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Exploiting π shielding interactions of η^6 arene chromium (0) complexes: New auxiliaries derived from the biogenic chiral pool

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Abstract

A family of highly selective chiral auxiliaries containing arene chromium (0) complexes has been prepared using biogenic precursors from the chiral pool. The systems, derived from isomannide, prolinol, and xylofuranose were applied to the asymmetric Diels–Alder reaction of derived acrylate esters. Factors influencing stereoselectivity with the auxiliaries have been investigated and delineated including the impact of mixed ligands on the chromium (0) complex. Under optimal conditions, the auxiliaries give >95% e.e. and 98:2 *exo:endo* ratio in cycloaddition with cyclopentadiene.
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Keywords: Chiral auxiliary; Chiral pool; Chromium (0) arene complexes

1. Introduction

Of the many tactics employed to achieve facial selectivity in asymmetric cycloadditions, π shielding of one face of the dienophile to attack has become a common and effective strategy [1]. Examples include both chiral catalysts and auxiliaries, where the interaction of the chiral controller and dienophile range from passive (steric shielding) through active (π–π stacking) [1]. We have been engaged in the design of auxiliaries and catalysts where pendant aryl substituents interact with a proximal acrylate to establish a high degree of facial selectivity in cycloaddition viz. **1**. Interactions between the two entities can be modulated *via* the corresponding arene chromium carbonyl complexes [2,3], mixed ligand derivatives provide access to a range of π basic through π acidic characteristics **2** [4]. The criteria for two entities to engage in a π stack are satisfied when π clouds interact through space at a distance of between 3 and 3.5 Å, with optimal overlap at approximately 3.4 Å [5]. Based on this criterion we wished to investigate the concept of face selection in a series of readily available auxiliaries derived from the chiral pool, and surveyed a variety of inexpensive building blocks. We ultimately decided to pursue monobenzylated derivatives of xylofuranose **3**, isomannide **4** and *N*-benzyl prolinol **5** based on the fact that: (a) molecular modeling analysis suggested that derived acrylate esters could position at π-stacking distance from the aryl, (b) the ligands themselves are commercially available and also easily accessible from other feedstocks [6], (c) the electronics of the benzyl group could be modulated at ease via arene chromium (0) complexation, and (d) in the case of **5** both enantiomeric forms are available.

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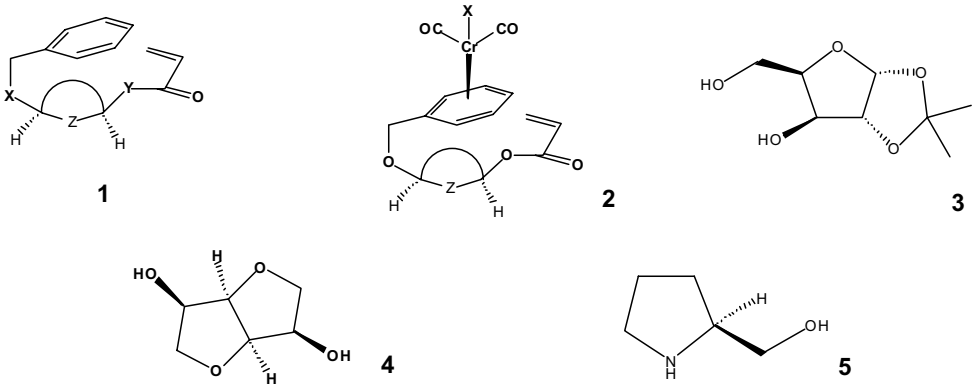


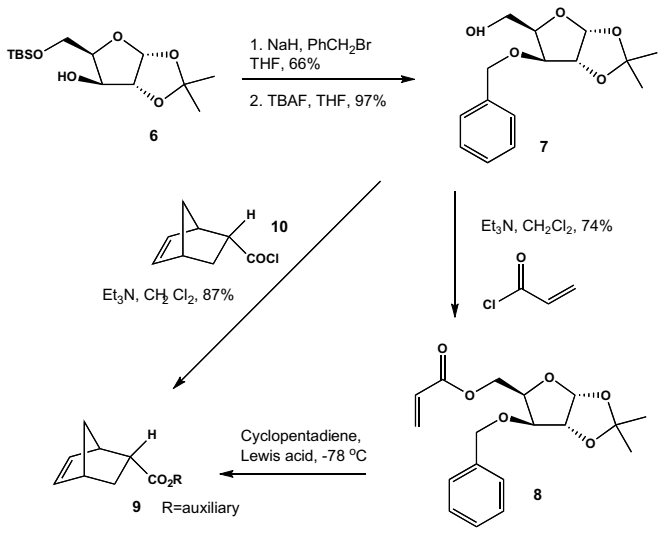
[STRUCTURES 1-5]

2. Results and discussion

Our initial goal was to prepare acrylate ester derivatives of each building block that would allow assessment of stereocontrol imparted the by benzyl chromium (0) complexed appendages in cycloaddition reactions. This would subsequently allow us to modulate and refine steric and electronic parameters of the arene group and delineate factors contributing to selectivity.

2.1. Xylofuranoses

Xylofuranonse **3** is a commercially available acetonide and the primary and secondary alcohols permit a wide range of derivatives to be produced. Conversion to the mono TBS ether (TBSCl, imidazole, DMF) proceeded in quantitative yield, and the ether **6** could then be transformed to benzyl derivative **7** *via* selective deprotection (Scheme 1). Conversion to the acrylate **8** proceeded in moderate yield, allowing us to immediately probe cycloaddition to cyclopentadiene under the influence of various Lewis acids. To aid in determination of facial- and diastereoselectivity, samples of authentic adducts **9** (R = H or alkyl) were also prepared from **10** and **7** [7]. Initial results with alkyl aluminum species were disappointing, though clear preference for *endo* addition were evident (Table 1, entry 3). With the exception of zinc, other metal derivatives yielded little benefit, and additional aluminum species were investigated. Aluminum chloride proved most effective, giving appreciable diastereoselectivity and *endo* preference when multiple equivalents were employed (Table 1, entry 17).



Scheme 1. Preparation and cycloaddition of benzyloxy xylofuranose acrylates.

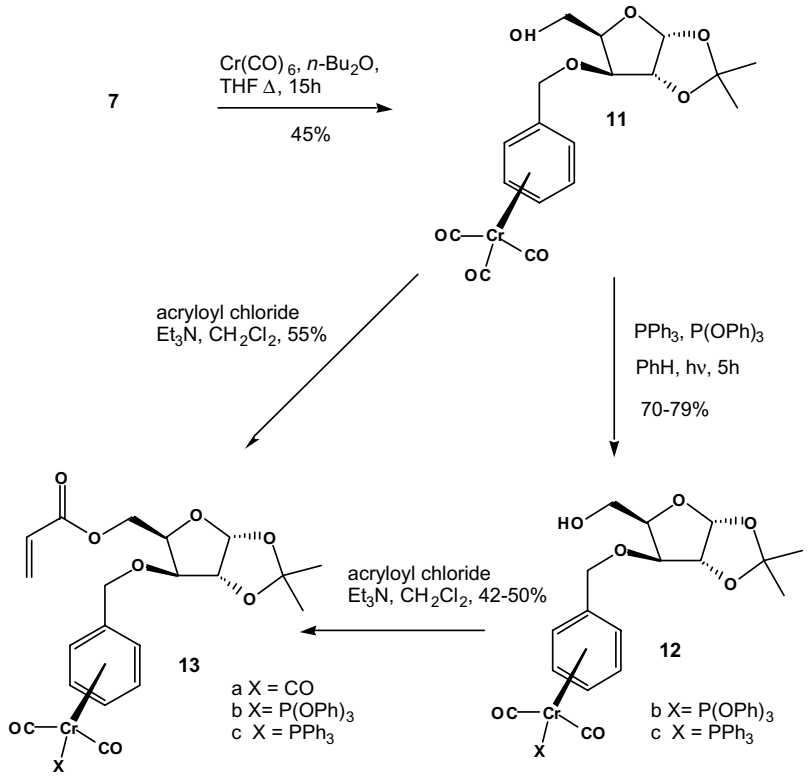
With results in hand, we sought to quantitate the impact of the corresponding arene chromium (0) derivatives, and their synthesis was investigated from ligand **7** (Scheme 2). Direct complexation was effective and in addition to tricarbonyl derivative **11**, representative mixed ligand phosphines and phosphites **12** were produced by photolytic ligand exchange. The family of derivatives was converted to analogous acrylates **13** without incident, and the substrates subjected to cycloadditions using the optimized conditions for **8**.

Though some improvement was evident using the bulky derivative **13c** (Table 1, entry 20), the poor result for **13a** and, particularly **13b** were surprising, and may be a consequence of (observed) *in situ* decomplexation under the conditions of cycloaddition and workup. Molecular modeling studies (PM3) suggested however that sufficient overlap between the acrylate and benzyl entities was present to establish π shielding [2], and since the benzyl group of **13b** is approximately isoelectronic with that of **8**, points to an undesirable steric realignment. Possibly compounding these geometric constraints is the need for multiple equivalents of Lewis acid in the process, a presumed consequence of the abundance of metal chelating sites (ether groups) in the auxiliary. Accordingly, we elected to investigate an alternate oxygenated auxiliary to determine if multiple Lewis acid chelation sites were the barrier, and initiated studies on isomannide derivatives.

Table 1
Cycloaddition of acrylates **8/13** with cyclopentadiene

Entry	Substrate	Lewis acid (eq.)	% 9	Temp. (Time)	*Endo*/*Exo*	%de
1	**8**	Et_2AlCl (1.2)	–	−78 °C (16h)	–	–
2	**8**	Et_2AlCl (1.2)	15	−25 °C (16 h)	75:25	0
3	**8**	$EtAlCl_2$ (1.2)	25	−78 °C (16 h)	99:1	23
4	**8**	$EtAlCl_2$ (1.2)	30	−25 °C (16 h)	89:11	3
5	**8**	$EtAlCl_2$ (1.2)	30	0 °C (4 h)	92:8	0
6	**8**	$TiCl_4$ (1.2)	<1	−78 °C (16 h)	–	–
7	**8**	$BF_3 \cdot OEt_2$ (1.2)	<1	−78 °C (16 h)	–	–
8	**8**	$SnCl_4$ (1.2)	–	−78 °C (16 h)	–	–
9	**8**	$SnCl_4$ (1.2)	–	−50 °C (16 h)	–	–
10	**8**	$SnCl_4$ (1.2)	18	−25 °C (2 h)	95:5	40
11	**8**	$ZnBr_2$ (1.2)	98	+25 °C (16 h)	90:10	3
12	**8**	$AlCl_3$ (1.2)	90	−78 °C (4 h)	>99:1	45
13	**8**	$AlCl_3$ (3.0)	85	−78 °C (16 h)	>99:1	63
14	**8**	$AlCl_3$ (3.5)	75	−78 °C (16 h)	>99:1	60
15	**8**	$AlCl_3$ (4.5)	71	−78 °C (16 h)	>99:1	59
16	**8**	$AlCl_3$ (5.0)	70	−78 °C (16 h)	>99:1	38
17	**8**	$AlCl_3$ (4.0)	71	−78 °C (12 h)	>99:1	77
18	**13a**	$AlCl_3$ (4.0)	64	−78 °C (48 h)	>99:1	33
19	**13b**	$AlCl_3$ (4.0)	65	−78 °C (48 h)	>99:1	50
20	**13c**	$AlCl_3$ (4.0)	70	−78 °C (48 h)	>99:1	83

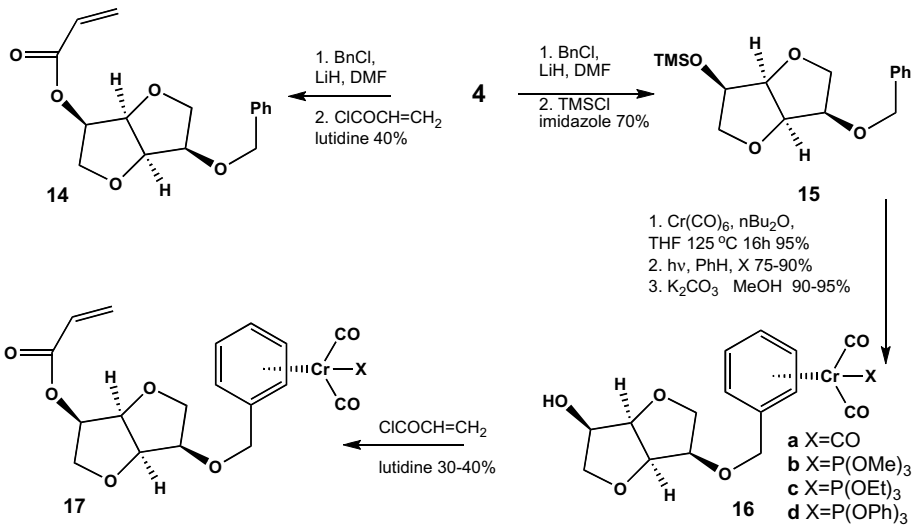
All cycloaddition conducted in CH_2Cl_2. Cycloadducts derived from **13** were decomplexed in Et_2O, then analyzed by chiral HPLC (Chiracel OD, 10% 2-propanol:90% hexanes eluent, 1 mL/min flow rate) using a racemic *endo* product as both an internal and external control (t_R *endoS* = 18.9 min *endoR* = 20.2 min).



Scheme 2. Preparation of η_6 arene complexed xylofuranose acrylates.

2.2. Isomannides

Isomannide is a commercially available building block which has already seen use as an auxiliary for cycloadditions. Loupy has reported that cycloaddition to this acrylate may be influenced by π-stacking interactions, helping to account for the good levels of asymmetric induction observed [8]. To investigate this system further, and attempt modulation of the π–π interactions, ligand **4** was transformed into a monobenzylated common precursor,



Scheme 3. Preparation of control and η_6 arene isomannide acrylates.

which could be converted to arene complexes or control substrate **14** as desired (Scheme 3). For the complexes, bis protected ether **15** was subjected to η^6 complexation followed by ligand substitution to give ligand precursors which were deprotected to give alcohols **16** and converted to give a family of acrylates **17**. Surprisingly, though acrylates **17a**–**c** were stable, the bulkier triphenylphosphite analog **17d** was not isolable, resulting in decomplexation (to **14**) even under a variety of conditions. Cycloaddition of the acrylates **14** and **17** was then conducted using cyclopentadiene, and various Lewis acid combinations.

Following decomplexation, the d.e. of the cycloadduct **9** was assessed using chiral HPLC (OD column), yielding some important findings (Table 2). Aluminum trichloride proved ineffective (entries 1–2) but appreciable d.e. is obtained using chloroalkyl aluminums with **14**, confirming prior reports [8], and revealing a consistent and marked benefit of complexation (viz. entries 3–4, 7–8, and 12–13). Additional improvements were possible using the dichloroethyl aluminum, a trend observed in both η^6 complexed and uncomplexed series. In all cases examined the *endo R* enantiomeric cycloaddition product predominated. Since π–π interactions were reasoned to contribute to diastereocontrol in substrate **14**, it was surprising to find that in the case of the π deficient **17a**, diastereocontrol is enhanced over **14** (entries 7–8), contrary to that observed in the analogous 8-phenylmethyl acrylate complexes [9]. The more electron rich mixed ligand systems performed even better, the trend seemingly reflecting a mix of steric and electronic factors (entries 9–10). Lower temperatures led to even higher selectivity, ultimately giving a system with extremely high facial and diastereocontrol (entry 14). In an attempt to rationalize these findings, a number of spectroscopic studies were undertaken using ligands **14** and **17**.

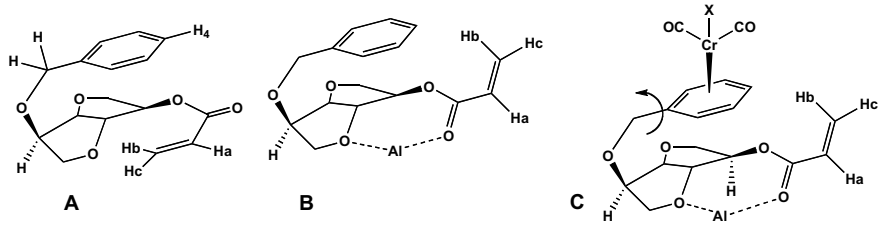
Assuming an *s*-trans enoate geometry is adopted in the Lewis acid catalyzed cycloaddition, a π–π stacked model

Table 2
Cycloaddition of acrylates **14/17** with cyclopentadiene

Entry	Substrate	Lewis acid (eq.)	%9	Temp. (Time)	*Endo*/*Exo*	%de
1	**14**	$AlCl_3$ (1.0)	55	−78 °C (12 h)	>99:1	36
2	**14**	$AlCl_3$ (3.0)	69	−78 °C (2 h)	>99:1	31
3	**14**	Et_2AlCl (1.0)	42	−78 °C (2 h)	>99:1	70
4	**17a**	Et_2AlCl (1.0)	72	−78 °C (2 h)	>99:1	80
5	**14**	$EtAlCl_2$ (1.0)	39	−10 °C to r.t. (6 h)	>99:1	67
6	**14**	$EtAlCl_2$ (1.0)	66	−40 °C (2 h)	>99:1	84
7	**14**	$EtAlCl_2$ (1.0)	42	−78 °C (2 h)	>99:1	88
8	**17a**	$EtAlCl_2$ (1.0)	81	−78 °C (2 h)	>99:1	95
9	**17b**	$EtAlCl_2$ (1.0)	53	−78 °C (2 h)	>99:1	97
10	**17c**	$EtAlCl_2$ (1.0)	71	−78 °C (2 h)	>99:1	97
11	**14**	$EtAlCl_2$ (0.5)	55	−78 °C (2 h)	>99:1	86
12	**14**	$EtAlCl_2$ (2.0)	74	−78 °C (2 h)	>99:1	88
13	**17a**	$EtAlCl_2$ (2.0)	22	−78 °C (2 h)	>99:1	94
14	**17c**	$EtAlCl_2$ (1.0)	73	−90 °C (2 h)	>99:1	99

All cycloaddition conducted in CH_2 Cl_2. Cycloadducts derived from **17** were decomplexed in Et_2O, then analyzed by chiral HPLC (Chiracel OD, 10% 2-propanol:90% hexanes eluent, 1 mL/min flow rate) using a racemic *endo* adduct prepared by alternate methods as both an internal and external control.

(A) does not account for the observed *endo R* cycloadduct, which would require addition to the (π shielded) upper face, and which also imposes unfavorable geometry on the ester function. Fluorescence quenching studies indicated a concentration dependent interaction between the acrylate and aryl moieties of **14** in the absence of Lewis acid [2]. No quenching was observed with the analogous arene complexes **17** (or control *alkane* analogs of **14**), either in the presence or absence of Lewis acid, which may indicate the metal carbonyl tripod either imparts a conformational bias to the benzyl group, or electronically insulates the arene. Chemical shift analysis of the acrylate protons in **14** and **17** ($CDCl_3$, 25 °C) did not reveal a trend for upfield shift consistent with π stacking with the phenyl ring, instead giving near uniform values for the entire series, even in the presence of Lewis acid (Table 3). More revealing were nOe studies, which failed to show any nOe between the vinyl group protons and either the aryl moiety or benzylic hydrogens, in both **14** and **17**. *However, in the presence of $EtAlCl_2$, nOe's were observed between the phenyl H_4 and the acrylate H_b (5%) and H_c (2%), suggesting that a conformational change ensues when Lewis acid coordinates to the enoate.* Taken together, the data suggest conformation B, where approach of the diene is directed to the underside of the enoate, leading to the observed endo *R* cycloadduct. The correlation of steric bulk with d.e. in the case of derivatives **17**, can be satisfied with structure C, the metal carbonyl group serving to amplify π shielding of the upper face of the enoate. Other possibilities include interaction of (the metal complexed) arene with the acrylate by some form of charge transfer process that is not detected by fluorescence quenching, or the participation of the metal carbonyl tripod itself in binding to the Lewis acid. From these results, though the precise origins of stereoselectivity remain to be defined, it is clear that the isomannide template is an effective building block for use in asymmetric cycloaddition chemistry. Additionally, the per-oxygenated skeleton does not share the requirement for multiple equivalents of Lewis acid observed with the xylofuranoses.



[STRUCTURES A-C]

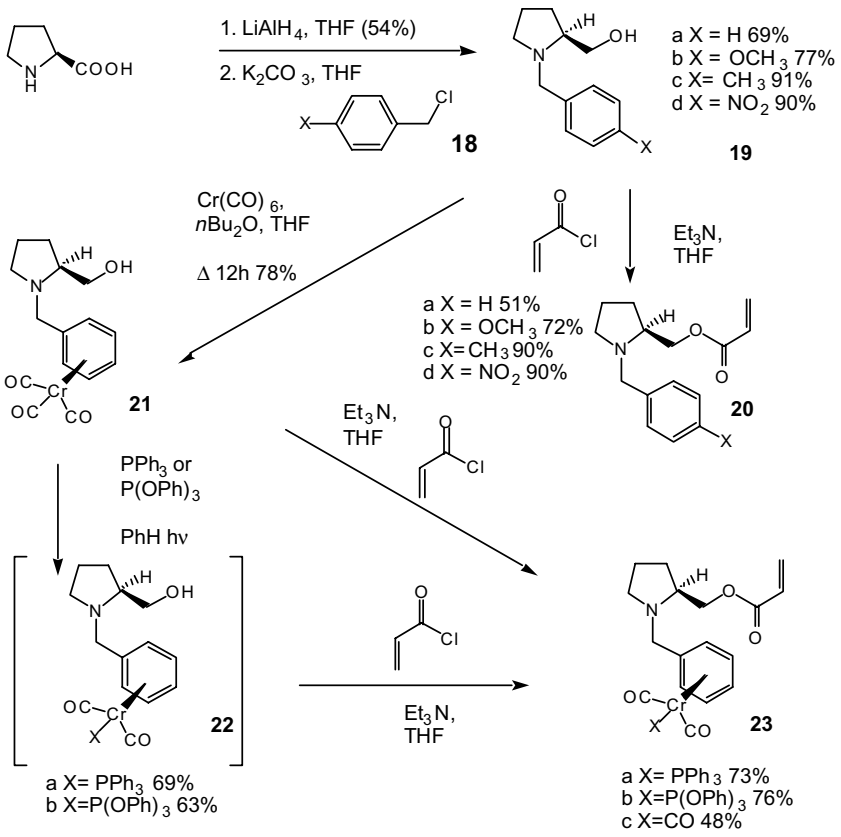
Table 3
^{1}H NMR analysis of isomannide acrylates (δ)[a]

Entry	Substrate	Ha	Hb	Hc
1	**14**	6.18	5.87	6.46
2	**14** (+$EtAlCl_2$)	6.10	5.85	6.43
3	**17a**	6.12	5.82	6.40
4	**17b**	6.22	5.87	6.54
5	**17c**	6.24	5.88	6.57

[a] Designation of Ha, Hb, Hc as shown in structures A–C.

2.3. N-benzyl prolinols

Proline derivatives have seen widespread use in catalysts and auxiliaries, and *N*-benzyl prolinol is now commercially available [10]. To initiate our studies L-proline was converted to its prolinol derivative and a variety of benzyl chlorides **18** were used to assemble the *N*-benzyl prolinols **19** (Scheme 4). Conversion to the corresponding acrylates **20** allowed us to probe the efficiency and stereoselectivity of cycloaddition on the basic template, using a series of Lewis acids with cyclopentadiene. Initial results (Table 4) confirmed the viability of the design criteria with moderate to good endo selectivity achieved and appreciable diastereocontrol. Through a survey of various Lewis acids, boron trifluoride performed best, with reproducible success under a variety of conditions. Product chemical yields ranged from poor to excellent, and the auxiliary could be recovered in good (~90%) yield by reduction of the ester linkage. In all cases, the major product obtained was the *endo R* isomer, confirmed by comparison with authentic material [11]. The most striking results were observed with 4-substituted derivatives **20b–d**, where a strong correlation between diastereoselectivity and electron donor ability of the substituent X emerged. As the same trends were not reflected in endo:exo ratios, we became especially interested in the (mixed ligand) arene chromium complexes, with their unique potential to modulate through-space electronics. Thus, commencing with **19a**, high yielding direct complexation was achieved to give alcohol **21**, presumably *via* intramolecular delivery of the $Cr(CO)_3$ tripod from an intermediate oxo-Cr complex (Scheme 4) [12]. Ligand exchange was effective without need for masking of the



Scheme 4. Synthesis and Cycloaddition to *N*-benzyl prolinol acrylates.

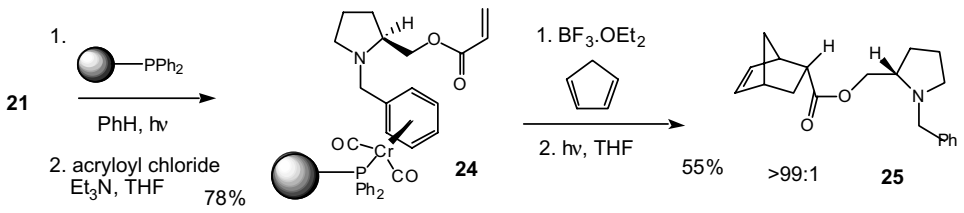
Table 4
Cycloaddition of acrylates **20/23** with cyclopentadiene

Entry	Substrate	Lewis acid (eq.)	% 9	Temp. (Time)	*Endo*/*Exo*	%de
1	**20a**	$BF_3 \cdot OEt_2$ (1.2)	<1	−78 °C (48 h)	–	–
2	**20a**	$BF_3 \cdot OEt_2$ (1.2)	6	−50 °C (12 h)	20:1	95
3	**20a**	$BF_3 \cdot OEt_2$ (1.2)	57	−25 °C (6 h)	8.8:1	55
4	**20a**	$BF_3 \cdot OEt_2$ (2.0)	24	−25 °C (6 h)	5.8:1	81
5	**20a**	$SnCl_4$ (1.2)	23	−25 °C (6 h)	1.5:1	21
6	**20a**	$SnCl_4$ (1.2)	10	−50 °C (12 h)	3.7:1	81
7	**20a**	$TiCl_4$ (1.2)	<1	−25 °C (6 h)	–	–
8	**20a**	$TiCl_2(OiPr)_2$ (1.2)	<1	−25 °C (6 h)	–	–
9	**20a**	$AlEt_2Cl$ (1.2)	10	−25 °C (6 h)	10:1	93
10	**20a**	$AlEtCl_2$ (1.2)	5	−25 °C (6 h)	1:40	80
11	**20b**	$BF_3 \cdot OEt_2$ (1.2)	90	−25 °C (12 h)	39:1	83
12	**20c**	$BF_3 \cdot OEt_2$ (1.2)	65	−25 °C (12 h)	22:1	68
13	**20d**	$BF_3 \cdot OEt_2$ (1.2)	77	−25 °C (12 h)	20:1	22
14	**23a**	$BF_3 \cdot OEt_2$ (1.2)	99	−25 °C (24 h)	35:1	98
15	**23b**	$BF_3 \cdot OEt_2$ (1.2)	86	−25 °C (24 h)	32:1	97
16	**23c**	$BF_3 \cdot OEt_2$ (1.2)	77	−25 °C (24 h)	28:1	96

All cycloadditions conducted in CH_2Cl_2. Cycloadducts derived from **23** were decomplexed in Et_2O, then analyzed. *Exo*:*endo* ratios determined by GC–MS (HP-5, evap. temp. 220 °C; operating temp. 60 °C 5 min then 4 °C/min ramp rate to 145 °C); *endo* 18.32 min. *exo* 18.58 min; de determined by HPLC (Chiracel OD, 3% 2-propanol:97% hexanes eluent, 1 mL/min flow rate) in comparison to reference standards (t_R*exoS* = 4.84 min *exoR* = 5.48 min, t_R *endoS* = 5.95 min *endoR* = 6.97min).

alcohol group, allowing **22a** and **22b** to be expeditiously converted to the corresponding acrylates **23**.

Cycloaddition was efficient with all three substrates (Table 4) and expected correlations between π donor ability and endo preference/diastereoselectivity were observed within the series. Clearly, substrate **23c** presents a more electron deficient π face than **20a** suggesting that the steric bulk of the metal carbonyl tripod contributes substantively to diastereoselectivity. Substantial diastereoselectivity was obtained in the case of **23a**, suggesting the platform to be

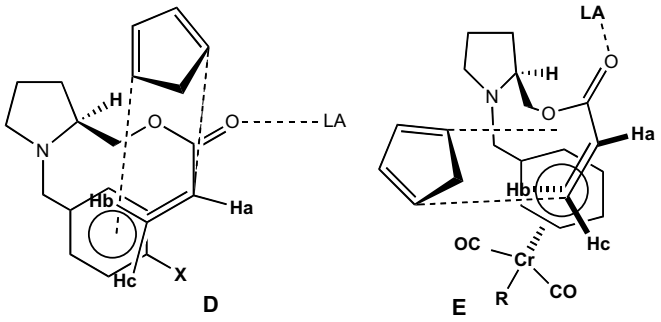


Scheme 5. Preparation and cycloaddition of polymer supported derivative.

suitable for application in other areas, and confirming the fact that a high degree of electronic control can be achieved by ligand substitution on Cr (entries 14–16), consistent with arene π basicity.

One such avenue of interest to us lies in preparation of solid-supported variants of this system. Prompted by original reports from the Semmelhack et al. [13], and Thomas groups [14], we have prior experience of the so-called 'traceless linker' approach for solid-supported synthesis. Specifically we have used polystyrene bound mixed ligand phosphine–chromium arene complexes to conduct polymer supported synthesis of a library of steroid derivatives [15]. Given the ease of uncoupling of products from the solid support following synthesis (UV release) we thus sought application of the technology in this series of auxiliaries. Accordingly, irradiation of **21** in the presence of polysytrene–diphenylphosphine complex resulted in formation of the mixed ligand derivative, which was converted to acrylate ester **24** without incident (Scheme 5). Cycloaddition proceeded with essentially *complete diastereoselectivity*, and the adduct **25** could be uncoupled from the support merely by exposure to light.

In an attempt to rationalize these findings, spectroscopic studies were undertaken using ligands **20** & **23.** Assuming an *s*-trans enoate geometry is adopted in the Lewis acid catalyzed cycloaddition, a π–π stacked/shielded model is consistent with the observed *endo R* cycloadduct, which implies approach of diene with the methylene group anti to the (mobile) benzyl substituent Structures D–E. However, chemical shift analysis of the acrylate protons in **20** and **23** ($CDCl_3$, 25 °C) revealed only minor perturbations in the presence of Lewis acid. If pronounced π stacking effects were operational, upfield shift of these protons would be expected (viz. structure D) [1]. Additional nOe experiments were conducted on substrates and in the case of **20c** irradiation of the aryl methyl group resulted in <2% enhancement of the acrylate vinyl protons. Based on these data, a *face-to-edge* arrangement (structure E) seems most plausible and must contribute to the remarkable selectivity and high degree of control observed at −25 °C. The effectiveness of **23** and especially solid supported variant **24** as chiral auxiliaries is encouraging particularly given their efficient syntheses. Further, given the clear facial preference observed it can be expected that a number of applications beyond cycloaddition to acrylate derivatives will be forthcoming, and it may become particularly useful in applications involving electrostatic interactions.



[STRUCTURES D-E]

3. Conclusion

The goal of the investigation was to highlight the use of electronically tunable chiral auxiliaries derived from the biogenic chiral pool as templates for asymmetric π-facial cycloaddition chemistry. Derived acrylates show appreciable endo- and diastereoselectivity in cycloadditions, and the selectivity can clearly be enhanced by introduction of pendant η^6 arene chromium carbonyl complexes. The metal carbonyl complexed ligands can be recycled with ease by ester reduction (LAH) of the product adducts. Spectroscopic studies suggest that a form of vinyl-face π shielding determines stereochemical bias in the cycloaddition reactions, features which will find applications in a variety of related asymmetric processes and in the design of new catalysts and auxiliaries. Though all three ligands studied are amenable to formation of benzyl η^6 arene complexes and show some degree of stereoselectivity, the isomannide and proline derived systems proved most versatile. In the latter case the affordability of the building block coupled with high degree of control at −25 °C suggest this as a candidate for further development in asymmetric reactions where π shielding of an enophile is desirable, and in the case of **24** for application in parallel screening methodology. More significantly, studies confirm that a very tight degree of electronic control can be afforded by mixed ligand arene Cr (0) derivatives, and applications in the design of electronic and charge activated materials may be forthcoming.

4. Experimental

General methods for the preparation, handling and fluorescence quenching studies of chromium complexes have been published [2]. Ether, THF and *n*-Butyl ether were distilled from sodium benzophenone ketyl. Hexanes and benzene were distilled from calcium hydride. Dichloromethane was distilled from P_2O_5 before use. DMF was dried stirring with BaO for 12 h at room temperature, followed by distillation from alumina at reduced pressure. Solvents used for complexations were deoxygenated by three cycles of freezing under vacuum, purging with nitrogen gas and thawing. Acroleins were distilled from calcium hydride immediately prior to use. Hexacarbonyl chromium was purchased from Strem Chemicals Inc. and used as supplied. All other chemicals were purchased from Aldrich and used as supplied. Silica gel chromatography (SGC) was conducted using Merck silica gel under standard flash chromatographic conditions. Photo-irradiations were conducted using a Hanovia 450W medium pressure Hg lamp enclosed in a light box. Ultrasonications were performed using a Branson 450 unit. Unless otherwise noted, NMR were recorded in $CDCl_3$ solution on a Varian Unity Innova instrument at 300 MHz for ^1H and 75 MHz for ^{13}C spectra. Peaks are listed parts per million downfield from TMS and coupling constants expressed in Hertz. Structural assignments of complexes were additionally supported by induced (hν, Et_2O, 12h) decomplexation and comparison to authentic uncomplexed ligands.

4.1. 4-O-t-butyldimethylsilyl-xylofuranose-2,3-acetonide (6)

A 100 mL round bottom flask was charged with a solution of 1, 2-*O*-isopropylidene-xylofuranose (5 g, 26.29 mmol) and imidazole (5.369 g, 78.86 mmol) in dry DMF (25 mL). The solution was cooled to 0 °C and a solution of TBDMSCl (4.359 g, 28.917 mmol) in dry DMF (25 mL) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 16 h. DMF was removed by distillation under reduced pressure and the residue was taken up in CH_2 Cl_2(30 mL), and successively washed with water (1×40 mL), then brine (1×20 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The residual oil was subjected to SGC (13:87 EtOAc:hexanes) to afford the title compound (7.987 g, 99.8%) as a colorless oil [16]; ^1H NMR (δ) 5.96 (d, $J = 3.6$ Hz, 1H), 4.51 (d, $J = 3.3$ Hz, 1H), 4.40 (d, $J =$ 3.3 Hz, 1H), 4.33 (t, $J = 3.3$ Hz, 1H), 4.15–4.11 (m, 2H), 1.49 (s, 3H), 1.32 (s, 3H), 0.89 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (δ) 111.4, 105.0, 85.6, 80.7, 74.8, 61.7, 26.8, 26.3, 25.9(3C), 18.3, −5.3(2C).

4.2. 4-O-t-butyldimethylsilyl-3-O-benzyl-xylofuranose2,3-acetonide

A 25 mL round bottom flask was charged with a solution of 4-*O*-*t*-butyldimethylsilyl-xylofuranose-*2,3-acetonide* (8.029 g, 26.372 mmol) in THF (10 mL). The flask was cooled to 0 °C and a suspension of NaH (1.266 g of 60%, 31.647 mmol) in THF (5 mL) was added dropwise. The resulting solution was stirred for 10 min at 0 °C, after which the solution was warmed to room temperature and benzyl bromide (3.47 mL, 4.962 g, 29.009 mmol) and of tetra-*n*-butyl-ammonium iodide (25 mg, 0.04 mmol) added. The resulting mixture was stirred at room temperature for 3 h, heated to 50 °C for an additional 2 h, then condensed *in vacuo*. The residue was dissolved in CH_2Cl_2, and the solution washed with water (1×20 mL), and brine (1×10 mL). The solution was dried over $MgSO_4$, then concentrated *in vacuo*. The crude oil was subjected to SGC (2:98 to 5:95 EtOAc:hexanes) to afford the title compound (6.868 g, 66%) as a colorless oil [17]; ^1H NMR (δ) 7.24–7.29 (m, 5H), 5.85 (d, $J = 3.9$ Hz, 1H), 4.61 (d, $J = 12$ Hz, 1H), 4.52 (d, $J = 12$ Hz, 1H), 4.53 (d, $J = 3.9$ Hz, 1H), 4.21–4.15 (m, 1H), 3.93 (d, $J = 3.3$ Hz, 1H), 3.88–3.67 (m, 2H), 1.42 (s, 3H), 1.25 (s, 3H), 0.83 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (δ) 138.0, 128.6, 128.0, 127.8, 111.2, 105.3, 82.8, 81.6, 81.1, 72.5, 61.6, 27.1, 26.5, 26.1, 18.5, −5.07, −5.19.

4.3. 3-O-benzyl-xylofuranose-2,3-acetonide (7)

A 100 mL round bottom flask was charged with 4-*O*-TBDMS-3-*O*-benzyl-xylofuranose-*2,3-acetonide* (1.410 g, 3.570 mmol) in THF (50 mL) and the solution cooled to 0 °C. Tetra-*n*-butyl ammonium fluoride (5.354 mmol, 5.354 mL of 1 M in THF) was added dropwise and the reaction was stirred for an additional 10 min at 0 °C and then 1 h at room temperature. The solvent was evaporated, and residue dissolved in EtOAc (40 mL) and the solution was washed with water (3×100 mL) and brine (1×100 mL) then dried over $MgSO_4$. The solution was filtered, and the filtrate condensed *in vacuo*, and the residue was purified by SGC (40:60 EtOAc:hexanes) to give the title compound (968 mg, 97%) as a colorless oil [7]; ^1H NMR (δ) 7.39–7.31 (m, 5H), 5.99 (d, $J = 2.1$ Hz, 1H), 4.73 (d, $J = 7.2$ Hz, 1H), 4.64 (d, $J = 2.4$ Hz, 1H), 4.49 (d, $J = 7.2$ Hz, 1H), 4.30–4.27 (m, 1H), 4.02 (d, $J = 2.1$ Hz, 1H), 3.97–3.83 (m, 2H), 1.6 (br.s, OH), 1.49 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (δ) 137.3, 128.9, 128.4, 127.9, 112.0, 105.3, 83.0, 82.7, 80.3, 72.1, 61.2, 27.0, 26.5.

4.4. 3-O-benzyl-xylofuranose-2,3-acetonide-acrylate (8)

A 10 mL round bottom flask was charged with 3-*O*-benzyl-xylofuranose-*2,3-acetonide* (45 mg, 0.161 mmol), triethylamine (0.11 mL, 0.805 mmol), and CH_2Cl_2 (2 mL). The solution was cooled to −10 °C with the aid of an ice-salt bath and acryloyl chloride (0.401 mmol, 0.033 mL) was added dropwise over 10 min. The reaction mixture was stirred at −10 °C for 10 min, then the resulting light brown slurry warmed to room temperature. The residue was dissolved in CH_2Cl_2 (5 mL) and the solution washed with water (3×5 mL) and brine (1×10 mL), then dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified *via* SGC (15:85, EtOAc:hexanes) to yield the

title compound (40 mg, 74%) as a colorless oil [7]; ^{1}H NMR (δ) 7.34–7.31 (m), 6.41 (dd, $J = 17.1$ Hz and $J = 1.2$ Hz, 1H), 6.12 (dd, $J = 17.1$ Hz, 10.5 Hz, 1H), 5.97 (d, $J = 3.6$ Hz, 1H), 5.83 (dd, $J = 10.5$, 1.2 Hz, 1H), 4.69 (d, $J = 12.3$ Hz, 1H), 4.64 (d, $J = 3.9$ Hz, 1H), 4.51–4.32 (m, 3H), 3.97 (d, $J = 2.7$ Hz, 1H), 1.60 (br.s, OH) 1.49 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (δ) 166.1, 137.3, 131.4, 128.8, 128.3, 128.2, 127.9, 112.1, 105.5, 82.3, 81.8, 78.3, 72.1, 62.5, 27.0, 26.5.

4.5. 3-*O*-benzyl-xylofuranose-2,3-acetonide: arene chromium tricarbonyl complex (**11**)

A 200 mL round bottom flask was charged with 3-*O*-benzyl-xylofuranose-*2,3-acetonide* (1.875 g, 6.689 mmol), chromium hexacarbonyl (2.944 g, 13.378 mmol) and a mixture of *n*-Bu_2O/THF (96 mL of 6:1 *n*-Bu_2O:THF). The resulting mixture was degassed using the triple cycle freeze-thaw procedure and then refluxed for 16 h. The mixture was cooled to room temperature, filtered through a plug of silica and then the solvent was removed *in vacuo*. The crude yellow oil was purified by SGC (20:80 to 33:67 EtOAc:hexanes) to yield the title compound (631.7 mg, 45%) as a yellow oil; ^{1}H NMR (Acetone-d_6, δ) 5.86 (d, $J = 3.6$ Hz, 1H), 5.70–5.50 (m, 5H), 4.80–4.30 (m, 3H), 4.30–4.75 (m, 1H), 3.97 (d, $J = 3.3$ Hz, 1H), 3.94–3.68 (m, 2H), 1.41 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (Acetone-d_6, δ) 233.6, 205.6, 111.5, 109.5, 105.2, 94.5, 93.4, 82.9, 81.2.0, 69.9, 59.5, 26.5, 25.9; IR (neat) 3021 (br), 3045, 2942, 1978, 1905, 1896, 1450, and 1025 cm^{-1}; $C_{18}H_{20}O_8Cr$ requires: C, 51. 93; H, 4.84. Found: C, 52.17; H, 5.09.

4.6. Benzyloxy xylofuranose-2,3-acetonide: arene chromium dicarbonyl triphenylphosphite complex (**12b**)

3-*O*-benzyl-xylofuranose-*2,3-acetonide*: arene chromium tricarbonyl complex (785 mg, 1.885 mmol) was dissolved in degassed benzene (20.0 mL, triple freeze pump thaw cycles). Degassed triphenylphosphite (4.94 mL, 18.854 mmol) was then added *via* cannula. The resulting mixture was irradiated (Hg lamp) for 6 h, then the solvent removed*in vacuo*. The crude residue was purified by SGC (15:75 EtOAc:hexanes) to yield the title compound (823 mg, 70%) as a yellow solid. m.p. 36–40 °C; ^{1}H NMR (Acetone-d_6, δ) 7.75–7.00 (m, 20H), 5.85 (m, 1H), 5.00–3.20 (m, 7H), 1.41 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (Acetone-d_6, δ) 205.5, 136.0, 130.1, 129.7, 129.5, 124.4, 122.0, 121.9, 120.9, 111.0, 105.1, 91.8, 89.3, 88.8, 79.7, 68.7, 26.5, and 25.7; $C_{35}H_{35}O_{10}CrP$ requires: C, 60.17; H, 5.05. Found: C, 60.36; H, 5.21.

4.7. Benzyloxy xylofuranose-2,3-acetonide: arene chromium dicarbonyl triphenylphosphine complex (**12c**)

3-*O*-benzyl-xylofuranose-*2,3-acetonide:* arene chromium tricarbonyl complex (371 mg, 0.892 mmol) was dissolved in degassed benzene (5.0 mL). A degassed solution of triphenylphosphine (2.337 g, 8.922 mmol) in benzene (5.0 mL) was then added *via* cannula. The resulting mixture was irradiated (medium pressure Hg lamp) for 6 h, then the solvent removed *in vacuo*. The crude residue was purified by SGC (30:70 EtOAc:Hexanes) to give the title compound (580 mg, 79%) as a red oil; ^{1}H NMR (Acetone-d_6, δ) 7.80–7.12 (m, 20H), 5.91 (bs, 1H), 5.00–3.60 (m, 7H), 1.45 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (Acetone-d_6, δ) 205.5, 140.1, 139.8, 133.2, 133.1, 129.3, 128.5, 128.1, 127.8, 111.2, 105.2, 102.1, 90.4, 82.4, 81.2, 71.4, 59.6, 26.6, and 25.8; $C_{35}H_{35}O_7CrP$ requires: C, 64.61; H, 5.42. Found: C, 64.88; H, 5.63.

4.8. 3-*O*-benzyl-xylofuranose-2,3-acetonide: acrylate arene chromium tricarbonyl complex (**13a**)

A 50 mL round bottom flask was charged with 3-*O*-benzyl-xylofuranose-*2,3-acetonide* arene chromium carbonyl complex (1.496 g, 3.587 mmol) and degassed CH_2Cl_2 (22 mL). The resulting solution was cooled to −10 °C and degassed Et_3N (17.938 mmol, 2.52 mL) and degassed acryloyl chloride (0.729 mL, 8.969 mmol) were added, respectively. After 10 min the reaction mixture was warmed to room temperature and after 1 h the solvent was removed *in vacuo*. The crude residue was purified by SGC (30:70, Et_2O:hexanes) to yield the title compound (927 mg, 55%) as a yellow oil; ^{1}H NMR (Acetone-d_6, δ) 6.43 (dd, $J = 17.4$ Hz, $J = 1.8$ Hz, 1H), 6.17 (dd, $J = 17.4$ Hz, $J = 9.9$ Hz, 1H), 6.00–5.88 (m, 2H), 5.70–5.50 (m, 5H), 4.84 (d, $J = 3.9$ Hz, 1H), 4.57–4.25 (m, 6H), 4.16(d, $J = 3.3$ Hz, 1H), 1.43 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (Acetone-d_6, δ) 233.6, 205.6, 165.4, 130.9, 128.5, 111.5, 108.9, 105.5, 94.5, 93.4, 82.9, 82.0, 78.0, 69.9, 62.2, 26.4, 25.7; IR (neat) 3089 (br), 3051, 1953, 1859, 1830, 1715, 1481, and 1036 cm^{-1}; $C_{21}H_{22}O_9Cr$ requires: C, 53.62; H, 4.71. Found: C, 53.81; H, 4.95.

4.9. Benzyl xylofuranose-2,3-acetonide acrylate ester: dicarbonyl phosphite complex (**13b**)

A 25 mL round bottom flask was charged with 3-*O*-benzyl-xylofuranose-*2,3-acetonide*: arene chromium carbonyl complex (296 g, 0.423 mmol) and degassed CH_2 Cl_2 (10 mL). The resulting solution was cooled to −10 °C and degassed Et_3N (2.115 mmol, 0.297 mL) and degassed acryloyl chloride (0.086 mL, 1.057 mmol) were added respectively. After 10 min the reaction mixture was warmed to room temperature and after 1 h the solvent was removed *in vacuo*. The crude residue was purified by SGC (15:85 Et_2O:hexanes) to yield the title compound (133 mg, 42%) as a yellow oil; ^{1}H NMR (Acetone-d_6, δ) 7.38–7.10 (m, 20H), 6.34 (ddd, $J = 9.9$ Hz, $J = 2.1$ Hz, $J = 17.1$ Hz, 1H), 6.12 (dd, $J = 4.5$ Hz, $J = 17.1$ Hz, 1H), 5.93 (ddd, $J = 4.5$ Hz, $J = 9.9$ Hz, $J = 1.8$ Hz, 1H), 5.80 (d, $J = 3.9$ Hz, 1H), 4.88–4.76 (m, 2H), 4.43 (d, $J = 3.9$ Hz, 1H), 4.20–4.00 (m, 1H), 3.72 (d, $J = 3$ Hz, 1H), 3.63–3.30 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (Acetone-d_6,

δ) 205.5, 152.5, 130.9, 129.8, 129.5, 128.4, 124.5, 122.0, 121.9, 119.4, 115.3, 111.4, 105.4, 91.5, 89.6, 89.3, 77.9, 62.2, 26.4, and 25.8; $C_{38}H_{37}O_{11}CrP$ requires: C, 60.64; H, 4.95. Found: C, 60.91; H, 5.18.

4.10. Benzyl xylofuranose-2,3-acetonide acrylate ester: dicarbonyl phosphine complex (**13c**)

A 25 mL round bottom flask was charged with 3-*O*-benzyl-xylofuranose-*2,3-acetonide:* arene chromium dicarbonyl triphenylphosphine complex (105 mg, 0.161 mmol) and degassed CH_2Cl_2(10 mL). The resulting solution was cooled to −10 °C and degassed Et_3N (0.805 mmol, 0.113 mL) and degassed acryloyl chloride (0.033 mL, 0.402 mmol) were added, respectively. After 10 min the reaction mixture was warmed to room temperature and after 1 h the solvent was removed *in vacuo*. The crude residue was purified by SGC (15:85, Et_2O:hexanes) to yield the title compound (48 mg, 42%) as a red oil; ^{1}H NMR (Acetone-d_6, δ) 7.60–7.20 (m, 20H), 6.39–6.33 (m, 1H), 6.24–6.05 (m, 1H), 5.98–5.52 (m, 2H), 5.00–3.60 (m, 7H), 1.45 (s, 3H), 1.30 (s, 3H);^{13}C NMR (Acetone-d_6, δ) 205.5, 140.1, 139.8, 133.2, 133.1, 129.3, 128.5, 128.1, 127.8, 111.2, 105.2, 102.1, 90.4, 82.4, 81.2, 71.4, 59.6, 26.6, 25.8; $C_{38}H_{37}O_8CrP$ requires: C, 64.77; H, 5.29. Found: C, 64.93; H, 5.51.

4.11. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-ol

A 250 mL round bottom flask was charged with isomannide (11.0 g, 75.0 mmol), lithium hydride (0.6 g, 75.0 mmol) and dry DMF (50 mL). The mixture stirred at r.t. for 15 min then freshly distilled benzyl chloride (8.6 mL, 75.0 mmol) cannulated into the solution. The mixture was then sonicated for 24 h. The mixture was then washed with water (3 × 200 mL) extracted with EtOAc (3 × 200 mL), and the organic solution condensed *in vacuo*. The residue was purified by SGC (hexanes:EtOAc to 50:50 to 10:90 eluent) to give the title compound (12.01 g, 68%) as white powder m.p. 89–90.5 °C (dec); ^{1}H NMR (δ) 7.36–7.28 (m, 5H), 4.77 (d, $J = 11.8$ Hz, 1H), 4.55 (t, $J = 8.1$ Hz, 2H), 4.48 (t, $J = 5.1$ Hz, 1H), 4.28 (br, 1H), 4.09–4.05 (q, $J = 5.9$ Hz, 1H), 4.03–3.96 (q, $J = 7.1$ Hz, 2H), 3.74 (d, $J = 6.6$ Hz, 1H), 3.72–3.69 (t, $J = 4.5$ Hz, 1H) and 2.88–2.83 (t, $J = 7.5$ Hz, 1H); ^{13}C NMR (δ) 137.5, 128.5, 127.9, 81.7, 80.6, 79.0, 74.8, 72.6, 72.2 and 71.4; IR (neat) 3500–3330 (br), 2988, 1445, and 987 cm^{-1}; MS (m/e) 237 (M + 1, 35.1%), 236 (M^+, 9.0), 235 (M − 1, 73.7); $[\alpha]_D = +112.72$ ($c = 0.4$, $CHCl_3$). Anal. Calc. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.13; H, 6.89%.

4.12. {[(3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl]oxy}trimethylsilane (**15**)

TMSCl (5.9 mL, 46.4 mmol) was cannulated into a precooled (−10 °C) solution of (3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3,2-*b*]furan-3-ol (2.19 g, 9.28 mmol) and imidazole (6.3 g, 92.8 mmol) in dry DMF (30 mL). The reaction mixture was stirred at r.t. for 24 h then poured over iced HCl (1% (v/v), 2 × 100 mL), washed with saturated $NaHCO_3$ (2 × 100 mL), then water (2 × 100 mL), and then extracted with EtOAc (3 × 100 mL). The organic extracts were combined, condensed *in vacuo*, and the residual oil purified by SGC (95:5 through 50:50 hexanes/EtOAc) to give the title compound (2.85 g, 99%) as a colorless oil; ^{1}H NMR (δ) 7.33–7.24 (m, 5H), 4.70 (d, $J = 11.9$ Hz, 1H), 4.61 (t, $J = 8.0$ Hz, 2H), 4.48 (t, $J = 4.3$ Hz, 1H), 4.34 (t, $J = 3.9$ Hz, 1H), 4.07–4.00 (m, 1H), 3.96–3.92 (q, $J = 4.7$ Hz, 2H), 3.72 (d, $J = 8.3$ Hz, 1H), 3.68–3.60 (q, $J = 7.8$ Hz, 1H), and 0.14 (s, 9H); ^{13}C NMR (δ) 137.6, 128.4, 128.2, 127.7, 81.8, 80.1, 79.3, 73.6, 72.2, 70.9, and −0.24; IR (neat) 3500–3330 (br), 3045, 2238, 1556, 1442, and 1022 cm^{-1}; MS (m/e) 307 (M − 1, 46.8%), 309 (M + 1, 72.1); $[\alpha]_D = +149.5$ ($c = 0.33$, $CHCl_3$); Anal. Calc. for $C_{16}H_{24}O_4Si$: C, 62.30; H, 7.84. Found: C, 62.76; H, 8.02%.

4.13. {[(3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl]oxy}trimethyl silane chromium (0) tricarbonyl (16a)

A mixture of {[(3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3,2-*b*]furan-3-yl]oxy} trimethyl silane (1.6 g, 5.3 mmol) and chromium hexacarbonyl (2.3 g, 10.6 mmol) in nBu$_2$O:THF (60:10, 70 mL) was heated using standard complexation conditions for 16 h. On cooling the mixture was filtered and the solution condensed *in vacuo.* The residual oil was purified by SGC (95:5 through 70:30 hexanes/EtOAc) to give the title compound (1.04 g, 44%) as yellow oil; ^{1}H NMR (δ) 6.92 (s, 1H), 5.23 (m, 4H), 5.12 (m, 1H), 4.43–4.30 (m, 2H), 4.20–4.02 (m, 3H), 3.92–3.80 (m, 2H), 3.64–3.48 (m, 2H), 2.75 (d, $J = 10.2$ Hz, 1H) and 0.001 (s, 9H); ^{13}C NMR (δ) 232.5, 107.2, 92.6, 92.3, 91.7, 81.8, 80.3, 80.0, 73.1, 71.9, 71.3, 70.4, and −0.33; IR (neat) 3025, 2940, 1976, 1901, 1889, 1454, and 1023 cm^{-1}; MS (m/e) 445 (M + 1, 11.8%), 372 (M-TMS, 34.6); $[\alpha]_D = +85.12$ ($c = 0.46$, $CHCl_3$). Anal. Calc. for $C_{19}H_{24}CrO_7Si$: C, 51.34; H, 5.44. Found: C, 51.48; H, 5.51%.

4.14. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro[3,2-b]furan-3-ol mono (trimethyl phosphite) chromium (0) dicarbonyl (**16b**)

Protected arene complex, {[(3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3,2-*b*]furan-3-yl]oxy} trimethyl silane chromium (0) tricarbonyl (0.18 g, 0.40 mmol), was dissolved in dry benzene (5 mL) in a quartz test tube, then trimethylphosphite (0.24 mL, 2.00 mmol) added to the tube, and the solution degassed using a slow stream of Argon gas. The vessel was capped and the mixture irradiated (Hanovia 450W Hg lamp) for 8h, following which the solvent was condensed *in vacuo*. The residue was dissolved in

MeOH (10 mL) and potassium carbonate (0.28 g, 2.00 mmol) added. After stirring at r.t. for 12 h, the mixture was filtered through a plug of silica gel (EtOAc, 50 mL), the filtrate condensed *in vacuo*, and the resulting oil purified by SGC (40:60 through 10:90 hexanes:EtOAc) to give the title compound (0.12 g, 78%) as yellow oil; ^{1}H NMR (CD_3OD, δ) 4.69 (m, 1H), 4.21 (m, 2H), 4.07 (d, $J = 11.5$ Hz, 1H), 3.94–3.87 (t, $J = 11.2$ Hz, 2H), 3.77 (m, 1H), 3.59 (m, 1H), 3.48 (m, 1H), 3.31 (d, $J = 5.7$ Hz, 2H), 3.06 (m, 1H), 3.00 (q, $J = 6.3$ Hz, 1H), 2.88 (d, $J = 10.8$ Hz, 2H) and 2.71 (s, 9H); ^{13}C NMR (δ) 240.5, 240.1, 105.0, 92.8, 92.6, 92.2, 91.9, 84.7, 83.1, 82.9, 82.4, 75.2, 74.7, 74.3, 73.5, and 52.9; IR (neat) 3450 (br), 3120, 2966, 2286, 1920, 1852, 1434, and 967 cm^{-1}; $[\alpha]_D = +74.16$ ($c = 0.25$, $CHCl_3$). Anal. Calc. for $C_{18}H_{25}CrO_9P$: C, 46.16; H, 5.38. Found: C, 46.34; H, 5.47%.

4.14.1. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-ol mono (triethyl phosphite) chromium (0) dicarbonyl (**16c**)

Using identical procedure to that used for 16b, {[(3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro [3, 2-*b*]furan-3-yl]oxy} trimethyl silane chromium (0) tricarbonyl (0.13 g, 0.29 mmol) and triethylphosphite (0.25 mL, 1.45 mmol) gave the title compound (0.14 g, 97%) as a yellow oil; ^{1}H NMR (δ) 4.95 (m, 4H), 4.63 (m, 1H), 4.36 (d, $J = 8.4$ Hz, 2H), 4.16 (m, 1H), 4.00 (m, 3H), 3.88 (m, 2H), 3.79 (q, $J = 9.3$ Hz, 6H), 3.60 (m, 1H), 3.19 (m, 1H), 2.80–2.63 (br, 1H) and 1.17 (t, $J = 7.2$ Hz, 9H); ^{13}C NMR (δ) 237.5, 237.1, 100.7, 89.4, 89.3, 88.9, 81.4, 80.0, 79.3, 73.8, 71.9, 71.6, 70.9, 70.6, 63.1, 59.2 and 15.7; IR (neat) 3464 (br), 3038, 2919, 1915, 1838, 1506, 1396, 1268, 1038, and 766 cm^{-1}; $[\alpha]_D = +27.98$ ($c = 0.28$, $CHCl_3$). Anal. Calc. for $C_{21}H_{31}CrO_9P$: C, 49.41; H, 6.12. Found: C, 49.55; H, 6.18%.

4.14.2. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl acrylate (**14**)

Acryloyl chloride (1.62 mL, 20 mmol) was added at −40 °C to a solution of (3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3,2-*b*]furan-3-ol (1.2 g, 5.0 mmol) and triethylamine (2.0 mL, 15.0 mmol) in CH_2Cl_2 (40 mL). After stirring 6 h. at r.t., the reaction was quenched by addition of water (50 mL), then extracted with CH_2Cl_2 (3×100 mL). The extracts were dried over Na_2SO_4 then the solution filtered, condensed *in vacuo* and the residue purified by SGC (50: 50 hexanes:CH_2Cl_2) to give the title compound (1.44 g, 99%) as pale yellow oil; ^{1}H NMR (δ) 7.36 (d, $J = 5.7$ Hz, 4H), 7.31 (m, 1H), 6.49–6.43 (dd, $J = 15.9$ Hz, 1.2 Hz, 1H), 6.21–6.12 (dd, $J = 13.8$ Hz, 4.8 Hz, 1H), 5.87 (d, $J = 9.9$ Hz, 1H), 5.20 (q, $J = 6.3$ Hz, 1H), 4.76 (d, $J = 4.2$ Hz, 1H), 4.73, (m, 1H), 4.57 (d, $J = 012$ Hz, 1H), 4.51 (t, $J = 4.8$ Hz, 1H), 4.06–4.00 (m, 3H), 3.93 (t, $J = 7.6$ Hz, 1H) and 3.65 (t, $J = 8.4$ Hz, 1H); ^{13}C NMR (δ) 165.4, 137.4, 131.6, 128.4, 127.9, 127.6, 127.4, 80.6, 80.1, 78.7, 74.2, 72.4, 70.9 and 70.4; IR (neat) 3092, 2375, 1698, 1446, 1123, and 781 cm^{-1}; MS (m/e) 290 (M^+, 55.4%), 291 (M + 1, 17.5), 293 (M+3, 67.2); $[\alpha]_D = +26.59$ ($c = 0.19$, $CHCl_3$). Anal. Calc. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.28; H, 6.32%.

4.15. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl acrylate chromium tricarbonyl (**17a**)

Acryloyl chloride (2.59 mL, 31.84 mmol) was added at −40 °C to a solution of (3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3, 2-*b*]furan-3-ol acrylate chromium tricarbonyl (2.37 g, 6.37 mmol) and triethylamine (3.55 mL, 25.47 mmol) in CH_2Cl_2 (40 mL). After stirring at r.t. for 6 h, the reaction was quenched by addition of water (50 mL), then extracted with CH_2 Cl_2 (3×150 mL), and the extracts dried over Na_2SO_4. The solution was filtered, condensed *in vacuo* and the residue purified by SGC (80:20 through 50:50 hexanes/EtOAc) to give the title compound (1.64 g, 60%) as yellow oil; ^{1}H NMR (δ) 6.40 (d, $J = 8.4$ Hz, 1H), 6.16–6.08 (dd, $J = 17.2$ Hz, 6.9 Hz, 1H), 5.82 (d, $J = 10.3$ Hz, 1H), 5.38 (m, 4H), 5.33 (d, $J = 6.3$ Hz, 1H), 5.26 (d, $J = 5.6$ Hz, 1H), 5.15 (d, $J = 5.6$ Hz, 1H), 4.74 (t, $J = 5.7$ Hz, 1H), 4.56 (d, $J = 4.7$ Hz, 1H), 4.45 (d, $J = 11.4$ Hz, 1H), 4.16–4.06 (m, 4H) and 3.66 (t, $J = 8.2$ Hz, 1H); ^{13}C NMR (δ) 232.5, 165.4, 131.6, 127.5, 106.8, 92.7, 92.6, 92.5, 92.4, 91.8, 80.7, 80.1, 79.8, 73.9, 70.8, 70.7, and 68.8; IR (neat) 3088, 3042, 1945, 1866, 1834, 1712, 1488 and 1039 cm^{-1}; $[\alpha]_D = +54.25$ ($c = 0.4$, $CHCl_3$). Anal. Calc. for $C_{19}H_{20}CrO_8$: C, 53.53; H, 4.26. Found: C, 53.48; H, 4.17%.

4.16. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl acrylate mono(trimethyl phosphite)chromium (0) dicarbonyl (**17b**)

Using similar procedure for **17a**, acryloyl chloride (0.09 mL, 1.10 mmol), (3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)perhydro[3,2-*b*]furan-3-ol acrylate mono trimethylphoshite chromium (0) dicarbonyl (0.17 g, 0.38 mmol) and 2,6-lutidine (0.17 mL, 1.47 mmol) gave the title compound (0.067 g, 35%) as yellow oil; ^{1}H NMR (δ) 6.54 (d, $J = 8.7$ Hz, 1H), 6.24–6.18 (dd, $J = 12.3$ Hz, 6.9 Hz, 1H), 5.87 (d, $J = 10.4$ Hz, 1H), 5.28 (m, 4H), 5.15 (q, $J = 5.7$ Hz, 1H), 4.76–4.72 (m, 2H), 4.54–4.48 (m, 2H), 4.13–3.88 (m, 5H), 3.74 (s, 9H) and 3.63 (t, $J = 8.7$ Hz, 1H); ^{13}C NMR (δ) 237.2, 236.5, 165.8, 137.2, 132.1, 104.9, 93.1, 92.8, 92.2, 91.8, 90.3, 80.7, 80.2, 78.7, 74.3, 72.5, 71.0, 70.4, and 31.5; IR (neat) 3085, 2987, 1844, 1812, 1698, 1415, and 965 cm^{-1}; $[\alpha]_D = +102.71$ ($c = 0.14$, $CHCl_3$). Anal. Calc. for $C_{21}H_{27}CrO_{10}P$: C, 48.28; H, 5.21. Found: C, 48.71; H, 5.54%.

4.17. (3R,3aS,6R,6aR)-6-(benzyloxy)perhydro-[3,2-b]furan-3-yl acrylate mono (triethyl phosphite) chromium (0) dicarbonyl (**17c**)

Using similar procedure for **17a**, acryloyl chloride (0.05 mL, 0.61 mmol), (3*R*,3*aS*,6*R*,6*aR*)-6-(benzyloxy)-

perhydro[3,2-*b*]furan-3-ol acrylate mono triethylphoshite chromium (0) dicarbonyl (0.104 g, 0.367 mmol) and 2,6-lutidine (0.095 mL, 0.815 mmol) gave the title compound (0.029 g, 25%) as yellow oil; ^{1}H NMR (δ) 6.57 (d, $J = 9.0$ Hz, 1H), 6.26–6.20 (dd, $J = 11.7$ Hz, 6.0 Hz, 1H), 5.88 (d, $J = 10.2$ Hz, 1H), 5.24 (m, 4H), 5.13 (q, $J = 5.1$ Hz, 1H), 4.72–4.68 (m, 2H), 4.56–4.51 (m, 2H), 4.15–3.91 (m, 5H), 3.58 (q, $J = 8.7$ Hz, 6H), 3.45 (t, $J = 7.2$ Hz, 1H) and 2.25 (t, $J = 6.3$ Hz, 9H); ^{13}C NMR (δ) 236.2, 234.9, 165.1, 137.1, 132.3, 101.8, 92.9, 92.6, 92.1, 91.6, 90.9, 80.8, 80.2, 79.2, 74.4, 72.6, 70.9, 70.1, 58.7, and 28.5; IR (neat) 3132, 3076, 1832, 1805, 1702, 1427, and 986 cm^{-1}; $[\alpha]_D = +168.59$ ($c = 0.14$, $CHCl_3$). Anal. Calc. for $C_{24}H_{33}CrO_{10}P$: C, 51.07; H, 5.89. Found: C, 51.12; H, 5.92%.

4.18. 4-Methoxy N-benzyl prolinol (**19b**)

A solution of L-prolinol (1.16 g, 11.49 mmol) and 4-methyloxybenzylchloride (1.83 g, 11.71 mmol) in THF (40 mL) was stirred with anhydrous K_2CO_3 (6 g) for 16 h at r.t. Dilute HCl was added to acidify the aqueous layer to pH 1. The aqueous layer was separated, extracted with EtOAc (1×20 mL), cooled to 0 °C, basified with ammonium hydroxide, and extracted with CH_2Cl_2 (4×20 mL). The combined extracts were dried (Na_2SO_4) concentrated *in vacuo*, then the residue purified by SGC (EtOAc:hexanes = 66:34) to yield the title compound (1.95 g, 77%) as a viscous oil; ^{1}H NMR (δ) 7.20 (d, 2H, $J = 8.4$ Hz), 6.85 (d, 2H, $J = 8.4$ Hz), 3.88 (d, 1H, $J = 12.9$ Hz), 3.80 (s, 3H), 3.61 (dd, 1H, $J = 3.3$ Hz, 10.5 Hz), 3.41 (dd, 1H, $J = 10.5$ Hz, 1.8 Hz), 3.30 (d, 1H, $J = 12.9$ Hz), 2.90–3.00 (m, 1H), 2.64–2.76 (m, 1H), 2.33 (s, 3H), 2.22–2.32 (m, 1H), 1.60–2.00 (m, 4H); ^{13}C NMR (δ) 159.2, 131.6, 130.0, 113.9, 64.3, 62.0, 58.0, 55.4, 54.6, 28.1, 23.6.

4.19. 4-Methyl N-benzyl prolinol (**19c**)

Similar procedure to **19b**, L-prolinol (1.17 g, 11.58 mmol) and α-bromo-*p*-xylene (2.2 g, 11.88 mmol) gave the title compound (1.673 g, 71%) as a viscous oil; ^{1}H NMR (δ) 7.18 (d, 2H, $J = 7.5$ Hz), 7.12 (d, 2H, $J = 8.1$ Hz), 3.91 (d, 1H, $J = 12.9$ Hz), 3.64 (dd, 1H, $J = 3.3$ Hz, 10.5 Hz), 3.42 (dd, 1H, $J = 10.5$ Hz, 1.8 Hz), 3.32 (d, 1H, $J = 13.2$ Hz), 2.80–3.00 (m, 2H), 2.60–2.80 (m, 1H), 2.33 (s, 3H), 2.20–2.30 (m, 1H), 1.50–2.00 (m, 4H); ^{13}C NMR (δ) 138.8, 136.5, 129.2, 128.9, 64.4, 62.0, 58.4, 54.6, 28.1, 23.6.

4.20. 4-Nitro N-benzyl prolinol (**19d**)

Using similar procedure to **19b**, L-prolinol (1.34 g, 13.27 mmol) and 4-nitrobenzyl chloride (2.5 g, 14.59 mmol) yielded the title compound (1.64 g, 52%) as a viscous oil; ^{1}H NMR (δ) 8.13 (d, 2H, $J = 8.1$ Hz), 7.45 (d, 2H, $J = 8.4$ Hz), 4.02–4.09 (m, 1H), 3.62 (dd, 1H, $J = 3.3$ Hz, 10.8 Hz), 3.44 (d, $J = 13.8$ Hz), 2.88–2.95 (m, 1H), 2.72–2.77 (m, 1H), 2.60 (s, 1H), 2.19–2.28 (m, 1H), 1.66–1.97 (m, 4H); ^{13}C NMR (δ) 147.6, 147.3, 129.4, 123.8, 64.9, 62.4, 58.4, 54.8, 27.8, 23.7.

4.21. N-benzyl prolinol acrylate (20 X = H)

To solution of *N*-benzyl prolinol (777 mg, 4.068 mmol) in THF (10 mL) was added acryloyl chloride (0.8 mL, 10.170 mmol) and Et_3N (3 mL, 20.340 mmol) at 0 °C. The solution was warmed to r.t. and stirred for 6 h. The solution was washed with brine (1×5 mL) and to the organic layer was added 5 N HCl solution at 0 °C to bring the pH 1. The aqueous layer was neutralized with ammonium hydroxide solution to bring the pH 9, then extracted with ethyl acetate (3×20 mL) and the combined extracts dried over Na_2SO_4. The mixture was filtered and then condensed *in vacuo* and the residue purified by SGC (hexanes:ethyl acetate = 80:20) to give the title compound (509.5 mg, 51%) as a colorless oil; ^{1}H NMR (δ) 7.22–7.36 (m, 5H), 6.42 (dd, 1H, $J = 17.5$ Hz, 1.5 Hz), 6.15 (dd, 1H, $J = 11$ Hz, 17.5 Hz), 5.82 (dd, 1H, $J = 11$ Hz, 1.5 Hz), 4.08–4.22 (m, 3H), 3.43 (d, 1H, $J = 13.5$ Hz), 2.84–2.98 (m, 2H), 2.22–2.30 (m, 1H), 1.92–2.02 (m, 1H), 1.64–1.80 (m, 3H); ^{13}C NMR (δ) 166.2, 139.7, 131.0, 129.1, 128.8, 128.5, 127.1, 67.5, 62.1, 59.7, 54.7, 28.7, 23.2.

4.22. 4-Methoxy N-benzyl prolinol acrylate (**20b**)

Using similar procedure to **20a**, compound **19b** (580 mg, 2.62 mmol) and acryloyl chloride (0.5 mL, 6.56 mmol) gave the title compound (520 mg, 72%) as a colorless oil; ^{1}H NMR (δ) 7.22 (d, 2H, $J = 8.1$ Hz), 6.88 (d, 2H, $J = 8.7$ Hz), 6.40 (d, 1H, $J = 17.4$ Hz), 6.14 (dd, 1H, $J = 10.5$ Hz, 17.1 Hz), 5.82 (dd, 1H, $J = 10.5$ Hz, 1.2 Hz), 3.72–4.2 (m, 6H), 3.36 (d, 1H, $J = 12.3$ Hz), 2.67–2.93 (m, 2H), 2.24 (dd, 1H, $J = 17.1$ Hz, 9 Hz), 1.87 (m, 1H), 1.59–1.74 (m, 3H); ^{13}C NMR (δ) 166.4, 158.8, 131.7, 130.9, 130.2, 128.7, 113.8, 67.5, 61.9, 59.0, 55.5, 54.5, 28.7, 23.1.

4.23. 4-Methyl N-benzyl prolinol acrylate (**20c**)

Using similar procedure to **20a**, compound **19c** (2 g, 8.24 mmol) and acryloyl chloride (1.6 mL, 20.6 mmol) gave the title compound (1.92 g, 91%) as a colorless oil; ^{1}H NMR (δ) 7.20 (d, 2H, $J = 7.8$ Hz), 7.11 (d, 2H, $J = 7.5$ Hz), 6.41 (dd, 1H, $J = 17.1$ Hz, 1.5), 6.14 (dd, 1H, $J = 10.5$ Hz, 17.7 Hz), 5.82 (dd, 1H, $J = 10.5$ Hz, 1.5 Hz), 4.02–4.23 (m, 3H), 3.40 (d, 1H, $J = 12.9$ Hz), 2.83–2.96 (m, 2H), 2.23 (s, 3H), 2.20–2.30 (m, 1H), 1.92–2.00 (m, 1H), 1.63–1.78 (m, 3H).

4.24. 4-Nitro N-benzyl prolinol acrylate (**20d**)

Using similar procedure to **20a**, compound **19d** (936 mg, 3.965 mmol) and acryloyl chloride (0.4 mL, 4.758 mmol) gave the title compound (1.05 g, 91%) as a colorless oil;

^{1}H NMR (δ) 8.12 (dd, 2H, $J = 8.7$ Hz, 6.6 Hz), 7.46 (dd, 2H, $J = 9$ Hz, 2.4 Hz), 6.36 (dd, 1H, $J = 17.1$ Hz, 1.5 Hz), 6.08 (dd, 1H, $J = 10.5$ Hz, 17.1 Hz), 5.79 (dd, 1H, $J = 10.5$ Hz, 1.5 Hz), 3.60–3.65 (m, 2H), 3.42–3.65 (m, 2H), 2.72–2.95 (m, 2H), 2.16–2.28 (m, 1H), 1.62–1.72 (m, 4H).

4.25. N-benzyl prolinol chromium tricarbonyl complex (**21**)

A mixture of $Cr(CO)_6$ (2.3 g, 10.47 mmol), *N*-benzyl prolinol (1 g, 5.236 mmol), THF (20 mL), and *n*-butyl ether (140 mL) was subjected to triple freeze-pump-thaw cycles then heated at 125–130 °C in the dark for 20 h. The solution was concentrated to 20 mL then filtered through a plug of silica gel and evaporated to dryness. The residue was purified by SGC (hexanes:EtOAc = 50:50) to give the title compound (1 g, 78%) as a pale yellow oil; ^{1}H NMR (Acetone-d_6, δ) 5.52–5.70 (m, 5H), 3.98 (d, 1H, $J = 13.2$ Hz), 3.50–3.60 (m, 2H), 3.05–3.28 (m, 2H), 2.74 (s, 1H), 2.31–2.37 (m, 1H), 1.49–2.10 (m, 4H); ^{13}C NMR (Acetone-d_6, δ) 234.1, 205.5, 112.1, 95.1, 94.9, 94.6, 92.9, 66.8, 64.8, 58.3, 54.7, 28.0, 23.2; IR (neat) 3020, 2945, 1979, 1903, 1885, 1450, and 1020 cm^{-1}; $C_{15}H_{17}NO_4Cr$ requires: C, 55.05; H, 5.23. Found: C, 55.36; H, 5.41.

4.26. N-benzyl prolinol chromium tricarbonyl complex-acrylate ester (**23c**)

A solution **21** (50 mg 1.53 mmol) in THF (20 mL) was degassed (triple freeze-pump-thaw cycle) then acryloyl chloride (0.3 mL, 3.83 mmol) and Et_3 N (1.1 mL, 7.65 mmol) added at 0 °C. The solution was warmed to r.t. and stirred for 6 h. Silica gel (1 g) was added and the resulting slurry concentrated *in vacuo* then transferred to a flash column and the mixture purified by SGC (hexanes:EtOAc = 80:20) under a positive pressure of argon. The title compound (368 mg, 63%) was isolated as a pale yellow oil; ^{1}H NMR (Acetone-d_6,δ) 6.36 (dd, 1H, $J = 2.1$ Hz, 17.1 Hz), 6.16 (dd, 1H, $J = 10.5$ Hz, 17.1 Hz), 5.89(dd, 1H, $J = 1.5$ Hz, 10.5 Hz), 5.60–5.80 (m, 4H), 5.50–5.60 (m, 1H), 4.02–4.24 (m, 2H), 3.92 (d, 1H, $J = 13.8$ Hz), 3.24 (d, 1H, $J = 13.8$ Hz), 3.02–3.16 (m, 1H), 2.86–3.02 (m, 1H), 2.34–2.46 (m, 1H), 1.90–2.10 (m, 1H), 1.60–1.80 (m, 3H); ^{13}C NMR (Acetone-d_6,δ) 233.0, 205.3, 165.9, 130.5, 128.8, 95.1, 94.8, 94.6, 93.0, 66.9, 62.2, 58.1, 54.4, 28.1, and 23.3; IR (neat) 3091, 3008, 1851, 1696, 1405 and 967 cm^{-1} $C_{18}H_{19}NO_5Cr$ requires: C, 56.69; H, 5.02. Found: C, 56.84; H, 5.33.

4.27. N-benzyl prolinol chromium dicarbonyl monophosphine complex-acrylate ester (**23a**)

A solution of triphenylphosphine (6.3 g, 23.85 mmol) in benzene (5 mL) was degassed (triple freeze-pump-thaw cycles) then cannulated into a flask containing complex **21** (780 mg, 2.385 mmol). The mixture was again degassed (double freeze-pump-thaw cycles) and then placed in a photolysis chamber and irradiated (Hanovia 450W Hg lamp) for 6 h. The solution was condensed in vacuo and the residue purified by SGC (gradient of hexanes, through hexanes:ethyl acetate = 95:5 to hexanes:ethyl acetate = 1:1) to give the corresponding monotriphenylphosphine complex compound **22a** (923.9 mg, yield: 69%) as a yellow oil which was used immediately in the next step. To this crude residue was added a solution of acryloyl chloride (0.306 mL, 4.113 mmol) in THF (60 mL) then Et_3N (1.224 mL, 8.23 mmol). The mixture was degassed at 0 °C then warmed to r.t. and stirred for 6 h. The solution was filtered through a plug of silica gel then concentrated *in vacuo* and the residue purified by SGC (hexanes:EtOAc = 50:50) to give the title compound (734 mg, 73%) as a yellow oil; ^{1}H NMR (Acetone-d_6,δ) 7.20–7.80 (m, 20H), 6.37 (dd, 1H, $J = 1.5$ Hz, 17.1 Hz), 6.16 (dd, 1H, $J = 10.2$ Hz, 17.1 Hz), 5.87 (dd, 1H, $J = 1.5$ Hz, 10.2 Hz), 4.60–5.00 (m, 2H), 4.00–4.20 (m, 2H), 3.85 (d, 1H, $J = 12.9$ Hz), 3.12 (d, 1H, $J = 12.9$ Hz), 2.90–3.00 (m, 1H), 2.20–2.40 (m, 1H), 1.60–1.80 (m, 3H); ^{13}C NMR (Acetone-d_6,δ) 205.7, 166.0, 140.4, 139.9, 133.2, 133.1, 130.6, 129.2, 128.8, 128.1, 128.0, 104.2, 92.2, 91.6, 90.4, 90.2, 89.8, 67.1, 61.8, 59.0, 54.3, 28.3, and 23.1; IR (neat) 3080, 3041, 1940, 1871, 1826, 1705, 1502, and 1029 cm^{-1}; $C_{35}H_{34}NO_4CrP$ requires: C, 68.29; H, 5.57. Found: C, 68.50; H, 5.71.

4.28. N-benzyl prolinol chromium dicarbonyl monophosphite complex-acrylate ester (**23b**)

Using similar procedures employed for **23a**, triphenylphosphite (4.27 g, 13.76 mmol) and complex **21** (450 mg, 1.376 mmol) gave crude **22b** (527 mg, 63%) which was reacted directly with acryloyl chloride (0.297 mL, 3.792 mmol) and Et_3N (1.17 mL, 7.585 mmol) to yield the title compound (433 mg, 76%) as a yellow oil; ^{1}H NMR (Acetone-d_6,δ) 7.00–7.80 (m, 20H), 6.39 (dd, 1H, $J = 0.9$ Hz, 17.1 Hz), 6.17 (dd, 1H, $J = 10.2$ Hz, 17.1 Hz), 5.88 (dd, 1H, $J = 10.2$ Hz, 0.9 Hz), 4.80–5.00 (m, 1H), 4.61 (s, 1H), 4.00–4.20 (m, 2H), 3.47 (d, 1H, $J = 12.9$ Hz), 2.77 (d, 2H, $J = 12.9$ Hz), 1.40–2.36 (m, 4H); ^{13}C NMR (Acetone-d_6, δ) 205.6, 165.7, 152.8, 152.7, 130.7, 130.2, 129.8, 128.8, 124.5, 122.1, 122.0, 107.7, 92.5, 92.1, 90.7, 90.4, 88.5, 67.0, 61.9, 58.4, 54.1, 28.3, and 23.1; IR (neat) 3136, 3071, 1829, 1810, 1715, 1421, and 989 cm^{-1}; $C_{35}H_{34}N\ O_7CrP$ requires: C, 63.34; H, 5.16. Found: C, 63.59; H, 5.41.

4.29. Preparation of polymer bound complex (**24**)

Degassed (triple freeze-pump-thaw cycles) anhydrous THF (10 mL) was cannulated to a mixture of compound **21** (651.6 mg, 1.99 mmol) and polymer-supported triphenylphosphine (331 mg, 1 mmol). The mixture was again degassed (double freeze-pump-thaw cycles) then placed in a photolysis chamber and irradiated (Hanovia 450W Hg lamp) for 48 h. The mixture was filtered and the residue

washed with anhydrous THF (10 mL) then anhydrous ether (10 mL). The residue was suspended in THF (20 mL) then acryloyl chloride (0.254 mL, 3.239 mmol) followed by Et_3N (1 mL, 6.477 mmol) was added at 0 °C. The solution was warmed to r.t. then stirred for 24 h, filtered, then washed with water (10 mL), THF (10 mL) ether (10 mL) and acetone (10 mL) then dried *in vacuo* to yield the title compound (533 mg, 78%) as a yellow solid which used immediately for cycloaddition reactions; ^{31}P NMR (121 MHz, Acetone-d_6, δ) 91.87 ppm.

4.30. Authentic endo adduct (9) via acyl chloride **10**

$SOCl_2$ (1.59 mL, 21.776 mmol) was added to a solution of 5-norbonene-2-carboxylic acid (2.006 g, 14.517 mmol) in dry CH_2Cl_2(8 mL) and the resulting mixture stirred for 12 h. The solvent was removed *in vacuo* and the residual oil was distilled under reduced pressure to give **10** (1.759 g, 77%) as a colorless liquid [7]. To a solution of 3-*O*-benzyl-xylofuranose-*2,3-acetonide* (200 mg, 0.713 mmol) in CH_2Cl_2 (5 mL) at −10 °C, was added **10** (279.34 mg, 1.784 mmol) and Et_3N (0.5 mL, 3.567 mL). The resulting mixture was warmed to r.t. and stirred for 2 h then washed with water (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by SGC (10:90 EtOAc:hexanes) to yield **9** (248 mg, 87%) as a pale yellow oil [7]; ^1H NMR (500 MHz, $CDCl_3$) 7.40–7.26 (m, 5H, Ph), 6.20–6.14 (m, 1H, *endo-R*, *S*-H-5′), 6.14–6.06 (m, 2H, *exo*-H-5′and 6′), 5.95 (d, $J = 2.1$ Hz, 1H), 5.94–5.88 (m, 1H, *endo-R*, *S*-H-6′), 4.67 (d, $J = 12$ Hz, 1H, O$\underline{CH_2}$Ph), 4.62 (d, $J = 3.6$ Hz, 1H, CH), 4.50 (dd, $J = 12$ Hz and $J = 2.7$ Hz, 1H, O$\underline{CH_2}$Ph), 4.38–4.18 (m, 3H, CH, and C$\underline{H_2}$O), 3.95 (t, $J = 2.7$ Hz, 1H), 3.22 (s, 1H, *endo-R*-H-4′), 3.17 (s, 1H, *endo-S*-H-4′), 3.02 (s, 1H, *exo*-H-4′), 3.00–2.88 (m, 1H, H-1′), 2.27–2.20 (m, 1H, *exo*-H-7′), 1.94–1.86 (m, 1H, *endo*-H-7′and *exo*-H-7′) 1.49 (s, 3H, CH_3), 1.43–1.38 (m, 2H) 1.32 (s, 3H, CH_3), 1.30–1.24 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, DEPT) 175.4, 138.0, 132.5, 132.4, 128.8, 128.4, 127.9, 112.0, 105.4, 82.3, 81.9, 81.8, 78.4, 72.1, 49.8, 46.0, 42.3, 42.7, 29.9, 27.0, 26.4.

4.31. Specimen procedure for cycloaddition reactions with **17a**

$EtAlCl_2$ (0.33 mL, 0.33 mmol) was added to a solution of **17a** (0.14 g, 0.34 mmol) in dry (5 mL) and the solution stirred at −78 °C for 1 h. Freshly distilled cyclopentadiene (0.06 mL, 0.82 mmol) was added to the solution *via* syringe, and the mixture stirred at −78 °C for a further 2 h. The reaction was quenched with water (10 mL) and the mixture extracted with ether (3 × 50 mL). The ethereal extracts were condensed *in vacuo*, the residue resuspended in CH_2Cl_2 (10 mL) and exposed to direct sunlight for 2 h. The solution was then filtered through a plug of silica gel, condensed *in vacuo* and the residue purified by SGC (95:5 through 60:40 hexanes:EtOAc) to give decomplexed adduct **9** (R = benzyl isommanoyl) (0.094 g, 81%) as colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.27 (m, 4H), 7.27–7.24 (dd, $J = 5.1$ Hz, 2.4 Hz, 1H), 6.15–6.12 (dd, $J = 5.7$ Hz, 3.0 Hz, 1H), 5.95–5.92 (dd, $J = 5.7$ Hz, 2.7 Hz, 1H), 5.01–4.97 (q, $J = 6.0$ Hz, 1H), 4.72–4.68 (d, $J = 12.0$ Hz, 1H), 4.61 (t, $J = 5.1$ Hz, 1H), 4.41 (t, $J = 5.1$ Hz, 1H), 4.00–3.86 (m, 4H), 3.63 (t, $J = 8.2$ Hz, 1H), 3.18 (s, 1H), 2.96–2.93 (m, 1H), 2.84 (s, 1H), 1.87–1.79 (m, 2H), 1.39–1.36 (dd, $J = 10.5$ Hz, 3.9 Hz, 2H) and 1.23–1.20 (dd, $J = 8.1$ Hz, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 137.4, 137.1, 132.2, 128.1, 127.6, 80.3, 79.8, 78.5, 73.5, 72.1, 71.0, 69.9, 49.3, 45.8, 42.5, 42.2, and 28.8; IR (neat) 3123, 2978, 1723, 1475, and 1056 cm^{-1}; MS (m/e) 354 (M − 2, 17.9%), 355 (M − 1, 11.9), 356 (M^+, 25.5), 357(M+1, 12.8); $[\alpha]_D = +134.91$ ($c = 0.22$,$CHCl_3$); HPLC (Daicel OD, 90:10 hexanes:IPA as eluent, 1 mL/min, $\lambda = 254$ nm) t_R 18.13 min minor(S), t_R 19.80 min major (R); Anal. Calc. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.82; H, 6.82%. Alternatively, reductive cleavage of adducts could be conducted [$LiAlH_4$, 0 °C, 2 h] to liberate the corresponding *endo R* norbornene-2-methanol [11]; ^1H NMR (300 MHz, $CDCl_3$) 6.10–6.14(m, 1H), 5.92–5.96(m, 1H), 3.19–3.4(m, 2H), 2.91(s. 1H), 2.79(s, 1H), 2.22–2.32(m, 1H), 1.76–1.84(m, 2H), 1.23–1.45(m, 2H), 0.47–0.54(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.6, 132.4, 66.7, 49.7, 43.8, 42.4, 41.9, 29.0; $[\alpha]_D = +95°$ ($c = 0.6$, 95% EtOH).

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