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Enantiomerically Pure 5-Substituted 2-Oxo-cyclopentanecarboxylates by Conjugate Addition of Cuprates to Asymmetric Shielded 2-Oxo-cyclopentenecarboxylates

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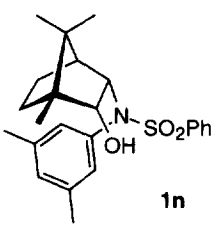
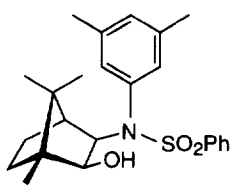
Abstract: Asymmetric shielded 2-oxo-cyclopentenecarboxylates **6n** and **6x** were prepared by transesterification of 2-oxo-cyclopentanecarboxylate **2** with camphor derived concave alcohols **1n** and **1x** and by subsequent introduction of a double bond via phenylselenides. Diastereoselective conjugate addition of equimolar amounts of mixed cuprates at -78 °C and deprotection by ethanolysis gave enantiomerically pure 5-substituted 2-oxo-cyclopentanecarboxylates **13-18** and *ent*-**13-18**, valuable as chiral building blocks in natural product synthesis.

Conjugate additions of cuprates to enoates have been widely employed for asymmetric carbon-carbon-bond formations in syntheses of chiral building blocks.[1] Particularly successful was the conjugate addition of organocopper compounds to enoates of camphor derived chiral auxiliaries.[1-3] Best results were obtained on additions to enoates derived from concave alcohols **1n** and **1x**, which generally proceeded with an extremely high diastereoselectivity (>99%) and in excellent yields (>90%).[3] Recently we extended these studies to cyclic enoates and demonstrated the usefulness of asymmetric protected 2-oxo-cyclohexenecarboxylates for the EPC synthesis of 6-substituted 2-oxo-cyclohexanecarboxylates.[4] In conjunction with a project aiming at the EPC synthesis of (-)-chokol A[5] we have investigated conjugate additions to asymmetric protected 2-oxo-cyclopentenecarboxylates derived from **1n** and **1x** and are now able to present an EPC synthesis of 5-substituted 2-oxo-cyclopentanecarboxylates.

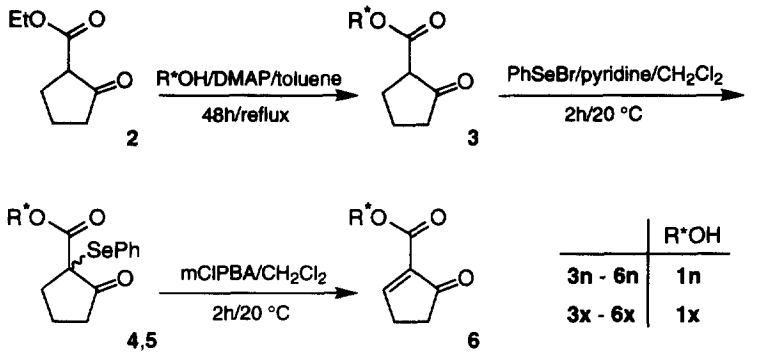


1n



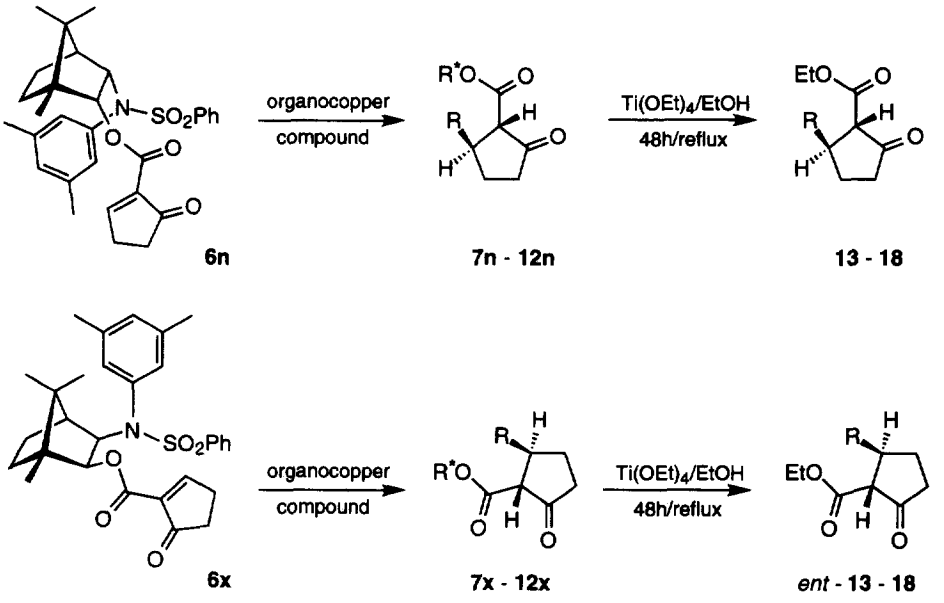
1x

Asymmetric shielded 2-oxo-cyclopentanecarboxylates were readily available from auxiliaries **1n** or **1x** and racemic 2-oxo-cyclopentanecarboxylate **2**. We obtained the well crystallizing esters **3n** (98%) and **3x** (99%) in excellent yields using a DMAP[6] mediated transesterification reaction[7] first reported by Taber.[8] Phenylselenylation[9] of **3n** and **3x** gave mixtures of diastereomeric selenides (**4n**:**5n** = **4x**:**5x** = 80:20) which were separated by chromatography. Oxidative deselenylation of **4n** or **5n** and **4x** or **5x** afforded enoates **6n** and **6x** in good yields (81-90%), respectively.



Scheme 1

Preparative scale synthesis of enoates **6n** (75%) and **6x** (78%) was manufactured by a one pot procedure starting from **3n** and **3x** without isolation of the intermediate selenides. In contrast to an anticipation[10] the enoates **6n** and **6x** were stable and could be stored without precautions.



	R*OH
7n - 12n	**1n**
7x - 12x	**1x**

	R
7,13	CH_3
8,14	nBu
9,15	tBu

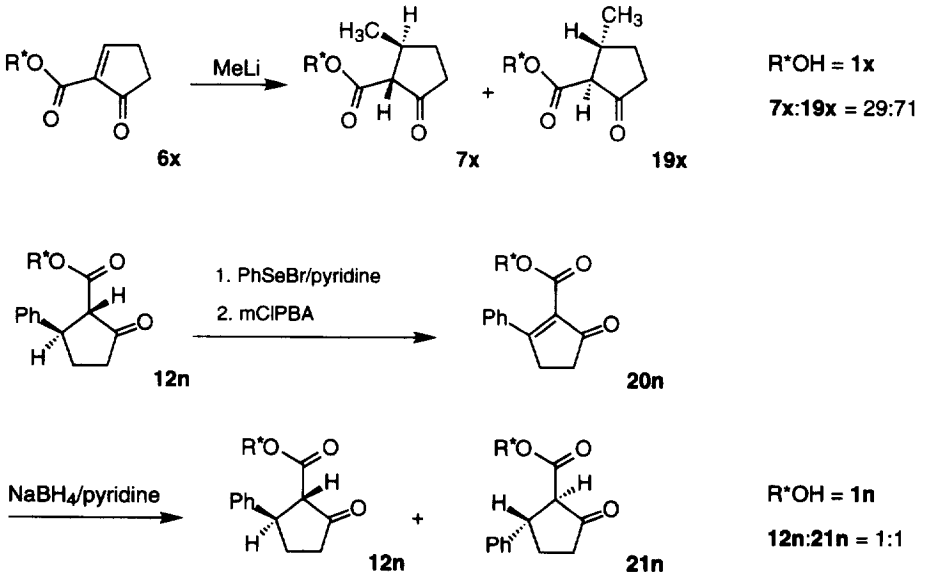
	R
10,16	H_2C=CH
11,17	H_2C=C-CH_3
12,18	Ph

Scheme 2

Table 1. Cuprate Addition to Asymmetric Shielded Enoates and Deprotection by Ethanolysis.

Enone	R	Cuprate Precursor	Cuprate Adduct	Yield (%)	Ethyl-ester	Yield (%)	$[\alpha]_D^{20}$
6n	CH_3	R-Li	**7n**	73	**13**	76	+94.00
6n	nBu	R-Li	**8n**	80	**14**	88	+81.58
6n	tBu	R-Li	**9n**	59	**15**	93	+94.61
6n	H_2C=CH	R-MgBr	**10n**	68	**16**	82	+85.05
6n	H_2C=C(CH_3)	R-Li	**11n**	63	**17**	81	+69.88
6n	Ph	R-Li	**12n**	56	**18**	79	+18.55
6x	CH_3	R-Li	**7x**	74	*ent*-**13**	75	-95.70
6x	nBu	R-Li	**8x**	69	*ent*-**14**	85	-81.26
6x	tBu	R-Li	**9x**	75	*ent*-**15**	90	-95.69
6x	H_2C=CH	R-MgBr	**10x**	80	*ent*-**16**	82	-85.61
6x	H_2C=C(CH_3)	R-Li	**11x**	75	*ent*-**17**	79	-70.21
6x	Ph	R-Li	**12x**	71	*ent*-**18**	76	-18.30

Next we studied the addition of Lipshutz cuprates[11] to **6n** and **6x** (see Table 1) and obtained 5-substituted 2-oxo-cyclopentanecarboxylates **7n-12n** and **7x-12x** in good yields (56-80%) and with an extremely high level of diastereoselection. In contrast to results obtained from cuprate addition to **6x** the conjugate addition of methyllithium gave a mixture of diastereomers with opposite diastereoselection (**7x**:**19x** = 29:71). Chromatographic separation afforded diastereomerically pure **19x** which we required for HPLC analysis.



Scheme 3

Table 2. ^{13}C NMR Shifts ($CDCl_3$, δ in ppm) of the Auxiliary Protected Derivatives **3n-12n** and **21n**.[a]

	3na[b]	**3nb**[b]	**4n**	**5n**	**6n**	**7n**	**8n**	**9n**	**10n**	**11n**	**12n**[c]	**21n**
C-1	51.67	51.11	51.77	51.63	51.30	51.26	51.31	51.64	51.27	51.43	51.33	51.72
C-2	76.93	76.53	77.72	77.75	76.26	77.27	77.43	78.36	77.58	77.78	77.80	77.42
C-3	59.13	59.20	59.27	59.17	59.26	59.42	59.36	59.39	59.32	59.32	59.20	59.20
C-4	49.88	49.42	49.12	49.31	49.80	49.45	49.40	49.06	49.40	49.26	49.33	49.26
C-5	19.59	19.54	19.61	19.58	19.61	19.51	19.51	19.59	19.50	19.50	19.49	19.54
C-6	26.89	26.79	26.70	26.91	26.69	26.68	26.60	26.26	26.59	26.47	26.43	26.47
C-7	45.53	45.61	45.66	45.65	45.57	45.68	45.71	45.92	45.68	45.73	45.64	45.69
Ar–CH_3	21.13	20.99	21.27	21.22	21.14	21.14	21.14	21.21	21.12	21.16	21.12	21.26
Ar–CH_3	20.94	20.87	20.92	20.96	20.93	20.93	20.94	20.92	20.92	20.91	20.89	20.96
CH_3	19.54	19.47	19.52	19.53	19.49	19.51	19.51	19.50	19.46	19.50	19.44	19.54
CH_3	19.47	19.30	19.23	19.21	19.41	19.39	19.39	19.37	19.36	19.35	19.32	19.29
CH_3	14.20	13.99	14.39	14.35	14.16	14.18	14.24	14.53	14.23	14.39	14.31	14.47
NAr C-1	136.76	136.26	136.34	136.43	136.50	137.22	137.25	137.81	137.09	137.22	136.98	136.80
NAr C-2	129.93	128.74	130.98	130.60	128.55	130.03	130.07	130.92	129.87	130.48	129.96	130.32
NAr C-3	138.17	138.27	138.42	138.33	138.18	138.18	138.16	138.33	138.15	138.23	138.13	138.50
NAr C-4	129.46	129.16	129.27	129.31	129.19	129.29	129.30	129.43	129.30	129.33	129.27	129.53
NAr C-5	138.13	136.92	136.61	136.84	137.01	137.04	137.02	137.09	137.01	137.02	136.98	137.02
NAr C-6	127.45	127.96	127.10	127.29	127.99	127.47	127.47	127.47	127.48	127.42	127.45	127.50
SO_2Ar C-1	139.03	139.58	138.68	138.94	139.36	139.06	139.06	138.65	139.05	138.88	139.01	138.87
SO_2Ar C-2, C-6	128.17	128.41	128.33	128.39	128.24	128.09	128.10	128.13	128.10	128.12	128.12	128.35
SO_2Ar C-3, C-5	128.17	128.22	128.12	128.13	128.13	128.09	128.10	127.97	128.06	128.07	128.03	128.17
SO_2Ar C-4	132.56	132.66	132.58	132.59	132.56	132.38	132.36	132.29	132.38	132.36	132.36	132.56
COO	168.48	168.78	169.66	168.90	160.90	168.66	168.64	169.41	167.83	167.92	167.64	168.76
C-1'	55.28	54.99	59.80	58.85	137.18	63.23	62.03	57.40	60.72	59.38	61.26	61.43
C-2'	212.56	212.80	209.01	207.92	202.72	212.24	212.05	212.54	210.64	210.72	210.10	211.39
C-3'	38.48	38.23	37.65	37.19	35.59	38.82	38.51	38.96	38.07	38.26	38.67	39.40
C-4'	21.40	21.27	19.93	19.27	27.18	29.15	22.62	22.24	26.54	26.17	29.06	30.17
C-5'	27.70	27.07	34.83	34.46	171.53	35.49	40.08	49.70	43.38	46.55	44.70	46.63

[a] Further data are presented in the experimental part.

[b] We obtained an unseparable mixture of 1'R and 1'S configurated β-ketoesters, **3na**:**3nb** = 52:48.

[c] **12n** showed both signals of the kentone and the enol form (ketone:enol = 67:33).

HPLC analysis of the unpurified cuprate addition products outlined excellent selectivities (**7x**:**19n** = 99.5:0.5; **12n**: **21n** = 98:2). After purification of the raw products by flash chromatography and crystallization we were in fact unable, with help of HPLC and NMR, to find more but single diastereomers.

Preparation of **21n** (diastereomer to **12n**) was manufactured by an oxidation to enoate **20n** followed by reduction with sodium borohydride (see Scheme 3). Addition of the complex hydride resulted without diastereoselection (**12n**:**21n** = 1:1), but we were able to separate the mixture by chromatography.

Table 3. ^{13}C NMR Shifts ($CDCl_3$, δ in ppm) of the Auxiliary Protected Derivatives **3x-12x** and **19x**.[a]

	3xa[b]	**3xb**[b]	**4x**	**5x**	**6x**	**7x**	**8x**	**9x**	**10x**	**11x**	**12x**[c]	**19n**
C-1	50.33	50.80	51.11	50.71	50.38	50.42	50.52	50.99	50.55	50.69	50.60	50.96
C-2	82.00	81.63	82.51	82.44	81.03	82.18	82.32	83.18	82.47	82.54	82.61	81.88
C-3	67.47	67.41	67.41	67.45	67.43	67.52	67.53	67.54	67.52	67.46	67.42	67.47
C-4	48.69	48.56	48.56	48.66	48.63	48.46	48.49	48.36	48.49	48.44	48.45	48.65
C-5	27.69	27.80	27.96	27.86	27.58	27.68	27.76	27.99	27.75	27.75	27.73	27.95
C-6	32.13	32.13	32.23	32.23	32.04	32.12	32.18	32.35	32.19	32.21	32.22	32.21
C-7	47.43	47.23	47.23	47.24	47.33	47.35	47.35	47.39	47.39	47.29	47.27	47.22
Ar-CH_3	21.06	21.06	21.30	21.08	21.04	20.99	20.99	21.01	21.04	21.00	21.02	21.11
Ar-CH_3	20.96	20.96	21.30	21.08	21.04	20.99	20.99	21.01	21.04	21.00	21.02	21.11
CH_3	21.30	21.36	21.30	21.50	21.28	21.31	21.38	21.52	21.42	21.39	21.29	21.19
CH_3	20.96	20.96	20.57	20.56	20.67	20.69	20.69	20.73	20.72	20.64	20.61	20.58
CH_3	11.19	11.19	11.37	11.49	11.31	11.24	11.28	11.34	11.30	11.32	11.26	11.39
NAr C-1	137.06	136.23	136.09	136.26	136.71	137.18	137.27	137.60	137.20	137.08	137.25	136.44
NAr C-2	d	d	d	d	d	131.46	d	d	d	d	d	d
NAr C-3	d	d	d	d	d	138.08	d	d	d	d	d	d
NAr C-4	129.33	129.58	129.28	129.39	129.32	129.31	129.31	129.35	129.36	129.34	129.33	129.61
NAr C-5	d	d	d	d	d	137.00	d	d	d	d	d	d
NAr C-6	d	d	d	d	d	129.00	d	d	d	d	d	d
SO_2Ar C-1	138.79	138.65	138.33	138.60	138.94	138.51	138.57	138.32	138.58	138.49	138.59	138.48
SO_2Ar C-2, C-6	128.30	128.65	128.62	128.62	128.34	128.20	128.25	128.18	128.29	128.29	128.30	128.62
SO_2Ar C-3, C-5	128.09	128.09	128.05	128.03	128.07	128.00	127.99	128.02	128.03	127.97	127.97	128.10
SO_2Ar C-4	132.68	132.49	132.64	132.60	132.53	132.38	132.34	132.30	132.41	132.37	132.36	132.64
COO	168.81	168.32	169.58	168.50	160.67	168.29	168.16	168.75	167.58	167.33	167.24	168.70
C-1'	55.32	55.22	59.71	58.45	137.12	63.35	62.05	57.09	60.91	59.16	60.97	63.27
C-2'	212.67	212.67	208.93	207.44	202.79	212.02	211.66	211.99	210.51	210.16	209.72	212.51
C-3'	38.33	38.65	37.90	37.21	35.60	38.90	38.55	38.94	38.24	38.34	38.69	39.59
C-4'	20.75	20.57	19.88	19.16	26.69	29.15	22.62	22.13	26.58	26.29	29.47	30.15
C-5'	27.32	27.32	34.45	34.31	171.64	35.47	40.02	49.26	43.35	46.45	44.74	36.87

[a] Further data are presented in the experimental part.

[b] We obtained an unseparable mixture of 1'R and 1'S configurated β-ketoesters, **3xa**:**3xb** = 73:27.

[c] **12x** showed both signals of the ketone and the enol form (ketone:enol = 68:32).

[d] Signals were not detectable due to signal broadening caused by hindered rotation.

Removal of the chiral auxiliary from the sterically highly crowded 2-oxo-cyclopentanecarboxylates **7n-12n** and **7x-12x** was accomplished using a $Ti(OEt)_4$ mediated transesterification reaction[12] which allowed recycling of **1n** and **1x** (78-89%) and gave the enantiomerically pure ethylesters **13-18** and *ent*-**13-18** in good yields (Table 1). Comparison of the optical rotation of **13** allowed the determination of absolute configuration at C-5', because **13** was previously prepared from (R)-Pulegone[13].

The steric course of cuprate additions to **6n** and **6x** can be rationalized by an attack of the organocopper nucleophile from the less hindered halfspace of the *s-trans* enoate reactive species (Scheme 2), as it was found for simpler acyclic enoates[3] and 2-oxo-cyclohexenecarboxylates.[4]

In conclusion, the present conjugate addition approach to 5-substituted 2-oxo-cyclopentanecarboxylates enable a short and extremely stereoselective route to valuable intermediates in natural product synthesis.

EXPERIMENTAL SECTION

Melting points were determined with a Büchi glass capillary melting point apparatus (Dr. Tottoli) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker AC 300 using TMS as an internal standard. The HPLC system consisted of a Knauer pump type 64, a Reodyne injection valve, a Knauer column (Eurosper 80-5, 250x5 mm, 5 µm), a Knauer UV/VIS photometer (detection at 254 nm), and a Hewlett Packard integrator (3393 A). GC chromatograms were performed at a Hewlett Packard chromatograph (HP 5890) using a capillary column (HP1, 23 m x 0.2 mm x 0.33 µm, crosslinked with methylsilicon); injection port 220 °C, initial temp. increased (15 °C/min) to final temp. (180 °C), mass spectrometric detector (HP 5970 MSD). Optical rotations were measured on a Perkin Elmer 241 polarimeter. Microanalyses were determined at the Institute of Organic Chemistry, University of Heidelberg.

General Procedure A: *Esterification of* **1** *to* **3**. A solution of **1** (40.0 g, 97 mmol), **2** (30.2 g, 193 mmol) and DMAP (23.6 g, 193 mmol) in toluene (600 ml) was refluxed. After 300 ml of the solvent were distilled off within 2 d the mixture was evaporated *in vacuo*, the residue dissolved in CH_2Cl_2. The organic layer was washed with 1 M HCl, dried (Na_2SO_4) and the solvent removed at reduced pressure. Excess **2** was distilled off at 90 °C/0.03 mbar and the residue recrystallized from ether to yield pure **3**.

General Procedure B: *Phenylselenylation of* **3** *to* **4** *and* **5**. A solution of PhSeBr (1.35 g, 5.70 mmol) in CH_2Cl_2 (50 ml) was cooled to 0 °C, pyridine (0.46 g, 5.80 mmol) and a solution of **3** (3.00 g, 5.70 mmol) in CH_2Cl_2 (50 ml) were added and the mixture was stirred for 2 h at 20 °C. After extraction with 1 M HCl, the organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure to give a mixture of crude selenides (**4n**:**5n** = **4x**:**5x** = 80:20).

General Procedure C: *Oxidative Elimination of* **4** or **5** *to Enoates* **6**. To a solution of the selenide (0.50 g, 0.72 mmol) in CH_2Cl_2 (20 ml) a solution of mCPBA (120 mg, 0.72 mmol) in CH_2Cl_2 (10 ml) was added. The mixture was stirred for 2 h at 20 °C, extracted with saturated $NaHCO_3$ and $NaHSO_3$ solution, the organic layer was dried (Na_2SO_4), the solvent distilled off *in vacuo* and the residue crystallized from ether.

General Procedure D: *Preparation of Enoates* **6**. A solution of PhSeBr (4.72 g, 20.0 mmol) in CH_2Cl_2 (100 ml) was cooled to 0 °C, pyridine (1.61 g, 20.4 mmol) and a solution of **3** (10.47 g, 20.0 mmol) in CH_2Cl_2 (100 ml) was added and the mixture was stirred for 2 h at 20 °C. After extraction with 1 M HCl, the organic layer was dried (Na_2SO_4) and a solution of mCPBA (3.97 g, 23.0 mmol) in CH_2Cl_2 (100 ml) was added. The mixture was stirred for 2 h at 20 °C, extracted with saturated $NaHCO_3$ and $NaHSO_3$ solution, the organic layer was dried (Na_2SO_4), the solvent distilled off *in vacuo* and the residue was crystallized from ether to yield **6**.

General Procedure E: *Conjugate Addition of Lipshutz Cuprates to* **6**. A solution of lithium 2-thienylcyanocuprate (8.00 ml, 0.25 M in THF, 2.00 mmol) was cooled to −78 °C, a solution of the organolithium (organomagnesium) compound (2.00 mmol) was added and the mixture was stirred at −78 °C for 1 h. A solution of **6** (1.05 g, 2.00 mmol) in THF (20 ml) was added and stirring was continued at −78 °C for 2 h. The reaction mixture was quenched with NH_4Cl solution (5%), stirred at 20 °C for 1 h and extracted with CH_2Cl_2.

The organic layer was dried (Na_2SO_4) and the solvent distilled off *in vacuo*. Purification of the residue by flash chromatography (100 g, silica gel, hexane/EtOAc = 9:1) and crystallization gave pure adducts **7–12**.

General Procedure F: *Transesterification of* **7-12** *to* **13-18**.
The camphor derived ester (2.00 mmol) and $Ti(OEt)_4$ (456 mg, 2.00 mmol) were dissolved in ethanol (50 ml) and refluxed for 48 h. After removal of the solvent *in vacuo* the residue was dissolved in CH_2Cl_2 (50 ml), 1 M HCl (50 ml) was added and the mixture was stirred for 1 h at 20 °C. The organic layer was separated, dried (Na_2SO_4) and the solvent distilled off *in vacuo*. Crystallization of the residue from ethanol gave the auxiliary (**1n** or **1x**) and kugelrohr distillation of the filtrate afforded the enantionerically pure ethyl esters **13-18**.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-2-oxo-cyclopentane-carboxylate (3n)

Esterification of **1n** (procedure A) gave **3n** (49.4 g, 98%), colourless crystals, mp 174 °C. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of 1'R and 1'S configurated β-ketoesters, **3na**:**3nb** = 70:30) δ(**3na**) = 0.79 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.03-1.32 (m, 3H), 1.66 (m_c, 2H), 1.93 (m_c, 1H), 2.03 (s, 3H, Ar–CH_3), 2.24-2.62 (m, 4H), 2.33 (s, 3H, Ar–CH_3), 2.79 (m_c, 1H), 3.23 (t, *J* = 9.1 Hz, 1H, 1'-H), 4.16 (m_c, 1H, 3-H), 5.46 (d, *J* = 8.8 Hz, 1H, 2-H), 5.71 (s, 1H, NAr 2-H), 6.86 (s, 1H, NAr 4-H), 7.05 (s, 1H, NAr 6-H), 7.32-7.40 (m, 4H, SO_2ArH), 7.53 (m_c, 1H, SO_2ArH); δ(**3nb**, separated signals) = 0.83 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 2.08 (s, 3H, Ar–CH_3), 2.27 (s, 3H, Ar–CH_3), 3.26 (t, *J* = 9.5 Hz, 1H, 1'-H), 5.35 (d, *J* = 8.8 Hz, 1H, 2-H), 6.06 (s, 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 6.89 (s, 1H, NAr 6-H). ^{13}C NMR (75 MHz, $CDCl_3$, **3na**:**3nb** = 52:48) see table 2. Anal. Calcd for $C_{30}H_{37}NO_5S$: C, 68.80; H, 7.14; N, 2.67; S, 6.11. Found C, 68.65; H, 7.15; N, 2.87; S, 5.92.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-2-oxo-cyclopentane-carboxylate (3x)

Esterification of **1x** (procedure A) gave **3x** (50.0 g, 99%), colourless crystals, mp 201 °C. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of 1'R and 1'S configurated β-ketoesters, **3xa**:**3xb** = 73:27) δ(**3xa**) = 0.61 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.20-2.60 (m, 17H), 3.42 (t, *J* = 9.1 Hz, 1H, 1'-H), 3.81 (d, *J* = 7.1 Hz, 1H, 3-H), 5.24 (d, *J* = 7.1 Hz, 1H, 2-H), 5.71 (s, br., 1H, NAr 2-H), 6.84 (s, 1H, NAr 4-H), 7.06 (s, br., 1H, NAr 6-H), 7.30-7.40 (m, 4H, SO_2ArH), 7.50 (m_c, 1H, SO_2ArH). δ(**3xb**, separated signals) = 0.56 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 3.26 (t, *J* = 8.8 Hz, 1H, 1'-H), 3.76 (d, *J* = 7.1 Hz, 1H, 3-H), 5.33 (d, *J* = 7.1 Hz, 1H, 2-H), 6.88 (s, 1H, NAr 4-H). ^{13}C NMR (75 MHz, $CDCl_3$, **3xa**:**3xb** = 74:26) see table 3. Anal. Calcd for $C_{30}H_{37}NO_5S$: C, 68.80; H, 7.14; N, 2.67; S, 6.11. Found C, 68.92; H, 7.06; N, 2.84; S, 6.11.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R*)-2-oxo-1-phenyl-selenyl-cyclopentanecarboxylate (4n)

Phenylselenylation of **3n** (procedure B), separation by flash chromatography (300 g silica gel, hexane:EtOAc = 8:2) and crystallization from ether yielded **4n** (1.59 g, 41%), colourless crystals, mp 164 °C. TLC (silica gel, hexane:EtOAc = 8:2) R_f = 0.44. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.77 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.21 (m_c, 1H), 1.59 (m_c, 1H), 1.82 (m_c, 1H), 1.93-2.19 (m, 4H), 2.00 (s, 3H, Ar–CH_3), 2.26-2.53 (m, 2H), 2.36 (s, 3H, Ar–CH_3), 2.73-2.97 (m, 2H), 4.16 (dd, *J* = 8.4 and 4.0 Hz, 1H, 3-H), 5.48 (d, *J* = 8.4 Hz, 1H, 2-H), 5.58 (s, 1H, NAr 2-H), 6.85 (s, 1H, NAr 4-H), 7.17 (s, 1H, NAr 6-H), 7.26-7.40 (m, 7H, SeArH, SO_2ArH), 7.53 (m_c, 1H, SO_2ArH), 7.72 (m_c, 2H, SeArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 126.92 (SeAr C-1), 128.82 (SeAr C-3, C-5), 129.47 (SeAr C-4), 137.43 (SeAr C-2, C-6),

further signals see table 2. Anal. Calcd for $C_{36}H_{41}NO_5SSe$: C, 63.70; H, 6.10; N, 2.07. Found C, 63.94; H, 6.14; N, 2.32.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R*)-2-oxo-1-phenyl-selenyl-cyclopentanecarboxylate (4x)

Phenylselenylation of **3x** (procedure B), separation by flash chromatography (300 g silica gel, hexane:EtOAc = 8:2) and crystallization from hexane yielded **4x** (1.19 g, 32%), colourless crystals, mp 213 °C. TLC (silica gel, hexane:EtOAc = 8:2) R_f = 0.44. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.55 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.02 (m_c, 1H), 1.40 (m_c, 1H), 1.52 (m_c, 1H) 1.64 (m_c, 1H) 1.72 (d, J = 4.3 Hz, 1H, 4-H), 1.90-2.20 (m, 6H), 2.20-2.50 (m, 4H), 2.72 (dt, J = 18.4 and 8.1 Hz, 1H), 2.89 (dt, J = 15.1 and 7.6 Hz, 1H), 3.75 (d, J = 7.1 Hz, 1H, 3-H), 5.36 (d, J = 7.1 Hz, 1H, 2-H), 5.49 (s, br., 1H, NAr 2-H), 6.87 (s, 1H, NAr 4-H), 7.13 (s, br., 1H, NAr 6-H), 7.25-7.40 (m, 7H, SeArH, SO_2ArH), 7.53 (m_c, 1H, SO_2ArH), 7.72 (m_c, 2H, SeArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 127.03 (SeAr C-1), 128.78 (SeAr C-3, C-5), 129.59 (SeAr C-4), 137.50 (SeAr C-2, C-6), further signals see table 3. Anal. Calcd for $C_{36}H_{41}NO_5SSe$: C, 63.70; H, 6.10; N, 2.07. Found C, 63.60; H, 6.18; N, 2.20.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S*)-2-oxo-1-phenyl-selenyl-cyclopentanecarboxylate (5n)

Phenylselenylation of **3n** (procedure B), separation by flash chromatography (300 g silica gel, hexane:EtOAc = 8:2) and crystallization from hexane yielded **5n** (0.81 g, 21%), colourless crystals, mp 118 °C. TLC (silica gel, hexane:EtOAc = 8:2) R_f = 0.22. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.80 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.08 (m_c, 1H), 1.24 (m_c, 1H), 1.67 (m_c, 2H), 1.80-2.12 (m, 3H), 2.04 (s, 3H, Ar–CH_3), 2.16-2.50 (m, 3H), 2.34 (s, 3H, Ar–CH_3), 3.12 (ddd, J = 14.6, 9.0 and 7.3 Hz, 1H), 4.20 (dd, J = 8.6 and 3.3 Hz, 1H, 3-H), 5.51 (d, J = 8.6 Hz, 1H, 2-H), 5.72 (s, 1H, NAr 2-H), 6.87 (s, 1H, NAr 4-H), 7.25-7.42 (m, 8H, NAr 6-H, SeArH, SO_2ArH), 7.54 (m_c, 1H, SO_2ArH), 7.75 (m_c, 2H, SeArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 127.12 (SeAr C-1), 128.99 (SeAr C-3, C-5), 129.49 (SeAr C-4), 137.36 (SeAr C-2, C-6), further signals see table 2. Anal. Calcd for $C_{36}H_{41}NO_5SSe$: C, 63.70; H, 6.10; N, 2.07. Found C, 63.89; H, 6.23; N, 2.28.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S*)-2-oxo-1-phenyl-selenyl-cyclopentanecarboxylate (5x)

Phenylselenylation of **3x** (procedure B), separation by flash chromatography (300 g silica gel, hexane:EtOAc = 8:2) and crystallization from hexane yielded **5x** (0.84 g, 22%), colourless crystals, mp 152 °C. TLC (silica gel, hexane:EtOAc = 8:2) R_f = 0.22. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.58 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.05 (m_c, 1H), 1.20-2.50 (m, 15H), 3.20 (ddd, J = 14.4, 9.3 and 7.2 Hz, 1H), 3.78 (d, J = 7.1 Hz, 1H, 3-H), 5.36 (d, J = 7.1 Hz, 1H, 2-H), 5.57 (s, br., 1H, NAr 2-H), 6.88 (s, 1H, NAr 4-H), 7.20 (s, br., 1H, NAr 6-H), 7.27-7.40 (m, 7H, SeArH, SO_2ArH), 7.52 (m_c, 1H, SO_2ArH), 7.73 (m_c, 2H, SeArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.10 (SeAr C-1), 128.87 (SeAr C-3, C-5), 129.55 (SeAr C-4), 137.76 (SeAr C-2, C-6), further signals see table 3. Anal. Calcd for $C_{36}H_{41}NO_5SSe$: C, 63.70; H, 6.10; N, 2.07. Found C, 63.92; H, 6.25; N, 2.22.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-2-oxo-cyclopentene-carboxylate (6n)

Reaction of **3n** (procedure D) afforded **6n** (7.90 g, 75%); oxidation of **4n** (procedure C) gave **6n** (344 mg, 90%); oxidation of **5n** (procedure C) yielded **6n** (318 mg, 83%); colourless crystals, mp 170 °C. ^{1}H NMR

(300 MHz, $CDCl_3$) δ = 0.84 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.13-1.28 (m, 2H), 1.52 (m_c, 1H), 1.80-1.93 (m, 2H), 2.03 (s, 3H, Ar–CH_3), 2.28 (s, 3H, Ar–CH_3), 2.57 (m_c, 2H, 3'-H), 2.80 (m_c, 2H, 4'-H), 4.19 (dd, *J* = 8.7 and 2.9 Hz, 1H, 3-H), 5.47 (d, *J* = 8.7 Hz, 1H, 2-H), 5.98 (s, 1H, NAr 2-H), 6.81 (s, 1H, NAr 4-H), 6.90 (s, 1H, NAr 6-H), 7.32-7.42 (m, 4H, SO_2ArH), 7.53 (m_c, 1H, SO_2ArH), 8.63 (t, *J* = 2.7 Hz, 1H, 5'-H). ^{13}C NMR (75 MHz, $CDCl_3$) see table 2. Anal. Calcd for $C_{30}H_{35}NO_5S$: C, 69.07; H, 6.78; N, 2.69; S, 6.13. Found C, 69.05; H, 6.69; N, 2.86; S, 6.13.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-2-oxo-cyclopentene-carboxylate (6x)

Reaction of **3x** (procedure D) afforded **6x** (8.14 g, 78%); oxidation of **4x** (procedure C) gave **6x** (309 mg, 81%); oxidation of **5x** (procedure C) yielded **6x** (384 mg, 88%); colourless crystals, mp 185 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.62 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.08 (m_c, 1H), 1.40 (m_c, 1H), 1.55 (m_c, 1H), 1.70 (m_c, 1H), 2.00 (m_c, 4H, Ar–CH_3, 4-H), 2.31 (s, br., 3H, Ar–CH_3), 2.57 (m_c, 2H, 3'-H), 2.80 (m_c, 2H, 4'-H), 3.82 (d, *J* = 7.2 Hz, 1H, 3-H), 5.36 (d, *J* = 7.2 Hz, 1H, 2-H), 5.76 (s, br., 1H, NAr 2-H), 6.84 (s, 1H, NAr 4-H), 6.99 (s, br., 1H, NAr 6-H), 7.35 (m_c, 4H, SO_2ArH), 7.51 (m_c, 1H, SO_2ArH), 8.67 (t, *J* = 2.7 Hz, 1H, 5'-H). ^{13}C NMR (75 MHz, $CDCl_3$) see table 3. Anal. Calcd for $C_{30}H_{35}NO_5S$: C, 69.07; H, 6.78; N, 2.69; S, 6.13. Found C, 68.99; H, 6.70; N, 2.91; S, 6.21.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-5-methyl-2-oxo-cyclopentanecarboxylate (7n)

Starting material **6n**; procedure E; cuprate precursor MeLi (1.29 ml, 1.55 M in ether); gave **7n** (788 mg, 73%), colourless crystals from 2-PrOH, mp 140 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.82 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.14-1.36 (m, 2H), 1.27 (d, *J* = 6.5 Hz, 3H, CH_3), 1.54 (m_c, 1H), 1.71 (t, *J* = 3.5 Hz, 1H, 4-H), 2.00 (s, 3H, Ar–CH_3), 2.05-2.55 (m, 5H), 2.32 (s, 3H, Ar–CH_3), 2.77 (m_c, 1H, 5'-H), 3.15 (d, *J* = 11.6 Hz, 1H, 1'-H), 4.25 (dd, *J* = 8.5 and 3.5 Hz, 1H, 3-H), 5.39 (d, *J* = 8.5 Hz, 1H, 2-H), 5.76 (s, 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 7.13 (s, 1H, NAr 6-H), 7.30-7.43 (m, 4H, SO_2ArH), 7.49 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.29 (CH_3), for further signals see table 2. Anal. Calcd for $C_{31}H_{39}NO_5S$: C, 69.24; H, 7.33; N, 2.60; S, 5.95. Found C, 69.48; H, 7.39; N, 2.87; S, 6.04.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-5-methyl-2-oxo-cyclopentanecarboxylate (7x)

Starting material **6x**; procedure E; cuprate precursor MeLi (1.29 ml, 1.55 M in ether); gave **7x** (799 mg, 74%), colourless crystals from 2-PrOH, mp 170 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.59 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.09 (m_c, 1H), 1.27 (d, *J* = 6.5 Hz, 3H, CH_3), 1.38 (m_c, 1H), 1.47-1.74 (m, 3H), 1.78 (d, *J* = 4.4 Hz, 1H, 4-H), 1.96 (s, br., 3H, Ar–CH_3), 2.15-2.45 (m, 6H, Ar–CH_3, aliphatic H), 2.80 (m_c, 1H, 5'-H), 3.18 (d, *J* = 11.6 Hz, 1H, 1'-H), 3.85 (d, *J* = 7.1 Hz, 1H, 3-H), 5.29 (d, *J* = 7.1 Hz, 1H, 2-H), 5.59 (s, br., 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 7.11 (s, br., 1H, NAr 6-H), 7.27-7.36 (m, 4H, SO_2ArH), 7.48 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 19.35 (CH_3), for further signals see table 3. HPLC (hexane:EtOAc:AcOH = 93:5:2, flow 2.0 ml/min) R_t(**7x**) = 12.99 min, R_t(**19x**) = 15.94 min; unpurified product: **7x**:**19x** = 99.5:0.5, crystals: only **7x** detectable. Anal. Calcd for $C_{31}H_{39}NO_5S$: C, 69.24; H, 7.33; N, 2.60; S, 5.95. Found C, 69.29; H, 7.38; N, 2.77; S, 6.00.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-5-butyl-2-oxo-cyclopentanecarboxylate (8n)

Starting material **6n**; procedure E; cuprate precursor nBuLi (1.40 ml, 1.43 M in hexane); gave **8n** (928 mg, 80%), colourless crystals from 2-PrOH, mp 150 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.80-0.90 (m, 2H),

0.81 (s, 3H, CH_3), 0.87 (s, 3H, CH_3) overlapped with (t, J = 6.9 Hz, 3H, nBu CH_3), 1.00-1.60 (m, 8H), 1.04 (s, 3H, CH_3), 1.71 (t, J = 3.3 Hz, 1H, 4-H), 1.82 (m_c, 1H), 2.01 (s, 3H, Ar–CH_3), 2.11 (m_c, 1H), 2.30-2.50 (m, 2H), 2.32 (s, 3H, Ar–CH_3), 2.74 (m_c, 1H, 5'-H), 3.19 (d, J = 11.3 Hz, 1H, 1'-H), 4.25 (dd, J = 8.7 and 3.3 Hz, 1H, 3-H), 5.46 (d, J = 8.7 Hz, 1H, 2-H), 5.77 (s, 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 7.12 (s, 1H, NAr 6-H), 7.30-7.40 (m, 4H, SO_2ArH), 7.50 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.96 (nBu C-4), 26.69 (nBu C-3), 29.18 (nBu C-2), 34.06 (nBu C-1), for further signals see table 2. Anal. Calcd for $C_{34}H_{45}NO_5S$: C, 70.43; H, 7.84; N, 2.41; S, 5.52. Found C, 70.46; H, 7.96; N, 2.59; S, 5.56.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-5-butyl-2-oxo-cyclopentanecarboxylate (8x)

Starting material **6x**; procedure E; cuprate precursor nBuLi (1.40 ml, 1.43 M in hexane); gave **8x** (798 mg, 69%), colourless crystals from 2-PrOH, mp 182 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.59 (s, 3H, CH_3), 0.86 (t, J = 7.0 Hz, 3H, nBu CH_3), 0.92 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.08 (m_c, 1H), 1.23-1.74 (m, 10H), 1.79 (d, J = 4.4 Hz, 1H, 4-H), 1.99 (s, br., 3H, Ar–CH_3), 2.20-2.45 (m, 6H, Ar–CH_3, aliphatic H), 2.78 (m_c, 1H, 5'-H), 3.21 (d, J = 11.2 Hz, 1H, 1'-H), 3.85 (d, J = 7.1 Hz, 1H, 3-H), 5.29 (d, J = 7.1 Hz, 1H, 2-H), 5.60 (s, br., 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 7.11 (s, br., 1H, NAr 6-H), 7.28-7.40 (m, 4H, SO_2ArH), 7.49 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.96 (nBu C-4), 26.61 (nBu C-3), 29.15 (nBu C-2), 34.02 (nBu C-1), for further signals see table 3. Anal. Calcd for $C_{34}H_{45}NO_5S$: C, 70.43; H, 7.84; N, 2.41; S, 5.52. Found C, 70.29; H, 7.77; N, 2.63; S, 5.66.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-5-*tert*-butyl-2-oxo-cyclopentane-carboxylate (9n)

Starting material **6n**; procedure E; cuprate precursor tBuLi (1.15 ml, 1.74 M in pentane); gave **9n** (684 mg, 59%); colourless crystals from 2-PrOH, mp 184 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.80 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 0.98-1.18 (m, 2H), 1.04 (s, 9H, tBu CH_3), 1.05 (s, 3H, CH_3), 1.60-1.80 (m, 3H), 2.00 (s, 3H, Ar–CH_3), 2.07-2.28 (m, 2H), 2.34 (s, 3H, Ar–CH_3), 2.38-2.47 (m, 2H), 2.79 (dt, J = 7.0 and 11.0Hz, 1H, 5'-H), 3.43 (d, J = 11.0 Hz, 1H, 1'-H), 4.37 (dd, J = 8.8 and 3.5 Hz, 1H, 3-H), 5.45 (d, J = 8.8 Hz, 1H, 2-H), 5.70 (s, 1H, NAr 2-H), 6.85 (s, 1H, NAr 4-H), 7.24 (s, 1H, NAr 6-H), 7.30-7.43 (m, 4H, SO_2ArH), 7.49 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 27.50 (tBu CH_3), 32.45 (tBu C), for further signals see table 2. Anal. Calcd for $C_{34}H_{45}NO_5S$: C, 70.43; H, 7.84; N, 2.41; S, 5.52. Found C, 70.36; H, 7.89; N, 2.68; S, 5.73.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-5-*tert*-butyl-2-oxo-cyclopentane-carboxylate (9x)

Starting material **6x**; procedure E; cuprate precursor tBuLi (1.15 ml, 1.74 M in pentane); gave **9x** (870 mg, 75%); colourless crystals from 2-PrOH, mp 221 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.58 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.00 (s, 9H, tBu CH_3), 1.09 (m_c, 1H), 1.40 (m_c, 1H), 1.52 (m_c, 1H), 1.60-1.76 (m, 2H), 1.80 (d, J = 4.3 Hz, 1H, 4-H), 2.02 (s, br., 3H, Ar–CH_3), 2.14 (m_c, 1H), 2.29 (s, br., 3H, Ar–CH_3), 2.36-2.46 (m, 2H), 2.81 (dt, J = 7.3 and 9.9 Hz, 1H, 5'-H), 3.44 (d, J = 9.9 Hz, 1H, 1'-H), 3.94 (dd, J = 7.2 Hz, 1H, 3-H), 5.25 (d, J = 7.2 Hz, 1H, 2-H), 5.61 (s, br., 1H, NAr 2-H), 6.83 (s, 1H, NAr 4-H), 7.20 (s, br., 1H, NAr 6-H), 7.27-7.42 (m, 4H, SO_2ArH), 7.48 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 27.44 (tBu CH_3), 32.59 (tBu C), for further signals see table 3. Anal. Calcd for $C_{34}H_{45}NO_5S$: C, 70.43; H, 7.84; N, 2.41; S, 5.52. Found C, 70.29; H, 7.91; N, 2.68; S, 5.52.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5S)-2-oxo-5-vinyl-cyclopentanecarboxylate (10n)

Starting material **6n**; procedure E; cuprate precursor H_2C=CHMgBr (2.00 ml, 1.00 M in THF); gave **10n** (748 mg, 68%), colourless crystals from hexane, mp 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ketone:enol = 97:3) δ(ketone) = 0.82 (s, 3H, CH_3), 0.84 (m_c, 1H), 0.87 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.16-1.37 (m, 3H), 1.72 (t, J = 3.4 Hz, 1H, 4-H), 1.80 (m_c, 1H), 2.01 (s, 3H, Ar–CH_3), 2.08 (m_c, 1H), 2.30 (m_c, 1H), 2.31 (s, 3H, Ar–CH_3), 2.45 (m_c, 1H), 3.33 (d, J = 11.4 Hz, 1H, 1'-H), 3.44 (m_c, 1H, 5'-H), 4.24 (dd, J = 8.6 and 3.4 Hz, 1H, 3-H), 5.11 (d, J = 10.3 Hz, 1H, =CH_2), 5.27 (d, J = 17.1 Hz, 1H, =CH_2), 5.46 (d, J = 8.6 Hz, 1H, 2-H), 5.77 (s, 1H, NAr 2-H), 5.98 (ddd, J = 17.1, 10.3 and 6.2 Hz, 1H, =CH–), 6.83 (s, 1H, NAr 4-H), 7.11 (s, 1H, NAr 6-H), 7.30-7.40 (m, 4H, SO_2ArH), 7.50 (m_c, 1H, SO_2ArH); δ(enol, separated signals) = 10.63 (s, 1H, =C–OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 115.32 (=CH_2), 138.61 (=CH–), for further signals see table 2. Anal. Calcd for $C_{32}H_{39}NO_5S$: C, 69.91; H, 7.17; N, 2.55; S, 5.82. Found C, 69.67; H, 7.17; N, 2.78; S, 5.84.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5R)-2-oxo-5-vinyl-cyclopentanecarboxylate (10x)

Starting material **6x**; procedure E; cuprate precursor H_2C=CHMgBr (2.00 ml, 1.00 M in THF); gave **10x** (880 mg, 80%), colourless crystals from 2-PrOH, mp 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.59 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.08 (m_c, 1H), 1.37 (m_c, 1H), 1.53 (m_c, 1H), 1.60-1.75 (m, 2H), 1.79 (d, J = 4.2 Hz, 1H, 4-H), 1.98 (s, br., 3H, Ar–CH_3), 2.30 (m_c, 4H, Ar–CH_3, aliphatic H), 2.40-2.50 (m, 2H), 3.37 (d, J = 11.2 Hz, 1H, 1'-H), 3.47 (m_c, 1H, 5'-H), 3.84 (d, J = 7.1 Hz, 1H, 3-H), 5.08 (d, J = 10.4 Hz, 1H, =CH_2), 5.23 (d, J = 17.2 Hz, 1H, =CH_2), 5.29 (d, J = 7.1 Hz, 1H, 2-H), 5.60 (s, br., 1H, NAr 2-H), 6.00 (ddd, J = 17.2, 10.4 and 6.0 Hz, 1H, =CH–), 6.83 (s, 1H, NAr 4-H), 7.09 (s, br., 1H, NAr 6-H), 7.26-7.36 (m, 4H, SO_2ArH), 7.48 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 115.13 (=CH_2), 138.84 (=CH–), for further signals see table 3. Anal. Calcd for $C_{32}H_{39}NO_5S$: C, 69.91; H, 7.17; N, 2.55; S, 5.82. Found C, 69.75; H, 7.25; N, 2.79; S, 6.06.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-5-isopropenyl-2-oxo-cyclopentane-carboxylate (11n)

Starting material **6n**; procedure E; cuprate precursor isopropenyllithium which was prepared from 2-bromo-propene (242 mg, 2.00 mmol) dissolved in THF (10 ml) and tBuLi (2.30 ml, 1.74 M, 4.00 mmol) at -78 °C (2 h); gave **11n** (712 mg, 63%), colourless crystals from 2-PrOH, mp 140 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ketone:enol = 87:13) δ(ketone) = 0.80 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.05-1.28 (m, 3H), 1.60-1.70 (m, 2H), 1.81 (m_c, 1H), 1.88 (s, 3H, =C–CH_3), 2.00 (s, 3H, Ar–CH_3), 2.12 (m_c, 1H), 2.33 (s, 3H, Ar–CH_3), 2.43-2.52 (m, 2H), 3.46 (dt, J = 6.1 and 11.2 Hz, 1H, 5'-H), 3.56 (d, J = 11.2 Hz, 1H, 1'-H), 4.26 (dd, J = 8.7 and 3.3 Hz, 1H, 3-H), 4.88 (s, 1H, =CH_2), 5.00 (s, 1H, =CH_2), 5.47 (d, J = 8.7 Hz, 1H, 2-H), 5.69 (s, 1H, NAr 2-H), 6.84 (s, 1H, NAr 4-H), 7.18 (s, 1H, NAr 6-H), 7.32-7.39 (m, 4H, SO_2ArH), 7.50 (m_c, 1H, SO_2ArH); δ(enol, separated signals) = 0.77 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.73 (s, 3H, =C–CH_3), 2.08 (s, 3H, Ar–CH_3), 2.25 (s, 3H, Ar–CH_3), 3.79 (m_c, 1H, 5'-H), 4.12 (m_c, 1H, 3-H), 4.71 (s, 1H, =CH_2), 4.84 (s, 1H, =CH_2), 5.42 (d, J = 9.0 Hz, 1H, 2-H), 6.12 (s, 1H, NAr 2-H), 6.80 (s, 1H, NAr 4-H), 7.31 (s, 1H, NAr 6-H), 10.57 (s, 1H, =C–OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.36 (CH_3), 111.36 (=CH_2), 144.42 (=C–), for further signals see table 2. Anal. Calcd for $C_{33}H_{41}NO_5S$: C, 70.30; H, 7.35; N, 2.49; S, 5.67. Found C, 70.39; H, 7.49; N, 2.45; S, 5.87.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-5-isopropenyl-2-oxo-cyclopentane-carboxylate (11x)

Starting material **6x**; procedure E; cuprate precursor isopropenyllithium (preparation see **11n**); gave **11x** (848 mg, 75%), colourless crystals from 2-PrOH, mp 168 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.58 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.07 (m_c, 1H), 1.37 (m_c, 1H), 1.52 (m_c, 1H), 1.59-1.73 (m, 2H), 1.77 (d, *J* = 4.6 Hz, 1H, 4-H), 1.87 (s, 3H, =C-CH_3), 1.99 (s,.br., 3H, Ar-CH_3), 2.29 (s, br., 3H, Ar-CH_3), 2.33 (m_c, 1H), 2.44-2.53 (m, 2H), 3.50 (dt, *J* = 6.0 and 10.3 Hz, 1H, 5'-H), 3.55 (d, *J* = 10.3 Hz, 1H, 1'-H), 3.84 (d, *J* = 7.1 Hz, 1H, 3-H), 4.86 (s, 1H, =CH_2), 4.96 (s, 1H, =CH_2), 5.29 (d, *J* = 7.1 Hz, 1H, 2-H), 5.58 (s, br., 1H, NAr 2-H), 6.84 (s, 1H, NAr 4-H), 7.10 (s, br., 1H, NAr 6-H), 7.27-7.37 (m, 4H, SO_2ArH), 7.48 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.35 (CH_3), 111.04 (=CH_2), 144.56 (=C-), for further signals see table 3. Anal. Calcd for $C_{33}H_{41}NO_5S$: C, 70.30; H, 7.35; N, 2.49; S, 5.67. Found C, 70.26; H, 7.43; N, 2.64; S, 5.77.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-2-oxo-5-phenyl-cyclopentanecarboxylate (12n)

Starting material **6n**; procedure E; cuprate precursor PhLi (1.00 ml, 2.00 M in hexane/ether); gave **12n** (672 mg, 56%), colourless crystals from 2-PrOH, mp 138 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ketone:enol = 73:27) δ(ketone) = 0.79 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.00-1.30 (m, 2H), 1.69 (m_c, 1H), 1.99 (s, 3H, Ar-CH_3), 2.00 (m_c, 1H), 2.30 (s, 3H, Ar-CH_3), 2.40-2.80 (m, 5H), 3.70 (d, *J* = 11.2 Hz, 1H, 1'-H), 4.07 (m_c, 1H, 5'H), 4.21 (dd, *J* = 8.6 and 3.3 Hz, 1H, 3-H), 5.43 (d, *J* = 8.6 Hz, 1H, 2-H), 5.76 (s, 1H, NAr 2-H), 6.79 (s, 1H, NAr 4-H), 7.08-7.55 (m, 11H, SO_2ArH, NAr 6-H, CArH). δ(enol, separated signals) = 0.58 (s, 3H, CH_3), 0.71 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 2.10 (s, 3H, Ar-CH_3), 2.31 (s, 3H, Ar-CH_3), 4.36 (m_c, 1H, 5'-H), 5.31 (d, *J* = 9.0 Hz, 1H, 2-H), 6.15 (s, 1H, NAr 2-H), 6.82 (s, 1H, NAr 4-H), 10.71 (s, 1H, =C-OH). ^{13}C NMR (75 MHz, $CDCl_3$, ketone:enol = 67:33) δ(ketone) = 126.67 (Ph C-4), 127.05 (Ph C-2, C-6), 128.56 (Ph C-3, C-5), 141.58 (Ph C-1), for further signals see table 2; δ(enol) = 13.64 (CH_3), 19.28 (CH_3), 19.32 (CH_3), 19.44 (C-5), 21.02 (Ar-CH_3), 21.12 (Ar-CH_3), 25.84 (C-6), 30.34 (C-4'), 31.51 (C-3'), 46.14 (C-5'), 45.18 (C-7), 49.91 (C-4), 50.49 (C-1), 58.99 (C-3), 75.19 (C-2), 103.87 (C-1'), 126.01 (Ph C-4), 126.85 (Ph C-2, C-6), 127.52 (NAr C-2), 128.03 (SO_2Ar C-3, C-5), 128.31 (SO_2Ar C-2, C-6; Ph C-3, C-5), 128.85 (NAr C-4), 129.96 (NAr C-6), 132.51 (SO_2Ar C-4), 136.31 (NAr C-1), 137.79 (NAr C-3, C-5), 139.55 (SO_2Ar C-1), 146.94, (Ph C-1), 169.24 (COO), 177.23 (C-2'). HPLC (hexane:EtOAc:AcOH = 93:5:2, flow 1.5 ml/min) R_t(**12n**) = 10.67 min, R_t(**21n**) = 17.12 min; unpurified product: **12n**:**21n** = 98:2, crystals only **12n** detectable. Anal. Calcd for $C_{36}H_{41}NO_5S$: C, 72.09; H, 6.90; N, 2.34; S, 5.33. Found C, 71.83; H, 6.93; N, 2.55; S, 5.45.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-2-oxo-5-phenyl-cyclopentanecarboxylate (12x)

Starting material **6x**; procedure E; cuprate precursor PhLi (1.00 ml, 2.00 M in hexane/ether); gave **12x** (852 mg, 71%), colourless crystals from 2-PrOH, mp 167 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ketone:enol = 15:85) δ(ketone, separated signals) = 0.54 (s, 3H, CH_3), 0.81 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 3.79 (d, *J* = 7.1 Hz, 1H, 3-H). δ(enol) = -0.02 (s, 3H, CH_3), 0.36 (s, 3H, CH_3), 0.52 (s, 3H, CH_3), 1.00 (m_c, 1H), 1.29 (m_c, 1H), 1.40 (m_c, 1H), 1.51-1.73 (m, 2H), 1.76 (d, *J* = 4.5 Hz, 1H, 4-H), 1.99 (s, br., 3H, Ar-CH_3), 2.38 (s, br., 3H, Ar-CH_3), 2.45-2.80 (m, 3H), 3.74 (d, *J* = 7.2 Hz, 1H, 3-H), 4.61 (d, *J* = 8.0 Hz, 1H, 5'-H), 5.27 (d, *J* = 7.2 Hz, 1H, 2-H), 5.68 (s, br., 1H, NAr 2-H), 6.84 (s, 1H, NAr 4-H), 7.01 (s, br., 1H, NAr 6-H), 7.15 (m_c, 1H, CArH), 7.27-7.40 (m, 8H, SO_2Ar, CArH), 7.50 (m_c, 1H, SO_2ArH), 11.09 (s, 1H, =C-OH). ^{13}C NMR (75 MHz, $CDCl_3$, ketone:enol = 68:32) δ(ketone) = 126.64 (Ph C-4), 127.07 (Ph C-2,

C-6), 128.49 (Ph C-3, C-5), 141.62 (Ph C-1), for further signals see table 3; δ(enol) =11.05 (CH_3), 20.22 (CH_3), 20.38 (CH_3), 21.02 (Ar–CH_3), 27.68 (C-5), 30.76 (C-4'), 31.26 (C-3'), 32.22 (C-6), 45.70 (C-5'), 46.86 (C-7), 48.31 (C-4), 50.20 (C-1), 67.31 (C-3), 80.58 (C-2), 103.27 (C-1'), 126.00 (Ph C-4), 126.87 (Ph C-2, C-6), 128.00 (SO_2Ar C-3, C-5), 128.30 (SO_2Ar C-2, C-6), 128.34 (Ph C-3, C-5), 129.22 (NAr C-4), 132.41 (SO_2Ar C-4), 137.25 (NAr C-1), 138.59 (SO_2Ar C-1), 146.93, (Ph C-1), 169.86 (COO), 178.44 (C-2'). Anal. Calcd for $C_{36}H_{41}NO_5S$: C, 72.09; H, 6.90; N, 2.34; S, 5.33. Found C, 72.07; H, 7.04; N, 2.58; S, 5.25.

Ethyl-(1S,5R)-5-methyl-2-oxo-cyclopentanecarboxylate (13)

Transesterification of **7n** (1.08 g, procedure F) gave **1n** (687mg, 83%) and **13** (259 mg, 76%), colourless oil, bp 80 °C/0.15 mbar. $[\alpha]_D^{20}$ = + 94.00 (*c* = 1.03, $CHCl_3$); $[\alpha]_D^{25}$ = + 68.01 (neat, d_4^{25} = 1.032); ref[13] $[\alpha]_D^{25}$ = + 66.90 (neat). ^1H NMR (300 MHz, $CDCl_3$) δ = 1.18 (d, *J* = 6.4 Hz, 3H, CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3), 1.47 (m_c, 1H, 4-H), 2.19 (m_c, 1H, 4-H), 2.31 (ddd, *J* = 19.3, 11.1 and 8.2 Hz, 1H, 3-H), 2.42 (m_c, 1H, 3-H), 2.59 (m_c, 1H, 5-H), 2.74 (d, *J* = 11.4 Hz, 1H, 1-H), 4.21 (q, *J* = 7.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.15 (CH_3), 19.20 (CH_3 at C-5), 29.28 (C-4), 36.35 (C-5), 38.65 (C-3), 61.18 (OCH_2), 63.04 (C-1), 169.15 (COO), 211.79 (C-2). GC initial temp. 80 °C (8 min), R_t = 12.40 min. MS (70 eV) *m/z* (%), 170 (8) [M^+]. Anal. Calcd for $C_9H_{14}O_3$: C, 63.50; H, 8.30. Found C, 63.21; H, 8.37.

Ethyl-(1R,5S)-5-methyl-2-oxo-cyclopentanecarboxylate (*ent*-13)

Transesterification of **7x** (1.08 g, procedure F) gave **1x** (678 mg, 82%) and *ent*-**13** (255 mg, 75%), colourless oil, bp 77 °C/0.08 mbar. $[\alpha]_D^{20}$ = - 95.70 (*c* = 1.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) data identical with **13**. GC initial temp. 80 °C (8 min), R_t = 12.39 min. MS (70 eV) *m/z* (%), 170 (8) [M^+]. Anal. Calcd for $C_9H_{14}O_3$: C, 63.50; H, 8.30. Found C, 63.39; H, 8.15.

Ethyl-(1S,5R)-5-butyl-2-oxo-cyclopentanecarboxylate (14)

Transesterification of **8n** (1.16 g, procedure F) gave **1n** (694 mg, 84%) and **14** (372 mg, 88%), colourless oil, bp 120 °C/0.15 mbar. $[\alpha]_D^{20}$ = + 81.58 (*c* = 1.13, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3), 1.30-1.60 (m, 7H), 2.22 (m_c, 1H, 4-H), 2.29 (ddd, *J* = 19.3, 11.1 and 8.2 Hz, 1H, 3-H), 2.40 (m_c, 1H, 3-H), 2.55 (m_c, 1H, 5-H), 2.79 (d, *J* = 11.2 Hz, 1H, 1-H), 4.19 (q, *J* = 7.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.85 (C-4'), 14.11 (CH_3), 22.61 (C-4), 27.34 (C-3'), 29.31 (C-2'), 34.64 (C-1'), 38.41 (C-3), 41.38 (C-5), 61.17 (OCH_2), 62.02 (C-1), 169.60 (COO), 212.02 (C-2). GC initial temp. 120 °C (10 min), R_t = 13.89 min. MS (70 eV) *m/z* (%), 212 (8) [M^+]. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.88; H, 9.51. Found C, 68.03; H, 9.72.

Ethyl-(1R,5S)-5-butyl-2-oxo-cyclopentanecarboxylate (*ent*-14)

Transesterification of **8x** (1.16 g, procedure F) gave **1x** (646 mg, 78%) and *ent*-**14** (360 mg, 85%), colourless oil, bp 120 °C/0.14 mbar. $[\alpha]_D^{20}$ = - 81.26 (*c* = 1.22, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) data identical with **14**. GC initial temp. 120 °C (10 min), R_t = 13.92 min. MS (70 eV) *m/z* (%), 212 (8) [M^+]. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.88; H, 9.51. Found C, 67.99; H, 9.68.

Ethyl-(1S,5R)-5-*tert*-butyl-2-oxo-cyclopentanecarboxylate (15)

Transesterification of **9n** (1.16 g, procedure F) gave **1n** (728 mg, 89%) and **15** (396 mg, 93%), colourless oil, bp 100 °C/0.14 mbar. $[\alpha]_D^{20}$ = + 94.61 (*c* = 0.98, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ = 0.88 (s, 9H, tBu CH_3), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3), 1.55 (m_c, 1H, 4-H), 2.03 (m_c, 1H, 4-H), 2.18-2.43 (m, 2H, 3-H), 2.52 (dt, *J* = 6.5 and 11.7 Hz, 1H, 5-H), 2.94 (d, *J* = 11.7 Hz, 1H, 1-H), 4.16 (q, *J* = 7.1 Hz, 2H, OCH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.02 (CH_3), 22.46 (C-4), 27.16 (tBu CH_3), 32.25 (tBu C), 38.88 (C-3), 51.64 (C-5), 57.69 (C-1), 61.25 (OCH_2), 170.68 (COO), 212.58 (C-2). GC initial temp. 120 °C (10 min), R_t = 13.02 min. MS (70 eV) *m/z* (%), 212 (4) [M^+]. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.88; H, 9.51. Found C, 67.75; H, 9.39.

Ethyl-(1R,5S)-5-*tert*-butyl-2-oxo-cyclopentanecarboxylate (*ent*-15)

Transesterification of **9x** (1.16 g, procedure F) gave **1x** (703 mg, 85%) and *ent*-**15** (382 mg, 90%), colourless oil, bp 100°C/0.14 mbar. $[\alpha]_D^{20}$ = - 95.69 (*c* = 1.22, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) identical with **15**. GC initial temp. 120 °C (10 min), R_t = 13.07 min. MS (70 eV) *m/z* (%), 212 (4) [M^+]. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.88; H, 9.51. Found C, 67.84; H, 9.38.

Ethyl-(1S,5S)-2-oxo-5-vinyl-cyclopentanecarboxylate (16)

Transesterification of **10n** (1.10 g, procedure F) gave **1n** (715 mg, 86%) and **16** (298 mg, 82%), colourless oil, bp 90 °C/0.15 mbar. $[\alpha]_D^{20}$ = + 85.05 (*c* = 1.11, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$): data identical with previous described *rac*-**16**[14]. GC initial temp. 100 °C (9 min), R_t = 11.88 min. MS (70 eV) *m/z* (%), 182 (21) [M^+]. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.90; H, 7.76. Found C, 65.81; H, 7.79.

Ethyl-(1R,5R)-2-oxo-5-vinyl-cyclopentanecarboxylate (*ent*-16)

Transesterification of **10x** (1.10 g, procedure F) gave **1x** (650 mg, 79%) and *ent*-**16** (300 mg, 82%), colourless oil, bp 90 °C/ 0.12 mbar. $[\alpha]_D^{20}$ = - 85.61 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) data identical with previous described *rac*-**16**[14]. GC initial temp. 100 °C (9 min), R_t = 11.82 min. MS (70 eV) *m/z* (%), 182 (24) [M^+]. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.90; H, 7.76. Found C, 65.65; H, 7.81.

Ethyl-(1S,5R)-5-isopropenyl-2-oxo-cyclopentanecarboxylate (17)

Transesterification of **11n** (1.13 g, procedure F) gave **1n** (670 mg, 81%) and **17** (320 mg, 81%), colourless oil, bp 85 °C/0.05 mbar. $[\alpha]_D^{20}$ = + 69.88 (*c* = 1.02, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.24 (t, *J* = 7.1 Hz, 3H, CH_3), 1.70 (m_c, 1H, 4-H), 1.75 (s, 3H, =C-CH_3), 2.24 (m_c, 1H, 4-H), 2.33 (ddd, *J* = 19.4, 11.2 and 8.2 Hz, 1H, 3-H), 2.45 (m_c, 1H, 3-H), 3.11 (d, *J* = 11.4 Hz, 1H, 1-H), 3.17 (dt, *J* = 5.8 and 11.4 Hz, 1H, 5-H), 4.18 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.78 (s, 1H, =CH_2), 4.81 (s, 1H, =CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.09 (CH_3), 20.34 (=C-CH_3), 26.23 (C-4), 38.26 (C-3), 47.68 (C-5), 59.80 (C-1), 61.27 (OCH_2), 110.98 (=CH_2), 144.22 (=C-), 169.09 (COO), 211.03 (C-2). GC initial temp. 100 °C (9 min), R_t = 13.48 min. MS (70 eV) *m/z* (%), 196 (32) [M^+]. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.31; H, 8.23. Found C, 67.19; H, 8.23.

Ethyl-(1R,5S)-5-isopropenyl-2-oxo-cyclopentanecarboxylate (*ent*-17)

Transesterification of **11x** (1.13 g, procedure F) gave **1x** (736 mg, 89%) and *ent*-**17** (310 mg, 79%), colourless oil, bp 85 °C/ 0.05 mbar. $[\alpha]_D^{20}$ = - 70.21 (*c* = 1.18, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) data identical with **17**. GC initial temp. 100 °C (9 min), R_t = 13.44 min. MS (70 eV) *m/z* (%), 196 (26) [M^+]. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.31; H, 8.23. Found C, 67.42; H, 8.30.

Ethyl-(1S,5R)-2-oxo-5-phenyl-cyclopentanecarboxylate (18)

Transesterification of **12n** (1.20 g, procedure F) gave **1n** (681 mg, 82%) and **18** (368 mg, 79%), colourless oil, bp 120 °C/0.05 mbar. $[\alpha]_D^{20}$ = + 18.55 (*c* = 0.99, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.23 (t, *J* =

7.1 Hz, 3H, CH_3), 2.00 (m_c, 1H, 4-H), 2.38-2.67 (m, 3H, 3-H, 4-H), 3.33 (d, J = 12.0 Hz, 1H, 1-H), 3.80 (dt, J =6.0 and 12.0 Hz, 1H, 5-H), 4.17 (m_c, 2H, OCH_2), 7.20-7.40 (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.13 (CH_3), 28.89 (C-4), 38.66 (C-3), 46.18 (C-5), 61.45 (OCH_2), 62.43 (C-1), 126.82 (C-2', C-6'), 127.20 (C-4'), 128.81 (C-3', C-5'), 141.07 (C-1'), 168.73 (COO), 210.56 (C-2). GC initial temp. 140 °C (12 min), R_t = 15.86 min. MS (70 eV) *m/z* (%), 232 (8) [M^+]. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.38; H, 6.96. Found C, 72.42; H, 7.11.

Ethyl-(1R,5S)-2-oxo-5-phenyl-cyclopentanecarboxylate (*ent*-18)

Transesterification of **12x** (1.20 g, procedure F) gave **1x** (716 mg, 86%) and *ent*-**18** (354 mg, 76%), colourless oil, bp 120 °C/ 0.05 mbar. $[\alpha]_D^{20}$ = - 18.30 (c = 0.98, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) data identical with **18**. GC initial temp. 140 °C (12 min), R_t = 15.91 min. MS (70 eV) *m/z* (%), 232 (7) [M^+]. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.38; H, 6.96. Found C, 72.42; H, 7.02.

Conjugate Addition of Methyllithium to **6x**: A solution of **6x** (1.04 g, 2.00 mmol) in THF (20 ml) was cooled to –78 °C, MeLi (1.25 ml, 1.60 M in ether, 2.00 mmol) was added dropwise and the mixture was stirred at –78 °C for 30 min. Then NH_4Cl solution (5%) was added, the mixture was extracted with CH_2Cl_2, the organic layer was dried (Na_2SO_4) and the solvent evaporated to give a mixture of **7x** and **19x** (29:71, HPLC). Separation by flash chromatography (100 g silica gel, hexane:EtOAc:AcOH = 8:1:1) and crystallization from 2-PrOH gave pure **7x** (181 mg, 17%), colourless crystals mp 170 °C; and **19x** (423 mg, 39%), colourless crystals mp 143 °C. HPLC (hexane:EtOAc:AcOH = 93:5:3, flow 2.0 ml/min) R_t(**7x**) = 13.01 min, R_t(**19x**) = 15.81 min.

(1R,2S,3R,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1S,5R)-5-methyl-2-oxo-cyclopentanecarboxylate (19x)

^1H NMR (300 MHz, $CDCl_3$) δ = 0.53 (s, 3H, CH_3), 0.77 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 1.02 (m_c, 1H), 1.31 (d, J =6.5 Hz, 3H, CH_3), 1.35-1.65 (m, 5H), 1.72 (d, J = 4.0 Hz, 1H, 4-H), 1.90-2.40 (m, 6H, 2 Ar–CH_3), 2.50 (m_c, 2H), 2.81 (d, J = 10.4 Hz, 1H, 1'-H), 3.19 (m_c, 1H, 5'-H), 3.78 (d, J = 7.0 Hz, 1H, 3-H), 5.31 (d, J = 7.0 Hz, 1H, 2-H), 5.50 (s, br., 1H, NAr 2-H), 6.86 (s, 1H, NAr 4-H), 7.00 (s, br., 1H, NAr 6-H), 7.36 (m_c, 4H, SO_2ArH), 7.52 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.05 (CH_3), for further signals see table 3. Anal. Calcd for $C_{31}H_{39}NO_5S$: C, 69.24; H, 7.33; N, 2.60. Found C, 68.97; H, 7.56; N, 2.60.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-2-oxo-5-phenyl-cyclopentenecarboxylate (20n)

A solution of PhSeBr (472 mg, 2.00 mmol) in CH_2Cl_2 (10 ml) was cooled to 0 °C, pyridine (158 mg, 2.00 mmol) and a solution of **12n** (1.20 g, 2.00 mmol) in CH_2Cl_2 (10 ml) was added and the mixture was stirred for 2 h at 20 °C. After extraction with 1 M HCl, the organic layer was dried (Na_2SO_4) and a solution of mCPBA (397 mg, 2.30 mmol) in CH_2Cl_2 (10 ml) was added. The mixture was stirred for 2 h at 20 °C, extracted with saturated $NaHCO_3$ and $NaHSO_3$ solution, the organic layer was dried (Na_2SO_4) and the solvent was distilled off *in vacuo*. Purification of the residue by flash chromatography (100 g, silica gel, hexane:EtOAc = 8:2) and crystallization from ether/hexane gave **20n** (420 mg, 35%), colourless crystals, mp 184 °C. ^1H NMR (300 MHz, $CDCl_3$) δ = 0.82 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 1.01-1.14 (m, 2H), 1.05 (s, 3H, CH_3), 1.60-1.76 (m, 2H), 2.05 (s, 3H, Ar–CH_3), 2.15 (m_c, 1H), 2.25 (s, 3H, Ar–CH_3), 2.70 (t, J = 5.0 Hz, 2H, 3'-H), 2.98 (dt, J = 18.6 and 5.0 Hz, 1H, 4'-H), 3.23 (dt, J = 18.6 and 5.0 Hz, 1H, 4'-H), 4.39 (dd, J = 8.6 and 3.0 Hz, 1H, 3-H), 5.59 (d, J = 8.6 Hz, 1H, 2-H), 5.94 (s, 1H, NAr 2-H), 6.82 (s, 1H, NAr 4-H), 6.96 (s, 1H, NAr 6-H), 7.33-7.56 (m, 8H, SO_2ArH, CArH), 7.72-7.80 (m, 2H, CArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.51 (CH_3), 19.43 (CH_3), 19.57 (CH_3), 19.69 (C-5), 21.01 (Ar–CH_3), 21.19 (Ar–CH_3), 26.52 (C-6), 30.38 (C-4'), 35.16 (C-3'), 46.08 (C-7), 49.37 (C-4), 51.76 (C-1), 59.11 (C-3), 78.03 (C-2), 127.75

(NAr C-2), 128.10 (SO_2Ar C-3, C-5), 128.19 (SO_2Ar C-2, C-6), 128.26 (CAr C-3, C-5), 128.60 (CAr C-2, C-6), 129.54 (NAr C-4), 130.39 (NAr C-6), 130.97 (CAr C-4), 132.39 (SO_2Ar C-4), 133.33 (C-1'), 134.38 (CAr C-1), 137.14 (NAr C-3), 138.13 (NAr C-1), 138.24 (NAr C-5), 138.81 (SO_2Ar C-1), 164.44, (COO), 176.04 (C-5'), 203.14 (C-2'). Anal. Calcd for $C_{36}H_{39}NO_5S$: C, 72.33; H, 6.59; N, 2.34. Found C, 72.21; H, 6.58; N, 2.54.

Reduction of **20n** *with sodium borohydride:* A solution of **20n** (150 mg, 0.25 mmol) in pyridine (5 ml) was reacted with $NaBH_4$ (9.5 mg, 0.25 mmol) at 20 °C for 2.5 h and then hydrolysed by the addition of 2 M HCl (10 ml). The mixture was extracted with ethyl acetate, the organic layer was washed with NH_4Cl solution (5%), dried (Na_2SO_4) and the solvent evaporated to give a mixture of **12n** and **21n** (1:1, HPLC). Separation by flash chromatography (100 g silica gel, hexane:EtOAc = 9:1) and crystallization gave pure **12n** (50 mg, 33%), colourless crystals from 2-PrOH mp 138 °C; and **21n** (40 mg, 27%), colourless crystals from ether/hexane mp 118 °C. HPLC (hexane:EtOAc:AcOH = 91:7:2, flow 2.0 ml/min), R_t(**12n**) = 7.76 min, R_t(**21n**) = 13.33 min.

(1R,2R,3S,4S)-{3-[N-Benzenesulfonyl-N-(3,5-dimethylphenyl)-amino]-2-bornyl}-(1R,5S)-2-oxo-5-phenyl-cyclopentanecarboxylate (21n)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.77 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.95-1.17 (m, 2H), 1.01 (s, 3H, CH_3), 1.68-1.47 (m, 3H), 2.02 (s, 3H, Ar–CH_3), 2.10 (m_c, 1H), 2.36 (s, 3H, Ar–CH_3), 2.56-2.72 (m, 2H), 2.84 (ddd, *J* = 18.1, 11.6 and 9.0 Hz, 1H), 3.43 (d, *J* = 10.2 Hz, 1H, 1'-H), 4.37 (m_c, 2H, 3-H, 5'-H), 5.42 (d, *J* = 8.6 Hz, 1H, 2-H), 5.70 (s, 1H, NAr 2-H), 6.87 (s, 1H, NAr 4-H), 7.09 (s, 1H, NAr 6-H), 7.23 (m_c, 1H, CArH), 7.30-7.46 (m, 8H, SO_2ArH, CArH), 7.52 (m_c, 1H, SO_2ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 126.85 (Ph C-4), 127.27 (Ph C-2, C-6), 128.63 (Ph C-3, C-5), 142.16 (Ph C-1), for further signals see table 2. Anal. Calcd for $C_{36}H_{41}NO_5S$: C, 72.09; H, 6.90; N, 2.34. Found C, 71.90; H, 6.91; N, 2.49.

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