Palladium-Catalyzed Asymmetric Allylic Alkylation of 3-Aminooxindoles to Access Chiral Homoallylic Aminooxindoles

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Supporting Information

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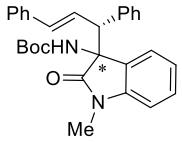
1. General remarks

Reagents were purchased from commercial sources and were directly used unless otherwise noted. Both catalysts and ligands **L1-10** were purchased from commercial sources [Daicel Chiral Technologies (China) Co., LTD]. 3-Aminooxindoles **1** were prepared according to the known method.[1] 1,3-Diphenylallyl acetates **2** were prepared according to the known method.[2] ^{1}H NMR and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded in $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). Datas are reported as the follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm).

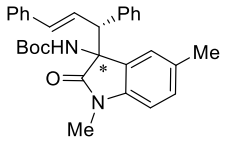
2. General procedure for the synthesis of compounds 3

In a 4 mL of flame-dried vial with a stir bar, the reactions were performed with **1** (0.1 mmol), **2** (0.15 mmol), $[\eta^3\text{-}C_3H_5ClPd]_2$ (0.005 mmol, 1.8 mg), **L3** (0.01 mmol, 6.2 mg), LiHMDS (0.1 mmol, 16.7 mg) in THF (0.1 mL) and TMSCl (0.15 mmol, 16.3 mg) in 2.0 mL of DCM at 25 °C under N_2 atmosphere. After completion of the reaction indicated by TLC, the mixture was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1~4:1) to afford the compounds **3a-x**. It is noted that it is very difficult to separate the two isomers for most products **3a-x** because of the impurity between the two diastereoisomers. Thus the characterization data of two mixed diastereoisomers of most products **3a-v** was given in the following parts.

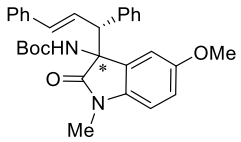


***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3a:** White solid; 43.2 mg, 95% yield (mixture of two diastereomers); 3:1 dr, 92/90% ee (major/minor); $[\alpha_{major}]_D^{25}$ = 54.5 (*c* 0.50, $CHCl_3$), $[\alpha_{minor}]_D^{25}$ = 65.2 (*c* 1.00, $CHCl_3$); mp 130.3-132.2 ºC. The ee was determined by HPLC (Chiralpak IA-3, ^{i}PrOH/hexane = 30/70, flow rate 0.5 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 14.6 min, t_{major} = 24.2 min; minor diastereomer: t_{minor} = 11.3 min, t_{major} = 26.6 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.33-7.20 (m, 7H), 7.12 (s, 3H), 7.06-7.03 (m, 1H), 6.98 (s, 2H), 6.68-6.67 (m, 2H), 6.50 (d, *J* = 6.4 Hz, 1H), 5.25 (bs, 1H), 3.89 (s, 1H), 2.91 (s, 3H), 1.18 (bs, 9H); δ (minor) 7.36 (d, *J* = 6.8 Hz, 2H), 7.32-7.28 (m, 3H), 7.25-7.20 (m, 2H), 7.15-7.14 (m, 3H), 7.09-7.05 (m, 1H), 7.01 (s, 2H), 6.71 (s, 1H), 6.62 (d, *J* = 15.2 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.28 (s,

1H), 3.92 (s, 1H), 2.93 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.7, 153.9, 143.6, 136.7, 136.5, 134.7, 129.0, 128.6, 128.1, 127.9, 127.6, 126.8, 125.1, 123.4, 122.4, 107.7, 80.6, 64.9, 56.6, 28.1, 26.0; δ (minor) 175.7, 153.9, 143.5, 136.9, 136.6, 134.7, 128.9, 128.6, 128.1, 127.9, 127.7, 126.7, 125.1, 123.3, 122.3, 107.7, 80.5, 64.9, 56.6, 28.1, 26.0. HRMS (ESI-TOF) calcd. for $C_{29}H_{31}N_2O_3$ $[M + H]^+$ 455.2329; found: 455.2328.

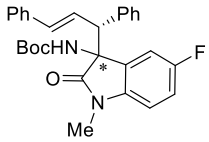


***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-1,5-dimethyl-2-oxoindolin-3-yl)carbamate 3b:** White solid; 45.8 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 95/92% ee (major/minor); $[\alpha]_D^{25}$ = 106.9 (*c* 0.68, $CHCl_3$); mp 166.2-168.1 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 22.0 min, t_{major} = 28.3 min; minor diastereomer: t_{minor} = 8.8 min, t_{major} = 12.9 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.45 (d, *J* = 7.2 Hz, 1.3H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.22 (m, 1H), 7.15-7.00 (m, 5H), 6.78-6.59 (m, 3.7H), 6.43-6.38 (m, 1H), 5.35-5.26 (m, 1H), 3.90 (d, *J* = 10.0 Hz, 1H), 2.91 (s, 0.7H), 2.68 (s, 2.3H), 2.44 (s, 2.3H), 2.36 (s, 0.7H), 1.35-1.05 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.5, 175.4, 153.9, 153.3, 141.7, 141.2, 137.0, 136.7, 136.3, 136.1, 134.6, 131.7, 129.5, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 128.0, 127.8, 127.6, 127.5, 126.7, 125.2, 124.2, 124.0, 107.7, 107.4, 80.5, 65.4, 64.9, 56.5, 56.2, 28.1, 26.0, 25.8, 21.5, 21.3. HRMS (ESI-TOF) calcd. for $C_{30}H_{33}N_2O_3$ $[M + H]^+$ 469.2486; found: 469.2483.

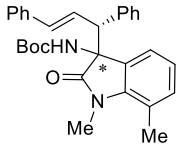


***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-5-methoxy-1-methyl-2-oxoindolin-3-yl)carbamate 3c:** White solid; 47.5 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 96/94% ee (major/minor); $[\alpha]_D^{25}$ = 168.2 (*c* 1.10, $CHCl_3$); mp 169.4-171.3 ºC. The ee was determined by HPLC (major diastereomer: Chiralpak IA-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 16.7 min, t_{major} = 28.1 min; minor diastereomer: Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 6.6 min, t_{major} = 7.8 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.44 (s, 1H), 7.38-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.21 (m, 0.5H), 7.14-7.10 (m, 1H), 7.09-6.94 (m, 3.5H), 6.82-6.59 (m, 5H), 6.44-6.39 (m, 1H), 5.36-5.27 (m, 1H), 3.91 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 2.3H), 3.81 (s, 0.7H), 2.91 (s, 0.7H), 2.68 (s, 2.3H), 1.33-1.07 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.2, 155.8, 155.7, 153.9, 153.5, 137.7, 137.1, 136.9, 136.6, 136.2, 136.0, 134.7, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.6, 127.5, 126.7, 125.1, 113.4, 112.8, 111.2, 108.1, 80.6,

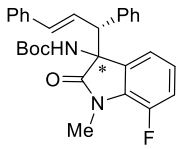
65.5, 65.2, 56.5, 56.1, 56.0, 55.9, 28.1, 26.1, 25.9. HRMS (ESI-TOF) calcd. for $C_{30}H_{32}N_2NaO_4$ [M + Na]$^+$ 507.2254; found: 507.2251.



***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-5-fluoro-1-methyl-2-oxoindolin-3-yl)carbamate 3d:** White solid; 46.3 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 93/91% ee (major/minor); $[\alpha]_D^{25}$ = 80.0 (*c* 0.75, $CHCl_3$); mp 113.2-115.1 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 13.7 min, t_{major} = 30.1 min; minor diastereomer: t_{minor} = 10.4 min, t_{major} = 19.5 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.45-7.29 (m, 4.5H), 7.21-6.89 (m, 6H), 6.79-6.61 (m, 3.5H), 6.43-6.40 (m, 1H), 5.37-5.31 (m, 1H), 3.93 (d, *J* = 10.0 Hz, 1H), 2.92 (s, 0.7H), 2.70 (s, 2.3H), 1.33-1.08 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.4, 175.3, 159.1 (d, *J* = 240.0 Hz, 1C), 153.5, 140.1, 135.7, 135.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 126.8, 124.4, 115.3 (d, *J* = 23.0 Hz, 1C), 111.4 (d, *J* = 26.0 Hz, 1C), 108.5, 108.2, 80.8, 65.4, 65.1, 56.6, 56.1, 28.1, 26.1, 26.0. HRMS (ESI-TOF) calcd. for $C_{29}H_{29}FN_2NaO_3$ [M + Na]$^+$ 495.2054; found: 495.2053.

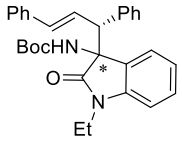


***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-1,7-dimethyl-2-oxoindolin-3-yl)carbamate 3e:** White solid; 45.4 mg, 97% yield (mixture of two diastereomers); 4:1 dr, 95/94% ee (major/minor); $[\alpha]_D^{25}$ = 91.2 (*c* 0.50, $CHCl_3$); mp 102.4-104.0 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 30.6 min, t_{major} = 21.8 min; minor diastereomer: t_{minor} = 10.4 min, t_{major} = 25.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.42-7.22 (m, 5.7H), 7.12-6.91 (m, 5.6H), 6.75-6.58 (m, 3.7H), 5.37-5.28 (m, 1H), 3.86 (d, *J* = 10.4 Hz, 1H), 3.16 (s, 0.7H), 2.92 (s, 2.3H), 2.27 (s, 0.7H), 2.24 (s, 2.3H), 1.32-1.06 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 176.3, 153.8, 153.5, 141.8, 141.2, 136.7, 136.6, 136.3, 136.0, 134.6, 132.8, 132.5, 128.9, 128.8, 128.6, 128.4, 128.3, 127.9, 127.8, 127.5, 126.7, 126.6, 125.1, 122.2, 122.1, 121.0, 80.4, 64.8, 64.4, 57.0, 56.4, 29.3, 28.0, 18.8, 18.7. HRMS (ESI-TOF) calcd. for $C_{30}H_{32}N_2NaO_3$ [M + Na]$^+$ 491.2305; found: 491.2303.

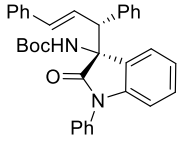


***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-7-fluoro-1-methyl-2-oxoindolin-3-yl)carbamate 3f:** White solid; 46.3 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 96/91% ee (major/minor); $[\alpha]_D^{25}$ = 87.3 (*c* 1.00, $CHCl_3$); mp 184.7-186.0 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80,

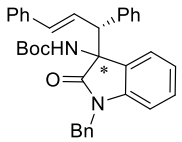
flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 28.9 min, t_{major} = 19.3 min; minor diastereomer: t_{minor} = 8.3 min, t_{major} = 19.1 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41-7.33 (m, 6H), 7.20-7.16 (m, 1H), 7.11-6.94 (m, 4H), 6.72-6.57 (m, 3.3H), 6.38-6.32 (m, 0.7H), 5.35-5.34 (m, 1H), 3.86 (d, J = 10.4 Hz, 1H), 3.09 (s, 0.5H), 2.86 (s, 2.5H), 1.30-1.05 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.3, 153.4, 142.9, 136.5, 136.1, 135.5, 131.7, 130.4, 128.8, 128.6 (d, J = 34.0 Hz, 1C), 128.4, 128.3, 128.0, 127.7, 126.7, 126.6, 126.4, 124.6, 122.8, 119.0, 117.2, 80.7, 75.0, 56.7, 56.1, 28.5, 28.2. HRMS (ESI-TOF) calcd. for $C_{29}H_{29}FN_2NaO_3$ [M + Na]$^+$ 495.2054; found: 495.2052.



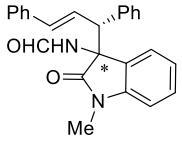
***Tert*-butyl (3-((*R*,*E*)-1,3-diphenylallyl)-1-ethyl-2-oxoindolin-3-yl)carbamate 3g:** White solid; 38.9 mg, 83% yield (mixture of two diastereomers); 3:1 dr, 94/64% ee (major/minor); $[\alpha]_D^{25}$ = 30.2 (c 0.50, $CHCl_3$); mp 171.0-172.6 ºC. The ee was determined by HPLC (Chiralpak IA-3, ^{i}PrOH/hexane = 30/70, flow rate 0.5 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.9 min, t_{major} = 22.2 min; minor diastereomer: t_{minor} = 10.4 min, t_{major} = 21.3 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.45-7.29 (m, 6.5H), 7.23-7.00 (m, 5H), 6.77-6.56 (m, 4.5H), 5.37-5.27 (m, 1H), 3.92 (d, J = 10.4 Hz, 1H), 3.74-3.65 (m, 1H), 3.11 (s, 1H), 1.34-1.05 (m, 9H), 0.90 (t, J = 7.2 Hz, 0.75H), 0.50 (t, J = 7.2 Hz, 2.25H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.0, 153.6, 143.5, 136.2, 134.6, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 127.9, 127.6, 126.7, 123.5, 122.1, 108.1, 80.5, 64.9, 56.3, 34.7, 34.4, 28.1, 12.4, 11.6. HRMS (ESI-TOF) calcd. for $C_{30}H_{32}N_2NaO_2$ [M + Na]$^+$ 491.2305; found: 491.2303.



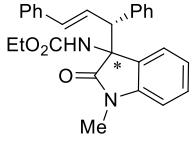
***Tert*-butyl ((*R*)-3-((*R*,*E*)-1,3-diphenylallyl)-2-oxo-1-phenylindolin-3-yl)carbamate 3h:** White solid; 42.3 mg, 82% yield (mixture of two diastereomers); 6:1 dr, 93% ee (major); $[\alpha]_D^{25}$ = 24.2 (c 0.50, $CHCl_3$); mp 177.8-179.1 ºC. The ee was determined by HPLC (Chiralpak IA-3, ^{i}PrOH/hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 20.1 min, t_{major} = 26.4 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.47 (t, J = 8.4 Hz, 3H), 7.38-7.26 (m, 6H), 7.22-7.14 (m, 3H), 7.05 (t, J = 7.6 Hz, 2H), 6.80-6.69 (m, 6H), 6.45 (s, 1H), 5.40 (s, 1H), 3.97 (d, J = 9.6 Hz, 1H), 1.28 (bs, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 174.9, 153.7, 144.3, 136.2, 134.1, 129.6, 129.5, 129.3, 129.1, 128.9, 128.8, 128.4, 128.1, 127.9, 127.7, 127.2, 126.8, 123.5, 122.8, 109.3, 80.7, 65.2, 56.4, 28.2. HRMS (ESI-TOF) calcd. for $C_{34}H_{32}N_2NaO_3$ [M + Na]$^+$ 539.2305; found: 539.2303.



***Tert*-butyl (1-benzyl-3-((*R*,*E*)-1,3-diphenylallyl)-2-oxoindolin-3-yl)carbamate 3i:** White solid; 42.5 mg, 80% yield (mixture of two diastereomers); 4:1 dr, 96/91% ee (major/minor); $[\alpha]_D^{25}$ = 9.6 (*c* 0.50, $CHCl_3$); mp 165.4-167.0 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 29.3 min, t_{major} = 14.1 min; minor diastereomer: t_{minor} = 6.2 min, t_{major} = 23.9 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.53-7.47 (m, 2.5H), 7.43-7.37 (m, 3H), 7.35-7.30 (m, 2.5H), 7.22-7.05 (m, 7H), 6.84-6.81 (m, 1.5H), 6.77-6.74 (m, 1H), 6.70-6.60 (m, 2H), 6.48-6.38 (m, 1.5H), 5.47-5.41 (m, 1H), 4.87 (bs, 1H), 4.48 (bs, 1H), 4.10 (d, *J* = 8.0 Hz, 0.2H), 4.05 (d, *J* = 9.2 Hz, 0.8H), 1.40-1.25 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 176.1, 153.9, 153.6, 143.9, 143.0, 136.7, 136.4, 136.3, 135.4, 131.8, 130.4, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 127.8, 127.7, 127.6, 127.3, 127.1, 127.0, 126.8, 126.7, 126.6, 126.4, 125.6, 125.1, 123.9, 123.5, 122.4, 122.3, 109.5, 109.1, 80.6, 64.7, 64.5, 56.2, 56.1, 44.4, 44.3, 28.1. HRMS (ESI-TOF) calcd. for $C_{35}H_{34}N_2NaO_3$ $[M + Na]^+$ 553.2462; found: 553.2457.

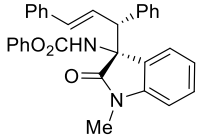


***N*-(3-((*R*,*E*)-1,3-diphenylallyl)-1-methyl-2-oxoindolin-3-yl)formamide 3j:** White solid; 37.5 mg, 98% yield (mixture of two diastereomers); 3:1 dr, 95/95% ee (major/minor); $[\alpha]_D^{25}$ = 60.2 (*c* 0.50, $CHCl_3$); mp 136.1-137.9 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.0 min, t_{major} = 10.1 min; minor diastereomer: t_{minor} = 11.3 min, t_{major} = 8.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 8.02 (d, *J* = 4.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40-7.37 (m, 2.5H), 7.32-7.29 (m, 2.5H), 7.24-7.20 (m, 1H), 7.17-7.13 (m, 2H), 7.10-7.02 (m, 3H), 6.82-6.73 (m, 2H), 6.69-6.64 (m, 1H), 6.60-6.54 (m, 1.5H), 6.42 (s, 0.5H), 4.03 (d, *J* = 9.6 Hz, 0.7H), 3.99 (d, *J* = 9.6 Hz, 0.3H), 2.97 (s, 2H), 2.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 174.5, 174.4, 160.1, 159.7, 144.2, 143.6, 136.4, 136.0, 135.6, 135.3, 134.8, 129.5, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 126.8, 126.7, 124.8, 124.7, 123.4, 123.1, 122.5, 122.4, 108.3, 108.0, 64.1, 64.0, 56.0, 55.8, 26.2, 26.0. HRMS (ESI-TOF) calcd. for $C_{25}H_{22}N_2NaO_2$ $[M + Na]^+$ 405.1573; found: 405.1564.

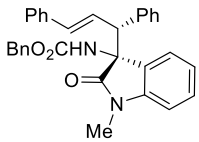


Ethyl (3-((*R*,*E*)-1,3-diphenylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3k: White solid; 41.3 mg, 97% yield (mixture of two diastereomers); 5:1 dr, 99% ee (major); $[\alpha]_D^{25}$ = 79.5 (*c* 3.66, $CHCl_3$); mp 168.8-172.0 ºC. The ee was

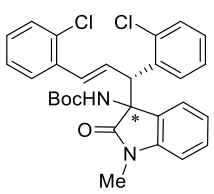
determined by HPLC (Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 1mL/min, λ = 254 nm, major diastereomer: t_{minor} = 11.1 min, t_{major} = 6.6 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.48-7.36 (m, 5H), 7.32-7.28 (m, 2H), 7.17-7.14 (m, 1H), 7.11-7.08 (m, 1H), 7.04-7.00 (m, 2H), 6.81-6.72 (m, 4H), 6.52 (d, J = 8.0 Hz, 1H), 5.58 (s, 1H), 4.02-3.95 (m, 3H), 2.76 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.3, 154.4, 144.2, 136.2, 135.8, 135.4, 129.5, 128.9, 128.6, 128.5, 128.4, 127.7, 127.6, 126.7, 125.0, 123.3, 122.4, 108.1, 65.1, 61.4, 56.1, 25.9, 14.5. HRMS (ESI-TOF) calcd. for $C_{27}H_{27}N_2O_3$ $[M + H]^+$ 427.2016; found: 427.2013.



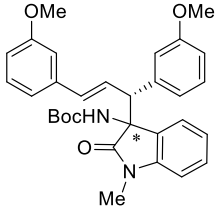
Phenyl ((*R*)-3-((*R*,*E*)-1,3-diphenylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3l: White solid; 44.9 mg, 95% yield (mixture of two diastereomers); 5:1 dr, 96% ee (major); $[\alpha]_D^{25}$ = 22.5 (*c* 0.50, $CHCl_3$); mp 179.5-181.1 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 14.9 min, t_{major} = 21.4 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.52-7.49 (m, 3H), 7.39 (t, J = 7.4 Hz, 2H), 7.34-7.29 (m, 2H), 7.27-7.22 (m, 3H), 7.17 (t, J = 7.6 Hz, 1H), 7.12-7.09 (m, 2H), 7.06-7.02 (m, 3H), 6.85 (d, J = 15.6 Hz, 1H), 6.79-6.73 (m, 3H), 6.50 (d, J = 8.0 Hz, 1H), 5.93 (bs, 1H), 4.05 (d, J = 10.0 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 174.8, 152.5, 150.6, 144.4, 136.2, 135.7, 129.7, 129.3, 129.0, 128.6, 127.8, 127.7, 126.8, 125.6, 124.9, 123.5, 122.6, 121.6, 108.3, 65.3, 56.2, 26.0. HRMS (ESI-TOF) calcd. for $C_{31}H_{26}N_2NaO_3$ $[M + Na]^+$ 497.1836; found: 497.1846.



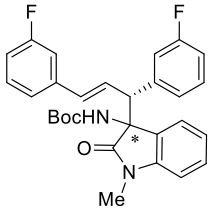
Benzyl ((*R*)-3-((*R*,*E*)-1,3-diphenylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3m: White solid; 46.9 mg, 96% yield (mixture of two diastereomers); 5:1 dr, >99% ee (major); $[\alpha]_D^{25}$ = 68.0 (*c* 0.60, $CHCl_3$); mp 95.2-96.9 ºC. The ee was determined by HPLC (Chiralpak OD-H, ^{i}PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.8 min, t_{major} = 12.9 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.45 (d, J = 7.6 Hz, 3H), 7.38-7.26 (m, 8H), 7.17 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 7.03 (t, J = 7.4 Hz, 2H), 6.82-6.66 (m, 5H), 6.54 (s, 1H), 5.69 (bs, 1H), 4.99-4.85 (m, 2H), 3.97 (d, J = 9.6 Hz, 1H), 2.78-2.68 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.2, 154.3, 144.2, 136.1, 135.8, 135.5, 129.5, 128.8, 128.5, 128.4, 127.7, 127.6, 126.8, 124.7, 123.4, 122.4, 108.2, 67.4, 65.3, 56.1, 25.9. HRMS (ESI-TOF) calcd. for $C_{32}H_{29}N_2O_3$ $[M + H]^+$ 489.2173; found: 489.2169.



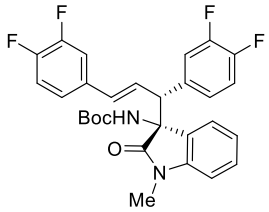
***Tert*-butyl (3-((*R*,*E*)-1,3-bis(2-chlorophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3n:** Yellow oil; 23.6 mg, 45% yield (mixture of two diastereomers); 2:1 dr, 60/66% ee (major/minor); $[\alpha]_D^{25}$ = 31.9 (*c* 1.39, $CHCl_3$). The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 12.3 min, t_{major} = 17.2 min; minor diastereomer: t_{minor} = 6.9 min, t_{major} = 8.1 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.53-7.40 (m, 1.4H), 7.36-7.27 (m, 3H), 7.24-6.87 (m, 7H), 6.73-6.63 (m, 1H), 6.55-6.50 (m, 1H), 6.42-6.35 (m, 0.6H), 5.45-5.35 (m, 1H), 4.86-4.80 (m, 1H), 3.07 (s, 1H), 2.87 (s, 2H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.8, 175.2, 153.9, 153.6, 144.5, 143.1, 134.8, 134.6, 134.5, 134.1, 133.9, 133.3, 133.1, 131.7, 131.2, 130.0, 129.9, 129.8, 129.7, 129.5, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 128.0, 127.6, 127.2, 127.0, 126.9, 126.2, 126.1, 124.3, 123.4, 122.6, 122.2, 108.1, 107.4, 80.6, 64.9, 64.4, 50.6, 28.1, 26.2, 26.1. HRMS (ESI-TOF) calcd. for $C_{29}H_{28}Cl_2N_2NaO_3$ $[M + Na]^+$ 545.1369; found: 545.1365.



***Tert*-butyl (3-((*R*,*E*)-1,3-bis(3-methoxyphenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3o:** White solid; 44.2 mg, 82% yield (mixture of two diastereomers); 4:1 dr, 91/84% ee (major/minor); $[\alpha]_D^{25}$ = 89.8 (*c* 0.5, $CHCl_3$); mp 141.6-143.0 ºC. The ee was determined by HPLC (Chiralpak OD-3, ^{i}PrOH/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.4 min, t_{major} = 6.8 min; minor diastereomer: t_{minor} = 5.7 min, t_{major} = 6.3 min).^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41 (d, *J* = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.23-7.19 (m, 0.5H), 7.16-7.13 (m, 1H), 7.10-7.05 (m, 1H), 6.98-6.91 (m, 2H), 6.85-6.76 (m, 1.5H), 6.73-6.70 (m, 1H), 6.64-6.62 (m, 1H), 6.58-6.49 (m, 2H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.10 (s, 1H), 5.35-5.27 (m, 1H), 3.88 (d, *J* = 10.4 Hz, 1H), 3.83 (s, 2.4H), 3.79 (s, 0.6H), 3.65 (s, 0.6H), 3.50 (s, 2.4H), 2.95 (s, 0.6H), 2.73 (s, 2.4H), 1.33-1.03 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.5, 159.9, 159.7, 159.2, 158.7, 153.8, 153.5, 144.2, 143.7, 137.8, 137.3, 134.5, 129.8, 129.5, 129.2, 129.0, 128.8, 128.7, 125.2, 123.1, 122.7, 122.6, 122.3, 122.2, 121.3, 119.3, 119.2, 114.1, 113.6, 113.5, 112.6, 112.0, 107.7, 80.6, 64.8, 56.0, 55.4, 55.3, 55.2, 55.1, 28.0, 26.0. HRMS (ESI-TOF) calcd. for $C_{31}H_{35}N_2O_5$ $[M + H]^+$ 515.2540; found: 515.2535.

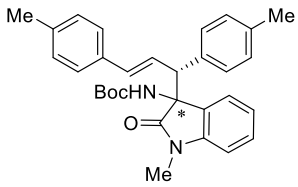


***Tert*-butyl (3-((*R*,*E*)-1,3-bis(3-fluorophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3p:** White solid; 33.4 mg, 68% yield (mixture of two diastereomers); 4:1 dr, 87/83% ee (major/minor); $[\alpha]_D^{25}$ = 69.7 (*c* 0.50, $CHCl_3$); mp 163.8-165.5 ºC. The ee was determined by HPLC (major diastereomer: Chiralpak OD-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 7.3 min, t_{major} = 6.5 min; minor diastereomer: Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 5.9 min, t_{major} = 6.4 min).^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41 (d, *J* = 8.0 Hz, 0.8H), 7.35-7.30 (m, 1.4H), 7.22-7.13 (m, 2.6H), 7.10-7.05 (m, 1.2H), 7.03-6.91 (m, 1.7H), 6.85-6.73 (m, 2H), 6.69-6.67 (m, 0.9H), 6.63-6.53 (m, 2.7H), 6.32 (d, *J* = 10.4 Hz, 0.7H), 5.26-5.24 (m, 1H), 3.99-3.90 (m, 1H), 2.95 (s, 1H), 2.76 (s, 2H), 1.33-1.21 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.3, 163.2 (d, *J* = 245.0 Hz, 1C), 163.1 (d, *J* = 244.0 Hz, 1C), 162.3 (d, *J* = 245.0 Hz, 1C), 162.0 (d, *J* = 245.0 Hz, 1C), 153.9, 153.6, 144.1, 143.4, 138.4 (d, *J* = 7.0 Hz, 1C), 134.0, 130.4 (d, *J* = 9.0 Hz, 1C), 130.2 (d, *J* = 8.0 Hz, 1C), 129.6, 129.5 (d, *J* = 8.0 Hz, 1C), 129.3, 129.2 (d, *J* = 8.0 Hz, 1C), 126.0, 124.6 (d, *J* = 3.0 Hz, 1C), 124.5 (d, *J* = 3.0 Hz, 1C), 123.2, 122.8 (d, *J* = 3.0 Hz, 1C), 122.7, 122.6, 115.8 (d, *J* = 22.0 Hz, 1C), 115.4 (d, *J* = 22.0 Hz, 1C), 115.2 (d, *J* = 22.0 Hz, 1C), 114.9 (d, *J* = 21.0 Hz, 1C), 114.6 (d, *J* = 21.0 Hz, 1C), 113.3 (d, *J* = 22.0 Hz, 1C), 113.1 (d, *J* = 21.0 Hz, 1C), 108.1, 107.9, 80.8, 80.7, 65.1, 64.8, 55.9, 55.6, 28.1, 26.0, 25.9. HRMS (ESI-TOF) calcd. for $C_{29}H_{29}F_2N_2O_3$ $[M + H]^+$ 491.2141; found: 491.2139.

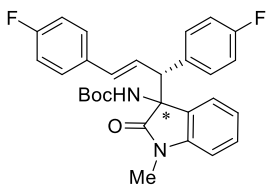


***Tert*-butyl ((*R*)-3-((*R*,*E*)-1,3-bis(3,4-difluorophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3q:** White solid; 48.4 mg, 92% yield (mixture of two diastereomers); 4:1 dr, 92/81% ee (major/minor); $[\alpha]_D^{25}$ = 102.9 (*c* 0.81, $CHCl_3$); mp 188.5-190.1 ºC. The ee was determined by HPLC (Chiralpak OD-H, ^{i}PrOH/hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.7 min, t_{major} = 8.0 min; minor diastereomer: t_{minor} = 5.8 min, t_{major} = 7.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41-7.28 (m, 2H), 7.23-7.09 (m, 3.7H), 6.89-6.82 (m, 1H), 6.79-6.72 (m, 0.5H), 6.65-6.58 (m, 1.8H), 6.55-6.39 (m, 3H), 5.21 (s, 1H), 3.87 (d, *J* = 10.4 Hz, 1H), 2.95 (s, 0.6H), 2.80 (s, 2.4H), 1.25-1.21 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.3, 153.5, 150.8 (dd, *J* = 15.0 Hz, 249.0 Hz, 1C), 150.5 (dd, *J* = 16.0 Hz, 253.0 Hz, 1C), 149.8 (dd, *J* = 12.0 Hz, 248.0 Hz, 1C), 149.5 (dd, *J* = 12.0 Hz, 247.0 Hz, 1C), 144.0, 143.2, 139.7, 134.1, 133.8, 133.1, 132.9, 129.8, 129.4, 125.0, 123.2, 122.7, 117.8 (d, *J* = 18.0 Hz, 1C),

117.2 (d, J = 17.0 Hz, 1C), 116.7 (d, J = 16.0 Hz, 1C), 116.5 (d, J = 17.0 Hz, 1C), 115.2 (d, J = 17.0 Hz, 1C), 115.1 (d, J = 18.0 Hz, 1C), 112.9, 108.3, 108.0, 81.0, 80.9, 65.0, 64.7, 54.9, 28.1, 26.1, 26.0. HRMS (ESI-TOF) calcd. for $C_{29}H_{26}F_4N_2NaO_3^+$ $[M + Na]^+$ 549.1772; found: 549.1771.

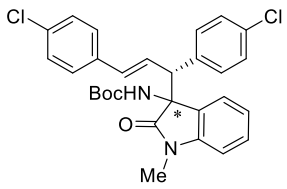


***Tert*-butyl (3-((*R*,*E*)-1,3-di-p-tolylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3r:** White solid; 45.9 mg, 95% yield (mixture of two diastereomers); 4:1 dr, 91/89% ee (major/minor); $[\alpha]_D^{25}$ = 115.7 (*c* 0.50, $CHCl_3$); mp 158.6-160.4 ºC. The ee was determined by HPLC (Chiralpak OD-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 10.5 min, t_{major} = 5.7 min; minor diastereomer: t_{minor} = 5.6 min, t_{major} = 6.0 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41-7.28 (m, 2.7H), 7.23-7.04 (m, 4.3H), 6.99-6.91 (m, 1H), 6.82 (d, J = 8.0 Hz, 1.4H), 6.73-6.69 (m, 1H), 6.62-6.50 (m, 3.6H), 5.38-5.26 (m, 1H), 3.86 (d, J = 10.4 Hz, 1H), 2.96 (s, 0.7H), 2.73 (s, 2.3H), 2.36 (s, 2.3H), 2.31 (s, 0.7H), 2.25 (s, 2.3H), 2.19 (s, 0.7H), 1.31-1.04 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.6, 153.9, 153.6, 144.1, 143.7, 138.2, 137.6, 137.0, 134.3, 134.0, 133.6, 133.1, 129.5, 129.3, 129.1, 128.9, 128.3, 126.6, 126.5, 124.1, 123.4, 123.2, 122.2, 122.1, 108.1, 107.7, 80.4, 64.9, 56.1, 55.9, 28.1, 26.1, 21.4, 21.3, 21.1, 21.0. HRMS (ESI-TOF) calcd. for $C_{31}H_{34}N_2NaO_3$ $[M + Na]^+$ 505.2462; found: 505.2460.

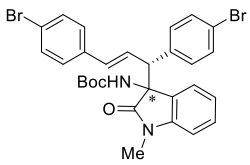


***Tert*-butyl (3-((*R*,*E*)-1,3-bis(4-fluorophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3s:** White solid; 48.1 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 93/91% ee (major/minor); $[\alpha]_D^{25}$ = 121.2 (*c* 2.88, $CHCl_3$); mp 156.3-158.0 ºC. The ee was determined by HPLC (major diastereomer: Chiralpak IA-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 16.1 min, t_{major} = 48.2 min; minor diastereomer: Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 6.0 min, t_{major} = 7.0 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.41-7.27 (m, 3.5H), 7.22-7.13 (m, 1H), 7.09-6.97 (m, 2.5H), 6.91-6.88 (m, 0.7H), 6.80-6.63 (m, 4.3H), 6.60-6.49 (m, 2H), 5.27 (s, 1H), 3.89 (d, J = 10.4 Hz, 1H), 2.92 (s, 1H), 2.74 (s, 2H), 1.28-1.19 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.5, 162.8 (d, J = 247.0 Hz, 1C), 162.0 (d, J = 242.0 Hz, 1C), 154.0, 144.0, 143.3, 134.3, 133.8, 132.6, 131.8, 130.4, 130.0 (d, J = 8.0 Hz, 1C), 129.4, 129.1, 128.4 (d, J = 7.0 Hz, 1C), 124.5, 123.2, 122.6, 122.5, 115.8 (d, J = 24.0 Hz, 1C), 115.5, 114.9, 114.6 (d, J = 21.0 Hz, 1C), 107.8, 80.8, 80.7, 65.2, 64.8, 55.8, 55.2, 28.1, 26.0, 25.8. HRMS (ESI-TOF) calcd. for $C_{29}H_{28}F_2N_2NaO_3$ $[M + Na]^+$ 513.1960; found:

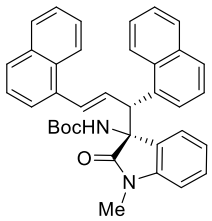
513.1958.



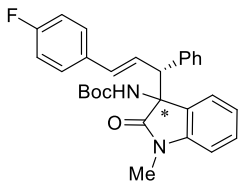
***Tert*-butyl (3-((*R*,*E*)-1,3-bis(4-chlorophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3t:** White solid; 50.8 mg, 97% yield (mixture of two diastereomers); 4:1 dr, 99/94% ee (major/minor); $[\alpha]_D^{25}$ = 92.5 (*c* 2.05, $CHCl_3$); mp 156.3-158.0 ºC. The ee was determined by HPLC (Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.2 min, t_{major} = 7.8 min; minor diastereomer: t_{minor} = 6.2 min, t_{major} = 7.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.40-7.27 (m, 4.8H), 7.23-7.13 (m, 1.2H), 7.09-7.05 (m, 1.4H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1.2H), 6.81-6.70 (m, 1H), 6.66-6.51 (m, 3.4H), 5.35-5.25 (m, 1H), 3.95-3.87 (m, 1H), 2.92 (s, 2H), 2.75 (s, 1H), 1.25-1.19 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.4, 175.3, 153.9, 153.6, 144.0, 144.3, 135.3, 134.9, 134.5, 134.4, 134.2, 133.8, 133.7, 133.5, 133.4, 130.1, 129.8, 129.5, 129.2, 129.0, 128.8, 128.1, 128.0, 127.9, 127.8, 125.3, 123.2, 122.6, 122.5, 108.3, 107.9, 80.8, 80.7, 65.1, 64.8, 55.8, 55.4, 28.1, 26.0, 25.9. HRMS (ESI-TOF) calcd. for $C_{29}H_{28}Cl_2N_2NaO_3$ $[M + Na]^+$ 545.1369; found: 545.1370.



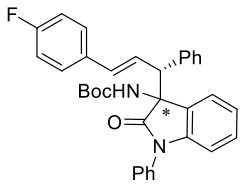
***Tert*-butyl (3-((*R*,*E*)-1,3-bis(4-bromophenyl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3u:** White solid; 60.0 mg, 98% yield (mixture of two diastereomers); 4:1 dr, 97/94% ee (major/minor); $[\alpha]_D^{25}$ = 107.8 (*c* 1.40, $CHCl_3$); mp 162.6-163.9 ºC. The ee was determined by HPLC (major diastereomer: Chiralpak OD-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 9.6 min, t_{major} = 7.6 min; minor diastereomer: Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, t_{minor} = 6.6 min, t_{major} = 7.9 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.49-7.39 (m, 3H), 7.32-7.20 (m, 4H), 7.15-7.05 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.68-6.52 (m, 4H), 5.23 (bs, 1H), 3.86 (d, *J* = 10.0 Hz, 1H), 2.92 (s, 0.7H), 2.75 (s, 2.3H), 1.25-1.20 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.4, 175.3, 153.9, 153.5, 144.0, 143.3, 135.3, 134.9, 134.8, 132.0, 131.8, 131.0, 130.8, 130.4, 130.2, 129.5, 129.2, 128.3, 128.2, 125.4, 123.2, 122.6, 122.5, 122.4, 121.9, 121.7, 121.6, 108.2, 108.0, 80.8, 80.7, 65.0, 64.7, 55.4, 28.1, 26.0, 25.9. HRMS (ESI-TOF) calcd. for $C_{29}H_{28}Br_2N_2NaO_3$ $[M + Na]^+$ 633.0359; found: 633.0356.



***Tert*-butyl ((*R*)-3-((*R*,*E*)-1,3-di(naphthalen-1-yl)allyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3v:** White solid; 36.6 mg, 66% yield (mixture of two diastereomers); 5:1 dr, 94% ee (major); $[\alpha]_D^{25}$ = 87.8 (*c* 0.70, $CHCl_3$); mp 89.3-90.9 ºC. The ee was determined by HPLC (Chiralpak OD-3, ^{i}PrOH/hexane = 20/80, flow rate 0.7 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 7.3 min, t_{major} = 6.8 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 8.43 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 6.8 Hz, 1H), 7.86-7.78 (m, 3H), 7.65-7.59 (m, 3H), 7.52-7.46 (m, 6H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.20-7.16 (m, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.73-6.67 (m, 2H), 6.49 (d, *J* = 7.6 Hz, 1H), 5.56 (bs, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 2.46 (d, *J* = 2.0 Hz, 3H), 1.27-1.23 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.6, 153.7, 144.5, 134.1, 133.8, 133.7, 132.1, 131.5, 131.1, 129.3, 128.7, 128.6, 128.0, 126.5, 126.2, 126.1, 125.9, 125.7, 125.6, 124.4, 124.3, 123.8, 123.5, 123.3, 122.5, 108.0, 80.6, 64.8, 49.2, 28.1, 25.7. HRMS (ESI-TOF) calcd. for $C_{37}H_{34}N_2NaO_3$ $[M + Na]^+$ 577.2462; found: 577.2458.



***Tert*-butyl (3-((*R*,*E*)-3-(4-fluorophenyl)-1-phenylallyl)-1-methyl-2-oxoindolin-3-yl)carbamate 3w:** White solid; 29.8 mg, 63% yield (mixture of two diastereomers); 2:1 dr, 90/95% ee (major/minor); $[\alpha]_D^{25}$ = 133.46 (*c* 0.76, $CHCl_3$); mp 149.6-151.2 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 9.7 min, t_{major} = 15.2 min; minor diastereomer: t_{minor} = 11.9 min, t_{major} = 27.7 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.42-7.25 (m, 6H), 7.18-7.00 (m, 3H), 6.76-6.47 (m, 6H), 5.31 (bs, 1H), 3.91-3.86 (m, 1H), 2.77-2.68 (m, 3H), 1.31-1.04 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.8, 175.5, 162.7 (d, *J* = 244.0 Hz, 1C), 162.1 (d, *J* = 244.0 Hz, 1C), 153.6, 144.0, 136.1, 136.0, 132.5, 131.9, 130.1 (d, *J* = 8.0 Hz, 1C), 129.4, 129.3, 128.9, 128.8, 128.5, 128.3 (d, *J* = 8.0 Hz, 1C), 127.7, 127.6, 126.8, 124.7, 123.2 (d, *J* = 4.0 Hz, 1C), 122.7, 122.6, 122.4, 122.3, 115.8 (d, *J* = 21.0 Hz, 1C), 114.5 (d, *J* = 21.0 Hz, 1C), 108.0, 80.7, 65.3, 56.1, 55.3, 28.1, 25.9. HRMS (ESI-TOF) calcd. for $C_{29}H_{29}FN_2NaO_3^+$ $[M + Na]^+$ 495.2054; found: 495.2052.

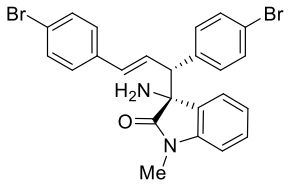


***Tert*-butyl (3-((*R*,*E*)-3-(4-fluorophenyl)-1-phenylallyl)-2-oxo-1-phenylindolin-3-yl)carbamate 3x:** White solid; 43.8 mg, 82% yield (mixture of two diastereomers); 2:1 dr, 96/91% ee (major/minor); $[\alpha]_D^{25}$ = 127.5 (*c* 1.0, $CHCl_3$); mp 81.5-83.1 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 15.3 min, t_{major} =

24.2 min; minor diastereomer: t_{minor} = 17.7 min, t_{major} = 15.3 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major + minor) 7.49-7.28 (m, 8H), 7.21-7.16 (m, 2H), 7.09-7.05 (m, 2H), 6.81-6.52 (m, 8H), 5.40 (bs, 1H), 4.01-3.97 (m, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major + minor) 175.0, 162.8 (d, J = 247.0 Hz, 1C), 162.3 (d, J = 245.0 Hz, 1C), 153.7, 136.2, 136.1, 134.1, 132.5, 132.1, 130.5 (d, J = 8.0 Hz, 1C), 129.6, 129.5, 129.4, 129.2, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 126.8, 124.8, 123.6 (d, J = 7.0 Hz, 1C), 122.9, 115.8 (d, J = 22.0 Hz, 1C), 114.9 (d, J = 21.0 Hz, 1C), 109.4, 109.3, 80.9, 65.3, 56.5, 55.6, 28.3. HRMS (ESI-TOF) calcd. for $C_{34}H_{32}FN_2O_3^+$ $[M + H]^+$ 535.2391; found: 535.2389.

3. Procedure for the synthesis of compounds 4-6

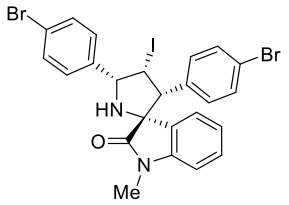
In a 50 mL of bottle with a stir bar, the reaction was performed with **3u** (208.1 mg, 0.34 mmol), TFA (0.1 mL, 1.3 mmol) in 5.0 mL DCM at 0 °C for 1 h. After completion of the reaction indicated by TLC, the mixture was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford the compound **4**.



(*R*)-3-amino-3-((*R*,*E*)-1,3-bis(4-bromophenyl)allyl)-1-methylindolin-2-one 4: White solid; 50.7 mg, 99% yield; >20:1 dr, 95% ee (major); $[\alpha]_D^{25}$ = 58.0 (*c* 1.22, $CHCl_3$); mp 75.3-77.1 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 26.3 min, t_{major} = 19.2 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.39 (d, J = 8.4 Hz, 2H), 7.28-7.19 (m, 6H), 7.05 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.75-6.69 (m, 1H), 6.59-6.55 (m, 2H), 3.78 (d, J = 10.0 Hz, 1H), 2.96 (s, 3H), 1.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 179.1, 143.2, 137.2, 135.9, 133.4, 131.8, 130.9, 130.5, 130.4, 129.5, 128.2, 126.2, 124.0, 122.8, 121.6, 121.2, 108.2, 64.4, 58.2, 26.0. HRMS (ESI-TOF) calcd. for $C_{24}H_{21}Br_2N_2O$ $[M + H]^+$ 511.0015; found: 511.0012.

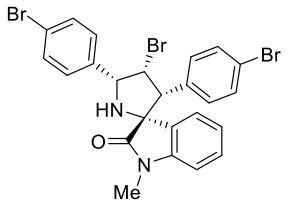
In a 10 mL of bottle with a stir bar. To a solution of **4** (51.0 mg, 0.1 mmol) in 2.0 mL acetonitrile was added I_2 (76.2 mg, 0.3 mmol) and $NaHCO_3$ (16.8 mg, 0.2 mmol) under -20 °C, and the mixture was stirred for 3 h. After completion of the reaction indicated by TLC, the reaction mixture was quenched with saturated sodium thiosulfate aqueous solution and 2 mL DCM, then the aqueous phase was extracted with DCM (3 ×4 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1)

to afford the compound **5**.



(3*R*,3'*R*,4'*R*,5'*R*)-3',5'-bis(4-bromophenyl)-4'-iodo-1-methylspiro[indoline-3,2'-pyrrolidin]-2-one 5: White solid; 60.0 mg, 94% yield; >20:1 dr, 90% ee (major); $[\alpha]_D^{25}$ = 63.0 (*c* 1.24, $CHCl_3$); mp 147.7-149.4 ºC. The ee was determined by HPLC (Chiralpak OD-H, ^{i}PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 10.1 min, t_{major} = 11.7 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.72 (d, *J* = 8.4 Hz, 2H), 7.56-7.45 (m, 3H), 7.31-7.25 (m, 3H), 7.21-7.13 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.04 (dd, *J* = 9.8 Hz, 12.2 Hz, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 3.83 (d, *J* = 12.4 Hz, 1H), 2.78 (s, 3H), 2.59 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 178.0, 143.3, 139.0, 138.7, 132.1, 132.0, 131.8, 131.3, 130.6, 130.0, 129.8, 129.6, 128.3, 123.5, 122.9, 122.6, 122.2, 108.4, 72.0, 66.0, 31.3, 25.9, 21.2. HRMS (ESI-TOF) calcd. for $C_{24}H_{20}Br_2IN_2O$ $[M + H]^+$ 636.8982; found: 636.8978.

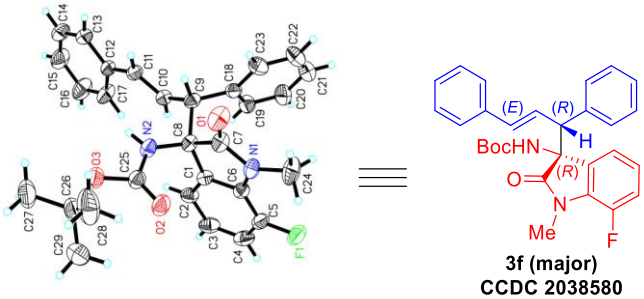
In a 10 mL of bottle with a stir bar. To a solution of **4** (51.0 mg, 0.1 mmol) in 2.0 mL acetonitrile was added NBS (53.2 mg, 0.3 mmol) and $NaHCO_3$ (16.8 mg, 0.2 mmol) under -20 °C, and the mixture was stirred for 4 h. After completion of the reaction indicated by TLC, the reaction mixture was quenched with saturated sodium thiosulfate aqueous solution and 2 mL DCM, then the aqueous phase was extracted with DCM (3 × 4 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford the compounds **6**.



(3*R*,3'*R*,4'*R*,5'*R*)-4'-bromo-3',5'-bis(4-bromophenyl)-1-methylspiro[indoline-3,2'-pyrrolidin]-2-one 6: White solid; 55.6 mg, 94% yield; >20:1 dr, 95% ee (major); $[\alpha]_D^{25}$ = 40.0 (*c* 0.50, $CHCl_3$); mp 239.9-241.6 ºC. The ee was determined by HPLC (Chiralpak AD-H, ^{i}PrOH/hexane = 10/90, flow rate 0.5 mL/min, λ = 254 nm, major diastereomer: t_{minor} = 45.1 min, t_{major} = 38.6 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.59-7.53 (m, 4H), 7.23-7.18 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.99 (d, *J* = 8.8 Hz, 1H), 4.48 (dd, *J* = 7.2 Hz, 12.0 Hz 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 3.14 (m, 3H), 2.73 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 178.8, 142.6, 138.9, 132.7, 131.9, 131.3, 130.7, 129.6, 129.4, 129.1, 124.8, 122.9, 122.4, 121.7, 108.5, 70.7, 68.3, 63.2, 54.0, 26.7. HRMS

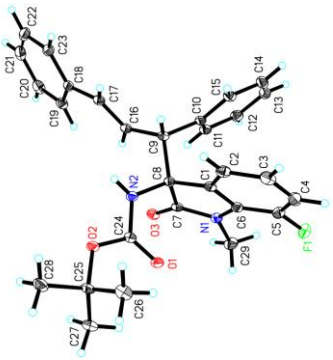
(ESI-TOF) calcd. for $C_{24}H_{20}Br_3N_2O$ $[M + H]^+$ 588.9120; found: 588.9123.

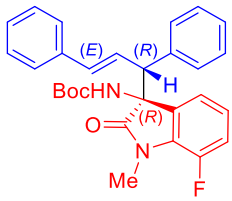
4. Crystallographic information for diastereomers of compound 3f



Chiral	Date
Identification code	ZC-2-2
Empirical formula	$C_{29}H_{29}FN_2O_3$
Formula weight	472.54
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2
a/Å	25.4371(5)
b/Å	6.95612(16)
c/Å	15.3764(2)
α/°	90
β/°	99.6850(16)
γ/°	90
Volume/Å^3	2681.98(9)
Z	4
ρ_{calc}g/cm^3	1.170
μ/mm^{-1}	0.654
F(000)	1000.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.83 to 147.416
Index ranges	-31 ≤ h ≤ 25, -7 ≤ k ≤ 8, -18 ≤ l ≤ 19
Reflections collected	10381
Independent reflections	4740 [R_{int} = 0.0168, R_{sigma} = 0.0214]
Data/restraints/parameters	4740/1/325
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0879
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0907
Largest diff. peak/hole / e Å^{-3}	0.12/-0.11

Flack/Hooft parameter	0.04(7)/0.08(7)



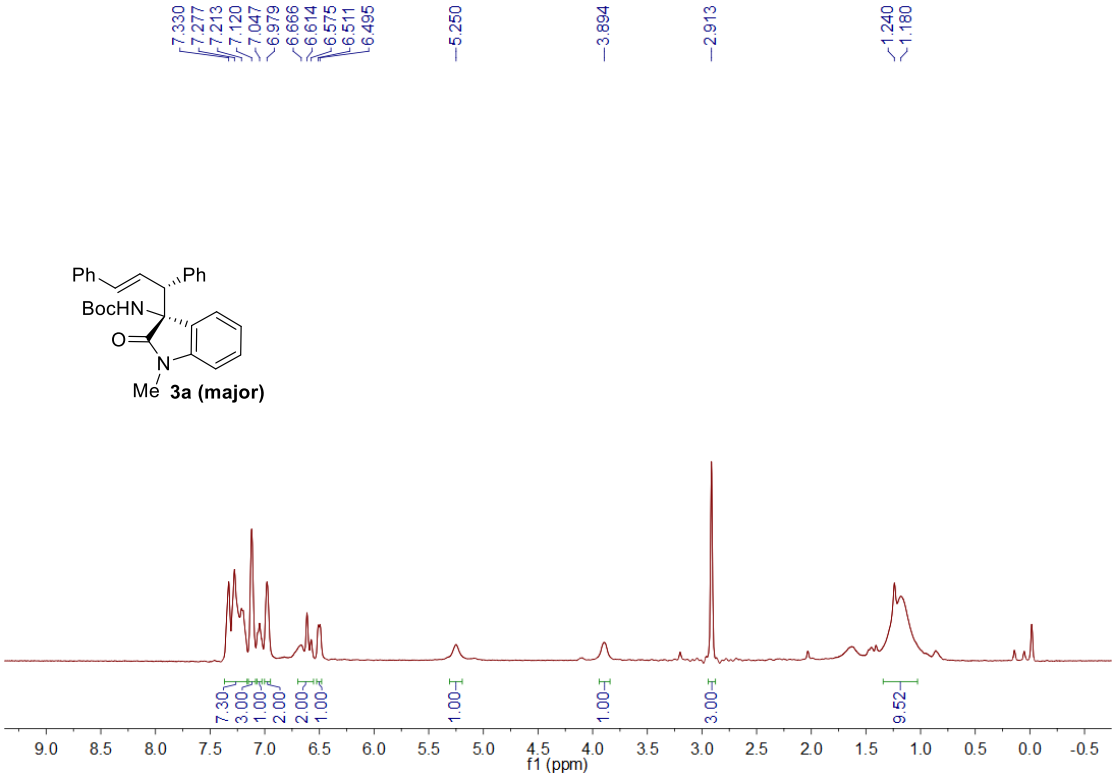


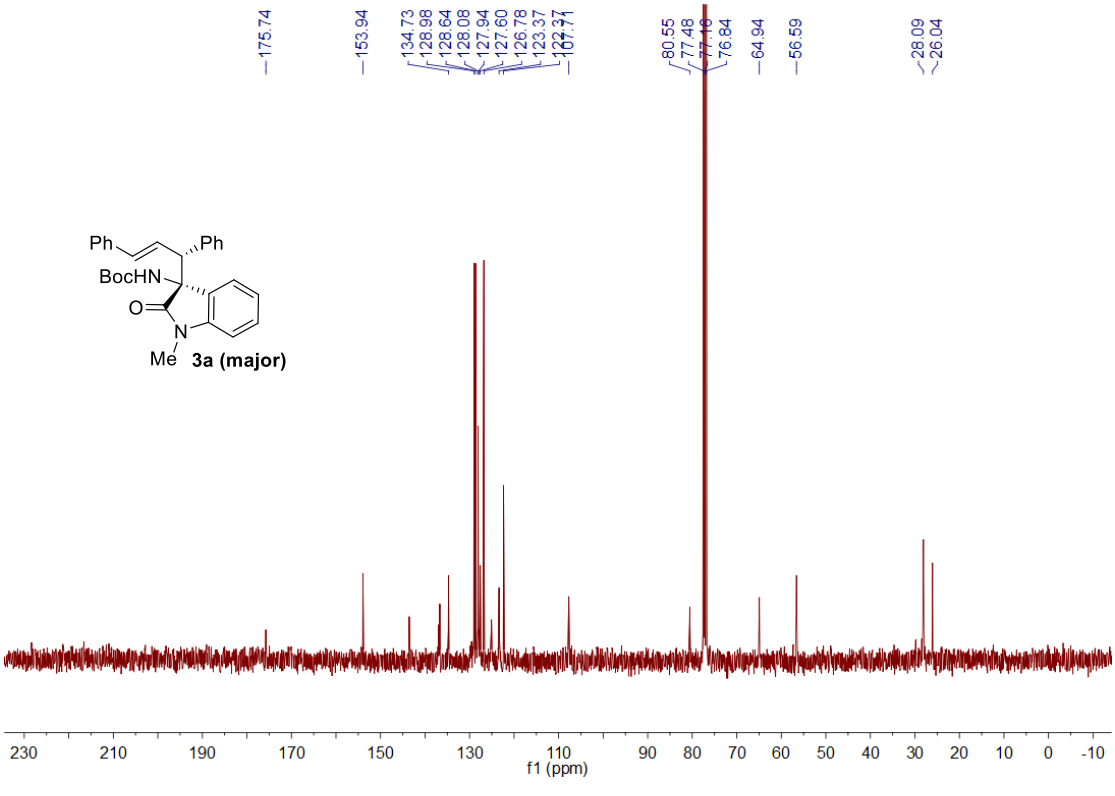
3f (minor)
CCDC 2038579

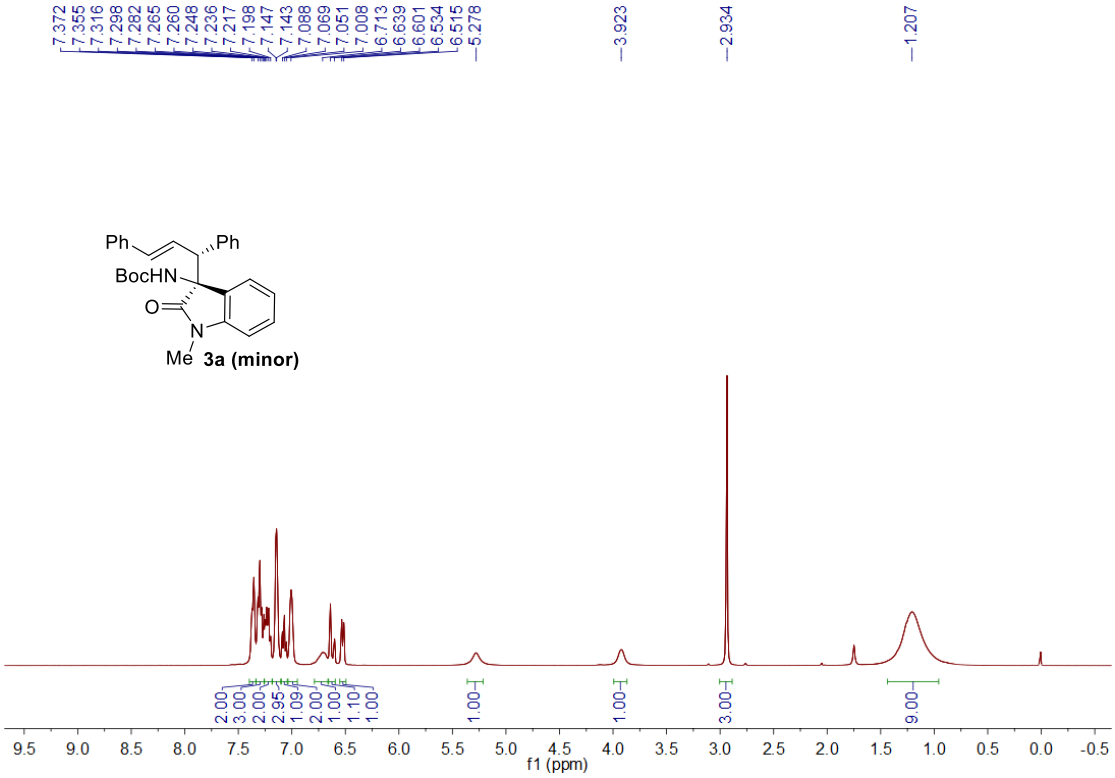
Chiral	Date
Identification code	ZC-3
Empirical formula	$C_{29}H_{29}FN_2O_3$
Formula weight	472.54
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	11.32490(16)
b/Å	10.11966(12)
c/Å	11.47015(15)
α/°	90
β/°	106.0020(14)
γ/°	90
Volume/Å^3	1263.59(3)
Z	2
ρ_{calc}g/cm^3	1.242
μ/mm^{-1}	0.694
F(000)	500.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.018 to 147.432
Index ranges	-14 ≤ h ≤ 11, -12 ≤ k ≤ 11, -14 ≤ l ≤ 13
Reflections collected	8662
Independent reflections	4383 [R_{int} = 0.0245, R_{sigma} = 0.0285]
Data/restraints/parameters	4383/1/325
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0700
Final R indexes [all data]	R_1 = 0.0274, wR_2 = 0.0709
Largest diff. peak/hole / e Å^{-3}	0.18/-0.16
Flack/Hooft parameter	0.00(8)/0.08(7)

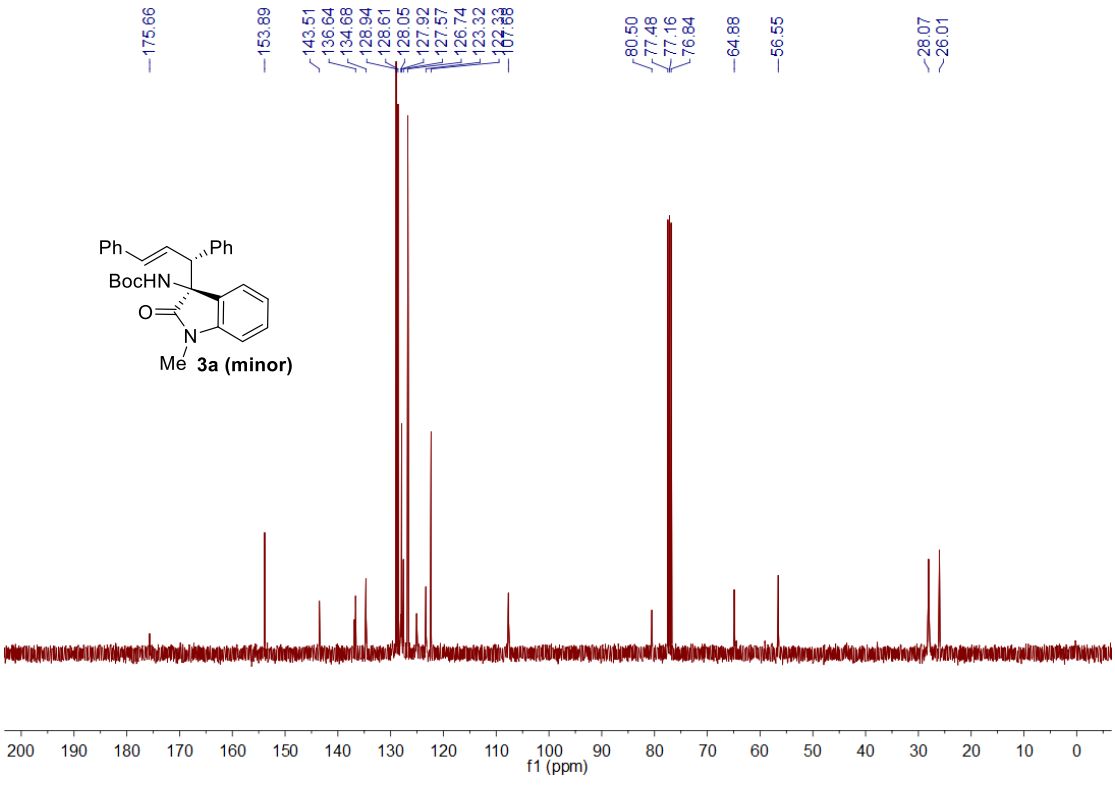
5. NMR and HPLC spectra for compounds 3-6

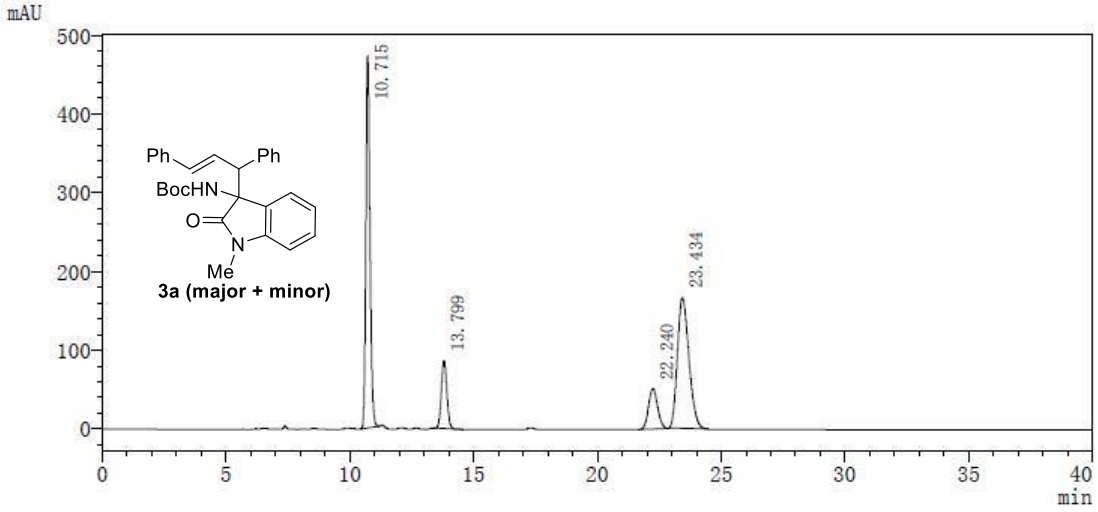
NMR and HPLC of 3a





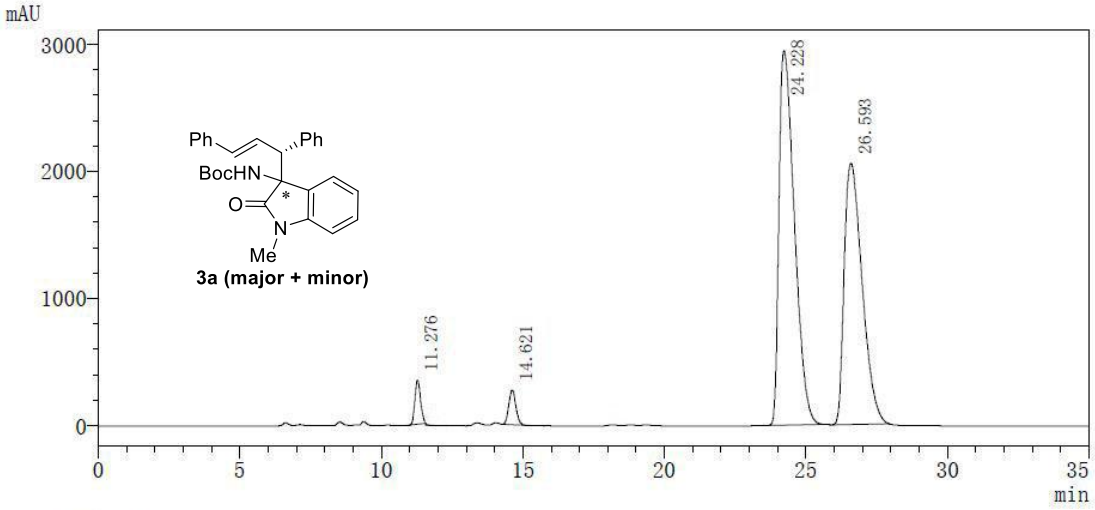

7.372
7.355
7.316
7.298
7.282
7.265
7.260
7.248
7.236
7.217
7.198
7.147
7.143
7.088
7.069
7.051
7.008
6.713
6.639
6.601
6.534
6.515
5.278
3.923
2.934
1.207
Ph
Ph
BocHN
O
N
Me
3a (minor)
2.00
3.00
2.00
2.95
1.09
2.00
1.00
1.10
1.00
1.00
1.00
3.00
9.00
f1 (ppm)


175.66
153.89
143.51
136.64
134.68
128.94
128.61
128.05
127.92
127.57
126.74
123.32
80.50
77.48
77.16
76.84
64.88
56.55
28.07
26.01
Ph
Ph
BocHN
O
N
Me
3a (minor)
f1 (ppm)



1 254nm 4nm

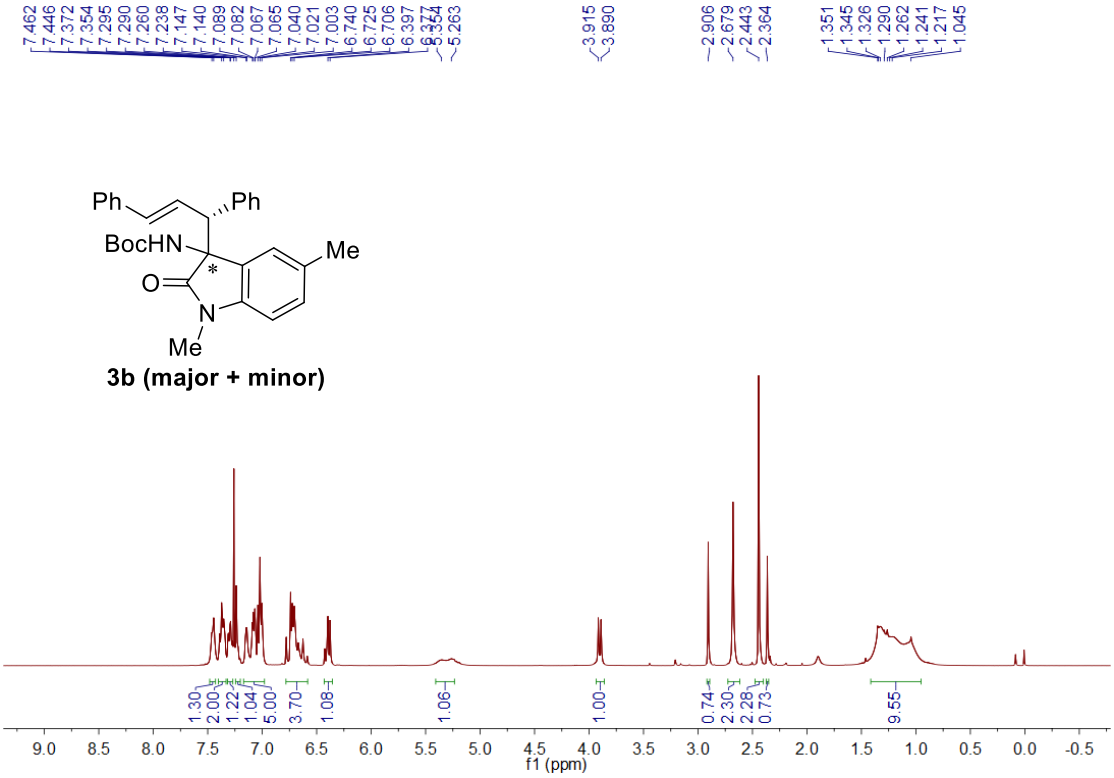
ID#	Rt. Time	Area	Height	Area %
1	10.715	5486367	472736	40.560
2	13.799	1335541	86415	9.873
3	22.240	1310491	51416	9.688
4	23.434	5394157	165992	39.878

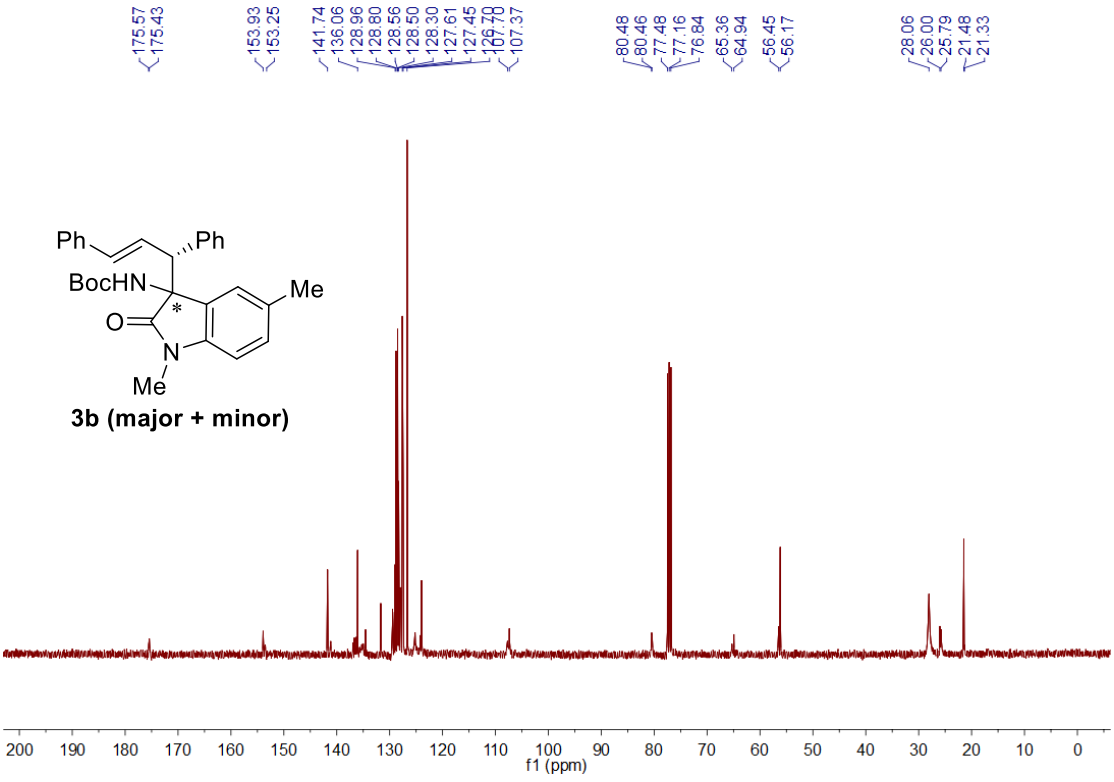


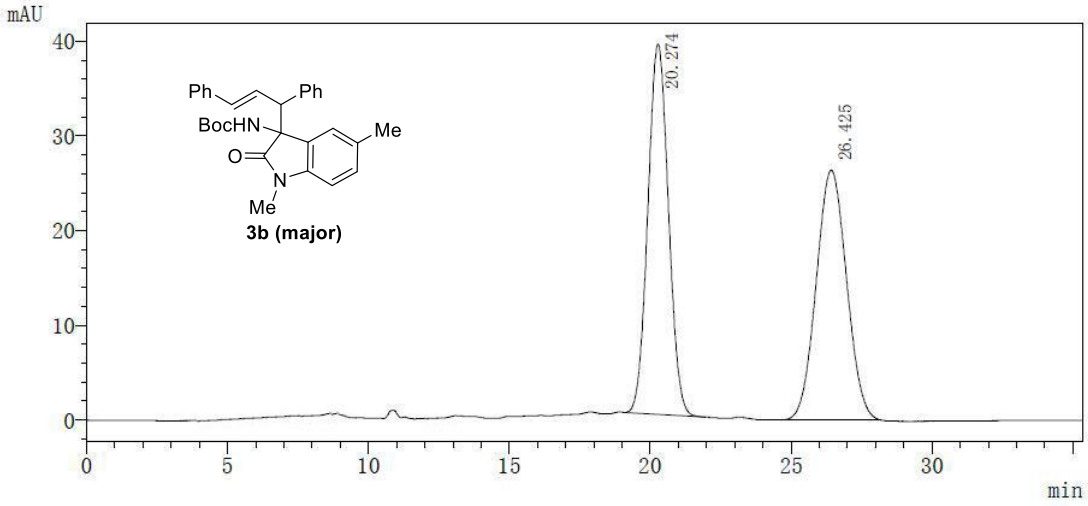
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	11.276	4799466	346894	2.268
2	14.621	4746694	274494	2.243
3	24.228	111651709	2944486	52.764
4	26.593	90408257	2055313	42.725

NMR and HPLC of 3b

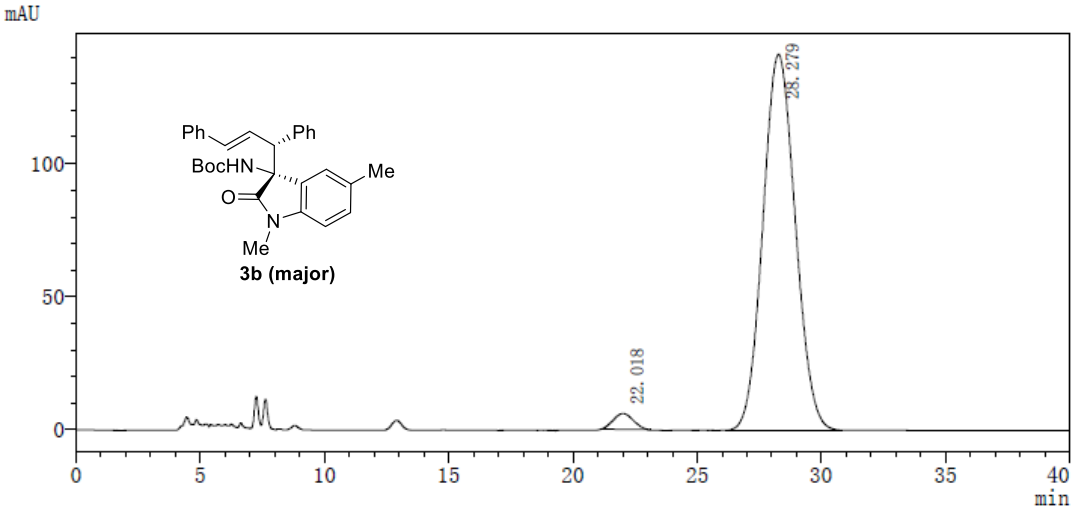






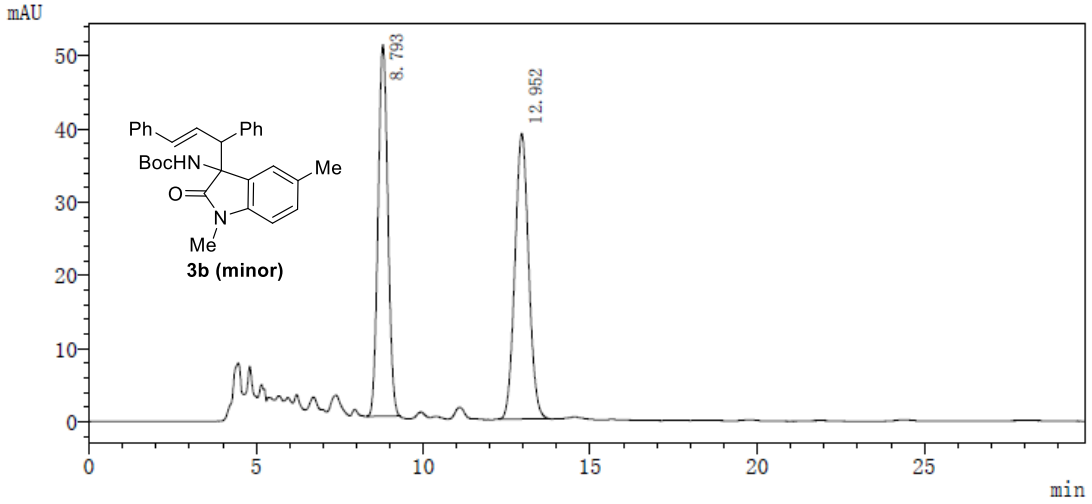
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	20.274	1986077	39066	50.208
2	26.425	1969634	26349	49.792



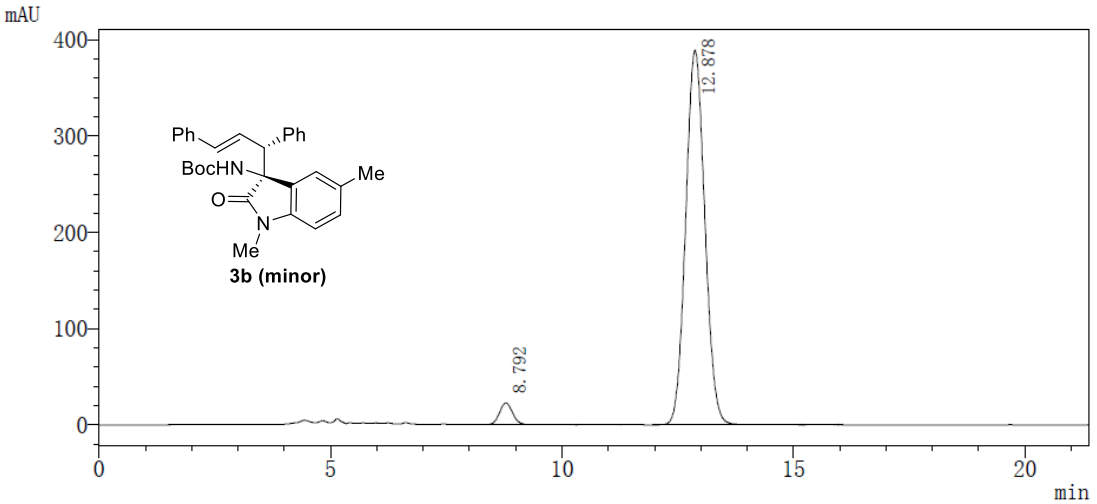
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	22.018	334045	5926	2.538
2	28.279	12827937	141257	97.462



1 254nm 4nm

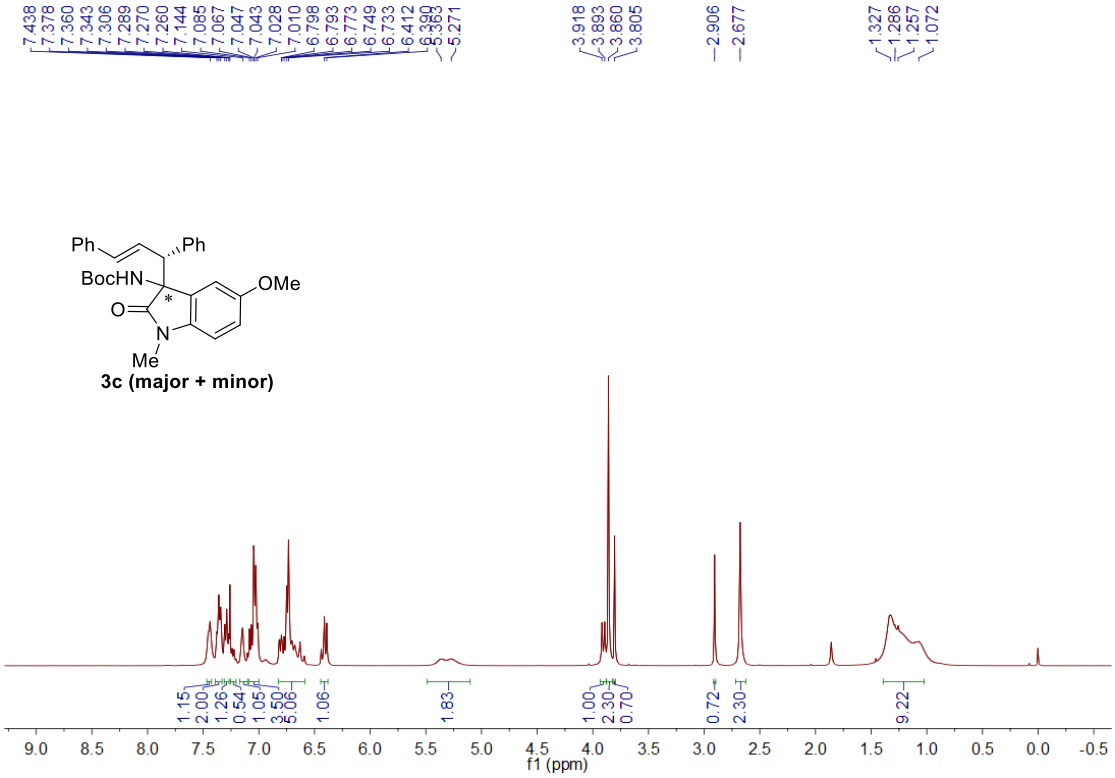
ID#	Rt. Time	Area	Height	Area %
1	8.793	1043335	50828	48.164
2	12.952	1122881	39057	51.836

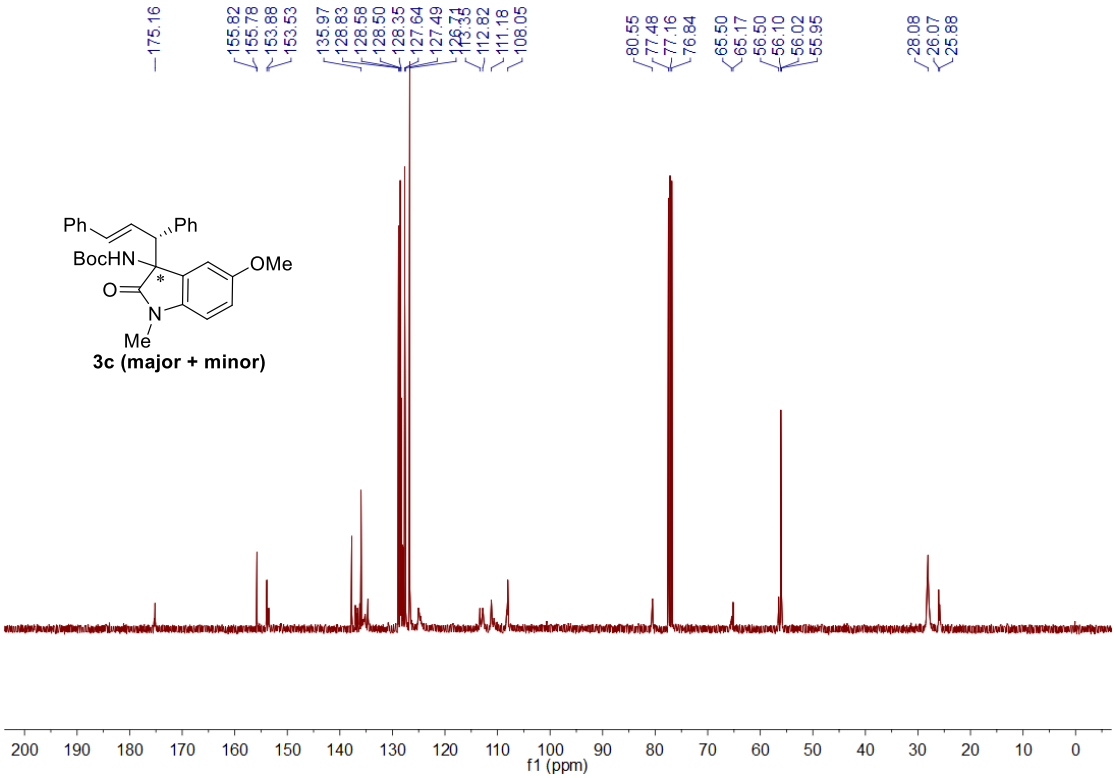


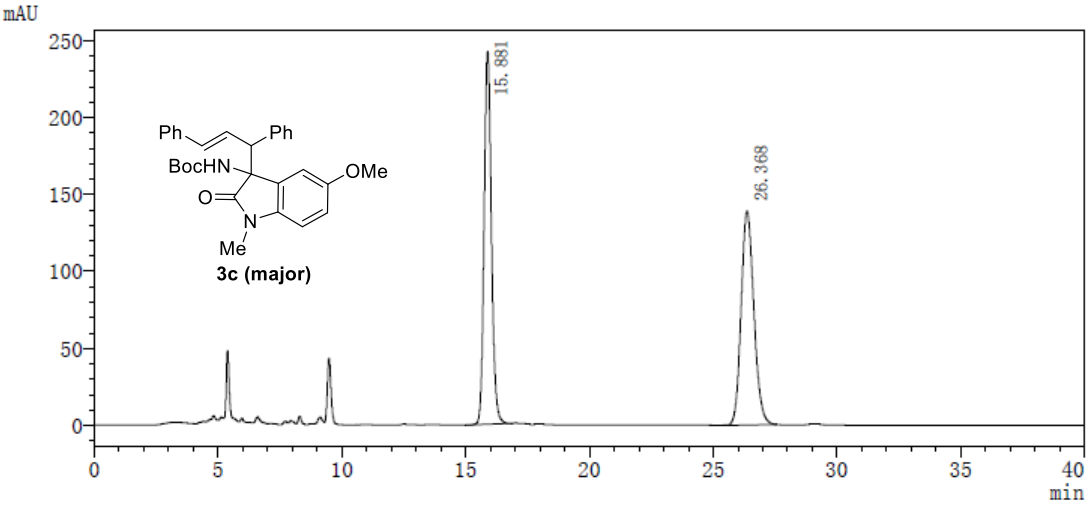
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	8.792	437822	22546	3.763
2	12.878	11197597	389189	96.237

NMR and HPLC of 3c

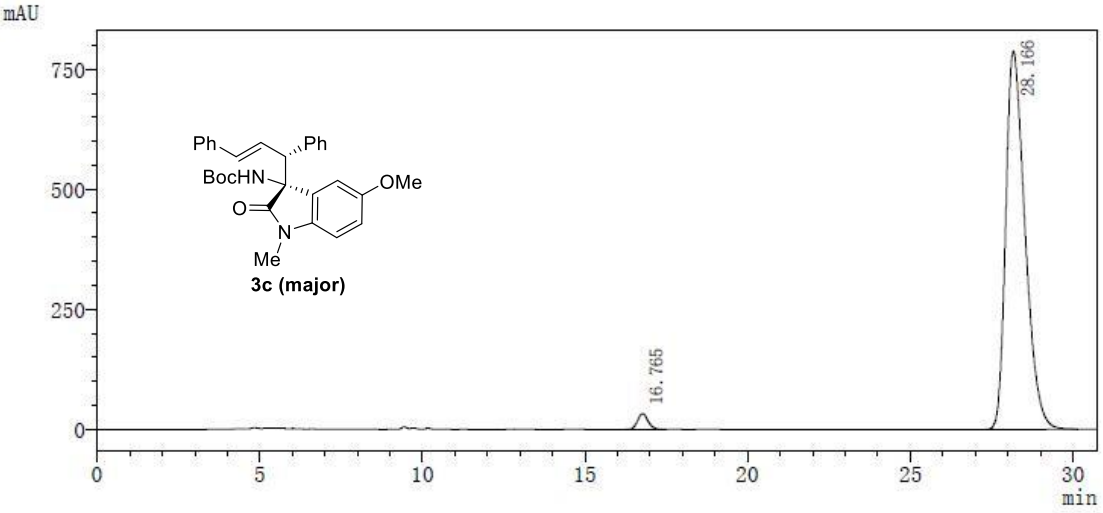






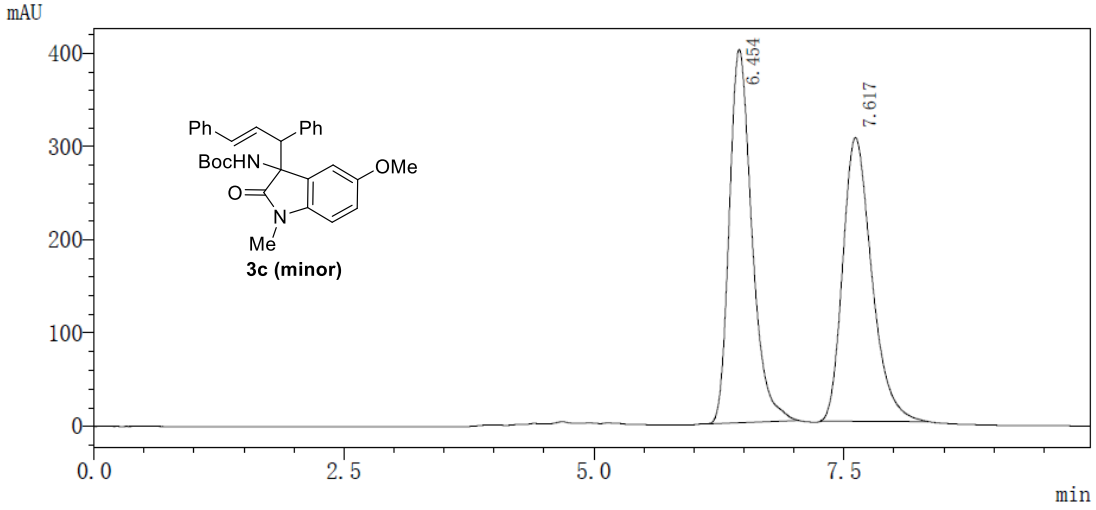
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	15.881	4969324	242604	49.988
2	26.368	4971746	139236	50.012



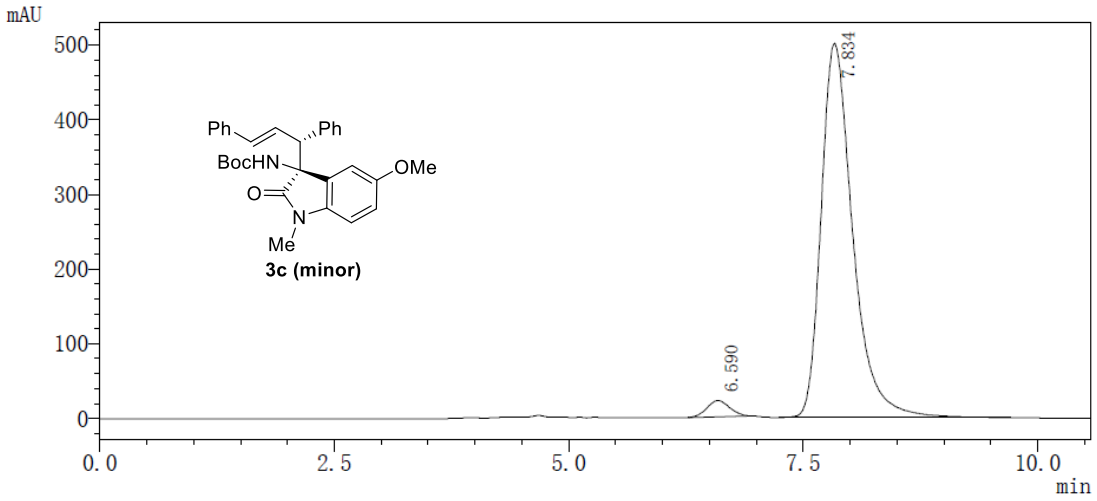
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	16.765	746242	33078	2.244
2	28.166	32513797	786865	97.756



1 254nm 4nm

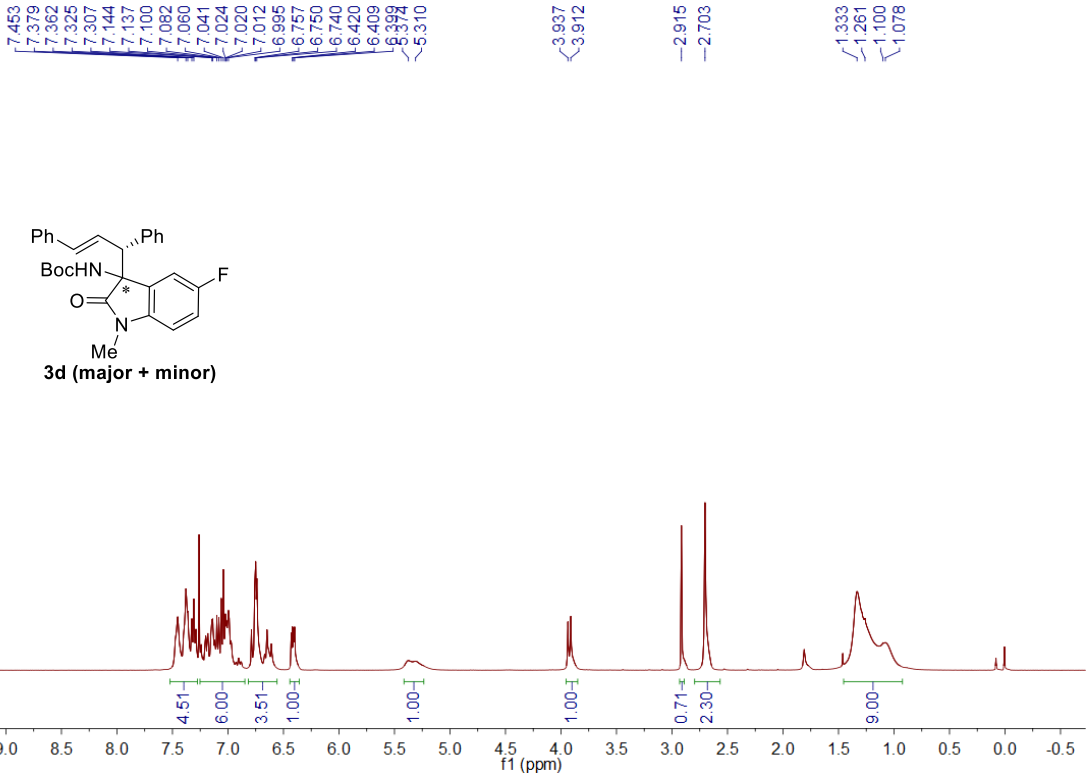
ID#	Rt. Time	Area	Height	Area %
1	6.454	6298950	399975	50.643
2	7.617	6138954	303844	49.357

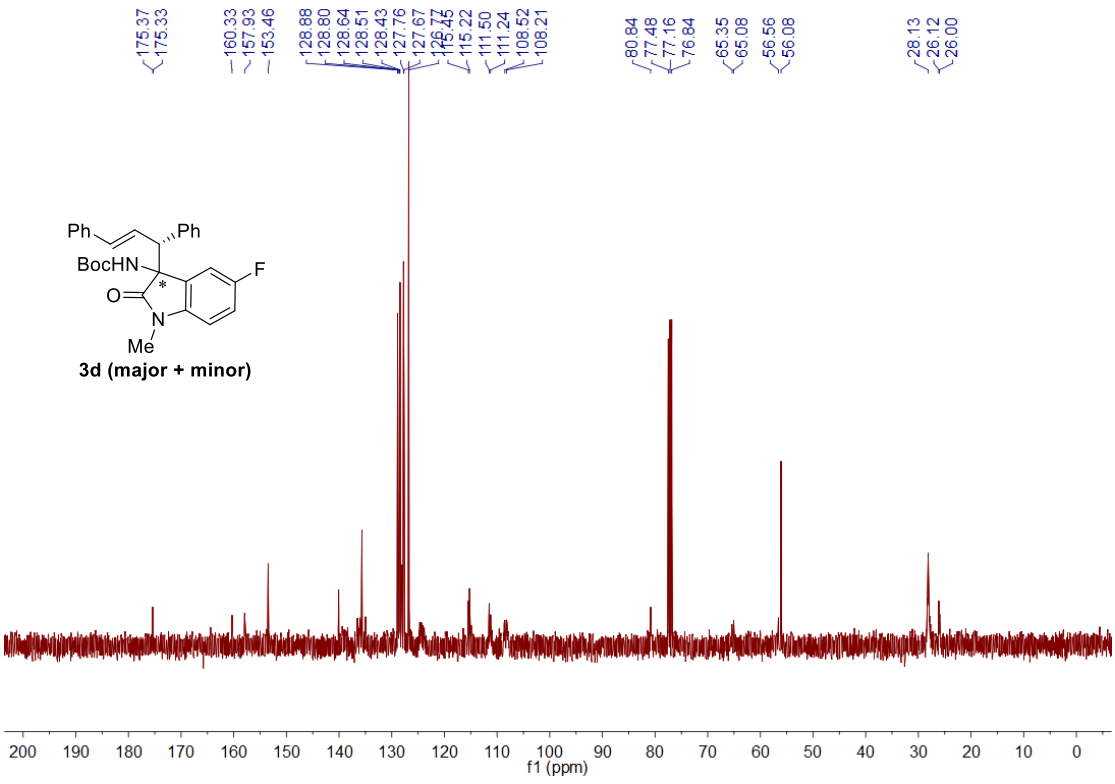


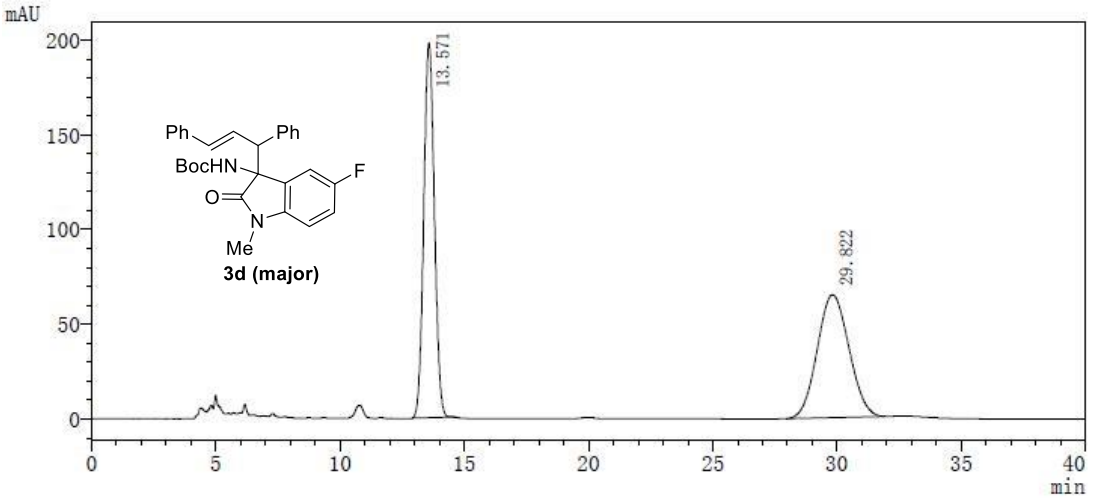
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	6.590	358371	21689	2.957
2	7.834	11760547	500987	97.043

NMR and HPLC of 3d

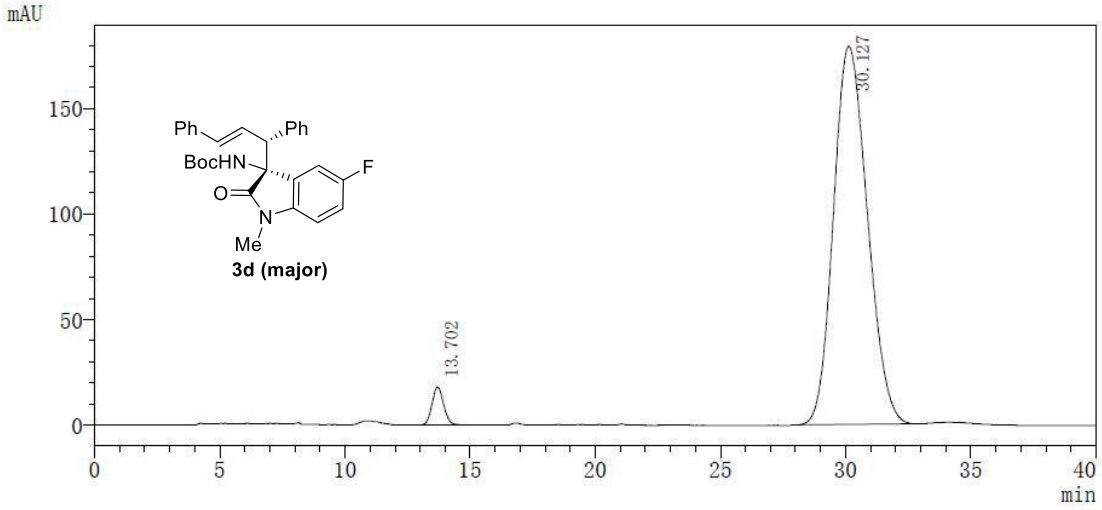






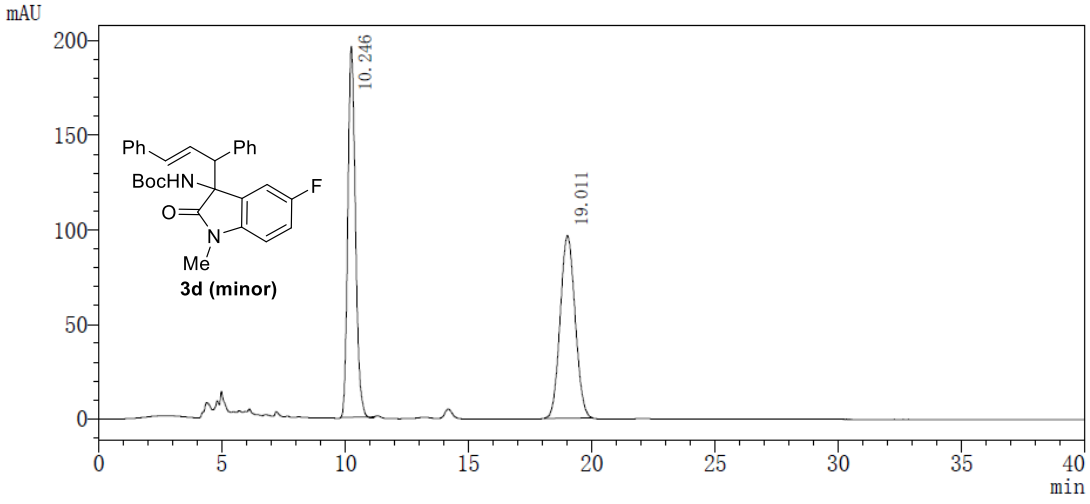
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	13.571	5902705	197979	50.577
2	29.822	5768018	64875	49.423



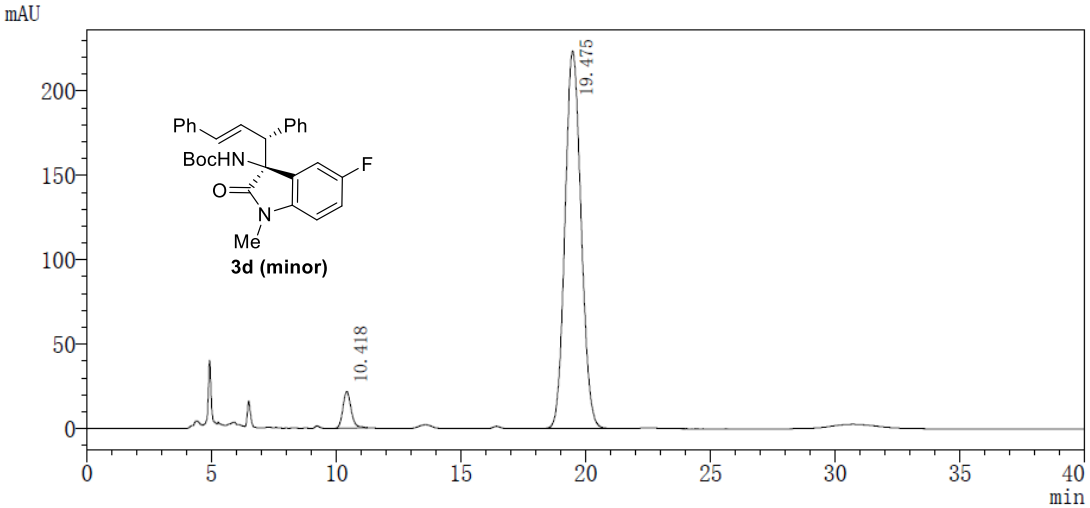
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	13.702	571369	17894	3.266
2	30.127	16925221	179231	96.734



1 254nm 4nm

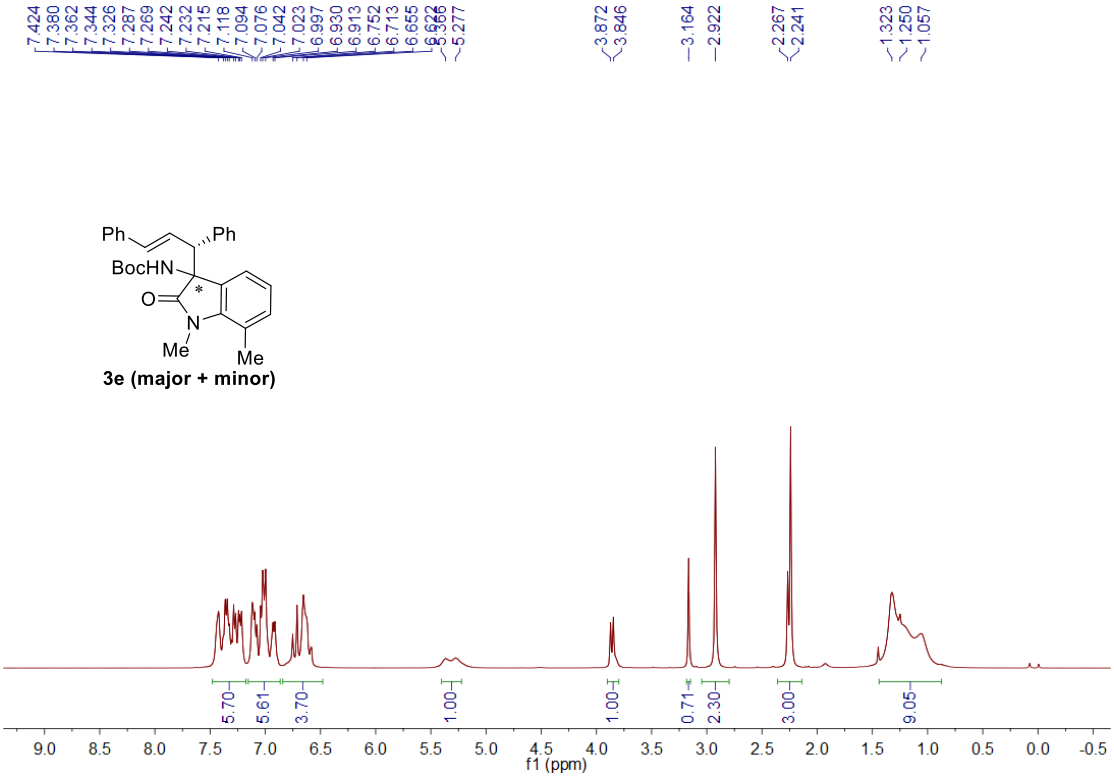
ID#	Rt. Time	Area	Height	Area %
1	10.246	4194508	196174	50.776
2	19.011	4066221	96419	49.224

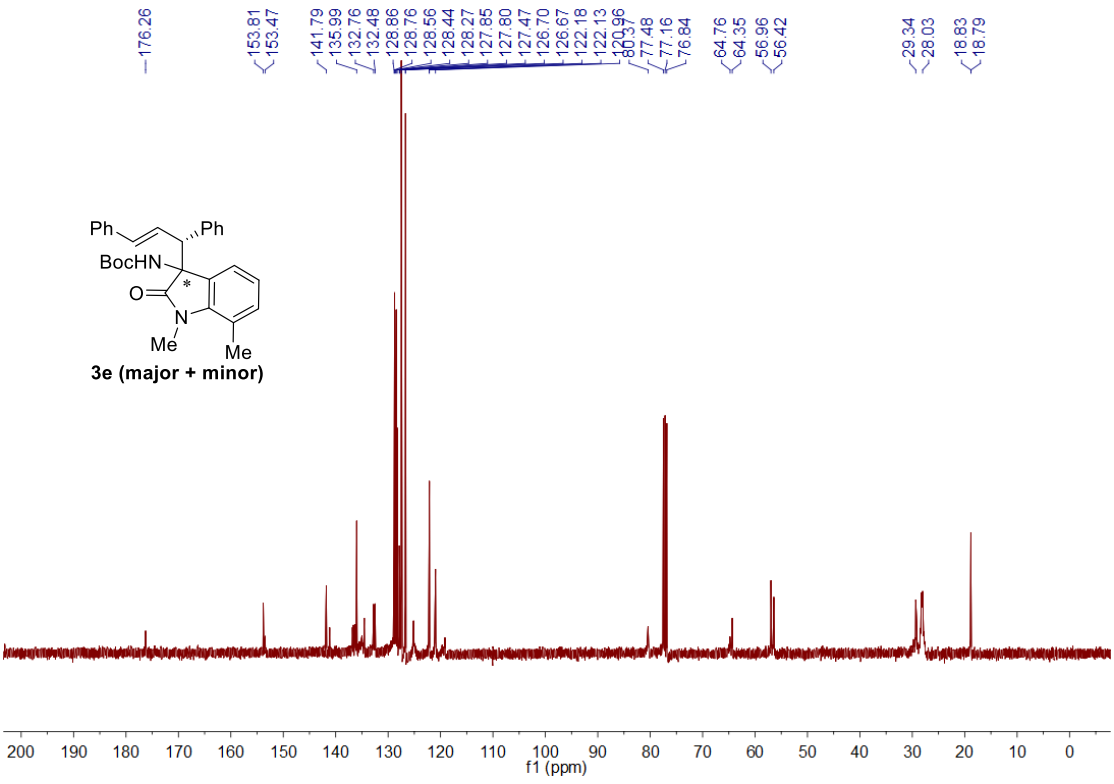


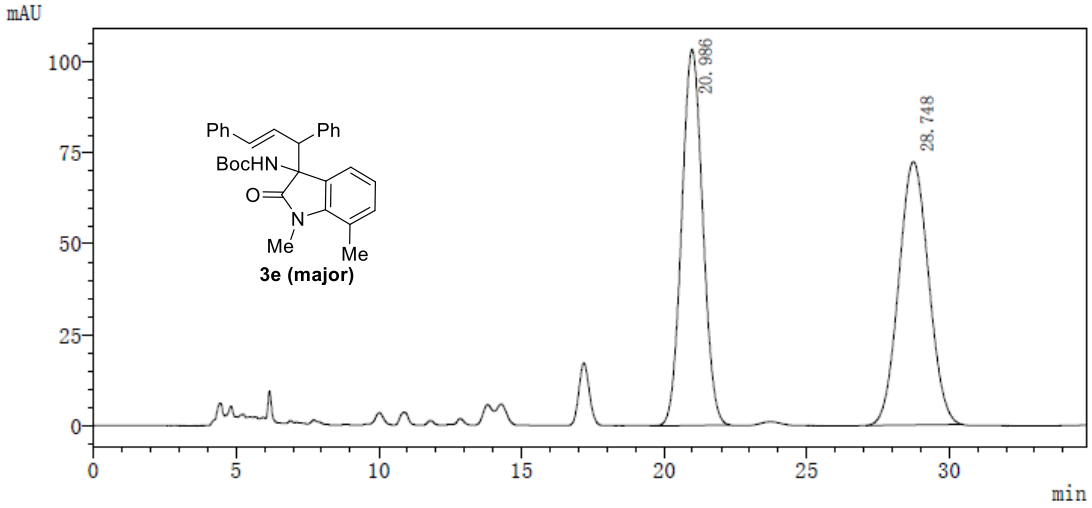
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	10.418	499805	21748	4.748
2	19.475	10026926	223617	95.252

NMR and HPLC of 3e

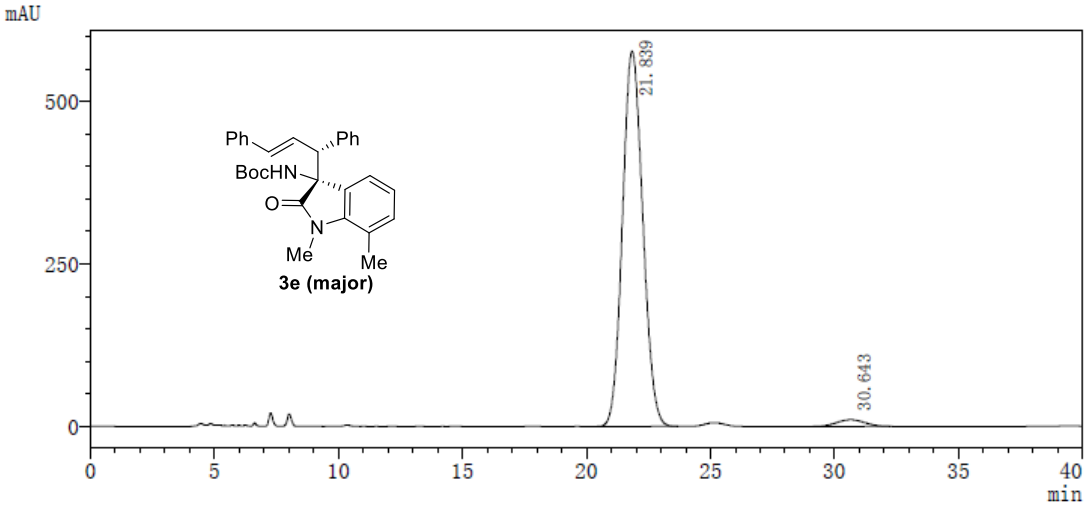






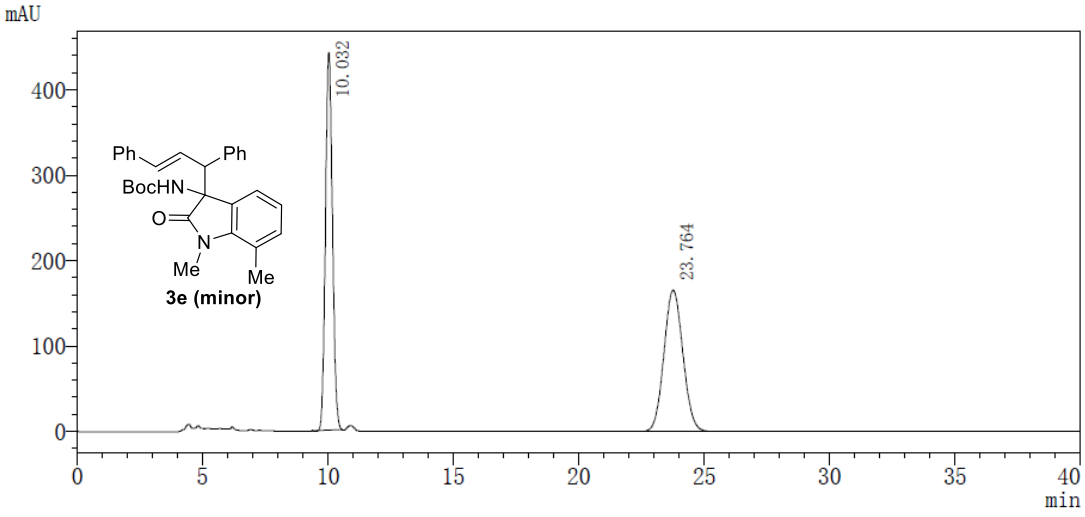
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	20.986	5292465	103385	50.148
2	28.748	5261264	72416	49.852



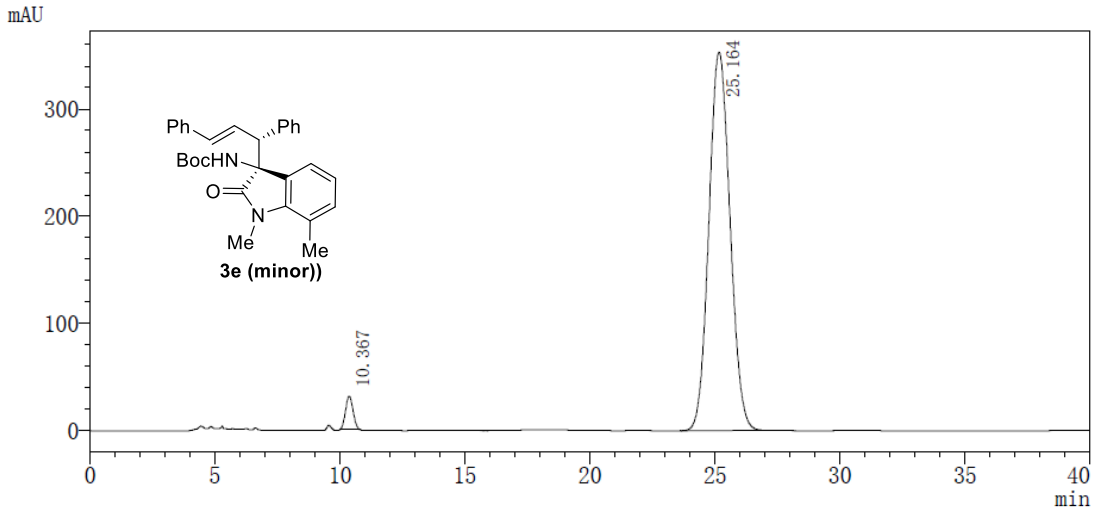
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	21.839	33038134	577508	97.541
2	30.643	832999	10351	2.459



1 254nm 4nm

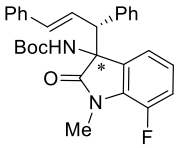
ID#	Rt. Time	Area	Height	Area %
1	10.032	8609496	442441	49.888
2	23.764	8648301	165223	50.112



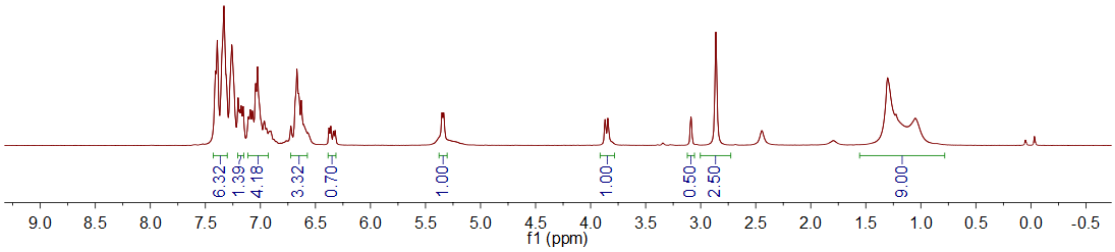
1 254nm 4nm

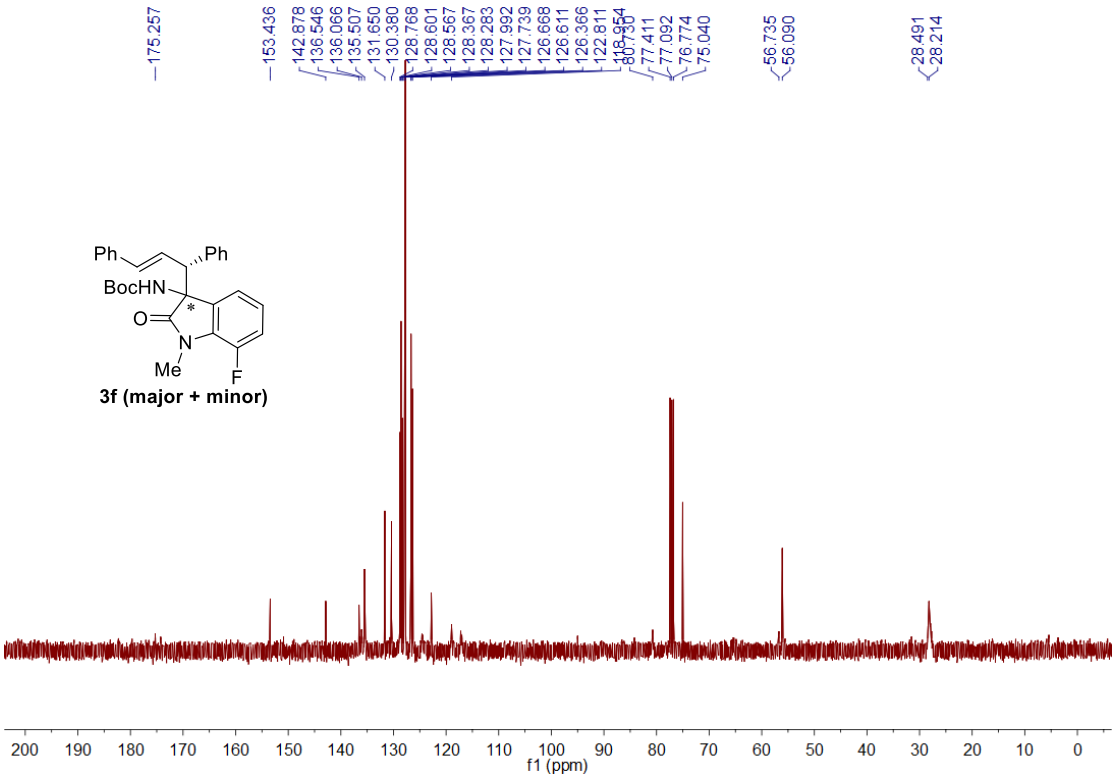
ID#	Rt. Time	Area	Height	Area %
1	10.367	655363	31223	3.055
2	25.164	20797006	353151	96.945

NMR and HPLC of 3f

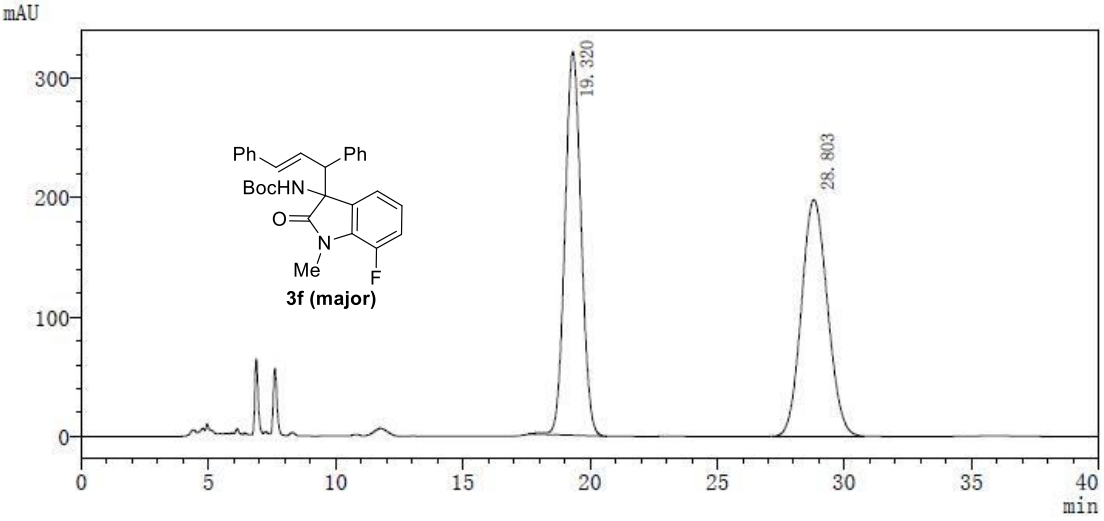


3f (major + minor)



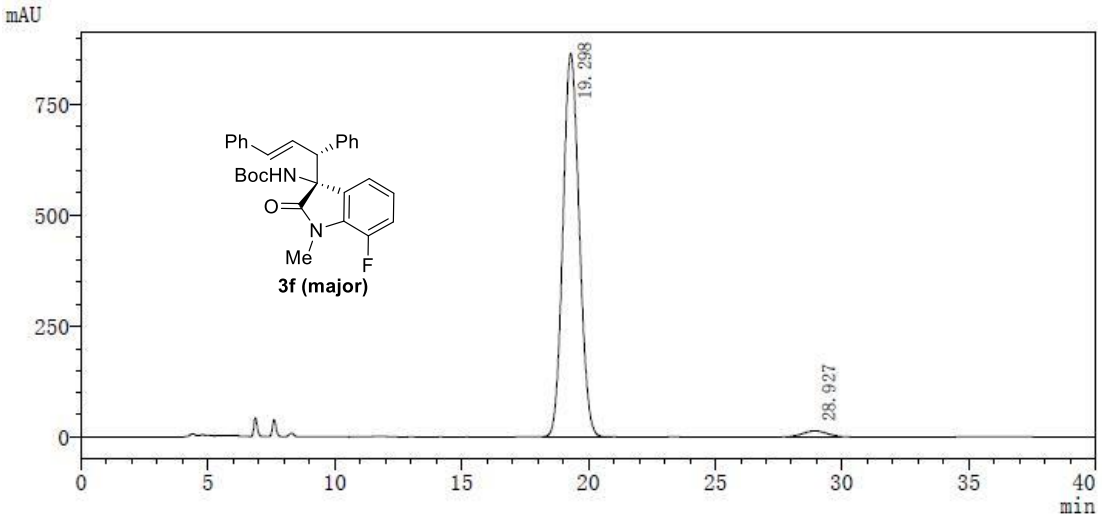


3f (major + minor)



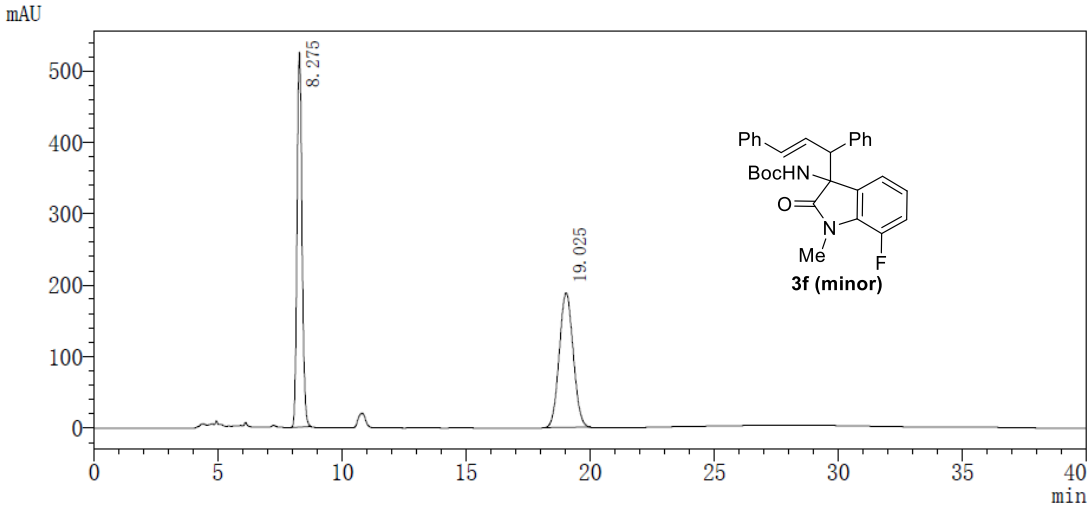
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	19.320	14183354	321047	50.179
2	28.803	14081914	197890	49.821



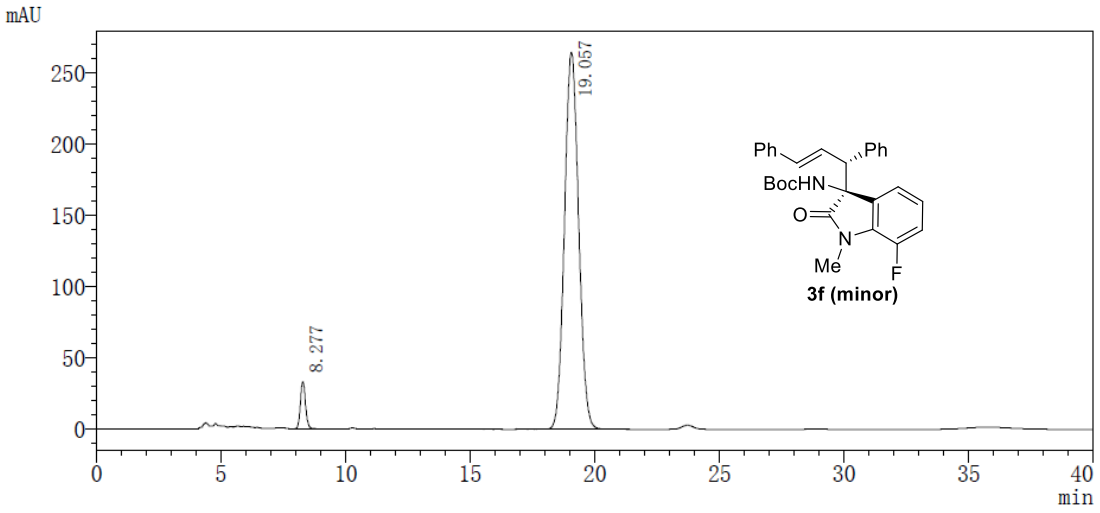
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	19.298	38488241	863592	97.912
2	28.927	820635	12723	2.088



1 254nm 4nm

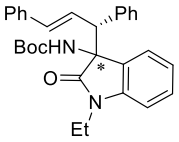
ID#	Rt. Time	Area	Height	Area %
1	8.275	7372438	525352	50.003
2	19.025	7371498	188670	49.997



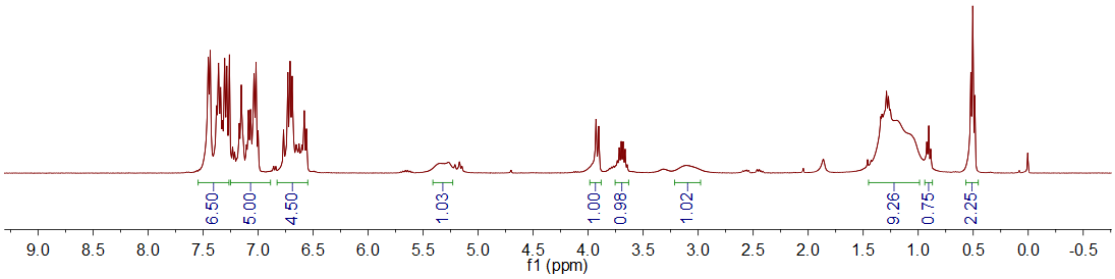
1 254nm 4nm

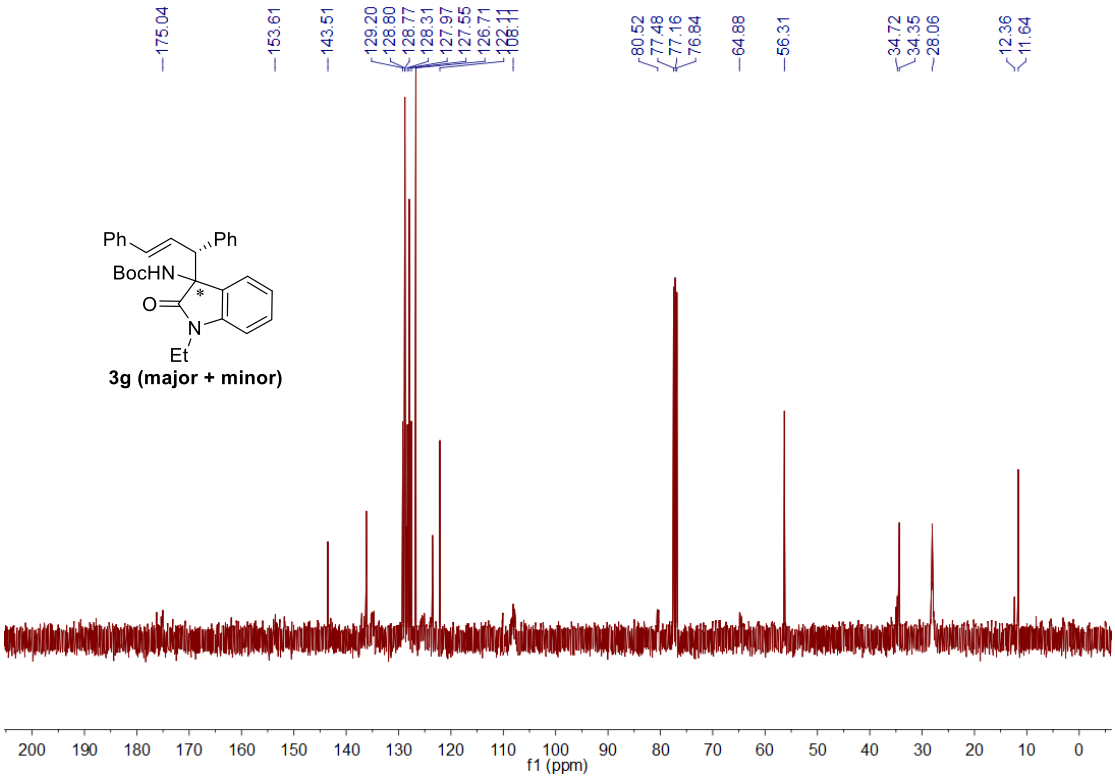
ID#	Rt. Time	Area	Height	Area %
1	8.277	469984	33122	4.310
2	19.057	10433889	264674	95.690

NMR and HPLC of 3g

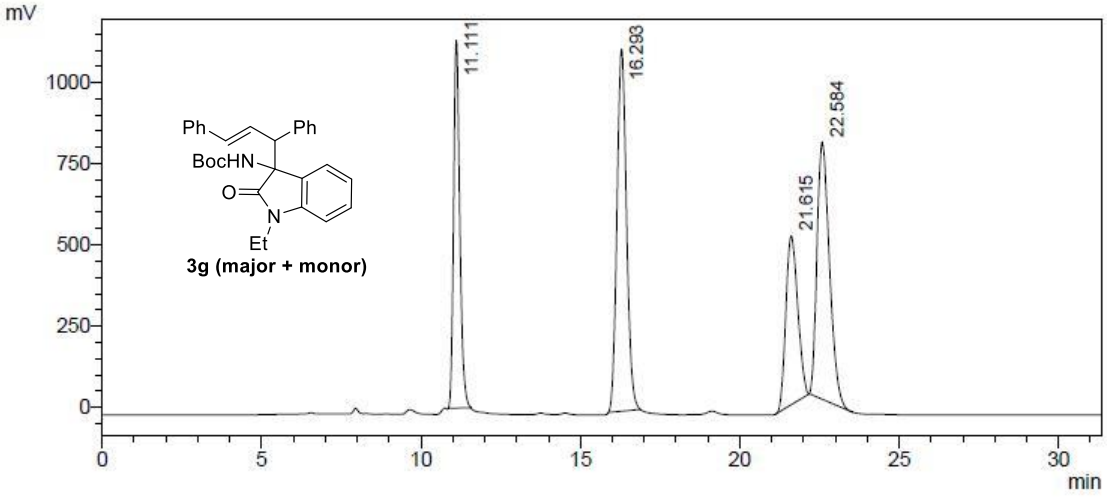


3g (major + minor)



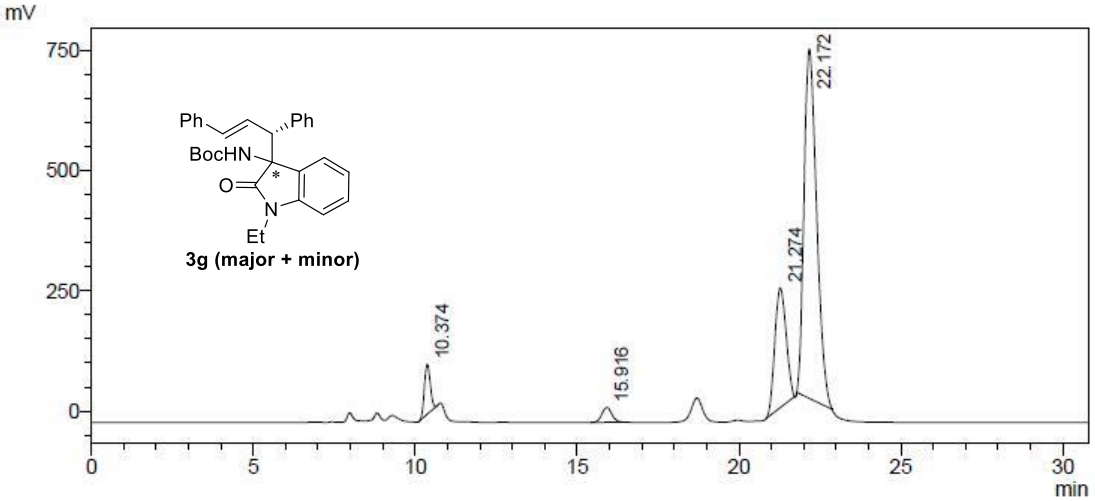


3g (major + minor)



1 254nm 4nm

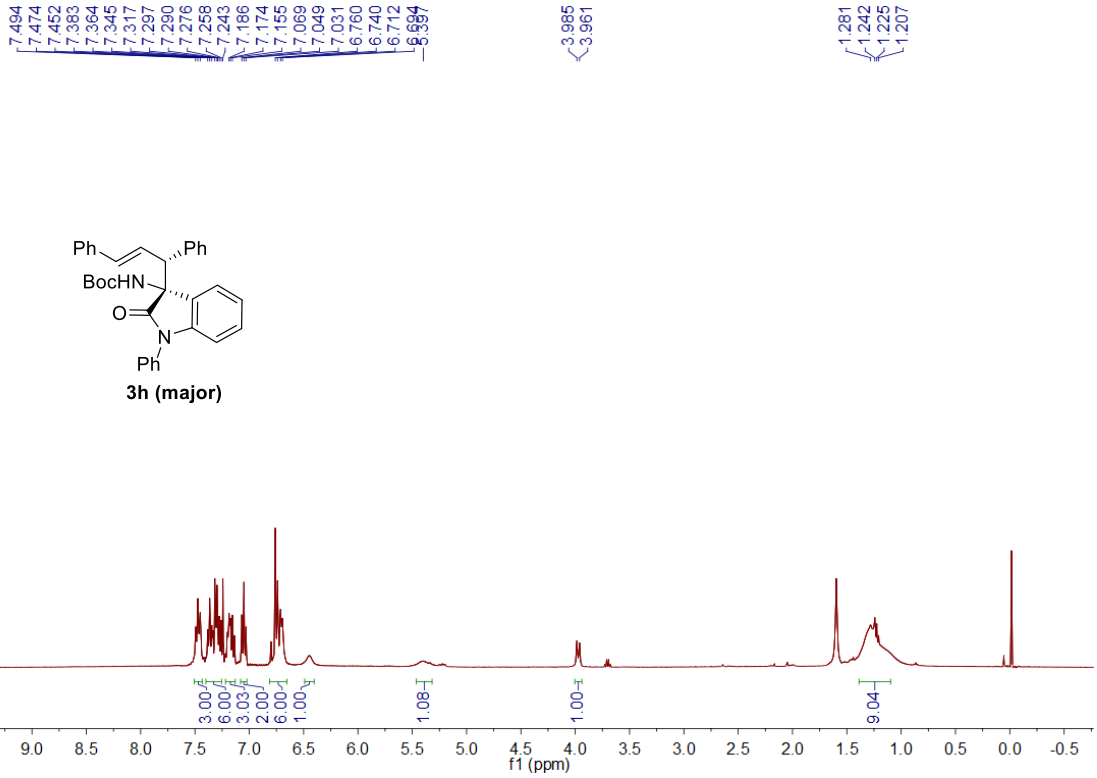
ID#	Ret. Time	Area	Height	Area%
1	11.111	15262369	1132983	20.786
2	16.293	23191300	1115449	31.585
3	21.615	13436880	519557	18.300
4	22.584	21535404	792525	29.329

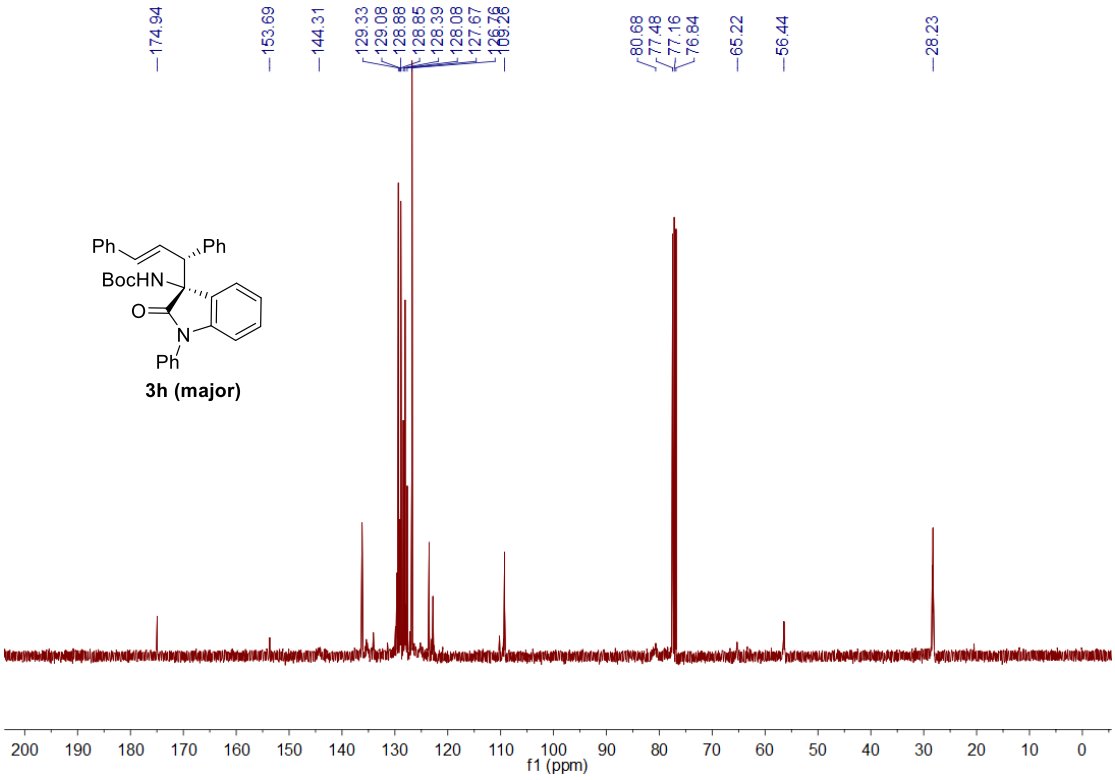


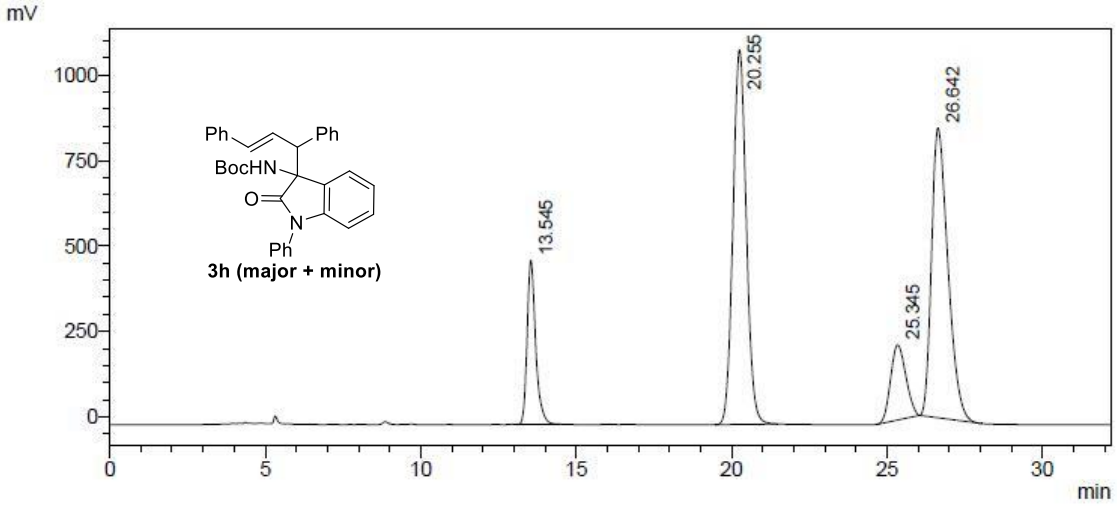
1 254nm 4nm

ID#	Ret. Time	Area	Height	Area%
1	10.374	1317496	103947	4.772
2	15.916	657421	31105	2.381
3	21.274	6038243	249088	21.871
4	22.172	19595276	726097	70.976

NMR and HPLC of 3h

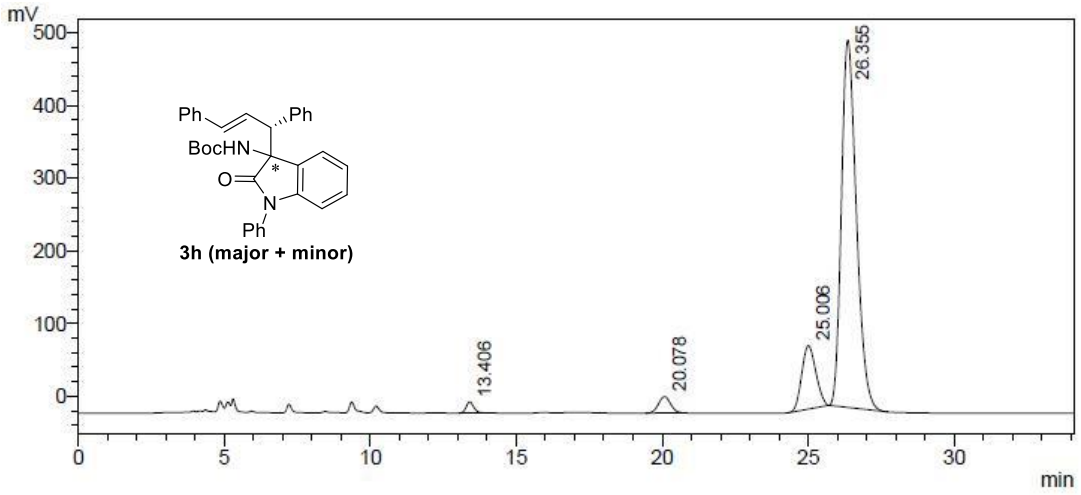






1 254nm 4nm

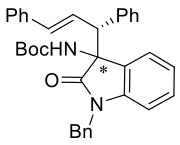
ID#	Ret. Time	Area	Height	Area%
1	13.545	9170381	478998	11.414
2	20.255	32589506	1095792	40.562
3	25.345	7490285	219320	9.323
4	26.642	31095497	847801	38.702



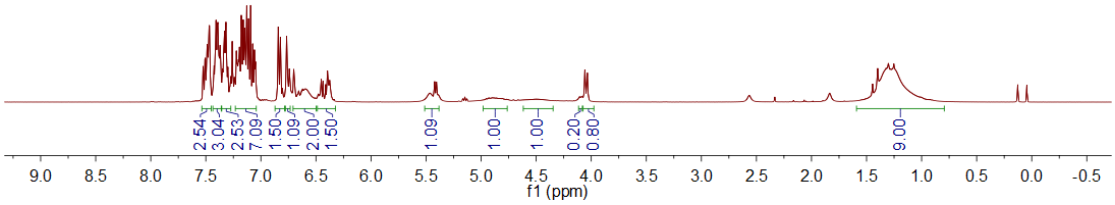
1 254nm 4nm

ID#	Ret. Time	Area	Height	Area%
1	13.406	269643	15218	1.233
2	20.078	651293	22625	2.979
3	25.006	2952108	87467	13.503
4	26.355	17989073	505846	82.284

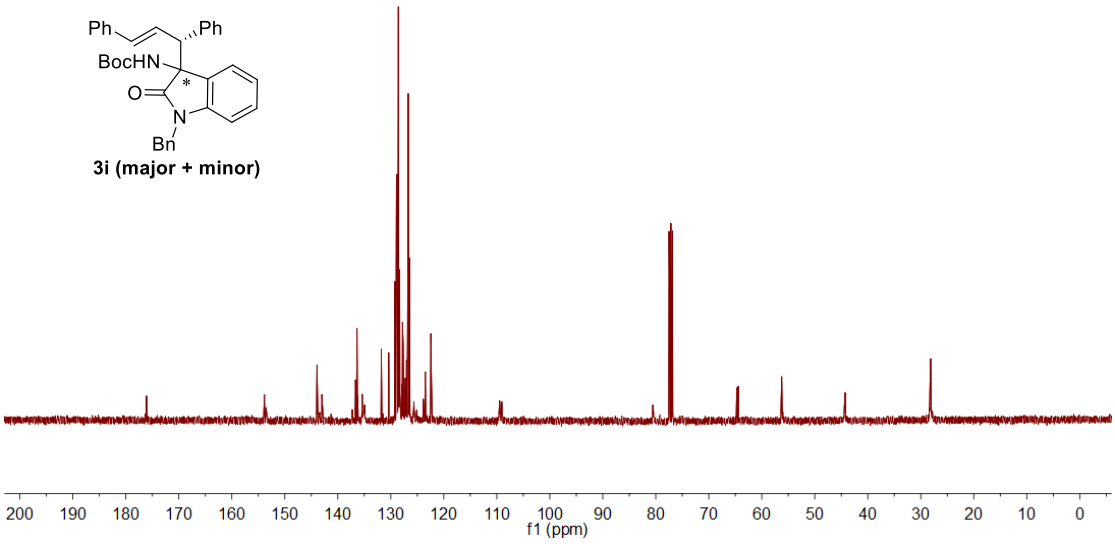
NMR and HPLC of 3i

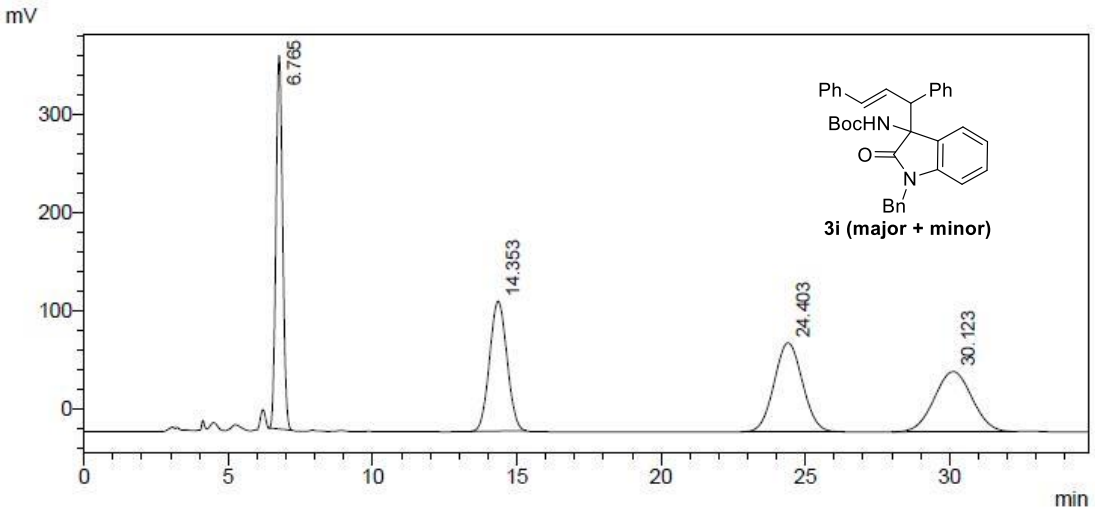


3i (major + minor)



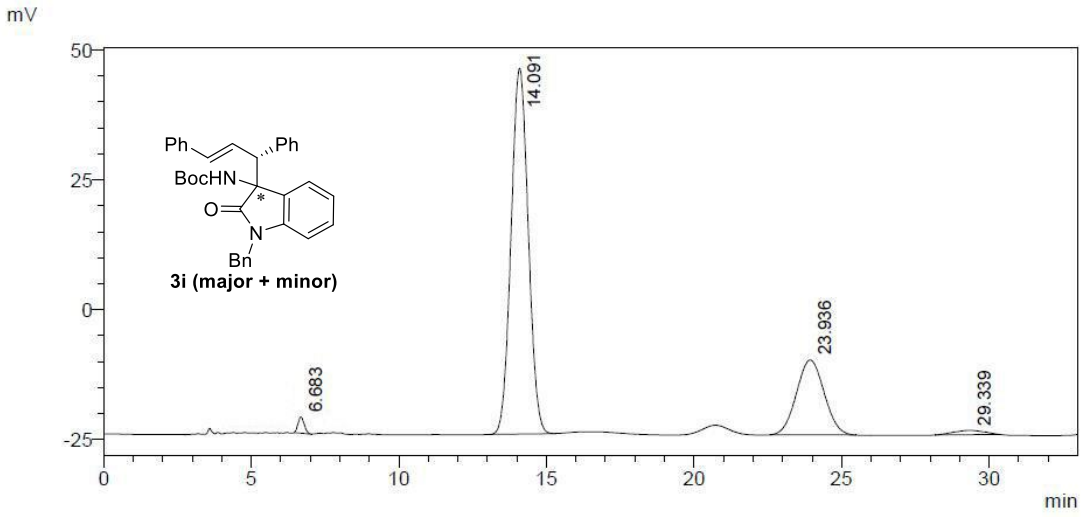
3i (major + minor)





1 254nm 4nm

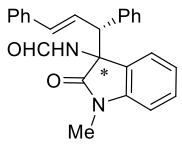
ID#	Ret. Time	Area	Height	Area%
1	6.765	6104150	381107	26.028
2	14.353	5568065	132507	23.742
3	24.403	6203118	90699	26.450
4	30.123	5577228	61378	23.781



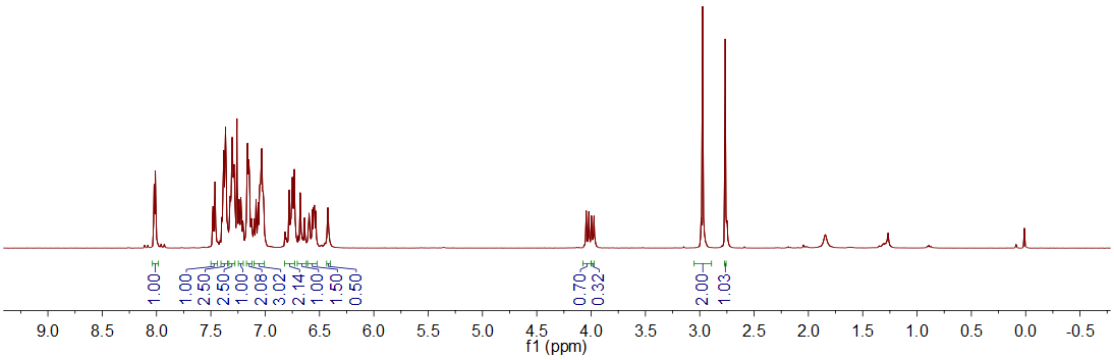
<Peak Table
PDA

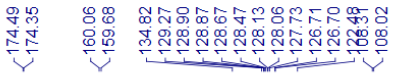
Peak#	Ret. Time	Area	Height	Area%
1	6.683	45922	3125	1.176
2	14.091	2854354	70449	73.118
3	23.936	942868	14411	24.153
4	29.339	60617	831	1.553

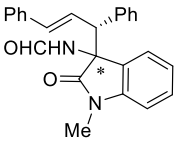
NMR and HPLC of 3j



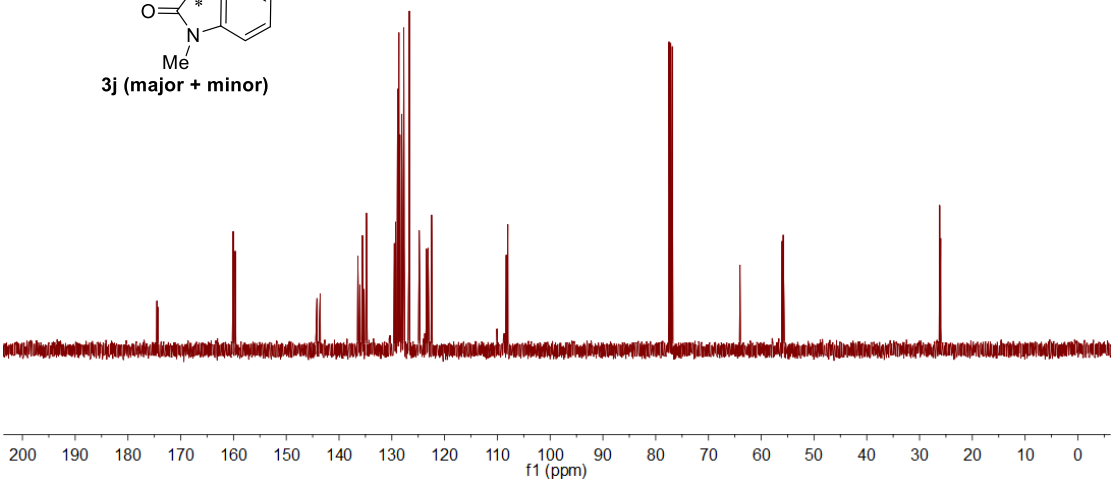
3j (major + minor)

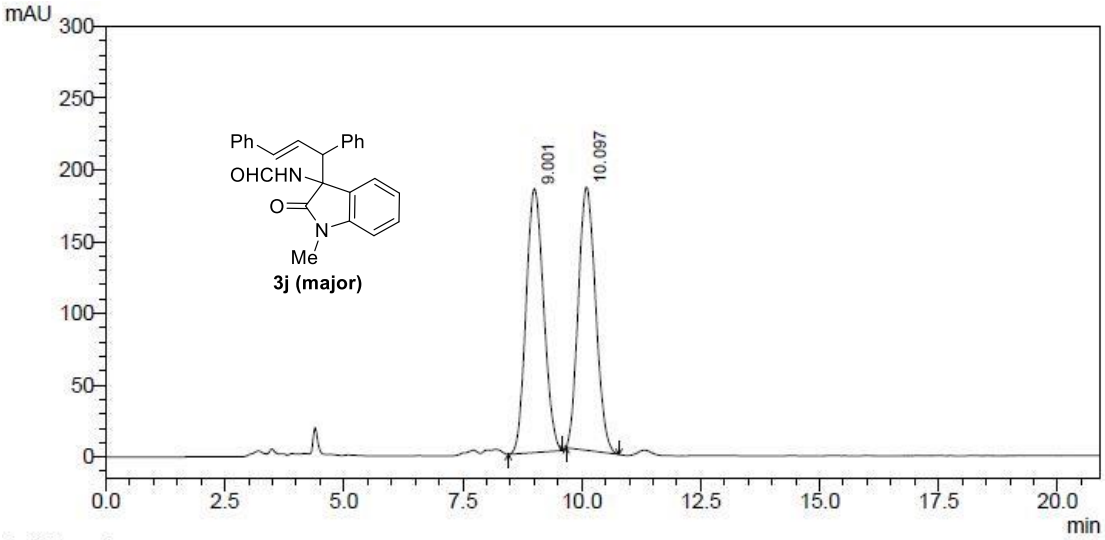






3j (major + minor)

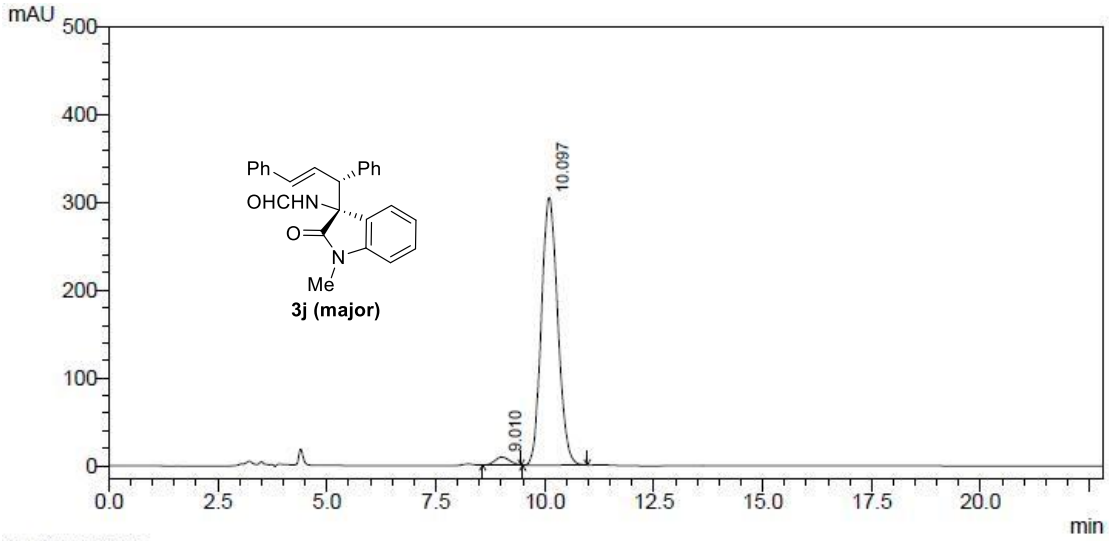




1 254nm 4nm

PDA

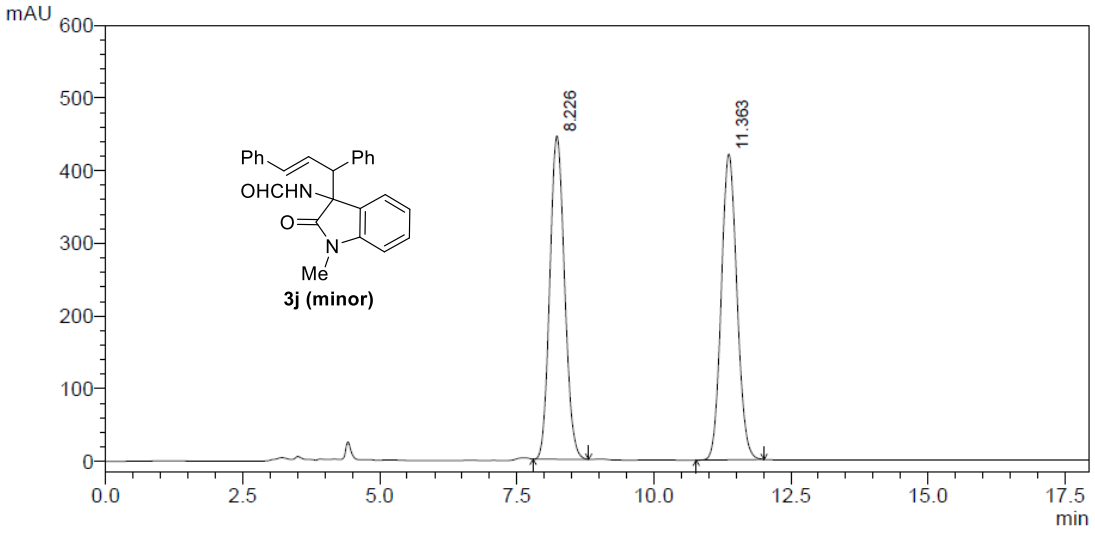
ID#	Rt. Time	Area	Height	Area %
1	9.001	4718848	183807	50.394
2	10.097	4645096	183358	49.606



1 254nm 4nm

PDA

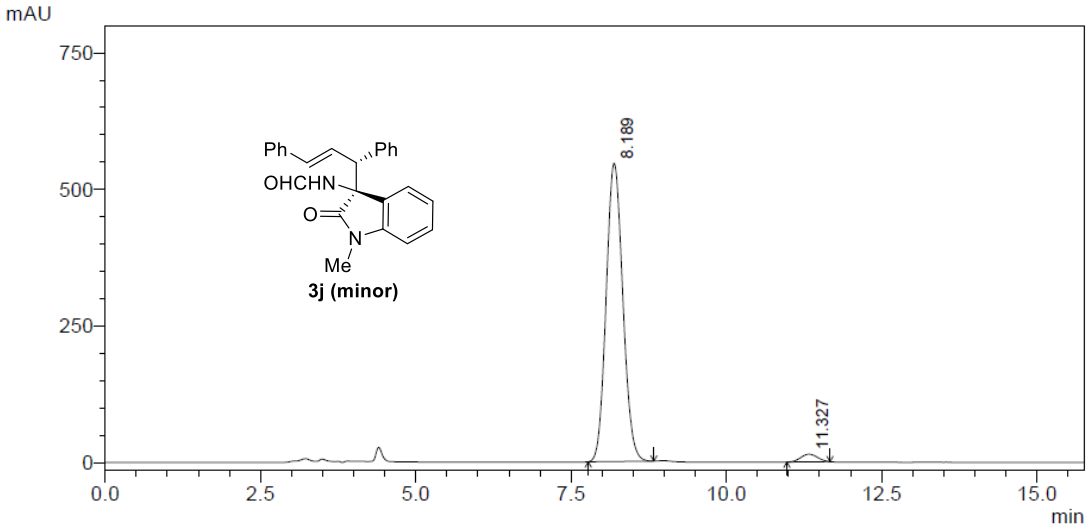
ID#	Rt. Time	Area	Height	Area %
1	9.010	209989	9071	2.570
2	10.097	7961552	304802	97.430



1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	8.226	8342900	444910	49.919
2	11.363	8369905	420738	50.081

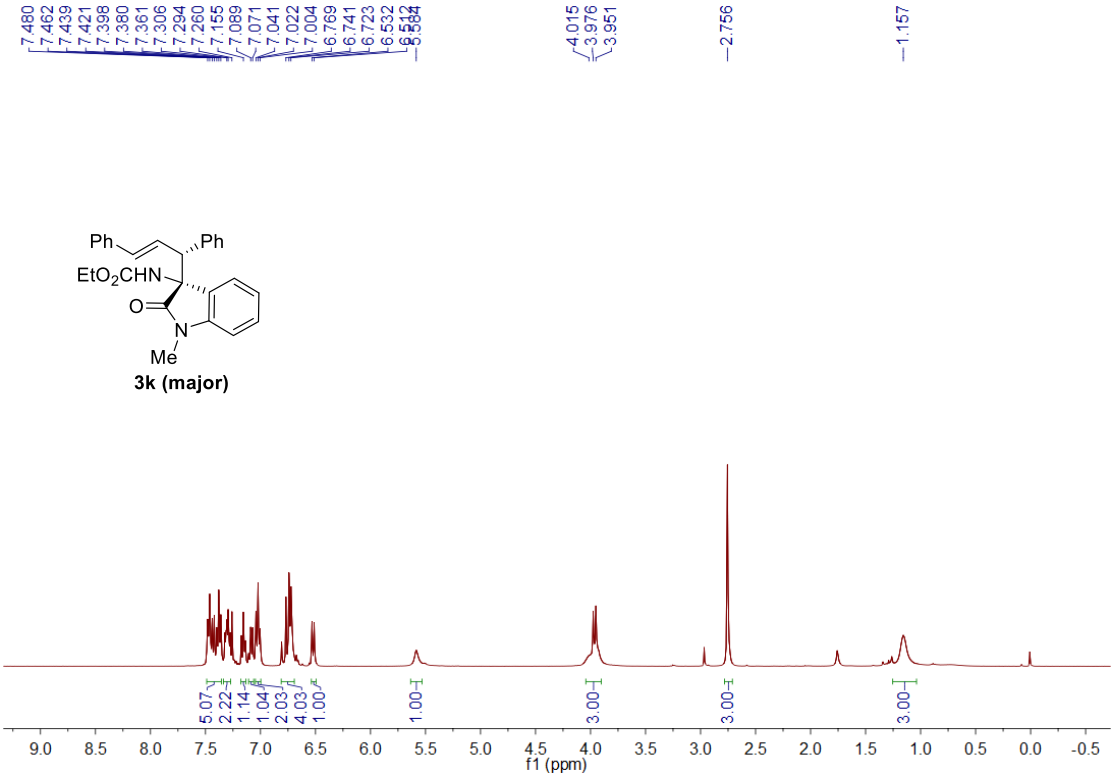


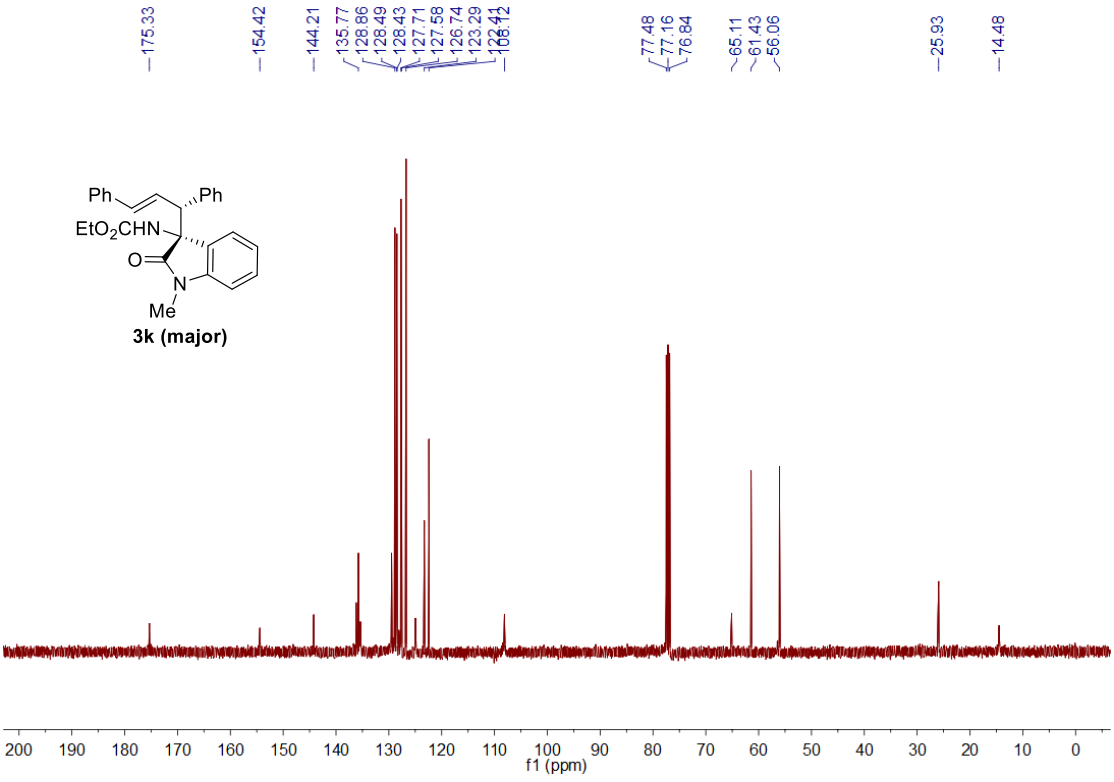
1 254nm 4nm

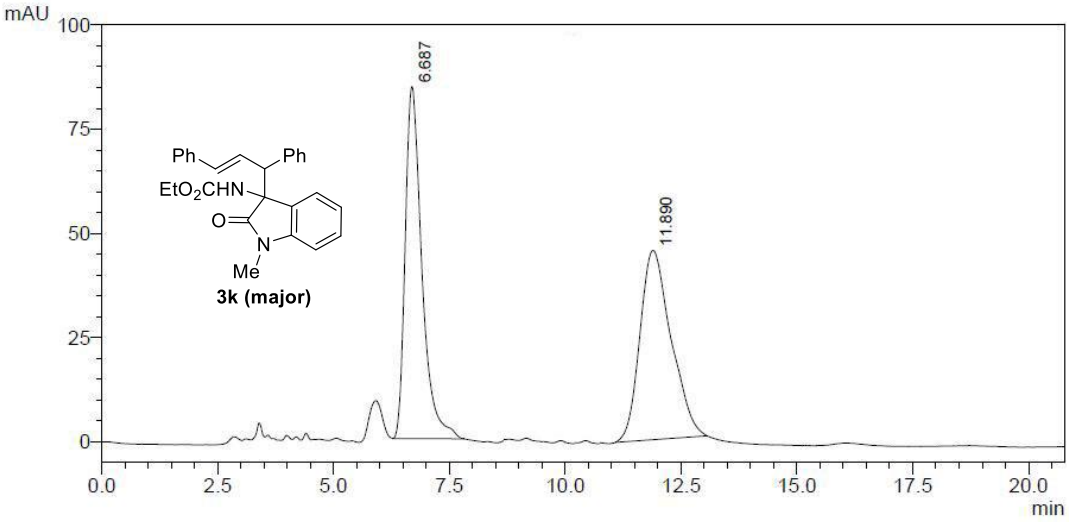
PDA

ID#	Rt. Time	Area	Height	Area%
1	8.189	10208830	546544	97.470
2	11.327	264999	14082	2.530

NMR and HPLC of 3k

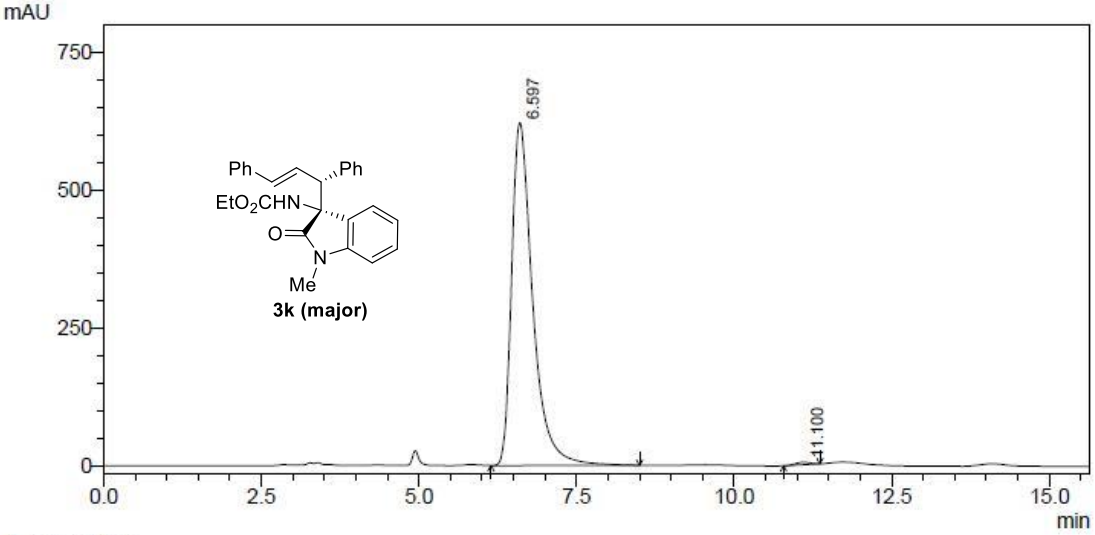






<Peak Table>
PDA

Peak#	Ret. Time	Area	Height	Area %
1	6.687	2113531	84432	49.881
2	11.890	2123604	45405	50.119

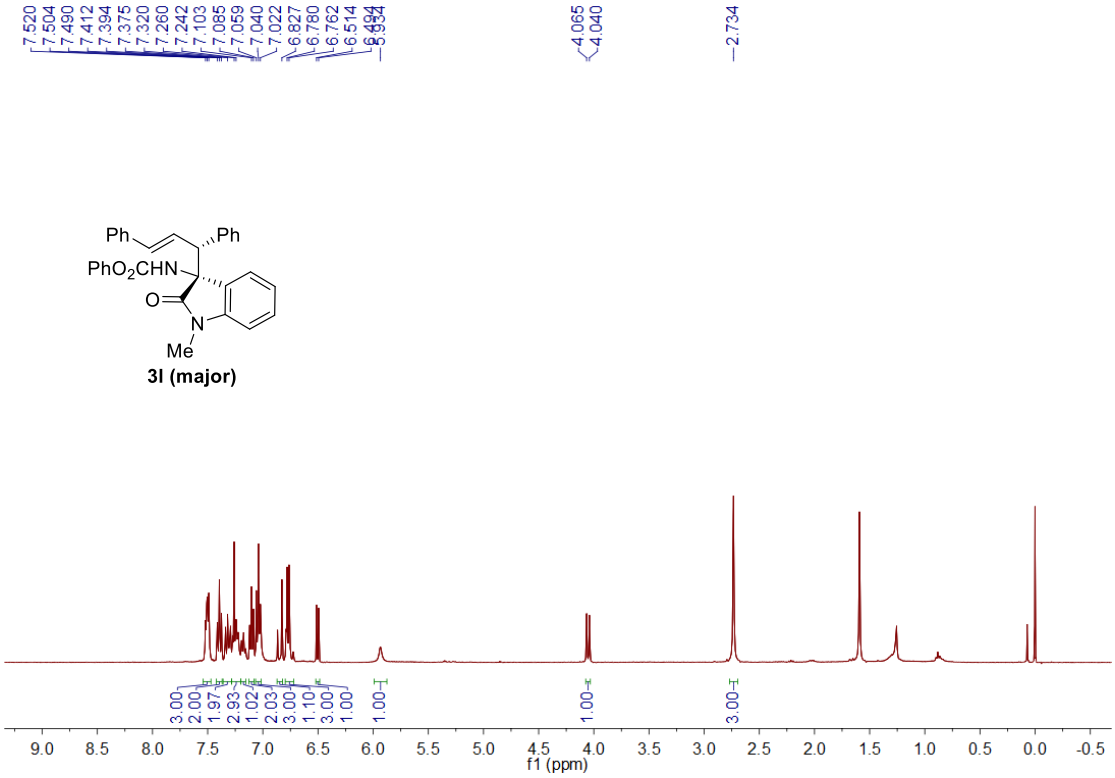


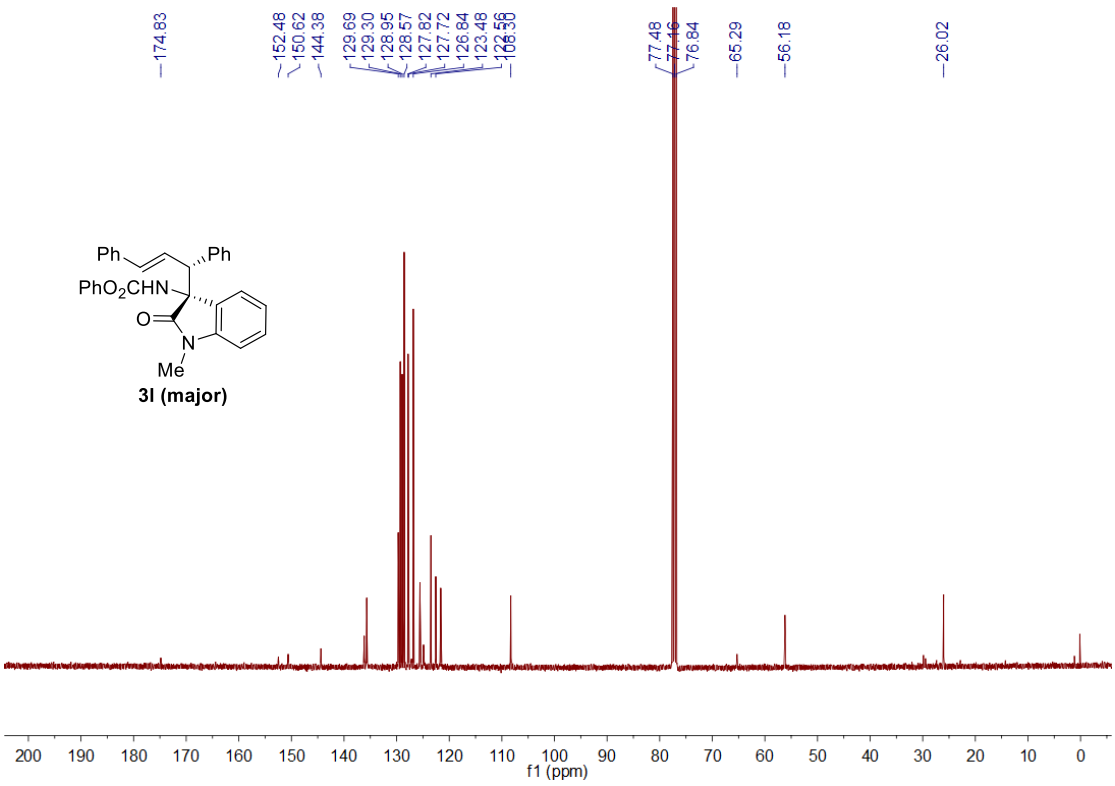
1 254nm 4nm

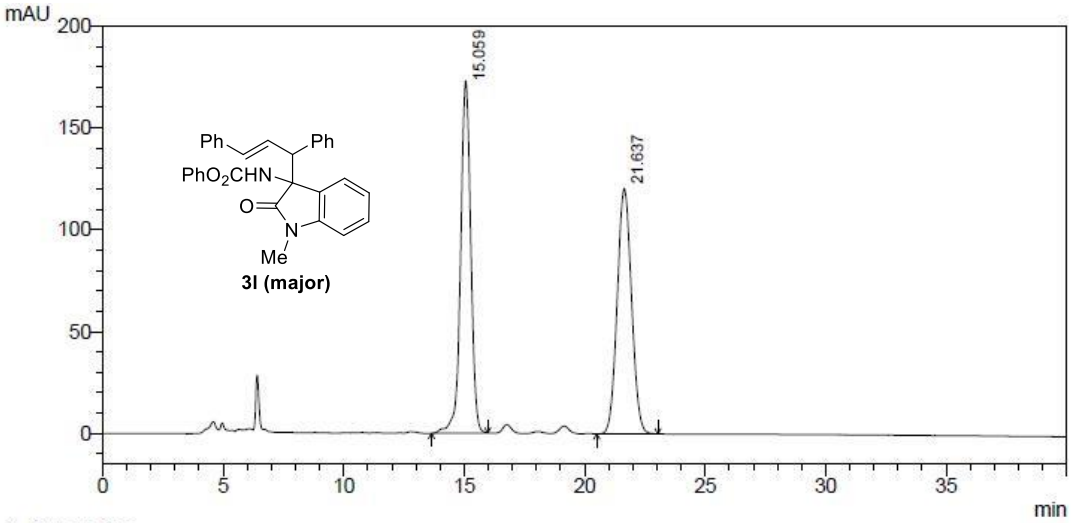
PDA

ID#	Rt. Time	Area	Height	Area %
1	6.597	14479668	622167	99.484
2	11.100	75149	4659	0.516

NMR and HPLC of 3l



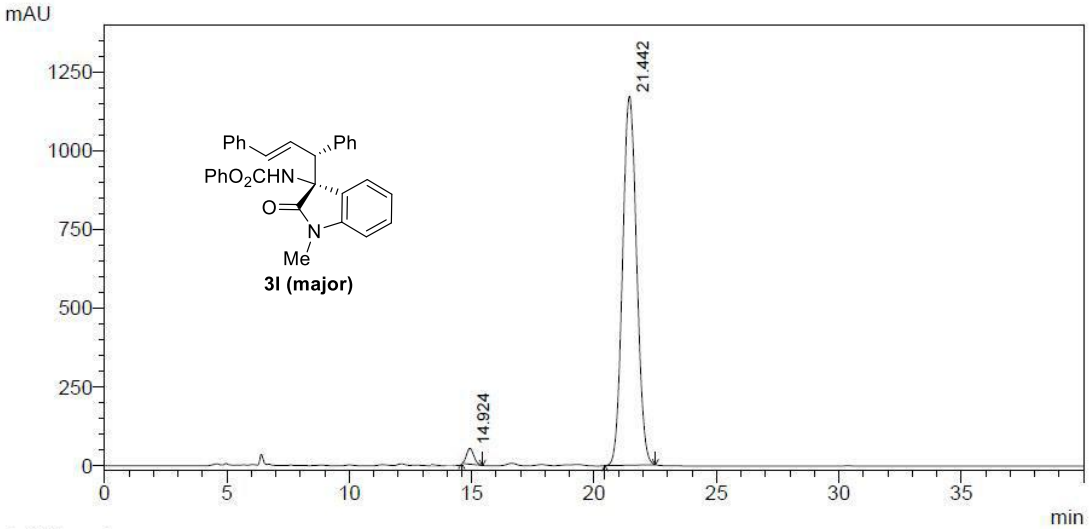




1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	15.059	5076562	173009	50.488
2	21.637	4978518	120469	49.512

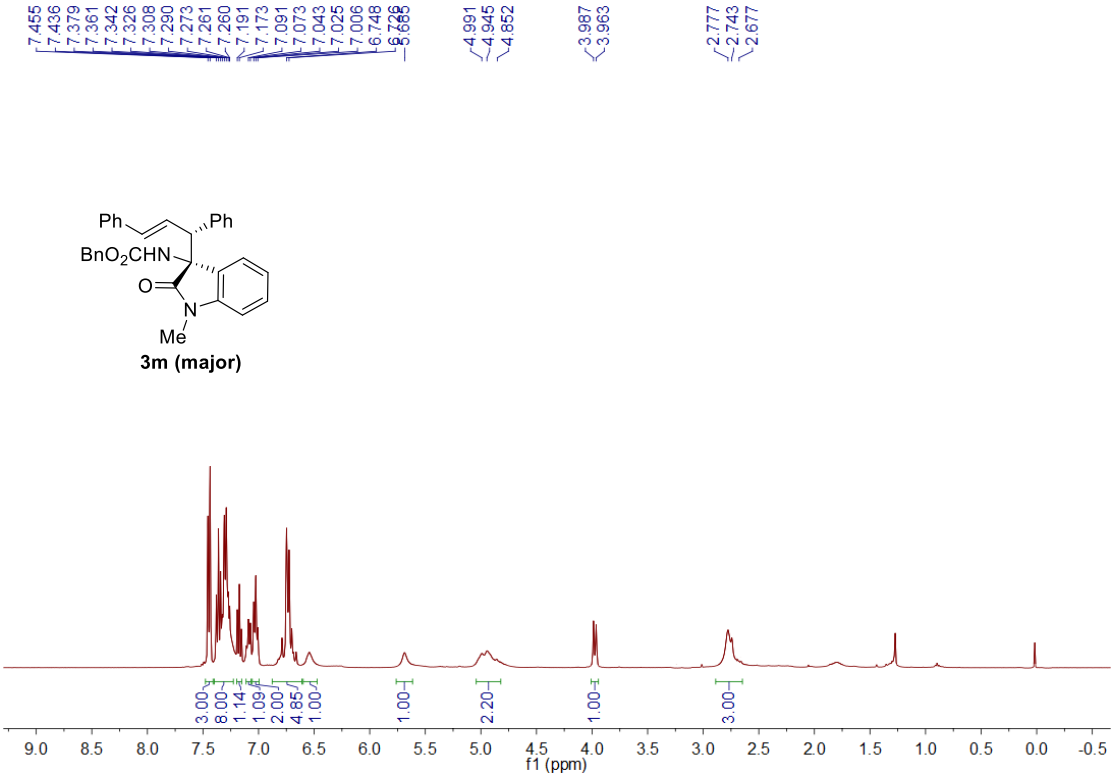


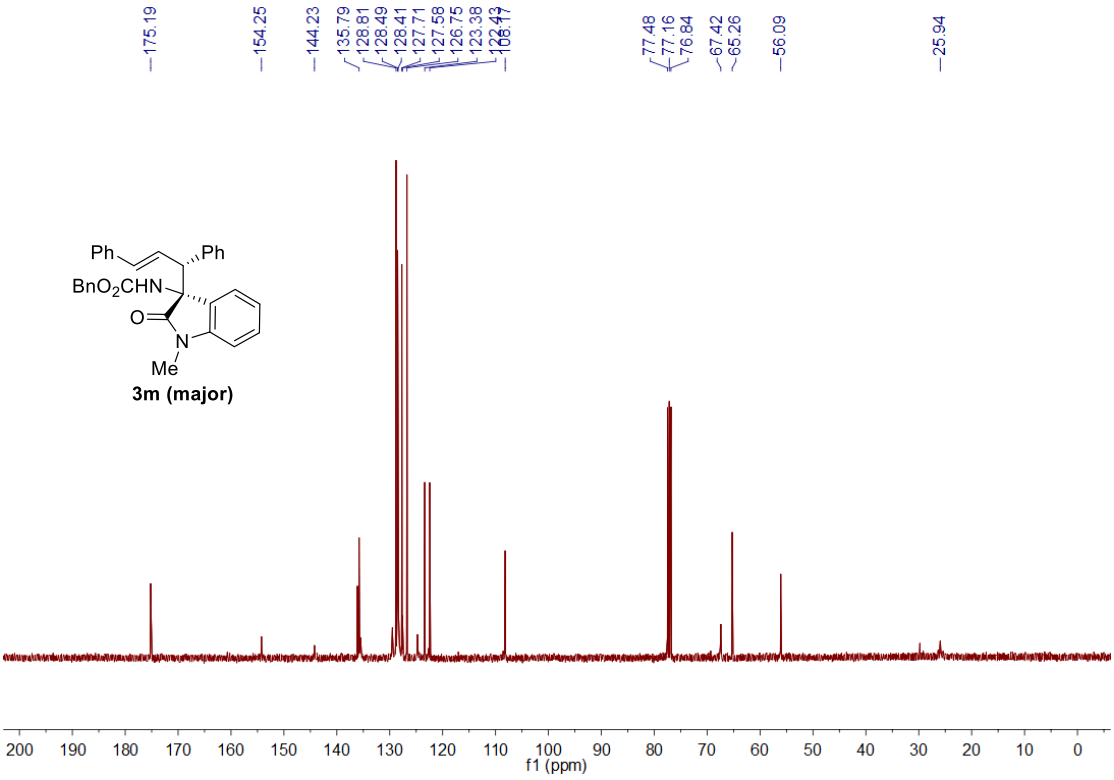
1 254nm 4nm

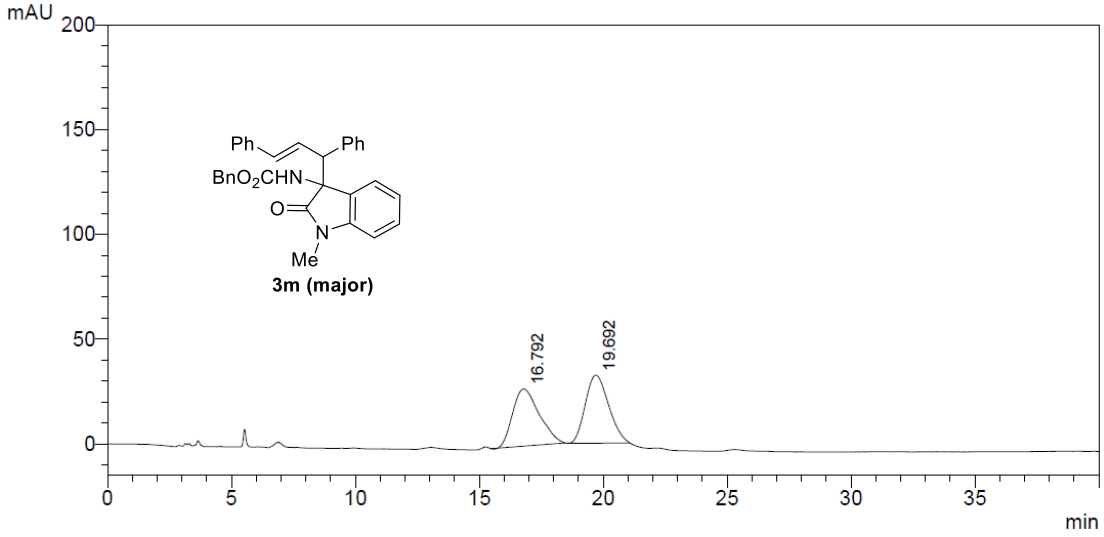
PDA

ID#	Rt. Time	Area	Height	Area %
1	14.924	1045873	50241	2.177
2	21.442	47003355	1172574	97.823

NMR and HPLC of 3m

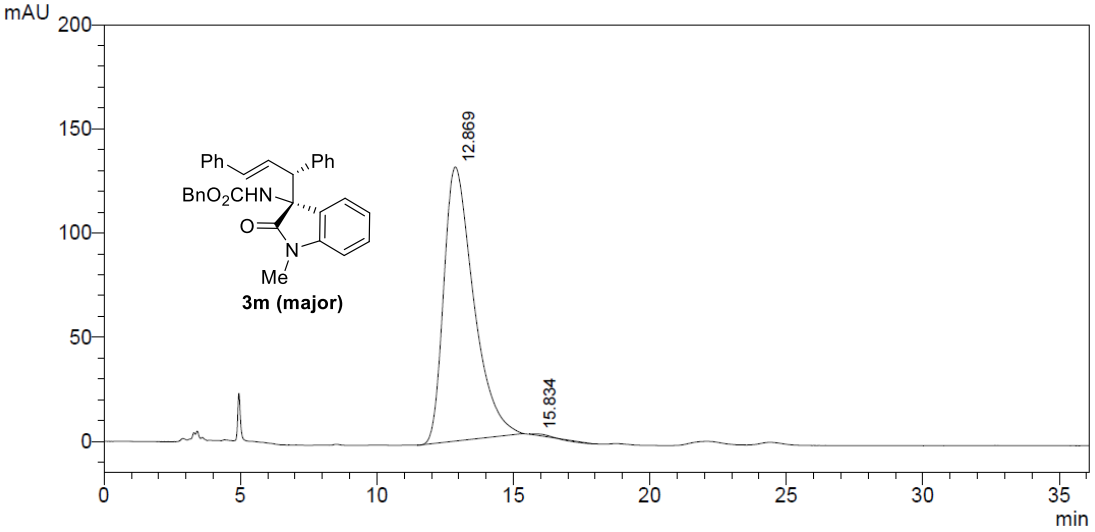






<Peak Table>
PDA

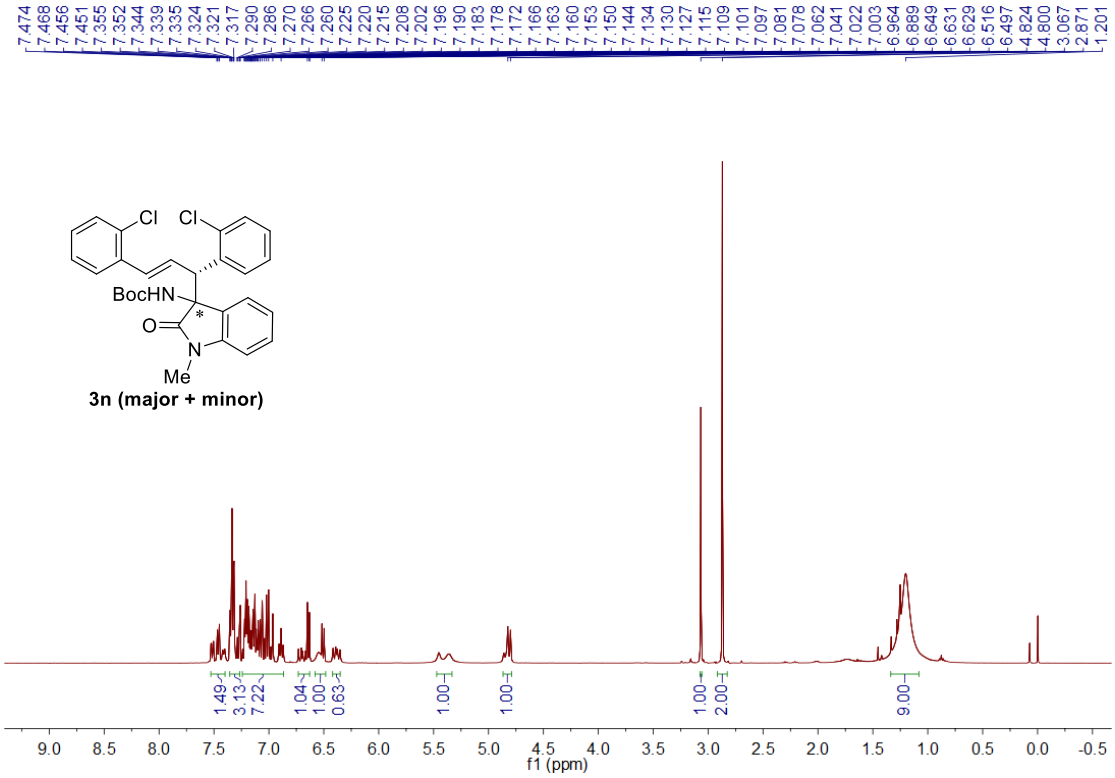
Peak#	Ret. Time	Area	Height	Area %
1	16.792	2021744	27227	48.773
2	19.692	2123464	32432	51.227

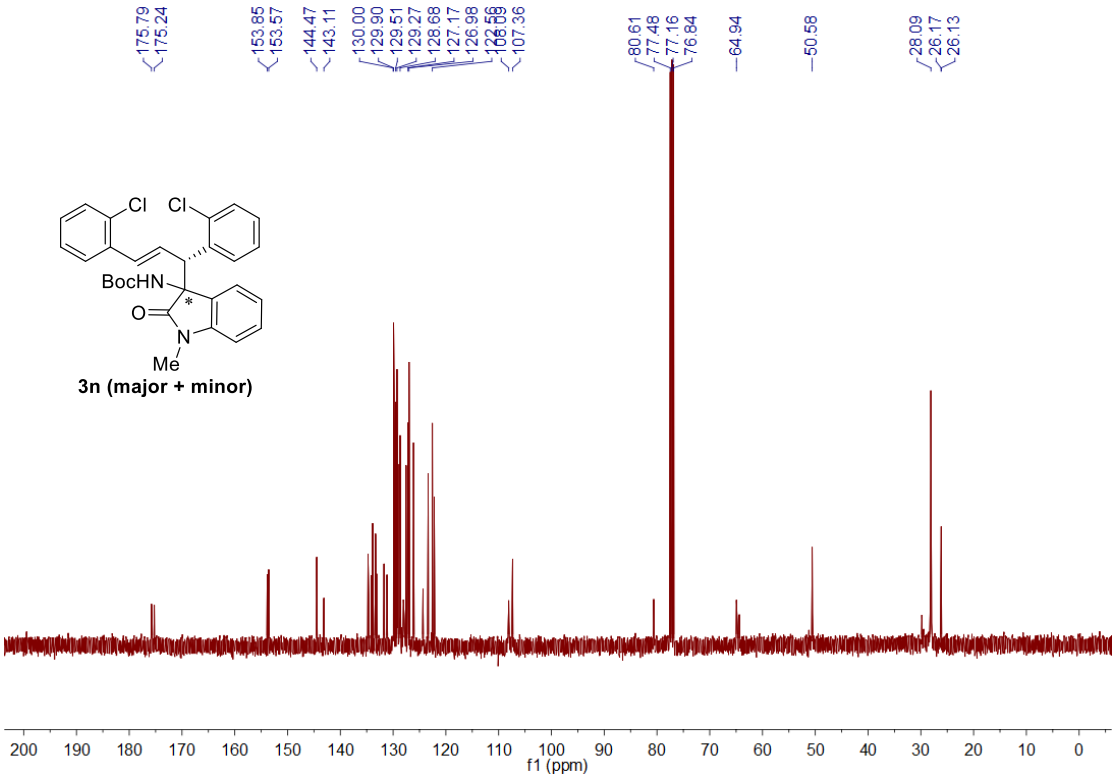


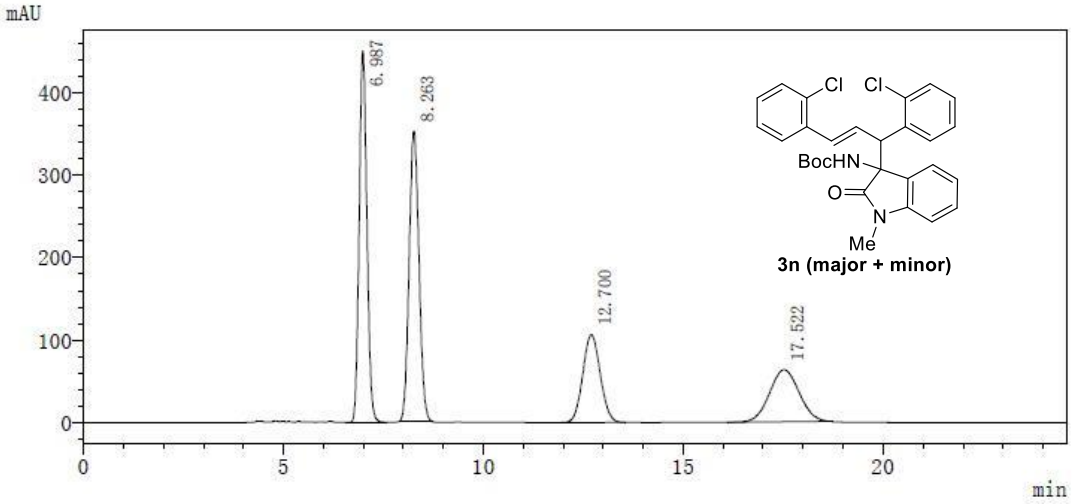
<Peak Table>
PDA

Peak#	Ret. Time	Area	Height	Area %
1	12.869	10015309	131526	99.926
2	15.834	7381	621	0.074

NMR and HPLC of 3n

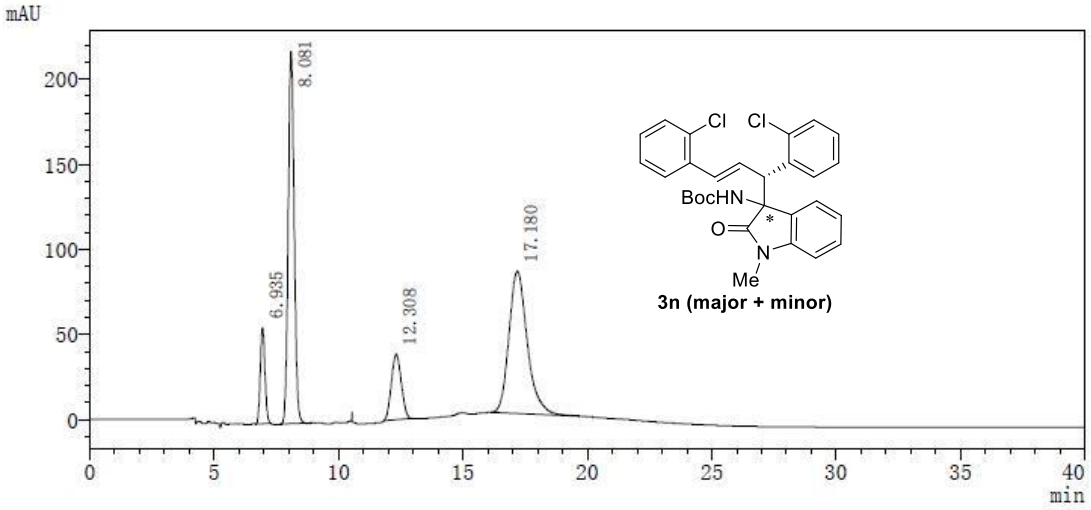






1 254nm 4nm

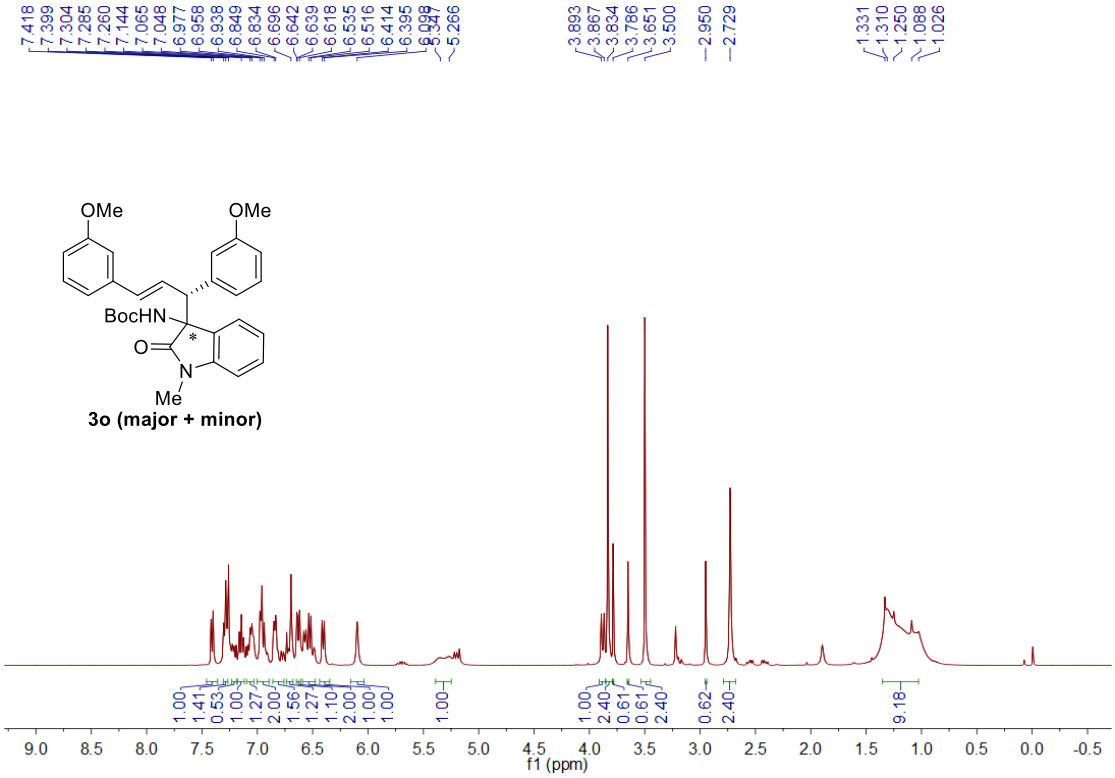
ID#	Rt. Time	Area	Height	Area %
1	6.987	6071948	450481	32.666
2	8.263	6006636	352260	32.315
3	12.700	3238702	106433	17.424
4	17.522	3270639	63211	17.596

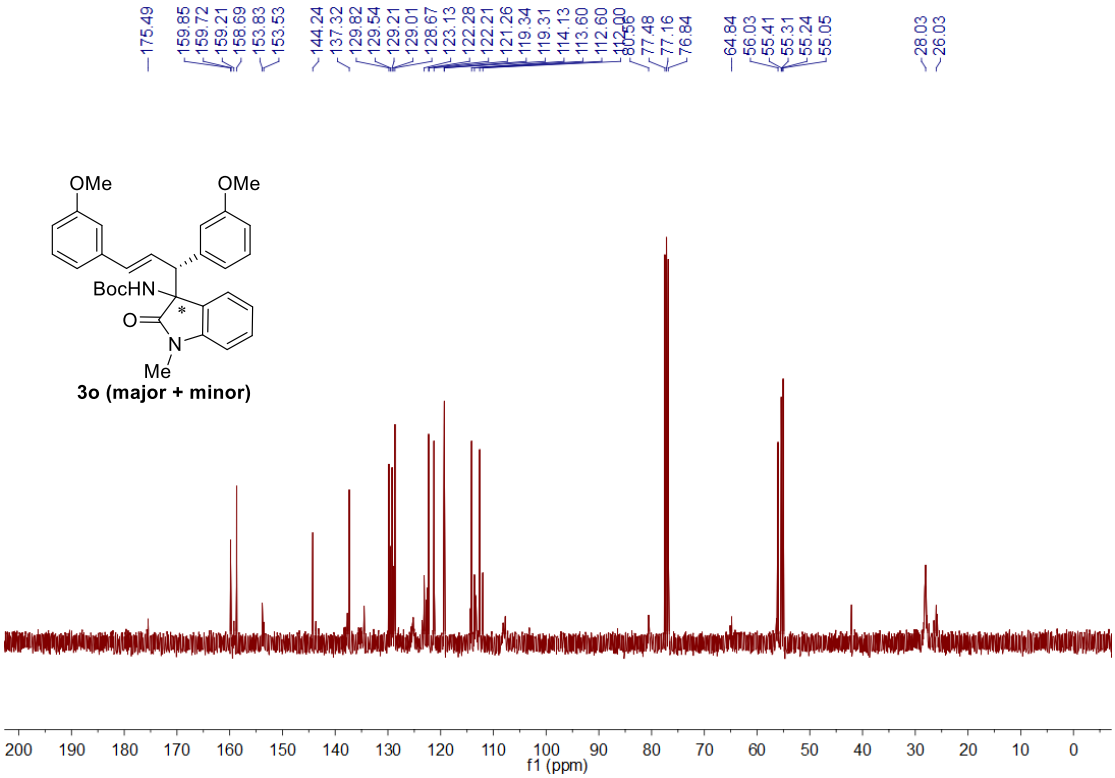


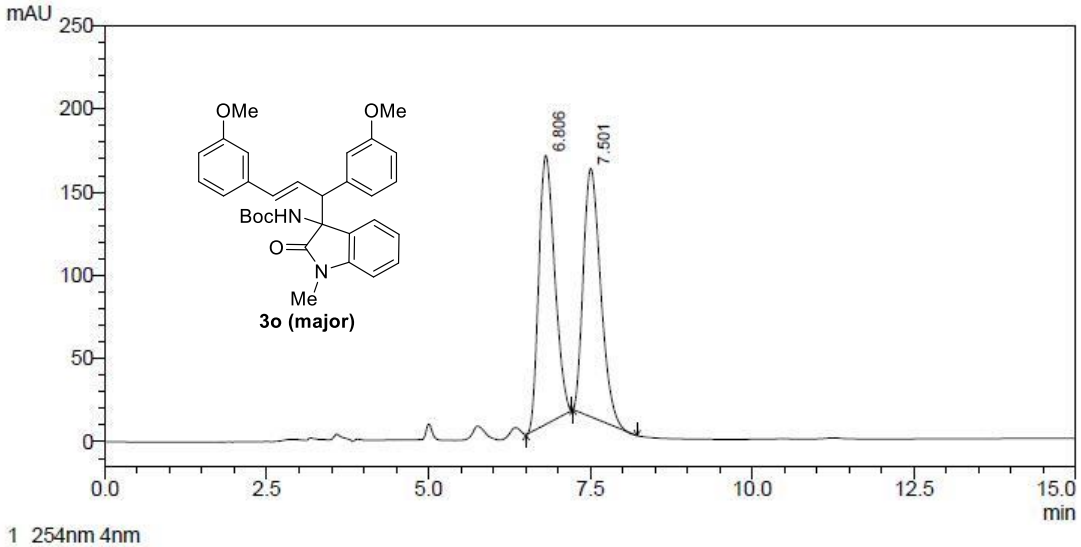
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	6.935	740123	56870	7.589
2	8.081	3655859	218878	37.488
3	12.308	1066466	38452	10.936
4	17.180	4289682	83660	43.987

NMR and HPLC of 3o



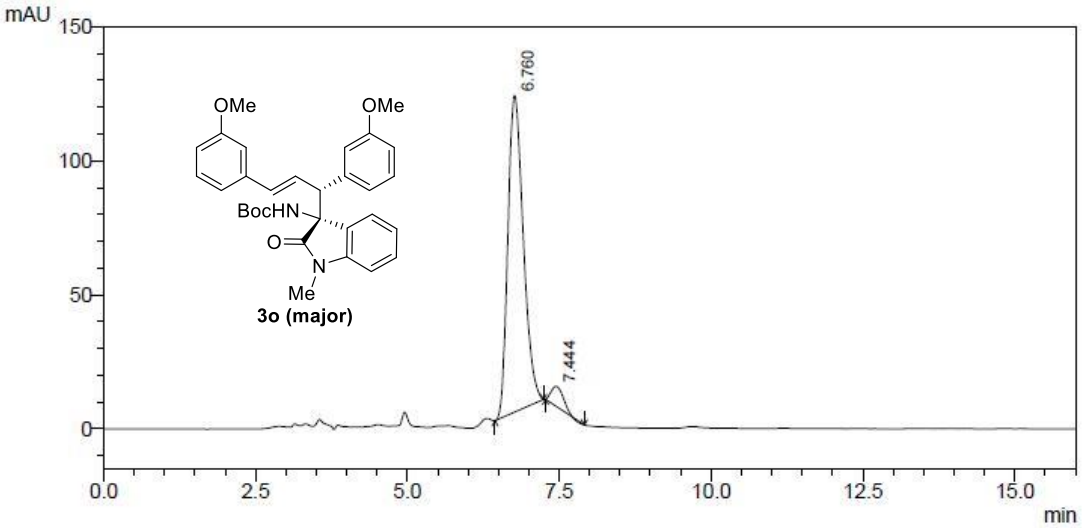




1 254nm 4nm

PDA

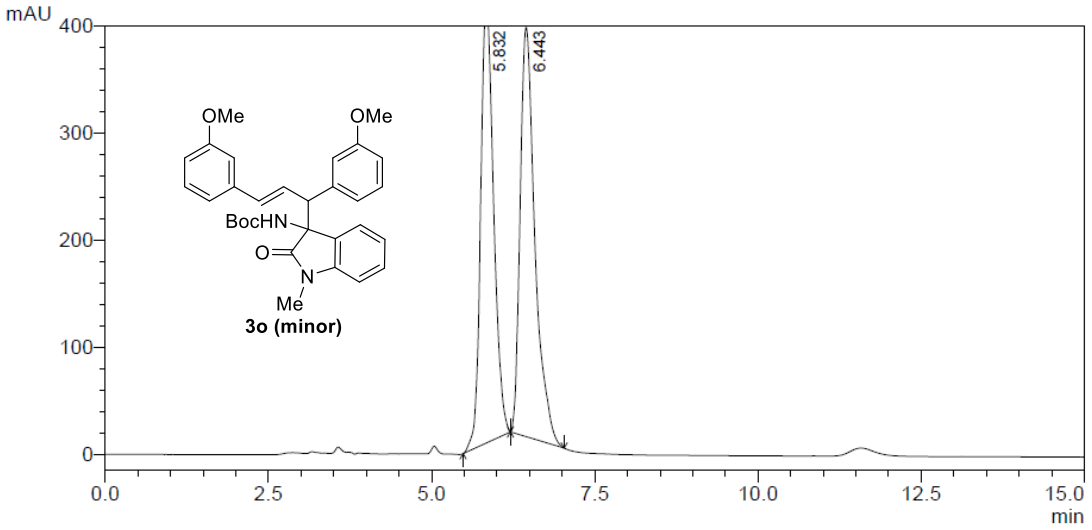
ID#	Rt. Time	Area	Height	Area %
1	6.806	2762724	161659	49.840
2	7.501	2780482	149188	50.160



1 254nm 4nm

PDA

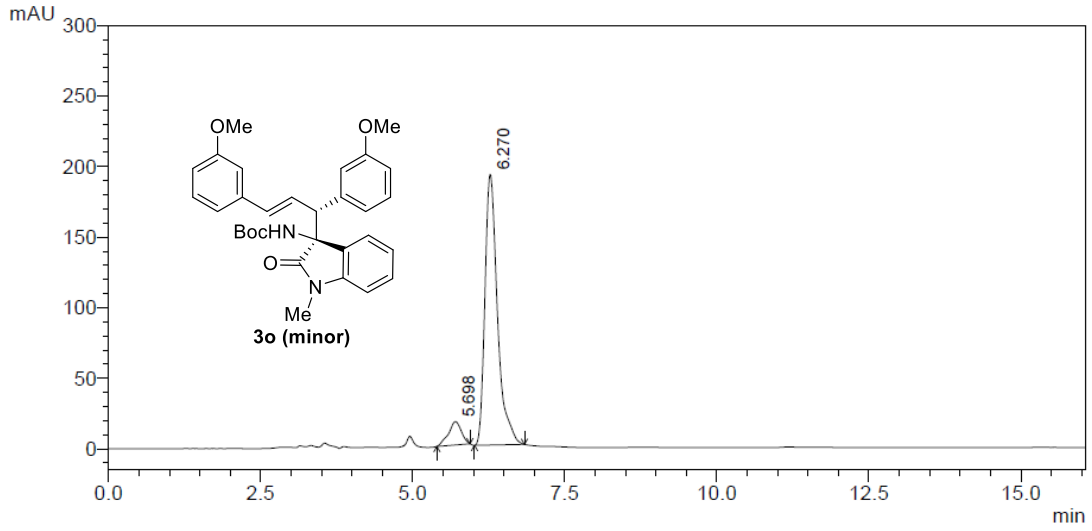
ID#	Rt. Time	Area	Height	Area %
1	6.760	2090746	118231	95.434
2	7.444	100033	7392	4.566



1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area%
1	5.832	5711969	413425	48.776
2	6.443	5998601	381396	51.224

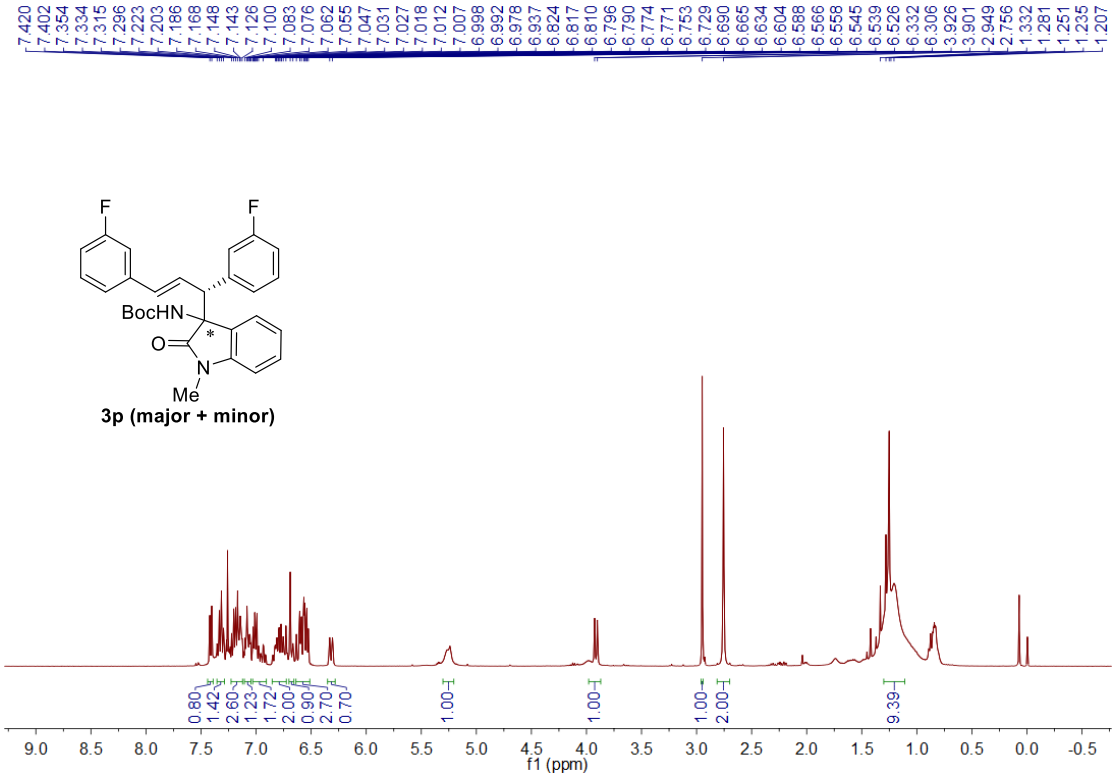


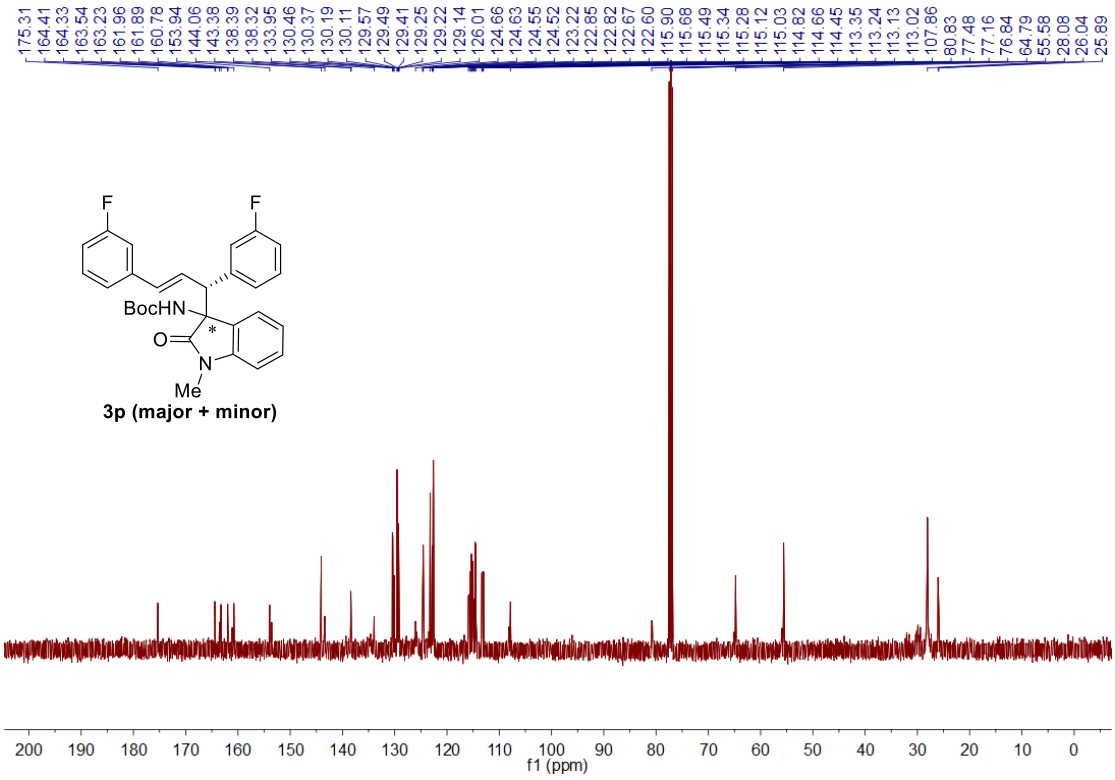
1 254nm 4nm

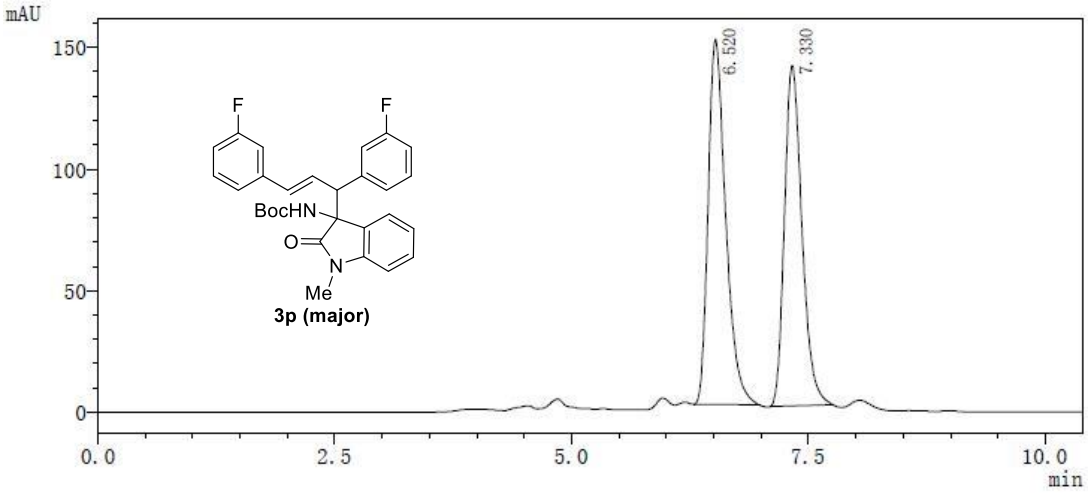
PDA

ID#	Rt. Time	Area	Height	Area %
1	5.698	244168	16596	8.141
2	6.270	2754943	191829	91.859

NMR and HPLC of 3p

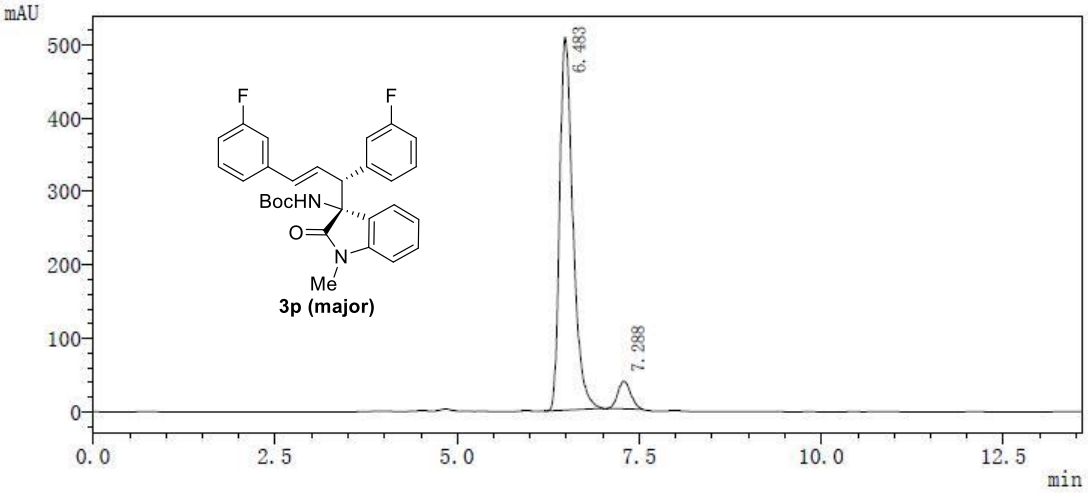






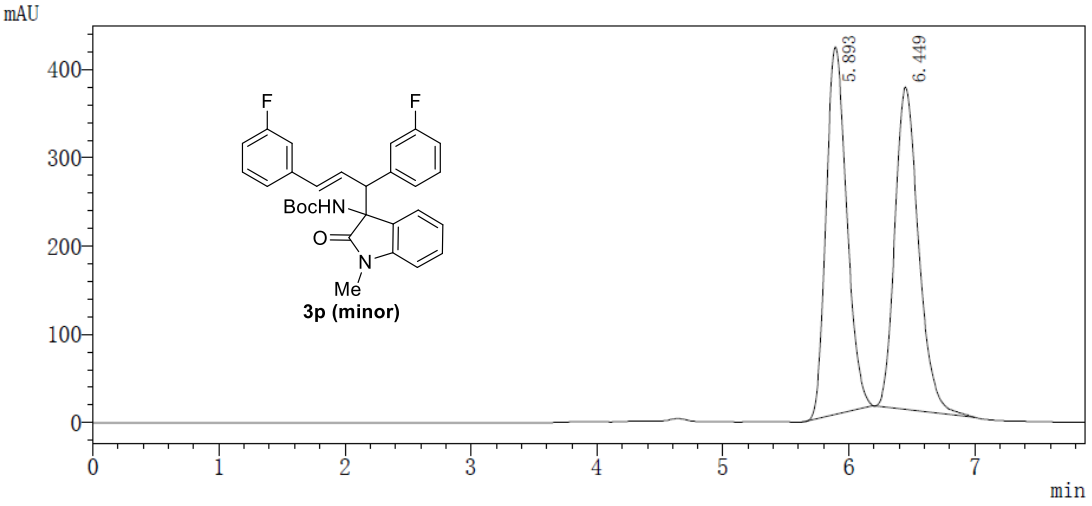
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	6.520	1938782	150114	51.879
2	7.330	1798370	140033	48.121



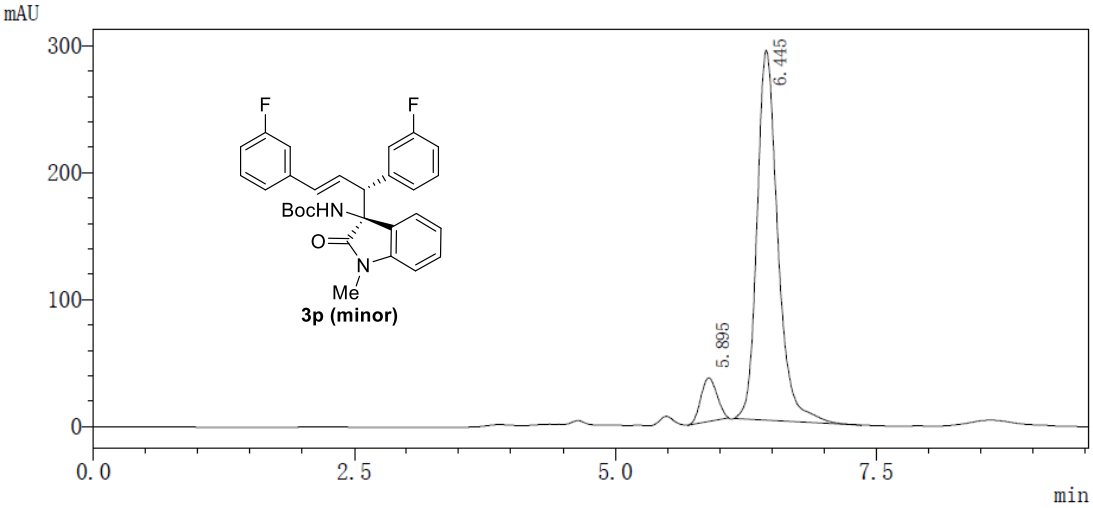
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	6.483	6431564	508135	93.258
2	7.288	464928	37813	6.742



1 254nm 4nm

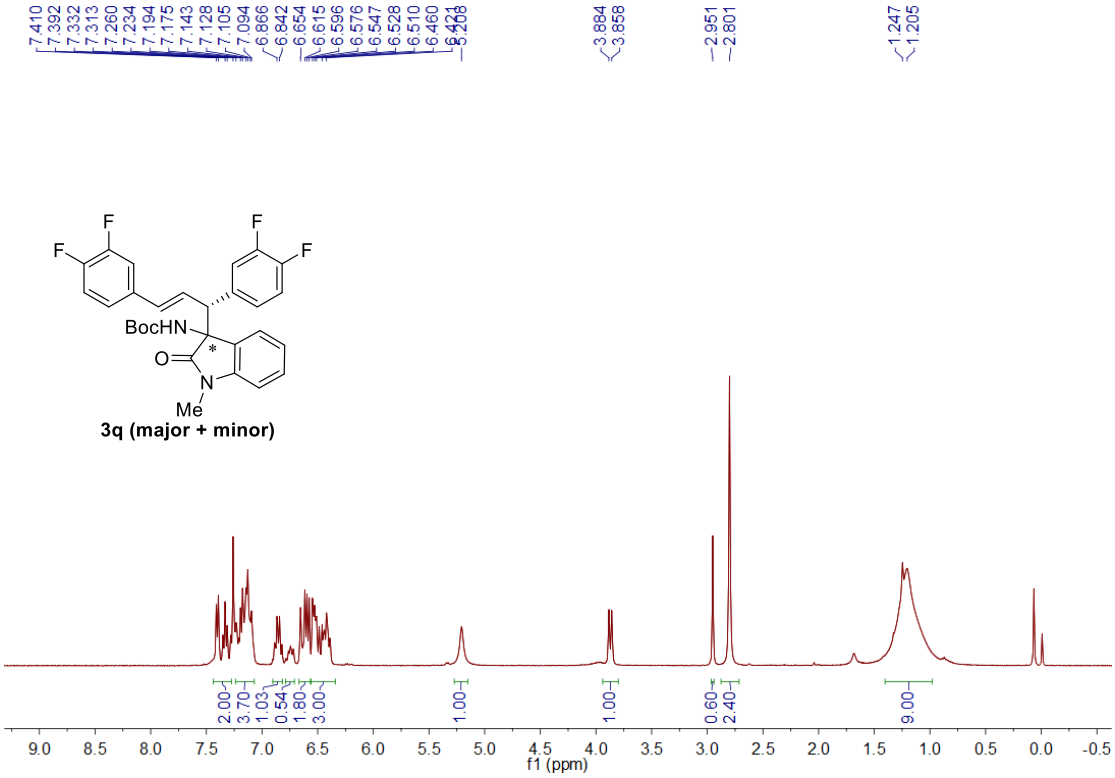
ID#	Rt. Time	Area	Height	Area %
1	5.893	4765468	416381	49.907
2	6.449	4783217	365216	50.093

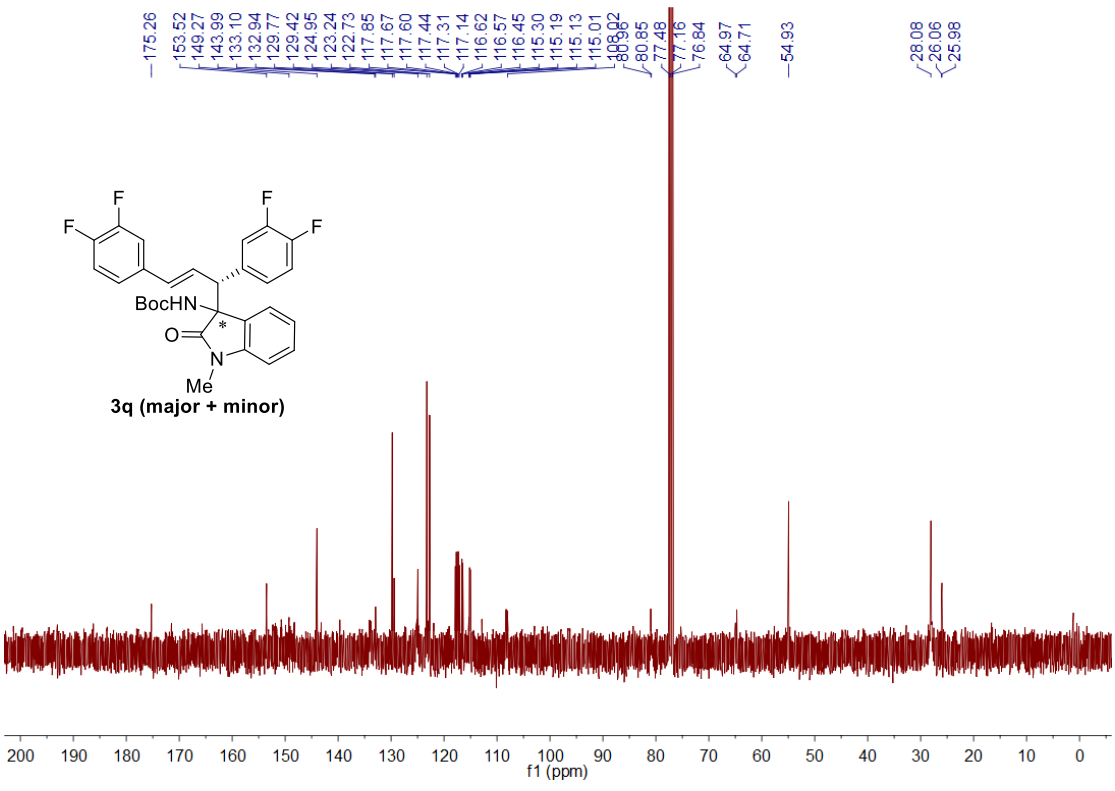


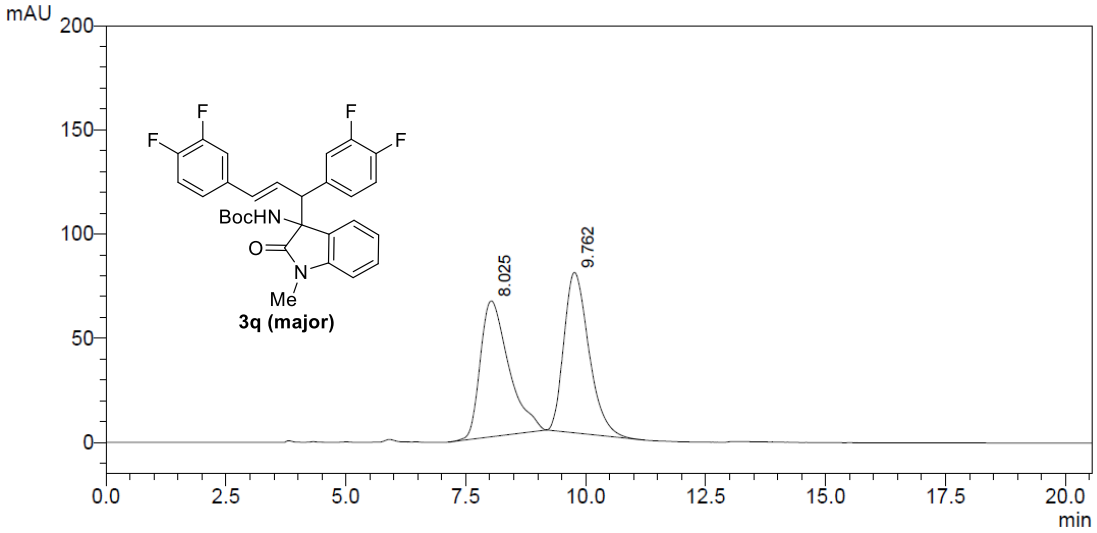
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	5.895	365677	34168	8.304
2	6.445	4038083	291250	91.696

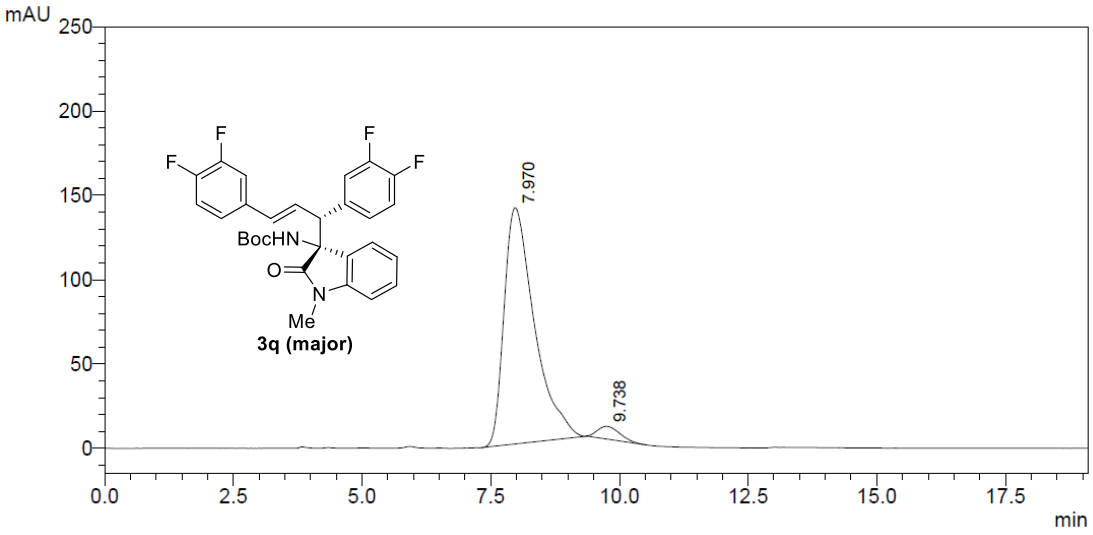
NMR and HPLC of 3q



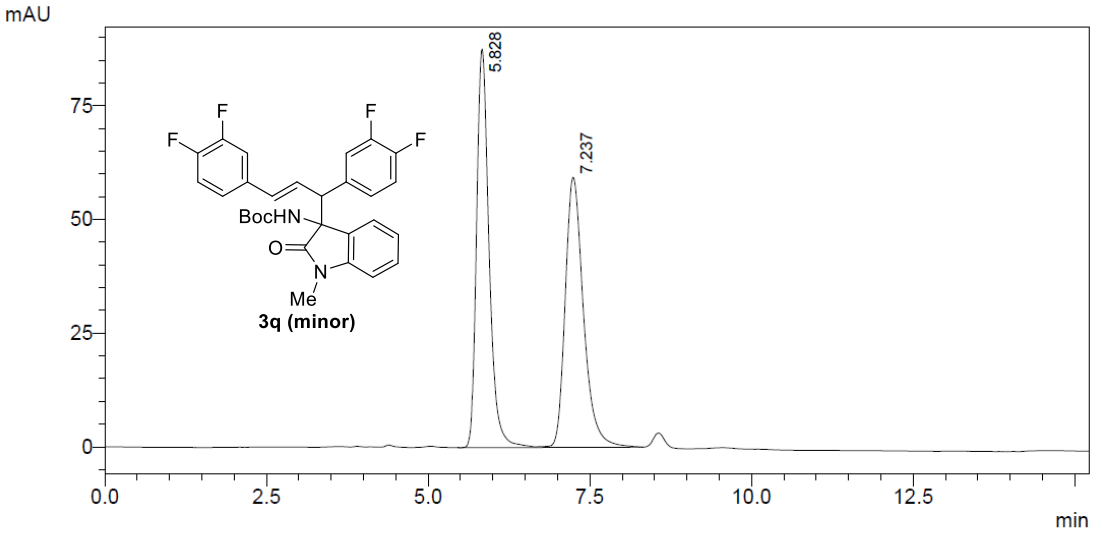




Peak	Ret. Time	Area	Height	Area %
1	8.025	2698786	65228	49.136
2	9.762	2793748	76963	50.864

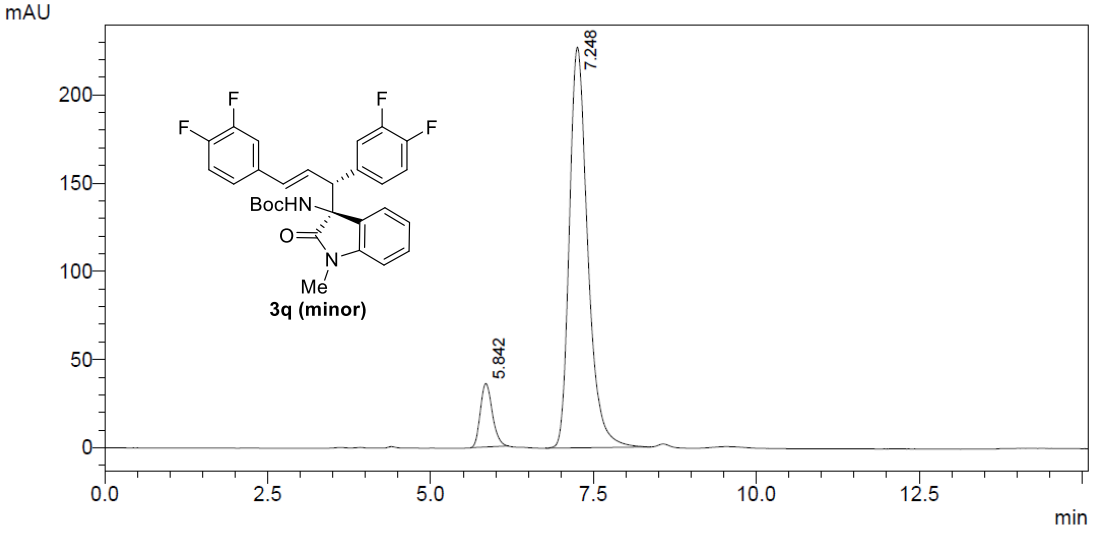


Peak	Ret. Time	Area	Height	Area %
1	7.970	5760632	140089	96.208
2	9.738	227066	7467	3.792



<Peak Table>
PDA

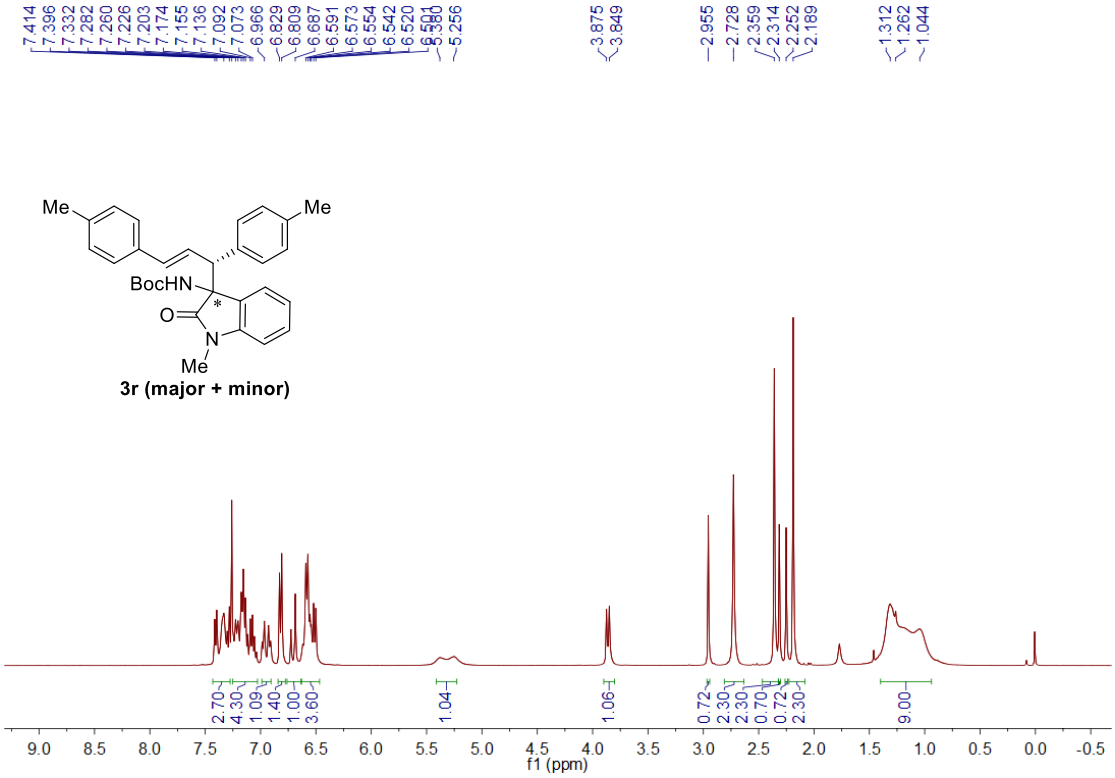
Peak#	Ret. Time	Area	Height	Area %
1	5.828	1181771	87642	50.324
2	7.237	1166546	59374	49.676

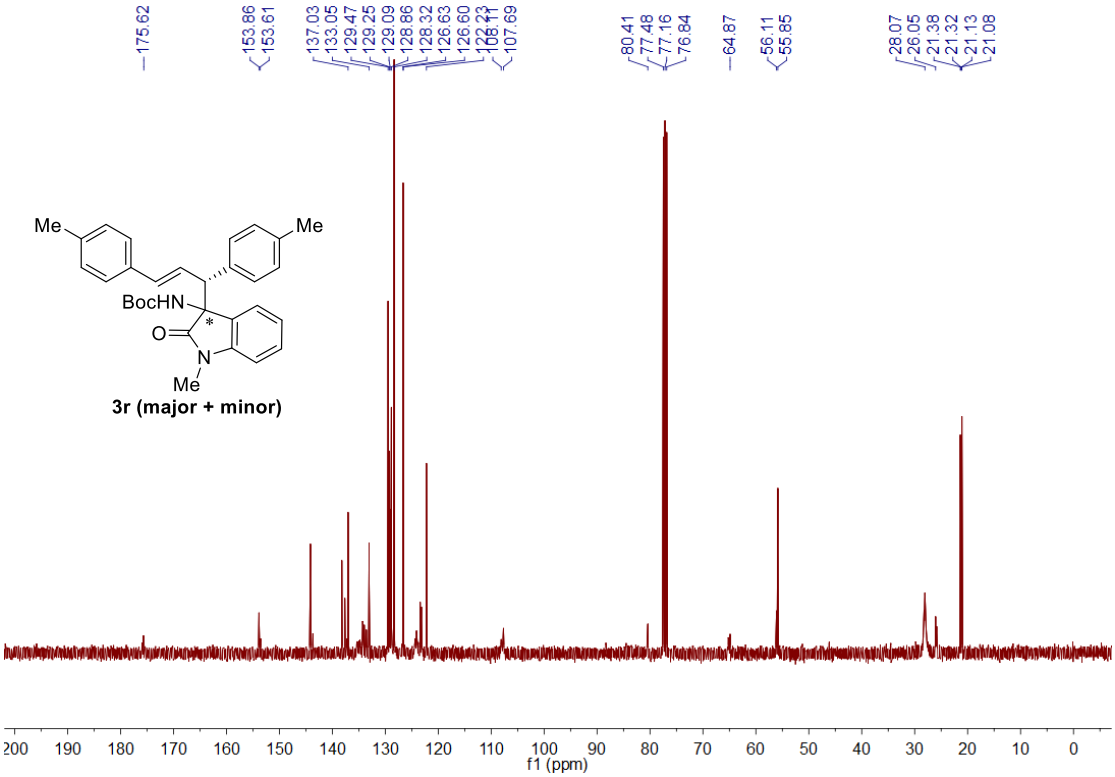


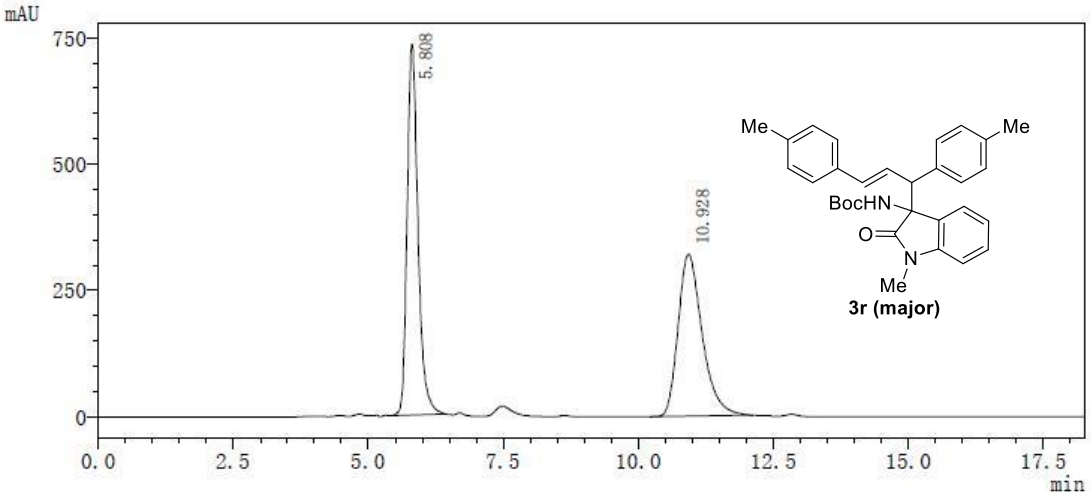
<Peak Table>
PDA

Peak#	Ret. Time	Area	Height	Area %
1	5.842	463057	36000	9.403
2	7.248	4461547	227198	90.597

NMR and HPLC of 3r

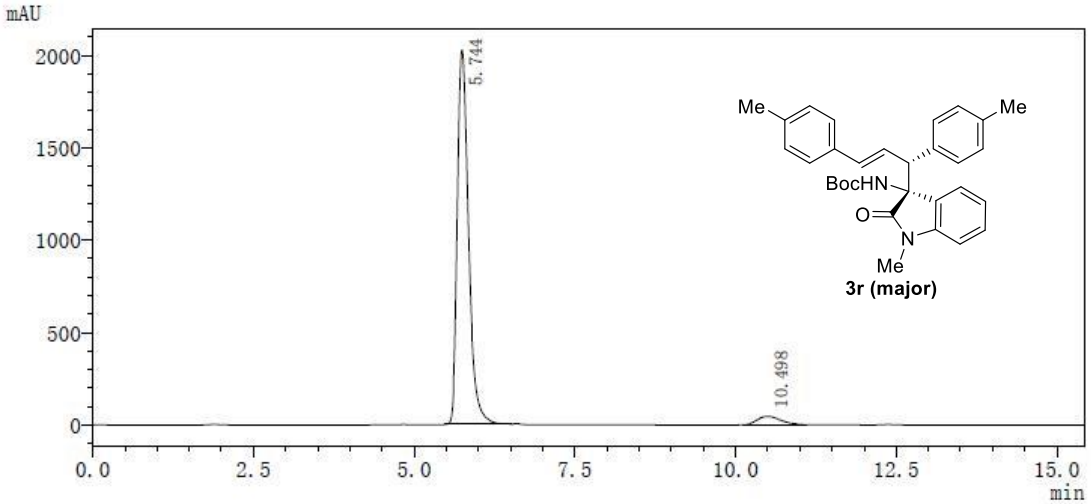






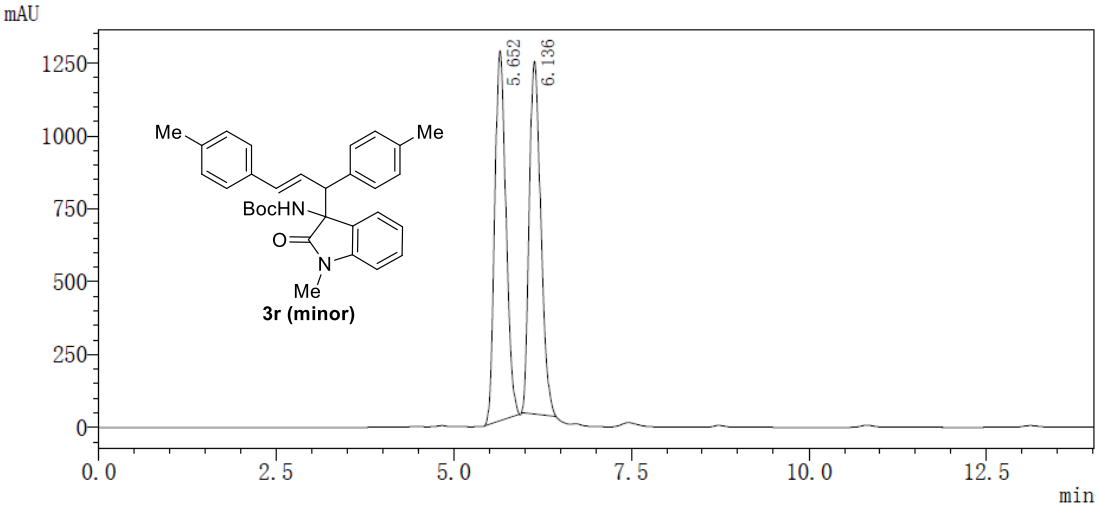
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	5.808	10234444	733003	50.886
2	10.928	9878027	319490	49.114



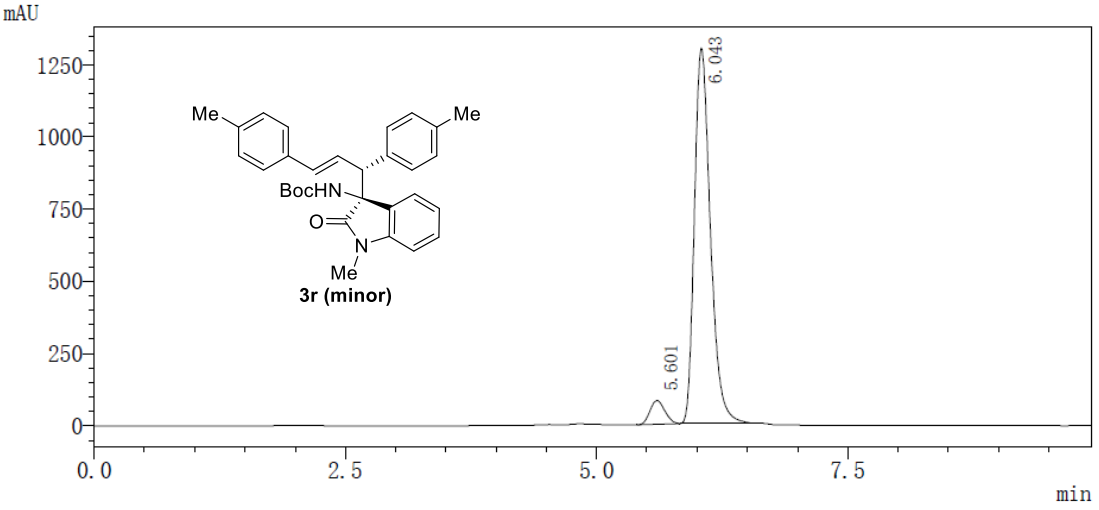
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	5.744	24370249	2027392	95.517
2	10.498	1143708	44819	4.483



1 254nm 4nm

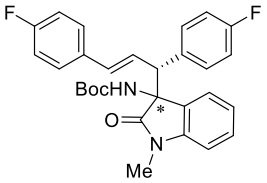
ID#	Rt. Time	Area	Height	Area %
1	5.652	14084443	1269761	50.581
2	6.136	13761142	1211749	49.419



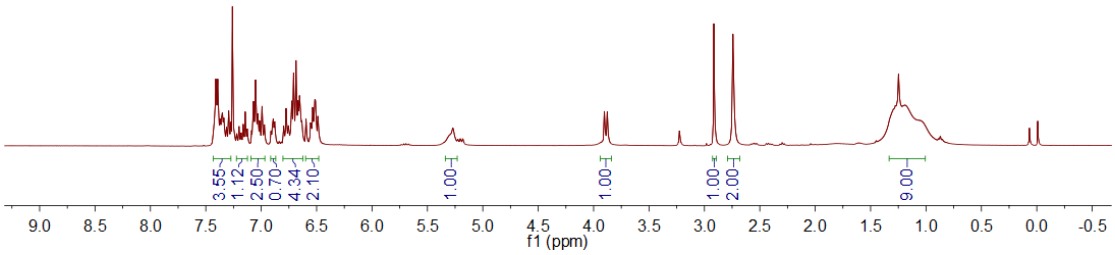
1 254nm 4nm

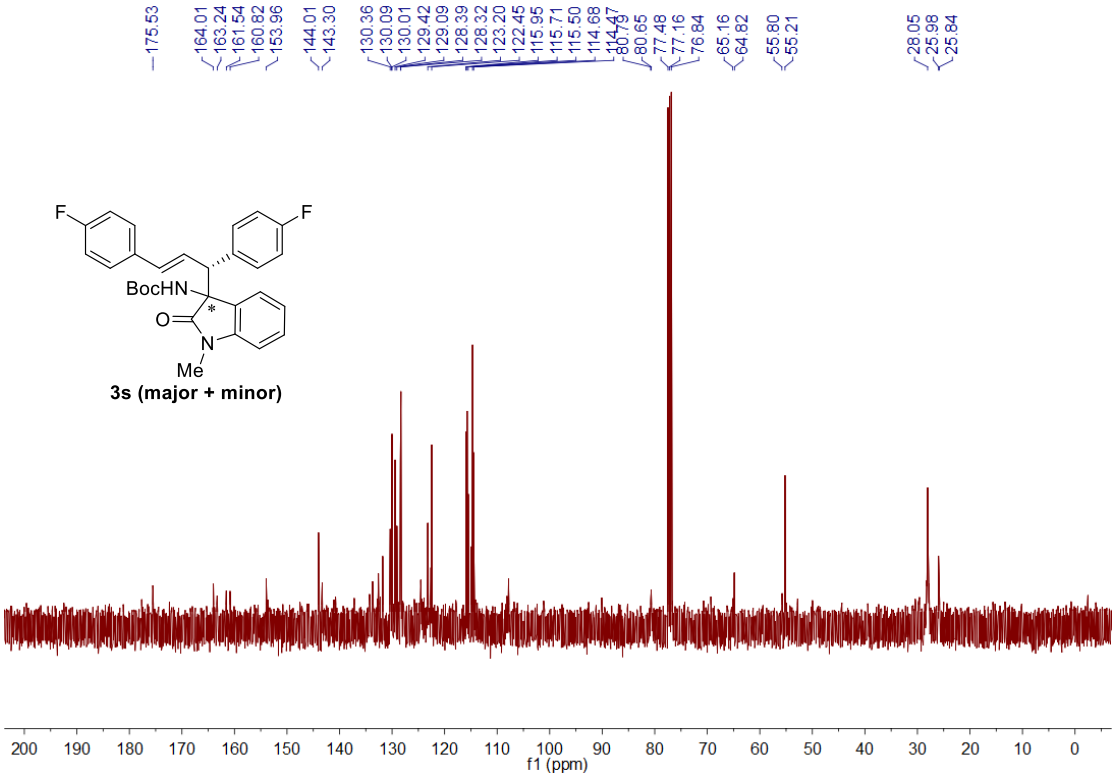
ID#	Rt. Time	Area	Height	Area %
1	5.601	844574	82480	5.551
2	6.043	14369425	1300247	94.449

NMR and HPLC of 3s

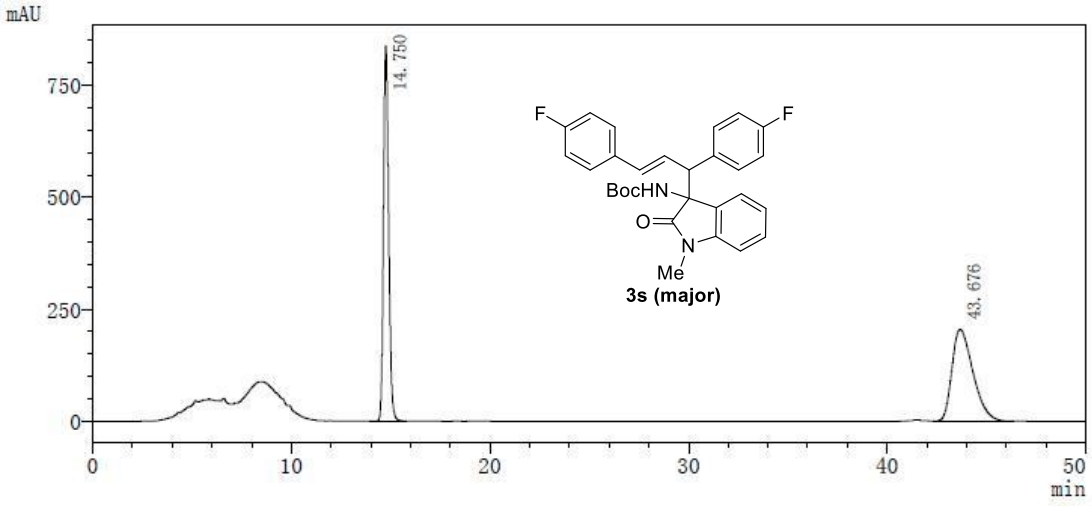


3s (major + minor)



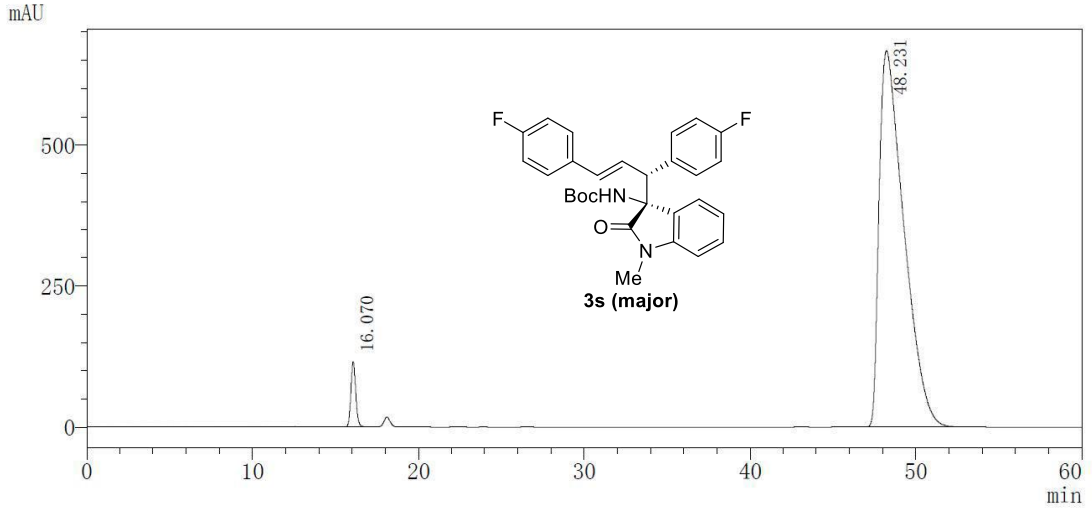


3s (major + minor)



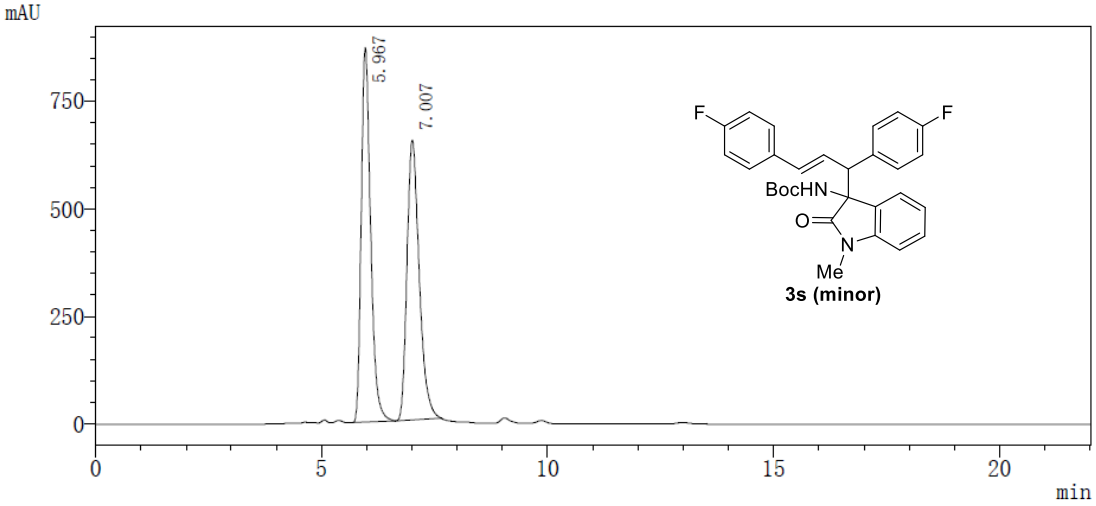
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	14.750	15081921	835935	50.023
2	43.676	15067842	204525	49.977



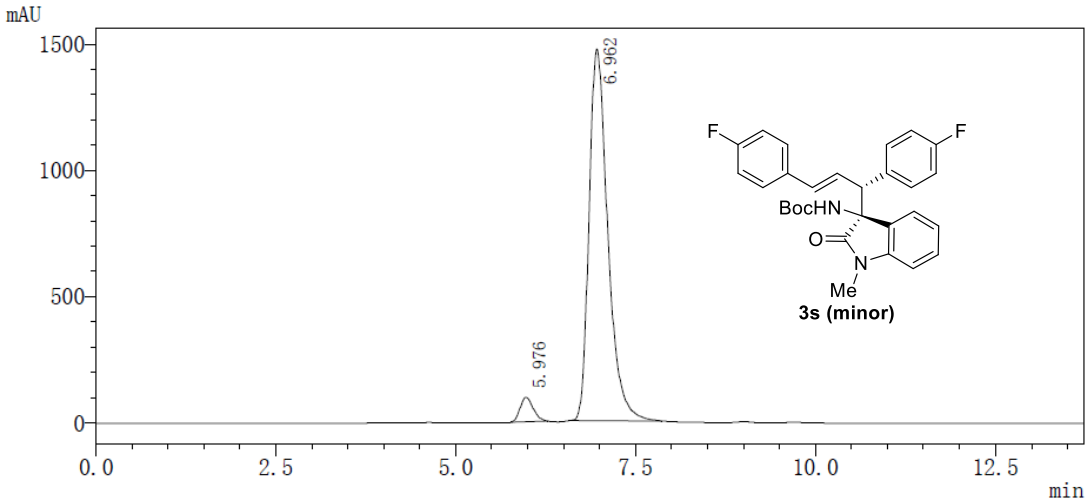
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	16.070	2334074	115665	3.272
2	48.231	69003154	667057	96.728



1 254nm 4nm

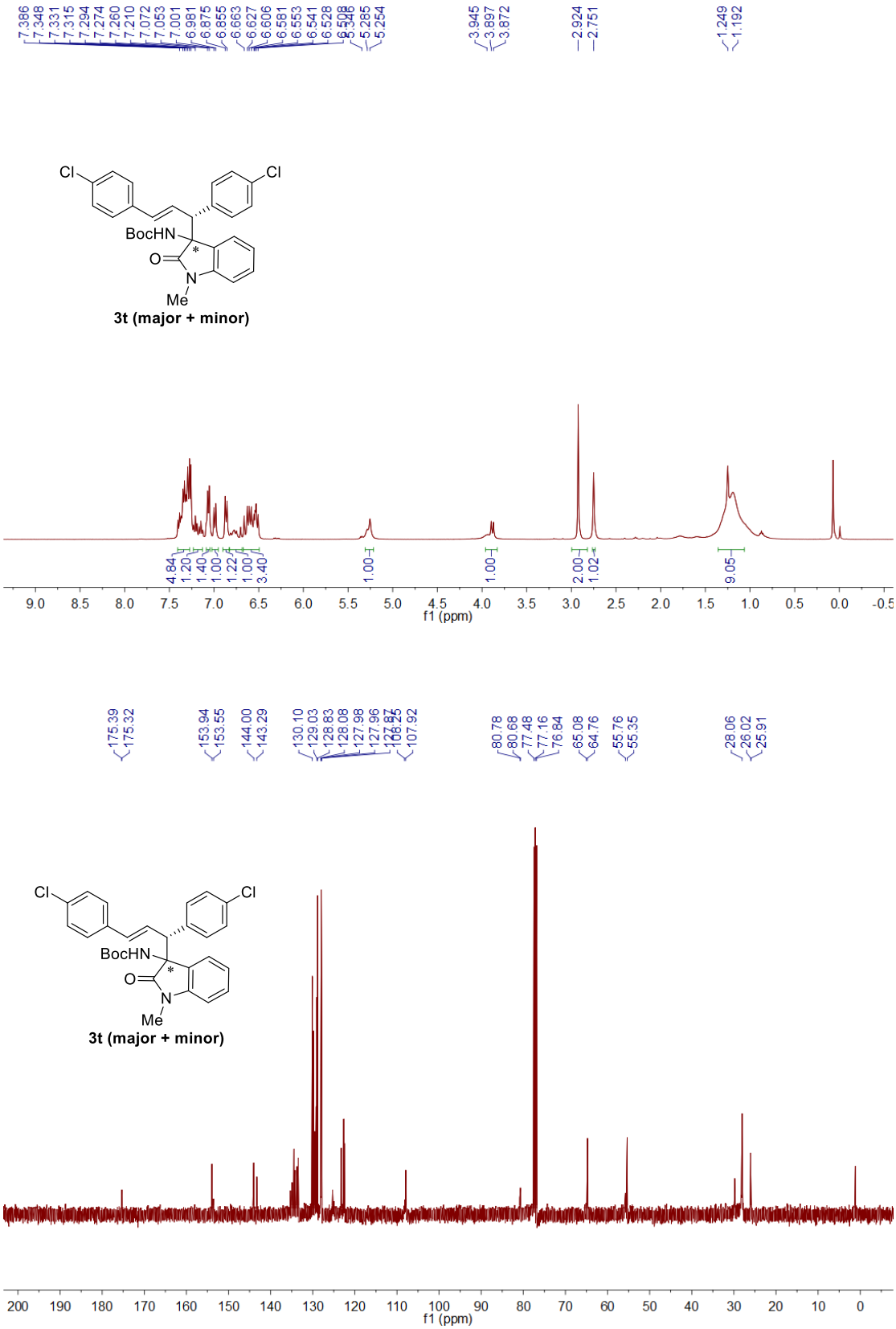
ID#	Rt. Time	Area	Height	Area %
1	5.967	12574660	870217	50.695
2	7.007	12229891	650840	49.305

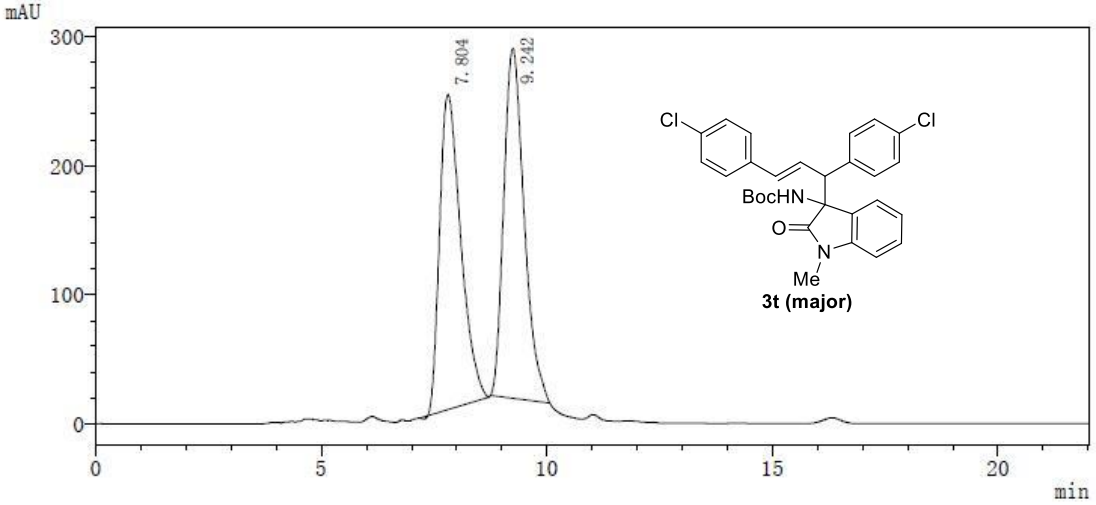


1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	5.976	1227096	96560	4.394
2	6.962	26696578	1471927	95.606

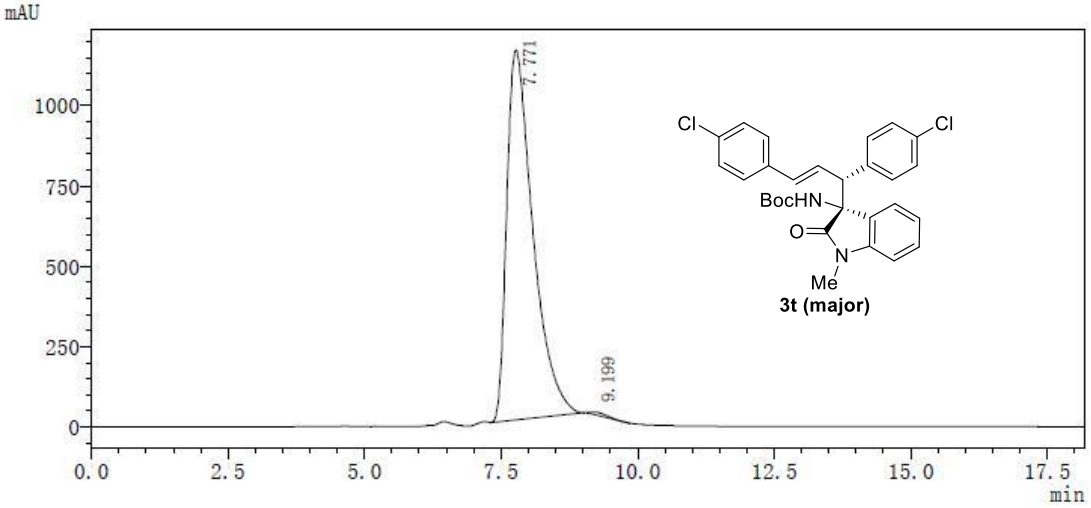
NMR and HPLC of 3t





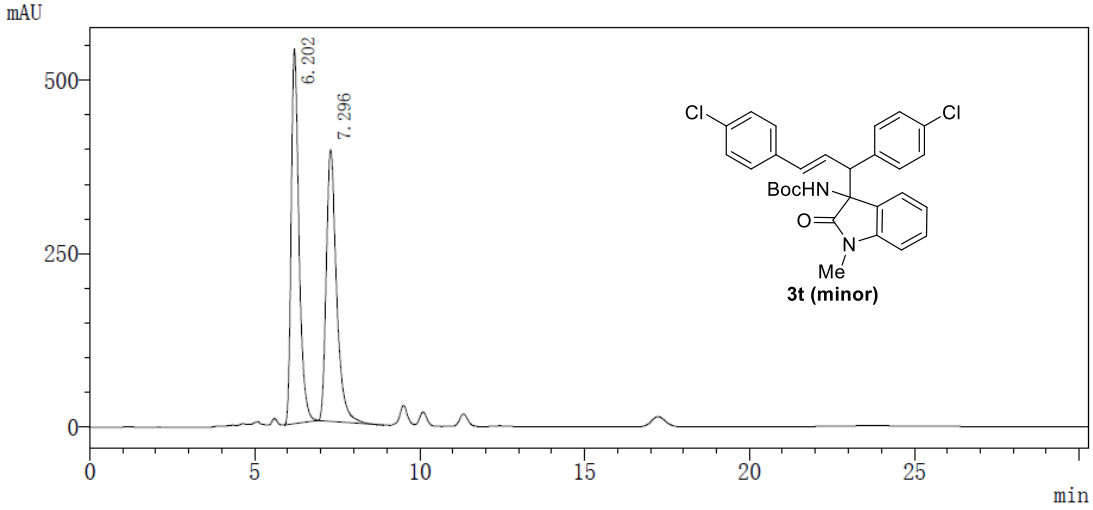
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	7.804	7981186	243788	48.438
2	9.242	8495836	271003	51.562



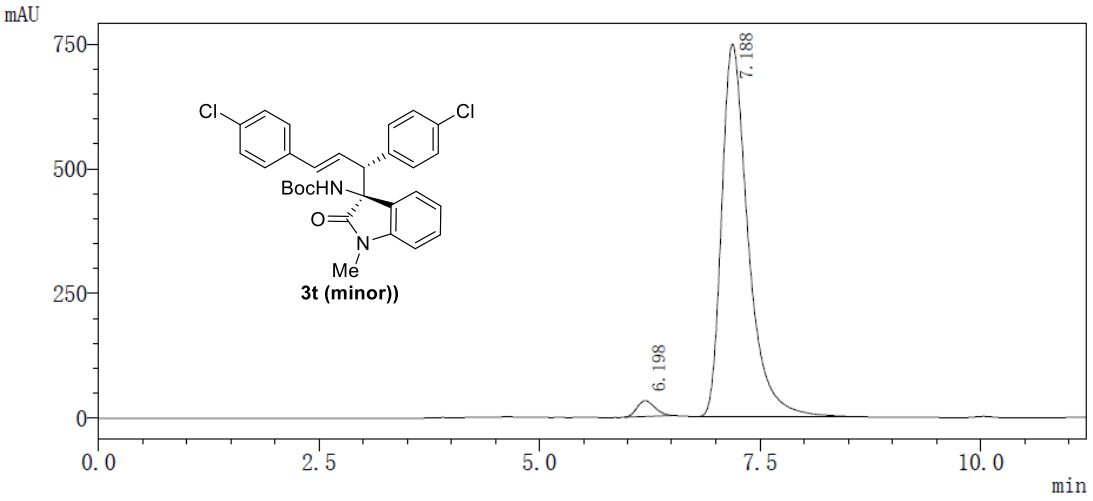
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	7.771	38415880	1149870	99.538
2	9.199	178300	7807	0.462



1 254nm 4nm

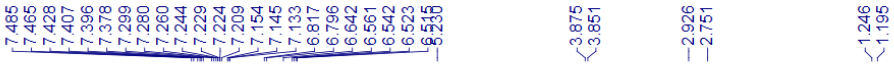
ID#	Rt. Time	Area	Height	Area %
1	6.202	8773325	540312	50.548
2	7.296	8583236	391419	49.452

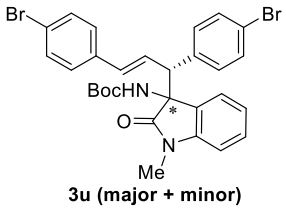


1 254nm 4nm

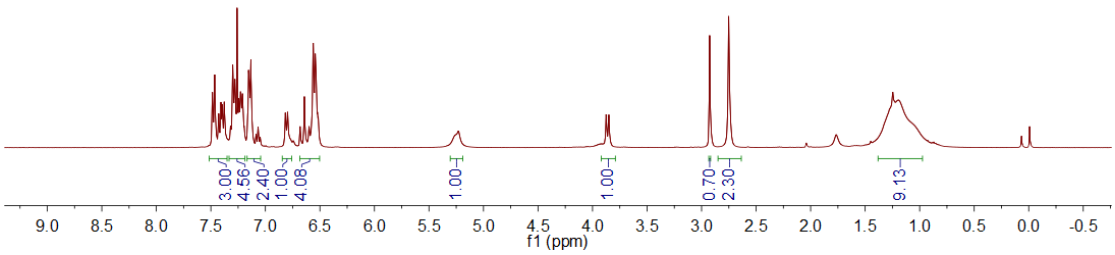
ID#	Rt. Time	Area	Height	Area %
1	6.198	451009	31887	2.810
2	7.188	15598220	746941	97.190

NMR and HPLC of 3u

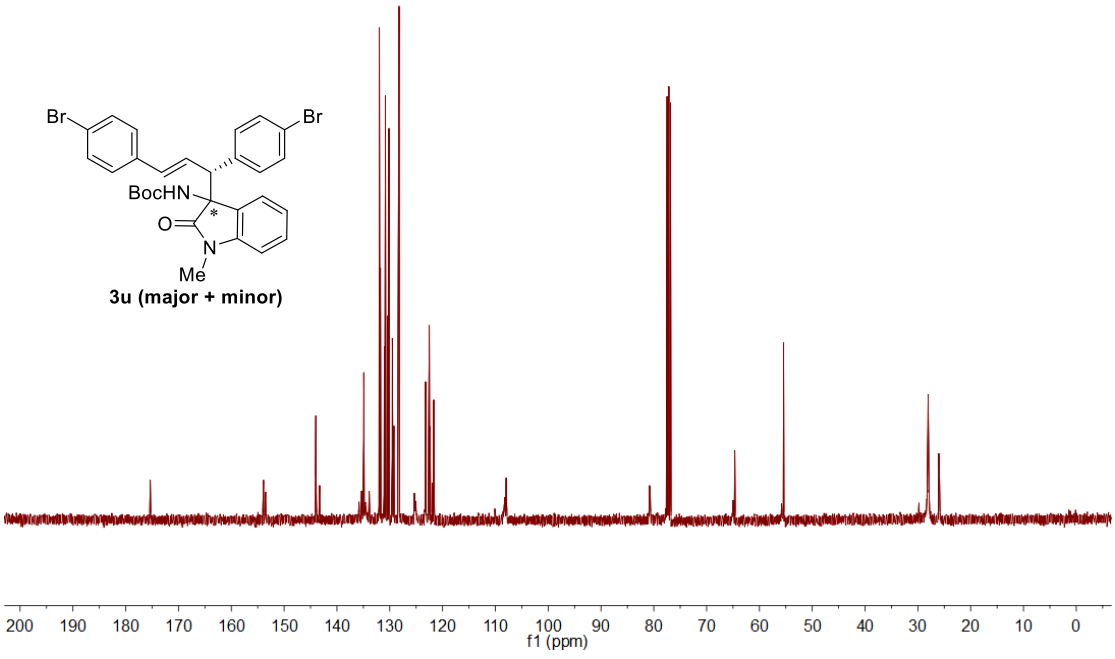


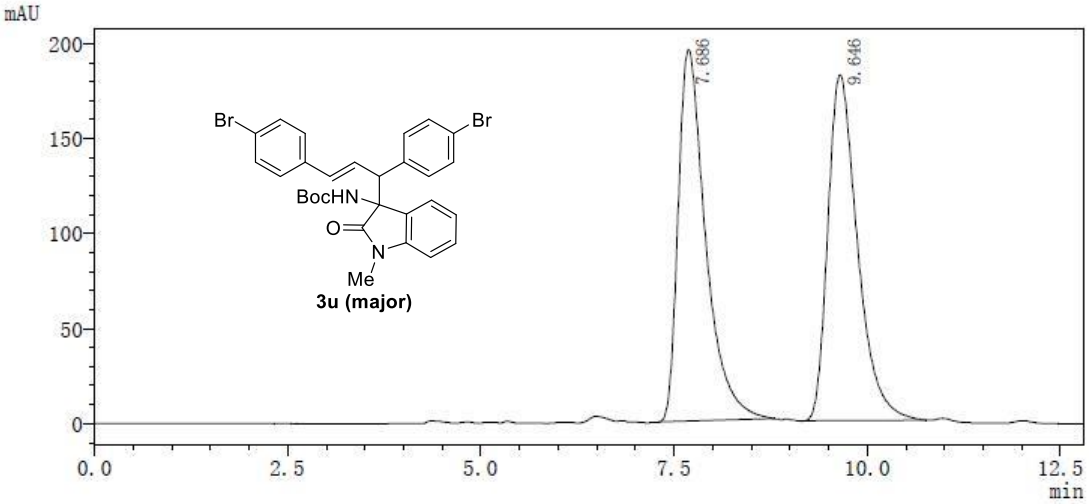


3u (major + minor)



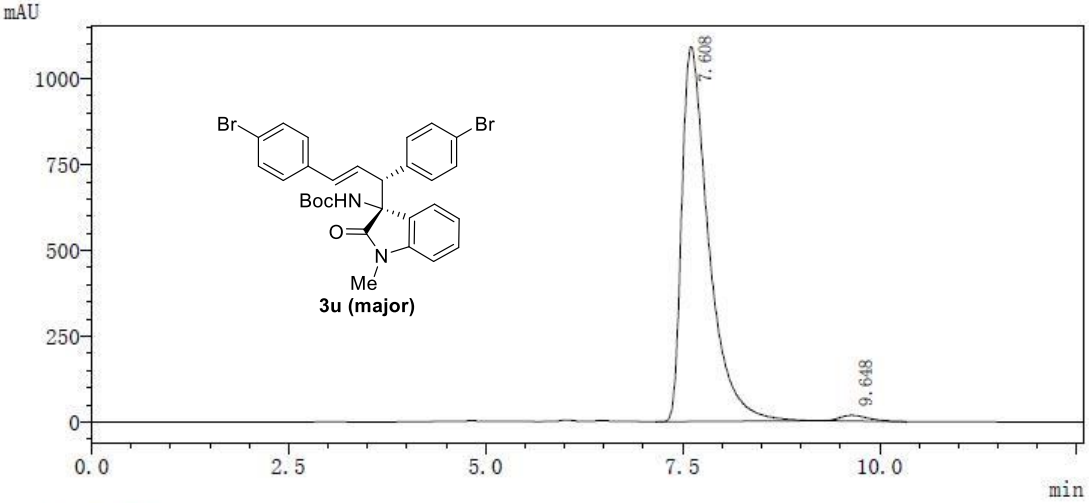
3u (major + minor)





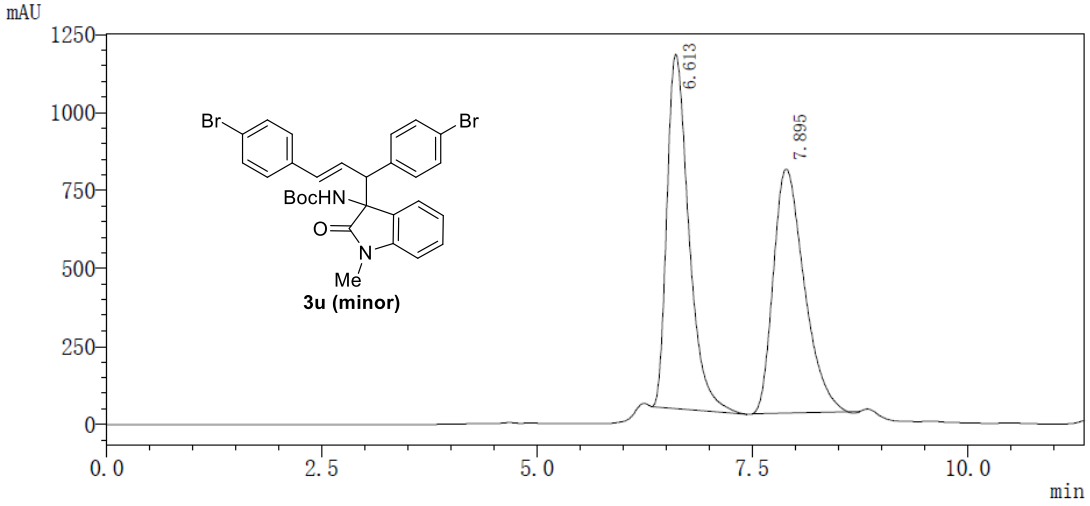
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	7.686	4839742	195526	49.865
2	9.646	4865929	182042	50.135



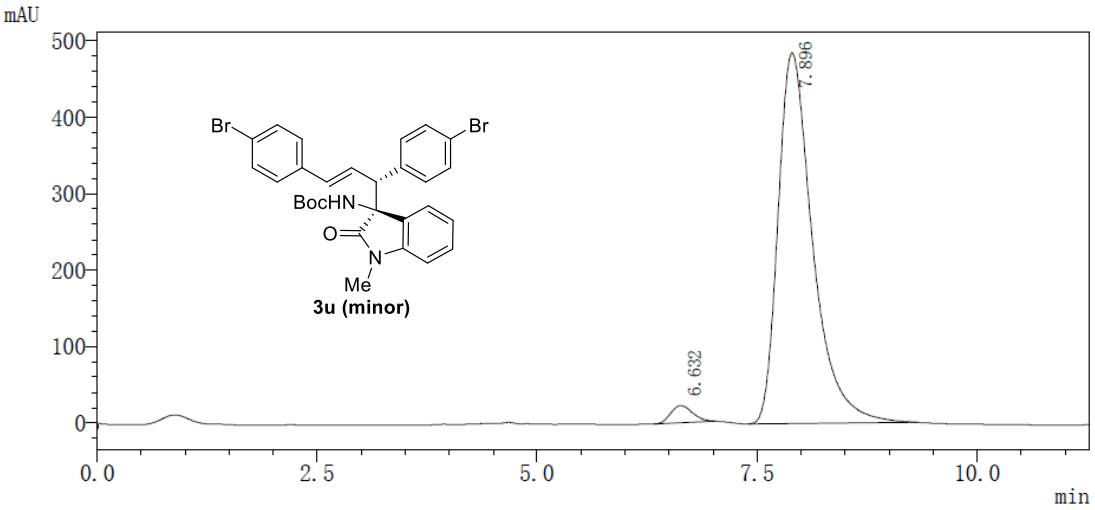
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	7.608	25967169	1091382	98.504
2	9.648	394255	16083	1.496



1 254nm 4nm

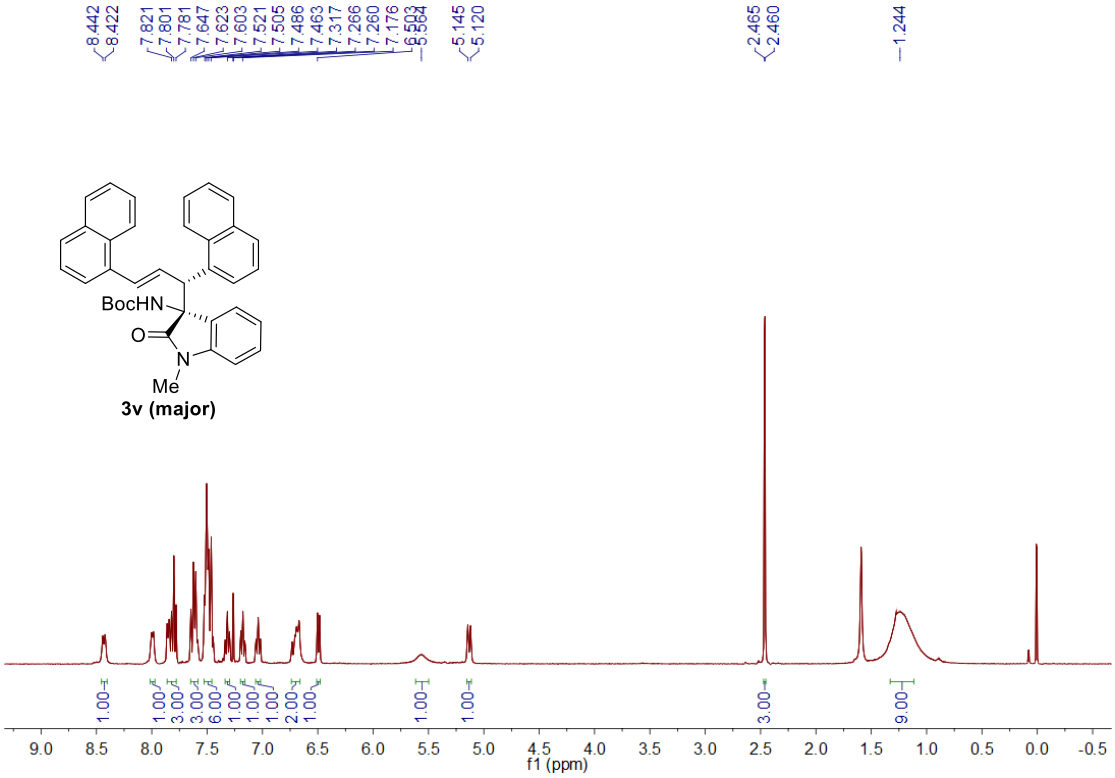
ID#	Rt. Time	Area	Height	Area %
1	6.613	20167231	1134827	50.752
2	7.895	19569646	782497	49.248

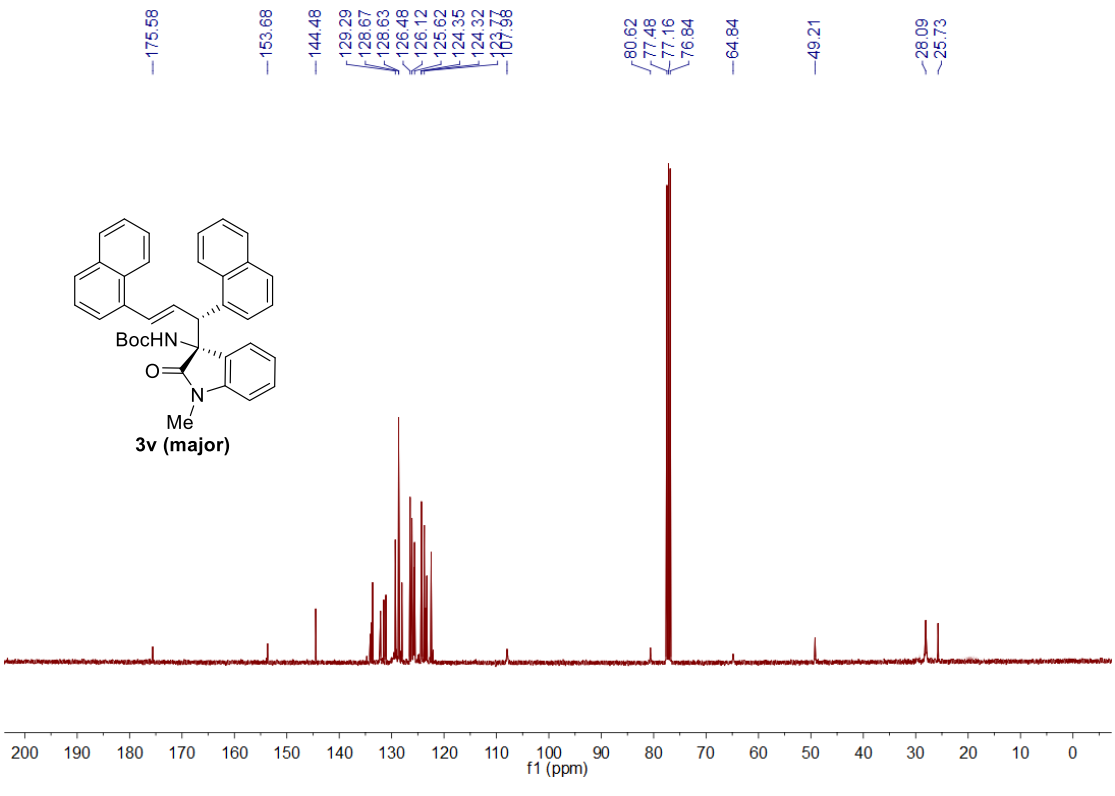


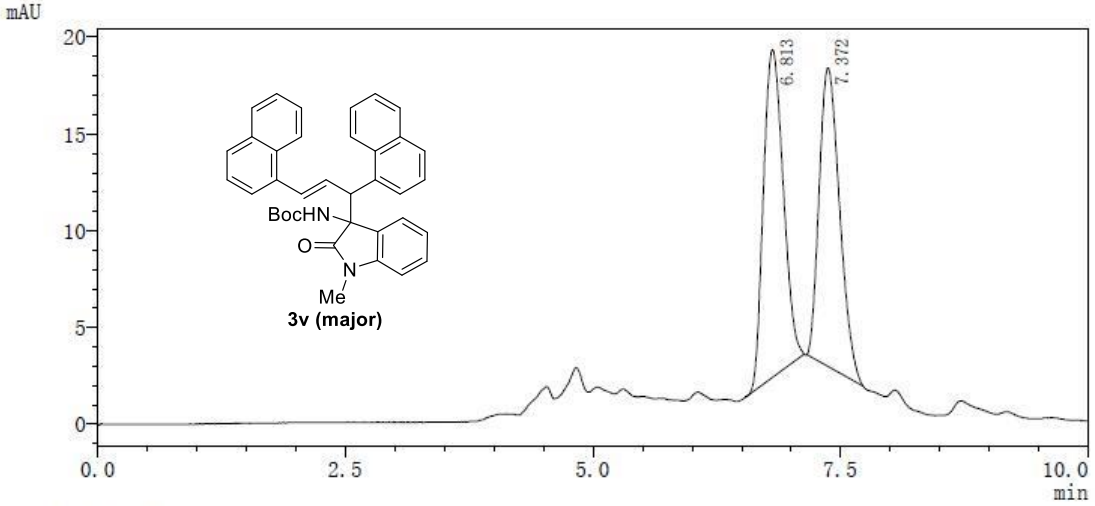
1 254nm 4nm

ID#	Rt. Time	Area	Height	Area %
1	6.632	389147	22528	2.847
2	7.896	13280419	484916	97.153

NMR and HPLC of 3v

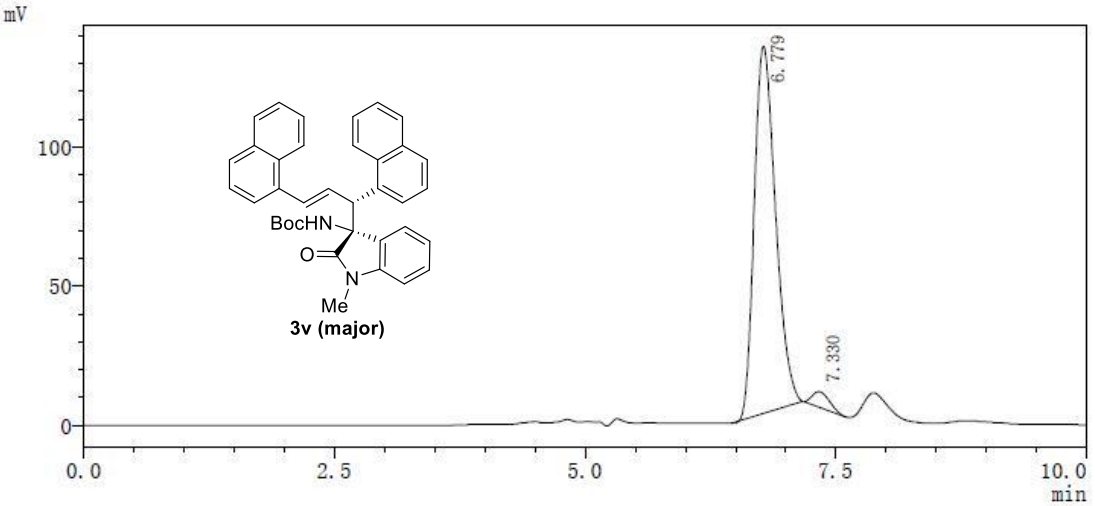






1 254nm 4nm

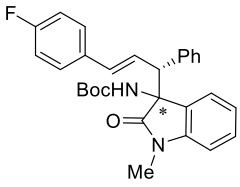
ID#	Rt. Time	Area	Height	Area %
1	6.813	236490	16923	51.664
2	7.372	221259	15434	48.336



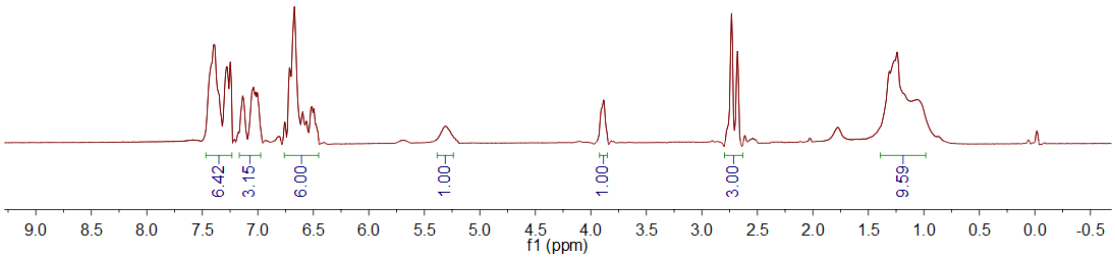
1 254nm 4nm

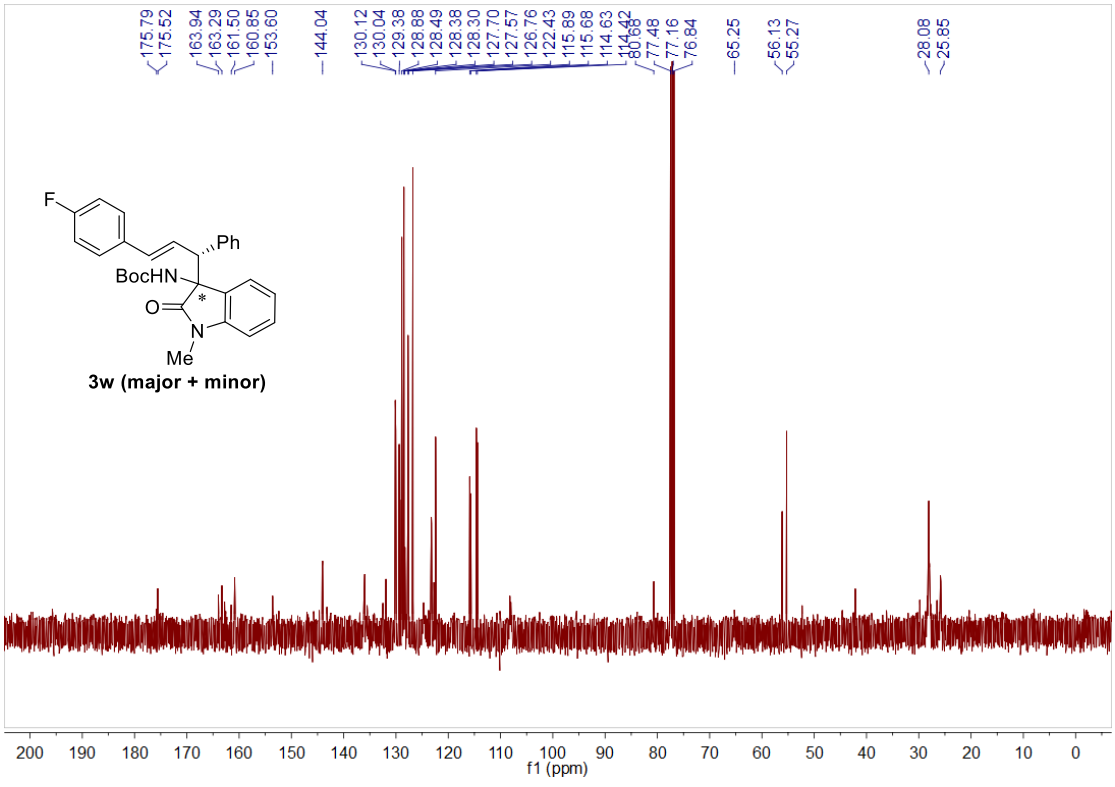
ID#	Rt. Time	Area	Height	Area %
1	6.779	1957217	131780	96.776
2	7.330	65211	5478	3.224

NMR and HPLC of 3w



3w (major + minor)





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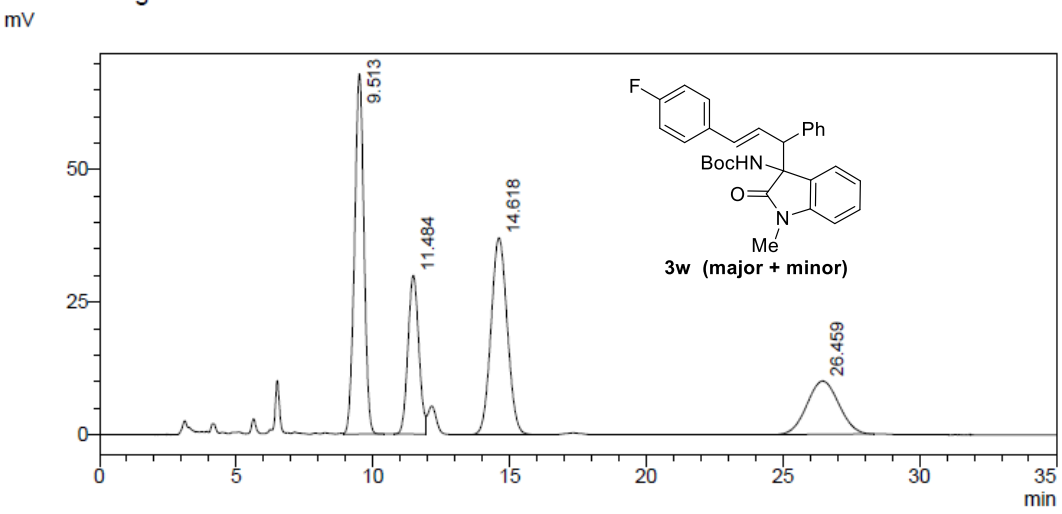
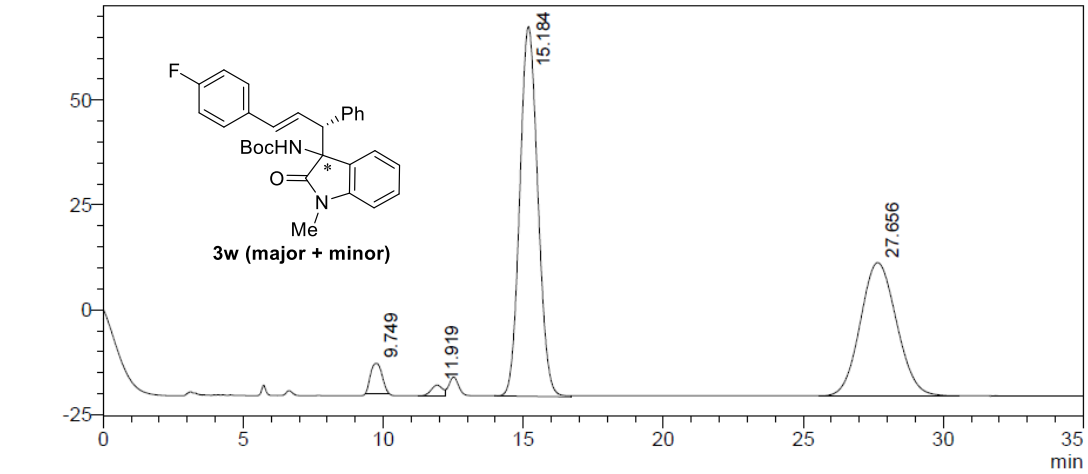


字符

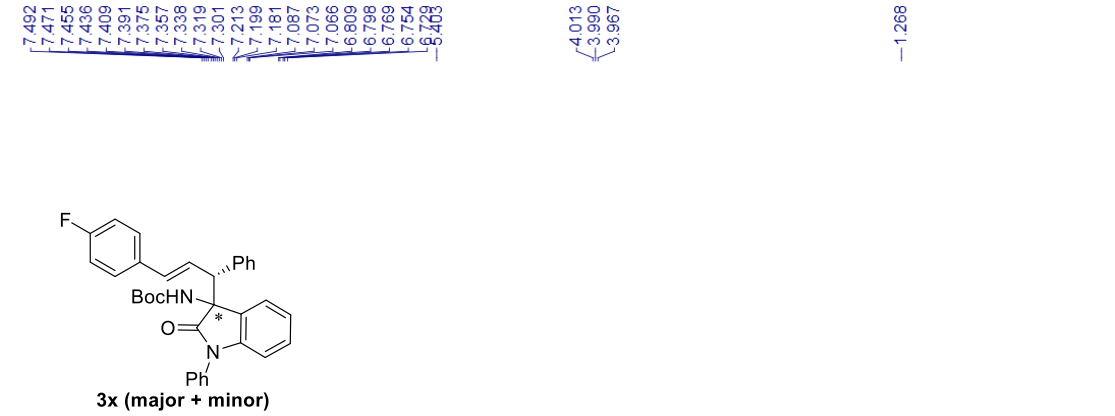
Peak	Ret. Time	Area	Height	Area%
1	9.513	1630843	67935	33.925
2	11.484	829997	29950	17.266
3	14.618	1528353	37096	31.793
4	26.459	818001	10047	17.016

<Chromatogram>

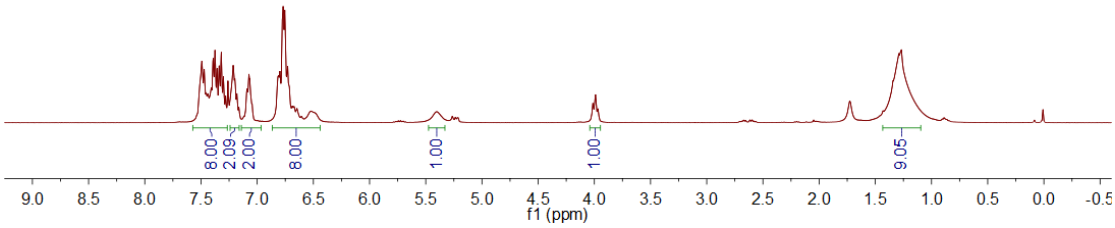


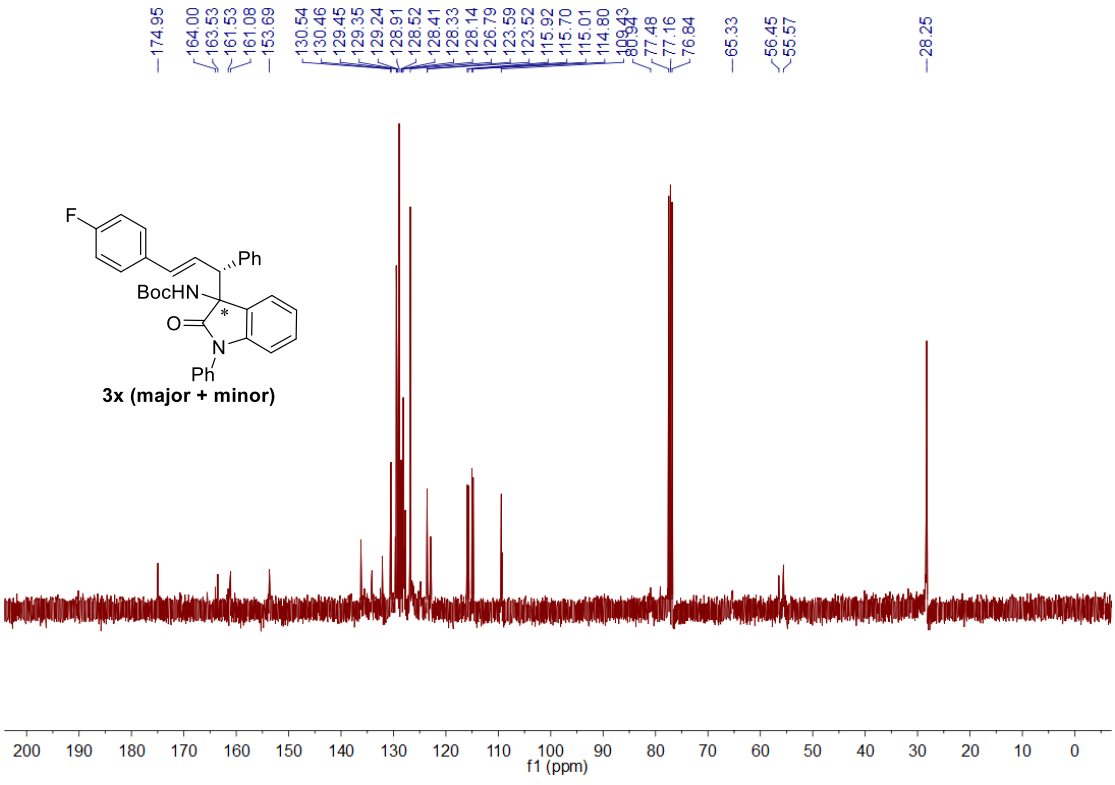
Peak	Ret. Time	Area	Height	Area%
1	9.749	198691	7093	2.807
2	11.919	69959	2518	0.988
3	15.184	3952182	88156	55.829
4	27.656	2858273	31768	40.376

NMR and HPLC of 3x



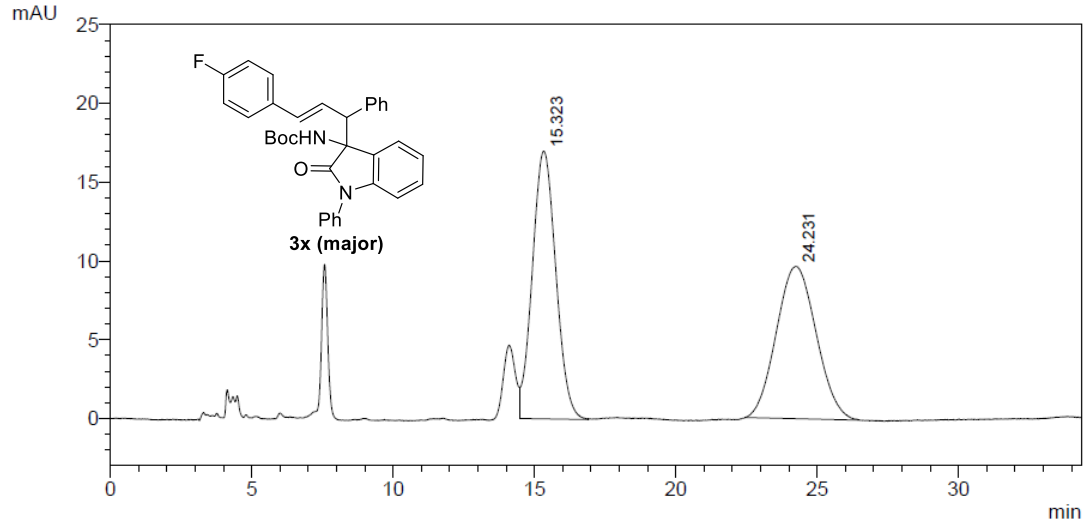
3x (major + minor)



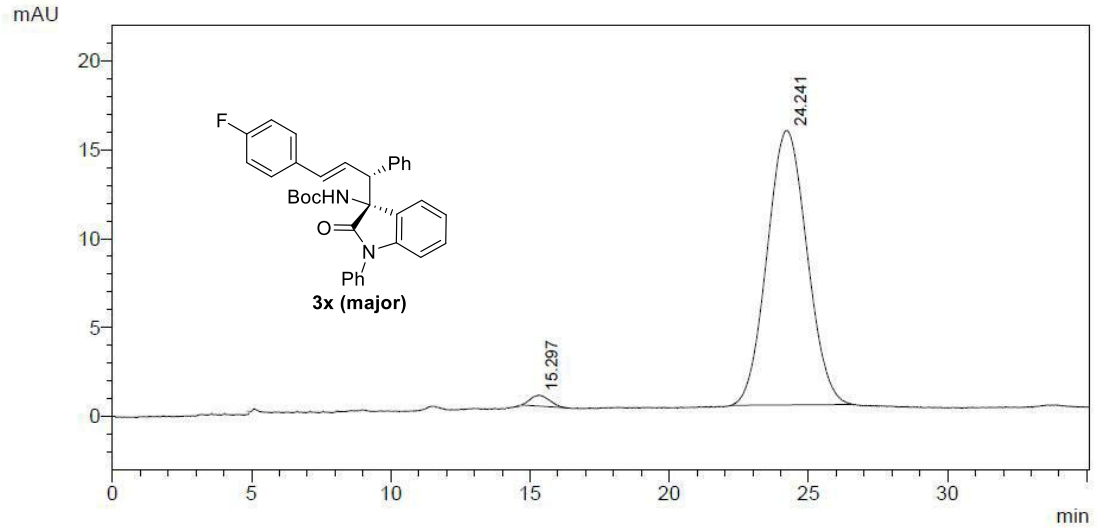


3x (major + minor)

<Chromatogram>



Peak	Ret. Time	Area	Height	Area %
1	15.323	983679	16985	50.886
2	24.231	949432	9662	49.114



Peak	Ret. Time	Area	Height	Area %
1	15.297	28681	617	1.829
2	24.241	1539676	15451	98.171

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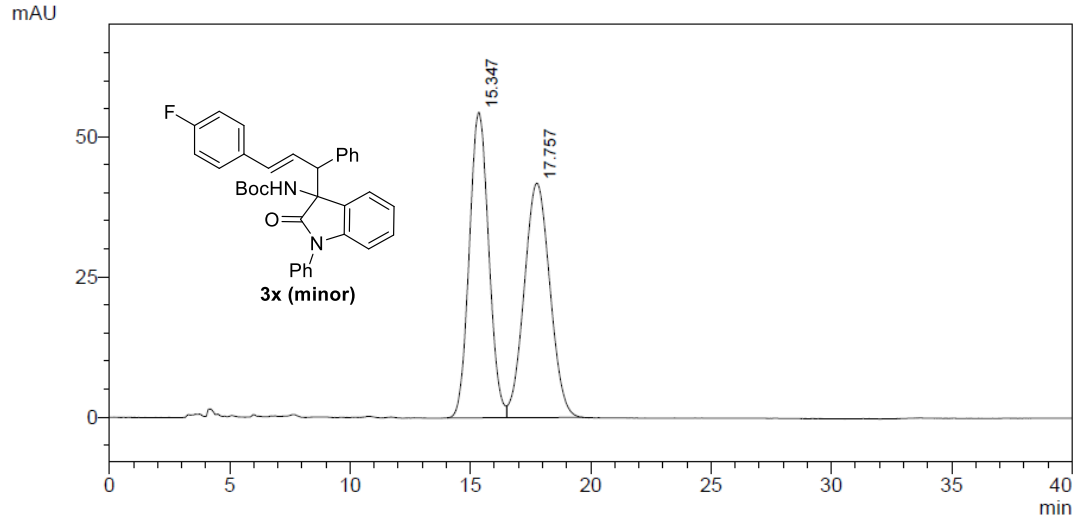

Peak	Ret. Time	Area	Height	Area %
1	15.347	3064867	54453	49.702
2	17.757	3101592	41771	50.298

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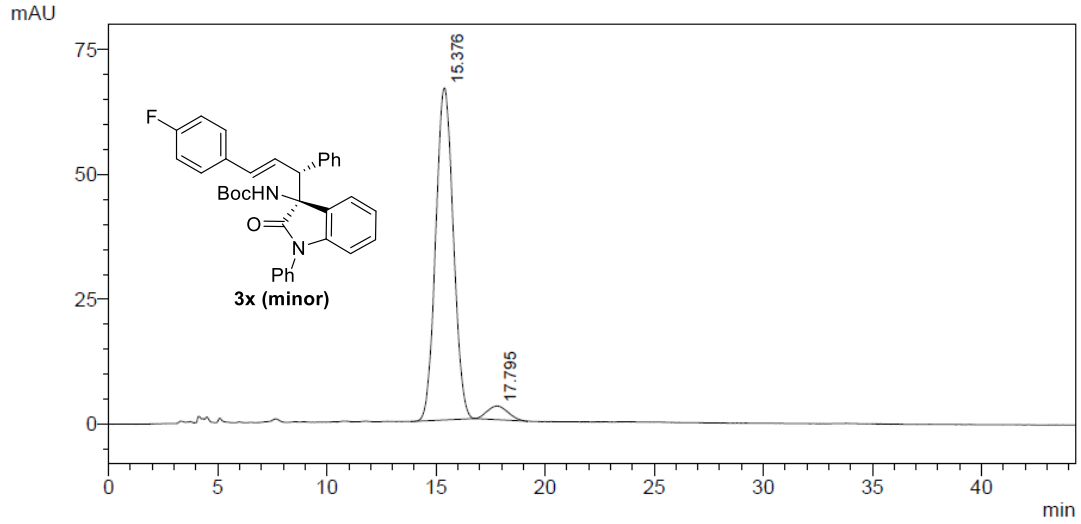
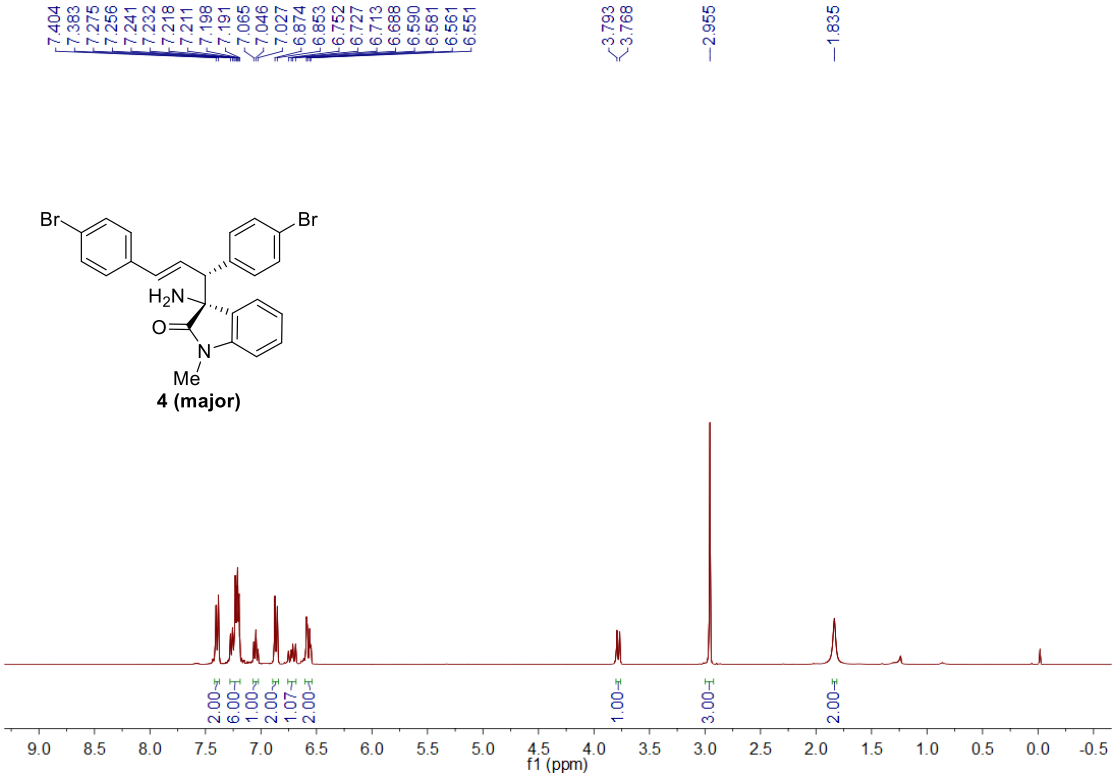
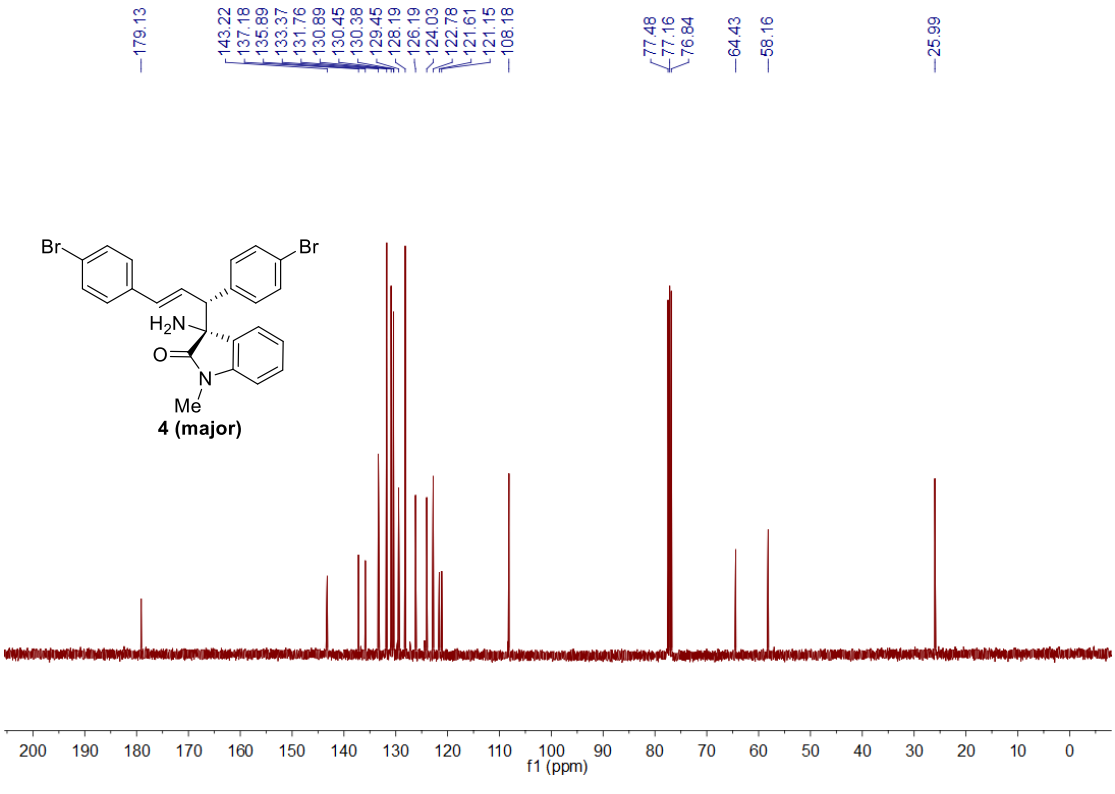


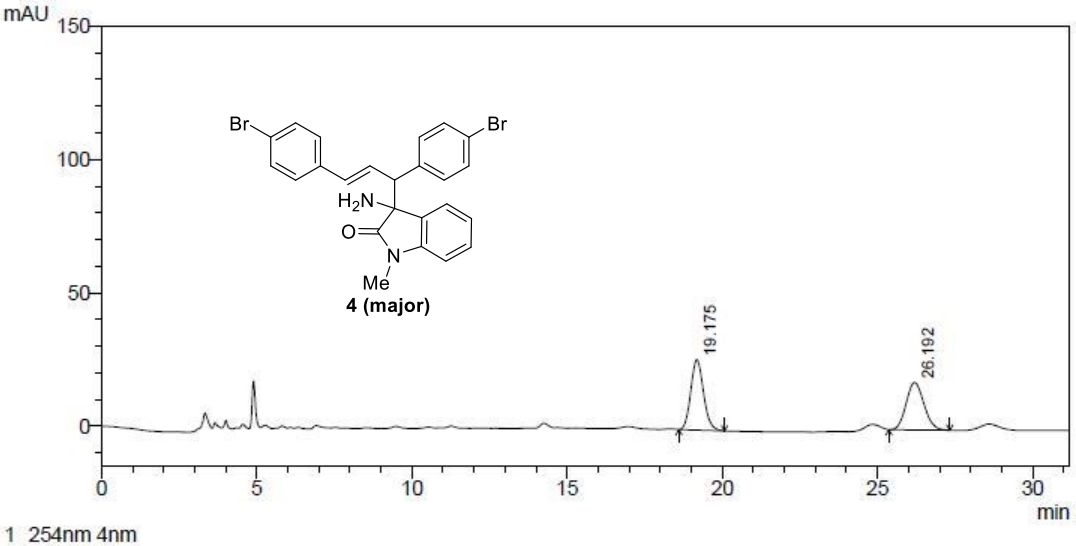
<Peak Table>
PDA

Peak#	Ret. Time	Area	Height	Area %
1	15.376	3738106	66547	95.375
2	17.795	181260	2740	4.625

NMR and HPLC of 4



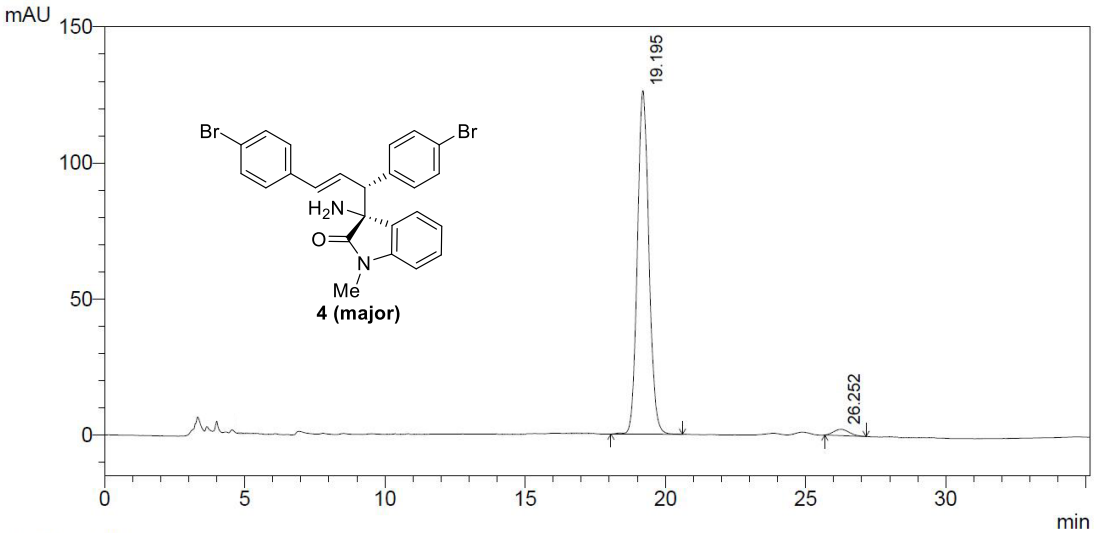




1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	19.175	754304	26390	51.468
2	26.192	711276	17855	48.532

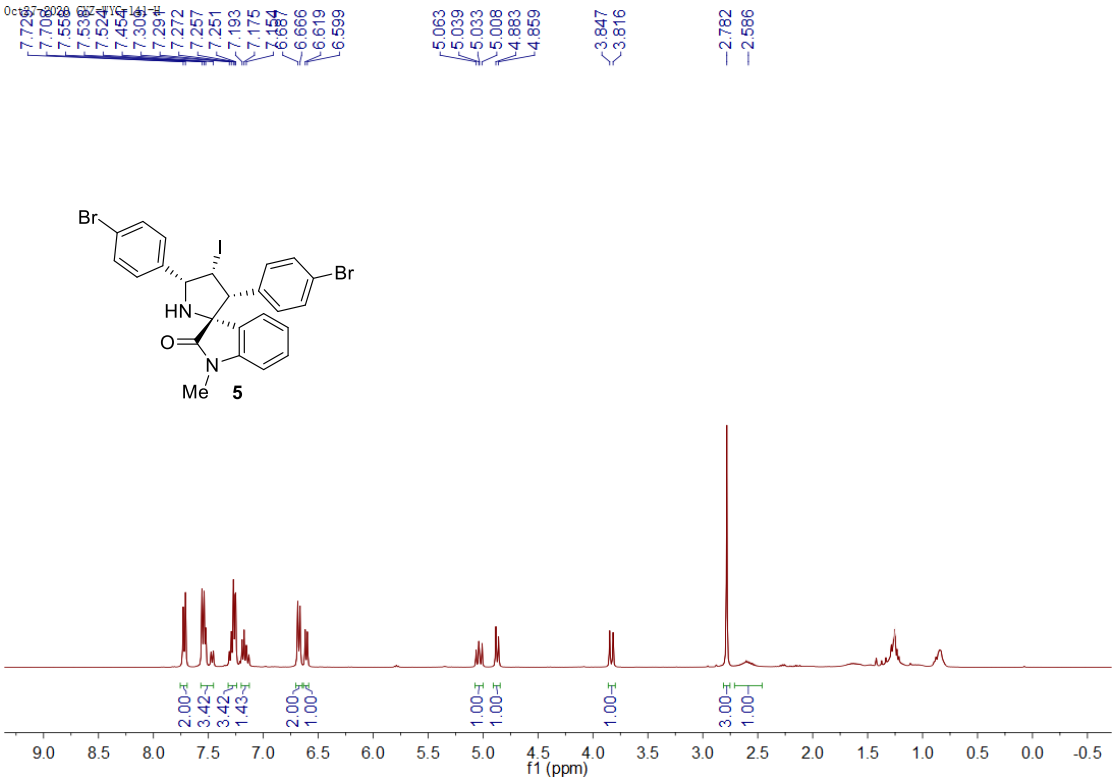


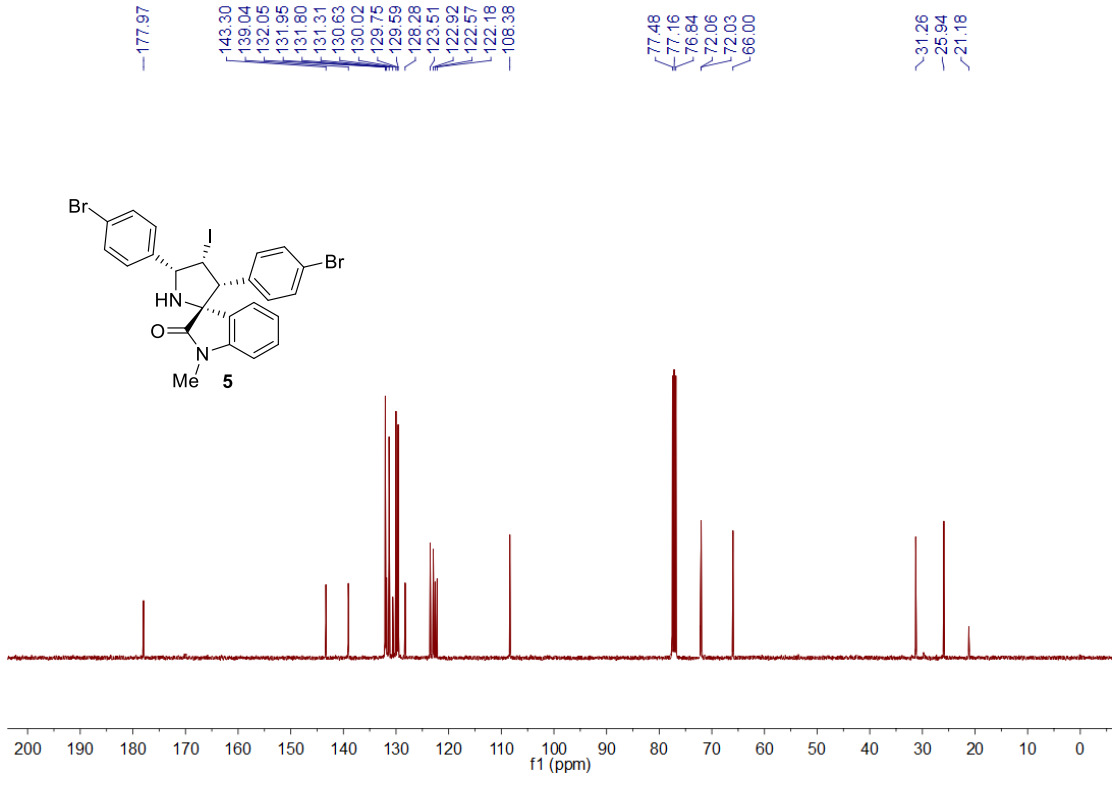
1 254nm 4nm

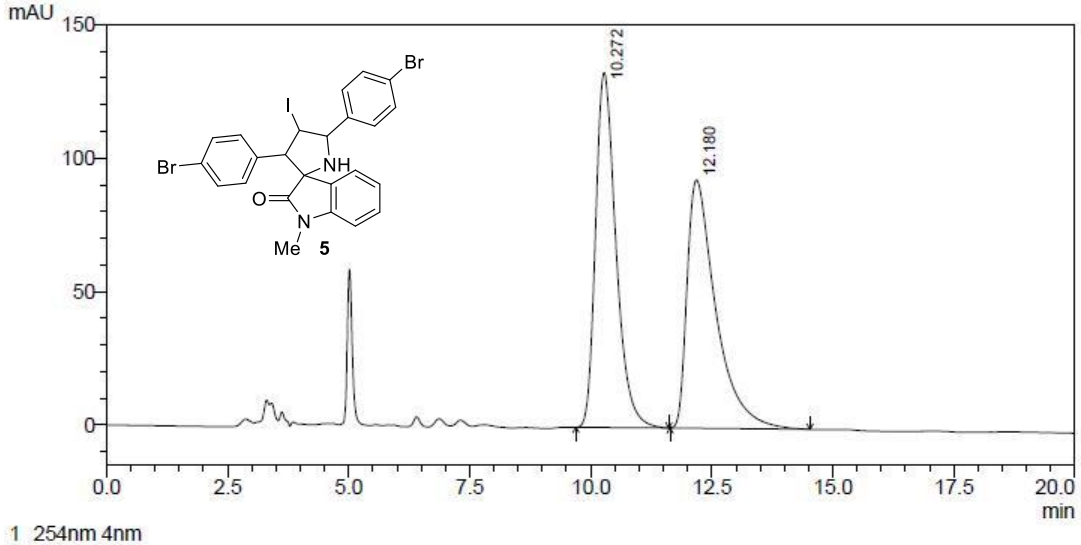
PDA

ID#	Rt. Time	Area	Height	Area %
1	19.195	3601678	126372	97.635
2	26.252	87253	2305	2.365

NMR and HPLC of 5



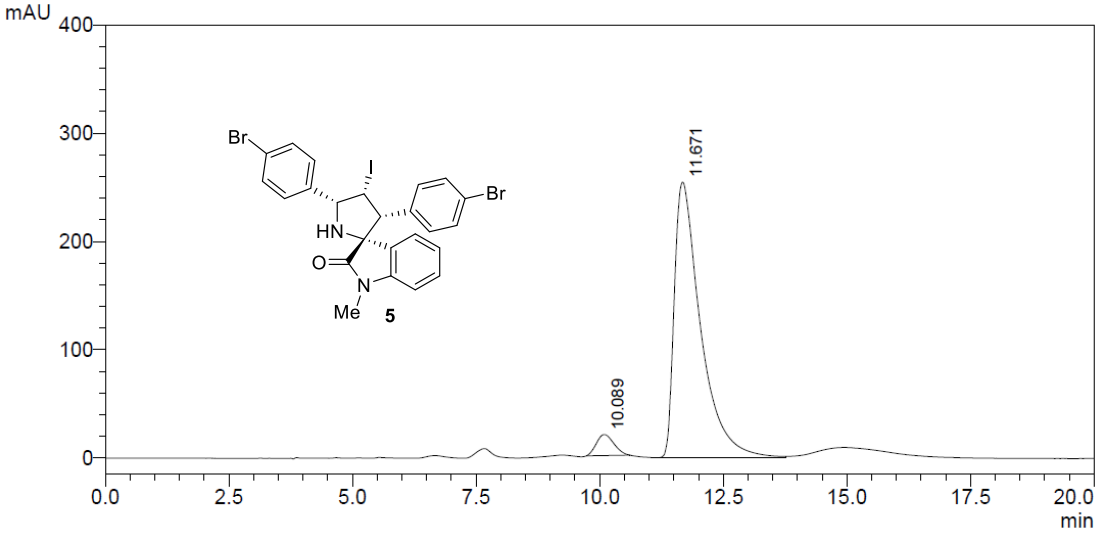




1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	10.272	3901984	132989	50.350
2	12.180	3847697	93012	49.650

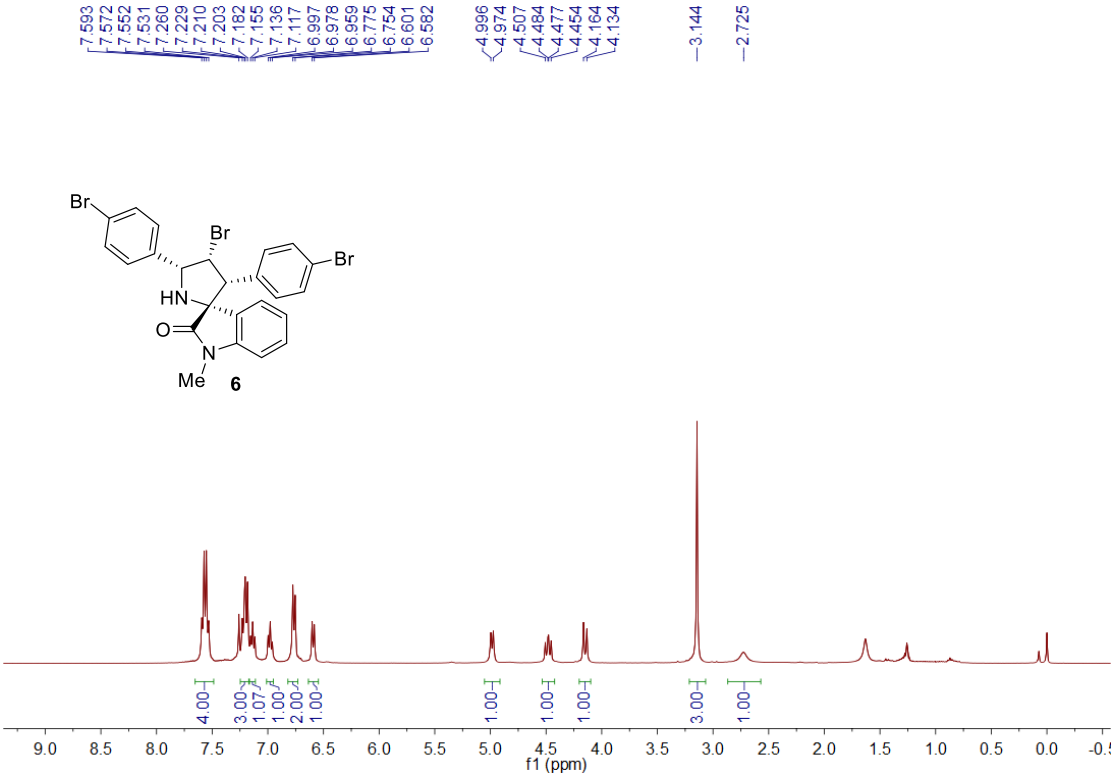


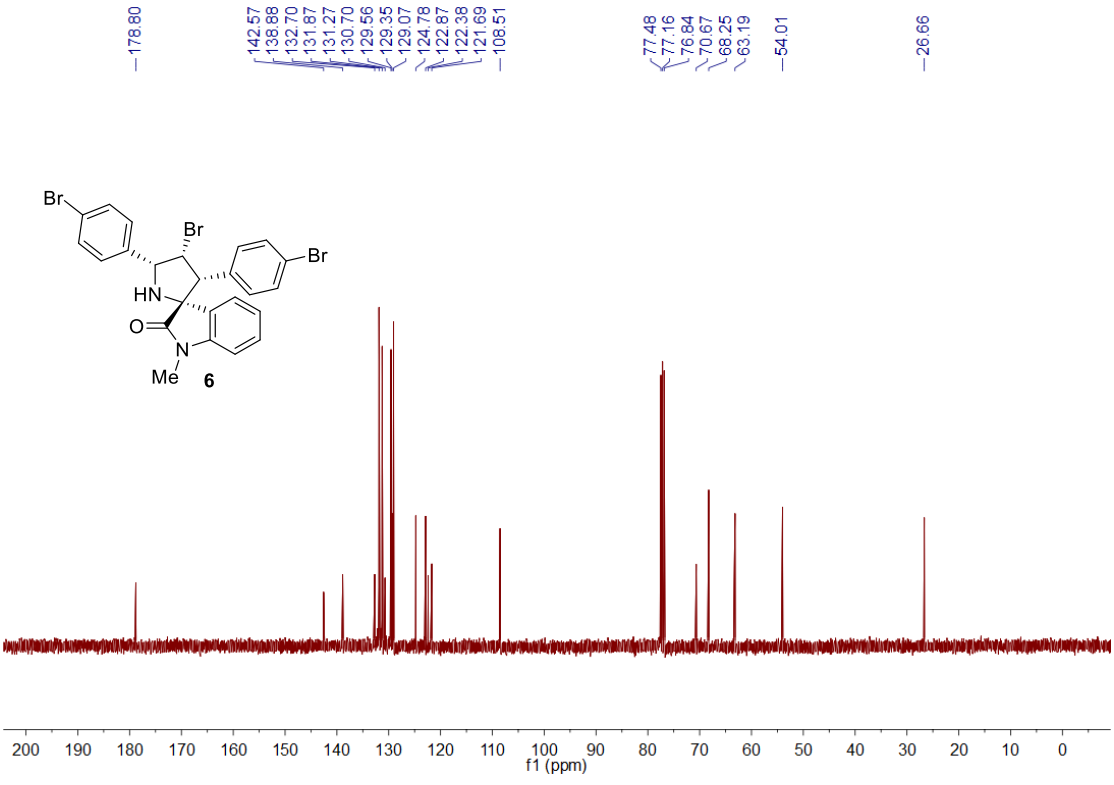
<Peak Table>

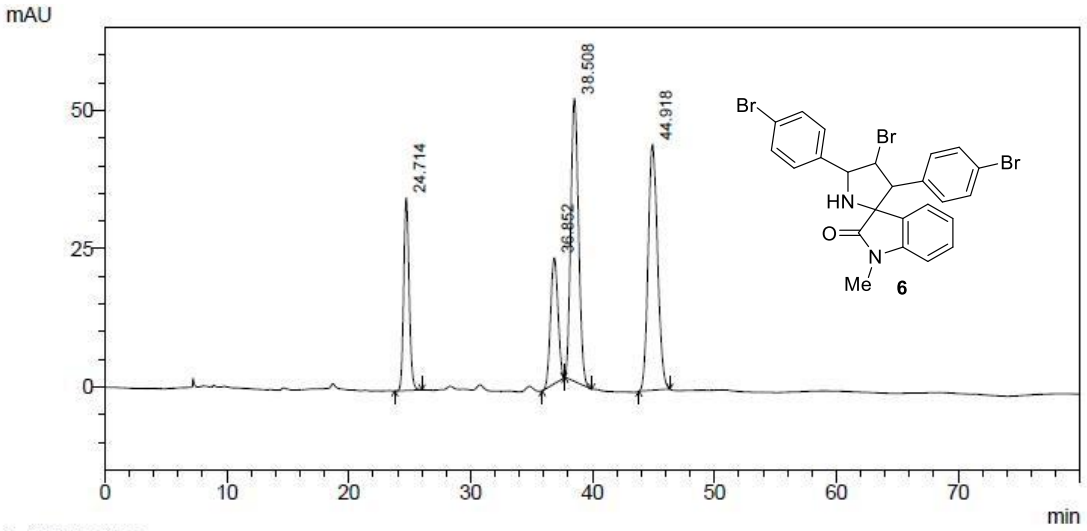
PDA

Peak#	Ret. Time	Area	Height	Area %
1	10.089	480957	19458	4.873
2	11.671	9388737	254476	95.127

NMR and HPLC of 6



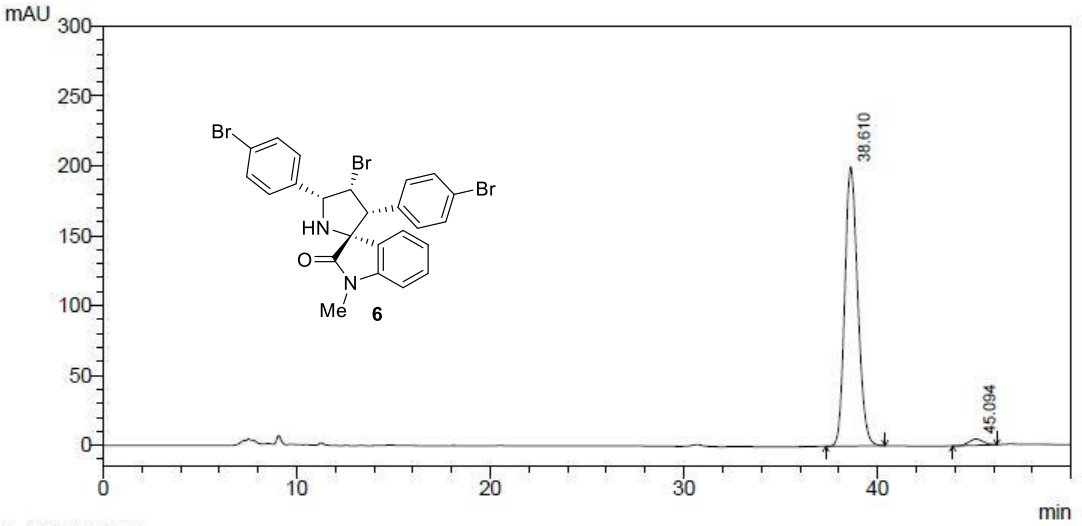




1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	24.714	1080690	34799	16.098
2	36.852	960113	22767	14.302
3	38.508	2275967	51094	33.904
4	44.918	2396275	44419	35.696

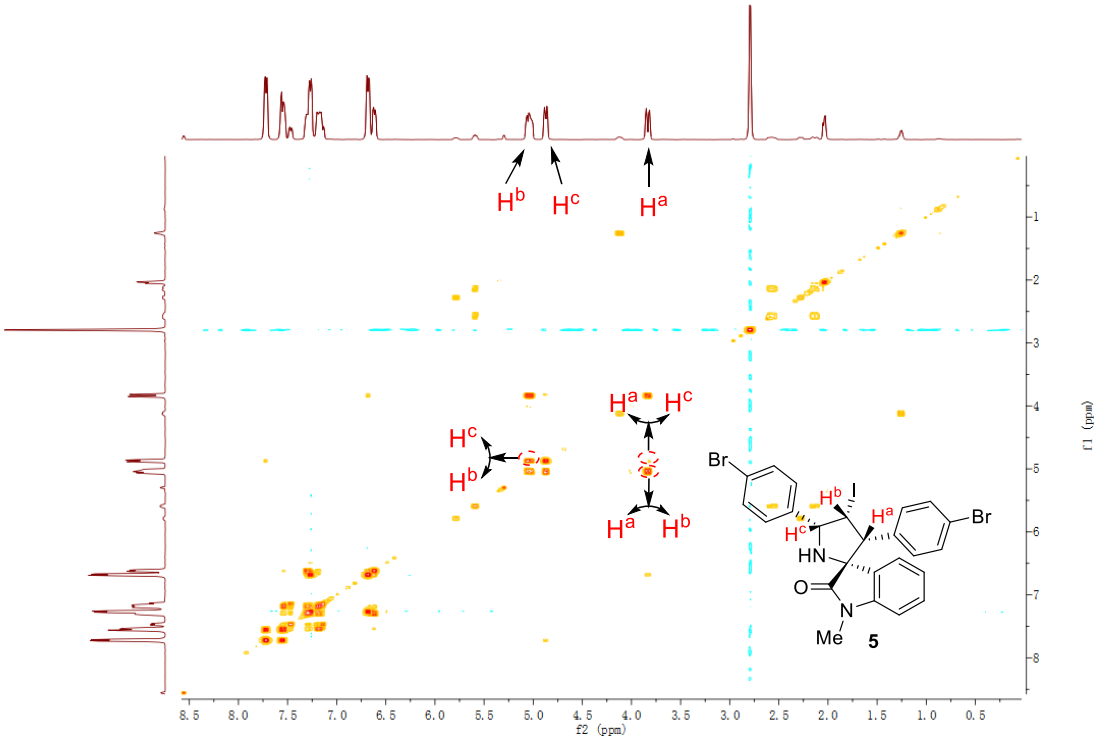


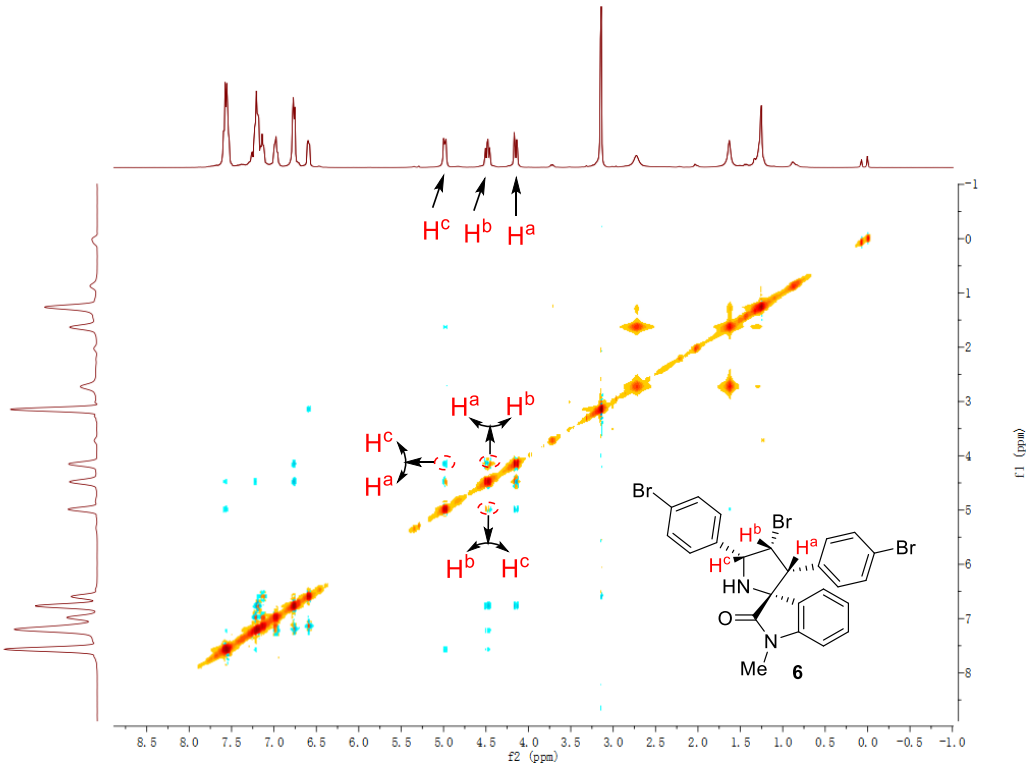
1 254nm 4nm

PDA

ID#	Rt. Time	Area	Height	Area %
1	38.610	9279811	199784	97.625
2	45.094	225727	4424	2.375

6. H-H noesy spectra for compounds 5 and 6





7. References

[1] (a) B.-D. Cui, W.-Y. Han, Z.-J. Wu, X.-M. Zhang, W.-C. Yuan, *J. Org. Chem.*, 2013, **78**, 8833; (b) T. Sengoku, D. Hayashi, M. Takahashi, H. Yoda, *Eur. J. Org. Chem.*, 2018, **2018**, 1813.

[2] E. P. Sánchez-Rodríguez, F. Hochberger-Roa, R. Corona-Sánchez, J. E. Barquera-Lozada, R. A. Toscano, M. Urrutigoïty, M. Gouygou, M. C. Ortega-Alfarod, J. G. López-Cortés, *Dalton Trans.*, 2017, **46**, 1510.