The Enantioselective Addition of 1-Fluoro-1-nitro(phenylsulfonyl)methane to Isatin-Derived Ketimines

Supporting Information

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Content

1 General information

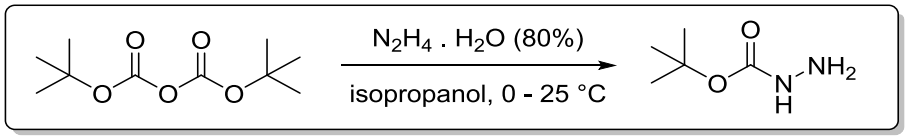
Chemicals and solvents were either purchased from commercial suppliers in p.a. purity or purified by standard method. Reactions were monitored by thin-layer chromatography (TLC), silica plates Merck 60 F 254 were used. Compounds were detected by irradiation with UV light and subsequently plates visualized by treatment detection reagent AMC or ninhydrin or vanillin or $KMnO_4$ followed by heating. The detection reagent AMC was prepared from phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 ml) and H_2O (940 ml). The detection solution of ninhydrin was prepared from ninhydrin (1.5 g) in 100 ml of n-butanol and then was added acetic acid (3 ml). The solution of vanilline was prepared from vanilline (15 g) in ethanol (250 ml) and conc. sulfuric acid (2.5 ml). Column chromatography was performed by using silica gel Fluka (40-63 µm). The solvents for column chromatography separation were purified by distillation. ^1H, ^{19}F and ^{13}C NMR spectra were recorded with Varian UNITY INOVA 300, Bruker AVANCE III 400 and Bruker AVANCE III 600. Chemical shifts are given in ppm relative to $CDCl_3$, and coupling constants *J* are given in Hz. The NMR spectra were recorded in $CDCl_3$ as solvent at room temperature, TMS served as internal standard (δ = 0.0 ppm) for ^1H NMR, $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR, and TFA was used as external standard for ^{19}F NMR. High-resolution mass spectra were recorded with a LCQ Fleet spectrometer. Chiral HPLC was carried out by using a Shimadzu chromatograph with SPD-M20A spectrophotometric detector. Chiral column Daicel Chiralpak AD was used for separation of enantiomers. Specific optical rotations were measured on AU-Tomatica polarimeter, Autopol III and as solvent was used $CHCl_3$. Specific optical rotations are given in concentrations *c* [g/100 mL]. Infrared spectroscopy spectra were measured on a Nicolet Avatar 370 FTIR. The method used for measuring was a diffuse reflectance (DRIFT) in KBr. IR absorptions are given in wavenumbers as cm^{-1}.

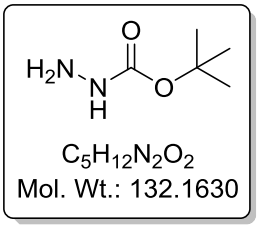
2 Preparation of Starting Materials

2.1 Preparation of Aza-Wittig reagents

tert-Butyl hydrazinecarboxylate (XA)

tert-Butyl hydrazinecarboxylate was prepared according to the following procedure (Schema 1).[1]





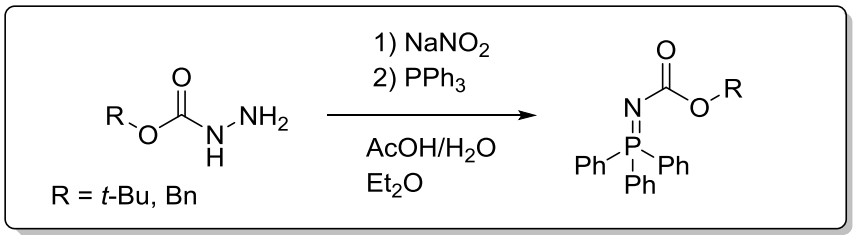
To a solution hydrazine monohydrate (80%, 3.25 g, 52.0 mmol) in 5 ml isopropanol was added dropwise a solution of Boc_2O (5.00 g, 23.0 mmol) in 25 ml isopropanol. After addition reaction mixture turned cloudy and stirring was continued at room temperature until complete disappearance of the starting material. The solvent was removed and residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Then CH_2Cl_2 was evaporated

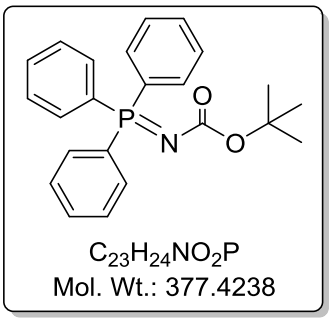
and product was obtained as white oil in yield 93 %. The produkt was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.06 (bs, 1H), 3.68 (s, 2H), 1.43 (s, 9H) ppm.

tert-Butyl (triphenyl-λ^5-phosphanylidene)carbamate (XB)

tert-Butyl (triphenyl-λ^5-phosphanylidene)carbamate was prepared according to the following procedure (Schema 2).[2]

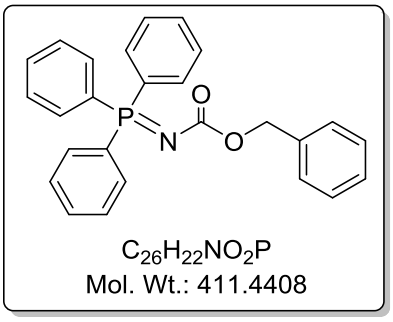




To solution of *tert*-Butyl hydrazinecarboxylate (1.0 g, 7.566 mmol) in 3.0 ml CH_3COOH and 6. 0 ml H_2O cooled to 0 °C was added $NaNO_2$ (0.574 g, 8.323 mmol) Reaction was stirred for 45 min at 0 °C. When we obtain full conversion of starting materials, then reaction mixture was extracted with Et_2O (2 x 25 ml). The combined organic layers were washed with 20 ml H_2O, 20 ml sat. aq. solution of $NaHCO_3$ and 20 ml sat. aq. solution of NaCl. The organic layer was dried by Na_2SO_4. The solution of azide in Et_2O was used in the next step. CAUTION: To avoid risks of explosion, do not warm the ethereal solution of the azide and do not concentrate to dryness! The ether solution of azide was cooled to 0 °C and then Ph_3P (1.9845g, 7,566 mmol) was added in small portion. We can see strong evolution of nitrogen occurred during the addition Ph_3P. The reaction was stirred for 1 h at 0 °C and then another 1 h at 25 °C. The product was obtained as precipitate (crystals) in yield 73 %, which was washed ice Et_2O and dried in vacuo.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77-7.70 (m, 6H), 7.57-7.51 (m, 3H), 7.48-7.42 (m, 6H) 1.37 (s, 9H) ppm.

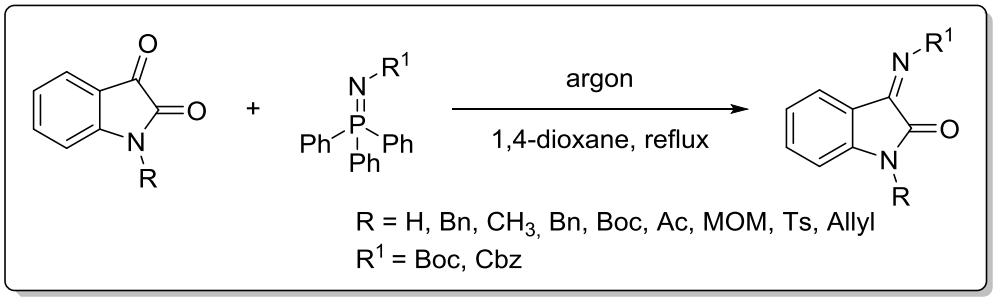
Benzyl (triphenyl-λ^5-phosphanylidene)carbamate (XC)



Benzyl (triphenyl-λ^5-phosphanylidene)carbamate was prepared according to the same procedure as *tert*-Butyl (triphenyl-λ^5-phosphanylidene)carbamate (Schema 2).[2] Product was obtained in yield 53 % as white solid.

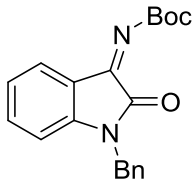
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77-7.70 (m, 6H), 7.58-7.53 (m, 3H), 7.48-7.42 (m, 6H), 7.29-7.24 (m, 5H), 5.06 (s, 2H) ppm.

2.2 General Procedure for the Synthesis of *N*-Alkoxycarbonyl Ketimines (A)



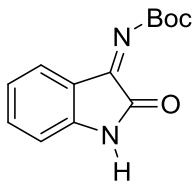
In an oven–dried Schlenk flask under argon atmosphere, isatin (10 mmol) and aza-Wittig reagent (11 mmol) were placed. After an injection of anhydrous 1,4-dioxane (10 mL), the mixture was heated under reflux until complete disappearance of the starting materials. Then the reaction was cooled to room temperature. After an evaporation of the volatile organic solvents, the crude residue was purified by column chromatography (silica gel, hexane/ethyl acetate) and afforded the resulting ketimine as described below.[3]

***tert*-Butyl (*Z*)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate (1a)**


$C_{20}H_{20}N_2O_3$
Mol. Wt.: 336.39

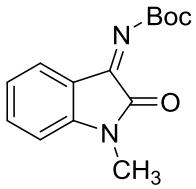
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1a** as yellow solid in 53 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (bs, 1H), 7.26-7.38 (m, 6H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.90 (s, 2H), 1.65 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{20}N_2O_3Na$ $[M + Na]^+$: 359.1372, found 359. The measured data correspond to the literature.[3]

***tert*-Butyl (*Z*)-(2-oxoindolin-3-ylidene)carbamate (1b)**


$C_{13}H_{14}N_2O_3$
Mol. Wt.: 246.27

Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1b** as yellow solid in 86 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 (bs, 1H), 7.64-7.62 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{13}H_{14}N_2O_3Na$ $[M + Na]^+$: 269.0902, found 269. The measured data correspond to the literature. [3]

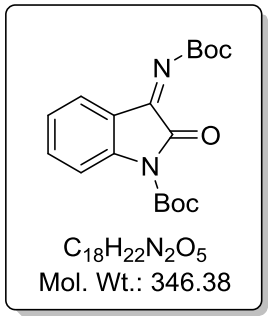
***tert*-Butyl (*Z*)-(1-methyl-2-oxoindolin-3-ylidene)carbamate (1c)**


$C_{14}H_{16}N_2O_3$
Mol. Wt.: 260.29

Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1c** as yellow solid in 74 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.0 Hz, 1H), 7.48 (dt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 6H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz,

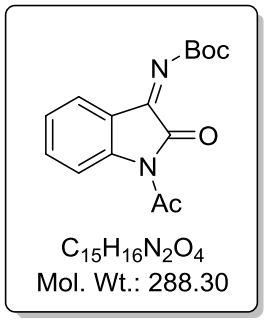
1H), 3.21 (s, 3H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{14}H_{16}N_2O_3Na$ $[M + Na]^+$: 283.1059, found 283. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-3-((*tert*-butoxycarbonyl)imino)-2-oxoindoline-1-carboxylate (1d)**



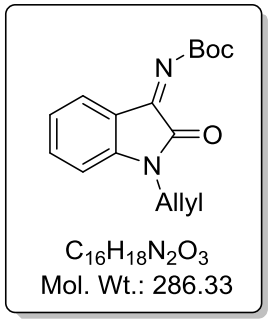
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1d** as yellow solid in 37 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 1.63 (s, 9H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{19}H_{23}N_2O_6Na$ $[M + MeOH + Na]^+$: 401.1689, found 401. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-acetyl-2-oxoindolin-3-ylidene)carbamate (1e)**



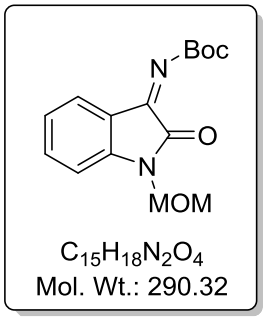
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1e** as yellow solid in 70 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 4.0 Hz, 1H), 7.29 (7, *J* = 8.0 Hz, 1H), 2.70 (s, 3H), 1.63 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{15}H_5N_2O_4$ $[M - H]^+$: 287.1032, found 287. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-allyl-2-oxoindolin-3-ylidene)carbamate (1f)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1f** as yellow solid in 75 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 4.0 Hz, 1H), 7.45 (dt, *J* = 8.0 Hz. *J'* = 4.0 Hz, 1H), 7.26-7.38 (m, 6H), 7.08 (t, *J* = 4.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.77-5.86 (m, 1H), 5.27-5.31 (m, 2H), 4.33 (s, 2H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{16}H_{28}N_2O_3Na$ $[M + Na]^+$: 309.1215, found 309. The measured data correspond to the literature. [3]

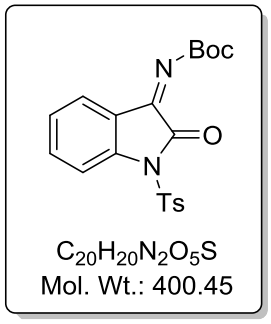
***tert*-Butyl (*Z*)-(1-(methoxymethyl)-2-oxoindolin-3-ylidene)carbamate (1g)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1g** as yellow solid in 81 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68 (bs, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 5.11 (s, 2H), 3.35 (s,

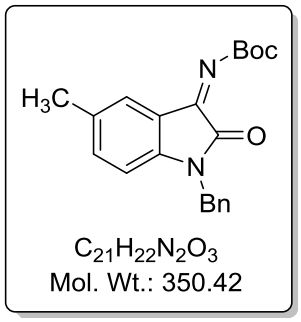
3H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{15}H_{18}N_2O_4Na$ $[M + Na]^+$: 313.1164, found 313. The measured data correspond to the literature.[3]

***tert*-Butyl (*Z*)-(2-oxo-1-tosylindolin-3-ylidene)carbamate (1h)**



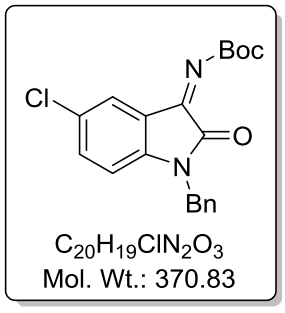
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1h** as yellow solid in 62 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0 Hz, 3H), 7.69 (bs, 1H), 7.59 (dt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 1.59 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{22}H_{22}N_2O_7SNa$ $[M + 2MeOH + Na]^+$: 487.1515, found 487. The measured data correspond to the literature.[3]

***tert*-Butyl (*Z*)-(1-benzyl-5-methyl-2-oxoindolin-3-ylidene)carbamate (1i)**



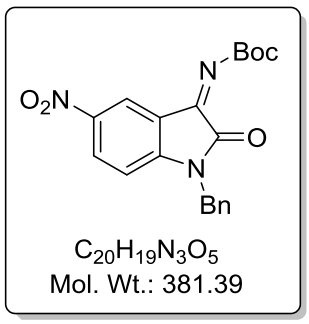
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1i** as yellow solid in 46 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46 (bs, 1H), 7.27-7.34 (m, 5H), 7.15 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 6.57-6.60 (m, 1H), 4.87 (s, 2H), 2.28 (s, 3H), 1.65 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{21}H_{22}N_2O_3Na$ $[M + Na]^+$: 373.1528, found 373. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)carbamate (1j)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (6:1 to 4:1) to give **1j** as yellow solid in 42 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62 (bs, 1H), 7.26-7.36 (m, 6H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.89 (s, 2H), 1.64 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{19}ClN_2O_3Na$ $[M + Na]^+$: 393.0982, found 393. The measured data correspond to the literature.[3]

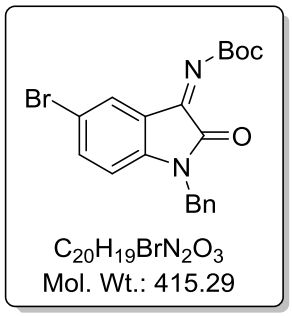
***tert*-Butyl (*Z*)-(1-benzyl-5-nitro-2-oxoindolin-3-ylidene)carbamate (1k)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1k** as yellow solid in 21 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.30 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.39-7.27 (m, 6H), 685 (d, *J* = 8.0 Hz, 1H), 4.97 (s, 2H),

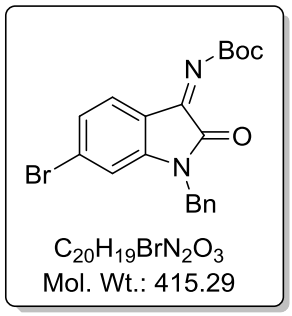
1.66 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{19}N_3O_5Na$ $[M + Na]^+$: 404.1222, found 404. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-benzyl-5-bromo-2-oxoindolin-3-ylidene)carbamate (1l)**



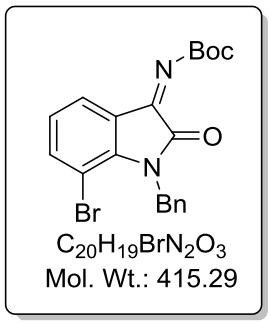
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1l** as yellow solid in 17 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 (bs, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27-7.36 (m, 5H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.89 (s, 2H), 1.64 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{19}N_2O_3Na$ $[M + 2H + Na]^+$: 439.0633, found 439. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-benzyl-6-bromo-2-oxoindolin-3-ylidene)carbamate (1m)**



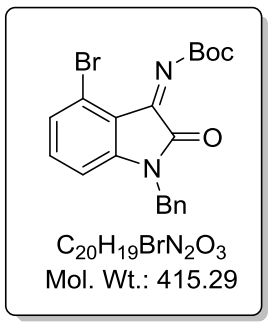
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1m** as yellow solid in 22 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 12.0 Hz, 1H), 7.40-7.31 (m, 5H), 7.24 (d, J = 12.0 Hz, 1H), 6.91 (s, 1H), 4.89 (s, 2H), 1.66 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{22}BrN_2O_3Na$ $[M + H_2 + Na]^+$: 439.0633, found 439. The measured data correspond to the literature. [3]

***tert*-Butyl (*Z*)-(1-benzyl-7-bromo-2-oxoindolin-3-ylidene)carbamate (1n)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1n** as yellow solid in 32 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 12.0 Hz, 1H), 7.55 (d, *J* = 12.0 Hz, 1H), 7.35-7.28 (m, 3H), 7.22 (d, *J* = 12.0 Hz, 2H), 6.97 (d, *J* = 12.0 Hz, 1H), 5.39 (s, 2H), 1.62 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{22}BrN_2O_3Na$ $[M + H_2 + Na]^+$: 439.0633, found 439. The measured data correspond to the literature. [3]

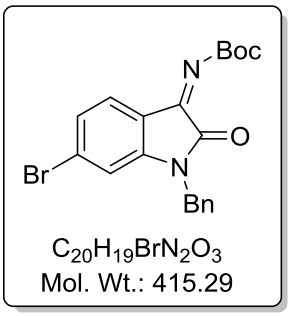
***tert*-Butyl (*Z*)-(1-benzyl-4-bromo-2-oxoindolin-3-ylidene)carbamate (1o)**



Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1o** as yellow solid in 50 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34-7.18 (m, 7H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.90 (s, 2H), 1.65 (s, 9H) ppm. **MS** (ESI) calcd. for

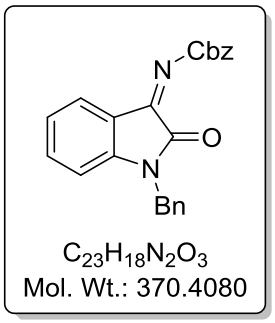
$C_{20}H_{22}BrN_2O_3Na$ [M + H_2 +Na]$^+$: 439.0633, found 439. The measured data correspond to the literature. [3]

tert-Butyl (_Z_)-(1-benzyl-6-bromo-2-oxoindolin-3-ylidene)carbamate (1o)



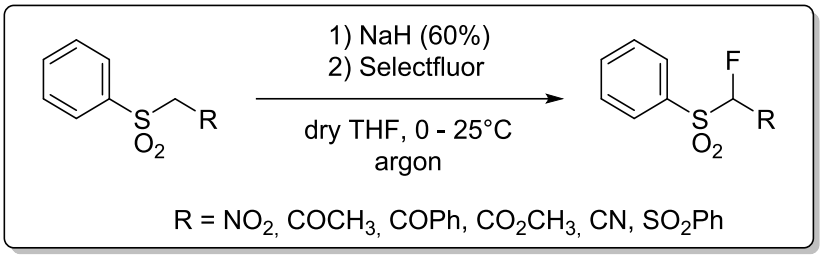
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1o** as yellow solid in 22 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 12.0 Hz, 1H), 7.40-7.31 (m, 5H), 7.24 (d, J = 12.0 Hz, 1H), 6.91 (s, 1H), 4.89 (s, 2H), 1.66 (s, 9H) ppm. **MS** (ESI) calcd. for $C_{20}H_{22}BrN_2O_3Na$ [M + H_2 +Na]$^+$: 439.0633, found 439. The measured data correspond to the literature. [3]

Benzyl (_Z_)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate (1p)



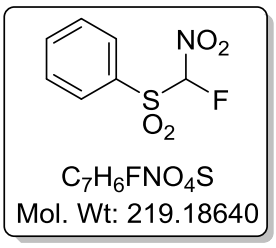
Product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1) to give **1p** as yellow solid in 55 % yield. **^{1}H NMR** (400 MHz, DMSO) δ = 7.59-7.45 (m, 2H), 7.43-7.21 (m, 10H), 7.13-6.94 (m, 2H), 5.31 (s, 2H), 4.90 (s, 2H) ppm. **MS** (ESI) calcd. for $C_{23}H_{18}N_2O_3Na$ [M + Na]$^+$: 393.1215, found 393. The measured data correspond to the literature. [3]

2.3 General Procedure for the Synthesis of α-Substituted ((Fluoro(methyl)sulfonyl)benzene (B)



To a stirring mixture of NaH (1.0 eq.) in dry THF (5 mL) was added 1-substutited (phenylsulfonyl)methane at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C overnight, and monitored by TLC and by ^{1}H NMR. Reaction was canceled adding DCM (20 mL). The mixture was washed with water (2 x 25 mL) and brine (2 x 25 mL). The organic phase was dried with $MgSO_4$, filtered and filtrate was concentrated under reduced pressure. The crude product was purified on silica gel by column chromatography to give product **2a-f** in good yield.

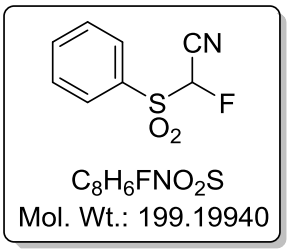
((Fluoro(nitro)methyl)sulfonyl)benzene (2a)



Compound **2a** was prepared by general procedure **B**. To a stirring mixture of NaH (2.485 mmol; 1.0 eq.) in dry THF (5 mL) was added nitro(phenylsulfonyl)methane (2.485 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (2.485 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C for 4 days, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2a** as white solid in 52 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0 Hz, 2H), 7.85 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.68 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 6.41 (d, *J* = 48.6 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.68, 131.38, 130.64 (2C), 129.92 (2C), 111.77 (d, *J* = 283.6 Hz, 1C) ppm. **^{19}F NMR** (376MHz, $CDCl_3$) δ = -141.60 (d, *J* = 48.9 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_7H_5FNO_4S$ $[M - H]^-$: 217.9923, found 218.

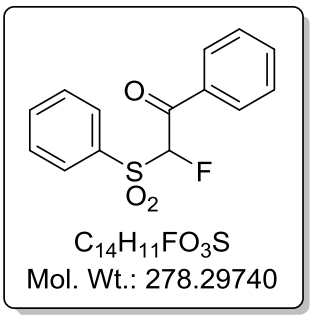
2-Fluoro-2-(phenylsulfonyl)acetonitrile (2b)



Compound **2b** was prepared by general procedure **B**. To a stirring mixture of NaH (2.816 mmol; 1.0 eq.) in dry THF (5 mL) was added 2-(phenylsulfonyl)acetonitrile (2.816 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (2.816 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C for 4 days, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2b** as white solid in 45 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.0 Hz, 2H), 7.86 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.70 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 5.69 (d, J = 48.0 Hz, 1F) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 136.46, 132.20, 130.58 (2C), 129.88 (2C), 109.75, (d, *J* = 29 Hz, 1C), 88.01 (d, *J* = 230.0 Hz, 1C) ppm. **^{19}F NMR** (376MHz, $CDCl_3$) δ = -178.72 (d, *J* = 48.9 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_8H_5FNO_2S$ $[M - H]^-$: 198.0025, found 198.

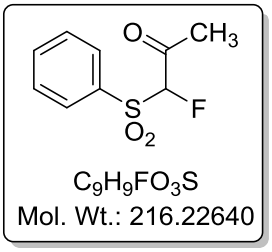
2-Fluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-one (2c)



Compound **2c** was prepared by general procedure **B**. To a stirring mixture of NaH (1.921 mmol; 1.0 eq.) in dry THF (5 mL) was added 1-phenyl-2-(phenylsulfonyl)ethan-1-one (1.921 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (1.921 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C overnight, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2c** as white solid in 63 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 7.88 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 7.74 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.68 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 48.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 175.25, 135.30 (2C), 135.03 (2C), 129.90 (2C), 129.80, 129.78, 129.37 (2C), 128.87 (2C), 100.29 (d, *J* = 231.0 Hz, 1C) ppm. **^{19}F NMR** (376MHz, $CDCl_3$) δ = -179.52 (d, J = 48.9 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_{14}H_{10}FO_3S$ $[M - H]^-$: 277.0335, found 277.

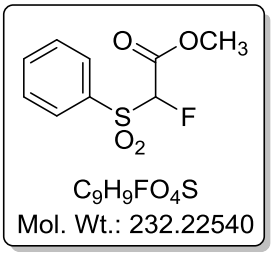
1-Fluoro-1-(phenylsulfonyl)propan-2-one (2d)



Compound **2d** was prepared by general procedure **B**. To a stirring mixture of NaH (2.522 mmol; 1.0 eq.) in dry THF (5 mL) was added 1-(phenylsulfonyl)propan-2-one (2.522 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (2.522 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C overnight, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2d** as white solid in 61 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 7.76 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 2H), 5.47 (d, *J* = 52.0 Hz, 1H), 2.36 (d, *J* = 4.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 175.22, 135.37 (2C), 139.65 (2C), 129.55 (3C), 101.43 (d, J = 232.0 Hz, 1C), 27.49 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -179.58 (qd, *J* = 48.9 Hz, *J'* = 3.8 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_9H_8FO_3S$ $[M - H]^-$: 215.0178, found 215.

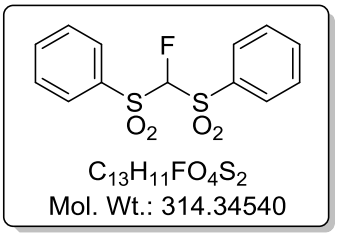
Methyl 2-fluoro-2-(phenylsulfonyl)acetate (2e)



Compound **2e** was prepared by general procedure **B**. To a stirring mixture of NaH (2.334 mmol; 1.0 eq.) in dry THF (5 mL) was added methyl 2-(phenylsulfonyl)acetate (2.334 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (2.334 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C overnight, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2e** as white solid in 56 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2 H), 7.76 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 2H), 5.59 (d, *J* = 48 Hz, 1H), 3.86 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.34, 135.38, 134.47, 129.76 (2C), 129.44 (2C), 97.26 (d, *J* = 231.0 Hz, 1C), 53.79 ppm. **^{19}F NMR** (376MHz, $CDCl_3$) δ = -180.47(d, *J* = 48.9 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_9H_9FO_4SNa$ $[M + Na]^+$: 255.0103, found 255.

Bis(phenylsulfonyl)fluoromethane (2f)

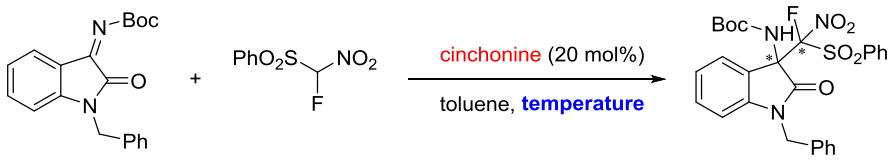


Compound **2f** was prepared by general procedure **B**. To a stirring mixture of NaH (1.687 mmol; 1.0 eq.) in dry THF (5 mL) was added bis(phenylsulfonyl)methane (1.687 mmol; 1.0 eq.) at 0 °C under argon atmosphere. After stirring for 2 h, a solution of Selectfluor (1.687 mmol; 1.0 eq.) in dry THF (5 mL) was added dropwise at 0 °C. Then reaction mixture was stirred at 25 °C overnight, and monitored by TLC and by ^{1}H NMR. After work up, product was purified by silica gel column chromatography with mobile phase hexane/ethyl acetate (7:1 to 3:1) to give **2f** as white solid in 52 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.0 Hz, 4H), 7.76 (tt, *J* = 8.0 Hz, *J'* = 4.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 4H), 5.73 (d, *J* = 44.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 135.69 (2C), 135.28 (2C), 130.15 (4C), 129.46 (4C), 105.69 (d, 264.0 Hz, 1C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -168.20 (d, *J* = 45.1 Hz, 1F) ppm. **MS** (ESI) calcd. for $C_{13}H_{10}FO_4S_2$ [M – H]$^-$: 313.0005, found 313.

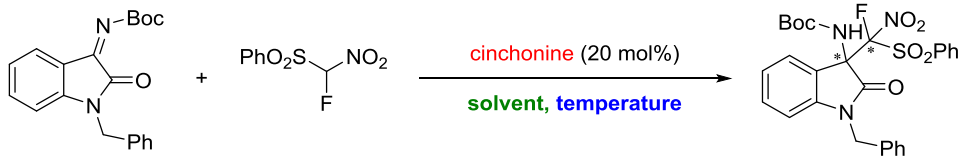
3 Screening and Optimization Studies

Table1: Temperature screening



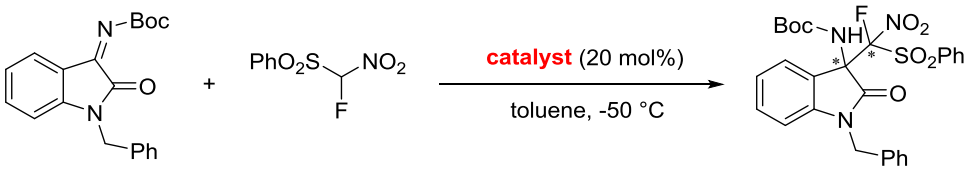
Entry	Temp [°C]	Time [h]	yield [%]	*d.r.*	*e.e.* [%]
1	+25	4 h	97	2:1	77/82
2	0	8 h	95	2,8:1	85/85
3	-50	18 h	85	3,3:1	96/95
4	-78	7 d	68	4:1	97/96

Table 2: Solvents screening



Entry	Solvent	Temp [°C]	Time [h]	yield [%]	*d.r.*	*e.e.* [%]	Problem
1	toluene	-50	19 h	82	3.5:1	96/96	-
2	heptane	-50	96 h	-	-	-	no reaction; solubility of ketimine
3	DCM	-50	19 h	57	2:1	79/86	-
4	Et_2O	-50	96 h	60	1:1	10/12	solubility of ketimine; 80% conv.
5	THF	-50	96 h	65	1.9:1	22/35	80% conversion
6	MTBE	-50	96 h	75	3:1	65/63	-
7	acetone	-50	96 h	26	1.5:1	12/18	solubility of ketimine; 65% conv.
8	MeOH	-50	96 h	-	-	-	no reactinon; solubility of ketimine
9	EtOAc	-50	96 h	18	2.8:1	61/63	solubility of ketimine; 30% conv.
10	$CHCl_3$	-50	19 h	84	3:1	88/89	-
11	DMF	-50	96 h	-	-	-	no reaction
12	toluene	0	8 h	95	2.8:1	85/85	-
13	*o*-xylene	0	8 h	83	2.9:1	86/85	-
14	toluene	+25	4 h	97	2:1	77/82	-
15	benzene	+25	4 h	99	1.4:1	74/83	-
16	1,4-dioxane	+25	24 h	92	1:1	12/39	-
17	DMSO	+25	96 h	-	-	-	no reaction

Table 3: Catalysts screening and catalyst loading



	Entry	Catalyst	Temp [°C]	Time [d]	yield [%]	*d.r.*[a]	*e.e.* [%]
	1	-	+25	7 d	-	-	-
	2	DABCO	+25	1 d	62	3:1	racemic
	3	QN	-50	17 h	64	3.4:1	-51/-47
	4	QD	-50	17 h	71	3:1	77/83
	5	CN	-50	18 h	82	3.5:1	96/96
Catalysts	**6**	CD	-50	24 h	97	3.5:1	-33/-31
	7	Takemoto's	-50	18 h	96	3.3:1	-27/-25
	8	Soós's I with QN	-50	18 h	96	3.7:1	64/56
	9	Soos's II with CN	-50	20 h	91	5.1:1	-71/-67
	10	Soós's III with CD	-50	20 h	96	5.9:1	70/62
	11	β-ICP	-50	24 h	94	5.3:1	-33/+56
	12	$(DHQ)_2AQN$	-50	24 h	90	4:1	35/28
	13	Rawal's with QN	-50	5 d	-	-	-
	14	Rawal's with CN	-50	7d	76	4.5:1	-75/-16
	15	CN (10 mol%)	-50	24 h	80	3.5:1	97/95
Catalysts loading	**16**	CN (5 mol%)	-50	24 h	24	3.7:1	97/96
	17	CN (2.5 mol%)	-50	24 h	24	3.6:1	97/95
	18	QN	25	18 h	98	1.5:1	-3/-3
Cinchona Catalysts at 25 °C	**19**	CN	25	4 h	97	2:1	77/82
	20	QD	25	4 h	94	1.2:1	19/62
	21	CD	25	4 h	93	1.6:1	-60/-70

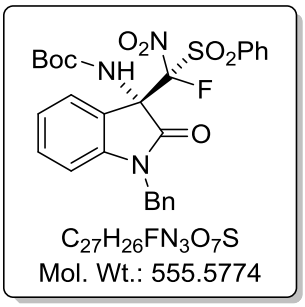
4 The Enantioselective Addition of 1-Fluoro-1-nitro(phenylsulfonyl)methane to Isatine-Derived Ketimines

4.1 General procedure (C)

In a Schlenk flask, chiral catalyst CN (0.02 mmol, 20 mol%) and sulfone **2a-f** (0.11 mmol, 1.1 eq.) were placed. After an injection of toluene (0.5 mL) reaction mixture was cold to -50 °C. Then ketamine **1a-p** (0.10 mmol, 1.0 eq.) was added in 1.0 mL of toluene at -50 °C. After that the mixture was stirred until complete disappearance of the ketamine (monitored by TLC and ^{1}H NMR), the mixture was purified by flash chromatography (silica gel, hexane/ethyl acetate) and afforded the resulting product as described below.

4.2 Characterization data for new compounds

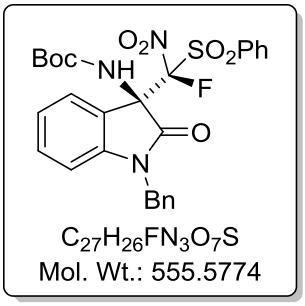
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a)



Adduct **3a** was prepared from 33.6 mg (0.10 mmol) ketimine **1a** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3a** was obtained as colorless oil in 83.6% yield (46.4 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.06 (dd, *J* = 12.0 Hz, *J'* = 6.0 Hz, 2H), 7.76 (dt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.59 (dt, *J* = 12Hz, *J'* = 6.0 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.05 (d, *J* = 6.0 Hz, 1H), 6.96 (t, *J* = 6.0 Hz, 1H), 6.82 (s, 1H), 6.66 (d, *J* = 6.0 Hz, 1H), 5.05 (d, *J* = 18.0 Hz, 1H), 4.59 (d, *J* = 18.0 Hz, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.15, 152.80, 143.94, 136.38, 134.94, 133.24, 131.85 (2C), 131.29, 129.17 (2C), 128.73 (2C), 127.70, 127.31 (2C), 123.94, 123.48, 122.47, 118.75 (d, *J* = 302.0 Hz, 1C), 109.69, 81.53, 65.6 (d, *J* = 25.8 Hz, 1C), 44.83, 28.05 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.43 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -9.3° (c = 0.755 in $CHCl_3$). **IR** (KBr): ν = 3428, 2976, 2926, 2849, 1725, 1611, 1590, 1489, 1469, 1450, 1393, 1360, 1277, 1255, 1159, 1080, 1014, 784, 754, 721, 698, 684, 617, 565, 545, 524 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{26}FN_3O_7S$ [M + Na] = 578.13677, found: 578.13686. **HPLC analysis** *ee (major diastereoisomer)* = 96 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 207 nm, retention time: t_{major} = 15.023 min, t_{minor} = 7.857 min).

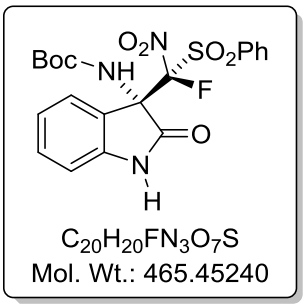
***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a')**



Adduct **3a'** was prepared from 33.6 mg (0.10 mmol) ketimine **1a** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3a'** was obtained as colorless oil in 11.9% yield (6.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 6.0 Hz, 2H), 7.79 (d, *J* = 6.0 Hz, 2H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.35 – 7.32 (m, 4H), 7.30 – 7.27 (m, 2H), 7.12 (t, *J* = 6.0 Hz, 1H), 6.98 (s, 1H), 6.71 (d, *J* = 6.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.37, 152.72, 144.10, 136.79, 134.92, 131.84, 131.17, 131.06 (2C), 129.70 (2C), 128.81(2C), 127.73, 127.33 (2C), 127.03, 122.79, 122.25, 118.14 (d, *J* = 285.4 Hz, 1C), 109.76, 81.51, 65.82 (d, *J* = 27.2 Hz, 1C), 44.91, 28.09 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.85 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +35.6° (c = 0.745 in $CHCl_3$). **IR** (KBr): ν = 3410, 3065, 2980, 29296, 1728, 1610, 1591, 1488, 1470, 1450, 1352, 1276, 1255, 1157, 1080, 1014, 909, 879, 840, 795, 754, 724, 698, 683, 604, 572, 550, 526, 460 cm^{-1}.**HRMS** (ESI) m/z calcd for $C_{27}H_{26}FN_3O_7S$ [M + Na] = 578.13677, found: 578.13687. **HPLC analysis** *ee (minor diastereoisomer)* = 96 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 206 nm, retention time: t_{major} = 36.006 min, t_{minor} = 9.223 min).

***tert*-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b)**

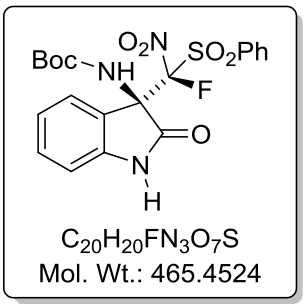


Adduct **3b** was prepared from 24.6 mg (0.10 mmol) ketimine **1b** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3b** was obtained as colorless oil in 70.3 % yield (32.7 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 6.0 Hz, 2H), 7.95 (s, 1H), 7.76 (tt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.27 (t, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.96 (d, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 6.0 Hz, 2H), 1.31 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.98, 152.92, 141.83, 136.47, 133.06, 131.61, 131.42, 129.31 (2C), 129.01, 128.21, 124.32, 123.48, 122.82, 110.59, 81.86, 65.63 (d, *J* = 37.8 Hz, 1C), 28.03 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 122.03 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +17.9° (c = 1.395 in $CHCl_3$). **IR** (KBr): ν = 3409, 3296, 2981, 2929, 1760, 1728, 1705, 1619, 1588, 1500, 1475, 1450, 1394, 1367, 1279, 1256, 1159, 1078, 1044, 1019, 912, 847, 795, 753, 717, 683, 635, 604, 574, 543, 522, 459 cm^{-1}. **HRMS** (ESI) m/z

calcd for $C_{20}H_{20}FN_3O_7S$ [M + Na] = 488.08982, found: 488.08988. **HPLC analysis** *ee (major diastereoisomer)* = 98,4 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 226 nm, retention time: t_{major} = 14.537 min, t_{minor} = 12.208 min).

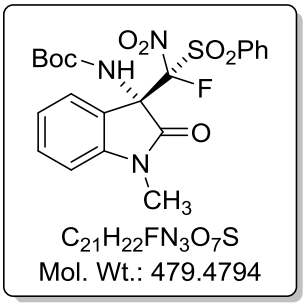
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')



Adduct **3b'** was prepared from 24.6 mg (0.10 mmol) ketimine **1b** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3b'** was obtained as colorless oil in 22.4 % yield (10.4 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 6.0 Hz, 2H), 7.79 (t, *J* = 6.0 Hz, 1H), 7.75 (d, *J* = 6.0 Hz, 1H), 7.71 (s, 1H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.35 (t, *J* = 6.0 Hz, 1H), 7.14 (t, *J* = 6.0 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 6.0 Hz, 1H), 1.33 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.13, 152.89, 141.77, 136.82, 131.74, 131.32, 131.02 (2C), 129.69 (2C), 127.34, 122.85, 122.58, 117.95 (d, *J* = 285.4 Hz, 1C), 112.22, 110.42, 81.83, 65.77 (d, *J* = 25.7 Hz, 1C), 28.05 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 122.08 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -32.8° (c = 0.320 in $CHCl_3$). **IR** (KBr): ν = 3377, 3101, 3067, 2979, 2929, 1745, 1610, 1595, 1490, 1470, 1448, 1390, 1365, 1345, 1320, 1280, 1256, 1156, 1108, 1077, 1042, 1015, 987, 919, 891, 841, 796, 769, 725, 687, 621, 574, 528, 509, 490, 452 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{20}H_{20}FN_3O_7S$ [M + Na] = 488.08982, found: 488.089457. **HPLC analysis** *ee (minor diastereoisomer)* = 73,8 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 206 nm, retention time: t_{major} = 14.929 min, t_{minor} = 17.929 min).

tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c)

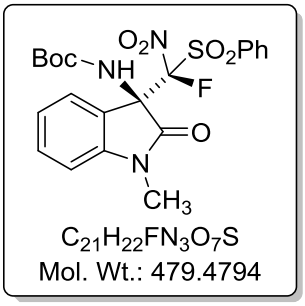


Adduct **3c** was prepared from 26.0 mg (0.10 mmol) ketimine **1c** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3c** was obtained as colorless oil in 79.1% yield (37.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (dt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.76 (t, *J* = 6.0 Hz, 1H), 7.58 (tt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 2H), 7.37 (td, J = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.10 (d, *J* = 6.0 Hz, 1H), 6.99 (t, *J* = 6.0 Hz, 1H), 6.83 (d, *J* = 6.0 Hz, 1H), 6.61 (s, 1H), 3.20 (s, 3H), 1.27 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.74, 152.59, 144.79, 136.32, 133.13, 131.44 (2C), 131.42, 129.27 (2C), 124.37, 123.35, 122.38, 118.82 (d, *J* = 288.4 Hz, 1C), 108.70, 81.47, 65.16 (d, *J* =

25.8 Hz, 1C), 27.96 (3C), 27.10 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.82 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -11.4° (c = 1.055 in $CHCl_3$). **IR** (KBr): ν = 3408, 3064, 2987, 2936, 1747, 1716, 1613, 1590, 1491, 1471, 1448, 1390, 1370, 1349, 1278, 1257, 1159, 1128, 1104, 1080, 1044, 895, 843, 795, 760, 724, 689, 608, 571, 536, 527, 465. cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{21}H_{22}FN_3O_7S$ [M + Na] = 502.10547, found: 502.10564. **HPLC analysis** *ee (major diastereoisomer)* = 94 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 211 nm, retention time: t_{major} = 21.162 min, t_{minor} = 14.467 min).

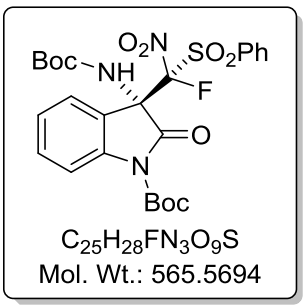
tert-Butyl ((_R_)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c')



Adduct **3c'** was prepared from 26.0 mg (0.10 mmol) ketimine **1c** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3c'** was obtained as colorless oil in 11.1 % yield (5.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 6.0 Hz, 2H), 7.77 (d, *J* = 6.0 Hz, 2H), 7.59 (t, *J* = 12.0 Hz, 2H), 7.43 (t, *J* = 12.0 Hz, 1H), 7.15 (t, *J* = 12.0 Hz, 1H), 6.87 (d, *J* = 12.0 Hz, 2H), 3.24 (s, 3H), 1.29 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.08, 151.62, 143.83, 135.73, 130.83, 130.31 (2C), 128.64 (2C), 126.01, 121.79, 121.18, 117.05 (d, *J* = 285.4 Hz, 1C), 107.62, 80.42, 64.62 (d, *J* = 25.8 Hz, 1C), 27.02 (3C), 26.14 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 122.00 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +54.5° (c = 0.275 in $CHCl_3$). **IR** (KBr): ν = 3430, 3068, 2979, 2926, 1740, 1611, 1589, 1493, 1493, 1473, 1450, 1393, 1356, 1276, 1255, 1159, 1129, 1076, 1013, 975, 893, 834, 784, 754, 719, 685, 616, 565, 543, 526, 464 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{21}H_{22}FN_3O_7S$ [M + Na] = 502.1162, found: 520.10569. **HPLC analysis** *ee (minor diastereoisomer)* = 93 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 208 nm, retention time: t_{major} = 25.287 min, t_{minor} = 15.879 min).

tert-Butyl (_S_)-3-((_tert_-butoxycarbonyl)amino)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d)

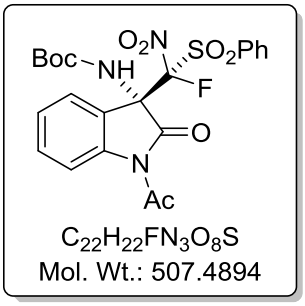


Adduct **3d** was prepared from 34.6 mg (0.10 mmol) ketimine **1d** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3d** was obtained as colorless oil in 76.3% yield (43.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 6.0 Hz, 1H), 7.87 (d, *J* = 6.0 Hz, 1H), 7.75 (t, *J* = 6.0 Hz, 1H), 7.57 (t, *J* = 12.0 Hz,

2H), 7.38 (dt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.08-.7.03 (m, 2H), 6.73 (s, 1H), 1.56 (s, 9H), 1.25 (s, 9H) ppm. **^{13}C NMR** (600 MHz, $CDCl_3$) δ = 166.45, 152.56, 148.31, 140.98, 136.36, 132.96, 131.62 (2C), 131.58, 129.25 (2C), 125.16, 123.51, 121.57, 118.33 (d, *J* = 287.0 Hz, 1C), 117.38, 115.52, 84.87, 82.08, 65.60 (d, *J* = 25.7 Hz, 1C), 27.97 (3C), 27.88 (3C). ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.24 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -9.3° (c = 1.080 in $CHCl_3$). **IR** (KBr): ν = 2981, 2933, 1810, 1727, 1714, 1590, 1499, 1479, 1450, 1395, 1371, 1355, 1313, 1281, 1250, 1151, 1074, 1008, 840, 794, 756, 716, 685, 598, 573, 561, 528 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}FN_3O_9S$ [M + Na] = 588.14225, found: 588.14251. **HPLC analysis** *ee (major diastereoisomer)* = 96 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 95:5, 0.5 mL/min, λ = 190 nm, retention time: t_{major} = 18.175 min, t_{minor} = 17.021 min).

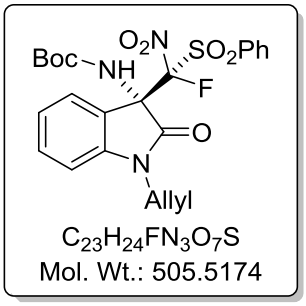
tert-Butyl ((*S*)-1-acetyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e)



Adduct **3e** was prepared from 28.8 mg (0.10 mmol) ketimine **1e** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3e** was obtained as colorless oil in 69.4 % yield (35.2 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 12.0 Hz, 1H), 7.86 (d, *J* = 12.0 Hz, 2H), 7.75 (dt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.55 (d, *J* = 6.0 Hz, 2H), 7.41 (t, *J* = 6.0 Hz, 1H), 7.08 (t, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.62 (s, 1H), 2.59 (s. 3H), 1.28 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.00, 169.2 (d), 152.69, 141.31, 136.43, 132.70, 131.79, 131.26 (2C), 129.41 (2C), 125.86, 123.47, 121.72, 118.25 (d, *J* = 286.9 Hz, 1C), 116.90,82.35, 65.45 (d, *J* = 22.7 Hz, 1C), 27.88 (3C), 26.23 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.11 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -50.9° (c = 0.845 in $CHCl_3$). **IR** (KBr): ν = 3434, 2985, 2938, 1789, 1714, 1590, 1490, 1475, 1446, 1370, 1334, 1310, 1275, 1171, 1158, 1103, 1080, 1039, 1015, 910, 845, 794, 777, 716, 685, 610, 597, 568, 544, 471, 439 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{22}H_{22}FN_3O_8S$ [M + Na] = 530.10038, found: 530.10055. **HPLC analysis** *ee (major diastereoisomer)* = 94 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 95:5, 1.0 mL/min, λ = 220 nm, retention time: t_{major} = 13.7656 min, t_{minor} = 12.316 min).

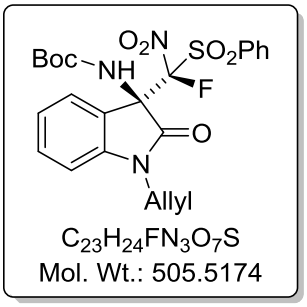
***tert*-butyl ((*S*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f)**



Adduct **3f** was prepared from 28.6 mg (0.10 mmol) ketimine **1f** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3f** was obtained as colorless oil in 83.4 % yield (42.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 12.0 Hz, *J''* = 6.0 Hz, 2H), 7.75 (tt, *J* = 12.0 Hz, *J''* = 6.0 Hz, 1H), 7.57 (t, *J* = 6.0 Hz, 2H), 7.32 (t, *J* = 6.0 Hz, 1H), 7.09 (d, *J* = 6.0 Hz, 1H), 6.97 (t, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 6.0 Hz, 1H), 6.68 (s, 1H), 5.79-5.73 (m, 1H), 5.22 (dd, *J* = 54.0 Hz, *J''* = 18.0 Hz, 2H), 4.45 (dd, *J* = 18.0 Hz, *J''* = 6.0 Hz, 1H), 4.11 (dd, *J* = 18.0 Hz, *J''* = 6.0 Hz, 1H), 1.29 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.56, 152.66, 144.02, 136.32, 133.15, 131.58 (2C), 131.26, 130.51, 129.22 (2C), 124.25, 123.32, 122.37, 118.79 (d, *J* = 286.9 Hz, 1C), 117.95, 109.58, 81.46, 65.26 (d, *J* = 25.8 Hz, 1C), 43.26, 28.02 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.62 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +1.6° (c = 1.825 in $CHCl_3$). **IR** (KBr): ν = 3377, 3101, 3067, 2979, 2929, 1746, 1716, 1610, 1595, 1490, 1470, 1448, 1390, 1365, 1345, 1320, 1280, 1256, 1156, 1108, 1077, 1042, 1015, 987, 919, 891, 841, 796, 763, 725, 687, 621, 574, 528, 509, 490, 452 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}FN_3O_7S$ [M + Na] = 528.12112, found: 528.12121. **HPLC analysis** *ee (major diastereoisomer)* = 96 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 95:5, 1.0 mL/min, λ = 215 nm, retention time: t_{major} = 24.081 min, t_{minor} = 13.147 min).

***tert*-Butyl ((*R*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')**

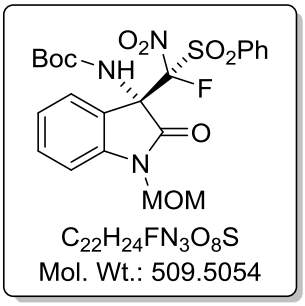


Adduct **3f'** was prepared from 28.6 mg (0.10 mmol) ketimine **1f** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3f'** was obtained as colorless oil in 6.1 % yield (3.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 12.0 Hz, 2H), 7.78 (m, 2H), 7.58 (dt, *J* = 12.0 Hz, *J''* = 6.0 Hz, 2H), 7.38 (dt, *J* = 12.0 Hz, *J''* = 6.0 Hz, 1H), 7.14 (dt, *J* = 12.0 Hz, *J''* = 6.0 Hz, 1H), 6.90 (s, 1H), 6.85 (d, *J* = 6.0 Hz, 1H), 5.86-5.80 (m, 1H), 5.28 (dd, *J* = 54.0 Hz, *J''* = 18.0 Hz, 2H), 4.53 (dd, *J* = 12.0 Hz, *J''* = 6.0 Hz, 1H), 4.16 (dd, *J* = 12.0 Hz, *J''* = 6.0 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.67, 152.44, 143.89, 136.54, 131.61, 130.94, 130.79 (2C), 130.38, 129.44 (2C), 126.82, 122.49, 121.97, 117.85 (d, *J* = 285.4 Hz, 1C), 117.74, 109.34,

81.21, 65.45 (d, *J* = 25.7 Hz, 1C), 43.04, 27.83 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.96 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -29.0° (c = 0.500 in $CHCl_3$). **IR** (KBr): ν = 3542, 3485, 3464, 3416, 2979, 2931, 1733, 1710, 1634, 1616, 1594, 1488, 1446, 1378, 1366, 1359, 1324, 1281, 1254, 1159, 1108, 1070, 1042, 987, 919, 892, 843, 797, 765, 722, 689, 6, 526, 490, 452 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{23}H_{24}FN_3O_7S$ [M + Na] = 528.12112, found: 528.12135. **HPLC analysis** *ee (minor diastereoisomer)* = 95 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 95:5, 1.0 mL/min, λ = 205 nm, retention time: t_{major} = 36.880 min, t_{minor} = 14.990 min).

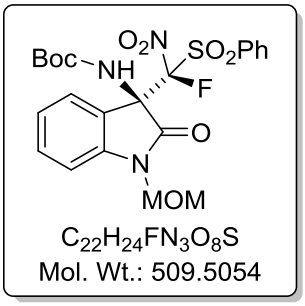
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g)



Adduct **3g** was prepared from 29.0 mg (0.10 mmol) ketimine **1g** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3g** was obtained as colorless oil in 77.8% yield (39.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 6.0 Hz, 2H), 7.76 (t, *J* = 6.0 Hz, 1H), 7.58 (t, *J* = 6.0 Hz, 2H), 7.36 (t, *J* = 6.0 Hz, 1H), 7.03 (m, 3H), 6.77 (s, 1H), 5.13 (d, *J* = 12.0 Hz, 1 H)), 5.03 (d, *J* = 12.0 Hz, 1H), 3.23 (s, 3H), 1.30 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.38, 152.72, 143.13, 136.32, 133.08, 131.62 (2C), 131.49, 129.19 (2C), 123.88, 123.86, 121.90, 118.49 (d, *J* = 286.9 Hz, 1C), 110.09, 81.57, 72.26, 65.74 (d, *J* = 25.7 Hz, 1C), 56.44, 27.98 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.66 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +12.7° (c = 1.340 in $CHCl_3$). **IR** (KBr): ν = 3389, 2978, 2932, 2847, 1748, 1720, 1612, 1596, 1489, 1471, 1449, 1392, 1347, 1256, 1235, 1194, 1157, 1124, 1106, 1077, 1026, 917, 839, 764, 724, 688, 618, 597, 574, 565, 529, 509, 452 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{22}H_{24}FN_3O_8S$ [M + Na] = 532.11603, found: 532.11614. **HPLC analysis** *ee (major diastereoisomer)* = 93 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 210 nm, retention time: t_{major} = 11.302 min, t_{minor} = 8.245 min).

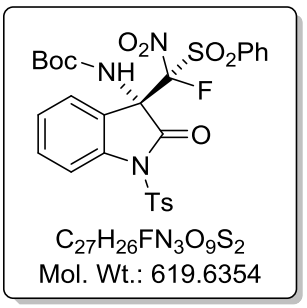
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g')



Adduct **3g'** was prepared from 29.0 mg (0.10 mmol) ketimine **1g** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3g'** was obtained as colorless oil in 16.0 % yield (8.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (t, *J* = 6.0 Hz, 2H), 7.78 (t, *J* = 6.0 Hz, 2H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.42 (t, *J* = 6.0 Hz, 1H), 7.19 (t, *J* = 6.0 Hz, 1H), 7.08 (d, *J* = 6.0 Hz, 1H), 6.96 (s, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 3.38 (s, 3H), 1.31 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.71, 152.72, 143.25, 136.81, 131.75, 131.41, 131.00 (2C), 129.68 (2C), 126.93, 123.23, 121.75, 117.95 (d, *J* = 285.4 Hz, 1C), 110.06, 81.58, 72.29, 66.09 (d, *J* = 27.2 Hz, 1C), 56.67, 28.04 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.82 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -40.5° (c = 0.605 in $CHCl_3$). **IR** (KBr): ν = 3429, 3067, 2979, 2933, 2849, 1747, 1724, 1611, 1590, 1489, 1470, 1450, 1394, 1358, 1277, 1255, 1190, 1160, 1121, 1100, 1079, 1026, 975, 913, 833, 785, 756, 721, 684, 618, 561, 544, 523, 489, 460 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{22}H_{24}FN_3O_8S$ [M + Na] = 532.11603, found: 532.11611. **HPLC analysis** *ee (minor diastereoisomer)* = 93 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 207 nm, retention time: t_{major} = 14.633 min, t_{minor} = 8.684 min).

tert-Butyl ((*S/R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h)



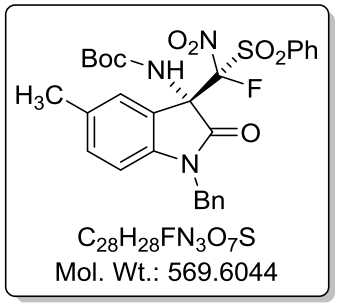
Adduct **3h** was prepared from 40.0 mg (0.10 mmol) ketimine **1h** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3h** was obtained as colorless oil in 31% yield (19.2 mg).

^{1}H NMR major diastereoisomer (600 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 6.0 Hz, 4H), 7.82 (d, *J* = 6.0 Hz, 2H), 7.79 (t, *J* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.41 (t, *J* = 6.0 Hz, 1H), 7.26-7.25 (m, 1H), 7.10 (t, *J* = 12.0 Hz, 1H), 6.98 (d, *J* = 6.0 Hz, 1H), 6.77 (s, 1H), 2.39 (s, 3H), 1.14 (s, 9H) ppm. **^{13}C NMR** major diastereoisomer (151 MHz, $CDCl_3$) δ = 167.37, 152.57, 145.64, 140.56, 136.67, 134.11, 132.48, 131.93, 131.54 (2C), 130.99, 129.71, 129.43 (2C), 128.43 (2C), 125.52, 123.83, 122.02, 117.48 (d, *J* = 286.4 Hz, 1C), 113.79, 81.99, 65.91 (d, *J* = 27.2 Hz, 1C), 27.74 (3C), 21.67 ppm. **^{19}F NMR** major diastereoisomer (376 MHz, $CDCl_3$) δ = 121.36 (s, 1F) ppm.

^{1}H NMR minor diastereoisomer (600 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 12.0 Hz, 1H), 7.88 (d, *J* = 6.0 Hz, 4H), 7.78 (t, *J* = 12.0 Hz, 1H), 7.70 (t, *J* = 6.0 Hz, 2H), 7.62-7.56 (m, 2H), 7.48 (t, *J* = 6.0 Hz, 1H), 7.25-7.24 (m, 3H), 6.85 (s, 1H), 2.37 (s, 3H), 1.14 (s, 9H) ppm. **^{13}C NMR** minor diastereoisomer (151 MHz, $CDCl_3$) δ = 167.86, 152.66, 145.68, 140.82, 136.97, 134.07, 132.48, 131.84, 131.51 (2C), 130.99, 129.47 (2C), 129.41 (2C), 128.55, 126.90, 124.75, 121.65, 117.48 (d, *J* = 286.9 Hz, 1C), 113.64, 81.99, 65.73 (d, *J* = 27.2 Hz, 1C), 27.74 (3C), 21.66 ppm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = 121.75 (s, 1F) ppm.

$[\alpha]_D^{rt}$ = +18° for mixture of diastereoisomers (c = 0.830 in $CHCl_3$). **IR** (KBr): ν = 3557, 3482, 3416, 1640, 1619 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{26}FN_3O_9S$ [M + Na] = 642.09867, found: 642.09883. **HPLC analysis** *ee (major diastereoisomer)* = 70 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 205 nm, retention time: t_{major} = 7.837 min, t_{minor} = 12.770 min). **HPLC analysis** *ee (minor diastereoisomer)* = 75 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 205 nm, retention time: t_{major} = 9.315 min, t_{minor} = 15.346 min).

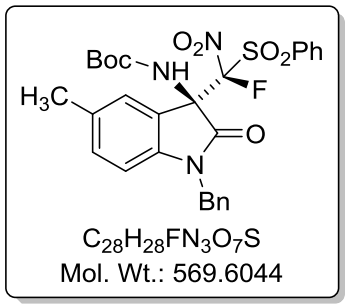
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i)



Adduct **3i** was prepared from 35.0 mg (0.10 mmol) ketimine **1i** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3i** was obtained as colorless oil in 85 % yield (48.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 6.0 Hz, 2H), 7.75 (dt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.58 (t, *J* = 6.0 Hz, 2H), 7.28-7.24 (m, 4H), 7.18 (d, *J* = 12.0 Hz, 2H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.83 (s, 1H), 6.77 (s, 1H), 6.54 (d, *J* = 6.0 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 2.19 (s, 3H), 1.33 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.99, 152.81, 141.52, 136.24, 135.03, 133.34, 133.15, 131.81 (2C), 131.66, 129.08 (2C), 128.67 (2C), 127.63, 127.28 (2C), 124.62, 122.33, 118.96 (d, *J* = 286.9 Hz, 1C), 109.45, 81.46, 65.51 (d, *J* = 25.7 Hz, 1C), 44.84, 28.08 (3C), 20.96 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.25 (s, 1F) ppm. $[\alpha]_D^{rt}$ = +45.6° (c = 1.130 in $CHCl_3$). **IR** (KBr): ν = 3416, 2979, 2928, 1728, 1592, 1498, 1449, 1362, 1275, 1254, 1157, 1080, 1012, 878, 814, 756, 726, 698, 683, 579, 533, 459 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{28}H_{28}FN_3O_7S$ [M + Na] = 592.15242, found: 592.15250. **HPLC analysis** *ee (major diastereoisomer)* = 98 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 190 nm, retention time: t_{major} = 15.232 min, t_{minor} = 8.458 min).

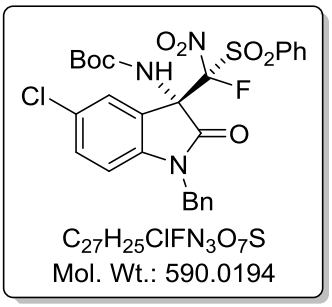
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i')



Adduct **3i'** was prepared from 35.0 mg (0.10 mmol) ketimine **1i** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3i'** was obtained as colorless oil in 4 % yield (2.0 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 12.0 Hz, 2H), 7.79 (t, *J* = 12.0 Hz, 1H), 7.61-7.58 (m, 3H), 7.35 – 7.30 (m, 5H), 7.06 (d, *J* = 6.0 Hz, 1H), 6.97 (s, 1H), 6.58 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 18.0 Hz, 1H), 4.68 (d, *J* = 18.0 Hz, 1H), 2.34 (s, 3H), 1.33 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.21, 152.74, 141.65, 136.74, 135.02, 132.42, 131.92, 131.51, 131.04 (2C), 129.67 (2C), 128.76 (2C), 127.66 (2C), 127.32 (2C), 122.15, 118.20 (d, *J* = 285.4 Hz, 1C), 109.48, 81.43, 65.95 (d, *J* = 25.7 Hz, 1C), 44.88, 28.10 (3C), 21.08 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 122.81 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = -1.6° (c = 0.100 in $CHCl_3$). **IR** (KBr): ν = 3554, 3473, 3416, 3224, 2926, 1730, 1619, 1497, 13612, 1165 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{28}H_{28}FN_3O_7S$ [M + Na] = 592.15242, found: 592.15254. **HPLC analysis** *ee (minor diastereoisomer)* = 96 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 210 nm, retention time: t_{major} = 23.944 min, t_{minor} = 10.423 min).

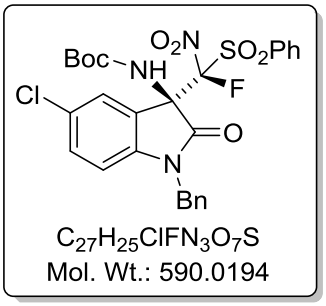
tert-Butyl ((*S*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j)



Adduct **3j** was prepared from 37.0 mg (0.10 mmol) ketimine **1j** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3j** was obtained as colorless oil in 84 % yield (49.5mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 12.0 Hz, *J'* = 6.0 Hz, 2H), 7.78 (t, *J* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.29-7.26 (m, 3H), 7.21-7.19 (m, 3H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.73 (s, 1H), 6.58 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.67 (d, 12.0 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.67, 152.80, 142.55, 136.53, 134.45, 132.91, 131.65 (2C), 131.28, 129.27 (2C), 128.86, 128.80 (2C), 127.87, 127.27 (2C), 124.69, 124.02, 118.51 (d, *J* = 288.4 Hz, 1C), 110.74, 81.92, 65.17 (d, *J* = 25.7 Hz, 1C), 45.03, 28.09 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.27 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +31.5° (c = °1.510 in $CHCl_3$). **IR** (KBr): ν = 3411, 3068, 2980, 2932, 1747, 1726, 1608, 1591, 1486, 1450, 1431, 1356, 1277, 1256, 1158, 1108, 1080, 1043, 1011, 974, 877, 815, 755, 725, 698, 683, 609, 579, 531, 462 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}ClFN_3O_7S$ [M + Na] = 612.09780, found: 612.09805. **HPLC analysis** *ee (major diastereoisomer)* = 97 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 217 nm, retention time: t_{major} = 9.742 min, t_{minor} = 6.606 min).

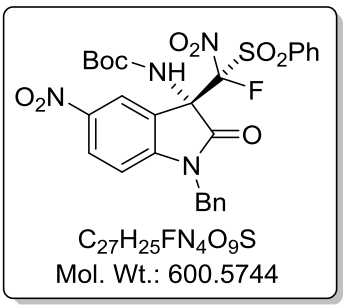
***tert*-Butyl ((*R*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')**



Adduct **3j'** was prepared from 37.0 mg (0.10 mmol) ketimine **1j** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3j'** was obtained as colorless oil in 5 % yield (3.0 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 6.0 Hz, 2H), 7.80 (tt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.76 (d, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 6.0 Hz, 2H), 7.35-7.31 (m, 4H), 7.29-7.26 (m, 1H), 7.24 (dd, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 6.99 (s, 1H), 6.60 (d, *J* = 6.0 Hz, 1H), 5.12 (d, *J* = 18 Hz, 1H), 4.70 (d, *J* = 18 Hz, 1H), 1.36 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.02, 152.74, 142.62, 136.94, 134.45, 131.58, 131.10, 131.07 (2C), 129.77 (2C), 128.88 (2C), 128.35, 127.89, 127.38, 127.26 (2C), 123.83, 117.74 (d, *J* = 286.9 Hz, 1C), 110.72, 81.87, 65.66 (d, *J* = 25.7 Hz, 1C), 45.04, 28.12 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 122.00 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +6 (c = 0.335 in $CHCl_3$). **IR** (KBr): ν = 3554, 3467, 3414, 1751, 1721, 1634, 1616, 1592, 1491, 1449, 1431, 1356, 1275, 1257, 1159, 1114, 1078, 1042, 1027, 1006, 878, 818, 629, 615, 582 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}ClFN_3O_7S$ [M + Na] = 612.09780, found: 612.09809. **HPLC analysis** *ee (minor diastereoisomer)* = 95 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 217 nm, retention time: t_{major} = 10.891 min, t_{minor} = 7.085 min).

***tert*-Butyl ((*S*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k)**

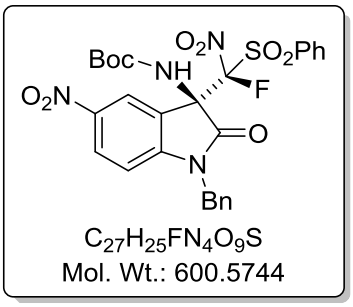


Adduct **3k** was prepared from 38.1 mg (0.10 mmol) ketimine **1k** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3k** was obtained as colorless oil in 81% yield (48.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.17 (dd, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 6.0 Hz, 2H), 7.78 (t, *J* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 2H), 7.34-7.26 (m, 5H), 6.75 (d, *J* = 6.0 Hz, 1H), 6.73 (s, 1H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.85 (d, *J* = 6.0 Hz, 1H), 1.37 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.19, 152.96, 149.52, 143.87, 136.71, 133.83, 132.65, 131.50 (2C), 129.50 (2C), 129.00 (2C), 128.19, 127.95, 127.36 (2C), 123.61, 120.63, 118.17 (d, *J* = 288.4 Hz, 1C), 109.54, 82.48, 64.70 (d, *J* = 24.2 Hz, 1C), 45.46, 28.11 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.58 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +29.8° (c = 0.605 in $CHCl_3$). **IR** (KBr): ν = 3411, 3070, 2980, 2929, 1756, 1724, 1605, 1592, 1525, 1490, 1449, 1387, 1339,

1278, 1256, 1157, 1080, 1011, 895, 880, 829, 753, 723, 683, 573, 468 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}FN_4O_9S$ [M + Na] = 623.12185, found: 623.12206. **HPLC analysis** *ee (major diastereoisomer)* = 96 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 321 nm, retention time: t_{major} = 19.181 min, t_{minor} = 14.616 min).

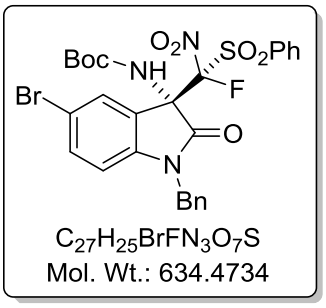
tert-Butyl ((*R*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')



Adduct **3k'** was prepared from 38.1 mg (0.10 mmol) ketimine **1k** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3k'** was obtained as colorless oil in 5.2% yield (3.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 6.0 Hz, 1H), 8.22 (dd, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 2H), 7.82 (tt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.62 (t, *J* = 12.0 Hz, 2H), 7.38-7.28 (m, 5H), 7.09 (s, 1H), 6.79 (d, *J* = 12.0 Hz, 1H), 5.15 (d, *J* = 24.0 Hz, 1H), 4.83 (d, *J* = 24.0 Hz, 1H), 1.37 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.76, 152.90, 149.44, 143.47, 137.16, 133.76, 131.23, 131.07 (2C), 129.86 (2C), 129.04 (2C), 128.19, 127.79, 127.26 (2C), 123.30, 122.89, 117.33 (d, *J* = 285.4 Hz, 1C), 109.58, 82.37, 65.24 (d, *J* = 27.2 Hz, 1C), 45.34, 28.09 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -122.34 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +17.1° (c = 0.175 in $CHCl_3$). **IR** (KBr): ν = 3422, 3067, 2926, 2854, 1751, 1723, 1605, 1592, 1526, 14889, 1449, 1385, 1359, 1338, 1279, 1257, 1183, 1159, 1102, 1080, 1043, 1018, 898, 876, 828, 752, 721, 683, 575, 562, 459 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}FN_4O_9S$ [M + Na] = 623.12185, found: 623.12203. **HPLC analysis** *ee (minor diastereoisomer)* = 94 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 318 nm, retention time: t_{major} = 17.976 min, t_{minor} = 22.945 min).

tert-Butyl ((*S*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l)

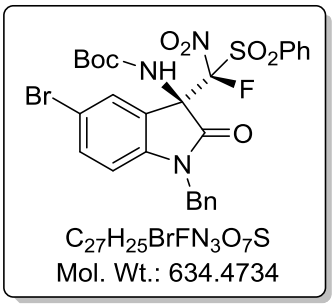


Adduct **3l** was prepared from 41.5 mg (0.10 mmol) ketimine **1l** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3l** was obtained as colorless oil in 86% yield (54.7 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 6.0 Hz, 2H), 7.75 (t, *J* = 6.0 Hz, 1H), 7.56 (t, *J* = 6.0 Hz, 2H), 7.31-7.23 (m, 4H), 7.18-7.14 (m, 3H), 6.69 (s, 1H), 6.50 (d, *J* = 6.0 Hz, 1H), 4.97 (d, *J* = 18.0 Hz, 1H), 4.64 (d, *J* = 18.0 Hz, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.53,

152.78, 143.05, 136.53, 134.41, 134.17, 132.90, 131.61 (2C), 129.26 (2C), 128.80 (2C), 127.87, 127.40, 127.27 (2C), 124.31, 118.53 (d, *J* = 288.4 Hz, 1C), 115.97, 111.21, 81.94, 65.04 (d, *J* = 24.2 Hz, 1C), 45.01, 28.08 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.21 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +35.0° (c = 1.330 in $CHCl_3$). **IR** (KBr): ν = 3408, 2980, 2949, 1747, 1725, 1592, 1483, 1450, 1426, 1360, 1276, 1256, 1157, 1080, 1010, 878, 816, 755, 723, 699, 683, 607, 576, 534, 458 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}BrFN_3O_7S$ [M + Na] = 656.04728, found: 656.04740. **HPLC analysis** *ee (major diastereoisomer)* = 98 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 98:2, 1.0 mL/min, λ = 195 nm, retention time: t_{major} = 50.715 min, t_{minor} = 25.168 min).

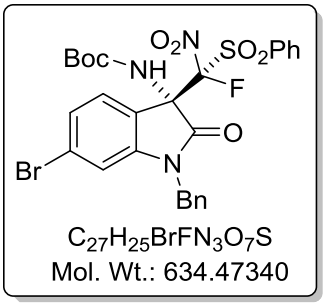
tert-Butyl ((*R*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')



Adduct **3l'** was prepared from 41.5 mg (0.10 mmol) ketimine **1l** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3l'** was obtained as colorless oil in 9 % yield (5.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 6.0 Hz, 1H), 7.91-7.89 (m, 3H), 7.80 (tt, *J* = 12.0 Hz, *J'* = 6.0 Hz, 1H), 7.61 (t, *J* = 12.0 Hz, 2H), 7.38 (dd, *J* = 6.0 Hz, *J'* = 2.0 Hz, 1H), 7.35-7.30 (m, 3H), 7.29-7.27 (m, 1H), 6.99 (s, 1H), 6.56 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 1.36 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.91, 152.74, 143.11, 136.94, 134.41, 133.98, 131.07 (2C), 130.07, 129.76 (2C), 129.72, 128.88 (2C), 127.89, 127.26 (2C), 124.14, 117.75 (d, *J* = 285.4 Hz, 1C), 115.49, 111.19, 81.89, 65.58 (d, *J* = 25.7 Hz, 1C), 45.01, 28.12 (3C) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = 121.99 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +17.5° (c = 0.285 in $CHCl_3$). **IR** (KBr): ν = 3545, 3485, 3443, 3416, 3240, 1724, 1640, 1619, 1512, 1365, 1228, 1156, 629, 612 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{26}FN_3O_7S$ [M + H] = 634.065338, found: 634.066606. **HPLC analysis** *ee (minor diastereoisomer)* = 95 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 98:2, 1.0 mL/min, λ = 226 nm, retention time: t_{major} = 65.870 min, t_{minor} = 28.306 min).

***tert*-Butyl ((*S/R*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m)**



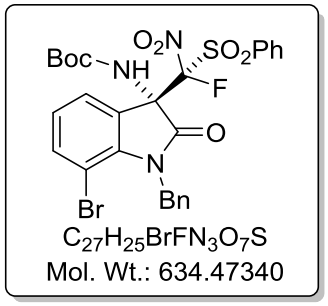
Adduct **3m** was prepared from 41.5 mg (0.10 mmol) ketimine **1m** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3m** was obtained as colorless oil in 87% yield (55.2 mg).

^{1}H NMR major diastereoisomer (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 6.0 Hz, 2H), 7.78 (t, *J* = 6.0 Hz, 1H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.36-7.25 (m, 2H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.09 (d, *J* = 6.0 Hz, 1H), 6.99 (s, 1H), 6.93 (d, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 6.0 Hz, 2H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** major diastereoisomer (151 MHz, $CDCl_3$) δ = 168.97, 152.84, 145.18, 136.51, 134.34, 131.71 (2C), 131.52, 129.27 (2C), 128.85 (2C), 127.23 (2C), 126.40, 125.83, 125.34, 125.15, 121.37, 118.39 (d, *J* = 286.9 Hz, 1C), 113.16, 81.85, 65.16 (d, *J* = 25.7 Hz, 1C), 44.98, 28.08 (3C) ppm. **^{19}F NMR** major diastereoisomer (376 MHz, $CDCl_3$) δ = 121.40 (s, 1F) ppm.

^{1}H NMR minor diastereoisomer (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 6.0 Hz, 2H), 7.80 (t, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 6.0 Hz, 1H), 7.61 (t, *J* = 6.0 Hz, 2H), 7.36-7.25 (m, 7H), 6.85 (s, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** minor diastereoisomer (151 MHz, $CDCl_3$) δ = 169.29, 152.72, 145.32, 136.93, 134.32, 132.93 (2C), 131.02 (2C), 130.62, 129.76 (2C), 128.93 (2C), 128.24, 127.92, 125.83, 125.32, 121.19, 117.69 (d, *J* = 286.9 Hz, 1C), 113.16, 81.80, 65.44 (d, *J* = 27.2 Hz, 1C), 44.98, 28.08 (3C) pm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = 122.06 (s, 1F) ppm.

Data for mixture of distereoisomers: $[\alpha]_D^{rt}$ = +24.9° (c = 1.025 in $CHCl_3$). **IR** (KBr): ν = 2980, 2926, 1745, 1718, 1604, 1598, 1488, 1449, 1359, 1341, 1278, 1257, 1156, 1078, 1009, 842, 755, 716, 701, 680, 579 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}BrFN_3O_7S$ [M + Na] = 656.04728, found: 656.047198. **HPLC analysis** *ee (major diastereoisomer)* = 95 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 242 nm, retention time: t_{major} = 13.095 min, t_{minor} = 7.383 min). **HPLC analysis** *ee (minor diastereoisomer)* = 93 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 242 nm, retention time: t_{major} = 19.890 min, t_{minor} = 8.181 min).

***tert*-Butyl ((*S/R*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n)**



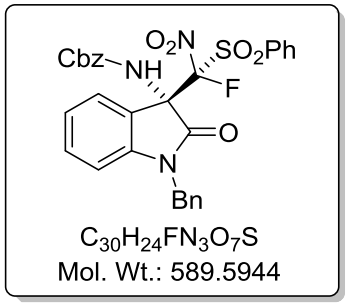
Adduct **3n** was prepared from 41.5 mg (0.10 mmol) ketimine **1n** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3n** was obtained as colorless oil in 80% yield (50.8 mg).

^{1}H NMR major diastereoisomer (600 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 12.0 Hz, 2H), 7.72 (t, *J* = 6.0 Hz, 1H), 7.55 (t, *J* = 6.0 Hz, 2H), 7.41 (d, *J* = 6.0 Hz, 1H), 7.31 (d, *J* = 6.0 Hz, 1H), 7.25-7.20 (m, 2H), 7.13 (d, *J* = 6.0 Hz, 2H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.93 (s, 1H), 6.86 (t, *J* = 6.0 Hz, 1H), 5.31 (d, *J* = 12.0 Hz, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** major diastereoisomer (151 MHz, $CDCl_3$) δ = 170.14, 152.86, 141.54, 137.31, 136.93, 136.50, 132.90, 131.88 (2C), 129.12 (2C), 128.35 (2C), 126.96, 126.44 (2C), 126.18, 124.56, 122.70, 118.41 (d, *J* = 286.9 Hz, 1C), 102.88, 81.88, 65.01 (d, *J* = 25.7k Hz, 1C), 45.70, 28.06 (3C) ppm. **^{19}F NMR** major diastereoisomer (376 MHz, $CDCl_3$) δ = 121.28 (s, 1F) ppm.

^{1}H NMR minor diastereoisomer (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 6.0 Hz, 2H), 7.79 (q, *J* = 6.0 Hz, 2H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.0 Hz, 1H), 7.02 (m, 2H), 7.31-7.23 (m, 4H), 6.93 (s, 1H), 5.38 (d, *J* = 6.0 Hz, 2H), 1.32 (s, 9H) ppm. **^{13}C NMR** minor diastereoisomer (151 MHz, $CDCl_3$) δ = 170.28, 152.65, 141.75, 137.22, 136.72, 136.61, 131.60, 131.02 (2C), 129.73 (2C), 128.44 (2C), 127.02, 126.44 (3C), 125.46, 123.85, 117.74 (d, *J* = 286.9 Hz, 1C), 102.72, 81.85, 65.31 (d, *J* = 25.7 Hz, 1C), 45.84, 28.06 (3C) ppm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = 121.83 (s, 1F) ppm.

Data for mixture of distereoisomers: $[\alpha]_D^{rt}$ = +34.4° (c = 2.095 in $CHCl_3$). **IR** (KBr): ν = 3440, 3064, 2980, 2932, 1748, 1718, 1589, 1449, 1356, 1281, 1257, 1159, 1120, 1075, 1015, 776, 752, 728, 725, 683 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{27}H_{25}BrFN_3O_7S$ [M + Na] = 656.04728, found: 656.046997. **HPLC analysis** *ee (major diastereoisomer)* = 95 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 240 nm, retention time: t_{major} = 8.934 min, t_{minor} = 5.461 min). **HPLC analysis** *ee (minor diastereoisomer)* = 92 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 240 nm, retention time: t_{major} = 16.925 min, t_{minor} = 6.276 min).

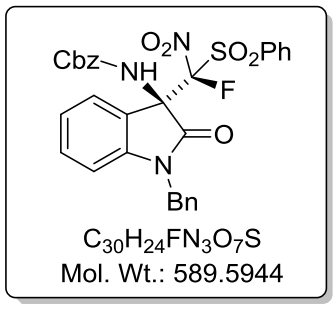
Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p)



Adduct **3p** was prepared from 37.0 mg (0.10 mmol) ketimine **1p** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3p** was obtained as colorless oil in 28 % yield (16.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 12.0 Hz, 2H), 7.75 (t, *J* = 12.0 Hz, 1H), 7.58 (t, *J* = 12.0 Hz, 2H), 7.38-7.33 (m, 4H), 7.30-7.27 (m, 3H), 7.24 (t, *J* = 6.0 Hz, 2H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.14 (s, 1H), 7.06 (d, *J* = 6.0 Hz, 1H), 6.98 (t, *J* = 6.0 Hz, 1H), 6.64 (d, *J* = 6.0 Hz, 1H) 5.04-4.99 (m, 3H), 4.62 (bs, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.76, 153.59, 144.02, 136.49, 135.24, 134.78, 133.02, 131.79 (2C), 131.56, 129.22 (2C), 128.76 (2C), 128.54 (2C), 128.39, 128.28, 127.73, 127.18 (2C), 124.05, 123.64, 121.88, 118.45 (d, *J* = 286.9 Hz, 1C), 109.91, 67.78, 66.94, 65.54 (d, *J* = 27.2 Hz, 1C), 44.85 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -121.75 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +29.5° (c = 0.625 in $CHCl_3$). **IR** (KBr): ν = 3557, 3539, 3470, 3411, 3399, 2929, 1733, 1637, 1613, 1589, 1500, 1488, 1470, 1449, 1353, 1257, 1245, 1186, 1159, 1075, 752, 615 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{30}H_{24}FN_3O_7S$ [M + Na] = 612.12112, found: 612.12113. **HPLC analysis** *ee (major diastereoisomer)* = 75 %, (Daicel Chiracel IB column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 207 nm, retention time: t_{major} = 16.529 min, t_{minor} = 15.101 min).

Benzyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p')

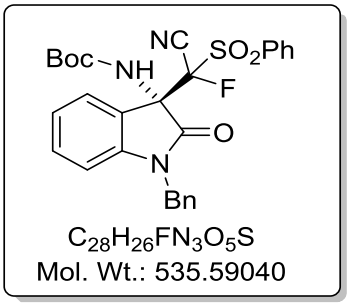


Adduct **3p'** was prepared from 37.0 mg (0.10 mmol) ketimine **1p** and sulfone **2a** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3p'** was obtained as colorless oil in 7 % yield (4.2 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 6.0 Hz, 2H), 7.82-7.78 (m, 2H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.37-7.34 (m, 8H), 7.31-7.27 (m, 4H), 7.14 (t, *J* = 6.0 Hz, 1H), 6.68 (d, *J* = 6.0 Hz, 1H), 5.12 (d, *J* = 6.0 Hz, 1H), 5.03-4.97 (m, 2H), 4.68 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 168.94, 153.49, 144.14, 136.89, 135.27, 134.75, 131.61 (2C), 131.44, 131.03 (2C), 129.73 (2C), 128.85 (2C), 128.55, 128.45, 128.39, 128.36, 127.77, 127.21 (2C), 122.97, 121.65, 117.90 (d, *J* = 285.4 Hz, 1C), 109.95, 67.81, 65.71 (d, *J* = 27.2 Hz, 1C), 62.96 (d, *J* = 13.6 Hz, 1C), 44.91. ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -121.08 (s, 1F) ppm. **$[\alpha]_D^{rt}$** = +6.1° (c = 0.245 in $CHCl_3$).

IR (KBr): ν = 3536, 3473, 3411, 3234, 2920, 2854, 1733, 1640, 1616, 1589, 1497, 1467, 1446, 1356, 1254, 1192, 1156, 1081, 755, 618 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{30}H_{25}FN_3O_7S$ [M + H] = 590.139176, found: 590.138765. **HPLC analysis** *ee (minor diastereoisomer)* = 64 %, (Daicel Chiracel AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 203 nm, retention time: t_{major} = 12.476 min, t_{minor} = 10.662 min).

tert-Butyl ((*S*/*R*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q)



Adduct **3q** was prepared from 37.0 mg (0.10 mmol) ketimine **1a** and sulfone **2b** 24.1 mg (0.11 mmol, 1.1 equiv). Product **3q** was obtained as colorless oil in 46 % yield (24.6 mg).

^{1}H NMR major diastereoisomer (600 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 6.0 Hz, 2H), 7.81 (t, *J* = 6.0 Hz, 1H), 7.71 (d, *J* = 6.0 Hz, 1H), 7.63 (t, *J* = 6.0 Hz, 2H), 7.45 (d, *J* = 6.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.10 (t, *J* = 6.0 Hz, 1H), 6.75 (d, *J* = 12.0 Hz, 1H), 6.52 (s, 1H), 5.07 (d, *J* = 18.0 Hz, 1H), 4.94 (d, *J* = 18.0 Hz, 1H), 1.34 (s, 9H) ppm. **^{13}C NMR** major diastereoisomer (151 MHz, $CDCl_3$) δ = 169.69, 152.92, 143.80, 136.59, 134.75, 132.69, 131.32, 131.24 (2C), 129.55 (2C), 128.69 (2C), 127.58 (2C), 127.17, 127.09, 122.92, 110.47, 110.27, 109.94, 97.45 *J* = 246.1 Hz, 1C), 81.67, 64.76 (d, *J* = 19.6 Hz, 1C), 45.12, 23.03 (3C) ppm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = -152.27 (s, 1F) ppm.

^{1}H NMR minor diastereoisomer (600 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 6.0 Hz, 2H), 7.84 (t, *J* = 6.0 Hz, 1H), 7.73 (d, *J* = 6.0 Hz, 1H), 7.67 (t, *J* = 6.0 Hz, 2H), 7.37 (d, *J* = 6.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.12 (t, *J* = 6.0 Hz, 1H), 6.73 (d, *J* = 12.0 Hz, 1H), 6.47 (s, 1H), 5.20 (d, *J* = 18.0 Hz, 1H), 4.80 (d, *J* = 18.0 Hz, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** minor diastereoisomer (151 MHz, $CDCl_3$) δ = 169.69, 152.83, 144.01, 136.72, 134.86, 132.57, 131.32, 131.28 (2C), 129.59 (2C), 128.75 (2C), 127.69 (2C), 127.30, 127.09, 122.74, 110.68, 110.47, 109.77, 97.67 (d, *J* = 240.1 Hz, 1C), 81.84, 64.58 (d, *J* = 25.8 Hz, 1C), 44.87, 27.98 (3C) ppm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = -152.38 (d, *J* = 48.9 Hz, 1F) ppm.

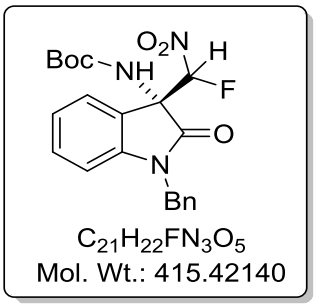
Data for mixture of distereoisomers: $[\alpha]_D^{rt}$ = +2.1° (c = 0.660 in $CHCl_3$). **IR** (KBr): ν = 3416, 3402, 3378, 3058, 3031, 2989, 2977, 2929, 1721, 1613, 1583, 1491, 1470, 1449, 1356, 1314, 1275, 1186, 1165, 1081, 1063, 976, 926, 875, 755, 722, 695, 683, 594, 582, 549, 528 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{28}H_{27}FN_3O_5S$ [M + H] = 536.164997, found: 536.166741. **HPLC analysis** *ee (major diastereoisomer)* = 62.9 %, (Daicel Chiracel IC column, heptane/*iso*-

propanol, 85:15, 1.0 mL/min, λ = 234 nm, retention time: t_{major} = 24.286 min, t_{minor} = 43.994 min), *ee (minor diastereoisomer)* = 31,1 %, (Daicel Chiracel IC column, heptane/*iso*-propanol, 85:15, 1.0 mL/min, λ = 237 nm, retention time: t_{major} = 14.887 min, t_{minor} = 16.956 min).

5 General procedure for desulfonation[4]

***tert*-Butyl ((*S*)-1-benzyl-3-((*S*/*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a, 4b)**

To adduct **3a** (40.0 mg, 0.072 mmol) in toluene (2.0 ml) were added *N*-benzylnicotinamide (46.3 mg, 0.216 mmol, 3.0 eq.) and AIBN (2.4 mg, 0.014 mmol). The reaction mixture was heated at 60 °C for 1 h in a microwave reactor. Product **4a, 4b** was isolated by column chromatography (Hex/EtOAc 15:1 to 8:1) in 84 % yield (25.1 mg).[4]



^{1}H NMR major diastereoisomer (600 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 6.0 Hz, 1H), 7.37-7.32 (m, 4H), 7.29-7.26 (m, 2H), 7.09 (t, *J* = 6.0 Hz, 1H), 6.73 (t, *J* = 6.0 Hz, 1H), 6.17 (d, *J* = 48 Hz, 1H), 5.52 (s, 1H), 5.05 (d, *J* = 18.0 Hz, 1H), 4.85 (d, *J* = 18.0 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C NMR** major diastereoisomer (151 MHz, $CDCl_3$) δ = 170.60, 153.94, 143.79, 134.79, 131.10, 128.96, 128.88 (2C), 127.88, 127.31 (2C), 125.70, 123.62, 110.12, 107.59 (d, *J* = 246.1 Hz, 1C), 81.81, 62.25 (d, *J* = 21.1 Hz, 1C), 44.73, 28.11 (3C) ppm. **^{19}F NMR** minor diastereoisomer (376 MHz, $CDCl_3$) δ = -157.23 (d, *J* = 48.9 Hz, 1F) ppm.

^{1}H NMR minor diastereoisomer (600 MHz, $CDCl_3$) δ = 7.37-7.32 (m, 4H), 7.29-7.26 (m, 3H), 7.13 (d, *J* = 6.0 Hz, 1H), 7.05 (t, *J* = 6.0 Hz, 1H), 6.73 (t, *J* = 6.0 Hz, 1H), 6.50 (d, *J* = 48.0 Hz, 1H), 6.11 (s, 1H), 5.17 (d, *J* = 18.0 Hz, 1H), 4.78 (bs, 1H), 1.34 (s, 9H) ppm. **^{13}C NMR** minor diastereoisomer (151 MHz, $CDCl_3$) δ = 170.25, 152.95, 143.58, 134.62, 128.96, 128.86 (2C), 127.81, 127.17 (2C), 123.88, 123.49, 122.22, 110.09, 108.36 (d, *J* = 244.6 Hz, 1C), 81.74, 62.25 (d, *J* = 21.1 Hz, 1C), 44.70, 28.04 (3C) ppm. **^{19}F NMR** minor diastereoisomer(376 MHz, $CDCl_3$) δ = -154.61 (d, *J* = 48.9 Hz, 1F) ppm.

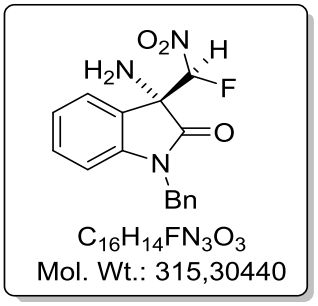
Data for mixture of distereoisomers: $[\alpha]_D^{rt}$ = -10.8° (c = 0.375 in $CHCl_3$). **IR** (KBr): ν = 3497, 3422, 2980, 2962, 2935, 2854, 1709, 1655, 1616, 1586, 1512, 1500, 1488, 1467, 1455, 1437, 1371, 1314, 1278, 1251, 1198, 1156, 1042, 1027, 1009, 905, 881, 842, 764, 728, 695, 573, 525 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{21}H_{22}FN_3O_5$ [M + Na] = 438.143570, found: 438.142989. **HPLC analysis** *ee (major diastereoisomer)* = 94.5 %, (Daicel Chiracel IA column, heptane/*iso*-

propanol, 80:20, 1.0 mL/min, λ = 207 nm, retention time: t_{major} = 22.552 min, t_{minor} = 8.675 min), *ee (minor diastereoisomer)* = 93.9 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 207 nm, retention time: t_{major} = 18.236 min, t_{minor} = 11.479 min).

6 General procedure for removed of Boc group

To mixture of adduct **4a, 4b** (1.0 eq.) in DCM (2.0 ml) was added TFA (46.3 mg, 2.50 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 2 h. Product **5a** and **5b** was isolated by column chromatography (Hex/EtOAc 10:1 to 3:1).[5]

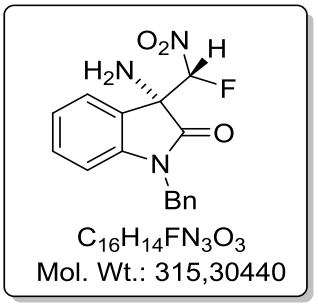
(*S*)-3-Amino-1-benzyl-3-((*S*)-fluoro(nitro)methyl)indolin-2-one (5a)



Amine **5a** was prepared from mixture 28.7 mg (0.069 mmol) of adduct **4a, 4b** in 2.0 ml DCM and CF_3COOH 190 µl (2.50 mmol, 31.8 equiv). Product **5a** was obtained as colorless oil in 48 % yield (10.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 6.0 Hz, 1H), 7.36-7.32 (m, 4H), 7.30-7.24 (m, 2H), 7.07 (t, *J* = 6.0 Hz, 1H), 6.73 (d, *J* = 6.0 Hz, 1H), 6.07 (d, *J* = 48.0 Hz, 1H), 5.03 (d, *J* = 18.0 Hz, 1H), 4.84 (d, *J* = 18.0 Hz, 1H), 2.13 (s, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 173.40 (d, *J* = 24.0 Hz, 1C), 143.09, 134.68, 130.96, 128.92 (2C), 127.93, 127.26 (2C), 124.40, 123.61, 111.05, 110.34, 109.43, 62.06 (d, *J* = 78.0 Hz, 1C), 44.39. ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -150.56 (d, *J* = 45.1 Hz, 1F) ppm. **$[\alpha]_D^{rt}$** = -37.9° (c = 0.580 in $CHCl_3$). **IR** (KBr): ν = 3548, 3485, 3458, 3431, 3414, 2926, 1637, 1610, 1571, 1491, 1467, 1455, 1437, 1388, 1278, 1180, 1144, 1081, 1003, 940, 908, 860, 791, 755, 698, 629 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{16}H_{14}FN_3O_3Na$ [M + Na] = 338.091140, found: 338.091135. **HPLC analysis** *ee (major diastereoisomer)* = 97 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 98:2, 1.0 mL/min, 20.0 °C, λ = 206 nm, retention time: t_{major} = 128.479 min, t_{minor} = 120.400 min).

(*S*)-3-Amino-1-benzyl-3-((*R*)-fluoro(nitro)methyl)indolin-2-one (5b)



Amine **5b** was prepared from mixture 28.7 mg (0.069 mmol) of adduct **4a, 4b** in 2.0 ml DCM and CF_3COOH 190 µl (2.50 mmol,

31.8 equiv). Product **5a** was obtained as colorless oil in 47 % yield (10.2 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.35-7.32 (m, 2H), 7.30-7.26 (m, 4H), 7.20 (d, *J* = 6.0 Hz, 1H), 7.09 (t, *J* = 6.0 Hz, 1H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.11 (d, *J* = 48.0 Hz, 1H), 5.09 (d, *J* = 18.0 Hz, 1H), 4.76 (d, *J* = 18.0 Hz, 1H), 2.20 (s, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 173.80, 143.22, 134.56, 131.08, 128.98 (2C), 127.97, 127.04 (2C), 124.55, 123.69, 111.78, 110.23, 110.16, 62.2 (d, *J* = 24.2 Hz, 1C), 44.29 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -159.52 (d, *J* = 48.9 Hz, 1F) ppm. **$[\alpha]_D^{rt}$** = -20.0° (c = 0.525 in $CHCl_3$). **IR** (KBr): ν = 3548, 3431, 3402, 2923, 2851, 1640, 1610, 1568, 1494, 1470, 1452, 1452, 1434, 1368, 1350, 1180, 1141, 1126, 1087, 911, 889, 866, 812, 758, 740, 698 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{16}H_{14}FN_3O_3Na$ [M + Na] = 338.091140, found: 338.091135. **HPLC analysis** *ee (minor diastereoisomer)* = 96 %, (Daicel Chiracel IA column, heptane/*iso*-propanol, 98:2, 1.0 mL/min, 20.0 °C, λ = 210 nm, retention time: t_{major} = 120.745 min, t_{minor} = 112.176 min).

7 Determination of absolute configuration in compound 3a – X-Ray section

The product **3a** was recrystallized from Et_2O giving colored crystals after slow evaporation at room temperature. The assignment of the absolute configuration of product **3a** was carried out by X-ray crystallography analysis.

Crystallographic data for **3a** were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube CuKα (λ = 1.54178 Å) at a temperature of 150(2) K. The structures were solved by direct methods (XT[39a])[i] and refined by full matrix least squares based on F^2 (SHELXL2014[ii]). The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety. The absolute structure determination was based on anomalous dispersion.

Crystal data for **3a** $C_{27}H_{26}FN_3O_7S$, M_r =555.57, m.p. = 202-204 °C; Monoclinic, *C* 2 (No 5), a = 27.2206 (7) Å, b = 8.3665 (2) Å, c = 13.1113 (3) Å, β = 114.033 (1)°, V = 2727.13 (12) Å^3 , Z = 4, D_x = 1.353 Mg m^{-3}, colourless prism of dimensions 0.29 × 0.20 × 0.09 mm, multi-scan absorption correction (μ = 1.55 mm^{-1}) T_{min} = 0.77, T_{max} = 0.87; a total of 46990 measured reflections (θ_{max}= 77.3˚), from which 5761 were unique (R_{int} = 0.028) and 5691 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged (Δ/σ_{max}= 0.001) to R = 0.026 for observed reflections and w$R(F^2)$ = 0.068, *GOF* = 1.04 for 356 parameters and all 5761 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.19, $\Delta\rho_{min}$ -0.22 e.Å^{-3}). Absolute structure parameter (Parsons[iii]) -0.002(7).
X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC- 1575684 for **3a** and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/getstructures).

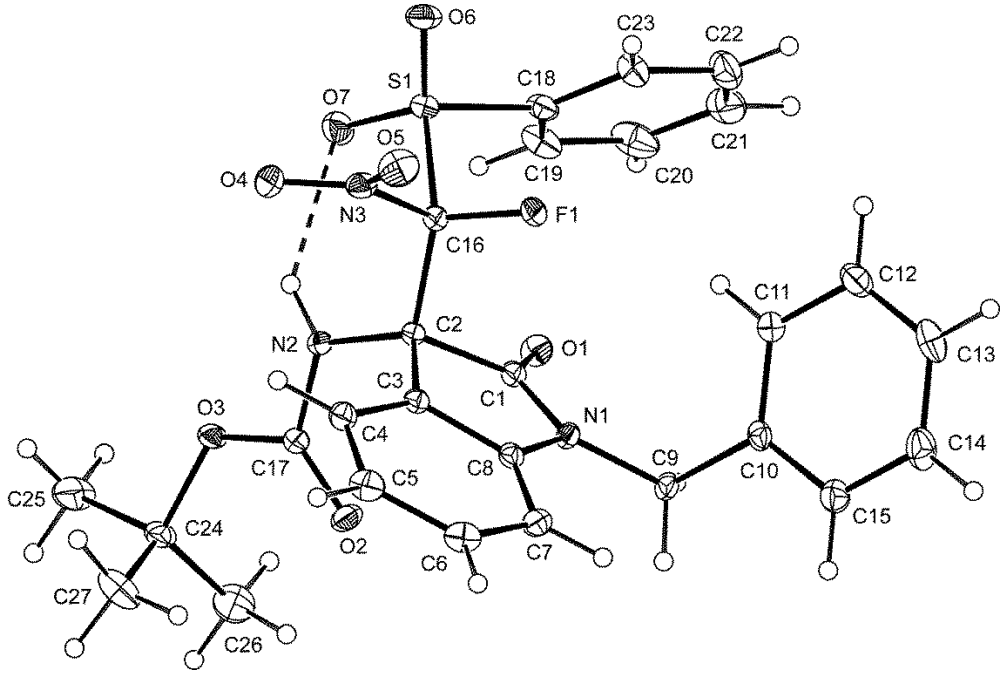


Figure 1. View on the molecular structure of **3a**, the displacement ellipsoids at 30% probability level. The dashed line indicates the intramolecular hydrogen bond N2-H2…O7, N2…O7 2.894(2) Å; angle on H2 138.7°.

Crystal data

$C_{27}H_{26}FN_3O_7S$	$F(000) = 1160$
$M_r = 555.57$	$D_x = 1.353$ Mg m^{-3}
Monoclinic, $C2$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 27.2206$ (7) Å	Cell parameters from 9946 reflections
$b = 8.3665$ (2) Å	$\theta = 4.0–77.3°$
$c = 13.1113$ (3) Å	$\mu = 1.55$ mm^{-1}
$\beta = 114.033$ (1)°	$T = 150$ K
$V = 2727.13$ (12) Å^3	Prism, colourless
$Z = 4$	0.29 × 0.20 × 0.09 mm

Data collection

Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS diffractometer	5761 independent reflections
Radiation source: IμS micro-focus sealed tube	5691 reflections with $I > 2\sigma(I)$
Helios Cu multilayer optic monochromator	$R_{int} = 0.028$
Detector resolution: 10.4167 pixels mm^{-1}	$\theta_{max} = 77.5°$, $\theta_{min} = 3.6°$
ϕ and ω scans	$h = -34\rightarrow34$
Absorption correction: multi-scan *SADABS2014*/5 - Bruker AXS area detector scaling and absorption correction	$k = -10\rightarrow10$
$T_{min} = 0.77$, $T_{max} = 0.87$	$l = -16\rightarrow16$
46990 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.1845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.068$	$\Delta\rangle_{max} = 0.19$ e Å^{-3}
$S = 1.04$	$\Delta\rangle_{min} = -0.22$ e Å^{-3}
5761 reflections	Extinction correction: *SHELXL2017*/1 (Sheldrick 2017), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
356 parameters	Extinction coefficient: 0.00161 (12)
1 restraint	Absolute structure: Flack x determined using 2582 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: mixed	Absolute structure parameter: 0.002 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.61070 (7)	0.4497 (2)	0.60942 (14)	0.0196 (3)
C2	0.65505 (7)	0.5072 (2)	0.56939 (14)	0.0179 (3)
C3	0.63824 (7)	0.6794 (2)	0.53781 (14)	0.0186 (3)
C4	0.65529 (7)	0.7902 (2)	0.48114 (15)	0.0245 (4)
H4	0.682536	0.764335	0.456129	0.029*
C5	0.63139 (8)	0.9412 (3)	0.46159 (17)	0.0292 (4)
H5	0.642371	1.019119	0.422465	0.035*
C6	0.59180 (8)	0.9787 (2)	0.49866 (18)	0.0289 (4)
H6	0.576359	1.082536	0.485160	0.035*
C7	0.57421 (7)	0.8672 (2)	0.55531 (15)	0.0235 (4)
H7	0.547376	0.893308	0.581442	0.028*
C8	0.59733 (7)	0.7171 (2)	0.57199 (14)	0.0189 (3)
C9	0.53894 (7)	0.5736 (2)	0.65276 (15)	0.0218 (4)
H9A	0.527622	0.460941	0.651847	0.026*
H9B	0.507868	0.634195	0.599390	0.026*
C10	0.55460 (7)	0.6414 (2)	0.76865 (15)	0.0211 (3)
C11	0.60258 (8)	0.5953 (3)	0.85544 (16)	0.0287 (4)
H11	0.625627	0.521376	0.841520	0.034*
C12	0.61701 (9)	0.6565 (3)	0.96211 (17)	0.0357 (5)
H12	0.650020	0.625447	1.020646	0.043*
C13	0.58357 (10)	0.7622 (3)	0.98319 (17)	0.0364 (5)
H13	0.593439	0.803890	1.056269	0.044*
C14	0.53557 (10)	0.8076 (3)	0.89792 (18)	0.0381 (5)
H14	0.512315	0.879850	0.912591	0.046*
C15	0.52124 (9)	0.7474 (3)	0.79043 (17)	0.0305 (4)
H15	0.488369	0.779613	0.731919	0.037*
C16	0.70925 (7)	0.5061 (2)	0.67411 (14)	0.0207 (4)
C17	0.61054 (7)	0.3918 (2)	0.38778 (14)	0.0199 (3)
C18	0.71715 (8)	0.2276 (3)	0.81235 (15)	0.0260 (4)
C19	0.68604 (9)	0.0916 (3)	0.77229 (18)	0.0359 (5)
H19	0.680809	0.047711	0.701782	0.043*
C20	0.66272 (11)	0.0212 (3)	0.8378 (2)	0.0451 (6)

H20	0.641486	-0.072468	0.812262	0.054*
C21	0.67026 (10)	0.0866 (3)	0.9397 (2)	0.0423 (5)
H21	0.653506	0.038928	0.983120	0.051*
C22	0.70199 (10)	0.2210 (3)	0.97928 (19)	0.0395 (5)
H22	0.707227	0.264387	1.049920	0.047*
C23	0.72612 (9)	0.2922 (3)	0.91608 (16)	0.0311 (4)
H23	0.748387	0.383627	0.943105	0.037*
C24	0.57587 (8)	0.2747 (2)	0.20150 (15)	0.0277 (4)
C25	0.59880 (12)	0.1446 (4)	0.1538 (2)	0.0566 (8)
H25A	0.633667	0.179013	0.156135	0.085*
H25B	0.574052	0.123614	0.076226	0.085*
H25C	0.603556	0.046883	0.197976	0.085*
C26	0.52235 (10)	0.2225 (4)	0.2000 (2)	0.0455 (6)
H26A	0.527835	0.130787	0.249934	0.068*
H26B	0.498105	0.192113	0.123857	0.068*
H26C	0.506444	0.310900	0.225261	0.068*
C27	0.57203 (12)	0.4329 (4)	0.1442 (2)	0.0481 (6)
H27A	0.556262	0.512475	0.176795	0.072*
H27B	0.549265	0.421495	0.064335	0.072*
H27C	0.608067	0.467671	0.154030	0.072*
F1	0.70166 (4)	0.57409 (14)	0.76043 (9)	0.0245 (2)
N1	0.58310 (6)	0.58082 (19)	0.61666 (12)	0.0189 (3)
N2	0.65707 (6)	0.4079 (2)	0.48144 (12)	0.0211 (3)
H2	0.685589	0.343630	0.497776	0.025*
N3	0.74998 (6)	0.6113 (2)	0.65288 (14)	0.0273 (4)
O1	0.60431 (5)	0.31305 (18)	0.63135 (11)	0.0266 (3)
O2	0.56979 (5)	0.46323 (19)	0.37442 (12)	0.0297 (3)
O3	0.61730 (5)	0.28772 (16)	0.31713 (10)	0.0247 (3)
O4	0.76361 (6)	0.5612 (2)	0.58111 (12)	0.0355 (4)
O5	0.76456 (6)	0.7341 (2)	0.70662 (14)	0.0387 (4)
O6	0.79957 (5)	0.3755 (2)	0.80540 (12)	0.0338 (3)
O7	0.74248 (7)	0.2154 (2)	0.63975 (12)	0.0353 (3)
S1	0.74799 (2)	0.31548 (6)	0.73193 (3)	0.02497 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0177 (8)	0.0244 (9)	0.0162 (8)	-0.0014 (6)	0.0063 (6)	-0.0005 (6)
C2	0.0148 (8)	0.0233 (8)	0.0147 (7)	-0.0001 (6)	0.0051 (6)	-0.0011 (6)
C3	0.0166 (8)	0.0221 (8)	0.0156 (7)	-0.0013 (6)	0.0051 (6)	-0.0011 (6)
C4	0.0214 (8)	0.0305 (10)	0.0223 (8)	-0.0025 (7)	0.0095 (7)	0.0024 (7)
C5	0.0282 (9)	0.0259 (9)	0.0306 (10)	-0.0056 (8)	0.0089 (8)	0.0046 (8)
C6	0.0285 (10)	0.0217 (9)	0.0309 (10)	-0.0006 (8)	0.0064 (8)	-0.0002 (7)
C7	0.0205 (8)	0.0245 (9)	0.0236 (8)	0.0001 (7)	0.0071 (7)	-0.0054 (7)
C8	0.0175 (8)	0.0227 (8)	0.0152 (7)	-0.0033 (7)	0.0055 (6)	-0.0018 (6)
C9	0.0162 (8)	0.0308 (9)	0.0205 (8)	-0.0037 (7)	0.0097 (6)	-0.0035 (7)
C10	0.0227 (8)	0.0244 (8)	0.0193 (8)	-0.0047 (7)	0.0118 (7)	0.0001 (7)
C11	0.0258 (9)	0.0387 (11)	0.0232 (9)	0.0028 (8)	0.0116 (8)	0.0015 (8)
C12	0.0337 (11)	0.0499 (13)	0.0203 (9)	-0.0045 (9)	0.0076 (8)	0.0022 (9)
C13	0.0545 (14)	0.0345 (11)	0.0236 (9)	-0.0087 (10)	0.0193 (9)	-0.0063 (8)
C14	0.0564 (13)	0.0320 (10)	0.0345 (11)	0.0071 (11)	0.0272 (10)	-0.0029 (9)
C15	0.0341 (10)	0.0328 (10)	0.0272 (9)	0.0060 (9)	0.0151 (8)	0.0011 (8)
C16	0.0175 (8)	0.0278 (9)	0.0163 (8)	-0.0005 (7)	0.0064 (7)	-0.0009 (7)
C17	0.0188 (8)	0.0225 (8)	0.0178 (8)	0.0006 (7)	0.0067 (6)	-0.0009 (6)
C18	0.0240 (9)	0.0293 (10)	0.0199 (8)	0.0017 (8)	0.0040 (7)	0.0052 (7)
C19	0.0411 (12)	0.0315 (11)	0.0253 (10)	-0.0034 (9)	0.0035 (9)	0.0041 (8)
C20	0.0444 (13)	0.0384 (12)	0.0391 (12)	-0.0118 (10)	0.0033 (10)	0.0135 (10)
C21	0.0402 (12)	0.0452 (13)	0.0414 (12)	0.0003 (11)	0.0166 (10)	0.0204 (11)
C22	0.0491 (13)	0.0433 (13)	0.0288 (10)	0.0021 (11)	0.0187 (10)	0.0076 (10)
C23	0.0355 (10)	0.0332 (11)	0.0233 (9)	-0.0010 (9)	0.0105 (8)	0.0023 (8)
C24	0.0262 (9)	0.0330 (11)	0.0170 (8)	0.0066 (7)	0.0018 (7)	-0.0050 (7)
C25	0.0476 (14)	0.076 (2)	0.0300 (12)	0.0263 (14)	-0.0010 (10)	-0.0268 (13)
C26	0.0364 (12)	0.0544 (15)	0.0371 (12)	-0.0129 (11)	0.0062 (10)	-0.0164 (11)
C27	0.0607 (16)	0.0500 (15)	0.0246 (11)	-0.0017 (13)	0.0082 (11)	0.0077 (10)
F1	0.0238 (5)	0.0321 (6)	0.0165 (5)	-0.0009 (4)	0.0072 (4)	-0.0038 (4)
N1	0.0163 (6)	0.0225 (7)	0.0193 (7)	-0.0006 (6)	0.0089 (5)	-0.0011 (6)
N2	0.0168 (7)	0.0287 (8)	0.0162 (7)	0.0047 (6)	0.0052 (6)	-0.0025 (6)
N3	0.0169 (7)	0.0378 (10)	0.0246 (8)	-0.0016 (7)	0.0056 (6)	0.0051 (7)
O1	0.0266 (6)	0.0233 (6)	0.0314 (6)	-0.0012 (6)	0.0132 (5)	0.0025 (6)
O2	0.0181 (6)	0.0401 (8)	0.0277 (7)	0.0058 (6)	0.0062 (5)	-0.0105 (6)
O3	0.0234 (6)	0.0293 (7)	0.0166 (6)	0.0087 (5)	0.0031 (5)	-0.0044 (5)
O4	0.0236 (7)	0.0568 (10)	0.0295 (7)	0.0004 (7)	0.0142 (6)	0.0045 (7)
O5	0.0308 (8)	0.0367 (9)	0.0453 (9)	-0.0122 (7)	0.0122 (7)	-0.0056 (7)
O6	0.0195 (6)	0.0475 (9)	0.0284 (7)	0.0032 (6)	0.0035 (5)	0.0090 (6)
O7	0.0411 (8)	0.0390 (8)	0.0257 (7)	0.0142 (7)	0.0135 (6)	0.0017 (6)

S1	0.0210 (2)	0.0327 (2)	0.01901 (19)	0.00502 (18)	0.00584 (15)	0.00366 (18)

Geometric parameters (Å, º) for (cu_mu568_vesely)

C1—O1	1.209 (2)	C16—S1	1.8921 (19)
C1—N1	1.355 (2)	C17—O2	1.208 (2)
C1—C2	1.575 (2)	C17—O3	1.337 (2)
C2—N2	1.440 (2)	C17—N2	1.365 (2)
C2—C3	1.517 (2)	C18—C19	1.387 (3)
C2—C16	1.553 (2)	C18—C23	1.390 (3)
C3—C4	1.381 (3)	C18—S1	1.755 (2)
C3—C8	1.395 (2)	C19—C20	1.390 (4)
C4—C5	1.396 (3)	C19—H19	0.9500
C4—H4	0.9500	C20—C21	1.380 (4)
C5—C6	1.386 (3)	C20—H20	0.9500
C5—H5	0.9500	C21—C22	1.383 (4)
C6—C7	1.393 (3)	C21—H21	0.9500
C6—H6	0.9500	C22—C23	1.385 (3)
C7—C8	1.381 (3)	C22—H22	0.9500
C7—H7	0.9500	C23—H23	0.9500
C8—N1	1.406 (2)	C24—O3	1.480 (2)
C9—N1	1.462 (2)	C24—C27	1.504 (3)
C9—C10	1.511 (2)	C24—C25	1.511 (3)
C9—H9A	0.9900	C24—C26	1.513 (3)
C9—H9B	0.9900	C25—H25A	0.9800
C10—C15	1.380 (3)	C25—H25B	0.9800
C10—C11	1.393 (3)	C25—H25C	0.9800
C11—C12	1.388 (3)	C26—H26A	0.9800
C11—H11	0.9500	C26—H26B	0.9800
C12—C13	1.375 (3)	C26—H26C	0.9800
C12—H12	0.9500	C27—H27A	0.9800
C13—C14	1.383 (3)	C27—H27B	0.9800
C13—H13	0.9500	C27—H27C	0.9800
C14—C15	1.394 (3)	N2—H2	0.8958
C14—H14	0.9500	N3—O5	1.217 (2)
C15—H15	0.9500	N3—O4	1.218 (2)
C16—F1	1.355 (2)	O6—S1	1.4317 (15)
C16—N3	1.527 (2)	O7—S1	1.4273 (16)
O1—C1—N1	127.70 (17)	O3—C17—N2	110.40 (14)
O1—C1—C2	124.91 (17)	C19—C18—C23	121.8 (2)

N1—C1—C2	107.37 (15)	C19—C18—S1	118.94 (16)
N2—C2—C3	115.76 (15)	C23—C18—S1	119.24 (16)
N2—C2—C16	111.86 (14)	C18—C19—C20	118.4 (2)
C3—C2—C16	108.60 (14)	C18—C19—H19	120.8
N2—C2—C1	112.03 (14)	C20—C19—H19	120.8
C3—C2—C1	101.18 (14)	C21—C20—C19	120.3 (2)
C16—C2—C1	106.55 (14)	C21—C20—H20	119.8
C4—C3—C8	120.53 (17)	C19—C20—H20	119.8
C4—C3—C2	130.85 (17)	C20—C21—C22	120.6 (2)
C8—C3—C2	108.57 (15)	C20—C21—H21	119.7
C3—C4—C5	118.20 (18)	C22—C21—H21	119.7
C3—C4—H4	120.9	C21—C22—C23	120.1 (2)
C5—C4—H4	120.9	C21—C22—H22	120.0
C6—C5—C4	120.72 (18)	C23—C22—H22	120.0
C6—C5—H5	119.6	C22—C23—C18	118.7 (2)
C4—C5—H5	119.6	C22—C23—H23	120.6
C5—C6—C7	121.36 (19)	C18—C23—H23	120.6
C5—C6—H6	119.3	O3—C24—C27	108.43 (17)
C7—C6—H6	119.3	O3—C24—C25	101.90 (16)
C8—C7—C6	117.37 (17)	C27—C24—C25	112.5 (2)
C8—C7—H7	121.3	O3—C24—C26	111.25 (17)
C6—C7—H7	121.3	C27—C24—C26	112.1 (2)
C7—C8—C3	121.76 (17)	C25—C24—C26	110.2 (2)
C7—C8—N1	128.16 (16)	C24—C25—H25A	109.5
C3—C8—N1	109.97 (15)	C24—C25—H25B	109.5
N1—C9—C10	112.19 (14)	H25A—C25—H25B	109.5
N1—C9—H9A	109.2	C24—C25—H25C	109.5
C10—C9—H9A	109.2	H25A—C25—H25C	109.5
N1—C9—H9B	109.2	H25B—C25—H25C	109.5
C10—C9—H9B	109.2	C24—C26—H26A	109.5
H9A—C9—H9B	107.9	C24—C26—H26B	109.5
C15—C10—C11	119.09 (18)	H26A—C26—H26B	109.5
C15—C10—C9	120.62 (17)	C24—C26—H26C	109.5
C11—C10—C9	120.28 (17)	H26A—C26—H26C	109.5
C12—C11—C10	120.5 (2)	H26B—C26—H26C	109.5
C12—C11—H11	119.7	C24—C27—H27A	109.5
C10—C11—H11	119.7	C24—C27—H27B	109.5
C13—C12—C11	120.1 (2)	H27A—C27—H27B	109.5
C13—C12—H12	120.0	C24—C27—H27C	109.5
C11—C12—H12	120.0	H27A—C27—H27C	109.5

C12—C13—C14	119.93 (19)	H27B—C27—H27C	109.5
C12—C13—H13	120.0	C1—N1—C8	111.88 (14)
C14—C13—H13	120.0	C1—N1—C9	122.82 (15)
C13—C14—C15	120.1 (2)	C8—N1—C9	124.80 (15)
C13—C14—H14	120.0	C17—N2—C2	116.97 (14)
C15—C14—H14	120.0	C17—N2—H2	123.5
C10—C15—C14	120.3 (2)	C2—N2—H2	117.8
C10—C15—H15	119.9	O5—N3—O4	127.44 (18)
C14—C15—H15	119.9	O5—N3—C16	118.07 (16)
F1—C16—N3	106.21 (14)	O4—N3—C16	114.48 (17)
F1—C16—C2	108.84 (14)	C17—O3—C24	119.67 (13)
N3—C16—C2	109.53 (14)	O7—S1—O6	120.77 (10)
F1—C16—S1	105.59 (11)	O7—S1—C18	110.61 (10)
N3—C16—S1	103.37 (12)	O6—S1—C18	108.72 (9)
C2—C16—S1	122.20 (13)	O7—S1—C16	107.83 (8)
O2—C17—O3	126.79 (16)	O6—S1—C16	101.99 (9)
O2—C17—N2	122.81 (16)	C18—S1—C16	105.61 (9)

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

i. [1] SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8
ii. [1] SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.
iii. [1] Parsons,S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst*. **B69**, 249-259.

8 Literature

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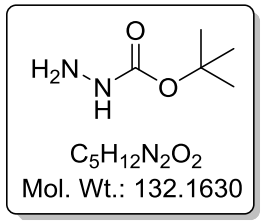
2. P. Calí, M. Begtrup *Synthesis* **2002**, *1*, 63.
3. (a) W. J. Yan, D. Wang, J. C. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett*., **2012**, *14*, 2512. (b) F-L. Hu, Y. Wei, M. Shi, S. Pindi, G. Li, *Org. Biomol. Chem.*, **2013**, *11*, 1921
4. Y. Seo, H. Kim, D. W. Chae, Y. G. Kim, *Tetrahedron: Asymmetry* **2014**, *25*, 625.
5. M. Montesinos-Magraner, C. Vila, R. Cantón, G. Blay, I. Fernández, M. C. Muñoz, J. R. Pedro, *Angew. Chem. Int. Ed.*, **2015**, *54*, 6320.

9 NMR Spectra of Compounds

FM207_av
standard 1H

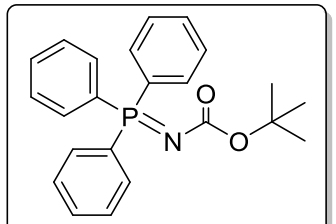
tert-Butyl hydrazinecarboxylate (XA)



$C_5H_{12}N_2O_2$
Mol. Wt.: 132.1630

FM3_aza_Wittig
standard 1H

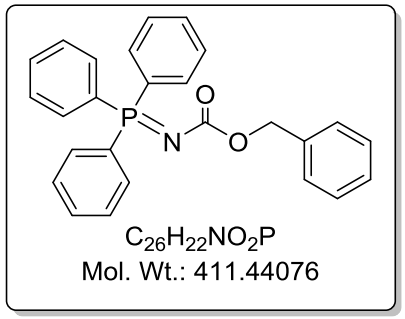
tert-Butyl (triphenyl-λ5-phosphanylidene)carbamate (XB)



$C_{23}H_{24}NO_2P$
Mol. Wt.: 377.4238

FM16_av3
standard 1H

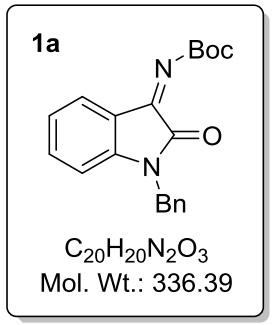
Benzyl (triphenyl-λ5-phosphanylidene)carbamate (XC)



$C_{26}H_{22}NO_2P$
Mol. Wt.: 411.44076

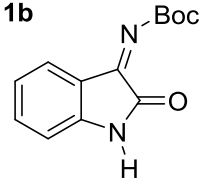
MU 697.1.fid
1H

tert-Butyl (*Z*)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate (1a)



tert-Butyl (*Z*)-(2-oxoindolin-3-ylidene)carbamate (Xb)

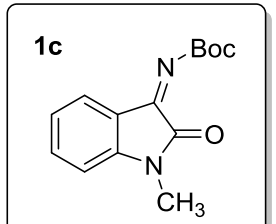
1b



$C_{13}H_{14}N_2O_3$
Mol. Wt.: 246.27

MU 534.1.fid
1H

tert-Butyl (*Z*)-(1-methyl-2-oxoindolin-3-ylidene)carbamate (1c)

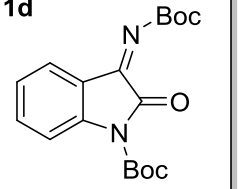


$C_{14}H_{16}N_2O_3$
Mol. Wt.: 260.29

FM 29.1.fid
1H

tert-Butyl (*Z*)-3-((*tert*-butoxycarbonyl)imino)-2-oxoindoline-1-carboxylate (1d)

1d

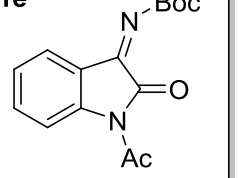


$C_{18}H_{22}N_2O_5$
Mol. Wt.: 346.38

FM 28.1.fid
1H

tert-Butyl (*Z*)-(1-acetyl-2-oxoindolin-3-ylidene)carbamate (Xe)

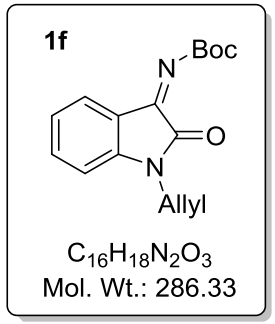
1e



$C_{15}H_{16}N_2O_4$
Mol. Wt.: 288.30

MU 753.1.fid
1H

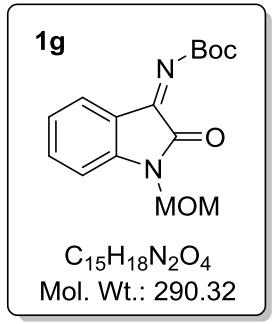
tert-Butyl (*Z*)-(1-allyl-2-oxoindolin-3-ylidene)carbamate (1f)



$C_{16}H_{18}N_2O_3$
Mol. Wt.: 286.33

FM 48.1.fid
1H

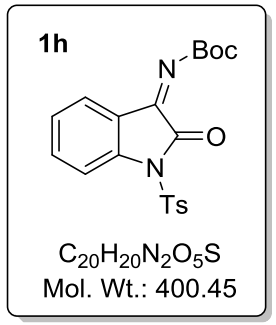
tert-Butyl (*Z*)-(1-(methoxymethyl)-2-oxoindolin-3-ylidene)carbamate (1g)



$C_{15}H_{18}N_2O_4$
Mol. Wt.: 290.32

FM 34.1.fid
1H

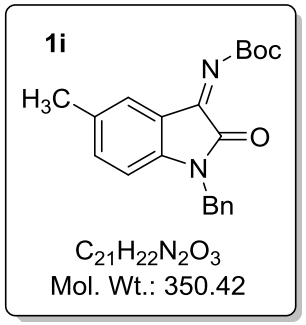
tert-Butyl (*Z*)-(2-oxo-1-tosylindolin-3-ylidene)carbamate (1h)



$C_{20}H_{20}N_2O_5S$
Mol. Wt.: 400.45

FM 111.1.fid
1H

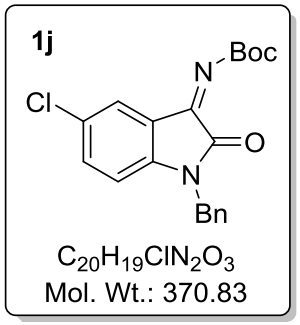
tert-Butyl (*Z*)-(1-benzyl-5-methyl-2-oxoindolin-3-ylidene)carbamate (1i)



$C_{21}H_{22}N_2O_3$
Mol. Wt.: 350.42

FM 113.1.fid
1H

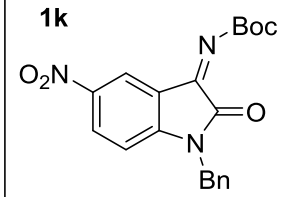
tert-Butyl (*Z*)-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)carbamate (Xj)



FM212_acav2
standard 1H

tert-butyl (*Z*)-(1-benzyl-5-nitro-2-oxoindolin-3-ylidene)carbamate (1k)

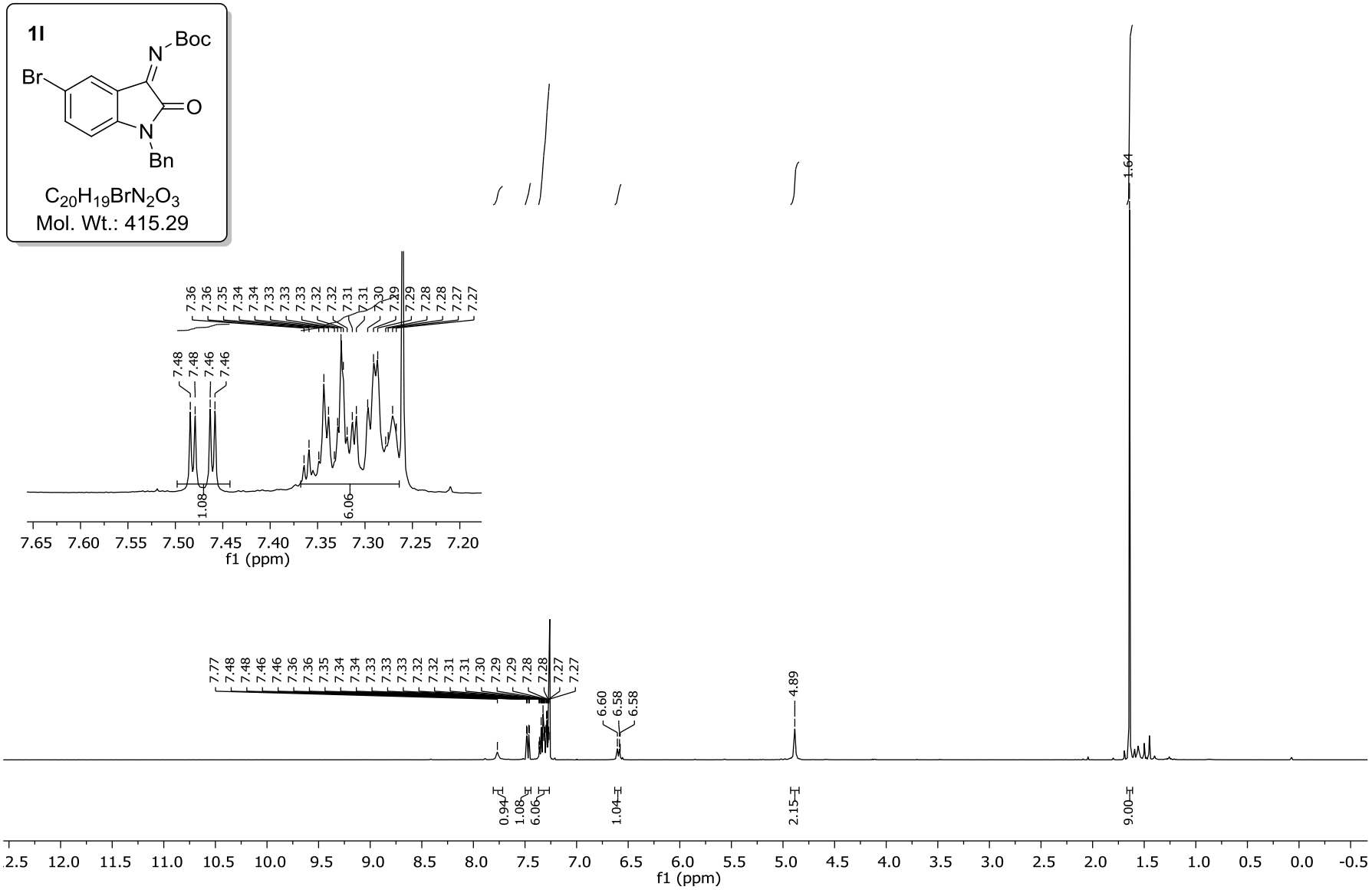
1k



$C_{20}H_{19}N_3O_5$
Mol. Wt.: 381.39

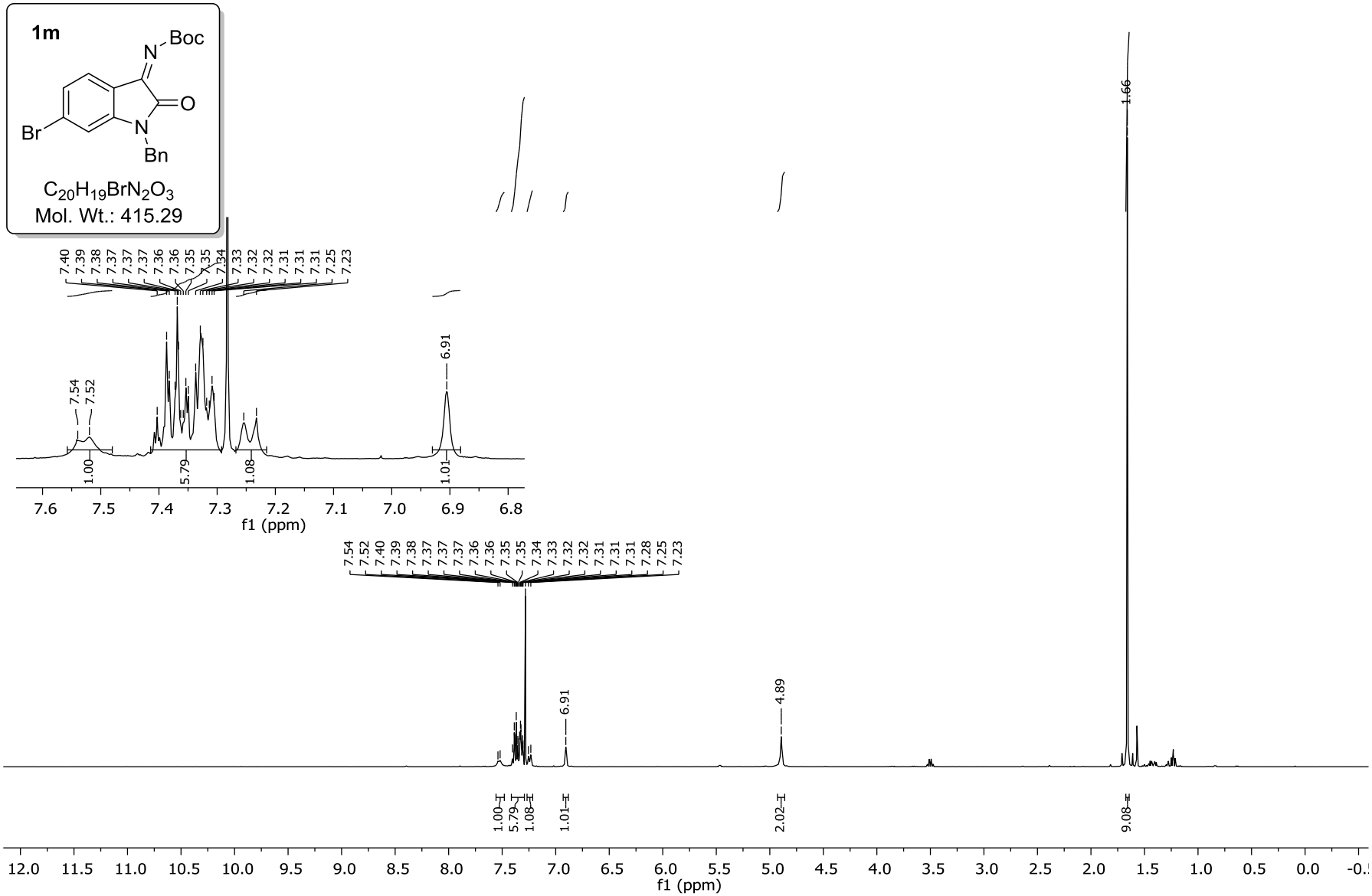
FM 107.1.fid
1H

tert-Butyl (*Z*)-(1-benzyl-5-bromo-2-oxoindolin-3-ylidene)carbamate (1l)



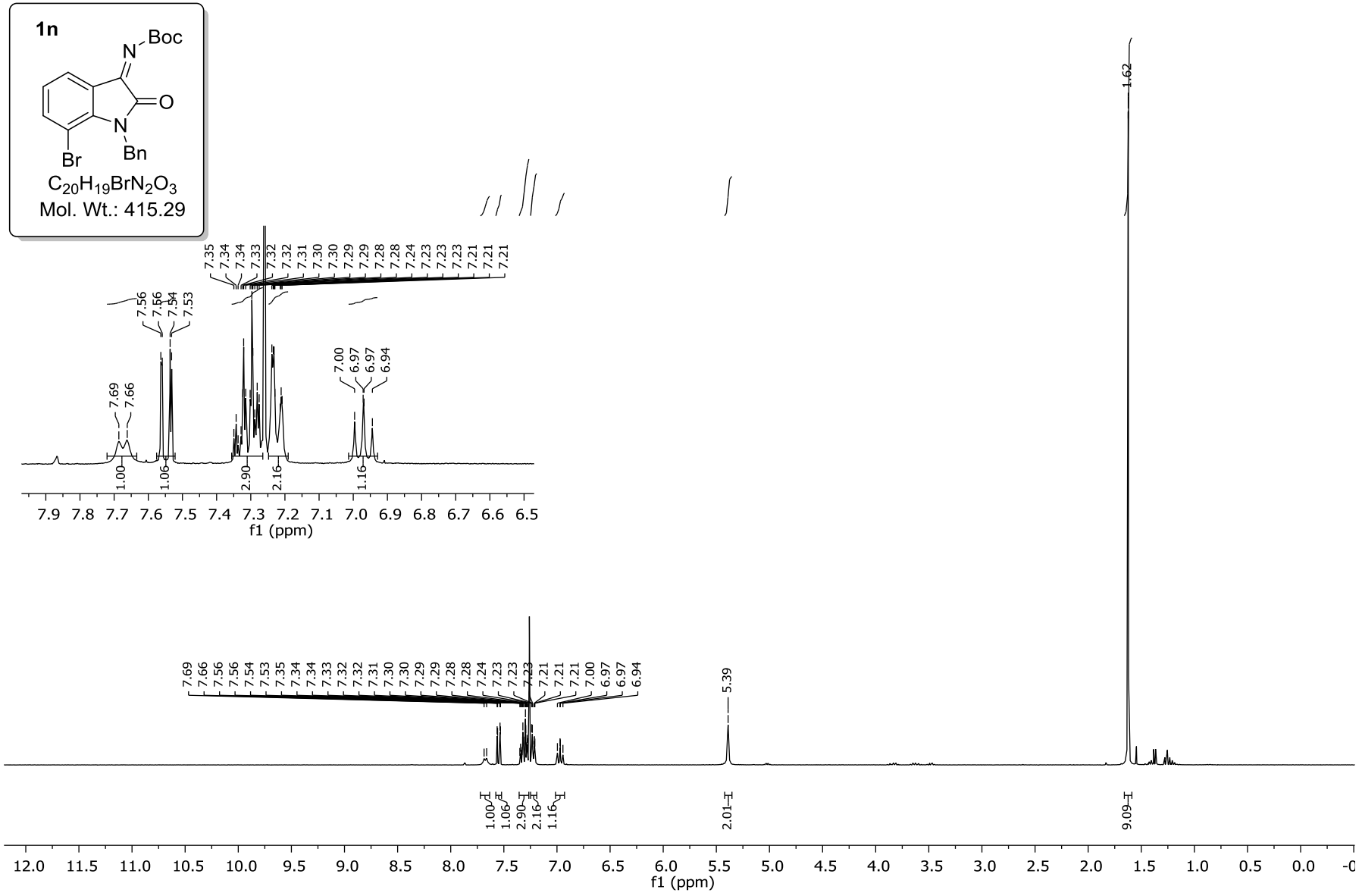
MU 1063

tert-Butyl (*Z*)-(1-benzyl-6-bromo-2-oxoindolin-3-ylidene)carbamate (1m)



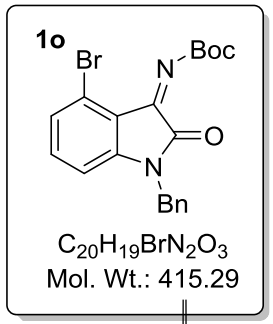
MU 1059

tert-Butyl (*Z*)-(1-benzyl-7-bromo-2-oxoindolin-3-ylidene)carbamate (1n)



FM 106.1.fid
1H

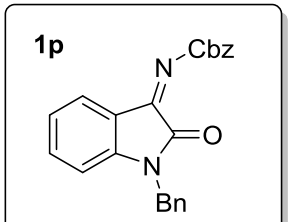
tert-Butyl (*Z*)-(1-benzyl-4-bromo-2-oxoindolin-3-ylidene)carbamate (1o)



$C_{20}H_{19}BrN_2O_3$
Mol. Wt.: 415.29

FM31_acav_DMSO
standard 1H

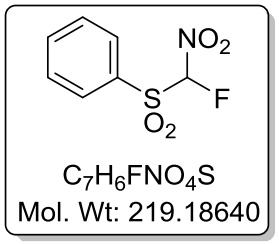
Benzyl (Z)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate (1p)



$C_{23}H_{18}N_2O_3$
Mol. Wt.: 370.40800

MU 732_NO2.1.fid
1H

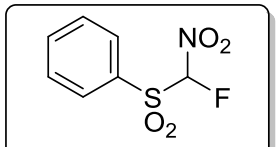
((Fluoro(nitro)methyl)sulfonyl)benzene (2a)



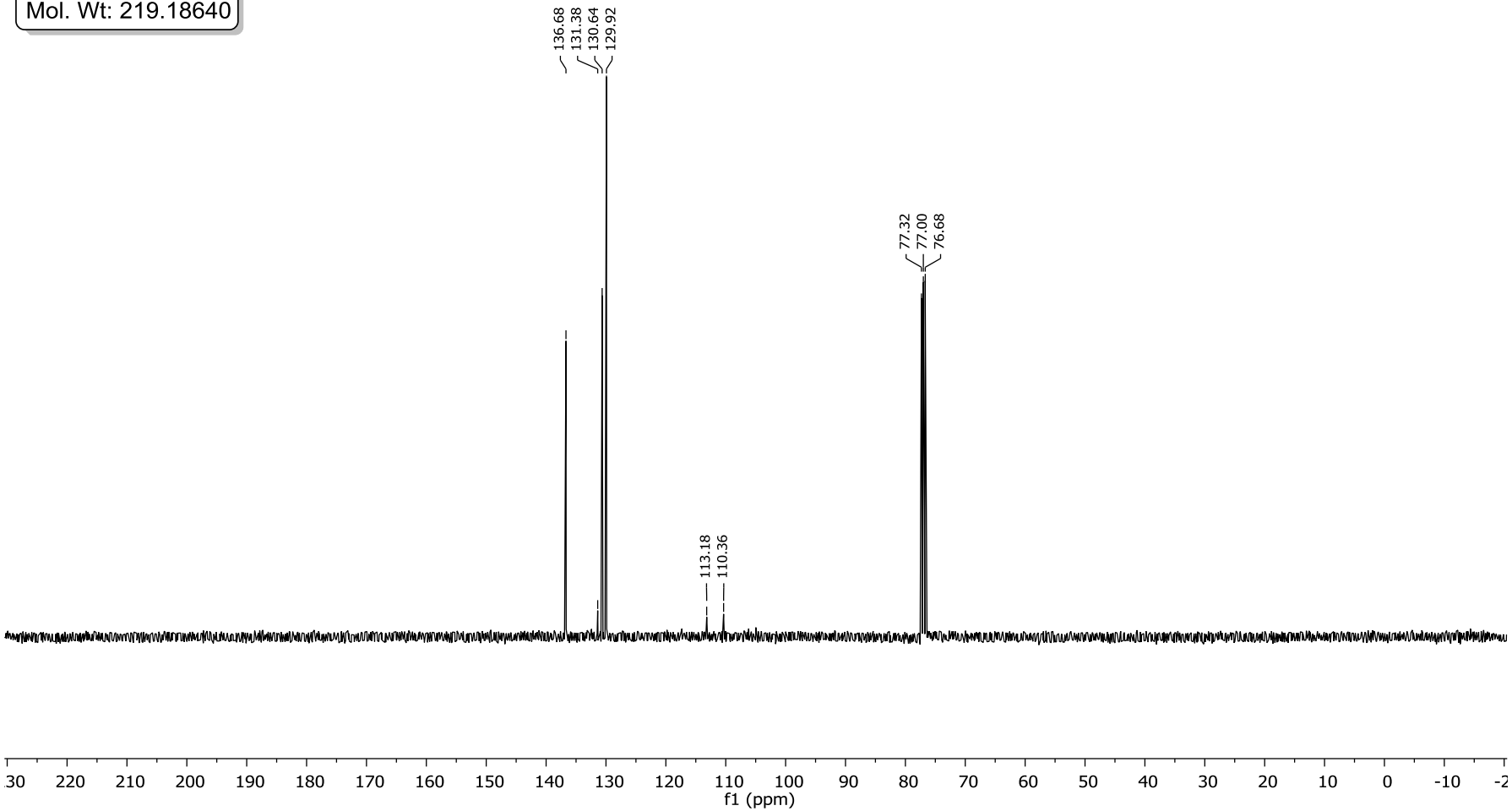
$C_7H_6FNO_4S$
Mol. Wt: 219.18640

MU 732_NO2.2.fid
13C

((Fluoro(nitro)methyl)sulfonyl)benzene (2a)

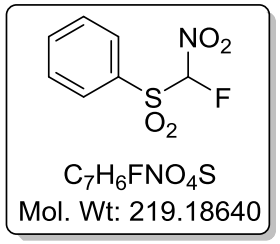


$C_7H_6FNO_4S$
Mol. Wt: 219.18640



MU 732_F.1.fid
19F

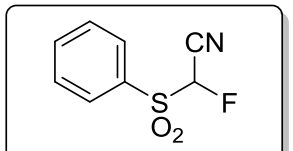
((Fluoro(nitro)methyl)sulfonyl)benzene (2a)



$C_7H_6FNO_4S$
Mol. Wt: 219.18640

MU 606_CN.1.fid
1H

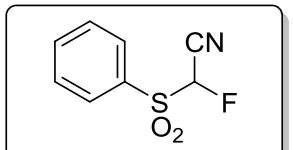
2-Fluoro-2-(phenylsulfonyl)acetonitrile (2b)



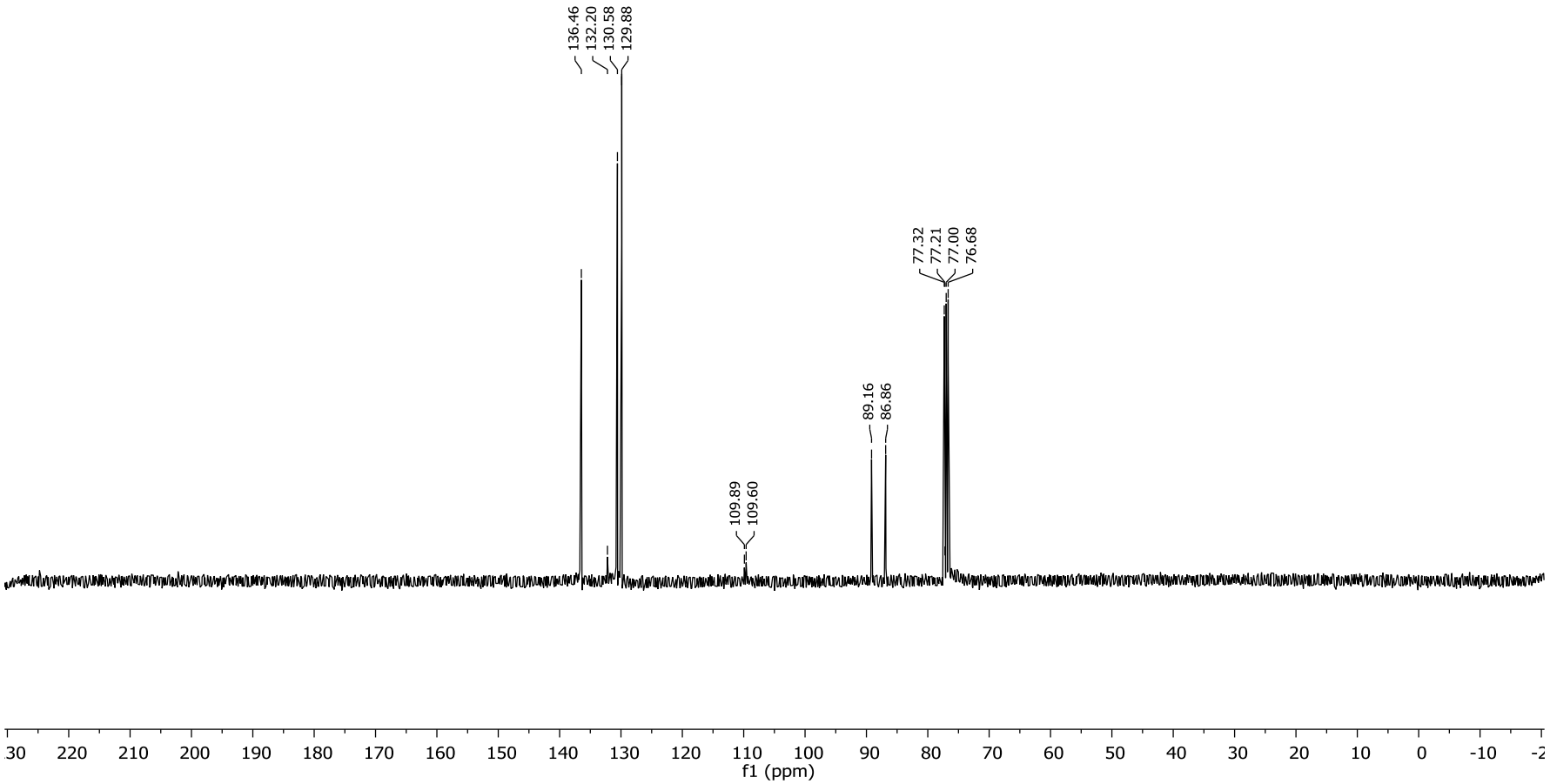
$C_8H_6FNO_2S$
Mol. Wt.: 199.19940

MU 606_CN_C.2.fid
13C

2-Fluoro-2-(phenylsulfonyl)acetonitrile (2b)

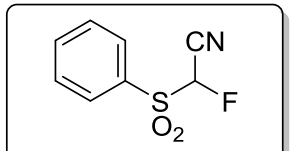


$C_8H_6FNO_2S$
Mol. Wt.: 199.19940

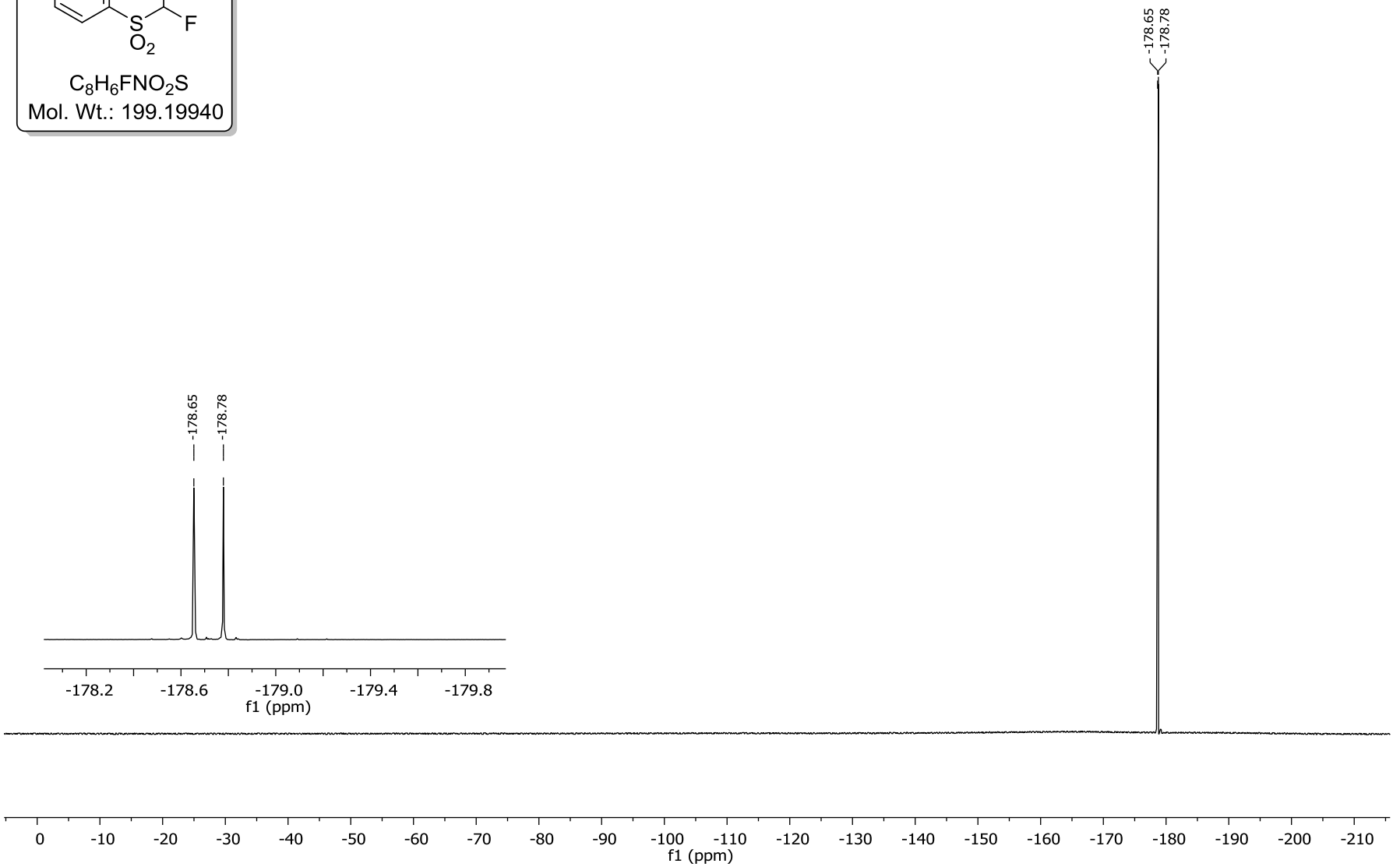


MU 606_F.1.fid
19F

2-Fluoro-2-(phenylsulfonyl)acetonitrile (2b)

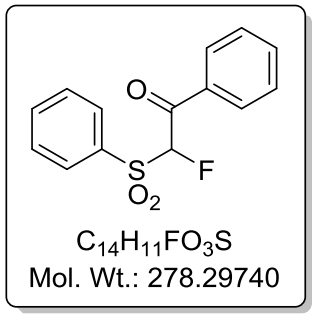


$C_8H_6FNO_2S$
Mol. Wt.: 199.19940

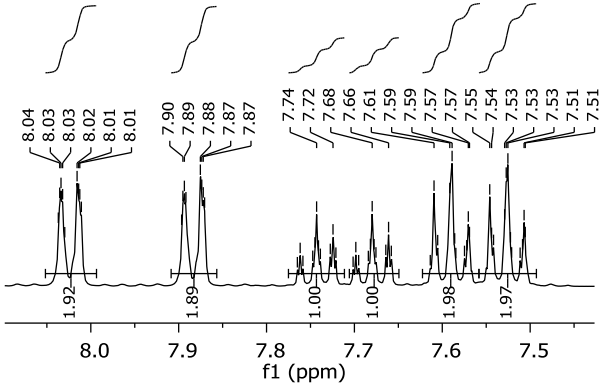


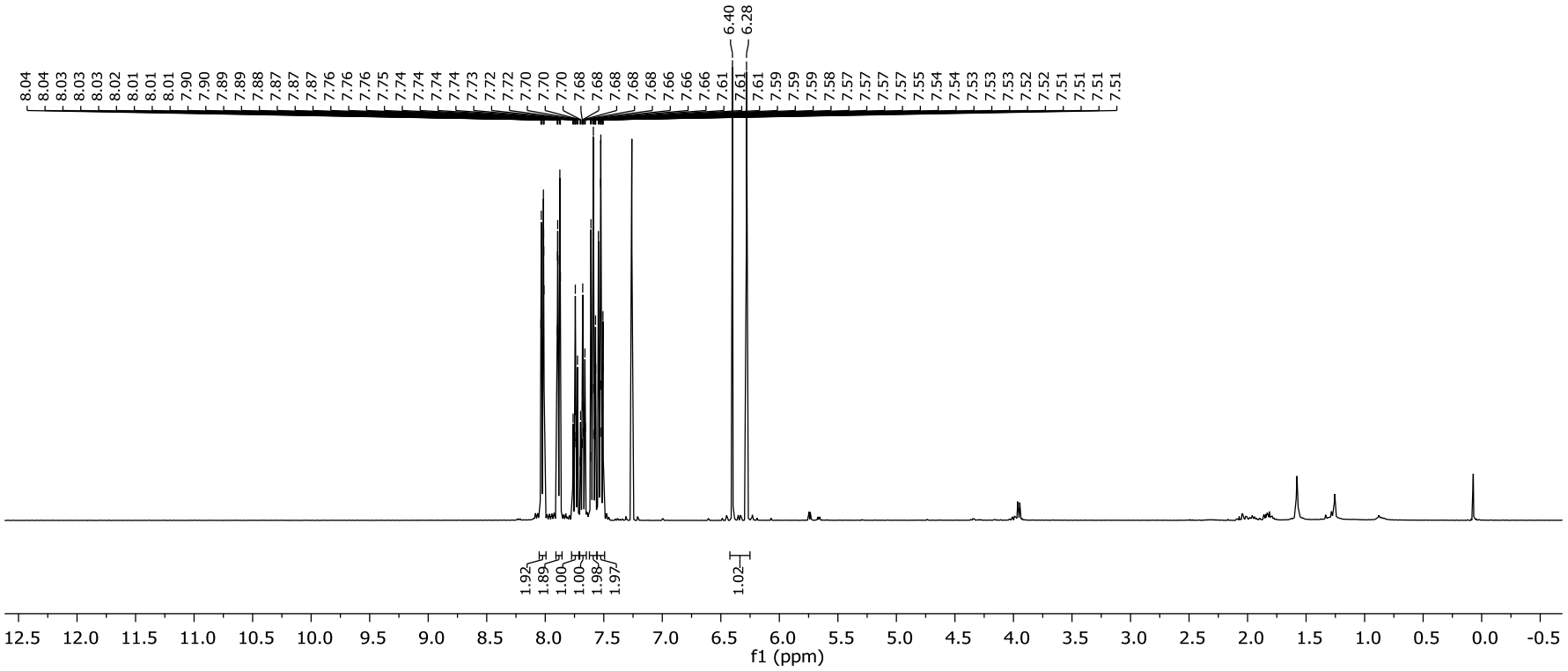
MU 588_COPh_C.1.fid
1H

2-fluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-one (2c)



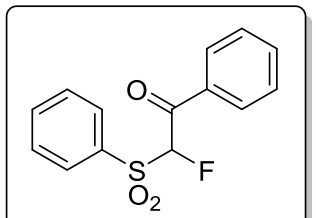
$C_{14}H_{11}FO_3S$
Mol. Wt.: 278.29740



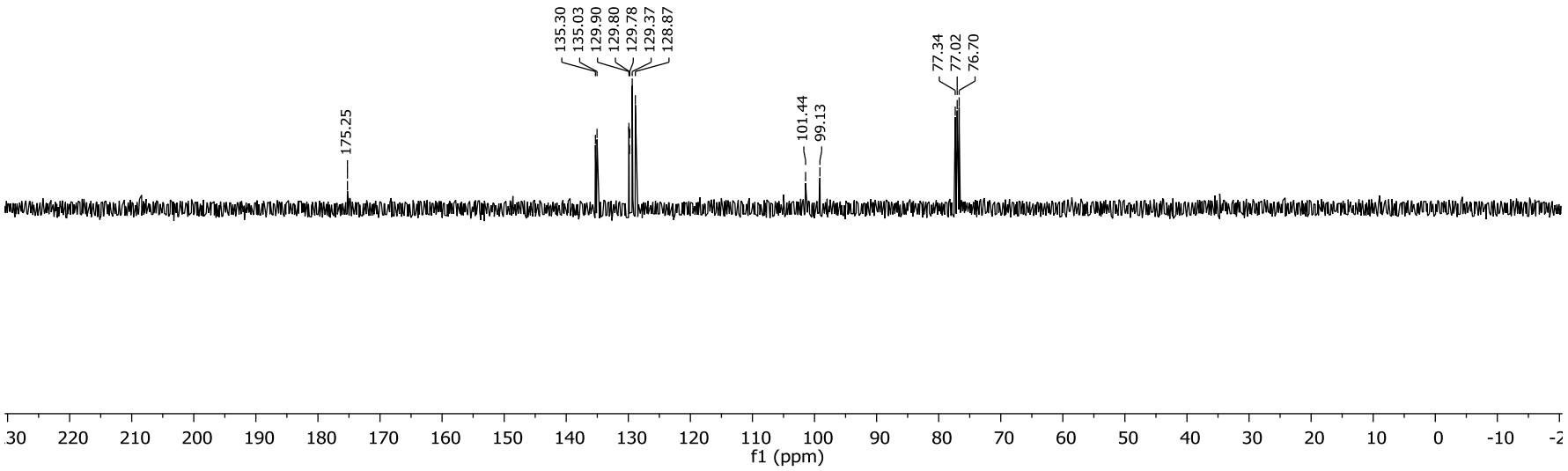


MU 588_COPh.2.fid
13C

2-fluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-one (2c)

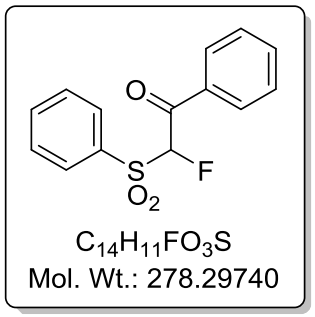


$C_{14}H_{11}FO_3S$
Mol. Wt.: 278.29740



MU 588_F.1.fid
19F

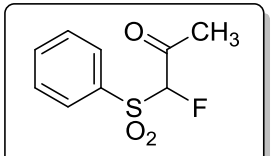
2-fluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-one (2c)



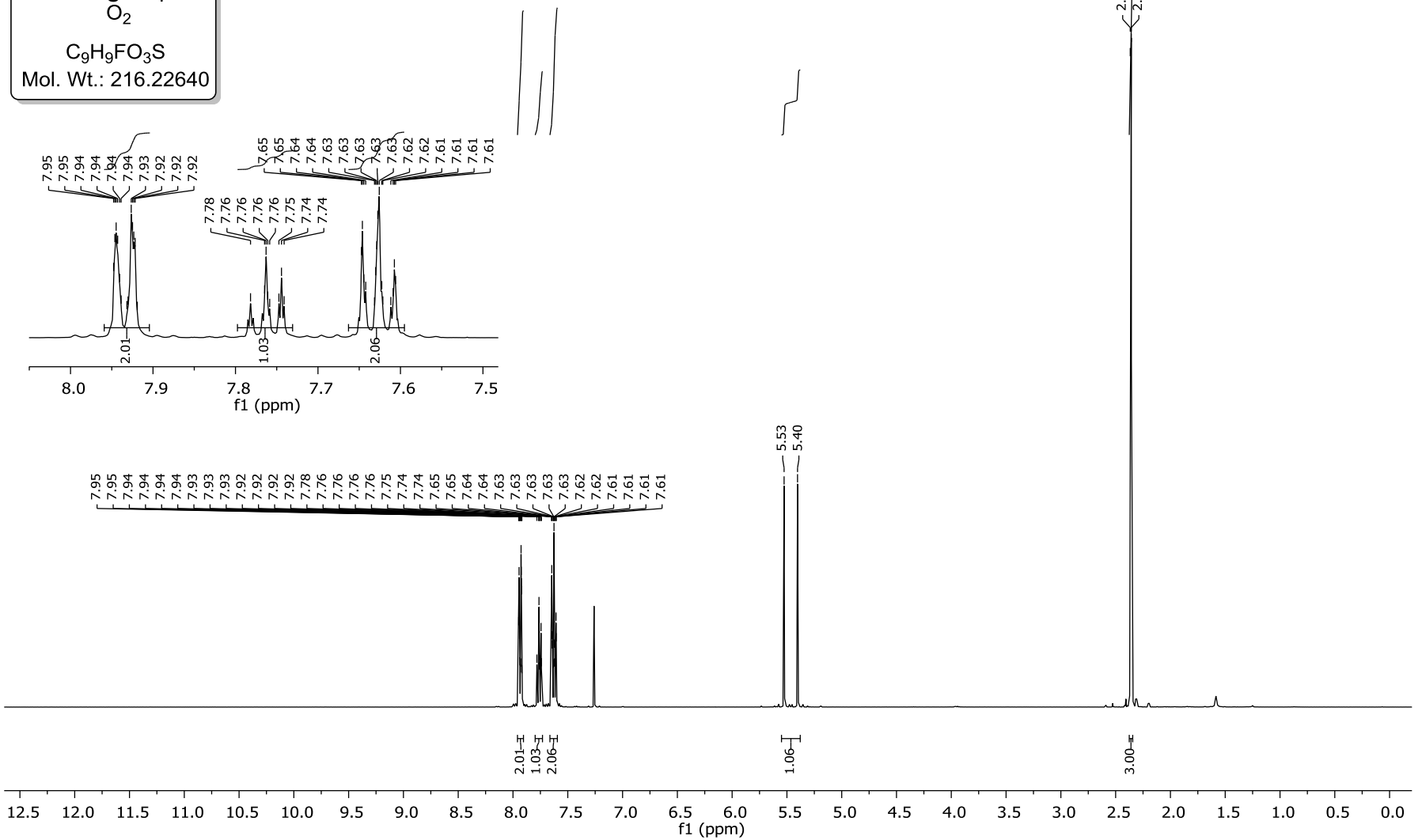
$C_{14}H_{11}FO_3S$
Mol. Wt.: 278.29740

MU 633_COMe_C.1.fid
1H

1-Fluoro-1-(phenylsulfonyl)propan-2-one (2d)

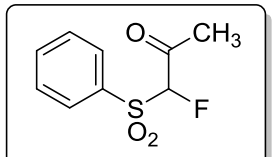


$C_9H_9FO_3S$
Mol. Wt.: 216.22640

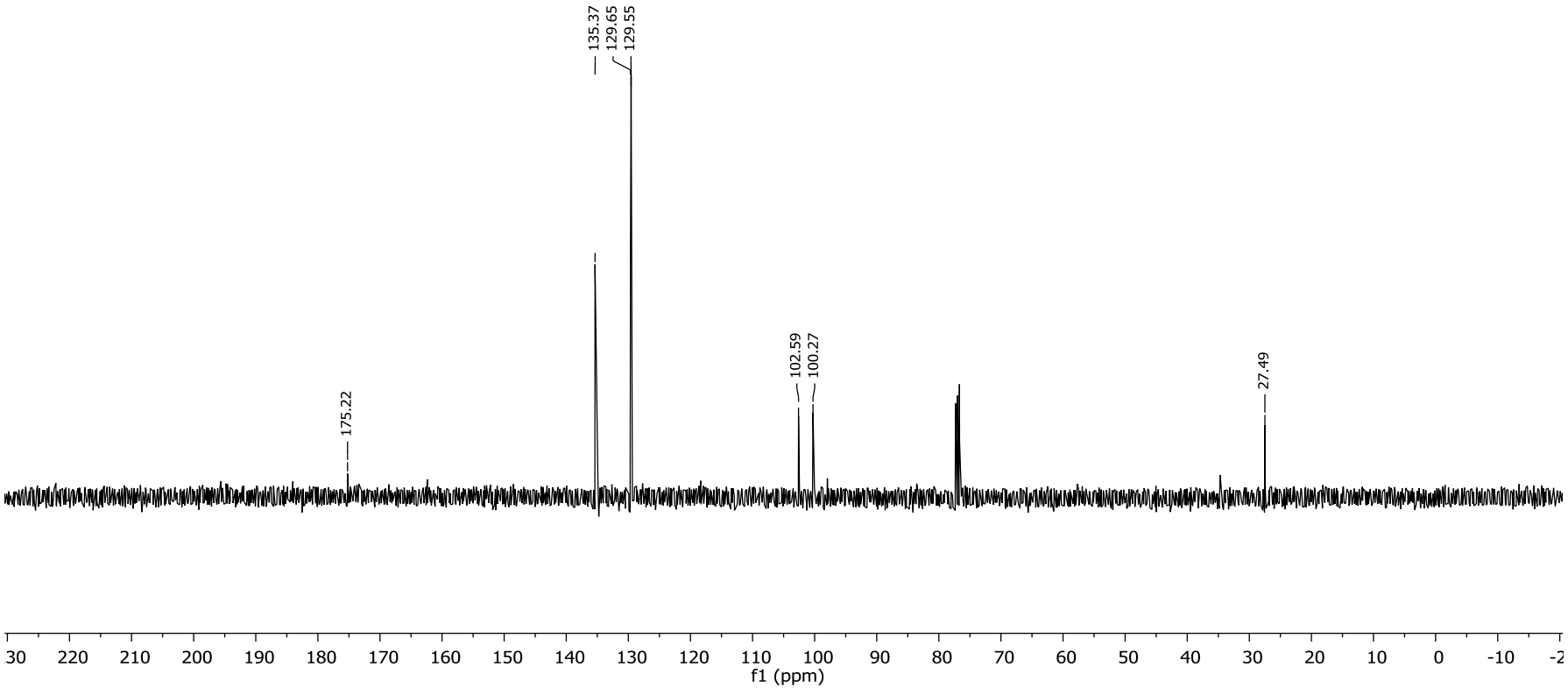


MU 633_COMe_C.2.fid
13C

1-Fluoro-1-(phenylsulfonyl)propan-2-one (2d)

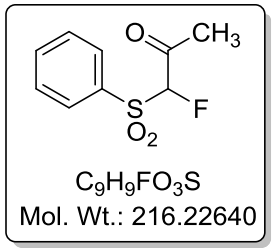


$C_9H_9FO_3S$
Mol. Wt.: 216.22640



MU 633_F.1.fid
19F

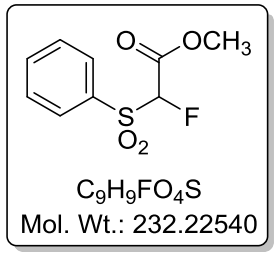
1-Fluoro-1-(phenylsulfonyl)propan-2-one (2d)



$C_9H_9FO_3S$
Mol. Wt.: 216.22640

MU 488_COOMe.1.fid
1H

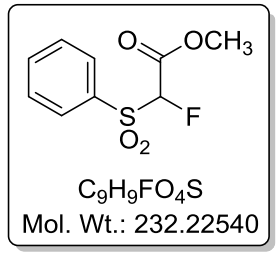
Methyl 2-Fluoro-2-(phenylsulfonyl)acetate (2e)



$C_9H_9FO_4S$
Mol. Wt.: 232.22540

MU 488_COOMe_C.2.fid
13C

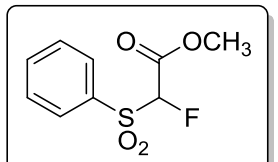
Methyl 2-fluoro-2-(phenylsulfonyl)acetate (2e)



$C_9H_9FO_4S$
Mol. Wt.: 232.22540

MU 488_F.1.fid
19F

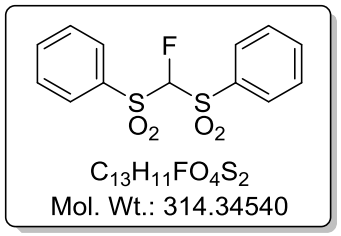
Methyl 2-fluoro-2-(phenylsulfonyl)acetate (2e)



$C_9H_9FO_4S$
Mol. Wt.: 232.22540

MU 381_PhSO2_C.1.fid
1H

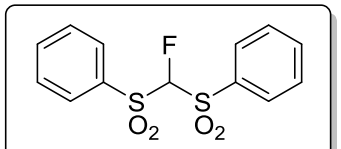
Bis(phenylsulfonyl)fluoromethane (2f)



$C_{13}H_{11}FO_4S_2$
Mol. Wt.: 314.34540

MU 381_PhSO2_C.2.fid
13C

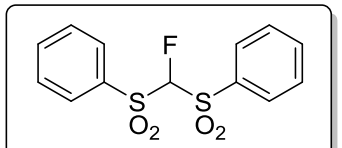
Bis(phenylsulfonyl)fluoromethane (2f)



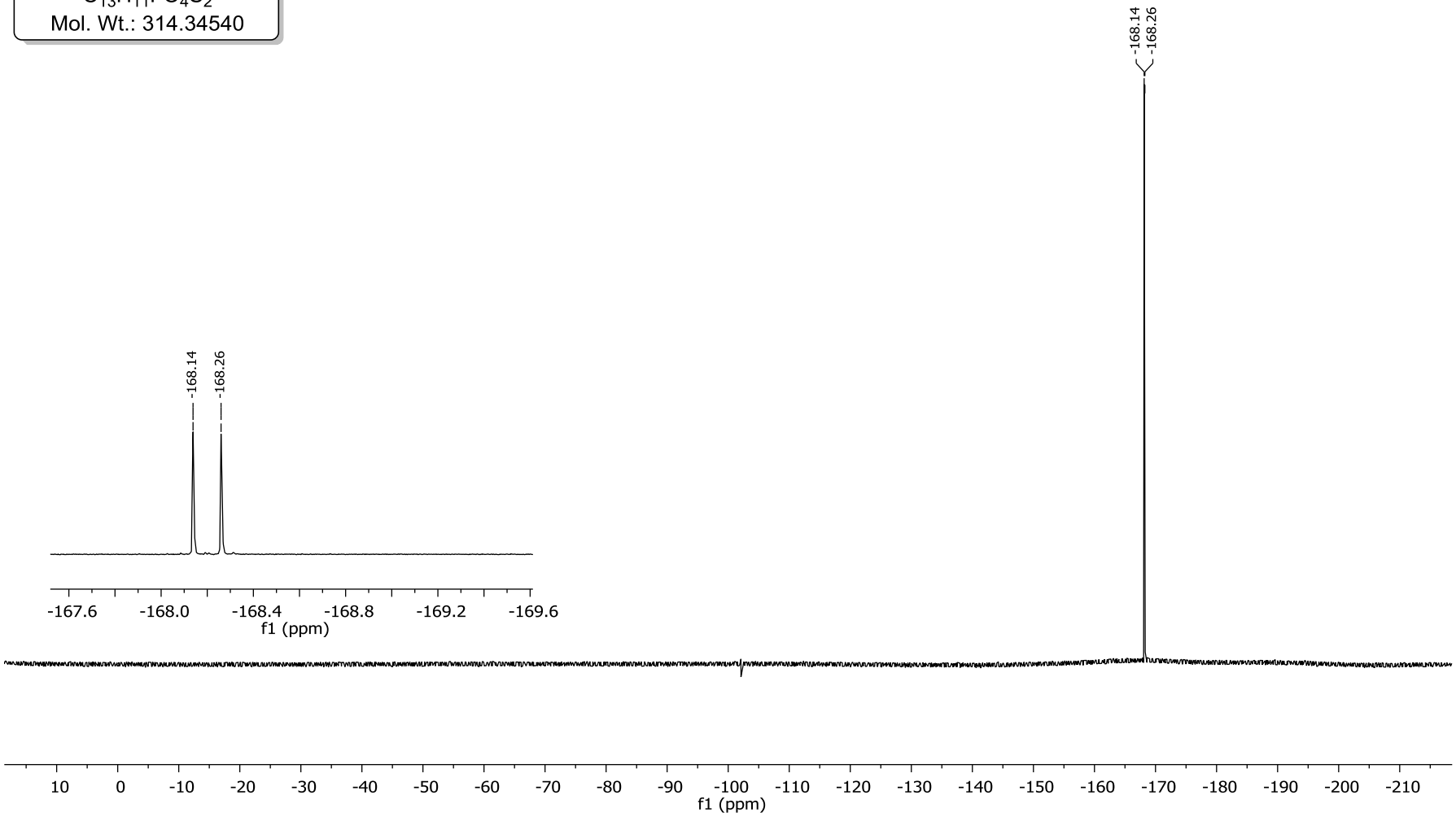
$C_{13}H_{11}FO_4S_2$
Mol. Wt.: 314.34540

MU 381_F.1.fid
19F

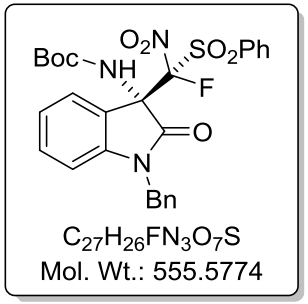
Bis(phenylsulfonyl)fluoromethane (2f)



$C_{13}H_{11}FO_4S_2$
Mol. Wt.: 314.34540

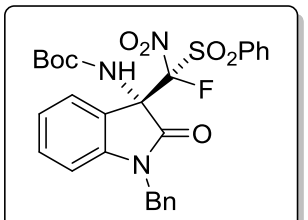


tert-Butyl ((S)-1-benzyl-3-((R)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a)



$C_{27}H_{26}FN_3O_7S$
Mol. Wt.: 555.5774

tert-Butyl ((*S*)-1-benzyl-3-((R)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a)

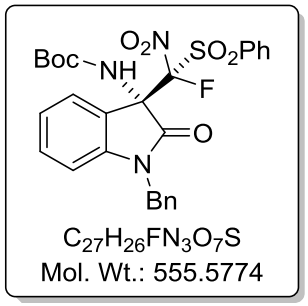


$C_{27}H_{26}FN_3O_7S$

Mol. Wt.: 555.5774

MU 600_major_NMR.3.fid
19F

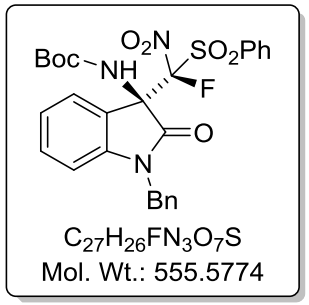
tert-Butyl ((*S*)-1-benzyl-3-((R)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a) - MAJOR



$C_{27}H_{26}FN_3O_7S$
Mol. Wt.: 555.5774

MU600_minor_cryo.1.fid
MU600_minor_cryo

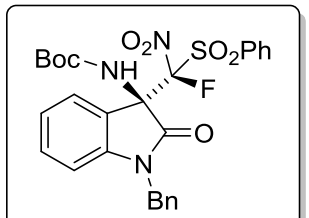
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a')



$C_{27}H_{26}FN_3O_7S$
Mol. Wt.: 555.5774

MU600_minor cryo.2.fid
MU600_minor cryo

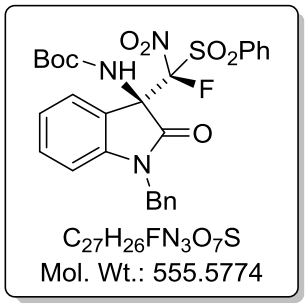
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a')



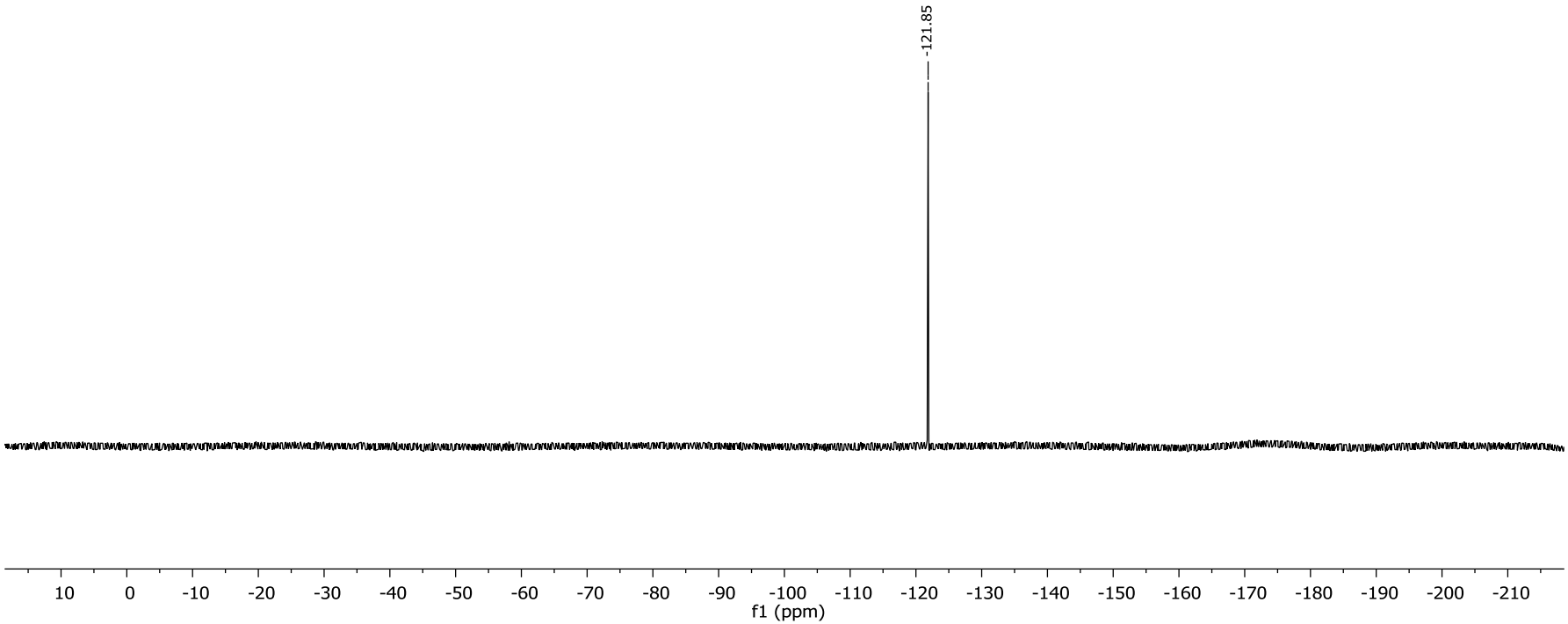
$C_{27}H_{26}FN_3O_7S$
Mol. Wt.: 555.5774

MU 600_minor_NMR.3.fid
19F

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a')

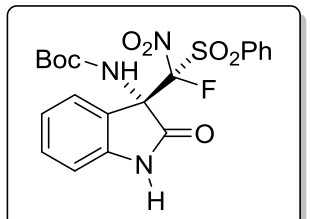


$C_{27}H_{26}FN_3O_7S$
Mol. Wt.: 555.5774



MU 602_Major

tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b)

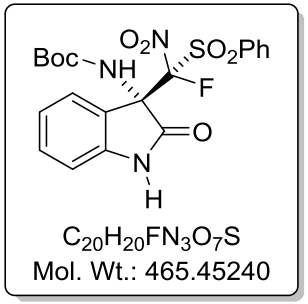


$C_{20}H_{20}FN_3O_7S$

Mol. Wt.: 465.45240

MU 602_Major

tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b)

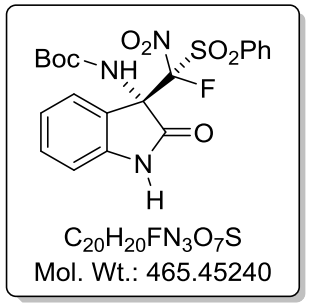


$C_{20}H_{20}FN_3O_7S$

Mol. Wt.: 465.45240

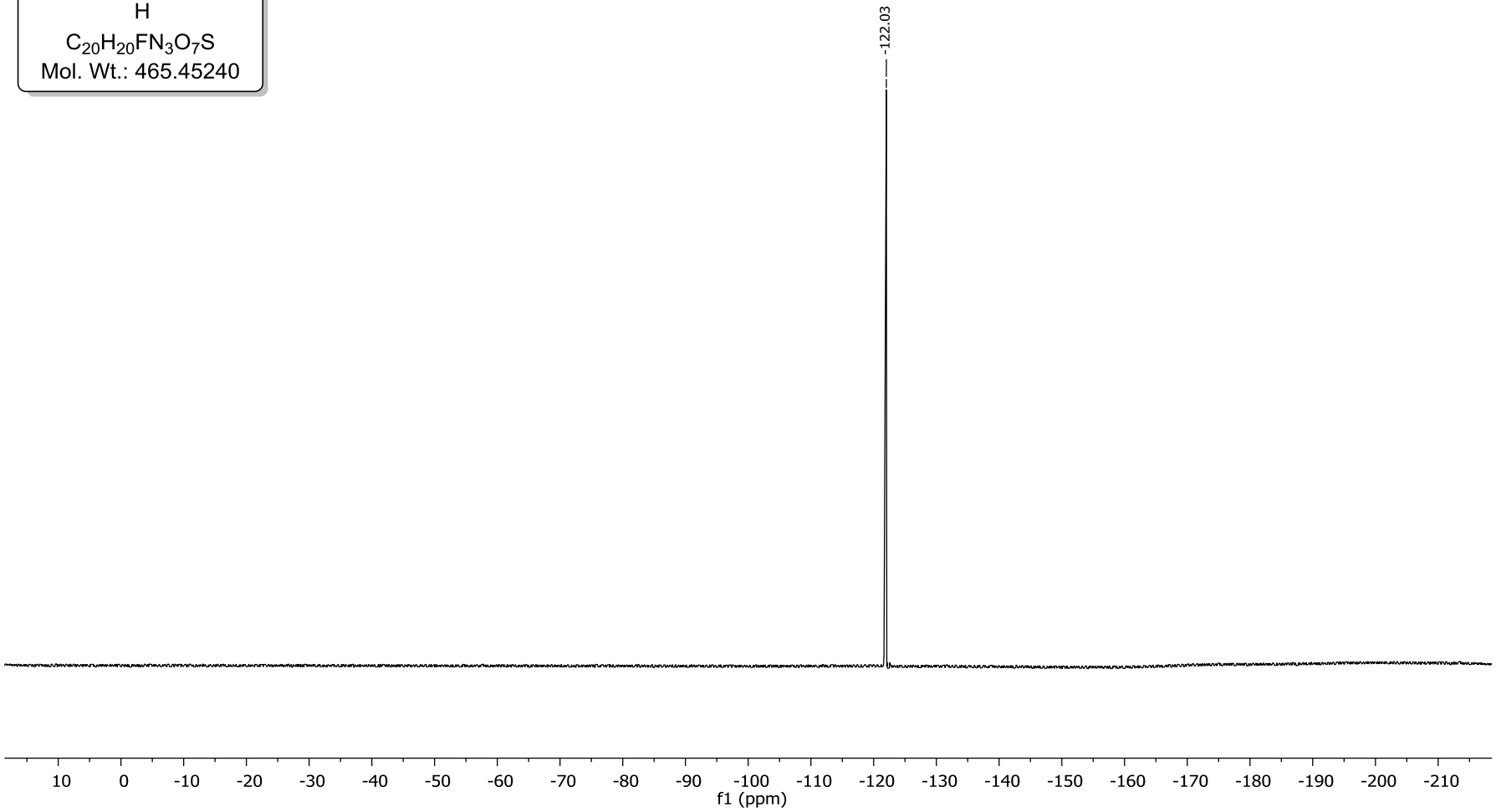
MU 602_Major

tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b)



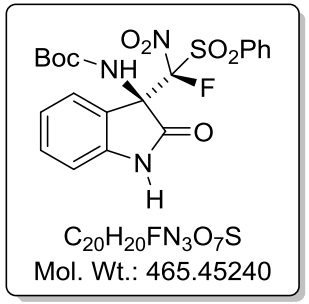
$C_{20}H_{20}FN_3O_7S$

Mol. Wt.: 465.45240



MU 602_Minor

tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')

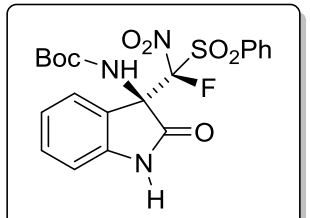


$C_{20}H_{20}FN_3O_7S$

Mol. Wt.: 465.45240

MU 602_Minor

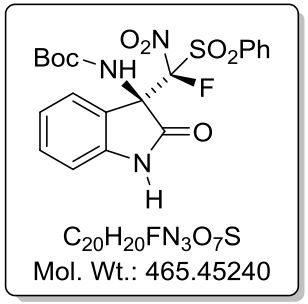
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')



$C_{20}H_{20}FN_3O_7S$
Mol. Wt.: 465.45240

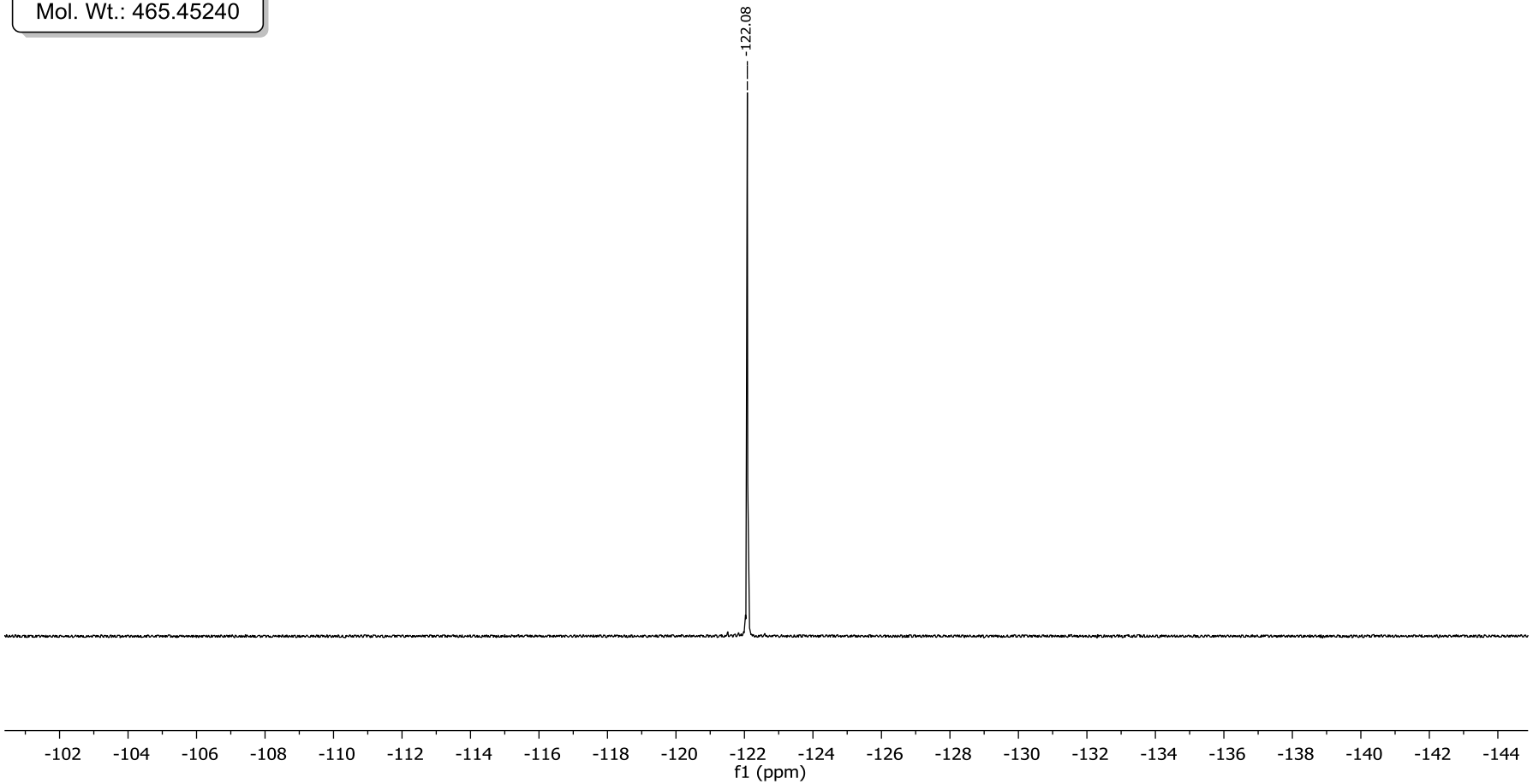
MU 602_Minor

tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')



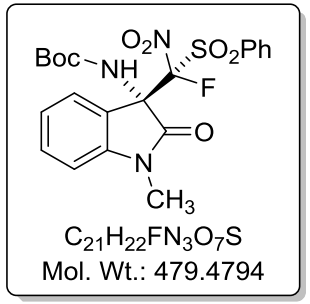
$C_{20}H_{20}FN_3O_7S$

Mol. Wt.: 465.45240



MU603 22022017 cryo.1.fid
MU603 22022017 cryo 1H

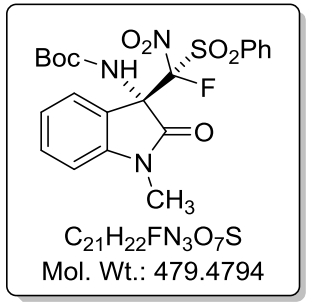
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c)



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU603_major_cryo.2.fid
MU603_major_cryo

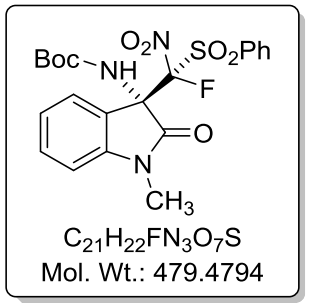
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c)



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU 603_major.3.fid
19F

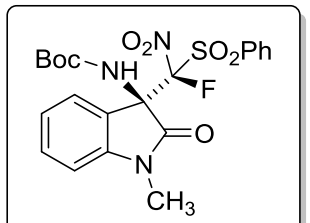
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c)



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU603_minor_cryo.3.fid
MU603_minor_cryo

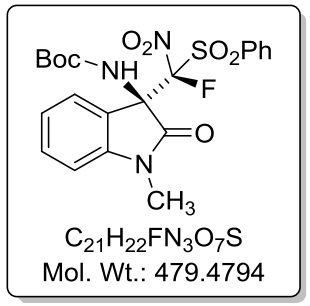
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c')



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU603_minor_cryo.4.fid
MU603_minor_cryo

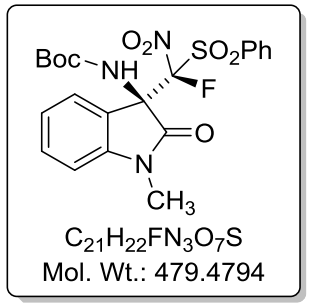
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c')



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU 603_minor.3.fid
1H

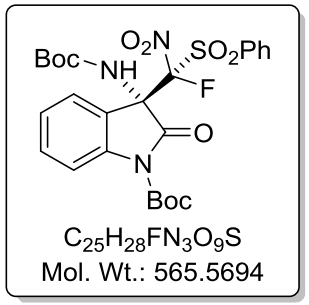
tert-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c')



$C_{21}H_{22}FN_3O_7S$
Mol. Wt.: 479.4794

MU 604_Major

tert-Butyl (*S*)-3-((tert-butoxycarbonyl)amino)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d)

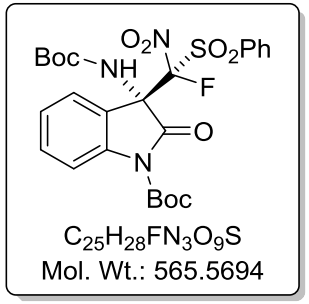


$C_{25}H_{28}FN_3O_9S$

Mol. Wt.: 565.5694

MU 604_Major

tert-Butyl (*S*)-3-((tert-butoxycarbonyl)amino)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d)

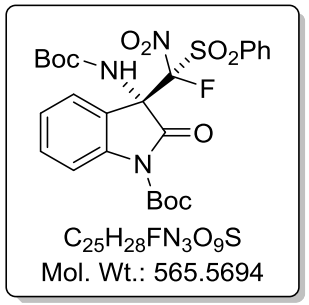


$C_{25}H_{28}FN_3O_9S$

Mol. Wt.: 565.5694

MU 604_major.3.fid
19F

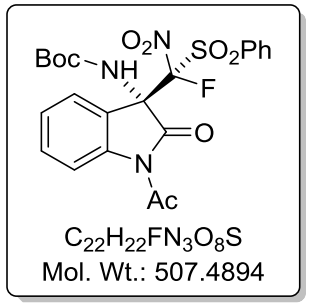
tert-Butyl (*S*)-3-((*tert*-butoxycarbonyl)amino)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d)



$C_{25}H_{28}FN_3O_9S$
Mol. Wt.: 565.5694

MU605_major cryo.1.fid
MU605_major cryo 1H

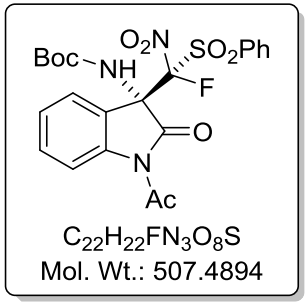
tert-Butyl ((*S*)-1-acetyl-3-((i)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e)



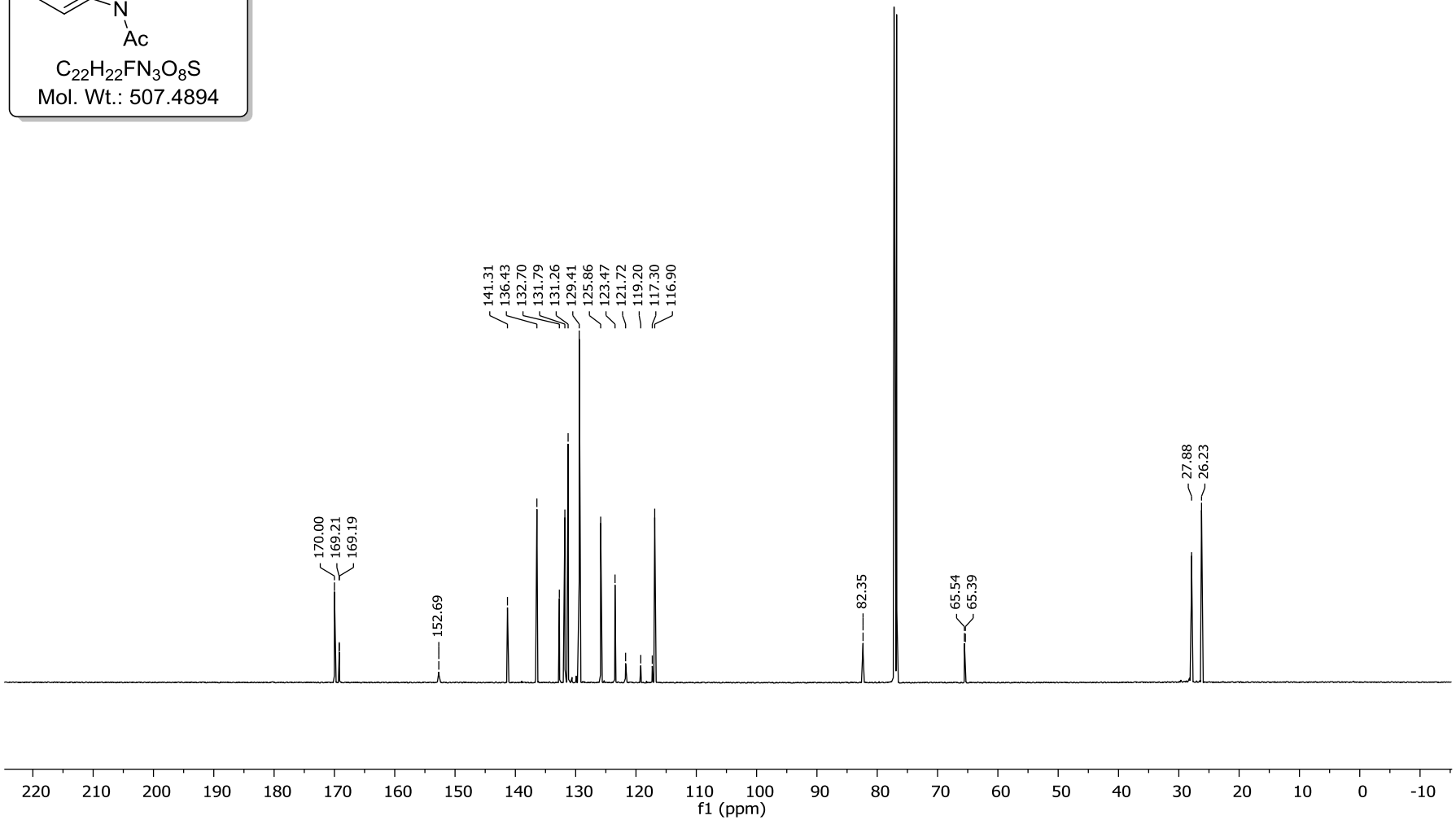
$C_{22}H_{22}FN_3O_8S$
Mol. Wt.: 507.4894

MU605_major_cryo.2.fid
MU605_major_cryo

tert-Butyl ((*S*)-1-acetyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e)

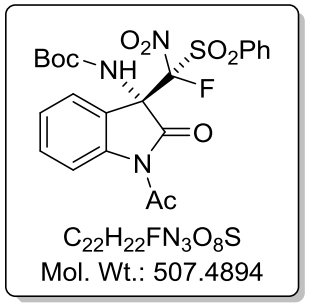


$C_{22}H_{22}FN_3O_8S$
Mol. Wt.: 507.4894

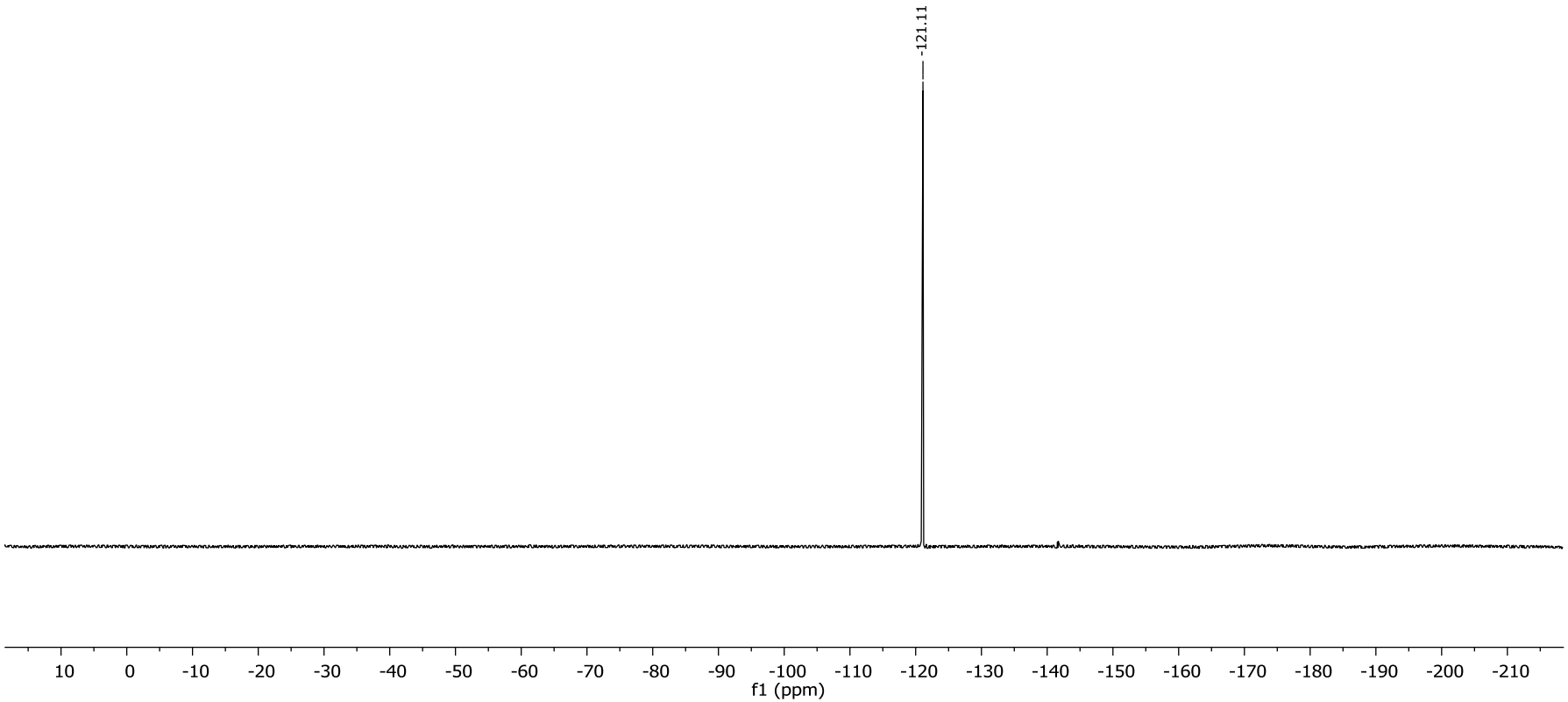


MU 605_major.3.fid
19F

tert-Butyl ((*S*)-1-acetyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e)

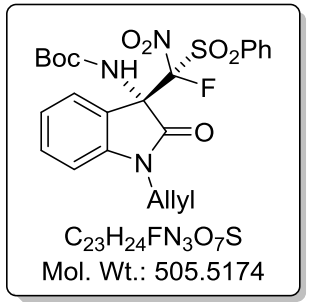


$C_{22}H_{22}FN_3O_8S$
Mol. Wt.: 507.4894



MU755_major cryo.3.fid
MU755_major cryo zg30

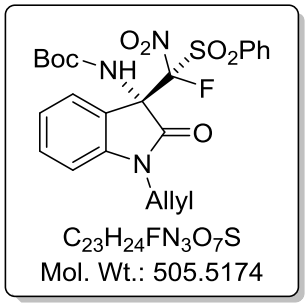
tert-Butyl ((*S*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f)



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU755_major cryo.4.fid
MU755_major cryo 13C

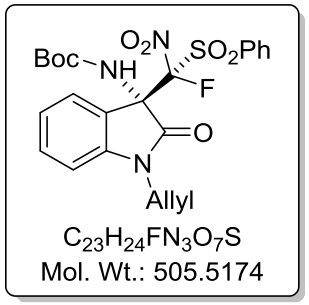
tert-Butyl ((*S*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f)



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU 755_major.2.fid
19F

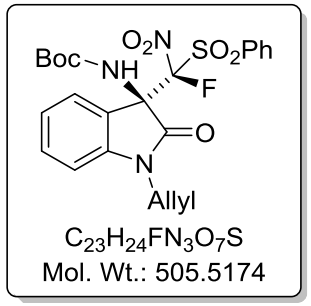
tert-butyl ((*S*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f)



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU755_minor cryo.5.fid
MU755_minor cryo zg30

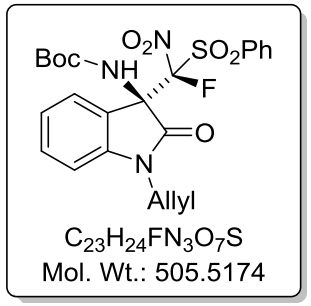
tert-butyl ((*R*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU755_minor cryo.6.fid
MU755_minor cryo 13C

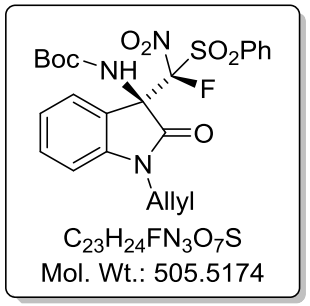
tert-butyl ((*R*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU 755_minor.2.fid
19F

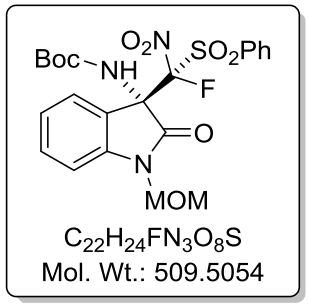
tert-butyl ((*R*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')



$C_{23}H_{24}FN_3O_7S$
Mol. Wt.: 505.5174

MU653_major cryo.1.fid
MU653_major cryo

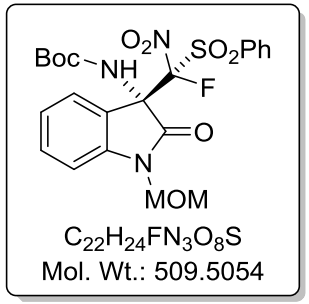
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g)



$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054

MU653_major cryo.4.fid
MU653_major cryo 13C

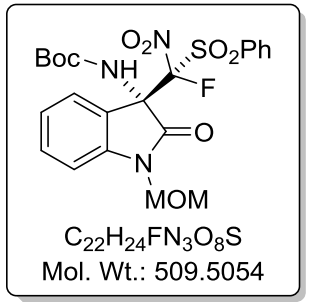
tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g)



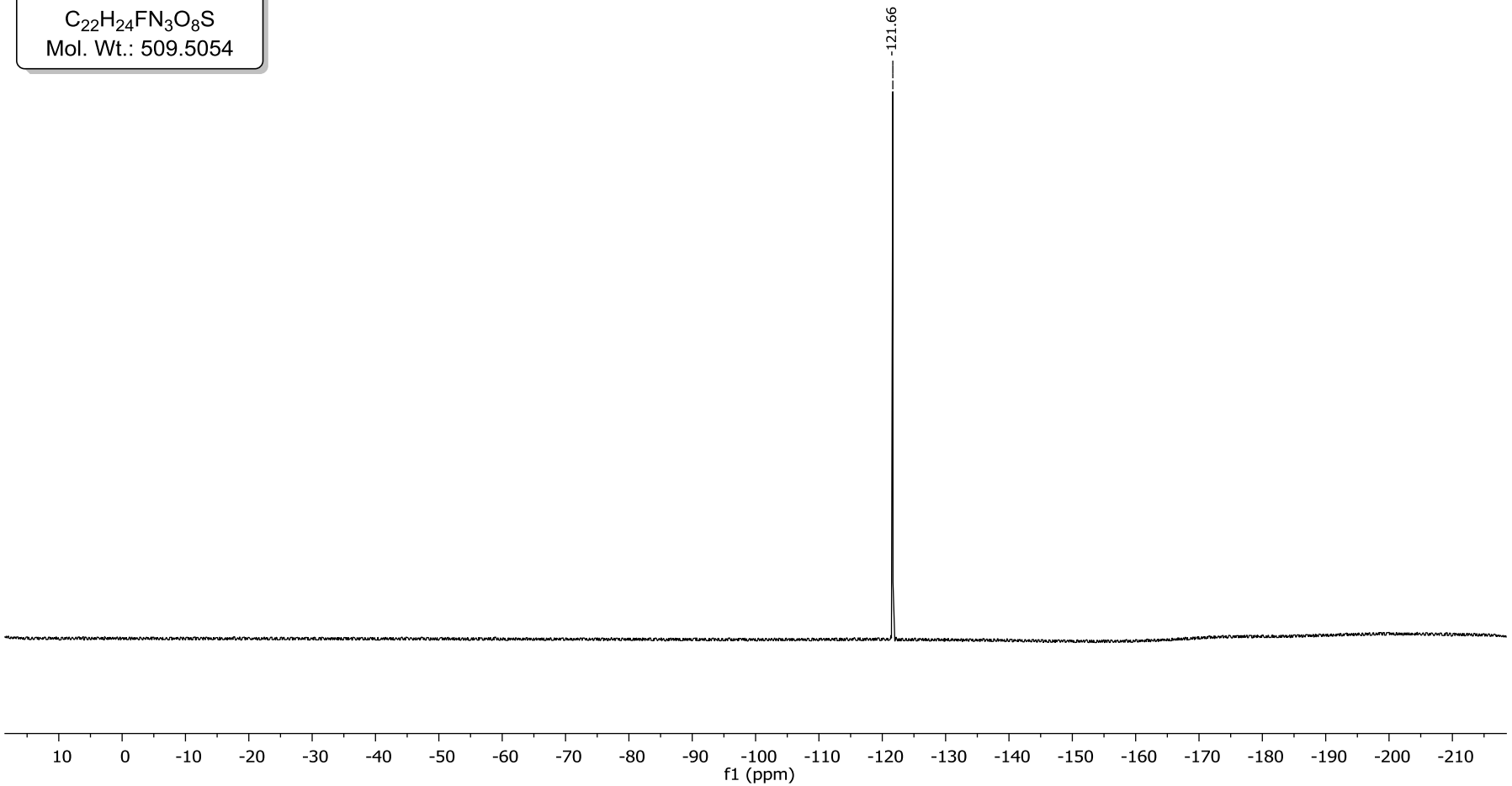
$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054

MU 653_major_1acv.3.fid
19F

tert-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g)

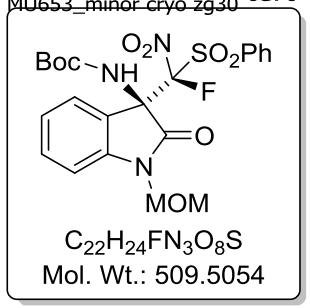


$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054



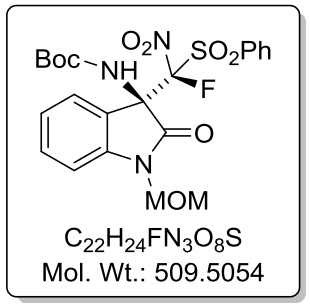
MU653_minor cryo.3.fid
MU653_minor cryo zg30

tert- Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g')



$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054

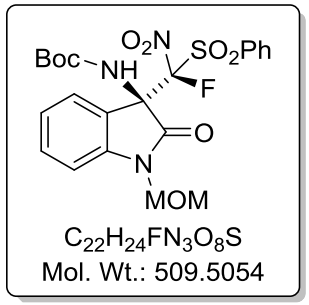
MU653_minor cryo.4.fid
MU653_minor cryo 13C *tert*- Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g')



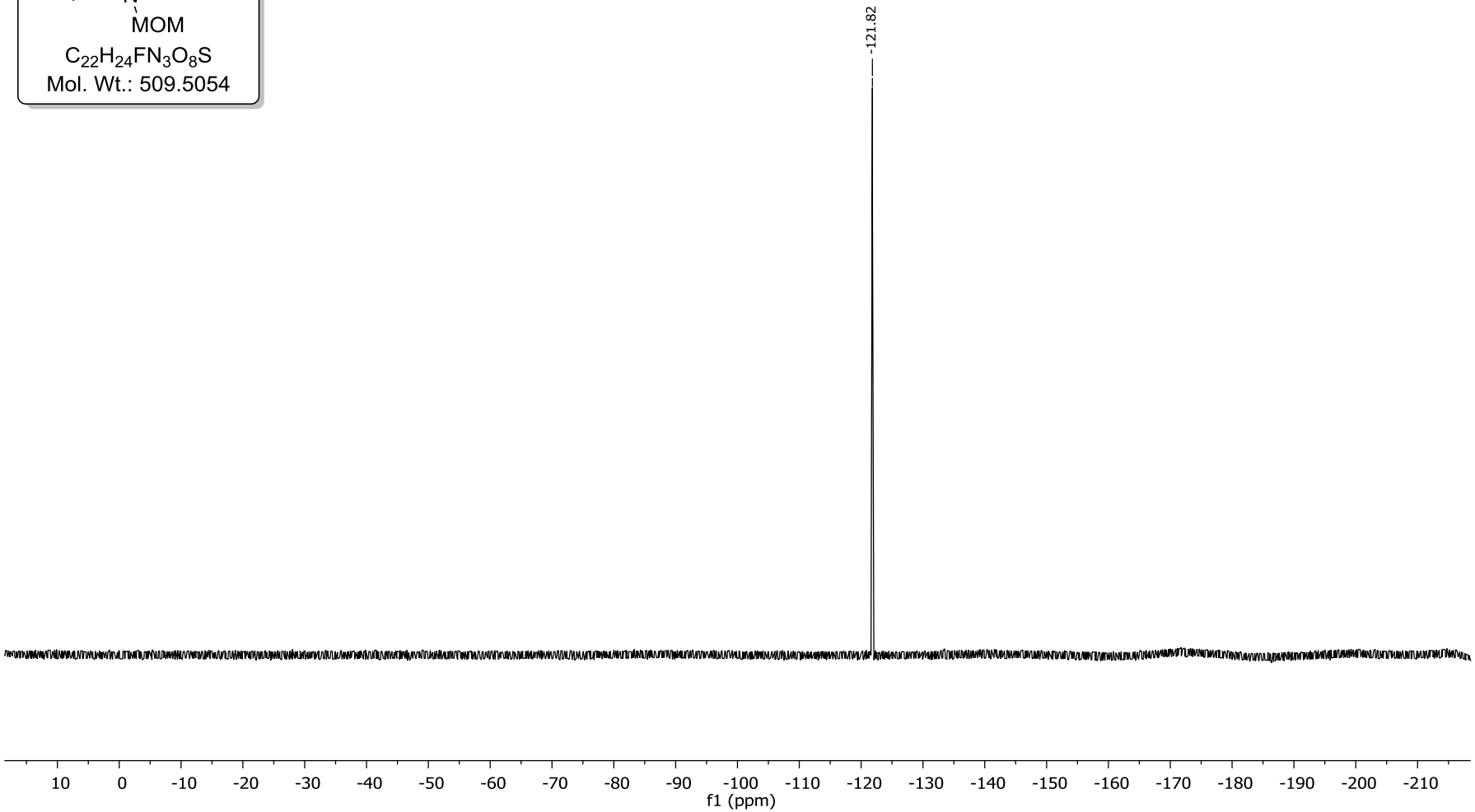
$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054

MU 653_minor_1acv.3.fid
19F

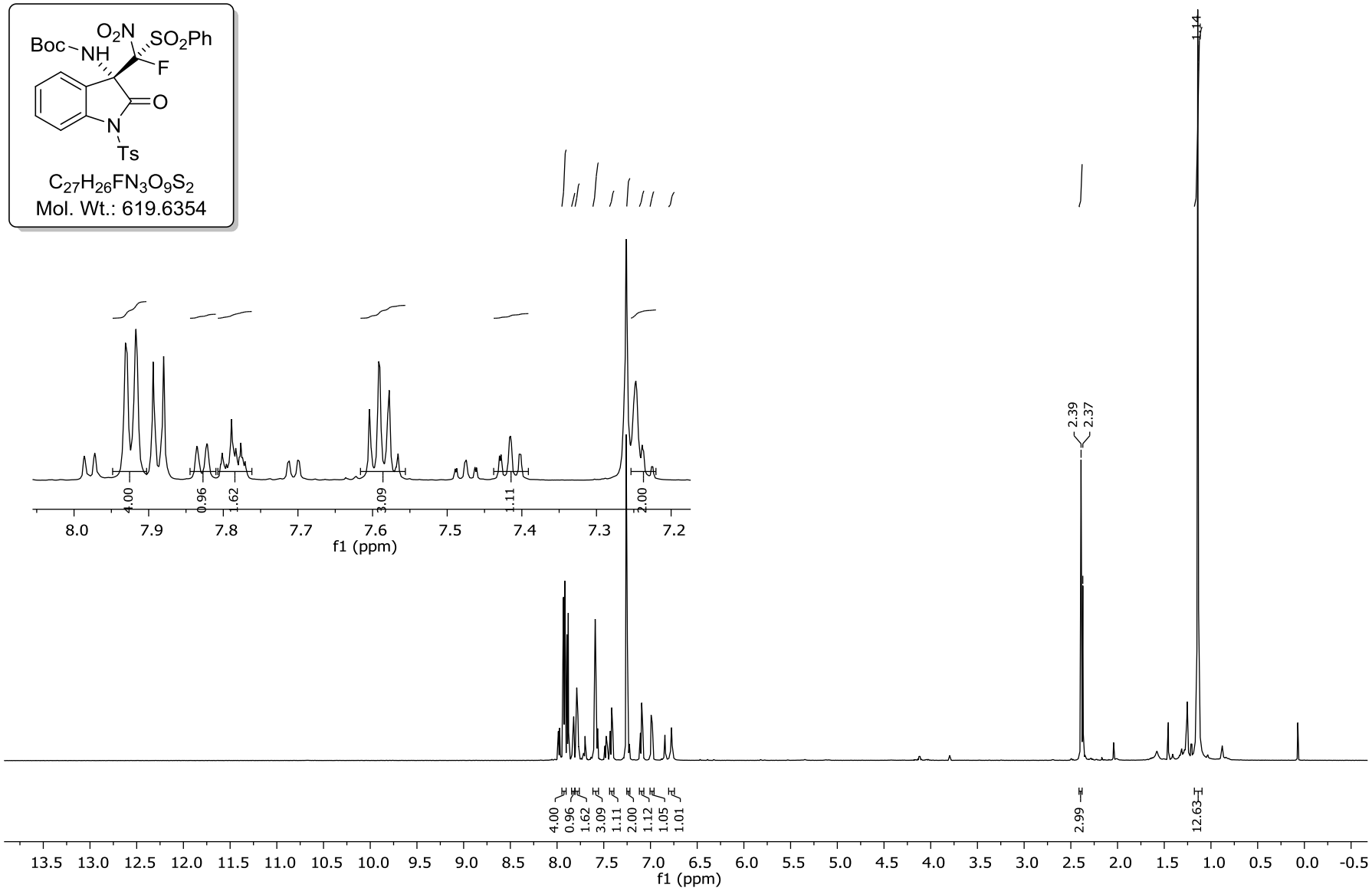
tert- Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g')



$C_{22}H_{24}FN_3O_8S$
Mol. Wt.: 509.5054

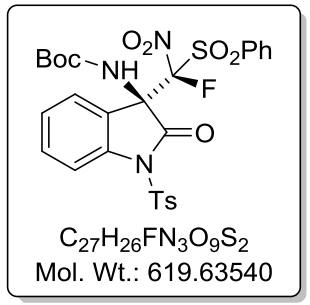


MU654 cryo.5.fid
MU654 cryo zg30 *tert*-Butyl ((*S*/*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – mixture of diastereoisomers



MU 654_Minor

tert-Butyl ((*S*/*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – mixture of diastereoisomers

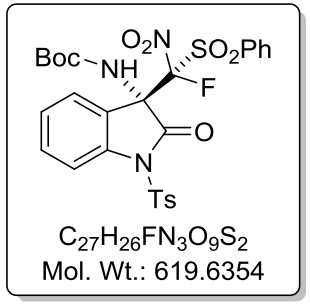


$C_{27}H_{26}FN_3O_9S_2$

Mol. Wt.: 619.63540

MU654 cryo.6.fid
MU654 cryo 13C

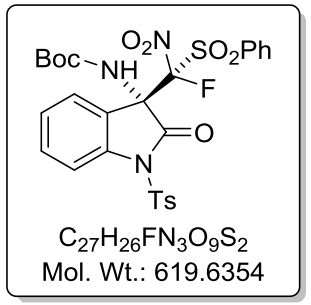
tert-Butyl ((*S*/*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – mixture of diastereoisomers



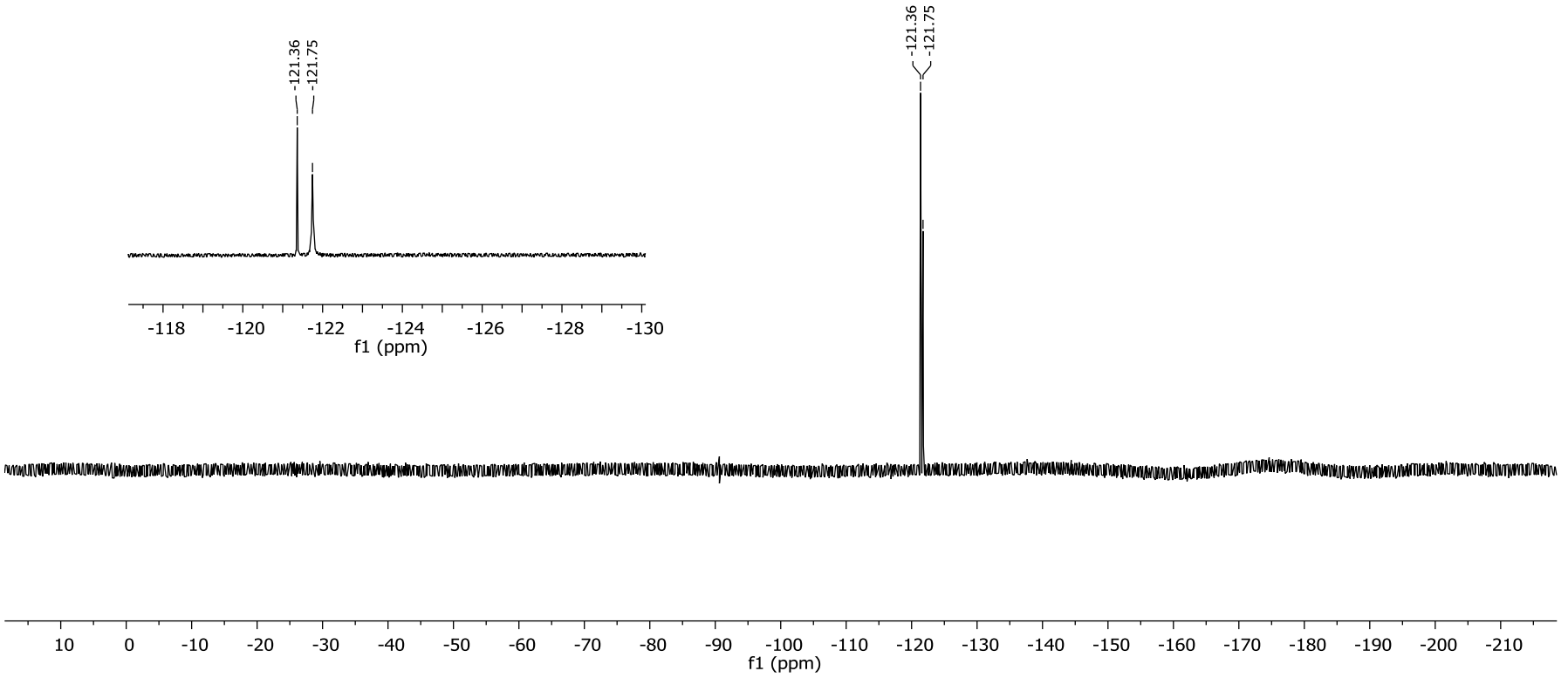
$C_{27}H_{26}FN_3O_9S_2$
Mol. Wt.: 619.6354

MU 654_chiral_1acv.3.fid
19F

tert-Butyl ((*S*/*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – mixture of diastereoisomers

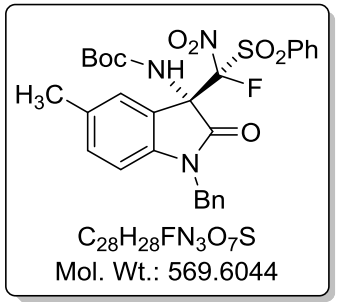


$C_{27}H_{26}FN_3O_9S_2$
Mol. Wt.: 619.6354



MU722_major.1.fid
MU722_major

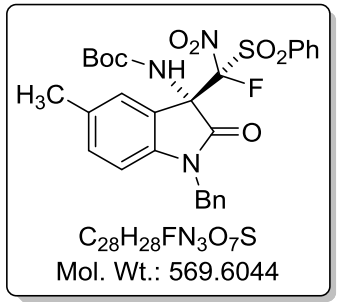
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i)



$C_{28}H_{28}FN_3O_7S$
Mol. Wt.: 569.6044

MU722_major cryo.4.fid
MU722_major cryo 13C

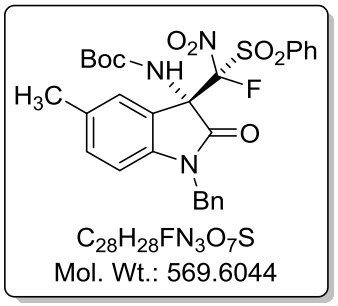
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i)



$C_{28}H_{28}FN_3O_7S$
Mol. Wt.: 569.6044

MU 722_chiral_1acv.3.fid
19F

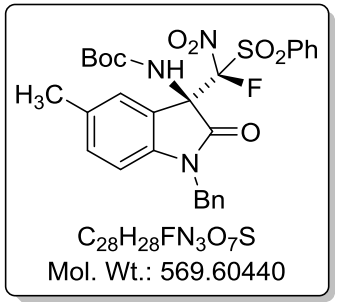
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i)



$C_{28}H_{28}FN_3O_7S$
Mol. Wt.: 569.6044

MU 722_Minor

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i')

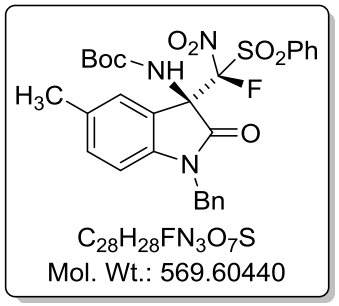


$C_{28}H_{28}FN_3O_7S$

Mol. Wt.: 569.60440

MU 722_Minor

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i')

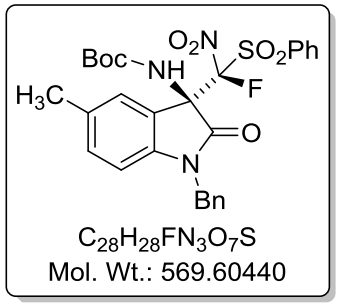


$C_{28}H_{28}FN_3O_7S$

Mol. Wt.: 569.60440

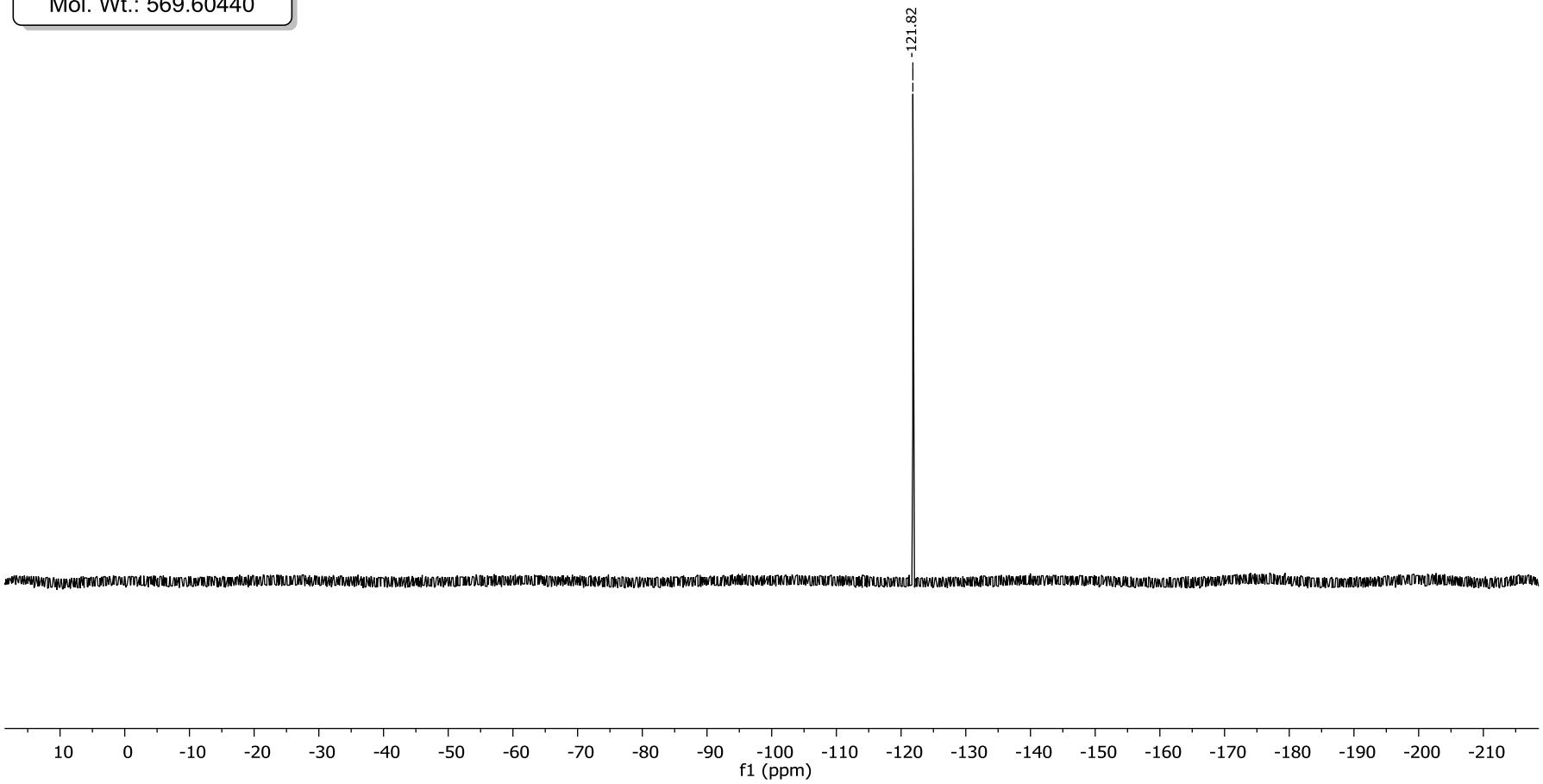
MU 722_Minor

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i')



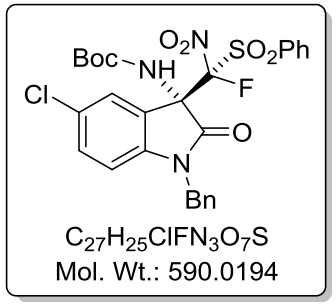
$C_{28}H_{28}FN_3O_7S$

Mol. Wt.: 569.60440



MU721_major.1.fid
MU721_major

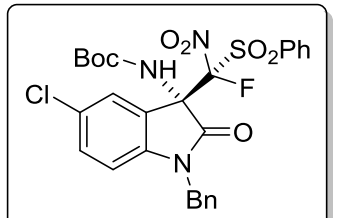
tert-Butyl ((*S*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j)



$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194

MU721_major cryo.4.fid
MU721_major cryo 13C

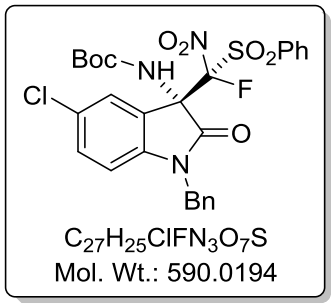
tert-Butyl ((*S*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j)



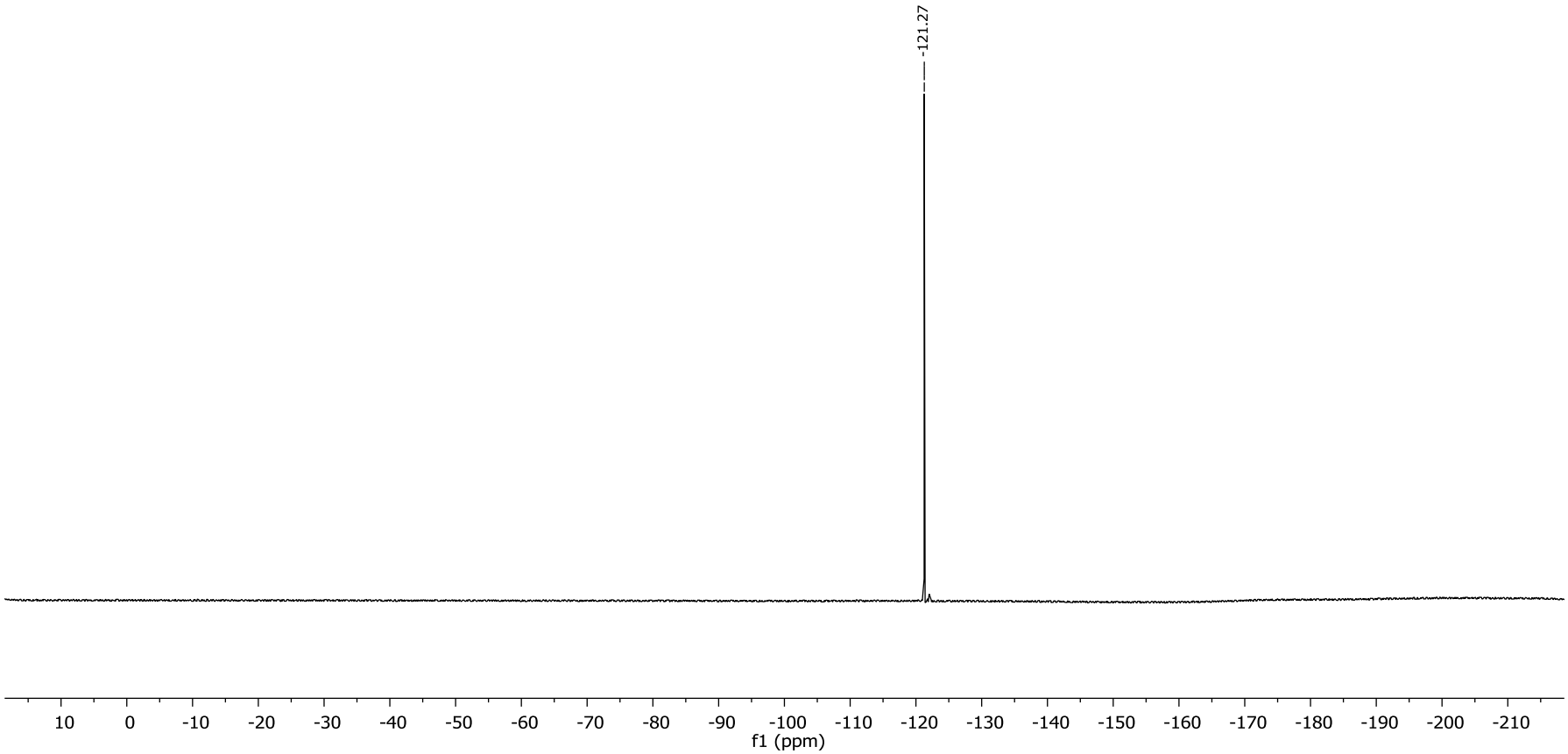
$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194

MU 721_chiral_2cv.2.fid
19F

tert-Butyl ((*S*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j)

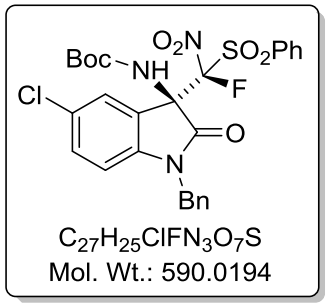


$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194



MU721_minor cryo.1.fid
MU721_minor cryo 1H

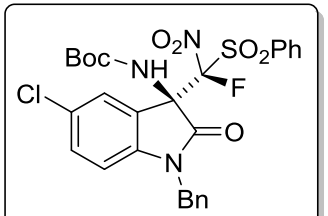
tert-Butyl ((*R*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')



$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194

MU721_minor cryo.2.fid
MU721_minor cryo 13C

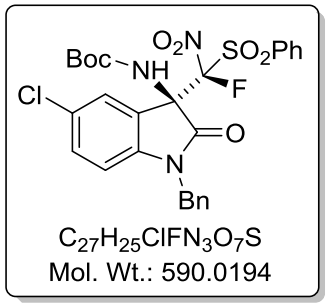
tert-Butyl ((*R*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')



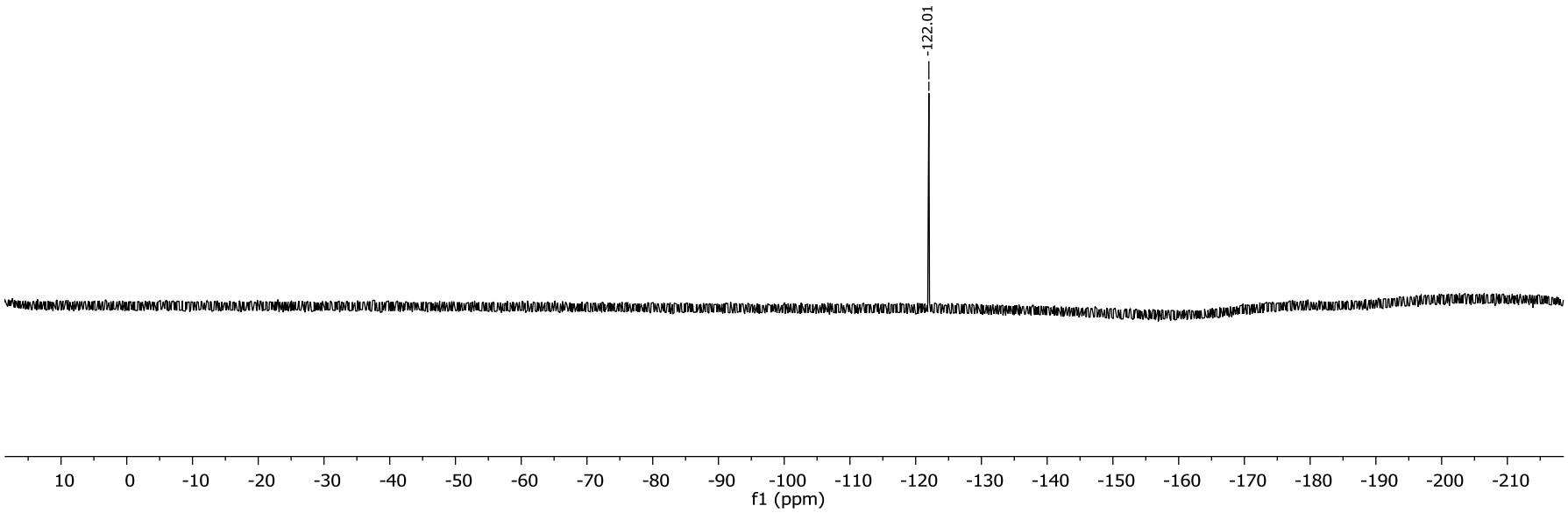
$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194

MU 721_minor_cp.2.fid
19F

tert-Butyl ((*R*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')

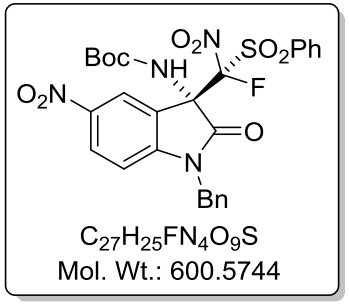


$C_{27}H_{25}ClFN_3O_7S$
Mol. Wt.: 590.0194



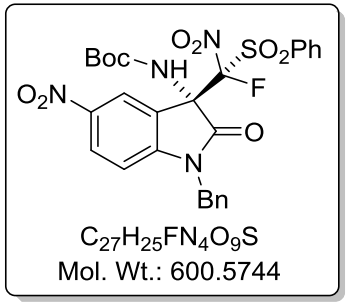
MU754_major cryo.1.fid
MU754_major cryo 1H

tert-butyl ((*S*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k)



$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744

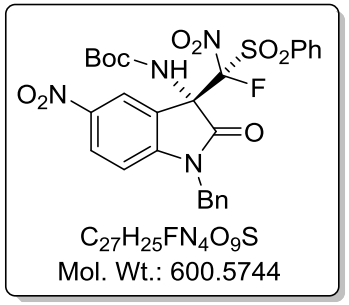
MU754_major cryo.2.fid
MU754_major cryo 13C *tert*-butyl ((*S*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k)



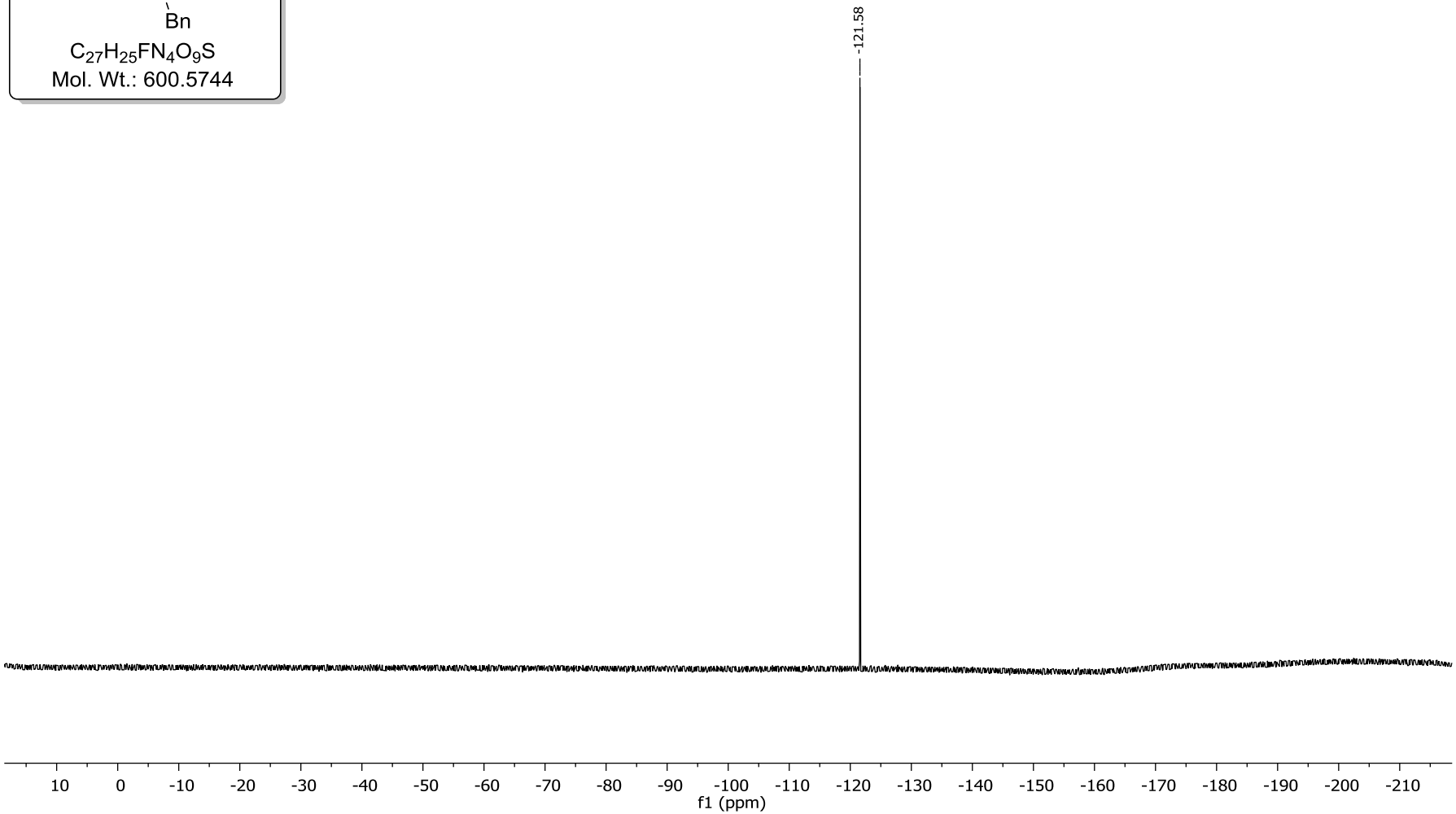
$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744

MU 754_chiral_2ac.2.fid
19F

tert-butyl ((*S*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k)

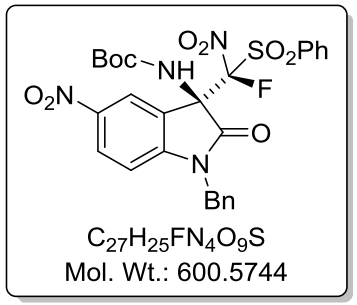


$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744



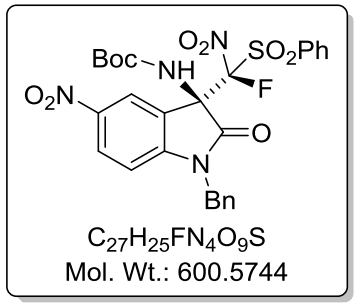
MU754_minor cryo.1.fid
1H

tert-butyl ((*R*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')



$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744

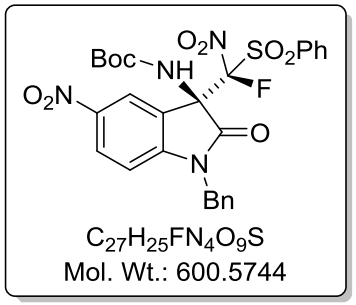
MU754_minor cryo.10.fid
MU754_minor cryo 13C *tert*-butyl ((*R*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')



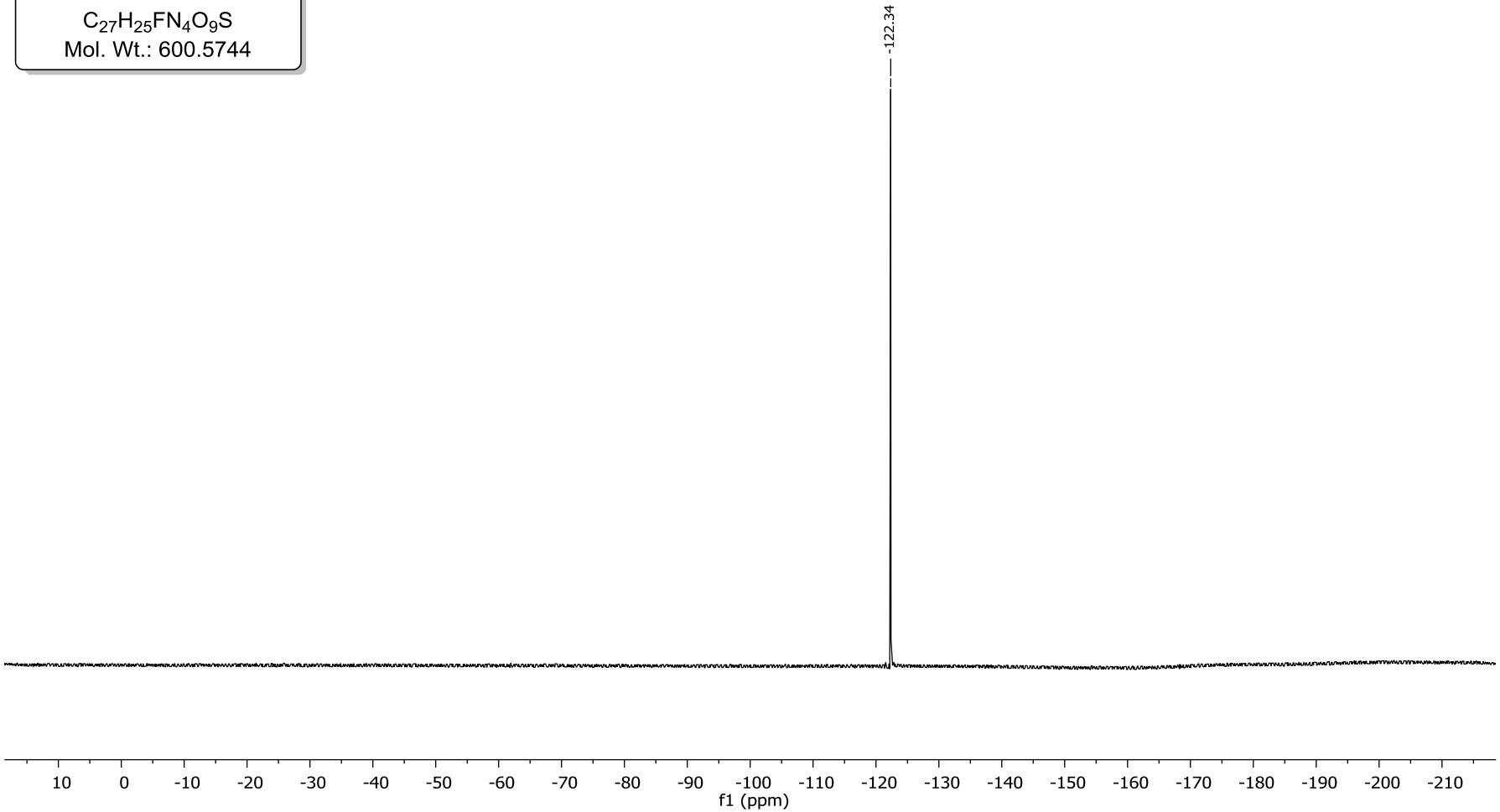
$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744

MU754_minor cryo.2.fid
19F

tert-butyl ((*R*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')

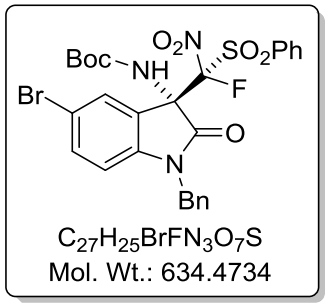


$C_{27}H_{25}FN_4O_9S$
Mol. Wt.: 600.5744



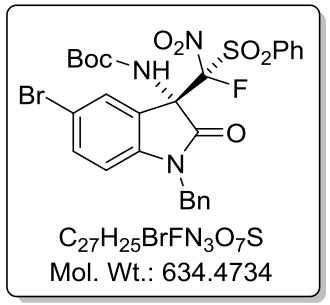
MU724_major cryo.1.fid
MU724_major cryo

tert-butyl ((*S*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l)



$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

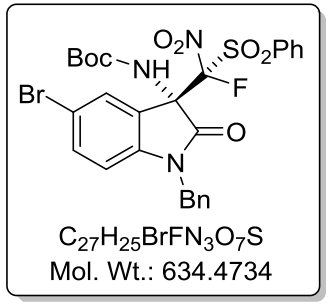
MU724_major cryo.4.fid
MU724_major cryo 13C *tert*-butyl ((*S*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l)



$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

MU 724_chiral_1ac.3.fid
19F

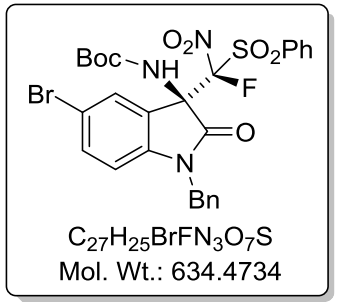
tert-butyl ((*S*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l)



$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

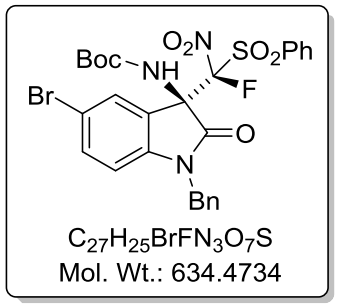
MU724_minor cryo.1.fid
MU724_minor cryo 1H

tert-butyl ((*R*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')



$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

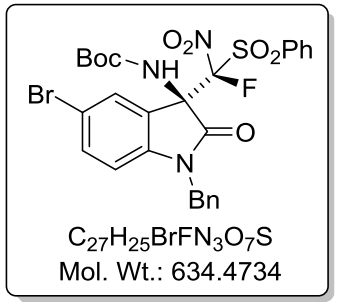
MU724_minor cryo.2.fid
MU724_minor cryo 13C *tert*-butyl ((*R*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')



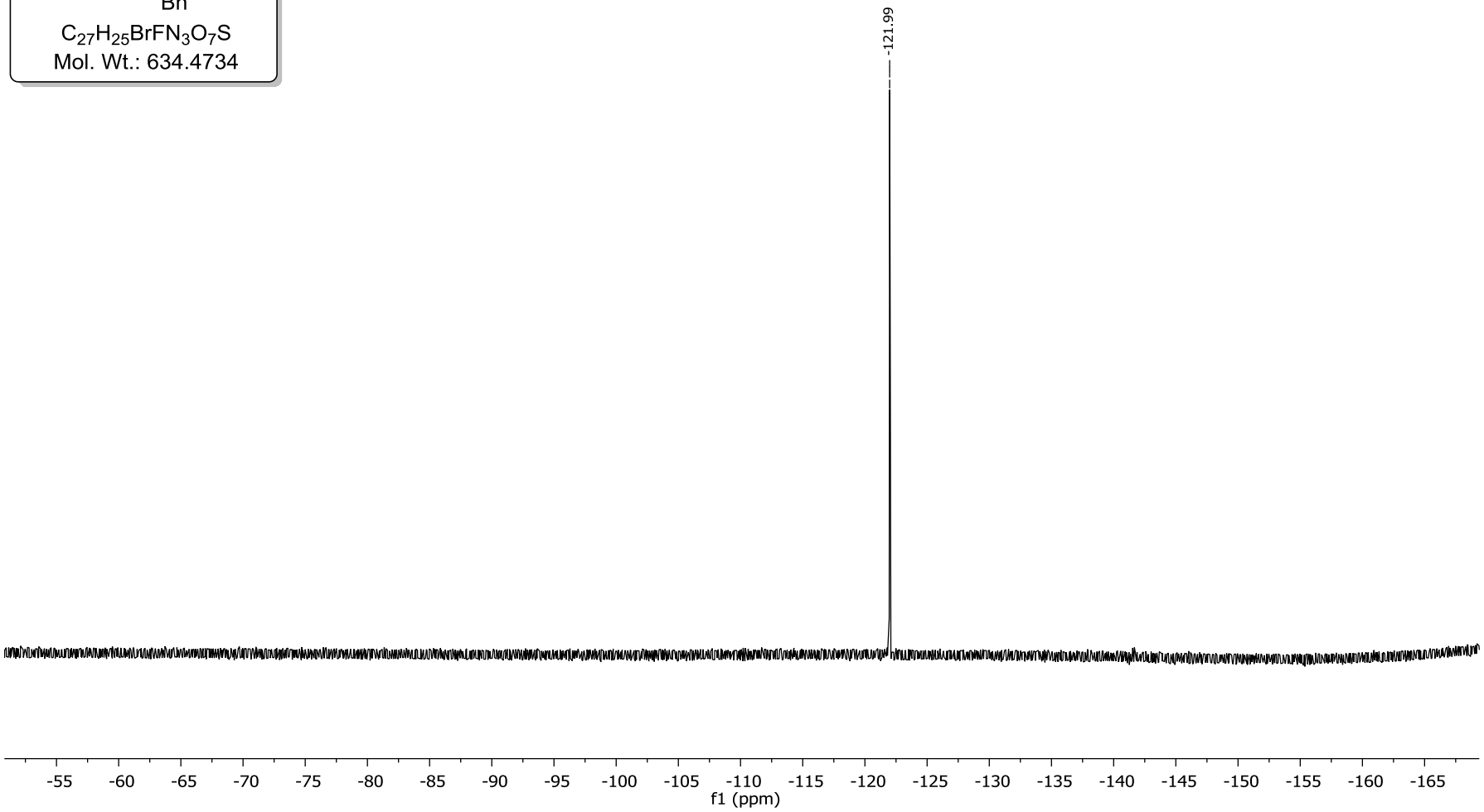
$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

MU 724_minor_cp.2.fid
19F

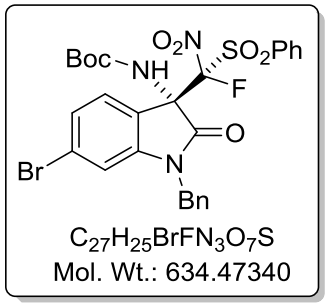
tert-butyl ((*R*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')



$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.4734

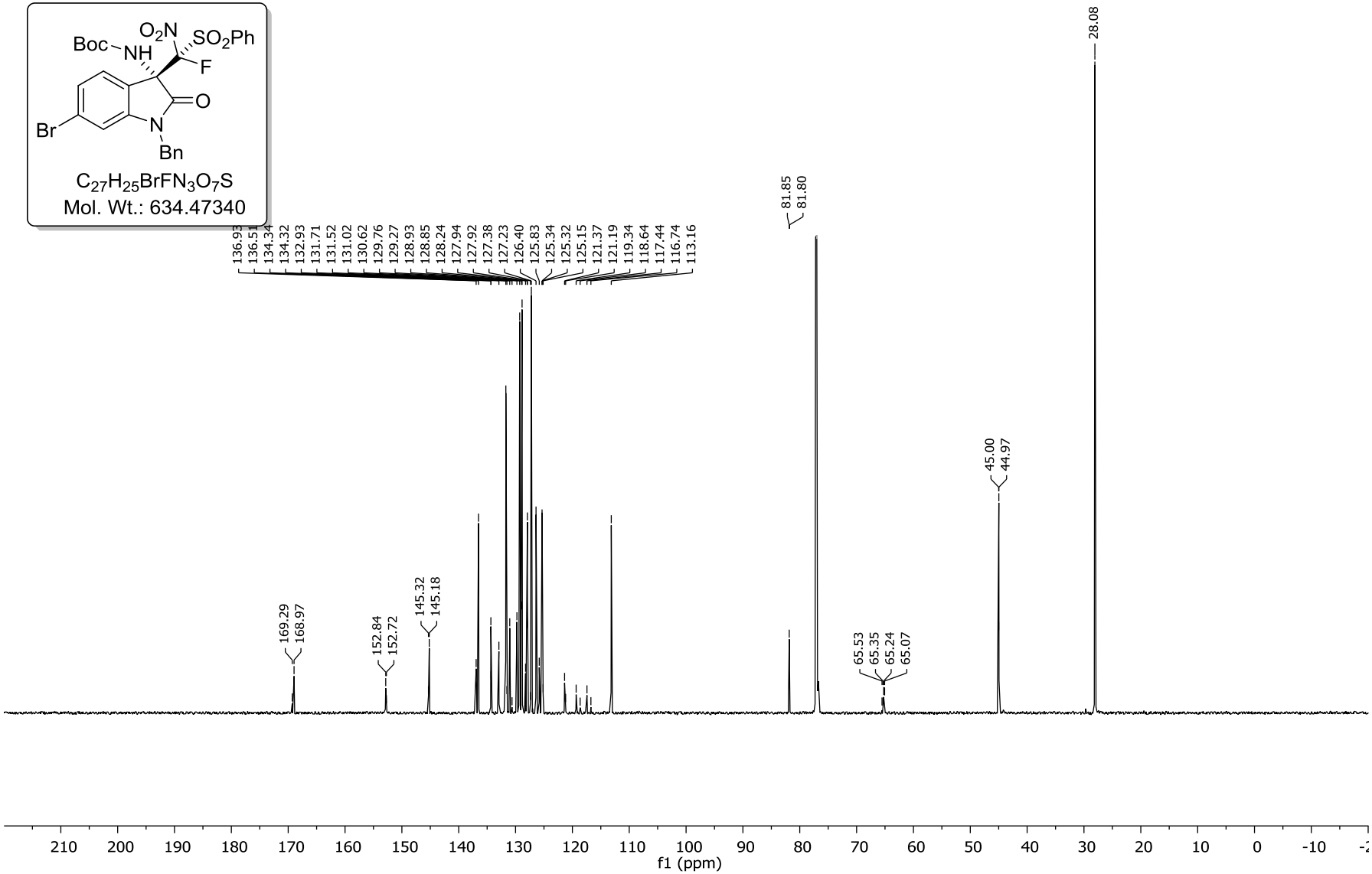


MU 1064 *tert*-Butyl ((*S*/*R*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m) - mixture of diastereoisomers

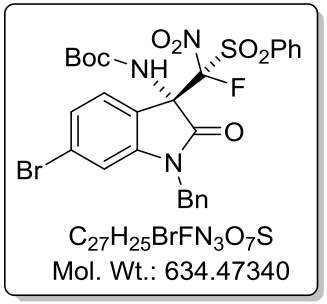


MU 1064

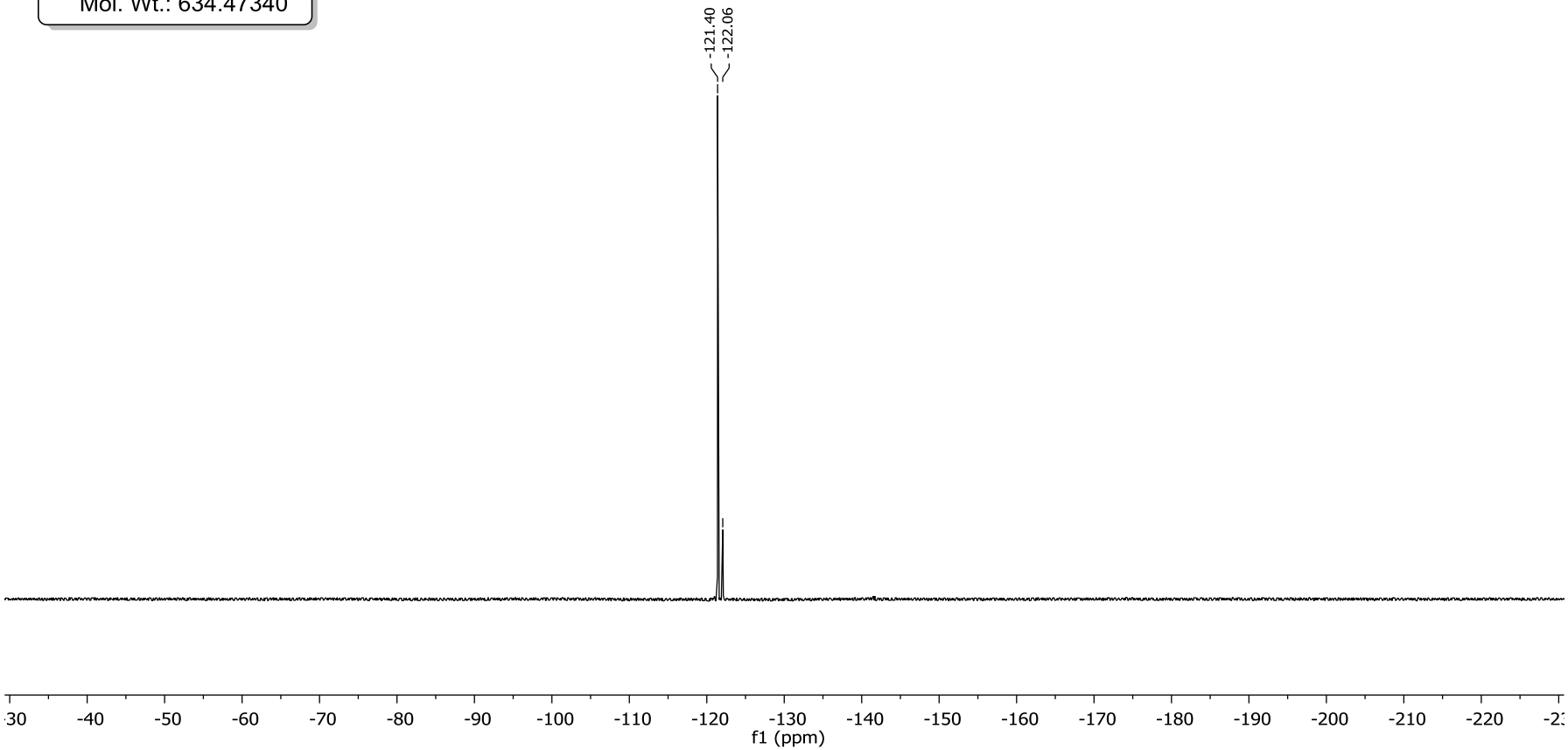
tert-Butyl ((*S/R*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m) - mixture of diastereoisomers



tert-Butyl ((*S/R*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m) - mixture of diastereoisomers

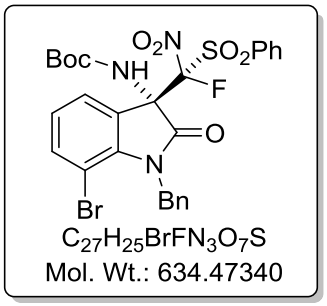


$C_{27}H_{25}BrFN_3O_7S$
Mol. Wt.: 634.47340



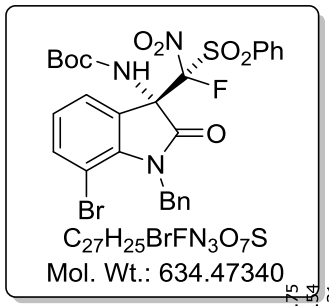
MU 1060

tert-Butyl ((*S/R*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n) - mixture of diastereoisomers



MU 1060

tert-Butyl ((*S/R*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n) - mixture of diastereoisomers



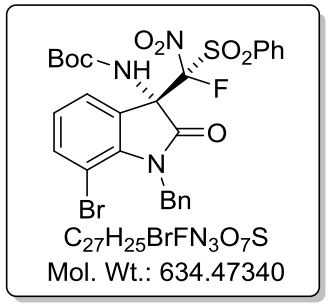
$C_{27}H_{25}BrFN_3O_7S$

Mol. Wt.: 634.47340

C

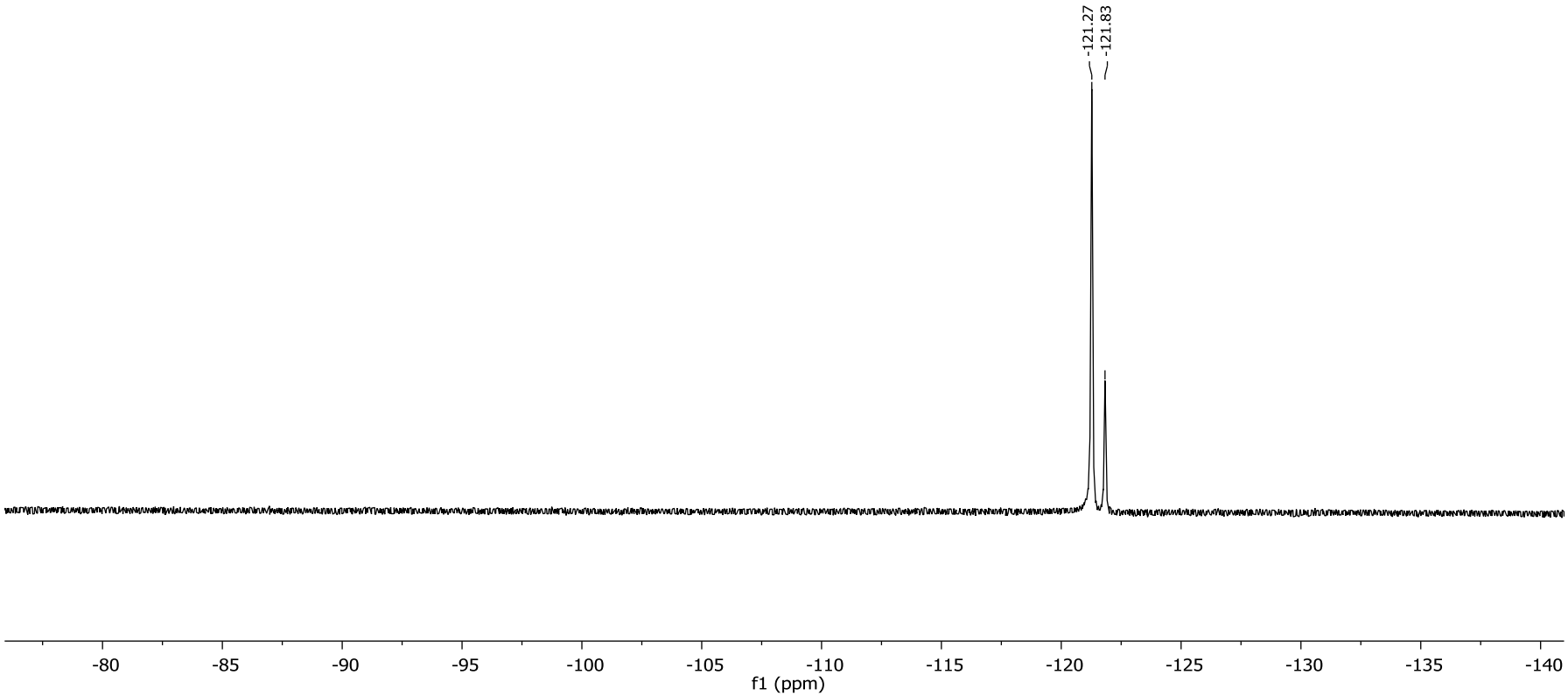
MU 1060

tert-Butyl ((*S/R*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n) - mixture of diastereoisomers



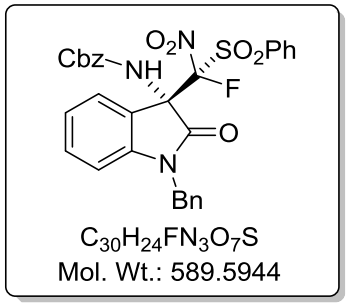
$C_{27}H_{25}BrFN_3O_7S$

Mol. Wt.: 634.47340



MU 709_Major

Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p)

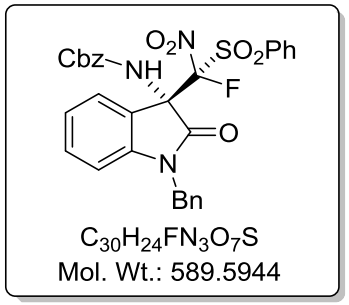


$C_{30}H_{24}FN_3O_7S$

Mol. Wt.: 589.5944

MU 709_Major

Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p)

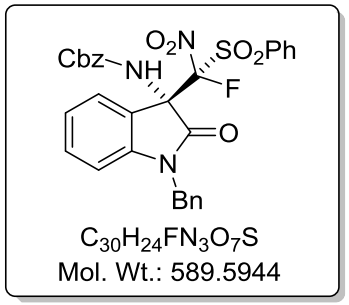


$C_{30}H_{24}FN_3O_7S$

Mol. Wt.: 589.5944

MU 709_Major

Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p)

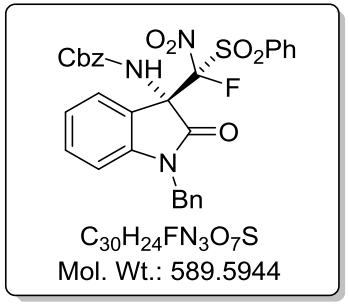


$C_{30}H_{24}FN_3O_7S$

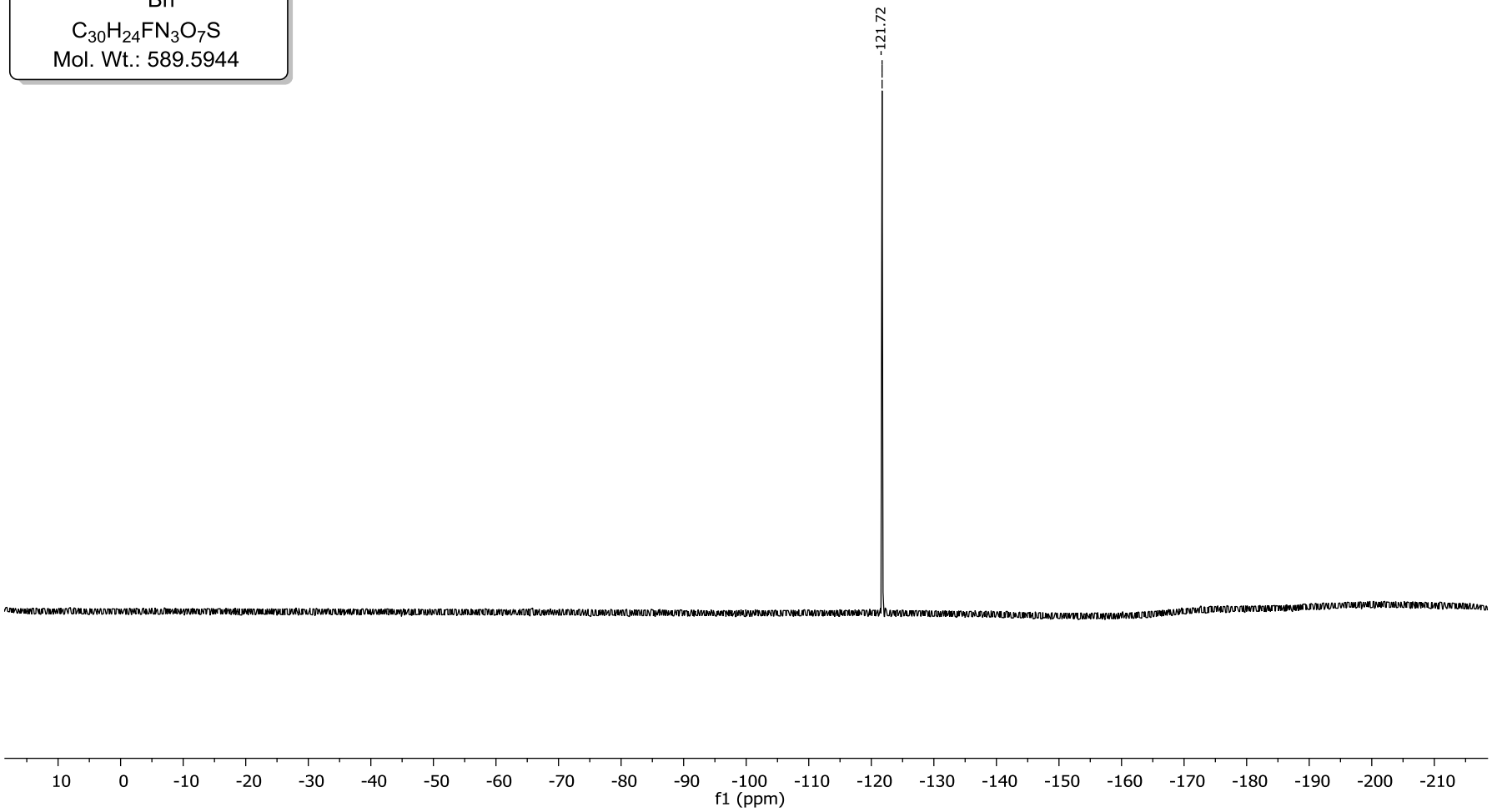
Mol. Wt.: 589.5944

MU 709_major_cp.2.fid
19F

Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p)

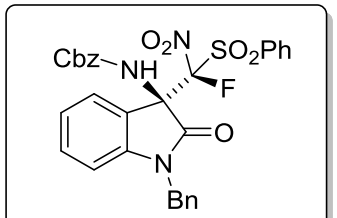


$C_{30}H_{24}FN_3O_7S$
Mol. Wt.: 589.5944



MU 709_Minor

Benzyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p')

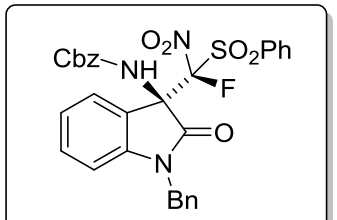


$C_{30}H_{24}FN_3O_7S$

Mol. Wt.: 589.5944

MU 709_Minor

Benzyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p')

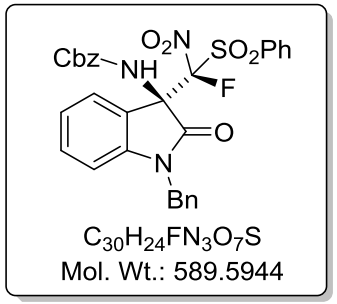


$C_{30}H_{24}FN_3O_7S$

Mol. Wt.: 589.5944

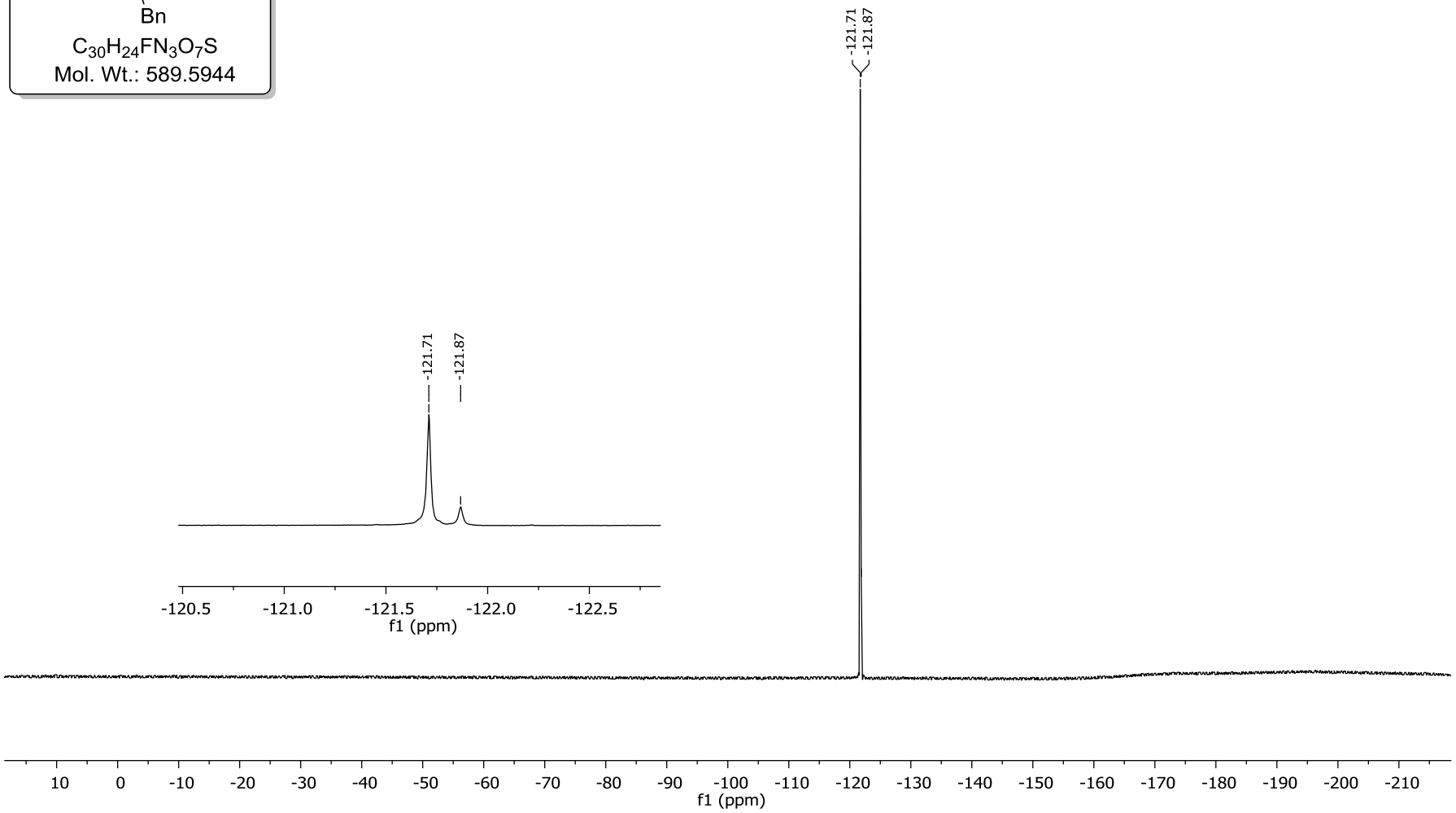
MU 709_Minor

Benzyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p')



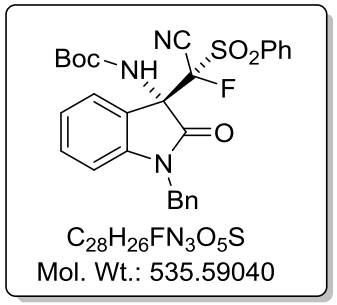
$C_{30}H_{24}FN_3O_7S$

Mol. Wt.: 589.5944



MU 728_Major

tert-butyl ((*S*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q)

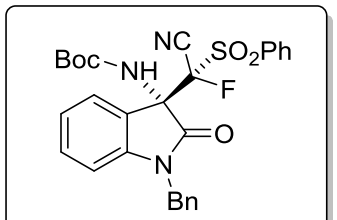


$C_{28}H_{26}FN_3O_5S$

Mol. Wt.: 535.59040

MU 728_Major

tert-butyl ((*S*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q)

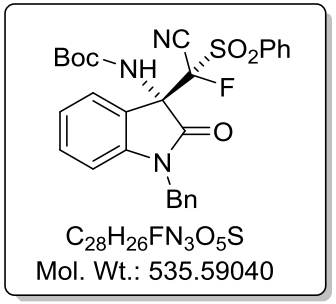


$C_{28}H_{26}FN_3O_5S$

Mol. Wt.: 535.59040

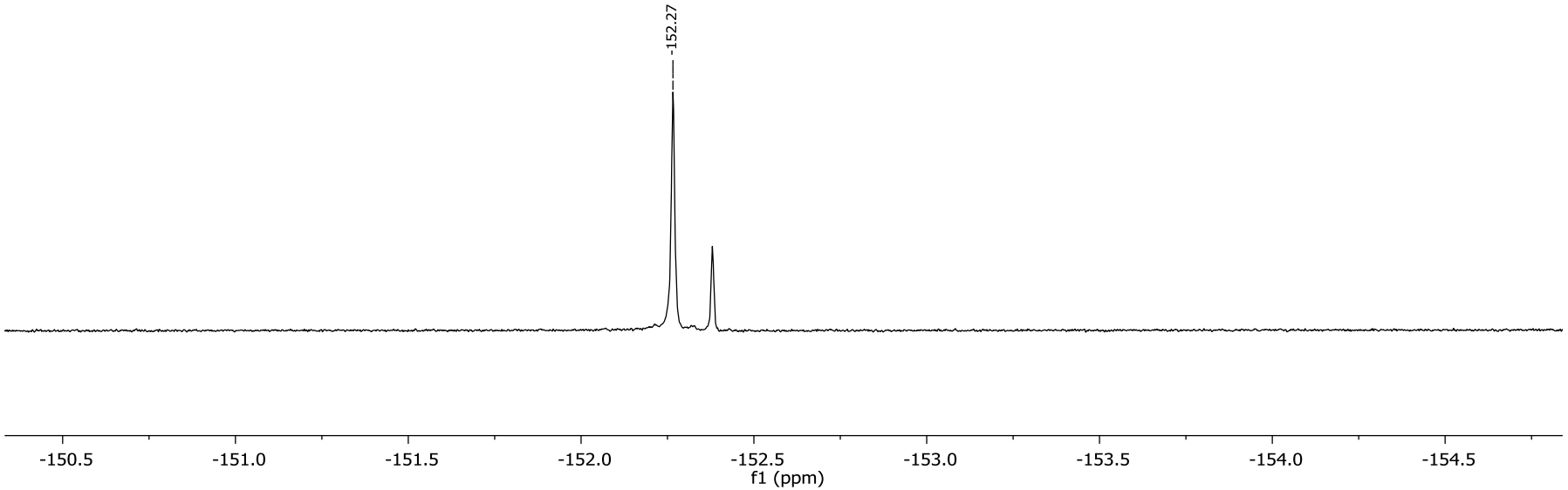
MU 728_Major

tert-butyl ((*S*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q)



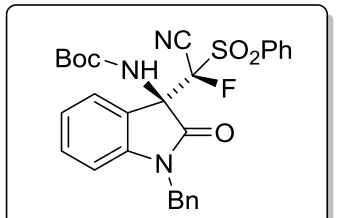
$C_{28}H_{26}FN_3O_5S$

Mol. Wt.: 535.59040



MU 728_Minor

tert-butyl ((*R*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q')

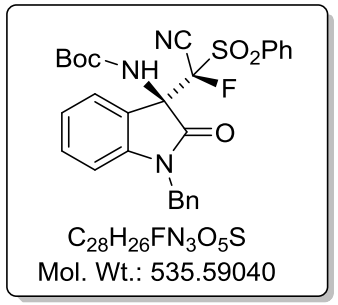


$C_{28}H_{26}FN_3O_5S$

Mol. Wt.: 535.59040

MU 728_Minor

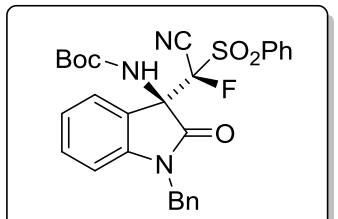
tert-butyl ((*R*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q')



$C_{28}H_{26}FN_3O_5S$
Mol. Wt.: 535.59040

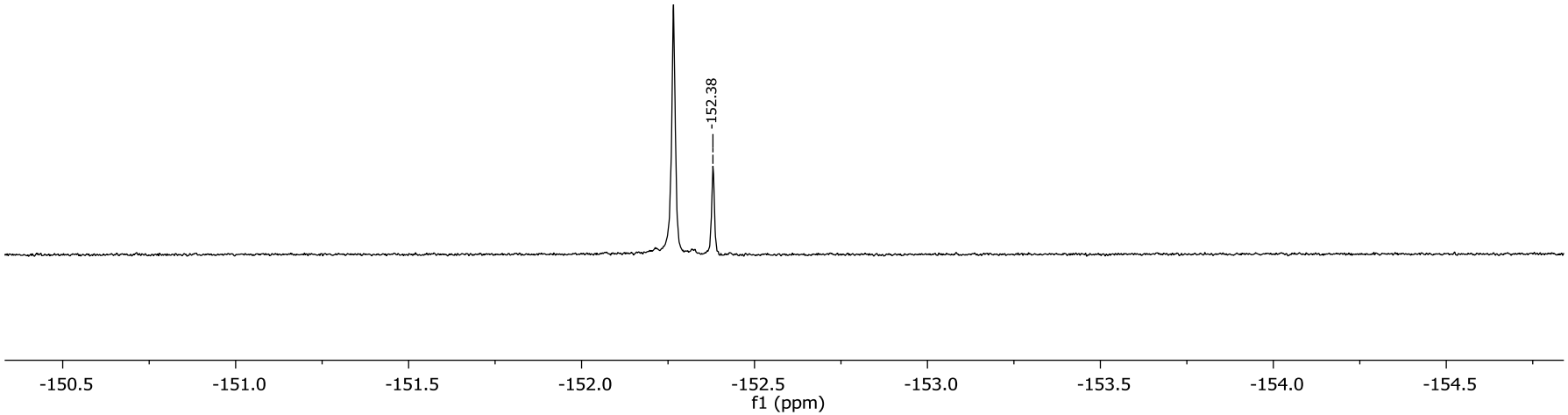
MU 728_Minor

tert-butyl ((*R*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q')



$C_{28}H_{26}FN_3O_5S$

Mol. Wt.: 535.59040

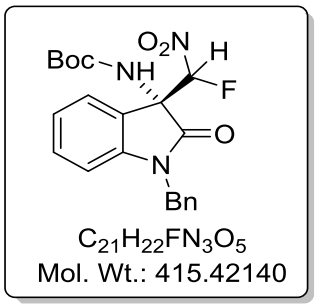


MU 838

Mixture of diastereoisomer 4a/4b

tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)

tert-Butyl ((*S*)-1-benzyl-3-((*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)

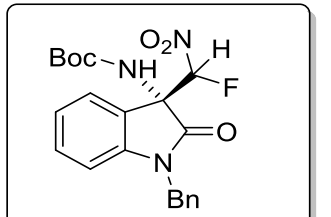


$C_{21}H_{22}FN_3O_5$

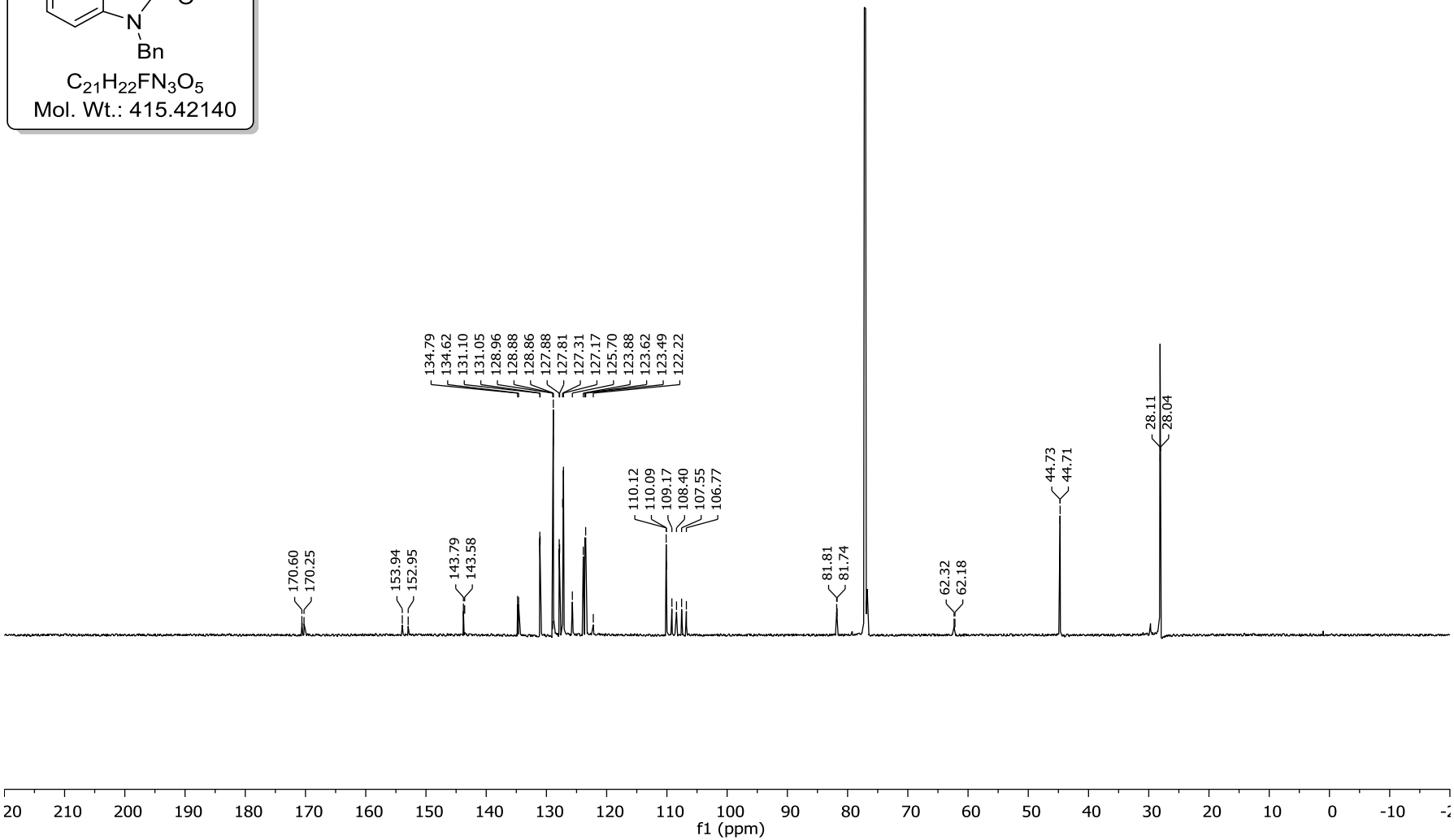
Mol. Wt.: 415.42140

MU838 cryo.2.fid
MU838 cryo 13C

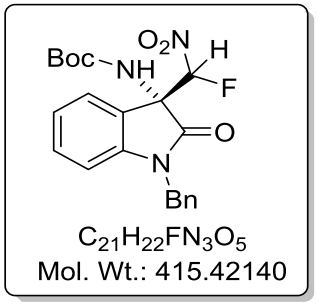
Mixture of diastereoisomer 4a/4b
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)
tert-Butyl ((*S*)-1-benzyl-3-((*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)



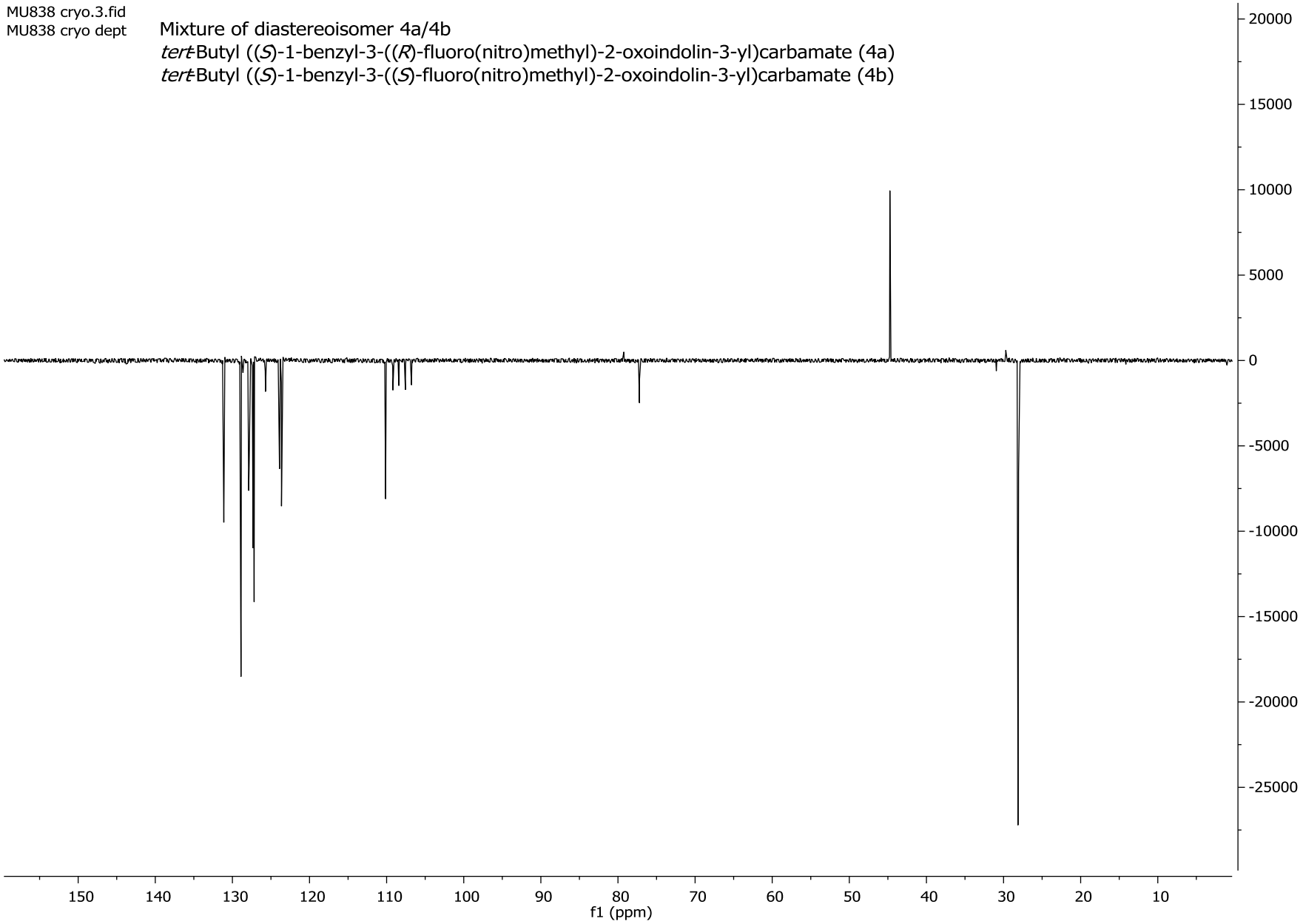
$C_{21}H_{22}FN_3O_5$
Mol. Wt.: 415.42140



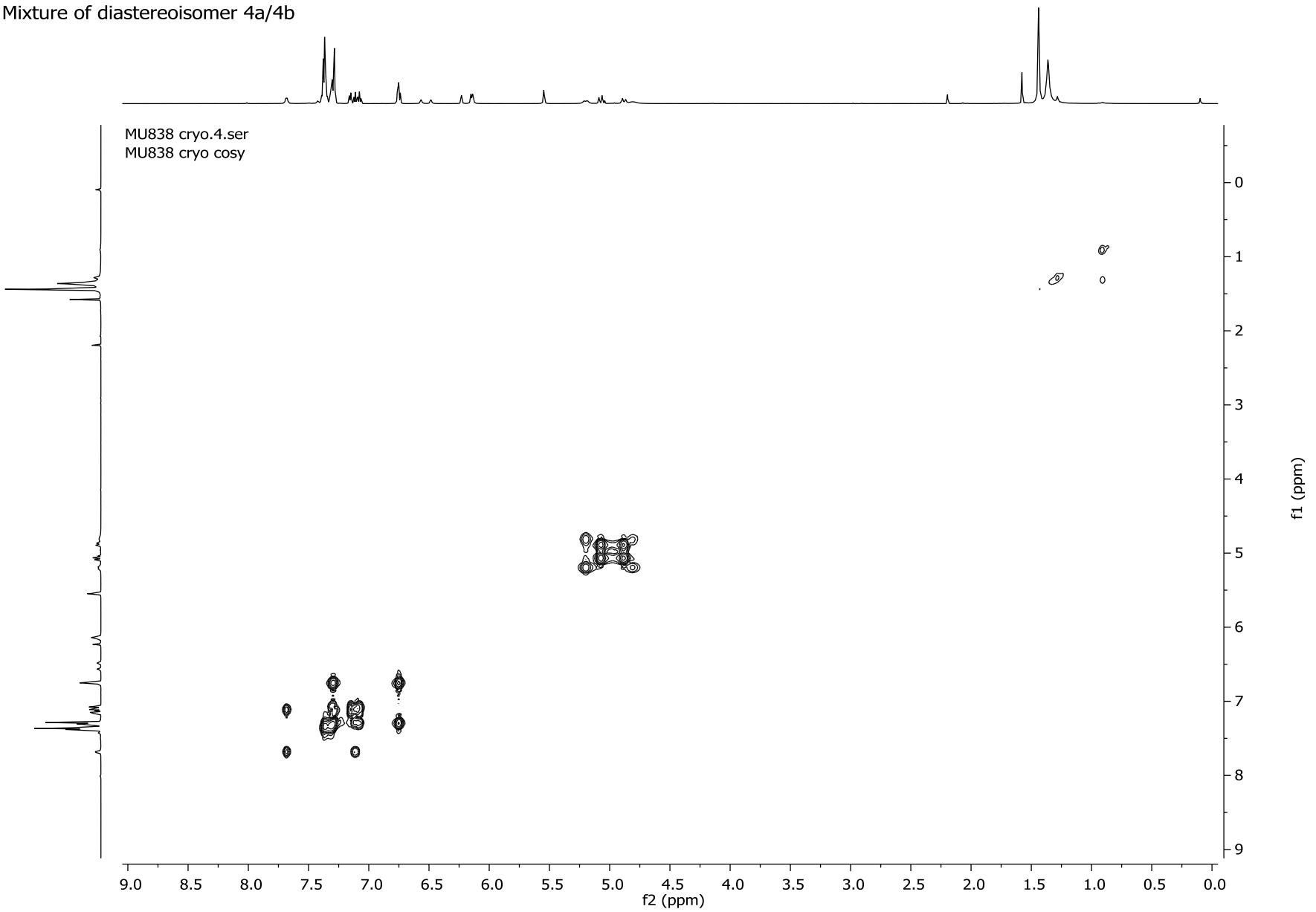
Mixture of diastereoisomer 4a/4b
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)
tert-Butyl ((*S*)-1-benzyl-3-((*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)

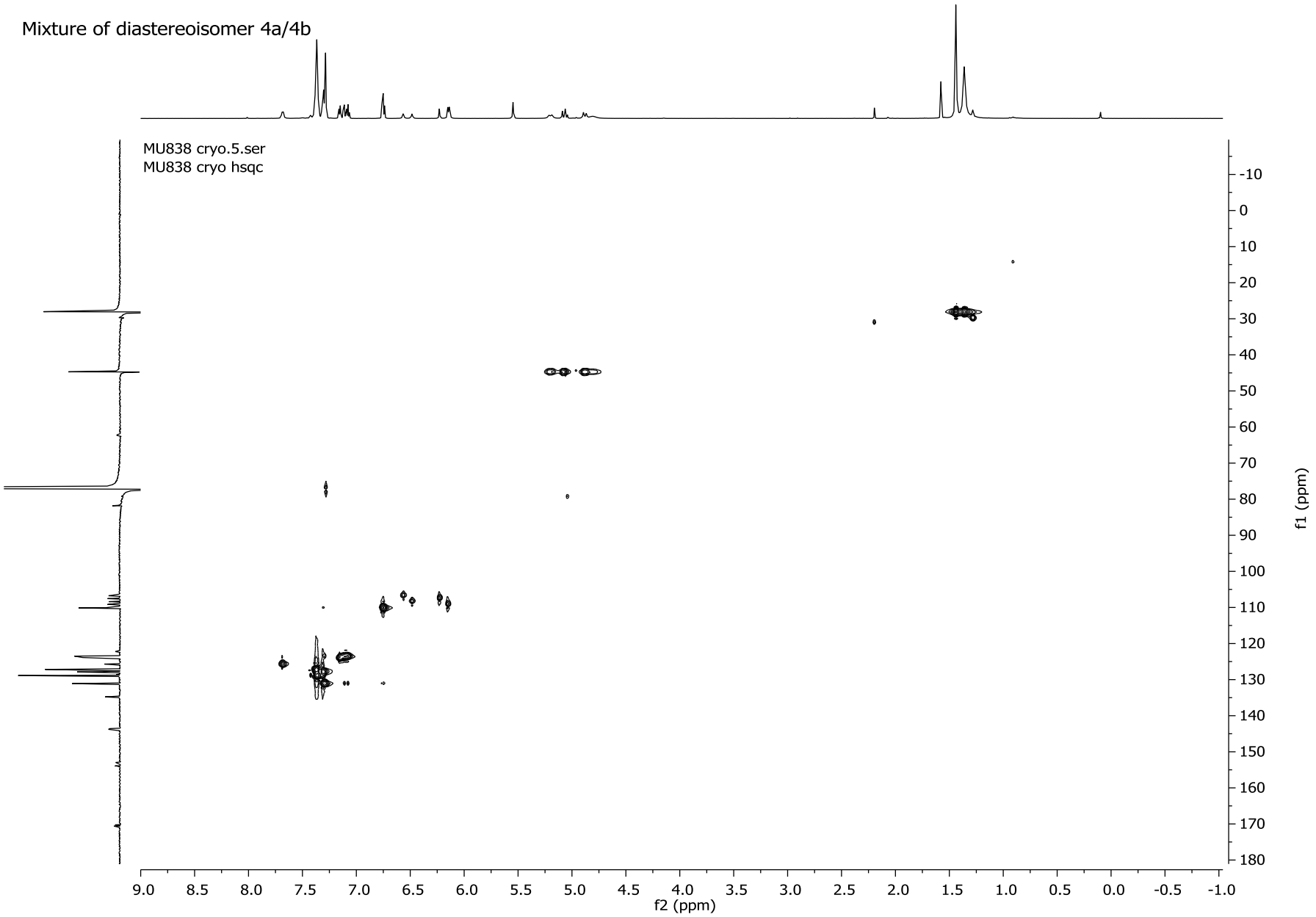


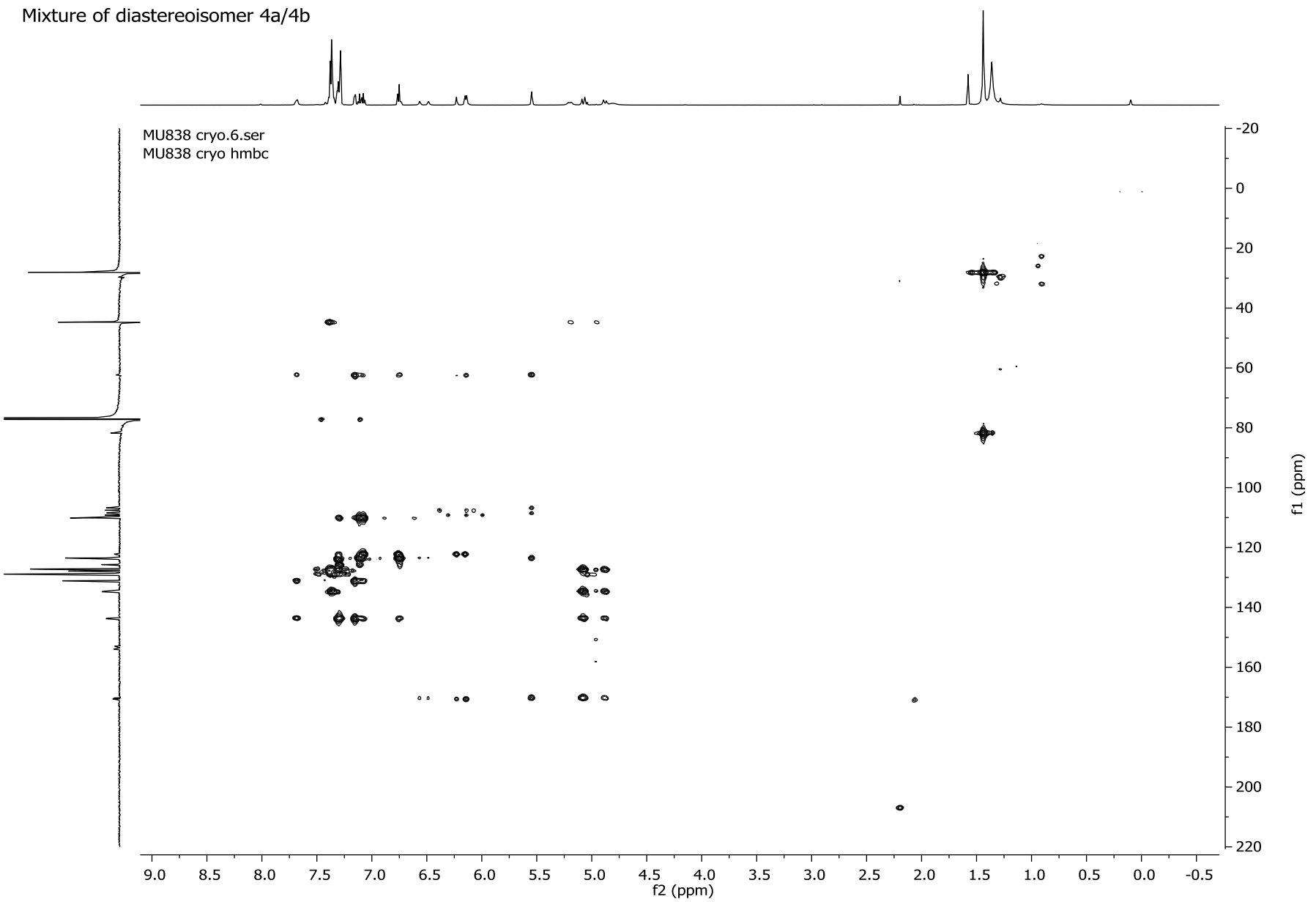
$C_{21}H_{22}FN_3O_5$
Mol. Wt.: 415.42140


MU838 cryo.3.fid
MU838 cryo dept
Mixture of diastereoisomer 4a/4b
tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)
tert-Butyl ((*S*)-1-benzyl-3-((*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Mixture of diastereoisomer 4a/4b

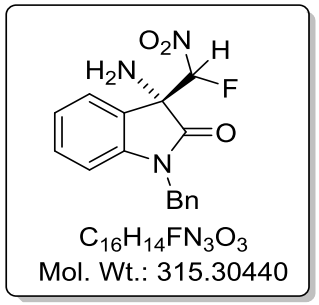



Mixture of diastereoisomer 4a/4b
MU838 cryo.5.ser
MU838 cryo hsqc
f2 (ppm)
f1 (ppm)


Mixture of diastereoisomer 4a/4b
MU838 cryo.6.ser
MU838 cryo hmbc
f2 (ppm)
f1 (ppm)

MU 1031_Major

(*S*)-3-amino-1-benzyl-3-((*S*)-fluoro(nitro)methyl)indolin-2-one (5a)

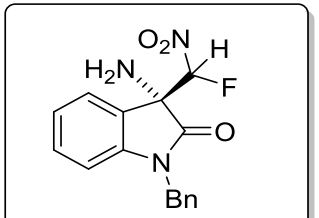


$C_{16}H_{14}FN_3O_3$

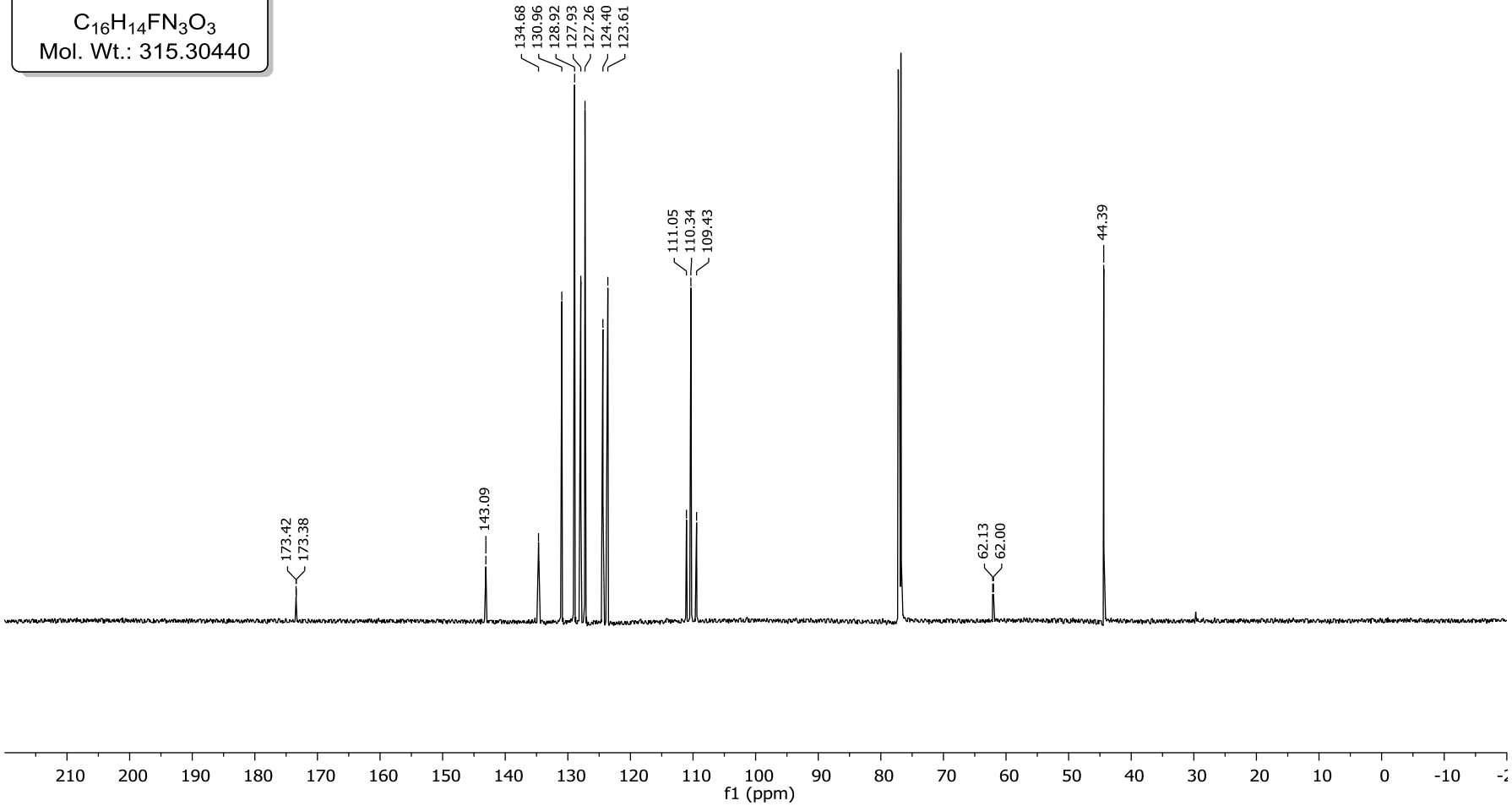
Mol. Wt.: 315.30440

MU 1031_Major

(*S*)-3-amino-1-benzyl-3-((*S*)-fluoro(nitro)methyl)indolin-2-one (5a)

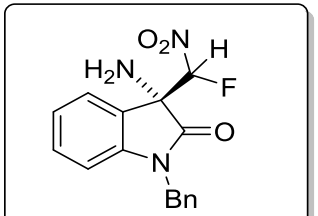


$C_{16}H_{14}FN_3O_3$
Mol. Wt.: 315.30440



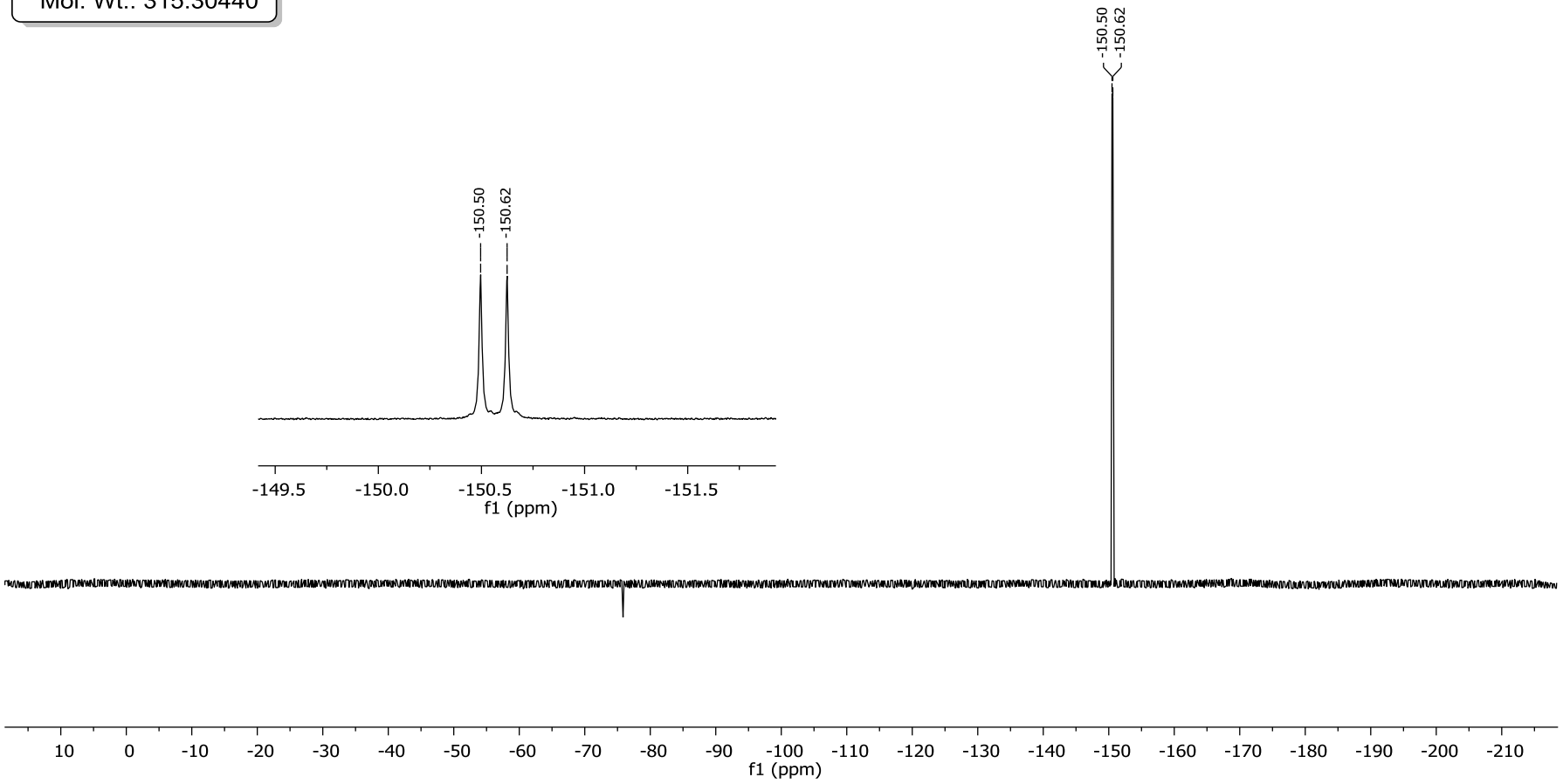
MU 1031_Major

(*S*)-3-amino-1-benzyl-3-((*S*)-fluoro(nitro)methyl)indolin-2-one (5a)



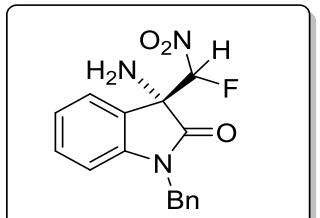
$C_{16}H_{14}FN_3O_3$

Mol. Wt.: 315.30440



MU 1031_Minor

(*S*)-3-amino-1-benzyl-3-((*R*)-fluoro(nitro)methyl)indolin-2-one (5b)

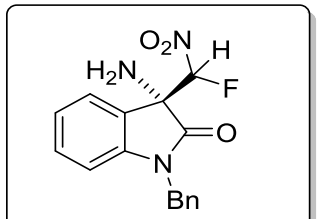


$C_{16}H_{14}FN_3O_3$

Mol. Wt.: 315.30440

MU 1031_Minor

(*S*)-3-amino-1-benzyl-3-((*R*)-fluoro(nitro)methyl)indolin-2-one (5b)

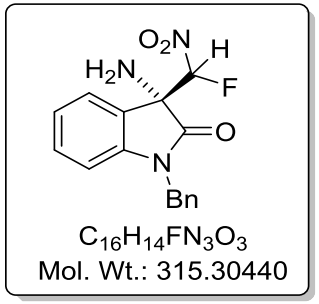


$C_{16}H_{14}FN_3O_3$

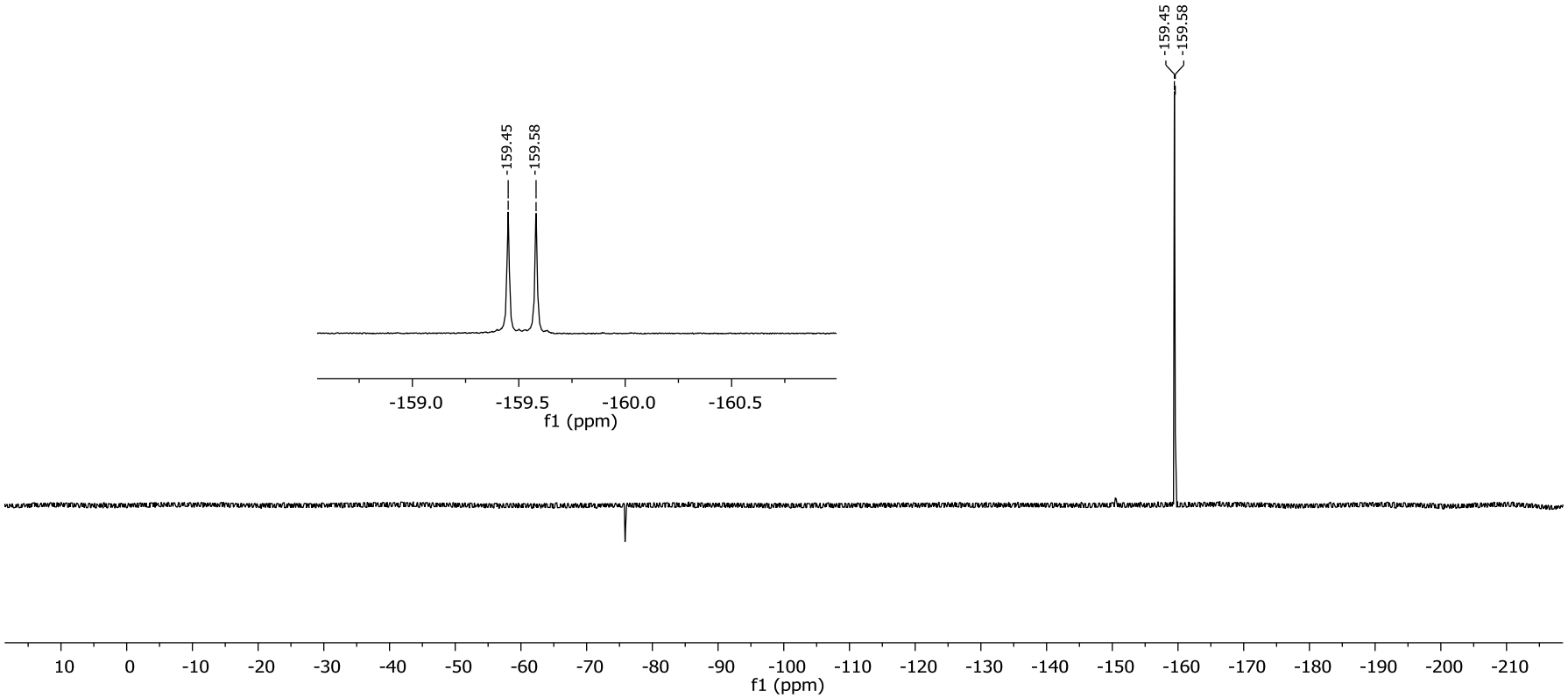
Mol. Wt.: 315.30440

MU 1031_Minor

(*S*)-3-amino-1-benzyl-3-((*R*)-fluoro(nitro)methyl)indolin-2-one (5b)



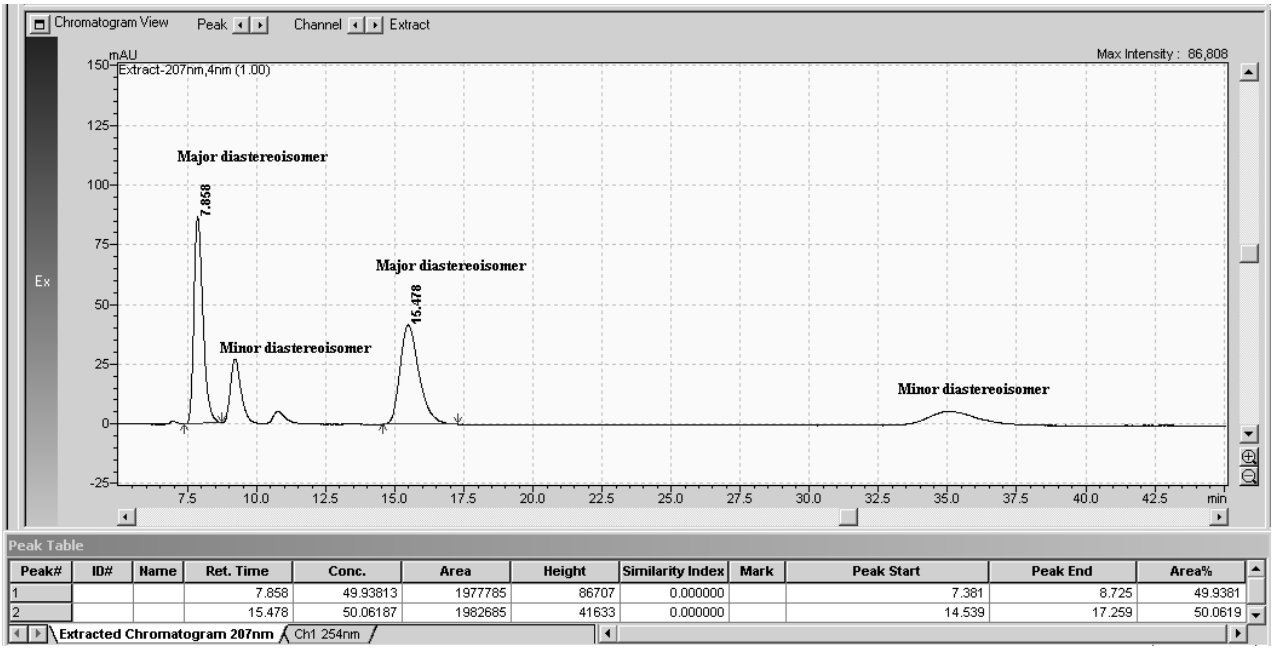
$C_{16}H_{14}FN_3O_3$
Mol. Wt.: 315.30440



10 HPLC Analysis of Compounds

tert-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a) – Racemic major diastereoisomer

HPLC MU 478: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 ML, 207 nm.



Peak Table

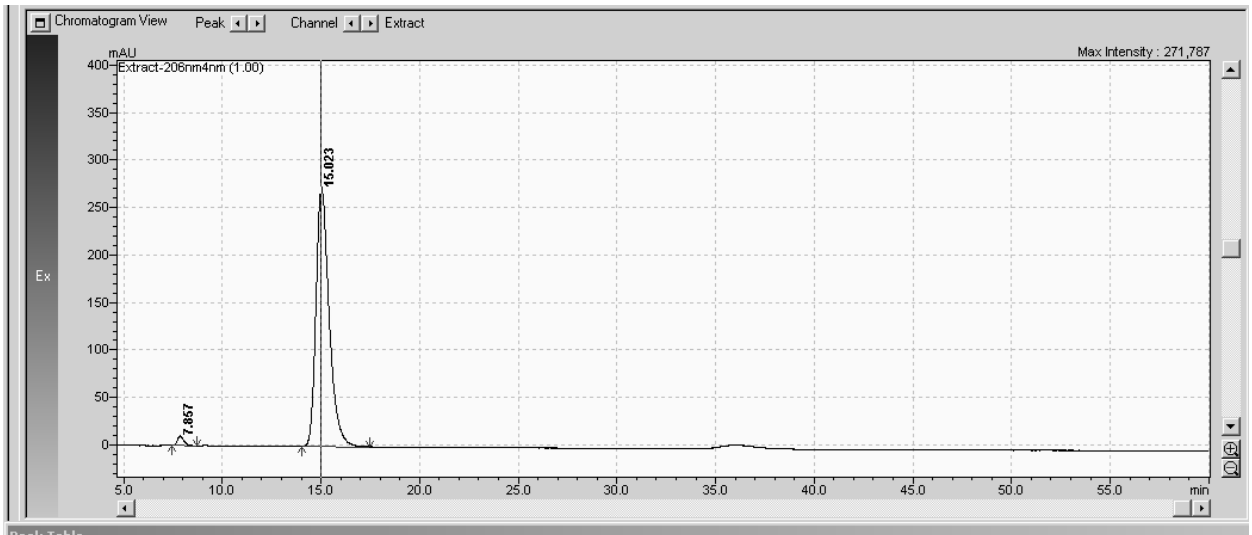
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.858	49.93813	1977785	86707	0.000000		7.381	8.725	49.9381
2			15.478	50.06187	1982685	41633	0.000000		14.539	17.259	50.0619

Extracted Chromatogram 207nm | Ch1 254nm

tert-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a) – Chiral major diastereoisomer

HPLC MU 600: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 206 nm.

ee = 96 %

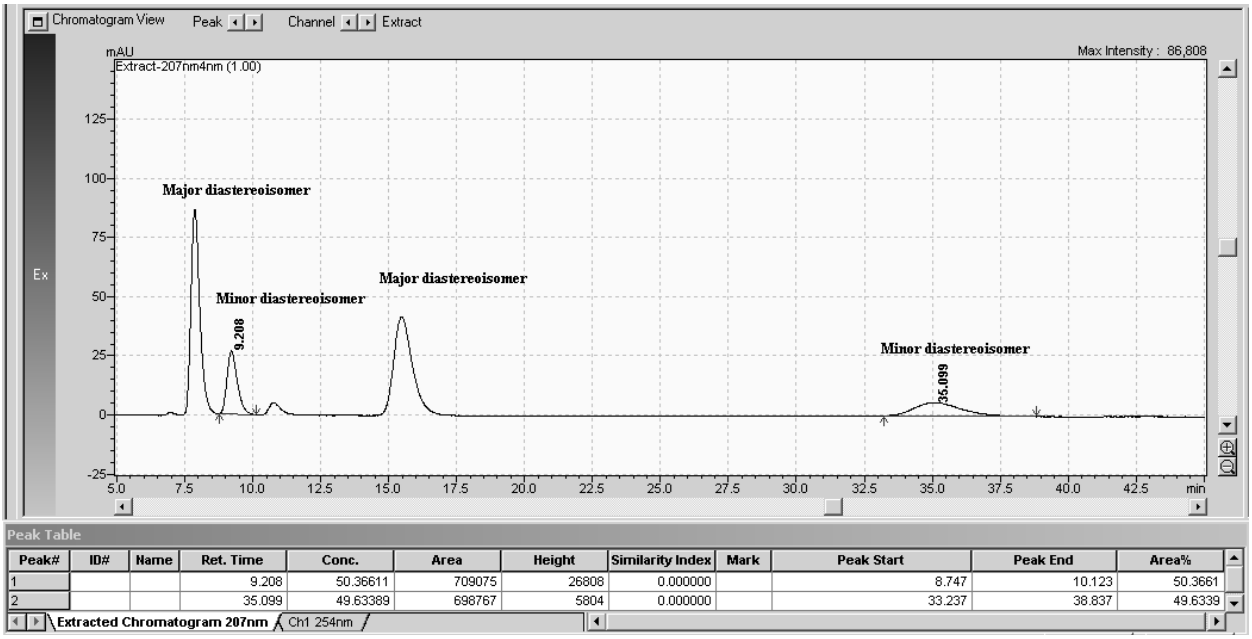


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.857	1.77862	229298	10151	0.000000	S	7.424	8.704	1.7786
2			15.023	98.22138	12662553	273543	0.000000		14.037	17.472	98.2214

***tert*-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a') – Racemic minor diastereoisomer**

HPLC MU 478: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 ML, 207 nm.



Peak Table

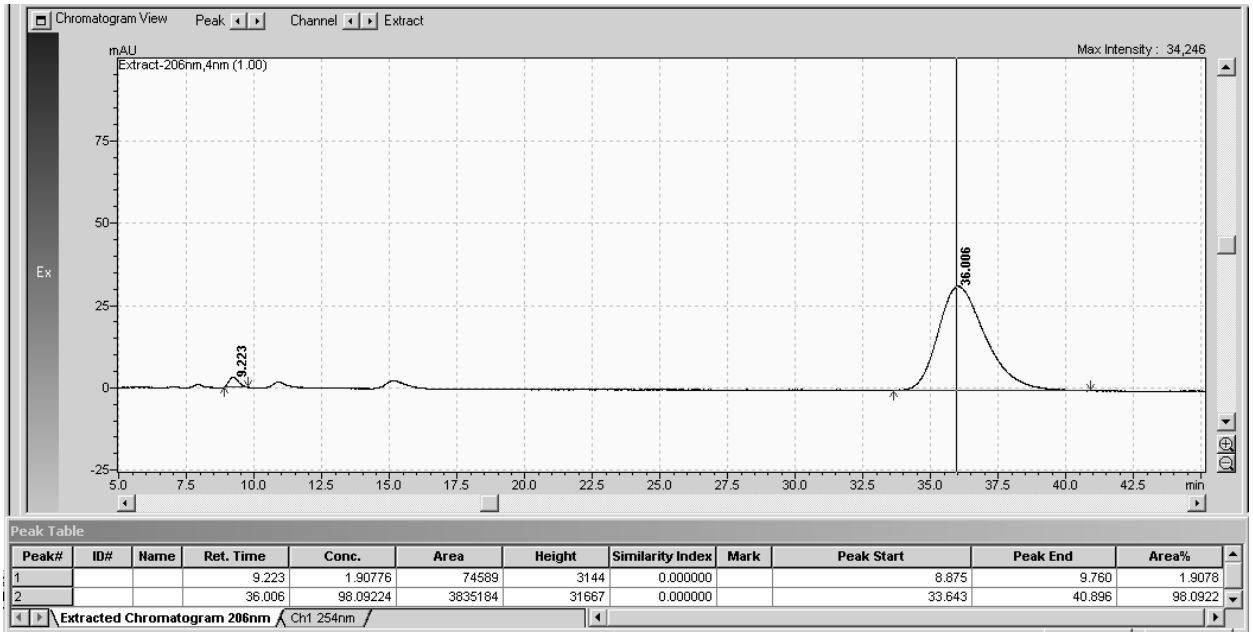
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			9.208	50.36611	709075	26808	0.000000		8.747	10.123	50.3661
2			35.099	49.63389	698767	5804	0.000000		33.237	38.837	49.6339

Extracted Chromatogram 207nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3a') – Chiral minor diastereoisomer**

HPLC MU 600: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 206 nm.

ee = 96 %



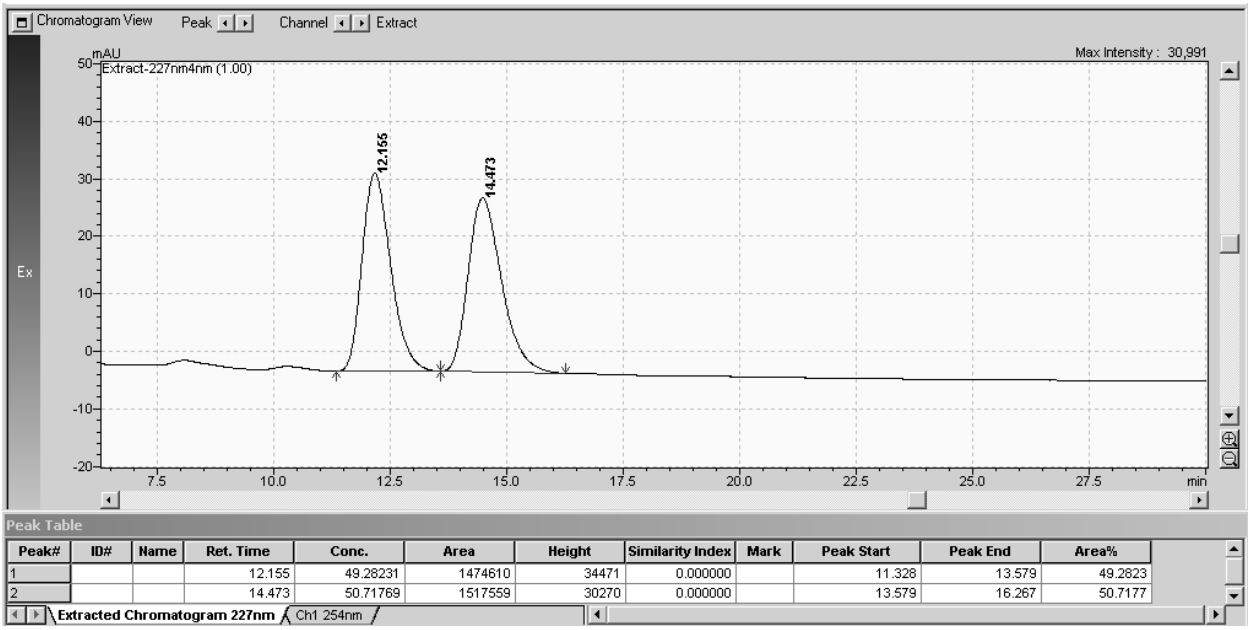
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			9.223	1.90776	74589	3144	0.000000		8.875	9.760	1.9078
2			36.006	98.09224	3835184	31667	0.000000		33.643	40.896	98.0922

Extracted Chromatogram 206nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b) – Racemic major diastereoisomer**

HPLC MU 614: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 226 nm.

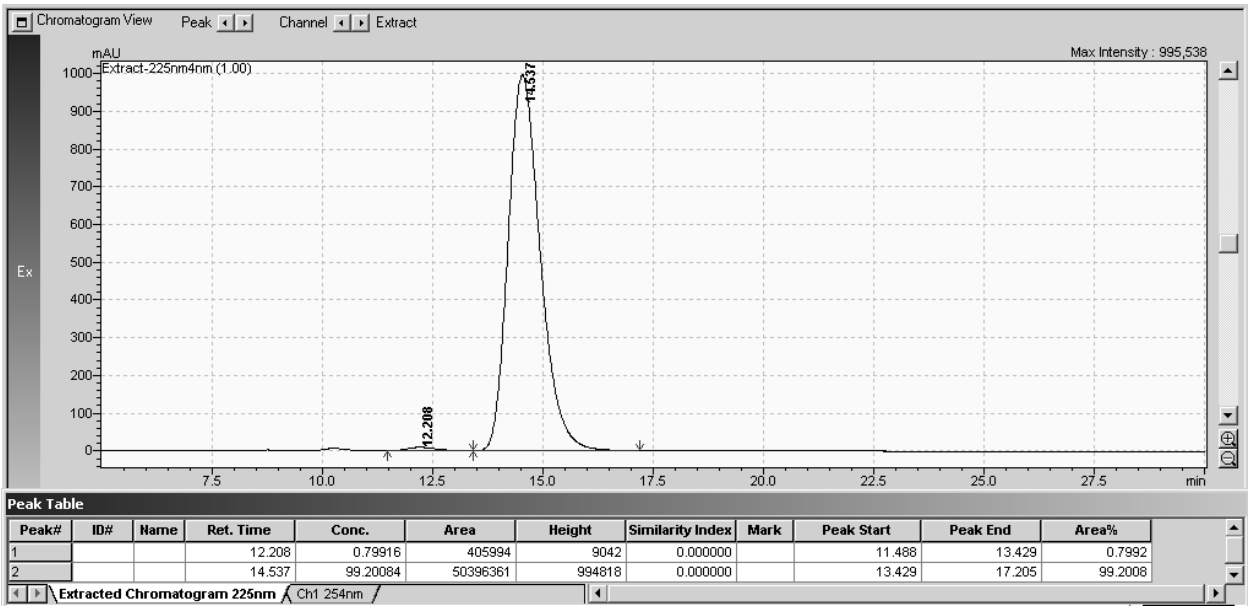


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.155	49.28231	1474610	34471	0.000000		11.328	13.579	49.2823
2			14.473	50.71769	1517559	30270	0.000000		13.579	16.267	50.7177

***tert*-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b) – Chiral major diastereoisomer**

HPLC MU 602: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 226 nm.

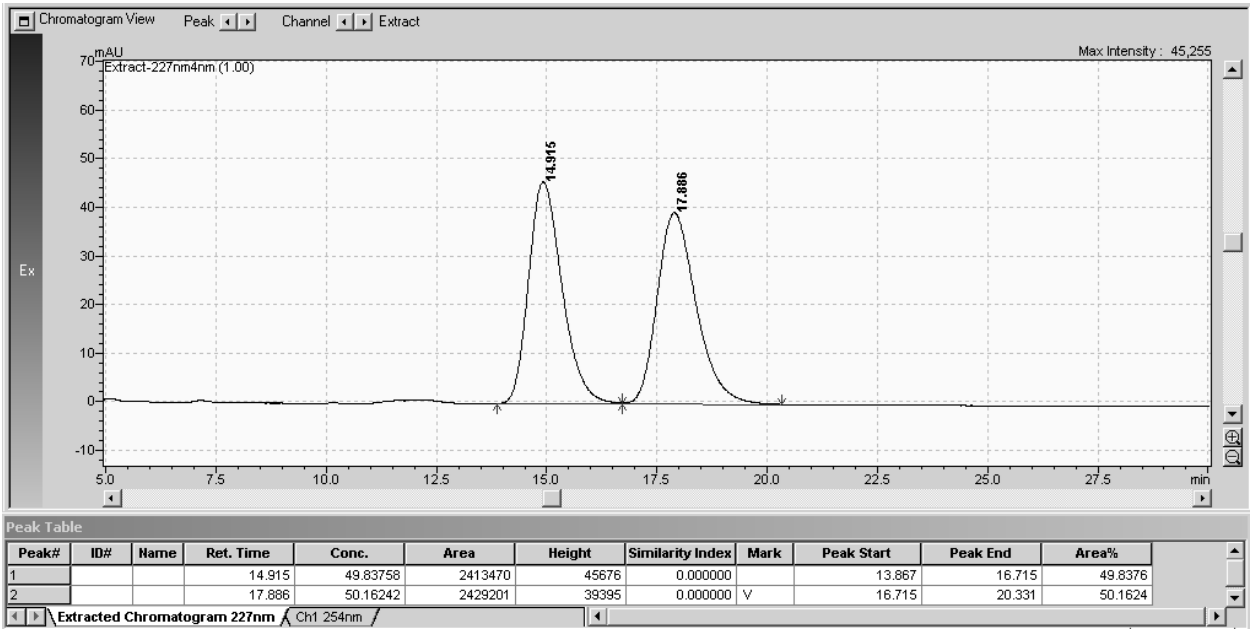
ee = 98,4%



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.208	0.79916	405994	9042	0.000000		11.488	13.429	0.7992
2			14.537	99.20084	50396361	994818	0.000000		13.429	17.205	99.2008

***tert*-Butyl ((*R*/*S*)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b') – Racemic minor diastereoisomer**

HPLC MU 614: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 227 nm.

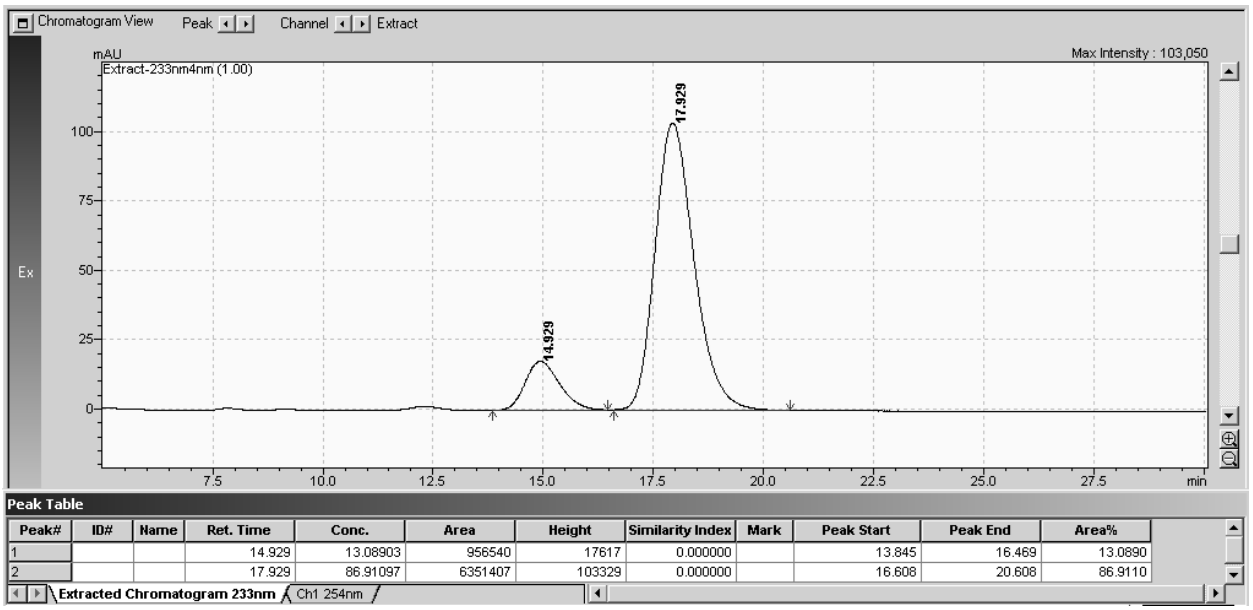


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.915	49.83758	2413470	45676	0.000000		13.867	16.715	49.8376
2			17.886	50.16242	2429201	39395	0.000000	V	16.715	20.331	50.1624

***tert*-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3b') – Chiral minor diastereoisomer**

HPLC MU 602: Chiral column AD, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 227 nm.

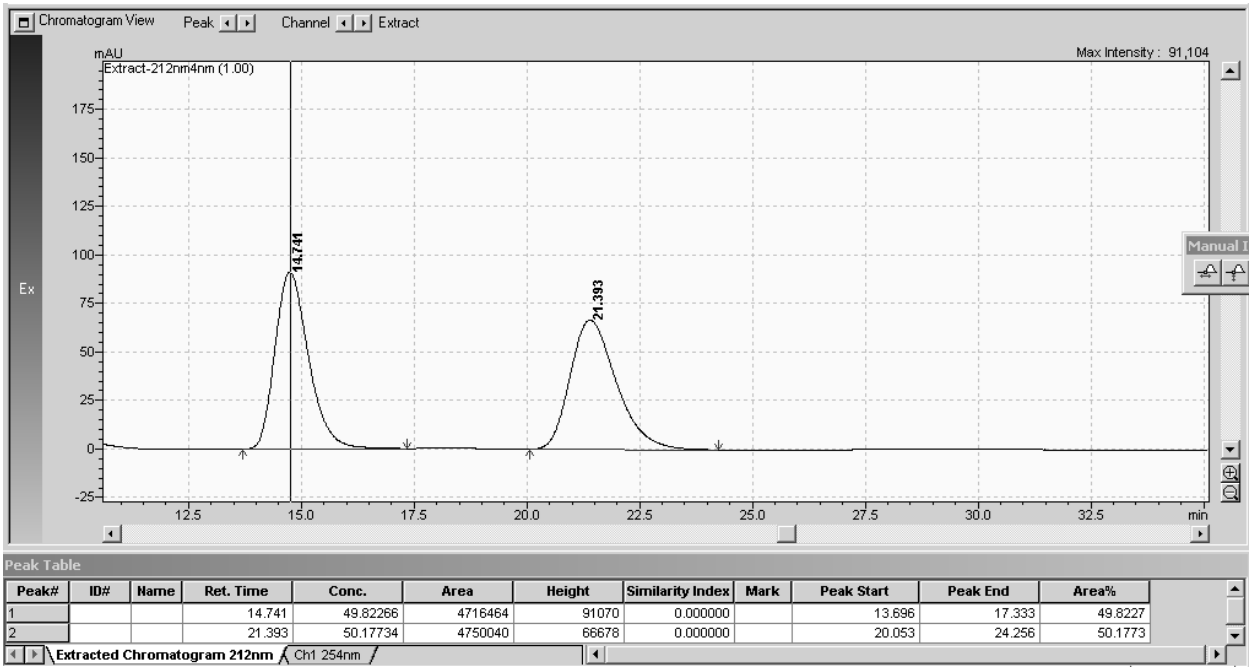
ee = 73,8%



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.929	13.08903	956540	17617	0.000000		13.845	16.469	13.0890
2			17.929	86.91097	6351407	103329	0.000000		16.608	20.608	86.9110

tert-Butyl ((_R_/_S_)-3-((_R_/_S_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c) – Racemic major diastereoisomer

HPLC MU 615: Chiral column AD, *n*-heptane/isopropanol (90:10), 1 mL, 25 °C, 212 nm.



Peak Table

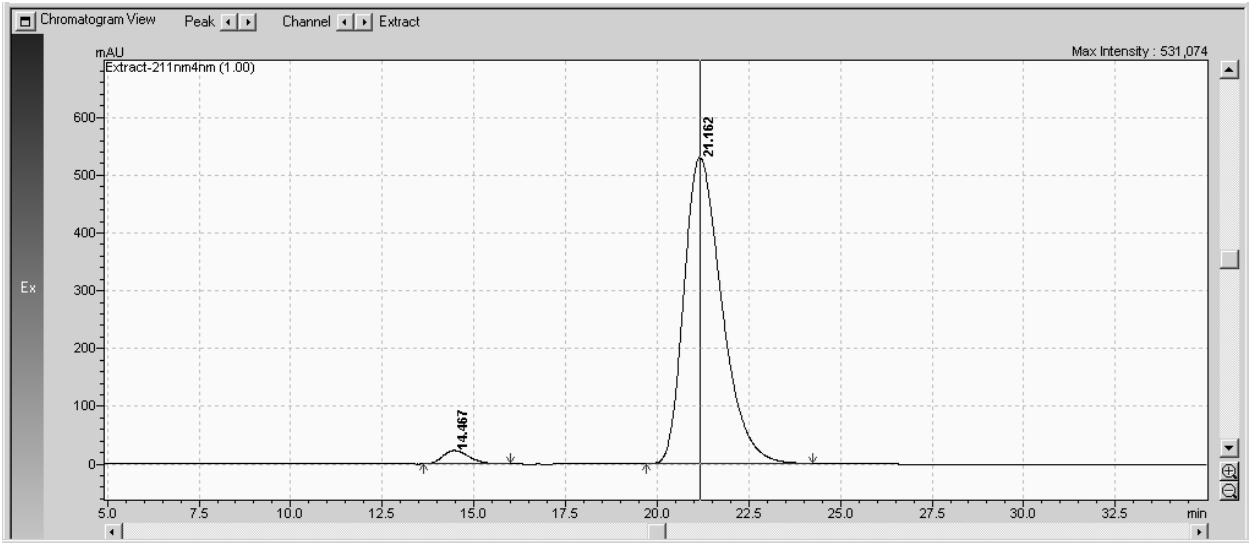
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.741	49.82266	4716464	91070	0.000000		13.696	17.333	49.8227
2			21.393	50.17734	4750040	66678	0.000000		20.053	24.256	50.1773

Extracted Chromatogram 212nm | Ch1 254nm

tert-Butyl ((_S_)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c) – Chiral major diastereoisomer

HPLC MU 603: Chiral column AD, *n*-heptane/isopropanol (90:10), 1 mL, 25 °C, 211 nm.

ee = 94 %



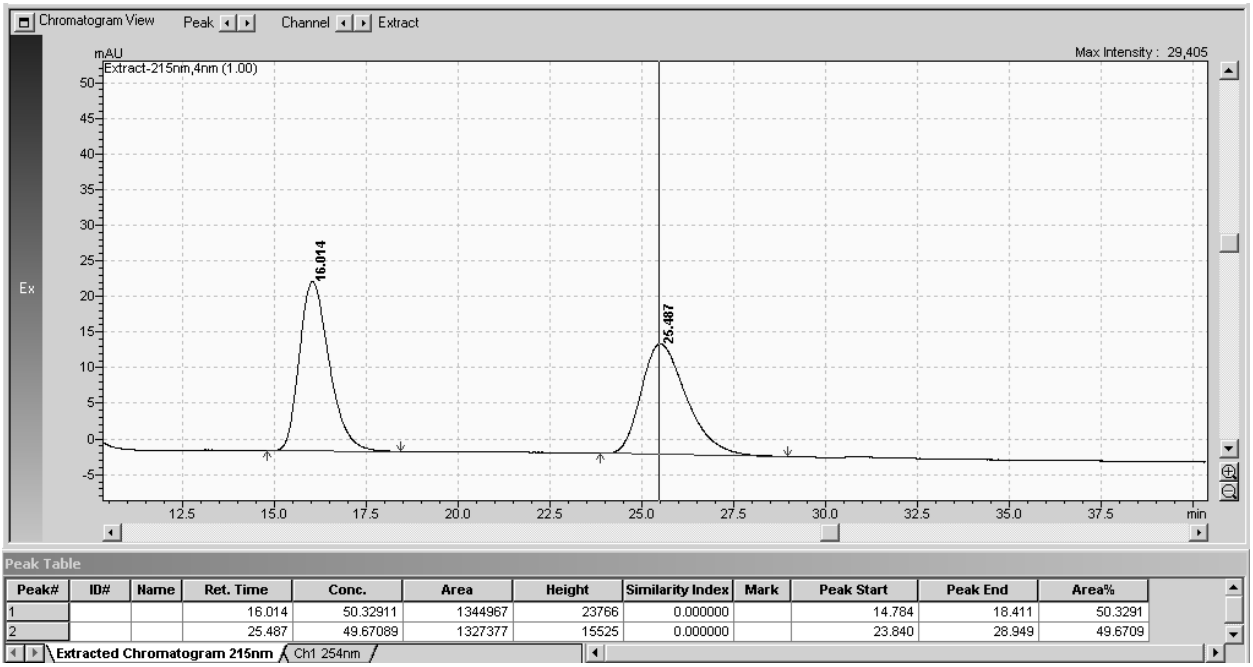
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.467	3.00789	1180642	23342	0.000000		13.611	16.011	3.0079
2			21.162	96.99211	38070905	530295	0.000000		19.691	24.256	96.9921

Extracted Chromatogram 211nm | Ch1 254nm

tert-Butyl ((_R_/_S_)-3-((_R_/_S_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c') – Racemic minor diastereoisomer

HPLC MU 615: Chiral column AD, *n*-heptane/isopropanol (90:10), 1 mL, 25 °C, 215 nm.



Peak Table

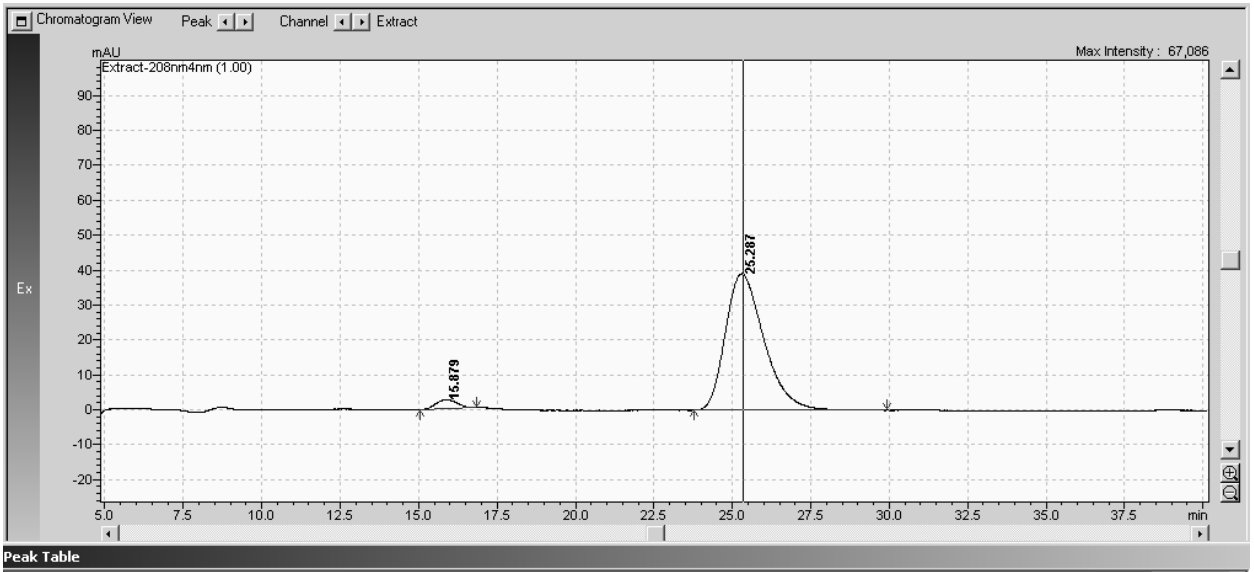
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			16.014	50.32911	1344967	23766	0.000000		14.784	18.411	50.3291
2			25.487	49.67089	1327377	15525	0.000000		23.840	28.949	49.6709

Extracted Chromatogram 215nm | Ch1 254nm

tert-Butyl ((_R_)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3c') –Chiral minor diastereoisomer

HPLC MU 603: Chiral column AD, *n*-heptane/isopropanol (90:10), 1 mL, 25 °C, 208 nm.

ee = 93 %



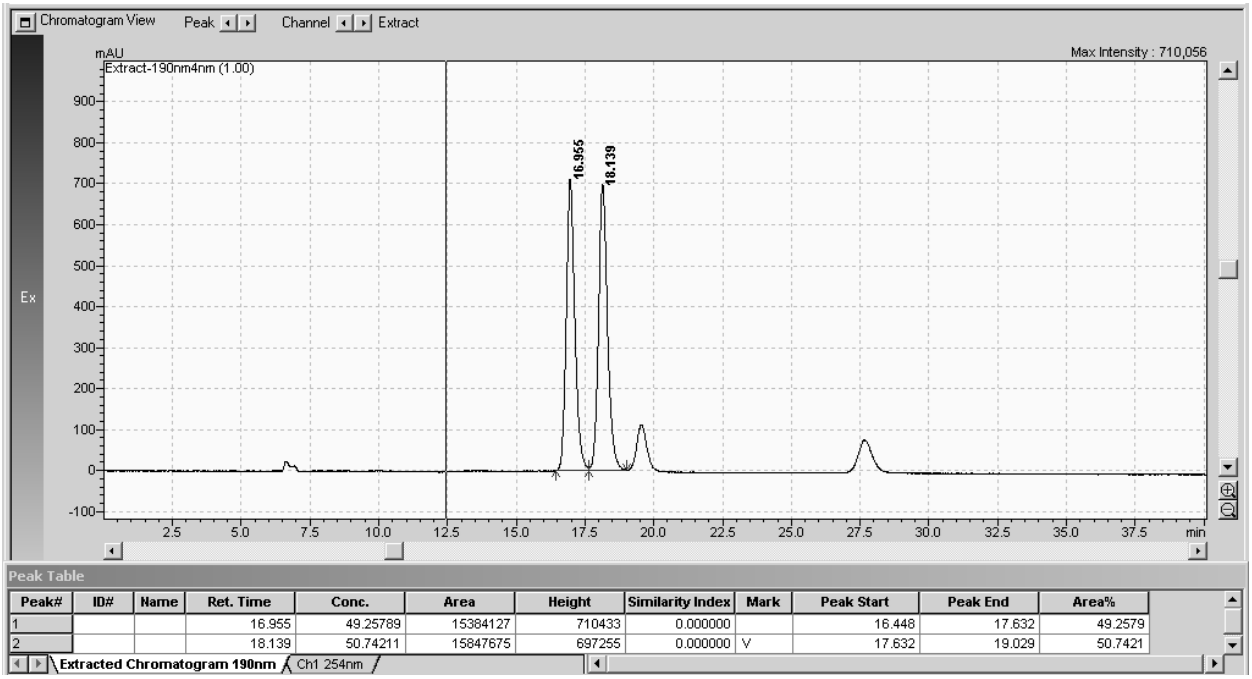
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			15.879	3.61146	125616	2648	0.000000		15.029	16.853	3.6115
2			25.287	96.38854	3352643	39135	0.000000		23.797	29.909	96.3885

Extracted Chromatogram 208nm | Ch1 254nm

***tert*-Butyl (*R*/*S*)-3-((tert-butoxycarbonyl)amino)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d) – Racemic major diastereoisomer**

HPLC MU 618: Chiral column IA, n-heptane/isopropanol (95:5), 0.5 mL, 25 °C, 190 nm.



Peak Table

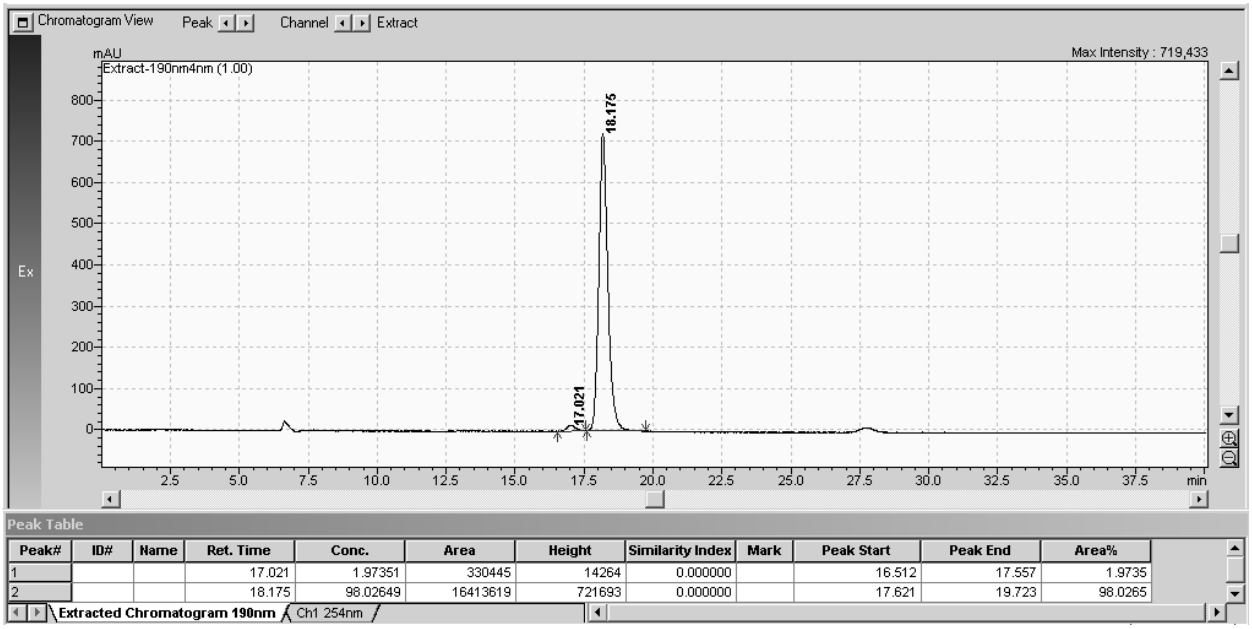
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			16.955	49.25789	15384127	710433	0.000000		16.448	17.632	49.2579
2			18.139	50.74211	15847675	697255	0.000000	V	17.632	19.029	50.7421

Extracted Chromatogram 190nm | Ch1 254nm

***tert*-Butyl (*S*)-3-((*tert*-butoxycarbonyl)amino)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d) – Chiral major diastereoisomer**

HPLC MU 604: Chiral column IA, n-heptane/isopropanol (95:5), 0.5 mL, 25 °C, 190 nm.

ee = 96 %



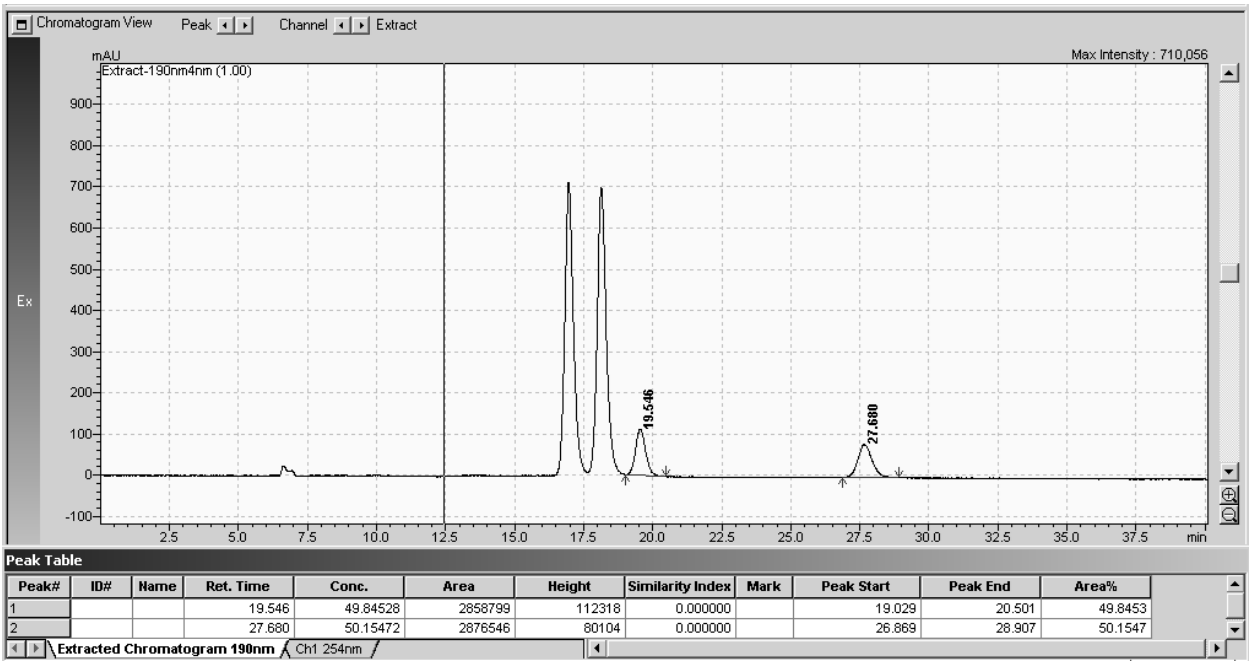
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			17.021	1.97351	330445	14264	0.000000		16.512	17.557	1.9735
2			18.175	98.02649	16413619	721693	0.000000		17.621	19.723	98.0265

Extracted Chromatogram 190nm | Ch1 254nm

***tert*-Butyl (*R*/*S*)-3-((*tert*-butoxycarbonyl)amino)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d') – Racemic minor diastereoisomer**

HPLC MU 618: Chiral column IA, n-heptane/isopropanol (95:5), 0.5 mL, 25 °C, 190 nm.



Peak Table

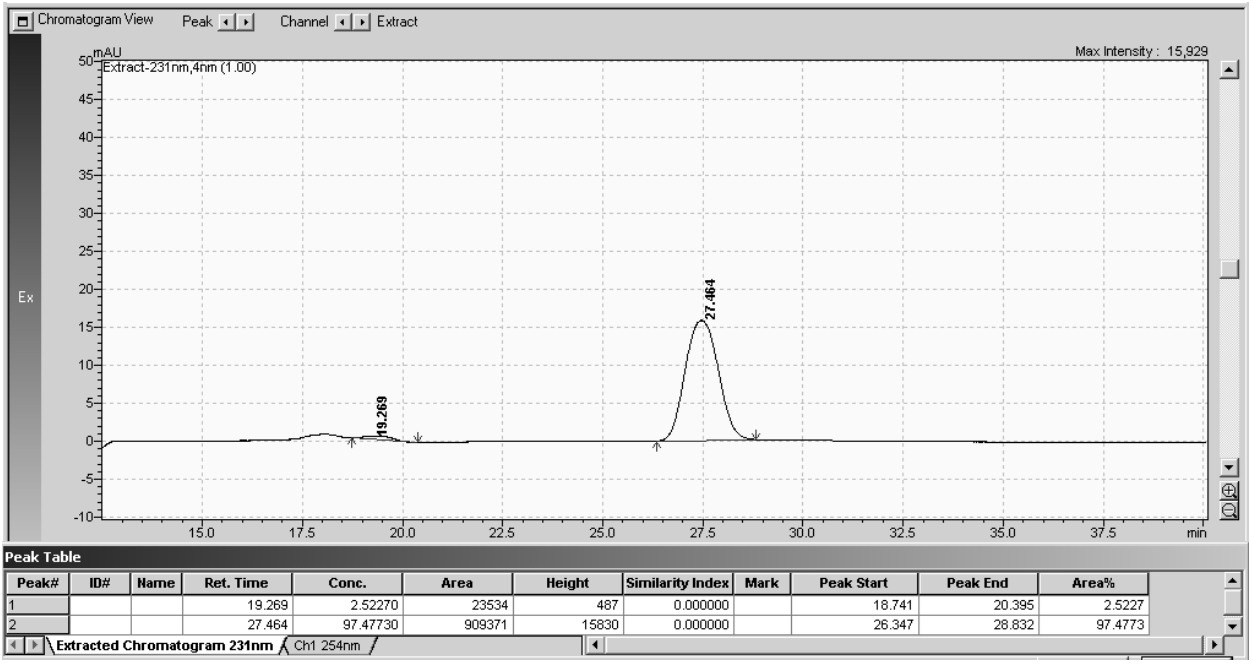
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			19.546	49.84528	2858799	112318	0.000000		19.029	20.501	49.8453
2			27.680	50.15472	2876546	80104	0.000000		26.869	28.907	50.1547

Extracted Chromatogram 190nm | Ch1 254nm

***tert*-Butyl (*R*)-3-((*tert*-butoxycarbonyl)amino)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindoline-1-carboxylate (3d') – Chiral minor diastereoisomer**

HPLC MU 604: Chiral column IA, n-heptane/isopropanol (95:5), 0.5 mL, 25 °C, 231 nm.

ee = 95 %



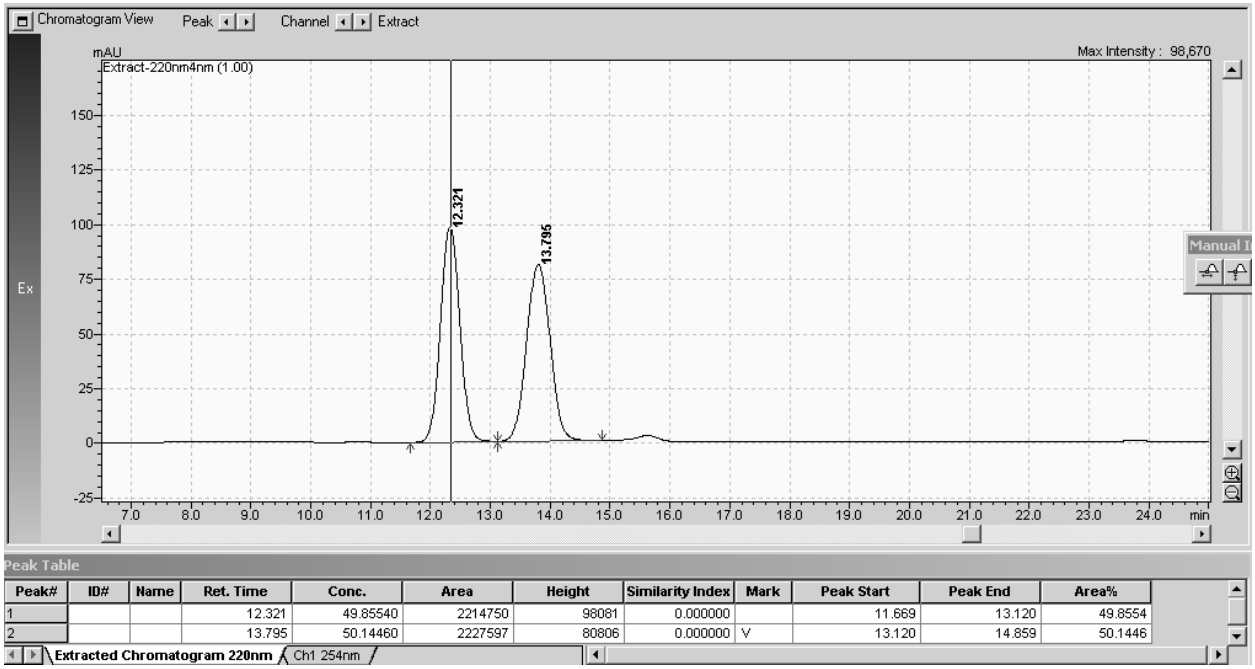
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			19.269	2.52270	23534	487	0.000000		18.741	20.395	2.5227
2			27.464	97.47730	909371	15830	0.000000		26.347	28.832	97.4773

Extracted Chromatogram 231nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-acetyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e) - Racemic major diasteroisomer**

HPLC MU 619: Chiral column IA, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 220 nm.



Peak Table

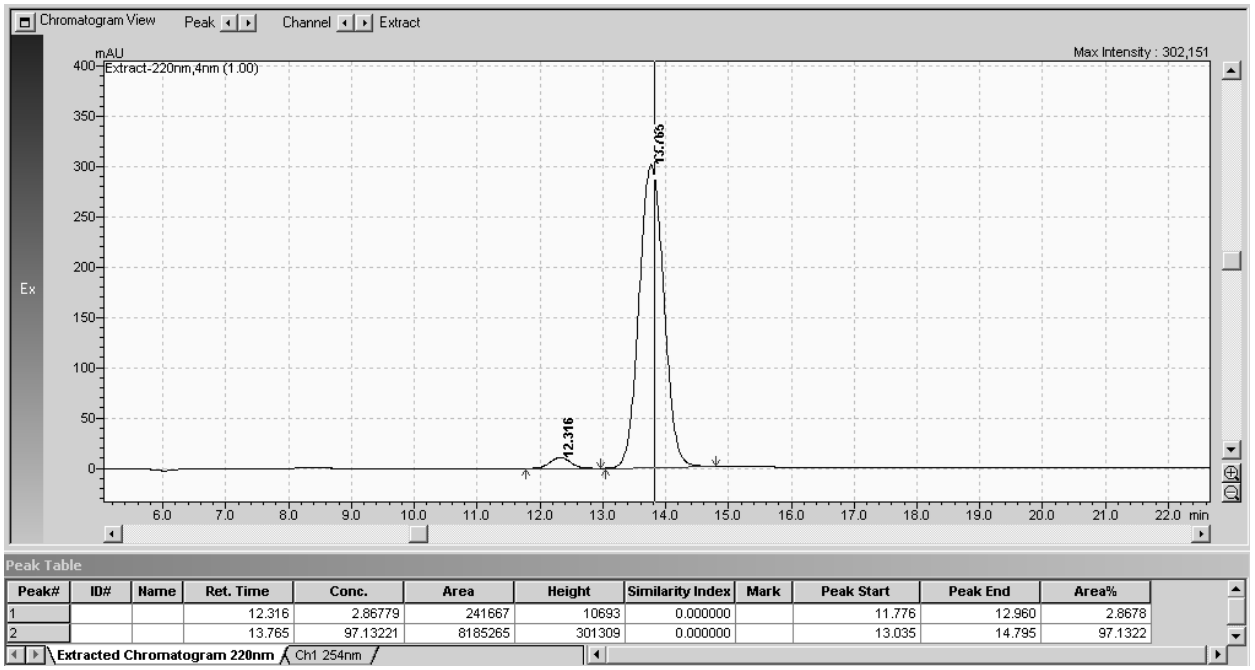
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.321	49.85540	2214750	98081	0.000000		11.669	13.120	49.8554
2			13.795	50.14460	2227597	80806	0.000000	V	13.120	14.859	50.1446

Extracted Chromatogram 220nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-acetyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e) - Chiral major diasteroisomer**

HPLC MU 605: Chiral column IA, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 220 nm.

ee = 94 %



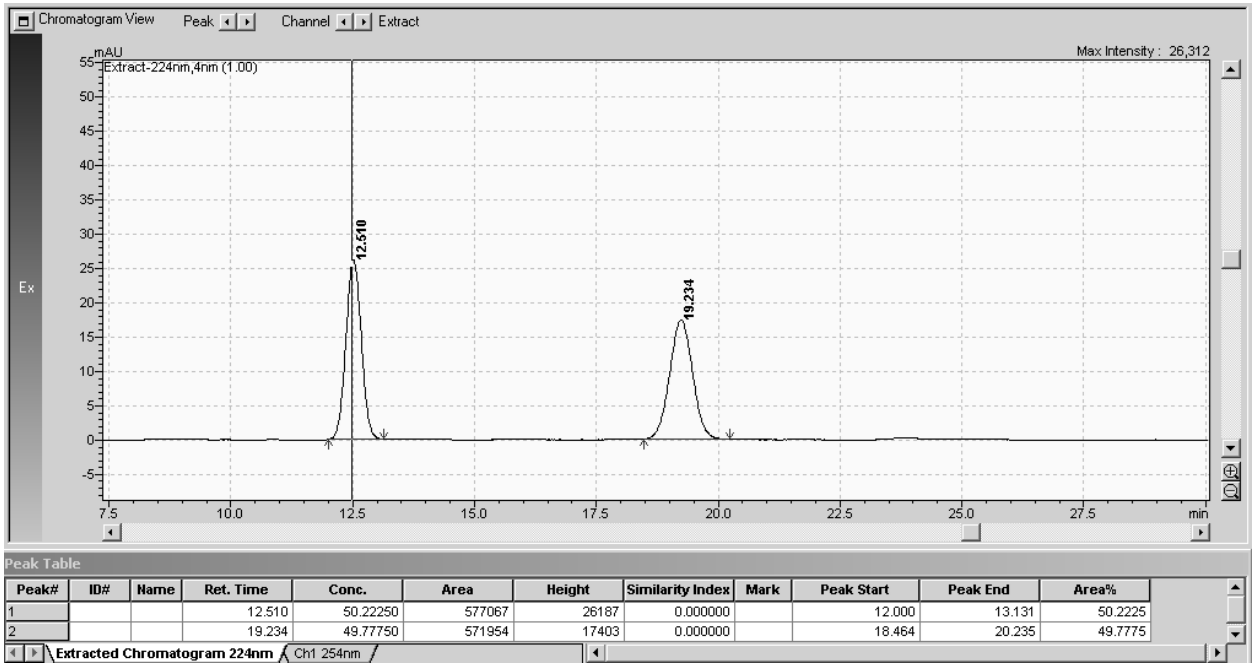
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.316	2.86779	241667	10693	0.000000		11.776	12.960	2.8678
2			13.765	97.13221	8185265	301309	0.000000		13.035	14.795	97.1322

Extracted Chromatogram 220nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-acetyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e') - Racemic minor diastereoisomer**

HPLC MU 619: Chiral column IA, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 224 nm.



Peak Table

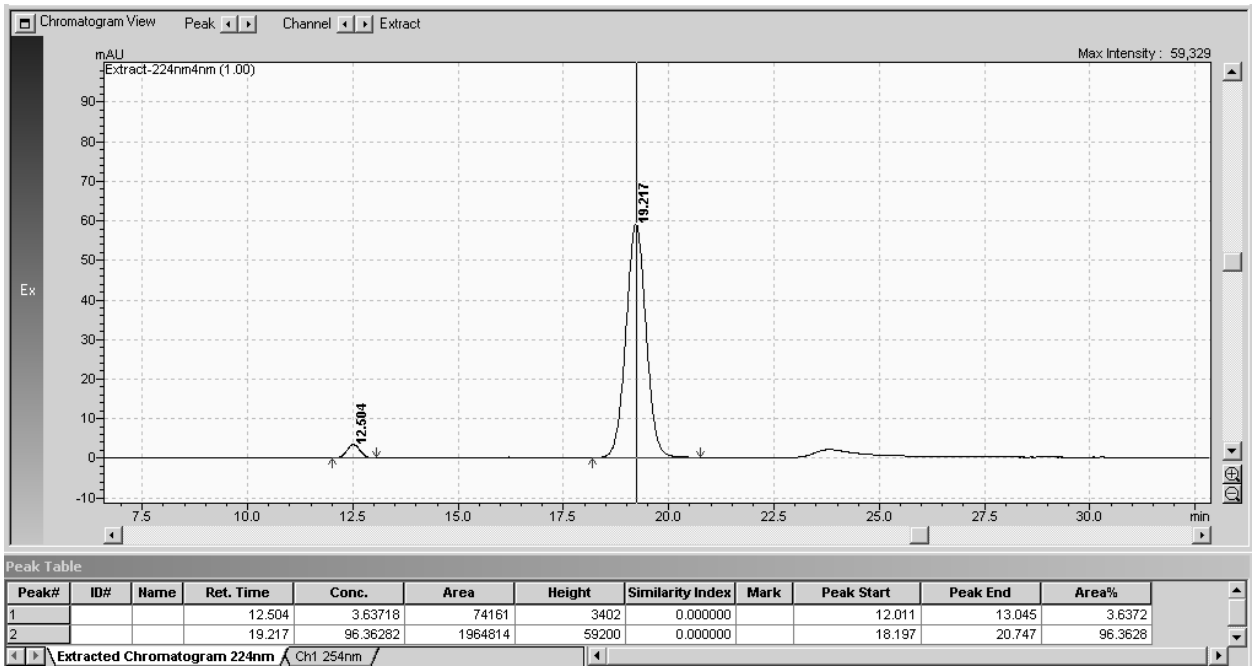
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.510	50.22250	577067	26187	0.000000		12.000	13.131	50.2225
2			19.234	49.77750	571954	17403	0.000000		18.464	20.235	49.7775

Extracted Chromatogram 224nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-acetyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3e') - Chiral minor diastereoisomer**

HPLC MU 605: Chiral column IA, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 224 nm.

ee = 93 %



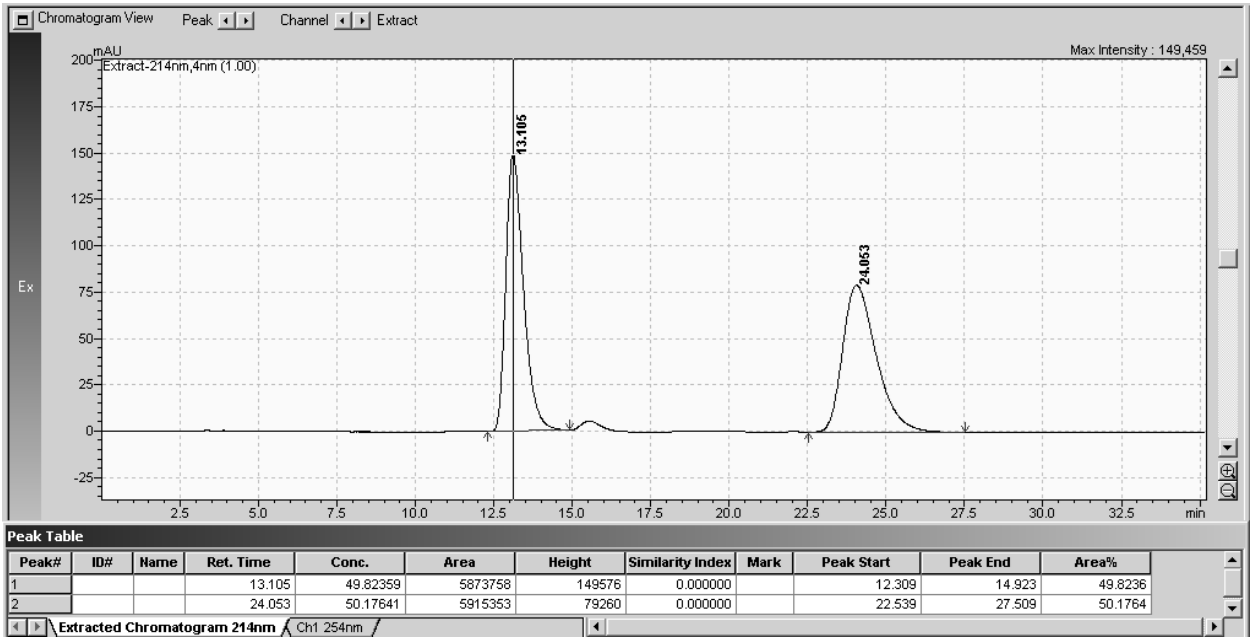
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			12.504	3.63718	74161	3402	0.000000		12.011	13.045	3.6372
2			19.217	96.36282	1964814	59200	0.000000		18.197	20.747	96.3628

Extracted Chromatogram 224nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-allyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f) – Racemic major diasteroisomer**

HPLC MU 757: Chiral column AD, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 214 nm.

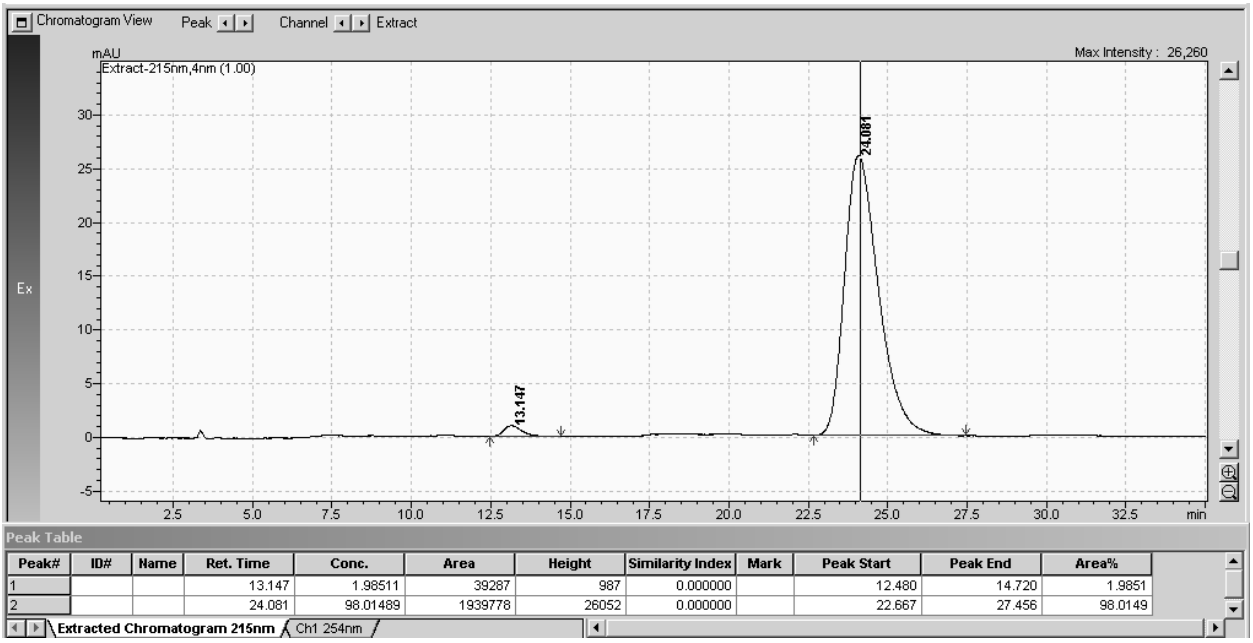


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			13.105	49.82359	5873758	149576	0.000000		12.309	14.923	49.8236
2			24.053	50.17641	5915353	79260	0.000000		22.539	27.509	50.1764

***tert*-Butyl ((*S*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f) – Chiral major diasteroisomer**

HPLC MU 755: Chiral column AD, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 215 nm.

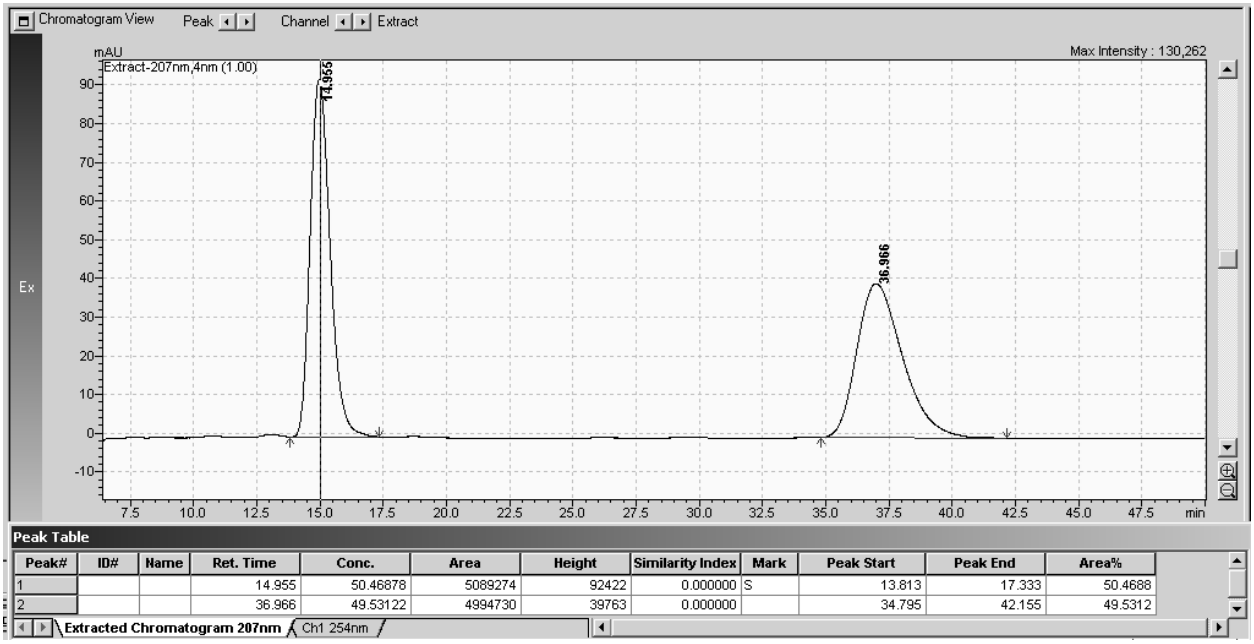
ee = 96 %



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			13.147	1.98511	39287	987	0.000000		12.480	14.720	1.9851
2			24.081	98.01489	1939778	26052	0.000000		22.667	27.456	98.0149

***tert*-Butyl ((*R*/*S*)-1-allyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f') – Racemic minor diastereoisomer**

HPLC MU 757: Chiral column AD, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 207 nm.



Peak Table

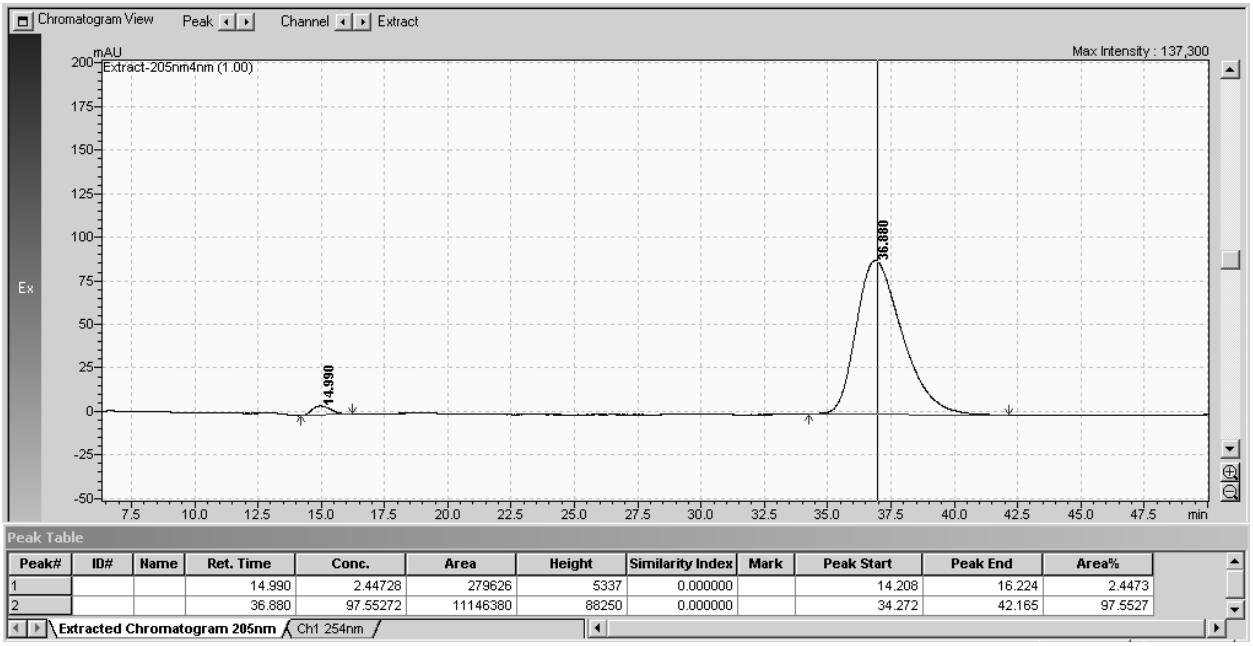
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.955	50.46878	5089274	92422	0.000000	S	13.813	17.333	50.4688
2			36.966	49.53122	4994730	39763	0.000000		34.795	42.155	49.5312

Extracted Chromatogram 207nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-allyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3f') – Chiral minor diastereoisomer**

HPLC MU 755: Chiral column AD, n-heptane/isopropanol (95:5), 1 mL, 25 °C, 205 nm.

ee = 95 %



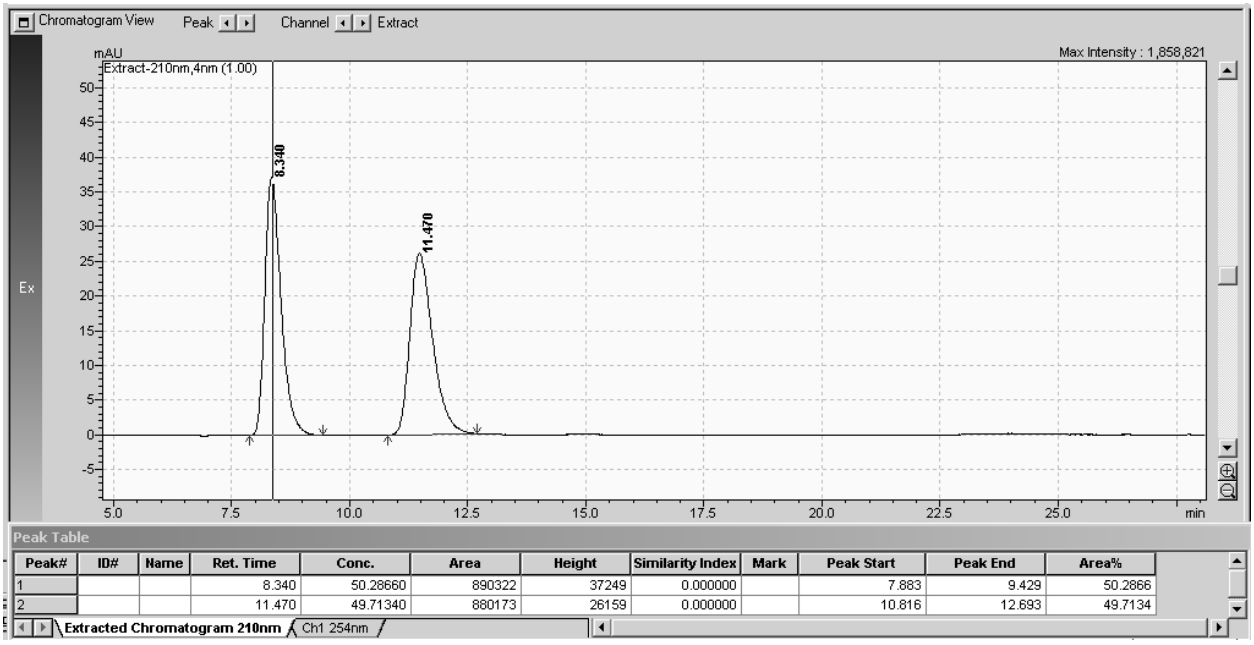
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.990	2.44728	279626	5337	0.000000		14.208	16.224	2.4473
2			36.880	97.55272	11146380	88250	0.000000		34.272	42.165	97.5527

Extracted Chromatogram 205nm | Ch1 254nm

tert-Butyl ((_R_/_S_)-3-((_R_/_S_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g) – Racemic major diastereoisomer

HPLC MU 647: Chiral column AD, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 210 nm.



Peak Table

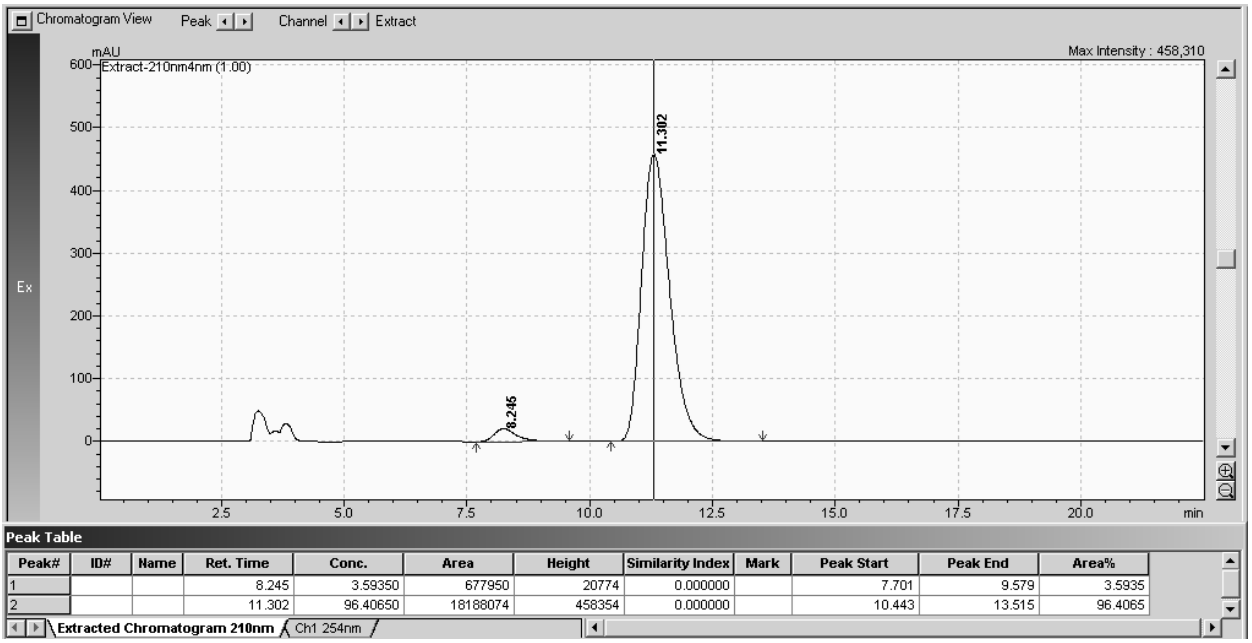
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.340	50.28660	890322	37249	0.000000		7.883	9.429	50.2866
2			11.470	49.71340	880173	26159	0.000000		10.816	12.693	49.7134

Extracted Chromatogram 210nm | Ch1 254nm

tert-Butyl ((_S_)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g) – Chiral major diastereoisomer

HPLC MU 653: Chiral column AD, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 210 nm.

ee = 93 %



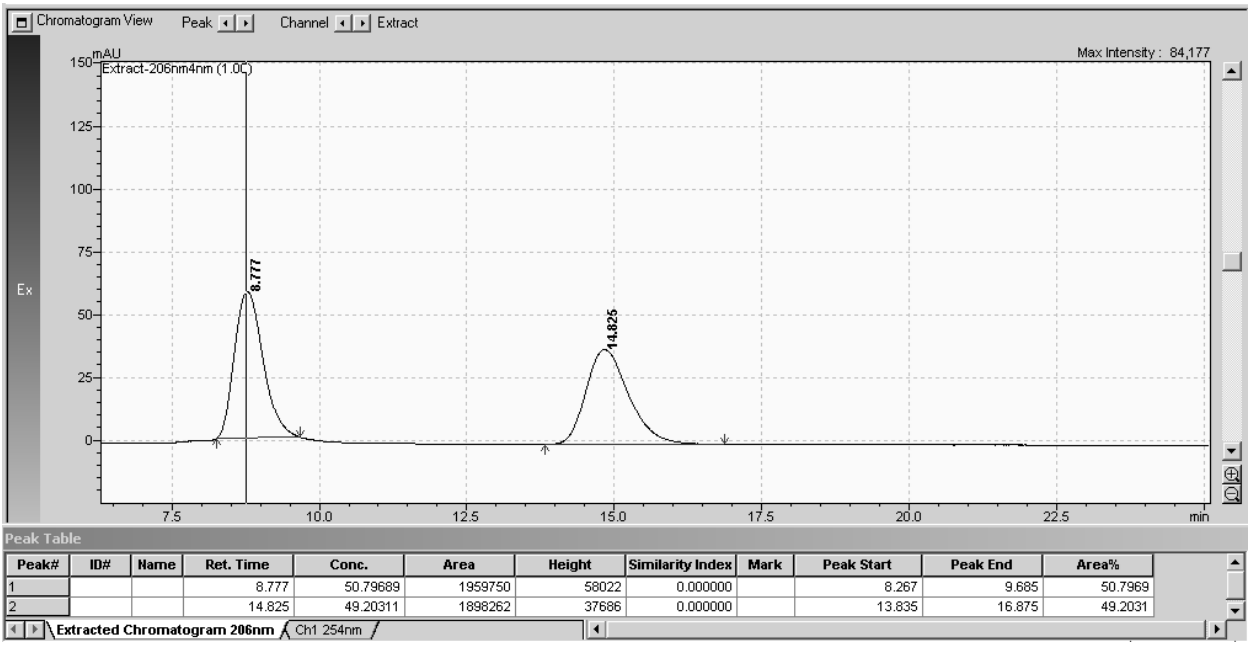
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.245	3.59350	677950	20774	0.000000		7.701	9.579	3.5935
2			11.302	96.40650	18188074	458354	0.000000		10.443	13.515	96.4065

Extracted Chromatogram 210nm | Ch1 254nm

tert-Butyl ((_R_/_S_)-3-((_R_/_S_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g') – Racemic minor diastereoisomer

HPLC MU 647: Chiral column AD, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 206 nm.



Peak Table

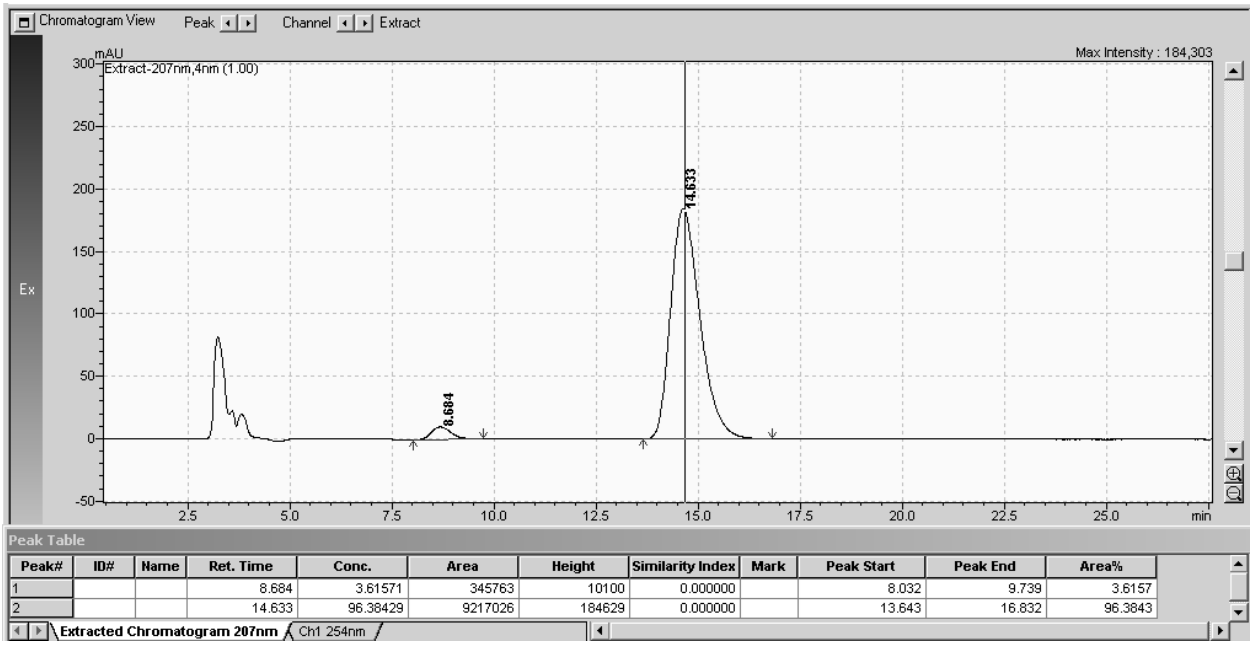
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.777	50.79689	1959750	58022	0.000000		8.267	9.685	50.7969
2			14.825	49.20311	1898262	37686	0.000000		13.835	16.875	49.2031

Extracted Chromatogram 206nm | Ch1 254nm

tert-Butyl ((_R_)-3-((_R_)-fluoro(nitro)(phenylsulfonyl)methyl)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3g') – Chiral minor diastereoisomer

HPLC MU 653: Chiral column AD, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 207 nm.

_ee_ = 93 %



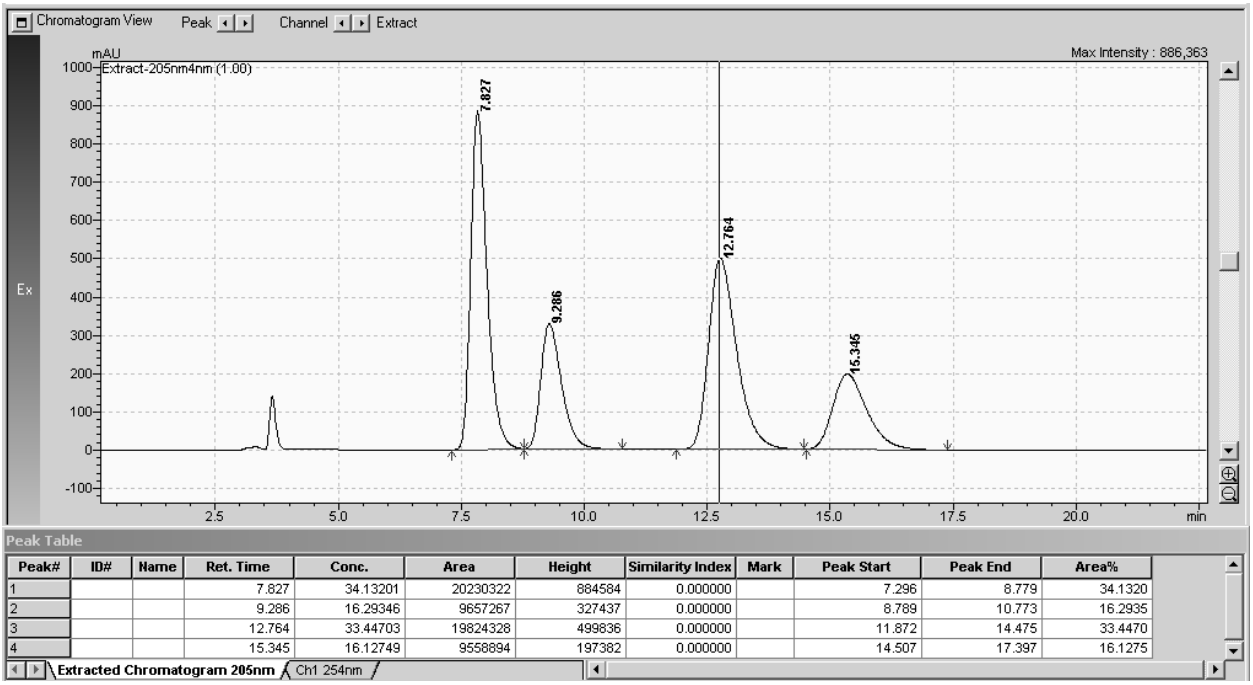
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.684	3.61571	345763	10100	0.000000		8.032	9.739	3.6157
2			14.633	96.38429	9217026	184629	0.000000		13.643	16.832	96.3843

Extracted Chromatogram 207nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – Racemic major +minor diastereoisomer**

HPLC MU 651: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 205 nm.



Peak Table

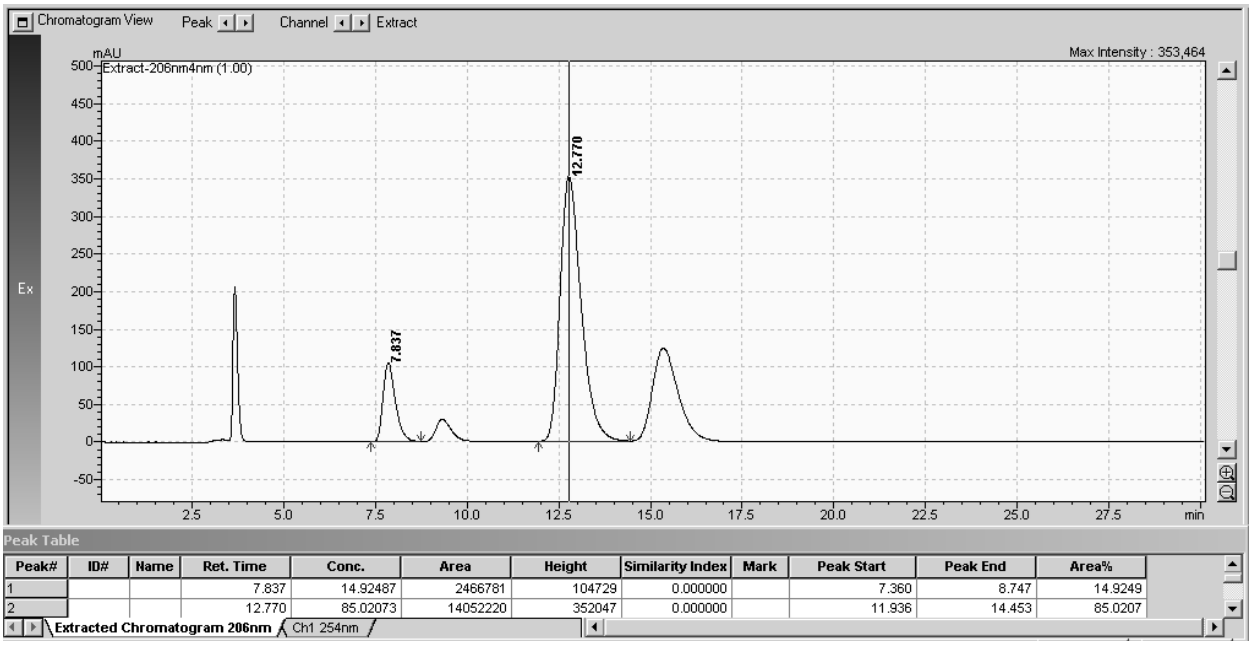
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.827	34.13201	20230322	884584	0.000000		7.296	8.779	34.1320
2			9.286	16.29346	9657267	327437	0.000000		8.789	10.773	16.2935
3			12.764	33.44703	19824328	499836	0.000000		11.872	14.475	33.4470
4			15.345	16.12749	9558894	197382	0.000000		14.507	17.397	16.1275

Extracted Chromatogram 205nm | Ch1 254nm

***tert*-Butyl ((*S*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h) – Chiral major diastereoisomer**

HPLC MU 651: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 205 nm.

ee = 70 %;



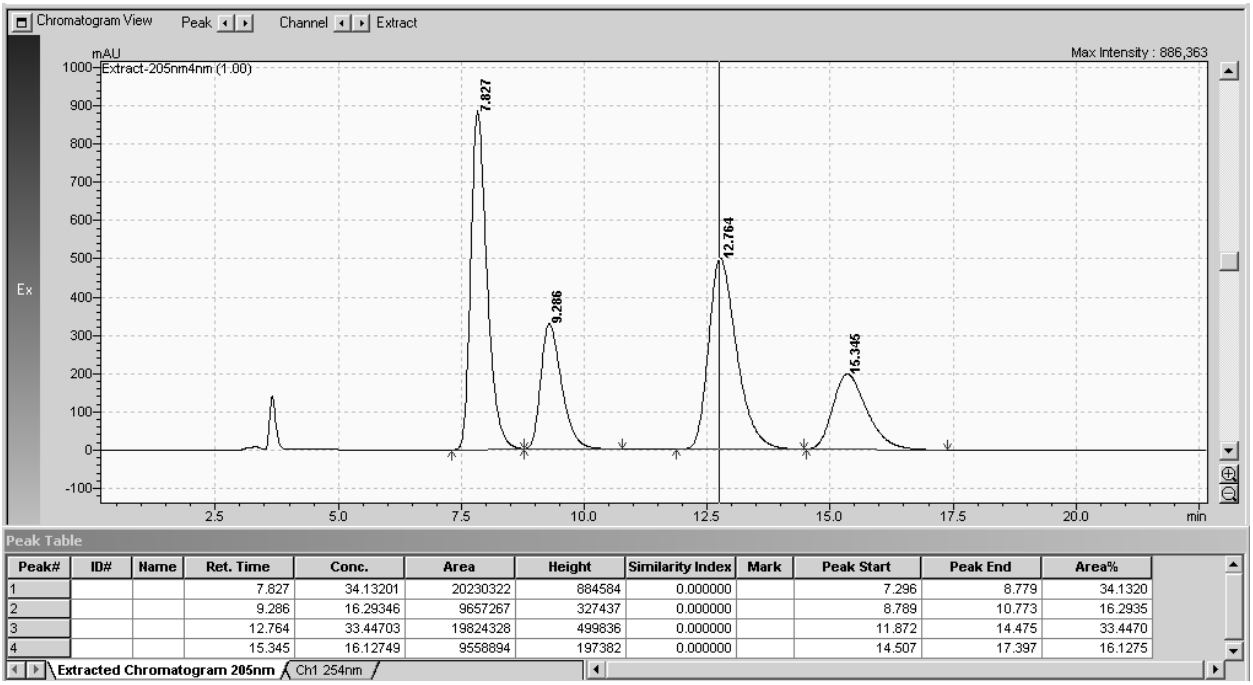
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.837	14.92487	2466781	104729	0.000000		7.360	8.747	14.9249
2			12.770	85.02073	14052220	352047	0.000000		11.936	14.453	85.0207

Extracted Chromatogram 206nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h') – Racemic major +minor diastereoisomer**

HPLC MU 651: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 205 nm.

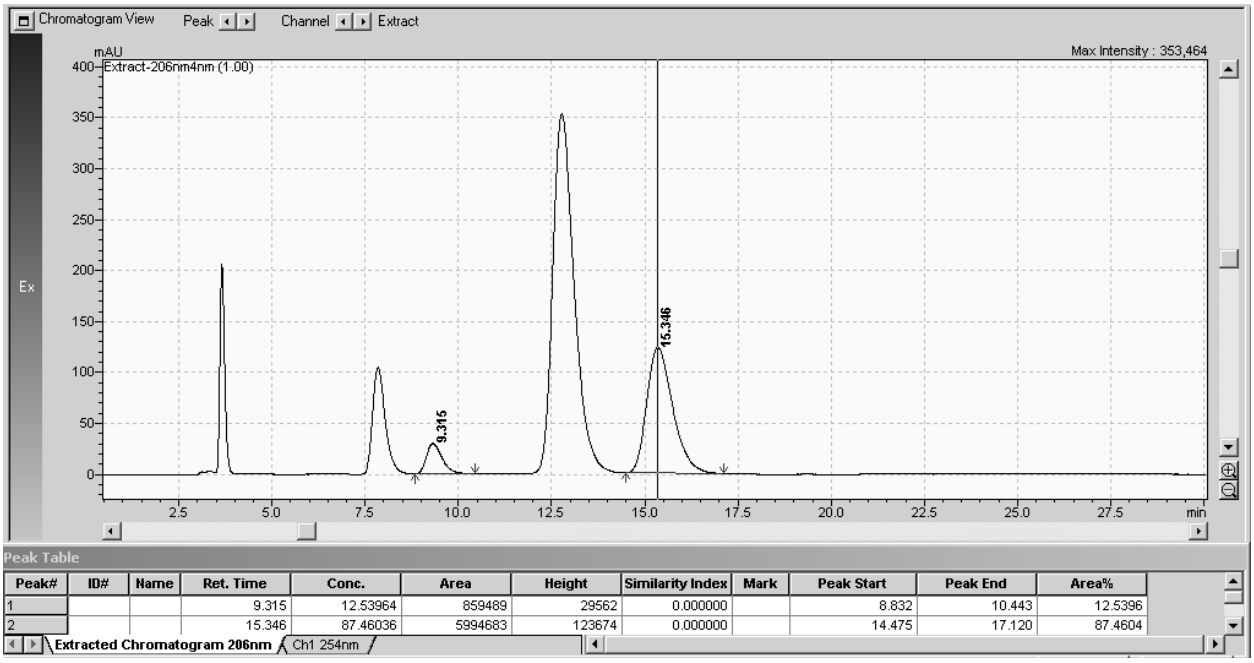


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.827	34.13201	20230322	884584	0.000000		7.296	8.779	34.1320
2			9.286	16.29346	9657267	327437	0.000000		8.789	10.773	16.2935
3			12.764	33.44703	19824328	499836	0.000000		11.872	14.475	33.4470
4			15.345	16.12749	9558894	197382	0.000000		14.507	17.397	16.1275

***tert*-Butyl ((*R*)-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxo-1-tosylindolin-3-yl)carbamate (3h') –Chiral minor diastereoisomer**

HPLC MU 651: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 205 nm.

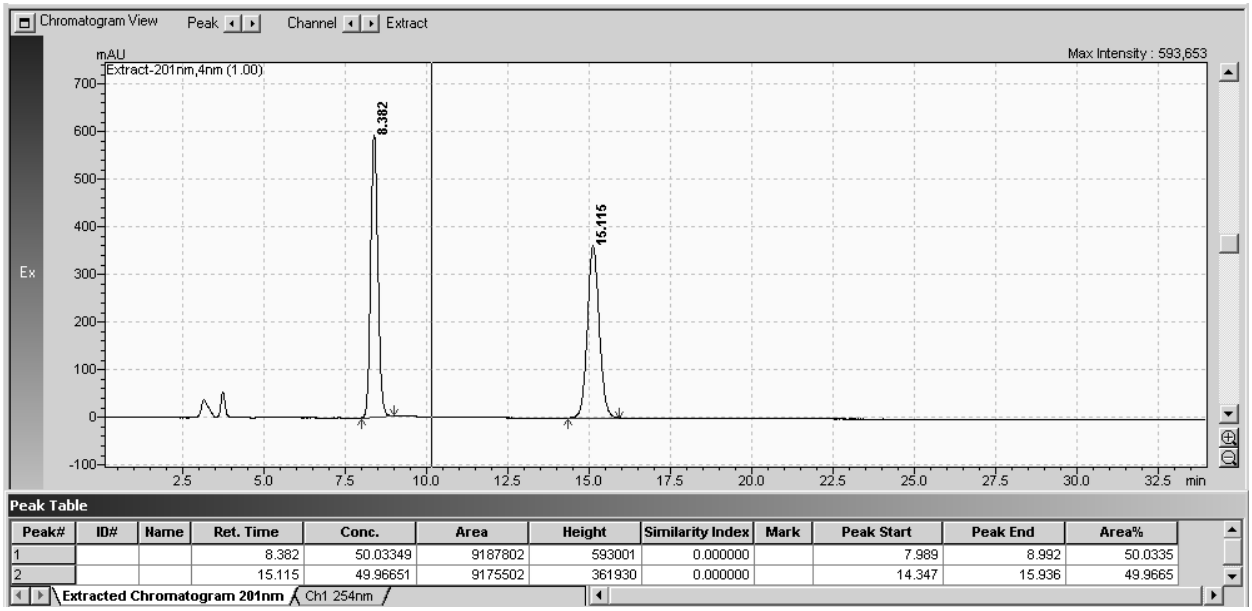
ee = 75 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			9.315	12.53964	859489	29562	0.000000		8.832	10.443	12.5396
2			15.346	87.46036	5994683	123674	0.000000		14.475	17.120	87.4604

***tert*-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i) – Racemic major diastereoisomer**

HPLC MU 720: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 190 nm.

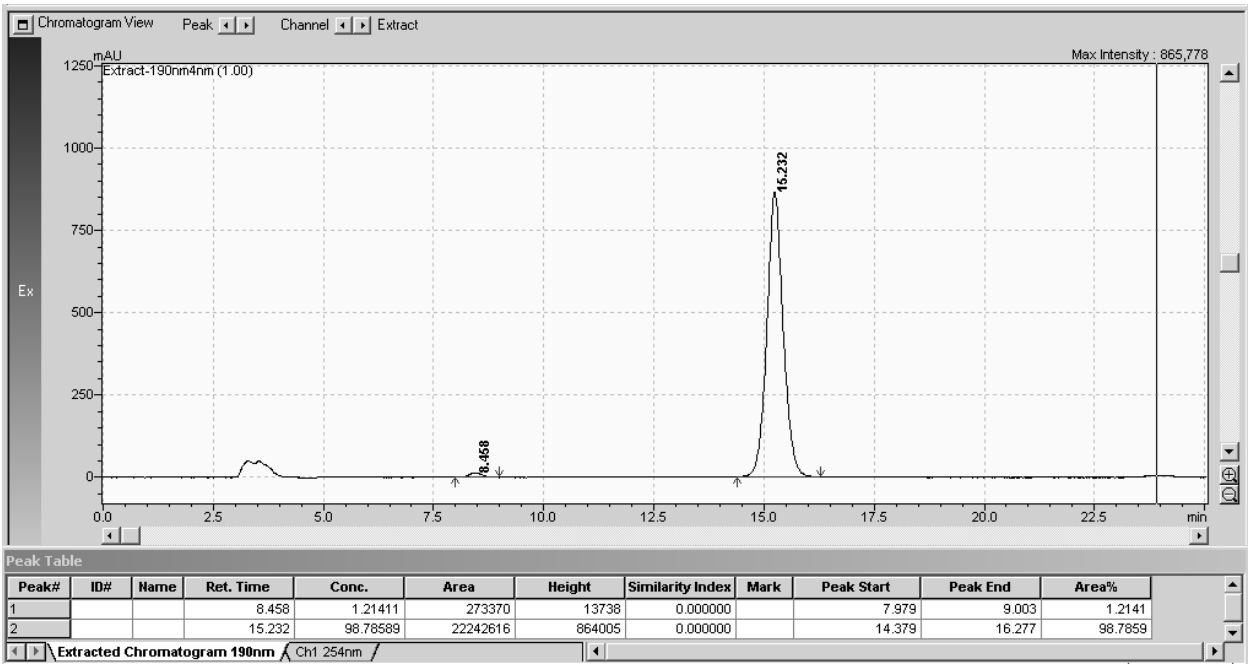


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.382	50.03349	9187802	593001	0.000000		7.989	8.992	50.0335
2			15.115	49.96651	9175502	361930	0.000000		14.347	15.936	49.9665

***tert*-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i) – Chiral major diastereoisomer**

HPLC MU 722: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 190 nm.

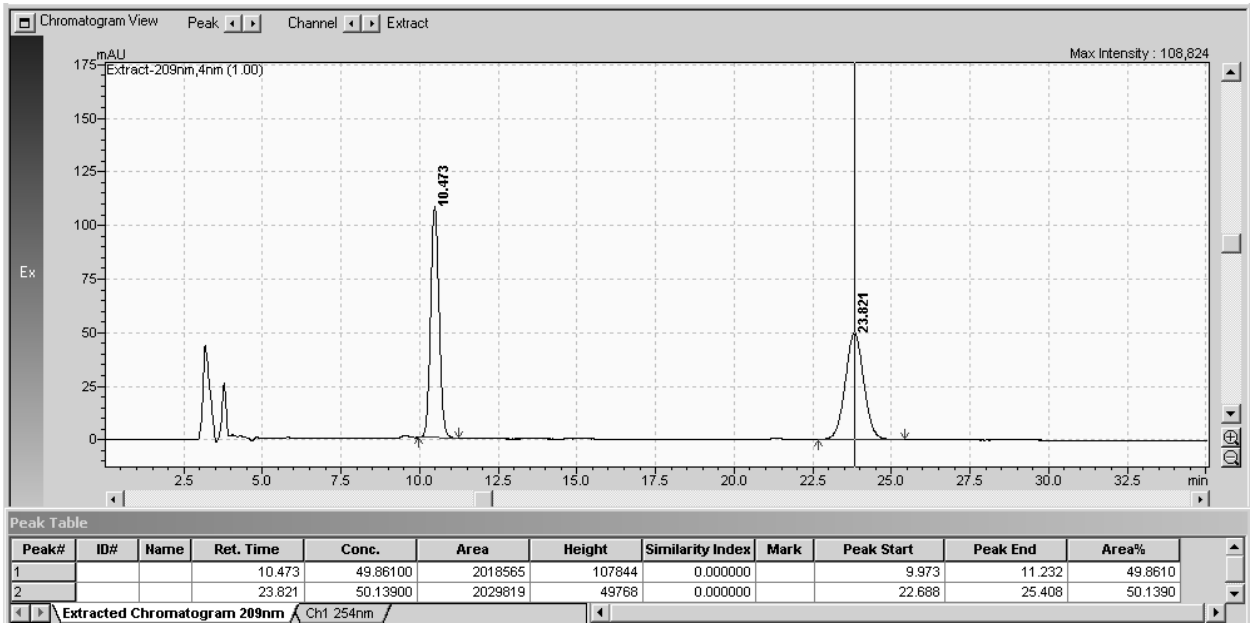
ee = 98 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.458	1.21411	273370	13738	0.000000		7.979	9.003	1.2141
2			15.232	98.78589	22242616	864005	0.000000		14.379	16.277	98.7859

***tert*-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i') – Racemic minor diasteroisomer**

HPLC MU 720: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 209 nm.

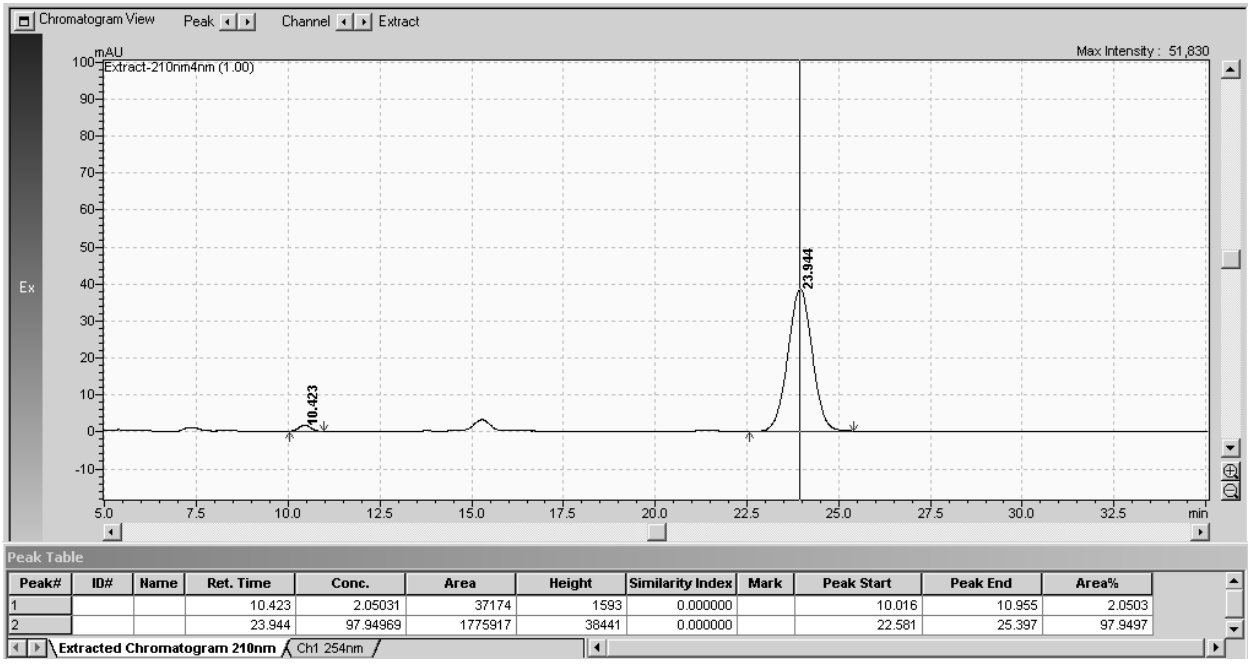


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			10.473	49.86100	2018565	107844	0.000000		9.973	11.232	49.8610
2			23.821	50.13900	2029819	49768	0.000000		22.688	25.408	50.1390

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-5-methyl-2-oxoindolin-3-yl)carbamate (3i') - Chiral minor diastereoisomer**

HPLC MU 722: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 210 nm.

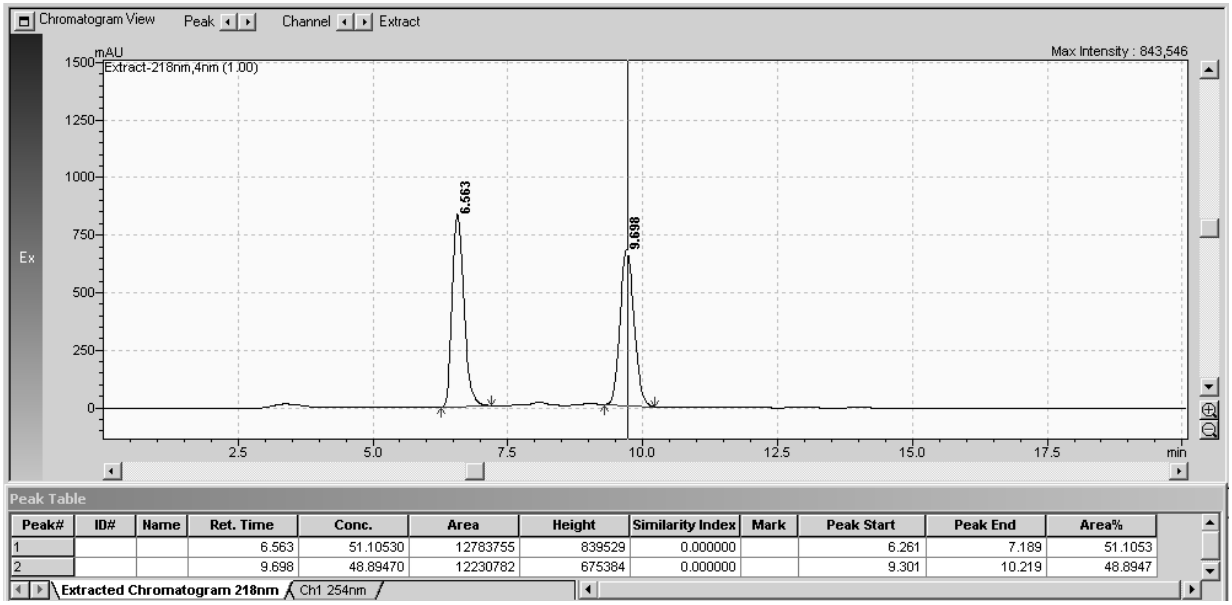
ee = 96 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			10.423	2.05031	37174	1593	0.000000		10.016	10.955	2.0503
2			23.944	97.94969	1775917	38441	0.000000		22.581	25.397	97.9497

***tert*-Butyl ((*R*/*S*)-1-benzyl-5-chloro-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j) – Racemic major diastereoisomer**

HPLC MU 719: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 218 nm.

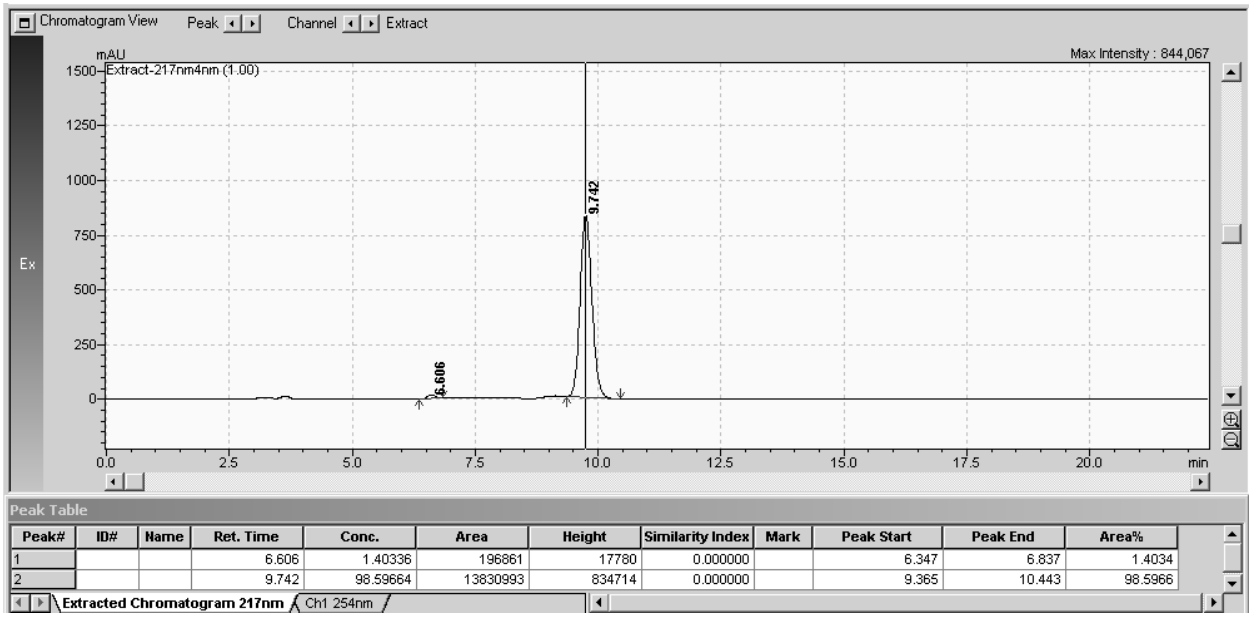


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			6.563	51.10530	12783755	839529	0.000000		6.261	7.189	51.1053
2			9.698	48.89470	12230782	675384	0.000000		9.301	10.219	48.8947

***tert*-Butyl ((*S*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j) – Chiral major diastereoisomer**

HPLC MU 721: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 217 nm.

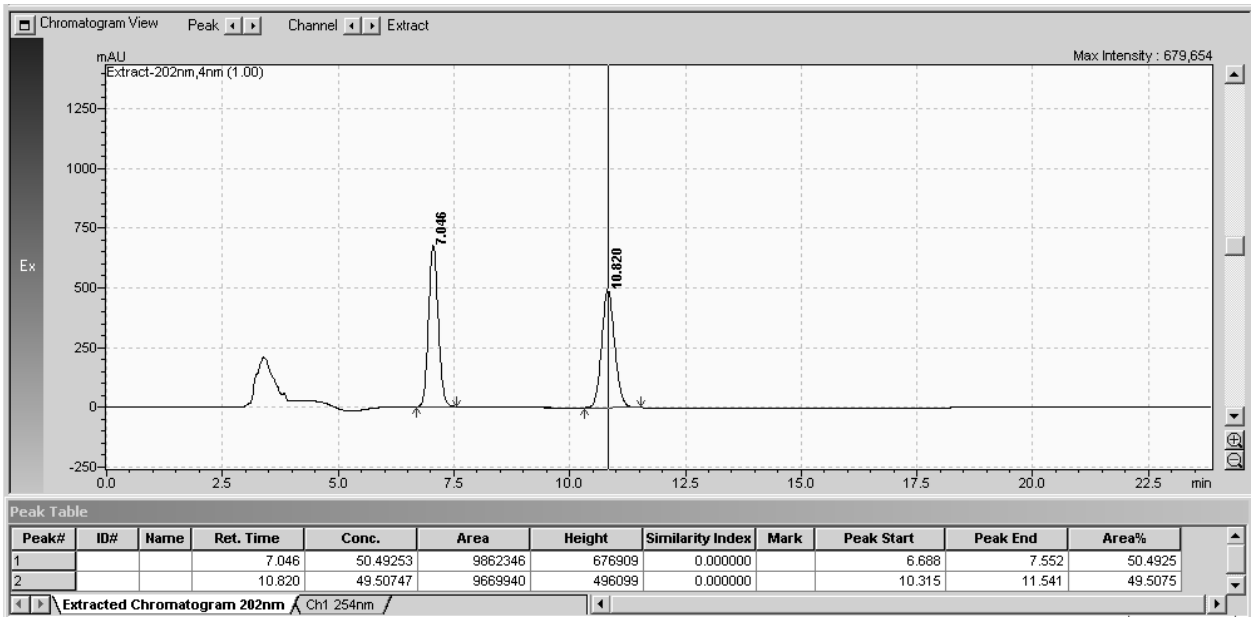
ee = 97 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			6.606	1.40336	196861	17780	0.000000		6.347	6.837	1.4034
2			9.742	98.59664	13830993	834714	0.000000		9.365	10.443	98.5966

***tert*-Butyl ((*R*/*S*)-1-benzyl-5-chloro-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j') – Racemic minor diastereoisomer**

HPLC MU 719: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 217 nm.



Peak Table

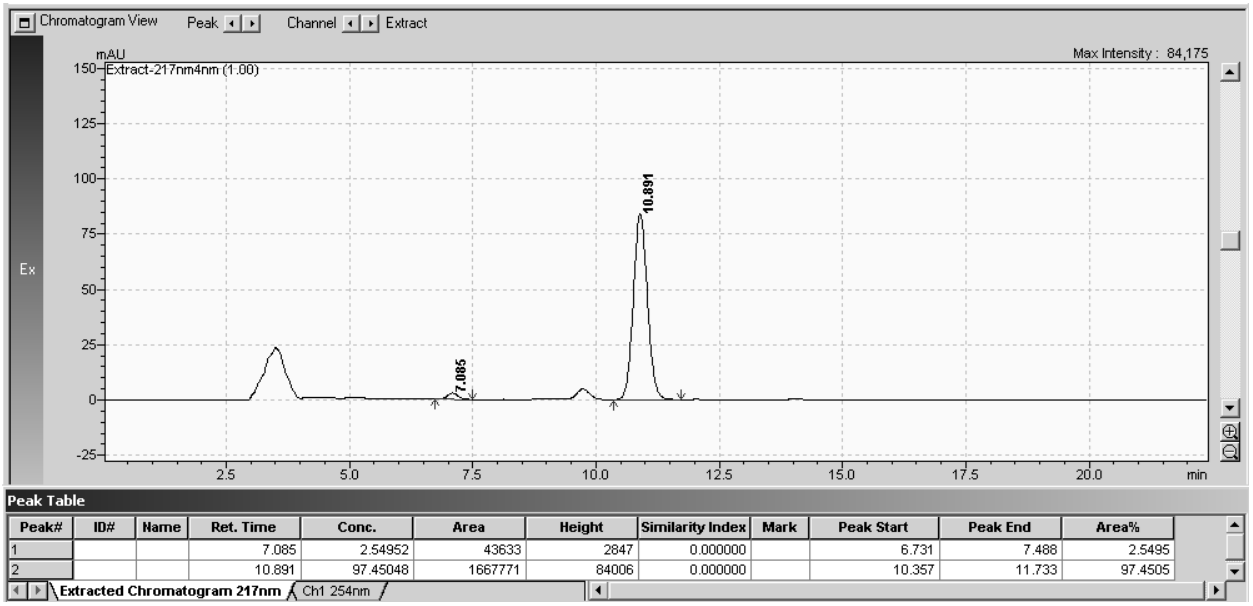
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.046	50.49253	9862346	676909	0.000000		6.688	7.552	50.4925
2			10.820	49.50747	9669940	496099	0.000000		10.315	11.541	49.5075

Extracted Chromatogram 202nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-benzyl-5-chloro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3j') – Chiral minor diastereoisomer**

HPLC MU 721: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 217 nm.

ee = 95 %;



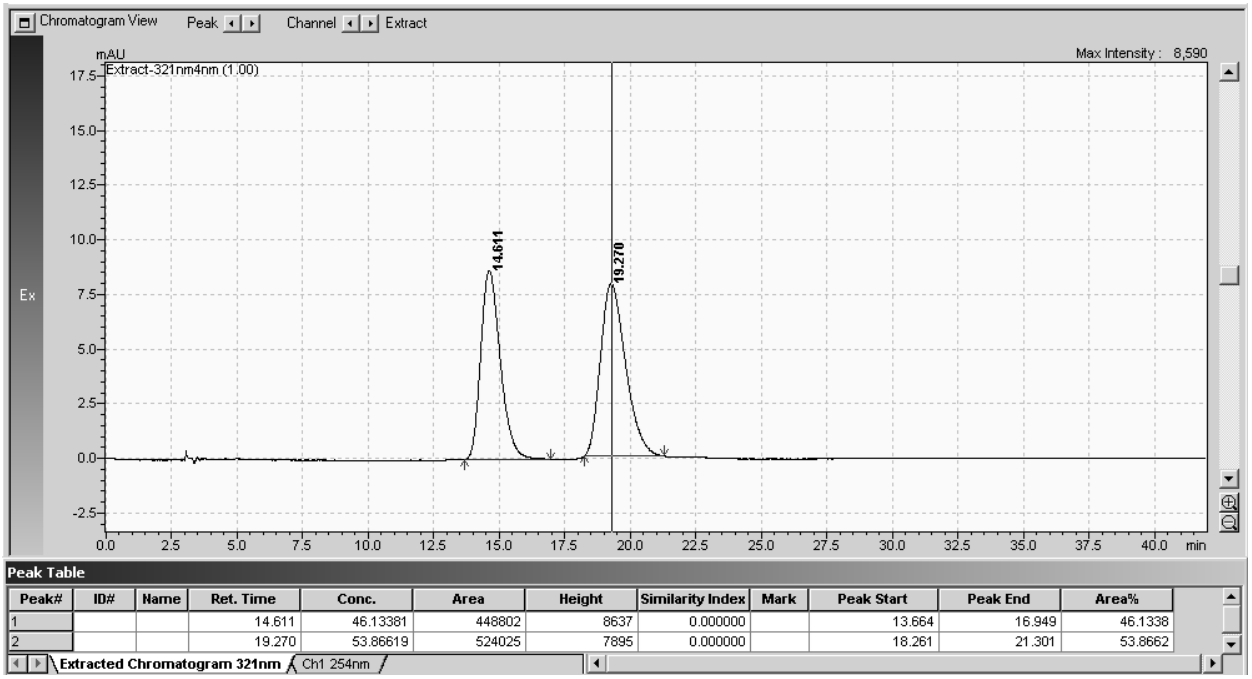
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.085	2.54952	43633	2847	0.000000		6.731	7.488	2.5495
2			10.891	97.45048	1667771	84006	0.000000		10.357	11.733	97.4505

Extracted Chromatogram 217nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-5-nitro-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k) – Racemic major diastereomer**

HPLC MU 756: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 321 nm.



Peak Table

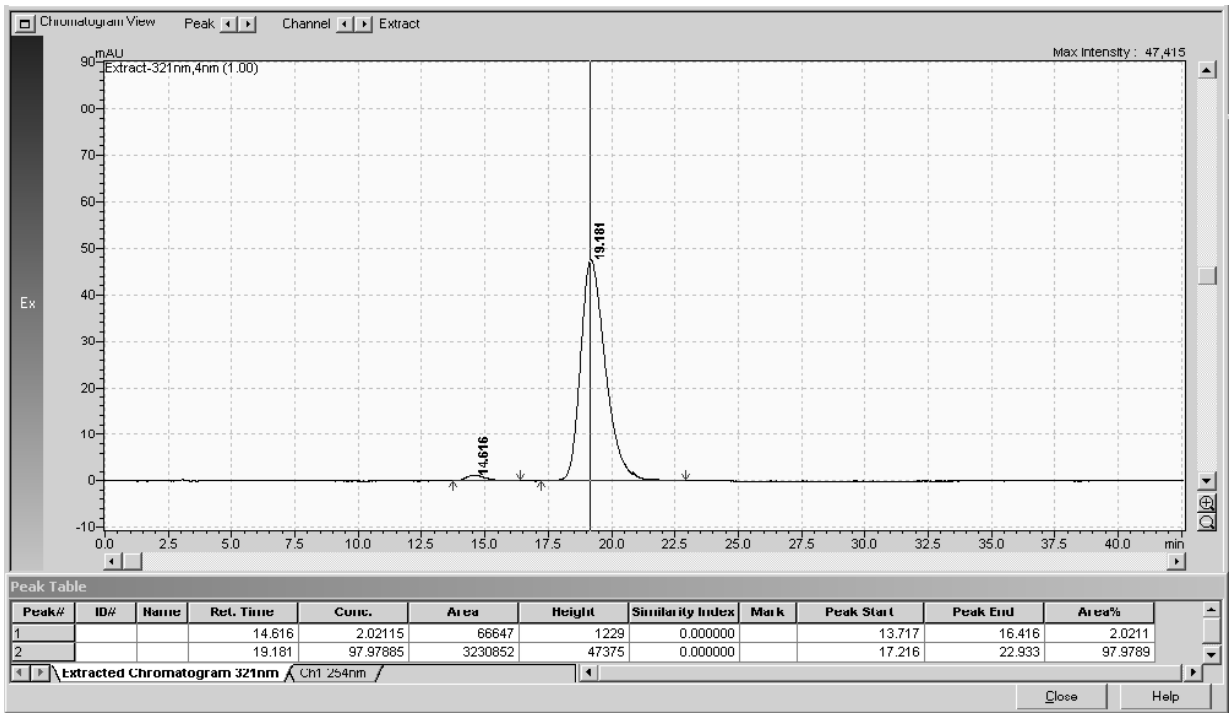
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.611	46.13381	448802	8637	0.000000		13.664	16.949	46.1338
2			19.270	53.86619	524025	7895	0.000000		18.261	21.301	53.8662

Extracted Chromatogram 321nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k) – Chiral major diastereoisomer**

HPLC MU 754: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 321 nm.

ee = 96 %;



Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.616	2.02115	66647	1229	0.000000		13.717	16.416	2.0211
2			19.181	97.97885	3230852	47375	0.000000		17.216	22.933	97.9789

Extracted Chromatogram 321nm | Ch1 254nm

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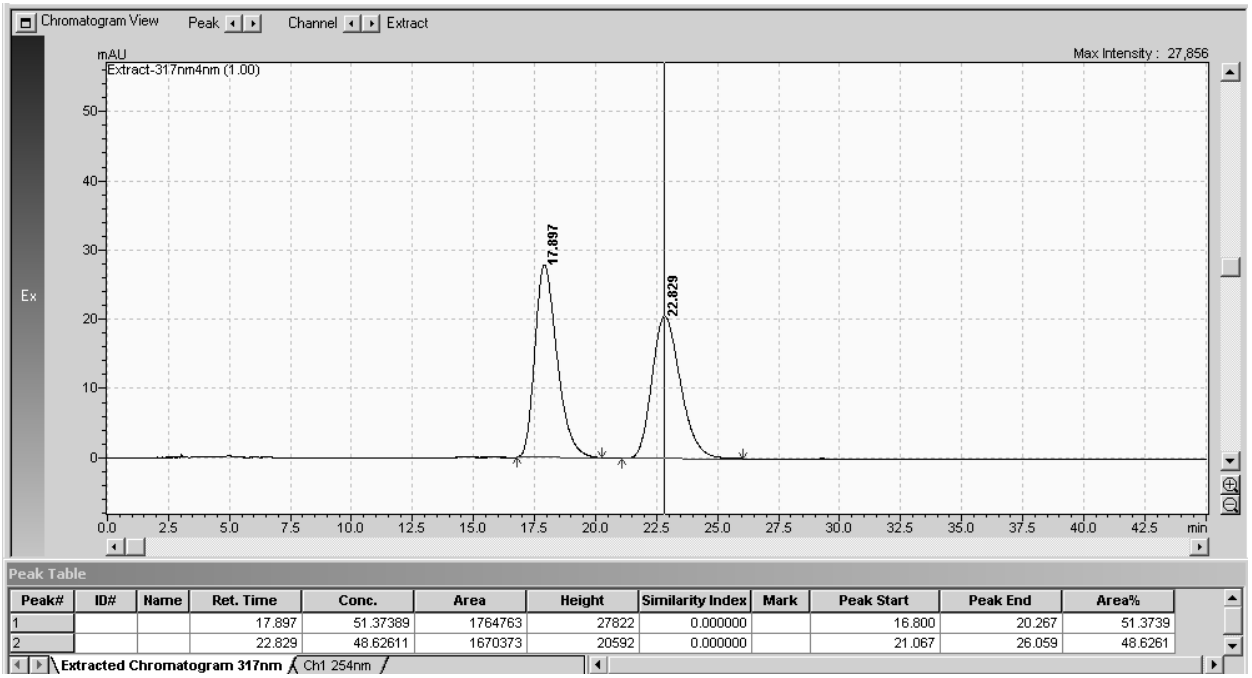
***tert*-Butyl ((*R*/*S*)-1-benzyl-5-nitro-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k') – Racemic minor diastereoisomer**

HPLC MU 756: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 317 nm.

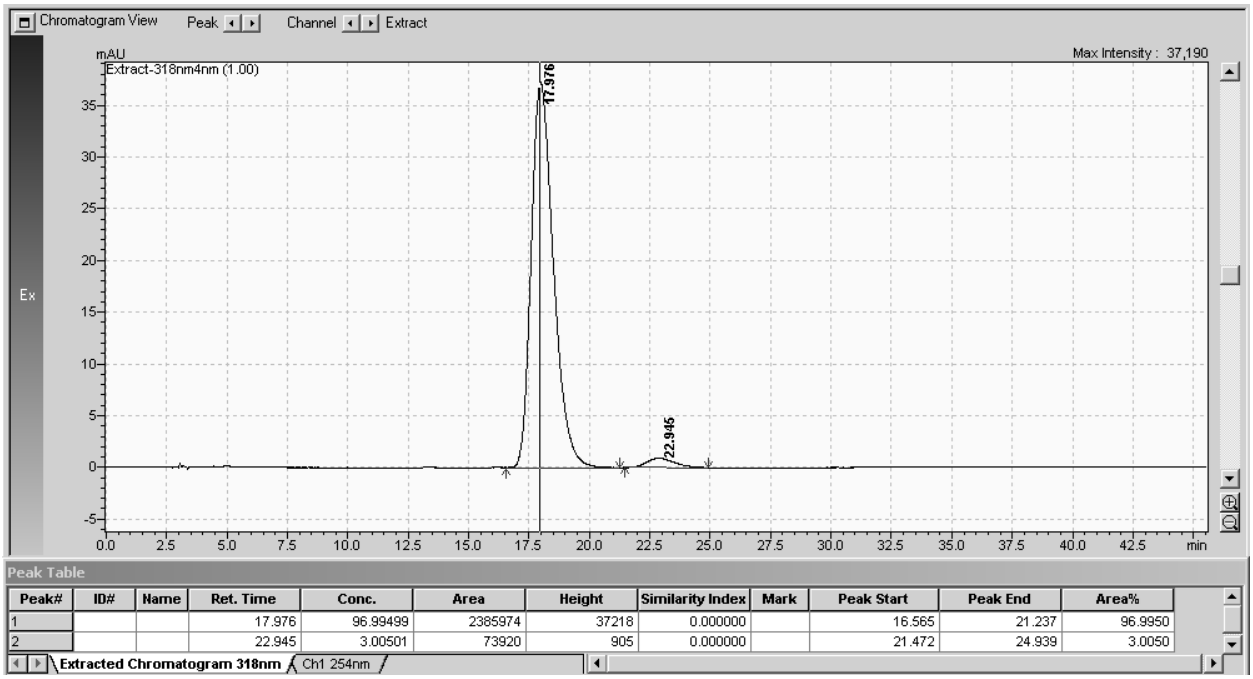


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			17.897	51.37389	1764763	27822	0.000000		16.800	20.267	51.3739
2			22.829	48.62611	1670373	20592	0.000000		21.067	26.059	48.6261

***tert*-Butyl ((*R*)-1-benzyl-5-nitro-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3k') – Chiral minor diastereoisomer**

HPLC MU 754: Chiral column AD, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 318 nm.

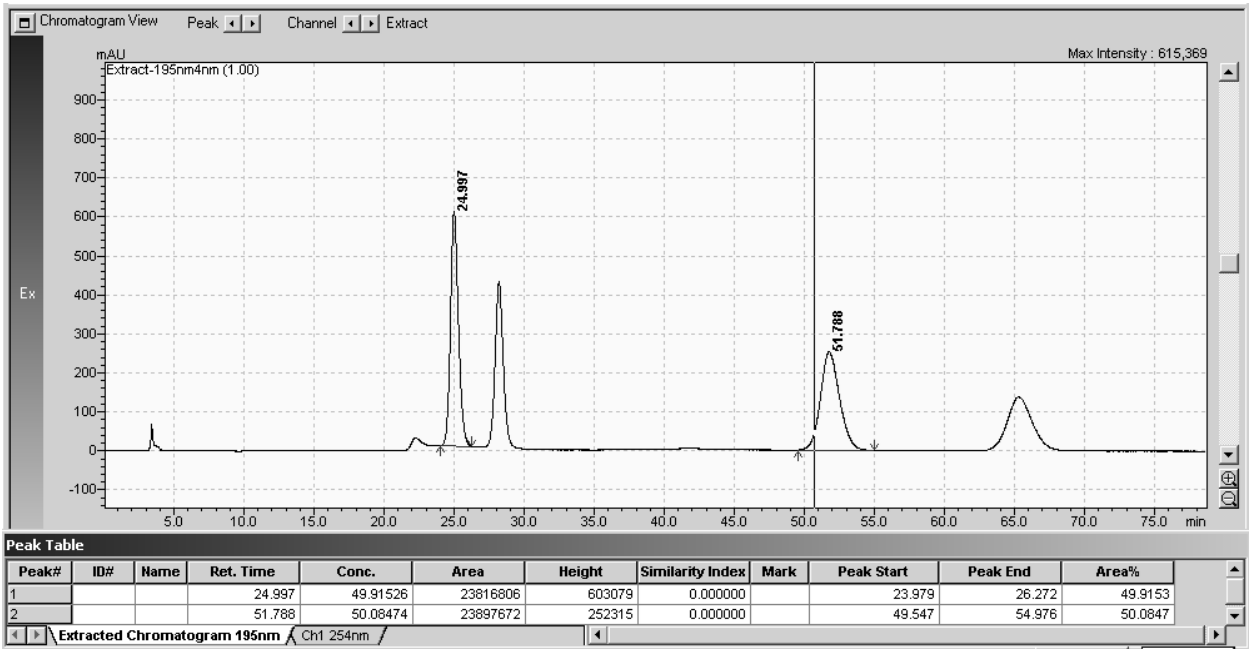
ee = 94 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			17.976	96.99499	2385974	37218	0.000000		16.565	21.237	96.9950
2			22.945	3.00501	73920	905	0.000000		21.472	24.939	3.0050

***tert*-Butyl ((*R*/*S*)-1-benzyl-5-bromo-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l) - Racemic major diastereoisomer**

HPLC MU 718: Chiral column IA, n-heptane/isopropanol (98:2), 1 mL, 25 °C, 205 nm.



Peak Table

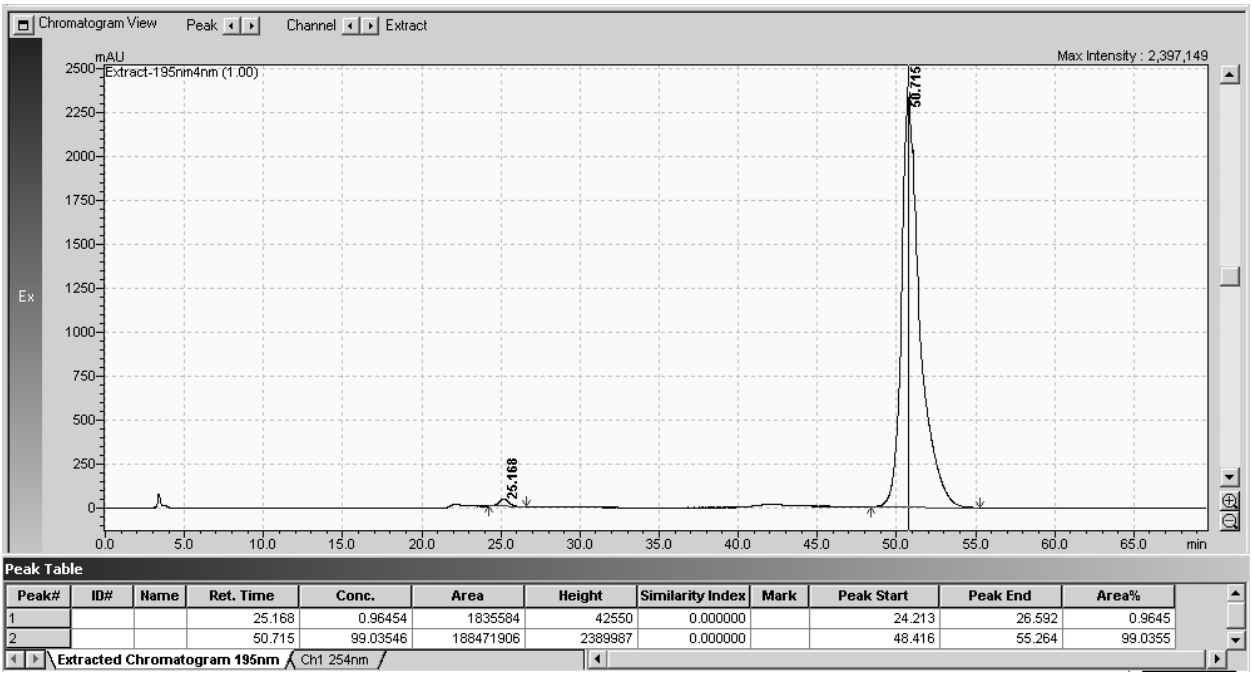
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			24.997	49.91526	23816806	603079	0.000000		23.979	26.272	49.9153
2			51.788	50.08474	23897672	252315	0.000000		49.547	54.976	50.0847

Extracted Chromatogram 195nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l) – Chiral major diastereoisomer**

HPLC MU 724: Chiral column IA, n-heptane/isopropanol (98:2), 1 mL, 25 °C, 195 nm.

ee = 98 %;



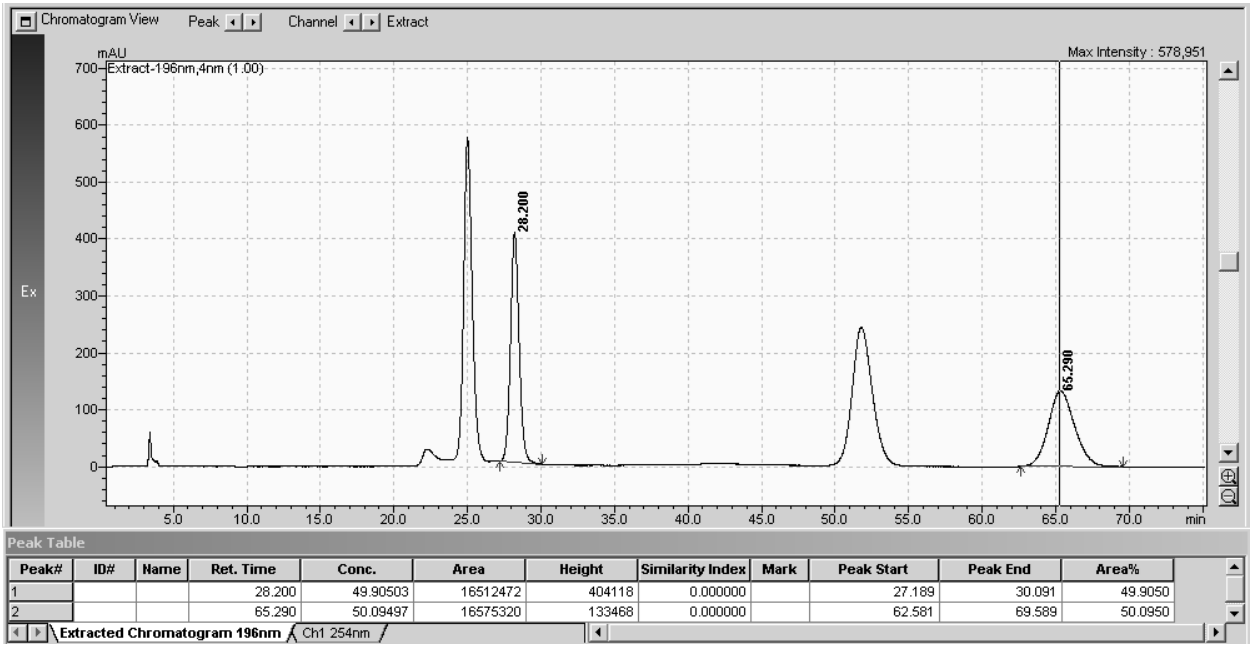
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			25.168	0.96454	1835584	42550	0.000000		24.213	26.592	0.9645
2			50.715	99.03546	188471906	2389987	0.000000		48.416	55.264	99.0355

Extracted Chromatogram 195nm | Ch1 254nm

***tert*-Butyl ((*R/S*)-1-benzyl-5-bromo-3-((*R/S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l') – Racemic minor diastereoisomer**

HPLC MU 718: Chiral column IA, n-heptane/isopropanol (98:2), 1 mL, 25 °C, 196 nm.

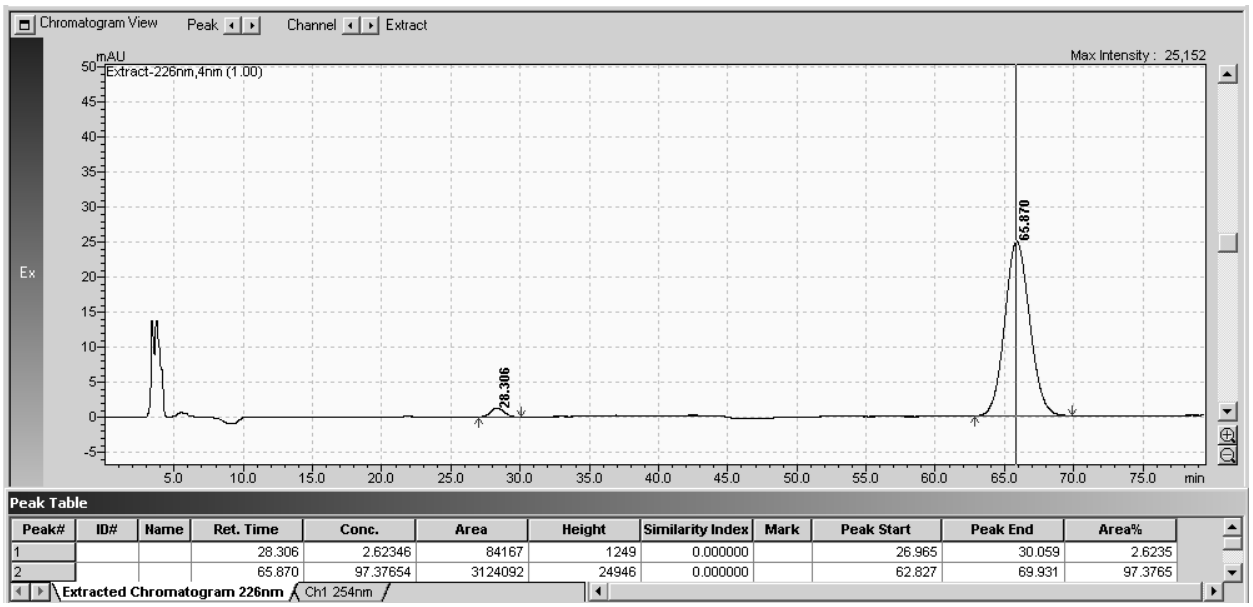


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			28.200	49.90503	16512472	404118	0.000000		27.189	30.091	49.9050
2			65.290	50.09497	16575320	133468	0.000000		62.581	69.589	50.0950

***tert*-Butyl ((*R*)-1-benzyl-5-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3l') – Chiral minor diastereoisomer**

HPLC MU 724: Chiral column IA, n-heptane/isopropanol (98:2), 1 mL, 25 °C, 226 nm.

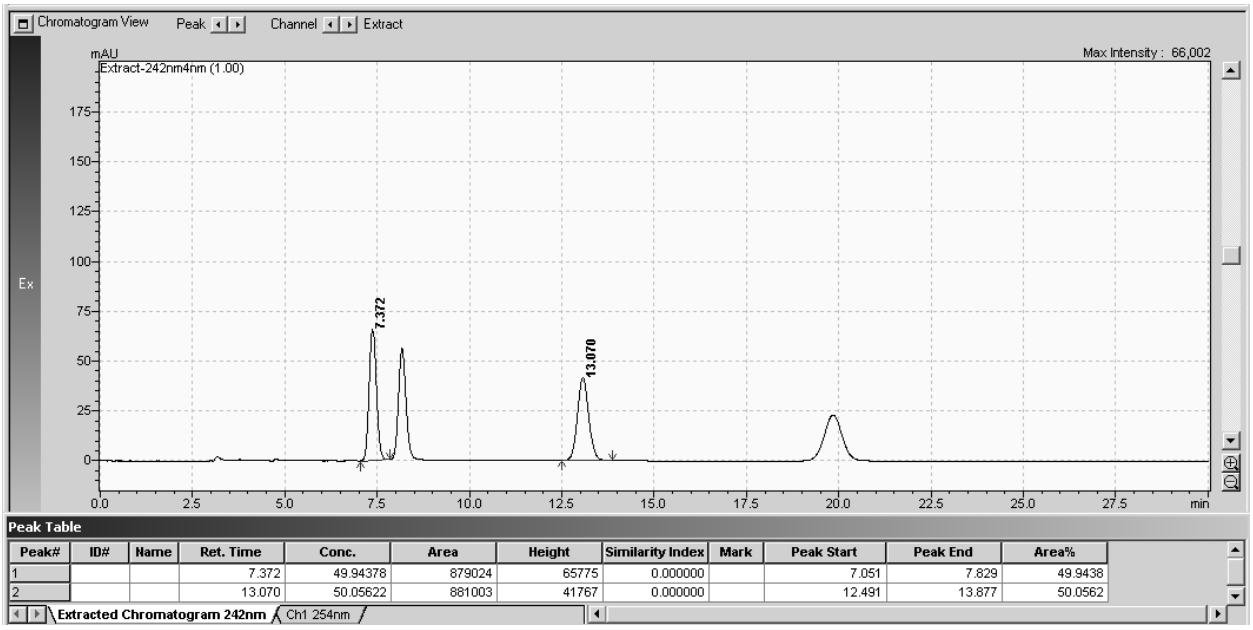
ee = 95 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			28.306	2.62346	84167	1249	0.000000		26.965	30.059	2.6235
2			65.870	97.37654	3124092	24946	0.000000		62.827	69.931	97.3765

***tert*-Butyl ((*R*/*S*)-1-benzyl-6-bromo-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m) - Racemic major diastereoisomer**

HPLC MU 1065: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 242 nm.



Peak Table

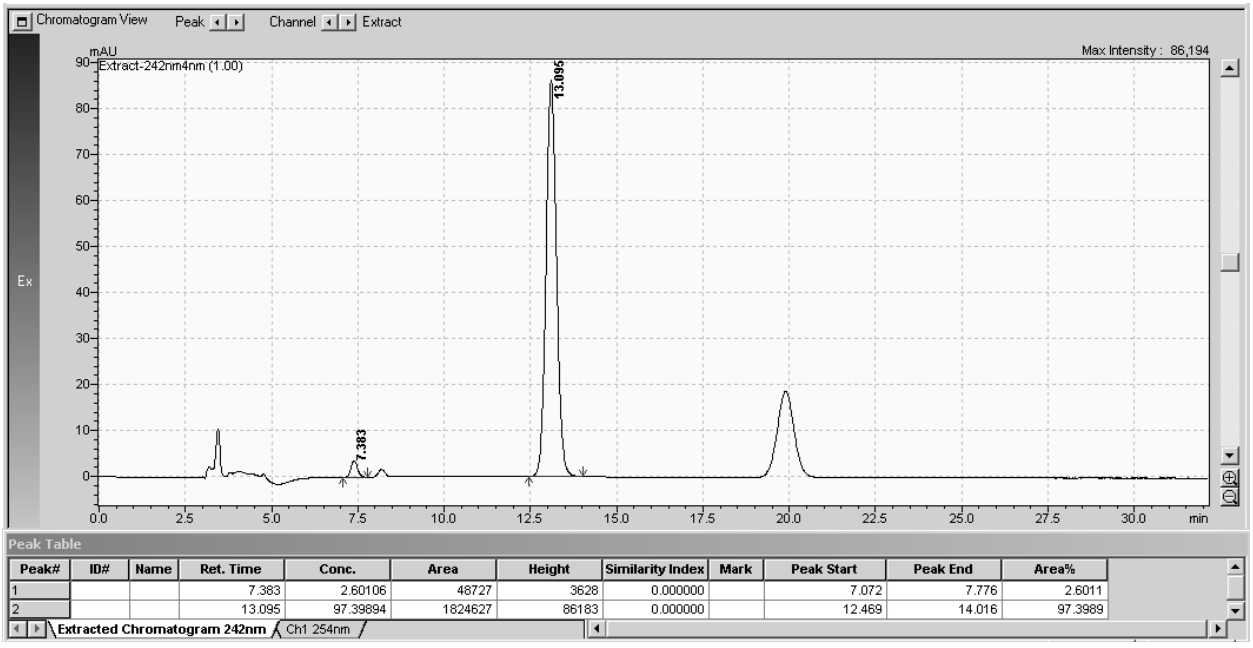
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.372	49.94378	879024	65775	0.000000		7.051	7.829	49.9438
2			13.070	50.05622	881003	41767	0.000000		12.491	13.877	50.0562

Extracted Chromatogram 242nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m) – Chiral major diastereoisomer**

HPLC MU 1064: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 242 nm.

ee = 95 %



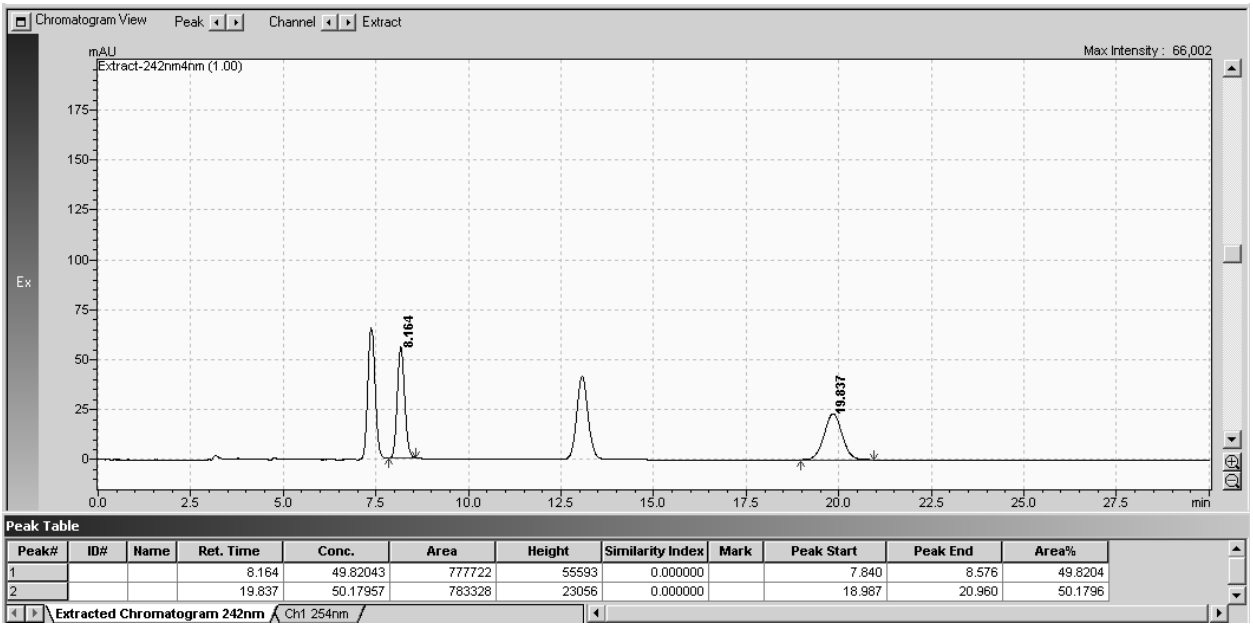
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.383	2.60106	48727	3628	0.000000		7.072	7.776	2.6011
2			13.095	97.39894	1824627	86183	0.000000		12.469	14.016	97.3989

Extracted Chromatogram 242nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-6-bromo-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m') - Racemic minor diastereoisomer**

HPLC MU 1065: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 242 nm.



Peak Table

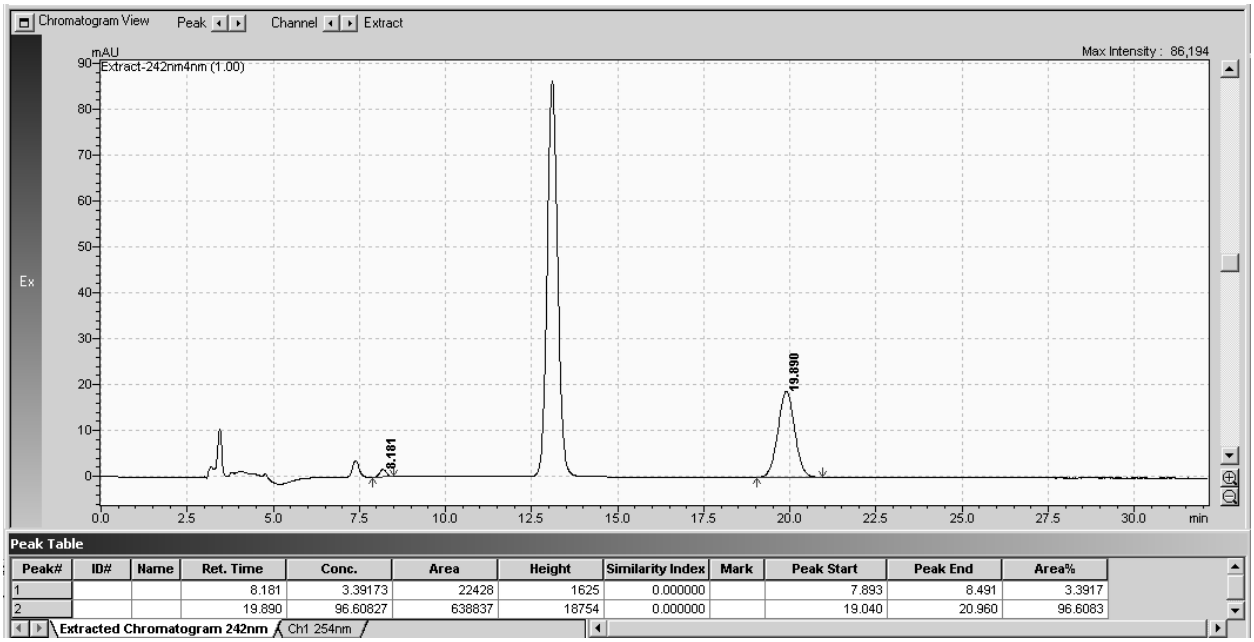
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.164	49.82043	777722	55593	0.000000		7.840	8.576	49.8204
2			19.837	50.17957	783328	23056	0.000000		18.987	20.960	50.1796

Extracted Chromatogram 242nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-benzyl-6-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3m') – Chiral minor diastereoisomer**

HPLC MU 1064: Chiral column IA, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 242 nm.

ee = 93 %



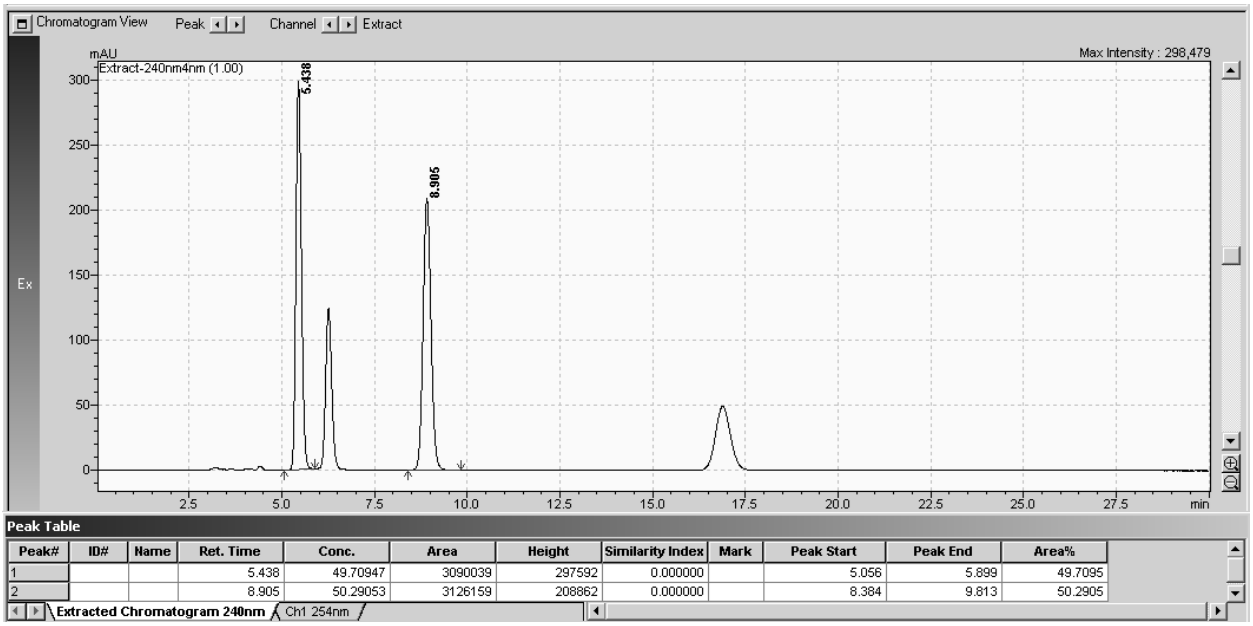
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.181	3.39173	22428	1625	0.000000		7.893	8.491	3.3917
2			19.890	96.60827	638837	18754	0.000000		19.040	20.960	96.6083

Extracted Chromatogram 242nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-7-bromo-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n) - Racemic major diastereoisomer**

HPLC MU 1061: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 240 nm.



Peak Table

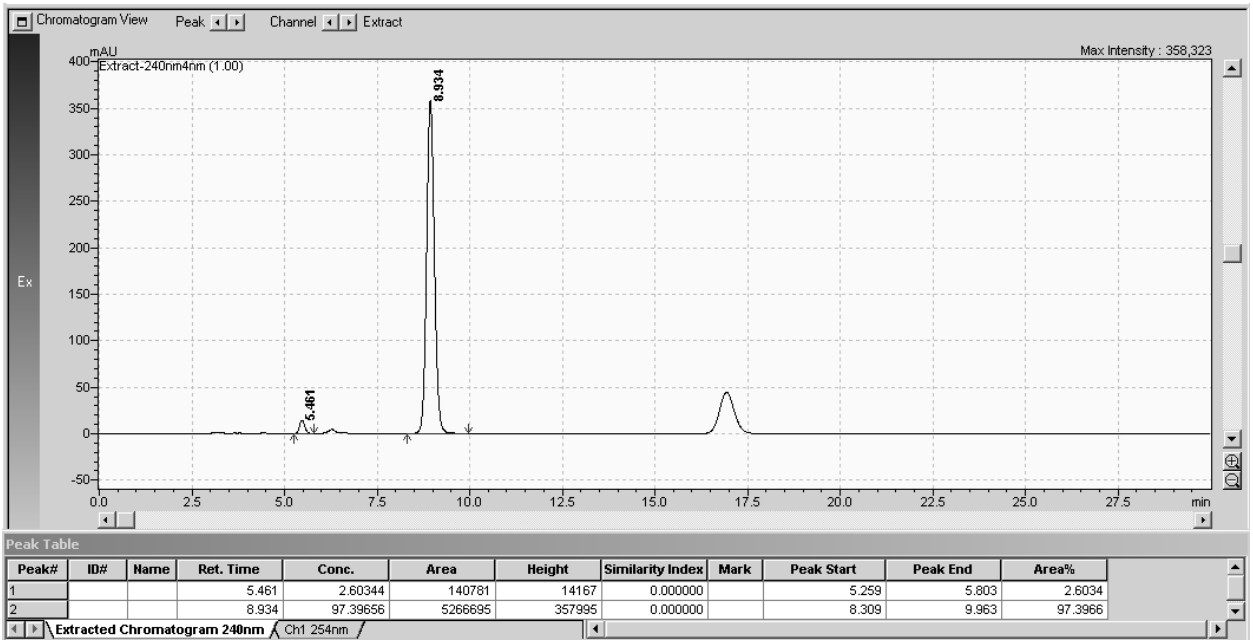
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.438	49.70947	3090039	297592	0.000000		5.056	5.899	49.7095
2			8.905	50.29053	3126159	208862	0.000000		8.384	9.813	50.2905

Extracted Chromatogram 240nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n) – Chiral major diastereoisomer**

HPLC MU 1060: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 240 nm.

ee = 95 %



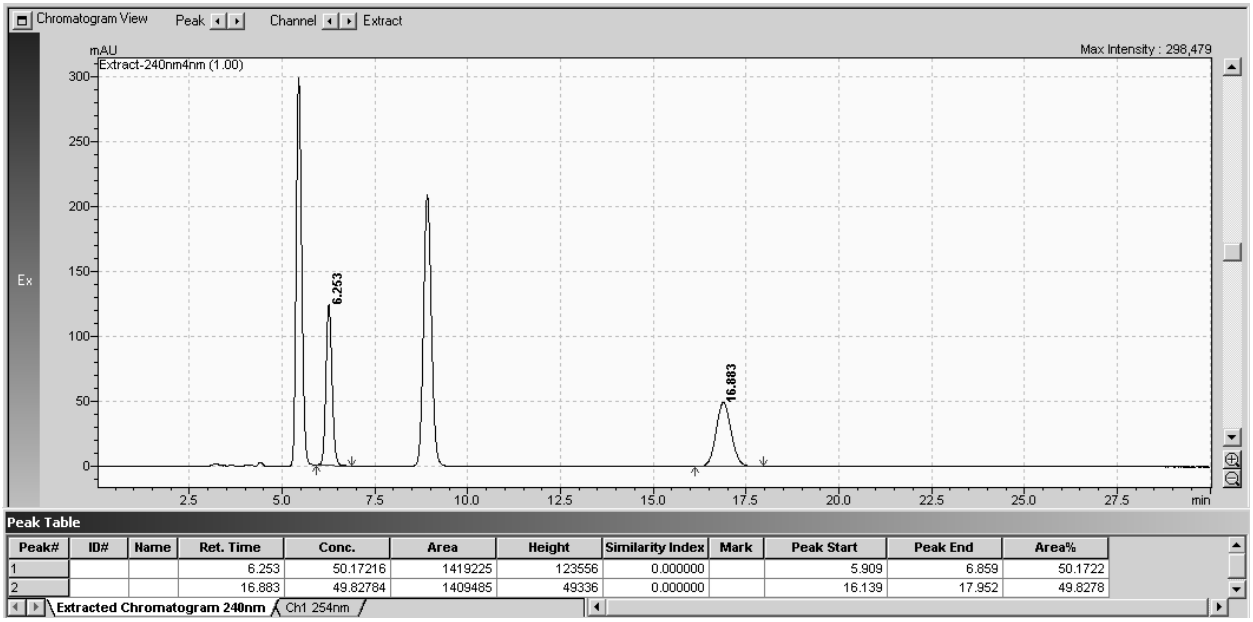
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.461	2.60344	140781	14167	0.000000		5.259	5.803	2.6034
2			8.934	97.39656	5266695	357995	0.000000		8.309	9.963	97.3966

Extracted Chromatogram 240nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-7-bromo-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n') - Racemic minor diastereoisomer**

HPLC MU 1061: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 240 nm.



Peak Table

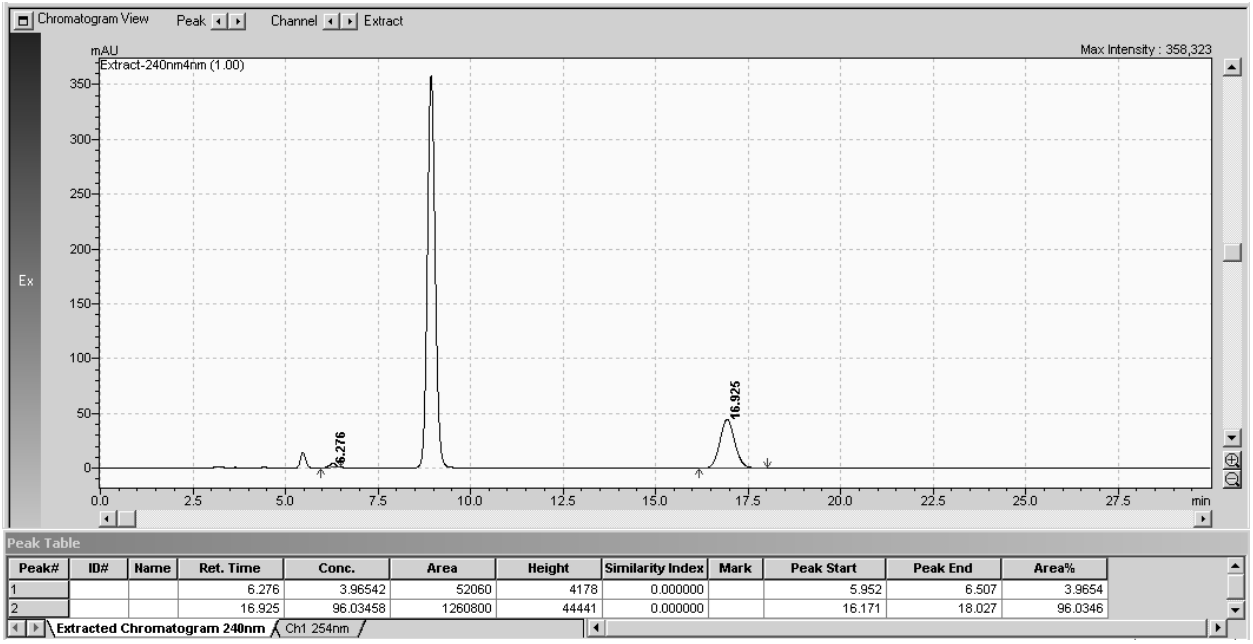
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			6.253	50.17216	1419225	123556	0.000000		5.909	6.859	50.1722
2			16.883	49.82784	1409485	49336	0.000000		16.139	17.952	49.8278

Extracted Chromatogram 240nm | Ch1 254nm

***tert*-Butyl ((*R*)-1-benzyl-7-bromo-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3n') – Chiral minor diastereoisomer**

HPLC MU 1060: Chiral column IA, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 240 nm.

ee = 92 %



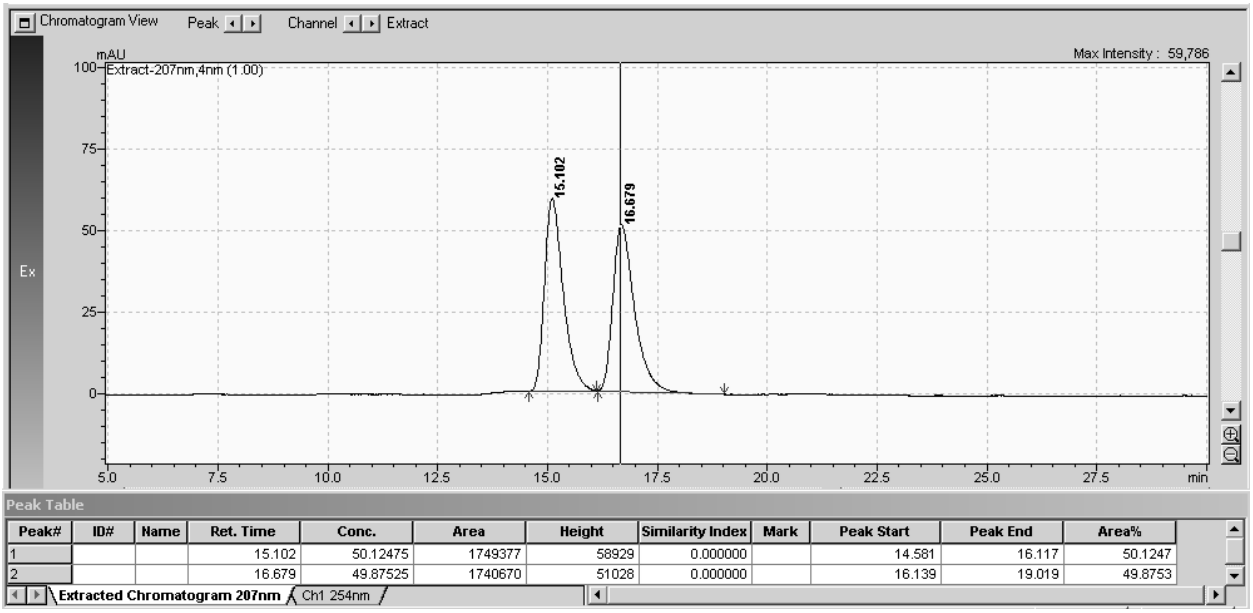
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			6.276	3.96542	52060	4178	0.000000		5.952	6.507	3.9654
2			16.925	96.03458	1260800	44441	0.000000		16.171	18.027	96.0346

Extracted Chromatogram 240nm | Ch1 254nm

Benzyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p) – Racemic major diastereomer

HPLC MU 708: Chiral column IB, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 207 nm.



Peak Table

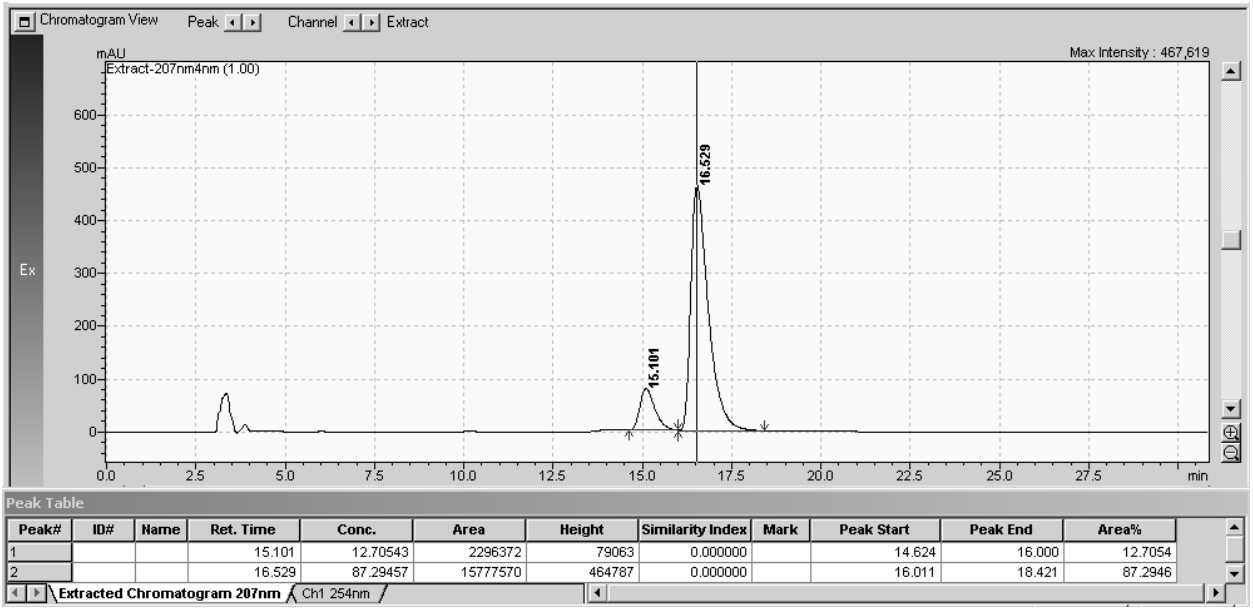
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			15.102	50.12475	1749377	58929	0.000000		14.581	16.117	50.1247
2			16.679	49.87525	1740670	51028	0.000000		16.139	19.019	49.8753

Extracted Chromatogram 207nm | Ch1 254nm

Benzyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p) – Chiral major diastereomer

HPLC MU 709: Chiral column IB, n-heptane/isopropanol (90:10), 1 mL, 25 °C, 207 nm.

ee = 75 %;



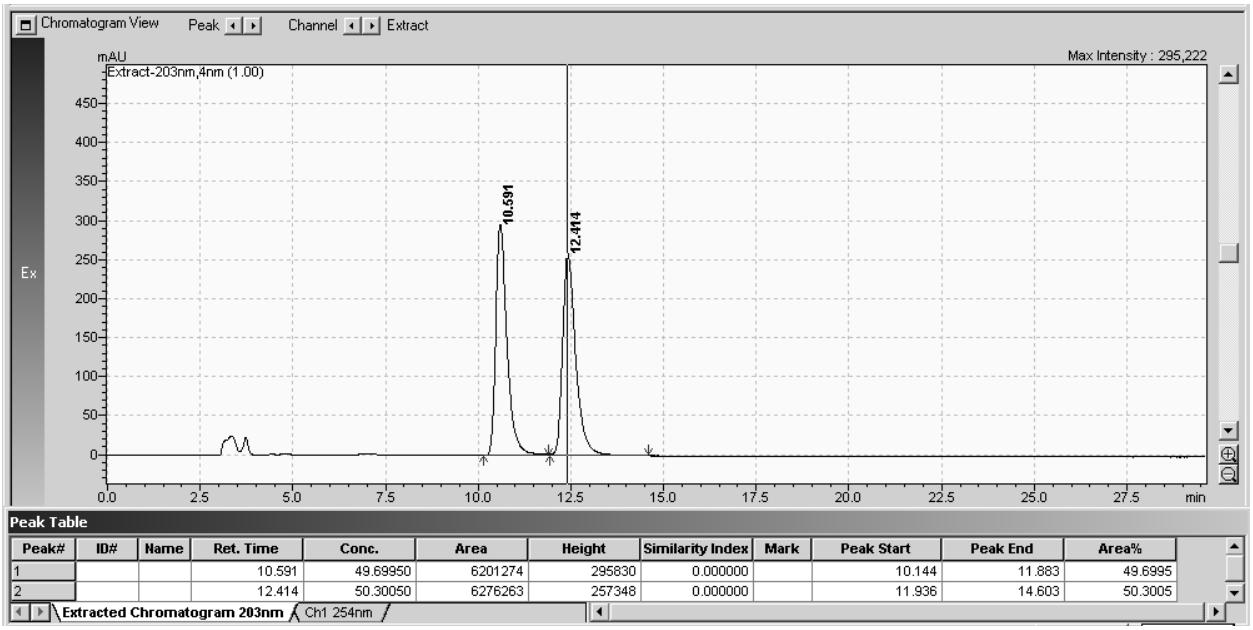
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			15.101	12.70543	2296372	79063	0.000000		14.624	16.000	12.7054
2			16.529	87.29457	15777570	464787	0.000000		16.011	18.421	87.2946

Extracted Chromatogram 207nm | Ch1 254nm

Benzyl ((*R/S*)-1-benzyl-3-((*R/S*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p') - Racemic minor diastereoisomer

HPLC MU 708: Chiral column IB, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 203 nm.



Peak Table

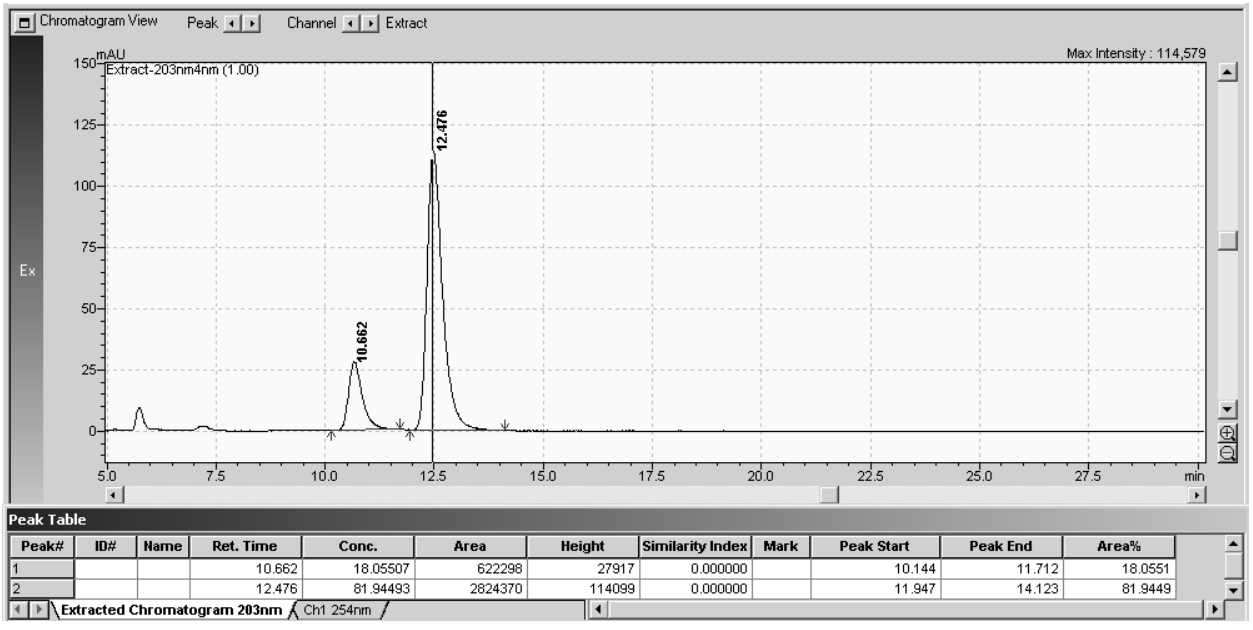
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			10.591	49.69950	6201274	295830	0.000000		10.144	11.883	49.6995
2			12.414	50.30050	6276263	257348	0.000000		11.936	14.603	50.3005

Extracted Chromatogram 203nm | Ch1 254nm

Benzyl ((*R*)-1-benzyl-3-((*R*)-fluoro(nitro)(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3p') - Chiral minor diastereoisomer

HPLC MU 709: Chiral column IB, n-heptane/isopropanol (80:20), 1 mL, 25 °C, 317 nm.

ee = 64 %;



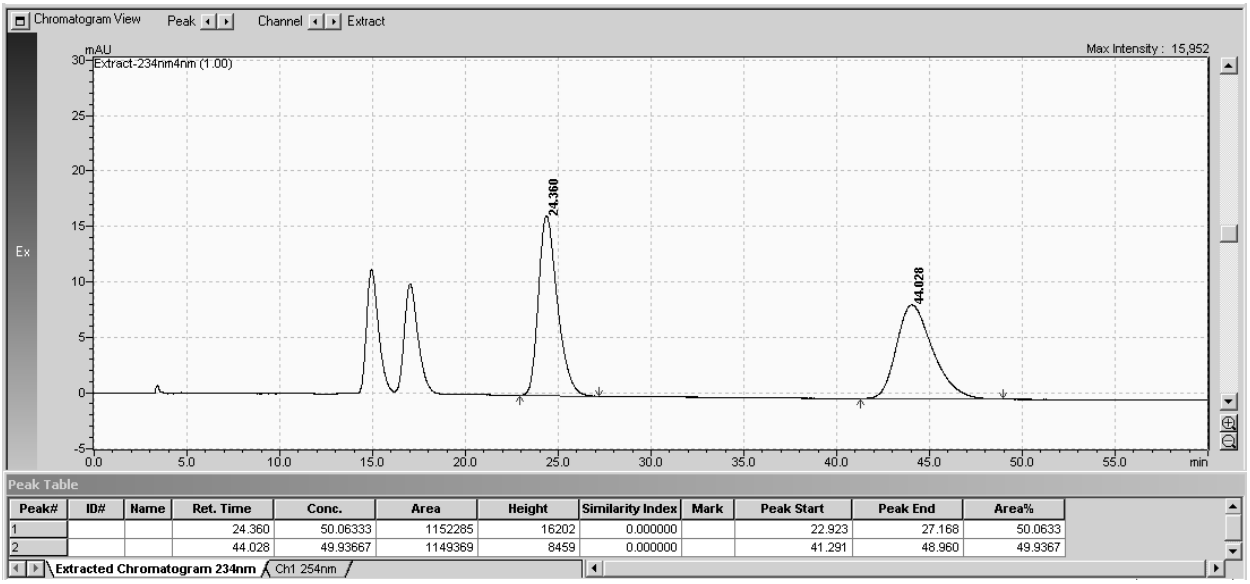
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			10.662	18.05507	622298	27917	0.000000		10.144	11.712	18.0551
2			12.476	81.94493	2824370	114099	0.000000		11.947	14.123	81.9449

Extracted Chromatogram 203nm | Ch1 254nm

tert*-Butyl ((*S*/*R*)-1-benzyl-3-((*S*/*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q) – Racemic *mixture of diastereoisomers

HPLC MU 638: Chiral column IC, n-heptane/isopropanol (85:15), 1 mL, 25 °C, 233 nm.

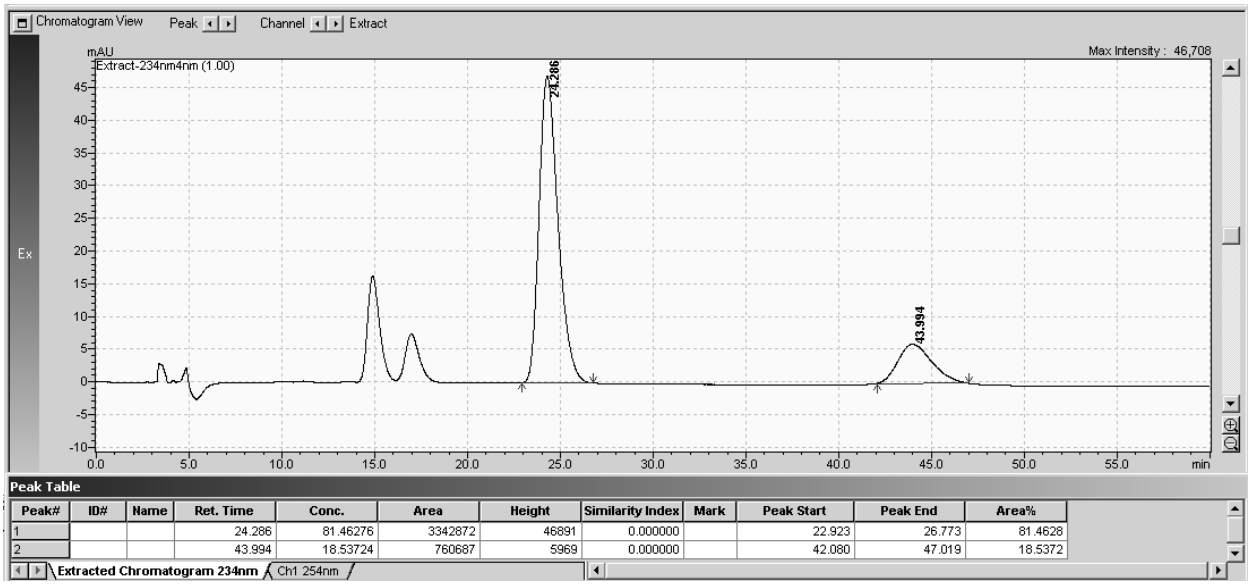


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			24.360	50.06333	1152285	16202	0.000000		22.923	27.168	50.0633
2			44.028	49.93667	1149369	8459	0.000000		41.291	48.960	49.9367

tert*-Butyl ((*S*)-1-benzyl-3-((*R*)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q) – Chiral *mixture of diastereoisomers

HPLC MU 728: Chiral column IC, n-heptane/isopropanol (85:15), 1 mL, 25 °C, 234 nm.

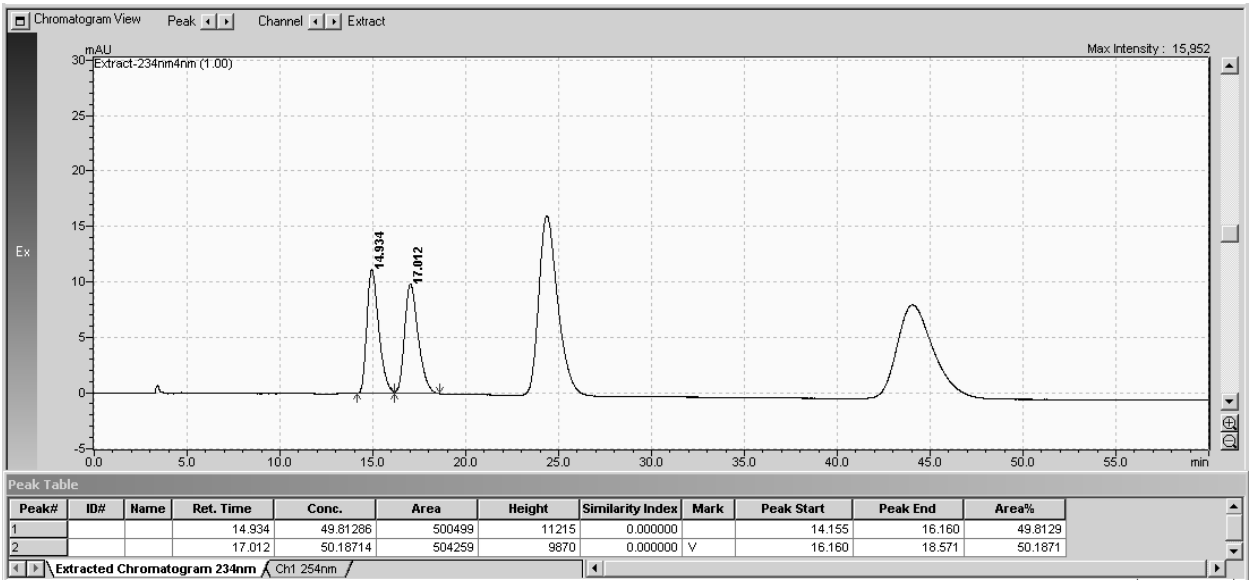
ee = 63 %;



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			24.286	81.46276	3342872	46891	0.000000		22.923	26.773	81.4628
2			43.994	18.53724	760687	5969	0.000000		42.080	47.019	18.5372

tert-Butyl ((_S/R_)-1-benzyl-3-((_S/R_)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q') – Racemic _mixture of diastereoisomers_

HPLC MU 638: Chiral column IC, n-heptane/isopropanol (85:15), 1 mL, 25 °C, 234 nm.



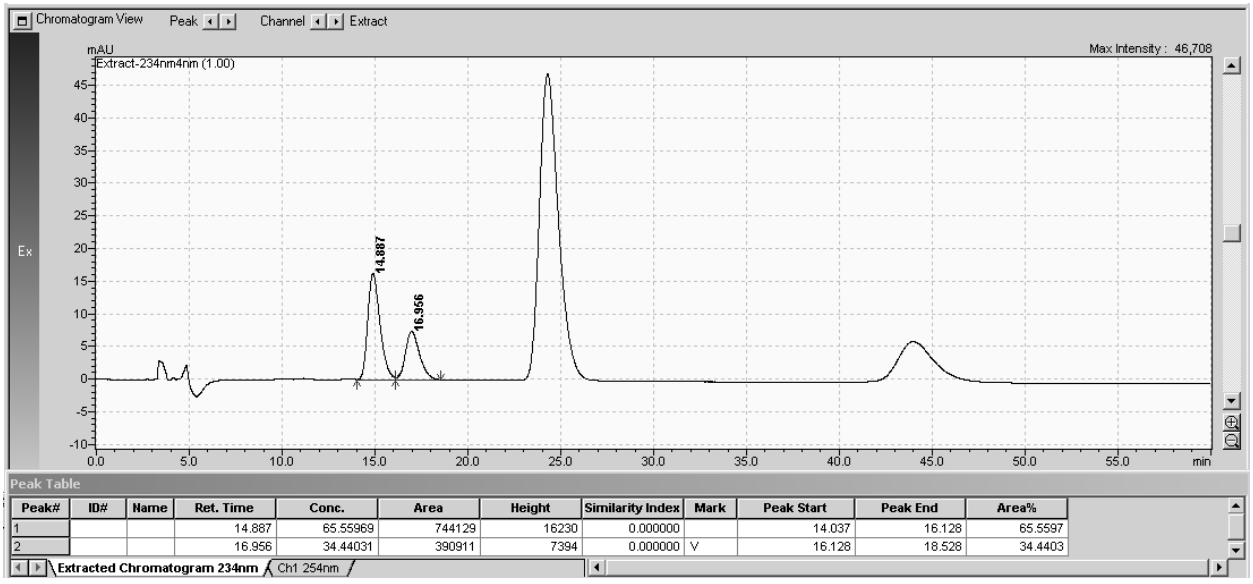
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.934	49.81286	500499	11215	0.000000		14.155	16.160	49.8129
2			17.012	50.18714	504259	9870	0.000000	V	16.160	18.571	50.1871

Extracted Chromatogram 234nm | Ch1 254nm

tert-Butyl ((_R_)-1-benzyl-3-((_R_)-cyanofluoro(phenylsulfonyl)methyl)-2-oxoindolin-3-yl)carbamate (3q') – Chiral _mixture of diastereoisomers_

HPLC MU 728: Chiral column IC, n-heptane/isopropanol (85:15), 1 mL, 25 °C, 234 nm.

_ee_ = 31 %;

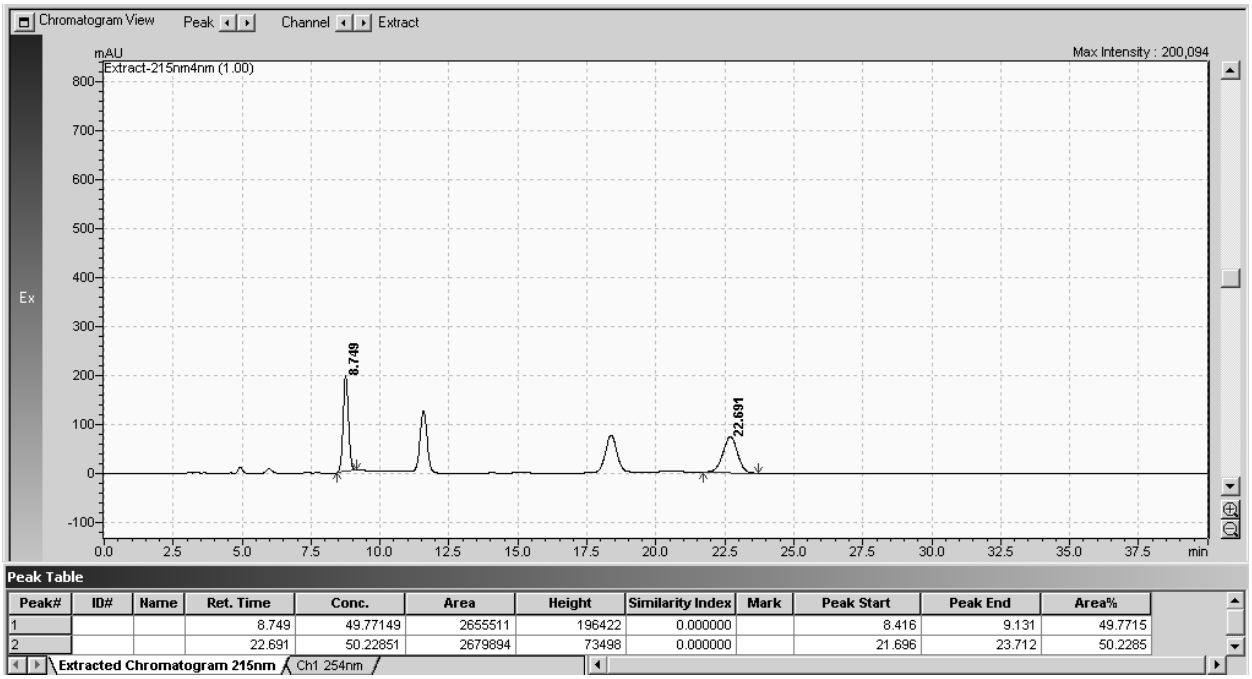


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			14.887	65.55969	744129	16230	0.000000		14.037	16.128	65.5597
2			16.956	34.44031	390911	7394	0.000000	V	16.128	18.528	34.4403

Extracted Chromatogram 234nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)**

HPLC MU 858: Chiral column IA, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 215 nm.



Peak Table

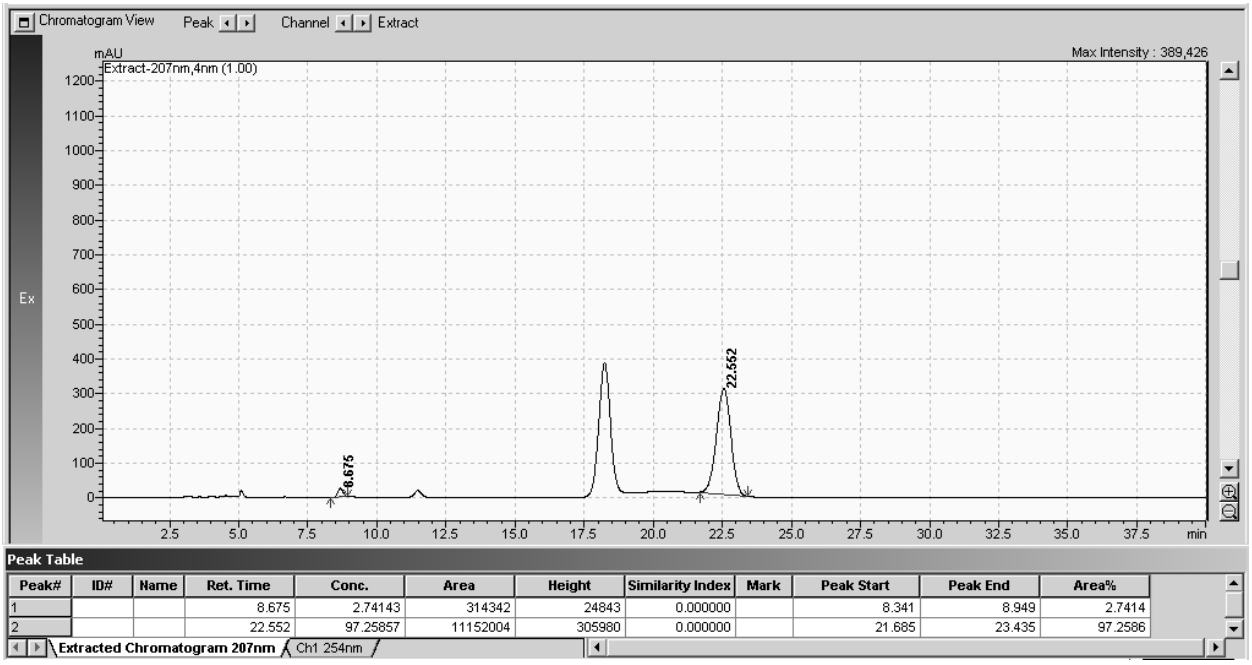
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.749	49.77149	2655511	196422	0.000000		8.416	9.131	49.7715
2			22.691	50.22851	2679894	73498	0.000000		21.696	23.712	50.2285

Extracted Chromatogram 215nm | Ch1 254nm

***tert*-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4a)**

HPLC MU 838: Chiral column IA, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 207 nm.

ee = 95 %



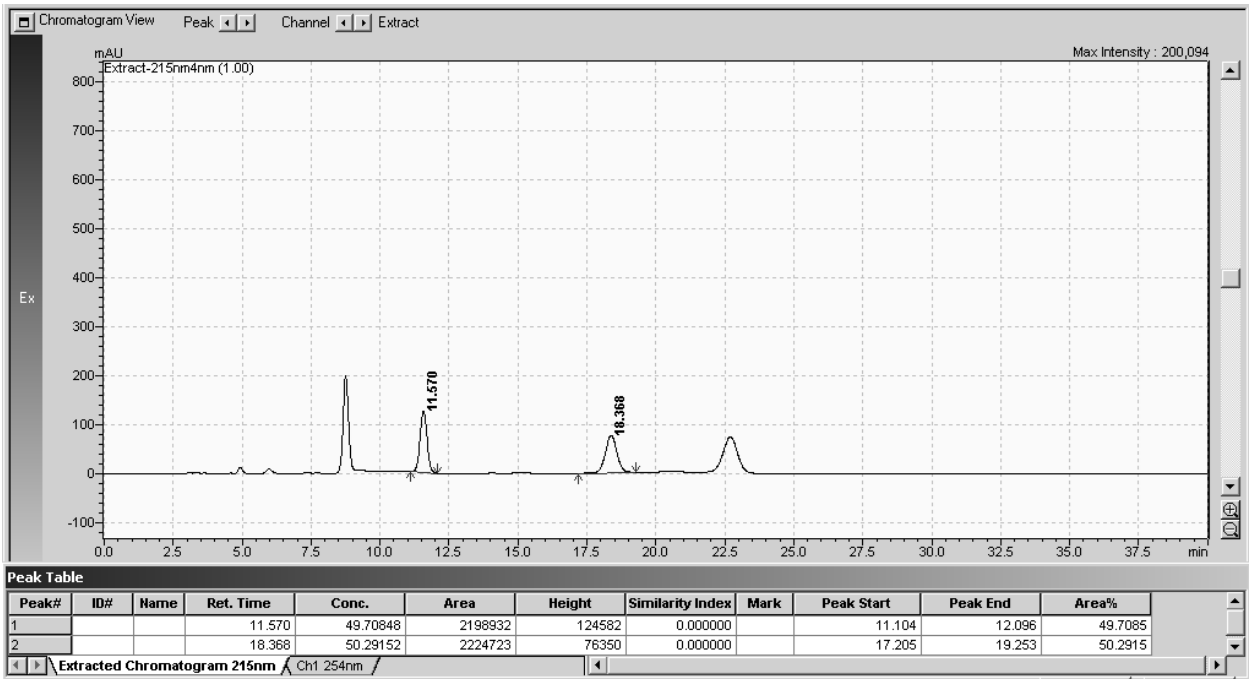
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.675	2.74143	314342	24843	0.000000		8.341	8.949	2.7414
2			22.552	97.25857	11152004	305980	0.000000		21.685	23.435	97.2586

Extracted Chromatogram 207nm | Ch1 254nm

***tert*-Butyl ((*R*/*S*)-1-benzyl-3-((*R*/*S*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)**

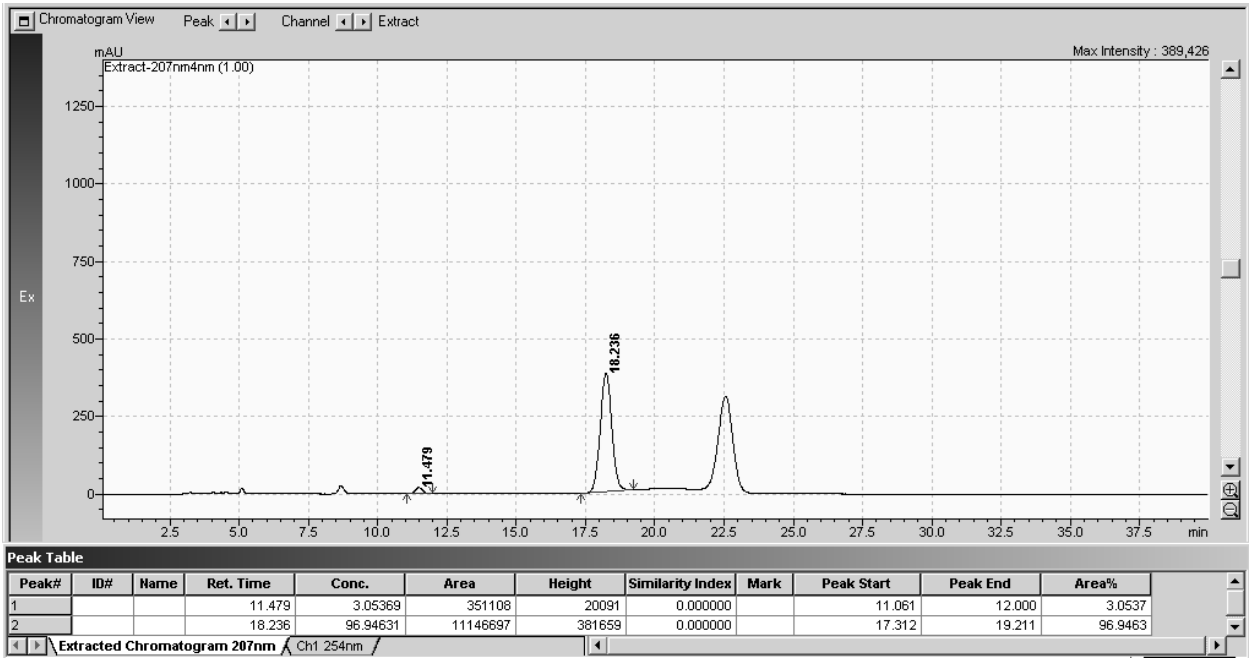
HPLC MU 858: Chiral column IA, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 215 nm.



***tert*-Butyl ((*S*)-1-benzyl-3-((*R*)-fluoro(nitro)methyl)-2-oxoindolin-3-yl)carbamate (4b)**

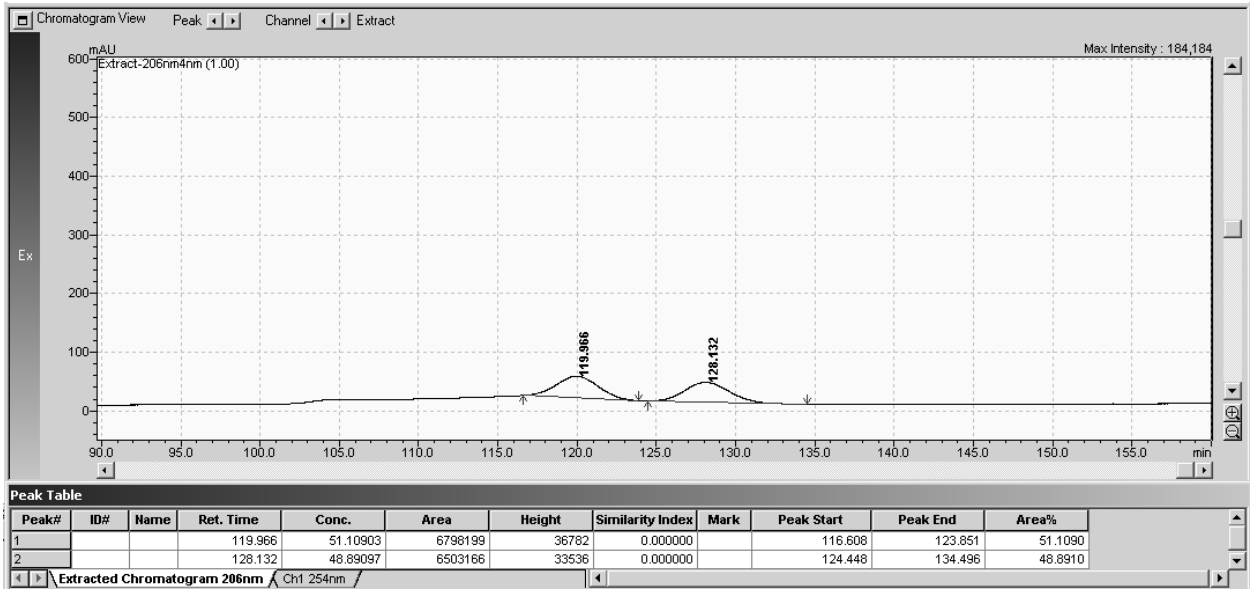
HPLC MU 838: Chiral column IA, *n*-heptane/isopropanol (80:20), 1 mL, 25 °C, 207 nm.

ee = 94 %



(*S*/*R*)-3-Amino-1-benzyl-3-((*S*/*R*)-fluoro(nitro)methyl)indolin-2-one (5a) – Racemic major diastereomer

HPLC MU 1036: Chiral column IA, *n*-heptane/isopropanol (98:2), 1 mL, 20°C, 206 nm.



Peak Table

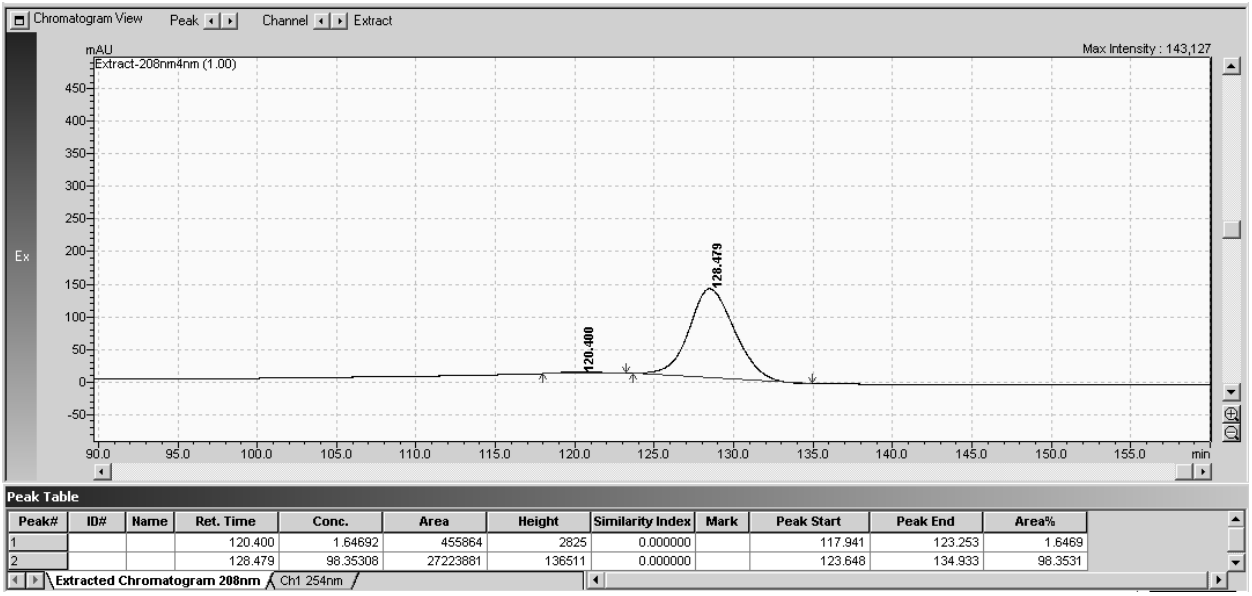
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			119.966	51.10903	6798199	36782	0.000000		116.608	123.851	51.1090
2			128.132	48.89097	6503166	33536	0.000000		124.448	134.496	48.8910

Extracted Chromatogram 206nm | Ch1 254nm

(*S*)-3-Amino-1-benzyl-3-((*S*)-fluoro(nitro)methyl)indolin-2-one (5a) – Chiral major diastereoisomer

HPLC MU 1031: Chiral column IA, *n*-heptane/isopropanol (98:2), 1 mL, 20°C, 206 nm.

ee = 97 %



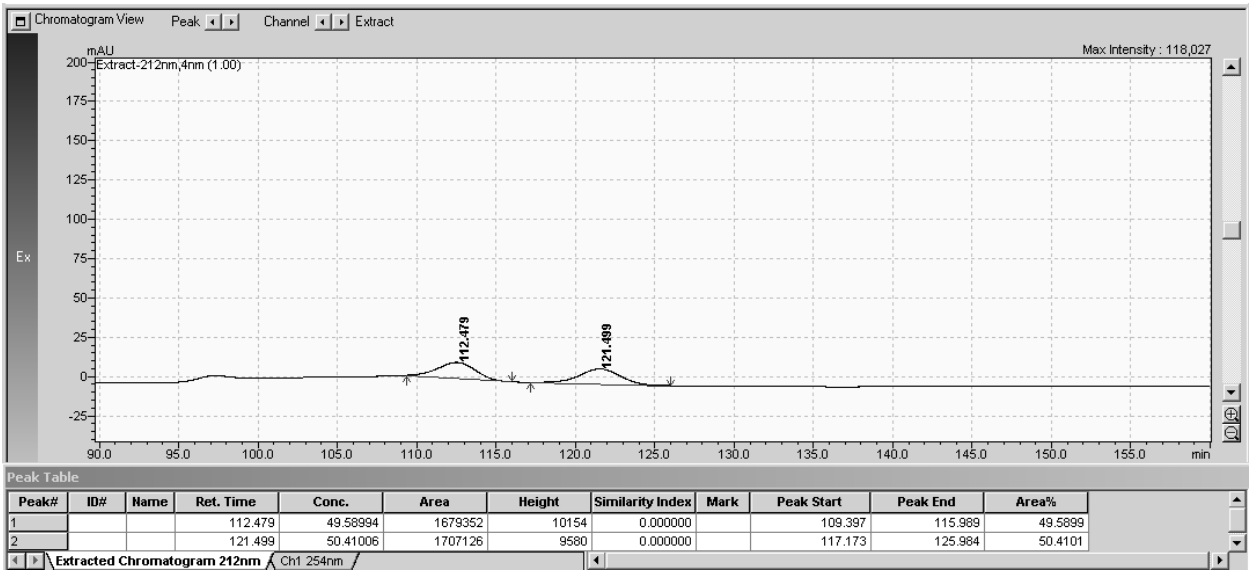
Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			120.400	1.64692	455864	2825	0.000000		117.941	123.253	1.6469
2			128.479	98.35308	27223881	136511	0.000000		123.648	134.933	98.3531

Extracted Chromatogram 208nm | Ch1 254nm

(*S*/*R*)-3-Amino-1-benzyl-3-((*S*/*R*)-fluoro(nitro)methyl)indolin-2-one (5b) - Racemic minor diastereoisomer

HPLC MU 1036: Chiral column IA, *n*-heptane/isopropanol (98:2), 1 mL, 20°C, 212 nm.



Peak Table

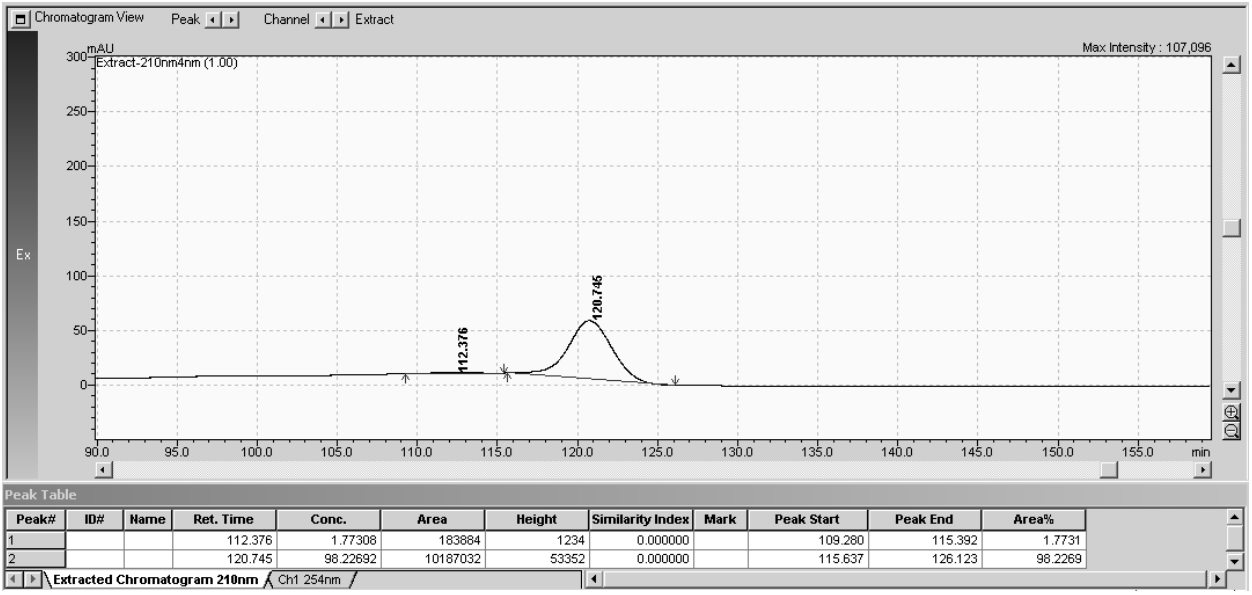
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			112.479	49.58994	1679352	10154	0.000000		109.397	115.989	49.5899
2			121.499	50.41006	1707126	9580	0.000000		117.173	125.984	50.4101

Extracted Chromatogram 212nm | Ch1 254nm

(*S*)-3-Amino-1-benzyl-3-((*R*)-fluoro(nitro)methyl)indolin-2-one (5b) – Chiral minor diastereoisomer

HPLC MU 1031: Chiral column IA, *n*-heptane/isopropanol (98:2), 1 mL, 20°C, 210 nm.

ee = 96 %



Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			112.376	1.77308	183884	1234	0.000000		109.280	115.392	1.7731
2			120.745	98.22692	10187032	53352	0.000000		115.637	126.123	98.2269

Extracted Chromatogram 210nm | Ch1 254nm

[i] SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8
[ii] SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.
[iii] Parsons,S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst*. **B69**, 249-259.