Supplementary Information

A C_2 -Symmetric Chiral Bis-Sulfoxide Ligand in Rhodium-Catalyzed Reaction: Asymmetric 1, 4- Addition of Sodium Tetraarylborates to Chromenones

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Experimental Section.

General Methods.

All commercially available reagents were used as received without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. (*R*)-*tert*-butane-thiosulfinate was prepared according to our method.¹ All reactions were performed under argon atmosphere in flame-dried glassware. ¹H NMR and ¹³C NMR were acquired at 300 MHz and 75 MHz and respectively. Optical rotation were recorded on PE polarimeter 341. Enantiomeric excess was determined by HPLC analysis on Chiralcel AD, OD, As or OJ column (Daicel Chemical Industries, LTD). Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer.

Synthesis of ligand

(R,R)-1,2-Bis(tert-Butylsulfinyl)benzene, (R,R)-1

At -78 °C, n-BuLi (4.4 mL, 2.5M in hexane, 11.0 mmol) was added dropwise to a solution of (R)-tert-Butylsulfinylbenzene **2**² (1.82 g, 10.0 mmol) in tetrahydrofuran (15 mL). The resulting mixture was stirred for 1 h at -78 °C and (R)-tert-butanethiosulfinate **3** (1.94 g, 11.0 mmol) was added to the mixture. After 0.5 h at -78 °C the reaction was allowed to warm to room temperature. The resulting mixture was quenched with water (10 mL), the organic phase separated and aqueous layer was extracted with CH₂Cl₂ (3 x 15 mL). The combined organic layer was dried over MgSO₄ and concentrated to a small volume. Flash chromatography of the crude material with Petroleum/EtOAc (2:1) afforded (R,R)-**1** as a white solid. (1.28g, 45%). $[\alpha]_D^{20} = +289.5$ (C=0.10, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 1.25 (s, 9H), 7.68-7.71(m, 2H), 7.98-8.01(m, 2H)ppm.. ¹³C NMR (75MHz, CDCl₃): δ = 23.1, 59.0, 126.1, 131.5, 131.6, 140.9 ppm. HRMS: Calcd. for C₁₄H₂₂O₂S₂+Na: 309.0959, found: 309.0972.

References

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2. (a) Chen, J. M.; Li, D.; Ma, H. F.; Cun, L. F.; Zhu, J.; Deng, J. G.; Liao, J. *Tetrahedron Lett.* **2008**, 49, 6921. (b) Fur, N. L.; Mojovic, L.; Ple, N.; Turck, A.; Reboul, V.; Metzner, P. *J. Org. Chem.* **2006**, 71, 2609.

General procedure for enantioselective rhodium-catalyzed addition of arylboronic acids to enones/esters

Under an argon atmosphere and at room temperature, to a 10mL Schlenk tube with a teflon cap was added ligand (*R,R*)-**1** (3.4 mg, 2.4 mol%), $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (1.94 mg, 2 mol %) and 1 mL CH_2Cl_2 , the mixture was stirred at 25°C for 30 min. $\text{ArB}(\text{OH})_2$ **6** (1.0 mmol), enone/ester **4** (0.5 mmol), degassed KOH aq. (2.5M in H_2O , 0.1 ml, 0.25 mmol) was added sequentially. The mixture was stirred for 3h at 40°C (monitored by TLC) and directly charged onto a column (silica gel) and flash chromatographed with a mixture of Petroleum/EtOAc to afford the product **7**.

(*R*) -3-Phenyl-cyclohexanone **7ap**

The ee was determined by HPLC using a Chiralcel OD-H column, hexane/2-propanol, 99/1, flow rate 1.0 ml/min, t_R : 15.1 min (minor), 16.1 min (major), $[\alpha]_D^{20} = +20.7$ ($c=0.73$, CHCl_3).

98% ee, 96% yield. ^1H NMR (300MHz, CDCl_3): δ = 1.80-1.89(m, 2H), 2.07-2.16(m, 2H), 2.37-2.59(m, 4H), 3.01(m, 1H), 7.21-7.26(m, 3H), 7.33-7.36 (m, 2H)ppm. ^{13}C NMR (75MHz, CDCl_3): δ = 25.5, 32.7, 41.1, 44.7, 48.9, 126.5, 126.6, 128.6, 144.3, 210.9 ppm.

3-(4-Fluorophenyl)cyclohexanone **7aq**

The ee was determined by HPLC using a Chiralcel AD-H column, hexane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 9.6 min (minor), 10.9 min (major), $[\alpha]_D^{20} = +18.8$ ($c=0.37$, CHCl_3).

97% ee, 97% yield. ^1H NMR (300 MHz, CDCl_3): δ = 1.77-1.85(m, 2H), 2.05-2.17(m, 2H), 2.38-2.56(m, 4H), 2.98-3.00(m, 1H), 6.98-7.04(m, 2H), 7.15-7.20(m, 2H)ppm. ^{13}C NMR (75MHz, CDCl_3): δ = 25.3, 32.8, 41.0, 43.9, 48.9, 115.3(d, $J=21.1\text{Hz}$), 127.9(d, $J=7.8\text{Hz}$), 139.96, 140.0(d, $J=3.2\text{Hz}$), 161.4(d, $J=243.2\text{Hz}$), 210.6 ppm.

3-(4-Chlorophenyl)cyclohexanone **7ar**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 10.8 min (minor), 11.3min (major). $[\alpha]_D^{20} = +19.3$ (c=0.93, CHCl_3).

97% ee, 97% yield. ^1H NMR(300MHz, CDCl_3): δ =1.76-1.83(m, 2H), 2.03-2.15(m, 2H), 2.35-2.54(m, 4H), 2.96-2.98(m, 1H), 7.14(d, J =8.4Hz, 2H), 7.28 (d, J =8.4Hz, 2H)ppm.

^{13}C NMR (75MHz, CDCl_3): δ =25.3, 32.6, 41.0, 44.0, 48.7, 128.0, 128.6, 132.3, 142.7, 210.3 ppm.

3-(4-Methylphenyl)cyclohexanone **7as**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 9.0min (minor), 9.6 min (major), $[\alpha]_D^{20} = +19.2$ (c=0.87, CHCl_3).

95% ee, 95% yield. ^1H NMR (300MHz, CDCl_3): δ =1.79-1.86(m, 2H), 2.05-2.16(m, 2H), 2.33(s, 3H), 2.37-2.57(m, 4H), 2.97(m, 1H), 7.10-7.16(m, 4H)ppm. ^{13}C NMR (75MHz, CDCl_3): δ =20.9, 25.5, 32.9, 41.1, 44.3, 49.0, 126.4, 129.3, 136.2, 141.4, 211.1 ppm.

3-(4-*tert*-Butyl-phenyl)cyclohexanone **7at**

The ee was determined by HPLC using a Chiralcel AS-H column, heaxane/2-propanol, 95/5, flow rate 1.0 ml/min, t_R : 9.0 min (minor), 10.8 min (major), $[\alpha]_D^{20} = +10.8$ (c=0.67, CHCl_3).

97% ee, 87% yield. ^1H NMR (300MHz, CDCl_3): δ = 1.31(s, 9H), 1.79-1.87(m, 2H), 2.07-2.17 (m, 2H), 2.39-2.59(m, 2H), 2.98(m, 1H), 7.16(d, J =8.3Hz, 2H), 7.36(d, J =8.3Hz, 2H)ppm. ^{13}C NMR (75MHz, CDCl_3): δ =25.5, 31.3, 32.8, 34.4, 41.2, 44.2, 49.0, 125.5, 126.2, 141.3, 149.5, 211.2 ppm.

3-(4-Chlorophenyl)cyclohexanone **7au**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 10.6min (minor), 11.3 min (major), $[\alpha]_D^{20} = +10.7$ (c=1.0, CHCl₃).

98% ee, 99% yield. ¹H NMR (300 MHz, CDCl₃): δ =1.74-1.82(m, 2H), 2.01-2.14(m, 2H), 2.39-2.53(m, 4H), 2.94-3.00(m, 1H), 7.06-7.08(m, 1H), 7.16-7.25(m, 3H)ppm. ¹³C NMR(75MHz, CDCl₃): δ =25.2, 32.4, 40.9, 44.2, 48.4, 124.7, 126.6, 126.7, 129.6, 134.2, 146.2, 210.2 ppm.

3-(3-Methylphenyl)cyclohexanone **7av**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 8.2 min (minor), 8.5 min (major), $[\alpha]_D^{20} = +21.7$ (c=0.93, CHCl₃).

96% ee, 97% yield. ¹H NMR (300 MHz, CDCl₃): δ = 1.70-1.88(m, 2H), 2.06-2.17(m, 2H), 2.35(s, 3H), 2.38-2.58(m, 4H), 2.96-2.97(m, 1H), 7.01-7.07(m, 3H), 7.22-7.26(m, 1H) ppm. ¹³C NMR (75MHz, CDCl₃): δ =21.4, 25.5, 32.8, 41.1, 44.7, 48.9, 123.5, 127.3, 127.4, 128.5, 138.2, 144.3, 211.0 ppm.

3-(2-Methylphenyl)cyclohexanone **7aw**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 10.5min (minor), 11.5 min (major), $[\alpha]_D^{20} = +46.2$ (c=0.85, CHCl₃).

96% ee, 90% yield. ¹H NMR (300 MHz, CDCl₃): δ = 1.80-1.88(m, 2H), 2.16-2.20(m, 2H), 2.33(s, 3H), 2.40-2.46(m, 2H), 2.51-2.54(m, 2H), 3.20-3.27(m, 1H), 7.11-7.16(m, 2H), 7.18-7.26(m, 2H)ppm. ¹³C NMR (75MHz, CDCl₃): δ =19.2, 25.7, 31.9, 40.2, 41.2, 48.3, 125.0, 126.3, 126.4, 130.6, 135.0, 142.2, 211.3ppm.

3-(3,5-dimethylphenyl)cyclohexanone **7ax**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 99/1, flow rate 1.0 ml/min, t_R : 11.3 min (minor), 14.9 min (major), $[\alpha]_D^{20} = +12.5$ ($c=0.95$, CHCl_3). 97% ee, 95% yield. ^1H NMR(300 MHz, CDCl_3): $\delta=1.74$ -1.88(m, 2H), 2.05-2.18(m, 2H), 2.32(s, 6H), 2.39-2.44(m, 2H), 2.52-2.57(m, 2H), 2.93-2.98(m, 1H), 6.85-6.89(m, 3H) ppm. ^{13}C NMR (75MHz, CDCl_3): $\delta=21.3$, 25.6, 32.8, 41.2, 44.7, 49.0, 124.4, 128.3, 138.1, 144.3, 211.1 ppm.

3-(1-naphthyl)cyclohexanone **7ay**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 85/15, flow rate 1.0 ml/min, t_R : 11.4 min (minor), 12.2 min (major), $[\alpha]_D^{20} = +53.8$ ($c=0.92$, CHCl_3). 92% ee, 93% yield. ^1H NMR(300MHz, CDCl_3) $\delta=1.95$ -2.00(m, 2H), 2.04-2.25(m, 2H), 2.46-2.53(m, 2H), 2.62-2.76(m, 2H), 3.81-3.90(m, 1H), 7.39-7.56(m, 4H), 7.76(d, $J=8.0\text{Hz}$, 1H), 7.88(d, $J=9.0\text{Hz}$, 1H), 8.04 (d, $J=8.2\text{Hz}$, 1H)ppm. ^{13}C NMR (75MHz, CDCl_3): $\delta=25.6$, 32.3, 39.4, 41.4, 48.6, 122.4, 122.7, 126.2, 126.5, 122.6, 127.3, 129.1, 131.0, 134.0, 140.1, 211.0 ppm.

3-(2-naphthyl)cyclohexanone **7az**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 85/15, flow rate 0.5 ml/min, t_R : 10.7min (minor), 11.4 min (major), $[\alpha]_D^{20} = +7.6$ ($c=0.79$, CHCl_3). 93% ee, 98% yield. ^1H NMR(300MHz, CDCl_3) $\delta=1.86$ -1.99(m, 2H), 2.16-2.22(m, 2H), 2.42-2.48(m, 2H), 2.66-2.68(m, 2H), 3.17-3.19(m, 1H), 7.37(d, $J=8.5\text{Hz}$, 1H), 7.44-7.50(m, 2H),

7.65(s, 1H), 7.79-7.84(m, 3H)ppm. ^{13}C NMR (75MHz, CDCl_3): δ =25.5, 32.8, 41.2, 44.8, 48.8, 124.8, 125.3, 125.6, 126.2, 127.6, 127.7, 128.4, 132.4, 133.6, 141.8, 210.8 ppm.

3-phenylcyclopentanone **7bp**

The ee was determined by GC using a GAMMA β -DEXTM 225 column (column temperature = 155 °C, H_2 = 12 Psi). t_R : 19.6 min (minor), 19.8 min (major), $[\alpha]_D^{20}$ = +89.6 (c =0.79, CHCl_3).

94% ee, 98% yield. ^1H NMR(300MHz, CDCl_3) δ =1.98-2.02(m, 1H), 2.30-2.49(m, 4H), 2.62-2.71(m, 1H), 3.40-3.48(m, 1H), 7.23-7.28(m, 3H), 7.33-7.38(m, 2H)ppm. ^{13}C NMR(75MHz, CDCl_3): δ =31.0, 38.7, 42.0, 45.6, 126.5, 126.5, 128.5, 142.9, 218.1 ppm.

3-phenylcycloheptanone **7cp**

The ee was determined by HPLC using a Chiralcel OD-H column, hexane/2-propanol, 98/2, flow rate 0.5 ml/min, t_R : 11.0 min (minor), 11.6min (major), $[\alpha]_D^{20}$ = +59.3 (c =0.60, CHCl_3).

93% ee, 95% yield, ^1H NMR(300MHz, CDCl_3) δ =1.51(m, 1H), 1.72-1.75(m, 2H), 2.03-2.07 (m, 3H), 2.57-2.67(m, 3H), 2.90-2.94(m, 2H), 7.16-7.22(m, 3H), 7.26-7.32 (m, 2H) ppm. ^{13}C NMR(75MHz, CDCl_3): δ =24.1, 29.1, 39.1, 42.6, 43.8, 51.2, 126.2, 126.3, 128.5, 146.8, 213.3 ppm.

4-phenyl-tetrahydro-2H-pyran-2-one **7dp**

The ee was determined by GC using a GAMMA β -DEXTM 225 column (column temperature = 155 °C, H_2 = 12 Psi). t_R : 30.0 min (minor), 30.8 min (major), $[\alpha]_D^{20}$ = +6.3(c =1.0, CHCl_3).

94% ee, 87% yield. ^1H NMR (300MHz, CDCl_3) δ =2.00-2.16(m, 2H), 2.64(dd, J =10.6Hz,

$J=17.6\text{Hz}$, 1H), 2.88-2.96(m, 1H), 3.22-3.26(m, 1H), 4.38-4.52(m, 2H), 7.20-7.39(m, 5H)ppm.

^{13}C NMR (75MHz, CDCl_3): $\delta=30.3, 37.4, 37.4, 68.6, 126.4, 127.2, 128.9, 142.8, 170.6$ ppm.

4-phenylpentan-2-one **7ep**

The ee was determined by HPLC using a Chiralcel AS-H column, heaxane/2-propanol, 98/2,

flow rate 0.5 ml/min, t_R : 15.5 min (minor), 18.4 min (major), $[\alpha]_D^{20} = +32.5$ ($c=0.51$, CHCl_3).

98% ee, 97% yield. ^1H NMR(300 MHz, CDCl_3) $\delta= 2.01$ (d, $J=6.9\text{Hz}$, 3H), 2.06(s, 3H), 2.61-

2.80(m, 2H), 3.28-3.34(m, 1H), 7.17-7.32(m, 5H)ppm. ^{13}C NMR(75MHz, CDCl_3): $\delta=21.9, 30.5,$

35.4, 51.9, 126.2, 126.7, 128.5, 146.1, 207.7 ppm.

4-phenylheptan-2-one **7fp**

The ee was determined by HPLC using a Chiralcel AD-H column, heaxane/2-propanol, 98/2,

flow rate 0.5 ml/min, t_R : 10.1 min (minor), 10.4 min (major), $[\alpha]_D^{20} = +30.5$ ($c=0.51$, CHCl_3).

97% ee, 95% yield. ^1H NMR(300MHz, CDCl_3) $\delta= 0.85$ (t, $J=7.2\text{Hz}$, 3H), 1.14-1.21(m, 2H),

1.54-1.61(m, 2H), 2.00(s, 3H), 2.71(d, $J=5.5\text{Hz}$, 2H), 3.14(t, $J=7.4\text{Hz}$, 1H), 7.16-7.20(m, 3H),

7.26-7.31(m, 2H)ppm. ^{13}C NMR (75MHz, CDCl_3): 13.9, 20.5, 30.6, 38.7, 41.1, 50.9, 126.3, 127.4,

128.4, 144.6, 208.0ppm.

Table 2. Conditions screening for the 1,4-addition of sodium tetraphenylborate to chromene **5a**

entry	Rh (mol%)	Ph ₄ BNa (equiv.)	solvent	Solvent/H ₂ O (v/v)	temp (°C)	time (h)	yield (%)	e.e (%)
1	5.0	3.0	CH ₂ Cl ₂	15:1	25	24	37	99
2	5.0	3.0	CH ₂ Cl ₂	15:1	40	24	68	99
3	10.0	3.0	CH ₂ Cl ₂	15:1	40	24	72	99
3	5.0	3.0	cyclohexane	15:1	40	24	53	99
4	5.0	3.0	dioxane	15:1	40	24	trace	n.d.
5	5.0	3.0	THF	15:1	40	24	trace	n.d.
6	5.0	3.0	toluene	15:1	40	24	trace	n.d.
7	5.0	3.0	MeOH	15:1	40	24	trace	n.d.
8	5.0	3.0	DCE	15:1	40	24	37	99
9	5.0	3.0	CH ₂ Cl ₂	20:1	40	24	70	99
10	5.0	3.0	CH ₂ Cl ₂	10:1	40	24	60	99
11	5.0	2.0	CH ₂ Cl ₂	15:1	40	24	49	99
12	5.0	4.0	CH₂Cl₂	15:1	40	24	75	99

General procedure for enantioselective rhodium-catalyzed addition of sodium tetraarylborate to chromenes

Under an argon atmosphere and at room temperature, to a 10mL Schlenk tube with a teflon cap was added ligand (*R,R*)-**1** (3.4 mg, 6 mol%), [RhCl(C₂H₄)₂]₂ (1.94 mg, 5 mol %) and 1.5 mL CH₂Cl₂, the mixture was stirred at 25°C for 30 min. then sodium tetraarylborate (0.8 mmol, 4.0 equiv), chromene **4** (0.2 mmol) and degassed H₂O (0.1mL, 6 mmol) was added sequentially. The mixture was stirred for 24h at 40°C and directly charged onto a column (silica gel) and flash chromatographed with a mixture of Petroleum/EtOAc to afford the product **5**.

(R)-flavanone 8a

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10 flow rate 1.0 ml/min, t_R : 8.2 min (minor), 10.3 min (major), $[\alpha]_D^{20} = +67$ (c=0.10, EtOH). 99.7% ee, 75 % yield. ^1H NMR(300 MHz, CDCl_3) δ = 2.90(dd, 1H, J =3.0Hz, J =16.9Hz), 3.10(dd, 1H, J =13.2Hz, J =16.8Hz), 5.48(dd, 1H, J =2.9Hz, J =13.2Hz), 7.04-7.08(m, 2H), 7.39-7.51(m, 6H), 7.94(dd, 1H, J =1.7Hz, J =7.9Hz)ppm. ^{13}C NMR (75MHz, CDCl_3): δ =44.6, 79.6, 118.1, 120.9, 121.6, 126.1, 127.0, 128.7, 128.8, 136.2, 138.7, 161.5, 191.9 ppm.

6-chloro-2-phenylchroman-4-one 8b

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 85/15 flow rate 1.0 ml/min, t_R : 9.2 min (minor), 13.0 min (major), $[\alpha]_D^{20} = +45$ (c=0.20, EtOH). 99.4% ee, 71% yield. ^1H NMR(300MHz, CDCl_3): δ = 2.91 (dd, 1H, J =3.1Hz, J =17.0Hz), 3.08(dd, 1H, J =13.0Hz, J =17.0Hz), 5.48 (dd, 1H, J =3.1Hz, J =13.1Hz), 7.02(d, 1H, J =8.9Hz), 7.40-7.49 (m, 6H), 7.89(d, 1H, J =2.6Hz)ppm. ^{13}C NMR (75MHz, CDCl_3): 44.2, 79.8, 119.9, 121.7, 126.1, 126.4, 127.1, 128.8, 128.9, 136.0, 138.2, 159.9, 190.8 ppm.

6-methyl-2-phenylchroman-4-one 8c

The ee was determined by HPLC using a Chiralcel OD-H column, hexane/2-propanol, 85/15 flow rate 1.0 ml/min, t_R : 6.9 min (minor), 8.3 min (major), $[\alpha]_D^{20} = +68$ (c=0.16, EtOH), 99.0% ee, 62% yield. ^1H NMR (300MHz, CDCl_3) δ =2.33(s, 3H), 2.88(dd, 1H, J =3.0Hz, J

=16.9Hz), 3.07(dd, 1H, $J=13.2\text{Hz}$, $J=16.9\text{Hz}$), 5.48(dd, 1H, $J=3.0\text{Hz}$, $J=13.2\text{Hz}$), $\delta=6.97$ (d, 1H, $J=8.4\text{Hz}$), 7.33(dd, 1H, $J=2.1\text{Hz}$, $J=8.5\text{Hz}$), 7.31-7.51(m, 6H), 7.72(d, $J=1.4\text{Hz}$, 1H)ppm. ^{13}C NMR(75MHz, CDCl_3): $\delta=20.4$, 44.7, 79.6, 117.9, 120.5, 126.1, 126.6, 128.7, 128.8, 131.1, 137.2, 138.8, 159.6, 192.3 ppm.

6-methoxy-2-phenylchroman-4-one **8d**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 9.6 min (minor), 11.8 min (major), $[\alpha]_D^{20} = +55$ (c=0.21, EtOH). 99.3% ee, 68% yield. ^1H NMR(300 MHz, CDCl_3): $\delta=2.88$ (dd, 1H, $J=3.0\text{Hz}$, $J=17.0\text{Hz}$), 3.08(dd, 1H, $J=13.4\text{Hz}$, $J=17.0\text{Hz}$), 3.82(s, 3H), 5.44(dd, 1H, $J=2.9\text{Hz}$, $J=13.4\text{Hz}$), 7.00(d, 1H, $J=9.0\text{Hz}$), 7.13(dd, 1H, $J=3.0\text{Hz}$, $J=9.0\text{Hz}$), 7.35(d, 1H, $J=3.1\text{Hz}$), 7.39-7.50 (m, 5H). ^{13}C NMR(75MHz, CDCl_3): 44.6, 55.8, 79.7, 107.3, 119.4, 120.7, 125.4, 126.1, 128.7, 128.8, 138.8, 154.2, 156.2, 192.1 ppm.

6-fluoro-2-phenylchroman-4-one **8e**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 85/15, flow rate 1.0 ml/min, t_R : 8.5 min (minor), 11.8 min (major), $[\alpha]_D^{20} = +14$ (c=0.24, EtOH). 98.9 % ee, 58 % yield. ^1H NMR(300 MHz, CDCl_3): $\delta=2.91$ (dd, 1H, $J=2.9\text{Hz}$, $J=17.0\text{Hz}$), 3.08(dd, 1H, $J=13.3\text{Hz}$, $J=17.0\text{Hz}$), 5.47(dd, 1H, $J=2.9\text{Hz}$, $J=13.2\text{Hz}$), 7.05(dd, 1H, $J=4.2\text{Hz}$, $J=9.0\text{Hz}$), 7.24 (dd, 1H, $J=3.4\text{Hz}$, $J=4.4\text{Hz}$), 7.39-7.50(m, 5H), 7.58(dd, 1H, $J=3.1\text{Hz}$, $J=8.2\text{Hz}$) ppm. ^{13}C NMR(75MHz, CDCl_3): 44.34, 44.35, 79.8, 111.9, 112.2, 119.8, 119.9, 121.3, 121.4, 123.6, 123.9, 126.1, 128.90, 128.91, 138.4, 155.7, 157.8, 158.9, 191.2, 191.23 ppm.

6-bromo-2-phenylchroman-4-one **8f**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 11.0 min (minor), 15.8 min (major), $[\alpha]_D^{20} = +60$ (c=0.12, EtOH). 99.3% ee, 63% yield. ^1H NMR(300 MHz, CDCl_3): δ = 2.91(dd, 1H, J =3.0Hz, J =17.0Hz), 3.09 (dd, 1H, J =13.2Hz, J =17.1Hz), 5.47(dd, 1H, J =3.0Hz, J =13.1Hz), 6.97(d, 1H, J =8.8Hz), 7.40-7.49(m, 5H), 7.59(dd, 1H, J =2.5Hz, J =8.8Hz), 8.03(d, 1H, J =2.5Hz)ppm. ^{13}C NMR(75MHz, CDCl_3): 44.2, 79.8, 114.3, 120.2, 126.1, 128.9, 129.0, 129.5, 138.2, 138.8, 160.4, 190.7 ppm.

7-bromo-2-phenylchroman-4-one **8g**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 10.5 min (minor), 15.3 min (major), $[\alpha]_D^{20} = +40$ (c=0.16, EtOH). 98.9 % ee, 67 % yield. ^1H NMR(300 MHz, CDCl_3): δ = 2.90 (dd, 1H, J =2.9Hz, J = 16.9Hz), 3.08(dd, 1H, J =13.2Hz, J =16.9Hz), 5.49(dd, 1H, J =2.8Hz, J = 13.0Hz), 7.20 (d, 1H, J =8.3Hz), 7.27(s, 1H), 7.40-7.46(m, 5H), 7.79(d, 1H, J =8.4Hz) ppm. ^{13}C NMR (75MHz, CDCl_3): 44.4, 80.0, 119.8, 121.4, 125.3, 126.1, 128.3, 128.9, 129.0, 130.6, 138.2, 161.7, 191.0 ppm.

7-methyl-2-phenylchroman-4-one **8h**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 7.8 min (minor), 11.6 min (major), $[\alpha]_D^{20} = +57$ (c=0.18, EtOH). 99.0 % ee, 57 %yield. ^1H NMR(300 MHz, CDCl_3): δ = 2.37(s, 3H), 2.86(dd, 1H, J =2.9Hz, J =16.9Hz), 3.06(dd, 1H, J =13.2Hz, J =16.8Hz), 5.47(dd, 1H, J =2.7Hz, J =13.2Hz), 6.08(d, 1H,

$J=6.8\text{Hz}$), 7.39-7.50(m, 5H), 7.83(d, 1H, $J=6.8\text{Hz}$)ppm. ^{13}C NMR(75MHz, CDCl_3): 22.0, 44.6, 79.6, 118.1, 118.7, 123.0, 126.1, 126.9, 128.7, 128.8, 138.9, 147.8, 161.6, 191.7 ppm.

2-phenyl-2H-benzo[h]chromen-4(3H)-one **8i**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 9.7 min (minor), 12.0 min (major), $[\alpha]_D^{20} = +83$ ($c=0.10$, EtOH), 99.5 % ee, 59 % yield. ^1H NMR(300 MHz, CDCl_3): $\delta=3.00(\text{dd}, 1\text{H}, J=3.2\text{Hz}, J=16.8\text{Hz})$, 3.19 (dd, 1H, $J=13.7\text{Hz}, J=16.7\text{Hz}$), 5.70(dd, 1H, $J=3.2\text{Hz}, J=13.5\text{Hz}$), 7.43-7.66(m, 8H), 7.82(d, 1H, $J=8.3\text{Hz}$), 7.91(d, 1H, $J=8.8\text{Hz}$), 8.35(d, 1H, $J=8.3\text{Hz}$) ppm. ^{13}C NMR (75MHz, CDCl_3): 44.0, 80.3, 115.4, 121.2, 121.7, 123.6, 124.8, 126.1, 126.2, 127.8, 128.7, 128.8, 129.7, 137.5, 138.7, 159.8, 191.6 ppm.

2-p-tolylchroman-4-one **8j**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10 flow rate 1.0 ml/min, t_R : 7.5 min (minor), 8.8 min (major), $[\alpha]_D^{20} = +80$ ($c=0.29$, EtOH), 99.4 % ee, 70 % yield. ^1H NMR(300MHz, CDCl_3): $\delta=2.39(\text{s}, 3\text{H})$, 2.87(dd, 1H, $J=2.9\text{Hz}, J=16.9\text{Hz}$), 3.10(dd, 1H, $J=13.3\text{Hz}, J=16.9\text{Hz}$), 5.45(dd, 1H, $J=2.7\text{Hz}, J=13.3\text{Hz}$), 7.03-7.08(m, 2H), 7.25(d, 2H, $J=7.8\text{Hz}$), 7.37(d, 2H, $J=8.0\text{Hz}$), 7.51(t, 1H, $J=7.2\text{Hz}$), 7.93(dd, 1H, $J=1.7\text{Hz}, J=8.1\text{Hz}$) ppm. ^{13}C NMR (75MHz, CDCl_3): 21.2, 44.5, 79.5, 118.1, 120.8, 121.5, 126.2, 127.0, 129.5, 135.7, 136.2, 138.7, 161.6, 192.2 ppm.

2-m-tolylchroman-4-one **8k**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 6.8 min (minor), 9.9 min (major), $[\alpha]_D^{20} = +57$ (c=0.36, EtOH).

97.7 % ee, 64 % yield. ^1H NMR(300 MHz, CDCl_3): δ = 2.47(s, 3H), 2.95(dd, 1H, $J=2.3\text{Hz}$, $J=16.8\text{Hz}$), 3.16(dd, 1H, $J=13.3\text{Hz}$, $J=16.8\text{Hz}$), 5.50(d, 2H, $J=13.4\text{Hz}$), 7.10-7.14(m, 2H), 7.27(d, 1H, $J=7.2\text{Hz}$), 7.33-7.40(m, 3H), 7.57(t, 1H, $J=7.4\text{Hz}$), 8.01(dd, 1H, $J=1.2\text{Hz}$, $J=8.1\text{Hz}$)ppm. ^{13}C NMR (75MHz, CDCl_3): 21.4, 44.6, 79.6, 118.1, 120.8, 121.5, 123.2, 126.8, 127.0, 128.7, 129.5, 136.1, 138.5, 161.5, 192.0 ppm.

2-(3-chlorophenyl)chroman-4-one **8l**

The ee was determined by HPLC using a Chiralcel OD-H column, heaxane/2-propanol, 90/10, flow rate 1.0 ml/min, t_R : 7.0 min (minor), 10.1 min (major), $[\alpha]_D^{20} = +37$ (c=0.14, EtOH).

97.1 % ee, 25 % yield. ^1H NMR(300 MHz, CDCl_3): δ =2.88(dd, 1H, $J=2.6\text{Hz}$, $J=16.9\text{Hz}$), 3.04(dd, 1H, $J=13.2\text{Hz}$, $J=16.8\text{Hz}$), 5.46(dd, 1H, $J=2.8\text{Hz}$, $J=13.1\text{Hz}$), 7.08(t, 2H, $J=7.5\text{Hz}$), 7.37-7.56(m, 5H), 7.93(dd, 1H, $J=1.0\text{Hz}$, $J=8.2\text{Hz}$) ppm. ^{13}C NMR (75MHz, CDCl_3): 44.6, 78.7, 118.0, 120.8, 121.9, 124.1, 126.3, 127.1, 128.9, 130.2, 134.8, 136.4, 140.7, 161.2, 191.4 ppm.

CJ-1 44 (0.753) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (43:44)

12-May-2009
TOF MS ES+
4.41e3

	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	15.122	1241214	49.87	46453	55.70
2	16.372	1247880	50.13	36839	44.30

	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.896	40274	0.91	2044	2.28
2	17.565	4394271	99.09	87605	97.72

1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.955	1531759	150482	50.139	52.529
2	11.548	1523250	135991	49.861	47.471
Total		3055009	286473	100.000	100.000

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		3.2392	29.968	0.000	17886			
2		96.7608	30.847	0.000	534300	BB	12.7	
Totals:		100.0000		0.000	552186	BB	18.5

1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.181	7997706	251673	49.716	58.821
2	18.576	8089050	176186	50.284	41.179
Total		16086756	427859	100.000	100.000

1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.521	2446278	222670	50.038	50.187
2	10.914	2442561	221008	49.962	49.813
Total		4888839	443678	100.000	100.000