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Design of a New and Highly Effective Chiral Auxiliary for Diels-Alder Reaction of 1-Aminodiene

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I. Description of methodological approach and of the dipole calculation

Computations were performed with the density functional methods (B3LYP 6-31G**) by using the Gaussian 98 Revision A.7 program package. A full optimization of each minimum and transition structure has always been performed. A check at the curvature and its eigenvector was systematically taken in order to guarantee the quality of the obtained results.

The [4+2] cycloaddition occurs from diene in *s-gauche* conformation. The aim of this study is to analyze the influence of the oxygen substitution by a sulfur on the TS*s-cis*/TS*s-trans* relative energy. The activation energies were thus calculated by summing the energies of the fully optimized isolated reactants considering the dienes presenting the dienyl moiety in a *s-gauche* conformation.

Dipole moment:

A Boys localization procedure allow to obtain the centroids of charges of localized molecular orbitals. The summation of those contributions coming from the orbitals describing the functional group fragment enables to define a group moiety dipole moment.

The center of the electronic charges is obtained by eq. 1, n_i being equal to 2 except for the MLO connecting the two fragment where n_i equals 1.

$$x_- = \frac{\sum_i n_i x_i}{\sum_i n_i} \quad (\text{eq. 1})$$

The nuclear center coordinates were similarly obtained by summation of nucleus coordinates (eq. 2).

$$x_+ = \frac{\sum_A Z_A x_A}{\sum_A Z_A} \quad (\text{eq. 2})$$

where Z_A is the charge of the nucleus A.

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II. Cartesian coordinates, total energies (a.u.) at the B3LYP 6-31G level and number of imaginary frequencies of the considered dienes and transition states**

N*-(butadienyl)-oxazolidin-2-one *s-trans

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-.976691	-.611809	1.625406
2	6	0	-.942476	-.685389	3.087146
3	6	0	.138541	-.577359	3.872685
4	6	0	-.072541	.051801	.880079
5	1	0	-1.808362	-1.113710	1.135493
6	1	0	-1.907889	-.857175	3.562786
7	1	0	1.139066	-.458486	3.466156
8	1	0	.052204	-.609533	4.953679
9	1	0	.741127	.619796	1.318341
10	7	0	-.071503	.110755	-.507414
11	6	0	.953003	.731147	-1.214768
12	6	0	-.952255	-.642435	-1.380400
13	8	0	1.889339	1.338814	-.760164
14	1	0	-2.005487	-.442174	-1.159475
15	8	0	.740517	.535836	-2.549119
16	6	0	-.534241	-.094806	-2.759060
17	1	0	-1.238127	.657674	-3.128921
18	1	0	-.413541	-.874389	-3.513100
19	1	0	-.777348	-1.721450	-1.275331

E(B3LYP 6-31G**) = -477.349501

Number of imaginary frequencies = 0

N*-(butadienyl)-oxazolidin-2-one *s-cis

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	.568353	.276371	1.743057
2	6	0	.394134	.222120	3.195421
3	6	0	-.768395	.207387	3.863372
4	6	0	-.309542	-.273975	.884399
5	1	0	1.454873	.762533	1.352245
6	1	0	1.319121	.209120	3.771976
7	1	0	-1.725059	.288993	3.354526
8	1	0	-.796602	.129635	4.945339
9	1	0	-1.171418	-.821307	1.256105
10	7	0	-.271083	-.230633	-.515189
11	6	0	.688415	.408666	-1.287722
12	6	0	-1.105933	-1.097636	-1.337649
13	8	0	1.618725	1.082481	-.918222
14	1	0	-2.159612	-1.032228	-1.050022
15	8	0	.427032	.152307	-2.608478
16	6	0	-.840430	-.511676	-2.731476
17	1	0	-1.599865	.225849	-3.014403
18	1	0	-.762480	-1.268299	-3.513778
19	1	0	-.787053	-2.145721	-1.258470

E(B3LYP 6-31G**) = -477.344749

Number of imaginary frequencies = 0

N-(butadienyl)-oxazolidin-2-thione *s-trans*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.213144	-.788249	1.678803
2	6	0	-1.201491	-.857338	3.141057
3	6	0	-.131891	-.737669	3.940199
4	6	0	-.300047	-.119198	.948579
5	1	0	-2.032951	-1.301311	1.180999
6	1	0	-2.171918	-1.038853	3.602076
7	1	0	.872561	-.609610	3.546890
8	1	0	-.232567	-.771252	5.019863
9	1	0	.503276	.454517	1.397073
10	7	0	-.279803	-.071341	-.441468
11	6	0	.700260	.548171	-1.183602
12	6	0	-1.203550	-.821844	-1.286932
13	16	0	2.007464	1.401418	-.650046
14	1	0	-2.242206	-.610277	-1.016639
15	8	0	.447538	.348048	-2.497570
16	6	0	-.838193	-.282083	-2.674804
17	1	0	-1.545868	.476288	-3.024391
18	1	0	-.734643	-1.058195	-3.434481
19	1	0	-1.028459	-1.899724	-1.179624

E(B3LYP 6-31G**) = -800.299120

Number of imaginary frequencies = 0

N-(butadienyl)-oxazolidin-2-thione *s-cis*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	.393165	.091608	1.883274
2	6	0	.152104	.024370	3.325709
3	6	0	-1.040201	.061099	3.937755
4	6	0	-.470716	-.418715	.986571
5	1	0	1.312045	.551153	1.539676
6	1	0	1.048337	-.041073	3.942183
7	1	0	-1.965713	.198826	3.385315
8	1	0	-1.123740	-.024713	5.016219
9	1	0	-1.356559	-.942396	1.334293
10	7	0	-.411752	-.387947	-.415262
11	6	0	.462132	.259869	-1.253188
12	6	0	-1.296864	-1.276175	-1.180382
13	16	0	1.744631	1.241479	-.910451
14	1	0	-2.322688	-1.221940	-.805856
15	8	0	.127895	-.024764	-2.541107
16	6	0	-1.144219	-.698882	-2.584672
17	1	0	-1.921952	.037428	-2.816475
18	1	0	-1.107286	-1.451546	-3.373174
19	1	0	-.949839	-2.314705	-1.109668

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E(B3LYP 6-31G**) = -800.291937

Number of imaginary frequencies = 0

TSs-*trans* of the reaction between *N*-(butadienyl)-oxazolidin-2-one and ethylene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.243031	1.360686	-.357842
2	6	0	-2.632536	1.276520	-.502713
3	6	0	-3.286622	.065394	-.711473
4	6	0	-.434726	.231097	-.424891
5	1	0	-.815846	2.297365	-.008163
6	1	0	-3.220706	2.149277	-.227245
7	1	0	-2.824393	-.694832	-1.332385
8	1	0	-4.372923	.050587	-.739169
9	1	0	-.695453	-.619899	-1.037256
10	7	0	.938443	.273282	-.167591
11	6	0	1.766325	-.793008	-.471452
12	8	0	1.450250	-1.836466	-.991283
13	6	0	-2.802701	-1.092449	1.018130
14	6	0	-1.427033	-1.097698	1.221048
15	1	0	-3.433759	-.515508	1.685501
16	1	0	-3.276932	-1.979554	.607901
17	6	0	1.665691	1.388421	.407889
18	1	0	1.203253	1.733182	1.339129
19	8	0	3.040920	-.487135	-.086111
20	6	0	3.051991	.750509	.644581
21	1	0	3.224933	.527437	1.702264
22	1	0	3.873309	1.365036	.271202
23	1	0	1.705106	2.236507	-.287930
24	1	0	-.822537	-1.933954	.886223
25	1	0	-.986653	-.476636	1.992566

E(B3LYP 6-31G**) = -555.9110583

Number of imaginary frequencies = 1

TSs-*cis* of the reaction between *N*-(butadienyl)-oxazolidin-2-one and ethylene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.184540	1.124860	-.664150
2	6	0	-2.582716	1.090843	-.728539
3	6	0	-3.310738	-.094213	-.735065
4	6	0	-.436041	-.044769	-.633170
5	1	0	-.687173	2.060783	-.438585
6	1	0	-3.112128	2.023748	-.547467
7	1	0	-2.924009	-.970287	-1.244931
8	1	0	-4.396243	-.049410	-.707380

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9	1	0	-.794585	-.931337	-1.139860
10	7	0	.961978	-.070259	-.460731
11	6	0	1.660536	.759810	.406414
12	6	0	-2.771324	-1.019456	1.140713
13	6	0	-1.388275	-1.089793	1.247349
14	1	0	-3.311143	-.289061	1.732542
15	1	0	-3.333633	-1.920811	.913248
16	6	0	1.746793	-1.255746	-.775970
17	1	0	1.649321	-1.536844	-1.828580
18	8	0	2.950864	.307452	.502307
19	6	0	3.159321	-.763394	-.430841
20	1	0	3.677650	-.368924	-1.311903
21	1	0	3.782263	-1.523222	.044105
22	1	0	1.439645	-2.110498	-.156311
23	1	0	-.877024	-2.024003	1.033328
24	1	0	-.844022	-.381501	1.859994
25	8	0	1.254030	1.725588	1.004753

E(B3LYP 6-31G**) = -555.9066216

Number of imaginary frequencies = 1

TSs-trans of the reaction between *N*-(butadienyl)-oxazolidin-2-thione and ethylene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.474349	-1.257606	-.729940
2	6	0	2.844368	-1.007152	-.866936
3	6	0	3.387166	.264047	-.702467
4	6	0	.577368	-.237660	-.432045
5	1	0	1.143256	-2.291889	-.683230
6	1	0	3.513155	-1.864738	-.887900
7	1	0	2.835906	1.133588	-1.043726
8	1	0	4.466269	.385765	-.741782
9	1	0	.734841	.779435	-.761139
10	7	0	-.774858	-.488084	-.166358
11	6	0	-1.754885	.468547	-.173369
12	16	0	-1.613661	2.077496	-.529150
13	6	0	2.895445	.785209	1.314001
14	6	0	1.535217	.608791	1.537264
15	1	0	3.599422	.086396	1.752745
16	1	0	3.280194	1.793175	1.187827
17	6	0	-1.317315	-1.814762	.113492
18	1	0	-.721013	-2.329264	.872944
19	8	0	-2.936357	-.101025	.164987
20	6	0	-2.726805	-1.460276	.602600
21	1	0	-2.806781	-1.484960	1.694323
22	1	0	-3.510863	-2.082274	.168442
23	1	0	-1.323791	-2.427695	-.796468
24	1	0	.853615	1.451528	1.492388
25	1	0	1.179784	-.259045	2.080973

E(B3LYP 6-31G**) = -878.861492

Number of imaginary frequencies = 1

TSs-*cis* of the reaction between *N*-(butadienyl)-oxazolidin-2-thione and ethylene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.265068	.490978	-1.191560
2	6	0	-2.664354	.500276	-1.246655
3	6	0	-3.450039	-.460550	-.619328
4	6	0	-.580645	-.508203	-.514276
5	1	0	-.718460	1.367728	-1.516557
6	1	0	-3.142743	1.406938	-1.609984
7	1	0	-3.116708	-1.491704	-.569182
8	1	0	-4.531122	-.350981	-.630815
9	1	0	-.996623	-1.505812	-.465481
10	7	0	.821061	-.533725	-.337151
11	6	0	1.652468	.493818	.028035
12	16	0	1.324956	2.098188	.254668
13	6	0	-2.936269	-.258856	1.468639
14	6	0	-1.561306	-.367239	1.626547
15	1	0	-3.403763	.714319	1.566896
16	1	0	-3.571031	-1.096884	1.742857
17	6	0	1.498734	-1.824662	-.183958
18	1	0	1.261813	-2.493982	-1.014873
19	8	0	2.903507	-.001045	.225551
20	6	0	2.960596	-1.383147	-.177355
21	1	0	3.411761	-1.436963	-1.174310
22	1	0	3.585984	-1.922768	.535209
23	1	0	1.196441	-2.306874	.755881
24	1	0	-1.125987	-1.315230	1.930344
25	1	0	-.949053	.511144	1.790435

E(B3LYP 6-31G**) = -878.8541537

Number of imaginary frequencies = 1

III. Experimental procedures and analyses for all new compounds

General.

All reagents were used directly as obtained commercially. The ^1H , ^{13}C and ^{15}N NMR spectra were recorded on Bruker AM-500 and Varian-Gemini 200 and 300 spectrometers, in CDCl_3 solution; chemical shifts are reported in ppm (δ) downfield from TMS (internal reference) for ^1H and ^{13}C NMR and from NH_3 (external reference) for ^{15}N NMR. GC analyses were realized on MN OPTIMAS-5 column or on Chirasil DEX CB column. HPLC analyses were performed on NOVAPAK AD column with UV-detector at 203 nm. The IR spectra were measured as NaCl pastille or as thin film on a Perkin-Elmer 1710 instrument. The HRMS were performed in the laboratory of Prof. R. Flammang (Université Mons-Hainaut, Belgium). Column chromatographies were performed on a silica gel MERCK 60 (40-63 μm). Optical rotation values, given in $\text{deg mL dm}^{-1} \text{g}^{-1}$, were taken on a Perkin-Elmer 241MC apparatus.

Synthesis of (4*R*,1*E*)-3-(3'-oxobut-1'-enyl)-4-phenyloxazolidin-2-thione (2).

Thiocarbonylbisimidazole (6.5 g, 36.50 mmol) was added to a solution of (1*R*,1*Z*)-4-(2'-hydroxy-1'-phenylethylamino)but-3-en-2-one (5 g, 24.35 mmol) in dichloromethane (100 mL). The solution was stirred overnight before being washed with water. The organic layer was dried (MgSO_4) and then concentrated in vacuo to give the titled compound as an oil (5.72 g, 95%): $[\alpha]^{25}_{\text{D}} -56.7$ ($c = 1.1$, CHCl_3) ^1H NMR (CDCl_3 , 300 MHz) δ 8.27 (d, $J = 15.0$ Hz, 1H), 7.45-7.20 (m, 5H), 5.43 (d, $J = 15.0$ Hz, 1H), 5.27 (dd, $J = 4.2, 9.0$ Hz, 1H), 4.95 (dd, $J = 9.0, 9.0$ Hz, 1H), 4.45 (dd, $J = 4.2, 9.0$ Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 196.7, 187.8, 138.6, 136.7, 129.9, 129.6, 126.0, 114.9, 76.1, 61.8, 27.3; ^{15}N NMR (CDCl_3 , 50 MHz) δ 152.4; IR (neat) ν 1635, 1558, 1380, 1232, 1190 cm^{-1} ; MS (CI) m/z (%) 247 (M^+ , 10), 143 (100); HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}+1$: 248.0711; found: 248.0728.

Synthesis of (4*R*,3*RS*)-3-(3'-hydroxybut-1'-enyl)-4-phenyloxazolidin-2-thione (3).

Sodium borohydride (1.7 g, 45.20 mmol) was added portionwise over 10 min to an ice-cooled solution of (4*R*,1*E*)-3-(3'-oxobut-1'-enyl)-4-phenyloxazolidin-2-thione (2) (5.59 g, 22.60 mmol) in methanol (120 mL) and the resulting solution was stirred at room temperature for two hours. Water (20 mL) was added dropwise and the resulting solution was stirred for 15 min whereupon the solution was concentrated under reduced pressure. The residue was extracted with dichloromethane (2 x 20 mL), the combined organic layers were dried (MgSO_4) and concentrated in vacuo to give the titled compound as a 1:1 mixture of diastereoisomers (4.8 g, 85%): ^1H NMR

(CDCl₃, 300 MHz) δ 7.50-7.10 (m, 6H), 5.23 (m, 1H), 4.98 (dd, J = 6.3, 14.7 Hz, 1H), 4.88 (dd, J = 3.3, 9.0 Hz, 1H), 4.37 (dd, J = 4.8, 9.0 Hz, 1H), 4.29 (dq, J = 6.3, 6.3 Hz, 1H), 1.19 and 1.08 (two d, for 2 diastereoisomers, J = 6.3 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 186.1, 136.9, 129.3, 128.9, 125.6, 125.1 (125.0), 121.1 (120.9), 74.9 (74.8), 66.8 (66.7), 62.1, 23.6 (23.4); IR (neat) ν 3356 (br), 1664, 1425, 1371, 1320, 1243, 1172 cm⁻¹; MS (CI) m/z (%) 249 (M⁺, 15), 104 (100); HRMS calcd for C₁₃H₁₅NO₂S+1: 250.0902; found: 250.0903.

Synthesis of (4*R*,1*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-thione (4).

Trifluoroacetic anhydride (3.09 mL, 21.73 mmol) was added dropwise to a stirred solution of (4*R*,3'*RS*)-3-(3'-hydroxybut-1'-enyl)-4-phenyloxazolidin-2-thione (3) (3.0 g, 12.08 mmol), 4-dimethyl-aminopyridine (15 mg, 0.12 mmol) and pyridine (2.29 mL, 27.78 mmol) in dry acetonitrile (40 mL) under argon atmosphere and the resulting solution was stirred at room temperature for 30 min. Triethylamine (4.48 mL, 32.62 mmol) was added and the resulting mixture was boiled under reflux for 4 hours, allowed to cool to room temperature and the solvent removed in vacuo. Saturated sodium bicarbonate solution (20 mL) was added and the residue extracted with dichloromethane (2 x 30 mL). The combined organic layers were dried (MgSO₄), concentrated in vacuo and purified by column chromatography on silica gel (elution with CH₂Cl₂) to give the titled compound as a yellow solid (2.0 g, 72%): [α]_D²⁵ -160.0 (c = 0.6, CHCl₃); mp 96-97 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.45-7.20 (m, 5H), 7.37 (d, J = 14.0 Hz, 1H), 6.27 (ddd, J = 10.5, 11.0 16.0 Hz, 1H), 5.52 (dd, J = 10.5, 14.0 Hz, 1H), 5.26 (dd, J = 4.5, 9.0 Hz, 1H), 4.99 (d, J = 16.0 Hz, 1H), 4.99 (d, J = 11.0 Hz, 1H), 4.89 (dd, J = 9.0, 9.0 Hz, 1H), 4.39 (dd, J = 4.5, 9.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 185.9, 137.2, 133.8, 129.5, 129.1, 127.6, 125.6, 117.5, 116.6, 74.9, 62.0; ¹⁵N NMR (CDCl₃, 50 MHz) δ 150.7; GC (MN OPTIMAS-5, 150→250, 5°C/min) 20.2 min; IR (NaCl) ν 1646, 1432, 1398, 1369, 1241, 1185 cm⁻¹; MS (CI) m/z (%) 232 (M+1, 30), 61 (100); HRMS calcd for C₁₃H₁₃NOS+1: 232.0796; found: 232.0793. Anal. Calcd for C₁₃H₁₃NOS: C, 67.50; H, 5.66; N, 6.05; S, 13.86. Found: C, 67.34; H, 5.70; N, 5.95; S, 13.76.

General procedure for cycloadditions.

Cycloadditions were performed by stirring and boiling under reflux a solution of one equivalent (~0.5 mmol) of diene, one to two equivalents of dienophile and phenanthrene (internal reference for conversion determination) in acetonitrile (~100 μ L). The solution was concentrated in vacuo to give the desired cycloadduct after purification by column chromatography. The conversions and selectivities were measured on the crude mixtures in GC, except mentioned. NMR data are given for the major stereoisomer.

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and methyl acrylate.

¹H NMR (CDCl₃, 500 MHz) δ 7.45-7.15 (m, 5H), 5.40 (m, 1H), 5.05 (m, 1H), 5.01 (dd, *J* = 4.0, 9.0 Hz, 1H), 4.81 (m, 1H), 4.50 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.00 (dd, *J* = 4.0, 9.0 Hz, 1H), 3.68 (s, 3H), 2.85 (ddd, *J* = 5.5, 5.5, 5.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 173.95, 158.15, 141.13, 130.11, 128.63, 128.24, 126.63, 124.17, 70.73, 59.08, 51.80, 48.21, 44.08, 23.26, 21.50; GC (MN Chirasil DEX CB, 150→225, 5°C/min) 33.4 min (66%), 36.0 min (12%), 36.3 (12%), 37.1 (10%); IR (NaCl) ν 1747, 1734 cm⁻¹; MS (CI) *m/z* (%) 302 (M+1, 50), 270(37), 192 (100); HRMS calcd for C₁₇H₁₉NO₄+1: 302.1392; found: 302.1395.

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and trimethylphosphonoacrylate.

[α]_D²⁵ -265.9 (*c* = 0.8, CHCl₃); mp 182-183 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.30-7.20 (m, 5H), 6.54 (d, *J* = 5.0, 1H), 5.69 (dd, *J* = 2.0, 8.0 Hz, 1H), 5.16 (dd, *J* = 5.5, 10.5, 1H), 5.03 (m, 1H), 4.69 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.13 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.86 (d, *J* = 4.5, 3H), 3.84 (d, *J* = 4.5 Hz, 3H), 3.74 (s, 3H), 2.51 (ddd, *J* = 4.5, 4.5, 13.5 Hz, 1H), 2.30 (m, 1H), 2.14 (m, 1H), 1.86 (ddd, *J* = 5.5, 5.5, 19.0, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 168.8 (d, *J* = 6.6 Hz), 158.2, 141.7, 128.8, 128.5, 128.2, 126.8, 123.9 (d, *J* = 8.9 Hz), 70.9, 58.9, 54.6 (d, *J* = 6.6 Hz), 53.4 (d, *J* = 5.0 Hz), 53.0, 52.9 (d, *J* = 146.5 Hz), 48.9 (d, *J* = 5.2 Hz), 22.5, 21.0 (d, *J* = 12.1); GC (MN OPTIMAS-5, 150→250, 5°C/min) 45.2 min (76%), 45.9 min (14%), 49.3 (10%); IR (NaCl) ν 1745, 1719, 1263 cm⁻¹; MS (CI) *m/z* (%) 438 (M+1, 10), 410 (65), 247 (100); HRMS calcd for C₂₁H₂₈NO₇P+1: 438.1682; found: 438.1689.

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and dimethylacetylenedicarboxylate.

¹H NMR (CDCl₃, 500 MHz) δ 7.40-7.22 (m, 5H), 5.40 (m, 1H), 5.26 (m, 2H), 4.80 (dd, *J* = 6.5, 8.5, 1H), 4.60 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.14 (dd, *J* = 6.5, 8.5 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H),^a 2.72 (m, 1H), 2.53 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 167.5, 166.3, 158.1, 139.6, 135.1, 132.7, 128.6, 128.5, 127.5, 124.6, 123.2, 70.5, 57.7, 52.6, 52.4, 49.2, 26.7; IR (NaCl) ν 1762 (br), 1683, 1648 cm⁻¹; MS(CI) *m/z* (%) 358.5 (M+1, 8), 357 (35), 355 (65), 162 (100), HRMS calcd for C₁₉H₁₉NO₆+1: 358.1290; found: 358.1288.

^a in the second isomer: 3.74 and 3.61 (integration: 17%)

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and *N*-methyl maleimide.

¹H NMR (CDCl₃, 500 MHz) δ 7.40-7.20 (m, 5H), 5.71 (m, 1H), 5.59 (m, 1H), 4.95 (dd, *J* = 3.0, 8.5 Hz, 1H), 4.80 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.48 (m, 1H),^a 4.07 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.60 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.10 (dd, *J* = 7.5, 7.5 Hz, 1H), 2.89^b (s, 3H), 2.67 (dd, *J* = 7.5, 16.0 Hz, 1H), 2.05 (m, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 179.0, 177.2, 158.2, 141.2, 129.4, 128.6, 126.2, 125.9, 125.8, 71.5, 59.4, 50.3, 41.7, 38.3, 24.9, 23.5; GC (MN OPTIMAS-5, 150→250, 5°C/min) 46.9 min (93%), 47.1 min (7%); IR (NaCl) ν 1756, 1695 cm⁻¹; MS(CI) *m/z* (%) 327 (M+1, 3), 310 (28), 278 (100); HRMS calcd for C₁₈H₁₈N₂O₄ +1: 327.1344; found: 327.1339.

^a in the minor diastereoisomer: 4.39 (dd, *J* = 4.3, 8.8 Hz, 1H)

^b in the minor diastereoisomer: 2.94 (s, 3H)

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and DEAD.

¹H NMR (CDCl₃, 500 MHz) δ 7.50-7.10 (m, 5H), 6.49(m, 1H), 5.45^a (dddd, *J* = 10, 5, 2, 2 Hz, 1H), 5.18^b (m, 1H), 5.06^c (m, 1H), 4.59 (dd, *J* = 9, 8.8 Hz, 1H), 4.30 (m, 2H), 4.19 (m, 2H), 4.15 (dd, *J* = 18.5, 5Hz, 1H), 4.03 (dd, *J* = 9, 6.4 Hz, 1H), 3.60 (dd, *J* = 18.5, 2 Hz, 1H), 1.35 (t, *J* = 7 Hz, 3H), 1.25 (t, *J* = 7 Hz, 3H);¹³C NMR (CDCl₃, 125 MHz)^d δ 157.4 (157.2), 154.7 (153.8), 154.2 (153.7), 139.5, 128.6, 128.3, 126.7, 125.6 (124.6), 122.9 (123.6), 70.6 (70.5), 62.7, 62.3, 60.2, 56.8 (57.9), 42.3 (41.5), 14.1, 14.6 (14.3) ; GC (MN OPTIMAS-5, 150→250, 5°C/min) 31.1 min (38%), 32.0 min (62%); IR (NaCl) ν 1768, 1717 cm⁻¹; MS (CI) *m/z* (%) 390 (M+1, 2), 249 (37), 177 (75), 164 (100); HRMS calcd for C₁₉H₂₃N₃O₆: 389.1587; found: 389.1574.

^a in the minor isomer: 5.39 (m, 1H)

^b in the minor isomer: 5.28 (m, 1H)

^c in the minor isomer: 4.89 (m, 1H)

^d values in parentheses correspond to the minor diastereoisomer

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and dimethylfumarate.

¹H NMR (CDCl₃, 500 MHz) δ 7.40-7.15 (m, 5H), 5.35 (m, 1H), 5.08 (m, 1H), 4.95 (m, 1H),^a 4.89 (dd, *J* = 4.0, 8.5 Hz, 1H), 4.46 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.01 (dd, *J* = 4.0, 8.5 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 3.11-3.03 (m, 2H), 2.30 (m, 1H), 1.93 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 174.5, 173.1, 157.9, 140.6, 129.3, 128.8, 127.9, 126.7, 125.9, 70.7, 58.9, 52.2, 52.1, 48.0, 46.3, 38.1, 27.4; GC (MN OPTIMAS-5, 150→225, 5°C/min) 34.8 min (44%), 37.6 min (31%), 38.7 min (25%); IR (NaCl) ν 1760 (br), 1673, 1629 cm⁻¹; MS (CI) *m/z* (%) 360 (M+1, 12), 328 (14), 218 (24), 164 (100); HRMS calcd for C₁₉H₂₁NO₆ +1: 360.1447; found: 360.1453.

^a in the second isomer: 4.71 (dd, *J* = 7.5, 16.5 Hz, 1H)

Characterization of cycloadduct of the reaction between 4 and methyl acrylate.

¹H NMR (CDCl₃, 500 MHz) δ 7.40-7.15 (m, 5H), 5.60-5.50 (m, 2H), 5.33 (dd, *J* = 2.5, 8.5 Hz, 1H), 5.14 (m, 1H), 4.69 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.27 (dd, *J* = 2.0, 8.5 Hz, 1H), 3.74 (s, 3H),^a 3.16 (m, 1H), 2.17-1.95 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.3, 173.5, 140.3, 130.6, 129.0, 128.6, 126.4, 123.1, 74.9, 62.7, 52.5, 52.0, 42.9, 23.0, 22.1; GC (MN OPTIMAS-5, 150→250, 5°C/min) 33.6 min (93%), 35.4 min (2%), 36.7 (5%); IR (NaCl) ν 1733, 1669, 1436, 1279 cm⁻¹; MS (CI) *m/z* (%) 318 (M+1, 3), 317 (10), 225 (100); HRMS calcd for C₁₇H₁₉NO₃S: 317.1085; found: 317.1086.

^a in the second isomer: 3.76 (s, 3H)

Characterization of cycloadduct of the reaction between 4 and trimethylphosphonoacrylate.

[α]_D²⁵ -245.2 (*c* = 0.9, CHCl₃); mp 190-191 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.29-7.16 (m, 5H), 6.35 (s, 1H),^a 5.62 (d, *J* = 8.0 Hz, 1H), 5.16 (m, 1H), 5.10 (m, 1H), 4.80 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 6.5, 3H), 3.84 (d, *J* = 6.5 Hz, 3H), 3.77 (s, 3H), 2.52 (ddd, *J* = 6.5, 6.5, 13.5 Hz, 1H), 2.32 (m, 1H), 2.12 (m, 1H), 1.87 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 189.4, 168.8 (d, *J* = 7.2 Hz), 140.4, 128.9, 128.7, 128.6, 126.7, 122.7 (d, *J* = 8.9 Hz), 74.9, 62.5, 54.3 (d, *J* = 6.9 Hz), 53.8 (d, *J* = 8.0 Hz), 53.2, 53.1 (d, *J* = 5.4 Hz), 52.6 (d, *J* = 133.0 Hz), 22.2, 21.0 (d, *J* = 12.1)^b; GC (MN OPTIMAS-5, 150→250, 5°C/min) 44.6 min (84%), 47.2 min (16%); IR (NaCl) ν 1727, 1714 cm⁻¹; MS (CI) *m/z* (%) 426 (M+1, 20), 60 (100); HRMS calcd for C₁₉H₂₄NO₆PS+1: 426.1140; found: 426.1147.

^a in the second isomer: 6.11 (d, *J* = 12.5 Hz, 1H)

^b in the second isomer: 21.8 (d, *J* = 3.1 Hz)

Characterization of cycloadduct of the reaction between 4 and dimethylacetylenedicarboxylate.

¹H NMR (CDCl₃, 500 MHz) δ 7.40-7.20 (m, 5H), 6.20 (m, 1H), 5.33 (m, 2H), 5.03 (m, 1H), 4.80 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.43 (dd, *J* = 3.0, 9.0 Hz, 1H), 3.86 (s, 6H), 2.80 (m, 1H), 2.57 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 188.2, 167.3, 166.2, 138.9, 135.1, 132.3, 129.2, 129.0, 128.7, 127.3, 124.8, 122.0, 74.8, 61.2, 53.3, 52.7, 52.5, 26.7; GC (MN OPTIMAS-5, 150→250, 5°C/min) 38.5 min (5%), 45.6 min (95%); IR (NaCl) ν 1728, 1648 (w), 1434, 1270 cm⁻¹; MS (CI) *m/z* (%) 374 (M+1, 7), 287 (85), 285 (56), 180 (100); HRMS calcd for C₁₉H₁₉NO₅S: 373.0984; found: 373.0989.

Characterization of cycloadduct of the reaction between diene 4 and *N*-methylmaleimide.

¹H NMR (CDCl₃, 500 MHz) δ 7.37-7.09 (m, 5H), 5.65-5.72 (m, 1H), 5.59-5.54 (m, 1H), 5.17 (d, *J* = 8.0 Hz, 1H), 5.12 (m, 1H), 4.95 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.27 (d, *J* = 8.0 Hz, 1H), 4.11 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.18 (dd, *J* = 8.0, 8.0 Hz, 1H), 2.88 (s, 3H), 2.66 (dd, *J* = 7.5, 16.0 Hz, 1H), 2.15-2.07 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 187.6, 179.0, 177.4, 140.0, 129.6, 128.7, 128.6, 125.5, 125.2, 75.6, 62.9, 53.9, 40.6, 38.0, 24.9, 24.0; GC (MN OPTIMAS-5, 150→250, 5°C/min) 63.9

min; IR (NaCl) ν 1774 (w), 1697, 1437, 1296 cm^{-1} ; MS (CI) m/z (%) 343 (M+1, 7), 223 (48), 205 (92), 84 (100); HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{S}+1$: 343.1116; found: 343.1111.

Characterization of cycloadduct of the reaction between diene 4 and DEAD.

^1H NMR (CDCl_3 , 500 MHz) δ 7.26-7.04 (m, 5H), 7.14 (m, 1H), 5.40^a (m, 2H), 5.32^b (dd, J = 9.3, 3.8 Hz, 1H), 4.78 (dd, J = 9.3, 9.3 Hz, 1H), 4.30 (dd, J = 9.3, 3.8 Hz, 1H), 4.30 (q, J = 7 Hz, 2H), 4.21 (q, J = 7 Hz, 2H), 3.90^c (dd, J = 18.3, 4.9 Hz, 1H), 3.60 (dd, J = 18.3, 2 Hz, 1H), 1.34 (t, J = 7 Hz, 3H), 1.27 (t, J = 7 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz)^d δ 187.6 (187.5), 154.5 (153.8), 154.1 (153.7), 139.1 (139.3), 128.8 (128.6), 128.7 (128.5), 126.4, 125.3 (124.4), 122.4 (122.1), 75.1 (74.9), 65.6 (65.3), 63.4 (63.3), 62.5 (62.4), 59.7 (60.7), 42.3 (41.4), 14.6 (14.5), 14.1; GC (MN OPTIMAS-5, 150→270, 5°C/min) 29.4 min (75%), 29.0 (25%); IR (NaCl) ν 1744, 1667 cm^{-1} ; MS (CI) m/z (%) 406 (M+1, 3), 370 (21), 259 (72), 223 (100); HRMS calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_5\text{S}+1$: 406.1436; found: 406.1423.

^a in the minor isomer: 5.43 (m, 1H) and 5.22 (m, 1H)

^b in the minor isomer: 5.09 (dd, 1H)

^c in the minor isomer: 4.06 (dd, 1H)

^d values in parentheses correspond to the minor diastereoisomer

Characterization of cycloadduct of the reaction between diene 4 and dimethylfumurate.

^1H NMR (CDCl_3 , 500 MHz) δ 7.40-7.10 (m, 5H), 5.80 (m, 1H),^a 5.42 (m, 1H), 5.15 (dd, J = 2.5, 8.5 Hz, 1H),^b 5.12 (m, 1H), 4.62 (dd, J = 8.5, 8.5 Hz, 1H),^c 4.29 (dd, J = 2.5, 8.5 Hz, 1H),^d 3.75 (s, 3H), 3.74 (s, 3H), 3.28 (dd, J = 6.5, 12.5 Hz, 1H),^e 3.12 (m, 1H), 2.43-2.30 (m, 1H), 2.10-1.85 (m, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 188.7, 174.2, 173.0, 139.9, 129.1, 128.9, 127.9, 126.8, 123.6, 74.8, 62.5, 52.3, 52.2, 52.0, 45.8, 38.4, 27.4; GC (MN OPTIMAS-5, 150→290, 5°C/min) 46.6 min(1%), 47.9 (70%), 51.8 (18%), 55.8(11%); IR (NaCl) ν 1734, 1653 (w), 1435, 1286 cm^{-1} ; MS (CI) m/z (%) 376 (M+1, 5), 375 (20), 237 (100); HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_5\text{S}+1$: 376.1218; found: 376.1216.

^a in the second isomer: 5.59 (m, 1H)

^b in the second isomer: 5.21 (dd, J = 5.0, 9.5 Hz, 1H)

^c in the second isomer: 4.81 (dd, J = 9.0, 9.0 Hz, 1H)

^d in the second isomer: 4.46 (dd, J = 4.5, 9.0 Hz, 1H)

^e in the third isomer 3.23 (dd, J = 5.0, 7.5 Hz, 1H)

S14

IV. ^{13}C NMR spectra of all new compounds

Compound 2

Compound 3

S15

Compound 4

cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and methyl acrylate.

S16

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and trimethylphosphonoacrylate.

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and dimethylacetylenedicarboxylate.

S17

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and *N*-methyl maleimide.

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and DEAD.

S18

Characterization of cycloadduct of the reaction between (4*R*,1'*E*)-3-(buta-1',3'-dienyl)-4-phenyloxazolidin-2-one and dimethylfumarate.

Characterization of cycloadduct of the reaction between 4 and methyl acrylate. **Characterization of cycloadduct of the reaction between 4 and trimethylphosphonoacrylate.**

S20

Characterization of cycloadduct of the reaction between 4 and dimethylacetylenedicarboxylate.

Characterization of cycloadduct of the reaction between diene 4 and *N*-methylmaleimide.

S21

Characterization of cycloadduct of the reaction between diene 4 and DEAD. **Characterization of cycloadduct of the reaction between diene 4 and dimethylfumarate.**