Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Chiral bifunctional thiourea-tertiary amine catalyzed enantioselective hydroxyamination of oxindoles

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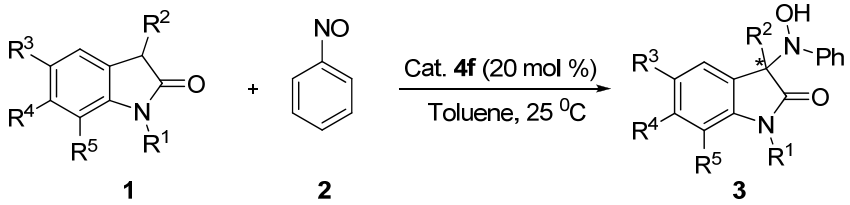
1.General methods

Commercial grade solvent was dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). ^{1}H NMR spectra were recorded at 300 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, $\delta = 7.26$ and DMSO-d^6，$\delta = 2.54$). ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta = 77.0$ and DMSO-d^6，$\delta = 40.6$). Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. Reactions were monitored by TLC and visualized with ultraviolet light. Enantiomeric excess (*ee*) was determined by HPLC analysis on chiralpak AD-H, or OD-H columns. IR spectra were recorded on a ThermoFisher Nicolet Avatar 360 FTIR spectrometer on a KBr beamsplitter. Optical rotations are reported as follows: $[\alpha]^{20}_{D}$ (C in g/per 100 mL, THF).

2.General procedure for hydroxyamination of oxindoles with nitrosobenzene

Substrates **1a-p**,[1] nitrosobenzene **2**[2] and catalysts **4a-m**[3] were prepared according to literature methods.

2.1 General procedure for hydroxyamination of oxindoles 1a-j with nitrosobenzene.



2-oxindole **1** (0.6 mmol), nitrosobenzene **2** (0.2 mmol) and catalyst **4f** (0.04 mmol) were stirred in 4.0 mL toluene at 25°C for 4-11 h in air. Then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether / ethylacetate) to afford the corresponding products **3**.

(R)-1,3-dibenzyl-3-(hydroxy(phenyl)amino)indolin-2-one (**3a**)

Yield 86%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.48 (d, *J*=9.1Hz, 1H), 7.38-7.40 (m, 1H), 7.23 (s, 1H), 6.98-7.18 (m, 11H), 6.85 (d, *J*=7.2Hz, 2H), 6.47 (d, *J*=7.1Hz, 2H), 6.16-6.19 (m, 1H), 4.56 (d, *J*=16.1Hz, 1H), 4.45 (d, *J*=16.1Hz, 1H), 3.78 (d, *J*=12.4Hz, 1H), 3.53 (d, *J*=12.4Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=175.2, 148.4, 143.1, 134.8, 134.3, 130.6, 129.0, 128.4, 127.7, 127.4, 126.9, 126.6, 126.5, 126.3, 126.2, 125.7, 124.1, 121.9, 109.1, 76.5, 43.2, 41.8; IR (KBr): ν=3346, 3060, 3030, 2924, 1709, 1694, 1610, 1487, 1466, 1454, 1373, 1359, 1176, 760, 730, 700, 648 cm^{-1}; ESI-HRMS: Calcd for $[C_{28}H_{24}N_2NaO_2, M+Na]^+$: 443.1730, FOUND: 443.1723. The *ee* was determined by HPLC analysis using a chiralcel AD column,

hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 24.69 min (major), 26.46 min (minor), 83% *ee*, $[\alpha]_D^{20}$=-28 (c 0.2, DCM).

(R)-1-benzyl-3-(4-fluorobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3b**)

Yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.36 (d, *J*=7.51Hz, 1H), 6.99-7.25 (m, 10H), 6.78 (t, *J*=7.0Hz, 2H), 6.68 (t, *J*=8.7Hz, 2H), 3.75 (d, *J*=7.1Hz, 2H), 6.8 (d, *J*=7.1Hz, 2H), 6.22 (d, *J*=6.9Hz, 1H), 4.57 (d, *J*=16.1Hz, 1H), 4.44 (d, *J*=16.1Hz, 1H), 3.75 (d, *J*=12.5Hz, 1H), 3.48 (d, *J*=12.6Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.6, 161.8 (J_{C-F}=243.4Hz), 147.5, 143.1, 134.6, 132.1 (J_{C-F}=7.9Hz), 129.8, 129.4, 128.4, 127.9, 127.4 (J_{C-F}=7.0Hz), 127.2, 126.7, 126.0, 124.0, 122.2, 114.6 (J_{C-F}=20.9Hz), 109.3, 77.2, 43.2, 40.1; IR (KBr): ν =3370, 3058, 2933, 2856, 1708, 1612, 1510, 1488, 1468, 1379, 1223, 1171, 1160, 1009, 943, 777, 755, 700 cm^{-1}; ESI-HRMS: Calcd for $[C_{28}H_{23}FN_2NaO_2, M+Na]^+$: 461.1636, FOUND: 461.1626. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 21.64 min (major), 25.52 min (minor), 80% *ee*, $[\alpha]_D^{20}$=-25 (c 0.1, DCM).

(R)-1-benzyl-3-(3-chlorobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3c**)

Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.37 (d, *J*=7.8Hz, 1H), 7.0-7.25 (m, 11H), 6.92 (t, *J*=7.8Hz, 1H), 6.84 (s, 1H), 6.74 (d, *J*=7.7Hz, 1H), 6.54 (d, *J*=7.0Hz, 2H), 6.22-6.25 (m, 1H), 4.46-4.58 (m, 2H), 3.75 (d, *J*=12.4Hz, 1H), 3.51 (d, *J*=12.5Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.4, 147.3, 143.0, 136.2, 134.6, 133.5, 130.6, 129.5, 128.5, 127.9, 127.2, 126.9, 126.7, 126.4, 125.7, 124.0, 122.3, 109.3, 76.4, 43.3, 41.1; IR (KBr): ν =3357, 3058, 2923, 2854, 1710, 1609, 1597, 1486, 1466, 1372, 1210, 1193, 1008, 945, 815, 773, 755, 696 cm^{-1}; ESI-HRMS: Calcd for $[C_{28}H_{23}ClN_2NaO_2, M+Na]^+$: 477.1340, FOUND: 477.1335. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 20.36 min (major), 21.68 min (minor), 81% *ee*, $[\alpha]_D^{20}$=-34 (c 0.2, DCM).

(R)-1-benzyl-3-(4-chlorobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3d**)

Yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.33 (d, *J*=7.3Hz, 2H), 7.01-7.24 (m, 9H), 6.97 (d, *J*=8.4Hz, 2H), 6.75 (d, *J*=8.3Hz, 2H), 6.47 (d, *J*=7.4Hz, 2H), 6.23 (d, *J*=7.1Hz, 1H), 4.63 (d, *J*=16.1Hz, 1H), 4.40 (d, *J*=16.1Hz, 1H), 3.73 (d, *J*=12.4Hz, 1H), 3.46 (d, *J*=12.4Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.9, 148.2, 143.1, 134.6, 132.8, 132.6, 132.0, 129.3, 128.4, 127.9, 127.8, 127.7, 127.2, 126.3, 126.2, 126.0, 124.0, 122.1, 109.3, 76.2, 43.2, 41.0; IR (KBr):

ν =3362, 3057, 2923, 2851, 1707, 1612, 1488, 1468, 1377, 1211, 1171, 945, 859, 815, 754, 698 cm^{-1}; ESI-HRMS: Calcd for $[C_{28}H_{23}ClN_2NaO_2, M+Na]^+$: 477.1340, FOUND: 477.1329. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 25.25 min (major), 27.49 min (minor), 82% *ee*, $[\alpha]_D^{20}$ =-45 (c 0.1, DCM).

(R)-1-benzyl-3-(4-bromobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3e**)

Yield 83%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.37 (d, *J*=6.7Hz,1H), 7.02-7.23 (m, 12H), 6.73 (d, *J*=8.3Hz, 2H), 6.47 (d, *J*=7.7Hz, 2H), 6.23 (d, *J*=8.1Hz,1H), 4.67 (d, *J*=16.1Hz, 1H), 4.40 (d, *J*=16.0Hz, 1H), 3.74 (d, *J*=12.5Hz, 1H), 3.48 (d, *J*=12.4Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ= 175.0, 148.2, 143.1, 134.7, 133.3, 132.3, 130.9, 129.3,128.5, 127.8, 127.2, 126.3, 125.9, 124.0, 122.1, 120.8, 119.7, 109.3, 76.1, 43.3, 41.1; IR (KBr): ν =3362, 3057, 2923, 2852, 1707, 1612, 1487, 1468, 1377, 1211, 1171, 1011, 858, 813, 754, 697 cm^{-1}; ESI-HRMS: Calcd for $[C_{28}H_{23}BrN_2NaO_2, M+Na]^+$: 521.0835, FOUND: 521.0836. The *ee* was determined by HPLC analysis using a chiralcel OD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 8.07 min (major), 8.71 min (minor), 80% *ee*, $[\alpha]_D^{20}$ =-47 (c 0.1, DCM).

(R)-1-benzyl-3-(hydroxy(phenyl)amino)-3-(3-methylbenzyl)indolin-2-one (**3f**)

Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.33-7.40 (m, 2H), 7.23-7.27 (m, 1H), 6.98-7.20 (m, 8H), 6.89-6.91 (m, 2H), 6.68 (s, 1H), 6.62 (d, *J*=6.6Hz, 1H), 6.46 (d, *J*=7.2Hz, 2H), 6.17-6.20 (m, 1H), 4.63 (d, *J*=16.1Hz, 1H), 4.42 (d, *J*=16.1Hz, 1H), 3.71-3.77 (m, 1H), 3.46-3.52 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=175.3, 148.4, 143.2, 137.2, 134.9, 134.2, 131.4, 129.0, 128.4, 127.7, 127.6, 127.5, 127.2, 126.9, 126.8, 126.6, 126.3, 125.7, 124.1, 121.8, 109.1, 76.4, 43.2, 41.7, 21.1; IR (KBr): ν =3349, 3051, 3027, 2924, 1708, 1609, 1486, 1466, 1373, 1211, 1174, 1010, 945, 917, 776, 698 cm^{-1}; ESI-HRMS: Calcd for $[C_{29}H_{26}N_2NaO_2, M+Na]^+$: 457.1886, FOUND: 457.1871. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 75:25, flow rate = 1.0 mL/min, 220 nm. t_R = 19.09 min (major), 21.83 min (minor), 77% *ee*, $[\alpha]_D^{20}$ = -35 (c 0.1, DCM).

(R)-1-benzyl-3-(hydroxy(phenyl)amino)-3-(4-methoxybenzyl)indoli n-2-one (**3g**)

Yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.36 (d, *J*=7.5Hz, 1H), 7.25 (d, *J*=6.9Hz, 2H), 7.01-7.20 (m, 8H), 6.75 (d, *J*=8.6Hz, 2H), 6.55 (d, *J*=8.6Hz, 2H), 6.45 (d, *J*=7.2Hz, 2H), 6.18-6.21 (m, 1H), 4.64 (d, *J*=16.1Hz, 1H), 4.42 (d, *J*=16.1Hz, 1H), 3.74 (d, *J*=12.6Hz,

1H), 3.70 (s, 3H), 3.46 (d, *J*=12.6Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.8, 158.3, 147.7, 143.2, 134.7, 131.6, 129.2, 128.3, 127.8, 127.0, 126.3, 126.1, 126.0, 124.0, 122.0, 113.1, 109.2, 76.6, 54.9, 43.1, 40.7; IR (KBr): ν =3362, 3054, 2929, 1704, 1611, 1512, 1486, 1467, 1248, 1177, 1110, 945, 859, 775, 755, 699 cm^{-1}; ESI-HRMS: Calcd for $[C_{29}H_{26}N_2NaO_3, M+Na]^+$: 473.1836, FOUND: 473.1835. The *ee* was determined by HPLC analysis using a chiralcel OD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 8.78 min (major), 9. 56 min (minor), 77% *ee*, $[\alpha]_D^{20}$ = -50 (c 0.1, DCM).

(R)-3-benzyl-1-ethyl-3-(hydroxy(phenyl)amino)indolin-2-one (**3h**)

Yield 51%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.47 (s, 1H), 7.31 (d, *J*=7.3Hz, 1H), 7.17-7.22 (m, 2H), 7.12 (t, *J*=7.9Hz, 3H), 6.93-7.05 (m, 5H), 6.77 (d, *J*=7.0Hz, 2H), 6.41 (d, *J*=7.7Hz, 1H), 3.68 (d, *J*=12.3Hz, 1H), 3.34-3.45 (m, 2H), 3.19-3.30 (m, 1H), 0.63 (t, *J*=7.1Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.8, 148.5, 142.9, 134.2, 130.4, 128.9, 127.6, 127.4, 127.0, 126.4, 125.5, 123.8, 121.7, 107.9, 76.1, 41.9, 34.0, 11.6; IR (KBr): ν =3357, 3057, 2934, 1700, 1610, 1487, 1467, 1452, 1377, 1214, 1099, 1028, 915, 769, 754, 699 cm^{-1}; ESI-HRMS: Calcd for $[C_{23}H_{22}N_2NaO_2, M+Na]^+$: 381.1573, FOUND: 381.1561. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0

mL/min, 220 nm. t_R = 12.69 min (major), 13.33 min (minor), 81% *ee*, $[\alpha]_D^{20}$ = -11 (c 0.2, DCM).

(R)-3-benzyl-5-bromo-3-(hydroxy(phenyl)amino)-1-methylindolin-2-one (**3i**)

Yield 85%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=7.35 (d, *J*=1.5Hz, 1H), 7.17-7.29 (m, 4H), 6.96-7.13(m, 5H), 6.77 (d, *J*=5.9Hz, 2H), 6.27 (d, *J*=8.3Hz, 1H), 3.61 (d, *J*=12.4Hz, 1H), 3.33 (d, *J*=12.4Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=174.7, 148.0, 142.8, 133.6, 131.7, 130.2, 129.0, 128.9, 127.9, 127.6, 126.6, 126.0, 123.7, 114.6, 109.1, 76.6, 42.0, 25.7; IR (KBr): ν =3293, 3061, 2924, 1707, 1607, 1485, 1364, 1271, 1100, 808, 773, 701 cm^{-1}; ESI-HRMS: Calcd for $[C_{22}H_{19}BrN_2NaO_2, M+Na]^+$: 445.0522, FOUND: 445.0518. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 12.48 min (minor), 14.32 min (major), 75% *ee*, $[\alpha]_D^{20}$ = -44 (c 0.2, DCM).

(R)-3-(3-chlorobenzyl)-3-(hydroxy(phenyl)amino)-1-methylindolin-2-one (**3j**)

Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$):δ= 7.52 (s, 1H), 7.10-7.23 (m, 5H), 6.96-7.07 (m, 3H), 6.89 (t, *J*=7.7Hz, 1H), 6.73 (s, 1H), 6.69 (d, *J*=7.6Hz, 1H), 6.42 (d, *J*=7.7Hz, 1H), 3.61 (d, *J*=12.4Hz, 1H), 3.36 (d, *J*=12.4Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):δ=

175.2, 148.3, 143.6, 136.3, 133.1, 130.2, 129.2, 128.6, 128.5, 127.7, 126.6, 126.3, 126.1, 125.7, 123.7, 122.1, 107.9, 76.1, 41.4, 25.6; IR (KBr): ν =3323, 3055, 2930, 1698, 1612, 1485, 1471, 1379, 1089, 949, 752, 670 cm^{-1}; ESI-HRMS: Calcd for [$C_{22}H_{19}ClN_2NaO_2$, M+Na]$^+$: 401.1027, FOUND: 401.1022. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 11.48 min (major), 13.40 min (minor), 77% *ee*, $[\alpha]_D^{20}$ = -3 (c 0.2, DCM).

2.2 General procedure for hydroxyamination of oxindoles 1k-p with nitrosobenzene.

2-oxindole **1** (0.6 mmol), nitrosobenzene **2** (0.2 mmol) and catalyst **4f** (0.04 mmol) were stirred in 4.0 mL toluene at 25°C for 1.5-3 h in air. The precipitate was filtered, washed with methylene dichloride and dried to afford the product as a white solid.

(R)-3-benzyl-3-(hydroxy(phenyl)amino)indolin-2-one (**3k**)[4a,b]

Yield 86%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=9.92 (s, 1H), 9.09 (s, 1H), 7.43 (d, *J*=7.1Hz, 1H), 6.82-7.19 (m, 12H), 6.35 (d, *J*=7.4Hz, 1H), 3.41-3.52 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d^6):δ=175.5, 150.0, 142.0, 134.9, 130.2, 128.5, 127.6, 127.4, 126.2, 126.0, 124.4, 123.0, 120.7, 108.8, 76.0, 41.7. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 23.36 min (major), 26.40 min

(minor), 90% *ee*, $[\alpha]_D^{20}$ = -89 (c 0.2, THF).

(R)-3-(4-chlorobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3l**)[4b]

Yield 85%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=9.97 (s, 1H), 9.11 (s, 1H), 7.42 (d, *J*=7.1Hz, 1H), 6.90-7.11 (m, 9H), 6.81 (d, *J*=8.0Hz, 2H), 6.37 (d, *J*=7.4Hz, 1H), 3.35-3.50 (m,2H); ^{13}C NMR (75 MHz, DMSO-d^6):δ= 175.3, 150.0, 141.9, 134.0, 132.0, 131.1, 128.7, 127.4, 126.1, 124.5, 122.9, 120.9, 108.9, 75.9, 41.0. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 23.80 min (major), 28.42 min (minor), 82% *ee*, $[\alpha]_D^{20}$ = -104 (c 0.2, THF).

(R)-3-(3-bromobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3m**)

Yield 91%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=10.03 (s, 1H), 9.13 (s, 1H), 7.44 (d, *J*=6.1Hz, 1H), 7.22 (d, *J*=6.5Hz, 1H), 6.98-7.11 (m, 9H), 6.79 (d, *J*=6.6Hz, 1H), 6.39 (d, *J*=7.2Hz, 1H) 3.37-3.52 (m,2H); ^{13}C NMR (75 MHz, DMSO-d^6):δ= 175.3, 149.9, 141.9, 137.8, 132.9, 129.5, 129.4, 129.2, 128.8, 127.5, 127.2, 126.1, 124.5, 123.0, 120.9, 120.7, 108.9, 75.9, 41.2; IR (KBr): ν =3237, 2918, 1702, 1618, 1469, 773, 753, 692 cm^{-1}; ESI-HRMS: Calcd for [$C_{21}H_{17}BrN_2NaO_2$, M+Na]$^+$: 431.0366, FOUND: 431.0364. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol

90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 18.31 min (major), 24.89 min (minor), 82% *ee*, $[\alpha]_D^{20}$ = -63 (c 0.2, THF).

(R)-3-(4-bromobenzyl)-3-(hydroxy(phenyl)amino)indolin-2-one (**3n**)[4b]

Yield 84%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=9.98 (s, 1H), 9.12 (s, 1H), 7.43 (d, *J*=7.2Hz, 1H), 7.21 (d, *J*=8.2Hz, 2H), 7.11-7.16 (m, 4H), 6.90-7.07 (m, 3H), 6.76 (d, *J*=8.2Hz, 2H), 6.39 (d, *J*=7.6Hz, 1H) 3.37-3.49 (m,2H); ^{13}C NMR (75 MHz, DMSO-d^6):δ= 175.3, 150.0, 141.9, 134.4, 132.4, 130.3, 128.7, 127.5, 127.3, 126.1, 124.5, 122.9, 120.9, 119.7, 108.9, 75.9, 41.0. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 25.53 min (major), 30.61 min (minor), 76% *ee*, $[\alpha]_D^{20}$ = -95 (c 0.2, THF).

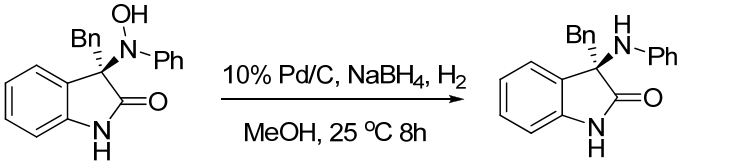
(R)-3-benzyl-6-chloro-3-(hydroxy(phenyl)amino)indolin-2-one (**3o**)

Yield 71%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=10.13 (s, 1H), 9.18 (s, 1H), 7.41 (d, *J*=7.8Hz, 1H), 6.96-7.15 (m, 10H), 6.84 (s, 1H), 6.37 (s, 1H), 3.39-3.49 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d^6): δ=175.5, 149.7, 143.5, 134.6, 132.7, 130.2, 127.6, 126.5, 124.8, 123.1, 120.5, 108.8, 75.9, 41.4; IR (KBr): ν=3269, 3030, 2919, 1716, 1669, 1617, 1489,1479, 1453, 1356, 1069, 964, 907, 857, 820, 765, 696; ESI-HRMS: Calcd for $[C_{21}H_{17}ClN_2NaO_2, M+Na]^+$: 387.0871, FOUND: 387.0883. The *ee* was determined by HPLC analysis using

a chiralcel OD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 220 nm. t_R = 7.10 min (major), 12.45 min (minor), 75% *ee*, $[\alpha]_D^{20}$=-52 (c 0.2, THF).

(R)-3-benzyl-7-fluoro-3-(hydroxy(phenyl)amino)indolin-2-one (**3p**) Yield 71%; ^{1}H NMR (300 MHz, DMSO-d^6):δ=10.48 (s, 1H), 9.21 (s, 1H), 7.26-7.29 (m, 1H), 7.13-7.18 (m, 4H), 7.02-7.04 (m, 4H), 6.83-6.97 (m, 2H), 6.80-6.83 (m, 2H), 3.41-3.51 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d^6): δ=175.4, 149.8, 145.8 (J_{C-F}= 240Hz), 134.6, 130.2, 127.6, 126.5, 124.8, 123.1, 122.2, 121.6 (J_{C-F}=5.6Hz), 115.6 (J_{C-F}= 17.0Hz), 76.4, 41.7; IR (KBr): ν=3263, 3032, 2928, 1719, 1688, 1644, 1602, 1491, 1454, 1215, 1183, 916, 834, 796, 760, 699; ESI-HRMS: Calcd for $[C_{21}H_{17}FN_2NaO_2, M+Na]^+$: 371.1166, FOUND: 371.1167. The *ee* was determined by HPLC analysis using a chiralcel AD column, hexane/2-propanol 95:5, flow rate = 1.0 mL/min, 220 nm. t_R = 20.33 min (minor), 31.09 min (major), 78% *ee*, $[\alpha]_D^{20}$=-49 (c 0.2, THF).

2.3 Procedure for cleave of the N-O bond.[4b]



3k, 90% *ee* **5k**, 71% yield, 92% *ee*

3k (0.2 mmol), Pd/C (4.9 mg, 10%) and sodium borohydride (0.6 mmol) were were stirred in 1.0 mL methanol at 25°C for 8 h in

hydrogen. Then the reaction mixture was filtered through celite and the filtrate was concentrated in vacuum. Column chromatography on silica gel (petroleum ether / ethylacetate 7:1) afford the corresponding products **5k**.

(R)-3-benzyl-3-(phenylamino)indolin-2-one (**5k**)

Yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$):δ=8.32 (s, 1H), 7.10-7.21 (m, 6H), 6.89-6.95 (m, 4H), 6.67-6.69 (m, 2H), 6.29 (d, *J*=7.7Hz, 2H), 4.68 (s, 1H), 3.26 (dd, *J*=27.4Hz, *J*=12.4Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=180.3, 145.1, 140.0, 133.1, 130.4, 129.4, 129.0, 127.8, 127.2, 124.5, 122.7, 119.0, 114.8, 110.5, 66.1, 46.3; IR (KBr): ν=3340, 3136, 3028, 1709, 1604, 1524, 1499, 1471, 1320, 1224, 1186, 751, 701, 667; ESI-HRMS: Calcd for $[C_{21}H_{18}N_2NaO, M+Na]^+$: 337.1311, FOUND: 337.1319. The *ee* was determined by HPLC analysis using a chiralcel OD column, hexane/2-propanol 90:10, flow rate = 1.0 mL/min, 254 nm. t_R = 9.87 min (major), 11.69 min (minor), 92% *ee*, $[\alpha]_D^{20}$=-5 (c 0.18, DCM).

References

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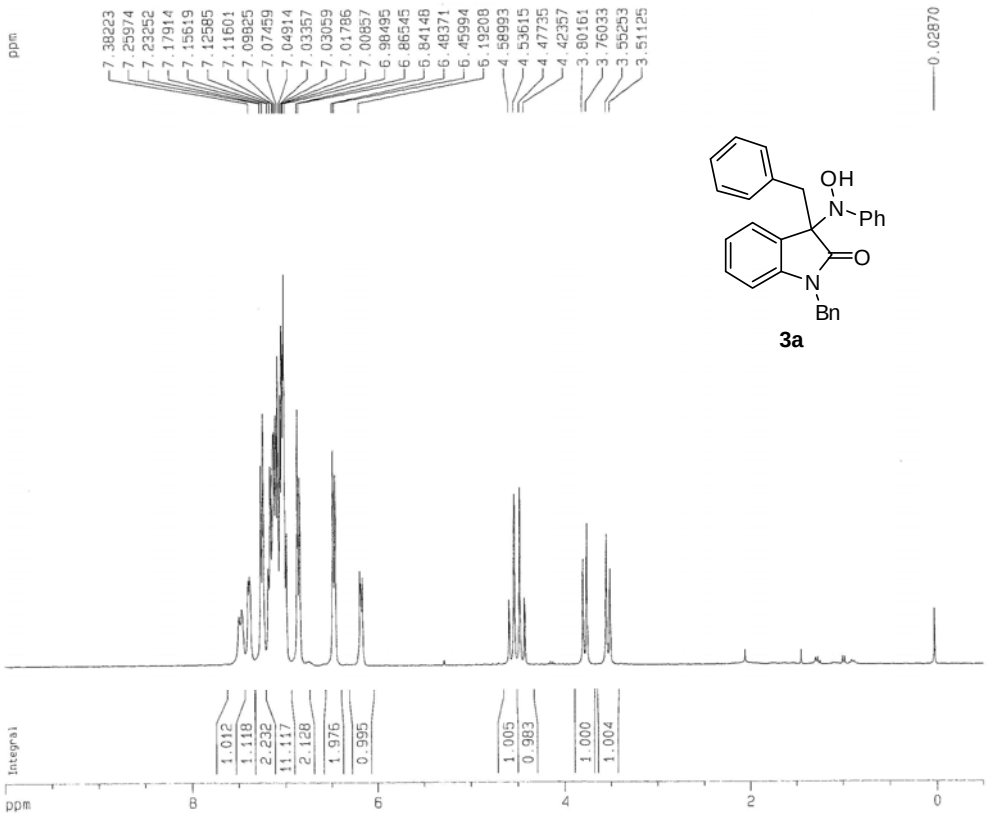
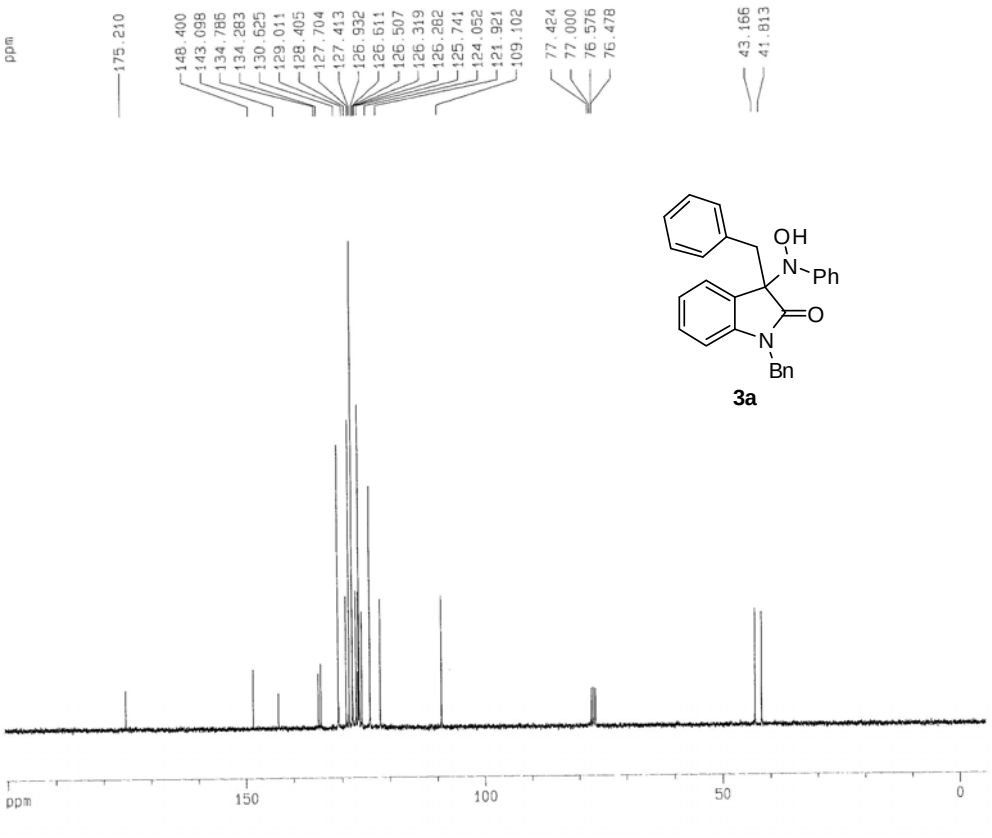
3874.

2. (a) G. H. Coleman, C. M. McCloskey and F. A. Stuart, *Org. Syn.*, 1955, **3**, 668; (b) E. L. Robert and R. L. Marion, *J. Org. Chem.*, 1937, **2**, 68.
3. L. Li, E. G. Klauber and D. Seidel, *J. Am. Chem. Soc.*, 2008, **130**, 12248.
4. (a) T. Zhang, L. Cheng, L. Liu, D. Wang and Y. -J. Chen, *Tetrahedron: Asymmetry*, 2010, **21**, 2800; (b) K. Shen, X.-H. Liu, G. Wang, L.-L. Lin and X.-M. Feng, *Angew. Chem. Int. Ed.*, 2011, **50**, 4684.

5. NMR spectra

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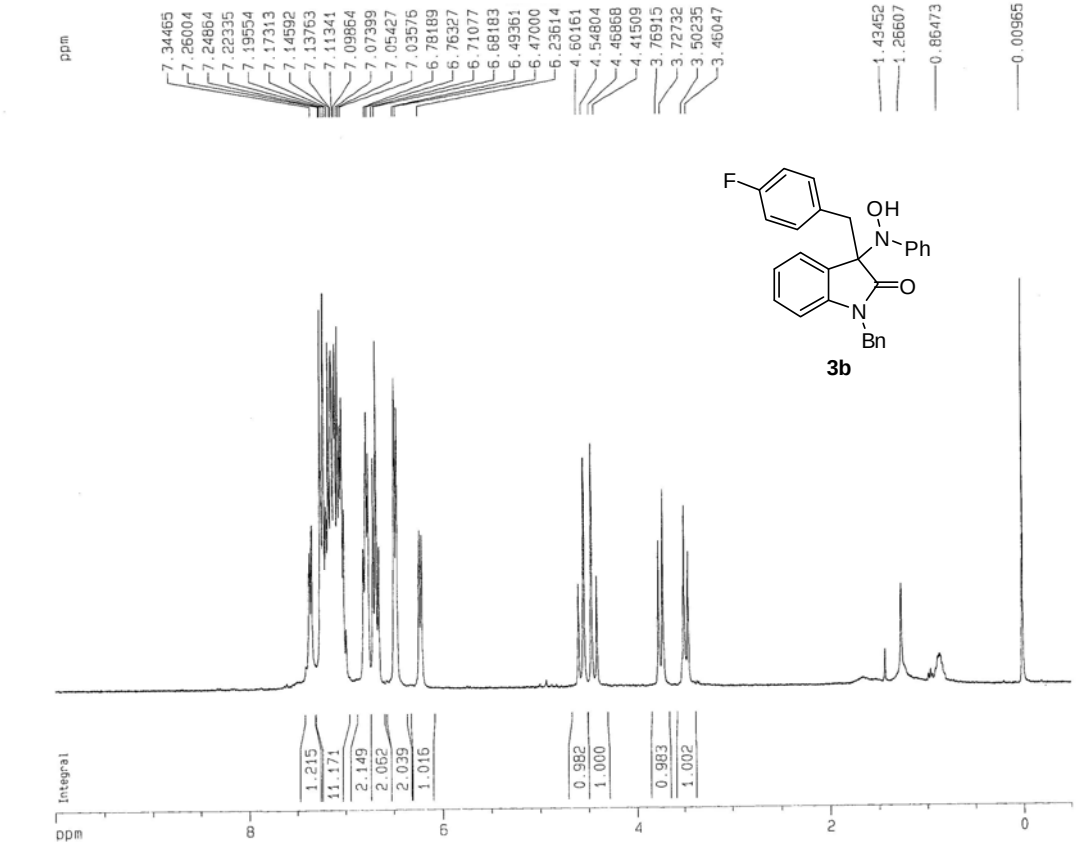
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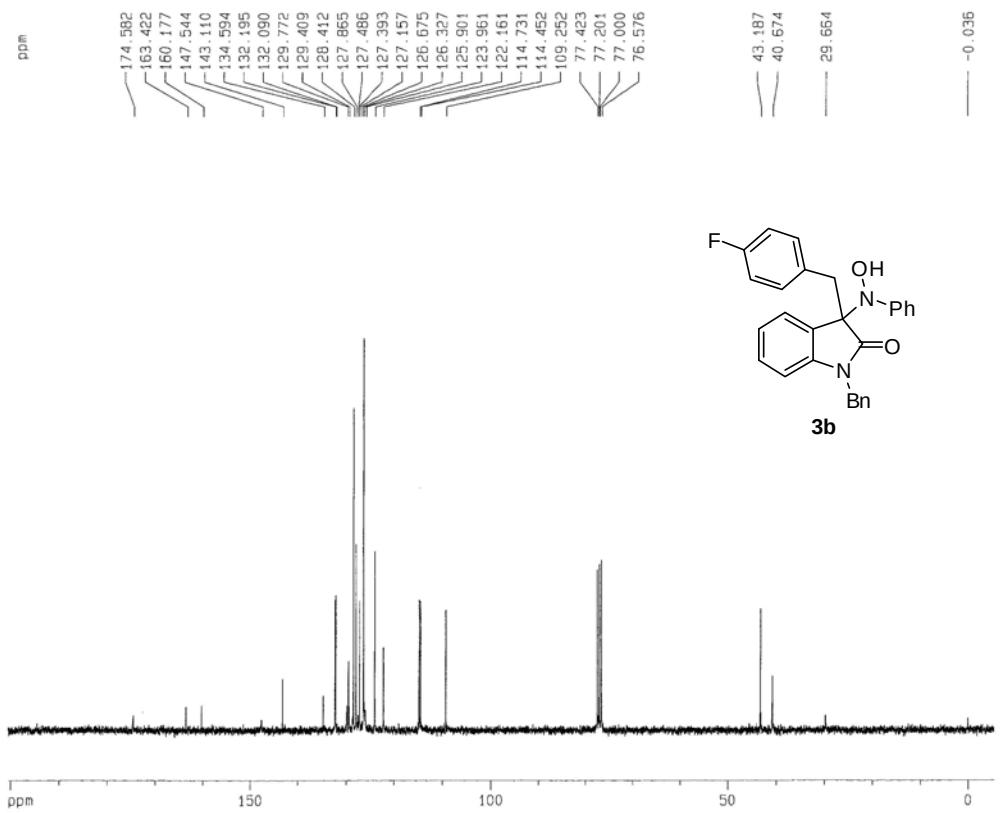
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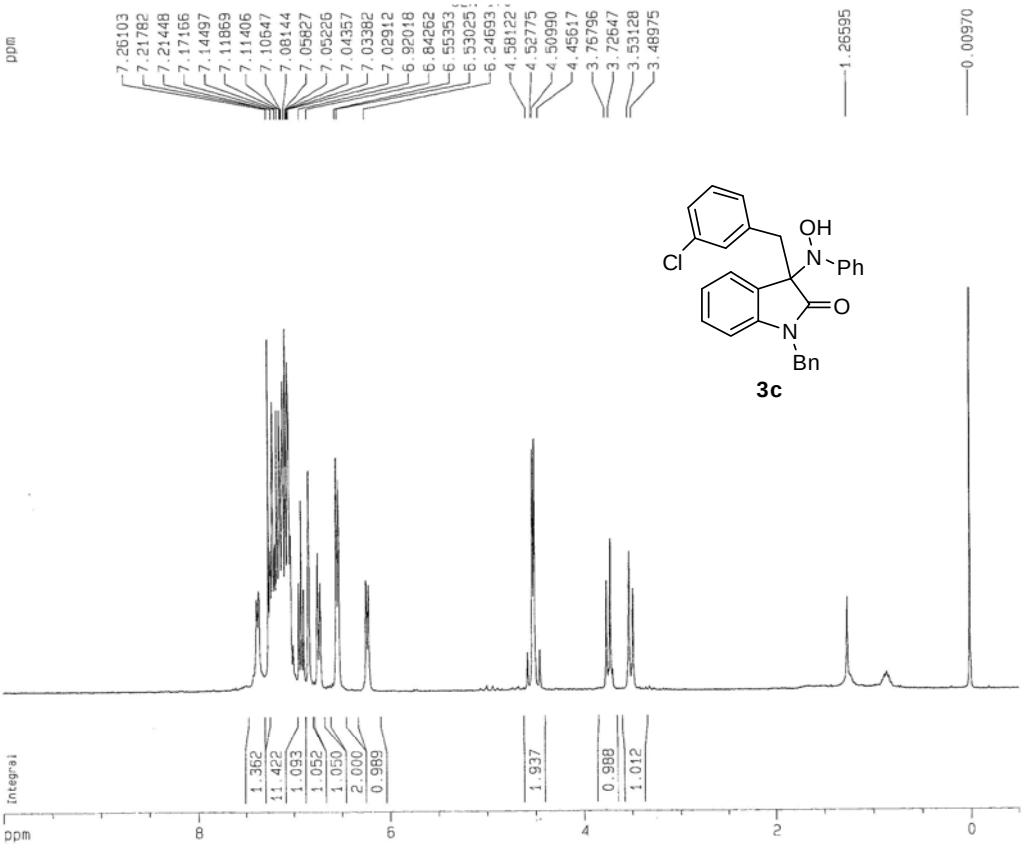
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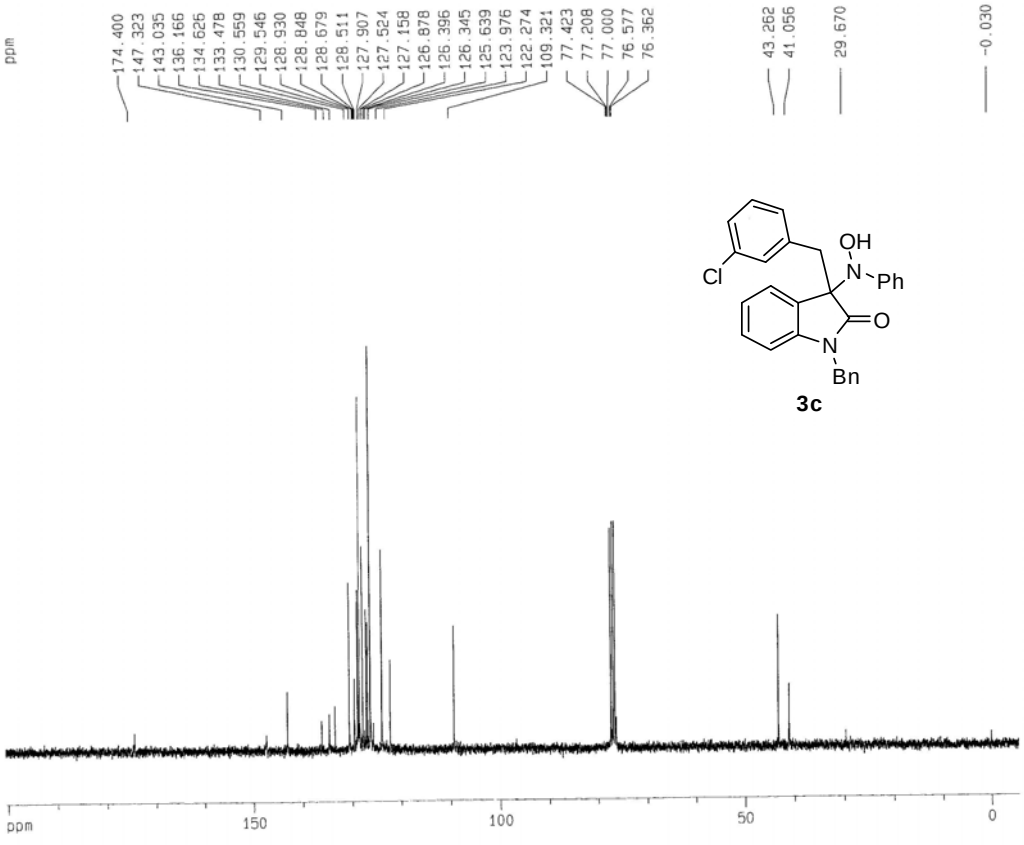

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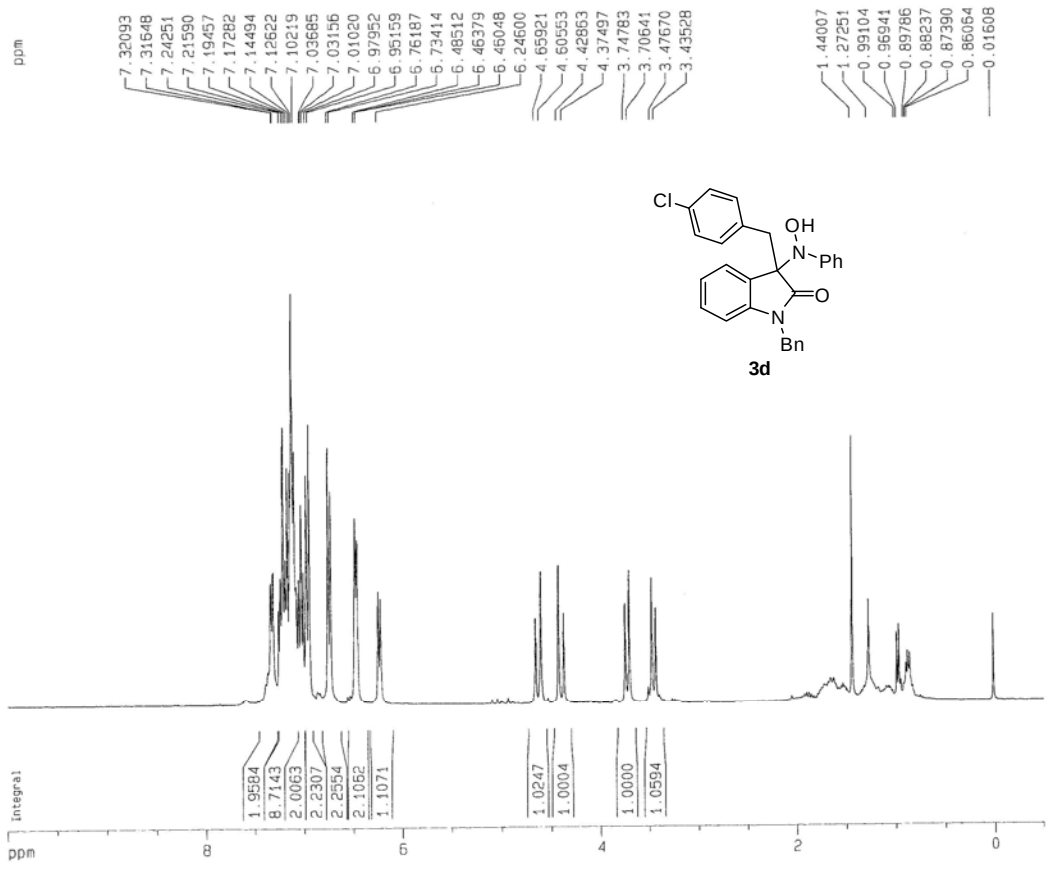

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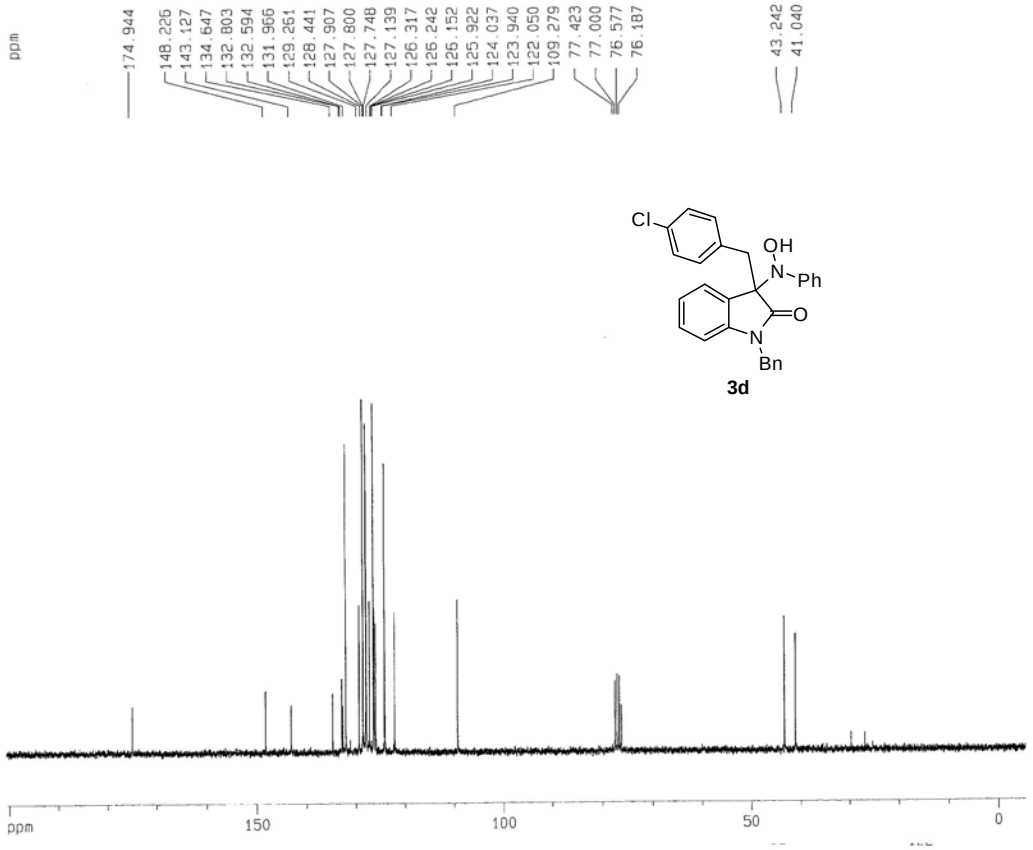
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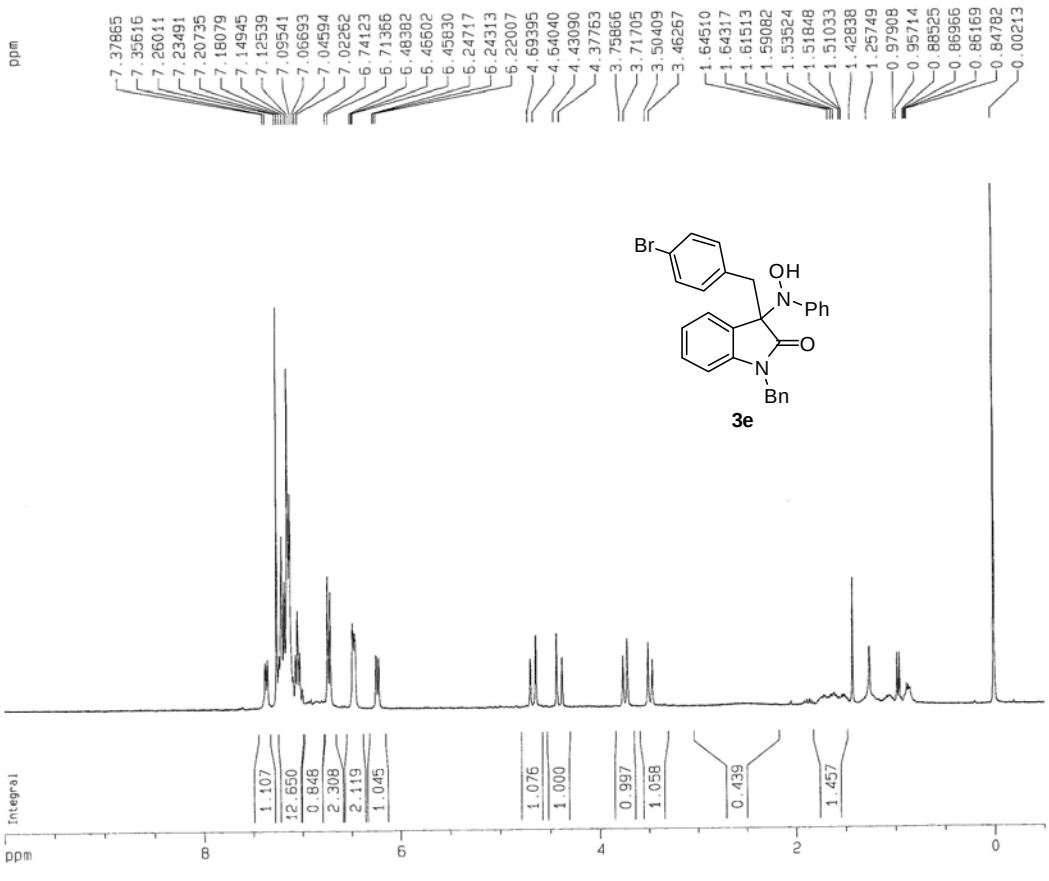
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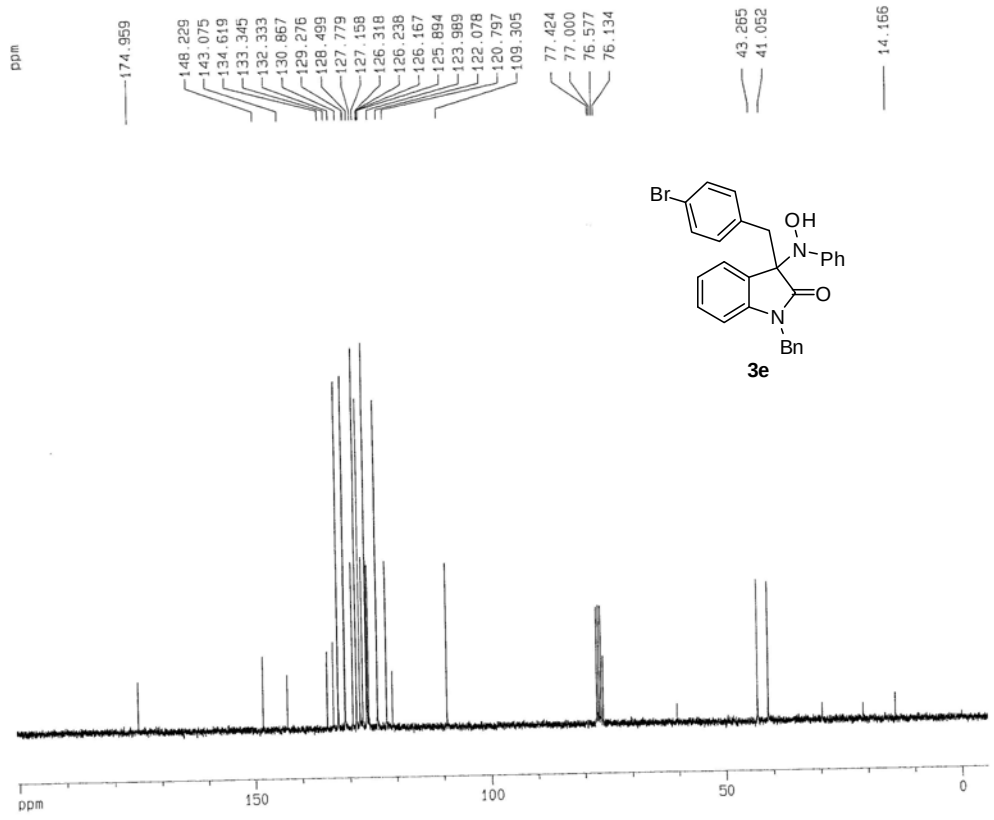

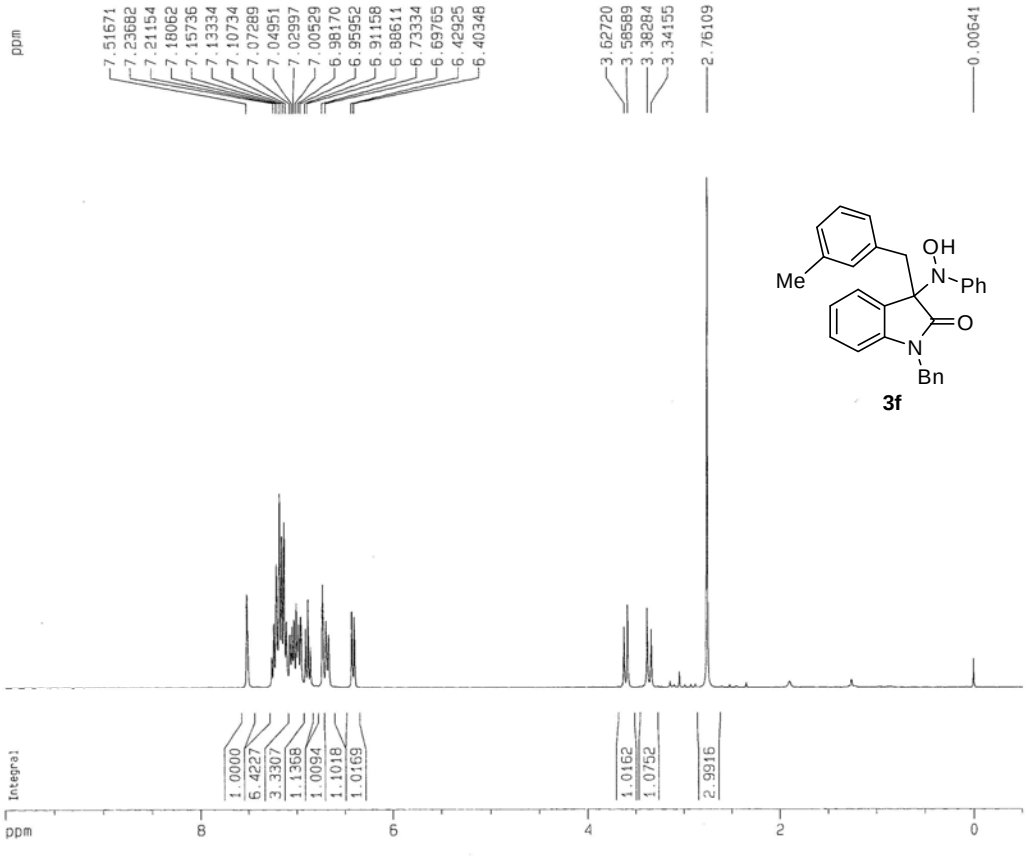

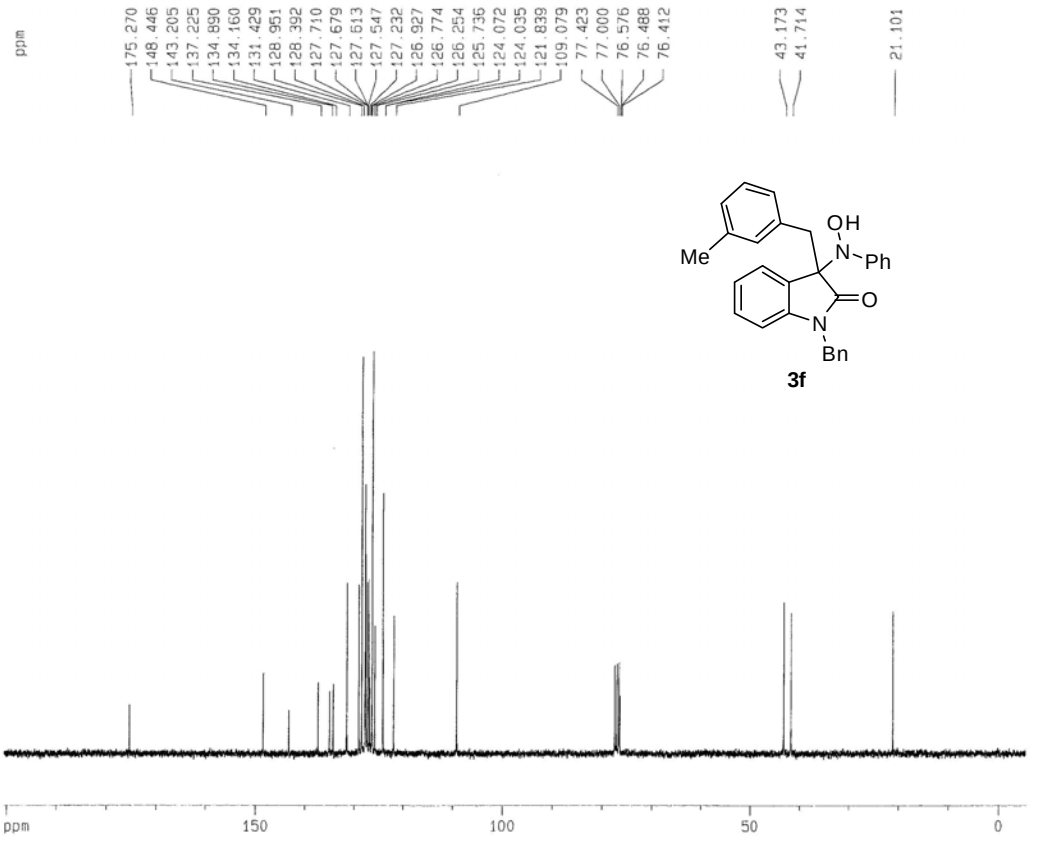
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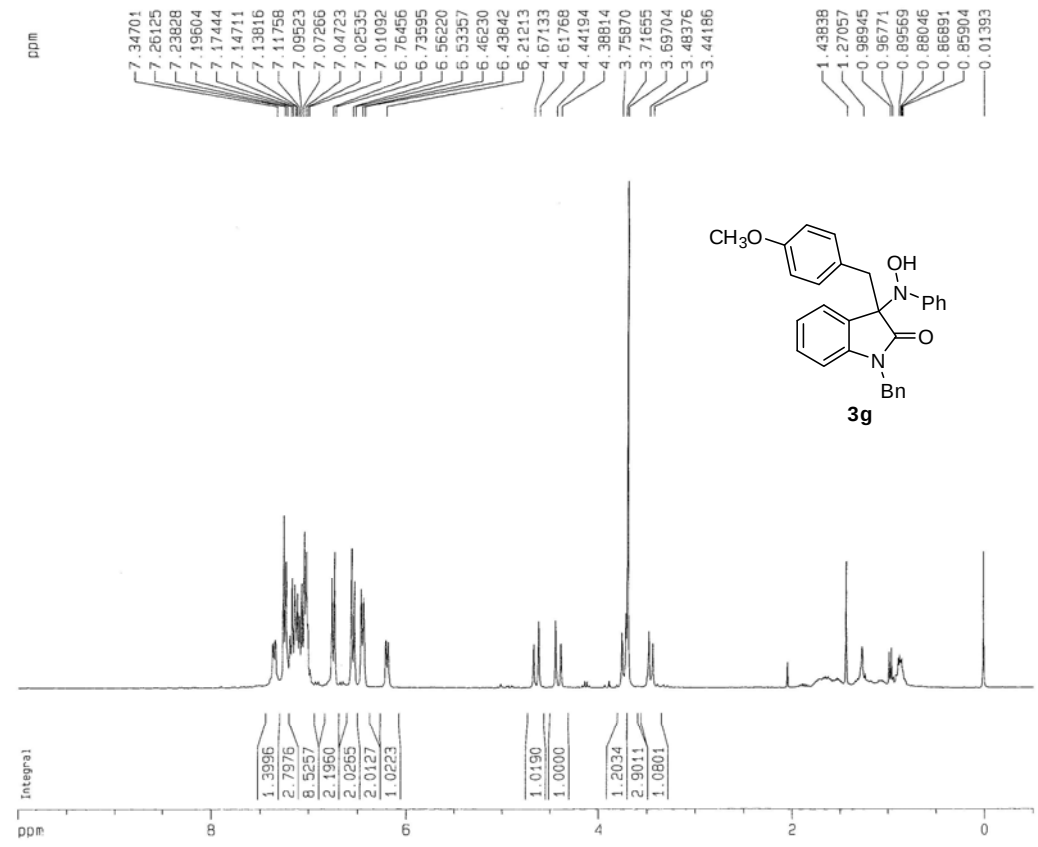
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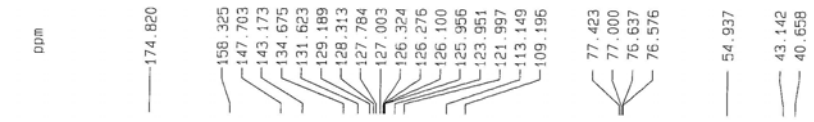
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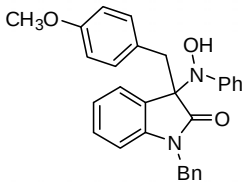
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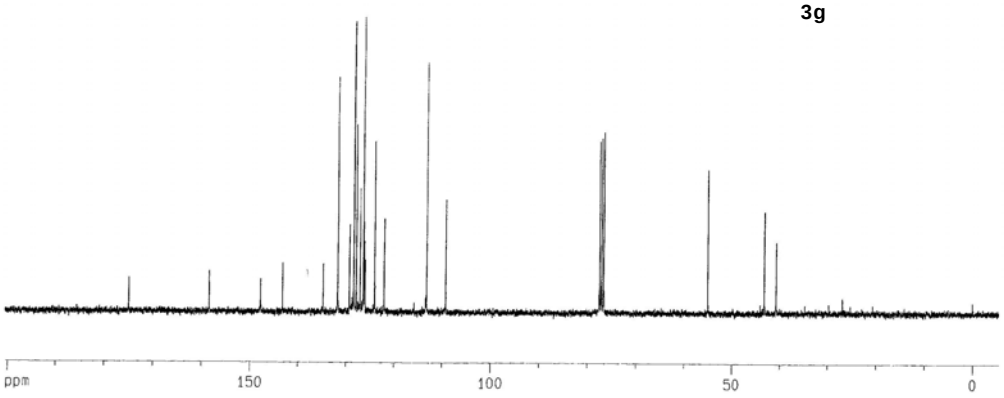
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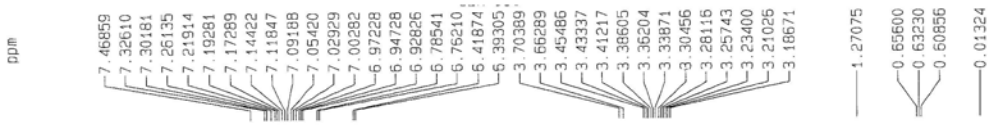
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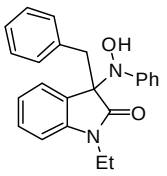
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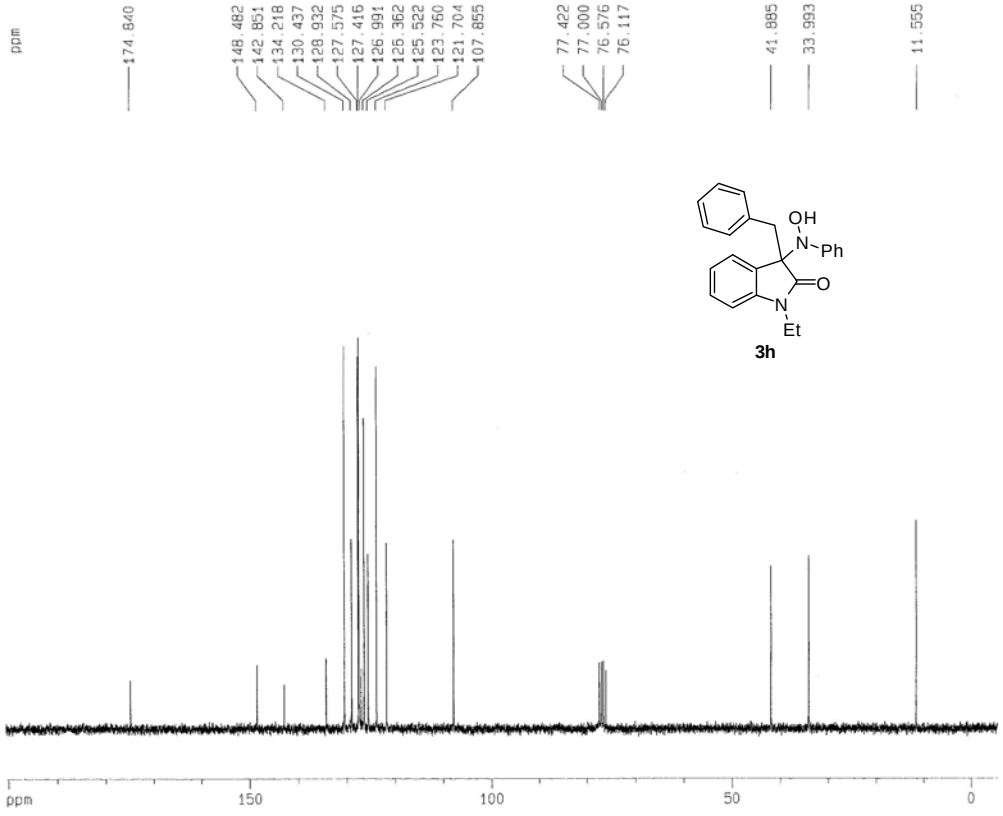
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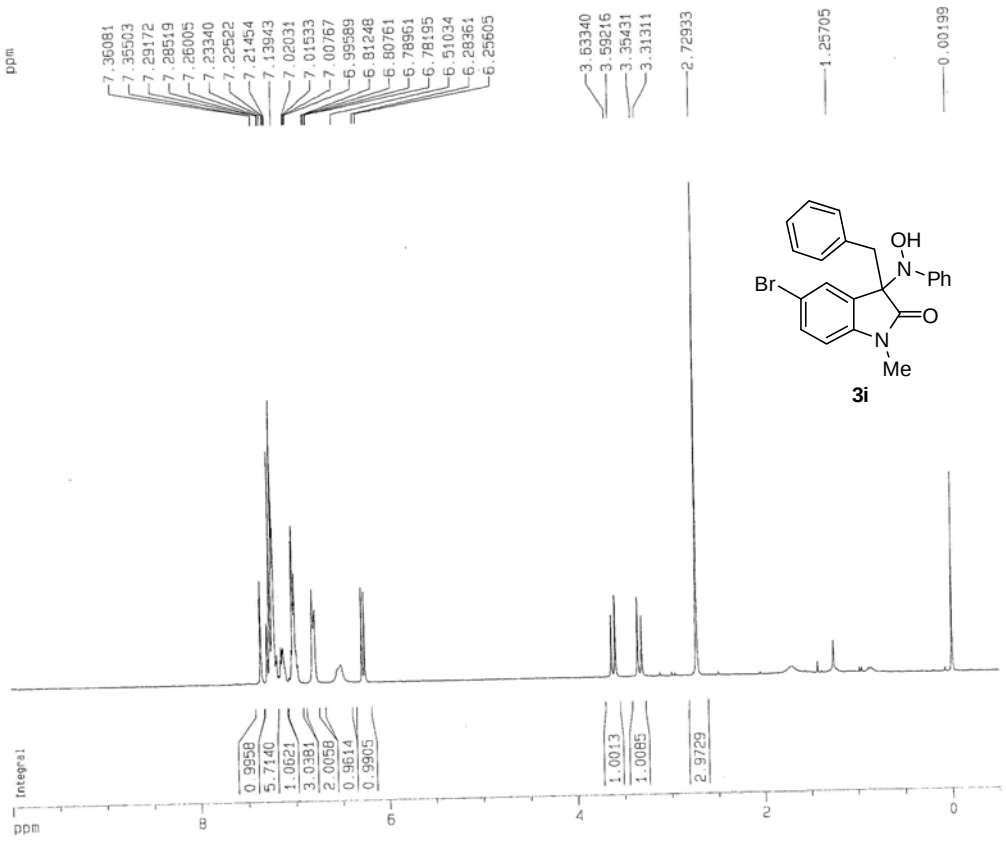
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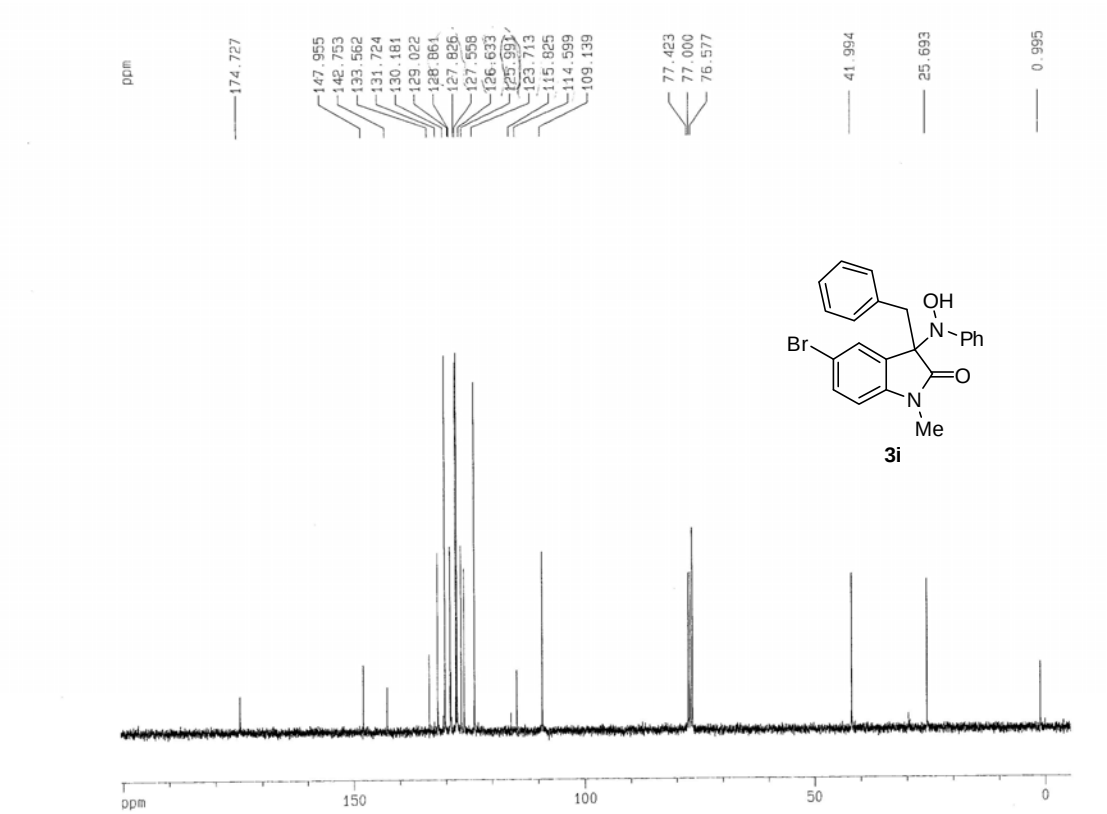
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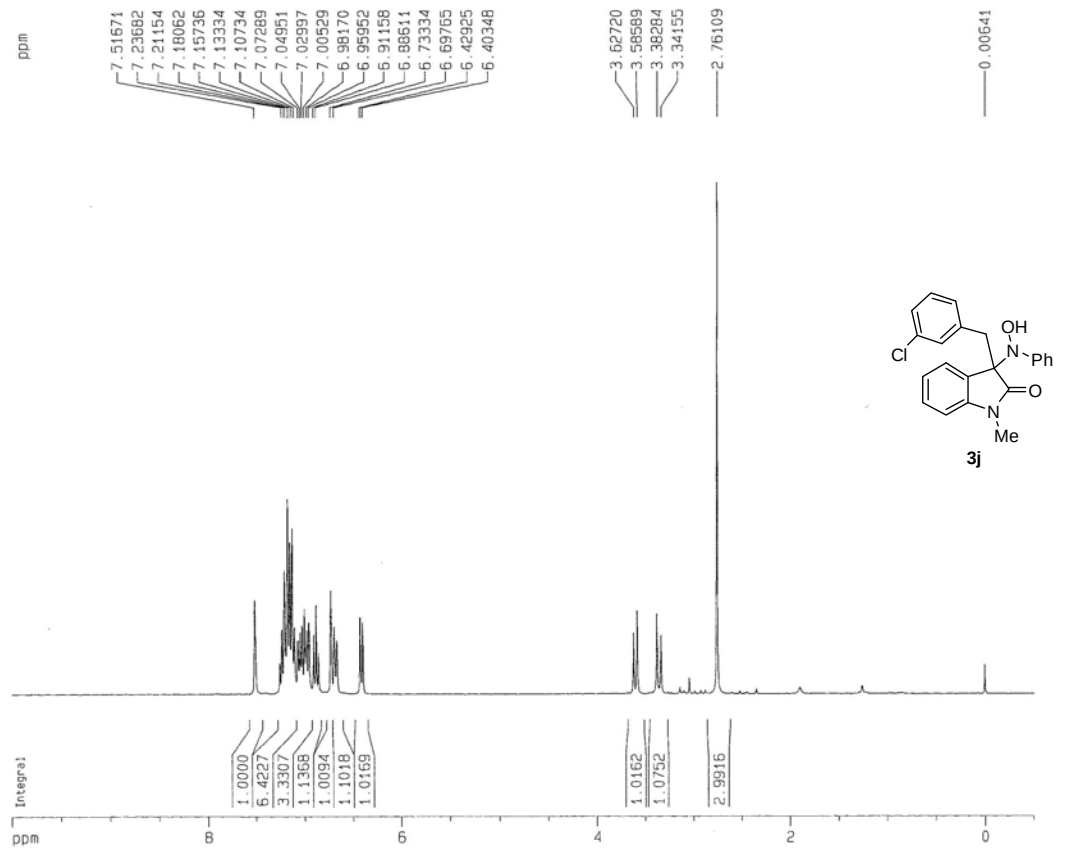
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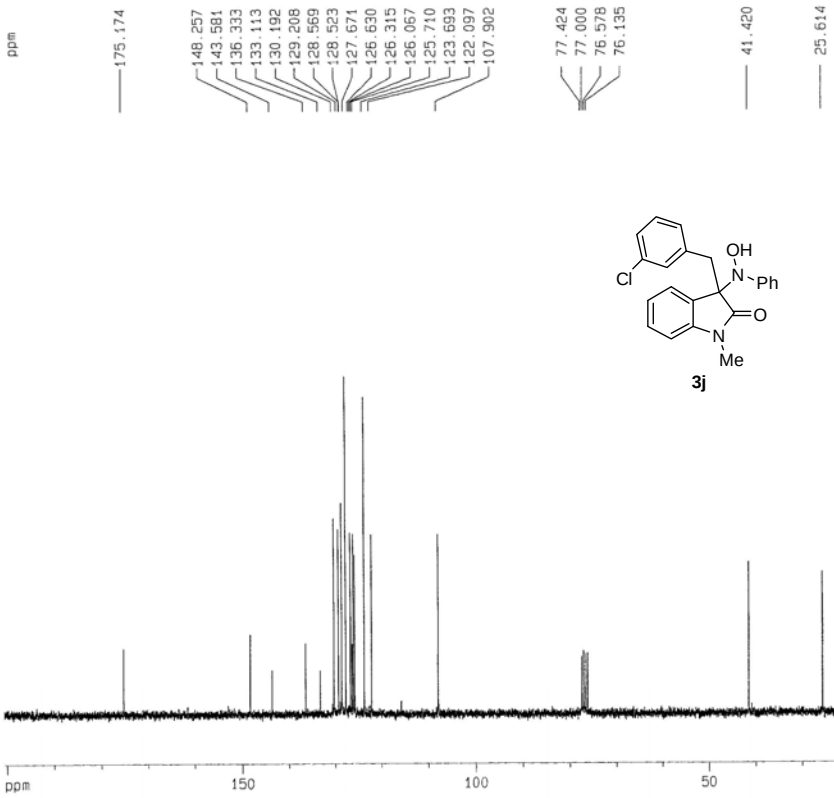
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126.067
125.710
123.693
122.097
107.902
77.424
77.000
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25.614
Cl
OH
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Ph
O
N
Me
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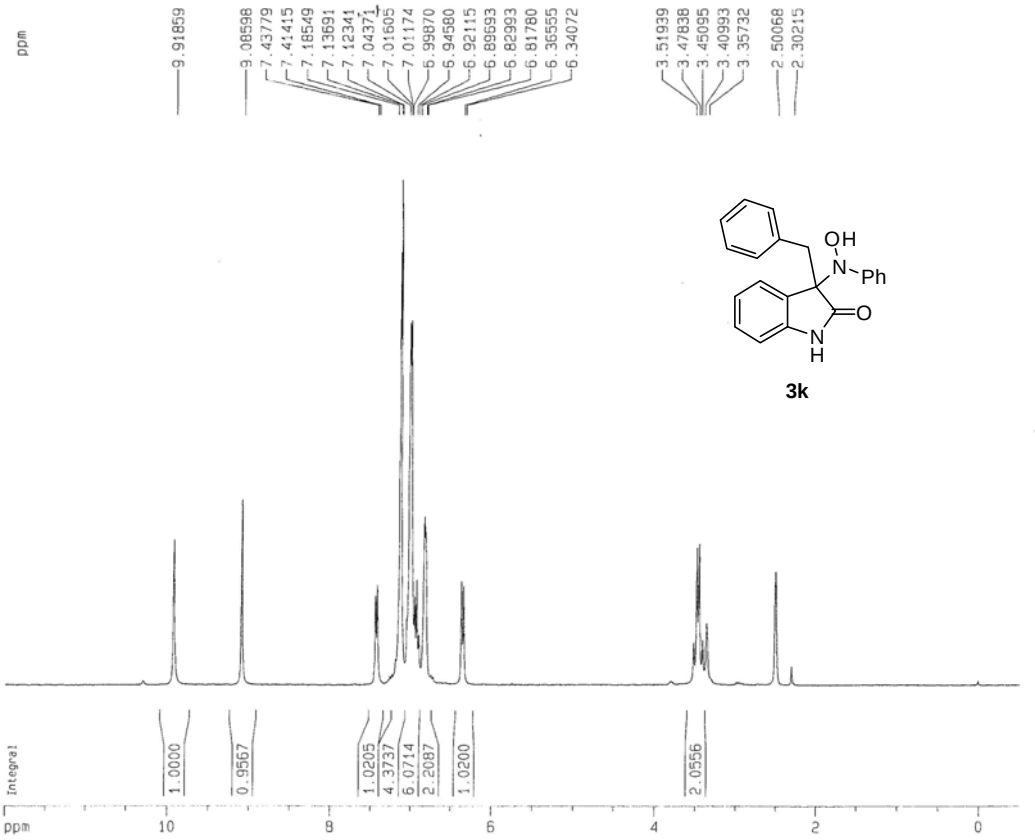
3j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7.18549
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6.94580
6.92115
6.89593
6.82993
6.81780
6.36555
6.34072
3.51939
3.47838
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3.35732
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OH
N
Ph
O
N
H
Integral
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ppm
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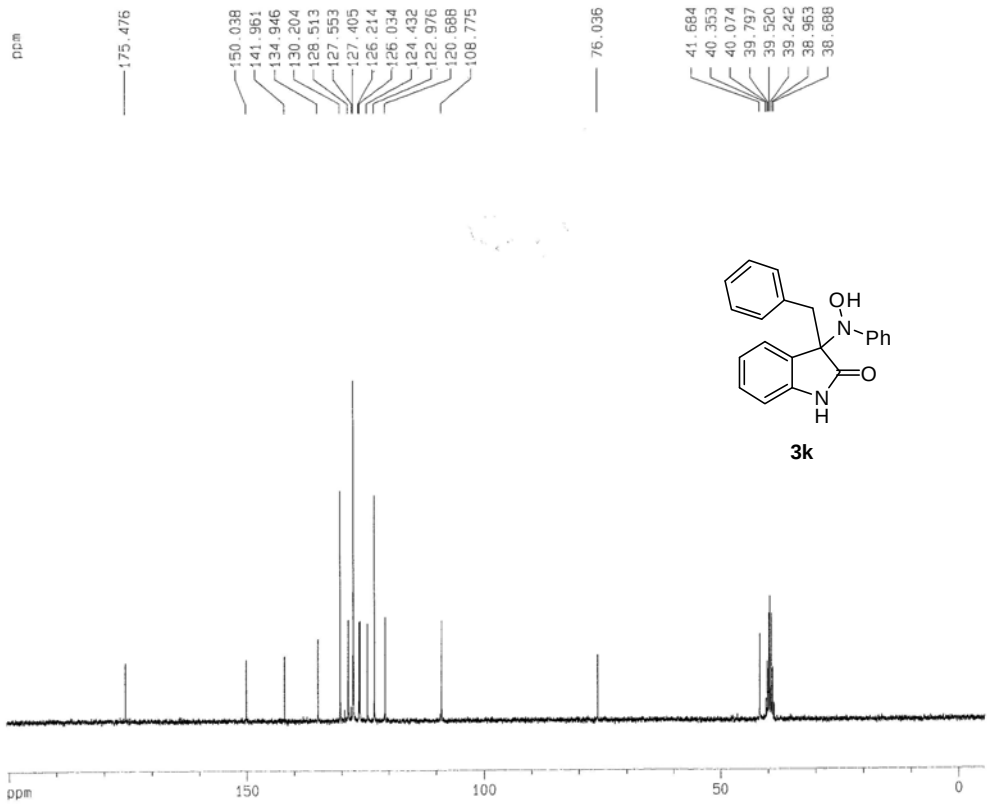
3k



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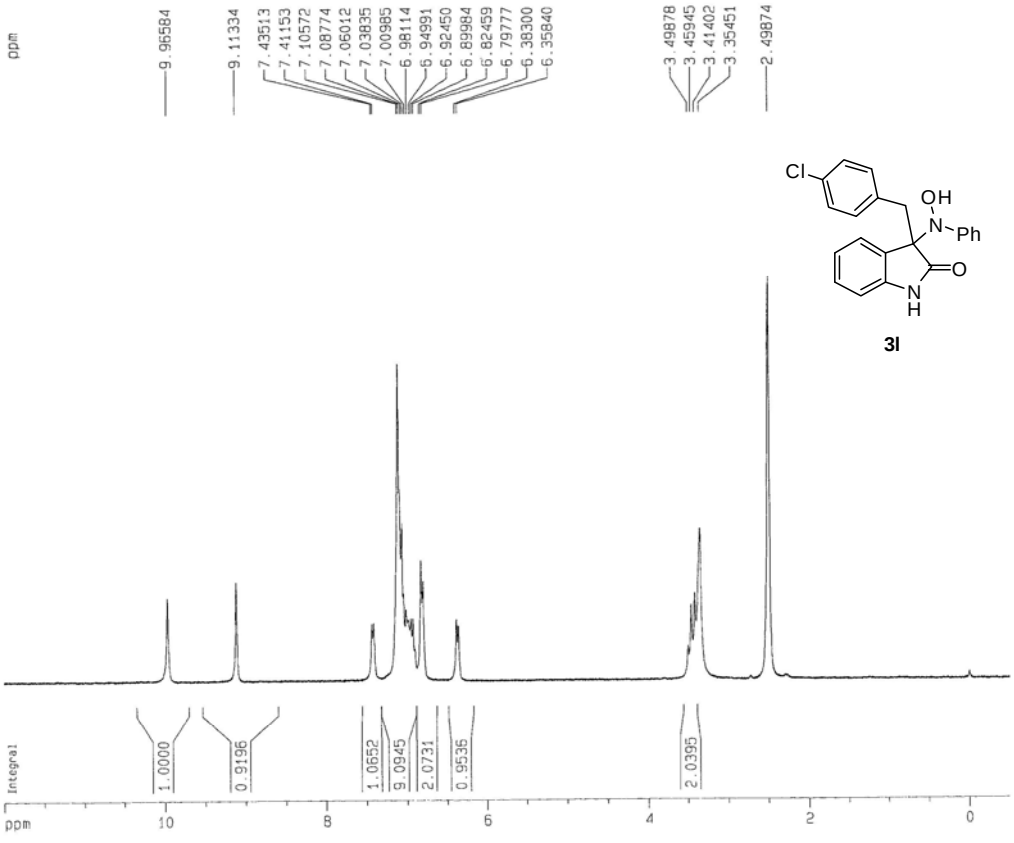

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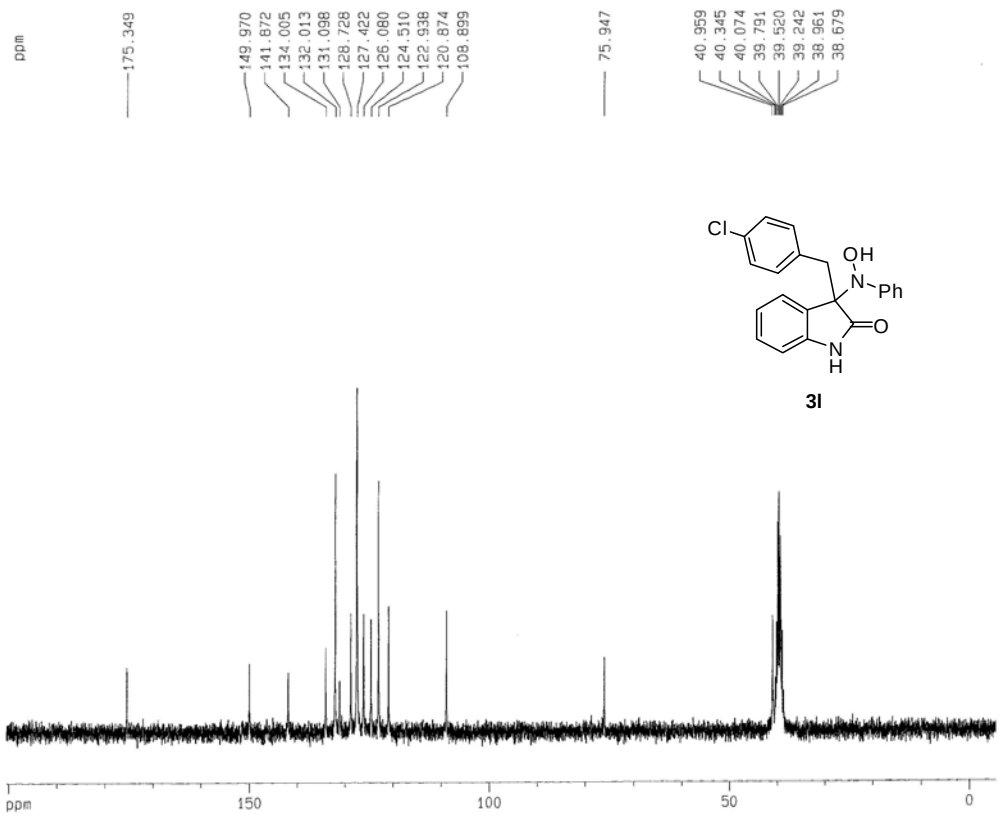
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108.899
75.947
40.959
40.345
40.074
39.791
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Cl
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Ph
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N
H
ppm
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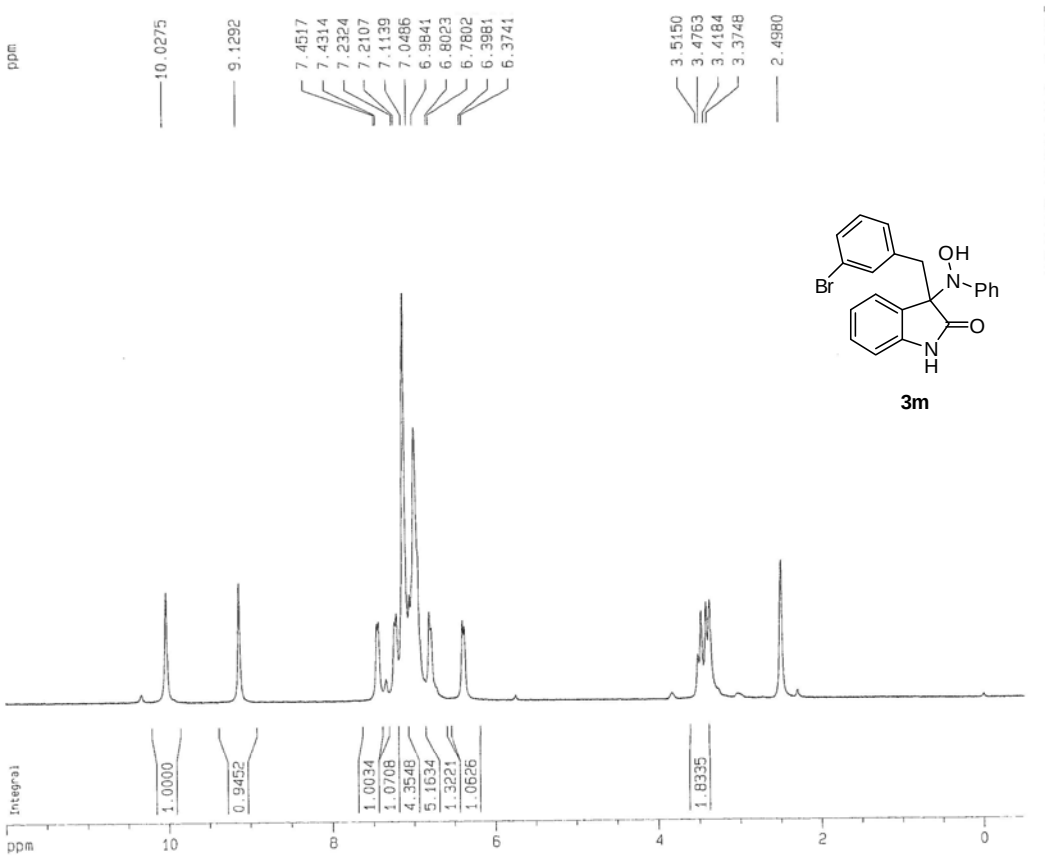
0

3l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6.3981
6.3741
3.5150
3.4763
3.4184
3.3748
2.4980
Br
OH
N
Ph
O
N
H
Integral
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1.0034
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ppm
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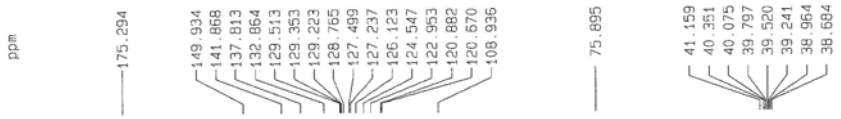
2
0

3m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122.953
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120.670
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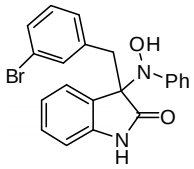
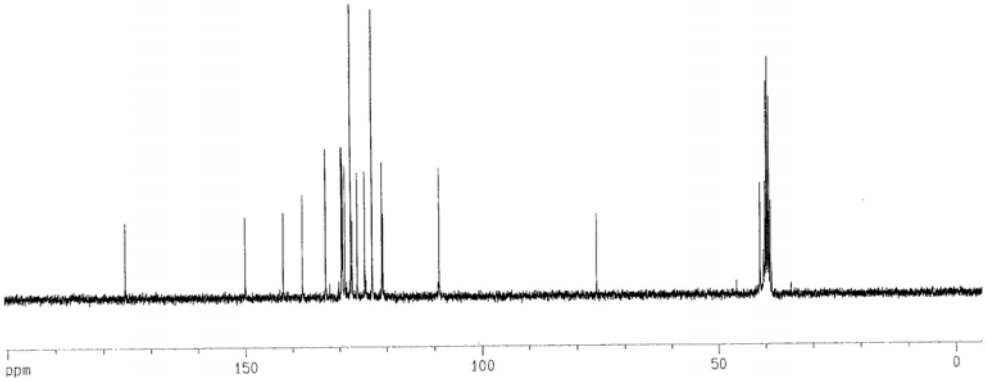
38.684


Br
OH
N
Ph
O
N
H

3m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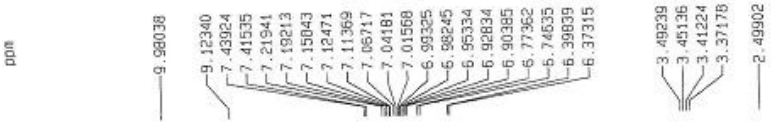
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7.01560
6.99325
6.98245
6.95334
6.92834
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3.45136
3.41224
3.37178
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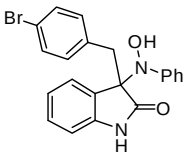
Br
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Ph
O
N
H

3n

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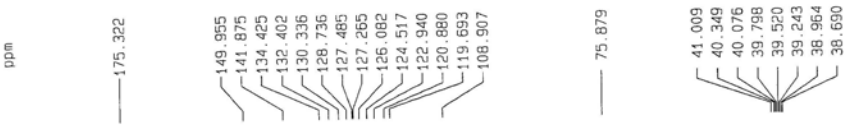
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39.798
39.520
39.243
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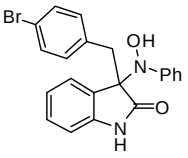
38.690


Br
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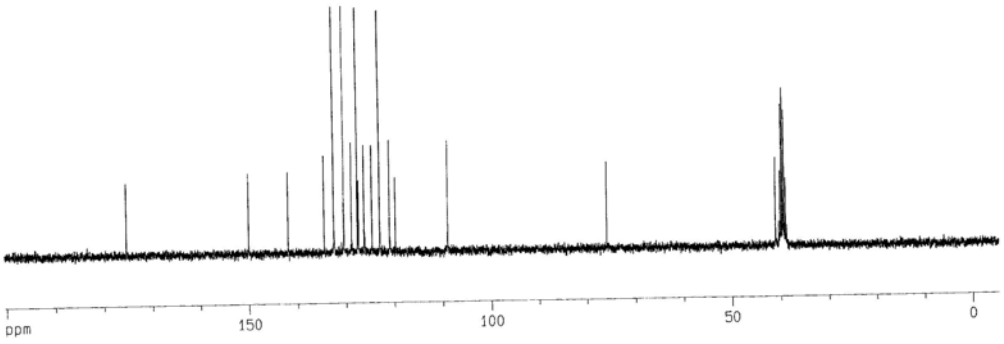
Ph
O
N
H

3n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JLN-219
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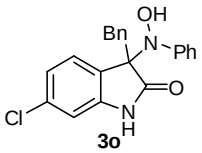
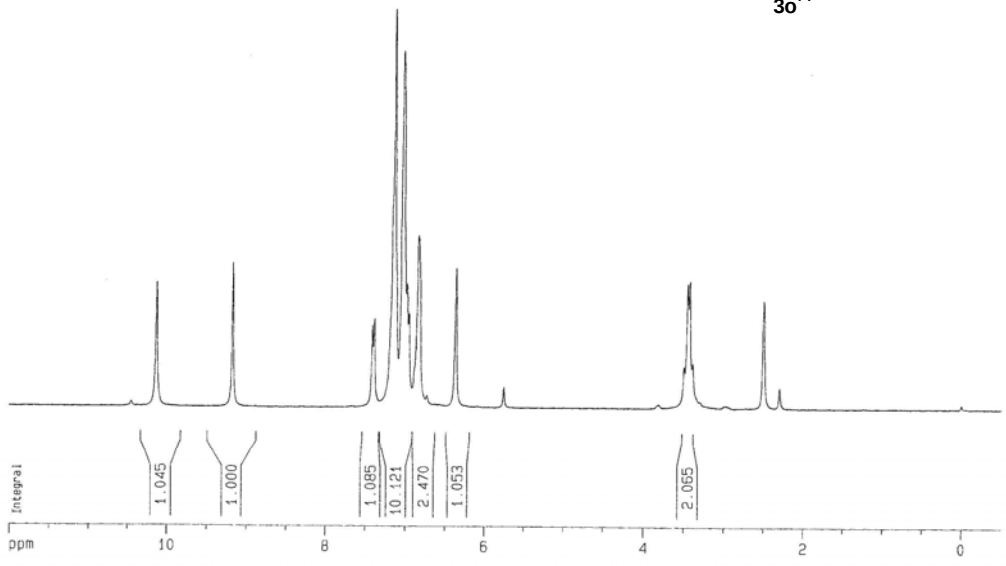
3.3877
2.4998


OH
Bn
N
Ph
O
Cl
N
H

3o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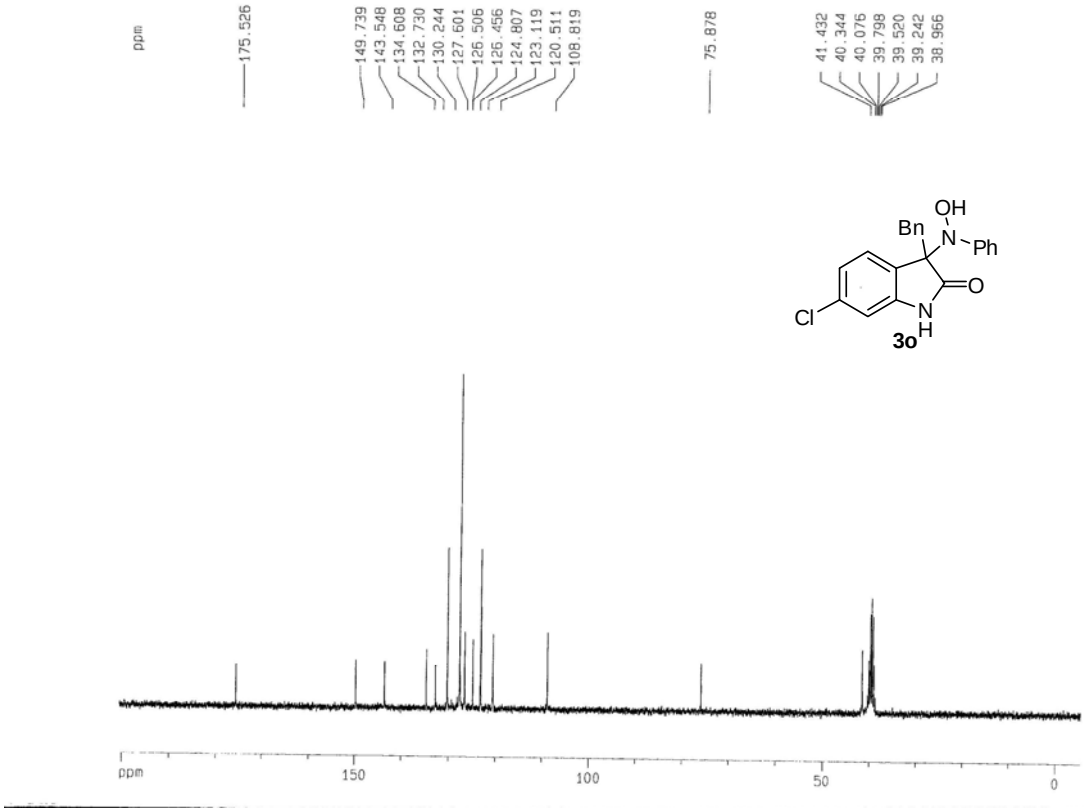
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75.878
41.432
40.344
40.076
39.798
39.520
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OH
Bn
N
Ph
O
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N
H
3o
ppm
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50
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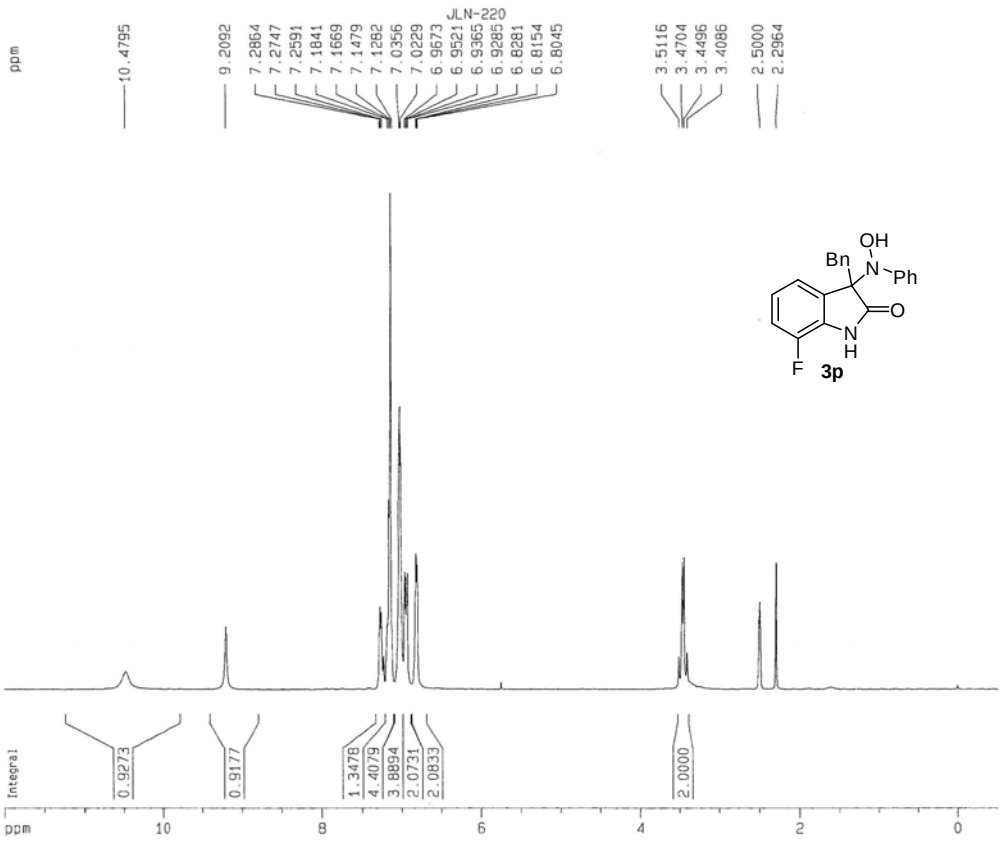
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7.0229
6.9673
6.9521
6.9365
6.9285
6.8281
6.8154
6.8045
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2.2964
OH
Bn
N
Ph
O
N
H
F
3p
Integral
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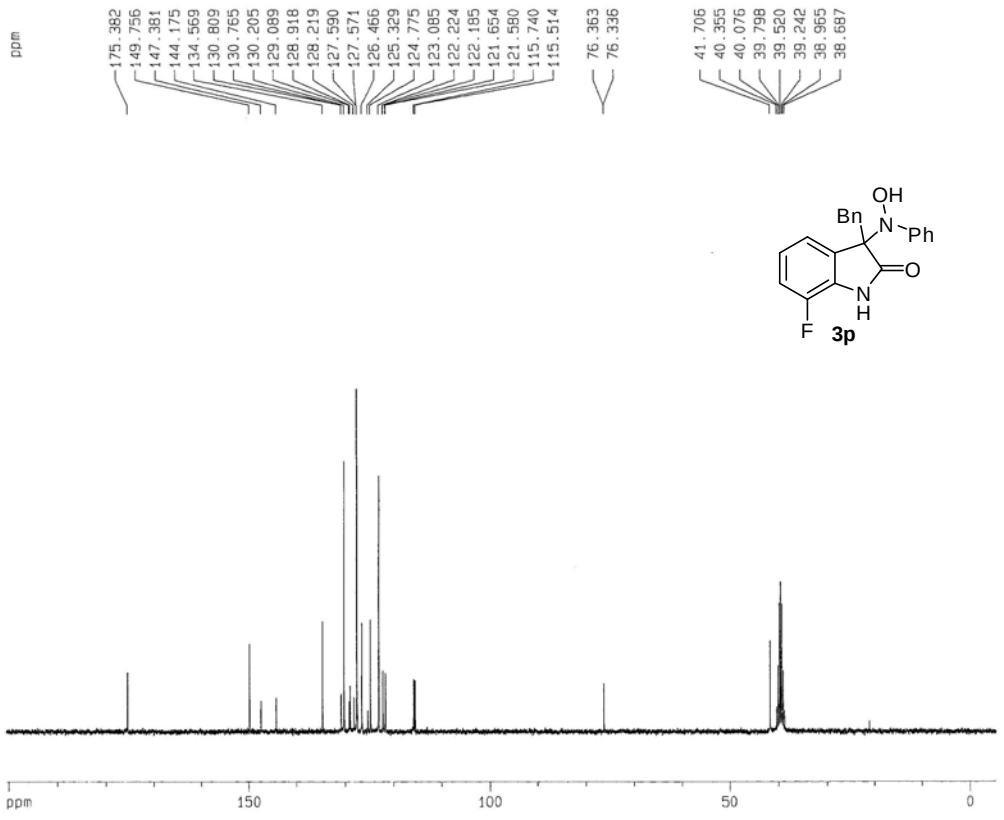
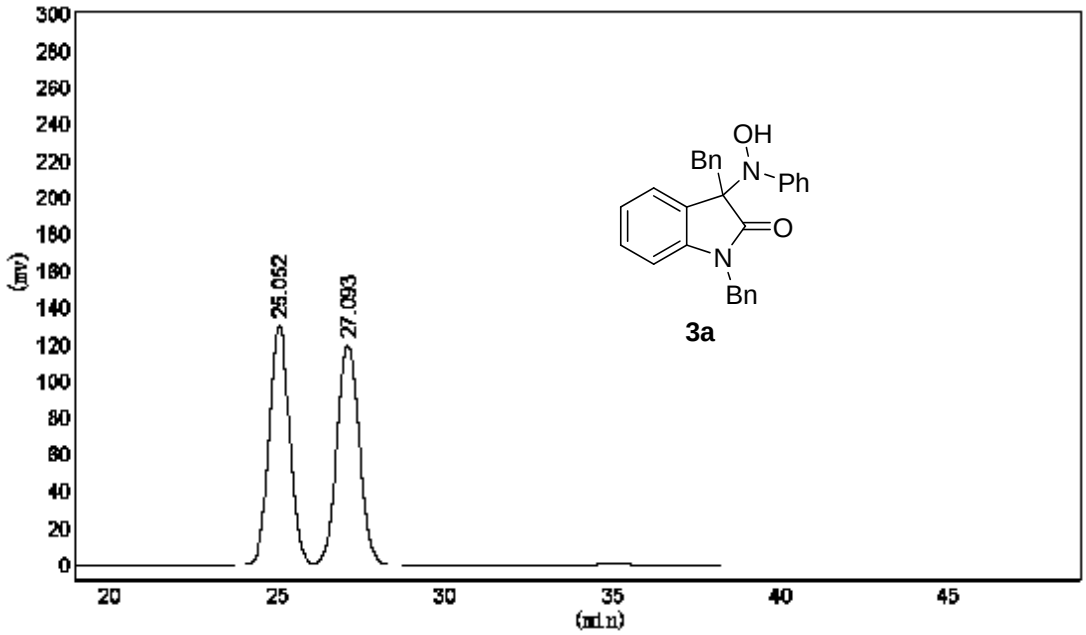
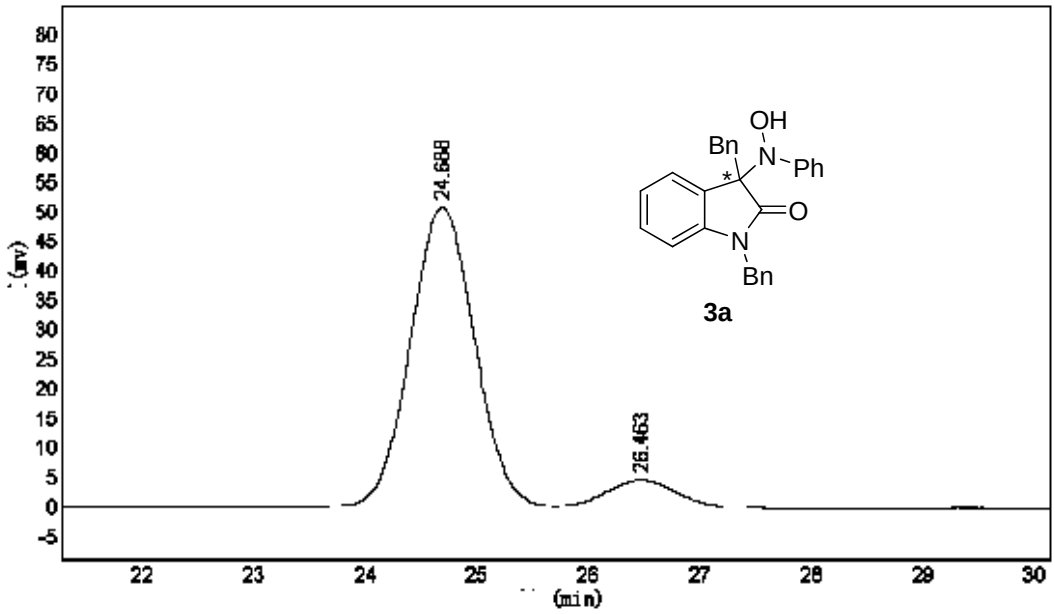


6. HPLC chromatograms

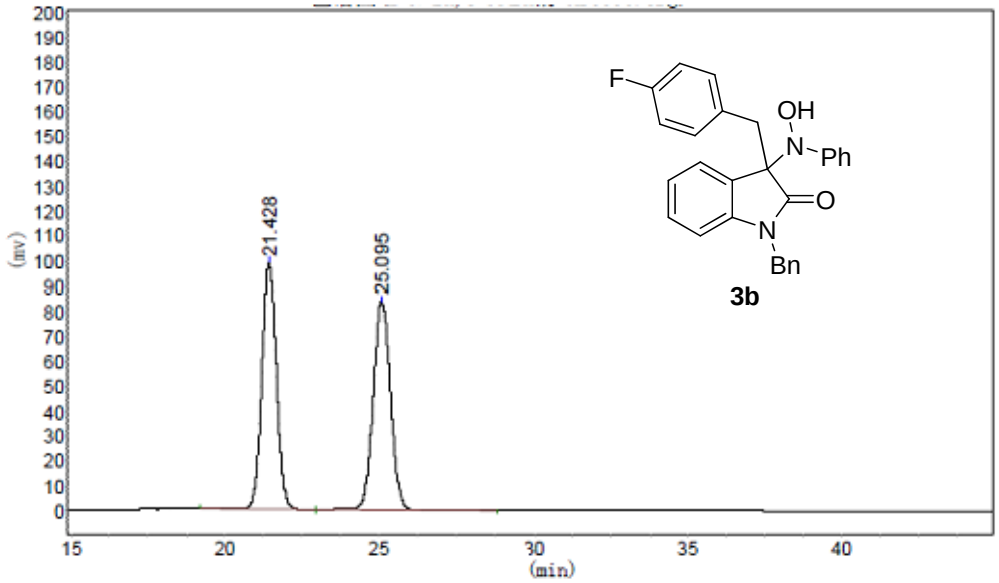


Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	25.052	129893.602	5485543.000	49.9666
2	27.093	118919.102	5492882.500	50.0334



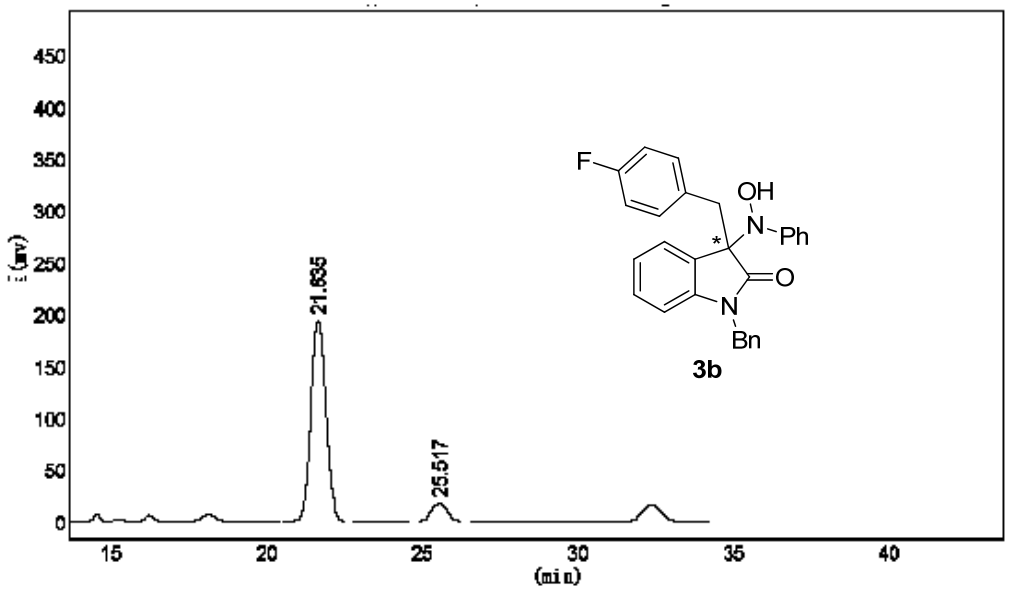
3a

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	24.688	50691.500	2009745.250	91.4494
2	26.463	4541.935	187913.094	8.5506

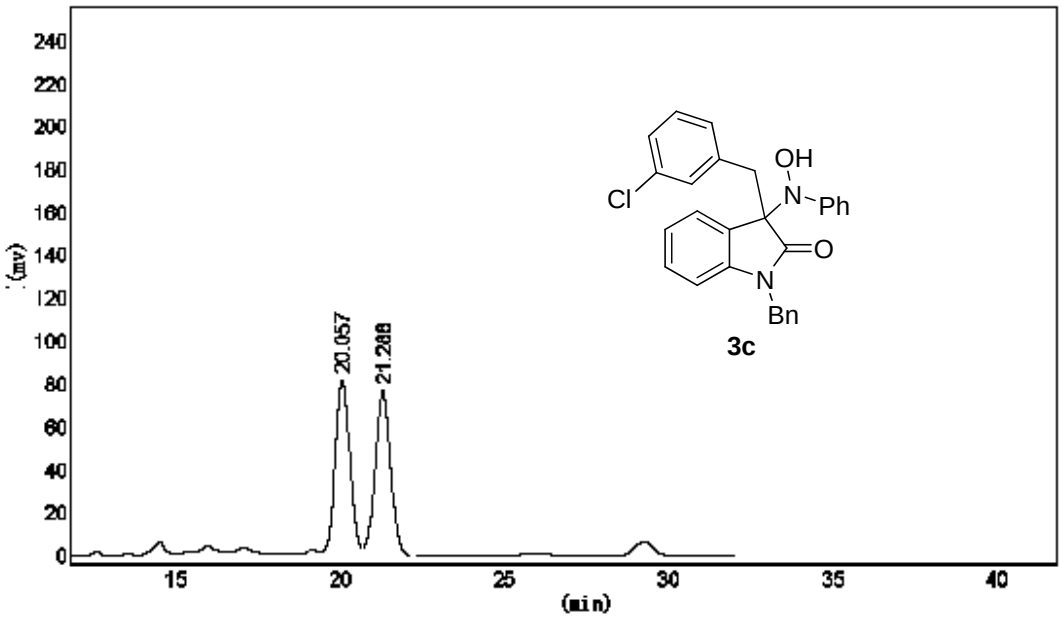


3b

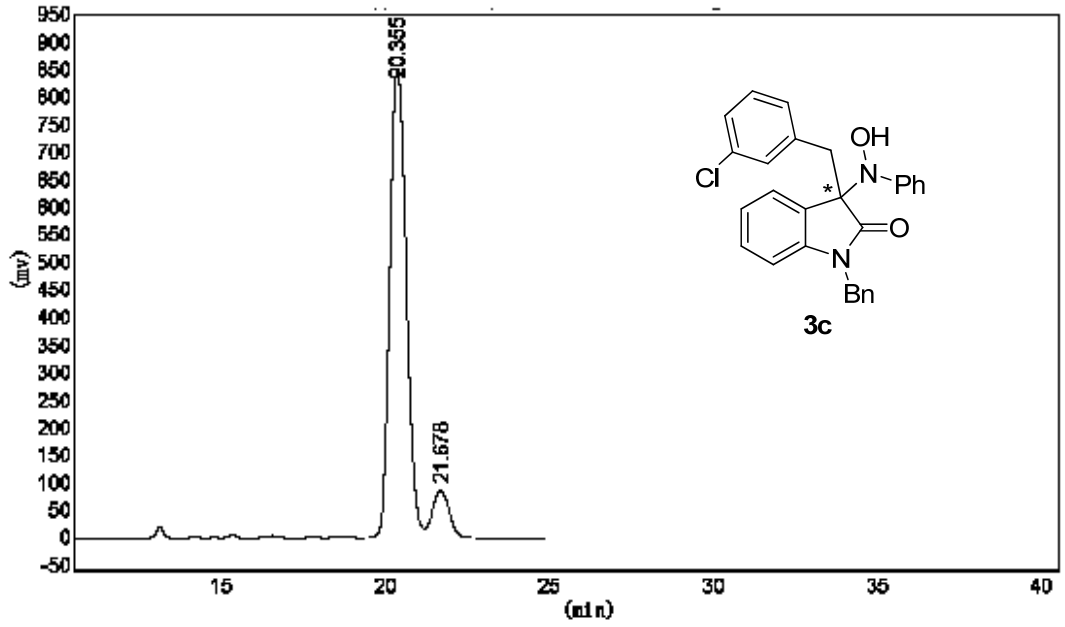
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	21.428	98929.477	3272745.000	49.8815
2	25.095	84156.602	3288291.750	50.1185



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	21.635	194533.281	6556853.000	90.0229
2	25.517	18501.555	726687.875	9.9771

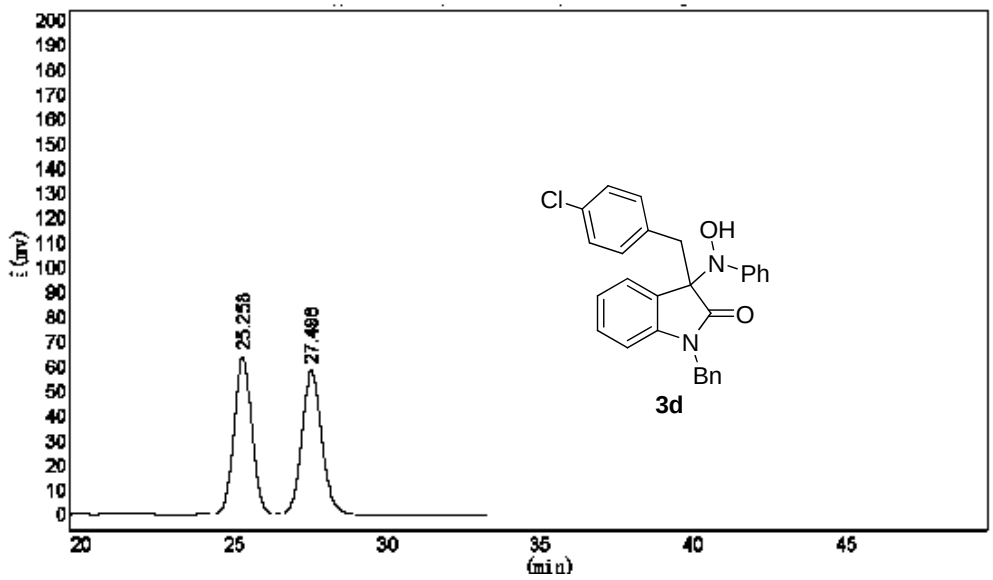


Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.057	79198.633	2365076.750	49.8512
2	21.288	74588.977	2379194.000	50.1488



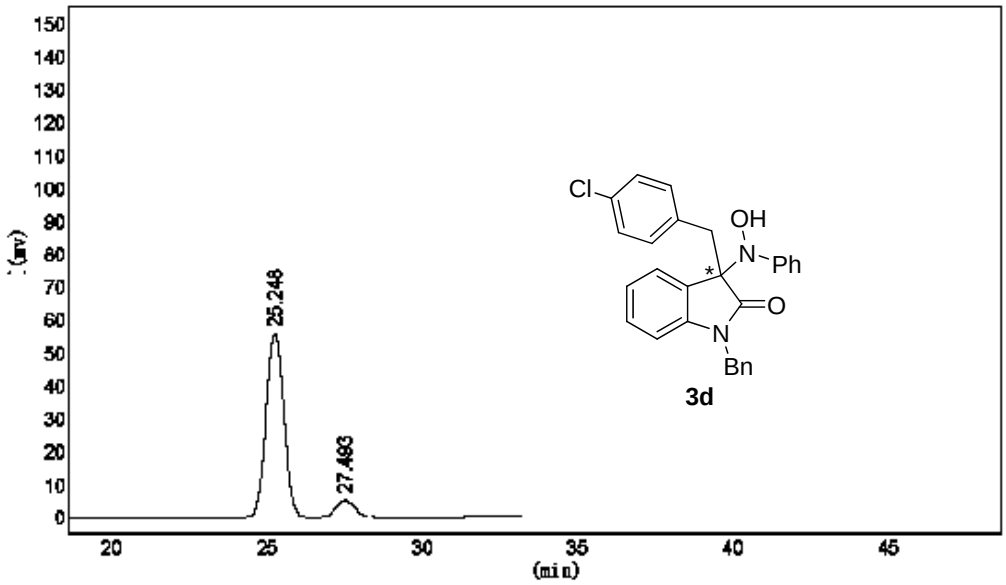
c

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.355	850176.125	29464098.000	90.6298
2	21.678	85257.508	3046305.500	9.3702

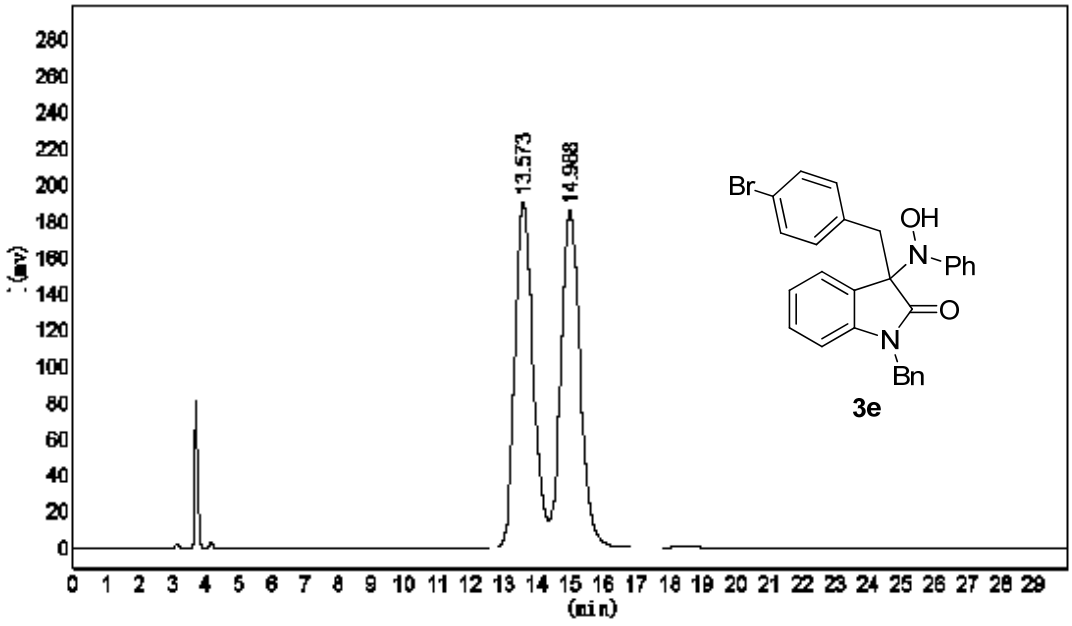


c

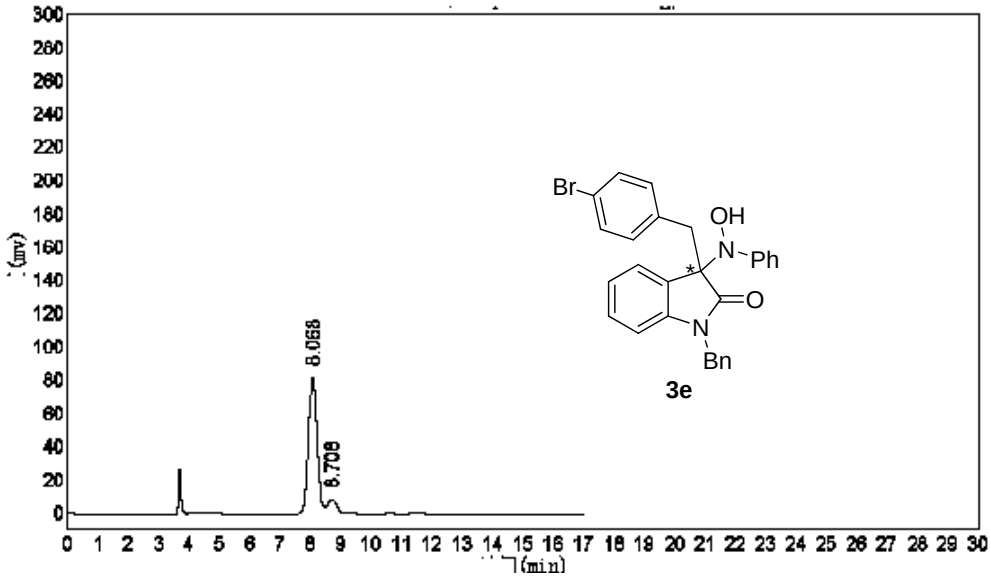
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	25.258	63639.457	2567564.250	49.3016
2	27.498	58085.191	2640308.500	50.6984



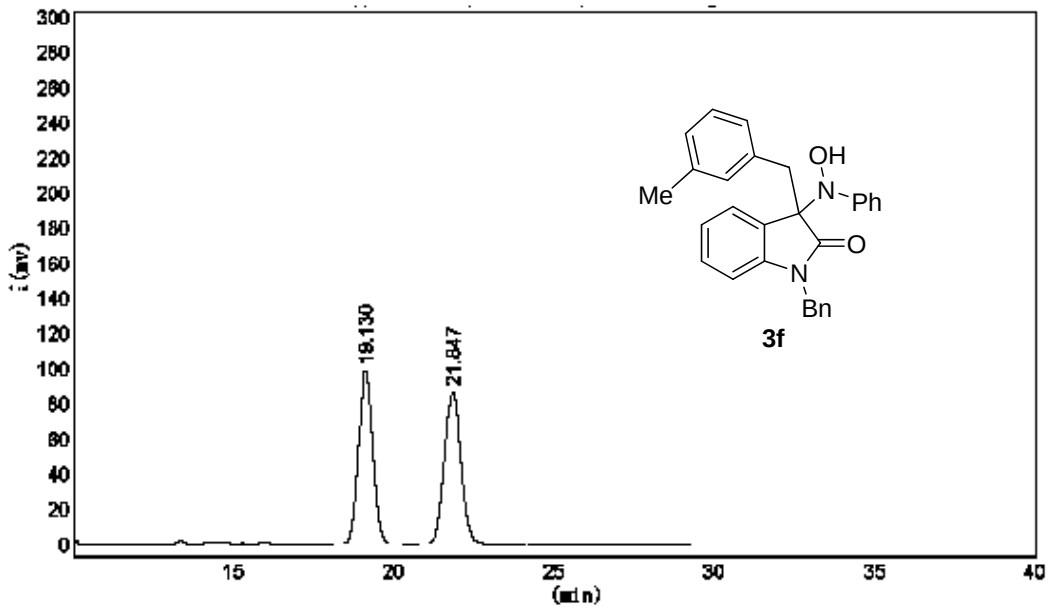
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	25.248	55853.023	2238038.250	90.8797
2	27.493	5241.358	224599.984	9.1203



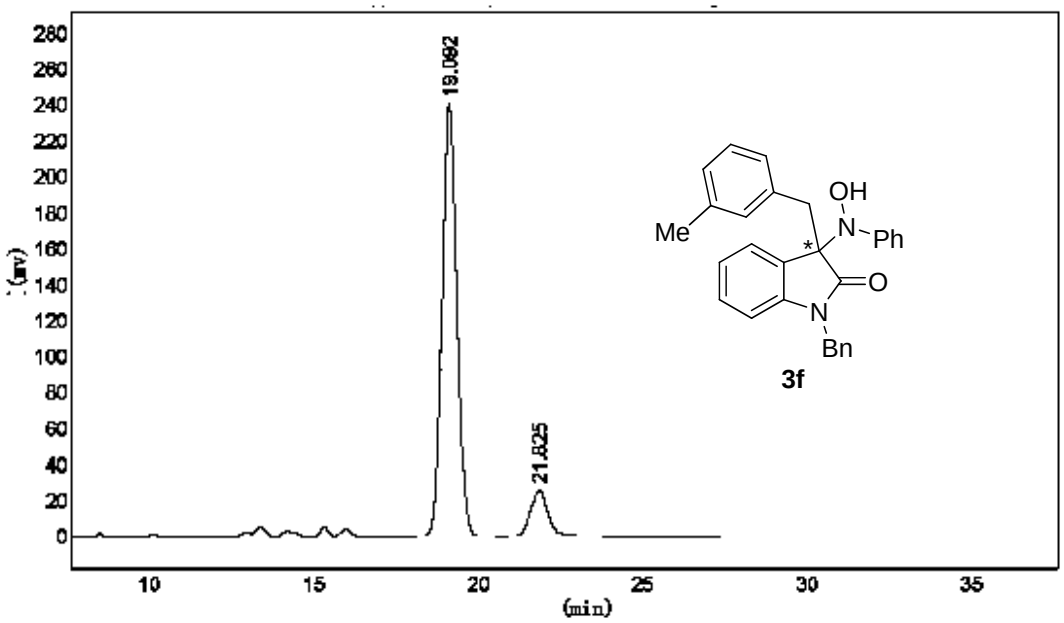
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	13.573	190267.891	7249819.000	49.2460
2	14.988	185583.219	7471822.000	50.7540



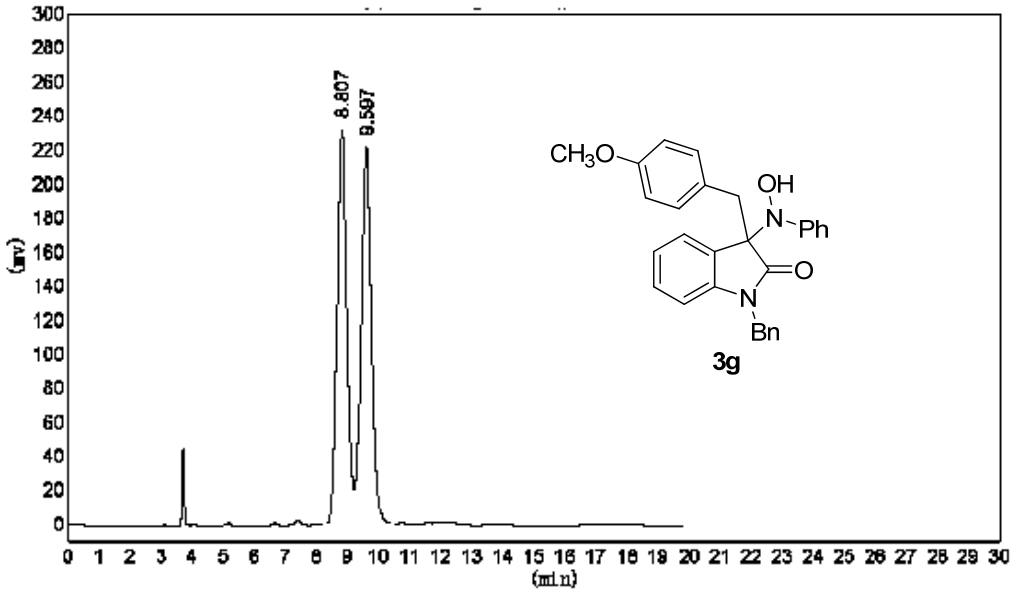
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	8.068	82317.703	1592853.500	90.0175
2	8.708	8866.564	176638.750	9.9825



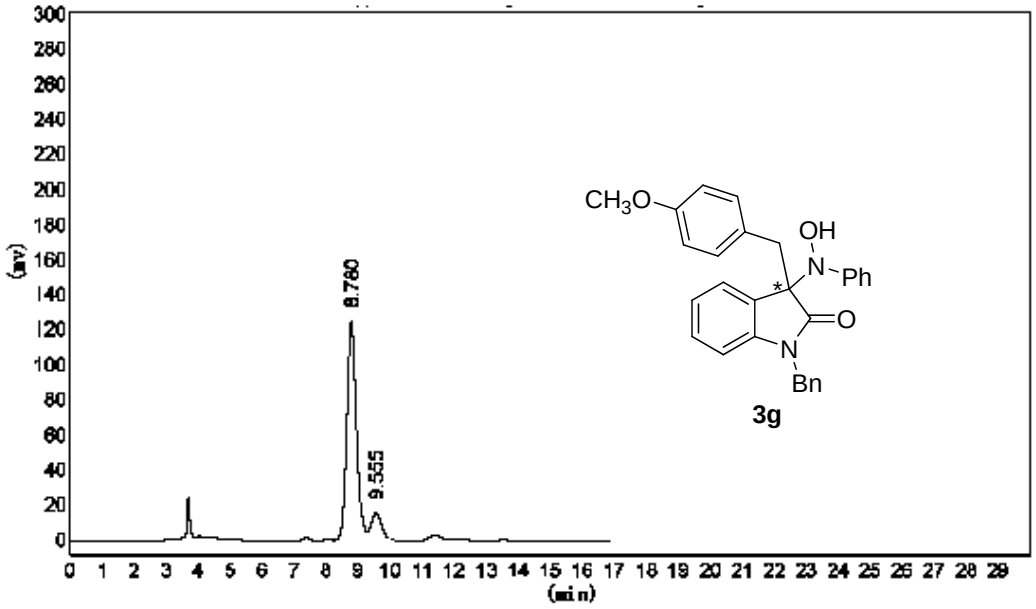
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	19.130	98693.656	3111489.500	49.4147
2	21.847	86421.984	3185192.750	50.5853



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	19.092	240699.344	7634962.500	88.5298
2	21.825	25650.889	989207.125	11.4702

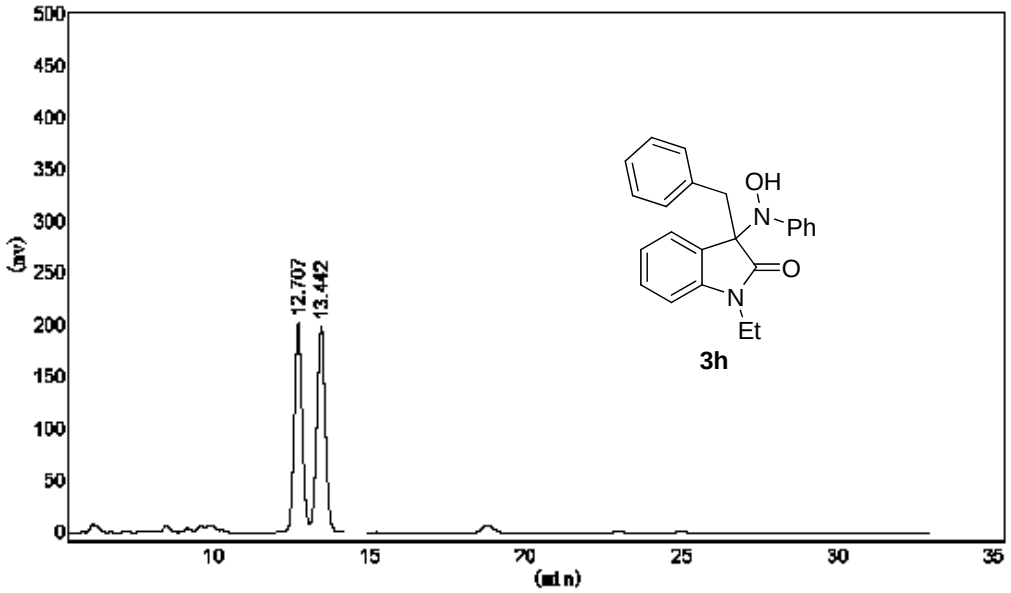


Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	8.807	231549.938	5131710.000	49.6916
2	9.597	220645.313	5195408.000	50.3084



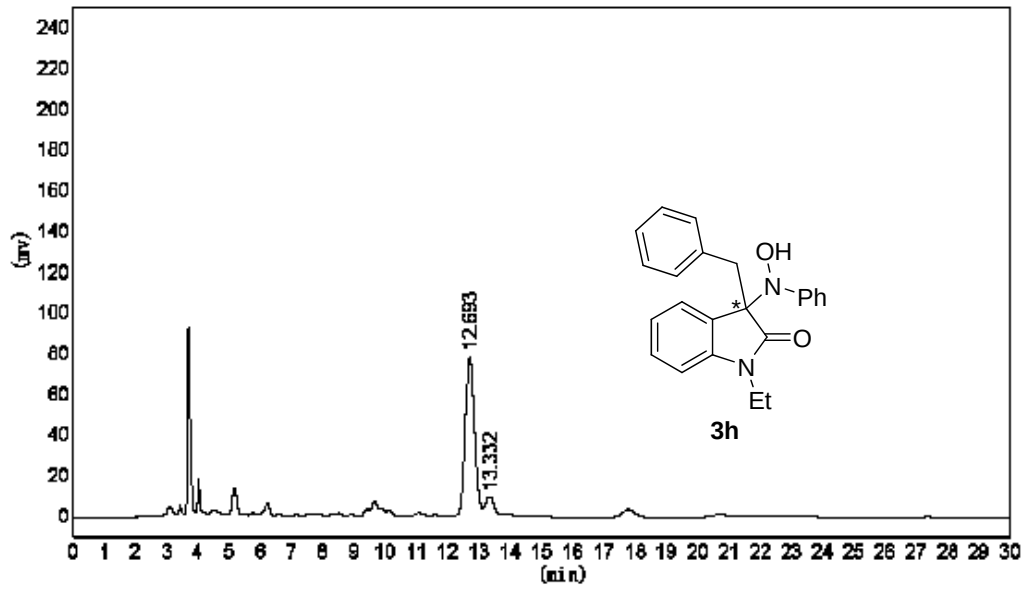
3g

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	8.780	125378.000	2701510.750	88.5159
2	9.555	15626.189	350493.875	11.4841

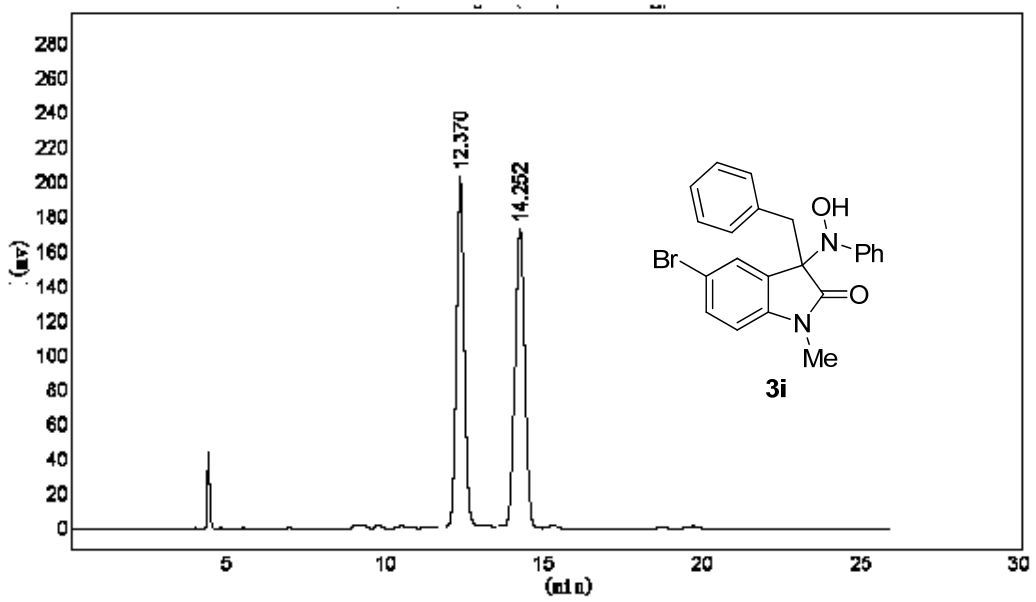


3h

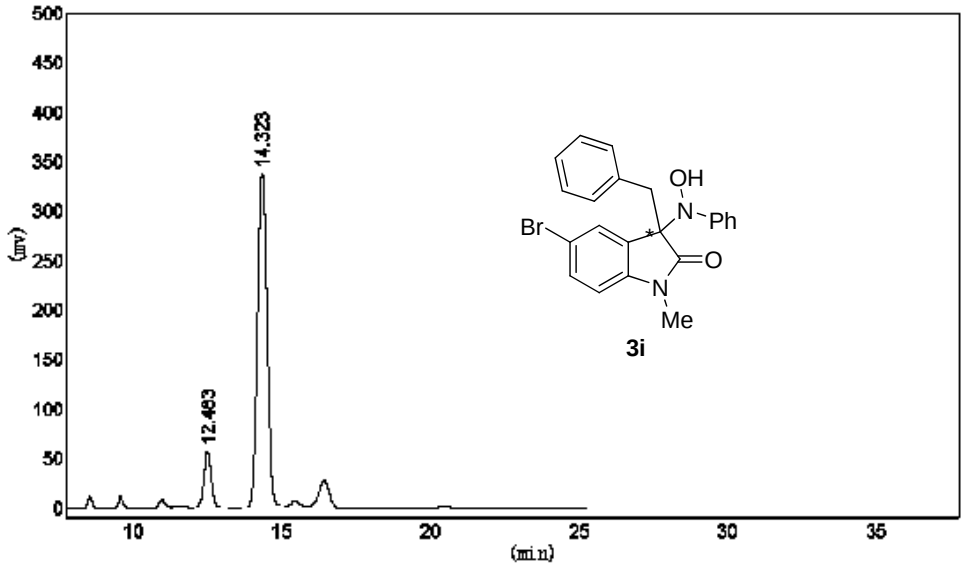
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	12.707	202063.250	3758233.500	48.7530
2	13.442	198124.719	3950481.500	51.2470



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	12.693	78077.680	1538623.875	90.6350
2	13.332	8818.305	158979.797	9.3650

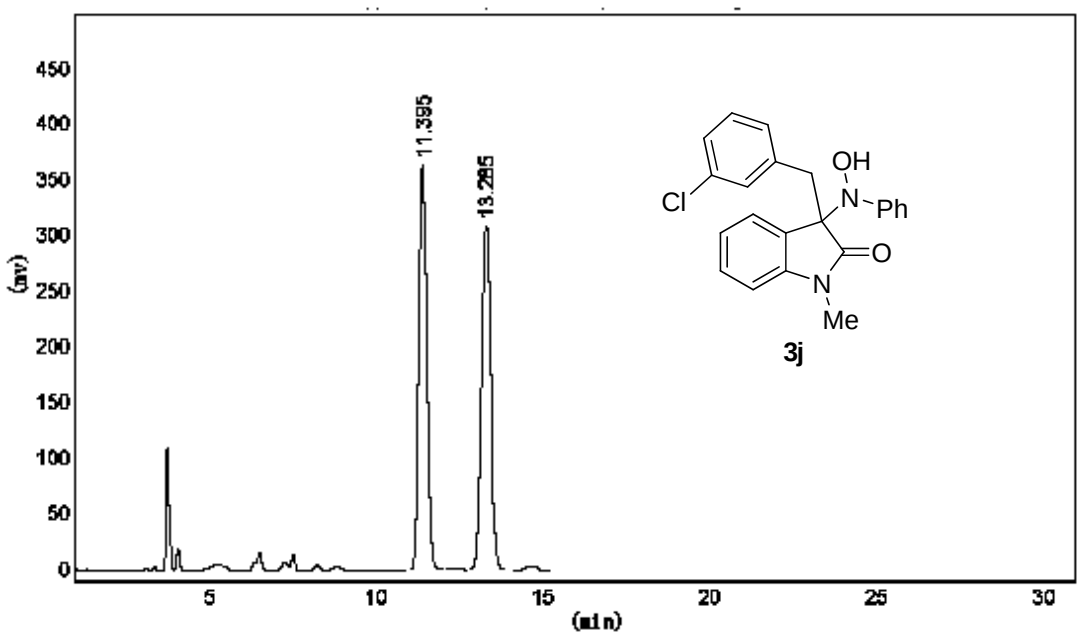


Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	12.370	201963.891	3645128.500	49.9703
2	14.252	172260.391	3649466.250	50.0297



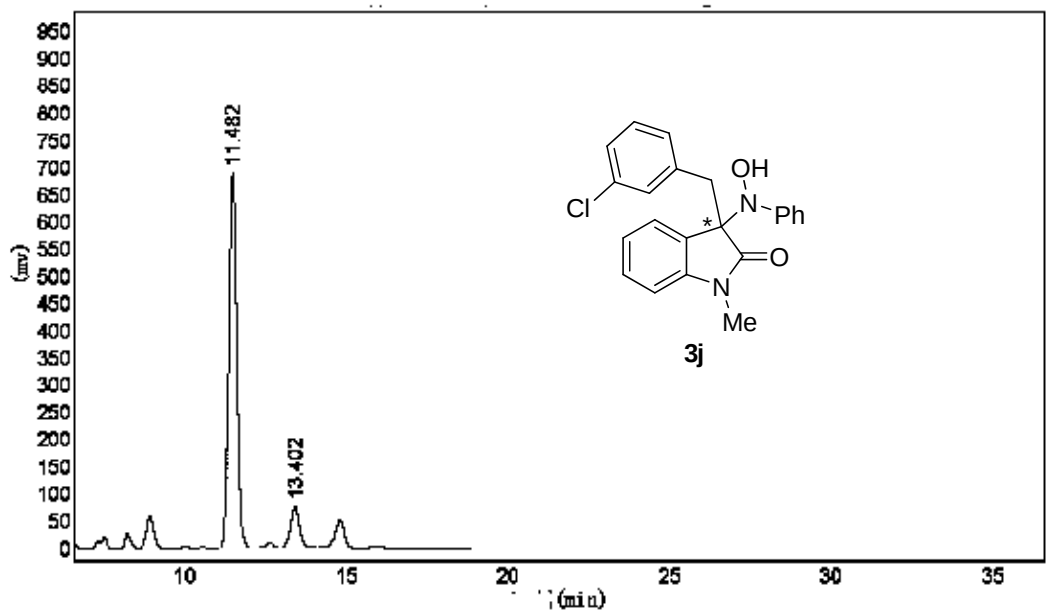
3i

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	12.483	57358.094	1033680.563	12.4628
2	14.323	337738.438	7260446.000	87.5372



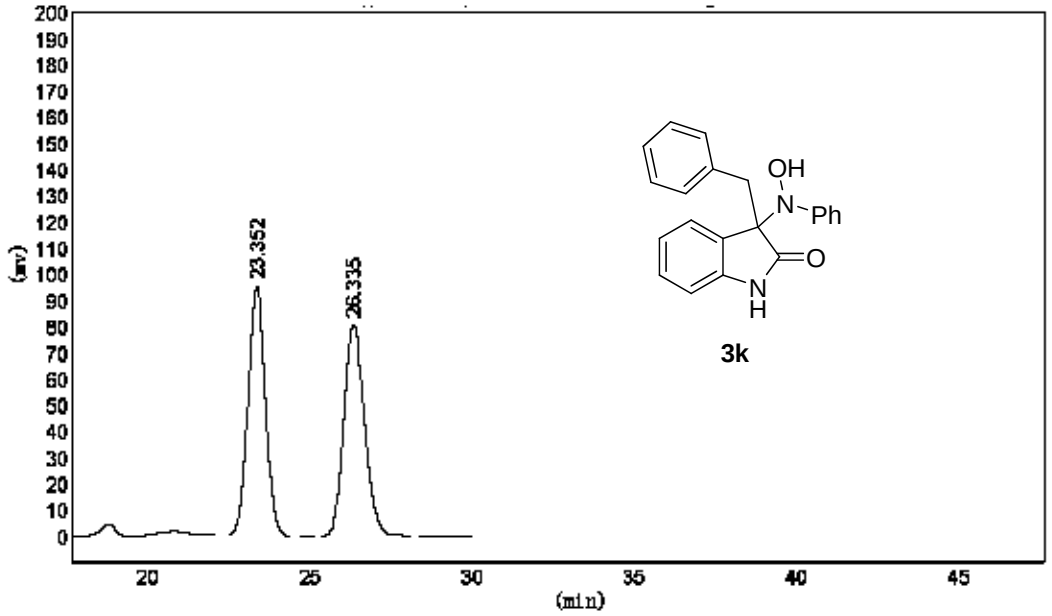
3j

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	11.395	364566.719	5912731.500	50.0326
2	13.285	309658.969	5905020.000	49.9674



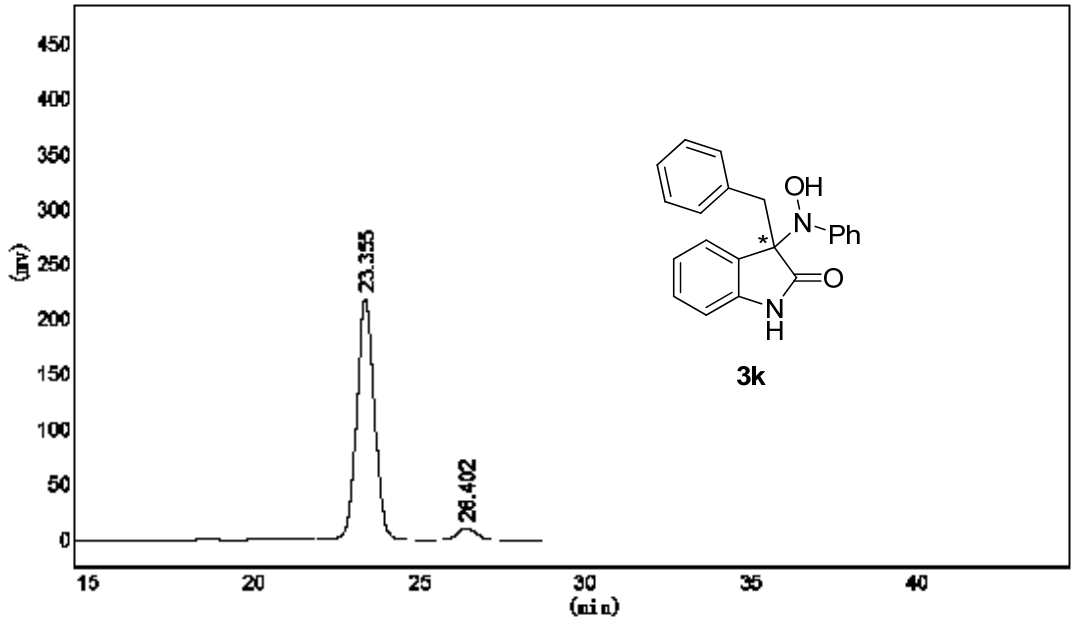
3j

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	11.482	689435.563	11494634.000	88.7106
2	13.402	76354.242	1462824.750	11.2894



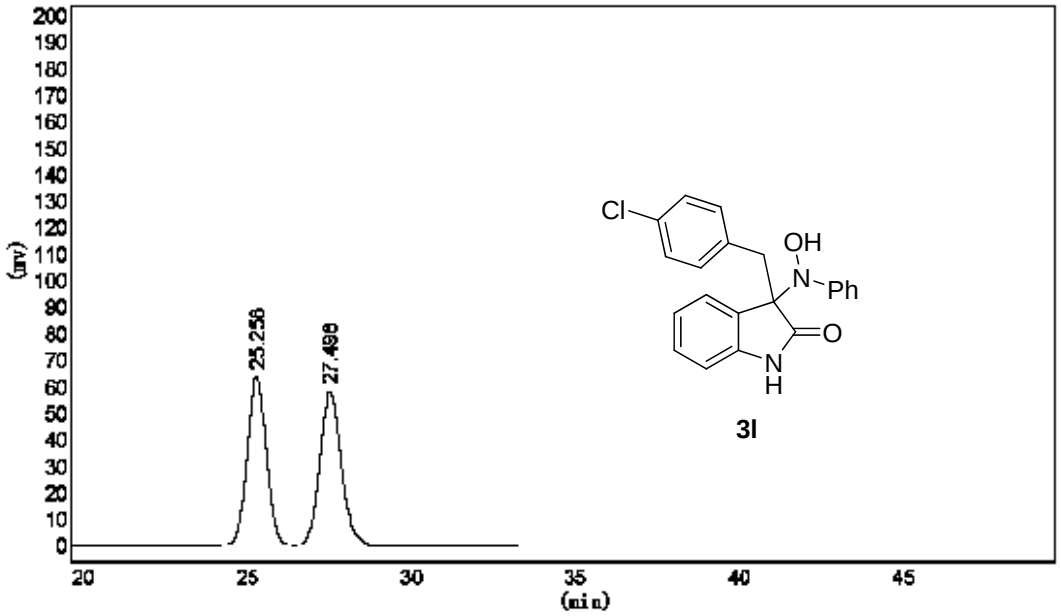
3k

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	23.352	95154.875	3564904.250	49.6129
2	26.335	80752.125	3620536.250	50.3871



C

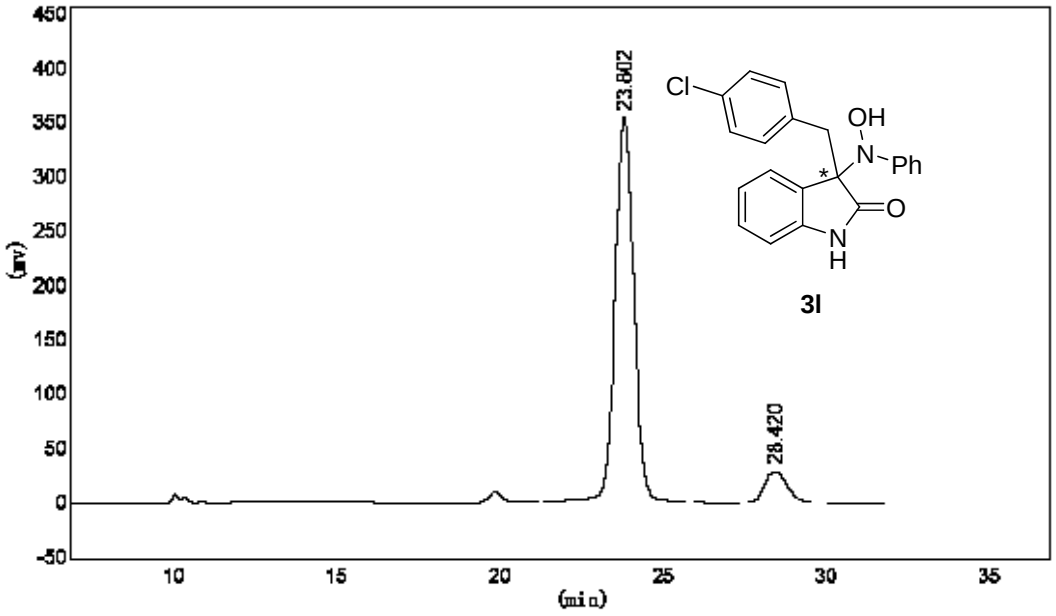
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	23.355	218264.813	8104260.000	94.8476
2	26.402	10503.429	440244.813	5.1524



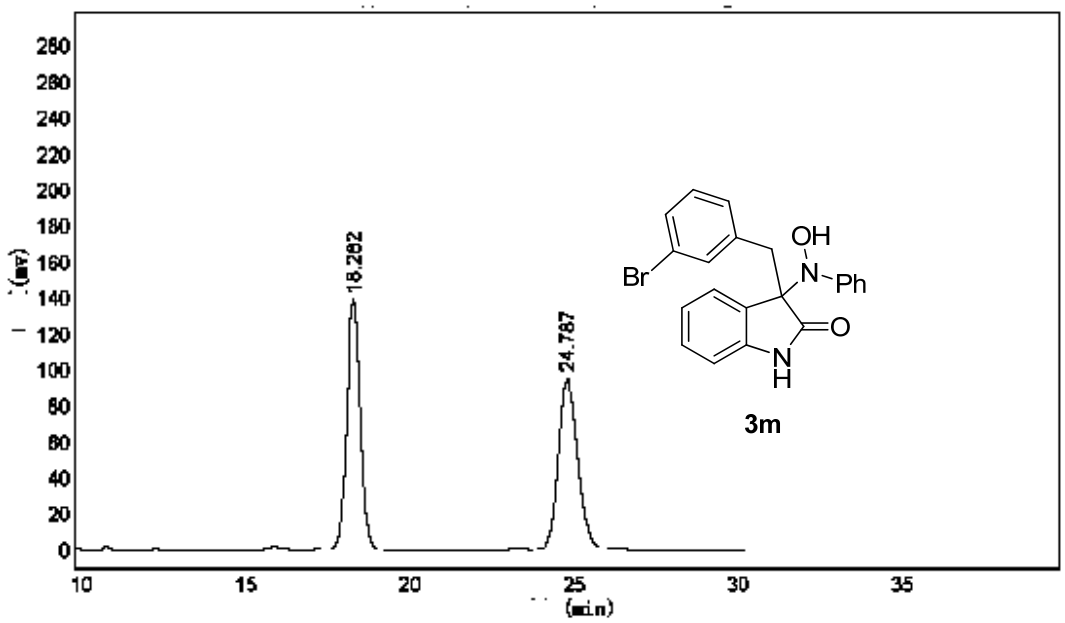
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)

c

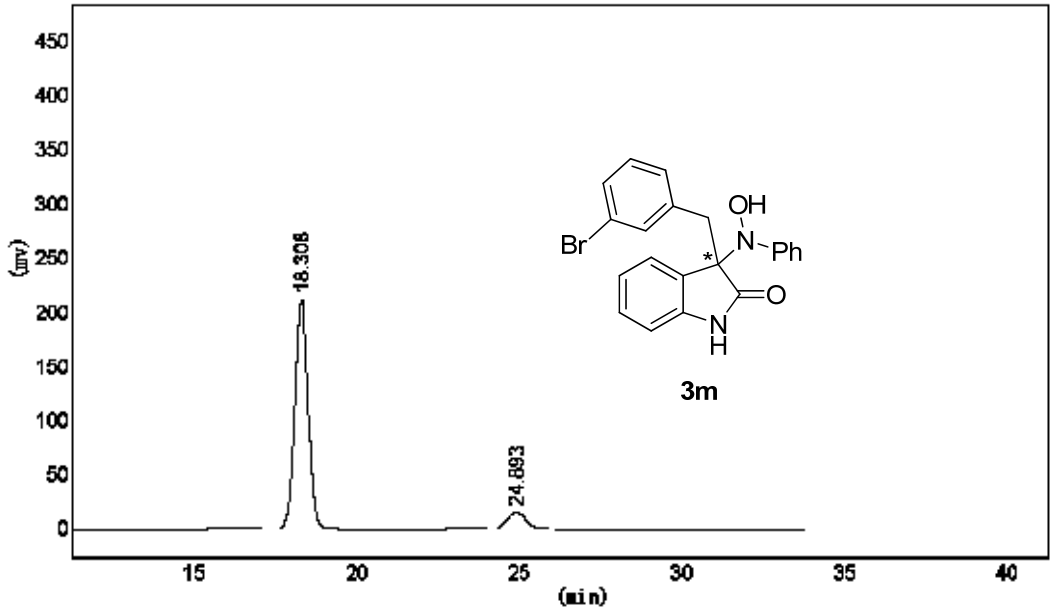
1	25.258	63639.457	2567564.250	49.3016
2	27.498	58085.191	2640308.500	50.6984



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	23.802	353945.438	14191307.000	90.8197
2	28.420	29523.873	1434497.625	9.1803

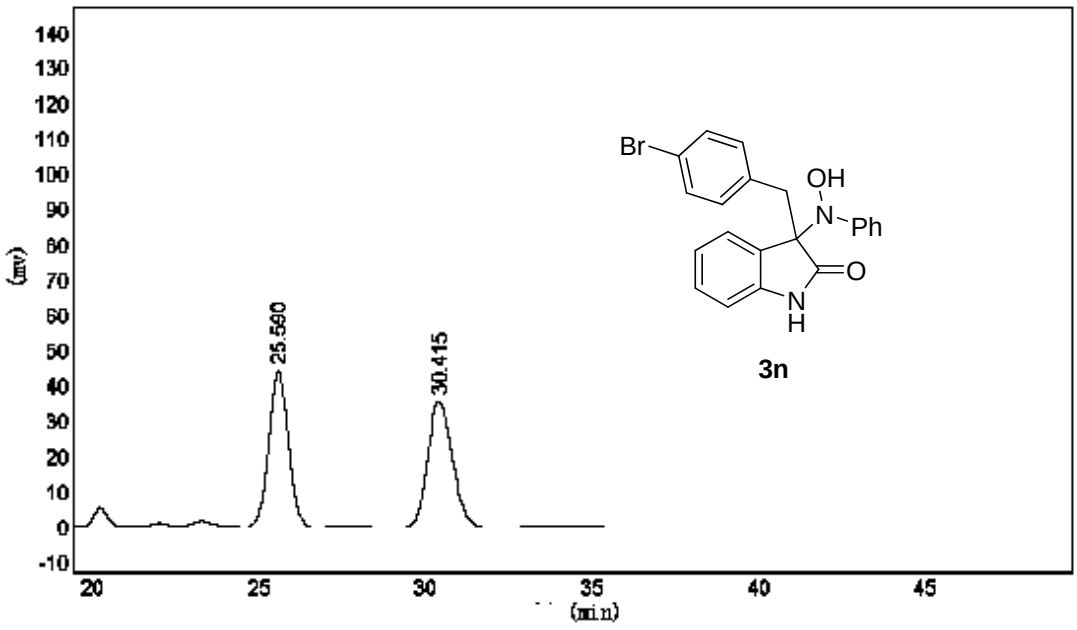


Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.282	138636.078	3967913.000	51.0167
2	24.787	94130.883	3809755.750	48.9833



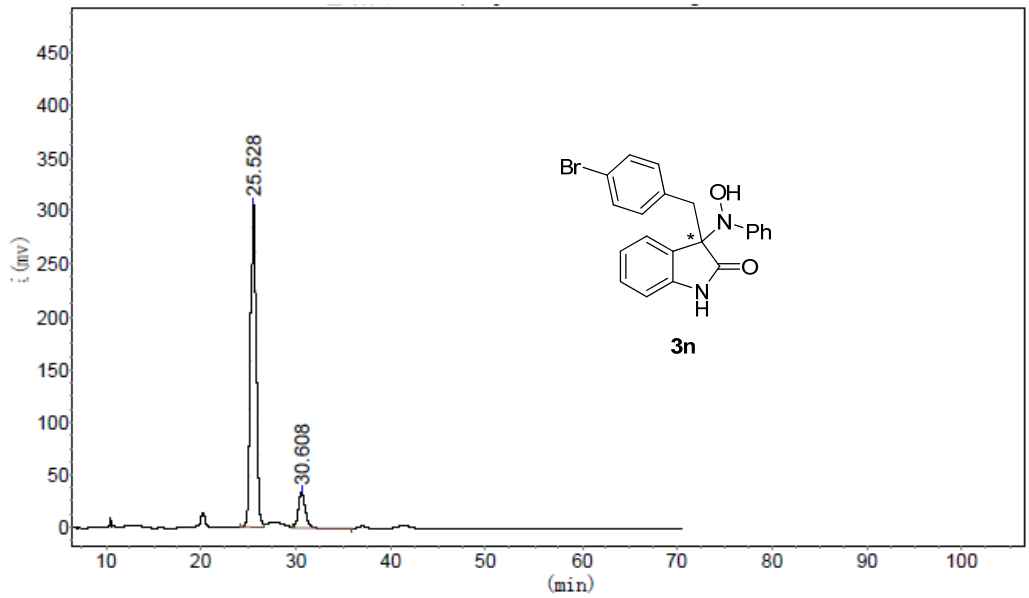
3m

Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.308	211036.531	6053562.500	91.1069
2	24.893	14646.946	590897.375	8.8931

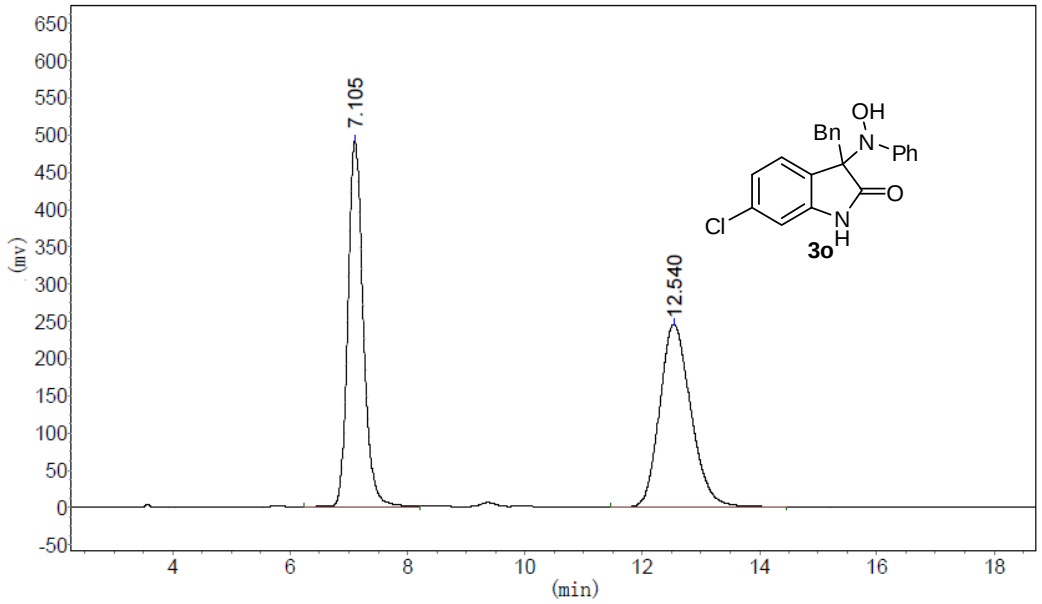


3n

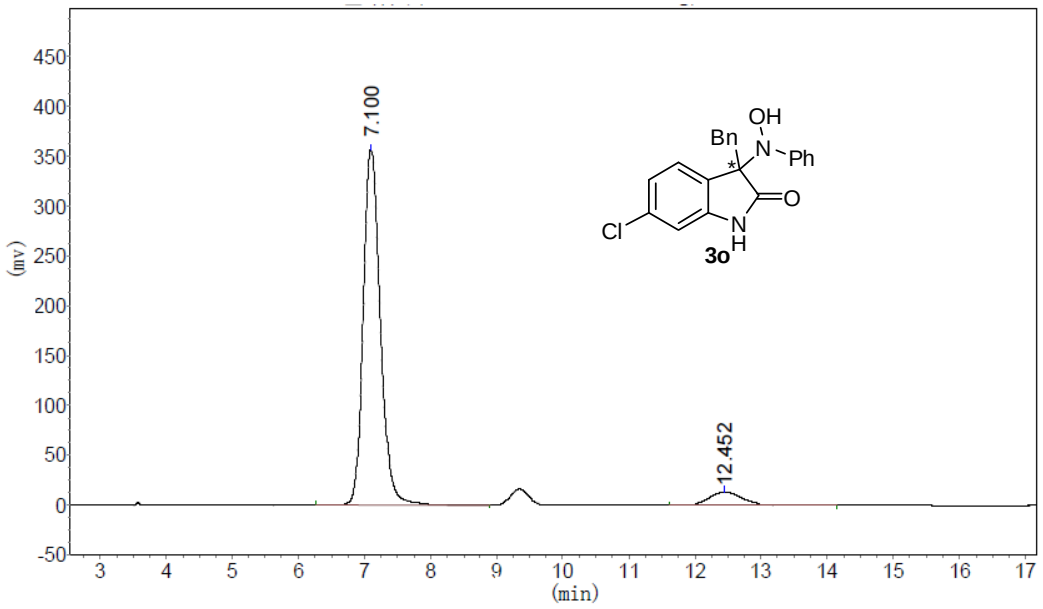
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	25.590	44059.523	1781857.625	49.2518
2	30.415	35699.344	1835997.250	50.7482



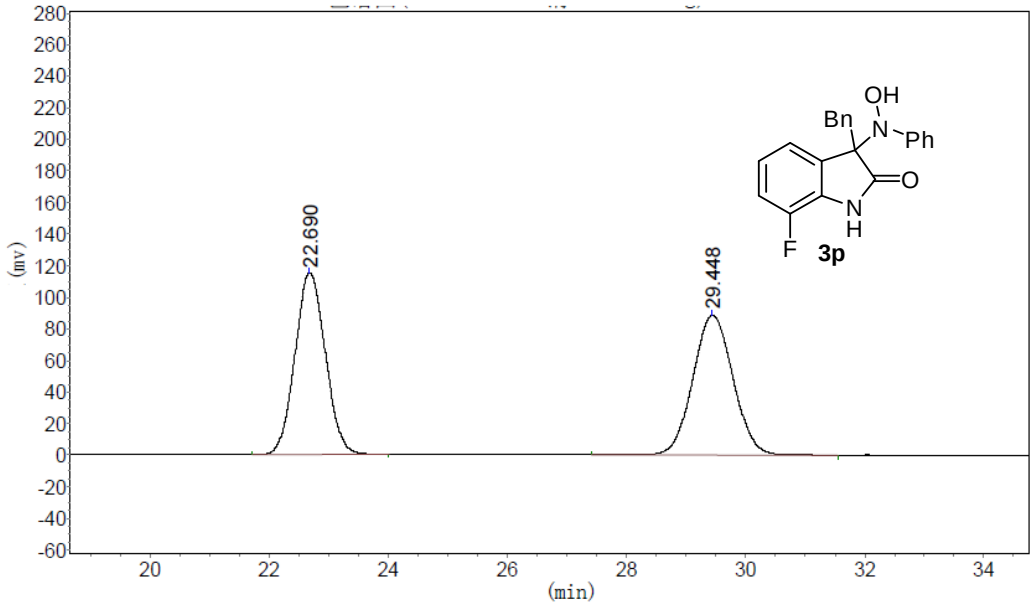
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	25.528	306808.781	12676039.000	87.8658
2	30.608	34345.645	1750558.375	12.1342



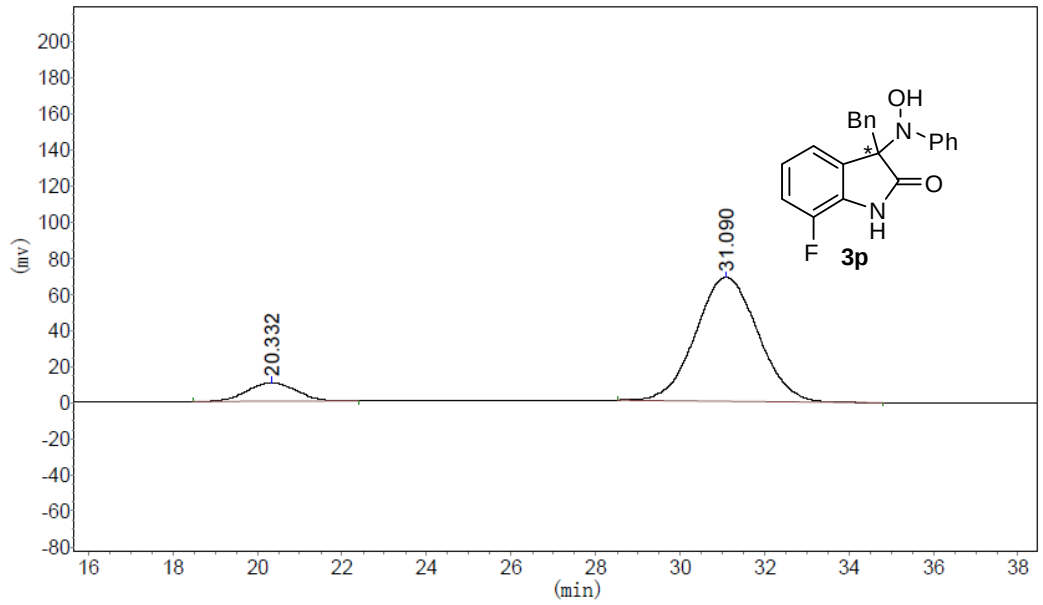
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.105	492218.156	8990405.000	49.8369
2	12.540	245709.922	9049236.000	50.1631



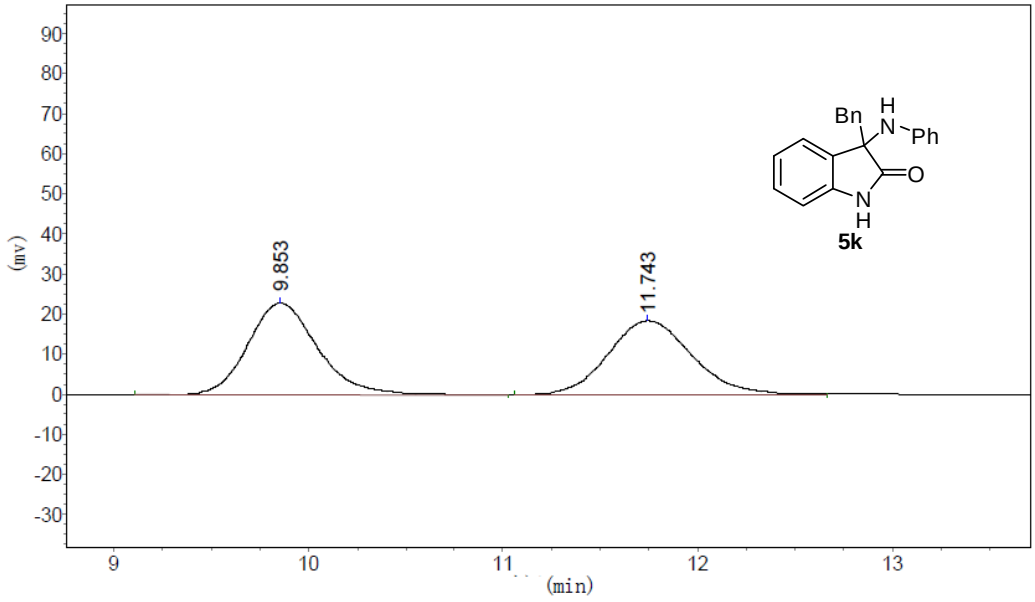
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.100	356760.094	6399166.500	93.0299
2	12.452	13447.665	479449.375	6.9701



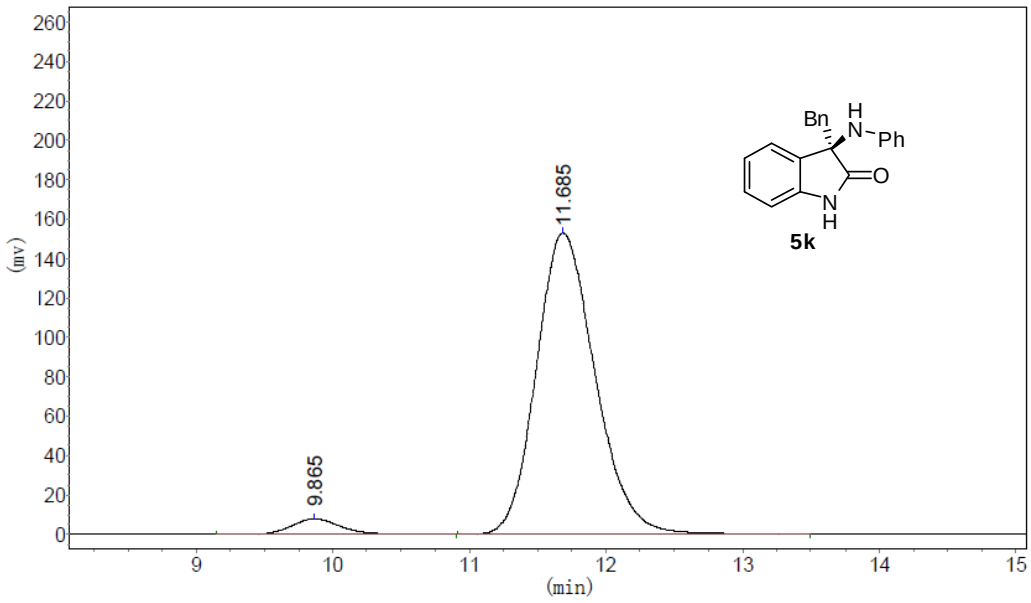
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	22.690	114958.344	4084648.750	49.6990
2	29.448	88170.172	4134124.750	50.3010



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.332	10594.243	844779.438	10.8098
2	31.090	68517.234	6970180.000	89.1902



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	9.853	22869.055	568481.063	50.6500
2	11.743	18518.225	553889.813	49.3500



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	9.865	7993.940	200825.875	4.1961
2	11.685	152990.391	4585138.500	95.8039