Highly Enantioselective and Efficient Synthesis of Flavanones Including Pinostrobin through the Rhodium-Catalyzed Asymmetric 1,4-Addition

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Supporting Information

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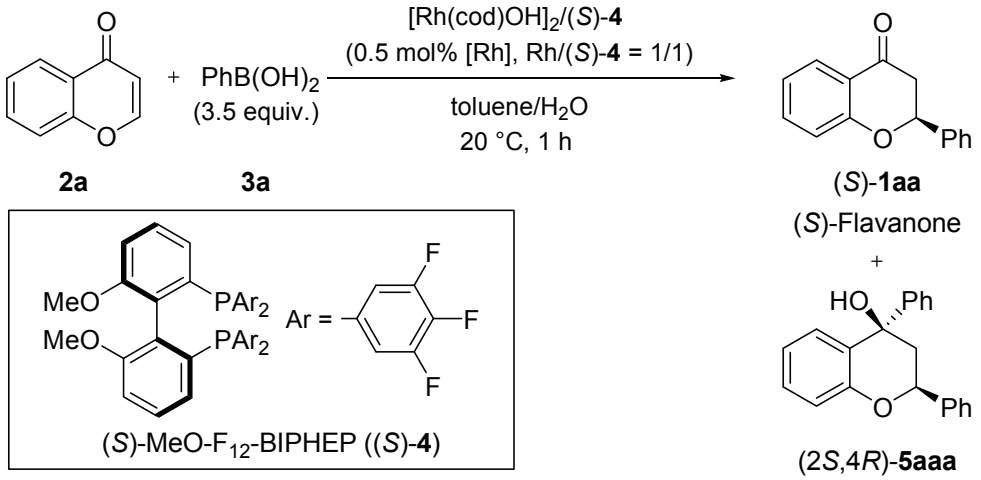
General information.

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dichloromethane and toluene were purchased from Kanto Chemical Co. and then were stored in Schlenk tubes under an argon atmosphere. Acetonitrile and *o*-xylene were purified by distillation prior to use. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. Chromone analogues (**2a**-**2h**) were purified by recrystalization prior to use. As a usual workup procedure, the reaction mixture was extracted with ethyl acetate (EtOAc). The organic layers were dried over Na_2SO_4, filtrated with suction, and then concentrated under reduced pressure. Preparative column chromatography was carried out by using silica gel (Fuji Silysia BW-127 ZH, 100－270 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured at 400 MHz and 101 MHz, respectively, and chemical shifts are given relative to tetramethylsilane (TMS). ^{19}F NMR spectra were measured at 376 MHz, and chemical shifts are given relative to CCl_3F using C_6F_6 as secondary reference (–162.9 ppm).

Experimental details.

General procedure for the 1,4-addition of phenylboronic acid (3a) to chromone (2a).[1, 2]



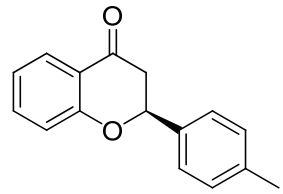
A 20 mL Schlenk flask was flushed with argon and charged with (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), and 0.50 mL of deoxygenated dichloromethane. The mixture was stirred at room temperature for 10 min, and then the solvent was removed under reduced pressure. Then, chromone (**2a**) (149 mg, 1.02 mmol), phenylboronic acid (**3a**) (435 mg, 3.57 mmol), 2.0 mL of deoxygenated toluene and 1.0 mL of deoxygenated water were added to the Schlenk flask. The resulting mixture was stirred at 20 °C for 1 h, and thensaturated aqueous $NaHCO_3$ solution was added to the reaction mixture. The resulting mixture was extracted with EtOAc, and treated in a usual manner to give a crude product. The residue was purified by silica gel column chromatography (hexane/EtOAc = 8/1) to give (*S*)-**1aa** and (2*S*,4*R*)-**5aaa**.

(*S*)-**1aa**: white solid (212 mg, 93% yield, 99.0% ee); mp 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (dd, J = 2.9, 16.8 Hz, 1H), 3.10 (dd, J = 13.4, 16.8 Hz, 1H), 5.48 (dd, J = 2.9, 13.4 Hz, 1H), 7.04–7.08 (m, 2H), 7.37–7.53 (m, 6H), 7.94 (dd, J = 1.7, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.6, 79.5, 118.1, 120.9, 121.6, 127.0, 128.7, 128.8, 136.1, 138.6, 161.5, 191.9; IR (KBr) 3352, 3074, 2898, 1691, 1608, 1575, 1464, 1373, 1298, 1224 and 907 cm^{-1}; $[\alpha]_D^{23}$ = –66° (*c* 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D^{20}$ = +67° (*c* 0.10, EtOH), 99.7% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1aa**; 8.8 min (99.5%), t_R of (*R*)-**1aa**; 11.0 min (0.5%).

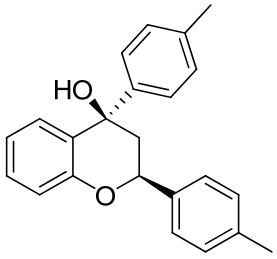
(2*S*,4*R*)-**5aaa**: white solid (8.8 mg, 3% yield, 99.0% ee); mp 56–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 1H), 2.53 (dd, J = 2.9, 13.2 Hz, 1H), 2.59 (dd, J = 11.2, 13.2 Hz, 1H), 4.91 (dd, J = 2.9, 11.2 Hz, 1H), 6.99–7.03 (m, 2H), 7.27–7.37 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.2, 73.5, 75.6, 116.8, 121.1, 126.1, 127.0, 127.2, 127.6, 127.7, 128.1, 128.2, 128.5, 129.5, 140.3, 147.3, 154.8; IR (KBr) 3348, 3061, 3034, 2959, 2885, 1954, 1888, 1809, 1607, 1582, 1485, 1454, 1337, 1229, 1121, 1069, 1015, 872, 756 and 698 cm^{-1}; $[\alpha]_D^{25}$ = +75° (*c* 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*R*,4*S*)-**5aaa**; 7.0 min (0.5%), t_R of (2*S*,4*R*)-**5aaa**; 10.2 min (99.5%).

(2*S*)-2,3-Dihydro-2-(4-methylphenyl)-4*H*-1-benzopyran-4-one (1ab) [1] **and**
(2*S*,4*R*)-2,4-bis(4-methylphenyl)-3,4-dihydro-2*H*-1-benzopyran-4-ol (5abb).

(2*S*)-2,3-Dihydro-2-(4-methylphenyl)-4*H*-1-benzopyran-4-one (**1ab**) and (2*S*,4*R*)-3,4-dihydro-2,4-bis(4-methylphenyl)-2*H*-1-benzopyran-4-ol (**5abb**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 4-methylphenylboronic acid (**3b**) (116 mg, 0.850 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 20 °C for 1 h by the general procedure described above.



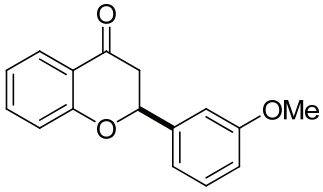
(*S*)-**1ab**: white solid (33.2 mg, 82% yield, 99.2% ee); mp 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.86 (dd, J = 2.8, 16.8 Hz, 1H), 3.10 (dd, J = 13.2, 16.8 Hz, 1H), 5.45 (dd, J = 2.8, 13.2 Hz, 1H), 7.04–7.08 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.51 (ddd, J = 1.8, 7.2, 8.3 Hz, 1H), 7.93 (dd, J = 1.6, 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.2, 44.5, 79.5, 118.1, 120.9, 121.6, 126.2, 127.0, 129.4, 135.7, 136.1, 138.7, 161.6, 192.2; IR (KBr) 3360, 3058, 2891, 1693, 1603, 1578, 1516, 1461, 1371, 1304, 1226, 1115, 1667, 979, 907 and 810 cm^{-1}; $[\alpha]_D^{23}$ = –47° (*c* 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D^{20}$ = +80° (*c* 0.29, EtOH), 99.4% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ab**; 7.5 min (99.6%), t_R of (*R*)-**1ab**; 8.7 min (0.4%).



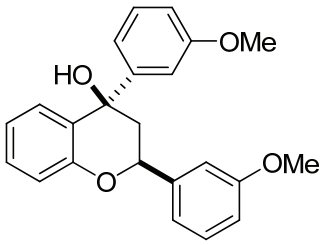
(2*S*,4*R*)-**5abb**: white solid (3.8 mg, 7% yield, >99% ee); mp 66–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.35 (s, 3H), 2.37 (s, 1H), 2.45–2.65 (m, 2H), 4.87 (dd, J = 2.2, 11.7 Hz, 1H), 6.94–7.04 (m, 2H), 7.09–7.38 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 21.1, 47.1, 73.4, 75.6, 116.8, 120.9, 126.2, 127.0, 127.4, 127.6, 128.9, 129.2, 129.4, 137.4, 137.4, 137.9, 144.5, 154.9; IR (KBr) 3366, 3028, 2957, 2920, 1909, 1609, 1581, 1514, 1485, 1454, 1115, 1076, 1043, 1015, 916, 821, 808, 756 and 725 cm^{-1}; $[\alpha]_D^{25}$ = +117° (*c* 0.1, $CHCl_3$); HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*S*,4*R*)-**5abb**; 10.7 min (>99%), t_R of (2*R*,4*S*)-**5abb**; 16.3 min (0%); Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.32; H, 6.78.

(–)-2,3-Dihydro-2-(3-methoxyphenyl)-4*H*-1-benzopyran-4-one (1ac) [3] **and**
(2*S,4*R**)-2,4-bis(3-methoxyphenyl)-3,4-dihydro-2*H*-1-benzopyran-4-ol (5acc).**

(–)-2,3-Dihydro-2-(3-methoxyphenyl)-4*H*-1-benzopyran-4-one (**1ac**) and (2*S**,4*R**)-3,4-dihydro-2,4-bis(3-methoxyphenyl)-2*H*-1-benzopyran-4-ol (**5acc**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 3-methoxyphenylboronic acid (**3c**) (77.5 mg, 0.510 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 20 °C for 1 h by the general procedure described above.

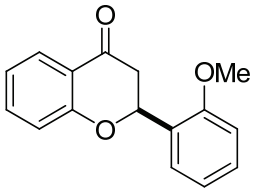


(–)-**1ac**: white solid (39.1 mg, 90% yield, 99.6% ee); mp 65–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (dd, J = 2.9, 16.8 Hz, 1H), 3.08 (dd, J = 13.2, 16.8 Hz, 1H), 3.84 (s, 3H), 5.46 (dd, J = 2.9, 13.2 Hz, 1H), 6.92 (ddd, J = 0.8, 2.4, 8.2 Hz, 2H), 7.03–7.07 (m, 4H), 7.38 (t, J = 8.2 Hz, 1H), 7.51 (ddd, J = 1.8, 7.2, 8.2, 1H), 7.93 (dd, J = 1.6, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.6, 55.3, 79.4, 118.2, 114.0, 118.1, 118.3, 120.7, 121.6, 127.0, 129.9, 136.2, 140.3, 159.9, 161.5, 191.9. IR (KBr) 3360, 3058, 2891, 1693, 1602, 1577, 1461, 1371, 1304, 1226 and 907 cm^{-1}; $[\alpha]_D^{27}$ = –28° (c 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ac**; 10.5 min (99.8%), t_R of (+)-**1ac**; 14.7 min (0.2%).



(2*S**,4*R**)-**5acc**: yellow oil (1.4 mg, 2% yield, 99.4% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (br, 1H), 2.52–2.61 (m, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 4.92 (dd, J = 3.8, 10.3 Hz, 1H), 6.82–7.03 (m, 8H), 7.23–7.32 (m, 3H), 7.36 (dd, J = 1.6 Hz, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.1, 55.2, 55.3, 73.5, 75.7, 111.8, 112.8, 113.1, 113.5, 116.8, 118.4, 119.6, 121.1, 127.1, 127.6, 129.2, 129.5, 129.6, 142.0, 149.1, 154.7, 159.5, 159.8; IR (neat) 3365, 3059, 3070, 3042, 2959, 2921, 1607, 1581, 1508, 1483, 1456, 1228, 1157, 1076, 1043, 1012, 918, 877, 840 and 758 cm^{-1}; $[\alpha]_D^{28}$ = +43° (c 0.3, $CHCl_3$); HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*S**,4*R**)-**5acc**; 17.5 min (99.7%), t_R of (2*R**,4*S**)-**5acc**; 30.0 min (0.3%); Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 75.96; H, 6.39.

(–)-2,3-Dihydro-2-(2-methoxyphenyl)-4*H*-1-benzopyran-4-one (1ad).[3]

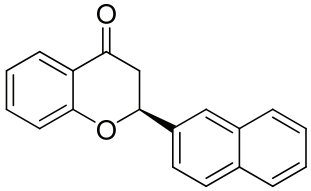


(–)-2,3-Dihydro-2-(2-methoxyphenyl)-4*H*-1-benzopyran-4-one (**1ad**) was obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 2-methoxyphenylboronic acid (**3d**) (310 mg, 2.04 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 20 °C for 2 h by the general procedure described above.

(–)-**1ad**: yellow oil (35.9 mg, 83% yield, 99.6% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (dd, J = 12.4, 16.9 Hz, 1H), 2.98 (dd, J = 3.9, 16.9 Hz, 1H), 3.84 (s, 3H), 5.86 (dd, J = 2.9, 13.2 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 7.03–7.08 (m, 3H), 7.38 (m, 1H), 7.64 (dd, J = 1.4, 7.8 Hz, 1H), 7.94 (dd, J = 1.4, 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 43.7, 55.3, 74.6, 110.5, 118.1, 120.9, 121.0, 121.4, 126.4, 127.0, 127.4, 129.4, 135.9, 155.7, 162.0, 192.7; IR (KBr) 3364, 3036, 3011, 2937, 2928, 2905, 1691, 1683, 1607, 1576, 1495, 1461, 1463, 1438, 1367, 1321, 1304, 1245, 1227 1149, 1118, 1028, 993, 907 and 756 cm^{-1}; $[\alpha]_D^{25}$ = –195° (c 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 0.3 mL/min, 254 nm): t_R of (+)-**1ad**; 22.7 min (0.2%), t_R of (–)-**1ad**; 24.7 min (99.8%).

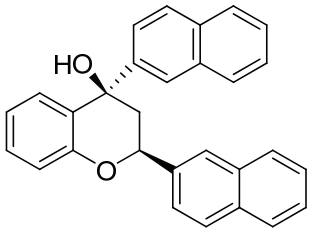
(*S*)-2,3-Dihydro-2-(2-naphthyl)-4*H*-1-benzopyran-4-one (1ae)[4] **and**
(2*S*,4*R*)-2,4-bis(2-naphthyl)-3,4-dihydro-2*H*-1-benzopyran-4-ol (5aee).

(*S*)-2,3-Dihydro-2-(2-naphthyl)-4*H*-1-benzopyran-4-one (**1ae**) and (2*S*,4*R*)-3,4-dihydro-2,4-bis(2-naphthyl)-2*H*-1-benzopyran-4-ol (**5aee**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 2-naphthylboronic acid (**3e**) (87.7 mg, 0.510 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 0 °C for 0.7 h by the general procedure described above.



(*S*)-**1ae**: white solid (38.5 mg, 83% yield, 99.2% ee); mp 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (dd, J = 2.9, 16.8 Hz, 1H), 3.22 (dd, J = 13.2, 16.8 Hz, 1H), 5.68 (dd, J = 2.9, 13.2 Hz, 1H), 7.09–7.13 (m, 2H), 7.54–7.63 (m, 4H), 7.90–7.99 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.7, 79.8, 118.2, 121.2, 121.9, 123.9, 125.6, 126.7, 126.8, 127.3, 128.0, 128.4, 129.0, 133.4, 133.6, 136.3, 136.5, 161.8, 192.2; IR (KBr) 3483, 3051, 2893, 1697, 1607, 1574, 1462, 1396, 1342, 1300, 1221 1148, 1667, 1028 and 907 cm^{-1}; $[\alpha]_D^{27}$ = –85° (c 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D$ = +56.3° (c 0.5, EtOH), 91% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H,

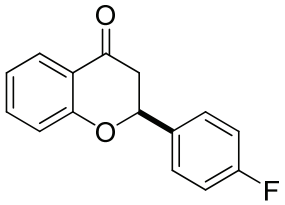
hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ae**; 13.7 min (99.6%), t_R of (*R*)-**1ae**; 21.8 min (0.4%).



(2*S*,4*R*)-**5aee**: white solid (2.0 mg, 3% yield, 99.2% ee); mp 112–115°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 1H), 2.71–2.78 (m, 2H), 5.08–5.17 (m, 1H), 7.05–7.12 (m, 2H), 7.34–7.61 (m, 8H), 7.70–7.94 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.1, 73.7, 75.8, 116.9, 121.3, 123.9, 124.4, 125.1, 126.1, 126.2, 126.3, 126.4, 127.0, 127.2, 127.5, 127.7, 127.8, 128.0, 128.4, 128.4, 128.5, 129.7, 132.7, 132.8, 133.1, 133.2, 137.7, 122.6, 154.9; IR (KBr) 3308, 3055, 2958, 2922, 2853, 1921, 1708, 1630, 1603, 1582, 1506, 1483, 1454, 1352, 1279, 1227, 1126, 1080, 1043, 1018, 922, 901, 860 and 746 cm^{-1}; $[\alpha]_D^{19}$ = +223° (*c* 0.2, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*R*,4*S*)-**5aee**; 12.2 min (0.4%), t_R of (2*S*,4*R*)-**5aee**; 20.8 min (99.6%); Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.50; H, 5.86.

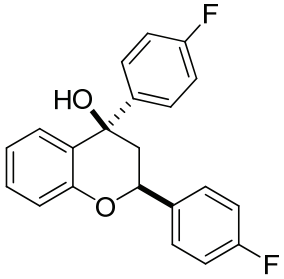
(–)-2,3-Dihydro-2-(4-fluorophenyl)-4*H*-1-benzopyran-4-one (1af) [5] **and**
(2*S,4*R**)-2,4-bis(4-fluorophenyl)-3,4-dihydro-2*H*-1-benzopyran-4-ol (5aff).**

(–)-2,3-Dihydro-2-(4-fluorophenyl)-4*H*-1-benzopyran-4-one (**1af**) and (2*S**,4*R**)-3,4-dihydro-2,4-bis(4-fluorophenyl)-2*H*-1-benzopyran-4-ol (**5aff**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 4-fluorophenylboronic acid (**3f**) (357 mg, 2.55 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 10 °C for 2 h by the general procedure described above.



(–)-**1af**: colorless oil (32.9 mg, 80% yield, 99.8% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dd, *J* = 2.9, 16.8 Hz, 1H), 3.08 (dd, *J* = 13.3, 16.8 Hz, 1H), 5.46 (dd, *J* = 2.9, 13.3 Hz, 1H), 7.03–7.15 (m, 4H), 7.45–7.53 (m, 3H), 7.93 (dd, *J* = 1.6, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.6, 78.8, 115.7 ($^2J_{F\text{-}C}$ = 21.5 Hz), 118.0, 120.6, 121.7, 127.0, 128.0 ($^3J_{F\text{-}C}$ = 8.9 Hz), 134.5 ($^4J_{F\text{-}C}$ = 2.9 Hz), 136.2, 161.3, 162.7 ($^1J_{F\text{-}C}$ = 246 Hz), 191.6; ^{19}F NMR (376 MHz) δ –114.0 to –113.9 (m, 1F); IR (KBr) 3364, 3074, 2899, 1894, 1693, 1605, 1578, 1464, 1367, 1304, 1226 1117, 1069, 1028, 989 and 907 cm^{-1}; $[\alpha]_D^{27}$ = –45° (*c* 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min, 254 nm): t_R of (–)-**1af**; 15.2 min

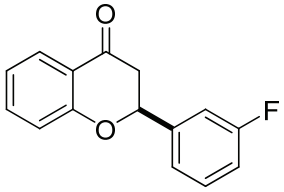
(99.9%), t_R of (+)-**1af**; 16.8 min (0.1%).



(2*S**,4*R**)-**5aff**: white solid (1.2 mg, 2% yield, >99% ee); mp 72–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 1H), 2.43–2.59 (m, 2H), 4.86 (dd, J = 2.3, 11.7 Hz, 1H), 6.94–7.07 (m, 6H), 7.24–7.36 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.5, 73.1, 75.0, 115.0 ($^2J_{F\text{-}C}$ = 21.7 Hz), 115.5 ($^2J_{F\text{-}C}$ = 21.7 Hz), 116.8, 121.4, 126.9, 127.5, 127.9 ($^3J_{F\text{-}C}$ = 8.3 Hz), 128.9 ($^3J_{F\text{-}C}$ = 8.2 Hz), 129.7, 140.0 ($^4J_{F\text{-}C}$ = 3.0 Hz), 143.1 ($^4J_{F\text{-}C}$ = 3.3 Hz), 154.6, 162.2 ($^1J_{F\text{-}C}$ = 246.9 Hz), 162.3 ($^1J_{F\text{-}C}$ = 246.8 Hz); ^{19}F NMR (376 MHz) δ –116.0 to –115.9 (m, 1F), –115.1 to –115.0 (m, 1F); IR (KBr) 3375, 3072, 3039, 2959, 2922, 1892, 1606, 1582, 1508, 1483, 1456, 1416, 1408, 1227, 1157, 1121, 1076, 1043, 1015, 878 and 758 cm^{-1}; $[\alpha]_D^{20}$ = +59° (*c* 0.2, $CHCl_3$); HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*S**,4*R**)-**5aff**; 10.2 min (>99%), t_R of (2*R**,4*S**)-**5aff**; 16.0 min (0%); Anal. Calcd for $C_{21}H_{16}F_2O_2$: C, 74.55; H, 4.77. Found: C, 74.16; H, 5.04.

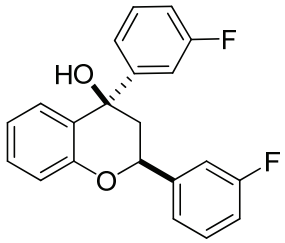
(–)-2,3-Dihydro-2-(3-fluorophenyl)-4*H*-1-benzopyran-4-one (1ag) [6] **and (2*S**,4*R**)-2,4-bis(3-fluorophenyl)-3,4-dihydro-2*H*-1-benzopyran-4-ol (5agg).**

(–)-2,3-Dihydro-2-(3-fluorophenyl)-4*H*-1-benzopyran-4-one (**1ag**) and (2*S**,4*R**)-3,4-dihydro-2,4-bis(3-fluorophenyl)-2*H*-1-benzopyran-4-ol (**5agg**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), chromone (**2a**) (24.8 mg, 0.170 mmol), 3-fluorophenylboronic acid (**3g**) (309 mg, 2.21 mmol), deoxygenated toluene (0.50 mL) and deoxygenated water (0.30 mL) at 40 °C for 2 h by the general procedure described above.



(–)-**1ag**: colorless oil (33.1 mg, 80% yield, 99.0% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (dd, J = 2.9, 16.8 Hz, 1H), 3.04 (dd, J = 13.3, 16.8 Hz, 1H), 5.46 (dd, J = 2.9, 13.3 Hz, 1H), 7.04–7.09 (m, 3H), 7.22–7.25 (m, 2H), 7.39–7.42 (m, 1H), 7.50–7.53 (m, 1H), 7.93 (dd, J = 1.6 Hz, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.6, 78.6, 113.1 ($^2J_{F\text{-}C}$ = 22.3 Hz), 115.5 ($^2J_{F\text{-}C}$ = 20.8 Hz), 118.1, 120.9, 121.5 ($^3J_{F\text{-}C}$ = 3.0 Hz), 121.8, 127.1, 130.4 ($^4J_{F\text{-}C}$ = 8.2 Hz), 136.3, 141.2 ($^4J_{F\text{-}C}$ = 7.5 Hz), 161.2, 162.7 ($^1J_{F\text{-}C}$ = 246 Hz), 191.6; ^{19}F NMR (376 MHz) δ –113.0 to –112.9 (m, 1F); IR (neat) 3364, 3074, 2899, 1894, 1693, 1605, 1578, 1464, 1367, 1304, 1226 and 907 cm^{-1}; $[\alpha]_D^{25}$ = –66° (*c* 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H,

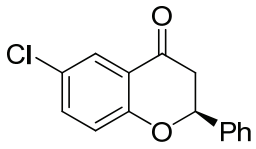
hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (–)-**1ag**; 7.7 min (99.5%), t_R of (+)-**1ag**; 9.3 min (0.5%).



(2*S**,4*R**)-**5agg**: yellow oil (3.7 mg, 6% yield, 97.2% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 1H), 2.59–2.48 (m, 2H), 5.44 (dd, J = 4.7, 9.4 Hz, 1H), 6.96–7.13 (m, 8H), 7.28–7.36 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.3, 73.1, 74.8, 113.1 ($^2J_{F\text{-}C}$ = 22.3 Hz) , 114.2 ($^2J_{F\text{-}C}$ = 23.1 Hz), 114.8 ($^2J_{F\text{-}C}$ = 20.8 Hz), 115.0 ($^2J_{F\text{-}C}$ = 20.8 Hz), 116.9, 121.5, 121.5 ($^4J_{F\text{-}C}$ = 2.9 Hz), 122.8 ($^4J_{F\text{-}C}$ = 3.0 Hz), 126.6, 127.5, 129.7 ($^3J_{F\text{-}C}$ = 8.2 Hz), 129.9, 130.1 ($^2J_{F\text{-}C}$ = 8.1 Hz), 142.8 ($^3J_{F\text{-}C}$ = 7.4 Hz), 149.8 ($^3J_{F\text{-}C}$ = 5.9 Hz), 154.5, 162.7 ($^1J_{F\text{-}C}$ = 250 Hz), 162.9 ($^1J_{F\text{-}C}$ = 245 Hz); ^{19}F NMR (376 MHz) δ –113.7 to –113.5 (m, 2F); IR (neat) 3367, 3077, 3042, 2959, 2920, 1896, 1607, 1582, 1510, 1483, 1456, 1412, 1362, 1229, 1158, 1074, 1043, 1013, 918, 879, 840 and 758 cm^{-1}; $[\alpha]_D^{19}$ = +42° (*c* 0.07, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min, 254 nm): t_R of (2*R**,4*S**)-**5agg**; 12.7 min (1.4%), t_R of (2*S**,4*R**)-**5agg**; 15.2 min (98.6%); Anal. Calcd for $C_{21}H_{16}F_2O_2$: C, 74.55; H, 4.77. Found: C, 74.28; H, 4.96.

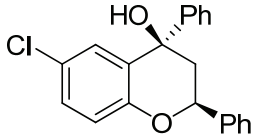
(*S*)-6-Chloro-2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one (1ba) [1] **and**
(2*S*,4*R*)-6-chloro-3,4-dihydro-2,4-diphenyl-2*H*-1-benzopyran-4-ol (5baa).

(*S*)-6-Chloro-2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one (**1ba**) and (2*S*,4*R*)-6-chloro-3,4-dihydro-2,4-diphenyl-2*H*-1-benzopyran-4-ol (**5baa**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), 6-chlorochromone (**2b**) (30.7 mg, 0.170 mmol), phenylboronic acid (**3a**) (104 mg, 0.850 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 40 °C for 1.5 h by the general procedure described above.



(*S*)-**1ba**: white solid (38.0 mg, 86% yield, 99.6% ee); mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dd, J = 2.9, 17.0 Hz, 1H), 3.05 (dd, J = 13.2, 17.0 Hz, 1H), 5.44 (dd, J = 2.9, 13.2 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 7.36–7.47 (m, 6H), 7.86 (d, J = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.1, 79.7, 119.8, 121.6, 126.0, 126.2, 127.0, 128.8, 128.9, 135.8, 138.1, 159.8, 190.6; IR (KBr) 3336, 3063, 1681, 1601, 1501, 1456, 1383, 1317, 1275 1213, 1132, 1062, 989, 908, 893 and 766 cm^{-1}; $[\alpha]_D^{27}$ = –23° (*c* 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D^{20}$ = +40° (*c* 0.20, EtOH), 99.4% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1,

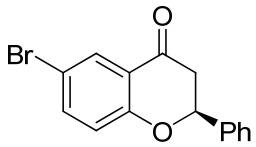
flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ba**; 9.7 min (99.8%), t_R of (*R*)-**1ba**; 12.5 min (0.2%).



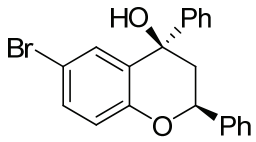
(2*S*,4*R*)-**5baa**: white solid (4.3 mg, 8% yield, 97.6% ee); mp 51–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H), 2.49–2.59 (m, 2H), 4.88 (dd, J = 4.6, 9.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 7.20–7.41 (m, 11H), 7.50 (d, J = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 46.7, 73.4, 75.8, 118.2, 125.9, 126.0, 126.9, 127.4, 127.9, 128.2, 128.3, 128.5, 128.7, 129.5, 139.8, 146.6, 153.4; IR (KBr) 3368, 3061, 3032, 2959, 2919, 1954, 1884, 1811, 1607, 1603, 1574, 1479, 1448, 1412, 1357, 1261, 1231, 1126, 1091, 1018, 922, 860, 818, 758 and 698 cm^{-1}; $[\alpha]_D^{21}$ = +49° (c 0.2, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*R*,4*S*)-**5baa**; 6.8 min (1.2%), t_R of (2*S*,4*R*)-**5baa**; 9.3 min (98.8%); Anal. Calcd for $C_{21}H_{17}ClO_2$: C, 74.89; H, 5.09. Found: C, 74.56; H, 5.36.

(*S*)-6-Broro-2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one (1ca) [1] **and**
(2*S*,4*R*)-6-bromo-3,4-dihydro-2,4-diphenyl-2*H*-1-benzopyran-4-ol (5caa).

(*S*)-6-Broro-2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one (**1ca**) and (2*S*,4*R*)-6-bromo-3,4-dihydro-2,4-diphenyl-2*H*-1-benzopyran-4-ol (**5caa**) were obtained from (*S*)-**4** (2.4 mg, 3.0 μmol), $[Rh(cod)OH]_2$ (0.68 mg, 1.5 μmol), 6-bromochromone (**2c**) (22.5 mg, 0.100 mmol), phenylboronic acid (**3a**) (122 mg, 1.00 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 35 °C for 3 h by the general procedure described above.



(*S*)-**1ca**: white solid (24.5 mg, 81% yield, >99% ee); mp 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dd, J = 2.9, 17.0 Hz, 1H), 3.05 (dd, J = 13.2, 17.0 Hz, 1H), 5.44 (dd, J = 2.9, 13.2 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 7.36–7.47 (m, 6H), 7.86 (d, J = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 46.7, 73.4, 75.8, 118.2, 125.9, 126.0, 126.9, 127.4, 127.9, 128.2, 128.3, 128.5, 128.7, 129.5, 139.8, 146.6, 153.4; IR (KBr) 3350, 3058, 2891, 1693, 1602, 1577, 1461, 1371, 1304, 1226 and 907 cm^{-1}; $[\alpha]_D^{27}$ = –47° (*c* 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D^{20}$ = +60° (*c* 0.12, EtOH), 99.3% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*R*)-**1ca**; 12.3 min (0%), t_R of (*S*)-**1ca**; 17.3 min (>99%).

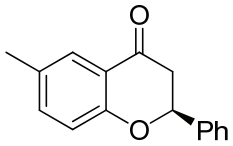


(2*S*,4*R*)-**5caa**: yellow solid (1.2 mg, 3% yield, >99% ee); mp 66–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H), 2.49–2.59 (m, 2H), 4.88 (dd, J = 4.6, 9.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 7.20–7.41 (m, 11H),

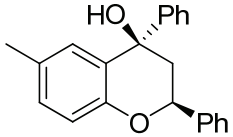
7.50 (d, J = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 46.8, 73.4, 75.9, 113.2, 118.7, 126.1, 126.9, 128.0, 128.3, 128.4, 128.6, 129.3, 130.4, 132.4, 139.8, 146.6, 153.9; IR (KBr) 3420, 3059, 3030, 2959, 2922, 1954, 1888, 1698, 1601, 1572, 1475, 1448, 1406, 1339, 1261, 1231, 1128, 1070, 1020, 920, 818, 772, 758 and 698 cm^{-1}; $[\alpha]_D^{25}$ = +36° (c 0.06, $CHCl_3$); HPLC (Daicel Chiralcel OJ-H, hexane/i-PrOH = 30/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*S*,4*R*)-**5caa**; 35.3 min (>99%), t_R of (2*R*,4*S*)-**5caa**; 43.3 min (0%); Anal. Calcd for $C_{21}H_{17}BrO_2$: C, 66.16; H, 4.49. Found: C, 66.51; H, 4.71.

(*S*)-2,3-Dihydro-6-methyl-2-phenyl-4*H*-1-benzopyran-4-one (1da) [1] **and**
(2*S*,4*R*)-3,4-dihydro-2,4-diphenyl-6-methyl -2*H*-1-benzopyran-4-ol (5daa).

(*S*)-2,3-Dihydro-6-methyl-2-phenyl-4*H*-1-benzopyran-4-one (**1da**) [1] and (2*S*,4*R*)-3,4-dihydro-6-methyl-2,4-diphenyl-2*H*-1-benzopyran-4-ol (**5daa**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), 6-methylchromone (**2d**) (27.2 mg, 0.170 mmol), phenylboronic acid (**3a**) (166 mg, 1.36 mmol), deoxygenated dichloromethane. (0.50 mL) and deoxygenated water (0.30 mL) at 30 °C for 2 h by the general procedure described above.



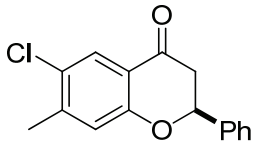
(*S*)-**1da**: white solid (35.2 mg, 87% yield, 99.6% ee); mp 108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.87 (dd, J = 2.9, 16.9 Hz, 1H), 3.05 (dd, J = 13.3, 16.9 Hz, 1H), 5.44 (dd, J = 2.9, 13.3 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 7.30–7.47 (m, 6H), 7.86 (d, J = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.3, 44.6, 79.4, 117.8, 120.4, 126.0, 126.5, 128.6, 128.7, 130.9, 137.1, 138.8, 159.5, 192.1; IR (KBr) 3358, 3033, 2895, 1934, 1699, 1614, 1573, 1494, 1375, 1313, 1226 and 907 cm^{-1}; $[\alpha]_D^{25}$ = –47° (c 0.1, $CHCl_3$) {lit.[1] $[\alpha]_D^{20}$ = +68° (c 0.16, EtOH), 99.0% ee, (*R*)}; HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1da**; 8.0 min (99.8%), t_R of (*R*)-**1da**; 9.7 min (0.2%).



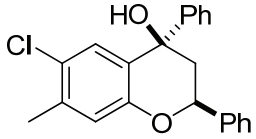
(2*S*,4*R*)-**5daa**: white solid (3.0 mg, 6% yield, >99% ee); mp 70–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.32 (s, 1H), 2.48–2.68 (m, 2H), 4.88 (dd, J = 2.5, 11.5 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 7.04–7.43 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.7, 47.4, 73.6, 75.5, 116.6, 126.1, 126.8, 127.1, 127.6, 127.7, 128.1, 128.2, 128.5, 130.3, 130.3, 140.5, 147.5, 152.7; IR (KBr) 3369, 3059, 3030, 2957, 2920, 1954, 1890, 1810, 1616, 1601, 1585, 1495, 1448, 1416, 1339, 1277, 1229, 1132, 1070, 1020, 920, 864, 818, 773, 754 and 700 cm^{-1}; $[\alpha]_D^{21}$ = +39° (c 0.06, $CHCl_3$); HPLC (Daicel Chiralcel OJ-H, hexane/i-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*S*,4*R*)-**5daa**; 10.7 min (>99%), t_R of (2*R*,4*S*)-**5daa**; 14.7 min (0%); Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.30; H, 6.63.

(–)-6-Chloro-2,3-dihydro-7-methyl-2-phenyl-4*H*-1-benzopyran-4-one (1ea) [7] **and**
(2*S,4*R**)-6-chloro-3,4-dihydro-2,4-diphenyl-7-methyl-2*H*-1-benzopyran-4-ol (5eaa).**

(–)-6-Chloro-2,3-dihydro-7-methyl-2-phenyl-4*H*-1-benzopyran-4-one (**1ea**) [7] and (2*S**,4*R**)-6-chloro-3,4-dihydro-2,4-diphenyl-7-methyl-2*H*-1-benzopyran-4-ol (**5eaa**) were obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), 6-chloro-7-methylchromone (**2e**) (33.1 mg, 0.170 mmol), phenylboronic acid (**3a**) (166 mg, 1.36 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 40 °C for 1.5 h by the general procedure described above.

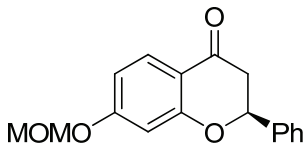


(–)-**1ea**: white solid (41.6 mg, 90% yield, 99.8% ee); mp 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.88 (dd, J = 3.0, 17.0 Hz, 1H), 3.05 (dd, J = 13.1, 17.0 Hz, 1H), 5.45 (dd, J = 2.9, 13.1 Hz, 1H), 6.96 (s, 1H), 7.39–7.47 (m, 5H), 7.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.9, 44.3, 79.7, 119.9, 120.2, 126.1, 126.7, 127.9, 128.9, 128.9, 138.4, 145.3, 159.8, 190.7; IR (KBr) 3360, 3069, 2895, 1693, 1610, 1560, 1456, 1337, 1238, 1217 and 907 cm^{-1}; $[\alpha]_D^{25}$ = –43° (c 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, Hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (–)-**1ea**; 10.2 min (99.9%), t_R of (+)-**1ea**; 19.0 min (0.1%).



(2*S**,4*R**)-**5eaa**: white solid (4.9 mg, 8% yield, 94.2% ee); mp 62–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 1H), 2.37 (s, 3H), 2.48–2.59 (m, 2H), 4.88 (dd, J = 4.5, 9.6 Hz, 1H), 6.88 (s, 1H), 7.21–7.42 (m, 11H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.0, 47.0, 73.3, 75.8, 118.8, 126.1, 126.3, 126.4, 126.9, 127.7, 127.9, 128.2, 128.3, 128.5, 137.4, 140.0, 146.8, 153.2; IR (KBr) 3362, 3061, 3032, 2956, 2912, 1948, 1886, 1616, 1564, 1485, 1448, 1398, 1339, 1240, 1213, 1163, 1069, 1022, 918, 864, 824, 773 and 698 cm^{-1}; $[\alpha]_D^{21}$ = +29° (c 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (2*R**,4*S**)-**5eaa**; 8.8 min (2.9%), t_R of (2*S**,4*R**)-**5eaa**; 11.3 min (97.1%); Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 75.32; H, 5.46. Found: C, 75.06; H, 5.79.

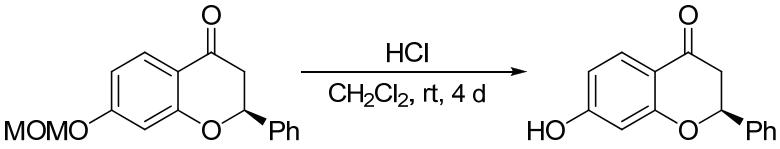
(*S*)-2,3-Dihydro-7-(methoxymethoxy)-2-phenyl-4*H*-1-benzopyran-4-one (1ga).[8]



(*S*)-2,3-Dihydro-7-(methoxymethoxy)-2-phenyl-4*H*-1-benzopyran-4-one (**1ga**) was obtained from (*S*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), 7-(methoxymethoxy)chromone (**2g**) (35.1 mg, 0.170 mmol), phenylboronic acid (**3a**) (166 mg, 1.36 mmol), deoxygenated dichloromethane (0.50 mL) and deoxygenated water (0.30 mL) at 30 °C for 2 h by the general procedure described above.

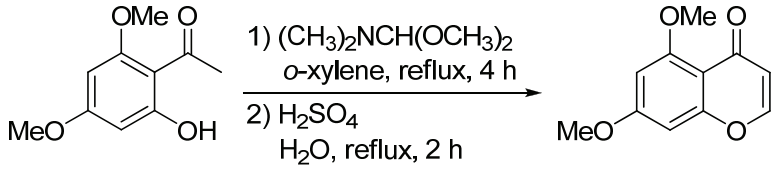
(*S*)-**1ga**: white solid (44.0 mg, 91% yield, 99.4% ee); mp 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (dd, J = 2.9, 16.9 Hz, 1H), 3.04 (dd, J = 13.3, 16.9 Hz, 1H), 3.48 (s, 3H), 5.21 (d, J = 0.8 Hz, 2H), 5.44 (dd, J = 2.9, 13.3 Hz, 1H), 6.72 (m, 2H), 7.38–7.49 (m, 5H), 7.86 (m, 1H); ^{13}C NMR (101 Hz, $CDCl_3$) δ 44.4, 56.4, 79.9, 94.1, 103.6, 111.2, 115.6, 126.1, 128.7, 128.8, 128.8, 138.7, 163.2, 163.6, 190.7; IR (KBr) 3346, 3031, 2890, 1683, 1607, 1574, 1489, 1368, 1304, 1226 and 907 cm^{-1}; $[\alpha]_D^{25}$ = –69° (*c* 0.1, $CHCl_3$); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ga**; 11.7 min (99.7%), t_R of (*R*)-**1ga**; 16.8 min (0.3%). Although this enantiomer had not been reported, the absolute configuration became clear by absolute configuration of (*S*)-**1fa**.

(*S*)-2,3-Dihydro-7-hydroxy-2-phenyl-4*H*-1-benzopyran-4-one (1fa).[9]



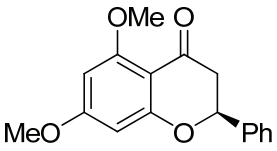
A solution of (*S*)-**1ga** (27.3 mg, 96.0 μmol) in 5.0 mL CH_2Cl_2 was treated with diluted HCl (0.10 mL of conc. HCl in 1.0 mL of CH_2Cl_2) at room temperature for 4 days under atomospheric condition. Then, H_2O (5.0 mL) was added to the solution and the resulting mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtrated with suction and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to give (*S*)-**1fa** as a white solid (20.3 mg, 88% yield, 99.0% ee); mp 186–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (dd, J = 2.8, 16.8 Hz, 1H), 3.06 (dd, J = 12.8, 16.8 Hz, 1H), 5.47 (dd, J = 2.8, 13.2 Hz, 1H), 6.34 (br, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.57 (dd, J = 2.4, 8.6 Hz, 1H), 7.37–7.49 (m, 5H), 7.87 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 44.3, 79.9, 103.5, 110.7, 115.0, 126.1, 128.8, 128.9, 129.4, 138.7, 163.1, 163.7, 191.2; IR (KBr) 3426, 3111, 3035, 2958, 2725, 1653, 1578, 1495, 1366, 1337, 1300, 1230, 1259, 1169, 1115, 1003, 858 and 806 cm^{-1}; $[\alpha]_D^{22}$ = –134° (*c* 0.1, $CHCl_3$) {lit.[9] $[\alpha]_D^{26}$ = +63.8° (*c* 0.14, MeOH), 97% ee, (*R*)}; HPLC (Daicel Chiralcel AD-H, Hexane/*i*-PrOH = 9/1, flow rate = 1.0 ml/min, 254 nm): t_R of (*R*)-**1fa**; 15.5 min (0.5%), t_R of (*S*)-**1fa**; 17.0 min (99.5%).

5,7-Dimethoxychromone (2h).[10, 11]



2-Hydroxy-4,6-dimethoxyacetophenone (1.96 g, 10.0 mmol) , *N*, *N*-dimethylformamide dimethyl acetal (1.55 g, 1.73 mL, 12.9 mmol) and *o*-xylene (7.5 mL) were added to the flame-dried 50 mL two-necked, round-bottomed flask under nitrogen. The mixture was heated at reflux for 4 h. Then, the reaction mixture was cooled to 0 °C and the precipitates were separated by filtration. The precipitates, conc. H_2SO_4 (2.5 mL) and H_2O (11 mL) were added to 50 mL two-necked, round-bottomed flask. The mixture was heated at reflux for 2 h under atmospheric condition. Then, the mixture was cooled to room temperature and neutralized by saturated aqueous Na_2CO_3 solution. The resulting mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtrated with suction and concentrated under reduced pressure. The residue was purified by recrystallization (CH_2Cl_2/hexane) to give **2h** as a red crystal (1.82 g, 88% yield): mp 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.93 (s, 3H), 6.18 (d, J = 6.0 Hz, 1H), 6.35 (d, J = 2.3 Hz, 1H), 6.43 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.6, 56.3, 92.7, 96.0, 110.2, 114.4, 152.5, 160.0, 160.9, 163.8, 176.5; IR (KBr) 3520, 3059, 3009, 2976, 2943, 2843, 1655, 1599, 1570, 1462, 1420, 1400, 1286, 1217, 1159, 1113, 1178, 1057, 949, 864 and 824 cm^{-1}.

(*S*)-2,3-Dihydro-5,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (1ha).[12]

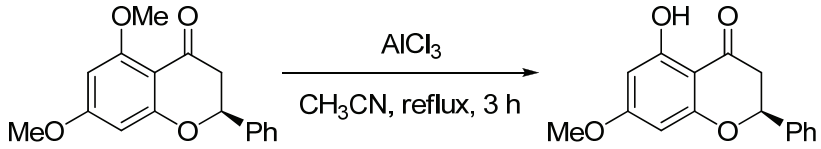


(*S*)-2,3-Dihydro-5,7-Dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (**1ha**) was obtained from (*S*)-**4** (1.2 mg, 1.5 μmol), $[Rh(cod)OH]_2$ (0.34 mg, 0.75 μmol), 5,7-dimethoxychromone (**2h**) (61.9 mg, 0.300 mmol), phenylboronic acid (**3a**) (293 mg, 2.40 mmol), deoxygenated toluene (1.0 mL) and deoxygenated water (0.50 mL) at 60 °C for 3 h by the general procedure described above.

(*S*)-**1ha**: white solid (79.1 mg, 93% yield, 99.6% ee); mp 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (dd, J = 2.9, 16.5 Hz, 1H), 3.01 (dd, J = 13.2, 16.5 Hz, 1H), 3.81 (s, 3H), 3.88 (s, 3H), 5.40 (dd, J = 2.9, 13.2 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 6.15 (d, J = 2.3 Hz, 1H), 7.38–7.46 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 45.5, 55.5, 56.0, 79.1, 93.1, 93.4, 105.9, 126.0, 128.6, 128.7, 138.7, 162.2, 164.9, 165.9, 189.1; IR (KBr) 3325, 3063, 2966, 2941, 2885, 2842, 1676, 1609, 1570, 1468, 1423, 1371, 1259, 1217, 1178, 1159, 1111, 1167, 823, 766 and 700 cm^{-1}; $[\alpha]_D^{20}$ = –29° (*c* 0.1, $CHCl_3$) {lit.[12] $[\alpha]_D^{22}$ = –28° (*c* 2.0,

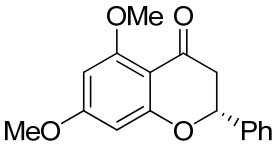
MeOH-CH_3Cl, 1:1), (*S*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**1ha**; 19.5 min (99.8%), t_R of (*R*)-**1ha**; 26.0 min (0.2%).

(*S*)-(–)-Pinostrobin (6).[12]



(*S*)-5,7-Dimethoxy-2-phenyl-4-chromanone (**1ha**) (100 mg, 0.352 mmol), aluminium chloride (188 mg, 1.41 mmol) and acetonitrile (7.0 mL) were added to the flame-dried 25 mL two-necked, round-bottomed flask under argon and the mixture was heated at reflux for 3 h. Then, the reaction mixture was cooled to room temperature. 4.0 mL of 2 M HCl aq. was added and the resulting mixture was extracted with EtOAc. The combined organic layers were washed with water, brine, dried and evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 2/1) to give (*S*)-**6** as a yellow solid (85.2 mg, 90% yield, 99.6% ee): mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (dd, J = 3.0, 17.2 Hz, 1H), 3.10 (dd, J =13.0, 17.2 Hz, 1H), 3.82 (s, 3H), 5.43 (dd, J = 3.0, 13.0 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 6.09 (d, J = 2.3 Hz, 1H), 7.40–7.46 (m, 5H), 12.03 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 43.4, 55.7, 79.2, 94.3, 95.1, 103.1, 126.1, 128.9, 138.4, 162.8, 164.1, 168.0, 195.8; IR (KBr) 3061, 3032, 2970, 2934, 1645, 1620, 1580, 1443, 1381, 1340, 1261, 1157, 1090, 993, 961, 916, 887, 841, 800, 766, 743 and 698 cm^{-1}; $[\alpha]_D^{21}$ = –49° (*c* 0.1, $CHCl_3$) {lit.[12] $[\alpha]_D^{22}$ = –48° (*c* 1.0, $CHCl_3$), (*S*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**6**; 12.5 min (99.8%), t_R of (*R*)-**6**; 17.3 min (0.2%).

(*R*)-2,3-Dihydro-5,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (1ha).[12]

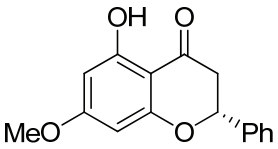


(*R*)-2,3-Dihydro-5,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (**1ha**) was obtained from (*R*)-**4** (4.2 mg, 5.1 μmol), $[Rh(cod)OH]_2$ (1.2 mg, 2.6 μmol), 5,7-dimethoxychromone (**2h**) (35.1 mg, 0.170 mmol), phenylboronic acid (**3a**) (207 mg, 1.70 mmol), deoxygenated toluene (1.0 mL) and deoxygenated water (0.50 mL) at 40 °C for 1 h by the general procedure described above.

(*R*)-**1ha**: white solid (44.4 mg, 92% yield, 99.4% ee); $[\alpha]_D^{21}$ = +29° (*c* 0.1, $CHCl_3$) {lit.[12] $[\alpha]_D^{22}$ = –28° (*c* 2.0, MeOH-CH_3Cl, 1:1), (*S*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0

mL/min, 254 nm): t_R of (*S*)-**1ha**; 20.0 min (0.3%), t_R of (*R*)-**1ha**; 25.7 min (99.7%).

(*R*)-(+)-Pinostrobin (6).[12]

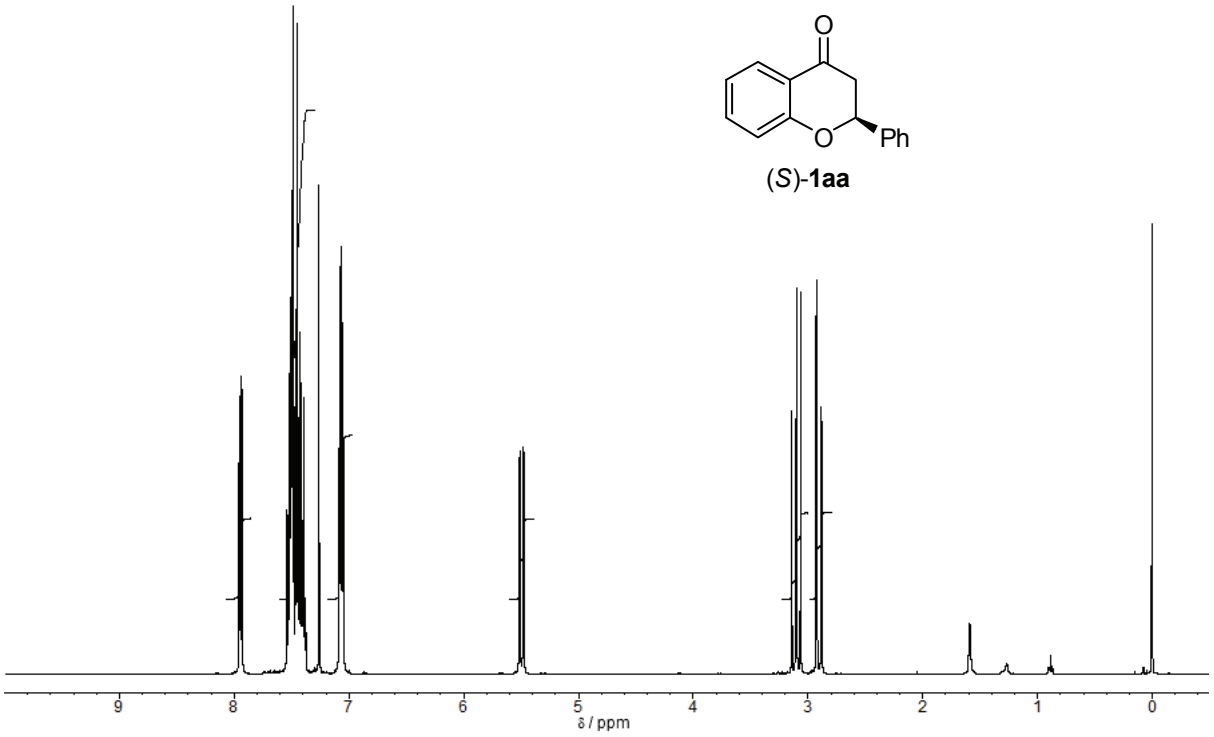


(*R*)-(+)-Pinostrobin (**6**) was obtained from (*R*)-**1ha** (50.0 mg, 0.176 mmol), aluminium chloride (93.8 mg, 0.703 mmol) and 3.5 mL of acetonitrile by the procedure described for (*S*)-**6**.

(*R*)-**6**: yellow solid (42.2 mg, 88% yield, 99.2% ee); $[\alpha]_D^{19}$ = +49° (*c* 0.1, $CHCl_3$) {lit.[12] $[\alpha]_D^{22}$ = –48° (*c* 1.0, $CHCl_3$), (*S*)}; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, 254 nm): t_R of (*S*)-**6**; 10.4 min (0.4%), t_R of (*R*)-**6**; 16.0 min (99.6%).

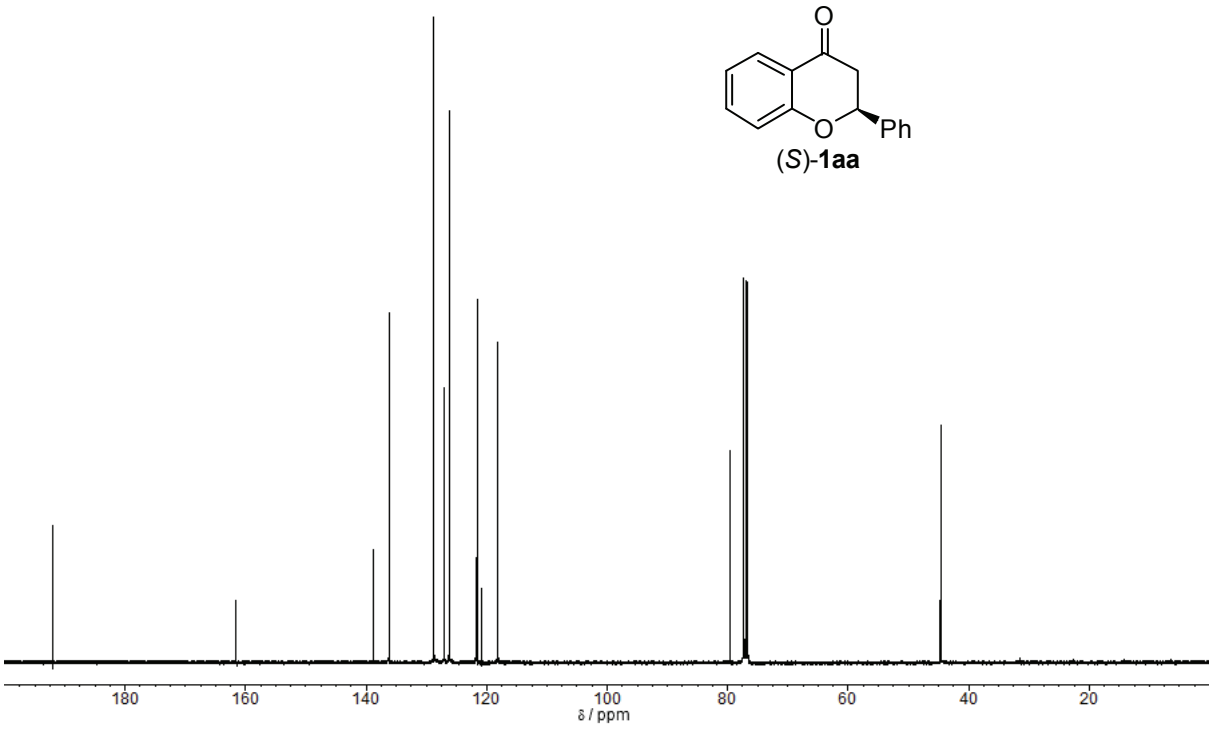
NMR and HPLC charts

^{1}H NMR (400 MHz, $CDCl_3$)



(*S*)-**1aa**

^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1aa**

HPLC

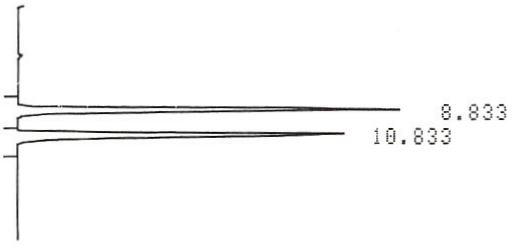
CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 12938

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	8.833	942197	S		99.5356	
2	11	4395	T		0.4643	
	TOTAL	946593			100	

Ph

H column
panol = 9/1
nL/min.

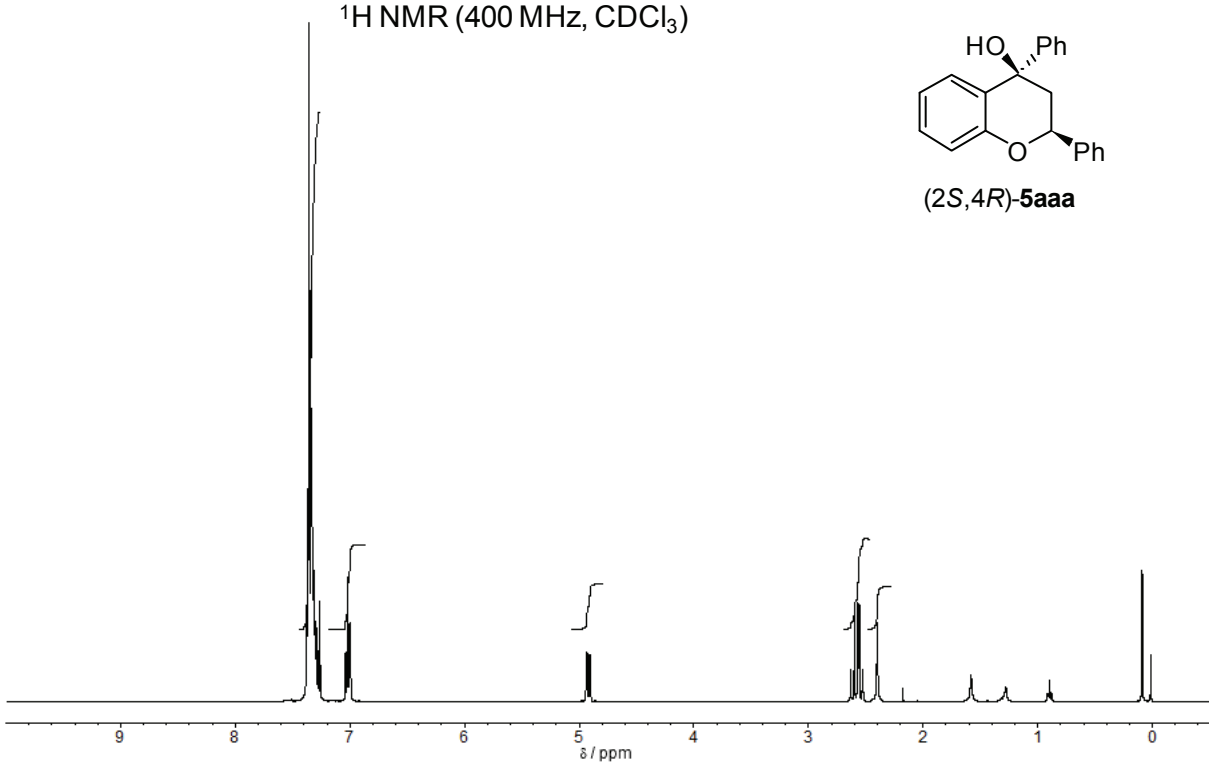
(±)-**1aa**



CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 12914

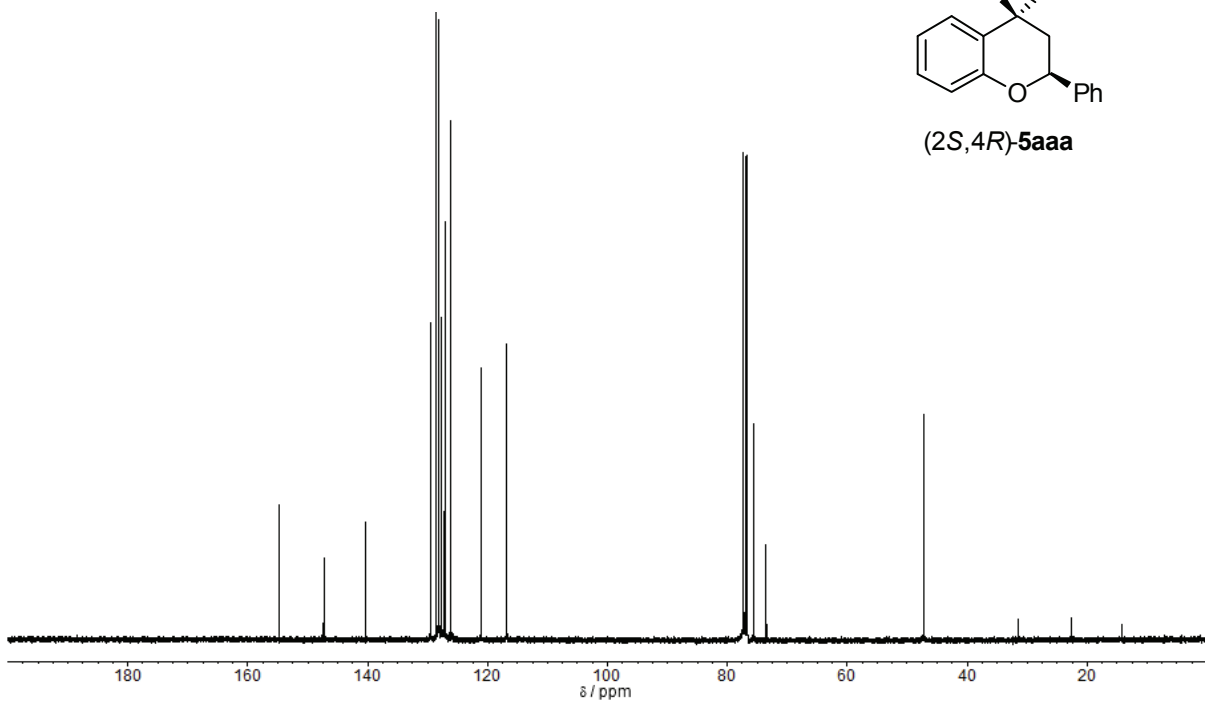
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	8.833	690011			50.0501	
2	10.833	688629	V		49.9499	
	TOTAL	1378640			100	

^{1}H NMR (400 MHz, $CDCl_3$)



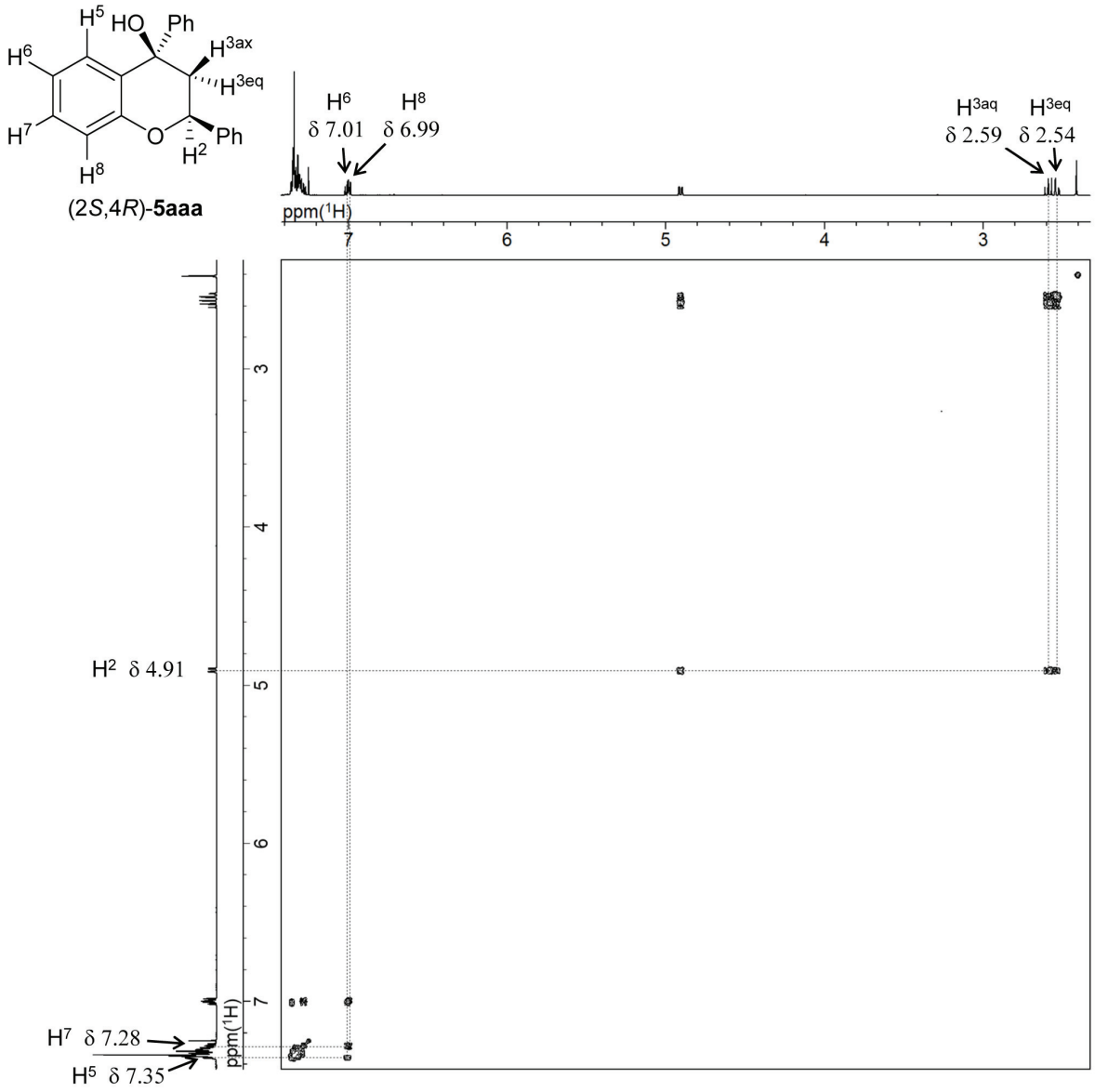
(2*S*,4*R*)-**5aaa**

^{13}C NMR (101 MHz, $CDCl_3$)

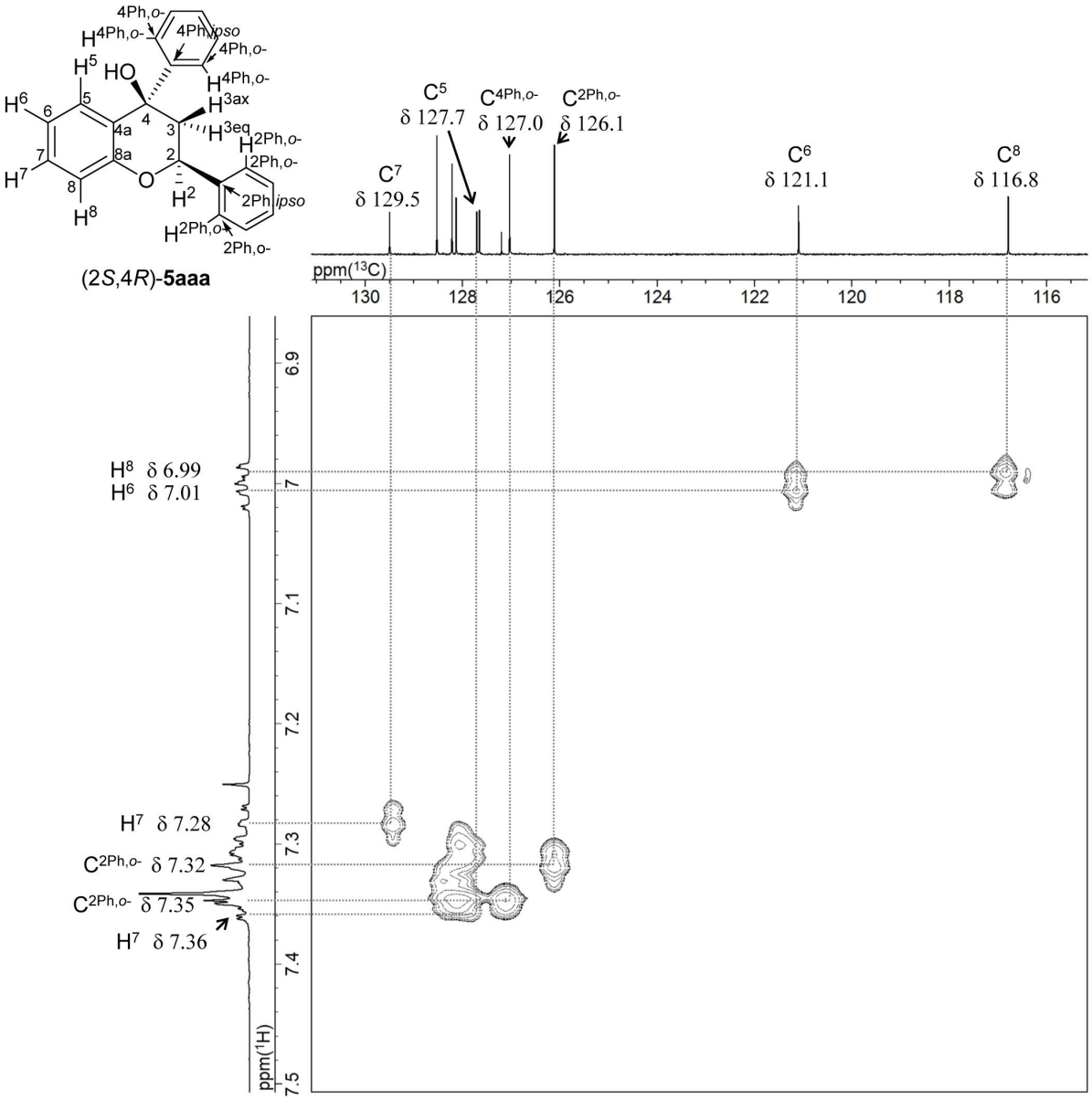


(2*S*,4*R*)-**5aaa**

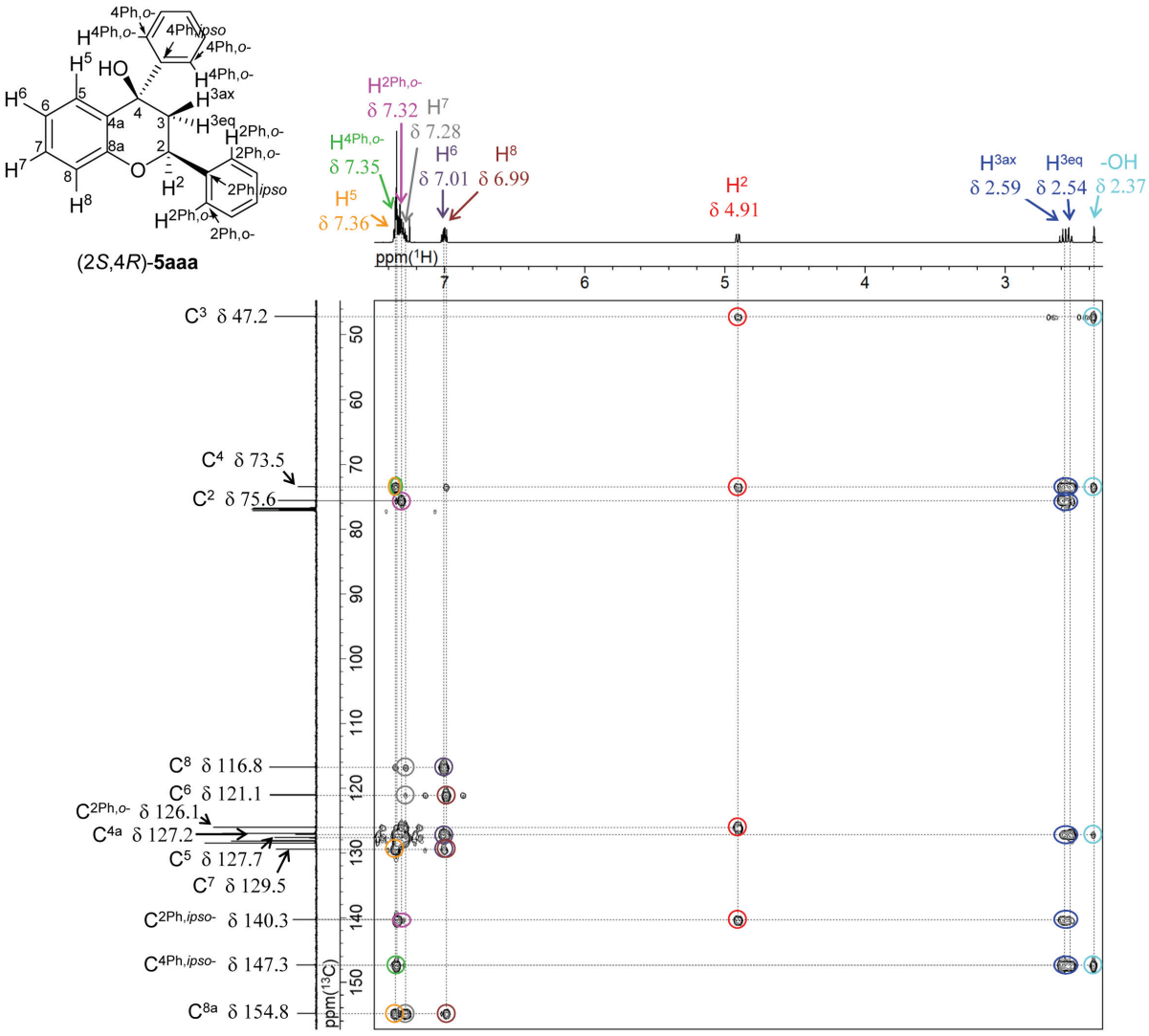
H-H COSY


H5
HO
Ph
H3ax
H3eq
H6
H7
O
Ph
H2
H8
(2S,4R)-5aaa
H6 δ 7.01
H8 δ 6.99
H3aq δ 2.59
H3eq δ 2.54
ppm(1H)
7
6
5
4
3
H2 δ 4.91
H7 δ 7.28
H5 δ 7.35
ppm(1H)

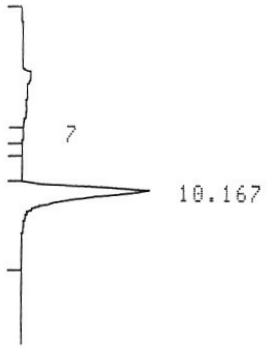
HSQC


4Ph,o-
H4Ph,o-
4Ph,ipso
4Ph,o-
H5
HO
H4Ph,o-
H6
6
5
4
H3ax
4a
3
H3eq
H2Ph,o-
7
8a
2
2Ph,o-
H7
8
O
H2
2Ph,ipso
H8
H2Ph,o-
2Ph,o-
(2S,4R)-5aaa
C5
δ 127.7
C4Ph,o-
δ 127.0
C2Ph,o-
δ 126.1
C7
δ 129.5
C6
δ 121.1
C8
δ 116.8
ppm(13C)
130
128
126
124
122
120
118
116
H8 δ 6.99
H6 δ 7.01
H7 δ 7.28
C2Ph,o- δ 7.32
C2Ph,o- δ 7.35
H7 δ 7.36
6.9
7
7.1
7.2
7.3
7.4
7.5
ppm(1H)

HMBC


(2S,4R)-5aaa
H2Ph,o- δ 7.32
H7 δ 7.28
H4Ph,o- δ 7.35
H6 δ 7.01
H8 δ 6.99
H5 δ 7.36
H2 δ 4.91
H3ax δ 2.59
H3eq δ 2.54
-OH δ 2.37
ppm(1H)
C3 δ 47.2
C4 δ 73.5
C2 δ 75.6
C8 δ 116.8
C6 δ 121.1
C2Ph,o- δ 126.1
C4a δ 127.2
C5 δ 127.7
C7 δ 129.5
C2Ph,ipso- δ 140.3
C4Ph,ipso- δ 147.3
C8a δ 154.8
ppm(13C)

HPLC



CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14719

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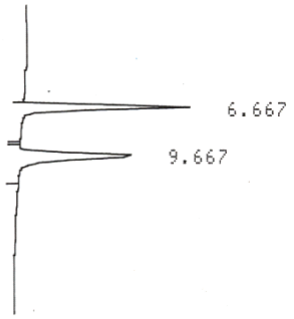
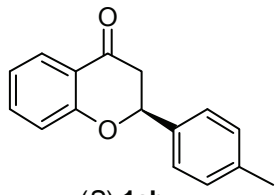
(±)-*trans*-**5aaa**



CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14297

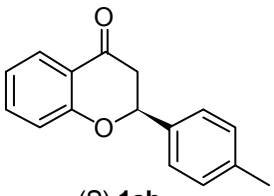
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	6.667	10099			50.1011	
2	9.667	10059			49.8989	
	TOTAL	20158			100	

^{1}H NMR (400 MHz, $CDCl_3$)



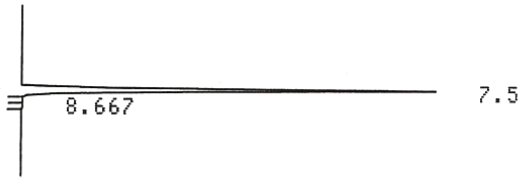
(*S*)-**1ab**

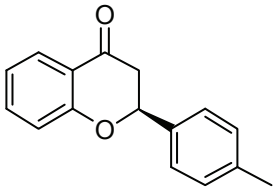
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1ab**

HPLC



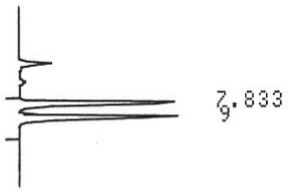


(*S*)-**1ab**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7393

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	7.5	743457			99.6415	
2	8.667	2675			0.3585	
	TOTAL	746131			100	

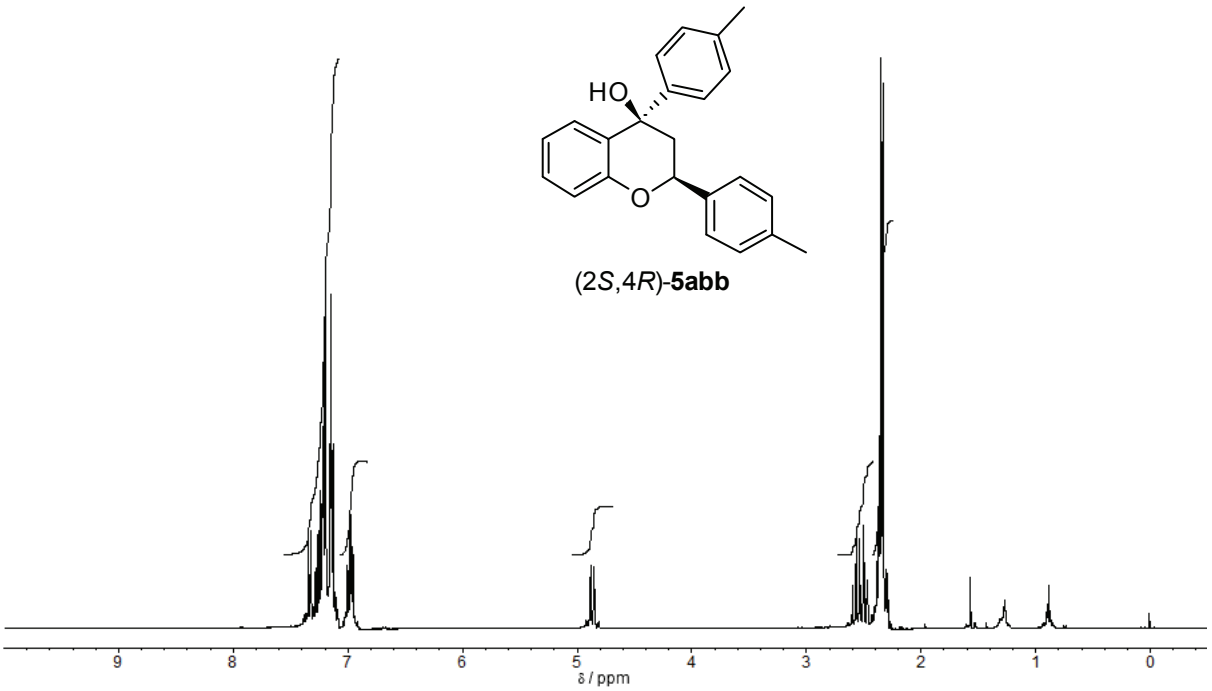


(±)-**1ab**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7354

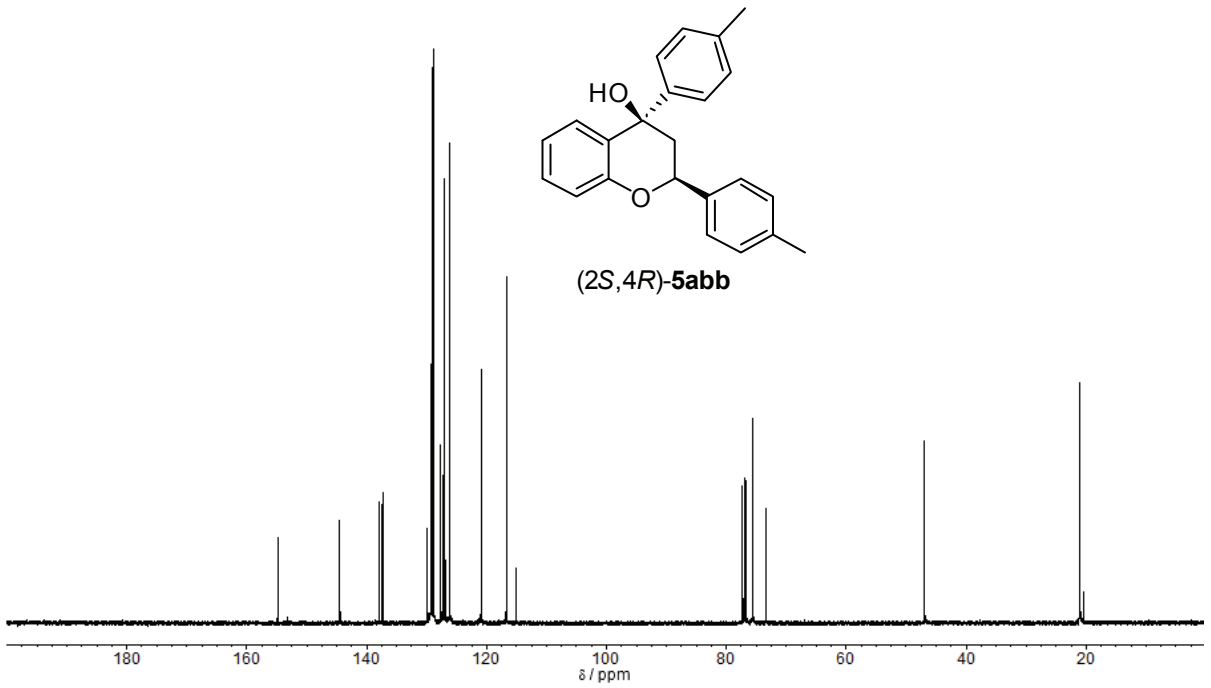
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	7.833	1112071			50.0664	
2	9	1109121	V		49.9336	
	TOTAL	2221192			100	

^{1}H NMR (400 MHz, $CDCl_3$)



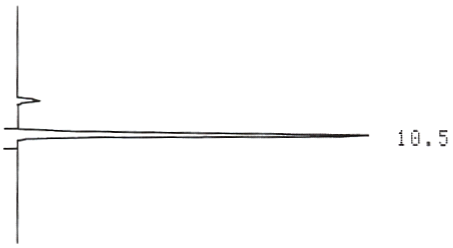
(2*S*,4*R*)-**5abb**

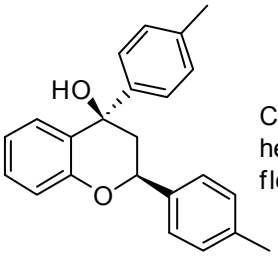
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S*,4*R*)-**5abb**

HPLC



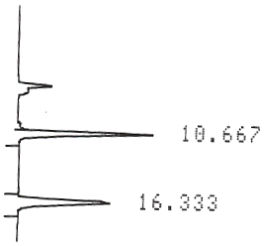


Chiralcel AD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

(2*S*,4*R*)-**5abb**

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 15077

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.5	168054			100	
	TOTAL	168054			100	

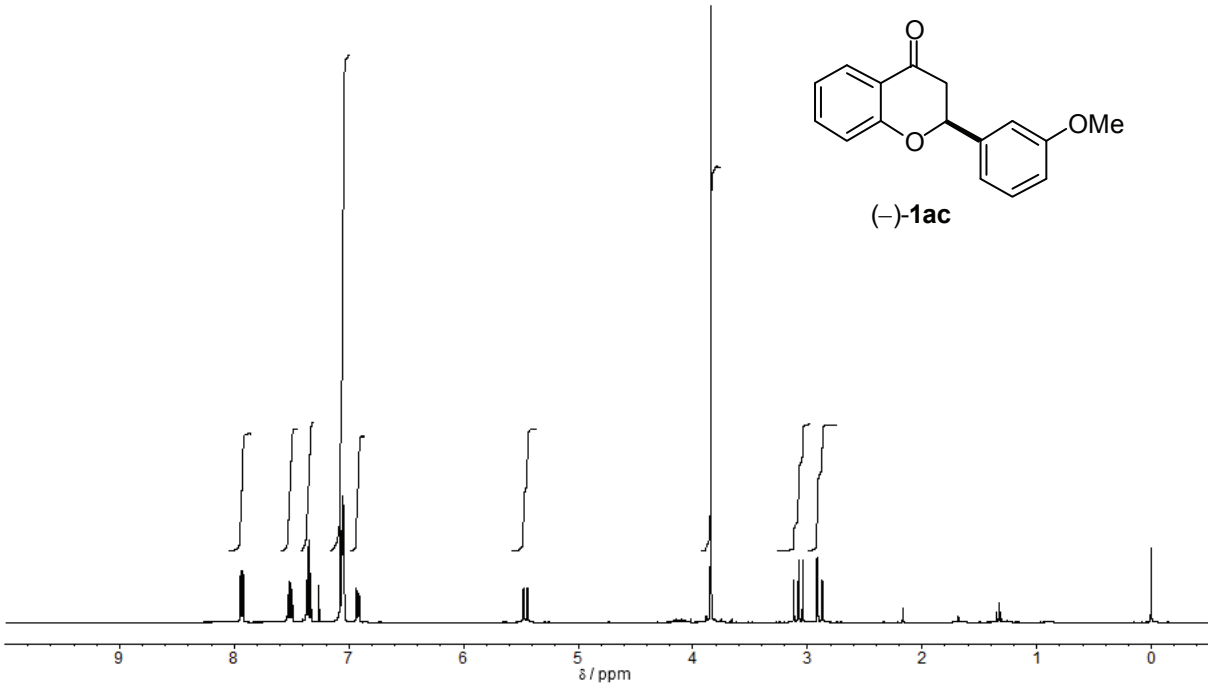


(±)-*trans*-**5abb**

CHROMATOPAC C-R6A FILE
SAMPLE NO 0 METHOD 61
REPORT NO 15076

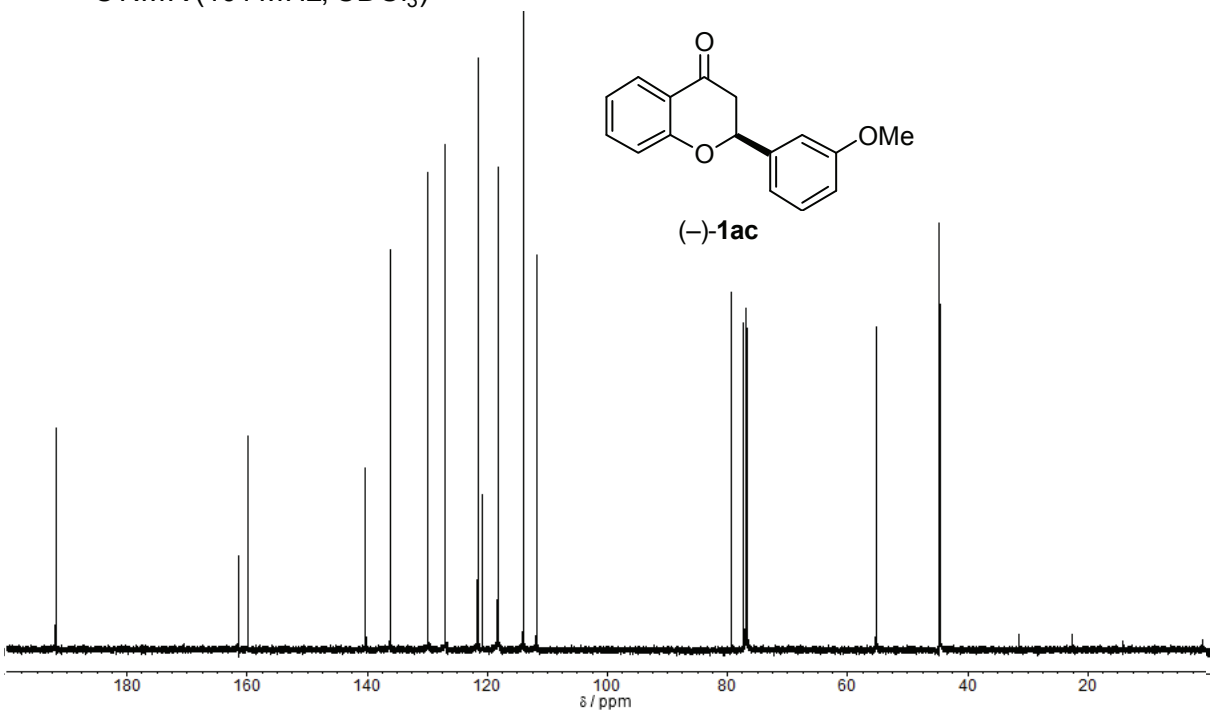
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.667	14772			50.3514	
2	16.333	14566			49.6486	
	TOTAL	29338			100	

^{1}H NMR (400 MHz, $CDCl_3$)



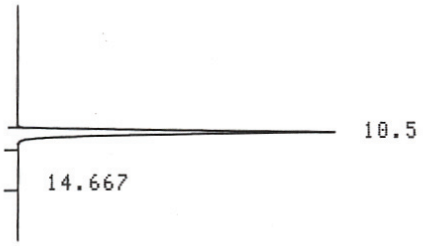
(–)-**1ac**

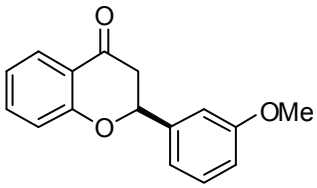
^{13}C NMR (101 MHz, $CDCl_3$)



(–)-**1ac**

HPLC





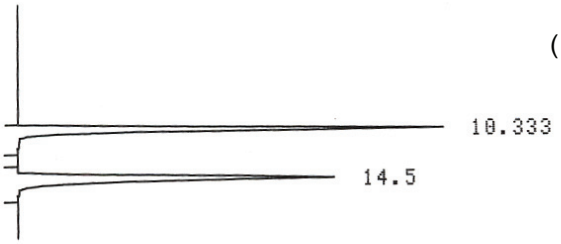
(–)-**1ac**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7487

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.5	1253619			99.8023	
2	14.667	2483	V		0.1977	
		125[illegible]			100	

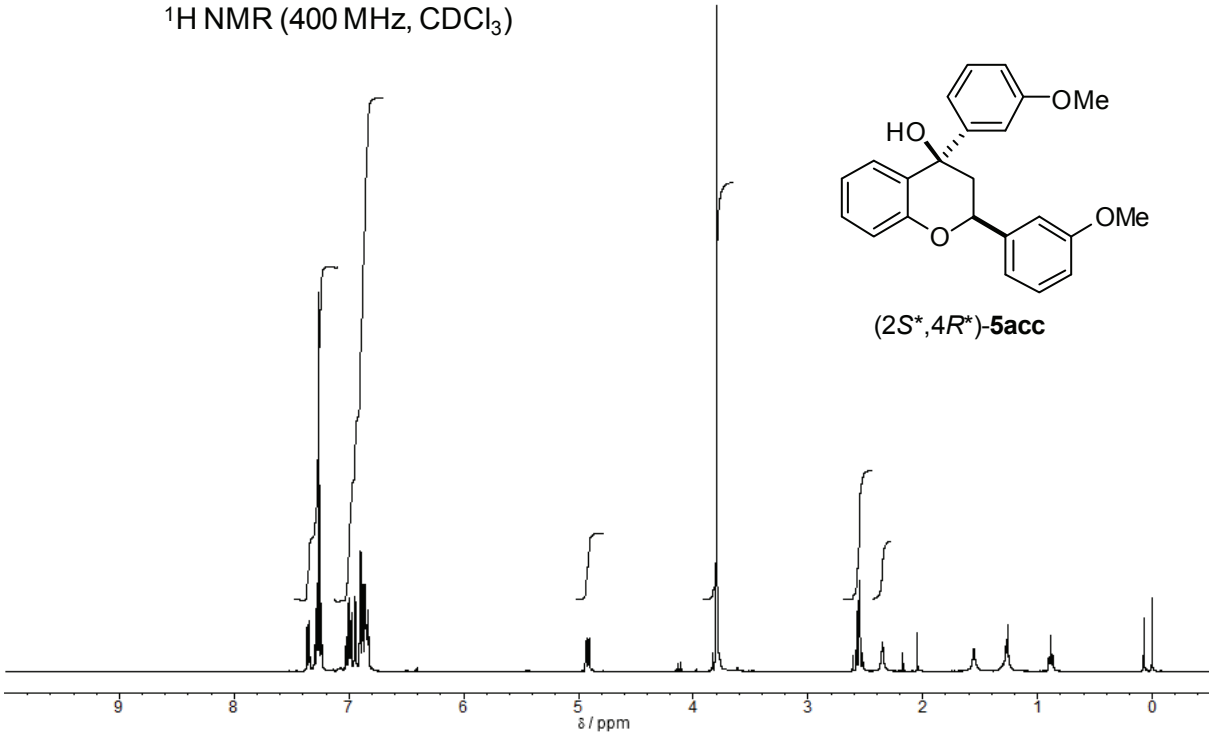
(±)-**1ac**



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7483

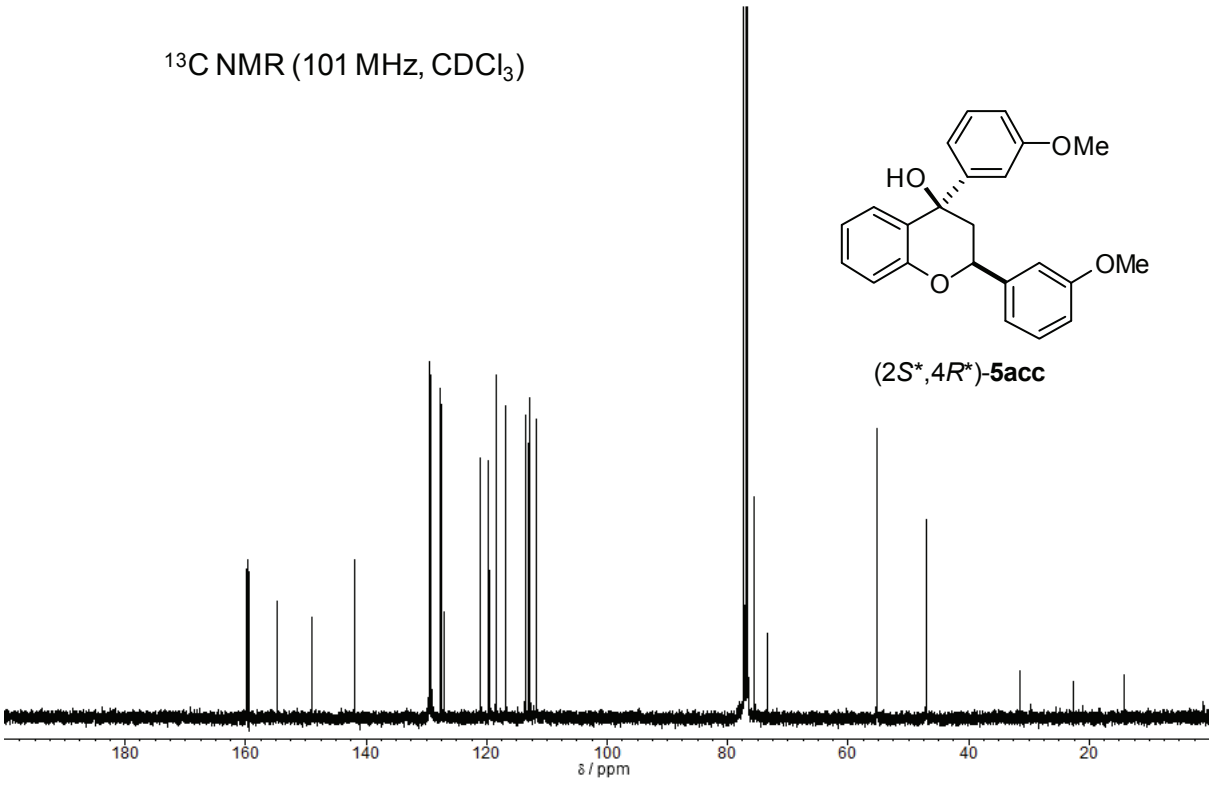
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.333	833382			49.9103	
2	14.5	836376			50.0897	
	TOTAL	1669757			100	

^{1}H NMR (400 MHz, $CDCl_3$)



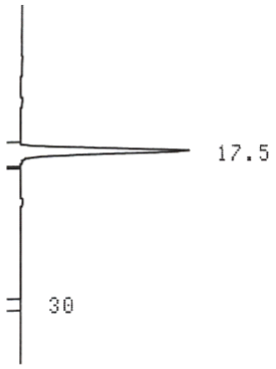
(2*S**,4*R**)-**5acc**

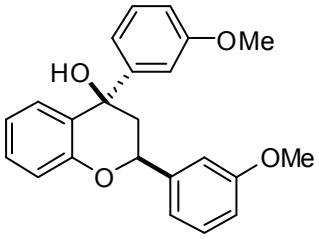
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S**,4*R**)-**5acc**

HPLC



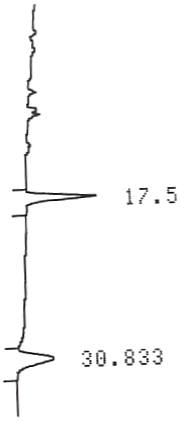


Chiralcel AD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

(2*S**,4*R**)-**5acc**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8755

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	17.5	423256			99.696	
2	30	1290			0.3039	
	TOTAL	424547			100	

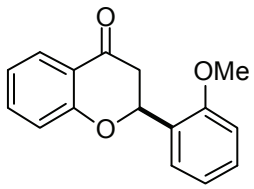


(±)-*trans*-**5acc**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8740

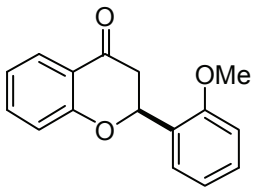
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	17.5	41729			51.4126	
2	30.833	39436			48.5874	
	TOTAL	81164			100	

^{1}H NMR (400 MHz, $CDCl_3$)



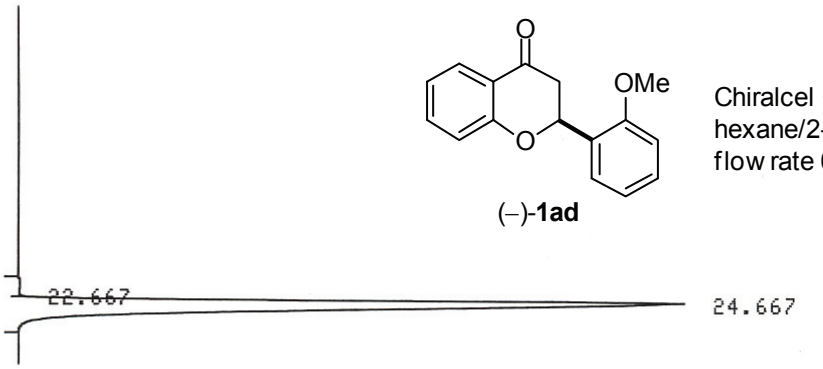
(–)-**1ad**

^{13}C NMR (101 MHz, $CDCl_3$)



(–)-**1ad**

HPLC

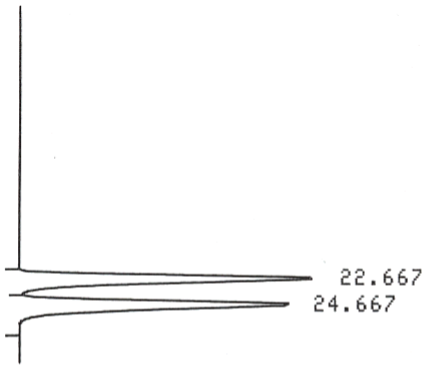


(–)-**1ad**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 0.3 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7522

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	22.667	18779			0.1706	
2	24.667	10990032			99.8294	
	TOTAL	11008811			100	

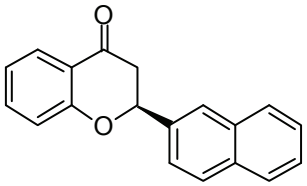


(±)-**1ad**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 7509

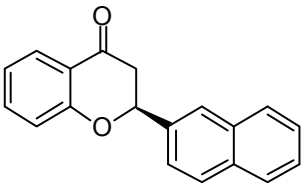
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	22.667	2241325			49.852	
2	24.667	2254637	V		50.148	
	TOTAL	4495962			100	

^{1}H NMR (400 MHz, $CDCl_3$)



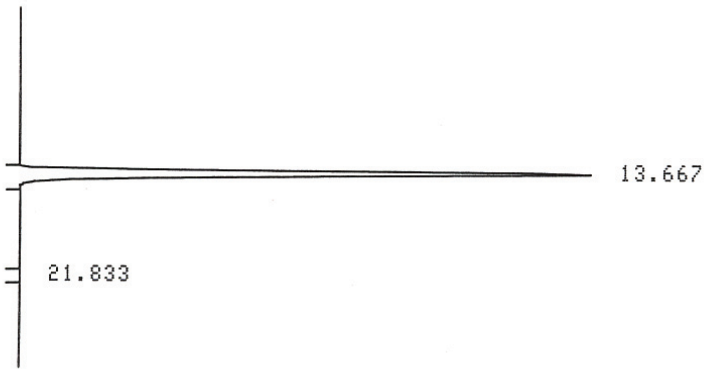
(*S*)-**1ae**

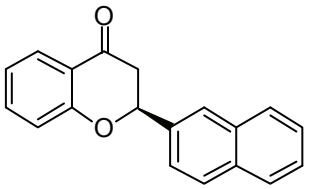
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1ae**

HPLC



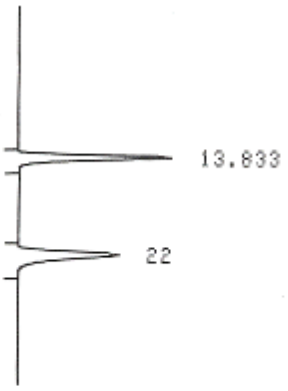


(*S*)-**1ae**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

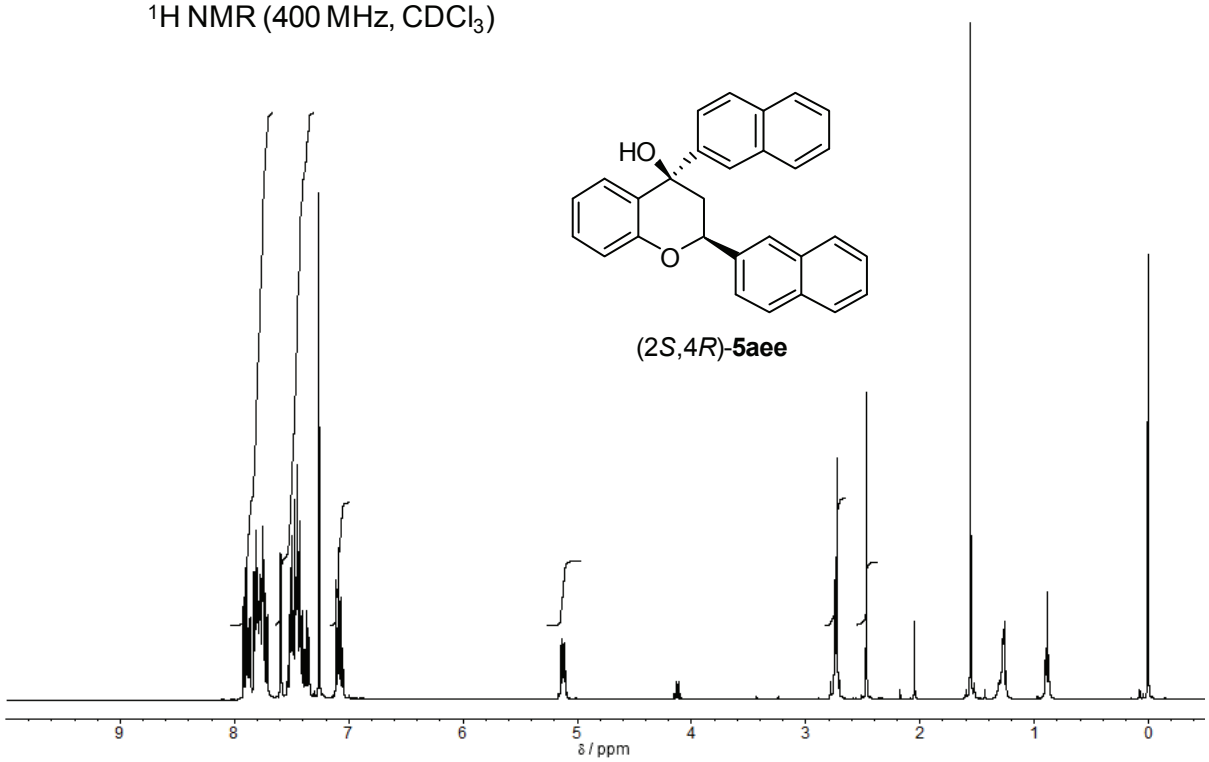
```
CHROMATOPAC   C-R6A                  FILE        2
SAMPLE NO   0                        METHOD      0061
REPORT NO   13373

PKNO      TIME      AREA   MK  IDNO     CONC       NAME

   1    13.667   1431836                99.5502
   2    21.833      6469                 0.4498
           ---------          -------------
        TOTAL    1438305                100
```

(±)-**1ae**



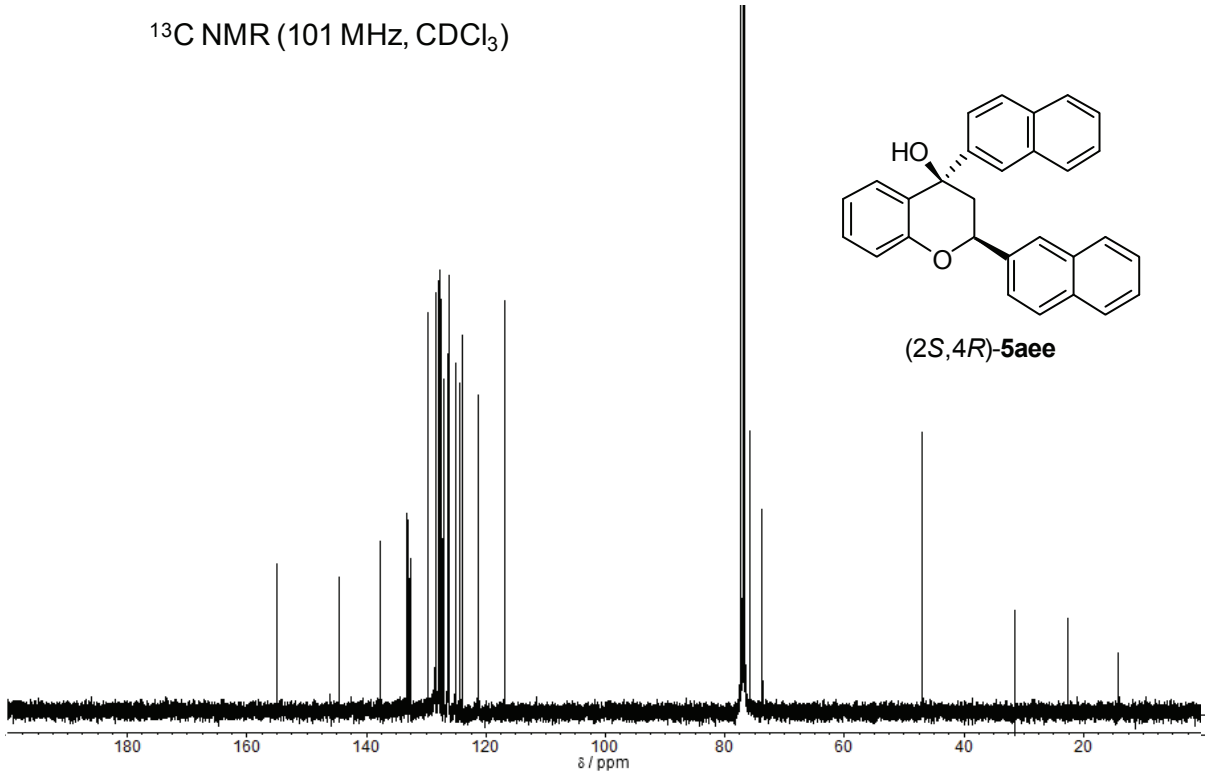

```
CHROMATOPAC   C-R6A                  FILE        2
SAMPLE NO   0                        METHOD      0061
REPORT NO   13366

PKNO      TIME      AREA   MK  IDNO     CONC       NAME

   1    13.833    393987                49.9296
   2    22        395098                50.0704
           ---------          -------------
        TOTAL     789085                100
```

^{1}H NMR (400 MHz, $CDCl_3$)



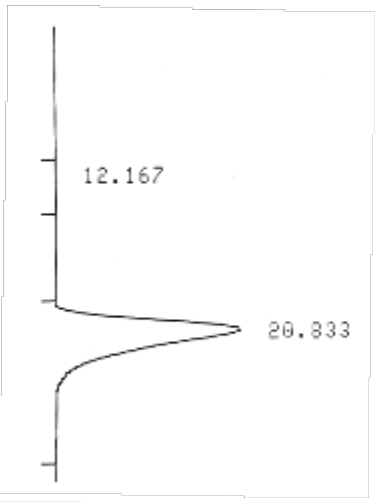
(2*S*,4*R*)-**5aee**

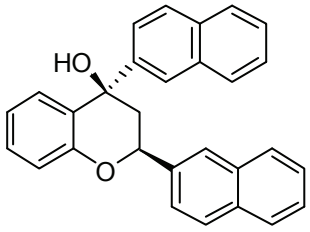
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S*,4*R*)-**5aee**

HPLC





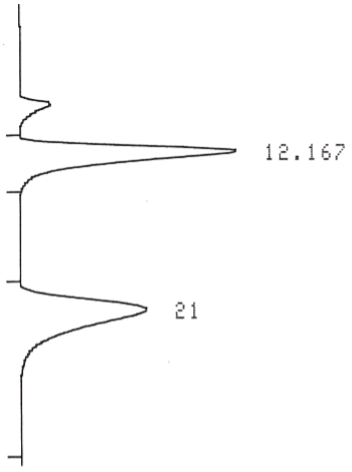
(2*S*,4*R*)-**5aee**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14965

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.167	5762			0.3598	
2	20.833	1595827			99.6402	
	TOTAL	1601590			100	

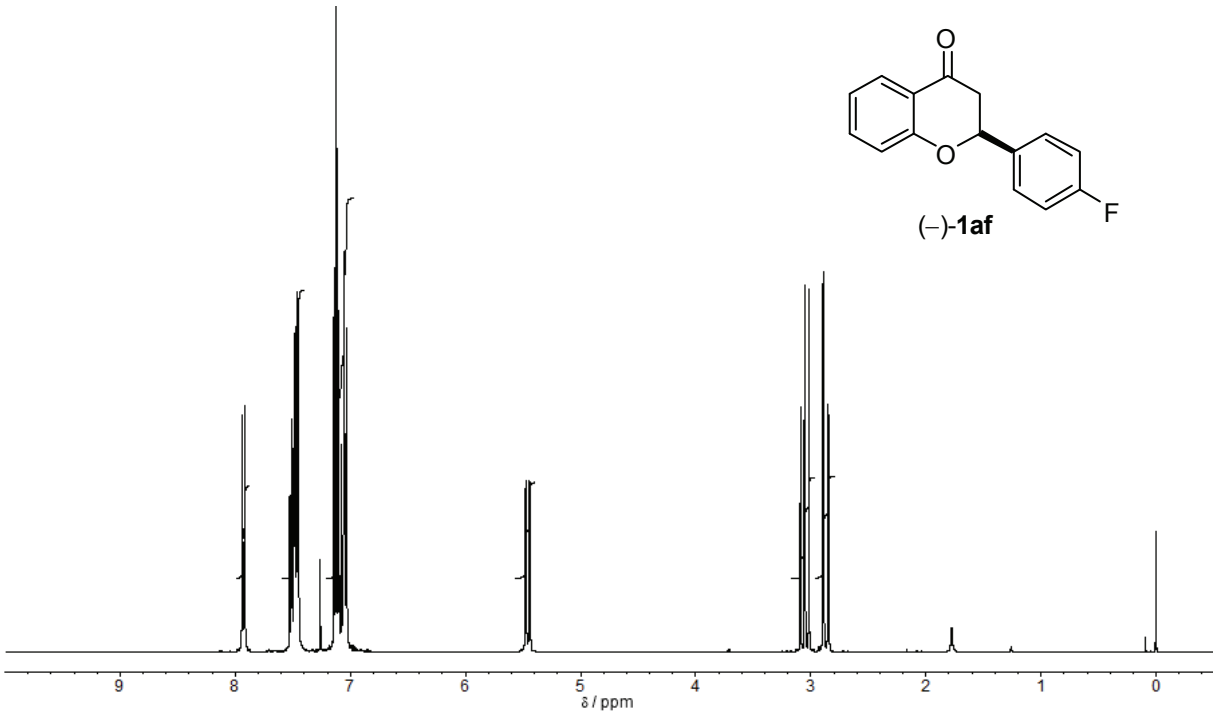
(±)-*trans*-**5aee**



CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14954

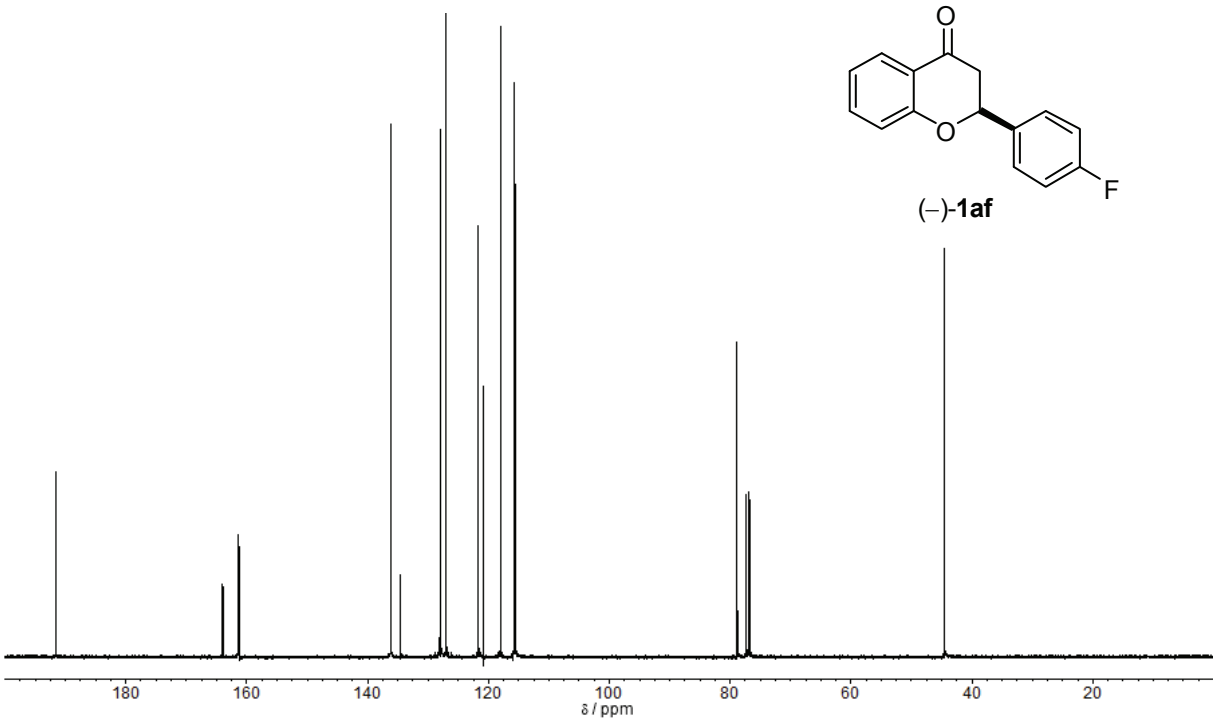
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.167	2121670			49.3907	
2	21	2174015			50.6093	
	TOTAL	4295686			100	

^{1}H NMR (400 MHz, $CDCl_3$)



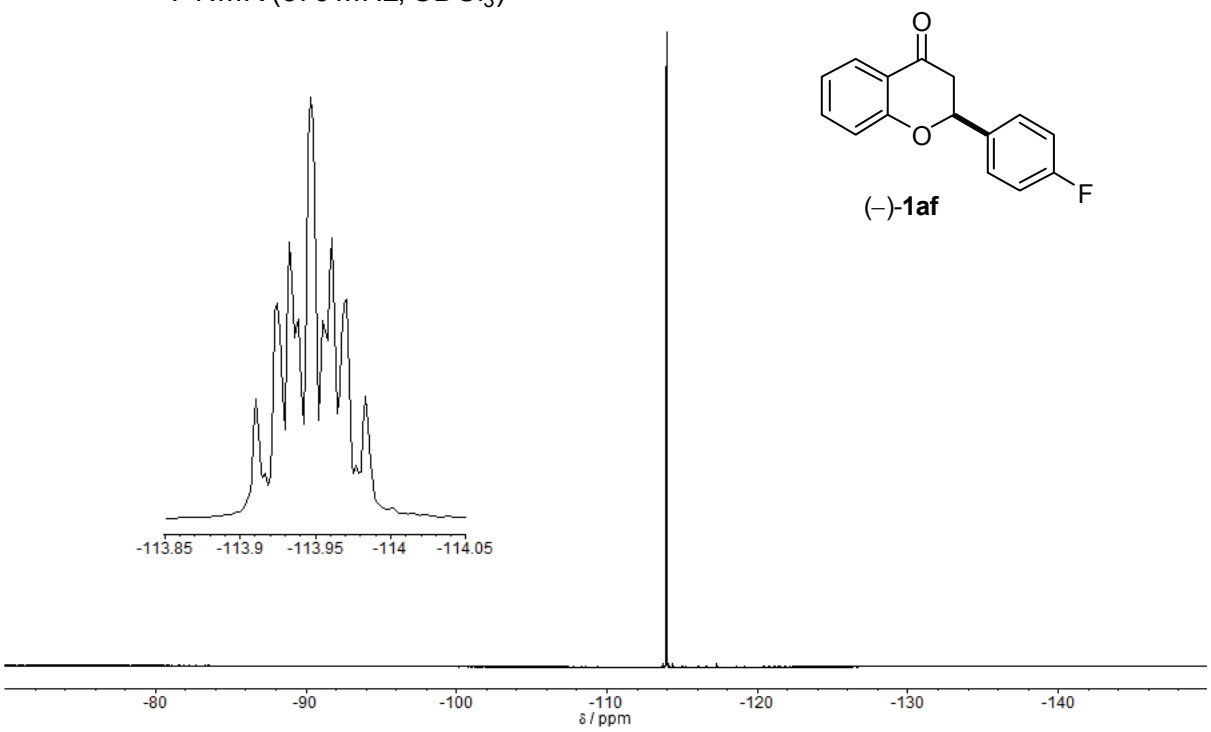
(–)-**1af**

^{13}C NMR (101 MHz, $CDCl_3$)

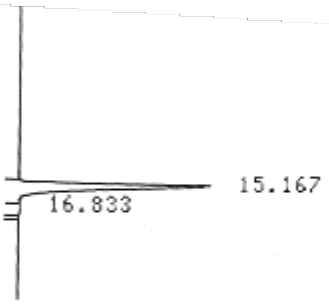


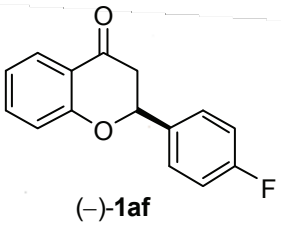
(–)-**1af**

^{19}F NMR (376 MHz, $CDCl_3$)



HPLC



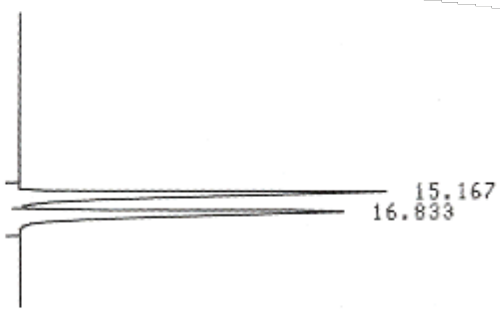


(–)-**1af**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 0.5 mL/min.

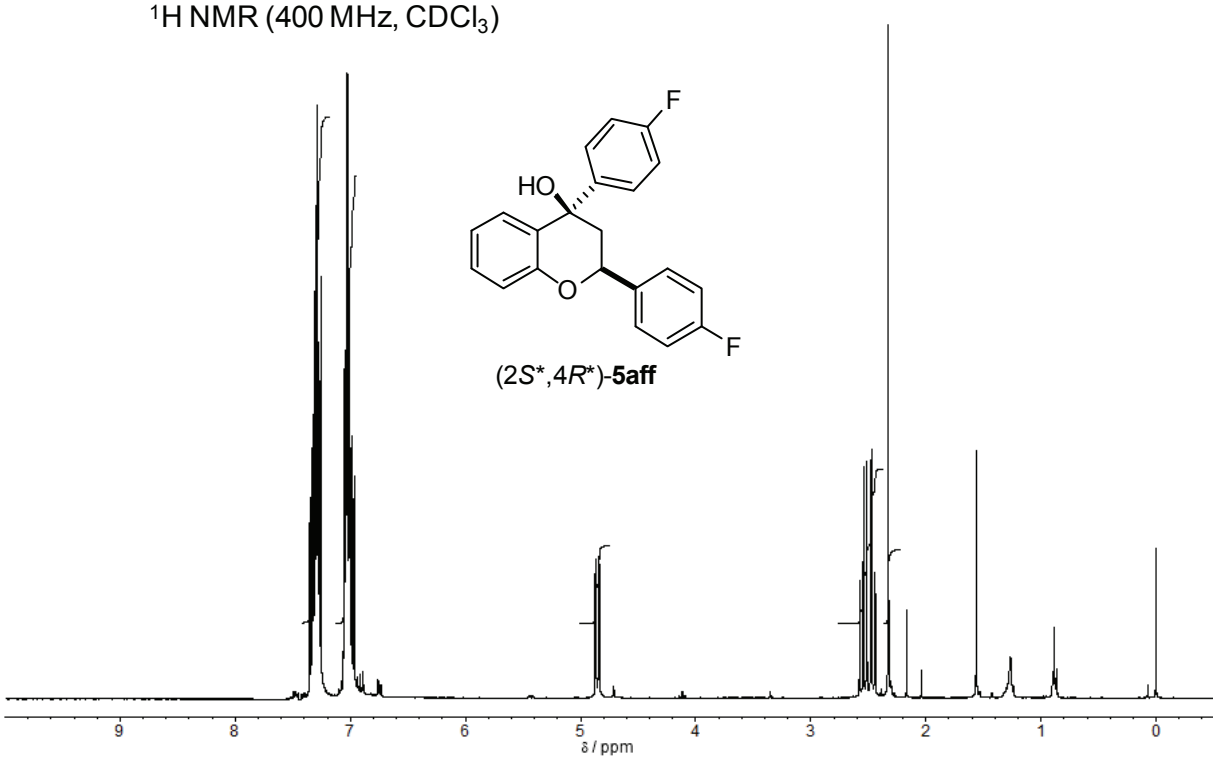
```
CHROMATOPAC   C-R6A                FILE        0
SAMPLE NO   0                      METHOD      0061
REPORT NO   7502

PKNO      TIME      AREA  MK  IDNO      CONC       NAME

   1    15.167   2063143 S               99.8769
   2    16.833      2542 T                0.1231
           ---------           -------------
        TOTAL    2065685                 100
```

(±)-**1af**



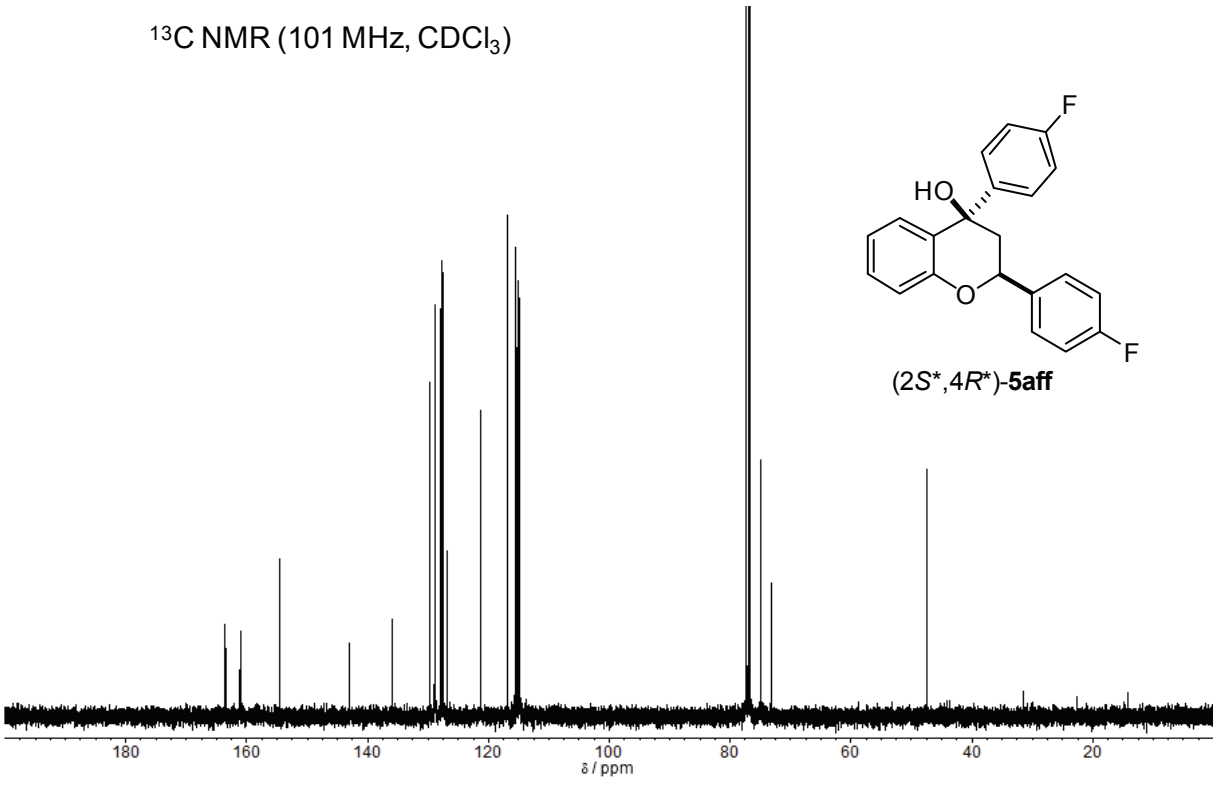

```
CHROMATOPAC   C-R6A                FILE        0
SAMPLE NO   0                      METHOD      0061
REPORT NO   7494

PKNO      TIME      AREA  MK  IDNO      CONC       NAME

   1    15.167   3831300                50.0027
   2    16.833   3830881  V             49.9973
           ---------           -------------
        TOTAL    7662181                 100
```

^{1}H NMR (400 MHz, $CDCl_3$)



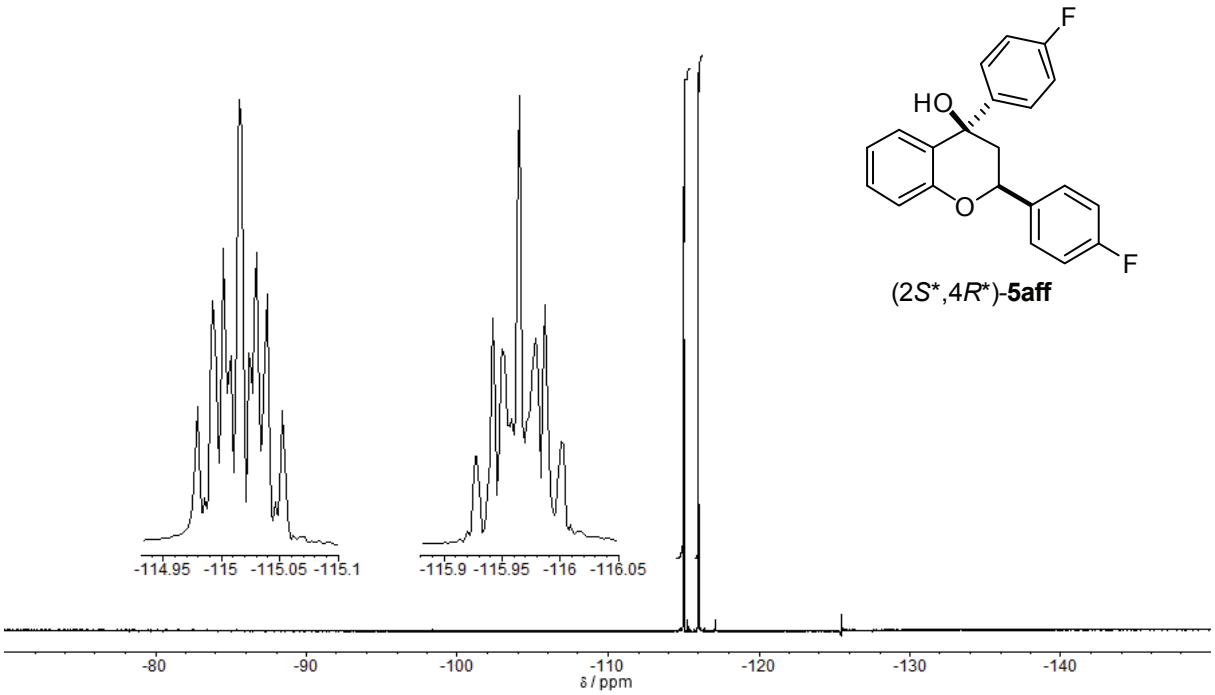
(2*S**,4*R**)-**5aff**

^{13}C NMR (101 MHz, $CDCl_3$)

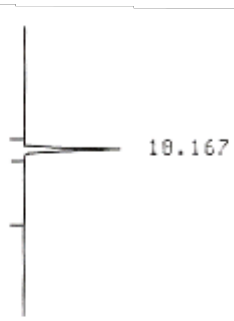


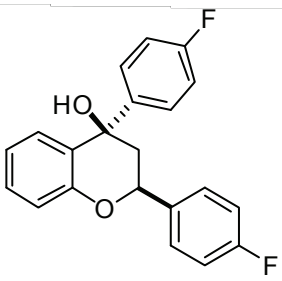
(2*S**,4*R**)-**5aff**

^{19}F NMR (376 MHz, $CDCl_3$)



HPLC

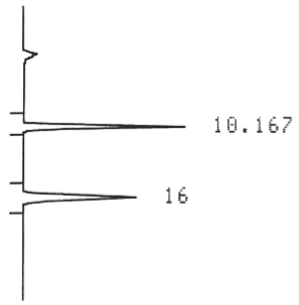




Chiralcel AD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

(2*S**,4*R**)-**5aff**

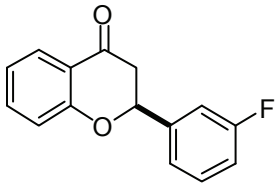
```
CHROMATOPAC   C-R6A                  FILE        0
SAMPLE NO   0                        METHOD      0061
REPORT NO   8777

PKNO      TIME      AREA  MK  IDNO      CONC       NAME

   1    10.167    140794                100
              ---------              -------------
         TOTAL     140794                100
```



(±)-*trans*-**5aff**

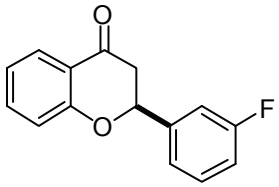
```
CHROMATOPAC   C-R6A                  FILE        0
SAMPLE NO   0                        METHOD      0061
REPORT NO   8757

PKNO      TIME      AREA  MK  IDNO      CONC       NAME

   1    10.167    248992                50.306
   2    16        245962                49.694
              ---------              -------------
         TOTAL     494954                100
```

^{1}H NMR (400 MHz, $CDCl_3$)



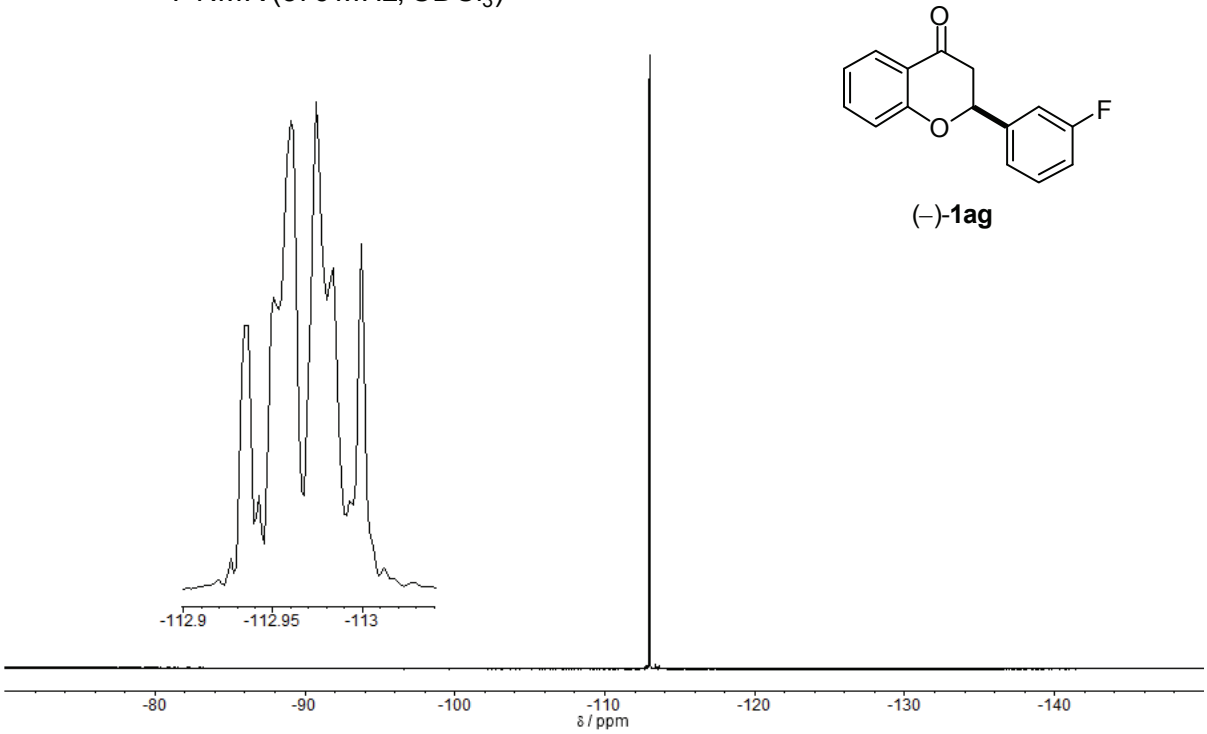
(–)-**1ag**

^{13}C NMR (101 MHz, $CDCl_3$)

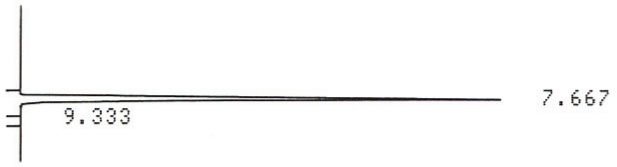


(–)-**1ag**

^{19}F NMR (376 MHz, $CDCl_3$)

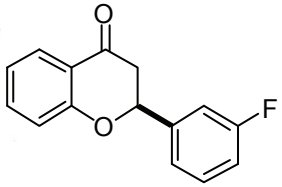


HPLC



CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 13249

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	7.667	2874571			99.5252	
2	9.333	13714	V		0.4748	
	TOTAL	2888284			100	



(–)-**1ag**

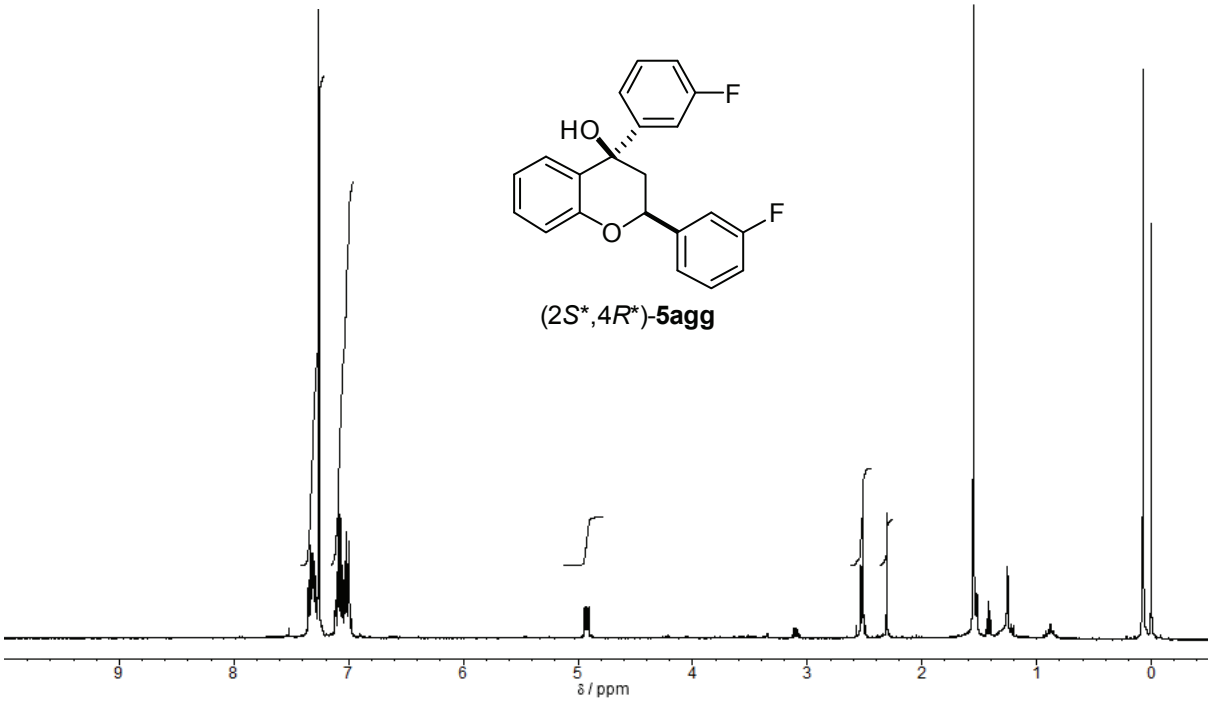
Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 0.5 mL/min.

(±)-**1ag**

CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 13237

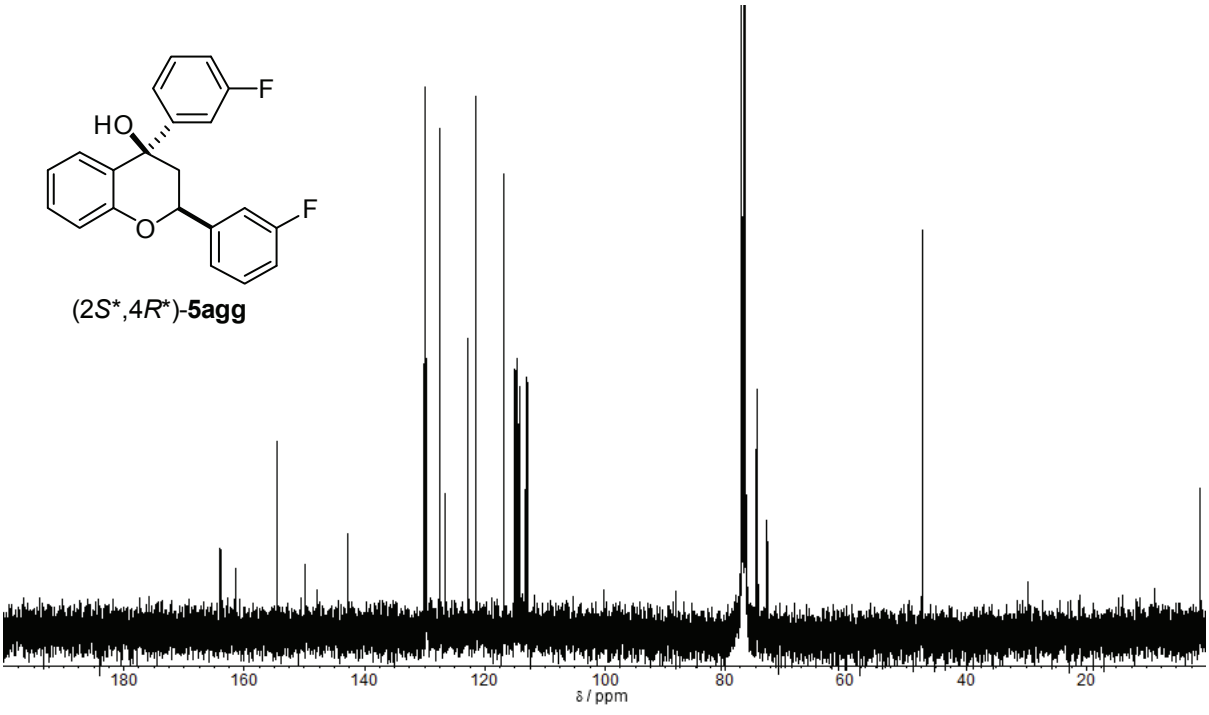
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	7.667	503295			49.9485	
2	9.333	504333	V		50.0515	
	TOTAL	1007628			100	

^{1}H NMR (400 MHz, $CDCl_3$)



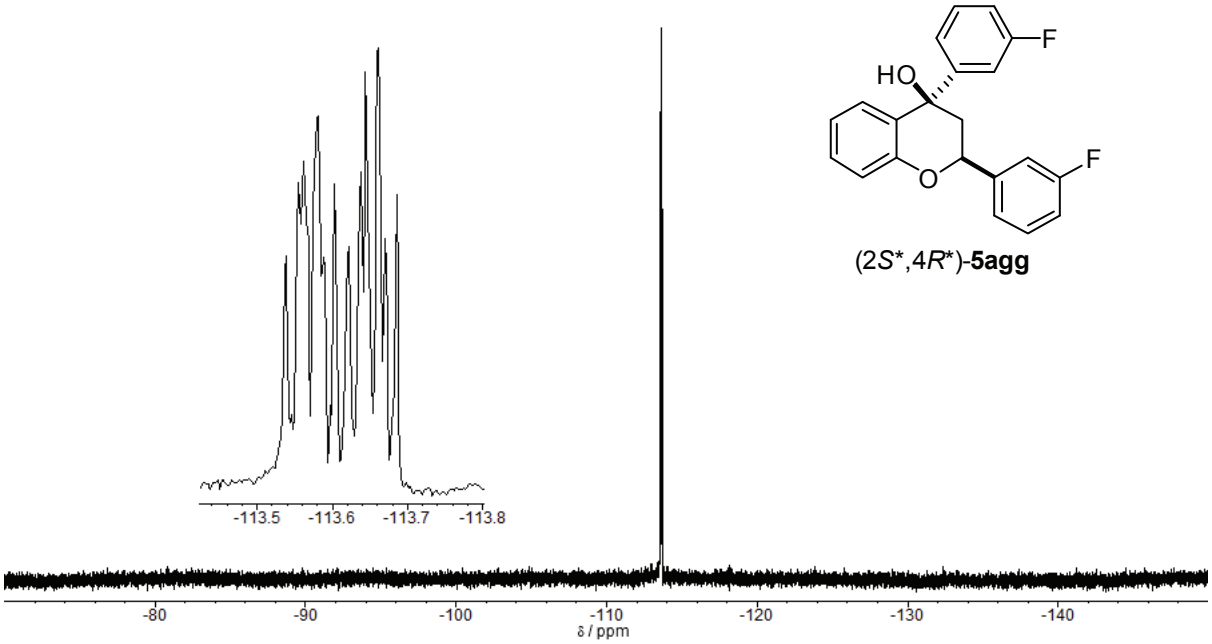
(2*S**,4*R**)-**5agg**

^{13}C NMR (101 MHz, $CDCl_3$)

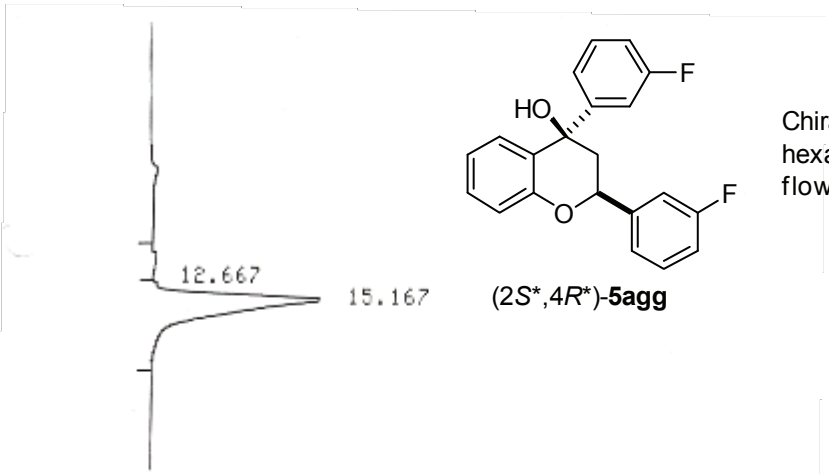


(2*S**,4*R**)-**5agg**

^{19}F NMR (376 MHz, $CDCl_3$)



HPLC



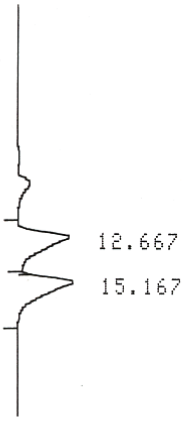
Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 0.5 mL/min.

(2*S**,4*R**)-**5agg**

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14787

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.667	6416			1.3837	
2	15.167	457248			98.6162	
		---			---	
	TOTAL	463664			100	

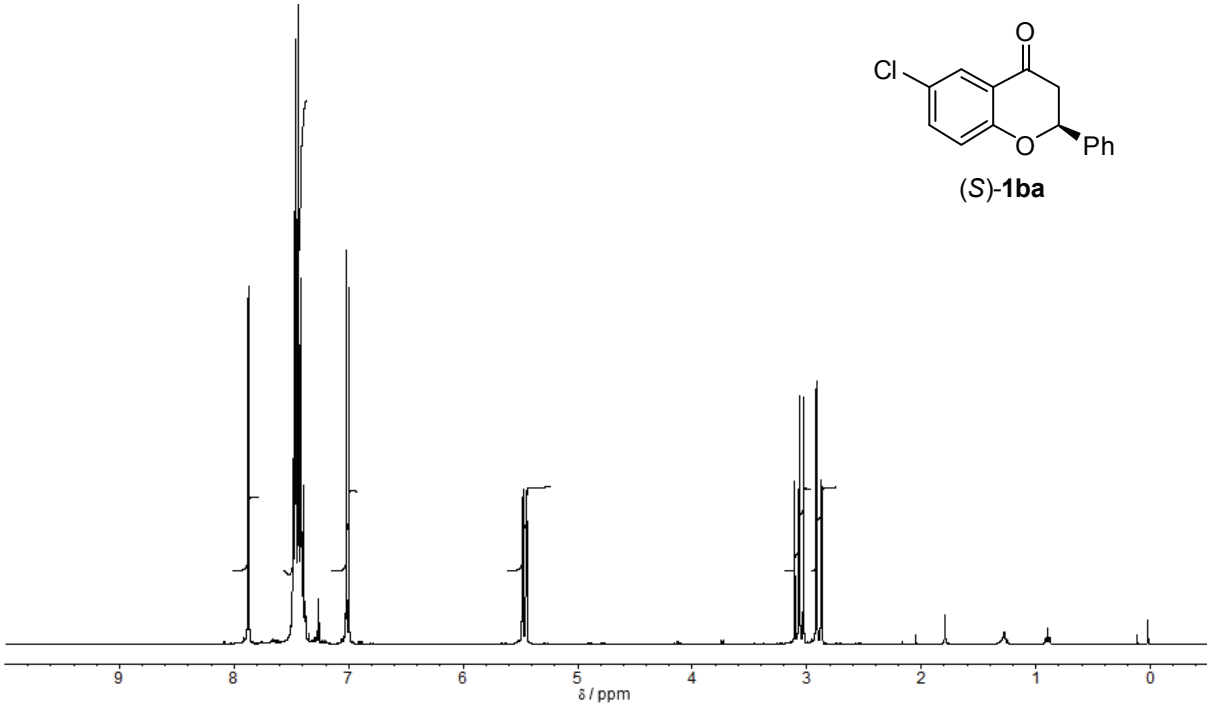
(±)-*trans*-**5agg**



CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14789

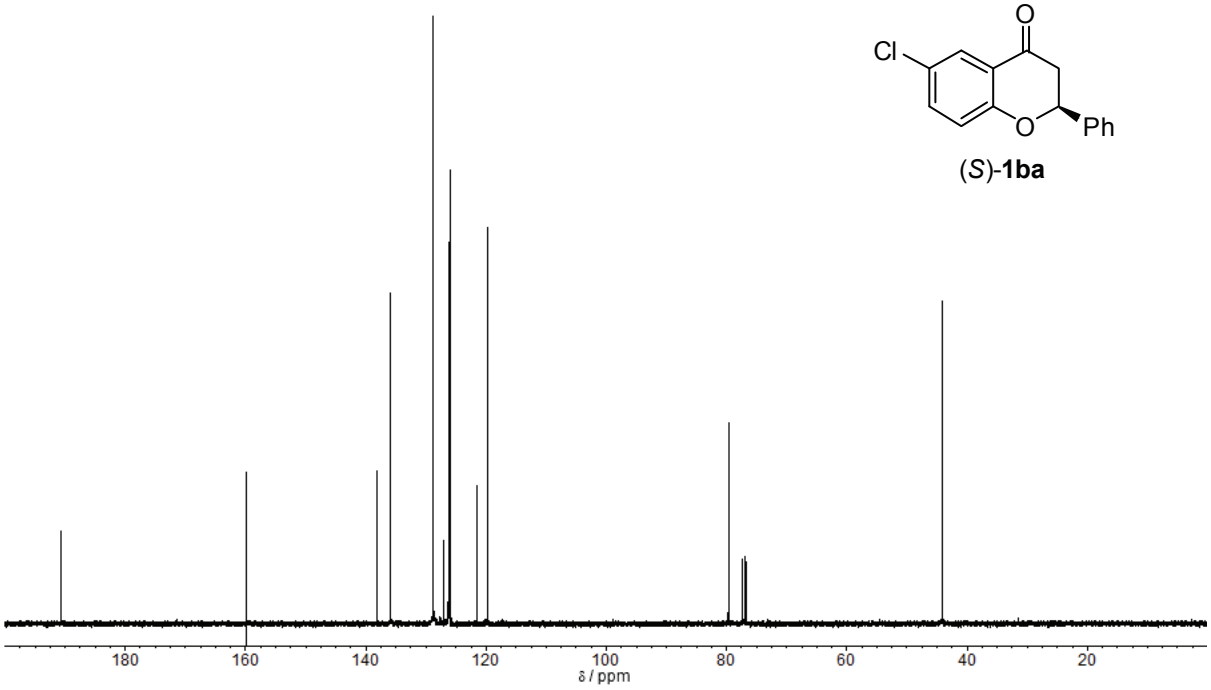
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.667	60110			49.2787	
2	15.167	61869			50.7213	
		---			---	
	TOTAL	121979			100	

^{1}H NMR (400 MHz, $CDCl_3$)



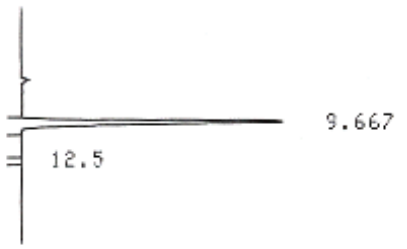
(*S*)-**1ba**

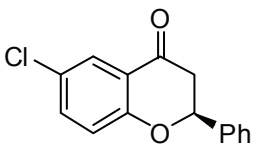
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1ba**

HPLC





(*S*)-**1ba**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 13312

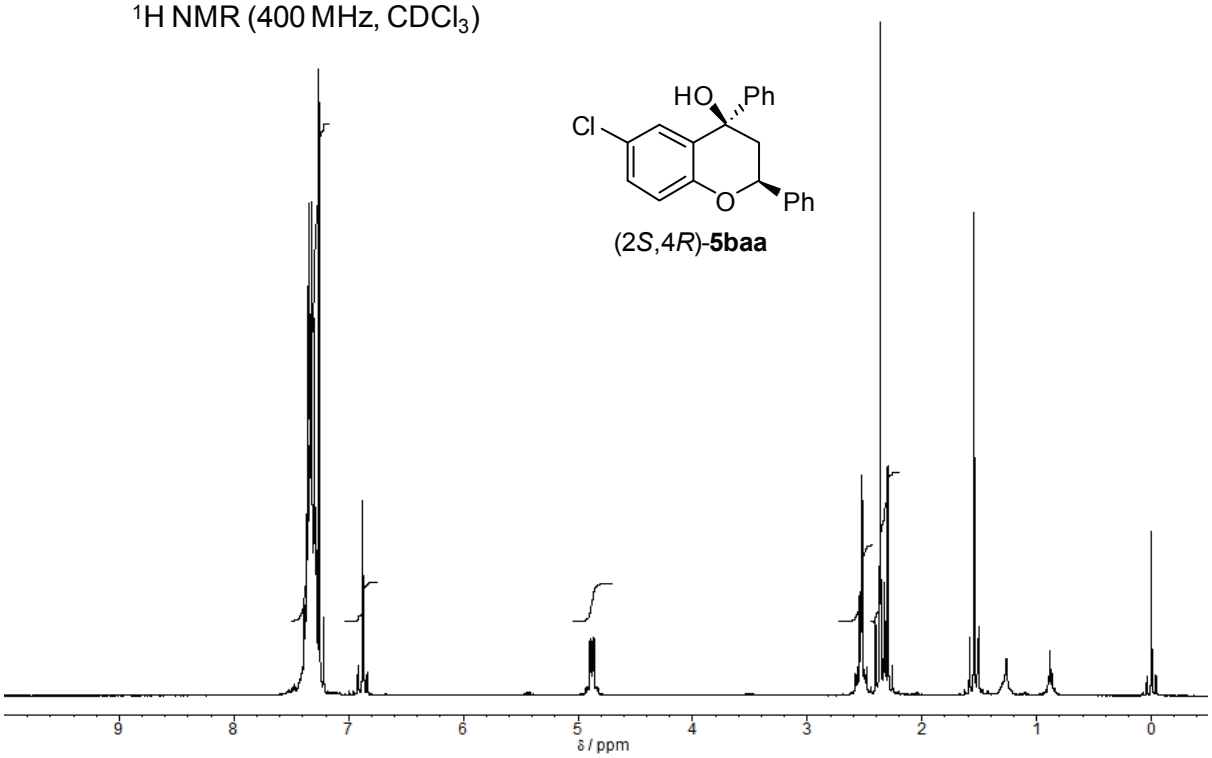
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9.667	1052580			99.753	
2	12.5	2606			0.247	
	TOTAL	1055187			100	

(±)-**1ba**

CHROMATOPAC C-R6A FILE 2
SAMPLE NO 0 METHOD 0061
REPORT NO 13300

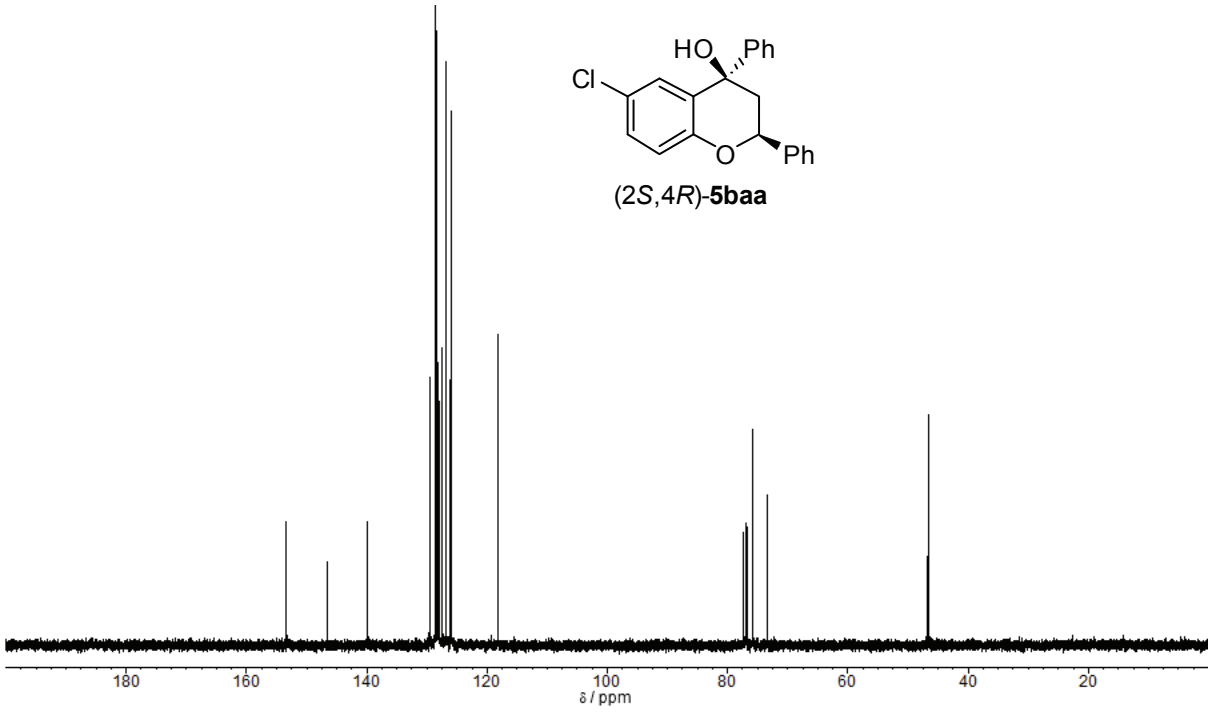
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9.333	806313			49.9702	
2	12.333	807274			50.0298	
	TOTAL	1613587			100	

^{1}H NMR (400 MHz, $CDCl_3$)



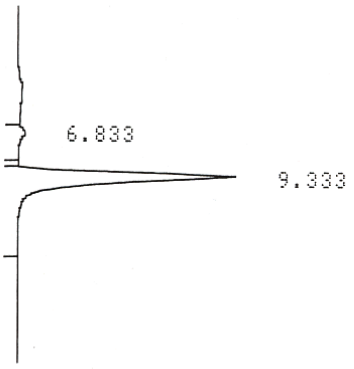
(2*S*,4*R*)-**5baa**

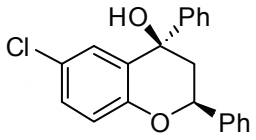
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S*,4*R*)-**5baa**

HPLC



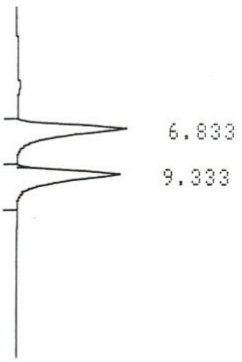


(2*S*,4*R*)-**5baa**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14721

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	6.833	1979			1.1603	
2	9.333	168556			98.8396	
	TOTAL	170535			100	

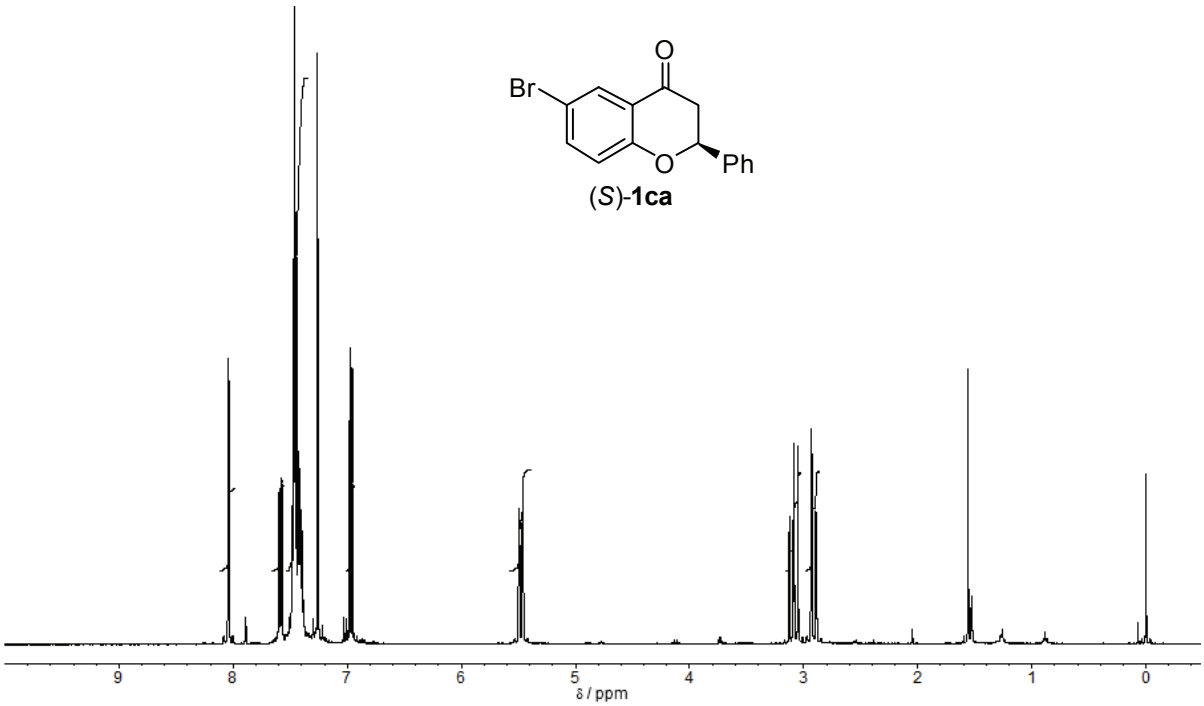


(±)-*trans*-**5baa**

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14726

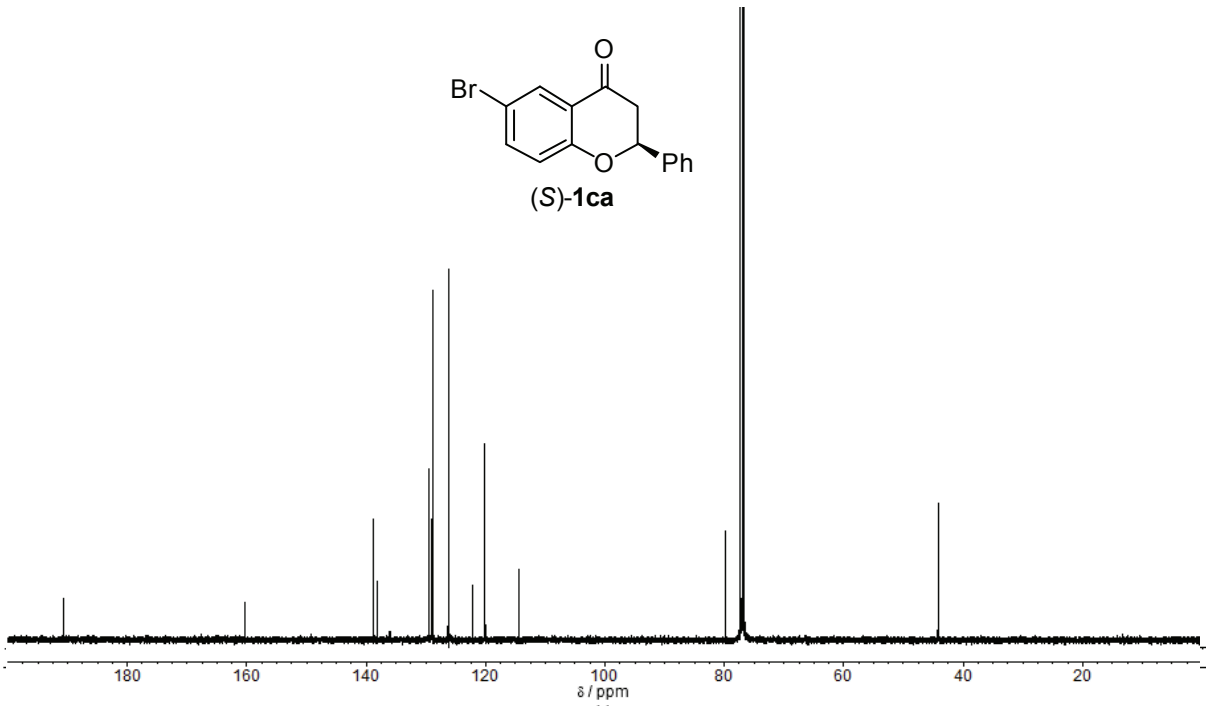
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	6.833	178295			51.7348	
2	9.333	166337			48.2652	
	TOTAL	344632			100	

^{1}H NMR (400 MHz, $CDCl_3$)



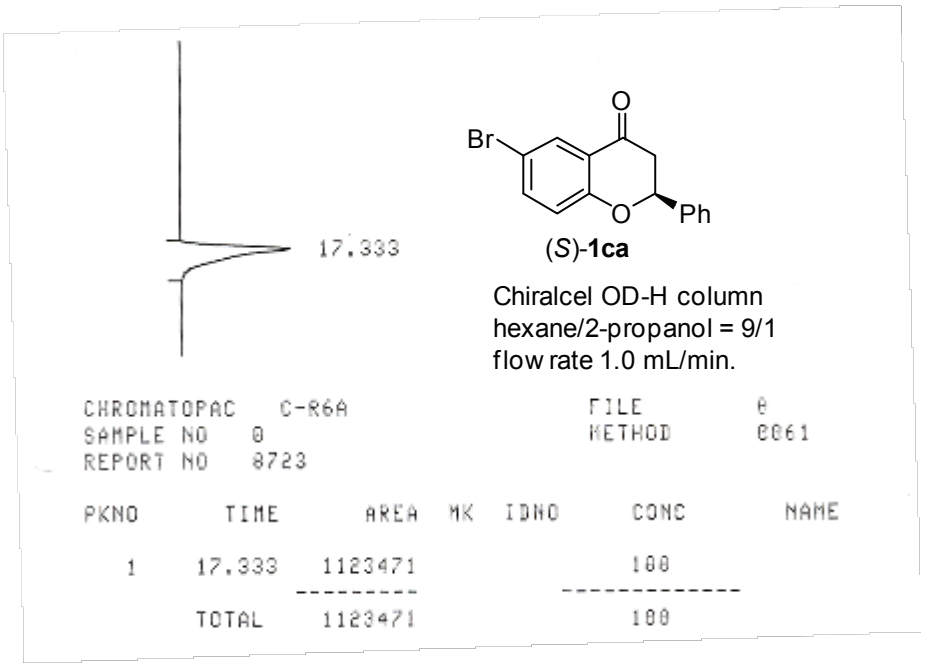
(*S*)-**1ca**

^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1ca**

HPLC

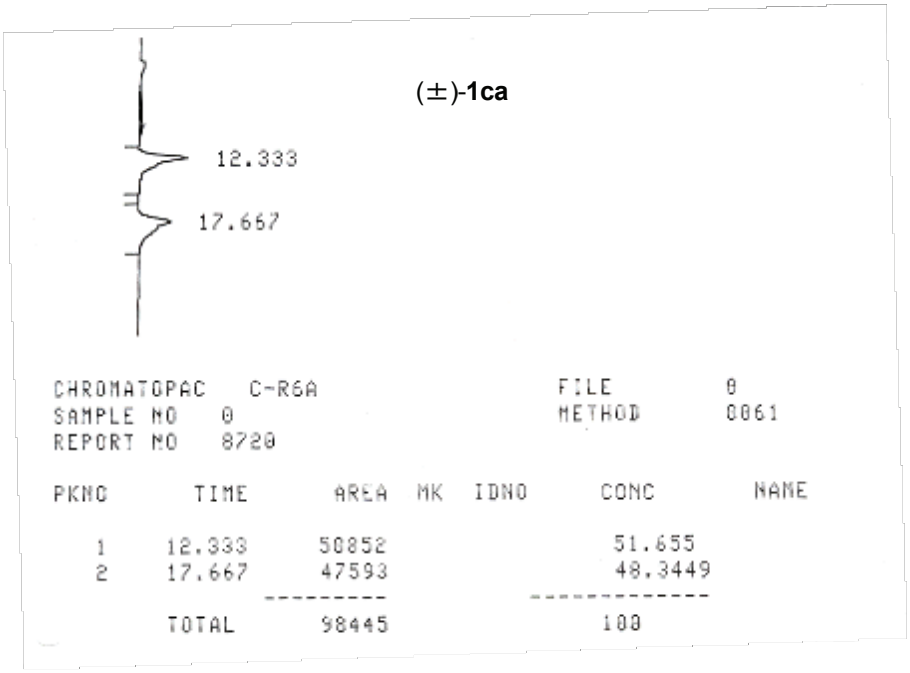


(*S*)-**1ca**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8723

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	17.333	1123471			100	
	TOTAL	1123471			100	

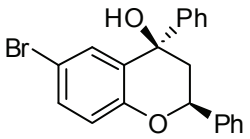


(±)-**1ca**

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8720

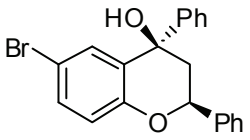
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.333	50852			51.655	
2	17.667	47593			48.3449	
	TOTAL	98445			100	

^{1}H NMR (400 MHz, $CDCl_3$)



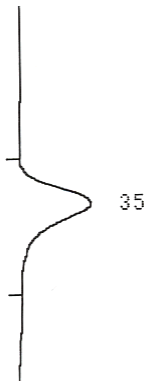
(2*S*,4*R*)-**5caa**

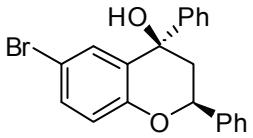
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S*,4*R*)-**5caa**

HPLC

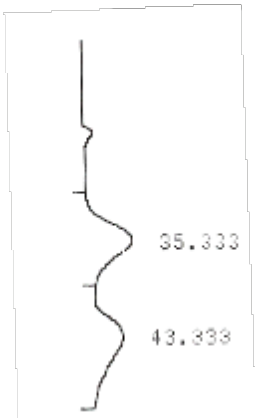




(2*S*,4*R*)-**5caa**

Chiralcel OJ-H column
hexane/2-propanol = 30/1
flow rate 1.0 mL/min.

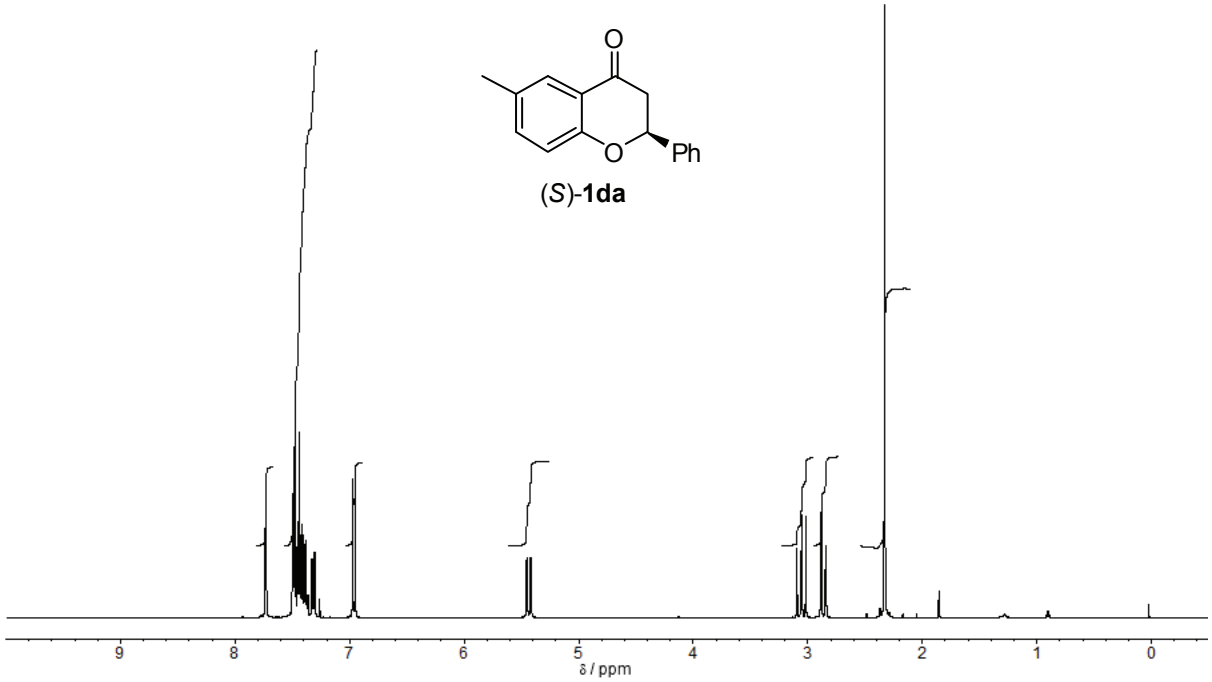
CHROMATOPAC C-R6A				FILE	0
SAMPLE NO 0				METHOD	0061
REPORT NO 8735					
PKNO	TIME	AREA	MK IDNO	CONC	NAME
1	35	300968		100	
	TOTAL	300968		100	



(±)-*trans*-**5caa**

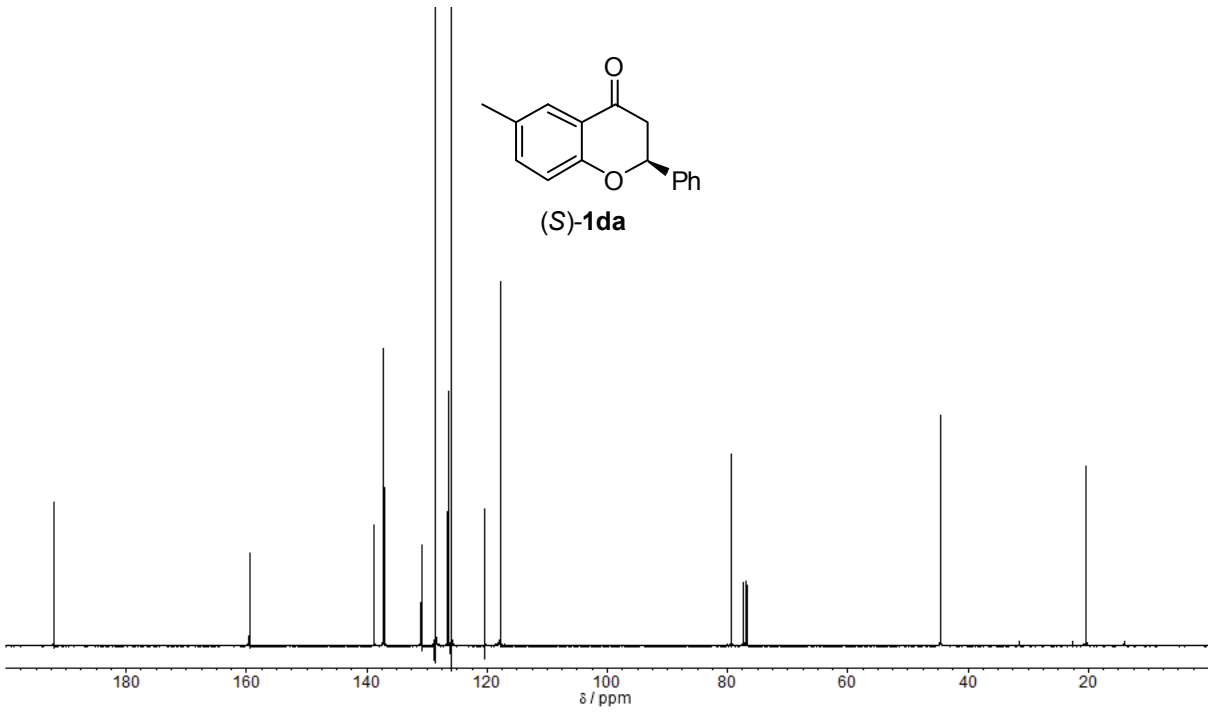
CHROMATOPAC C-R6A				FILE	0
SAMPLE NO 0				METHOD	0061
REPORT NO 3729					
PKNO	TIME	AREA	MK IDNO	CONC	NAME
1	35.333	188682		50.8533	
2	43.333	182310	V	49.1412	
	TOTAL	370993		100	

^{1}H NMR (400 MHz, $CDCl_3$)



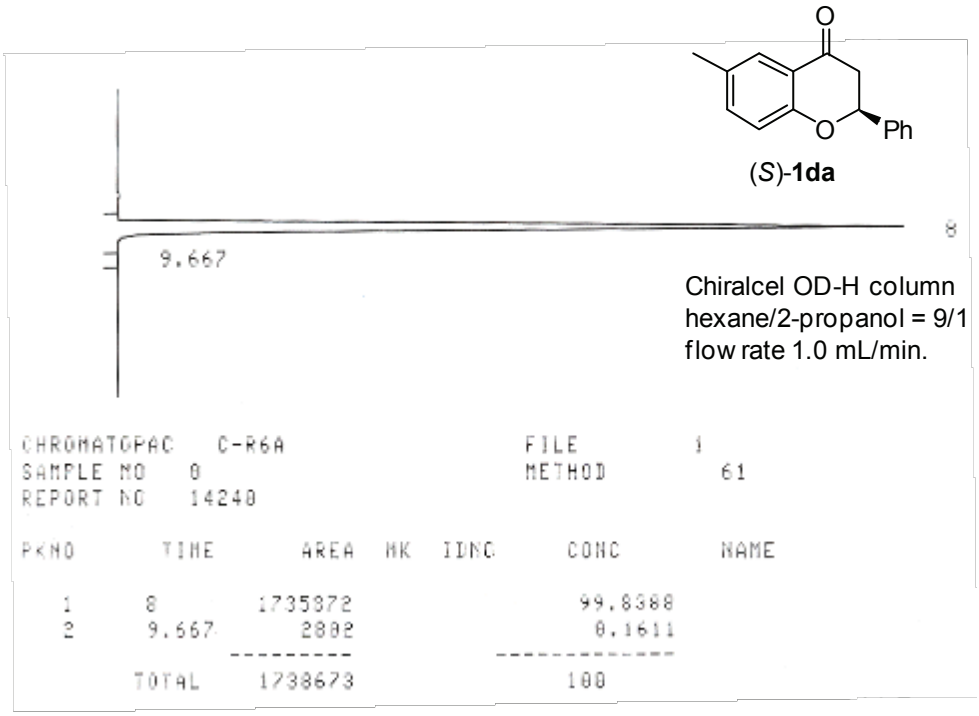
(*S*)-**1da**

^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1da**

HPLC



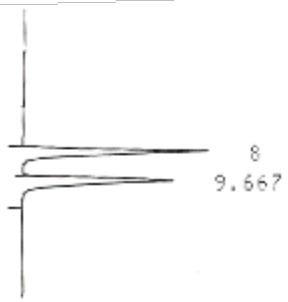
(*S*)-**1da**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14240

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	8	1735372			99.8388	
2	9.667	2802			0.1611	
	TOTAL	1738673			100	

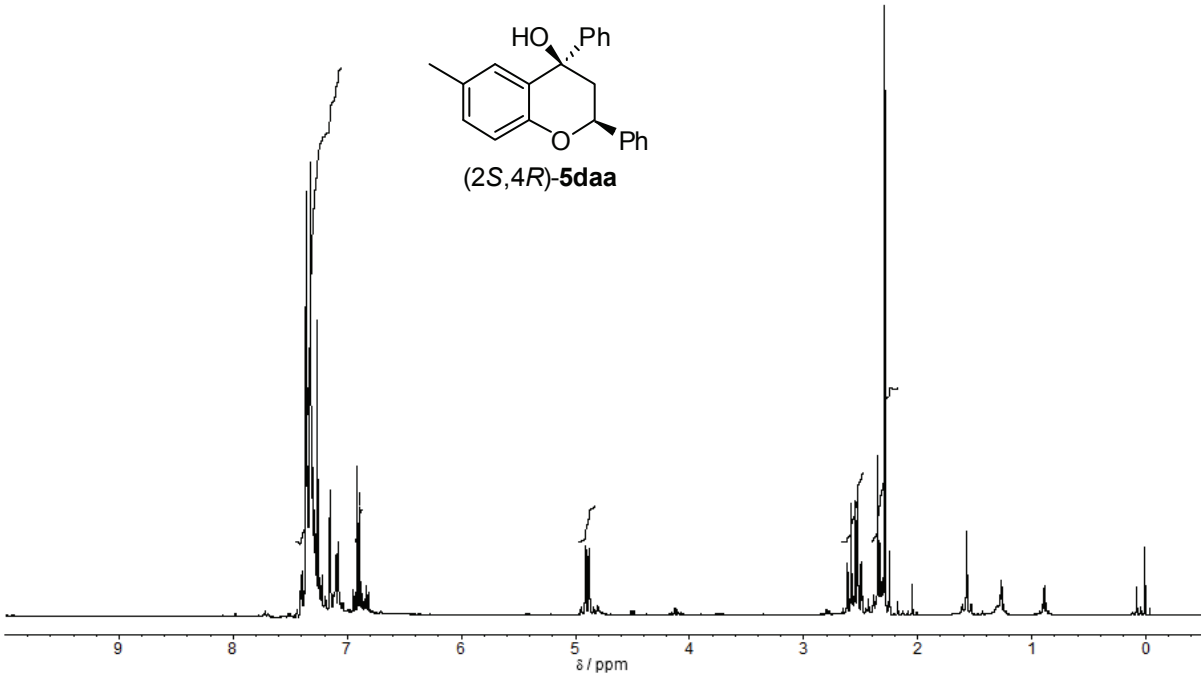
(±)-**1da**



CHROMATOPAC C-R6A FILE 1
SAMPLE NO 6 METHOD 61
REPORT NO 14237

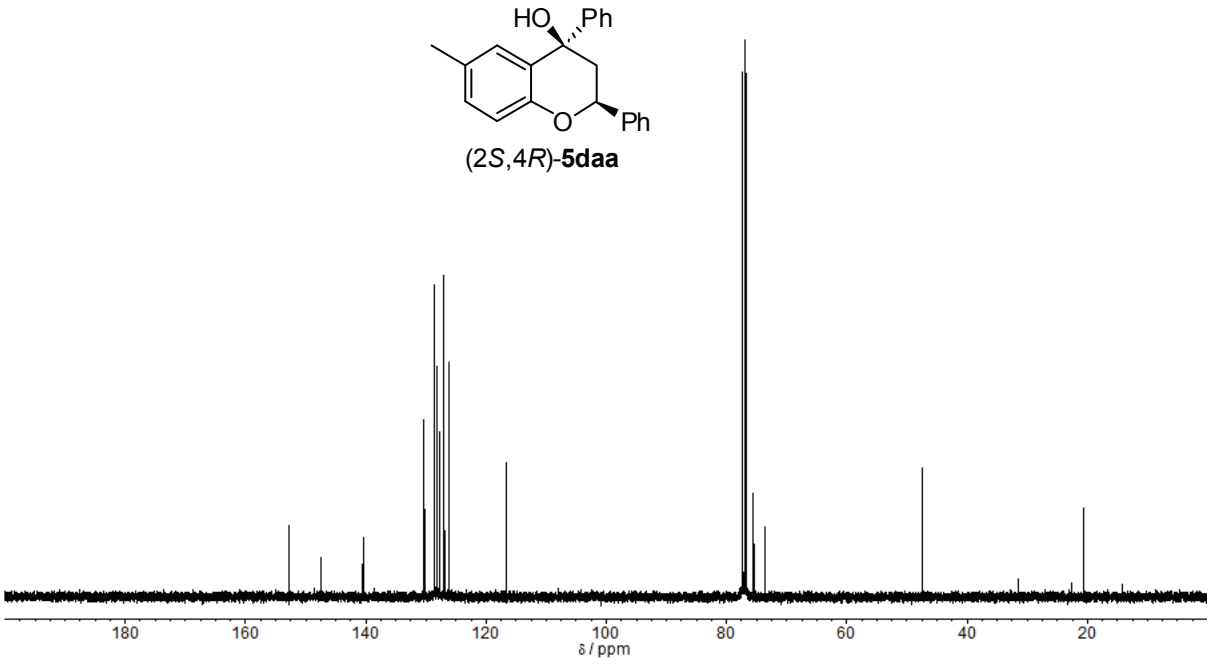
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	8	74613			49.9134	
2	9.667	74872			50.0866	
	TOTAL	149485			100	

^{1}H NMR (400 MHz, $CDCl_3$)



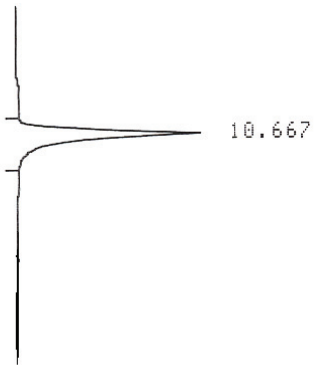
(2*S*,4*R*)-**5daa**

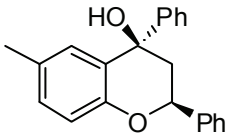
^{13}C NMR (101 MHz, $CDCl_3$)



(2*S*,4*R*)-**5daa**

HPLC



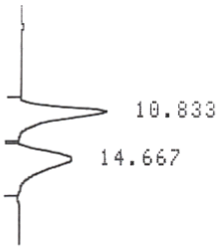


(2*S*,4*R*)-**5daa**

Chiralcel OJ-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8812

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.667	1550271			100	
	TOTAL	1550271			100	

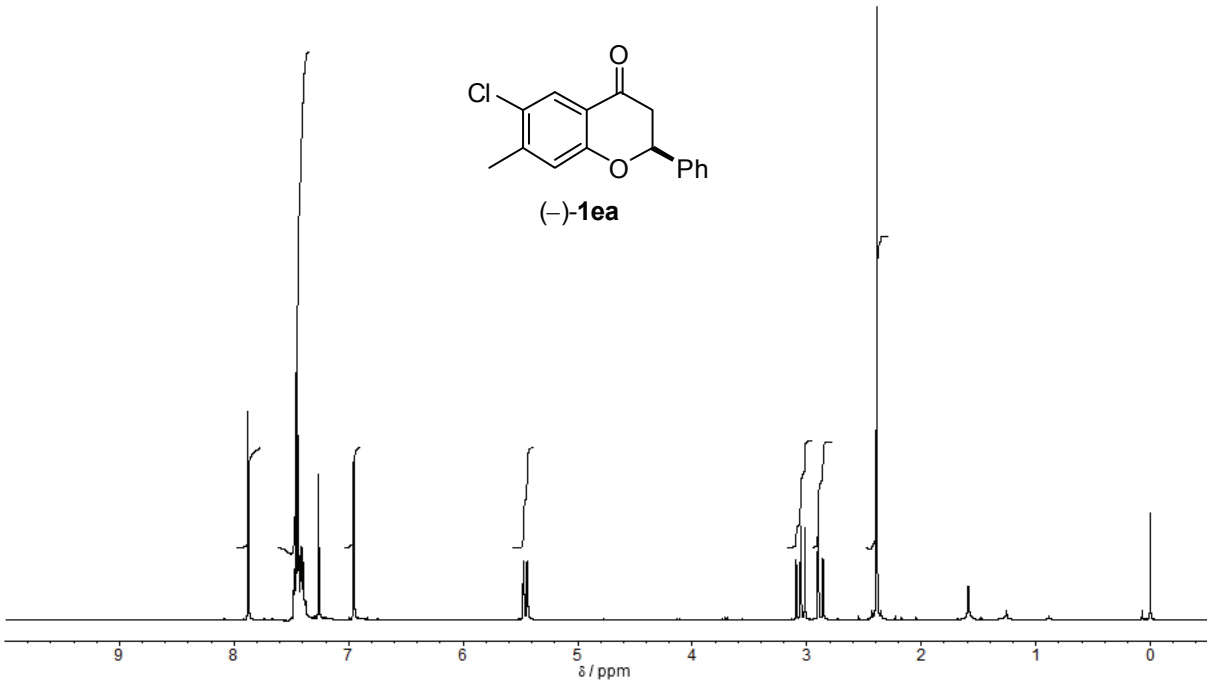


(±)-*trans*-**5daa**

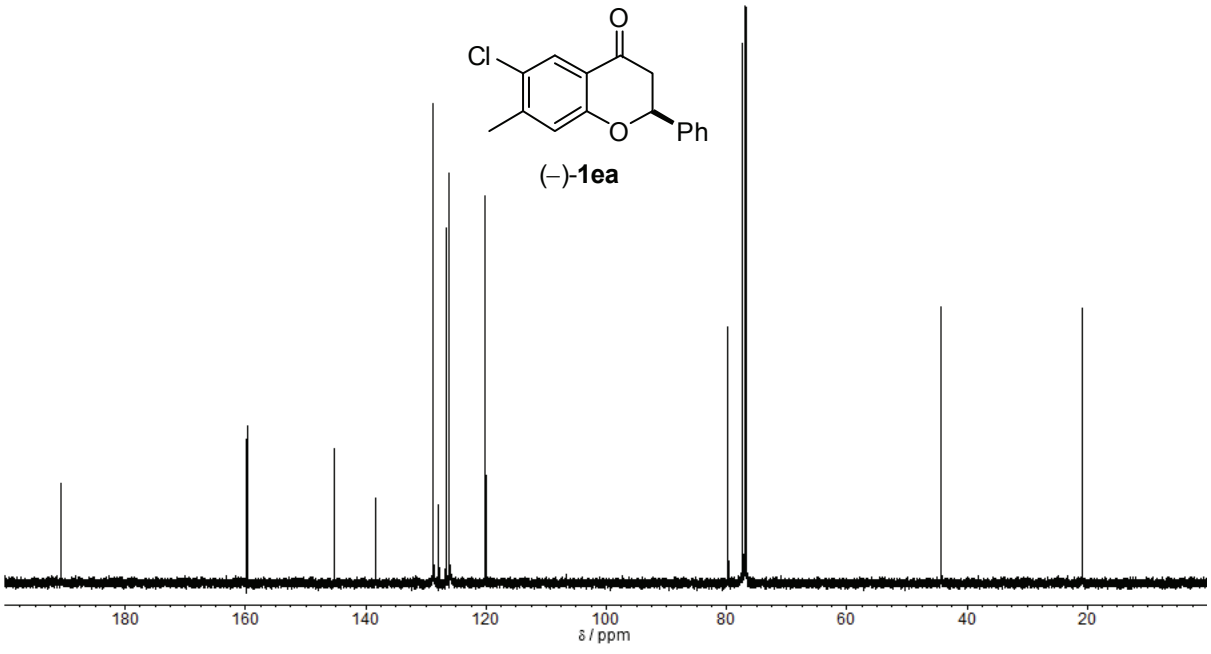
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8804

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.833	120498			50.9918	
2	14.667	115810			49.0082	
	TOTAL	236308			100	

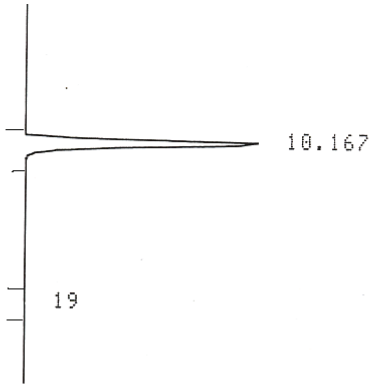
^{1}H NMR (400 MHz, $CDCl_3$)

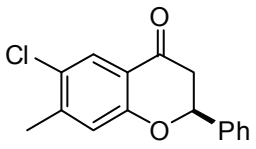


^{13}C NMR (101 MHz, $CDCl_3$)



HPLC





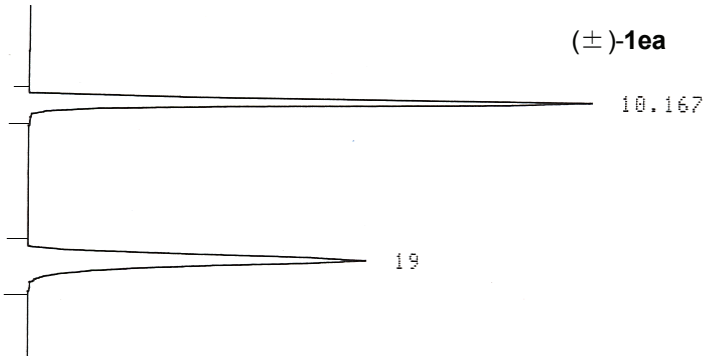
(–)-**1ea**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 41
REPORT NO 14213

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.167	1049037			99.8547	
2	19	1526			0.1453	
	TOTAL	1050564			100	

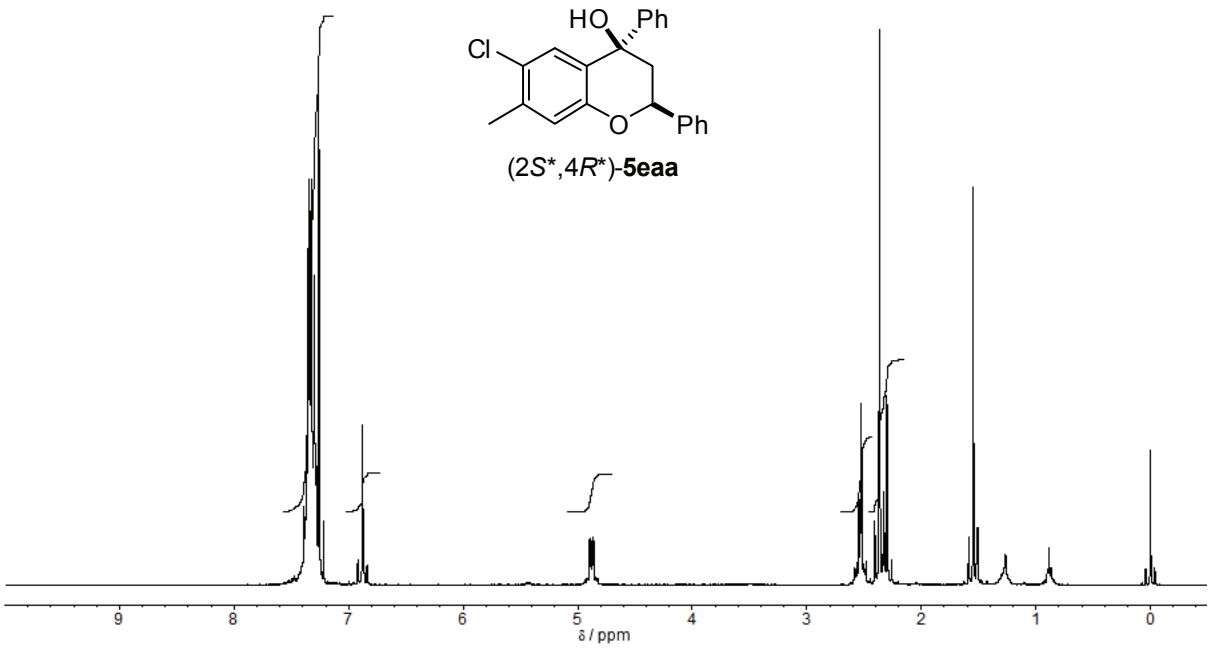
(±)-**1ea**



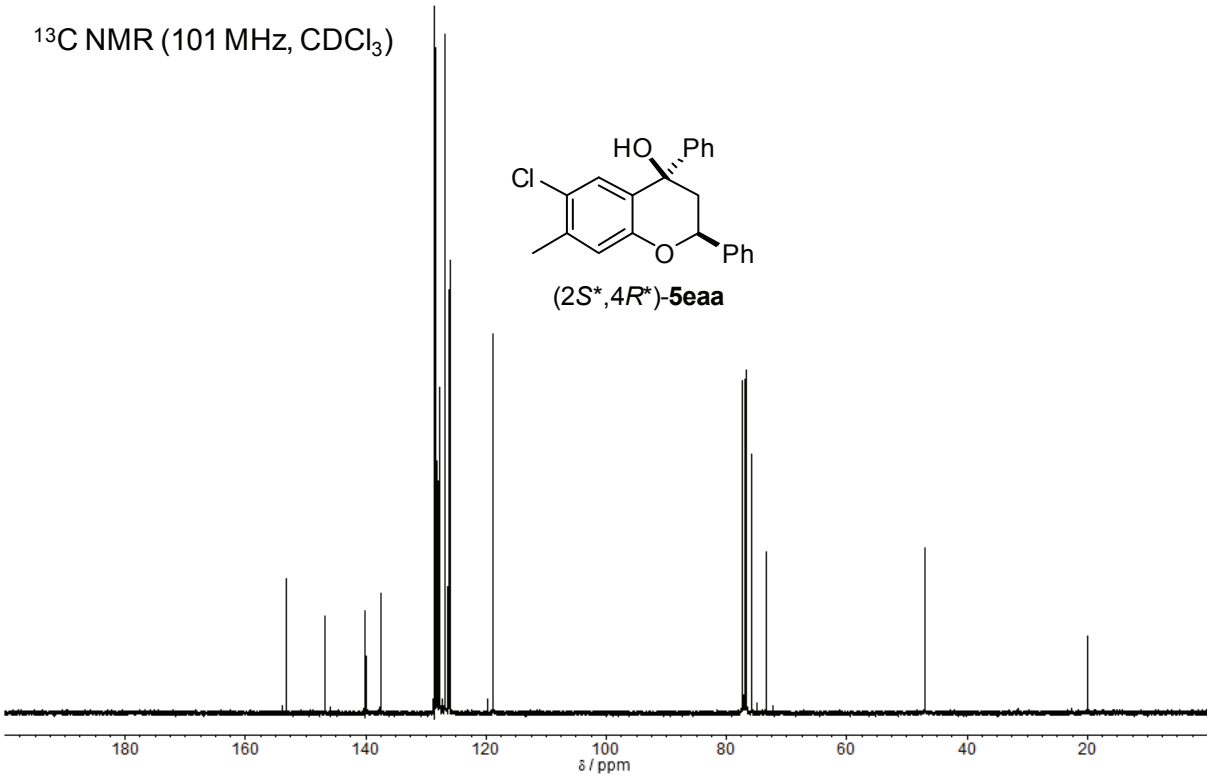
CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 41
REPORT NO 14209

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.167	1225875			49.9944	
2	19	1226148			50.0056	
	TOTAL	2452022			100	

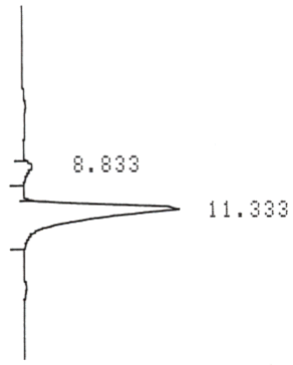
^{1}H NMR (400 MHz, $CDCl_3$)

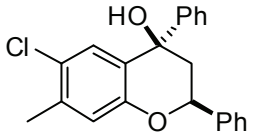


^{13}C NMR (101 MHz, $CDCl_3$)



HPLC

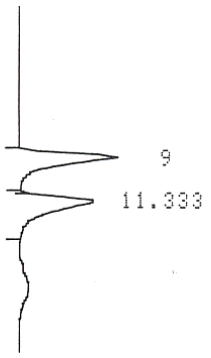




(2*S**,4*R**)-**5eaa**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

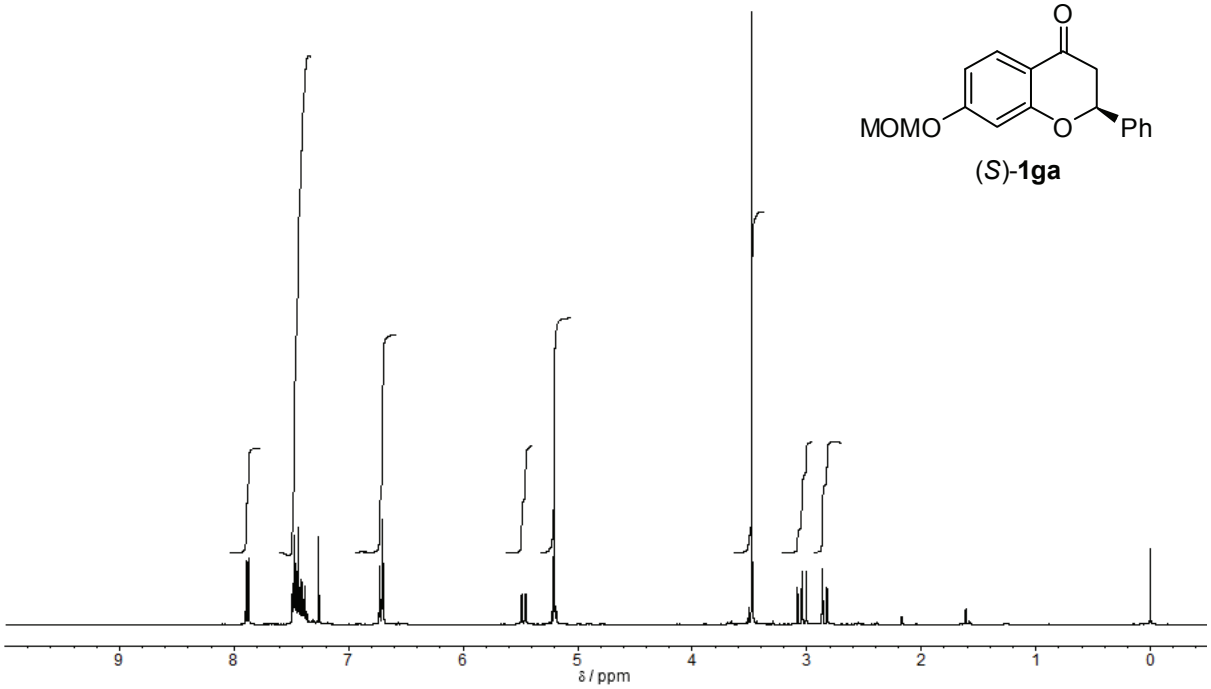
CHROMATOPAC C-R6A					FILE	1
SAMPLE NO 0					METHOD	61
REPORT NO 14735						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	8.833	4666			2.8909	
2	11.333	156746			97.1091	
	TOTAL	161412			100	



(±)-*trans*-**5eaa**

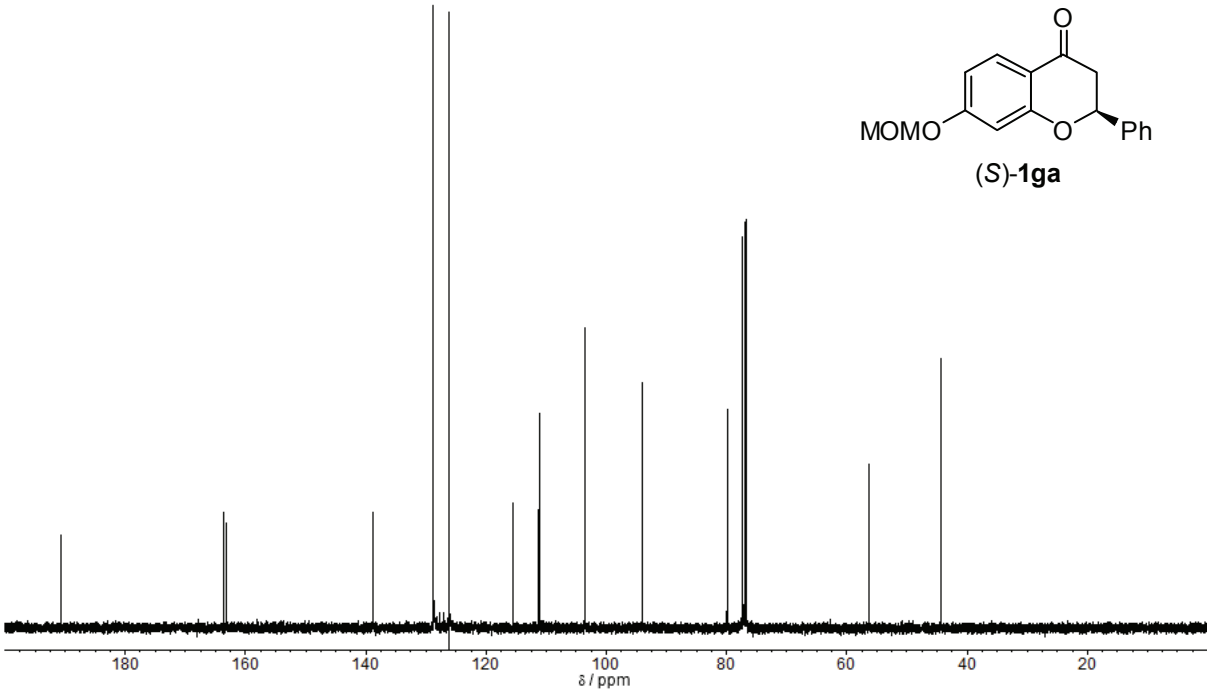
CHROMATOPAC C-R6A					FILE	1
SAMPLE NO 0					METHOD	61
REPORT NO 14737						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	9	315433			50.9022	
2	11.333	304251			49.0978	
	TOTAL	619684			100	

^{1}H NMR (400 MHz, $CDCl_3$)



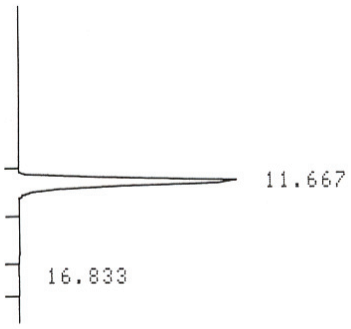
(*S*)-**1ga**

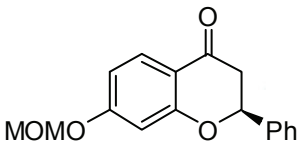
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1ga**

HPLC

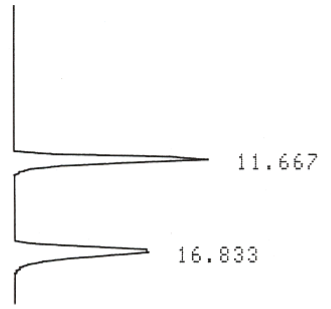




(*S*)-**1ga**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

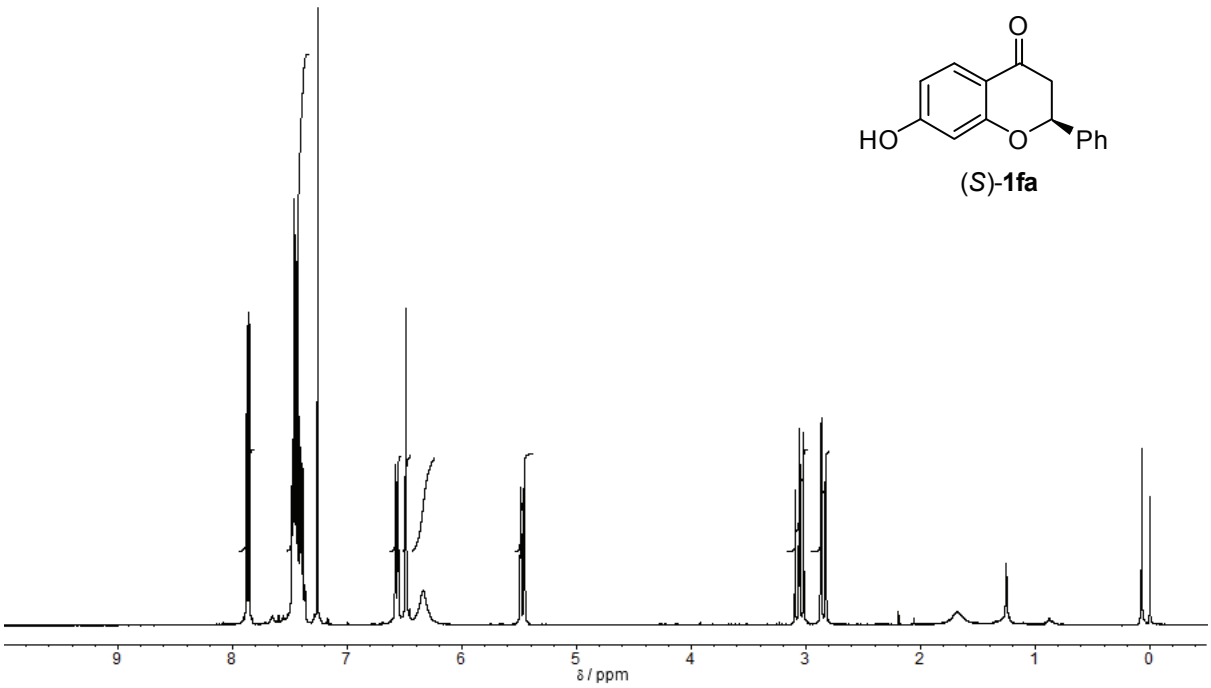
CHROMATOPAC C-R6A					FILE	1
SAMPLE NO 0					METHOD	61
REPORT NO 14228						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	11.667	558565			99.6874	
2	16.833	1752			0.3126	
	TOTAL	560316			100	



(±)-**1ga**

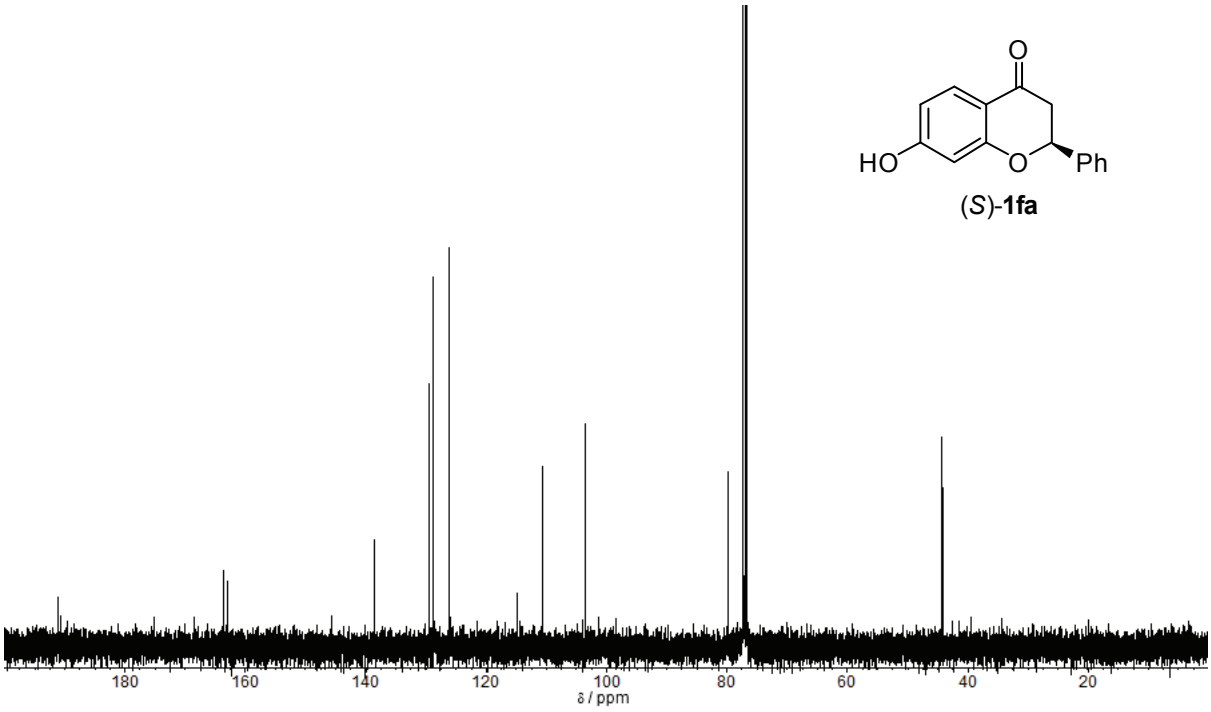
CHROMATOPAC C-R6A					FILE	1
SAMPLE NO 0					METHOD	41
REPORT NO 14188						
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	11.667	468472			49.9755	
2	16.833	468930	V		50.0245	
	TOTAL	937402			100	

^{1}H NMR (400 MHz, $CDCl_3$)



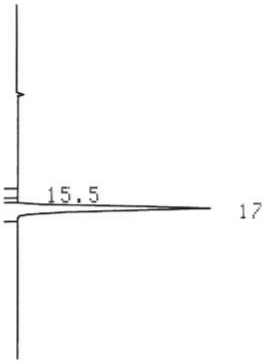
(*S*)-**1fa**

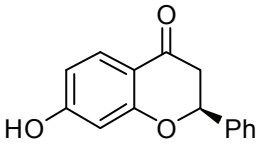
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**1fa**

HPLC



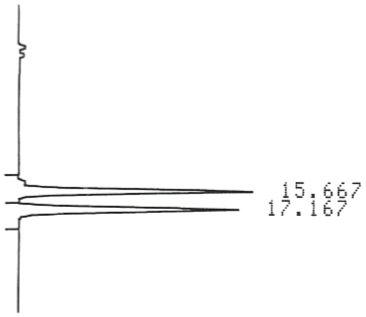


(*S*)-**1fa**

Chiralcel AD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8801

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	15.5	2416			0.5483	
2	17	438238			99.4516	
	TOTAL	440654			100	

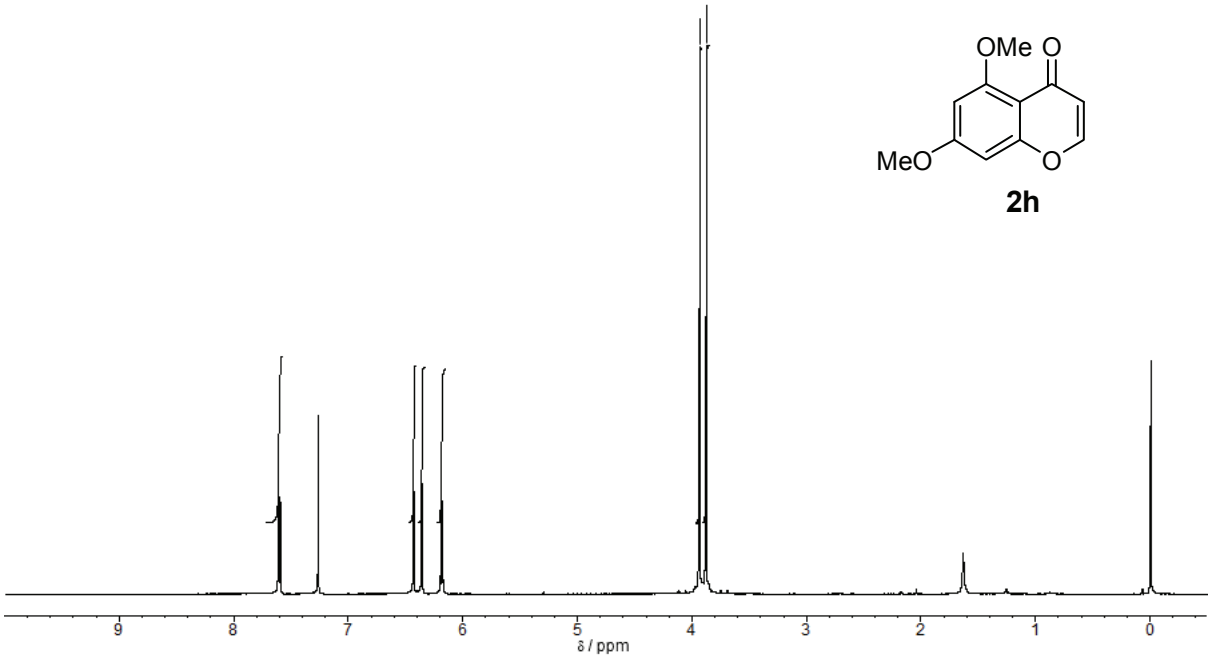


(±)-**1fa**

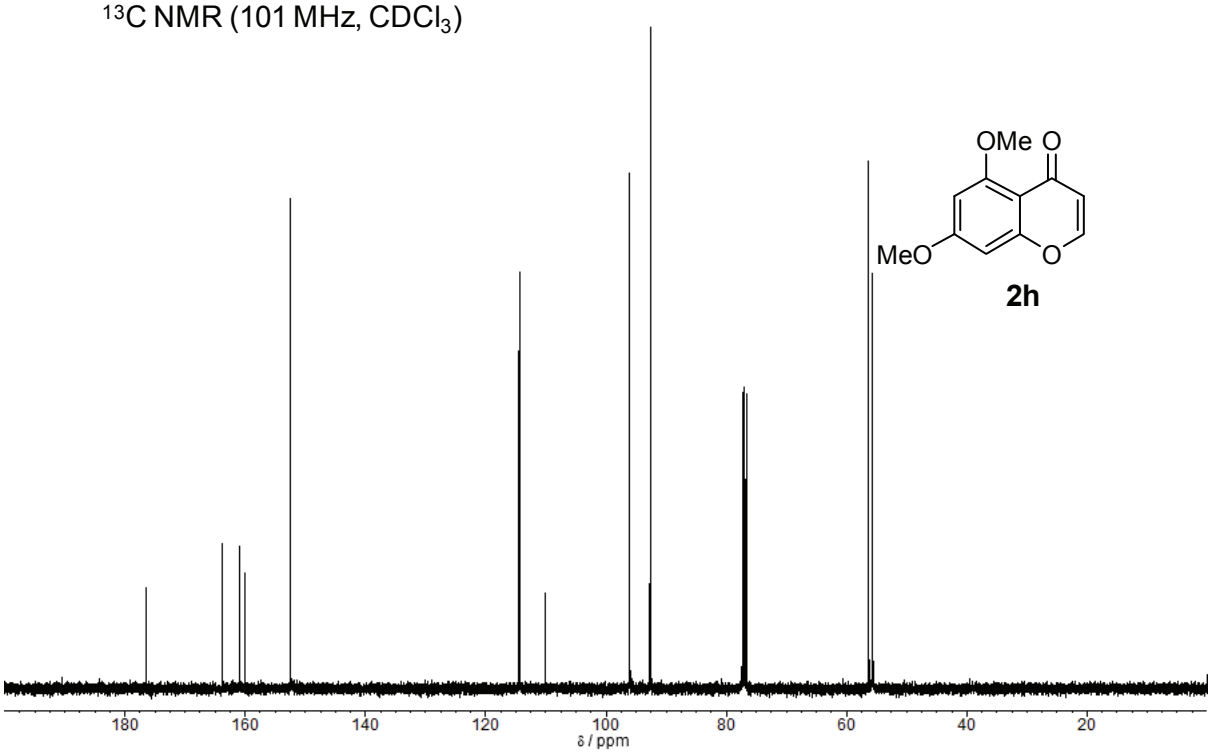
CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8781

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	15.667	535832			50.9536	
2	17.167	515776	V		49.0464	
	TOTAL	1051608			100	

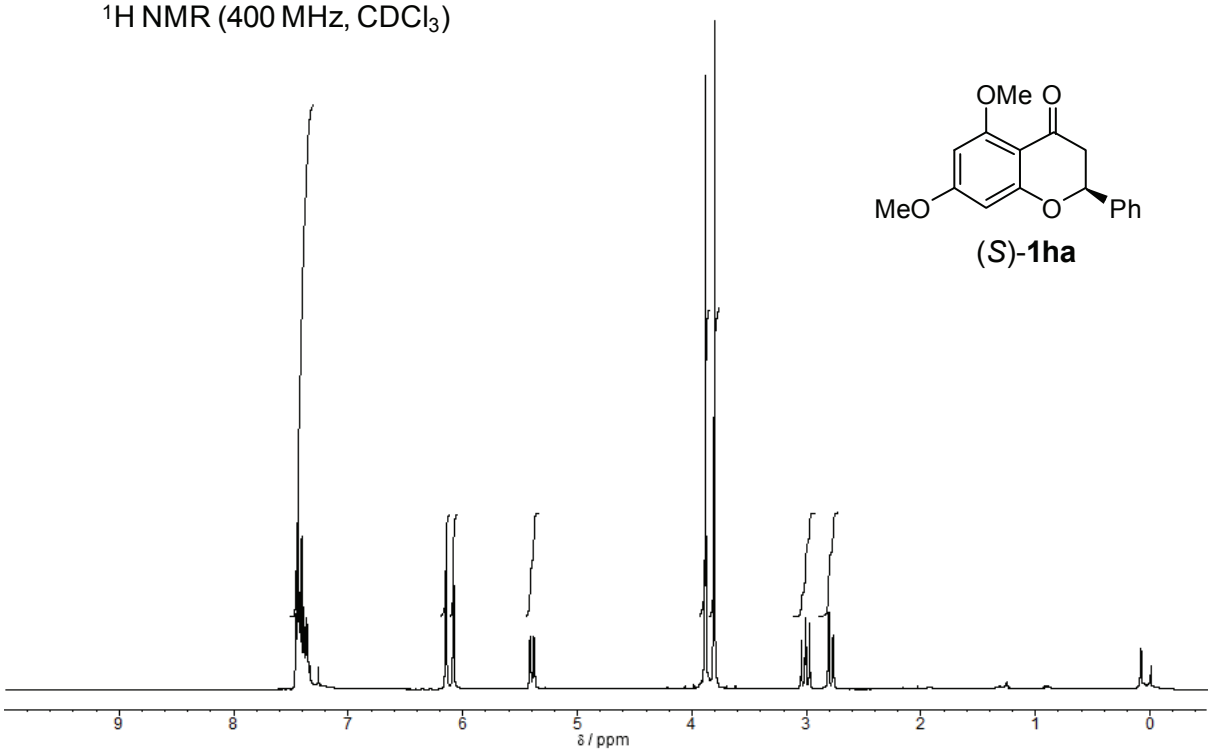
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

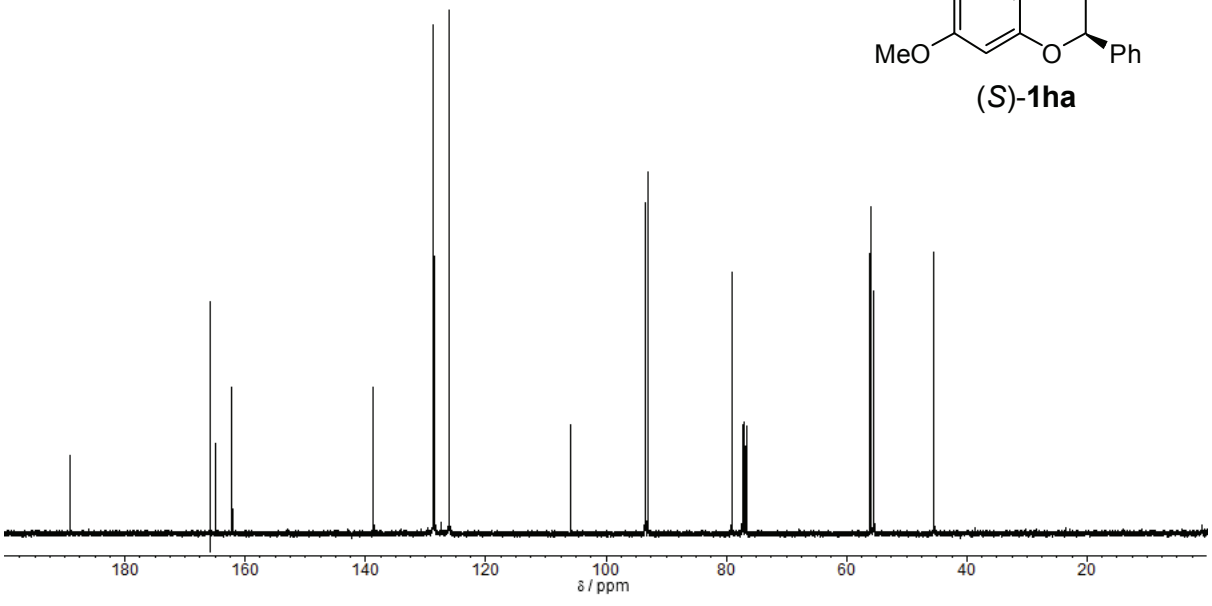


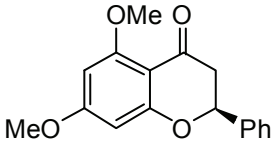
^{1}H NMR (400 MHz, $CDCl_3$)



(*S*)-**1ha**

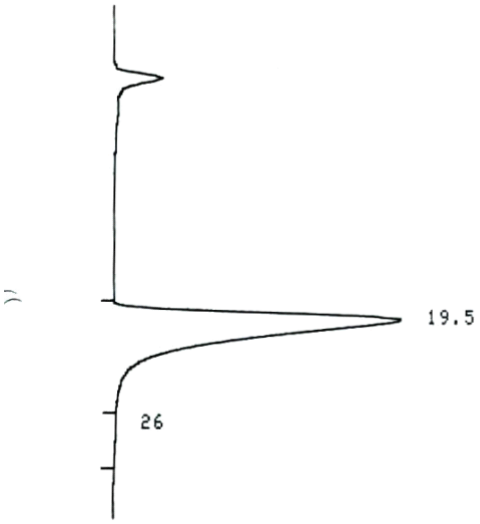
^{13}C NMR (101 MHz, $CDCl_3$)

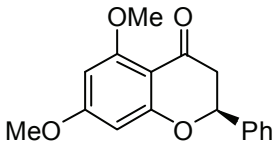




(*S*)-**1ha**

HPLC



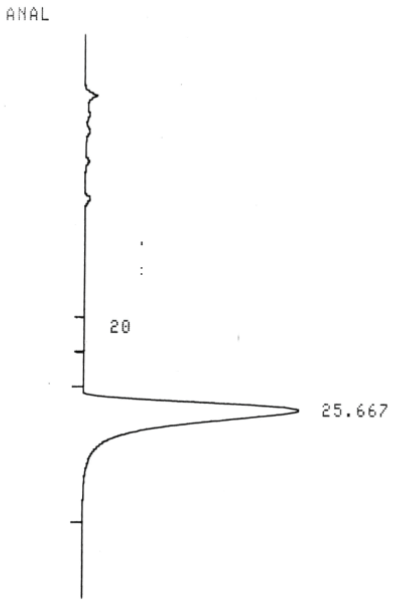


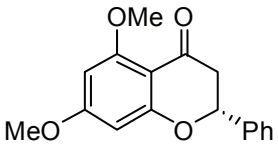
(*S*)-**1ha**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 15009

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	19.5	342772			99.7778	
2	26	763			0.2222	
	TOTAL	343535			100	



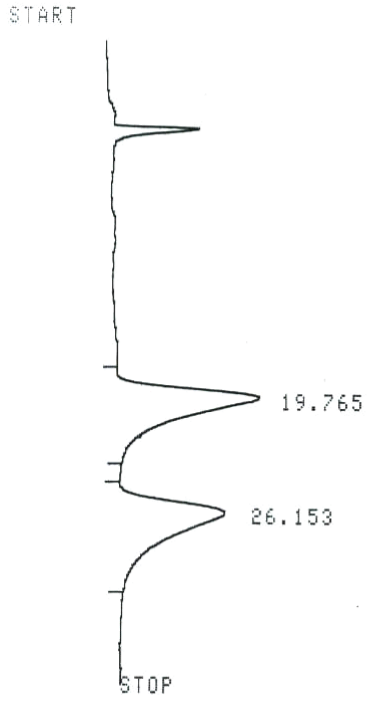


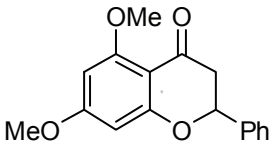
(*R*)-**1ha**

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14926

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	20	1926			0.3409	
2	25.667	562917			99.6591	
	TOTAL	564843			100	

HPLC





(±)-**1ha**

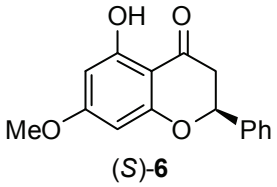
Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 15004

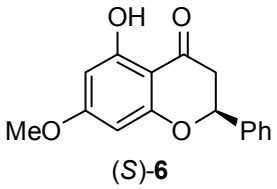
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	19.765	71961			51.1761	
2	26.153	68653			48.8239	
	TOTAL	140614			100	

^{1}H NMR (400 MHz, $CDCl_3$)



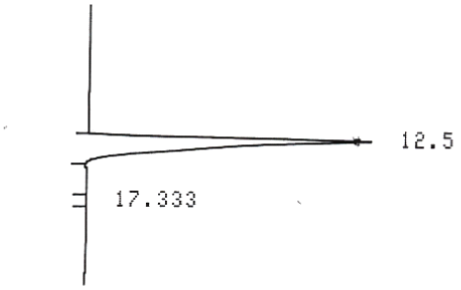
(*S*)-**6**

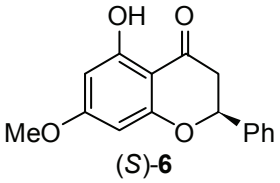
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-**6**

HPLC





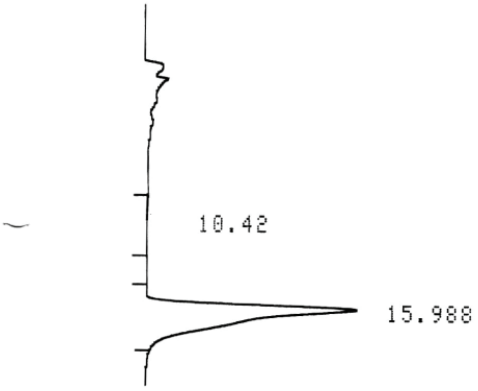
(*S*)-**6**

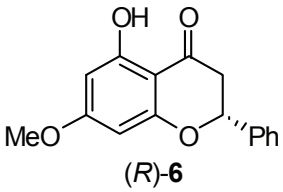
Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8863

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	12.5	297080			99.7841	
2	17.333	643			0.2159	
	TOTAL	297723			100	

A.SAVE
START





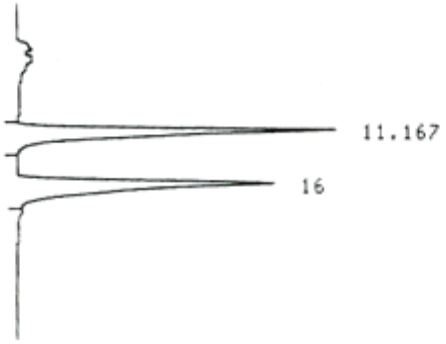
(*R*)-**6**

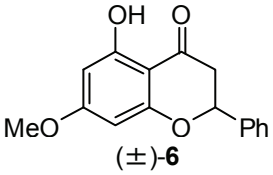
CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 14986

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	10.42	466			0.3832	
2	15.988	121173			99.6168	
	TOTAL	121639			100	

HPLC





(±)-**6**

Chiralcel OD-H column
hexane/2-propanol = 9/1
flow rate 1.0 mL/min.

CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 0061
REPORT NO 8570

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	11.167	615540			50.0504	
2	16	614299			49.9496	
	TOTAL	1229839			100	

Confirmation of relative conformation of 5aaa.

The relative configuration of 1,2-,1,4-adduct **5aaa** was determined to be (2*S*,4*R*)- form by NOESY spectrum or DFT calculation of the chemical shifts of ^{1}H NMR as follows. In the NOESY spectrum (page S78), no NOE was observed between hydroxy proton and H^2, which suggested *trans* relationship between two phenyl groups (Figure S1). This finding was used for the determination of the relative configurations of the other **5** compounds.

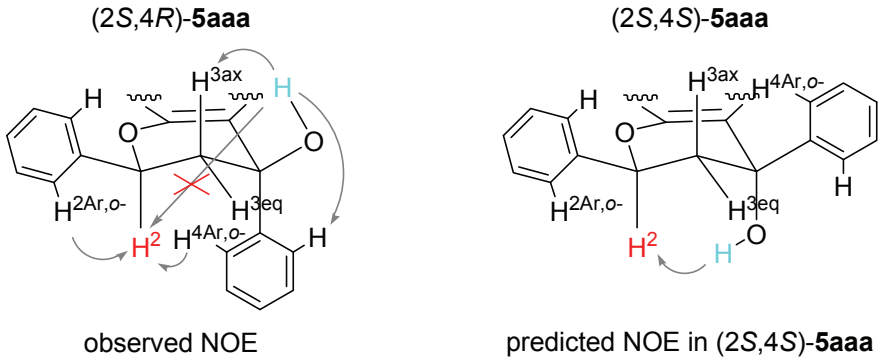
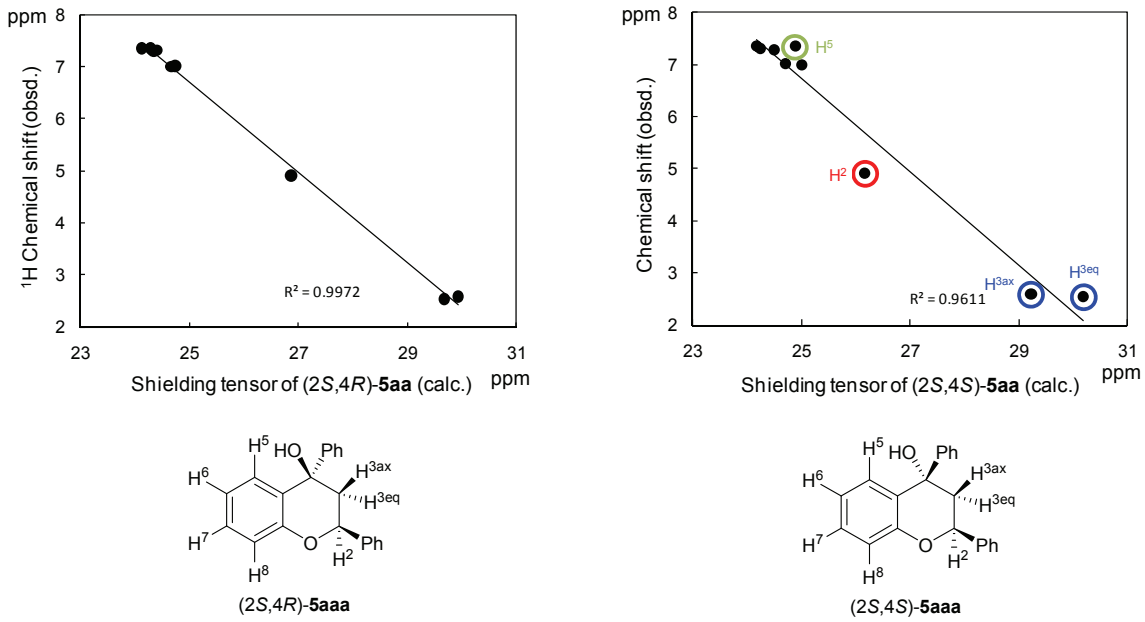


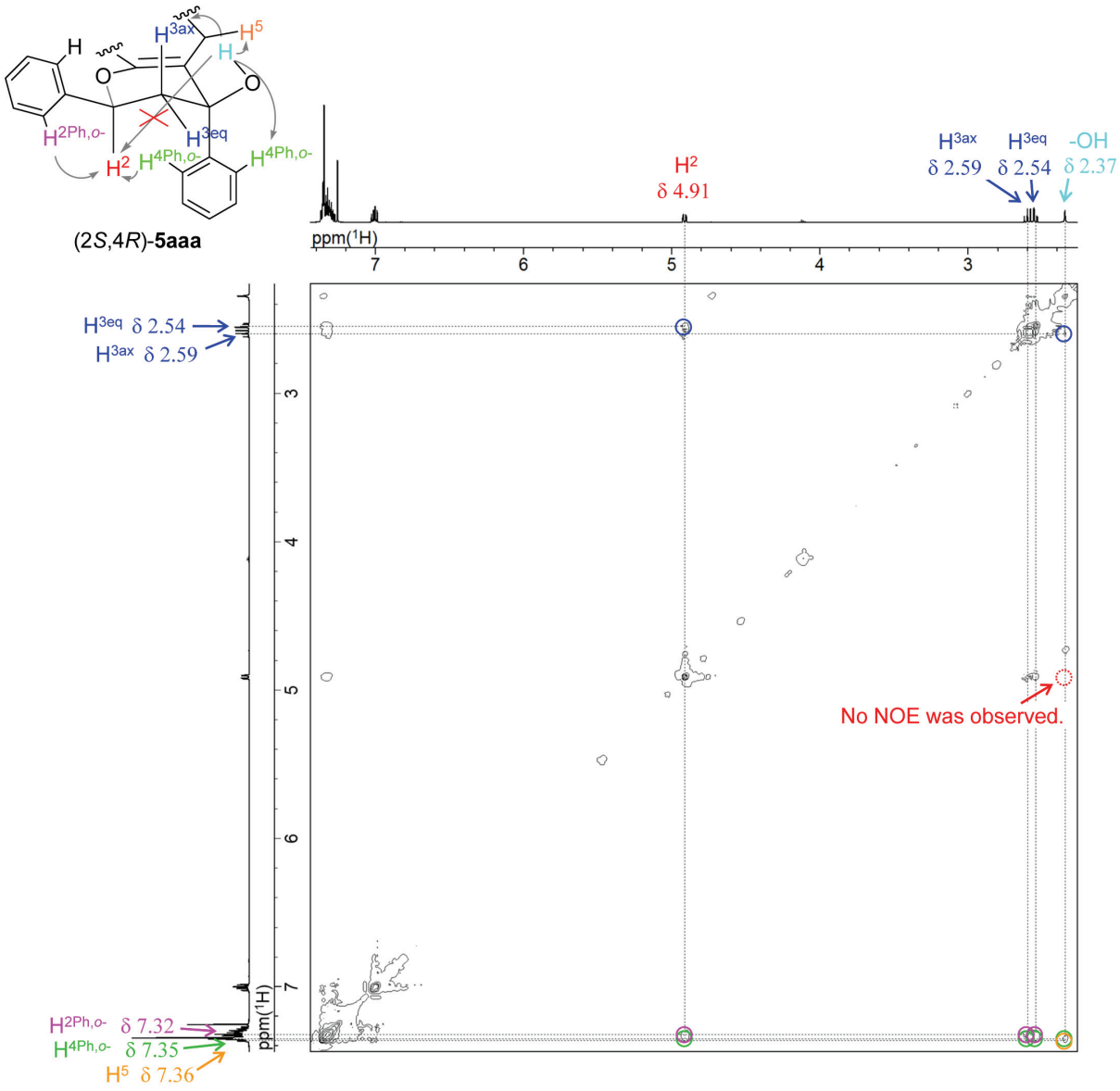
Figure S1

Just to be safe, the relative configuration of **5aaa** was confirmed by DFT calculations of chemical shifts (pages S79, S80). The chemical shifts (shielding tensors) of **5aaa** in both diastereomers were calculated at the GIAO/B3LYP/6-311++G(d,p) after optimization at the B3LYP/6-31G(d) using Gaussian 03. Although the calculated shielding tensors of (2*S*,4*R*)-5**aaa** are highly correlated with the observed chemical shifts of **5aaa** in ^{1}H NMR, those of (2*S*,4*S*)-5**aaa** are not lined up with observed ones at the H^2, H^3 and H^5 protons (Figure S2). Therefore, the calculated results indicate that the relative configuration of **5aaa** is (2*S*,4*R*)-form.

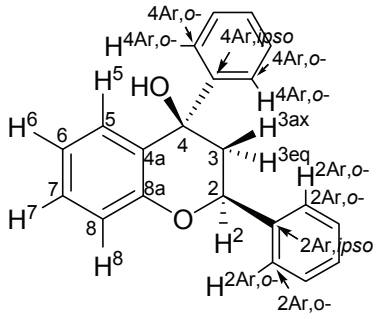
Figure S2 Correlation of ^{1}H chemical shift between observed and calculated values.



NOESY


H3ax
H5
H
H
O
O
H2Ph,o-
H3eq
H2
H4Ph,o-
H4Ph,o-
(2S,4R)-5aaa
H2
δ 4.91
H3ax
δ 2.59
H3eq
δ 2.54
-OH
δ 2.37
ppm(1H)
7
6
5
4
3
H3eq δ 2.54
H3ax δ 2.59
No NOE was observed.
H2Ph,o- δ 7.32
H4Ph,o- δ 7.35
H5 δ 7.36
ppm(1H)

Correlation of chemical shifts between calculated values of (2*S*,4*R*)-5aaa and observed values.



(2*S*,4*R*)-**5aaa**

δ ^{1}H values of NMR of 5aaa, which was suspected to be (2*S*,4*R*)-form.

The chemical shifts were measured in $CDCl_3$.

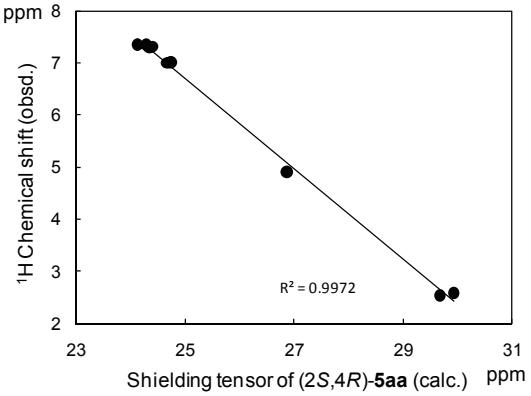
Calculated values of (2*S*,4*R*)-5aaa.

The structure was optimized at the B3LYP/6-31G(d). Shielding tensors were calculated at the GIAO/B3LYP/6-311++G(d,p).

^{1}H NMR

H	δ ^{1}H	Shielding tensor[a)]
2	4.91	26.8654
3eq	2.54	29.6813
3ax	2.59	29.9312
5	7.35	24.1264
6	7.01	24.7409
7	7.28	24.3510
8	6.99	24.6701
2Ar, *o*-	7.31	24.4040[b)]
4Ar, *o*-	7.35	24.2822[b)]

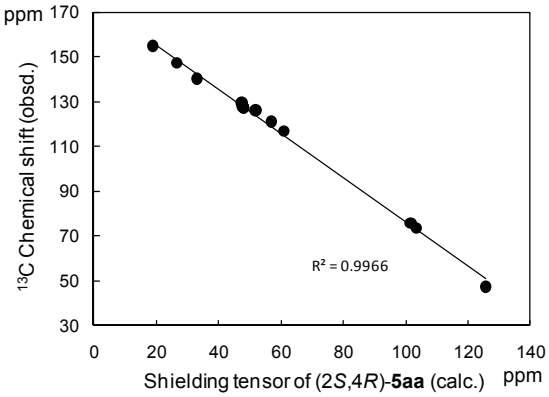
a) GIAO/B3LYP/6-311++G(d,p)//B3LYP/6-31G(d).
b) Average of *ortho*-protons.



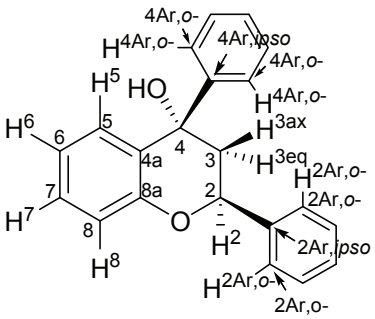
^{13}C NMR

C	δ ^{13}C	Shielding tensor[a)]
2	75.6	101.5741
3	47.2	125.7145
4	73.5	103.3493
4a	127.2	47.8664
5	127.7	47.8088
6	121.1	56.9964
7	129.5	47.4528
8	116.8	60.9940
8a	154.8	18.8446
2Ar, *o*-	126.1	51.7899[b)]
4Ar, *o*-	127.0	49.0948[b)]
2Ar, *ipso*	140.3	33.0732
4Ar, *ipso*	147.3	26.6303

a) GIAO/B3LYP/6-311++G(d,p)//B3LYP/6-31G(d).
b) Average of *ortho*-carbons.



Correlation of chemical shifts between calculated values of (2*S*,4*S*)-5aaa and observed values.



(2*S*,4*S*)-**5aaa**

δ values of ^{1}H NMR of 5aaa, which was suspected to be (2*S*,4*R*)-form.

The chemical shifts were measured in $CDCl_3$.

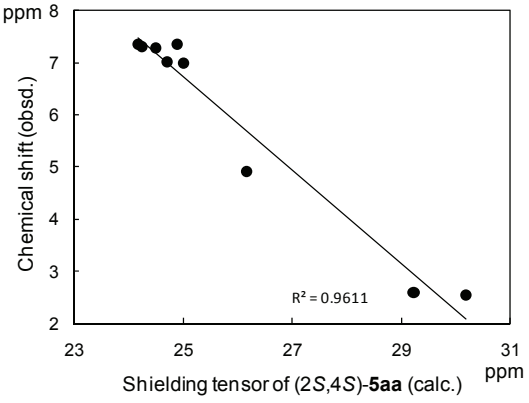
Calculated values of (2*S*,4*S*)-5aaa.

The structure was optimized at the B3LYP/6-31G(d). Shielding tensors were calculated at the GIAO/B3LYP/6-311++G(d,p).

^{1}H NMR

H	δ ^{1}H	Shielding tensor[a)]
2	4.91	26.1672
3eq	2.54	30.1872
3ax	2.59	29.2292
5	7.35	24.8937
6	7.01	25.0079
7	7.28	24.5019
8	6.99	24.7155
2Ar, *o*-	7.31	24.2474[b)]
4Ar, *o*-	7.35	24.1753[b)]

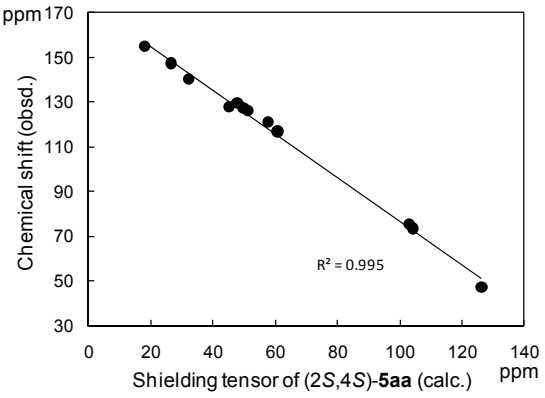
a) GIAO/B3LYP/6-311++G(d,p)//B3LYP/6-31G(d).
b) Average of *ortho*-protons.



^{13}C NMR

C	δ ^{13}C	Shielding tensor[a)]
2	75.6	103.0183
3	47.2	126.1932
4	73.5	104.1029
4a	127.2	49.7654
5	127.7	45.0343
6	121.1	57.6883
7	129.5	47.7891
8	116.8	60.6858
8a	154.8	18.0955
2Ar, *o*-	126.1	51.3416[b)]
4Ar, *o*-	127.0	51.1403[b)]
2Ar, *ipso*	140.3	32.2266
4Ar, *ipso*	147.3	26.5441

a) GIAO/B3LYP/6-311++G(d,p)//B3LYP/6-31G(d).
b) Average of *ortho*-carbons.



Cartesian Coordinates of 5aaa.

(2*S*,4*R*)-5aaa

Optimization was performed at the B3LYP/6-31G(d). Optimized structure was verified from the vibrational frequency calculations in which no imaginary frequency.

Total energy: -961.515200562 a.u.

C	1.851936	3.830164	−0.781381	H	−2.451586	−2.196572	−0.858683
C	0.612665	3.222271	−0.945584	C	−4.856920	0.595841	0.330746
C	0.370598	1.960670	−0.384411	H	−3.094483	1.830953	0.482541
C	1.371882	1.303673	0.350532	C	−5.363863	−0.662989	0.002796
C	2.614131	1.937081	0.499528	H	−4.879338	−2.648864	−0.687773
C	2.862622	3.187834	−0.057366	H	−5.529620	1.385868	0.654517
H	2.030826	4.807579	−1.221656	H	−6.430850	−0.857502	0.071409
H	−0.186234	3.699686	−1.504477	C	1.763464	−1.221997	0.267696
H	3.380695	1.428086	1.076520	C	2.015344	−2.412479	0.966766
H	3.832210	3.660059	0.071324	C	2.077234	−1.166682	−1.095405
O	−0.883846	1.450524	−0.585300	C	2.562464	−3.517200	0.316509
C	1.108808	−0.047532	1.006617	H	1.793715	−2.459778	2.027548
C	−0.423935	−0.250547	1.095263	C	2.620244	−2.276472	−1.748576
H	−0.647589	−1.278210	1.395793	H	1.912387	−0.249107	−1.651673
H	−0.831314	0.417101	1.867175	C	2.864582	−3.455249	−1.046002
C	−1.113796	0.074403	−0.231509	H	2.756749	−4.428327	0.876724
H	−0.679840	−0.554270	−1.021829	H	2.858671	−2.211246	−2.807001
C	−2.609498	−0.155789	−0.181649	H	3.291606	−4.316910	−1.552351
C	−3.125135	−1.413152	−0.517318	O	1.664076	−0.074569	2.331913
C	−3.487498	0.848457	0.241980	H	1.300069	0.692136	2.804180
C	−4.493317	−1.668360	−0.421763				

(2*S*,4*S*)-5aaa

Optimization was performed at the B3LYP/6-31G(d). Optimized structure was verified from the vibrational frequency calculations in which no imaginary frequency.

Total energy: -961.514398710 Hartree

C	−1.369547	3.959084	−0.404588	H	3.262639	−1.079305	2.132834
C	−0.120647	3.351116	−0.441973	C	4.667504	−0.571161	−1.439709
C	0.013291	2.004483	−0.079186	H	2.840207	0.505316	−1.834821
C	−1.109225	1.248941	0.297744	C	5.413492	−1.279209	−0.495246
C	−2.354717	1.889865	0.339041	H	5.479323	−2.005113	1.535367
C	−2.494772	3.230843	−0.003687	H	5.063373	−0.415556	−2.439996
H	−1.464868	5.005494	−0.682463	H	6.389955	−1.677848	−0.757176
H	0.770820	3.896194	−0.736331	C	−2.102368	−1.079656	0.104059
H	−3.225632	1.313228	0.636194	C	−2.237299	−1.256112	−1.281993
H	−3.471500	3.704136	0.035394	C	−3.029193	−1.703606	0.946236
O	1.282809	1.494158	−0.141789	C	−3.254299	−2.050471	−1.806528
C	−0.963194	−0.221632	0.677868	H	−1.552166	−0.754770	−1.960333
C	0.408013	−0.738891	0.186413	C	−4.050095	−2.501830	0.421894
H	0.613536	−1.714760	0.643730	H	−2.966160	−1.546181	2.017790
H	0.410685	−0.887990	−0.898354	C	−4.163749	−2.683259	−0.954738
C	1.513783	0.255843	0.548985	H	−3.339445	−2.172733	−2.883160
H	1.464001	0.451135	1.628743	H	−4.758918	−2.976215	1.095791
C	2.894127	−0.241248	0.181226	H	−4.956481	−3.303952	−1.363562
C	3.651525	−0.943683	1.125580	O	−0.970974	−0.250517	2.117997
C	3.414132	−0.057549	−1.105592	H	−0.825532	−1.174926	2.385054
C	4.901819	−1.464414	0.790134				

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