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Thermal and Lewis acid Promoted Intramolecular Diels-Alder Reaction of Furanose Tethered 1,3,9-Decatriene Systems: A Synthetic and Computational Investigation

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Abstract: The intramolecular Diels–Alder (IMDA) reaction of furanose tethered 1,3,9-decatrienes (**4a-4r**) was investigated under thermal conditions and in the presence of a Lewis acid. The stereoselectivity was determined by establishing the structures of adducts through single crystal X-ray diffraction and ^{1}H NMR spectroscopy. It was found that contrary to expectations, the thermal IMDA reaction of (3*E*) and (3*Z*)-1,3,9-decatrienes proceeded with nearly equal rate and furnished IMDA adducts (**6**-**25**) with moderate stereoselectivity. In some cases, rearranged products (**9**, **12**, **17** and **24**) arising out of 1,5-sigmatropic shift, *cis*-*trans* isomerization followed by IMDA reaction were formed. In contrast, Lewis acid promoted IMDA reaction afforded only one adduct albeit in lower yields. Not surprisingly, *cis*-boat transition states were favored over *trans*-boat transition states. Experimental results were corroborated with transition state modeling of these reactions by applying density functional theory based electronic structure calculation.

Introduction

The intramolecular Diels-Alder (IMDA) reaction is a powerful technique that offers an efficient, atom economic and versatile solution to the problem of constructing multicyclic molecules[1] and biologically active natural products.[2] However, the full potential of this important reaction will be realized only when the stereochemical outcome of such IMDA reactions can be predicted. This goal remains elusive despite

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significant progress made towards understanding various factors that control stereochemistry of adducts formed. While several acyclic 1,3,9-decatrienes have been prepared and subjected[3] to thermal and Lewis acid catalyzed IMDA reaction in order to study the stereoselectivity of adduct formation, IMDA reactions of 1,3,9-decatrienes tethered on a cyclic chiral scaffold offering an entry into functionalized chiral cyclic systems have received[4] comparatively less attention.

In a study involving 1,3,9-decatrienes tethered on a six membered chiral dioxane scaffold, Nay and co-workers[4] obtained two adducts, one *endo* and the other *exo*. Only one adduct and that too *exo* was observed by Miyashita *et al*.[5] when they subjected a 1,3,9-decatrienes tethered on a chiral cyclohexane derivative to the IMDA reaction. Paddon-Row and co-workers have described the *cis*/*trans* selectivity in thermal and Lewis acid promoted IMDA reactions of ethylene-tethered and benzo-tethered 1,3,9-decatriene systems and its validity by DFT methods[6a-d] in the analysis of IMDA reaction transition state structures. They also describe the *exo*-selective IMDA reaction of benzo-tethered 1,3,9-decatrienes promoted by sterically hindered aluminium tris(2,6-diphenyl phenoxide) (ATPH) catalyst. It is well known[7] that in thermal inter- and intramolecular Diels-Alder reactions acyclic (3*Z*)-1,3-dienes are substantially less reactive than their (3*E*)-counterparts. As a result, their use in Diels-Alder reaction is limited.[8]

We describe here the preparation and isolation of various (3*E*)- and (3*Z*)- 1,3,9-decatrienes (**4a**-**4r**) tethered onto a D-*xylo*-furanose template (Scheme 1 and 2) and their thermal and Lewis acid promoted IMDA reactions. To the best of our knowledge, this is the first report that describes the IMDA reaction of (3*E*)- as well as the corresponding (3*Z*)- 1,3,9-decatrienes. Equally noteworthy is our finding that both geometric isomers react at nearly the same rate and with almost identical stereoselectivity. We propose an empirical method for assigning stereochemistry of isochromenone system based on the difference in the chemical shift of the olefinic protons. We describe the formation of a byproduct arising out of a rearrangement followed by the IMDA reaction. We also present results obtained by applying

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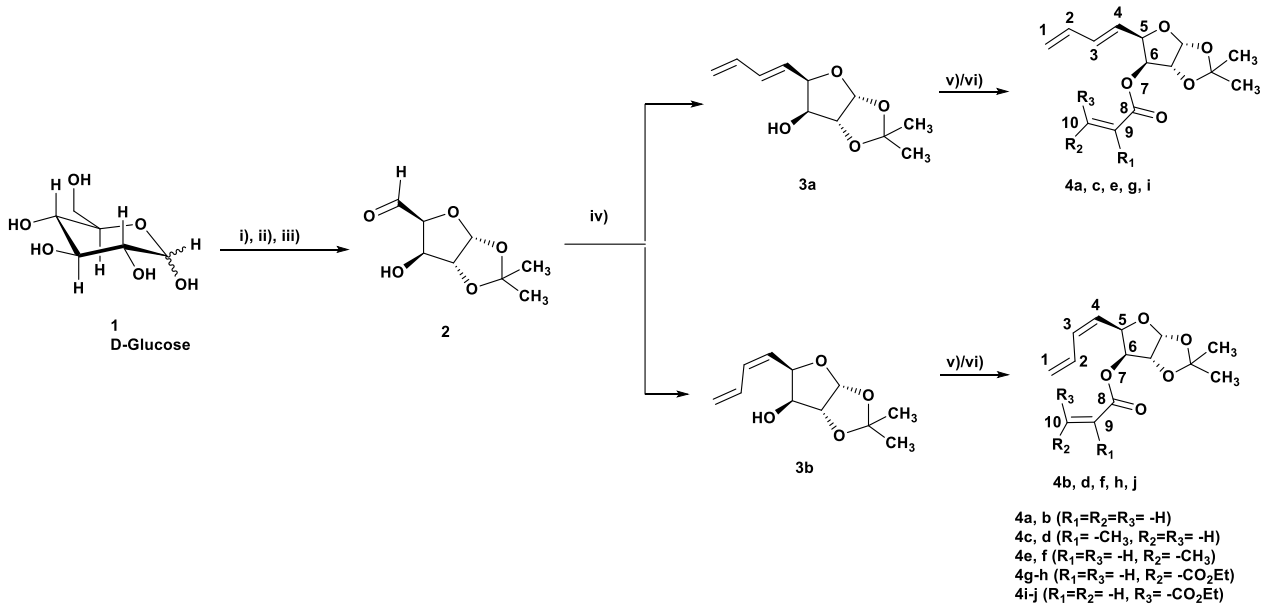
density functional theory based computational techniques to transition state modeling of these reactions and show that these are in accordance with experimental results.

Results and discussion

Synthesis of IMDA substrates:



Scheme 1 Synthesis of furanose derived acyclic 1,3,9-decatrienes. Reagents and conditions: i) I_2, acetone, aq. $Na_2S_2O_3$ solution, 24 h, 50%; ii) 60% Aq. acetic acid, 21 h, 96%; iii) $NaIO_4$, MeOH:H_2O [1:1], 0 °C, 1 h, 100%; iv) Allyl triphenylphosphonium bromide, KHMDS (0.5 M solution in toluene), THF, 0 °C to rt; v) Acryloyl chloride or methacryloyl chloride or *trans*-crotonyl chloride, Et_3N, CH_2Cl_2, 0 °C to rt, 3 h; vi) Monoethyl ester of fumaric acid or monoethyl ester of maleic acid, DCC, DMAP, CH_2Cl_2, 0 °C to rt, 3-24 h.

IMDA precursor 1,3,9-decatrienes (**4a**-**4r**), differing in the nature of dienophile were prepared in five straightforward steps (Scheme 1 and 2). Thus, 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**2**), readily obtained in three steps from D-glucose[9] (**1**) was subjected to the Wittig[10] reaction to furnish the (3*E*)- (**3a**) and (3*Z*)-diene (**3b**) which were easily separated by flash column chromatography.

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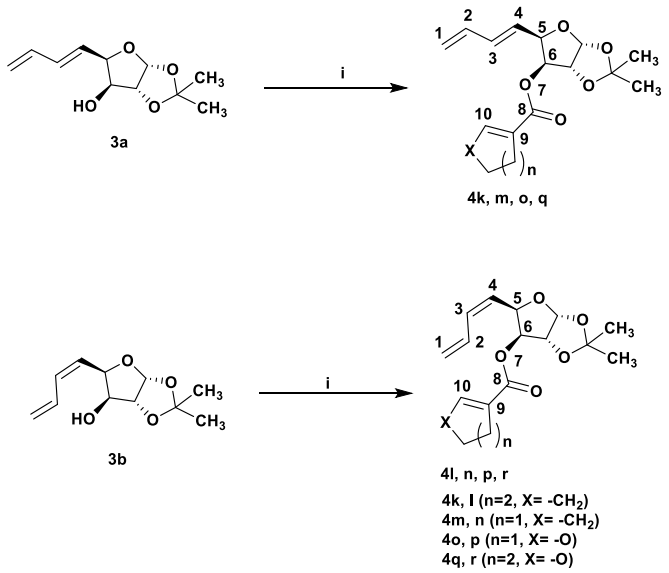
Esterification[11] with acryloyl chloride or methacryloyl chloride or *trans*-crotonyl chloride afforded 1,3,9-decatrienes **4a**-**4f** (Scheme 1). Steglich esterification[12] with monoethyl ester of fumaric acid or monoethyl ester of maleic acid or cyclohexene-1-carboxylic acid or cyclopentene-1-carboxylic acid or 4,5-dihydrofuran-3-carboxylic acid or 3,4-dihydro-2*H*-pyran-5-carboxylic acid afforded 1,3,9-decatrienes **4g**-**4r** (Scheme 1 and 2).



Scheme 2 Synthesis of furanose derived 1,3,9-decatrienes having acyclic diene and cyclic dienophile. Reagents and conditions: i) Cyclohexene-1-carboxylic acid or cyclopentene-1-carboxylic acid or 4,5-dihydrofuran-3-carboxylic acid or 3,4-dihydro-2*H*-pyran-5-carboxylic acid, DCC, DMAP, CH_2Cl_2, 0 °C to rt, 3-28 h.

Thermal IMDA reactions

In principle, the IMDA reaction of 1,3,9-decatrienes (**4a**-**4r**) is expected to give four adducts (Scheme 3). When a solution (1M in toluene) of the acrylate derived (3*E*)-1,3,9-decatrienes (**4a**) was boiled under reflux at ambient pressure, a complex mixture of several products along with a significant amount of starting material was obtained even after 48 hours. Three adducts (**6**, **7**, **8**) and a rearranged product (**9**) were formed in a combined yield of 84% along with less polar byproducts when the reaction was

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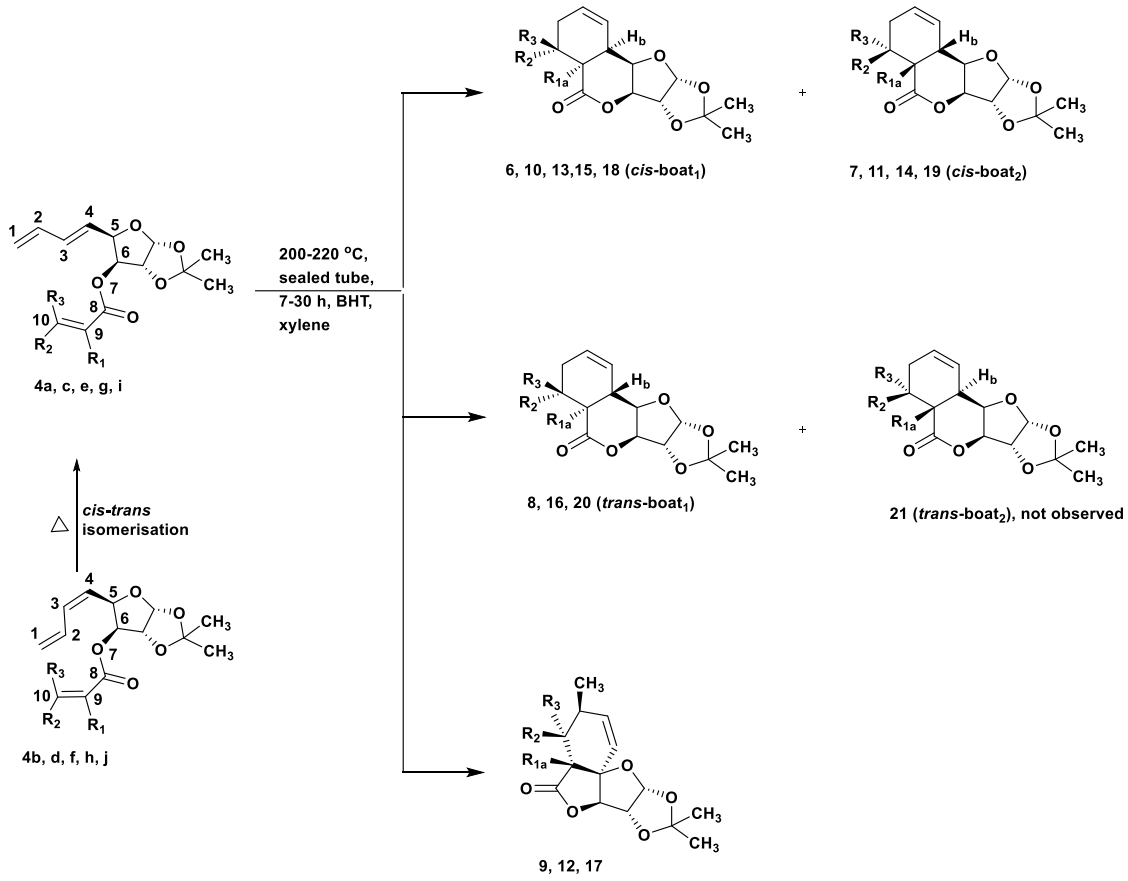
conducted at 200-220 °C for 7 h in a sealed tube with xylene as the solvent in the presence of sub-stoichiometric amounts of 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT). These conditions were used for conducting the IMDA reaction with the rest of the 1,3,9-decatrienes. The methacrylate derived (3*E*)-1,3,9-decatriene (**4c**) afforded two adducts (**10**, **11**) and a rearranged product (**12**) in a total yield of 31%. The crotonate derived (3*E*)-1,3,9-decatriene (**4e**) furnished adducts (**13**, **14**) in low yield (9%). In the case of the fumarate (**4g**) and the maleate derived 1,3,9-decatriene (**4i**) possessing an activated dienophile, two (**15**, **16**) and three adducts (**18**, **19**, **20**) in 43% and 60% yield respectively were obtained. Fumarate derived 1,3,9-decatriene (**4g**) also provide a rearranged product **17** in 8% yield.



Scheme 3 Thermal IMDA reactions of acyclic ester derived 1,3,9-decatrienes

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Table 1 Thermal IMDA reactions (see Scheme 3 and 4)

Sr. No.	IMDA substrate	Cycloadducts	R_1/R_{1a}	R_2	R_3	T [°C]	t [h]	Transition states			Adducts total yield [%]
								cis-boat$_1$ [%]	*cis*-boat$_2$ [%]	*trans*-boat$_1$ [%]	
1	**4a**	**6**, **7** and **8**	H	H	H	207	7	38	16	22	84[a]
2	**4b**	**6**, **7** and **8**	H	H	H	207	7	35	17	21	79[a]
3	**4c**	**10** and **11**	CH_3	H	H	215	18	8	23	-	35[a]
4	**4d**	**10** and **11**	CH_3	H	H	215	18	6	20	-	31[a]
5	**4e**	**13** and **14**	H	CH_3	H	218	30	6	3	-	9[b]
6	**4f**	**13** and **14**	H	CH_3	H	218	30	5	2	-	7[b]
7	**4g**	**15** and **16**	H	CO_2Et	H	210	17	24	-	19	51[a]
8	**4h**	**15** and **16**	H	CO_2Et	H	210	17	22	-	20	49[a]
9	**4i**	**18**, **19** and **20**	H	H	CO_2Et	212	16	25	19	16	60
10	**4j**	**18**, **19** and **20**	H	H	CO_2Et	212	16	23	20	14	57
11	**4k**	**22**	$-(CH_2)_3-CH_2-$		H	219	29	-	32	-	32
12	**4l**	**22**	$-(CH_2)_3-CH_2-$		H	219	29	-	30	-	30
13	**4m**	**23**	$-(CH_2)_2-CH_2-$		H	220	24	-	33	-	52[a]
14	**4n**	**23**	$-(CH_2)_2-CH_2-$		H	220	24	-	29	-	47[a]
15	**4o**	**25**	$-(CH_2)_2-O-$		H	217	32	-	27	-	27
16	**4p**	**25**	$-(CH_2)_2-O-$		H	217	32	-	26	-	26
17	**4q**	-	$-(CH_2)_3-O-$		H	216	35	-	-	-	-[c]
18	**4r**	-	$-(CH_2)_3-O-$		H	216	35	-	-	-	-[c]

[a]Total yield including rearranged product. [b]IMDA adduct along with trace amount of rearranged product was observed. [c]Dihydropyran derived (3*E*)- and (3*Z*)-1,3,9-decatriene after IMDA reaction gives an unseparable mixture of products.

The acrylate, methacrylate, crotonate, fumarate, and maleate derived (3*Z*)-1,3,9-decatrienes (**4b, 4d, 4f, 4h, 4j**) afforded an almost identical product profile as that obtained from (3*E*)-1,3,9-decatrienes (**4a, 4c, 4e, 4g, 4i**). The order of the reactivity of the five furanose tethered substrates towards the IMDA reaction as judged from the time taken for the (3*E*)-1,3,9-decatriene to disappear was: acrylate **4a** > maleate **4i** > fumarate **4g** > methacrylate **4c** > crotonate **4e**. A very similar order of reactivity was observed in case of (3*Z*)-1,3,9-decatrienes. The reaction rate of crotonate derived 1,3,9-decatrienes (**4e** and **4f**) was significantly slower. Considerable decomposition was also observed.

The thermal IMDA reactions of cyclohexene derived (3*E*)-1,3,9-decatrienes (**4k**) stereoselectively afforded adduct (**22**) in 32% yield (Scheme 4). Similarly, cyclopentene derived (3*E*)-1,3,9-decatrienes

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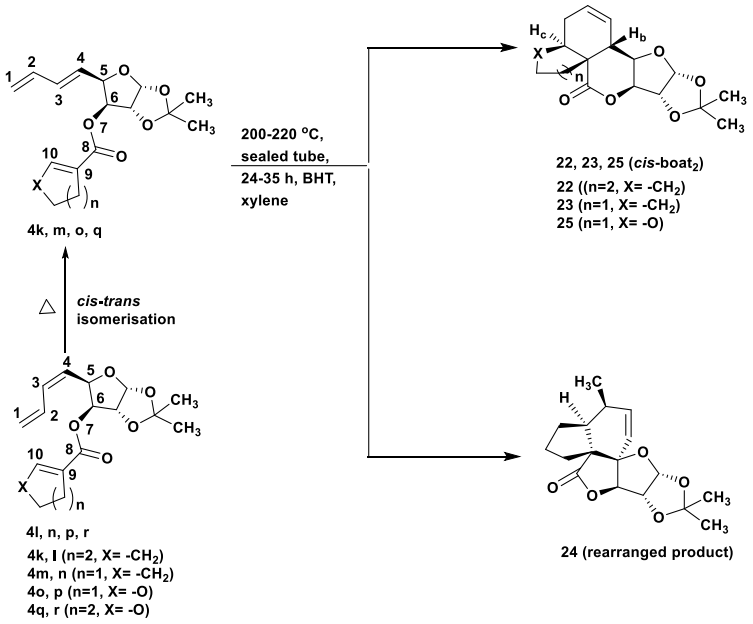
(**4m**) underwent the thermal IMDA reaction to afford adduct **23** in 33% yield along with a rearranged product **24** (Scheme 4). Adduct **25** was obtained in (27%) yield by the thermal IMDA reactions of dihydrofuran derived (3*E*)-1,3,9-decatrienes (**4o**).



Scheme 4 Thermal IMDA reactions of cyclic ester derived 1,3,9-decatrienes

A comparable product profile was obtained when geometrical isomers of (3*Z*)-1,3,9-decatrienes underwent thermal IMDA reactions. The order of reactivity of these 1,3,9-decatrienes was as follows: cyclopentene **4m** > cyclohexene **4k** > dihydrofuran **4o**. The dihydropyran derived (3*E*)- and (3*Z*)-1,3,9-decatrienes (**4q** and **4r**) afforded an unseparable mixture of products.

Selectivity in thermal IMDA reactions:

Fig. 1 depicts *cis*/*trans* boat transition state conformers of the (3*E*)/(3*Z*)-1,3,9-decatriene precursors (**4a**-**4j**) leading to four possible cycloadducts. Formation of adduct (**21**) was not observed (Scheme 3) in 1,3,9-decatrienes (**4a**-**4j**)

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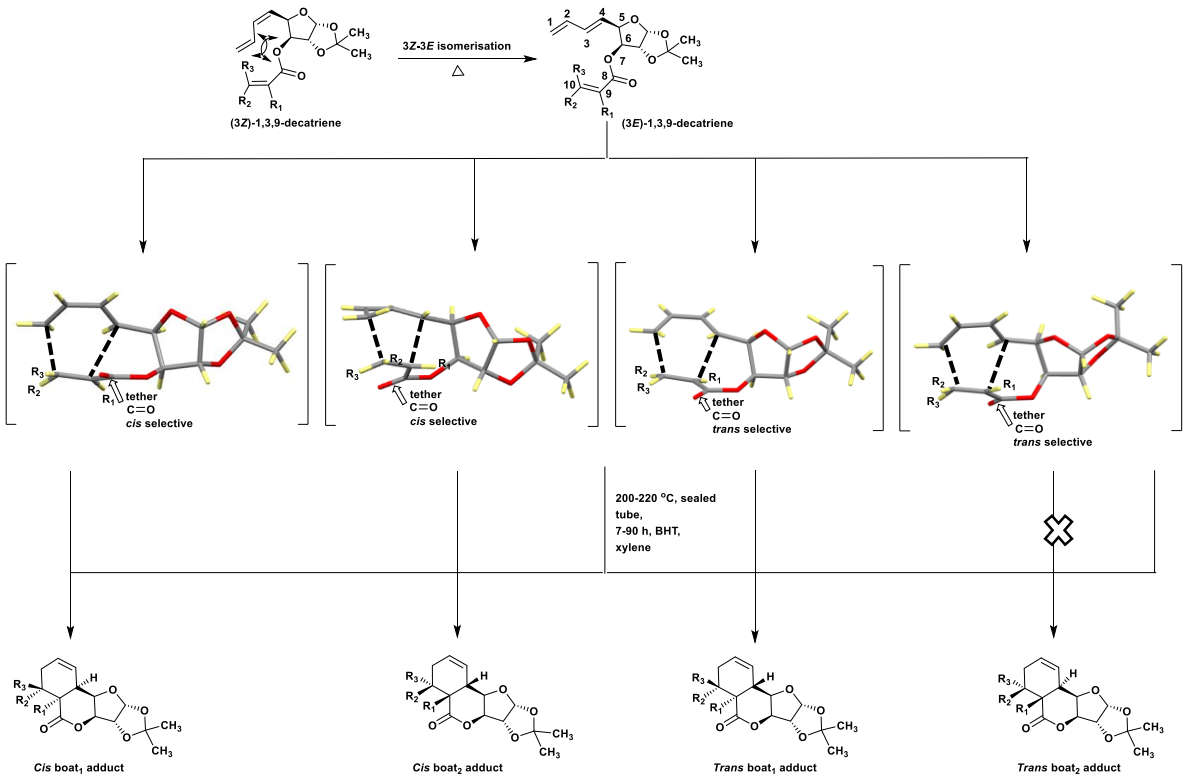
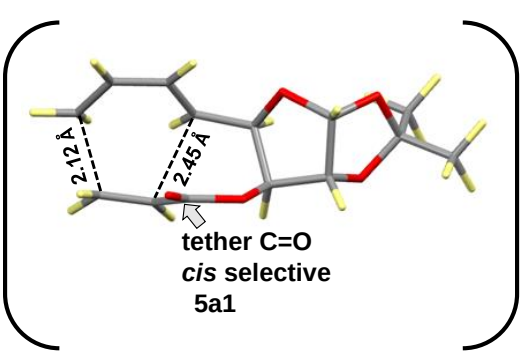
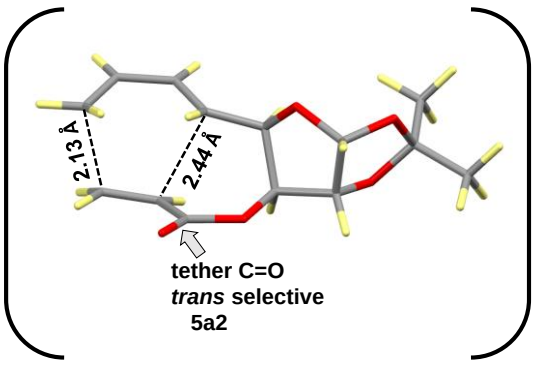


Fig. **1** Thermal 3*Z*-3*E* isomerization of furanose tethered 1,3,9-decatrienes

because the *trans* boat$_2$ transition state is sterically unfavorable. This is in accordance with previous literature reports[4]. As can be seen in Scheme 3 adducts (**6**, **10**, **13**, **15** and **18**) are formed from *cis* boat$_1$ transition states (Fig. 2, **5a1**, **5a6**, **5a9**, **5a11** and **5a13**) and adducts (**7**, **11**, **14**, and **19**) are formed from *cis* boat$_2$ transition states (Fig. 2, **5a3**, **5a7**, **5a10** and **5a14**) respectively. The *trans* fused adducts (**8**, **16**, and **20**) arise from *trans* boat$_1$ transition states (**5a2, 5a12** and **5a15**). Adducts **22**, **23** and **25** are selectively formed from *cis* boat$_2$ transition states (Fig. 2, **5a19**, **5a23** and **5a27**) respectively.





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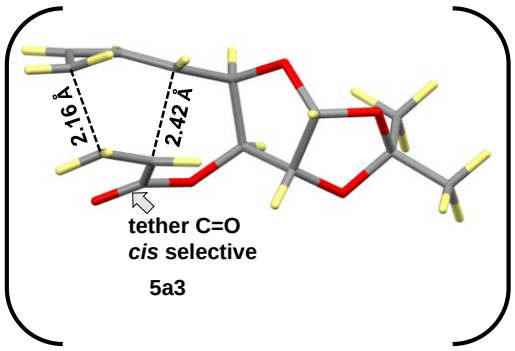

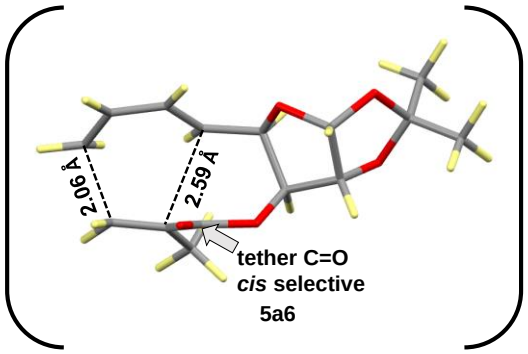

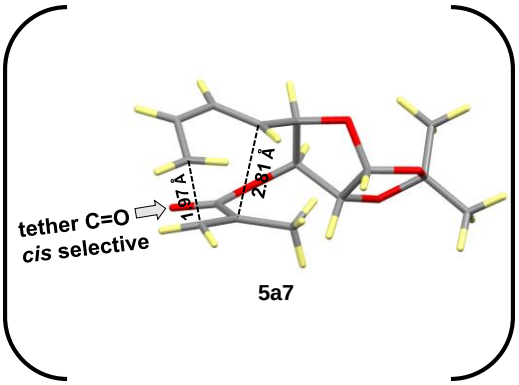

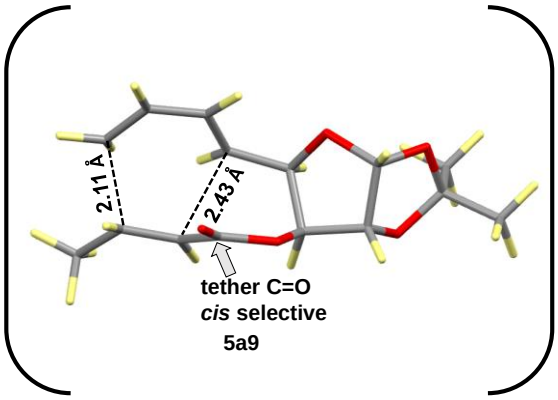

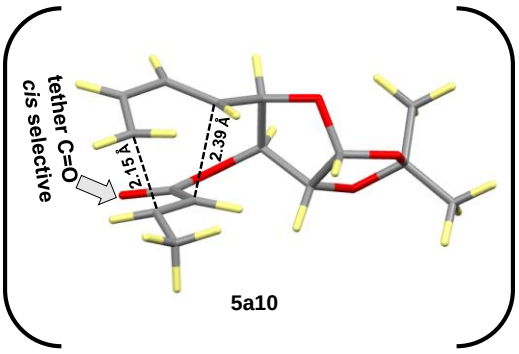

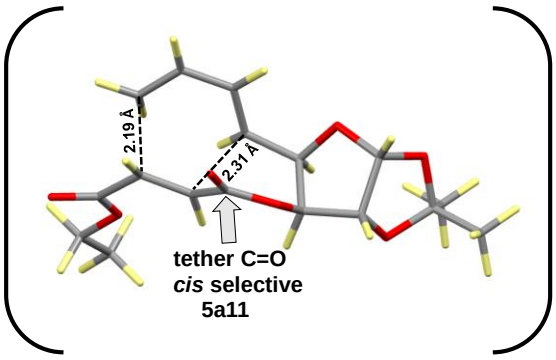

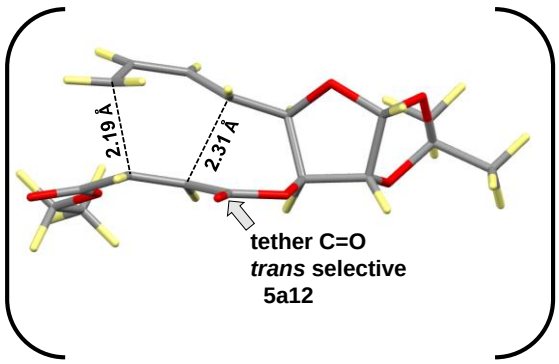

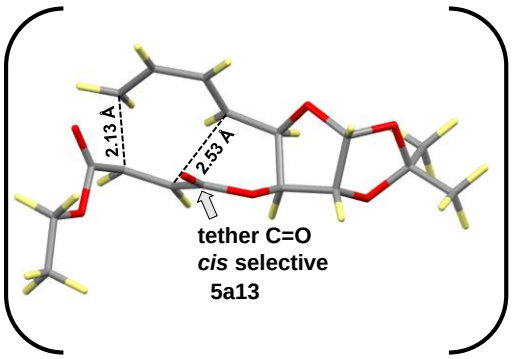

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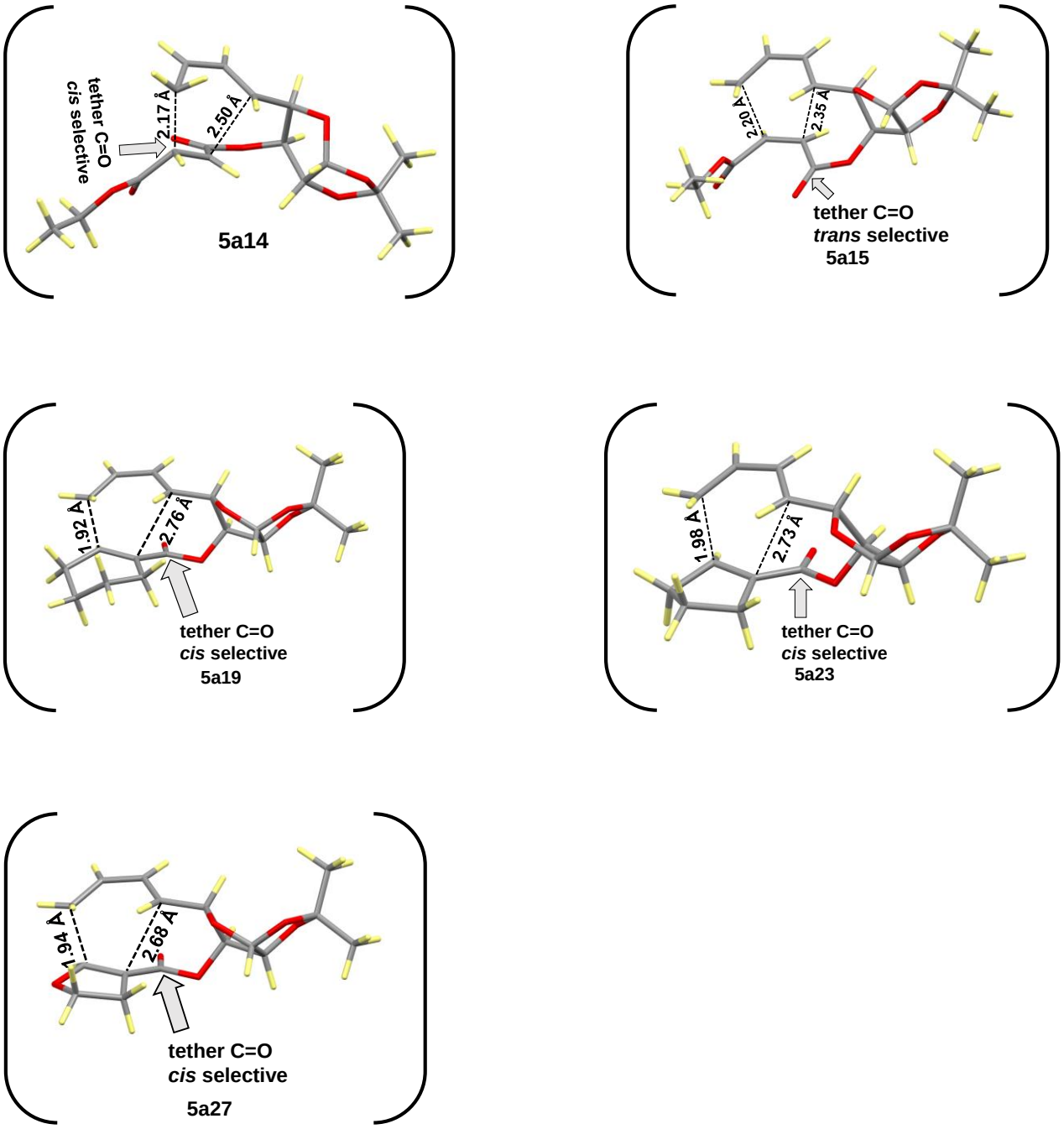

Fig. 2 Transition states for thermal IMDA reactions

Adducts are formed in the ratio *cis*$_1$:*cis*$_2$:*trans*$_1$ = 2:1:1.3 when there are no substituents in the diene and dienophile portions (Table-1, entries 1 and 2). The *trans* transition state is not favoured when the dienophile bears an C9-methyl substituent (Table-1, entries 3 and 4). The *cis* selectivity is also reversed and adducts are formed in the ratio *cis*$_1$:*cis*$_2$ = 1:3. A substituent such as methyl group at the C10-position

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(Table-1, entries 5 and 6) in the dienophile results in very low yields (~8%). An electron withdrawing substituent (such as $–CO_2Et$) present on the dienophile (Table-1, entries 7-10) had no substantial effect on the yield. The *cis*-boat$_2$ transition state was not observed in the case of fumarate derived 1,3,9-decatrienes (**4g**-**4h**). The maleate derived 1,3,9-decatrienes (**4i**) and (**4j**) also formed adducts in the ratio *cis*$_1$:*cis*$_2$:*trans*$_1$ = 1:0.76:0.64. Cyclohexene, cyclopentene and dihydrofuran derived 1,3,9-decatrienes (**4k**-**4p**) selectively afforded only one IMDA adduct arising from the *cis* boat$_2$ transition states but in low yields (Table-1, entries 11-16).

Influence of geometrical isomerism on the IMDA reaction

As shown in Scheme 3 and 4, the IMDA reaction of (3*Z*)-1,3,9-decatrienes (**4b**, **4d**, **4f**, **4h**, **4j**, **4l**, **4n** and **4p**) afforded a mixture of adducts that was almost identical to that obtained with (3*E*)-1,3,9-decatrienes. There is severe steric hindrance between the diene in the cisoid conformation and the furanose tether in these (3*Z*)-1,3,9-decatrienes (Fig. 1). Thus, thermal as well as Lewis acid promoted IMDA reaction can occur only with the (3*E*)-1,3,9-decatrienes. This indicates that the (3*Z*)-1,3,9-decatrienes undergo geometrical isomerization and the resulting (3*E*)-1,3,9-decatrienes undergo the IMDA reaction. Such (3*Z*)-(3*E*) isomerization, followed by IMDA reaction has been previously observed by Overman and co-workers.[7b-7c]

Lewis acid promoted IMDA reactions

In the presence of a Lewis acid (Et_2AlCl, 1.0 M solution in *n*-hexane) 1,3,9-decatrienes (**4a**-**4p**) afforded only one of the four possible cycloadducts in CH_2Cl_2 at 0-25 ^oC in lower yields (23-35%) along with degradation products (Table 2). Adducts (**6**, **10**, **15**, and **18**) *via* the *cis*-boat$_1$ transition state (Table 2) were obtained with high stereoselectivity by Lewis acid promoted IMDA reaction of 1,3,9-decatrienes (**4a**-**4d** and **4g**-**4j**). In case of 1,3,9-decatrienes (**4e**) and (**4f**) the *cis*-boat$_2$ transition state was exclusively preferred. The Lewis acid promoted IMDA reactions of 1,3,9-decatrienes (**4k**-**4p**) afforded adducts **22**,

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23, and **25** selectively *via* the *cis*-boat$_2$ transition state but in lower yield (Table 2). The rearranged product was not formed under these conditions. The IMDA reaction did not proceed in presence of other Lewis acids (5 mol % $TiCl_4$, DCM, 0-25 ^oC, 48 h and $ZnCl_2.OEt_2$, pyridine, DCM, 25 ^oC, 28 h).

Table 2 Lewis acid promoted IMDA reactions[a] (see Scheme 3 and 4 for IMDA substrate and adduct structure)

Sr. No.	IMDA substrate	Cycloadducts	R_1/R_{1a}	R_2	R_3	T [^oC]	t [h]	Transition states	
								cis-boat$_1$ [%]	*cis*-boat$_2$ [%]
1	**4a**	**6**	H	H	H	0-R.T.	38	32	-
2	**4b**	**6**	H	H	H	0-R.T.	38	29	-
3	**4c**	**10**	CH_3	H	H	0-R.T.	72	30	-
4	**4d**	**10**	CH_3	H	H	0-R.T.	90	28	-
5	**4e**	**14**	H	CH_3	H	0-R.T.	95	-	31
6	**4f**	**14**	H	CH_3	H	0-R.T.	90	-	26
7	**4g**	**15**	H	CO_2Et	H	0-R.T.	80	30	-
8	**4h**	**15**	H	CO_2Et	H	0-R.T.	82	28	-
9	**4i**	**18**	H	H	CO_2Et	0-R.T.	78	35	-
10	**4j**	**18**	H	H	CO_2Et	0-R.T.	84	26	-
11	**4k**	**22**	$-(CH_2)_3-CH_2-$		H	0-R.T.	49	-	29
12	**4l**	**22**	$-(CH_2)_3-CH_2-$		H	0-R.T.	50	-	31
13	**4m**	**23**	$-(CH_2)_2-CH_2-$		H	0-R.T.	45	-	27
14	**4n**	**23**	$-(CH_2)_2-CH_2-$		H	0-R.T.	46	-	24
15	**4o**	**25**	$-(CH_2)_2-O-$		H	0-R.T.	62	-	23
16	**4p**	**25**	$-(CH_2)_2-O-$		H	0-R.T.	59	-	21

[a]Reagents and conditions: Et_2AlCl (1.0 M solution in *n*-hexane), DCM, 0-25 ^oC, 38-95 h.

Structural determination of IMDA adducts

While the proton count of high field ^1H NMR spectra of compounds (**6**-**25**) obtained from the IMDA reaction indicated these products to be IMDA adducts, ^1H NMR spectroscopy was not sufficient for structural assignment. Fortunately we were able to grow crystals of adducts (**6**, **7**, **8** and **11**) and hence structural assignments could be unambiguously made by single crystal X-ray diffraction (see Fig. 3 for the ORTEP drawing of these adducts).

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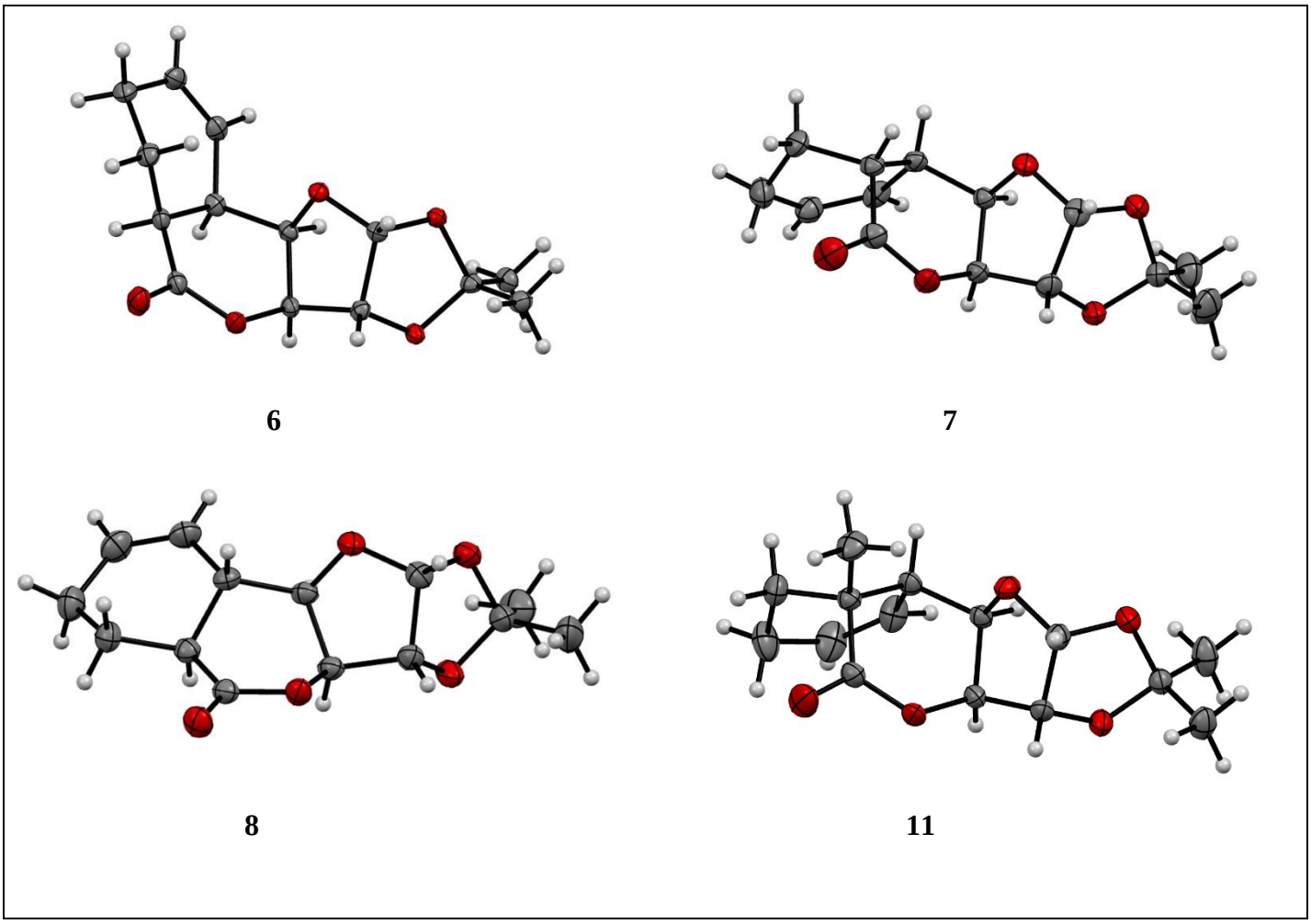

Fig. **3** ORTEP drawings of compounds **6**, **7**, **8** and **11** at 50% probability of thermal ellipsoids.

Structural assignments of oily IMDA adducts were based on:

a) Co-relation between the difference in the chemical shift (Δδ) of the olefinic protons and the stereochemistry of $–R_{1a}$ and $–H_b$ (see Table 3). Δδ is large when $-R_{1a}$ and $-H_b$ are β, β; medium when α, α and small when α, β. It is observed that such Δδs of previously reported IMDA adducts follow this trend (see Supporting Information pp. S158-S159). Mondal *et al*. have used the difference in chemical shifts of acetonide methyl protons for stereochemical assignment of IMDA adducts.[13]

b) The fact that adducts arising out of the *trans* $boat_2$ transition state are not[4b, 6a-6c] formed. We have also not observed such adducts in our work.

c) 1D, 2D NOESY and HMBC studies.

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Table 3 Stereochemistry of oily IMDA adducts (see Scheme 3 and 4)

Sr. No.	Adduct	Nature	-R_{1a}	-H_b	Δδ (ppm)	Transition state
			From XRD			
1	**7**	Crystalline	β	β	0.387	*cis*-boat$_2$
2	**11**		β	β	0.435	*cis*-boat$_2$
3	**6**		α	α	0.272	*cis*-boat$_1$
4	**8**		α	β	0.060	*trans*-boat$_1$
			From Δδ values			
5	**10**	Oily	α	α	0.311	*cis*-boat$_1$
6	**14**		β	β	0.122	*cis*-boat$_2$
7	**13**		α	α	0.113	*cis*-boat$_1$
8	**15**		α	α	0.116	*cis*-boat$_1$
9	**16**		α	β	0.100	*trans*-boat$_1$
10	**19**		β	β	0.374	*cis*-boat$_2$
11	**18**		α	α	0.126	*cis*-boat$_1$
12	**20**		α	β	0.098	*trans*-boat$_1$
13	**22**		β	β	0.412	*cis*-boat$_2$
14	**23**		β	β	0.416	*cis*-boat$_2$
15	**25**		β	β	0.367	*cis*-boat$_2$

In case of the adduct pair (**10**) and (**11**), the oily adduct is assigned structure (**10**) based on its Δδ value (0.311 ppm) which is only slightly lower than that exhibited (0.435 ppm) by the crystalline adduct (**11**). Maleate derived 1,3,9-decatrienes (**4i**-**4j**) afforded three oily adducts of which the one exhibiting the lowest Δδ value (0.098 ppm) is assigned structure (**20**). The adduct exhibiting a high Δδ value (0.374 ppm) is assigned structure (**19**) and that exhibiting a lower Δδ value of 0.126 ppm is assigned structure (**18**). 1D-NOESY spectrum of adduct (**20**) does not show an NOE enhancement between –R_{1a} and –H_b and hence the formed ring junction geometry is *trans*. NOE enhancement between –R_{1a} and –H_b of adduct (**19**) indicate that both these groups are on the same face of the molecule. Furthermore, an NOE enhancement between –R_{1a} and the anomeric proton displayed by adduct (**19**) indicates that –R_{1a} is β. Thus –R_{1a} and –H_b are β, β in adduct (**19**) and hence α, α in adduct (**18**) thereby supporting structural assignment based on Δδ values. These structural assignments are in accordance with those reported by Paddon-Row and others[6a-6c] in case of their acyclic maleate derived 1,3,9-decatrienes.

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In case of the fumarate derived 1,3,9-decatrienes (**4g**-**4h**) two adducts are obtained of which the one exhibiting a significantly lower Δδ value of 0.100 ppm is assigned structure (**16**), arising out of the *trans*-boat$_1$ transition state. The *trans* ring junction geometry in adduct (**16**) is confirmed by 1D and 2D NOESY spectra. The other adduct is assigned structure (**15**) arising out of the *cis*-boat$_1$ transition state since its Δδ value (0.116 ppm) is comparable to that exhibited (0.126 ppm) by adduct (**18**). The *cis* ring junction geometry in adduct (**15**) is also confirmed by an NOE enhancement between –R_{1a} and –H_b in its 1D-NOESY spectrum.

Crotyl derived 1,3,9-decatrienes (**4e**-**4f**) gave two adducts of which the one exhibiting a Δδ value (0.113 ppm) similar to that of adduct (**15**) is assigned structure (**13**) obtained from *cis*-boat$_1$ transition state. The other adduct with a slightly higher Δδ value (0.122 ppm) is assigned structure (**14**) arising out of the *cis*-boat$_2$ transition state. Adduct **22** was obtained from the *cis*-boat$_2$ transition state for cyclohexene derived 1,3,9-decatrienes (**4k**-**4l**), since it exhibits a high Δδ value (0.412 ppm). Cyclopentene and dihydrofuran derived 1,3,9-decatrienes (**4m**-**4p**) afforded one adduct each and that too exhibiting a high Δδ value (0.416 and 0.367 ppm) respectively. Thus, these adducts are assigned structures **23** and **25** arising out of the *cis*-boat$_2$ transition state. The 1D-NOESY spectra of adducts **22**, **23** and **25** (see Scheme 4 for adduct structures) do not show an NOE enhancement between -H_b and -H_c indicating that these two protons are not on the same face of molecule. Additionally, an NOE enhancement between -H_b and the anomeric proton displayed by adduct **23** and **25** indicates that -H_b is β. The HMBC spectra of adducts **22**, **23** and **25** do not show co-relation between -H_b and the carbon having -H_c proton. Thus –H_b and -H_c are β, α in adduct **22**, **23** and **25** thereby supporting structural assignments based on Δδ values.

Structural determination of rearranged products

Structural determination of rearranged products was done by using spectroscopic techniques. The rearranged products exhibited a higher carbonyl stretching frequency (1772-1793 cm^{-1}) in the IR

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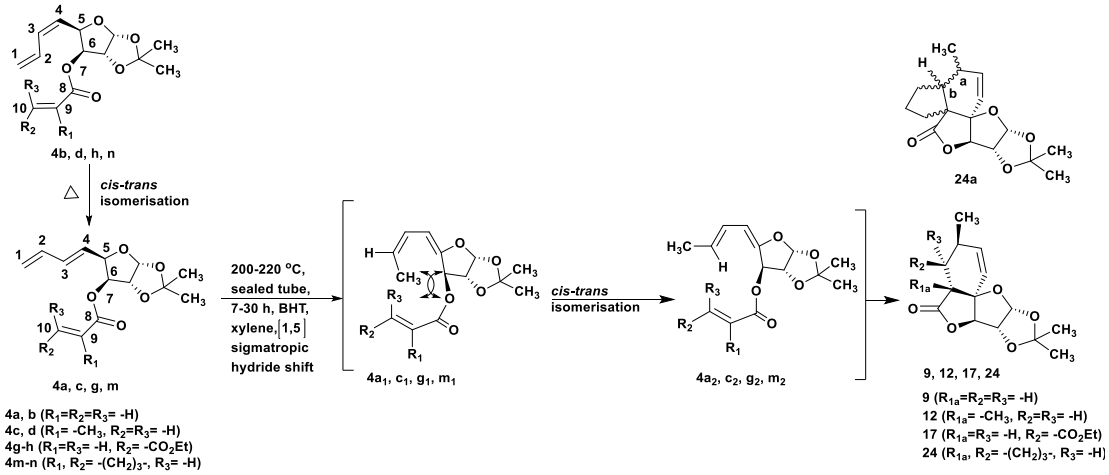
spectrum than that exhibited (1724-1758 cm^{-1}) by the corresponding IMDA adducts indicating a ring contraction in the cyclic lactone portion of the molecule. The proton count exhibited by rearranged products and IMDA adducts is identical. However, in case of the rearranged product (**9**), signals from one of the low field carbohydrate protons and two protons in the aliphatic region were replaced by a signal that was characteristic of a methyl group adjacent to a carbon atom bearing one hydrogen atom.



Scheme 5 Structural determination of rearranged products

A DEPT study of the rearranged product (**17** and **24**), obtained from the fumarate derived 1,3,9-decatriene (**4g**) and the cyclopentene derived 1,3,9-decatriene (**4m**) respectively, indicated the presence of an additional quaternary center. On the basis of these spectroscopic analyses we assigned structure **24a** to the rearranged product (Scheme 5). The configurations at positions **a** and **b** in **24a** were

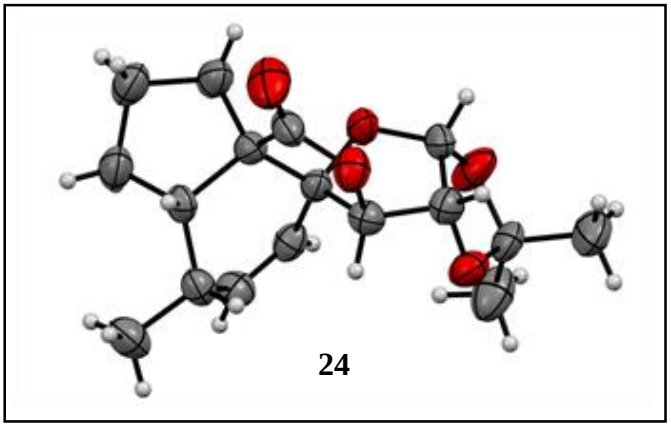


Fig. 4 ORTEP drawing of compound **24** at 50% probability of thermal ellipsoid

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confirmed to be *S* and *S* from the single crystal X-ray analysis (see Fig. 4 for an ORTEP drawing of this compound) of the rearranged product (**24**). Scheme 5 also depicts the formation of the rearranged product (**24**). Thus, the cyclopentene derived 1,3,9-decatriene (**4m**) undergoes a [1,5] sigmatropic hydride shift to give the sterically crowded furanose tethered *cis*-piperylene derived 1,3,9-decatriene (**4m$_1$**). *Cis-trans* isomerization of the 1,3,9-decatriene (**4m$_1$**) gives the *trans*-piperylene derived 1,3,9-decatriene (**4m$_2$**) which readily undergoes IMDA reaction to form the rearranged product (**24**). Such rearrangements have been previously observed.[14] On this basis, the rearranged products from the acrylate (**4a**, **4b**), maleate (**4c**, **4d**) and fumarate derived 1,3,9-decatriene (**4g**, **4h**) are assigned structures **9**, **12** and **17** (Scheme 5) respectively.

Functionally embellished furo[3,2-*b*]furanone scaffolds has been widely encountered as a characteristic sub-structure among a diverse range of natural products.[15a-e] The obtained rearranged products can be converted into derivatives of 2,6-dioxabicyclo[3.3.0]octane-3,7-dione (bis-lactone) which is a useful intermediate in some important biologically active compounds.[16a-c] These rearranged products are structurally similar to the arteannuin B core and so, could be possible intermediates for its synthesis in fewer number of steps than what is reported.[13]

Theoretical Results

Thirty two different transition states (TS) are envisaged for nine different reactants considered at present leading to thirty two products of which fifteen products are observed. To provide mechanistic insights about these reactions leading to isolated products, theoretical calculations were carried out on minimum energy structure of reactants, transition states and products by applying density functional theory.[17] Optimized geometrical parameters of TS structures are supplied in supplementary information. Transition state structures with selected bond distance parameters are displayed in Fig. 2. All the transition states calculated have boat like structures. For the TS structure (**5a1**), C1-C10 and C4-C9 distances are calculated as 2.11 and 2.46 Å respectively. Bonds C1-C2, C3-C4 and C9-C10 in TS

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elongates to 1.39 Å from 1.33 Å in the reactant structure. As expected, in TS C2-C3 bond shrinks to 1.41 Å from 1.54 Å of reactant geometry. Calculated bond distances suggest shift of π bond in this intramolecular Diels-Alder (IMDA) reaction of diene leading to the formation of product (**6**) from acrylate, (**4a**). It is worth to mention that TS structure is confirmed by Hessian calculation producing only one imaginary frequency (456 cm^{-1}) and the corresponding normal mode connects to the reactant (**4a**) and product (**6**). Bond distance parameters and the imaginary frequency of TS structures (**5a2**), (**5a3**) and (**5a4**) are also in the same range. It is to be noted that in case of TS (**5a4**) leading (transition states of theoretically expected adducts are shown in Fig. 5 see supporting information) to product (**t1**) which is not observed experimentally, C1-C10 distance is the minimum (2.03 Å) and C4-C9 distance is the maximum (2.60 Å) out of these four possible TS structures. Table 4 lists calculated Gibbs free energy for reaction energy at 298K by applying M06-2X functional leading to thirty two different possible products from nine reactants. The Table also provides barrier energy in terms of electronic energy calculated considering B3LYP as well as M06-2X functional. Barrier energy is also calculated in terms of Gibb's free energy at 298 K and 500 K by applying M06-2X functional. Full geometry optimizations and Hessian calculations have been carried out at B3LYP level. Single point energy calculations have been performed at M06-2X level with the B3LYP structures. Calculated B3LYP free energy parameters have been improved considering the electronic energy difference between M06-2X and B3LYP level as the correction factor and modified values are shown in Table 4 as free energy at M06-2X level. For acrylate (**4a**), the calculated barrier height (Gibbs free energy) is the minimum (21.8 kcal/mol) at 500 K for TS (**5a1**) implying product (**6**) to be the major product corroborating experimental finding. When barrier height is calculated from total electronic energy, M06-2X functional does predict TS (**5a1**) to be the lowest lying TS for acrylate. Since the calculated barrier height for product **t1** is less than that for product **7**, full geometry optimization and frequency calculation has also been carried out for these four TS (**5a1**, **5a2**, **5a3**, **5a4**) applying M06-2X functional. However, predicted barrier energy values are in the same order.

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Similarly for methacrylate (**4c**), the barrier height for TS (**5a7**) is the lowest among four possible routes when it is calculated from electronic energy as well as Gibbs's free energy. This explains the product (**11**) to be observed as the major product supporting experimental observation. Geometrical parameters of all the four TS structures are very close as shown in Fig. 2. In case of reactant crotylacrylate (**4e**), M06-2X predicts barrier energy to be the minimum for TS (**5a9**) showing product (**13**) as the major product. Calculated Gibb's free energy at 500K does also support similar observation. Similarly for reactant fumarate the observed major product (**16**) may be explained based on the calculated barrier energy for the concerned TS (**5a11**) based on energy calculated following M06-2X functional. Again for maleate the barrier energy parameter based on M06-2X can explain the observed major product.

For cyclohexene derived 1,3,9-decatriene (**4k**), three TS structures are predicted. TS for fourth possible conformer could not be obtained and this may be attributed to the fact that possible steric hindrance may not allow the formation of the product. Calculated smaller barrier height for TS, **5a19** explains the observed major product (**22**). Similarly in case of cyclopentene (**4m**) as well as dihydrofuran (**4o**) derived 1,3,9-decatriene, the formation of major product **23** and **25** can be explained based on computed low barrier energy for TS, **5a23** and **5a27**. In case of dihydropyran derived 1,3,9-decatriene (**4q**), theoretically it is predicted the product formed through TS, **5a31** as the major product. However, synthetically a mixture of products is obtained and individual product from this mixture is inseparable. All these reactions are predicted to be exothermic showing formation of products to be thermodynamically feasible.

Table 4 Calculated Electronic and Gibbs free energy (kcal mol^{-1}) for reaction barrier and reaction energy of different reaction paths

Reactant[a]	Transition State[b]	Barrier Energy				Product[c,d]	Reaction Energy[e]
		Electronic Energy		Gibb's Free Energy (M06-2X)			
		B3LYP	M06-2X	298 K	500K		
4a	**5a1**	18.9	14.4	21.0	21.8	6	-23.2
4a	**5a2**	18.8	15.3	18.8	23.1	8	-20.9

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4a	**5a3**	26.1	21.3	25.1	28.6	7	-25.2
4a	**5a4**[h]	20.9	17.6	21.1	25.0	t1	-24.7
4c	**5a5**[h]	24.9	20.4	23.7	30.9	t2	-18.7
4c	**5a6**	23.7	18.3	21.9	25.2	10	-20.5
4c	**5a7**	19.1	15.0	16.0	24.7	11	-20.0
4c	**5a8**[h]	20.2	15.3	19.3	26.5	t3	-17.6
4e	**5a9**	23.3	17.2	22.9	23.8	13	-17.1
4e	**5a9-a**[h]	23.2	17.9	22.6	24.5	t4	-18.8
4e	**5a10**	30.2	23.6	27.5	29.7	14	-18.9
4e	**5a10-a**[h]	25.7	20.9	24.7	27.3	t5	-15.5
4g	**5a11**	18.1	11.7	15.1	18.1	15	-16.0
4g	**5a11-a**[h]	22.9	15.9	18.0	20.4	t6	-18.1
4g	**5a12**	25.5	16.3	18.8	19.9	t7	-22.7
4g	**5a12-a**[h]	18.3	12.6	15.8	18.8	16	-18.2
4i	**5a13**	22.1	16.5	19.4	26.6	18	-23.8
4i	**5a14**	29.5	23.9	26.8	33.4	19	-27.1
4i	**5a15**	20.8	16.7	19.3	26.7	20	-24.7
4i	**5a16**[h]	23.4	19.7	21.8	27.7	t8	-26.5
4k[f]	**5a17**[h]	24.1	21.1	27.9	31.9	t9	-20.4
4k	**5a18**[h]	26.3	23.3	30.1	34.0	t10	-19.8
4k	**5a19**	20.1	17.5	24.3	28.5	22	-21.2
4m[f]	**5a21**[h]	18.3	14.6	20.6	24.3	t11	-26.7
4m	**5a22**[h]	20.4	17.8	23.7	19.3	t12	-26.8
4m	**5a23**	15.6	12.7	18.7	22.7	23	-28.9
4o[f]	**5a25**[h]	21.1	17.1	22.5	26.4	t13	-24.2
4o	**5a26**[h]	22.0	18.4	23.7	27.4	t14	-24.7
4o	**5a27**	18.8	15.9	21.0	24.3	25	-26.6
4q[f]	**5a29**[h]	26.5	23.2	27.7	31.0	g	-18.5
4q	**5a30**[h]	28.6	25.1	30.1	33.7	g	-19.0
4q	**5a31**[h]	22.1	19.2	24.4	28.3	g	-20.9

[a]Refer to Scheme 1 and 2 for reactant structures. [b]Refer to Fig. 2 for experimentally formed TS structures. [c]Refer to Scheme 3 and 4 for product structures. [d]Products (t1 to t14) are not observed. [e]Gibb's free energy at 298K applying B3LYP functional. [f]For these reactants, TS for the 4th possible conformer (**5a20**, **5a24**, **5a28**, **5a32**) could not be obtained by present DFT calculations. [g]A mixture of unseparable products are obtained. [h]Transition states of theoretically expected adducts are shown in Fig. 5 (see supporting information page no. S200-S202).

Conclusion

We have conducted the first systematic survey of the IMDA reaction of furanose tethered 1,3,9-decatriene and have shown that under thermal conditions adducts are formed from *cis*-boat and *trans*-boat$_1$ transition states. The *trans*-boat$_2$ transition state was not observed. Our model may be used to predict the stereochemical outcome of such IMDA reactions. Our work has also uncovered an alternative pathway for the synthesis of Arteannuin B core. Only one adduct was obtained but in low yields (21-

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35%) when the reaction was carried out in presence of a Lewis acid promoter. The furanose tether was found to be resistant to harsh reaction conditions such as high temperature and long reaction time.

The following empirical rules can be deduced:

1) *Cis-trans* geometry in the diene portion has no effect on yield and stereochemistry of the IMDA reaction.
2) Highest yields (~75%) are obtained when there are no substituents in the diene and dienophile portion of 1,3,9-decatrienes.
3) Yields are further reduced (~30%) when there is a substituent at the C9 position of the dienophile.
4) Thermal IMDA reactions of 1,3,9-decatrienes having cyclic dienophiles selectively afford IMDA adducts obtained from the *cis*-boat$_2$ transition state.
5) Lewis acid promoted IMDA reactions are stereoselective but low yielding.

Our studies indicate that acyclic 1,3,9-decatrienes such as acrylate (**4a**), crotylacrylate (**4e**), fumarate (**4g**) and maleate (**4i**) predominantly adopt the *cis*-boat$_1$ transition state whereas the acyclic methacrylate derived 1,3,9-decatriene (**4c**) and cyclic 1,3,9-decatrienes (cyclohexene **4k**, cyclopentene **4m**, dihydrofuran **4o** and dihydropyran **4q**) adopt the *cis*-boat$_2$ transition state. Similar conclusions are drawn by the analysis of IMDA reaction transition state structures by using DFT methods thereby giving important insights into furanose tethered adducts. We thus reassert the validity of DFT method in modeling reaction path of IMDA reaction and note that DFT functional M06-2X is able to predict reaction barrier in correct orders for most of these reactions.

Experimental section

General Information

Unless noted, all commercial reagents and solvents were used without further purification. All reactions were carried out under N_2 atmosphere in anhydrous solvents such as DCM, THF, MeOH, toluene, xylene and acetone. Anhydrous THF was distilled from sodium benzophenone and dichloromethane was distilled from calcium hydride. Aluminum TLC sheets (silica gel 60 F_{254}) of 0.25

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mm thickness were used to monitor the reactions. The spots were visualized with short wavelength UV light or by charring after being sprayed with a solution prepared from one of the following solutions: phosphomolybdic acid (5.0 g) in 95% EtOH (100 mL), 10% ethanolic H_2SO_4 and 2,4-dinitrophenyl hydrazine (2,4-DNP). Melting points were determined by capillary apparatus and are uncorrected. Yields refer to spectroscopically (^1H, ^{13}C NMR) homogeneous material obtained after column chromatography performed on silica gel (100-200 and 230-400 mesh size). Air-sensitive reagents were transferred by syringe or a double-ended needle. Optical rotations were measured by using a polarimeter at the indicated temperature with a sodium lamp (D line, 589 nm). Infrared spectra were recorded by using an FT/IR spectrometer with ATR PRO450-S and the absorption is expressed in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were obtained by using 500, 600 and 125.0, 150.0 MHz NMR spectrometers, respectively. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the solvent peak: $CDCl_3$ (δ 7.26 for ^1H NMR and δ 77.16 for ^{13}C NMR). The peak patterns of ^1H NMR are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; br, broad. The coupling constants, *J*, are reported in hertz (Hz). Assignment of carbon signals was assisted by DEPT experiments. To assign the structures under consideration, the relative stereochemistry was assigned using one and two dimensional NOE and HMBC experiments. High-resolution mass spectra were obtained by using positive electrospray ionization (ESI) by Time of Flight (TOF) method.

Computational Methods

The minimum-energy structures of reactants, transition states and products were obtained by applying density functional theory (DFT) based electronic structure calculations. A popular hybrid density functional, namely, Becke three parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) as well as a modern density functional, namely, M06-2X was used for these calculations. The quasi-Newton-Raphson-based algorithm was used to carry out geometry optimization by adopting Gaussian type split valence atomic basis function, 6-31G(d,p) for all the atoms.

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All transition state structures were characterized by one and only one imaginary frequency representing the correct reaction coordinate. The Gibbs free energies were obtained by including the thermal and entropic contributions to the energies obtained from the optimized structures. Calculated Gibbs free energy values employed for discussions in the text are the obtained through this approach. These energy values were further refined through zero point energy corrections for the calculation of reaction barrier and reaction energy. All electronic structure calculations are carried out employing GAMESS suite of ab initio package.

Experimental procedure and product characterization data

1,2:5,6-*O*-Diisopropylidene-α-D-glucofuranose (**1a**)**:**

D-Glucose (6.9 g, 38.3 mmol) was converted into 1,2:5,6-*O*-diisopropylidene-α-D-glucofuranose (**1a**) (yellowish crystals, 5.0 g, 50.2%) by reaction with excess of acetone in presence of I_2 as described by Bennet and co-workers,[18a] mp 107-109 ºC (110-111 ºC, lit.[18b]), R_f = 0.6 (50% EtOAc/*n*-hexanes). $[\alpha]_{25}^{D}$ = -13.3 (*c* 1, $CHCl_3$) (lit.[18c] $[\alpha]_{25}^{D}$ = -12.5 ($CHCl_3$)).

1,2-*O*-Isopropylidene-α-D-glucofuranose (**1b**)**:**

1,2:5,6-*O*-Diisopropylidene-α-D-glucofuranose (**1a**) (6.5 g, 25 mmol) was converted into 1,2-*O*-isopropylidene-α-D-glucofuranose (**1b**) (white crystals, 5.3 g, 96.4%) by stirring with 60% aqueous AcOH at 25-30 ºC for 21 h as described by Madsen and co-workers,[18d] mp 153-154 ºC (H_2O) (lit.[18e] 159–160 ºC), R_f = 0.4 (80% EtOAc/*n*-hexanes). $[\alpha]_{25}^{D}$ = -3.67 (c 0.53, H_2O) (lit.[18f] $[\alpha]_{25}^{D}$ = -12.2 (H_2O)).

1,2-*O*-Isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**2**)**:**

1,2-*O*-Isopropylidene-α-D-glucofuranose (**1b**) (5.2 g, 23.61 mmol) was oxidized to 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**2**) (4.44 g, 100%) by reaction with aqueous sodium metaperiodate in MeOH at 0 ºC for 1 h as described by Madsen and co-workers,[18d] mp 162-164 ºC

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(lit.[18g] mp 162–164 ºC (monomer, H_2O)), (lit.[18h] mp 181-182 ºC (dimer, EtOAc/*n*-hexane)). R_f = 0.5 (60% EtOAc/*n*-hexanes).

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-ol (3a) and (3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-buta-1,3-dien-1-yl)-2,2-dimethyl tetrahydrofuro[2,3-*d*]-[1,3]dioxol-6-ol (3b):

To a solution of allyl triphenylphosphonium bromide (4.074 g, 10.63 mmol) in THF (6 mL) at 0 ºC was added a solution of potassium hexamethyldisilazide (23.1 mL, 0.5 M solution in toluene, 11.55 mmol). The yellow suspension was stirred at 0 ºC for 1 h and a solution of 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**2**) (1 g, 5.32 mmol) in THF (3 mL) was added. The resultant brown suspension was allowed to warm to 25-30 ºC, stirred for 3 h and quenched with saturated NH_4Cl solution (50 mL). Diethyl ether (50 mL) was added and a white solid was removed by filtration through a pad of celite. The separated aqueous layer was extracted with diethyl ether (3 × 40 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give a crude product, which was purified by flash column chromatography over silica gel by using *n*-hexane/ethyl acetate (83:17) to afford alcohol (**3a**) (0.35 g, 31%) as an off white solid and alcohol (**3b**) (0.1 g, 9%) as a yellowish oily liquid.

Isomer (3a): R_f = 0.74 (50% EtOAc/*n*-hexanes), m.p. 122-124 ºC; $[\alpha]_{25}^{D}$ = -73.64 (*c* 0.865, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 3399, 2974, 1604, 1370, 1211, 1162, 963, 939, 907; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.38 (dt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.72 (dd, *J* = 15.5, 5.5 Hz, 1H), 5.28 (d, *J* = 17.0 Hz, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 5.0 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.09 (d, *J* = 2.5 Hz, 1H), 1.71 (br s, 1H) 1.51 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8, 135.1, 125.7, 118.8, 111.6, 104.5, 84.9, 80.4, 76.0, 26.6, 26.1; HRMS (ESI): calcd. for $C_{11}H_{17}O_4$ $[M+H]^+$ 213.1127, found 213.1125.

Isomer (3b): R_f = 0.72 (50% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$= -26.42 (*c* 1.03, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 3426, 2922, 1639, 1594, 1375, 1213, 1162, 911, 711; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (dt, *J* = 17.0,

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10.5, 6.5 Hz, 1H), 6.28 (t, *J* = 11.0 Hz, 1H), 5.97 (d, *J* = 3.5 Hz, 1H), 5.52 (dd, *J* = 11.0, 7.0 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 5.07 (d, *J* = 7.0 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.15 (d, *J* = 2.0 Hz, 1H), 1.80 (br s, 1H), 1.53 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.8, 131.7, 124.0, 120.7, 111.6, 104.5, 84.9, 77.5, 76.8, 26.7, 26.1; HRMS (ESI): calcd for $C_{11}H_{16}O_4Na$ ($M+Na^+$) 235.0946, found 235.0952.

General procedure for the esterification of alcohols (3a) and (3b) by using acid chloride

To a stirred solution of the alcohol (**3a** or **3b**) (1 mmol) and triethylamine (2.5 mmol) in DCM (2.5 mL) was added acryloyl chloride or methacryloyl chloride or *trans*-crotonyl chloride (2.2 mmol) dropwise at 0 ^oC. The resulting mixture was stirred at room temperature for 3 h, quenched with water (10 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with water (2 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude product that was purified by column chromatography over silica gel by using *n*-hexane/ethyl acetate (92.5:7.5) as an eluent to afford the desired acrylate (**4a-4f**) respectively.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl acrylate (**4a**)**:** Yield = 0.460 g, 61%; yellowish oily liquid; R_f = 0.82 (80% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -21.19 (*c* 0.645, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2921, 1728, 1655, 1626, 1377, 1260, 1160, 963, 891, 857, 730; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (dt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 6.43 (distorted dd, *J* = 17.5, 7.5 Hz, 1H), 6.21 (t, *J* = 11.0 Hz, 1H), 6.11 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.88 (d, *J* = 17.5 Hz, 1H), 5.42 (t, *J* = 19.0, 8.5 Hz, 1H), 5.30 (distorted d, *J* = 16.0 Hz, 1H), 5.28 (d, *J* = 2.5 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 5.21 (d, *J* = 8.0, 2.5 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 1.57 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 135.9, 135.4, 132.1, 127.6, 125.2, 118.9, 112.1, 104.6, 83.6, 79.6, 77.7, 26.7, 26.3; HRMS (ESI): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1244.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl acrylate (**4b**)**:** Yield = 0.060 g, 30%; yellowish oily liquid; R_f = 0.80 (80% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ =

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-40.60 (*c* 0.36, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2925, 1729, 1634, 1375, 1259, 1161,920, 807, 721; ^1H NMR (500 MHz, $CDCl_3$): δ 6.65 (dt, *J* = 17.0, 10.5, 6.0 Hz, 1H), 6.44 (distorted d, *J* = 17.5 Hz, 1H), 6.21 (t, *J* = 11.0 Hz, 1H), 6.11 (distorted dd, *J* = 17.0, 10.5 Hz, 1H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.88 (d, *J* = 10.5 Hz, 1H), 5.43 (t, *J* = 10.5, 8.5 Hz, 1H), 5.30 (distorted d, *J* = 15.5 Hz, 1H), 5.28 (d, *J* = 2.5 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 5.21 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 1.57 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.8, 134.3, 132.2, 131.6, 127.6, 122.9, 120.8, 112.1, 104.6, 83.7, 77.9, 75.2, 26.8, 26.2; HRMS (ESI): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1234.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl methacrylate (**4c**)**:** Yield = 0.480 g, 46%; yellowish oily liquid; R_f = 0.84 (20% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -33.256 (*c* 0.6, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2988, 2931, 1725, 1637, 1606, 1375, 1215, 1154, 952, 901, 865, 737; ^1H NMR (500 MHz, $CDCl_3$): δ 6.39 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.30 (dt, *J* = 16.5, 10.5, 6.5 Hz, 1H), 6.10 (s, 1H), 5.96 (d, *J* = 3.5 Hz, 1H), 5.63 (dd, *J* = 15.0, 6.5 Hz, 1H), 5.59 (s, 1H), 5.24 (d, *J* = 16.5 Hz, 1H), 5.23 (d, *J* = 3.0 Hz, 1H), 5.12 (d, *J* = 9.5 Hz, 1H), 4.84 (dd, *J* = 6.5, 2.5 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 1.92 (s, 3H), 1.55 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 135.8, 135.6, 135.0, 126.4, 125.2, 118.6, 111.9, 104.5, 83.5, 79.5, 77.7, 26.6, 26.1, 18.1; HRMS (ESI-MS): *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$: 303.1208; found: 303.1215.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl methacrylate (4d): Yield = 0.025 g, 31%; yellowish oily liquid; R_f = 0.83 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -73.773 (*c* 0.705, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2988, 2925, 1725, 1637, 1375, 1215, 1153, 951, 917, 864, 757; ^1H NMR (500 MHz, $CDCl_3$): δ 6.65 (dt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 6.20 (t, *J* = 11.5, 11.0 Hz, 1H), 6.13 (s, 1H), 5.96 (d, *J* = 3.5 Hz, 1H), 5.61 (s, 1H), 5.44 (t, *J* = 10.5, 8.5 Hz, 1H), 5.30 (d, *J* = 16.5 Hz, 1H), 5.25 (distorted d, *J* = 8.5 Hz, 1H), 5.24 (distorted d, *J* = 3.0 Hz, 1H), 5.22 (distorted dd, *J* = 8.5, 2.0 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 1.93 (s, 3H), 1.57 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 135.5, 134.0, 131.4, 126.5, 123.0, 120.6, 111.9, 104.5, 83.5, 77.9, 75.2, 26.7, 26.1, 18.1; HRMS (ESI-MS): *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$: 303.1208; found: 303.1215.

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(*E*)-(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl but-2-enoate (**4e**)**:** Yield = 0.050 g, 26%; yellowish oily liquid; R_f = 0.82 (20% EtOAc/*n*-hexanes). $[\alpha]_{25}^{D}$ = -19.577 (*c* 0.44, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2987, 2924, 1744, 1644, 1605, 1375, 1215, 1159, 958, 916, 858, 726; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.38 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.30 (dt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.60 (dd, *J* = 15.0, 6.5 Hz, 1H), 5.24 (distorted d, *J* = 18.0 Hz, 1H), 5.22 (distorted d, *J* = 3.5 Hz, 1H), 5.16 (distorted d, *J* = 19.0 Hz, 1H), 5.14 (distorted d, *J* = 19.5 Hz, 1H), 5.13 (distorted d, *J* = 9.5 Hz, 1H), 4.81 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.55 (d, *J* = 4.0 Hz, 1H), 3.08 (d, *J* = 7.0 Hz, 3H), 1.53 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 135.8, 134.9, 129.5, 125.2, 119.0, 118.6, 111.9, 104.4, 83.4, 79.3, 77.5, 38.8, 26.6, 26.1; HRMS (ESI-MS): *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$: 303.1208; found: 303.1217.

(*E*)-(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]diox-ol-6-yl but-2-enoate (**4f**)**:** Yield = 0.045 g, 29.6%; yellowish oily liquid; R_f = 0.81 (20% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -56.850 (*c* 0.615, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2988, 2923, 1745, 1643, 1375, 1250, 1159, 960, 917, 808, 736; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (dt, *J* = 16.5, 10.5, 6.0 Hz, 1H), 6.20 (t, *J* = 11.0 Hz, 1H), 5.95 (d, *J* = 3.0 Hz, 1H), 5.40 (t, *J* = 10.0, 9.0 Hz, 1H), 5.30 (d, *J* = 16.5 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 5.21 (distorted d, *J* = 17.5 Hz, 1H), 5.17 (distorted d, *J* = 15.5 Hz, 1H), 5.16 (distorted dd, *J* = 6.5, 3.5 Hz, 1H), 4.54 (d, *J* = 3.5 Hz, 1H), 3.10 (d, *J* = 7.0 Hz, 3H), 1.55 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 134.1, 131.5, 129.5, 122.8, 120.6, 119.0, 111.9, 104.4, 83.5, 77.7, 75.2, 38.7, 26.6, 26.1; HRMS (ESI-MS): *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$: 303.1208; found: 303.1205.

General procedure for the Steglich esterification of alcohols 3a and 3b

A stirred solution of the alcohol (**3a** or **3b**) (1 mmol), 4-dimethylaminopyridine (DMAP) (0.2 mmol) and monoethyl ester of fumaric acid or monoethyl ester of maleic acid or cyclohexene-1-carboxylic acid or cyclopentene-1-carboxylic acid or 4,5-dihydrofuran-3-carboxylic acid or 3,4-dihydro-2*H*-pyran-5-

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carboxylic acid (1.3 mmol) in dry DCM (10 mL) was cooled in an ice-water bath at 0 ^{o}C under N_2 atmosphere. Dicyclohexyl carbodiimide (DCC) (1.5 mmol) was added in one portion. After stirring for 30 min. at 0 ^{o}C the reaction mixture was allowed to warm up to R. T. followed by stirring for another 3-28 h. The reaction mass was filtered through a pad of celite and extracted with DCM (3 × 30 mL). The combined organic layers were washed with water (2 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude product that was purified by column chromatography over silica gel by using *n*-hexane/ethyl acetate (94:6) as an eluent to afford the desired 1,3,9-decatrienes (**4g**-**4r**) respectively.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl ethyl fumarate (**4g**)**:** Yield = 0.070 g, 44%; yellowish oily liquid; R_f = 0.84 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -30.00 (*c* 0.4, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2919, 1765, 1728, 1638, 1383, 1236, 1088, 892, 788; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (distorted dd, *J* = 15.5 Hz, 2H), 6.39 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.30 (dt, *J* = 16.5, 10.5, 6.5 Hz, 1H), 5.97 (d, *J* = 3.5 Hz, 1H), 5.60 (dd, *J* = 15.5, 7.0 Hz, 1H), 5.27 (d, *J* = 3.0 Hz, 1H), 5.22 (distorted dd, *J* = 16.0, 1.5 Hz, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 4.84 (dd, *J* = 6.5, 2.5 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 4.26 (q, *J* = 7.5 Hz, 2H), 1.54 (s, 3H), 1.33 (s, 3H), 1.32 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7, 163.8, 135.9, 135.5, 135.0, 132.4, 124.9, 119.1, 112.3, 104.6, 83.6, 79.5, 78.5, 61.6, 26.8, 26.3, 14.2; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1454.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl ethyl fumarate (**4h**)**:** Yield = 0.060 g, 37%; yellowish oily liquid; R_f = 0.82 (15% EtOAc/*n*-hexanes). $[\alpha]_{25}^{D}$ = -106.4 (*c* 1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2922, 1736, 1701, 1643, 1381, 1235, 1159, 1089, 892, 763; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.85 (distorted dd, *J* = 16.2, 15.6 Hz, 2H), 6.63 (dt, *J* = 16.8, 10.8, 6.6 Hz, 1H), 6.20 (t, *J* = 11.4, 10.8 Hz, 1H), 5.97 (d, *J* = 3.6 Hz, 1H), 5.40 (t, *J* = 10.2, 8.4 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 5.31 (d, *J* = 3.0 Hz, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.54 (s, 3H), 1.33 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C

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NMR (125 MHz, $CDCl_3$): δ 165.3, 164.0, 136.1, 135.4, 135.1, 128.9, 123.5, 117.8, 112.7, 104.7, 84.5, 80.8, 79.1, 61.1, 26.9, 26.4, 15.4; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{22}O_7Na$ $[M+Na]^+$ 361.1263, found 361.1274.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl ethyl maleate (**4i**)**:** Yield = 0.110 g, 68%; yellowish oily liquid; R_f = 0.83 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -43.5 (*c* 1.025, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2934, 1731, 1700, 1639, 1603, 1383, 1212, 1158, 1017, 912, 856, 729; ^1H NMR (500 MHz, $CDCl_3$): δ 6.39 (distorted dd, *J* = 15.0, 10.5 Hz, 1H), 6.32 (distorted dt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 6.27 (distorted d, *J* = 12.0 Hz, 1H), 6.19 (distorted d, *J* = 12.0 Hz, 1H), 5.92 (d, *J* = 3.5 Hz, 1H), 5.64 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.26 (distorted s, 1H), 5.23 (d, *J* = 2.5 Hz, 1H), 5.13 (distorted t, *J* = 8.5, 2.0 Hz, 1H), 4.81 (dd, *J* = 7.0, 2.5 Hz, 1H), 4.70 (d, *J* = 4.0 Hz, 1H), 4.24 (qd, *J* = 7.5, 2.0 Hz, 2H), 1.54 (s, 3H), 1.33 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 164.0, 135.9, 135.4, 130.7, 128.8, 125.2, 118.8, 112.0, 104.5, 83.0, 79.2, 78.4, 61.3, 26.6, 26.2, 13.9; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{22}O_7Na$ $[M+Na]^+$ 361.1263, found 361.1270.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl ethyl maleate (4j): Yield = 0.410 g, 59%; yellowish oily liquid; R_f = 0.81 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -36.5 (*c* 1.075, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2923, 1735, 1701, 1642, 1428, 1381, 1235, 1159, 1088, 892, 762; ^1H NMR (500 MHz, $CDCl_3$): δ 6.63 (dt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 6.29 (distorted d, *J* = 12.0 Hz, 1H), 6.21 (distorted t, *J* = 9.5, 8.0 Hz, 1H), 6.20 (distorted d, *J* = 12.0 Hz, 1H), 5.93 (d, *J* = 4.0 Hz, 1H), 5.45 (t, *J* = 10.5, 9.0 Hz, 1H), 5.28 (dd, *J* = 16.5, 10.5 Hz, 2H), 5.24 (distorted d, *J* = 3.0 Hz, 1H), 5.20 (d, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.25 (qd, *J* = 7.5, 1.5 Hz, 2H), 1.56 (s, 3H), 1.34 (s, 3H), 1.32 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 164.1, 134.4, 131.5, 131.0, 128.7, 122.9, 120.8, 112.1, 104.6, 83.1, 78.7, 74.7, 61.1, 26.8, 26.3, 14.3; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1446.

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(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl cyclohex-1-enecarboxylate (4k): Yield = 0.136 g, 68%; yellowish oily liquid; R_f = 0.81 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -96.381 (*c* 1.050, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2938, 1711, 1644, 1620, 1382, 1231, 1213, 1162, 1080, 959, 893, 742; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (distorted quint, *J* = 4.0, 2.0 Hz, 1H), 6.39 (distorted dd, *J* = 15.0, 10.5 Hz, 1H), 6.32 (dt, *J* = 16.5, 10.5, 6.0 Hz, 1H), 5.94 (d, *J* = 3.5 Hz, 1H), 5.64 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.23 (d, *J* = 15.0 Hz, 1H), 5.21 (s, 1H), 5.12 (distorted dd, *J* = 10.5, 1.5 Hz, 1H), 4.82 (dd, *J* = 7.0, 2.5 Hz, 1H), 4.57 (d, *J* = 4.0 Hz, 1H), 2.24-2.17 (m, 4H), 1.66-1.61 (m, 2H), 1.59-1.56 (m, 2H), 1.54 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 141.1, 136.0, 135.1, 129.7, 125.6, 118.6, 112.0, 104.6, 83.7, 79.7, 77.4, 26.7, 26.2, 25.8, 24.0, 22.0, 21.3; HRMS (ESI-MS): *m*/*z* calcd. for $C_{18}H_{24}O_5Na$ $[M+Na]^+$ 343.1521, found 343.1529.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl cyclohex-1-enecarboxylate (4l): Yield = 0.094 g, 47%; yellowish oily liquid; R_f = 0.80 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -116.10 (*c* 1.025, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2934, 1713, 1645, 1375, 1215, 1163, 1074, 917, 862, 740, 700; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (distorted sextet, *J* = 4.0, 2.0 Hz, 1H), 6.65 (distorted dt, *J* = 10.5, 6.0 Hz, 1H), 6.21 (t, *J* = 11.0 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.45 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.30 (d, *J* = 16.5 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.23 (d, *J* = 3.0 Hz, 1H), 5.21 (distorted dd, *J* = 8.5, 3.0 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 2.26-2.17 (m, 4H), 1.67-1.63 (m, 2H), 1.62-1.59 (m, 2H), 1.57 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 141.3, 134.1, 131.7, 129.8, 123.3, 120.6, 112.0, 104.7, 83.8, 77.6, 75.3, 26.8, 26.2, 25.9, 24.1, 22.0, 21.4; HRMS (ESI-MS): *m*/*z* calcd. for $C_{18}H_{24}O_5Na$ $[M+Na]^+$ 343.1521, found 343.1526.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl cyclopent-1-enecarboxylate (4m): Yield = 0.130 g, 65%; yellowish oily liquid; R_f = 0.81 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -111.200 (*c* 1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2919, 1715, 1627, 1605, 1374, 1258, 1162, 1081, 1014, 855, 735; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.39 (distorted dd, *J* =

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15.0, 10.5 Hz, 1H), 6.31 (dt, *J* = 16.5, 10.5, 6.5 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.64 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.23 (d, *J* = 11.5 Hz, 1H), 5.22 (s, 1H), 5.12 (d, *J* = 9.5 Hz, 1H), 4.82 (dd, *J* = 7.0, 6.5, 2.5, 3.0 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 2.55-2.48 (m, 4H), 1.95 (quint, *J* = 7.5 Hz, 2H), 1.54 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.0, 145.3, 136.1, 135.9, 135.3, 125.6, 118.7, 112.1, 104.7, 83.8, 79.7, 77.4, 33.5, 31.3, 26.8, 26.3, 23.1; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{23}O_5$ $[M+H]^+$ 307.1545, found 307.1549.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl cyclopent-1-enecarboxylate (4n): Yield = 0.085 g, 42%; yellowish oily liquid; R_f = 0.79 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -70.000 (*c* 1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2921, 1711, 1629, 1596, 1374, 1212, 1159, 1034, 955, 901, 814; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (s, 1H), 6.65 (dt, *J* = 17.0, 10.5, 6.5, 6.0 Hz, 1H), 6.20 (t, *J* = 11.5, 11.0 Hz, 1H), 5.96 (d, *J* = 3.5 Hz, 1H), 5.45 (t, *J* = 10.5, 8.5 Hz, 1H), 5.29 (d, *J* = 16.5 Hz, 1H), 5.25 (d, *J* = 4.5 Hz, 1H), 5.24 (s, 1H), 5.21 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.59 (d, *J* = 4.0 Hz, 1H), 2.57-2.49 (m, 4H), 1.96 (quint, *J* = 7.5 Hz, 2H), 1.57 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.0, 145.5, 135.8, 134.1, 131.7, 123.3, 120.6, 112.1, 104.7, 83.8, 77.6, 75.4, 33.5, 31.3, 26.9, 26.3, 23.1; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1364, found 329.1367.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4,5-dihydrofuran-3-carboxylate (4o): Yield = 0.095 g, 47%; yellowish oily liquid; R_f = 0.82 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -98.182 (*c* 1.1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2986, 1703, 1619, 1375, 1253, 1214, 1083, 1005, 873, 753; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (t, *J* = 2.0 Hz, 1H), 6.39 (distorted dd, *J* = 15.0, 10.5, 2.0 Hz, 1H), 6.32 (distorted dt, *J* = 16.0, 10.5, 6.5 Hz, 1H), 5.94 (d, *J* = 4.0 Hz, 1H), 5.63 (dd, *J* = 15.5, 7.0 Hz, 1H), 5.23 (td, *J* = 9.5, 8.0, 3.0, 2.0 Hz, 2H), 5.13 (distorted dd, *J* = 10.0, 2.0 Hz, 1H), 4.82 (dd, *J* = 7.0, 3.0 Hz, 1H), 4.59 (d, *J* = 4.5 Hz, 1H), 4.57 (t, *J* = 10.0 Hz, 2H), 2.83 (tt, *J* = 10.0, 2.0, 1.5 Hz, 2H), 1.54 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 158.5, 136.0, 135.2,

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125.6, 118.7, 112.0, 108.4, 104.6, 83.7, 79.7, 77.0, 73.4, 27.6, 26.7, 26.2; HRMS (ESI-MS): *m*/*z* calcd. for $C_{16}H_{20}O_6Na$ $[M+Na]^+$ 331.1157, found 331.1158.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4,5-dihydrofuran-3-carboxylate (4p): Yield = 0.070 g, 35%; yellowish oily liquid; R_f = 0.80 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -149.80 (*c* 1, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2925, 1688, 1619, 1381, 1258, 1131, 1088, 1033, 912, 870, 744; ^1H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, *J* = 1.5, 2.0 Hz, 1H), 6.66 (dtd, *J* = 17.0, 11.0, 7.0, 5.5, 2.0, 1.5, 1.0 Hz, 1H), 6.20 (distorted td, *J* = 11.0, 1.0 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.43 (distorted dd, *J* = 10.5, 8.0 Hz, 1H), 5.30 (td, *J* = 16.5, 1.0 Hz, 1H), 5.26 (d, *J* = 3.0 Hz, 1H), 5.24 (distorted t, *J* = 2.0 Hz, 1H), 5.19 (ddd, *J* = 8.0, 3.0, 1.5 Hz, 1H), 4.59 (d, *J* = 3.0 Hz, 1H), 4.57 (t, *J* = 10.0, 9.5 Hz, 2H), 2.84(distorted tt, *J* = 10.0, 9.5, 2.0, 1.5 Hz, 2H), 1.56 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 158.6, 134.1, 131.7, 123.2, 120.6, 112.0, 108.4, 104.6, 83.8, 77.2, 75.4, 73.5, 27.6, 26.8, 26.2; HRMS (ESI-MS): *m*/*z* calcd. for $C_{16}H_{20}O_6Na$ $[M+Na]^+$ 331.1157, found 331.1160.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*E*)-Buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 3,4-dihydro-2*H*-pyran-5-carboxylate (4q): Yield = 0.102 g, 51%; yellowish oily liquid; R_f = 0.83 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -112.80 (*c* 1, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2929, 1693, 1624, 1387, 1257, 1176, 1075, 919, 845, 755, 733; ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 6.38 (distorted dd, *J* = 15.5, 10.5 Hz, 1H), 6.32 (distorted dt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.94 (d, *J* = 4.0 Hz, 1H), 5.64 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 3.0 Hz, 1H), 5.11 (distorted dd, *J* = 10.5, 2.0 Hz, 1H), 4.81 (dd, *J* = 7.0, 2.5 Hz, 1H), 4.58 (d, *J* = 4.0 Hz, 1H), 4.05 (distorted td, *J* = 6.0, 1.5 Hz, 2H), 2.23 (q, *J* = 6.5 Hz, 2H), 1.86 (quint, *J* = 6.5 Hz, 2H), 1.54 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 156.3, 136.0, 135.0, 125.7, 118.5, 111.9, 105.3, 104.6, 83.7, 79.6, 77.0, 66.8, 26.7, 26.2, 21.0, 19.1; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{22}O_6Na$ $[M+Na]^+$ 345.1313, found 345.1307.

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(3a*R*,5*R*,6*S*,6a*R*)-5-((*Z*)-buta-1,3-dien-1-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 3,4-dihydro-2*H*-pyran-5-carboxylate (4r): Yield = 0.086 g, 43%; yellowish oily liquid; R_f = 0.81 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -140.88 (*c* 1.025, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2934, 1704, 1629, 1375, 1257, 1176, 1072, 1012, 916, 862, 740; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H), 6.65 (dt, *J* = 16.5, 10.5, 6.0 Hz, 1H), 6.20 (t, *J* = 11.0 Hz, 1H), 5.94 (d, *J* = 3.5 Hz, 1H), 5.44 (distorted dd, *J* = 11.0, 8.0 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 9.5 Hz, 1H), 5.23 (distorted d, *J* = 3.0 Hz, 1H), 5.20 (dd, *J* = 8.0, 3.0 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.05 (t, *J* = 5.0, 5.5 Hz, 2H), 2.25 (q, *J* = 5.5, 5.0 Hz, 2H), 1.87 (quint, *J* = 5.5, 5.0 Hz, 2H), 1.56 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 156.4, 134.0, 131.7, 123.3, 120.5, 111.9, 105.3, 104.6, 83.8, 77.2, 75.3, 66.8, 26.8, 26.2, 21.0, 19.2; HRMS (ESI-MS): *m*/*z* calcd. for $C_{17}H_{22}O_6Na$ $[M+Na]^+$ 345.1313, found 345.1311.

General procedure for the IMDA reaction

A solution of 1,3,9-decatriene (**4a-4r)** (1 mmol) in anhydrous xylene (3 mL) was heated to 210-215 ^oC in a sealed tube in the presence of BHT (0.4 mmol) for 7-35 h. The resulting mixture was concentrated under reduced pressure to afford a crude product that was purified by flash column chromatography over silica gel by using *n*-hexane/ethyl acetate (90:10) as an eluent to afford the desired adducts.

(4a*S*,6a*S*,6b*R*,9a*R*,10a*R*,10b*R*)-8,8-Dimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo [4',5':4,5] furo[3,2-*c*]isochromen-5(6a*H*)-one (**6**), **(4a*R*,6a*S*,6b*R*,9a*R*,10a*R*,10b*S*)-8,8-dimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromen-5(6a*H*)-one** (**7**), **(4a*S*,6a*S*,6b*R*,9a*R*,10a*R*,10b*S*)-8,8-dimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo [4',5':4,5]furo[3,2-*c*]isochromen-5(6a*H*)-one** (**8**) **and (3*R*,4a*R*,6a*R*,6b*R*,9a*R*,-10a*R*)-3,8,8-trimethyl-4,4a,6b,9a-tetrahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isobenzo-furan-5(6a*H*)-one (9):**

Acrylate (**4a**) (0.175 g, 0.657 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**6**) (0.066 g, 38%), adduct (**7**) (0.028 g, 16%), adduct (**8**) (0.038 g, 22%) as white

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crystalline solids and rearranged product (**9**) (0.014 g, 8%) as a yellowish oily liquid. Acrylate (**4b**) (0.050 g, 0.19 mmol) likewise afforded adduct (**6**) (0.0175 g, 35%), adduct (**7**) (0.0085 g, 17%), adduct (**8**) (0.0105 g, 21%) and rearranged product (**9**) (0.003 g, 6%).

Adduct (6): R_f = 0.45 (15% EtOAc/*n*-hexanes), m.p. 164-166 ^oC; $[\alpha]_{25}^{D}$ = -70.83 (*c* 0.5, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 3022, 2904, 1724, 1658, 1379, 1298, 1195, 1075, 730; ^1H NMR (500 MHz, $CDCl_3$): δ 5.97-5.93 (m, 1H), 5.89 (d, *J* = 3.5 Hz, 1H), 5.70-5.67 (m, 1H), 4.69 (d, *J* = 3.0 Hz, 1H), 4.50 (t, *J* = 3.0 Hz, 1H), 2.87 (t, *J* = 3.0 Hz, 1H), 2.73-2.68 (m, 1H), 2.24-2.00 (m, 4H), 1.50 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1, 129.8, 123.8, 112.2, 104.4, 83.4, 82.7, 73.8, 36.7, 32.6, 26.4, 26.1, 24.2, 23.7; HRMS (ESI-MS): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1223.

Adduct (7): R_f = 0.52 (15% EtOAc/*n*-hexanes), m.p. 176-178 ^oC; $[\alpha]_{25}^{D}$ = +2.63 (*c* 0.3, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2968, 2915, 1732, 1648, 1434, 1293, 1261, 1195, 1152, 682; ^1H NMR (500 MHz, $CDCl_3$): δ 5.93 (d, *J* = 4.0 Hz, 1H), 5.93-5.90 (m, 1H), 5.53 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.67 (d, *J* = 4.0 Hz, 1H), 4.59 (d, *J* = 2.5 Hz, 1H), 4.36 (t, *J* = 3.0 Hz, 1H), 3.06-3.00 (m, 1H), 2.44-2.41 (m, 1H), 2.22-2.09 (m, 3H) 1.65-1.58 (m, 1H), 1.52 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 131.7, 123.4, 112.2, 104.8, 83.8, 81.6, 75.9, 34.3, 34.1, 26.5, 26.1, 22.7, 21.8; HRMS (ESI-MS): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1223.

Adduct (8): R_f = 0.50 (15% EtOAc/*n*-hexanes), m.p. 162-164 ^oC; $[\alpha]_{25}^{D}$ = +25.62 (*c* 0.5, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2916, 2849, 1733, 1652, 1434, 1261, 1194, 1153, 681; ^1H NMR (500 MHz, $CDCl_3$): δ 5.98 (d, *J* = 4.0 Hz, 1H), 5.84-5.81 (m, 1H), 5.78–5.75 (m, 1H), 4.78 (d, *J* = 3.5 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.39 (dd, *J* = 6.0, 3.5 Hz, 1H), 2.44-2.39 (m, 1H), 2.25-2.07 (m, 3H), 1.61-1.57 (m, 1H), 1.49 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 128.1, 126.8, 112.0, 105.2, 83.1, 81.7, 80.7, 39.6, 38.2, 26.7, 26.2, 24.2, 22.2; HRMS (ESI-MS): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1223.

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Rearranged product (9): R_f = 0.59 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = +6.77 (*c* 0.15, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): ν_{max} 2920, 2851, 1743, 1639, 1376, 1259, 967, 909, 722; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.98 (d, *J* = 3.5 Hz, 1H), 5.96 (dd, *J* = 10.0, 5.0 Hz, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 4.82 (d, *J* = 3.5 Hz, 1H), 4.67 (s, 1H), 2.88 (distorted t, *J* = 10.0, 8.0 Hz, 1H), 2.35 (br s, 1H), 1.90 (distorted dd, *J* = 10.0, 4.5 Hz, 2H), 1.59 (s, 3H), 1.34 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6, 137.1, 124.6, 112.7, 106.1, 87.5, 83.2, 74.7, 52.1, 32.0, 29.5, 26.8, 26.5, 18.9; HRMS (ESI-MS): calcd for $C_{14}H_{19}O_5$ $[M+H]^+$ 267.1232, found 267.1230.

(4a*S*,6a*S*,6b*R*,9a*R*,10a*R*,10b*R*)-4a,8,8-Trimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]-dioxolo[4',5':4,5]furo[3,2-*c*]isochromen-5(6a*H*)-one (**10**)**, (4a*R*,6a*S*,6b*R*,9a*R*,10a*R*,10b*S*)-4a,-8,8-trimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-c]- isochromen-5(6a*H*)-one** (**11**) **and (3*R*,4a*R*,6a*R*,6b*R*,9a*R*,10a*R*)-3,4a,8,8-tetramethyl-4,4a,6b,9a-tetrahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isobenzofuran-5(6a*H*)-one** (**12**)

Methacrylate (**4c**) (0.360 g, 1.3 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**10**) (0.029 g, 8%) and rearranged product (**12**) (0.014 g, 4%) as yellowish oily liquids, and adduct (**11**) (0.083 g, 23%) as a white crystalline solid. Methacrylate (**4d**) (0.100 g, 0.357 mmol) likewise afforded adduct (**10**) (0.006 g, 6%), adduct (**11**) (0.020 g, 20%) and rearranged product (**12**) (0.005 g, 5%).

Adduct (10): R_f = 0.42 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -3.000 (*c* 0.4, $CHCl_3$); IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2918, 2852, 1729, 1691, 1380, 1295, 1150, 1023, 831 758; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.94 (d, *J* = 9.5 Hz, 1H), 5.89 (d, *J* = 3.5 Hz, 1H), 5.63 (distorted dd, *J* = 9.5, 3.0 Hz, 1H), 4.72 (s, 1H), 4.69 (d, *J* = 3.5 Hz, 1H), 4.45 (s, 1H), 2.44 (s, 1H), 2.13 (d, *J* = 2.5 Hz, 2H), 1.75 (d, *J* = 10.0 Hz, 2H) 1.51 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 128.9, 123.7, 112.4, 104.6, 83.8, 82.4, 74.1, 39.5, 37.2, 32.0, 27.2, 26.7, 26.3, 21.0; HRMS (ESI-MS): *m/z* $[M+H]^+$ calcd for $C_{15}H_{21}O_5$: 281.1390; found: 281.1393.

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Adduct (11): R_f = 0.50 (15% EtOAc/*n*-hexanes), m.p. 58–60 ºC; $[\alpha]_{25}^{D}$ = -2.170 (*c* 0.365, $CHCl_3$); IR (neat, cm^{-1}): ν_{max} 2965, 2919, 1729, 1649, 1380, 1295, 1176, 1151, 682, 655; ^1H NMR (500 MHz, $CDCl_3$): δ 5.95 (d, *J* = 4.0 Hz, 1H), 5.94 (distorted s, 1H), 5.50 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.68 (d, *J* = 3.5 Hz, 1H), 4.64 (d, *J* = 2.0 Hz, 1H), 4.34 (t, *J* = 2.5, 2.0 Hz, 1H), 2.79 (d, *J* = 2.5 Hz, 1H), 2.17 (dt, *J* = 13.0, 4.5, 4.0 Hz, 1H), 2.03 (t, *J* = 3.0 Hz, 3H), 1.52 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.9, 130.7, 124.9, 112.3, 104.6, 83.7, 81.6, 76.9, 40.6, 39.6, 33.4, 28.3, 26.6, 26.2, 22.2; HRMS (ESI-MS): *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{21}O_5$: 281.1389; found: 281.1399.

Rearranged product (12): R_f = 0.58 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -1.714 (*c* 0.350, $CHCl_3$); IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2921, 2853, 1738, 1705, 1691, 1438, 1381, 1235, 1088, 891, 794; ^1H NMR (500 MHz, $CDCl_3$): δ 5.95 (d, *J* = 3.5 Hz, 1H), 5.87 (distorted d, *J* = 10.5 Hz, 1H), 5.83 (distorted d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 3.5 Hz, 1H), 4.61 (s, 1H), 2.32 (d, *J* = 5.5 Hz, 1H), 2.02 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.58 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H), 1.16 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.7, 135.5, 124.4, 112.4, 106.3, 87.5, 83.1, 81.8, 56.2, 34.8, 31.8, 26.3, 25.8, 19.9, 18.0; HRMS (ESI-MS): *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{21}O_5$: 281.1389; found: 281.1393.

(4*R*,4a*S*,6a*S*,6b*R*,9a*R*,10b*R*)-4,8,8-Trimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo [4',5':4,5]furo[3,2-*c*]isochromen-5(6a*H*)-one (13) and (4*S*,4a*R*,6a*S*,6b*R*,9a*R*,10b*S*)-4,8,8-trimethyl-4,4a,6b,9a,10a,10b-hexahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromen-5(6a*H*)-one (14)

Crotyl acrylate (**4e**) (0.360 g, 1.3 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**13**) (0.022 g, 6%) and adduct (**14**) (0.011 g, 3%) as yellowish oily liquids. Crotyl acrylate (**4f**) (0.100 g, 0.357 mmol) likewise afforded adduct (**13**) (0.005 g, 5%) and adduct (**14**) (0.002 g, 2%).

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Adduct (13): R_f = 0.58 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = +1.928 (*c* 0.825, $CHCl_3$); IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2959, 2850, 1731, 1660, 1467, 1236, 1088, 891, 793; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.02-5.92 (m, 1H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 4.84 (dd, *J* = 16.5, 4.0 Hz, 1H), 4.67 (s, 1H), 4.56 (d, *J* = 8.0 Hz, 1H), 2.54 (d, *J* = 13.0 Hz, 1H), 2.23-2.14 (m, 2H), 2.07-2.02 (m, 2H), 1.59(s, 3H), 1.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.9, 130.7, 124.9, 112.3, 104.6, 83.7, 81.6, 76.9, 40.6, 39.6, 33.4, 28.3, 26.7, 26.2, 22.2; HRMS (ESI-MS): *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{21}O_5$: 281.1389; found: 281.1387.

Adduct (14): R_f = 0.42 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -8.308 (*c* 0.650, $CHCl_3$); IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2920, 2851, 1729, 1645, 1467, 1382, 1236, 1089, 890, 785; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (d, *J* = 3.5 Hz, 1H), 5.84 (distorted d, *J* = 8.0 Hz, 1H), 5.72 (d, *J* = 9.5 Hz, 1H), 4.72 (d, *J* = 3.5 Hz, 1H), 4.64 (s, 1H), 4.58 (t, *J* = 3.0, 2.5 Hz, 1H), 3.06 (s, 1H), 2.45-2.31 (m, 2H), 1.75-1.70 (m, 2H) 1.51 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 130.5, 124.7, 111.0, 104.3, 83.5, 81.4, 76.9, 40.4, 38.0, 33.3, 28.1, 26.5, 26.1, 22.0; HRMS (ESI-MS): *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{21}O_5$: 281.1389; found: 281.1395.

(4*R*,4a*R*,6a*S*,6b*R*,9a*R*,10a*R*,10b*R*)-Ethyl 8,8-dimethyl-5-oxo-4,4a,5,6a,6b,9a,10a,10b-octahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromene-4-carboxylate (15), (4*R*,4a*R*,6a*S*,6b*R*,-9a*R*,10a*R*,10b*S*)-ethyl 8,8-dimethyl-5-oxo-4,4a,5,6a,6b,9a,10a,10b-octahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromene-4-carboxylate (16) and (3*S*,4*S*,4a*R*,6a*R*,6b*R*,9a*R*,10a*R*)-ethyl 3,8,8-trimethyl-5-oxo-4,4a,5,6a,6b,9a-hexahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isobenzofuran-4-carboxylate (17)

Fumarate derived 1,3,9-decatriene (**4g**) (0.200 g, 0.59 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**15**) (0.048 g, 24%) as a yellowish oily liquid, and adduct (**16**) (0.038 g, 19%) and rearranged product (**17**) (0.016 g, 8%) as white crystalline solids. Fumarate derived 1,3,9-decatriene (**4j**) (0.050 g, 0.15 mmol) likewise afforded adduct (**15**) (0.011 g, 22%), adduct (**16**) (0.010 g, 20%) and rearranged product (**17**) (0.0035 g, 7%).

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Adduct (15): R_f = 0.48 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -9.684 (*c* 0.475, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2918, 1734, 1578, 1468, 1236, 1088, 891, 782, 758; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.91 (d, *J* = 3.5 Hz, 1H), 5.87-5.84 (m, 1H), 5.74 (distorted dd, *J* = 10.0, 2.5 Hz, 1H), 4.72 (distorted d, *J* = 5.5 Hz, 1H), 4.71 (distorted d, *J* = 1.5 Hz, 1H), 4.59 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.16 (t, *J* = 6.5, 5.0 Hz, 1H), 2.46-2.44 (m, 2H), 2.03 (q, *J* = 7.5 Hz, 1H), 1.52 (s, 3H), 1.33 (s, 3H), 1.29 (distorted d, *J* = 2.5 Hz, 1H), 1.27 (distorted t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 170.6, 126.8, 123.5, 112.5, 104.6, 83.1, 82.0, 73.9, 61.1, 39.3, 38.1, 31.7, 26.6, 26.2, 25.2, 14.2; HRMS (ESI-MS): calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1448.

Adduct (16): R_f = 0.51 (15% EtOAc/*n*-hexanes), m.p. 90-92 ºC; $[\alpha]_{25}^{D}$ = +4.400 (*c* 1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 1758, 1716, 1654, 1375, 1315, 1240, 1186, 1158, 1014, 957, 862, 754, 666; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99 (d, *J* = 4.0 Hz, 1H), 5.87 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.78-5.75 (m, 1H), 4.80 (d, *J* = 4.0 Hz, 1H), 4.69 (d, *J* = 4.0 Hz, 1H), 4.45 (dd, *J* = 6.5, 4.0 Hz, 1H), 4.25-4.14 (m, 2H), 2.76 (td, *J* = 11.5, 11.0, 6.0 Hz, 1H), 2.62 (dd, *J* = 13.5, 11.5 Hz, 1H), 2.51-2.43 (m, 2H), 2.20-2.12 (m, 1H), 1.51 (s, 3H), 1.33 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 172.1, 126.6, 126.3, 112.4, 105.6, 83.2, 82.0, 80.8, 61.1, 39.9, 39.2, 29.8, 28.6, 26.9, 26.4, 14.2; HRMS (ESI-MS): calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1444.

Rearranged product (17): R_f = 0.53 (15% EtOAc/*n*-hexanes), m.p. 108-110 ºC; $[\alpha]_{25}^{D}$ = -1.714 (*c* 0.350, $CHCl_3$); IR (ATR) ṽ (cm^{-1}): 2922, 1793, 1732, 1466, 1379, 1235, 1161, 1085, 885, 790; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99 (d, *J* = 10.0 Hz, 1H), 5.99 (d, *J* = 4.0 Hz, 1H), 5.89 (d, *J* = 10.0 Hz, 1H), 4.83 (d, *J* = 3.5 Hz, 1H), 4.62 (s, 1H), 4.23 (q, *J* = 7.5 Hz, 2H), 3.32 (d, *J* = 13.0 Hz, 1H), 2.88 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.63 (sextet, *J* = 6.5, 6.0 Hz, 1H), 1.59 (s, 3H), 1.33 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.021 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 170.2, 135.4, 124.4, 112.7, 106.1, 88.7, 86.9, 83.2, 61.3, 45.2, 43.4, 30.7, 26.4, 25.7, 15.8, 14.3; HRMS (ESI-MS): calcd for $C_{17}H_{23}O_7$ *m/z* $[M+H]^+$ 339.1444; found: 339.1452.

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(4*S*,4a*R*,6a*S*,6b*R*,9a*R*,10a*R*,10b*R*)-Ethyl 8,8-dimethyl-5-oxo-4,4a,5,6a,6b,9a,10a,10b-octahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromene-4-carboxylate (18), (4*R*,4a*S*,6a*S*,6b*R*,-9a*R*,10a*R*,10b*S*)-ethyl 8,8-dimethyl-5-oxo-4,4a,5,6a,6b,9a,10a,10b-octahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]isochromene-4-carboxylate (19) and (4*S*,4a*R*,6a*S*,6b*R*,9a*R*,10a*R*,-10b*S*)-ethyl 8,8-dimethyl-5-oxo-4,4a,5,6a,6b,9a,10a,10b-octahydro-3*H*-[1,3]dioxolo-[4',5':4,5]furo[3,2-*c*]isochromene-4-carboxylate (20)

Maleate derived 1,3,9-decatriene (**4i**) (0.200 g, 0.59 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**18**) (0.050 g, 25%), adduct (**19**) (0.038 g, 19%) and adduct (**20**) (0.032 g, 16%) as yellowish oily liquids. Maleate derived 1,3,9-decatriene (**4j**) (0.050 g, 0.15 mmol) likewise afforded adduct (**18**) (0.0115 g, 23%), adduct (**19**) (0.010 g, 20%) and adduct (**20**) (0.007 g, 14%).

Adduct (18): R_f = 0.47 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = +12.000 (*c* 0.1, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2922, 1776, 1730, 1647, 1465, 1374, 1257, 1193, 1081, 888, 750, 629; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.91 (d, *J* = 3.5 Hz, 1H), 5.88-5.84 (m, 1H), 5.74 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.72 (d, *J* = 4.5 Hz, 1H), 4.71 (d, *J* = 2.5 Hz, 1H), 4.59 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.20 (distorted dd, *J* = 5.5, 2.5 Hz, 1H), 3.17-3.13 (m, 2H), 2.45 (distorted dd, *J* = 7.0, 3.0 Hz, 2H), 1.52 (s, 3H), 1.33 (s, 3H) 1.28 (distorted t, *J* = 9.0, 5.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.8, 170.0, 130.1, 123.1, 112.6, 104.9, 83.8, 81.8, 75.5, 61.2, 38.5, 36.2, 26.7, 26.3, 23.5, 22.8, 14.2; HRMS (ESI): calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1444.

Adduct (19): R_f = 0.54 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = +4.333 (*c* 0.6, $CHCl_3$); IR **(**ATR**)** ṽ (cm^{-1}): 2936, 1763, 1729, 1649, 1385, 1309, 1240, 1158, 1017, 965, 866, 751, 670; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.97 (d, *J* = 3.5 Hz, 1H), 5.92-5.89 (m, 1H), 5.54 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 3.5 Hz, 1H), 4.60 (d, *J* = 1.5 Hz, 1H), 4.39 (distorted t, *J* = 2.5 Hz, 1H), 4.20-4.13 (m, 2H), 3.54 (distorted dd, *J* = 6.5, 1.5 Hz, 1H), 3.47 (distorted dd, *J* = 5.5, 1.5 Hz, 1H), 3.13 (s, 1H), 2.60 (d, *J* = 17.5 Hz, 1H), 2.35-2.30 (m, 1H), 1.53 (s, 3H), 1.33 (s, 3H) 1.28 (distorted t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.6,

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172.1, 126.6, 126.2, 112.3, 105.5, 83.1, 82.0, 80.8, 61.1, 39.9, 39.1, 28.6, 26.9, 26.4, 22.8, 14.2; HRMS (ESI): calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1443.

Adduct (20): R_f = 0.52 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -18.581 (*c* 0.775, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2920, 1767, 1725, 1647, 1436, 1374, 1297, 1184, 1159, 1016, 967, 888, 859, 765; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99 (d, *J* = 3.5 Hz, 1H), 5.87 (d, *J* = 9.5 Hz, 1H), 5.78–5.76 (m, 1H), 4.80 (d, *J* = 3.5 Hz, 1H), 4.69 (d, *J* = 3.5 Hz, 1H), 4.45 (distorted dd, *J* = 5.5, 4.0 Hz, 1H), 4.26-4.14 (m, 2H), 2.76 (td, *J* = 11.5, 6.0 Hz, 1H), 2.62 (t, *J* = 13.0, 11.5 Hz, 1H), 2.50-2.47 (m, 2H), 2.17 (td, *J* = 13.0, 3.0 Hz, 1H), 1.51 (s, 3H), 1.34 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.2, 170.6, 126.8, 123.4, 112.5, 104.5, 83.1, 81.9, 73.9, 61.1, 39.3, 38.1, 26.6, 26.2, 25.2, 22.8, 14.2; HRMS (ESI): calcd for $C_{17}H_{23}O_7$ $[M+H]^+$ 339.1444, found 339.1447.

(7a*S*,9a*S*,9b*R*,12a*R*,13a*R*,13b*S*)-11,11-Dimethyl-3,3a,4,5,6,7,9b,12a,13a,13b-decahydro-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]benzo[*i*]isochromen-8(9a*H*)-one (22)

Cyclohexene derived 1,3,9-decatriene (**4k**) (0.250 g, 0.78 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**22**) (0.080 g, 32%) as a yellowish oily liquid. Cyclohexene derived 1,3,9-decatriene (**4l**) (0.100 g, 0.31 mmol) likewise afforded adduct (**22**) (0.030 g, 30%).

Adduct (22): R_f = 0.61 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -4.333 (*c* 1.2, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2924, 1731, 1693, 1453, 1377, 1257, 1164, 1078, 1019, 841, 750; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93 (d, *J* = 4.0 Hz, 1H), 5.86-5.82 (m, 1H), 5.43 (distorted dd, *J* = 10.0, 2.5 Hz, 1H), 4.67 (d, *J* = 4.0 Hz, 1H), 4.58 (d, *J* = 2.5 Hz, 1H), 4.42 (t, *J* = 3.0 Hz, 1H), 3.20 (d, *J* = 2.0 Hz, 1H), 2.46 (distorted dd, *J* = 12.5, 11.0, 2.5, 1.0 Hz, 1H), 2.31-2.23 (m, 2H), 1.71 (distorted dd, *J* = 17.0, 5.5, 4.0 Hz, 2H), 1.61-1.57 (m, 1H), 1.53 (s, 3H), 1.50-1.42 (m, 2H), 1.41-1.38 (m, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.6, 129.4, 123.3, 112.4, 104.8, 83.7, 81.2, 76.9, 43.7, 37.5, 35.9, 31.9, 29.5, 27.4, 26.7, 26.3, 25.6, 20.9; HRMS (ESI-MS): calcd for $C_{18}H_{25}O_5$ $[M+H]^+$ 321.1702, found 321.1707.

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(3a*S*,6a*R*,8a*S*,8b*R*,11a*R*,12a*R*,12b*S*)-10,10-Dimethyl-3a,4,5,6,8b,11a,12a,12b-octahydro-3*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]cyclopenta[*i*]isochromen-7(8a*H*)-one (23) and (3*R*,3a*R*,6a*S*,-8a*R*,8b*R*,11a*R*,12a*R*)-3,10,10-trimethyl-3a,4,5,6,8b,11a-hexahydro-3*H*-indeno[4'',3a'':3',4']-furo[2',3':4,5]furo[2,3-*d*][1,3]dioxol-7(8a*H*)-one (24)

Cyclopentene derived 1,3,9-decatriene (**4m**) (0.150 g, 0.49 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**23**) (0.049 g, 33%) as a yellowish oily liquid and rearranged product (**24**) (0.028 g, 19%) as a white crystalline solid. Cyclopentene derived 1,3,9-decatriene (**4n**) (0.075 g, 0.24 mmol) likewise afforded adduct (**23**) (0.022 g, 29%) and rearranged product (**24**) (0.013 g, 18%).

Adduct (23): R_f = 0.57 (15% EtOAc/*n*-hexanes); $[\alpha]_{25}^{D}$ = -15.644 (*c* 1.125, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2927, 1731, 1707, 1633, 1458, 1375, 1258, 1163, 1078, 1018, 950, 864, 784, 655; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93 (d, *J* = 3.5 Hz, 1H), 5.88-5.85 (m, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 4.66 (d, *J* = 4.0 Hz, 1H), 4.61 (d, *J* = 2.0 Hz, 1H), 4.40 (t, *J* = 3.0 Hz, 1H), 2.81 (d, *J* = 1.5 Hz, 1H), 2.71-2.64 (m, 1H), 2.41 (distorted dd, *J* = 8.5, 1.5 Hz, 1H), 2.39 (distorted d, *J* = 10.0 Hz, 1H), 2.25-2.19 (m, 2H), 2.03-1.97 (m, 2H), 1.84 (t, *J* = 9.5, 7.5 Hz, 1H), 1.76 (distorted t, *J* = 9.5 Hz, 1H), 1.53 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.2, 128.9, 123.3, 112.4, 104.8, 83.6, 80.9, 76.5, 47.4, 43.5, 40.1, 33.6, 29.3, 26.6, 26.2, 24.9, 21.0; HRMS (ESI-MS): calcd for $C_{17}H_{23}O_5$ $[M+H]^+$ 307.1545, found 307.1548.

Rearranged product (24): R_f = 0.59 (15% EtOAc/*n*-hexanes), m.p. 122-124 ^oC; $[\alpha]_{25}^{D}$ = +12.878 (*c* 1.025, $CHCl_3$); IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 1772, 1633, 1455, 1376, 1209, 1159, 1033, 855, 753; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.04 (dd, *J* = 10.0, 3.0 Hz, 1H), 5.94 (d, *J* = 4.0 Hz, 1H), 5.68 (ddd, *J* = 10.0, 1.5, 1.0 Hz, 1H), 4.80 (d, *J* = 4.0 Hz, 1H), 4.47 (s, 1H), 2.39 (distorted dt, *J* = 11.0, 6.5, 5.0 Hz, 1H), 2.29 (distorted qdd, *J* = 10.0, 3.0 Hz, 1H), 2.04 (distorted dtd, *J* = 13.0, 5.25, 2.0, 1.5 Hz, 1H), 1.87 (distorted dt, *J* = 13.5, 9.0 Hz, 1H), 1.83-1.77 (m, 1H), 1.69-1.63 (m, 2H), 1.54 (s, 3H), 1.31 (s, 3H), 1.23-1.15 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.2, 135.3, 130.2, 112.4, 106.0, 90.6,

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87.4, 83.3, 59.2, 50.9, 34.3, 31.2, 29.3, 26.4, 26.0, 25.7, 18.4; HRMS (ESI-MS): calcd for $C_{17}H_{23}O_5$ $[M+H]^+$ 307.1545, found 307.1550.

(3a*S*,6a*S*,8a*S*,8b*R*,11a*R*,12a*R*,12b*S*)-10,10-Dimethyl-3,3a,5,6,8b,11a,12a,12b-octahydro-[1,3]dioxolo[4',5':4,5]furo[3,2-*c*]furo[2,3-*i*]isochromen-7(8a*H*)-one (25)

Dihydrofuran derived 1,3,9-decatriene (**4o**) (0.220 g, 0.71 mmol) when subjected to the general procedure for the IMDA reaction afforded adduct (**25**) (0.059 g, 27%) as a yellowish oily liquid. Dihydrofuran derived 1,3,9-decatriene (**4p**) (0.050 g, 0.16 mmol) likewise afforded adduct (**25**) (0.013 g, 26%).

Adduct (25): R_f = 0.58 (15% EtOAc/*n*-hexanes), m.p. 158-160 ºC; $[\alpha]_{22}^{D}$ = –2.125 (*c* 0.8, $CHCl_3$); IR **(**ATR**)** $\tilde{\nu}$ (cm^{-1}): 2992, 1719, 1615, 1460, 1368, 1252, 1181, 1068, 1010, 955, 851, 665; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (d, *J* = 3.5 Hz, 1H), 5.88 (distorted dd, *J* = 10.0, 3.5 Hz, 1H), 5.51 (dd, *J* = 10.0, 1.0 Hz, 1H), 4.69 (d, *J* = 3.5 Hz, 1H), 4.66 (d, *J* = 2.0 Hz, 1H), 4.47 (distorted t, *J* = 2.5 Hz, 1H), 4.33 (d, *J* = 4.5 Hz, 1H), 4.08-3.97 (m, 2H), 2.89 (distorted d, *J* = 2.0 Hz, 1H), 2.62 (ddd, *J* = 11.7, 7.8, 3.6 Hz, 1H), 2.51-2.45 (m, 1H), 2.41-2.31 (m, 2H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 127.5, 123.0, 112.6, 104.8, 83.5, 81.4, 80.0, 76.1, 65.4, 46.2, 41.2, 34.2, 26.6, 26.2, 26.0; HRMS (ESI-MS): calcd for $C_{16}H_{21}O_6$ $[M+H]^+$ 309.1364, found 309.1331.

General procedure for the Lewis acid promoted IMDA reaction

To a solution of 1,3,9-decatriene (**4a**-**4p**) (1 mmol) in dry DCM (3 mL) was added BHT (0.4 mmol) followed by dropwise addition of Et_2AlCl (5 mmol, 1.0 M solution in *n*-hexane) at 0 ºC over 15 min. under N_2 atmosphere. The resulting mixture was warmed and stirred to 25-30 ºC and stirred for 38-95 h. It was concentrated under reduced pressure to afford a crude product that was purified by flash column chromatography over silica gel by using *n*-hexane/ethyl acetate (90:10) to afford the desired adducts.

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Supplementary data

Electronic supplementary information (ESI) available: Copies of ^{1}H, ^{13}C, DEPT, 2D NMR and HRMS spectra for all new compounds, computational details including cartesian coordinates for all transition state structures and its energies, cifs and anisotropic displacement ellipsoid plots for compounds **6**, **7**, **8**, **11** and **24** (CCDC nos. 1032856−1032859 and 1053326 respectively). See DOI:

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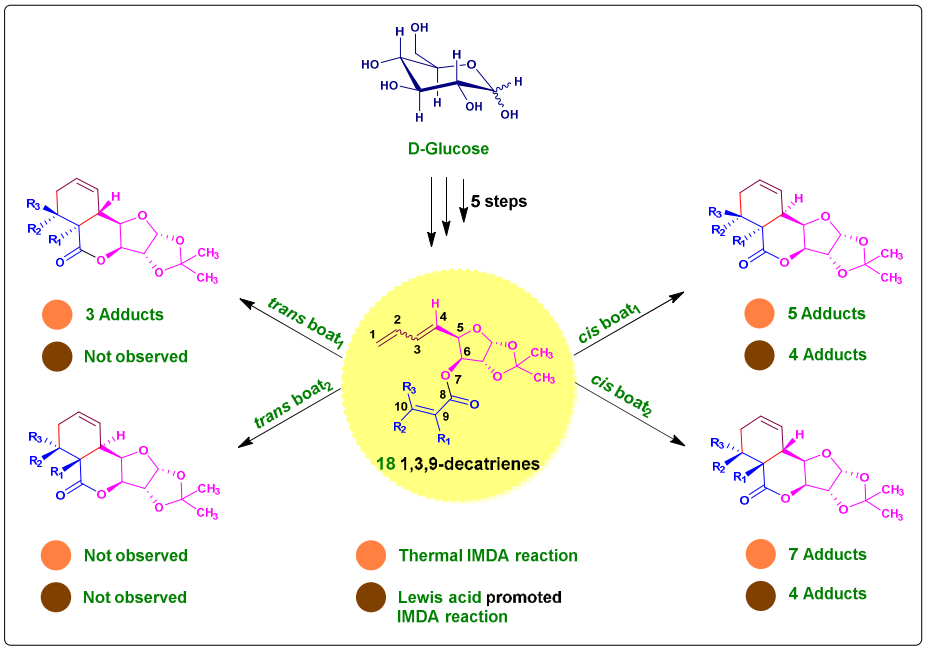
Graphical abstract

Thermal and Lewis acid Promoted Intramolecular Diels-Alder Reaction of Furanose Tethered 1,3,9-Decatriene Systems: A Synthetic and Computational Investigation

The intramolecular Diels–Alder (IMDA) reaction of furanose tethered 1,3,9-decatrienes (**4a-4r**) was investigated under thermal conditions and in the presence of a Lewis acid.



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