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Exploring structural effects of levoglucosenone derived chiral auxiliaries in asymmetric Diels–Alder cycloadditions

Ariel M. Sarotti,[a] Rolando A. Spanevello,[a] Carine Duhayon,[b] Jean-Pierre Tuchagues[b] and Alejandra G. Suárez[a,*]

[a]*Instituto de Química Orgánica de Síntesis, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario—CONICET. Suipacha 531, S2002LRK Rosario, Argentina*
[b]*Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse Cedex, France*

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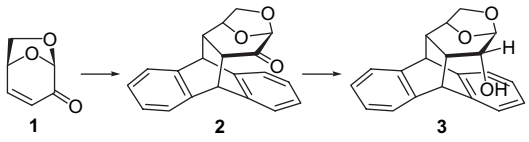
Abstract—New chiral auxiliaries derived from levoglucosenone were developed in a simple and efficient way and evaluated as chiral inductors in asymmetric Diels–Alder reactions between the corresponding acrylate derivatives and cyclopentadiene. The results showed an important influence of the absolute configuration of the C(2) center of the auxiliary on the level of stereoinduction obtained.

1. Introduction

Among the plethora of natural molecules from the chiral pool, carbohydrates probably play an unsurpassed role as chiral auxiliaries in asymmetric synthesis regarding optical purity, number of stereogenic centers, availability and economics. Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) (**1**) is a versatile and readily available member of the carbohydrate derived chiral pool, which has been intensively used as chiral synthon in the synthesis of a wide variety of compounds.[1,2] This bicyclic enone, is the major product of the pyrolysis of cellulose or cellulose-containing materials, such as waste paper.[1,3] Our interest in this field is focused on the potential use of this chiral building block in the synthesis of new asymmetric inductors.

The Diels–Alder reaction is among the most popular and successful synthetic applications of carbohydrate auxiliaries, particularly when they are attached to the dienophile. Recently, we reported the synthesis of the first chiral auxiliary derived from levoglucosenone. The asymmetric inductor was obtained by a [4+2] cycloaddition reaction of **1** with anthracene followed by a diastereoselective reduction of the C(2) keto functionality in high overall yield (Scheme 1).[4] The auxiliary was used as chiral template in an asymmetric Diels–Alder reaction of the corresponding acrylic ester derivative with cyclopentadiene and shown to be efficient for asymmetric induction.[4,5]



Scheme 1.

To investigate the relationship between the structure of the synthetic chiral auxiliary and its effectiveness in asymmetric synthesis, we developed different chiral auxiliaries structurally related to **3**. The new chiral auxiliaries were conceived in order to determine the relationship between the absolute configuration of the carbinolic center and the steric hindrance of the α-face of the molecule with the induction capacity. Subsequently, their relative effectiveness in asymmetric Diels–Alder reaction was evaluated.

2. Results and discussion

2.1. Synthesis of chiral auxiliaries

2.1.1. Syntheses of alcohols 3 and 4. As described in our previous report we have developed a convenient access to large amounts of the cycloadduct **2** through the reaction of **1** with anthracene and catalytic amount of $FeCl_3$.[4] The structural assignment was based on NMR studies; moreover, owing to the high crystallinity of this compound, it was possible

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* Corresponding author. Tel./fax: +54 341 437 0477; e-mail: asuarez@fbioyf.unr.edu.ar

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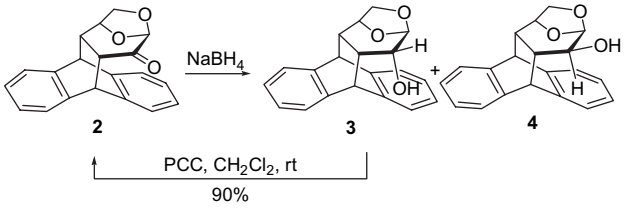
to determine the crystal structure by X-ray. The ORTEP representation of cycloadduct **2** (Fig. 1) clearly shows that the annelated aromatic ring lies below the plane of the 1,6-anhydro bridge.

Figure 1 shows that cycloadduct **2** is composed of an anhydropyranoside residue [C(1)–C(6)] fused to an anthracenyl moiety [C(7)–C(20)] with a ketone group at C(2) (C–O bond length of 1.201(3) Å and bond angles of 116.7(2), 120.4(2), and 122.9(2)°). As in most 1,6-anhydropyranoses, the two outer C–O bonds of the C(5)–O(2)–C(1)–O(1)–C(6) bond sequence are longer than the average C–O bond length, while the inner two C–O bonds are shorter than this average C–O bond length.[6] The C–O bond lengths in the crystalline structure of **2** for the above sequence are 1.446(2), 1.409(3), 1.409(3), and 1.449(3) Å. The acetal ring in **2** adopts an envelope $^{O(2)}$E conformation and the pyranone ring a $^{3}C_{O(2)}$ conformation. As a result of the fused ring system, the pyranose ring conformation differs somewhat from other 1,6-anhydropyranosides.[7,8] Evidence for the flattening of this ring in solution was also observed by ^{1}H NMR spectroscopy, where the coupling constant between H(3) and H(4) is large ($J_{3,4}$=9.8 Hz), indicating a small dihedral angle between these cis hydrogen atoms (12.1° in the crystalline state). In addition, H(5) appears as a doublet, coupled only with H(6), which means that the coupling constant $J_{4,5}$ of **2** is unusually small (~0 Hz) indicating a dihedral angle close to 90°, found to be 74.0° in the crystalline state.

The diastereoselective conversion of **2** to the corresponding alcohol derivatives relies mainly on the competitive steric hindrance exerted by the 1,6-anhydro bridge above the plane of the pyranose ring and the aromatic rings below it. We have already shown that reduction of **2** with DIBAL-H in dichloromethane at −80 °C gives only compound **3** in quantitative yield. For this reason, the initial attempt for the synthesis of the epimeric alcohol **4** was to invert the configuration of the carbinolic center via a Mitsunobu or related reactions. Unfortunately, none of the applied methodologies yielded **4**. After several attempts with different reducing agents, we found that reduction of the C(2) ketone of **2** with sodium borohydride afforded a mixture of epimeric alcohols (Scheme 2), in different ratio depending on the reaction conditions (Table 1).



Scheme 2.

Table 1. Reduction of **2** with $NaBH_4$ at room temperature

Entry	Solvent	Yield (%)[a]	Ratio **3/4**
1	EtOH/H_2O 9:1	93	56/44
2	CH_2Cl_2/MeOH 1:3	100	81/19
3	CH_2Cl_2/MeOH 3:1	100	70/30
4	CH_2Cl_2/MeOH 20:1	100	62/38
5	CH_2Cl_2/MeOH 99:1	92	53/47

[a] Yield corresponds to isolated material.

Analysis of the results shown in Table 1 demonstrates that $NaBH_4$ in EtOH (entry 1) or CH_2Cl_2/MeOH 99:1 (entry 5) led to approximately equal amounts of the epimeric products. These results suggest that under these experimental conditions the steric contribution of the 1,6-anhydro bridge and the annelated anthracene ring, play an equivalent role in deciding the reaction outcome. In order to increase the overall yield of alcohol **4**, compound **3** can be reoxidized with PCC in excellent yield to regenerate ketone **2**. Separation of alcohols **3** and **4** was easily performed by flash chromatography. Although both epimeric alcohols are crystalline compounds, only the structure of compound **3** could be solved by X-ray crystallography (Fig. 2).

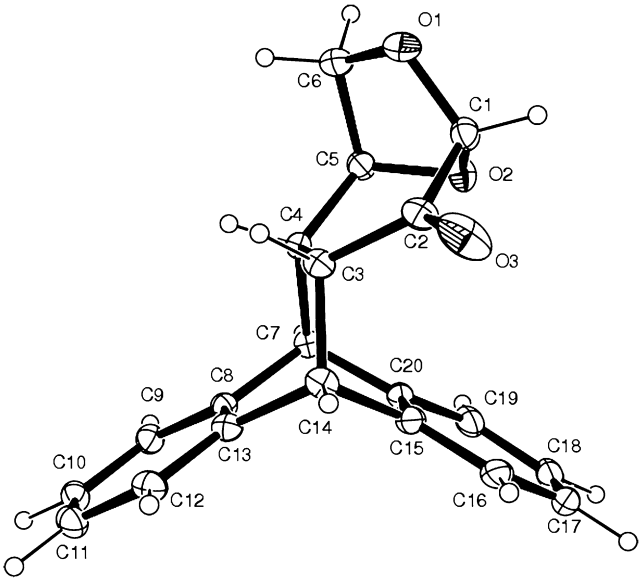


Figure 1. X-ray crystallographic structure of **2**.

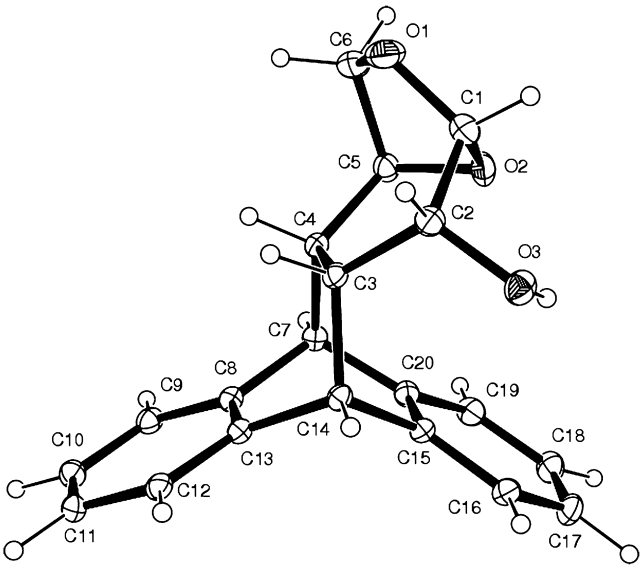
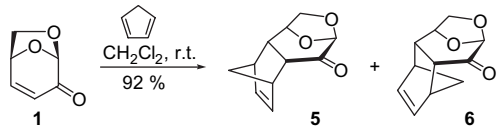


Figure 2. X-ray crystallographic structure of **3**.

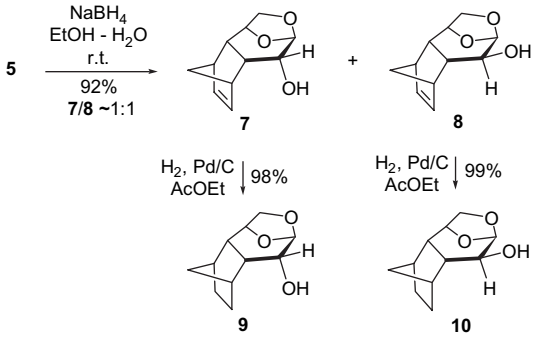
The crystal structure of **3** shows that this alcohol includes an hexopyranoside residue [C(1)–C(6)] fused to an anthracenyl moiety [C(7)–C(20)] with an hydroxyl group at C(2) (C–O bond length of 1.421(3) Å). The pyranose ring assumes a ^1H_O conformation placing the hydroxy group of C(2) in a pseudo equatorial position. The acetal ring adopts an envelope E_5 conformation. The flattening of the pyranose ring is observed both in solution and in the crystalline state. The coupling constants between H(3) and H(4) obtained from the ^1H NMR spectra is large ($J_{3,4}$=10.4 Hz), according to the small dihedral angle (1.4°) found in the solid state. In other 1,6-anhydropyranoses in a chair conformation, $J_{3,4}$ (axial–equatorial) is usually within the range of 4.2–5.8 Hz.[7,8] Besides, H(5) is not coupled with H(4) ($J_{4,5}$= 0 Hz), indicating a dihedral angle of approximately 90°, found 87.7° in the crystal, whereas 1.5–2.5 Hz coupling constant (equatorial–equatorial) would be expected for a chair conformation.[7,8] The C–O bond length of the five membered ring are 1.446(2), 1.421(2), 1.428(3) and 1.436(3) Å corresponding to the sequence C(5)–O(2)–C(1)–O(1)–C(6). These values are in good agreement with the bond sequence described for the 1,6-anhydro bridge present in other derivatives.[6] The *R* configuration of the C(2) of **2** is consistent with the small $J_{1,2}$ (~0 Hz) and large $J_{2,3}$ (10.4 Hz) coupling constants, corresponding, in the solid state, to dihedral angles of 67.0 and 13.4°. A small $J_{1,2}$ is also observed in related derivatives of **2** in which H(1) appears as a singlet in the *R* isomer.[7] The packing of the molecules in the crystal is due to van der Waals forces. The hydroxyl hydrogen is the only hydrogen atom available for hydrogen bonding, but no hydrogen-bond interaction was detected in the crystal packing.

2.1.2. Syntheses of alcohols 9 and 10. The synthesis of chiral auxiliaries with smaller carbon skeleton in the α-face of the molecule was achieved by the introduction of a cyclopentadiene residue. The cycloaddition reaction of levoglucosenone and cyclopentadiene was previously described by Horton and Bhate.[9] However, after several reaction attempts with **1** and dicyclopentadiene in refluxing chlorobenzene, a mixture of adducts **5** (*endo*) and **6** (*exo*) was obtained in a 69% overall yield and in a 78/22 *endo*/*exo* ratio. In order to increase the amount of the desired product **5** different reaction conditions were tested. We found that the [4+2] cycloaddition in dichloromethane at room temperature with freshly distilled cyclopentadiene afforded adduct **5** in 86% yield with only 6% of isomer **6** (Scheme 3). This milder experimental conditions favor the formation of the kinetic products and may account for the higher *endo* selectivity observed.



Scheme 3.

The adduct **5** was readily reduced by sodium borohydride in aqueous ethanol at room temperature affording a 1:1 mixture of alcohols **7** and **8** in very good yield. Separation of the two isomers was easily achieved by column chromatography. Hydrogenation of the double bond in each alcohol was performed to avoid possible future inconvenience, yielding the new chiral inductors **9** and **10** (Scheme 4).

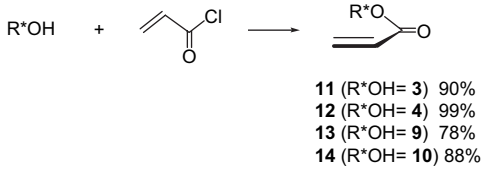


Scheme 4.

2.2. Asymmetric Diels–Alder reactions of acrylates derived from 3, 4, 9, and 10

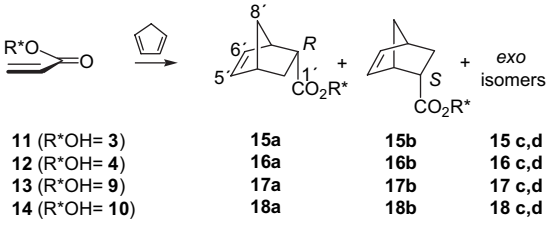
Once the syntheses of the inductors **4**, **9**, and **10** were achieved in a straightforward manner, we tested their synthetic usefulness as chiral auxiliaries. There are several possibilities to prove the inductive capacity and our initial choice was a Diels–Alder reaction. For this reason, we examined the use of the acrylic esters derived from the chiral auxiliaries as dienophiles. The cycloaddition reaction of the corresponding acrylates with cyclopentadiene would produce a bicyclic system having significant synthetic utility for the construction of complex natural products.[10]

Acrylates **11**–**14** were simply prepared in very good to excellent yields by reaction of acryloyl chloride with the corresponding alcohol in the presence of triethylamine at 0 °C (Scheme 5). We also include acrylate **11** previously reported,[4,5] because **3** is a complementary auxiliary of **4** that only differs at the stereocenter containing the hydroxyl group.



Scheme 5.

The Diels–Alder reactions between acrylates **11**–**14** and cyclopentadiene were carried out under thermal conditions and in the presence of Lewis acids affording the four expected diastereoisomers as depicted in Scheme 6.



Scheme 6.

The stereochemical assignments of each product were based on the ^{1}H and ^{13}C NMR data, as well as 2D NMR techniques. The *endo* adducts **15**–**18a**,**b** showed larger chemical shift differences for the vinylic protons H(5′) and H(6′) in contrast to the similarity in chemical shift for the corresponding protons in the *exo* isomers **15**–**18c**,**d**, which is consistent with the absence of any shielding effects exerted by the chiral auxiliary moiety. In contrast, the olefinic protons in the *endo* adducts are relatively closer to the auxiliary moiety and their anisotropy induces larger chemical shift differences between H(5′) and H(6′). The foregoing assignment agreed with chemical shift data obtained from the ^{13}C NMR spectra of the adducts. Thus, the carbon signal of the methylene bridge (C-8′) is much more shielded (ca. 3.3 ppm) in the *exo* adducts than in the *endo* ones, as already reported for similar carbocycles.[11,12] Furthermore, the C(1′) and C(6′) signals are more shielded (ca. 1.6 ppm and 3.5 ppm, respectively) in the *endo* than in the *exo* adducts.

The absolute configuration of the *endo* adducts was determined by hydrolysis with LiOH under standard conditions and correlation of their optical rotation with the reported ones for the pair of enantiomers of 5-norbornene-2-carboxylic acid.[13] The carboxylic acids derived from **15a**, **16a**, and **18a** displayed an $[\alpha]_D^{21}$ +148.4 (*c* 0.73, $CHCl_3$), +149.9 (*c* 0.90, $CHCl_3$), and +150.2 (*c* 0.44, $CHCl_3$), respectively, indicating that the 2*R* configuration corresponds to these *endo* isomers. The carboxylic acid derived from a 13:87 mixture of **17a**,**b** displayed an $[\alpha]_D^{19}$ −107.7 (*c* 1.58, $CHCl_3$) [lit.[13] −151.5 (*c* 2.0, $CHCl_3$)] indicating that adduct **17b** has a 2*S* configuration. It is important to point out that chiral auxiliaries were recovered almost quantitatively in all hydrolysis reactions performed.

Table 2 shows the results of the Diels–Alder reactions of acrylates **3**, **4**, **9**, and **10** with cyclopentadiene performed in the presence and absence of Lewis acids. Diethylaluminum chloride (Et_2AlCl) and ethylaluminum dichloride ($EtAlCl_2$) were chosen to promote the cycloaddition reaction in this study, because they produce the best yields and selectivity among the Lewis acids tested.

The *endo*/*exo* and *endo*/*endo* ratios of cycloadducts derived from acrylates **11** and **12** were determined from the relative intensities of the signals attributed to hydrogens H(5′) and H(6′) in the ^{1}H NMR spectra of the mixture of adducts. When the cycloaddition reaction was performed with acrylate **14**, the mixture of adducts was previously separated by column chromatography, to isolate **18a** from the mixture of **18b**,**c**,**d**. The *endo*/*exo* and *endo*/*endo* ratios were calculated from the ^{1}H NMR spectra of each fraction. The mixture of adducts **17a**–**d** was also separated by column chromatography to afford two fractions *endo* **17a**,**b** and *exo* **17c**,**d**. The ratio **17a**/**17b** was calculated from the ^{1}H NMR spectra by a deconvolution method. The result was corroborated by analysis of the ^{1}H NMR spectra performed in deuterated benzene, whereas the signals of *endo* **17a** and **17b** are clearly separated.

All cycloadditions were *endo* selective, as predicted by the Alder's rule, which has been rationalized in terms of interplay between stabilizing secondary orbital interactions and steric effects in the transition state.[14] The reactions

Table 2. Diels–Alder reactions (Scheme 6)

Entry	Auxiliary	Lewis acid (equiv)	Solvent	Temp (°C)	Time (h)	Yield (%)[a]	*endo R*/*S*	*endo*/*exo*
1	**3**	—	PhMe	110	1.5	100	70/30	71/29
2	**3**	—	PhMe	25	48	86	74/26	74/26
3	**3**	—	CH_2Cl_2	25	52	87	71/29	79/21
4	**3**	Et_2AlCl (2)	CH_2Cl_2	25	1	80	22/78	92/8
5	**3**	Et_2AlCl (2)	CH_2Cl_2	−30	1	86	10/90	98/2
6	**3**	$EtAlCl_2$ (2)	CH_2Cl_2	25	<1	60	34/66	96/4
7	**3**	$EtAlCl_2$ (2)	CH_2Cl_2	−40	<1	91	15/85	98/2
8	**4**	—	PhMe	110	1.5	97	49/51	73/27
9	**4**	—	PhMe	25	56	96	43/57	76/24
10	**4**	—	CH_2Cl_2	25	48	100	49/51	82/18
11	**4**	Et_2AlCl (2)	CH_2Cl_2	25	1	70	53/47	94/6
12	**4**	Et_2AlCl (2)	CH_2Cl_2	−40	1	81	57/43	97/3
13	**4**	$EtAlCl_2$ (2)	CH_2Cl_2	25	1	83	71/29	92/8
14	**4**	$EtAlCl_2$ (2)	CH_2Cl_2	−40	1	98	75/25	96/4
15	**9**	—	PhMe	110	2	80	52/48	71/29
16	**9**	—	PhMe	25	46	97	52/48	74/26
17	**9**	—	CH_2Cl_2	25	46	90	48/52	82/18
18	**9**	Et_2AlCl (2)	CH_2Cl_2	25	1	97	26/74	93/7
19	**9**	Et_2AlCl (2)	CH_2Cl_2	−40	1	92	13/87	96/4
20	**9**	$EtAlCl_2$ (2)	CH_2Cl_2	25	1	84	23/77	83/17
21	**9**	$EtAlCl_2$ (2)	CH_2Cl_2	−40	1	87	16/84	93/7
22	**10**	—	PhMe	110	6.5	83	44/56	68/32
23	**10**	—	PhMe	25	72	89	43/57	72/28
24	**10**	—	CH_2Cl_2	25	72	99	47/53	75/25
25	**10**	Et_2AlCl (2)	CH_2Cl_2	25	1	79	62/38	91/9
26	**10**	Et_2AlCl (2)	CH_2Cl_2	−40	1	82	63/37	92/8
27	**10**	$EtAlCl_2$ (2)	CH_2Cl_2	25	1	82	59/41	91/9
28	**10**	$EtAlCl_2$ (2)	CH_2Cl_2	−40	1	98	63/37	96/4

[a] Yield corresponds to isolated products.

performed under thermal conditions showed moderate *endo*/*exo* ratio. The π-facial selectivity is low for chiral auxiliary **3**, and almost nil for **4**, **9**, and **10**. This is probably due to the fact that the conformation of acrylate is not fixed in the absence of Lewis acid.

On the other hand, reactions promoted in the presence of Lewis acids showed an important enhancement in stereoselectivity. All cycloaddition reactions proceeded in very good yields and high *endo*/*exo* selectivity. However, the π-facial selectivity showed dependence on the chiral inductor employed. A closer examination of the experimental results in Table 2 reveals that the absolute configuration at the carbinolic center has a great influence on the effectiveness of asymmetric induction in the cycloaddition reaction. Comparing the results in entries 5, 7, 19, and 21 to those in entries to 12, 14, 26, and 28, make it evident that chiral auxiliaries **3** and **9** with *R* configuration at the carbinolic center are superior to **4** and **10**, which have *S* configuration at C(2). This observation suggests that for this class of chiral inductors the configuration of the C(2) stereocenter is a key feature for the effectiveness of the π-facial selectivity. On the other hand, the difference between the anthracenyl and cyclopentadienyl moieties attached to the α-face of the levoglucosenone scaffold has almost no influence on the *endo*/*endo* selectivity for chiral auxiliaries **3** and **9** (entries 5 and 7, compared to 19 and 21). However, by employing inductors **4** and **10** the π-facial selectivity is different (entries 12 and 14 compared to 26 and 28).

In order to draw an overall comparison of the effectiveness of the different chiral auxiliaries developed in this study, Figure 3 shows the best values obtained for *endo*/*exo* and π-facial selectivity.

The *endo*/*exo* ratios shown in Figure 3 demonstrate that the auxiliaries give very good levels of stereoselectivity. The *endo*/*endo* ratios observed showed dependence on the C(2) configuration. Chiral auxiliaries **3** and **9** having the *R* configuration at the carbinolic position showed better induction than their corresponding epimers. The steric hindrance of the α-face of **3** and **9** had almost no influence on the *endo*/*endo* ratio. However, for alcohols **4** and **10**, the π-facial selectivity is directly related to the higher steric hindrance exerted by the anthracenyl residue (diastereomeric excess **16a**,**b** 50% and **18a**,**b** 26%).

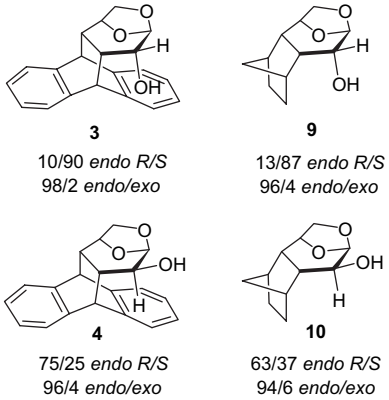


Figure 3.

3. Conclusion

We have developed new chiral auxiliaries derived from levoglucosenone and explored the structural factors that affect their inductive effectiveness in Diels–Alder reactions. The chiral auxiliaries are easily removed from the adducts by hydrolysis to provide the free carboxylic acid in very good yields and they can be reused. The level of induction obtained, in addition to the fact that the starting material is inexpensive, make these systems excellent models to be further employed in other asymmetric reactions.

4. Experimental

4.1. General

The melting points were taken on a Leitz Wetzlar Microscope Heating Stage Model 350 apparatus and are uncorrected. Optical rotation was measured in a Jasco DIP 1000 polarimeter. Infrared spectra were obtained on an IRPrestige-21 Fourier Transform Spectrophotometer Shimadzu. Elemental analyses were determined by Atlantic Microlab, Inc., Norcross, GA, U.S.A. High-resolution mass spectra were performed on a Micromass AutoSpec. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 spectrometer with tetramethylsilane as an internal standard and deuterochloroform as solvent. Assignments marked with * and ** can be interchanged.

All reactions were monitored by thin layer chromatography carried out on 0.25 mm E. Merck silica gel plates ($60F_{254}$) were developed using UV light and anisaldehyde–sulfuric acid–acetic acid with subsequent heating. Flash column chromatography using Merck silica gel 60H, was performed by gradient elution created by mixtures of hexanes and increasing amounts of ethyl acetate.

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated.

Levoglucosenone **1** was obtained from the pyrolysis of waste paper or microcrystalline cellulose (Anedra).[1,3] Compound **1** was obtained with sufficient purity for synthetic transformations and was used without further purification. It displayed spectroscopic properties that are in agreement with those reported in the literature.[15]

4.2. Synthesis of chiral auxiliaries

4.2.1. Cycloaddition of 1 with anthracene. Preparation of compound 2. To a solution of **1** (1.940 g, 15.39 mmol) in dichloromethane (33 mL) was added anthracene (4.046 g, 22.70 mmol) and anhydrous $FeCl_3$ (0.348 g, 2.15 mmol). The mixture was stirred at room temperature for 5.5 h. The reaction was diluted with dichloromethane and washed with aqueous 5% sodium and potassium tartrate. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over anhydrous magnesium sulfate. Concentration and

purification by flash chromatography furnished **2** (4.305 g, 14.15 mmol, 92% yield) as a white crystalline solid. Compound **2**: mp=235–236 °C (hexane/ethyl acetate); $[\alpha]_D^{26}$ −109.7 (*c* 0.50, $CHCl_3$); IR (KBr) ν_{max}: 1732 (C=O), 1478, 1458, 1223, 1117, 987 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–7.01 (m, 8H, aromatics), 4.83 (d, $J_{3,3a}$=3.2 Hz, 1H, H-3a), 4.67 (d, $J_{5,6}$=4.4 Hz, 1H, H-5), 4.59 (s, 1H, H-1), 4.30 (d, $J_{4,4a}$=1.8 Hz, 1H, H-4a), 3.72–3.61 (m, 2H, H-6*endo*,*exo*), 2.84 (dd, $J_{3,4}$=9.8 Hz, $J_{3,3a}$=3.2 Hz, 1H, H-3), 2.19 (dd, $J_{3,4}$=9.8 Hz, $J_{4,4a}$=1.8 Hz, 1H, H-4); ^{13}C NMR ($CDCl_3$) δ 198.6 (C, C-2), 143.8 (C, aromatic), 140.9 (C, aromatic), 140.4 (C, 2C, aromatics), 126.2 (CH, aromatic), 126.1 (CH, 2C, aromatics), 125.9 (CH, aromatic), 124.5 (CH, 2C, aromatics), 123.9 (CH, aromatic), 122.8 (CH, aromatic), 99.0 (CH, C-1), 76.7 (CH, C-5), 69.4 (CH_2, C-6), 49.7 (CH, C-4a), 46.6 (CH, C-3a), 45.1 (CH, C-3), 43.2 (CH, C-4). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.94; H, 5.28.

4.2.2. Reduction of 2 with $NaBH_4$. Compounds 3 and 4. To a solution of **2** (3.200 g, 10.51 mmol) in 96% ethanol (305 mL) was added dropwise a solution of $NaBH_4$ (0.948 g, 25.06 mmol) in water (14.8 mL) containing four drops of 40% KOH solution. After stirring for 40 min at 60 °C solvent was evaporated under reduced pressure and the crude was dissolved with ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4) and evaporated. Flash column chromatography provided **3** (1.818 g, 5.93 mmol, 56%) and **4** (1.199 g, 3.91 mmol, 37%) as white crystalline solids.

Compound **3**: mp=225–226 °C (hexane/ethyl acetate); $[\alpha]_D^{31}$ +58.3 (*c* 0.73, $CHCl_3$); IR (KBr) ν_{max}: 3521, 2958, 2900, 1458, 1138, 1095, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.02 (m, 8H, aromatics), 4.95 (s, 1H, H-1), 4.70 (d, $J_{3,3a}$=2.1 Hz, 1H, H-3a), 4.47 (d, $J_{5,6exo}$=3.9 Hz, 1H, H-5), 4.19 (d, $J_{4,4a}$=2.1 Hz, 1H, H-4a), 3.87 (dd, $J_{2\text{-}OH}$=12.4 Hz, $J_{2,3}$=10.4 Hz, 1H, H-2), 3.66 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.58 (dd, J_{gem}=6.9 Hz, $J_{5,6exo}$=3.9 Hz, 1H, H-6*exo*), 2.58 (td, $J_{3,4}$=$J_{2,3}$=10.4 Hz, $J_{3,3a}$=2.1 Hz, 1H, H-3), 1.98 (dd, $J_{3,4}$=10.4 Hz, $J_{4,4a}$=2.1 Hz, 1H, H-4), 1.61 (d, $J_{2\text{-}OH}$=12.4 Hz, OH); ^{13}C NMR ($CDCl_3$) δ 144.2 (C, aromatic), 143.3 (C, aromatic), 143.1 (C, aromatic), 141.7 (C, aromatic), 126.3 (CH, aromatic), 126.1 (CH, aromatic), 125.9 (CH, aromatic), 125.6 (CH, aromatic), 124.8 (CH, aromatic), 124.5 (CH, aromatic), 123.3 (CH, aromatic), 122.7 (CH, aromatic), 102.4 (CH, C-1), 76.0 (CH, C-5), 71.0 (CH_2, C-6), 69.2 (CH, C-2), 51.0 (CH, C-4a), 46.0 (CH, C-3a), 42.1 (CH, C-4), 36.2 (CH, C-3). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 77.70; H, 5.91.

Compound **4**: mp=239–240 °C (hexane/ethyl acetate); $[\alpha]_D^{25}$ −32.5 (*c* 0.49, $CHCl_3$); IR (KBr) ν_{max}: 3407, 2962, 2900, 1718, 1458, 1054, 999 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.07 (m, 8H, aromatics), 4.96 (d, $J_{1,2}$=3.2 Hz, 1H, H-1), 4.60 (d, $J_{5,6exo}$=4.7 Hz, 1H, H-5), 4.46 (d, $J_{3,3a}$=2.8 Hz, 1H, H-3a), 4.19 (s, 1H, H-4a), 3.71 (dd, J_{gem}=6.9 Hz, $J_{5,6exo}$=4.7 Hz, 1H, H-6*exo*), 3.62 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.09 (br s, 1H, H-2), 2.16–1.99 (m, 3H, H-3, H-4 and OH); ^{13}C NMR ($CDCl_3$) δ 144.8 (C, aromatic), 141.6 (C, aromatic), 141.3 (C, aromatic), 140.9 (C, aromatic), 126.2 (CH, aromatic), 125.9 (CH, aromatic), 125.7 (CH, aromatic), 125.6 (CH, aromatic), 125.5 (CH, aromatic), 124.7 (CH, aromatic), 124.1 (CH, aromatic), 122.4 (CH, aromatic), 99.6 (CH, C-1), 76.3 (CH, C-5), 70.4 (CH_2, C-6), 70.1 (CH, C-2), 50.1 (CH, C-4a), 48.2 (CH, C-3a), 46.2 (CH, C-4), 41.7 (CH, C-3); HRMS calcd for $C_{20}H_{18}O_3Na$ $[M+Na]^+$ 329.1148, found 329.1167.

4.2.3. Cycloaddition of 1 with cyclopentadiene. Compounds 5 and 6. To a solution of **1** (1.242 g, 9.85 mmol) in dichloromethane (12 mL) was added freshly distilled cyclopentadiene (2.5 mL, 30.38 mmol). The mixture was stirred at room temperature for 4 days. Evaporation of solvent and purification by flash chromatography gave adducts *endo* **5** (1.631 g, 8.49 mmol, 86%) as a white crystalline solid and *exo* **6** (106 mg, 0.55 mmol, 6%) as an oil.

Compound **5**: mp=67–68 °C (hexane/ether); $[\alpha]_D^{23}$ −223.0 (*c* 1.08, $CHCl_3$) [lit.[9] mp=62–63 °C; $[\alpha]_D^{25}$ −222.0 (*c* 1, $CHCl_3$)]; IR (KBr) ν_{max}: 2977, 1725 (C=O), 1132, 1126, 1111, 1095, 989, 917, 887, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (dd, J_{8-9}=5.6 Hz, J_{9-10}=3.0 Hz, 1H, H-9), 6.01 (dd, J_{8-9}=5.6 Hz, J_{7-8}=2.9 Hz, 1H, H-8), 4.80 (s, 1H, H-1), 4.62 (d, J_{5-6exo}=4.3 Hz, 1H, H-5), 3.84 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.78 (dd, J_{gem}=6.9 Hz, J_{5-6}=4.3 Hz, 1H, H-6*exo*), 3.38 (br s, 1H, H-7), 3.03 (br s, 1H, H-10), 3.00 (dd, J_{3-4}=9.2 Hz, J_{3-7}=4.5 Hz, 1H, H-3), 2.38 (dd, J_{3-4}= 9.2 Hz, J_{4-10}=3.2 Hz, 1H, H-4), 1.46 (td, J_{gem}=8.6 Hz, J_{7-11}=1.8 Hz, J_{10-11}=1.8 Hz, 1H, H-11*anti*), 1.30 (br d, J_{gem}=8.6 Hz, 1H, H-11*syn*); ^{13}C NMR ($CDCl_3$) δ 200.2 (C, C-2), 135.5 (CH, C-8), 134.1 (CH, C-9), 99.3 (CH, C-1), 74.8 (CH, C-5), 70.2 (CH_2, C-6), 49.4 (CH_2, C-11), 46.9 (CH, 2C, C-7 and C-3), 46.3 (CH, C-10), 42.3 (CH, C-4).

Compound **6**: $[\alpha]_D^{21}$ −220.8 (*c* 1.15, $CHCl_3$) [lit.[9] $[\alpha]_D^{25}$ −220.0 (*c* 1, $CHCl_3$)]; IR (film) ν_{max}: 2972, 1722 (C=O), 1330, 1234, 1118, 986, 912, 876, 844, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.31 (dd, J_{8-9}=5.6 Hz, J_{9-10}=3.0 Hz, 1H, H-9), 6.20 (dd, J_{8-9}=5.6 Hz, J_{7-8}=3.0 Hz, 1H, H-8), 5.05 (s, 1H, H-1), 4.81 (d, J_{5-6exo}=4.7 Hz, 1H, H-5), 3.88 (dd, J_{gem}=7.0 Hz, J_{5-6}=4.7 Hz, 1H, H-6*exo*), 3.81 (d, J_{gem}=7.0 Hz, 1H, H-6*endo*), 3.30 (br s, 1H, H-7), 2.90 (br s, 1H, H-10), 2.26 (d, J_{3-4}=8.4 Hz, 1H, H-3), 1.74–1.59 (m, 2H, H-4 and H-11*anti*), 1.26 (td, J_{gem}=9.0 Hz, J_{7-11}= 1.5 Hz, J_{10-11}=1.5 Hz, 1H, H-11*syn*); ^{13}C NMR ($CDCl_3$) δ 201.1 (C, C-2), 139.4 (CH, C-8), 136.3 (CH, C-9), 99.1 (CH, C-1), 76.8 (CH, C-5), 69.9 (CH_2, C-6), 48.2 (CH, C-10), 46.9 (CH, C-7), 44.9 (CH, C-3), 44.5 (CH_2, C-11), 41.9 (CH, C-4).

4.2.4. Reduction of 5 with $NaBH_4$. Compounds 7 and 8. To a solution of **5** (1.631 g, 8.49 mmol) in 96% ethanol (15.5 mL) was added dropwise a solution of $NaBH_4$ (0.267 g, 7.06 mmol) in water (2.4 mL) containing two drops of 40% KOH solution. After stirring for 30 min at room temperature the solvent was evaporated under reduced pressure and the crude was dissolved with ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4) and evaporated. Flash column chromatography provided **7** (0.798 g, 4.11 mmol, 48%) and **8** (0.732 g, 3.77 mmol, 44%) as white crystalline solids.

Compound **7**: mp=93–94 °C (hexane/ether); $[\alpha]_D^{23}$ +36.6 (*c* 1.08, $CHCl_3$) [lit.[9] mp=85–86 °C; $[\alpha]_D^{25}$ +36.6 (*c* 1, $CHCl_3$)]; IR (KBr) ν_{max}: 3397, 2968, 2936, 1337, 1136,

1038, 909, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.32 (br s, 1H, H-8), 6.23 (br s, 1H, H-9), 5.07 (s, 1H, H-1), 4.32 (d, J_{5-6exo}=3.6 Hz, 1H, H-5), 3.82 (d, J_{2-3}=9.2 Hz, 1H, H-2), 3.73 (d, J_{gem}=6.5 Hz, 1H, H-6*endo*), 3.61 (dd, J_{gem}=6.5 Hz, J_{5-6}=3.6 Hz, 1H, H-6*exo*), 3.08 (br s, 1H, H-7), 2.91 (br s, 1H, H-10), 2.76 (td, J_{3-4}=10.0 Hz, J_{2-3}=9.2 Hz, J_{3-7}= 3.3 Hz, 1H, H-3), 2.11 (dd, J_{3-4}=10.0 Hz, J_{4-10}=3.1 Hz, 1H, H-4), 1.76 (br s, 1H, OH), 1.38 (d, J_{gem}=7.9 Hz, 1H, H-11*anti*), 1.25 (d, J_{gem}=7.9 Hz, 1H, H-11*syn*); ^{13}C NMR ($CDCl_3$) δ 137.7 (CH, C-8), 132.9 (CH, C-9), 101.9 (CH, C-1), 74.4 (CH, C-5), 71.2 (CH_2, C-6), 67.9 (CH, C-2), 50.0 (CH_2, C-11), 47.6 (CH, C-10), 46.4 (CH, C-7), 42.2 (CH, C-4), 39.4 (CH, C-3).

Compound **8**: mp=76–77 °C (hexane/ether); $[\alpha]_D^{21}$ −78.2 (*c* 1.04, $CHCl_3$) [lit.[9] mp=71–72 °C; $[\alpha]_D^{25}$ −79.0 (*c* 1, $CHCl_3$)]; IR (KBr) ν_{max}: 3278, 2966, 2886, 2868, 1171, 1121, 1095, 1067, 1047, 991, 890, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.28 (dd, J_{8-9}=5.6 Hz, J_{9-10}=3.0 Hz, 1H, H-9), 6.18 (dd, J_{8-9}=5.6 Hz, J_{7-8}=3.0 Hz, 1H, H-8), 5.14 (d, J_{1-2}=3.4 Hz, 1H, H-1), 4.41 (d, J_{5-6exo}=3.7 Hz, 1H, H-5), 3.77–3.68 (m, 2H, H-6*endo* and H-6*exo*), 3.19–3.12 (m, 2H, H-2 and H-7), 2.89 (br s, 1H, H-10), 2.29–2.16 (m, 2H, H-3 and H-4), 1.94 (d, *J*=10.8 Hz, 1H, OH), 1.44 (td, J_{gem}=8.2 Hz, J_{7-11}= 1.8 Hz, J_{10-11}=1.8 Hz, 1H, H-11*anti*), 1.28 (d, J_{gem}=8.2 Hz, 1H, H-11*syn*); ^{13}C NMR ($CDCl_3$) δ 135.7 (CH, 2C, C-8 and C-9), 99.9 (CH, C-1), 74.4 (CH, C-5), 71.1 (CH_2, C-6), 69.8 (CH, C-2), 50.3 (CH_2, C-11), 47.8 (CH, C-10), 46.9 (CH, C-3), 46.3 (CH, C-7), 44.2 (CH, C-4).

4.2.5. Hydrogenation of 7. Compound 9. To a solution of **7** (798 mg, 4.11 mmol) in ethyl acetate (35 mL) was added a catalytic amount of Pd/C and was stirred for 2 h under hydrogen atmosphere (1 bar) at room temperature. The suspension was filtered over Celite and the solvent was evaporated under reduced pressure providing **9** (786 mg, 4.01 mmol, 98%) as a white crystalline solid. Compound **9**: mp=94–95 °C (hexane/ether); $[\alpha]_D^{28}$ −55.2 (*c* 1.00, $CHCl_3$); IR (KBr) ν_{max}:3471, 3451, 3346, 2951, 2935, 2878, 1142, 1136, 1033, 914 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (s, 1H, H-1), 4.43 (d, J_{5-6exo}=4.7 Hz, 1H, H-5), 3.89 (dd, J_{2-3}= 10.1 Hz, $J_{2\text{-}OH}$=6.4 Hz, 1H, H-2), 3.69 (dd, J_{gem}=6.7 Hz, J_{5-6}=4.7 Hz, 1H, H-6*exo*), 3.62 (d, J_{gem}=6.7 Hz, 1H, H-6*endo*), 2.40–2.26 (m, 3H, H-7, H-10 and H-3), 1.93–1.36 (m, 8H, H-4, H-8, H-9, H-11 and OH); ^{13}C NMR ($CDCl_3$) δ 104.1 (CH, C-1), 73.7 (CH, C-5), 69.9 (CH, C-2), 69.4 (CH_2, C-6), 42.6 (CH, C-3), 39.7 (CH, C-10)*, 39.1 (CH_2, C-11), 38.3 (CH, C-4), 36.4 (CH, C-7)*, 24.5 (CH_2, 2C, C-8 and C-9); HRMS calcd for $C_{11}H_{16}O_3$ $[M]^+$ 196.1099. Found: 196.1095.

4.2.6. Hydrogenation of 8. Compound 10. To a solution of **8** (763 mg, 3.93 mmol) in ethyl acetate (33 mL) was added a catalytic amount of Pd/C and was stirred for 2 h under hydrogen atmosphere (1 bar) at room temperature. The suspension was filtered over Celite and the solvent was evaporated under reduced pressure providing **10** (763.8 mg, 3.89 mmol, 99%) as a white crystalline solid. Compound **10**: mp=80–81 °C; $[\alpha]_D^{19}$ −109.2 (*c* 1.02, $CHCl_3$); IR (KBr) ν_{max}: 3373, 2946, 2876, 1158, 1075, 1061, 1034, 1020, 1014, 951, 881 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (d, J_{1-2}=3.9 Hz, 1H, H-1), 4.46 (d, J_{5-6exo}=3.9 Hz, 1H, H-5), 3.80–3.71 (m, 2H, H-6*endo* and H-6*exo*), 3.65 (br s, 1H, H-2), 2.42 (br s, 1H, H-7)*, 2.31 (br s, 1H, H-10)*, 2.14 (br d, $J_{2\text{-}OH}$=9.2 Hz, 1H, OH), 1.96–1.25 (m, 8H, H-3, H-4, H-8, H-9 and H-11); ^{13}C NMR ($CDCl_3$) δ 99.7 (CH, C-1), 73.9 (CH, C-5), 70.9 (CH_2, C-6), 67.2 (CH, C-2), 42.7 (CH, C-3), 42.1 (CH, 2C, C-4 and C-10)*, 41.3 (CH, C-7)*, 39.5 (CH_2, C-11), 23.1 (CH_2, C-8)**, 22.6 (CH_2, C-9); HRMS calcd for $C_{11}H_{17}O_3$ $[M+H]^+$ 197.1178. Found: 197.1181.

4.3. Synthesis of acrylates

4.3.1. Acrylate 11. Acryloyl chloride (0.93 mL, 11.40 mmol) was added at 0 °C to a solution of **3** (644 mg, 2.1 mmol) in dichloromethane (30 mL) and triethylamine (1 mL, 7.2 mmol). After stirring for 4 h at 0 °C, the reaction was quenched by addition of water, extracted several times with methylenchloride and dried (Na_2SO_4). The residue was purified by flash column chromatography to give the acrylate **11** (681 mg, 1.89 mmol, 90%) as a white crystalline solid. Compound **11**: mp=208–209 °C (hexane/ethyl acetate); $[\alpha]_D^{29}$ −71.4 (*c* 0.66, $CHCl_3$); IR (KBr) ν_{max}: 2948, 2886, 1714 (C=O), 1630, 1468, 1458, 1408, 1296, 1195, 1142 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.05 (m, 8H, aromatics), 6.58 (dd, J_{vic}=17.3 Hz, J_{gem}=1.6 Hz, 1H, H-3′*cis*), 6.31 (dd, J_{vic}=17.3 Hz, J_{vic}=10.2 Hz, 1H, H-2′), 6.01 (dd, J_{vic}=10.2 Hz, J_{gem}=1.6 Hz, 1H, H-3′*trans*), 5.11 (d, $J_{2,3}$= 10.3 Hz, 1H, H-2), 4.93 (s, 1H, H-1), 4.50 (d, $J_{5,6exo}$=4.3 Hz, 1H, H-5), 4.24 (d, $J_{4,4a}$=2.8 Hz, 1H, H-4a), 4.23 (d, $J_{3,3a}$=2.1 Hz, 1H, H-3a), 3.68 (d, J_{gem}=6.7 Hz, 1H, H-6*endo*), 3.60 (dd, J_{gem}=6.7 Hz, $J_{5,6exo}$=4.3 Hz, 1H, H-6*exo*), 2.72 (td, $J_{3,4}$=$J_{2,3}$=10.3 Hz, $J_{3,3a}$=2.1 Hz, 1H, H-3), 2.06 (dd, $J_{3,4}$=10.3 Hz, $J_{4,4a}$=2.8 Hz, 1H, H-4); ^{13}C NMR ($CDCl_3$) δ 165.5 (C, C-1′), 143.5 (C, aromatic), 143.3 (C, aromatic), 141.9 (C, aromatic), 140.8 (C, aromatic), 132.0 (CH_2, C-3′), 127.9 (CH, C-2′), 125.8 (CH, aromatic), 125.7 (CH, aromatic), 125.5 (CH, aromatic), 125.4 (CH, 2C, aromatics), 123.9 (CH, aromatic), 123.1 (CH, aromatic), 122.9 (CH, aromatic), 100.3 (CH, C-1), 75.5 (CH, C-5), 70.2 (CH, C-2), 69.8 (CH_2, C-6), 51.0 (CH, C-4a), 45.8 (CH, C-3a), 40.5 (CH, C-4), 35.0 (CH, C-3); HRMS calcd for $C_{23}H_{20}O_4Na$ $[M+Na]^+$ 383.1259. Found 383.1267.

4.3.2. Acrylate 12. Acryloyl chloride (0.23 mL, 2.80 mmol) was added at 0 °C to a solution of **4** (415 mg, 1.36 mmol) in dichloromethane (18 mL) and triethylamine (0.6 mL, 4.31 mmol). After stirring for 20 min at 0 °C, the reaction was quenched by addition of water, extracted several times with methylenchloride and dried (Na_2SO_4). The residue was purified by flash column chromatography to give the acrylate **12** (485 mg, 1.35 mmol, 99%) as a colorless oil. Compound **12**: $[\alpha]_D^{27}$ −45.4 (*c* 1.07, $CHCl_3$); IR (film) ν_{max}: 2950, 1723 (C=O), 1466, 1405, 1193, 1165, 1142, 1018, 1000, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.06 (m, 8H, aromatics), 6.51 (dd, J_{vic}=17.2 Hz, J_{gem}=1.6 Hz, 1H, H-3′*cis*), 6.22 (dd, J_{vic}=17.2 Hz, J_{vic}=10.3 Hz, 1H, H-2′), 5.88 (dd, J_{vic}=10.3 Hz, J_{gem}=1.6 Hz, 1H, H-3′*trans*), 5.07 (d, J_{1-2}=3.2 Hz, 1H, H-1), 4.61 (br s, 1H, H-5), 4.48–4.42 (m, 2H, H-2 and H-3a), 4.21 (d, J_{4-4a}=1.3 Hz, 1H, H-4a), 3.76–3.68 (m, 2H, H-6*endo* and H-6*exo*), 2.35 (td, J_{3-4}= 10.5 Hz, J_{2-3}=6.0 Hz, J_{3-3a}=3.2 Hz, 1H, H-3), 2.10 (d, J_{3-4}=10.5 Hz, 1H, H-4); ^{13}C NMR ($CDCl_3$) δ 165.8 (C, C-1′), 144.8 (C, aromatic), 141.3 (C, aromatic), 140.9 (C, aromatic), 140.5 (C, aromatic), 131.4 (CH_2, C-3′), 128.0 (CH, C-2′), 126.3 (CH, aromatic), 126.0 (CH, aromatic), 125.9

(CH, aromatic), 125.8 (CH, 2C, aromatics), 124.6 (CH, aromatic), 124.3 (CH, aromatic), 122.3 (CH, aromatic), 97.4 (CH, C-1), 76.3 (CH, C-5), 72.0 (CH, C-2), 70.7 (CH_2, C-6), 50.1 (CH, C-4a), 47.7 (CH, C-3a), 46.4 (CH, C-4), 38.0 (CH, C-3); HRMS calcd for $C_{23}H_{21}O_4$ $[M+H]^+$ 361.1440. Found 361.1434.

4.3.3. Acrylate 13. Acryloyl chloride (0.26 mL, 3.20 mmol) was added at 0 °C to a solution of **9** (273.7 mg, 1.39 mmol) in dichloromethane (20 mL) and triethylamine (0.72 mL, 5.17 mmol). After stirring for 20 min at 0 °C, the reaction was quenched by addition of water, extracted several times with methylenchloride and dried (Na_2SO_4). The residue was purified by flash column chromatography to give the acrylate **13** (273.1 mg, 1.09 mmol, 78%) as a white crystalline solid. Compound **13**: mp=54–55 °C (hexane/ethyl acetate); $[\alpha]_D^{21}$ −116.2 (*c* 0.61, $CHCl_3$); IR (KBr) ν_{max}: 2955, 2928, 2891, 1715 (C=O), 1630, 1408, 1198, 1144, 1024, 889 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.42 (dd, J_{vic}=17.3 Hz, J_{gem}= 1.7 Hz, 1H, H-3′*cis*), 6.13 (dd, J_{vic}=17.3 Hz, J_{vic}=10.4 Hz, 1H, H-2′), 5.85 (dd, J_{vic}=10.4 Hz, J_{gem}=1.7 Hz, 1H, H-3′*trans*), 5.34 (s, 1H, H-1), 4.93 (d, J_{2-3}=10.7 Hz, 1H, H-2), 4.47 (d, J_{5-6exo}=2.4 Hz, 1H, H-5), 3.75–3.67 (m, 2H, H-6*endo* and H-6*exo*), 2.53–2.40 (m, 2H, H-3 and H-7)*, 2.13 (br s, 1H, H-10)*, 1.99–1.73 (m, 3H, H-4, H-8 and H-9), 1.48–1.33 (m, 4H, H-11, H-8 and H-9); ^{13}C NMR ($CDCl_3$) δ 165.1 (C, C-1′), 130.7 (CH_2, C-3′), 128.2 (CH, C-2′), 101.3 (CH, C-1), 73.8 (CH, C-5), 71.6 (CH, C-2), 69.5 (CH_2, C-6), 42.7 (CH, C-7)*, 40.6 (CH, C-10)*, 39.0 (CH_2, C-11), 38.3 (CH, C-4), 34.8 (CH, C-3), 24.3 (CH_2, C-8)**, 24.0 (CH_2, C-9)**; HRMS calcd for $C_{14}H_{19}O_4$ $[M+H]^+$ 251.1283. Found: 251.1285.

4.3.4. Acrylate 14. Acryloyl chloride (0.22 mL, 2.70 mmol) was added at 0 °C to a solution of **10** (227.2 mg, 1.16 mmol) in dichloromethane (17 mL) and triethylamine (0.6 mL, 4.3 mmol). After stirring for 20 min at 0 °C, the reaction was quenched by addition of water, extracted several times with methylenchloride and dried (Na_2SO_4). The residue was purified by flash column chromatography to give the acrylate **14** (254.7 mg, 1.02 mmol, 88%) as colorless oil. Compound **14**: $[\alpha]_D^{21}$ −115.3 (*c* 0.99, $CHCl_3$); IR (film) ν_{max}: 2956, 2879, 1729 (C=O), 1195, 1161, 1031, 1008 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.44 (dd, J_{vic}=17.2 Hz, J_{gem}=1.7 Hz, 1H, H-3′*cis*), 6.17 (dd, J_{vic}=17.2 Hz, J_{vic}=10.1 Hz, 1H, H-2′), 5.83 (dd, J_{vic}=10.1 Hz, J_{gem}=1.7 Hz, 1H, H-3′*trans*), 5.52 (d, $J_{1,2}$=3.4 Hz, 1H, H-1), 4.91 (dd, J_{1-2}=J_{2-3}=3.4 Hz, 1H, H-2), 4.49 (d, J_{5-6exo}=3.9 Hz, 1H, H-5), 3.84–3.75 (m, 2H, H-6*endo* and H-6*exo*), 2.42 (br s, 1H, H-7)*, 2.33 (br s, 1H, H-10)*, 2.01 (br s, 2H, H-3 and H-4), 1.86–1.26 (m, 6H, H-8, H-9 and H-11); ^{13}C NMR ($CDCl_3$) δ 165.8 (C, C-1′), 130.9 (CH_2, C-3′), 128.3 (CH, C-2′), 97.5 (CH, C-1), 74.2 (CH, C-5), 71.5 (CH_2, C-6), 70.5 (CH, C-2), 43.3 (CH, C-3), 42.2 (CH, C-4), 41.5 (CH, C-10)*, 39.5 (CH_2, C-11), 38.3 (CH, C-7)*, 23.4 (CH_2, C-8)**, 22.5 (CH_2, C-9)**; HRMS calcd for $C_{14}H_{19}O_4$ $[M+H]^+$ 251.1283. Found 251.1280.

4.4. Diels–Alder reactions between acrylates 11–14 and cyclopentadiene

4.4.1. Reaction of 11 with cyclopentadiene: general procedure. To a solution of acrylate **11** (37 mg, 0.10 mmol) in the appropriate solvent (4.1 mL) under an argon atmosphere was added dropwise a solution of the appropriate Lewis acid and the mixture was stirred for 20 min. Freshly distilled cyclopentadiene (0.1 mL, 1.3 mmol) was added dropwise and the mixture was stirred at the temperature and time indicated in Table 2. The reaction was quenched with water and extracted with dichloromethane and the organic phase was dried over Na_2SO_4. Evaporation of solvent and purification by flash chromatography gave the adducts **15a**, **15b**, **15c**, and **15d**.

Compound **15a**: white solid, mp=188–189 °C (hexane/ethyl acetate); $[\alpha]_D^{22}$ −4.6 (*c* 0.48, $CHCl_3$); IR (KBr) ν_{max}: 2985, 1728 (C=O), 1459, 1196, 1031, 900, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–7.05 (m, 8H, aromatics), 6.24 (dd, $J_{5'-6'}$= 5.5 Hz, $J_{4'-5'}$=3.1 Hz, 1H, H-5′), 5.84 (dd, $J_{5'-6'}$=5.5 Hz, $J_{6'-7'}$=2.3 Hz, 1H, H-6′), 4.95 (d, J_{2-3}=10.3 Hz, 1H, H-2), 4.81 (s, 1H, H-1), 4.45 (d, J_{5-6exo}=4.5 Hz, 1H, H-5), 4.27 (d, J_{3-3a}=2.2 Hz, 1H, H-3a), 4.24 (d, J_{4-4a}=3.0 Hz, 1H, H-4a), 3.63 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.57 (dd, J_{gem}= 6.9 Hz, $J_{5,6}$=4.5 Hz, 1H, H-6*exo*), 3.29–3.17 (m, 2H, H-7′ and H-2′), 3.00 (br s, 1H, H-4′), 2.62 (td, J_{3-4}=J_{2-3}= 10.3 Hz, J_{3-3a}=2.2 Hz, 1H, H-3), 2.14–2.00 (m, 2H, H-3′*exo* and H-4), 1.62 (td, J_{gem}=12.0 Hz, $J_{2'-3'endo}$=$J_{3'endo,4'}$= 2.7 Hz, 1H, H-3′*endo*), 1.50 (d, J_{gem}=8.2 Hz, 1H, H-8′), 1.39 (d, J_{gem}=8.2 Hz, 1H, H-8′); ^{13}C NMR ($CDCl_3$) δ 174.1 (C, C-1′), 143.8 (C, aromatic), 143.1 (C, aromatic), 142.0 (C, aromatic), 141.0 (C, aromatic), 138.0 (CH, C-5′), 131.9 (CH, C-6′), 125.9 (CH, aromatic), 125.7 (CH, aromatic), 125.6 (CH, aromatic), 125.5 (CH, aromatic), 125.3 (CH, aromatic), 124.0 (CH, aromatic), 123.1 (CH, 2C, aromatics), 100.5 (CH, C-1), 75.5 (CH, C-5), 70.1 (CH, C-2), 69.7 (CH_2, C-6), 51.1 (CH, C-4a), 49.8 (CH_2, C-8′), 45.9 (CH, C-2′), 45.8 (CH, C-3a), 43.3 (CH, C-7′), 42.6 (CH, C-4′), 40.4 (CH, C-4), 35.2 (CH, C-3), 29.3 (CH_2, C-3′); HRMS calcd for $C_{28}H_{26}O_4Na$ $[M+Na]^+$ 449.1723. Found 449.1712.

Compound **15b**: white solid, mp=178–179 °C (hexane/ethyl acetate); $[\alpha]_D^{21}$ −92.7 (*c* 1.25, $CHCl_3$); IR (KBr) ν_{max}: 2963, 1733 (C=O), 1458, 1173, 1137, 1028, 905, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.06 (m, 8H, aromatics), 6.24 (dd, $J_{5'-6'}$=5.6 Hz, $J_{4'-5'}$=3.0 Hz, 1H, H-5′), 6.13 (dd, $J_{5'-6'}$= 5.6 Hz, $J_{6'-7'}$=2.6 Hz, 1H, H-6′), 4.93 (d, J_{2-3}=10.3 Hz, 1H, H-2), 4.79 (s, 1H, H-1), 4.42 (d, J_{5-6exo}=4.5 Hz, 1H, H-5), 4.31 (d, J_{3-3a}=2.1 Hz, 1H, H-3a), 4.25 (d, J_{4-4a}= 2.8 Hz, 1H, H-4a), 3.63 (d, J_{gem}=6.7 Hz, 1H, H-6*endo*), 3.56 (dd, J_{gem}=6.7 Hz, J_{5-6exo}=4.5 Hz, 1H, H-6*exo*), 3.49 (br s, 1H, H-7′), 3.20 (td, $J_{2'-3'exo}$=9.4 Hz, $J_{2'-7'}$=$J_{2'-3'endo}$= 4.0 Hz, 1H, H-2′), 2.97 (br s, 1H, H-4′), 2.62 (td, J_{3-4}= J_{2-3}=10.3 Hz, J_{3-3a}=2.1 Hz, 1H, H-3), 2.12–1.97 (m, 2H, H-4 and H-3′*exo*), 1.57 (td, J_{gem}=8.3, $J_{2'-3'endo}$=4.0 Hz, $J_{3'endo-4'}$=1.9 Hz, 1H, H-3′*endo*), 1.46–1.32 (m, 2H, H-8′); ^{13}C NMR ($CDCl_3$) δ 174.2 (C, C-1′), 144.0 (C, aromatic), 142.9 (C, aromatic), 141.8 (C, aromatic), 141.1 (C, aromatic), 137.9 (CH, C-5′), 132.3 (CH, C-6′), 125.9 (CH, aromatic), 125.8 (CH, aromatic), 125.6 (CH, 2C, aromatics), 125.4 (CH, aromatic), 124.0 (CH, aromatic), 123.2 (CH, aromatic), 123.0 (CH, aromatic), 100.6 (CH, C-1), 75.5 (CH, C-5), 70.4 (CH, C-2), 69.5 (CH_2, C-6), 51.1 (CH, C-4a), 49.6 (CH_2, C-8′), 45.9 (CH, C-2′), 45.7 (CH, C-3a), 43.5 (CH, C-7′), 42.5 (CH, C-4′), 40.3 (CH, C-4), 35.4 (CH, C-3), 30.0 (CH_2, C-3′); HRMS calcd for $C_{28}H_{26}O_4Na$ $[M+Na]^+$ 449.1723. Found 449.1722.

Compound **15c**: white solid, mp=166–167 °C (hexane/ethyl acetate); $[\alpha]_D^{21}$ −54.2 (*c* 0.57, $CHCl_3$); IR (KBr) ν_{max}: 2971, 1728 (C=O), 1458, 1335, 1175, 1137, 1035, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.05 (m, 8H, aromatics), 6.28–6.15 (m, 2H, H-5′ and H-6′), 5.00 (d, J_{2-3}=10.3 Hz, 1H, H-2), 4.89 (s, 1H, H-1), 4.47 (d, J_{5-6exo}=4.5 Hz, 1H, H-5), 4.29 (d, J_{3-3a}=2.1 Hz, 1H, H-3a), 4.24 (d, J_{4-4a}=2.5 Hz, 1H, H-4a), 3.65 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.58 (dd, J_{gem}=6.9 Hz, J_{5-6}=4.5 Hz, 1H, H-6*exo*), 3.02 (br s, 1H, H-4′), 2.97 (br s, 1H, H-7′), 2.66 (td, J_{3-4}=J_{2-3}=10.3 Hz, J_{3-3a}=2.1 Hz, 1H, H-3), 2.46 (dd, $J_{2'-3'endo}$=8.4 Hz, $J_{2'-3'exo}$=4.0 Hz, 1H, H-2′), 2.18 (td, J_{gem}=11.6 Hz, $J_{2'-3'exo}$=$J_{4'-3'exo}$=4.0 Hz, 1H, H-3′*exo*), 2.03 (dd, J_{3-4}= 10.3 Hz, J_{4-4a}=2.5 Hz, 1H, H-4), 1.64–1.48 (m, 2H, H-3′*endo* and H-8′), 1.37 (br d, J_{gem}=8.6 Hz, 1H, H-8′); ^{13}C NMR ($CDCl_3$) δ 175.7 (C, C-1′), 143.6 (C, aromatic), 143.3 (C, aromatic), 142.0 (C, aromatic), 140.9 (C, aromatic), 138.2 (CH, C-5′), 135.7 (CH, C-6′), 125.9 (CH, aromatic), 125.7 (CH, aromatic), 125.5 (CH, 2C, aromatics), 125.4 (CH, aromatic), 124.0 (CH, aromatic), 123.1 (CH, aromatic), 123.0 (CH, aromatic), 100.3 (CH, C-1), 75.6 (CH, C-5), 70.0 (CH, C-2), 69.8 (CH_2, C-6), 51.0 (CH, C-4a), 47.1 (CH, C-7′), 46.0 (CH_2, C-8′), 45.9 (CH, C-3a), 43.2 (CH, C-2′), 41.7 (CH, C-4′), 40.5 (CH, C-4), 34.9 (CH, C-3), 30.3 (CH_2, C-3′); HRMS calcd for $C_{28}H_{27}O_4$ $[M+H]^+$ 427.1909. Found 427.1930.

Compound **15d**: white solid, mp=197–198 °C (hexane/ethyl acetate); $[\alpha]_D^{22}$ −34.2 (*c* 0.34, $CHCl_3$); IR (KBr) ν_{max}: 2944, 1727 (C=O), 1457, 1173, 1136, 1042, 900, 763 cm^{-1}; ^1H NMR ($CHCl_3$) δ 7.35–7.06 (m, 8H, aromatics), 6.31–6.20 (m, 2H, H-5′ and H-6′), 5.02 (d, J_{2-3}=10.4 Hz, 1H, H-2), 4.86 (s, 1H, H-1), 4.46 (d, J_{5-6exo}=4.5 Hz, 1H, H-5), 4.35 (d, J_{3-3a}=2.2 Hz, 1H, H-3a), 4.25 (d, J_{4-4a}=2.5 Hz, 1H, H-4a), 3.66 (d, J_{gem}=6.9 Hz, 1H, H-6*endo*), 3.58 (dd, J_{gem}=6.9 Hz, J_{5-6}=4.5 Hz, 1H, H-6*exo*), 3.33 (br s, 1H, H-4′), 2.98 (br s, 1H, H-7′), 2.67 (td, J_{3-4}=J_{2-3}=10.4 Hz, J_{3-3a}=2.2 Hz, 1H, H-3), 2.44 (td, $J_{2'-3'endo}$=8.7 Hz, $J_{2'-3'exo}$=4.0 Hz, $J_{2'-7'}$=1.7 Hz, 1H, H-2′), 2.06 (dd, J_{3-4}= 10.4 Hz, J_{4-4a}=2.5 Hz, 1H, H-4), 1.86 (td, J_{gem}=11.6 Hz, $J_{2'-3'exo}$=$J_{3'exo-4'}$=4.0 Hz, 1H, H-3′*exo*), 1.70–1.37 (m, 3H, H-3′*endo*, and H-8′); ^{13}C NMR ($CDCl_3$) δ 175.8 (C, C-1′), 143.7 (C, aromatic), 143.2 (C, aromatic), 142.0 (C, aromatic), 141.0 (C, aromatic), 138.4 (CH, C-5′), 135.4 (CH, C-6′), 125.9 (CH, aromatic), 125.8 (CH, aromatic), 125.6 (CH, 3C, aromatics), 124.0 (CH, aromatic), 123.1 (CH, 2C, aromatics), 100.4 (CH, C-1), 75.6 (CH, C-5), 70.1 (CH, C-2), 69.8 (CH_2, C-6), 51.1 (CH, C-4a), 46.6 (CH, C-7′, CH_2, C-8′), 45.9 (CH, C-3a), 43.0 (CH, C-2′), 41.5 (CH, C-4′), 40.4 (CH, C-4), 35.1 (CH, C-3), 30.9 (CH_2, C-3′); HRMS calcd for $C_{28}H_{27}O_4$ $[M+H]^+$ 427.1909. Found 427.1898.

4.4.2. Reaction of 12 with cyclopentadiene: general procedure. To a solution of acrylate **12** (37 mg, 0.10 mmol) in the appropriate solvent (4.1 mL) under an argon atmosphere was added dropwise a solution of the appropriate Lewis acid and the mixture was stirred for 20 min. Freshly distilled cyclopentadiene (0.1 mL, 1.3 mmol) was added dropwise and the mixture was stirred at the temperature and time indicated in Table 2. The reaction was quenched with water and extracted with dichloromethane and the organic phase was dried over Na_2SO_4. Evaporation of solvent and purification by flash chromatography gave two fractions.

Fraction 1: Compound **16a**: colorless oil; $[\alpha]_D^{28}$ +21.6 (*c* 1.58, $CHCl_3$); IR (film) ν_{max}: 2941, 1739 (C=O), 1458, 1337, 1163, 1142, 1108, 1037, 997, 948 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41–7.07 (m, 8H, aromatics), 6.33 (dd, $J_{5'-6'}$= 5.4 Hz, $J_{5'-4'}$=3.0 Hz, 1H, H-5′), 6.05 (dd, $J_{6'-5'}$=5.4 Hz, $J_{6'-7'}$=2.7 Hz, 1H, H-6′), 4.99 (d, J_{1-2}=3.0 Hz, 1H, H-1), 4.59 (br s, 1H, H-5), 4.36–4.32 (m, 2H, H-2 and H-3a), 4.20 (s, 1H, H-4a), 3.72–3.71 (m, 2H, H-6*endo* and H-6*exo*), 3.31 (br s, 1H, H-7′), 3.06 (td, $J_{2'-3'exo}$=9.3 Hz, $J_{2'-3'endo}$=3.7 Hz, $J_{2'-7'}$=3.7 Hz, 1H, H-2′), 2.95 (br s, 1H, H-4′), 2.33–2.22 (m, 1H, H-3), 2.09 (d, J_{3-4}=10.5 Hz, 1H, H-4), 1.94 (td, J_{gem}=11.8 Hz, $J_{3'exo-2'}$=9.3 Hz, $J_{3'exo-4'}$=3.6 Hz, 1H, H-3′*exo*), 1.55–1.46 (m, 2H, H-3′*endo* and H-8′), 1.30 (d, J_{gem}=7.9 Hz, 1H, H-8′); ^{13}C NMR ($CDCl_3$) δ 174.3 (C, C-1′), 144.8 (C, aromatic), 141.2 (C, aromatic), 141.0 (C, aromatic), 140.4 (C, aromatic), 138.2 (CH, C-5′), 131.7 (CH, C-6′), 126.2 (CH, aromatic), 125.9 (CH, aromatic), 125.8 (CH, 3C, aromatics), 124.5 (CH, aromatic), 124.0 (CH, aromatic), 122.4 (CH, aromatic), 97.6 (CH, C-1), 76.2 (CH, C-5), 71.4 (CH, C-2), 70.7 (CH_2, C-6), 50.1 (CH, C-4a), 49.6 (CH_2, C-8′), 47.8 (CH, C-3a), 46.4 (CH, C-4), 45.9 (CH, C-7′), 43.1 (CH, C-2′), 42.5 (CH, C-4′), 38.3 (CH, C-3), 29.0 (CH_2, C-3′); HRMS calcd for $C_{28}H_{27}O_4$ $[M+H]^+$ 427.1909. Found 427.1913.

Fraction 2: Compounds **16b**, **16c**, and **16d**: colorless oil; IR (film) ν_{max}: 2969, 2945, 1730 (C=O), 1458, 1336, 1165, 1142, 1033, 764, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43–7.06 (m, aromatic. **16b**, **16c**, and **16d**), 6.22 (dd, $J_{5'-6'}$=5.6 Hz, $J_{5'-4'}$=3.0 Hz, H-5′ of **16b**), 6.17–6.09 (m, H-5′ and H-6′ of **16c** and **16d**), 5.96 (dd, $J_{5'-6'}$=5.6 Hz, $J_{6'-7'}$=2.8 Hz, H-6′ of **16b**), 5.04 (br s, H-1 of **16c** and **16d**), 4.98 (d, J_{1-2}= 3.2 Hz, H-1 of **16b**), 4.60 (br s, H-5 of **16b**, **16c**, and **16d**), 4.42–4.29 (m, H-2 and H-3a of **16b**, **16c**, and **16d**), 4.20 (br s, H-4a of **16b**, **16c**, and **16d**), 3.71 (br s, H-6*endo* and H-6*exo* of **16b**, **16c**, and **16d**), 3.26 (br s, H-7′ of **16b**), 3.13–3.03 (m, H-2′ of **16b** and H-4′ of **16c** and **16d**), 2.93 (br s, H-4′ of **16b** and H-7′ of **16c** and **16d**), 2.38–2.23 (m, H-3 of **16b**, **16c**, and **16d**, H-2′ of **16c** and **16d**), 2.11–1.89 (m, H-4 of **16b**, **16c** and **16d**, H-3′*exo* of **16b**, **16c**, and **16d**), 1.64–1.26 (m, H-3′*endo* of **16b**, **16c**, and **16d**, H-8′ of **16b**, **16c**, and **16d**); ^{13}C NMR ($CDCl_3$) δ 176.0 (C, C-1′ of **16c** and **16d**), 174.4 (C, C-1′ of **16b**), 144.8 (C, aromatic, **16b**, **16c**, and **16d**), 141.3 (C, aromatic, **16b**, **16c**, and **16d**), 141.0 (C, aromatic, **16b**, **16c**, and **16d**), 140.5 (C, aromatic, **16b**, **16c**, and **16d**), 138.1 (CH, C-5′ of **16c**), 137.9 (CH, C-5′ of **16d**), 137.8 (CH, C-5′ of **16b**), 135.7 (CH, C-6′ of **16d**), 135.5 (CH, C-6′ of **16c**), 132.1 (CH, C-6′ of **16b**), 126.2 (CH, aromatic, **16b**, **16c**, and **16d**), 125.8 (CH, 4C, aromatic, **16b**, **16c**, and **12–d**), 124.6 (CH, aromatic, **16b**, **16c**, and **16d**), 124.2 (CH, aromatic, **16b**, **16c**, and **16d**), 122.3 (CH, aromatic, **16b**, **16c**, and **16d**), 97.5 (CH, C-1 of **16b**, **16c**, and **16d**), 76.3 (CH, C-5 of **16b**, **16c**, and **16d**), 71.7 (CH, C-2 of **16c** and **16d**), 71.6 (CH, C-2 of **16b**), 70.7 (CH_2, C-6 of **16b**, **16c**, and **16d**), 50.1 (CH, C-4a of **16b**, **16c**, and **16d**), 49.5 (CH_2, C-8′ of **16b**), 47.8 (CH, C-3a of **16c** and **16d**), 47.7 (CH, C-3a of **16b**), 46.9 (CH, C-7′ of **16c**), 46.7 (CH, C-7′ of **16d**), 46.4 (CH, C-4 of **16b**, **16c**, and **16d**), 46.2 (CH_2, C-8′ of **16c** and **16d**), 45.9 (CH, C-7′ of **16b**), 43.2 (CH, C-2′ of **16b**), 43.1 (CH, C-2′ of **16c**), 43.0 (CH, C-2′ of **16d**), 42.5 (CH, C-4′ of **16b**), 41.6 (CH, C-4′ of **16c** and **16d**), 38.2 (CH, C-3 of **16c** and **16d**), 38.0

(CH, C-3 of **16b**), 30.4 (CH_2, C-3′ of **16c** and **16d**), 29.1 (CH_2, C-3′ of **16b**).

4.4.3. Reaction of 13 with cyclopentadiene: general procedure. To a solution of acrylate **13** (35 mg, 0.14 mmol) in the appropriate solvent (5.6 mL) under an argon atmosphere was added dropwise a solution of the appropriate Lewis acid and the mixture was stirred for 20 min. Freshly distilled cyclopentadiene (0.1 mL, 1.3 mmol) was added dropwise and the mixture was stirred at the temperature and time indicated in Table 2. The reaction was quenched with water and extracted with dichloromethane and the organic phase was dried over Na_2SO_4. Evaporation of solvent and purification by flash chromatography gave two fractions.

Fraction 1: Compounds **17a** and **17b**: colorless oil; IR (film) ν_{max}: 2954, 2877, 1729 (C=O), 1336, 1184, 1143, 1110, 1026, 872, 717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.22 (dd, $J_{5'-6'}$=5.6 Hz, $J_{4'-5'}$=3.2 Hz, 1H, H-5′ of **17b**), 6.18 (dd, $J_{5'-6'}$=5.7 Hz, $J_{4'-5'}$=3.1 Hz, 1H, H-5′ of **17a**), 6.00 (dd, $J_{5'-6'}$=5.7 Hz, $J_{6'-7'}$=2.9 Hz, 1H, H-6′ of **17a**), 5.94 (dd, $J_{5'-6'}$=5.6 Hz, $J_{6'-7'}$=2.8 Hz, 1H, H-6′ of **17b**), 5.25 (s, 1H, H-1 of **17a** and **17b**), 4.78 (d, J_{2-3}=10.5 Hz, 1H, H-2 of **17a** and **17b**), 4.44 (d, J_{5-6exo}=3.7 Hz, 1H, H-5 of **17a** and **17b**), 3.72–3.64 (m, 2H, H-6*endo* and H-6*exo* of **17a** and **17b**), 3.23 (br s, 1H, H-7′ of **17a** and **17b**), 3.02–2.91 (m, 2H, H-2′ and H-4′ of **17a** and **17b**), 2.44–1.26 (m, 14H, H-3, H-3′, H-4, H-7, H-8, H-8′, H-9, H-10, and H-11); ^{13}C NMR ($CDCl_3$) δ 173.8 (C, C-1′ of **17b**), 173.7 (C, C-1′ of **17a**), 137.9 (CH, C-5′ of **17a**), 137.6 (CH, C-5′ of **17b**), 132.7 (CH, C-6′ of **17b**), 131.9 (CH, C-6′ of **17a**), 101.7 (CH, C-1 of **17a**), 101.5 (CH, C-1 of **17b**), 73.8 (CH, C-5 of **17a** and **17b**), 71.4 (CH, C-2 of **17a** and **17b**), 69.6 (CH_2, C-6 of **17a** and **17b**), 49.8 (CH_2, C-8′ of **17b**), 49.4 (CH_2, C-8′ of **17b**), 45.7 (CH, C-7′ of **17a**), 45.3 (CH, C-7′ of **17b**), 43.5 (CH, C-2′ of **17b**), 43.1 (CH, C-2′ of **17a**), 42.7 (CH, C-7 of **17a** and **17b**)*, 42.5 (CH, C-4′ of **17a**), 42.3 (CH, C-4′ of **17b**), 40.7 (CH, C-10 of **17a** and **17b**)*, 39.1 (CH_2, C-11 of **17a** and **17b**), 38.4 (CH, C-4 of **17a** and **17b**), 34.8 (CH, C-3 of **17a** and **17b**), 29.0 (CH_2, C-3′ of **17a** and **17b**), 24.4 (CH_2, C-8 of **17a** and **17b**)**, 24.3 (CH_2, C-9 of **17b**)**, 24.2 (CH_2, C-9 of **17a**)**.

Fraction 2: Compounds **17c** and **17d**: colorless oil; IR (film) ν_{max}: 2954, 2877, 1728 (C=O), 1333, 1173, 1143, 1111, 1021, 876 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.17–6.08 (m, 2H, H-5′ and H-6′ of **17c** and **17d**), 5.31 (s, 1H, H-1 of **17c** and **17d**), 4.84 (d, J_{2-3}=10.5 Hz, 1H, H-2 of **17c**), 4.83 (d, J_{2-3}=10.5 Hz, 1H, H-2 of **17d**), 4.45 (d, J_{5-6exo}=3.9 Hz, 1H, H-5 of **17c** and **17d**), 3.74–3.65 (m, 2H, H-6*endo* and H-6*exo* of **17c** and **17d**), 3.09 (br s, 1H, H-4′ of **17c** and **17d**), 2.92 (br s, 1H, H-7′ of **17c** and **17d**), 2.50–2.39 (m, 2H, H-3 and H-2′ of **17c** and **17d**), 2.30–2.21 (m, 1H, H-3′*exo* of **17c** and **17d**), 2.12–1.26 (m, 12H, H-3′*endo*, H-4, H-7, H-8, H-8′, H-9, H-10, and H-11 of **17c** and **17d**); ^{13}C NMR ($CDCl_3$) δ 175.3 (C, C-1′ of **17c**), 175.1 (C, C-1′ of **17d**), 138.1 (CH, C-5′ of **17c**), 137.8 (CH, C-5′ of **17d**), 135.7 (CH, C-6′ of **17c**), 135.6 (CH, C-6′ of **17d**), 101.6 (CH, C-1 of **17c** and **17d**), 73.9 (CH, C-5 of **17c** and **17d**), 71.8 (CH, C-2 of **17c**), 71.6 (CH, C-2 of **17d**), 69.6 (CH_2, C-6 of **17c** and **17d**), 46.5 (CH_2, C-8′ of **17c**), 46.2 (CH_2, C-8′ of **17d**), 46.2 (CH, C-7′ of **17c** and **17d**), 43.2 (CH, C-2′ of **17c**), 43.1 (CH, C-2′ of **17d**), 42.8 (CH, C-7 of **17c** and **17d**)*, 41.6 (CH, C-4′ of **17c** and **17d**), 40.7 (CH, C-10 of **17c**)*, 40.5 (CH, C-10 of **17d**)*, 39.1 (CH_2, C-11 of **17c** and **17d**), 38.5 (CH, C-4 of **17c** and **17d**), 35.1 (CH, C-3 of **17c**), 35.0 (CH, C-3 of **17d**), 30.2 (CH_2, C-3′ of **17c**), 30.0 (CH_2, C-3′ of **17d**), 24.5 (CH_2, C-8 of **17c** and **17d**)**, 24.3 (CH_2, C-9 of **17c**)**, 24.2 (CH_2, C-9 of **17d**)**.

4.4.4. Reaction of 14 with cyclopentadiene: general procedure. To a solution of acrylate **13** (35 mg, 0.14 mmol) in the appropriate solvent (5.6 mL) under an argon atmosphere was added dropwise a solution of the appropriate Lewis acid and the mixture was stirred for 20 min. Freshly distilled cyclopentadiene (0.1 mL, 1.3 mmol) was added dropwise and the mixture was stirred at the temperature and time indicated in Table 2. The reaction was quenched with water and extracted with dichloromethane and the organic phase was dried over Na_2SO_4. Evaporation of solvent and purification by flash chromatography gave two fractions.

Fraction 1: Compound **18a**: colorless oil; $[\alpha]_D^{24}$ −3.9 (*c* 1.56, $CHCl_3$); IR (film) ν_{max}: 2949, 2878, 1730 (C=O), 1336, 1159, 1033, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (dd, $J_{5'-6'}$=5.5 Hz, $J_{4'-5'}$=3.0 Hz, 1H, H-5′), 5.91 (dd, $J_{5'-6'}$=5.5 Hz, $J_{6'-7'}$=2.6 Hz, 1H, H-6′), 5.43 (d, J_{1-2}=3.5 Hz, 1H, H-1), 4.79 (br s, 1H, H-2), 4.46 (d, J_{5-6exo}=3.7 Hz, 1H, H-5), 3.83–3.74 (m, 2H, H-6*endo* and H-6*exo*), 3.24 (br s, 1H, H-7′), 3.00 (td, $J_{2'-3'exo}$=9.2 Hz, $J_{2'-3'endo}$=$J_{2'-7'}$=3.9 Hz, 1H, H-2′), 2.90 (br s, 1H, H-4′), 2.33 (br s, 2H, H-7 and H-10), 1.97–1.24 (m, 12H, H-3, H-4, H-8, H-9, H-11, H-3′, and H-8′); ^{13}C NMR ($CDCl_3$) δ 174.4 (C, C-1′), 137.8 (CH, C-5′), 132.0 (CH, C-6′), 97.7 (CH, C-1), 74.2 (CH, C-5), 71.6 (CH_2, C-6), 70.0 (CH, C-2), 49.5 (CH_2, C-8′), 45.7 (CH, C-7′), 43.4 (CH, C-3), 43.1 (CH, C-2′), 42.5 (CH, C-4′), 42.2 (CH, C-4), 41.4 (CH, C-10)*, 39.6 (CH_2, C-11), 38.4 (CH, C-7)*, 29.3 (CH_2, C-3′), 23.5 (CH_2, C-8)**, 22.4 (CH_2, C-9)**; HRMS calcd for $C_{19}H_{25}O_4$ 317.1753. Found 317.1742.

Fraction 2: Compounds **18b**, **18c**, and **18d**: colorless oil; IR (film) ν_{max}: 2951, 2878, 1730 (C=O), 1335, 1188, 1157, 1034, 714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19 (dd, $J_{5'-6'}$=5.6 Hz, $J_{4'-5'}$=3.0 Hz, H-5′ of **18b**), 6.12 (br s, H-5′ and H-6′ of **18c** and **18d**), 5.98 (dd, $J_{5'-6'}$=5.6 Hz, $J_{6'-7'}$=2.8 Hz, $H_{6'}$ of **18b**), 5.50–5.47 (m, H-1 of **18c** and **18d**), 5.43 (d, J_{1-2}=3.5 Hz, H-1 of **18b**), 4.85 (br s, H-2 of **18c** and **18d**), 4.75 (br s, H-2 of **18b**), 4.48–4.45 (m, H-5 of **18b**, **18c**, and **18d**), 3.84–3.74 (m, H-6 of **18b**, **18c**, and **18d**), 3.24 (br s, H-7′ of **18b**), 3.06–2.90 (m, H-2′ and H-4′ of **18b**, **18c**, and **18d**), 2.37–2.24 (m, H-7′ of **18c** and **18d**, H-3 and H-7* of **18b**, **18c**, and **18d**), 1.96–1.24 (m, H-3′, H-8, H-8′, H-9, H-10* and H-11 of **18b**, **18c**, and **18d**); ^{13}C NMR ($CDCl_3$) 175.9 (C, C-1′ of **18c** and **18d**), 174.4 (C, C-1′ of **18b**), 138.0 (CH, C-5′ of **18c**), 137.9 (CH, C-5′ of **18d**), 137.5 (CH, C-5′ of **18b**), 135.7 (CH, C-6′ of **18c**), 135.6 (CH, C-6′ of **18d**), 132.2 (CH, C-6′ of **18b**), 97.6 (CH, C-1 of **18b**, **18c**, and **18d**), 74.1 (CH, C-5 of **18b**, **18c**, and **18d**), 71.5 (CH_2, C-6 of **18b**, **18c**, and **18d**), 70.1 (CH, C-2 of **18b**, **18c**, and **18d**), 49.5 (CH_2, C-8′ of **18b**), 46.8 (CH, C-7′ of **18c**), 46.6 (CH, C-7′ of **18d**), 46.1 (CH_2, C-8′ of **18c** and **18d**), 45.9 (CH, C-7′ of **18b**), 43.2 (CH, C-3 of **18b**, **18c**, and **18d**), 43.1 (CH, C-2′ of **18b**), 43.0 (CH, C-2′ of **18c** and **18d**), 42.5 (CH, C-4′ of **18b**), 42.2 (CH, C-4 of **18b**, **18c**, and **18d**), 41.6 (CH, C-4′ of **18c**), 41.5 (CH, C-4′ of

18d), 41.4 (CH, C-10 of **18b**, **18c**, and **18d**)*, 39.5 (CH_2, C-11 of **18b**, **18c**, and **18d**), 38.3 (CH, C-7 of **18b**, **18c**, and **18d**)*, 30.4 (CH_2, C-3′ of **18c**), 30.3 (CH_2, C-3′ of **18d**), 29.1 (CH_2, C-3′ of **18b**), 23.4 (CH_2, C-8 of **18b**, **18c**, and **18d**)**, 22.5 (CH_2, C-9 of **18b**, **18c**, and **18d**)**.

4.5. Crystallography

X-ray data for **2** have been deposited at the Cambridge Crystallographic Data Centre, deposition numbers CCDC 615721 and CCDC 615722. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Crystal data for **2**: $C_{20}H_{16}O_3$; M=304.35, colorless block crystal, 0.20×0.30×0.50, orthorhombic, space group $P2_12_12_1$, a=8.530(5), b=12.541(5), c=13.627(5) Å, V=1458(1) Å^3, Z=4, T=180 K, ρ_c=1.39 g cm^{-3}, $F(000)$=640, μ (Mo Kα)=0.093 mm^{-1}. Crystal data for **3**: $C_{20}H_{18}O_3$; M=306.36, colorless plate, 0.10×0.35×0.50, orthorhombic, space group $P2_12_12_1$, a=8.6946(9), b=9.2618(9), c=18.186(2) Å, V=1464.5(2) Å^3, Z=4, T=180 K, ρ_c=1.39 g cm^{-3}, $F(000)$=648, μ (Mo Kα)=0.093 mm^{-1}. Intensity data were collected at low temperature on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo Kα radiation source (λ=0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The crystal was placed 48.9 mm from the CCD detector. More than the hemisphere of reciprocal space was covered by combination of four sets of exposures; each set had a different φ-angle (0, 90, 180, and 270°) and each exposure of 35 s covered 0.75° (**2**), 1° (**3**) in ω. Coverage of the unique set is 96%, complete up to 2θ=64.44° (**2**), 64.32° (**3**). Out of the 15511 (**2**), 15710 (**3**), reflections measured (2794 (R_{int}=0.02) (**2**), 2806 (R_{int}=0.03) (**3**)) unique 1887 (**2**), 1756 (**3**), reflections with $I>1.3\sigma(I)$ (**2**), $I>1.5\sigma(I)$ (**3**), were used in the refinements. The structures were solved by direct methods using SIR92, and refined by full-matrix least-squares procedures on F using the programs of the PC version of CRYSTALS.[16] Atomic scattering factors were taken from the International tables for X-ray Crystallography. Nonhydrogen atom positions were refined anisotropically. Hydrogen atoms were introduced in calculated positions in the last refinements (C–H=1.0 Å) and were allocated an overall refinable isotropic thermal parameter. Absorption corrections were introduced by semi-empirical methods based on equivalent reflections, using the program MULTISCAN.[17] The final full-matrix least-squares refinement, minimizing $[\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$, converged at the values of R=0.0362 (**2**), 0.0326 (**3**), and wR=0.0445 (**2**), 0.0403 (**3**). The molecular plots were obtained by using the ZORTEP program.[18]

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