

Supporting Information

Stereoselective Synthesis of C3-Tetrasubstituted oxindoles *via* Copper Catalyzed Asymmetric Propargylation

Jiao-Mei Wang,^{a,1} Yu Zhao,^{b,1} Chang-Sheng Yao,^{*,c} and Kai Zhang^{*,c}

^a School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou 221018, P R China

^b College of Chemistry and Chemical Engineering, Yan'an University, Yan'an, Shaanxi 716000, P R China

^c Jiangsu Key Lab of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, Jiangsu 221116, P R China

¹ Jiaomei Wang and Yu Zhao contributed equally to this work.

E-mail: zhangkai@jsnu.edu.cn.

Table of Contents

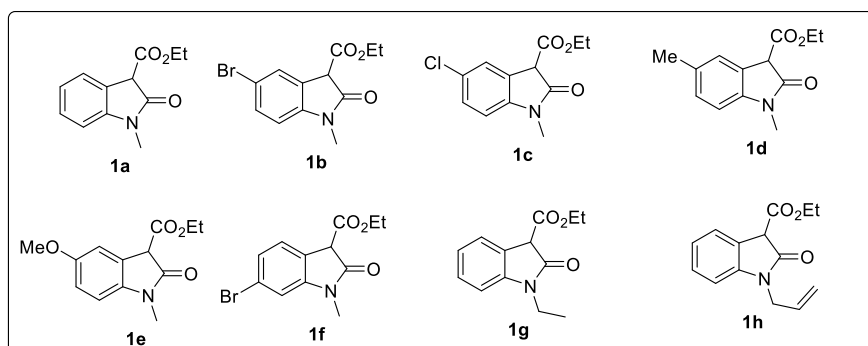
1. General Information.....	S2
2. Preparation of the Materials.....	S2
3. General Procedures of products.....	S3
4. Characterization Data of the Products.....	S4
5. X-Ray Structures of Product (<i>S,R</i>)-3i and (<i>R,S</i>)-3m.....	S11
6. Copies of ¹H and ¹³C NMR Spectra.....	S13
7. Copies of HPLC Chromatography.....	S50

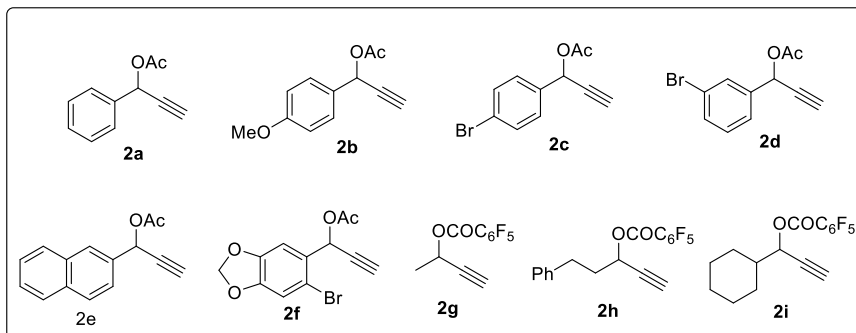
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^1H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers (CDCl_3 : 77.0 ppm). Enantiomeric excesses (ee) were determined by HPLC analysis on ThermoFisher UltiMate 3000 chiral HPLC with chiral AD-H, IC-H, OJ-H columns with hexane and *i*PrOH as solvents. The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI.

2. Preparation of the Substrates

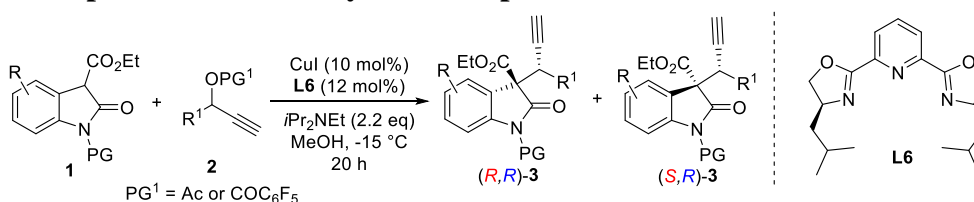
All the solvents were treated according to standard methods and all chemicals were used without purification. The 2-oxindole-3-carboxylate esters **1**¹ and terminal propargylic esters **2**² were known compounds or prepared from conventional methods.





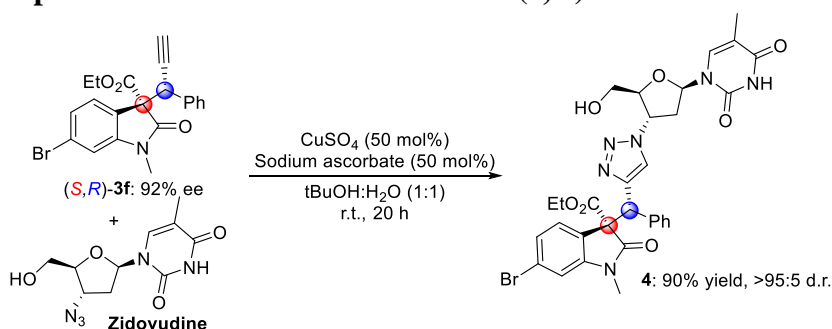
3. General Procedures of the Products

3.1 General procedure for the synthesis of products 3.



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.02 mmol, 10 mol%), chiral PyBOX ligand **L6** (0.024 mmol, 12 mol%) and MeOH (3 mL). The resulting solution was stirred for 1 h at room temperature. Then 2-oxindole-3-carboxylate esters **1** (0.2 mmol, 1.0 eq) and *i*Pr₂NEt (0.44 mmol, 2.2 eq) were added stirring for 5 min at room temperature before cooled to -15 °C. Then the propargylic acetate **2** (0.3 mmol, 1.5 eq) were introduced at -15 °C. The resulting solution was stirred until complete conversion of substrate **1** as monitored by TLC analysis. The resulting mixture was evaporated and purified by flash column chromatography on silica gel (PE/EA=20/1-10/1) to give product **3**. All the products **3** were prepared according to the above procedure.

3.2 General procedure for the Click reaction of (S,R)-3f.

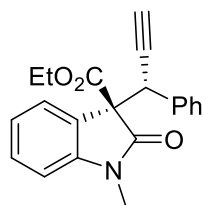


Procedure: Under argon atmosphere, a flame-dried 10 ml Schlenk tube was charged with

compound (*S,R*)-**3f** (0.1 mmol, 1.0 eq), zidovudine (0.11 mmol, 1.1 eq), tBuOH (1.0 mL) and a stir bar was added a freshly prepared solution of CuSO₄ (0.05 mmol, 0.5 eq) and sodium ascorbate (0.05 mmol, 0.5 eq) in H₂O (1.0 mL). The resulting solution was stirred at room temperature for 20 h. The resulting mixture was concentrated and subjected to column chromatography (DCM/MeOH = 20/1) to give product **4** as a white solid.

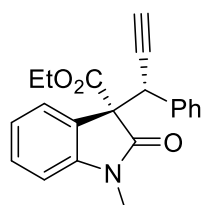
4. Characterization Data of Products

Ethyl (*R*)-1-methyl-2-oxo-3-((*R*)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((*R,R*)-**3a**)



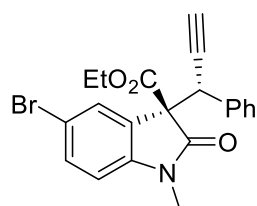
White solid, 36% yield; $[\alpha]_D^{23} = 1.532$ ($c = 1.00$ in CH₂Cl₂); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 4.84 min, t_R (minor) = 5.90 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.84 (d, $J = 7.5$ Hz, 1H), 7.37 – 7.23 (m, 1H), 7.21 – 6.82 (m, 6H), 6.52 (d, $J = 7.8$ Hz, 1H), 5.05 – 4.79 (m, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 2.77 (s, 3H), 2.45 (d, $J = 1.4$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.81, 167.21, 143.93, 133.99, 129.29, 128.92, 127.68, 127.39, 125.99, 125.27, 122.46, 107.83, 82.40, 73.20, 63.50, 62.36, 42.81, 26.05, 14.04; HRMS (ESI) for: C₂₁H₂₀NO₃ [M+H]⁺: calcd 334.1438, found 334.1447.

Ethyl (*S*)-1-methyl-2-oxo-3-((*R*)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((*S,R*)-**3a**)



White solid, 56% yield; $[\alpha]_D^{23} = 1.735$ ($c = 1.00$ in CH₂Cl₂); 95% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 8.90 min, t_R (minor) = 17.52 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.28 – 7.00 (m, 9H), 6.62 (d, $J = 7.8$ Hz, 1H), 4.84 (d, $J = 2.6$ Hz, 1H), 4.29 – 4.18 (m, 2H), 3.01 (s, 3H), 2.32 (d, $J = 2.5$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.10, 167.55, 144.13, 134.23, 129.38, 129.32, 127.84, 127.61, 125.19, 125.03, 122.09, 107.91, 80.73, 73.13, 63.25, 62.29, 43.13, 26.17, 13.95; HRMS (ESI) for: C₂₁H₂₀NO₃ [M+H]⁺: calcd 334.1438, found 334.1447.

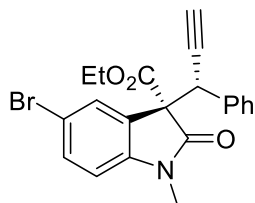
Ethyl (*R*)-5-bromo-1-methyl-2-oxo-3-((*R*)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((*R,R*)-**3b**)



White solid, 42% yield, $[\alpha]_D^{23} = -3.473$ ($c = 1.00$ in CH₂Cl₂); 90% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 5.29 min, t_R (minor) = 6.28 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.04 – 7.90 (m, 1H), 7.42 – 7.39 (m, 1H), 7.18 – 6.91 (m, 5H), 6.39 (d, $J = 8.3$ Hz, 1H), 4.89 (d, $J = 2.5$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.75 (s, 3H), 2.50 (d, $J = 2.1$ Hz, 1H), 1.29

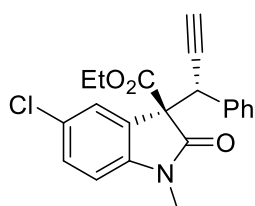
(t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.22, 166.49, 142.96, 133.56, 132.13, 129.07, 128.84, 127.87, 127.56, 127.14, 115.04, 109.20, 81.79, 73.77, 63.47, 62.63, 42.85, 26.13, 14.00; HRMS (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0544.

Ethyl (S)-5-bromo-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3b)



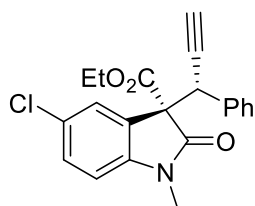
White solid, 51% yield, $[\alpha]_{\text{D}}^{23} = 1.390$ ($c = 1.00$ in CH_2Cl_2); 88% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 31.05 min, t_{R} (minor) = 37.83 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.41 – 7.38 (m, 1H), 7.24 – 7.23 – 7.18 (m, 5H), 7.08 (t, $J = 1.5$ Hz, 1H), 6.54 (d, $J = 8.3$ Hz, 1H), 4.85 (d, $J = 2.5$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.02 (s, 3H), 2.30 (d, $J = 1.2$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.58, 166.81, 143.24, 133.87, 132.18, 129.31, 128.64, 128.18, 127.84, 126.80, 114.58, 109.30, 80.23, 73.40, 63.32, 62.60, 43.23, 26.33, 13.96; HRMS (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0544.

Ethyl (R)-5-chloro-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3c)



White solid, 44% yield, $[\alpha]_{\text{D}}^{23} = 0.898$ ($c = 1.00$ in CH_2Cl_2); 90% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 5.20 min, t_{R} (minor) = 6.38 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.83 (t, $J = 1.6$ Hz, 1H), 7.30 – 7.22 (m, 1H), 7.14 – 6.91 (m, 5H), 6.45 – 6.42 (m, 1H), 4.91 – 4.88 (m, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.76 (s, 3H), 2.50 (d, $J = 1.5$ Hz, 1H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.31, 166.49, 142.47, 133.55, 129.23, 128.83, 127.86, 127.77, 127.55, 126.79, 126.36, 108.70, 81.80, 73.75, 63.56, 62.62, 42.83, 26.16, 14.00; HRMS (ESI) for: $\text{C}_{21}\text{H}_{19}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: calcd 368.1048, found 368.1057.

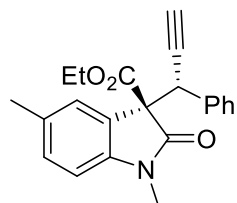
Ethyl (S)-5-chloro-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3c)



White solid, 53% yield, $[\alpha]_{\text{D}}^{23} = 0.879$ ($c = 1.00$ in CH_2Cl_2); 87% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 28.99 min, t_{R} (minor) = 46.50 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.28 – 7.15 (m, 6H), 6.96 (t, $J = 1.4$ Hz, 1H), 6.58 (d, $J = 8.3$ Hz, 1H), 4.85 (d, $J = 2.6$ Hz, 1H), 4.27 – 4.21 (m, 2H), 3.03 (s, 3H), 2.30 (d, $J = 2.5$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.80, 166.94, 142.89, 134.02, 129.44, 128.29, 127.97, 127.54, 126.59, 126.03, 108.92, 80.37, 73.52, 63.51, 62.71, 43.35,

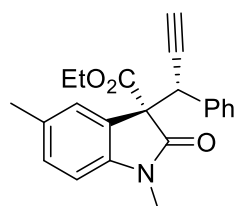
26.48, 14.08; **HRMS** (ESI) for: C₂₁H₁₈ClNO₃Na [M+Na]⁺: calcd 390.0867, found 390.0875.

Ethyl (R)-1,5-dimethyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3d)



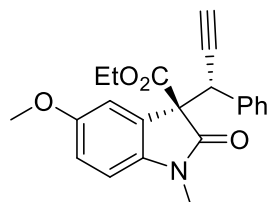
White solid, 34% yield, $[\alpha]_D^{23} = 0.334$ (c = 1.00 in CH₂Cl₂); 90% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 4.74 min, t_R (minor) = 5.53 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.65 (s, 1H), 7.14 – 6.88 (m, 5H), 6.41 (d, $J = 7.9$ Hz, 1H), 4.94 – 4.83 (m, 1H), 4.33 – 4.24 (m, 2H), 2.75 (s, 3H), 2.44 (d, $J = 3.6$ Hz, 1H), 2.42 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) 170.77, 167.39, 141.59, 134.12, 131.95, 129.60, 128.97, 127.63, 127.39, 126.65, 125.22, 107.54, 82.50, 73.07, 63.51, 62.34, 42.73, 26.07, 21.35, 14.04; **HRMS** (ESI) for: C₂₂H₂₂NO₃ [M+H]⁺: calcd 348.1594, found 348.1604.

Ethyl (S)-1,5-dimethyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3d)



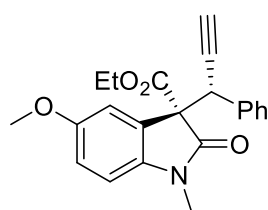
White solid, 50% yield, $[\alpha]_D^{23} = 1.600$ (c = 1.00 in CH₂Cl₂); 95% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 11.53 min, t_R (minor) = 14.99 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.22 – 7.08 (m, 5H), 7.05 (d, $J = 7.9$ Hz, 1H), 6.87 (s, 1H), 6.50 (d, $J = 7.9$ Hz, 1H), 4.82 (d, $J = 2.4$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 2.98 (s, 3H), 2.31 (d, $J = 3.9$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) 171.05, 167.74, 141.75, 134.29, 131.58, 129.60, 129.33, 127.77, 127.51, 125.85, 124.97, 107.59, 80.87, 73.02, 63.28, 62.23, 43.02, 26.15, 21.08, 13.95; **HRMS** (ESI) for: C₂₂H₂₁NO₃Na [M+Na]⁺: calcd 370.1414, found 370.1419.

Ethyl (R)-5-methoxy-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3e)



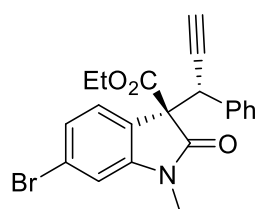
White solid, 38% yield, $[\alpha]_D^{23} = 1.007$ (c = 1.00 in CH₂Cl₂); 92% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 5.73 min, t_R (minor) = 7.67 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.48 (d, $J = 2.6$ Hz, 1H), 7.13 – 7.11 – 6.96 (m, 5H), 6.83 – 6.80 (m, 1H), 6.43 – 6.41 (m, 1H), 4.89 (d, $J = 2.7$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 3.86 (s, 3H), 2.74 (s, 3H), 2.46 (d, $J = 1.5$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) 170.47, 167.14, 155.60, 137.55, 133.98, 128.92, 128.68, 127.66, 127.55, 127.41, 127.29, 126.42, 113.64, 113.30, 108.08, 82.40, 73.24, 63.74, 62.35, 55.83, 42.69, 26.12, 14.03; **HRMS** (ESI) for: C₂₂H₂₂NO₄ [M+H]⁺: calcd 364.1543, found 364.1544.

Ethyl (S)-5-methoxy-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3e)



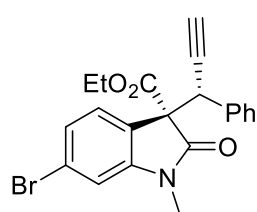
White solid, 49% yield, $[\alpha]_D^{23} = -3.965$ ($c = 1.00$ in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 15.61 min, t_R (minor) = 33.97 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.19 (m, 5H), 6.81 – 6.78 (m, 1H), 6.62 (d, $J = 2.5$ Hz, 1H), 6.55 (d, $J = 8.5$ Hz, 1H), 4.85 (d, $J = 2.5$ Hz, 1H), 4.27 – 4.19 (m, 2H), 3.73 (s, 3H), 3.01 (s, 3H), 2.29 (d, $J = 2.3$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.82, 167.42, 155.33, 137.74, 134.29, 129.41, 127.90, 127.65, 126.03, 114.13, 112.39, 108.25, 80.67, 73.09, 63.63, 62.30, 55.75, 43.09, 26.29, 13.96; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{21}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: calcd 386.1363, found 386.1361.

Ethyl (R)-6-bromo-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3f)



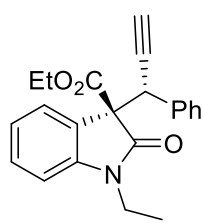
White solid, 45% yield, $[\alpha]_D^{23} = 1.489$ ($c = 1.00$ in CH_2Cl_2); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 5.24 min, t_R (minor) = 5.59 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.71 – 7.69 (m, 1H), 7.29 – 7.26 (m, 1H), 4.89 (d, $J = 2.5$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.75 (s, 3H), 2.46 (d, $J = 2.0$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.60, 166.59, 145.19, 133.62, 128.85, 127.91, 127.61, 127.29, 125.34, 124.20, 123.07, 111.38, 82.05, 73.51, 63.32, 62.57, 42.70, 26.15, 14.01; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0544.

Ethyl (S)-6-bromo-1-methyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3f)



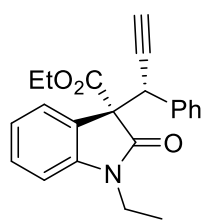
White solid, 50% yield, $[\alpha]_D^{23} = 0.739$ ($c = 1.00$ in CH_2Cl_2); 92% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 7.14 min, t_R (minor) = 14.16 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.24 – 7.10 (m, 6H), 6.85 – 6.76 (m, 2H), 4.86 (d, $J = 2.5$ Hz, 1H), 4.27 – 4.15 (m, 2H), 3.04 (s, 3H), 2.29 (d, $J = 2.4$ Hz, 1H), 1.21 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.97, 166.84, 145.50, 134.03, 129.35, 128.13, 127.86, 126.88, 124.91, 123.79, 123.15, 111.46, 80.30, 73.36, 63.16, 62.50, 43.02, 26.37, 13.93; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0544.

Ethyl (R)-1-ethyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3g)



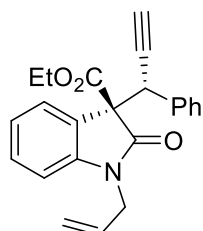
White solid, 37% yield, $[\alpha]_D^{23} = 1.416$ ($c = 1.00$ in CH_2Cl_2); 67% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 4.89 min, t_R (minor) = 5.66 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.87 (d, $J = 7.5$ Hz, 1H), 7.33 – 7.25 (m, 1H), 7.18 – 7.05 (m, 2H), 7.01 (t, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 7.5$ Hz, 2H), 6.57 (d, $J = 7.8$ Hz, 1H), 4.90 (d, $J = 2.5$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.62 – 3.53 (m, 1H), 3.24 – 3.15 (m, 1H), 2.44 (d, $J = 2.2$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 0.62 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.33, 167.35, 143.21, 134.26, 129.25, 129.23, 127.66, 127.56, 126.16, 125.57, 122.24, 108.05, 82.70, 73.04, 63.07, 62.29, 42.57, 34.55, 14.00, 11.52; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd 348.1594, found 348.1597.

Ethyl (S)-1-ethyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3g)



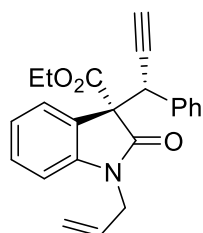
White solid, 43% yield, $[\alpha]_D^{23} = 1.341$ ($c = 1.00$ in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 6.38 min, t_R (minor) = 11.85 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.29 – 7.22 (m, 1H), 7.20 – 7.07 (m, 6H), 7.02 (t, $J = 7.5$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 4.87 – 4.80 (m, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.83 – 3.74 (m, 1H), 3.45 – 3.36 (m, 1H), 2.34 (d, $J = 3.7$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.93 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.65, 167.71, 143.28, 134.17, 129.45, 129.35, 127.77, 127.67, 125.32, 125.25, 121.89, 108.10, 80.88, 73.23, 62.92, 62.24, 42.88, 34.58, 13.92, 11.81; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{21}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: calcd 370.1414, found 370.1416.

Ethyl (R)-1-allyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((R,R)-3h)



White solid, 43% yield, $[\alpha]_D^{23} = 1.993$ ($c = 1.00$ in CH_2Cl_2); 92% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 4.86 min, t_R (minor) = 5.55 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.89 (d, $J = 7.4$ Hz, 1H), 7.32 – 6.89 (m, 7H), 6.54 (d, $J = 7.9$ Hz, 1H), 5.22 – 5.06 (m, 1H), 4.99 – 4.82 (m, 2H), 4.57 (d, $J = 17.5$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.18 – 4.07 (m, 1H), 3.85 – 3.78 (m, 1H), 2.45 (d, $J = 3.8$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 170.50, 167.25, 143.32, 134.30, 130.38, 129.27, 129.19, 127.70, 127.67, 125.96, 125.32, 122.41, 117.13, 108.97, 82.67, 73.07, 63.26, 62.35, 42.43, 42.23, 13.97; **HRMS** (ESI) for: $\text{C}_{23}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd 360.1594, found 360.1596.

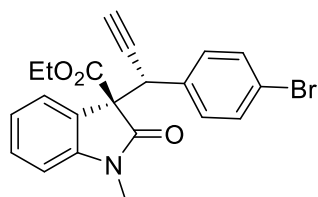
Ethyl (S)-1-allyl-2-oxo-3-((R)-1-phenylprop-2-yn-1-yl)indoline-3-carboxylate ((S,R)-3h)



White solid, 46% yield, $[\alpha]_D^{23} = 3.416$ ($c = 1.00$ in CH_2Cl_2); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 6.35 min, t_R (minor) = 9.54 min; $^1\text{H NMR}$ (400 MHz,

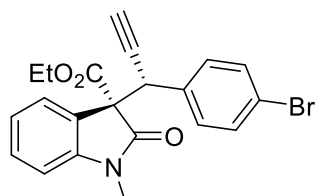
CDCl₃): δ (ppm) 7.37 – 6.93 (m, 8H), 6.61 (d, J = 7.8 Hz, 1H), 5.45 (m, 1H), 5.01 (d, J = 10.3 Hz, 1H), 4.92 – 4.76 (m, 2H), 4.44 – 4.17 (m, 3H), 4.05 – 3.99 (m, 1H), 2.36 (d, J = 2.6 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.77, 167.71, 143.35, 134.18, 130.70, 129.49, 129.32, 127.80, 127.74, 125.09, 124.95, 122.10, 117.33, 109.04, 80.98, 73.26, 63.13, 62.32, 42.74, 42.25, 13.92; **HRMS** (ESI) for: C₂₃H₂₁NO₃Na [M+Na]⁺: calcd 382.1414, found 382.1396.

Ethyl (R)-3-((R)-1-(4-bromophenyl)prop-2-yn-1-yl)-1-methyl-2-oxindoline-3-carboxylate ((R,R)-3i)



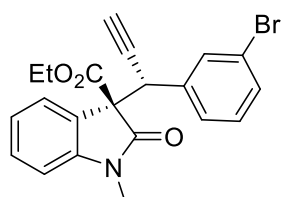
White solid, 40% yield, $[\alpha]_D^{23}$ = 0.741 (c = 1.00 in CH₂Cl₂); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), t_R (major) = 6.03 min, t_R (minor) = 7.03 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.81 (d, J = 7.5 Hz, 1H), 7.35 – 7.24 (m, 1H), 7.19 – 7.10 (m, 3H), 6.89 – 6.81 (m, 2H), 6.58 (d, J = 7.8 Hz, 1H), 4.91 – 4.83 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.83 (s, 3H), 2.46 (d, J = 3.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.66, 166.97, 143.86, 133.24, 130.68, 130.55, 129.50, 125.87, 124.93, 122.61, 121.88, 108.10, 81.85, 73.53, 63.22, 62.44, 42.10, 26.16, 13.98; **HRMS** (ESI) for: C₂₁H₁₉BrNO₃ [M+H]⁺: calcd 412.0543, found 412.0550.

Ethyl (S)-3-((R)-1-(4-bromophenyl)prop-2-yn-1-yl)-1-methyl-2-oxindoline-3-carboxylate ((S,R)-3i)



White solid, 56% yield, $[\alpha]_D^{23}$ = 0.997 (c = 1.00 in CH₂Cl₂); 96% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), t_R (major) = 11.46 min, t_R (minor) = 12.54 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.34 – 7.22 (m, 3H), 7.09 – 7.01 (m, 4H), 6.67 (d, J = 7.8 Hz, 1H), 4.79 (d, J = 2.4 Hz, 1H), 4.28 – 4.18 (m, 2H), 3.04 (s, 3H), 2.33 (d, J = 2.0 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.95, 167.44, 144.13, 133.44, 131.12, 130.76, 129.63, 124.96, 124.77, 122.27, 122.07, 108.19, 80.27, 73.47, 63.01, 62.41, 42.42, 26.24, 13.95; **HRMS** (ESI) for: C₂₁H₁₉BrNO₃ [M+H]⁺: calcd 412.0543, found 412.0550.

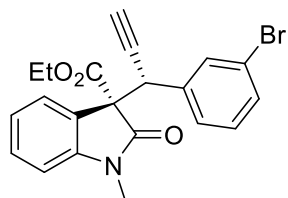
Ethyl (R)-3-((R)-1-(3-bromophenyl)prop-2-yn-1-yl)-1-methyl-2-oxindoline-3-carboxylate ((R,R)-3j)



White solid, 35% yield, $[\alpha]_D^{23}$ = 3.836 (c = 1.00 in CH₂Cl₂); 87% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C), t_R (major) = 5.11 min, t_R (minor) = 6.14 min; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.81 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.25 – 7.12 (m, 2H), 7.05 (d, J = 1.8 Hz, 1H), 6.97 – 6.87 (m, 2H), 6.57 (d, J = 7.8 Hz, 1H), 4.85 (t, J = 2.0 Hz, 1H), 4.28

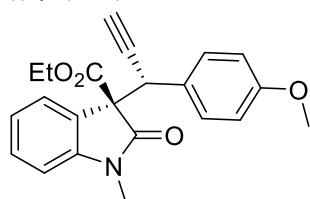
(q, $J = 7.1$ Hz, 2H), 2.83 (s, 3H), 2.47 (d, $J = 2.1$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.64, 166.93, 143.86, 136.37, 131.90, 130.80, 129.59, 128.86, 127.76, 125.89, 124.90, 122.67, 121.35, 108.01, 81.62, 73.76, 63.36, 62.47, 42.40, 26.14, 14.02; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0552.

Ethyl (S)-3-((R)-1-(3-bromophenyl)prop-2-yn-1-yl)-1-methyl-2-oxoindoline-3-carboxylate ((S,R)-3j)



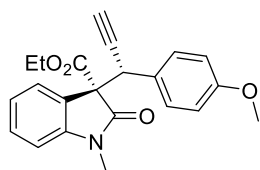
White solid, 46% yield, $[\alpha]_{\text{D}}^{23} = 2.632$ ($c = 1.00$ in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 9.43 min, t_{R} (minor) = 14.96 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.37 – 7.22 (m, 3H), 7.15 – 7.12 (m, 1H), 7.08 – 6.96 (m, 3H), 6.67 (d, $J = 7.8$ Hz, 1H), 4.81 (d, $J = 2.5$ Hz, 1H), 4.29 – 4.18 (m, 2H), 3.05 (s, 3H), 2.33 (d, $J = 3.7$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.85, 167.30, 144.12, 136.63, 132.32, 130.96, 129.64, 129.10, 128.10, 125.10, 124.65, 122.24, 121.56, 108.11, 79.94, 73.66, 63.04, 62.42, 42.60, 26.22, 13.94; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{19}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: calcd 412.0543, found 412.0552.

Ethyl (R)-3-((R)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-1-methyl-2-oxoindoline-3-carboxylate ((R,R)-3k)



White solid, 41% yield, $[\alpha]_{\text{D}}^{23} = 0.881$ ($c = 1.00$ in CH_2Cl_2); 82% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 8.23 min, t_{R} (minor) = 9.55 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.83 (d, $J = 7.4$ Hz, 1H), 7.35 – 7.22 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.87 – 6.85 (m, 2H), 6.56 – 6.54 (m, 3H), 4.86 (t, $J = 2.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.68 (s, 3H), 2.82 (s, 3H), 2.44 (d, $J = 4.1$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.89, 167.22, 158.94, 143.95, 130.02, 129.23, 126.10, 125.93, 125.37, 122.41, 112.78, 107.90, 82.67, 73.04, 63.55, 62.28, 55.08, 42.08, 26.12, 14.02; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{22}\text{NO}_4$ $[\text{M}+\text{H}]^+$: calcd 364.1543, found 364.1551.

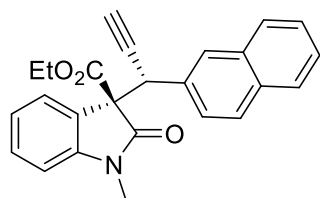
Ethyl (S)-3-((R)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-1-methyl-2-oxoindoline-3-carboxylate ((S,R)-3k)



White solid, 50% yield, $[\alpha]_{\text{D}}^{23} = 0.997$ ($c = 1.00$ in CH_2Cl_2); 74% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 13.61 min, t_{R} (minor) = 23.42 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.31 – 7.22 (m, 1H), 7.08 (m, 3H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.69 – 6.62 (m, 3H), 4.80 (t, $J = 2.1$ Hz, 1H), 4.26 – 4.19 (m, 2H), 3.73 (d, $J = 1.5$ Hz, 3H), 3.03 (d, $J = 1.6$ Hz, 3H), 2.30 (d, $J = 4.4$ Hz, 1H), 1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.20, 167.57,

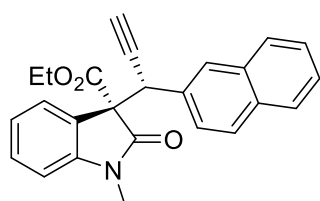
159.11, 144.17, 130.46, 129.31, 126.28, 125.21, 125.12, 122.06, 112.97, 107.95, 81.00, 72.94, 63.40, 62.23, 55.15, 42.39, 26.21, 13.96; **HRMS** (ESI) for: C₂₂H₂₁NO₄Na [M+Na]⁺: calcd 386.1363, found 386.1370.

Ethyl (R)-1-methyl-3-((R)-1-(naphthalen-2-yl)prop-2-yn-1-yl)-2-oxindoline-3-carboxylate ((R,R)-3I)



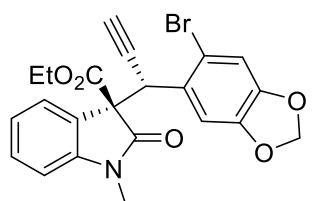
White solid, 39% yield, $[\alpha]_D^{23} = 0.718$ ($c = 1.00$ in CH₂Cl₂); 88% ee, determined by HPLC analysis (Chiralpak AD column, hexane/i-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 7.05 min, t_R (minor) = 9.29 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.91 (d, $J = 7.4$ Hz, 1H), 7.71 – 7.56 (m, 2H), 7.52 – 7.32 (m, 4H), 7.24 – 7.17 (m, 2H), 7.05 – 7.02 (m, 1H), 6.41 (d, $J = 7.7$ Hz, 1H), 5.10 – 5.06 (m, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.66 (s, 3H), 2.50 (d, $J = 3.5$ Hz, 1H), 1.28 (t, $J = 7.8$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) 170.80, 167.18, 143.89, 132.59, 132.57, 131.54, 129.31, 128.39, 127.91, 127.26, 126.83, 126.53, 125.98, 125.94, 125.74, 125.28, 122.47, 107.92, 82.40, 73.41, 63.54, 62.36, 42.87, 26.02, 14.02; **HRMS** (ESI) for: C₂₅H₂₂NO₃ [M+H]⁺: calcd 348.1594, found 348.1600.

Ethyl (S)-1-methyl-3-((R)-1-(naphthalen-2-yl)prop-2-yn-1-yl)-2-oxindoline-3-carboxylate ((S,R)-3I)



White solid, 52% yield, $[\alpha]_D^{23} = 1.024$ ($c = 1.00$ in CH₂Cl₂); 96% ee, determined by HPLC analysis (Chiralpak AD column, hexane/i-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 9.91 min, t_R (minor) = 19.58 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.81 – 7.58 (m, 4H), 7.49 – 7.38 (m, 2H), 7.34 – 7.19 (m, 2H), 7.12 – 6.97 (m, 2H), 6.58 (d, $J = 7.8$ Hz, 1H), 5.06 – 5.01 (m, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 2.99 (s, 3H), 2.36 (d, $J = 3.8$ Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) 171.18, 167.55, 144.17, 132.75, 132.71, 131.82, 129.41, 128.81, 127.97, 127.41, 127.14, 127.06, 126.12, 125.96, 125.35, 125.01, 122.08, 108.01, 80.77, 73.32, 63.36, 62.34, 43.20, 26.22, 13.96; **HRMS** (ESI) for: C₂₅H₂₂NO₃ [M+H]⁺: calcd 348.1594, found 348.1600.

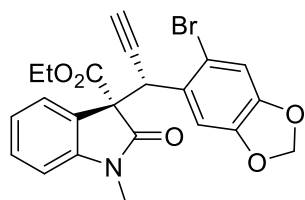
Ethyl (R)-3-((S)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)-1-methyl-2-oxindoline-3-carboxylate ((R,S)-3m)



White solid, 37% yield, $[\alpha]_D^{23} = -6.717$ ($c = 1.00$ in CH₂Cl₂); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/i-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (minor) = 6.68 min, t_R (major) = 8.26 min; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.67 (d, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 1.3$ Hz, 1H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.44 (d, $J = 1.3$ Hz, 1H), 5.90 – 5.82 (m, 2H), 5.43 (d, $J = 3.8$ Hz, 1H), 4.22 – 4.16 (m, 2H), 3.01 (s, 3H), 2.35 (d, $J =$

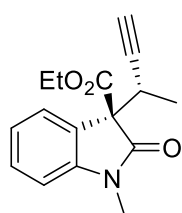
3.7 Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 170.85, 167.22, 147.73, 146.86, 144.57, 129.84, 128.45, 125.75, 125.54, 122.74, 115.78, 112.42, 109.54, 108.15, 101.70, 81.99, 72.80, 62.35, 62.14, 40.34, 26.40, 13.90; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{19}\text{BrNO}_5$ $[\text{M}+\text{H}]^+$: calcd 456.0441, found 456.0442.

Ethyl (S)-3-((S)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)-1-methyl-2-oxindoline-3-carboxylate ((S,S)-3m)



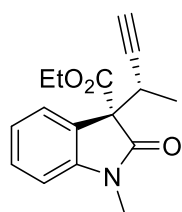
White solid, 38% yield, $[\alpha]_{\text{D}}^{23} = 3.518$ ($c = 1.00$ in CH_2Cl_2); 85% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (minor) = 9.36 min, t_{R} (major) = 16.27 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.53 (d, $J = 7.5$ Hz, 1H), 7.27 – 7.20 (m, 1H), 7.09 (d, $J = 1.3$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 1.3$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 5.96 – 5.87 (m, 2H), 5.39 (t, $J = 2.0$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.17 (s, 3H), 2.36 (d, $J = 4.0$ Hz, 1H), 1.22 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.65, 167.68, 147.96, 147.42, 143.68, 129.69, 128.13, 125.72, 124.51, 122.13, 115.55, 112.20, 109.83, 107.88, 101.96, 80.90, 73.16, 62.55, 62.34, 40.65, 26.46, 13.99; **HRMS** (ESI) for: $\text{C}_{22}\text{H}_{19}\text{BrNO}_5$ $[\text{M}+\text{H}]^+$: calcd 456.0441, found 456.0442.

Ethyl (R)-3-((S)-but-3-yn-2-yl)-1-methyl-2-oxindoline-3-carboxylate ((R,S)-3n)



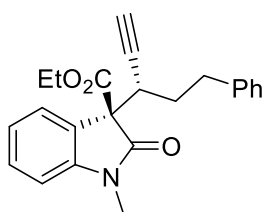
White solid, 43% yield, $[\alpha]_{\text{D}}^{23} = 0.708$ ($c = 1.00$ in CH_2Cl_2); 98% ee, determined by HPLC analysis (Chiralpak OJ column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (major) = 8.13 min, t_{R} (minor) = 9.06 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.58 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 4.30 – 4.12 (m, 2H), 3.71 – 3.65 (m, 1H), 3.24 (s, 3H), 2.09 (d, $J = 3.7$ Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.07 (d, $J = 5.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.77, 167.62, 144.19, 129.23, 126.19, 124.79, 122.83, 108.06, 83.97, 70.75, 62.17, 61.71, 31.70, 26.45, 15.56, 13.93; **HRMS** (ESI) for: $\text{C}_{16}\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd 272.1281, found 272.1283.

Ethyl (S)-3-((S)-but-3-yn-2-yl)-1-methyl-2-oxindoline-3-carboxylate ((S,S)-3n)



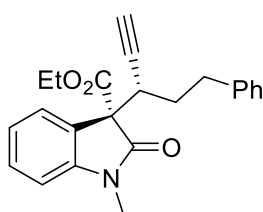
White solid, 56% yield, $[\alpha]_{\text{D}}^{23} = 0.351$ ($c = 1.00$ in CH_2Cl_2); 96% ee, determined by HPLC analysis (Chiralpak OJ column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_{R} (minor) = 10.04 min, t_{R} (major) = 11.31 min; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.38 – 7.32 (m, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.65 – 3.59 (m, 1H), 3.25 (s, 3H), 2.03 (d, $J = 2.9$ Hz, 1H), 1.22 – 1.19 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.99, 167.73, 144.50, 129.32, 125.76, 124.39, 122.57, 108.18, 82.99, 70.57, 62.09, 61.88, 31.62, 26.37, 15.82, 13.92; **HRMS** (ESI) for: $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: calcd 294.1101, found 294.1105.

Ethyl (R)-1-methyl-2-oxo-3-((S)-5-phenylpent-1-yn-3-yl)indoline-3-carboxylate ((R,S)-3o)



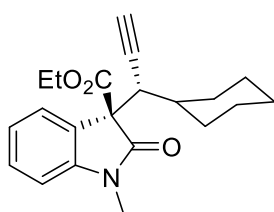
White solid, 39% yield, $[\alpha]_D^{23} = 0.906$ ($c = 1.00$ in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (minor) = 6.61 min, t_R (major) = 7.22 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.57 (d, $J = 7.5$ Hz, 1H), 7.39 – 7.01 (m, 7H), 6.83 (d, $J = 7.7$ Hz, 1H), 4.27 – 4.10 (m, 2H), 3.66 – 3.52 (m, 1H), 3.21 (s, 3H), 2.95 – 2.88 (m, 1H), 2.67 – 2.60 (m, 1H), 2.17 (d, $J = 4.0$ Hz, 1H), 1.68 – 1.58 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.71, 167.53, 144.06, 141.17, 129.22, 128.51, 128.31, 126.46, 125.93, 124.76, 122.85, 108.16, 82.39, 72.30, 62.23, 61.71, 37.31, 33.73, 31.09, 26.52, 13.91; **HRMS** (ESI) for: $\text{C}_{23}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd 362.1751, found 362.1752.

Ethyl (S)-1-methyl-2-oxo-3-((S)-5-phenylpent-1-yn-3-yl)indoline-3-carboxylate ((S,S)-3o)



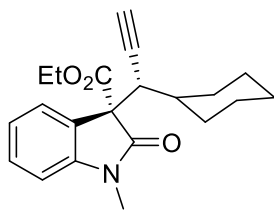
White solid, 51% yield, $[\alpha]_D^{23} = 0.426$ ($c = 1.00$ in CH_2Cl_2); 94% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (minor) = 6.83 min, t_R (major) = 7.31 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.41 – 6.99 (m, 8H), 6.84 (d, $J = 7.8$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.52 – 3.40 (m, 1H), 3.23 (s, 3H), 2.98 – 2.91 (m, 1H), 2.69 – 2.61 (m, 1H), 2.13 (d, $J = 3.9$ Hz, 1H), 1.89 – 1.51 (m, 2H), 1.17 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.99, 167.71, 144.49, 140.98, 129.35, 128.51, 128.36, 126.01, 125.73, 124.40, 122.62, 108.20, 81.57, 72.02, 62.14, 61.74, 36.88, 33.73, 31.37, 26.41, 13.89; **HRMS** (ESI) for: $\text{C}_{23}\text{H}_{23}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: calcd 384.1570, found 384.1575.

Ethyl (R)-3-((S)-1-cyclohexylprop-2-yn-1-yl)-1-methyl-2-oxoindoline-3-carboxylate ((R,S)-3p)



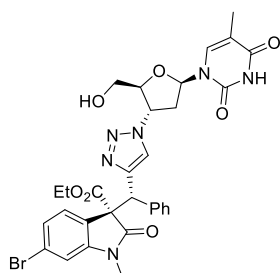
White solid, 33% yield, $[\alpha]_D^{23} = 0.983$ ($c = 1.00$ in CH_2Cl_2); 71% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 8.90 min, t_R (minor) = 12.29 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.64 (d, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 4.21 – 4.15 (m, 2H), 3.57 – 3.55 (m, 1H), 3.24 (s, 3H), 2.15 (d, $J = 2.2$ Hz, 1H), 1.74 – 1.33 (m, 5H), 1.30 – 1.24 (m, 1H), 1.21 (t, $J = 6.9$ Hz, 3H), 1.17 – 1.08 (m, 2H), 1.06 – 0.90 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.77, 167.98, 143.79, 129.05, 127.49, 125.49, 122.69, 108.05, 82.09, 72.73, 62.25, 61.45, 43.22, 38.43, 32.68, 29.79, 26.56, 26.39, 26.07, 25.86, 13.88; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{H}]^+$: calcd 340.1907, found 340.1916.

Ethyl (S)-3-((S)-1-cyclohexylprop-2-yn-1-yl)-1-methyl-2-oxoindoline-3-carboxylate ((S,S)-3p)



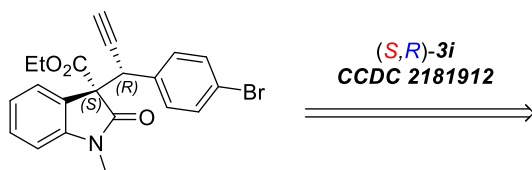
White solid, 42% yield, $[\alpha]_D^{23} = 0.193$ ($c = 1.00$ in CH_2Cl_2); 58% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 70:30 v/v, flow rate 1 mL/min, $\lambda = 254$ nm, 25 °C), t_R (major) = 33.63 min, t_R (minor) = 59.70 min; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.35 (t, $J = 7.7$ Hz, 1H), 7.29 – 7.24 (m, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 4.22 – 4.15 (m, 2H), 3.52 (t, $J = 2.9$ Hz, 1H), 3.23 (s, 3H), 2.13 (d, $J = 3.5$ Hz, 1H), 1.74 – 1.45 (m, 5H), 1.33 – 1.25 (m, 3H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.15 – 0.96 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 172.35, 168.32, 144.28, 129.28, 125.84, 124.39, 122.57, 108.18, 80.87, 72.65, 62.20, 61.29, 43.32, 37.66, 32.92, 30.13, 26.43, 26.40, 26.00, 25.78, 13.85; **HRMS** (ESI) for: $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: calcd 362.1727, found 362.1732.

Ethyl (S)-6-bromo-3-((R)-1-((2S,3S,5R)-2-(hydroxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)tetrahydrofuran-3-yl)-1H-1,2,3-triazol-4-yl)(phenyl)methyl)-1-methyl-2-oxindoline-3-carboxylate (4)

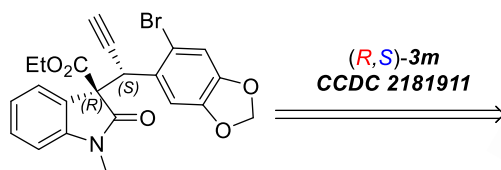
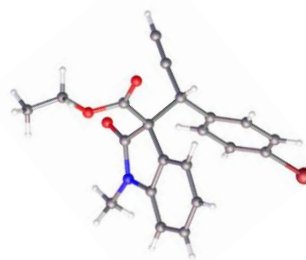


White solid, 90% yield, $[\alpha]_D^{23} = -1.290$ ($c = 1.00$ in CH_2Cl_2); >95:5 d.r.; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 9.47 (s, 1H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.44 (s, 1H), 7.39 (s, 1H), 7.22 – 7.00 (m, 4H), 6.95 (d, $J = 7.6$ Hz, 2H), 6.72 (s, 1H), 6.22 (t, $J = 6.5$ Hz, 1H), 5.37 – 5.34 (m, 2H), 4.44 – 4.33 (m, 1H), 4.25 – 4.06 (m, 2H), 3.98 (d, $J = 12.3$ Hz, 1H), 3.79 – 3.68 (m, 1H), 3.59 (s, 1H), 2.91 (t, $J = 6.9$ Hz, 2H), 2.79 (s, 3H), 1.88 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.72, 167.31, 163.90, 150.46, 147.28, 145.43, 137.80, 136.15, 129.47, 129.14, 127.75, 125.42, 125.01, 123.56, 122.69, 111.27, 111.17, 88.51, 85.15, 63.97, 62.31, 61.50, 59.11, 48.15, 37.39, 26.25, 13.80, 12.37; **HRMS** (ESI) for: $\text{C}_{31}\text{H}_{32}\text{BrN}_6\text{O}_7$ $[\text{M}+\text{H}]^+$: calcd 679.1510, found 679.1516.

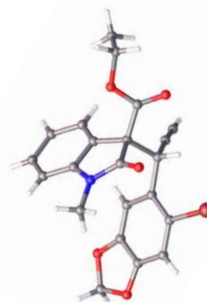
5. X-ray structure of (S,R)-3i and (R,S)-3m



(S,R)-3i
CCDC 2181912



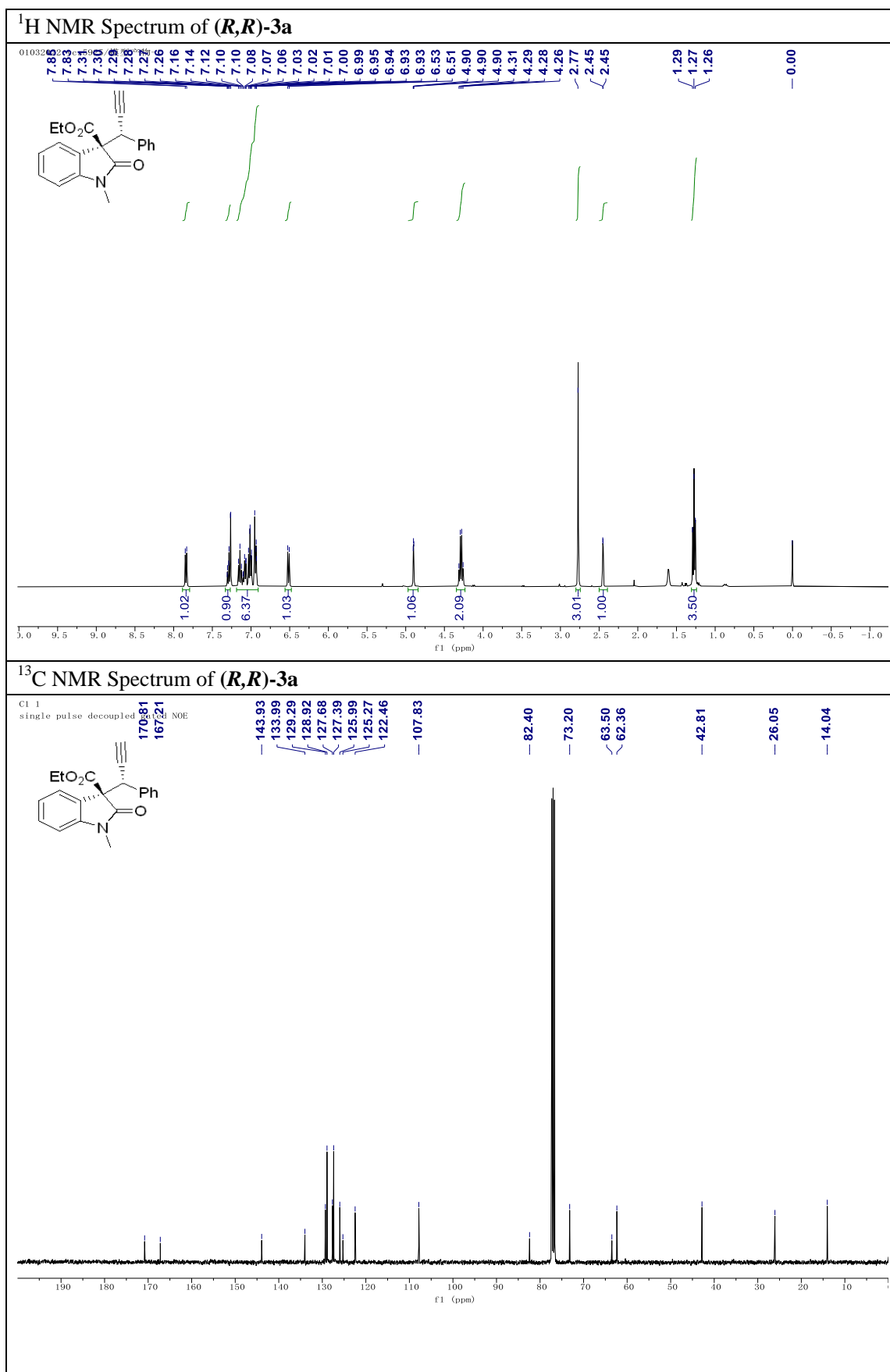
(R,S)-3m
CCDC 2181911



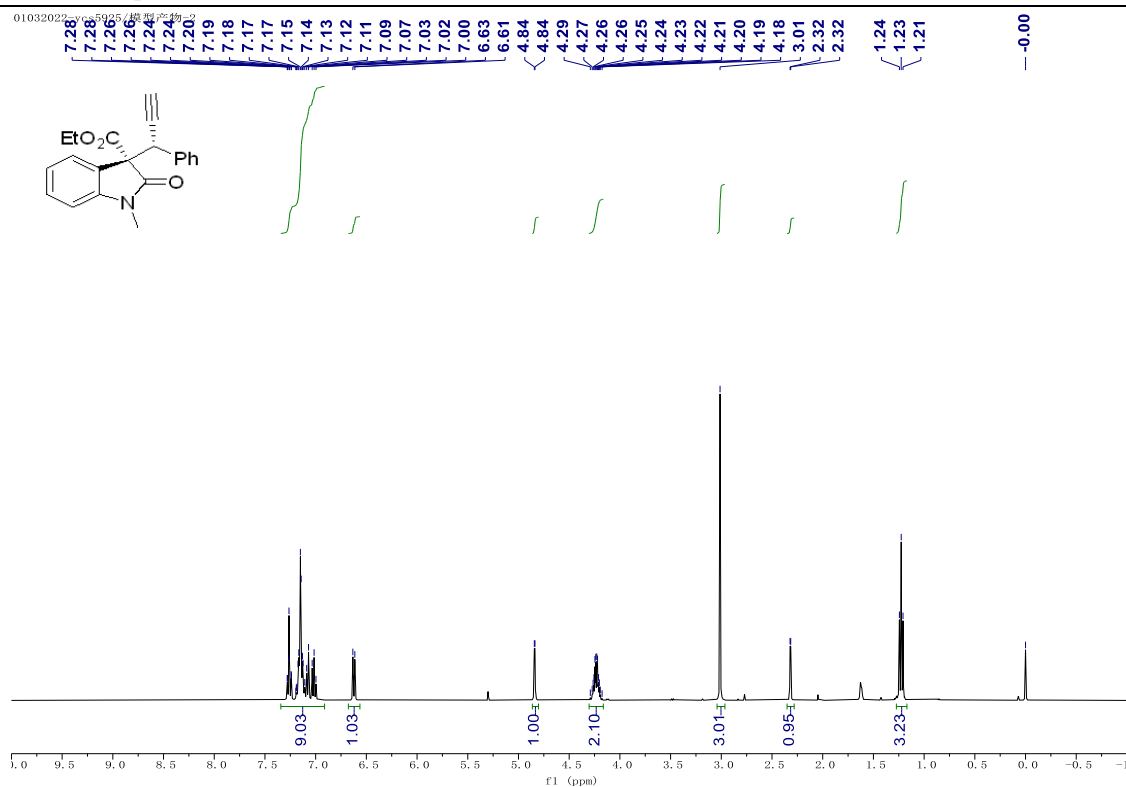
References

- (a) J. Gao, J. R. Chen, S. W. Duan, T. R. Li, L. Q. Lu and W. J. Xiao, *Asian J. Org. Chem.*, 2014, **3**, 530-535; (b) J. G. Wang, S. Osman, X. J. Lu, J. Y. Chen and X. D. Xia, *Heterocycl. Commun.*, 2020, **26**, 168-175.
- (a) G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2010, **132**, 10592-10608; (b) D. Y. Zhang, L. Shao, J. Xu and X. P. Hu, *ACS Catal.*, 2015, **5**, 5026-5030; (c) K. Zhang, L. Q. Lu, S. Yao, J. R. Chen, D. Q. Shi and W. J. Xiao, *J. Am. Chem. Soc.*, 2017, **139**, 12847-12854.

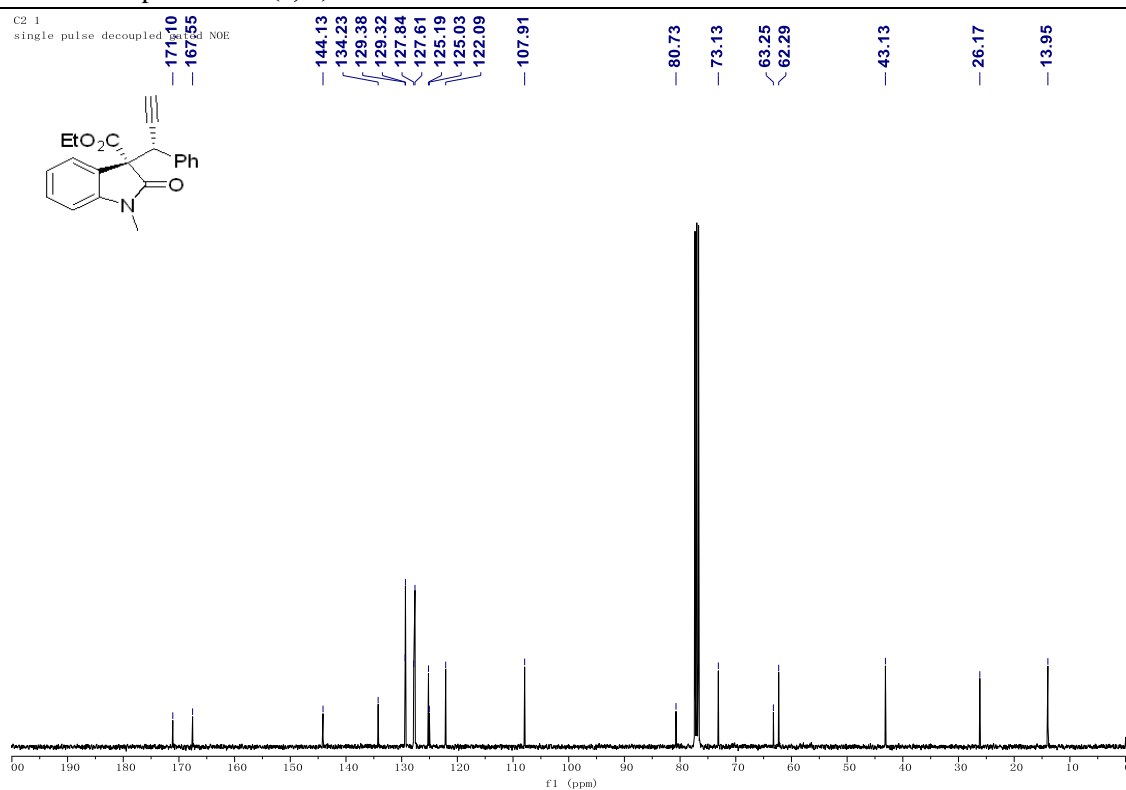
6. Copies of ^1H and ^{13}C NMR Spectra



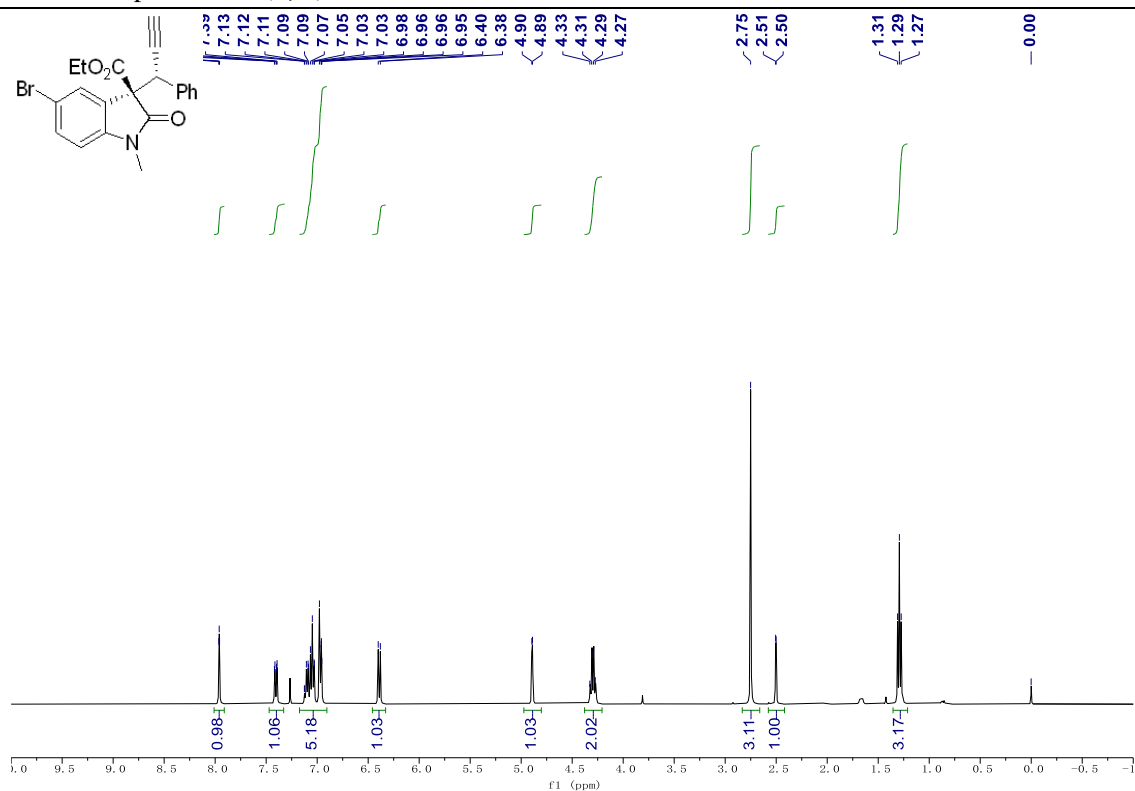
¹H NMR Spectrum of (*S,R*)-3a



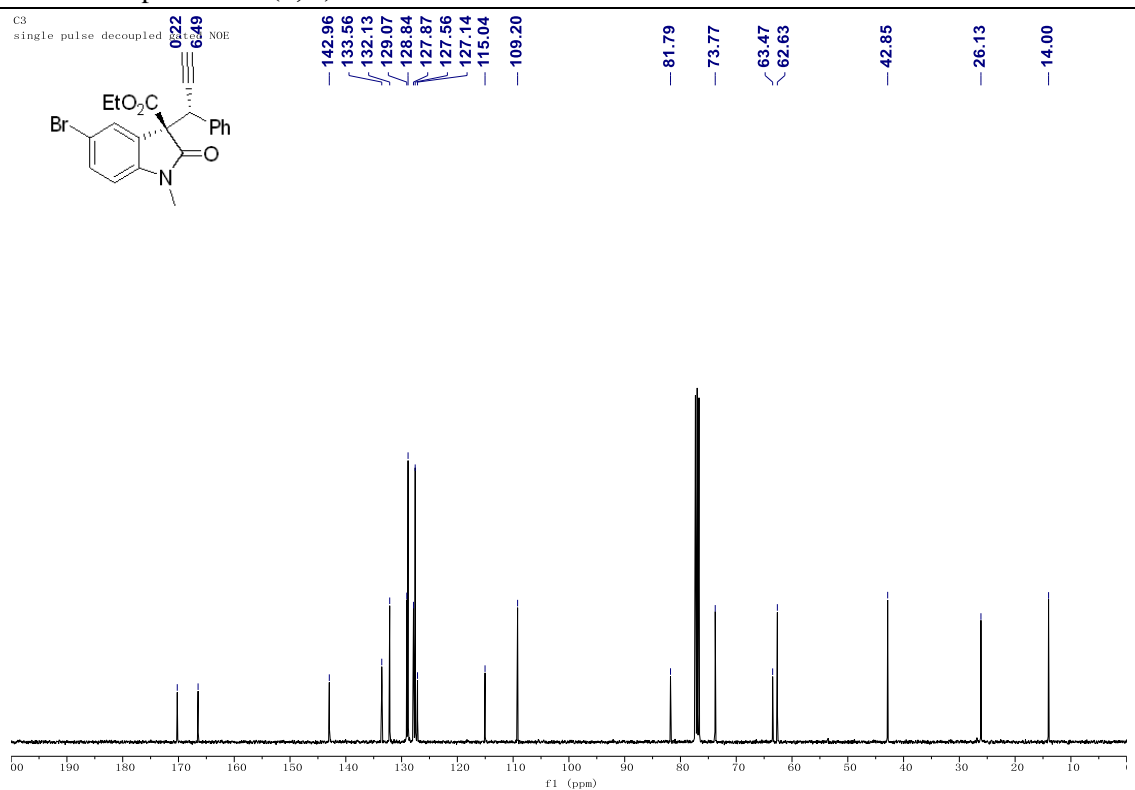
¹³C NMR Spectrum of (*S,R*)-3a

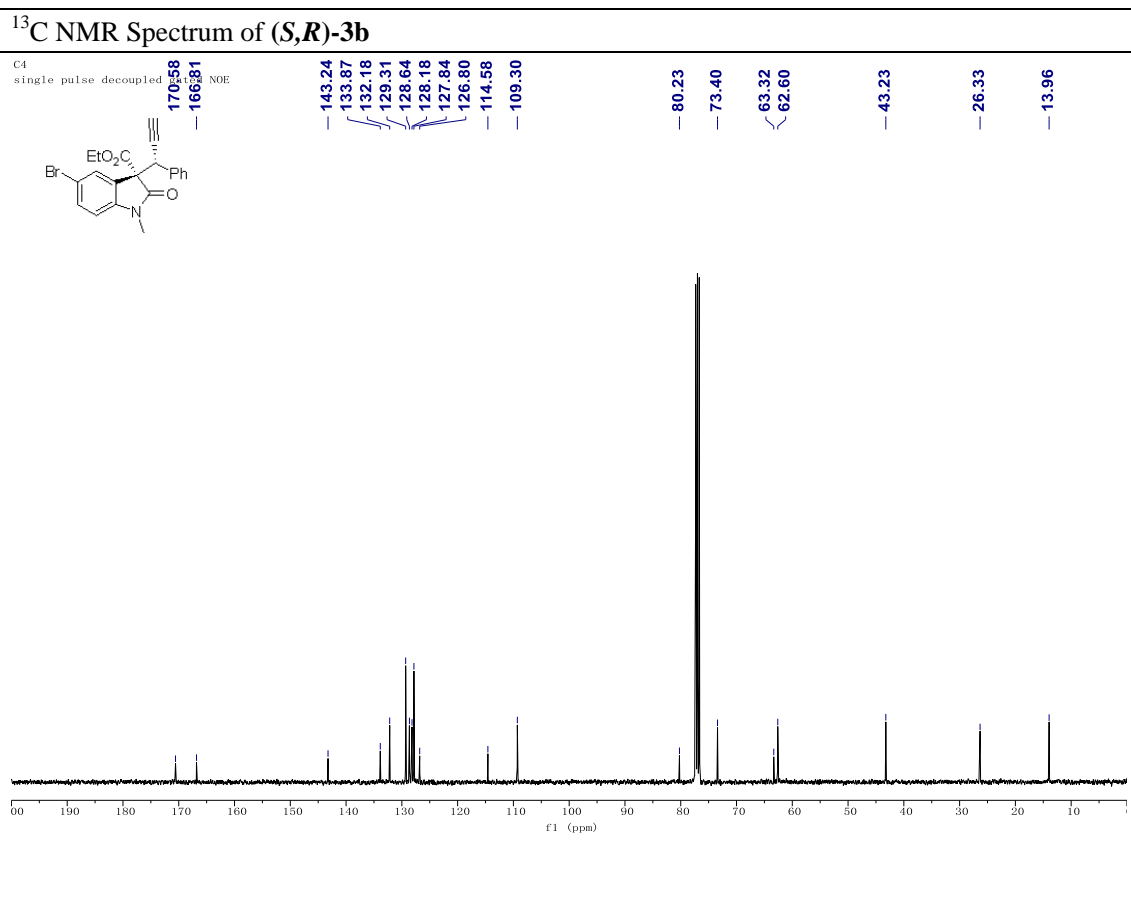
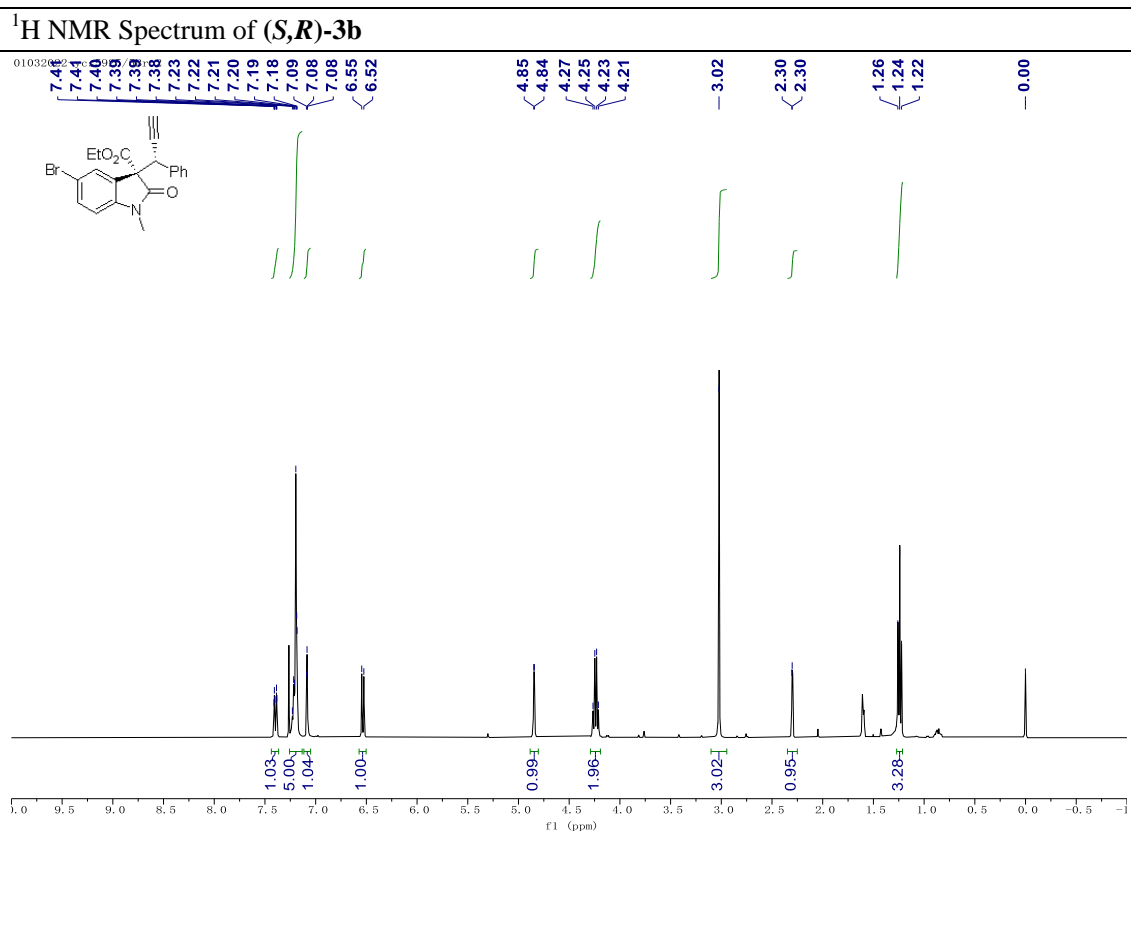


¹H NMR Spectrum of (*R,R*)-3b

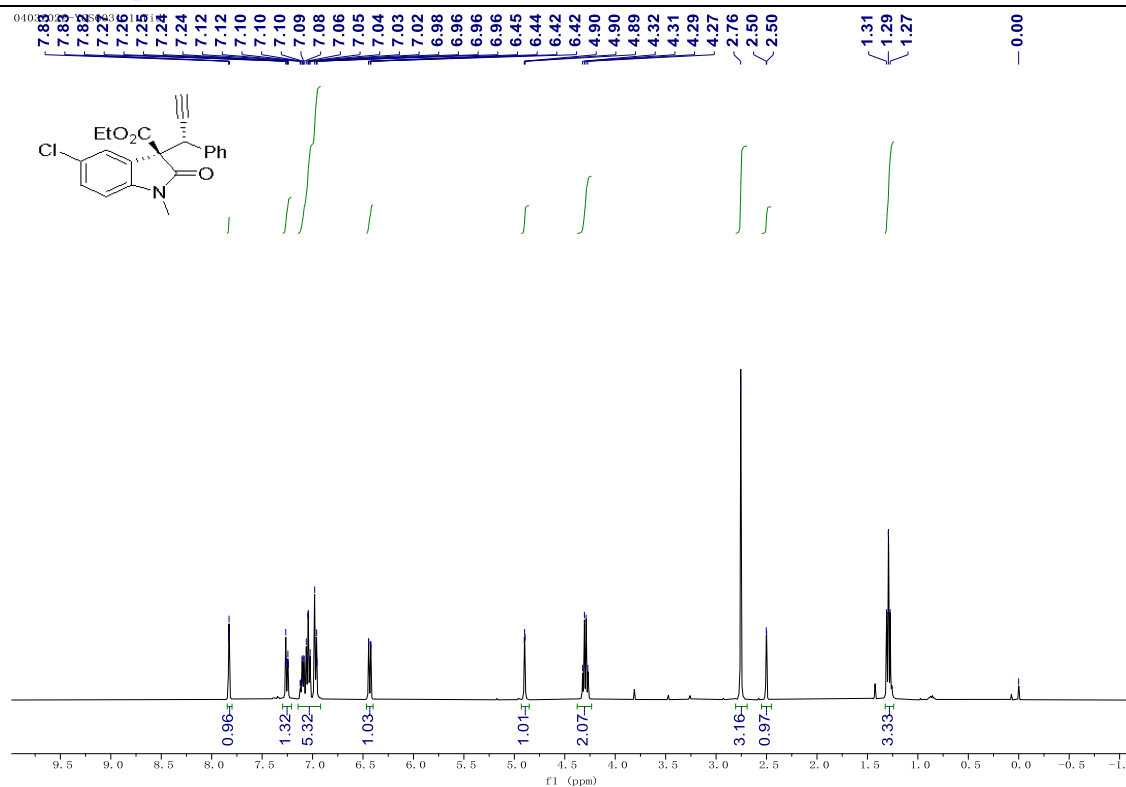


¹³C NMR Spectrum of (*R,R*)-3b

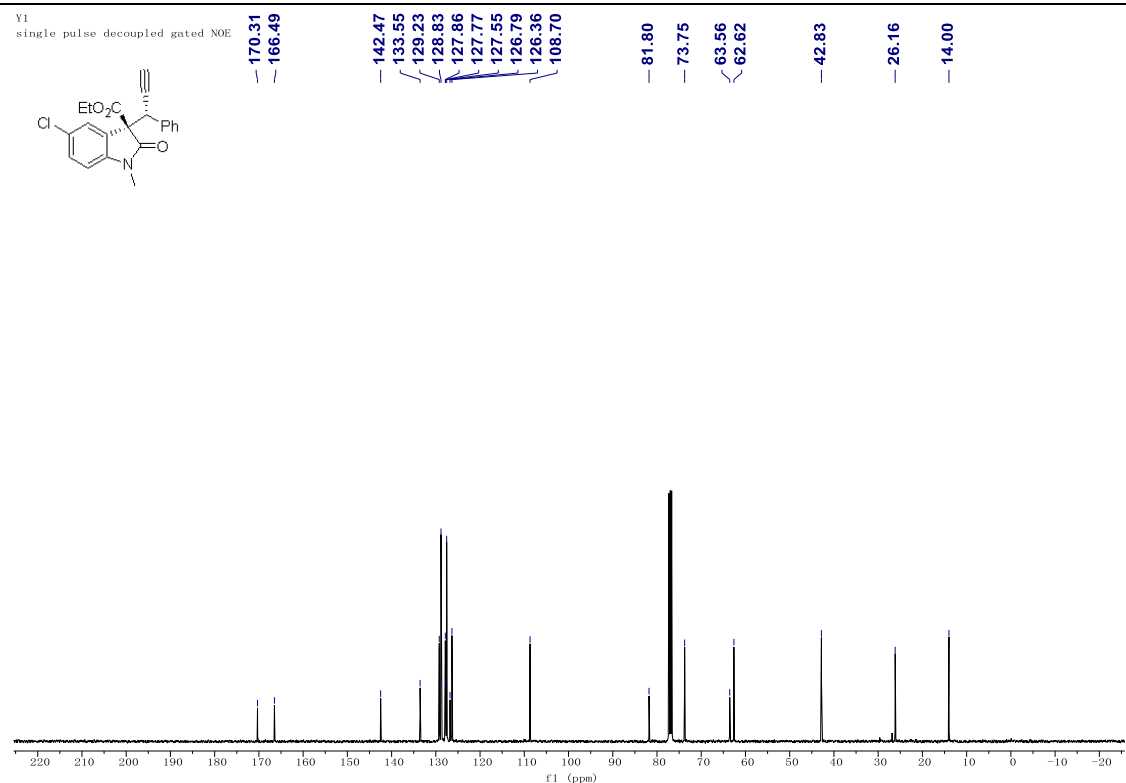




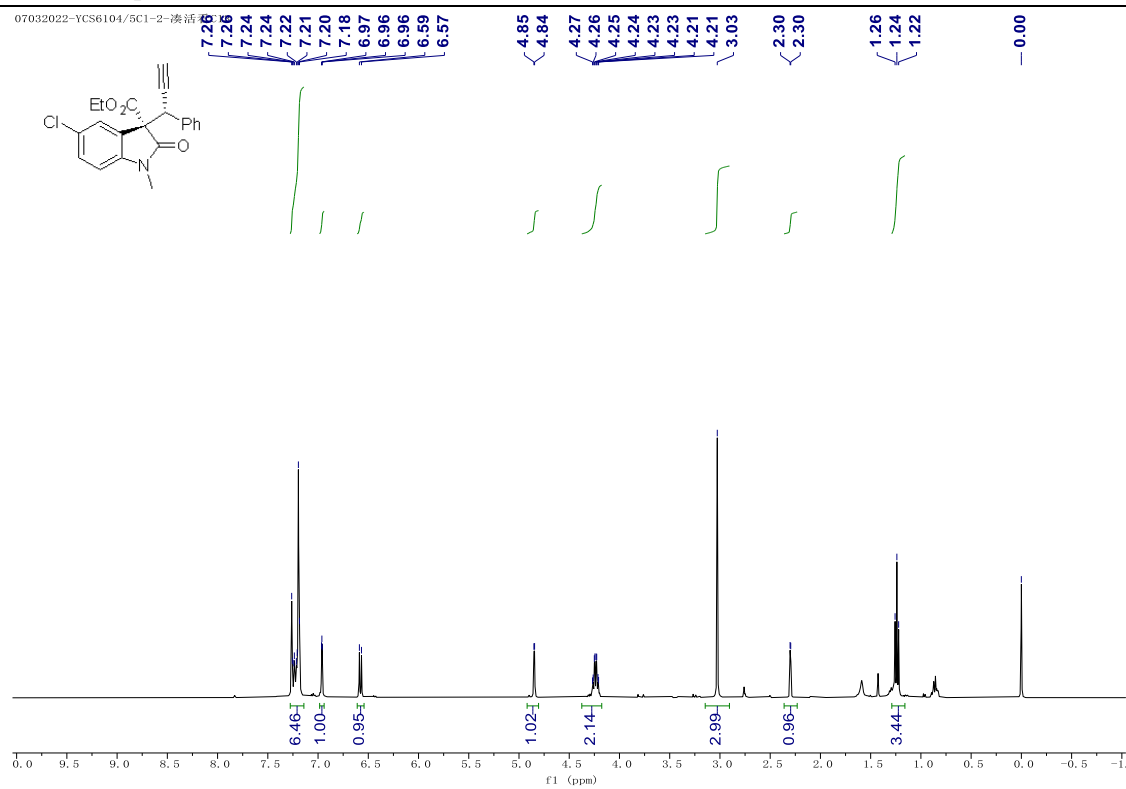
¹H NMR Spectrum of (*R,R*)-3c



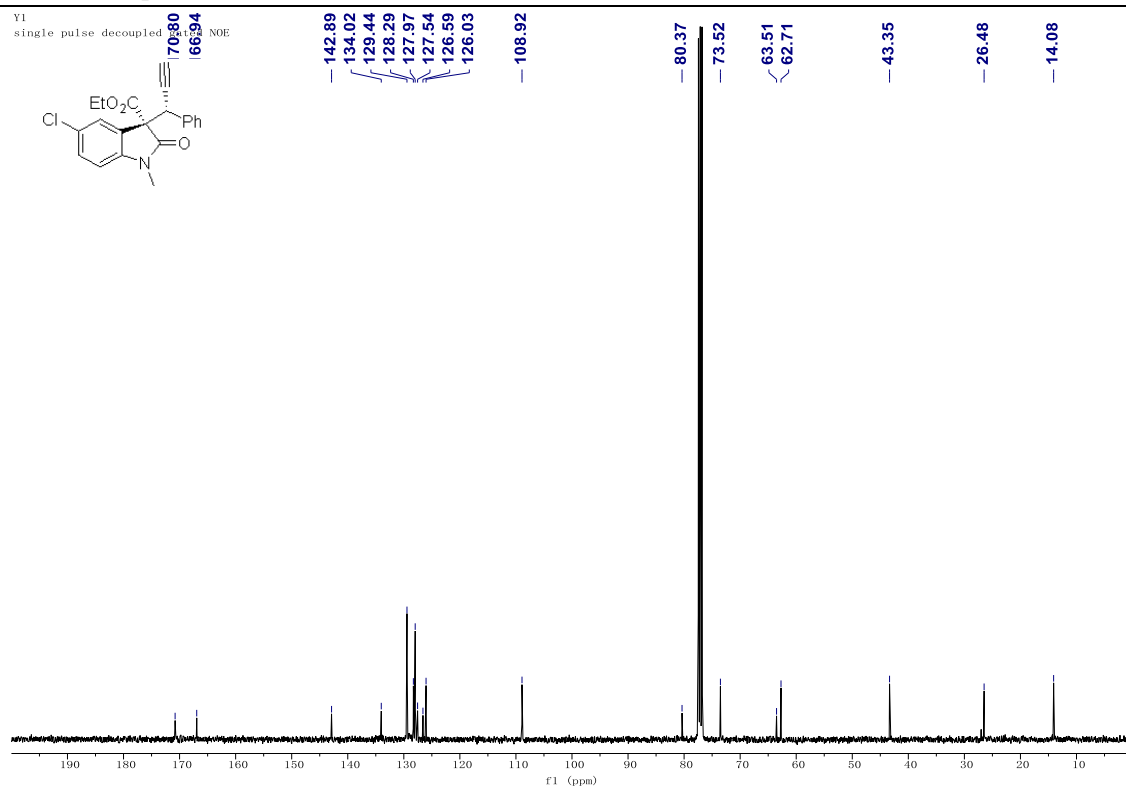
¹³C NMR Spectrum of (*R,R*)-3c



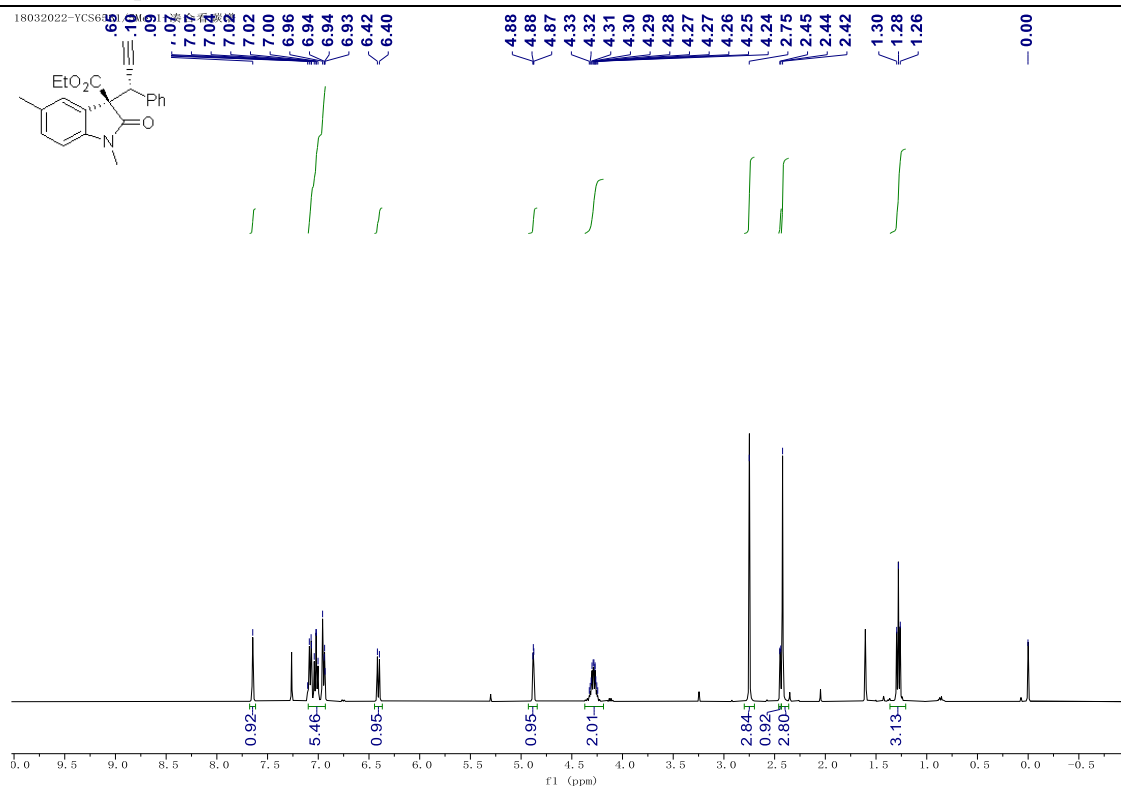
¹H NMR Spectrum of (*S,R*)-3c



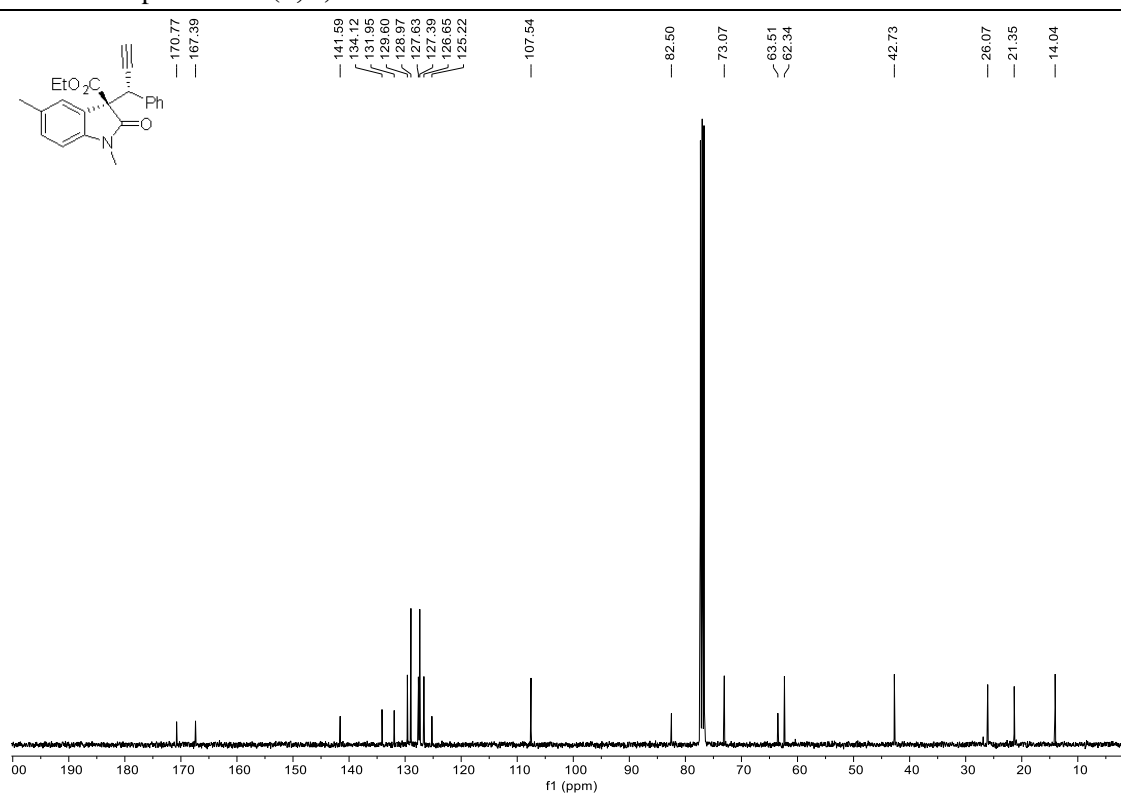
¹³C NMR Spectrum of (*S,R*)-3c



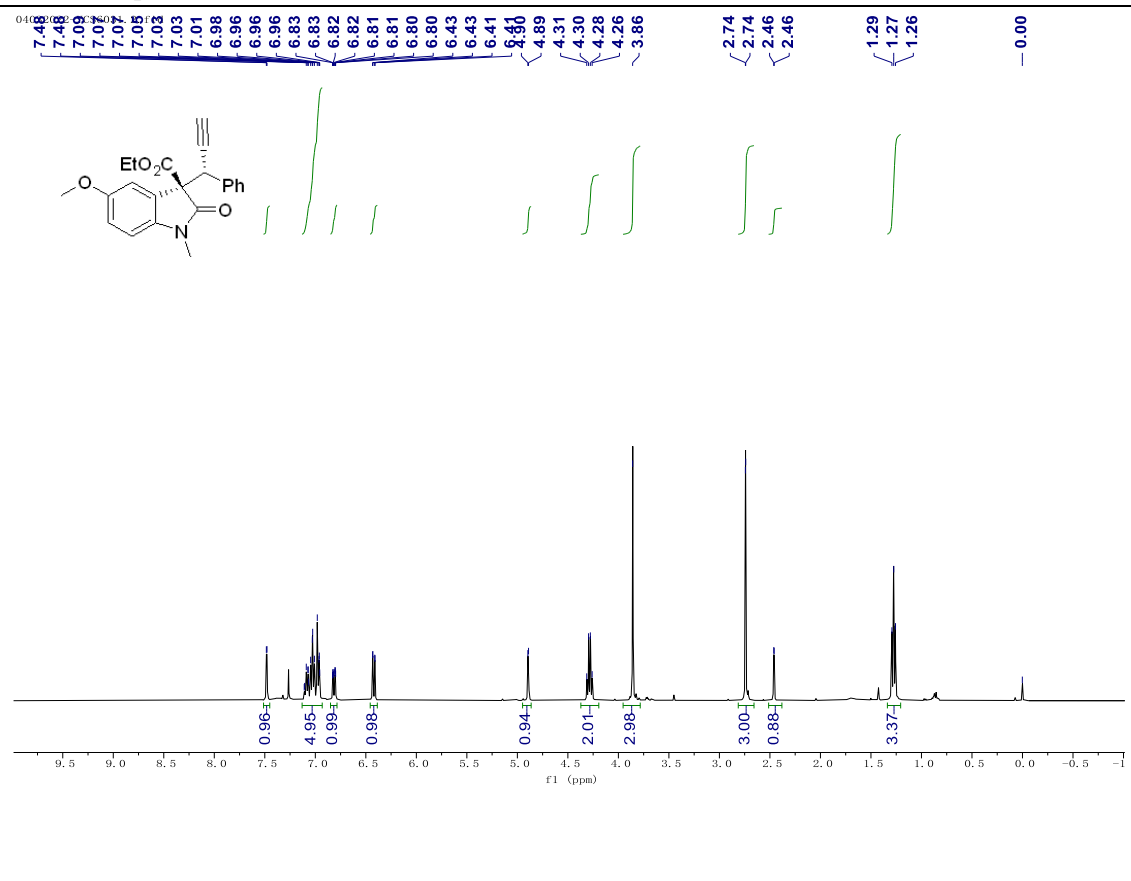
¹H NMR Spectrum of (*R,R*)-3d



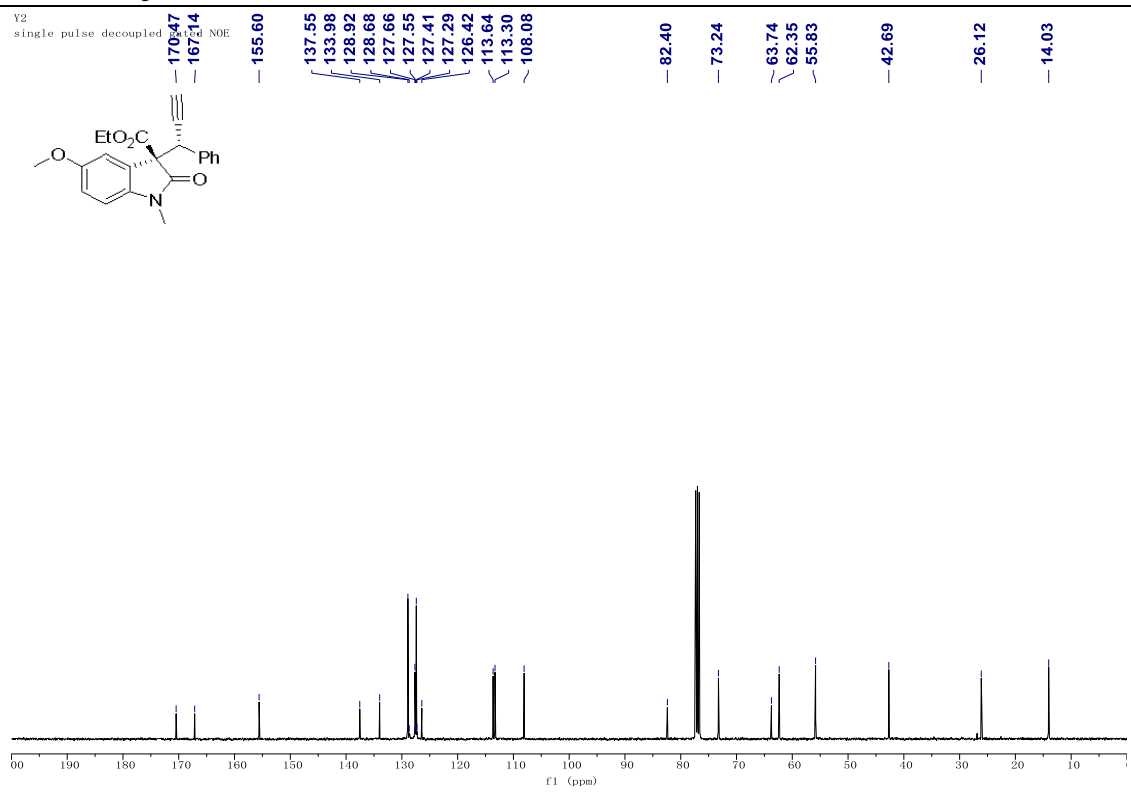
¹³C NMR Spectrum of (*R,R*)-3d



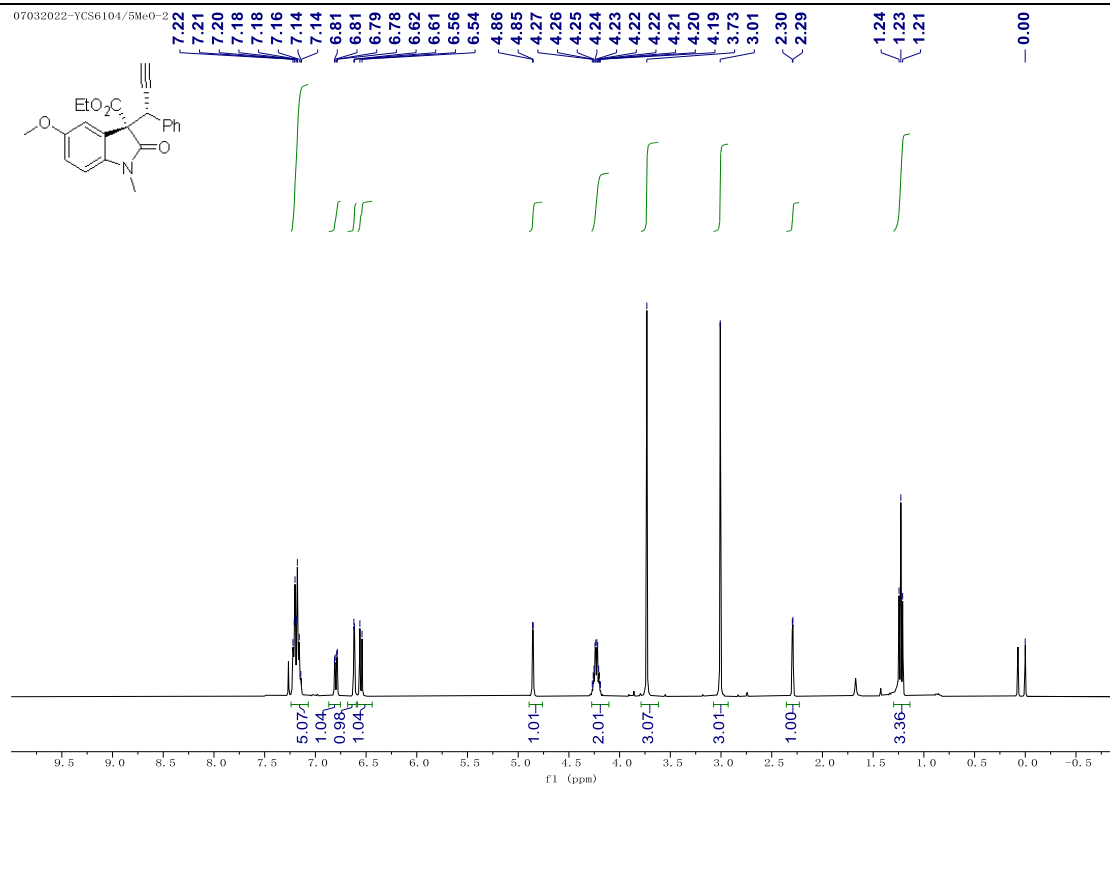
¹H NMR Spectrum of (*R,R*)-3e



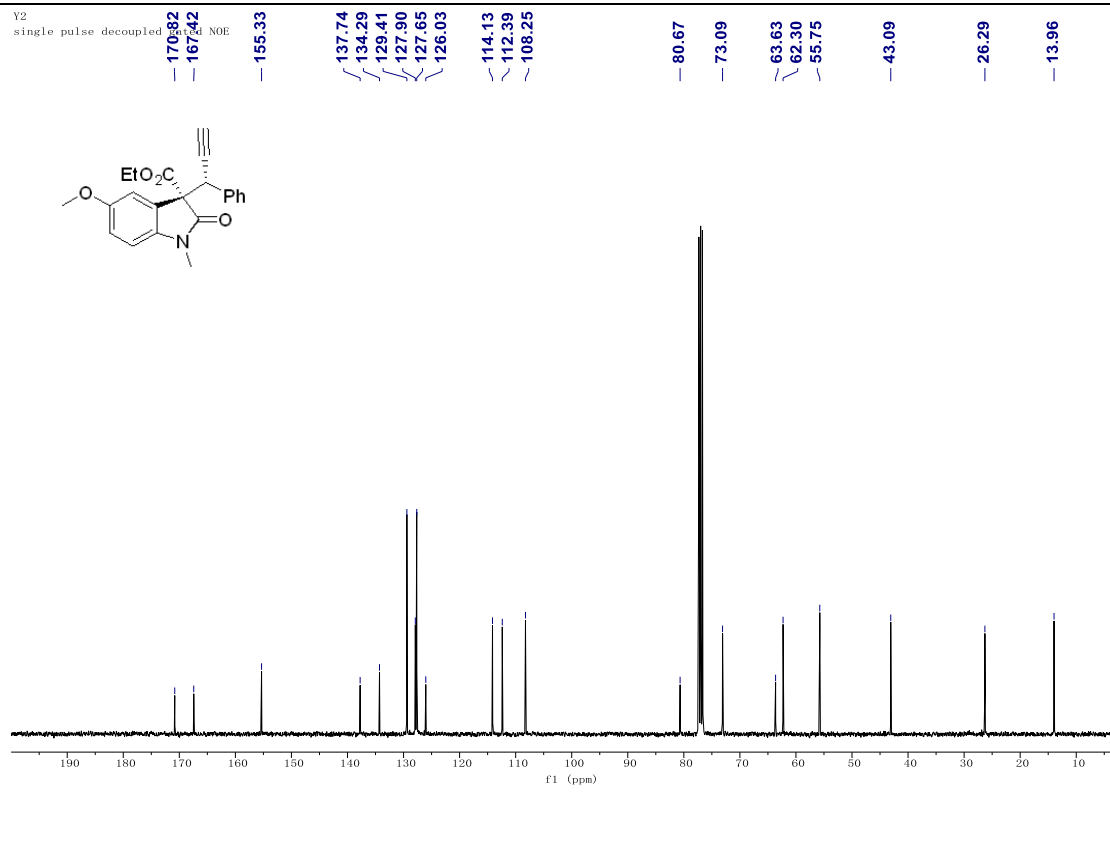
¹³C NMR Spectrum of (*R,R*)-3e



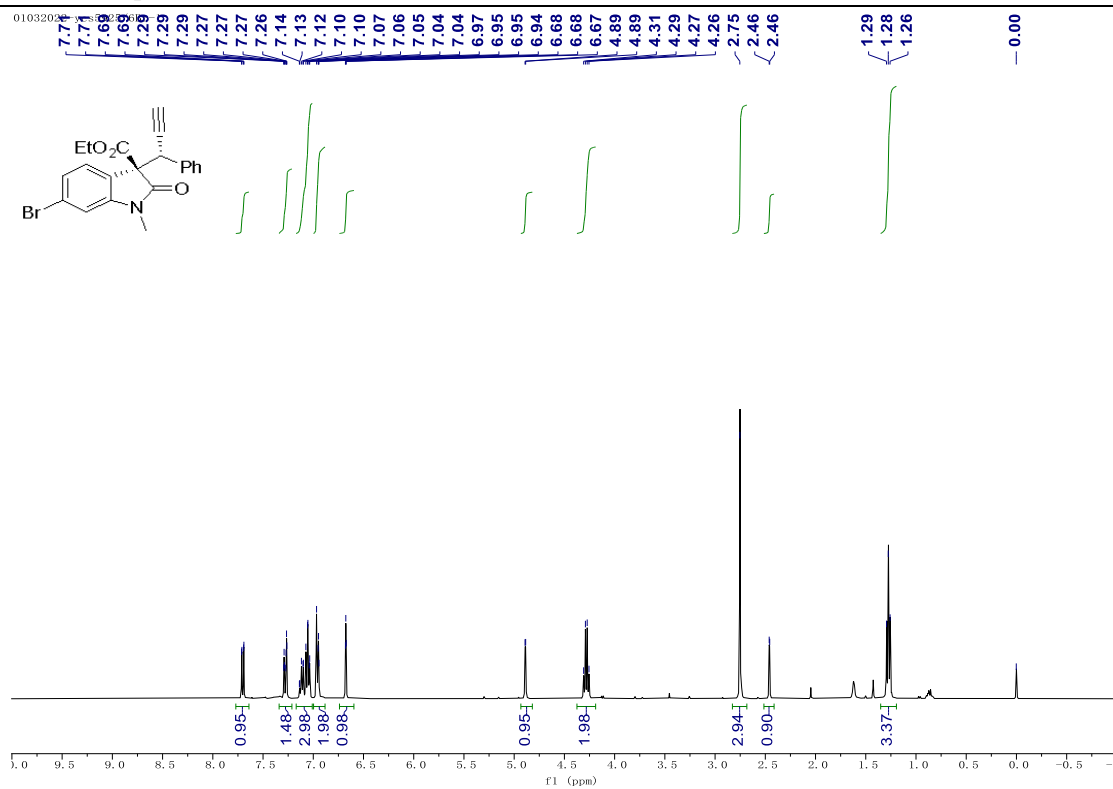
¹H NMR Spectrum of (S,R)-3e



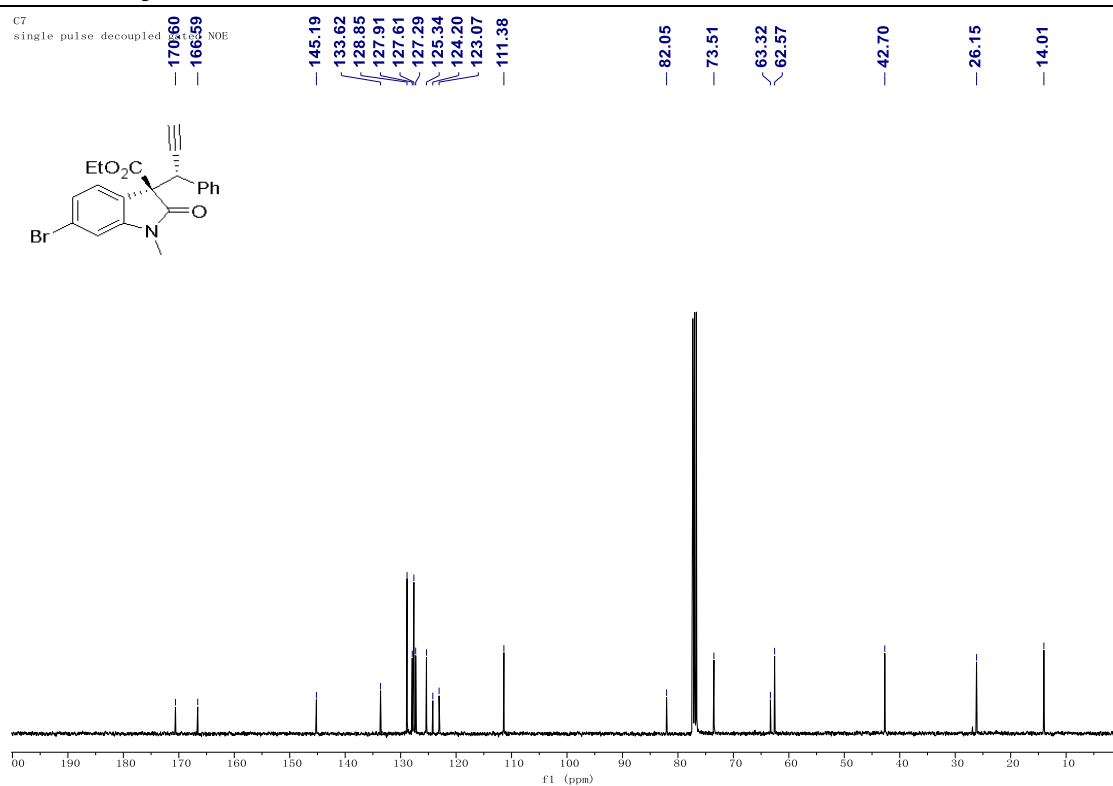
¹³C NMR Spectrum of (S,R)-3e



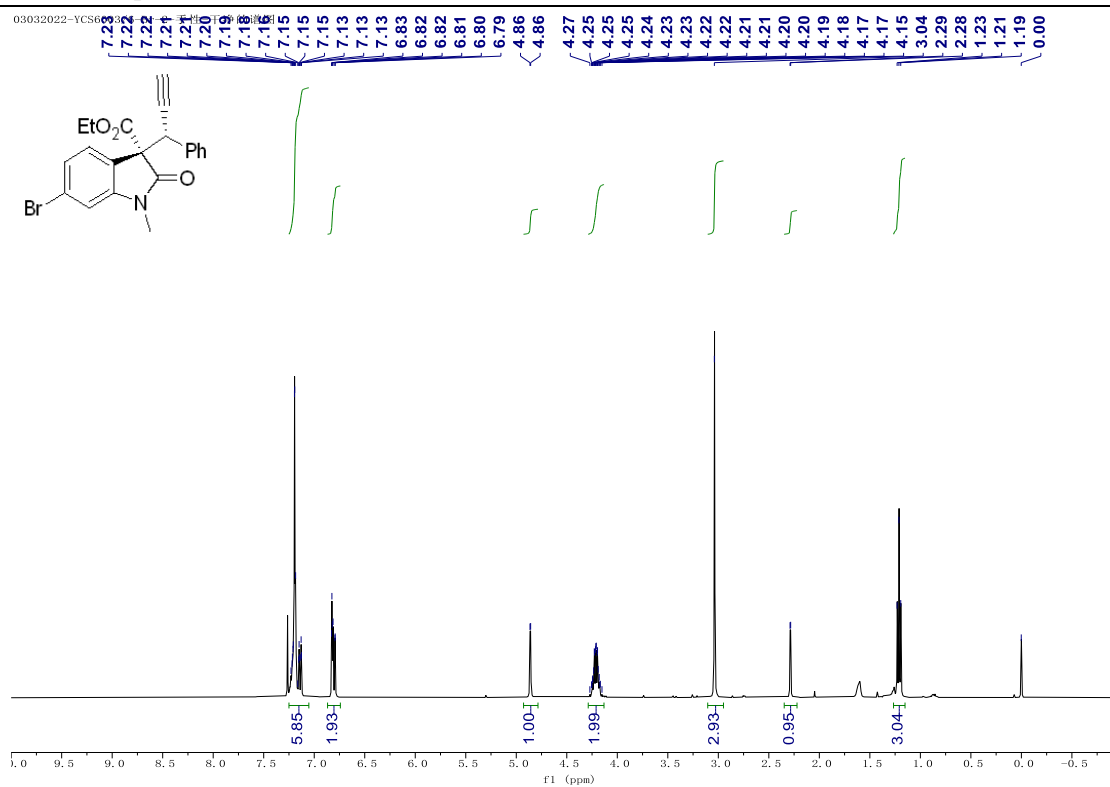
¹H NMR Spectrum of (*R,R*)-3f



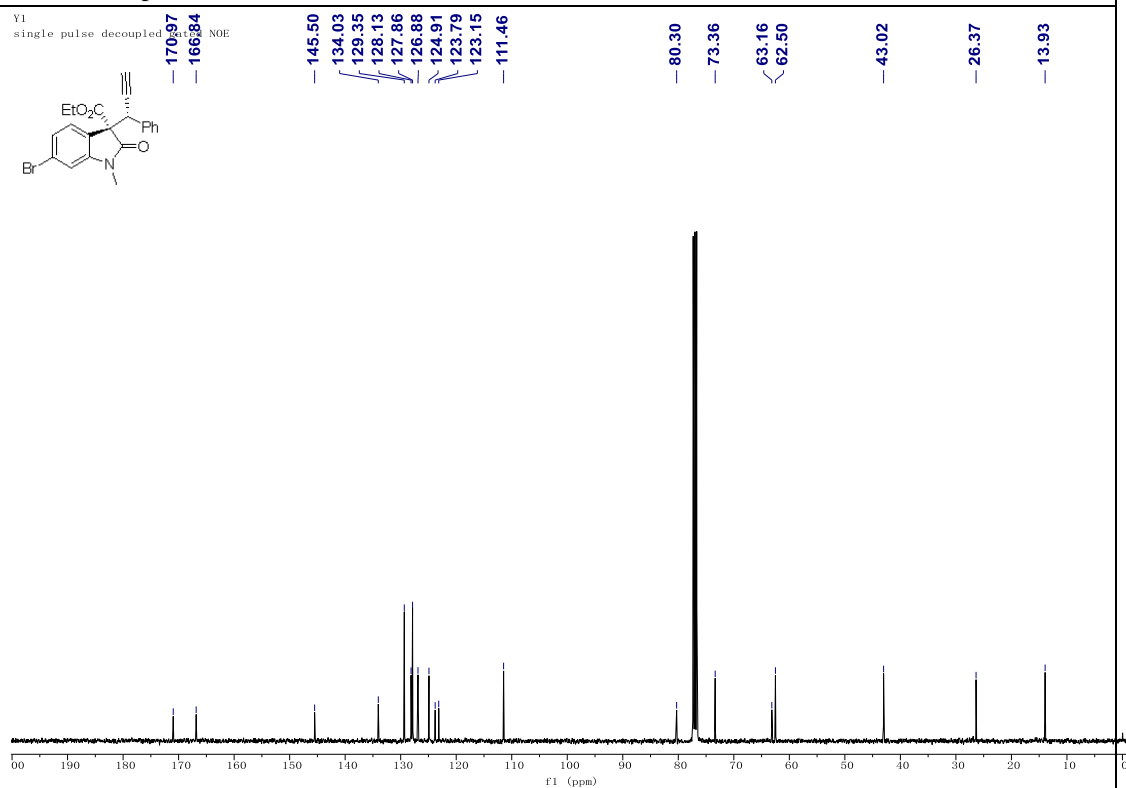
¹³C NMR Spectrum of (*R,R*)-3f

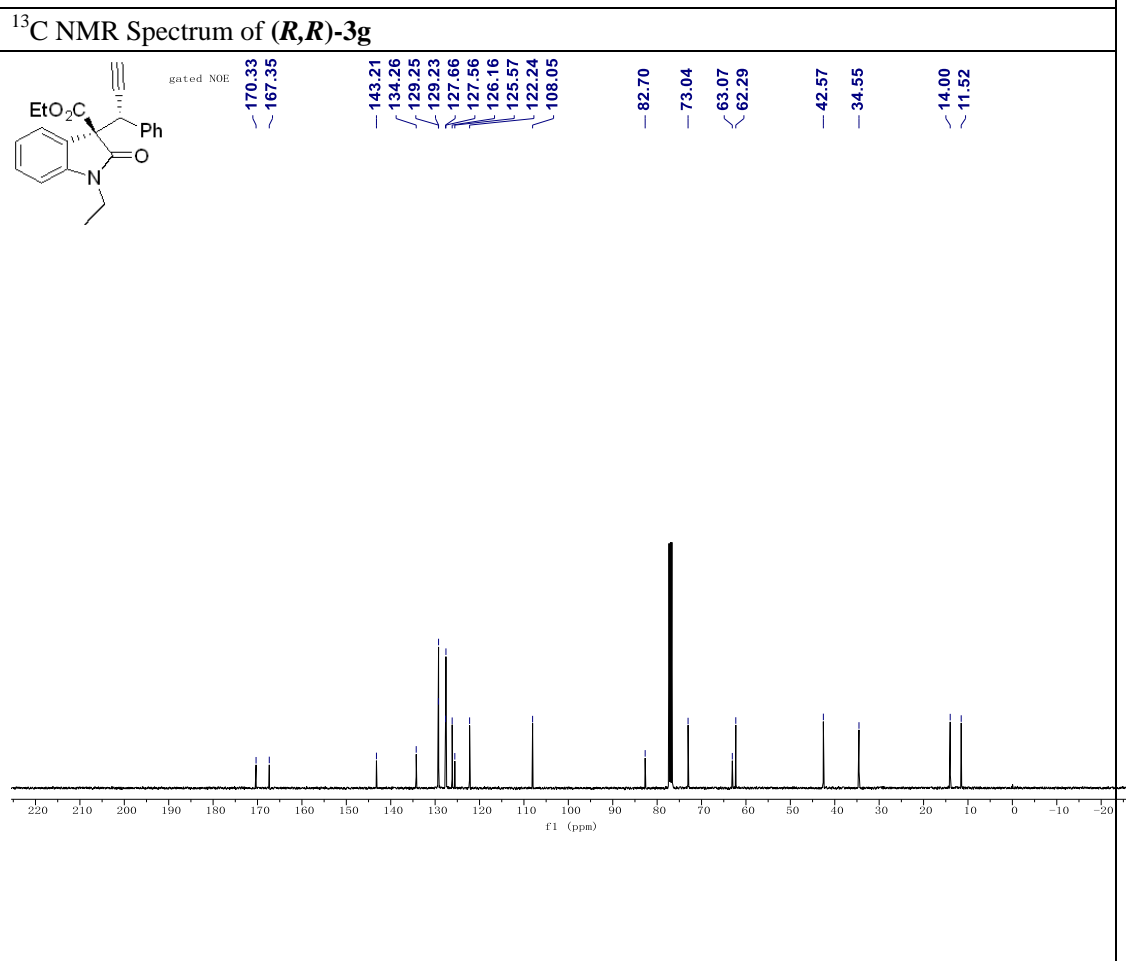
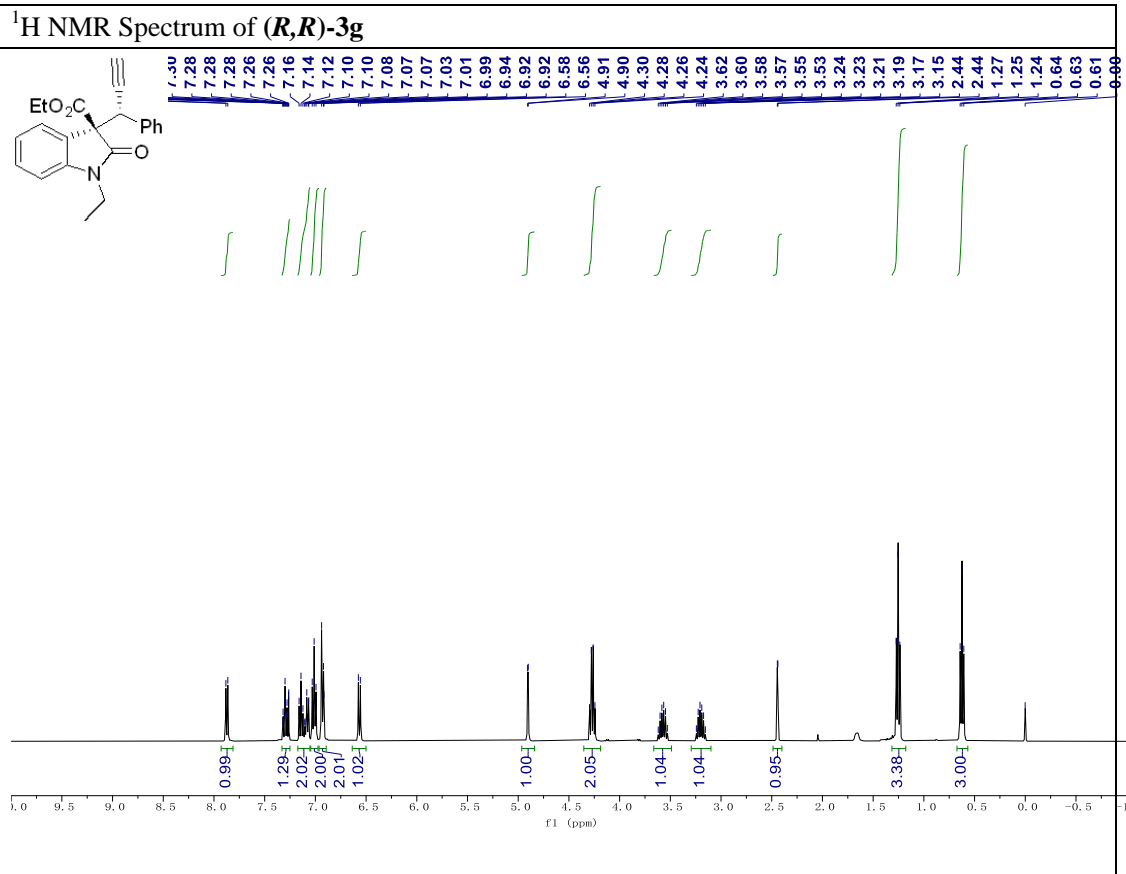


¹H NMR Spectrum of (S,R)-3f

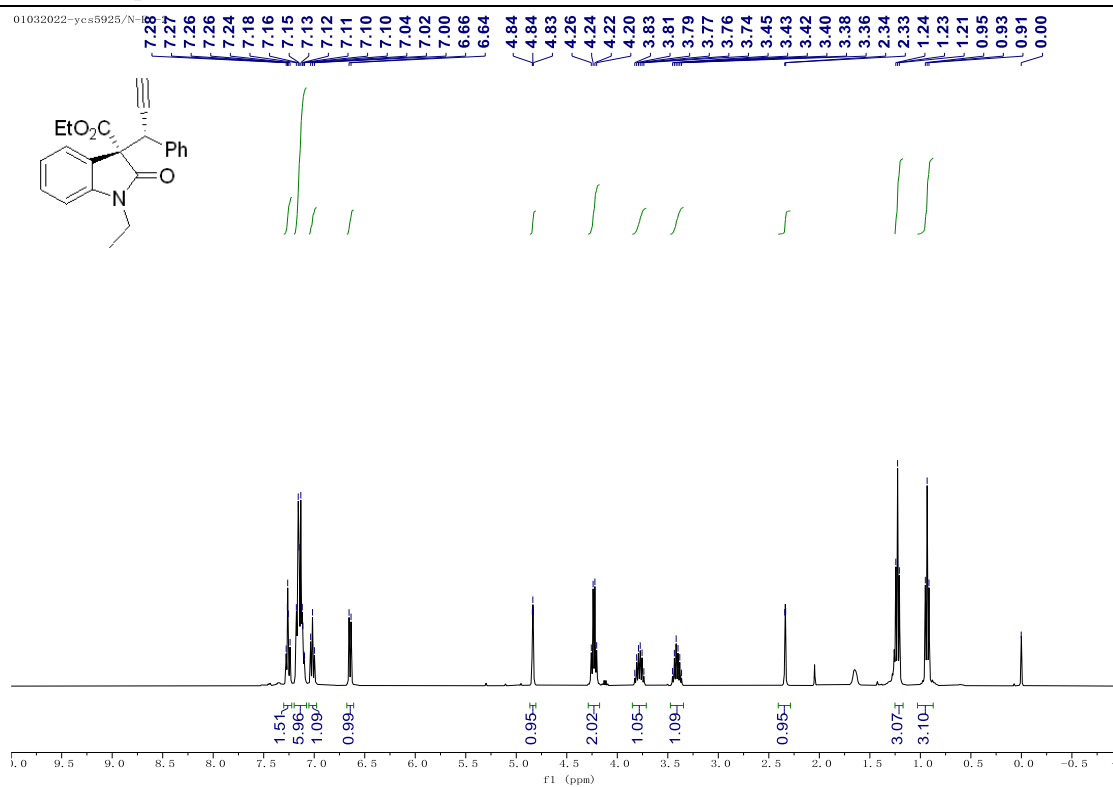


¹³C NMR Spectrum of (S,R)-3f

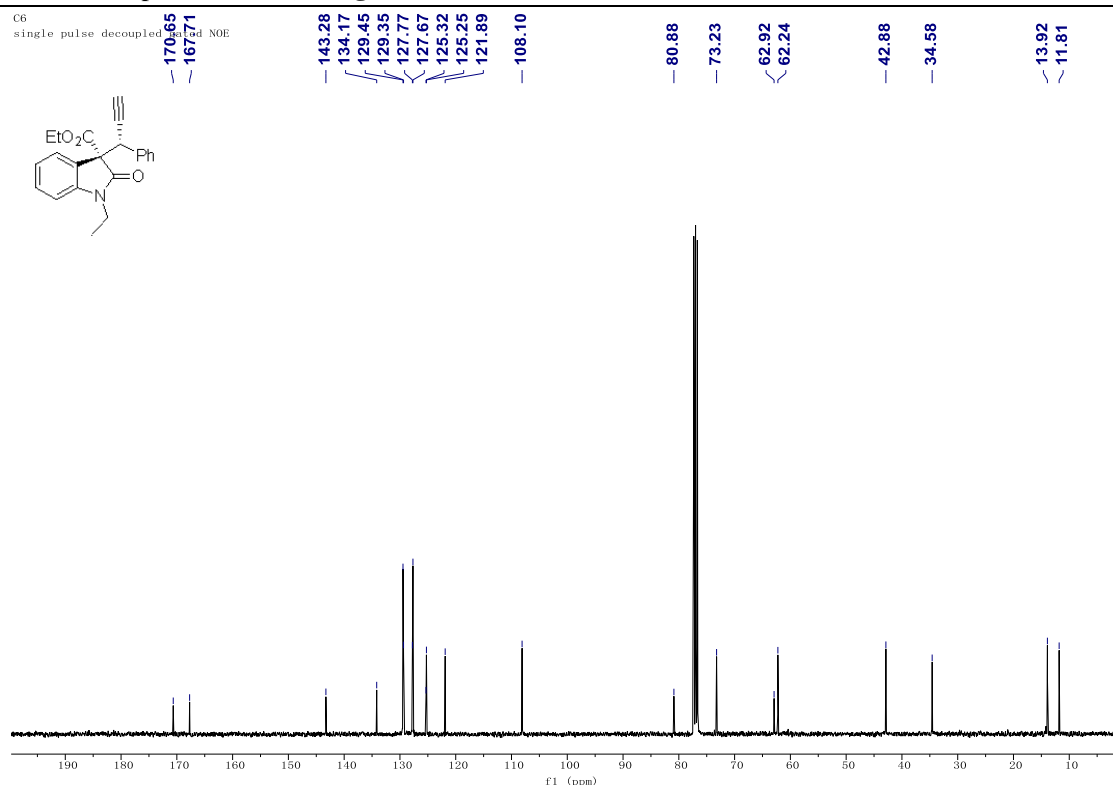




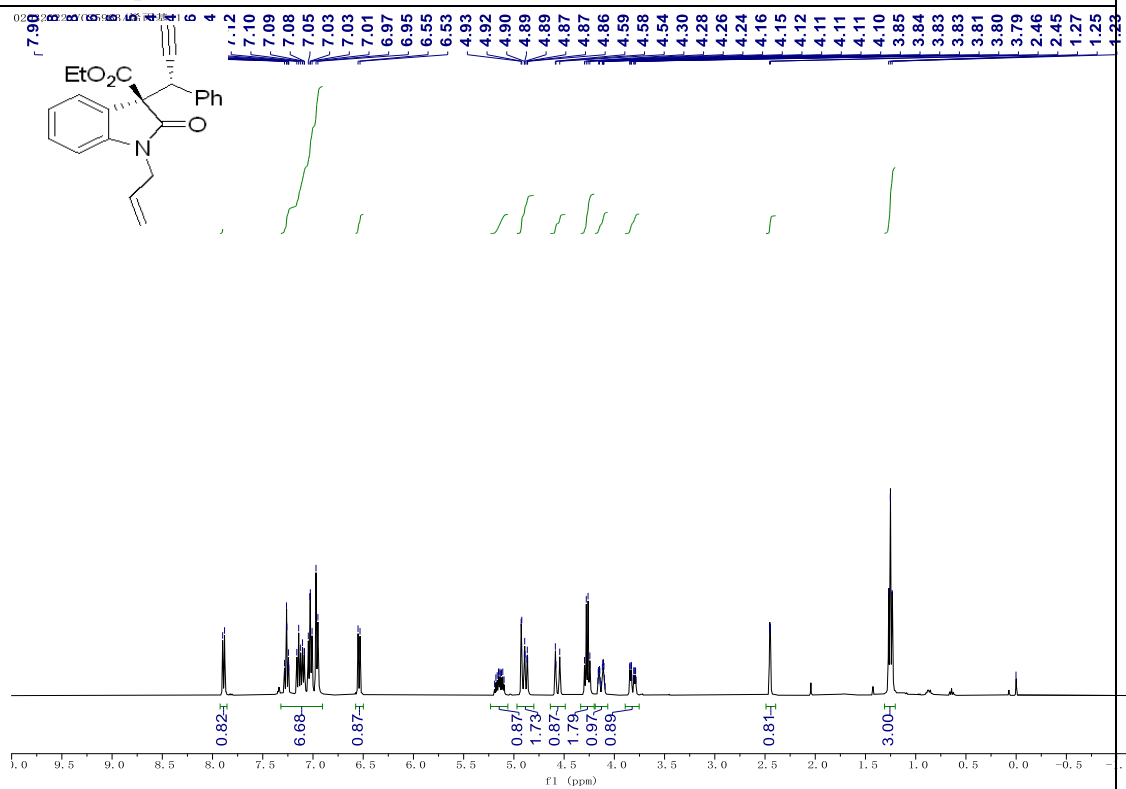
¹H NMR Spectrum of (*S,R*)-3g



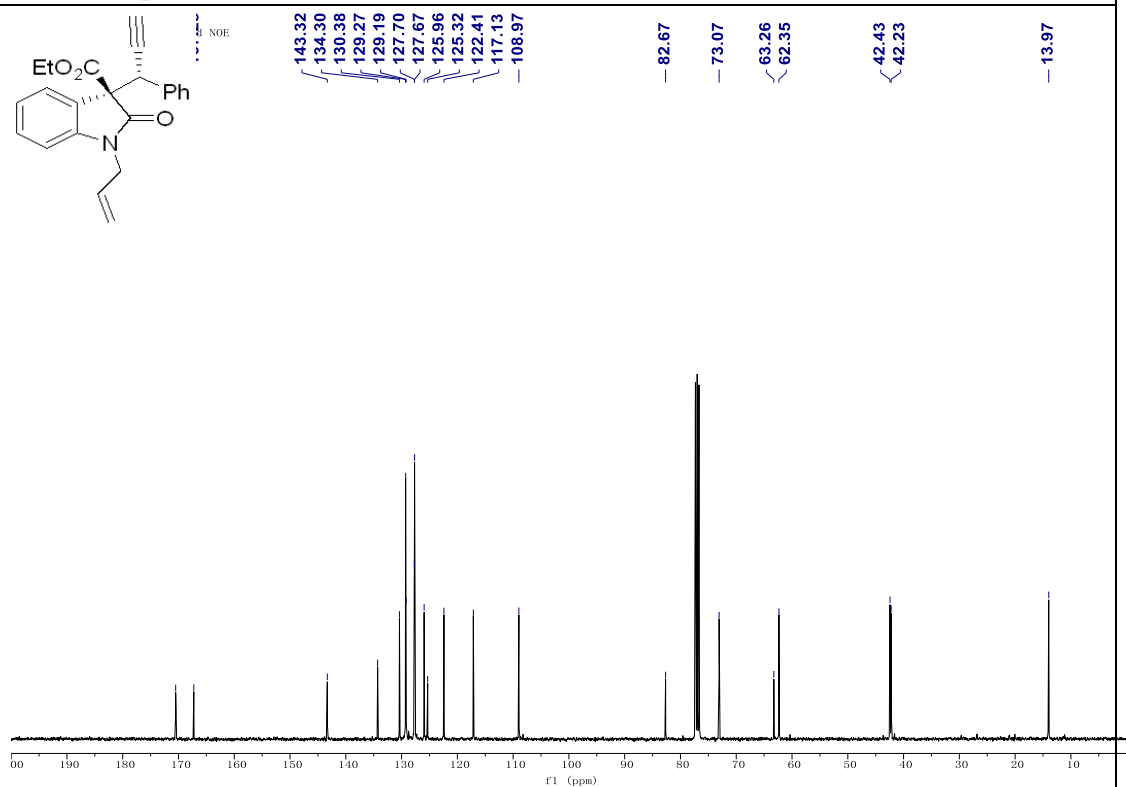
¹³C NMR Spectrum of (*S,R*)-3g



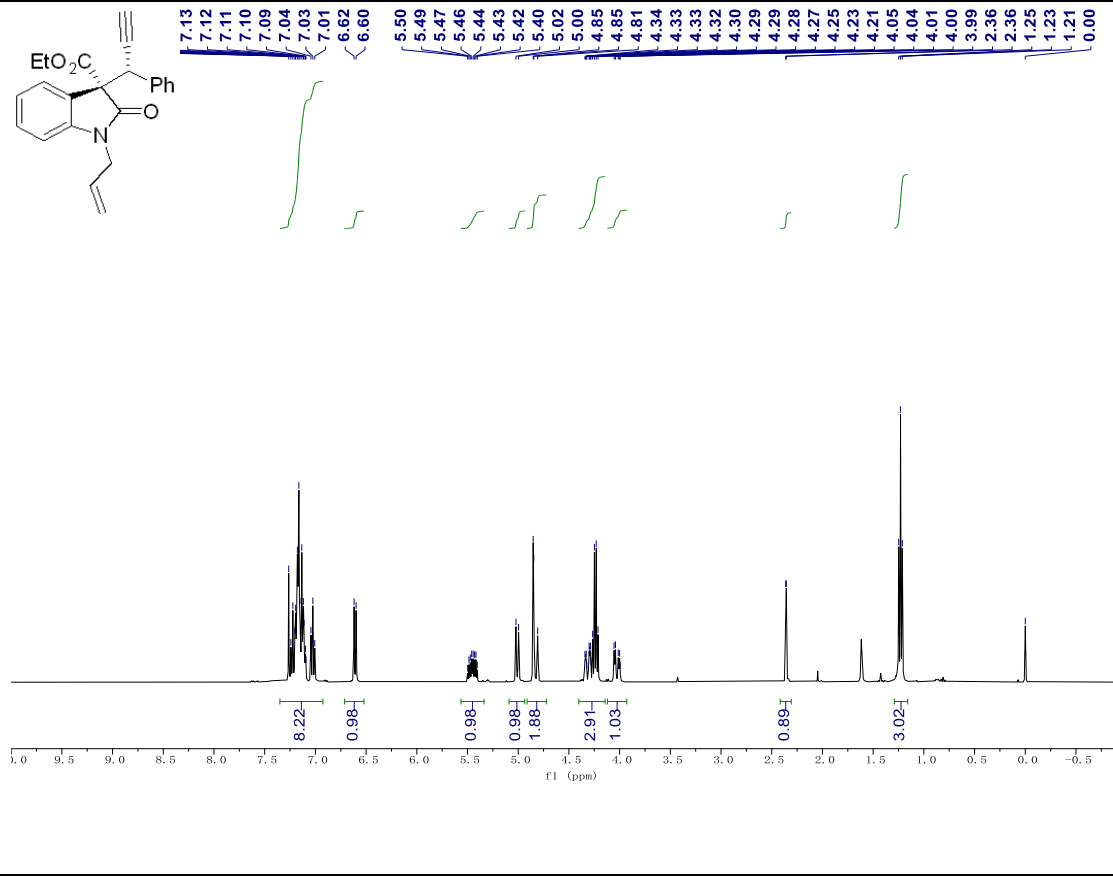
¹H NMR Spectrum of (*R,R*)-3h



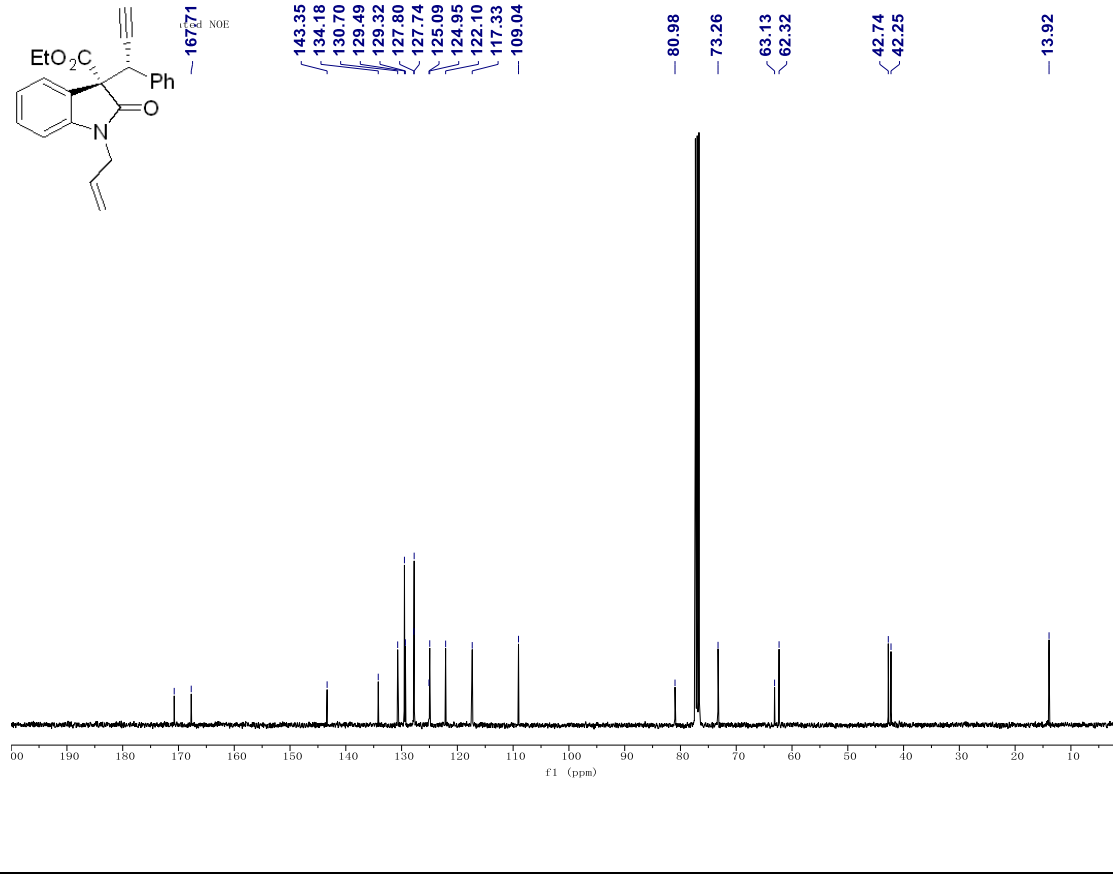
¹³C NMR Spectrum of (*R,R*)-3h



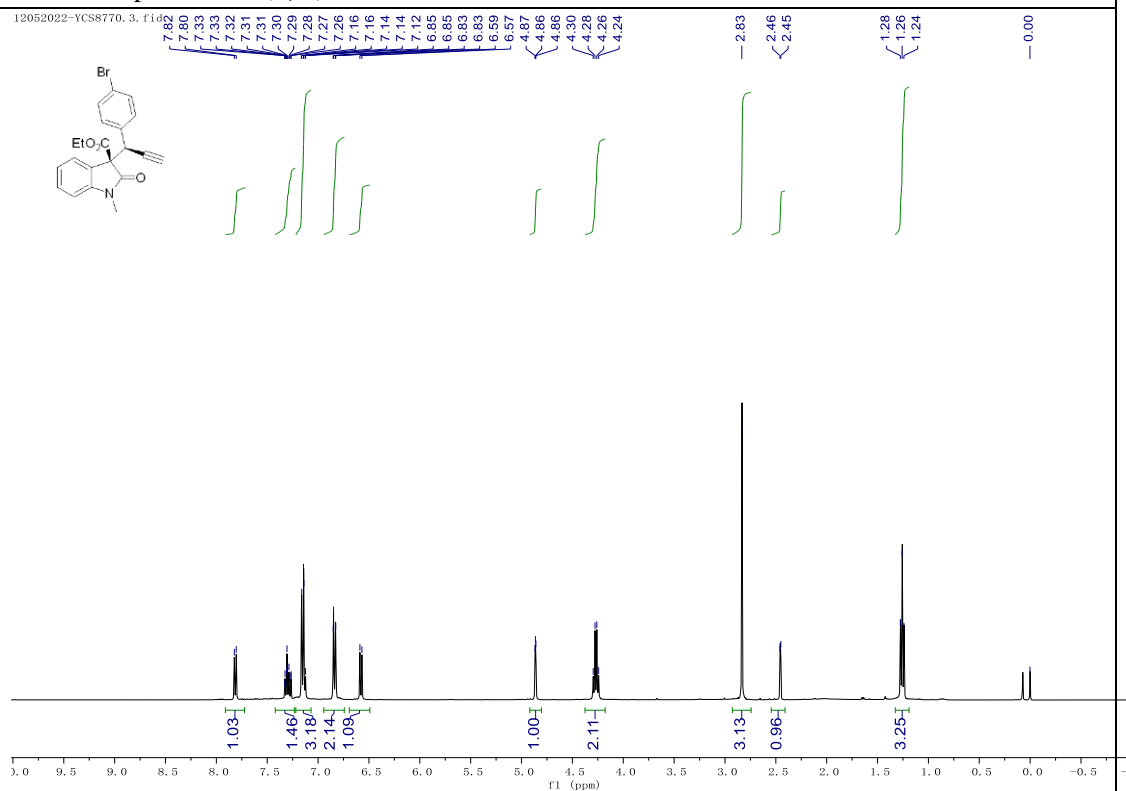
¹H NMR Spectrum of (S,R)-3h



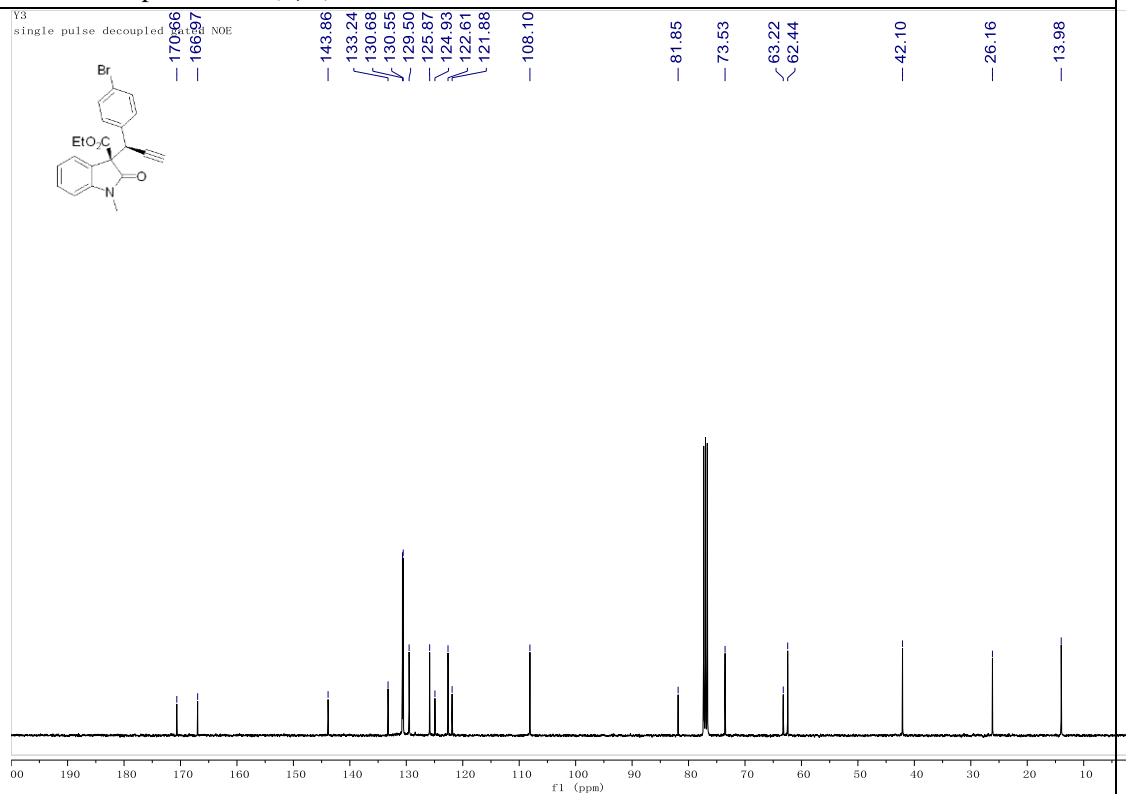
¹³C NMR Spectrum of (S,R)-3h



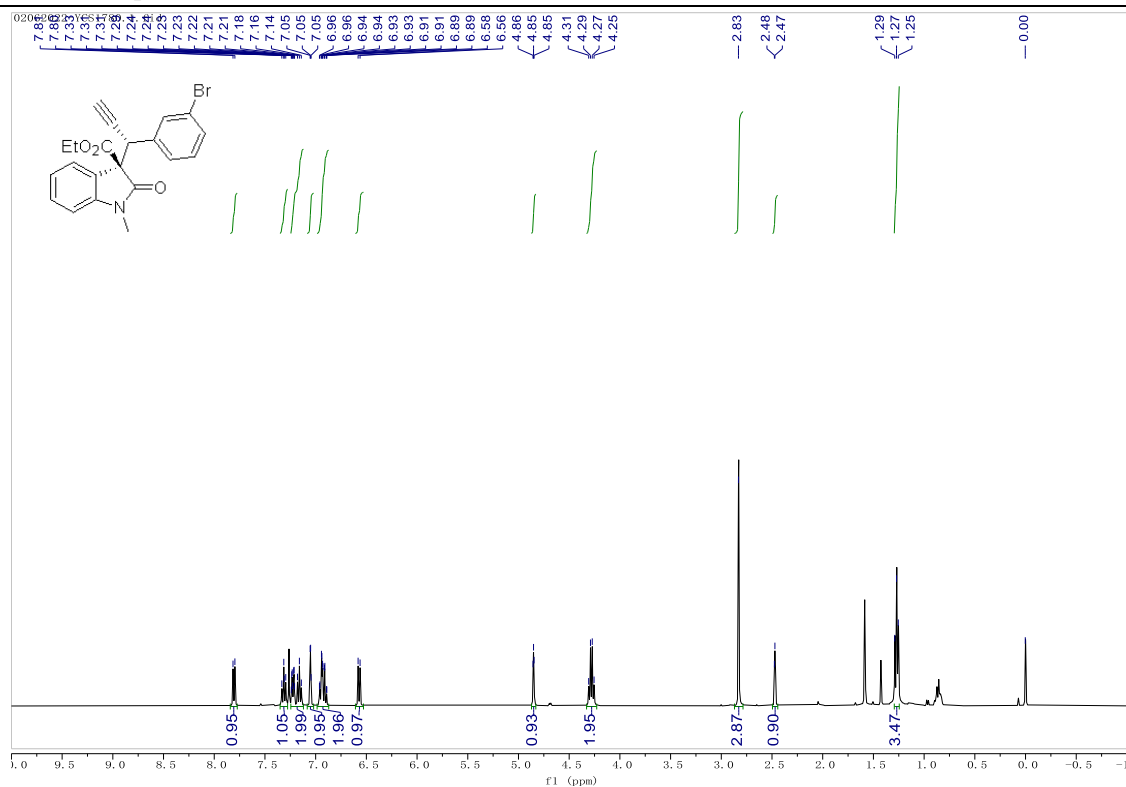
¹H NMR Spectrum of (*R,R*)-3i



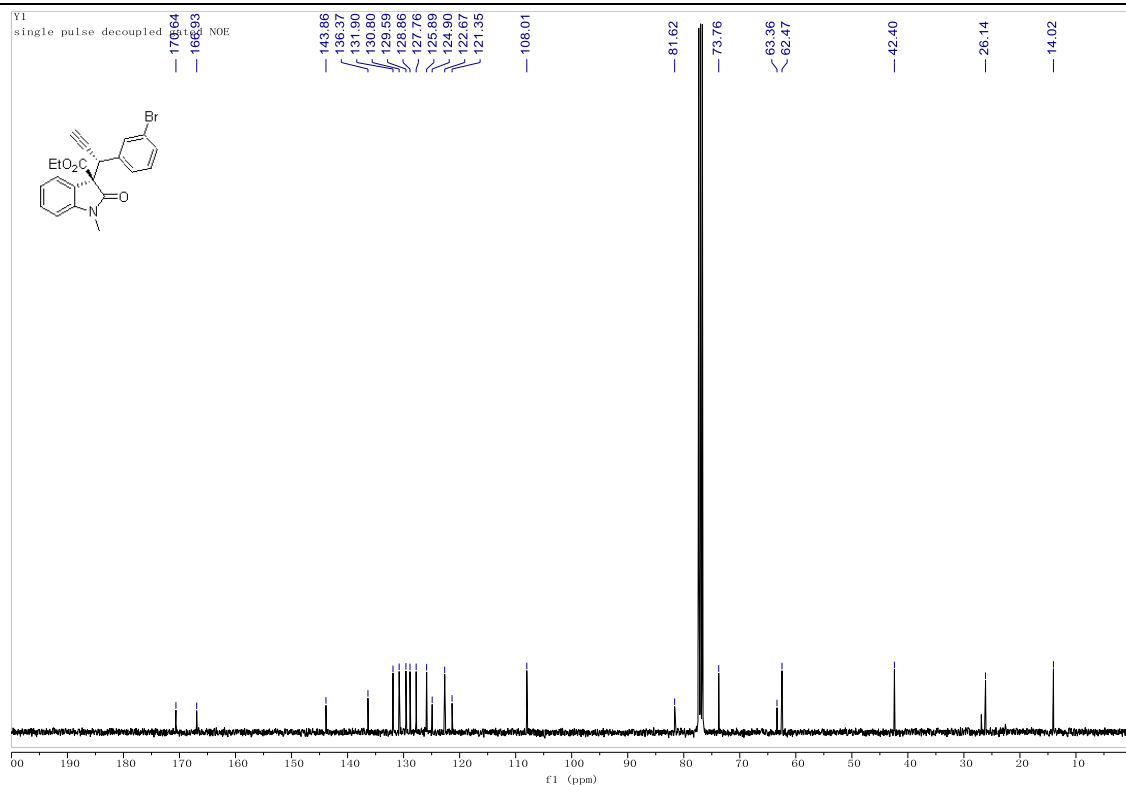
¹³C NMR Spectrum of (*R,R*)-3i



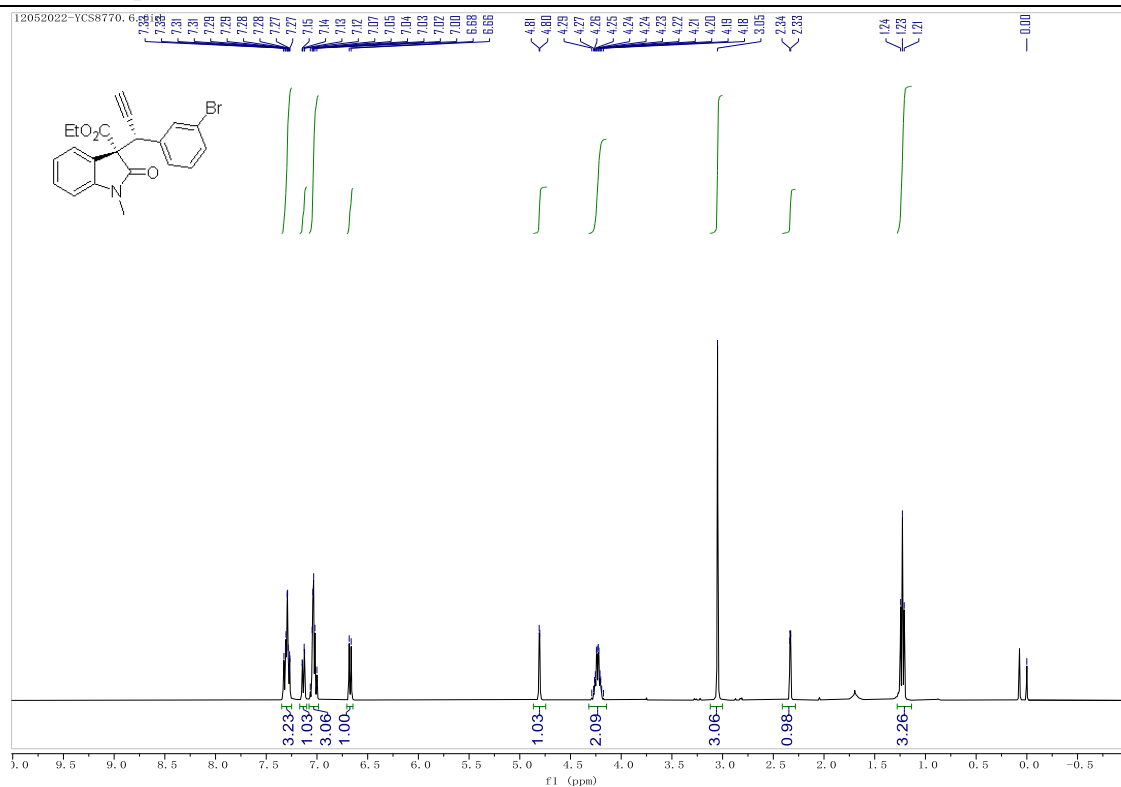
¹H NMR Spectrum of (*R,R*)-3j



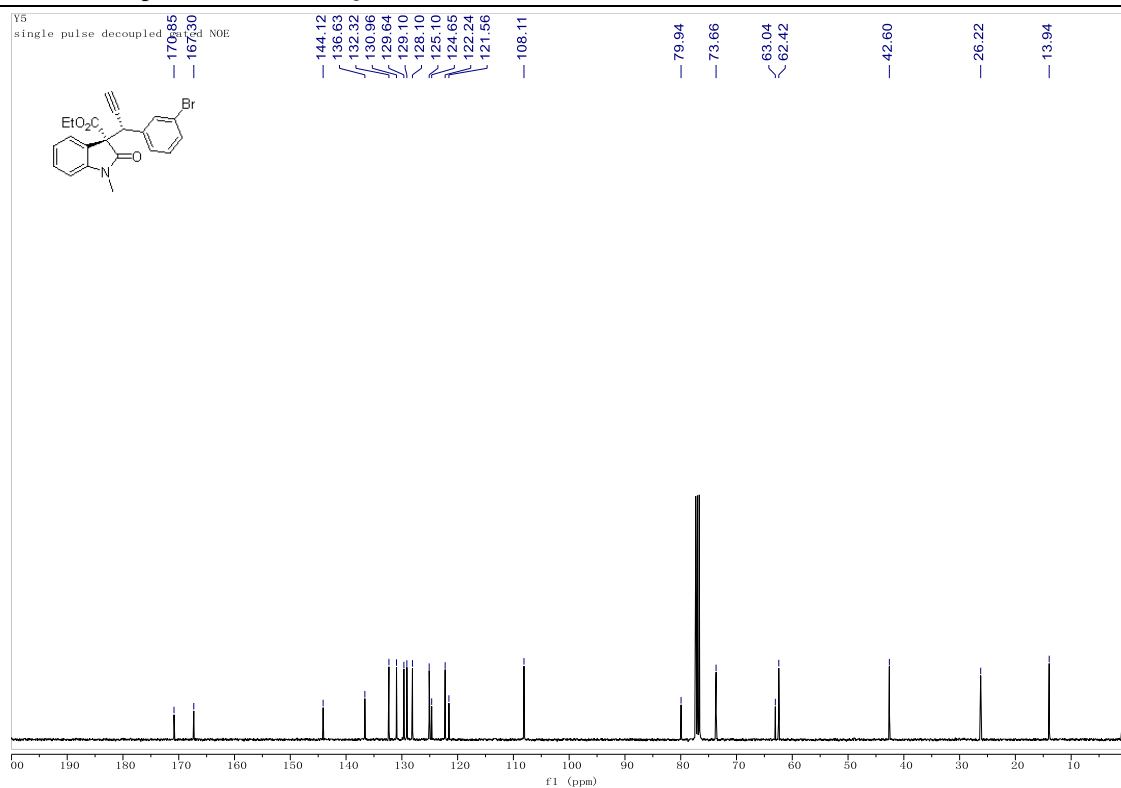
¹³C NMR Spectrum of (*R,R*)-3j



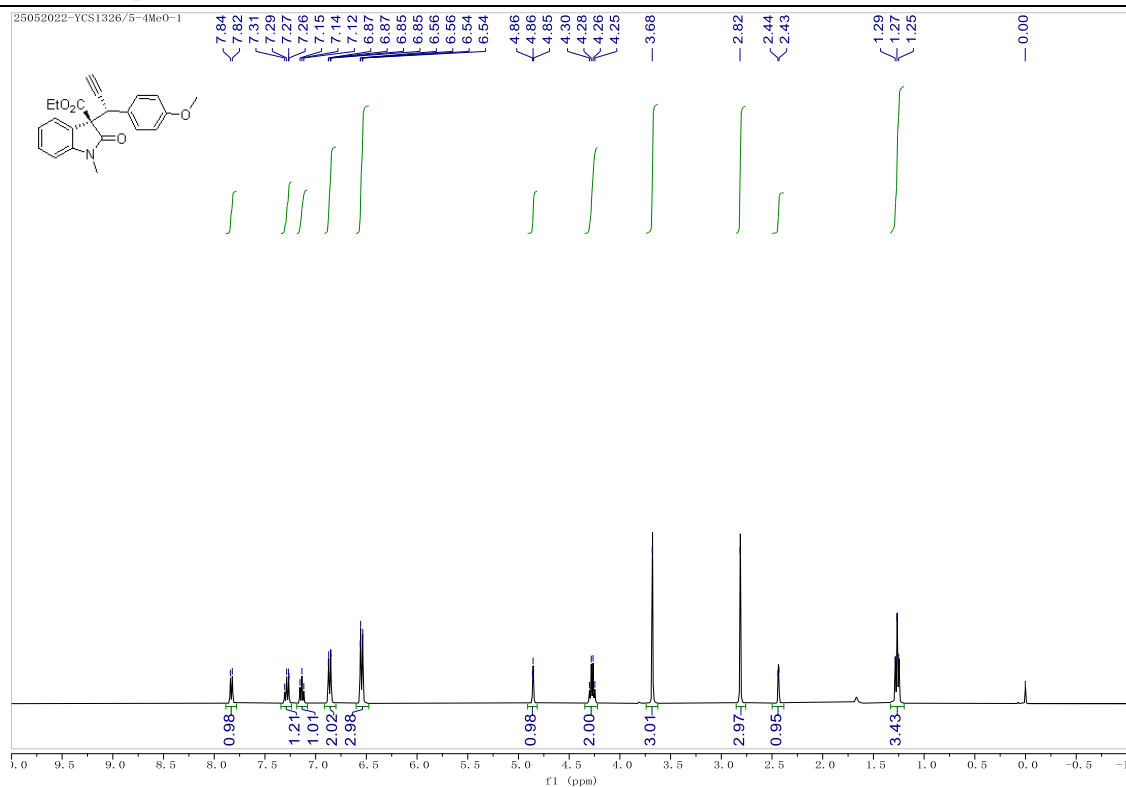
¹H NMR Spectrum of (*S,R*)-3j



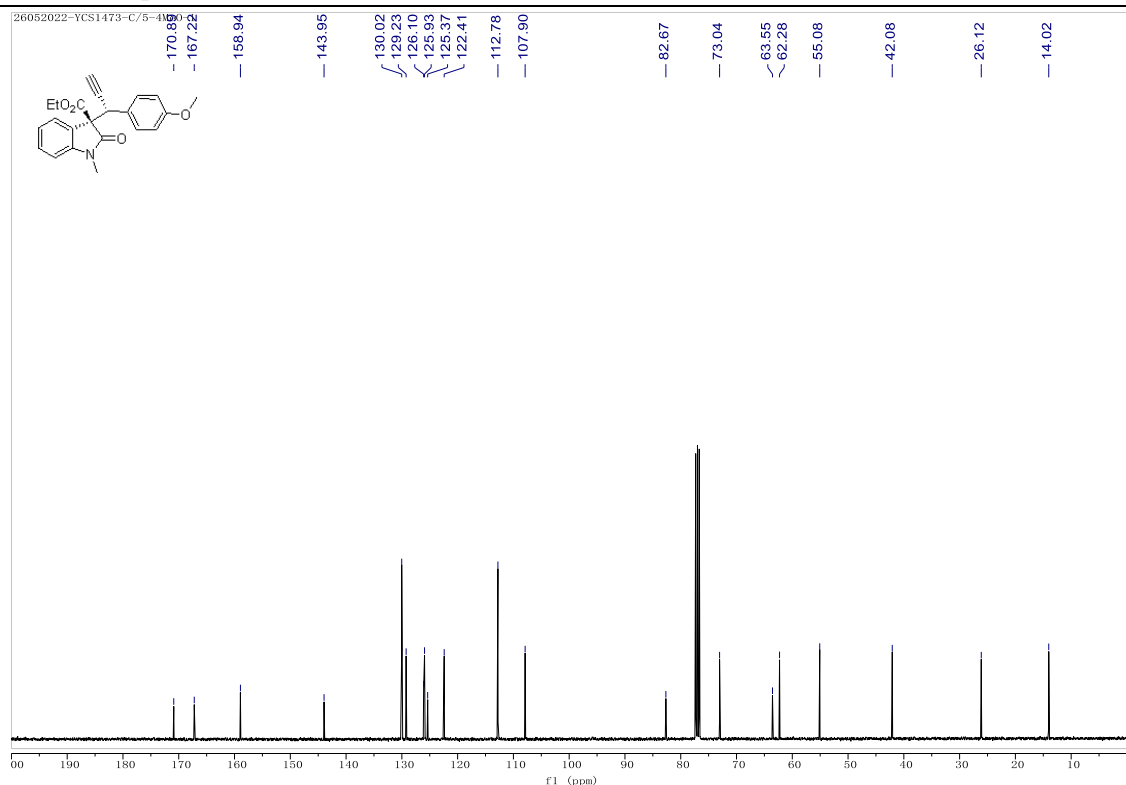
¹³C NMR Spectrum of (*S,R*)-3j



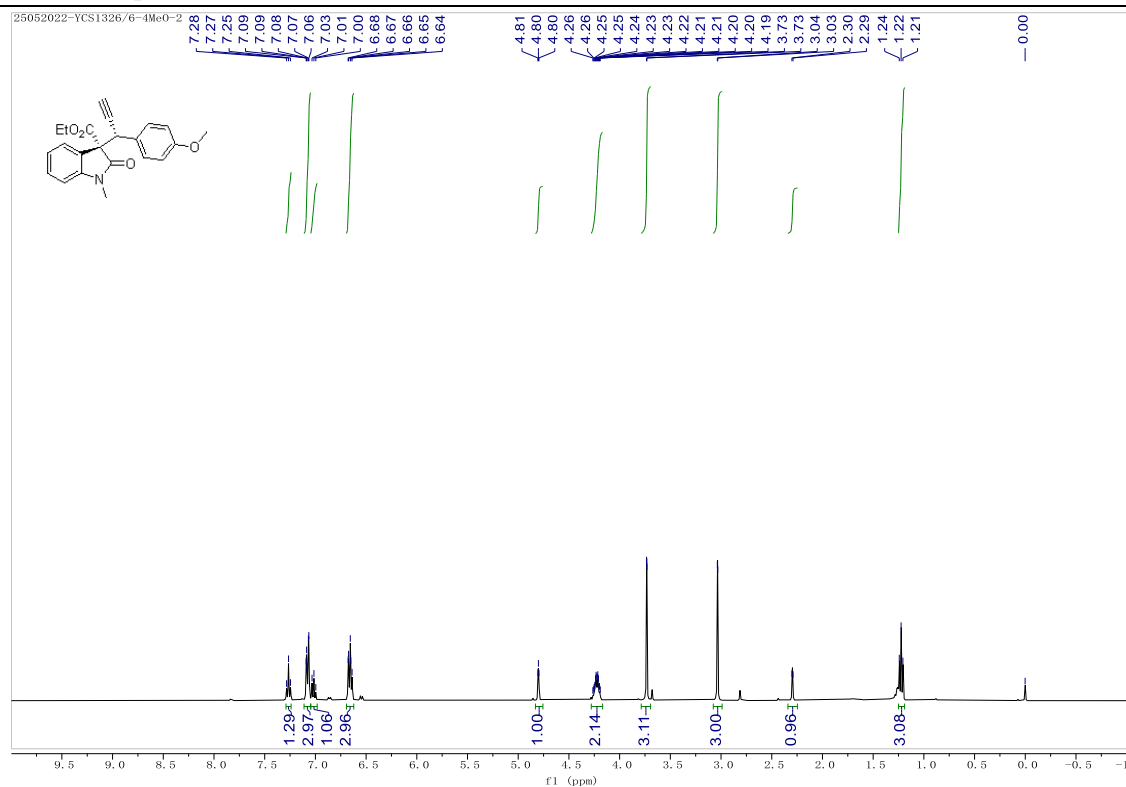
¹H NMR Spectrum of (*R,R*)-3k



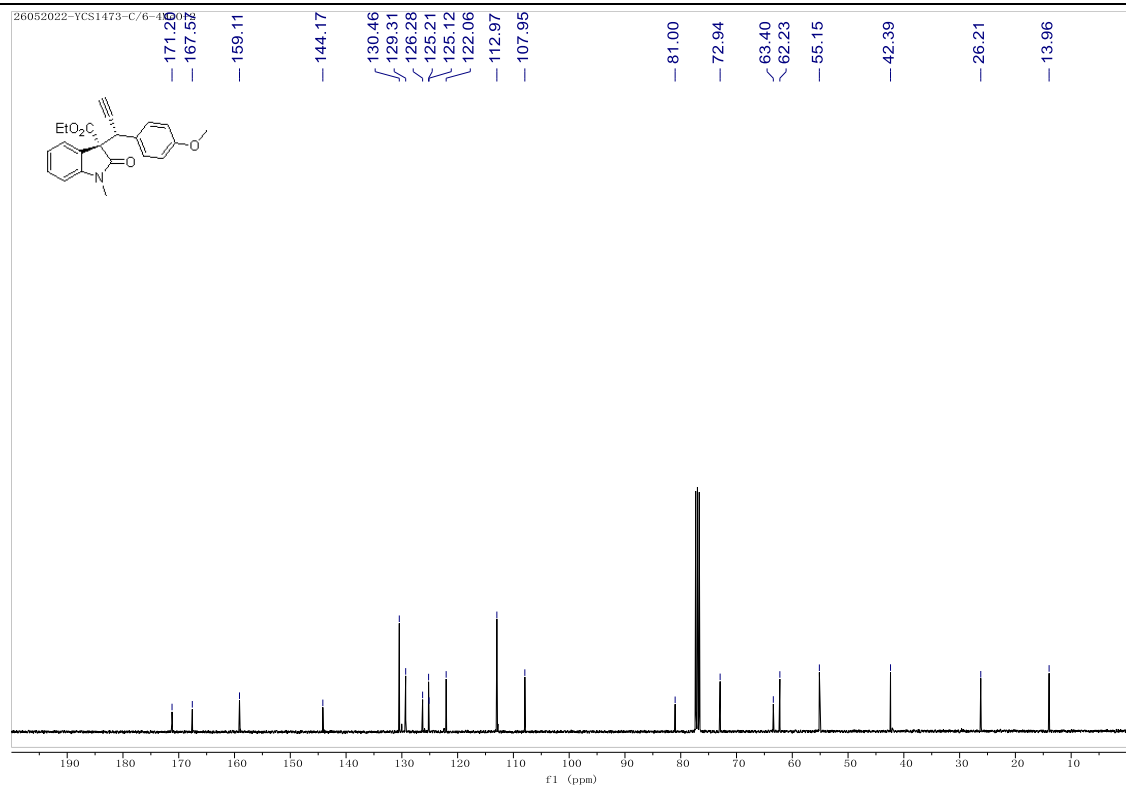
¹³C NMR Spectrum of (*R,R*)-3k



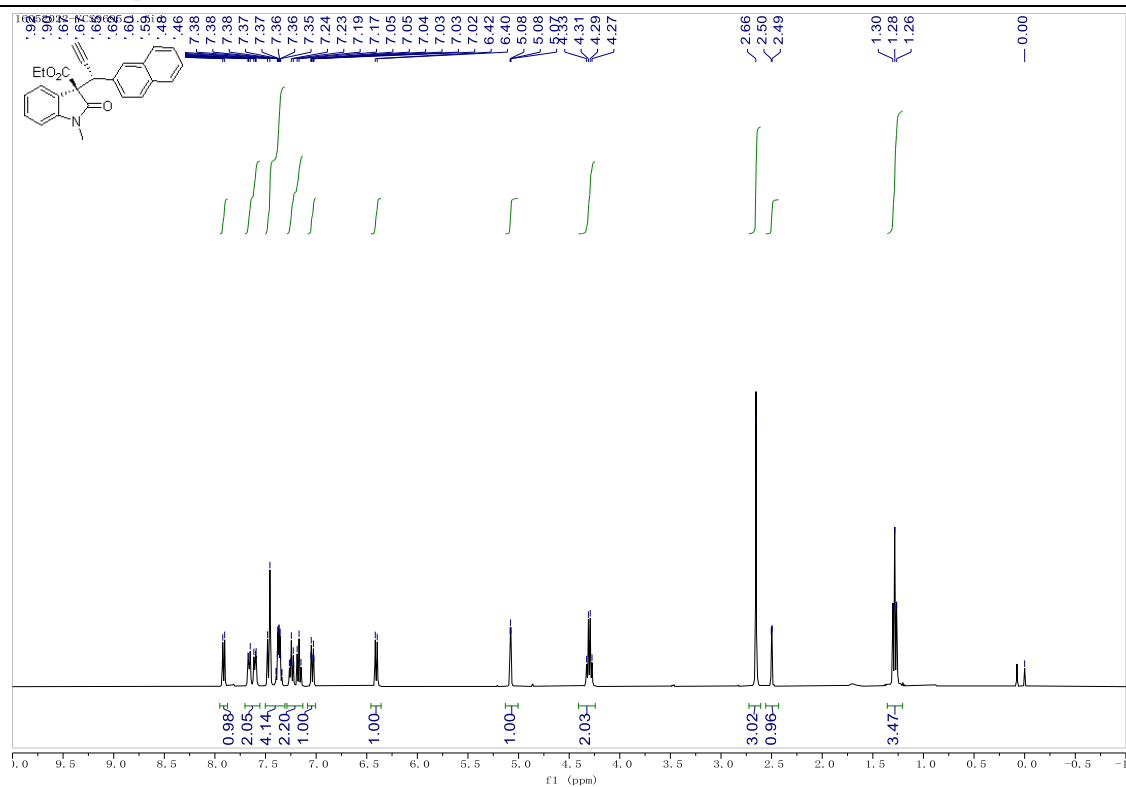
¹H NMR Spectrum of (*S,R*)-3k



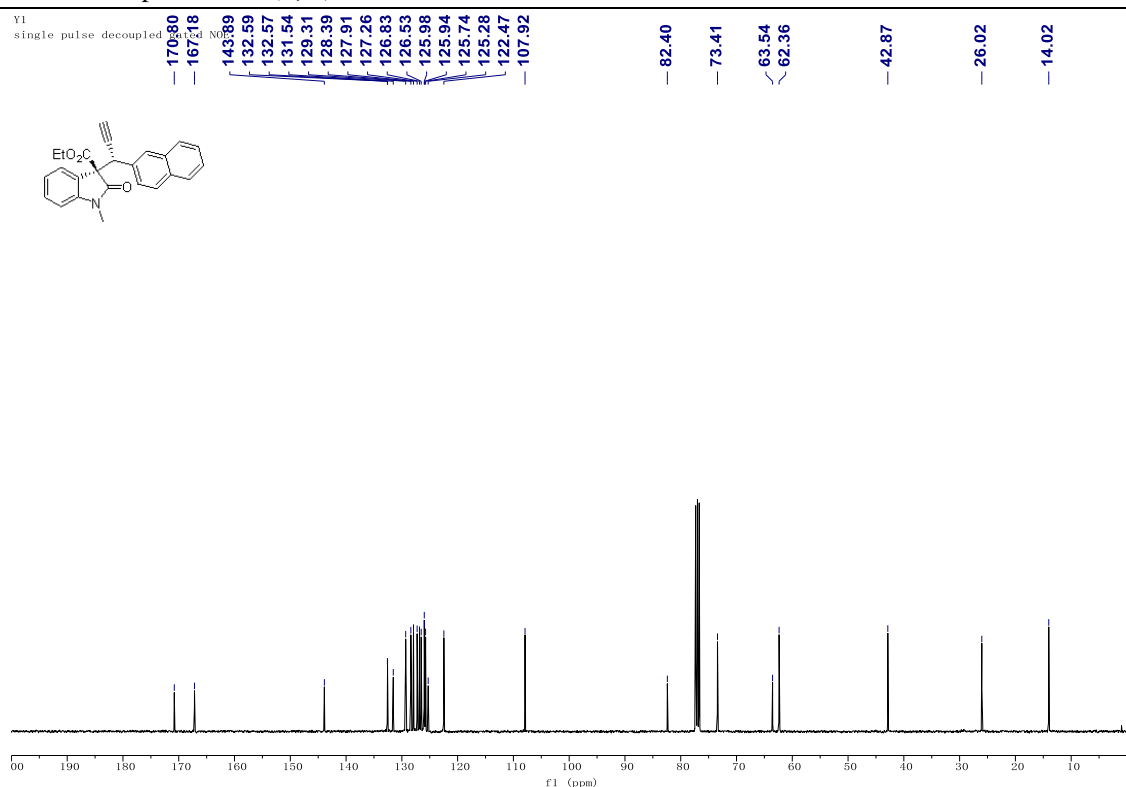
¹³C NMR Spectrum of (*S,R*)-3k



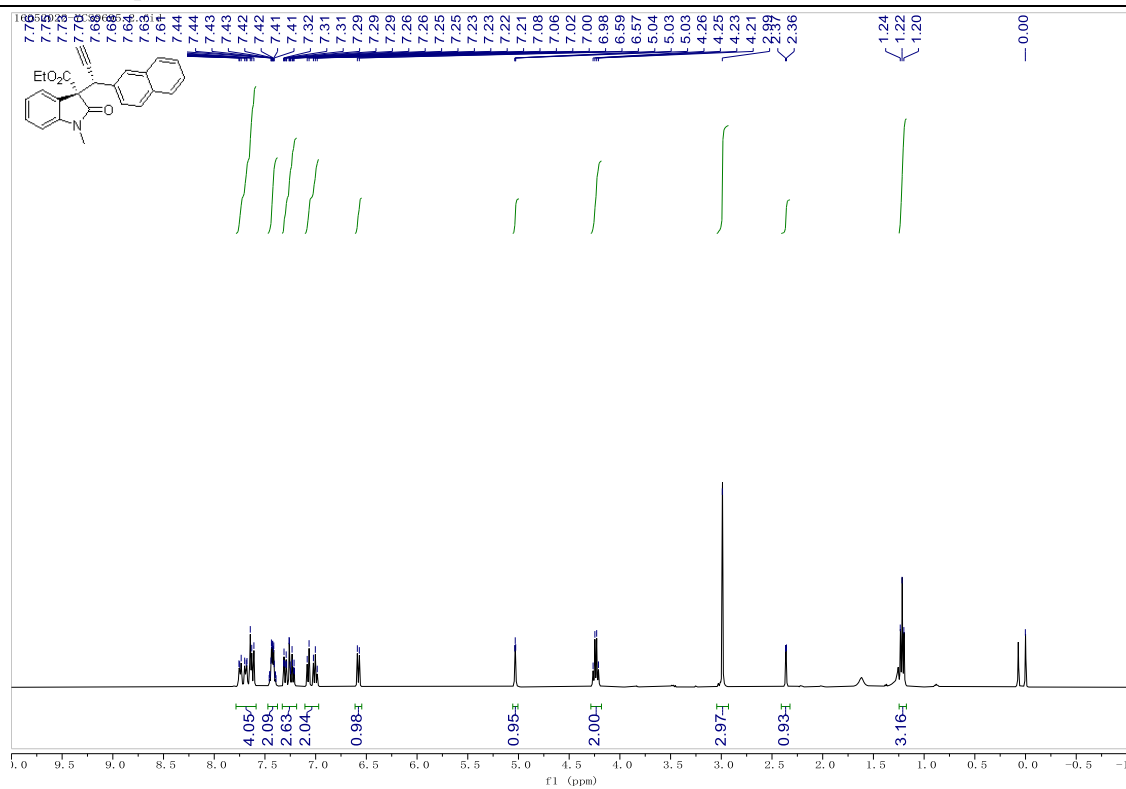
¹H NMR Spectrum of (*R,R*)-31



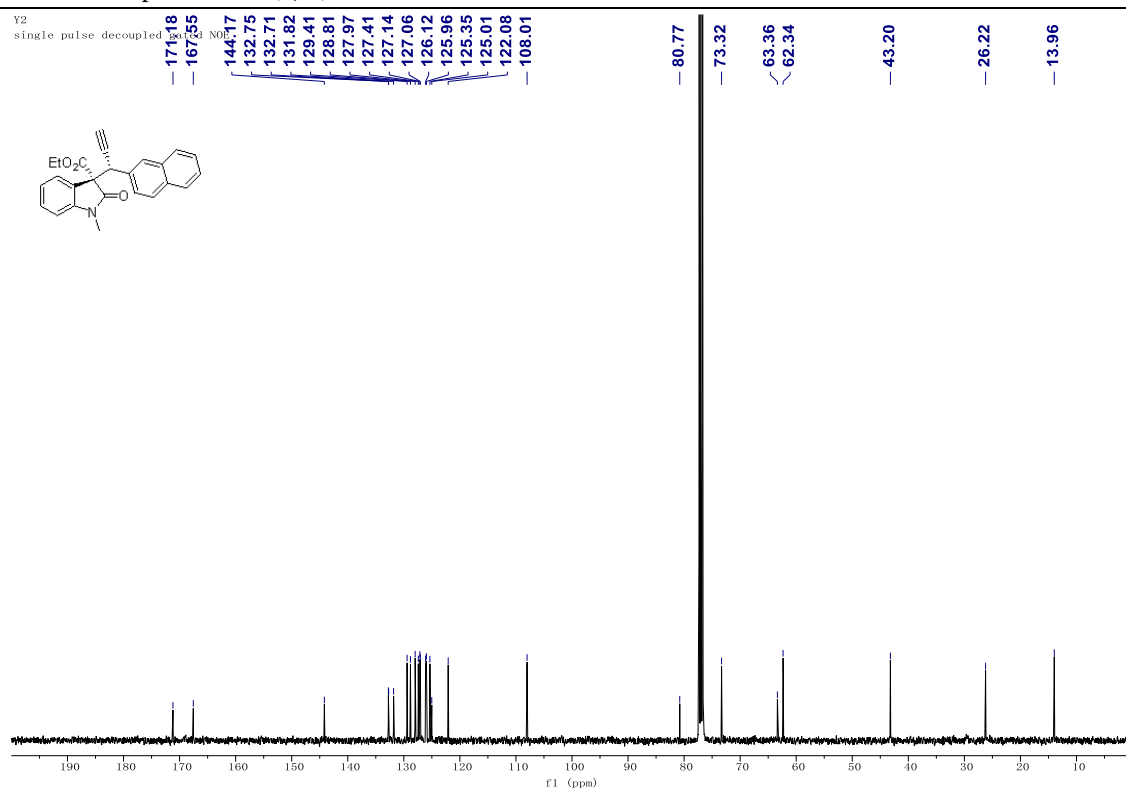
¹³C NMR Spectrum of (*R,R*)-31



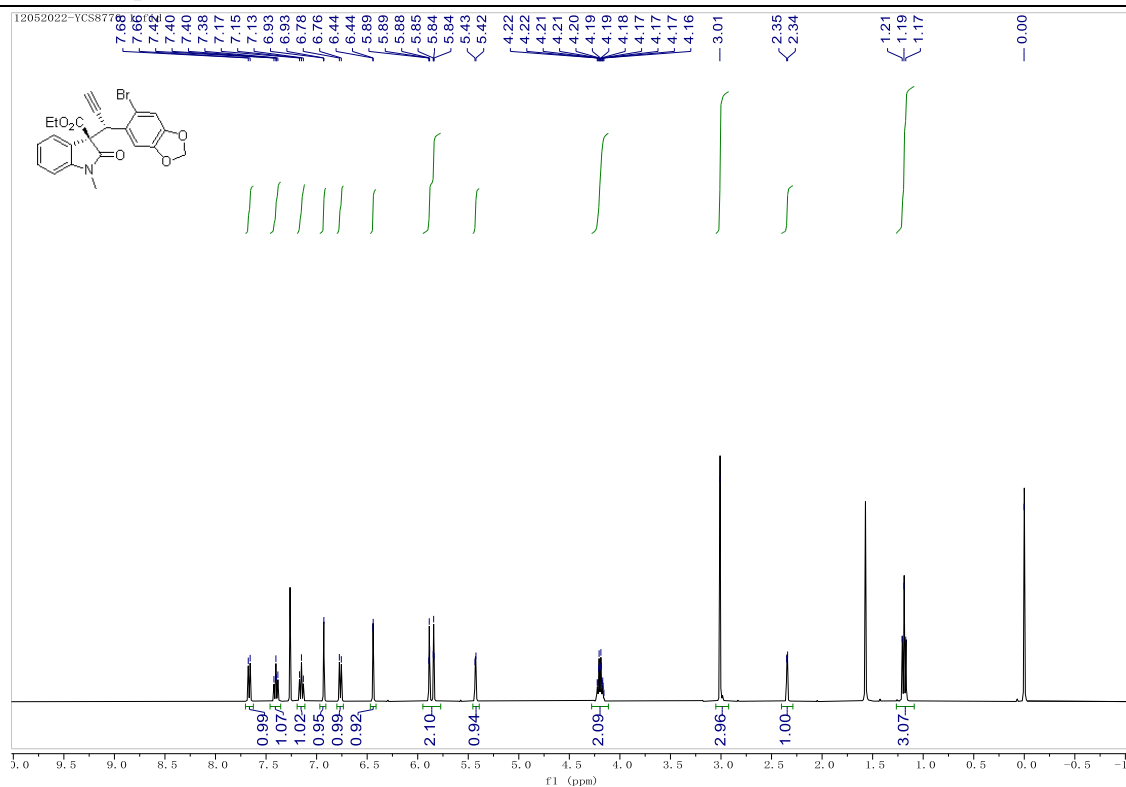
¹H NMR Spectrum of (*S,R*)-3I



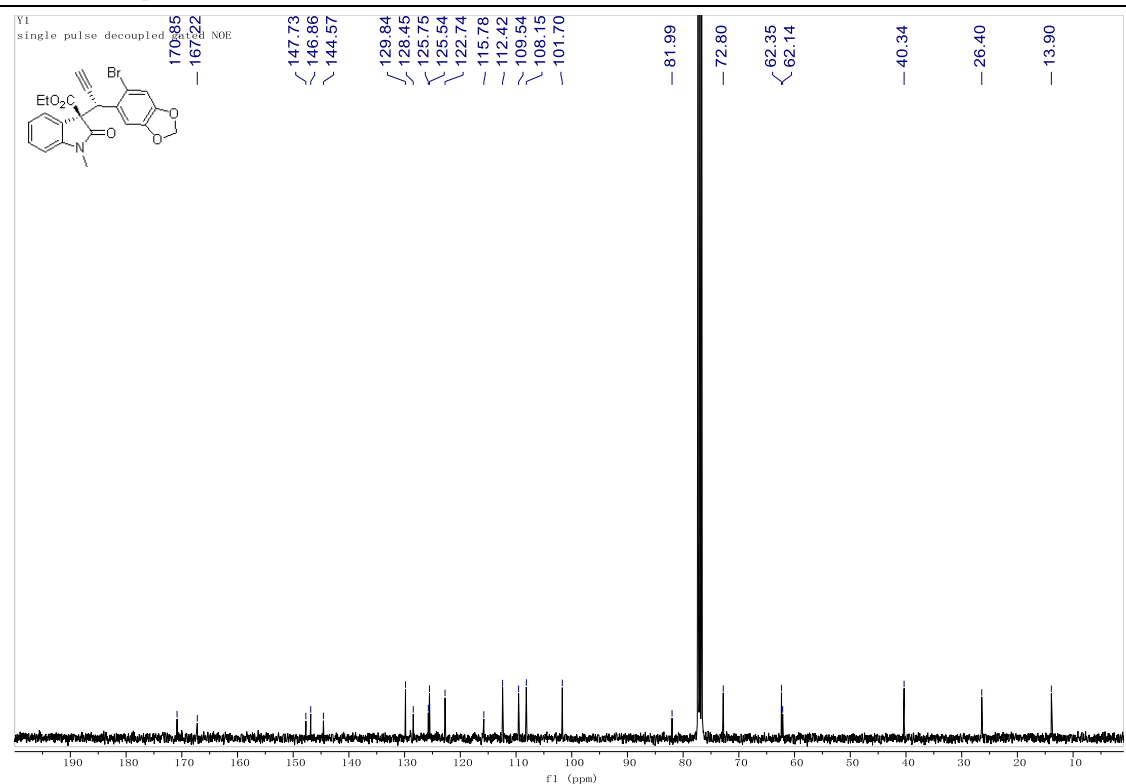
¹³C NMR Spectrum of (*S,R*)-3I



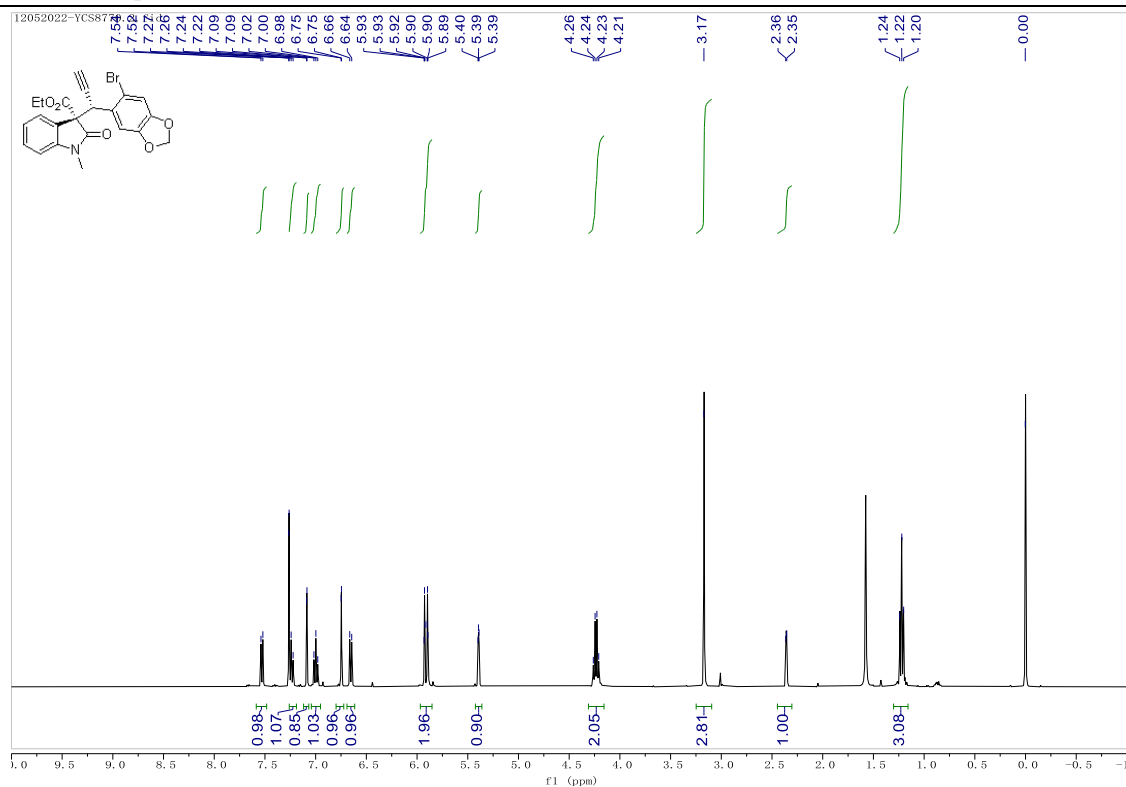
¹H NMR Spectrum of (*R,S*)-3m



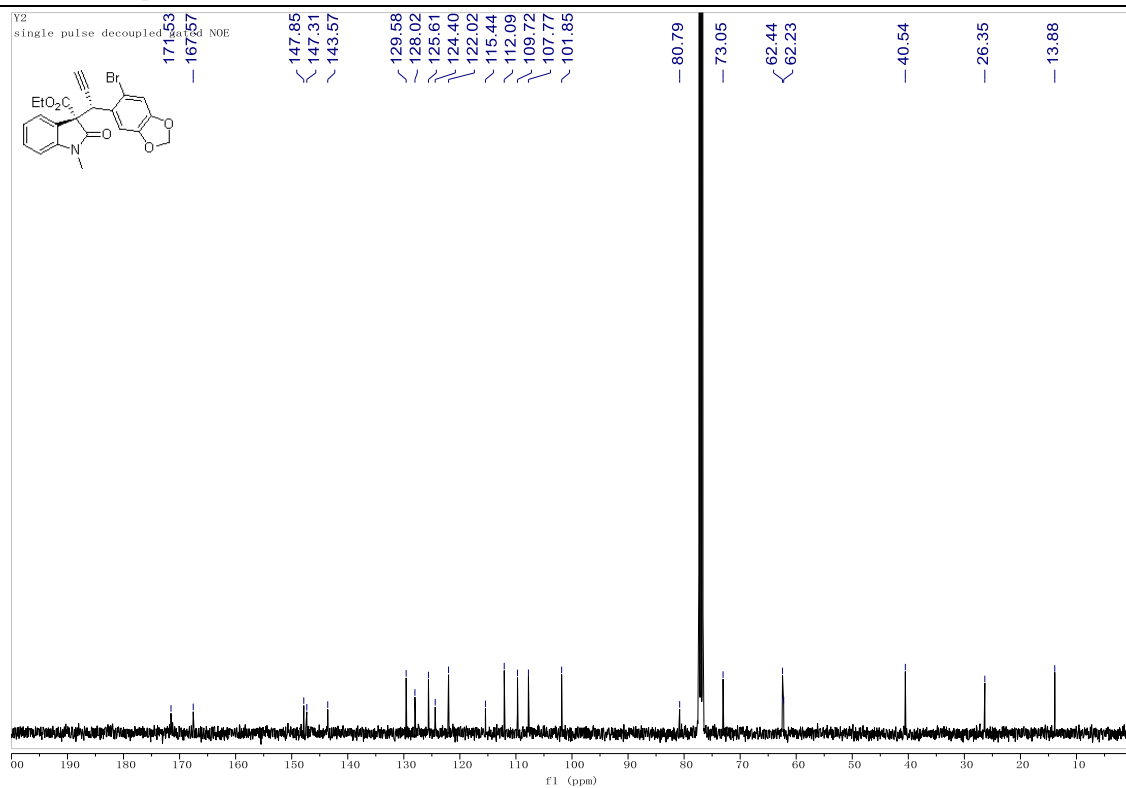
¹³C NMR Spectrum of (*R,S*)-3m



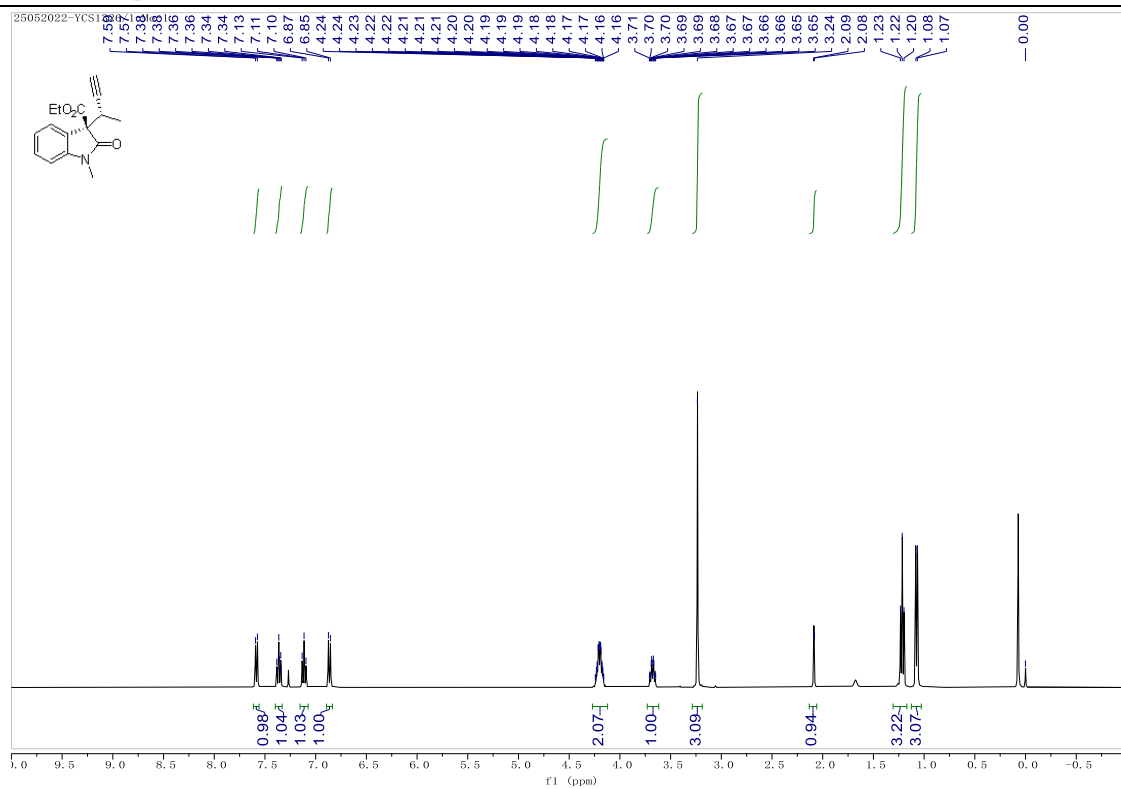
¹H NMR Spectrum of (*S,S*)-3m



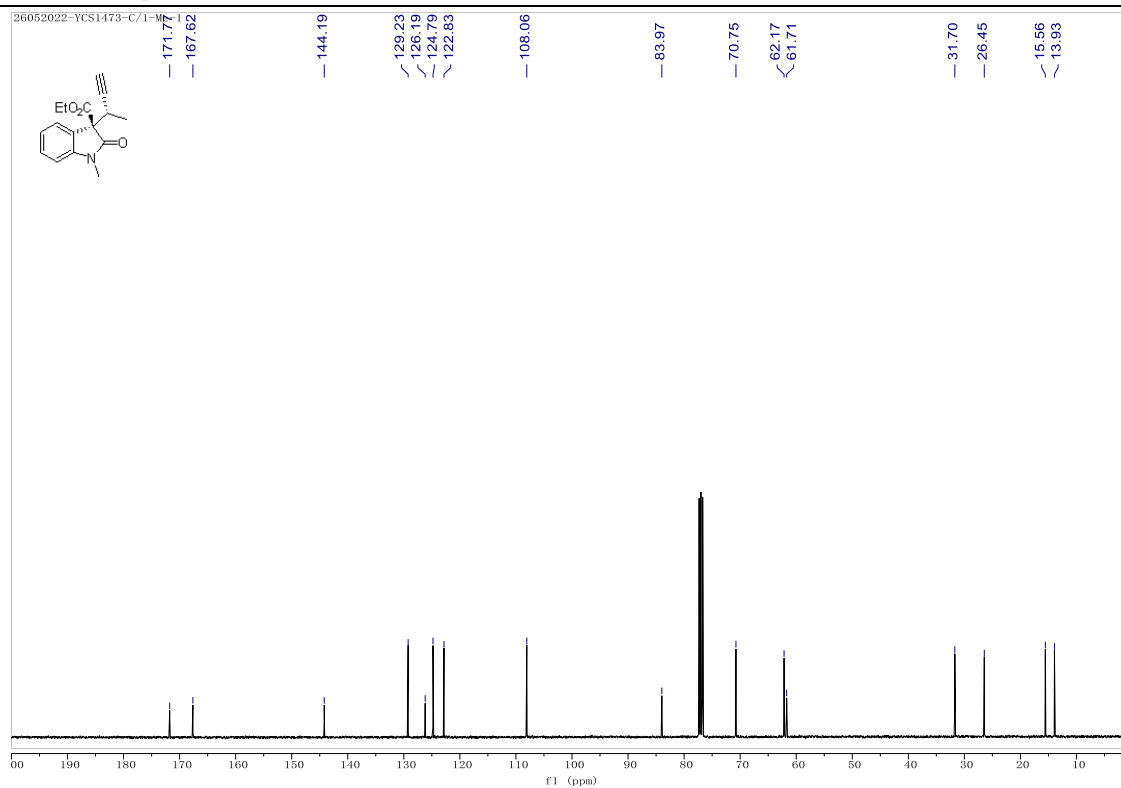
¹³C NMR Spectrum of (*S,S*)-3m



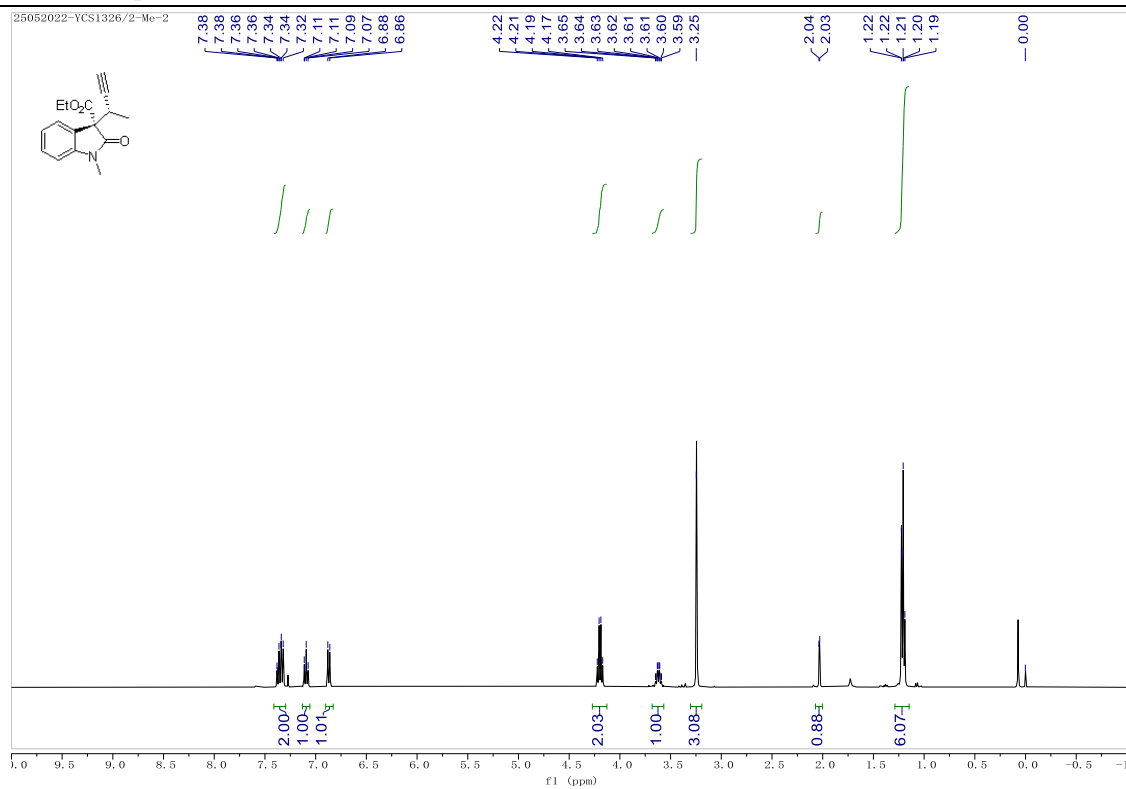
¹H NMR Spectrum of (*R,S*)-3n



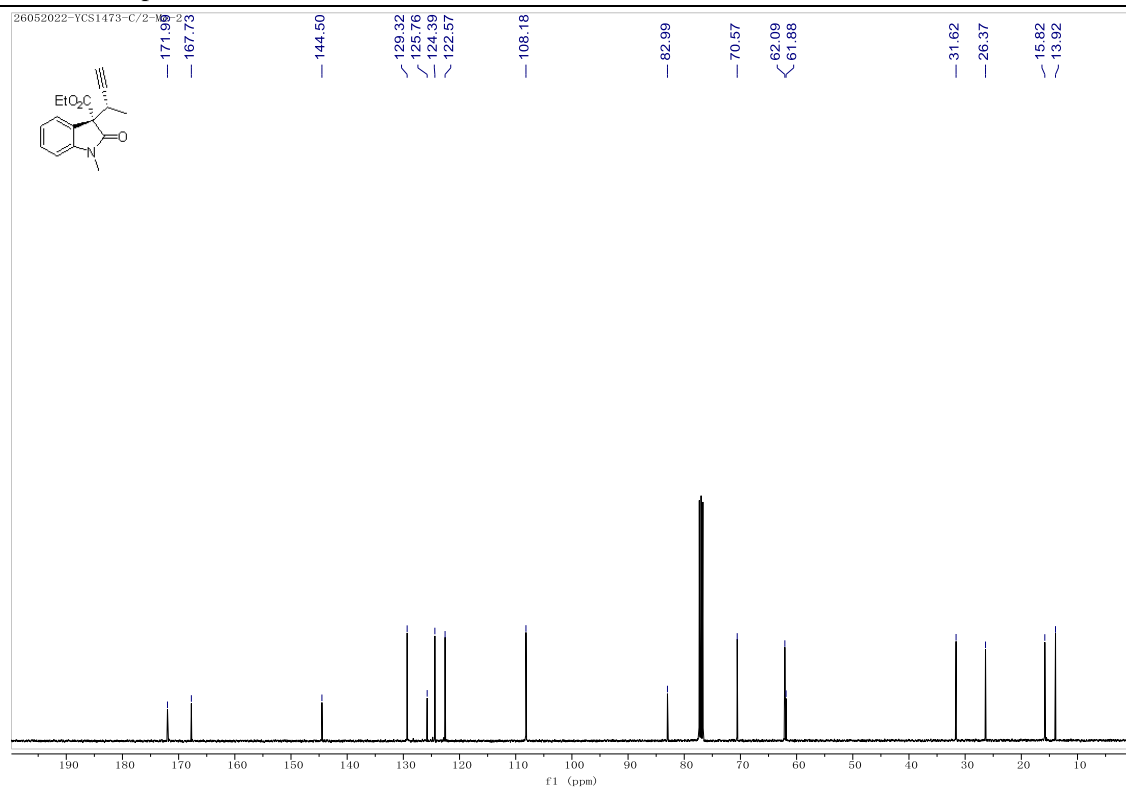
¹³C NMR Spectrum of (*R,S*)-3n



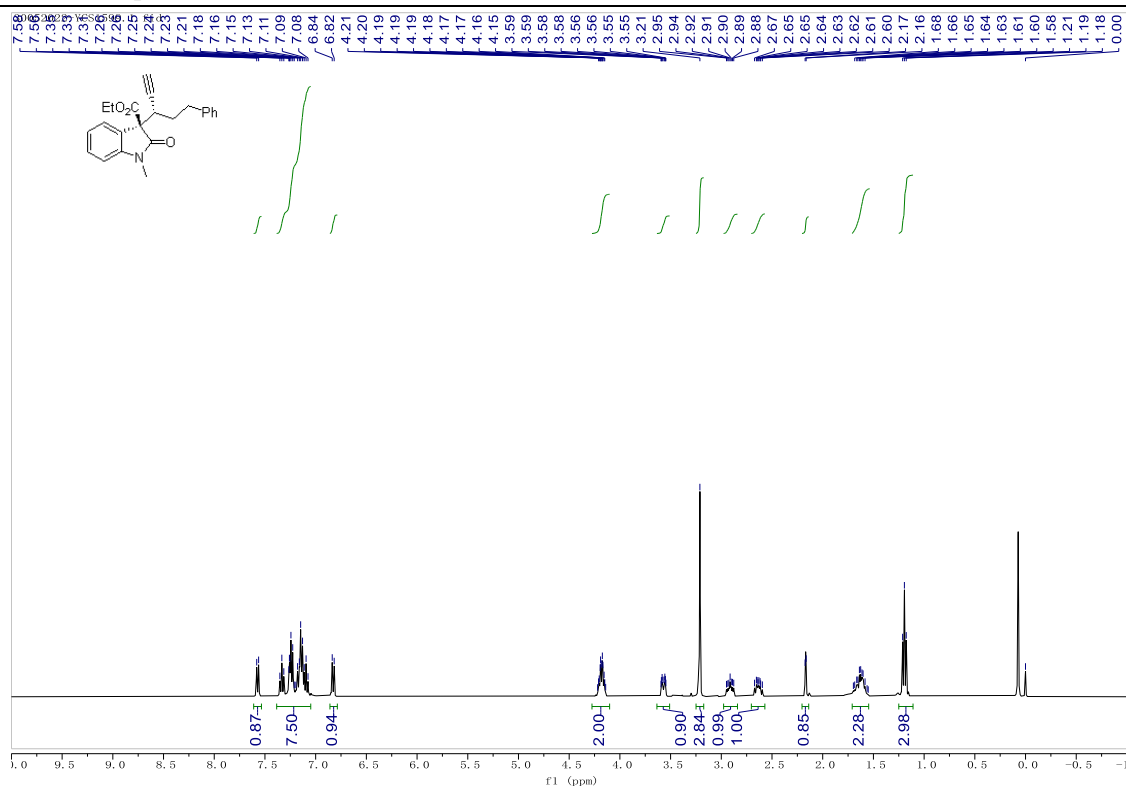
¹H NMR Spectrum of (S,S)-3n



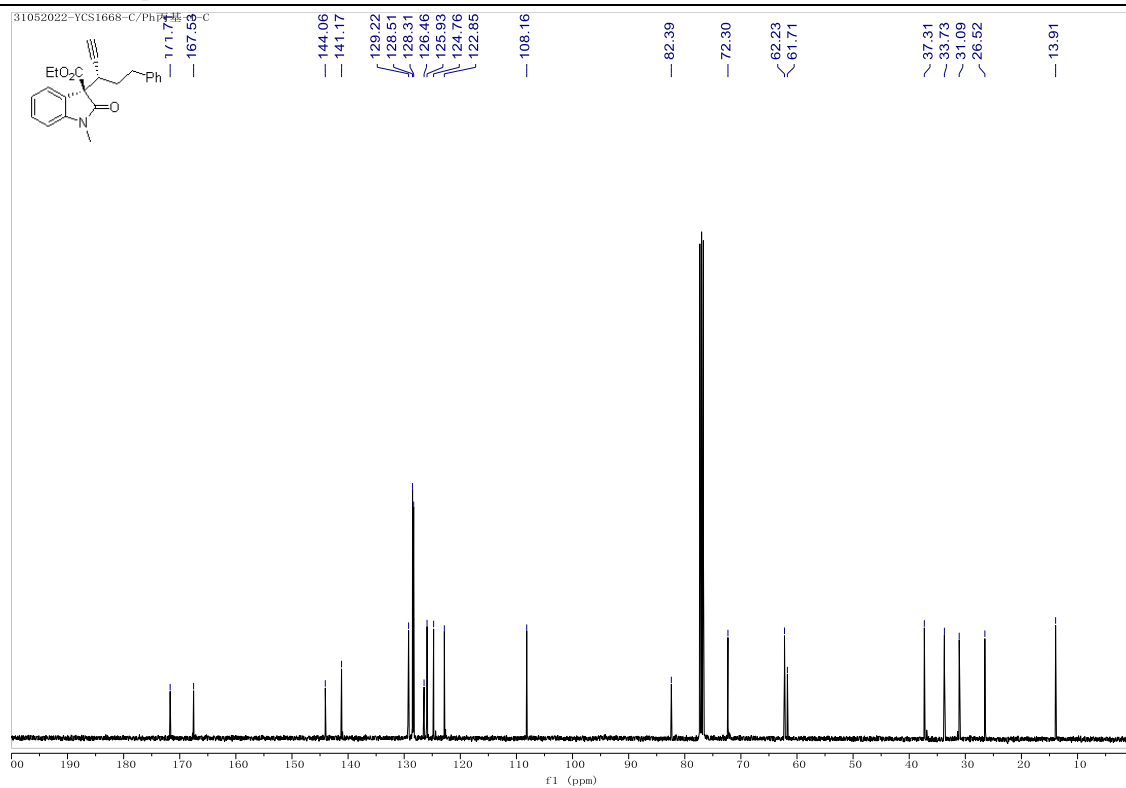
¹³C NMR Spectrum of (S,S)-3n



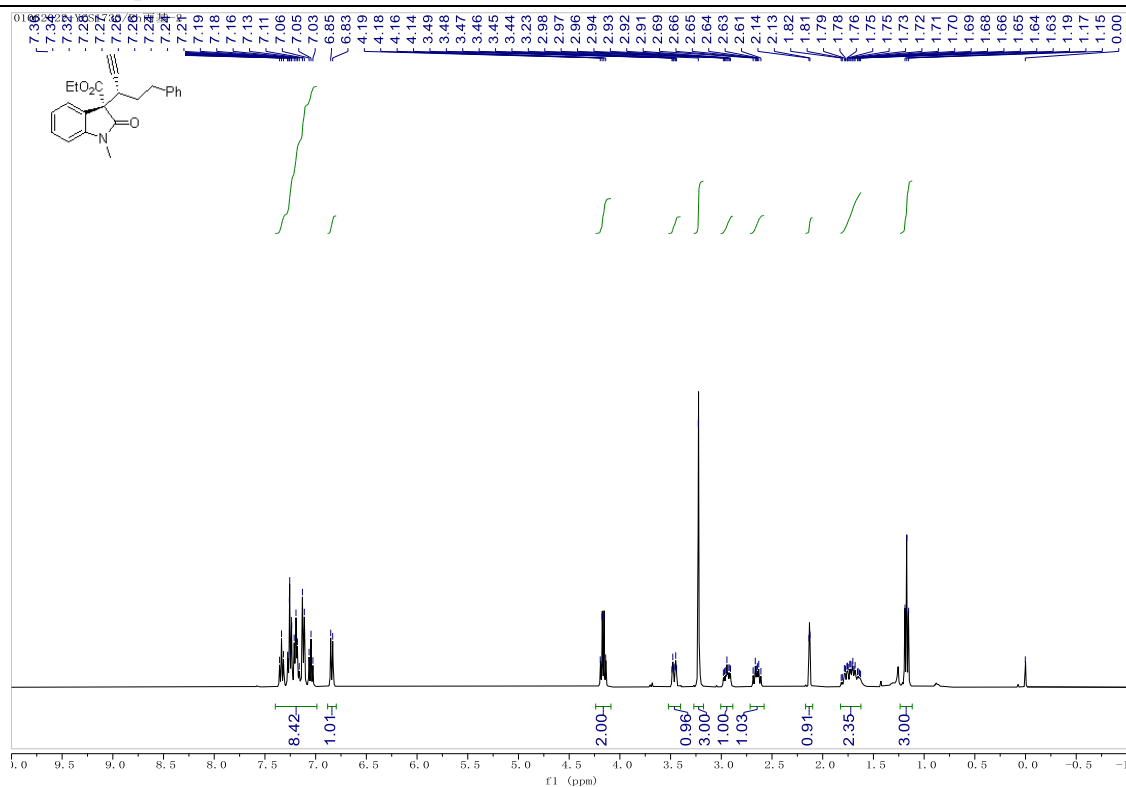
¹H NMR Spectrum of (*R,S*)-3o



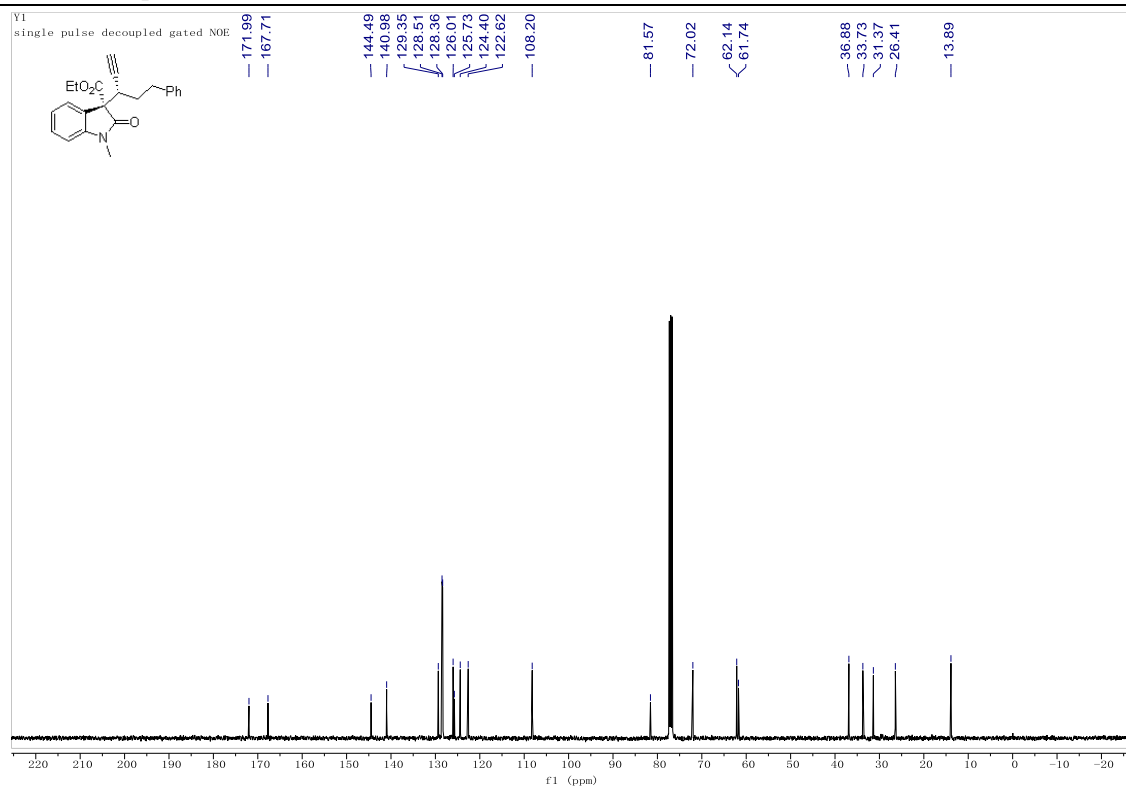
¹³C NMR Spectrum of (*R,S*)-3o



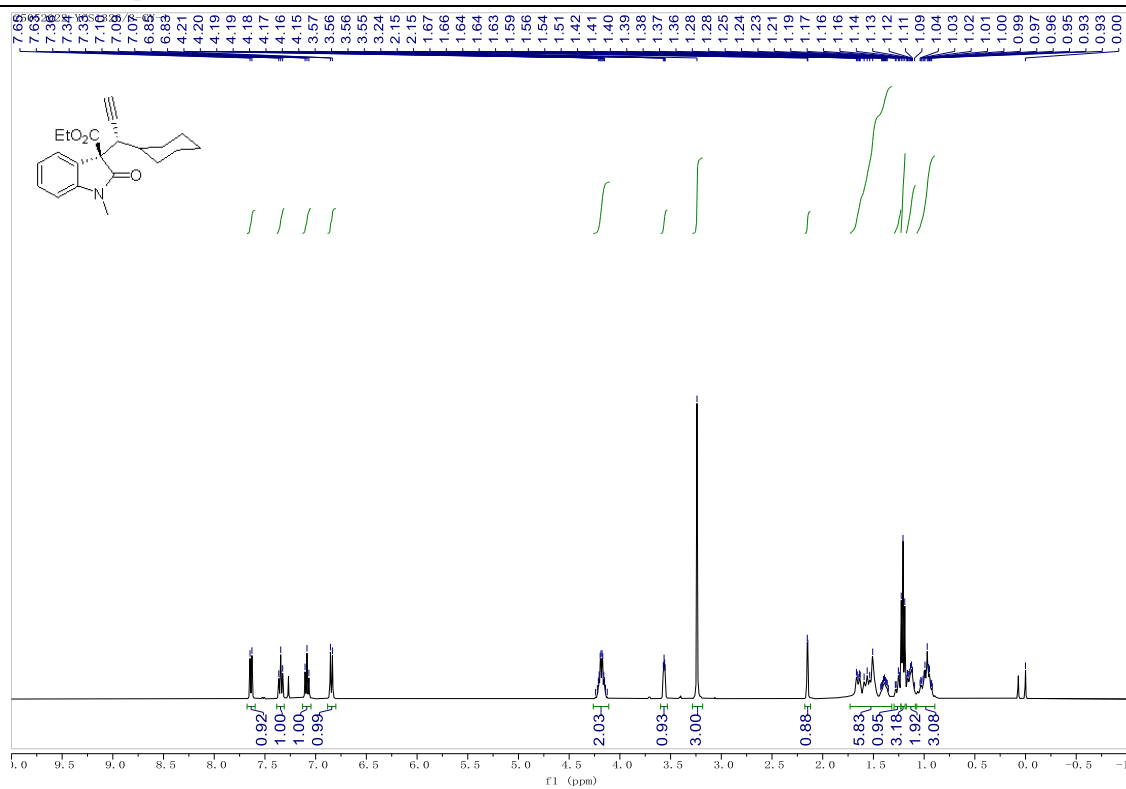
¹H NMR Spectrum of (*S,S*)-3o



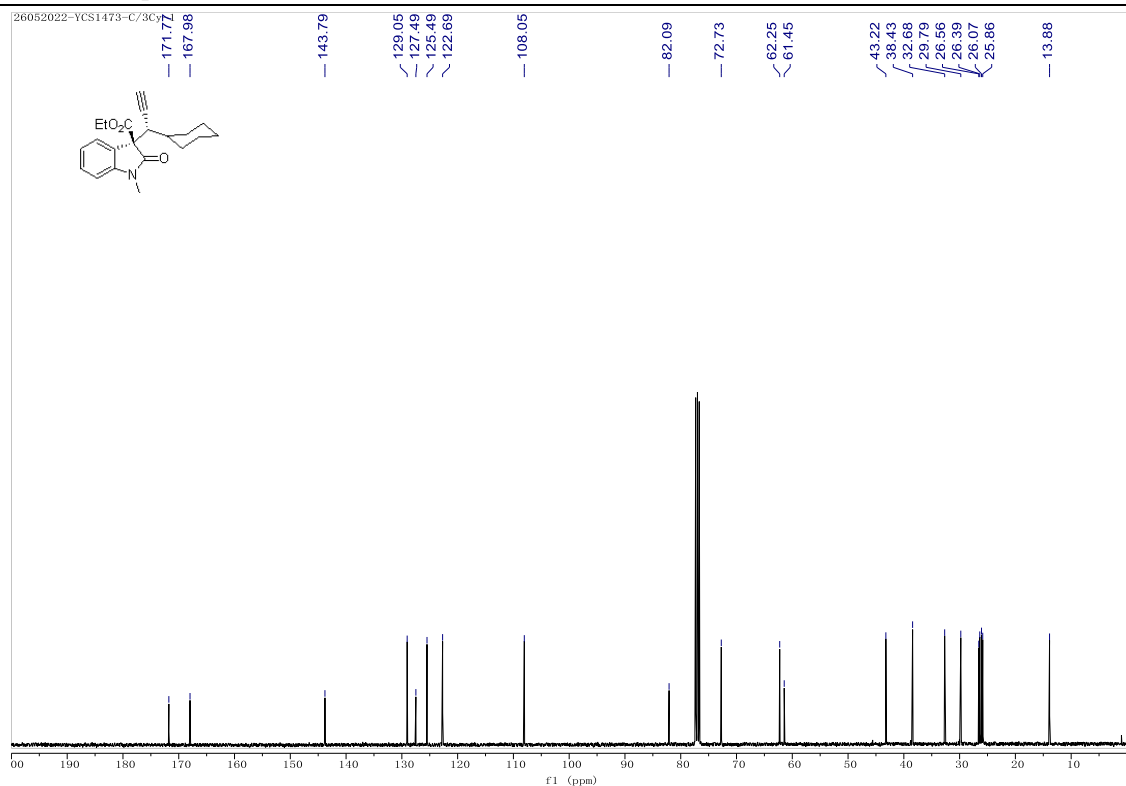
¹³C NMR Spectrum of (*S,S*)-3o



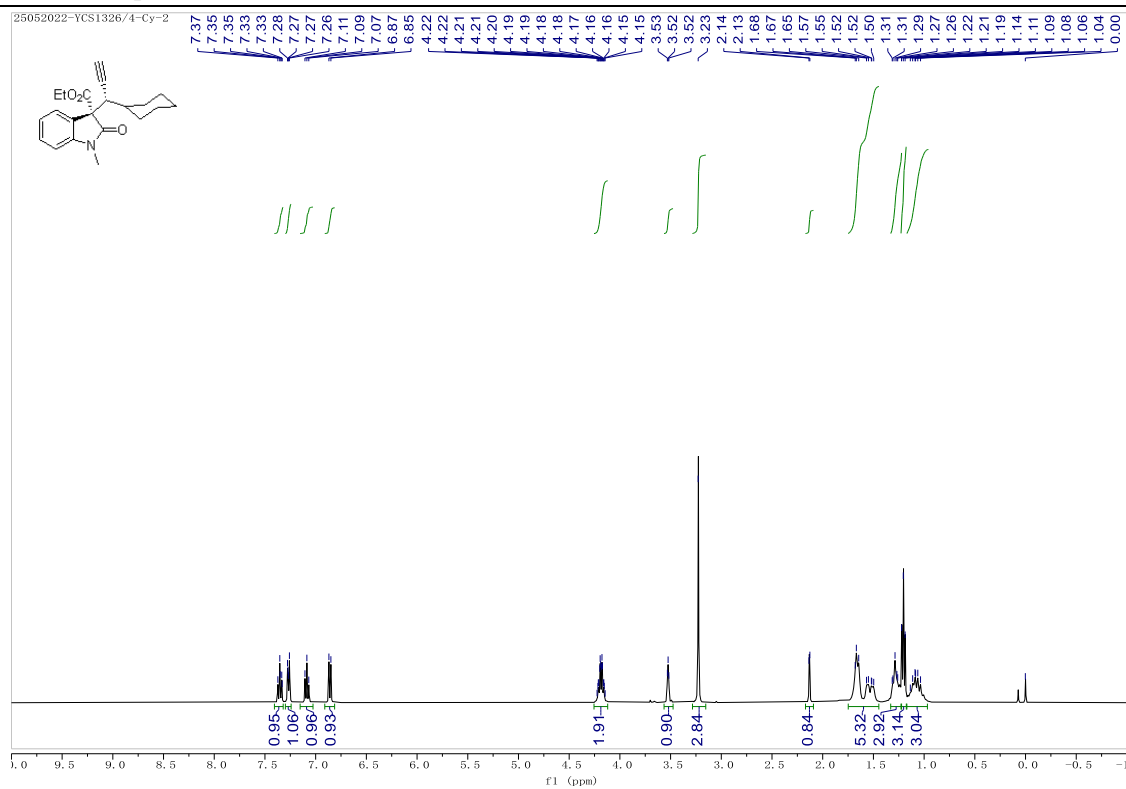
¹H NMR Spectrum of (*R,S*)-3p



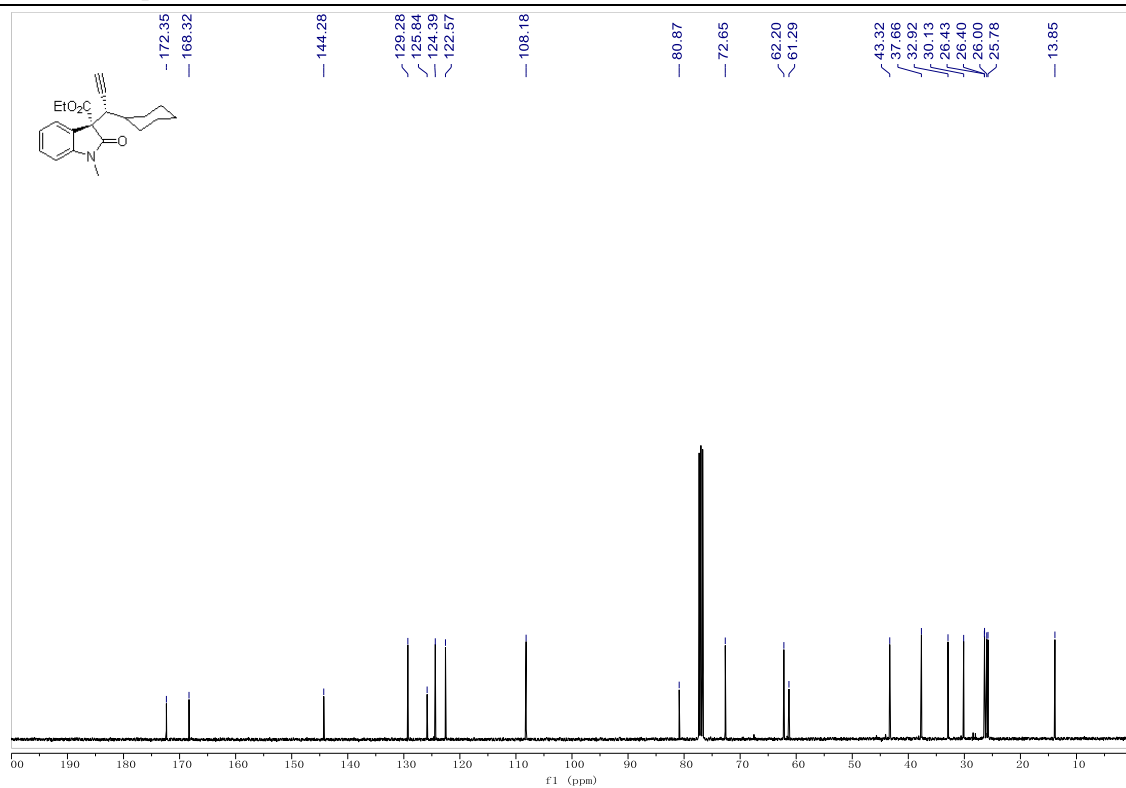
¹³C NMR Spectrum of (*R,S*)-3p



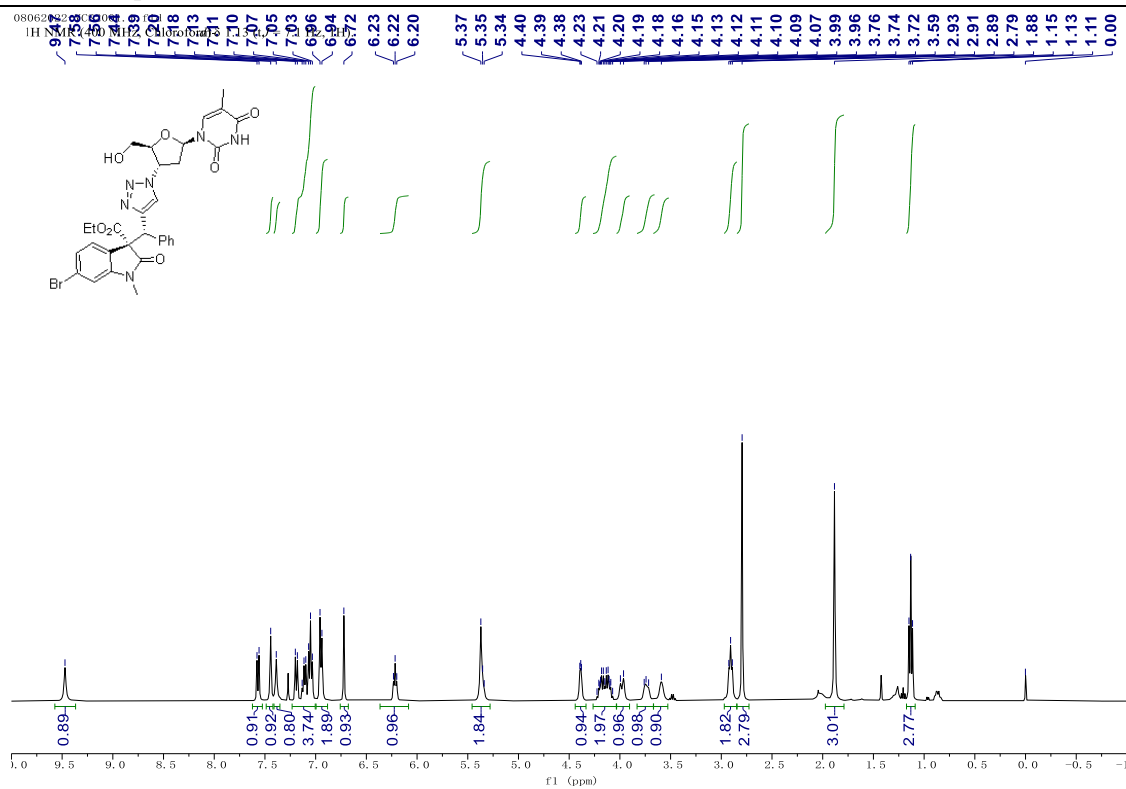
¹H NMR Spectrum of (S,S)-3p



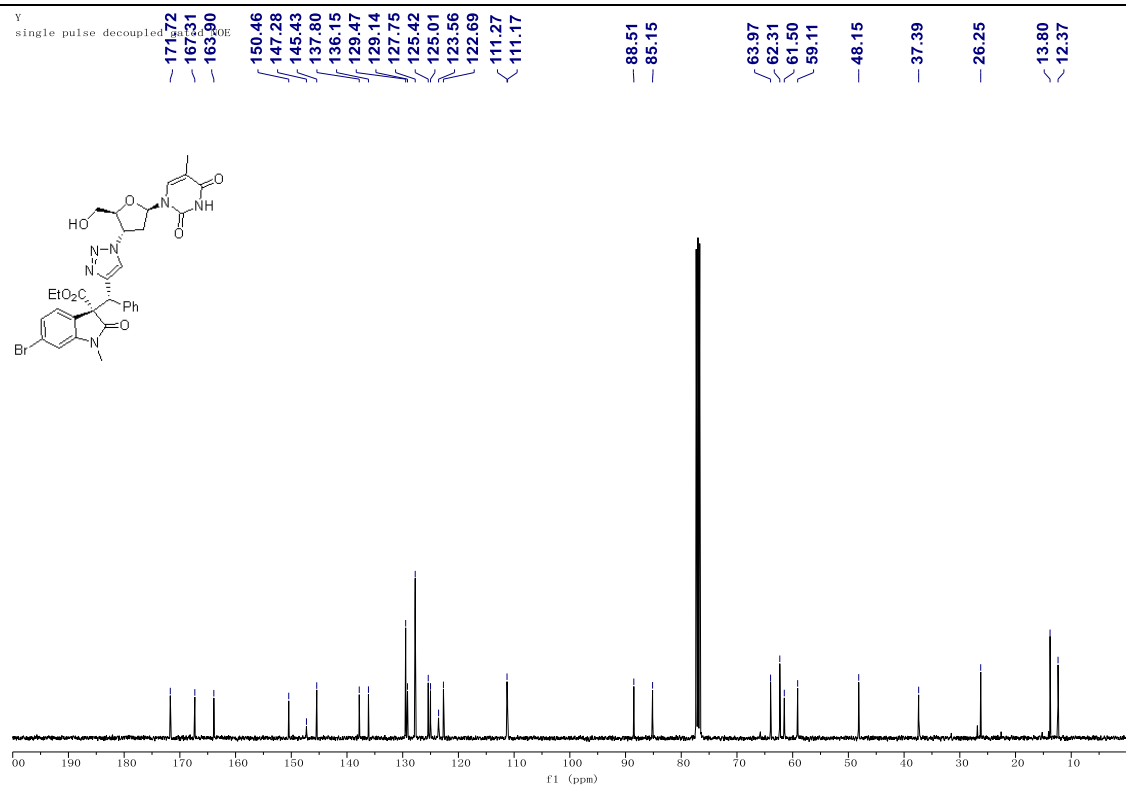
¹³C NMR Spectrum of (S,S)-3p



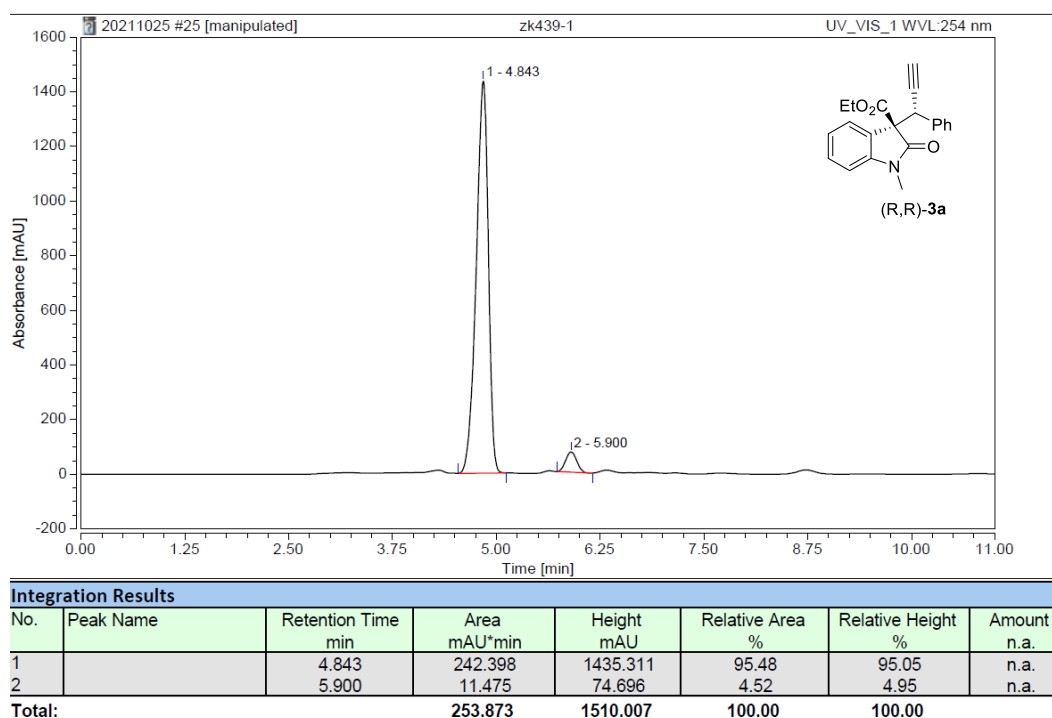
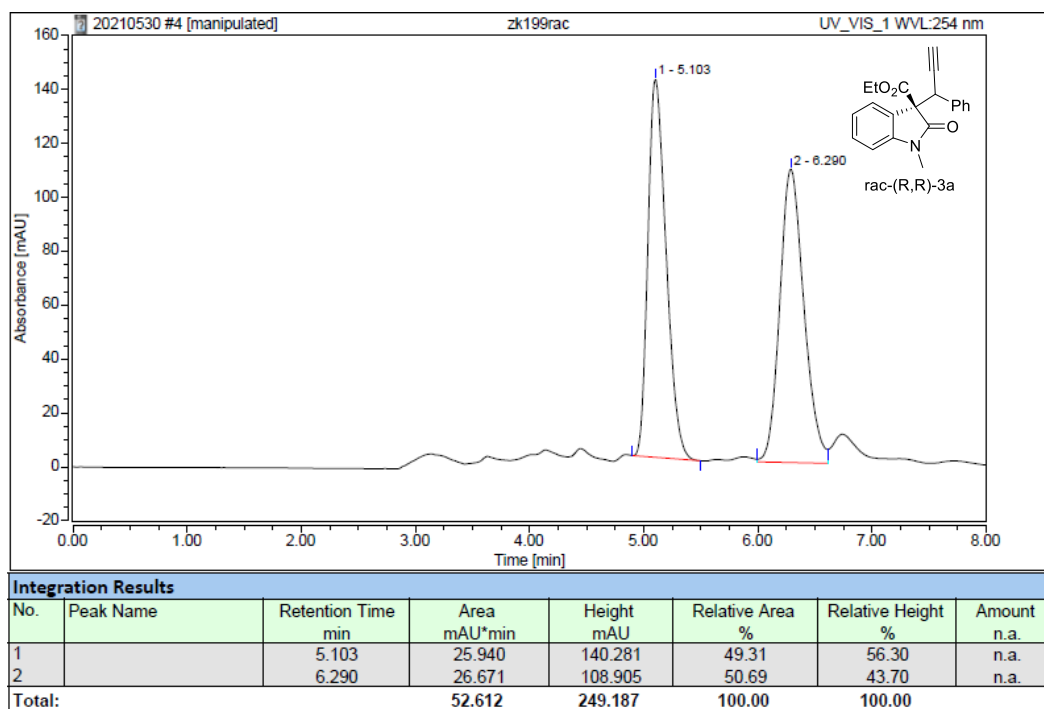
¹H NMR Spectrum of 4

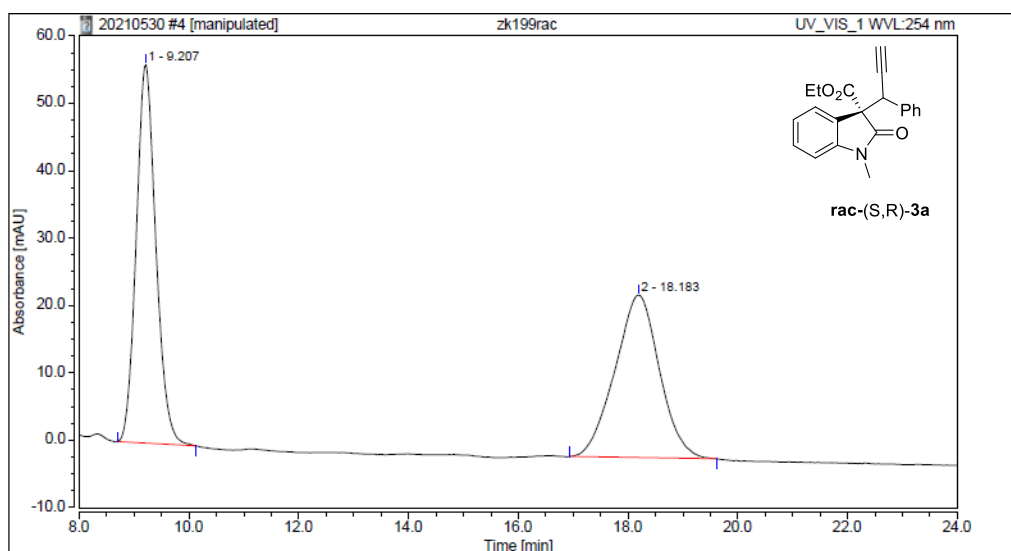


¹³C NMR Spectrum of 4

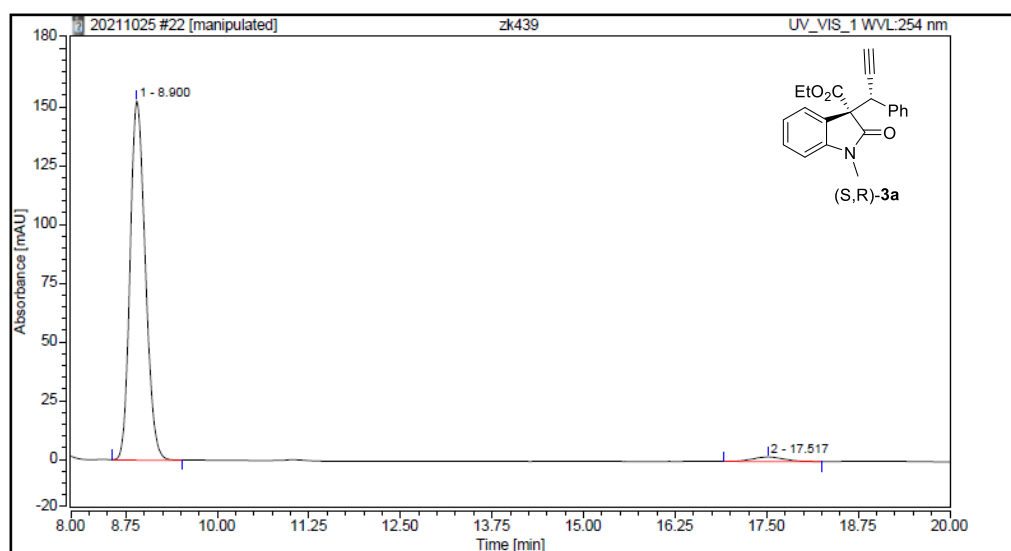


7. Copies of HPLC Chromatography

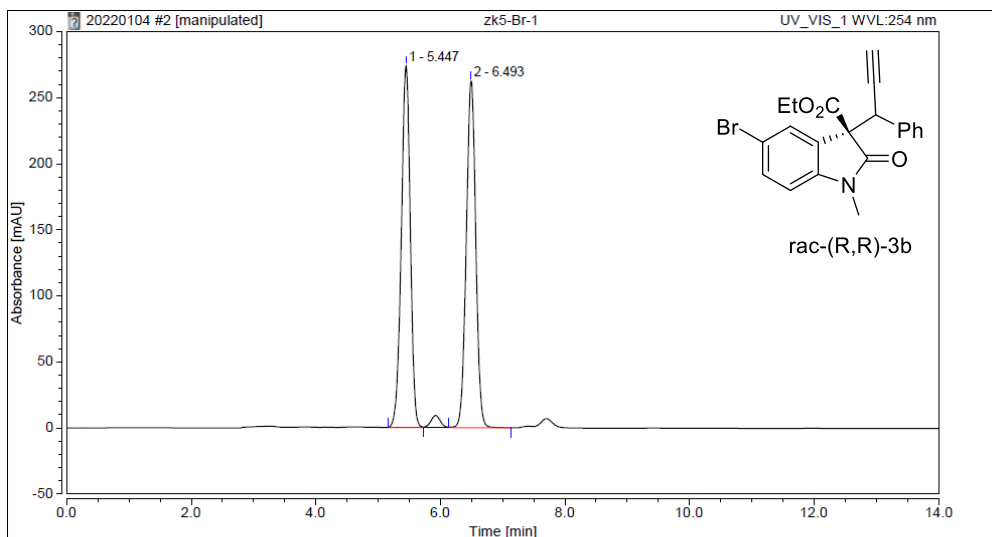




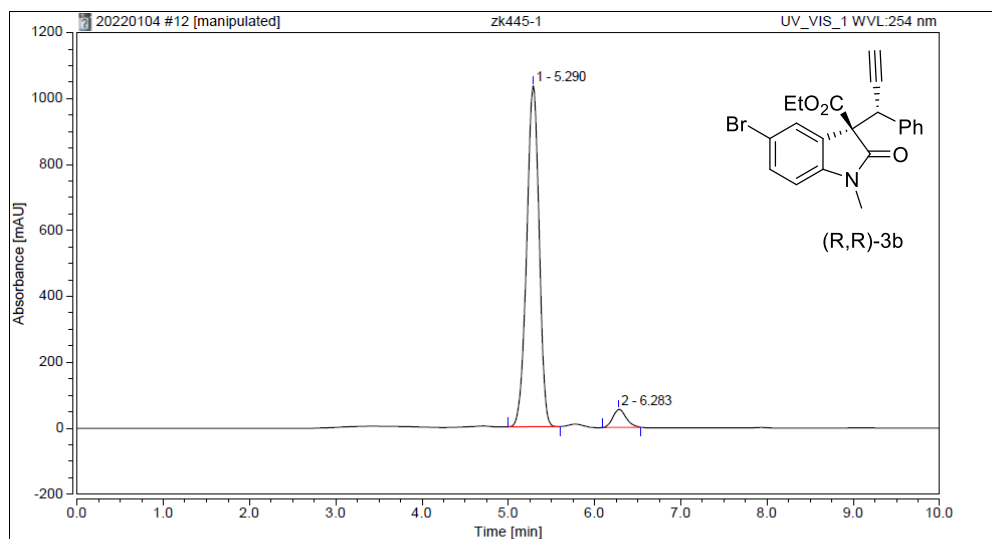
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.207	23.239	56.170	50.69	69.97	n.a.
2		18.183	22.609	24.103	49.31	30.03	n.a.
Total:			45.848	80.274	100.00	100.00	



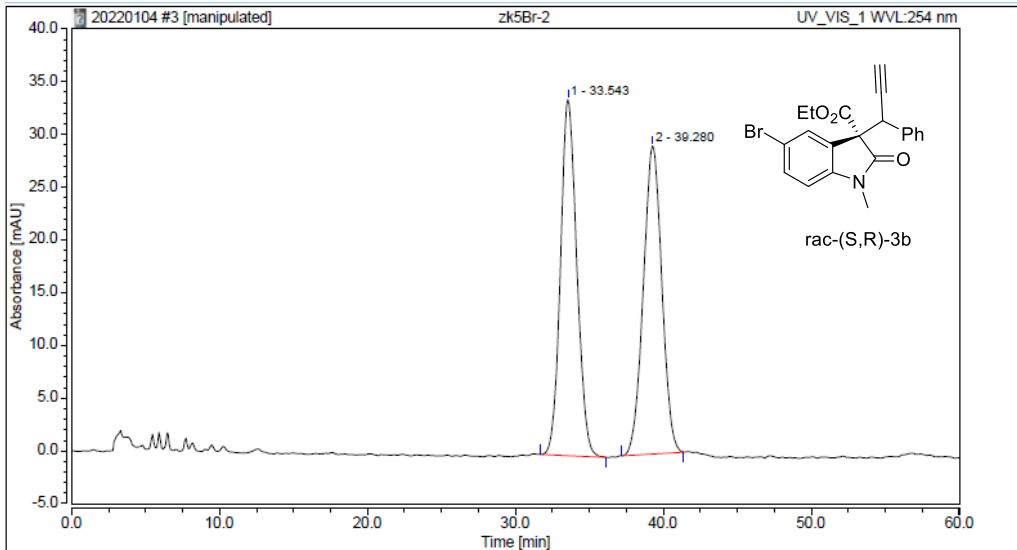
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.900	36.894	152.968	97.52	98.77	n.a.
2		17.517	0.940	1.907	2.48	1.23	n.a.
Total:			37.834	154.875	100.00	100.00	



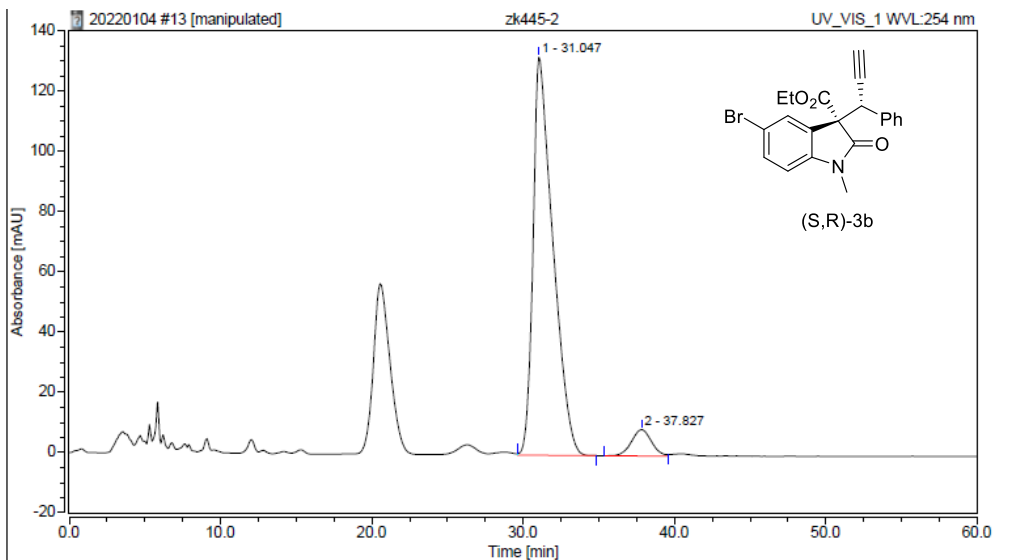
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.447	45.896	274.050	49.76	51.06	n.a.
2		6.493	46.343	262.692	50.24	48.94	n.a.
Total:			92.240	536.743	100.00	100.00	



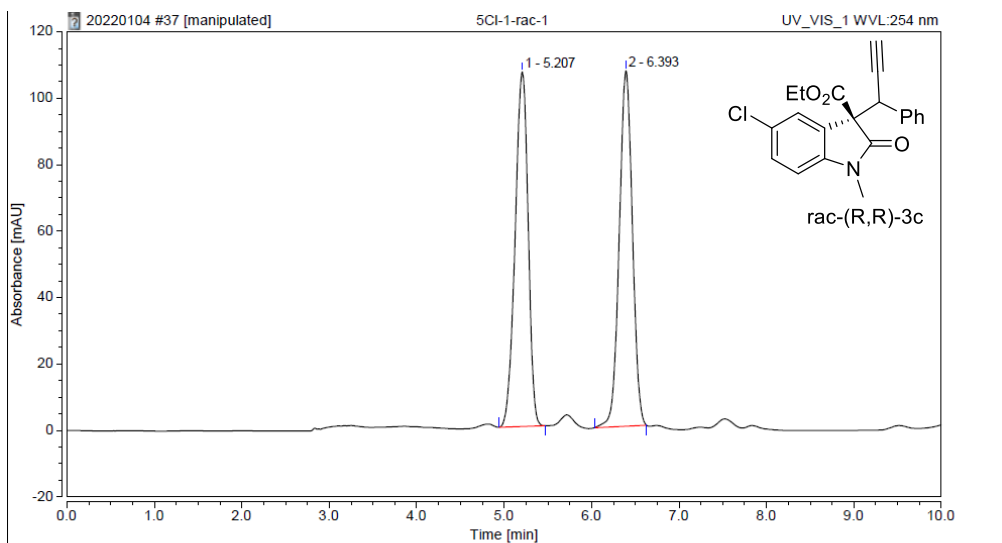
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.290	173.148	1034.111	94.71	95.02	n.a.
2		6.283	9.680	54.197	5.29	4.98	n.a.
Total:			182.828	1088.308	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		33.543	43.118	33.758	50.48	53.60	n.a.
2		39.280	42.302	29.222	49.52	46.40	n.a.
Total:			85.420	62.980	100.00	100.00	

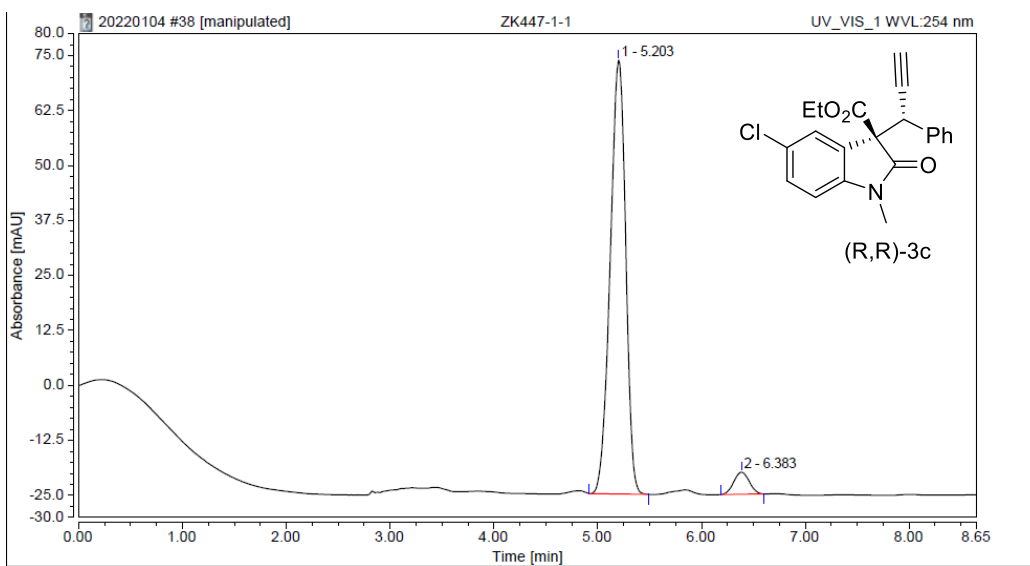


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		31.047	201.193	132.220	93.76	93.81	n.a.
2		37.827	13.393	8.729	6.24	6.19	n.a.
Total:			214.586	140.948	100.00	100.00	



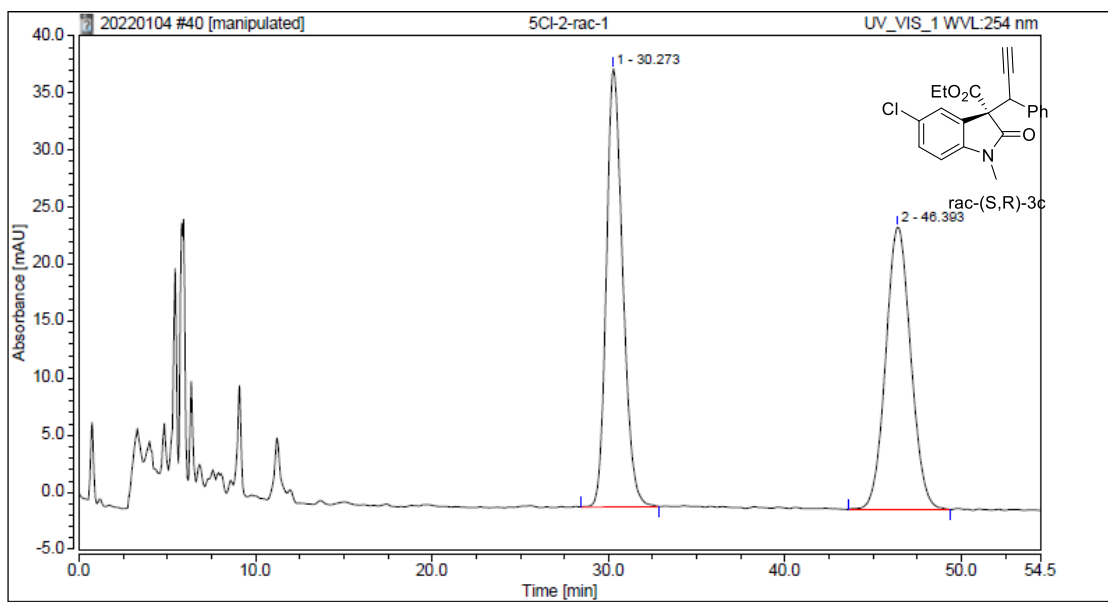
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.207	18.382	106.744	49.64	49.94	n.a.
2		6.393	18.645	107.015	50.36	50.06	n.a.
Total:			37.027	213.759	100.00	100.00	



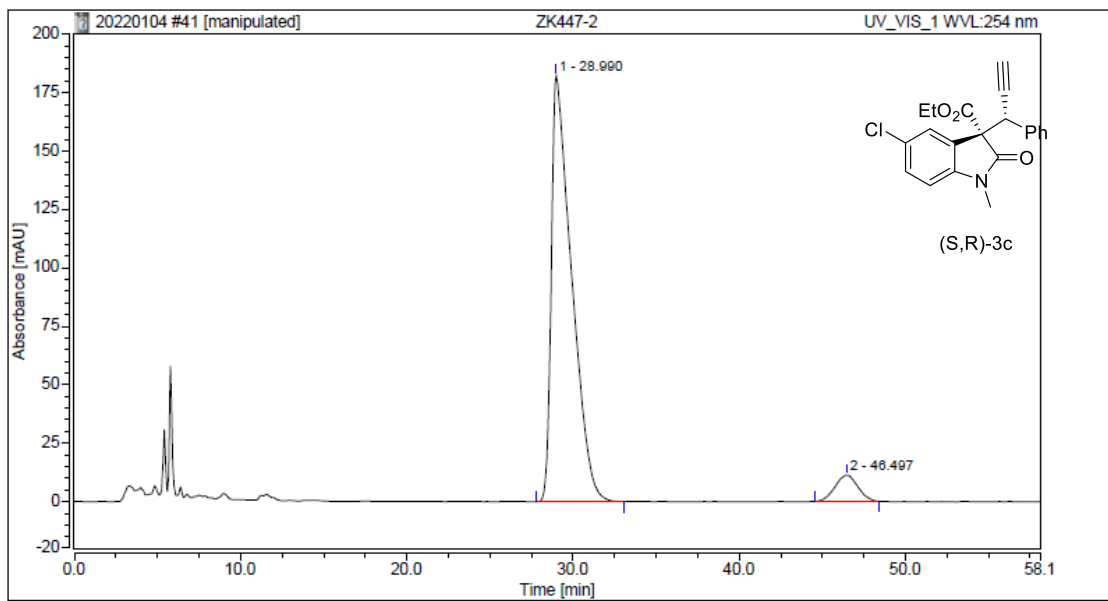
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.203	17.021	98.639	95.15	95.14	n.a.
2		6.383	0.868	5.039	4.85	4.86	n.a.
Total:			17.888	103.678	100.00	100.00	



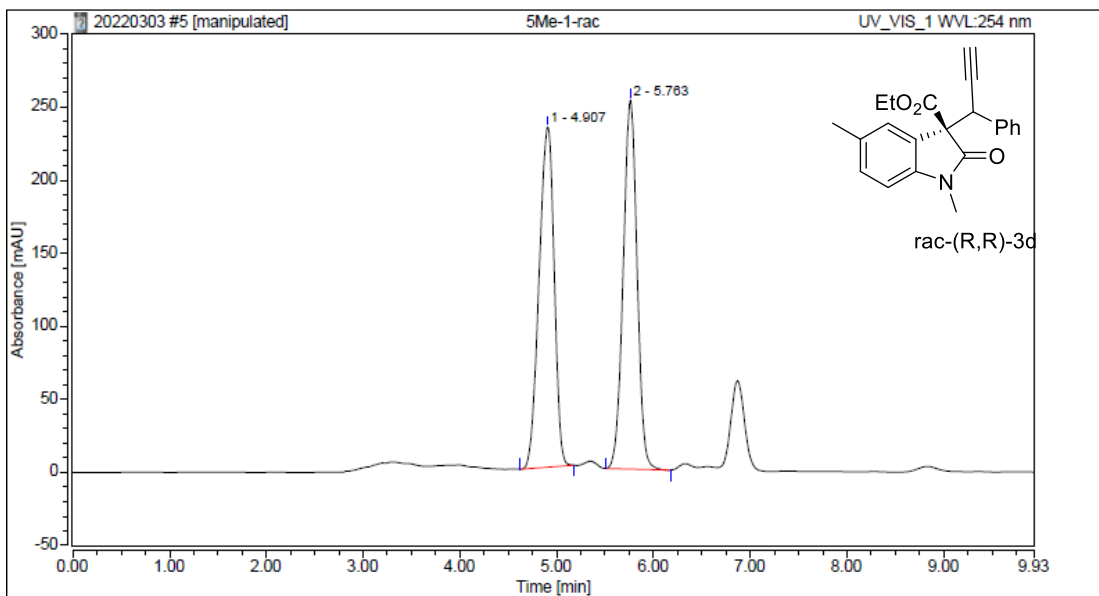
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.273	41.281	38.400	50.29	60.79	n.a.
2		46.393	40.809	24.771	49.71	39.21	n.a.
Total:			82.089	63.171	100.00	100.00	



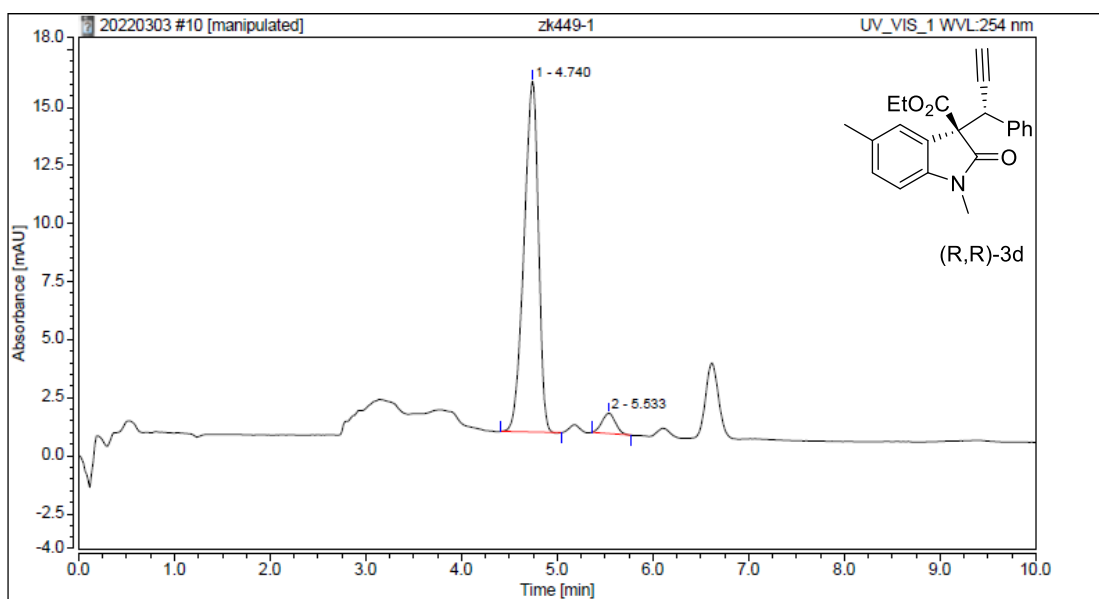
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.990	257.042	182.617	93.51	94.22	n.a.
2		46.497	17.836	11.199	6.49	5.78	n.a.
Total:			274.878	193.816	100.00	100.00	



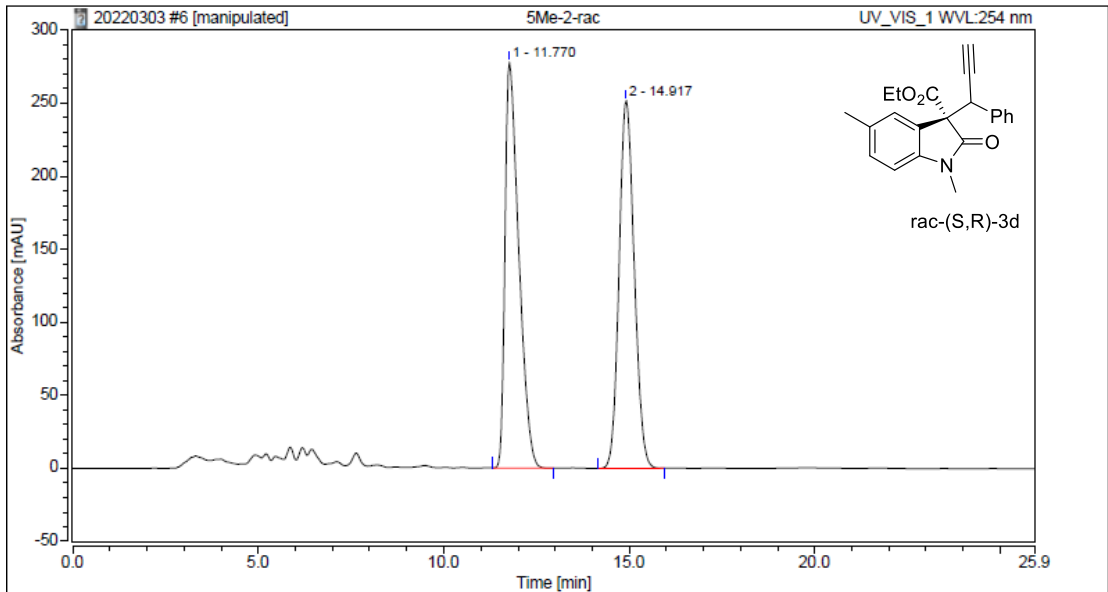
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.907	42.024	232.925	50.04	47.97	n.a.
2		5.763	41.965	252.606	49.96	52.03	n.a.
Total:			83.989	485.531	100.00	100.00	



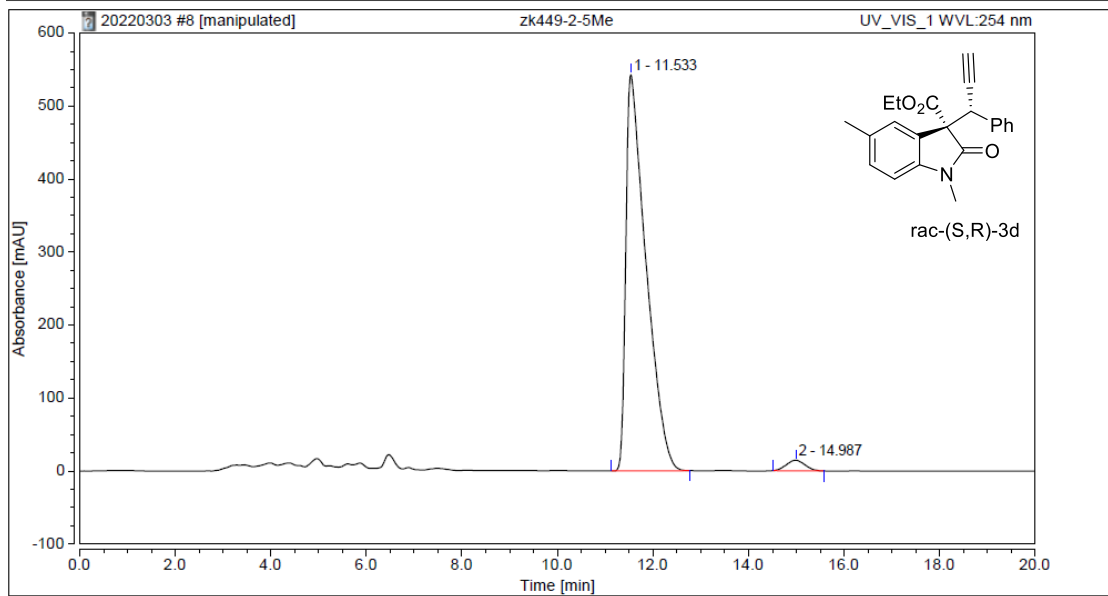
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.740	2.630	15.098	94.88	94.52	n.a.
2		5.533	0.142	0.875	5.12	5.48	n.a.
Total:			2.772	15.973	100.00	100.00	



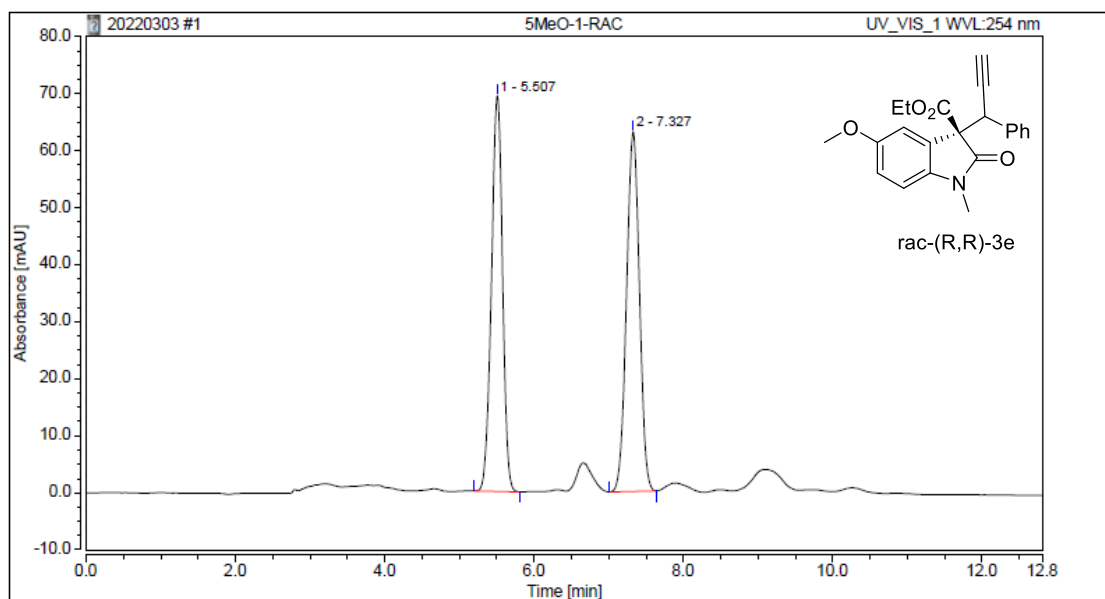
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.770	119.368	277.889	50.00	52.44	n.a.
2		14.917	119.388	251.991	50.00	47.56	n.a.
Total:			238.756	529.880	100.00	100.00	

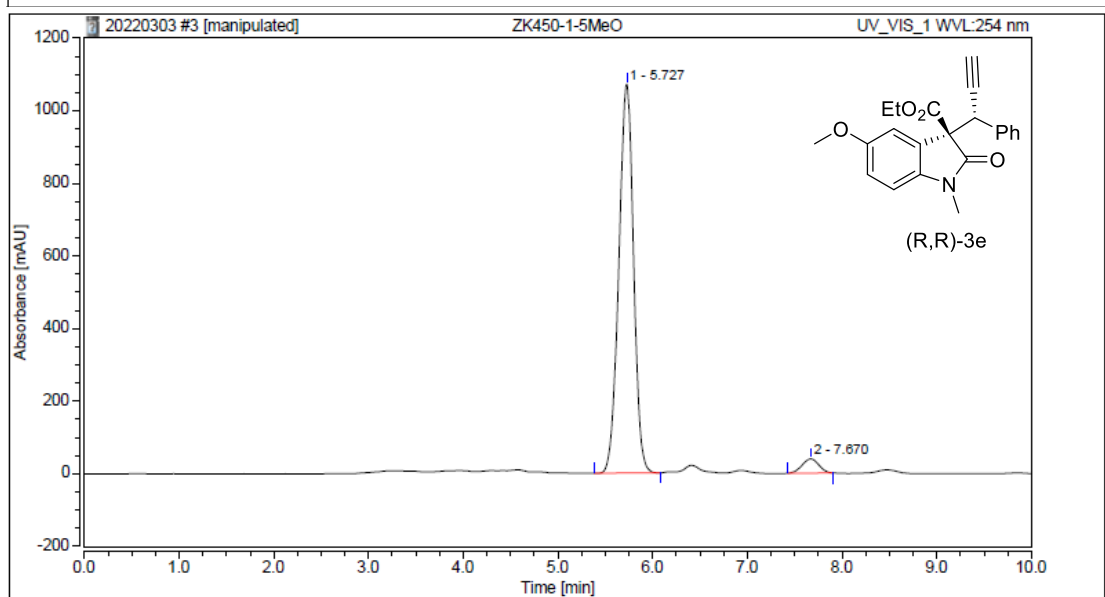


Integration Results

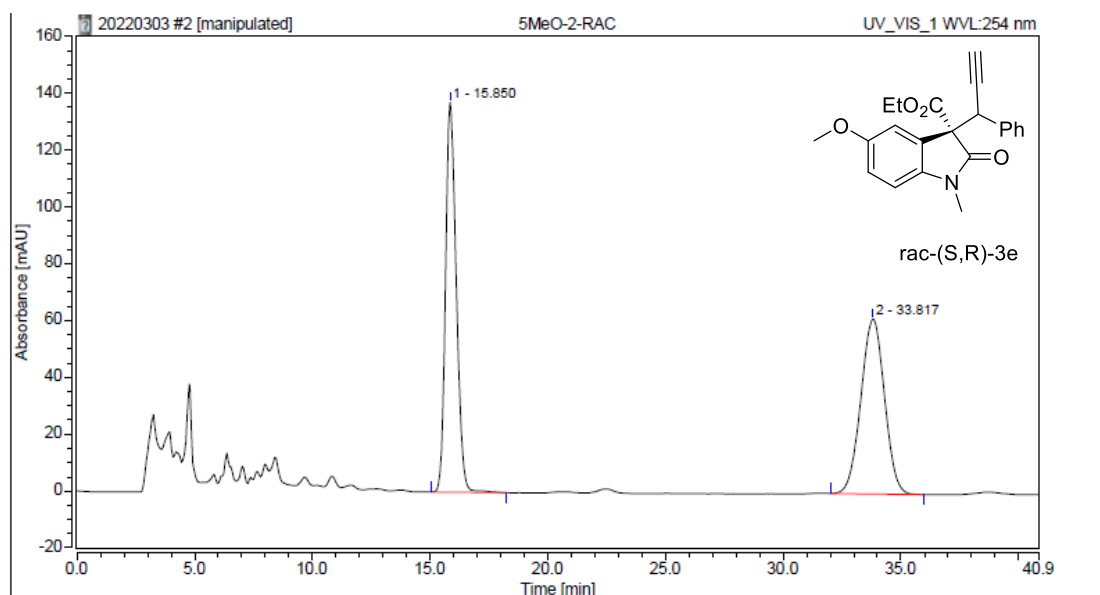
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.533	263.518	542.591	97.57	97.41	n.a.
2		14.987	6.568	14.410	2.43	2.59	n.a.
Total:			270.085	557.001	100.00	100.00	



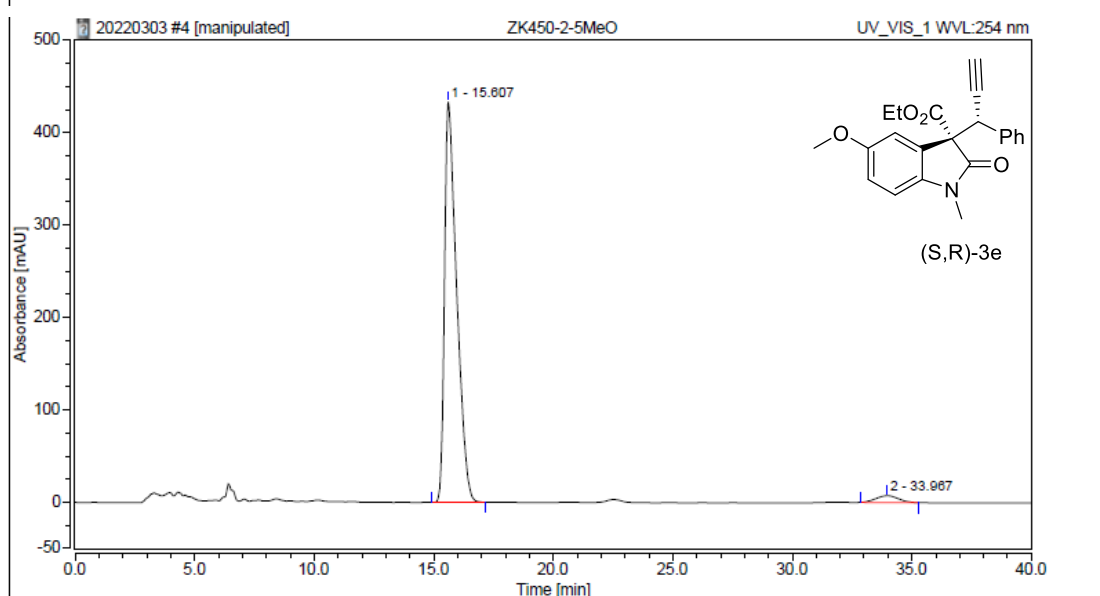
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.507	11.906	69.395	48.57	52.36	n.a.
2		7.327	12.608	63.130	51.43	47.64	n.a.
Total:			24.514	132.524	100.00	100.00	



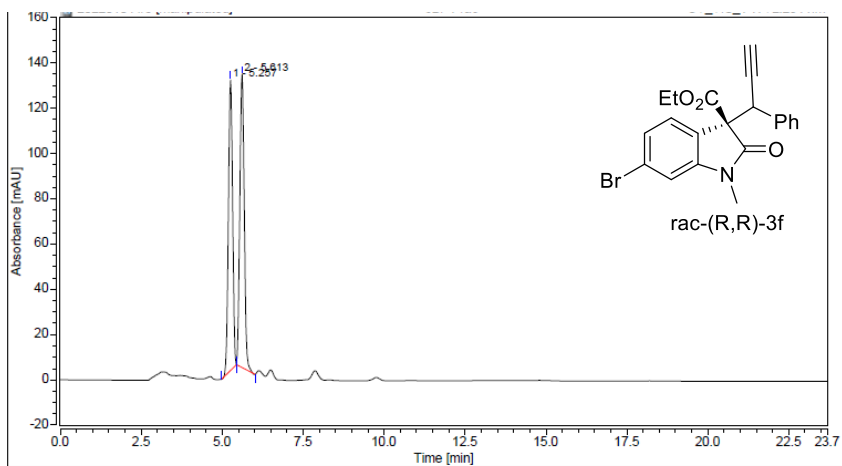
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.727	193.160	1070.976	96.03	96.49	n.a.
2		7.670	7.987	38.956	3.97	3.51	n.a.
Total:			201.147	1109.932	100.00	100.00	



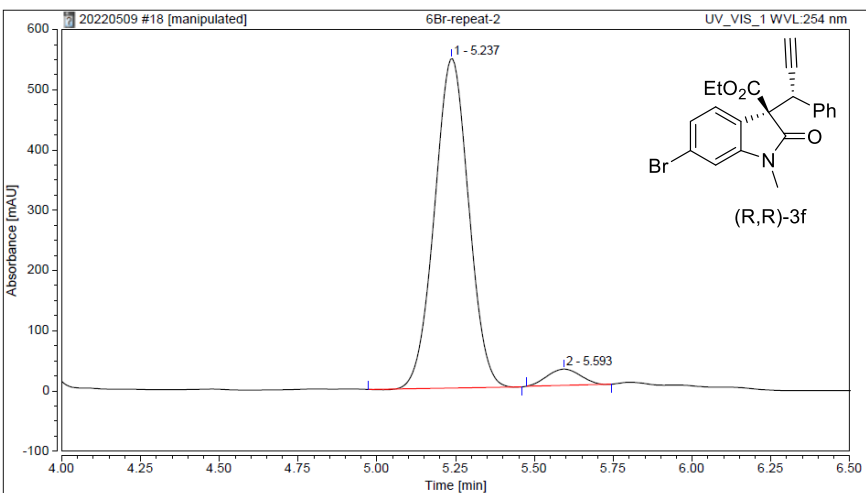
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.850	72.124	137.081	50.19	69.00	n.a.
2		33.817	71.574	61.590	49.81	31.00	n.a.
Total:			143.698	198.671	100.00	100.00	



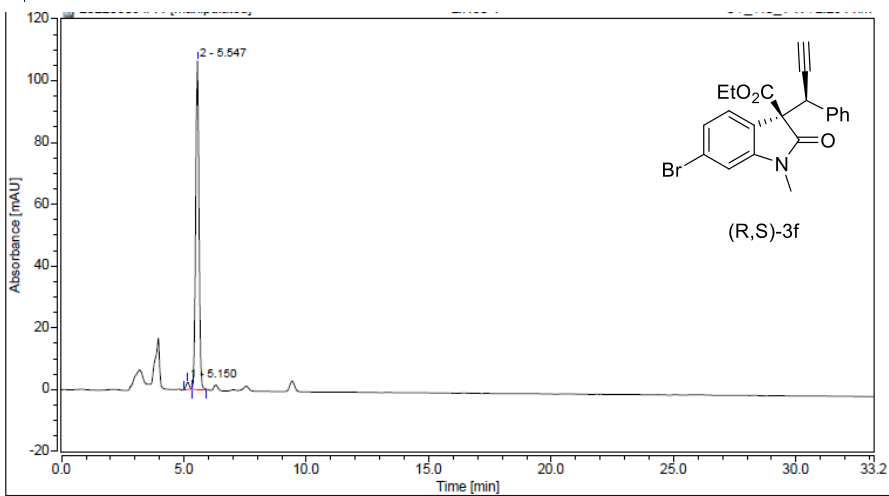
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.607	254.468	433.331	96.98	98.35	n.a.
2		33.967	7.930	7.250	3.02	1.65	n.a.
Total:			262.399	440.580	100.00	100.00	



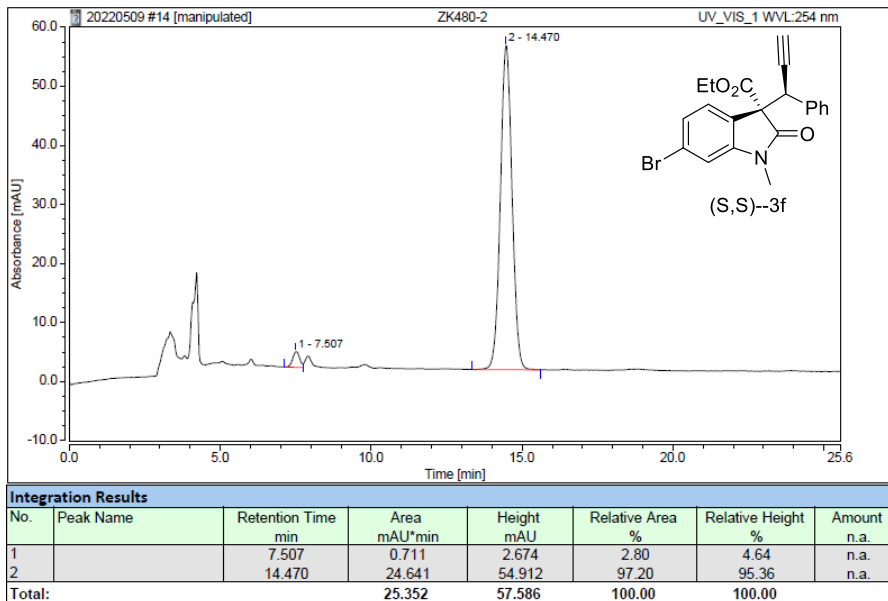
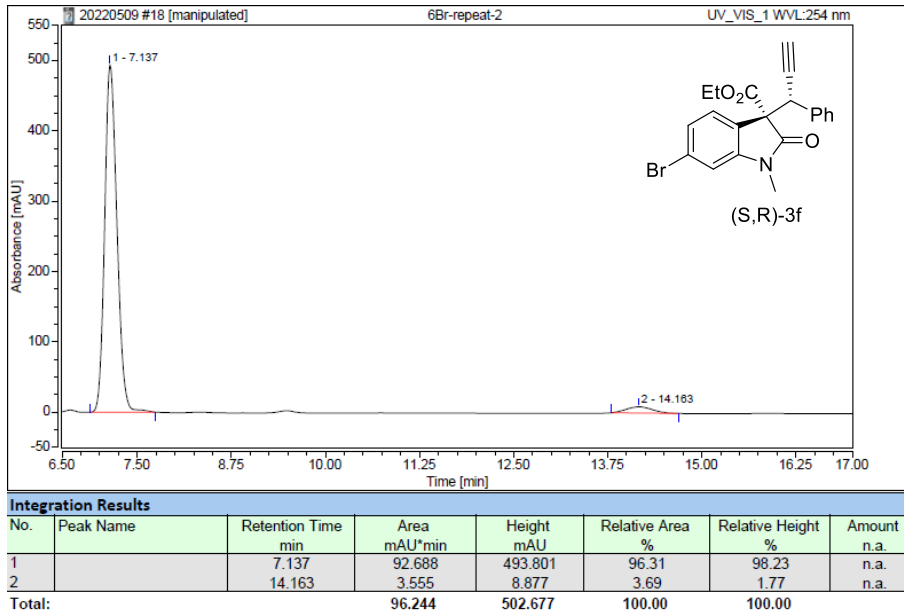
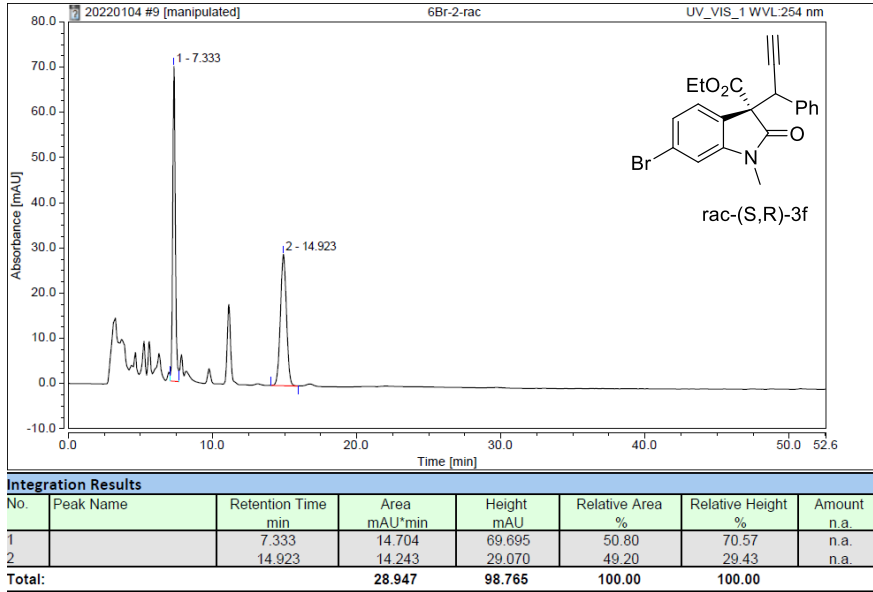
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.257	19.214	128.302	48.57	49.80	n.a.
2		5.613	20.348	129.333	51.43	50.20	n.a.
Total:			39.562	257.636	100.00	100.00	

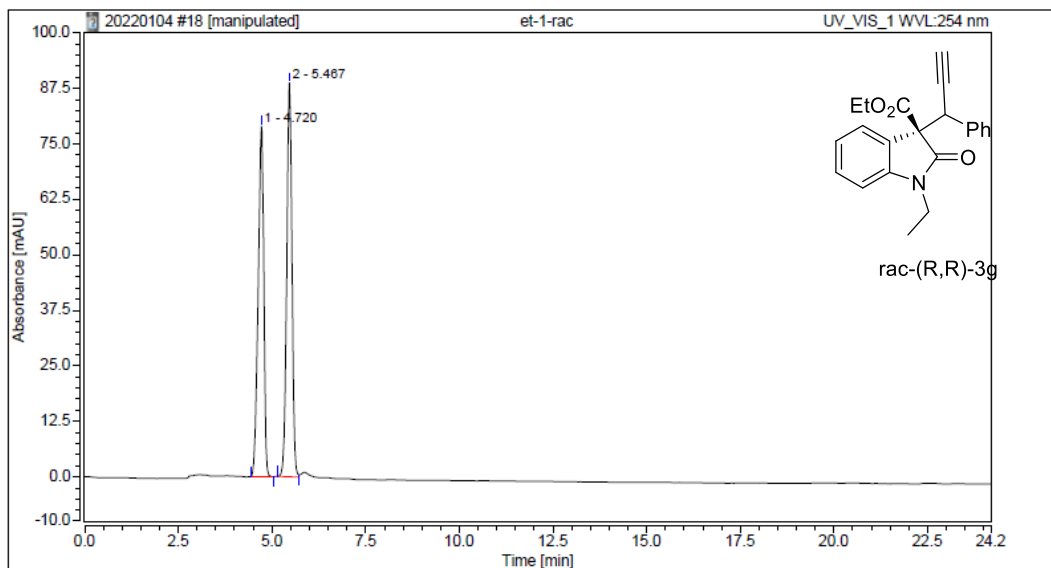


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.237	68.589	547.473	95.43	95.31	n.a.
2		5.593	3.283	26.963	4.57	4.69	n.a.
Total:			71.872	574.436	100.00	100.00	

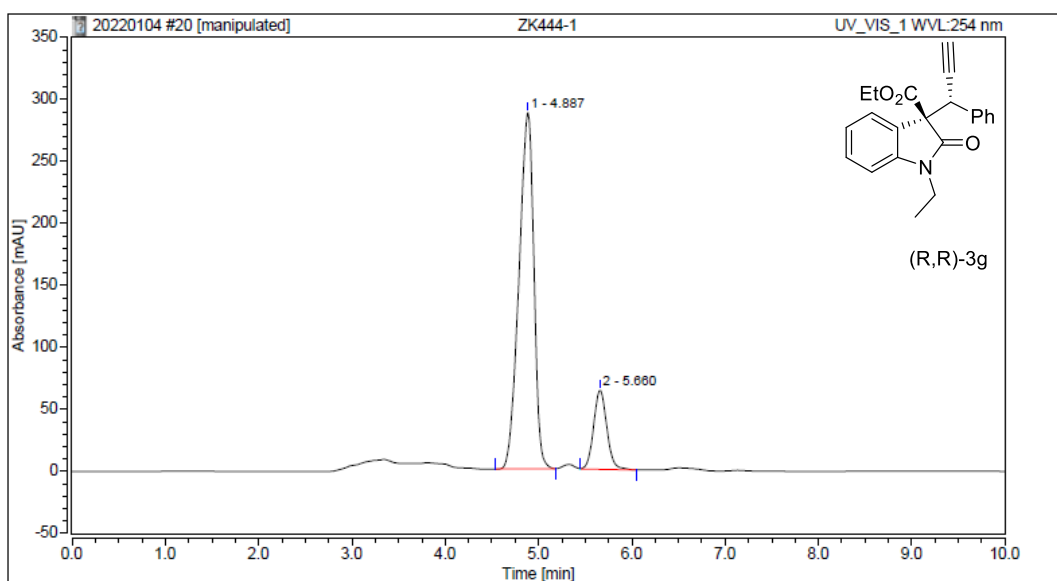


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.150	0.357	2.438	2.08	2.24	n.a.
2		5.547	16.754	106.422	97.92	97.76	n.a.
Total:			17.111	108.859	100.00	100.00	

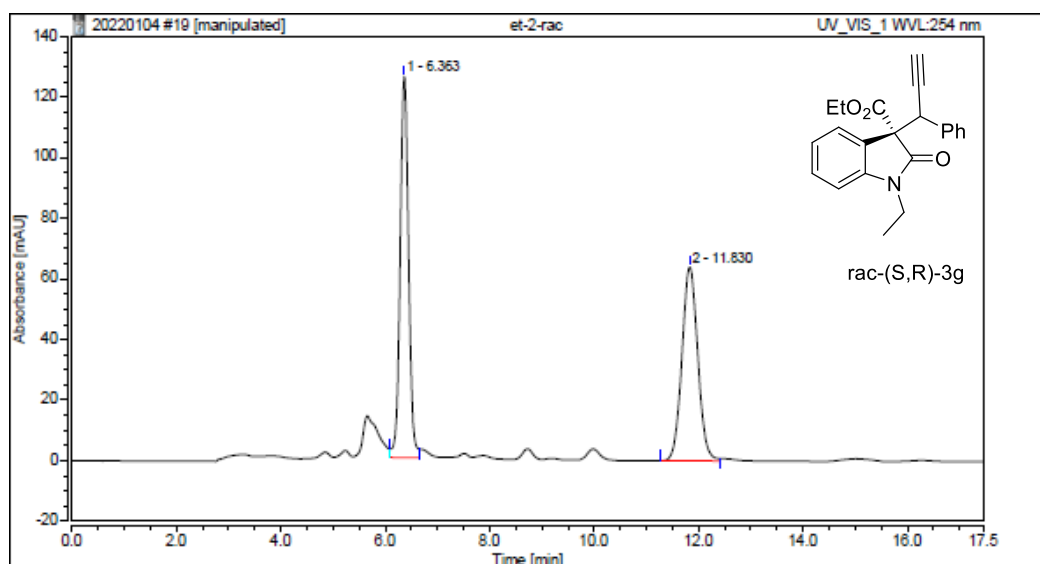




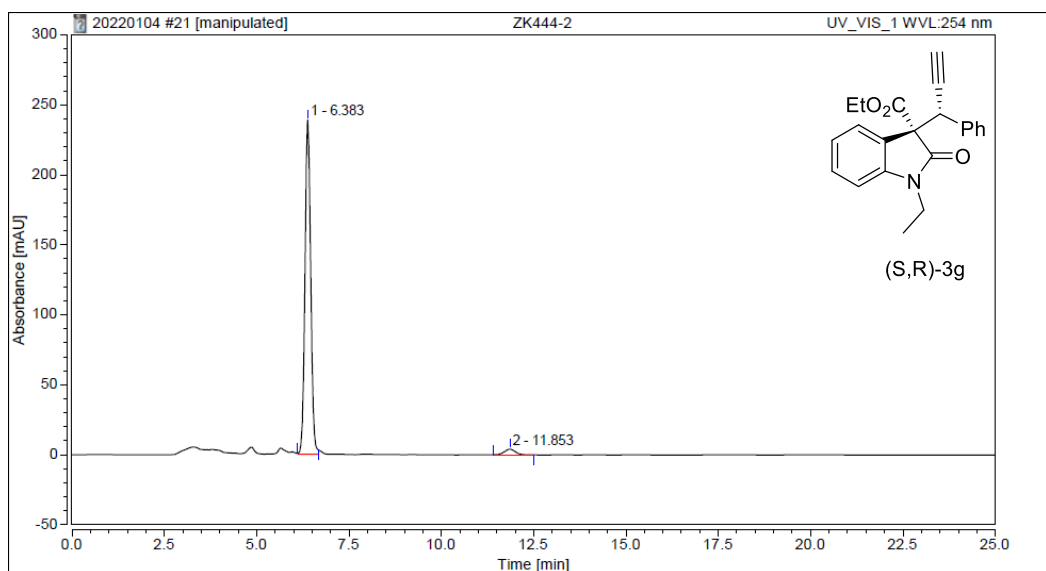
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.720	13.666	79.018	48.68	47.09	n.a.
2		5.467	14.404	88.782	51.32	52.91	n.a.
Total:			28.070	167.800	100.00	100.00	



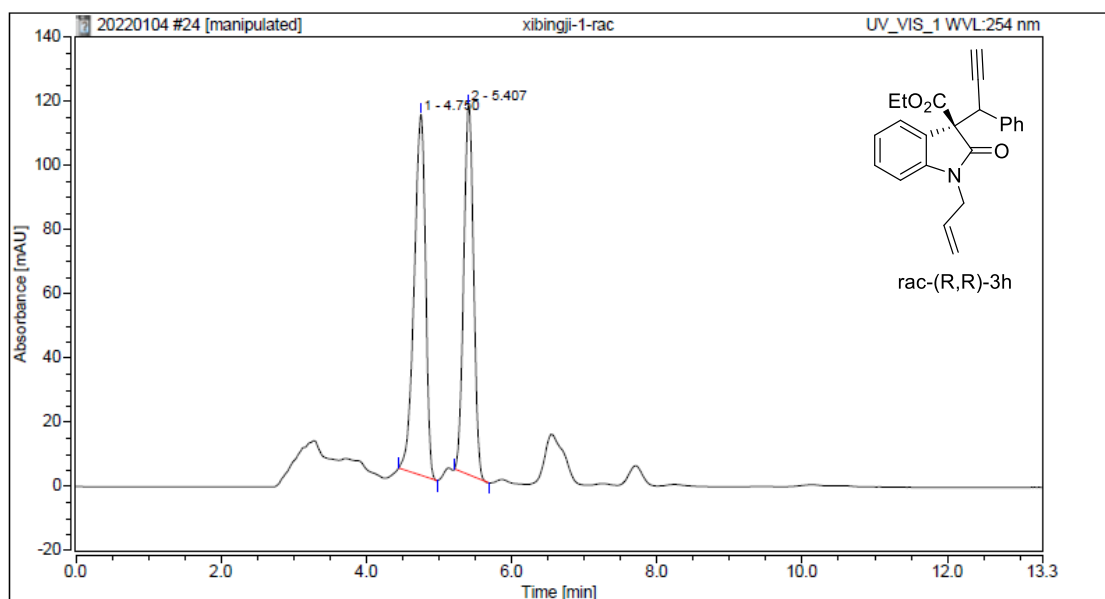
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.887	53.147	286.986	83.54	81.80	n.a.
2		5.660	10.470	63.858	16.46	18.20	n.a.
Total:			63.617	350.844	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.363	23.488	125.912	51.08	66.28	n.a.
2		11.830	22.492	64.071	48.92	33.72	n.a.
Total:			45.979	189.983	100.00	100.00	

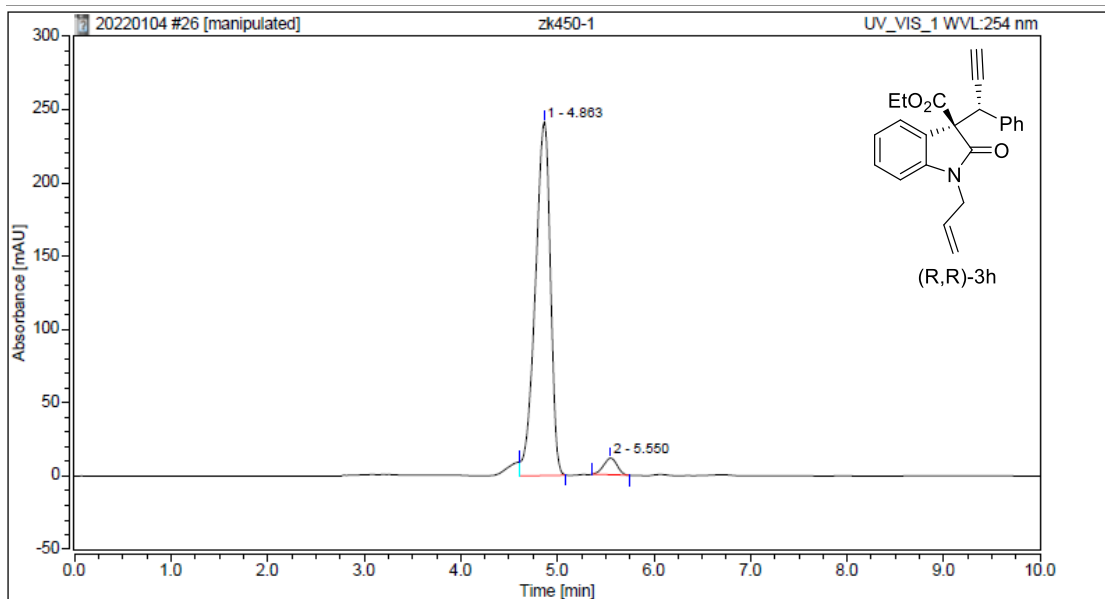


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.383	42.821	238.841	96.84	98.35	n.a.
2		11.853	1.397	4.005	3.16	1.65	n.a.
Total:			44.218	242.846	100.00	100.00	



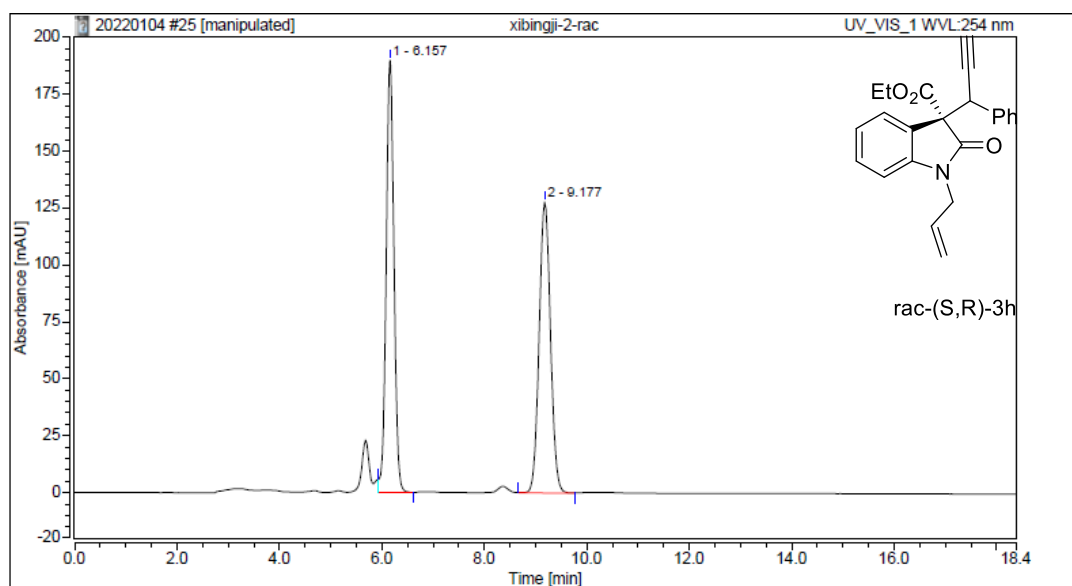
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.750	20.251	112.508	52.86	49.42	n.a.
2		5.407	18.058	115.137	47.14	50.58	n.a.
Total:			38.309	227.645	100.00	100.00	

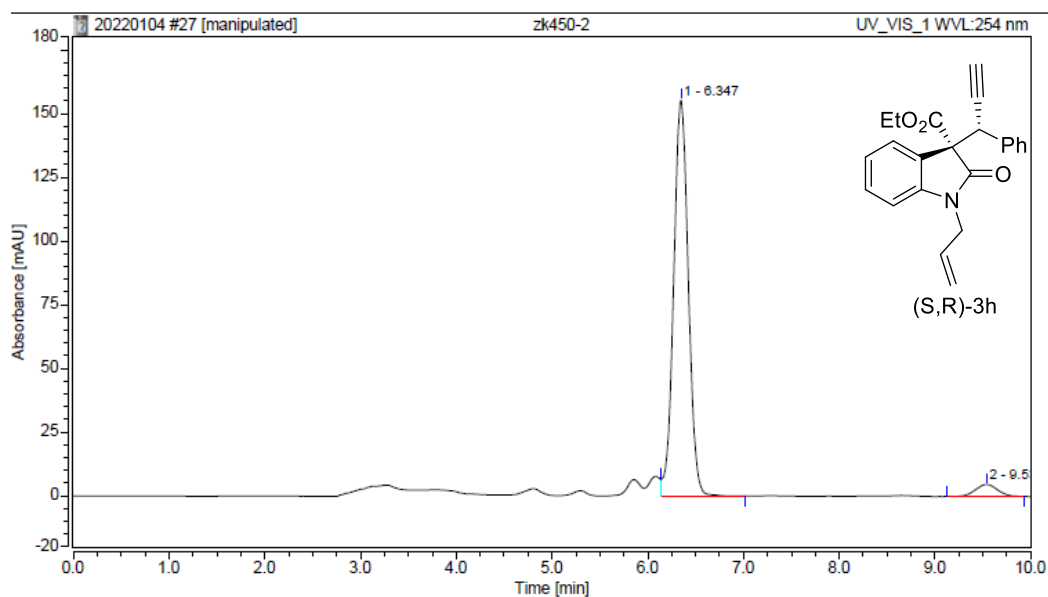


Integration Results

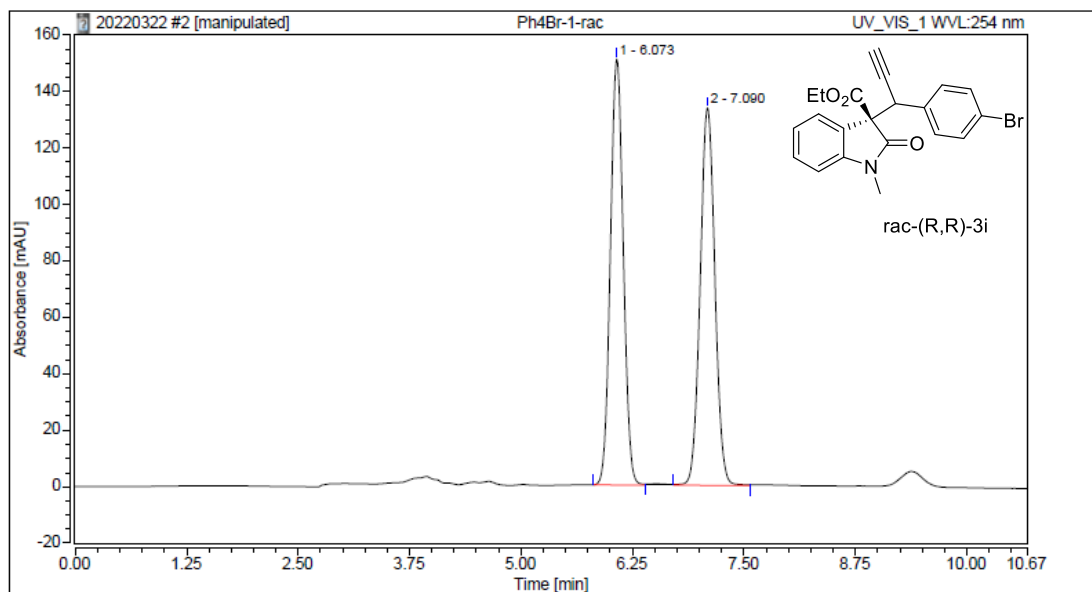
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.863	43.656	241.402	95.97	95.52	n.a.
2		5.550	1.834	11.332	4.03	4.48	n.a.
Total:			45.490	252.734	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.157	33.224	189.840	50.30	59.74	n.a.
2		9.177	32.829	127.951	49.70	40.26	n.a.
Total:			66.052	317.791	100.00	100.00	

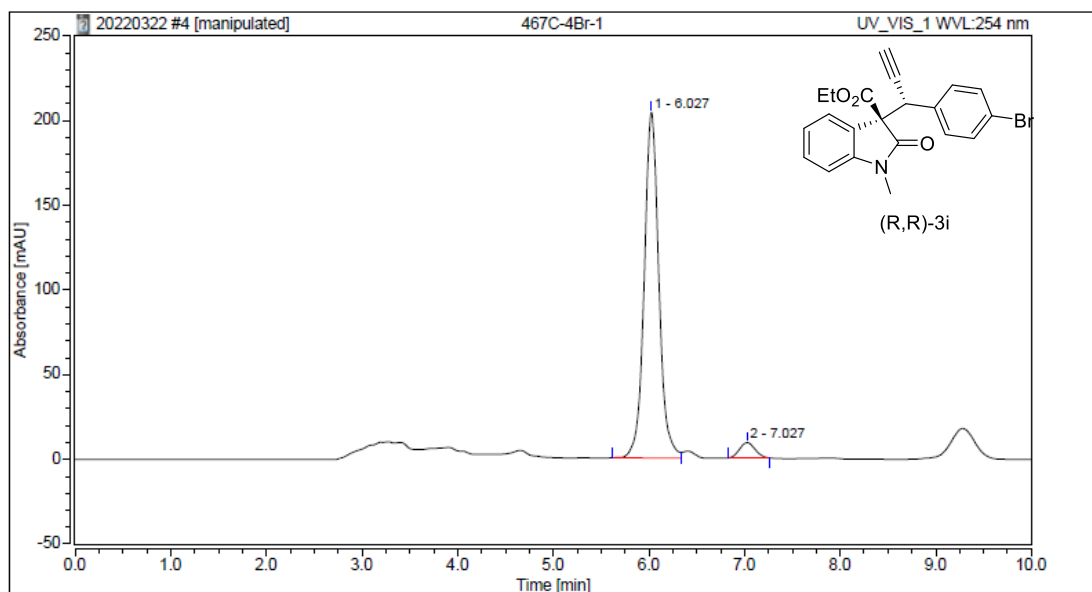


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.347	27.511	155.297	95.63	97.05	n.a.
2		9.537	1.259	4.723	4.37	2.95	n.a.
Total:			28.770	160.019	100.00	100.00	



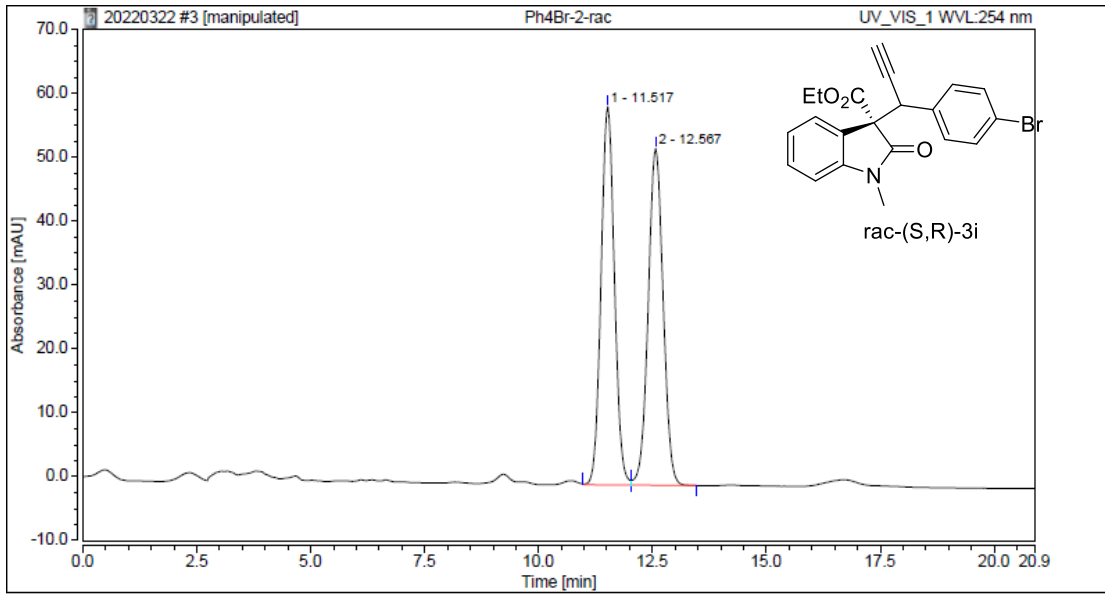
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.073	25.254	150.799	49.64	53.00	n.a.
2		7.090	25.620	133.738	50.36	47.00	n.a.
Total:			50.875	284.537	100.00	100.00	



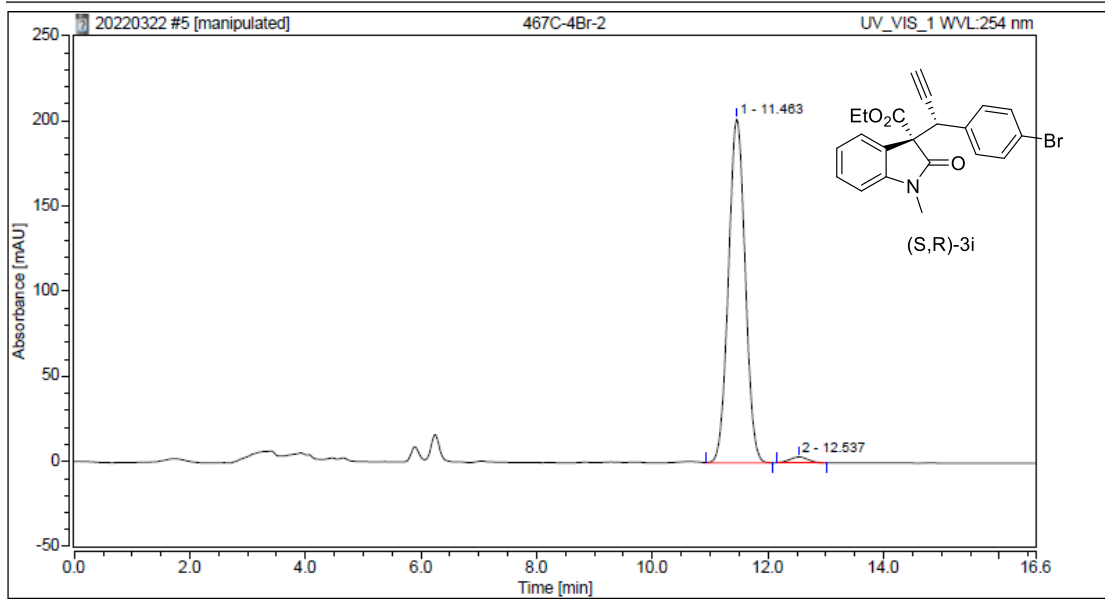
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.027	36.182	204.163	95.47	95.73	n.a.
2		7.027	1.718	9.109	4.53	4.27	n.a.
Total:			37.900	213.272	100.00	100.00	



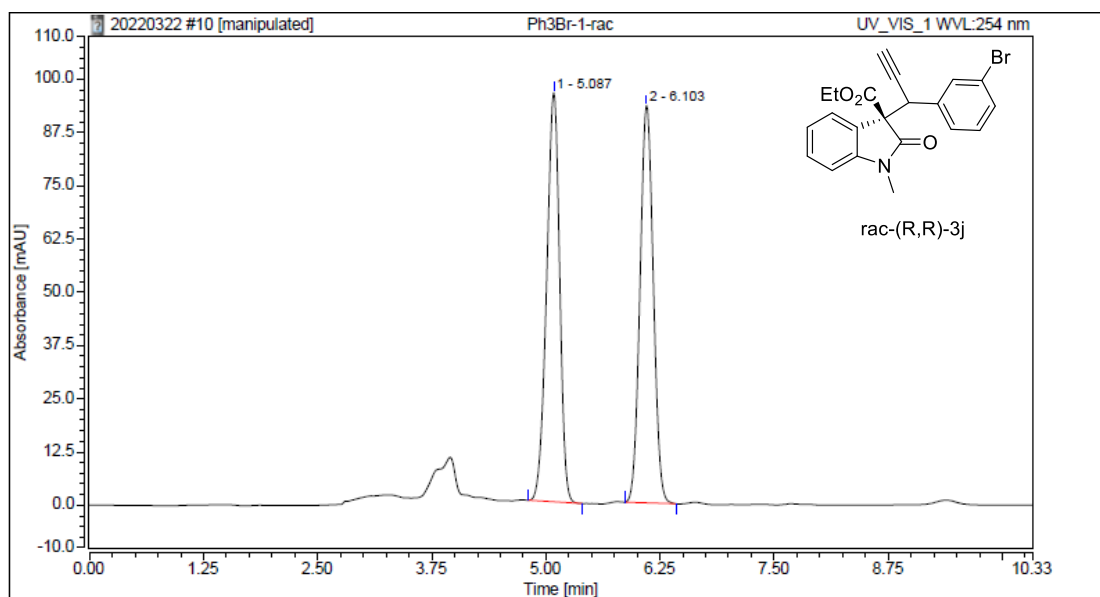
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.517	20.176	59.339	50.15	52.93	n.a.
2		12.567	20.053	52.768	49.85	47.07	n.a.
Total:			40.229	112.107	100.00	100.00	

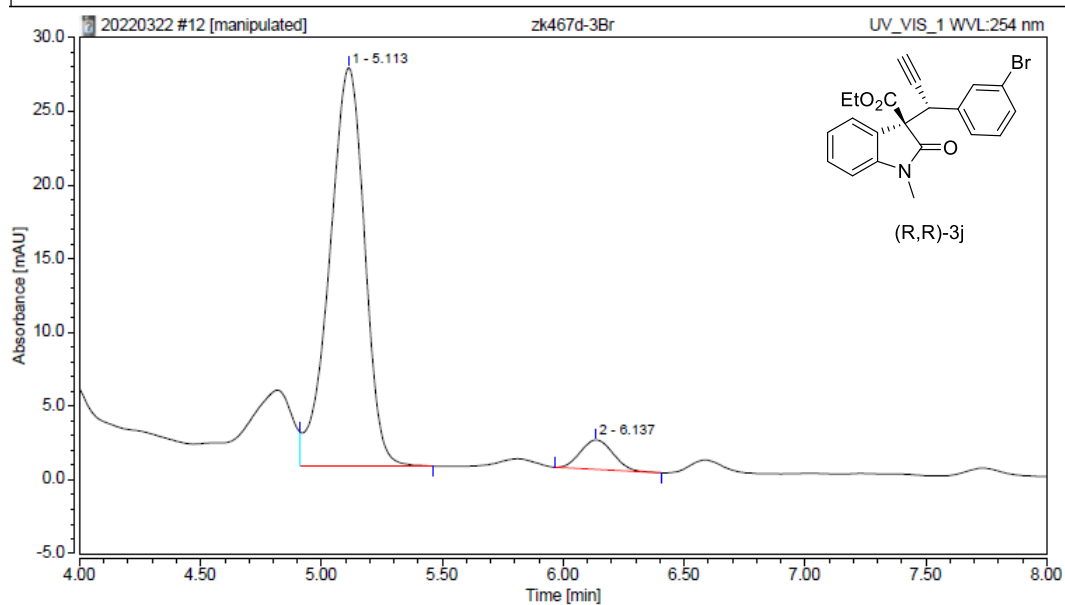


Integration Results

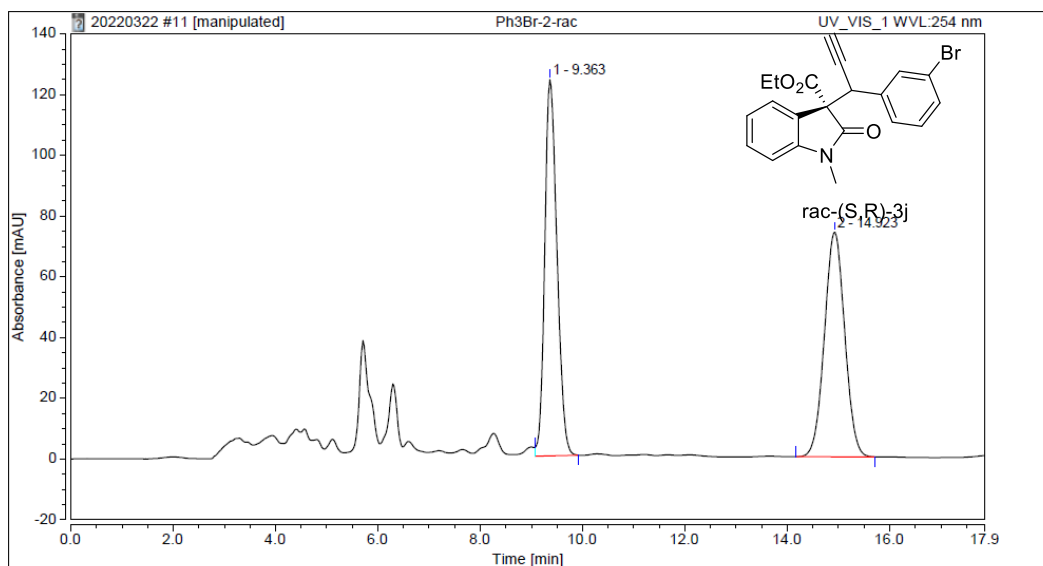
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.463	67.730	202.029	98.23	98.36	n.a.
2		12.537	1.222	3.372	1.77	1.64	n.a.
Total:			68.953	205.401	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.087	15.775	96.021	50.14	50.72	n.a.
2		6.103	15.684	93.288	49.86	49.28	n.a.
Total:			31.459	189.309	100.00	100.00	

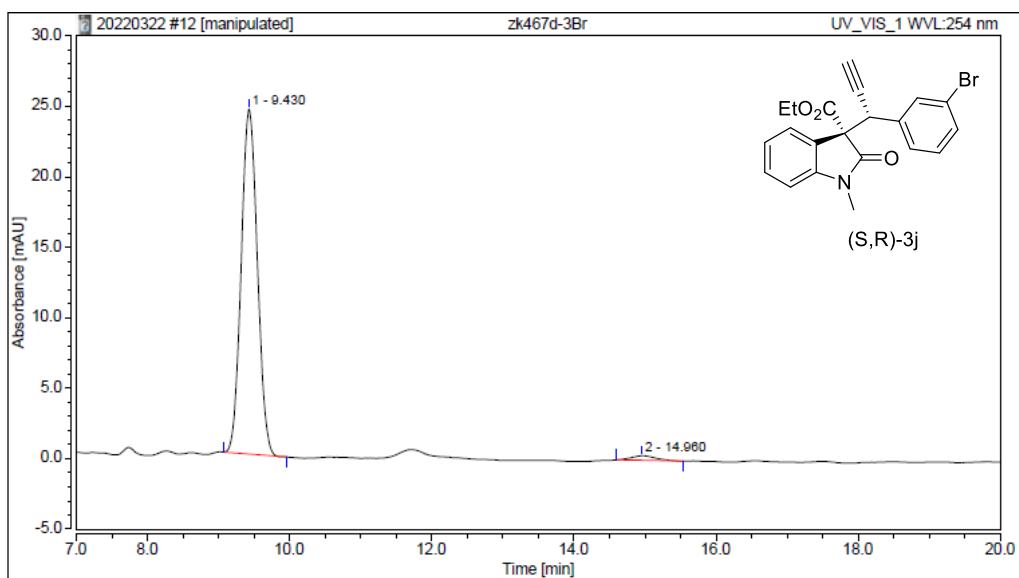


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.113	4.532	27.026	93.61	93.14	n.a.
2		6.137	0.309	1.992	6.39	6.86	n.a.
Total:			4.842	29.018	100.00	100.00	



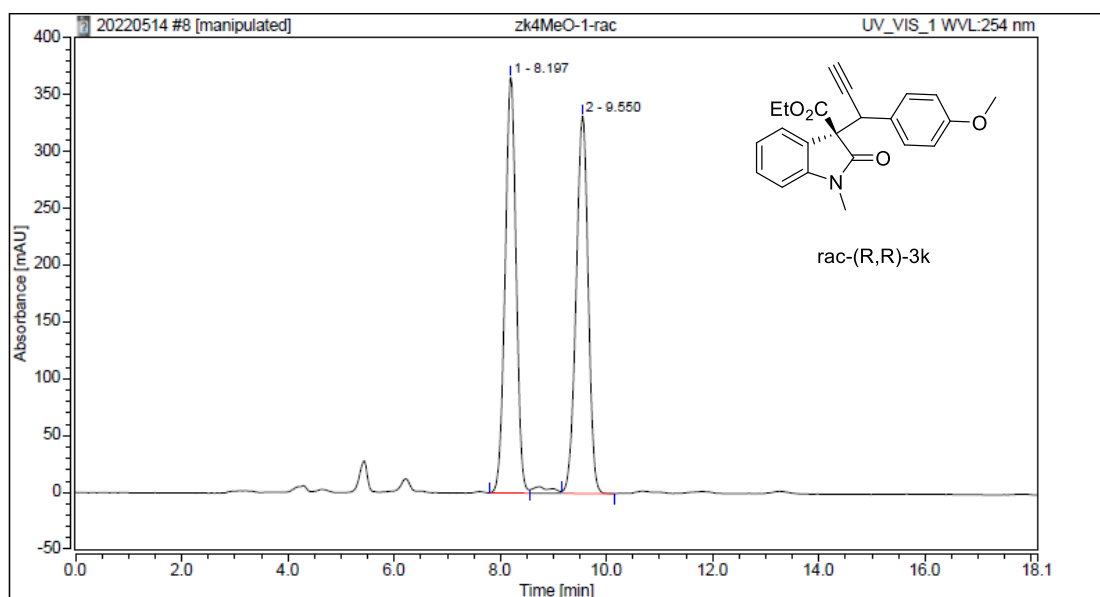
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.363	34.260	123.967	50.21	62.61	n.a.
2		14.923	33.973	74.028	49.79	37.39	n.a.
Total:			68.233	197.996	100.00	100.00	



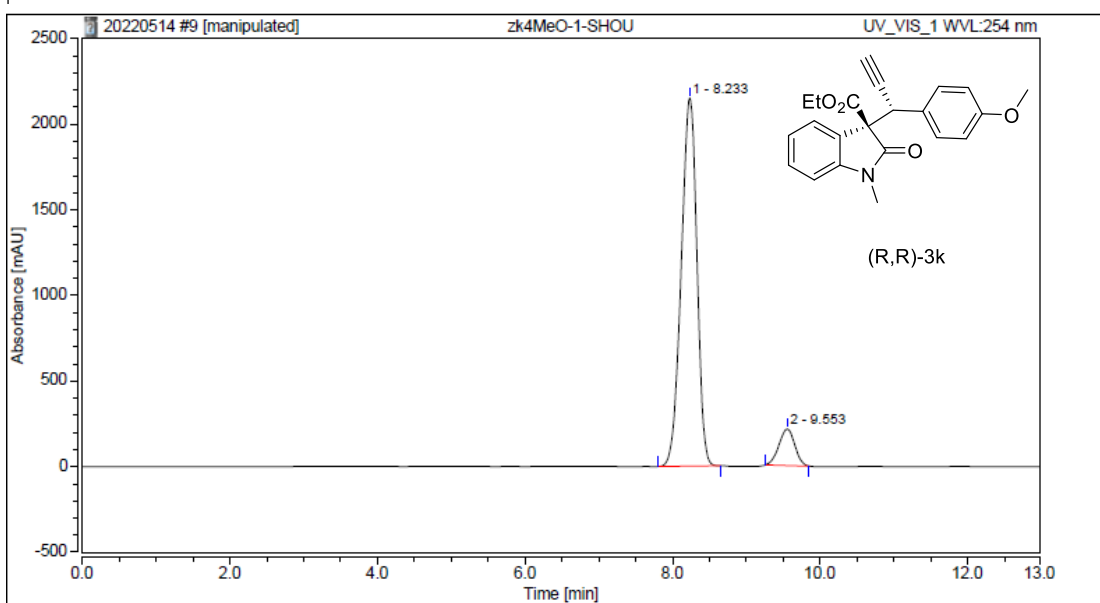
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.430	6.435	24.481	98.05	98.68	n.a.
2		14.960	0.128	0.326	1.95	1.32	n.a.
Total:			6.563	24.807	100.00	100.00	



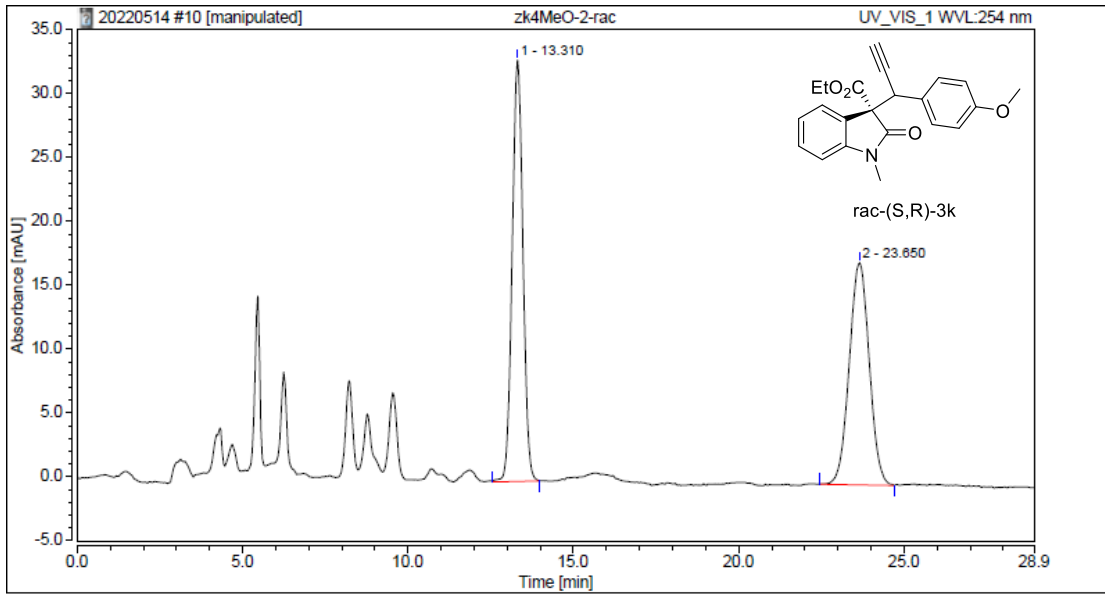
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.197	87.584	365.829	49.99	52.43	n.a.
2		9.550	87.620	331.907	50.01	47.57	n.a.
Total:			175.204	697.736	100.00	100.00	



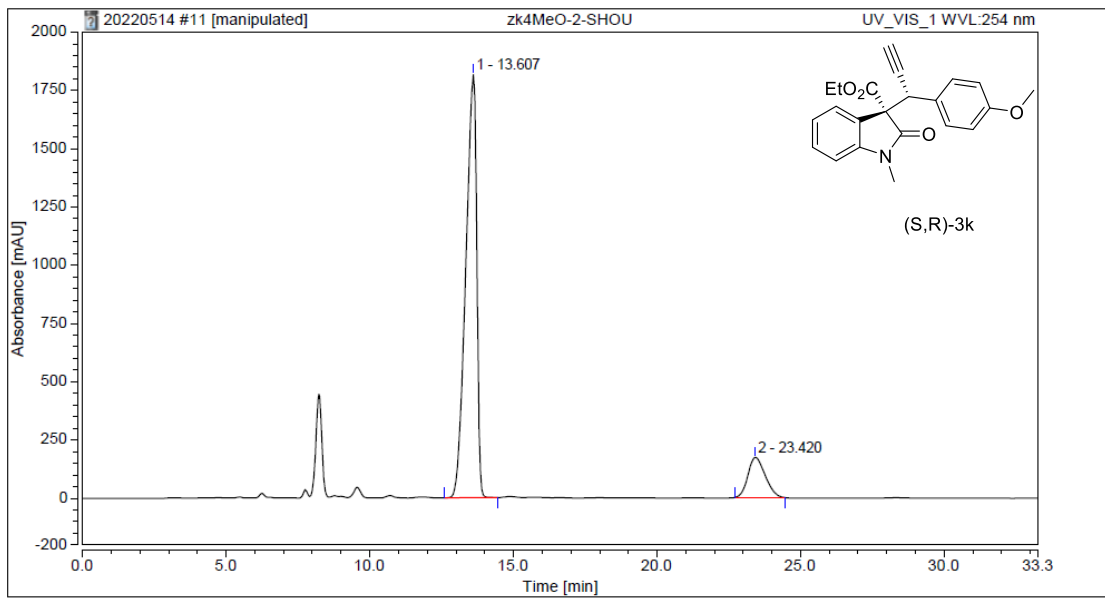
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.233	528.631	2149.837	90.92	91.01	n.a.
2		9.553	52.770	212.276	9.08	8.99	n.a.
Total:			581.401	2362.114	100.00	100.00	



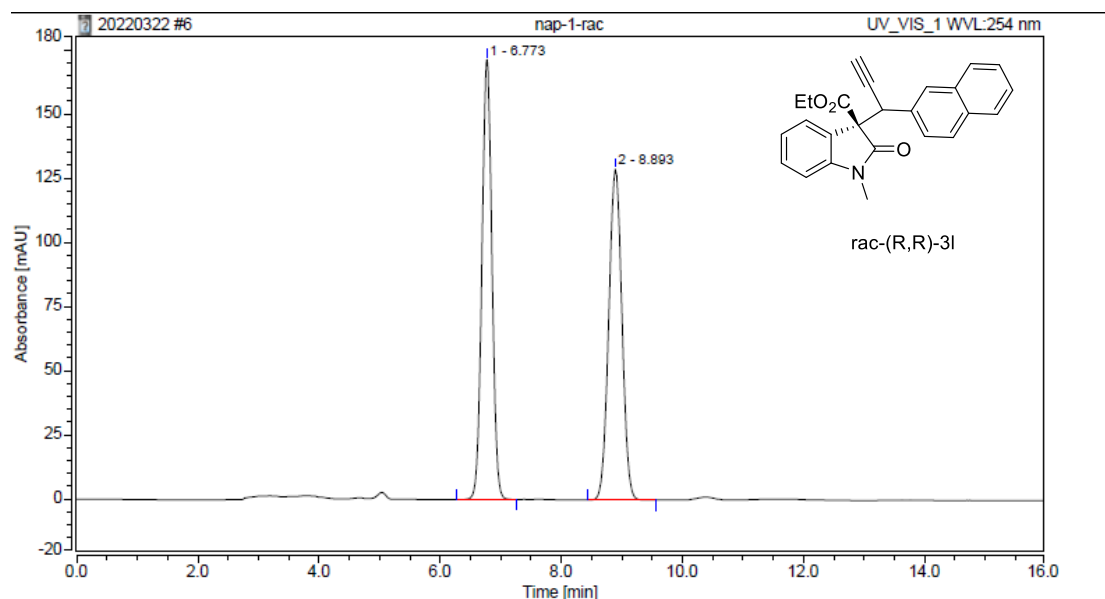
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.310	12.441	32.976	50.51	65.44	n.a.
2		23.650	12.188	17.418	49.49	34.56	n.a.
Total:			24.629	50.393	100.00	100.00	



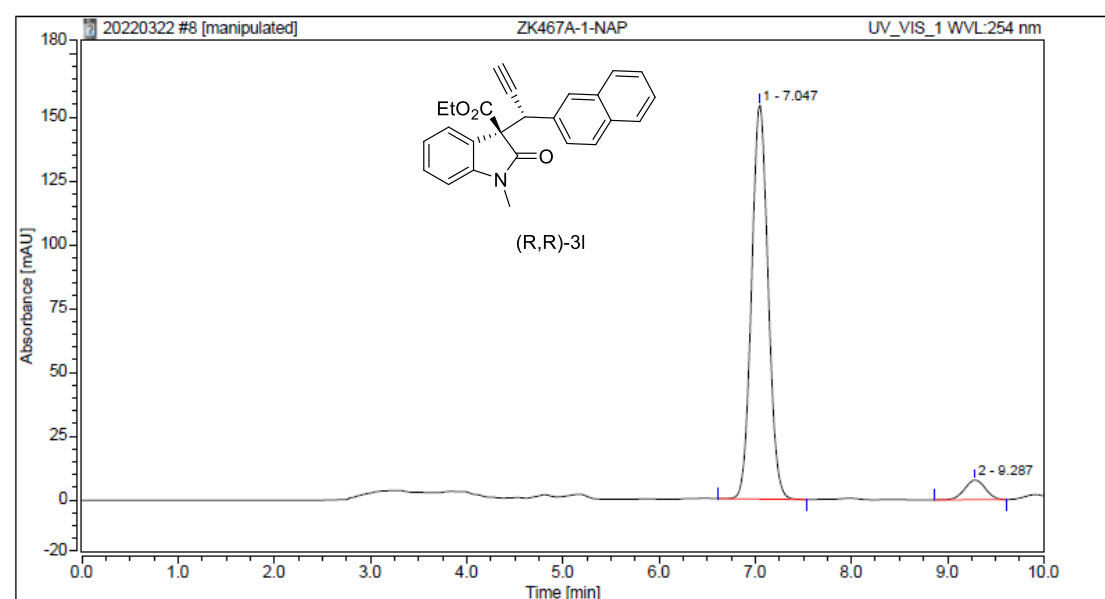
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.607	799.741	1815.027	86.98	91.33	n.a.
2		23.420	119.732	172.390	13.02	8.67	n.a.
Total:			919.474	1987.417	100.00	100.00	



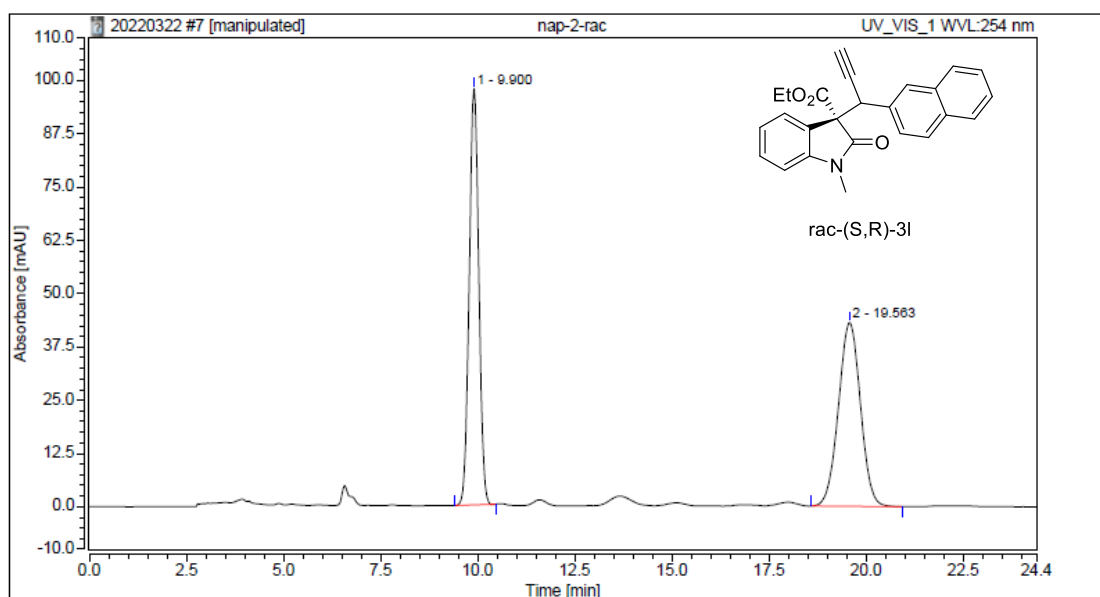
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.773	32.731	171.348	50.25	57.06	n.a.
2		8.893	32.401	128.924	49.75	42.94	n.a.
Total:			65.132	300.272	100.00	100.00	



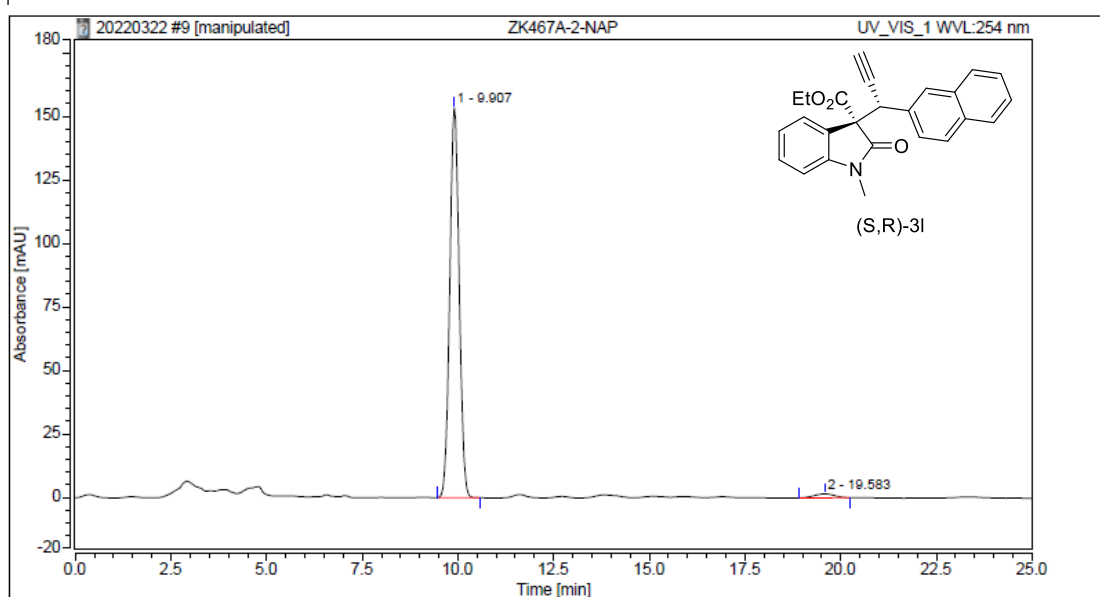
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.047	30.677	154.380	94.12	95.26	n.a.
2		9.287	1.916	7.686	5.88	4.74	n.a.
Total:			32.593	162.066	100.00	100.00	



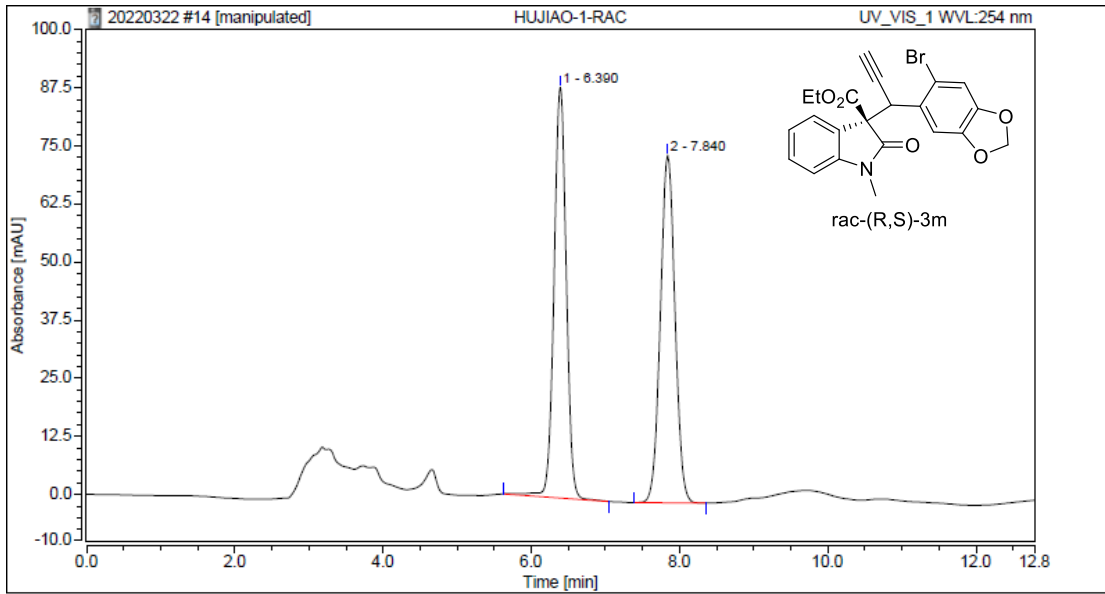
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.900	27.820	97.632	49.58	69.33	n.a.
2		19.563	28.287	43.193	50.42	30.67	n.a.
Total:			56.107	140.825	100.00	100.00	



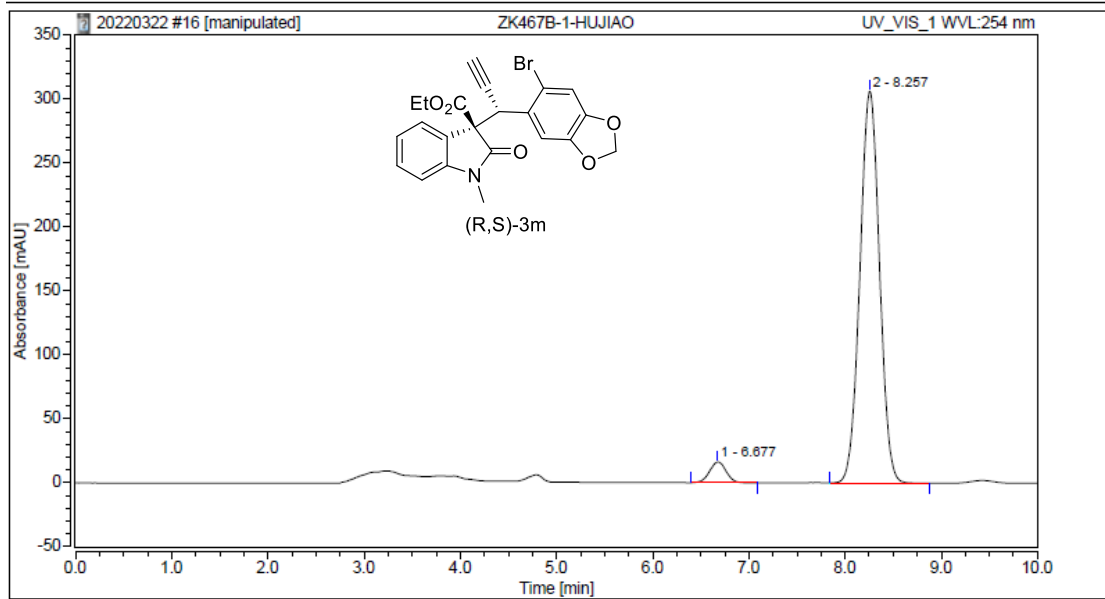
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.907	43.869	153.364	97.89	98.98	n.a.
2		19.583	0.946	1.573	2.11	1.02	n.a.
Total:			44.815	154.937	100.00	100.00	



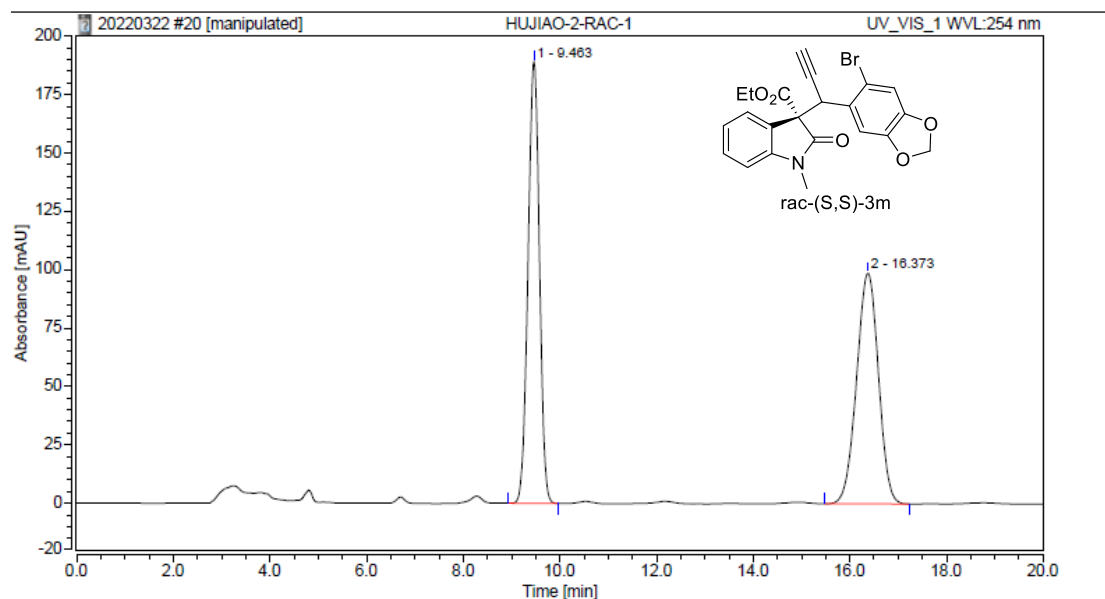
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.390	16.891	88.361	49.67	54.14	n.a.
2		7.840	17.114	74.849	50.33	45.86	n.a.
Total:			34.005	163.211	100.00	100.00	



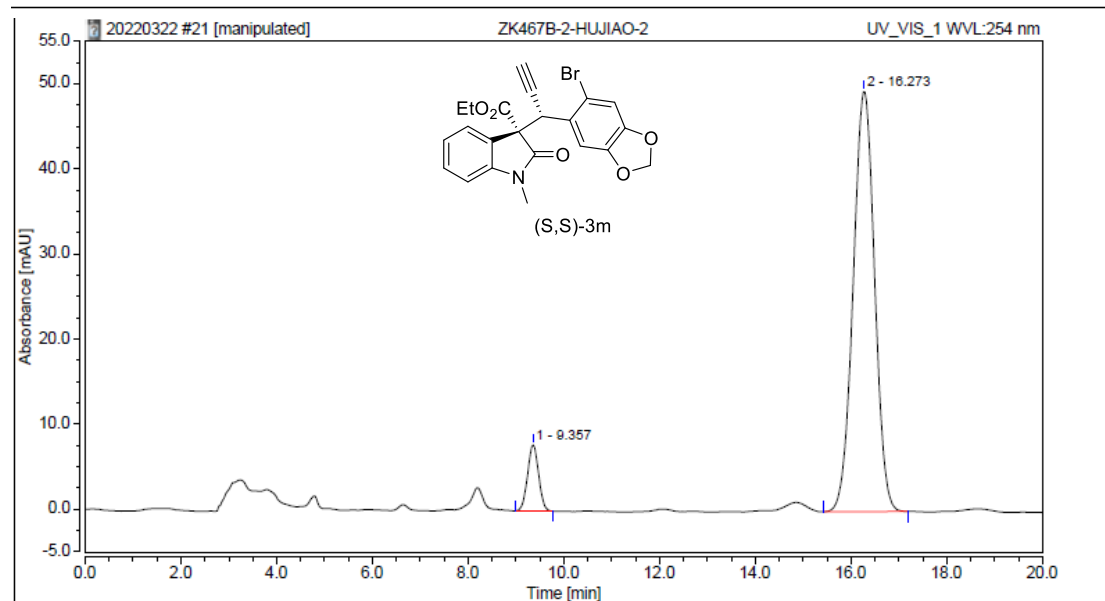
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.677	3.247	16.339	4.31	5.06	n.a.
2		8.257	72.166	306.338	95.69	94.94	n.a.
Total:			75.412	322.676	100.00	100.00	



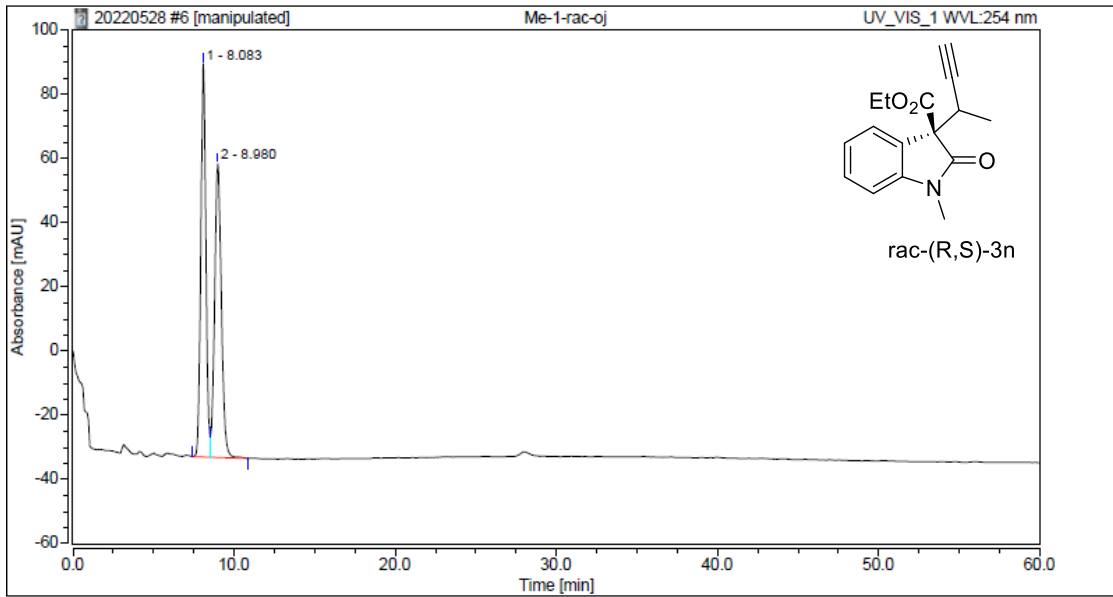
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.463	51.315	189.312	49.81	65.68	n.a.
2		16.373	51.706	98.934	50.19	34.32	n.a.
Total:			103.020	288.245	100.00	100.00	



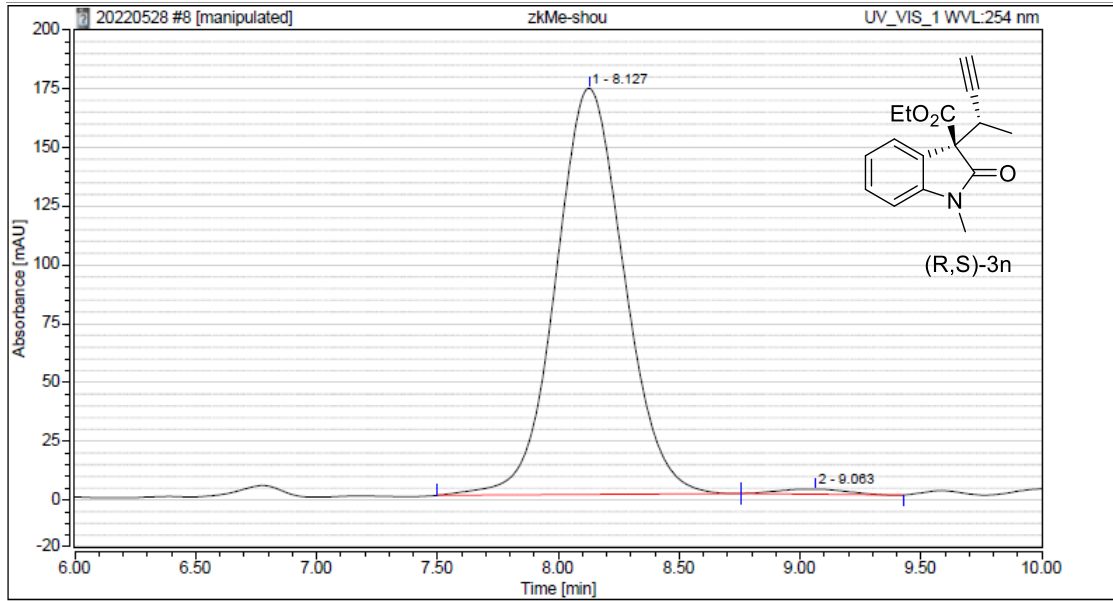
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.357	2.075	7.779	7.52	13.60	n.a.
2		16.273	25.529	49.439	92.48	86.40	n.a.
Total:			27.604	57.218	100.00	100.00	



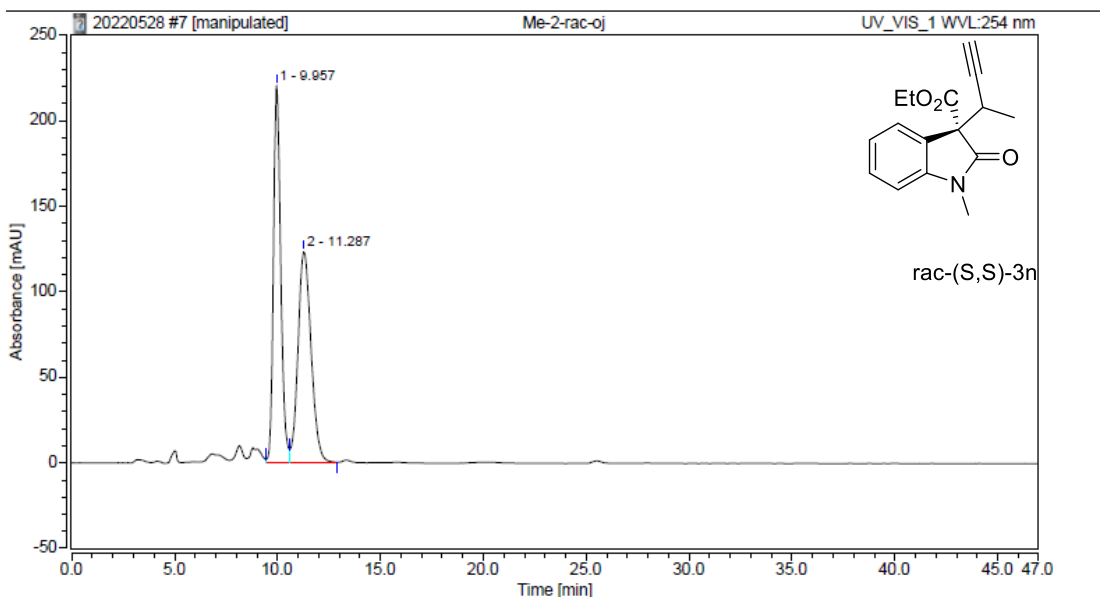
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.083	44.203	122.492	49.66	57.24	n.a.
2		8.980	44.801	91.504	50.34	42.76	n.a.
Total:			89.004	213.997	100.00	100.00	

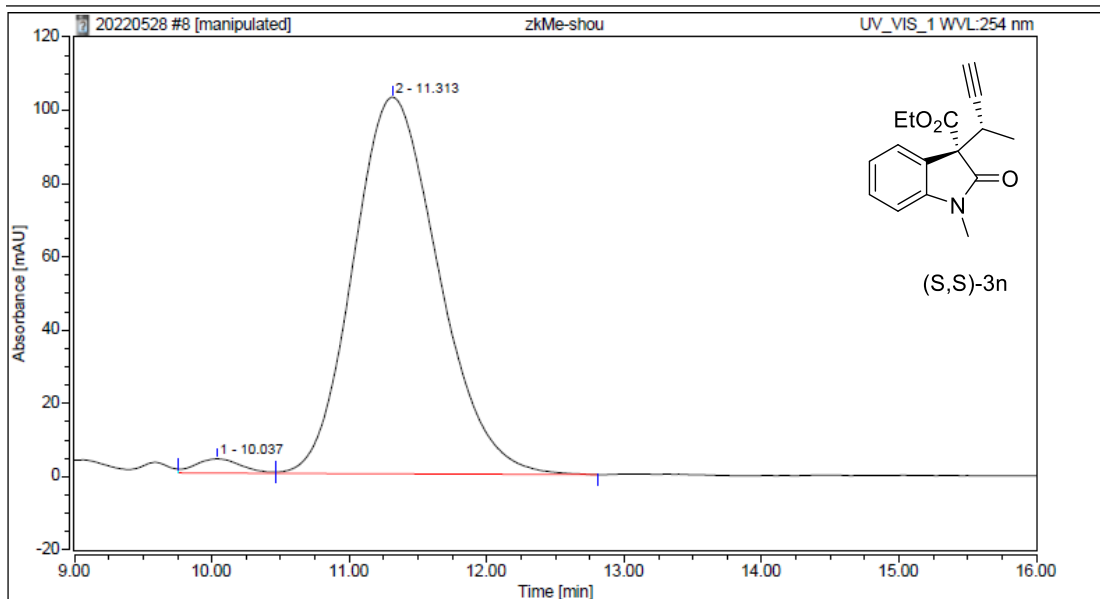


Integration Results

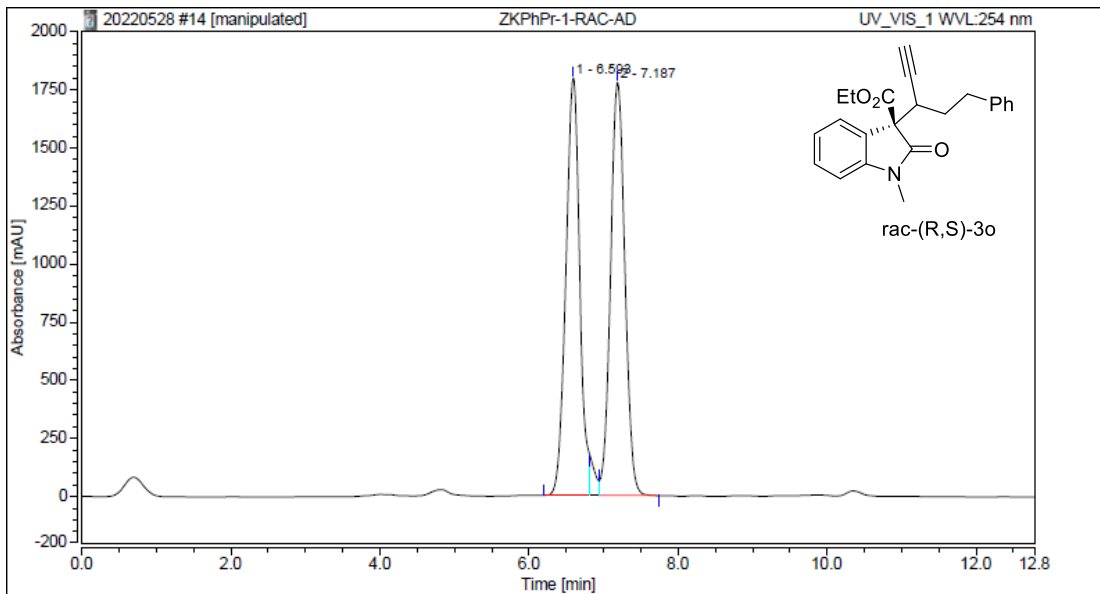
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.127	56.580	172.924	98.81	98.77	n.a.
2		9.063	0.680	2.161	1.19	1.23	n.a.
Total:			57.259	175.084	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.957	90.080	220.536	49.75	64.07	n.a.
2		11.287	90.986	123.667	50.25	35.93	n.a.
Total:			181.066	344.202	100.00	100.00	

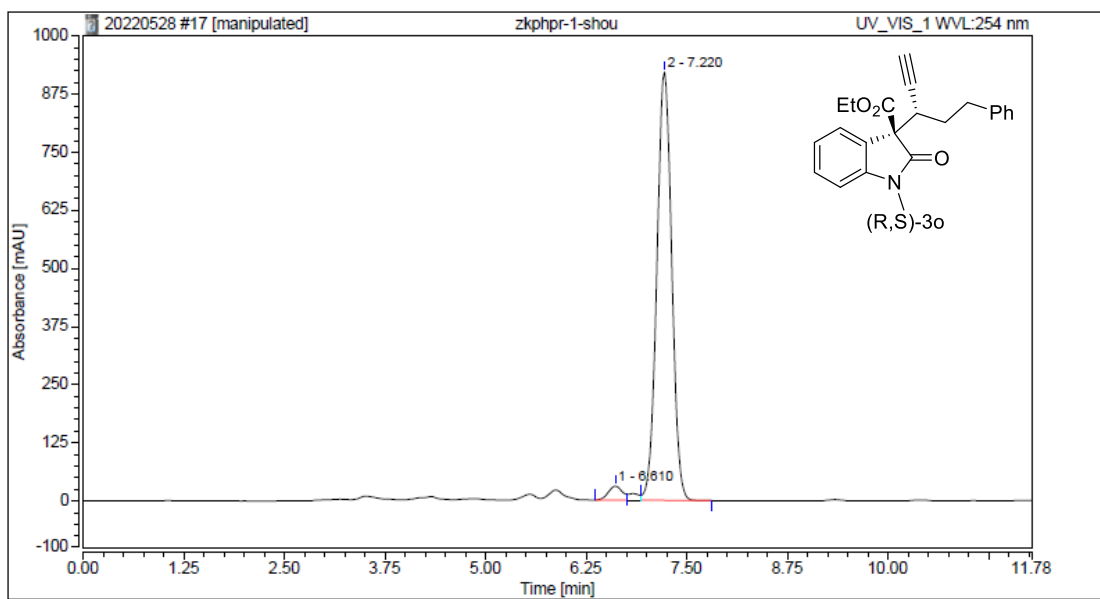


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.037	1.495	3.896	1.98	3.65	n.a.
2		11.313	73.911	102.710	98.02	96.35	n.a.
Total:			75.406	106.606	100.00	100.00	



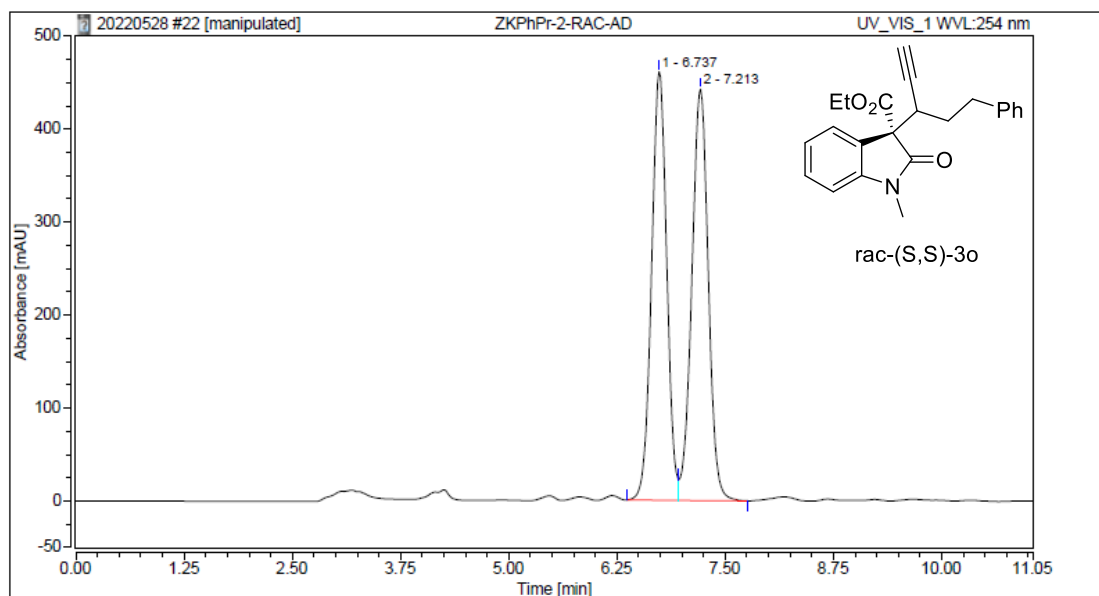
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.593	384.395	1796.578	49.20	50.26	n.a.
2		7.187	396.964	1777.825	50.80	49.74	n.a.
Total:			781.359	3574.404	100.00	100.00	

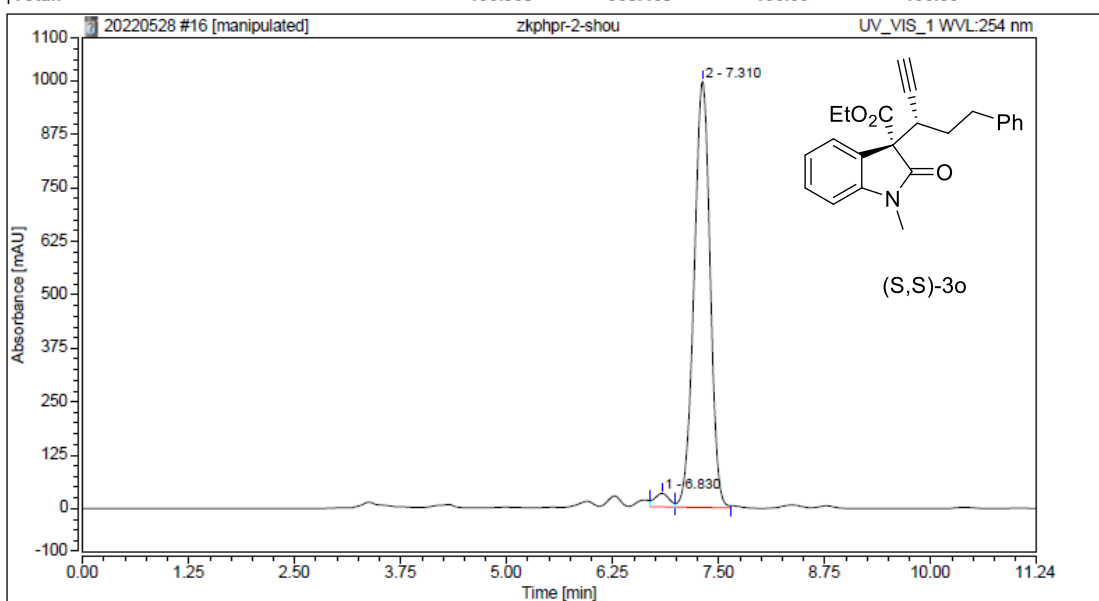


Integration Results

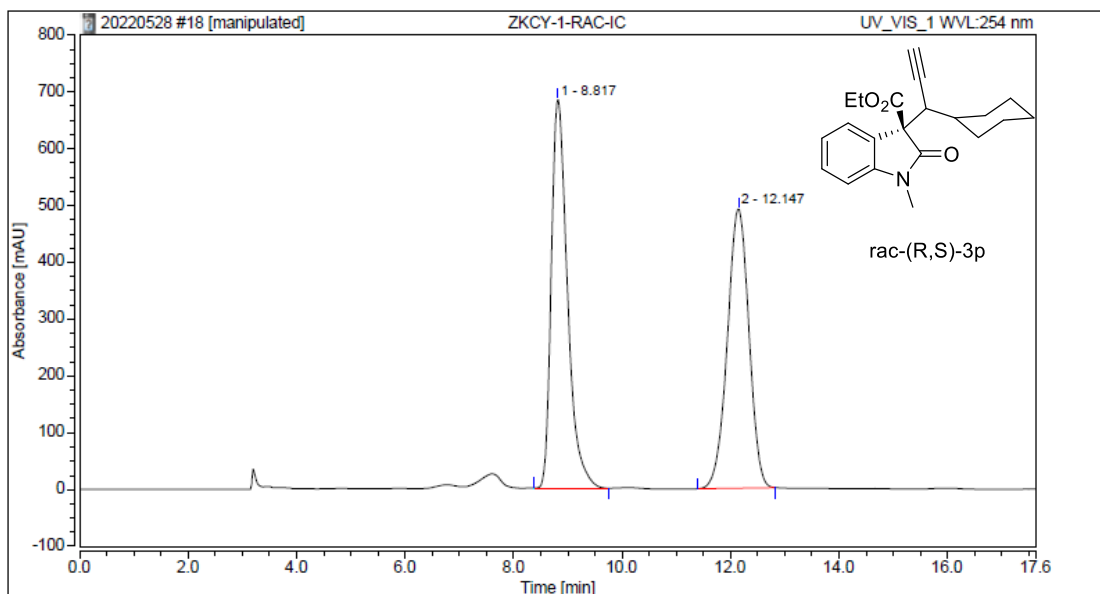
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.610	6.156	30.327	3.03	3.19	n.a.
2		7.220	196.961	921.272	96.97	96.81	n.a.
Total:			203.116	951.599	100.00	100.00	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.737	93.182	460.737	48.91	51.00	n.a.
2		7.213	97.321	442.726	51.09	49.00	n.a.
Total:			190.503	903.463	100.00	100.00	

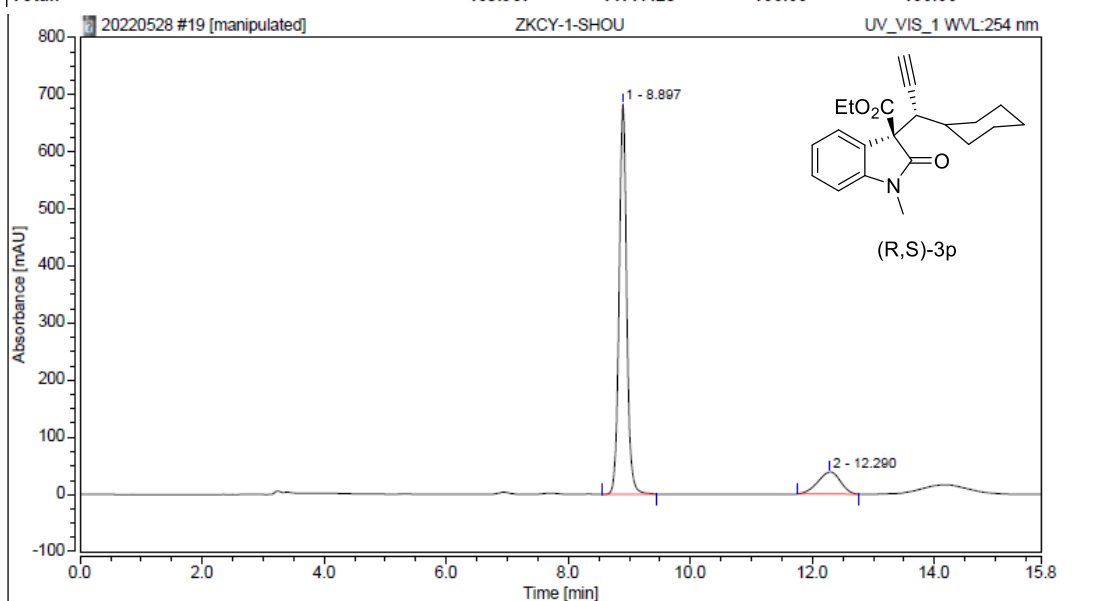


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.830	6.489	31.482	2.88	3.06	n.a.
2		7.310	219.066	995.887	97.12	96.94	n.a.
Total:			225.555	1027.369	100.00	100.00	



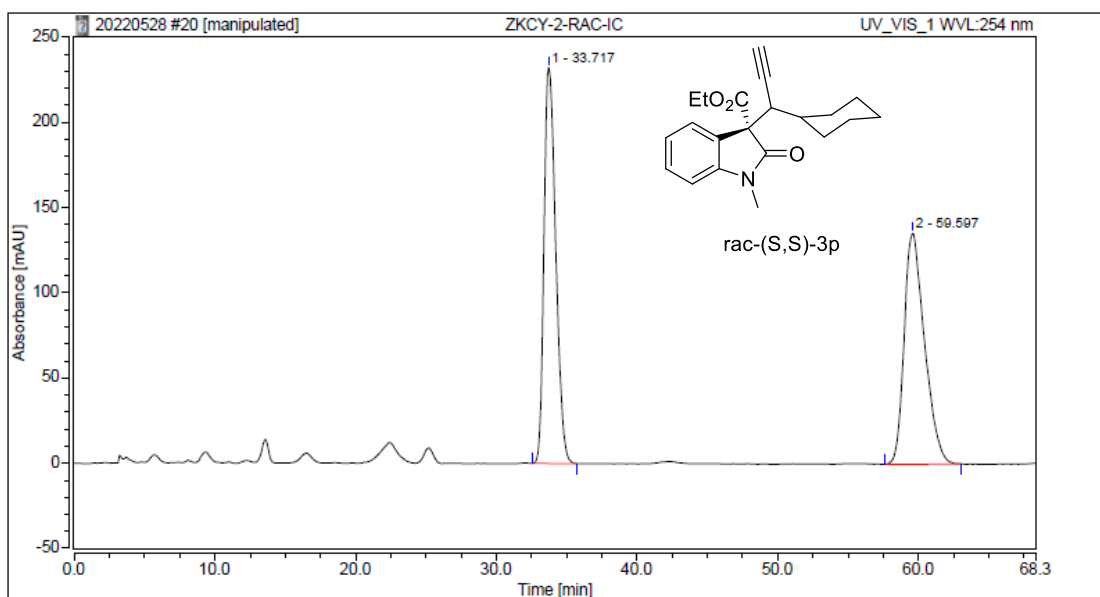
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.817	237.442	685.513	51.17	58.22	n.a.
2		12.147	226.544	491.910	48.83	41.78	n.a.
Total:			463.987	1177.423	100.00	100.00	



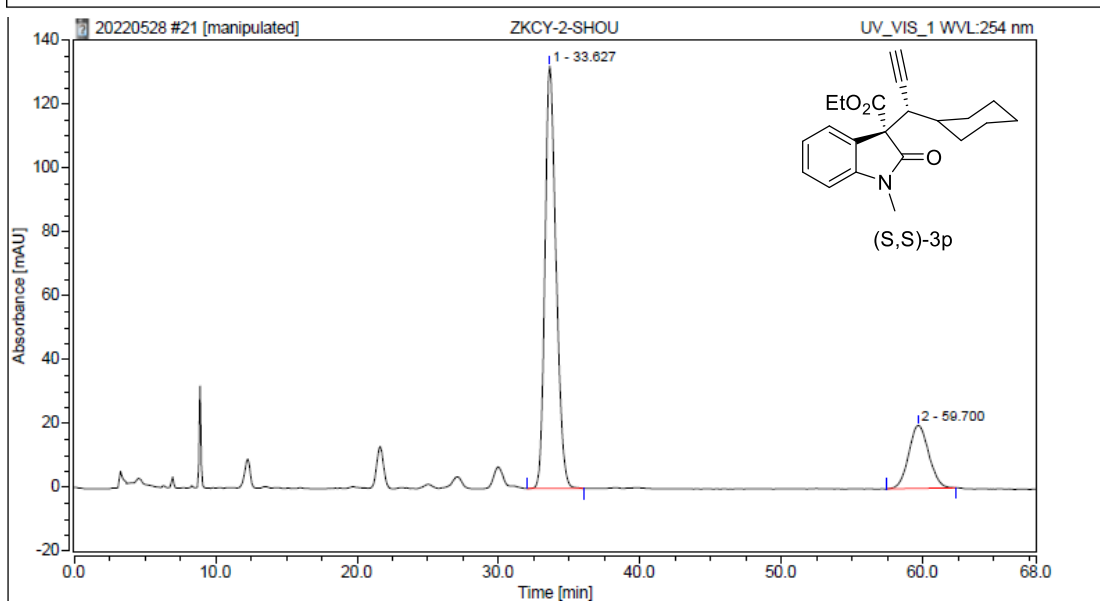
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.897	98.371	682.923	85.60	94.64	n.a.
2		12.290	16.548	38.645	14.40	5.36	n.a.
Total:			114.920	721.568	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.717	224.911	232.325	49.82	63.12	n.a.
2		59.597	226.533	135.769	50.18	36.88	n.a.
Total:			451.445	368.093	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.627	120.314	132.179	78.72	87.02	n.a.
2		59.700	32.518	19.716	21.28	12.98	n.a.
Total:			152.832	151.895	100.00	100.00	