

Supporting Information

Organocatalytic asymmetric Michael addition of 3-substituted oxindoles to α,β -unsaturated acyl phosphonates for the synthesis of 3,3'-disubstituted oxindoles with chiral squaramides

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Table of Contents

General Methods

General Procedure for Synthesis of 3,3'-Disubstituted Oxindoles 3

References

Copies of NMR and HPLC Spectra for 3,3'-Disubstituted Oxindoles 3

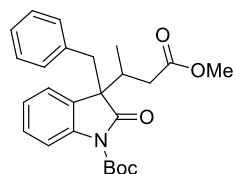
General Methods

^1H NMR spectra were recorded on Bruker 300 (300 MHz) spectrophotometers. Chemical shifts (δ) are reported from the solvent resonance as the internal standard (CDCl_3 : δ 7.26, $\text{DMSO}-d_6$: δ 2.50). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruple and m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker 300 (75 MHz) spectrophotometers (CDCl_3 : δ 77.2, $\text{DMSO}-d_6$: δ 39.5). Mass spectra were recorded on Bruker micrOTOF-Q II mass spectrometer. HPLC data was acquired using a Shimadzu LC-20A with Daicel AD-H, Daicel OD-H, Daicel IA, Daicel IC column.

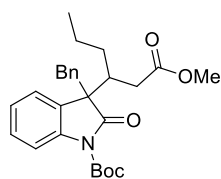
3-Mono Substituted Oxindoles (**1a-1x**) were prepared according to the reported procedures^[1] or similarly. α,β -Unsaturated acyl phosphonates (**2a-2h**) were prepared according to the reported procedures^[2] or similarly. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions have been carried out with distilled and degassed solvents in oven-dried glassware. All the solvents were treated according to general methods. Column chromatography was performed using silica gel H.

General Procedure for Synthesis of 3,3-Disubstituted Oxindoles 3

An oven-dried 20-mL reaction tube containing a stir bar was charged with oxindole **1** (0.1 mmol, 1.0 equiv), catalyst **4g** (0.02 mmol, 0.2 equiv) and Et_2O (1.0 mL). After 10 min of stirring at -20°C , α,β -unsaturated acyl phosphonates **2** (0.4 mmol, 4.0 equiv) with Et_2O (1.0 mL) was added. The stirring was maintained at the same temperature for 23 h, alcohol (0.4 mmol, 4.0 equiv)/amine (0.4 mmol, 4.0 equiv) and DBU (0.2 mmol, 2.0 equiv) were then added in the described sequence. After additionally 30 min of stirring at -20°C , the crude reaction mixture was poured into NH_4Cl (sat.) rapidly, extracted with DCM (3 x 5 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purified on silica gel afforded the pure addition products **3**.

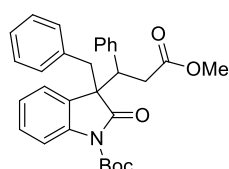


tert-butyl 3-benzyl-3-(4-methoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3ad): Colorless oil; 34.1 mg, 81% yield; 12.3:1 dr, 88% ee; $[\alpha]_D^{20} = +13.3$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 1/99$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 8.9$ min, $t_{\text{major}} = 12.2$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.15 (d, $J = 6.7$ Hz, 3 H), 1.58 (s, 9 H), 2.26 (dd, $J = 11.0$ Hz, $J = 15.1$ Hz, 1 H), 2.44 (dd, $J = 3.2$ Hz, $J = 15.1$ Hz, 1 H), 2.77-2.84 (m, 1 H), 3.07 (d, $J = 12.7$ Hz, 1 H), 3.40 (d, $J = 12.6$ Hz, 1 H), 3.67 (s, 3H), 6.79 (d, $J = 7.6$ Hz, 2 H), 6.99-7.06 (m, 3 H), 7.20-7.24 (m, 2 H), 7.30-7.33 (m, 1 H), 7.56 (d, $J = 7.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 28.0, 36.9, 37.7, 42.5, 51.7, 57.3, 83.9, 114.6, 123.5, 124.1, 126.6, 127.6, 128.3, 129.0, 129.7, 135.1, 140.1, 148.6, 172.8, 176.9; MS calcd for $\text{C}_{25}\text{H}_{29}\text{NNaO}_5$ $[\text{M} + \text{Na}]^+$: 446.1938, found 446.1937.



tert-butyl 3-benzyl-3-(1-methoxy-1-oxohexan-3-yl)-2-oxoindoline-1-carboxylate (3af): Colorless oil; 29.3 mg, 65% yield; 17.5:1 dr, 93% ee; $[\alpha]_D^{20} = +24.5$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak IA column, $i\text{PrOH}/\text{hexane} = 5/95$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 6.2$ min, $t_{\text{major}} = 8.6$ min); ^1H NMR (300

MHz, CDCl₃) δ 0.86 (t, J = 6.7 Hz, 3 H), 1.17-1.33 (m, 4 H), 1.52 (s, 9 H), 2.34 (dd, J = 7.4 Hz, J = 15.8 Hz, 1 H), 2.48 (dd, J = 4.8 Hz, J = 15.8 Hz, 1 H), 2.72-2.80 (m, 1 H), 3.24 (d, J = 12.5 Hz, 1 H), 3.33 (d, J = 12.5 Hz, 1 H), 3.61 (s, 3 H), 6.71 (d, J = 6.5 Hz, 2 H), 6.93-7.04 (m, 3 H), 7.13-7.22 (m, 2 H), 7.33 (d, J = 6.6 Hz, 1 H), 7.51 (d, J = 7.3 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.2, 21.0, 28.0, 33.5, 35.8, 42.1, 43.1, 51.7, 58.0, 83.8, 114.6, 123.6, 124.0, 126.5, 127.5, 128.2, 129.2, 129.7, 134.9, 140.0, 148.6, 173.4, 177.2; MS calcd for C₂₇H₃₃NNaO₅ [M + Na]⁺: 474.2251, found 474.2246.

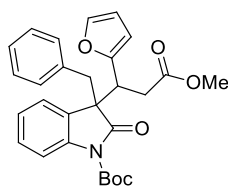


tert-butyl

3-benzyl-3-(3-methoxy-3-oxo-1-phenylpropyl)-2-

oxoindoline-1-carboxylate (3ag) White solid; 34.5 mg, 71% yield; 4.9:1 dr, 74% ee; [α]_D²⁰ = +8.8 (c = 1.0, CHCl₃); Mp: 157.2-158.9 °C; The ee was determined by HPLC (Chiralpak AD-H column, *i*PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 11.6 min,

t_{major} = 27.7 min); ¹H NMR (300 MHz, CDCl₃) δ 1.43 (s, 9 H), 2.89-3.00 (m, 2 H), 3.18 (d, J = 12.9 Hz, 1 H), 3.28 (d, J = 12.6 Hz, 1 H), 3.48 (s, 3 H), 3.84 (dd, J = 5.3 Hz, J = 10.2 Hz, 1 H), 6.78-6.81 (m, 2 H), 6.94-6.99 (m, 5 H), 7.11-7.13 (m, 3 H), 7.19-7.22 (m, 2 H), 7.37-7.45 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 27.8, 35.5, 41.7, 49.6, 51.7, 58.3, 83.6, 114.8, 123.7, 124.0, 126.5, 127.3, 127.7, 127.7, 128.0, 128.5, 129.2, 129.9, 135.2, 137.6, 140.3, 148.2, 171.8, 176.1; MS calcd for C₃₀H₃₁NNaO₅ [M + Na]⁺: 508.2094, found 508.2092.

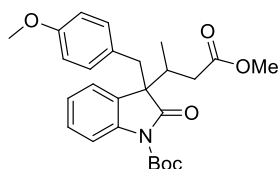


tert-butyl

3-benzyl-3-(1-(furan-2-yl)-3-methoxy-3-oxopropyl)-2-

oxoindoline-1-carboxylate (3ah) White solid; 29.0 mg, 61% yield; 3.2:1 dr, 80% ee; [α]_D²⁰ = +18.2 (c = 1.0, CHCl₃); Mp: 127.6-128.9 °C; The ee was determined by HPLC (Chiralpak AD-H column, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 5.6 min,

t_{major} = 9.4 min); 1.53 (s, 9 H), 2.80 (dd, J = 3.9 Hz, J = 15.7 Hz, 1 H), 2.92 (dd, J = 11.3 Hz, J = 15.7 Hz, 1 H), 3.14-3.34 (m, 2 H), 3.55 (s, 3 H), 3.93 (dd, J = 4.0 Hz, J = 11.3 Hz, 1 H), 6.17 (d, J = 3.2 Hz, 1 H), 6.28 (t, J = 3.1 Hz, 1 H), 6.74 (d, J = 6.2 Hz, 2 H), 6.93-7.03 (m, 3 H), 7.12-7.21 (m, 3 H), 7.42-7.50 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 28.0, 33.9, 41.6, 42.4, 51.8, 57.1, 83.9, 108.6, 110.4, 114.6, 123.8, 123.9, 124.8, 126.5, 127.6, 128.5, 129.8, 134.8, 139.8, 141.6, 148.5, 152.4, 171.7, 176.0; MS calcd for C₂₈H₂₉NNaO₆ [M + Na]⁺: 498.1887, found 498.1885.



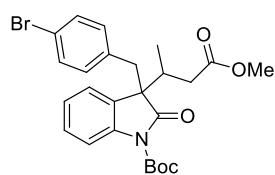
tert-butyl 3-(4-methoxy-4-oxobutan-2-yl)-3-(4-methoxybenzyl)-2-

oxoindoline-1-carboxylate (3bd): Colorless oil; 35.5 mg, 78% yield;

11.8:1 dr, 85% ee; [α]_D²⁰ = +22.8 (c = 1.0, CHCl₃); The ee was determined by HPLC (Chiralpak OD-H column, EtOH/hexane = 1/99,

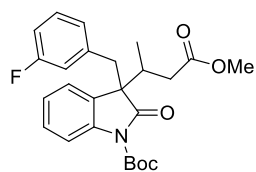
flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 8.9 min,

t_{major} = 12.2 min); ¹H NMR (300 MHz, CDCl₃) δ 1.07 (d, J = 6.7 Hz, 3 H), 1.53 (s, 9 H), 2.19 (dd, J = 11.0 Hz, J = 14.9 Hz, 1 H), 2.39 (dd, J = 2.9 Hz, J = 15.1 Hz, 1 H), 2.70-2.75 (m, 1 H), 2.97 (d, J = 12.9 Hz, 1 H), 3.28 (d, J = 12.9 Hz, 1 H), 3.61 (s, 3H), 3.63 (s, 3H), 6.50 (d, J = 8.5 Hz, 2 H), 6.65 (d, J = 8.5 Hz, 2 H), 7.12-7.22 (m, 2 H), 7.25 (d, J = 7.7 Hz, 1 H), 7.53 (d, J = 7.4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.9, 27.9, 36.8, 37.6, 41.5, 51.6, 54.9, 57.3, 83.8, 112.9, 114.6, 123.4, 124.0, 127.0, 128.2, 129.1, 130.7, 140.1, 148.6, 158.1, 172.7, 177.0; MS calcd for C₂₆H₃₁NNaO₆ [M + Na]⁺: 476.2044, found 476.2048.



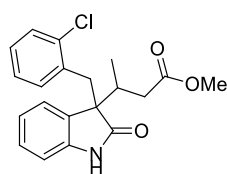
tert-butyl 3-(4-bromobenzyl)-3-(4-methoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3cd) Colorless oil; 30.1 mg, 60% yield; 36.5:1 dr, 93% ee; $[\alpha]_D^{20} = +29.4$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 1/99$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 13.1$ min,

$t_{\text{major}} = 22.7$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.07 (d, $J = 6.7$ Hz, 3 H), 1.54 (s, 9 H), 2.20 (dd, $J = 10.9$ Hz, $J = 15.1$ Hz, 1 H), 2.38 (dd, $J = 3.2$ Hz, $J = 15.1$ Hz, 1 H), 2.70-2.77 (m, 1 H), 2.97 (d, $J = 12.7$ Hz, 1 H), 3.30 (d, $J = 12.7$ Hz, 1 H), 3.62 (s, 3 H), 6.60 (d, $J = 8.3$ Hz, 2 H), 7.09 (d, $J = 8.3$ Hz, 2 H), 7.14-7.22 (m, 2 H), 7.25-7.27 (m, 1 H), 7.53 (d, $J = 7.7$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 27.9, 36.7, 37.7, 41.7, 51.7, 57.1, 84.2, 114.8, 120.7, 123.4, 124.2, 128.5, 128.6, 130.7, 131.4, 134.1, 140.0, 148.4, 172.6, 176.7; MS calcd for $\text{C}_{25}\text{H}_{28}\text{BrNNaO}_5$ $[\text{M} + \text{Na}]^+$: 524.1043, found 524.1052.



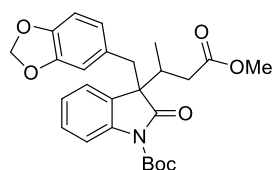
tert-butyl 3-(3-fluorobenzyl)-3-(4-methoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3dd) Colorless oil; 34.4 mg, 78% yield; 29.2:1 dr, 94% ee; $[\alpha]_D^{20} = +15.6$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 1/99$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 10.2$ min,

$t_{\text{major}} = 14.2$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.08 (d, $J = 6.7$ Hz, 3 H), 1.54 (s, 9 H), 2.20 (dd, $J = 10.8$ Hz, $J = 15.1$ Hz, 1 H), 2.37 (dd, $J = 3.2$ Hz, $J = 15.1$ Hz, 1 H), 2.72-2.76 (m, 1 H), 3.00 (d, $J = 12.7$ Hz, 1 H), 3.35 (d, $J = 12.7$ Hz, 1 H), 3.62 (s, 3 H), 6.49 (t, $J = 6.8$ Hz, 2 H), 6.70 (td, $J = 1.7$ Hz, $J = 8.9$ Hz, 1 H), 6.88-6.96 (m, 1 H), 7.13-7.23 (m, 2 H), 7.26-7.28 (m, 1 H), 7.54 (d, $J = 7.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.9, 27.9, 36.7, 37.7, 42.1, 51.7, 57.1, 84.1, 113.5 (d, $J = 20.9$ Hz), 114.6, 116.5 (d, $J = 21.4$ Hz), 123.3, 124.2, 125.4 (d, $J = 2.8$ Hz), 128.5, 128.6, 128.9 (d, $J = 8.2$ Hz), 137.6 (d, $J = 7.4$ Hz), 140.0, 148.5, 162.0 (d, $J = 243.8$ Hz), 172.6, 176.6; MS calcd for $\text{C}_{25}\text{H}_{28}\text{FNNaO}_5$ $[\text{M} + \text{Na}]^+$: 464.1844, found 464.1838.



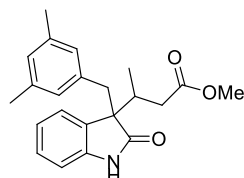
methyl 3-(3-(2-chlorobenzyl)-2-oxoindolin-3-yl)butanoate (3fd)

Deprotected the Boc group; White solid; 30.2 mg, 86% yield; 54.9:1 dr, 98% ee; $[\alpha]_D^{20} = -0.2$ ($c = 1.0$, CHCl_3); Mp: 120.2-121.5 $^{\circ}\text{C}$; The ee was determined by HPLC (Chiralpak AD-H column, $\text{EtOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 11.5$ min, $t_{\text{major}} = 15.2$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.07 (d, $J = 6.7$ Hz, 3 H), 2.22 (dd, $J = 11.0$ Hz, $J = 15.1$ Hz, 1 H), 2.53 (dd, $J = 2.9$ Hz, $J = 15.2$ Hz, 1 H), 2.68-2.75 (m, 1 H), 3.39 (d, $J = 13.6$ Hz, 1 H), 3.57 (d, $J = 13.6$ Hz, 1 H), 3.63 (s, 3 H), 6.68 (d, $J = 7.4$ Hz, 1 H), 6.85-6.97 (m, 3 H), 7.06-7.11 (m, 3 H), 7.30 (d, $J = 7.4$ Hz, 1 H), 8.63 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.7, 36.3, 36.8, 37.6, 51.7, 57.2, 109.2, 122.0, 125.1, 126.3, 127.8, 128.2, 129.2, 129.3, 129.5, 130.4, 134.4, 140.8, 173.0, 180.9; MS calcd for $\text{C}_{20}\text{H}_{20}\text{ClNNaO}_3$ $[\text{M} + \text{Na}]^+$: 380.1024, found 380.1018.



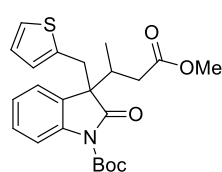
tert-butyl 3-(benzo[d][1,3]dioxol-5-ylmethyl)-3-(4-methoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3gd) Colorless oil; 34.4 mg, 84% yield; 13.8:1 dr, 89% ee; $[\alpha]_D^{20} = +23.5$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak IC column, $i\text{PrOH}/\text{hexane} = 20/80$,

flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 10.5 min, t_{major} = 7.5 min); ^1H NMR (300 MHz, CDCl_3) δ 1.06 (d, J = 6.7 Hz, 3 H), 1.55 (s, 9 H), 2.18 (dd, J = 11.0 Hz, J = 15.1 Hz, 1 H), 2.36 (dd, J = 3.2 Hz, J = 15.1 Hz, 1 H), 2.68-2.73 (m, 1 H), 2.93 (d, J = 12.9 Hz, 1 H), 3.27 (d, J = 12.9 Hz, 1 H), 3.61 (s, 3 H), 5.75-5.77 (m, 2 H), 6.20 (dd, J = 1.7 Hz, J = 8.0 Hz, 1 H), 6.24 (d, J = 1.6 Hz, 1 H), 6.41 (d, J = 8.0 Hz, 1 H), 7.12-7.26 (m, 3 H), 7.58 (d, J = 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.9, 27.9, 36.8, 37.6, 42.1, 51.6, 57.3, 83.9, 100.6, 107.4, 110.0, 114.6, 123.0, 123.4, 124.1, 128.3, 128.7, 128.9, 140.1, 146.0, 146.8, 148.7, 172.7, 176.9; MS calcd for $\text{C}_{26}\text{H}_{29}\text{NNaO}_7$ [$\text{M} + \text{Na}$] $^+$: 490.1836, found 490.1830.



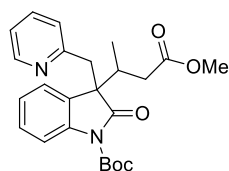
methyl 3-(3-(3,5-dimethylbenzyl)-2-oxoindolin-3-yl)butanoate (3hd)

Deprotected the Boc group; White solid; 21.4 mg, 61% yield; 7.3:1 dr, 78% ee; $[\alpha]_{\text{D}}^{20}$ = +62.0 (c = 1.0, CHCl_3); Mp: 118.6-119.8 $^{\circ}\text{C}$; The ee was determined by HPLC (Chiralpak IA column, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.8 min, t_{major} = 11.2 min); ^1H NMR (300 MHz, CDCl_3) δ 1.03 (d, J = 6.6 Hz, 3 H), 2.02 (s, 6 H), 2.23 (dd, J = 11.0 Hz, J = 15.0 Hz, 1 H), 2.53 (dd, J = 3.1 Hz, J = 15.0 Hz, 1 H), 2.64-2.73 (m, 1 H), 3.02 (d, J = 12.7 Hz, 1 H), 3.20 (d, J = 12.9 Hz, 1 H), 3.64 (s, 3 H), 6.41 (s, 2 H), 6.64 (s, 1 H), 6.65 (d, J = 7.3 Hz, 1 H), 7.04 (t, J = 7.2 Hz, 1 H), 7.13 (t, J = 7.6 Hz, 1 H), 7.25 (d, J = 5.9 Hz, 1 H), 8.00 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.9, 21.0, 36.8, 37.2, 40.8, 51.7, 57.5, 109.5, 122.0, 124.4, 127.7, 128.0, 128.0, 130.5, 135.4, 136.8, 141.1, 173.1, 180.4; MS calcd for $\text{C}_{22}\text{H}_{25}\text{NNaO}_3$ [$\text{M} + \text{Na}$] $^+$: 374.1727, found 374.1724.



tert-butyl 3-(4-methoxy-4-oxobutan-2-yl)-2-oxo-3-(thiophen-2-ylmethyl)indoline-1-carboxylate (3id)

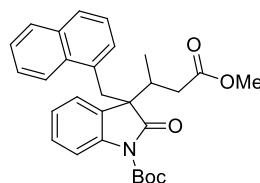
Colorless oil; 32.2 mg, 75% yield; 50.3:1 dr, 98% ee; $[\alpha]_{\text{D}}^{20}$ = +13.1 (c = 1.0, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, EtOH/hexane = 1/99, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.3 min, t_{major} = 17.8 min); ^1H NMR (300 MHz, CDCl_3) δ 1.09 (d, J = 6.7 Hz, 3 H), 1.57 (s, 9 H), 2.17 (dd, J = 10.9 Hz, J = 15.1 Hz, 1 H), 2.36 (dd, J = 3.2 Hz, J = 15.1 Hz, 1 H), 2.68-2.75 (m, 1 H), 3.27 (d, J = 14.0 Hz, 1 H), 3.59 (d, J = 14.0 Hz, 1 H), 3.62 (s, 3 H), 6.53 (d, J = 3.3 Hz, 1 H), 6.69 (t, J = 3.5 Hz, 1 H), 6.91 (d, J = 5.1 Hz, 1 H), 7.15-7.29 (m, 3 H), 7.65 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.8, 28.0, 36.2, 36.7, 37.7, 51.7, 56.9, 84.1, 114.8, 123.5, 124.3, 124.4, 126.2, 127.1, 128.6, 128.9, 136.7, 140.4, 148.7, 172.6, 176.6; MS calcd for $\text{C}_{23}\text{H}_{27}\text{NNaO}_5\text{S}$ [$\text{M} + \text{Na}$] $^+$: 452.1502, found 452.1502.



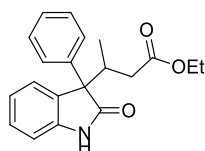
tert-butyl 3-(4-methoxy-4-oxobutan-2-yl)-2-oxo-3-(pyridin-2-ylmethyl)indoline-1-carboxylate (3jd)

Colorless oil; 36.6 mg, 86% yield; >99:1 dr, 96% ee; $[\alpha]_{\text{D}}^{20}$ = -4.5 (c = 1.0, CHCl_3); The ee was determined by HPLC (Chiralpak AD-H column, EtOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 5.3 min, t_{major} = 4.4 min); ^1H NMR (300 MHz, CDCl_3) δ 1.12 (d, J = 6.7 Hz, 3 H), 1.62 (s, 9 H), 2.17 (dd, J = 11.0 Hz, J = 15.2 Hz, 1 H), 2.37 (dd, J = 3.0 Hz, J = 15.2 Hz, 1 H), 2.66-2.72 (m, 1 H), 3.24 (d, J = 13.6 Hz, 1 H), 3.60 (s, 3 H), 3.66 (d, J = 13.6 Hz, 1 H), 6.82-6.90 (m, 2 H), 7.03 (t, J = 7.4 Hz, 1 H), 7.13 (t, J = 7.1 Hz, 2 H), 7.32 (td, J = 1.8 Hz, J = 7.7 Hz, 1 H), 7.58 (d, J = 7.7 Hz, 1 H),

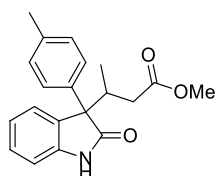
8.18 (d, $J = 4.0$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.5, 28.1, 36.6, 38.3, 43.8, 51.6, 55.5, 83.9, 114.5, 121.3, 123.4, 123.5, 123.9, 128.0, 129.0, 135.6, 140.1, 148.6, 149.2, 156.3, 172.8, 177.2; MS calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{NaO}_5$ $[\text{M} + \text{Na}]^+$: 447.1890, found 447.1889.



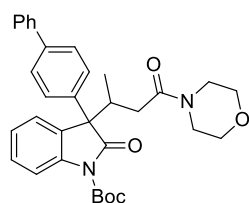
tert-butyl 3-(4-methoxy-4-oxobutan-2-yl)-3-(naphthalen-1-ylmethyl)-2-oxoindoline-1-carboxylate (3kd) Colorless oil; 38.9 mg, 82% yield; 26.2:1 dr, 96% ee; $[\alpha]_{\text{D}}^{20} = +27.1$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 12.1$ min, $t_{\text{major}} = 6.6$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.25 (d, $J = 6.7$ Hz, 3 H), 1.40 (s, 9 H), 2.27 (dd, $J = 10.8$ Hz, $J = 15.4$ Hz, 1 H), 2.41 (dd, $J = 3.2$ Hz, $J = 15.2$ Hz, 1 H), 2.89-2.96 (m, 1 H), 3.51 (d, $J = 13.5$ Hz, 1 H), 3.64 (s, 3 H), 3.96 (d, $J = 13.5$ Hz, 1 H), 6.87 (d, $J = 7.1$ Hz, 1 H), 7.00 (t, $J = 7.4$ Hz, 1 H), 7.08 (t, $J = 7.4$ Hz, 2 H), 7.24 (d, $J = 7.3$ Hz, 1 H), 7.31-7.41 (m, 2 H), 7.45 (d, $J = 8.0$ Hz, 1 H), 7.54 (d, $J = 8.1$ Hz, 1 H), 7.66 (d, $J = 7.4$ Hz, 1 H), 7.96 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 27.7, 37.0, 37.8, 51.7, 56.9, 83.6, 114.4, 123.8, 123.8, 124.3, 124.4, 125.1, 125.2, 127.4, 127.7, 128.1, 128.2, 128.8, 128.9, 131.5, 131.9, 133.4, 140.0, 148.5, 172.8, 177.0; MS calcd for $\text{C}_{29}\text{H}_{31}\text{NNaO}_5$ $[\text{M} + \text{Na}]^+$: 496.2094, found 496.2088.



ethyl 3-(2-oxo-3-phenylindolin-3-yl)butanoate (3ld) Deprotected the Boc group; White solid; 27.5 mg, 85% yield; 24.8:1 dr, 81% ee; $[\alpha]_{\text{D}}^{20} = +202.3$ ($c = 1.0$, CHCl_3); Mp: 188.9-190.5 °C; The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 5.3$ min, $t_{\text{major}} = 10.9$ min); ^1H NMR (300 MHz, CDCl_3) δ 0.83 (d, $J = 6.5$ Hz, 3 H), 1.22 (t, $J = 7.1$ Hz, 3 H), 2.24 (dd, $J = 11.4$ Hz, $J = 15.1$ Hz, 1 H), 2.46 (d, $J = 13.5$ Hz, 1 H), 3.33-3.38 (m, 1 H), 4.08 (q, $J = 7.1$ Hz, 2 H), 6.98 (d, $J = 7.7$ Hz, 1 H), 7.10 (t, $J = 7.4$ Hz, 1 H), 7.24-7.33 (m, 5 H), 7.45 (d, $J = 7.3$ Hz, 2 H), 9.03 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 15.1, 37.0, 37.2, 60.5, 60.8, 110.4, 122.3, 126.1, 127.5, 127.5, 128.5, 128.7, 129.6, 138.1, 141.6, 172.6, 180.2; MS calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3$ $[\text{M} + \text{Na}]^+$: 346.1414, found 346.1410.

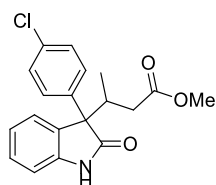


methyl 3-(2-oxo-3-(p-tolyl)indolin-3-yl)butanoate (3md) Deprotected the Boc group; Colorless oil; 22.6 mg, 70% yield; 14.8:1 dr, 79% ee; $[\alpha]_{\text{D}}^{20} = +155.0$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $\text{EtOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 5.3$ min, $t_{\text{major}} = 11.1$ min); ^1H NMR (300 MHz, CDCl_3) δ 0.81 (d, $J = 6.5$ Hz, 3 H), 2.25 (dd, $J = 11.5$ Hz, $J = 15.2$ Hz, 1 H), 2.29 (s, 3 H), 2.49 (dd, $J = 1.9$ Hz, $J = 15.1$ Hz, 1 H), 3.26-3.38 (m, 1 H), 3.63 (s, 3 H), 6.97 (d, $J = 7.7$ Hz, 1 H), 7.07-7.12 (m, 3 H), 7.24 (d, $J = 7.4$ Hz, 1 H), 7.29-7.36 (m, 3 H), 8.92 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.1, 20.9, 36.8, 37.1, 51.7, 60.5, 110.4, 122.3, 126.0, 127.3, 128.4, 129.4, 129.7, 135.0, 137.3, 141.6, 173.1, 180.4; MS calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3$ $[\text{M} + \text{Na}]^+$: 346.1414, found 346.1401.



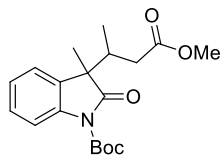
tert-butyl 3-([(1,1'-biphenyl]-4-yl)-3-(4-morpholino-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3nd) Colorless oil; 40.5 mg, 75% yield; 11.4:1 dr, 76% ee; $[\alpha]_{\text{D}}^{20} = +65.7$ ($c = 1.0$, CHCl_3); The ee was

determined by HPLC (Chiralpak OD-H column, *i*PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.3 min, t_{major} = 12.6 min); ^1H NMR (300 MHz, CDCl_3) δ 0.85 (d, J = 6.5 Hz, 3 H), 1.62 (s, 9 H), 2.28-2.39 (m, 2 H), 3.29 (s, 2 H), 3.46-3.62 (m, 7H), 7.25-7.35 (m, 3 H), 7.39-7.44 (m, 3 H) 7.50-7.56 (m, 6 H), 7.99 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.6, 28.0, 34.8, 38.5, 44.0, 60.4, 66.5, 84.5, 115.3, 124.2, 125.5, 126.9, 127.3, 127.5, 128.1, 128.2, 128.7, 128.8, 137.1, 140.2, 140.4, 140.6, 149.1, 169.9, 176.0; MS calcd for $\text{C}_{33}\text{H}_{36}\text{N}_2\text{NaO}_5$ $[\text{M} + \text{Na}]^+$: 563.2516, found 563.2501.



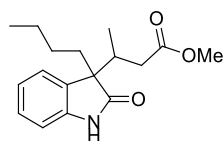
methyl 3-(3-(4-chlorophenyl)-2-oxoindolin-3-yl)butanoate (3od)

Deprotected the Boc group; White solid; 25.1 mg, 73% yield; 2.0:1 dr, 79%/69% ee; $[\alpha]_{\text{D}}^{20}$ = +158.6 (c = 1.0, CHCl_3); Mp: 171.8-173.2 °C; The ee was determined by HPLC (Chiralpak AD-H column, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 22.9 min, t_{major} = 12.9 min); ^1H NMR (300 MHz, CDCl_3) δ 0.82 (d, J = 6.4 Hz, 3 H), 2.21-2.30 (m, 1 H), 2.47 (td, J = 2.1 Hz, J = 15.2 Hz, 1 H), 3.29-3.38 (m, 1 H), 3.62 (s, 3 H), 6.98 (d, J = 7.7 Hz, 1 H), 7.08-7.13 (m, 1 H), 7.22-7.34 (m, 4 H), 7.45 (d, J = 7.1 Hz, 2 H), 8.92 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.1, 36.8, 37.3, 51.7, 60.7, 110.4, 122.3, 126.1, 127.5, 128.7, 128.8, 129.0, 129.5, 138.0, 141.6, 173.0, 180.1; MS calcd for $\text{C}_{19}\text{H}_{18}\text{ClNNaO}_3$ $[\text{M} + \text{Na}]^+$: 366.0867, found 366.0877.



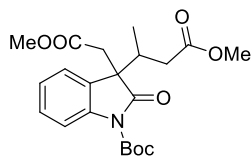
tert-butyl 3-(4-methoxy-4-oxobutan-2-yl)-3-methyl-2-oxoindoline-1-carboxylate (3pd)

Colorless oil; 29.2 mg, 84% yield; 5.7:1 dr, 70% ee; $[\alpha]_{\text{D}}^{20}$ = +27.4 (c = 1.0, CHCl_3); The ee was determined by HPLC (Chiralpak AD-H column, *i*PrOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 5.8 min, t_{major} = 5.5 min); ^1H NMR (300 MHz, CDCl_3) δ 0.97 (d, J = 6.7 Hz, 3 H), 1.43 (s, 3 H), 1.64 (s, 9H), 2.10 (dd, J = 11.0 Hz, J = 15.1 Hz, 1 H), 2.35 (dd, J = 3.3 Hz, J = 15.1 Hz, 1 H), 2.47-2.57 (m, 1H), 3.61 (s, 3 H), 7.12-7.20 (m, 2 H), 7.26-7.32 (m, 1 H), 7.83 (d, J = 8.1, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.6, 22.1, 28.1, 36.4, 38.4, 50.7, 51.6, 84.3, 114.8, 122.9, 124.4, 128.2, 131.7, 139.3, 149.2, 172.8, 178.1; MS calcd for $\text{C}_{19}\text{H}_{25}\text{NNaO}_5$ $[\text{M} + \text{Na}]^+$: 370.1625, found 370.1619.

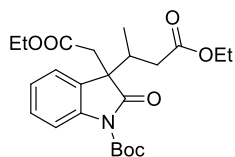


methyl 3-(3-butyl-2-oxoindolin-3-yl)butanoate (3qd)

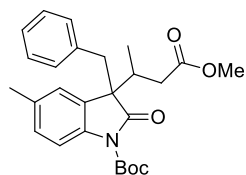
Deprotected the Boc group; Colorless oil; 22.0 mg, 76% yield; 7.8:1 dr, 68% ee; $[\alpha]_{\text{D}}^{20}$ = +20.8 (c = 1.0, CHCl_3); The ee was determined by HPLC (Chiralpak AD-H column, *i*PrOH/hexane = 20/80, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 5.4 min, t_{major} = 7.3 min); ^1H NMR (300 MHz, CDCl_3) δ 0.74 (t, J = 7.2 Hz, 3 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.97-1.10 (m, 2 H), 1.12-1.25 (m, 2 H), 1.76-2.00 (m, 2 H), 2.14 (dd, J = 11.0 Hz, J = 14.9 Hz, 1 H), 2.42-2.57 (m, 2 H), 3.61 (s, 3 H), 6.91 (d, J = 7.7 Hz, 1 H), 7.03 (t, J = 7.4 Hz, 1 H), 7.12 (d, J = 7.3 Hz, 1 H), 7.21 (t, J = 7.5 Hz, 1 H), 8.78 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 14.6, 22.9, 26.3, 34.9, 36.6, 37.1, 51.6, 55.9, 109.6, 122.4, 123.6, 127.9, 131.5, 141.4, 173.2, 181.8; MS calcd for $\text{C}_{17}\text{H}_{23}\text{NNaO}_3$ $[\text{M} + \text{Na}]^+$: 312.1570, found 312.1565.



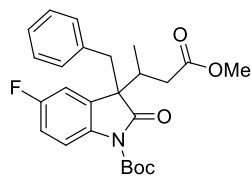
tert-butyl 3-(2-methoxy-2-oxoethyl)-3-(4-methoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3rd) Colorless oil; 32.1 mg, 79% yield; 45.7:1 dr, 93% ee; $[\alpha]_{\text{D}}^{20} = +21.6$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 7.4$ min, $t_{\text{major}} = 6.4$ min); ^1H NMR (300 MHz, CDCl_3) δ 0.97 (d, $J = 6.7$ Hz, 3 H), 1.64 (s, 9 H), 2.06 (dd, $J = 10.9$ Hz, $J = 15.2$ Hz, 1 H), 2.27 (dd, $J = 3.2$ Hz, $J = 15.3$ Hz, 1 H), 2.47-2.54 (m, 1 H), 2.90 (d, $J = 16.3$ Hz, 1 H), 3.19 (d, $J = 16.3$ Hz, 1 H), 3.40 (s, 3 H), 3.60 (s, 3 H), 7.11-7.16 (m, 2 H), 7.26-7.33 (m, 1 H), 7.84 (d, $J = 8.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 28.1, 36.1, 38.3, 39.9, 51.7, 51.7, 52.1, 84.2, 115.0, 122.6, 124.3, 128.7, 140.6, 140.7, 149.1, 170.0, 172.4, 176.8; MS calcd for $\text{C}_{21}\text{H}_{27}\text{NNaO}_7$ $[\text{M} + \text{Na}]^+$: 428.1680, found 428.1661.



tert-butyl 3-(2-ethoxy-2-oxoethyl)-3-(4-ethoxy-4-oxobutan-2-yl)-2-oxoindoline-1-carboxylate (3sd) Colorless oil; 33.8 mg, 78% yield; 12.1:1 dr, 97% ee; $[\alpha]_{\text{D}}^{20} = +13.4$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 5.4$ min, $t_{\text{major}} = 5.0$ min); ^1H NMR (300 MHz, CDCl_3) δ 0.92-0.99 (m, 6 H), 1.20 (t, $J = 7.1$ Hz, 3 H), 1.64 (s, 9 H), 2.05 (dd, $J = 11.0$ Hz, $J = 15.2$ Hz, 1 H), 2.26 (dd, $J = 3.1$ Hz, $J = 15.2$ Hz, 1 H), 2.44-2.52 (m, 1 H), 2.88 (d, $J = 16.0$ Hz, 1 H), 3.20 (d, $J = 16.0$ Hz, 1 H), 3.77-3.86 (m, 2 H), 4.06 (q, $J = 7.1$ Hz, 2 H), 7.12-7.15 (m, 2 H), 7.27-7.33 (m, 1 H), 7.84 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.6, 14.1, 14.1, 28.1, 36.4, 38.5, 40.3, 52.2, 60.6, 60.7, 84.2, 114.9, 122.7, 124.3, 128.7, 128.8, 140.7, 149.2, 169.4, 172.0, 176.8; MS calcd for $\text{C}_{23}\text{H}_{31}\text{NNaO}_7$ $[\text{M} + \text{Na}]^+$: 456.1993, found 456.1970.

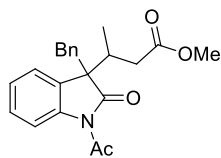


tert-butyl 3-benzyl-3-(4-methoxy-4-oxobutan-2-yl)-5-methyl-2-oxoindoline-1-carboxylate (3td) Colorless oil; 35.8 mg, 82% yield; 11.1:1 dr, 85% ee; $[\alpha]_{\text{D}}^{20} = +36.2$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak AD-H column, $i\text{PrOH}/\text{hexane} = 10/90$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 5.1$ min, $t_{\text{major}} = 5.6$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.09 (d, $J = 6.7$ Hz, 3 H), 1.52 (s, 9 H), 2.22 (dd, $J = 11.1$ Hz, $J = 15.1$ Hz, 1 H), 2.37-2.44 (m, 4 H), 2.70-2.77 (m, 1 H), 3.01 (d, $J = 12.7$ Hz, 1 H), 3.33 (d, $J = 12.7$ Hz, 1 H), 3.64 (s, 3 H), 6.74 (dd, $J = 1.4$ Hz, $J = 7.4$ Hz, 2 H), 6.95-7.05 (m, 5 H), 7.39 (d, $J = 8.3$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 21.2, 28.0, 36.9, 37.7, 42.5, 51.7, 57.3, 83.7, 114.4, 124.0, 126.5, 127.5, 128.8, 128.9, 129.8, 133.6, 135.2, 137.8, 148.7, 172.9, 177.0; MS calcd for $\text{C}_{26}\text{H}_{31}\text{NNaO}_5$ $[\text{M} + \text{Na}]^+$: 460.2094, found 460.2103.

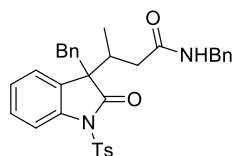


tert-butyl 3-benzyl-3-(4-methoxy-4-oxobutan-2-yl)-5-methyl-2-oxoindoline-1-carboxylate (3ud) Colorless oil; 28.6 mg, 65% yield; 36.1:1 dr, 93% ee; $[\alpha]_{\text{D}}^{20} = +12.5$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}/\text{hexane} = 5/95$, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 5.5$ min, $t_{\text{major}} = 7.6$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.12 (d, $J = 6.7$ Hz, 3 H), 1.54 (s, 9 H), 2.20 (dd, $J = 10.8$ Hz, $J = 15.1$ Hz, 1 H), 2.36 (dd, $J = 3.2$ Hz, $J = 15.1$ Hz, 1 H), 2.70-2.76 (m, 1 H), 2.99 (d, $J = 12.8$ Hz, 1 H), 3.37 (d, $J = 12.8$ Hz, 1 H), 3.65 (s, 3 H), 6.77 (dd, $J = 1.4$ Hz, $J = 7.5$ Hz, 2 H),

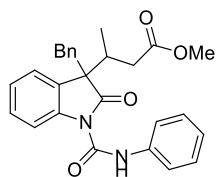
6.89 (td, $J = 2.7$ Hz, $J = 8.9$ Hz, 1 H), 6.98-7.05 (m, 4 H), 7.52 (dd, $J = 4.6$ Hz, $J = 8.9$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 28.0, 36.8, 37.7, 42.5, 51.8, 57.6, 84.1, 110.9 (d, $J = 24.1$ Hz), 114.8 (d, $J = 22.6$ Hz), 116.0 (d, $J = 7.8$ Hz), 126.8, 127.7, 129.7, 131.0 (d, $J = 7.7$ Hz), 134.7, 136.1, 148.5, 159.7 (d, $J = 242.1$ Hz), 172.5, 176.4; MS calcd for $\text{C}_{25}\text{H}_{28}\text{FNNaO}_5$ [$\text{M} + \text{Na}$] $^+$: 464.1844, found 464.1854.



methyl 3-(1-acetyl-3-benzyl-2-oxoindolin-3-yl)butanoate (3vd) White solid; 35.1 mg, 96% yield; 4.3:1 dr, 3% ee; $[\alpha]_{\text{D}}^{20} = +0.7$ ($c = 1.0$, CHCl_3); Mp: 143.5-149 $^{\circ}\text{C}$; The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}$ /hexane = 1/99, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 12.4$ min, $t_{\text{major}} = 26.7$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.03 (d, $J = 6.7$ Hz, 3 H), 2.22 (dd, $J = 10.9$ Hz, $J = 15.1$ Hz, 1 H), 3.47-3.53 (m, 4 H), 2.77-2.81 (m, 1 H), 3.10 (d, $J = 12.8$ Hz, 1 H), 3.34 (d, $J = 12.8$ Hz, 1 H), 3.65 (s, 3 H), 6.70 (d, $J = 6.5$ Hz, 2 H), 6.96-7.03 (m, 3 H), 7.21-7.27 (m, 2 H), 7.34 (dd, $J = 3.7$ Hz, $J = 5.6$ Hz, 1 H), 7.93-7.98 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.2, 26.4, 36.7, 38.0, 42.4, 51.7, 57.6, 116.2, 123.4, 124.9, 126.9, 127.7, 128.6, 129.1, 129.6, 134.9, 140.5, 170.3, 172.6, 179.3; MS calcd for $\text{C}_{22}\text{H}_{23}\text{NNaO}_4$ [$\text{M} + \text{Na}$] $^+$: 388.1519, found 388.1517.



N-benzyl-3-(3-benzyl-2-oxo-1-tosylindolin-3-yl)butanamide (3wd) White solid; 54.2 mg, 98% yield; 4.9:1 dr, 60% ee; $[\alpha]_{\text{D}}^{20} = +0.9$ ($c = 1.0$, CH_2Cl_2); Mp: 199.5-201.3 $^{\circ}\text{C}$; The ee was determined by HPLC (Chiralpak IA column, $i\text{PrOH}$ /hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 24.3$ min, $t_{\text{major}} = 11.0$ min); ^1H NMR (300 MHz, CDCl_3) δ 0.57 (d, $J = 6.5$ Hz, 3 H), 1.99 (t, $J = 11.7$ Hz, 1 H), 2.39-2.59 (m, 5 H), 3.08 (d, $J = 13.1$ Hz, 1 H), 3.29 (d, $J = 13.1$ Hz, 1 H), 4.25 (d, $J = 5.7$ Hz, 2 H), 6.50 (d, $J = 7.2$ Hz, 2 H), 6.73 (t, $J = 7.6$ Hz, 2 H), 6.90 (t, $J = 7.4$ Hz, 1 H), 7.21-7.32 (m, 7 H), 7.41 (d, $J = 8.1$ Hz, 2 H), 7.57 (d, $J = 7.9$ Hz, 2 H), 7.70 (d, $J = 8.3$ Hz, 2 H), 8.47 (t, $J = 5.7$ Hz, 1 H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 14.1, 21.1, 37.3, 38.7, 40.2, 42.2, 57.4, 112.2, 124.4, 125.3, 126.1, 126.7, 127.2, 127.2, 127.5, 128.2, 128.4, 128.6, 129.1, 130.0, 134.4, 135.3, 138.7, 139.4, 145.6, 170.5, 176.8; MS calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{NaO}_4\text{S}$ [$\text{M} + \text{Na}$] $^+$: 575.1975, found 575.1967.

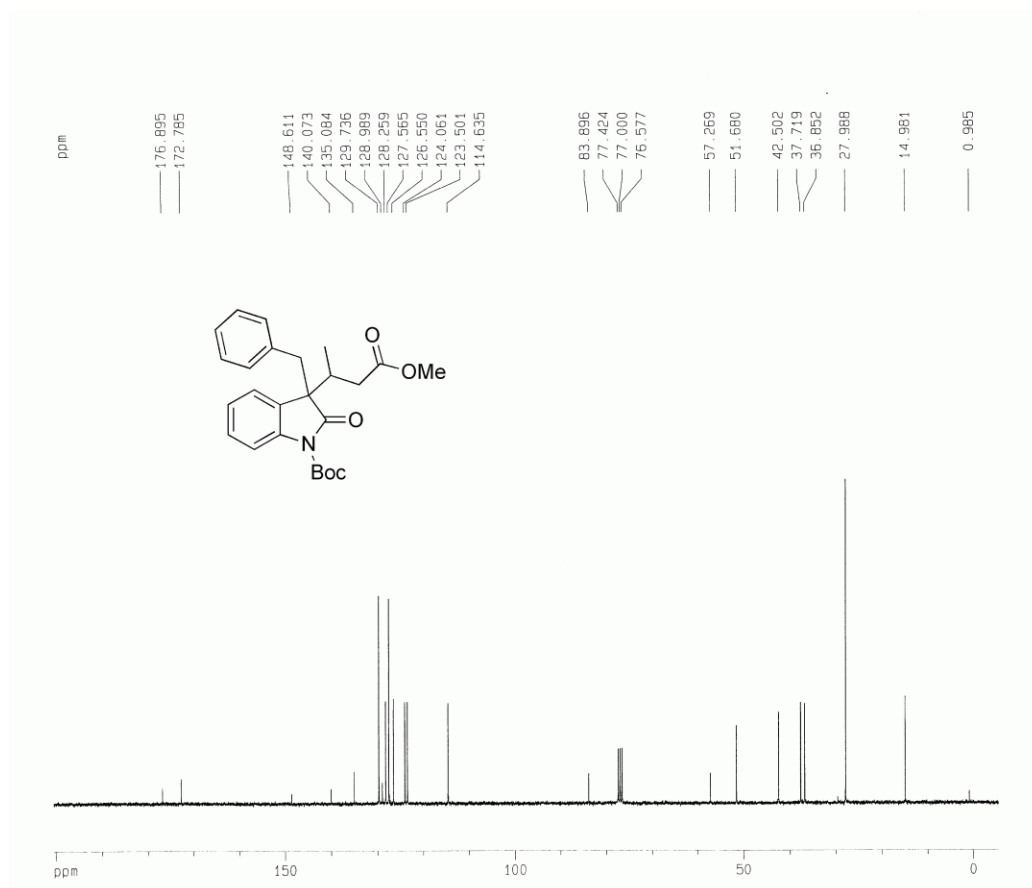
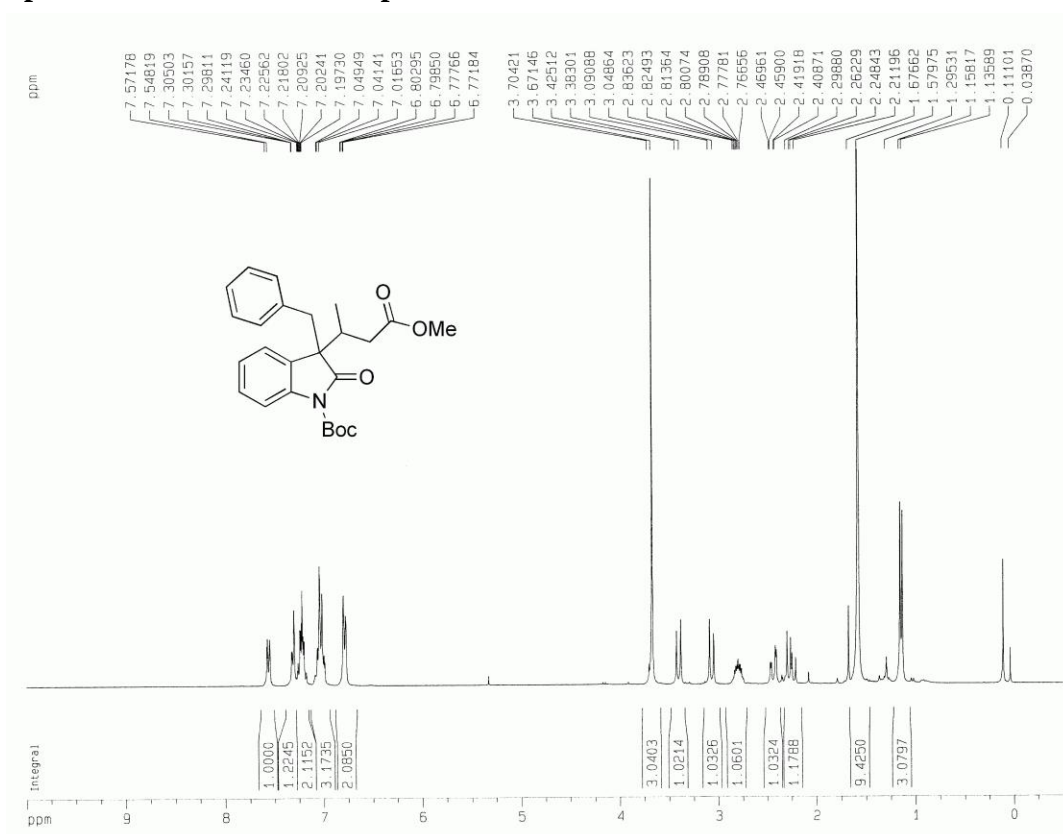


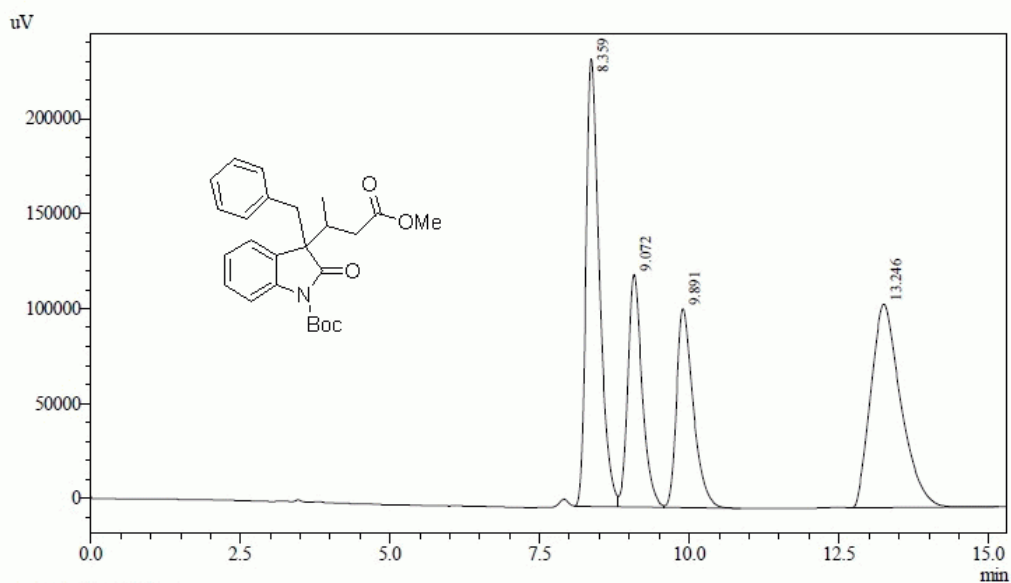
methyl 3-(3-benzyl-2-oxo-1-(phenylcarbamoyl)indolin-3-yl)butanoate (3xd) Colorless oil; 41.6 mg, 94% yield; 2.9:1 dr, 0%/35% ee; $[\alpha]_{\text{D}}^{20} = -4.3$ ($c = 1.0$, CHCl_3); The ee was determined by HPLC (Chiralpak OD-H column, $i\text{PrOH}$ /hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, major diastereomer: $t_{\text{minor}} = 6.1$ min, $t_{\text{major}} = 9.4$ min); ^1H NMR (300 MHz, CDCl_3) δ 1.10 (d, $J = 6.7$ Hz, 3 H), 2.34 (dd, $J = 10.9$ Hz, $J = 15.1$ Hz, 1 H), 2.50 (dd, $J = 3.2$ Hz, $J = 15.1$ Hz, 1 H), 2.78-2.87 (m, 1 H), 3.17 (d, $J = 12.9$ Hz, 1 H), 3.31 (d, $J = 12.9$ Hz, 1 H), 3.66 (s, 3 H), 6.74-6.76 (m, 2 H), 6.96-7.04 (m, 3 H), 7.14 (t, $J = 7.5$ Hz, 1 H), 7.22-7.29 (m, 2 H), 7.31-7.41 (m, 3 H), 7.56 (d, $J = 8.5$ Hz, 2 H), 8.08 (d, $J = 7.7$ Hz, 1 H), 10.65 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.0, 36.7, 38.0, 42.0, 51.7, 58.4, 116.3, 120.4, 123.3, 124.4, 124.6, 127.0, 127.9, 128.7, 128.7, 129.0, 129.5, 134.6, 137.0, 140.5, 148.8, 172.5, 181.6; MS calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$: 465.1785, found 465.1785.

References

- [1] For the preparation of 3-Mono Substituted Oxindoles (**1a-1x**), see: (a) F. Manoni and S. J. Connon, *Angew. Chem. Int. Ed.*, 2014, **53**, 2628; (b) A. Huang, J. J. Kodanko and L. E. Overman, *J. Am. Chem. Soc.*, 2004, **126**, 14043; (c) B. Tan, N. R. Candeias and C. F. Barbas, III, *J. Am. Chem. Soc.*, 2011, **133**, 4672; (d) Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura and M. Sodeoka, *J. Am. Chem. Soc.*, 2005, **127**, 10164; (e) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru and S. Kanemasa, *J. Am. Chem. Soc.*, 2006, **128**, 16488; (f) S.-W. Duan, J. An, J.-R. Chen and W.-J. Xiao, *Org. Lett.*, 2011, **13**, 2290; (g) L. Cheng, L. Liu, D. Wang and Y.-J. Chen, *Org. Lett.*, 2009, **11**, 3874.
- [2] For the preparation of α,β -unsaturated acyl phosphonates (**2a-2h**), see: (1) D. A. Evans, K. A. Scheidt, K. R. Fandrick, H. W. Lam and J. Wu, *J. Am. Chem. Soc.*, 2003, **125**, 10780; (2) D. A. Evans, J. S. Johnson and E. J. Olhava, *J. Am. Chem. Soc.*, 2000, **122**, 1635. (3) P. Bachu and T. Akiyama, *Chem. Commun.*, 2010, **46**, 4112; (4) C. Allais, F. Liéty-Muller, J. Rodriguez and T. Constantieux, *Eur. J. Org. Chem.*, **2013**, 4131; (5) C.-K. Pei, Y. Jiang, Y. Wei and M. Shi, *Angew. Chem. Int. Ed.*, 2012, **51**, 11328; (6) D. Sinha, S. Perera and J. C. Zhao, *Chem. Eur. J.*, 2013, **19**, 6976; (7) T. Liu, Y.-M. Wang, G.-P. Wu, H.-B. Song, Z.-H. Zhou and C.-C. Tang, *J. Org. Chem.*, 2011, **76**, 4119; (8) F. Palacios, J. Vicario, A. Maliszewska and D. Aparicio, *J. Org. Chem.*, 2007, **72**, 2682.

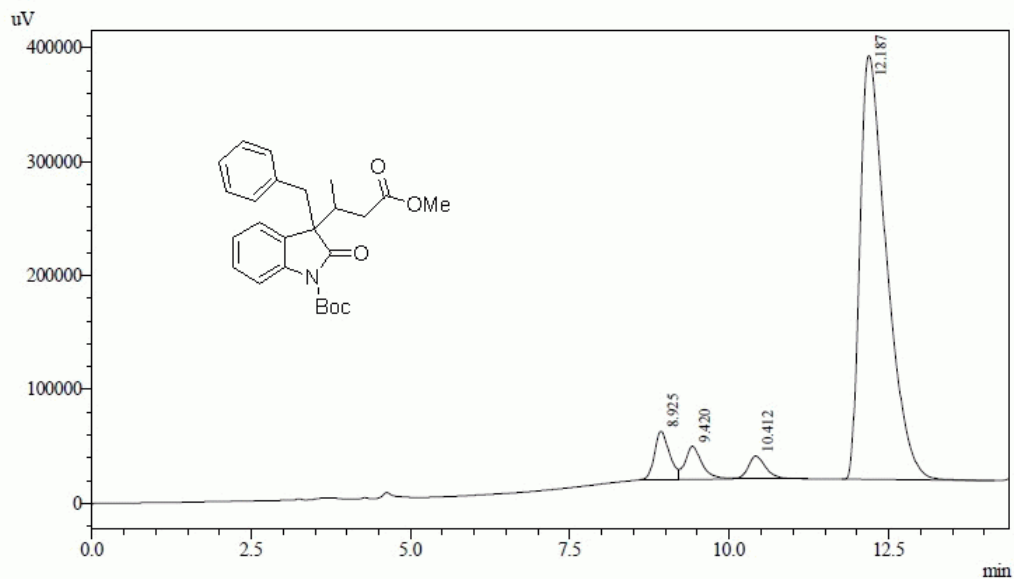
Copies of NMR and HPLC Spectra for 3,3-Disubstituted Oxindoles 3





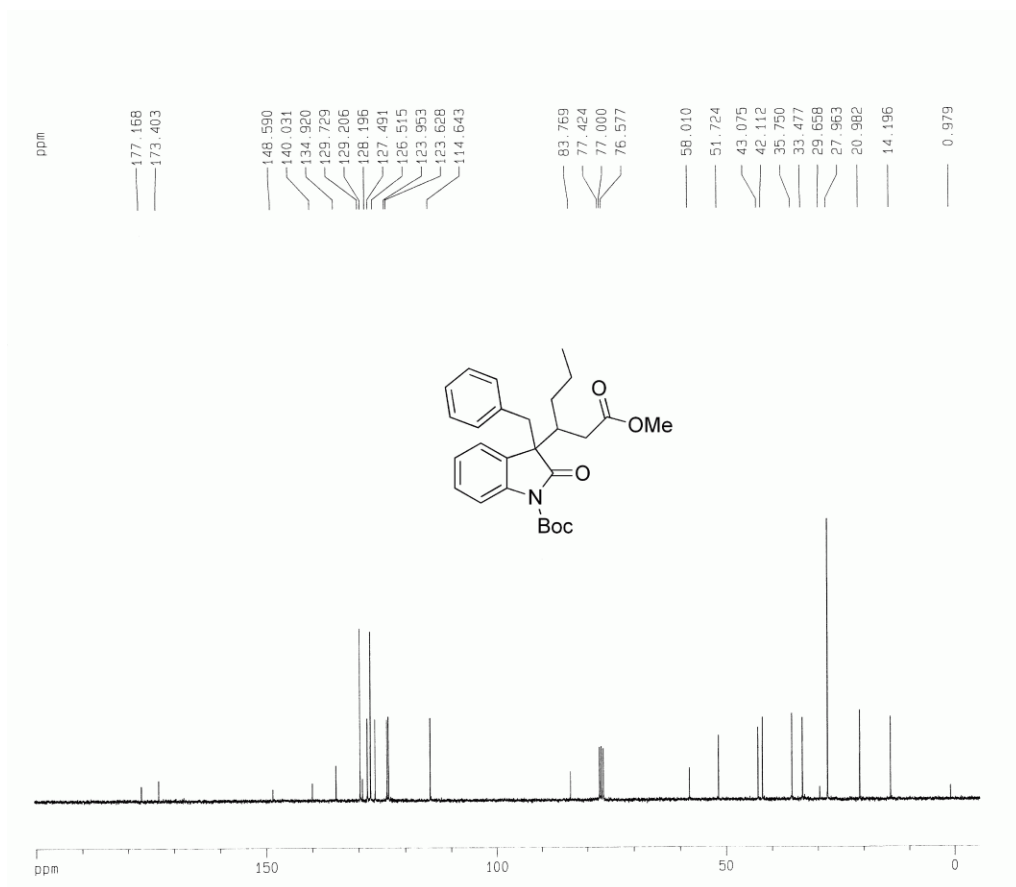
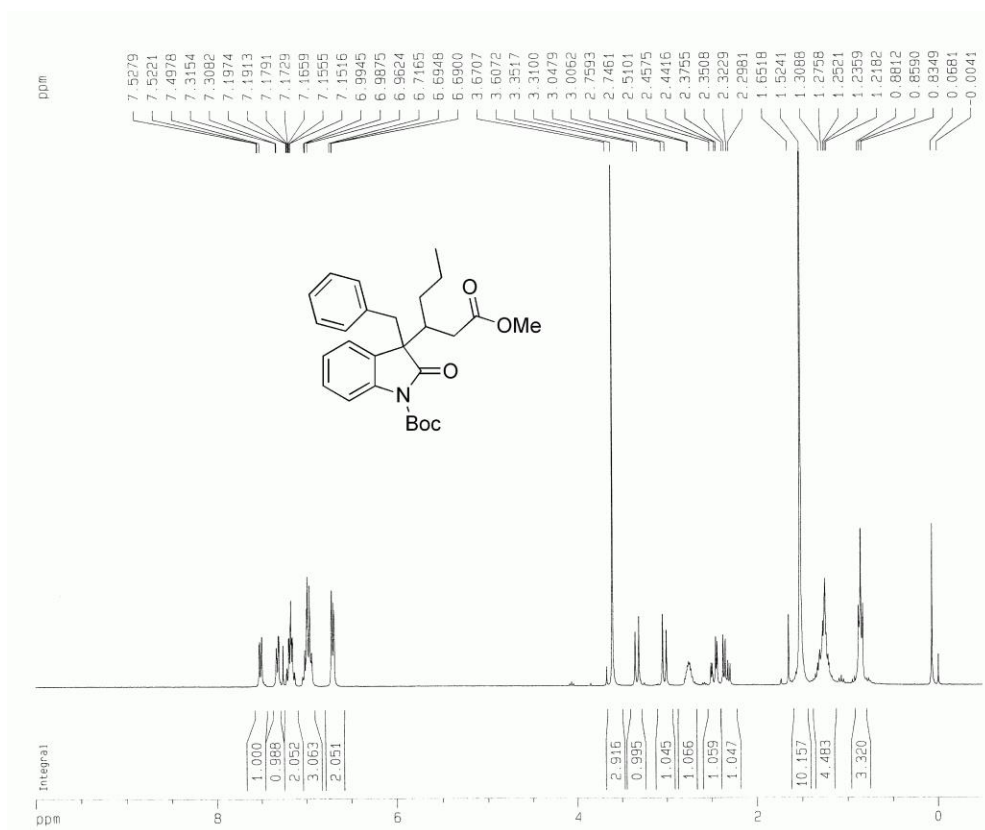
Detector A Ch1 254nm

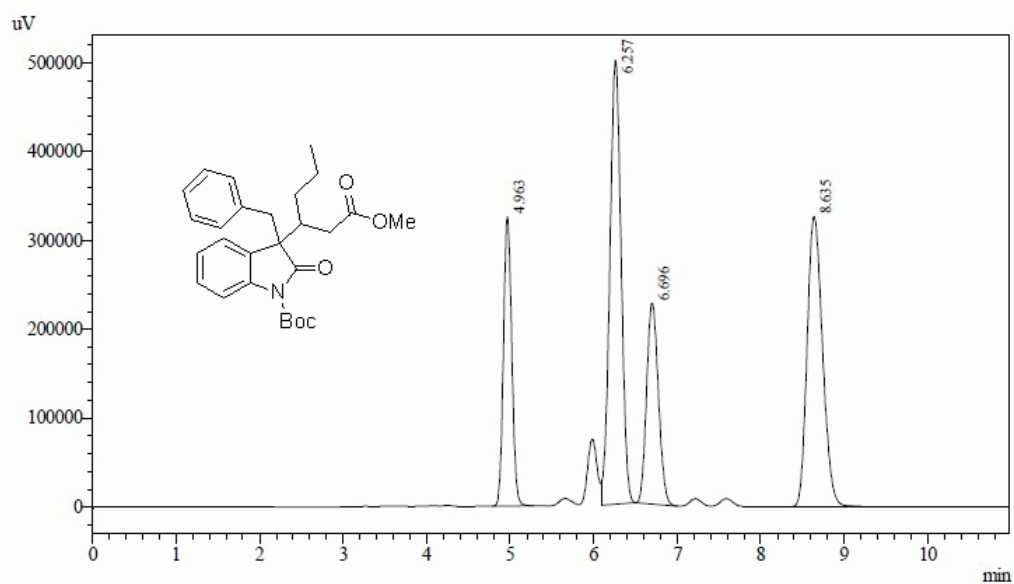
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2	9.072	2024140	122421	17.699	21.503
3	9.891	2026059	104627	17.716	18.377
4	13.246	3725473	106977	32.576	18.790
Total		11436422	569332	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.925	692550	42586	5.554	9.175
2	9.420	541237	29025	4.340	6.253
3	10.412	395057	20272	3.168	4.367
4	12.187	10841052	372297	86.938	80.205
Total		12469896	464181	100.000	100.000

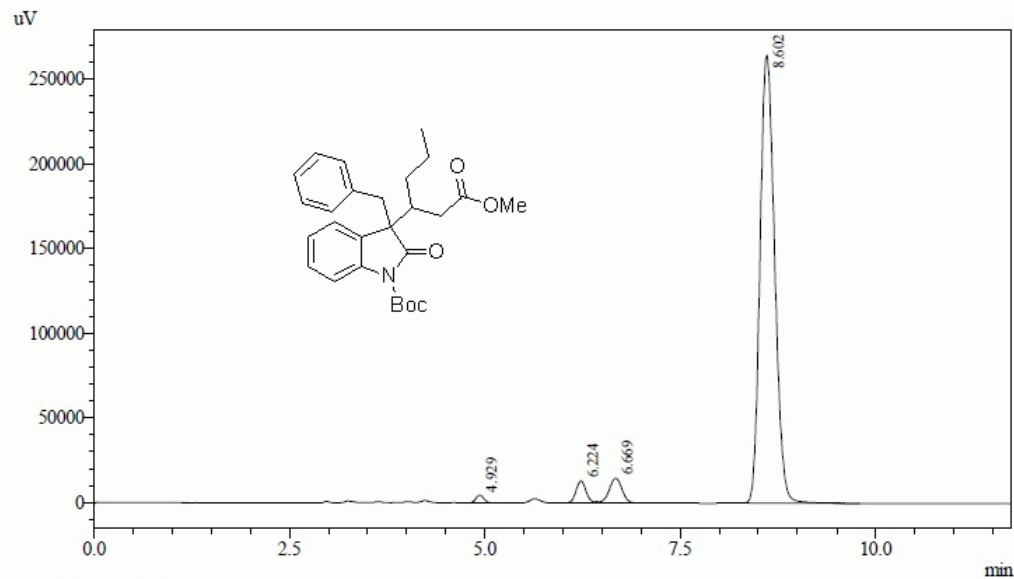




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

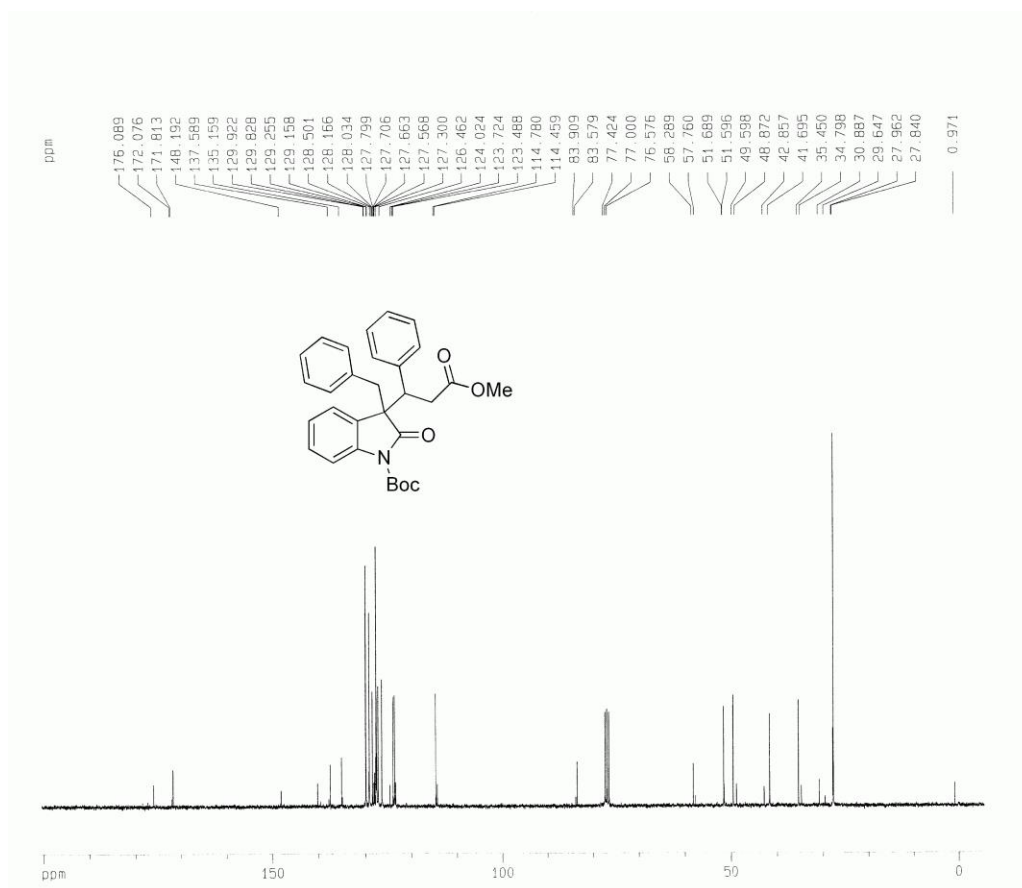
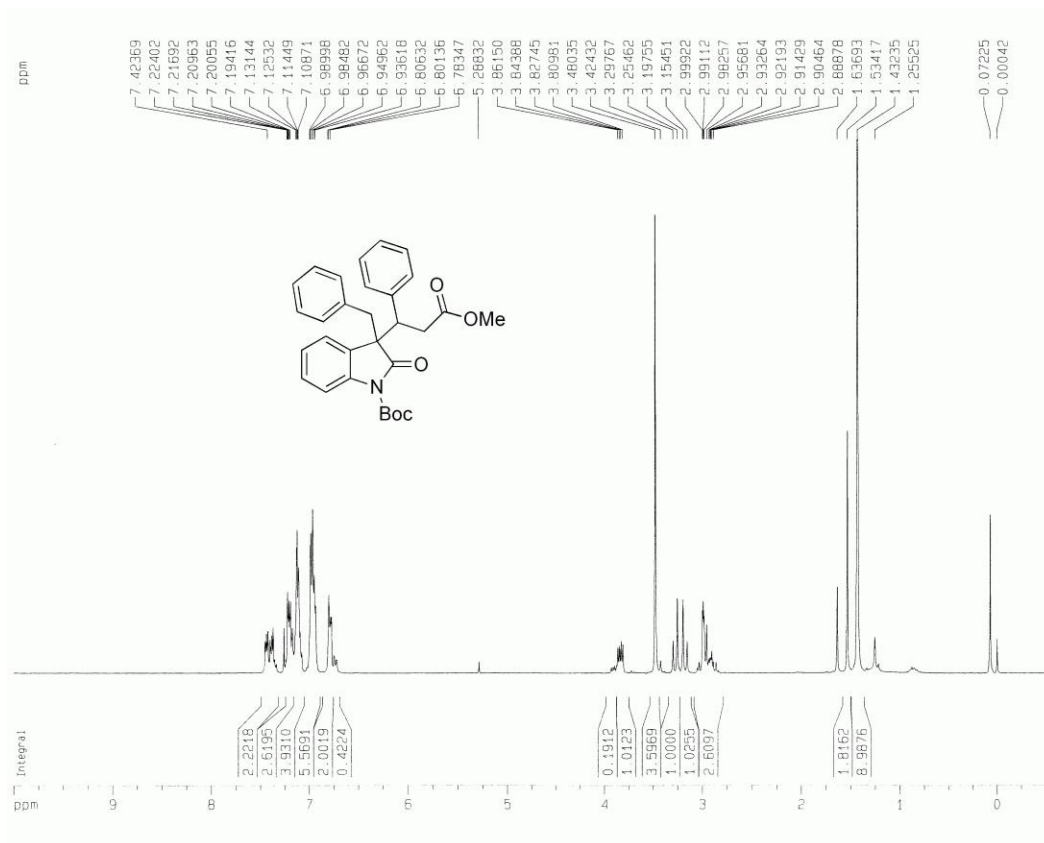
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1	4.963	2251151	326027	16.866	23.647
2	6.257	4675575	499880	35.030	36.257
3	6.696	2223519	226359	16.659	16.418
4	8.635	4197245	326450	31.446	23.678
Total		13347491	1378716	100.000	100.000

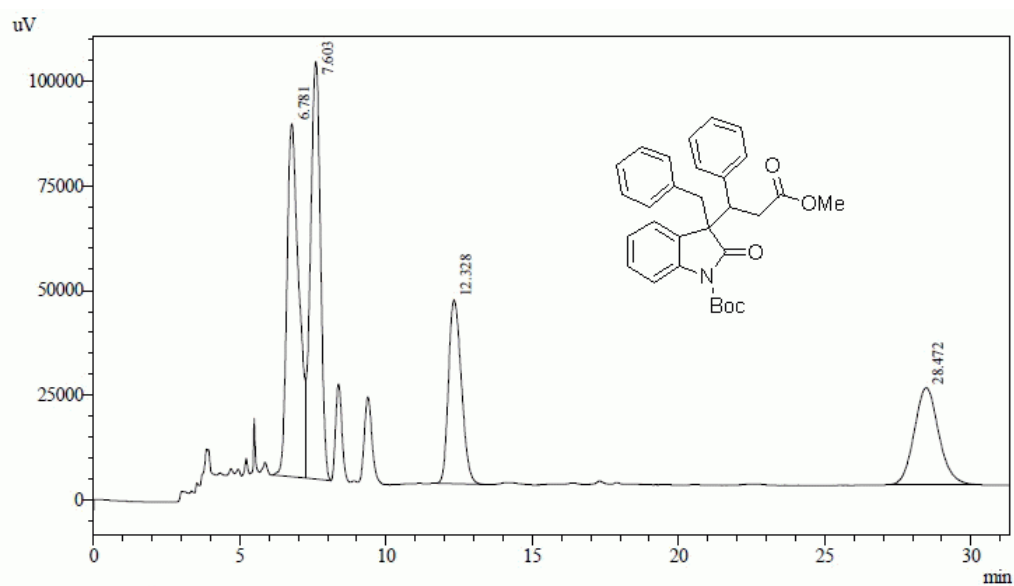


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.929	34368	4701	0.915	1.582
2	6.224	117393	13012	3.125	4.378
3	6.669	168348	14752	4.481	4.964
4	8.602	3436697	264745	91.479	89.077
Total		3756805	297210	100.000	100.000

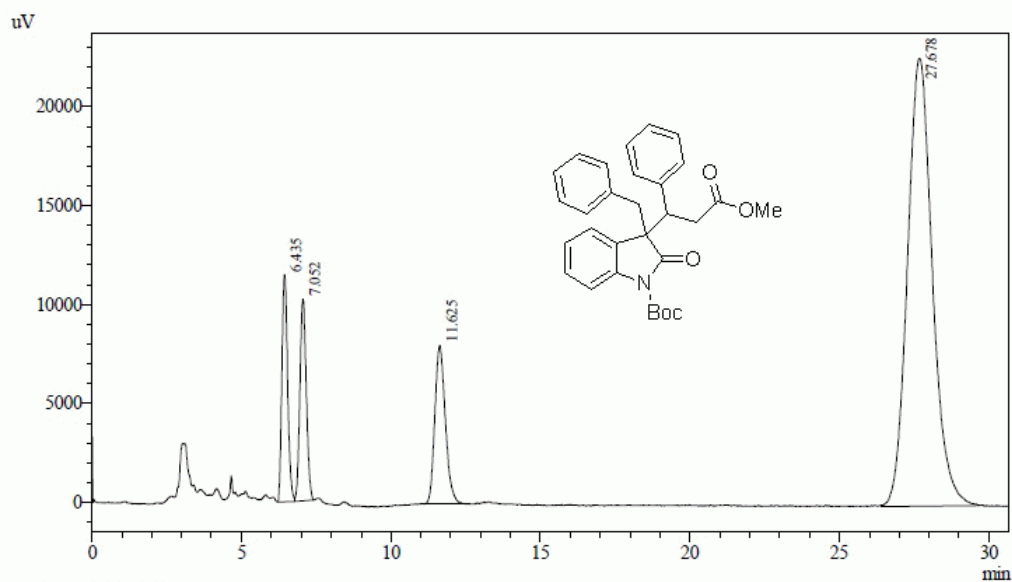




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

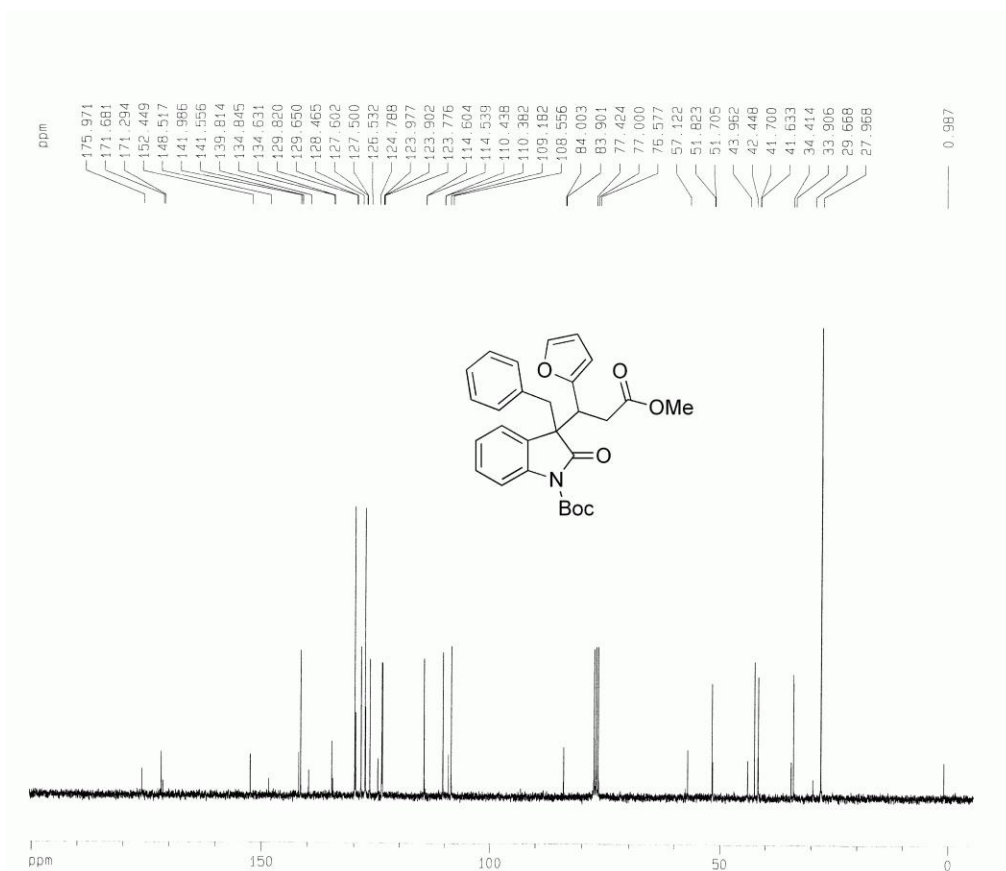
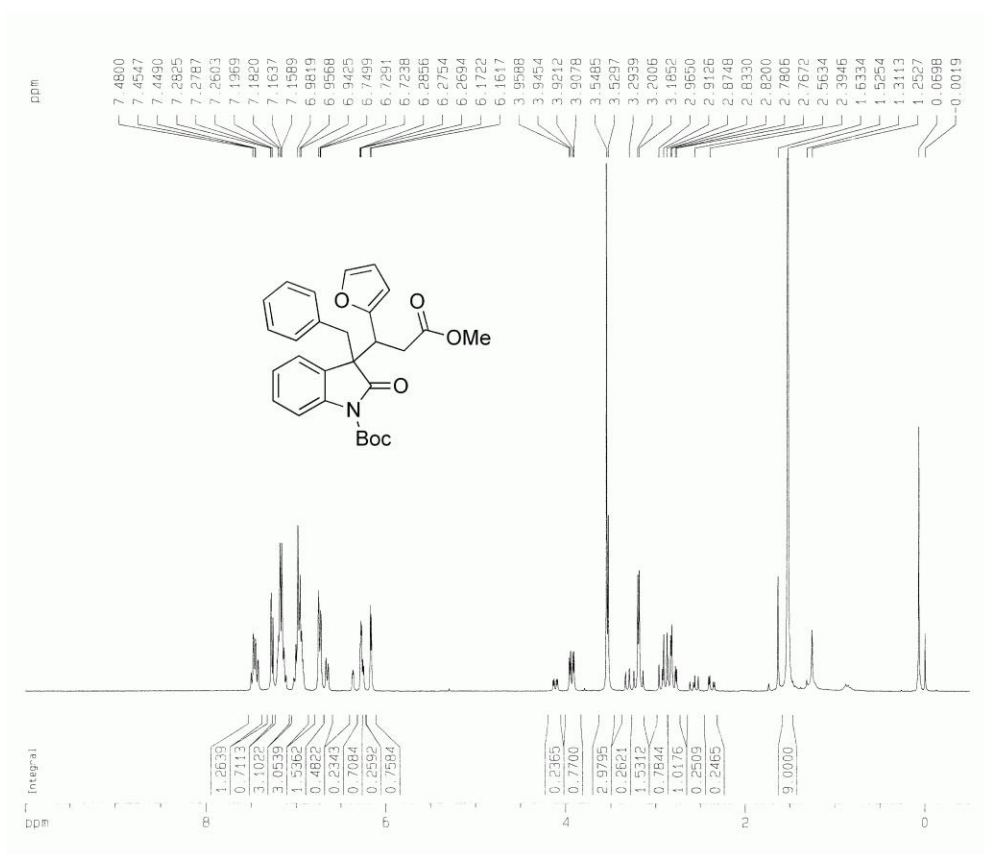
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.781	2393536	84416	31.995	33.569
2	7.603	2382593	99821	31.849	39.695
3	12.328	1351097	44025	18.061	17.507
4	28.472	1353694	23206	18.095	9.228
Total		7480919	251467	100.000	100.000

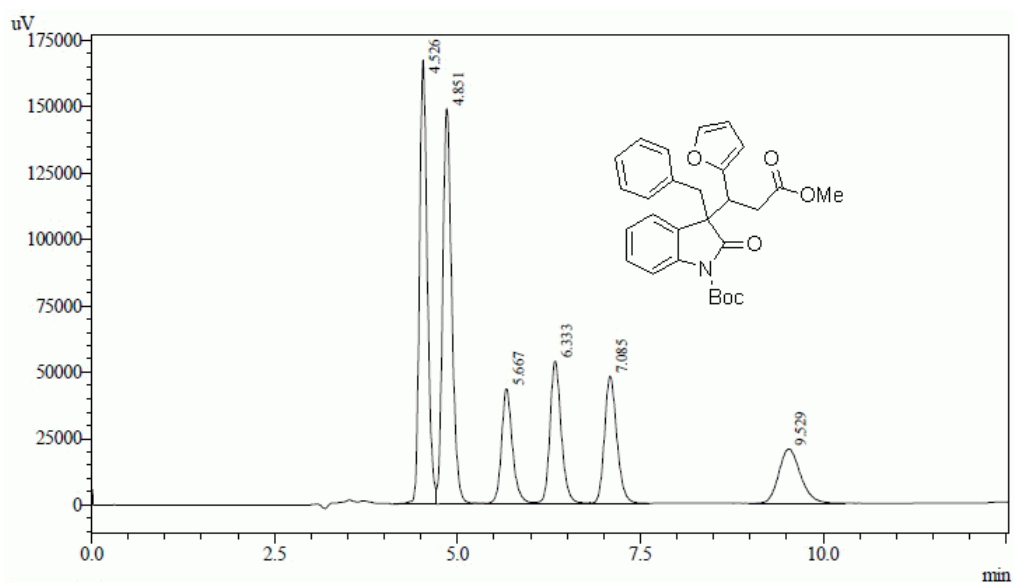


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.435	152172	11497	8.406	21.966
2	7.052	152262	10199	8.411	19.485
3	11.625	196940	8020	10.880	15.322
4	27.678	1308802	22626	72.302	43.227
Total		1810176	52342	100.000	100.000

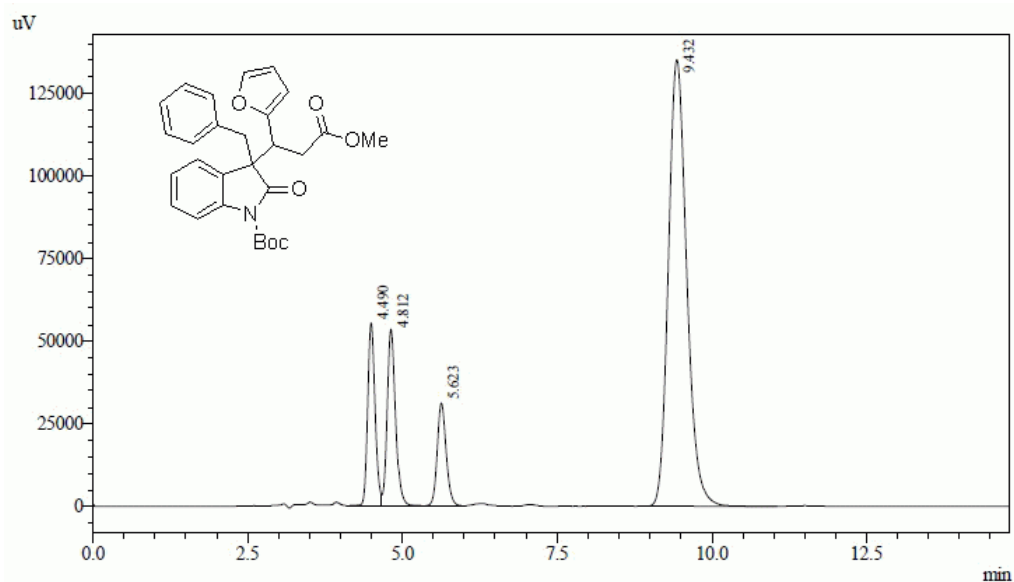




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

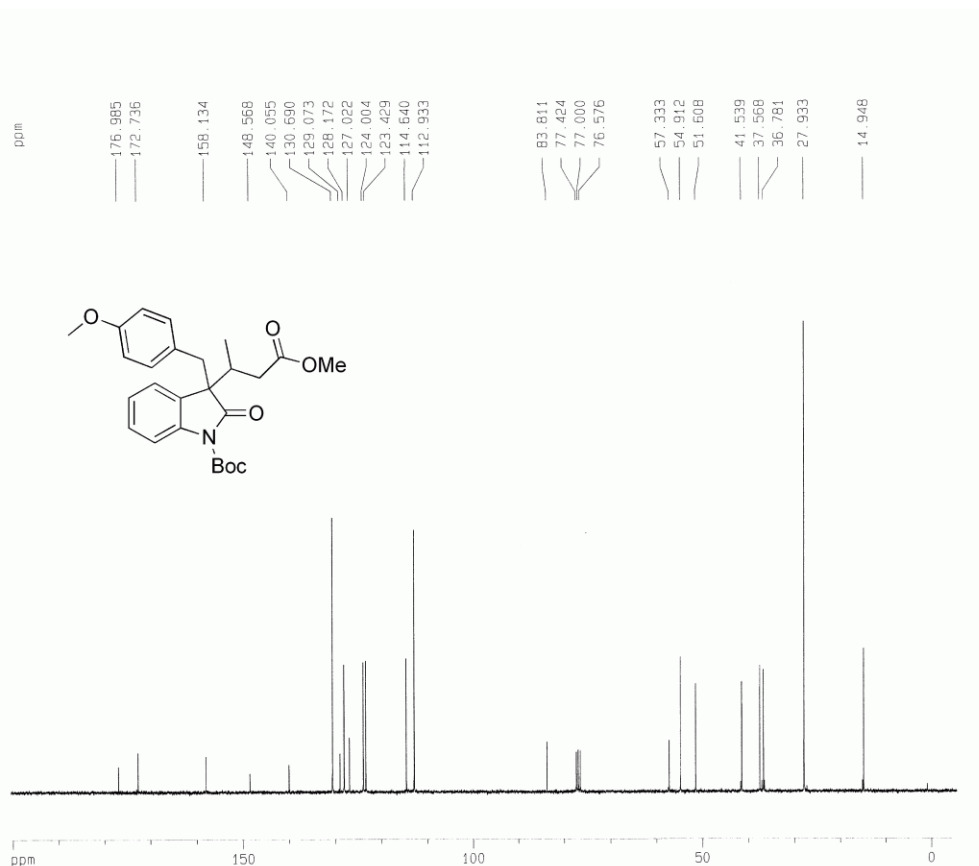
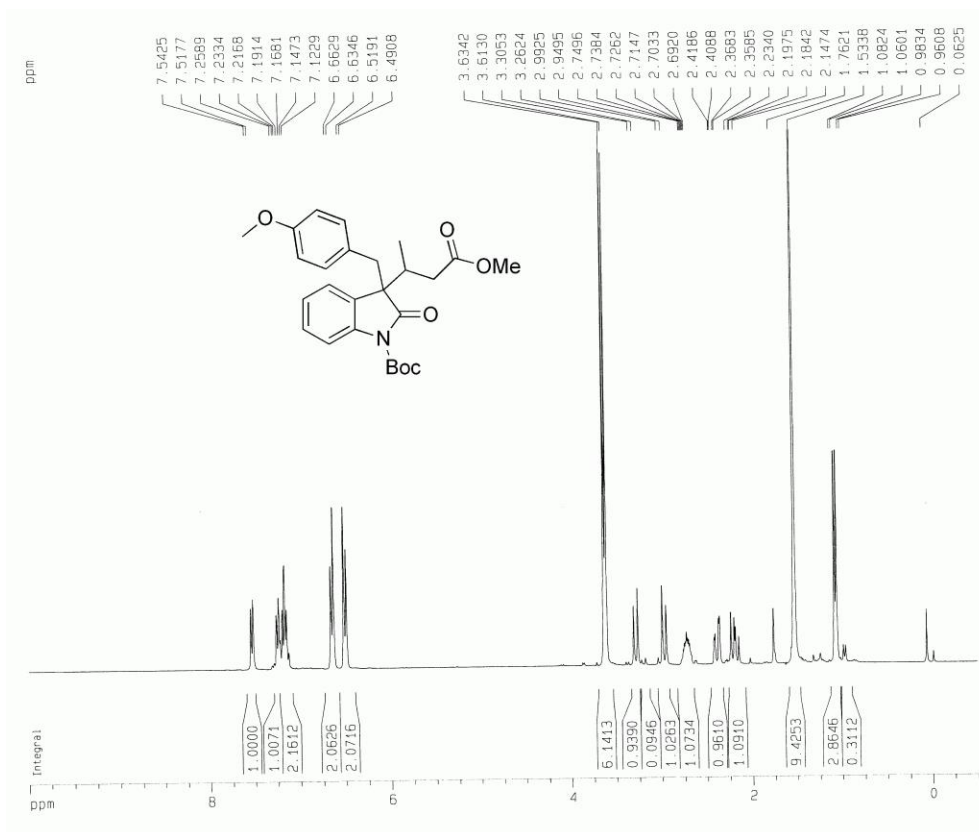
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.526	1257182	167122	27.580	34.736
2	4.851	1290279	148901	28.306	30.949
3	5.667	450581	43204	9.885	8.980
4	6.333	574961	53594	12.613	11.139
5	7.085	562522	47828	12.340	9.941
6	9.529	422861	20469	9.277	4.254
Total		4558387	481118	100.000	100.000

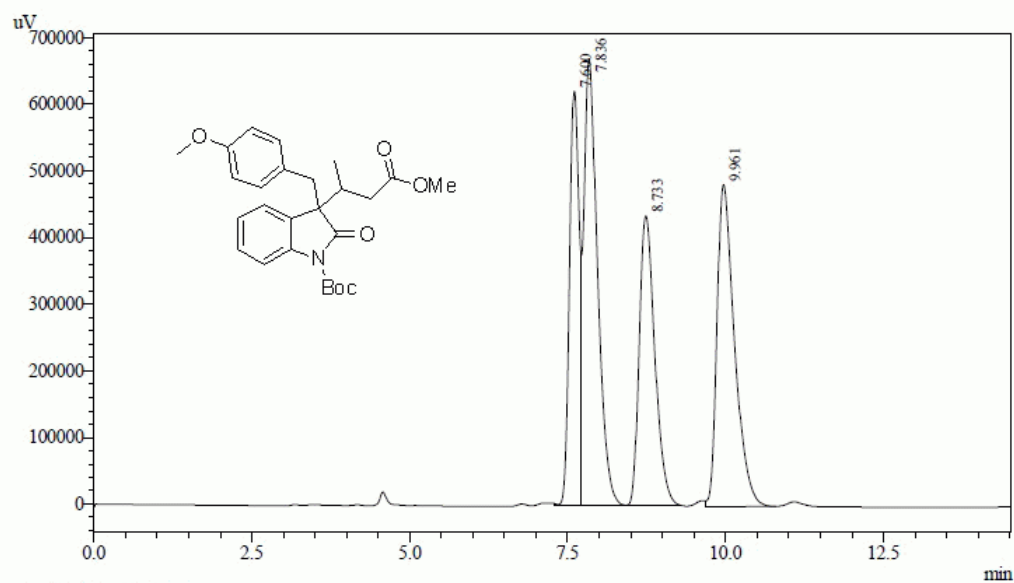


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.490	463908	55420	11.406	20.134
2	4.812	497445	53495	12.231	19.435
3	5.623	314837	31152	7.741	11.318
4	9.432	2791042	135185	68.623	49.113
Total		4067232	275251	100.000	100.000

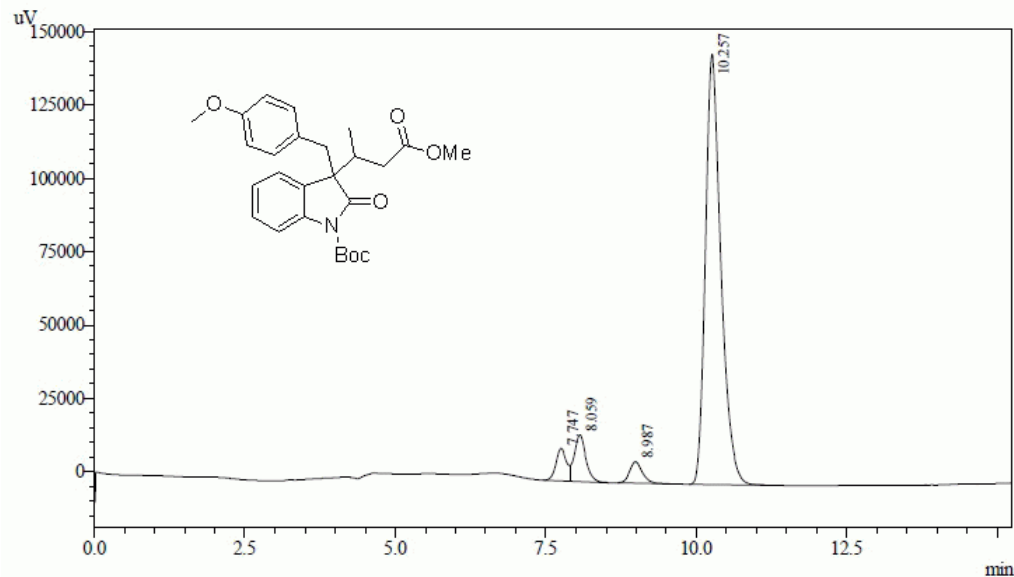




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

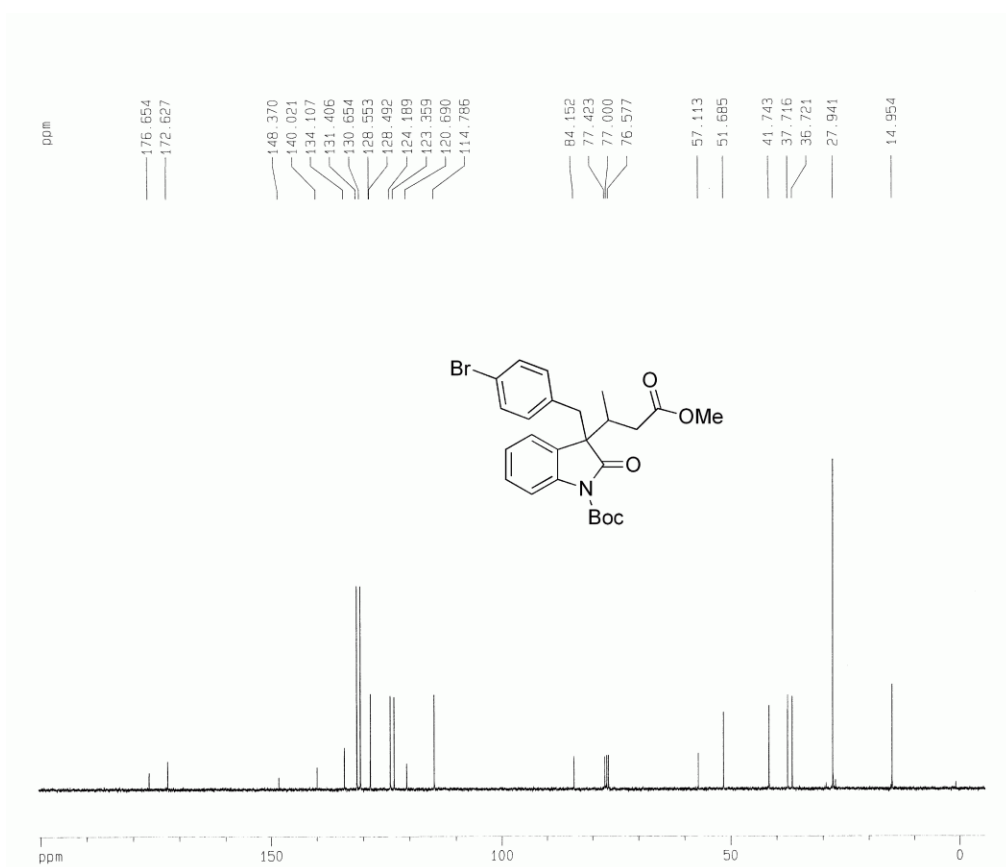
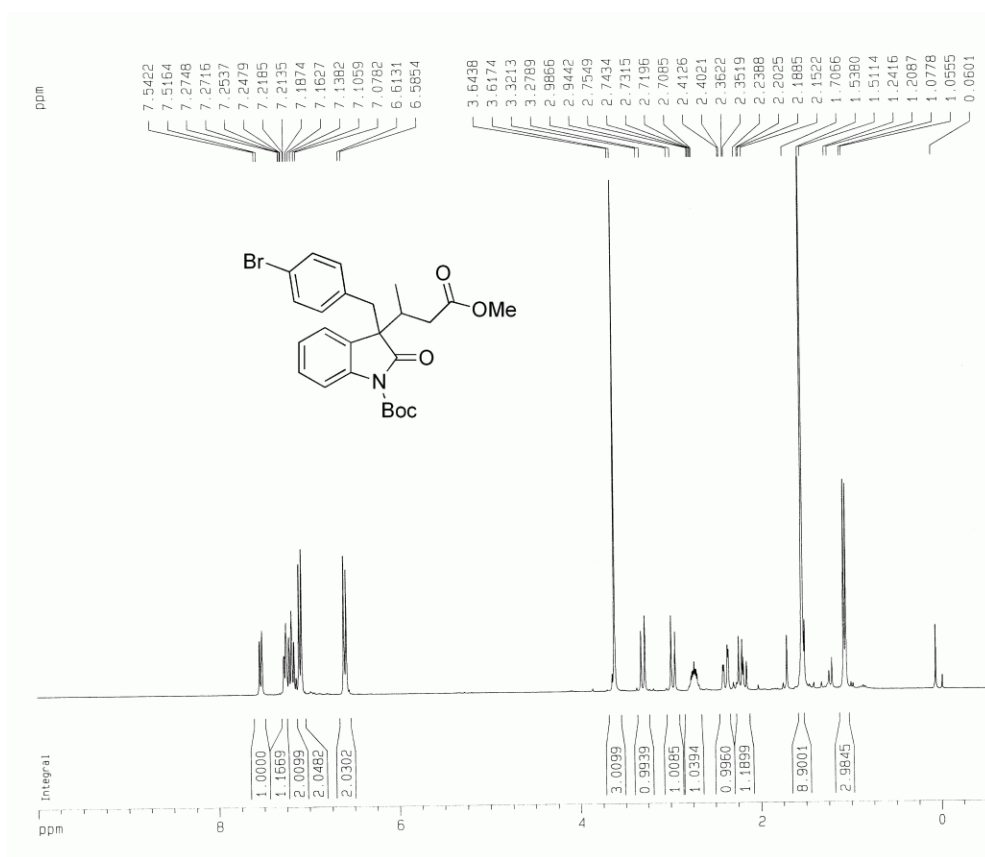
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.600	6621974	621606	19.786	28.129
2	7.836	10077659	670086	30.111	30.323
3	8.733	7474739	434589	22.334	19.666
4	9.961	9293555	483552	27.769	21.882
Total		33467927	2209834	100.000	100.000

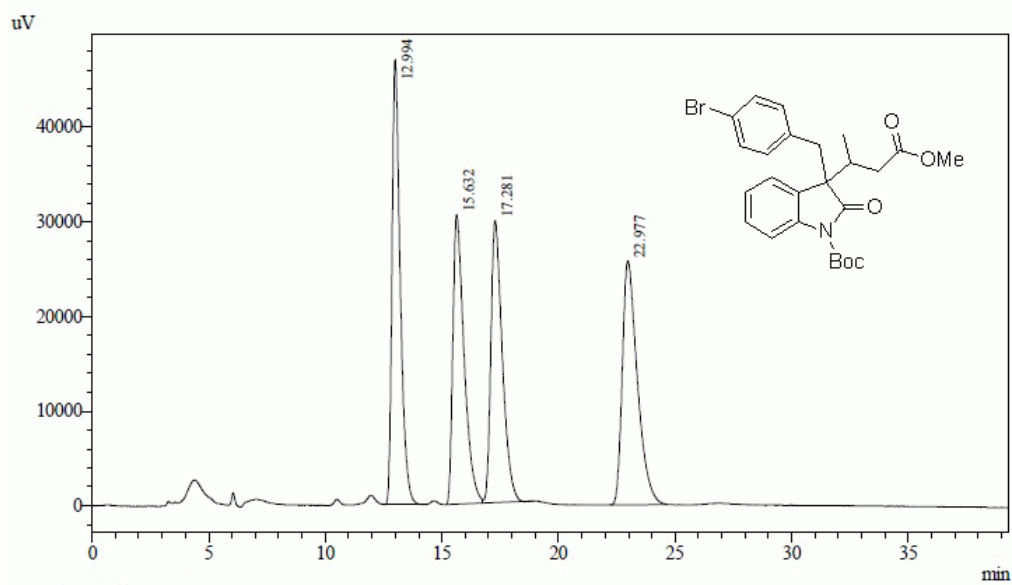


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.747	136180	11094	4.389	6.132
2	8.059	213239	15912	6.873	8.795
3	8.987	106706	7275	3.439	4.022
4	10.257	2646439	146629	85.298	81.051
Total		3102565	180910	100.000	100.000

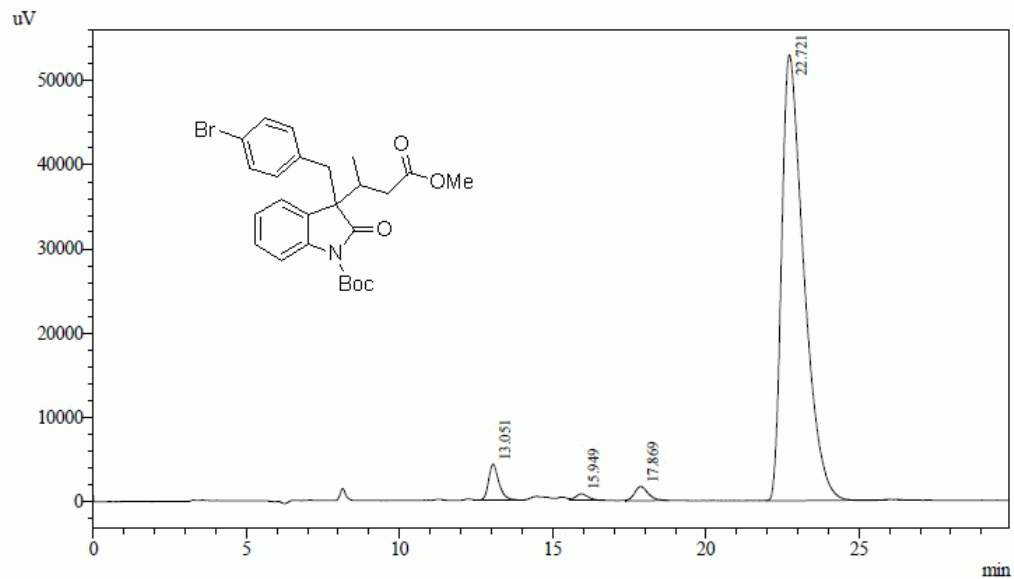




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

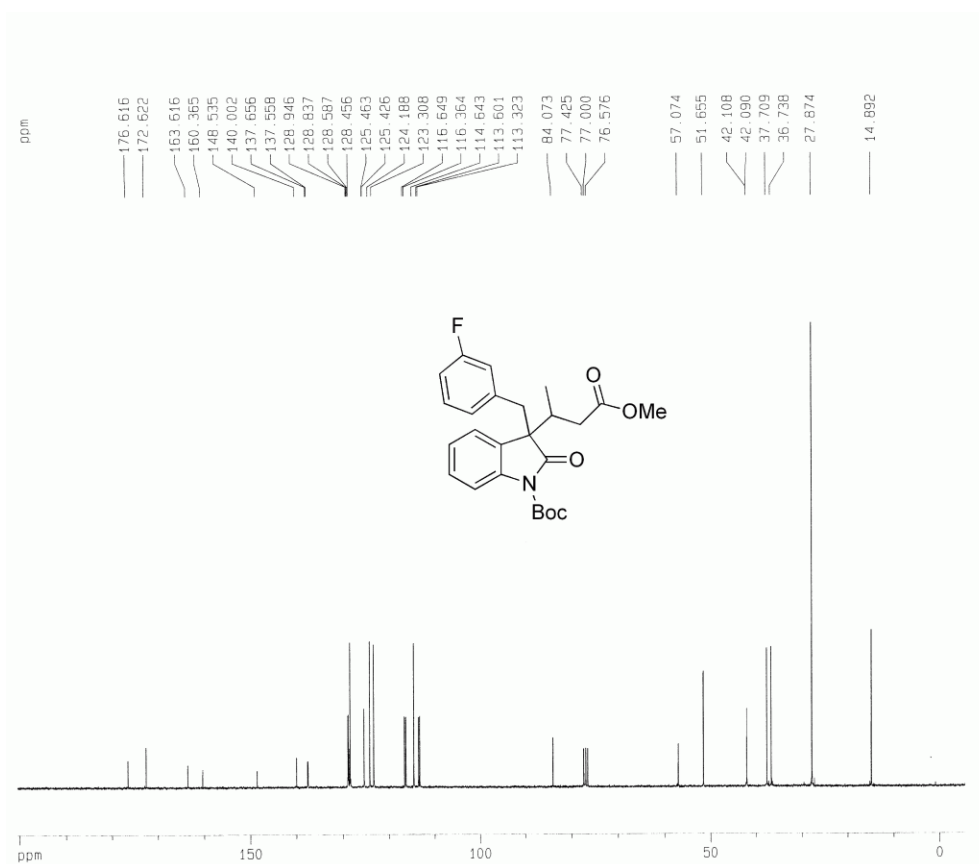
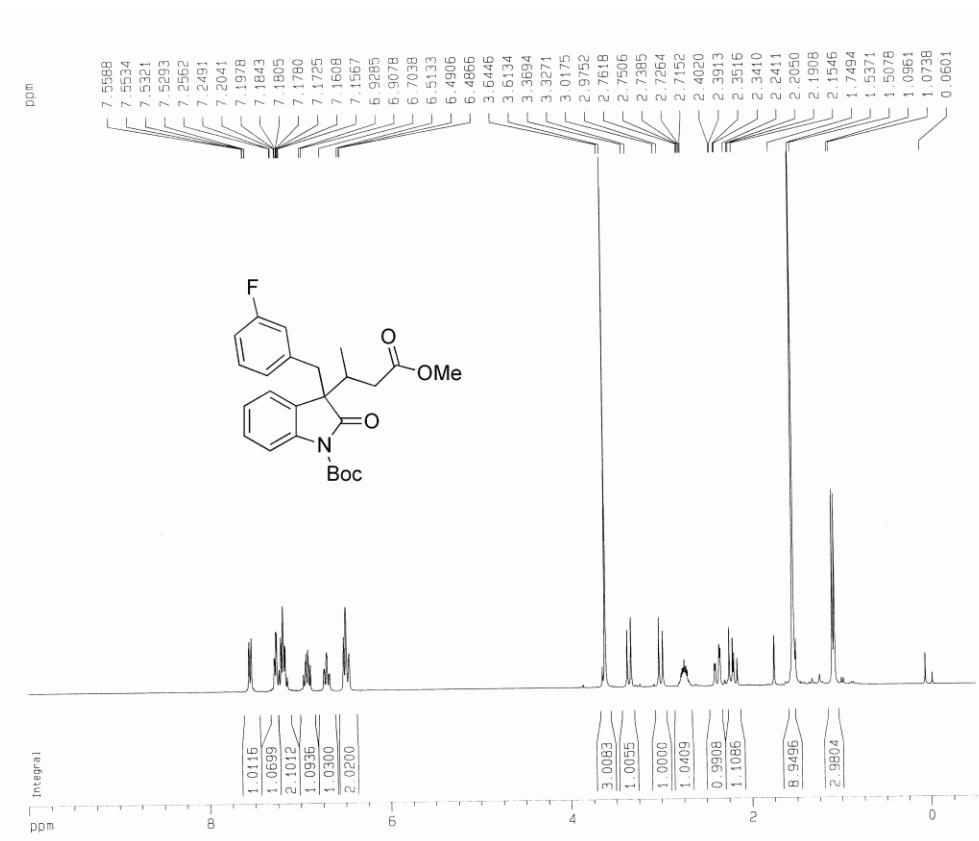
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.994	1148857	47065	26.407	35.314
2	15.632	1028358	30613	23.637	22.969
3	17.281	1016003	29824	23.353	22.378
4	22.977	1157341	25774	26.602	19.339
Total		4350559	133276	100.000	100.000

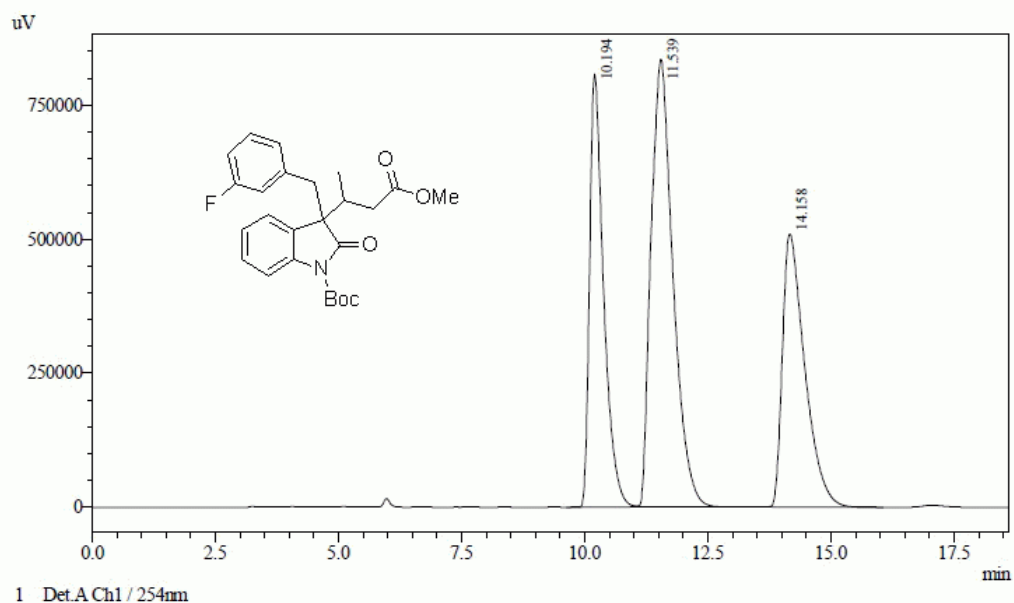


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

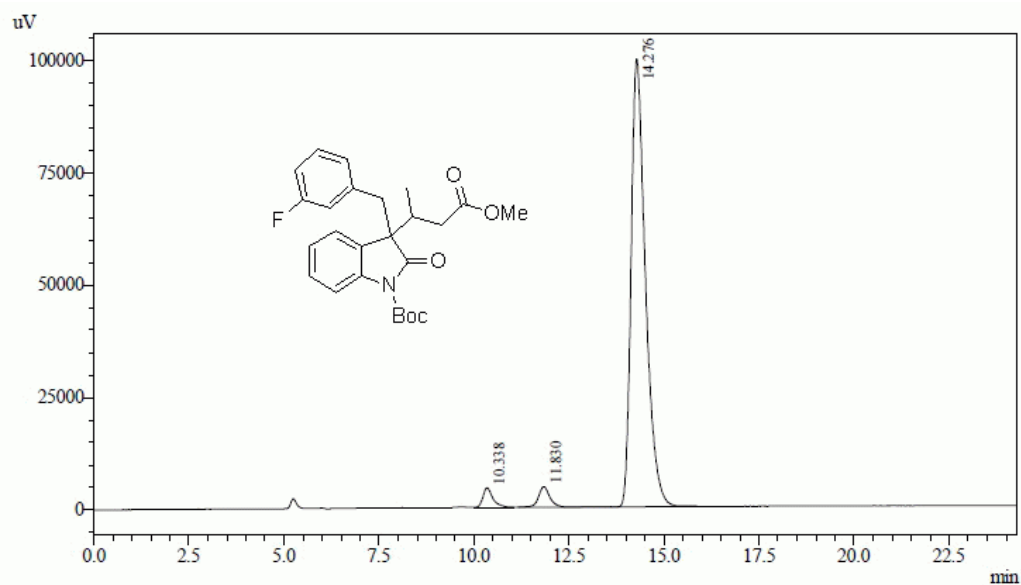
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.051	98066	4275	3.481	7.165
2	15.949	23330	778	0.828	1.304
3	17.869	51865	1690	1.841	2.832
4	22.721	2643666	52919	93.849	88.698
Total		2816928	59661	100.000	100.000





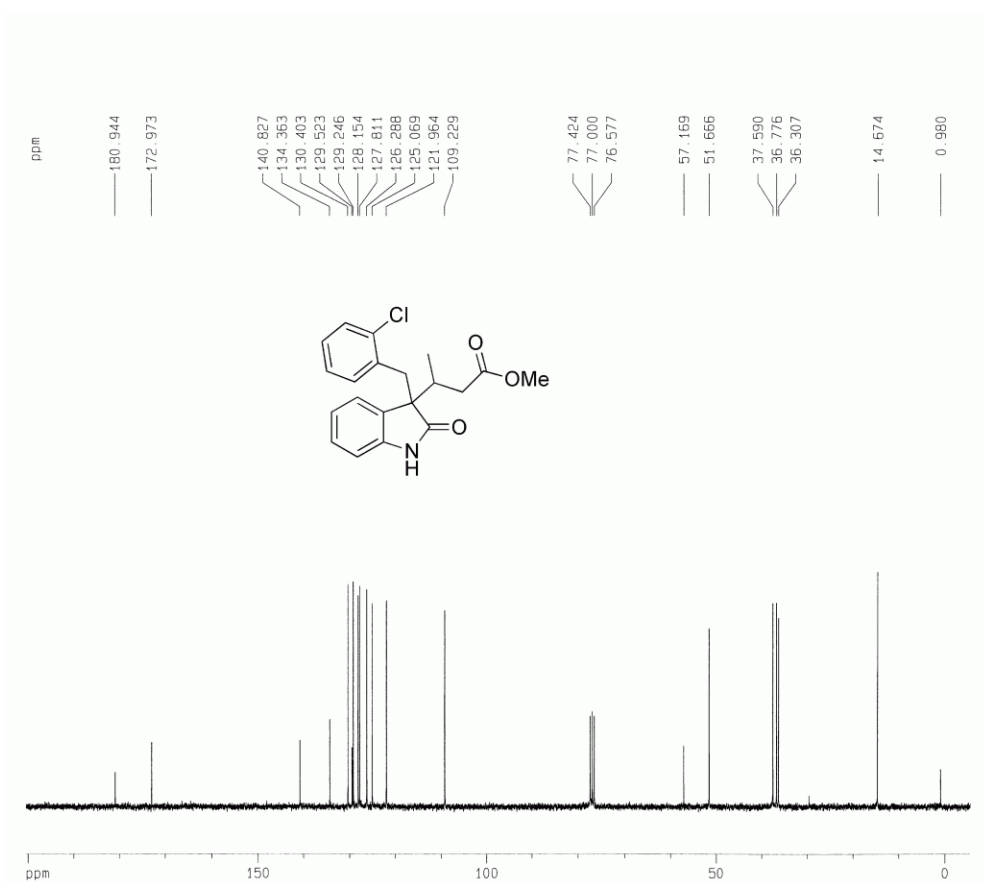
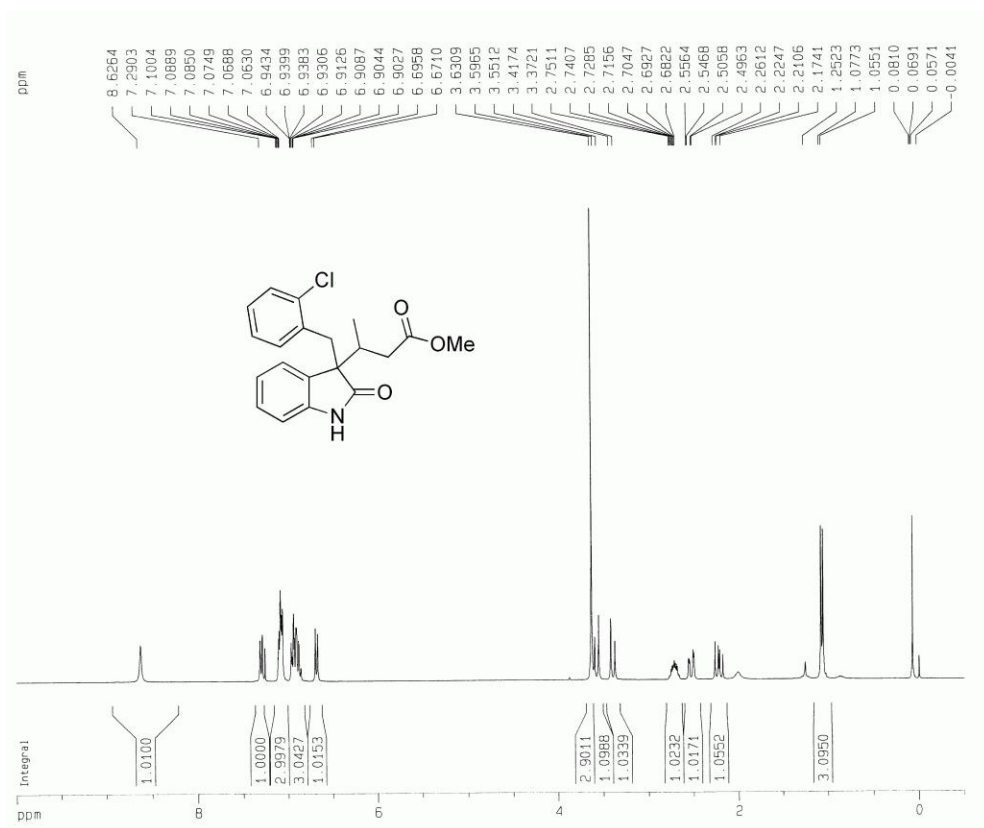
Detector A Ch1 254nm

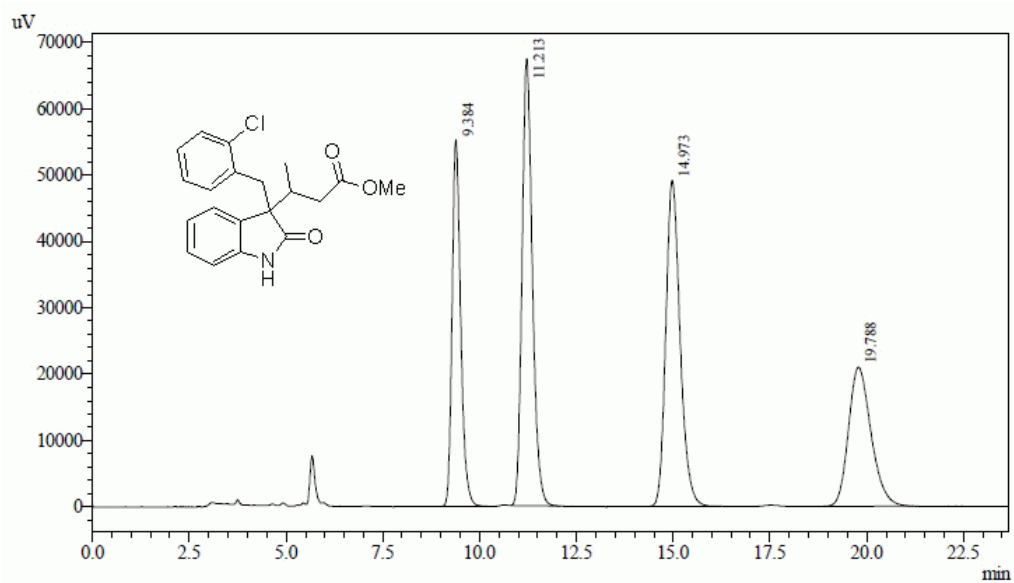
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.194	16005662	807404	27.654	37.517
2	11.539	25836862	835323	44.640	38.814
3	14.158	16036370	509380	27.707	23.669
Total		57878894	2152107	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.338	79182	4353	2.848	4.013
2	11.830	91991	4560	3.309	4.204
3	14.276	2608710	99561	93.842	91.783
Total		2779882	108474	100.000	100.000

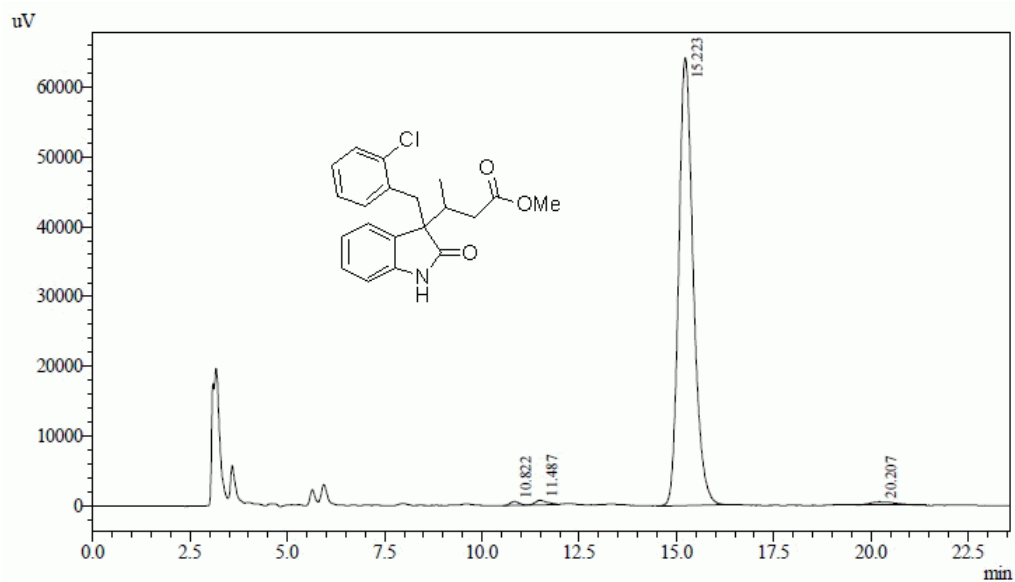




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

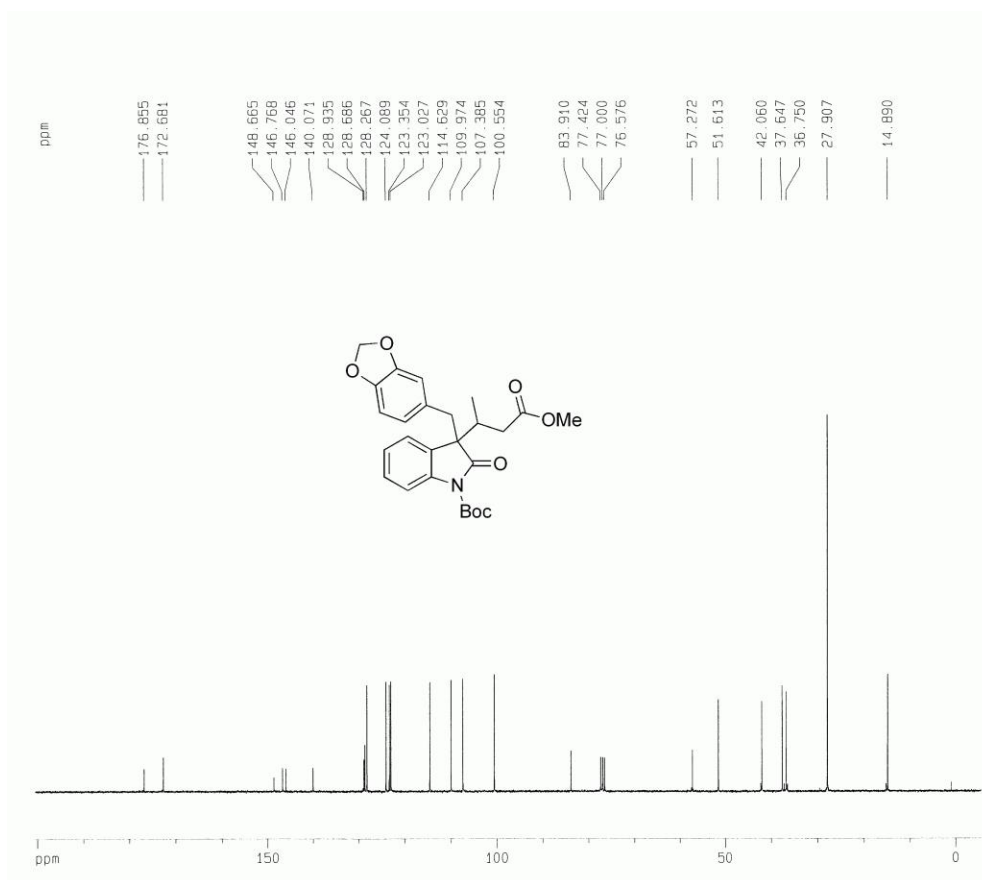
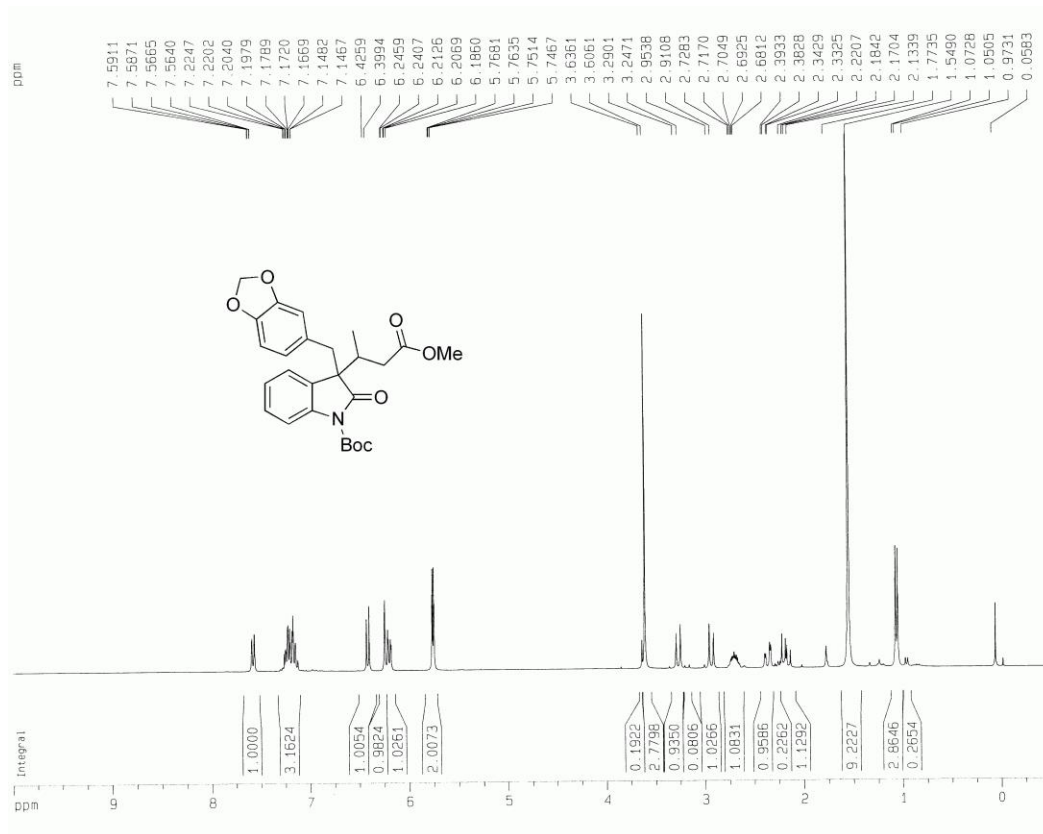
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.384	853539	55313	20.250	28.681
2	11.213	1247675	67383	29.600	34.940
3	14.973	1259706	49179	29.886	25.500
4	19.788	854163	20980	20.264	10.879
Total		4215083	192854	100.000	100.000

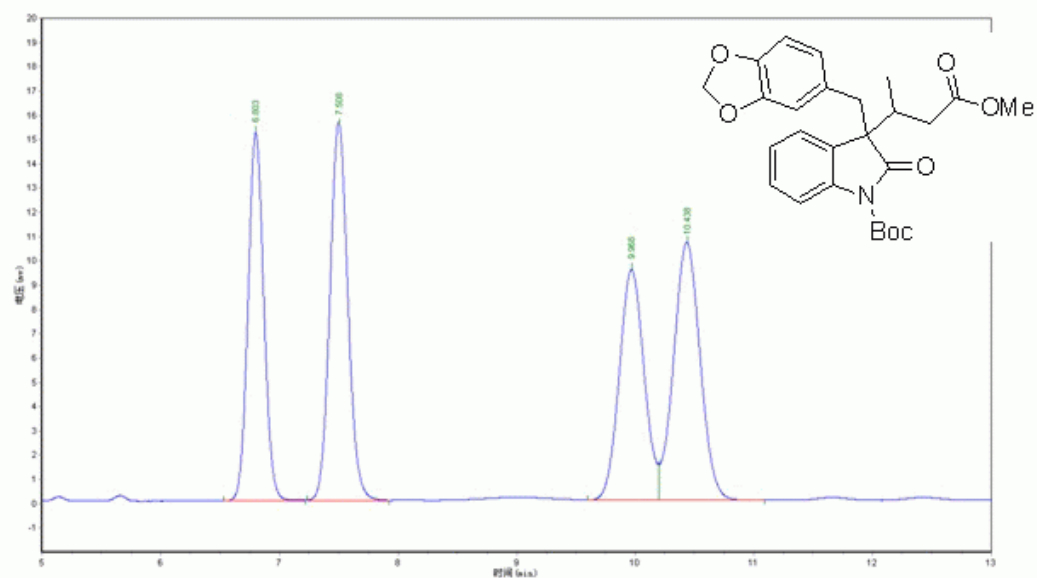


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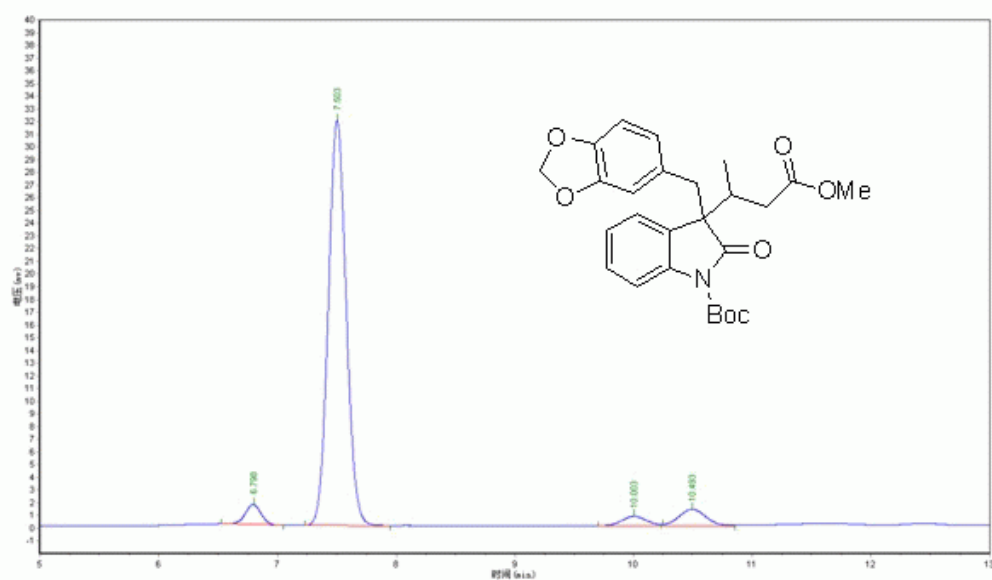
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.822	9003	560	0.525	0.850
2	11.487	14666	676	0.856	1.027
3	15.223	1668838	64102	97.353	97.412
4	20.207	21714	467	1.267	0.710
Total		1714221	65805	100.000	100.000

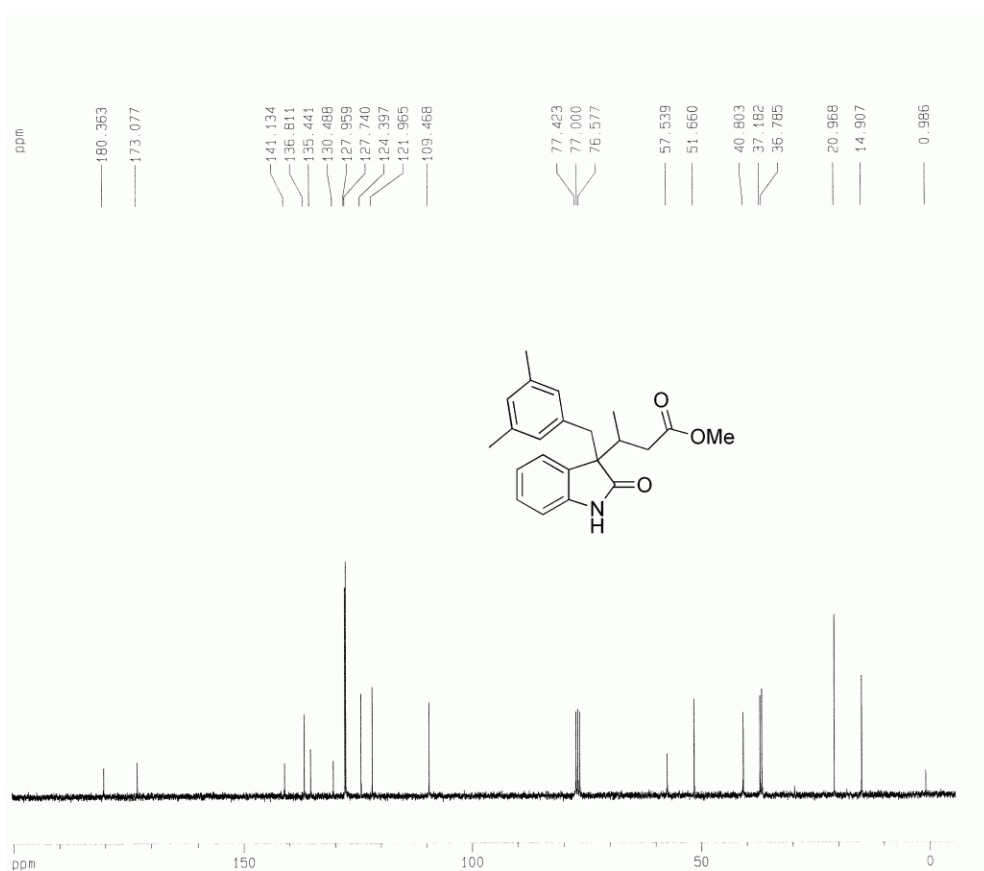
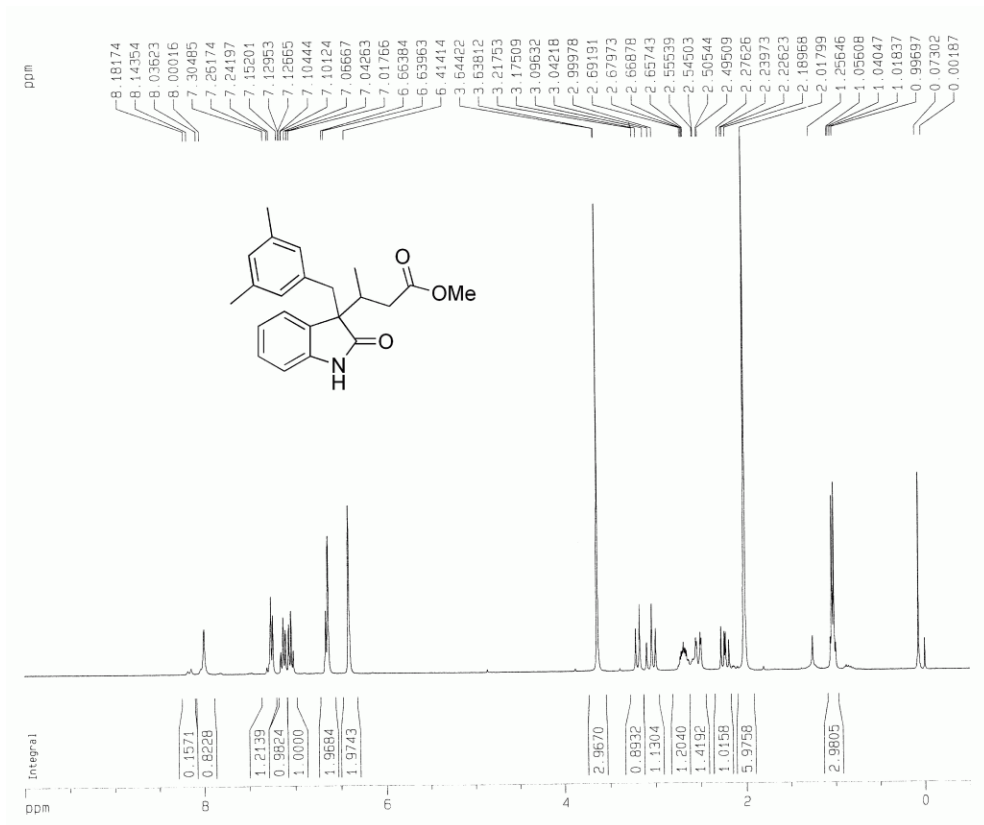


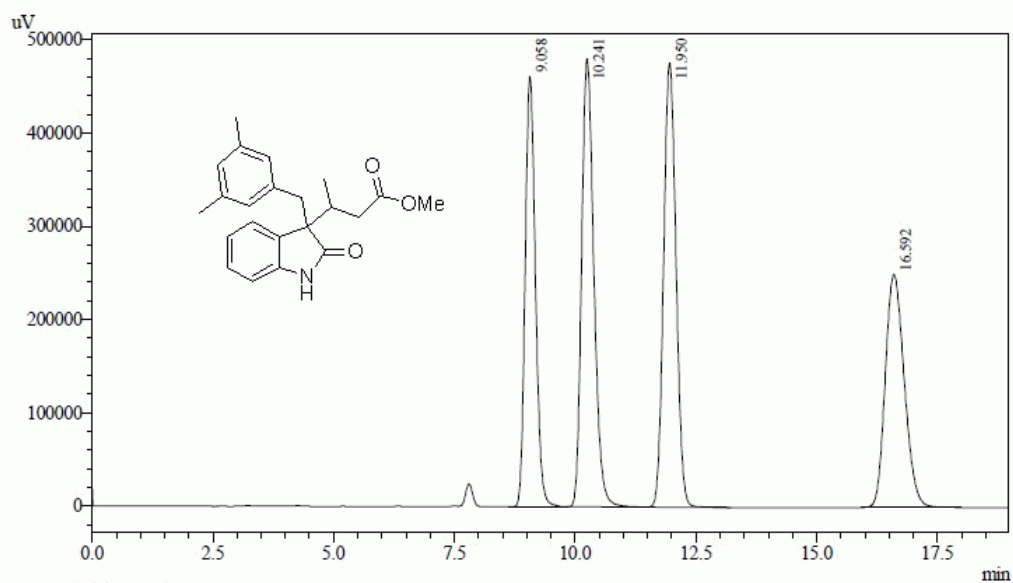


峰号	保留时间	峰高	峰面积	含量 μ
1	6.803	15174.077	139998.609	23.0156 μ
2	7.508	15541.444	163974.688	26.9573 μ
3	9.968	9496.200	138906.500	22.8361 μ
4	10.438	10615.857	165396.000	27.1910 μ



峰号	保留时间	峰高	峰面积	含量 μ
1	6.798	1585.800	14814.500	3.9126 μ
2	7.503	31841.639	333282.406	88.0211 μ
3	10.003	739.478	10742.404	2.8371 μ
4	10.493	1279.826	19799.873	5.2292 μ

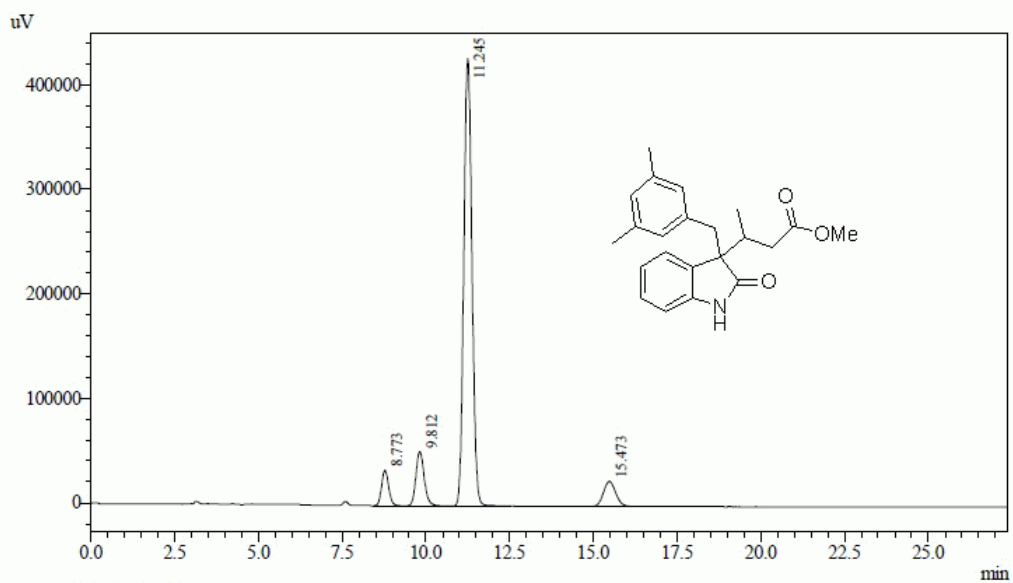




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

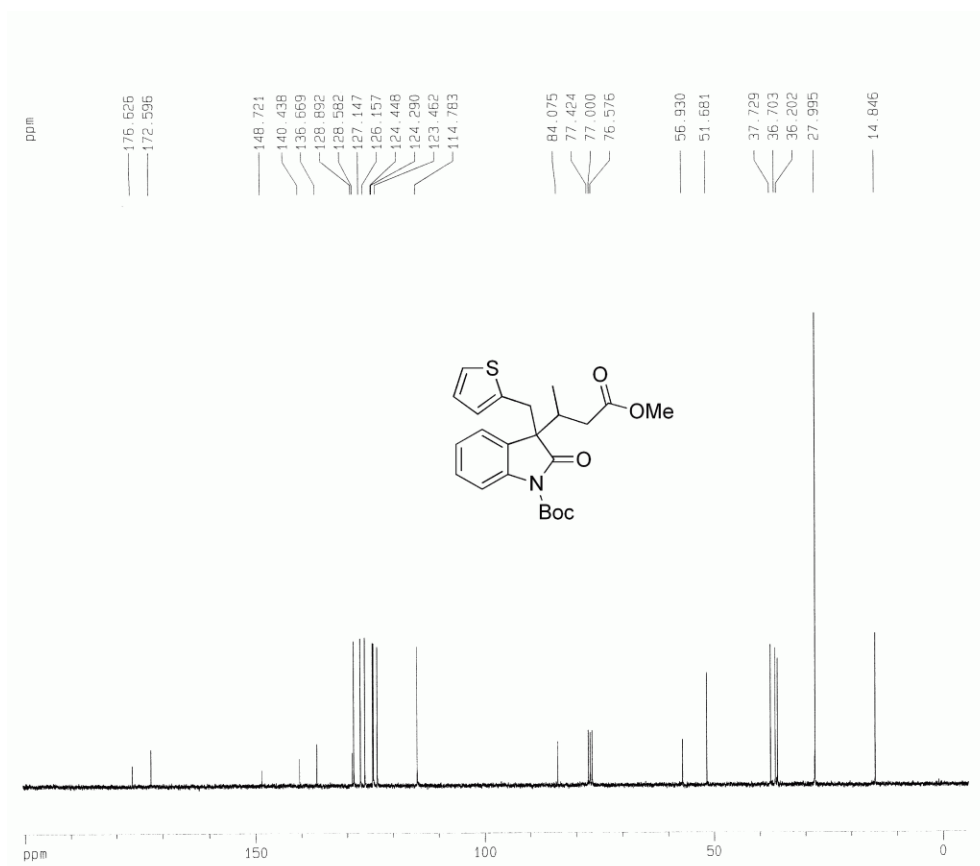
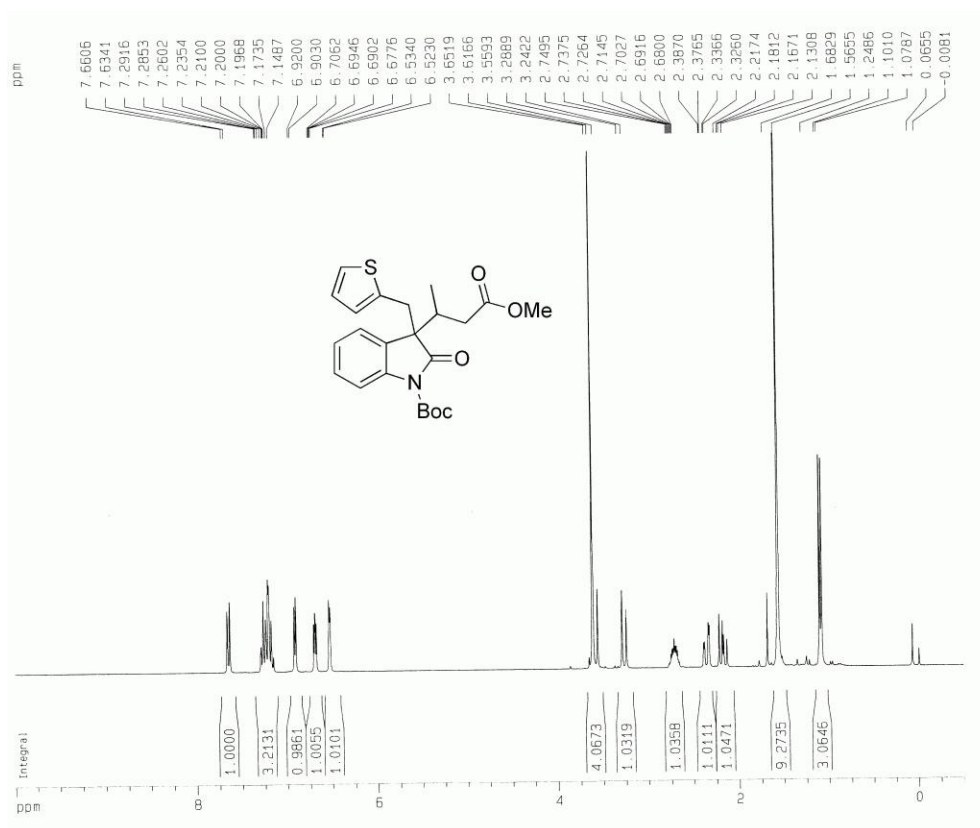
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.058	6807564	461471	22.250	27.667
2	10.241	8461929	480493	27.657	28.808
3	11.950	8490727	476302	27.751	28.556
4	16.592	6836056	249673	22.343	14.969
Total		30596276	1667939	100.000	100.000

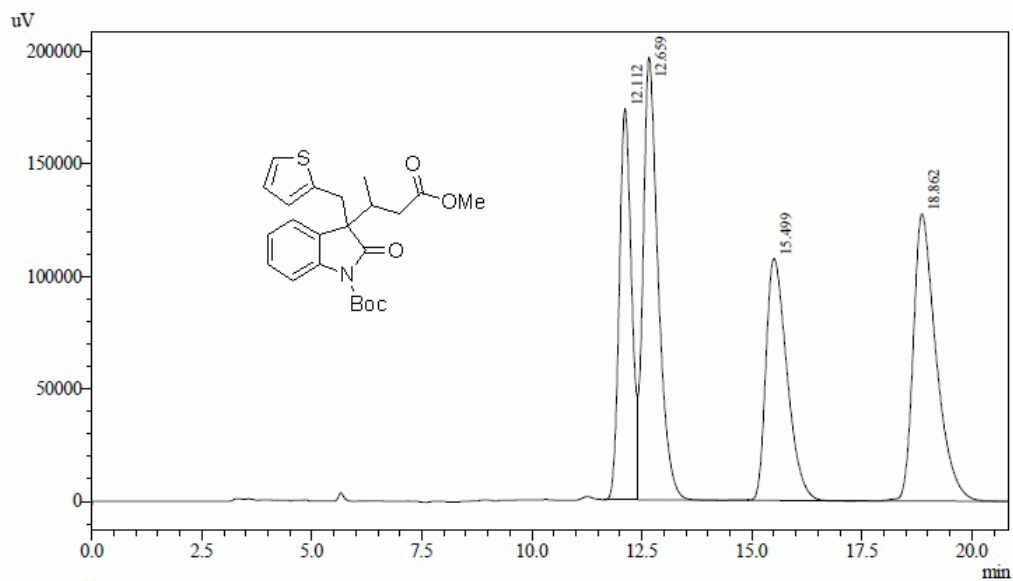


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

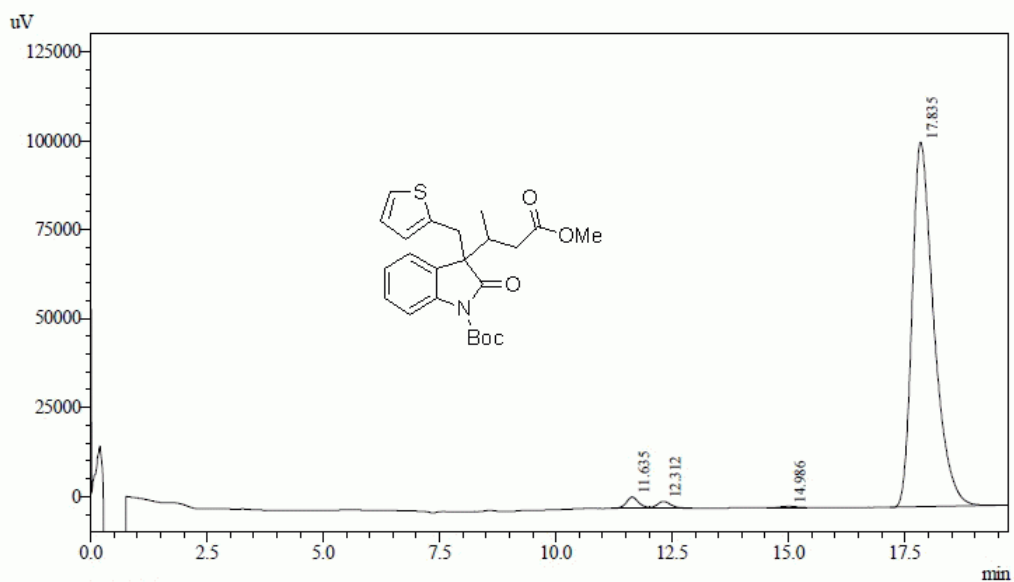
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.773	499787	34115	5.374	6.331
2	9.812	906077	52209	9.743	9.689
3	11.245	7278356	428531	78.266	79.528
4	15.473	615281	23989	6.616	4.452
Total		9299501	538845	100.000	100.000





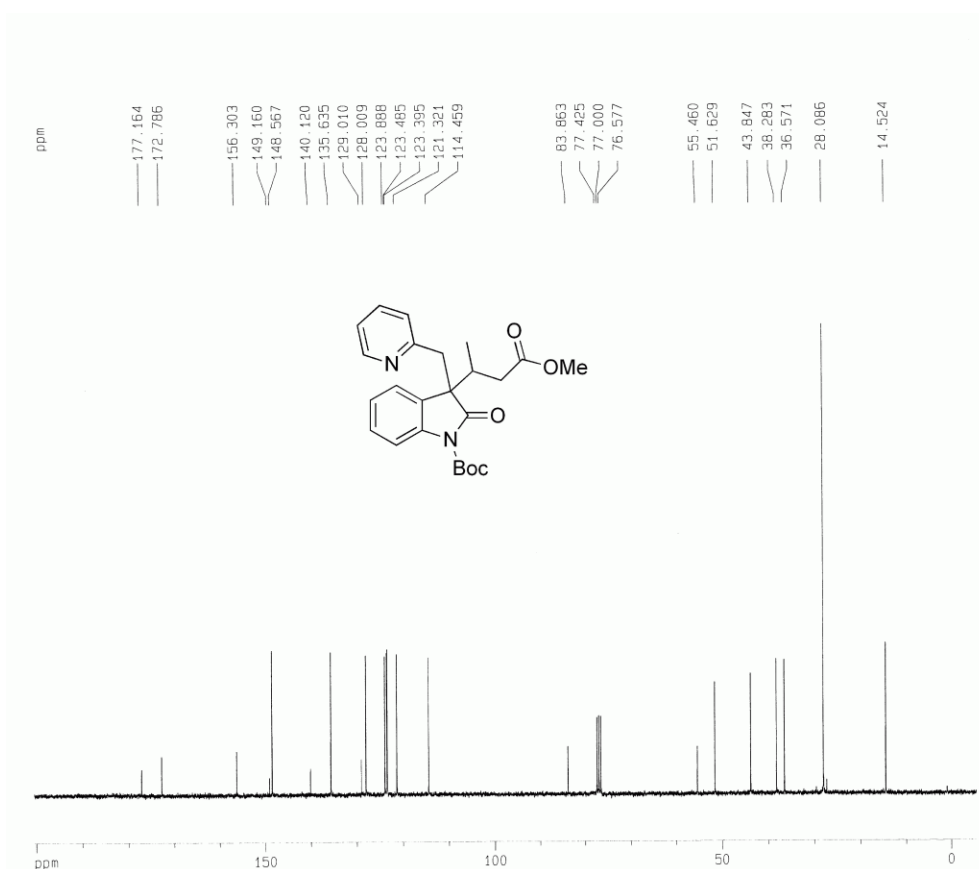
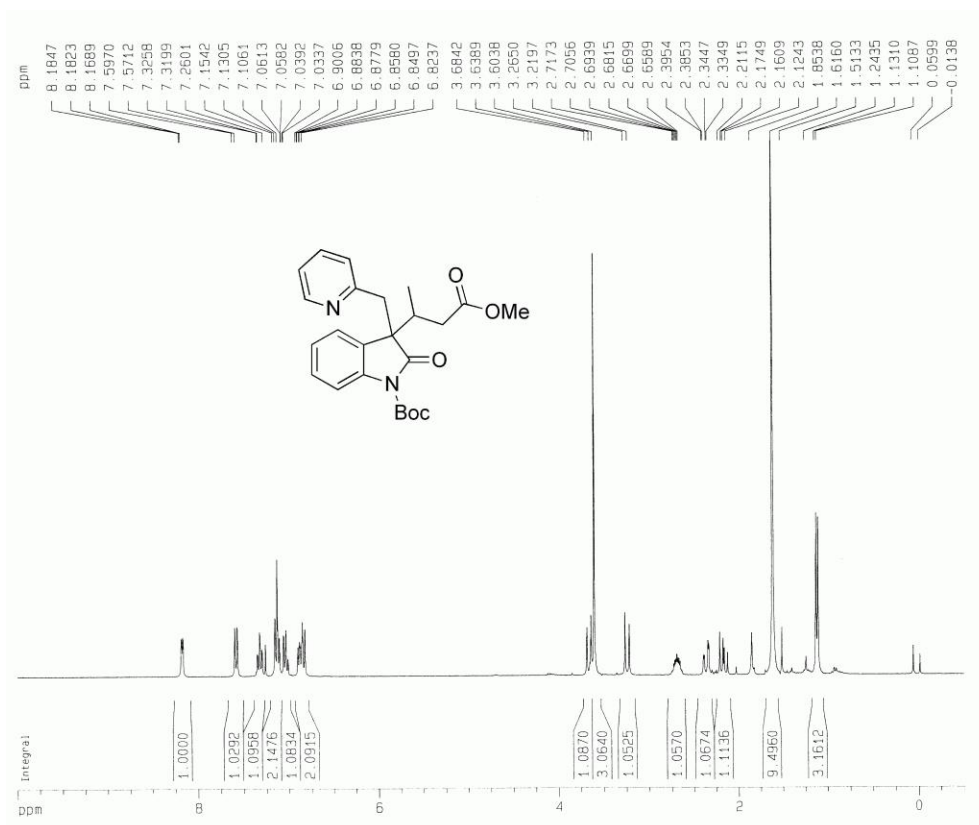
Detector A Ch1 254nm

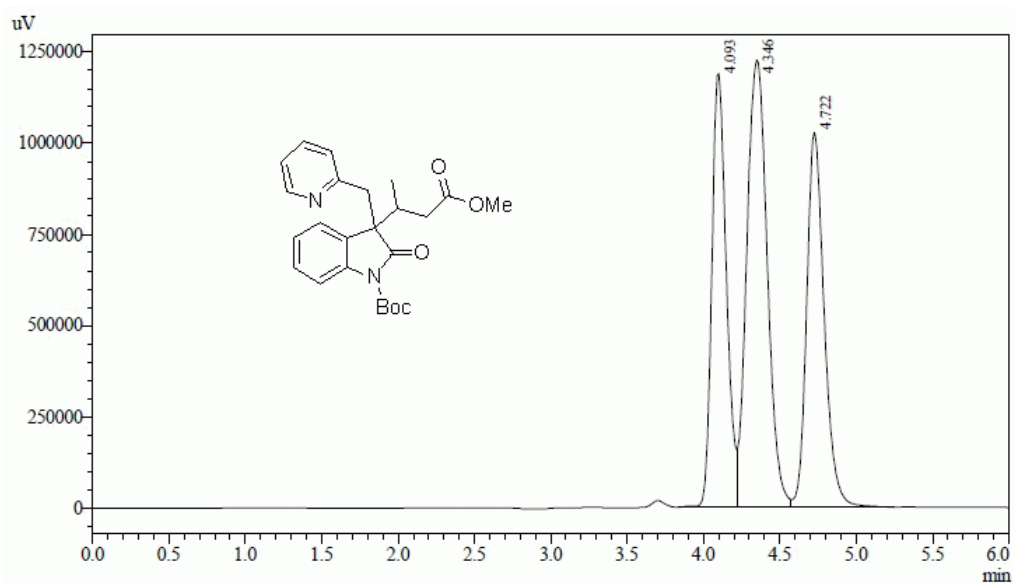
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.112	3356806	173971	20.649	28.702
2	12.659	4719631	196910	29.032	32.486
3	15.499	3567435	107607	21.944	17.753
4	18.862	4612830	127646	28.375	21.059
Total		16256702	606133	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.635	59285	3185	1.721	2.949
2	12.312	39992	1978	1.161	1.831
3	14.986	7842	359	0.228	0.333
4	17.835	3337209	102489	96.890	94.887
Total		3444328	108011	100.000	100.000

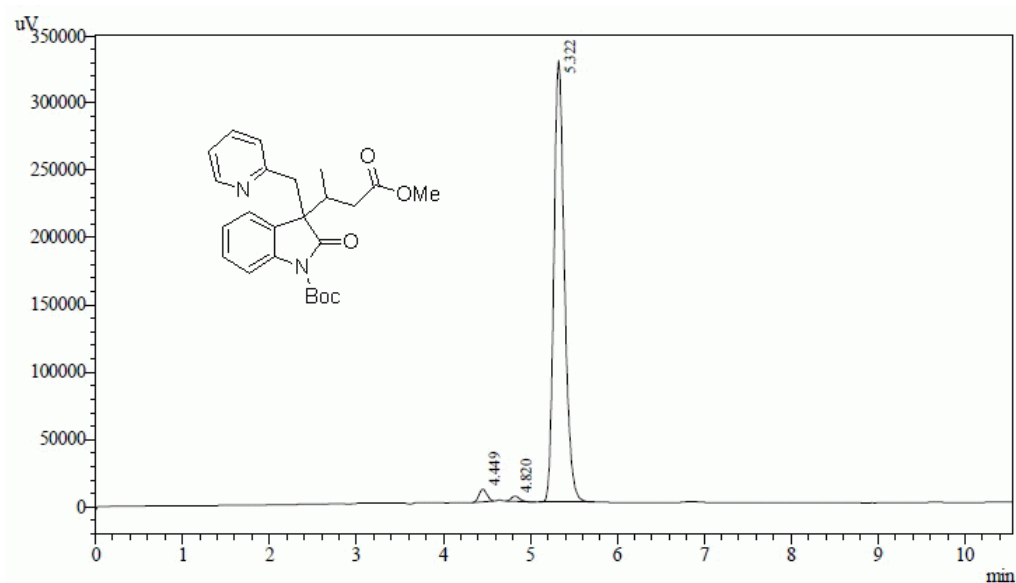




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

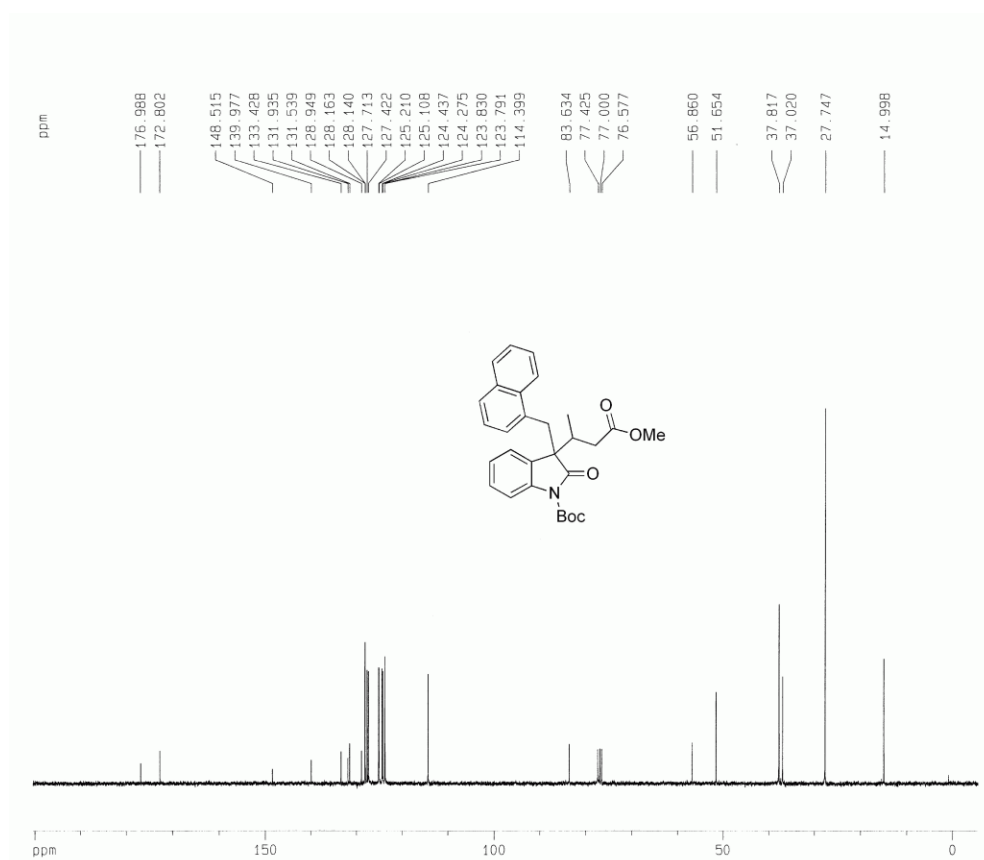
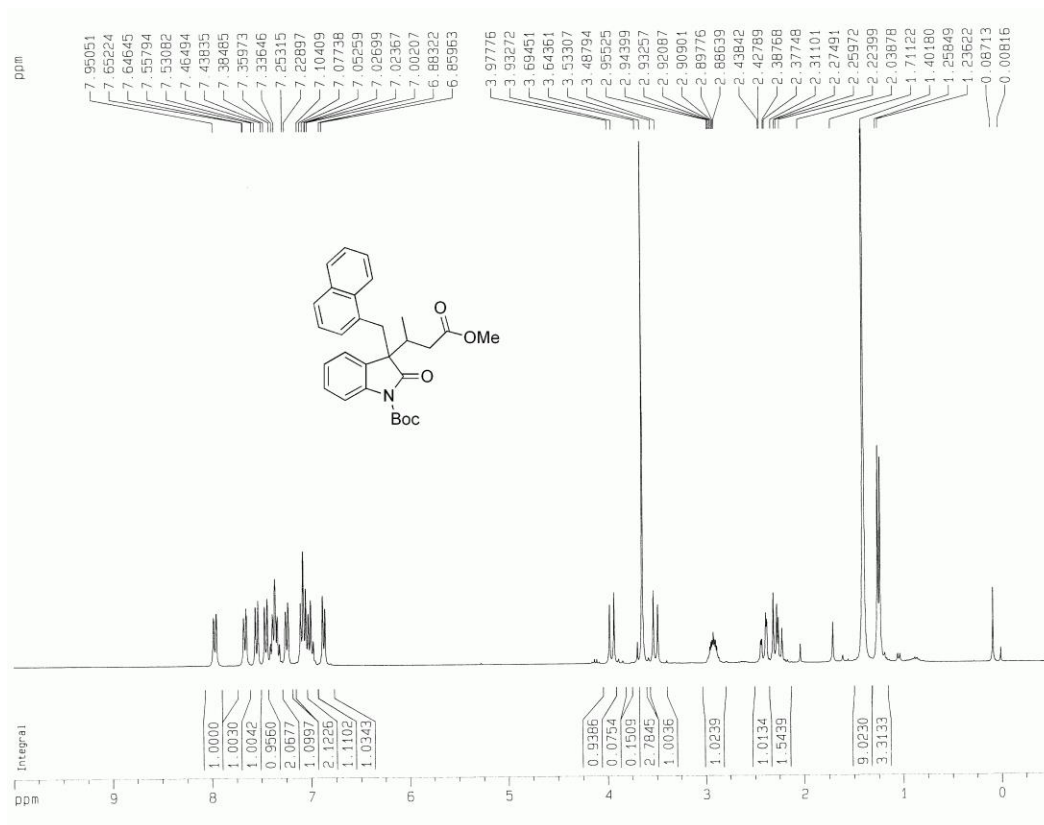
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.093	7894999	1189242	28.634	34.556
2	4.346	11445549	1225684	41.511	35.615
3	4.722	8231976	1026547	29.856	29.829
Total		27572523	3441473	100.000	100.000

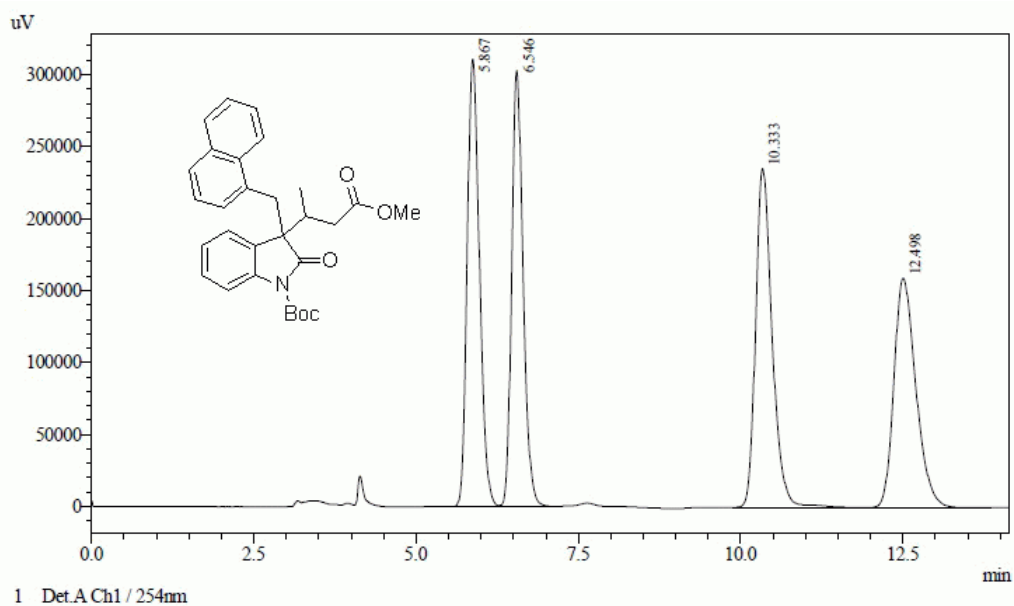


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

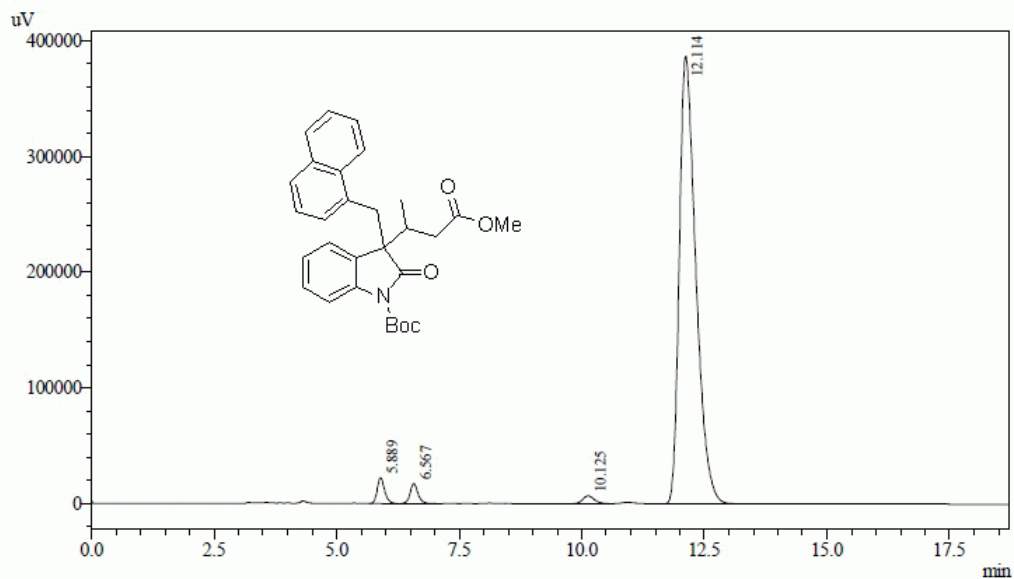
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.449	59419	9371	2.064	2.741
2	4.820	26223	3844	0.911	1.124
3	5.322	2792639	328615	97.025	96.134
Total		2878281	341830	100.000	100.000





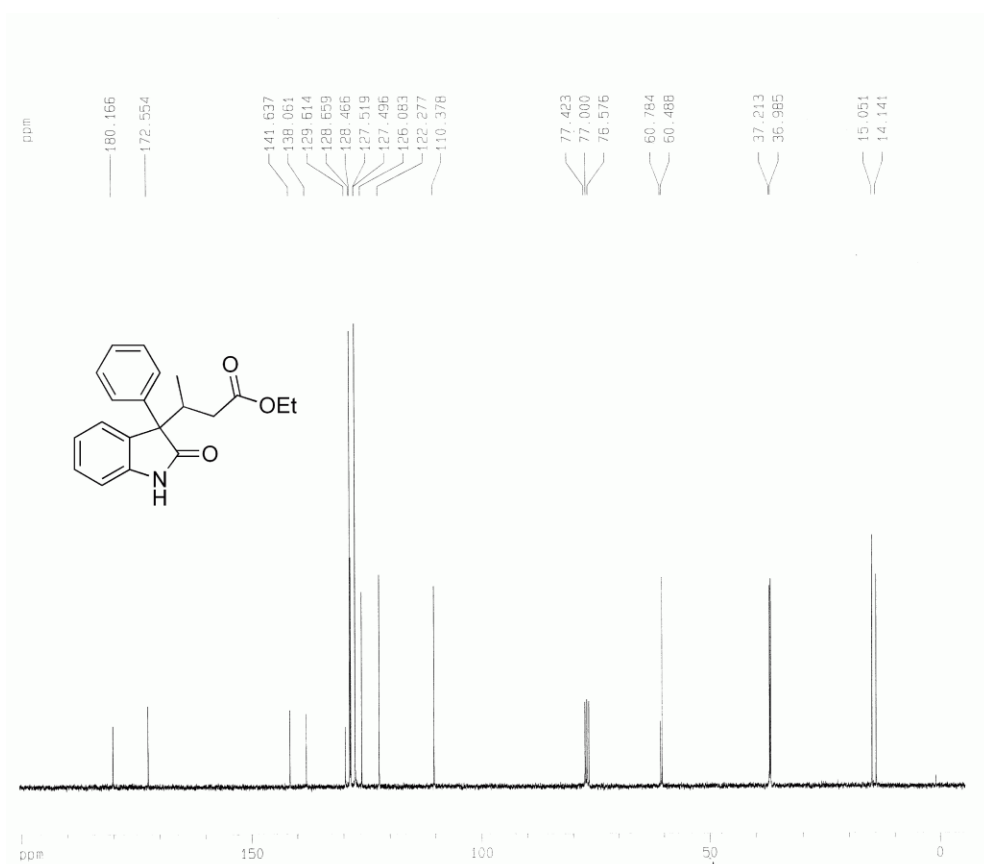
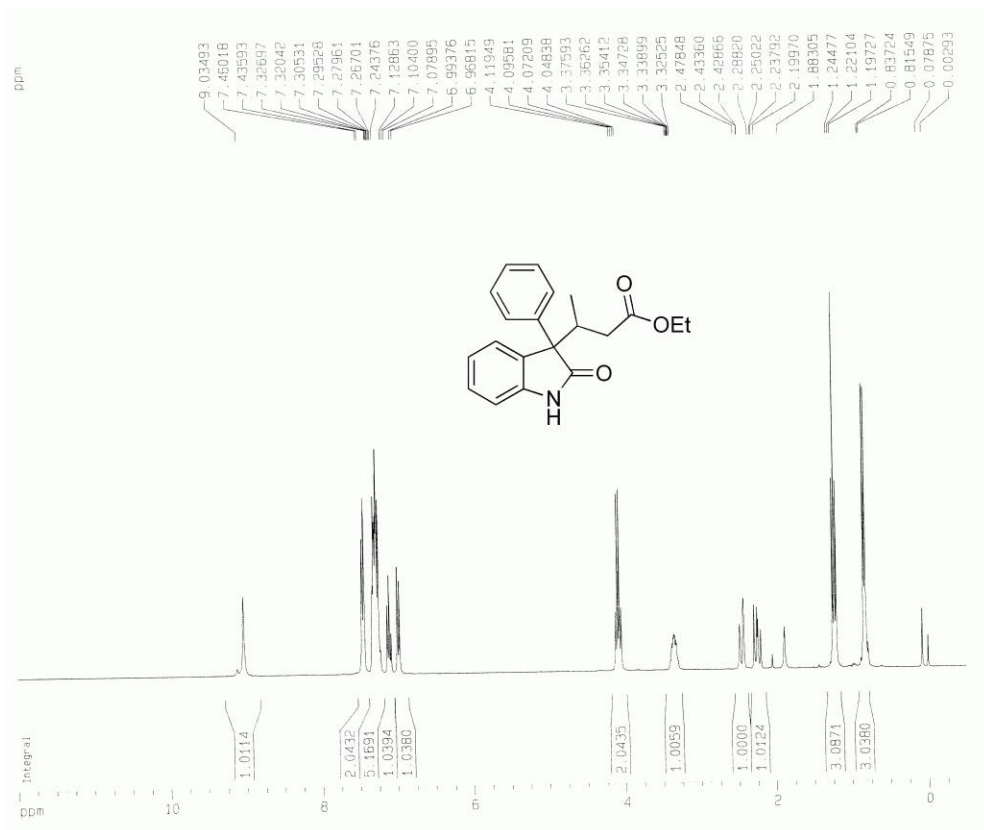
Detector A Ch1 254nm

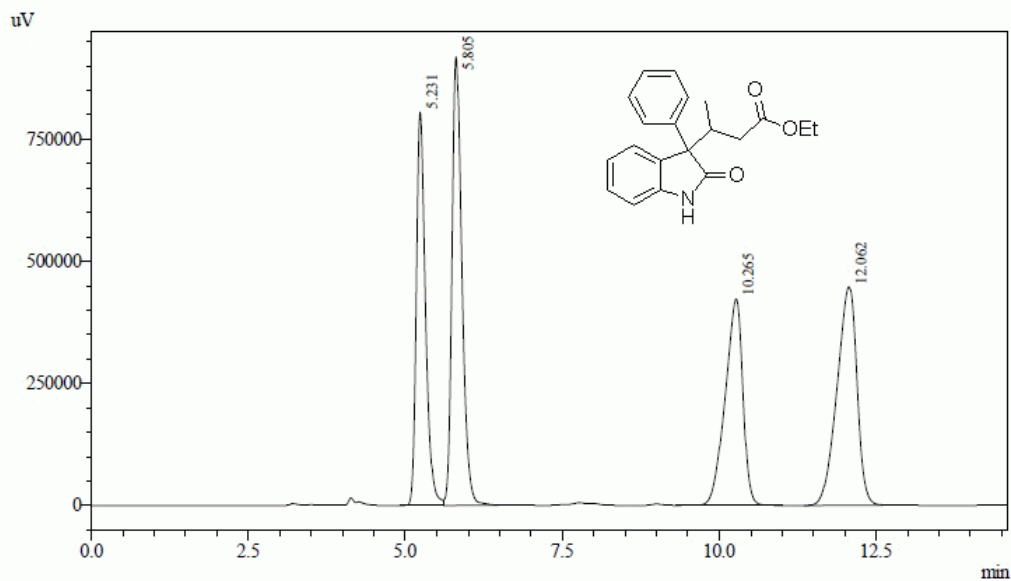
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.867	4092807	310761	26.053	30.824
2	6.546	3709376	302889	23.612	30.044
3	10.333	4163894	235137	26.506	23.323
4	12.498	3743384	159377	23.829	15.809
Total		15709461	1008165	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.889	239051	22563	2.488	5.197
2	6.567	199504	17591	2.076	4.051
3	10.125	114705	6853	1.194	1.578
4	12.114	9055607	387178	94.242	89.174
Total		9608867	434185	100.000	100.000

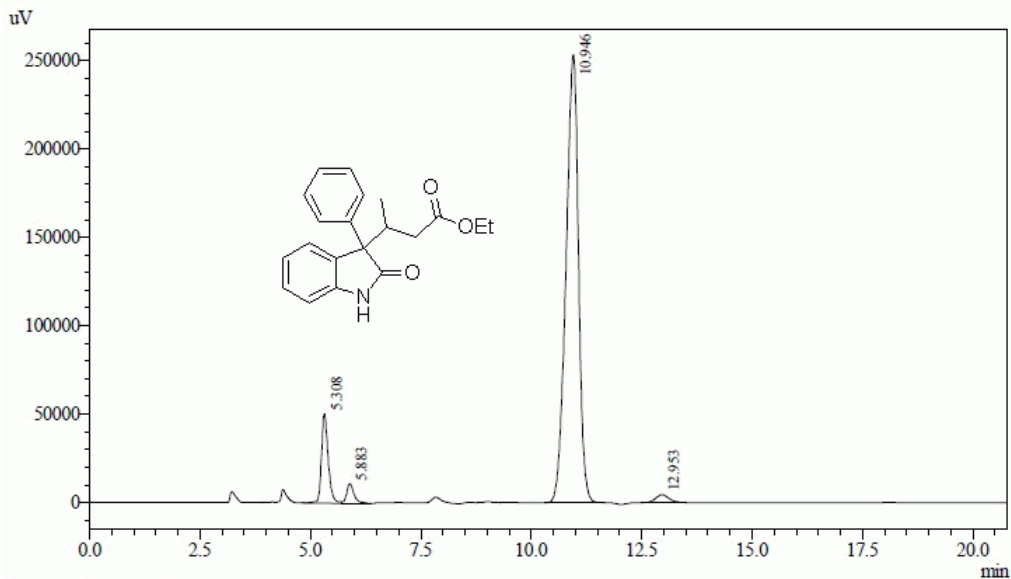




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

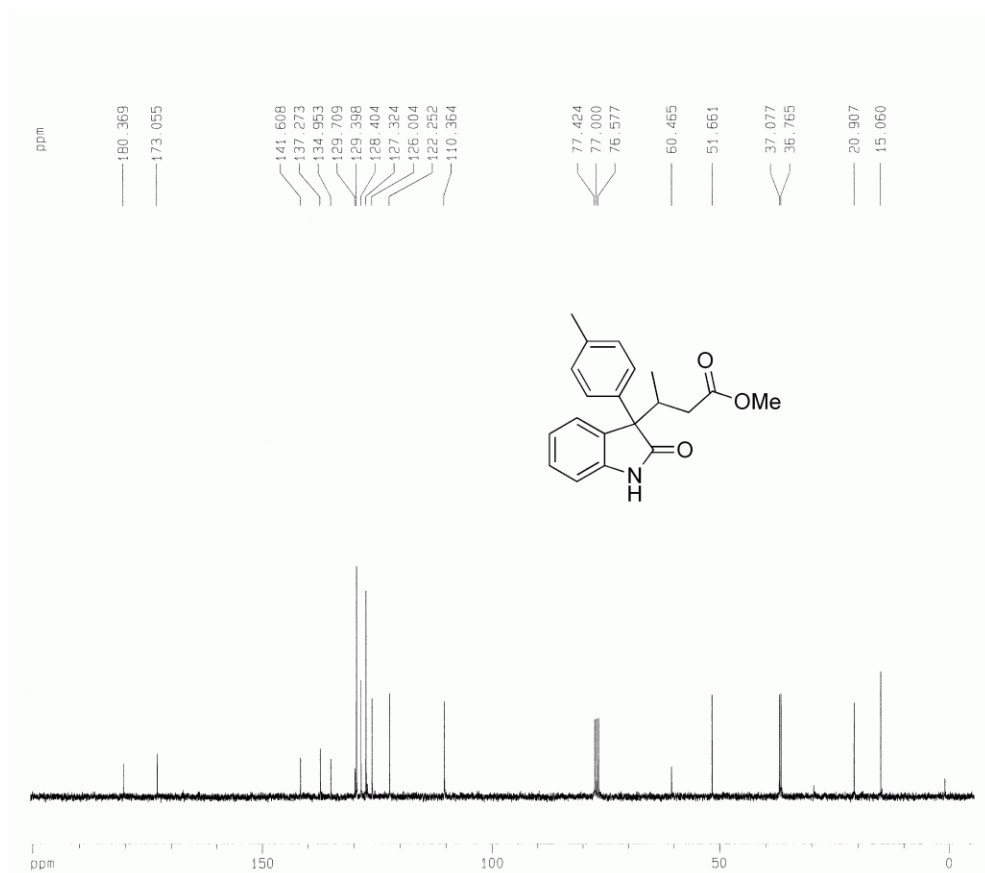
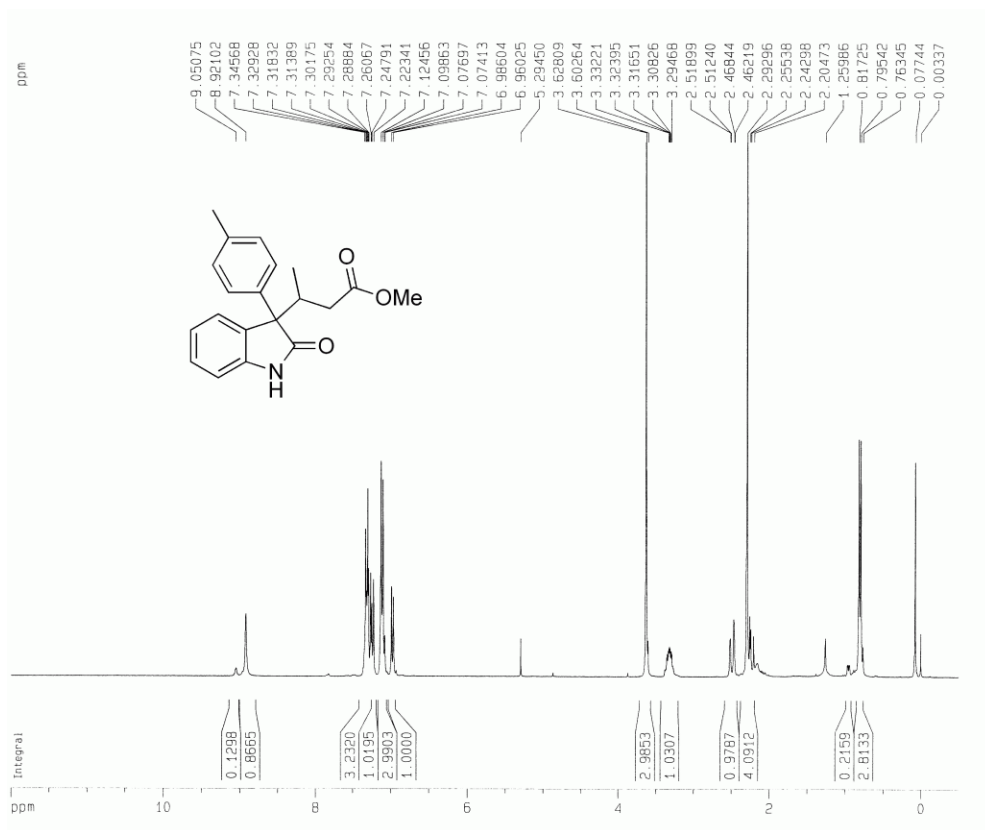
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.231	8264935	804766	22.722	31.043
2	5.805	9947769	918485	27.348	35.430
3	10.265	8308213	422264	22.841	16.288
4	12.062	9853741	446901	27.090	17.239
Total		36374658	2592416	100.000	100.000

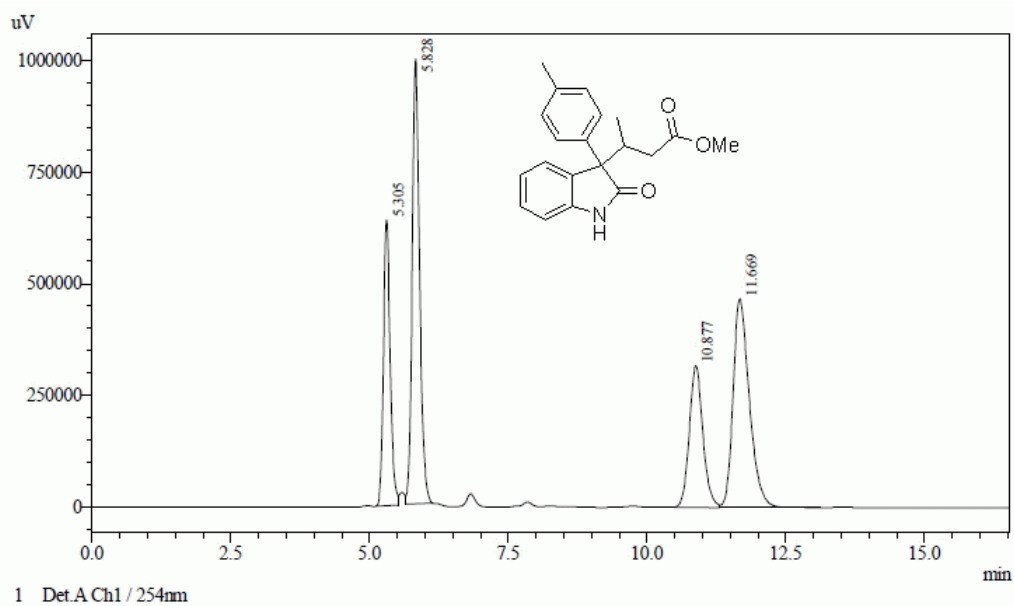


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

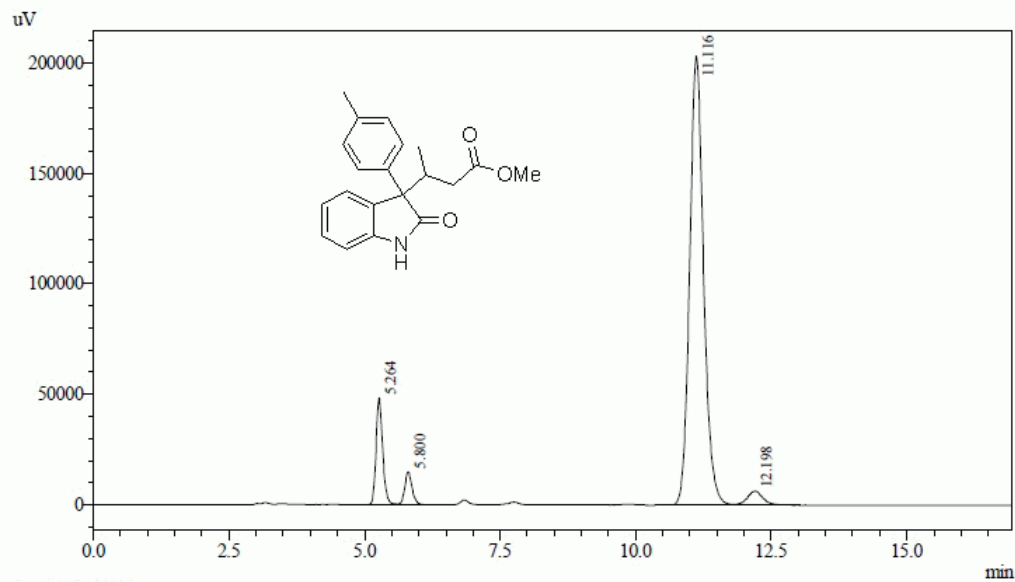
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.308	535192	50406	9.320	15.785
2	5.883	126060	11081	2.195	3.470
3	10.946	4985051	253396	86.810	79.354
4	12.953	96154	4439	1.674	1.390
Total		5742457	319322	100.000	100.000





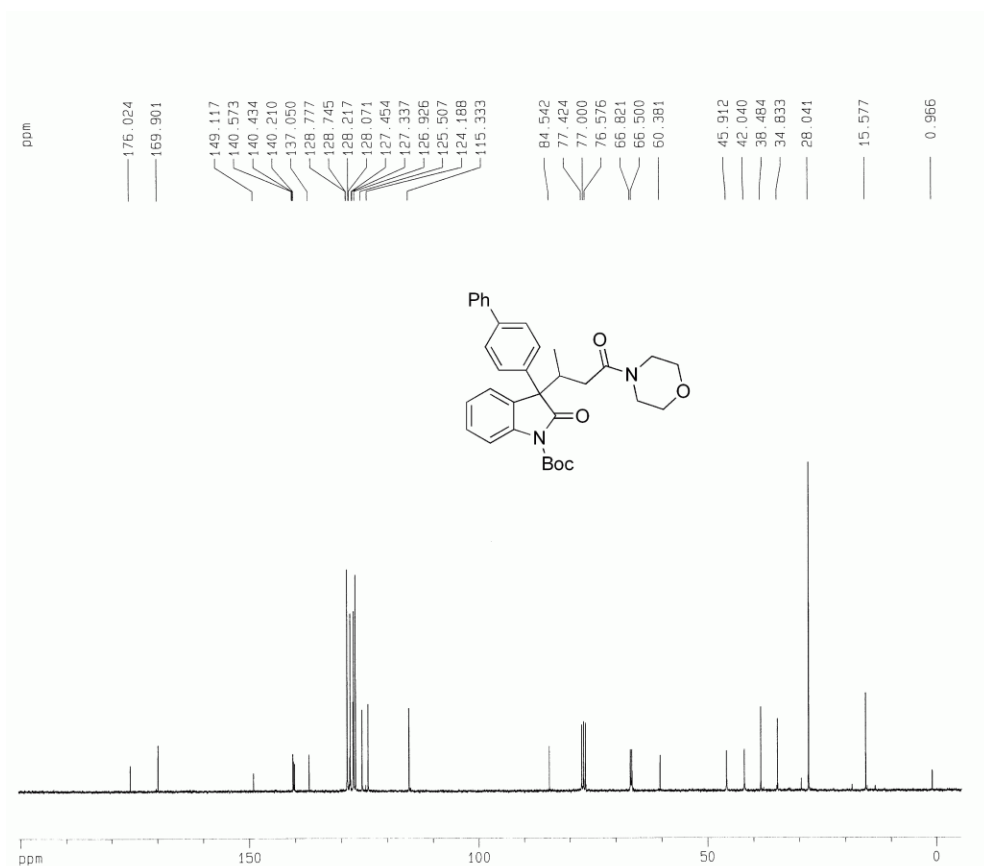
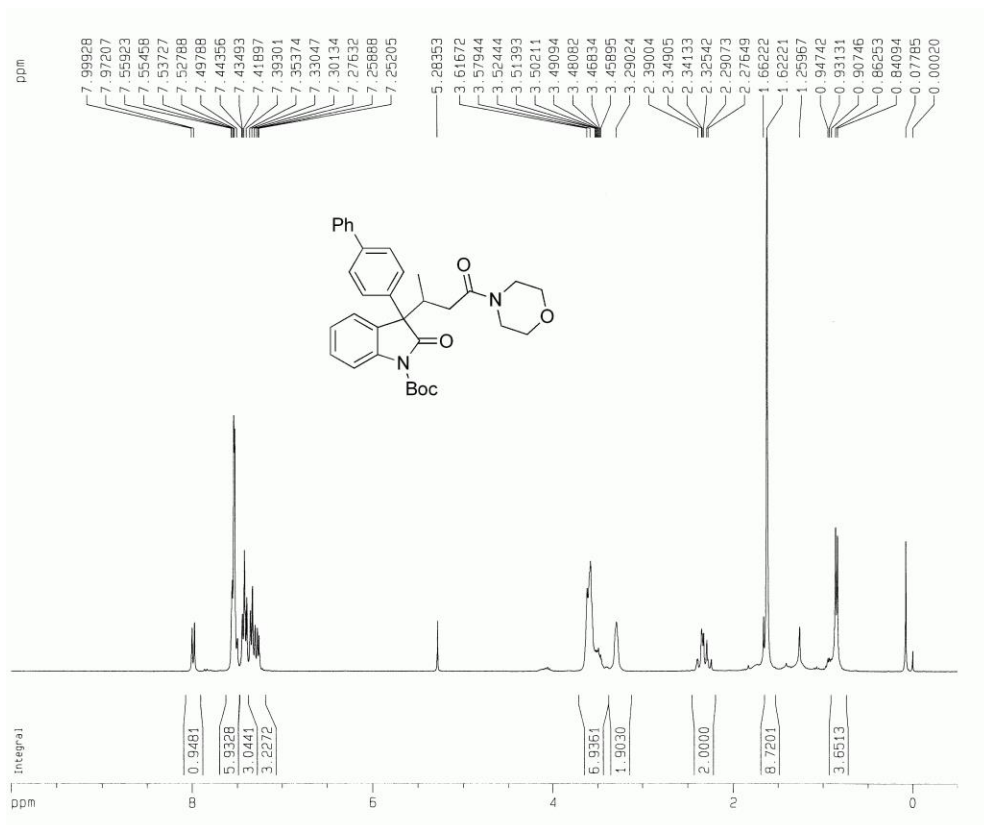
Detector A Ch1 254nm

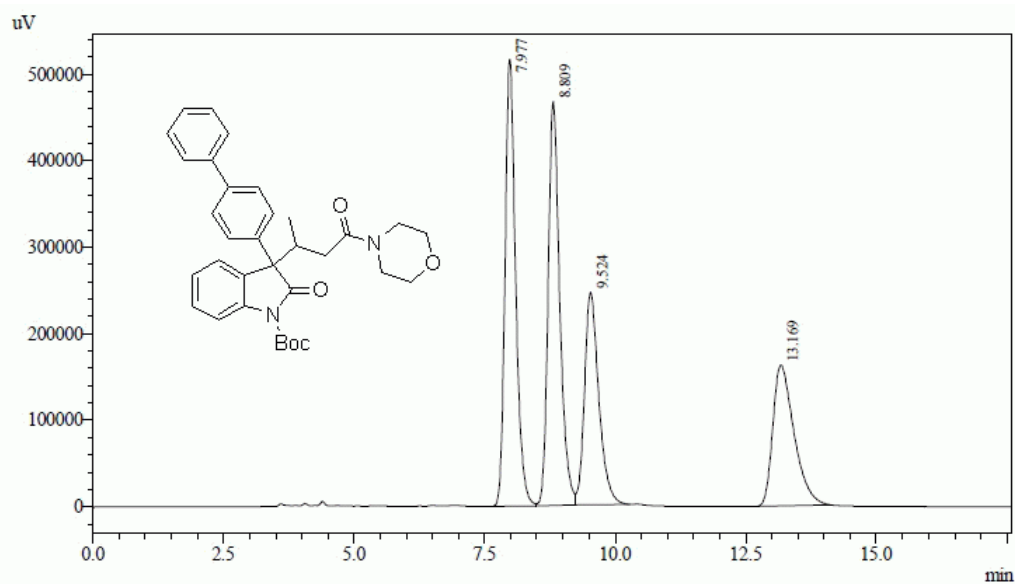
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.305	5390079	640590	18.276	26.468
2	5.828	9225323	995367	31.280	41.127
3	10.877	5393080	317377	18.286	13.114
4	11.669	9484680	466896	32.159	19.291
Total		29493161	2420231	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.264	414820	48387	9.617	17.719
2	5.800	143499	14911	3.327	5.460
3	11.116	3626158	203454	84.069	74.503
4	12.198	128859	6329	2.987	2.317
Total		4313336	273080	100.000	100.000

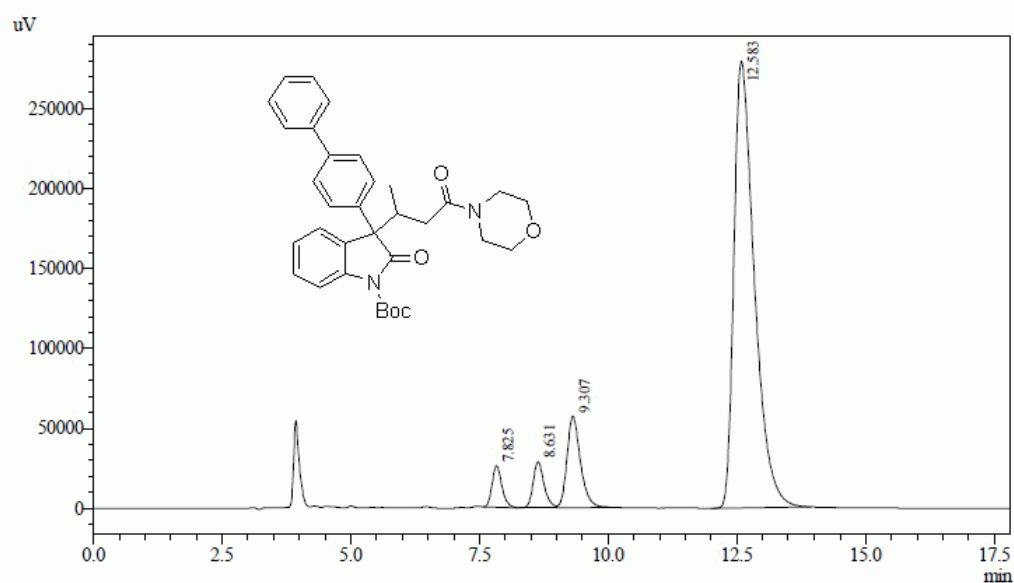




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

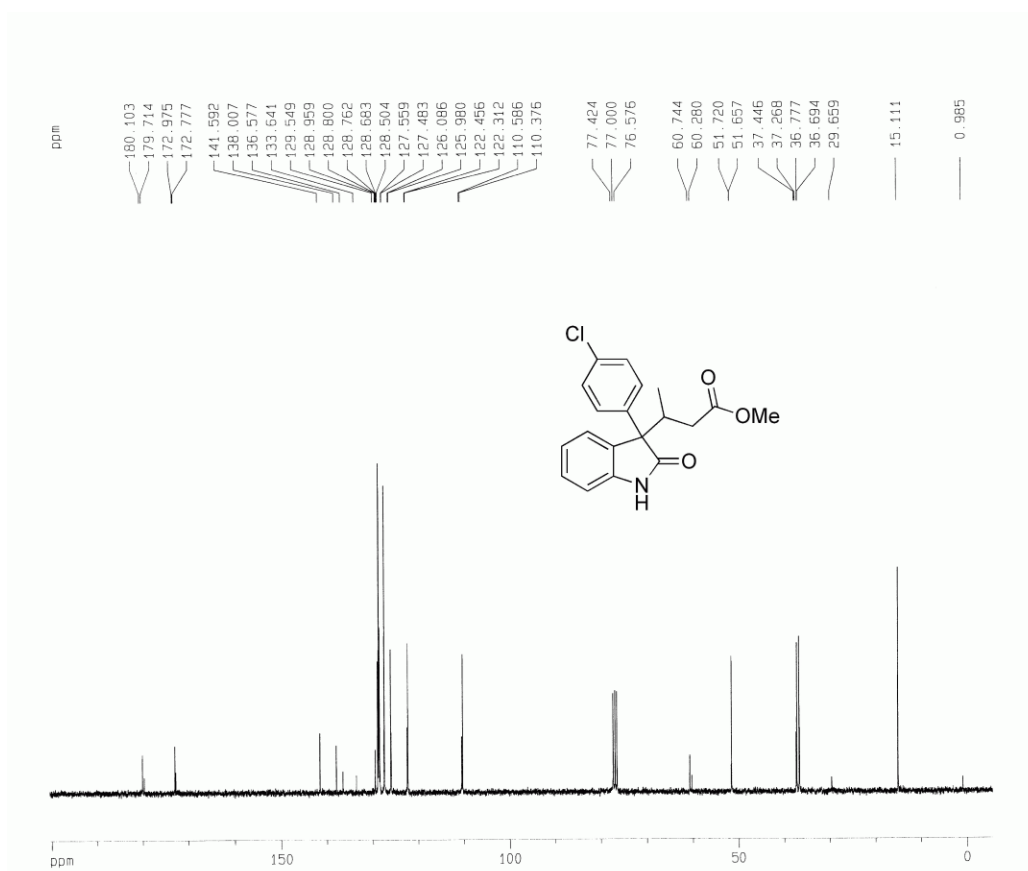
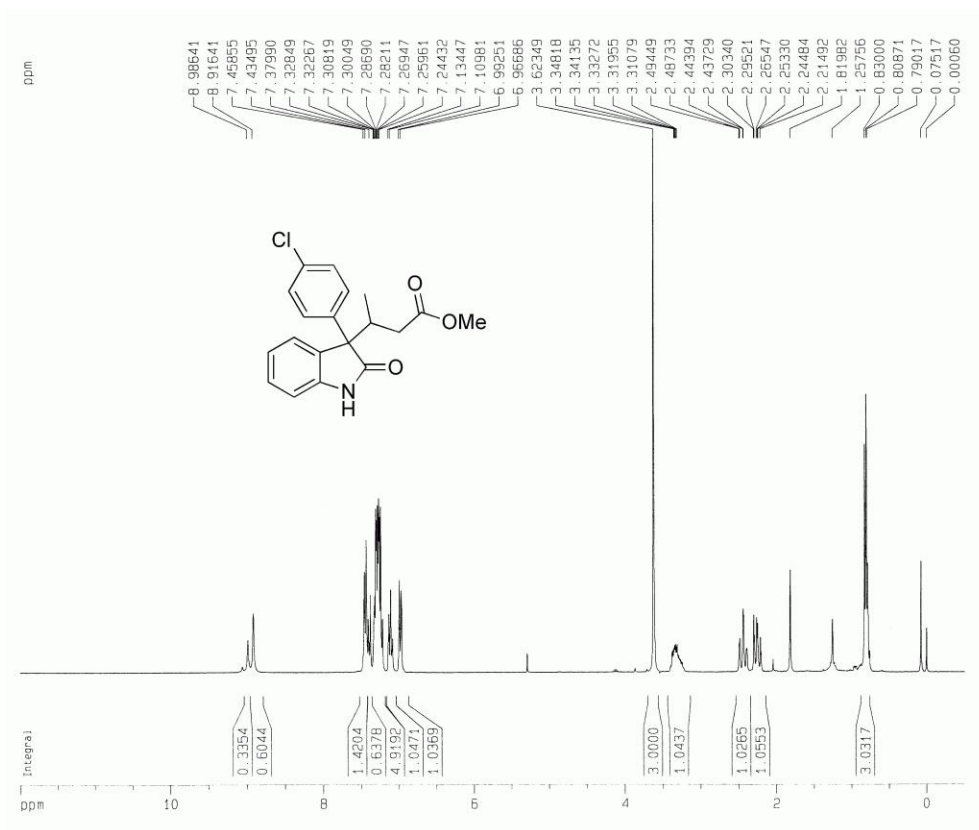
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.977	7272679	515956	30.587	37.105
2	8.809	7220611	466289	30.368	33.533
3	9.524	4680869	245526	19.687	17.657
4	13.169	4602888	162754	19.359	11.705
Total		23777047	1390525	100.000	100.000

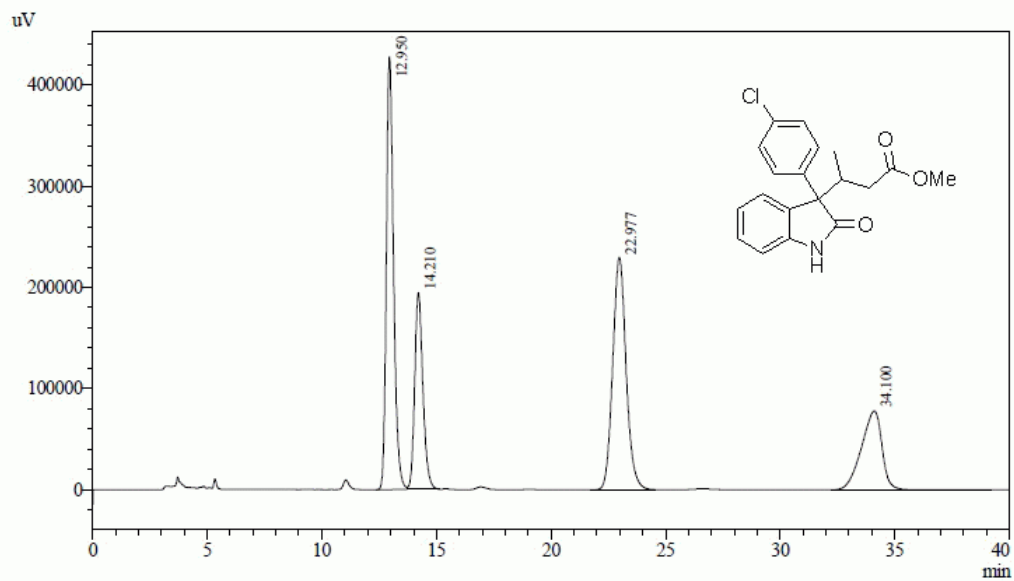


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.825	345179	25916	3.633	6.629
2	8.631	421767	28817	4.439	7.371
3	9.307	1033213	57042	10.873	14.591
4	12.583	7702031	279169	81.055	71.409
Total		9502189	390944	100.000	100.000

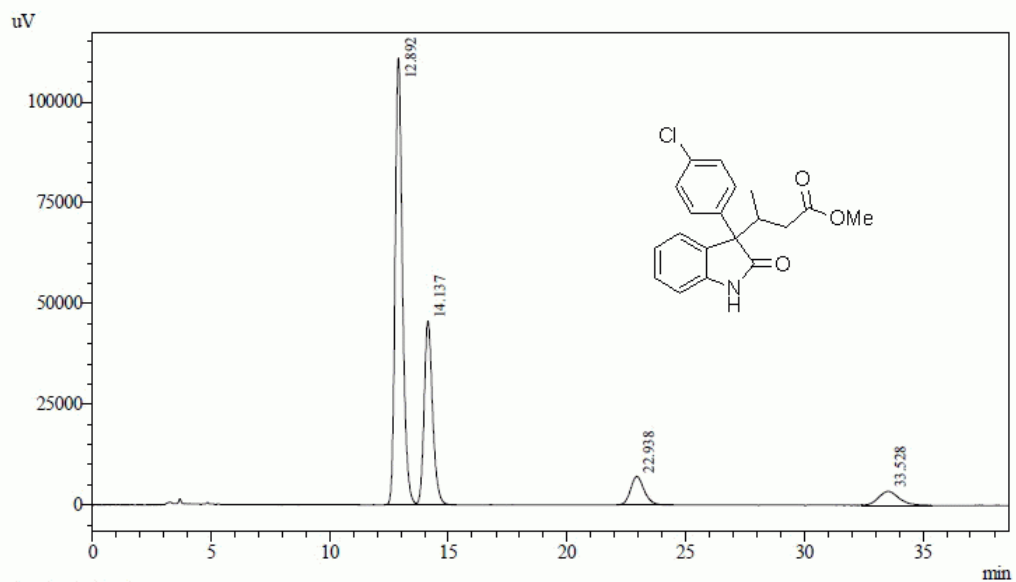




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

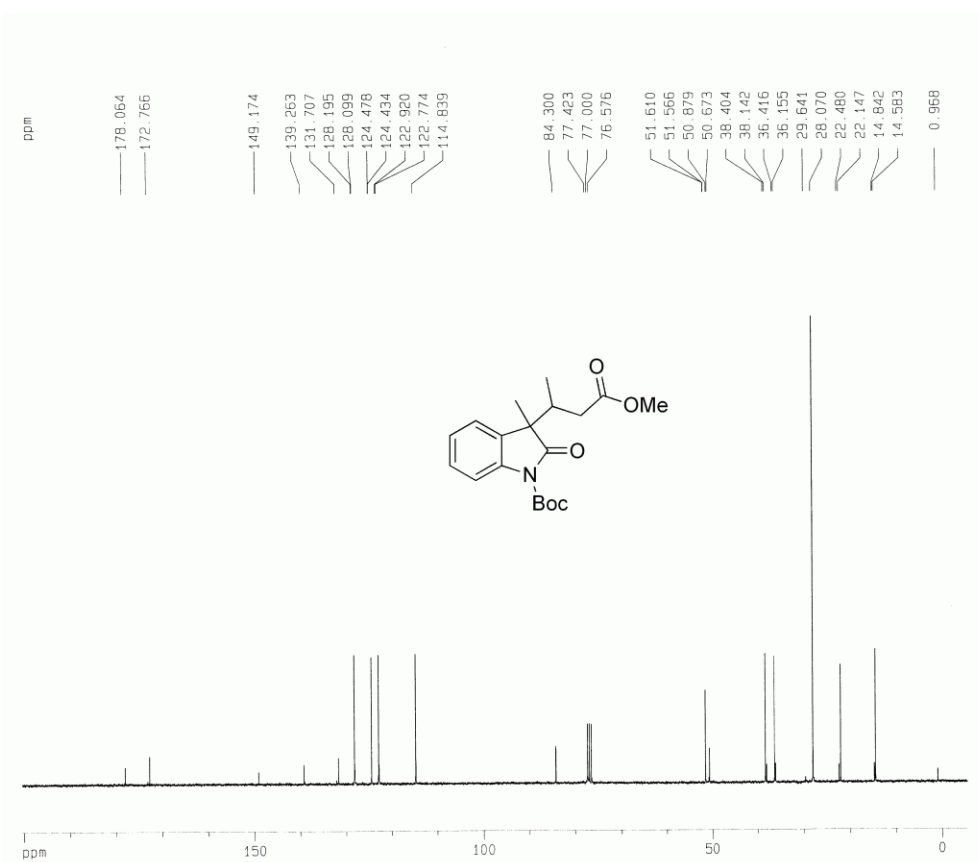
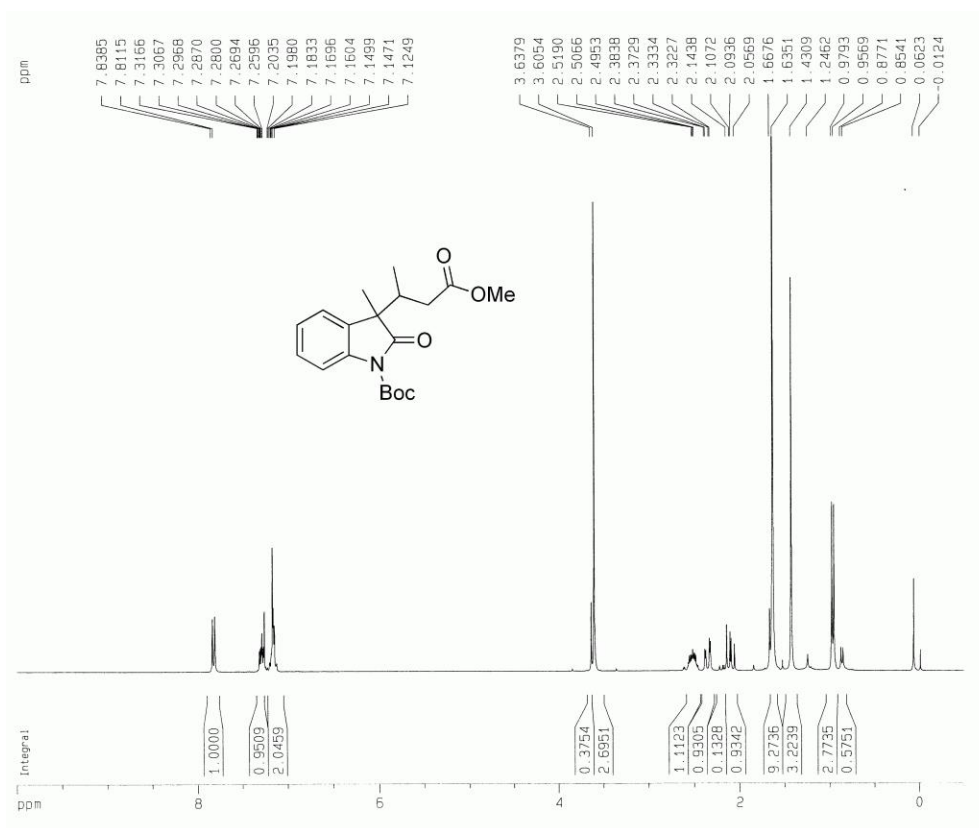
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.950	9328212	427881	32.865	46.012
2	14.210	4845638	194380	17.072	20.903
3	22.977	9335264	229716	32.890	24.702
4	34.100	4874121	77956	17.173	8.383
Total		28383234	929933	100.000	100.000

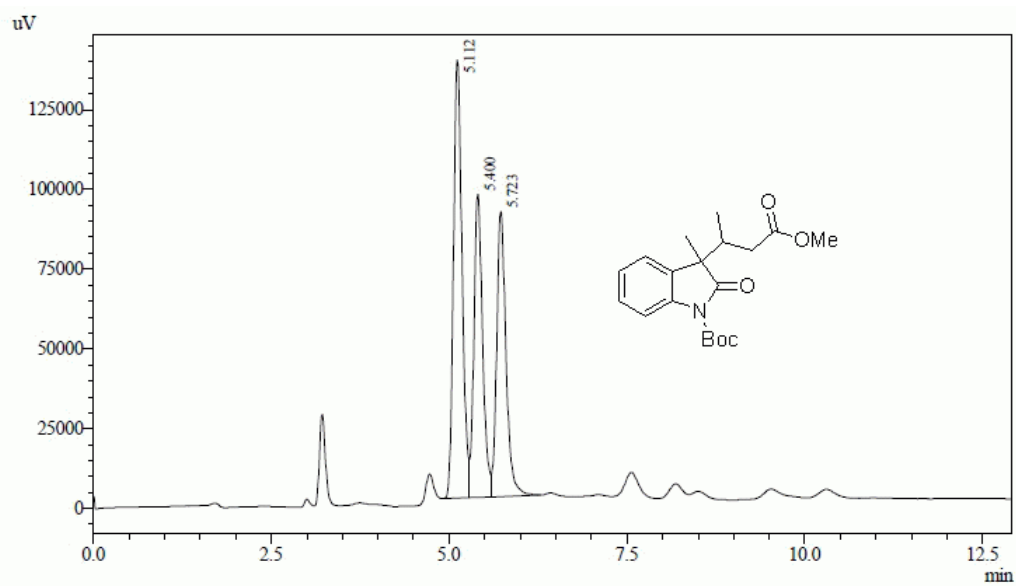


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.892	2400222	110998	59.503	66.364
2	14.137	1133068	45655	28.090	27.296
3	22.938	288645	7115	7.156	4.254
4	33.528	211833	3490	5.251	2.086
Total		4033767	167257	100.000	100.000

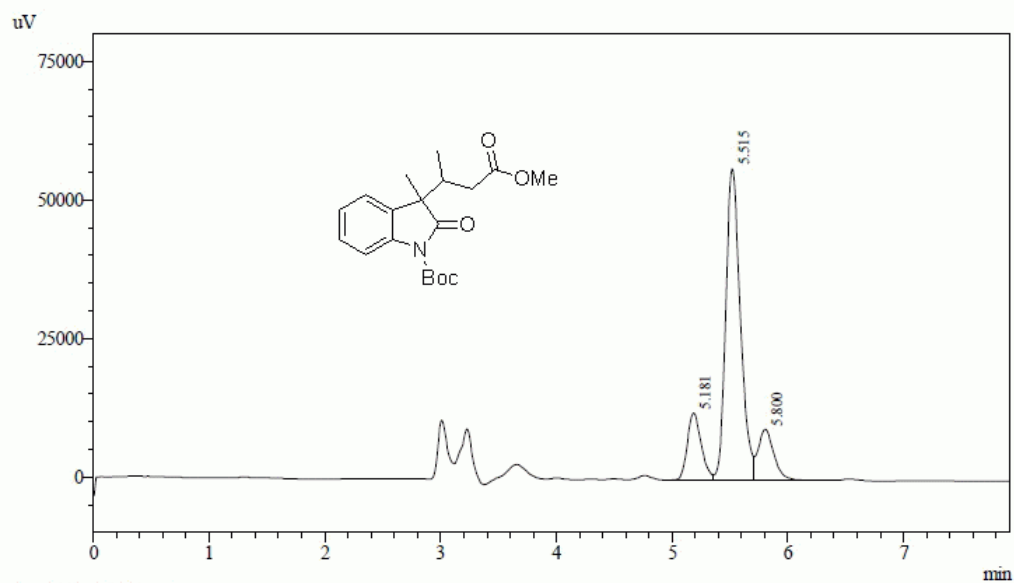




1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

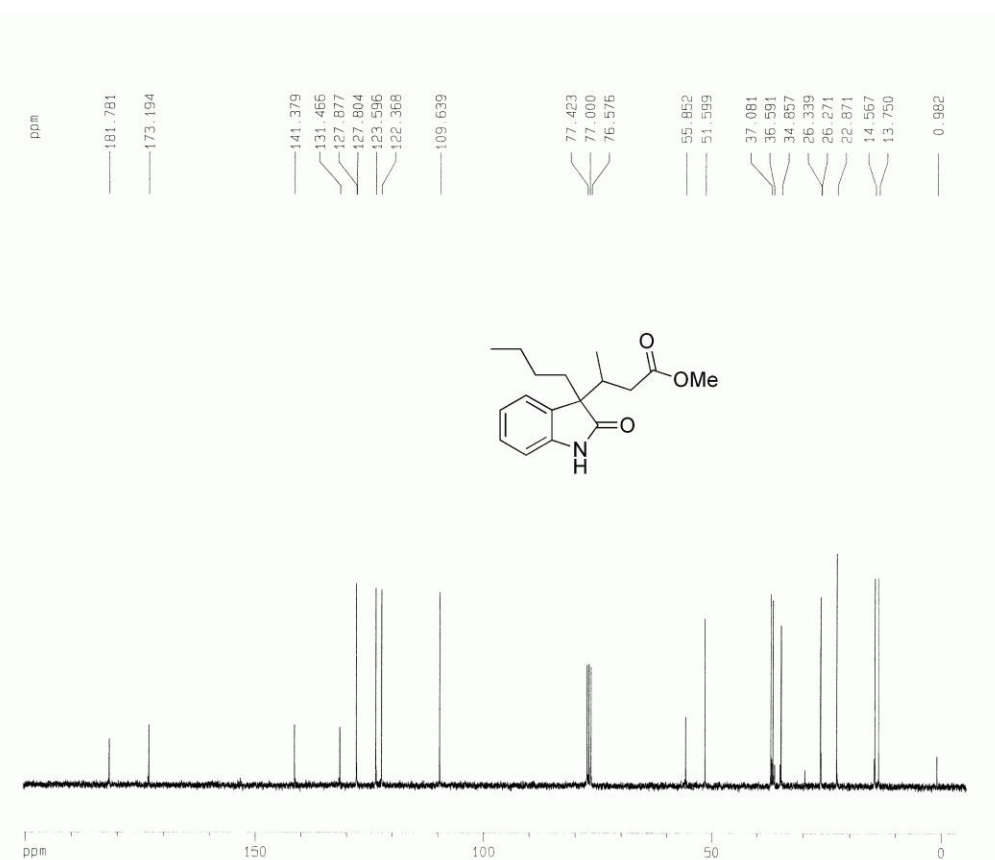
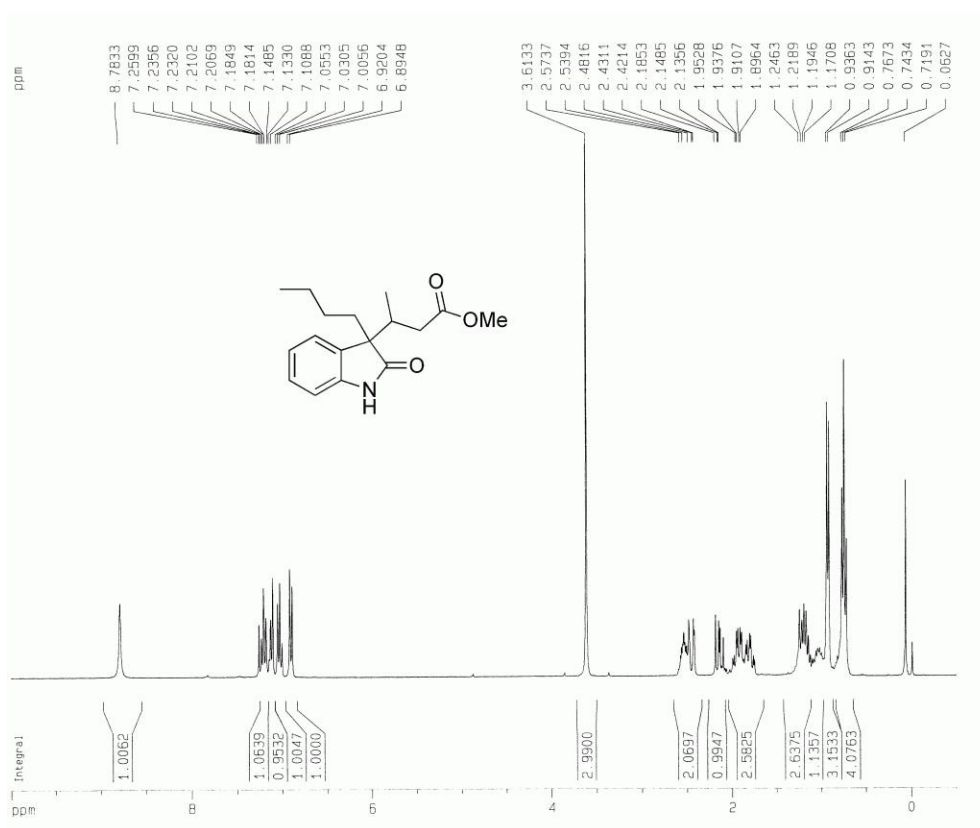
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.112	1155111	137351	41.587	42.702
2	5.400	808592	94974	29.112	29.527
3	5.723	813848	89323	29.301	27.770
Total		2777551	321648	100.000	100.000

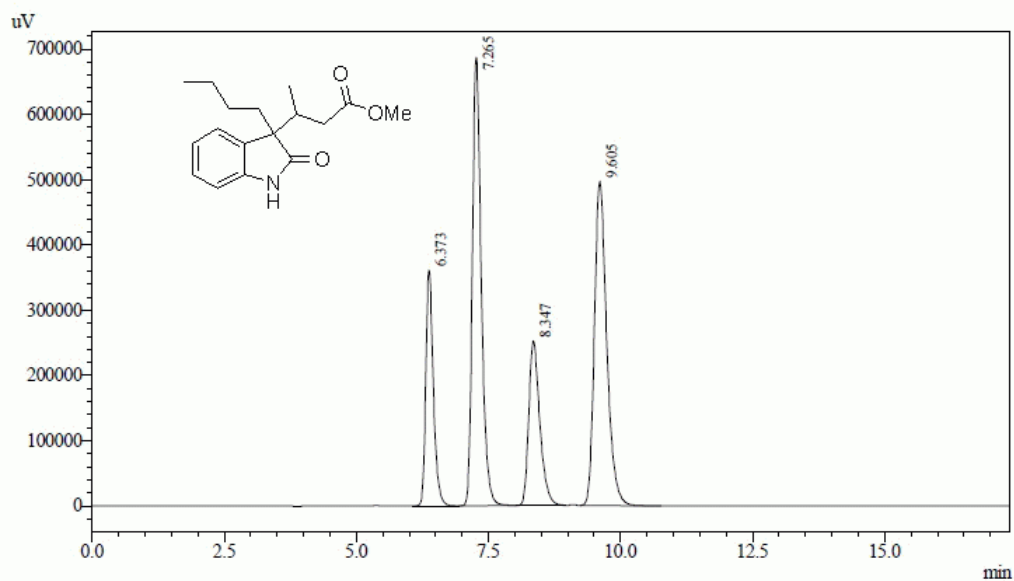


1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.181	101189	12102	14.831	15.603
2	5.515	494813	56290	72.524	72.576
3	5.800	86275	9169	12.645	11.821
Total		682277	77560	100.000	100.000

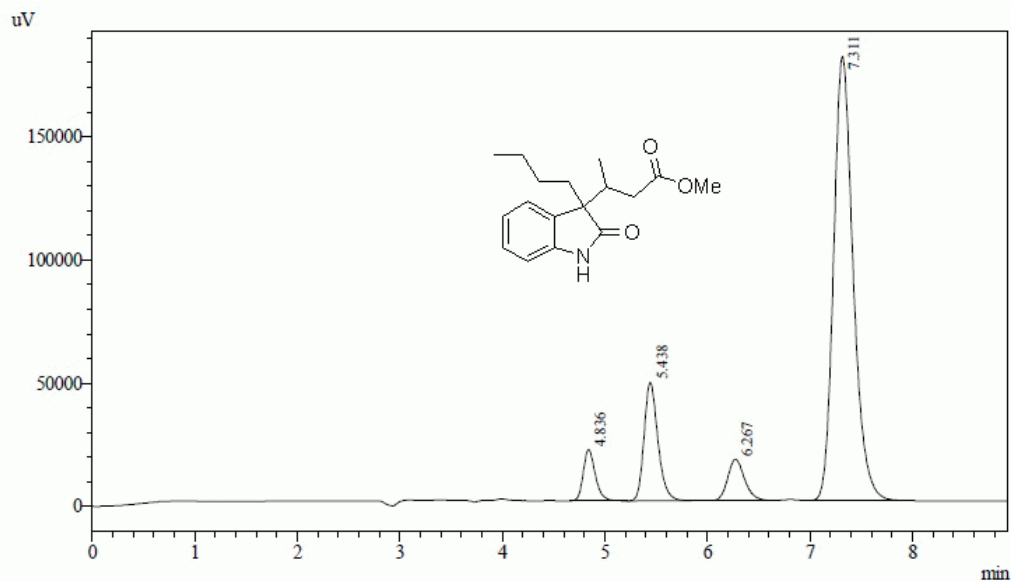




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

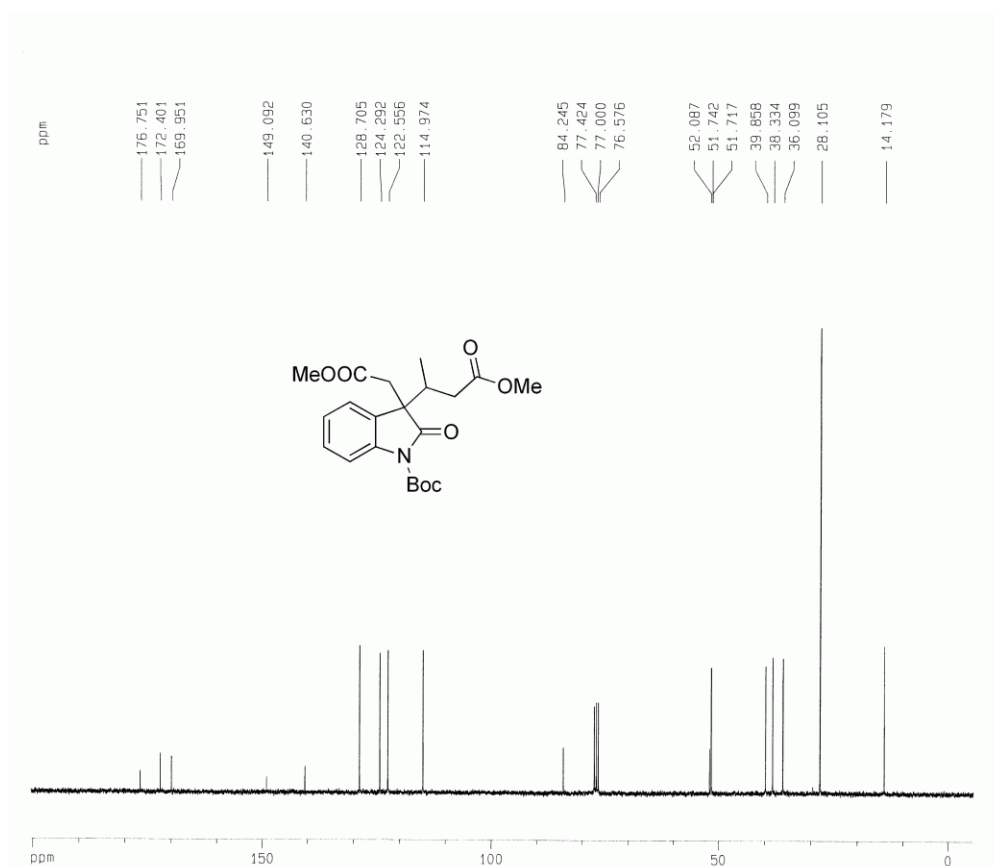
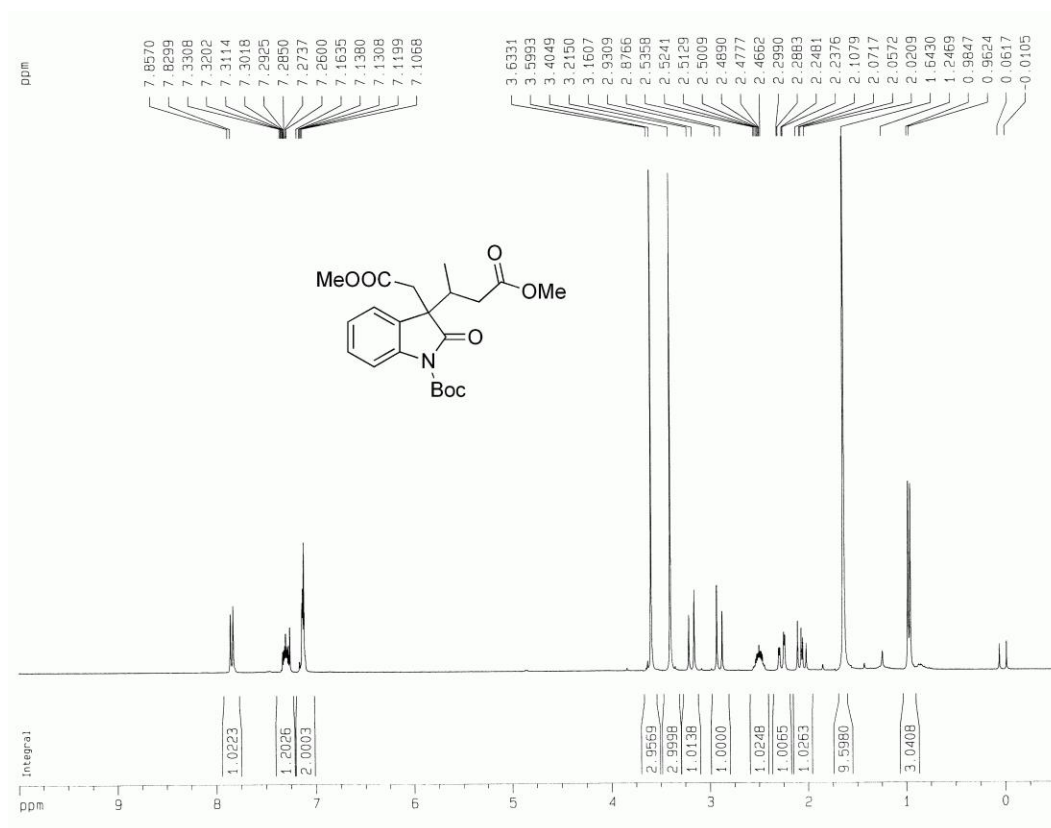
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.373	3588098	361288	15.365	20.103
2	7.265	8051151	686797	34.477	38.215
3	8.347	3674924	252271	15.737	14.037
4	9.605	8037734	496840	34.420	27.645
Total		23351907	1797195	100.000	100.000

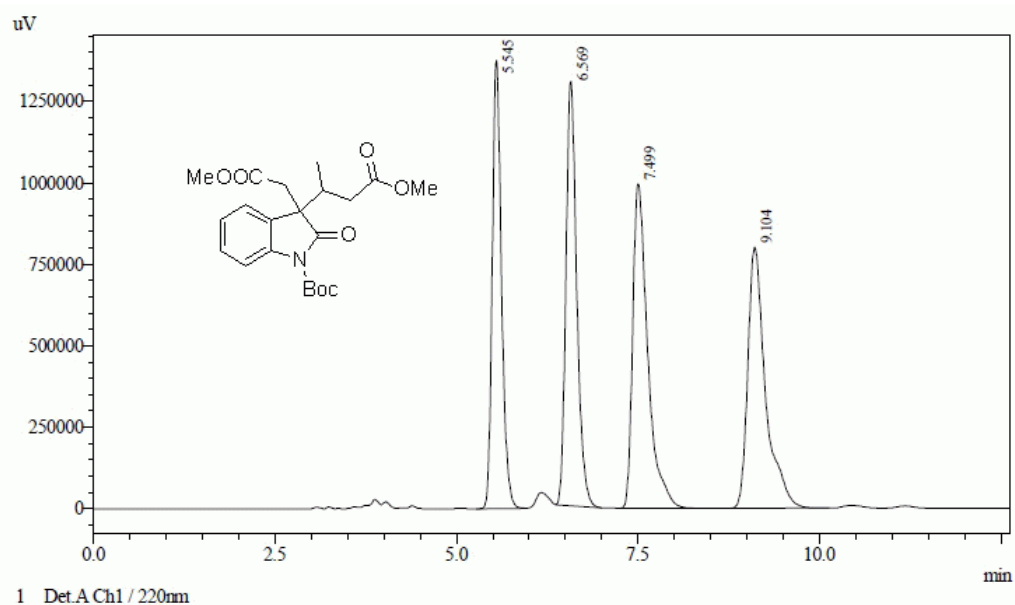


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

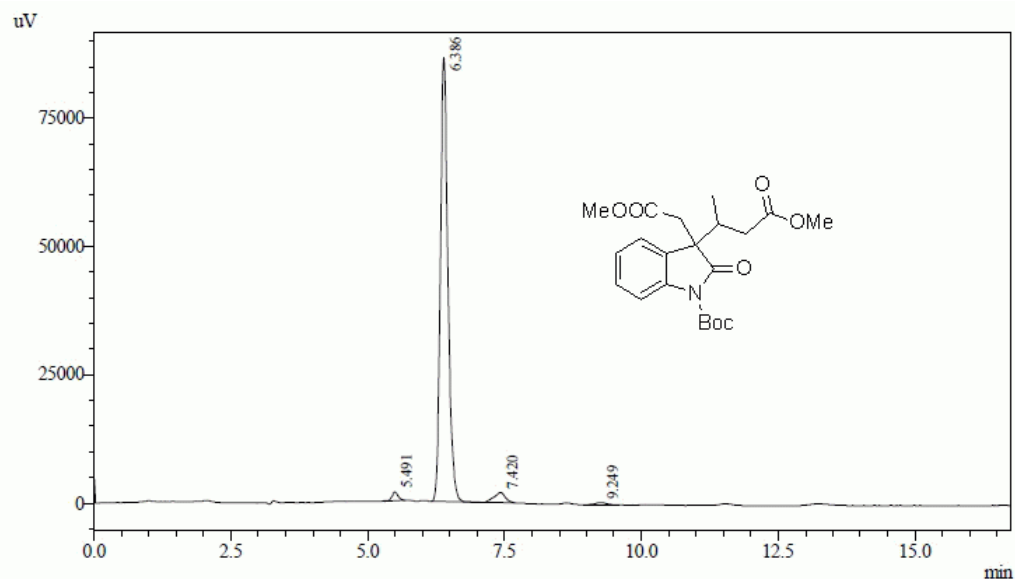
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.836	169479	20772	5.290	7.819
2	5.438	450546	47994	14.063	18.065
3	6.267	192971	16795	6.023	6.321
4	7.311	2390884	180116	74.625	67.795
Total		3203879	265677	100.000	100.000





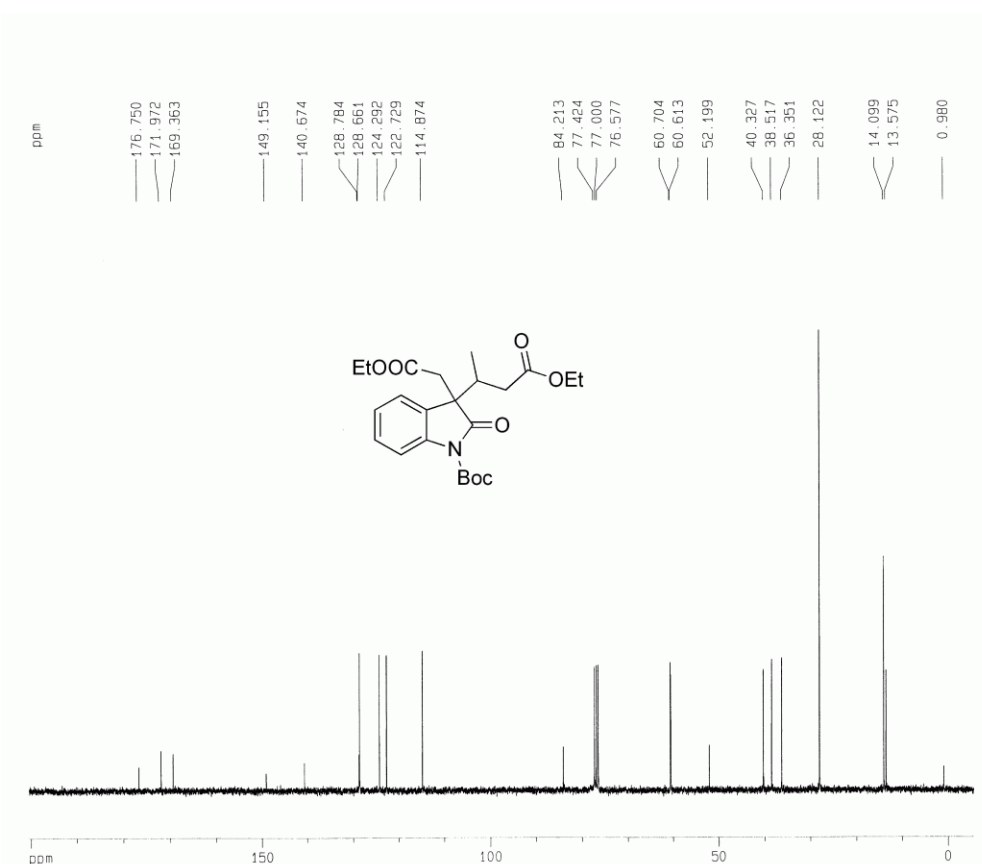
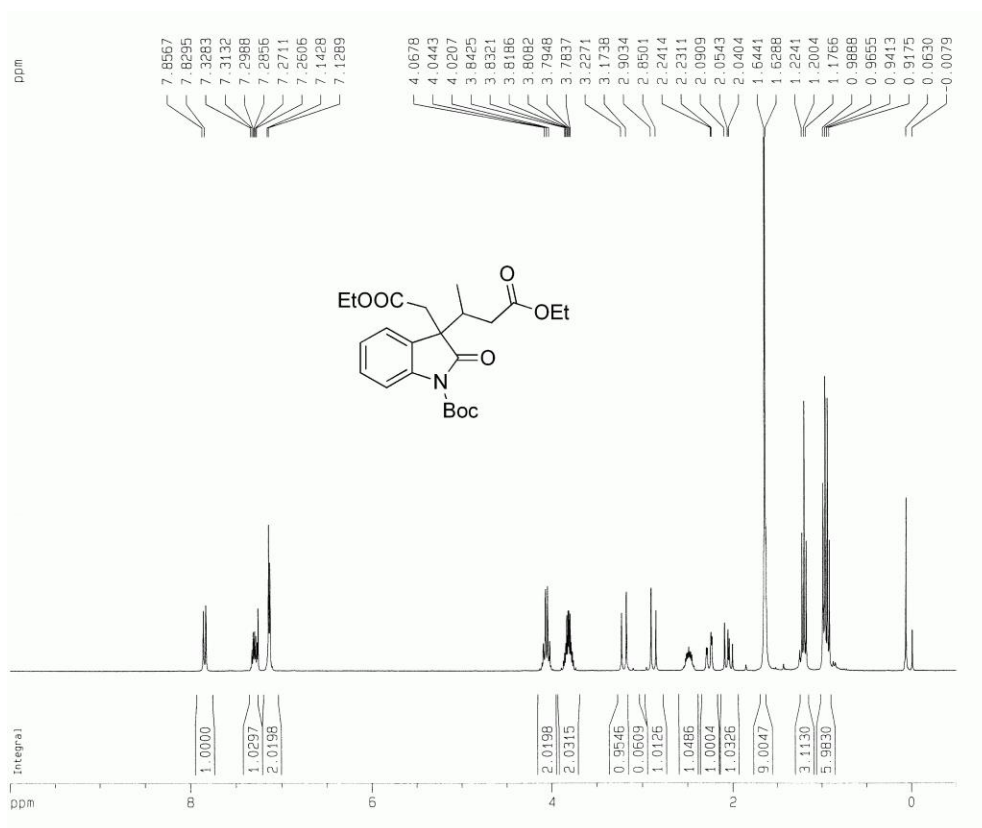
Detector A Ch1 220nm

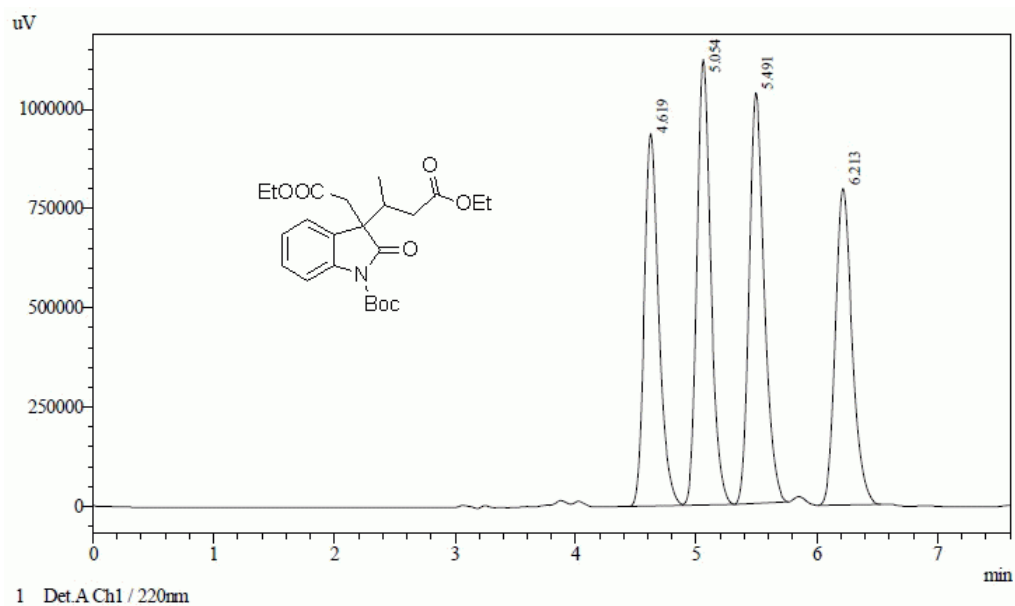
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.545	12126353	1376091	22.644	30.756
2	6.569	13453870	1301998	25.123	29.100
3	7.499	14332301	994970	26.764	22.238
4	9.104	13639041	801102	25.469	17.905
Total		53551566	4474161	100.000	100.000



Detector A Ch1 254nm

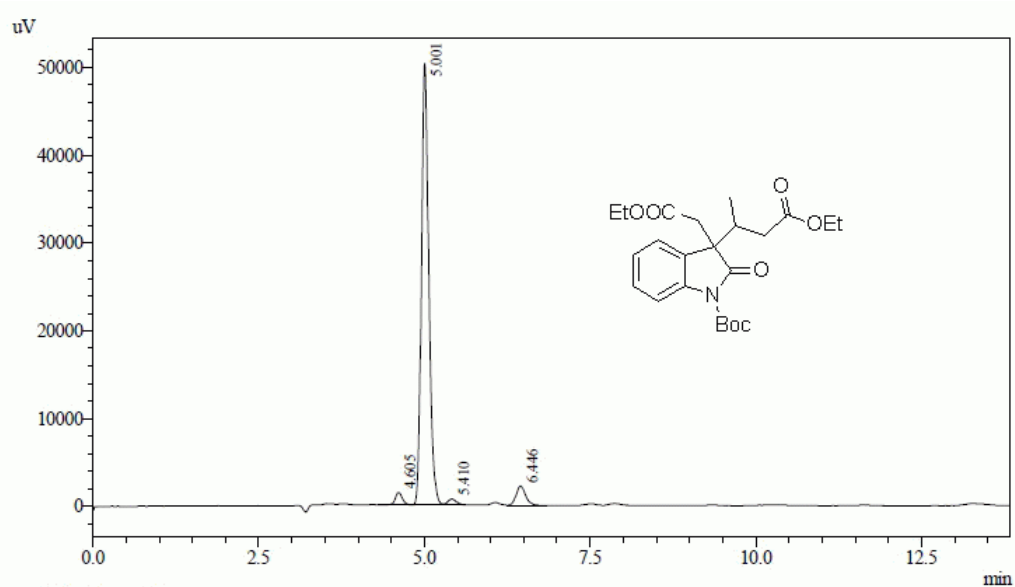
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.491	12785	1640	1.451	1.811
2	6.386	833132	86463	94.578	95.507
3	7.420	28901	1988	3.281	2.196
4	9.249	6074	440	0.690	0.486
Total		880892	90530	100.000	100.000





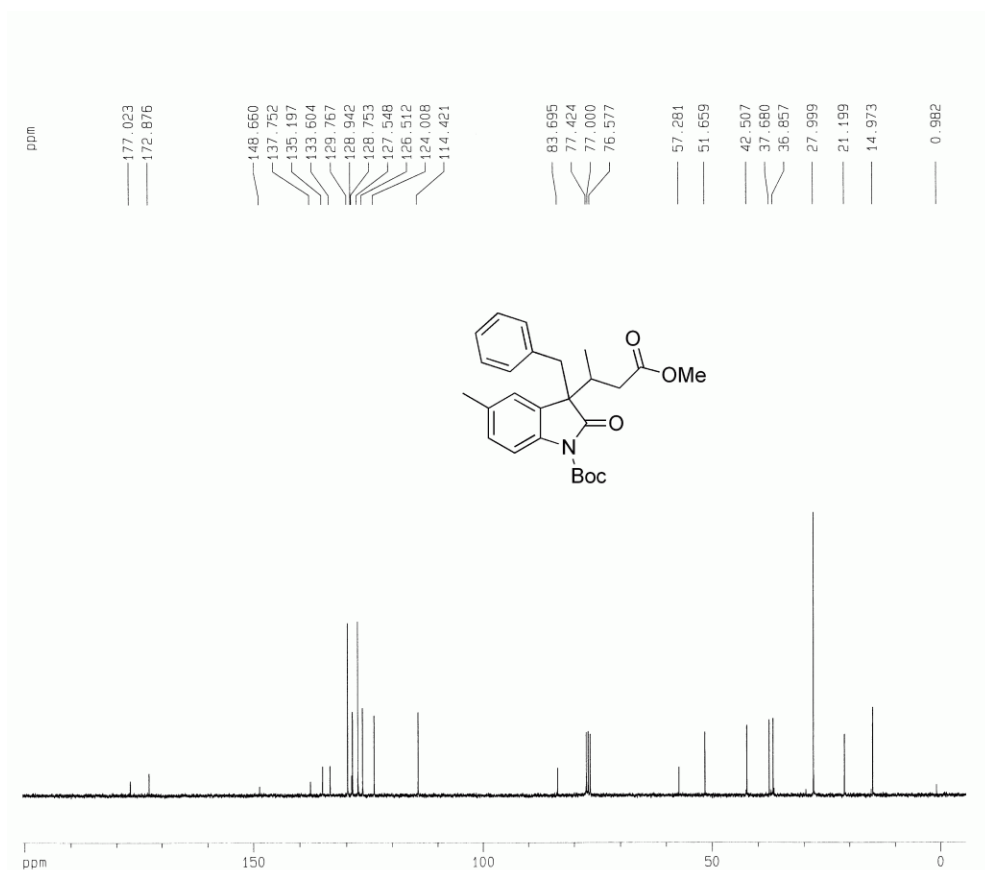
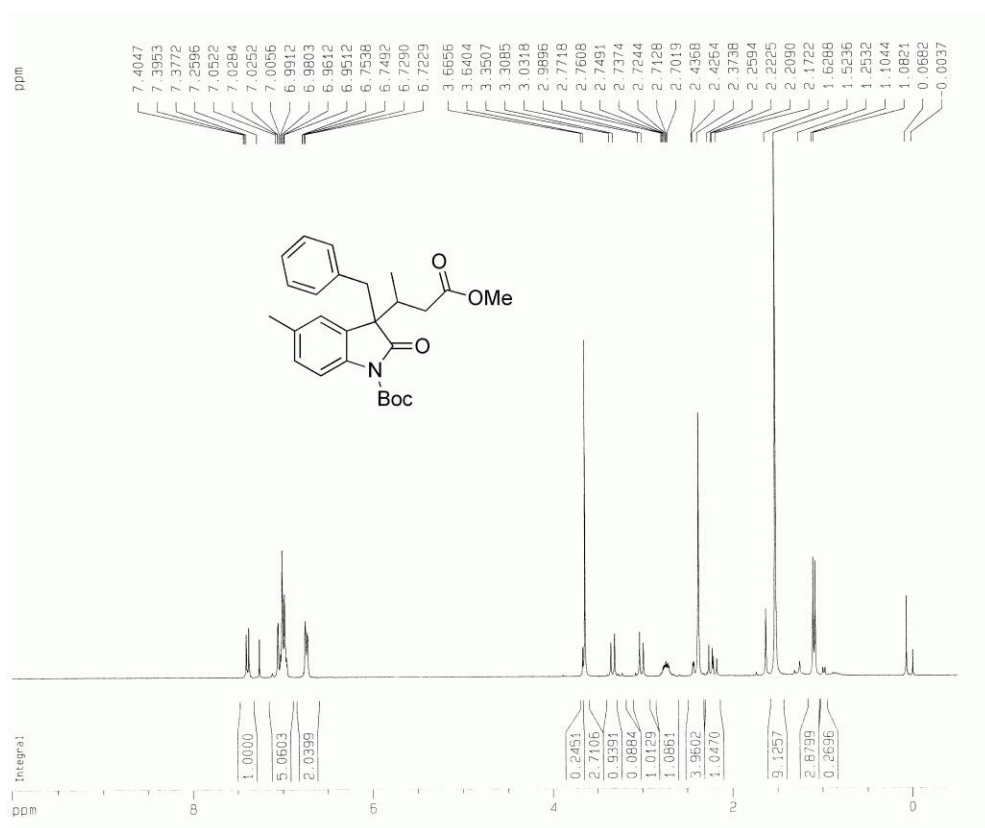
Detector A Ch1 220nm

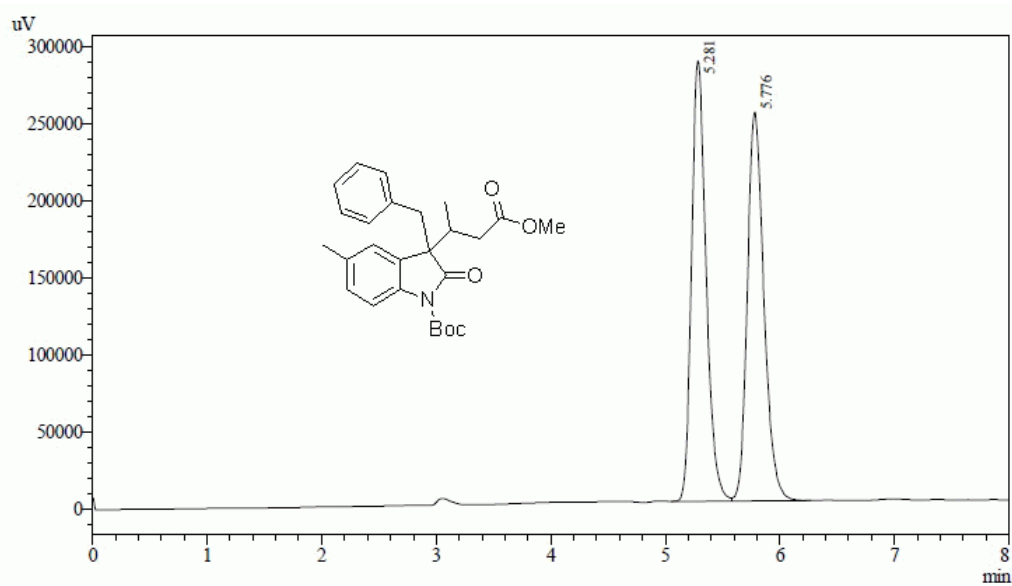
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.619	7843303	938564	23.352	24.118
2	5.054	8959334	1122053	26.675	28.833
3	5.491	9059725	1033211	26.974	26.550
4	6.213	7724305	797726	22.998	20.499
Total		33586666	3891554	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.605	10985	1444	2.554	2.644
2	5.001	390957	50295	90.915	92.061
3	5.410	6118	685	1.423	1.253
4	6.446	21964	2208	5.108	4.042
Total		430024	54632	100.000	100.000

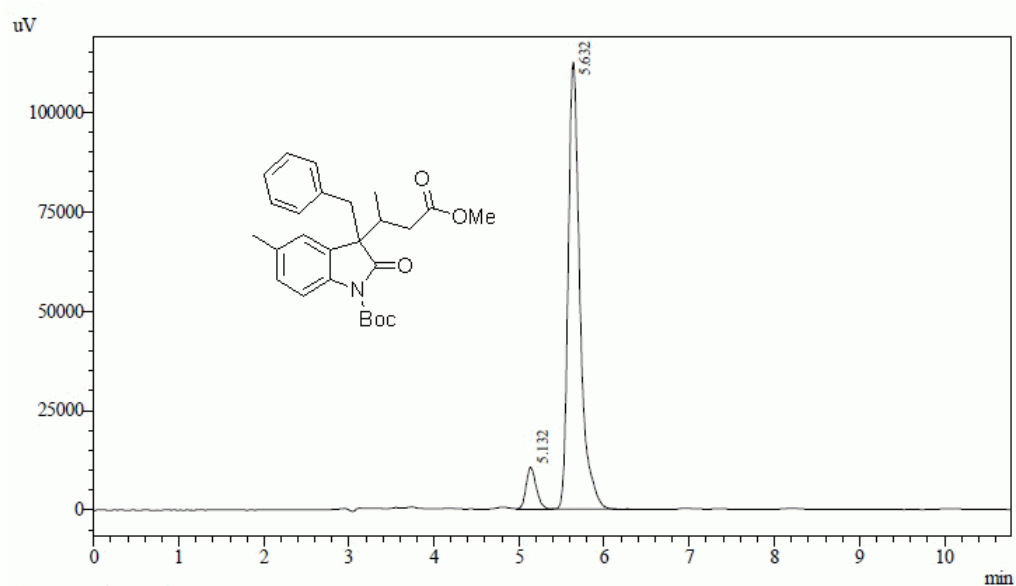




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

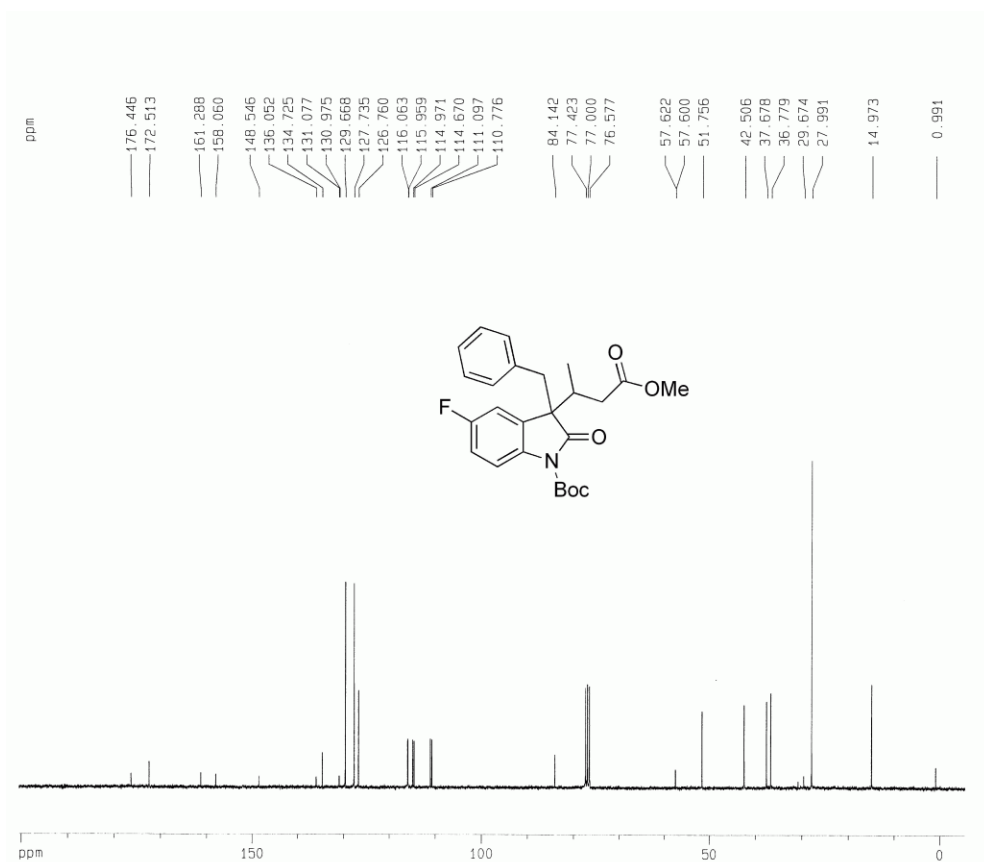
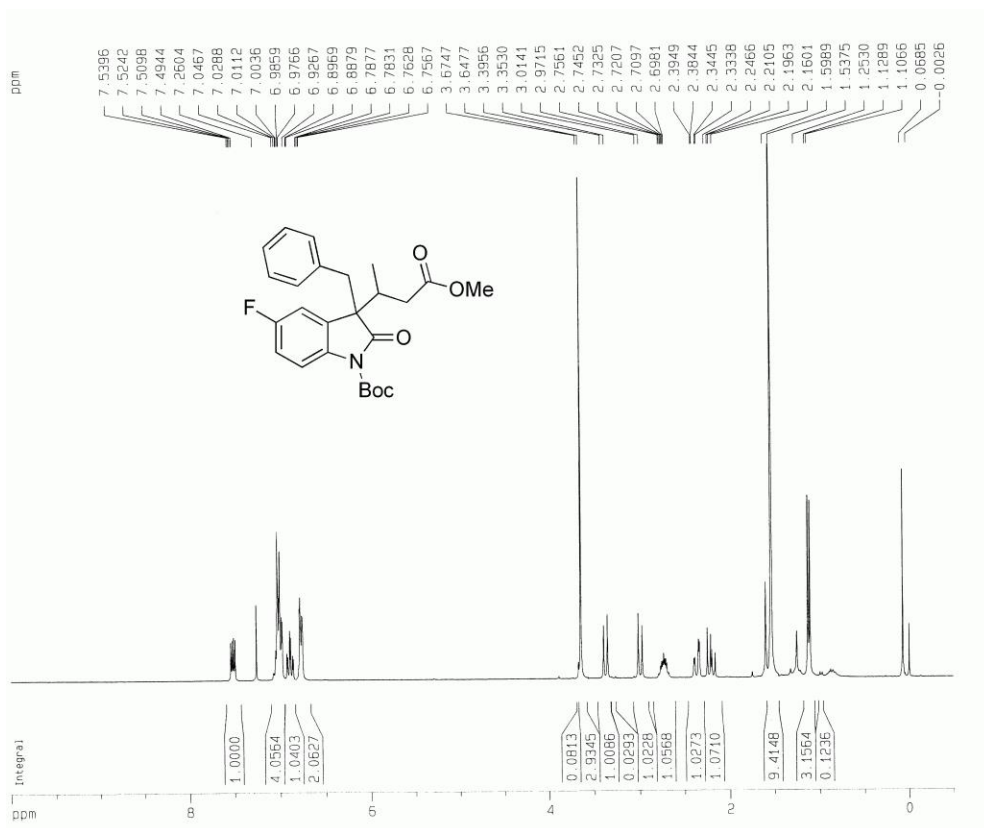
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.281	2527214	285760	49.949	53.111
2	5.776	2532422	252280	50.051	46.889
Total		5059636	538041	100.000	100.000

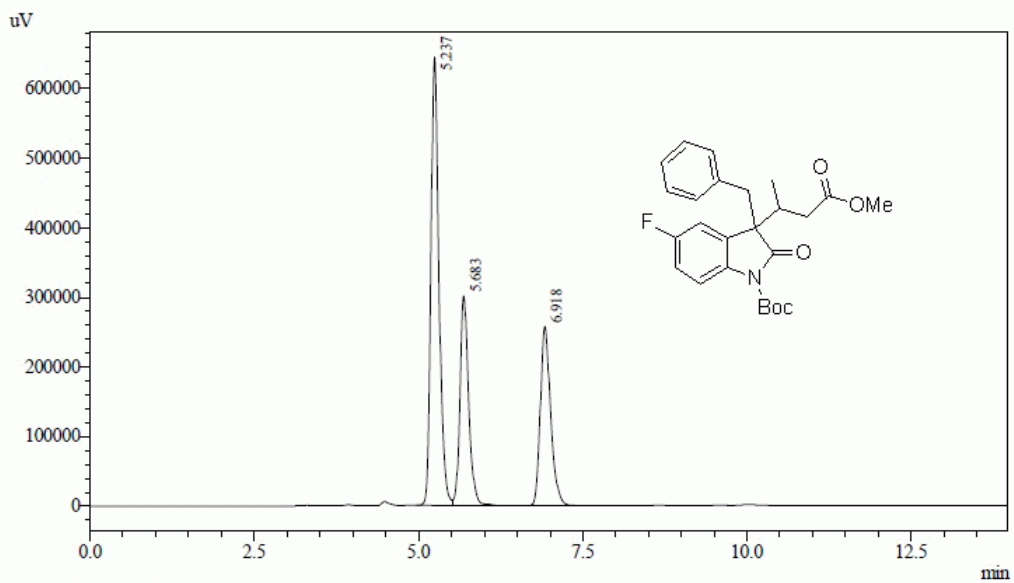


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.132	85947	10420	7.378	8.488
2	5.632	1078993	112348	92.622	91.512
Total		1164940	122768	100.000	100.000

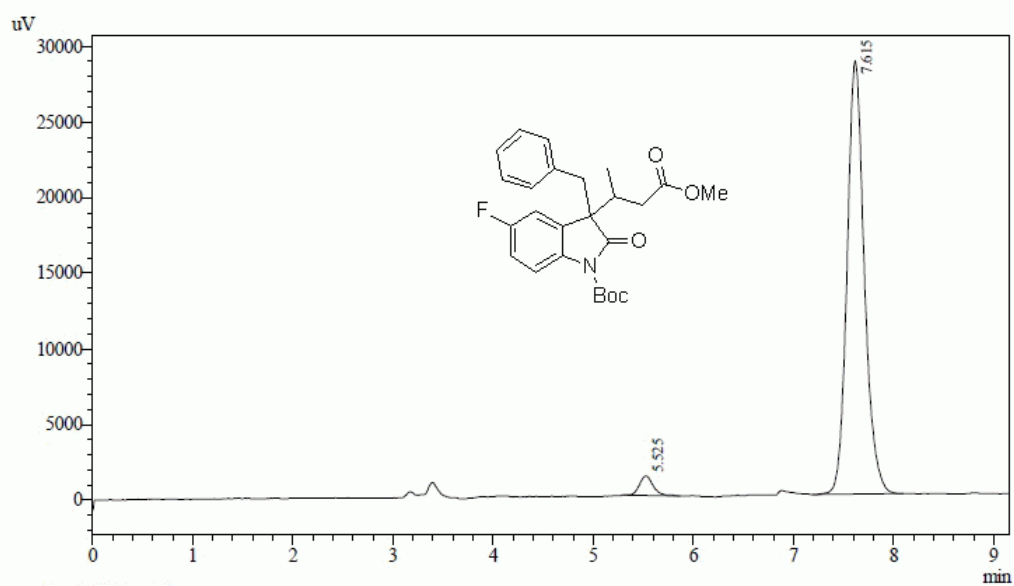




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

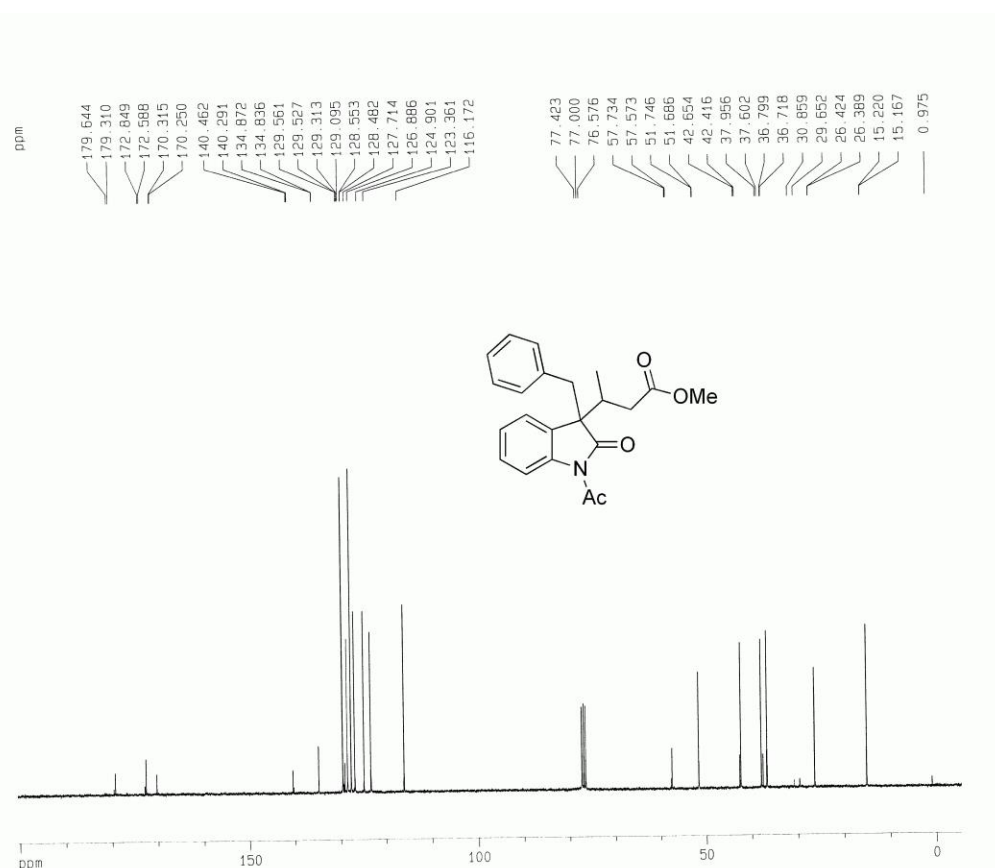
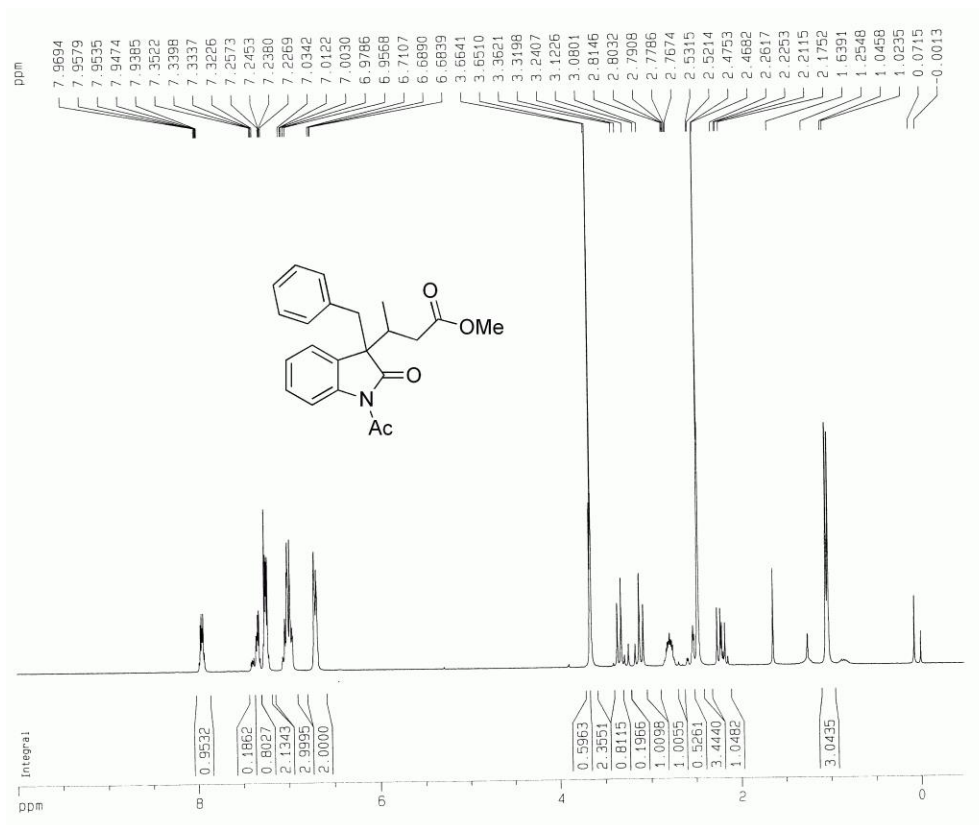
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.237	5501003	644149	49.517	53.547
2	5.683	2771792	301254	24.950	25.043
3	6.918	2836523	257561	25.533	21.411
Total		11109317	1202965	100.000	100.000

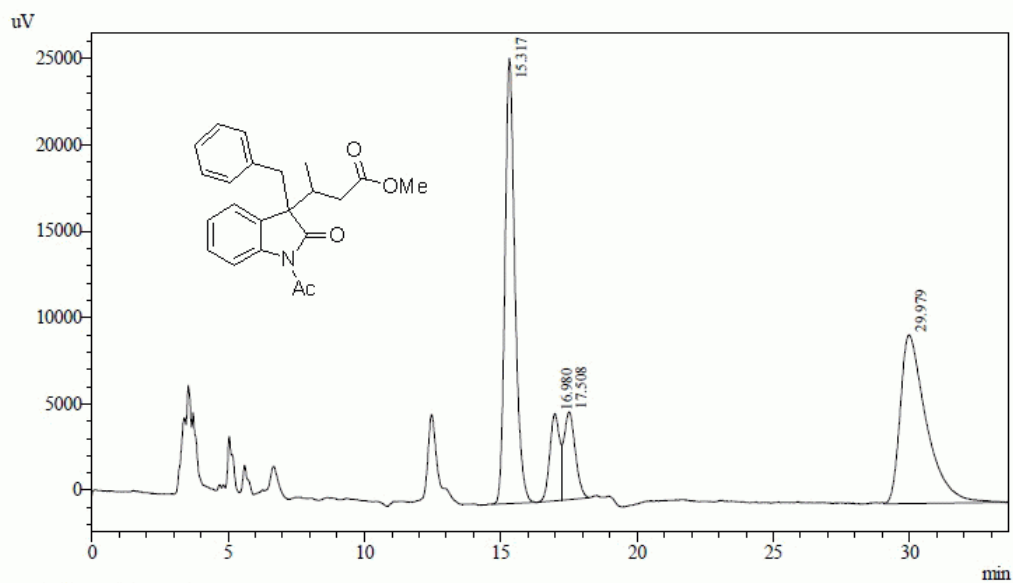


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.525	12320	1288	3.462	4.305
2	7.615	343513	28637	96.538	95.695
Total		355834	29926	100.000	100.000

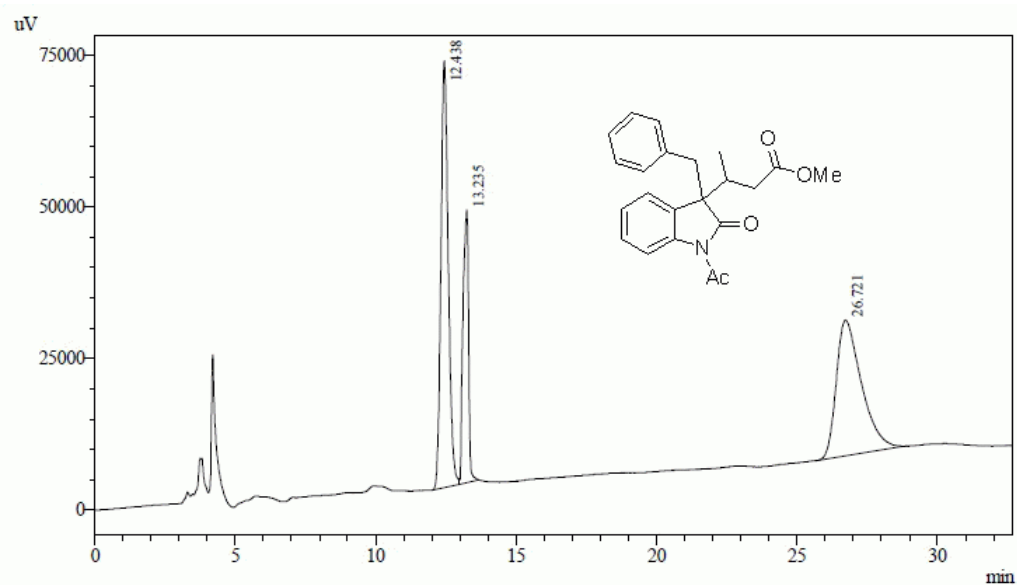




1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

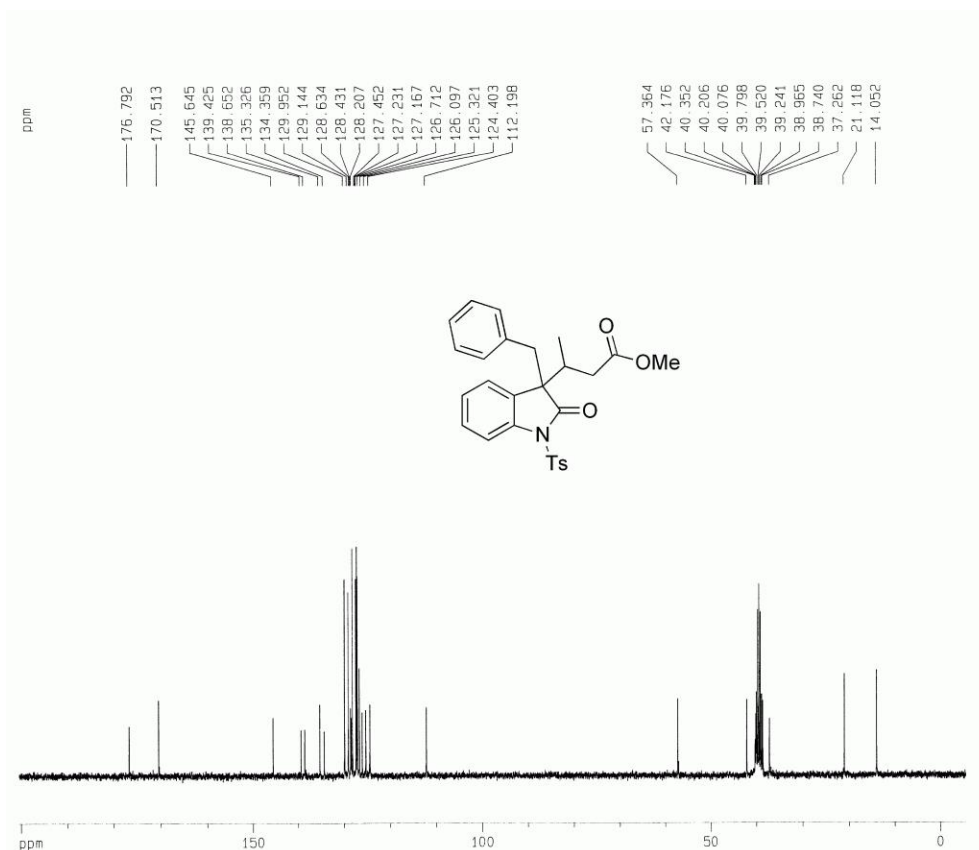
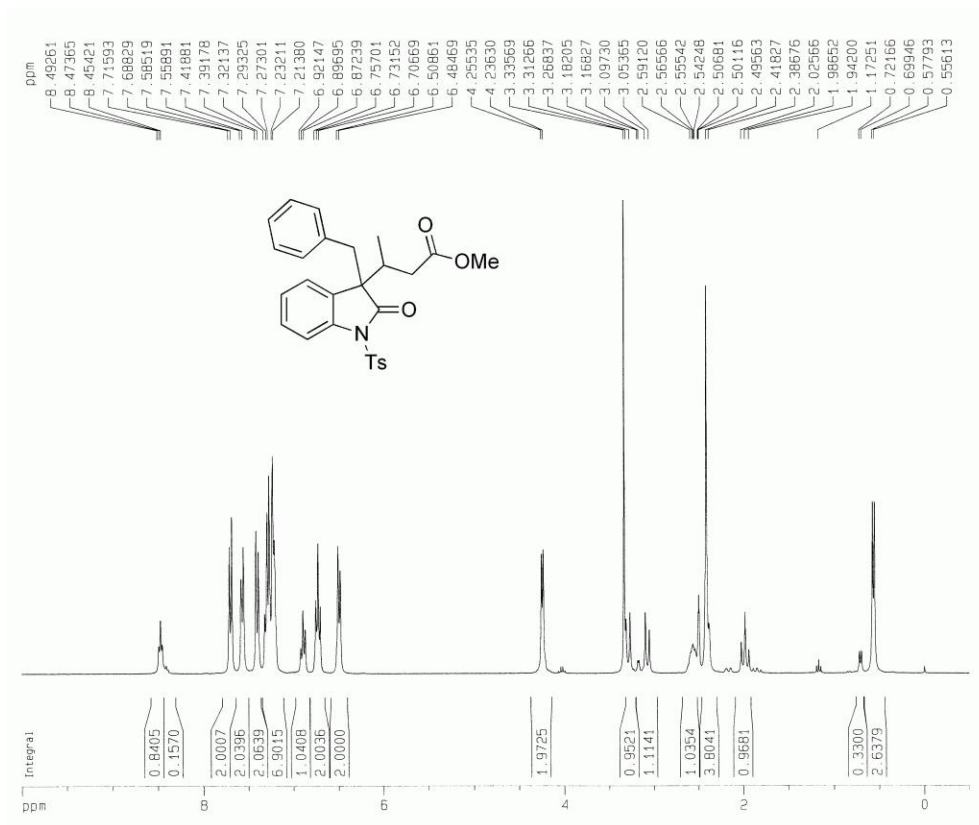
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.317	654943	25818	41.450	56.431
2	16.980	126939	5058	8.034	11.055
3	17.508	149789	5095	9.480	11.135
4	29.979	648396	9781	41.036	21.379
Total		1580068	45751	100.000	100.000

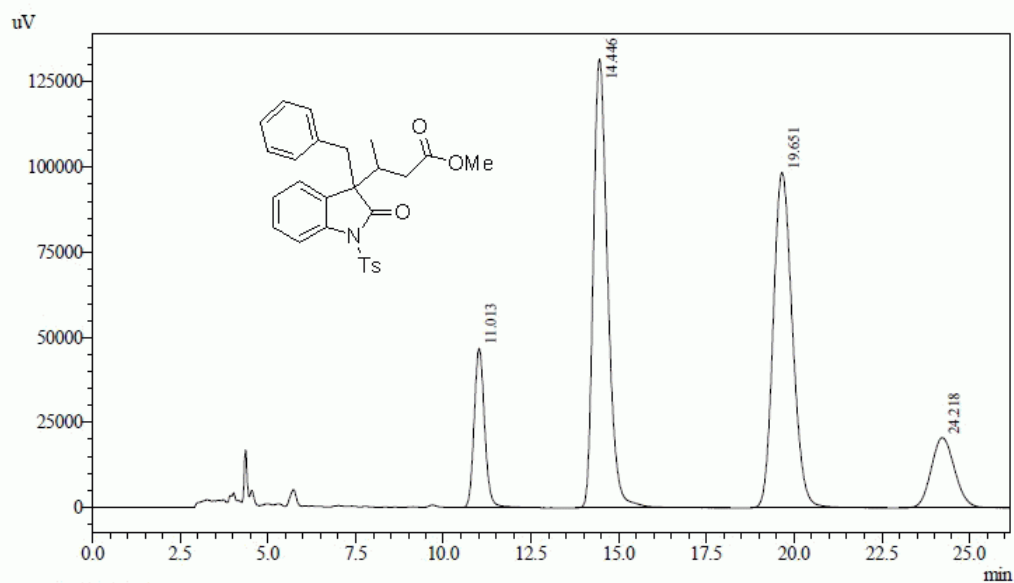


1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.438	1283256	70399	38.971	51.103
2	13.235	618449	45001	18.782	32.666
3	26.721	1391116	22360	42.247	16.231
Total		3292821	137759	100.000	100.000

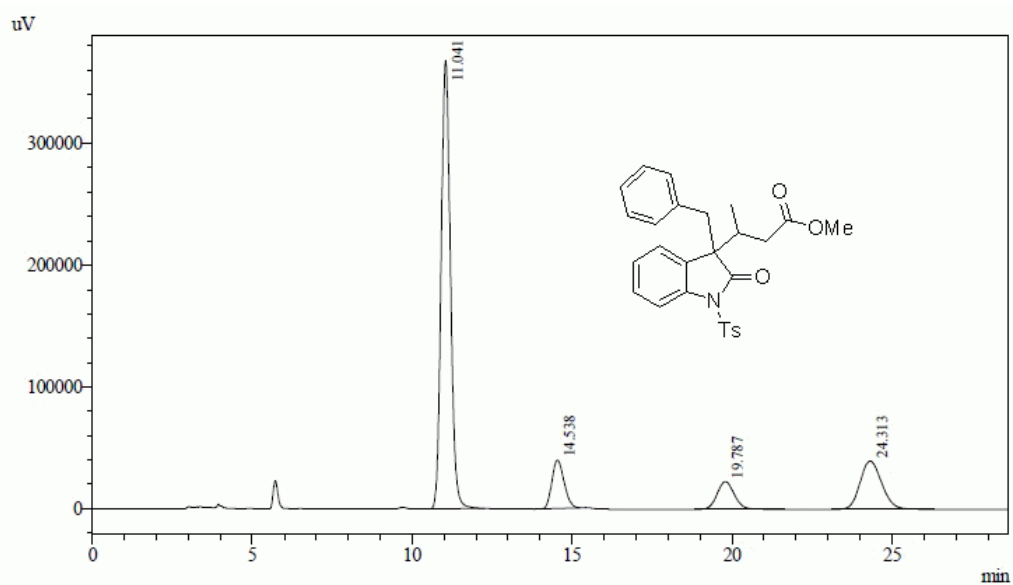




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

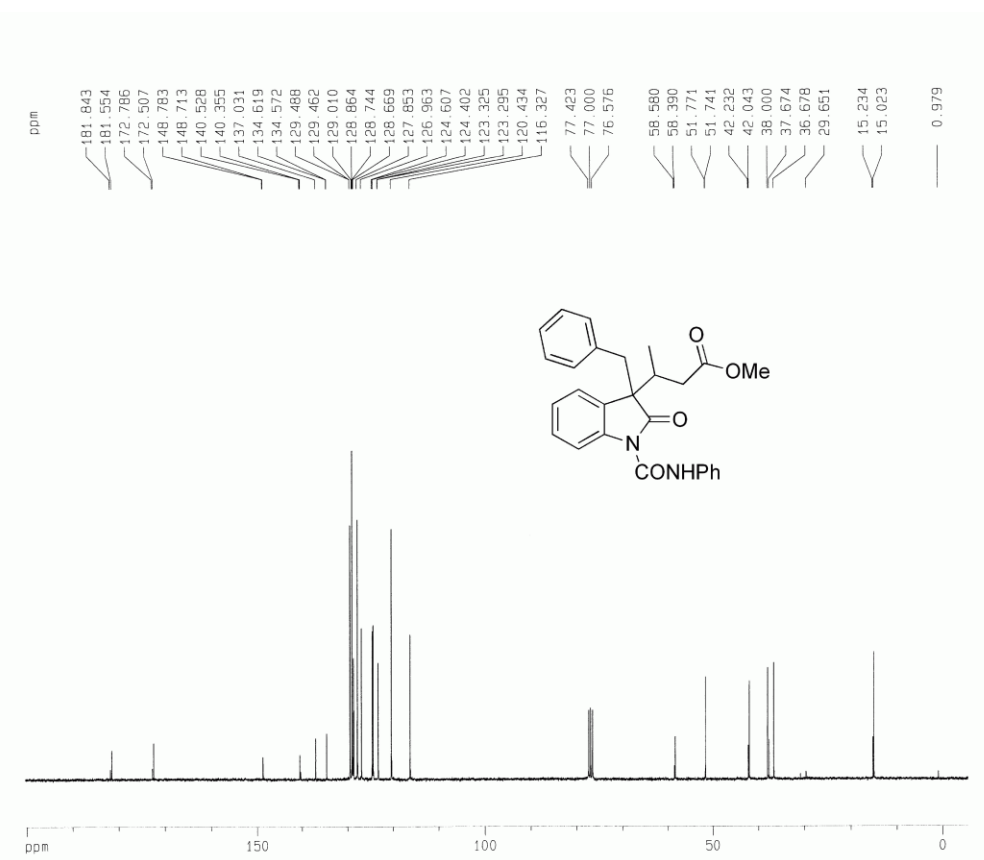
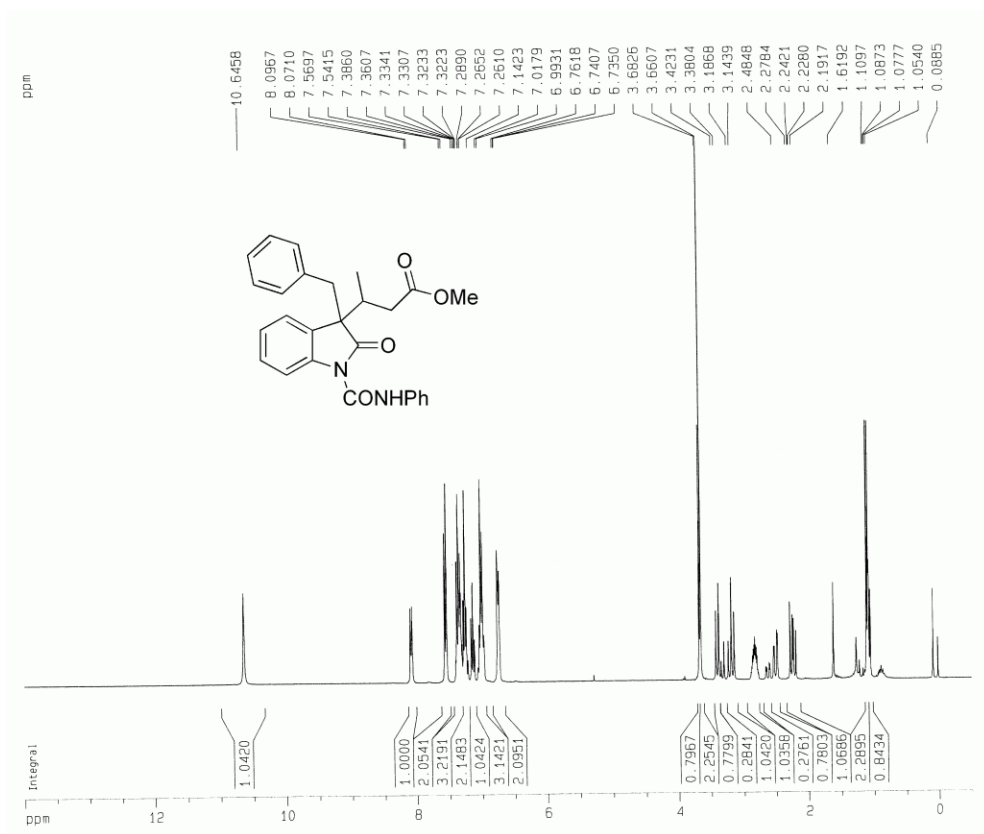
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.013	973739	46859	10.320	15.727
2	14.446	3753969	131941	39.785	44.283
3	19.651	3746086	98544	39.702	33.074
4	24.218	961779	20605	10.193	6.916
Total		9435573	297949	100.000	100.000

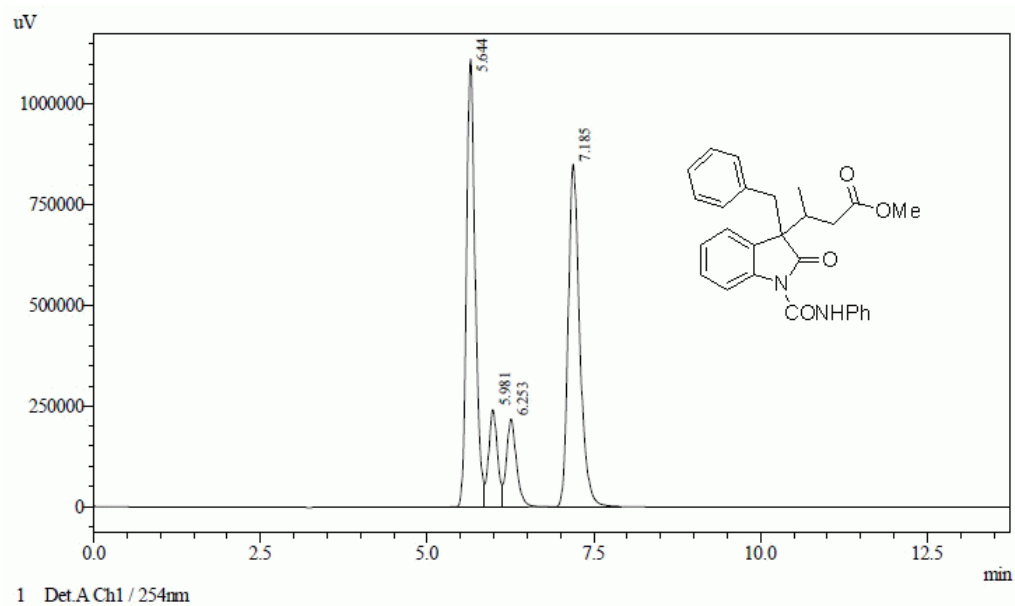


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

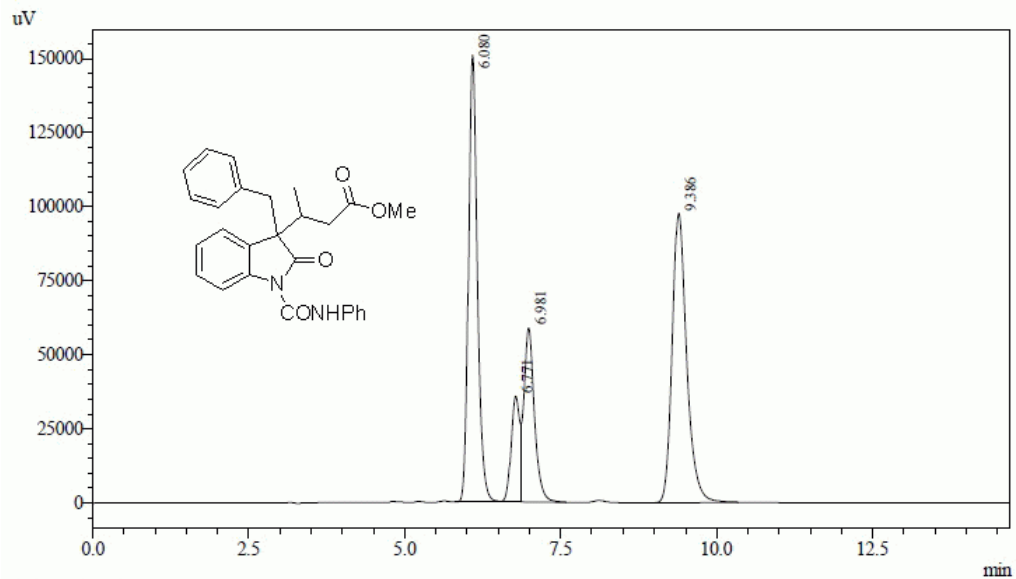
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.041	7441574	367868	66.365	78.286
2	14.538	1053325	39673	9.394	8.443
3	19.787	855481	22718	7.629	4.835
4	24.313	1862793	39645	16.613	8.437
Total		11213174	469904	100.000	100.000





Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.644	10137354	1113583	40.609	45.906
2	5.981	2254849	242353	9.033	9.991
3	6.253	2296518	218792	9.200	9.019
4	7.185	10274649	851060	41.159	35.084
Total		24963369	2425788	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.080	1484080	150881	36.248	43.970
2	6.771	338938	35819	8.278	10.438
3	6.981	704463	58781	17.206	17.130
4	9.386	1566813	97666	38.268	28.462
Total		4094293	343147	100.000	100.000