# Synthesis of phenyl 2-acryloyloxybornane-10-sulfonate diastereomers

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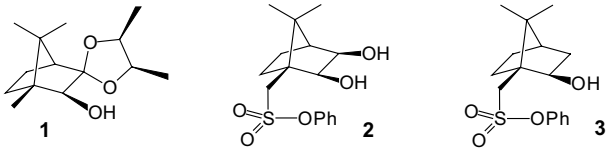
Several routes to phenyl 2-*exo*- and 2-*endo*-acryloyloxybornane-10-sulfonate have been investigated. Preparation of the former product is complicated by concomitant formation of 10-isobornylsultone, while addition of HCl is observed when the alcohol precursors are treated with acryloyl chloride in the presence of $Al_2O_3$. An X-ray crystal structure has been determined for one of the chlorinated derivatives.

**Keywords:** camphor-10-sulfonic acid, chiral auxiliaries, Baylis–Hillman substrates

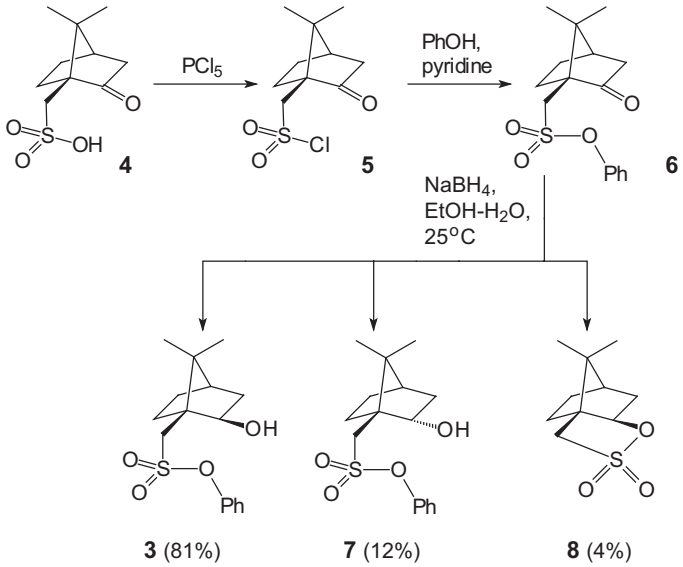
In recent years, the Baylis–Hillman reaction has enjoyed considerable attention[1] and, in our own laboratories, it has found application in the synthesis of various benzannulated heterocyclic systems.[2] The reaction typically proceeds with the formation of a new stereogenic centre and several approaches to achieving stereoselectivity have been reported.[3] In a previous asymmetric Baylis–Hillman study, using the camphor-derived chiral auxiliary **1**, we reported low diastereomeric excesses (<35%);[4] we have, however, observed excellent stereoselectivity (>99% d.e.) in the Simmons–Smith cyclopropanation of acetals of α,β-unsaturated aldehydes and phenyl 2,3-dihydroxybornane-10-sulfonate **2**.[5] Encouraged by the latter result, we decided to explore the use of phenyl 2-*exo*-hydroxybornane-10-sulfonate **3** as a chiral auxiliary for asymmetric Baylis–Hillman reactions.




The isobornyl derivative **3** was obtained following the approach summarised in Scheme 1. Thus, commercially available camphorsulfonic acid **4** was treated with phosphorus pentachloride ($PCl_5$),[6] to give camphorsulfonyl chloride **5** in 59% yield. Addition of phenol to the sulfonyl chloride **5** in pyridine then afforded phenyl camphor-10-sulfonate **6**[7] in 78% yield. Reduction of the carbonyl group in the camphor-10-sulfonate **6** was effected with $NaBH_4$ under various conditions (Table 1), the most efficient being the use of 10 equivalents of $NaBH_4$ in EtOH–$H_2O$ (2 : 1) at –8°C to afford the 2-*exo*-hydroxy product **3** in 81% yield. While preferential hydride delivery from the less hindered *endo*-face of the bicyclo substrate **6** accounts for the formation of the *exo*-alcohol **3** as the dominant product, the *endo*-hydroxy isomer **7** (12%) and the known sultone **8** (4%) were also isolated as competition products.

Interestingly, the sultone **8** was isolated as the sole product (94%) when the reaction was conducted at 25°C, its formation being attributed to deprotonation of the *exo*-alcohol **3** in the basic reaction medium, followed by cyclisation *via* nucleophilic displacement of phenoxide ion from the phenyl sulfonate ester group. There was, however, no evidence of the analogous *endo*-cyclised sultone due, presumably, to unfavourable orientation of the reactive centres. Assignment of the stereochemistry at the new stereogenic centre (C-2) in each of the products was based, largely, on analysis of the NMR signals for the 2-H nuclei and their correlation with the 5-, 6-, 8- and 10-H nuclei.

With the phenyl 2-*exo*-(**3**) and 2-*endo*-hydroxybornane-10-sulfonate (**7**) esters in hand, attention was given to generating the corresponding acrylate esters (Scheme 2). Several




**Scheme 1**

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**Table 1** Data for the reduction of phenyl camphor-10-sulfonate **6**

| Product | Reaction conditions | | | |
|---|---|---|---|---|
| | 1 eq. $NaBH_4$, EtOH, 0°C, 12 h Yield (%) | 1 eq. $NaBH_4$, 2-propanol, 0°C, 12 h Yield (%) | 10 eq. $NaBH_4$, $EtOH/H_2O$ (2:1), –8°C, 8 h Yield (%) | 10 eq. $NaBH_4$, abs. EtOH, 25°C, 12 h Yield (%) |
| **3** | 11.2 | 10.7 | 81 | 0 |
| **7** | 1.3 | 1.0 | 12 | 0 |
| **8** | 23.1 | 22.3 | 4 | 94 |

approaches were explored. In the first, the *exo*-hydroxy isomer **3** was treated with BuLi at –78°C, followed by acryloyl chloride at < –10°C. Since formation of the sultone **8** during the reduction of the camphor derivative **6** only appeared to occur significantly at temperatures above –10°C, competitive cyclisation of the alkoxide intermediate to the sultone **8** was not expected to intervene. In the event, the sultone **8** proved to be the major product (79%), with concomitant acylation of the displaced phenoxide ion affording phenyl acrylate **10** in 76% yield; the required acrylate ester **9** was isolated in only 5% yield. A second approach using DMAP, as a nucleophilic catalyst, $Et_3N$ and acryloyl chloride in dichloromethane failed to produce any of the required acrylate ester **9**. Finally, treatment of phenyl 2-*exo*-hydroxybornane-10-sulfonate **3** with $Al_2O_3$ and acryloyl chloride, in the absence of solvent, afforded the acrylate ester **9** in reasonable yield (55%), together with the hydrochlorinated product **11**. Formation of the latter product is attributed to the addition of HCl, liberated during the reaction, to the acrylate ester **9**. The structure of the hydrochlorinated product **11** was established by single crystal X-ray analysis (Fig. 1), which provided independent confirmation of the *exo*-orientation of the C-2 (C17) substituent. Molecular parameters for compound **11** are normal and the crystal structure is maintained by van der Waals forces and several C–H···O hydrogen bonds with C···O in the range 3.269(4)–3.334(4) Å.

Treatment of the *endo*-hydroxy isomer **7** with BuLi at –78°C, followed by acryloyl chloride at < –10°C afforded the 2-*endo*-acryloyloxy derivative **12** in 77% yield without competitive formation of the *endo*-sultone. However, as was the case with the *exo*-hydroxy isomer **3**, use of $Al_2O_3$ and acryloyl chloride,

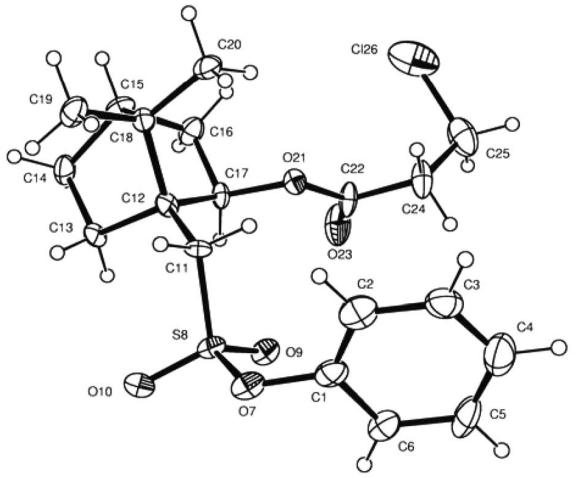
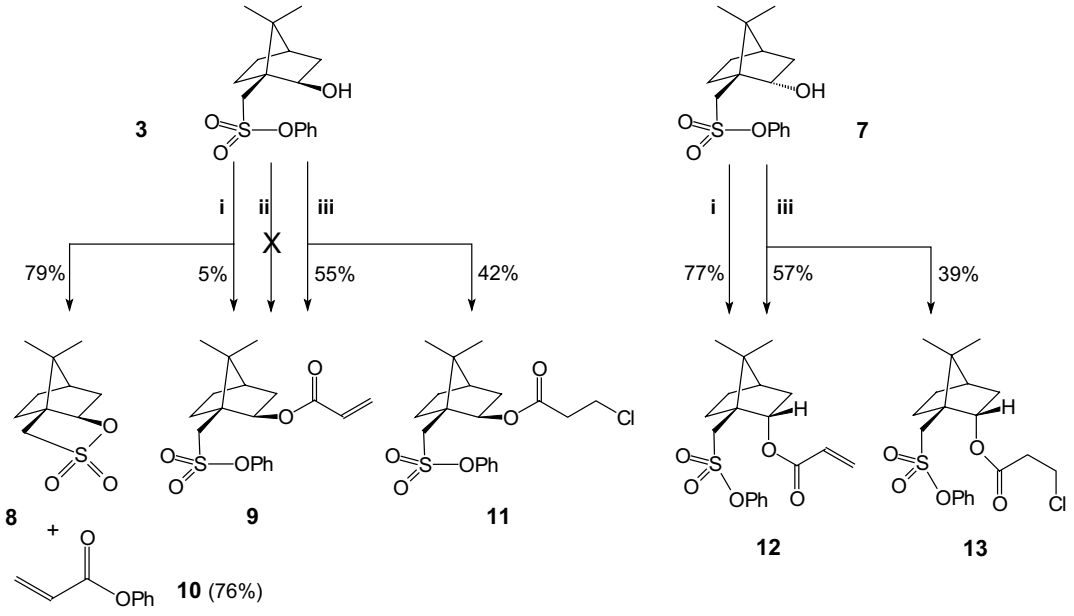



**Fig. 1** X-ray crystal structure of phenyl 2-*exo*-(3-chloropropanoyloxy)bornane-10-sulfonate **11**, showing the crystallographic numbering and thermal ellipsoids drawn at the 50% probability level.

in the absence of solvent, gave both the desired acrylate ester **12** (57%) and the corresponding hydrochlorinated product **13**.

Computer modelling, at the molecular mechanics level, of the putative, zwitterionic Baylis–Hillman intermediate **14** {following conjugate addition of 1,4-diazabicyclo-[2.2.2]octane (DABCO) to phenyl 2-*exo*-acryloyloxybornane-10-sulfonate **9**} (Fig. 2) suggests that the steric bulk of the phenyl sulfonate moiety at C-10 could well induce




**Scheme 2** Reagents and conditions: (i) BuLi, THF, –78°C then acryloyl chloride, –10°C; (ii) DMAP, $CH_2Cl_2$, –10°C then acryloyl chloride, $Et_3N$; (iii) $Al_2O_3$, acryloyl chloride, r.t.

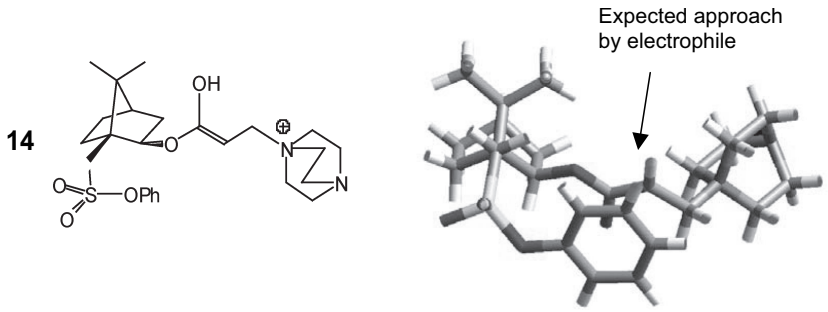



**Fig. 2** Line- and computer-modelled structures of the putative, zwitterionic Baylis–Hillman intermediate **14**, showing expected approach of the electrophilic aldehyde in a Baylis–Hillman reaction.

diastereofacial selectivity in the approach of an attacking electrophile. Future work is expected to focus on applications of phenyl 2-*exo*-hydroxybornane-10-sulfonate **3** as a chiral auxiliary in Baylis–Hillman and other reactions.

## Experimental

NMR spectra were recorded on Bruker AMX400 or AVANCE 400 MHz spectrometers at 303 K in $CDCl_3$, and calibrated using solvent signals. Low-resolution (EI) mass spectra were obtained on a Finnigan-Mat GCQ mass spectrometer and high-resolution (EI) mass spectra on a VG70-SEQ double-focusing magnetic sector spectrometer (Cape Technikon Mass Spectrometry unit or Department of Chemistry, University of the Witwatersrand). Optical rotations were measured on a Perkin Elmer 141 polarimeter using a 1 dm cell, with concentrations cited in g/100 ml. Computer modelling was conducted at the molecular mechanics level using the Accelrys Cerius$^2$ software package on an SGI $O^2$ computer. Optically pure compounds were derived from commercially available, homochiral, (1*R*)-(+)-camphor. Compounds **5**, **6**, **8** and **10** are known.[6-9]

*Phenyl (1*S*,2*R*,4*R*)-2*-exo-*hydroxybornane-10-sulfonate* **3,** *phenyl (1*S*,2*S*,4*R*)-2*-endo-*hydroxybornane-10-sulfonate* **7** *and 10-isobornyl sultone* **8**: A solution of phenyl (+)-camphor-10-sulfonate **6** (2.37 g, 7.7 mmol) in ethanol (5 ml) was added to a stirred solution of $NaBH_4$ (0.10 g, 2.7 mmol) in EtOH–$H_2O$ (10 ml, 5 ml) at –15°C over 20 min. The solution was stirred vigorously for 16 h at –8°C. 5% aq. HCl was added drop-wise to quench excess $NaBH_4$. Solvent was removed under reduced pressure, and the residue was dissolved in $Et_2O$ (8 ml), washed with brine (3 × 3 ml) and then dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give an oil, which was purified [flash chromatography on silica gel; hexane-EtOAc (8 : 2)] to afford three products:

(i) *phenyl (1*S*,2*R*,4*R*)-2*-exo-*hydroxybornane-10-sulfonate* **3**, as an oil (1.94 g, 81.0%) (Found: $M^+$, 310.12333. $C_{16}H_{22}O_4S$ requires *M*, 310.12388); $[\alpha]_D^{20}$ = –35.16° (*c* 4.42, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.85 (3H, s, 9-Me), 1.07 (3H, s, 8-Me), 1.12–1.87 (7H, complex of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 2.82 (1H, d, *J* = 4.4 Hz, 2-OH), 3.15 and 3.73 (2H, 2 × d, *J* = 13.67 Hz, 10-$CH_2$), 4.11 (1H, m, 2-CH) and 7.25–7.44 (5H, complex of multiplets, Ar-H); $\delta_C$ (100 MHz; $CDCl_3$) 20.5 (C-9), 19.8 (C-8), 27.3 (C-5), 30.2 (C-6), 39.2 (C-3), 44.4 (C-4), 49.0 (C-7), 50.0 (C-1), 50.3 (C-10), 76.1 (C-2) and 122.0, 127.3, 130.0 and 149.0 (Ar-C); *m/z* 310 ($M^+$, 0.3%) and 94 (100);

(ii) *phenyl* (*1*S, *2*S, *4*R)-*2*-endo-*hydroxybornane-10-sulfonate* **7**, as an oil (0.28 g, 11.5%) (Found: $M^+$, 310.12645. $C_{16}H_{22}O_4S$ requires *M*, 310.12388); $[\alpha]_D^{20}$ = + 17.95° (*c* 0.44, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.92 (3H, s, 9-Me), 0.93 (3H, s, 8-Me), 1.14–2.53 (7H, series of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 3.14 (1H, d, *J* = 2.2 Hz, 2-$OH_{endo}$), 3.34 (2H, s, 10-$CH_2$), 4.39 (1H, dd, *J* = 10.0 and 2.5 Hz, 2-$H_{exo}$) and 7.28, 7.32 and 7.42 (5H, complex of multiplets, Ar-H); $\delta_C$ (100 MHz; $CDCl_3$) 18.9 (C-8), 20.5 (C-9), 23.8 (C-6), 28.1 (C-5), 38.2 (C-3), 44.0 (C-4), 51.0 (C-7), 51.9 (C-1), 54.3 (C-10), 75.1 (C-2) and 122.0, 127.4, 130.0 and 148.7 (Ar-C); *m/z* 310 ($M^+$, 0.5%) and 94 (100); and

(iii) *10-isobornyl sultone* **8** (0.058 g, 3.5%), m.p. 109–112°C (Lit.[8] 114–116°C).

*Phenyl 2*-exo-*acryloyloxybornane-10-sulfonate* **9** *and phenyl 2*-exo-*(3-chloropropanoyloxy)-bornane-10-sulfonate* **11**

*Method 1*

Neutral $Al_2O_3$ (0.32 g, 3.1 mmol) was added to the alcohol **3** (0.61 g, 2.0 mmol) and acryloyl chloride (0.39 g, 4.3 mmol) was then added. The resulting dispersion was sealed and kept unstirred at 25°C for 72 h. The residue was taken up in EtOAc (3 × 1 ml), filtered and dried over anhydrous $MgSO_4$. Solvent was removed *in vacuo* to give an oil, which was chromatographed [HPLC; elution with hexane-EtOAc (8 : 2)] to afford two products:

(i) *(1*S*,2*R*,4*R*)-2*-exo-*acryloyloxybornane-10-sulfonate* **9** (0.40 g, 55%) (Found: $M^+$, 364.13395. $C_{19}H_{24}O_5S$ requires *M*, 364.13445); $[\alpha]_D^{20}$ = –30.52° (*c* 2.90, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.91 and 1.02 (6H, 2 × s, 8- and 9-Me), 1.22–1.98 (7H, series of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 3.14 and 3.67 (2H, 2 × d, *J* = 13.9 Hz, 10-$CH_2$), 5.01 (1H, dd, *J* = 3.1 and 7.9 Hz, 2-CH), 5.68 (1H, dd, *J* = 1.4 and 10.4 Hz, 3'-$H_a$), 5.92 (1H, dd, *J* = 10.4 and 17.3 Hz, 2'-H), 6.19 (1H, dd, *J* = 17.3 and 1.4 Hz, 3'-$H_b$) and 7.18–7.41 (5H, complex of multiplets, Ar–H); $\delta_C$ (100 MHz; $CDCl_3$) 19.9 and 20.3 (C-8 and C-9), 26.9, 29.9 and 39.3 (C-3, C-5 and C-6), 44.5 (C-4), 48.8 and 49.5 (C-1 and C-7), 49.3 (C-10), 77.5 (C-2), 121.9, 127.0, 129.8 and 149.0 (Ar–C), 128.5 (C-2'), 130.3 (C-3') and 164.6 (C-1'); *m/z* 364 ($M^+$, 0.8%) and 55 (100); and

(ii) *phenyl (1*S*,2*R*,4*R*)-2*-exo-*(3-chloropropanoyloxy)bornane-10-sulfonate* **11** (0.33 g, 42%) m.p. 117–119°C (Found: $M^+$, 400.10707. $C_{19}H_{25}ClO_5S$ requires *M*, 400.11112); $[\alpha]_D^{20}$ = –70.51° (*c* 2.14, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.92 and 1.03 (6H, 2 × s, 8- and 9-Me), 1.24–1.99 (7H, series of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 2.58 (2H, m, 2'-$CH_2$), 3.17 and 3.69 (2H, 2 × d, *J* = 13.9 Hz, 10-$CH_2$), 3.60 (2H, m, 3'-$CH_2$), 4.99 (1H, dd, *J* = 3.2 and 8.0 Hz, 2-CH) and 7.21–7.44 (5H, complex of multiplets, Ar-H); $\delta_C$ (100 MHz; $CDCl_3$) 19.9 and 20.3 (C-8 and C-9), 26.9, 30.1 and 39.3 (C-3, C-5 and C-6), 37.6 (C - 2'), 38.9 (C- 3'), 44.6 (C- 4), 48.8 and 49.6 (C-1 and C-7), 49.4 (C-10), 78.1 (C-2), 122.1, 127.2, 129.9 and 149.1 (Ar-C) and 168.7 (C-1'); *m/z* 400 ($M^+$, 2.0%) and 94 (100).

*Method 2*

Butyllithium (1.6 **M** solution in hexane; 0.28 ml, 0.5 mmol) was added drop-wise over 20 min, under dry $N_2$, to a stirred solution of phenyl (+)-2-*exo*-hydroxybornane-10-sulfonate **3** (0.13 g, 0.4 mmol) in dry THF (2 ml) at –78°C. After 1 h, acryloyl chloride (0.04 g, 0.5 mmol) was added drop-wise, the mixture was stirred at –10°C for 1 h and then allowed to warm to room temperature over 12 h. The THF was removed *in vacuo* and the residue was quenched with saturated aqueous $NaHCO_3$ (1 ml), extracted with $Et_2O$ (3 × 1 ml) and dried over anhydrous $MgSO_4$. Concentration under reduced pressure gave an oil, which was chromatographed [HPLC; elution with hexane–EtOAc (9 : 1)] to give phenyl 2-*exo*-acryloyloxybornane-10-sulfonate **9** (0.15 g, 5%) together with 10-isobornyl sultone **8** (0.09 g, 79%) and phenyl acrylate **10** (0.05 g, 82%).

*Phenyl 2*-endo-*acryloyloxybornane-10-sulfonate* **12** *and phenyl 2*-endo-*(3-chloropropanoyloxy)bornane-10-sulfonate* **13**

*Method 1*

The experimental procedure employed for the synthesis of 2-*exo*-acryloyloxybornane-10-sulfonate **9** and phenyl 2-*exo*-(3-chloropropanoyloxy)bornane-10-sulfonate **11** (Method 1) was followed, using neutral $Al_2O_3$ (0.14 g, 1.4 mmol), phenyl (+)-2-*endo*-hydroxybornane-10-sulfonate **7** (0.27 g, 0.9 mmol) and acryloyl chloride (0.18 g, 2.0 mmol). Work-up and chromatography [using

silica gel on a chromatotron, 1 mm plate; elution with hexane-EtOAc (8 : 2)] afforded two products:

(i) *phenyl (1S,2S,4R)-2-*endo-*acryloyloxybornane-10-sulfonate* **12** (0.18 g, 57%) (Found: $M^+$, 364.13465. $C_{19}H_{24}O_5S$ requires *M*, 364.13445); $[\alpha]_D^{20}$ = –61.03° (*c* 2.04, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.96 and 1.00 (6H, 2 × s, 8- and 9-Me), 1.09–2.65 (7H, series of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 3.26 and 3.35 (2H, 2 × d, *J* = 14.1 Hz, 10-$CH_2$), 5.26 (1H, dt, *J* = 2.6 and 9.8 Hz, 2-H), 5.80 (1H, dd, *J* = 1.3 and 10.5 Hz, 3'-$H_Z$), 6.11 (1H, dd, *J* = 10.5 and 17.4 Hz, 2'-H), 6.43 (1H, dd, *J* = 1.3 and 17.4 Hz, 3'-$H_E$), 7.22–7.39 (5H, complex of multiplets, Ar–H); $\delta_C$ (400 MHz; $CDCl_3$) 19.1 and 19.9 (C-8 and C-9), 25.3, 27.9 and 37.4 (C-3, C-5 and C-6), 44.2 (C-4), 49.7 and 50.8 (C-1 and C-7), 53.3 (C-10), 76.8 (C-2), 122.0 (C-13 and C-15), 127.0 (C-14), 128.6 (C-2'), 129.9 (C-12 and C-16), 130.8 (C-3'), 149.3 (C-2) and 166.0 (C-1'); *m/z* 364 ($M^+$, 0.1%) and 55 (100); and

(ii) *phenyl (1S,2S,4R)-2-*endo-*(3-chloropropanoyloxy)bornane-10-sulfonate* **13** (0.14 g, 39%) (Found: $M^+$, 400.10875. $C_{19}H_{25}ClO_5S$ requires *M*, 400.11112); $[\alpha]_D^{20}$ = –87.7° (*c* 1.02, $CHCl_3$); $\delta_H$ (400 MHz; $CDCl_3$) 0.96 and 0.99 (6H, 2 × s, 8- and 9-Me), 1.12–2.57 (7H, series of multiplets, 3-, 5- and 6-$CH_2$ and 4-H), 2.81 (2H, t, *J* = 6.9 Hz, 2'-$CH_2$), 3.26 and 3.32 (2H, 2 × d, *J* = 13.9 Hz, 10-$CH_2$), 3.76 (2H, dt, *J* = 1.1 and 7.0 Hz, 3'-$CH_2$), 5.26 (1H, d, *J* = 9.8 Hz, 2-CH), 7.21–7.44 (5H, complex of multiplets, Ar–H); $\delta_C$ (100 MHz; $CDCl_3$) 19.1 and 19.8 (C-8 and C-9), 25.3, 27.9 and 37.3 (C-3, C-5 and C-6), 37.7 (C-2'), 39.1 (C-3'), 44.1 (C-4), 49.6 and 50.9 (C-1 and C-7), 53.3 (C-10), 77.1 (C-2), 122.0, 127.1, 129.9, 149.2 (Ar-C) and 170.1 (C-1'); *m/z* 400 ($M^+$, 0.3%) and 135 (100).

*Method 2*

The experimental procedure employed for the synthesis of 2-*exo*-acryloyloxybornane-10-sulfonate **9** (Method 2) was followed, using butyllithium (1.6 M solution in hexane; 0.28 ml, 0.5 mmol), phenyl (+)-2-*endo*-hydroxybornane-10-sulfonate **7** (0.10 g, 0.3 mmol) and acryloyl chloride (0.033 g, 0.4 mmol) in dry THF (2 ml). Work-up and radial chromatography [using silica gel on a 1 mm plate; elution with hexane–EtOAc (8 : 2)] afforded transparent crystals of phenyl 2-*endo*-acryloyloxybornane-10-sulfonate **12** (0.09 g, 76.5%).

*X-Ray analysis of phenyl (1S,2S,4R)-2-exo-(3-chloropropanoyloxy) bornane-10-sulfonate* **11**

*Crystal data* **11**: $C_{19}H_{25}ClO_5S$, $M_r$ = 400.91, orthorhombic, $P2_12_12_1$, *a* = 7.0692(1), *b* = 7.5925(1), *c* = 36.0280(6) Å, *V* = 1933.73(5) Å$^3$, $D_x$ = 1.377 g cm$^{-3}$, *Z* = 4, μ = 0.332 mm$^{-1}$, *T* = 113K. Intensity data were collected from a colourless fragment cooled in a stream of nitrogen vapour (Cryostream cooler, Oxford Cryosystems) using a Nonius Kappa CCD diffractometer and Mo-Kα radiation (λ = 0.71073 Å). No phase change occurred on cooling the specimen from ambient temperature. Cell refinement and data reduction were performed with DENZO-SMN.[10] Data reduction included Lorentz-polarisation corrections and empirical absorption corrections with program SADABS.[11] The structure was solved with SHELXS-86[12] and refined on $F^2$ with SHELXL-97.[13] All H atoms were identified in difference electron density maps but were added in idealised positions in a riding model with isotropic displacement parameters 1.2 times those of their parent atoms. All non-hydrogen atoms were treated anisotropically. The final cycle of refinement was based on 3681 reflections and 238 variable parameters and converged at $R_1$ = 0.0430 (2450 reflections with $I > 2\sigma(I)$), $wR_2$ = 0.0973 and *S* = 0.994. The final difference electron density was 0.34 eÅ$^{-3}$. The correct choice of absolute structure was indicated by the Flack parameter value of –0.07(8). Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC 609071).

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