Highly Efficient Asymmetric *Trans*-Selective Aziridination of Diazoacetamides and N-Boc Imines Catalyzed by Chiral Brønsted Acids

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General Information. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

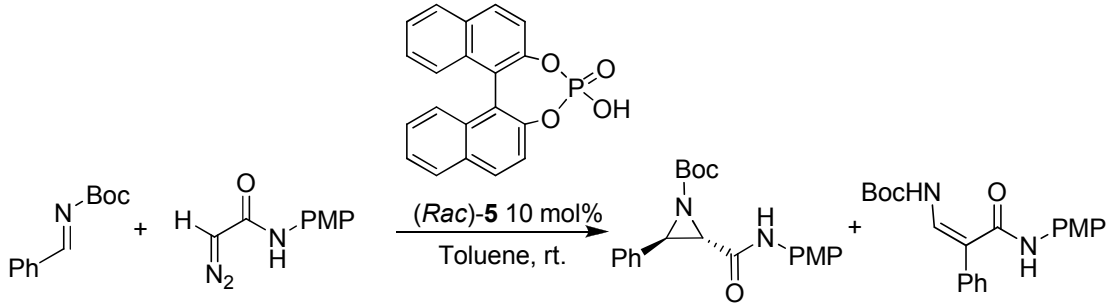
Flash chromatography (FC) was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX 400 and 500 spectrophotometers at ambient temperature as noted. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Data for ^{13}C NMR are reported as δ in ppm downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet).

Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis employing a Daicel Chiracel OD-H column. Optical rotations were measured in $CHCl_3$ on a *Schmidt + Haensdch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in S-2 g/100 mL). Absolute configuration of the products was determined by comparison with compounds previously published. The absolute configuration of the aziridination products was confirmed by comparison with the literature reported by Prof. Keiji Maruoka.[1]

High resolution mass spectrometry (HRMS) was recorded on QTOF perimer for ESI^+. Racemic phosphoric acid (*Rac*)-**5** were purchased from Sigma-Aldrich of highest purity and used without further purification. N-Boc[2], N-Cbz[3] protected imines, the diazoacetamide derivatives[4] and the chiral phosphoric acids (*R*)-**5a-g**[5] were prepared according to literature procedures.[2] The racemic products used to determine the e.e. values were synthesized using racemic phosphoric acid (*Rac*)-**5** as catalyst.

Synthesis of 1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-phenylaziridine-2-carbox amide



To an oven dried flask was added benzaldehyde benzaldehyde *N*-(*tert*-butoxycarbonyl)imine, (0.25 mmol) *N*-(4-methoxyphenyl)diazoacetamide (0.01 mmol) and 0.5 mL toluene, then catalyst (*rac*)-**5** (0.01 mmol, 3.4 mg) was added successively, the mixture was stirred at room temperature. After the completion of the reaction, (monitored by TLC, about 10 min) the solution was poured into saturated $NaHCO_3$ aq and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography (EtOAc/Hexane) on silica gel carefully.

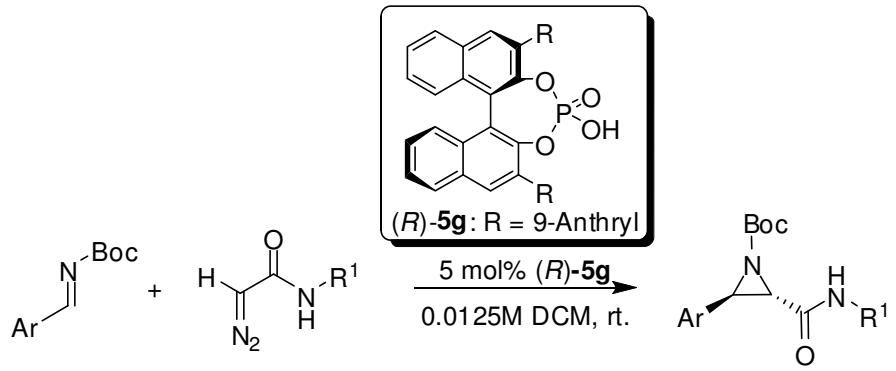
1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-phenylaziridine-2-carboxamide

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (1H, brs, N**H**), 7.44 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.39-7.28 (5H, m, PhCH**H**), 6.81 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.88 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.79 (3H, s, OC**H3**) 3.48 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.36 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 156.5, 134.1, 130.6, 129.0, 128.6, 127.2, 125.5, 121.5, 114.1, 82.6, 55.4, 46.1, 44.8, 27.8;

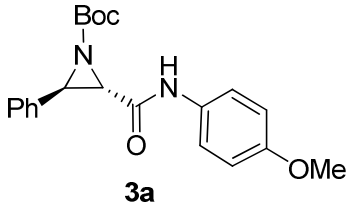
HRMS (ESI^+) calcd for $C_{21}H_{25}N_2O_4$, m/z 369.1736, found 369.1731.

General Procedure for the Asymmetric Aziridination Catalyzed by Chiral phosphoric acids



To an oven dried flask was added benzaldehyde benzaldehyde *N*-(*tert*-butoxycarbonyl)imine, (0.12 mmol) *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol) and 0.5 mL toluene, then catalyst (*R*)-**5g** (0.01 mmol, 1.8 mg) was added successively, the mixture was stirred at room temperature. After the completion of the reaction, (monitored by TLC, about 10 min) the solution was poured into saturated $NaHCO_3$ aq and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography (EtOAc/Hexane) on silica gel carefully.

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-phenylaziridine-2-carboxamide (3a)(Table 3, entry 1):



3a

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [97% (17.8 mg), 93% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 13.1 min (minor) and 26.3 min (major)).

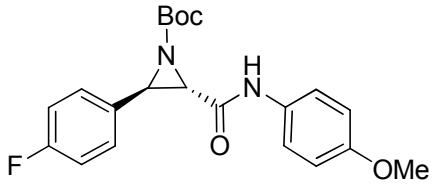
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (1H, brs, N**H**), 7.44 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.39-7.28 (5H, m, PhCH**H**), 6.81 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.88 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.79 (3H, s, OC**H3**) 3.48 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.36 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 156.5, 134.1, 130.6, 129.0, 128.6, 127.2, 125.5, 121.5, 114.1, 82.6, 55.4, 46.1, 44.8, 27.8;

HRMS (ESI^+) calcd for $C_{21}H_{25}N_2O_4$, m/z 369.1736, found 369.1733.

$[\alpha]_{26}^{D}$ = 68.3 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(4-fluorophenyl)aziridine-2-carboxamide (3b)(Table 3, entry 2):



3b

Prepared according to the general procedure with 4-fluorobenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 28.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [91% (17.6 mg), 94% ee].

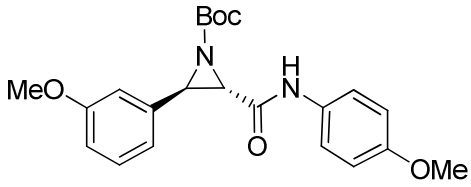
Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 10.4 min (minor) and 25.3 min (major)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (1H, brs, N**H**), 7.43 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.31-7.27 (2H, m, PhCH**H**), 7.07-7.05 (2H, m, PhCH**H**), 6.82 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.83 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.78 (3H, s, OC**H3**) 3.37 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.35 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.2, 154.8, 134.2, 129.1, 127.6, 124.7, 119.8, 115.5,

115.3, 82.7, 61.2, 45.5, 44.8, 27.8;
HRMS (ESI^+) exact mass calcd. For $C_{21}H_{24}FN_2O_4$: *m/z* 387.1642, found: *m/z* 387.1650.
$[\alpha]_{26}^{D}$ = 86.1 (*c* = 1.0, $CHCl_3$).

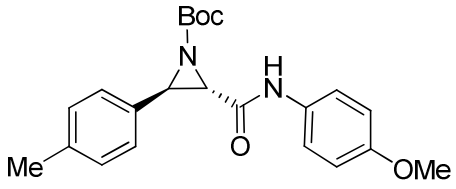
(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(3-methoxyphenyl)aziridine-2-carboxamide (3c)(Table 3, entry 4):



3c

Prepared according to the general procedure with 3-methoxybenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 29.2 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [96% (19.2 mg), 96% ee].
Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 14.2 min (minor) and 35.7 min (major)).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (1H, brs, N**H**), 7.44 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.30-7.26 (1H, m, PhCH**H**), 6.94-6.87 (3H, m, PhCH**H**), 6.81 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.86 (1H, d, *J* = 2.4 Hz, BocNC**H**), 3.82 (3H, s, OC**H3**) 3.79 (3H, s, OC**H3**) 3.44 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.39 (9H, s, *t*Bu);
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 159.9, 135.8, 130.5, 129.7, 121.5, 119.5, 114.4, 114.1, 112.3, 82.6, 55.4, 55.3, 46.0, 45.0, 27.8;
HRMS (ESI^+) exact mass calcd. For $C_{22}H_{27}FN_2O_5$: *m/z* 399.1842, found: *m/z* 399.1843.
$[\alpha]_{26}^{D}$ = 65.5 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(4-methylphenyl)aziridine-2-carboxamide (3d)(Table 3, entry 5):



3d

Prepared according to the general procedure with 4-methylbenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 27.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [90% (17.2 mg), 88% ee].
Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 14.2 min (minor) and 25.6

min (major)).

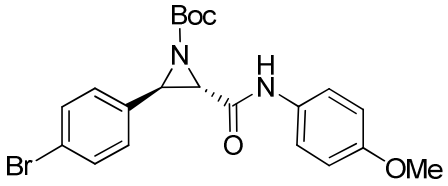
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, brs, N**H**), 7.42 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.25-7.11 (4H, m, PhCH**H**), 6.80 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.81 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.77 (3H, s, OC**H3**) 3.48 (1H, d, *J* = 2.8 Hz, BocNC**H**), 2.35 (1H, s, C**H**3), 1.33 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 158.9, 156.4, 138.5, 131.0, 130.6, 129.3, 127.1, 121.5, 114.0, 82.5, 55.4, 46.2, 454.7, 28.2, 21.2;

HRMS (ESI^+) exact mass calcd. For $C_{22}H_{27}N_2O_4$: *m/z* 383.1893, found: *m/z* 383.1891.

$[\alpha]_{26}^{D}$ = 61.8 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(4-bromophenyl)aziridine-2-carboxamide (3e)(Table 3, entry 6):



3e

Prepared according to the general procedure with 4-bromobenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 34.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a solid [95% (21.2 mg), 90% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 11.5 min (minor) and 18.4 min (major)).

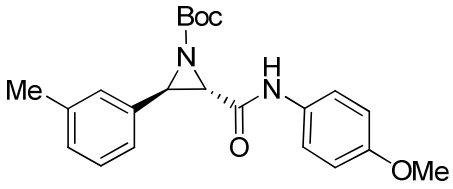
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, brs, N**H**), 7.42 (2H, d, *J* = 8.8 Hz, PhC**H**H), 7.31-7.03 (4H, m, PhCH**H**), 6.81 (2H, d, *J* = 8.8 Hz, PhC**H**H), 3.84 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.78 (3H, s, OC**H3**) 3.39 (1H, d, *J* = 2.8 Hz, BocNC**H**), 2.35 (1H, s, C**H**3), 1.35 (9H, s, *t*Bu);

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 161.9, 130.4, 129.9, 129.0, 128.9, 121.5, 115.7, 115.6, 114.1, 82.7, 55.4, 45.4, 44.9, 27.8;

HRMS (ESI^+) exact mass calcd. For $C_{21}H_{24}BrN_2O_4$: *m/z* 447.0841, found: *m/z* 447.0843.

$[\alpha]_{26}^{D}$ = 71.9 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(3-methylphenyl)aziridine-2-carboxamide (3f)(Table 3, entry 7):



3f

Prepared according to the general procedure with 3-methylbenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 27.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column

chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [96% (18.3 mg), 90% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 11.8 min (minor) and 17.5 min (major)).

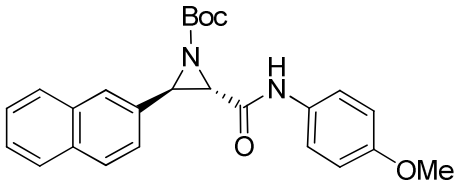
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, brs, N**H**), 7.42 (2H, d, *J* = 9.2 Hz, PhC**H**H), 7.25 (1H, s, PhCH**H**), 7.16-7.11 (3H, m, PhCH**H**), 6.80 (2H, d, *J* = 9.2 Hz, PhC**H**H), 3.80 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.77 (3H, s, OC**H3**) 3.48 (1H, d, *J* = 2.8 Hz, BocNC**H**), 2.35 (1H, s, C**H**3), 1.33 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 158.6, 156.5, 138.3, 133.8, 130.5, 129.4, 128.5, 127.7, 124.5, 121.5, 114.2, 82.5, 55.4, 46.4, 44.6, 27.8, 21.4;

HRMS (ESI^+) exact mass calcd. For $C_{22}H_{27}N_2O_4$: *m/z* 383.1893, found: *m/z* 383.1888.

$[\alpha]_{26}^{D}$ = 64.7 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-methoxyphenyl)-3-(2-naphthyl)aziridine-2-carboxamide (3g)(Table 3, entry 8):



3g

Prepared according to the general procedure with 2-naphthaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 31.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [91% (19.1 mg), 88% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 16.8 min (minor) and 30.4 min (major)).

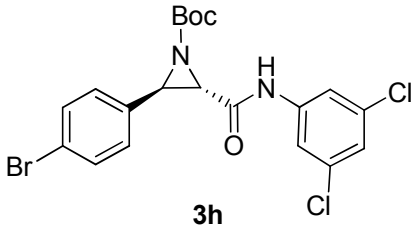
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, brs, N**H**), 7.85-7.81 (4H, m, PhC**H**H), 7.51-7.38 (5H, m, PhCH**H**), 6.80 (2H, d, *J* = 9.2 Hz, PhC**H**H), 4.03 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.78 (3H, s, OC**H3**) 3.57 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.32 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 160.3, 137.3, 133.3, 133.1, 131.3, 129.0, 128.4, 127.9, 127.7, 126.9, 126.6, 126.5, 124.7, 124.3, 119.8, 82.7, 68.8, 46.5, 44.9, 27.8;

HRMS (ESI^+) exact mass calcd. For $C_{25}H_{27}N_2O_4$: *m/z* 419.1893, found: *m/z* 419.1895.

$[\alpha]_{26}^{D}$ = 94.5 (*c* = 1.1, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(3,5-dichlorophenyl)-3-(4-bromophenyl)aziridine-2-carboxamide (3h)(Table 3, entry 9):



3h

Prepared according to the general procedure with 4-bromobenzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 34.0 mg) and *N*-(3,5-dichlorophenyl) diazoacetamide (0.05 mmol, 11.5 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [89% (21.6 mg), 98% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 6.6 min (minor) and 12.7 min (major)).

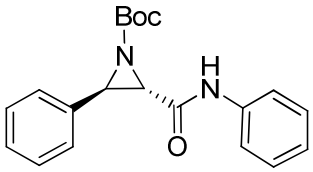
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (1H, brs, N**H**), 7.60-7.52 (2H, d, *J* = 2.4, PhC**H**H), 7.27-7.20 (2H, m, PhCH**H**), 6.94 (1H, t, *J* = 2.4 Hz, PhC**H**H), 3.91 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.40 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.53 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 160.4, 139.2, 134.8, 134.0, 132.7, 131.9, 128.2, 124.3, 117.6, 84.1, 46.0, 45.0, 28.0;

HRMS (ESI^+) exact mass calcd. For $C_{20}H_{20}BrCl_2N_2O_3$: *m/z* 484.9956, found: *m/z* 484.9958.

$[\alpha]_{26}^{D}$ = 95.3 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*,3-diphenylaziridine-2-carboxamide (3i)(Table 3, entry 10):



3i

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-phenyldiazoacetamide (0.05 mmol, 8.0 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [95% (16.1 mg), 92% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 9.9 min (minor) and 17.0 min (major)).

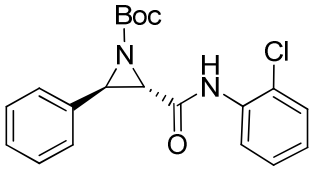
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (1H, brs, N**H**), 7.55 (2H, d, *J* = 8.0, PhC**H**H), 7.38-7.14 (7H, m, PhCH**H**), 7.13 (1H, d, *J* = 7.2 Hz, PhC**H**H), 3.83 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.50 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.30 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.1, 137.4, 134.3, 128.8, 128.6, 127.1, 124.5, 119.8, 82.8, 46.1, 45.1, 27.8;

HRMS (ESI^+) exact mass calcd. For $C_{20}H_{23}N_2O_3$: *m/z* 339.1630, found: *m/z* 339.1634.

$[\alpha]_{26}^{D}$ = 52.1 (*c* = 1.1, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(2-chlorophenyl)-3-phenylaziridine-2-carboxamide (3j)(Table 3, entry 11):



3j

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(2-chlorophenyl)diazoacetamide (0.05 mmol, 9.7 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a solid [95% (17.7 mg), 94% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 12.5 min (minor) and 24.1 min (major)).

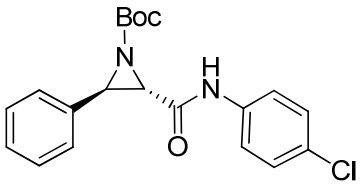
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (1H, brs, N**H**), 7.61 (1H, s, PhC**H**H), 7.43-7.29 (6H, m, PhCH**H**), 7.11 (1H, t, *J* = 8.0 Hz, PhC**H**H), 6.99 (1H, t, *J* = 8.0 Hz, PhC**H**H), 3.93 (1H, d, *J* = 2.4 Hz, BocNC**H**), 3.55 (1H, d, *J* = 2.4 Hz, BocNC**H**), 1.44 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.5, 138.7, 134.4, 129.7, 1228.7, 128.6, 127.0, 124.4, 119.7, 117.5, 83.2, 46.0, 45.3, 27.9;

HRMS (ESI^+) exact mass calcd. For $C_{20}H_{22}ClN_2O_3$: *m/z* 373.1241, found: *m/z* 373.1240.

$[\alpha]_{26}^{D}$ = 72.5 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(4-chlorophenyl)-3-phenylaziridine-2-carboxamide (3k)(Table 3, entry 12):



3k

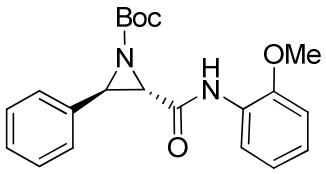
Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(4-chlorophenyl)diazoacetamide (0.05 mmol, 9.7 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a solid [96% (17.8 mg), 88% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 12.7 min (minor) and 25.1 min (major)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (1H, brs, N**H**), 7.50 (2H, d, *J* = 8.4 Hz, PhC**H**H), 7.40-7.25 (7H, m, PhCH**H**), 3.86 (1H, d, *J* = 2.4 Hz, BocNC**H**), 3.53 (1H, d, *J* = 2.4 Hz, BocNC**H**), 1.34 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.1, 136.0, 134.0, 129.5, 128.8, 128.7, 128.6, 127.1, 120.9, 83.0, 46.2, 44.9, 27.8;
HRMS (ESI^+) exact mass calcd. For $C_{20}H_{22}ClN_2O_3$: *m/z* 373.1241, found: *m/z* 373.1244.
$[\alpha]_{26}^{D}$ = 66.3 (*c* = 1.0, $CHCl_3$).

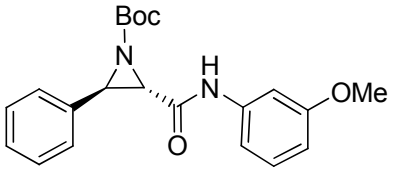
(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(2-methoxyphenyl)-3-phenylaziridine-2-carboxamide (3l)(Table 3, entry 13):



3l

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(2-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [93% (15.7 mg), 92% ee].
Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 12.4 min (minor) and 23.7 min (major)).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (1H, brs, N**H**), 7.40-7.34 (5H, m, PhC**H**H), 7.22-7.15 (2H, m, PhCH**H**), 7.06 (1H, d, *J* = 8.0 Hz, PhCH**H**), 6.65-6.62 (1H, m, PhC**H**H), 3.90 (1H, d, *J* = 2.4 Hz, BocNC**H**), 3.78 (3H, s, OC**H**3), 3.52 (1H, d, *J* = 2.4 Hz, BocNC**H**), 1.38 (9H, s, *t*Bu);
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.9, 138.6, 134.2, 129.8, 129.4, 129.0, 128.6, 127.1, 112.0, 110.7, 105.2, 87.8, 55.2, 46.0, 45.1, 27.8;
HRMS (ESI^+) exact mass calcd. For $C_{21}H_{25}N_2O_4$: *m/z* 369.1736, found: *m/z* 369.1738.
$[\alpha]_{26}^{D}$ = 58.3 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(3-methoxyphenyl)-3-phenylaziridine-2-carboxamide (3m)(Table 3, entry 14):



3m

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(3-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [94% (17.3 mg), 96% ee].
Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 12.4 min (minor) and 23.7

min (major)).

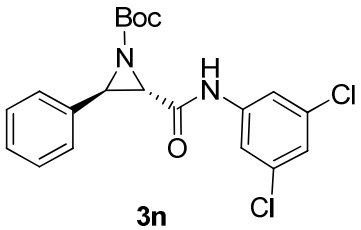
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (1H, brs, N**H**), 7.38-7.32 (5H, m, PhC**H**H), 7.17-7.10 (2H, m, PhCH**H**), 7.04 (1H, d, *J* = 8.4 Hz, PhCH**H**), 6.61-6.58 (1H, m, PhC**H**H), 3.89 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.74 (3H, s, OC**H**3), 3.52 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.36 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.4, 138.6, 134.4, 134.3, 129.7, 128.7, 127.0, 125.8, 124.4, 119.7, 117.7, 83.1, 55.2, 46.1, 45.2, 27.9;

HRMS (ESI$^+$) exact mass calcd. For $C_{21}H_{25}N_2O_4$: *m/z* 369.1736, found: *m/z* 369.1732.

$[\alpha]_{26}^{D}$ = 55.8 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(3,5-dichlorophenyl)-3-phenylaziridine-2-carboxamide (3n)(Table 3, entry 15):



3n

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (0.12 mmol, 25.0 mg) and *N*-(3,5-dichlorophenyl)diazoacetamide (0.05 mmol, 11.5 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [81% (16.4 mg), 95% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 5.3 min (minor) and 11.8 min (major)).

Prepare of (2*S*,3*R*)-1-(*t*-Butoxycarbonyl)-*N*-(3,5-dichlorophenyl)-3-phenylaziridine-2-carboxamide in 1.5 mmol scale (3o)(Table 3, entry 16):

Prepared according to the general procedure with benzaldehyde *N*-(*tert*-butoxycarbonyl)imine (3.0 mmol, 0.60g) and *N*-(3,5-dichlorophenyl)diazoacet- amide (1.5 mmol, 0.345g) in the presence of (*R*)-**5g** (52.5 mg, 5 mmol %) in DCM (60 mL) at room temperature over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 10:1 to 4:1) to give the title compound as a white solid [92% (0.61g), 96% ee].

Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 5.3 min (minor) and 11.8 min (major)).

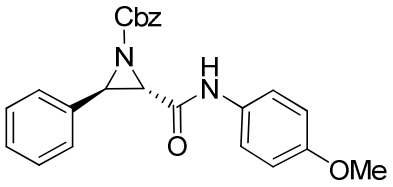
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (1H, brs, N**H**), 7.44-7.36 (7H, m, PhC**H**H), 6.94 (1H, t, *J* = 1.2 Hz, PhCH**H**), 3.96 (1H, d, *J* = 2.8 Hz, BocNC**H**), 3.51 (1H, d, *J* = 2.8 Hz, BocNC**H**), 1.52 (9H, s, *t*Bu);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 160.5, 139.4, 134.9, 134.8, 128.7, 128.6, 126.7, 124.2, 117.6, 83.8, 45.9, 45.7, 28.0;

HRMS (ESI$^+$) exact mass calcd. For $C_{20}H_{21}N_2O_3$: *m/z* 407.0851, found: *m/z* 407.0850.

$[\alpha]_{26}^{D}$ = 76.6 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(Benzylcarbonyl)-*N*-(4-methoxyphenyl)-3-phenylaziridine-2-carboxamide (3p)(Scheme 2, entry 1):



3p

Prepared according to the general procedure with benzaldehyde *N*-(benzylcarbonyl)imine (0.12 mmol, 30.0 mg) and *N*-(4-methoxyphenyl)diazoacetamide (0.05 mmol, 9.6 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 5:1 to 2:1) to give the title compound as a white solid [95% (19.0 mg), 97% ee]. Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 27.2 min (minor) and 36.8 min (major)).

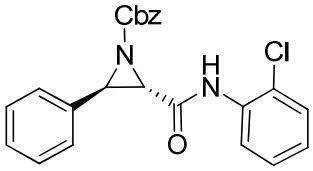
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, brs, N**H**), 7.38-7.27 (11H, m, PhC**H**H), 6.78 (2H, d, *J* = 8.8 Hz, PhCH**H**), 5.13 (2H, d, *J* = 9.2 Hz, PhC**H**2), 3.97 (1H, d, *J* = 2.4 Hz, CbzNC**H**), 3.77 (3H, s, OC**H**3), 3.37 (1H, d, *J* = 2.4 Hz, CbzNC**H**);

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 160.3, 135.2, 134.4, 130.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 126.6, 121.5, 114.0, 68.8, 55.4, 46.0, 45.6;

HRMS (ESI$^+$) exact mass calcd. For $C_{24}H_{23}N_2O_4$: *m/z* 403.1850, found: *m/z* 403.1854.

$[\alpha]_{26}^{D}$ = 72.9 (*c* = 1.0, $CHCl_3$).

(2*S*,3*R*)-1-(Benzylcarbonyl)-*N*-(2-chlorophenyl)-3-phenylaziridine-2-carboxamide (3q)(Scheme 2, entry 2):



3q

Prepared according to the general procedure with benzaldehyde *N*-(benzylcarbonyl)imine (0.12 mmol, 30.0 mg) and *N*-(2-chlorophenyl)diazoacetamide (0.05 mmol, 9.8 mg) over the course of 10 min. The crude material was purified by column chromatography on silica gel (eluting with EtOAc/Hexane = 6:1 to 2:1) to give the title compound as a white solid [94% (19.0 mg), 94% ee]. Enantiomeric purity was determined by HPLC analysis (Daicel Chiralcel OD-H, hexane/2-propanol = 80:20, flow rate = 1.0 mL/min, retention time; 20.3 min (minor) and 25.8 min (major)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (1H, brs, N**H**), 7.39-7.11 (11H, m, PhC**H**H), 6.97 (2H, d, *J* = 8.4 Hz, PhCH**H**), 6.64-6.61 (1H, m, PhCH**H**), 5.13 (2H, d, *J* = 9.2 Hz, PhC**H**2), 3.98 (1H, d, *J* = 2.4 Hz, CbzNC**H**), 3.40 (1H, d, *J* = 2.4 Hz, CbzNC**H**);

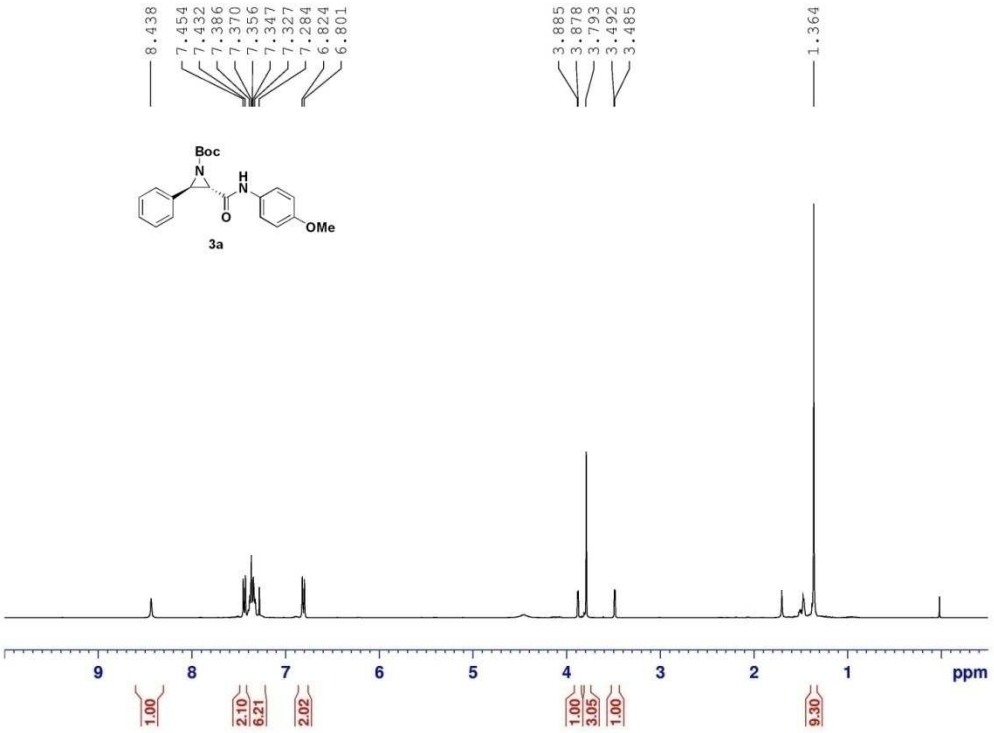
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 160.4, 138.4, 135.2, 134.4, 129.6, 128.8, 128.7, 128.5, 128.4, 128.2, 126.7, 112.0, 110.8, 105.4, 68.9, 46.0, 45.7;

HRMS (ESI$^+$) exact mass calcd. For $C_{23}H_{20}ClN_2O_3$: *m/z* 407.1084, found: *m/z* 407.1081.

$[\alpha]_{26}^{D}$ = 77.4 (*c* = 1.0, $CHCl_3$).

Reference:

1. Hashimoto, T.; Uchiyama, N.; Maruoka. K. *J. Am. Chem. Soc.* **2008**, *130*, 14380.
2. For the synthesis of the N-Boc imines see: (a) Wenzel, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008**, *130*, 12964. (b) Gizecki, P.; Ait Youcef, R.; Poulard, C.; Dhal, R.; Dujardin, G. *Tetrahedron Lett.* **2004**, *45*, 9589. (c) Kanazawa, A. M.; Denis, J.-N.; Greene, A. E. *J. Org. Chem.* **1994**, *59*, 1238.
3. For the synthesis of the N-Cbz imines see: Tillman, A. L.; Ye, J.-X.; Dixon, D. *J. Chem. Commun.* **2006**, 1191.
4. For the synthesis of the diazoacetamide derivatives see: (a) Blankley, C. J.; Stauter, F. J.; House, H. O. *Org. Synth.* **1969**, *49*, 22. (b) Crich, D.; Zou, Y.-K.; Brebion, F. *J. Org. Chem.* **2006**, *71*, 9172. (c) Ouihia, A.; Rene, L.; Badet, B. *Tetrahedron Lett.* **1992**, *33*, 5509.
5. For the synthesis of the chiral phosphoric acids see: (a) Cheng, X.; Goddard, R.; Buth, G.; List, B. *Angew. Chem. Int. Ed.* **2008**, *47*, 5079. (b) Cheon, C. H.; Yamamoto, H. *J. Am. Chem. Soc.* **2008**, *130*, 9246. (c) Yamanaka, M.; Itoh, J.; Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 6756. (d) Liu, Hua; Cun, Lin-Feng; Mi, Ai-Qiao; Jiang, Yao-Zhong; Gong, Liu-Zhu. *Org. Lett.* **2006**, *8*, 6023. (e) Storer, R. Ian; Carrera, Diane E.; Ni, Yike; MacMillan, David W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84. (f) Akiyama, Takahiko; Itoh, Junji; Yokota, Koji; Fuchibe, Kohei. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566.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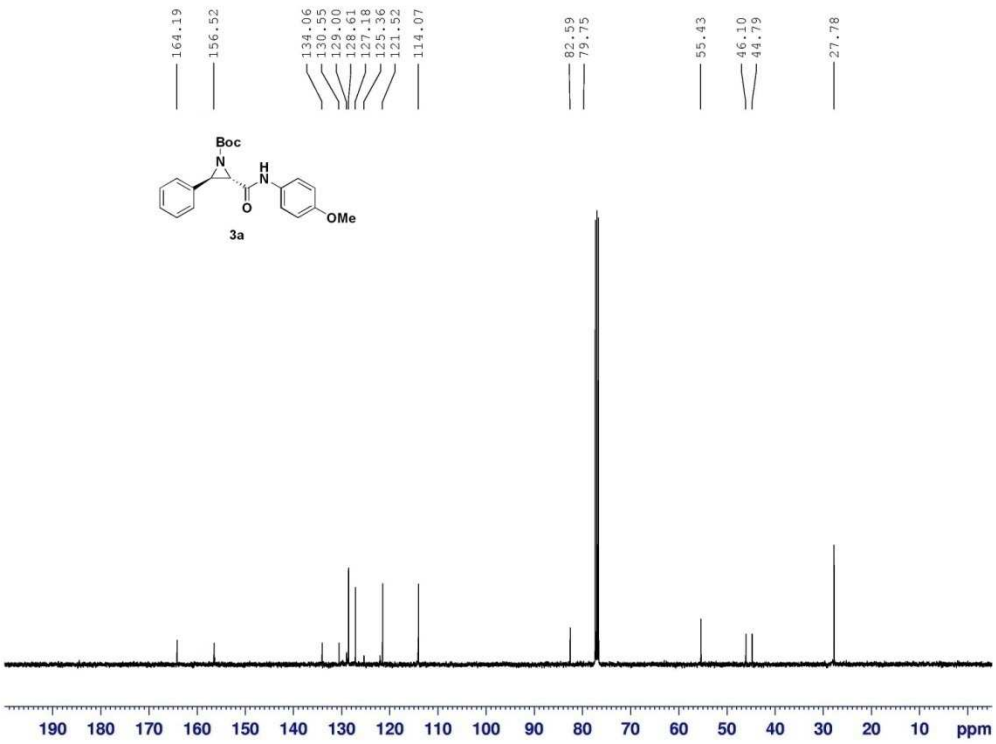
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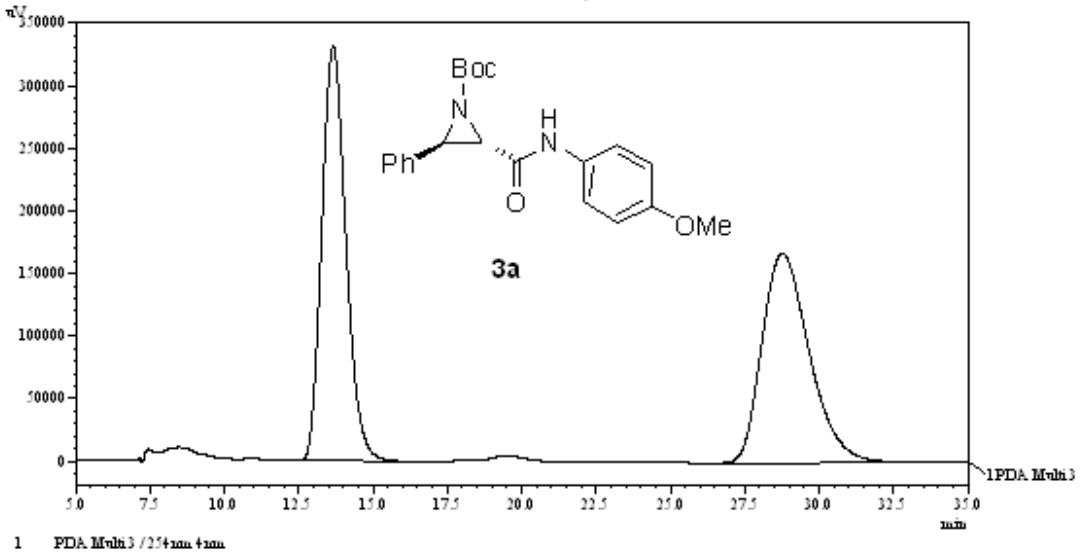

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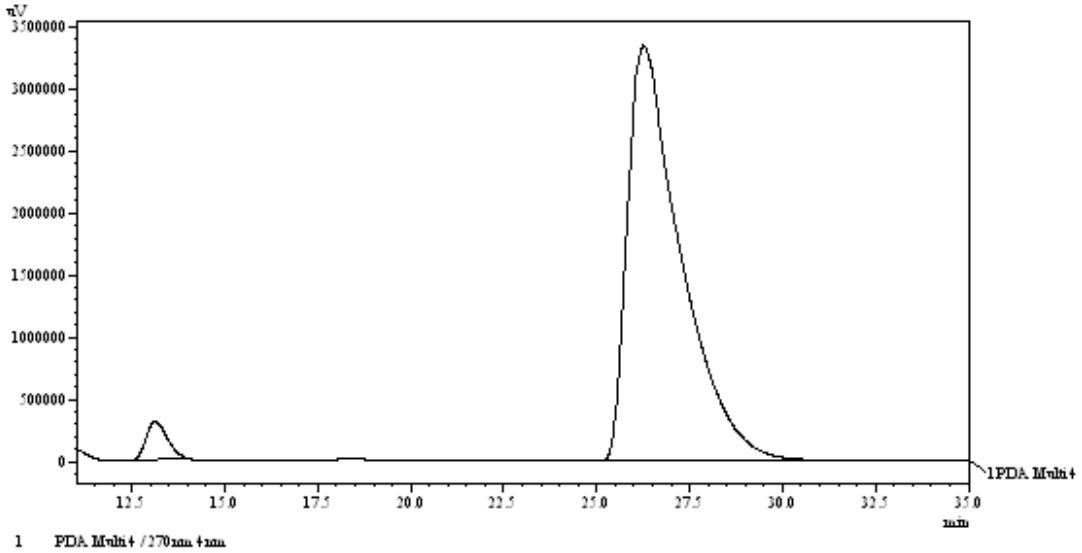

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Peak Table

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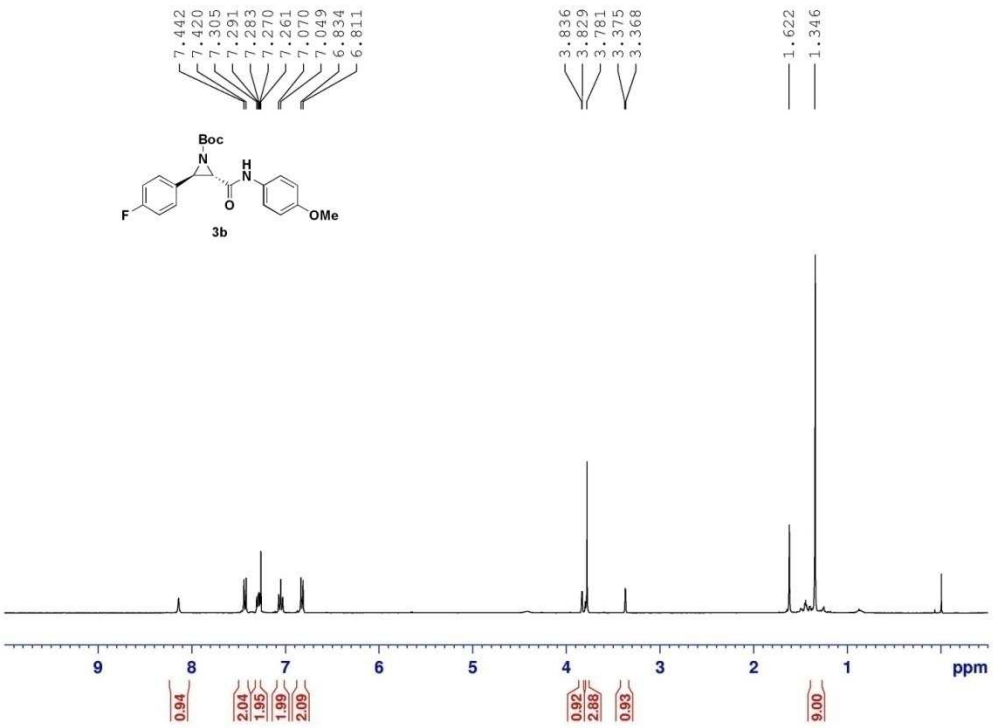
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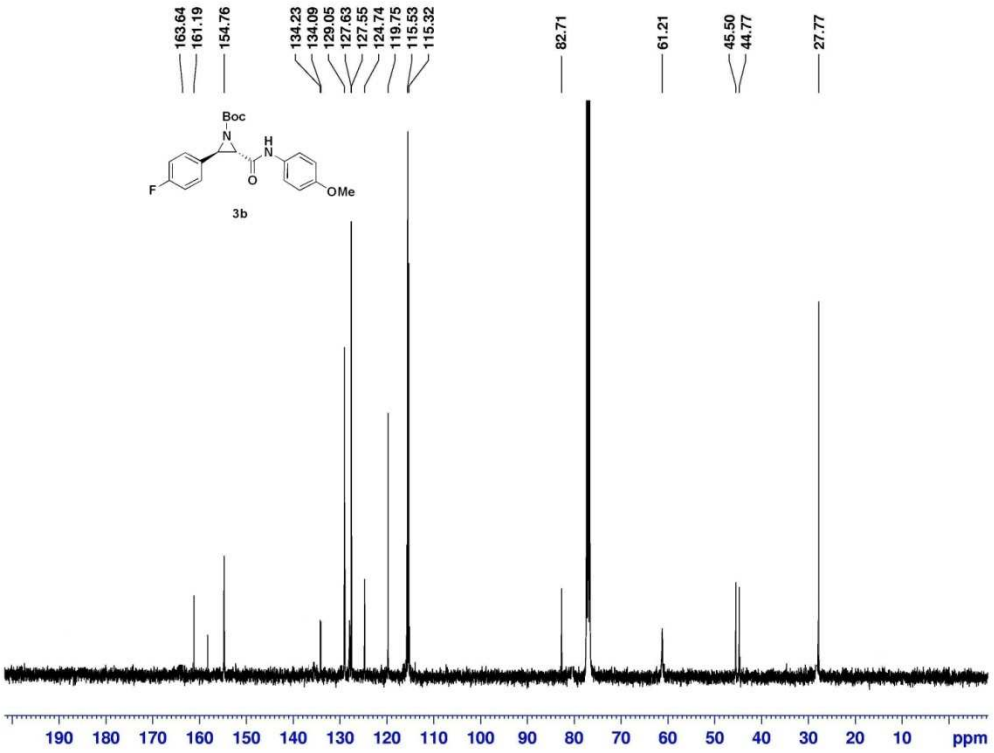
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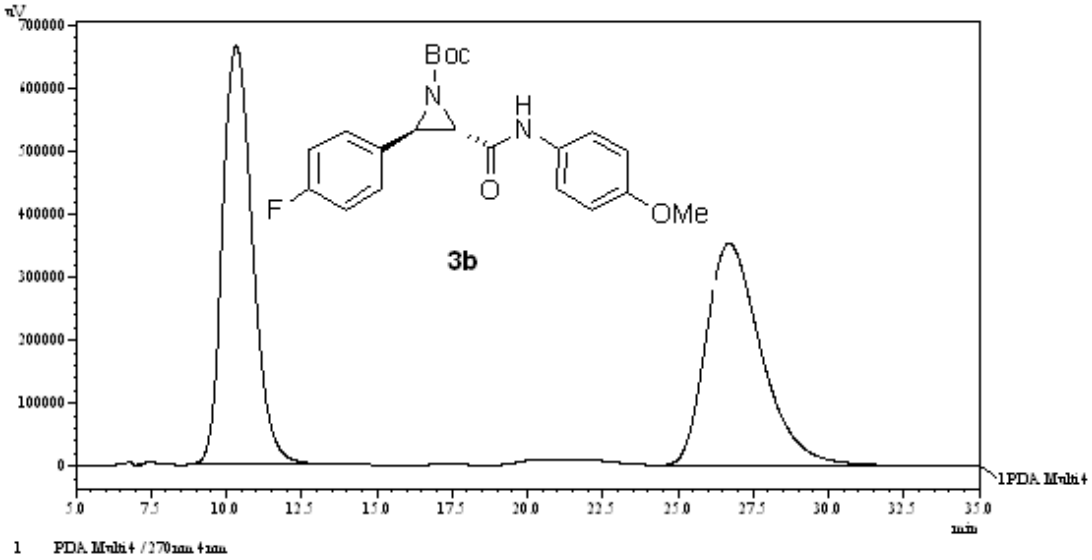

1 PDA Multi4 / 270nm 4nm

Peak Table

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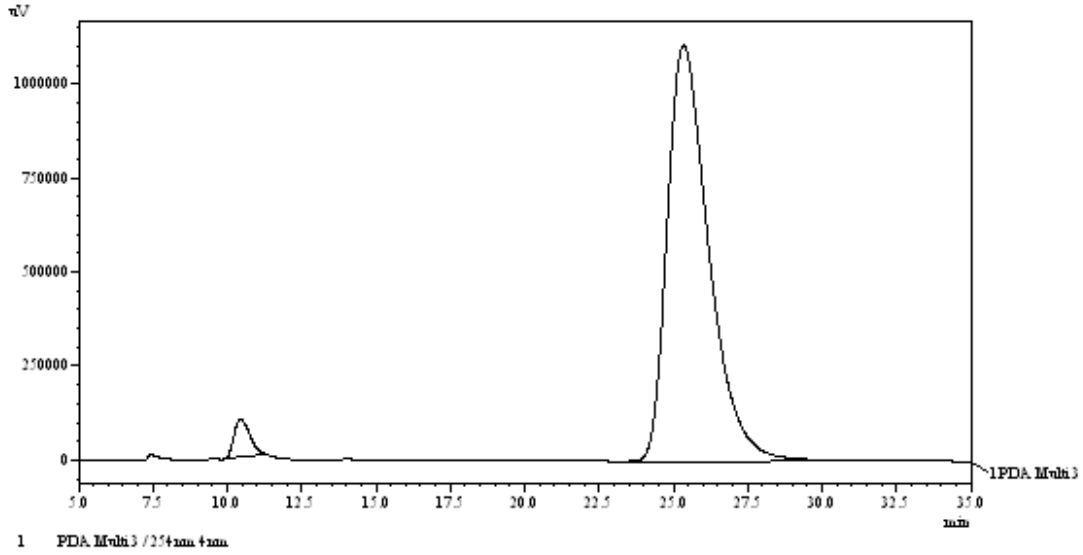
2	26.698	45275133	352906	49.683
Total		91127380	1016353	100.000

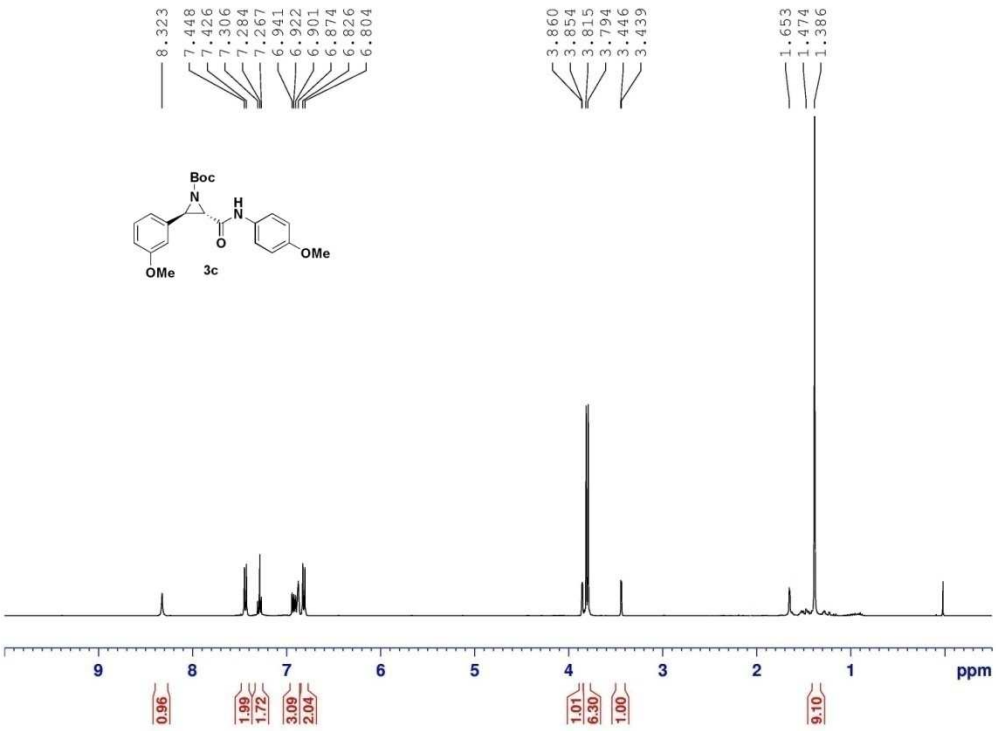


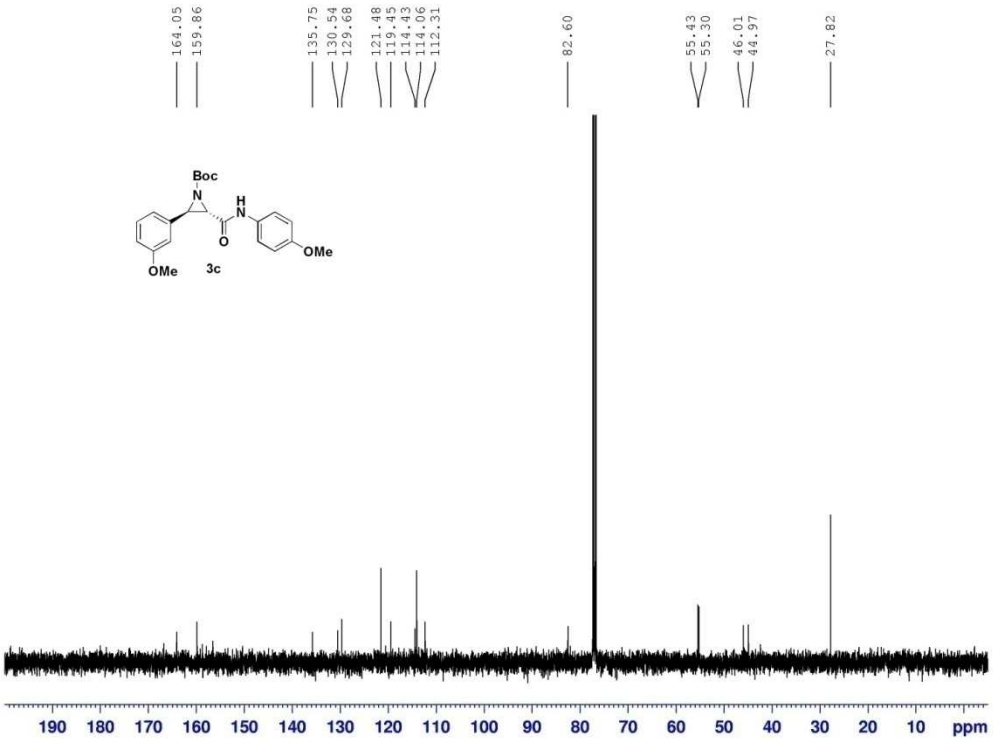
1 PDA Multi3 / 254nm 4nm

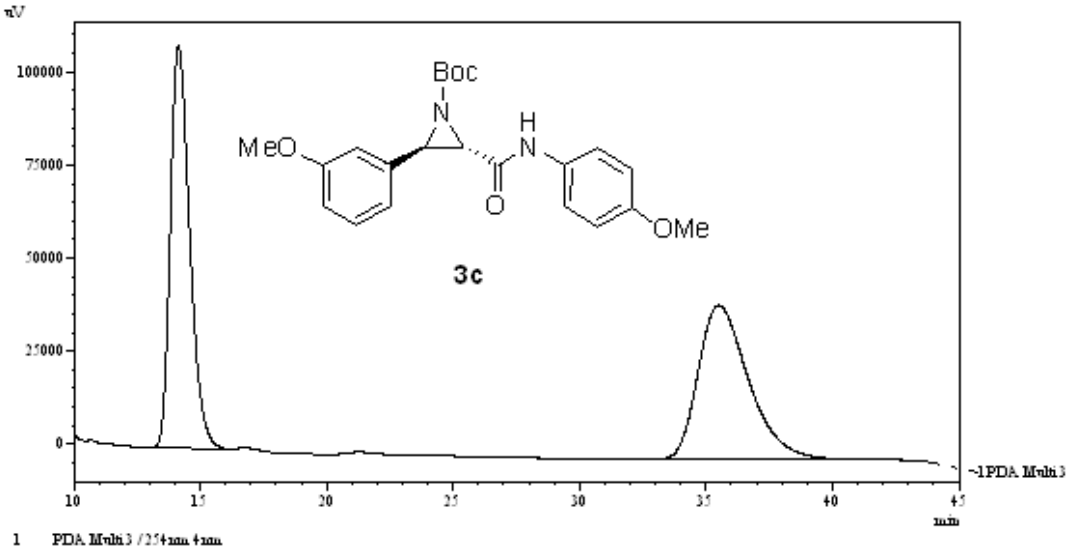
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.449	3572665	97393	3.207
2	25.344	107831153	1105976	96.793
Total		111403818	1203369	100.000


8.323
7.448
7.426
7.306
7.284
7.267
6.941
6.922
6.901
6.874
6.826
6.804
3.860
3.854
3.815
3.794
3.446
3.439
1.653
1.474
1.386
Boc
N
H
N
O
OMe
OMe
3c
9
8
7
6
5
4
3
2
1
ppm
0.96
1.99
1.72
3.09
2.04
1.01
6.30
1.00
9.10

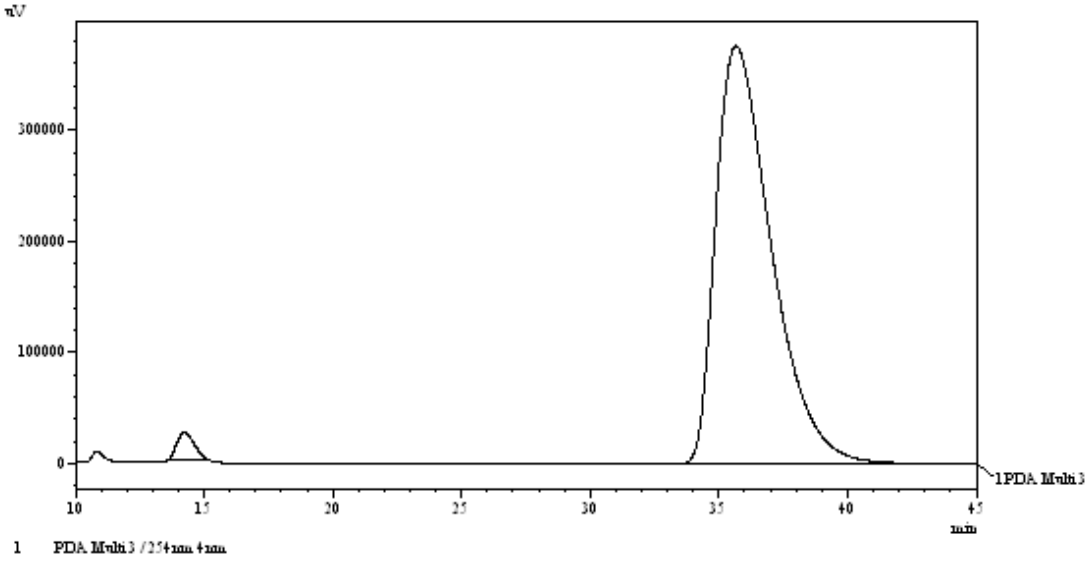

164.05
159.86
135.75
130.54
129.68
121.48
119.45
114.43
114.06
112.31
82.60
55.43
55.30
46.01
44.97
27.82
Boc
N
H
N
O
OMe
OMe
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



Peak Table

PDA Ch3 254nm 4nm

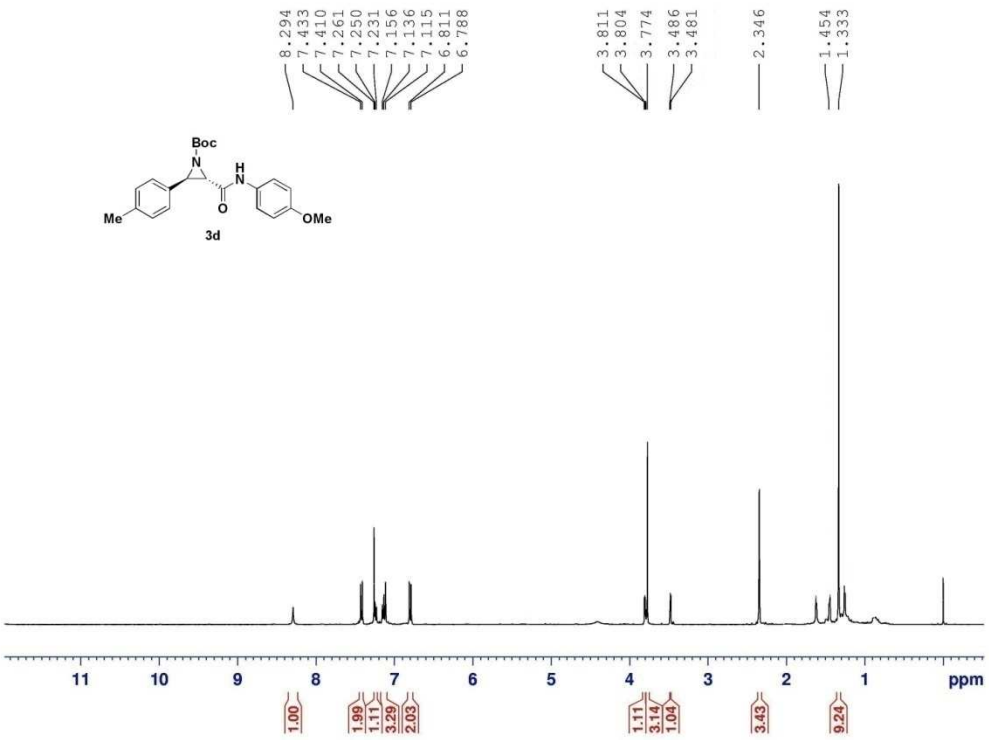
Peak#	Ret. Time	Area	Height	Area %
1	14.142	5737816	107899	50.294
2	35.498	5670799	41262	49.706
Total		11408615	149160	100.000

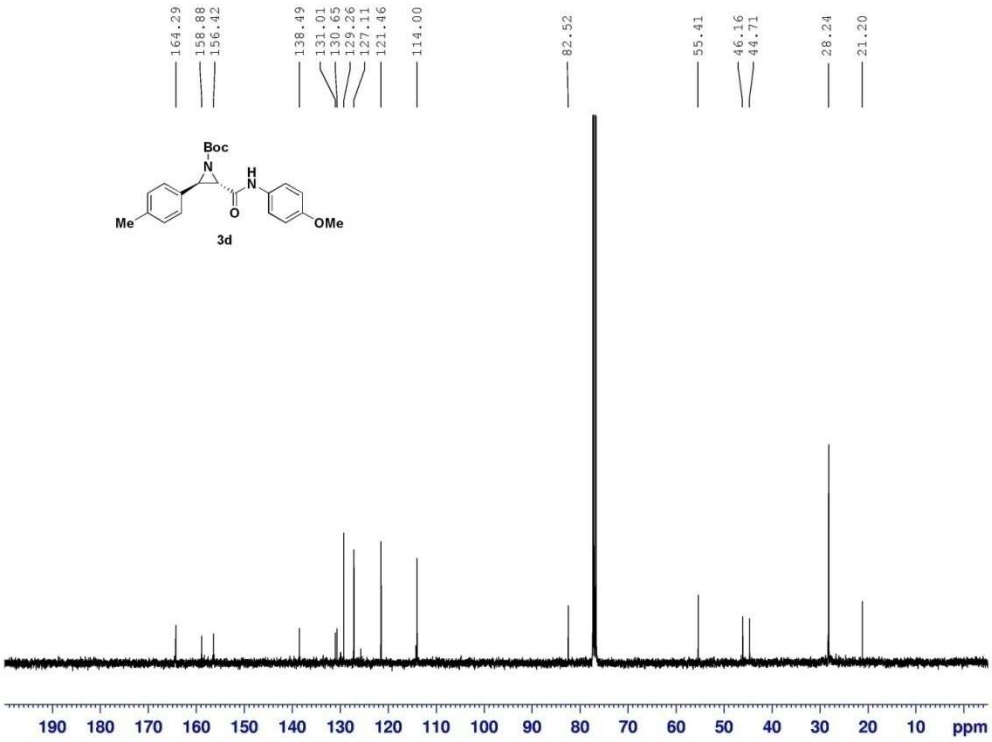


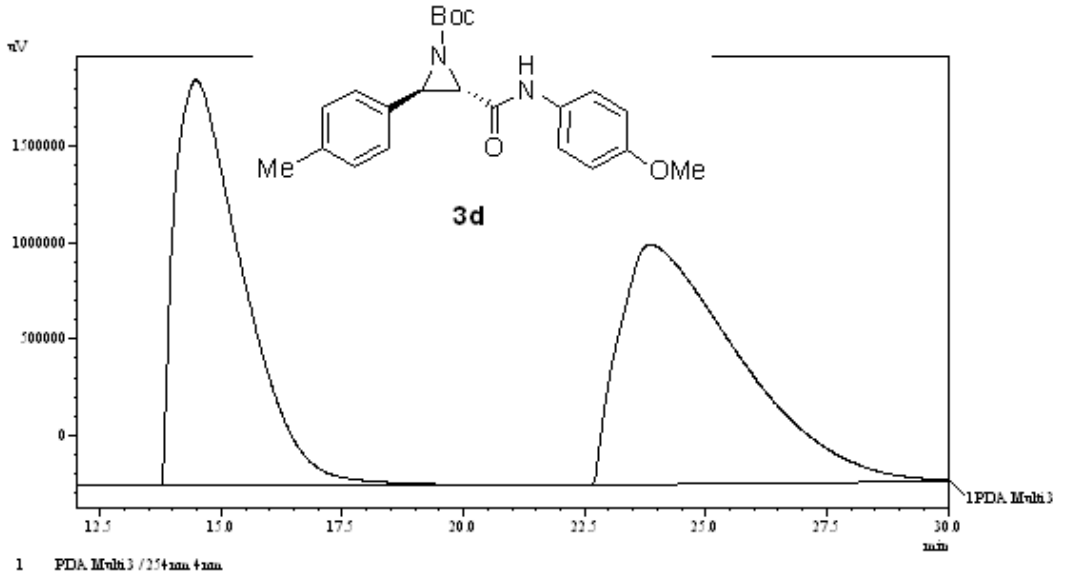
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.236	1194644	24916	2.062
2	35.666	56738030	376585	97.938
Total		57932674	401501	100.000


8.294
7.433
7.410
7.261
7.250
7.231
7.156
7.136
7.115
6.811
6.788
3.811
3.804
3.774
3.486
3.481
2.346
1.454
1.333
Boc
N
H
N
O
Me
OMe
3d
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
1.11
3.29
2.03
1.11
3.14
1.04
3.43
9.24


164.29
158.88
156.42
138.49
131.01
130.65
129.26
127.11
121.46
114.00
82.52
55.41
46.16
44.71
28.24
21.20
Boc
N
H
N
O
Me
OMe
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

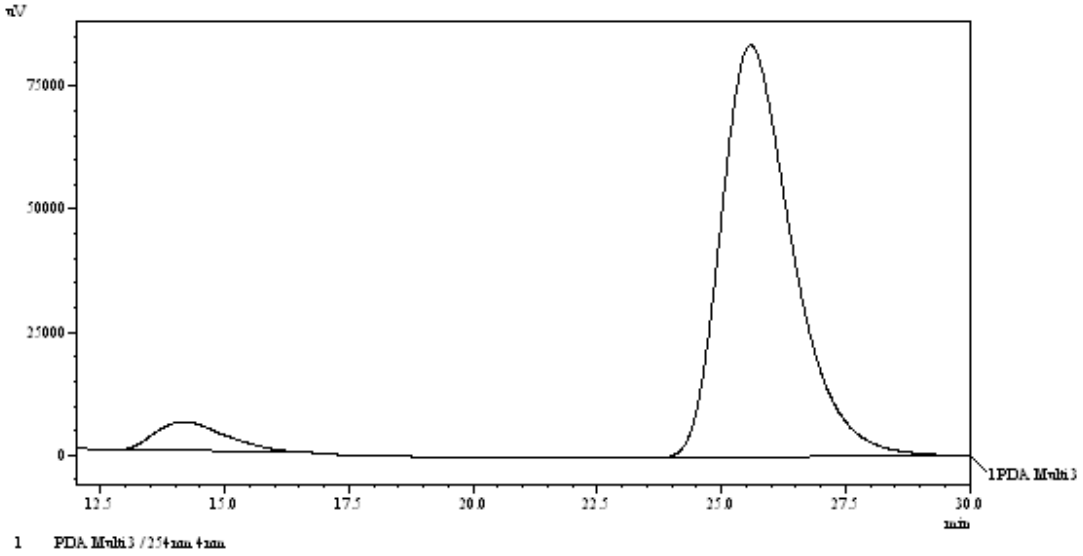


1 PDA Multi 3 / 254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.476	205564560	2105101	48.835
2	23.864	215374535	1243042	51.165
Total		420939095	3348143	100.000

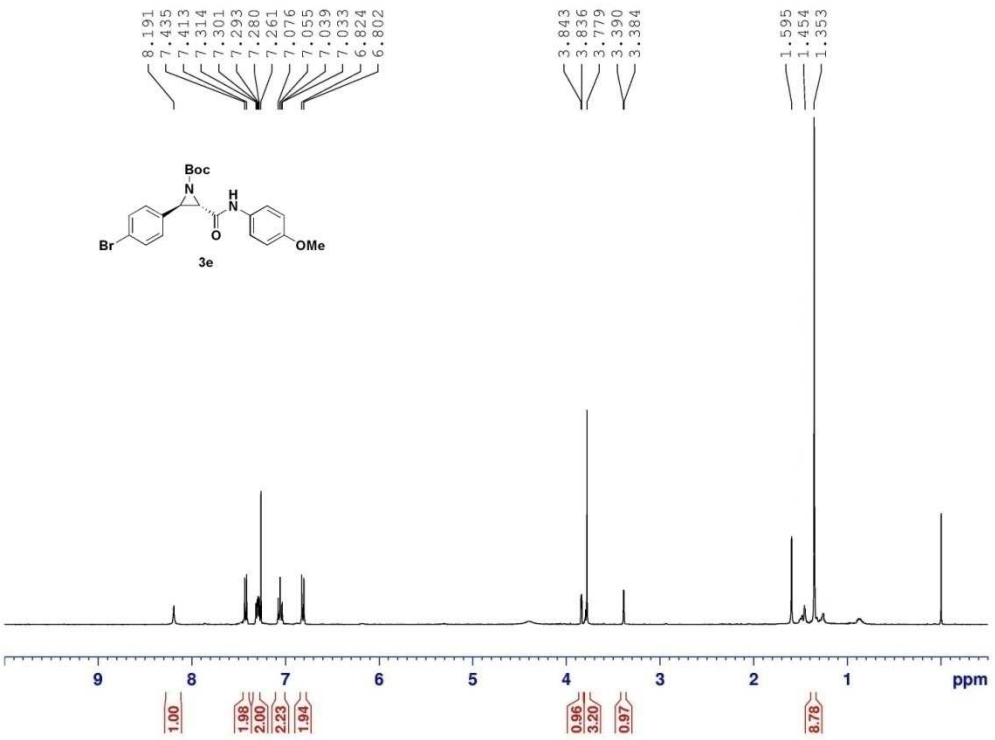


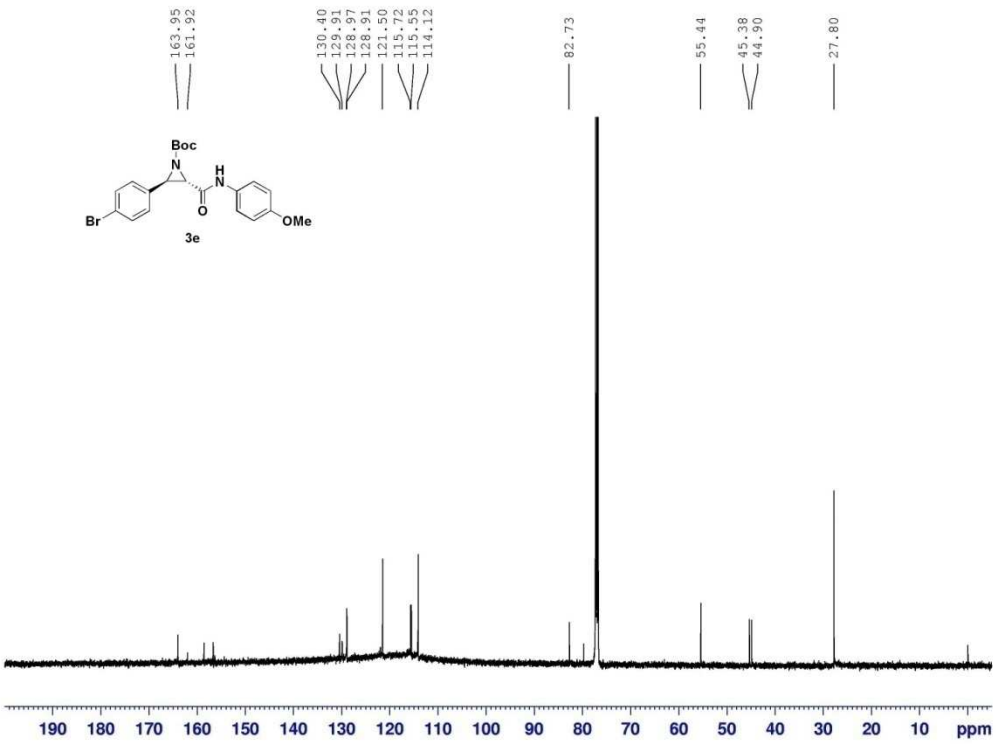
1 PDA Multi 3 / 254nm 4nm

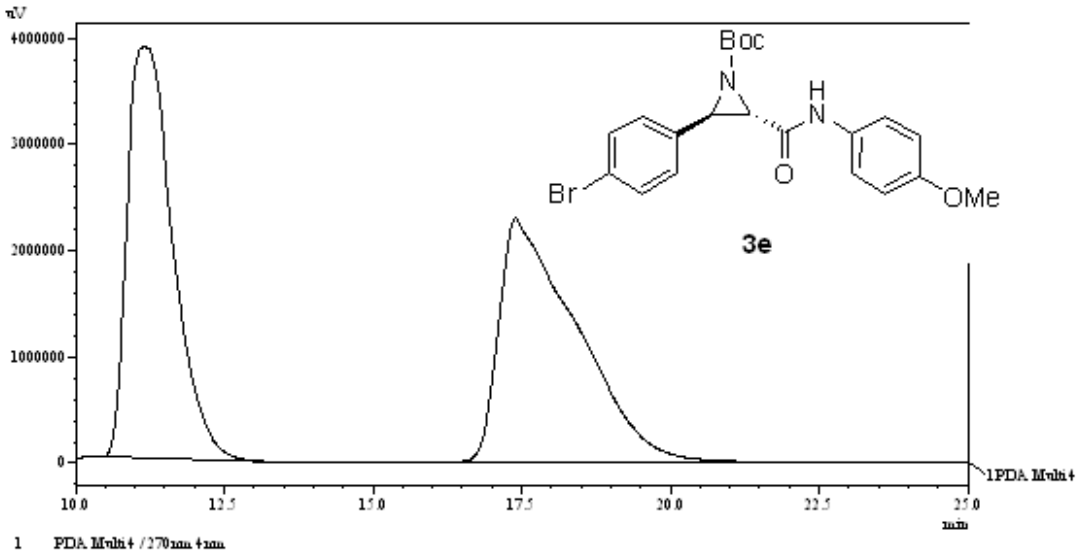
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	14.164	552161	5707	6.183
2	25.588	8378761	83740	93.817
Total		8930922	89447	100.000


8.191
7.435
7.413
7.314
7.301
7.293
7.280
7.261
7.076
7.055
7.039
7.033
6.824
6.802
3.843
3.836
3.779
3.390
3.384
1.595
1.454
1.353
Boc
N
H
N
O
Br
OMe
3e
9
8
7
6
5
4
3
2
1
ppm
1.00
1.98
2.00
2.23
1.94
0.96
3.20
0.97
8.78


163.95
161.92
130.40
129.91
128.97
128.91
121.50
115.72
115.55
114.12
82.73
55.44
45.38
44.90
27.80
Boc
N
H
N
O
Br
OMe
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

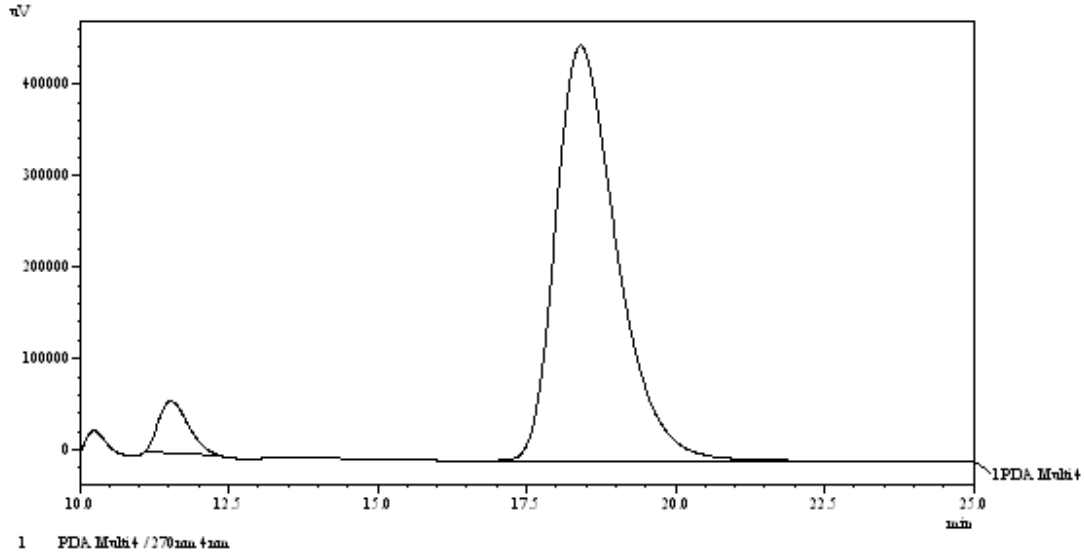


1 PDA Multi4 /270nm 4nm

Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	11.134	206630798	3868169	49.323
2	17.389	212306794	2304191	50.677
Total		418937592	6172360	100.000

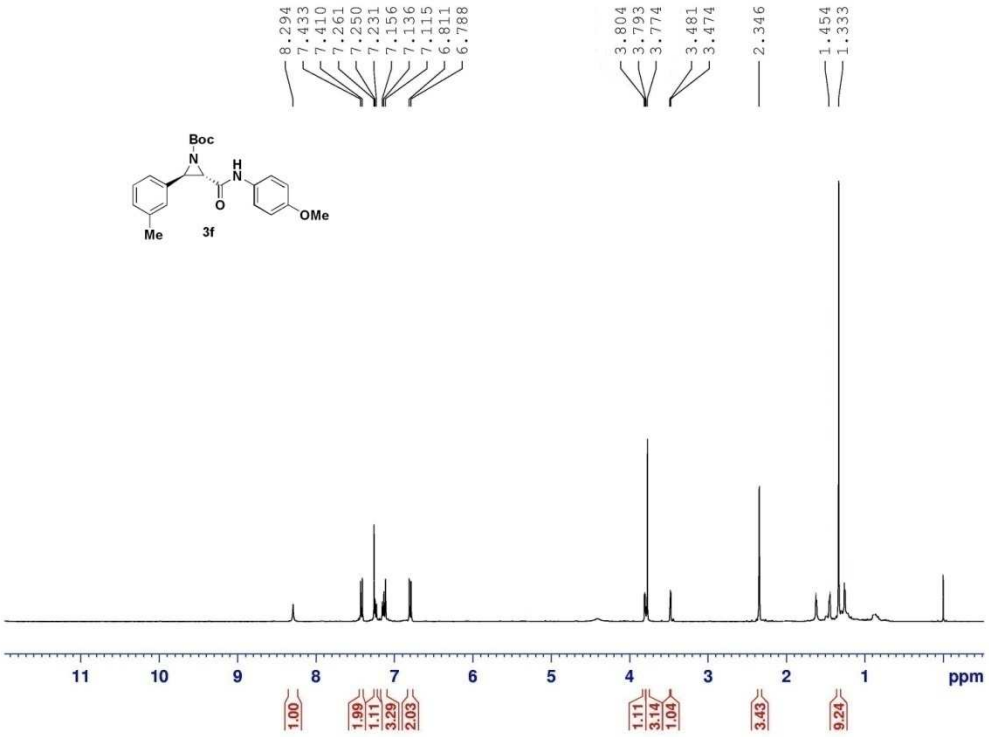


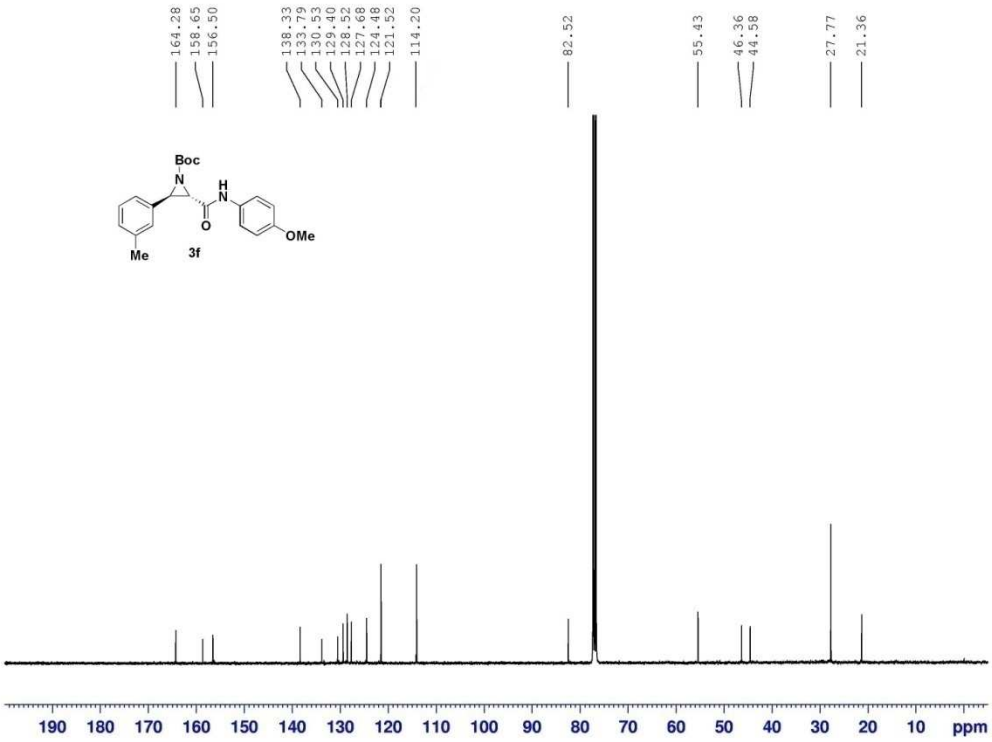
1 PDA Multi4 /270nm 4nm

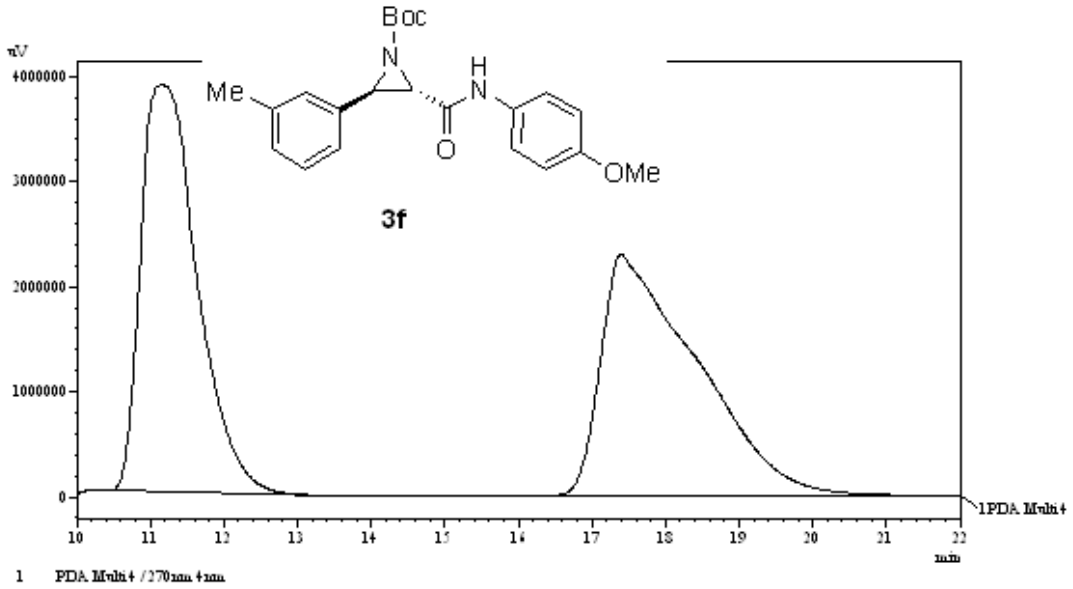
Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	11.528	1967911	56256	5.731
2	18.407	32369007	454081	94.269
Total		34336918	510336	100.000


8.294
7.433
7.410
7.261
7.250
7.231
7.156
7.136
7.115
6.811
6.788
3.804
3.793
3.774
3.481
3.474
2.346
1.454
1.333
Boc
N
H
N
O
OMe
Me
3f
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
1.11
3.29
2.03
1.11
3.14
1.04
3.43
9.24

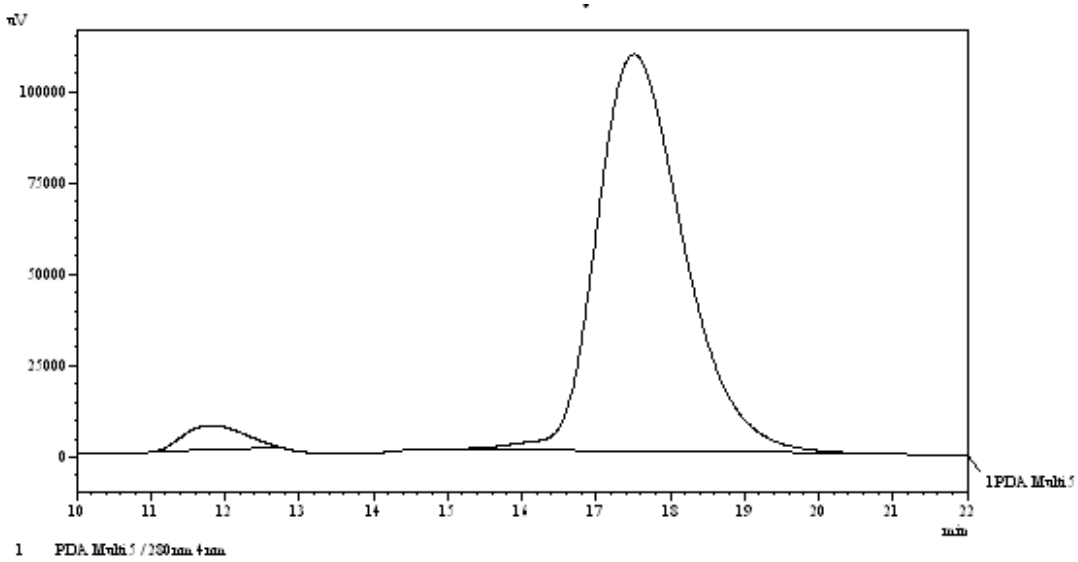

164.28
158.65
156.50
138.33
133.79
130.53
129.40
128.52
127.68
124.48
121.52
114.20
82.52
55.43
46.36
44.58
27.77
21.36
Boc
N
H
N
O
OMe
Me
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



Peak Table

PDA Ch4 270nm 4nm

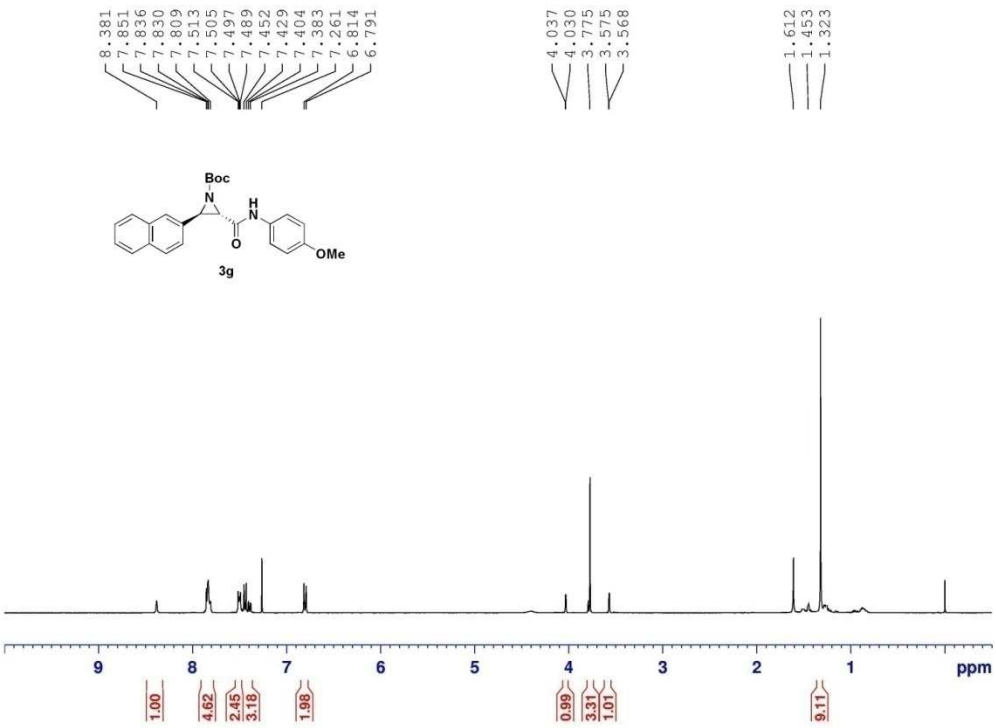
Peak#	Ret. Time	Area	Height	Area %
1	11.134	206630798	3868169	49.323
2	17.389	212306794	2304191	50.677
Total		418937592	6172360	100.000

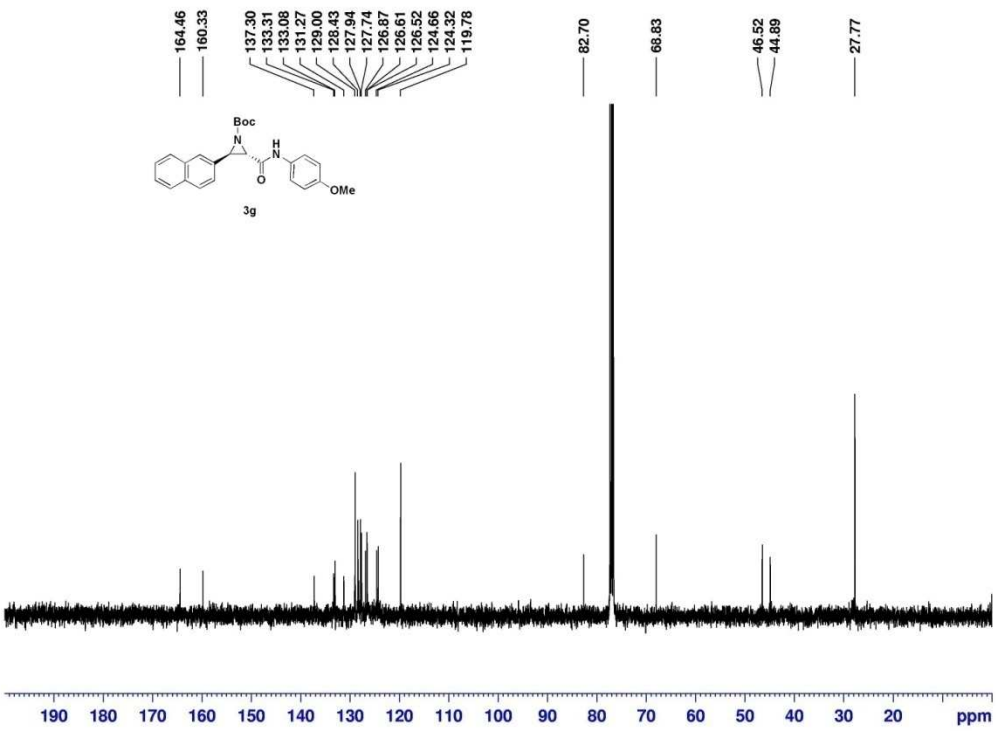


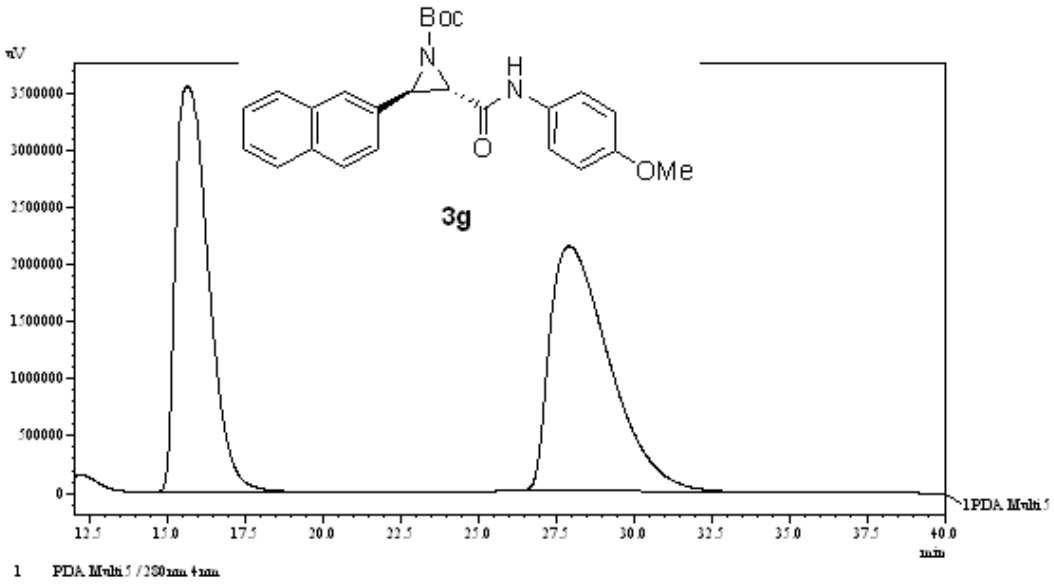
Peak Table

PDA Ch5 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	11.824	373577	6599	4.067
2	17.508	8810990	108410	95.933
Total		9184567	115010	100.000


8.381
7.851
7.836
7.830
7.809
7.513
7.505
7.497
7.489
7.452
7.429
7.404
7.383
7.261
6.814
6.791
4.037
4.030
3.775
3.575
3.568
1.612
1.453
1.323
Boc
N
H
N
O
OMe
3g
9
8
7
6
5
4
3
2
1
ppm
1.00
4.62
2.45
3.18
1.98
0.99
3.31
1.01
9.11


164.46
160.33
137.30
133.31
133.08
131.27
129.00
128.43
127.94
127.74
126.87
126.61
126.52
124.66
124.32
119.78
82.70
68.83
46.52
44.89
27.77
Boc
N
H
N
O
OMe
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

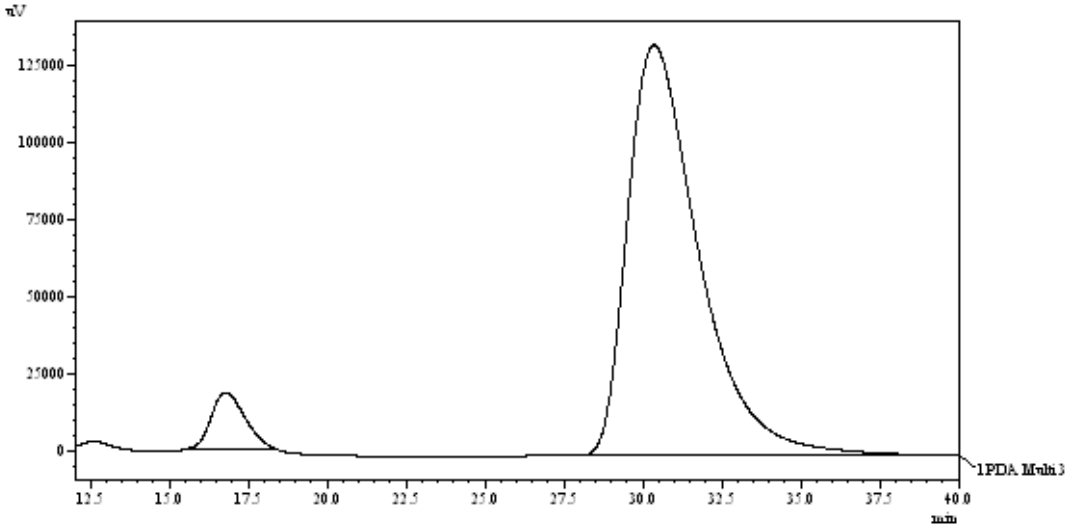


1 PDA Multi 5 / 280nm 4nm

Peak Table

PDA Ch5 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	15.655	261313694	3541573	47.878
2	27.915	284474263	2134982	52.122
Total		545787957	5676554	100.000

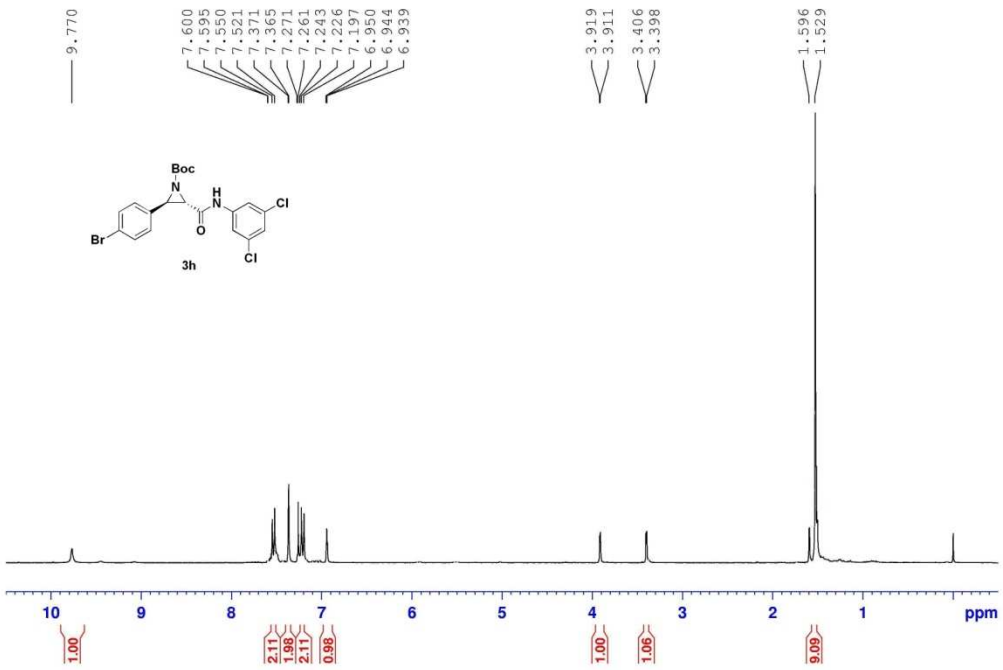


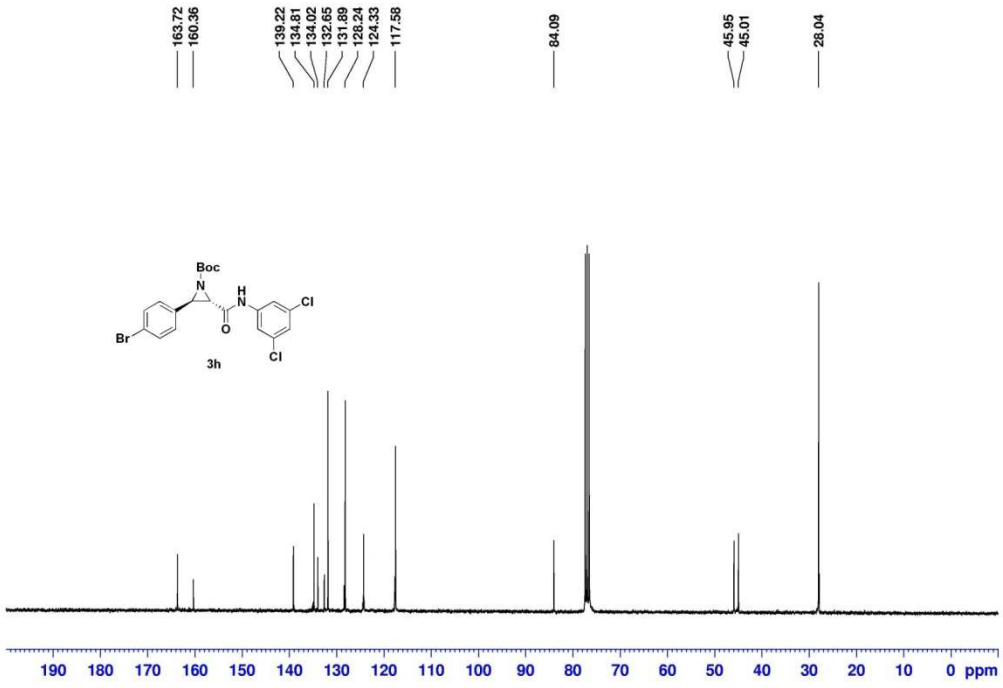
1 PDA Multi 3 / 254nm 4nm

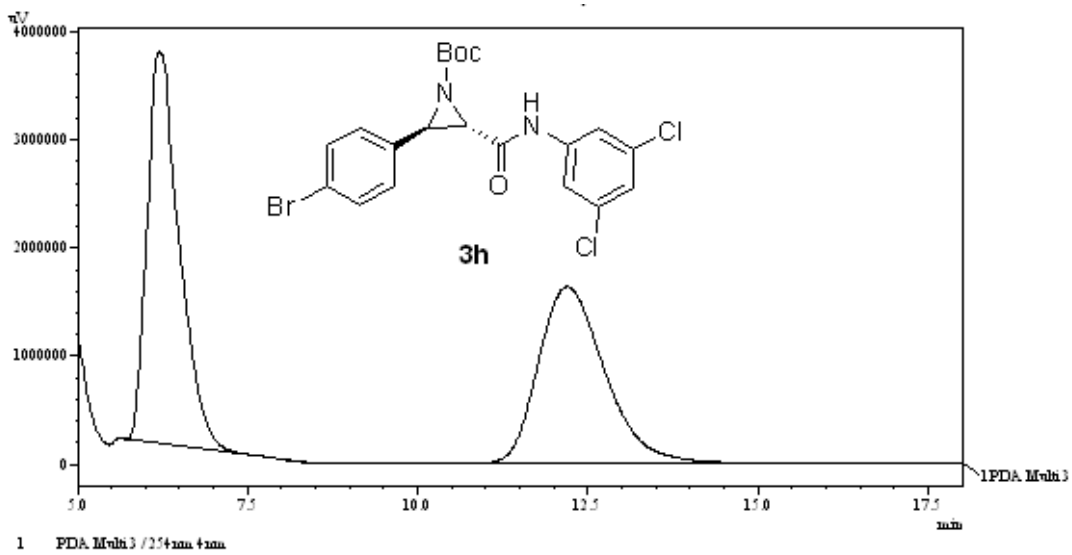
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.779	1364955	18379	6.138
2	30.353	20871543	133051	93.862
Total		22236498	151430	100.000


9.770
7.600
7.595
7.550
7.521
7.371
7.365
7.271
7.261
7.243
7.226
7.197
6.950
6.944
6.939
3.919
3.911
3.406
3.398
1.596
1.529
Boc
N
H
N
O
Br
Cl
Cl
3h
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.11
1.98
2.11
0.98
1.00
1.06
9.09


163.72
160.36
139.22
134.81
134.02
132.65
131.89
128.24
124.33
117.58
84.09
45.95
45.01
28.04
Boc
N
H
N
O
Br
Cl
Cl
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

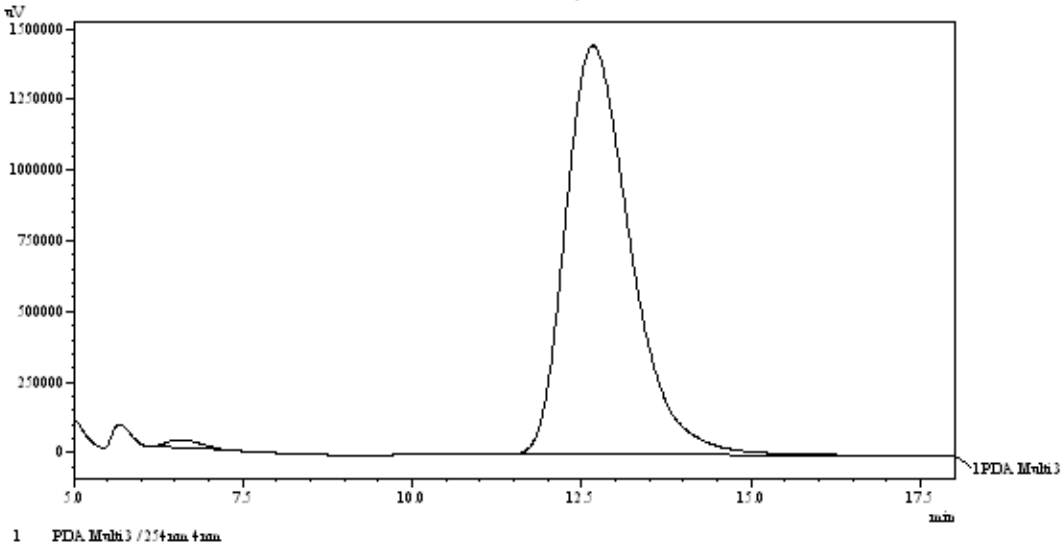


1 PDA Multi 3 / 254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	6.204	118457374	3618336	51.766
2	12.195	110375155	1631895	48.234
Total		228832529	5250230	100.000

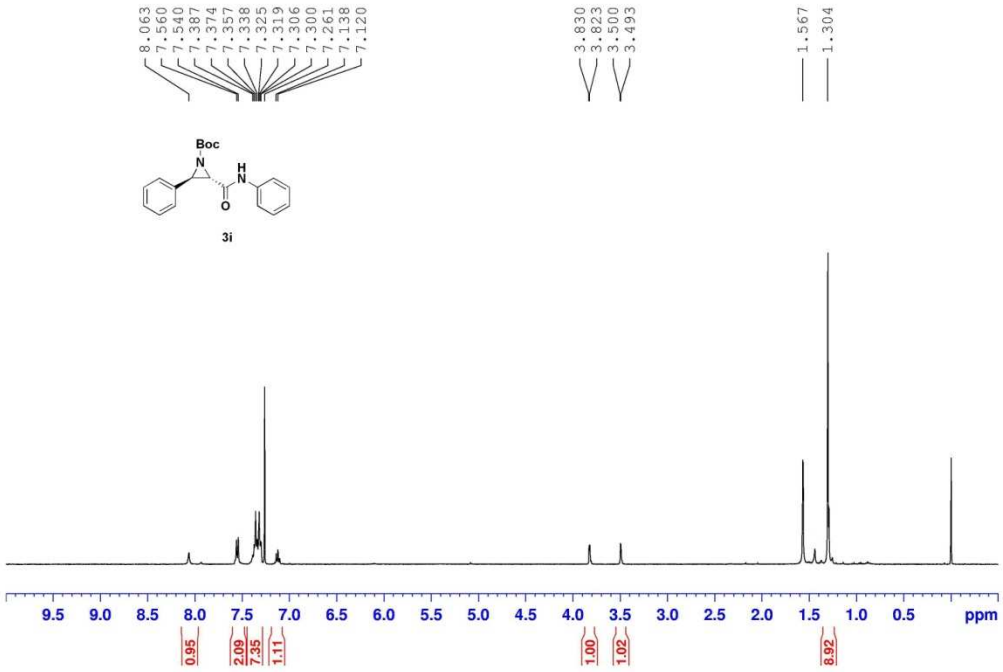


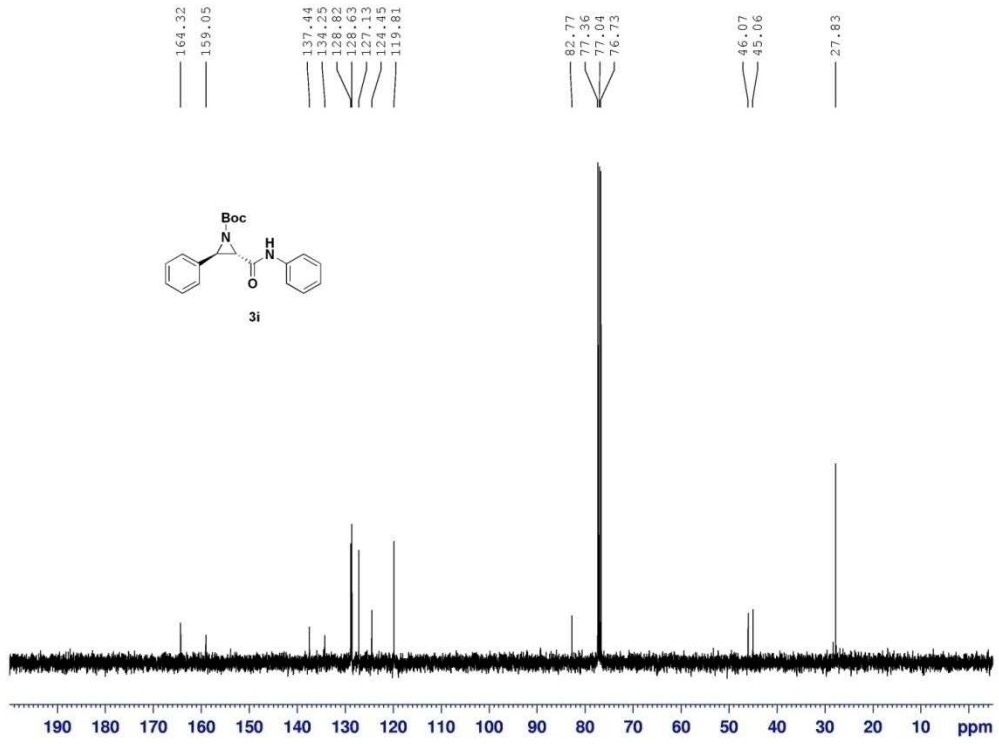
1 PDA Multi 3 / 254nm 4nm

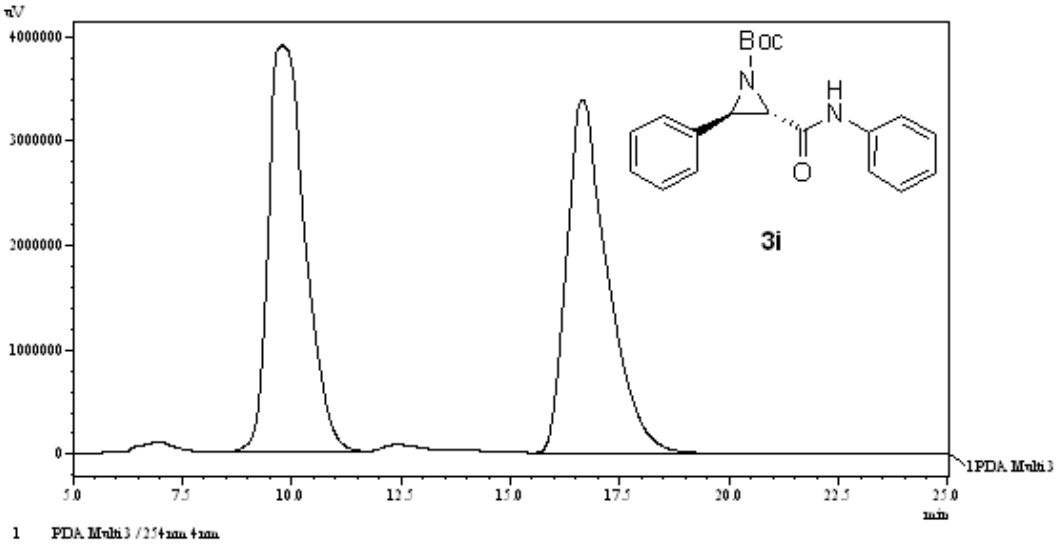
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	6.572	1069689	29404	1.094
2	12.666	96674214	1446984	98.906
Total		97743903	1476388	100.000


8.063
7.560
7.540
7.387
7.374
7.357
7.338
7.325
7.319
7.306
7.300
7.261
7.138
7.120
3.830
3.823
3.500
3.493
1.567
1.304
Boc
N
H
N
O
3i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.95
2.09
7.35
1.11
1.00
1.02
8.92


164.32
159.05
137.44
134.25
128.82
128.63
127.13
124.45
119.81
82.77
77.36
77.04
76.73
46.07
45.06
27.83
Boc
N
H
N
O
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

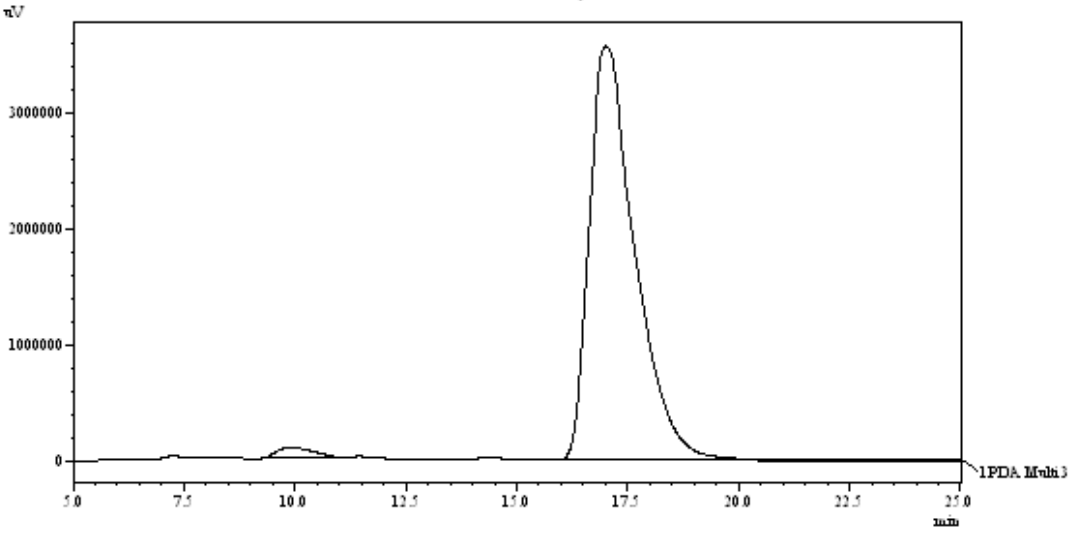


1 PDA Multi 3 / 254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.768	225893778	3882836	50.670
2	16.653	219923102	3384703	49.330
Total		445816879	7267539	100.000

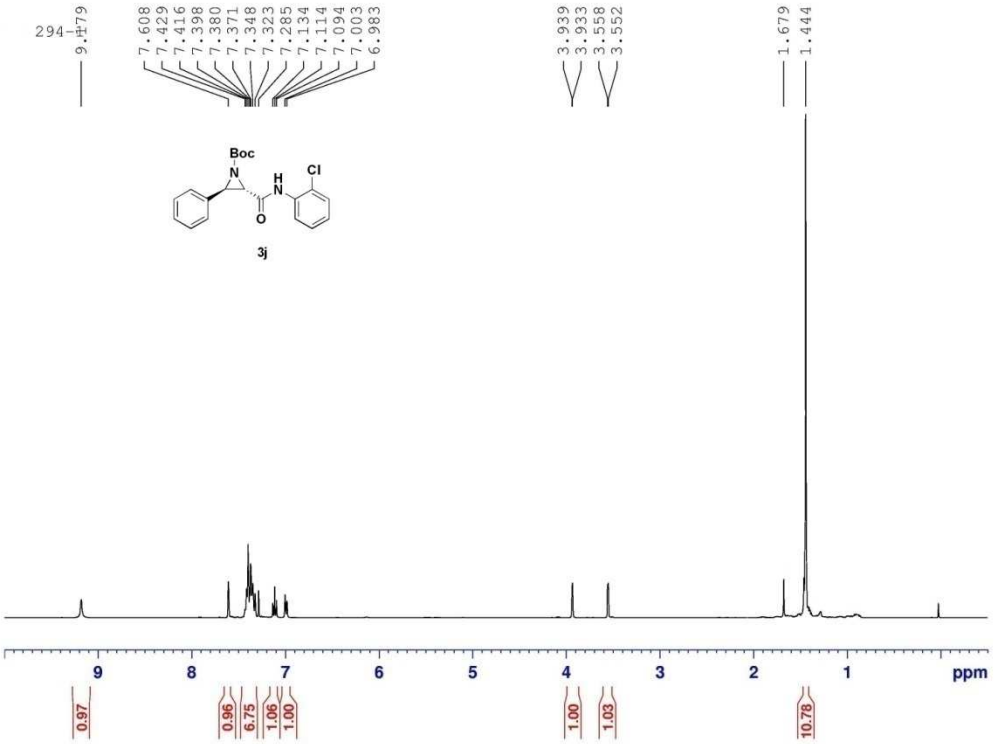


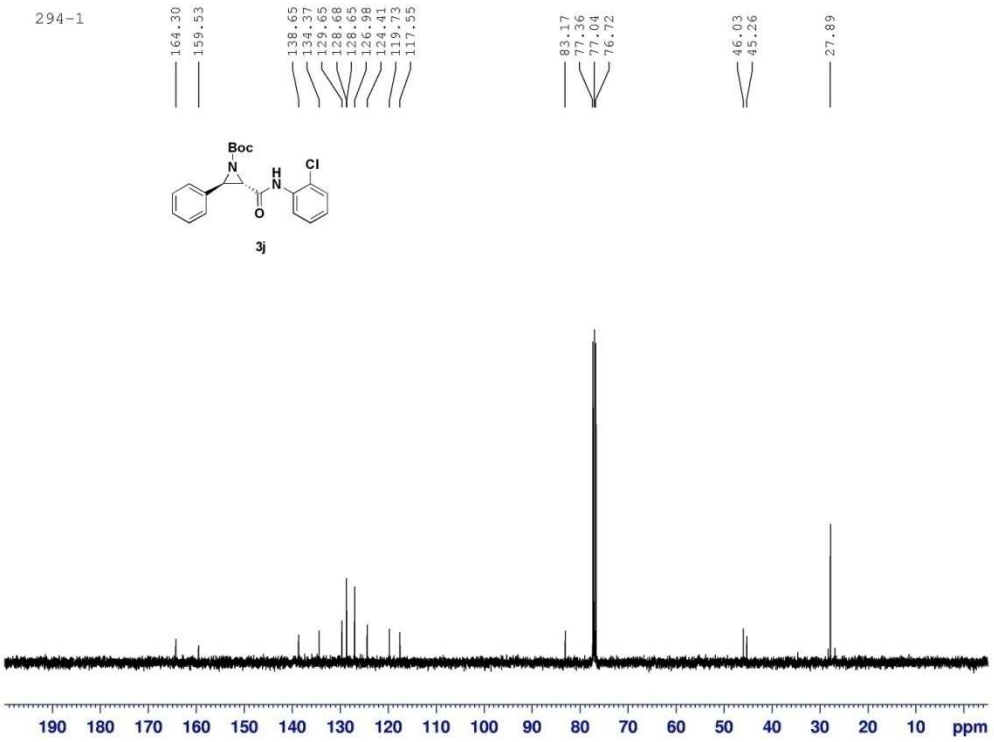
1 PDA Multi 3 / 254nm 4nm

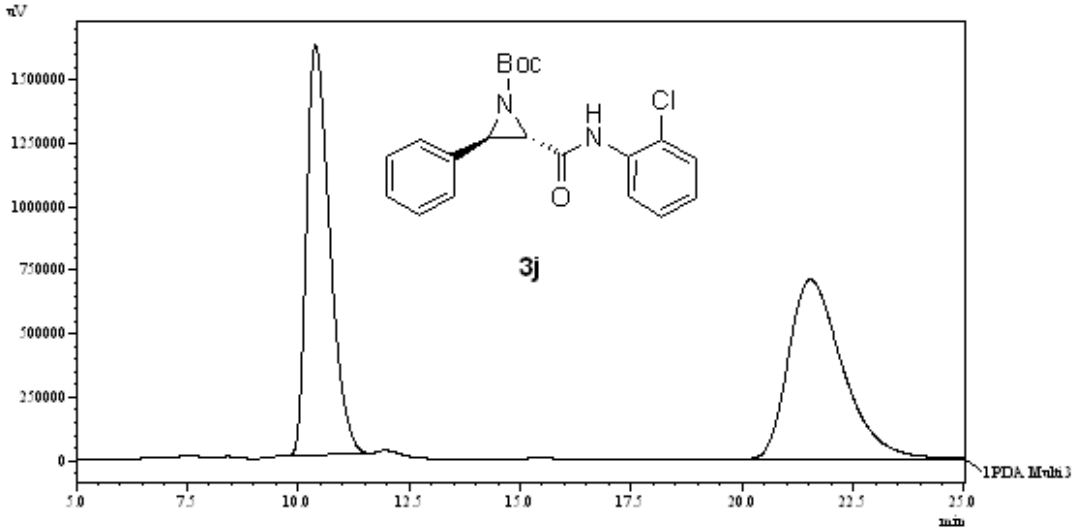
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.908	4653620	84224	1.785
2	16.997	256083663	3578496	98.215
Total		260737284	3662721	100.000


294-1
9.179
7.608
7.429
7.416
7.398
7.380
7.371
7.348
7.323
7.285
7.134
7.114
7.094
7.003
6.983
3.939
3.933
3.558
3.552
1.679
1.444
Boc
N
H
N
Cl
O
3j
9
8
7
6
5
4
3
2
1
ppm
0.97
0.96
6.75
1.06
1.00
1.00
1.03
10.78


294-1
164.30
159.53
138.65
134.37
129.65
128.68
128.65
126.98
124.41
119.73
117.55
83.17
77.36
77.04
76.72
46.03
45.26
27.89
Boc
N
H
N
Cl
O
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

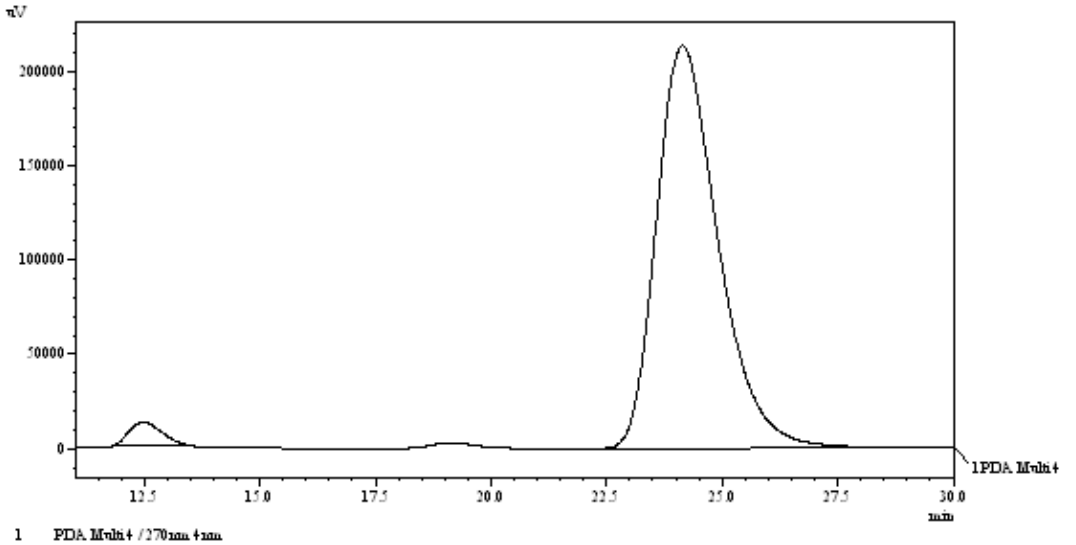


1 PDA Mvlh3 /254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.395	58631640	1612529	49.224
2	21.535	60479875	709880	50.776
Total		119111515	2322409	100.000

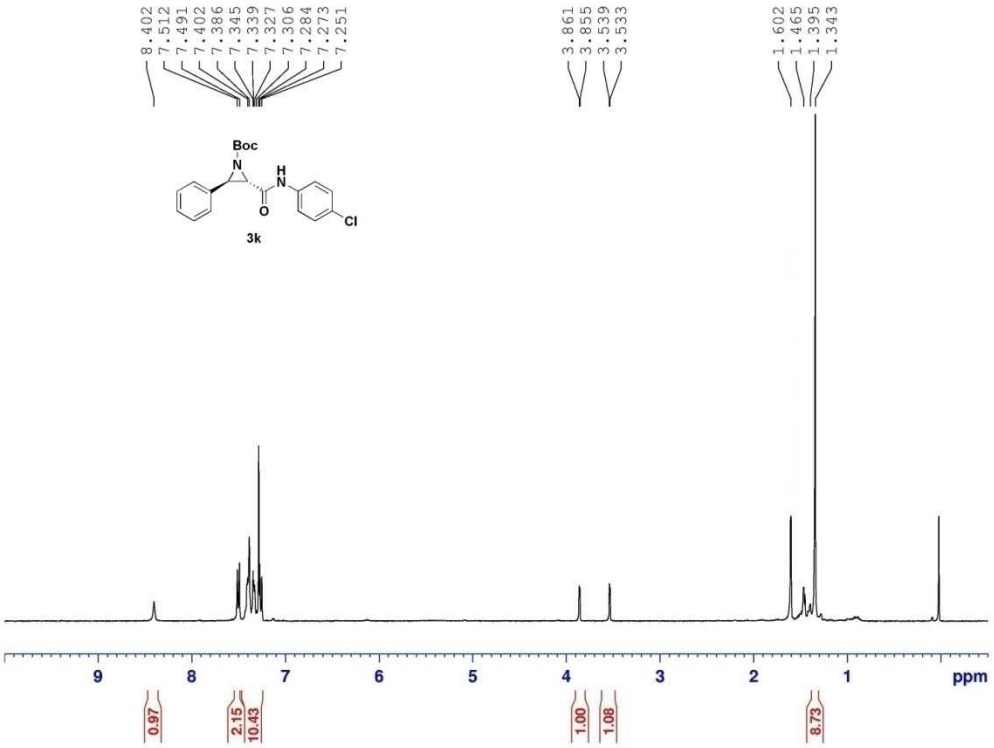


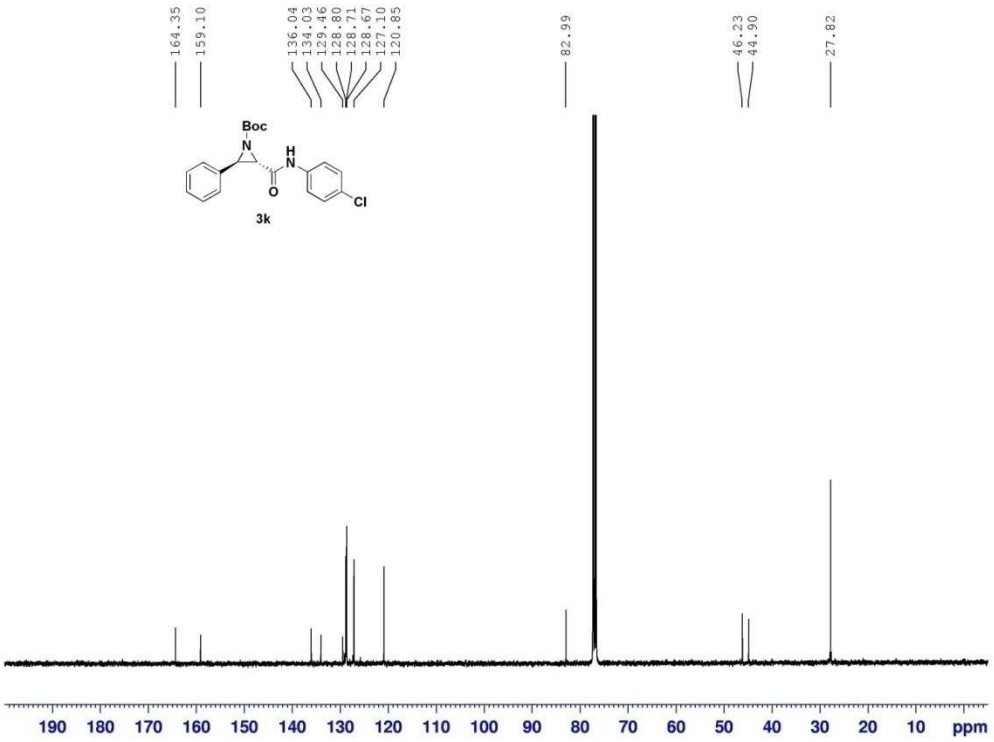
1 PDA Mvlh4 /270nm 4nm

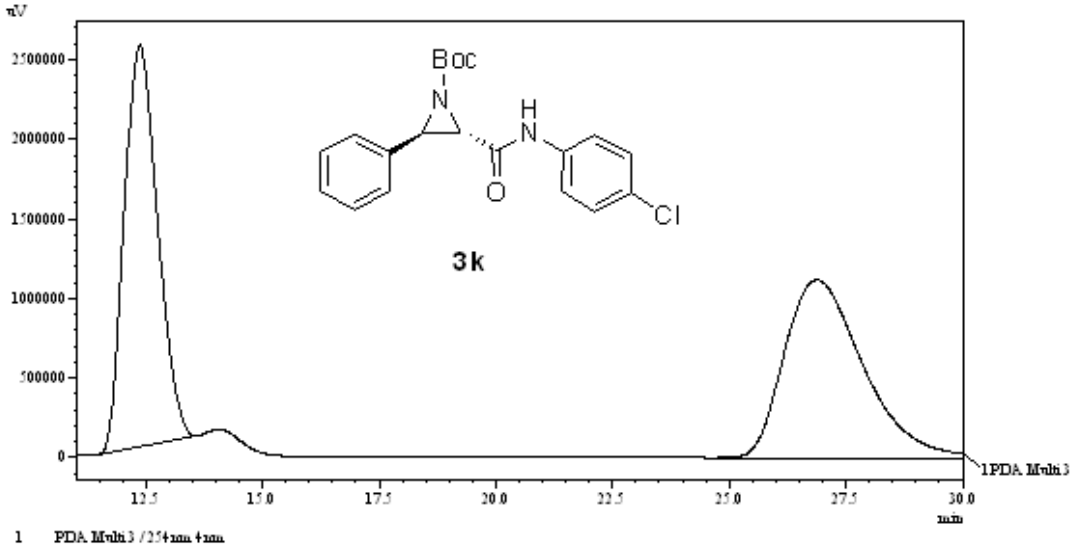
Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.468	601916	12270	2.951
2	24.136	19798129	213267	97.049
Total		20400045	225536	100.000


8.402
7.512
7.491
7.402
7.386
7.345
7.339
7.327
7.306
7.284
7.273
7.251
3.861
3.855
3.539
3.533
1.602
1.465
1.395
1.343
Boc
N
H
N
O
Cl
3k
9
8
7
6
5
4
3
2
1
ppm
0.97
2.15
10.43
1.00
1.08
8.73

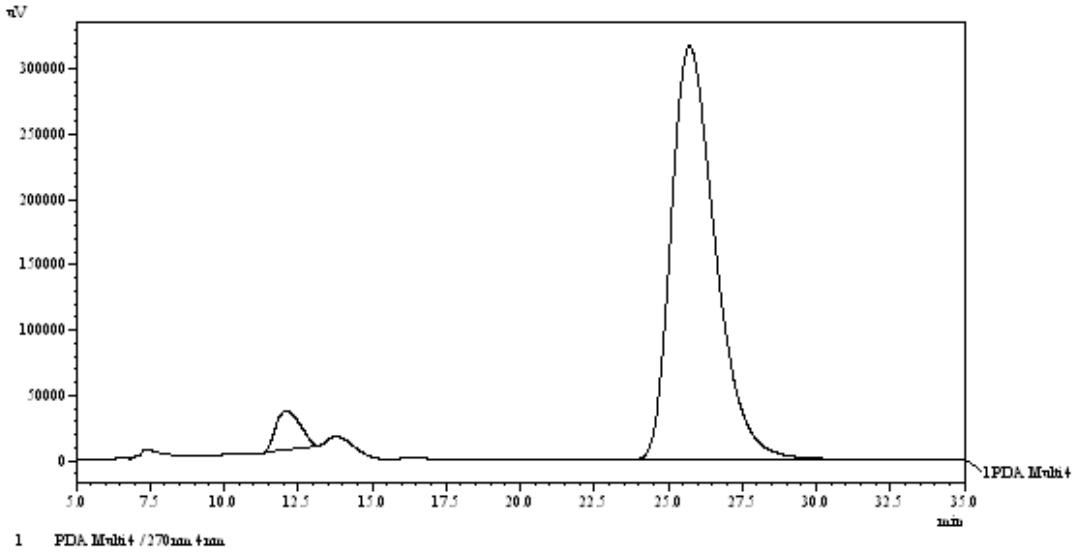

164.35
159.10
136.04
134.03
129.46
128.80
128.71
128.67
127.10
120.85
82.99
46.23
44.90
27.82
Boc
N
H
N
O
Cl
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



Peak Table

PDA Ch3 254nm 4nm

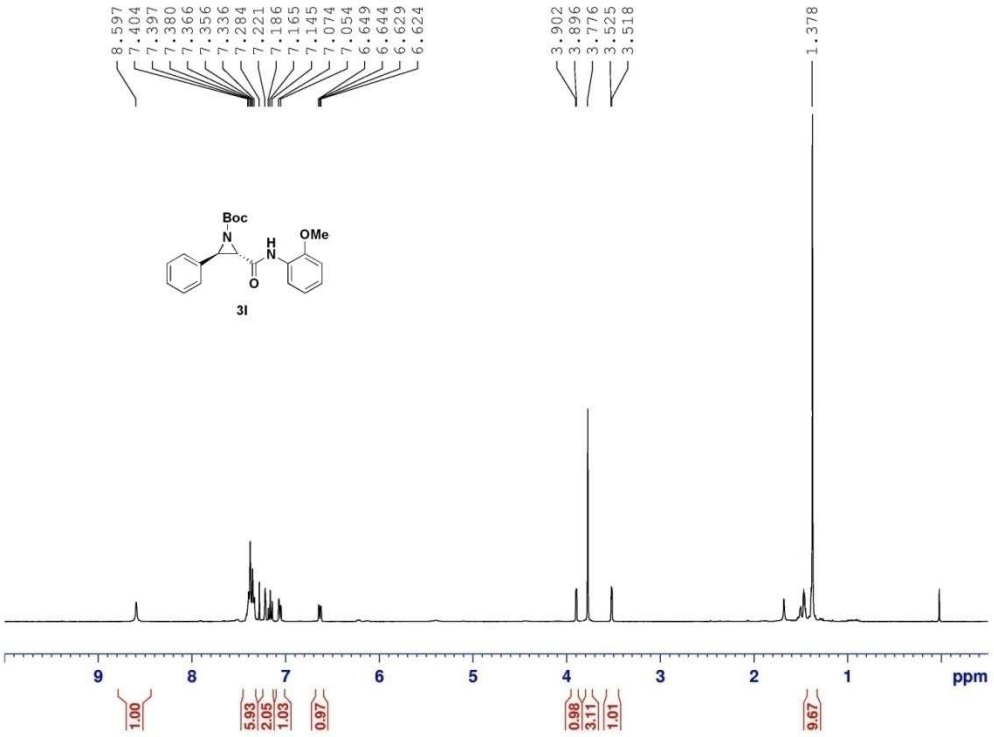
Peak#	Ret. Time	Area	Height	Area %
1	12.370	125557088	2523376	48.751
2	26.876	131989087	1117903	51.249
Total		257546175	3641278	100.000

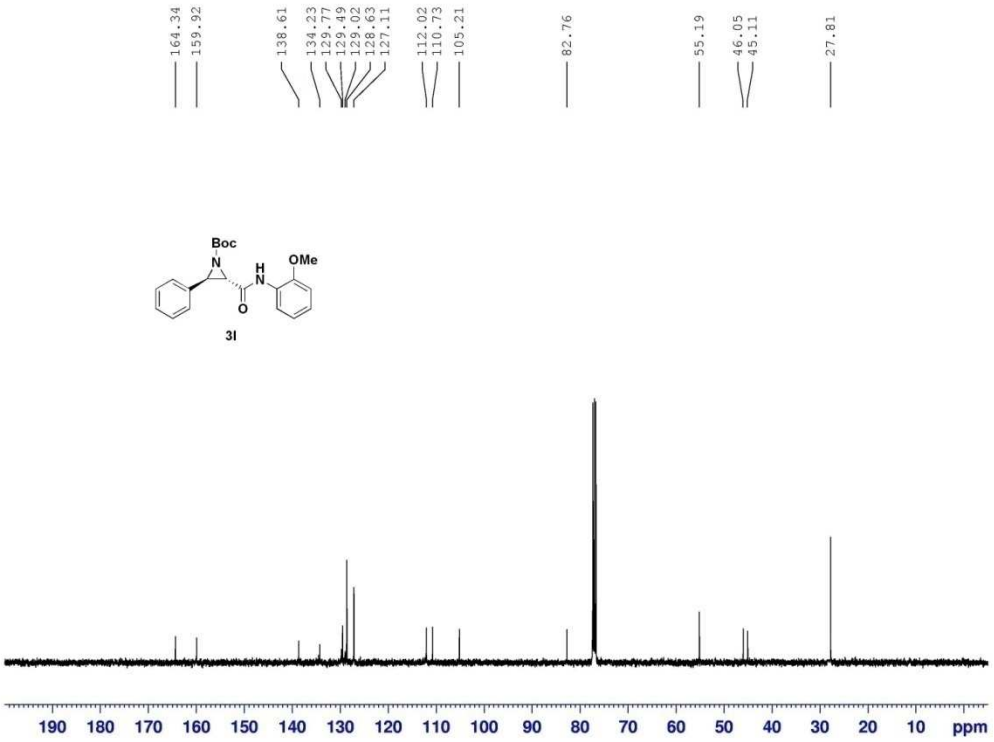


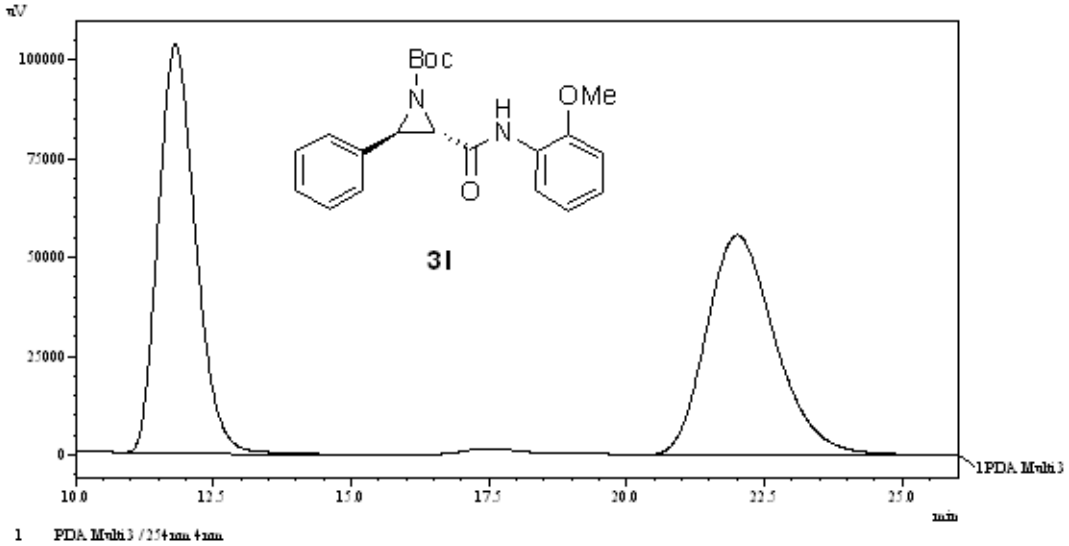
Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.094	1659819	29212	4.815
2	25.717	32809350	316619	95.185
Total		34469169	345831	100.000


8.597
7.404
7.397
7.380
7.366
7.356
7.336
7.284
7.221
7.186
7.165
7.145
7.074
7.054
6.649
6.644
6.629
6.624
3.902
3.896
3.776
3.525
3.518
1.378
Boc
N
H
N
OMe
O
3l
9
8
7
6
5
4
3
2
1
ppm
1.00
5.93
2.05
1.03
0.97
0.98
3.11
1.01
9.67


164.34
159.92
138.61
134.23
129.77
129.49
129.02
128.63
127.11
112.02
110.73
105.21
82.76
55.19
46.05
45.11
27.81
Boc
N
H
N
OMe
O
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



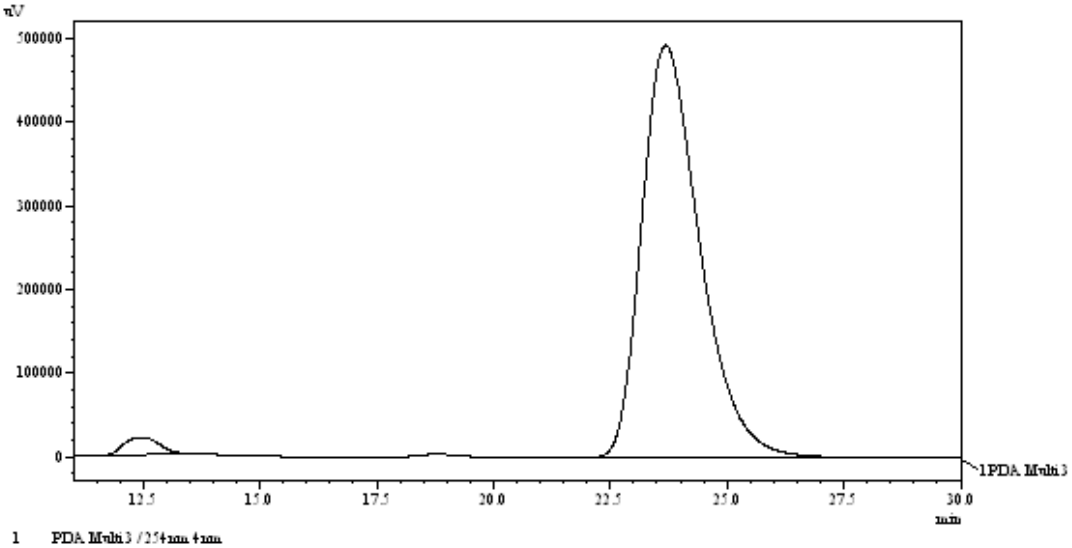
3l

1 PDA Multi 3 / 254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	11.811	4860390	103160	50.366
2	21.999	4789842	55536	49.634
Total		9650232	158696	100.000

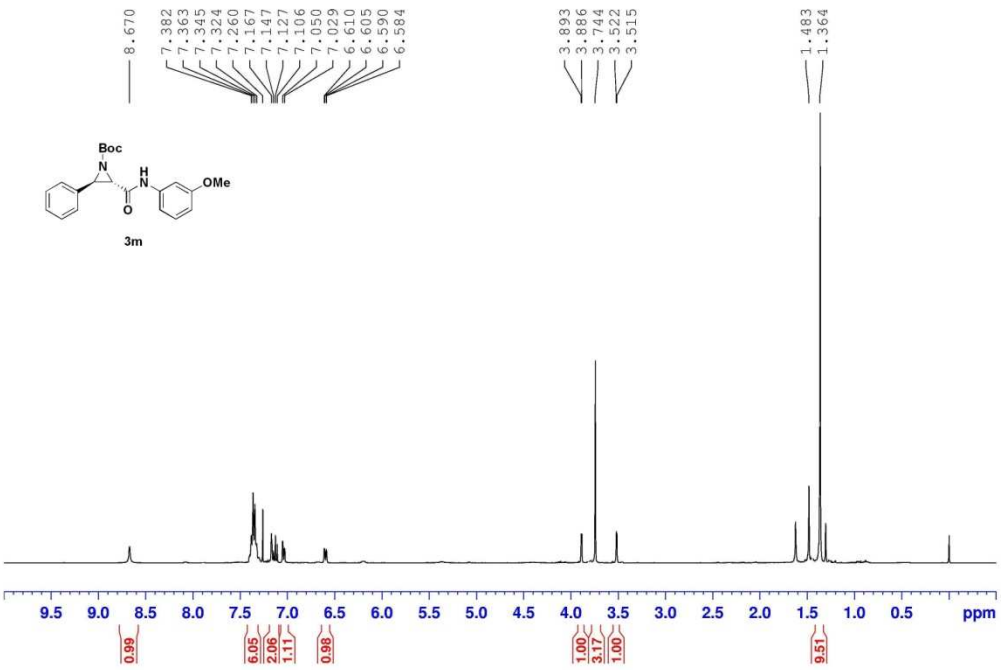


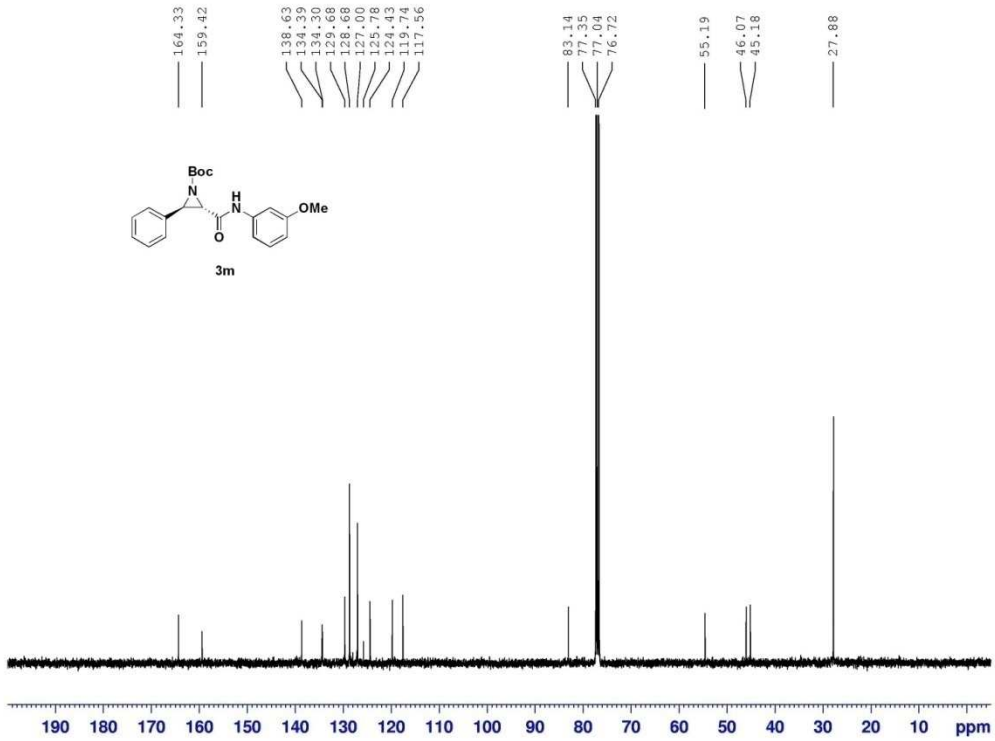
1 PDA Multi 3 / 254nm 4nm

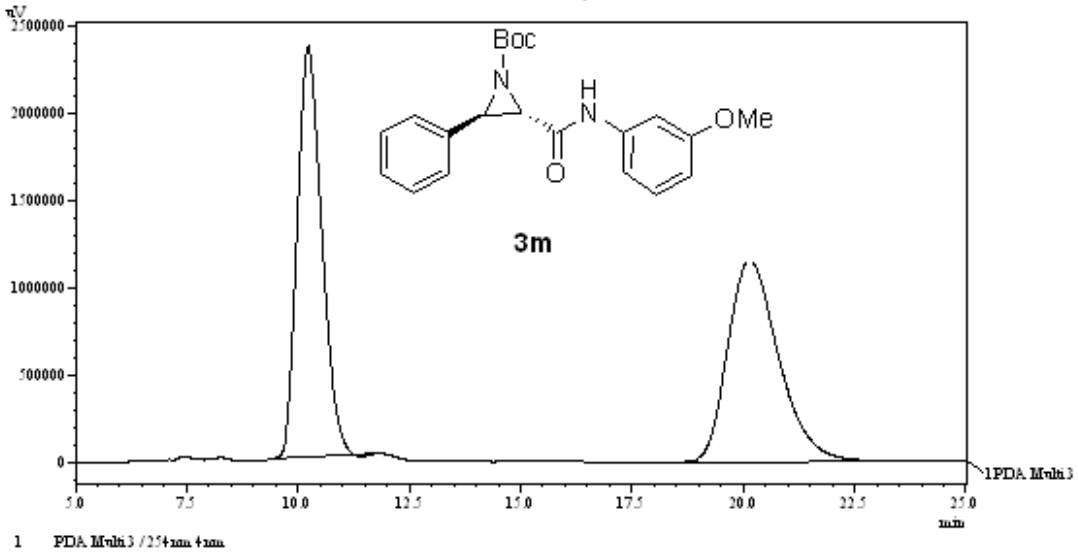
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.371	1036615	19418	2.363
2	23.683	42832120	493203	97.637
Total		43868735	512621	100.000


8.670
7.382
7.363
7.345
7.324
7.260
7.167
7.147
7.127
7.106
7.050
7.029
6.610
6.605
6.590
6.584
3.893
3.886
3.744
3.522
3.515
1.483
1.364
Boc
N
H
N
OMe
O
3m
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
6.05
2.06
1.11
0.98
1.00
3.17
1.00
9.51


164.33
159.42
138.63
134.39
134.30
129.68
128.68
127.00
125.78
124.43
119.74
117.56
83.14
77.35
77.04
76.72
55.19
46.07
45.18
27.88
Boc
N
H
N
OMe
O
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

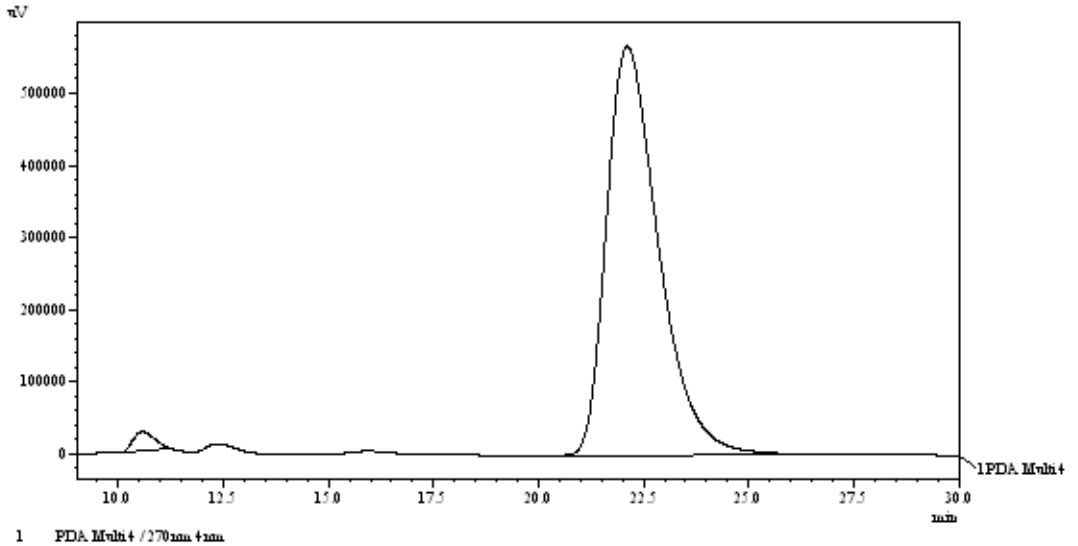


1 PDA Multi 3 /254nm 4nm

Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.226	90621639	2359738	49.610
2	20.139	92047991	1158247	50.390
Total		182669630	3517985	100.000

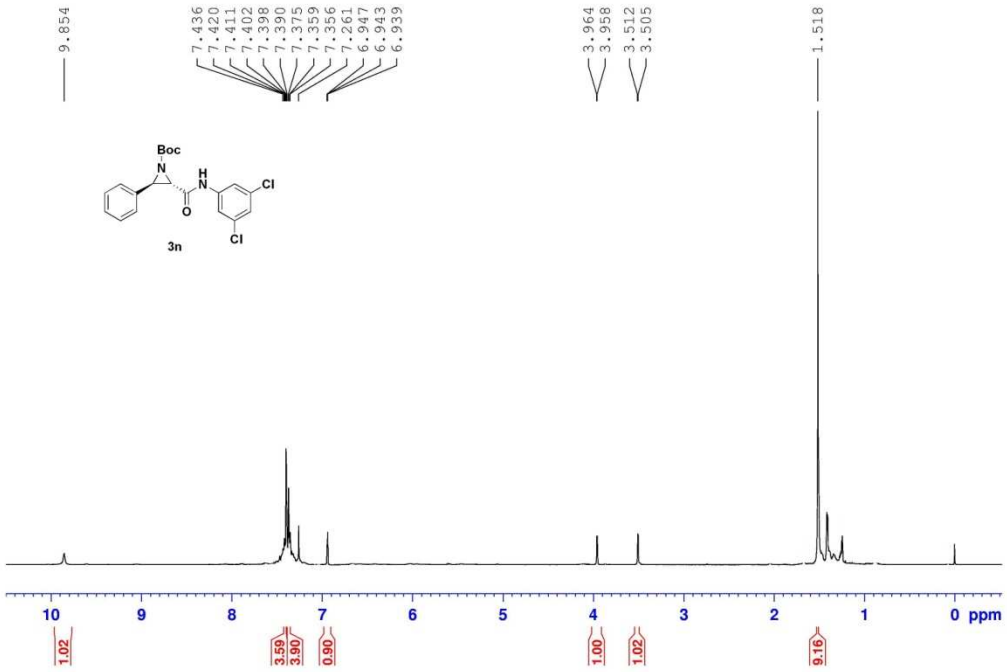


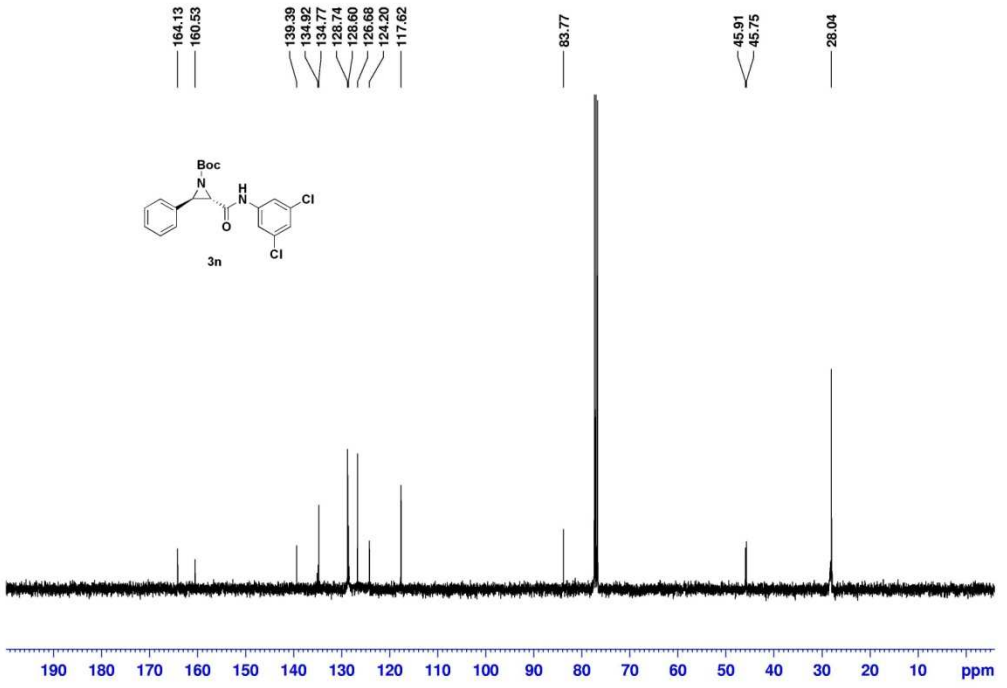
1 PDA Multi 4 /270nm 4nm

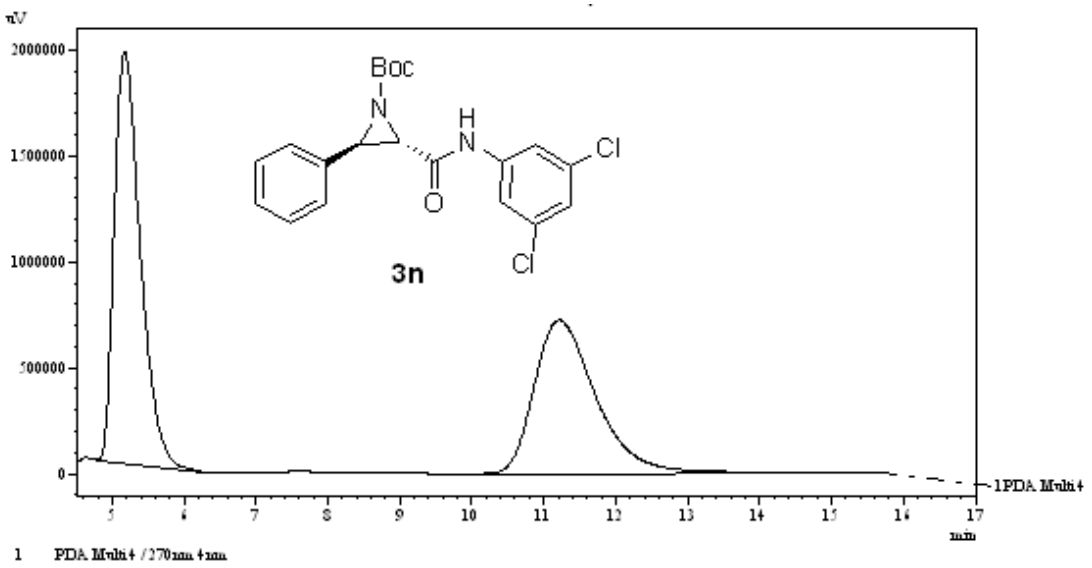
Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.562	904854	25683	1.816
2	22.109	48923823	566742	98.184
Total		49828677	592425	100.000


9.854
7.436
7.420
7.411
7.402
7.398
7.390
7.375
7.359
7.356
7.261
6.947
6.943
6.939
3.964
3.958
3.512
3.505
1.518
Boc
N
H
N
O
Cl
Cl
3n
10
9
8
7
6
5
4
3
2
1
0 ppm
1.02
3.59
3.90
0.90
1.00
1.02
9.16


164.13
160.53
139.39
134.92
134.77
128.74
128.60
126.68
124.20
117.62
83.77
45.91
45.75
28.04
Boc
N
H
N
O
Cl
Cl
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

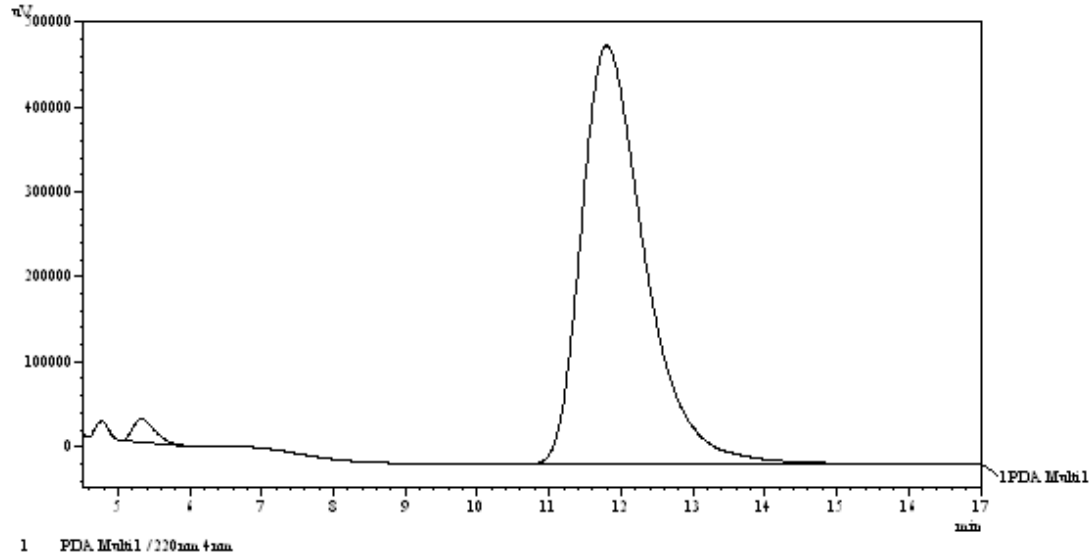


1 PDA Multi4 / 270nm 4nm

Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	5.173	49054850	1936254	52.981
2	11.211	43533976	724525	47.019
Total		92588826	2660779	100.000

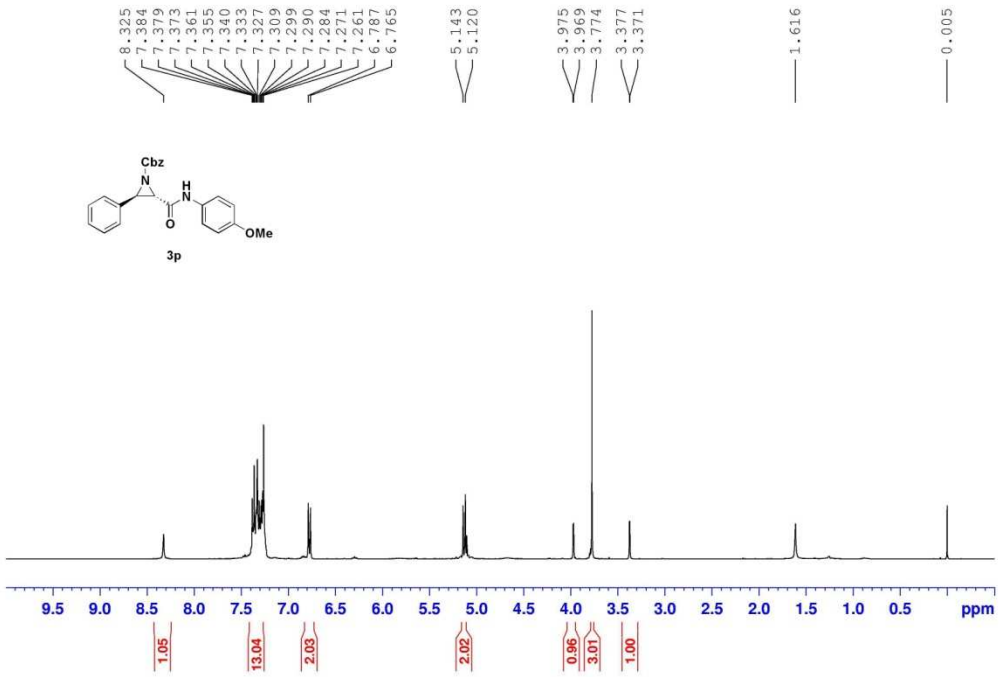


1 PDA Multi1 / 220nm 4nm

Peak Table

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	5.319	572920	27320	1.870
2	11.798	30061914	492261	98.130
Total		30634835	519581	100.000


8.325
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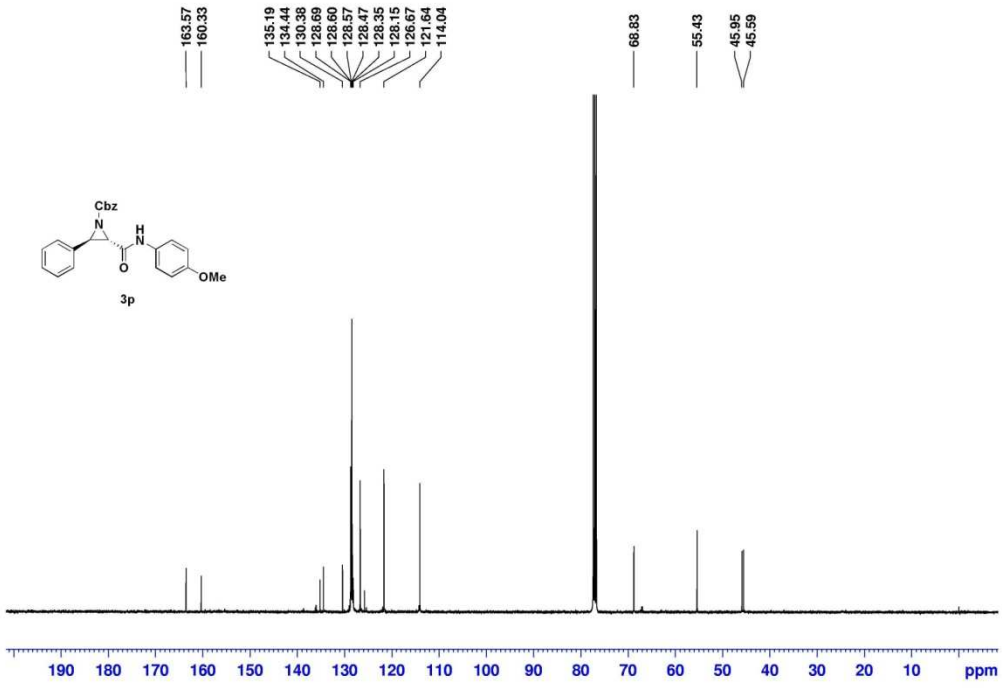
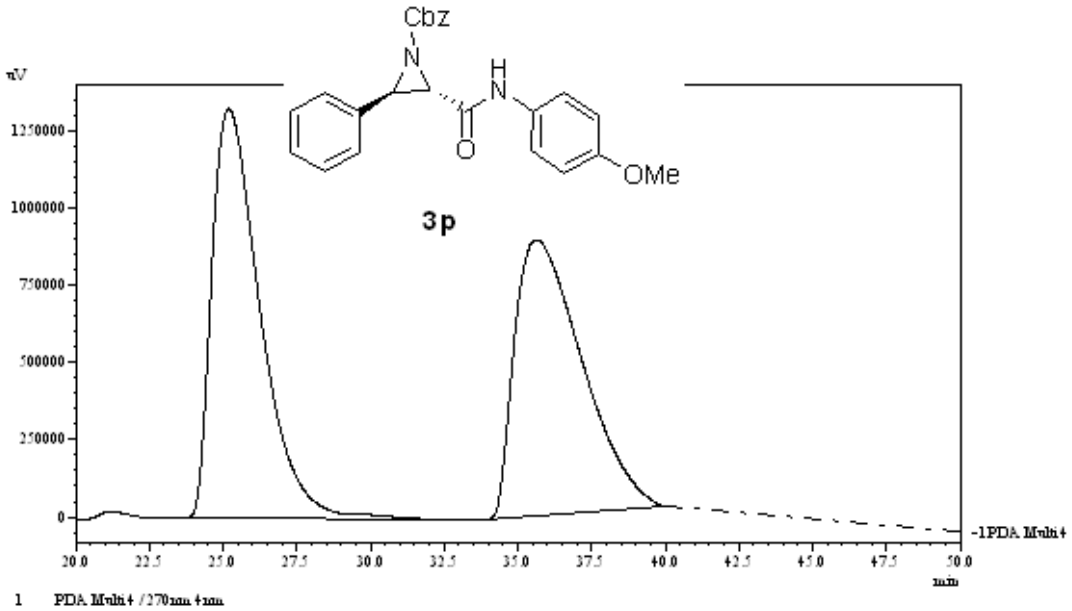
7.379
7.373
7.361
7.355
7.340
7.333
7.327
7.309
7.299
7.290
7.284
7.271
7.261
6.787
6.765
5.143
5.120
3.975
3.969
3.774
3.377
3.371
1.616
0.005
Cbz
N
H
N
O
OMe
3p
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.05
13.04
2.03
2.02
0.96
3.01
1.00

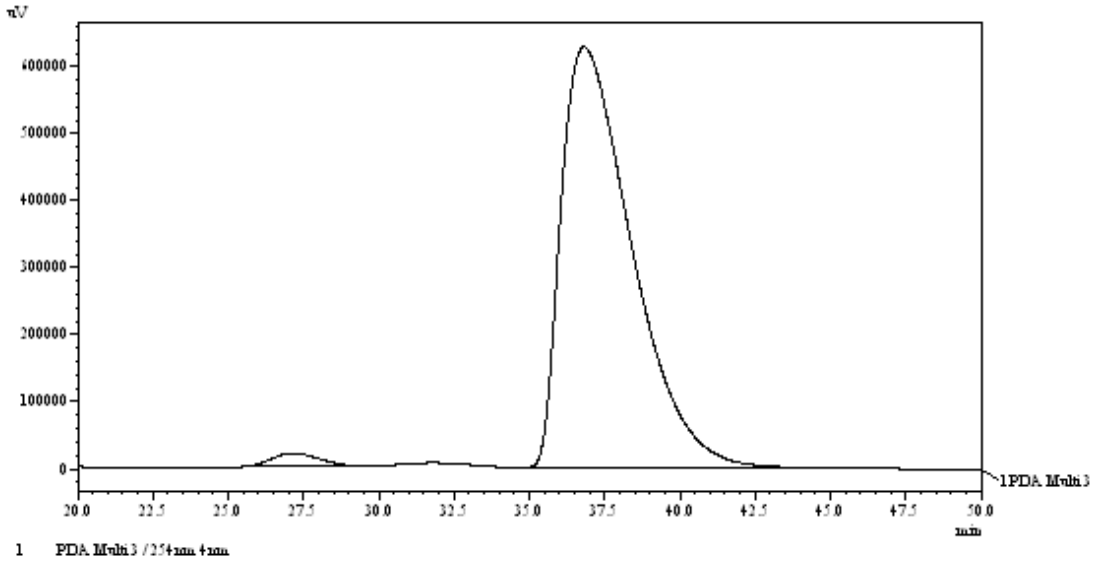

163.57
160.33
135.19
134.44
130.38
128.69
128.60
128.57
128.47
128.35
128.15
126.67
121.64
114.04
68.83
55.43
45.95
45.59
Cbz
N
H
N
O
OMe
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



Peak Table

PDA Ch4 270nm 4nm

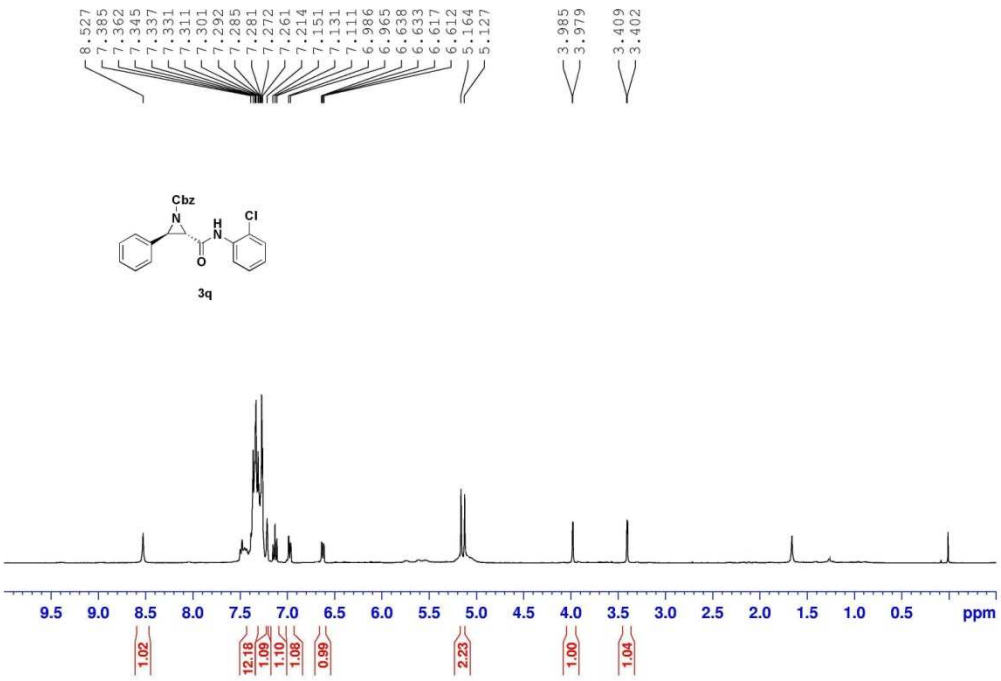
Peak#	Ret. Time	Area	Height	Area %
1	25.193	152853809	1331952	51.703
2	35.623	142782975	898177	48.297
Total		295636784	2230128	100.000

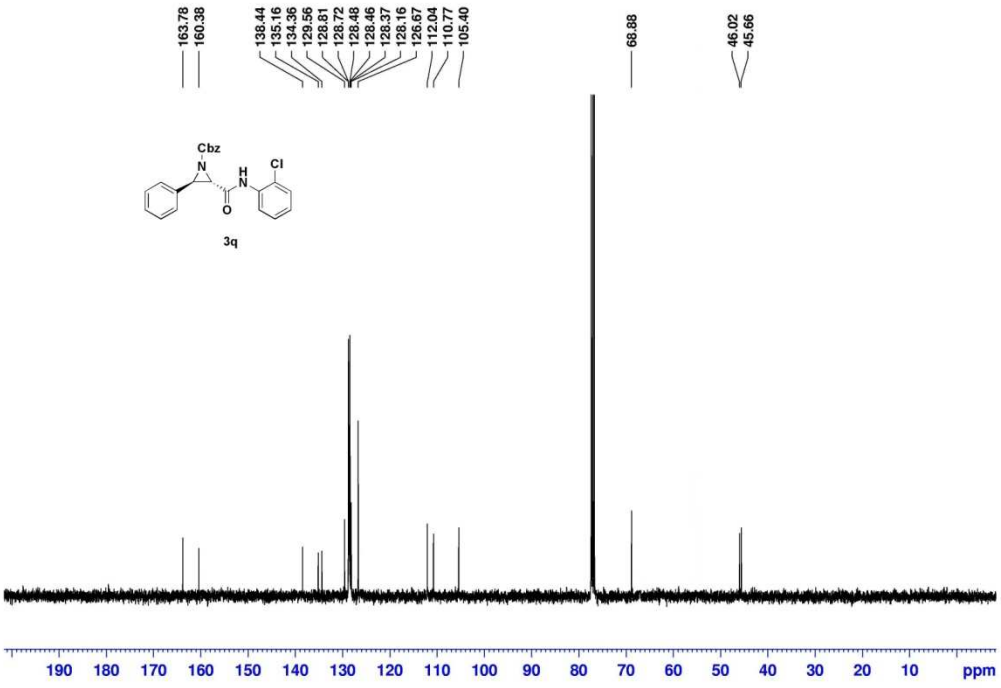


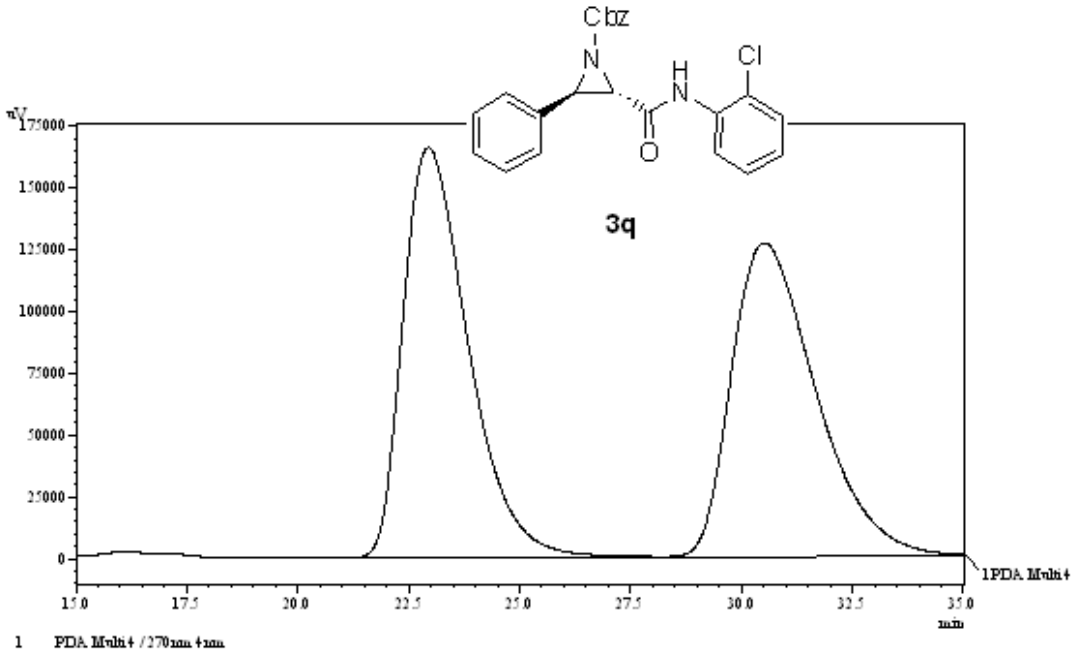
Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	27.157	1963306	18580	1.871
2	36.814	102968780	628324	98.129
Total		104932086	646904	100.000


8.527
7.385
7.362
7.345
7.337
7.331
7.311
7.301
7.292
7.285
7.281
7.272
7.261
7.214
7.151
7.131
7.111
6.986
6.965
6.638
6.633
6.617
6.612
5.164
5.127
3.985
3.979
3.409
3.402
Cbz
N
H
N
Cl
O
3q
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
12.16
1.09
1.10
1.08
0.99
2.23
1.00
1.04

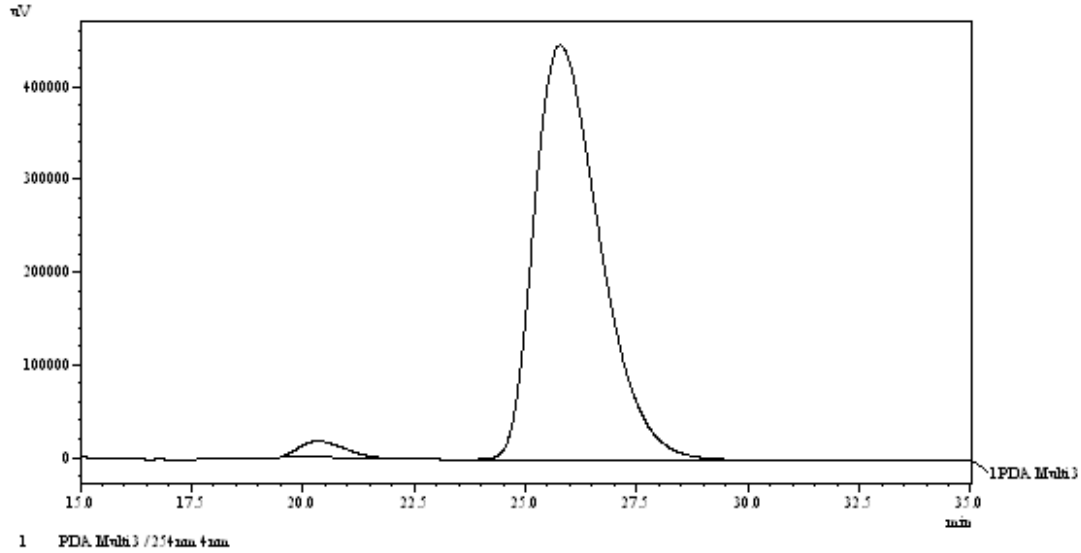

163.78
160.38
138.44
135.16
134.36
129.56
128.81
128.72
128.48
128.46
128.37
128.16
126.67
112.04
110.77
105.40
68.88
46.02
45.66
Cbz
N
H
N
Cl
O
3q
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



Peak Table

PDA Ch4 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	22.943	16949000	165850	50.106
2	30.511	16877124	126901	49.894
Total		33826123	292751	100.000



Peak Table

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.345	1211251	17477	2.570
2	25.779	45917033	447388	97.430
Total		47128284	464865	100.000