Supporting Information for:

Highly Enantioselective *L*-Thiaproline catalyzed *α*-Aminoxylation of Aldehydes in Aqueous Media

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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 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.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). 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 $SiMe_4$ (δ 0.0, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) 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. Carbon nuclear magnetic resonance spectra (^{13}C NMR) 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 77.03, triplet).

Enantioselectivities were determined by High Performance Liquid Chromatography (HPLC) analysis employing a Daicel Chirapak AD-H (0.46cm x 25 cm), OD-H (0.46cm x 25 cm) or OJ-H (0.46cm x 25 cm) column.

Optical rotations were measured in $CHCl_3$ on a *Schmidt + Haensdch* polarimeter (Polartronic MH8) with a 1 cm cell (*c* given in g/100 mL). Absolute configuration of the products was determined by comparison with compounds previously published.

Aldehydes **1i** and **1j** were prepared according to literature procedures.[1, 2] The enantiomers used to determine the ee values were synthesized with DL-proline as catalyst. All other reagents were available from commercial sources and used without further purification.

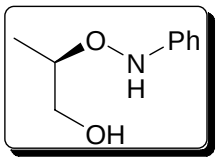
General experimental procedure for the *α*-aminoxylation of aldehydes to nitrosobenzene in the presence of water:

Water (0.10 mL) and tetrabutylammonium bromide (193.4 mg, 0.6 mmol) was added to a 5 mL drum vial containing nitrosobenzene **2** (32.1 mg, 0.3 mmol), corresponding aldehydes **1** (0.9 mmol) and a magnetic stirring bar. After stirring for 5 min at 0 °C, L-thiaproline (8 mg, 0.06 mmol) was then added. The reaction was first stirred at this temperature for about 10 min and then at room temperature until the green solution turned yellow which indicated complete consumption of the nitrosobenzene. As the *α*-aminoxy aldehyde product is rather labile, isolation and characterization was performed after conversion to the corresponding *α*-aminoxy alcohol **3** by treatment of the reaction mixture with $NaBH_4$. The excess $NaBH_4$ was quenched by the addition of water and then extracted with CH_2Cl_2 (3 x 30 ml). The combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The crude oil was purified by flash column chromatography (Hexane:EtOAc = 9/1~7/3) yielding pure *α*–aminoxy alcohols **3**.

Relative and absolute configurations of the products were compared with the known ^1H NMR, chiral HPLC analysis, and optical rotation values. The compounds in Table 3 are known in the literature.

Experimental data of Compounds 3a-3k

(*R*)-2-(N-phenylaminoxy)propan-1-ol (**3a**) [3]



α-aminoxy alcohol **3a** was prepared according to the general procedure from propanal (0.07 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (42.3 mg, 84% yield) after flash column chromatography on silica gel (Hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (2H, m), 7.04-6.96 (3H, m), 4.16-4.08 (1H, m), 3.80-3.70 (2H, m), 2.56 (1H, brs), 1.25 (3H, d, J = 6.4 Hz).

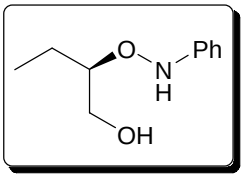
^{13}C NMR (100 MHz, $CDCl_3$): 148.5, 129.0, 122.4, 114.7, 80.0, 66.5, 15.4.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 10.6 min, t_R (major) =12.1 min; 96% ee.

$[\alpha]_D^{25}$ = + 2.9 (c = 1.0, $CHCl_3$).

(*R*)-2-(N-phenylaminoxy)butan-1-ol (**3b**) [3]



α-aminoxy alcohol **3b** was prepared according to the general procedure from butanal (0.08 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (40.9 mg, 75% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (2H, m), 7.07-6.96 (2H, m), 3.91-3.74 (3H, m), 2.67 (1H, brs), 1.78-1.53 (2H, m), 1.01 (3H, t, J = 7.5 Hz).

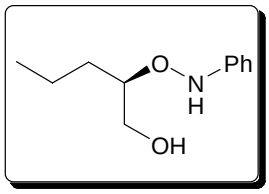
^{13}C NMR (100 MHz, $CDCl_3$): 148.4, 129.0, 122.4, 114.8, 85.3, 64.9, 22.9, 10.1.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 10.2 min, t_R (major) =11.6 min; 98% ee.

$[\alpha]_D^{23}$ = + 36.0 (c = 1.0, $CHCl_3$).

(*R*)-2-(N-phenylaminoxy)pentan-1-ol (**3c**) [3]



α-aminoxy alcohol **3c** was prepared according to the general procedure from pentanal (0.10 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (46.0 mg, 79% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.15 (3H, m), 6.98-6.94 (2H, m), 3.94-3.91 (1H, m), 3.85-3.82 (1H, m), 3.75-3.71 (1H, m), 2.93 (1H, brs), 1.67-1.61 (1H, m), 1.54-1.33 (3H, m), 0.97-0.89 (3H, m).

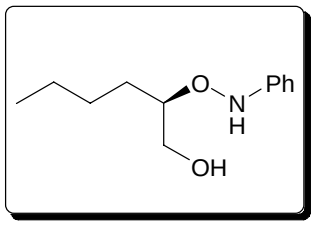
^{13}C NMR (100 MHz, $CDCl_3$): 148.4, 129.0, 122.3, 114.7, 83.7, 65.1, 32.0, 19.0, 14.2.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 10.0 min, t_R (major) =11.4 min; 97% ee.

$[\alpha]_D^{23}$ = + 28.6 (*c* = 1.0, $CHCl_3$).

(*R*)-2-(N-phenylaminoxy)hexan-1-ol (**3d**) [4]



α-aminoxy alcohol **3d** was prepared according to the general procedure from hexanal (0.11 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (46.4 mg, 74% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (2H, m), 7.06-6.96 (3H, m), 3.98-3.92 (1H, m), 3.87-3.84 (1H, m), 3.79-3.72 (1H, m), 2.68 (1H, brs), 1.69-1.50 (1H, m), 1.47-1.30 (4H, m), 0.92 (3H, t, *J* = 7.1 Hz).

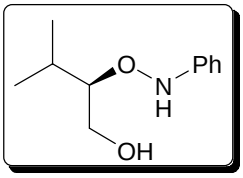
^{13}C NMR (100 MHz, $CDCl_3$): 148.4, 129.0, 122.5, 114.9, 84.0, 65.4, 29.6, 27.9, 22.0, 14.0.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 9.5 min, t_R (major) =11.4 min; 96% ee.

$[\alpha]_D^{23}$ = + 22.5 (*c* = 1.2, $CHCl_3$).

(*R*)-3-methyl-2-(N-phenylaminoxy)butan-1-ol (**3e**) [4]



α-aminoxy alcohol **3e** was prepared according to the general procedure from 3-methybutanal (0.10 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (44.8 mg, 76% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m), 7.03-6.99 (3H, m), 3.88-3.87 (2H, m), 3.76-3.74 (1H, m), 2.07-1.99 (1H, m), 1.05 (3H, d, J = 6.9 Hz), 1.01 (3H, d, J = 6.9 Hz).

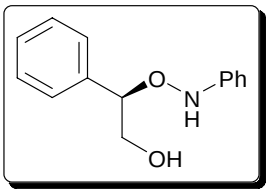
^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 129.0, 122.5, 115.0, 88.6, 63.6, 28.7, 18.7, 18.6.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 9.0 min, t_R (major) =10.1mins; 97% ee.

$[\alpha]_D^{22}$ = + 33.4 (c = 1.0, $CHCl_3$).

(*R*)-2-phenyl-2-(N-phenylaminoxy)ethanol (**3f**) [3]



α-aminoxy alcohol **3f** was prepared according to the general procedure from 2-phenylacetaldehyde (0.11 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (53.5 mg, 78% yield) after flash column chromatography on silica gel (hexane:ether = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (5H, m), 7.28-7.20 (2H, m), 6.99-6.94 (3H, m), 5.00 (1H, dd, J = 3.5, 8.1Hz), 3.99-3.92 (1H, m), 3.83-3.78 (1H, m), 2.58 (1H, brs).

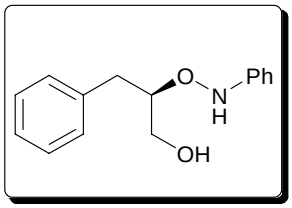
^{13}C NMR (100 MHz, $CDCl_3$): 147.9, 137.7, 129.0, 128.7, 128.5, 127.0, 122.5, 115.0, 86.4, 66.4.

HPLC: Chiralpak OD-H (hexane/*i*-PrOH, 95/5, flow rate 1 mL/min, λ= 230 nm),

t_R (major) = 25.8mins, t_R (minor) =30.2 min; 93% ee.

$[\alpha]_D^{24}$ = - 85.5 (c = 1.1, $CHCl_3$).

(*R*)-3-phenyl-2-(N-phenylaminoxy)propan-1-ol (**3g**) [3]



α-aminoxy alcohol **3g** was prepared according to the general procedure from 3-phenylpropanal (0.12 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (55.9 mg, 77% yield) after flash column chromatography on silica gel (hexane:ether = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.18 (6H, m), 7.08 (1H, brs), 6.94 (1H, t, J = 7.3 Hz), 6.82 (2H, d, J = 8.0 Hz), 4.16-4.10 (1H, m), 3.85 (1H, d, J = 11.8 Hz), 3.04 (1H, dd, J = 6.8, 13.7 Hz), 2.84 (1H, dd, J = 7.0, 13.7 Hz), 2.62 (1H, brs).

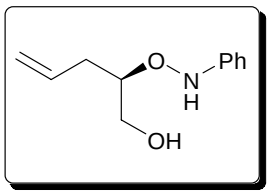
^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 137.8, 129.4, 128.9, 128.5, 126.4, 122.3, 114.6, 85.0, 64.1, 36.4.

HPLC: Chiralpak OD-H (hexane/*i*-PrOH, 91/9, flow rate 1 mL/min, λ= 230 nm),

t_R (major) = 57.9 min, t_R (minor) =62.4 min; >99% ee.

$[\alpha]_D^{22}$ = +55.2 (c = 1.3, $CHCl_3$).

(*R*)-2-(N-phenylaminoxy)pent-4-en-1-ol (**3h**) [4]



α-aminoxy alcohol **3h** was prepared according to the general procedure from 4-pentenal (0.09 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (51.0 mg, 88% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (2H, m), 7.06-6.96 (3H, m), 5.93-5.82 (1H, m), 5.18-5.11 (2H, m), 4.05-4.00 (1H, m), 3.87-3.75 (2H, m), 2.54-2.32 (3H, m), 1.66 (1H, brs).

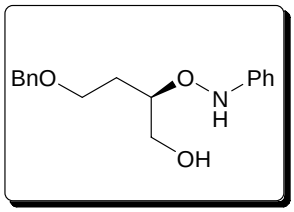
^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 134.0, 129.0, 122.5, 117.8, 114.8, 83.3, 64.6, 34.6.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 10.5 min, t_R (major) =12.5 min; 96% ee.

$[\alpha]_D^{23}$ = - 22.9 (c = 1.0, $CHCl_3$).

(*R*)-4-(benzyloxy)-2-(N-phenylaminoxy)butan-1-ol (new compound) (**3i**)



α-aminoxy alcohol **3i** was prepared according to the general procedure from 4-(benzyloxy)butanal (0.16 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (73.8 mg, 86% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.23 (6H, m), 7.05 (1H, brs), 6.98-6.94 (3H, m), 4.54-4.52 (2H, m), 4.14-4.11 (1H, m), 3.93- 3.87 (1H, m), 3.81-3.77 (1H, m), 3.66 (2H, t, J = 5.7 Hz), 2.81 (1H, t, J = 5.9 Hz), 2.06-1.89 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 138.0, 129.0, 128.5, 127.8, 122.4, 116.1, 114.8, 81.5, 73.2, 66.7, 64.8, 30.3.

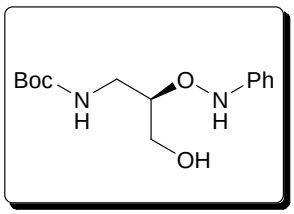
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 91/9, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 18.8 min, t_R (major) =24.1 min; 97% ee.

$[\alpha]_D^{22}$ = +15.5 (c = 1.1, $CHCl_3$).

HRMS (ESI) calcd for $C_{17}H_{21}NO_3$, m/z 288.1600, found 288.1599.

(R)-tert-butyl 3-hydroxy-2-(N-phenylaminoxy)propylcarbamate (new compound) (**3j**)



α-aminoxy alcohol **3j** was prepared according to the general procedure from tert-butyl-3-oxopropylcarbamate (0.16 mL, 0.9 mmol) to provide the title compound as a pale yellow liquid (67.2 mg, 79% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (3H, m), 6.98-6.94 (2H, m), 5.02 (1H, brs), 3.94-3.92 (1H, m), 3.80 (2H, s), 3.50-3.36 (2H, m), 1.45 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$): 157.1, 148.3, 129.0, 122.4, 114.6, 82.4, 80.0, 61.3, 39.6, 28.3.

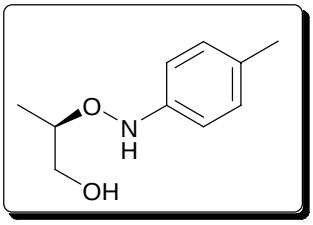
HPLC: Chiralpak OJ-H (hexane/*i*-PrOH, 95/5, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 24.8 min, t_R (major) =26.6 min; 93% ee.

$[\alpha]_D^{22}$ = - 8.2 (*c* = 1.3, $CHCl_3$).

HRMS (ESI) calcd for $C_{14}H_{23}N_2O_4$, m/z 282.1658, found 282.1659.

(*R*)-2-(p-toluidinoxy)propan-1-ol (new compound) (**3k**) [5]



α-aminoxy alcohol **3k** was prepared according to the general procedure from propanal (0.07 mL, 0.9 mmol) and nitrosotoluene (36.3 mg, 0.3 mmol) to provide the title compound as a pale yellow liquid (45.0 mg, 83% yield) after flash column chromatography on silica gel (hexane:EtOAc = 9/1~7/3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (2H, d, *J* = 8.1 Hz), 6.99 (1H, brs), 6.88 (2H, d, *J* = 8.3Hz), 4.13-4.07 (1H, m), 3.78-3.68 (2H, m), 2.28 (3H, s), 1.22 (3H, d, *J* = 6.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 145.8, 132.0, 129.5, 115.3 79.8, 66.6, 20.6, 15.4.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 230 nm),

t_R (minor) = 10.9 min, t_R (major) =12.4 min; 97% ee.

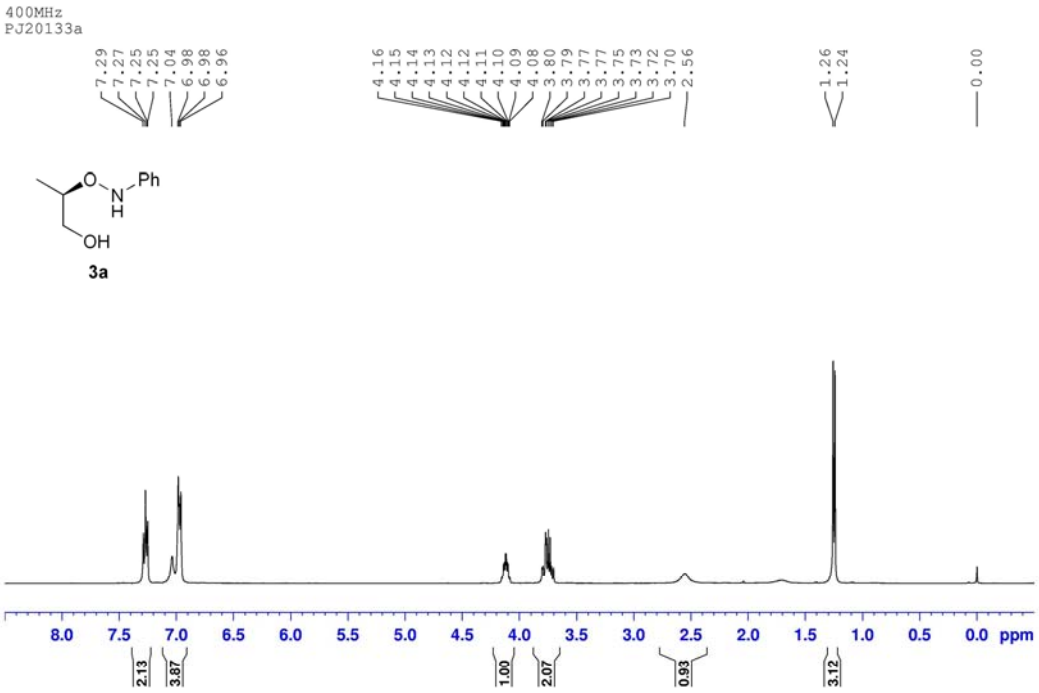
$[\alpha]_D^{25}$ = + 5.5 (*c* = 1.5, $CHCl_3$).

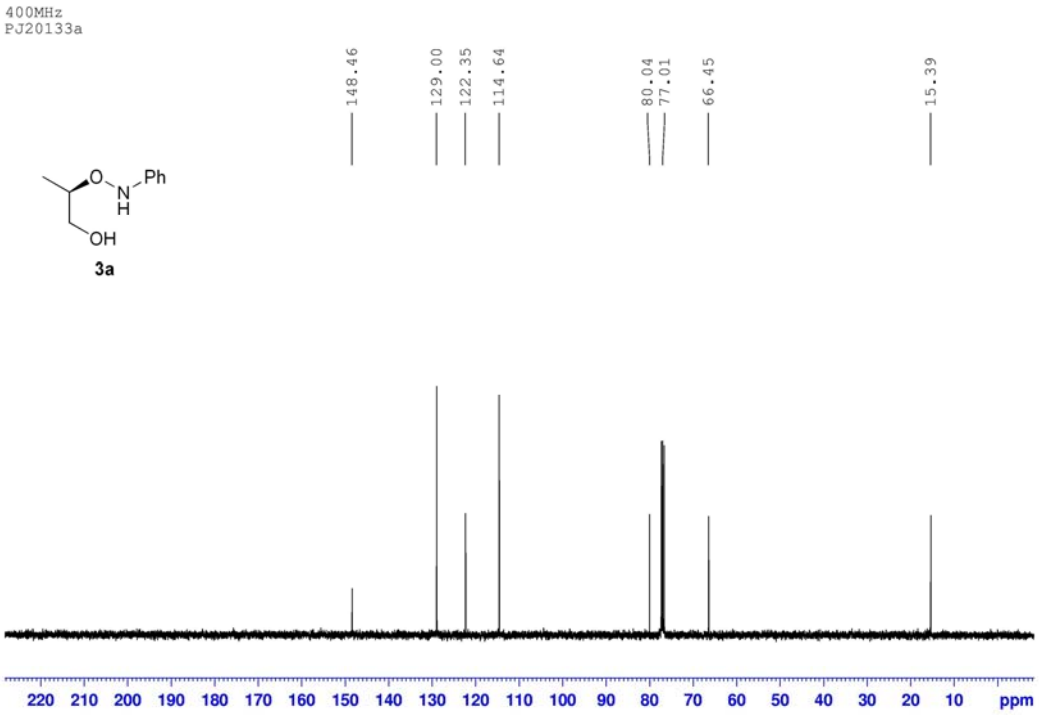
HRMS (ESI) calcd for $C_{10}H_{16}NO_2$, m/z 182.1181, found 182.1181.

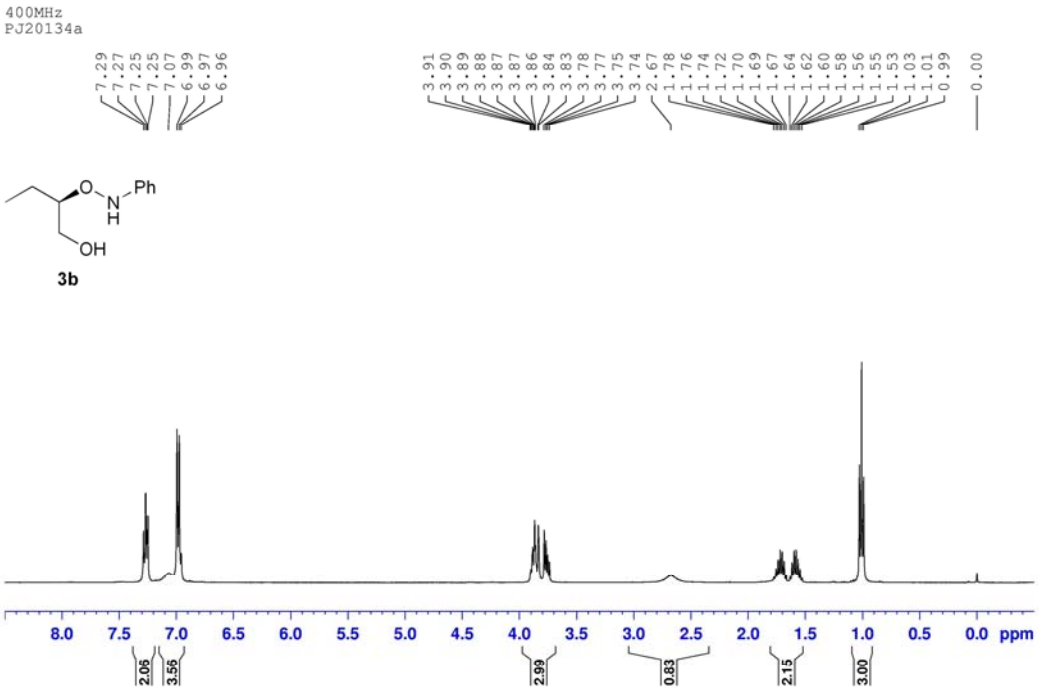
References:

1. For the preparation of **1i**: R. Iyengar, K. Schildknegt, M. Morton, J. Aube, *J. of Org. Chem.*, 2005, **70**, 10645.
2. For the preparation of **1j**: J. D. More and N. S. Finney, *Org. Lett.*, 2002, **4**, 3001
3. Y. Hayashi, J. Yamaguchi, T. Sumiya, K. Hibino and M. Shoji, *J. of Org. Chem.*, 2004, **69**, 5966
4. A. Córdova, H. Sundén, A. Bøgevig,, M. Johansson and F. Himo, *Chem. Eur. J.* 2004, **10**, 3673

^{1}H and ^{13}C NMR Spectra of Compounds 3a-3n



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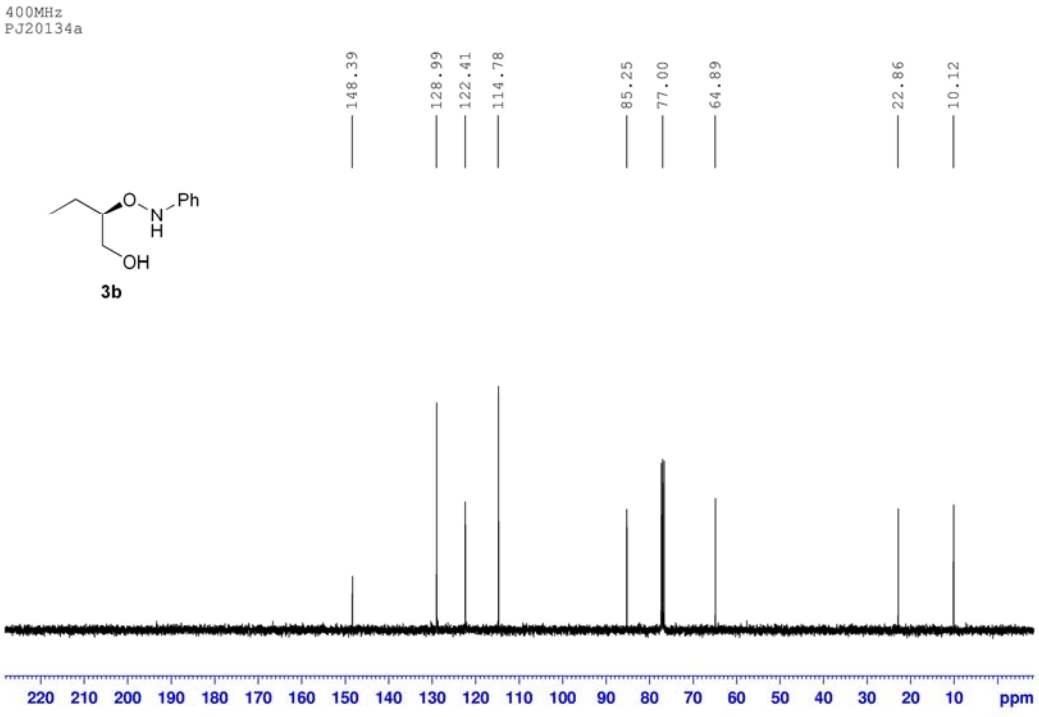
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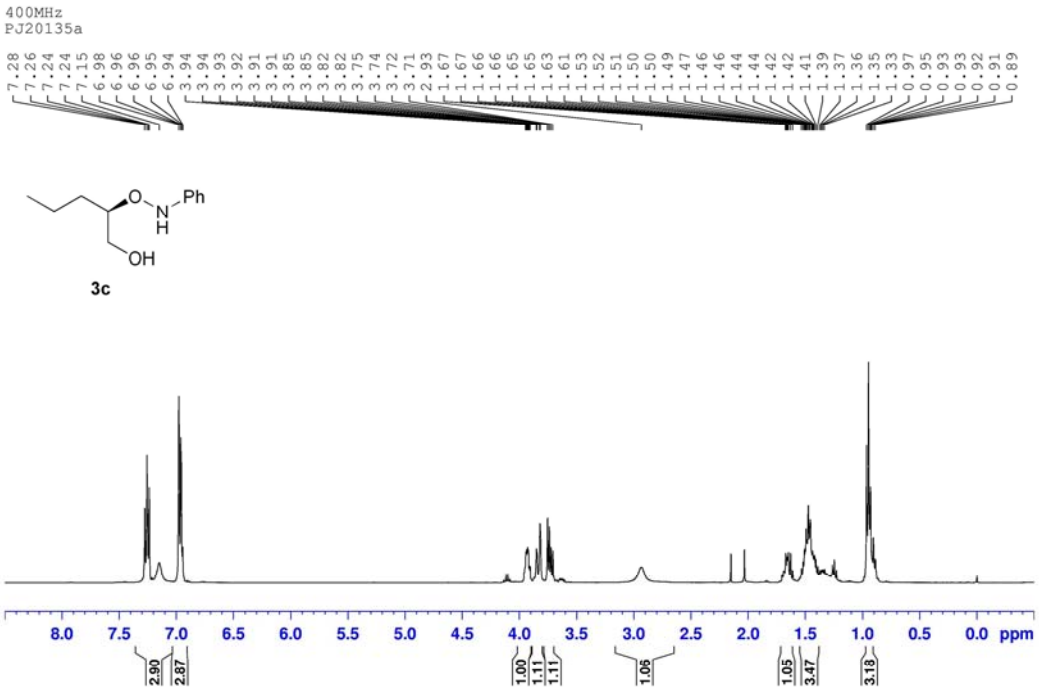
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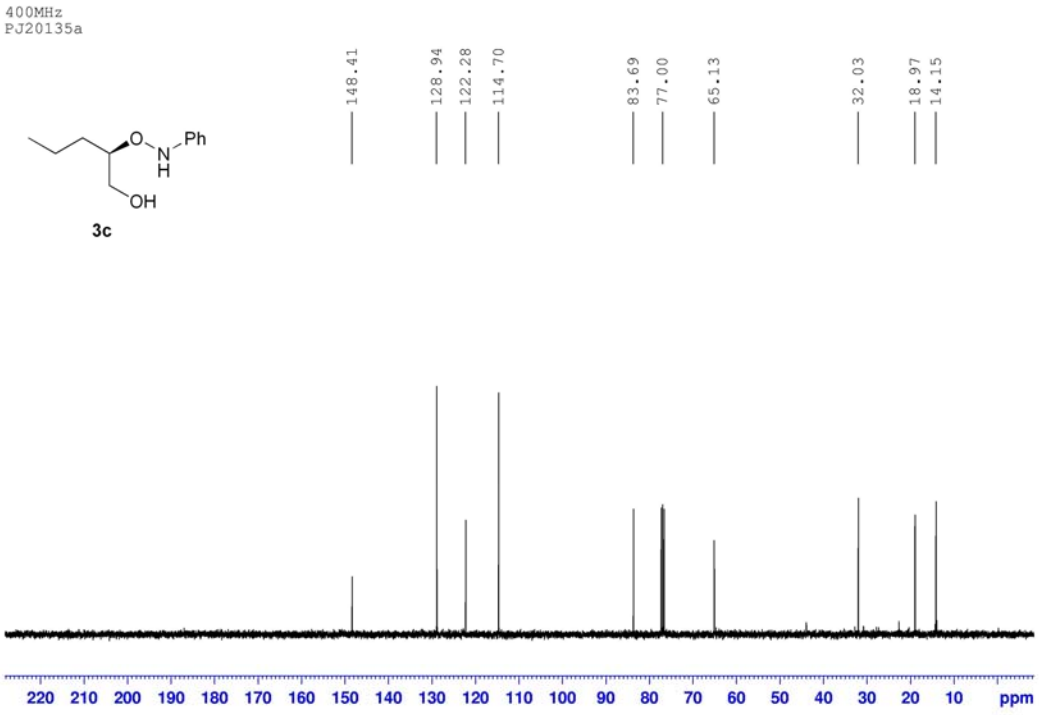
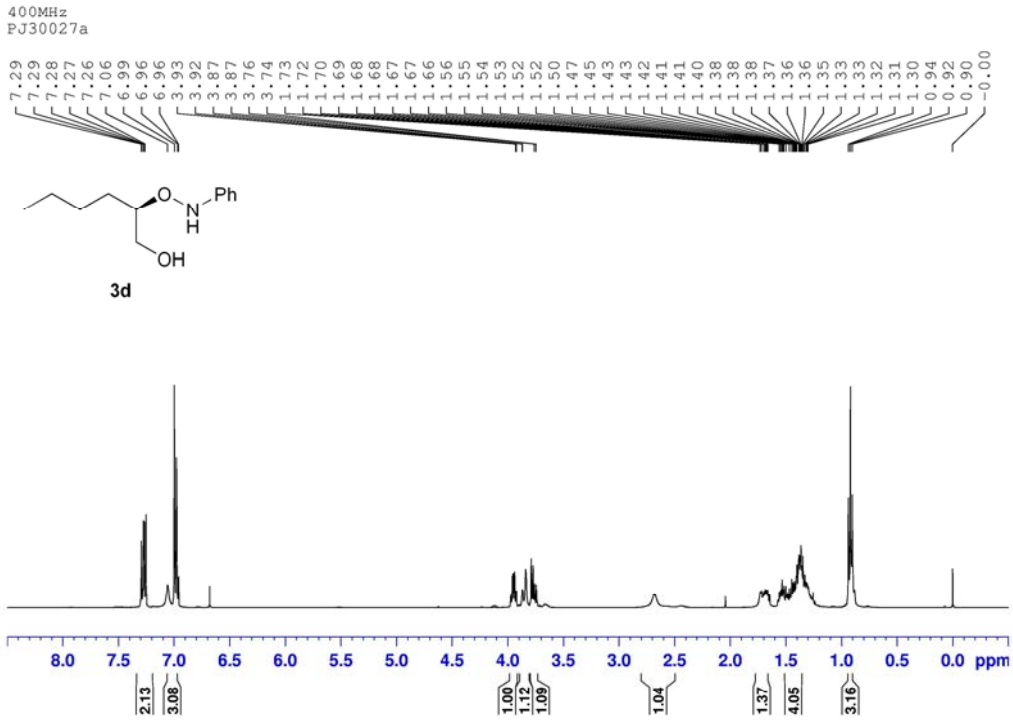
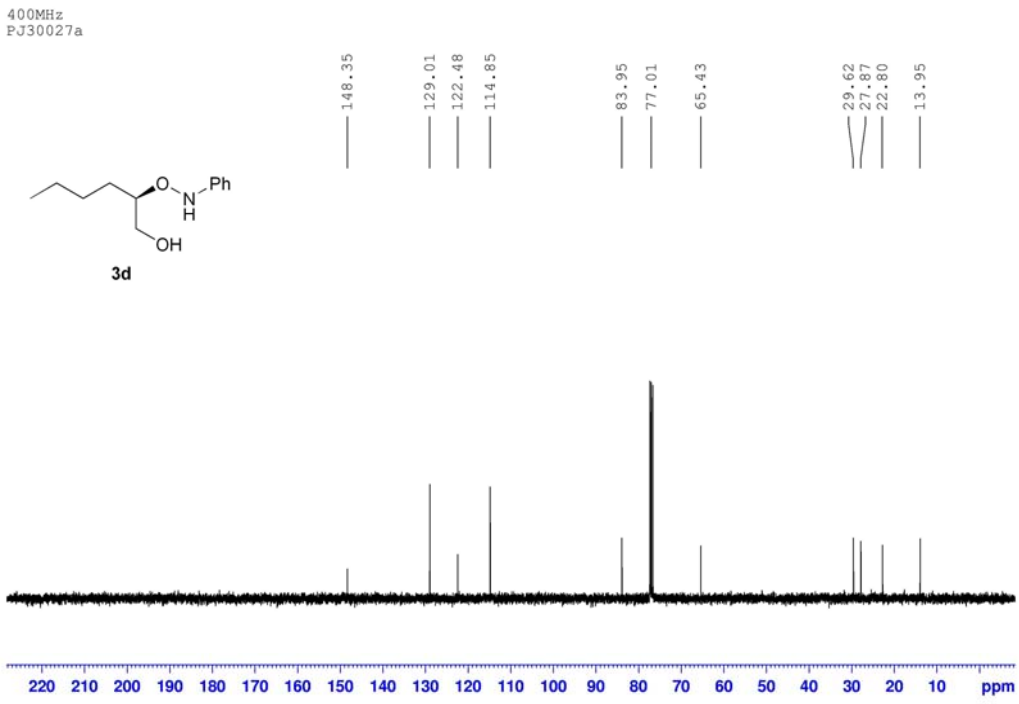
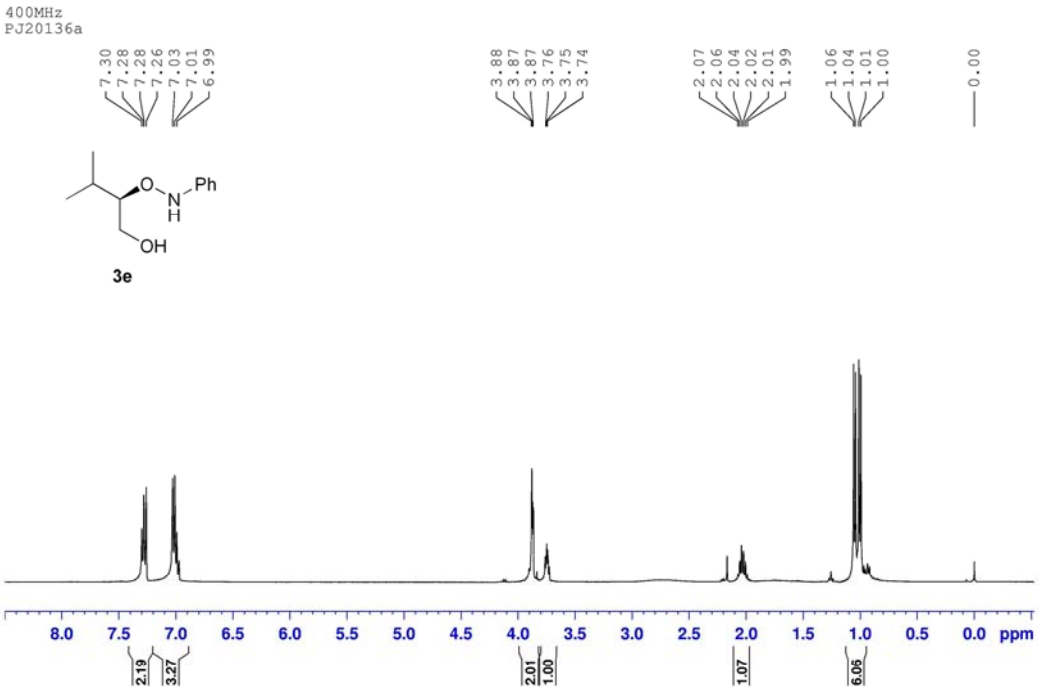
PJ20135a
7.28 7.26 7.24 7.24 7.15 6.98 6.96 6.96 6.95 6.94 3.94 3.94 3.93 3.92 3.91 3.91 3.85 3.85 3.82 3.82 3.75 3.74 3.72 3.71 2.93 1.67 1.67 1.66 1.66 1.65 1.65 1.63 1.61 1.53 1.52 1.51 1.50 1.50 1.49 1.47 1.46 1.46 1.44 1.44 1.42 1.42 1.41 1.39 1.37 1.36 1.35 1.33 0.97 0.95 0.93 0.93 0.92 0.91 0.89
O
N
H
Ph
OH
3c
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 0.0 ppm
2.90
2.87
1.00
1.11
1.11
1.06
1.05
3.47
3.18


400MHz
PJ20135a
148.41
128.94
122.28
114.70
83.69
77.00
65.13
32.03
18.97
14.15
O
N
H
Ph
OH
3c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


400MHz
PJ30027a
7.29 7.29 7.28 7.27 7.26 7.06 6.99 6.96 6.96 3.93 3.92 3.87 3.87 3.76 3.74 1.73 1.72 1.70 1.69 1.68 1.68 1.67 1.67 1.66 1.56 1.55 1.54 1.53 1.52 1.52 1.50 1.47 1.45 1.43 1.43 1.42 1.41 1.41 1.40 1.38 1.38 1.37 1.36 1.36 1.35 1.33 1.33 1.32 1.31 1.30 0.94 0.92 0.90 -0.00
O
N
H
Ph
OH
3d
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 0.0 ppm
2.13 3.08 1.00 1.12 1.09 1.04 1.37 4.05 3.16


400MHz
PJ30027a
148.35 129.01 122.48 114.85 83.95 77.01 65.43 29.62 27.87 22.80 13.95
O
N
H
Ph
OH
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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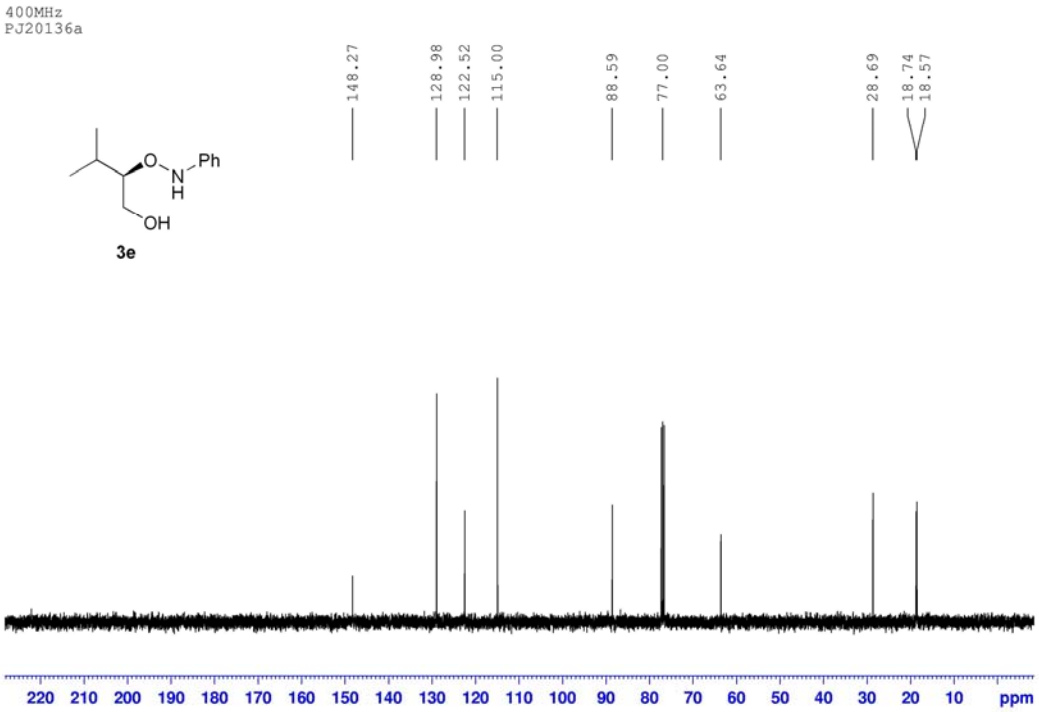
PJ20136a
7.30
7.28
7.28
7.26
7.03
7.01
6.99
3.88
3.87
3.87
3.76
3.75
3.74
2.07
2.06
2.04
2.02
2.01
1.99
1.06
1.04
1.01
1.00
0.00
O
N
H
Ph
OH
3e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.19
3.27
2.01
1.00
1.07
6.06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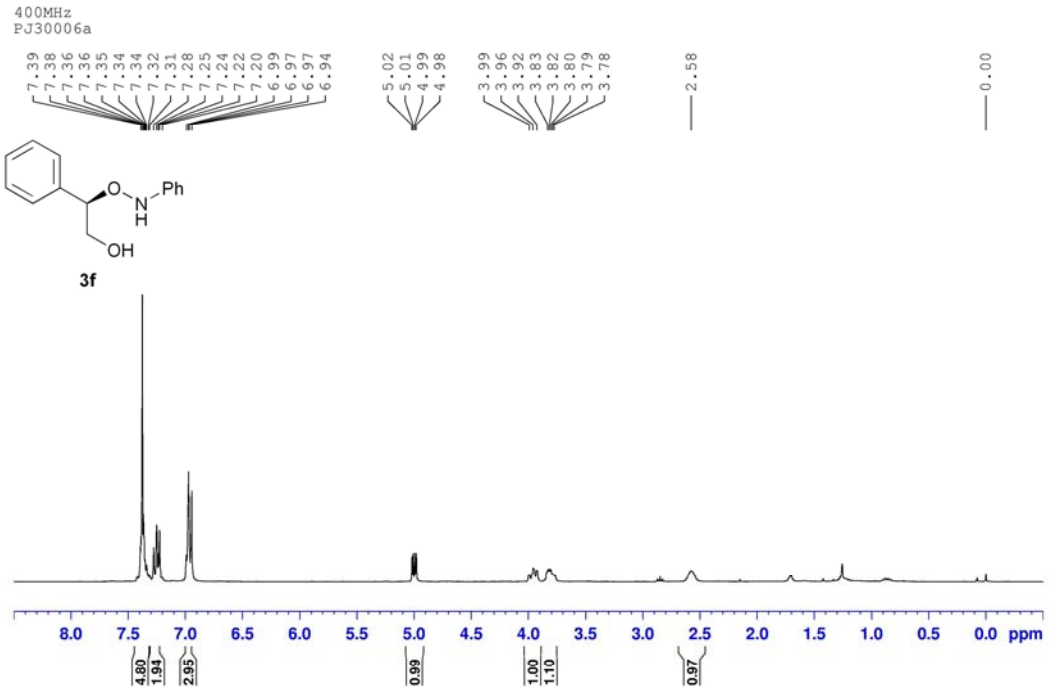
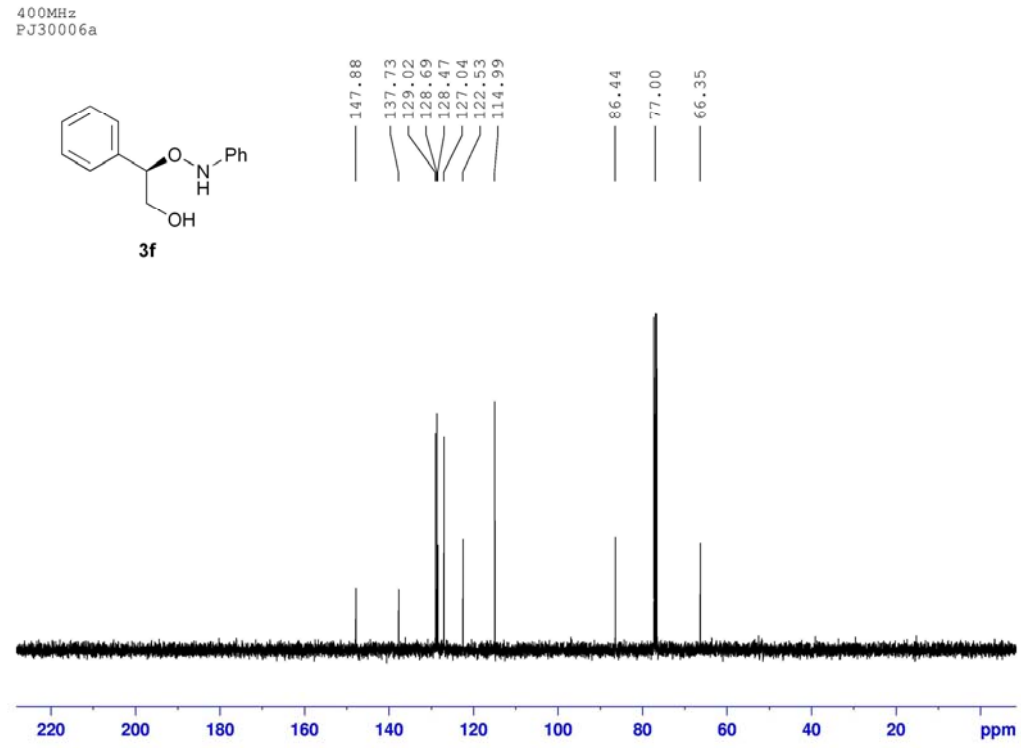
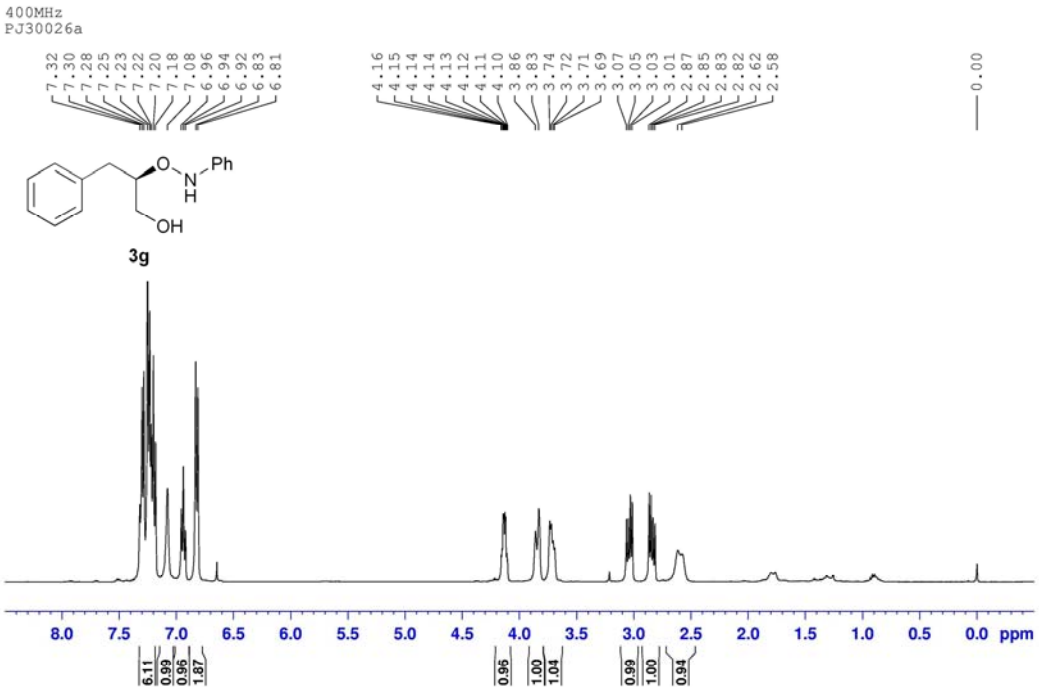
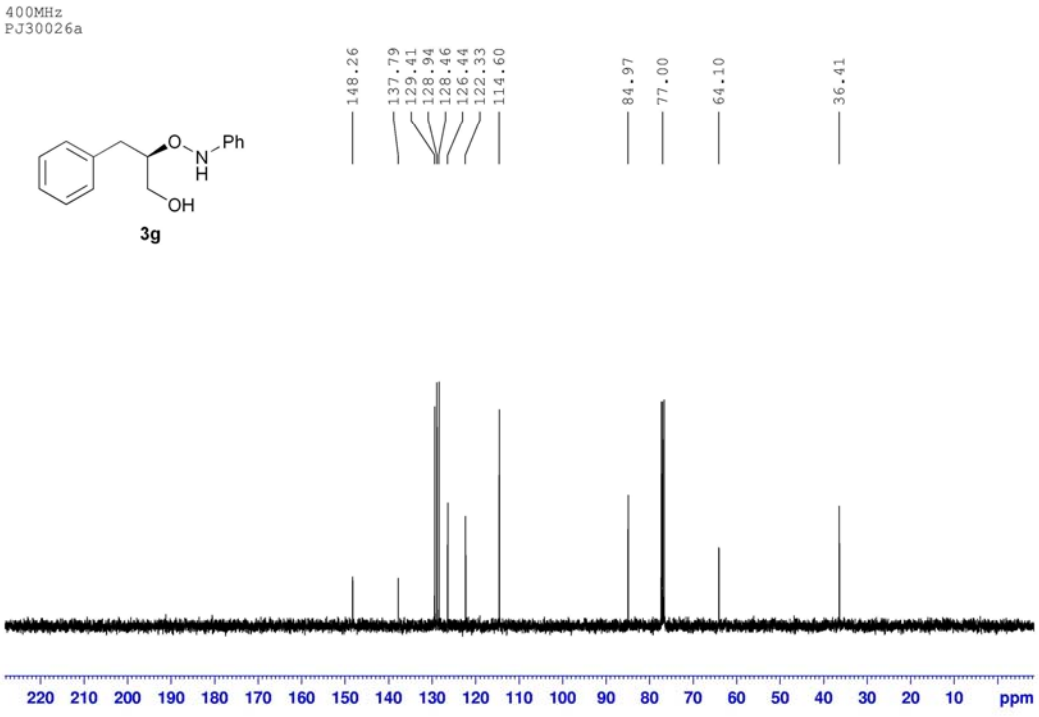
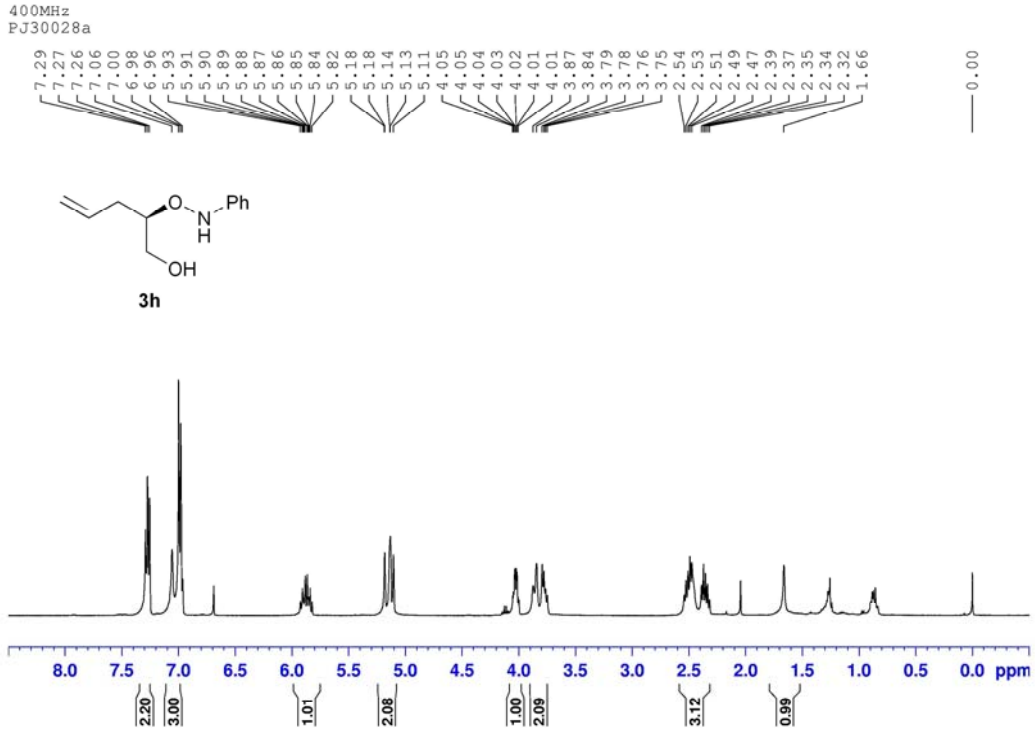
122.52
115.00
88.59
77.00
63.64
28.69
18.74
18.57
O
N
H
Ph
OH
3e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
PJ30006a
7.39
7.38
7.36
7.36
7.35
7.34
7.34
7.32
7.31
7.28
7.25
7.24
7.22
7.20
6.99
6.97
6.97
6.94
5.02
5.01
4.99
4.98
3.99
3.96
3.92
3.83
3.82
3.80
3.79
3.78
2.58
0.00
O
N
H
Ph
OH
3f
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
0.0
ppm
4.80
1.94
2.95
0.99
1.00
1.10
0.97


400MHz
PJ30006a
147.88
137.73
129.02
128.69
128.47
127.04
122.53
114.99
86.44
77.00
66.35
O
N
H
Ph
OH
3f
220
200
180
160
140
120
100
80
60
40
20
ppm


400MHz
PJ30026a
7.32
7.30
7.28
7.25
7.23
7.22
7.20
7.18
7.08
6.96
6.94
6.92
6.83
6.81
4.16
4.15
4.14
4.14
4.13
4.12
4.11
4.10
3.86
3.83
3.74
3.72
3.71
3.69
3.07
3.05
3.03
3.01
2.87
2.85
2.83
2.82
2.62
2.58
0.00
O
N
H
Ph
OH
3g
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
0.0
ppm
6.11
0.99
0.96
1.87
0.96
1.00
1.04
0.99
1.00
0.94


400MHz
PJ30026a
148.26
137.79
129.41
128.94
128.46
126.44
122.33
114.60
84.97
77.00
64.10
36.41
O
N
H
Ph
OH
3g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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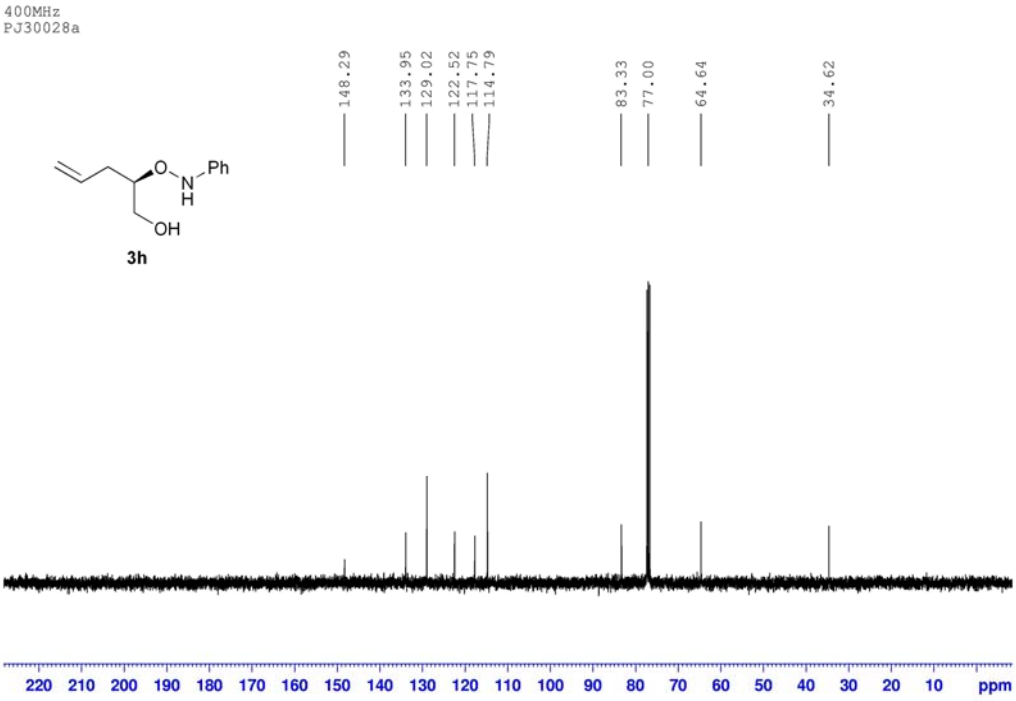
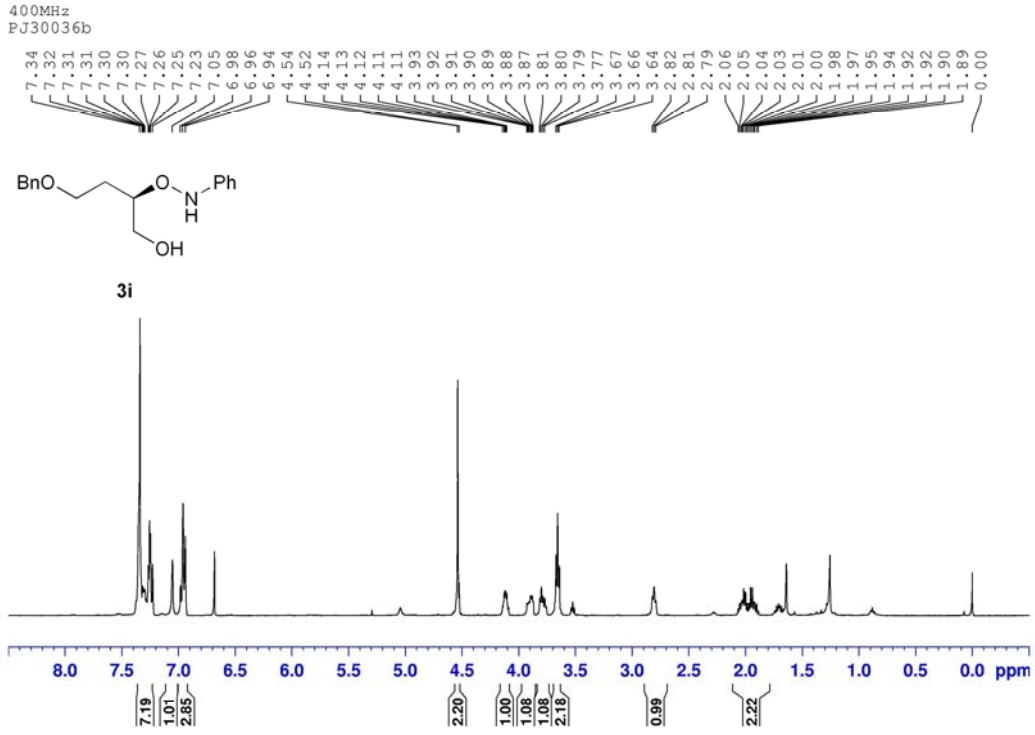
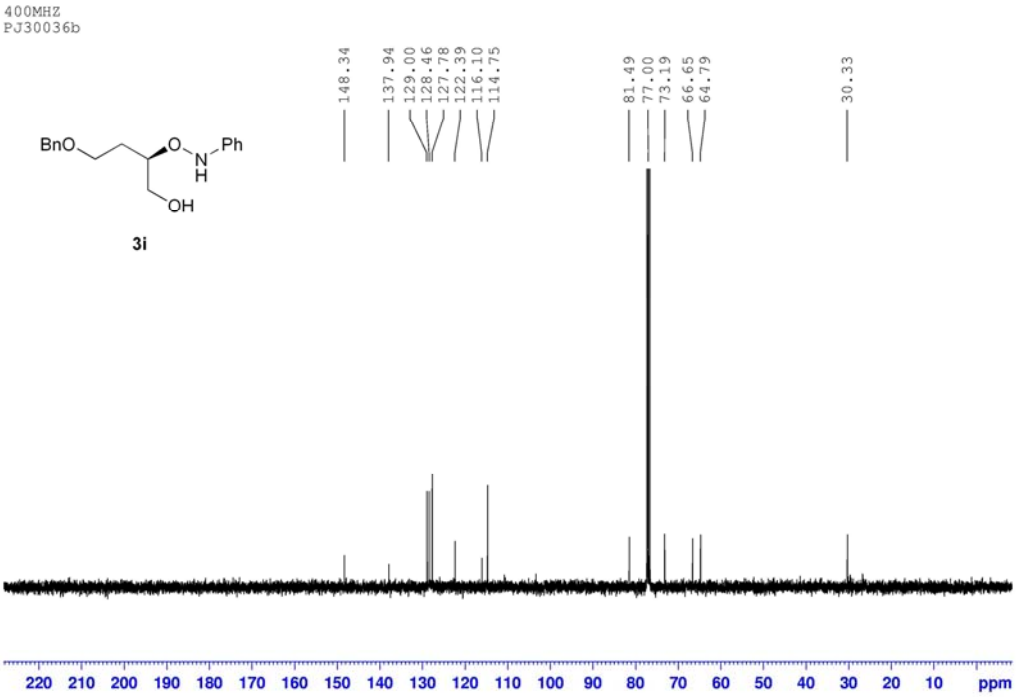
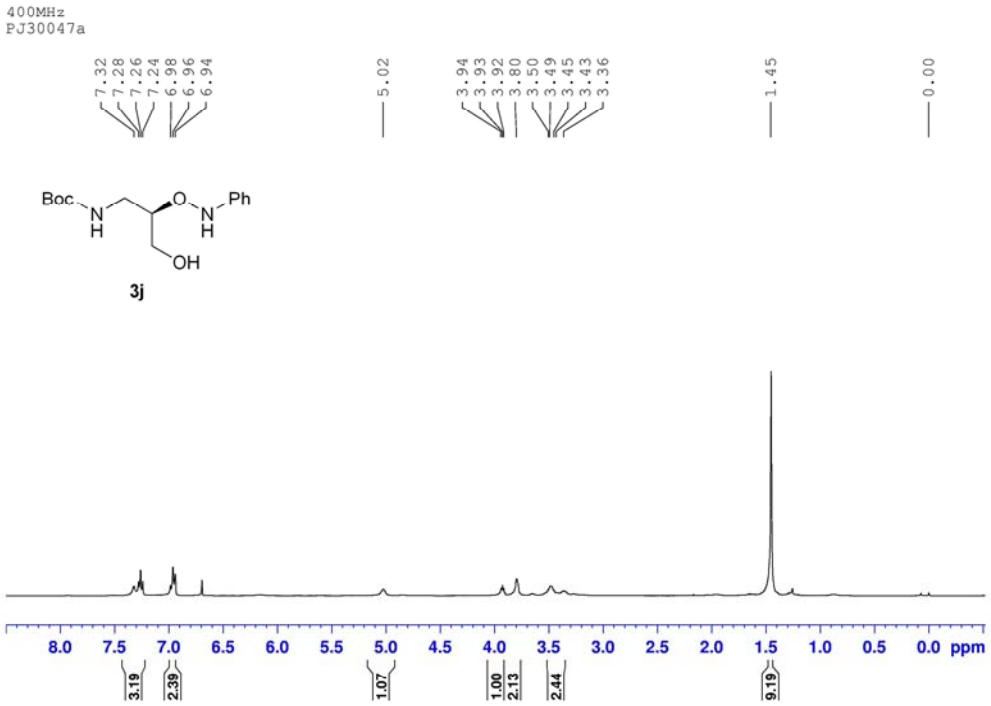
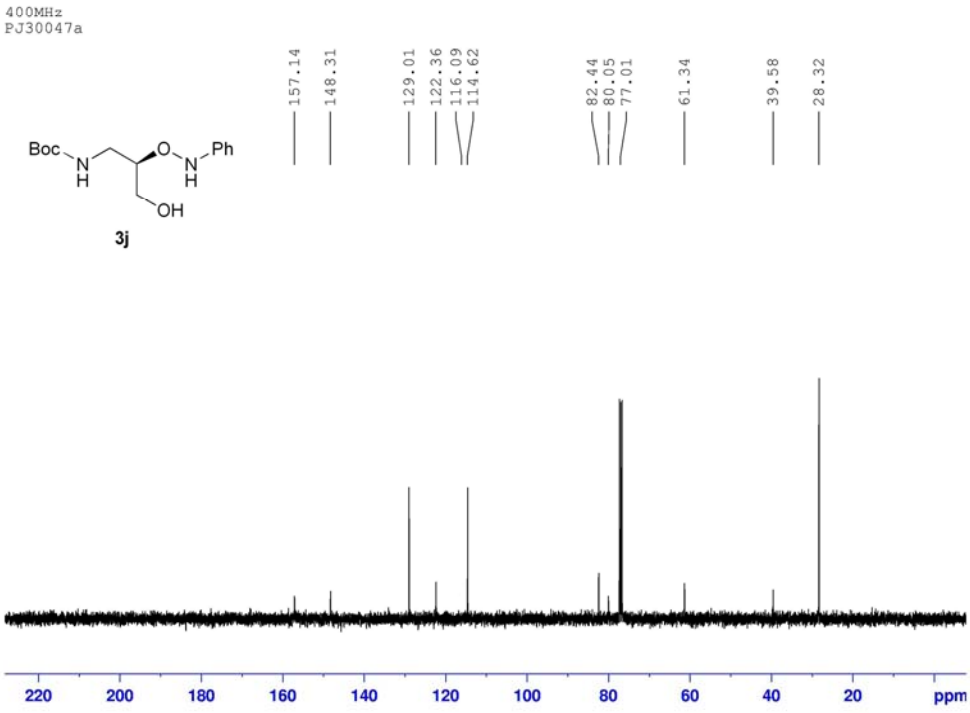
PJ30028a
7.29 7.27 7.26 7.06 7.00 6.98 6.96 5.93 5.91 5.90 5.89 5.88 5.87 5.86 5.85 5.84 5.82 5.18 5.18 5.14 5.13 5.11 4.05 4.04 4.03 4.02 4.01 4.01 3.87 3.84 3.79 3.78 3.76 3.75 2.54 2.53 2.51 2.49 2.47 2.39 2.37 2.35 2.34 2.32 1.66
0.00
O
N
H
Ph
OH
3h
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.20 3.00 1.01 2.08 1.00 2.09 3.12 0.99

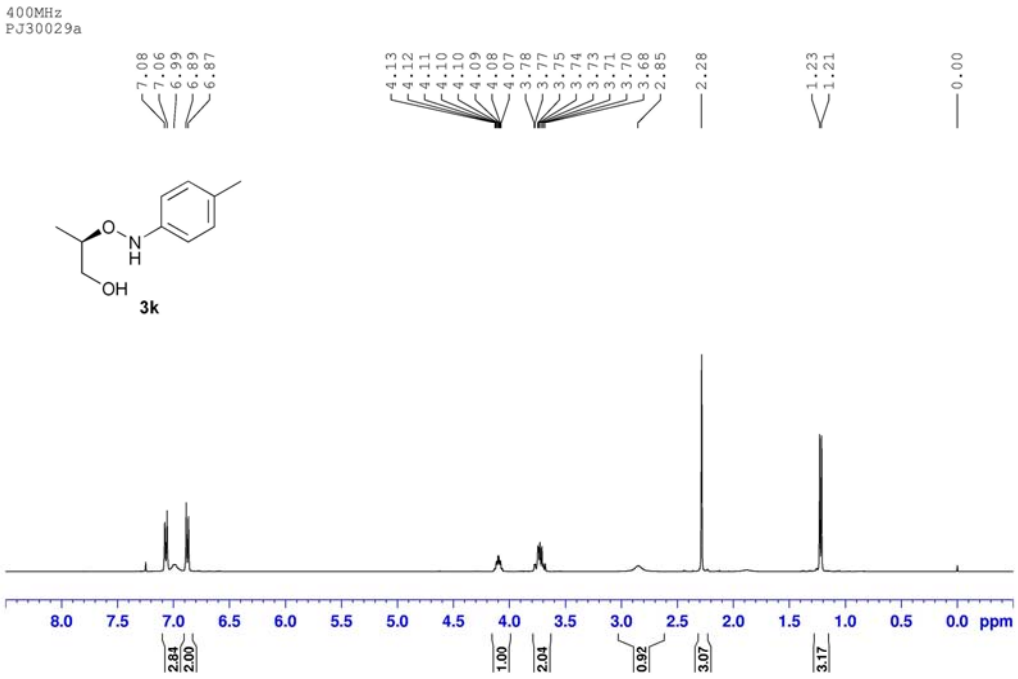

400MHz
PJ30028a
148.29 133.95 129.02 122.52 117.75 114.79 83.33 77.00 64.64 34.62
O
N
H
Ph
OH
3h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

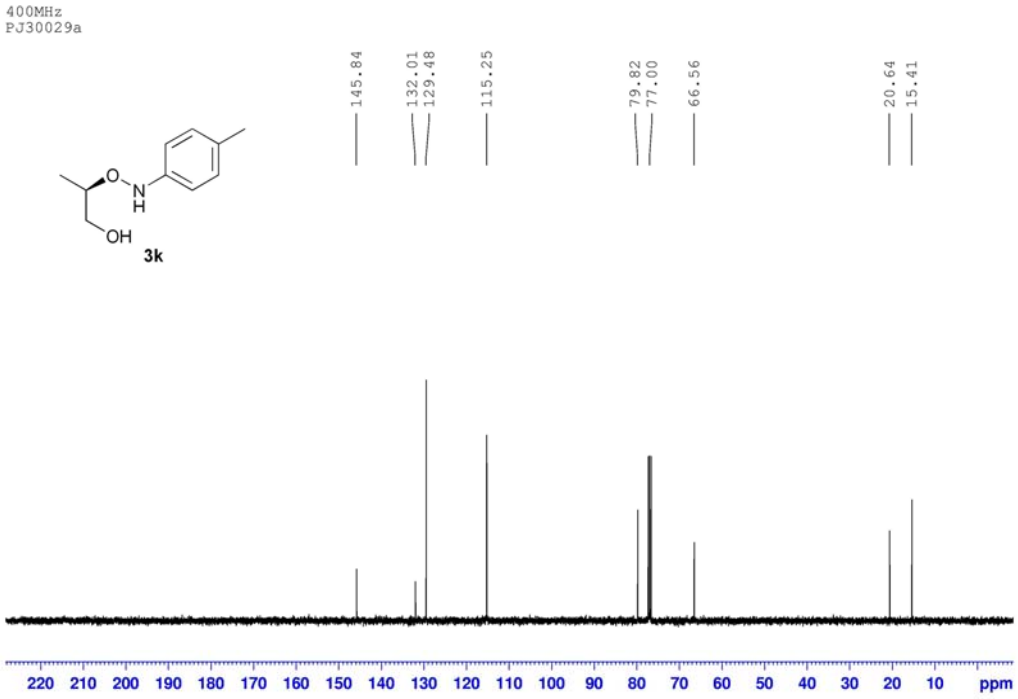

400MHz
PJ30036b
7.34 7.32 7.31 7.31 7.30 7.30 7.27 7.26 7.25 7.23 7.05 6.98 6.96 6.94 4.54 4.52 4.14 4.13 4.12 4.11 4.11 3.93 3.92 3.91 3.90 3.89 3.88 3.87 3.81 3.80 3.79 3.77 3.67 3.66 3.64 2.82 2.81 2.79 2.06 2.05 2.04 2.03 2.01 2.00 1.98 1.97 1.95 1.94 1.92 1.92 1.90 1.89 0.00
BnO
O
N
H
Ph
OH
3i
8.0 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 0.0 ppm
7.19 1.01 2.85 2.20 1.00 1.08 1.08 2.18 0.99 2.22


400MHZ
PJ30036b
148.34 137.94 129.00 128.46 127.78 122.39 116.10 114.75 81.49 77.00 73.19 66.65 64.79 30.33
BnO
O
N
H
Ph
OH
3i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

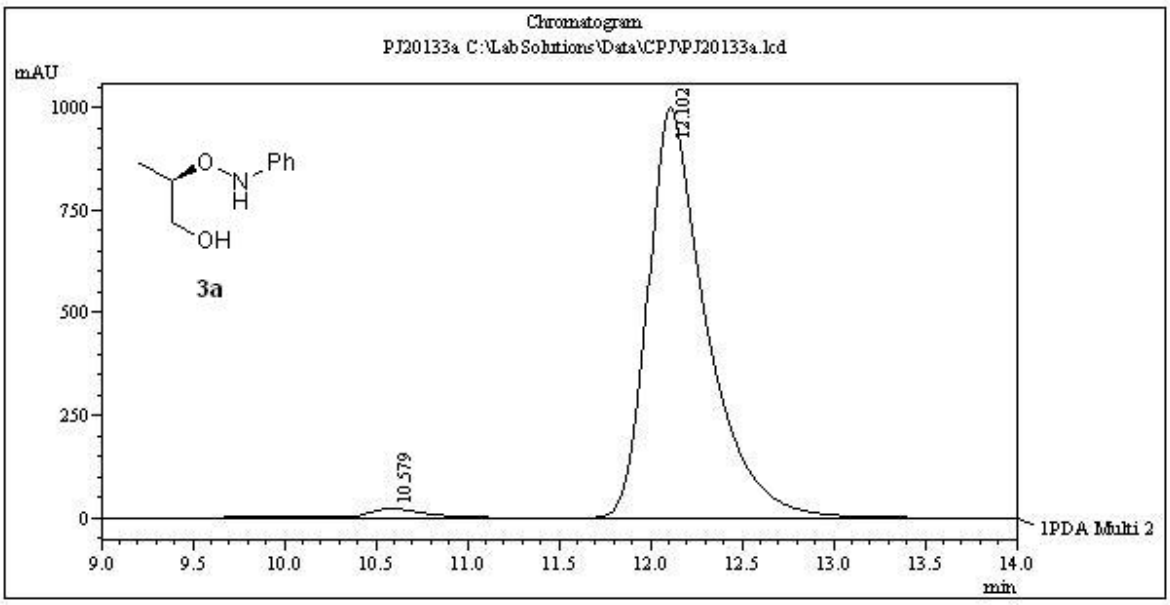

400MHz
PJ30047a
7.32
7.28
7.26
7.24
6.98
6.96
6.94
5.02
3.94
3.93
3.92
3.80
3.50
3.49
3.45
3.43
3.36
1.45
0.00
Boc
N
H
O
N
H
Ph
OH
3j
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.19
2.39
1.07
1.00
2.13
2.44
9.19


400MHz
PJ30047a
157.14
148.31
129.01
122.36
116.09
114.62
82.44
80.05
77.01
61.34
39.58
28.32
Boc
N
H
O
N
H
Ph
OH
3j
220
200
180
160
140
120
100
80
60
40
20
ppm


400MHz
PJ30029a
7.08
7.06
6.99
6.89
6.87
4.13
4.12
4.11
4.10
4.10
4.09
4.08
4.07
3.78
3.77
3.75
3.74
3.73
3.71
3.70
3.68
2.85
2.28
1.23
1.21
0.00
3k
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 0.0 ppm
2.84
2.00
1.00
2.04
0.92
3.07
3.17

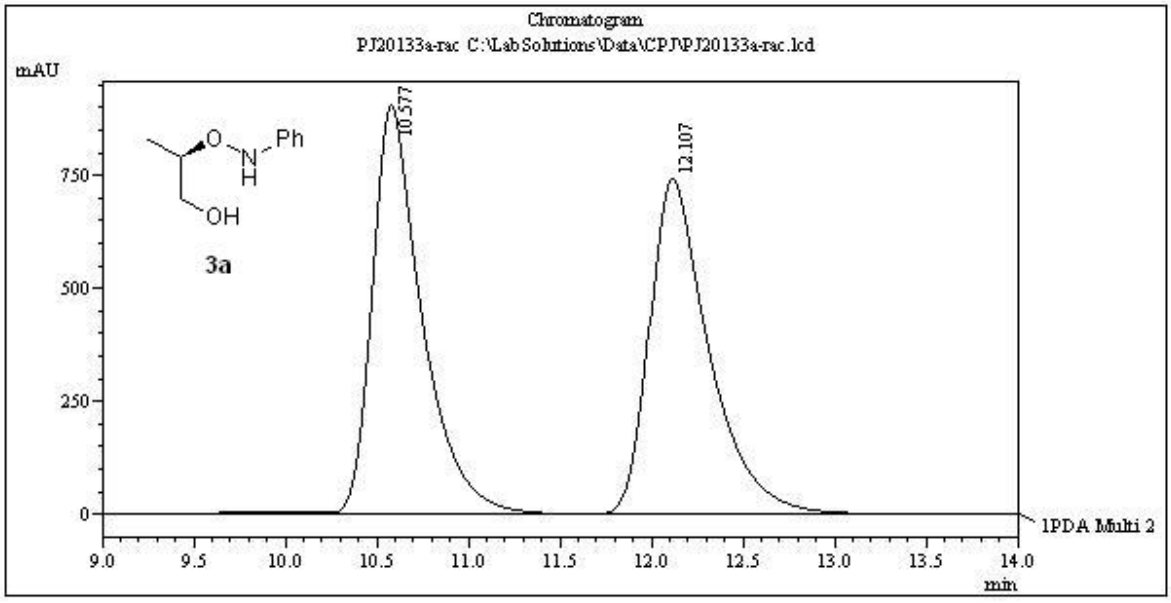

400MHz
PJ30029a
145.84
132.01
129.48
115.25
79.82
77.00
66.56
20.64
15.41
3k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

HPLC Spectra of Compounds 3a-3n



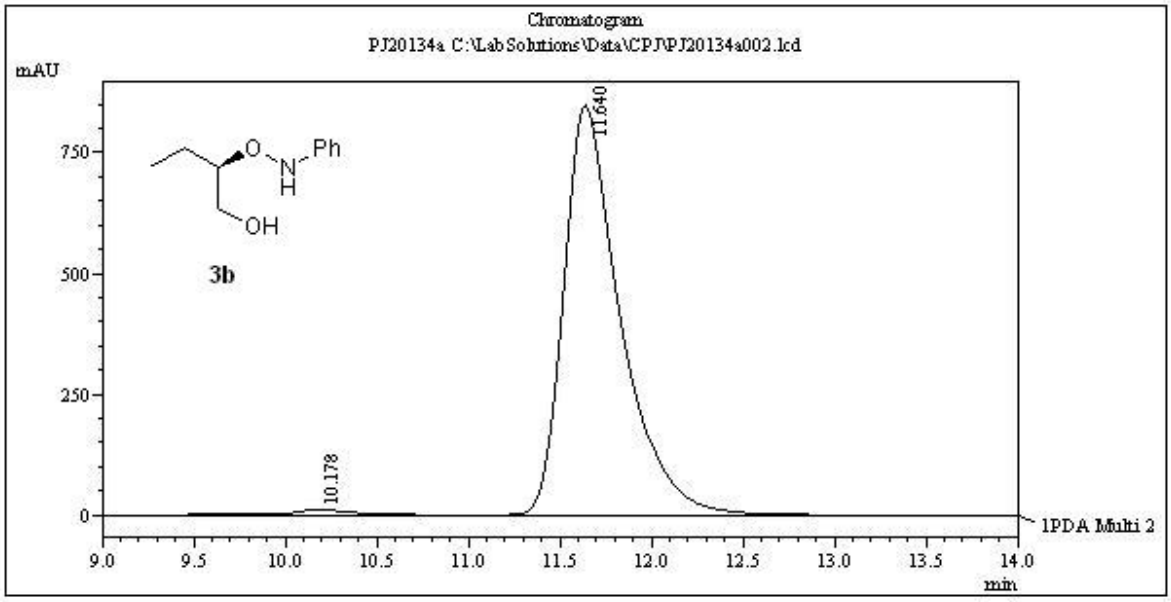
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.579	2.111
2	12.102	97.889
Total		100.000



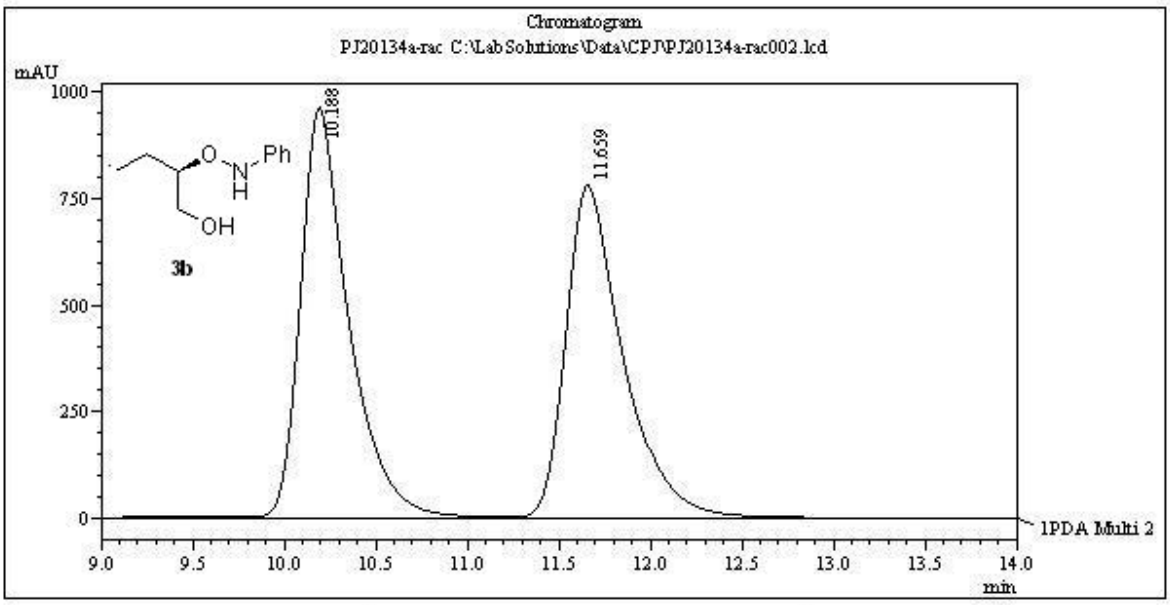
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.577	50.695
2	12.107	49.305
Total		100.000



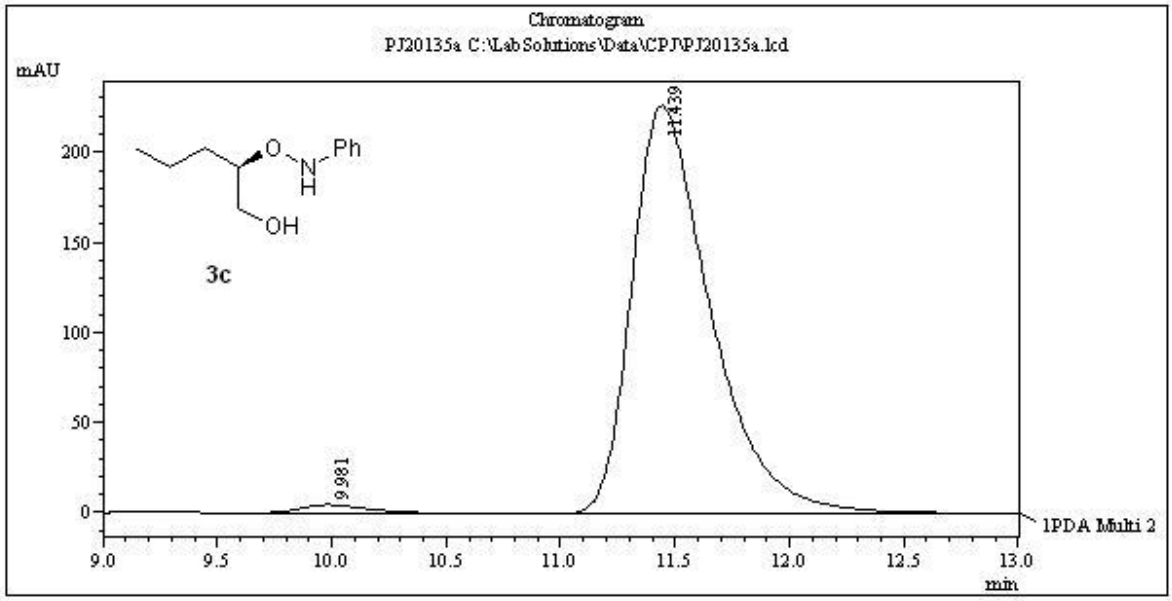
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.178	1.177
2	11.640	98.823
Total		100.000



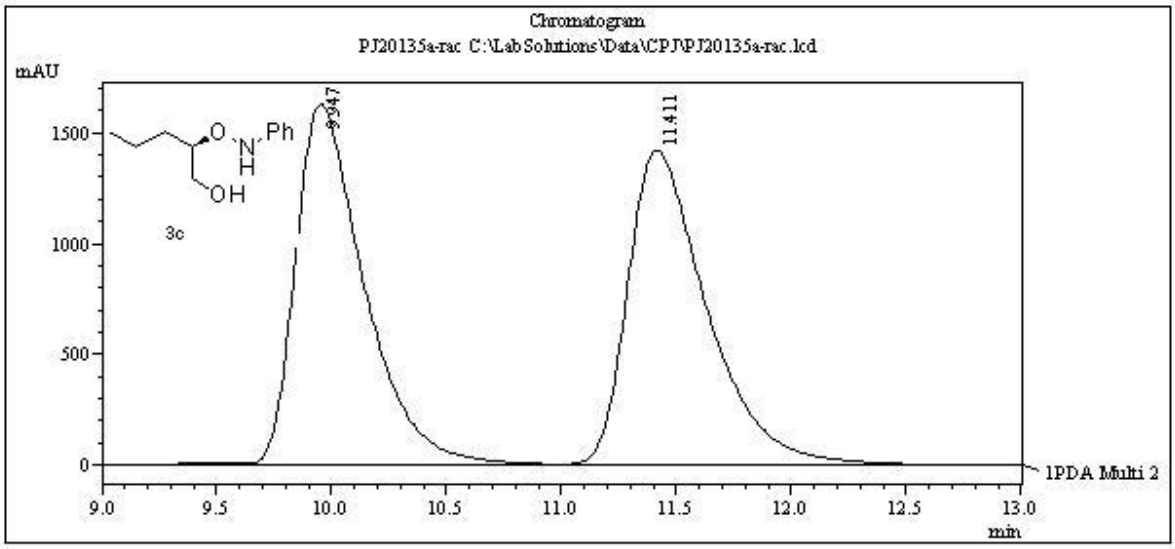
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.188	51.244
2	11.659	48.756
Total		100.000



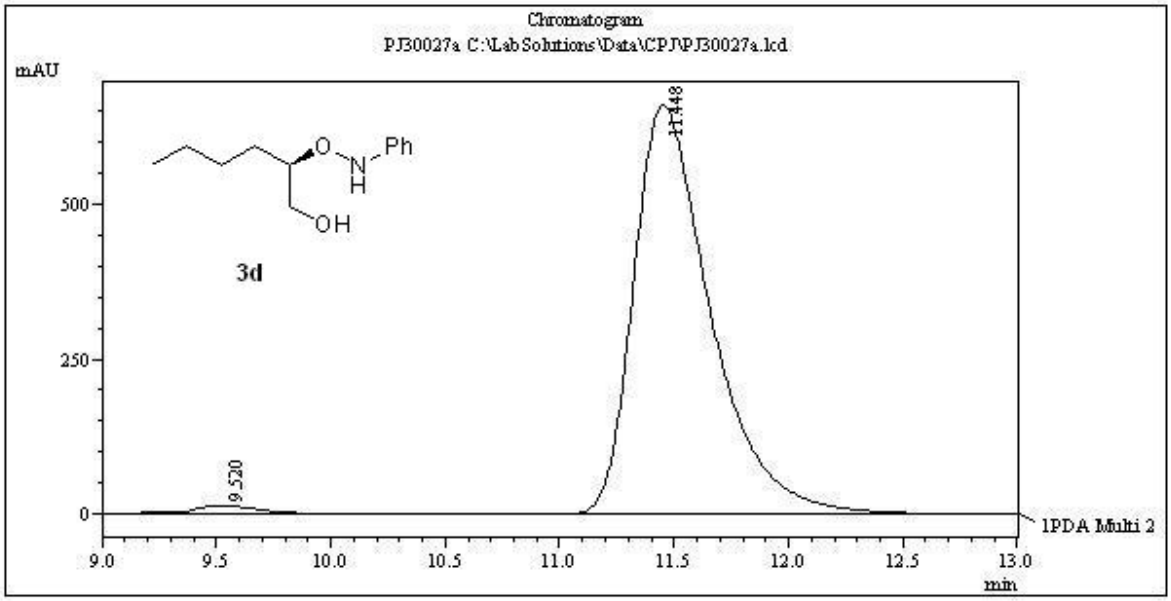
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	9.981	1.741
2	11.439	98.259
Total		100.000



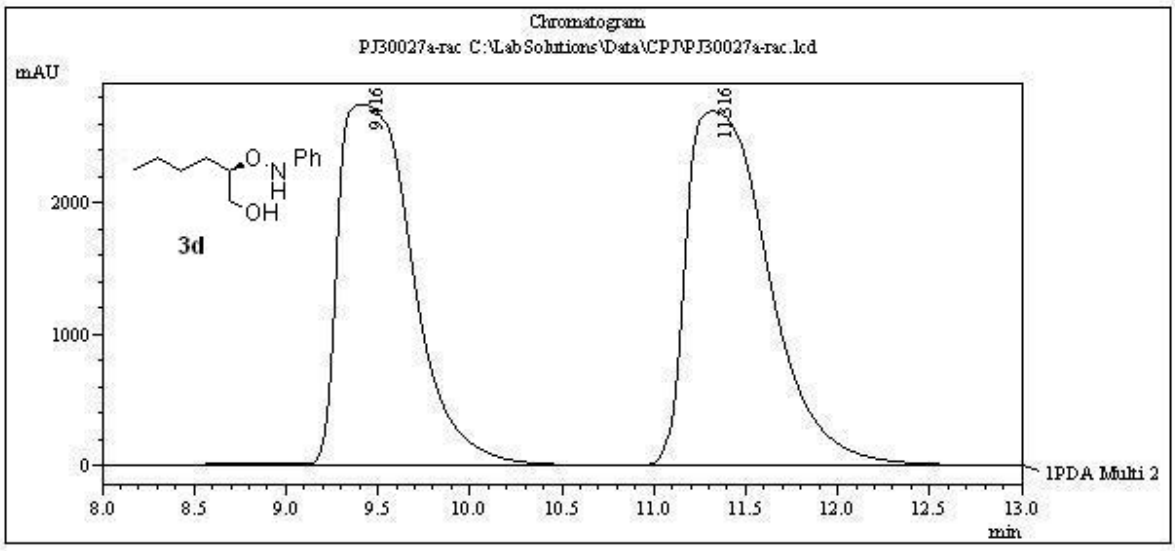
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	9.947	49.922
2	11.411	50.078
Total		100.000



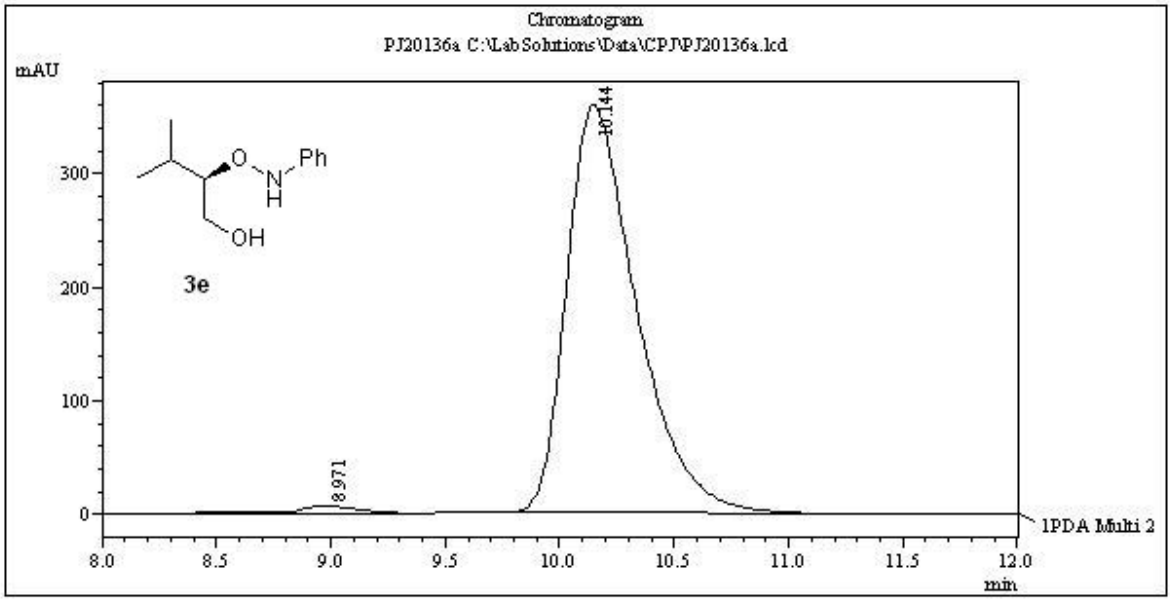
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	9.520	1.797
2	11.448	98.203
Total		100.000



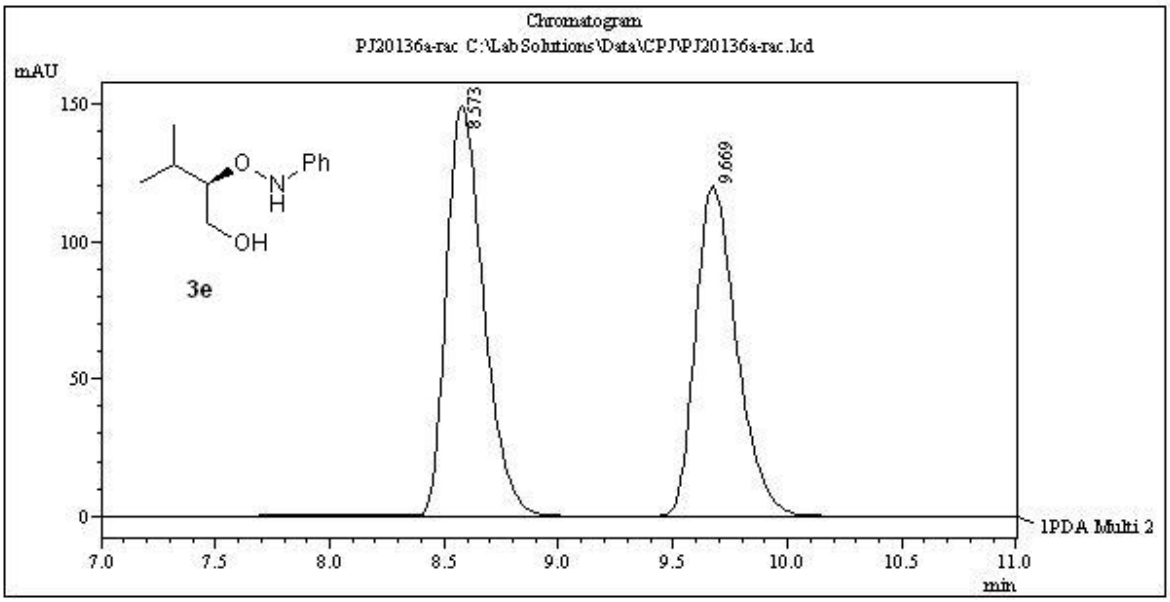
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	9.416	47.256
2	11.316	52.744
Total		100.000



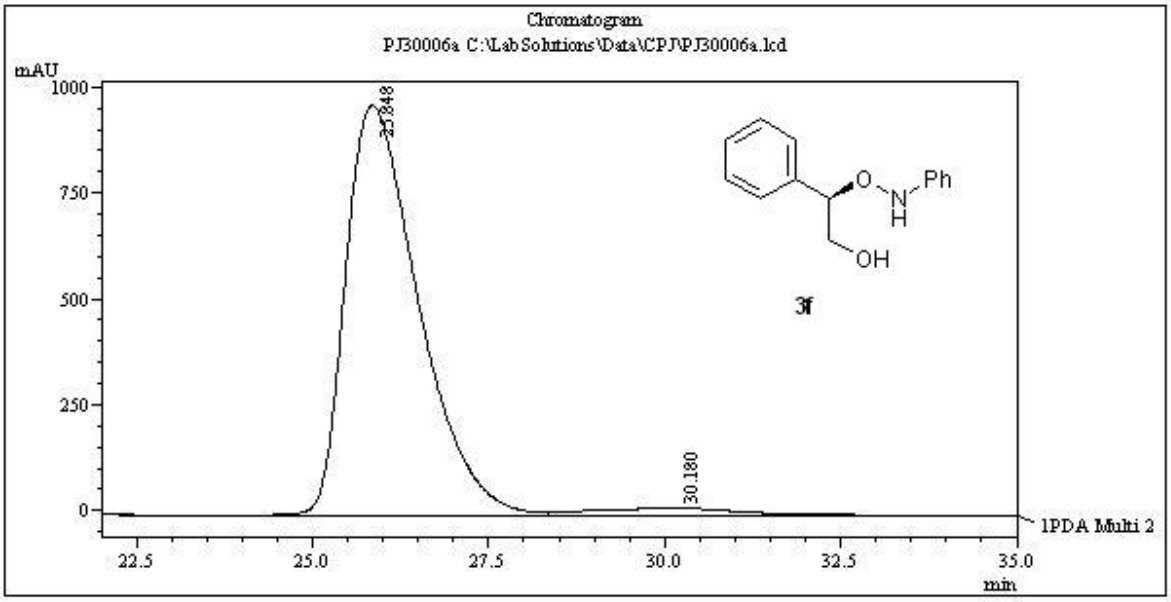
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	8.971	1.541
2	10.144	98.459
Total		100.000



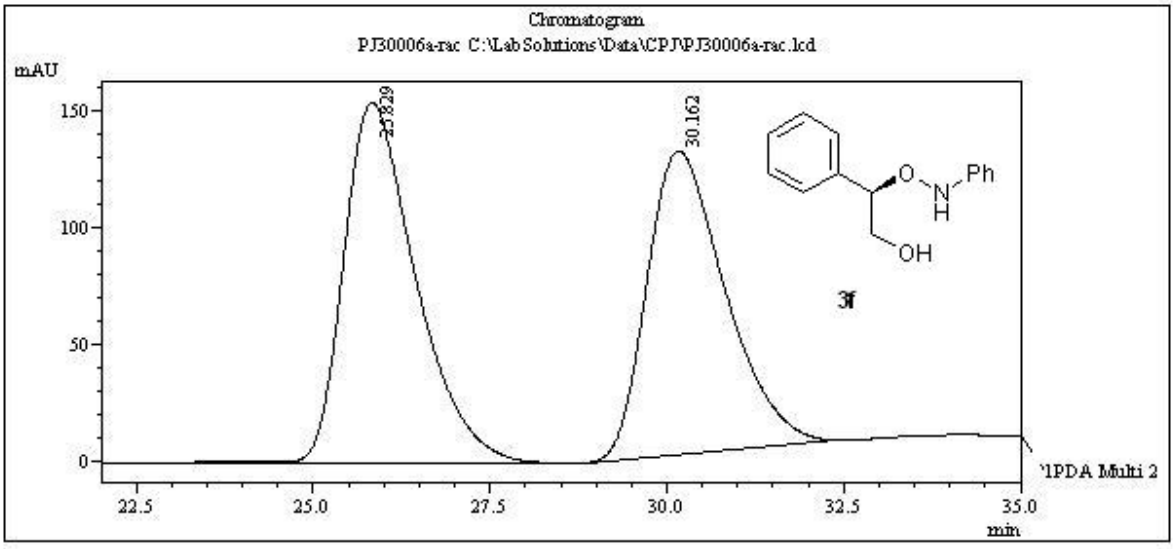
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	8.573	52.949
2	9.669	47.051
Total		100.000



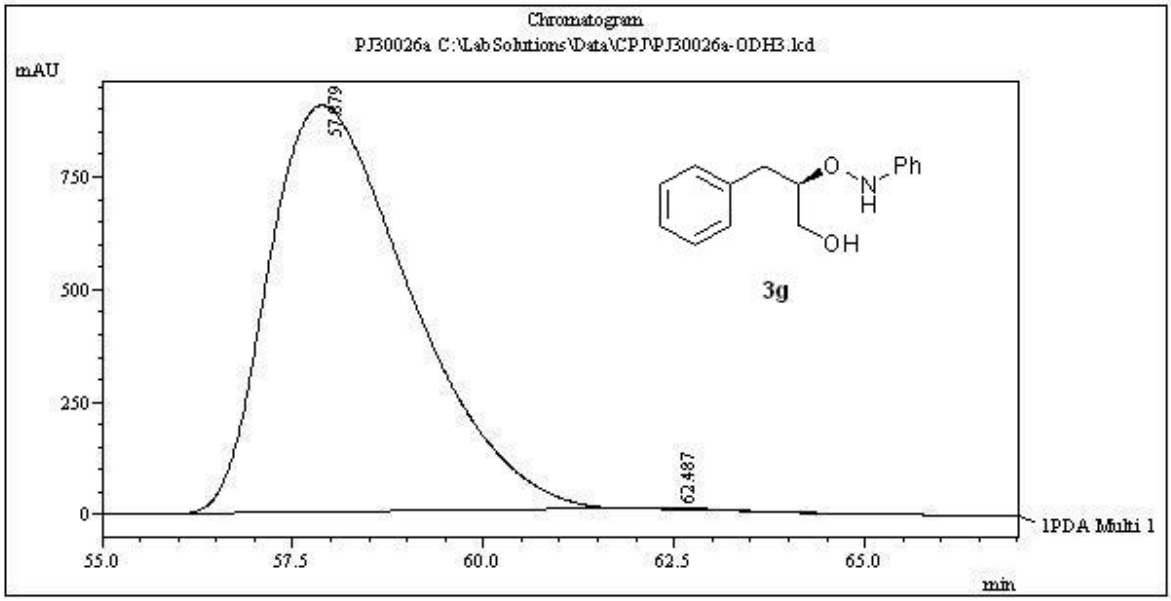
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	25.848	96.521
2	30.180	3.479
Total		100.000



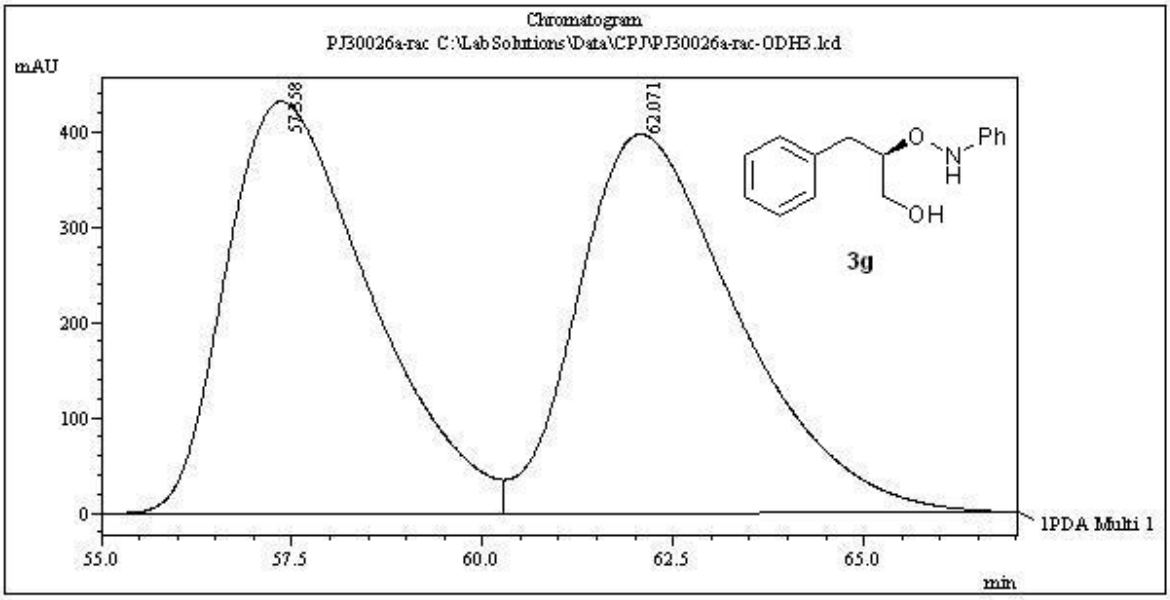
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	25.829	52.132
2	30.162	47.868
Total		100.000



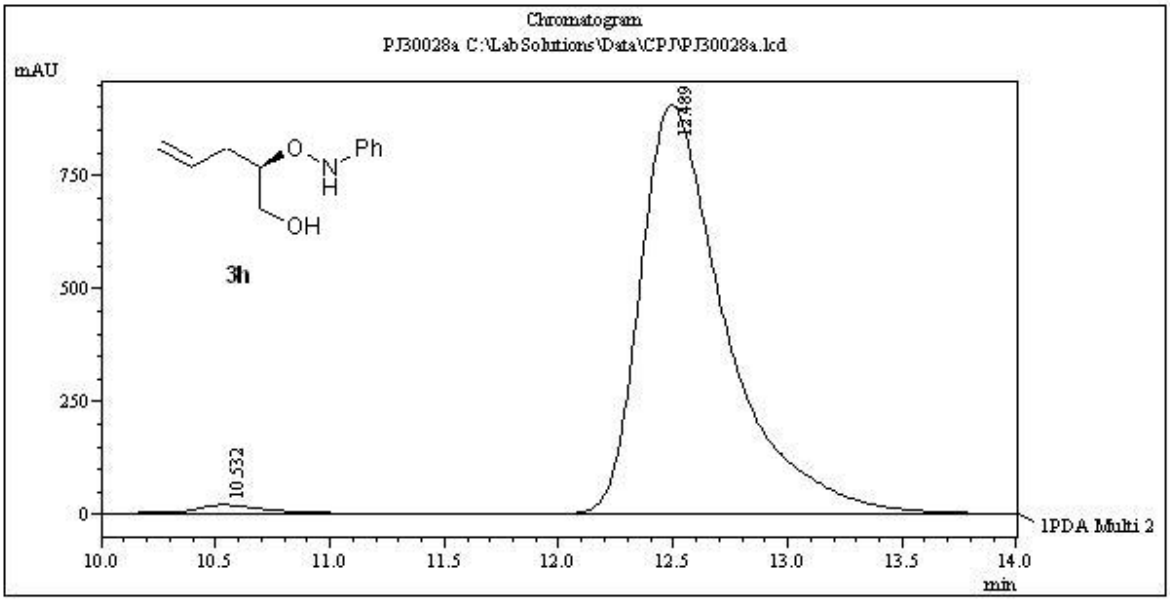
Peak Table
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area %
1	57.879	99.789
2	62.487	0.211
Total		100.000



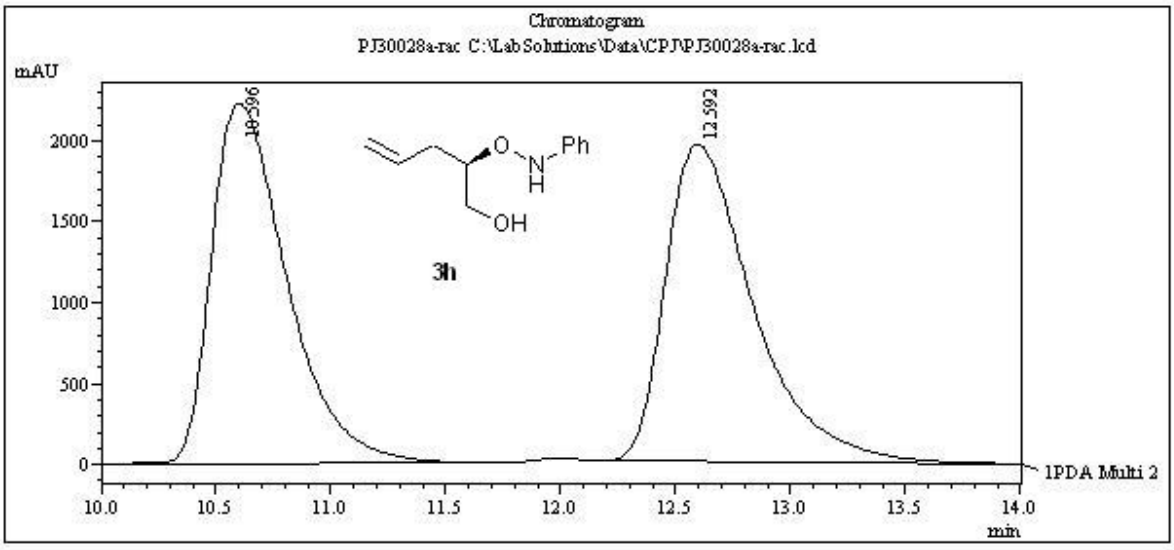
Peak Table
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area %
1	57.358	49.364
2	62.071	50.636
Total		100.000



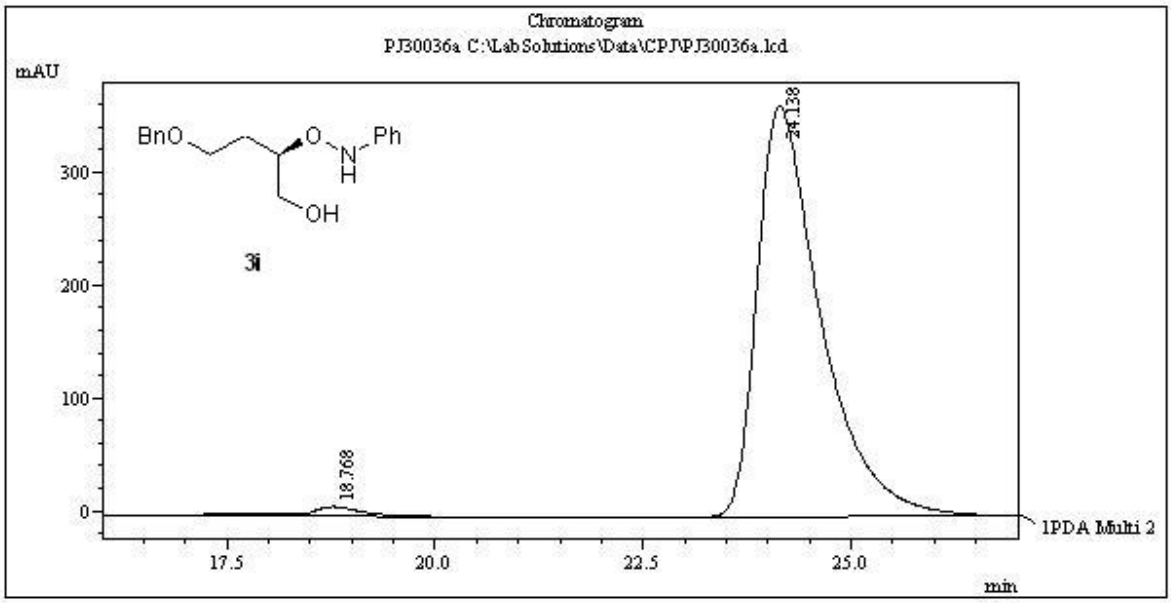
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.532	1.880
2	12.489	98.120
Total		100.000



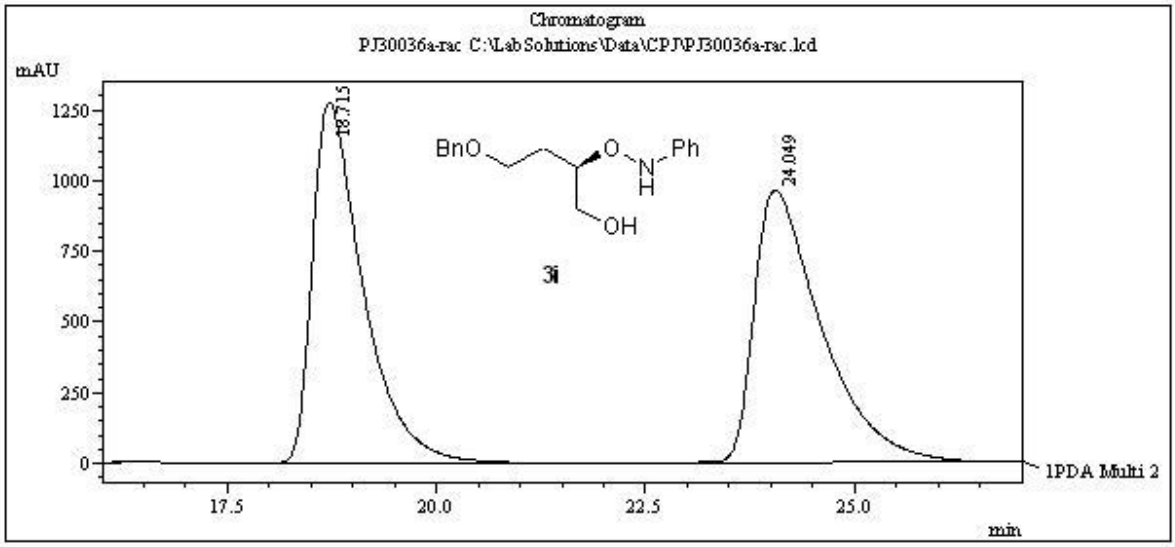
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.596	49.417
2	12.592	50.583
Total		100.000



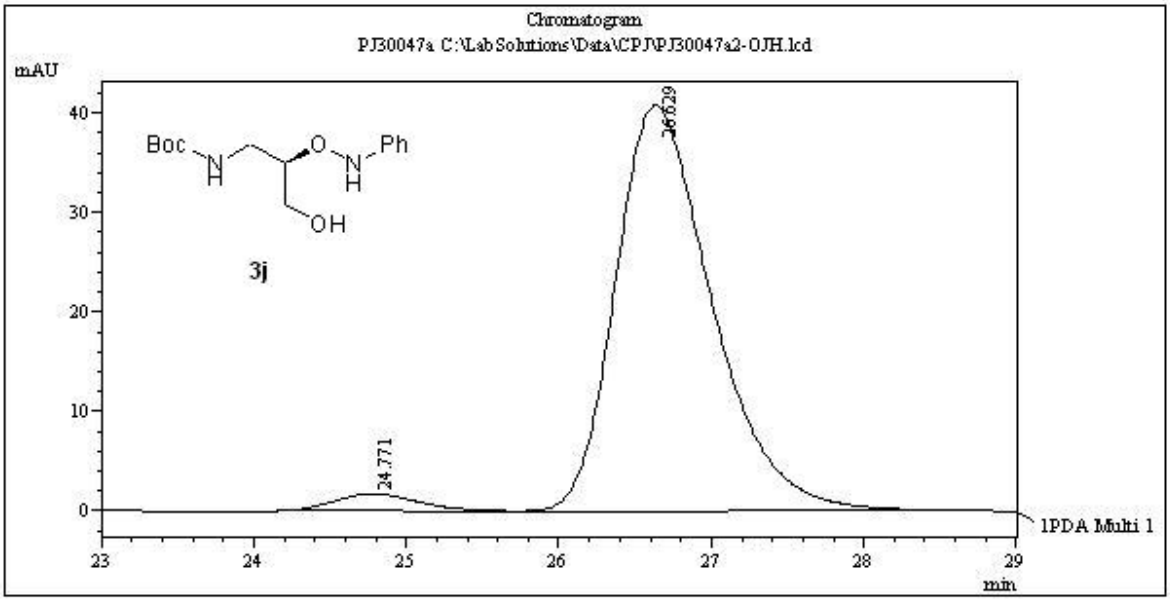
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	18.768	1.736
2	24.138	98.264
Total		100.000



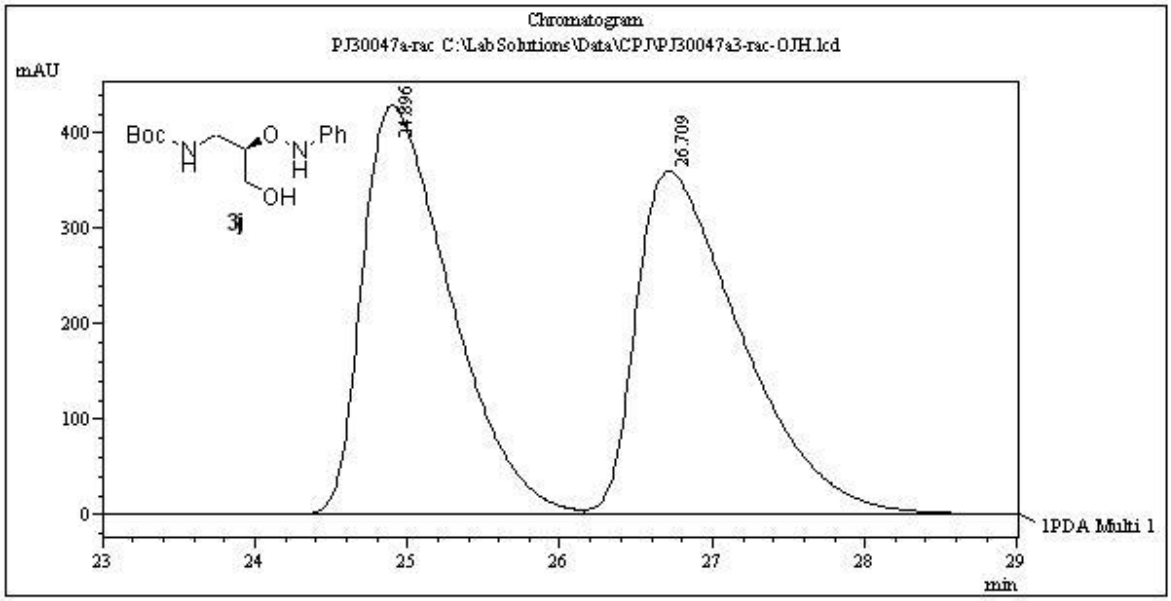
Peak Table
PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	18.715	49.796
2	24.049	50.204
Total		100.000



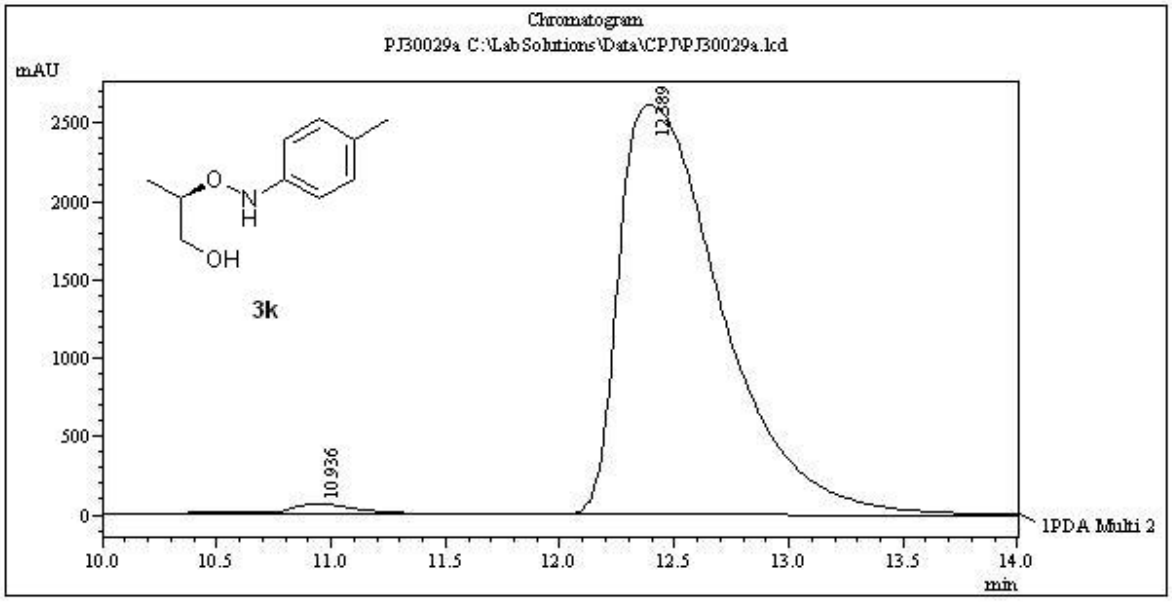
Peak Table
PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area %
1	24.771	3.411
2	26.629	96.589
Total		100.000



Peak Table
PDA Ch1 230nm 4nm

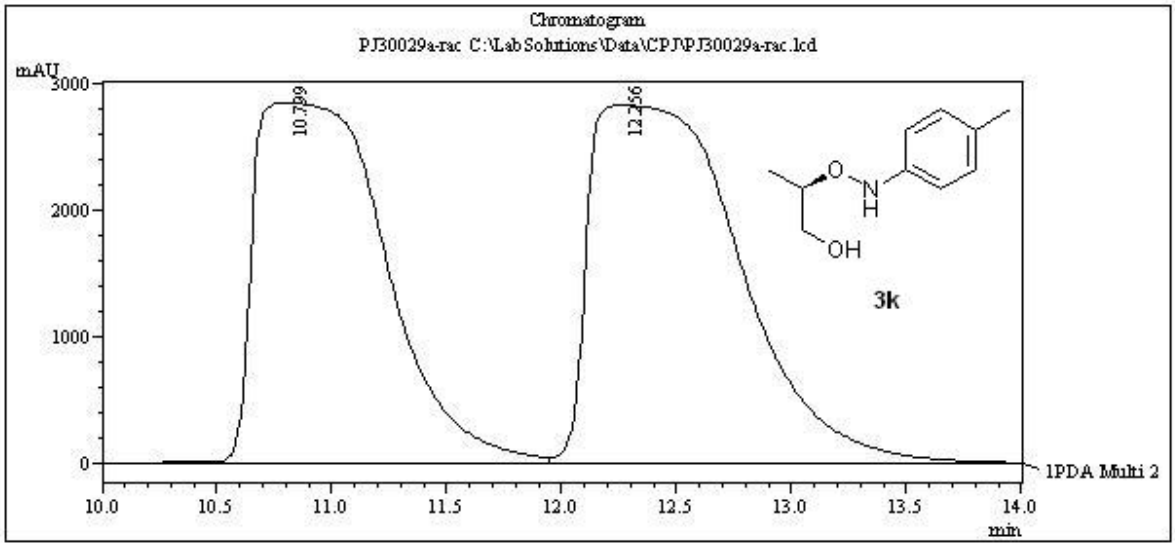
Peak#	Ret. Time	Area %
1	24.896	49.829
2	26.709	50.171
Total		100.000



Peak Table

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.936	1.744
2	12.389	98.256
Total		100.000



Peak Table

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area %
1	10.799	46.717
2	12.256	53.283
Total		100.000