Organocatalytic Vinyl and Friedel–Crafts Alkylations with Trifluoroborate Salts

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Supporting Information

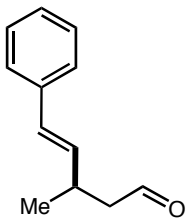
General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an ice-water bath for volatile compounds. Potassium tri(fluoro)borate salts were synthesized from commercially available boronic acids or esters using a modified Molander procedure.[3] Chromatographic purification of products was accomplished using force-flow chromatography on Silicycle silica gel according to the method of Still[4] and where noted, Iatrobeads 6RS-8060 was used in place of silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching and anisaldehyde stain.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz or 75 MHz), Mercury 400 (400 MHz or 100 MHz), or an Inova 500 (500MHz and 125 MHz) as noted, and are internally referenced to residual protio solvent signals (note: $CDCl_3$

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988.
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.
(3) (a) Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393. (b) Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867. Note: The cited procedures were found to be more efficient when reaction slurries were sonicated.
(4) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

referenced at δ 7.24). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the California Institute of Technology Mass Spectral Facility and the Princeton Mass Spectroscopy Facility. Gas liquid chromatography (GLC) was performed on Hewlett-Packard 6850 and 6890 Series gas chromatographs equipped with split-mode capillary injection system and flame ionization detectors using Bodman Chiraldex Γ-TA (30 m x 0.25 mm) column. Supercritical fluid chromatography (SFC) was performed on a Berger Minigram equipped with a diode array UV detector (λ = 214–258 nm) using a chiral column (25 cm) and guard column (5 cm) as noted for each compound.

General procedure: To a plastic vial (Wheaton HDPE) is added HF (48 wt%, 1.0 eq) followed by 1,2-dimethoxyethane (DME) (1M, relative to aldehyde) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*,5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (0.2 eq) and HCl (0.2 eq) and is then cooled to temperature (as noted). The reaction is started with the addition of the aldehyde (3.0 eq) to the DME solution immediately followed by the addition of the trifluoroborate salt (1.0 eq). The reaction is stirred at temperature and is often worked-up by an aqueous quench, which is then partitioned with dichloromethane, chloroform or ether, as noted. The combined organic layers are dried over Na_2SO_4 and concentrated *in vacuo*. The crude oil is then purified by column chromatography (conditions noted) to yield the desired product.

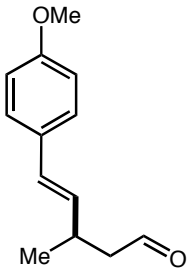


(*R*, *E*)-3-methyl-5-phenylpent-4-enal (Table 2, entry 1). Prepared according to the general procedure using crotonaldehyde and potassium *trans*-styryltrifluoroborate. To a plastic vial is added HF (48 wt%, 7.00 mg, 0.167 mmol) followed by DME (500 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (12.5 mg, 0.033 mmol) and HCl (4N in dioxane, 8.30 μL, 0.033 mmol) and is then cooled to –20 °C. Crotonaldehyde (58.0 μL, 0.50 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (37.3 mg, 0.167 mmol). The reaction is stirred at –20 °C for 24 hours and quenched with 1M HCl (1.0 mL) and is stirred with chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with CH_2Cl_2 (2 x 2.0 mL), dried over Na_2SO_4, filtered through celite (ether wash) and concentrated *in vacuo*. Purification by chromatography (silica gel, 20% ether in pentanes) yields the title compound as clear oil (27.9 mg, 96% yield, 87% ee). IR (film) 2962, 1718, 965.0, 747.0, 692.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, 1H, J = 2.1 Hz, C**H**O), 7.34-7.19 (m, 5H, aryl **H**), 6.42 (dd, 1H, J = 0.6, 15.9 Hz, C**H**=CH), 6.14 (dd, 1H, J = 7.5, 15.9 Hz, CH=C**H**), 2.94 (m, 1H, C**H**CH_3), 2.50 (ddd, 2H, J = 2.1, 6.9, 16.5 Hz, C$\mathbf{H}_2$), 1.16 (d, 3H, C$\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.33, 134.16, 129.32, 128.76, 127.50, 126.33, 50.60, 32.08, 20.65; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{12}H_{14}O$) requires *m*/*z* 174.1045, found *m*/*z* 174.1051; $[\alpha]_D$= –49.1 (c = 0.45, $CHCl_3$). The enantiomeric excess was determined on the alcohol product, which was prepared by a $NaBH_4$ reduction, by SFC analysis using a Chiralcel OD-H column (5% to 35% IPA, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 4.75 min, (*R*) isomer t_r = 5.35 min.

Determination of the absolute stereochemistry of (*R*,*E*)-3-methyl-5-phenylpent-4-enal by correlation to methyl [1-((*E*)-sytryl)ethyl]acetate.[5] Aldehyde **4**

(5) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723 (reported $[\alpha]_D$= –49.2 (c = 1.3, CCl_4) for a product that was 79% ee).

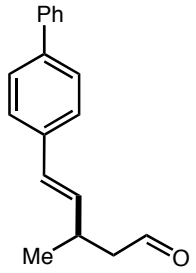
(22.0 mg, 0.126 mmol) was subjected to oxidation[6] using Oxone® (77.6 mg, 0.126 mmol) in DMF (1.26 mL) to quantitatively produce the corresponding acid (24.0 mg, 0.126 mmol). Subsequently, the acid was esterified using TMS diazomethane (2M in hexane, 130 μL) in a solution of 25% methanol in benzene (1.0 mL) at room temperature. Purification was accomplished via chromatography (prep TLC, 20% ether in pentanes) to yield (*R*, *E*)-methyl 3-methyl-5-phenylpent-4-enoate in 34% isolated yield. ^{1}H NMR and ^{13}C NMR (500 MHz, CCl_4 with TMS internal reference) spectral data matched literature values.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.18 (m, 5H, aryl **H**), 6.38 (d, 1H, J = 15.6 Hz, CH=C**H**), 6.12 (dd, 1H, J = 7.6, 15.9 Hz, C**H**=CH), 6.14 (dd, 1H, J = 7.5, 16.0 Hz, CH=C**H**), 3.65 (s, 3H, OC**H**$_3$), 2.84 (septet, 1H, J = 7.2 Hz, C**H**CH$_2$), 2.39 (ddd, 2H, J = 7.2, 14.4, 21.6 Hz, C**H**$_2$) 1.13 (d, 3H, J = 6.4 Hz, C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 134.4, 129.1, 128.7, 127.4, 126.3, 51.74, 41.73, 34.22, 20.42; $[\alpha]_D$= –57.8 (c = 0.502, CCl_4).



(*R*,*E*)-5-(4-methoxyphenyl)-3-methylpent-4-enal (Table 2, entry 2). Prepared according to the general procedure using crotonaldehyde and potassium *trans*-2-(4-methoxyphenyl)trifluoroborate. To a plastic vial is added HF (48 wt%, 3.5 mg, 0.083 mmol) followed by DME (250 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (6.25 mg, 0.017 mmol) and HCl (4N in dioxane, 4.2 μL, 0.017 mmol) and is then cooled to –40 °C. Crotonaldehyde (21.0 μL, 0.25 mmol) is charged to the DME solution followed by the addition of potassium *trans*-2-(4-methoxyphenyl)trifluoroborate (20.0 mg, 0.083 mmol). The reaction is stirred at –

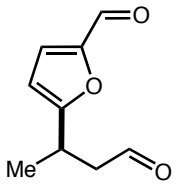
(6) Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, *5*, 1031.

40 °C for 20 hours and quenched with 1M HCl (1.0 mL) and is stirred with chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with CH_2Cl_2 (2 x 2.0 mL), dried over Na_2SO_4, filtered through celite (ether wash) and concentrated *in vacuo*. Purification by chromatography (prep TLC, 10% ether in pentanes) yields the title compound as clear oil (13.9 mg, 70% yield, 88% ee). IR (film) 2954, 1720, 1605, 1510, 1243, 1174, 1030, 964.8, 804.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, 1H, J = 2.1 Hz, C**H**O), 7.27 (d, 2H, J = 8.4 Hz, aryl **H**), 6.84 (d, 2H, J = 9.0 Hz, aryl **H**), 6.36 (d, 1H, J = 15.9 Hz, CH=C**H**), 6.01 (dd, 1H, J = 7.5, 15.9 Hz, C**H**=CH), 3.80 (s, 3H, OC**H**$_3$), 2.93 (m, 1H, C**H**CH_2), 2.50 (ddd, 2H, J = 2.1, 7.2, 16.2 Hz, C**H**$_2$), 1.17 (d, 3H, J = 6.6 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.54, 159.17, 132.01, 130.11, 128.68, 127.44, 114.15, 55.51, 50.73, 32.11, 20.79; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{13}H_{16}O_2$) requires *m/z* 204.1150, found *m/z* 204.1150; $[\alpha]_D$= –44.0 (c = 1.26, $CHCl_3$). The enantiomeric excess was determined by SFC analysis using a Chiralpak AS-H column (5% to 10% MeCN, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 4.03 min, (*R*) isomer t_r = 4.68 min.



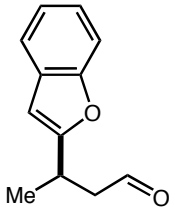
(*R*,*E*)-5-(4-biphenyl)-3-methylpent-4-enal (**Table 2, entry 3**)**.** Prepared according to the general procedure using crotonaldehyde and potassium *trans*-2-(biphenyl)trifluoroborate. To a plastic vial is added HF (48 wt%, 6.3 mg, 0.15 mmol) followed by DME (450 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (11.3 mg, 0.03 mmol) and HCl (4N in dioxane, 7.5 μL, 0.03 mmol) and is then cooled to –40 °C. Crotonaldehyde (37.5 μL, 0.45 mmol) is charged to the DME solution followed by the addition of potassium *trans*-2-(4-

biphenyl)trifluoroborate (42.9 mg, 0.15 mmol). The reaction is stirred at –40 °C for 24 hours and was directly subjected to purification by chromatography (Iatrobeads, 1% acetone and 5% ether in pentanes) to yield the title compound as light, yellow solid (20.6 mg, 91% yield, 95% ee). IR (film) 2924, 2854, 1724, 972.3, 761.7, 694.4 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, 1H, J = 2.0 Hz, C**H**O), 7.58-7.52 (m, 4H, aryl **H**), 7.43-7.39 (m, 4H, aryl **H**), 7.33-7.24 (m, 1H, aryl **H**), 6.44 (d, 1H, J = 16.0 Hz, CH=C**H**), 6.19 (dd, 1H, J = 7.5, 16.0 Hz, C**H**=CH), 2.97 (septet, 2H, J = 7.0 Hz, C**H**CH_2), 2.52 (ddd, 2H, J = 2.0, 7.0, 16.5 Hz, C$\mathbf{H}_2$), 1.18 (d, 3H, J = 7.0 Hz, C$\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.21, 140.95, 140.31, 136.41, 134.34, 128.99, 128.93, 127.46, 127.12, 126.77, 50.65, 32.15, 29.92, 20.67; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{13}H_{16}O_2$) requires *m*/*z* 250.1358, found *m*/*z* 250.1349; $[\alpha]_D$= –13.6 (c = 1.29, $CHCl_3$). The enantiomeric excess was determined by SFC analysis using a Chiralcel OJ-H column (5% to 15% MeCN, 2%/min gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 2.97 min, (*R*) isomer t_r = 3.23 min.



5-((*R*)-1-formylpropan-2-yl)furan-2-carbaldehyde (Table 2, entry 4). Prepared according to the general procedure using crotonaldehyde and potassium 2-(5-formylfuran-2-yl) trifluoroborate. To a plastic vial is added HF (48 wt%, 3.5 mg, 0.083 mmol) followed by DME (250 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (6.25 mg, 0.017 mmol) and HCl (4N in dioxane, 4.2 μL, 0.017 mmol) and is then cooled to –20 °C. Crotonaldehyde (21.0 μL, 0.25 mmol) is charged to the DME solution followed by the addition of potassium 2-(5-formylfuran-2-yl) trifluoroborate (20.0 mg, 0.083 mmol). The reaction is stirred at –20 °C for 20 hours and quenched with 1M HCl (1.0 mL) and is stirred with ether (1.5 mL)

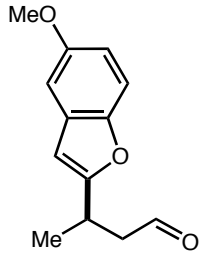
for 30 minutes. The organic layer is extracted with ether (2 x 2.0 mL), dried over Na_2SO_4, filtered through celite (ether wash) and concentrated *in vacuo* (ice-water bath). Purification by chromatography (silica gel, 10% ether in pentanes) yields the title compound as a clear, light yellow oil (11.7 mg, 85% yield, 95% ee). IR (film) 1719, 1670, 1513, 1020 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, 1H, J = 1.5 Hz, C**H**O), 9.51 (s, 1H, furyl C**H**O), 7.17 (d, 1H, J = 3.6 Hz, aryl **H**), 6.30 (dd, 1H, J = 0.9, 3.6, aryl **H**), 3.53 (m, 1H, C**H**CH_3), 2.81 (ddd, 2H, J = 1.5, 7.2, 17.7 Hz, C**H**$_2$), 1.35 (d, 3H, J = 7.2 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.53, 177.45, 152.56, 123.72, 108.38, 49.08, 28.55, 19.07; HRMS (EI+) exact mass calculated for [$M^{+\bullet}$] ($C_9H_{10}O_3$) requires *m/z* 166.0630, found *m/z* 166.0629; $[\alpha]_D$= –1.09 (c = 1.17, $CHCl_3$). The enantiomeric excess was determined by SFC analysis using a Chiralpak AS-H column (5% to 10% MeCN, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 2.73 min, (*R*) isomer t_r = 3.63 min.



***(R)*-3-(benzofuran-2-yl)butanal (Table 2, entry 5).** Prepared according to the general procedure using crotonaldehyde and potassium 2-benzofuranyltrifluoroborate.[7] To a plastic vial is added HF (48 wt%, 6.25 mg, 0.167 mmol) followed by DME (450 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (11.3 mg, 0.033 mmol) and HCl (4N in dioxane, 7.50 μL, 0.033 mmol) and is then cooled to –20 °C. Crotonaldehyde (37.3 μL, 0.45 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (33.6 mg, 0.150 mmol). The reaction is stirred at –20 °C for

(7) Murphy, J. M.; Tzschucke, C. C.; Hartwig, J. F. *Org. Lett.* **2007**, *9*, 757.

23 hours and then flushed though a silica gel plug (wash with 30% ether in pentanes). Concentration *in vacuo* (ice-water bath) provided the title compound as clear oil (25.5 mg, 90% yield, 97% ee). IR (film) 1722, 1454, 1253, 1168, 750.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H, C**H**O), 7.54-7.43 (m, 2H, aryl **H**), 7.29-7.19 (m, 2H, aryl **H**), 6.45 (t, 1H, J = 0.9 Hz, 3'-benzofuran **H**), 3.61 (m, 1H, C**H**CH_3), 2.85 (dd, 2H, J = 1.80, 17.1 Hz, C$\mathbf{H}_2$), 1.45 (d, 3H, J = 6.60 Hz, C$\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.06, 161.47, 154.81, 128.68, 123.81, 122.81, 120.75, 111.07, 101.58, 49.06, 28.38, 19.04; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{12}H_{12}O_2$) requires *m/z* 188.0837, found *m/z* 188.0844; $[\alpha]_D$= –17.1 (c = 1.22, $CHCl_3$). The enantiomeric excess was determined on the alcohol product, which was prepared by a $NaBH_4$ reduction, by SFC analysis using a Chiralpak AS-H column (5% to 50% MeOH, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 2.17 min, (*R*) isomer t_r = 2.40 min.



(*R*)-3-(5-methoxybenzofuran-2-yl)butanal (Table 2, entry 6). Prepared according to the general procedure using crotonaldehyde and potassium 2-(5-methoxybenzofuranly)trifluoroborate. To a plastic vial is added HF (48 wt%, 6.25 mg, 0.15 mmol) followed by DME (450 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (10.9 mg, 0.03 mmol) and HCl (4N in dioxane, 7.5 μL, 0.03 mmol) and is then cooled to –20 °C. Crotonaldehyde (37.5 μL, 0.45 mmol) is charged to the DME solution followed by the addition of potassium 2-(5-methoxybenzofuranyl)trifluoroborate (42.4 mg, 0.15 mmol). The reaction is stirred at –20 °C for 24 hours and quenched with 1M HCl (1.0 mL) and is stirred with chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with chloroform (2 x 2.0 mL),

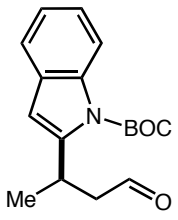
dried over Na_2SO_4, filtered through celite (ether wash) and concentrated *in vacuo*. Purification by chromatography (silica gel, 15% ether in pentanes) yields the title compound as clear oil (30.7 mg, 94% yield, 92% ee). IR (film) 1724, 1475, 1205, 1030 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 9.78 (t, 1H, J = 1.5 Hz, C**H**O), 7.29 (d, 1H, J = 8.4 Hz, aryl **H**), 6.98 (d, 1H, J = 2.4 Hz, aryl **H**), 6.81 (dd, 1H, J = 2.4, 9.0 Hz, aryl **H**), 6.38 (d, 1H, J = 0.9 Hz), 3.01 (s, 3H, OC**H**$_3$), 3.54 (m, 1H, C**H**CH_3), 2.79 (ddd, 2H, J = 1.5, 6.6, 17.4 Hz, C**H**$_2$), 1.39 (d, 3H, J = 0.9 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.32, 163.07, 156.46, 150.05, 129.72, 112.37, 111.60, 103.72, 101.93, 56.29, 49.30, 28.78, 19.18; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{13}H_{14}O_3$) requires *m/z* 218.0943, found *m/z* 218.0944; $[\alpha]_D$= –8.51 (c = 1.29, $CHCl_3$). The enantiomeric excess was determined by SFC using a Chiracel OJ-H column (5% to 10% MeCN, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 5.17 min, (*R*) isomer t_r = 5.61 min.

Determination of the absolute stereochemistry of (*R*)-3-(5-methoxybenzofuran-2-yl)butanal by correlation to (*R*)-3-(5-methoxybenzofuran-2-yl)butan-1-ol.[8] To a stirring solution of the aldehyde (25 mg, 0.11 mmol) in CH_2Cl_2(2.0 mL) and ethanol (20 μL) at 0 °C was added $NaBH_4$ (13 mg, 0.34 mmol). The reaction was quenched after 5 minutes by a saturated solution of Rochelle's salt (2.0 mL). The organic was extracted with ether (2 x 3.0 mL) and concentrated *in vacuo* to yield a clear oil (quantitative yield) with spectroscopic data matching literature values. IR (film) 3306 (br), 2922, 1458, 1201, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, 1H, J = 8.7 Hz, aryl **H**), 6.94 (d, 1H, J = 2.7 Hz, aryl **H**), 6.79 (dd, 1H, J = 2.7, 8.7 Hz, aryl **H**), 6.33 (s, 1H, aryl **H**), 3.81 (s, 3H, OC**H**$_3$), 3.69 (m, 2H, C**H**$_2CH_2$), 3.11 (m, 1H, C**H**CH_3), 2.06-1.95 (m, 1H, C**H**$_2$OH), 1.91-1.79 (m, 1H, C**H**$_2$OH), 1.57 (br s, 1H, O**H**), 1.34 (d, 3H, J = 7.2 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.11, 155.98, 149.73, 129.48, 111.81, 111.38, 103.45, 101.40, 60.97, 56.16, 38.53, 30.56, 19.38; HRMS (EI+) exact mass

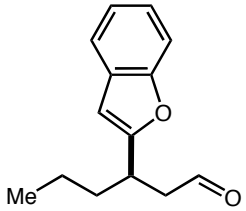
(8) Hughes, C. C.; Trauner, D. *Tetrahedron*, **2004**, *60*, 9675 (reported $[\alpha]_D$= –33.0 (c = 1.00, $CHCl_3$) for a product that was 91% ee).

calculated for [M+1] ($C_{13}H_{16}O_3$) requires *m*/*z* 220.1100, found *m*/*z* 220.1089; $[\alpha]_D$= –46.2 (c = 0.83, $CHCl_3$).[6] The enantiomeric excess was determined by SFC analysis using a Chiralcel OJ-H column (5% to 10% methanol, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 5.71 min, (*R*) isomer t_r = 6.56 min.

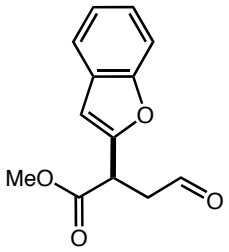
Determination of the absolute stereochemistry of (*R*)-3-(5-methoxybenzofuran-2-yl)butanal by obtaining a crystal structure of (*R*)-3-(5-methoxybenzofuran-2-yl)butyl 4-bromobenzoate (*vide S 17*). Esterification of (*R*)-3-(5-methoxybenzofuran-2-yl)butan-1-ol (22 mg, 0.10 mmol) proceeded in a solution of CH_2Cl_2 (1.0 mL) to which NEt_3 (21 μL, 0.15 mmol) and DMAP (1.2 mg, 0.01 mmol) were added. The solution was then cooled to 0 °C and *p*-Br benzoyl chloride (24 mg, 0.11 mmol) was added. The ice bath was removed and after 30 minutes at room temperature, 0.5 M HCl (2.0 mL) was added to quench the reaction. The organic layer was dried with Na_2SO_4, triturated diethyl ether, filtered (to remove salt impurities) and concentrated *in vacuo* to yield a yellow solid (34 mg, 85% yield). IR (film) 2929, 1719, 1591, 1477, 1271, 1205, 1102, 1012, 756.3 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4 Hz, aryl **H**), 7.47 (d, 2H, J = 8.4 Hz, aryl **H**), 7.22 (s, 1H, aryl **H**), 6.89 (d, 1H, J = 2.8 Hz, aryl **H**), 6.77 (dd, 1H, J = 2.8, 9.2 Hz, aryl **H**), 6.32 (s, 1H, aryl **H**), 4.33 (m, 2H, C**H**$_2$OC(O)), 3.78 (s, 3H, OC**H**$_3$), 3.11 (m, 1H, CH_3C**H**), 2.25-2.01 (m, 2H, C**H**$_2$), 1.37 (t, 3H, J = 7.2 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.95, 163.18, 155.97, 149.75, 131.76, 131.17, 129.40, 129.18, 128.11, 111.85, 111.32, 103.42, 101.62, 63.41, 56.10, 34.32m 31.20, 19.23; HRMS (EI+) exact mass calculated for [$M^{+\bullet}$] ($C_{20}H_{19}O_4Br$) requires *m*/*z* 402.0467, found *m*/*z* 402.0481; $[\alpha]_D$= –52.7 (c = 1.02, $CHCl_3$).



***tert*-butyl 2-((*R*)-1-formylpropan-2-yl)-1*H*-indole-1-carboxylate (Table 2, entry 7).** Prepared according to the general procedure using crotonaldehyde and potassium 2-(*tert*-butyl 1*H*-indole-1-carboxylate)trifluoroborate. To a plastic vial is added HF (48 wt%, 3.5 mg, 0.083 mmol) followed by DME (250 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*,5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (12.4 mg, 0.033 mmol) and HCl (4N in dioxane, 8.3 μL, 0.033 mmol) and is then cooled to –20 °C. Crotonaldehyde (21.0 μL, 0.25 mmol) is charged to the DME solution followed by the addition of potassium 2-(*tert*-butyl 1*H*-indole-1-carboxylate)trifluoroborate (26.9 mg, 0.083 mmol). The reaction is stirred at –20 °C for 24 hours and quenched with 1M HCl (1.0 mL) and is stirred with chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with chloroform (2 x 2.0 mL), dried over Na_2SO_4, filtered through celite (ether wash) and concentrated *in vacuo*. Purification by chromatography (silica gel, 10% ether in pentanes) yields the title compound as light yellow oil (19.0 mg, 79% yield, 91% ee). IR (film) 1728, 1455, 1370, 1327, 1157, 747.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, 1H, J = 1.8 Hz, C**H**O), 8.03 (dt, 1H, J = 0.6, 7.8 Hz, aryl **H**), 7.45 (m, 1H, aryl **H**), 7.26-7.15 (m, 2H, aryl **H**), 6.40 (t, 1H, J = 0.9, aryl **H**), 4.24 (m, 1H, C**H**CH_3), 2.57 (dd, 1H, C**H**$_2$), 2.89 (1H, dd, J = 1.8, 5.4 Hz, C**H**$_2$), 1.37 (t, 3H, J = 6.9 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.95, 150.69, 145.80, 129.22, 123.96, 123.00, 120.28, 115.94, 106.42, 84.47, 50.80, 28.45, 28.02, 21.06; HRMS (EI+) exact mass calculated for [$M^{+\bullet}$] ($C_{17}H_{21}NO_3$) requires *m*/*z* 287.1521, found *m*/*z* 287.1533; $[\alpha]_D$= –6.1 (c = 0.6, $CHCl_3$). The enantiomeric excess was determined by SFC analysis using a Chiralcel OD-H column (5% to 50% MeCN, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 2.51 min, (*R*) isomer t_r = 2.97 min.

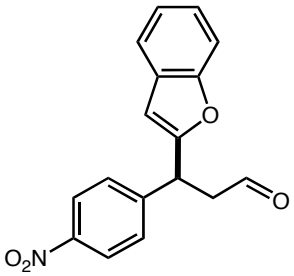


(*R*)-3-(benzofuran-2-yl) hexanal (Table 3, entry 2). Prepared according to the general procedure using hexenal and potassium 2-benzofuranyltrifluoroborate. To a plastic vial is added HF (48 wt%, 7.00 mg, 0.167 mmol) followed by DME (500 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (12.5 mg, 0.033 mmol) and HCl (4N in dioxane, 8.30 μL, 0.033 mmol) and is then cooled to 4 °C. Hexenal (58.0 μL, 0.50 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (37.3 mg, 0.167 mmol). The reaction is stirred at 4 °C for 12 hours and quenched with a saturated solution of Rochelle's salt (1.0 mL) and is partitioned with dichloromethane (2 x 1.5 mL). The combined organic layers are dried over Na_2SO_4, concentrated *in vacuo* and purified by chromatography (silica gel, 10% ether in pentanes) to yield the title compound as clear oil (34.9 mg, 97% yield, 93% ee). IR (film) 2959, 2932, 2873, 1725, 1456, 1253, 751.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (s, 1H, C**H**O), 7.49-7.38 (m, 2H, aryl **H**), 7.24-7.14 (m, 2H, aryl **H**), 6.42 (s, 1H, 3'-benzofuran **H**), 3.48-3.39 (m, 1H, $CH_2C\mathbf{H}CH_2$), 2.80 (ddd, 2H, J = 1.8, 7.5, 17.1 Hz, α-C$\mathbf{H}_2$), 1.85-1.58 (m, 2H, C$\mathbf{H}_2$), 1.37-1.24 (m, 2H, C$\mathbf{H}_2$), 0.89 (t, 3H, J = 6.9 Hz, C$\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.31, 147.98, 132.55, 123.73, 122.82, 120.73, 111.12, 102.85, 67.13, 47.70, 35.97, 33.69, 20.48, 14.07; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{14}H_{16}O_2$) requires *m/z* 216.1150, found *m/z* 216.1142; $[\alpha]_D$= –7.3 (c = 1.05, $CHCl_3$). The enantiomeric excess was determined on the alcohol product, which was prepared by a $NaBH_4$ reduction, and analyzed by SFC using a Chiralpak AS-H column (5% to 25% IPA, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 3.18 min, (*R*) isomer t_r = 3.36 min.



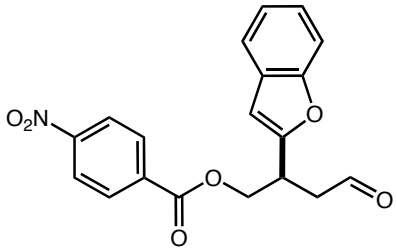
(*R*)-methyl 2-(benzofuran-2-yl)-3-formylpropanoate (Table 3, entry 3). Prepared according to the general procedure using (*E*)-methyl 3-formylacrylate and potassium 2-benzofuranyltrifluoroborate. To a plastic vial is added HF (48 wt%, 7.00 mg, 0.167 mmol) followed by DME (500 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (12.5 mg, 0.033 mmol) and HCl (4N in dioxane, 8.30 μL, 0.033 mmol) and is then cooled to –20 °C. (*E*)-Methyl 3-formylacrylate (58.0 μL, 0.50 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (37.3 mg, 0.167 mmol). The reaction is stirred at –20 °C for 18 hours and quenched with 1M HCl (1.0 mL) and is stirred in chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with chloroform (2 x 2.0 mL), dried over Na_2SO_4, concentrated *in vacuo* and purified by chromatography (silica gel, 25% ether in pentanes) to yield the title compound as clear oil (36.0 mg, 93% yield, 88% ee). IR (film) 1736, 1720, 1453, 1168, 750.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H, C**H**O), 7.52-7.40 (m, 2H, aryl **H**), 7.28-7.17 (m, 2H, aryl **H**), 6.58 (s, 1H, 3'-benzofuran **H**), 4.42 (dd, 1H, J = 5.1, 9.0 Hz, C**H**CH_2), 3.73 (s, 3H, OC**H**$_3$), 3.45 (ddd, 1H, J = 0.6, 9.0, 18.6 Hz, C**H**$_2$), 3.02 (ddd, 1H, J = 0.6, 5.1, 18.6 Hz, C**H**$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.82, 191.57, 147.97, 132.45, 128.33, 124.52, 123.18, 121.14, 111.42, 104.62, 53.120, 44.37, 39.39; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{13}H_{12}O_4$) requires *m*/*z* 232.0736, found *m*/*z* 232.0728; $[\alpha]_D$= –95.0 (c = 0.8, $CHCl_3$). The enantiomeric excess was determined on the diol product, which is prepared by reduction of the ester and aldehyde (21.5 mg, 0.093 mmol) in THF (1mL) using $LiAlH_4$ (1M in THF, 200 μL, 0.2 mmol) at –60 °C. SFC analysis was performed

using a Chiralpak AD-H column (5% to 15% methanol, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 10.23 min, (*R*) isomer t_r = 10.80 min.



(*S*)-3-(Benzofuran-2-yl)-3-(4-nitrophenyl)propanal (Table 3, entry 5). Prepared according to the general procedure using *p*-nitrocinnamaldehyde and potassium 2-benzofuranyltrifluoroborate. To a plastic vial is added HF (48 wt%, 3.50 mg, 0.083 mmol) followed by DME (250 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*, 5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (6.26 mg, 0.017 mmol) and HCl (4N in dioxane, 4.20 μL, 0.017 mmol). *p*-Nitrocinnamaldehye (44.3 mg, 0.250 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (18.7 mg, 0.083 mmol). The reaction is stirred at ambient temperature for 24 hours and quenched with a saturated solution of Rochelle's salt (1.0 mL) and is then partitioned with dichloromethane (2 x 1.5 mL). The combined organic layers are dried over Na_2SO_4, concentrated *in vacuo* and purified by chromatography (prep TLC, 25% dichloromethane in benzene) to yield the title compound as a light yellow oil (16.9 mg, 69% yield, 92% ee). IR (film) 1724, 1519, 1454, 1347, 1254, 752.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (s, 1H, C**H**O), 8.19 (d, 2H, J = 8.4 Hz, aryl **H**), 7.53-7.39 (m, 4H, aryl **H**), 7.28-7.18 (m, 2H, aryl **H**), 6.50 (s, 1H, 3'-benzofuran **H**), 4.90 (t, 1H, J = 7.2 Hz, CH_2C**H**), 3.32 (dd, 2H, J = 6.9, 17.7 Hz, C$\mathbf{H}_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.65, 157.20, 147.99, 129.13, 124.55, 124.30, 123.25, 121.11, 111.32, 104.11, 47.82, 39.16; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{17}H_{13}NO_4$) requires *m*/*z* 295.0845, found *m*/*z* 295.0853; $[\alpha]_D$= 48.7 (c = 1.0, $CHCl_3$). The enantiomeric

excess was determined on the alcohol product, which was prepared by a $NaBH_4$ reduction, and analyzed by SFC using a Chiralpak AS-H column (5% to 25% methanol, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 6.93 min, (*R*) isomer t_r = 7.22 min.



(*S*)-2-(benzofuran-2-yl)-3-formylpropyl 4-nitrobenzoate (Table 3, entry 4). Prepared according to the general procedure using (*E*)-3-formylallyl 4-nitrobenzoate and potassium 2-benzofuranyltrifluoroborate. To a plastic vial is added HF (48 wt%, 2.1 mg, 0.05 mmol) followed by DME (150 μL) and a magnetic stir bar. The catalyst and acid co-catalyst are charged to the vial with the addition of (2*S*,5*S*)-2-*tert*-butyl-5-((1-benzyl-1*H*-indol-3-yl)methyl)-3-methylimidazolidin-4-one (7.51 mg, 0.02 mmol) and HCl (4N in dioxane, 5.0 μL, 0.02 mmol). (*E*)-3-Formylallyl 4-nitrobenzoate (35.3 mg, 0.15 mmol) is charged to the DME solution followed by the addition of potassium 2-benzofuranyltrifluoroborate (11.2 mg, 0.05 mmol). The reaction is stirred at –20 °C for 23 hours and quenched with 1M HCl (1.0 mL) and is stirred with chloroform (1.5 mL) for 30 minutes. The organic layer is extracted with chloroform (2 x 2.0 mL), dried over Na_2SO_4, concentrated *in vacuo* and purified by chromatography (prep TLC, 40% dichloromethane in benzene) to yield the title compound as a yellow oil (13.3 mg, 75% yield, 89% ee). IR (film) 1725, 1526, 1348, 1272, 1120, 1103, 752.6, 718.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.84 (t, 1H, J = 1.2 Hz, C**H**O), 8.19 (dd, 4H, J = 2.1, 39.9 Hz, aryl **H**), 7.45 (dd, 2H, J = 7.5, 27.6 Hz, aryl **H**), 7.28-7.17 (m, 2H, aryl **H**), 6.57 (s, 1H, 3'-benzofuran **H**), 4.66 (dd, 2H, J = 6.3, 10.8 Hz, C**H**$_2$OBz), 4.07-3.98 (m, 1H, C**H**CH_2), 3.04 (ddd, 2H, J = 1.2, 6.6, 18.0 Hz, CHC**H**$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.20, 164.53, 156.03, 135.21, 130.98, 128.29, 124.44, 123.85 121.08, 111.25, 104.05, 66.47,

44.23, 33.31; HRMS (EI+) exact mass calculated for $[M]^{+\bullet}$ ($C_{19}H_{15}NO_6$) requires *m*/*z* 353.0899, found *m*/*z* 353.0885; $[\alpha]_D$= +6.29 (c = 1.06, $CHCl_3$). The enantiomeric excess was determined on the alcohol product, which was prepared by a $NaBH_4$ reduction, and analyzed by SFC using a Chiralpak AD-H column (30% to 50% methanol, linear gradient, 100 bar, 35 °C oven, flow = 4.0 mL/min); (*S*) isomer t_r = 5.78 min, (*R*) isomer t_r = 6.34 min.

Crystal Structure Analysis of:

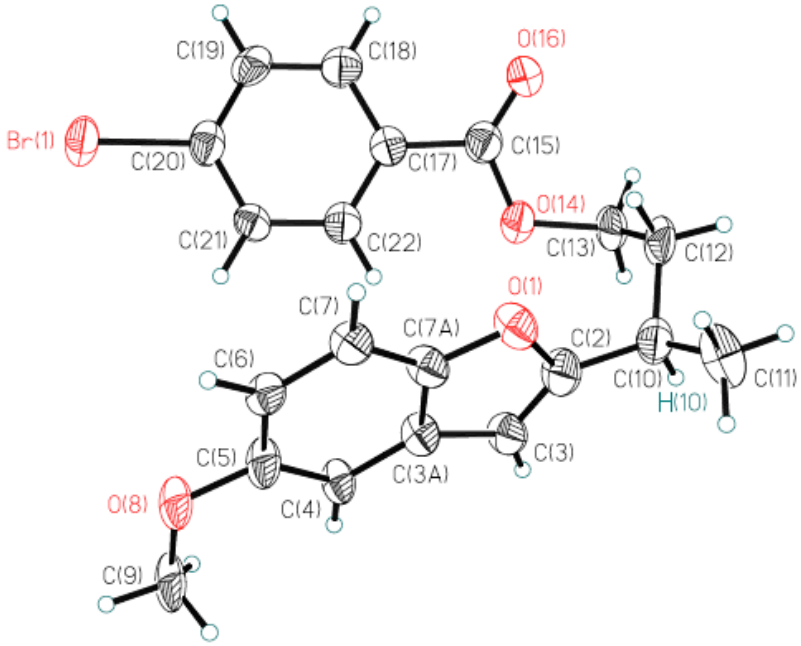
4-Bromobenzoic Acid (*R*)-3-(5-Methoxybenzofuran-2-yl)butyl Ester (DWCM003)

For Investigator: Sandra Lee

Advisor: David W. C. MacMillan

By Douglas M. Ho

Contents



4-Bromobenzoic Acid (*R*)-3-(5-Methoxybenzofuran-2-yl)butyl Ester (DWCM003)

Experimental

Evaporation of a carbon disulfide solution of the compound yielded a yellow oil. Upon standing at room temperature for a number of hours, the oil crystallized into colorless bundles of intergrown plates. A fragment approximately 0.03 mm x 0.08 mm x 0.25 mm in size was cut from one of the plates, mounted on a glass fiber with silicone grease and transferred to a Nonius KappaCCD diffractometer equipped with an MSC X-stream cryosystem and Mo Kα radiation (λ = 0.71073 Å). Fourteen hundred and forty frames of data were collected at 200(2) K with an ω oscillation range of 0.5°/frame, and an exposure time of 60 s/deg.[9] A total of 7927 reflections (θ_{max} = 22.46°) were indexed, integrated and corrected for Lorentz and polarization effects using *DENZO-SMN* and *SCALEPACK*.[10] The crystal did not exhibit any usable data beyond that θ_{max} value. Therefore, a standard 0.76961 Å (θ_{max} = 27.5°) data set was not warranted or pursued. Gaussian and ψ-scan absorption corrected data sets were also examined but did not lead to improved refinement results and were therefore not pursued further as well. Data reduction yielded 2296 unique reflections (R_{int} = 0.066) of which 1735 had $I > 2\sigma(I)$. Postrefinement of the unit cell parameters gave a = 5.8677(3) Å, b = 7.3771(5) Å, c = 20.8583(14) Å, α = 90°, β = 97.998(4)°, γ = 90°, and V = 894.1(1) Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in one of two possible monoclinic space groups, i.e., $P2_1$ or $P2_1/m$. The observed mean $|E^2-1|$ value was 0.948 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively). Nevertheless, the chiral space group $P2_1$ (No. 4) was selected since the compound was indicated to be optically pure.

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using *SHELXTL*.[11] The asymmetric unit was found to contain only a single molecule of 4-bromobenzoic acid (*R*)-3-(5-methoxybenzofuran-2-yl)butyl ester. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The

(9) *COLLECT.;* Nonius BV: Delft, The Netherlands, 1998.
(10) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; MacMomolecular Crystallography, Part A; Academic Press: New York, 1997; pp 307-326.
(11) Sheldrick, G. M. *SHELXTL*, version 5.04; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective carbons. The sample was also found to be twinned with the volume fractions of the twin components being 0.9774(6) and 0.0226(6). Convergence of this single molecule model gave $wR(F^2) = 0.1141$ for 2296 unique reflections of which 1735 had $I > 2\sigma(I)$, 227 parameters and 199 restraints. This model, however, gave atoms exhibiting large thermal vibrations, and was therefore abandoned in favor of a two-site whole molecule disorder model. Initial occupancy refinement tests yielded site occupancy factors of 0.45(4) and 0.55(4) for the atoms of the two sites indicating that each site was half-occupied within the errors of the experiment. A whole molecule disorder model consisting of two exactly half-occupied molecules was therefore selected. Distance, similarity and common plane restraints were employed due to the close proximity of the two half molecules. The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + 0.1541P]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to $R(F) = 0.0483$, $wR(F^2) = 0.0910$, and $S = 1.224$ for 1735 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0741$, $wR(F^2) = 0.1017$, and $S = 1.142$ for 2296 unique reflections, 451 parameters and 724 restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.256 to 0.354 eÅ^{-3}. The *R*-factor ratio between the $wR(F^2)$ values for the single molecule model and the whole molecule disorder model is $R = 0.1141 / 0.1017 = 1.12$ while $R_{224,2069,0.005} = 1.07$, i.e., $R > R_{224,2069,0.005}$.[12] Hence, the notion that the model without whole molecule disorder might be preferable is convincingly rejected at the 0.005 level. Scattering factors were taken from the International Tables for Crystallography, Volume C.[13]

The Flack parameter refined to 0.04(2) [*vs* the expectation values of 0 for the correct hand and 1 for the wrong hand] indicating that the coordinates below are for the correct hand of the molecule and that the absolute configuration at the chiral carbon is unequivocally *R* (IUPAC Numbering: Wanted = (3*R*), Found = (3*R*); Crystallographic

(12) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.
(13) Maslen, E. N.; Fox, A. G.; O'Keefe, M. A. *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, pp 476-516.

Atom Numbering: Wanted = (10*R* / 10'*R*), Found = (10*R* / 10'*R*)).[14] Due to the complexity of the molecule, the IUPAC butyl C-3 atom is given the crystallographic label C10 in the atoms list below. (The C10' atom listed below corresponds to the chiral atom in the second molecule of the two-site whole molecule disorder model employed.)

For comparison, a refinement of the inverted molecule having the wrong absolute structure, i.e., (3*S*), gave $R(F) = 0.0696$, $wR(F^2) = 0.1670$, and $S = 1.129$ for 1735 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0949$, $wR(F^2) = 0.1858$, and $S = 1.052$ for 2296 unique reflections, 451 parameters, and 724 restraints for the whole molecule disorder model. The Flack parameter based on the wrong absolute structure was 0.95(3). Based on these $wR(F^2)$ and Flack values, the (3*S*) isomer is soundly rejected.

Table 1. Crystal data

$C_{20}H_{19}BrO_4$	$Z = 2$
$M_r = 403.26$	$D_x = 1.498$ Mg m^{-3}
Monoclinic, $P2_1$ (No. 4)	Mo $K\alpha$ radiation
$a = 5.8677$ (3) Å	Cell parameters from 7927 reflections
$b = 7.3771$ (5) Å	$\theta = 1.97–22.46°$
$c = 20.8583$ (14) Å	$\mu = 2.32$ mm^{-1}
$\beta = 97.998$ (4)°	$T = 200$ (2) K
$V = 894.1$ (1) Å^3	Plate, Colorless

Table 2. Data collection

Nonius KappaCCD diffractomer	1735 reflections with $I > 2\sigma(I)$
ω scans; 1440 0.5° rotations	$R_{int} = 0.066$
Absorption correction: none	$\theta_{max} = 22.46°$
	$h = -6 \rightarrow 6$
7927 measured reflections	$k = -7 \rightarrow 7$
2296 independent reflections	$l = -22 \rightarrow 22$

(14) Flack, H. D. *Acta Crystallogr. Sect. A* **1983**, *39*, 876.

Table 3. Refinement

Refinement on F^2	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)] = 0.0483$ (obs data)	2296 unique reflections
$wR(F^2) = 0.0910$ (obs data)	451 parameters
$S = 1.224$ (obs data)	724 restraints
$R[F^2 > 2\sigma(F^2)] = 0.0741$ (uniq data)	$\lvert\Delta/\sigma\rvert_{max} = 0.001$
$wR(F^2) = 0.1017$ (uniq data)	$\Delta\rho_{max} = 0.354$ e Å^{-1}
$S = 1.142$ (uniq data)	$\Delta\rho_{min} = -0.256$ e Å^{-1}
Flack parameter: 0.038 (15)	Extinction correction: none
Absolute structure:[14]	Calculated weights $w = 1/[\sigma^2(F_o^2) + 0.1541P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 4. Atomic site parameters for dwcm003f

	x	*y*	*z*	*U*
Br1	-0.1992 (9)	0.8493	0.0767 (3)	0.0563 (13)
O1	0.5174 (14)	0.2757 (12)	0.3126 (5)	0.039 (2)
C2	0.7373 (17)	0.3442 (11)	0.3350 (5)	0.043 (3)
C3	0.8475 (15)	0.3863 (12)	0.2851 (5)	0.041 (3)
H3	0.9986	0.4350	0.2882	0.049
C3A	0.7002 (15)	0.3461 (10)	0.2259 (5)	0.032 (3)
C4	0.7143 (17)	0.3591 (12)	0.1597 (5)	0.033 (3)
H4	0.8492	0.4047	0.1449	0.039
C5	0.5301 (18)	0.3048 (12)	0.1170 (5)	0.039 (3)
C6	0.3296 (17)	0.2371 (13)	0.1375 (5)	0.033 (3)
H6	0.2042	0.2003	0.1064	0.039
C7	0.3131 (16)	0.2233 (14)	0.2031 (6)	0.035 (3)
H7	0.1780	0.1776	0.2178	0.042
C7A	0.4998 (15)	0.2785 (11)	0.2463 (5)	0.034 (2)
O8	0.5136 (20)	0.3079 (14)	0.0504 (5)	0.041 (3)
C9	0.7208 (24)	0.3394 (23)	0.0232 (6)	0.049 (4)
H9A	0.6869	0.3385	-0.0241	0.074
H9B	0.8326	0.2439	0.0375	0.074
H9C	0.7850	0.4575	0.0378	0.074
C10	0.7945 (20)	0.3537 (14)	0.4060 (5)	0.043 (3)
H10	0.9547	0.4025	0.4156	0.051
C11	0.7942 (32)	0.1714 (18)	0.4365 (6)	0.050 (4)
H11A	0.8329	0.1834	0.4836	0.075
H11B	0.9083	0.0940	0.4199	0.075
H11C	0.6412	0.1169	0.4263	0.075

C12	0.6356 (26)	0.4817 (19)	0.4395 (6)	0.046 (4)
H12A	0.4738	0.4422	0.4279	0.055
H12B	0.6757	0.4709	0.4870	0.055
C13	0.6563 (22)	0.6770 (18)	0.4202 (6)	0.041 (4)
H13A	0.5965	0.7557	0.4526	0.049
H13B	0.8206	0.7072	0.4200	0.049
O14	0.5282 (18)	0.7132 (15)	0.3560 (5)	0.046 (3)
C15	0.3100 (19)	0.7738 (12)	0.3535 (5)	0.041 (3)
O16	0.2201 (23)	0.8108 (20)	0.4005 (5)	0.054 (4)
C17	0.1954 (17)	0.7883 (11)	0.2855 (5)	0.032 (3)
C18	-0.0240 (18)	0.8709 (13)	0.2751 (5)	0.040 (3)
H18	-0.0920	0.9144	0.3109	0.048
C19	-0.1399 (16)	0.8885 (11)	0.2130 (5)	0.039 (3)
H19	-0.2874	0.9440	0.2059	0.047
C20	-0.0392 (15)	0.8246 (7)	0.1614 (4)	0.041 (3)
C21	0.1767 (15)	0.7427 (11)	0.1705 (5)	0.033 (3)
H21	0.2436	0.6994	0.1345	0.040
C22	0.2923 (17)	0.7252 (13)	0.2325 (5)	0.038 (3)
H22	0.4397	0.6695	0.2391	0.045
Br1'	-0.1809 (10)	0.9272 (11)	0.0755 (3)	0.0726 (15)
O1'	0.5261 (14)	0.3606 (12)	0.3134 (5)	0.042 (3)
C2'	0.7441 (16)	0.4309 (11)	0.3363 (5)	0.041 (3)
C3'	0.8558 (15)	0.4738 (13)	0.2866 (5)	0.040 (4)
H3'	1.0062	0.5237	0.2900	0.048
C3A'	0.7102 (14)	0.4318 (10)	0.2272 (5)	0.039 (3)
C4'	0.7269 (15)	0.4447 (13)	0.1611 (5)	0.033 (4)
H4'	0.8618	0.4914	0.1467	0.039
C5'	0.5443 (17)	0.3885 (12)	0.1181 (5)	0.046 (3)
C6'	0.3443 (17)	0.3195 (14)	0.1379 (5)	0.041 (5)
H6'	0.2205	0.2816	0.1066	0.049
C7'	0.3253 (17)	0.3058 (14)	0.2037 (6)	0.040 (3)
H7'	0.1902	0.2590	0.2180	0.047
C7A'	0.5104 (15)	0.3628 (11)	0.2471 (5)	0.039 (3)
O8'	0.5322 (19)	0.3919 (15)	0.0515 (5)	0.049 (3)
C9'	0.7420 (24)	0.4290 (24)	0.0260 (6)	0.046 (4)
H9A'	0.7126	0.4279	-0.0214	0.069
H9B'	0.8564	0.3361	0.0410	0.069
H9C'	0.8004	0.5484	0.0410	0.069
C10'	0.8007 (20)	0.4419 (14)	0.4073 (5)	0.046 (3)
H10'	0.9612	0.4898	0.4170	0.055
C11'	0.7986 (37)	0.2589 (20)	0.4377 (7)	0.074 (6)
H11D	0.8368	0.2703	0.4848	0.111
H11E	0.9125	0.1811	0.4210	0.111

H11F	0.6453	0.2051	0.4272	0.111
C12'	0.6431 (24)	0.5697 (19)	0.4409 (6)	0.047 (4)
H12C	0.4815	0.5293	0.4299	0.056
H12D	0.6849	0.5593	0.4884	0.056
C13'	0.6596 (23)	0.7647 (20)	0.4219 (6)	0.050 (4)
H13C	0.5968	0.8420	0.4540	0.060
H13D	0.8234	0.7973	0.4222	0.060
O14'	0.5337 (19)	0.8008 (14)	0.3575 (5)	0.049 (3)
C15'	0.3155 (19)	0.8615 (12)	0.3539 (5)	0.050 (3)
O16'	0.2219 (24)	0.9006 (19)	0.4000 (5)	0.074 (5)
C17'	0.2047 (18)	0.8735 (11)	0.2853 (5)	0.037 (3)
C18'	-0.0179 (17)	0.9502 (15)	0.2740 (5)	0.041 (3)
H18'	-0.0900	0.9912	0.3093	0.050
C19'	-0.1310 (16)	0.9655 (15)	0.2116 (4)	0.044 (3)
H19'	-0.2807	1.0169	0.2038	0.052
C20'	-0.0239 (15)	0.9052 (11)	0.1605 (5)	0.043 (3)
C21'	0.1951 (16)	0.8294 (13)	0.1707 (5)	0.041 (3)
H21'	0.2662	0.7886	0.1351	0.050
C22'	0.3081 (16)	0.8140 (13)	0.2331 (5)	0.035 (3)
H22'	0.4578	0.7624	0.2403	0.042

Table 5. Anisotropic atomic displacement parameters for dwcm003f

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.0435 (14)	0.087 (4)	0.035 (2)	0.000 (2)	-0.0086 (12)	0.006 (2)
O1	0.038 (4)	0.047 (6)	0.032 (4)	-0.016 (4)	0.002 (3)	-0.013 (5)
C2	0.038 (5)	0.053 (8)	0.035 (4)	-0.007 (6)	-0.008 (4)	-0.009 (6)
C3	0.030 (4)	0.057 (9)	0.033 (4)	-0.008 (6)	-0.003 (4)	-0.015 (8)
C3A	0.028 (4)	0.034 (6)	0.032 (4)	-0.016 (5)	-0.001 (4)	-0.007 (5)
C4	0.032 (5)	0.038 (9)	0.026 (5)	-0.015 (7)	-0.003 (4)	-0.005 (7)
C5	0.034 (5)	0.050 (8)	0.031 (5)	-0.016 (5)	-0.008 (4)	0.000 (5)
C6	0.026 (5)	0.033 (10)	0.036 (5)	-0.007 (5)	-0.003 (4)	-0.008 (6)
C7	0.029 (4)	0.038 (7)	0.037 (4)	-0.011 (4)	0.003 (4)	-0.006 (5)
C7A	0.033 (4)	0.038 (6)	0.032 (4)	-0.012 (4)	0.004 (3)	-0.012 (5)
O8	0.036 (4)	0.054 (7)	0.029 (4)	-0.018 (5)	-0.010 (4)	-0.003 (5)
C9	0.042 (6)	0.072 (11)	0.028 (6)	-0.024 (7)	-0.014 (5)	0.000 (7)
C10	0.041 (5)	0.051 (8)	0.034 (5)	0.000 (7)	-0.002 (4)	0.008 (7)
C11	0.084 (9)	0.032 (9)	0.033 (7)	-0.026 (9)	0.002 (7)	-0.010 (7)
C12	0.047 (6)	0.059 (9)	0.026 (5)	0.003 (6)	-0.014 (5)	-0.003 (6)
C13	0.043 (5)	0.052 (9)	0.024 (6)	-0.003 (7)	-0.008 (5)	-0.006 (7)
O14	0.036 (4)	0.066 (8)	0.033 (4)	0.004 (5)	-0.002 (3)	0.008 (5)

C15	0.036 (5)	0.049 (8)	0.039 (5)	-0.005 (6)	0.004 (4)	0.010 (6)
O16	0.043 (6)	0.087 (11)	0.031 (5)	0.012 (6)	0.005 (5)	0.007 (6)
C17	0.025 (4)	0.037 (8)	0.033 (4)	-0.017 (5)	0.002 (4)	0.001 (5)
C18	0.033 (4)	0.044 (8)	0.043 (5)	-0.009 (6)	0.006 (4)	0.004 (7)
C19	0.025 (4)	0.044 (8)	0.047 (4)	-0.008 (6)	0.000 (4)	0.003 (6)
C20	0.035 (5)	0.051 (8)	0.034 (5)	-0.012 (5)	0.001 (4)	0.015 (6)
C21	0.032 (4)	0.040 (8)	0.030 (4)	-0.007 (5)	0.011 (4)	0.011 (6)
C22	0.030 (5)	0.047 (8)	0.035 (5)	-0.010 (5)	0.004 (4)	0.008 (6)
Br1'	0.053 (2)	0.122 (4)	0.040 (2)	-0.006 (2)	-0.0018 (13)	-0.001 (3)
O1'	0.034 (3)	0.070 (7)	0.025 (3)	-0.012 (5)	0.010 (3)	-0.014 (6)
C2'	0.031 (5)	0.060 (9)	0.031 (4)	-0.006 (6)	0.004 (4)	-0.014 (6)
C3'	0.033 (5)	0.061 (10)	0.027 (5)	-0.006 (6)	0.005 (4)	-0.017 (6)
C3A'	0.027 (4)	0.062 (8)	0.028 (4)	-0.016 (5)	0.008 (4)	-0.011 (6)
C4'	0.015 (5)	0.056 (11)	0.028 (5)	-0.006 (6)	0.006 (4)	-0.006 (7)
C5'	0.028 (5)	0.083 (9)	0.030 (4)	-0.020 (6)	0.012 (4)	-0.006 (7)
C6'	0.024 (5)	0.062 (14)	0.035 (5)	-0.011 (6)	-0.004 (4)	-0.011 (6)
C7'	0.031 (4)	0.060 (8)	0.031 (4)	-0.014 (5)	0.015 (4)	-0.013 (5)
C7A'	0.030 (3)	0.065 (7)	0.025 (3)	-0.014 (5)	0.012 (3)	-0.011 (5)
O8'	0.031 (4)	0.085 (9)	0.031 (4)	-0.024 (6)	0.007 (3)	-0.004 (6)
C9'	0.045 (6)	0.065 (10)	0.030 (6)	-0.028 (7)	0.016 (5)	-0.002 (7)
C10'	0.041 (5)	0.066 (9)	0.030 (5)	0.005 (6)	0.004 (4)	-0.005 (6)
C11'	0.120 (12)	0.060 (11)	0.041 (8)	0.000 (13)	0.007 (10)	-0.016 (8)
C12'	0.040 (6)	0.075 (10)	0.029 (6)	0.001 (8)	0.014 (5)	-0.003 (6)
C13'	0.043 (5)	0.078 (9)	0.028 (6)	0.007 (7)	0.003 (4)	0.000 (7)
O14'	0.038 (4)	0.080 (9)	0.031 (4)	0.005 (5)	0.006 (3)	-0.002 (5)
C15'	0.035 (4)	0.077 (9)	0.038 (4)	0.004 (7)	0.007 (4)	0.001 (7)
O16'	0.047 (6)	0.137 (15)	0.038 (5)	0.015 (9)	0.012 (5)	-0.014 (9)
C17'	0.028 (4)	0.052 (7)	0.033 (4)	-0.015 (6)	0.007 (3)	0.003 (6)
C18'	0.034 (5)	0.058 (9)	0.035 (5)	-0.005 (6)	0.016 (4)	0.005 (6)
C19'	0.028 (5)	0.055 (8)	0.047 (5)	-0.009 (5)	0.002 (4)	0.009 (6)
C20'	0.041 (5)	0.054 (7)	0.034 (4)	-0.006 (6)	0.002 (4)	0.005 (6)
C21'	0.042 (4)	0.052 (9)	0.031 (4)	-0.011 (5)	0.008 (4)	0.009 (6)
C22'	0.023 (4)	0.046 (9)	0.037 (4)	-0.014 (5)	0.007 (4)	0.005 (5)

Table 6. Geometric parameters (Å, °) for dwcm003f

Br1—C20	1.890 (7)	Br1'—C20'	1.889 (7)
O1—C7A	1.374 (7)	O1'—C7A'	1.374 (7)
O1—C2	1.404 (7)	O1'—C2'	1.401 (7)
C2—C3	1.337 (8)	C2'—C3'	1.340 (8)
C2—C10	1.473 (8)	C2'—C10'	1.474 (8)

C3—C3A	1.437 (8)	C3'—C3A'	1.437 (8)
C3A—C7A	1.397 (7)	C3A'—C7A'	1.393 (7)
C3A—C4	1.397 (8)	C3A'—C4'	1.398 (7)
C4—C5	1.362 (8)	C4'—C5'	1.363 (8)
C5—O8	1.379 (7)	C5'—O8'	1.380 (7)
C5—C6	1.399 (8)	C5'—C6'	1.394 (8)
C6—C7	1.390 (8)	C6'—C7'	1.395 (8)
C7—C7A	1.379 (8)	C7'—C7A'	1.379 (8)
O8—C9	1.430 (7)	O8'—C9'	1.434 (7)
C10—C11	1.488 (12)	C10'—C11'	1.492 (12)
C10—C12	1.558 (11)	C10'—C12'	1.554 (11)
C12—C13	1.506 (13)	C12'—C13'	1.499 (13)
C13—O14	1.466 (8)	C13'—O14'	1.463 (8)
O14—C15	1.350 (8)	O14'—C15'	1.348 (7)
C15—O16	1.209 (7)	C15'—O16'	1.207 (7)
C15—C17	1.486 (8)	C15'—C17'	1.489 (8)
C17—C22	1.391 (9)	C17'—C22'	1.390 (9)
C17—C18	1.413 (8)	C17'—C18'	1.413 (8)
C18—C19	1.383 (8)	C18'—C19'	1.381 (8)
C19—C20	1.381 (8)	C19'—C20'	1.382 (8)
C20—C21	1.392 (8)	C20'—C21'	1.391 (8)
C21—C22	1.380 (9)	C21'—C22'	1.381 (9)

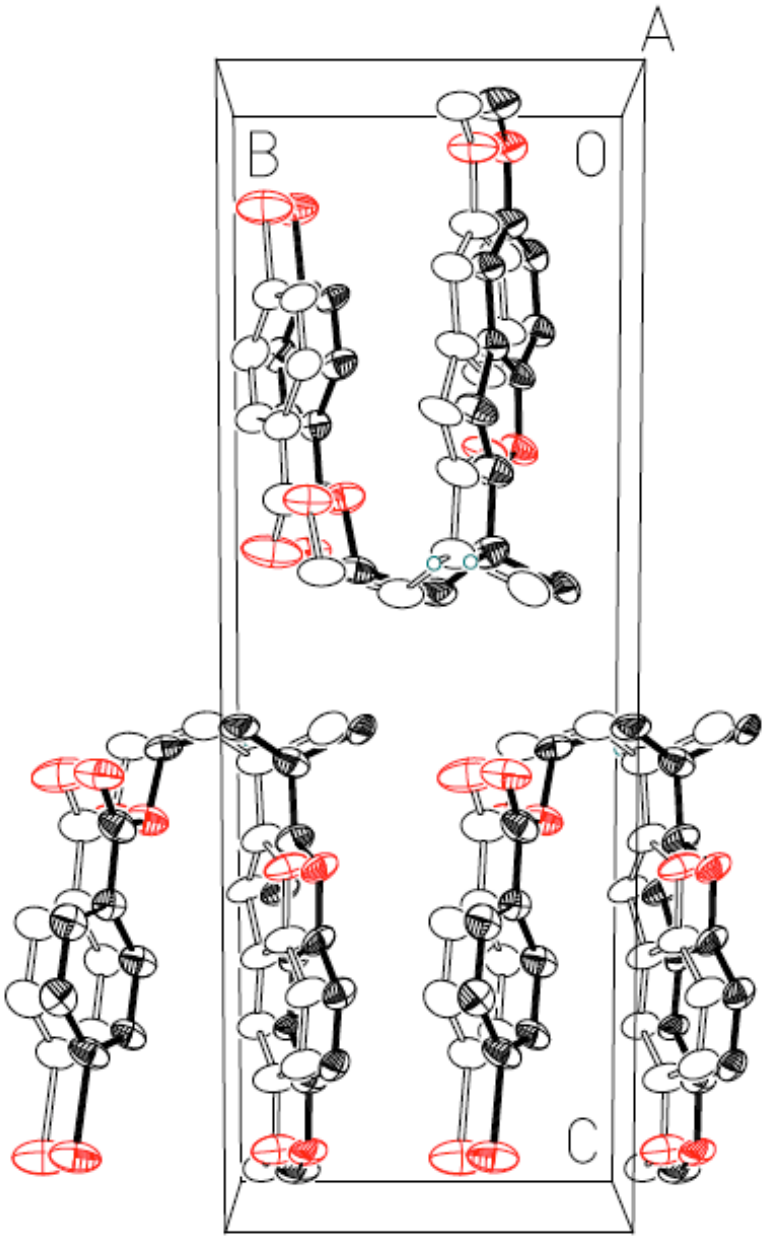
C7A—O1—C2	105.5 (5)	C7A'—O1'—C2'	105.6 (5)
C3—C2—O1	110.3 (5)	C3'—C2'—O1'	110.2 (5)
C3—C2—C10	134.8 (7)	C3'—C2'—C10'	134.3 (6)
O1—C2—C10	114.9 (6)	O1'—C2'—C10'	115.5 (6)
C2—C3—C3A	108.8 (5)	C2'—C3'—C3A'	108.7 (5)
C7A—C3A—C4	119.6 (6)	C7A'—C3A'—C4'	119.7 (5)
C7A—C3A—C3	104.1 (5)	C7A'—C3A'—C3'	104.3 (5)
C4—C3A—C3	136.3 (6)	C4'—C3A'—C3'	136.0 (6)
C5—C4—C3A	118.4 (6)	C5'—C4'—C3A'	118.1 (6)
C4—C5—O8	126.3 (6)	C4'—C5'—O8'	125.7 (6)
C4—C5—C6	122.0 (6)	C4'—C5'—C6'	122.2 (6)
O8—C5—C6	111.7 (6)	O8'—C5'—C6'	112.2 (6)
C7—C6—C5	120.3 (6)	C5'—C6'—C7'	120.3 (6)
C7A—C7—C6	117.6 (6)	C7A'—C7'—C6'	117.3 (6)
O1—C7A—C7	126.5 (6)	O1'—C7A'—C7'	126.4 (6)
O1—C7A—C3A	111.3 (5)	O1'—C7A'—C3A'	111.3 (5)
C7—C7A—C3A	122.2 (6)	C7'—C7A'—C3A'	122.3 (6)
C5—O8—C9	117.2 (6)	C5'—O8'—C9'	116.7 (6)

C2—C10—C11	111.9 (6)	C2'—C10'—C11'	111.3 (7)
C2—C10—C12	114.3 (6)	C2'—C10'—C12'	114.9 (6)
C11—C10—C12	108.6 (8)	C11'—C10'—C12'	108.5 (8)
C13—C12—C10	112.7 (8)	C13'—C12'—C10'	113.5 (8)
O14—C13—C12	111.6 (8)	O14'—C13'—C12'	112.0 (9)
C15—O14—C13	117.3 (7)	C15'—O14'—C13'	117.8 (7)
O16—C15—O14	124.2 (7)	O16'—C15'—O14'	124.6 (7)
O16—C15—C17	124.6 (7)	O16'—C15'—C17'	124.4 (7)
O14—C15—C17	111.2 (6)	O14'—C15'—C17'	111.0 (6)
C22—C17—C18	119.1 (6)	C22'—C17'—C18'	119.3 (6)
C22—C17—C15	123.5 (6)	C22'—C17'—C15'	123.7 (6)
C18—C17—C15	117.4 (6)	C18'—C17'—C15'	117.1 (6)
C19—C18—C17	120.2 (6)	C19'—C18'—C17'	120.2 (6)
C20—C19—C18	119.4 (6)	C18'—C19'—C20'	119.3 (6)
C19—C20—C21	121.4 (6)	C19'—C20'—C21'	121.5 (6)
C19—C20—Br1	119.0 (5)	C19'—C20'—Br1'	118.7 (5)
C21—C20—Br1	119.6 (6)	C21'—C20'—Br1'	119.8 (6)
C22—C21—C20	119.2 (6)	C22'—C21'—C20'	119.3 (7)
C21—C22—C17	120.7 (6)	C21'—C22'—C17'	120.6 (6)

Computer programs

Data collection: COLLECT.[8] Cell refinement: DENZO-SMN.[9] Data reduction: DENZO-SMN.[9] Program(s) used to solve structure: Siemens SHELXTL.[10] Program(s) used to refine structure: Siemens SHELXTL.[10] Molecular graphics: Siemens SHELXTL.[10] Software used to prepare material for publication: Siemens SHELXTL,[10] publCIF,[15] printCIF for Word.[16]

(15) Westrip, S. P. *publCIF*, version 1.0c; International Union of Crystallography, Abbey Square: Chester, U. K., 2006.
(16) *prinfCIF for word*; International Union of Crystallography, Abbey Square: Chester, U. K., 2005.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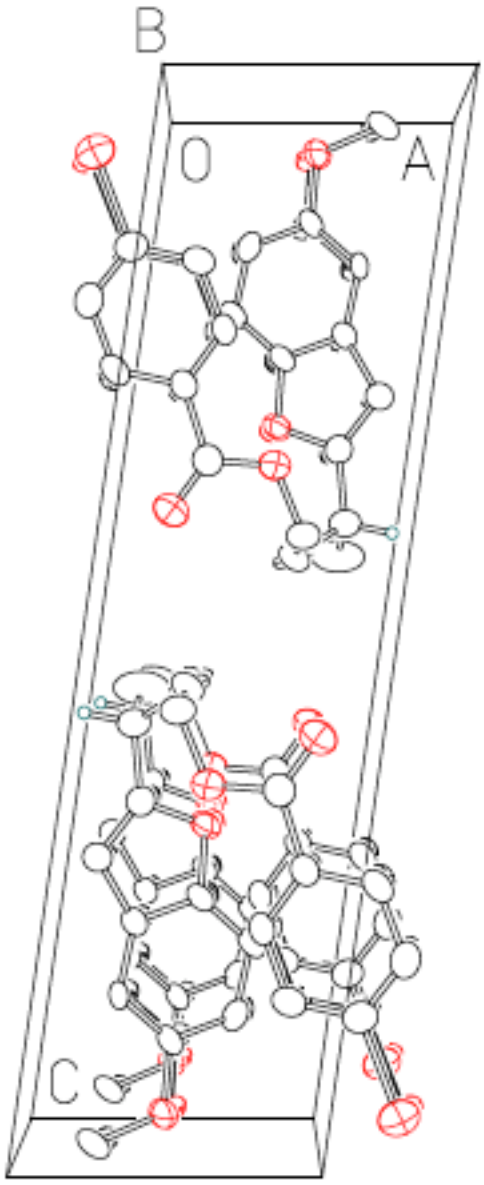
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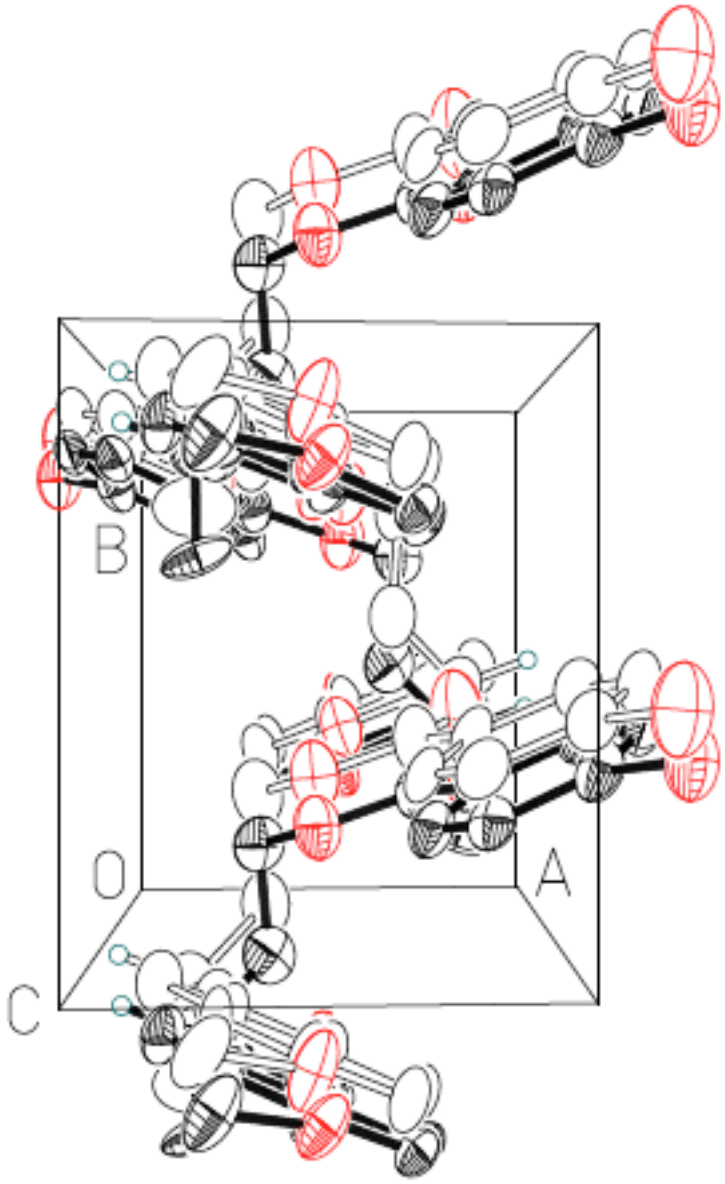
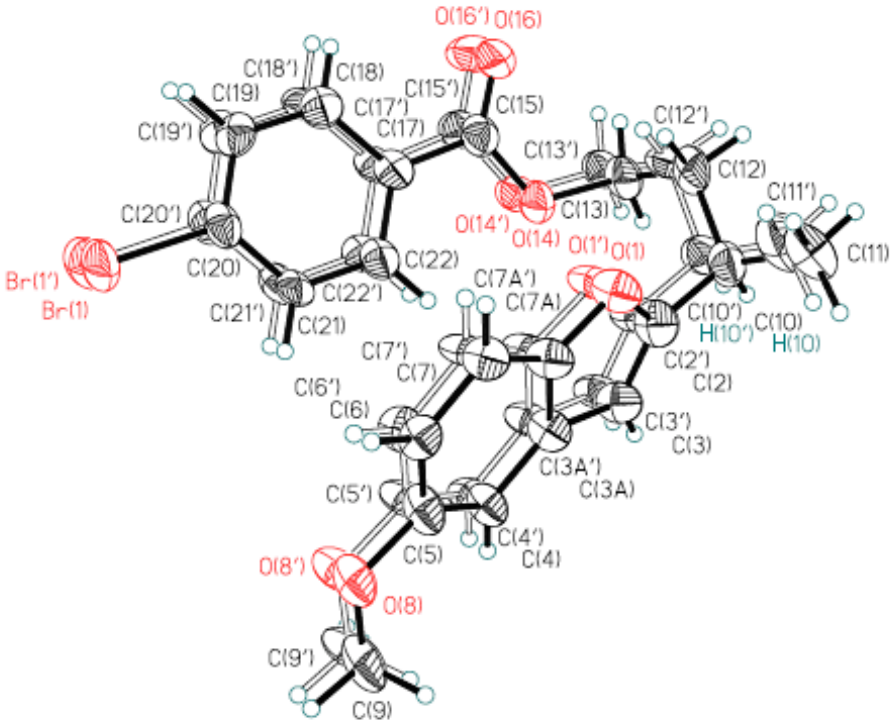
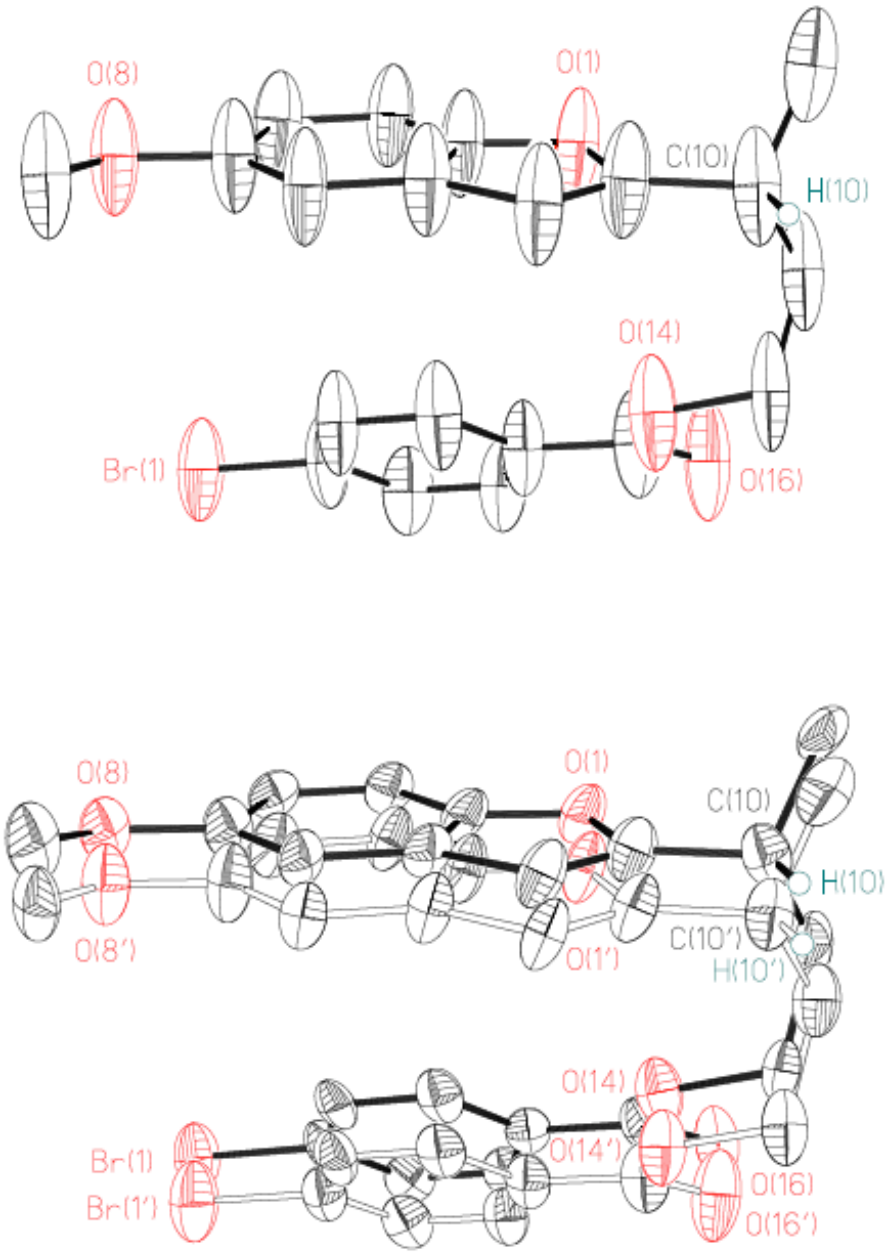
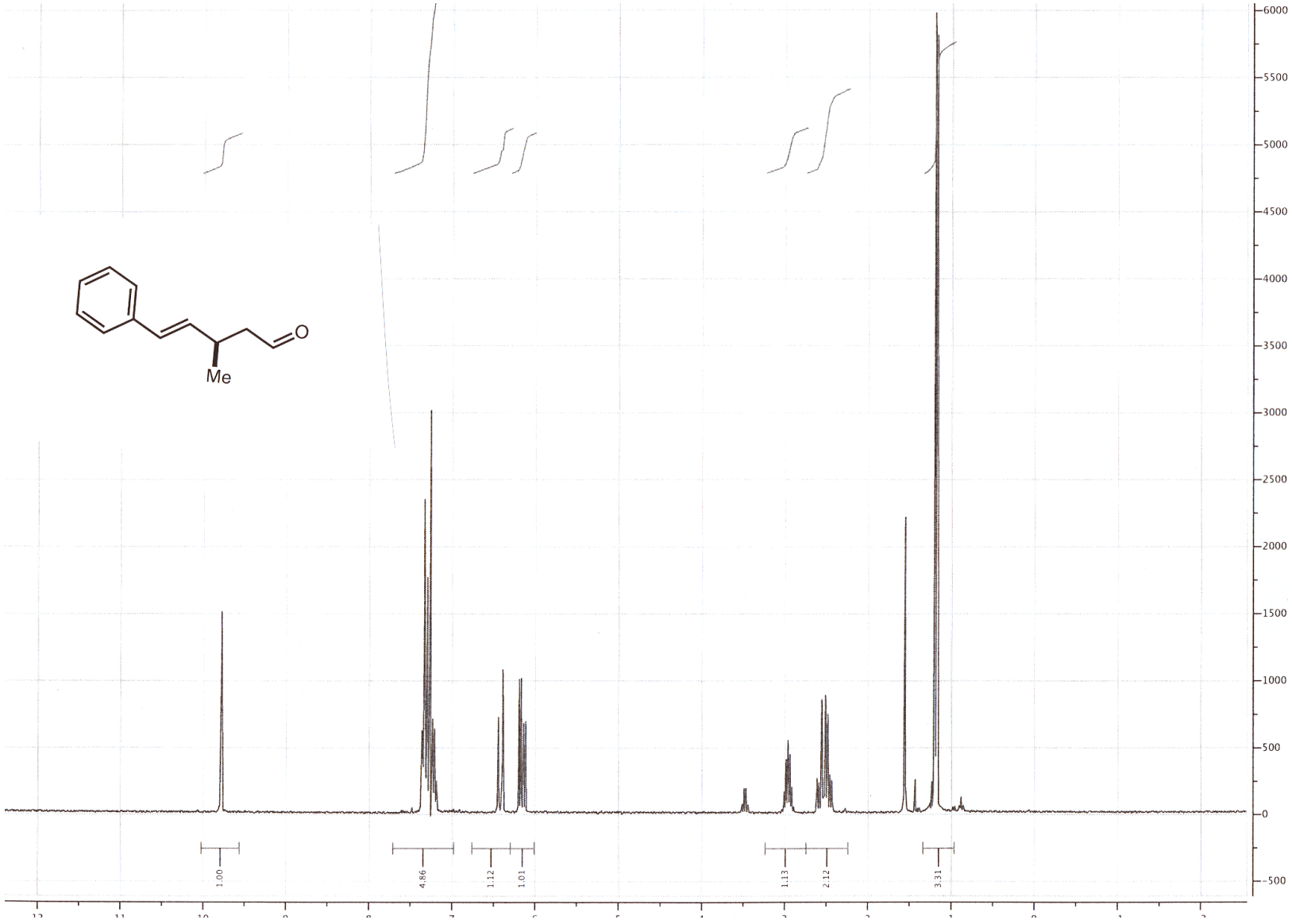
A
C


B
O
A
C

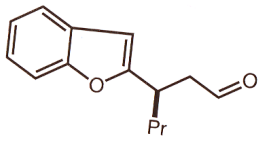

O(16')
O(16)
C(18')
C(18)
C(19)
C(15')
C(15)
C(17')
C(19')
C(17)
C(12')
C(13')
C(12)
C(11')
C(20')
O(14')
O(14)
C(13)
C(11)
O(1')
O(1)
Br(1')
C(20)
C(22)
C(7A')
C(7A)
Br(1)
C(22')
C(21')
C(21)
C(10')
C(10)
H(10')
H(10)
C(7')
C(2')
C(7)
C(2)
C(6')
C(6)
C(3')
C(3)
C(3A')
C(3A)
C(5')
C(4')
C(5)
C(4)
O(8')
O(8)
C(9')
C(9)


O(8)
O(1)
C(10)
H(10)
O(14)
Br(1)
O(16)
O(8)
O(1)
C(10)
H(10)
O(8')
O(1')
C(10')
H(10')
O(14)
O(14')
Br(1)
Br(1')
O(16)
O(16')


O
Me
1.00
4.86
1.12
1.01
1.13
2.12
3.31
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

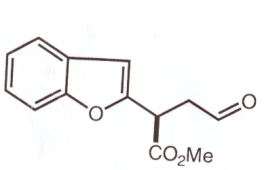
SL-III-296 product

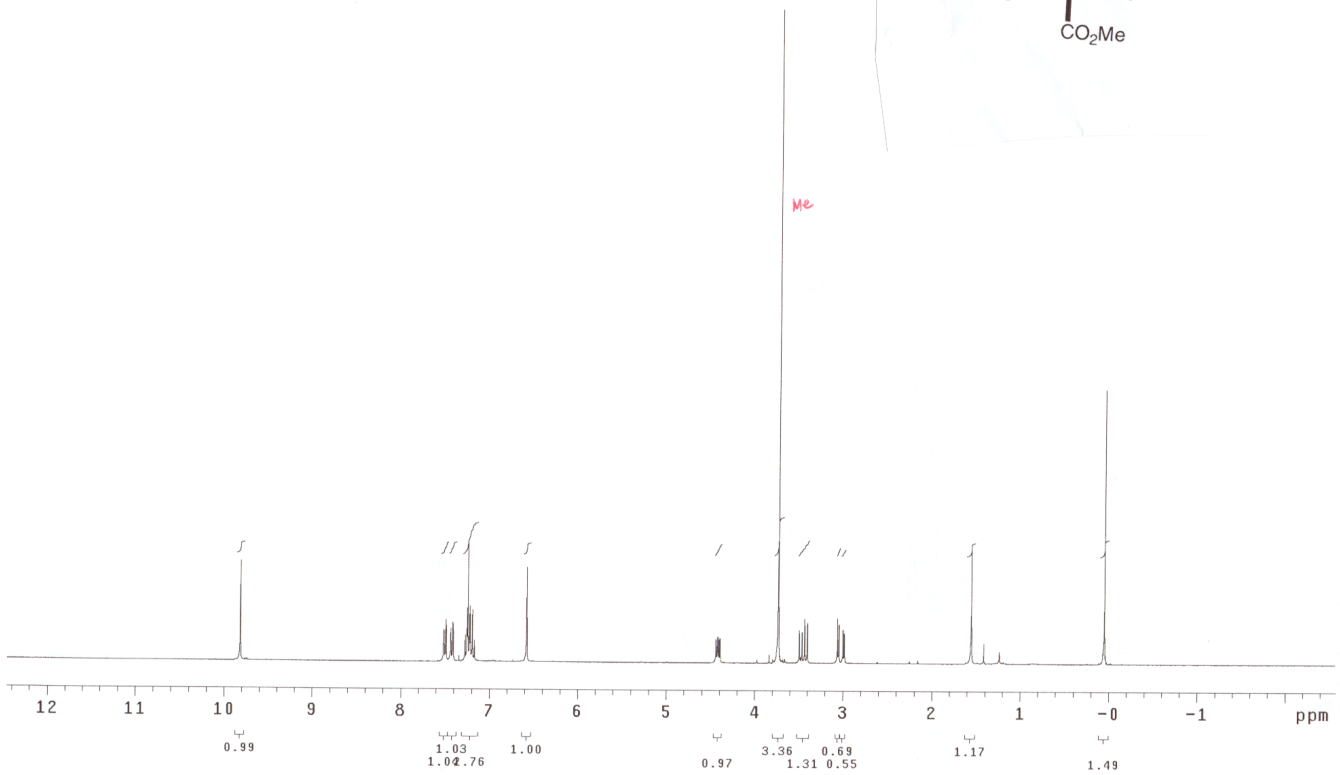
Pulse Sequence: s2pul



SL-III-300 A

Pulse Sequence: s2pul

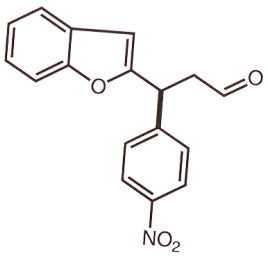


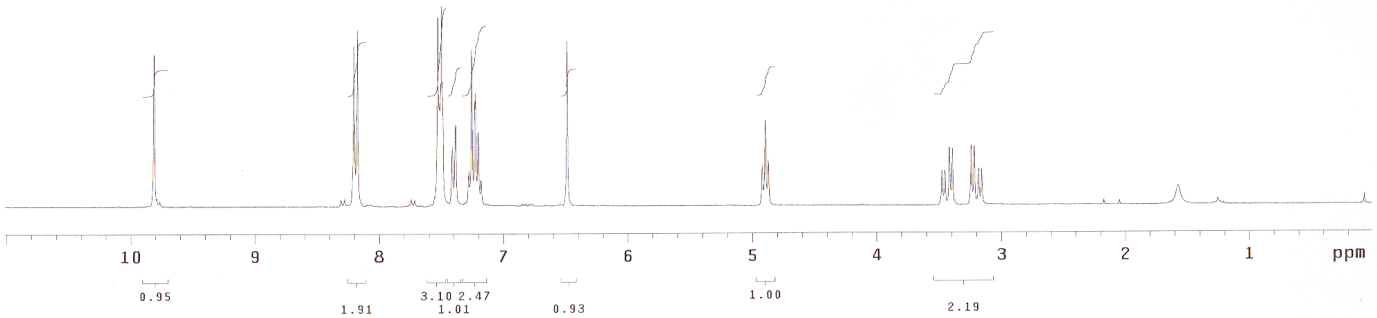


SL-IV-27 p-NO2 cinnamaldehyde

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc28_2005-12-13
File: 2802

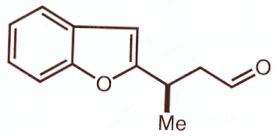
Pulse Sequence: s2pul
Solvent: cdcl3





SL-IV-31 crotonaldehyde

Pulse Sequence: s2pul

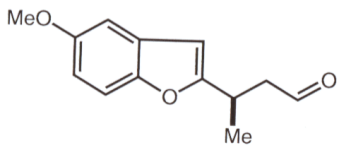


SC-IV-81R

Pulse Sequence: s2pul

Solvent: cd2cl2
Ambient temperature
Mercury-300 "hg2"

Relax. delay 1.000 sec
Pulse 47.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
48 repetitions
OBSERVE H1, 299.8172086 MHz
DATA PROCESSING
FT size 32768
Total time 7 min, 9 sec

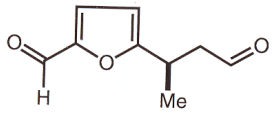


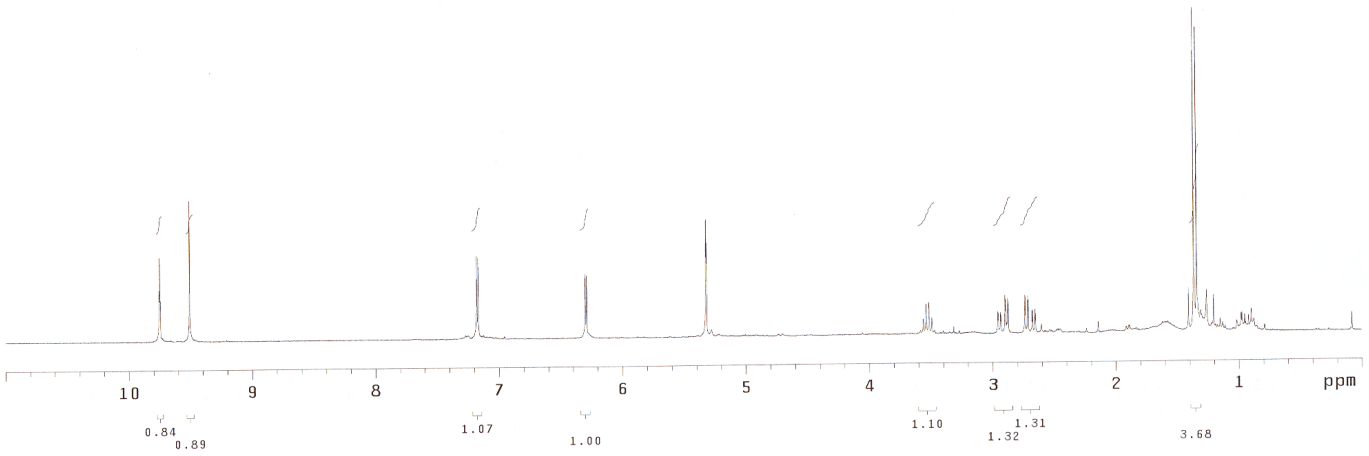
SL-IV-94

Pulse Sequence: s2pul

Solvent: cd2cl2
Ambient temperature
Mercury-300BB "hg1"

Relax. delay 1.000 sec
Pulse 36.6 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
48 repetitions
OBSERVE H1, 299.8666544 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec

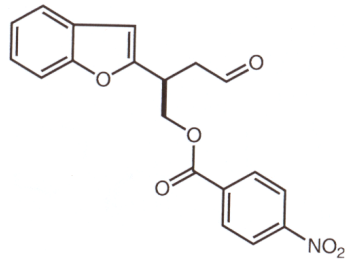


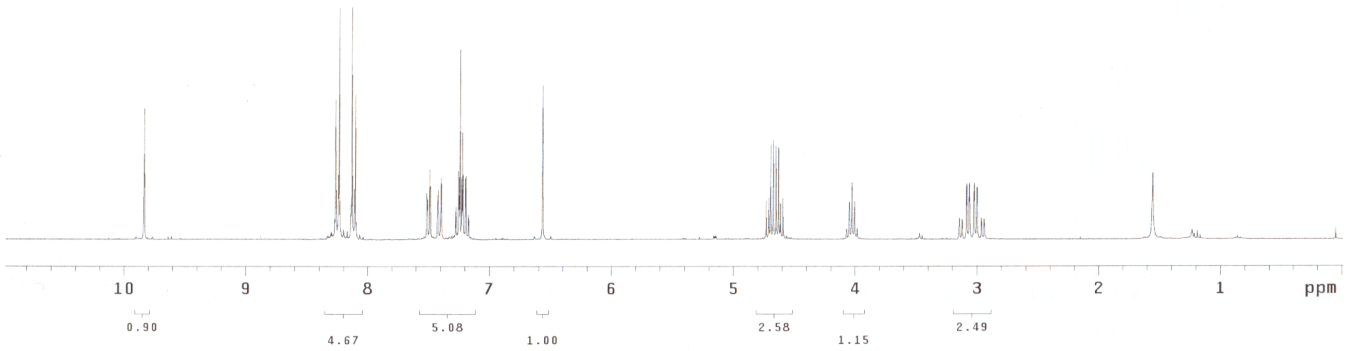


SL-IV-97

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc28_2006-02-23
File: 2802

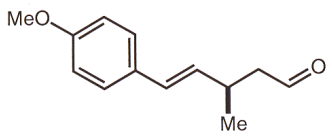
Pulse Sequence: s2pul
Solvent: cdcl3





SL-IV-135

Pulse Sequence: s2pul

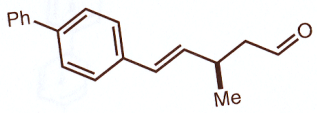


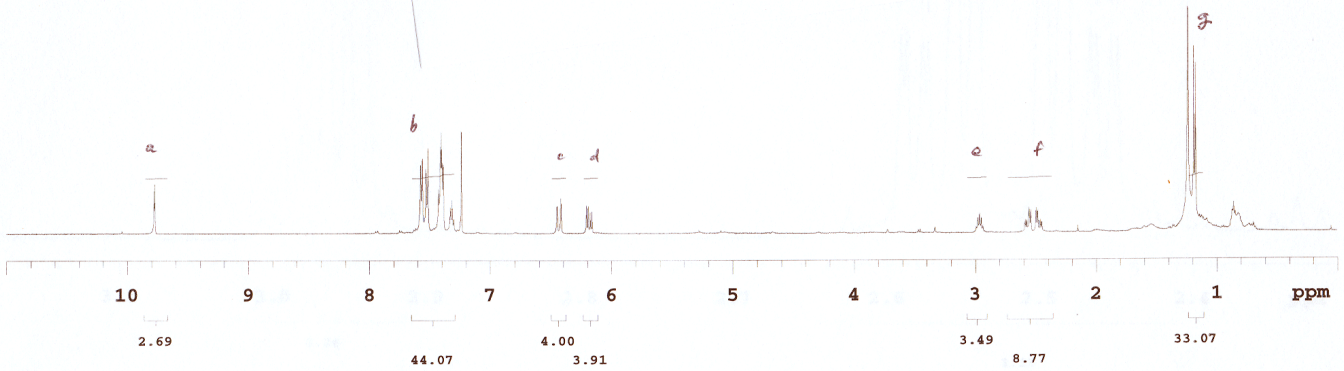
SL-IV-288

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-500 "nmrsun-5"

Relax. delay 1.100 sec
Pulse 50.0 degrees
Acq. time 1.892 sec
Width 10000.0 Hz
44 repetitions
OBSERVE H1, 499.7746306 MHz
DATA PROCESSING
FT size 65536
Total time 50 min, 6 sec



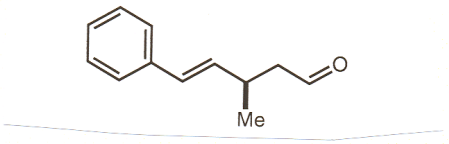


BergerSFC Chromatogram Report

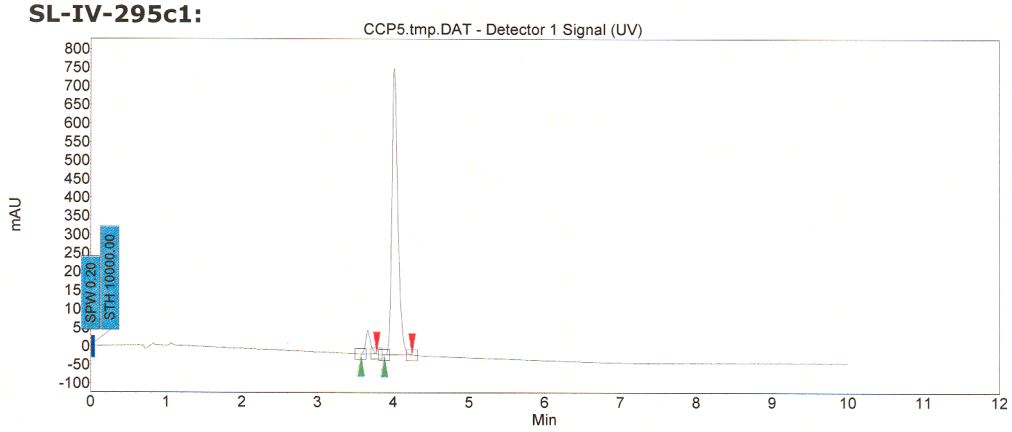
Date: 10/15/2007
Time: 5:08:12 PM
Vial number: 3
Sequence name: SL5
Filename: SL-IV-295c1

Method Name: ODH_IPA_5-35
User Name: SFC User
Acquisition Date: 2/1/2007 6:28:50 PM

Run Information:
N.A.



SL-IV-295c1:

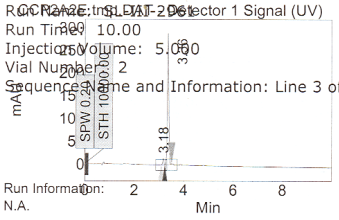


The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	3.57	3.66	3.78	0.00	6.27	63.4	4.7	6.272
1	UNKNOWN	3.88	4.01	4.24	0.00	93.73	770.6	70.2	93.728
Total						100.00	834.0	74.9	100.000

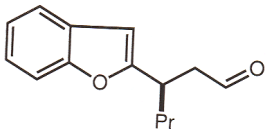
BergerSFC Chromatogram Report



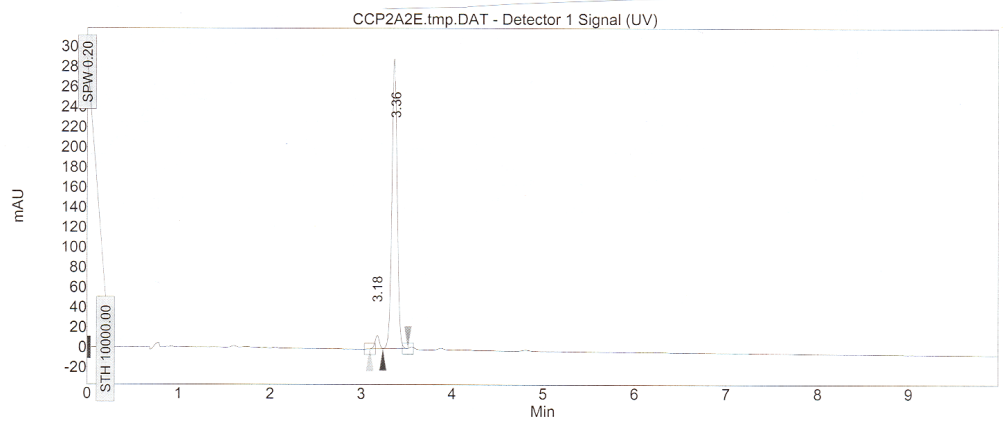
Run Name: SL-III-2961
Run Time: 10.00
Injection Volume: 5.000
Vial Number: 2
Sequence Name and Information: Line 3 of 3

Run Information:
N.A.

Method Name: ASH_IPA_5-25
User Name: SFC User
Acquisition Date: 11/3/2005 12:00:30 PM



SL-III-2961:



The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.10	3.18	3.24	0.00	3.60	13.4	0.7	3.604
2	UNKNOWN	3.24	3.36	3.51	0.00	96.40	289.6	19.5	96.396
Total						100.00	303.0	20.2	100.000

92.8%.

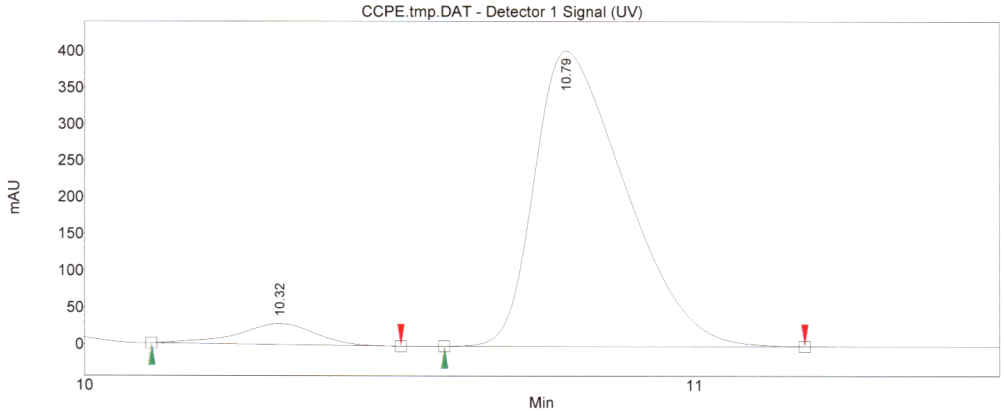
BergerSFC Chromatogram Report

Date: 10/18/2007
Time: 4:13:40 PM
Vial number: 2
Sequence name: SL-screen3
Filename: SL-III-300-B10

Method Name: ADH_MeOH_5-15R1
User Name: SFC User
Acquisition Date: 11/10/2005 8:28:09 PM

Run Information:
N.A.

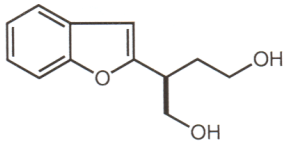
SL-III-300-B10:



The Chromatogram Noise is 0

Results Table:

Index	Name	Time	Width USP	Height	Area	Area
		[Min]	[Min]	[µV]	[µV.Min]	[%]
1	UNKNOWN	10.32	0.22	28.6	4.2	5.698
2	UNKNOWN	10.79	0.28	403.2	69.2	94.302
Total				431.8	73.3	100.000



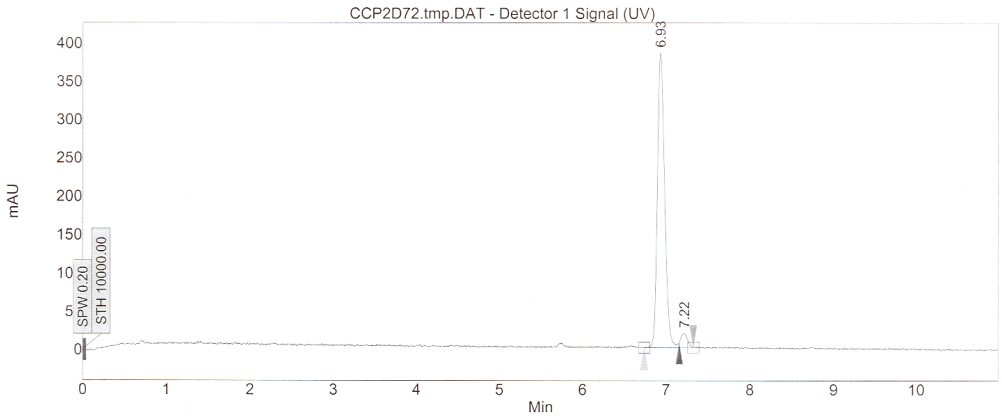
BergerSFC Chromatogram Report

Date: 12/20/2005
Time: 6:06:16 PM
Vial number: 1
Sequence name: SL-screen4
Filename: SL-IV-271

Method Name: ASH_MeOH_5-25
User Name: SFC User
Acquisition Date: 12/20/2005 5:53:14 PM

Run Information:
N.A.

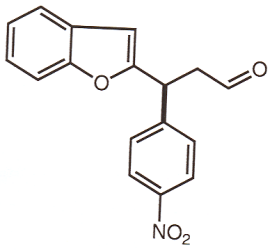
SL-IV-271:



The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.74	6.93	7.16	0.00	95.87	384.4	38.5	95.873
2	UNKNOWN	7.16	7.22	7.33	0.00	4.13	18.5	1.7	4.127
Total						100.00	402.9	40.2	100.000



91.7% ee

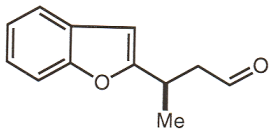
Mettl

BergerSFC Chromatogram Report

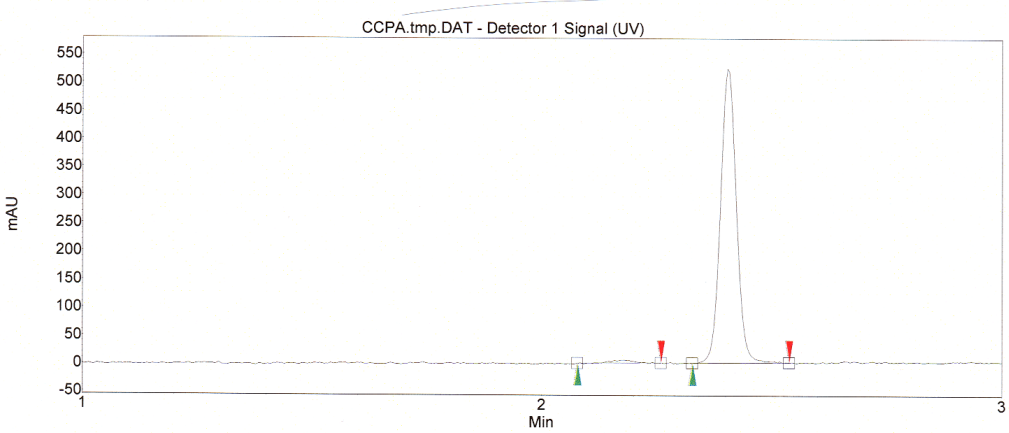
Date: 10/18/2007
Time: 3:59:57 PM
Vial number: 2
Sequence name: SL-screen5
Filename: SL-IV-312

Method Name: ASH_MeOH_5-50
User Name: SFC User
Acquisition Date: 12/20/2005 6:05:38 PM

Run Information:
N.A.



SL-IV-312:



The Chromatogram Noise is 0

Results Table:

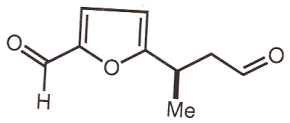
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.08	2.17	2.26	0.00	1.21	5.1	0.3	1.210
2	UNKNOWN	2.33	2.40	2.54	0.00	98.79	524.1	21.0	98.790
Total						100.00	529.1	21.3	100.000

BergerSFC Chromatogram Report

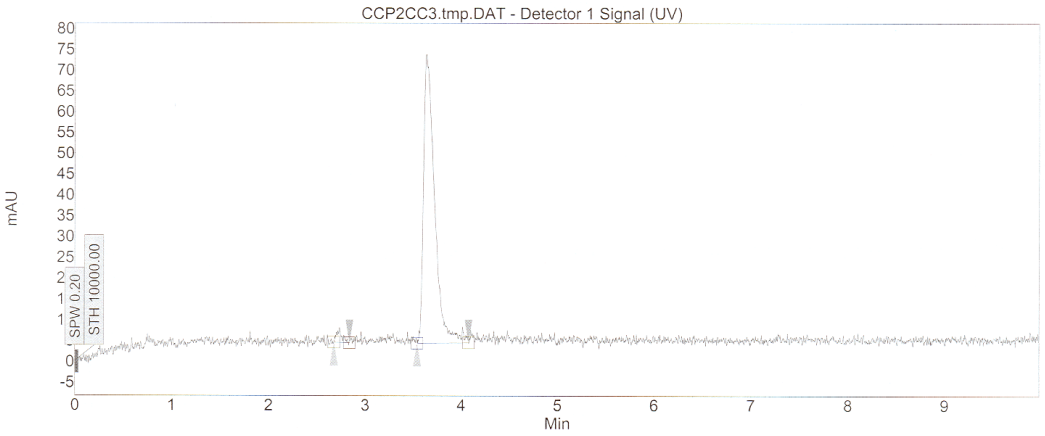
Date: 2/22/2006
Time: 11:09:53 AM
Vial number: 2
Sequence name: Nina4
Filename: SL-IV-943

Method Name: ASH_MeCN_5-10
User Name: SFC User
Acquisition Date: 2/22/2006 10:54:02 AM

Run Information:
N.A.



SL-IV-943:



The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	2.68	2.73	2.84	0.00	2.26	2.9	0.2	2.261
1	UNKNOWN	3.54	3.63	4.08	0.00	97.74	69.4	9.2	97.739
Total						100.00	72.2	9.4	100.000

95.5% ee

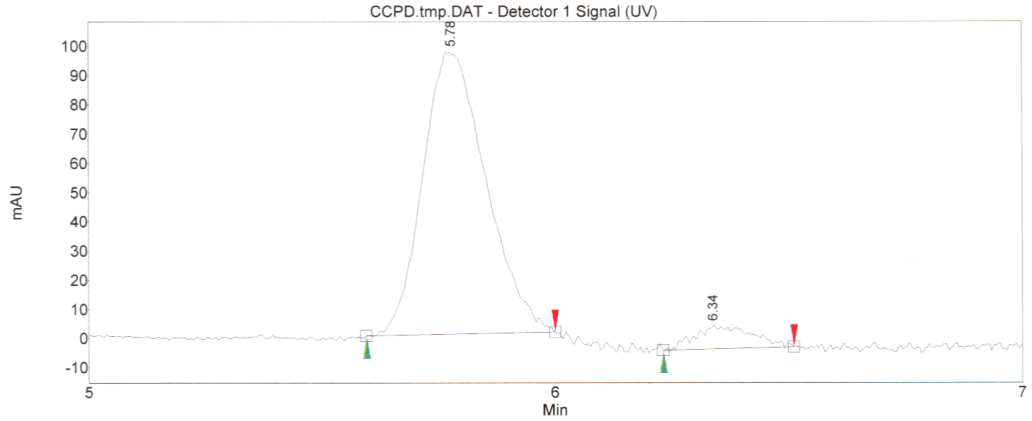
BergerSFC Chromatogram Report

Date: 10/18/2007
Time: 4:12:58 PM
Vial number: 1
Sequence name: Nina2
Filename: SL-IV-971

Method Name: ADH_MeOH_30-50
User Name: SFC User
Acquisition Date: 2/23/2006 10:23:54 PM

Run Information:
N.A.

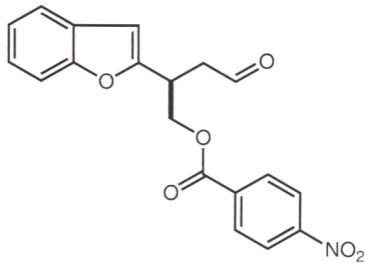
SL-IV-971:



The Chromatogram Noise is 0

Results Table:

Index	Name	Time	Width USP	Quantity	Height	Area	Area
		[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.78	0.25	93.21	96.0	15.2	93.209
2	UNKNOWN	6.34	0.20	6.79	7.5	1.1	6.791
Total				100.00	103.5	16.3	100.000



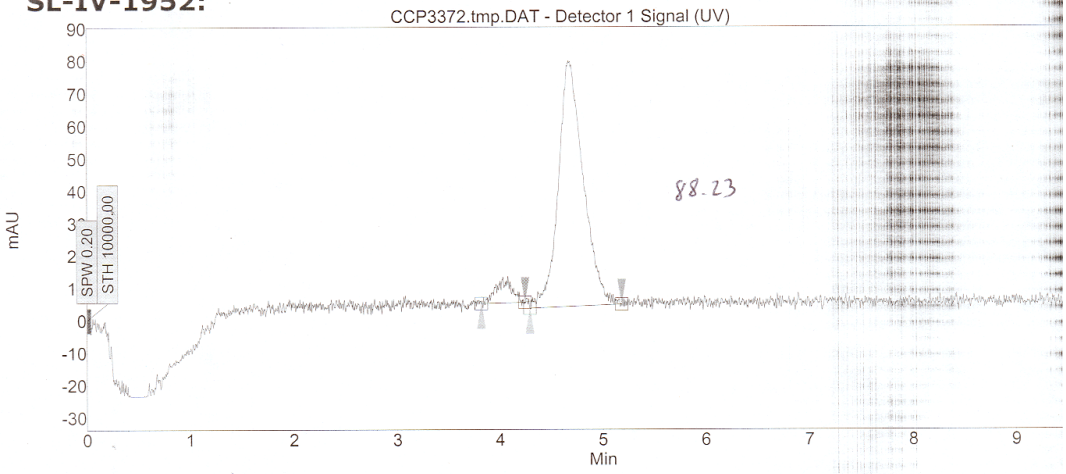
BergerSFC Chromatogram Report

Date: 6/5/2006
Time: 9:51:43 PM
Vial number: 8
Sequence name: sl-assay2
Filename: SL-IV-1952

Method Name: ASH_MeCN_5-10
User Name: SFC User
Acquisition Date: 6/5/2006 9:39:24 PM

Run Information:
N.A.

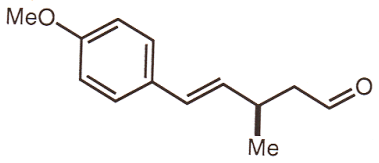
SL-IV-1952:



The Chromatogram Noise is 0

Results Table:

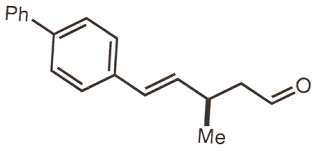
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.82	4.03	4.24	0.00	5.89	7.7	1.3	5.885
2	UNKNOWN	4.29	4.68	5.18	0.00	94.11	75.1	21.3	94.115
Total						100.00	82.8	22.6	100.000



BergerSFC Chromatogram Report

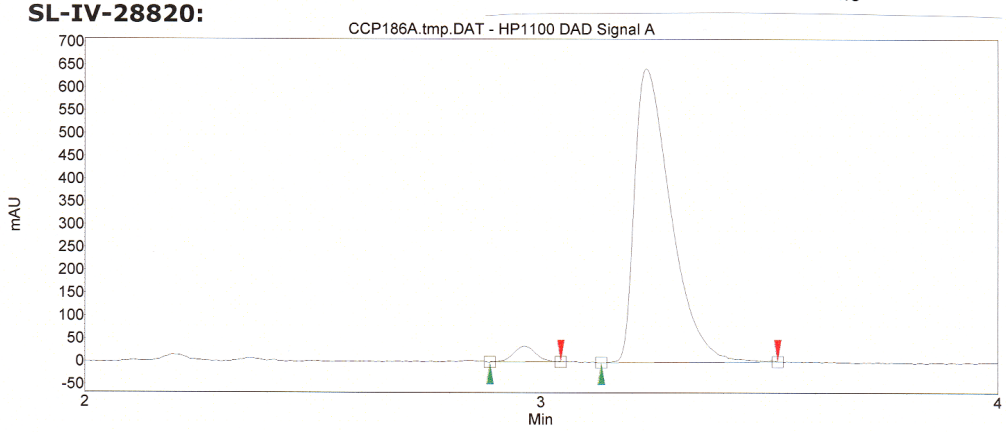
Date: 10/18/2007
Time: 3:10:53 PM
Vial number: 8
Sequence name: SL-1
Filename: SL-IV-28820

Method Name: OJH_MeCN_5-15r2
User Name: SFC User
Acquisition Date: 1/22/2007 2:33:14 PM



Run Information:
N.A.

SL-IV-28820:



The Chromatogram Noise is 0

Results Table:

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.89	2.96	3.04	0.00	3.20	34.8	2.0	3.203
2	UNKNOWN	3.13	3.23	3.52	0.00	96.80	643.8	59.4	96.797
Total						100.00	678.7	61.4	100.000