Supplementary Information

Stereochemical Considerations on Construction of the Poly-functionalized Bicyclo[3.3.1]nonenones by Successive Michael Reactions of 2-Cyclohexenones

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Figure S1. Determination of the Relative Stereochamistry by the ^{1}H NMR NOE or ROESY Experiments

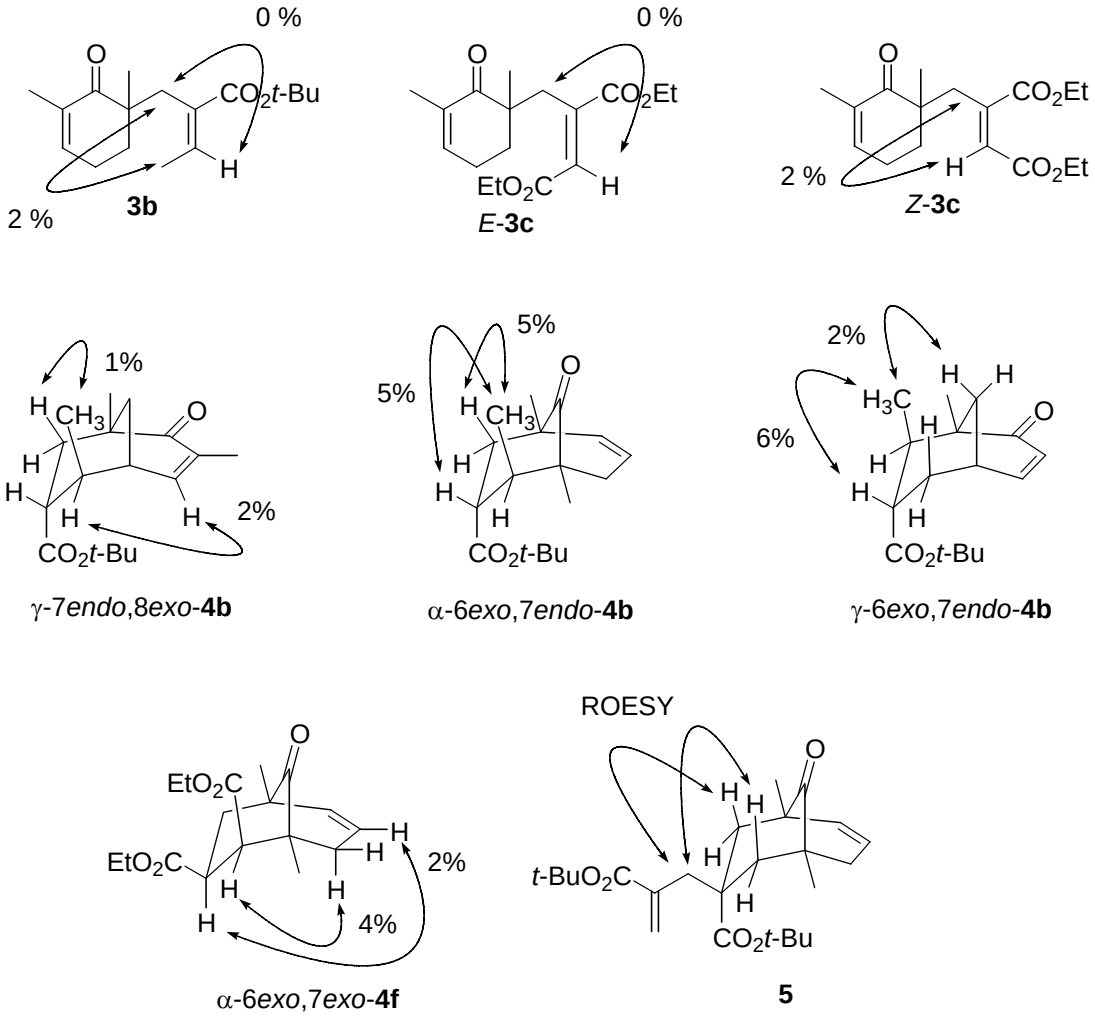
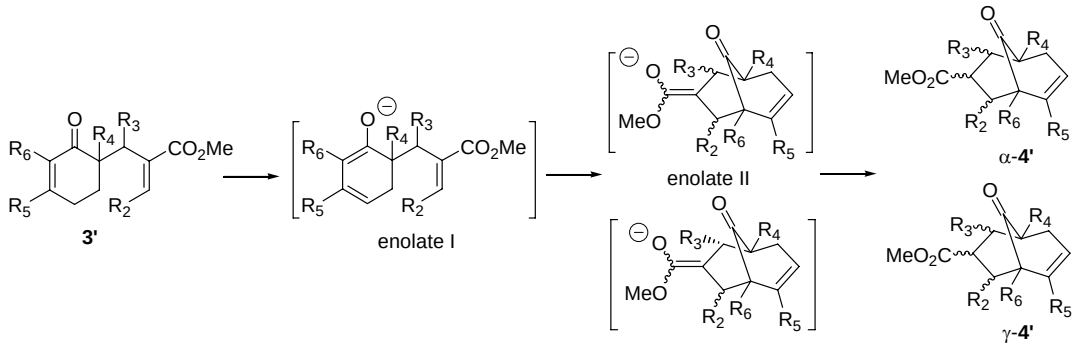


Table S1. Coupling Constants for the Determination of the Relative Stereochemistry

α-*endo*-**4a**	$J_{H4ax,H6ax}$ = 1.8 Hz, $J_{H6ax,H7}$ = 7.3 Hz, $J_{H7,H8ax}$ = 6.4 Hz
γ-*endo*-**4a**	$J_{H7,H8ax}$ = 7.5 Hz
α-7*endo*,8*exo*-**4b**	$J_{H4ax,H6ax}$ = 1.8 Hz, $J_{H6ax,H7}$ = 7.6 Hz, $J_{H7,H8}$ = 1.5 Hz
γ-7*endo*,8*exo*-**4b**	$J_{H7,H8ax}$ = 7.3 Hz
α-7*exo*,8*exo*-**4c**	$J_{H6ax,H7}$ = 13.7 Hz, $J_{H4ax,H6ax}$ = $J_{H6eq,H8}$ = 1.8 Hz, $J_{H7,H8}$ = 5.2 Hz
γ-7*exo*,8*exo*-**4c**	$J_{H7,H8ax}$ = 13.4 Hz, $J_{H6,H8ax}$ = 1.8 Hz, $J_{H6,H7}$ = 5.2 Hz
α-6*exo*,7*endo*-**4d**	$J_{H6,H8eq}$ = $J_{H6,H7}$ = 2.1 Hz, $J_{H7,H8ax}$ = 6.4 Hz
γ-6*exo*,7*endo*-**4d**	$J_{6ax,H7}$ = 6.7 Hz
α-6*exo*,7*exo*-**4e**	$J_{H6,H8eq}$ = 2.1 Hz, $J_{H6,H7}$ = 4.9 Hz, $J_{H7,H8eq}$ = 13.0 Hz
α-6*exo*,7*endo*-**4e**	$J_{H6,H8eq}$ = $J_{H6,H8eq}$ = 2.2 Hz, $J_{H6,H7}$ = 4.4 Hz, $J_{H7,H8ax}$ = 6.6 Hz
α-6*endo*,7*exo*-**4e**	$J_{H6,H7}$ = $J_{H7,H8ax}$ = 13.0 Hz, $J_{H7,H8eq}$ = 4.9 Hz
γ-6*exo*,7*exo*-**4e**	$J_{H6eq,H8}$ = 2.3 Hz, $J_{H6ax,H7}$ = 12.8 Hz, $J_{H7,H8}$ = 4.9 Hz
α-6*exo*,7*exo*-**4f**	$J_{H6,H7}$ = 4.9 Hz, $J_{H6,H8eq}$ = 1.8 Hz, $J_{H7,H8ax}$ = $J_{H7,H8eq}$ = 13.0 Hz
α-6*endo*,7*exo*-**4f**	$J_{H6,H7}$ = $J_{H7,H8ax}$ = 12.7 Hz, $J_{H7,H8eq}$ = 4.6 Hz
γ-6*exo*,7*exo*-**4f**	$J_{H6ax,H7}$ = 13.0 Hz, $J_{H6eq,H7}$ = $J_{H7,H8}$ = 5.2 Hz
α-6*exo*,7*exo*-**4g**	$J_{H6,H7}$ = $J_{H7,H8eq}$ =4.5 Hz, $J_{H6,H8eq}$ = 1.8 Hz, $J_{H7,H8ax}$ = 13.1 Hz
α-6*endo*,7*endo*-**4g**	$J_{H6,H7}$ = $J_{H7,H8ax}$ = 8.2 Hz, $J_{H7,H8eq}$ = 7.3 Hz
α-6*endo*,7*exo*-**4g**	$J_{H4ax,H6}$ = 1.2 Hz, $J_{H6,H7}$ = $J_{H7,H8ax}$ = 13.1 Hz, $J_{H7,H8eq}$ = 4.6 Hz
γ-6*exo*,7*exo*-**4g**	$J_{H6ax,H7}$ = 13.2 Hz, $J_{H6eq,H7}$ = 3.5 Hz, $J_{H7,H8}$ = 5.4 Hz
α-*endo*-**4h**	$J_{H7,H8ax}$ = 5.3 Hz
α-*exo*-**4h**	$J_{H4ax,H6ax}$ = 1.2 Hz, $J_{H6ax,H7}$ = $J_{H7,H8ax}$ = 12.8 Hz
γ-*endo*-**4h**	$J_{H7,H8ax}$ = 7.6 Hz

[a] The numbering is based on the bicyclo[3.3.1]non-2-one core.

Table S2. HF/6-31G* Calculated Energies in the Intramolecular Michael Reaction



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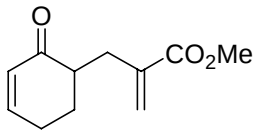
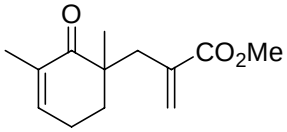
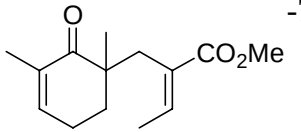
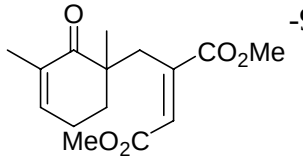
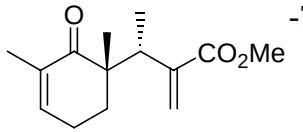
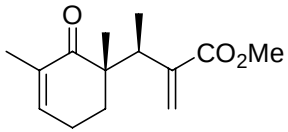
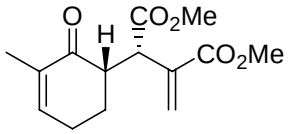
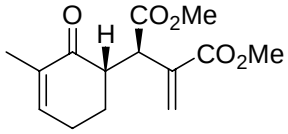
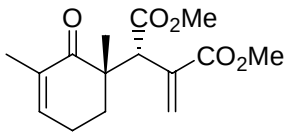
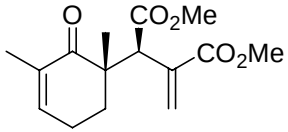
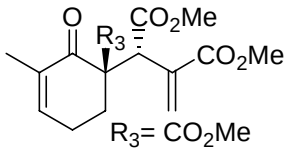
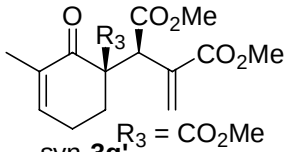
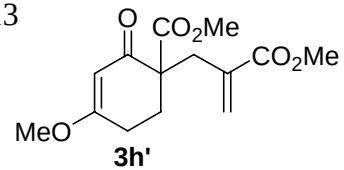
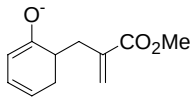
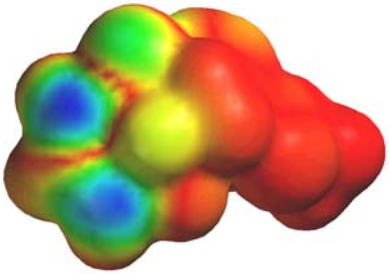
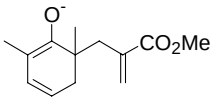
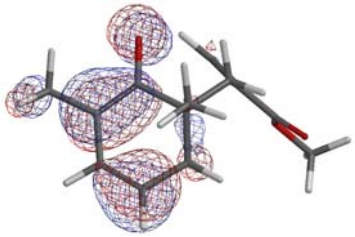
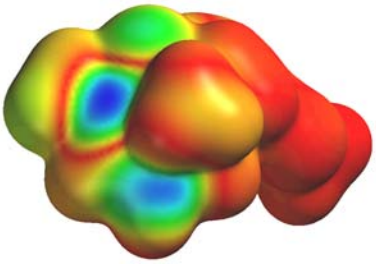
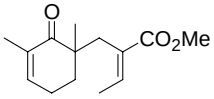
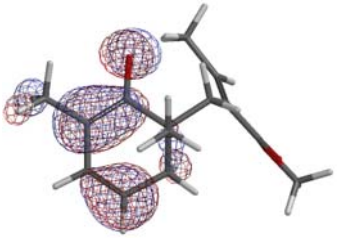
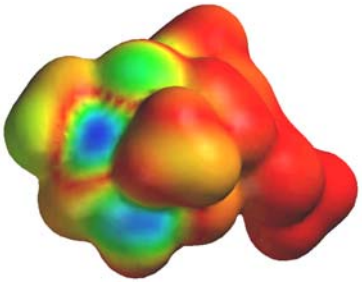
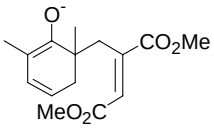
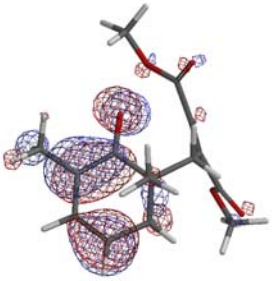
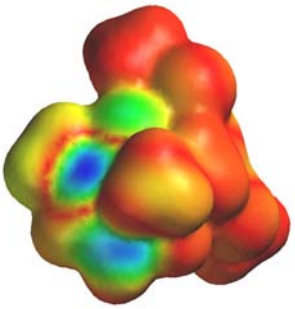
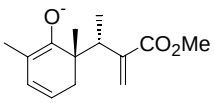
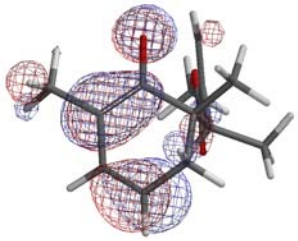
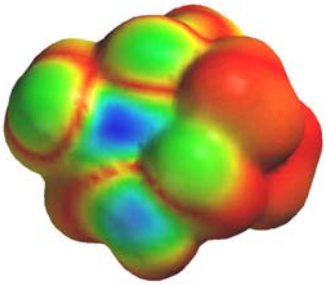
1		-648.627	α-chair	-684.605	-648.639		α-*endo*	-649.254
			α-boat	-648.591	-648.630		α-*exo*	-649.257
			γ-chair	-648.598	-648.645		γ-*endo*	-649.261
			γ-boat	-648.590	-648.636		γ-*exo*	-649.265
2	 **3a'**	-726.692	α-chair	-726.670	-726.706	**4a'**	α-*endo*	-727.321
			α-boat	-726.656	-726.697		α-*exo*	-727.323
			γ-chair	-726.663	-726.714		γ-*endo*	-727.330
			γ-boat	-726.655	-726.705		γ-*exo*	-727.335
3	 **3b'**	-765.724	α-chair	-765.697	-765.734	**4b'**	α-7*endo*,8*exo*[b]	-766.348
			α-boat	-765.683	-765.729		α-7*exo*,8*endo*[b]	-766.341
			γ-chair	-765.691	-765.745		γ-7*endo*,8*exo*[b]	-766.356
			γ-boat	-765.683	-765.738		γ-7*exo*,8*endo*[b]	-766.352

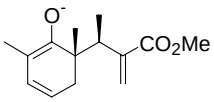
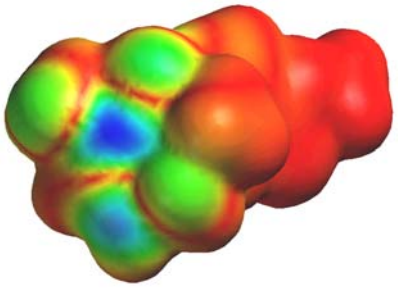
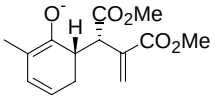
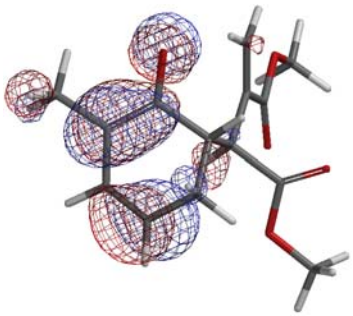
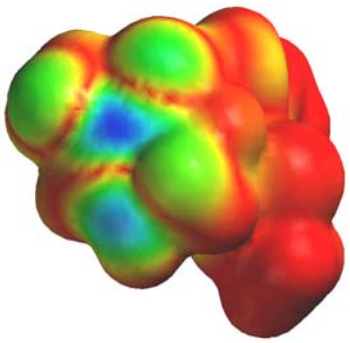
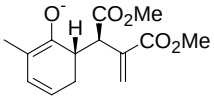
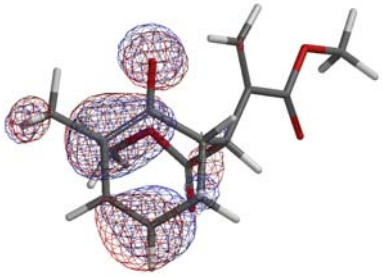
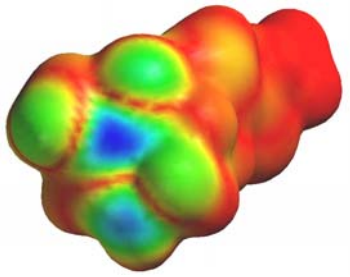
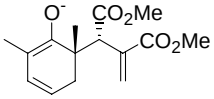
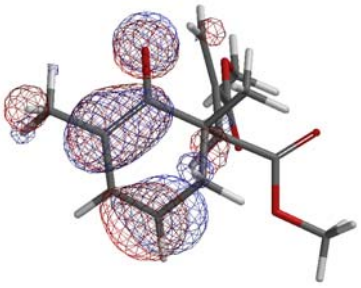
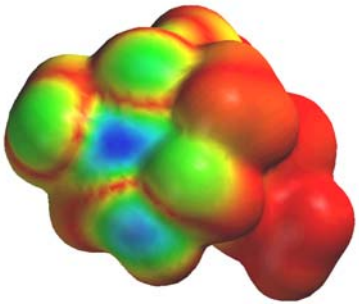
entry	substrate	enoate I[a]	transition state[a]		enolate II[a]	product[a]		
4	 **3c'**	-953.319	α-chair	-953.299	-953.339	**4c'**	α-7*endo*,8*exo*[b]	-953.941
			α-boat	-953.284	-953.331		α-7*exo*,8*endo*[b]	-953.934
			γ-chair	-953.297	-953.350		γ-7*endo*,8*exo*[b]	-953.957
			γ-boat	-953.283	-953.300		γ-7*exo*,8*endo*[b]	-953.948
5	 *anti*-**3d'**	-765.709	α-chair	-765.695	-765.733	**4d'**	α-6*exo*,7*endo*[b]	-766.346
			α-boat	-765.679	-765.719		α-6*exo*,7*exo*[b]	-766.347
			γ-chair	-765.686	-765.735		γ-6*endo*,7*endo*[b]	-766.353
			γ-boat	-765.683	-765.727		γ-6*endo*,7*exo*[b]	-766.362
6	 *syn*-**3d'**	-765.710	α-chair	-765.692	-765.727	**4d'**	α-6*endo*,7*edno*[b]	-766.344
			α-boat	-765.678	-765.722		α-6*endo*,7*exo*[b]	-766.350
			γ-chair	-765.689	-765.740		γ-6*exo*,7*endo*[b]	-766.354
			γ-boat	-765.678	-765.727		γ-6*exo*,7*exo*[b]	-766.356
7	 *anti*-**3e'**	-914.343	α-chair	-914.326	-914.364	**4e'**	α-6*exo*,7*endo*[b]	-914.969
			α-boat	-914.311	-914.333		α-6*exo*,7*exo*[b]	-914.970
			γ-chair	-914.309	-914.368		γ-6*endo*,7*endo*[b]	-914.977
			γ-boat	-914.312	-914.361		γ-6*endo*,7*exo*[b]	-914.977
8	 *syn*-**3e'**	-914.337	α-chair	-914.326	-914.362	**4e'**	α-6*endo*,7*edno*[b]	-914.972
			α-boat	-914.308	-914.352		α-6*endo*,7*exo*[b]	-914.978
			γ-chair	-914.321	-914.374		γ-6*exo*,7*endo*[b]	-914.982
			γ-boat	-914.311	-914.363		γ-6*exo*,7*exo*[b]	-914.983

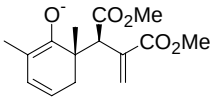
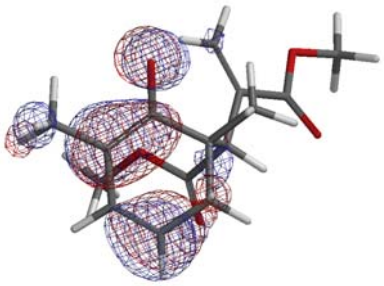
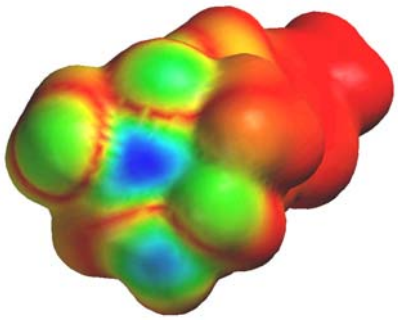
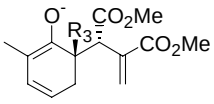
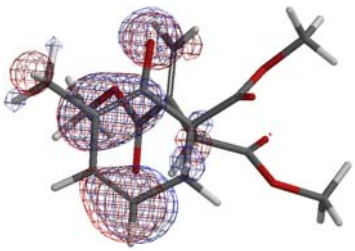
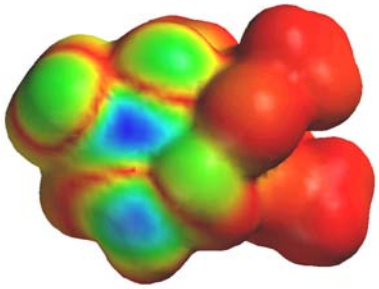
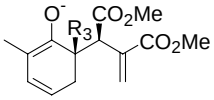
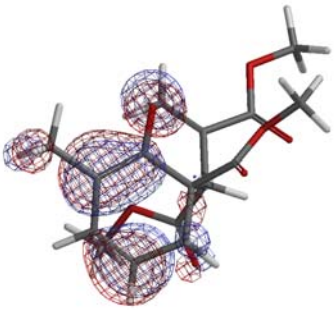
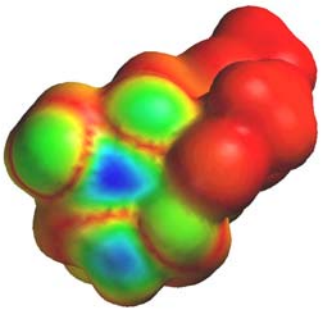
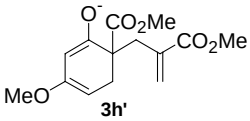
entry	substrate	enoate I[a]	transition state[a]		enolate II[a]	product[a]		
9	 *anti*-**3f'**	-953.311	α-chair	-953.295	-953.338	**3f'**	α-6*exo*,7*endo*[b]	-953.941
			α-boat	-953.279	-953.307		α-6*exo*,7*exo*[b]	-953.941
			γ-chair	-953.280	-953.340		γ-6*endo*,7*endo*[b]	-953.946
			γ-boat	-953.284	-953.333		γ-6*endo*,7*exo*[b]	-953.957
10	 *syn*-**3f'**	-953.307	α-chair	-953.295	-953.333	**3f'**	α-6*endo*,7*edno*[b]	-953.942
			α-boat	-953.280	-953.324		α-6*endo*,7*exo*[b]	-953.948
			γ-chair	-953.292	-953.347		γ-6*exo*,7*endo*[b]	-953.952
			γ-boat	-953.273	-953.328		γ-6*exo*,7*exo*[b]	-953.957
11	 *anti*-**3g'**	-1140.909	α-chair	-1140.889	-1140.931	**4g'**	α-6*exo*,7*endo*[b]	-1141.530
			α-boat	-1140.873	-1141.530		α-6*exo*,7*exo*[b]	-1141.530
			γ-chair	-1140.876	-1140.933		γ-6*endo*,7*endo*[b]	-1141.539
			γ-boat	-1140.875	-1140.930		γ-6*endo*,7*exo*[b]	-1141.544
12	 *syn*-**3g'**	-1140.902	α-chair	-1140.896	-1140.932	**4g'**	α-6*endo*,7*edno*[b]	-1141.536
			α-boat	-1140.874	-1140.919		α-6*endo*,7*exo*[b]	-1141.540
			γ-chair	-1140.892	-1140.945		γ-6*exo*,7*endo*[b]	-1141.544
			γ-boat	-1140.865	-1140.918		γ-6*exo*,7*exo*[b]	-1141.547
13	 **3h'**	-989.134	α-chair	-989.110	-989.146	**4h'**	α-*endo*	-989.754
			α-boat	-989.098	-989.137		α-*exo*	-989.757
			γ-chair	-989.110	-989.158		γ-*endo*	-989.768
			γ-boat	-989.100	-989.143		γ-*exo*	-989.765

[a] au. [b] The numbering is based on the bicyclo[3.3.1]non-2-ene core.

Figure S2. HOMO Orbital and HOMO Potential Map of the Enolate I by B3LYP/6-31G* calculations

Substrate	HOMO Orbital	HOMO Potential Map
		
 **3a'**		
 **3b'**		
 **3c'**		
 *anti*-**3d'**		

Substrate	HOMO Orbital	HOMO Potential Map
 *syn*-**3d'**		
 *anti*-**3e'**		
 *syn*-**3e'**		
 *anti*-**3f'**		

Substrate	HOMO Orbital	HOMO Potential Map
 *syn*-**3f'**		
 *anti*-**3g'** $R_3 = CO_2Me$		
 *syn*-**3g'** $R_3 = CO_2Me$		
 **3h'**