

# Asymmetric Domino 1,6-Addition/Annulation Reaction of 3-Cyano-4-alkenyl-2*H*-chromen-2-ones with Isatin-Derived MBH Carbonates: Enantioselective Synthesis of 3,3'-Cyclopentenylspirooxindoles Bearing 2*H*-Chromen-2-ones

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## Supporting Information

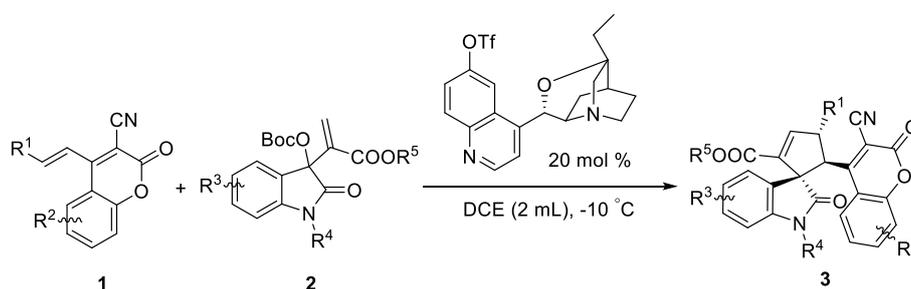
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## 1. General experimental information

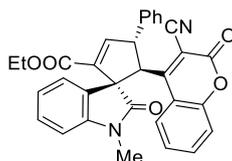
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ( $\text{CDCl}_3$  at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ( $\text{CDCl}_3$  at 77.16 ppm). Melting points of major diastereoisomer were recorded on a Büchi Melting Point B-545. Specific rotation of major diastereoisomer were determined by Perkin Elmer 341

## 2. General procedure for the synthesis of compounds 3.



In an ordinary vial equipped with a magnetic stirring bar, 3-cyano-4-alkenyl-2H-chromen-2-ones **1** (0.1 mmol) and isatin-derived MBH carbonates **2** (0.15 mmol), catalyst **C4** (0.02 mmol, 20 mol%) and dried DCE (2 mL), then the mixture was stirred at 0 °C. After completion of the reaction as indicated by TLC, the product **3** were isolated by flash chromatography on silica gel.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3aa)**



Pale yellow solid, 49.2 mg, 95% yield; 95:5 er;  $[\alpha]_{\text{D}}^{20} = +247.7$  (c. 2.21,  $\text{CH}_2\text{Cl}_2$ ); m.p. 106.8-107.3 °C.

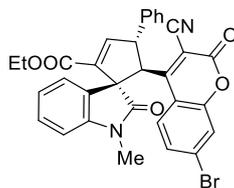
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 12.2$  min (major), 13.7 min (minor).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.76 (d,  $J = 8.2$  Hz, 1H), 7.67-7.46 (m, 4H), 7.43-7.23 (m, 5H), 7.22-6.99 (m, 3H), 6.55 (d,  $J = 7.6$  Hz, 1H), 6.19 (dd,  $J = 9.4, 1.8$  Hz, 1H), 4.83 (d,  $J = 9.4$  Hz, 1H), 4.02 (q,  $J = 7.1$  Hz, 2H), 2.91 (s, 3H), 1.08 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 162.0, 160.2, 156.8, 152.5, 148.7, 143.1, 140.2, 136.3, 135.3, 129.8, 129.4, 128.2, 127.9, 126.3, 125.7, 125.2, 123.1, 117.8, 117.6, 115.5, 108.3, 102.9, 66.5, 61.0, 58.1, 51.7, 26.4, 13.9.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{24}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  539.1577, found: 539.1579.

**Ethyl (1*R*,4*S*,5*S*)-5-(7-bromo-3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ba)**



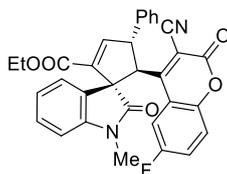
Pale yellow solid, 58.9 mg, 99% yield; 95:5 er;  $[\alpha]_{\text{D}}^{20} = +338.0$  (c. 2.62,  $\text{CHCl}_3$ ); m.p. 88.5-88.9 °C. **HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 9.9$  min (major), 11.7 min (minor).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.68-7.58 (m, 2H), 7.54-7.44 (m, 2H), 7.42-7.31 (m, 4H), 7.30-7.25 (m, 2H), 7.24-7.17 (m, 1H), 7.10 (t,  $J = 7.5$  Hz, 1H), 6.61 (d,  $J = 7.7$  Hz, 1H), 6.16 (dd,  $J = 9.5, 1.9$  Hz, 1H), 4.74 (d,  $J = 9.6$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 2.96 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 161.9, 159.5, 156.2, 152.6, 148.6, 143.1, 140.0, 138.4, 136.5, 130.0, 129.5, 128.7, 128.3, 127.9, 127.4, 126.0, 125.9, 123.2, 120.8, 116.9, 115.4, 108.5, 103.0, 66.5, 61.1, 58.2, 51.7, 26.5, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{BrN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  617.0683, found: 617.0670.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-6-fluoro-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ca)**



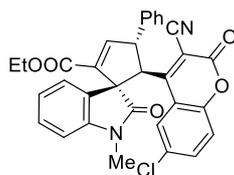
Pale yellow solid, 41.1 mg, 77% yield; 91.5:8.5 er;  $[\alpha]_{\text{D}}^{20} = +287.7$  (c. 1.60,  $\text{CHCl}_3$ ); m.p. 177.5-177.8 °C. **HPLC** (Chiralpak IB column, *i*-propanol/*n*-hexane = 25/75, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 8.7$  min (minor), 9.8 min (major).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.62-7.56 (m, 1H), 7.55-7.48 (m, 3H), 7.43-7.34 (m, 2H), 7.33-7.26 (m, 2H), 7.26-7.23 (m, 1H), 7.22-7.03 (m, 3H), 6.59 (d,  $J = 7.8$  Hz, 1H), 6.16 (dd,  $J = 9.4, 2.1$  Hz, 1H), 4.65 (d,  $J = 9.4$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 2.99 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 161.8, 159.3 (d,  $J = 3.0$  Hz, 1C), 159.0 (d,  $J = 247.5$  Hz, 1C), 157.8, 156.4, 148.6 (d,  $J = 2.0$  Hz, 1C), 148.5, 143.1, 140.0, 136.4, 129.9, 129.4, 128.3, 127.9, 126.0, 125.7, 123.1, 122.6 (d,  $J = 25.3$  Hz, 1C), 119.2 (d,  $J = 9.1$  Hz, 1C), 118.8 (d,  $J = 9.1$  Hz, 1C), 115.1, 112.1 (d,  $J = 27.3$  Hz, 1C), 108.3, 103.9, 66.4, 61.0, 58.4, 51.7, 26.3, 13.9.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{FN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  557.1483, found: 557.1496.

**Ethyl (1*R*,4*S*,5*S*)-5-(6-chloro-3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3da)**



Pale yellow solid, 45.7 mg, 83% yield; 92:8 er;  $[\alpha]_{\text{D}}^{20} = +321.1$  (c. 1.92,  $\text{CHCl}_3$ ); m.p. 197.1-198.3 °C.

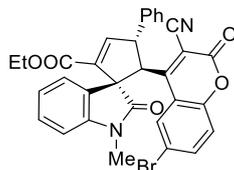
**HPLC** (Chiralpak OD-H column, *i*-propanol/*n*-hexane = 25/75, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.5$  min (minor), 12.5 min (major).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.76 (d,  $J = 2.2$  Hz, 1H), 7.60-7.46 (m, 4H), 7.44-7.35 (m, 2H), 7.35-7.29 (m, 1H), 7.26-7.23 (m, 1H), 7.23-7.16 (m, 1H), 7.15-7.03 (m, 2H), 6.58 (d,  $J = 7.7$  Hz, 1H), 6.17 (dd,  $J = 9.2, 2.1$  Hz, 1H), 4.67 (d,  $J = 9.2$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 3.01 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.3, 161.9, 159.4, 156.3, 150.8, 148.6, 143.1, 140.1, 136.4, 135.1, 131.2, 130.0, 129.5, 128.4, 128.0, 126.1, 125.8, 125.6, 123.2, 119.0, 118.9, 115.1, 108.4, 103.9, 66.5, 61.1, 58.4, 51.7, 26.4, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{ClN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  573,1188, found: 573.1215.

**Ethyl (1R,4S,5S)-5-(6-bromo-3-cyano-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ea)**



Pale yellow solid, 56.3 mg, 95% yield; 89.5:10.5 er;  $[\alpha]_{\text{D}}^{20} = +297.8$  (c. 2.19,  $\text{CHCl}_3$ ); m.p. 186.6-186.9 °C.

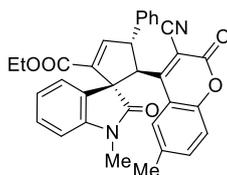
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 15.4$  min (major), 17.6 min (minor).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.90 (d,  $J = 2.0$  Hz, 1H), 7.64 (dd,  $J = 8.8, 2.1$  Hz, 1H), 7.59-7.49 (m, 3H), 7.44-7.35 (m, 2H), 7.34-7.27 (m, 1H), 7.26-7.14 (m, 2H), 7.12-7.01 (m, 2H), 6.59 (d,  $J = 7.7$  Hz, 1H), 6.18 (dd,  $J = 9.2, 2.2$  Hz, 1H), 4.66 (d,  $J = 9.3$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 3.03 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 161.9, 159.3, 156.2, 151.3, 148.6, 143.1, 140.1, 137.9, 136.4, 130.0, 129.5, 128.8, 128.3, 128.0, 126.1, 125.6, 123.2, 119.3, 119.2, 118.3, 115.1, 108.4, 103.9, 66.5, 61.1, 58.4, 51.7, 26.5, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{BrN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  617.0683, found: 617.0688.

**Ethyl (1R,4S,5S)-5-(3-cyano-6-methyl-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3fa)**



Pale yellow solid, 39.5 mg, 75% yield; 95:5 er;  $[\alpha]_{\text{D}}^{20} = +355.2$  (c. 2.80,  $\text{CHCl}_3$ ); m.p. 195.3-196.4 °C.

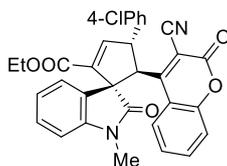
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.5$  min (major), 12.7 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.62-7.49 (m, 4H), 7.42-7.33 (m, 3H), 7.32-7.26 (m, 2H), 7.21-7.14 (m, 1H), 7.11-7.01 (m, 2H), 6.55 (d,  $J = 7.7$  Hz, 1H), 6.20 (dd,  $J = 9.4, 2.1$  Hz, 1H), 4.79 (d,  $J = 9.4$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 2.92 (s, 3H), 2.39 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.3, 162.0, 160.1, 157.1, 150.6, 148.8, 143.0, 140.3, 136.4, 136.3, 135.2, 129.8, 129.4, 128.2, 128.0, 126.3, 126.0, 125.6, 123.1, 117.5, 117.3, 115.7, 108.3, 102.7, 66.5, 61.0, 58.0, 51.6, 26.2, 21.0, 13.9.

**HRMS (ESI)** calcd. for  $\text{C}_{33}\text{H}_{26}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  553,1734, found: 553.1747.

**Ethyl (1R,4S,5S)-4-(4-chlorophenyl)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ga)**



Pale yellow solid, 27.2 mg, 50% yield; 92:8 er;  $[\alpha]_{\text{D}}^{20} = 241.9$  (c. 1.20,  $\text{CHCl}_3$ ); m.p. 198.9-199.5 °C.

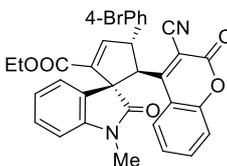
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 12.0$  min (major), 15.0 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.77-7.68 (m, 1H), 7.62-7.52 (m, 2H), 7.51-7.41 (m, 2H), 7.40-7.27 (m, 3H), 7.24-7.14 (m, 3H), 7.14-7.04 (m, 1H), 6.55 (d,  $J = 7.7$  Hz, 1H), 6.15 (dd,  $J = 9.3, 2.2$  Hz, 1H), 4.74 (d,  $J = 9.3$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 2.92 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 161.9, 160.0, 156.8, 152.6, 148.0, 143.1, 138.8, 136.9, 135.5, 134.2, 130.0, 129.7, 129.4, 126.2, 126.1, 125.8, 125.3, 123.2, 117.8, 117.7, 115.5, 108.4, 102.9, 66.6, 61.2, 58.1, 51.2, 26.4, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{ClN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  573,1188, found: 573.1206.

**Ethyl (1R,4S,5S)-4-(4-bromophenyl)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ha)**



Pale yellow solid, 36.3 mg, 61% yield; 92:8 er;  $[\alpha]_{\text{D}}^{20} = +327.6$  (c. 0.83,  $\text{CHCl}_3$ ); m.p. 115.1-115.8 °C.

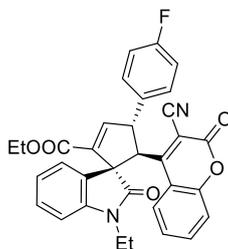
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 12.8$  min (major), 15.8 min (minor).

**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.72 (d,  $J = 8.3$  Hz, 1H), 7.62-7.52 (m, 2H), 7.52-7.45 (m, 2H), 7.44-7.36 (m, 2H), 7.33-7.26 (m, 1H), 7.24-7.14 (m, 3H), 7.09 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.55 (d,  $J = 7.7$  Hz, 1H), 6.14 (dd,  $J = 9.3, 2.1$  Hz, 1H), 4.74 (d,  $J = 9.4$  Hz, 1H), 4.03 (q,  $J = 7.1$  Hz, 2H), 2.92 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.2, 161.9, 159.9, 156.8, 152.6, 147.9, 143.1, 139.3, 136.9, 135.5, 132.6, 130.0, 129.7, 126.2, 126.1, 125.7, 125.3, 123.2, 122.3, 117.8, 115.5, 108.4, 102.9, 66.6, 61.2, 58.1, 51.2, 26.4, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{BrN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  617.0683, found: 617.0705.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-4-(4-fluorophenyl)-1'-ethyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ik)**



Pale yellow solid, 17.5 mg, 32% yield; 94:6 er;  $[\alpha]_{\text{D}}^{20} = 225.4$  (c. 0.87,  $\text{CH}_2\text{Cl}_2$ ); m.p. 159.3-160.2 °C.

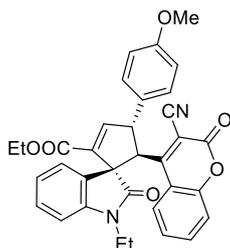
**HPLC** (Chiralpak IA column, EtOH/*n*-hexane = 15/85, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 11.6$  min (major), 13.2 min (minor).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.81 (d,  $J = 8.1$  Hz, 1H), 7.63 (d,  $J = 7.4$  Hz, 1H), 7.58 (t,  $J = 7.8$  Hz, 1H), 7.54-7.45 (m, 2H), 7.34-7.27 (m, 1H), 7.26-7.16 (m, 3H), 7.14-7.00 (m, 3H), 6.61 (d,  $J = 7.8$  Hz, 1H), 6.15 (dd,  $J = 9.5, 2.0$  Hz, 1H), 4.79 (d,  $J = 9.6$  Hz, 1H), 4.11-3.96 (m, 2H), 3.58 (dq,  $J = 14.4, 7.2$  Hz, 1H), 3.44 (dq,  $J = 14.2, 7.1$  Hz, 1H), 1.09 (t,  $J = 7.1$  Hz, 3H), 0.86 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.6, 162.6 (d,  $J = 248.3$  Hz, 1C), 161.9, 159.9, 156.8, 152.6, 148.3, 142.3, 137.0, 135.9 (d,  $J = 3.2$  Hz, 1C), 135.4, 130.0, 129.6 (d,  $J = 8.3$  Hz, 1C), 126.4, 126.2, 126.2, 125.5, 122.9, 117.9, 117.7, 116.3 (d,  $J = 21.7$  Hz, 1C), 115.6, 108.5, 103.0, 66.4, 61.1, 58.0, 51.0, 35.0, 14.0, 11.9.

**HRMS (ESI)** calcd. for  $\text{C}_{33}\text{H}_{25}\text{FN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  571.1640, found: 571.1645.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-4-(4-methoxyphenyl)-1'-ethyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3jk)**



Pale yellow solid, 24.3 mg, 43% yield; 97:3 er;  $[\alpha]_D^{20} = +243.0$  (c. 1.20,  $\text{CH}_2\text{Cl}_2$ ); m.p. 102.3-103.4 °C.

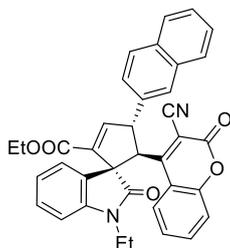
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 9.8$  min (major), 14.0 min (minor).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.85 (d,  $J = 8.3$  Hz, 1H), 7.65 (d,  $J = 7.4$  Hz, 1H), 7.61-7.53 (m, 1H), 7.45 (d,  $J = 8.7$  Hz, 2H), 7.35-7.15 (m, 4H), 7.09 (t,  $J = 7.6$  Hz, 1H), 6.89 (d,  $J = 8.7$  Hz, 2H), 6.61 (d,  $J = 7.7$  Hz, 1H), 6.13 (dd,  $J = 9.6, 1.9$  Hz, 1H), 4.83 (d,  $J = 9.7$  Hz, 1H), 4.10-3.97 (m, 2H), 3.77 (s, 3H), 3.59 (dq,  $J = 14.5, 7.2$  Hz, 1H), 3.44 (dq,  $J = 14.3, 7.1$  Hz, 1H), 1.09 (t,  $J = 7.1$  Hz, 3H), 0.85 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.7, 162.0, 160.2, 159.5, 156.9, 152.6, 149.0, 142.3, 136.4, 135.2, 132.0, 129.8, 129.0, 126.5, 126.3, 126.2, 125.4, 122.8, 118.0, 117.6, 115.6, 114.8, 108.4, 103.0, 66.3, 61.0, 58.0, 55.4, 51.0, 34.9, 14.0, 11.9.

**HRMS (ESI)** calcd. for  $\text{C}_{34}\text{H}_{28}\text{N}_2\text{NaO}_6$   $[\text{M} + \text{Na}]^+$  583.1840, found: 583.1853.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-4-(naphthalen-2-yl)-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3mk)**



Pale yellow solid, 23.6 mg, 41% yield; 95.5:4.5 er;  $[\alpha]_D^{20} = +201.2$  (c. 1.18,  $\text{CH}_2\text{Cl}_2$ ); m.p. 225.5-225.8 °C.

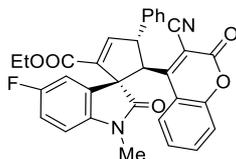
**HPLC** (Chiralpak OD-H column, *i*-propanol/*n*-hexane = 5/95, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 39.6$  min (minor), 44.8 min (major).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.96 (s, 1H), 7.93-7.79 (m, 4H), 7.76-7.65 (m, 2H), 7.60-7.44 (m, 3H), 7.37 (d,  $J = 2.1$  Hz, 1H), 7.32-7.21 (m, 2H), 7.20-7.07 (m, 2H), 6.64 (d,  $J = 7.7$  Hz, 1H), 6.37 (dd,  $J = 9.6, 2.0$  Hz, 1H), 4.99 (d,  $J = 9.7$  Hz, 1H), 4.09 (qt,  $J = 7.1, 3.6$  Hz, 2H), 3.62 (dq,  $J = 14.5, 7.3$  Hz, 1H), 3.46 (dq,  $J = 14.3, 7.1$  Hz, 1H), 1.13 (t,  $J = 7.1$  Hz, 3H), 0.87 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.7, 162.0, 160.0, 157.0, 152.6, 148.6, 142.4, 137.4, 137.0, 135.3, 133.5, 133.1, 130.0, 129.6, 128.0, 127.8, 127.2, 126.7, 126.6, 126.5, 126.4, 126.3, 125.5, 125.3, 123.0, 118.0, 117.6, 115.8, 108.5, 103.1, 66.5, 61.1, 57.8, 51.9, 35.0, 14.0, 11.9.

**HRMS (ESI)** calcd. for  $\text{C}_{37}\text{H}_{28}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  603.1890, found: 603.1873.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-5'-fluoro-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ab)**



Pale yellow solid, 54.1 mg, 99% yield; >20:1 dr, 93:7 er;  $[\alpha]_{\text{D}}^{20} = +289.5$  (c. 2.08,  $\text{CHCl}_3$ ); m.p. 213.6-214.2 °C.

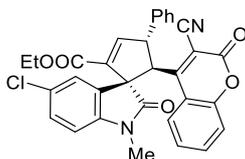
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 12.2$  min (major), 13.7 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.78-7.71 (m, 1H), 7.62-7.54 (m, 1H), 7.53-7.46 (m, 2H), 7.44-7.32 (m, 3H), 7.32-7.26 (m, 3H), 7.22-7.14 (m, 1H), 6.92 (td,  $J = 8.7, 2.6$  Hz, 1H), 6.52 (dd,  $J = 8.6, 4.0$  Hz, 1H), 6.16 (dd,  $J = 9.5, 2.2$  Hz, 1H), 4.83 (d,  $J = 9.6$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 2.92 (s, 3H), 1.12 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  177.0, 161.9, 160.6, 159.9, 157.4, 156.8, 152.6, 149.1, 139.9, 139.2, 139.2, 136.1, 135.5, 129.5, 128.3, 127.9, 127.8, 126.2, 125.3, 117.8, 117.8, 116.4, 116.1, 115.5, 114.4, 114.0, 109.0, 108.9, 103.0, 66.7, 61.2, 57.8, 51.8, 26.6, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{FN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  557.1483, found: 557.1474.

**Ethyl (1*R*,4*S*,5*S*)-5'-chloro-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ac)**



Pale yellow solid, 54.6 mg, 99% yield; >20:1 dr, 94:6 er;  $[\alpha]_{\text{D}}^{20} = +364.3$  (c. 2.16,  $\text{CHCl}_3$ ); m.p. 201.9-202.5 °C.

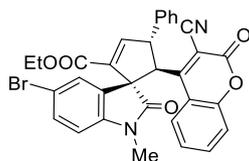
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 11.6$  min (major), 13.4 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.75 (d,  $J = 8.4$  Hz, 1H), 7.65-7.61 (m, 1H), 7.61-7.54 (m, 1H), 7.52-7.46 (m, 2H), 7.40-7.33 (m, 2H), 7.32-7.25 (m, 4H), 7.22-7.14 (m, 2H), 6.51 (d,  $J = 8.3$  Hz, 1H), 6.16 (dd,  $J = 9.7, 2.0$  Hz, 1H), 4.81 (d,  $J = 9.6$  Hz, 1H), 4.07 (q,  $J = 7.1$  Hz, 2H), 2.91 (s, 3H), 1.14 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.8, 161.9, 159.6, 156.7, 152.6, 149.2, 141.7, 139.8, 136.1, 135.5, 129.9, 129.5, 128.6, 128.4, 127.9, 127.8, 126.4, 126.2, 125.3, 117.8, 115.4, 109.3, 103.1, 66.5, 61.3, 57.8, 51.7, 26.6, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{ClN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  573.1188, found: 573.1170.

**Ethyl (1*R*,4*S*,5*S*)-5'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ad)**



Pale yellow solid, 60.7 mg, 99% yield; >20:1 dr, 93:7 er;  $[\alpha]_D^{20} = +337.6$  (c. 2.48,  $\text{CHCl}_3$ ); m.p. 191.5-192.2 °C.

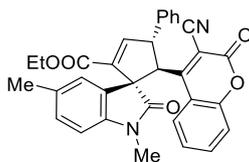
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.9$  min (major), 15.1 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.78-7.71 (m, 2H), 7.62-7.54 (m, 1H), 7.52-7.46 (m, 2H), 7.42-7.32 (m, 3H), 7.32-7.27 (m, 3H), 7.21-7.14 (m, 1H), 6.46 (d,  $J = 8.3$  Hz, 1H), 6.16 (dd,  $J = 9.6, 2.0$  Hz, 1H), 4.80 (d,  $J = 9.7$  Hz, 1H), 4.07 (q,  $J = 7.1$  Hz, 2H), 2.90 (s, 3H), 1.14 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.7, 161.8, 159.5, 156.7, 152.6, 149.1, 142.2, 139.8, 136.1, 135.5, 132.7, 129.5, 129.1, 128.4, 128.2, 127.9, 126.2, 125.3, 117.8, 115.7, 115.4, 109.8, 103.2, 66.5, 61.3, 57.9, 51.7, 26.5, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{32}\text{H}_{23}\text{BrN}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  617.0683, found: 617.0663.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-5'-dimethyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ae)**



Pale yellow solid, 52.3 mg, 99% yield; >20:1 dr, 95:5 er;  $[\alpha]_D^{20} = +475.5$  (c. 1.54,  $\text{CHCl}_3$ ); m.p. 196.1-197.2 °C.

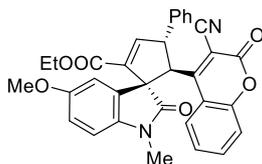
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.1$  min (major), 15.2 min (minor).

**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.79 (d,  $J = 7.7$  Hz, 1H), 7.60-7.47 (m, 3H), 7.46-7.41 (m, 1H), 7.40-7.32 (m, 2H), 7.32-7.23 (m, 4H), 7.15 (dd,  $J = 8.3, 1.1$  Hz, 1H), 7.01-6.94 (m, 1H), 6.43 (d,  $J = 7.8$  Hz, 1H), 6.17 (dd,  $J = 9.6, 2.1$  Hz, 1H), 4.80 (d,  $J = 9.7$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 2.86 (s, 3H), 2.34 (s, 3H), 1.11 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )**  $\delta$  176.9, 162.1, 160.0, 157.0, 152.4, 148.6, 140.5, 140.1, 136.4, 135.2, 132.7, 130.0, 129.4, 128.2, 127.9, 126.7, 126.5, 126.1, 125.2, 117.9, 117.6, 115.5, 108.0, 103.0, 66.6, 61.1, 58.1, 51.5, 26.4, 21.1, 14.0.

**HRMS (ESI)** calcd. for  $\text{C}_{33}\text{H}_{26}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  553.1734, found: 553.1731.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-5'-methoxy-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3af)**



Pale yellow solid, 55.2 mg, 99% yield; >20:1 dr, 94:6 er;  $[\alpha]_D^{20} = +407.6$  (c. 2.25, CHCl<sub>3</sub>); m.p. 84.6-85.1 °C.

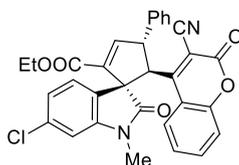
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 16.5$  min (major), 24.2 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  7.82-7.71 (m, 1H), 7.61-7.46 (m, 3H), 7.40-7.32 (m, 2H), 7.31-7.24 (m, 4H), 7.24-7.19 (m, 1H), 6.72 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.46 (d,  $J = 8.5$  Hz, 1H), 6.24-6.11 (m, 1H), 4.84 (d,  $J = 9.4$  Hz, 1H), 4.04 (q,  $J = 7.1$  Hz, 2H), 3.85 (s, 3H), 2.90 (s, 3H), 1.10 (t,  $J = 7.1$  Hz, 3H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  176.9, 162.0, 160.4, 157.0, 156.1, 152.5, 148.9, 140.2, 136.4, 135.4, 129.4, 128.2, 128.0, 127.3, 126.5, 125.2, 117.9, 117.6, 116.0, 115.9, 111.7, 109.1, 102.8, 66.9, 61.1, 58.0, 56.2, 51.8, 26.5, 14.0.

**HRMS (ESI)** calcd. for C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>NaO<sub>6</sub> [M + Na]<sup>+</sup> 569.1683, found: 569.1678.

**Ethyl (1*R*,4*S*,5*S*)-6'-chloro-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ag)**



Pale yellow solid, 54.3 mg, 99% yield; >20:1 dr, 93:7 er;  $[\alpha]_D^{20} = +318.5$  (c. 2.37, CHCl<sub>3</sub>); m.p. 122.1-122.8 °C.

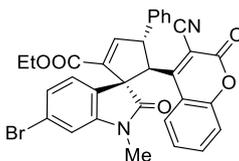
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 11.6$  min (major), 22.3 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  7.76-7.69 (m, 1H), 7.63-7.53 (m, 2H), 7.53-7.46 (m, 2H), 7.41-7.32 (m, 2H), 7.31-7.25 (m, 4H), 7.20 (dd,  $J = 8.3, 1.0$  Hz, 1H), 7.06 (dd,  $J = 8.0, 1.9$  Hz, 1H), 6.58 (d,  $J = 1.7$  Hz, 1H), 6.15 (dd,  $J = 9.4, 2.0$  Hz, 1H), 4.82 (d,  $J = 9.5$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 2.93 (s, 3H), 1.13 (t,  $J = 7.1$  Hz, 3H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  177.4, 161.9, 160.0, 156.8, 152.6, 149.0, 144.5, 139.9, 136.1, 135.7, 135.5, 129.5, 128.4, 127.9, 126.8, 126.1, 125.4, 124.6, 123.0, 117.9, 117.8, 115.6, 109.3, 103.0, 66.1, 61.3, 57.8, 51.9, 26.6, 14.0.

**HRMS (ESI)** calcd. for C<sub>32</sub>H<sub>23</sub>ClN<sub>2</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> 573.1188, found: 573.1196.

**Ethyl (1*R*,4*S*,5*S*)-6'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ah)**



Pale yellow solid, 63.3 mg, 99% yield; >20:1 dr, 92.5:7.5 er;  $[\alpha]_D^{20} = +291.2$  (c. 2.68, CHCl<sub>3</sub>); m.p. 137.1-137.8 °C.

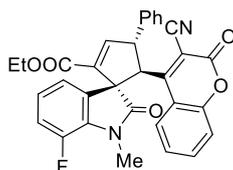
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 30/70, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 9.1$  min (major), 15.2 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)** δ 7.77-7.68 (m, 1H), 7.63-7.54 (m, 1H), 7.53-7.45 (m, 3H), 7.41-7.32 (m, 2H), 7.31-7.24 (m, 3H), 7.24-7.17 (m, 2H), 6.73 (d, *J* = 1.6 Hz, 1H), 6.15 (dd, *J* = 9.4, 2.1 Hz, 1H), 4.82 (d, *J* = 9.5 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.92 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 177.2, 161.8, 159.9, 156.8, 152.6, 148.9, 144.5, 139.9, 136.1, 135.5, 129.4, 128.3, 127.9, 127.1, 126.1, 125.9, 125.3, 125.1, 123.6, 117.9, 117.8, 115.5, 112.0, 103.0, 66.1, 61.2, 57.7, 51.9, 26.5, 14.0.

**HRMS (ESI)** calcd. for C<sub>32</sub>H<sub>23</sub>BrN<sub>2</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> 617.0683, found: 617.0695.

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-7'-fluoro-1'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ai)**



Pale yellow solid, 52.8 mg, 99% yield; >20:1 dr, 90:10 er; [α]<sub>D</sub><sup>20</sup> = +286.8 (c. 2.33, CHCl<sub>3</sub>); m.p. 178.2-178.5 °C.

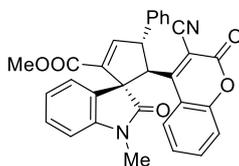
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min, λ = 254 nm) t<sub>R</sub> = 12.0 min (major), 15.0 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)** δ 7.76-7.69 (m, 1H), 7.63-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.44-7.33 (m, 3H), 7.33-7.26 (m, 4H), 7.24-7.17 (m, 1H), 7.09-6.99 (m, 1H), 6.99-6.88 (m, 1H), 6.18 (dd, *J* = 9.4, 2.1 Hz, 1H), 4.82 (d, *J* = 9.5 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.13 (d, *J* = 2.6 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)** δ 177.0, 161.9, 159.8, 156.8, 152.6, 149.0, 147.5 (d, *J* = 243.0 Hz, 1C), 140.0, 136.2, 135.5, 129.8, 129.7, 129.2 (d, *J* = 3.0 Hz, 1C), 128.3, 127.9, 126.2, 125.3, 123.7 (d, *J* = 6.0 Hz, 1C), 121.7 (d, *J* = 3.0 Hz, 1C), 118.0, 117.8, 117.7, 115.5, 103.0, 66.6 (d, *J* = 2.3 Hz, 1C), 61.2, 58.1, 51.7, 29.0, 28.9, 14.0.

**HRMS (ESI)** calcd. for C<sub>32</sub>H<sub>23</sub>FN<sub>2</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> 557.1483, found: 557.1509.

**Methyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3aj)**



Pale yellow solid, 40.2 mg, 80% yield; >20:1 dr, 94:6 er; [α]<sub>D</sub><sup>20</sup> = +266.2 (c. 1.18, CHCl<sub>3</sub>); m.p. 213.4-214.2 °C.

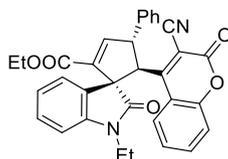
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min, λ = 254 nm) t<sub>R</sub> = 13.5 min (major), 20.4 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)** δ 7.79-7.72 (m, 1H), 7.64-7.48 (m, 4H), 7.40-7.33 (m, 2H), 7.31-7.24 (m, 4H), 7.23-7.05 (m, 3H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.20 (dd, *J* = 9.4, 2.2 Hz, 1H), 4.82 (d, *J* = 9.5 Hz, 1H), 3.63 (s, 3H), 2.91 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2, 162.5, 160.1, 156.9, 152.5, 148.9, 143.1, 140.2, 136.1, 135.3, 130.0, 129.5, 128.3, 128.0, 126.4, 126.1, 125.8, 125.2, 123.2, 117.9, 117.7, 115.6, 108.4, 103.0, 66.6, 58.1, 52.2, 51.8, 26.4.

HRMS (ESI) calcd. for  $\text{C}_{31}\text{H}_{22}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  525.1421, found: 525.1408.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ak)**



Pale yellow solid, 36.5 mg, 69% yield; >20:1 dr, 96.5:3.5 er;  $[\alpha]_{\text{D}}^{20} = +309.8$  (c. 2.54,  $\text{CHCl}_3$ ); m.p. 87.9-88.3 °C.

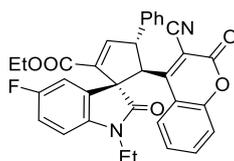
HPLC (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 11.7$  min (major), 16.6 min (minor).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.4$  Hz, 1H), 7.64 (d,  $J = 7.4$  Hz, 1H), 7.60-7.47 (m, 3H), 7.41-7.32 (m, 2H), 7.31-7.24 (m, 3H), 7.23-7.13 (m, 2H), 7.12-7.04 (m, 1H), 6.59 (d,  $J = 7.7$  Hz, 1H), 6.16 (dd,  $J = 9.6, 2.0$  Hz, 1H), 4.86 (d,  $J = 9.7$  Hz, 1H), 4.03 (qq,  $J = 7.4, 3.7$  Hz, 2H), 3.57 (dq,  $J = 14.4, 7.2$  Hz, 1H), 3.42 (dq,  $J = 14.0, 7.1$  Hz, 1H), 1.08 (t,  $J = 7.1$  Hz, 3H), 0.84 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 161.9, 160.0, 156.9, 152.6, 148.6, 142.3, 140.1, 136.8, 135.2, 129.9, 129.4, 128.2, 127.9, 126.5, 126.3, 126.2, 125.4, 122.9, 118.0, 117.6, 115.6, 108.4, 103.0, 66.4, 61.0, 57.8, 51.7, 35.0, 14.0, 11.9.

HRMS (ESI) calcd. for  $\text{C}_{33}\text{H}_{26}\text{N}_2\text{NaO}_5$   $[\text{M} + \text{Na}]^+$  553.1734, found: 553.1727.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-5'-fluoro-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3al)**



Pale yellow solid, 48.6 mg, 89% yield; >20:1 dr, 96.5:3.5 er;  $[\alpha]_{\text{D}}^{20} = +316.3$  (c. 2.00,  $\text{CHCl}_3$ ); m.p. 176.4-177.1 °C.

HPLC (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_{\text{R}} = 10.4$  min (major), 13.3 min (minor).

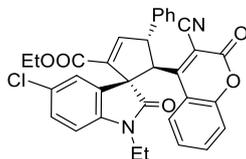
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.77 (m, 1H), 7.61-7.53 (m, 1H), 7.53-7.46 (m, 2H), 7.46-7.40 (m, 1H), 7.40-7.32 (m, 2H), 7.32-7.26 (m, 3H), 7.18 (dd,  $J = 8.3, 1.1$  Hz, 1H), 6.92 (td,  $J = 8.7, 2.6$  Hz, 1H), 6.55 (dd,  $J = 8.5, 4.0$  Hz, 1H), 6.13 (dd,  $J = 9.7, 2.1$  Hz, 1H), 4.86 (d,  $J = 9.8$  Hz, 1H), 4.05 (qd,  $J = 7.1, 2.2$  Hz, 2H), 3.57 (dt,  $J = 14.6, 7.3$  Hz, 1H), 3.41 (dq,  $J = 14.3, 7.2$  Hz, 1H), 1.12 (t,  $J = 7.1$  Hz, 3H), 0.82 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.4, 161.8, 159.7, 158.9 (d,  $J = 241.5$  Hz, 1C), 156.8, 152.7, 149.0, 139.8, 138.4, 136.5, 135.4, 129.5, 128.3, 128.0, 127.9, 126.5, 125.5, 117.9, 117.7, 116.3 (d,  $J = 23.3$

Hz, 1C), 115.6, 114.7 (d,  $J = 24.8$  Hz, 1C), 109.0 (d,  $J = 8.3$  Hz, 1C), 103.1, 66.6, 61.2, 57.6, 51.8, 35.2, 14.0, 11.8.

**HRMS (ESI)** calcd. for  $C_{33}H_{25}FN_2NaO_5$  [ $M + Na$ ] $^+$  571.1640, found: 571.1636.

**Ethyl (1R,4S,5S)-5'-chloro-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3am)**



Pale yellow solid, 51.2 mg, 91% yield; >20:1 dr, 97:3 er;  $[\alpha]_D^{20} = +334.2$  (c. 2.32,  $CHCl_3$ ); m.p. 201.1-201.5 °C.

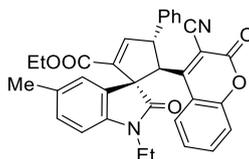
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 15/85, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 12.8$  min (major), 17.4 min (minor).

**$^1H$  NMR (300 MHz,  $CDCl_3$ )**  $\delta$  7.86-7.78 (m, 1H), 7.66 (d,  $J = 1.9$  Hz, 1H), 7.62-7.53 (m, 1H), 7.53-7.44 (m, 2H), 7.41-7.32 (m, 2H), 7.31-7.25 (m, 3H), 7.23-7.14 (m, 2H), 6.55 (d,  $J = 8.3$  Hz, 1H), 6.14 (dd,  $J = 9.9, 2.0$  Hz, 1H), 4.90 – 4.79 (m, 1H), 4.07 (qd,  $J = 7.0, 1.1$  Hz, 2H), 3.57 (dt,  $J = 14.1, 7.1$  Hz, 1H), 3.40 (dt,  $J = 14.2, 7.0$  Hz, 1H), 1.13 (t,  $J = 7.1$  Hz, 3H), 0.80 (t,  $J = 7.2$  Hz, 3H).

**$^{13}C$  NMR (75 MHz,  $CDCl_3$ )**  $\delta$  176.2, 161.8, 159.4, 156.7, 152.7, 149.0, 141.0, 139.7, 136.5, 135.4, 129.8, 129.5, 128.3, 128.0, 127.9, 126.9, 126.4, 125.5, 117.9, 117.8, 115.4, 109.4, 103.2, 61.2, 57.6, 51.7, 35.1, 14.0, 11.8.

**HRMS (ESI)** calcd. for  $C_{33}H_{25}ClN_2NaO_5$  [ $M + Na$ ] $^+$  587.1344, found: 587.1348.

**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-5'-methyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3an)**



Pale yellow solid, 39.6 mg, 73% yield; >20:1 dr, 96.5:3.5 er;  $[\alpha]_D^{20} = +355.1$  (c. 1.03,  $CHCl_3$ ); m.p. 187.9-188.7 °C.

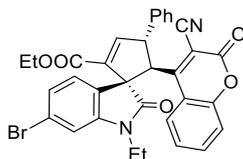
**HPLC** (Chiralpak AD-H column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 8.6$  min (major), 12.4 min (minor).

**$^1H$  NMR (300 MHz,  $CDCl_3$ )**  $\delta$  7.86 (d,  $J = 8.3$  Hz, 1H), 7.59-7.45 (m, 4H), 7.41-7.32 (m, 2H), 7.32-7.25 (m, 3H), 7.20-7.12 (m, 1H), 7.03-6.96 (m, 1H), 6.48 (d,  $J = 7.9$  Hz, 1H), 6.15 (dd,  $J = 9.9, 2.0$  Hz, 1H), 4.83 (d,  $J = 9.9$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 3H), 3.53 (dq,  $J = 14.2, 7.4$  Hz, 1H), 3.37 (dq,  $J = 14.1, 7.1$  Hz, 1H), 2.36 (s, 3H), 1.11 (t,  $J = 7.1$  Hz, 3H), 0.78 (t,  $J = 7.2$  Hz, 3H).

**$^{13}C$  NMR (75 MHz,  $CDCl_3$ )**  $\delta$  176.4, 162.1, 159.9, 157.0, 152.6, 148.5, 140.1, 139.8, 136.9, 135.2, 132.5, 130.1, 129.4, 128.2, 128.0, 127.3, 126.7, 126.2, 125.4, 118.1, 117.6, 115.6, 108.2, 103.2, 66.5, 61.0, 57.9, 51.5, 35.0, 21.1, 14.0, 11.9.

**HRMS (ESI)** calcd. for  $C_{34}H_{28}N_2NaO_5$  [ $M + Na$ ] $^+$  567.1890, found: 567.1870.

**Ethyl (1*R*,4*S*,5*S*)-6'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenyl-spiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ao)**



Pale yellow solid, 58.0 mg, 95% yield; >20:1 dr, 96.5:3.5 er;  $[\alpha]_D^{20} = +302.0$  (c. 2.40, CHCl<sub>3</sub>); m.p. 116.1-116.7 °C.

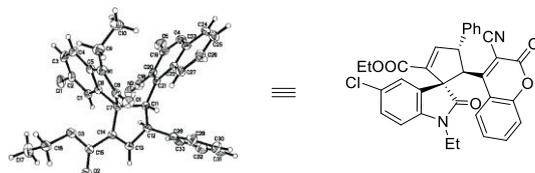
**HPLC** (Chiralpak IA column, *i*-propanol/*n*-hexane = 20/80, column temperature = 30 °C, flow rate = 1.0 mL/min,  $\lambda = 254$  nm)  $t_R = 9.2$  min (major), 18.7 min (minor).

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**  $\delta$  7.79 (d,  $J = 8.4$  Hz, 1H), 7.63-7.44 (m, 4H), 7.41-7.30 (m, 3H), 7.31-7.25 (m, 3H), 7.24-7.13 (m, 2H), 6.76 (s, 1H), 6.12 (dd,  $J = 9.6, 1.7$  Hz, 1H), 4.84 (d,  $J = 9.7$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 3.59 (dq,  $J = 14.4, 7.0$  Hz, 1H), 3.40 (dq,  $J = 14.4, 7.3$  Hz, 1H), 1.12 (t,  $J = 7.1$  Hz, 3H), 0.84 (t,  $J = 7.2$  Hz, 3H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**  $\delta$  176.7, 161.8, 159.8, 156.8, 152.7, 148.8, 143.9, 139.8, 136.5, 135.5, 129.5, 128.3, 127.9, 127.6, 126.3, 125.7, 125.5, 125.2, 123.7, 117.9, 115.6, 112.0, 103.1, 66.0, 61.2, 57.4, 51.9, 35.2, 14.0, 11.8.

**HRMS (ESI)** calcd. for C<sub>33</sub>H<sub>25</sub>BrN<sub>2</sub>NaO<sub>5</sub> [M + Na]<sup>+</sup> 631.0839, found: 631.0852.

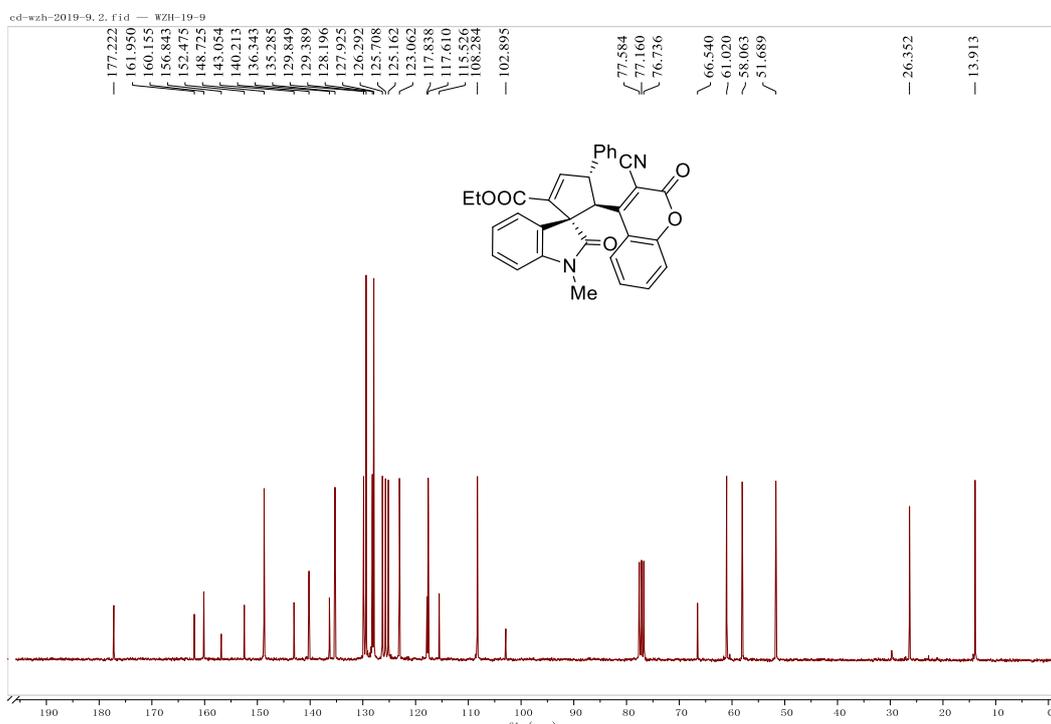
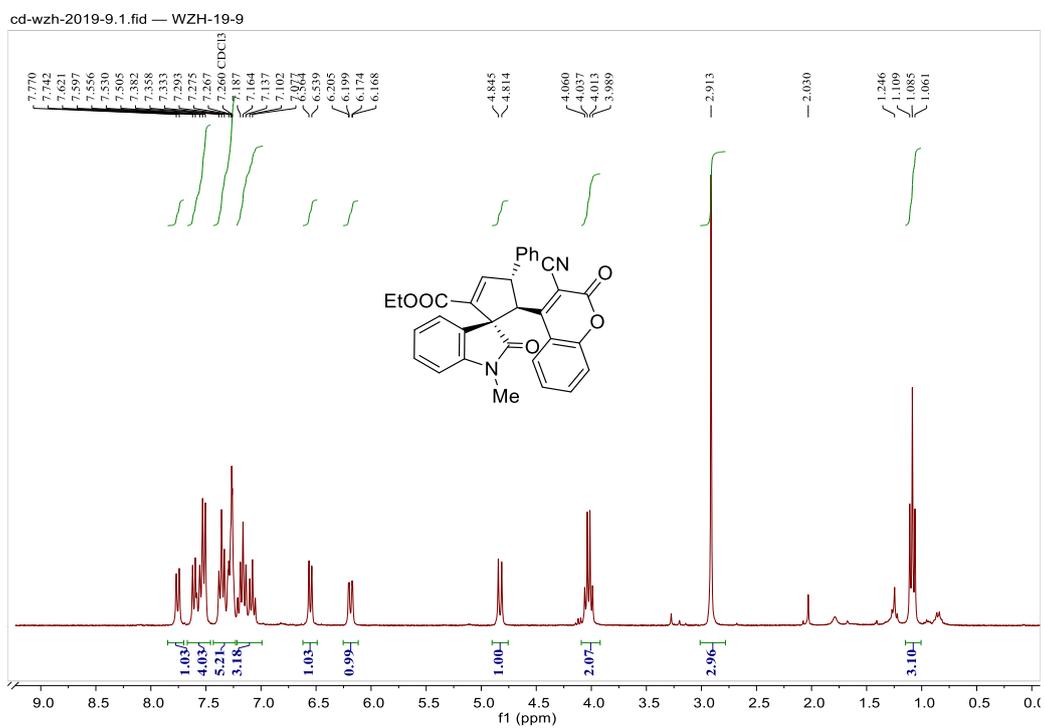
### 3. Crystal data and structure refinement for 3am

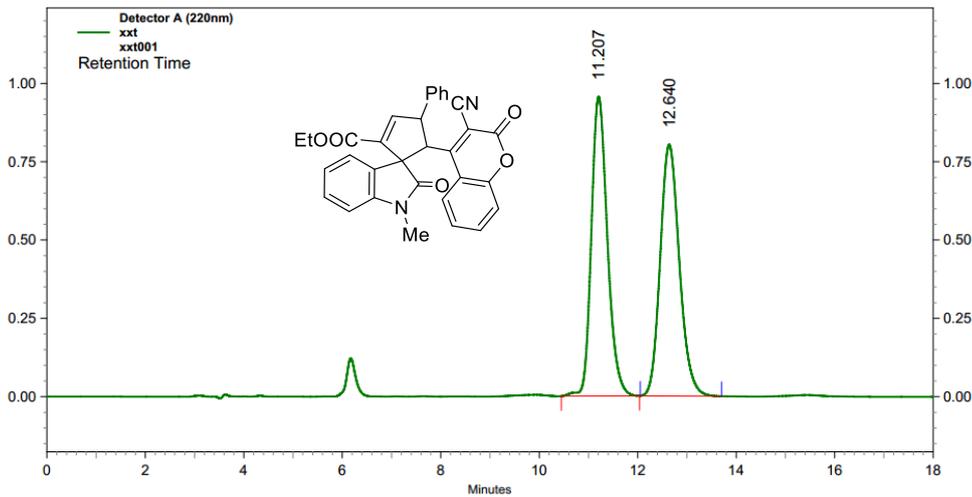


Identification code	<b>3am</b>
Solvent system for growing the single crystal	EtOH/DCM
Empirical formula	C <sub>33</sub> H <sub>25</sub> ClN <sub>2</sub> O <sub>5</sub>
Formula weight	565.00
Temperature/K	293(2)
Crystal system	triclinic
Space group	P1
a/Å	10.5960(5)
b/Å	11.6796(5)
c/Å	12.6988(6)
α/°	69.855(4)
β/°	70.549(4)
γ/°	88.791(4)
Volume/Å <sup>3</sup>	1383.43(12)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.356
μ/mm <sup>-1</sup>	1.603
F(000)	588.0
Crystal size/mm <sup>3</sup>	0.16 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.908 to 141.862
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	19847
Independent reflections	9547 [R <sub>int</sub> = 0.0386, R <sub>sigma</sub> = 0.0497]
Data/restraints/parameters	9547/3/743
Goodness-of-fit on F <sup>2</sup>	1.051
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0449, wR <sub>2</sub> = 0.1108
Final R indexes [all data]	R <sub>1</sub> = 0.0499, wR <sub>2</sub> = 0.1165
Largest diff. peak/hole / e Å <sup>-3</sup>	0.16/-0.22
Flack parameter	-0.004(10)

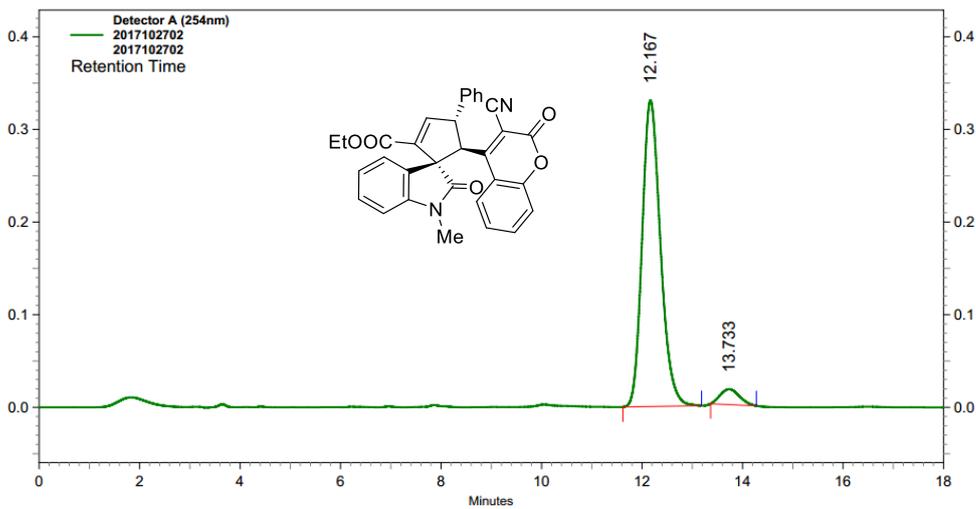
#### 4. $^1\text{H}$ , $^{13}\text{C}$ NMR and HPLC spectra for compounds 3

##### Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3aa)



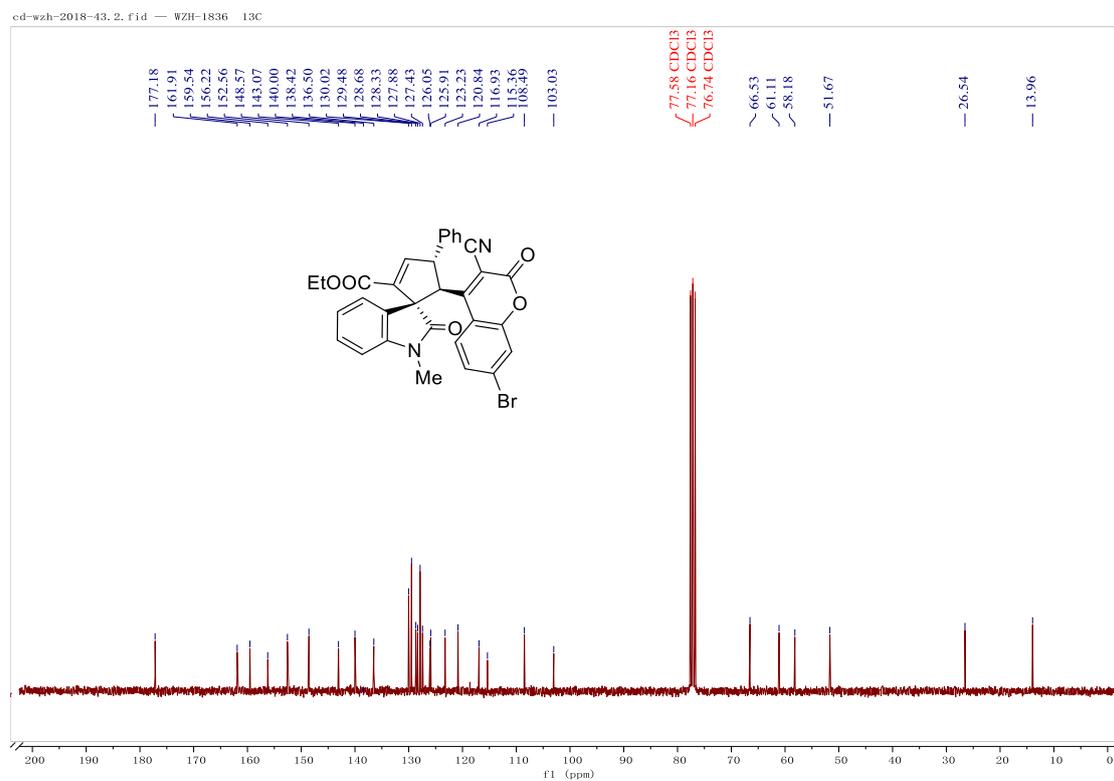
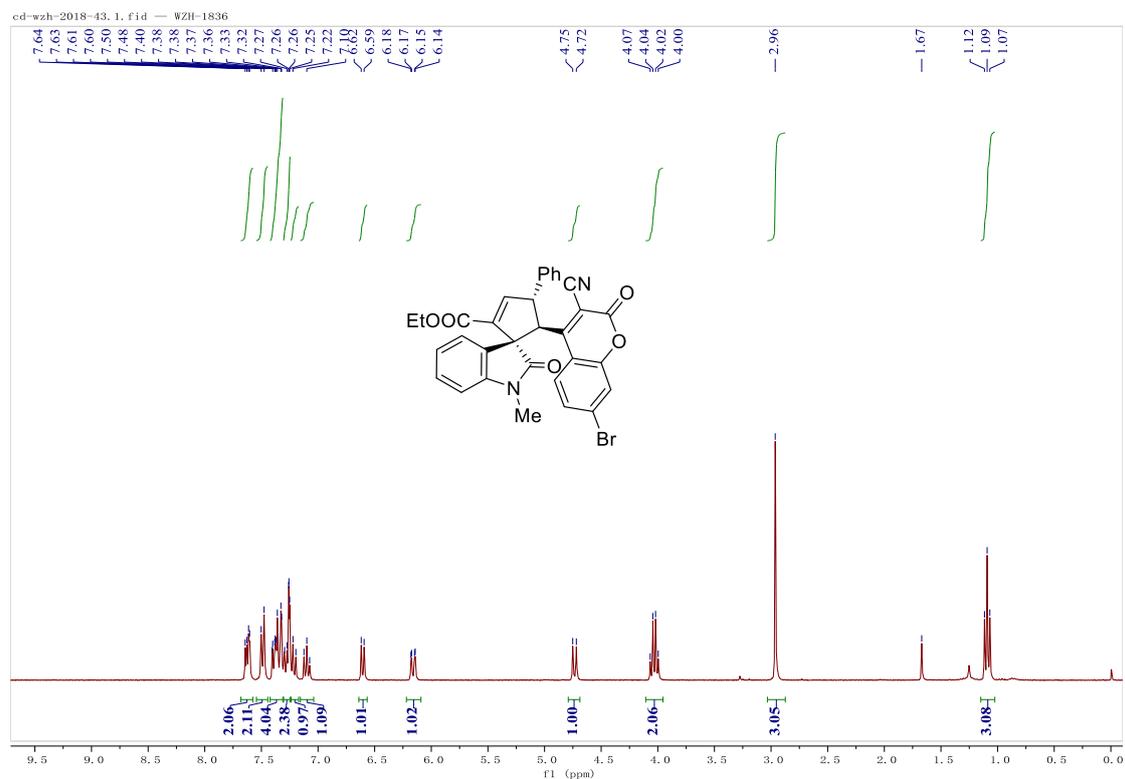


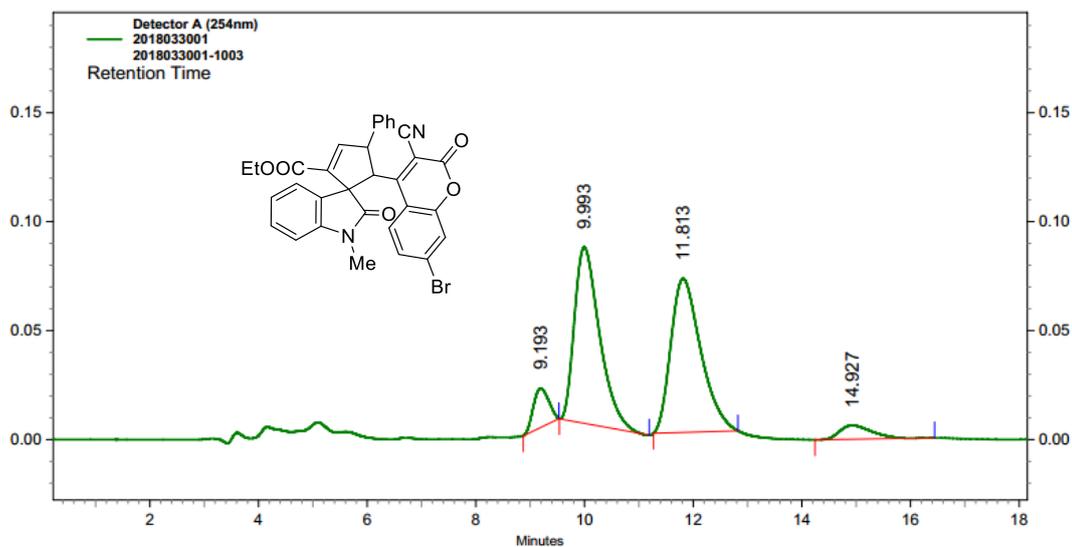
Detector A (220nm)					
PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.207	955593	54.36	21669374	49.94
2	12.640	802464	45.64	21722728	50.06
Totals		1758057	100.00	43392102	100.00



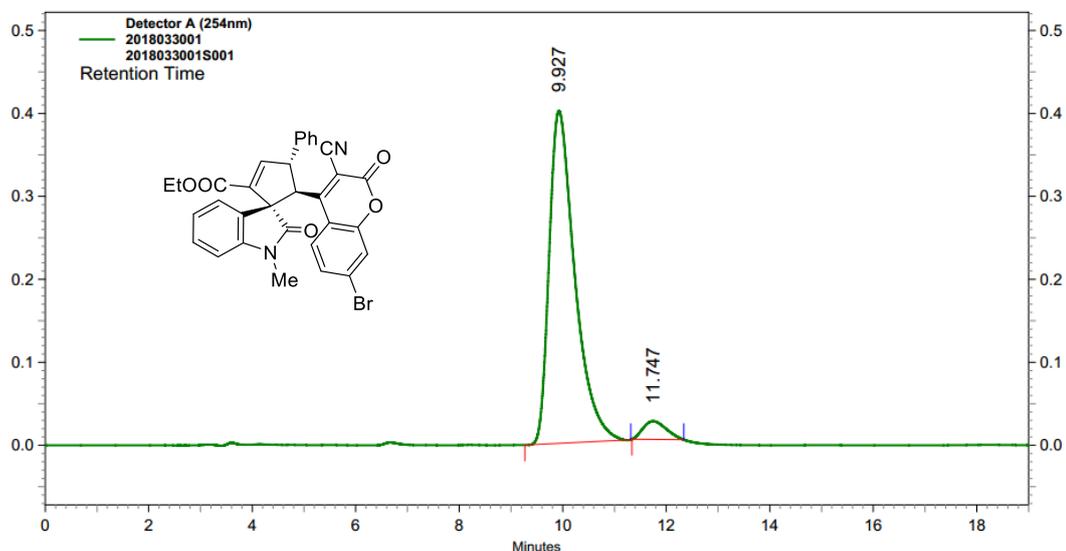
Detector A (254nm)					
PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.167	330330	95.20	8384211	94.99
2	13.733	16653	4.80	442528	5.01
Totals		346983	100.00	8826739	100.00

**Ethyl (1*R*,4*S*,5*S*)-5-(7-bromo-3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ba)**



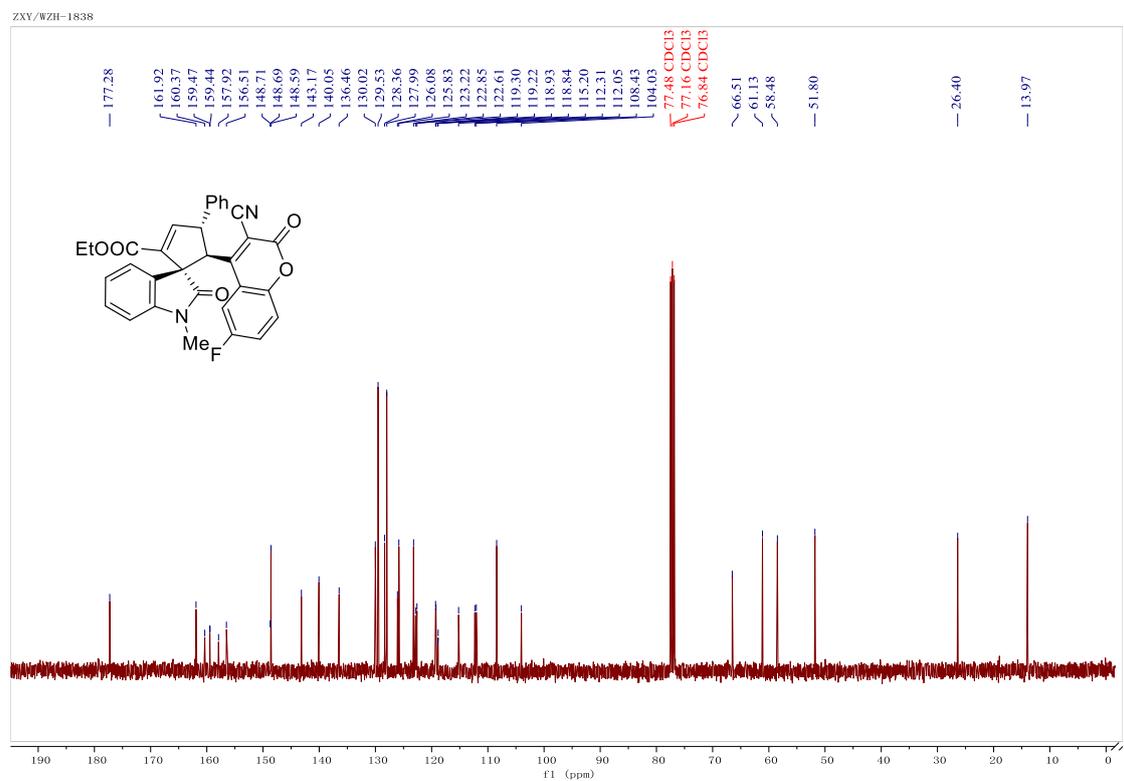
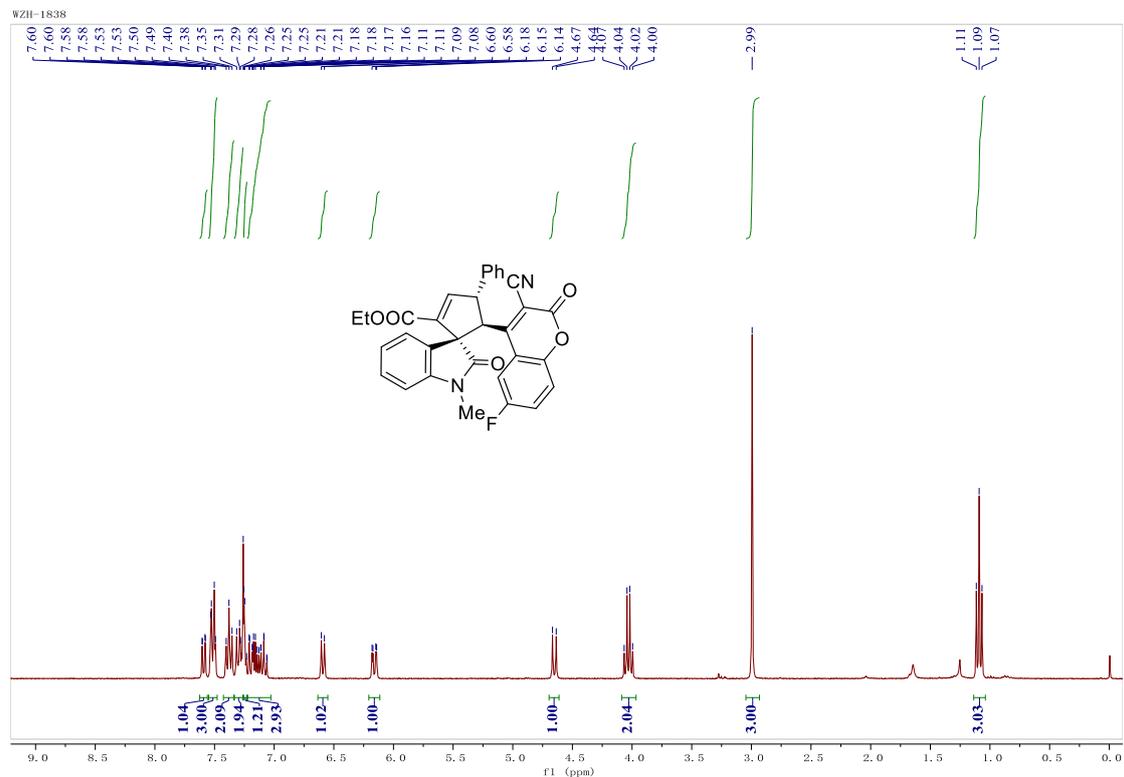


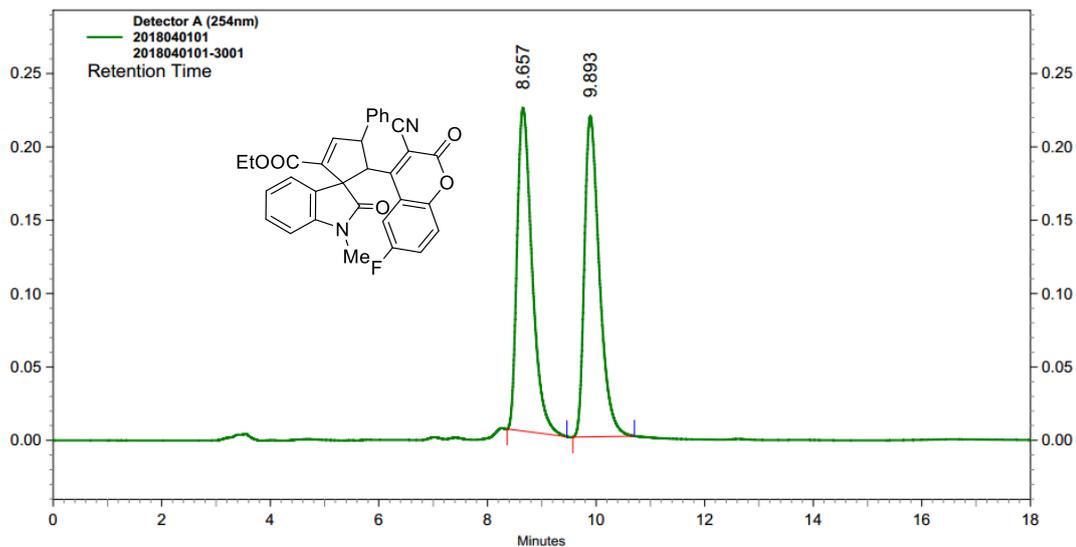
Detector A (254nm)	Pk #	Retention Time	Height	Height Percent	Area	Area Percent
	1	9.193	17973	10.23	354964	5.98
	2	9.993	80834	45.99	2608577	43.97
	3	11.813	70606	40.17	2711414	45.70
	4	14.927	6347	3.61	257840	4.35
<b>Totals</b>			175760	100.00	5932795	100.00



Detector A (254nm)	Pk #	Retention Time	Height	Height Percent	Area	Area Percent
	1	9.927	400867	94.81	13795464	95.25
	2	11.747	21951	5.19	688183	4.75
<b>Totals</b>			422818	100.00	14483647	100.00

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-6-fluoro-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ca)**

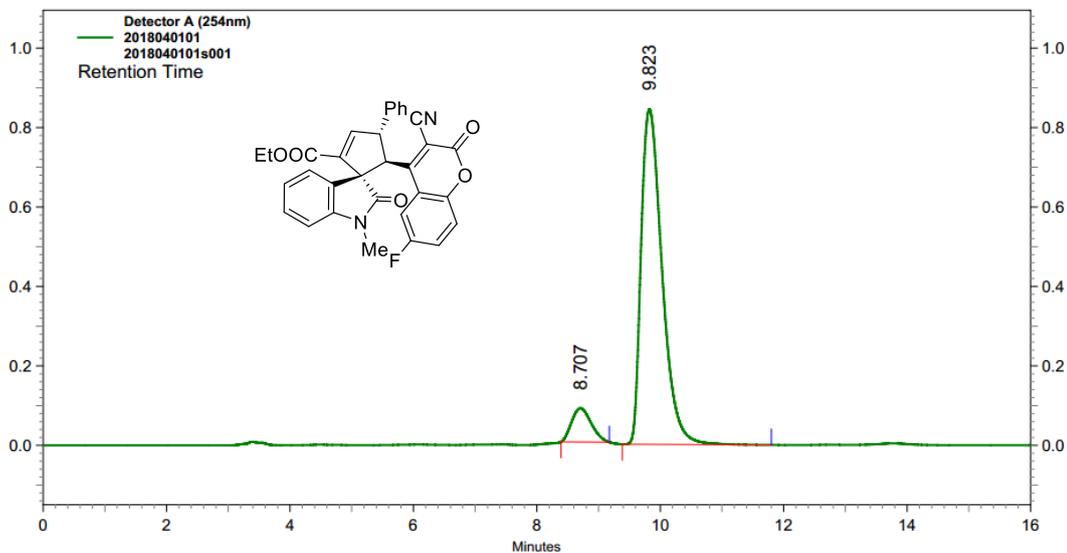




Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.657	220209	50.20	4230378	50.23
2	9.893	218446	49.80	4190815	49.77

Totals		438655	100.00	8421193	100.00
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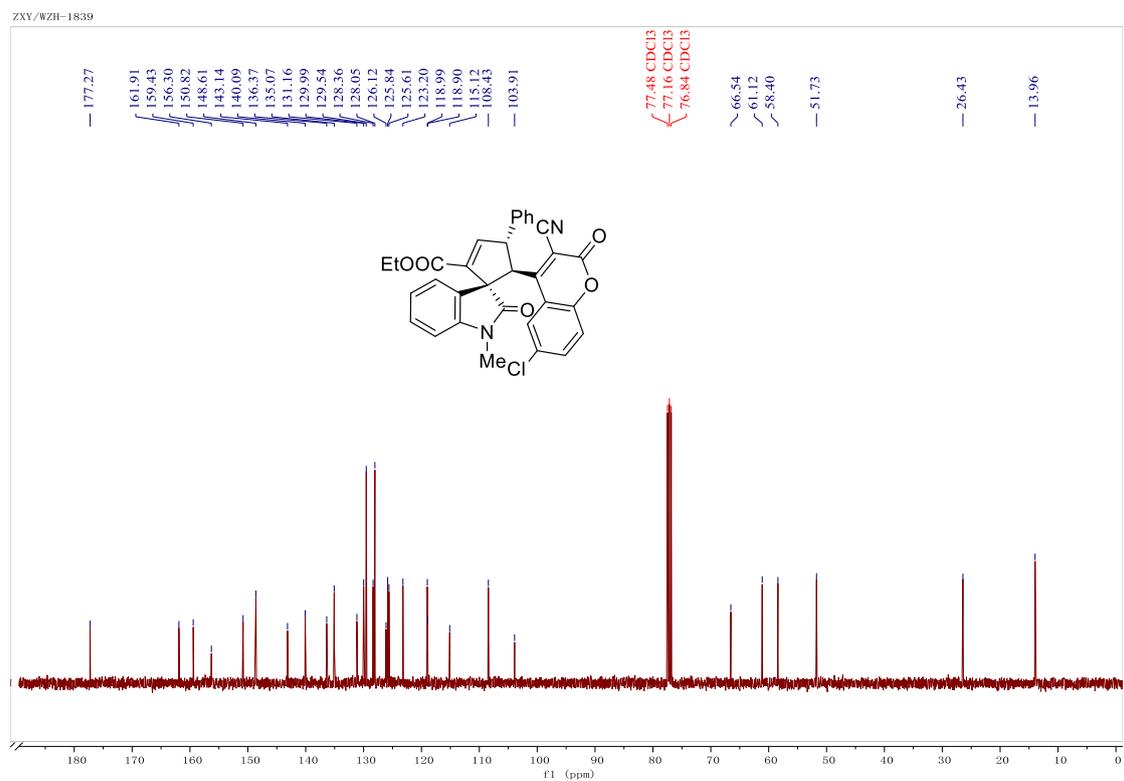
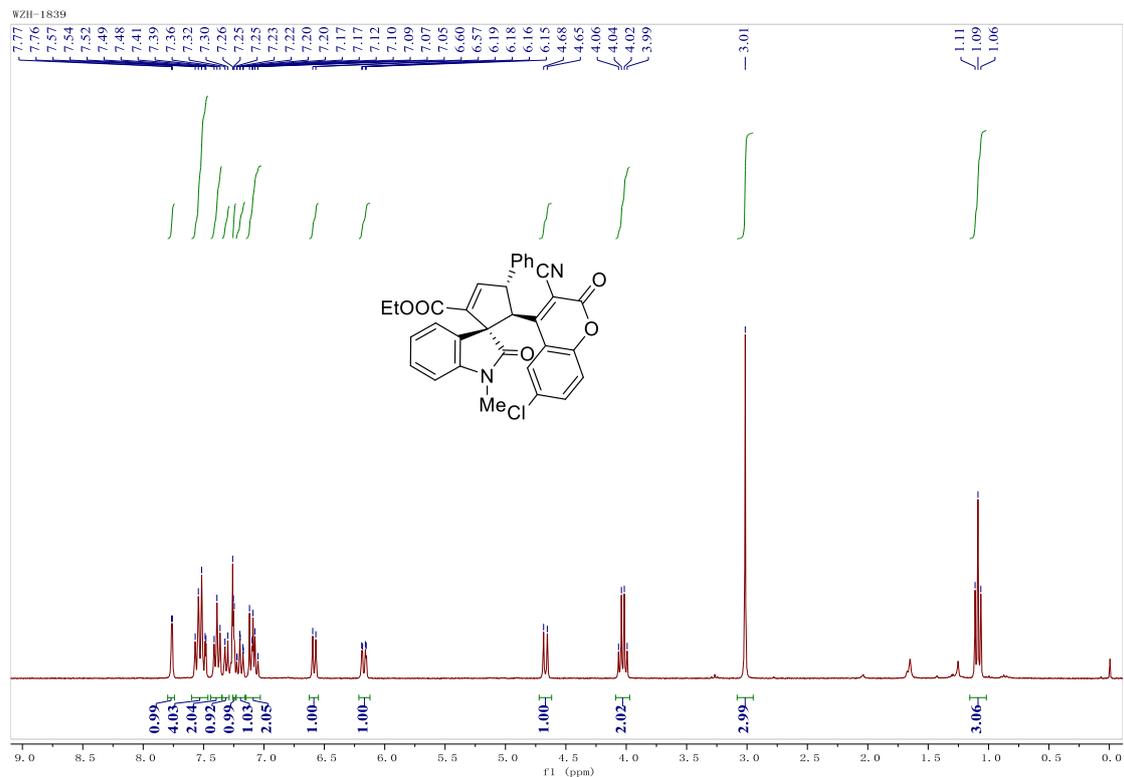


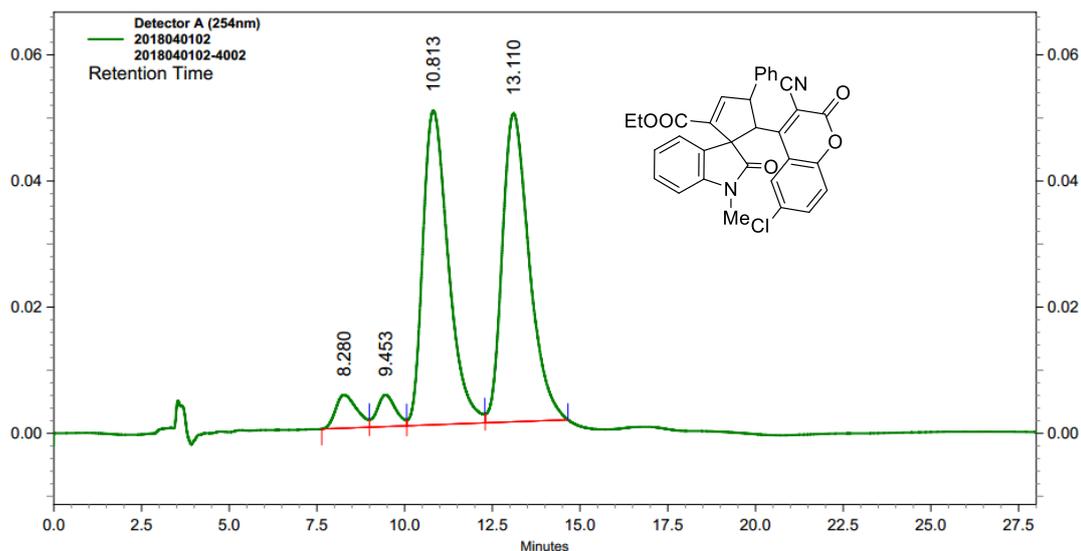
Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.707	85064	9.16	1872641	8.60
2	9.823	843963	90.84	19909360	91.40

Totals		929027	100.00	21782001	100.00
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**Ethyl (1*R*,4*S*,5*S*)-5-(6-chloro-3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3da)**

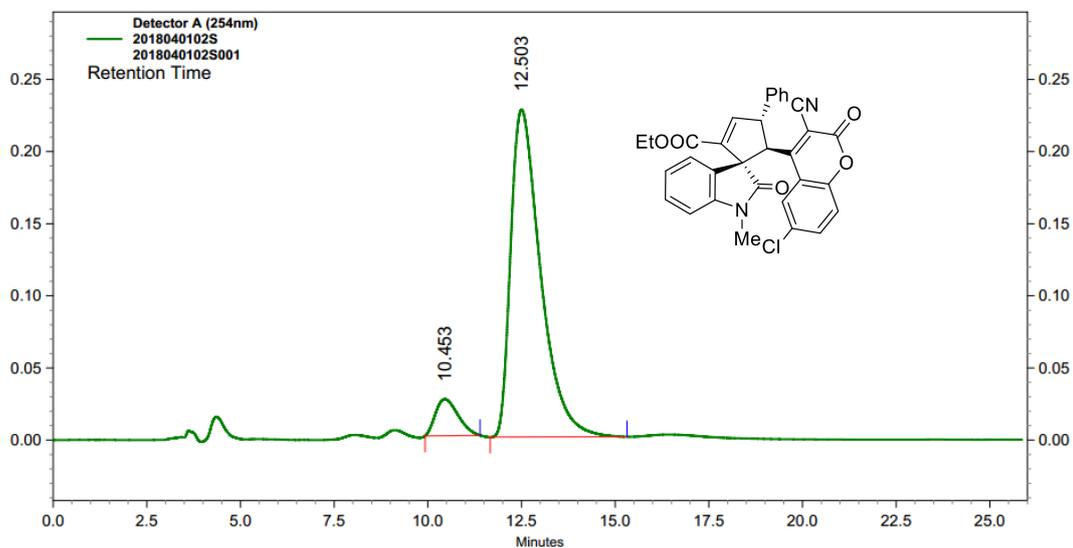




Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.280	5266	4.83	221701	3.99
2	9.453	5016	4.60	182877	3.29
3	10.813	49830	45.71	2525199	45.49
4	13.110	48896	44.86	2620820	47.22

Totals		109008	100.00	5550597	100.00
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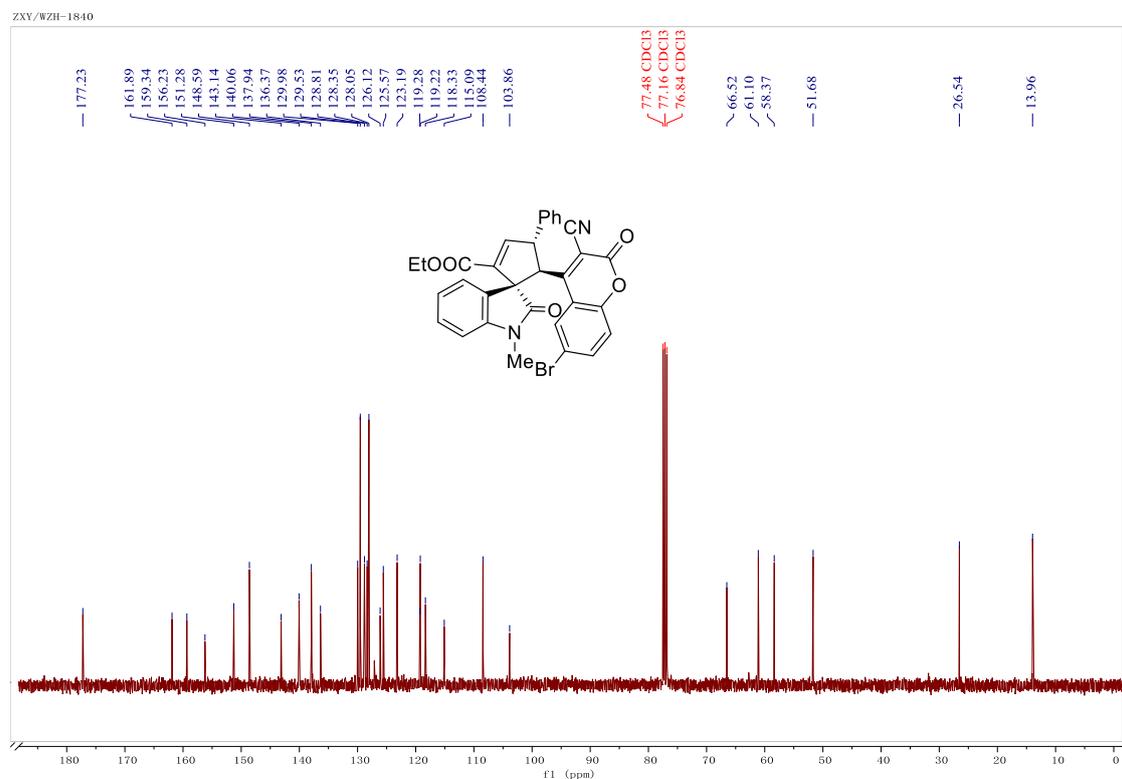
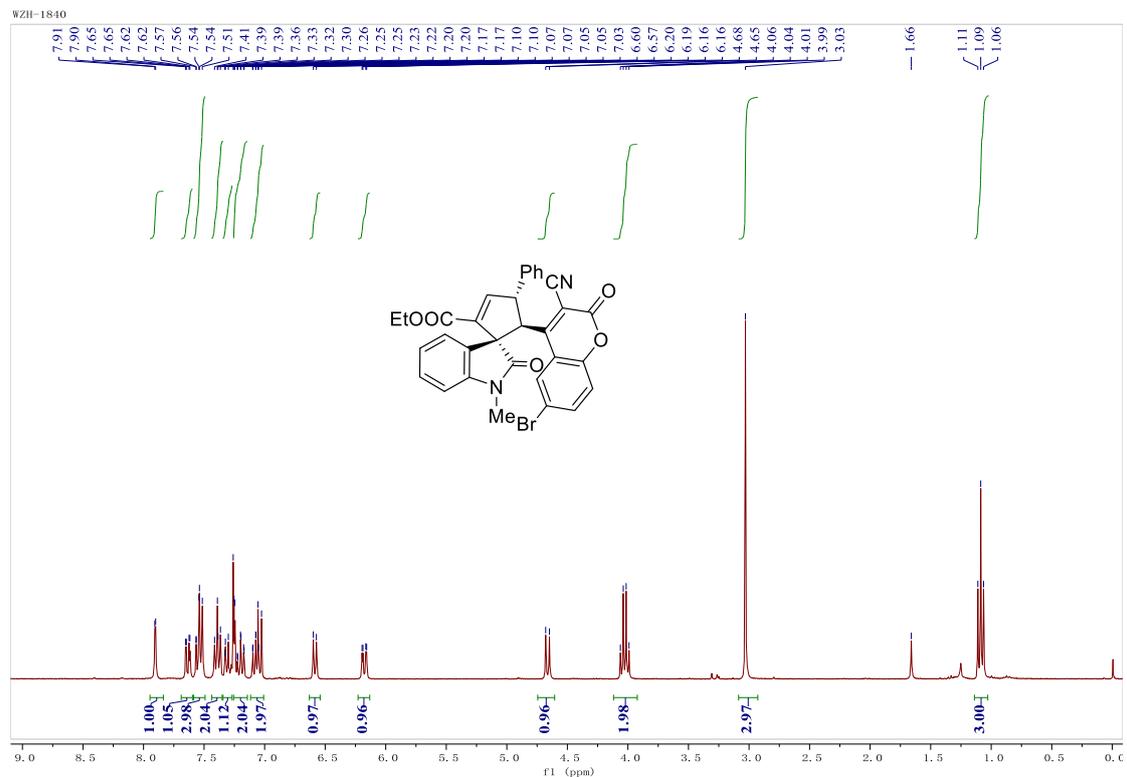


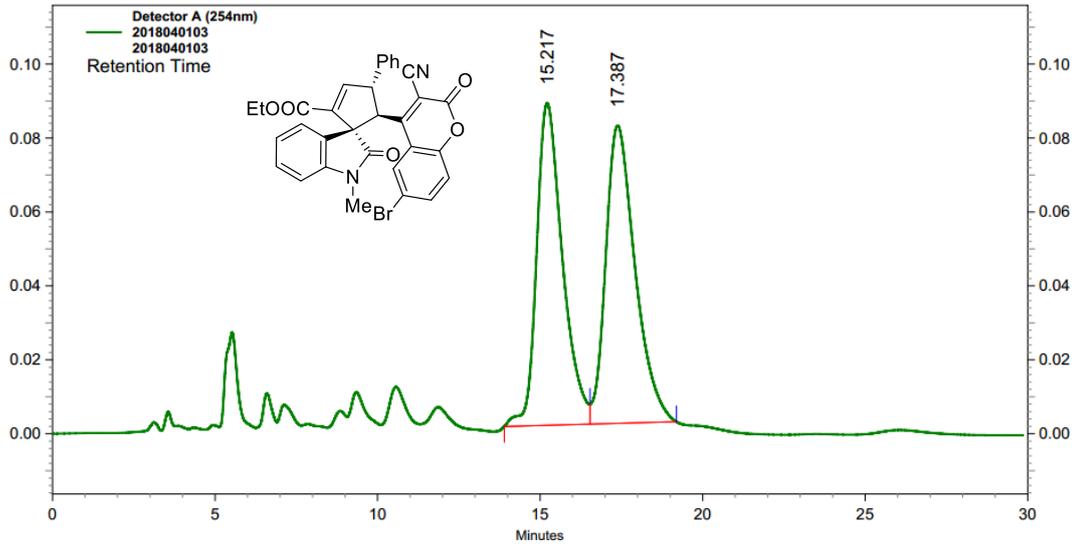
Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.453	25336	10.05	1068592	7.82
2	12.503	226883	89.95	12589408	92.18

Totals		252219	100.00	13658000	100.00
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**Ethyl (1*R*,4*S*,5*S*)-5-(6-bromo-3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ea)**

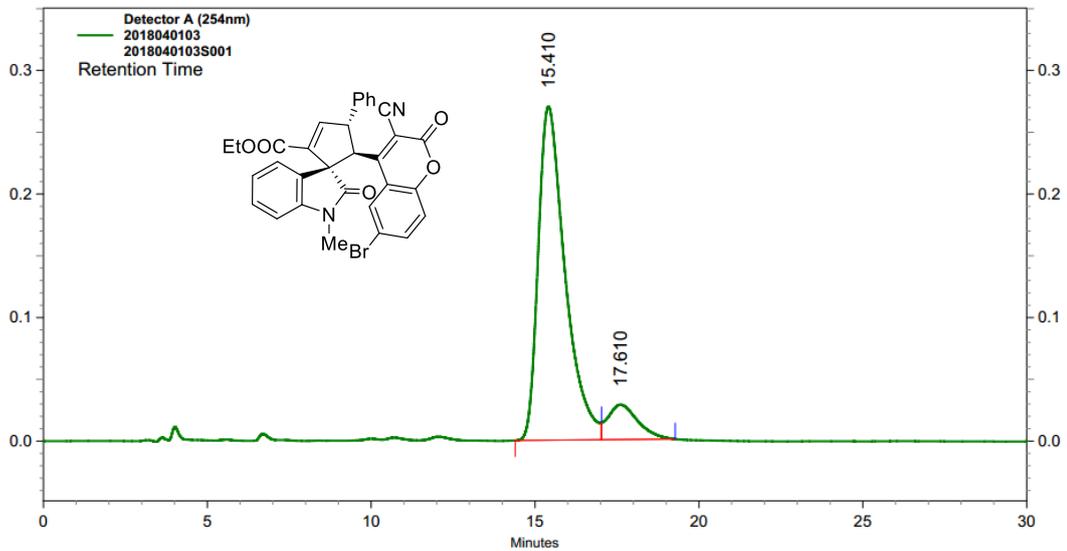




Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	15.217	87194	51.98	4831629	48.80
2	17.387	80549	48.02	5069987	51.20

Totals		167743	100.00	9901616	100.00
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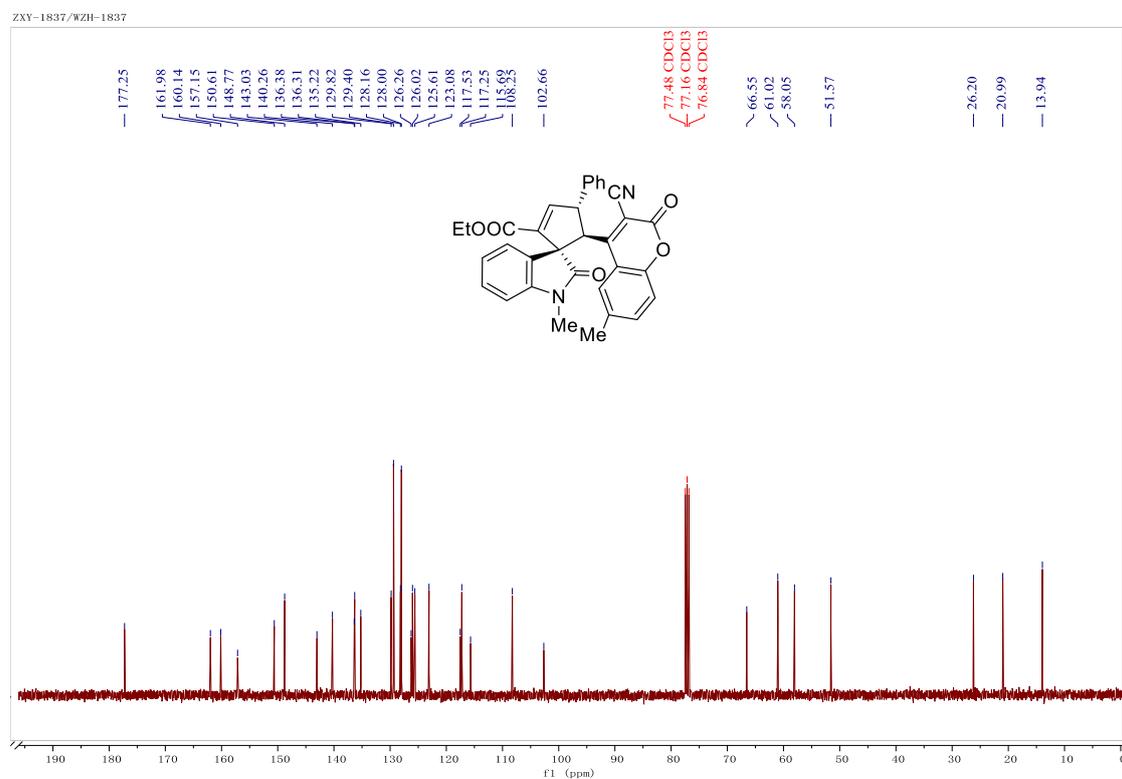
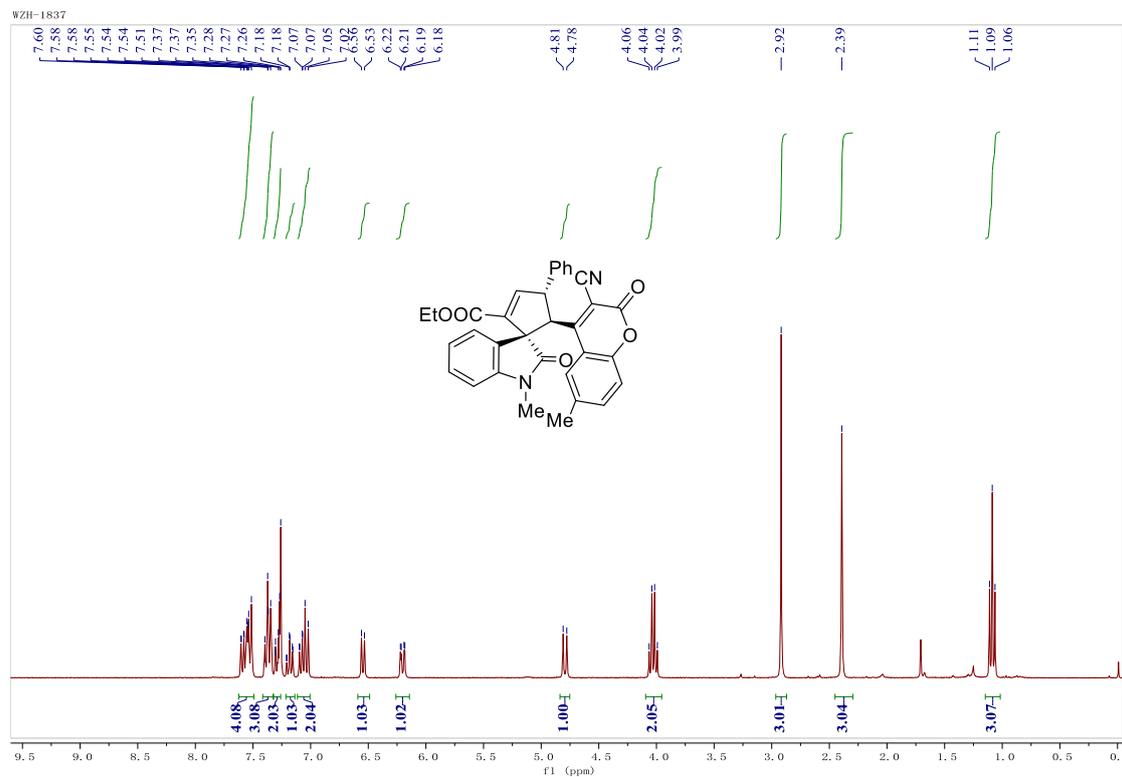


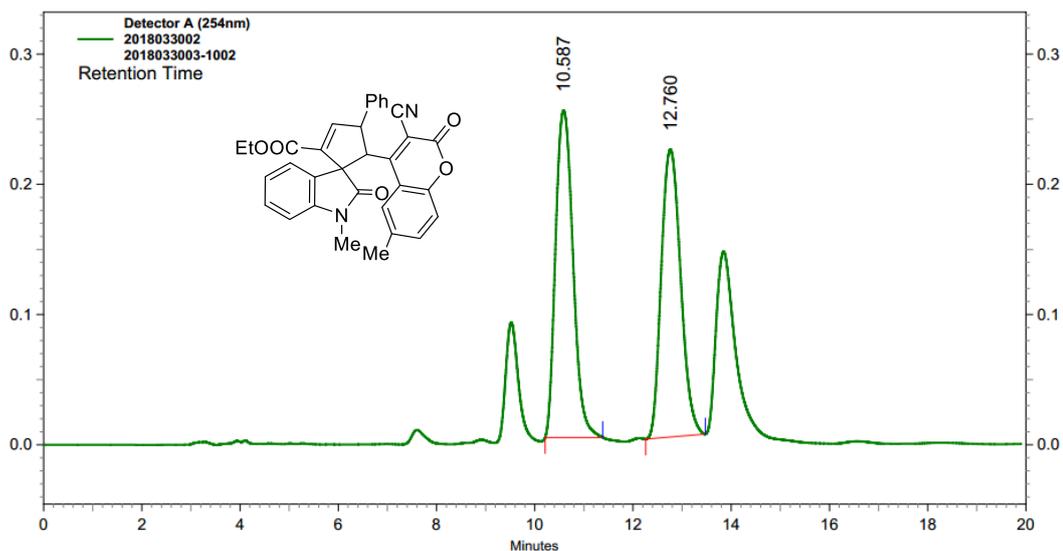
Detector  
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	15.410	270044	90.52	15418730	89.54
2	17.610	28265	9.48	1801252	10.46

Totals		298309	100.00	17219982	100.00
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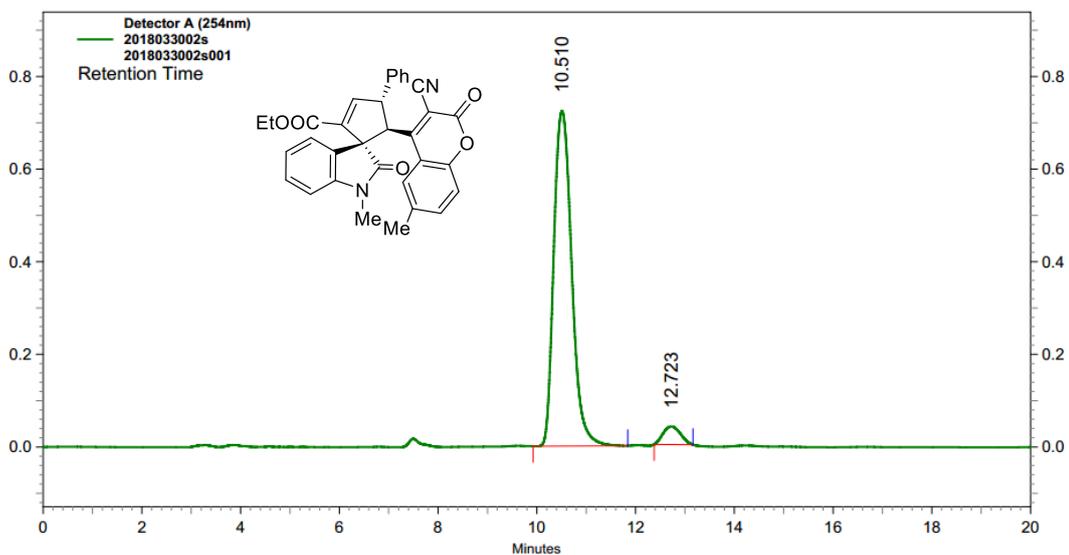
**Ethyl (1R,4S,5S)-5-(3-cyano-6-methyl-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3fa)**





**Detector A (254nm)**

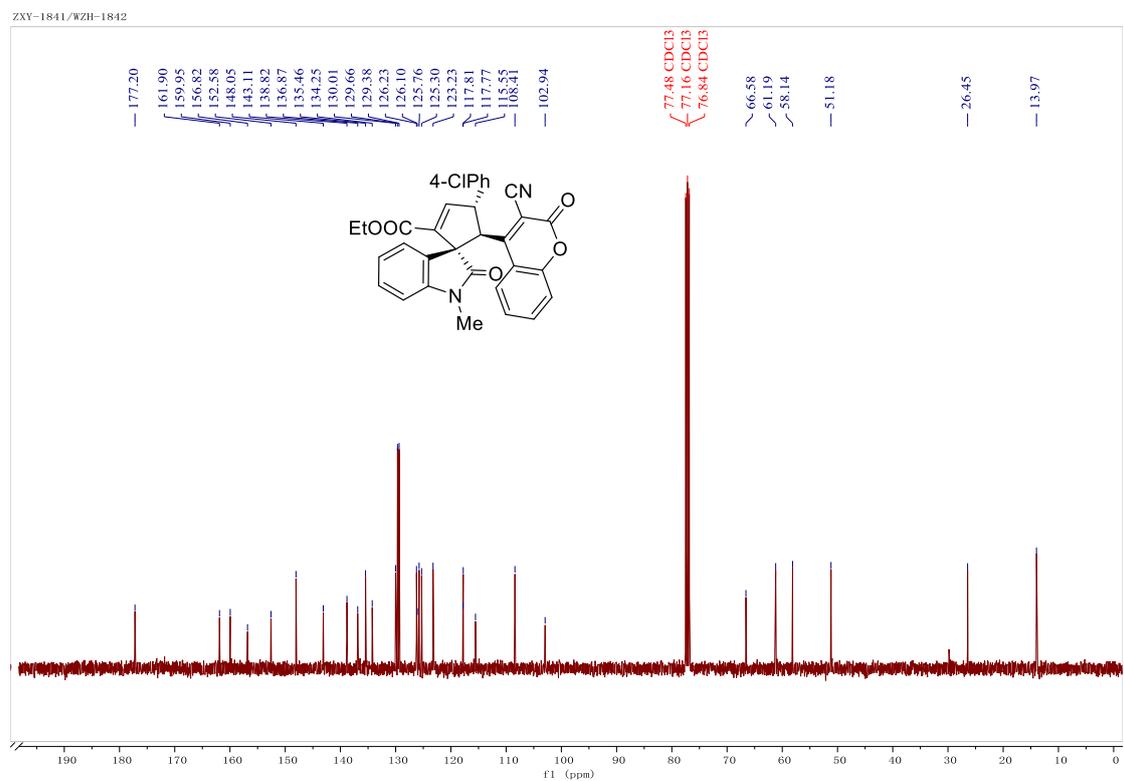
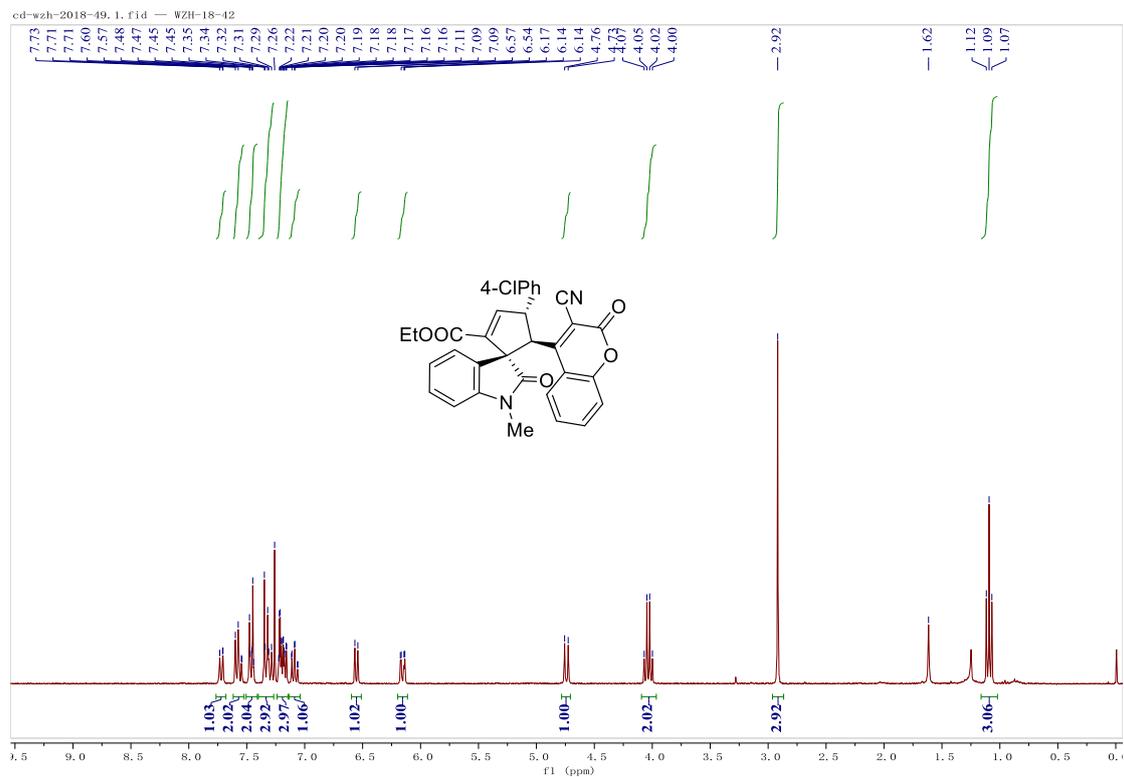
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.587	251171	53.21	6207916	50.65
2	12.760	220877	46.79	6049396	49.35
<b>Totals</b>		472048	100.00	12257312	100.00

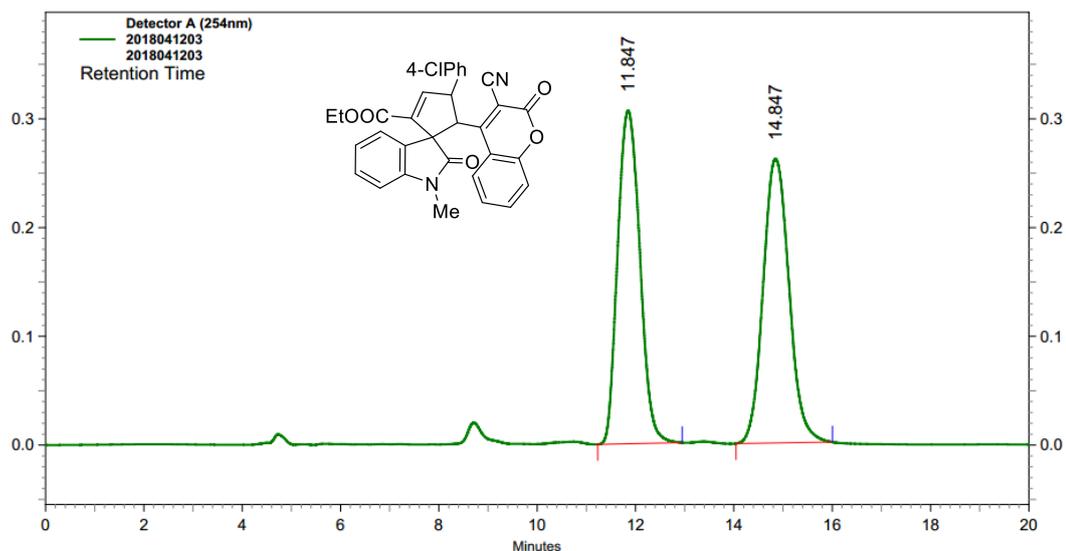


**Detector A (254nm)**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	10.510	723524	94.91	18196953	95.00
2	12.723	38842	5.09	956780	5.00
<b>Totals</b>		762366	100.00	19153733	100.00

**Ethyl (1*R*,4*S*,5*S*)-4-(4-chlorophenyl)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ga)**

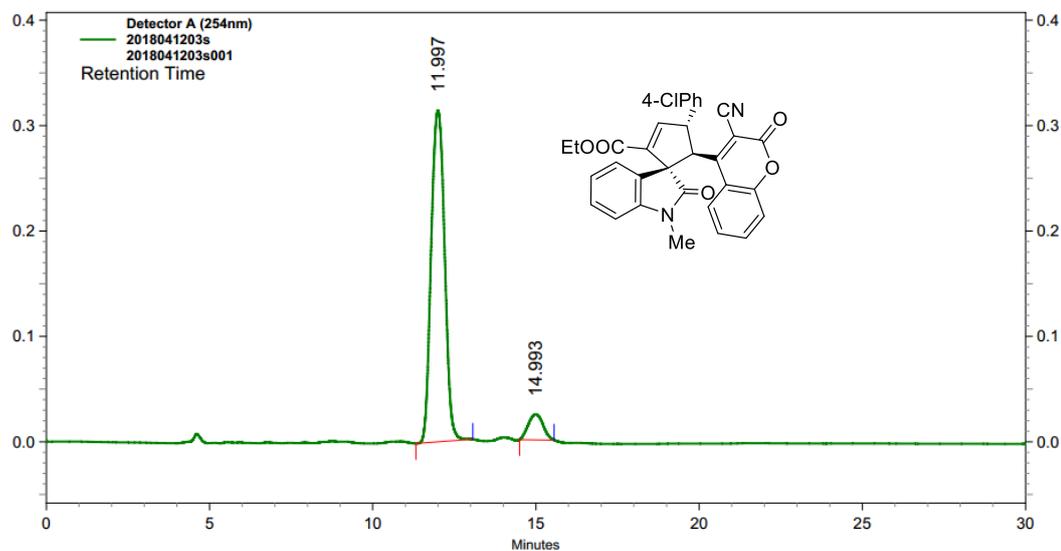




Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.847	306283	53.97	9617400	50.12
2	14.847	261252	46.03	9572651	49.88

Totals		567535	100.00	19190051	100.00
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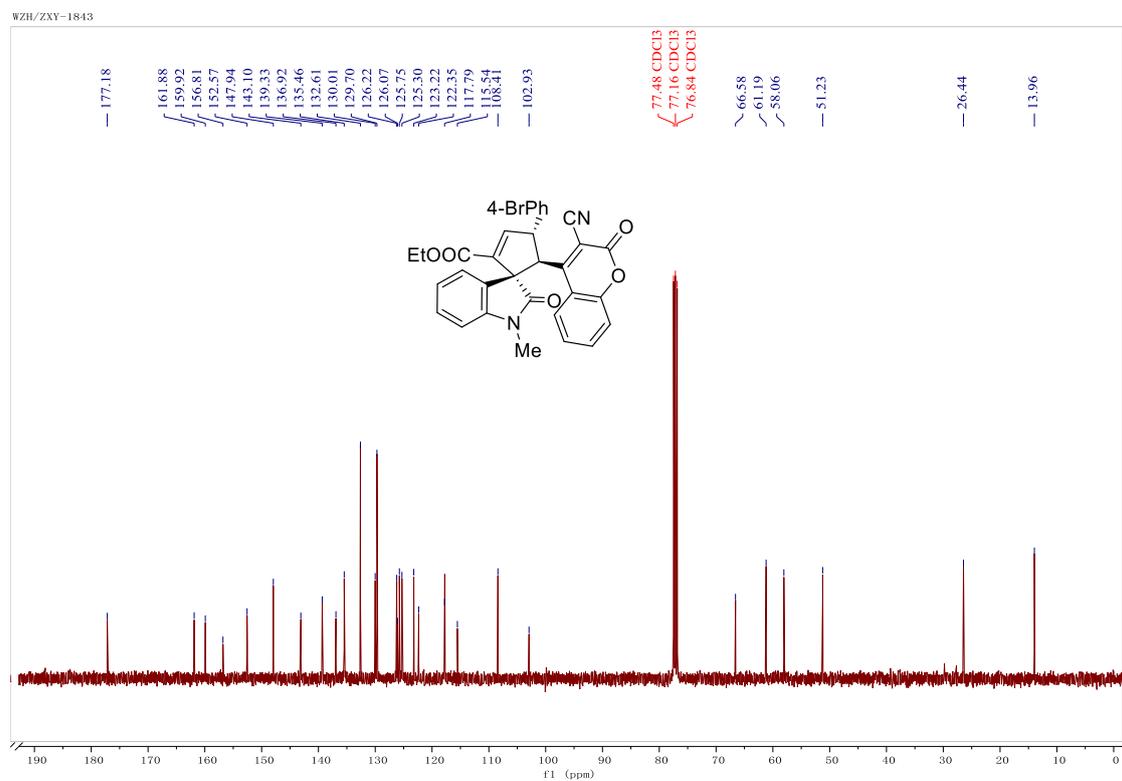
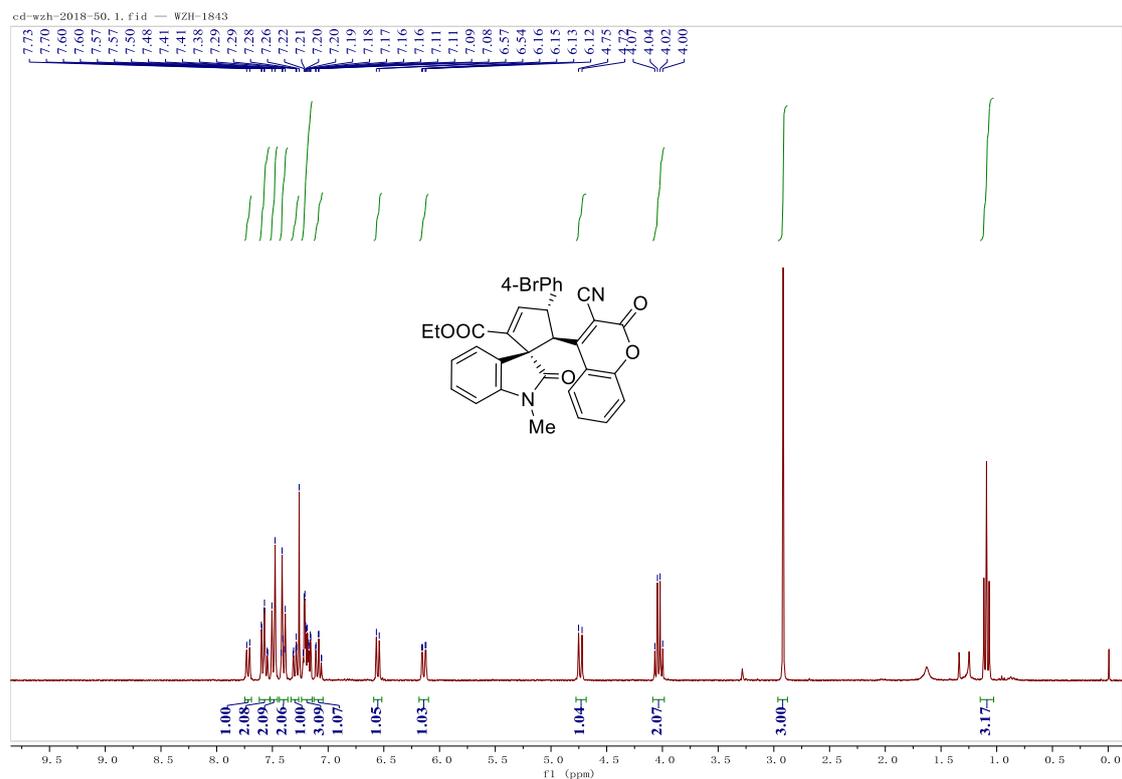


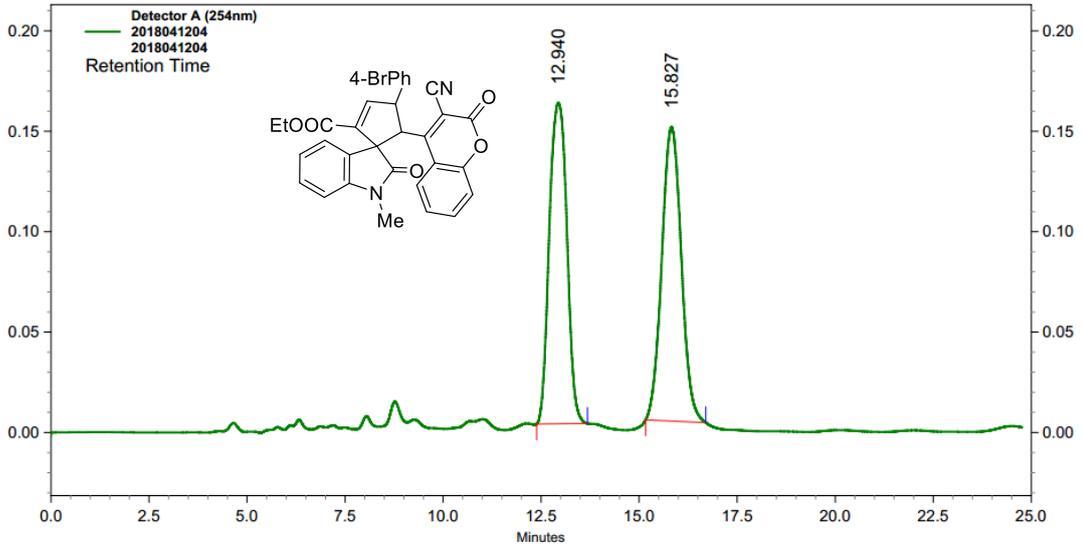
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.997	314270	92.82	8999890	92.14
2	14.993	24323	7.18	767239	7.86

Totals		338593	100.00	9767129	100.00
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**Ethyl (1*R*,4*S*,5*S*)-4-(4-bromophenyl)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ha)**

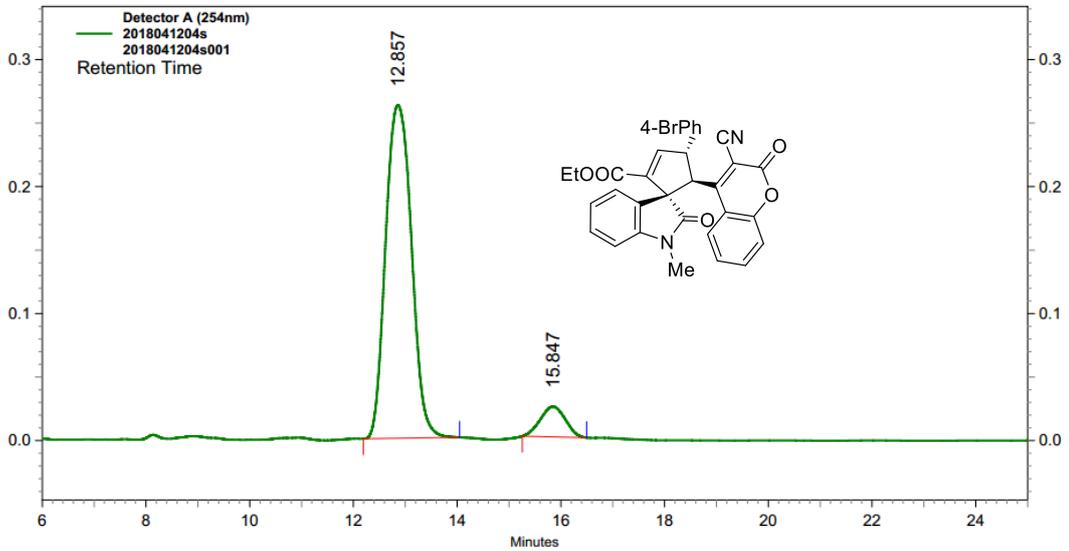




Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.940	159812	52.18	4989150	49.62
2	15.827	146448	47.82	5066212	50.38

Totals		306260	100.00	10055362	100.00
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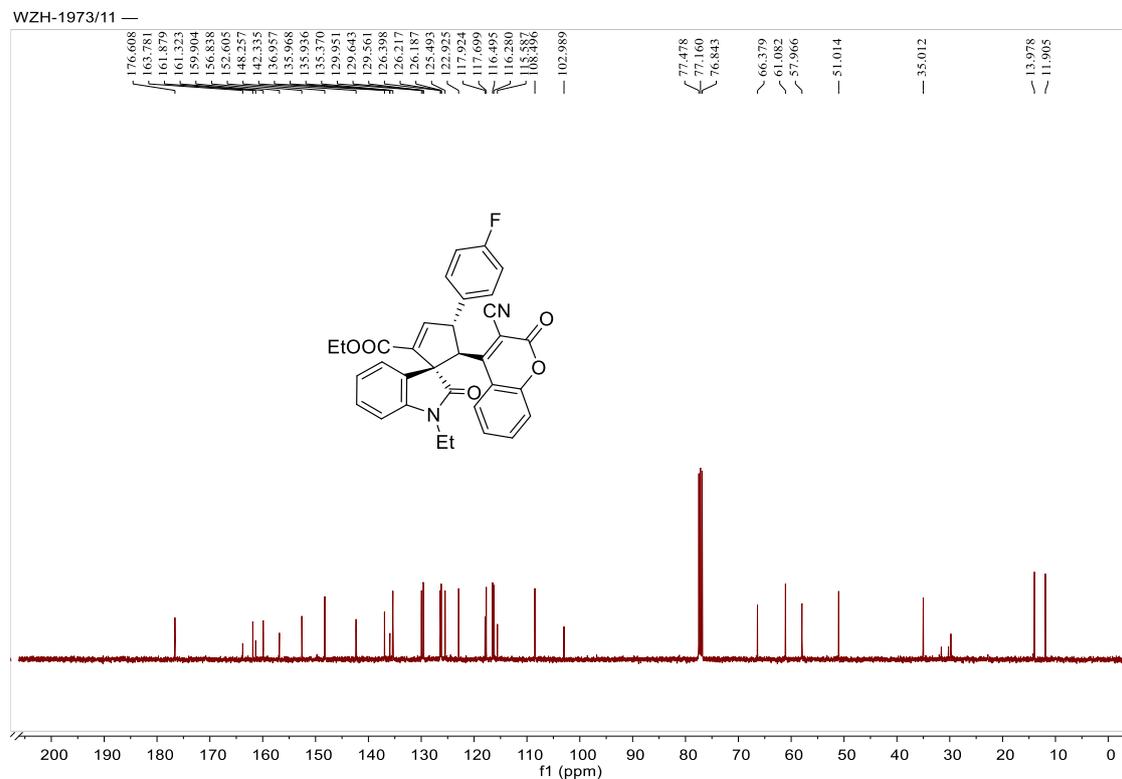
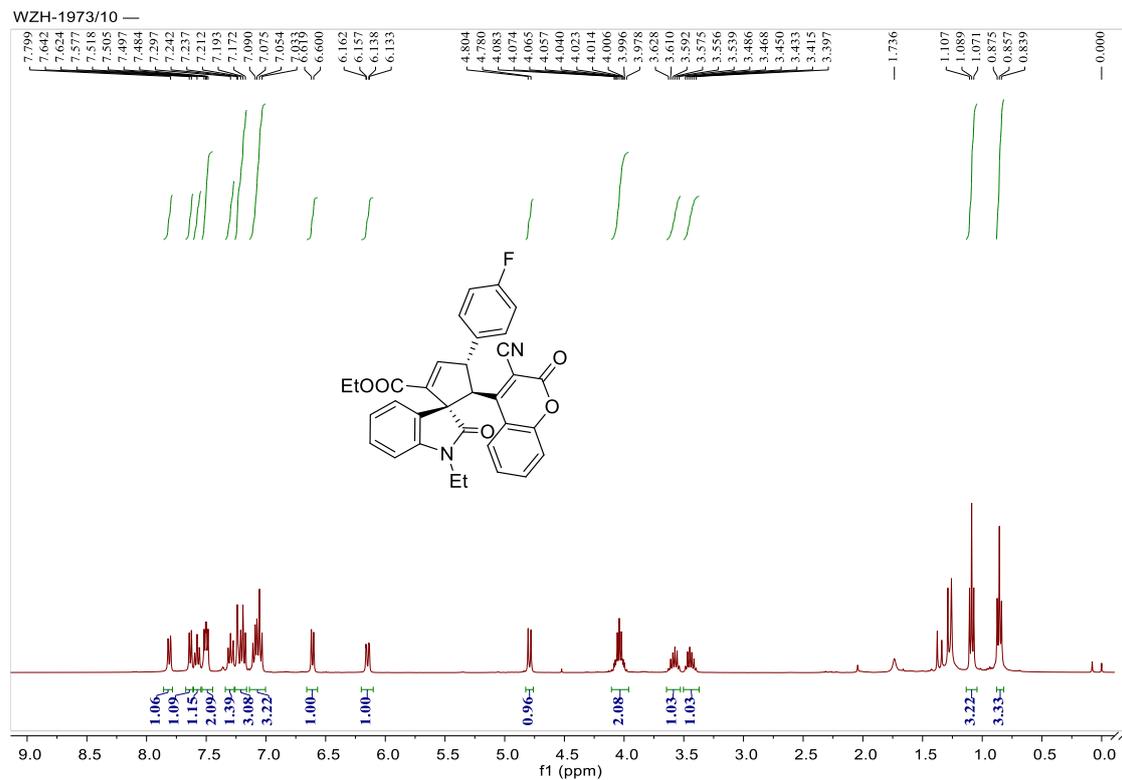


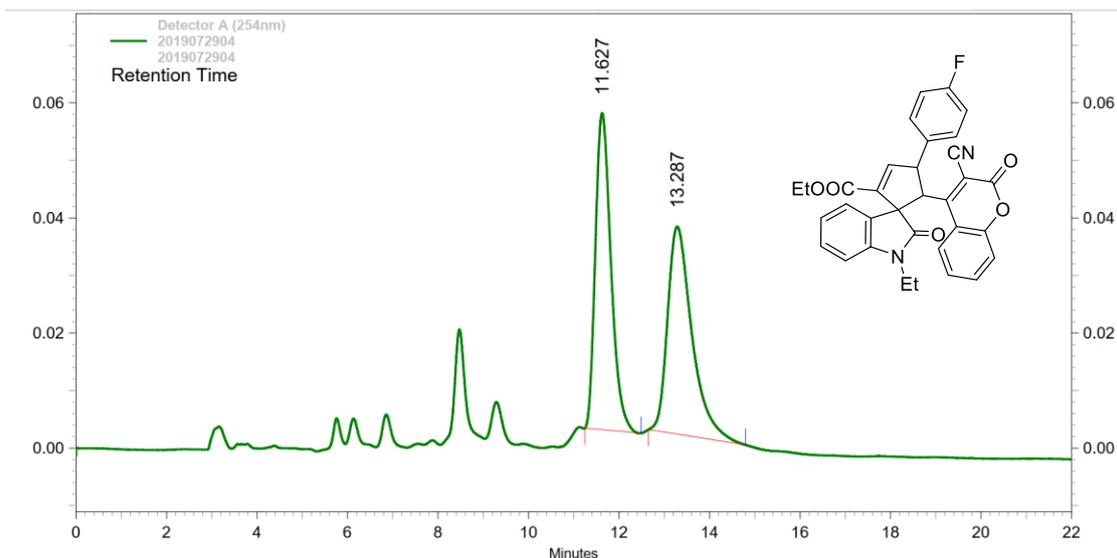
Detector A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.857	262255	91.67	9103585	91.92
2	15.847	23831	8.33	800123	8.08

Totals		286086	100.00	9903708	100.00
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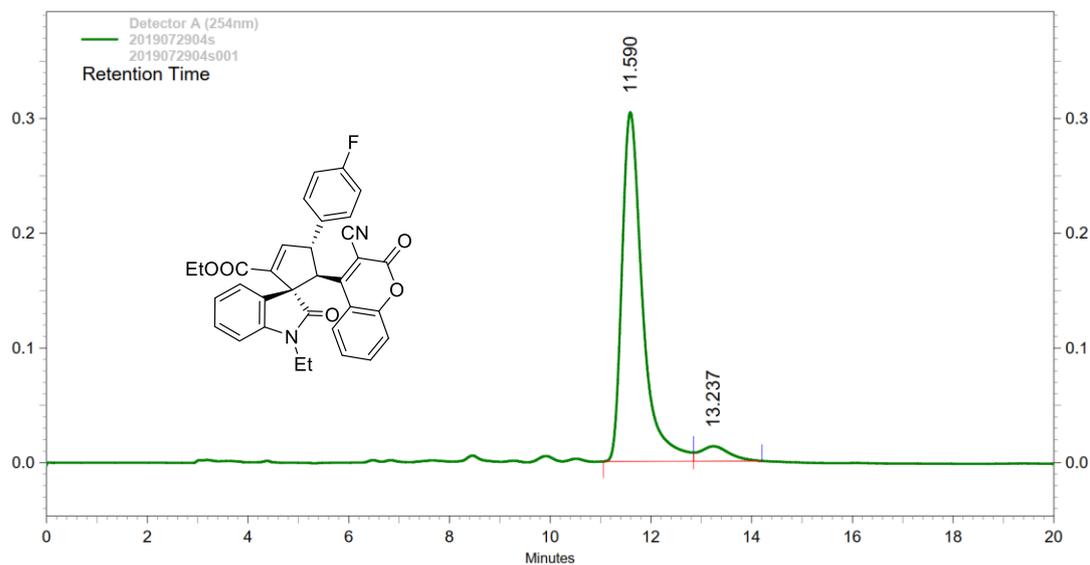
**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-4-(4-fluorophenyl)-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ik)**





**Detector A (254nm)**

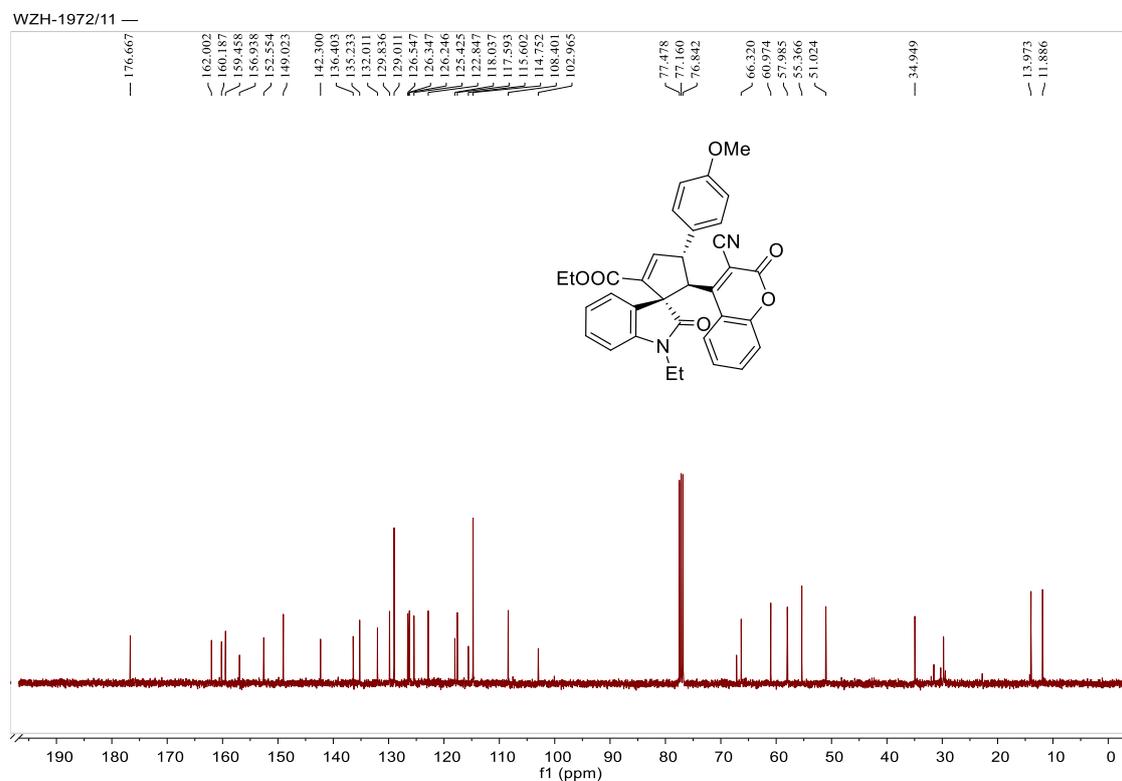
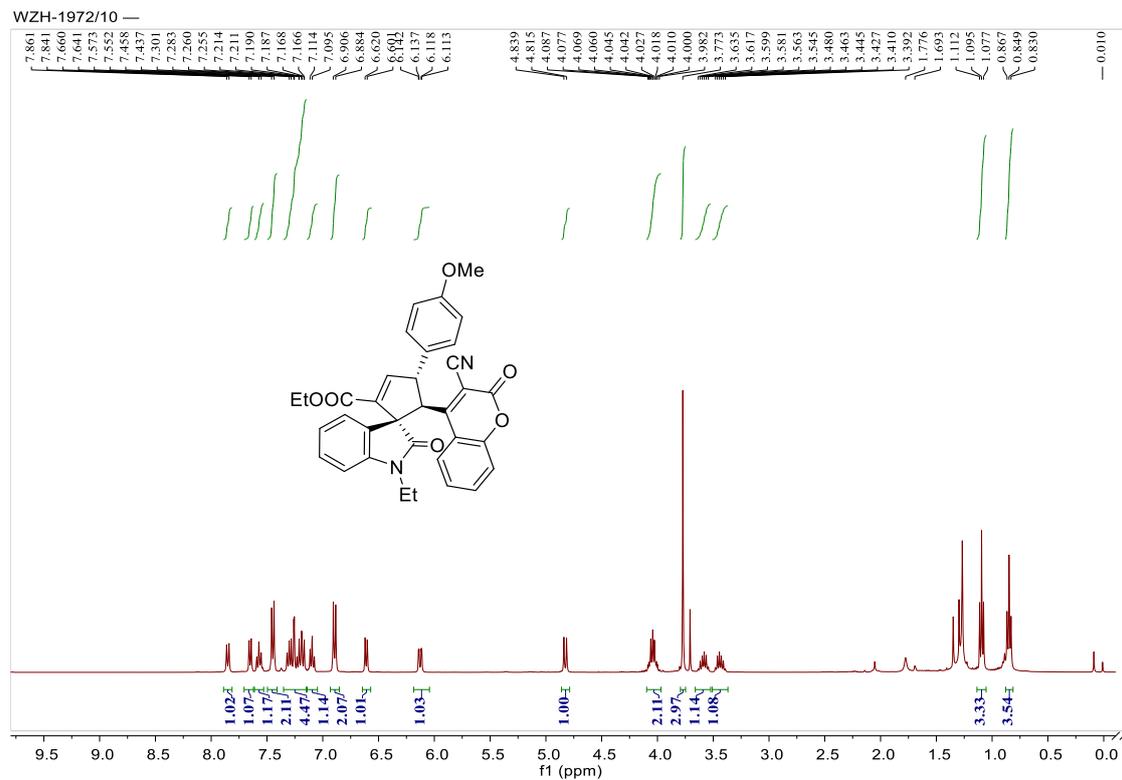
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.627	55021	60.39	1317103	49.31
2	13.287	36088	39.61	1353772	50.69
<b>Totals</b>		91109	100.00	2670875	100.00

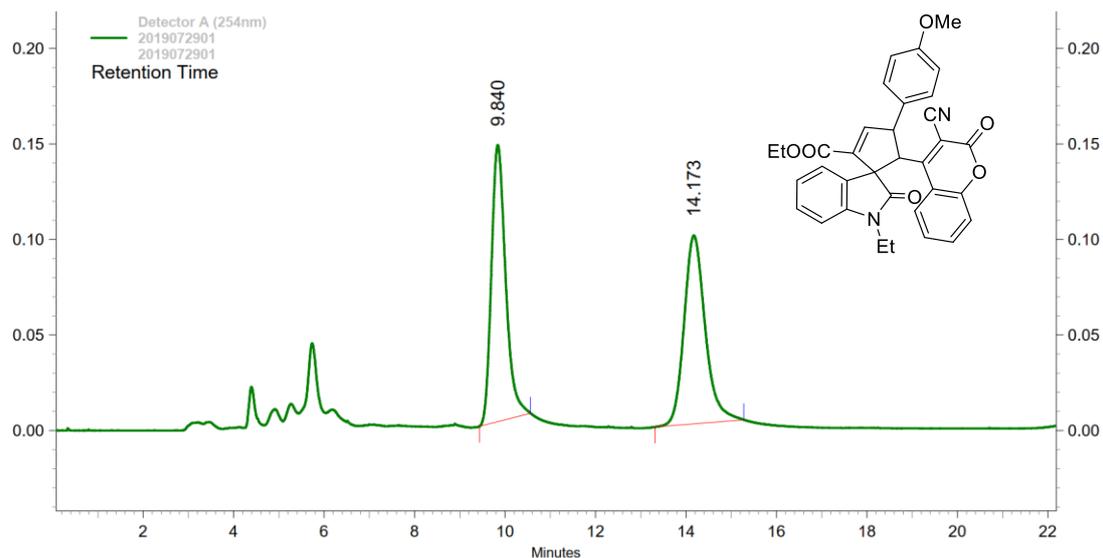


**Detector A 254nm**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.590	304188	95.92	8615529	94.20
2	13.237	12950	4.08	530502	5.80
<b>Totals</b>		317138	100.00	9146031	100.00

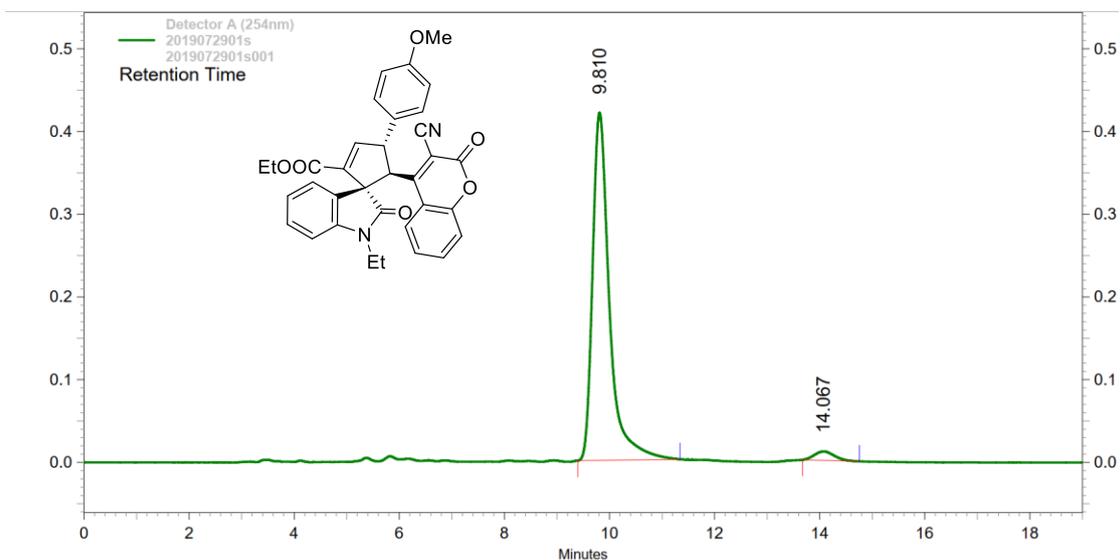
**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-4-(4-methoxyphenyl)-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3jk)**





**Detector A (254nm)**

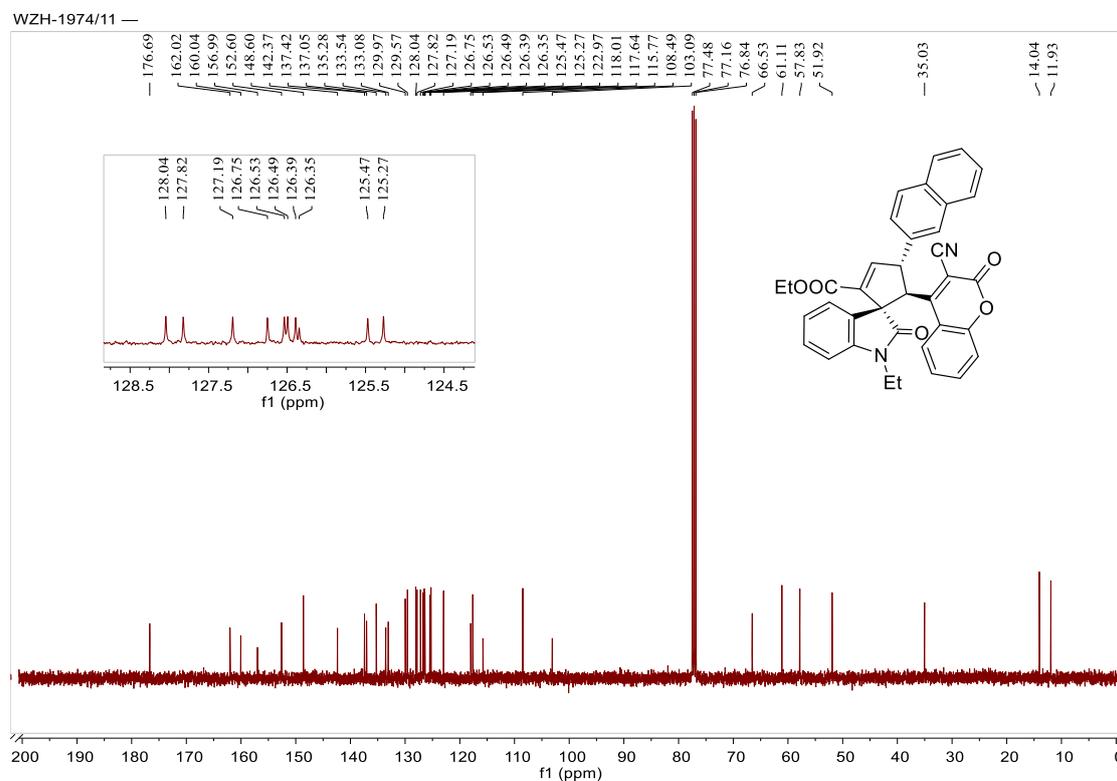
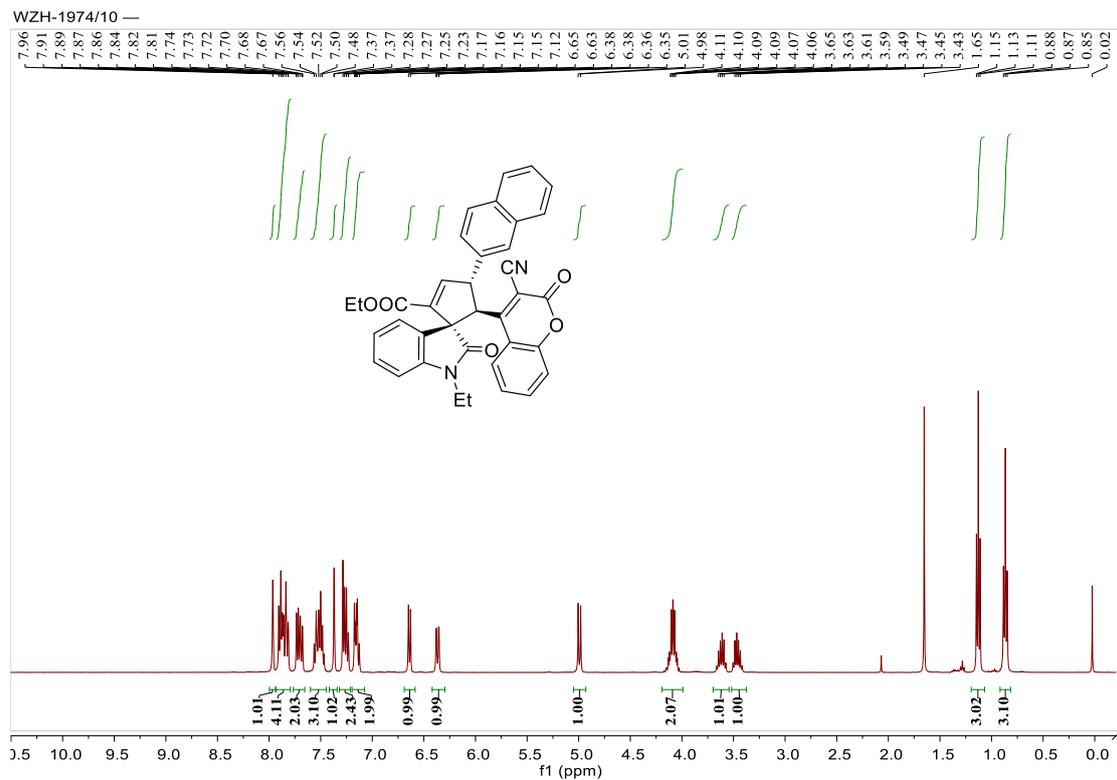
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.840	144689	59.49	3172054	49.77
2	14.173	98518	40.51	3200781	50.23
<b>Totals</b>		243207	100.00	6372835	100.00

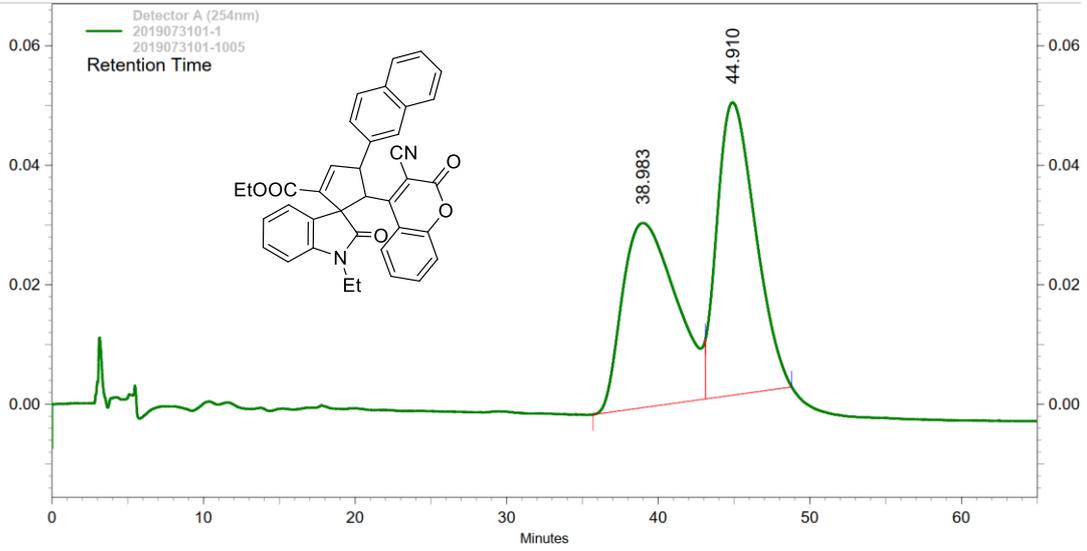


**Detector A 254nm**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.810	420332	97.52	9362122	97.02
2	14.067	10675	2.48	287097	2.98
<b>Totals</b>		431007	100.00	9649219	100.00

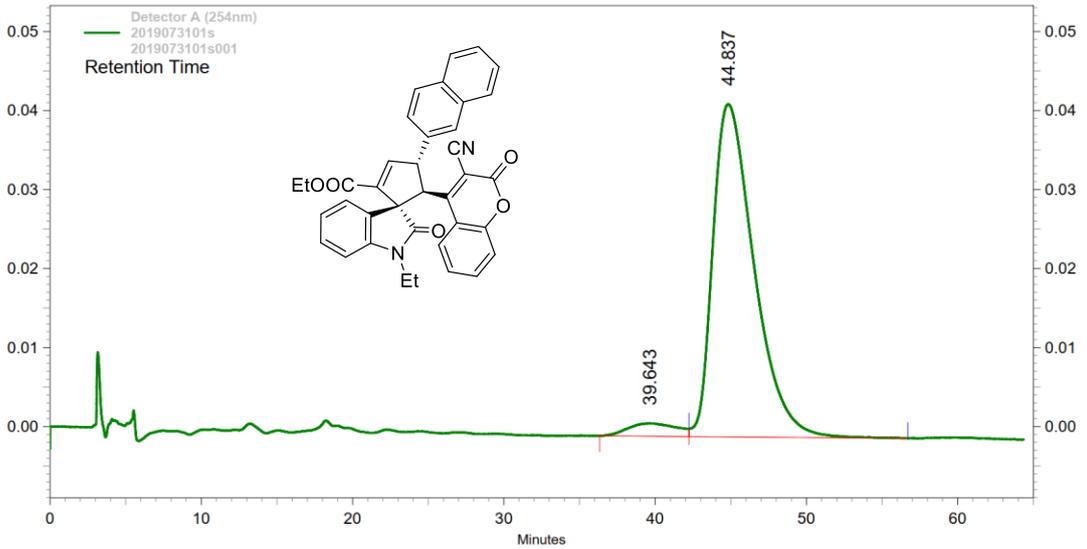
**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-4-(naphthalen-2-yl)-2'-oxospiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate**





Detector  
A. 254nm

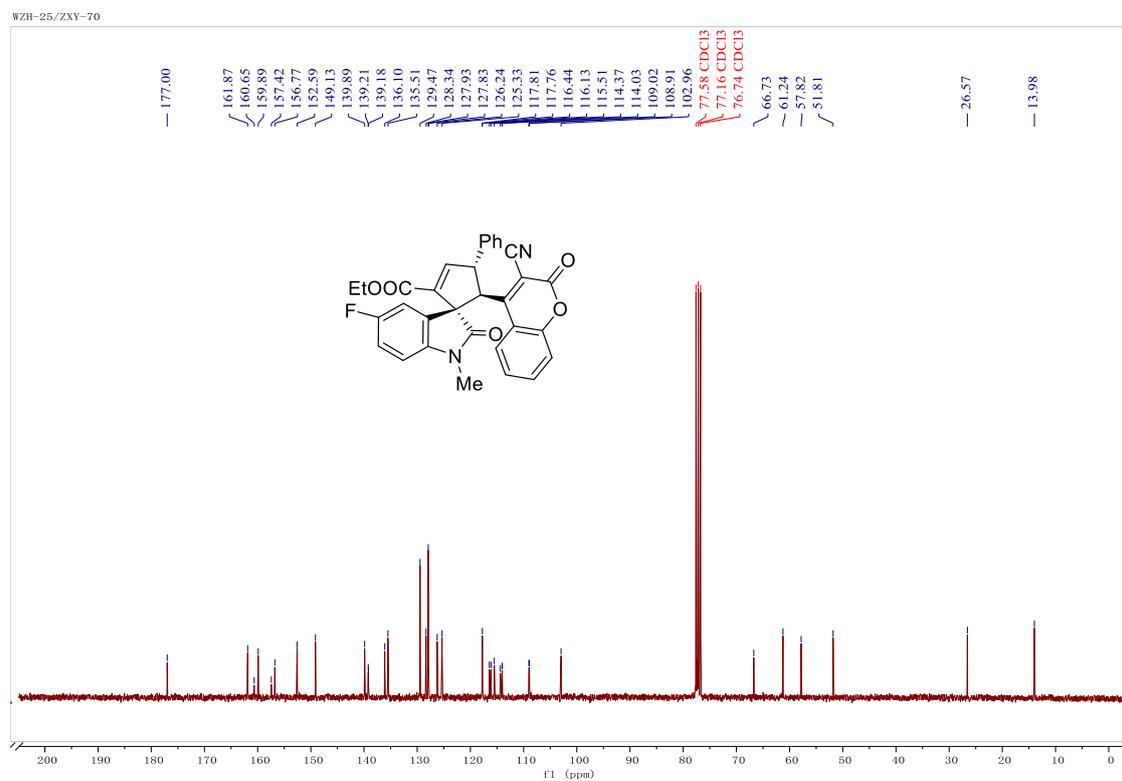
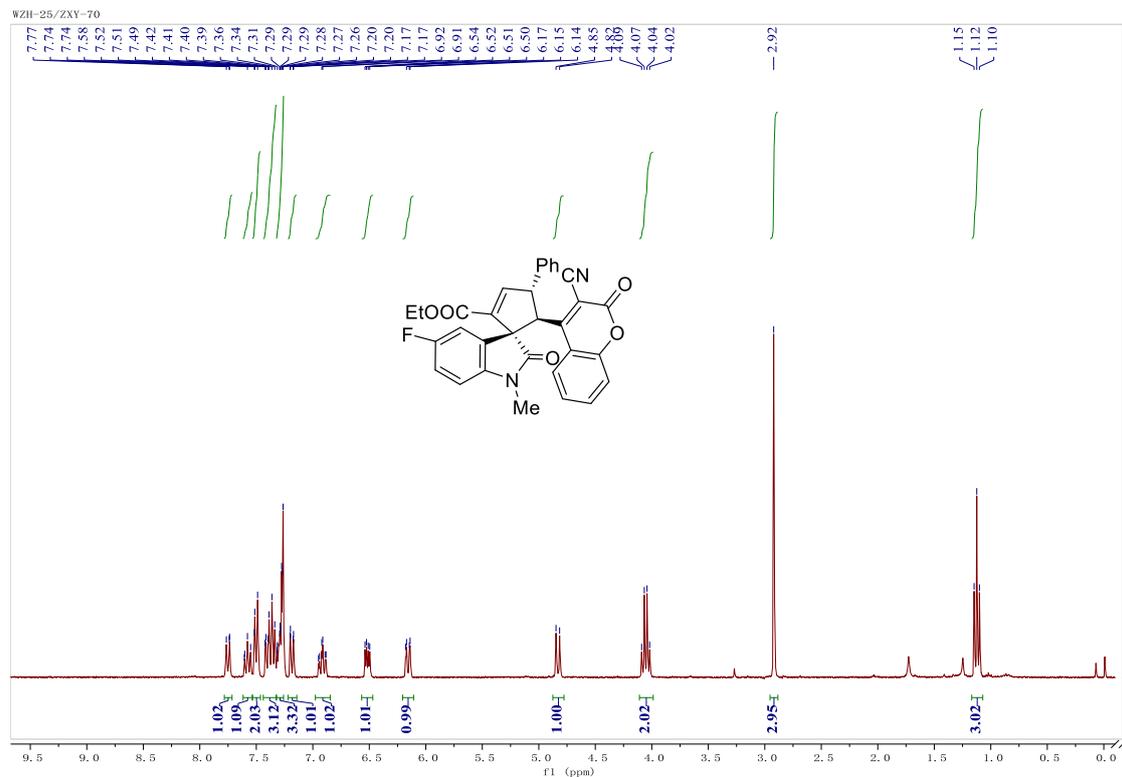
PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	38.983	30905	38.69	7617998	46.90
2	44.910	48979	61.31	8623763	53.10
<b>Totals</b>		79884	100.00	16241761	100.00

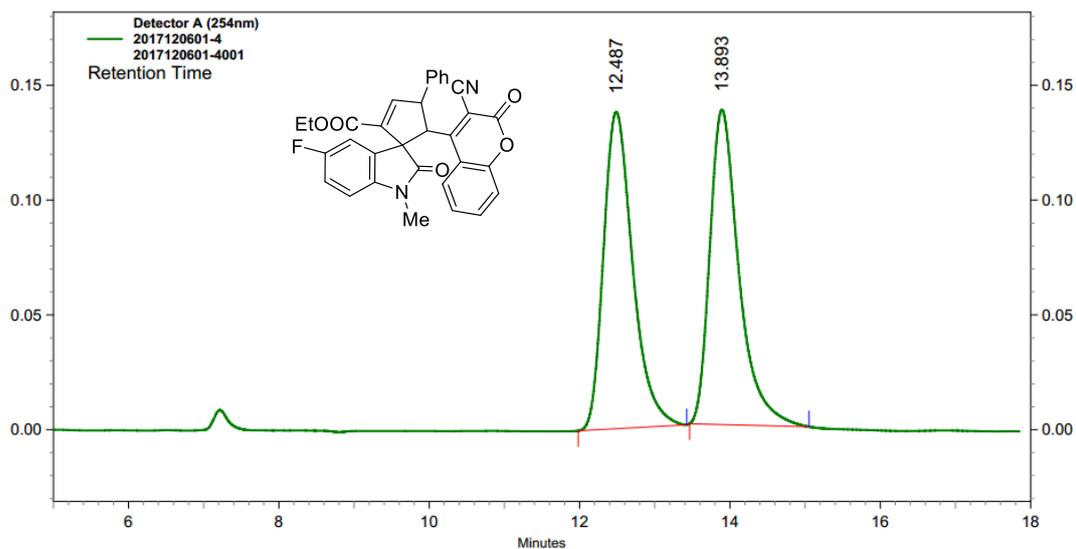


Detector  
A (254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	39.643	1632	3.73	364758	4.38
2	44.837	42119	96.27	7969100	95.62
<b>Totals</b>		43751	100.00	8333858	100.00

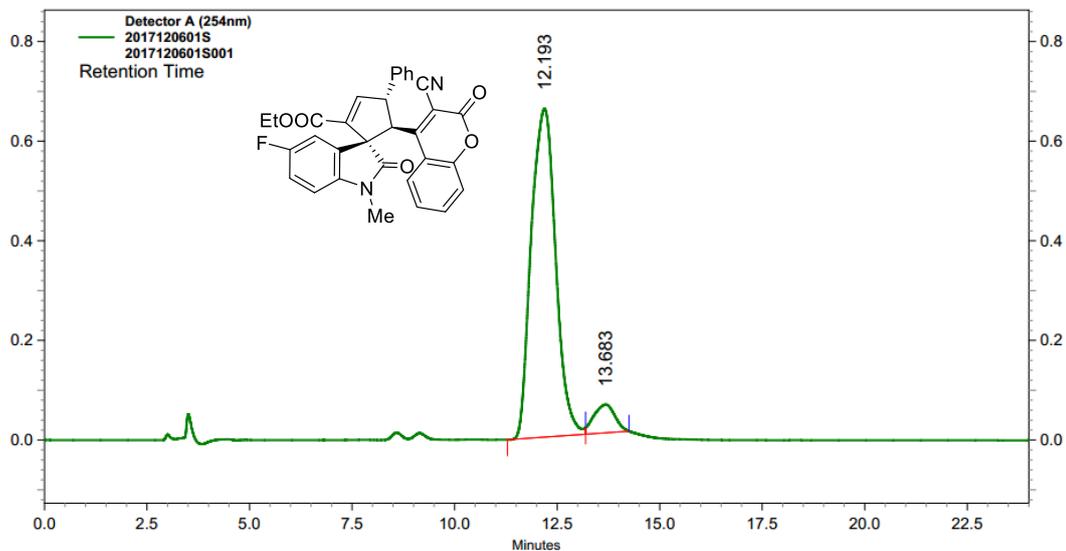
**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-5'-fluoro-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ab)**





**Detector A (254nm)**

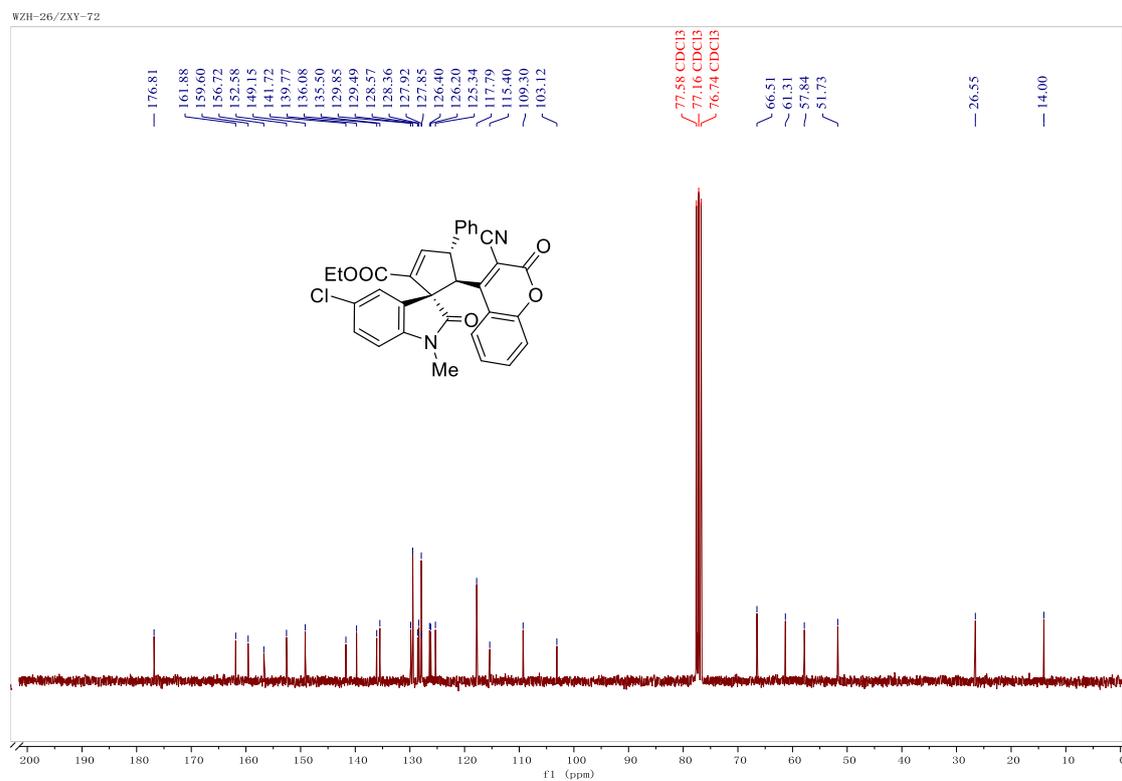
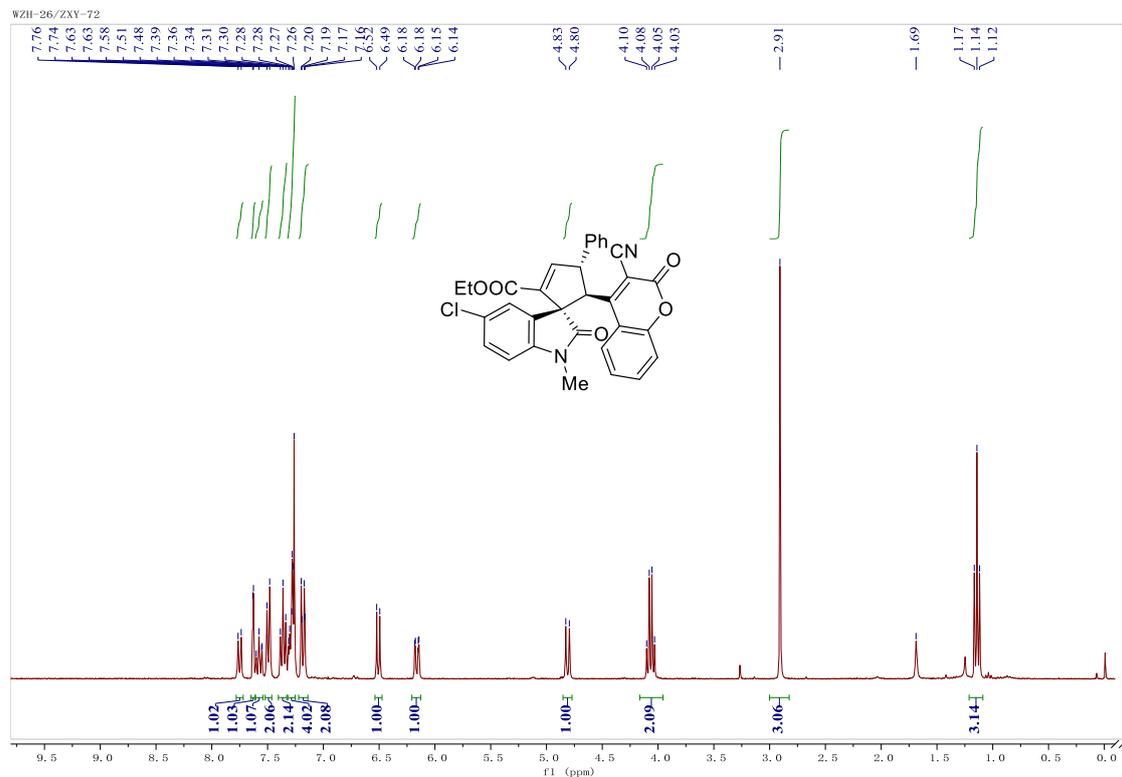
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.487	137896	50.15	3720370	50.17
2	13.893	137065	49.85	3694670	49.83
<b>Totals</b>					
		274961	100.00	7415040	100.00

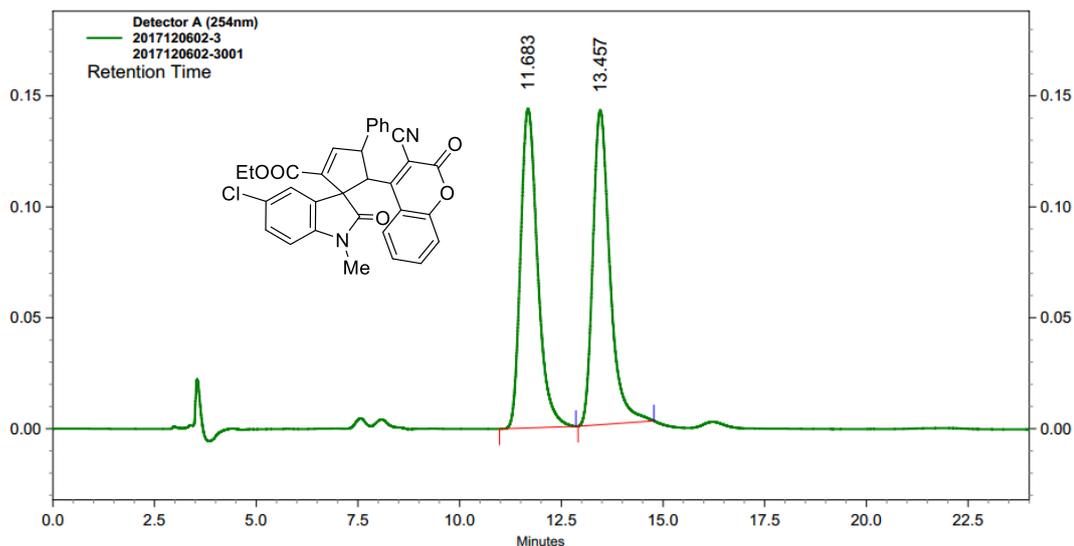


**Detector A (254nm)**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.193	659384	92.09	27314530	93.07
2	13.683	56606	7.91	2033650	6.93
<b>Totals</b>					
		715990	100.00	29348180	100.00

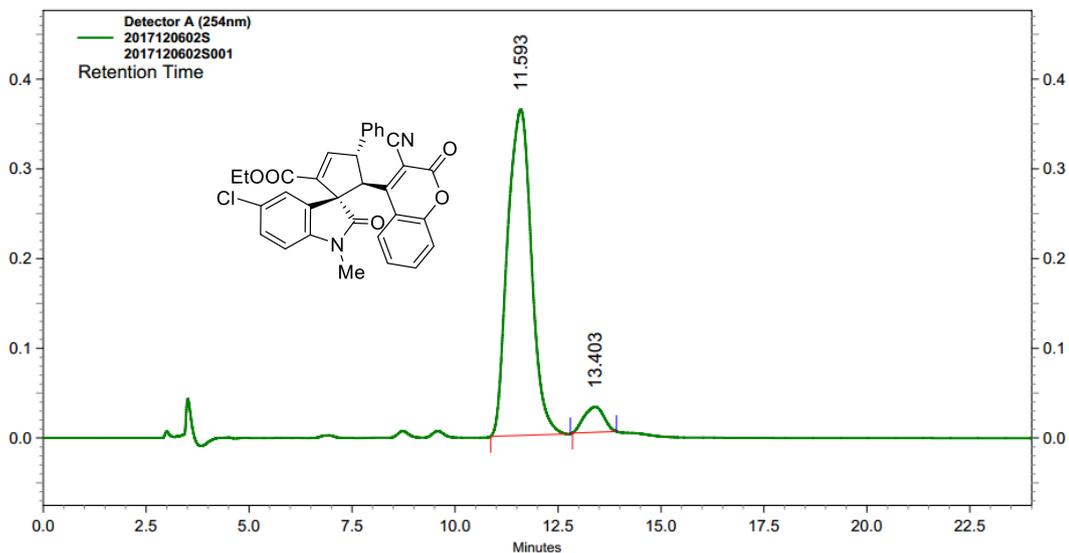
**Ethyl (1*R*,4*S*,5*S*)-5'-chloro-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ac)**





**Detector A (254nm)**

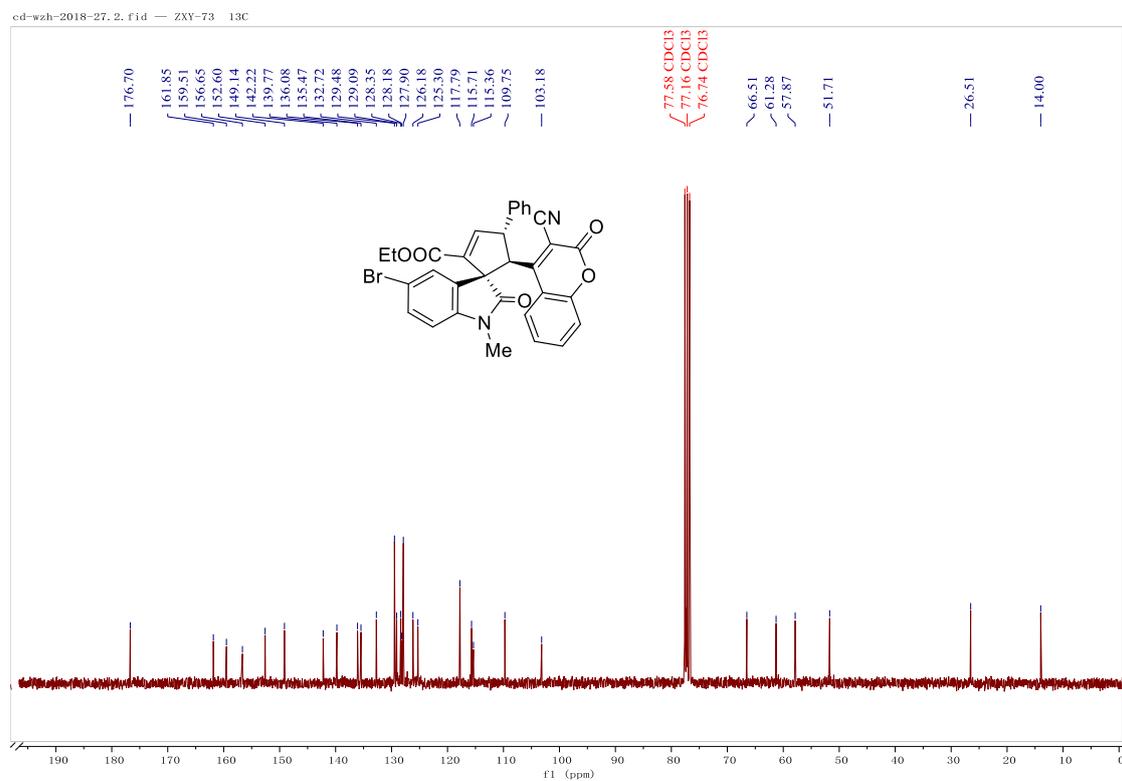
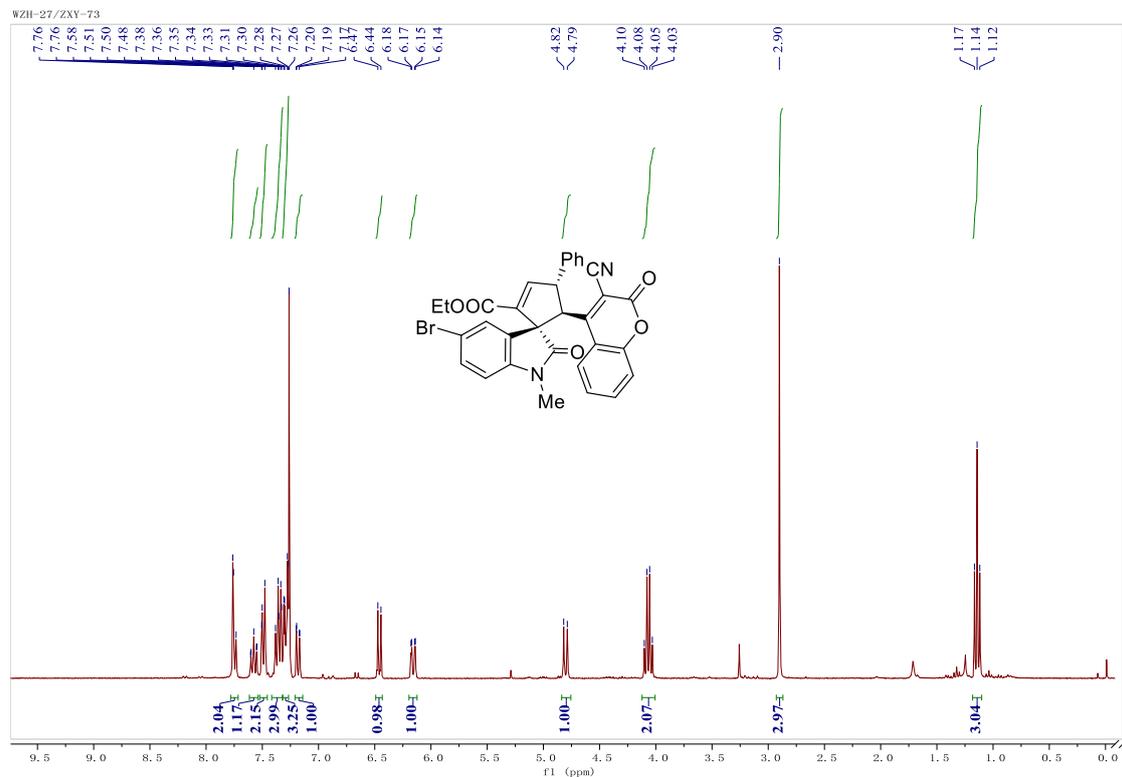
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.683	143884	50.38	4191163	50.32
2	13.457	141692	49.62	4137136	49.68
<b>Totals</b>		285576	100.00	8328299	100.00

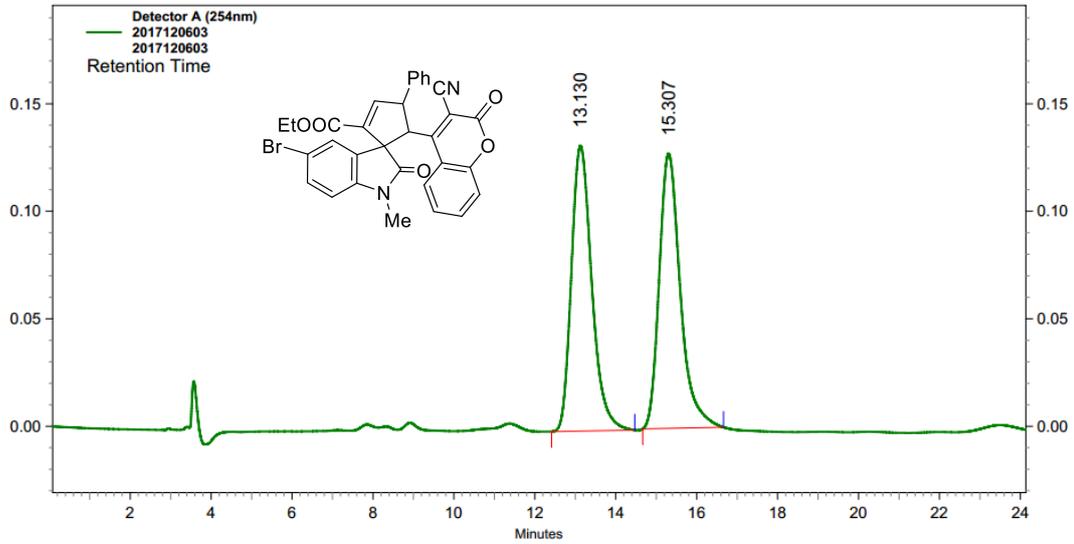


**Detector A (254nm)**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.593	363569	92.77	14608863	93.86
2	13.403	28343	7.23	955171	6.14
<b>Totals</b>		391912	100.00	15564034	100.00

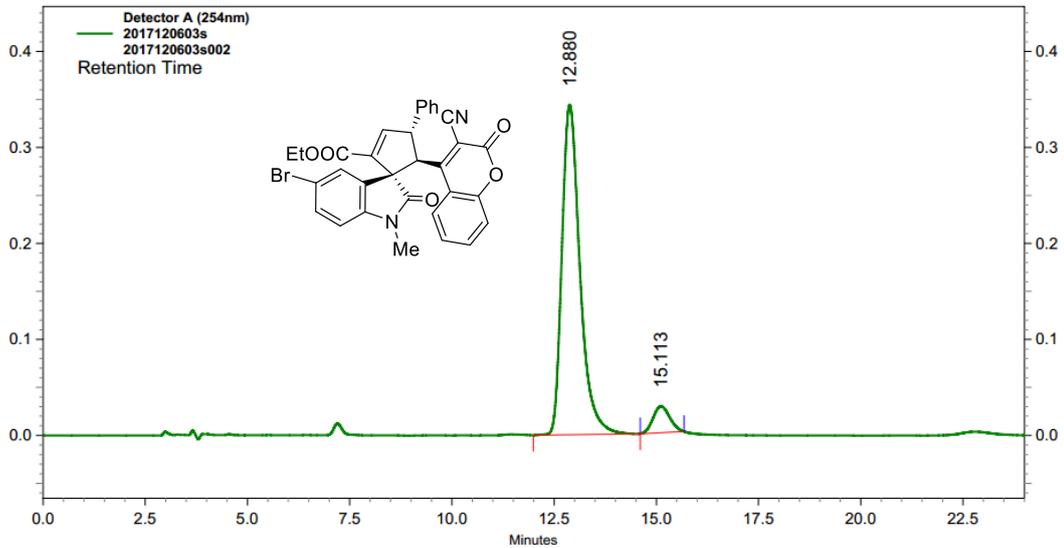
**Ethyl (1*R*,4*S*,5*S*)-5'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ad)**





Detector  
A (254nm)

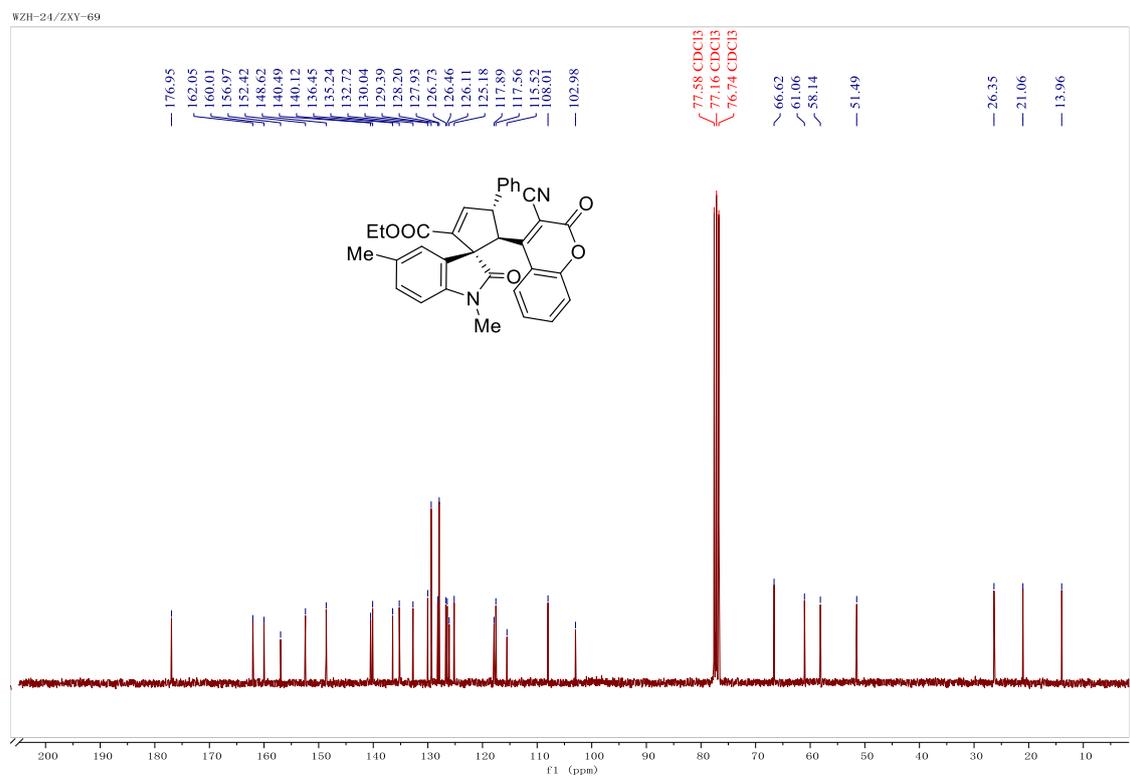
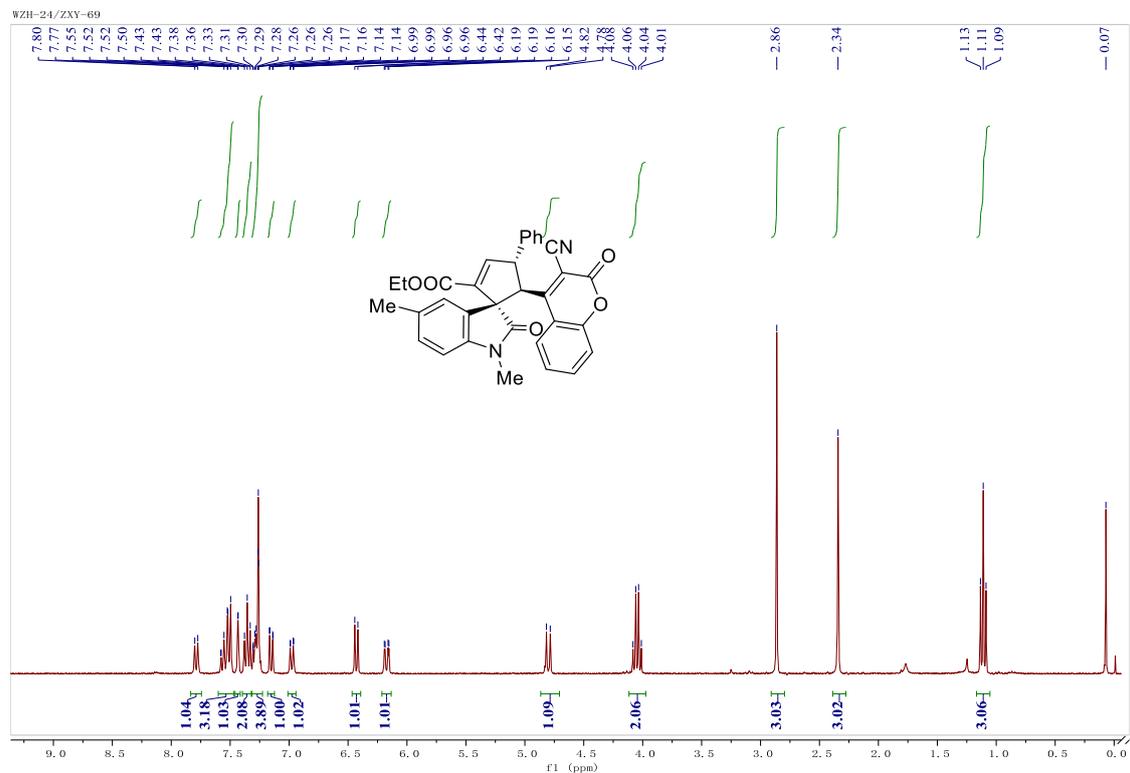
PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	13.130	132754	50.93	4645000	50.08
2	15.307	127883	49.07	4630679	49.92
<b>Totals</b>		260637	100.00	9275679	100.00

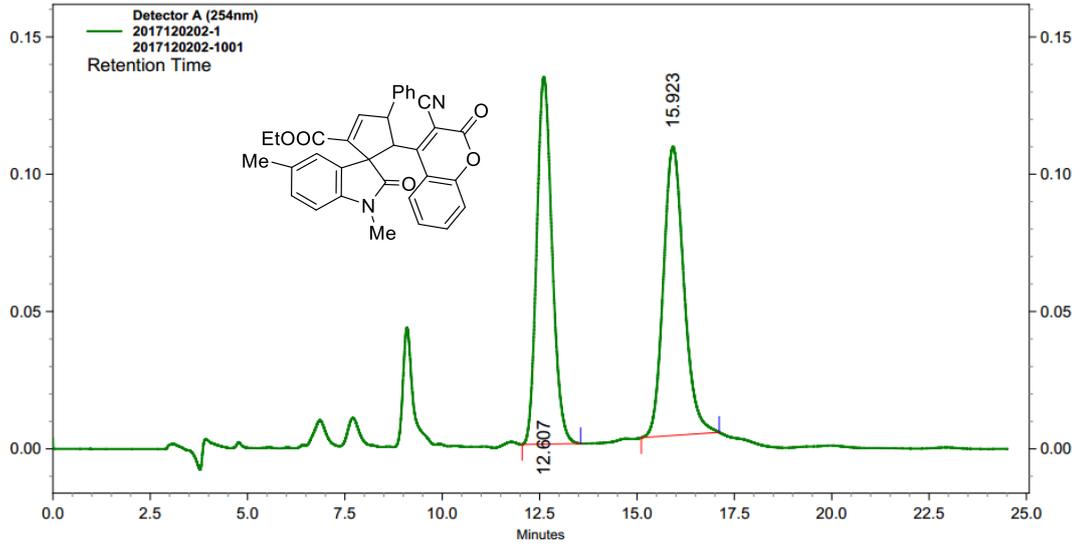


Detector  
A (254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.880	343615	92.56	10510622	93.07
2	15.113	27631	7.44	782385	6.93
<b>Totals</b>		371246	100.00	11293007	100.00

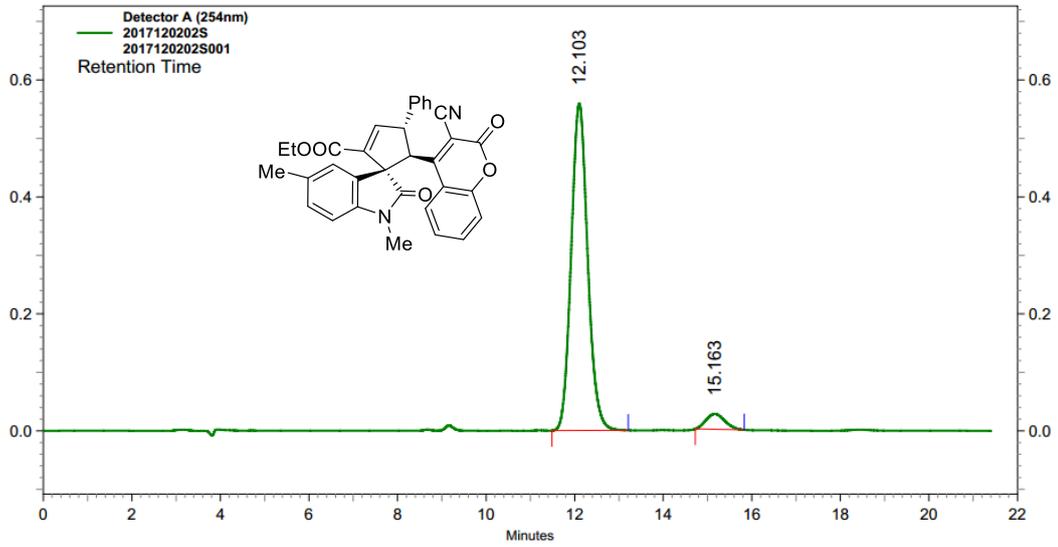
**Ethyl (1R,4S,5S)-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1',5'-dimethyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ae)**





**Detector A (254nm)**  
2017120202-1  
2017120202-1001

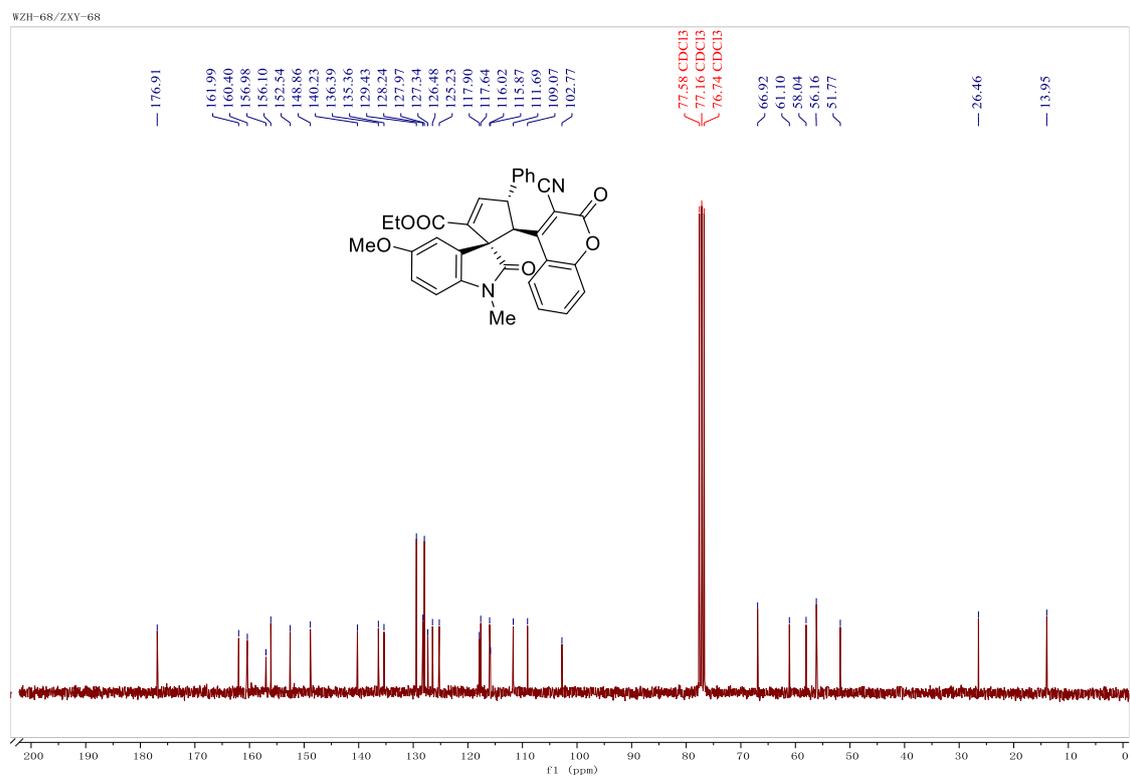
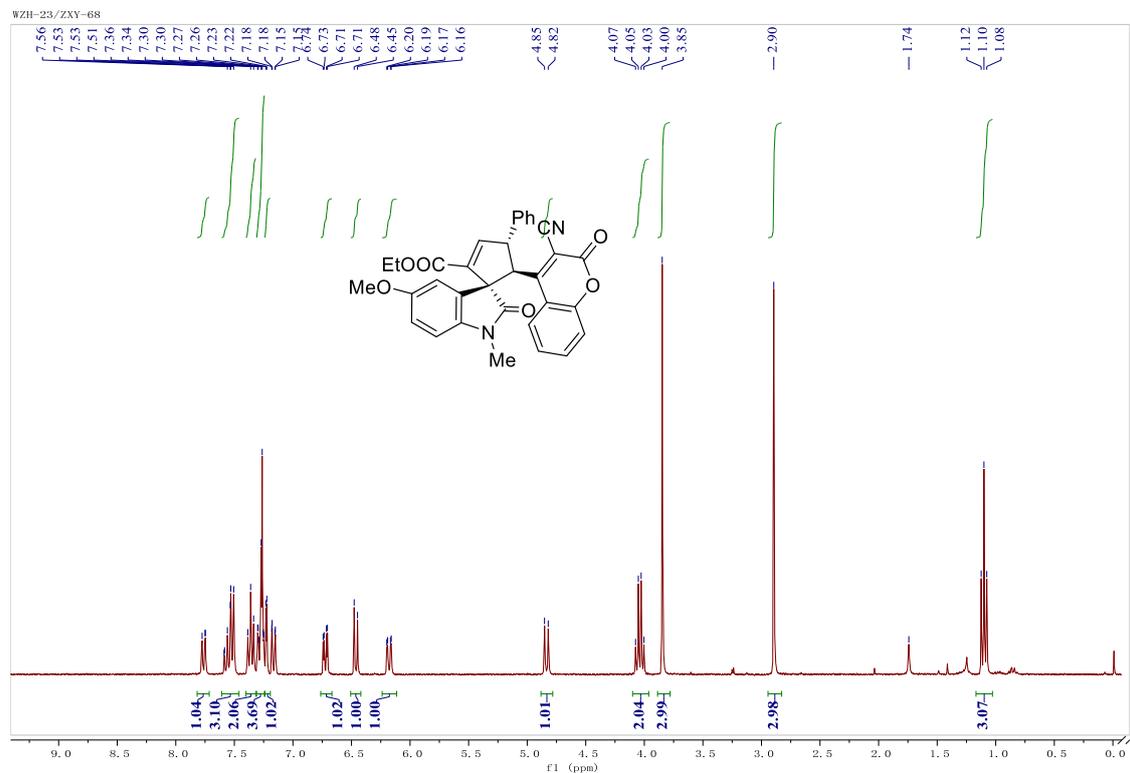
Retention Time	Height	Height Percent	Area	Area Percent
12.607	133768	55.98	3678403	48.81
15.923	105200	44.02	3858354	51.19
<b>Totals</b>	<b>238968</b>	<b>100.00</b>	<b>7536757</b>	<b>100.00</b>

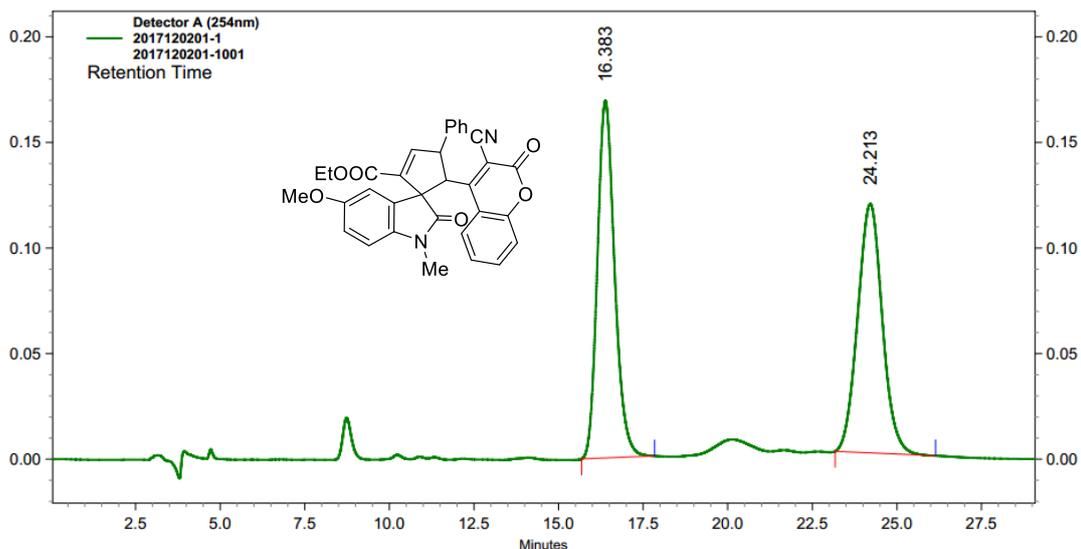


**Detector A (254nm)**  
2017120202S  
2017120202S001

Retention Time	Height	Height Percent	Area	Area Percent
12.103	558961	95.51	14478418	94.88
15.163	26295	4.49	781590	5.12
<b>Totals</b>	<b>585256</b>	<b>100.00</b>	<b>15260008</b>	<b>100.00</b>

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-5'-methoxy-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3af)**



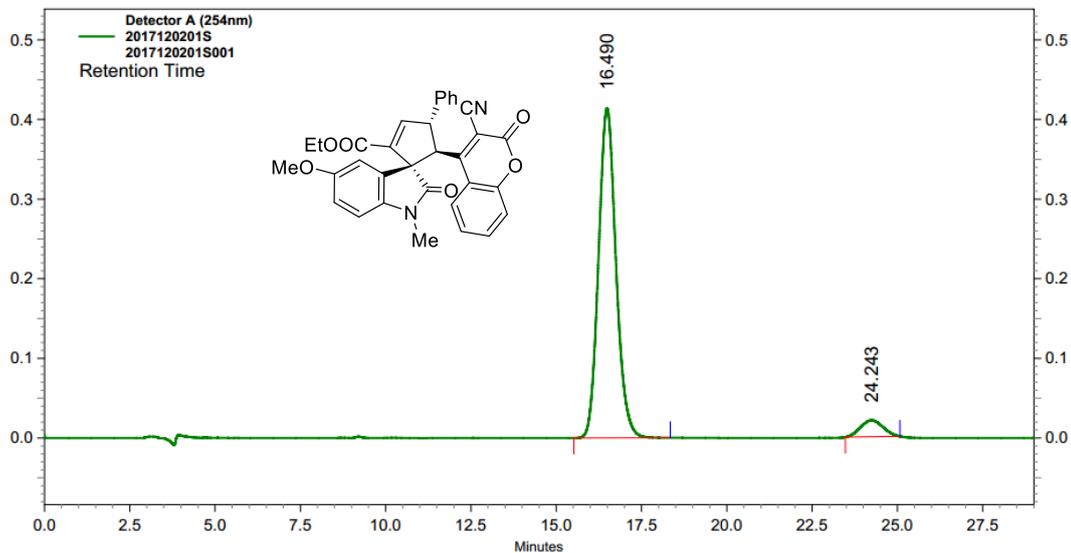


Detector

A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	16.383	169227	58.93	6006004	50.13
2	24.213	117926	41.07	5975346	49.87

Totals		287153	100.00	11981350	100.00
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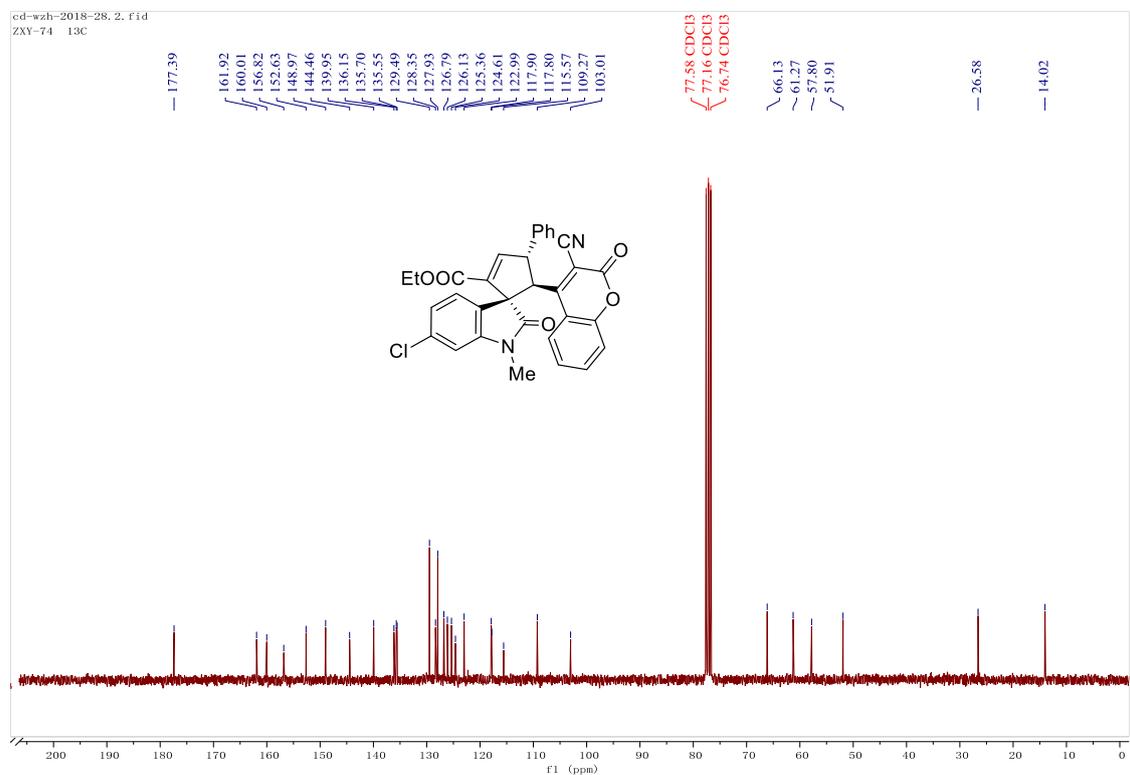
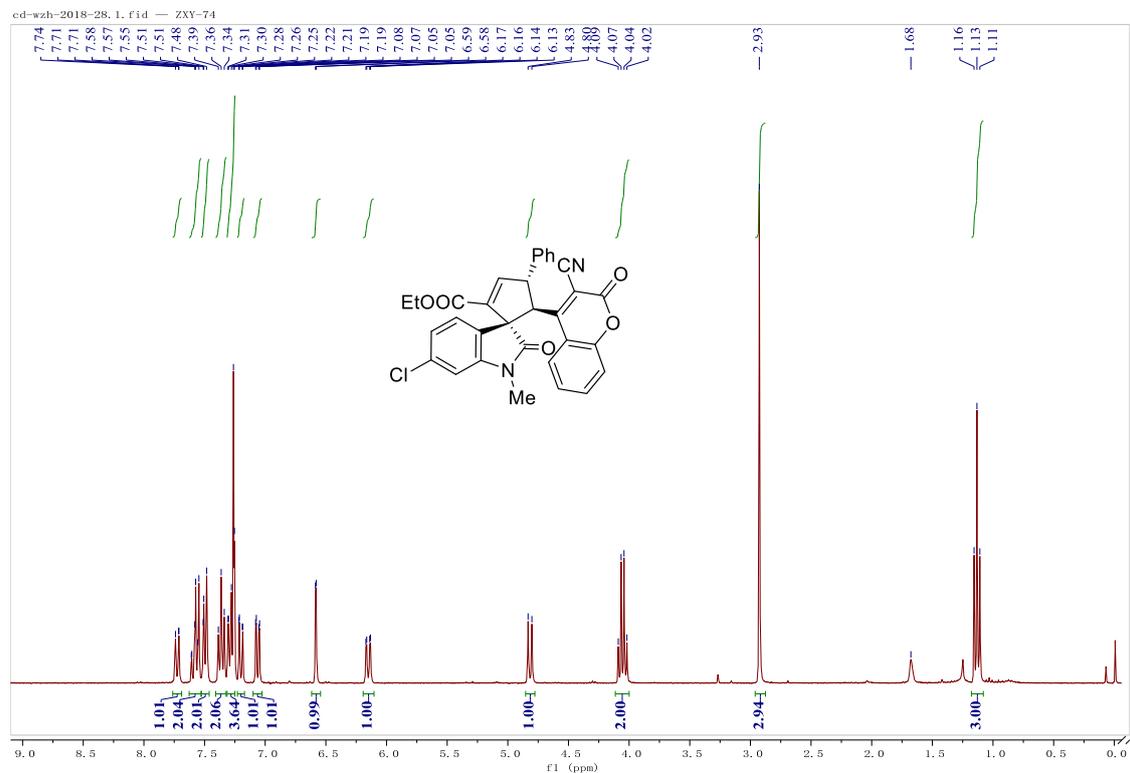
Detector

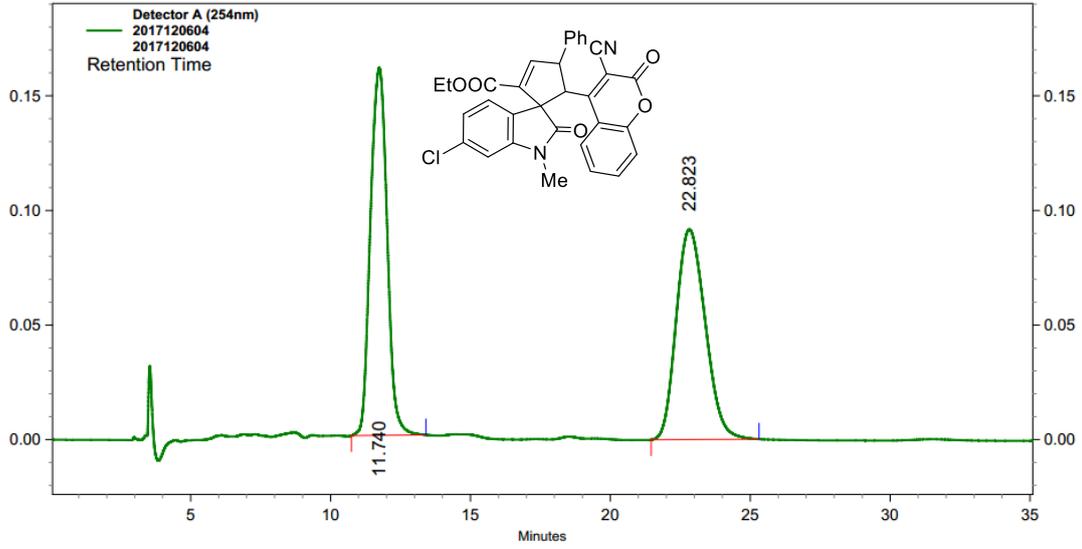
A (254nm)

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	16.490	414102	95.25	14746691	93.96
2	24.243	20644	4.75	947996	6.04

Totals		434746	100.00	15694687	100.00
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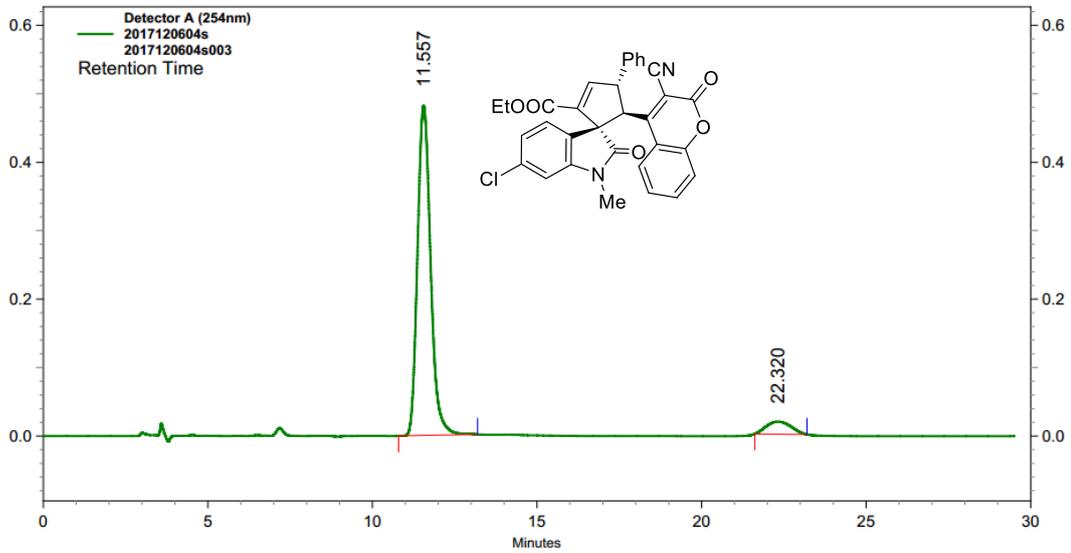
**Ethyl (1R,4S,5S)-6'-chloro-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ag)**





**Detector A (254nm)**

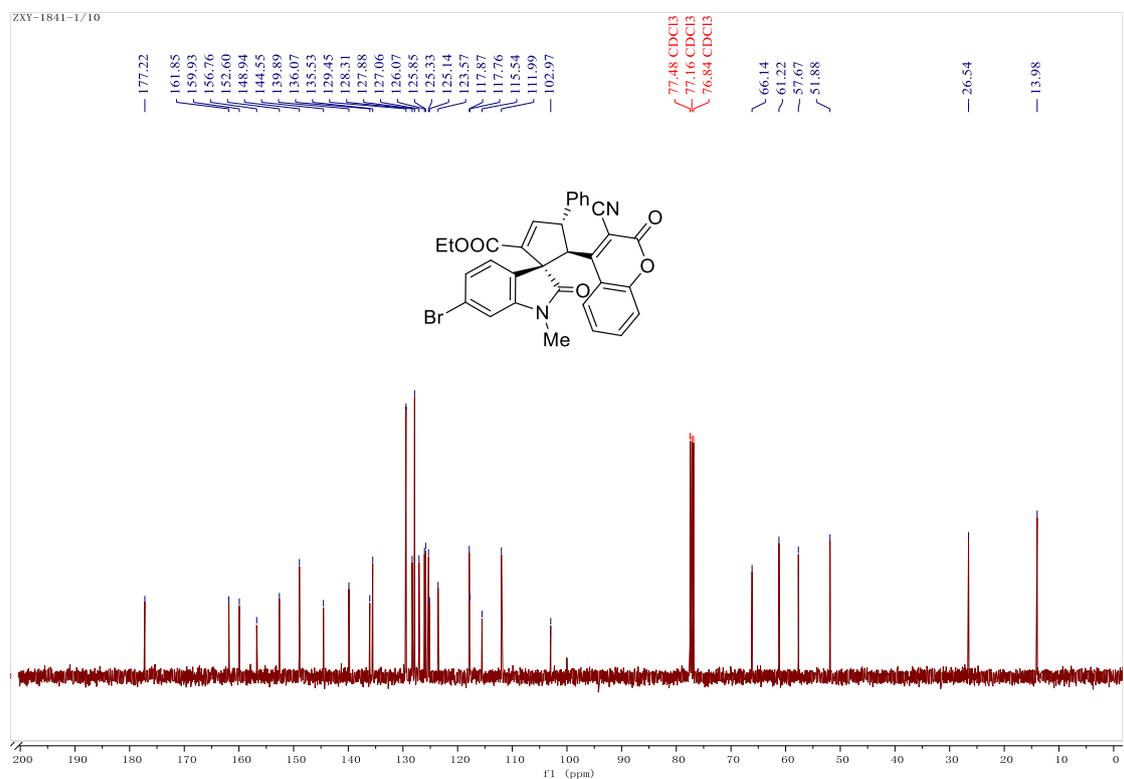
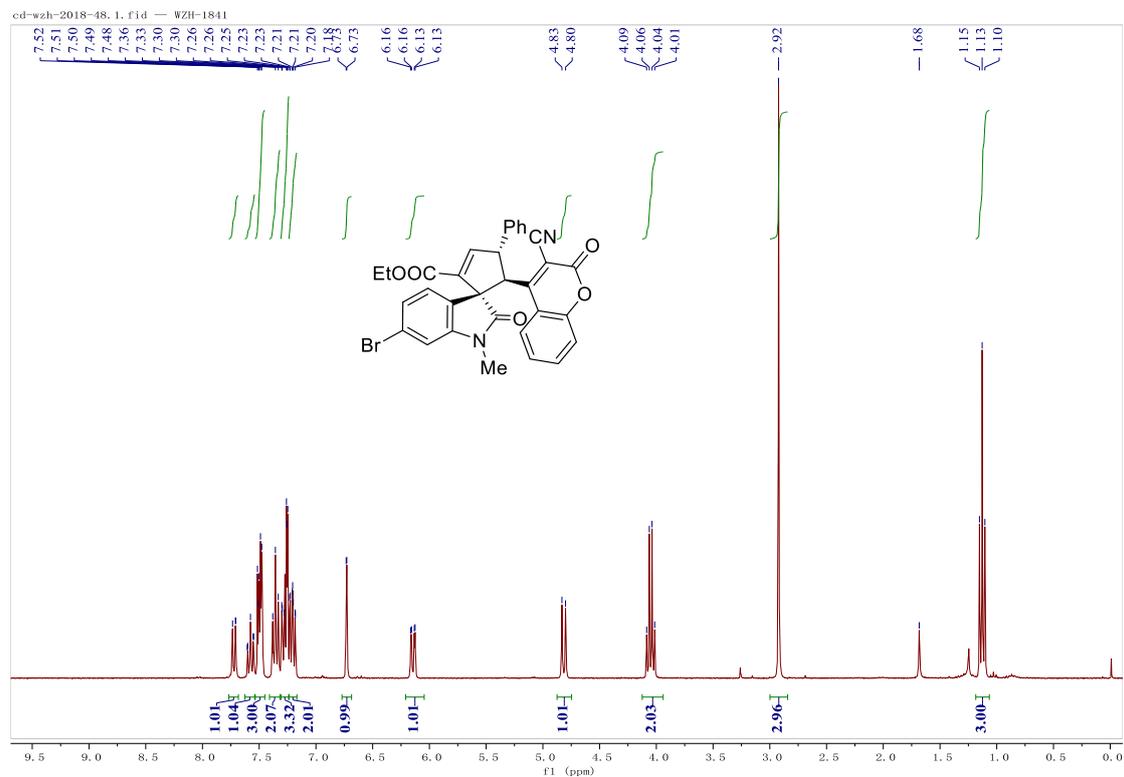
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.740	160347	63.61	6654746	50.02
2	22.823	91724	36.39	6649738	49.98
<b>Totals</b>		252071	100.00	13304484	100.00

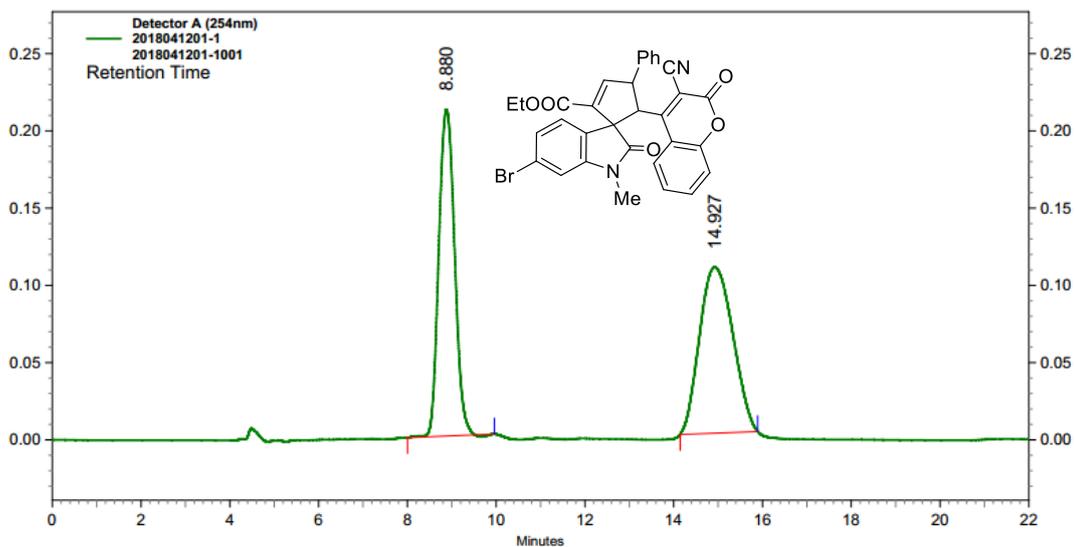


**Detector A (254nm)**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.557	481940	96.35	13350624	93.30
2	22.320	18257	3.65	959027	6.70
<b>Totals</b>		500197	100.00	14309651	100.00

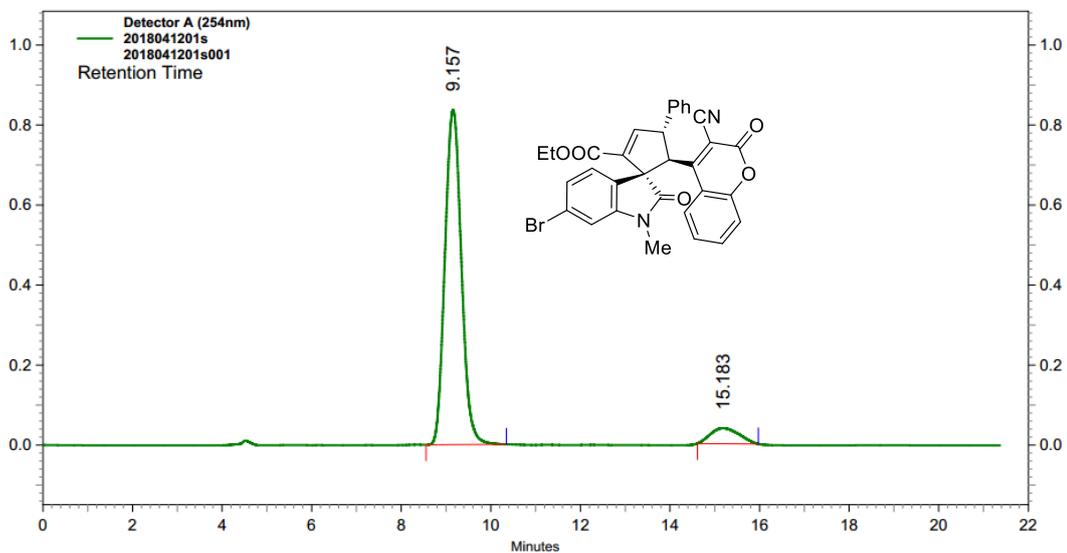
**Ethyl (1*R*,4*S*,5*S*)-6'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ah)**





**Detector A (254nm)**

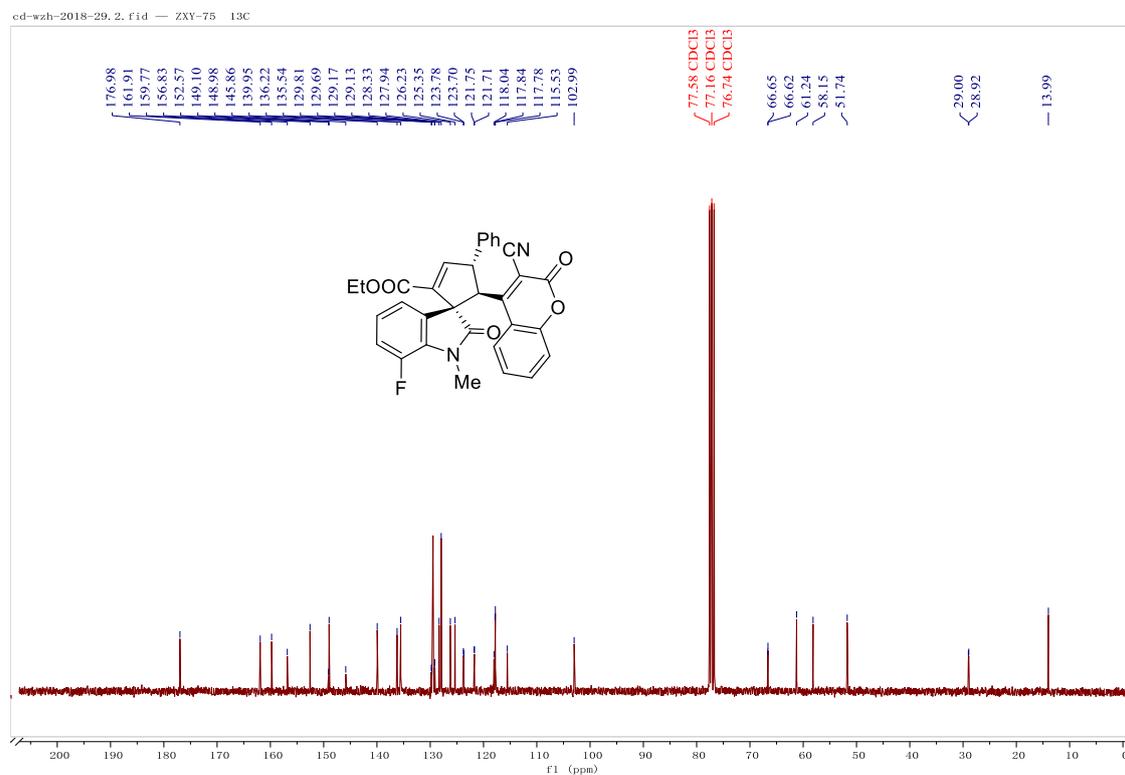
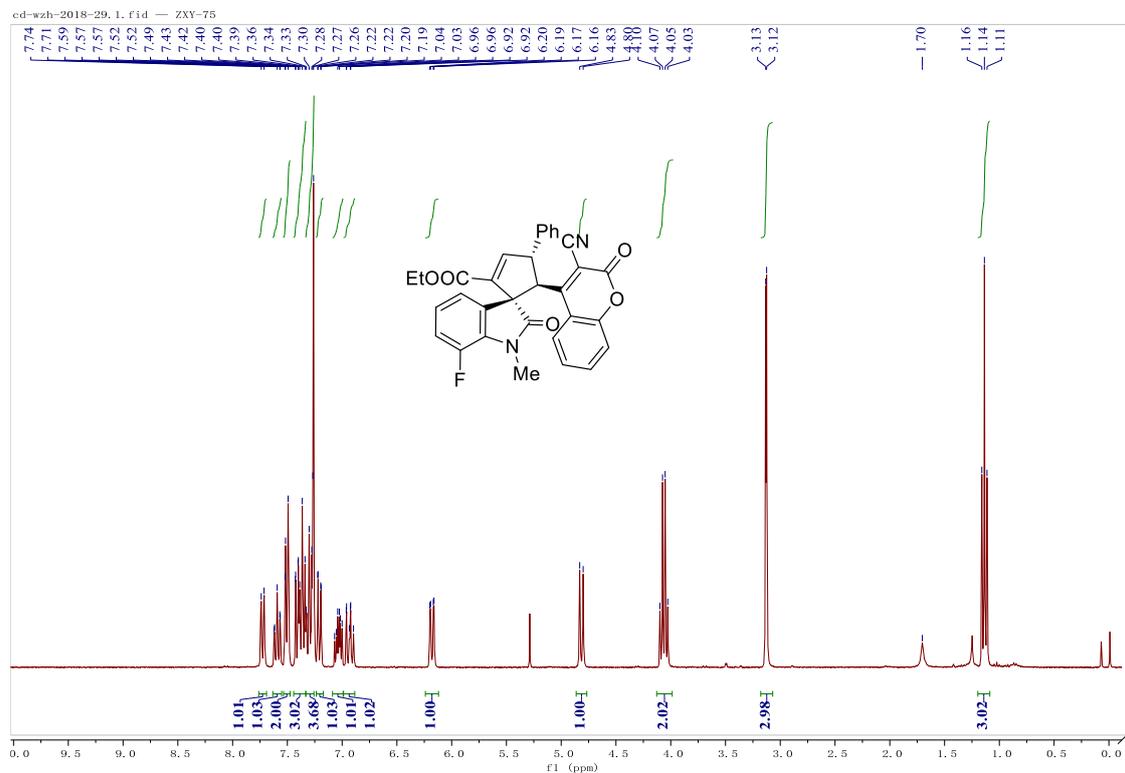
Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	8.880	211423	66.30	5214223	48.15
2	14.927	107443	33.70	5615568	51.85
<b>Totals</b>		<b>318866</b>	<b>100.00</b>	<b>10829791</b>	<b>100.00</b>

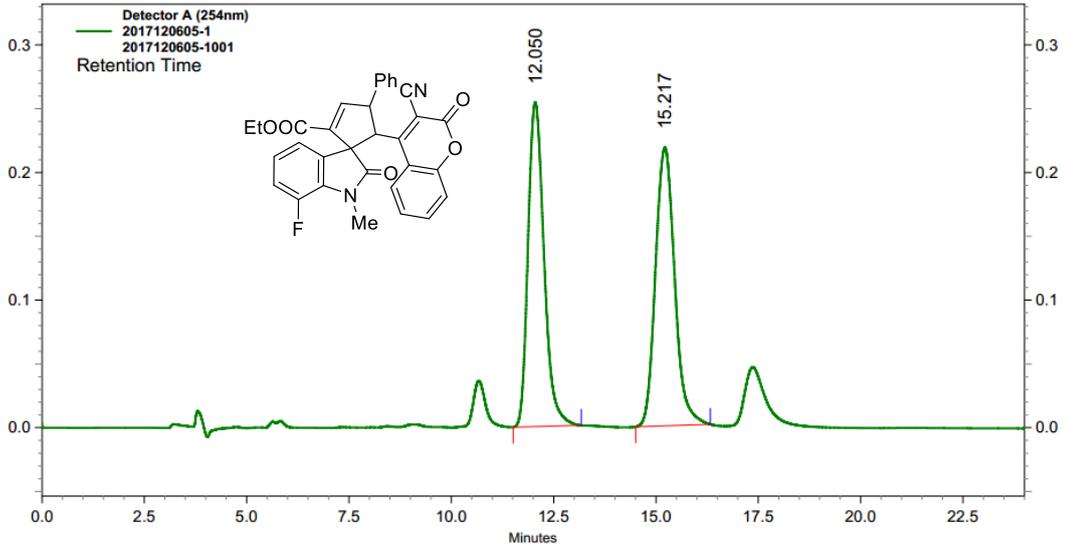


**Detector A (254nm)**

Pk #	Retention Time	Height	Height Percent	Area	Area Percent
1	9.157	836649	95.57	21357878	92.50
2	15.183	38765	4.43	1731070	7.50
<b>Totals</b>		<b>875414</b>	<b>100.00</b>	<b>23088948</b>	<b>100.00</b>

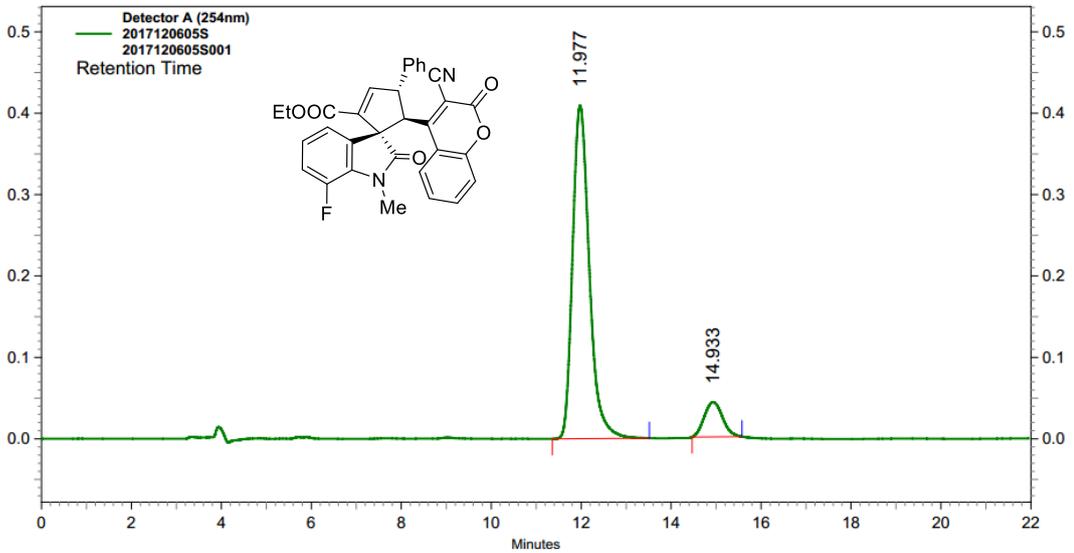
**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-7'-fluoro-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ai)**





Detector A (254nm)

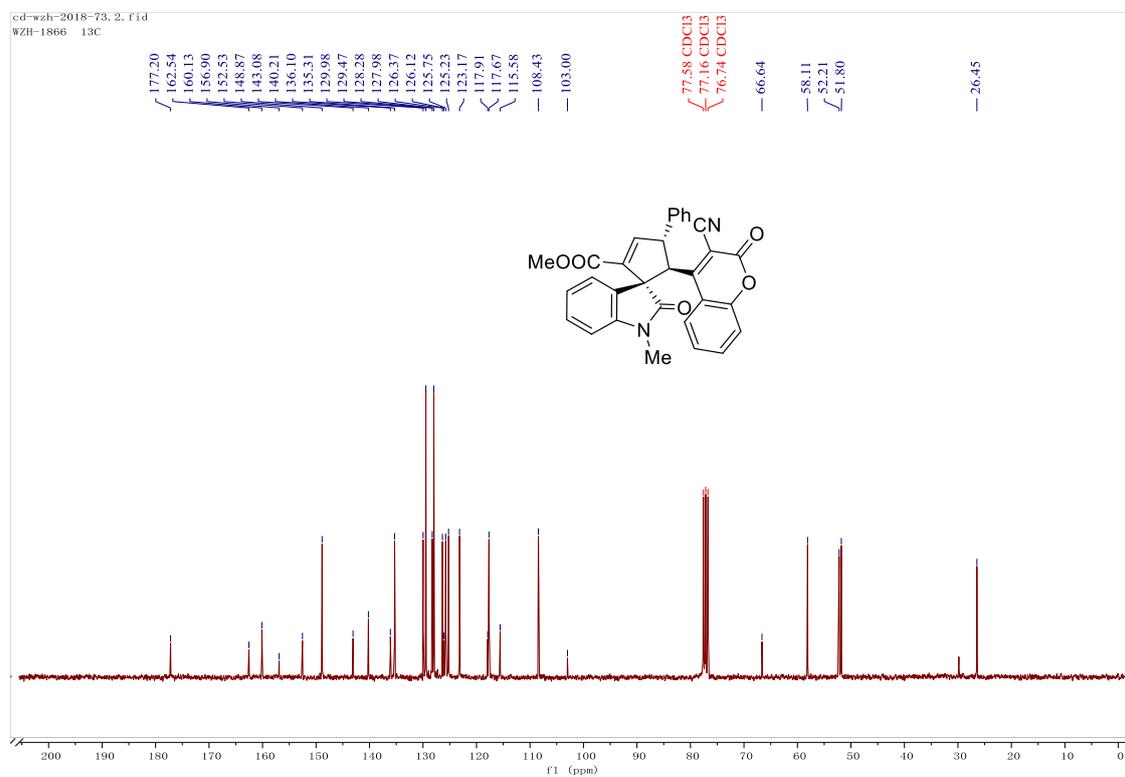
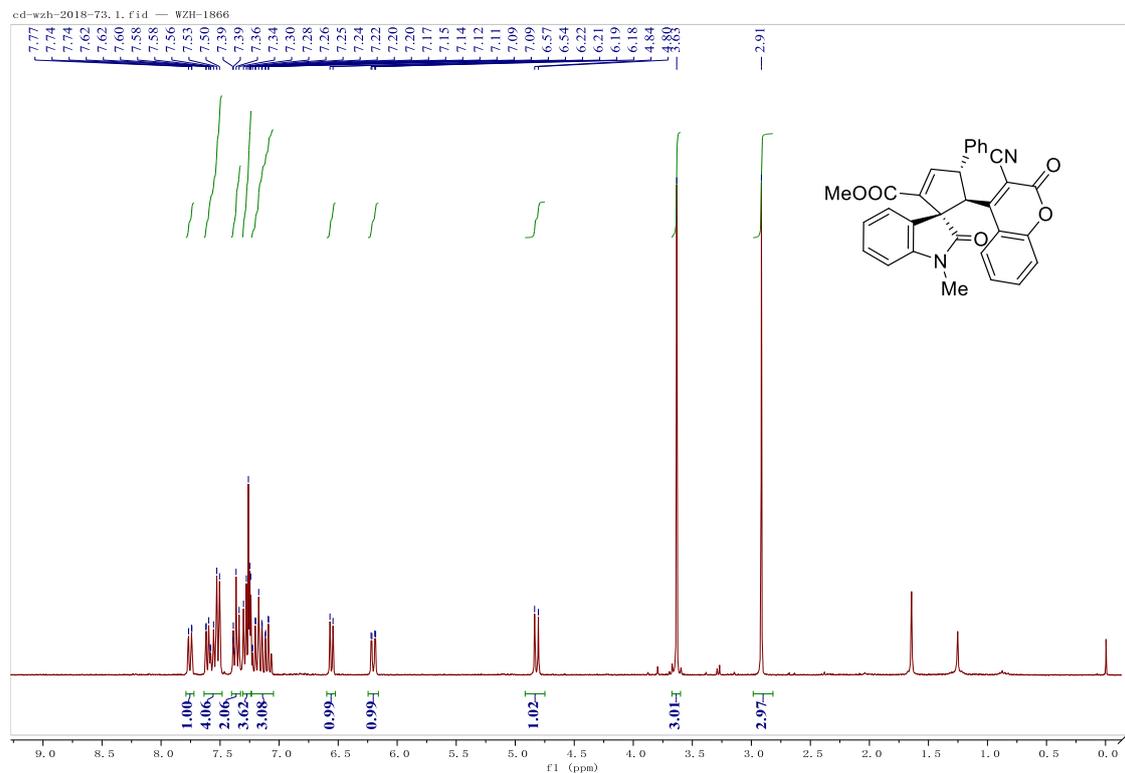
PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	12.050	254030	53.80	6906849	49.28
2	15.217	218144	46.20	7108249	50.72
Totals		472174	100.00	14015098	100.00

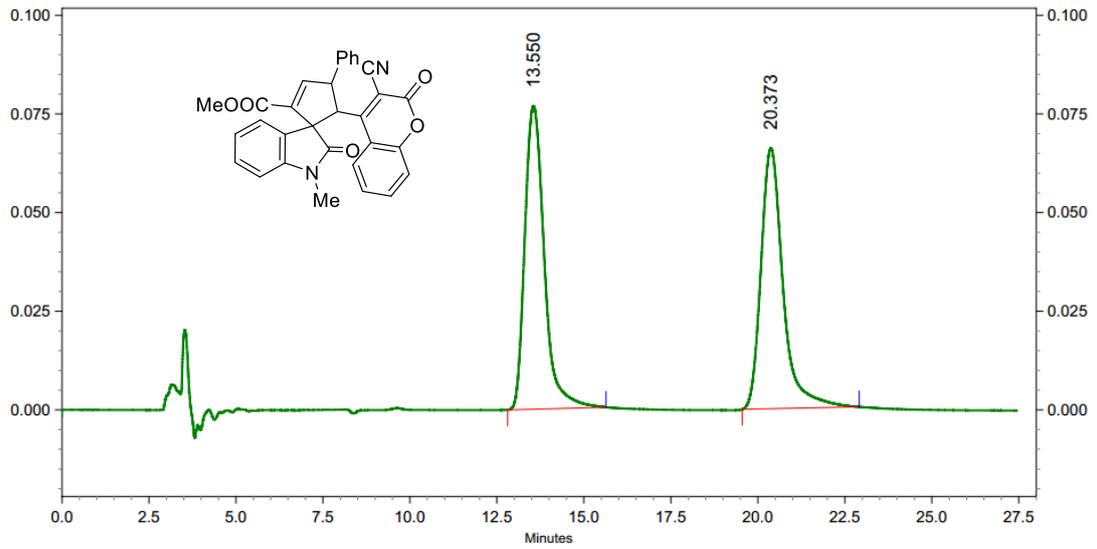


Detector A (254nm)

PK #	Retention Time	Height	Height Percent	Area	Area Percent
1	11.977	409141	90.56	10578182	89.71
2	14.933	42668	9.44	1213033	10.29
Totals		451809	100.00	11791215	100.00

**Methyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3a<sub>j</sub>)**



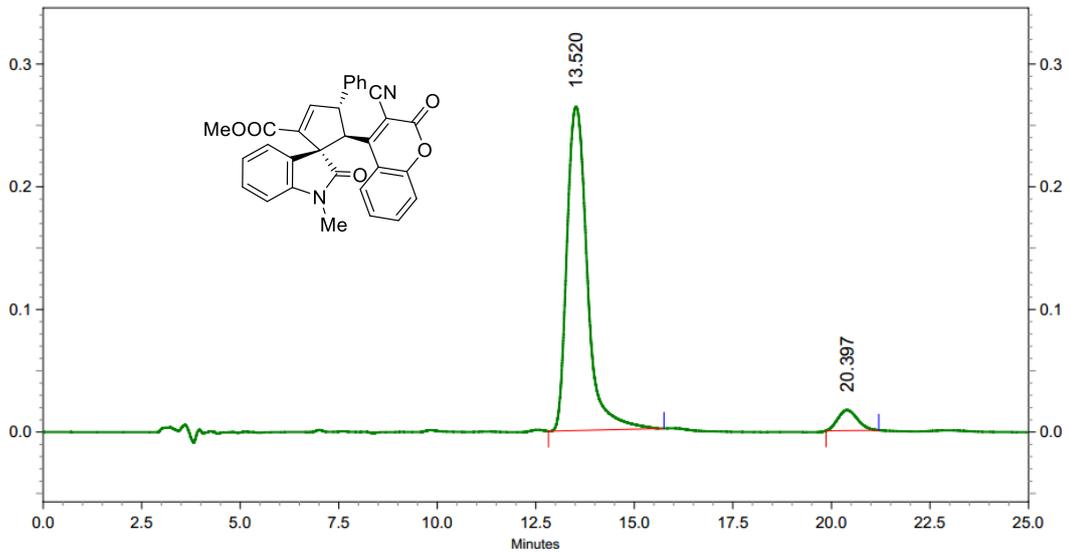


2017121204-5

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
13.550	76882	53.80	2984878	50.61
20.373	66010	46.20	2913398	49.39

Totals	142892	100.00	5898276	100.00
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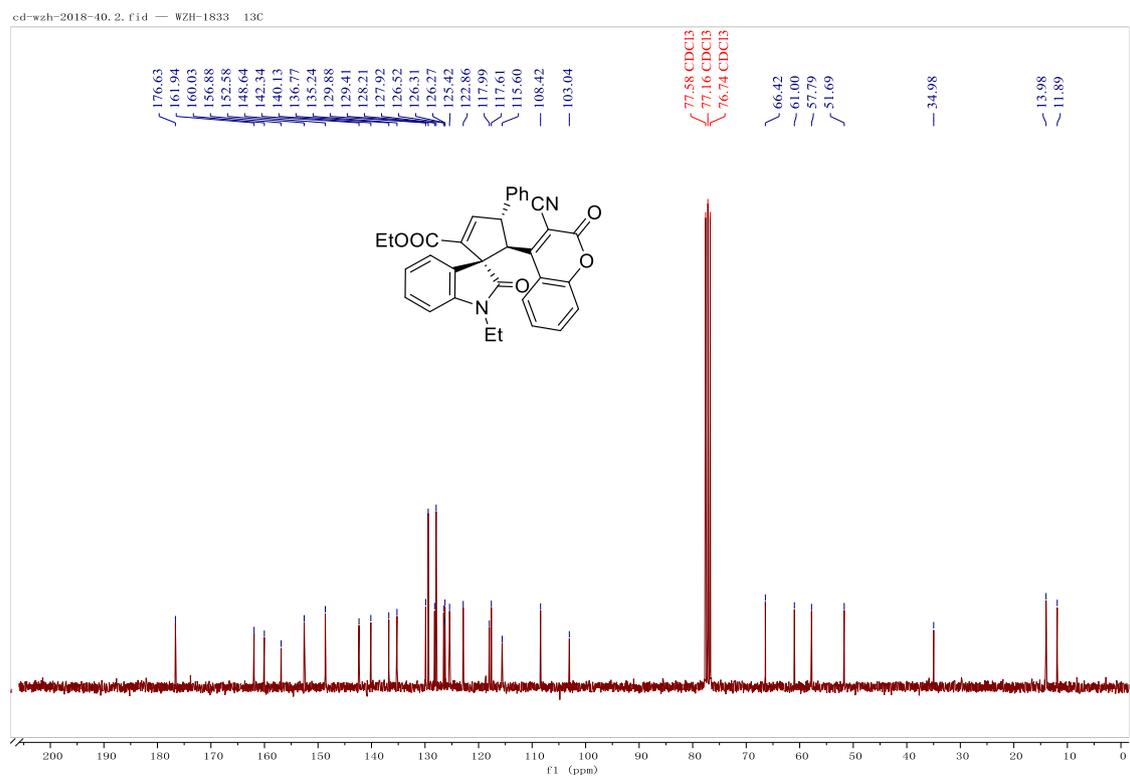
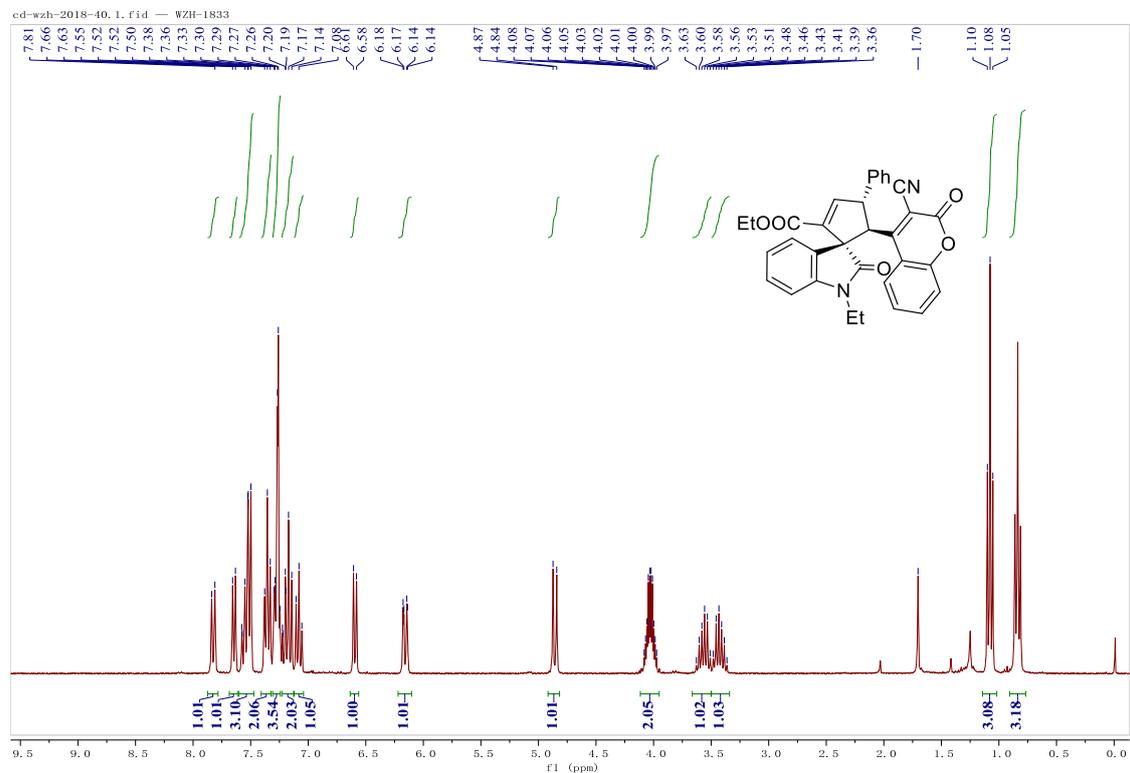
2017121204S-A

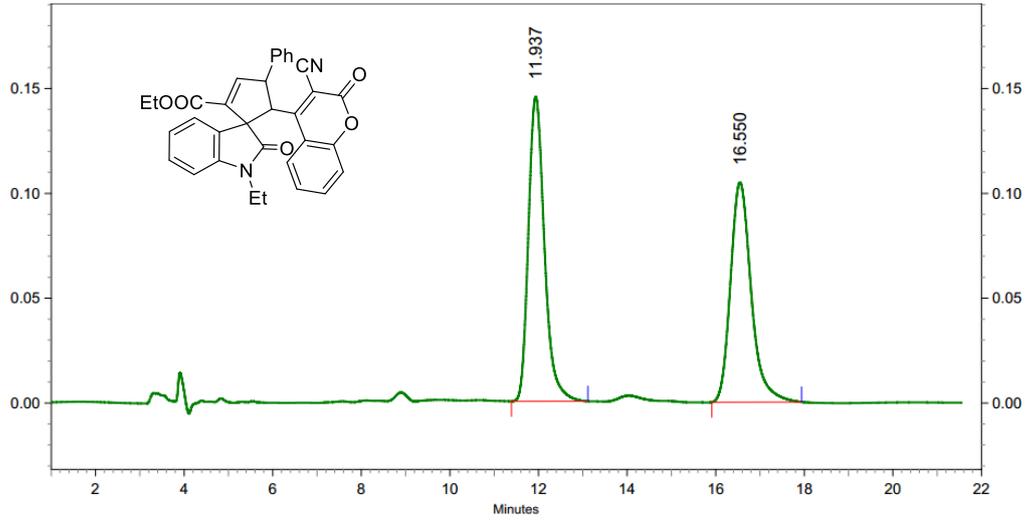
Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
13.520	264049	94.07	9489057	94.25
20.397	16652	5.93	578839	5.75

Totals	280701	100.00	10067896	100.00
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**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ak)**



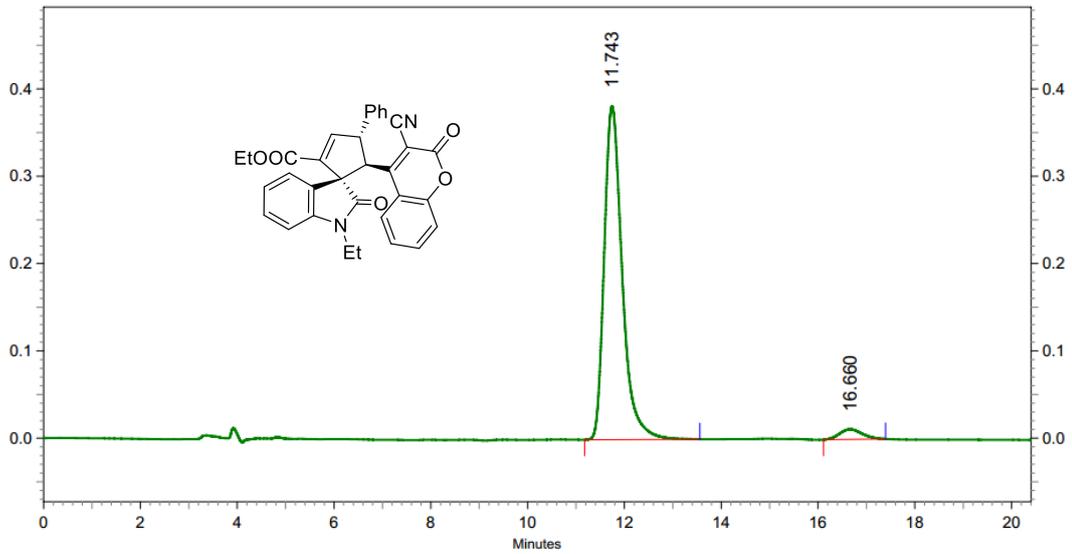


2017121201

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
11.937	145289	58.08	3653862	51.74
16.550	104851	41.92	3408196	48.26

Totals	Height	Height Percent	Area	Area Percent
	250140	100.00	7062058	100.00



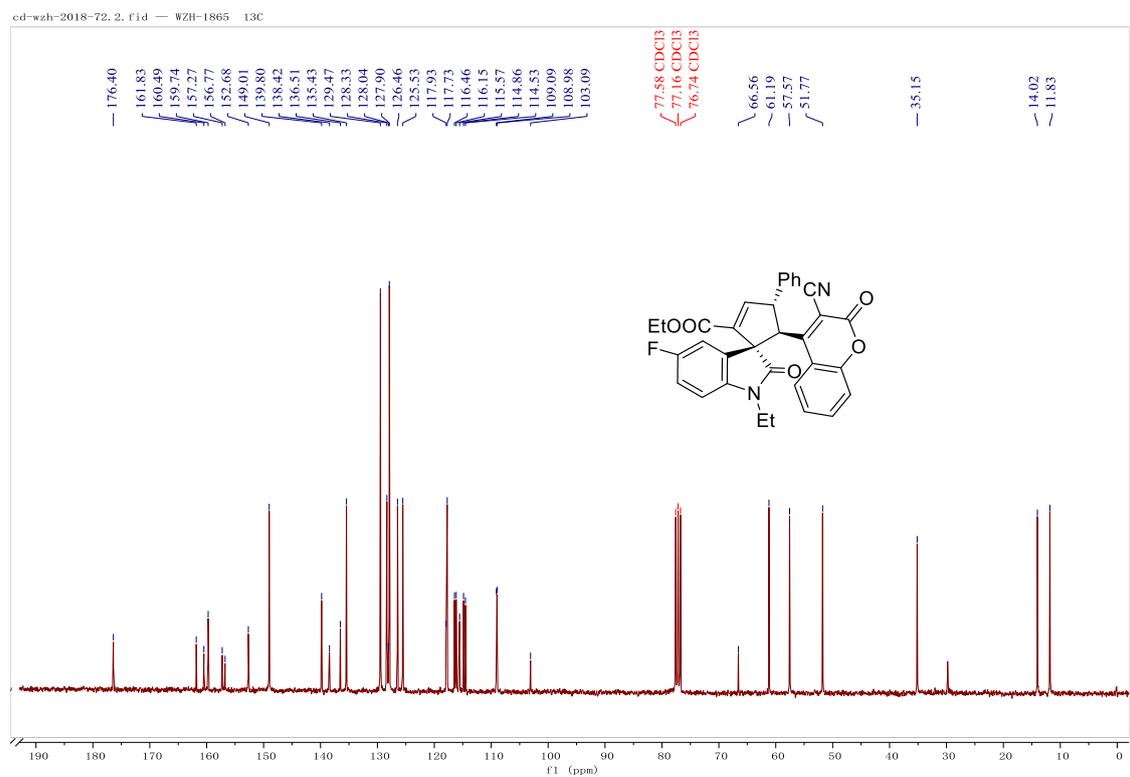
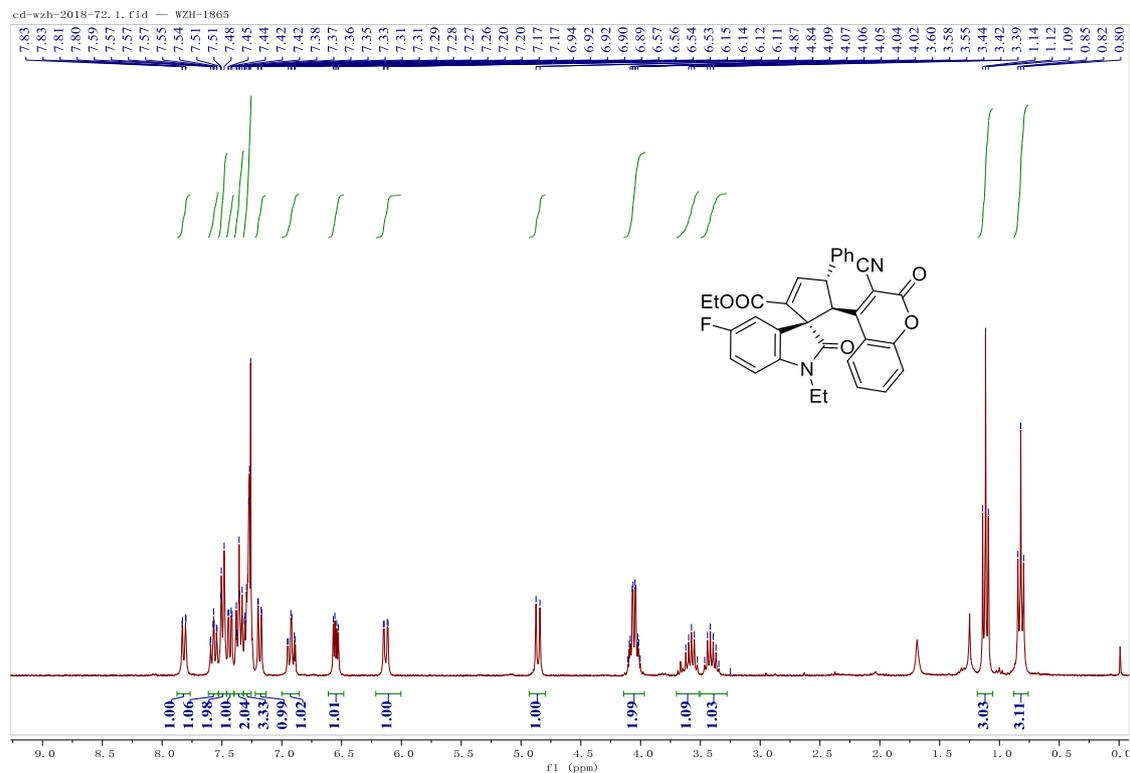
2017121201S

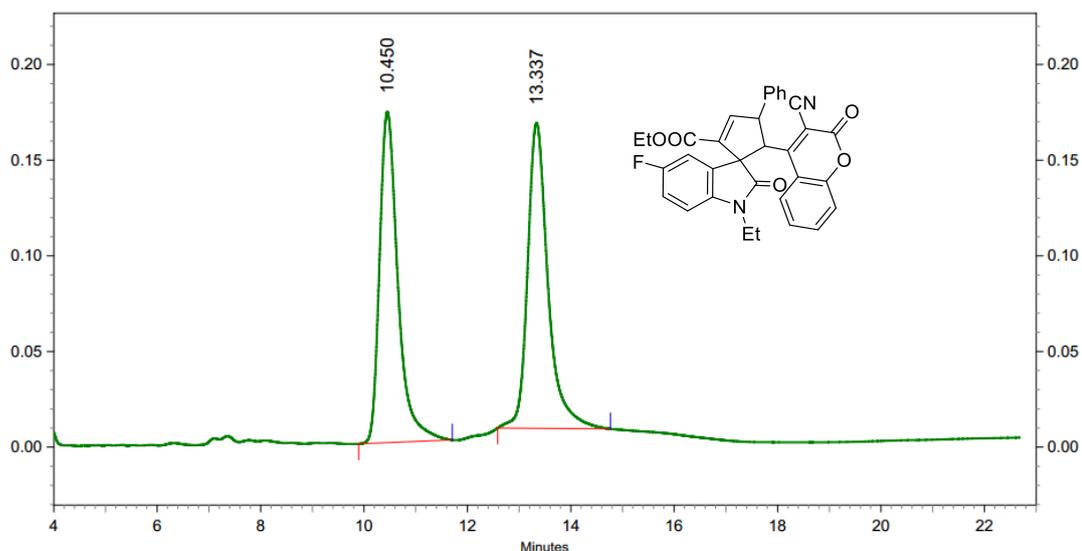
Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
11.743	382110	97.07	9843539	96.29
16.660	11521	2.93	378925	3.71

Totals	Height	Height Percent	Area	Area Percent
	393631	100.00	10222464	100.00

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-5'-fluoro-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3a)**



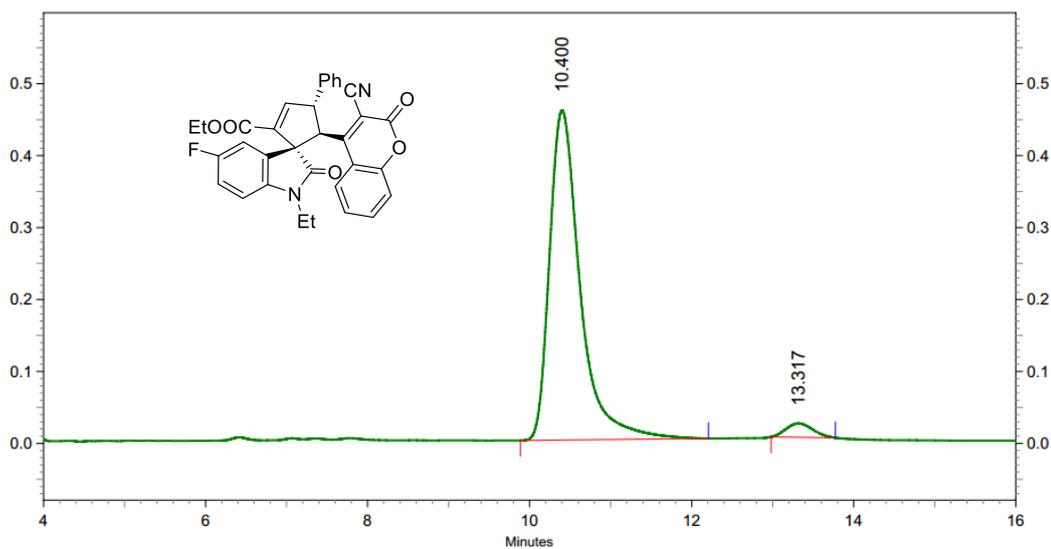


2018072302

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
10.450	173042	52.01	4276353	49.33
13.337	159643	47.99	4392061	50.67

Totals	Height	Height Percent	Area	Area Percent
	332685	100.00	8668414	100.00



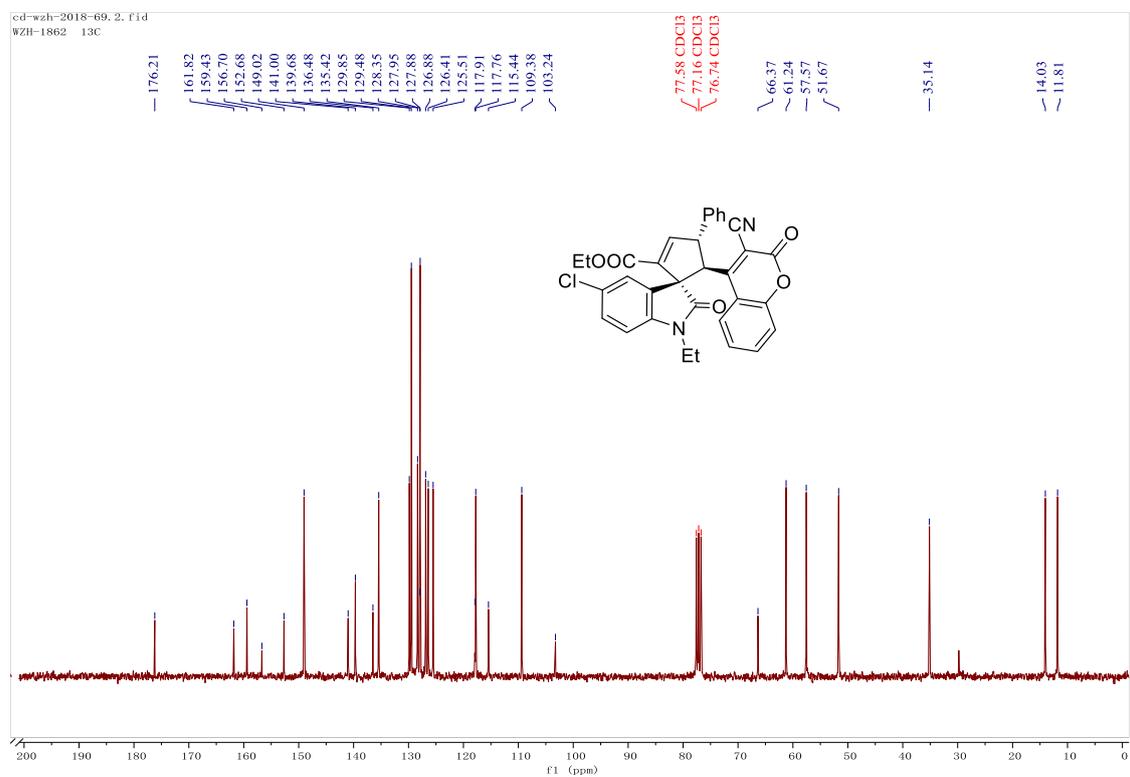
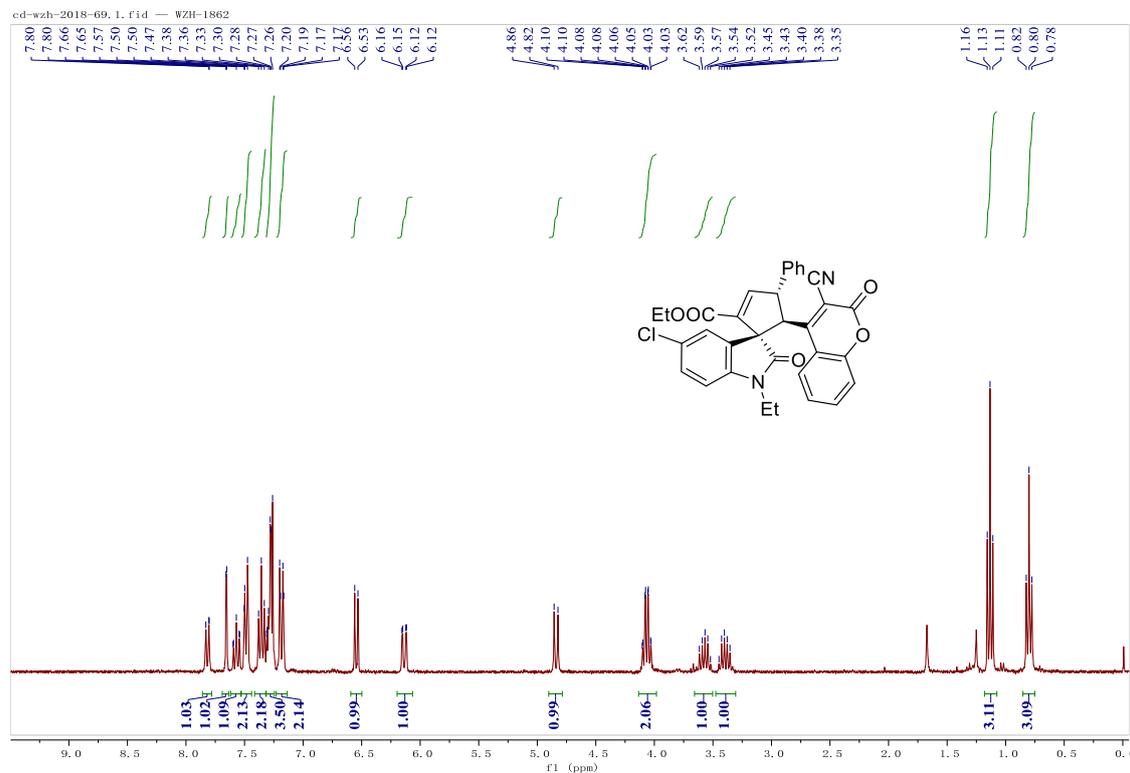
2018072302s

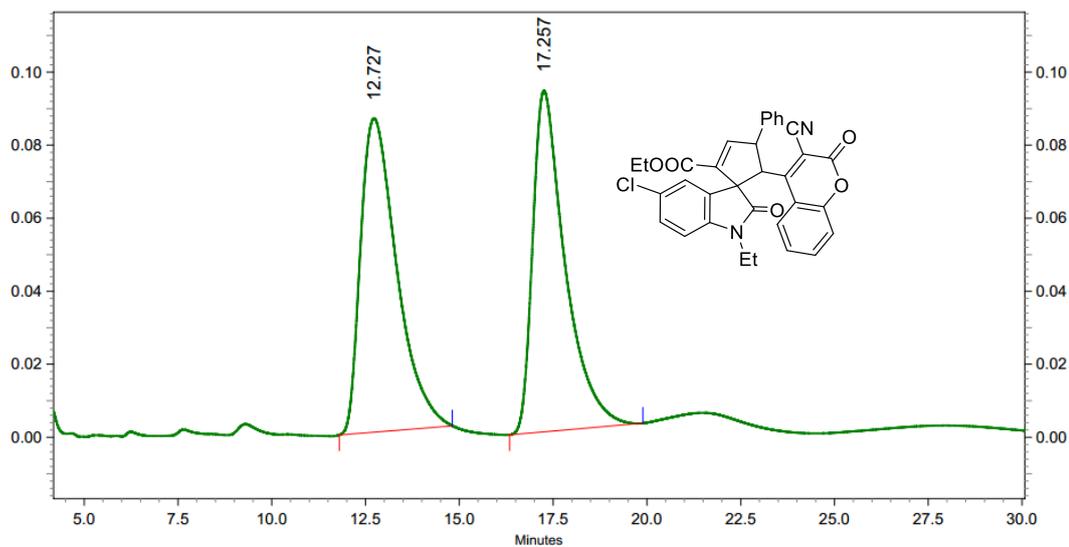
Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
10.400	458486	95.95	12016586	96.43
13.317	19354	4.05	444588	3.57

Totals	Height	Height Percent	Area	Area Percent
	477840	100.00	12461174	100.00

**Ethyl (1R,4S,5S)-5'-chloro-5-(3-cyano-2-oxo-2H-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3am)**



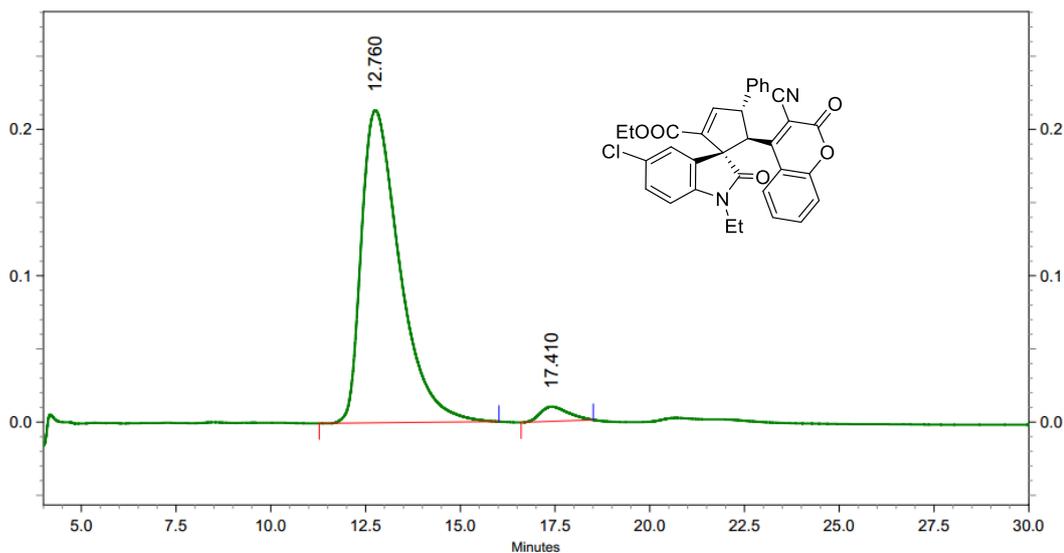


2018071201-5

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
12.727	85930	47.91	5769147	50.72
17.257	93418	52.09	5605388	49.28

Totals	Height	Height Percent	Area	Area Percent
	179348	100.00	11374535	100.00



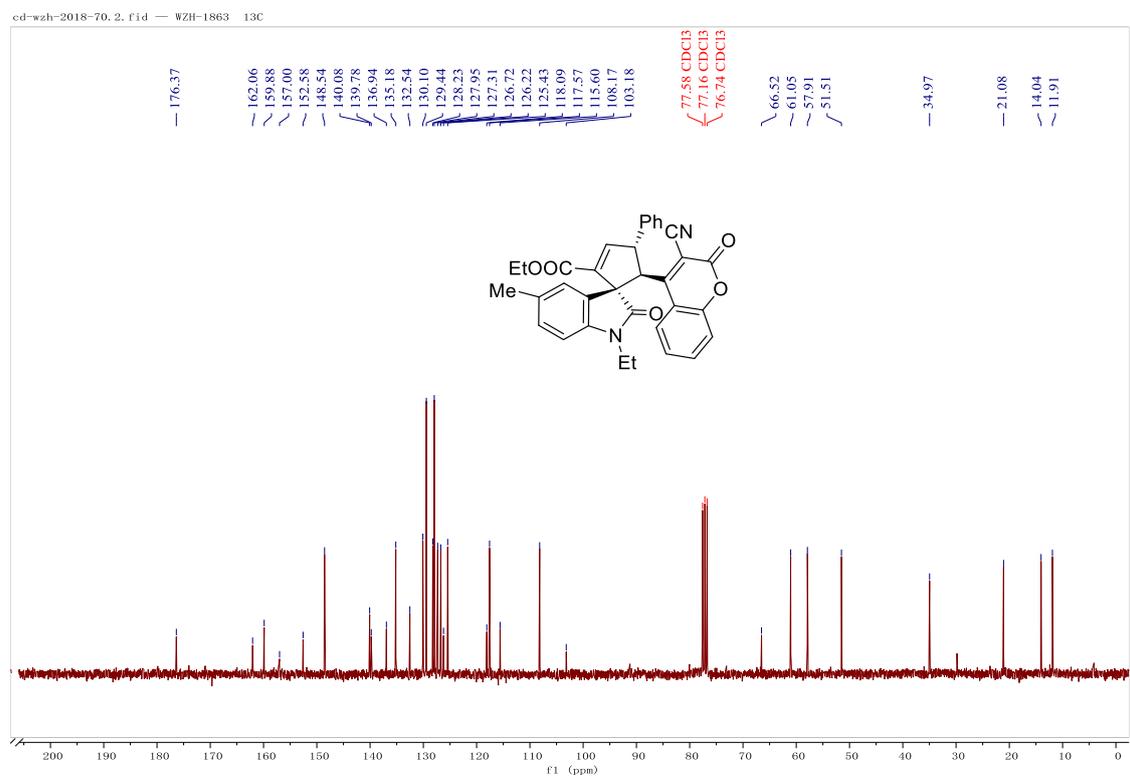
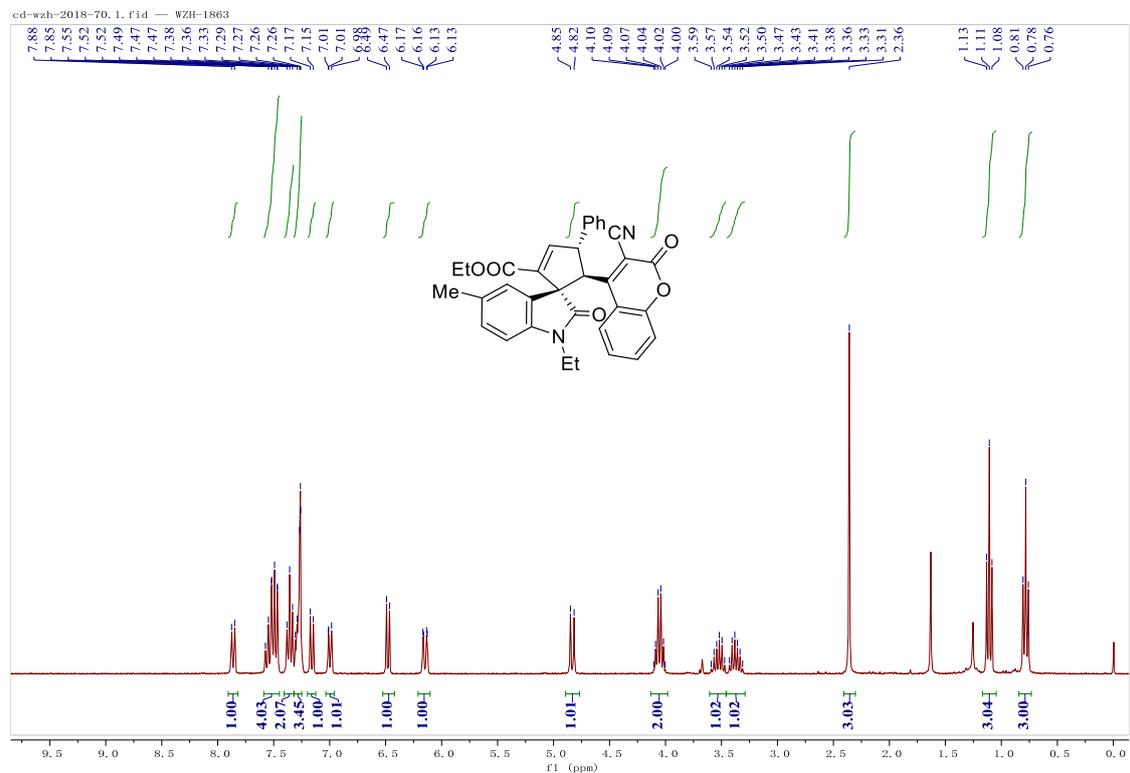
2018071201S

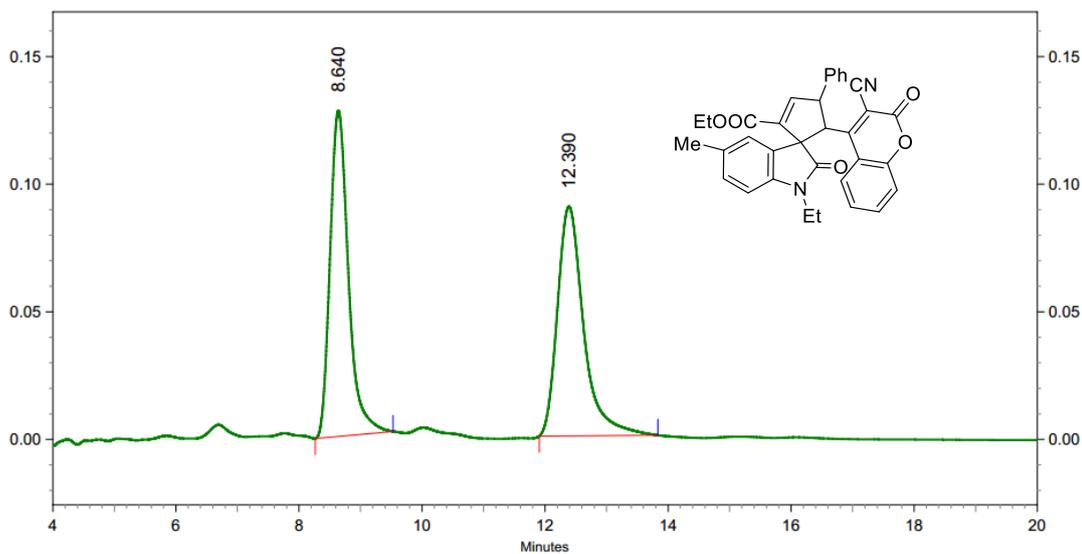
Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
12.760	213641	95.50	15044907	96.70
17.410	10069	4.50	513614	3.30

Totals	Height	Height Percent	Area	Area Percent
	223710	100.00	15558521	100.00

**Ethyl (1*R*,4*S*,5*S*)-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-5'-methyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3a)**



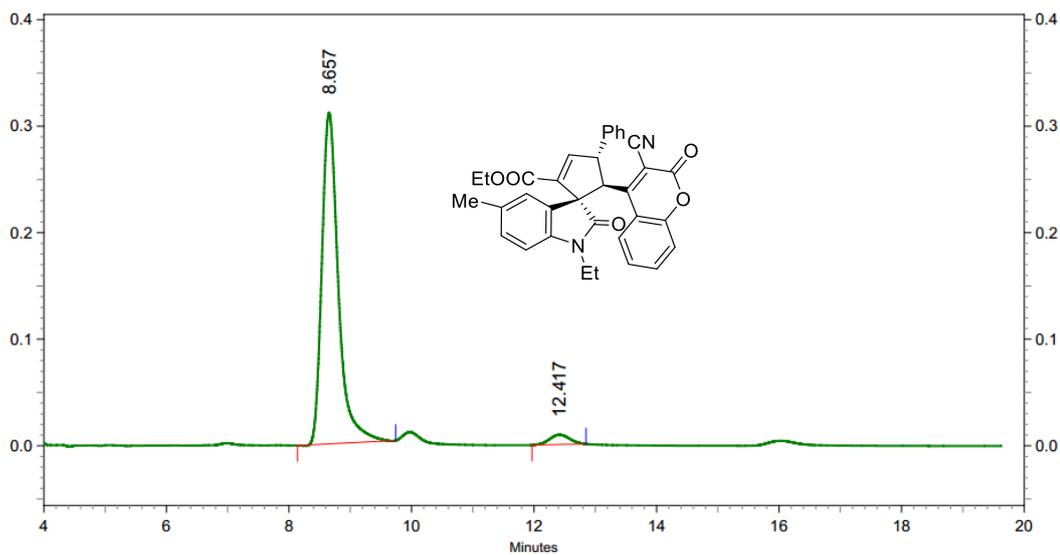


2018071202

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
8.640	127758	58.69	2643566	49.79
12.390	89920	41.31	2666026	50.21

Totals	Height	Height Percent	Area	Area Percent
	217678	100.00	5309592	100.00



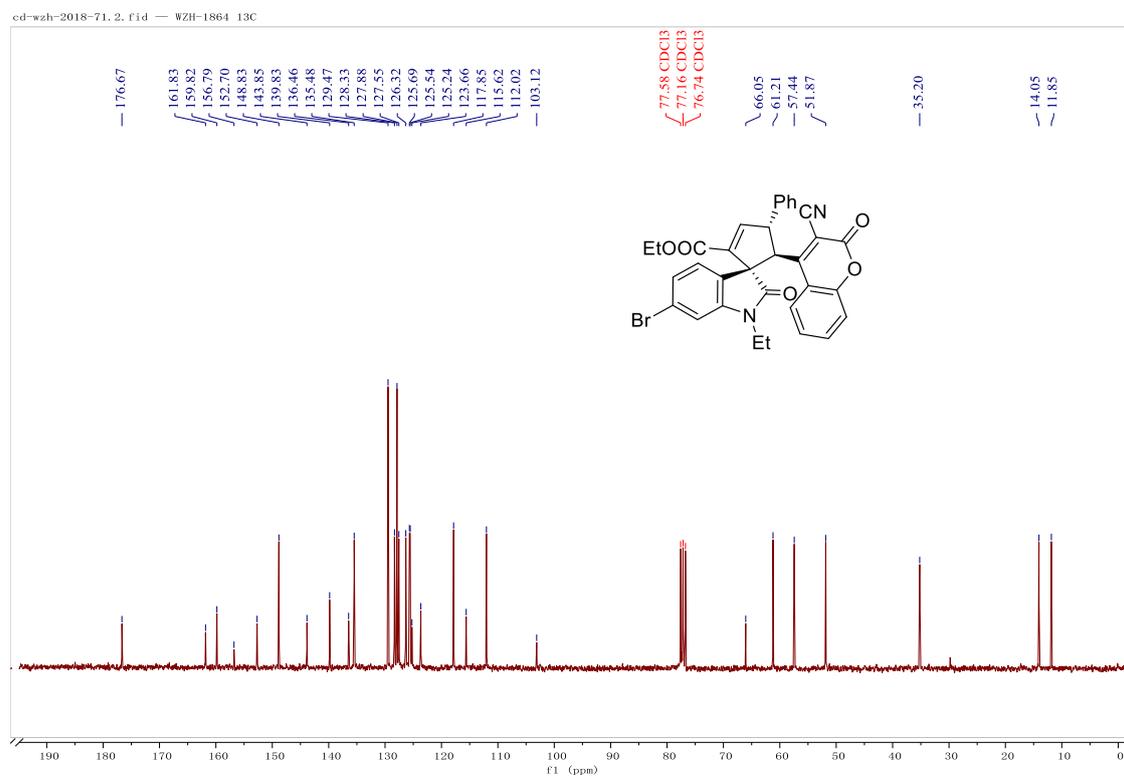
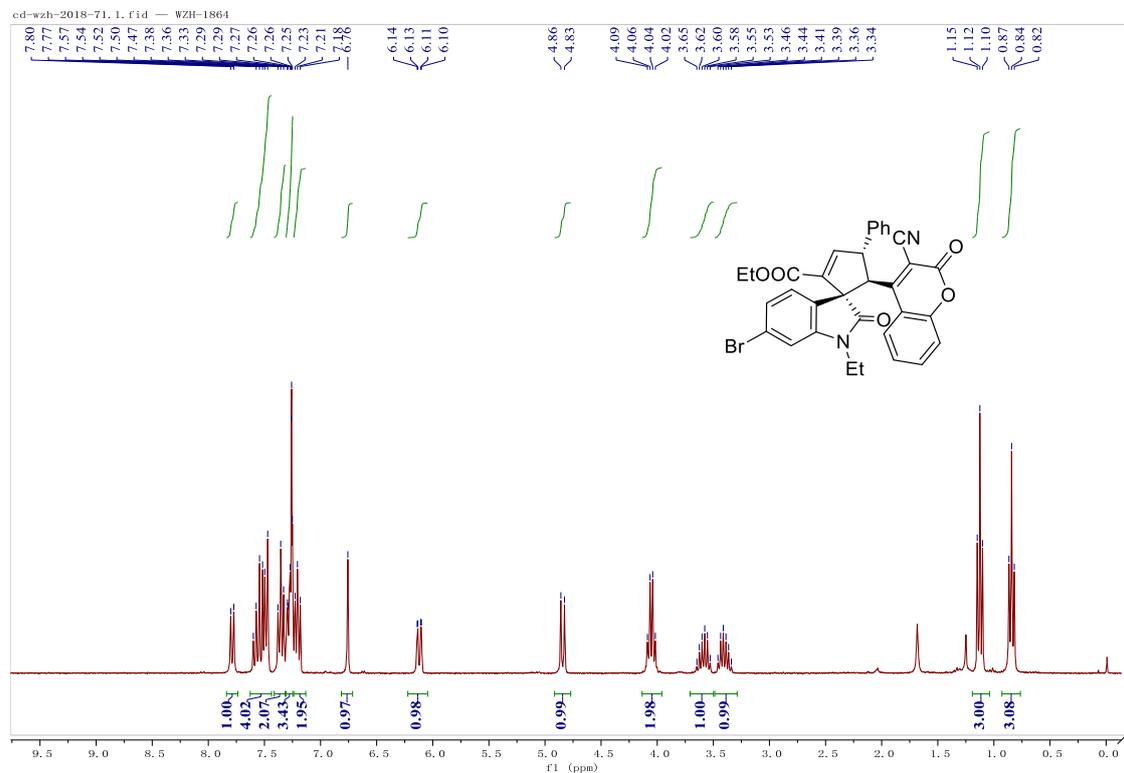
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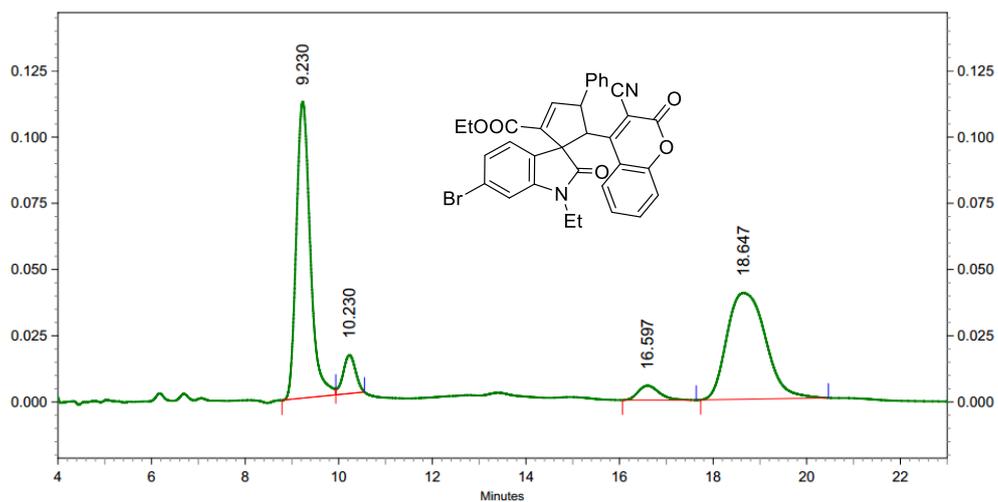
Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
8.657	311101	97.16	5800188	96.52
12.417	9089	2.84	209150	3.48

Totals	Height	Height Percent	Area	Area Percent
	320190	100.00	6009338	100.00

**Ethyl (1*R*,4*S*,5*S*)-6'-bromo-5-(3-cyano-2-oxo-2*H*-chromen-4-yl)-1'-ethyl-2'-oxo-4-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-2-carboxylate (3ao)**



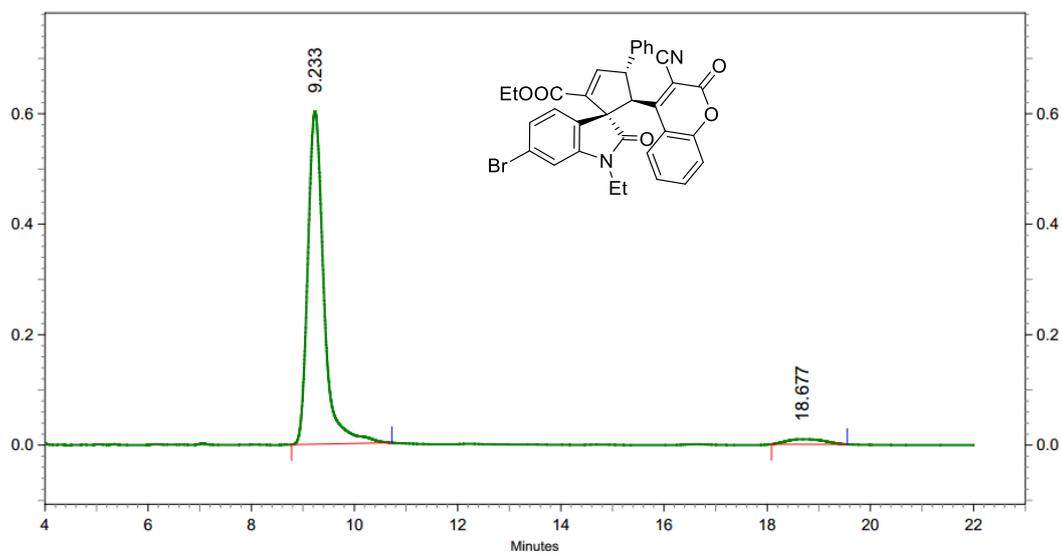


2018072301

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
9.230	111943	65.08	2315600	45.71
10.230	14530	8.45	268610	5.30
16.597	5430	3.16	170875	3.37
18.647	40105	23.32	2310223	45.61

Totals	172008	100.00	5065308	100.00
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2018072301s

Detector A (254nm)

Retention Time	Height	Height Percent	Area	Area Percent
9.233	602865	98.50	13004437	96.52
18.677	9187	1.50	468839	3.48

Totals	612052	100.00	13473276	100.00
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