O), 6.99 (dd, J = 9.0, 1.0 Hz, 2H, H_{meta}), 7.18 (dd, J = 9.0, 1.0 Hz, 2H, H_{ortho}). ¹³C NMR (125 MHz, CDCl₃) δ: 13.3 (C-9), 13.4 (C-10), 14.5 (C-11), 27.2 (C-4), 33.8 (C-8), 45.0 (C-5), 46.8 (C-7), 55.4 (CH₃O), 114.8 (C_{meta}), 120.2 (C-3a), 125.7 (C_{ipso}), 128.7 (C_{ortho}) , 139.0 (C-8a), 154.4 (C-2), 159.8 (C_{para}), 213.8 (C-6). MS; $C_{18}H_{21}NO_4$ [EI⁺] m/z (%): 315 (M⁺), 300 (14), 282 (12), 258 (35), 244 (27), 228 (24), 123 (31), 77 (30), 69 (26), 55 (31), 41 (38). HRMS (EI) m/z [M⁺] calcd for C₁₈H₂₁NO₄: 315.1471. Found: 315.1478.

Mixture of adducts 12a/12b. Use of the general procedure, with 0.50 g of **5**, 0.882 g of copper, 3.78 g of sodium iodide in 8.8 mL of acetonitrile and 1.05 g of **6**, gave 0.524 g (74%) of **12a/12b** as a brown powder. R_f 0.42 (hexane/EtOAc, 6:4); m.p. 105-107 °C (CH₂Cl₂-hexane); IR (KBr) 2972 (-CH₃), 2932 (-CH₂-), 1746 (-NCO₂-), 1707 (C=O), 1399 (C=C), 1301, 1251 (Ar-O), 3096 (CH₃O) cm⁻¹. Signals assigned to adduct **12a**: ¹H NMR (500 MHz, CDCl₃) δ : 0.96 (t, *J* = 7.5 Hz, 3H, CH₃), 1.08 (d, *J* = 6.5

Hz, 3H, H-9), 1.18 (d, J = 6.5 Hz, 3H, H-10), 1.79 (m, 1H, H- M References and notes 11), 1.97 (m, 1H, H-11), 2.10 (m, 2H, H-4b), 2.56 (m, 1H, H-8), 2.75 (ddd, 1H, J = -14.5, 5.0, 1.5 Hz, 1H, H-4a), 2.87 (m, 1H, H-5), 3.01 (qd, J = 8.0, 7.0 Hz, 1H, H-7), 3.84 (s, 3H, CH₃O), 6.98 (d, J = 8.0 Hz, 2H, H_{meta}), 7.18 (d, J = 8.0 Hz, 2H, H_{ortho}). ¹³C NMR (125 MHz, CDCl₃) & 9.3 (CH₃), 14.9 (C-10), 15.8 (C-9), 24.2 (C-11), 26.7 (C-4), 41.9 (C-8), 45.1 (C-5), 45.1 (C-7), 55.5 (CH₃O), 114.8 (C_{meta}), 122.5 (C-3a), 125.7 (C_{ipso}), 128.8 (C_{ortho}), 136.4 (C-8a), 154.4 (C-2), 159.7 (C_{para}), 213.6 (C-6). Signals assigned to adduct **12b**: ¹H NMR (500 MHz, CDCl₃) δ : 0.99 (t, J = 7.5 Hz, 3H, CH₃), 1.09 (d, J = 6.5 Hz, 3H, H-9), 1.17 (d, J =6.5 Hz, 3H, H-10), 1.33 (m, 1H, H-11), 1.71 (m, 1H, H-11), 2.10 (m, 1H, H-4b), 2.44 (dd, J = -14.5, 4.5 Hz, 1H, H-4a), 2.90 (td, J = 8.0, 4.5 Hz, 1H, H-8), 2.94 (m, 1H, H-5), 3.08 (dq, J = 7.0, 4.0 Hz, 1H, H-7), 3.84 (s, 3H, CH₃O), 6.99 (d, J = 8.0 Hz, 2H, H_{meta}), 7.18 (d, J = 8.0 Hz, 2H, H_{ortho}). ¹³C NMR (125 MHz, CDCl₃) δ : 12.4 (CH₃), 13.3 (C-10), 16.3 (C-9), 21.6 (C-11), 28.1 (C-4), 40.2 (C-8), 44.1 (C-5), 48.7 (C-7), 55.5 (CH₃O), 114.8 (C_{meta}), 120.4 (C-3a), 125.7 (Cipso), 128.6 (Cortho), 139.2 (C-8a), 154.3 (C-2), 159.7 (C_{para}), 213.4 (C-6). MS $C_{19}H_{23}NO_4$ [EI⁺] m/z (%): 329 (M⁺), 300 (67), 272 (22), 244 (100), 200 (32), 174 (16), 69 (29), 41 (13). HRMS (EI) m/z [M⁺] calcd for C₁₉H₂₃NO₄: 329.1627. Found: 329.1633.

Theoretical Methodology. All calculations were carried out with the Gaussian 09 program $package^{37}$ at the M06-X/6-31+G(d,p)¹⁹ level of density functional theory using the INT(GRID=ULTRAFINE) option. All optimizations to minima and transition states were carried out using the OPT=TIGHT option. The transition states were located with the OPT=QST3 options and stationary points were characterized by the determination of vibrational frequencies. The corresponding thermochemical analyses were carried out at 298.15 K and 1 atm of pressure. No scaling factors were used for the vibrational frequencies or zero-point energies. The electronic energies corrected by the inclusion of thermal free energies were used to obtain the relative free energies discussed in the text. The saddle points were confirmed by the presence of a single imaginary frequency, and the normal mode associated with this frequency was analyzed visually in order to confirm that the molecular motion corresponded to the cycloaddition. The minima showed only real vibrational frequencies. The presence of solvent was accounted for with the default method in Gaussian 09 (IEFPCM).²⁰ The minima and TS obtained in the gas phase were reoptimized under these conditions and vibrational frequency analyses were carried out again, also within the PCM formalism.

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Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/XXXX-XX.

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14

SUPPLEMENTARY DATA

Synthesis and structural studies of novel fused seven-membered carbocycles derived from exo-2-oxazolidinone dienes through (4 + 3) cycloadditions

Patricia Alcázar^a, Indira Cruz^a, Carlos González-Romero^a, Erick Cuevas-Yañez^b, Eduardo Díaz^c, Joaquín Tamariz^d, Hugo A. Jiménez-Vázquez^d, David Corona-Becerril^b, Rubén A. Toscano^c, and Aydeé Fuentes-Benítes^a,

^a Facultad de Química, Universidad Autónoma del Estado de México, Paseo Tollocan y Colón, 50000, Toluca, Estado de México, México.

^b Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM. Carretera Toluca-Atlacomulco, Km. 14.5, Toluca, 50200, Estado de México, México.

^c Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior, C.U. Coyoacán, 04510 México, D.F., México.

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

*Corresponding author: Tel.: +52 722 2175 109x113; fax: +52 722 2173 890. E-mail: mpagfuentesb@uaemex.mx

CONTENTS

General procedure for the synthesis of 2,4-dibromopentan-3-one (6)	S2-S2
Previous treatments for the [4 + 3] cycloaddition reaction	
of diverse <i>exo</i> -2-oxazolidinone dienes and the oxyallyl cation	S2-S3
General computational methods	S3-S8
¹ H, ¹³ C and 2D NMR spectra of compounds 8, 9a-b, 10a-b, 11a-b, and	
12a-b	S9-S36

General procedure for the synthesis of 2,4-dibromopentan-3-one (6).



3-Pentanone (5 mL, 47.14 mmol) and phosphorus tribromide (0.09 mL, 0.94 mmol) was placed in a flask protected from moisture with an anhydrous calcium chloride trap, magnetic stirring and a glass tube immersed in a trap with a saturated solution of sodium bicarbonate (10%). The mixture was stirred for 30 min. Then, bromine (4.8 mL, 94.3 mmol) was added dropwise; stirring and cooling (-10 to 0 °C) was continued for 1 hr. The reaction was stopped by addition of distilled water (20 mL), the organic phase was separated and the aqueous phase washed with ether (3 x 10 mL). The combined organic phase was washed with 10% aqueous solutions of sodium carbonate (3 x 15 mL) and 10% sodium bisulphite (3 x 10 mL), and later, dried over dry sodium sulphate and filtered. The solvent was removed under vacuum and the residue was purified by fractionated distillation at 65-70 °C and 10 mm Hg, obtaining 8.36 g (73%) of **7** as a light dark oil R_f 0.82; (hexane-EtOAc, 9:1). ¹H-NMR (300 MHz, CDCl₃) δ : 1.81 (d, *J* = 6.6, 3H), 4.99 (q, *J* = 6.6, Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 19.45 (C-1, C-5), 43.79 (C-2, C-4), 195.92 (C-3).

Previous treatments for the [4 + 3] cycloaddition reaction of diverse *exo*-2oxazolidinone dienes and the oxyallyl cation. Synthesis of 3-Benzyl- and 3-Aryl-5,7,8trimethyl-4,5,7,8-tetrahydro-3*H*-cyclohepta[*d*]oxazole-2,6-diones 8-12.

1. Activation of copper powder: In a 250 mL round-bottomed flask, containing copper powder (10 g) a solution of iodine in acetone (2% w/v) (100 mL) was added. The suspension was stirred for 30 min and filtered through a Büchner funnel. The solid was washed with 60 mL of a 1:1mixture of 35% (w/w) aqueous HCl and acetone, and afterwards with distilled water (100 mL) followed by acetone (50 mL). Copper powder with a metallic luster was obtained, which was dried under high vacuum for 30 min and stored in an inert atmosphere (N₂), in the dark, in a desiccator.

2. Activation of NaI. Sodium iodide used in cycloaddition reactions should be activated (dehydrated) before use. For this purpose, NaI was ground and then dehydrated in an oven at 100 °C for 5 h. It is necessary to cool it to room temperature in a desiccator prior to use.

COMPUTATIONAL DATA

Cartesian coordinates and energies of the stationary points mentioned in the text.

M06-2X/6-31+G(d,p)/PCM(benzene) cartesian coordinates and energies of the lowest-energy conformer of **10a**.

SCF	Done: E(RM062)	X) = -1398.92	604795 A.U.	after 1 cycles
Sum	of electronic	and zero-point	Energies=	-1398.601676
Sum	of electronic	and thermal En	ergies=	-1398.581638
Sum	of electronic	and thermal En	thalpies=	-1398.580694
Sum	of electronic	and thermal Fr	ee Energies=	-1398.651678
С	3.2859667446	0.0810842868	-0.950739036	
С	2.3892528404	0.1492068436	0.1146947585	
С	2.7622613616	-0.296775869	3 1.382984020	2
С	4.0276404519	-0.839400958	6 1.584552815	5
С	4.9142526168	-0.904969875	9 0.513811232	2
С	4.5592848617	-0.442001547	9 -0.75003245	94
Ν	1.0950720077	0.6930883295	-0.091985367	
С	-0.1460640229	0.135944744	2 0.291702244	8
С	-1.0756667611	1.054000816	5 -0.02110816	72
0	-0.4597405073	2.161789970	5 -0.57801992	9
С	0.884305309	1.94479826	-0.6306574314	
С	-0.3190627839	-1.25658665	67 0.82177711	67
С	-1.2937129286	-2.08175402	54 -0.0418327	182
С	-0.6235686416	-2.55924485	43 -1.3296243	314
0	1.6879292462	2.7338301135	-1.069114447	9
С	-2.5627323324	1.100436328	5 0.109981804	
С	-2.984033557	2.266161796	1.0144888531	
С	-3.1003984287	-0.26508007	8 0.6085033494	4
С	-2.5965735409	-1.34081229	2 -0.35281811	01
0	-3.2286342842	-1.60032394	39 -1.3563865	89
С	-4.6269050822	-0.28095418	08 0.67628843	92
Н	-2.9812473304	1.266058294	3 -0.89355558	68
Н	-0.6414011417	-1.22452776	94 1.86745311	
Н	0.6478040457	-1.766684039	8 0.816165456	9
Н	-1.6004735582	-2.95846769	95 0.54890500	76
Н	-2.68887659	-0.4502175047	1.6087228312	
Н	0.2277175993	-3.204325991	9 -1.09706417	99
Н	-4.9884799771	0.399649642	7 1.449804676	5
Н	-4.9898728959	-1.28470159	15 0.91126109	51
Н	-5.0555876146	0.013244076	5 -0.28518423	39
Н	-0.2597734547	-1.70147663	29 -1.9066973	974
Н	-1.3277597025	-3.10983565	65 -1.9539090	924
Н	-4.0650946732	2.415911187	8 0.981185378	8
Н	-2.5048117356	3.191435257	9 0.686122185	2
Н	-2.6867882761	2.071981945	2 2.050646994	9
Н	2.0675477201	-0.209523010	7 2.213029356	1
Н	4.3284475368	-1.193068778	6 2.564285361	7
C1	6.5047006212	-1.57560086	8 0.762581105	

H 5.2682611042 -0.4963346886 -1.5683609195 H 2.9887887535 0.4466506214 -1.9274503772

M06-2X/6-31+G(d,p)/PCM(benzene) cartesian coordinates and energies of the lowest-energy conformer of **10b**.

SCF	Done: E(RM062X)) = -1398.92638417 A.U. after 2 cycles
Sum	of electronic ar	nd zero-point Energies= -1398.601592
Sum	of electronic ar	nd thermal Energies= -1398.581566
Sum	of electronic ar	nd thermal Enthalpies= -1398.580621
Sum	of electronic ar	nd thermal Free Energies= -1398.650835
С	2.7235882012	0.8443186912 1.0602937415
С	2.4848114921	-0.0800791296 0.0432873509
С	3.4748448673	-0.3674504628 -0.8960338404
С	4.704451386 0	ð.2790265386 -0.8255265848
С	4.9234698506	1.2185411627 0.1779616954
С	3.9444193467	1.5091075881 1.1230876594
Ν	1.2345592793	-0.7491709483 -0.0298969086
С	-0.0586336455	-0.1724572933 -0.0104318165
С	-0.9226696452	-1.2025480182 -0.0561034364
0	-0.2100332812	-2.3920774677 -0.0974570746
С	1.123052953 -	-2.1201565241 -0.0938759031
С	-0.2669512001	1.3085009878 0.0354366833
С	-1.5273912498	1.800910044 -0.7026825588
С	-1.6289434196	3.3213450783 -0.6068956755
0	1.9926451411	-2.9589146918 -0.1419644961
С	-2.4068149445	-1.3619016648 0.0383833509
С	-3.1834925643	-0.2185458208 -0.6679829322
С	-4.694563137	-0.4096929808 -0.5546508216
С	-2.8196253379	-1.5638576392 1.5052285511
С	-2.75872676 1	1.1303289484 -0.1001036317
0	-3.3520023217	1.6412606306 0.8293232136
Н	-2.6457755075	-2.2785181969 -0.5149667999
Н	0.6012924557	1.7988293608 -0.4172211795
Н	-0.3198730972	1.6557514278 1.0761612835
Н	-1.4434300912	1.4917055594 -1.7505002076
Н	-2.8874444005	-0.2446983886 -1.7227219862
Н	-0.7401781572	3.7880549 -1.0402140951
Н	-4.9748270097	-1.4225805656 -0.8586884154
Н	-5.2169874048	0.2998325257 -1.2013506589
Н	-5.0334534281	-0.2387113467 0.4685772372
Н	-1.7192078685	3.6323429638 0.4366536369
Н	-2.5075198033	3.6883088901 -1.1431629131
Н	-3.8635285123	-1.8769984689 1.5794349506
Н	-2.6941355555	-0.6389056166 2.0764407966
Н	-2.2001345264	-2.3410254784 1.9600445241
Н	3.2841856364	-1.1033056037 -1.6692361806
Н	5.4841382371	0.0610214338 -1.546600067
C1	6.4572711518	2.0441680183 0.2566319949
Н	4.1396542913	2.2333287438 1.9057888549
Н	1.9617295793	1.0365958137 1.8088486588

M06-2X/6-31+G(d,p)/PCM(acetonitrile) cartesian coordinates and energies of the *endo* transition state of the cycloaddition between 7a and 1.

SCF	Don	e:	E(RM062	2X) =	-939.2437871	22 A.U.	after	2 cycles
Sum	of	elec	tronic	and	zero-point Ene	rgies=	-9	38.919074
Sum	of	elec	tronic	and	thermal Energi	es=	-9	38.898389

Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= -938.897444 -938.969283

С	-0.1267240816	-0.2650672648	-1.1754679546	
Ν	0.9947401126	-0.7496038029	-0.4907036689	
С	0.6924536315	-1.9272352809	0.1477966233	
0	-0.5657969988	-2.299932685	-0.2156374395	
С	-1.1289911906	-1.3031774769	-0.9977099245	
С	1.3878090171	-2.5835500987	0.8849512188	
2	2.1573439565	0.0185125088	-0.1866549749	
2	-2.405672516	-1.3500027286	-1.4046065805	
С	-3.3319705563	-2.4934970603	-1.1364831573	
2	-0.2660130787	0.9383019869	-1.7698675199	
2	-1.5457952748	2.1429764897	0.1686776951	
2	-1.8537508301	0.9247685122	0.8369424282	
)	-1.0121715308	0.2775668472	1.5419000793	
2	-3.1997734981	0.5470406263	0.6499402429	
2	-3.8217802667	-0.5070991761	1.4865042701	
2	-0.3727068002	2.9674376349	0.54776008	
ł	-2.7419201585	-0.5455075848	-2.0518491308	
ł	-1.1572277908	1.1547905356	-2.3446507138	
	0.5610548722	1.6371247227	-1.8137852369	
	-2.3003278747	2.5788524257	-0.4818603547	
ł	-3.818324948	1.1207954898	-0.0347634774	
ł	-0.059494104	3.6337926302	-0.2582336442	
ł	-4.7372100659	-0.903054176	1.0438560892	
ł	-4.0853376039	-0.083311644	2.4668672842	
	-3.1035890528	-1.3109647073	1.6754950015	
	0.45540063 2	.3326677432 0	.8700592998	
	-0.6605841685	3.5990971379	1.4018556119	
ł	-4.345050232	-2.1336768107	-0.9422449239	
ł	-2.9965044875	-3.089709638	-0.2853523791	
ł	-3.3855765582	-3.1492563306	-2.0130771878	
2	3.0551967844	0.3331598272	-1.2037955214	
2	4.1743012451	1.1096036588	-0.9057396144	
2	4.3921129719	1.5488262654	0.4004882193	
	3.4875235721	1.220384428	1.4118498385	
2	2.3577983027	0.4586934868	1.1207868381	
ł	2.8741723294	-0.0284770368	-2.2115489799	
ł	4.8780239518	1.3639935319	-1.6914268081	
H	5.266563941	2.1489401684	0.6307957313	
H	3.6555061047	1.5676704306	2.4261386429	
H	1.6163562444	0.2154274143	1.8759659984	

M06-2X/6-31+G(d,p)/PCM(acetonitrile) cartesian coordinates and energies of the exo transition state of the cycloaddition between 7a and 1.

SCF	Done: E(RM062X)) = -939.239941	.226 A.U. aft	ter 2 cycles
Sum	of electronic a	nd zero-point En	ergies=	-938.916071
Sum	of electronic an	nd thermal Energ	;ies=	-938.894651
Sum	of electronic an	nd thermal Entha	lpies=	-938.893706
Sum	of electronic an	nd thermal Free	Energies=	-938.969412
С	-3.2228068772	0.1125262502	-1.2160812811	
С	-2.5093212742	-0.1687260549	-0.0519531036	
С	-3.0022580864	0.1915277493	1.2002497278	
С	-4.2351902377	0.8363130658	1.2861811567	
С	-4.9547233341	1.1289751667	0.1276424574	
С	-4.4473284664	0.7701846956	-1.1219801193	
Ν	-1.2520992263	-0.8352581102	-0.1492039811	
С	-0.0960664127	-0.3165538054	-0.7656956415	

С	0.8896307905	-1.3973651575	-0.6162377921	
0	0.2555324943	-2.4438244145	0.053586146	
С	-1.0312082643	-2.0993631551	0.3325752553	
С	0.0394464272	0.8936459356	-1.3204747389	
С	1.8295854914	2.2994058771	0.7732681967	
С	1.6349381596	3.7099571175	0.3687185571	
0	-1.8002725876	-2.8316974202	0.9075397152	
С	2.1674687993	-1.4744921804	-0.992008092	
С	3.0375697442	-2.6753028084	-0.7907709805	
С	3.2028682755	0.5694160814	1.1415499242	
С	2.7615552646	1.4516325925	0.1269876773	
0	3.3105868857	1.6526764154	-0.995271081	
С	4.5750736566	0.0122823688	1.1649313801	
Н	2.5793014246	-0.6057635446	-1.5022808991	
Н	-0.789444217	1.5918334372	-1.3468139227	
Н	0.986482426	1.1820021066	-1.7636471046	
Н	1.2533372982	1.9144818571	1.6088800726	
Н	2.5289147469	0.3257326215	1.9567308996	
Н	0.6436730683	3.8095409247	-0.0959896371	
Н	4.5667942366	-1.0168530914	1.5368253884	
Н	5.1970817819	0.5886035461	1.8631582208	
Н	5.0297842822	0.0604907013	0.1735438696	
Н	2.3878008562	4.0144557171	-0.3597313614	
Н	1.6389351937	4.3759863424	1.2364281631	
Н	3.9932162182	-2.388028635	-0.3423650757	
Н	3.268184533	-3.1395527617	-1.7557700766	
Н	2.5582448375	-3.420615865	-0.1540335958	
Н	-2.4259457122	-0.0389825366	2.0908743096	
Н	-4.6291444283	1.1150295662	2.2579758947	
Н	-5.9112175923	1.6367843583	0.1982477844	
Н	-5.0071696359	0.9952293573	-2.0237864962	
Н	-2.8178035398	-0.183650311	-2.1790628165	

M06-2X/6-31+G(d,p)/PCM(acetonitrile) cartesian coordinates and energies of the endo transition state of the cycloaddition between 7b and 1.

SCF	Done: E(RM062)	() = -1101.4602	27899 A.U.	after 1 cycles
Sum	of electronic a	and zero-point E	nergies=	-1101.133308
Sum	of electronic a	and thermal Ener	gies=	-1101.111118
Sum	of electronic a	and thermal Enth	alpies=	-1101.110174
Sum	of electronic a	and thermal Free	e Energies=	-1101.184489
С	2.5308043984	-0.0219754312	0.9824931037	
С	2.1513563149	-0.4984559631	-0.270836854	7
С	3.0682645585	-0.5935302402	-1.315994869	2
С	4.3864639472	-0.1956364086	-1.102667682	3
С	4.7810828227	0.27588106 6	.1497923611	
С	3.8550001434	0.3586317237	1.1902302969	
Ν	0.7987164813	-0.8872471038	-0.506916504	8
С	-0.0920114322	-0.2387438044	-1.36877096	45
С	-1.3530924332	-0.9305877714	-1.17299638	42
0	-1.1587662005	-1.8728771214	-0.17341600	38
С	0.1080760159	-1.7551722335	0.300565337	
С	0.134573075	0.8875817869	-2.0835194468	
0	0.4932017542	-2.3409774311	1.2864693362	
С	-2.5542952088	-0.7114424891	-1.72484750	75
С	-3.7859012702	-1.4977716995	-1.41364909	23
С	-0.7729190153	2.4818471253	-0.354362991	
С	0.5621863373	2.9577464784	0.0838187296	
С	-1.5219254754	1.542558342	0.410668619	
С	-2.89218745	1.5644014623	0.1274587096	

С	-3.8674277143	0.8318505919	0.9740939483
0	-0.970346742	0.7605204612	1.2716752638
Н	-2.5999049691	0.0370083149	-2.5105347045
Н	-0.6233368864	1.244873043	-2.7691211236
Н	1.1259135701	1.3209100955	-2.1403367774
Н	-1.3039567172	3.0554305241	-1.1097126637
Н	-3.2503084179	2.2098166185	-0.6692663989
Н	0.4001008425	3.7416367665	0.8389788192
Н	-4.8687033196	0.8264515682	0.5424631246
Н	-3.9236300527	1.3045057085	1.9646790991
Н	-3.5303247004	-0.1972958844	1.1429753411
Н	1.132811445	3.4030401611	-0.7322660565
Н	1.1272243814	2.1546903893	0.5590058106
Н	-4.6411395407	-0.8321960252	-1.2697634451
Н	-3.6577922658	-2.113153238	-0.521617235
Н	-4.0288128393	-2.1552456495	-2.2555031631
Н	2.7472603798	-0.9762863215	-2.2800126961
Н	5.1053512642	-0.2638059106	-1.9122227792
Н	5.8097829222	0.5789397625	0.3148467073
Н	4.1597737735	0.7291588056	2.1633443291
Н	1.7902710833	0.059173659	1.7710780226
Na	-1.06417786	-0.711291722	2.9164833852

M06-2X/6-31+G(d,p)/PCM(acetonitrile) cartesian coordinates and energies of the *exo* transition state of the cycloaddition between **7b** and **1**.

SCF	Done: E(RM062	2X) = -1101.456	557611	A.U. after	r 2 cycles
Sum	of electronic	and zero-point	Energies=		-1101.128450
Sum	of electronic	and thermal Ene	ergies=	X Y	-1101.105588
Sum	of electronic	and thermal Ent	halpies=		-1101.104644
Sum	of electronic	and thermal Fre	ee Energies	s=	-1101.182841
Ν	-1.1688528922	-0.809422488	-0.1937	752932	
С	-0.0128689078	-0.3082702345	-0.813	6839532	
С	0.9689235112	-1.3817562011	-0.64214	461492	
0	0.3289587333	-2.426306149	0.0170044	4389	
С	-2.4037876184	-0.1053461262	-0.064	1411458	
С	-3.187938842	0.1097515714	-1.196012	28767	
С	-4.3830537117	0.8150431031	-1.0701	717311	
С	-4.7883568211	1.2872164874	0.179003	31322	
С	-3.9971059976	1.0610850175	1.30568	74645	
С	-2.7936854821	0.367889228	1.1867848	8135	
С	0.1323921244	0.8939855562	-1.388544	41965	
С	2.2574557742	-1.4487424082	-0.99020	630535	
С	3.1163082238	-2.6586669861	-0.7985	786045	
0	-1.7265972723	-2.790931778	0.88679	965019	
С	1.5661803303	2.1619888663	0.7714124	4518	
С	2.712381501	1.4859660804	0.29803970	0 5	
0	3.3692844047	1.8275416132	-0.74951	32884	
С	1.1515271943	3.4800339935	0.248417	3447	
С	3.1092830297	0.4770345305	1.1967613	1771	
С	4.4524775296	-0.1352832529	1.153758	85117	
Н	2.6705523624	-0.5794383134	-1.4992	597006	
Н	-0.6933198709	1.5947743579	-1.43573	104063	
Н	1.0804402486	1.1658916032	-1.840082	25401	
Н	1.0266275778	1.7395620936	1.6145992	2636	
Н	2.4344371396	0.205064047	2.00322764	425	
Н	0.0715118545	3.6220645126	0.3235140	639	
Н	4.4476650164	-1.1520889025	1.552073	37376	
Н	5.1249397591	0.4548142317	1.7945840	0352	

ННННННН	4.8607650511 1.4972598061 1.6214893316 4.108703675 3.2606862809 2.6660014229 -2.1602907823 -4.3127008932 -5.7222502795 -4.999646971 -2.8593256102 4.7495070746	-0.107580542 3.6172540863 4.2599262812 -2.3809111556 -3.1683136281 -3.3650643497 0.1891198908 1.4278845378 1.8314338244 0.9888535278 -0.2729115785 2.4782941691	0.1406132152 -0.7779525732 0.866432592 -0.4351581013 -1.7577685134 -0.0993467219 2.0501823222 2.2766822799 0.2743567846 -1.9457072752 -2.1574936701 -2.267461977	R	







DEPT spectra of compound 8.





















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