

**Organocatalytic Enantioselective Tandem Michael-Cyclization of Isatin Derived  
 $\beta$ ,  $\gamma$ -Unsaturated  $\alpha$ -Ketoesters with 3-Hydroxy-4*H*-Chromen-4-One or 2-  
Hydroxy-1,4-Naphthoquinone Derivatives**

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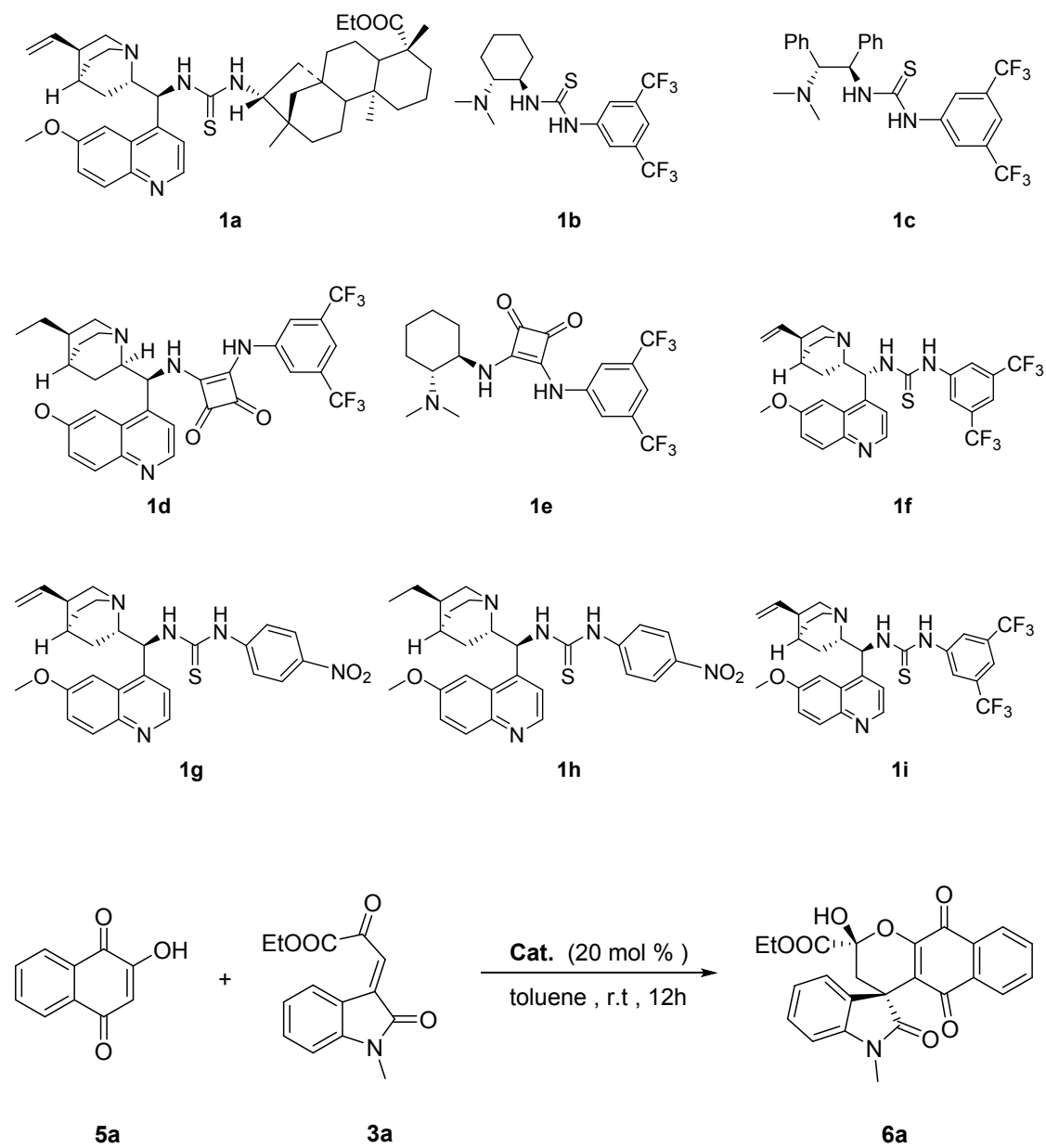
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## 1. General information :

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvents, without any precautions to exclude moisture unless otherwise noted. Organic solutions were concentrated under reduced pressure on an EYELA N-1001 rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates ( $0.2 \pm 0.03$  mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute, P. R. China. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using silica gel (particle size 0.04 – 0.05 mm).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Varian Inova (400 MHz and 100 MHz, respectively) spectrometer.  $^1\text{H}$  NMR data are reported as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants ( $J$ ) and assignment. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass GCT-TOF mass spectrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a Daicel Chiralpak IA, Chiralpak AD-H or Chiralpak OD-H column (0.46cm x 25 cm). X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations are reported as follows:  $[\alpha]_{\text{D}}^{25}$ . (c in g per 100 mL, solvent).

## 2. Optimization of reaction

**Table 1. Optimization of Organocatalysts**



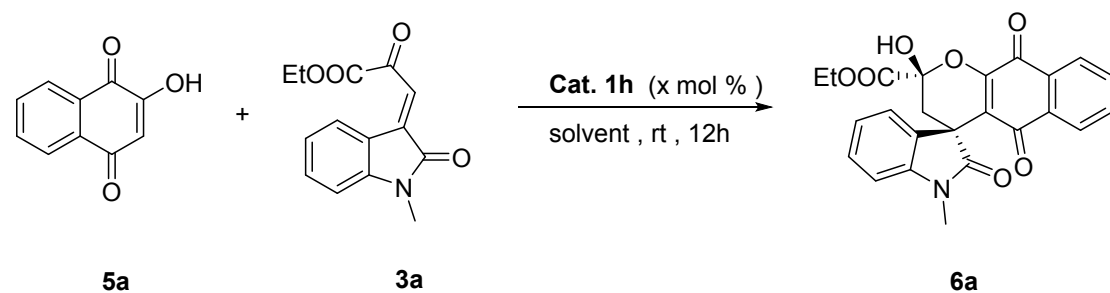
entry <sup>a</sup>	cat.	time (h)	yield (%) <sup>b</sup>	<i>dr</i> <sup>c</sup>	<i>ee</i> (%) <sup>d</sup>
1	<b>1a</b>	12	73	>20:1	66
2	<b>1b</b>	12	90	>20:1	-93
3	<b>1c</b>	12	50	>20:1	-86
4	<b>1d</b>	12	76	>20:1	38
5	<b>1e</b>	12	90	>20:1	-69
6	<b>1f</b>	12	77	>20:1	-70
7	<b>1g</b>	12	89	>20:1	95

8	<b>1h</b>	12	91	>20:1	99
9	<b>1i</b>	12	83	>20:1	93

<sup>a</sup>Unless noted, the reaction was conducted with **5a**(0.12 mmol), **3a**(0.1 mmol) and **cat.** (20 mol %) in toluene (1 mL) at room temperature for 12 h. <sup>b</sup>Isolated yield.

<sup>c</sup>Determined by <sup>1</sup>H NMR. <sup>d</sup>Determined by chiral HPLC analysis (Chiralpak IA-H).

**Table 2. Optimization of the Reaction Conditions**



entry <sup>a</sup>	solvent	Cat. <b>1h</b> (x mol %)	Conc. (mol/L)	yield (%) <sup>b</sup>	<i>dr</i> <sup>c</sup>	<i>ee</i> (%) <sup>d</sup>
1	toluene	20	0.1	91	>20:1	99
2	toluene	10	0.1	76	>20:1	99
3	toluene	5	0.1	50	>20:1	95
4	toluene	2.5	0.1	48	>20:1	70
5	DCM	10	0.1	83	>20:1	98
6	THF	10	0.1	80	>20:1	96
7	CH <sub>3</sub> CN	10	0.1	79	>20:1	97
8	MTBE	10	0.1	87	>20:1	95
9	DCM	5	0.1	75	>20:1	98
10	DCM	5	0.067	72	>20:1	96
11	DCM	5	0.2	81	>20:1	98

<sup>a</sup>Unless noted, the reaction was conducted with **5a** (0.12 mmol), **3a** (0.1 mmol) and **cat.1h** (x mol %) in solvent (1 mL) at room temperature for 12 h. <sup>b</sup>Isolated yield.

<sup>c</sup>Determined by <sup>1</sup>H NMR. <sup>d</sup>Determined by chiral HPLC analysis (Chiralpak IA-H.)

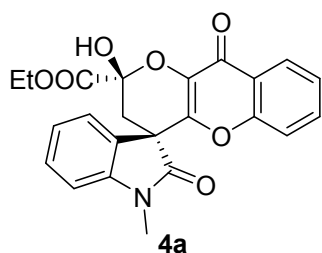
### 3. Experimental data

#### 3.1 Synthesis of compounds 4a–4w

**General procedure:** In an ordinary tube equipped with a magnetic stirring bar, the solution of **2** (0.15 mmol, 1.5 equiv), catalyst **1i** (3.0 mg, 5 mol %, 0.05 equiv) in DCM (1.0 mL) was stirred at  $-20\text{ }^{\circ}\text{C}$  for 30 min, and then **3** (0.1 mmol, 1 equiv) was added. The reaction was stirred under  $-20\text{ }^{\circ}\text{C}$  for 40 h, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 2:1 – 1.5:1) to give desired products **4a–4w**.

**A specific procedure for synthesis of compound 4a:** In an ordinary tube equipped with a magnetic stirring bar, the solution of **2a** (24.3 mg, 0.15 mmol, 1.5 equiv), catalyst **1i** (3.0 mg, 5 mol %, 0.05 equiv) in DCM (1.0 mL) was stirred at  $-20\text{ }^{\circ}\text{C}$  for 30 min, and then **3a** (25.9 mg, 0.1 mmol, 1 equiv) was added. The reaction was stirred under  $-20\text{ }^{\circ}\text{C}$  for 40 h, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 1.5:1) to give desired products **4a**.

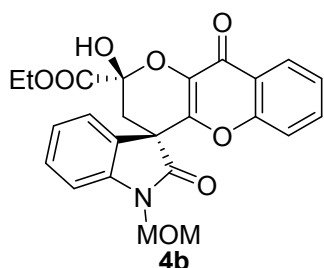
#### Ethyl 2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate **4a**



yellow solid, melting point:  $198\text{--}201\text{ }^{\circ}\text{C}$ , 40.9 mg, 97% yield, 98% *ee*,  $> 20:1$  *dr*,  $[\alpha]_{\text{D}}^{25} = + 63.0$  ( $c = 0.51$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0\text{ mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254\text{ nm}$ ,  $t$  (major) = 13.936,  $t$  (minor) = 24.650];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 0.5H), 8.21 (ddd,  $J = 13.2, 8.0, 1.2\text{ Hz}$ , 1H), 7.89 (d,  $J = 7.6\text{ Hz}$ , 0.5H), 7.54 – 7.49 (m, 1H), 7.45 (td,  $J = 8.0, 1.2\text{ Hz}$ , 0.5H), 7.38 (td,  $J = 8.0, 1.2\text{ Hz}$ , 0.5H), 7.33 – 7.29 (m, 1H), 7.23 – 7.18 (m, 1H), 7.15 – 7.03 (m, 2H), 6.98 (d,  $J = 7.8\text{ Hz}$ , 0.5H), 5.05 (s, 0.5H), 4.42 – 4.32 (dq,  $J = 7.2, 6.8\text{ Hz}$ , 2H), 3.38 (d,  $J = 8.0\text{ Hz}$ , 3H), 3.31 (d,  $J = 14.0\text{ Hz}$ , 0.5H), 3.07 (d,  $J = 14.8\text{ Hz}$ , 0.5H), 2.69 (d,  $J = 14.8\text{ Hz}$ , 0.5H), 2.33 (d,  $J = 14.0\text{ Hz}$ , 0.5H), 1.38 (dt,  $J = 15.8, 7.1\text{ Hz}$ , 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.71, 175.47, 171.97, 171.84, 168.43, 167.33, 155.05, 154.99, 147.63, 145.48, 143.87, 143.78, 137.11, 136.67, 133.58, 133.44, 130.23, 129.86, 129.54, 128.80, 127.69,

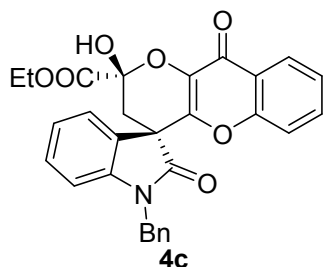
126.32, 126.08, 124.78, 124.77, 124.60, 123.76, 123.74, 123.71, 123.41, 118.07, 117.87, 109.66, 108.61, 94.90, 93.63, 63.71, 62.80, 50.16, 49.56, 37.60, 37.51, 27.41, 27.25, 14.15, 14.08; IR: 3276.4, 2961.7, 1740.5, 1714.4, 1627.4, 1611.0, 1468.6, 1260.0, 1192.0, 1034.8, 1020.7, 796.4, 758.9, 692.5  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{NNaO}_7$   $[\text{M}+\text{Na}]^+$  444.1054, found: 444.1065.

**Ethyl 2'-hydroxy-1-(methoxymethyl)-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4b**



yellow solid, melting point: 141–144  $^{\circ}\text{C}$ , 42.9 mg, 95% yield, 98% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +98.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 12.362,  $t$  (minor) = 17.090];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 0.3H), 8.22 (d,  $J = 7.2$  Hz, 0.4H), 8.18 (d,  $J = 7.6$  Hz, 0.6H), 7.93 (d,  $J = 7.6$  Hz, 0.6H), 7.51 – 7.49 (m, 1H), 7.42 (t,  $J = 7.2$  Hz, 0.3H), 7.36 (t,  $J = 7.6$  Hz, 0.7H), 7.33 – 7.28 (m, 1H), 7.23 (d,  $J = 2.9$  Hz, 0.3H), 7.21 – 7.15 (m, 1.2H), 7.11 – 7.04 (m, 1.7H), 5.29 (s, 0.7H), 5.29 (t,  $J = 10.1$  Hz, 1H), 5.21 (dd,  $J = 10.8, 5.2$  Hz, 1H), 4.36 (dq,  $J = 12.7, 5.7$  Hz, 2H), 3.42 (d,  $J = 7.6$  Hz, 3H), 3.30 (d,  $J = 13.6$  Hz, 0.7H), 3.11 (d,  $J = 14.8$  Hz, 0.3H), 2.72 (d,  $J = 14.8$  Hz, 0.35H), 2.39 (d,  $J = 14.0$  Hz, 0.65H), 1.37 (dt,  $J = 14.2, 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.59, 176.28, 171.92, 171.75, 168.29, 167.22, 155.00, 154.96, 147.42, 145.43, 142.10, 141.90, 136.94, 136.49, 133.73, 133.58, 130.34, 129.65, 129.37, 128.27, 127.82, 126.40, 126.18, 125.12, 124.86, 124.67, 123.90, 123.84, 123.74, 123.70, 117.73, 117.61, 110.10, 110.06, 94.80, 93.64, 72.17, 71.95, 63.68, 62.88, 56.61, 56.37, 50.50, 49.96, 37.78, 37.62, 14.14, 14.07; IR: 3514.9, 3282.1, 2961.4, 2928.7, 1738.7, 1720.6, 1631.9, 1620.9, 1484.3, 1467.9, 1368.6, 1341.2, 1217.1, 1194.4, 1147.4, 1103.9, 1039.2, 977.2, 923.7, 860.6, 775.0, 758.9, 701.2, 660.5, 613.3  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  452.1340, found: 452.1348.

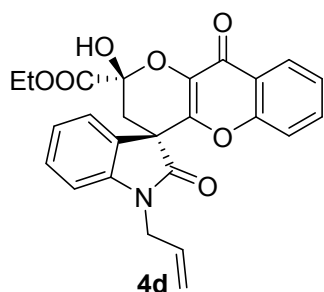
**Ethyl 1-benzyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4c**



white solid, melting point: 141–144  $^{\circ}\text{C}$ , 48.7 mg, 98%

yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 114.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 17.371,  $t$  (minor) = 25.698];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 0.45H), 8.23 (d,  $J = 8.0 \text{ Hz}$ , 0.45H), 8.18 (d,  $J = 8.0 \text{ Hz}$ , 0.55H), 7.94 (d,  $J = 7.6 \text{ Hz}$ , 0.55H), 7.55 – 7.50 (m, 1H), 7.42 – 7.33 (m, 5H), 7.32 – 7.30 (m, 1.5H), 7.23 (d,  $J = 8.4 \text{ Hz}$ , 1H), 7.12 (t,  $J = 7.6 \text{ Hz}$ , 0.5H), 7.06 (d,  $J = 7.6 \text{ Hz}$ , 0.7H), 7.02 (d,  $J = 3.2 \text{ Hz}$ , 0.5H), 7.00 (d,  $J = 4.4 \text{ Hz}$ , 0.3H), 6.92 (d,  $J = 8.0 \text{ Hz}$ , 0.4H), 6.85 (d,  $J = 7.6 \text{ Hz}$ , 0.5H), 5.33 (s, 0.6H), 5.26 (t,  $J = 15.6 \text{ Hz}$ , 1H), 4.81 (t,  $J = 15.2 \text{ Hz}$ , 1H), 4.37 (dq,  $J = 7.2, 5.2 \text{ Hz}$ , 2H), 3.38 (dd,  $J = 14.0, 2.0 \text{ Hz}$ , 0.6H), 3.13 (d,  $J = 15.2 \text{ Hz}$ , 0.4H), 2.76 (d,  $J = 14.8 \text{ Hz}$ , 0.4H), 2.42 (d,  $J = 14.0 \text{ Hz}$ , 0.6H), 1.38 (dt,  $J = 7.2, 5.2 \text{ Hz}$ , 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.95, 175.64, 171.97, 171.81, 168.39, 167.31, 154.00, 154.96, 147.84, 145.80, 136.90, 136.45, 135.44, 134.53, 133.66, 133.48, 130.15, 129.87, 129.44, 129.13, 128.94, 128.71, 128.32, 127.99, 127.78, 127.32, 127.30, 126.37, 126.13, 124.80, 124.70, 124.60, 123.79, 123.75, 123.69, 123.43, 117.76, 117.60, 110.65, 109.59, 94.90, 93.66, 63.64, 62.83, 50.17, 49.55, 44.63, 44.46, 37.42, 37.37, 14.13, 14.07; IR: 3484.2, 3281.4, 2959.1, 2923.7, 1739.1, 1714.4, 1632.2, 1610.4, 1485.9, 1466.6, 1364.0, 1346.3, 1284.3, 1263.4, 1216.9, 1197.6, 1182.2, 1145.9, 1081.0, 1038.4, 974.7, 947.8, 883.8, 808.3, 753.4, 734.7, 698.6, 630.1  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{29}\text{H}_{24}\text{NO}_7$   $[\text{M}+\text{H}]^+$  498.1547, found:498.1545.

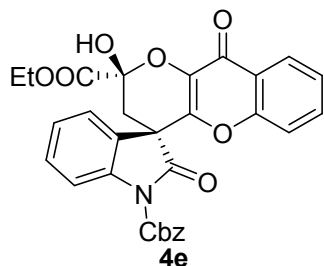
**Ethyl 1-allyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4d**



white solid, melting point: 158–160 °C, 43.4 mg, 97% yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 97.3$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 15.593,  $t$  (minor) = 19.550];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (s, 0.45H), 8.21 (dd,  $J = 17.2, 7.6 \text{ Hz}$ , 1H), 7.93 (d,  $J = 7.6 \text{ Hz}$ , 0.50H), 7.54 – 7.50 (m, 1H), 7.41 (t,  $J = 7.6 \text{ Hz}$ , 0.6H), 7.36 – 7.29 (m, 1.4H), 7.25 (d,  $J = 7.2 \text{ Hz}$ , 0.5H), 7.17 (t,  $J = 7.6 \text{ Hz}$ , 0.5H), 7.11 – 7.01 (m, 2H), 6.94 (d,  $J = 7.6 \text{ Hz}$ , 0.5H), 5.99 – 5.88 (m, 1H), 5.34 (dd,  $J = 16.8, 10.6 \text{ Hz}$ , 2H), 5.21 (s, 0.55H),

4.60 (dd,  $J = 16.8, 3.6$  Hz, 1H), 4.36 (dt,  $J = 7.6, 5.6$  Hz, 3H), 3.33 (d,  $J = 14.0$  Hz, 0.55H), 3.11 (d,  $J = 14.8$  Hz, 0.45H), 2.72 (d,  $J = 14.8$  Hz, 0.45H), 2.38 (d,  $J = 14.0$  Hz, 0.55H), 1.38 (dt,  $J = 14.4, 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.59, 175.22, 171.98, 171.82, 168.42, 167.32, 155.02, 149.97, 147.72, 145.61, 143.07, 142.90, 136.98, 136.52, 133.66, 133.50, 130.76, 130.16, 129.96, 129.83, 129.45, 128.72, 127.78, 126.37, 126.12, 124.80, 124.70, 124.61, 123.82, 123.74, 123.70, 123.37, 118.00, 117.85, 117.68, 117.44, 110.51, 109.49, 94.88, 93.64, 63.69, 62.83, 50.16, 49.53, 43.05, 42.92, 37.50, 37.47, 14.15, 14.08; IR: 3544.6, 3259.4, 2963.1, 2854.3, 1740.2, 1710.8, 1625.9, 1609.6, 1487.0, 1467.4, 1432.8, 1280.3, 1260.9, 1238.1, 1198.6, 1186.3, 1107.0, 1039.8, 1004.7, 977.5, 943.9, 884.7, 855.7, 797.5, 761.9, 702.3, 668.9, 655.5, 636.0, 619.9  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  448.1391, found: 448.1393.

**1- benzyl 2'-ethyl 2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-1,2'-dicarboxylate 4e**



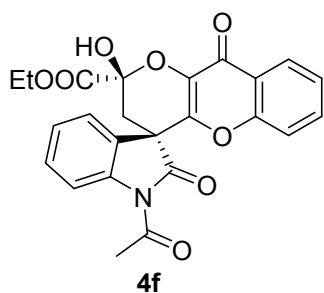
yellow solid, melting point: 196–198 °C, 39.5 mg, 73% yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 98.4$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 28.027,  $t$  (minor) = 41.336];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 0.45H), 8.23 (dd,  $J = 14.8, 7.6$  Hz, 1H), 7.93 (d,  $J = 7.6$  Hz, 0.55H), 7.54 (t,  $J = 7.6$  Hz, 1H), 7.40 – 7.29 (m, 6.45H), 7.23 – 7.01 (m, 3H), 6.92 (d,  $J = 7.6$  Hz, 0.5H), 6.85 (d,  $J = 7.6$  Hz, 0.5H), 5.27 (t,  $J = 15.6$  Hz, 1H), 5.11 (s, 0.55H), 4.82 (t,  $J = 14.0$  Hz, 1H), 4.39 (dq,  $J = 12.4, 7.2$  Hz, 2H), 3.39 (d,  $J = 14.0$  Hz, 0.55H), 3.14 (d,  $J = 14.8$  Hz, 0.45H), 2.75 (d,  $J = 15.2$  Hz, 0.45H), 2.41 (d,  $J = 14.0$  Hz, 0.55H), 1.40 (dt,  $J = 12.4, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.00, 175.66, 171.99, 171.85, 168.45, 167.34, 155.07, 155.02, 147.80, 143.05, 142.86, 136.95, 136.50, 135.47, 134.56, 133.69, 133.54, 130.18, 129.89, 129.50, 129.18, 128.99, 128.78, 128.38, 128.04, 127.80, 127.37, 127.36, 126.46, 126.22, 124.86, 124.75, 124.67, 123.84, 123.78, 123.47, 117.81, 117.64, 110.66, 109.64, 94.93, 93.64, 63.78, 62.90, 50.21, 49.56, 44.69, 44.52, 37.46, 14.18, 14.12; IR: 3482.3, 3279.6, 2960.8, 2922.9, 1743.1,



1715.8, 1640.6, 1609.8, 1488.3, 1467.7, 1432.2, 1369.4, 1282.4, 1262.1, 1196.7, 1184.7, 1146.1, 1109.0, 1040.2, 1013.5, 972.1, 860.0, 772.8, 753.5, 728.6, 696.9, 630.7  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{30}\text{H}_{24}\text{NO}_9$   $[\text{M}+\text{H}]^+$  542.1146, found:542.1153.

**Ethyl 1-acetyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4f**

yellow solid, melting point: 150–153  $^{\circ}\text{C}$ , 24.2 mg, 54% yield, 98% *ee*, > 20:1 *dr*,

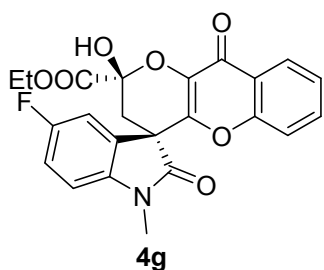


$[\alpha]_{\text{D}}^{25} = +113.3$  ( $c = 0.30$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 15.747,  $t$  (minor) = 20.035];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (d,  $J = 8.0$  Hz, 0.8H), 8.31 (d,  $J = 6.4$  Hz, 0.2H), 8.23 – 8.21 (m, 1H), 7.95 (d,  $J = 7.6$  Hz, 0.7H), 7.56 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.95 (d,  $J = 2.8$  Hz,

0.3H), 7.47 – 7.40 (m, 1H), 7.34 – 7.29 (m, 1.3H), 7.23 (d,  $J = 8.0$  Hz, 0.7H), 7.18 (d,  $J = 8.4$  Hz, 1H), 7.14 (d,  $J = 8.4$  Hz, 0.3H), 5.10 (s, 0.7H), 4.38 (dq,  $J = 15.6, 7.2$  Hz, 2H), 3.32 (d,  $J = 14.0$  Hz, 0.8H), 3.08 (d,  $J = 15.2$  Hz, 0.2H), 2.81 (d,  $J = 15.2$  Hz, 0.3H), 2.74 (d,  $J = 5.7$  Hz, 3H), 2.47 (d,  $J = 14.0$  Hz, 0.7H), 1.38 (dt,  $J = 15.2, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.06, 171.94, 170.71, 168.06, 155.10, 147.08, 140.19, 136.56, 133.94, 133.82, 129.91, 128.76, 127.90, 127.28, 126.85, 126.41, 126.22, 125.96, 125.62, 125.08, 124.91, 123.69, 123.42, 118.05, 117.96, 117.37, 116.65, 94.46, 93.56, 63.93, 63.21, 50.70, 50.51, 38.87, 38.56, 27.35, 27.01, 14.17, 14.13; IR: 3350.2, 2926.9, 2924.5, 1760.2, 1741.5, 1724.4, 1640.9, 1613.6, 1465.6, 1434.8, 1370.1, 1339.0, 1306.9, 1268.1, 1198.3, 1147.9, 1107.9, 1063.4, 973.7, 802.7, 763.4  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{20}\text{NO}_8$   $[\text{M}+\text{H}]^+$  450.1183, found:450.1188.

**Ethyl 5-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4g**

light red solid, melting point: 114–116  $^{\circ}\text{C}$ , 36.0 mg, 82% yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +135.8$  ( $c = 0.46$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (85:15),

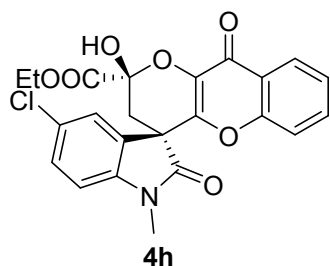


flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 30.576];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (s, 0.3H), 8.22 (dd,  $J = 8.0, 1.6$  Hz, 0.3H), 8.18 (dd,  $J = 8.0, 1.6$  Hz, 0.7H), 7.69

(dd,  $J = 8.4, 2.4$  Hz, 0.7H), 7.55 – 7.50 (m, 1H), 7.34 – 7.27 (m, 1H), 7.13 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.10 – 7.05 (m, 1H), 7.00 – 6.96 (m, 0.7H), 6.89 (dd,  $J = 8.4, 4.0$  Hz, 0.7H), 5.28 (d,  $J = 2.2$  Hz, 0.7H), 4.36 (m, 2H), 3.35 (dt,  $J = 14.4, 7.1$  Hz, 3H), 3.31 (d,  $J = 2.4$  Hz, 0.3H), 3.27 (d,  $J = 2.4$  Hz, 0.3H), 3.02 (d,  $J = 14.8$  Hz, 0.3H), 2.70 (d,  $J = 14.8$  Hz, 0.3H), 2.34 (d,  $J = 14.0$  Hz, 0.7H), 1.37 (dt,  $J = 14.4, 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.40, 175.14, 171.96, 171.75, 168.21, 167.19, 160.22 ( $J = 243.2$  Hz), 154.50 ( $J = 239.6$  Hz), 155.02, 154.09, 147.07, 144.79, 139.79, 139.77, 137.16, 136.60, 133.72, 133.57, 131.23, 131.14, 130.71 ( $J = 6.4$  Hz) 130.66 ( $J = 6.9$  Hz), 128.94, 126.36, 126.12, 124.90, 124.72, 123.71, 123.68, 118.00, 117.84, 116.75 ( $J = 23.6$  Hz), 116.08 ( $J = 26.1$  Hz), 115.93 ( $J = 23.6$  Hz), 112.15 ( $J = 25.4$  Hz), 110.44 ( $J = 8.1$  Hz), 109.03 ( $J = 8.1$  Hz), 94.79, 93.59, 63.73, 62.89, 50.41 ( $J = 1.7$  Hz), 49.86 ( $J = 1.6$  Hz), 37.43, 27.58, 27.41, 14.14, 14.07; IR: 3298.6, 2927.8, 1747.9, 1722.8, 1636.2, 1613.7, 1492.8, 1469.3, 1352.8, 1258.6, 1198.5, 1151.0, 1105.5, 1030.8, 972.2, 866.1, 797.3, 734.3, 683.5  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{FNO}_7$   $[\text{M}+\text{H}]^+$  440.1140, found:440.1146.

**Ethyl 5-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4h**



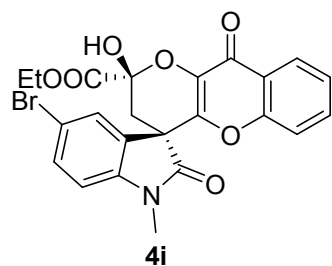
yellow solid, melting point: 128–131 °C, 35.0 mg, 77% yield, 94% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 188.8$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (85:15), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 30.714,  $t$  (minor) = 28.046];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (s,

0.3H), 8.21 (dd,  $J = 14.0, 8.0$  Hz, 1H), 7.90 (d,  $J = 1.6$  Hz, 0.7H), 7.55 – 7.51 (m, 1H), 7.42 (dd,  $J = 8.0, 1.6$  Hz, 0.3H), 7.35 (dd,  $J = 8.4, 2.0$  Hz, 0.7H), 7.32 – 7.28 (m, 1H), 7.21 (d,  $J = 1.6$  Hz, 0.3H), 7.14 (d,  $J = 8.4$  Hz, 0.7H), 7.10 (d,  $J = 8.8$  Hz, 0.3H), 6.97 (d,  $J = 8.4$  Hz, 0.3H), 6.90 (d,  $J = 8.4$  Hz, 0.7H), 5.18 (s, 0.7H), 4.37 (dq,  $J = 14.8, 7.2$  Hz, 2H), 3.35 (d,  $J = 9.5$  Hz, 3H), 3.28 (d,  $J = 14.0$  Hz, 0.7H), 3.03 (d,  $J = 14.8$  Hz, 0.3H), 2.69 (d,  $J = 14.8$  Hz, 0.3H), 2.33 (d,  $J = 14.0$  Hz, 0.7H), 1.37 (dt,  $J = 14.8, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.30, 175.04, 171.93, 171.73, 168.17, 167.16, 155.02, 154.96, 146.91, 144.69, 142.39, 137.18, 136.63, 133.73, 133.59,

131.22, 131.04, 130.38, 130.30, 130.25, 129.57, 128.84, 128.26, 126.39, 126.15, 124.92, 124.75, 124.39, 123.71, 118.03, 117.90, 110.64, 109.52, 94.77, 93.55, 63.78, 62.93, 50.18, 49.64, 37.44, 27.57, 27.39, 14.16, 14.09; IR: 3474.2, 2932.3, 1746.1, 1728.2, 1632.8, 1611.2, 1489.4, 1468.1, 1429.9, 1345.7, 1189.4, 1148.1, 1104.3, 1030.5, 977.3, 834.7, 808.9, 762.2, 703.7, 676.4  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClNO}_7$   $[\text{M}+\text{H}]^+$  456.0845, found:456.0832.

**Ethyl 5-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

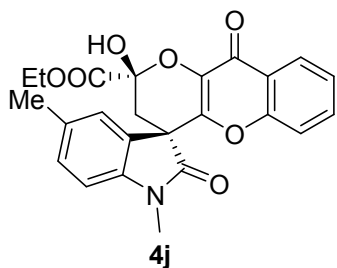
**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4i**



white solid, melting point: 124–127 °C, 44.5mg, 89% yield, 93% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 78.6$  ( $c = 0.60$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 22.013,  $t$  (minor) = 19.790];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 (s,

0.3H), 8.22 (dd,  $J = 8.0, 1.6$  Hz, 0.3H), 8.18 (dd,  $J = 8.0, 1.2$  Hz, 0.7H), 8.03 (d,  $J = 1.6$  Hz, 0.7H), 7.57 – 7.48 (m, 2H), 7.34 (d,  $J = 2.0$  Hz, 0.3H), 7.31 (d,  $J = 8.0$  Hz, 0.7H), 7.13 (d,  $J = 8.4$  Hz, 0.7H), 7.10 (d,  $J = 8.4$  Hz, 0.3H), 6.92 (d,  $J = 8.4$  Hz, 0.3H), 6.85 (d,  $J = 8.0$  Hz, 0.7H), 5.22 (s, 0.7H), 4.36 (dq,  $J = 14.4, 7.2$  Hz, 2H), 3.35 (d,  $J = 9.7$  Hz, 3H), 3.29 (d,  $J = 2.0$  Hz, 0.3H), 3.26 (d,  $J = 2.4$  Hz, 0.35H), 3.03 (d,  $J = 14.8$  Hz, 0.35H), 2.68 (d,  $J = 14.8$  Hz, 0.3H), 2.33 (d,  $J = 14.0$  Hz, 0.7H), 1.36 (dt,  $J = 14.4, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.18, 174.93, 171.91, 171.70, 168.14, 167.15, 154.99, 154.94, 146.89, 144.69, 142.90, 142.87, 137.17, 136.62, 133.72, 133.57, 133.20, 132.46, 131.54, 130.94, 130.66, 127.09, 126.35, 126.12, 124.90, 124.73, 123.72, 123.69, , 118.02, 117.91, 117.38, 116.15, 111.09, 110.03, 94.76, 93.55, 63.75, 62.91, 50.10, 49.56, 37.46, 37.44, 27.54, 27.36, 14.15, 14.08; IR: 3494.2, 3280.2, 2961.3, 1723.3, 1364.5, 1610.4, 1480.4, 1467.2, 1339.7, 1282.0, 1218.4, 1173.6, 1146.4, 1106.2, 1040.3, 977.1, 961.1, 813.5, 797.2, 764.6, 747.7, 669.0, 643.9  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClNO}_7$   $[\text{M}+\text{H}]^+$  500.0339, found:500.0339.

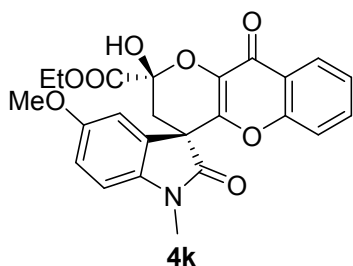
**Ethyl 2'-hydroxy-1,5-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4j**



white solid, melting point: 226–228 °C, 43.0 mg, 99% yield, 96% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 24.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 17.666,  $t$  (minor) = 15.895]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s,

0.5H), 8.22 (dd,  $J = 8.0, 1.6$  Hz, 0.5H), 8.18 (dd,  $J = 8.0, 1.6$  Hz, 0.5H), 7.69 (s, 0.5H), 7.53 – 7.48 (m, 1H), 7.32 – 7.28 (m, 1H), 7.22 (d,  $J = 8.0$  Hz, 0.5H), 7.17 – 7.13 (m, 1H), 7.09 (d,  $J = 8.4$  Hz, 0.5H), 7.02 (s, 0.5H), 6.91 (d,  $J = 7.6$  Hz, 0.5H), 6.85 (d,  $J = 8.0$  Hz, 0.5H), 5.08 (d,  $J = 2.2$  Hz, 0.5H), 4.35 (dt,  $J = 7.2, 5.0$  Hz, 2H), 3.34 (d,  $J = 8.0$  Hz, 3H), 3.29 (dd,  $J = 14.0, 2.4$  Hz, 0.5H), 3.04 (d,  $J = 14.8$  Hz, 0.5H), 2.66 (d,  $J = 14.8$  Hz, 0.5H), 2.31 (d,  $J = 14.0$  Hz, 0.5H), 2.30 (d,  $J = 8.8$  Hz, 3H), 1.37 (dt,  $J = 16.6, 7.2$  Hz, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.59, 175.37, 171.98, 171.84, 168.48, 167.37, 155.04, 154.99, 147.87, 145.70, 141.43, 141.36, 137.05, 136.59, 134.65, 133.52, 133.38, 132.99, 130.47, 129.86, 128.74, 128.73, 128.38, 126.28, 126.03, 124.71, 124.55, 124.47, 123.74, 123.71, 118.11, 117.94, 109.39, 108.30, 94.91, 93.64, 63.66, 62.76, 50.18, 49.61, 37.59, 27.41, 27.25, 21.32, 21.23, 14.14, 14.07; IR: 3494.7, 3282.8, 2961.6, 1745.8, 1718.6, 1636.8, 1611.3, 1499.5, 1359.2, 1282.1, 1260.8, 1196.1, 1103.7, 1037.9, 977.5, 964.8, 811.7, 796.6, 760.2, 699.6, 669.8, 647.7 cm<sup>-1</sup>; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  436.1391, found:436.1396.

**Ethyl 2'-hydroxy-5-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4k**



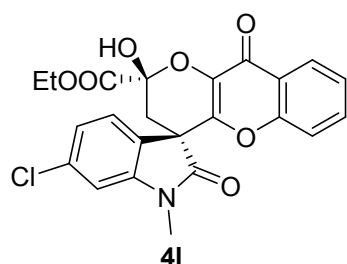
white solid, melting point: 191–193 °C, 44.1 mg, 98% yield, 98% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 141.6$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 22.303,  $t$  (minor) = 27.639]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95

(s, 0.5H), 8.20 – 8.16 (m, 1H), 7.55 (d,  $J = 2.0$  Hz, 0.5H), 7.53 – 7.49 (m, 1H), 7.29 (t,  $J = 1.2$  Hz, 1H), 7.11 (dd,  $J = 19.6, 8.4$  Hz, 1H), 6.93 (s, 1H), 6.89 (d,  $J = 2.4$  Hz, 0.5H), 6.84 (d,  $J = 18.8$  Hz, 1H), 5.07 (d,  $J = 1.6$  Hz, 0.5H), 4.34 (dq,  $J = 15.6, 7.2$

Hz, 2H), 3.74 (d,  $J = 8.0$  Hz, 3H), 3.33 (d,  $J = 7.6$  Hz, 3H), 3.28 (d,  $J = 2.0$  Hz, 0.5H), 3.04 (d,  $J = 14.8$  Hz, 0.5H), 2.67 (d,  $J = 14.8$  Hz, 0.5H), 2.32 (d,  $J = 14.0$  Hz, 0.5H), 1.36 (dt,  $J = 15.6, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.27, 175.05, 171.92, 171.81, 168.41, 167.37, 157.49, 156.38, 155.02, 154.97, 147.62, 145.52, 137.15, 137.06, 136.99, 136.59, 133.54, 133.42, 130.97, 129.96, 126.24, 126.02, 124.73, 124.57, 123.71, 123.69, 118.08, 117.92, 114.82, 114.58, 114.29, 110.57, 110.22, 108.92, 94.91, 93.60, 63.69, 62.77, 55.95, 55.82, 50.51, 49.89, 37.63, 37.45, 27.47, 27.31, 14.14, 14.06; IR: 3350.6, 2963.2, 2922.7, 1748.1, 1714.7, 1652.5, 1637.1, 1611.6, 1497.2, 147.0, 1363.4, 1339.6, 1260.9, 1236.3, 1202.1, 1160.5, 1144.2, 1108.8, 1039.5, 1025.3, 977.0, 806.5, 758.1, 694.3, 679.9, 646.6  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  452.1340, found: 452.1352.

**Ethyl 6-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4l**

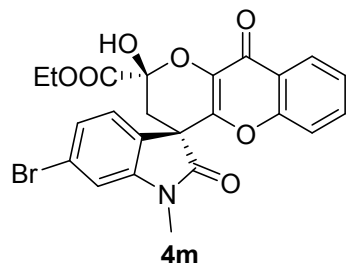


yellow solid, melting point: 111–113 °C, 38.3mg, 86% yield, 97% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 57.2$  ( $c = 0.65$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 22.883,  $t$  (minor) = 30.794];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58

(s, 0.3H), 8.22 (dd,  $J = 8.0, 1.2$  Hz, 0.3H), 8.18 (dd,  $J = 8.0, 1.6$  Hz, 0.7H), 7.82 (d,  $J = 8.0$  Hz, 0.7H), 7.55 – 7.51 (m, 1H), 7.34 – 7.28 (m, 1H), 7.15 (d,  $J = 7.4$  Hz, 1.3H), 7.10 (d,  $J = 8.4$  Hz, 0.3H), 7.05 – 7.03 (m, 1H), 6.97 (d,  $J = 2.0$  Hz, 0.7H), 5.19 (s, 0.7H), 4.36 (dq,  $J = 11.1, 5.6$  Hz, 2H), 3.35 (d,  $J = 9.2$  Hz, 3H), 3.27 (d,  $J = 14.4$  Hz, 0.7H), 3.03 (d,  $J = 14.8$  Hz, 0.3H), 2.67 (d,  $J = 14.8$  Hz, 0.3H), 2.31 (d,  $J = 14.0$  Hz, 0.7H), 1.36 (dt,  $J = 11.1, 5.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.76, 175.49, 171.96, 171.77, 168.28, 167.21, 155.03, 154.97, 147.06, 145.02, 144.88, 137.15, 136.64, 136.18, 135.45, 133.74, 133.61, 128.85, 128.11, 127.09, 126.39, 126.13, 124.92, 124.81, 123.74, 124.67, 123.73, 123.69, 123.29, 118.03, 117.85, 110.51, 109.38, 94.80, 93.58, 63.79, 62.93, 49.84, 49.25, 37.57, 37.40, 27.56, 27.38, 14.16, 14.09; IR: 3348.8, 3277.2, 2961.0, 2923.4, 1722.4, 1365.8, 1607.2, 1468.0, 1365.6, 1281.9, 1260.5, 1188.7, 1147.4, 1103.4, 1078.4, 1025.5, 971.2, 798.4, 759.1, 645.0,

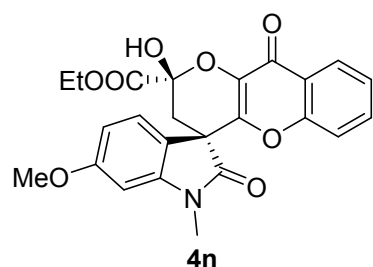
621.5  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{ClNO}_7$   $[\text{M}+\text{H}]^+$  456.0845, found:456.0833.

**Ethyl 6-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4m**



light yellow solid, melting point: 105–107 °C, 43.1 mg, 86% yield, 97% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +245.2$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 22.846,  $t$  (minor) = 31.330];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (s, 0.3H), 8.22 (dd,  $J = 8.0, 1.6$  Hz, 0.3H), 8.18 (dd,  $J = 8.0, 1.6$  Hz, 0.7H), 7.76 (d,  $J = 8.4$  Hz, 0.7H), 7.55 – 7.51 (m, 1H), 7.32 – 7.28 (m, 1.3H), 7.21 (d,  $J = 2.0$  Hz, 0.3H), 7.19 (d,  $J = 1.6$  Hz, 0.7H), 7.15 (d,  $J = 8.4$  Hz, 1H), 7.12 (d,  $J = 1.6$  Hz, 0.7H), 7.09 (d,  $J = 1.6$  Hz, 0.3H), 5.13 (d,  $J = 2.0$  Hz, 0.7H), 4.36 (dt,  $J = 14.4, 7.1$  Hz, 2H), 3.35 (d,  $J = 9.3$  Hz, 3H), 3.28 (dd,  $J = 14.4, 1.6$  Hz, 0.7H), 3.02 (d,  $J = 14.8$  Hz, 0.3H), 2.67 (d,  $J = 15.2$  Hz, 0.3H), 2.30 (d,  $J = 14.0$  Hz, 0.7H), 1.37 (dt,  $J = 14.4, 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.63, 175.35, 171.89, 171.72, 168.25, 167.19, 155.01, 154.96, 146.91, 145.14, 144.77, 137.16, 136.67, 133.73, 133.60, 129.17, 128.66, 127.69, 1127.61, 126.37, 126.23, 126.13, 125.12, 124.90, 124.73, 123.86, 123.70, 123.30, 118.02, 117.85, 113.27, 112.16, 94.79, 93.55, 63.80, 62.91, 49.89, 49.29, 37.49, 37.34, 27.55, 27.37, 14.15, 14.09; IR: 3396.7, 3280.6, 2961.7, 2924.1, 1723.6, 1636.6, 1602.5, 1468.6, 1365.5, 1282.9, 1260.5, 1188.9, 1149.5, 1101.7, 1025.4, 970.9, 798.9, 759.3, 707.0, 643.9, 620.5  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{BrNO}_7$   $[\text{M}+\text{H}]^+$  500.0339, found:500.0346.

**Ethyl 2'-hydroxy-6-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4n**

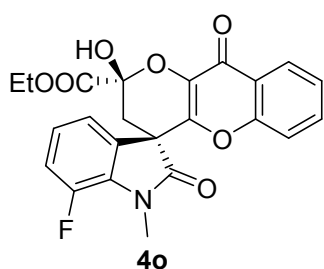


light red solid, melting point: 210–211 °C, 33.4 mg, 74% yield, > 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +186.0$  ( $c = 0.20$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 26.010];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (s, 0.4H), 8.24 – 8.19 (m, 1H), 7.76 (d,  $J = 8.0$  Hz, 0.5H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.30

(dd,  $J = 14.4, 7.2$  Hz, 1H), 7.15 (d,  $J = 8.4$  Hz, 0.5H), 7.10 (d,  $J = 8.4$  Hz, 1H), 6.66 – 6.59 (m, 1H), 6.56 – 6.54 (m, 1H), 4.94 (d,  $J = 1.8$  Hz, 0.6H), 4.36 (dd,  $J = 14.9, 7.3$  Hz, 2H), 3.86 (d,  $J = 7.6$  Hz, 3H), 3.34 (d,  $J = 6.0$  Hz, 3H), 3.28 (dd,  $J = 14.0, 2.0$  Hz, 0.6H), 3.02 (d,  $J = 15.2$  Hz, 0.4H), 2.65 (d,  $J = 15.2$  Hz, 0.4H), 2.29 (d,  $J = 14.0$  Hz, 0.6H), 1.38 (dd,  $J = 14.9, 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.34, 176.05, 171.99, 171.89, 168.52, 167.41, 161.64, 161.11, 155.07, 155.03, 147.89, 145.81, 145.16, 136.54, 133.43, 128.53, 126.36, 126.11, 124.75, 124.60, 124.56, 123.76, 121.88, 120.28, 118.11, 117.91, 108.28, 106.82, 97.87, 96.71, 94.98, 93.67, 63.75, 62.82, 55.88, 55.72, 49.74, 49.13, 37.77, 37.68, 27.42, 27.28, 14.18, 14.11; IR: 3334.4, 2962.9, 2938.6, 1740.2, 1707.5, 1629.4, 1612.5, 1470.9, 1456.4, 1373.9, 1288.0, 1262.2, 1194.5, 1149.8, 1101.2, 1062.6, 969.3, 927.7, 877.8, 804.3, 758.7, 691.5, 649.3, 639.4, 617.3  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  452.1340, found:452.1353

**Ethyl 7-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4o**

yellow solid, melting point: 190–192 °C, 43.5 mg, 99% yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 132.9$  ( $c = 0.54$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20),

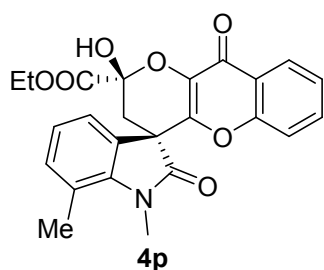


flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 19.841,  $t$  (minor) = 40.459];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (s, 0.4H), 8.21 (dd,  $J = 8.0, 1.2$  Hz, 0.4H), 8.17 (dd,  $J = 8.0, 1.2$  Hz, 0.6H), 7.71 (d,  $J = 7.2$  Hz, 0.6H), 7.55 – 7.50 (m, 1H), 7.33 – 7.28 (m, 1H), 7.18 – 7.16 (m, 1H),

7.14 (d,  $J = 2.4$  Hz, 0.4H), 7.12 – 7.07 (m, 1H), 7.02 – 6.97 (m, 1H), 5.20 (s, 0.6H), 4.35 (dq,  $J = 14.6, 7.2$  Hz, 2H), 3.56 (d,  $J = 2.8$  Hz, 3H), 3.28 (dd,  $J = 14.4, 1.6$  Hz, 0.6H), 3.03 (d,  $J = 14.8$  Hz, 0.4H), 2.70 (d,  $J = 14.8$  Hz, 0.4H), 2.34 (d,  $J = 14.0$  Hz, 0.6H), 1.36 (dt,  $J = 14.6, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.34, 175.14, 171.93, 171.75, 168.27, 167.19, 155.02, 154.97, 148.02 (d,  $J = 244.8$  Hz), 147.84 (d,  $J = 242.0$  Hz), 147.11, 137.02, 136.57, 133.71, 136.57, 132.35 (d,  $J = 2.5$  Hz), 131.41 (d,  $J = 2.7$  Hz), 130.56 (d,  $J = 8.4$  Hz), 130.53 (d,  $J = 8.8$  Hz), 126.33, 126.08, 125.45 (d,  $J = 6.5$  Hz), 124.86, 124.67, 123.84 (d,  $J = 8.6$  Hz), 123.68 (d,  $J = 4.2$  Hz), 123.58

(d,  $J = 3.2$  Hz), 119.65 (d,  $J = 3.3$  Hz), 118.28 (d,  $J = 19.0$  Hz), 118.03, 117.85, 117.47 (d,  $J = 18.8$  Hz), 94.81, 93.54, 63.72, 62.86, 50.33 (d,  $J = 1.9$  Hz), 49.69 (d,  $J = 2.1$  Hz), 37.76, 37.59, 30.02 (d,  $J = 5.8$  Hz), 29.84 (d,  $J = 6.2$  Hz), 14.13, 14.06; IR: 3516.5, 3277.3, 2961.2, 2922.7, 1736.5, 1715.6, 1624.6, 1610.9, 1477.8, 1466.6, 1364.9, 1336.3, 1284.1, 1260.1, 1245.1, 1196.8, 1108.1, 1080.2, 1048.3, 1023.4, 988.0, 963.4, 800.7, 758.6, 702.5, 642.4, 628.9  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{FNO}_7$   $[\text{M}+\text{H}]^+$  440.1140, found:440.1151.

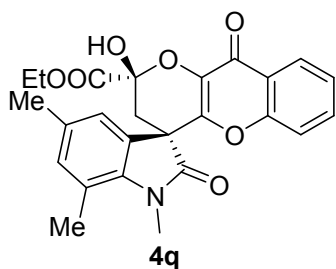
**Ethyl 2'-hydroxy-1,7-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4p**



yellow solid, melting point: 191–194 °C, 43.1 mg, 99% yield, > 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 92.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 31.735];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (s, 0.65H), 8.21 (dd,  $J = 8.0, 1.2$  Hz, 0.65H), 8.17 (dd,  $J = 8.0, 1.6$  Hz, 0.35H), 7.73 (d,  $J = 7.2$  Hz, 0.35H), 7.53 – 7.49 (m, 1H), 7.29 (t,  $J = 7.2$  Hz, 1H), 7.18 – 7.12 (m, 1.35H), 7.10 – 7.07 (m, 0.35H), 7.05 – 7.02 (m, 1.3H), 6.93 (t,  $J = 7.6$  Hz, 0.65H), 5.07 (s, 0.35H), 4.34 (dt,  $J = 16.0, 7.2$  Hz, 2H), 3.62 (s, 3H), 3.28 (d,  $J = 14.0$  Hz, 0.35H), 2.99 (d,  $J = 14.8$  Hz, 0.65H), 2.66 (d,  $J = 3.2$  Hz, 3H), 2.62 (d,  $J = 14.4$  Hz, 0.65H), 2.30 (d,  $J = 14.4$  Hz, 0.35H), 1.36 (dt,  $J = 16.0, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.28, 176.32, 171.95, 171.83, 168.44, 167.33, 155.06, 155.00, 147.92, 145.78, 141.50, 141.46, 137.04, 137.64, 133.93, 133.53, 133.38, 133.31, 130.50, 129.38, 126.25, 126.01, 125.51, 124.71, 124.59, 124.55, 123.70, 123.18, 121.64, 121.33, 120.03, 118.10, 117.90, 94.91, 93.63, 63.63, 62.73, 49.61, 49.04, 38.10, 37.95, 30.79, 30.75, 19.40, 19.01, 14.13, 14.05; IR: 3503.2, 3277.8, 2960.2, 2924.9, 1736.6, 1694.9, 1667.7, 1648.6, 1634.0, 1612.0, 1466.3, 1377.1, 1361.1, 1287.1, 1260.5, 1195.2, 1145.4, 1111.1, 1071.5, 1021.2, 965.3, 909.4, 795.5, 763.3, 749.9, 699.7, 643.2, 623.9  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  436.1391, found:436.1400.

**Ethyl 2'-hydroxy-1,5,7-trimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4q**

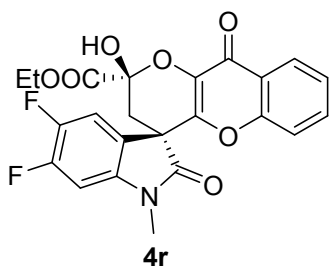




yellow solid, melting point: 200–202 °C, 35.9 mg, 80% yield, 98% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 45.0$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 21.379,  $t$  (minor) = 19.769]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.98 (s,

0.7H), 8.22 (dd,  $J = 8.0, 1.6$  Hz, 0.7H), 8.18 (dd,  $J = 8.0, 1.6$  Hz, 0.3H), 7.54 – 7.50 (m, 1.3H), 7.32 (d,  $J = 0.8$  Hz, 0.2H), 7.29 (d,  $J = 8.0$  Hz, 0.8H), 7.18 (d,  $J = 8.4$  Hz, 0.3H), 7.14 (d,  $J = 8.4$  Hz, 0.7H), 6.94 (s, 0.7H), 6.89 (s, 0.3H), 6.82 (s, 0.7H), 5.03 (d,  $J = 2.0$  Hz, 0.3H), 4.35 (dq,  $J = 16.8, 7.2$  Hz, 2H), 3.59 (s, 3H), 3.27 (dd,  $J = 14.0, 2.4$  Hz, 0.3H), 2.98 (d,  $J = 14.8$  Hz, 0.7H), 2.63 (d,  $J = 11.2$  Hz, 0.6H), 2.62 (s, 3H), 2.29 (d,  $J = 14.4$  Hz, 0.4H), 2.23 (d,  $J = 7.2$  Hz, 3H), 1.36 (dt,  $J = 16.8, 7.2$  Hz, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.16, 176.23, 171.99, 171.87, 168.52, 167.41, 155.08, 155.03, 148.16, 146.01, 139.04, 139.00, 137.00, 136.59, 134.37, 133.76, 133.48, 133.35, 132.69, 130.61, 129.42, 126.26, 126.11, 126.01, 124.68, 124.53, 123.74, 122.28, 120.99, 118.17, 117.99, 94.94, 93.64, 63.64, 62.73, 49.67, 49.12, 38.10, 38.06, 30.72, 20.97, 20.88, 19.23, 18.84, 14.14, 14.07; IR: 3151.5, 2961.7, 2921.9, 1757.4, 1710.4, 1660.6, 1632.5, 1612.4, 1485.3, 1468.8, 1442.9, 1371.2, 1287.2, 1260.4, 1200.4, 1139.1, 1099.0, 1077.0, 1025.7, 961.6, 870.6, 800.3, 761.7, 695.9, 648.9 cm<sup>-1</sup>; HRMS-ESI calcd. for  $\text{C}_{25}\text{H}_{24}\text{NO}_7$   $[\text{M}+\text{H}]^+$  450.1547, found:450.1558.

**5,6-difluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4r**



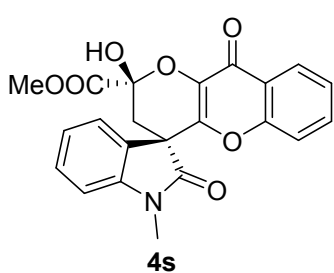
white solid, melting point: 113–115 °C, 43.9 mg, 96% yield, 93% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 98.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 22.295,  $t$  (minor) = 27.049]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s,

0.2H), 8.20 (dd,  $J = 8.0, 1.2$  Hz, 0.2H), 8.16 (dd,  $J = 8.0, 1.6$  Hz, 0.8H), 7.82 (dd,  $J = 10.0, 8.0$  Hz, 0.8H), 7.55 – 7.51 (m, 1H), 7.29 (t,  $J = 8.0$  Hz, 1H), 7.14 (d,  $J = 8.4$  Hz, 0.8H), 7.10 (t,  $J = 8.0$  Hz, 0.2H), 6.90 (dd,  $J = 9.2, 6.0$  Hz, 0.2H), 6.80 (dd,  $J = 9.6,$

6.4 Hz, 1H), 5.51 (s, 0.8H), 4.36 (dq,  $J = 13.6, 6.4$  Hz, 2H), 3.34 (d,  $J = 10.2$  Hz, 3H), 3.25 (dd,  $J = 14.0, 1.6$  Hz, 0.8H), 3.00 (d,  $J = 14.8$  Hz, 0.2H), 2.69 (d,  $J = 15.2$  Hz, 0.2H), 2.33 (d,  $J = 14.4$  Hz, 0.8H), 1.36 (dt,  $J = 13.6, 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  17.54, 175.30, 171.96, 171.70, 168.10, 167.14, 154.98, 154.93, 151.39, (d,  $J = 248.2$  Hz), 151.25 (d,  $J = 248.1$  Hz), 146.83 (d,  $J = 241.4$  Hz), 146.76, 146.71 (d,  $J = 244.3$  Hz), 140.26 (d,  $J = 11.6$  Hz), 137.19, 136.55, 136.55, 133.82, 133.68, 126.38, 126.13, 124.99 (d,  $J = 2.9$  Hz), 124.92 (d,  $J = 4.0$  Hz), 124.80, 123.68, 123.62, 118.01 (d,  $J = 11.7$  Hz), 117.95, 117.83 (d,  $J = 42.0$  Hz), 98.90, 98.67, 94.76, 93.61, 63.73, 62.96, 50.06, 49.52, 37.53, 37.41, 27.69, 27.51, 14.12, 14.06; IR: 3279.2, 3070.6, 2961.2, 2161.1, 2031.0, 1979.4, 1626.2, 1613.7, 1506.3, 1428.2, 1391.7, 1368.7, 1283.9, 1252.0, 1185.7, 1152.3, 1096.7, 1024.9, 1007.6, 960.4, 873.5, 786.3, 758.8, 688.3, 645.2, 618.4  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{18}\text{F}_2\text{NO}_7$   $[\text{M}+\text{H}]^+$  458.1046, found:458.1048.

**Methyl 2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4s**

light red solid, melting point: 205–207 °C, 39.9 mg, 98% yield, 98% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +71.5$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow

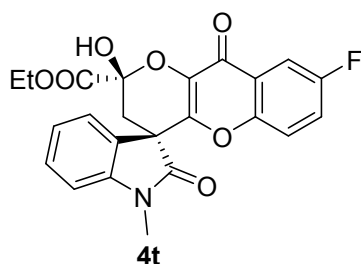


rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 20.279,  $t$  (minor) = 32.183];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 0.55H), 8.22 (dd,  $J = 8.0, 1.2$  Hz, 0.6H), 8.19 (dd,  $J = 8.4, 1.6$  Hz, 0.4H), 7.87 (d,  $J = 7.6$  Hz, 0.45H), 7.53 – 7.49 (m, 1H), 7.44 (td,  $J = 7.6, 1.2$  Hz, 0.6H), 7.38

(dt,  $J = 8.0, 1.2$  Hz, 0.4H), 7.33 – 7.29 (m, 1H), 7.20 (dd,  $J = 12.0, 6.4$  Hz, 1H), 7.15 – 7.12 (m, 0.55H), 7.09 – 7.06 (m, 1H), 7.04 (d,  $J = 8.0$  Hz, 0.6H), 6.97 (d,  $J = 7.6$  Hz, 0.4H), 5.01 (d,  $J = 2.0$  Hz, 0.45H), 3.91 (s, 3H), 3.37 (d,  $J = 10.8$  Hz, 3H), 3.30 (dd,  $J = 14.0, 2.4$  Hz, 0.45H), 3.07 (d,  $J = 14.8$  Hz, 0.55H), 2.69 (d,  $J = 15.2$  Hz, 0.55H), 2.33 (d,  $J = 14.0$  Hz, 0.45H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.71, 175.38, 171.94, 171.84, 168.87, 167.82, 155.06, 155.00, 147.64, 145.48, 143.86, 143.00, 137.03, 136.56, 133.62, 133.47, 130.27, 129.82, 129.57, 128.71, 127.64, 126.33, 126.08, 124.81, 124.79, 124.63, 123.75, 123.72, 123.69, 123.43, 118.08, 117.88, 109.69,

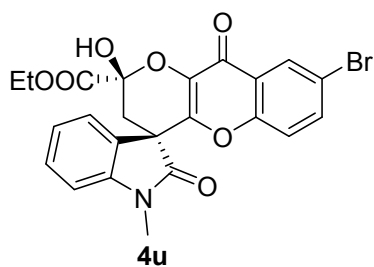
108.62, 94.97, 93.72, 54.07, 53.52, 50.15, 49.49, 37.64, 37.48, 27.43, 27.25; IR: 3316.0, 2961.4, 2922.7, 1752.1, 1725.6, 1637.8, 1610.0, 1468.3, 1432.1, 1366.3, 1351.3, 1280.3, 1270.1, 1260.5, 1219.0, 1188.0, 1146.9, 1124.0, 1070.1, 979.7, 966.8, 945.6, 811.9, 801.2, 760.7, 746.8, 660.7, 640.5, 616.8  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{22}\text{H}_{18}\text{NO}_7$   $[\text{M}+\text{H}]^+$  408.1078, found:408.1084.

**Ethyl 8'-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4t**



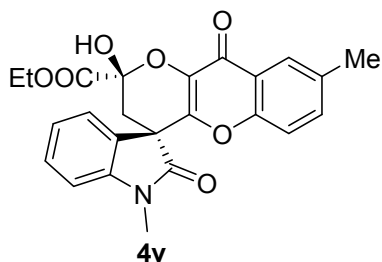
light red solid, melting point: 170–173 °C, 38.5 mg, 88% yield, 93% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +80.2$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 12.258,  $t$  (minor) = 22.094];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (s, 0.5H), 7.88 (dd,  $J = 7.6, 0.8$  Hz, 0.5H), 7.84 (dd,  $J = 8.0, 2.8$  Hz, 0.5H), 7.80 (dd,  $J = 8.0, 2.8$  Hz, 0.5H), 7.45 (td,  $J = 7.6, 1.2$  Hz, 0.5H), 7.38 (td,  $J = 7.6, 1.2$  Hz, 0.5H), 7.24 – 7.21 (m, 1.25H), 7.20 – 7.13 (m, 1.25H), 7.11 – 7.06 (m, 1H), 7.04 (d,  $J = 7.6$  Hz, 0.5H), 6.97 (d,  $J = 7.6$  Hz, 0.5H), 5.17 (s, 0.5H), 4.35 (tq,  $J = 14.4, 7.2$  Hz, 2H), 3.36 (d,  $J = 9.6$  Hz, 3H), 3.28 (d,  $J = 14.0$  Hz, 0.5H), 3.05 (d,  $J = 15.2$  Hz, 0.5H), 2.68 (d,  $J = 15.2$  Hz, 0.5H), 2.33 (d,  $J = 14.4$  Hz, 0.5H), 1.37 (dt,  $J = 14.4, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.58, 175.35, 171.24, 171.11, 168.33, 167.22, 159.24 ( $J = 245.3$  Hz), 159.17 ( $J = 245.1$  Hz), 151.33, 151.25, 148.05, 145.86, 143.82, 143.73, 136.77, 136.35, 130.33, 129.73, 129.63, 128.63, 127.70, 124.86, 124.84 ( $J = 6.3$  Hz), 124.75 ( $J = 4.6$  Hz), 123.78, 123.48, 120.06 ( $J = 14.6$  Hz), 121.75 ( $J = 14.5$  Hz), 120.26 ( $J = 8.1$  Hz), 120.06 ( $J = 8.0$  Hz), 110.94 ( $J = 27.1$  Hz), 110.70 ( $J = 26.9$  Hz), 109.72, 108.67, 100.09, 94.97, 93.70, 63.75, 62.86, 50.16, 49.57, 37.64, 37.48, 27.44, 27.27, 14.14, 14.08; IR: 3430.1, 2987.5, 1755.6, 1711.6, 1610.3, 1483.3, 1469.4, 1369.7, 1259.8, 1186.1, 1163.3, 1100.0, 1022.9, 994.4, 852.4, 831.0, 799.5, 757.7, 691.1, 642.2  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{FNO}_7$   $[\text{M}+\text{H}]^+$  440.1140, found:440.1143.

**Ethyl 8'-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4u**



light red solid, melting point: 136–138 °C, 32.5 mg, 65% yield, 92% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 355.0$  ( $c = 0.61$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 15.695,  $t$  (minor) = 31.396]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 0.5H), 8.32 (d,  $J = 2.4$  Hz, 0.5H), 8.27 (d,  $J = 2.0$  Hz, 0.5H), 7.88 (d,  $J = 7.6$  Hz, 0.5H), 7.58 (dt,  $J = 8.8, 2.4$  Hz, 1H), 7.47 – 7.36 (m, 1H), 7.24 – 7.18 (m, 1H), 7.10 – 7.04 (m, 1H), 7.03 (d,  $J = 4.8$  Hz, 0.5H), 6.99 – 6.96 (m, 1H), 5.22 (s, 0.5H), 4.35 (dq,  $J = 7.2, 4.4$  Hz, 2H), 3.36 (d,  $J = 10.0$  Hz, 3H), 3.27 (d,  $J = 14.0$  Hz, 0.5H), 3.05 (d,  $J = 15.2$  Hz, 0.5H), 2.68 (d,  $J = 15.2$  Hz, 0.5H), 2.34 (d,  $J = 14.4$  Hz, 0.5H), 1.36 (dt,  $J = 14.6, 7.1$  Hz, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.52, 175.27, 170.73, 170.59, 168.29, 167.18, 153.81, 153.75, 148.11, 145.88, 143.81, 143.71, 137.27, 136.81, 136.58, 136.42, 130.36, 129.65, 128.70, 128.53, 128.46, 127.73, 125.00, 124.98, 124.88, 123.80, 123.51, 120.07, 119.87, 118.24, 118.06, 109.73, 108.67, 95.01, 93.73, 63.75, 62.88, 50.15, 49.57, 37.66, 37.46, 27.45, 27.28, 14.15, 14.08; IR: 3331.6, 2926.6, 1741.1, 1723.1, 1626.8, 1606.3, 1467.2, 1418.4, 1352.2, 1242.0, 1227.8, 1098.5, 1074.8, 987.5, 963.1, 835.7, 754.6, 660.7 cm<sup>-1</sup>; HRMS-ESI calcd. for  $\text{C}_{23}\text{H}_{19}\text{BrNO}_7$   $[\text{M}+\text{H}]^+$  500.0339, found:500.0337.

**Ethyl 2'-hydroxy-1,8'-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4v**

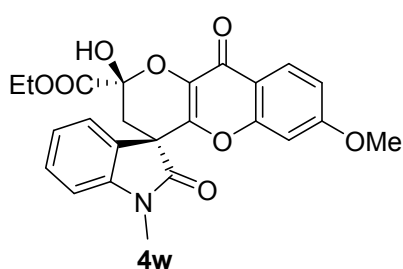


yellow solid, melting point: 106–108 °C, 42.2 mg, 97% yield, 98% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = + 52.8$  ( $c = 0.60$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 19.812,  $t$  (minor) = 41.106]; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (s, 0.5H), 7.97 (dd,  $J = 18.8, 1.2$  Hz, 1H), 7.88 (d,  $J = 7.6$  Hz, 0.5H), 7.43 (td,  $J = 8.0, 1.2$  Hz, 0.5H), 7.36 (td,  $J = 8.0, 1.2$  Hz, 0.5H), 7.32 – 7.29 (m, 1H), 7.21 – 7.14 (m, 1H), 7.07 (dd,  $J = 7.6, 0.8$  Hz, 0.5H), 7.02 (d,  $J = 8.4$  Hz, 1H), 6.97 (d,  $J = 3.2$  Hz, 0.5H), 6.95 (d,  $J = 2.4$  Hz, 0.5H), 5.15 (s, 0.5H), 4.39 (dq,  $J = 16.8, 7.2$  Hz, 2H), 3.35 (d,  $J = 8.4$  Hz, 3H), 3.28 (d,  $J = 14.0$  Hz, 0.5H), 3.04 (d,  $J =$

14.8 Hz, 0.5H), 2.66 (d,  $J = 14.8$  Hz, 0.5H), 2.36 (d,  $J = 5.6$  Hz, 3H), 2.32 (d,  $J = 14.0$  Hz, 0.5H), 1.36 (dt,  $J = 16.8, 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.74, 175.52, 172.02, 171.88, 168.45, 167.35, 153.37, 153.30, 147.52, 145.35, 143.84, 143.75, 136.96, 136.51, 134.90, 134.77, 134.74, 134.52, 130.17, 129.93, 129.47, 128.85, 127.68, 125.43, 125.18, 124.73, 123.72, 123.37, 117.79, 117.60, 109.62, 108.56, 94.85, 93.63, 63.62, 62.76, 50.15, 49.56, 37.62, 37.51, 27.38, 27.21, 20.86, 14.13, 14.06; IR: 3283.4, 2936.0, 1717.8, 1611.6, 1488.4, 1471.8, 1368.8, 1278.3, 1191.7, 1161.4, 1129.7, 1031.4, 961.7, 692.2, 662.7  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  436.1391, found:436.1381.

**Ethyl2'-hydroxy-7'-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4w**

yellow solid, melting point: 218–220 °C, 44.6 mg, 99% yield, 99% *ee*, > 20:1 *dr*,  $[\alpha]_{\text{D}}^{25} = +43.6$  ( $c = 0.50$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow



rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 16.022,  $t$  (minor) = 23.611];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (s, 0.5H), 8.11 (d,  $J = 9.2$  Hz, 0.5H), 8.05 (d,  $J = 8.8$  Hz, 0.5H), 7.92 (d,  $J = 7.2$  Hz, 0.5H), 7.45 (t,  $J = 8.4$  Hz, 0.5H), 7.39 (t,  $J =$

7.2 Hz, 0.5H), 7.24 – 7.17 (m, 1H), 7.11 – 7.04 (m, 1H), 6.98 (d,  $J = 8.0$  Hz, 0.5H), 6.85 (ddd,  $J = 15.6, 8.8, 2.0$  Hz, 1H), 6.49 (d,  $J = 2.4$  Hz, 0.5H), 6.44 (d,  $J = 2.0$  Hz, 0.5H), 5.41 (s, 0.5H), 4.36 (q,  $J = 7.2$  Hz, 2H), 3.77 (s, 3H), 3.37 (d,  $J = 8.0$  Hz, 3H), 3.25 (d,  $J = 14.0$  Hz, 0.5H), 3.04 (d,  $J = 14.8$  Hz, 0.5H), 2.67 (d,  $J = 14.8$  Hz, 0.5H), 2.34 (d,  $J = 14.0$  Hz, 0.5H), 1.37 (dt,  $J = 16.9, 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.74, 175.61, 171.50, 171.27, 168.44, 167.36, 164.14, 164.03, , 156.86, 156.77, 147.09, 144.90, 143.83, 143.73, 137.00, 136.50, 130.16, 129.94, 129.44, 128.86, 127.77, 127.58, 127.27, 124.75, 123.76, 123.40, 117.60, 117.49, 114.60, 114.49, 109.65, 108.65, 99.92, 94.86, 93.72, 63.52, 62.76, 55.89, 55.85, 50.07, 49.53, 37.76, 37.60, 27.40, 27.24, 14.12, 14.05; IR: 3287.6, 2962.2, 1733.3, 1609.8, 1446.5, 1422.9, 1368.4, 1265.9, 1167.8, 1153.7, 1100.4, 1028.0, 973.5, 833.4, 748.5, 694.1, 635.9  $\text{cm}^{-1}$ ; HRMS-ESI calcd. for  $\text{C}_{24}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  452.1340, found:452.1343.

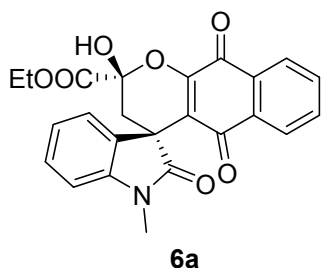
### 3.2 Synthesis of compounds 6a–6t

**General procedure:** In an ordinary tube equipped with a magnetic stirring bar, the solution of **5** (0.12 mmol, 1.2 equiv), catalyst **1h** (2.5 mg, 5 mol %, 0.05 equiv) in DCM (0.5 mL) was stirred at rt. for 30 min, and then **3** (0.1 mmol, 1 equiv) was added. The reaction was stirred under rt. for 12 h, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/DCM = 1:1 – 0:1) to give desired products **6a–6t**.

**A specific procedure for synthesis of compound 6a:** In an ordinary tube equipped with a magnetic stirring bar, the solution of **5a** (20.9 mg, 0.15 mmol, 1.5 equiv), catalyst **1h** (2.5 mg, 5 mol %, 0.05 equiv) in DCM (0.5 mL) was stirred at rt. for 30 min, and then **3a** (25.9 mg, 0.1 mmol, 1 equiv) was added. The reaction was stirred under rt. for 40 h, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 1.5:1) to give desired products **6a**.

#### Ethyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-

#### tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate **6a**

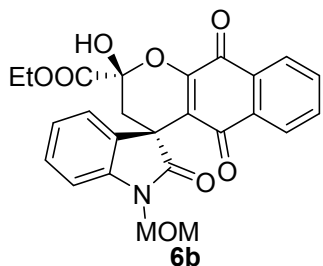


**6a**

foamy solid, 35.1 mg, 81% yield; 98% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26}$  = – 36.01 (*c* = 1.43, CH<sub>2</sub>Cl<sub>2</sub>); [Daicel Chiralpak IA, hexane/*i*-PrOH (75:25), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda$  = 254 nm, *t* (major) = 17.981, *t* (minor) = 22.054]; <sup>1</sup>H (400 Hz, CDCl<sub>3</sub>):  $\delta$  9.17 (s, 0.6H), 8.13 – 8.07 (m, 1H), 7.87 – 7.81 (m, 1H), 7.70 – 7.59 (m, 3H), 7.38 – 7.29 (m, 1H), 7.10 – 7.05 (m, 1H), 7.01 – 6.94 (m, 1H), 5.29 (s, 0.4H), 4.37 (q, *J* = 8.0 Hz, 2H), 3.39 (s, 1.85H), 3.38 (s, 1.15H), 3.03 (dd, *J* = 8.0, 4.0 Hz, 0.35H), 2.80 (d, *J* = 16.0 Hz, 0.65H), 2.56 (d, *J* = 16.0 Hz, 0.65H), 2.17 (d, *J* = 16.0 Hz, 0.35H), 1.38 (t, *J* = 8.0 Hz, 1.8H), 1.35 (t, *J* = 8.0 Hz, 1.2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  182.36, 179.70, 178.88, 178.66, 178.53, 168.29, 166.81, 155.24, 154.13, 143.94, 143.83, 134.47, 134.40, 133.78, 133.61, 132.08, 131.55, 131.50, 130.93, 130.87, 129.62, 128.85, 126.82, 126.69, 126.62, 126.53, 124.22, 122.36, 122.26, 121.75, 120.83, 109.42, 108.50, 97.10, 95.12, 64.15, 63.00, 46.82, 45.59, 37.46, 36.72, 27.24, 27.17, 14.16, 14.07; IR: 3431.3, 1751.2,

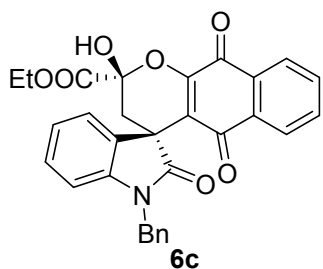
1714.3, 1682.4, 1611.4, 1384.3, 1273.2, 1140.0, 1047.0, 974.3, 755.5, 723.2, 684.6, 543.0, 416.1  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{20}\text{NO}_7$   $[\text{M}+\text{H}]^+$  434.1234, found: 434.1241.

**Ethyl-2-hydroxy-1'-(methoxymethyl)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6b**



foamy solid, 31.0 mg, 67% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -15.84$  ( $c = 1.19$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak OD-H, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 16.117,  $t$  (minor) = 7.124];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.83 (s, 0.6H), 8.14 – 8.07 (m, 1H), 7.88 – 7.83 (m, 1H), 7.71 – 7.69 (m, 0.5H), 7.68 – 7.62 (m, 2H), 7.38 – 7.28 (m, 1H), 7.22 – 7.15 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.98 (m, 0.5H), 5.32 (s, 0.4H), 5.30 – 5.22 (m, 2H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.52 (s, 1.4H), 3.49 (s, 1.6H), 3.02 (d,  $J = 16.0$  Hz, 0.5H), 2.82 (d,  $J = 16.0$  Hz, 0.5H), 2.58 (d,  $J = 16.0$  Hz, 0.55H), 2.22 (d,  $J = 16.0$  Hz, 0.45H), 1.39 (t,  $J = 8.0$  Hz, 1.55H), 1.35 (t,  $J = 8.0$  Hz, 1.45H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.34, 182.25, 180.72, 179.18, 178.86, 178.58, 168.17, 166.69, 155.19, 154.16, 142.19, 142.13, 134.51, 134.44, 133.84, 133.65, 131.60, 131.53, 131.52, 131.05, 130.94, 130.87, 129.49, 128.93, 126.91, 126.86, 126.75, 126.65, 126.63, 124.61, 122.82, 122.33, 121.64, 120.76, 110.86, 109.94, 96.95, 95.16, 72.41, 72.30, 64.18, 63.09, 57.05, 56.78, 47.11, 45.99, 37.93, 37.08, 14.15, 14.08; IR: 3411.4, 2935.3, 1750.6, 1722.1, 1684.0, 1655.7, 1594.9, 1467.8, 1300.9, 1202.5, 1133.1, 1044.3, 975.6, 952.3, 756.3, 724.5, 684.1  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NNaO}_8$   $[\text{M}+\text{H}]^+$  486.1159, found: 464.1148.

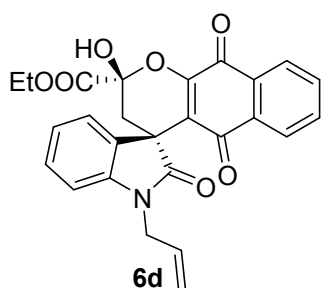
**Ethyl-1'-benzyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6c**



foamy solid, 26.5 mg, 52% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -27.12$  ( $c = 2.05$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 26.256,  $t$  (minor) = 24.481];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.14 (s, 0.6H), 8.16 – 8.08 (m, 1H), 7.94 – 7.85

(m, 1H), 7.72 – 7.69 (m, 0.4H), 7.68 – 7.64 (m, 2H), 7.49 – 7.46 (m, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.15 (m, 1H), 7.08 – 7.06 (m, 0.6H), 7.05 – 6.92 (m, 1H), 6.87 – 6.77 (m, 1H), 5.29 (s, 0.4H), 5.18 – 5.00 (m, 2H), 4.39 (q,  $J = 8.0$  Hz, 2H), 3.12 – 3.08 (m, 0.4H), 2.85 (d,  $J = 16.0$  Hz, 0.6H), 2.59 (d,  $J = 16.0$  Hz, 0.6H), 2.24 (d,  $J = 16.0$  Hz, 0.4H), 1.40 (t,  $J = 8.0$  Hz, 1.8H), 1.37 (t,  $J = 8.0$  Hz, 1.2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 182.26, 180.01, 178.89, 178.65, 178.63, 168.26, 166.80, 155.29, 154.24, 143.01, 142.92, 135.87, 134.86, 134.48, 134.41, 133.78, 133.62, 132.18, 131.57, 131.48, 130.94, 130.89, 129.22, 129.11, 128.93, 128.68, 128.10, 127.70, 127.49, 127.36, 126.84, 126.81, 126.78, 126.66, 126.62, 124.24, 122.34, 122.26, 121.67, 120.71, 110.51, 109.65, 97.08, 95.18, 64.21, 63.06, 46.85, 45.71, 44.90, 44.67, 37.79, 37.06, 14.17, 14.09; IR: 3415.8, 2983.5, 1750.6, 1712.6, 1682.6, 1655.3, 1357.6, 1333.3, 1221.7, 1155.1, 1027.7, 949.1, 855.9, 830.0, 793.1, 754.0, 723.3, 697.2, 476.4  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{30}\text{H}_{24}\text{NO}_7$   $[\text{M}+\text{H}]^+$  510.1547, found: 510.1562.

**Ethyl-1'-allyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6d**

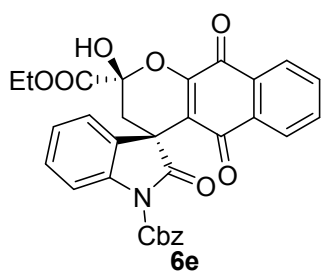


foamy solid, 32.1 mg, 70% yield; 96% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -40.95$  ( $c = 1.36$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 16.315,  $t$  (minor) = 14.892];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.10 (s, 0.6H), 8.13 – 8.07 (m, 1H), 7.89 – 7.83 (m, 1H), 7.70 – 7.68 (m, 0.4H), 7.67 – 7.62 (m, 2H), 7.35 – 7.24 (m, 1H), 7.07 – 6.98 (m, 2H), 6.96 – 6.93 (m, 0.6H), 6.04 – 5.91 (m, 1H), 5.53 – 5.45 (m, 1H), 5.36 – 5.29 (m, 1H), 5.17 (s, 0.4H), 4.59 – 4.41 (m, 2H), 4.40 – 4.35 (m, 2H), 3.06 – 3.02 (m, 0.4H), 2.81 (d,  $J = 16.0$  Hz, 0.6H), 2.56 (d,  $J = 16.0$  Hz, 0.6H), 2.18 (d,  $J = 16.0$  Hz, 0.4H), 1.39 (t,  $J = 8.0$  Hz, 1.8H), 1.35 (t,  $J = 8.0$  Hz, 1.2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.24, 179.61, 178.90, 178.66, 178.27, 168.28, 166.81, 155.24, 154.16, 143.05, 142.97, 134.46, 134.38, 133.76, 133.59, 132.15, 131.56, 131.52, 130.93, 130.88, 130.46, 129.22, 128.67, 126.85, 126.80, 126.77, 126.63, 126.60, 124.18,



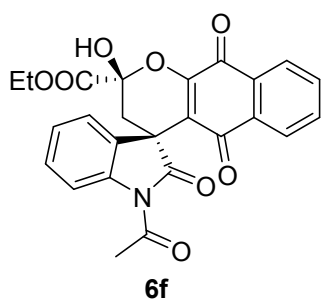
122.29, 121.72, 120.76, 118.62, 117.90, 110.33, 109.49, 97.06, 95.13, 64.18, 63.03, 46.81, 45.62, 43.32, 43.20, 37.68, 36.95, 14.16, 14.08; IR: 3412.3, 2984.3, 2925.6, 1750.3, 1655.8, 1435.0, 1333.2, 1271.9, 1201.5, 1046.3, 969.1, 948.1, 793.0, 755.3, 724.0, 683.9  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{26}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  460.1391, found: 460.1404.

**1'-benzyl-2-ethyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-1',2-dicarboxylate 6e**



foamy solid, 32.7 mg, 59% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -29.64$  ( $c = 1.28$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 26.872,  $t$  (minor) = 24.448];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.14 (s, 0.6H), 8.14 – 8.08 (m, 1H), 7.91 – 7.86 (m, 1H), 7.71 – 7.64 (m, 2.45H), 7.48 – 7.45 (m, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.15 (m, 1H), 7.08 – 7.06 (m, 0.55H), 7.05 – 6.91 (m, 1H), 6.87 – 6.77 (m, 1H), 5.19 (s, 0.4H), 5.16 – 5.00 (m, 2H), 4.38 (q,  $J = 8.0$  Hz, 2H), 3.09 (d,  $J = 16.0$  Hz, 0.4H), 2.84 (d,  $J = 16.0$  Hz, 0.6H), 2.59 (d,  $J = 16.0$  Hz, 0.6H), 2.24 (d,  $J = 16.0$  Hz, 0.4H), 1.42 – 1.35 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.26, 180.01, 178.90, 178.66, 178.63, 168.27, 166.80, 155.29, 154.25, 143.01, 142.92, 135.88, 134.87, 134.48, 134.41, 133.79, 133.62, 132.18, 131.57, 131.49, 130.95, 130.89, 129.22, 129.11, 128.93, 128.69, 128.10, 127.71, 127.49, 127.36, 126.84, 126.82, 126.79, 126.66, 126.62, 124.24, 122.35, 122.26, 121.67, 120.71, 110.51, 109.66, 97.08, 95.19, 64.21, 63.07, 46.85, 45.72, 44.91, 44.67, 37.80, 37.07, 14.17, 14.09; IR: 3415.8, 2925.4, 2853.2, 1750.3, 1712.9, 1682.3, 1271.1, 1155.0, 1046.5, 1027.7, 1011.3, 948.2, 830.1, 753.8, 723.2, 697.4, 553.1, 455.2  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{31}\text{H}_{24}\text{NO}_9$   $[\text{M}+\text{H}]^+$  554.1446, found: 554.1426.

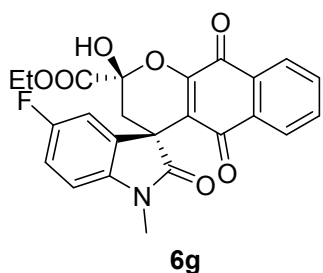
**Ethyl-1'-acetyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6f**



foamy solid, 25.8 mg, 56% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -3.82$  ( $c = 1.02$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$

nm, t (major) = 14.311, t (minor) = 12.719];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.34 – 8.29 (m, 1H), 8.15 – 8.10 (m, 1H), 7.89 – 7.84 (m, 1.2H), 7.73 – 7.65 (m, 2.8H), 7.40 – 7.32 (m, 1H), 7.18 – 7.08 (m, 1.3H), 5.25 (s, 0.7H), 4.42 – 4.36 (m, 2H), 3.00 (d,  $J = 16.0$  Hz, 0.7H), 2.83 (d,  $J = 16.0$  Hz, 0.3H), 2.74 (s, 2.2H), 2.73 (s, 1H), 2.32 (d,  $J = 16.0$  Hz, 0.8H), 1.41 – 1.36 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.37, 179.55, 178.69, 171.05, 167.93, 154.14, 140.11, 134.69, 134.64, 134.12, 133.92, 131.32, 131.28, 130.84, 130.28, 129.76, 129.19, 127.02, 126.84, 126.72, 126.49, 126.29, 124.87, 122.04, 121.70, 117.25, 116.59, 96.54, 95.11, 64.38, 63.34, 46.34, 38.73, 37.45, 26.98, 14.16, 14.11; IR: 3416.5, 2985.1, 1753.6, 1713.9, 1654.5, 1594.9, 1580.1, 1336.1, 1272.4, 1227.5, 1040.9, 956.1, 917.2, 830.1, 794.2, 721.1, 684.6,  $530.5\text{ cm}^{-1}$ ; HRMS-ESI:  $^+$  calcd. for  $\text{C}_{25}\text{H}_{20}\text{NO}_8$   $[\text{M}+\text{H}]$  462.1183, found: 462.1196.

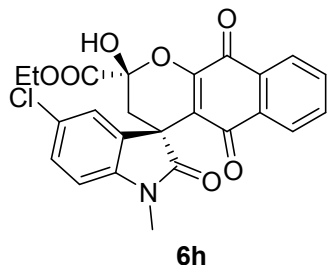
**Ethyl-5'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6g**



foamy solid, 31.5 mg, 70% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -14.28$  ( $c = 1.08$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0\text{ mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254\text{ nm}$ , t (major) = 13.975, t (minor) = 10.650];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.12 (s, 0.55H), 8.17 – 8.10 (m, 1H), 7.91 – 7.85 (m, 1H), 7.74 – 7.65 (m, 2H), 7.48 – 7.45 (m, 0.55H), 7.11 – 7.01 (m, 1H), 6.97 – 6.94 (m, 0.45H), 6.90 – 6.84 (m, 1H), 5.24 (s, 0.45H), 4.40 (q,  $J = 8.0$  Hz, 2H), 3.40 (s, 1.4H), 3.38 (s, 1.6H), 3.05 (d,  $J = 16.0$  Hz, 0.5H), 2.78 (d,  $J = 16.0$  Hz, 0.5H), 2.59 (d,  $J = 16.0$  Hz, 0.5H), 2.19 (d,  $J = 16.0$  Hz, 0.5H), 1.42 (t,  $J = 8.0$  Hz, 1.3H), 1.38 (t,  $J = 8.0$  Hz, 1.7H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.41, 182.36, 179.43, 178.75, 178.50, 178.21, 168.08, 166.67, 160.03 ( $J = 242$  Hz), 158.89 ( $J = 267$  Hz), 155.40, 154.20, 140.01, 140.00, 139.77, 139.75, 134.55 ( $J = 8$  Hz), 133.94, 133.76, 131.48, 130.90 ( $J = 6$  Hz), 126.94, 126.72 ( $J = 1$  Hz), 126.56, 121.38, 121.31, 120.23, 115.61 ( $J = 24$  Hz), 115.23 ( $J = 25$  Hz), 115.06 ( $J = 24$  Hz), 110.84, 110.59, 110.08, 110.00, 108.81, 108.72, 97.03, 95.03, 64.25, 63.11, 47.08, 45.90, 37.29, 36.55, 27.41, 27.34, 14.17, 14.08; IR: 3424.4, 2926.6, 1750.7, 1714.4, 1683.0, 1656.5, 1620.2, 1594.0, 1333.5, 1269.3, 1119.0, 959.6, 920.2, 876.6, 817.2, 720.7, 622.7,  $502.3\text{ cm}^{-1}$ ; HRMS-

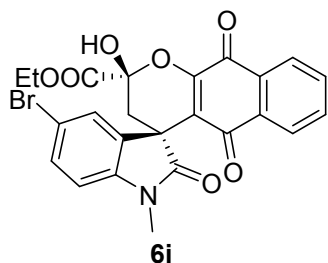
ESI: calcd. for C<sub>24</sub>H<sub>19</sub>FNO<sub>7</sub> [M+H]<sup>+</sup> 452.1140, found: 452.1136.

**Ethyl-5'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6h**



foamy solid, 41.1 mg, 88% yield; 97% *ee*, > 20/1 *dr*, [α]<sub>D</sub><sup>26</sup> = -22.49 (c = 1.44, CH<sub>2</sub>Cl<sub>2</sub>); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0 mL·min<sup>-1</sup>, λ = 254 nm, t (major) = 14.660, t (minor) = 8.947]; <sup>1</sup>H (400 Hz, CDCl<sub>3</sub>): δ 8.99 (s, 0.4H), 8.15 – 8.08 (m, 1H), 7.88 – 7.83 (m, 1H), 7.73 – 7.70 (m, 0.5H), 7.69 – 7.64 (m, 2H), 7.35 – 7.27 (m, 1.2H), 7.06 – 7.05 (m, 0.5H), 6.95 – 6.87 (m, 1H), 5.32 (s, 0.4H), 4.38 (q, *J* = 8.0 Hz, 2H), 3.38 (s, 1.4H), 3.36 (s, 1.6H), 3.01 (d, *J* = 16.0 Hz, 0.55H), 2.77 (d, *J* = 16.0 Hz, 0.45H), 2.57 (d, *J* = 16.0 Hz, 0.45H), 2.18 (d, *J* = 16.0 Hz, 0.55H), 1.40 (t, *J* = 8.0 Hz, 1.4H), 1.35 (t, *J* = 8.0 Hz, 1.6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 182.35, 179.56, 178.93, 178.69, 178.44, 168.31, 166.85, 155.18, 154.06, 141.52, 141.37, 134.43, 134.36, 133.95, 133.73, 133.55, 132.04, 131.77, 131.55, 130.92, 130.85, 129.58, 129.09, 127.61, 126.77, 126.71, 126.56, 123.09, 121.88, 120.94, 109.13, 108.18, 97.10, 95.16, 64.06, 62.96, 46.83, 45.67, 37.56, 36.77, 27.24, 27.17, 21.31, 21.23, 14.14, 14.05; IR: 3431.7, 2926.0, 1751.0, 1718.9, 1683.4, 1654.9, 1384.3, 1106.2, 989.3, 976.4, 728.9, 630.6, 518.5, 475.2, 416.8 cm<sup>-1</sup>; HRMS-ESI: calcd. for C<sub>24</sub>H<sub>19</sub>ClNO<sub>7</sub> [M+H]<sup>+</sup> 468.0845, found: 468.0842.

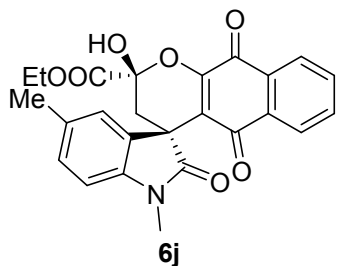
**Ethyl-5'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6i**



foamy solid, 47.1 mg, 92% yield; 97% *ee*, > 20/1 *dr*, [α]<sub>D</sub><sup>26</sup> = -27.45 (c = 1.51, CH<sub>2</sub>Cl<sub>2</sub>); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0 mL·min<sup>-1</sup>, λ = 254 nm, t (major) = 15.113, t (minor) = 9.027]; <sup>1</sup>H (400 Hz, CDCl<sub>3</sub>): δ 8.95 (s, 0.5H), 8.12 – 8.05 (m, 1H), 7.86 – 7.81 (m, 1H), 7.78 – 7.77 (m, 0.55H), 7.69 – 7.64 (m, 2H), 7.48 – 7.40 (m, 1H), 7.18 – 7.17 (m, 0.45H), 6.89 – 6.81 (m, 1H), 5.40 (s, 0.5H), 4.39 – 4.33 (m, 2H), 3.36 (s, 1.3H), 3.34 (s, 1.7H), 2.98 (d, *J* = 16.0 Hz, 0.6H), 2.76 (d, *J* = 16.0 Hz, 0.4H), 2.56 (d,

$J = 16.0$  Hz, 0.4H), 2.17 (d,  $J = 16.0$  Hz, 0.6H), 1.38 (t,  $J = 8.0$  Hz, 1.3H), 1.33 (t,  $J = 8.0$  Hz, 1.7H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.36, 182.32, 179.18, 178.69, 178.41, 177.97, 167.94, 166.60, 155.32, 154.19, 143.05, 142.87, 134.56, 134.47, 133.99, 133.91, 133.72, 133.33, 132.17, 131.59, 131.40, 131.38, 130.87, 130.79, 130.05, 126.88, 126.67, 126.66, 126.57, 125.58, 121.16, 120.13, 116.73, 115.10, 110.80, 109.86, 96.93, 95.06, 64.12, 63.10, 46.73, 45.61, 37.24, 36.56, 27.32, 27.24, 14.12, 14.04.; IR: 3440.0, 2924.8, 1718.1, 1682.4, 1654.7, 1621.9, 1465.7, 1332.3, 1202.3, 1105.0, 975.7, 953.8, 797.1, 724.8, 689.4, 614.8, 538.8, 418.6  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{19}\text{BrNO}_7$   $[\text{M}+\text{H}]^+$  512.0339, found: 512.0328.

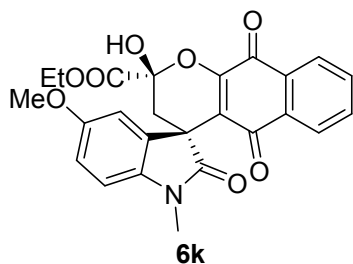
**Ethyl-2-hydroxy-1',5'-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6j**



foamy solid, 38.9 mg, 87% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -50.50$  ( $c = 1.67$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 11.020,  $t$  (minor) = 7.396];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.23 (s, 0.7H), 8.12 – 8.06 (m, 1H), 7.86 – 7.82

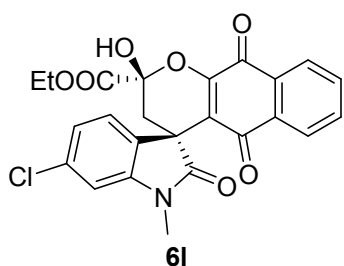
(m, 1H), 7.69 – 7.62 (m, 2H), 7.15 – 7.09 (m, 1H), 6.90 – 6.83 (m, 2H), 5.29 (s, 0.3H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.36 (s, 2H), 3.35 (s, 1H), 3.01 (d,  $J = 16.0$  Hz, 0.3H), 2.78 (d,  $J = 16.0$  Hz, 0.7H), 2.54 (d,  $J = 16.0$  Hz, 0.7H), 2.26 (s, 2H), 2.25 (s, 1H), 2.16 (d,  $J = 16.0$  Hz, 0.3H), 1.38 (t,  $J = 8.0$  Hz, 2H), 1.34 (t,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.40, 182.36, 179.32, 178.75, 178.46, 178.10, 168.01, 166.63, 155.37, 154.22, 142.60, 142.40, 134.59, 134.51, 133.95, 133.77, 133.72, 132.98, 131.45, 131.43, 130.92, 130.85, 129.56, 129.31, 128.74, 127.77, 127.40, 126.94, 126.73, 126.70, 126.60, 122.90, 121.23, 120.18, 110.34, 109.35, 96.97, 95.05, 64.21, 63.13, 46.84, 45.69, 37.27, 36.56, 27.38, 27.30, 14.16, 14.07; IR: 3410.4, 2925.3, 1749.9, 1721.9, 1682.4, 1618.5, 1333.2, 1271.5, 1104.2, 976.8, 913.2, 871.4, 721.3, 628.8, 530.1, 470.1  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  448.1391, found: 448.1382.

**Ethyl-2-hydroxy-5'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6k**



foamy solid, 33.3 mg, 72% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_D^{26} = -37.09$  ( $c = 1.41$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 13.584,  $t$  (minor) = 11.840];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.29 (s, 0.6H), 8.13 – 8.06 (m, 1H), 7.88 – 7.82 (m, 1H), 7.70 – 7.61 (m, 2H), 7.32 – 7.31 (m, 0.3H), 6.92 – 6.83 (m, 2H), 6.67 – 6.66 (m, 0.7H), 5.21 (s, 0.4H), 4.37 (q,  $J = 8.0 \text{ Hz}$ , 2H), 3.72 (s, 2H), 3.71 (s, 1H), 3.36 (s, 2H), 3.35 (s, 1H), 3.03 (d,  $J = 16.0 \text{ Hz}$ , 0.3H), 2.77 (d,  $J = 16.0 \text{ Hz}$ , 0.7H), 2.56 (d,  $J = 16.0 \text{ Hz}$ , 0.65H), 2.17 (d,  $J = 16.0 \text{ Hz}$ , 0.35H), 1.38 (t,  $J = 8.0 \text{ Hz}$ , 2H), 1.34 (t,  $J = 8.0 \text{ Hz}$ , 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.40, 182.34, 179.26, 178.90, 178.70, 178.13, 168.29, 166.86, 157.12, 155.65, 155.26, 154.10, 137.48, 137.08, 134.48, 134.41, 133.78, 133.62, 133.41, 132.82, 131.56, 130.94, 130.87, 126.82, 126.71, 126.62, 126.57, 120.80, 114.43, 113.32, 113.09, 109.84, 109.73, 108.65, 97.14, 95.12, 64.17, 63.01, 55.86, 55.80, 47.15, 45.95, 37.60, 36.63, 27.32, 27.26, 14.16, 14.07; IR: 3427.6, 2937.4, 1751.1, 1710.3, 1682.1, 1656.3, 1618.4, 1579.5, 1273.2, 1156.4, 976.7, 956.2, 872.1, 800.3, 760.2, 721.0, 693.9, 529.9  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  464.1340, found: 464.1326.

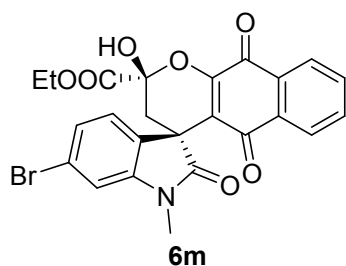
**Ethyl-6'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6l**



foamy solid, 32.3 mg, 69% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_D^{26} = -6.56$  ( $c = 1.70$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (80:20), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 210 \text{ nm}$ ,  $t$  (major) = 34.813,  $t$  (minor) = 32.136];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (s, 0.4H), 8.12 – 8.05 (m, 1H), 7.87 – 7.81 (m, 1H), 7.71 – 7.62 (m, 2H), 7.58 – 7.54 (m, 0.6H), 7.06 – 7.03 (m, 0.4H), 7.00 – 6.92 (m, 2H), 5.28 (s, 0.6H), 4.37 (q,  $J = 8.0 \text{ Hz}$ , 2H), 3.37 (s, 1H), 3.35 (s, 2H), 2.99 (d,  $J = 16.0 \text{ Hz}$ , 0.6H), 2.76 (d,  $J = 16.0 \text{ Hz}$ , 0.4H), 2.55 (d,  $J = 16.0 \text{ Hz}$ , 0.4H), 2.14 (d,  $J = 16.0 \text{ Hz}$ , 0.6H), 1.38 (t,  $J = 8.0 \text{ Hz}$ , 1.2H), 1.34 (t,  $J = 8.0 \text{ Hz}$ , 1.8H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.39, 182.37, 179.76, 178.74, 178.51, 178.50, 168.10, 166.66, 155.31, 154.17, 145.19, 145.00, 135.17, 134.63, 134.58, 134.50, 133.92,

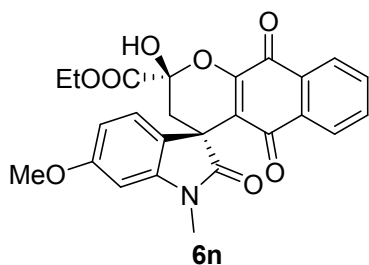
133.74, 131.43, 130.89, 130.82, 130.38, 129.79, 127.88, 126.90, 126.87, 126.68, 126.52, 124.04, 123.20, 122.23, 121.30, 120.86, 120.35, 110.29, 109.23, 96.99, 95.07, 64.20, 63.10, 46.47, 45.25, 37.26, 36.66, 27.36, 27.28, 14.14, 14.06; IR: 3423.7, 2926.4, 1750.8, 1720.8, 1656.3, 1620.8, 1607.3, 1333.3, 1302.7, 1161.4, 977.8, 717.9, 688.9, 590.1, 481.4  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{19}\text{ClNO}_7$   $[\text{M}+\text{H}]^+$  468.0845, found: 468.0844.

**Ethyl-6'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6m**



foamy solid, 28.2 mg, 55% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -4.69$  ( $c = 0.91$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 14.557,  $t$  (minor) = 13.511];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.92 (s, 0.4H), 8.13 – 8.07 (m, 1H), 7.88 – 7.81 (m, 1H), 7.71 – 7.63 (m, 2H), 7.52 – 7.50 (m, 0.6H), 7.22 – 7.08 (m, 2H), 6.94 – 6.92 (m, 0.4H), 5.21 (s, 0.6H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.37 (s, 1.3H), 3.35 (s, 1.7H), 3.00 (d,  $J = 16.0$  Hz, 0.6H), 2.76 (d,  $J = 16.0$  Hz, 0.4H), 2.55 (d,  $J = 16.0$  Hz, 0.4H), 2.14 (d,  $J = 16.0$  Hz, 0.6H), 1.39 (t,  $J = 8.0$  Hz, 1.35H), 1.35 (t,  $J = 8.0$  Hz, 1.65H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.40, 182.38, 179.65, 178.73, 178.50, 178.39, 168.11, 166.65, 155.34, 154.20, 145.32, 145.12, 134.59, 134.52, 133.94, 133.76, 131.44, 130.99, 130.91, 130.85, 130.34, 128.23, 127.02, 126.92, 126.71, 126.70, 126.54, 125.21, 123.55, 122.89, 122.55, 122.29, 121.25, 120.29, 113.05, 112.03, 96.99, 95.03, 64.26, 63.12, 46.54, 45.30, 37.21, 36.58, 27.37, 27.29, 14.16, 14.08; IR: 3427.4, 2926.5, 1750.7, 1717.0, 1655.8, 1603.2, 1466.5, 1432.5, 1302.1, 1272.6, 1126.7, 1101.6, 1066.6, 976.1, 953.2, 905.4, 791.9, 744.4, 674.2, 586.9, 509.3  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{19}\text{BrNO}_7$   $[\text{M}+\text{H}]^+$  512.0339, found: 512.0347.

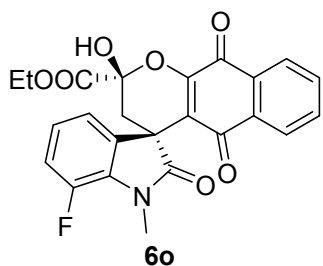
**Ethyl-2-hydroxy-6'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6n**



foamy solid, 29.2 mg, 63% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -86.40$  ( $c = 1.01$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak OD-H, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$

$^1$ ,  $\lambda = 254$  nm,  $t$  (major) = 12.908,  $t$  (minor) = 11.065];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.11 (s, 0.4H), 8.13 – 8.07 (m, 1H), 7.88 – 7.82 (m, 1H), 7.68 – 7.63 (m, 2H), 7.54 – 7.51 (m, 0.4H), 6.95 – 6.93 (m, 0.6H), 6.58 – 6.45 (m, 2H), 5.15 (s, 0.4H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.82 (s, 1.70H), 3.81 (s, 1.3H), 3.36 (s, 1.7H), 3.35 (s, 1.3H), 3.00 (d,  $J = 16.0$  Hz, 0.4H), 2.77 (d,  $J = 16.0$  Hz, 0.6H), 2.53 (d,  $J = 16.0$  Hz, 0.6H), 2.13 (d,  $J = 16.0$  Hz, 0.4H), 1.38 (t,  $J = 8.0$  Hz, 1.7H), 1.35 (t,  $J = 8.0$  Hz, 1.3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.48, 182.47, 180.33, 179.08, 178.73, 168.34, 166.87, 161.01, 160.59, 155.10, 153.98, 145.28, 145.08, 134.45, 134.39, 133.75, 133.60, 131.60, 131.58, 130.94, 130.88, 127.56, 126.80, 126.71, 126.61, 126.52, 123.62, 123.52, 122.93, 121.93, 121.06, 107.81, 106.07, 100.11, 97.65, 97.15, 96.46, 95.17, 64.15, 62.99, 55.72, 55.57, 46.35, 45.11, 37.66, 36.93, 27.25, 27.19, 14.17, 14.08.; IR: 3431.8, 2926.2, 1749.7, 1714.8, 1682.2, 1656.0, 1619.9, 1332.0, 1269.1, 1221.4, 1201.7, 980.4, 832.2, 796.7, 721.2, 687.2, 424.1  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_8$   $[\text{M}+\text{H}]^+$  464.1340, found: 464.1344.

**Ethyl-7'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6o**

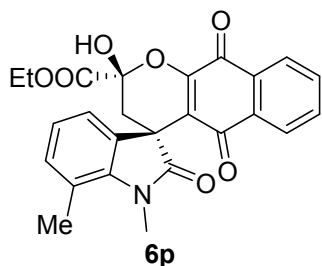


foamy solid, 27.5 mg, 61% yield; 93% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -23.30$  ( $c = 0.78$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 13.161,  $t$  (minor) = 15.137];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.00 (s, 0.55H), 8.14 – 8.08 (m, 1H), 7.89 – 7.83 (m, 1H), 7.70 – 7.65 (m, 2H), 7.45 – 7.43 (m, 0.4H), 7.11 – 7.05 (m, 0.6H), 7.03 – 6.98 (m, 1H), 6.91 – 6.83 (m, 1H), 5.15 (s, 0.45H), 4.38 (q,  $J = 8.0$  Hz, 2H), 3.59 – 3.58 (m, 3H), 3.02 (d,  $J = 16.0$  Hz, 0.4H), 2.76 (d,  $J = 16.0$  Hz, 0.6H), 2.58 (d,  $J = 16.0$  Hz, 0.6H), 2.18 (d,  $J = 16.0$  Hz, 0.4H), 1.39 (t,  $J = 8.0$  Hz, 1.7H), 1.35 (t,  $J = 8.0$  Hz, 1.3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 182.39, 182.36, 179.42, 178.79, 178.56, 178.34, 178.22, 168.18, 166.68, 155.21, 154.11, 148.11 ( $J = 244$  Hz), 145.57 ( $J = 248$  Hz), 144.31, 134.55 ( $J = 7$  Hz), 133.92, 133.75, 131.49, 131.47, 130.91 ( $J = 6$  Hz), 126.92, 126.72, 126.55, 124.91, 124.89, 124.84, 122.73, 122.70, 122.67, 121.43, 120.53, 118.13, 118.10, 117.61, 117.33 ( $J = 19$  Hz), 116.79 ( $J = 19$  Hz), 97.07, 95.02,

64.29, 63.10, 47.04, 47.02, 37.48, 36.80, 29.90, 29.85, 14.17, 14.09; IR: 3419.4, 2984.2, 1751.4, 1720.0, 1683.7, 1656.0, 1621.7, 1594.4, 1270.8, 1203.1, 1160.4, 1059.4, 1017.6, 924.4, 790.3, 735.4, 723.6, 565.2, 456.3  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{19}\text{FNO}_7$   $[\text{M}+\text{H}]^+$  452.1140, found: 452.1119.

**Ethyl-2-hydroxy-1',7'-dimethyl-2',5,10-trioxo-2,3,5,10-**

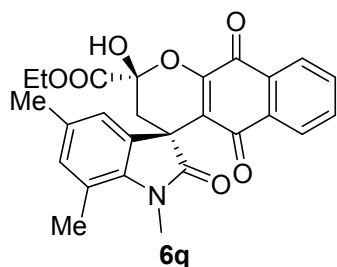
**tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6p**



foamy solid, 35.8 mg, 70% yield; 98% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -40.00$  ( $c = 1.33$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak OD-H, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 12.474,  $t$  (minor) = 8.329];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.26 (s, 0.7H), 8.13–8.07 (m, 1H), 7.88 – 7.82 (m, 1H), 7.70 – 7.62 (m, 2H), 7.08 – 7.01 (m, 1H), 6.96 – 6.82 (m, 2H), 5.15 (s, 0.3H), 4.36 (q,  $J = 8.0$  Hz, 2H), 3.64 (s, 3H), 3.01 (d,  $J = 16.0$  Hz, 0.2H), 2.73 (d,  $J = 16.0$  Hz, 0.8H), 2.66 (s, 2.2H), 2.65 (s, 0.8H), 2.53 (d,  $J = 16.0$  Hz, 0.8H), 2.14 (d,  $J = 16.0$  Hz, 0.2H), 1.38 (t,  $J = 8.0$  Hz, 2.2H), 1.34 (t,  $J = 8.0$  Hz, 0.8H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.54, 182.37, 180.36, 179.38, 178.69, 168.31, 166.82, 155.12, 154.07, 141.63, 141.46, 134.43, 134.36, 133.74, 133.59, 133.12, 132.69, 132.64, 132.15, 131.55, 130.93, 130.88, 126.80, 126.67, 126.60, 126.50, 124.68, 124.06, 122.13, 121.97, 121.19, 121.07, 120.19, 119.87, 97.14, 95.15, 64.11, 62.95, 46.30, 45.08, 37.88, 37.07, 30.66, 19.46, 19.06, 14.15, 14.06; IR: 3438.6, 2925.8, 1751.4, 1709.4, 1657.6, 1618.2, 1596.4, 1458.8, 1356.1, 1333.2, 1202.7, 1171.8, 977.9, 956.9, 787.7, 747.2, 598.8, 542.5  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  448.1391, found: 448.1402.

**Ethyl-2-hydroxy-1',5',7'-trimethyl-2',5,10-trioxo-2,3,5,10-**

**tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6q**

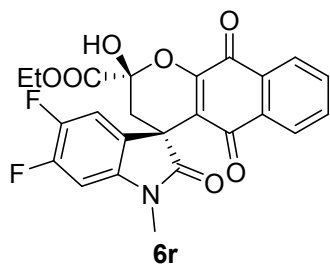


foamy solid, 32.3 mg, 70% yield; 94% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -44.40$  ( $c = 1.27$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 11.668,  $t$  (minor) = 7.381];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.32 (s, 0.8H), 8.13 – 8.10 (m, 1H), 7.86 – 7.84



(m, 1H), 7.70 – 7.63 (m, 2H), 6.87 – 6.83 (m, 1H), 6.69 (s, 1H), 5.10 (s, 0.2H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.61 (s, 3H), 2.72 (d,  $J = 16.0$  Hz, 1H), 2.61 (s, 3H), 2.51 (d,  $J = 16.0$  Hz, 1H), 2.20 (s, 2.4H), 2.19 (s, 0.6H), 1.38 (t,  $J = 8.0$  Hz, 2.4H), 1.34 (t,  $J = 8.0$  Hz, 0.6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.41, 180.24, 178.73, 166.89, 155.12, 138.98, 134.41, 133.72, 133.58, 132.77, 131.61, 130.97, 126.79, 126.56, 121.31, 120.94, 120.72, 97.18, 62.94, 46.36, 38.02, 30.61, 20.91, 18.89, 14.16; IR: 3425.9, 2923.9, 1750.3, 1709.5, 1682.6, 1658.8, 1579.1, 1477.9, 1332.4, 1203.7, 1100.9, 981.6, 956.2, 861.6, 779.1, 761.3, 647.6, 531.6  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{26}\text{H}_{24}\text{NO}_7$   $[\text{M}+\text{H}]^+$  462.1547, found: 462.1554.

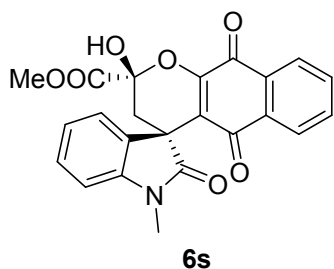
**Ethyl-5',6'-difluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6r**



foamy solid, 36.6 mg, 78% yield; 95% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -5.97$  ( $c = 1.79$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 15.728,  $t$  (minor) = 11.683];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.90 (s, 0.3H), 8.11 – 8.03 (m, 1H), 7.87 – 7.82

(m, 1H), 7.71 – 7.63 (m, 2H), 7.58 – 7.53 (m, 0.7H), 6.97 – 6.93 (m, 0.3H), 6.87 – 6.74 (m, 1H), 5.44 (s, 0.6H), 4.36 (q,  $J = 8.0$  Hz, 2H), 3.35 (s, 1H), 3.31 (s, 2H), 2.98 (d,  $J = 16.0$  Hz, 0.7H), 2.74 (d,  $J = 16.0$  Hz, 0.3H), 2.56 (d,  $J = 16.0$  Hz, 0.3H), 2.16 (d,  $J = 16.0$  Hz, 0.7H), 1.38 (t,  $J = 8.0$  Hz, 0.8H), 1.34 (t,  $J = 8.0$  Hz, 2.2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.43, 182.40, 178.67, 178.34, 167.94, 166.59, 154.16, 134.64, 134.56, 134.00, 133.81, 131.38, 130.87, 130.79, 126.94, 126.72, 126.66, 126.53, 121.04, 117.07, 116.86, 112.45, 112.24, 98.62, 98.39, 96.95, 95.07, 64.20, 63.16, 46.70, 45.52, 37.82, 36.61, 27.49, 27.41, 14.12, 14.04; IR: 3423.6, 2928.6, 1751.5, 1722.2, 1683.8, 1594.0, 1580.1, 1470.5, 1395.8, 1333.3, 1250.5, 1095.0, 948.4, 885.3, 833.2, 780.1, 763.0, 721.2, 691.3, 618.1, 505.3  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{24}\text{H}_{18}\text{F}_2\text{NO}_7$   $[\text{M}+\text{H}]^+$  470.1046, found: 470.1044.

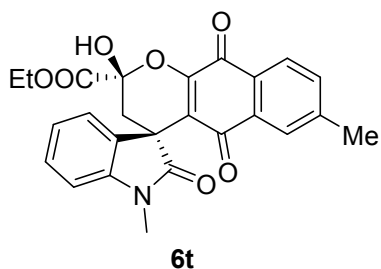
**Methyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6s**



foamy solid, 31.0 mg, 74% yield; >99% *ee*, > 20/1 *dr*,  
 $[\alpha]_{\text{D}}^{26} = -40.42$  ( $c = 1.41$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak IA,  
 hexane/*i*-PrOH (70:30), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254$   
 nm,  $t$  (major) = 17.990];  $^1\text{H}$  (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.22 (s,  
 0.7H), 8.13 – 8.06 (m, 1H), 7.85 – 7.80 (m, 1H), 7.70 –

7.63 (m, 2.3H), 7.38 – 7.29 (m, 1H), 7.09 – 6.94 (m, 2.7H), 5.29 (s, 0.3H), 3.92 (s,  
 3H), 3.39 (s, 2H), 3.37 (s, 1H), 3.02 (d,  $J = 16.0$  Hz, 0.3H), 2.81 (d,  $J = 16.0$  Hz,  
 0.7H), 2.56 (d,  $J = 16.0$  Hz, 0.7H), 2.17 (d,  $J = 16.0$  Hz, 0.3H);  $^{13}\text{C}$  NMR (101 MHz,  
 $\text{CDCl}_3$ )  $\delta$  182.33, 182.30, 179.68, 179.44, 178.67, 178.42, 168.71, 167.31, 155.12,  
 153.98, 134.50, 134.42, 133.79, 133.61, 131.99, 131.53, 131.48, 130.90, 130.82,  
 129.39, 129.34, 128.86, 126.84, 126.76, 126.70, 126.62, 126.54, 124.24, 122.37,  
 122.25, 122.19, 120.89, 109.44, 108.51, 97.15, 95.22, 54.37, 53.68, 46.80, 45.53,  
 37.45, 36.81, 27.25, 27.16; IR: 3432.1, 2926.2, 1754.3, 1712.4, 1655.6, 1579.5,  
 1474.4, 1437.9, 1356.2, 1333.1, 1202.1, 1096.2, 1026.8, 972.5, 796.0, 753.9, 723.4,  
 684.6,  $543.0 \text{ cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{23}\text{H}_{18}\text{NO}_7$   $[\text{M}+\text{H}]^+$  420.1078, found:  
 420.1074.

**Ethyl-2-hydroxy-1',7-dimethyl-2',5,10-trioxo-2,3,5,10-**  
**tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6t**



foamy solid, 37.9 mg, 85% yield; 93% *ee*, > 20/1 *dr*,  
 $[\alpha]_{\text{D}}^{26} = -0.69$  ( $c = 1.43$ ,  $\text{CH}_2\text{Cl}_2$ ); [Daicel Chiralpak  
 IA, hexane/*i*-PrOH (70:30), flow rate:  $1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda$   
 = 254 nm,  $t$  (major) = 16.323,  $t$  (minor) = 22.584];  $^1\text{H}$   
 (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  9.15 (s, 0.65H), 7.91 – 7.87 (m,

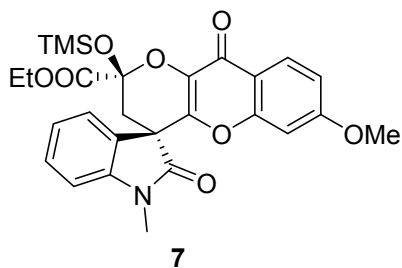
1H), 7.75 – 7.69 (m, 1H), 7.65 – 7.64 (m, 0.35H), 7.44 – 7.28 (m, 2H), 7.09 – 6.99  
 (m, 2H), 6.97 – 6.93 (m, 0.65H), 5.20 (s, 0.35H), 4.37 (q,  $J = 8.0$  Hz, 2H), 3.38 (s,  
 2H), 3.37 (s, 1H), 3.01 (d,  $J = 16.0$  Hz, 0.35H), 2.78 (d,  $J = 16.0$  Hz, 0.65H), 2.55 (d,  
 $J = 16.0$  Hz, 0.65H), 2.45 (s, 2H), 2.44 (s, 1H), 2.16 (d,  $J = 16.0$  Hz, 0.35H), 1.38 (t,  
 $J = 8.0$  Hz, 1.90H), 1.35 (t,  $J = 8.0$  Hz, 1.1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.31,  
 179.78, 179.21, 178.97, 178.63, 168.35, 166.87, 155.09, 153.98, 144.97, 144.73,  
 143.94, 143.83, 135.17, 135.11, 132.20, 131.60, 130.84, 130.78, 129.32, 129.31,

128.82, 127.16, 126.97, 126.89, 126.82, 126.72, 124.20, 122.34, 122.25, 121.63, 120.72, 109.40, 108.49, 97.04, 95.10, 64.12, 63.00, 46.83, 45.59, 37.50, 36.74, 27.23, 27.17, 21.84, 21.18, 14.16, 14.08; IR: 3431.4, 2925.4, 1749.7, 1682.0, 1611.4, 1305.0, 1162.6, 1047.7, 1025.7, 754.8  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{22}\text{NO}_7$   $[\text{M}+\text{H}]^+$  448.1391, found: 448.1386.

### 3.3 Synthesis of compound 7

In an ordinary tube equipped with a magnetic stirring bar, the solution of **4w** (45.1mg, 0.1 mmol, 1 equiv), TMSCl (75.6  $\mu\text{L}$ , 0.6 mmol, 6 equiv), in  $\text{CH}_3\text{CN}$  (1.0 mL) was stirred at rt for 30 min, and then triethylamine (83.0  $\mu\text{L}$ , 0.6 mmol, 6 equiv) was added. After 12h the reaction was completed, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ ethyl acetate = 2:1) to give desired product **7**.

#### Ethyl-7'-methoxy-1-methyl-2,10'-dioxo-2'-((trimethylsilyl)oxy)-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate **7**



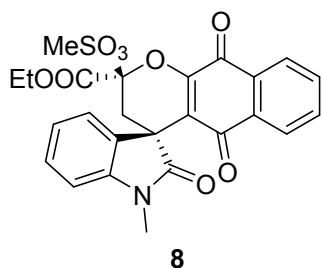
white solid, melting point: 71–73  $^{\circ}\text{C}$ , 27.3 mg, 52% yield; 97% *ee*, > 20/1 *dr*,  $[\alpha]_{\text{D}}^{26} = -30.59$  ( $c = 0.68$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak AD, hexane/*i*-PrOH (70:30), flow rate: 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254$  nm,  $t$  (major) = 16.431,  $t$  (minor) = 19.872];  $^1\text{H}$  NMR (400

MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.8$  Hz, 1H), 7.70 (dd,  $J = 7.6, 0.8$  Hz, 1H), 7.39 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.08 (td,  $J = 7.6, 1.2$  Hz, 1H), 6.97 (d,  $J = 7.6$  Hz, 1H), 6.87 (dd,  $J = 8.8, 2.4$  Hz, 1H), 6.50 (d,  $J = 2.4$  Hz, 1H), 4.31 (td,  $J = 7.2, 0.8$  Hz, 2H), 3.78 (s, 3H), 3.33 (s, 3H), 2.97 (d,  $J = 14.0$  Hz, 1H), 2.44 (d,  $J = 14.0$  Hz, 1H), 1.34 (t,  $J = 7.2$  Hz, 3H), 0.25 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.72, 171.07, 168.71, 164.01, 156.87, 146.96, 143.87, 136.55, 130.41, 129.43, 127.48, 127.04, 123.06, 117.68, 114.52, 108.69, 100.05, 95.35, 62.80, 55.88, 49.71, 40.95, 27.26, 14.16, 1.15; IR: 2987.8, 2943.8, 1767.6, 1725.3, 1768.7, 1600.5, 1623.4, 1430.3, 1294.9, 1276.7, 1246.7, 933.4, 904.8, 888.7, 838.8, 794.3  $\text{cm}^{-1}$ ; HRMS-ESI: calcd. for  $\text{C}_{27}\text{H}_{30}\text{NO}_8\text{Si}$   $[\text{M}+\text{H}]^+$  524.1735, found: 524.1745.

### 3.4 Synthesis of compound 8

In an ordinary tube equipped with a magnetic stirring bar, the solution of **6a** (64.9 mg, 0.15 mmol, 1 equiv), mesyl chloride (19.2  $\mu$ L, 0.25 mmol 1.67 equiv), in DCM (1.0 mL) was stirred at rt. for 30 min, and then triethylamine (34.6  $\mu$ L, 0.25 mmol, 1.67 equiv) was added. After 12h the reaction was finished, the reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to give desired product **8**.

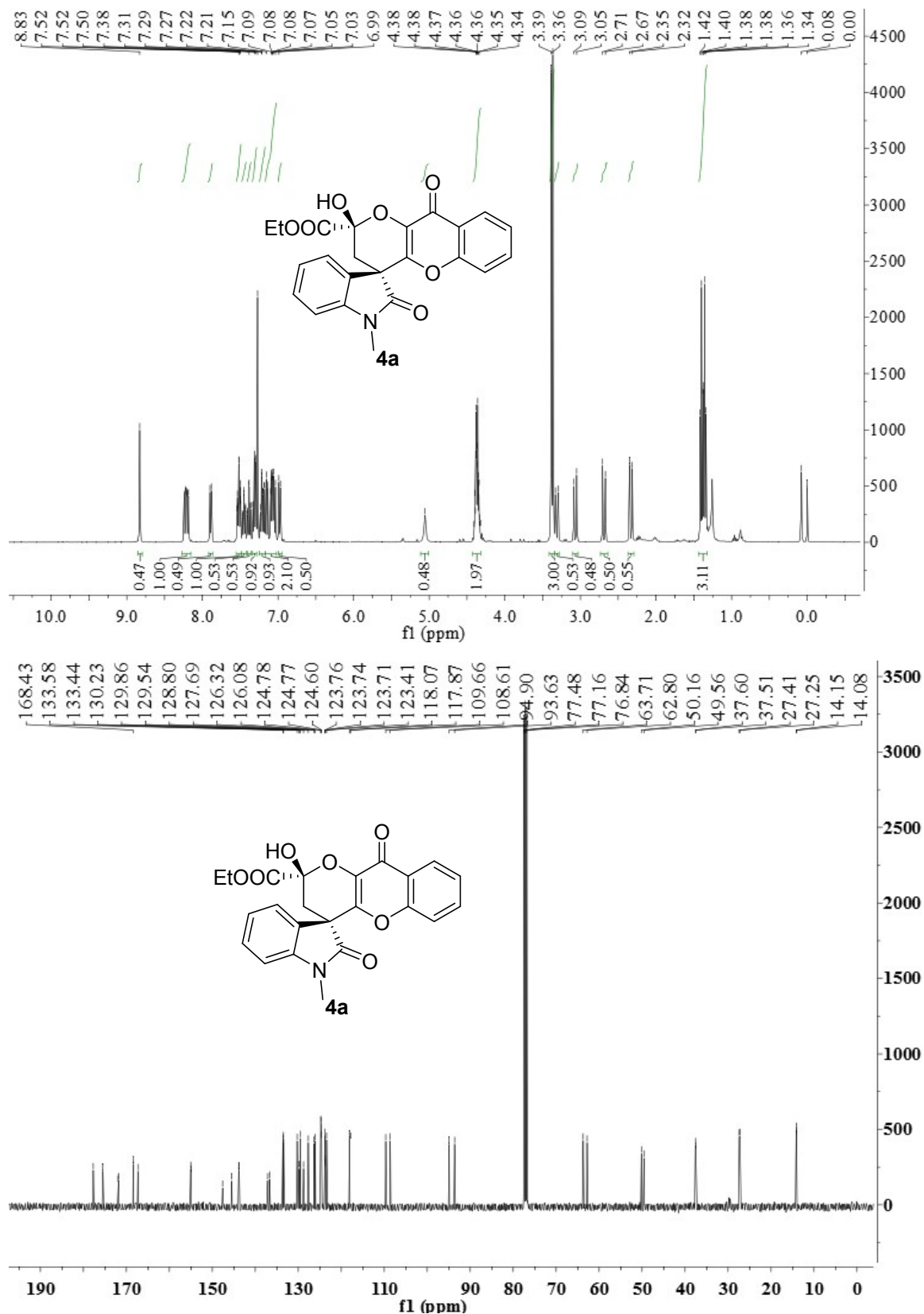
**Ethyl-1'-methyl-2-((methylsulfonyl)oxy)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate **8****



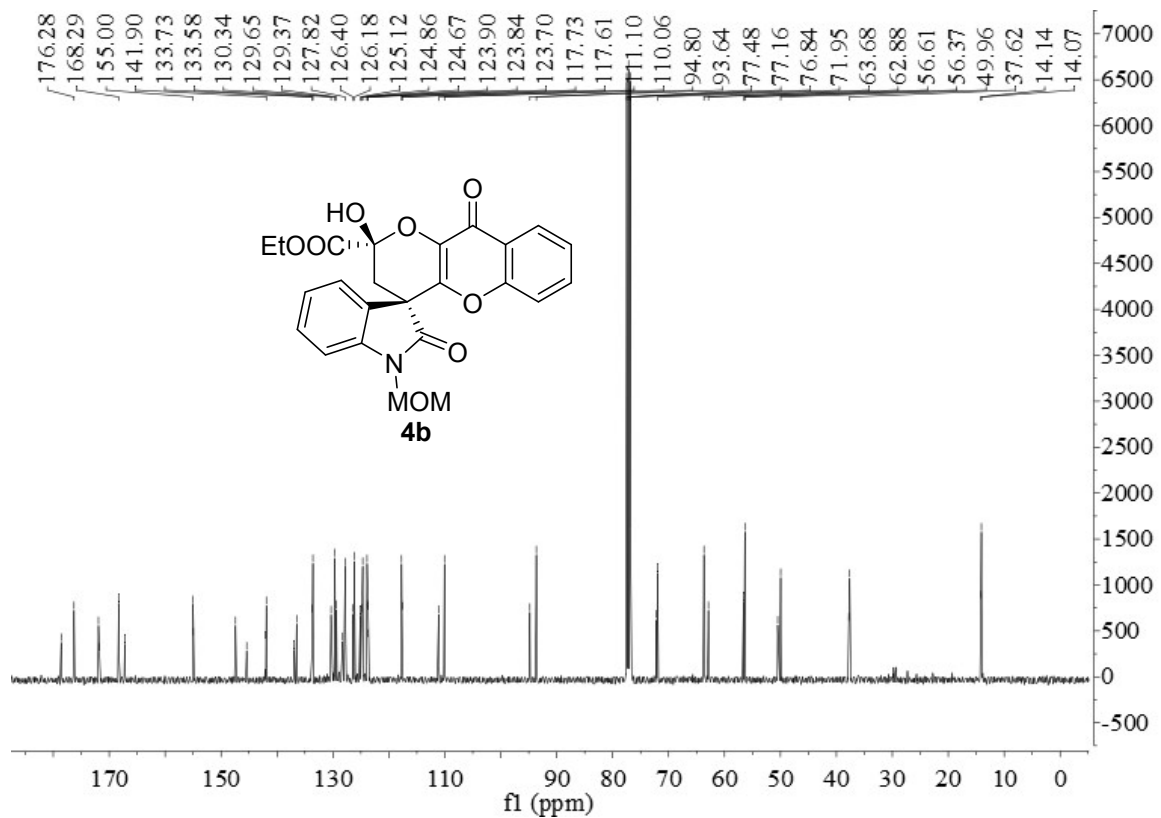
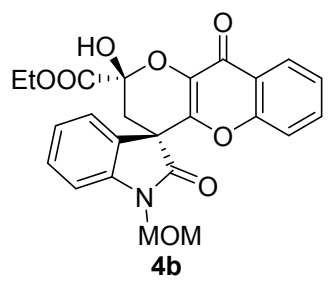
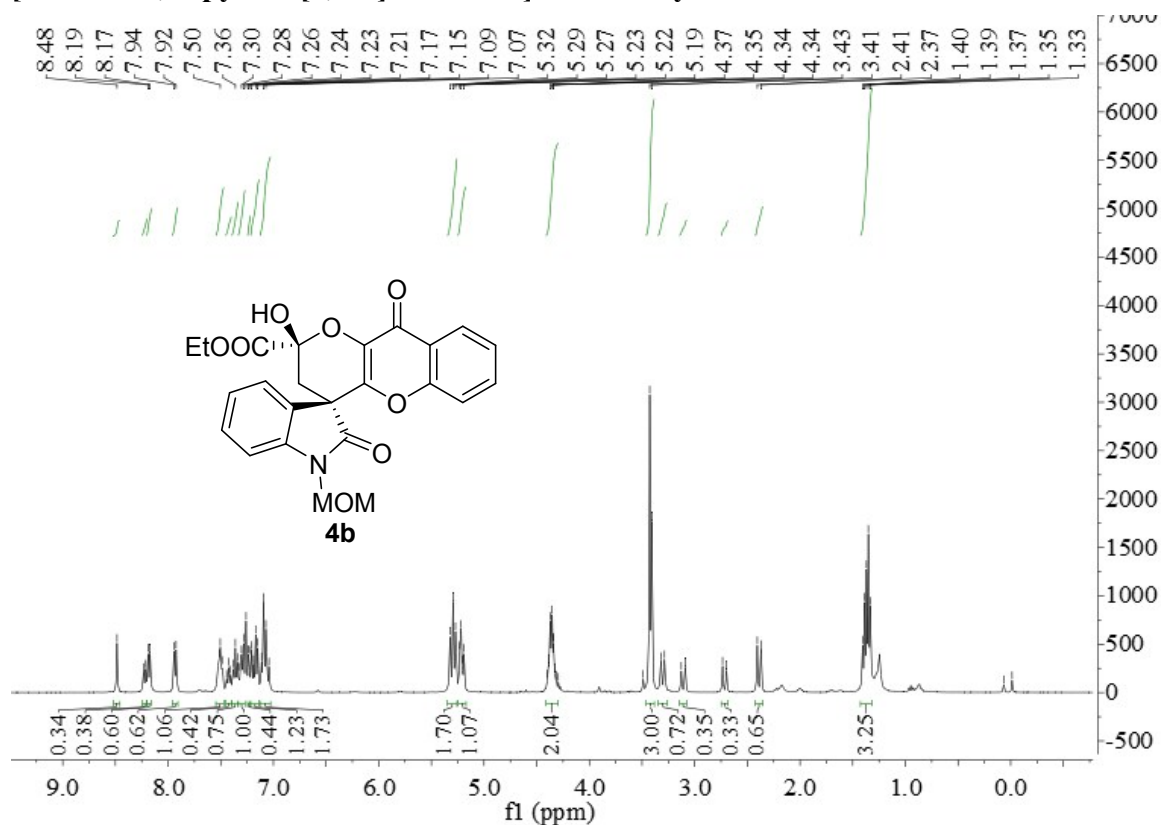
yellow solid, melting point: 124–126 °C, 73.7 mg, 96% yield; 94% *ee*, 8/1 *dr*,  $[\alpha]_D^{26} = -34.05$  ( $c = 0.79$ ,  $\text{CHCl}_3$ ); [Daicel Chiralpak IA, hexane/*i*-PrOH (70:30), flow rate: 1.0 mL·min<sup>-1</sup>,  $\lambda = 254$  nm,  $t$  (major) = 42.444,  $t$  (minor) = 17.437]; <sup>1</sup>H (400 Hz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (dd,  $J = 7.7, 1.2$  Hz, 1H), 7.86 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.73 – 7.64 (m, 2H), 7.45 (dd,  $J = 7.6, 0.8$  Hz, 1H), 7.36 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.03 (td,  $J = 7.6, 1.2$  Hz, 1H), 6.99 (d,  $J = 8.0$  Hz, 1H), 4.39 (qd,  $J = 7.2, 2.8$  Hz, 2H), 3.36 (s, 3H), 3.25 (s, 3H), 2.74 (d,  $J = 14.4$  Hz, 1H), 2.59 (d,  $J = 14.4$  Hz, 1H), 1.36 (t,  $J = 7.2$  Hz, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.00, 177.31, 164.76, 152.65, 144.02, 134.57, 134.06, 131.30, 130.89, 130.78, 129.39, 126.92, 126.76, 125.70, 122.79, 121.80, 109.00, 99.15, 64.10, 45.36, 41.30, 38.67, 27.25, 13.96; IR: 2987.8, 2943.8, 1767.6, 1725.3, 1768.7, 1600.5, 1623.4, 1430.3, 1294.9, 1276.7, 1246.7, 933.4, 904.8, 888.7, 838.8, 794.3 cm<sup>-1</sup>; HRMS-ESI: calcd. for  $\text{C}_{25}\text{H}_{21}\text{NNaO}_7\text{S}$   $[\text{M}+\text{Na}]^+$  534.0829, found: 534.0827.

#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

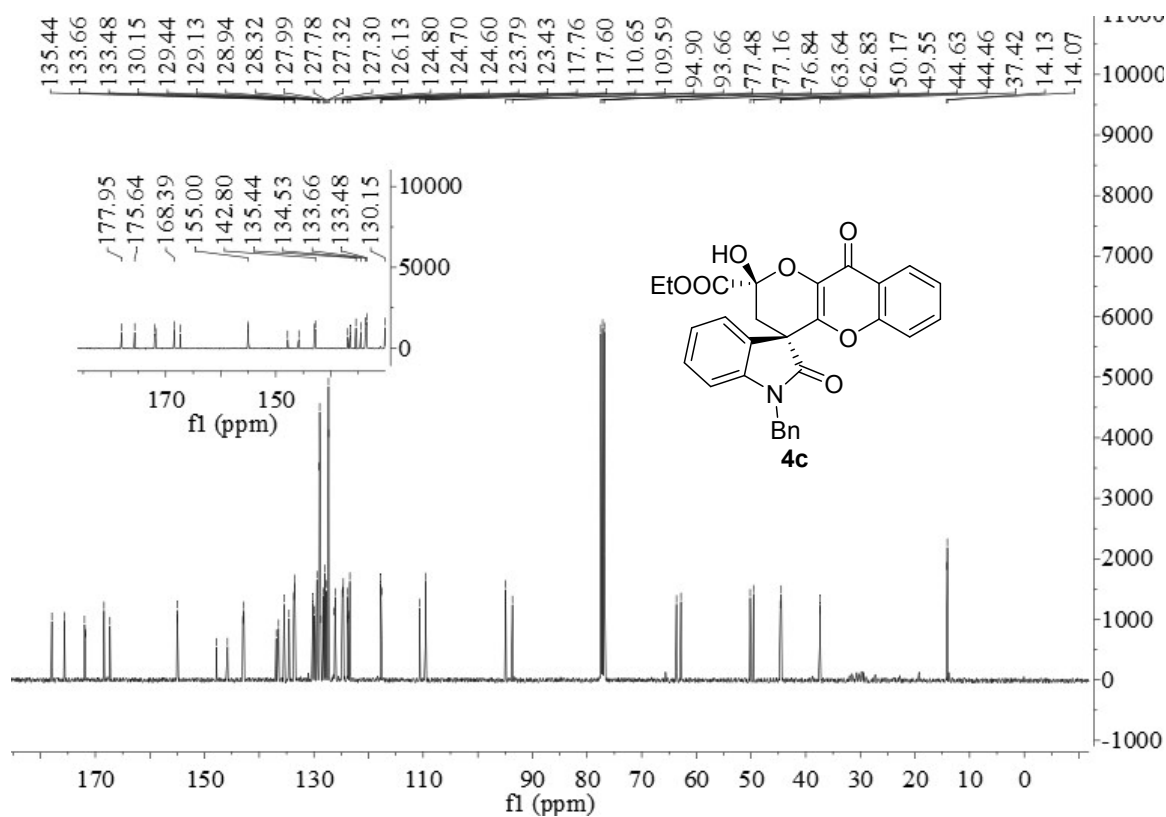
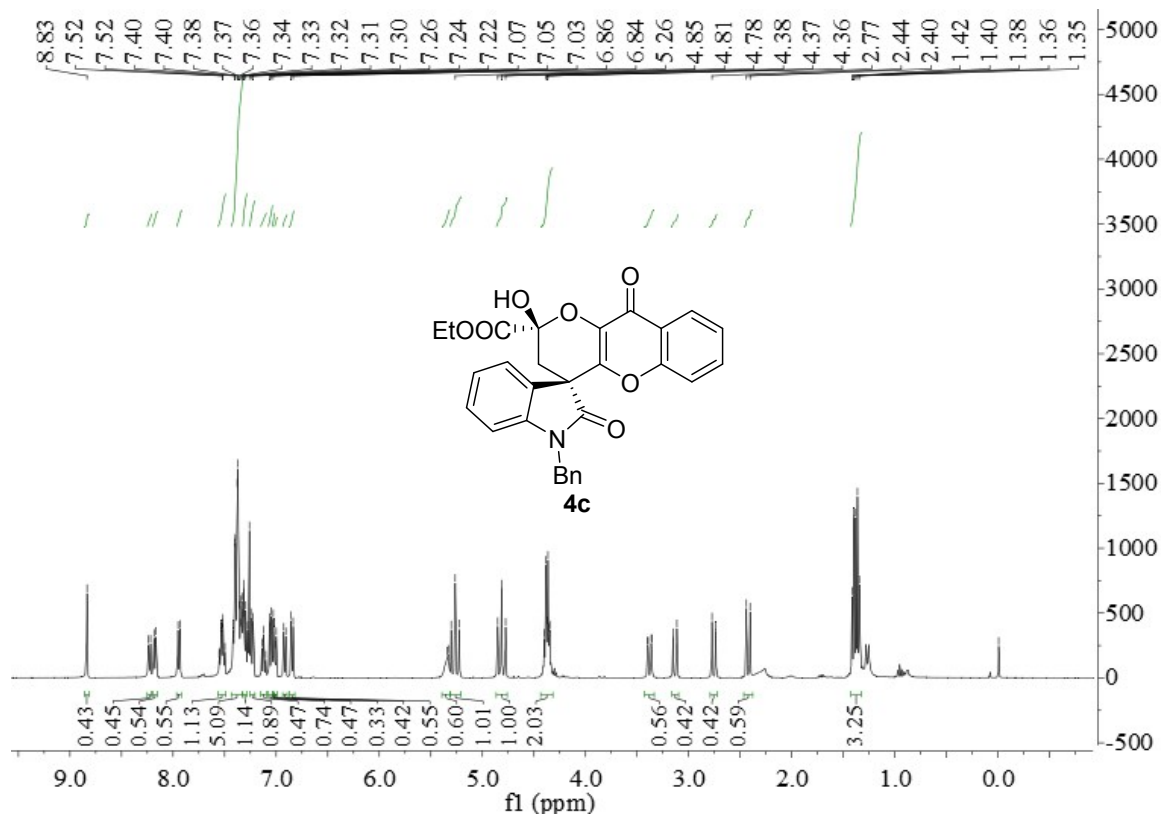
##### Ethyl-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4a



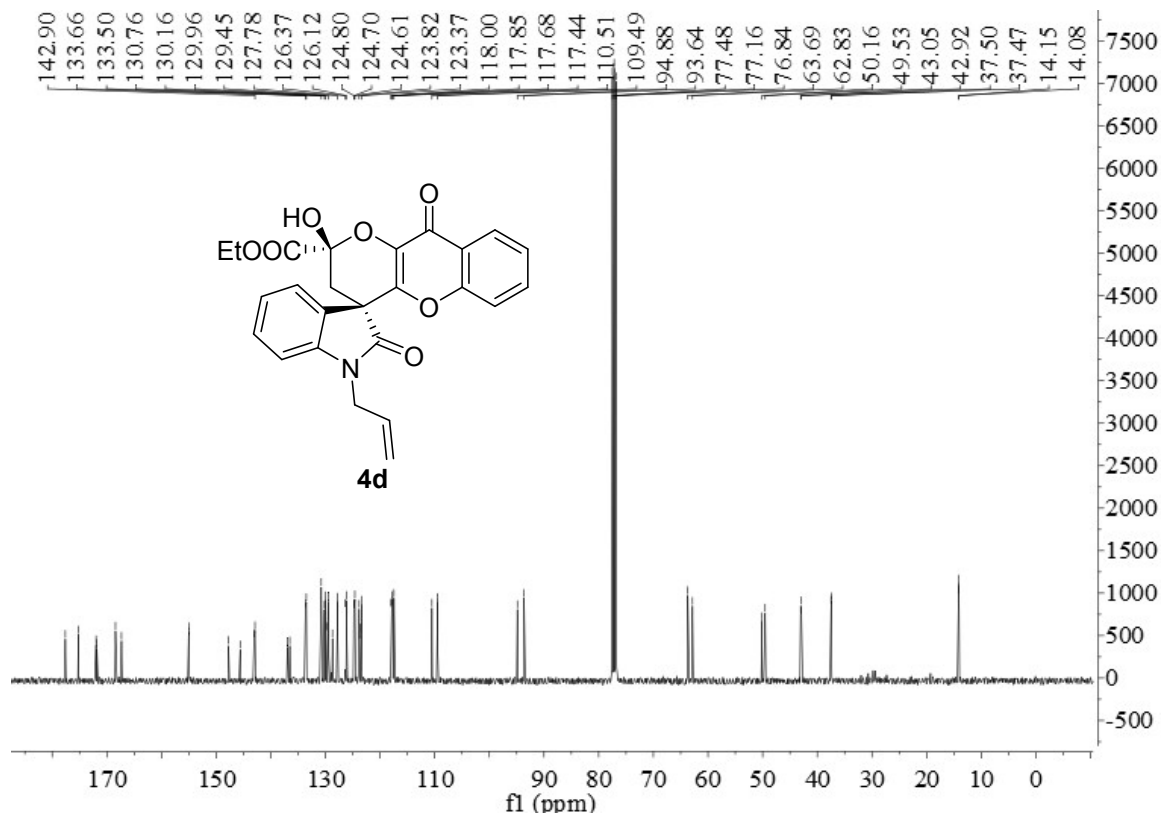
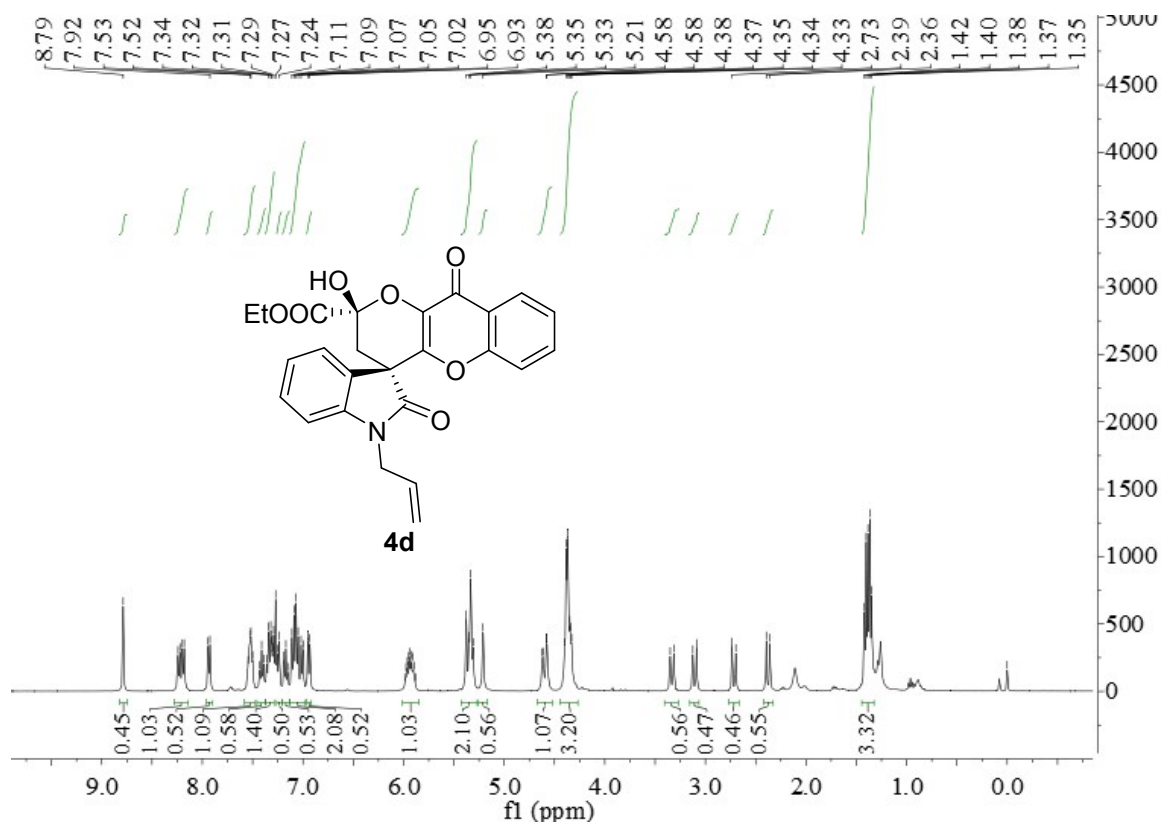
**Ethyl 2'-hydroxy-1-(methoxymethyl)-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4b**



**Ethyl 1-benzyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4c**



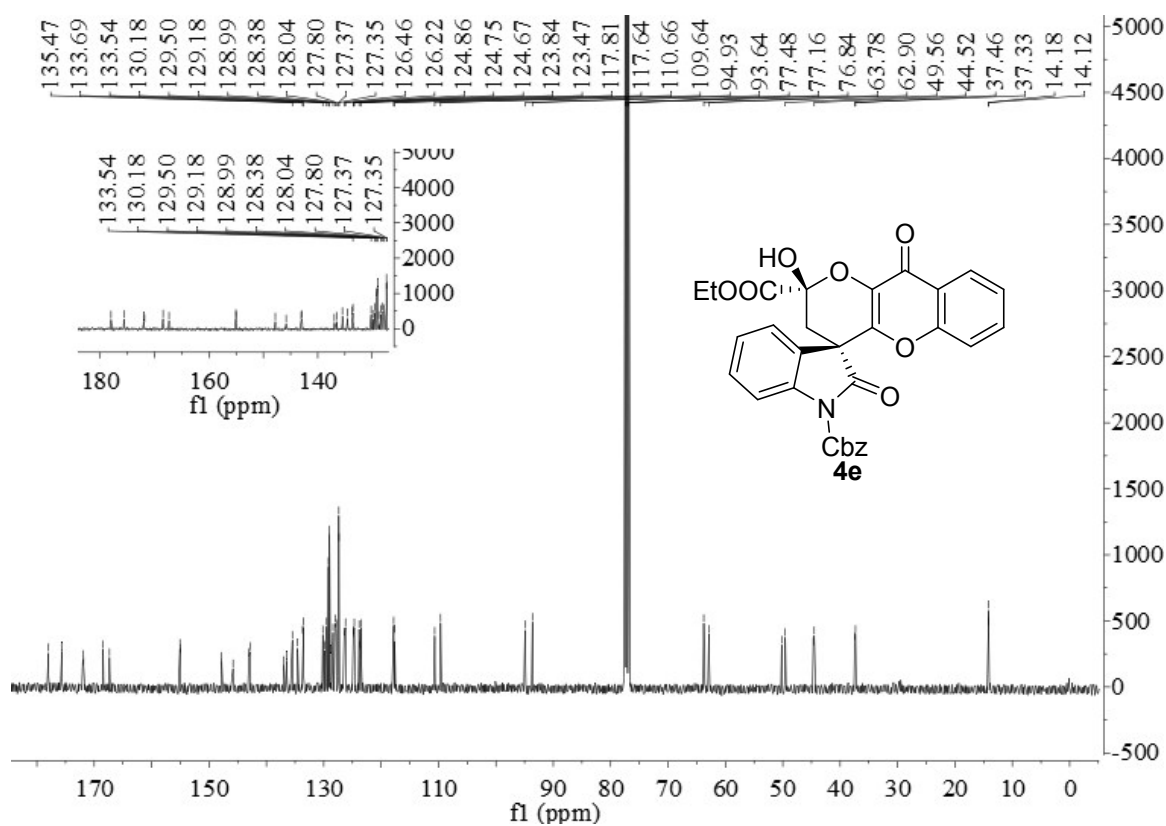
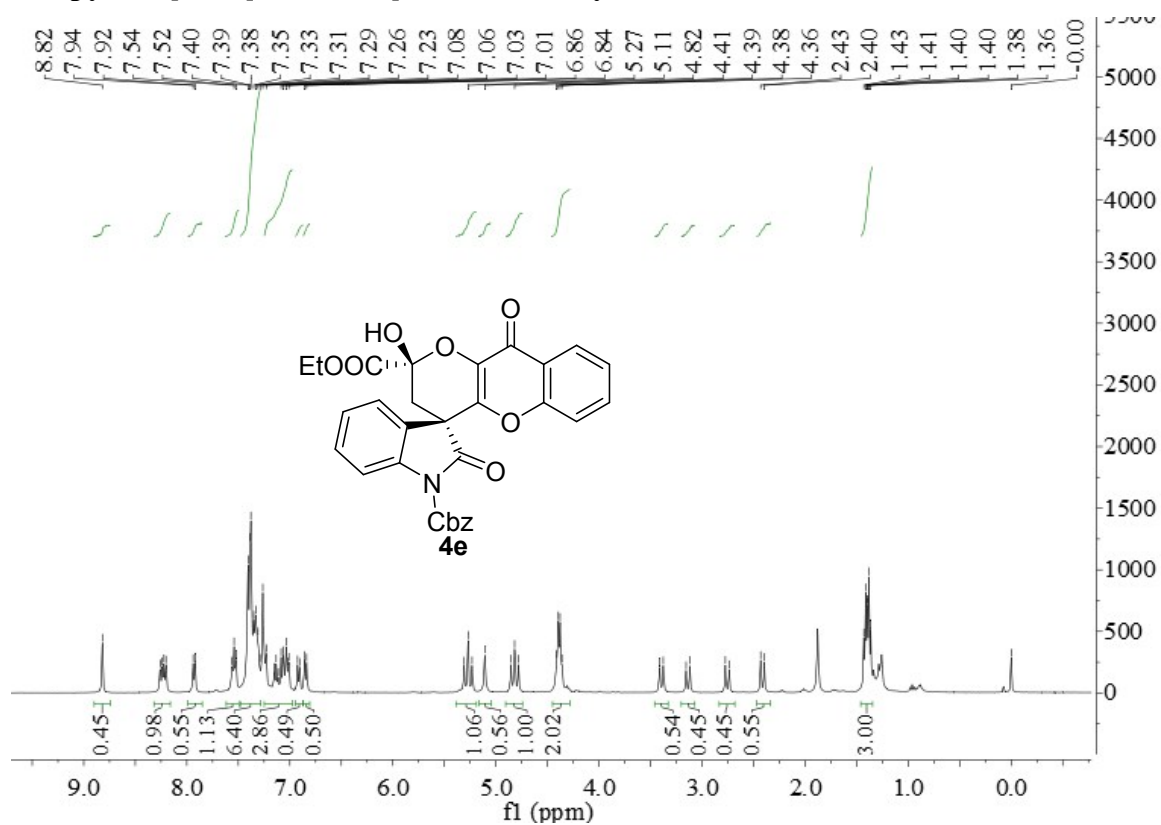
**Ethyl 1-allyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4d**



**1-benzyl 2'-ethyl 2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-**

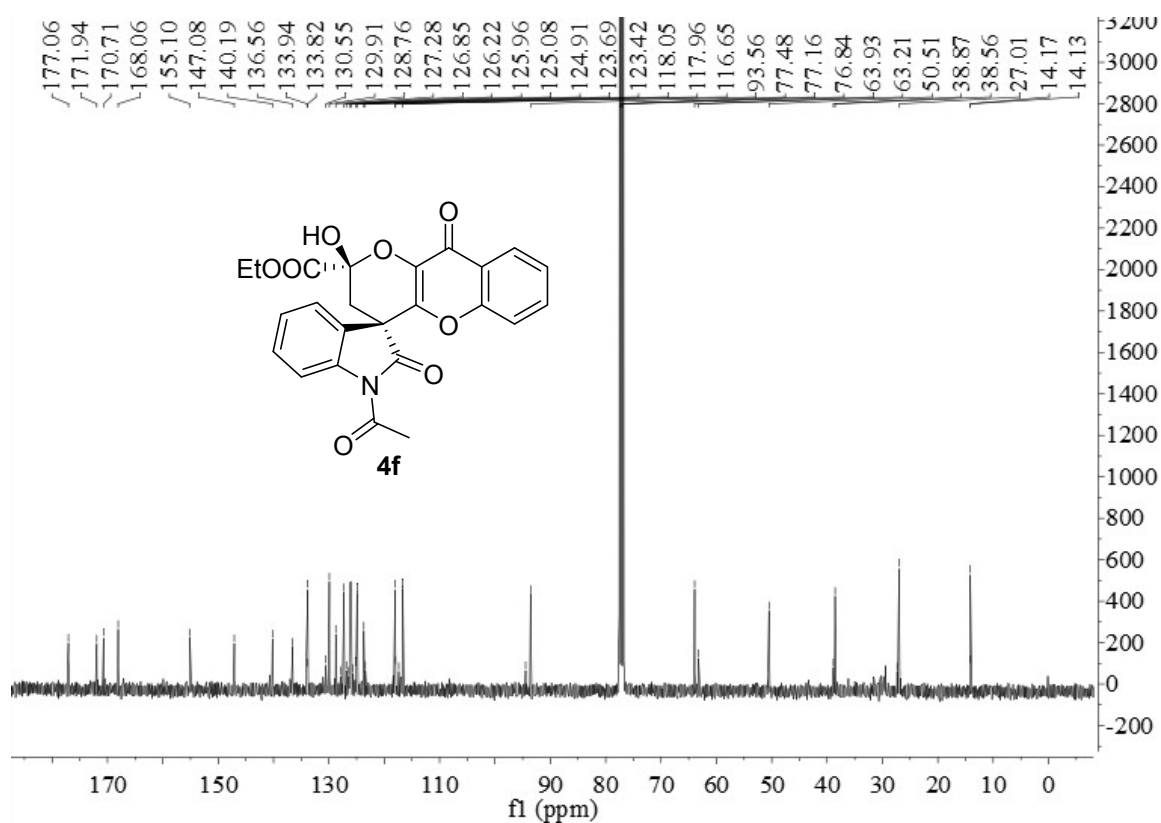
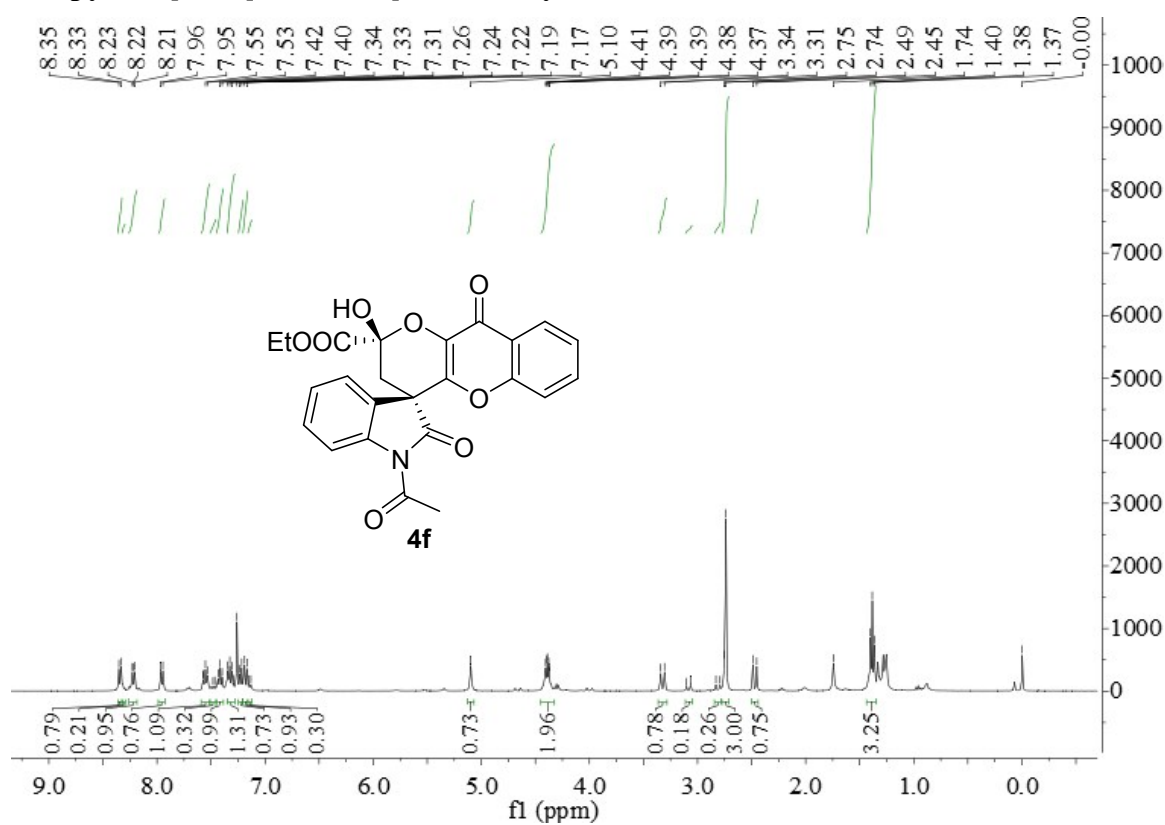


**3,4'-pyrano[3,2-*b*]chromene]-1,2'-dicarboxylate 4e**



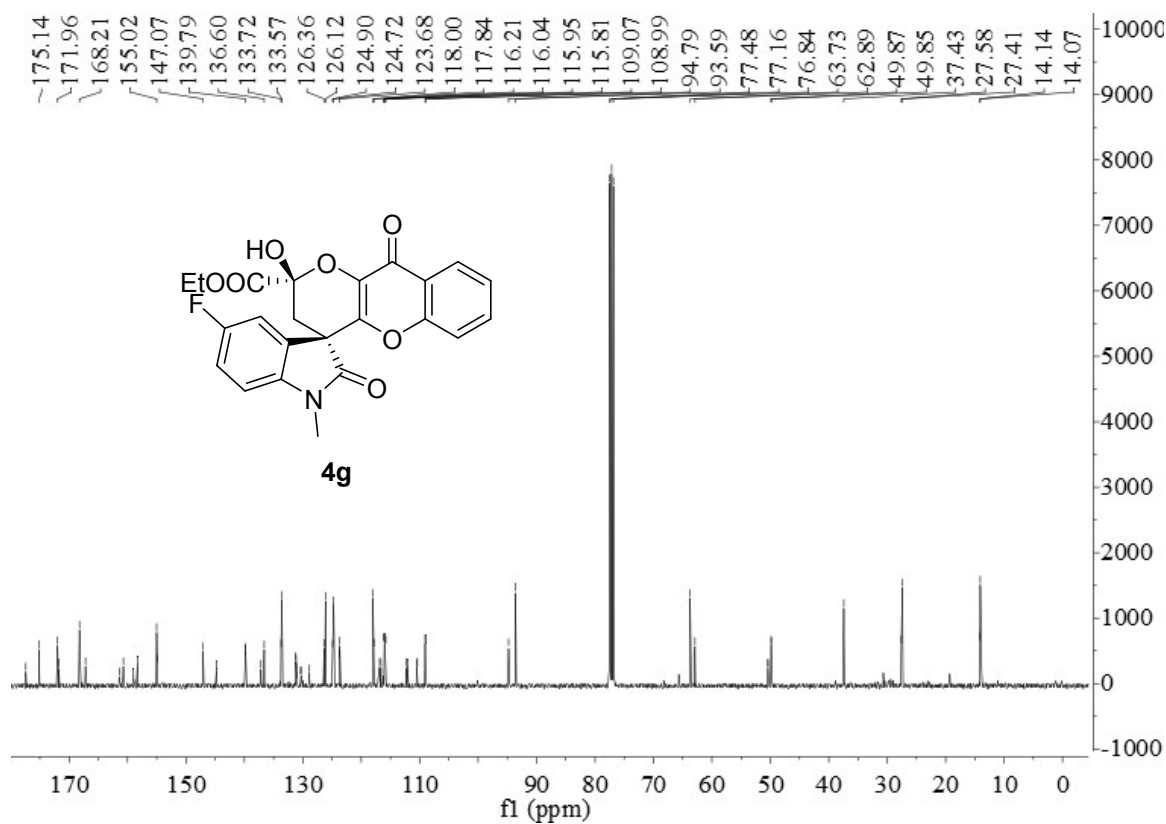
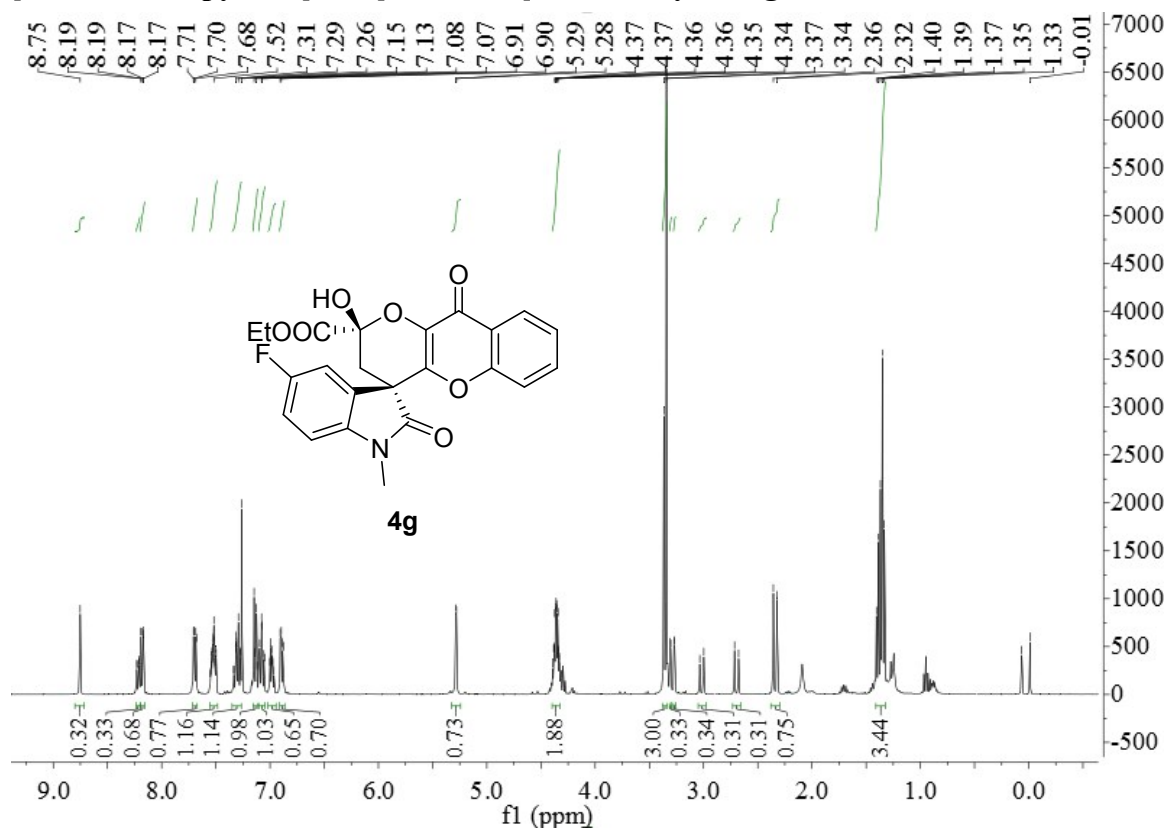
**Ethyl 1-acetyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-**

**3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4f**



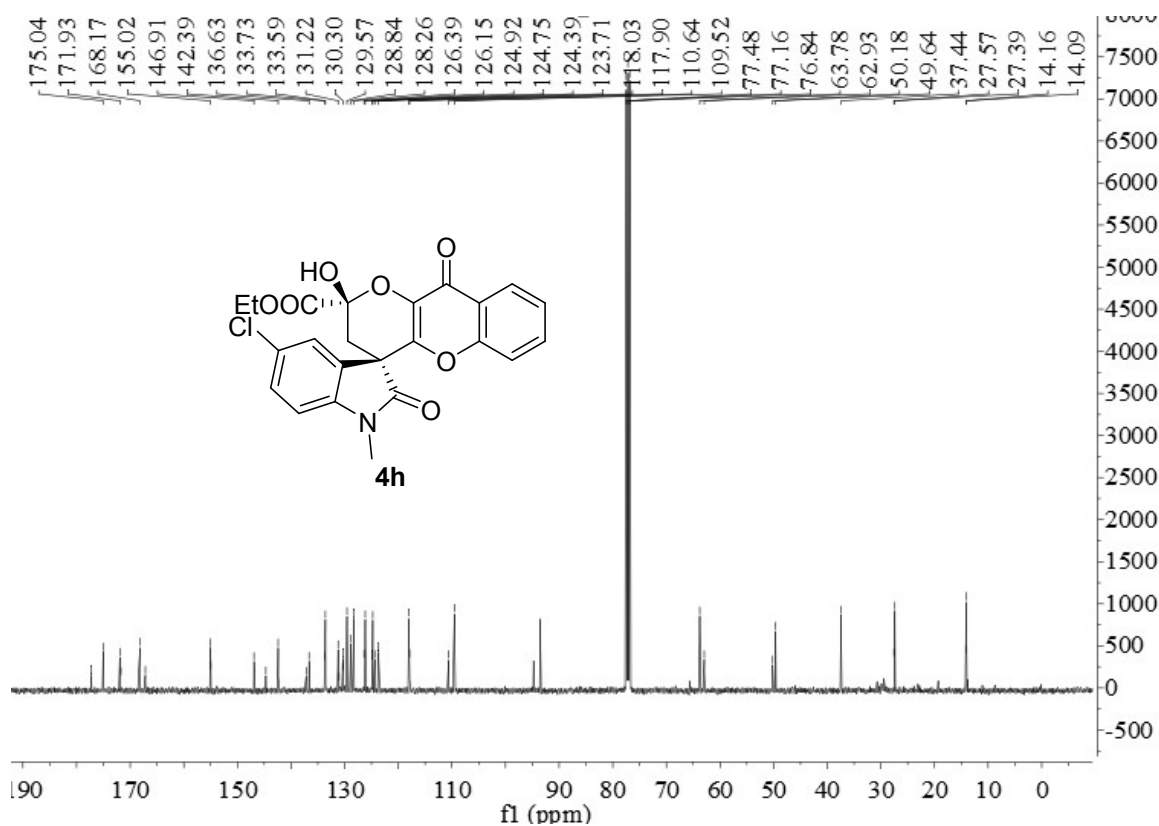
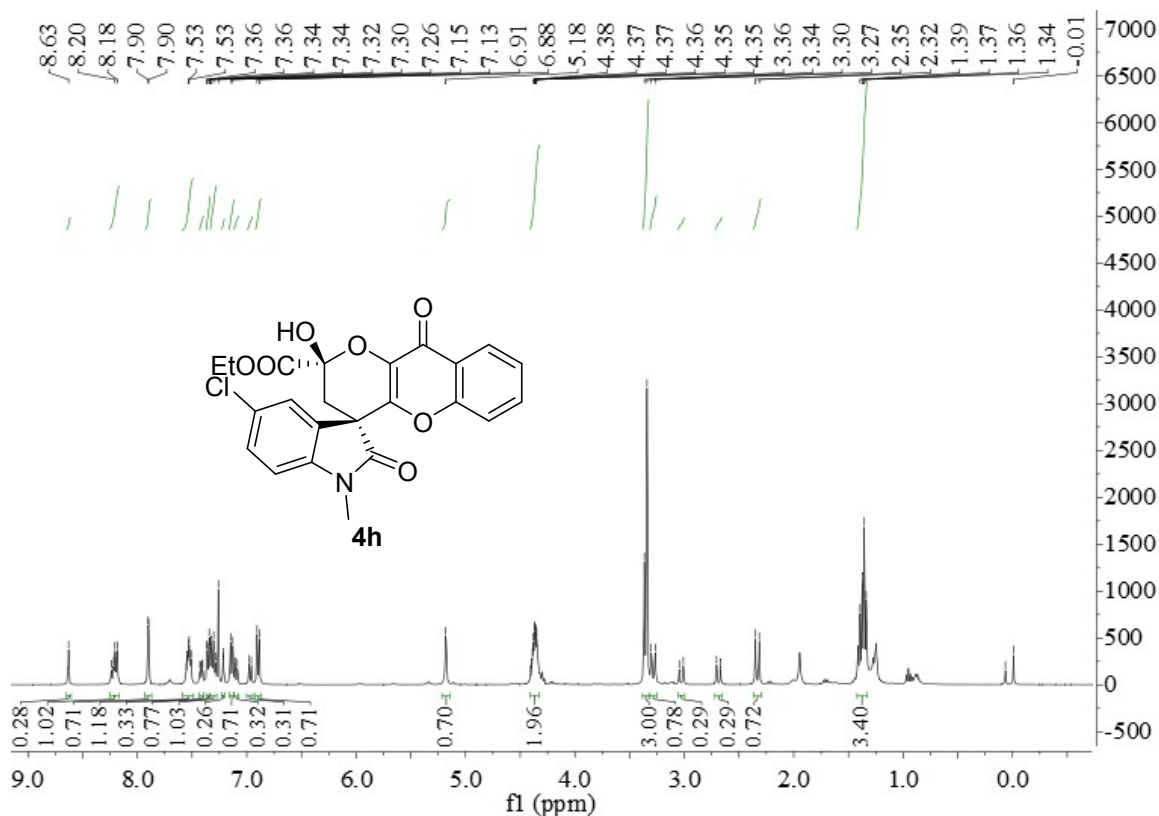
**Ethyl 5-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'--carboxylate 4g**



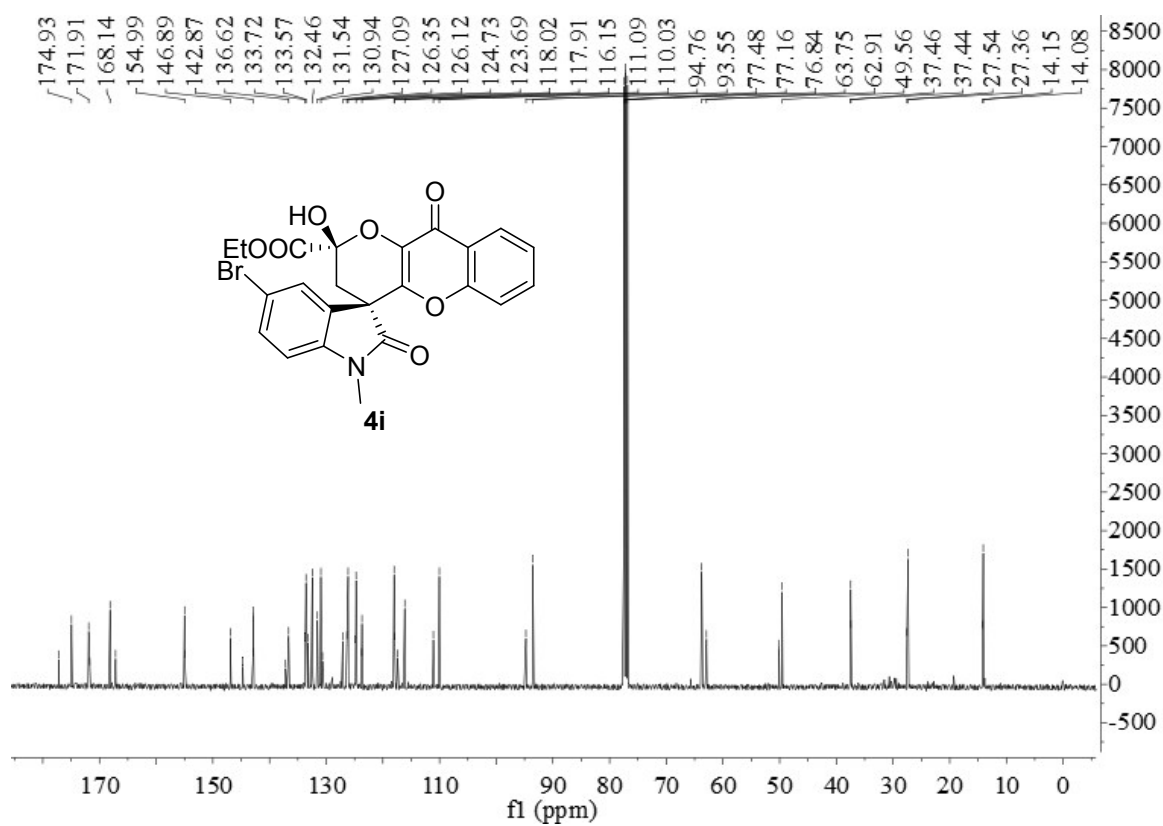
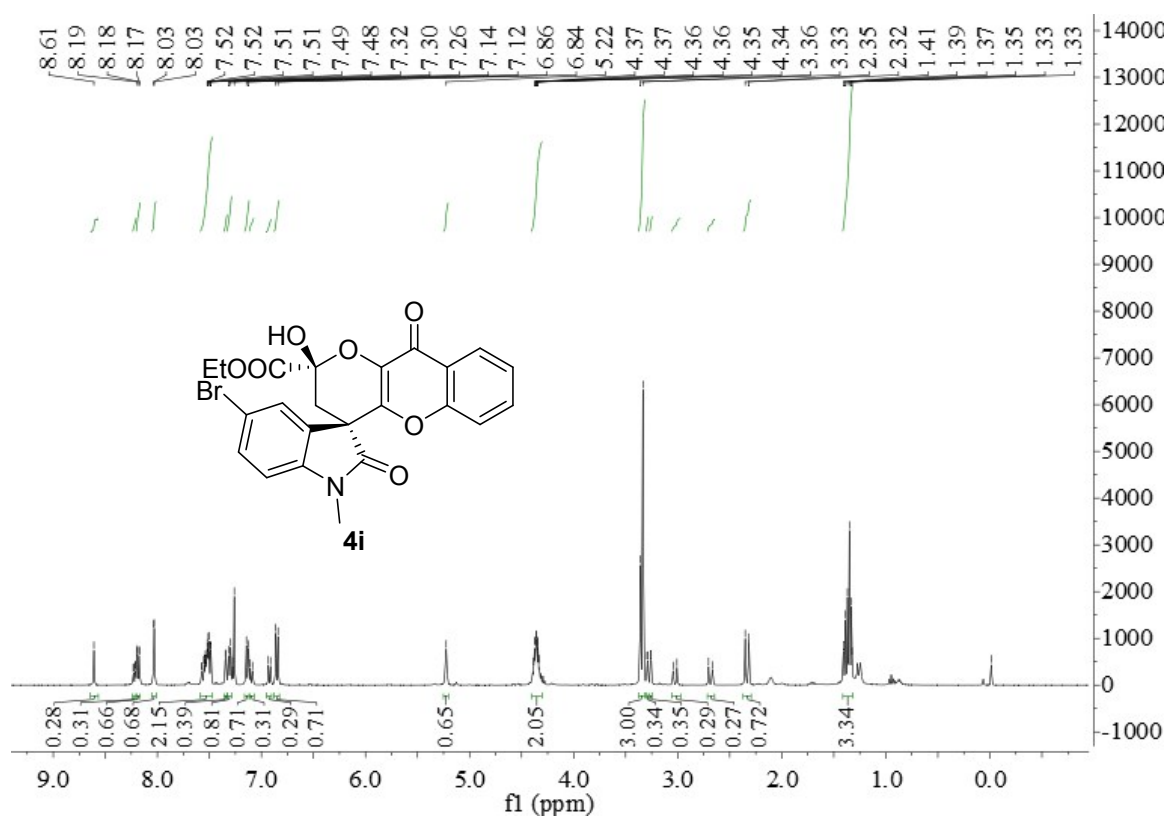
**Ethyl 5-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4h**



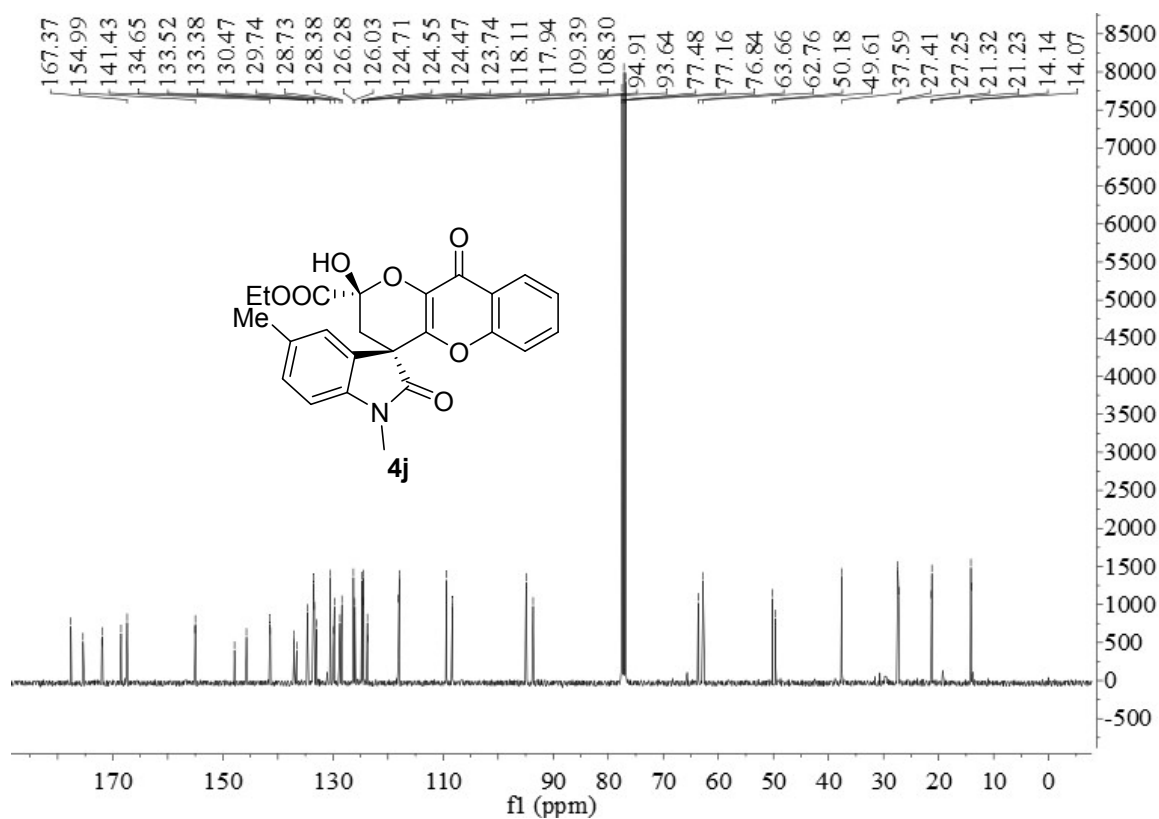
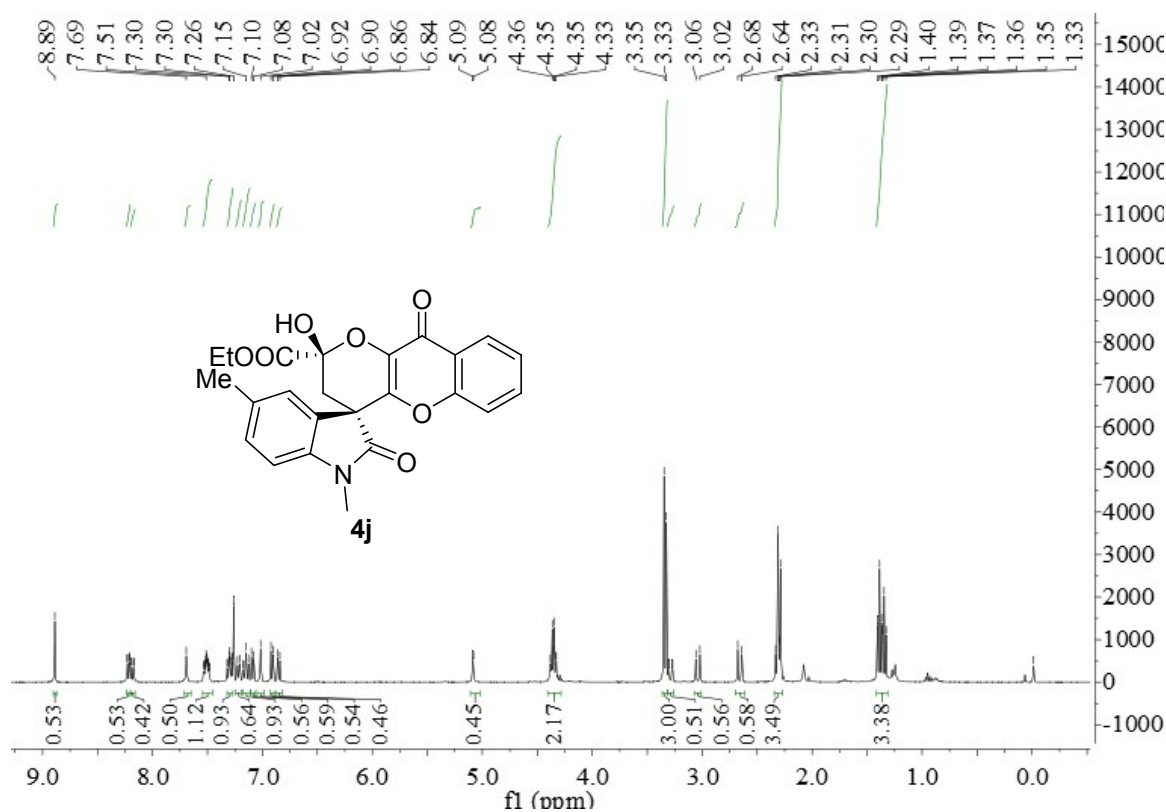
**Ethyl 5-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4i**



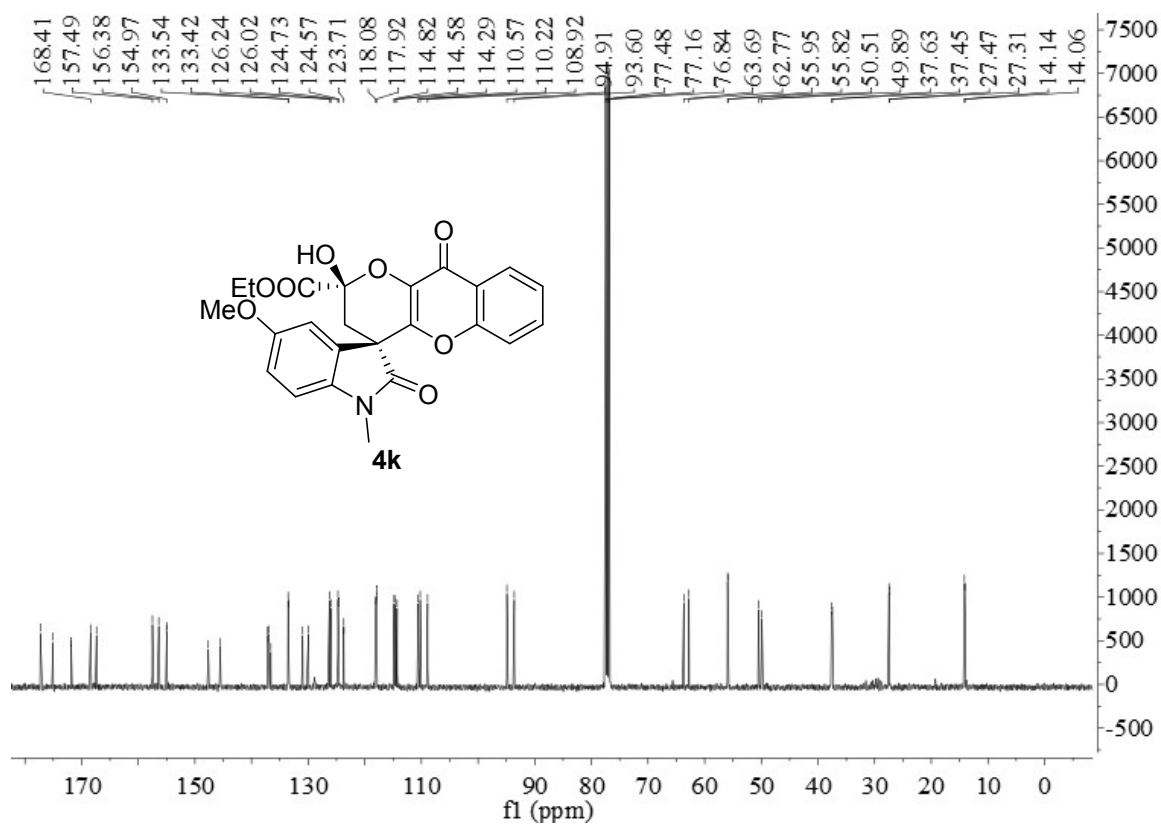
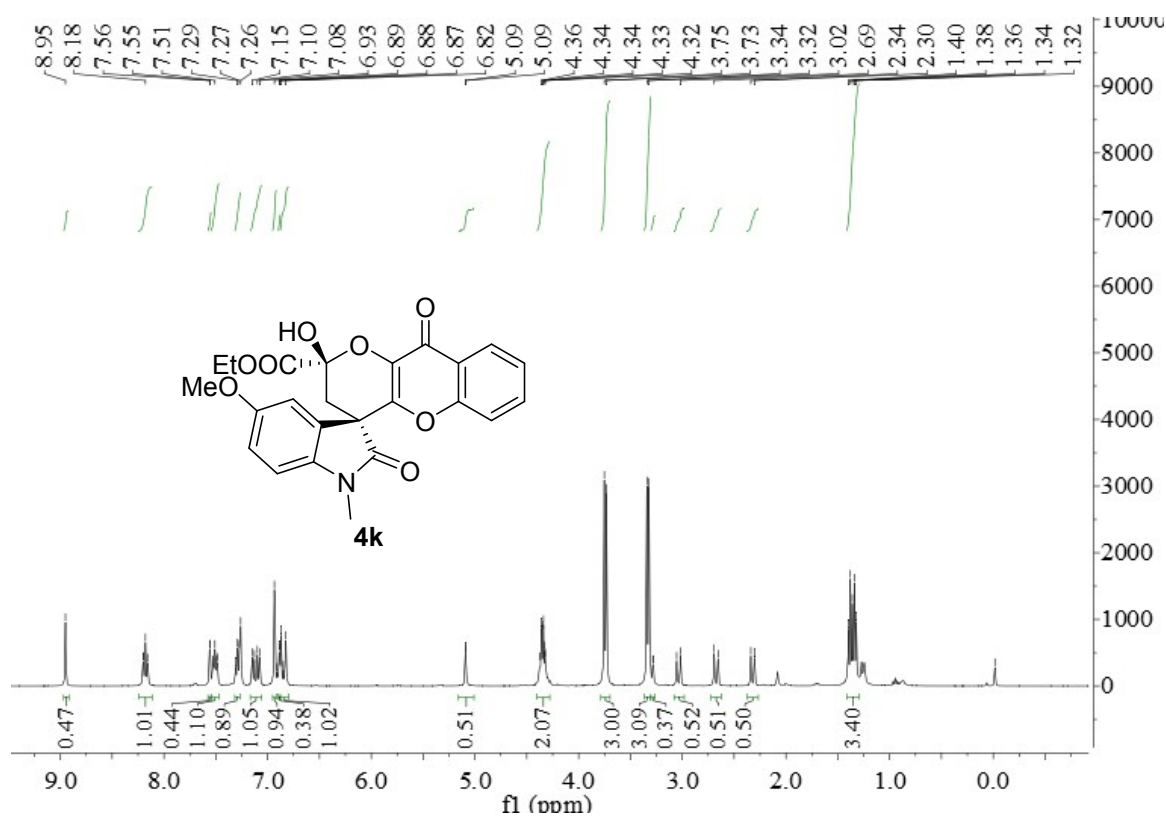
**Ethyl 2'-hydroxy-1,5-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4j**



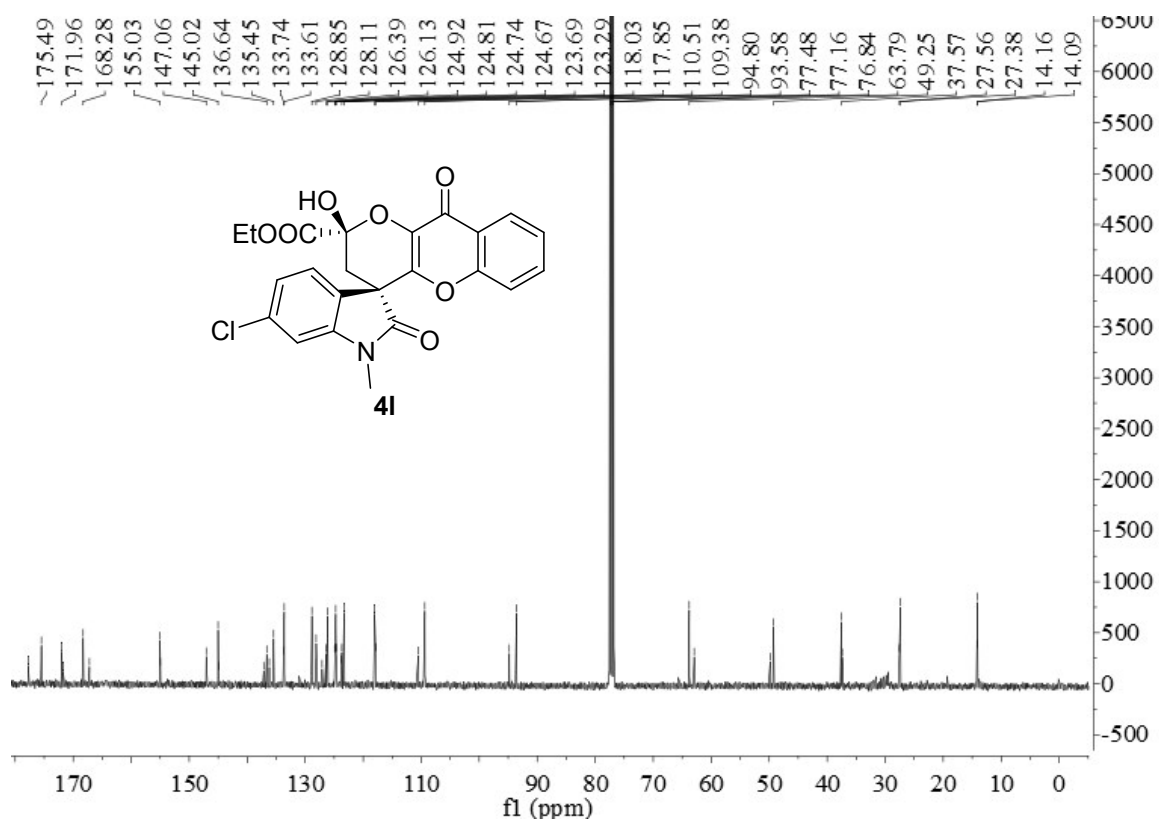
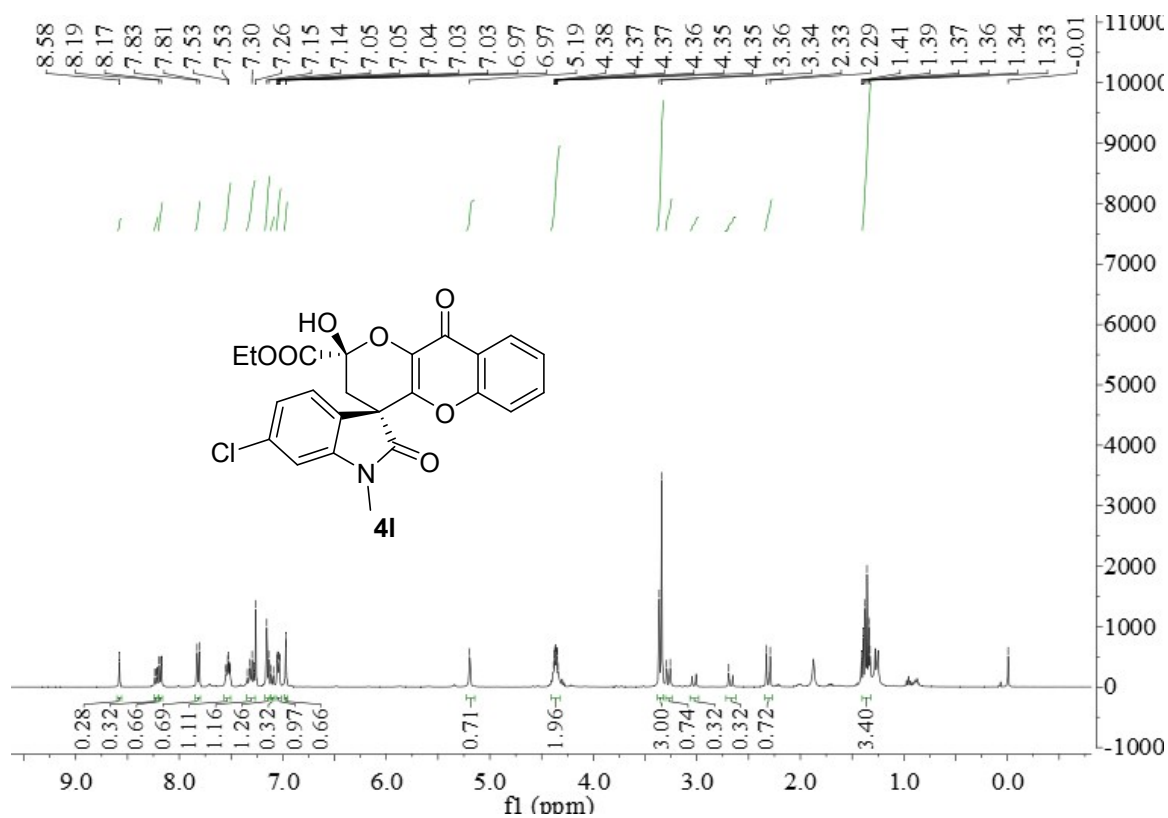
**Ethyl 2'-hydroxy-5-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4k**



**Ethyl 6-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

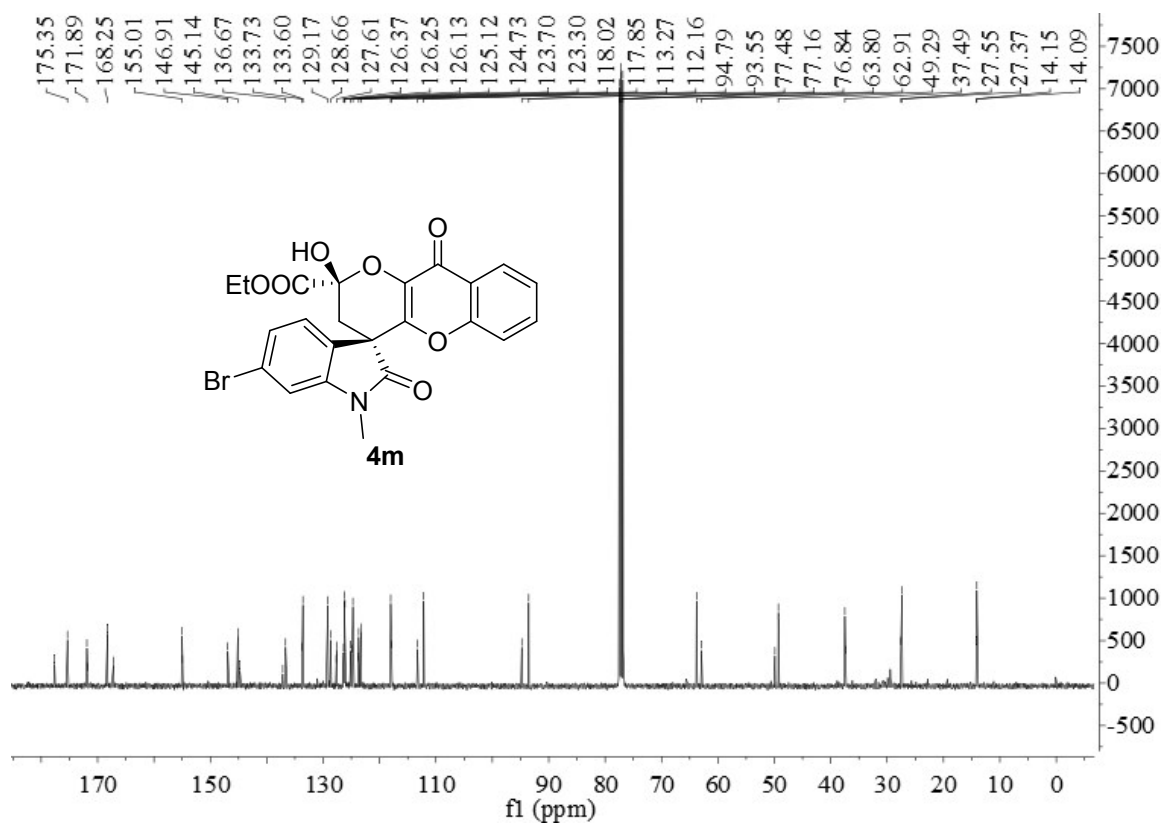
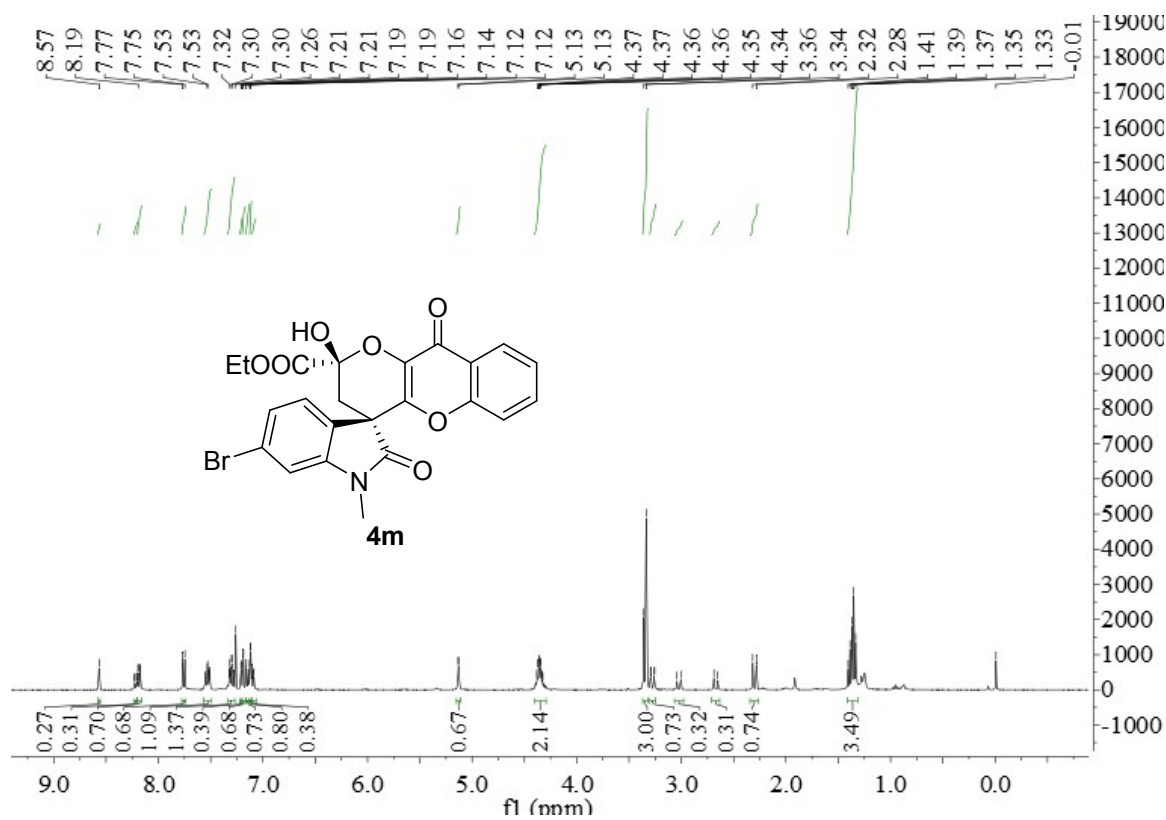
**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4I**



**Ethyl 6-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

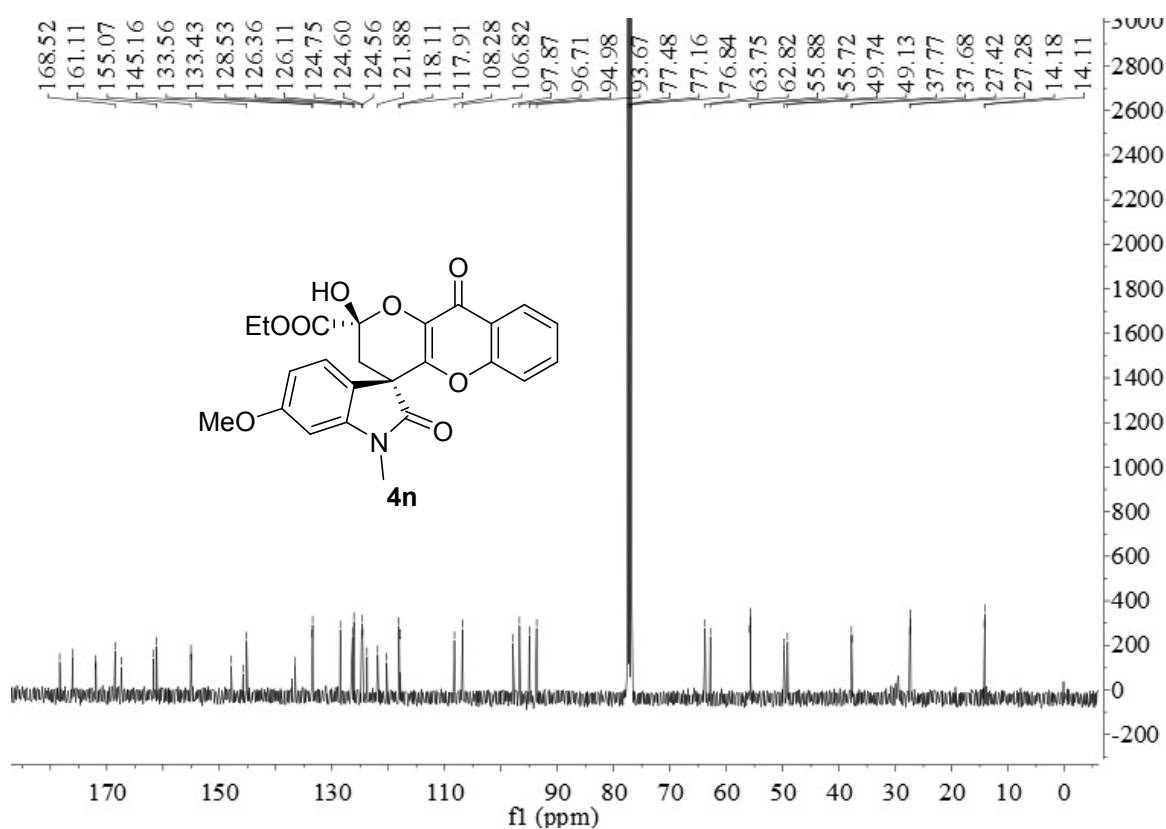
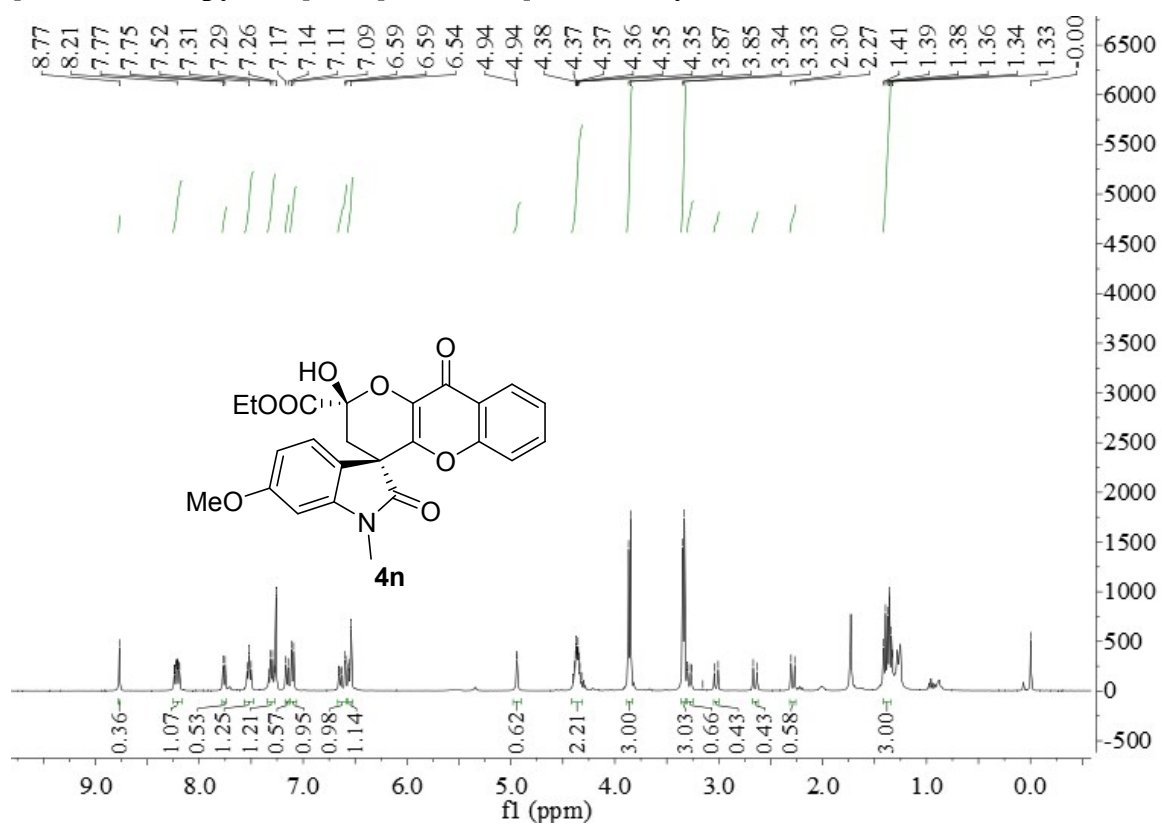


**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4m**



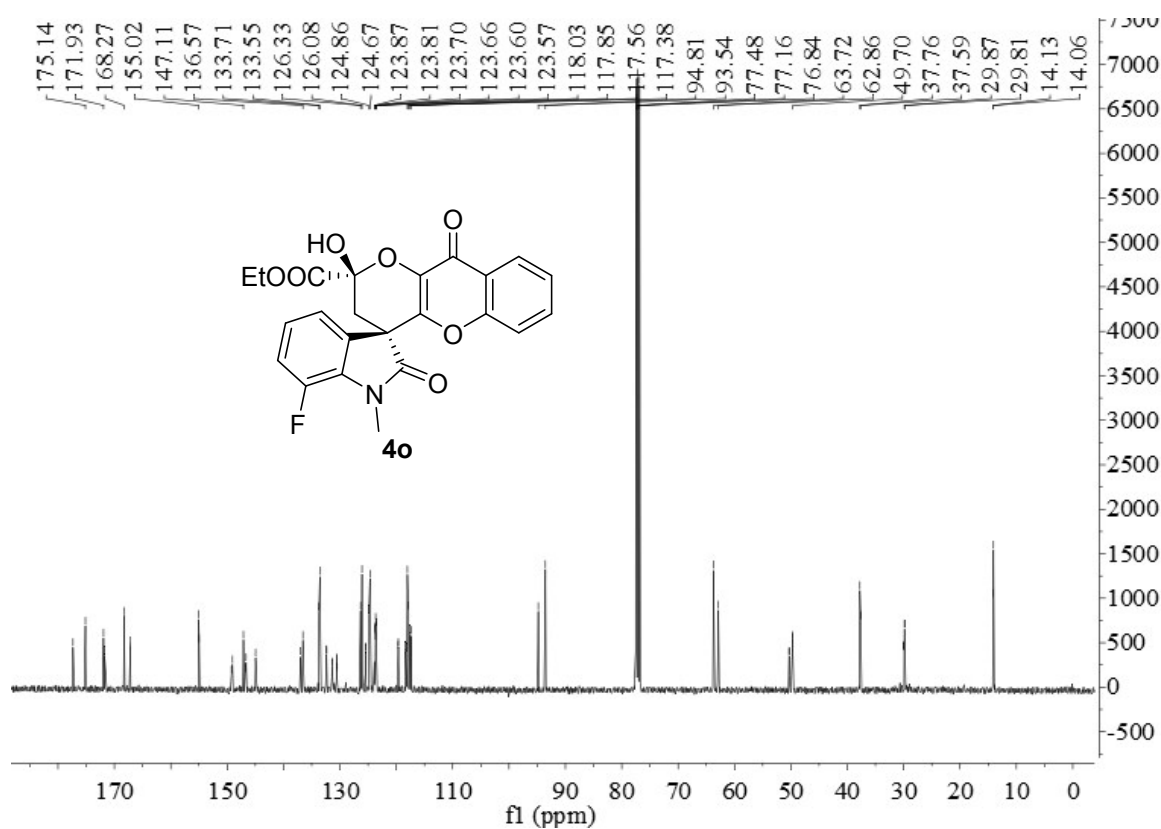
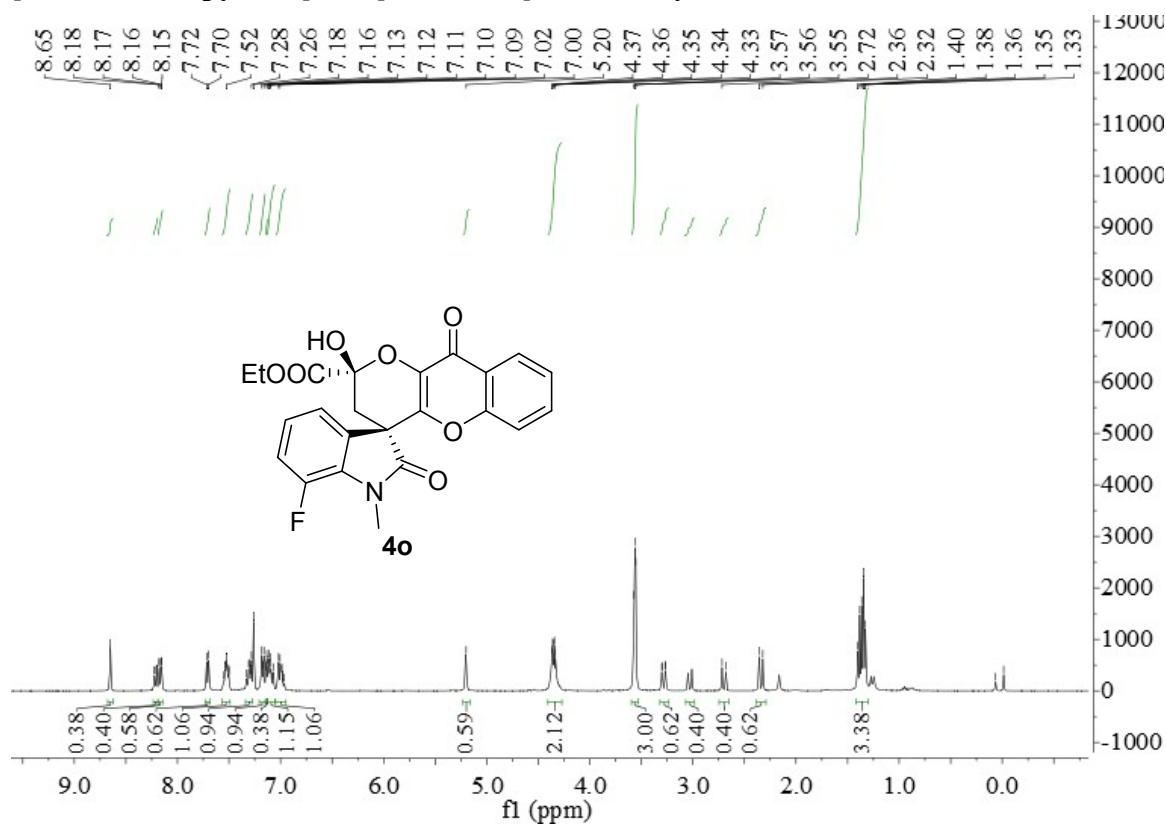
**Ethyl 2'-hydroxy-6-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4n**



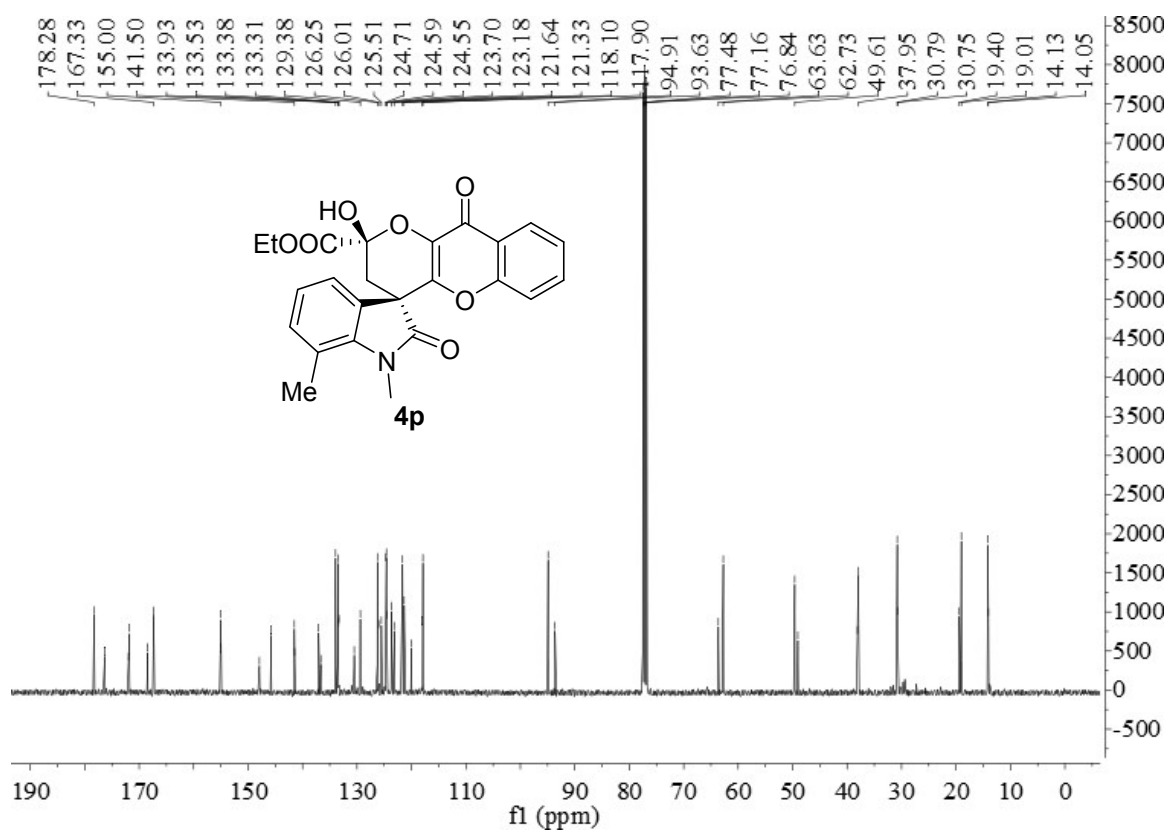
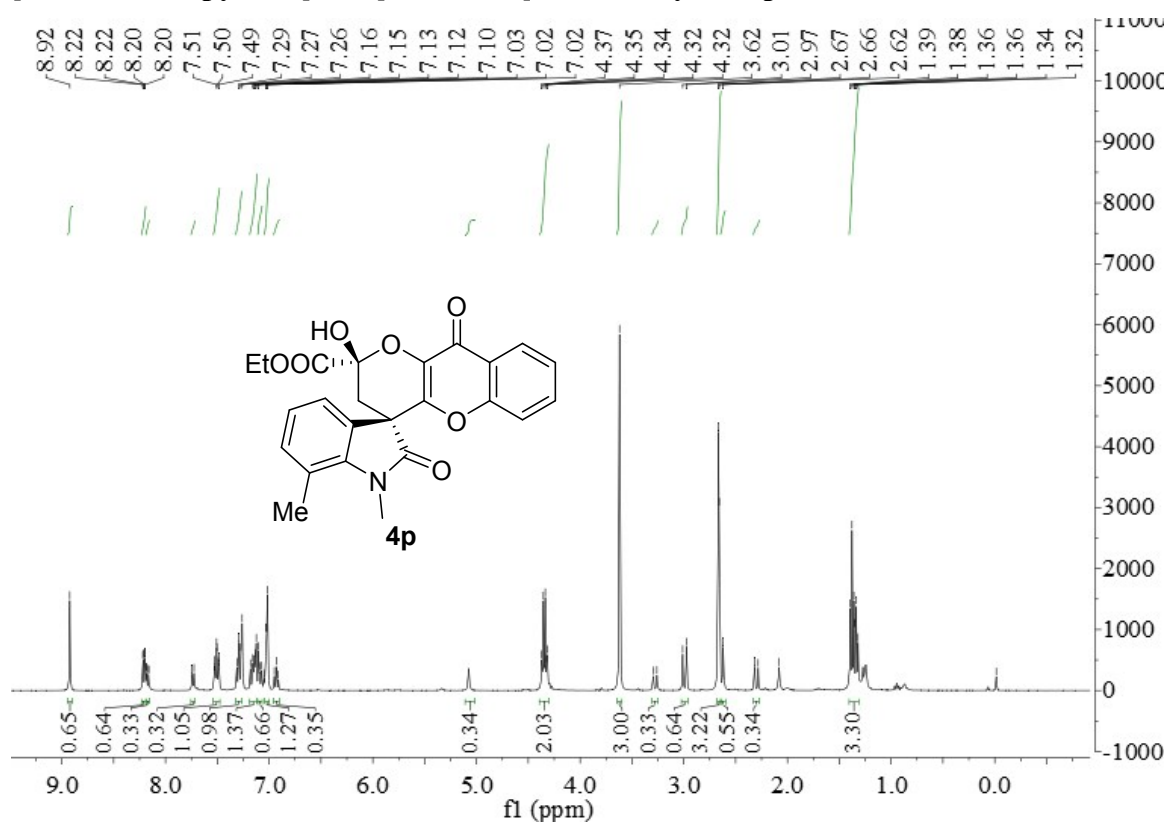
**Ethyl 7-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4o**



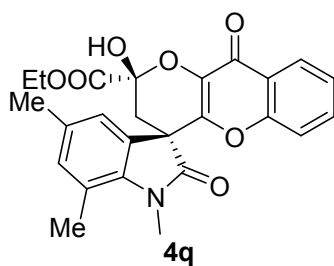
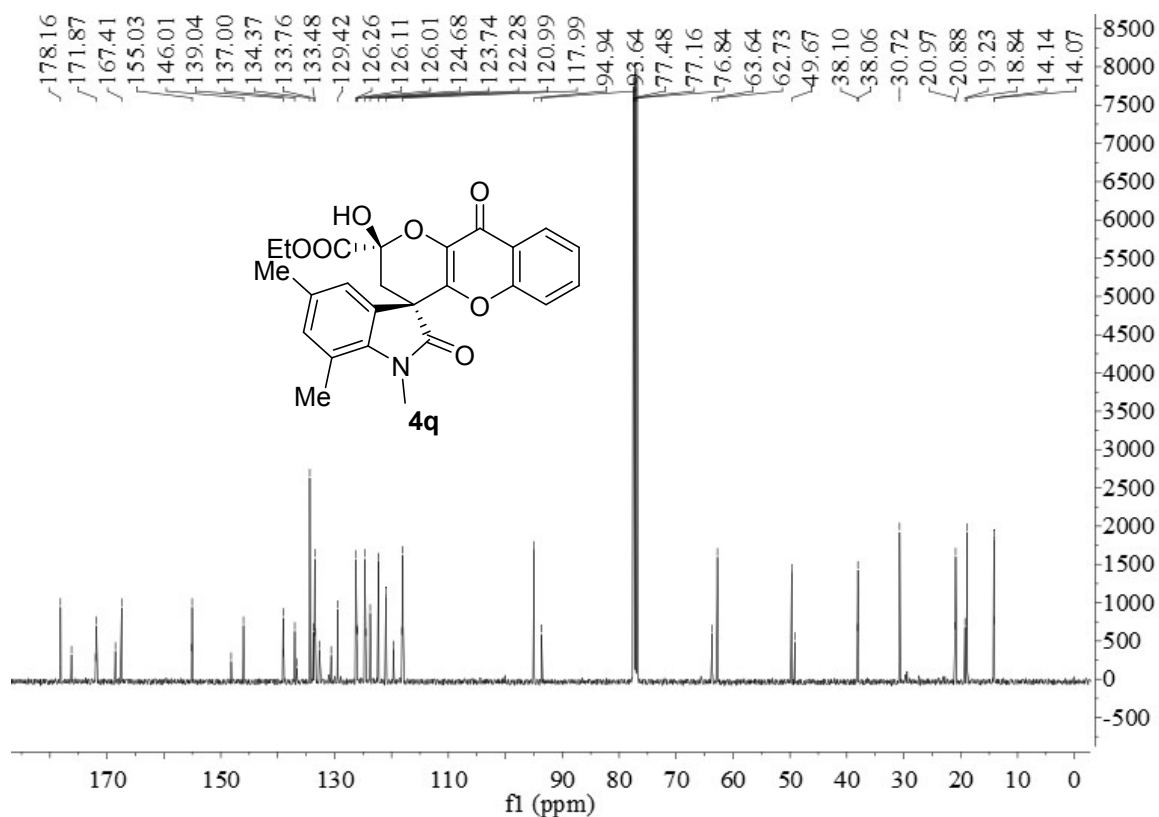
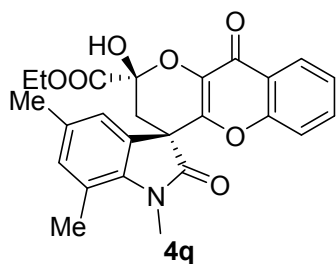
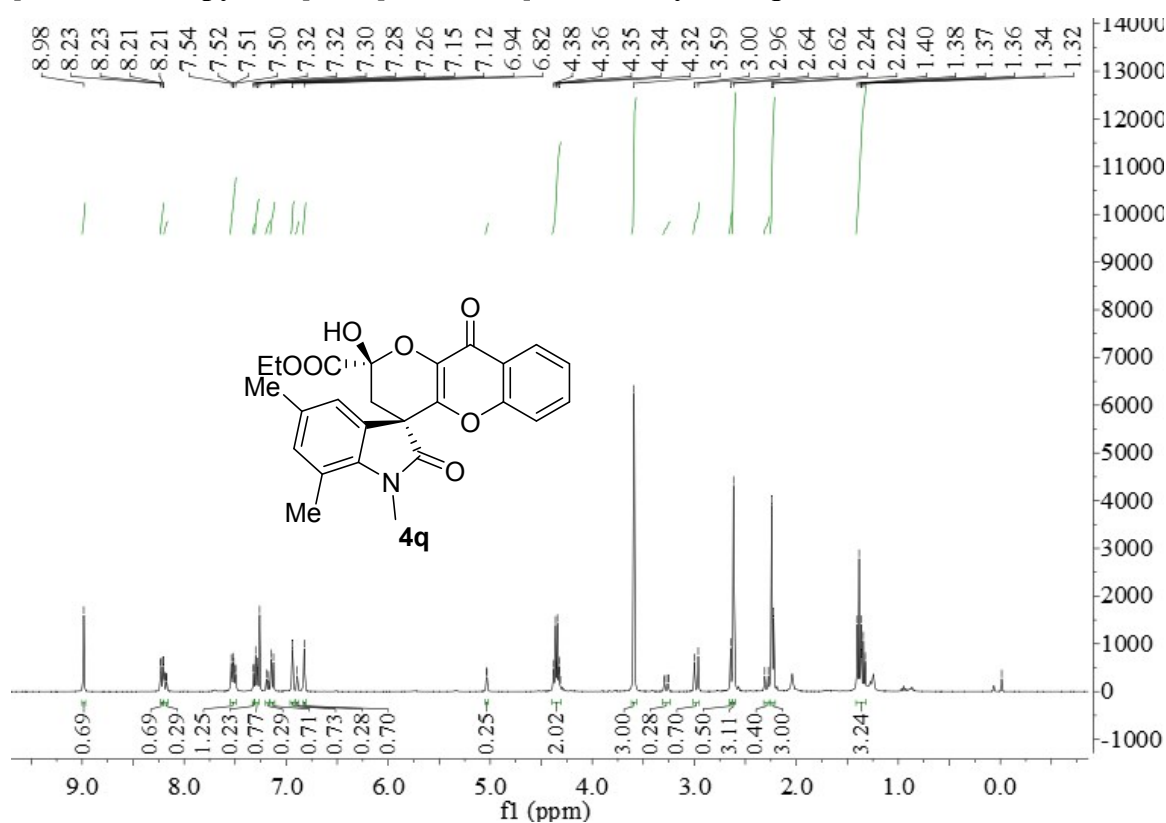
**Ethyl 2'-hydroxy-1,7-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4p**



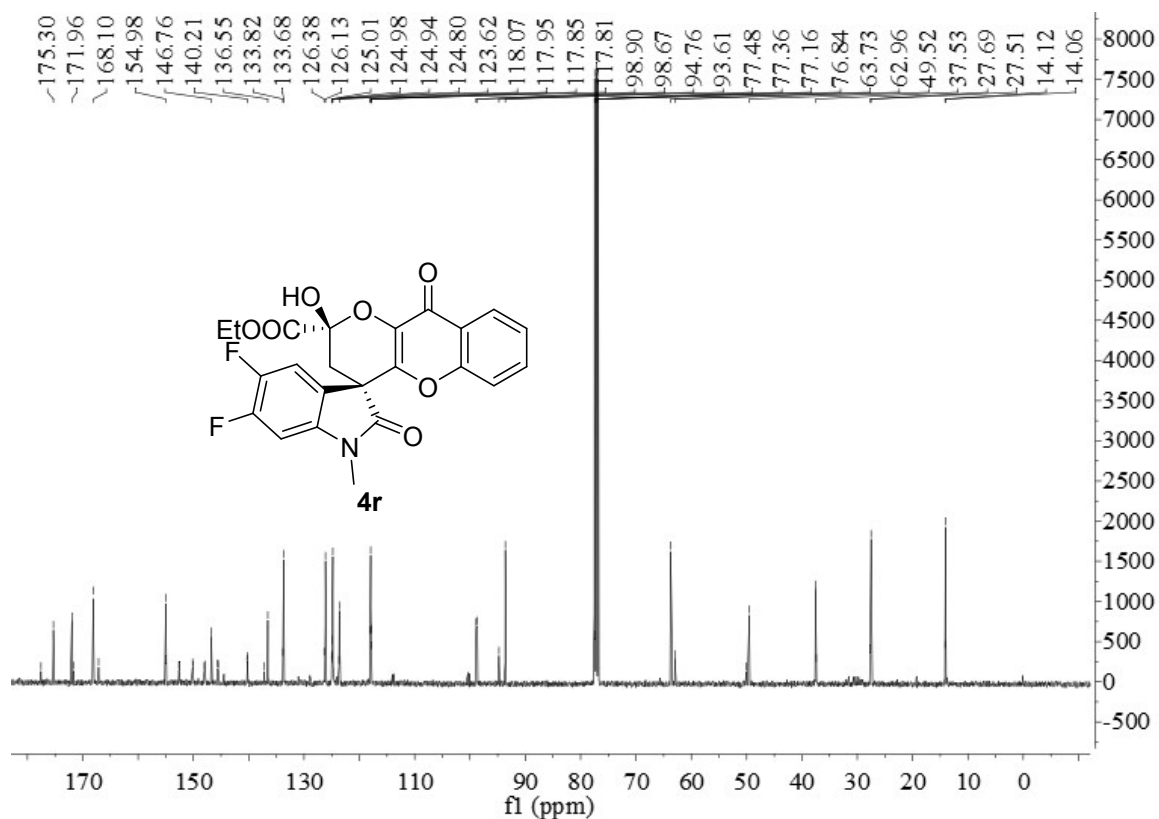
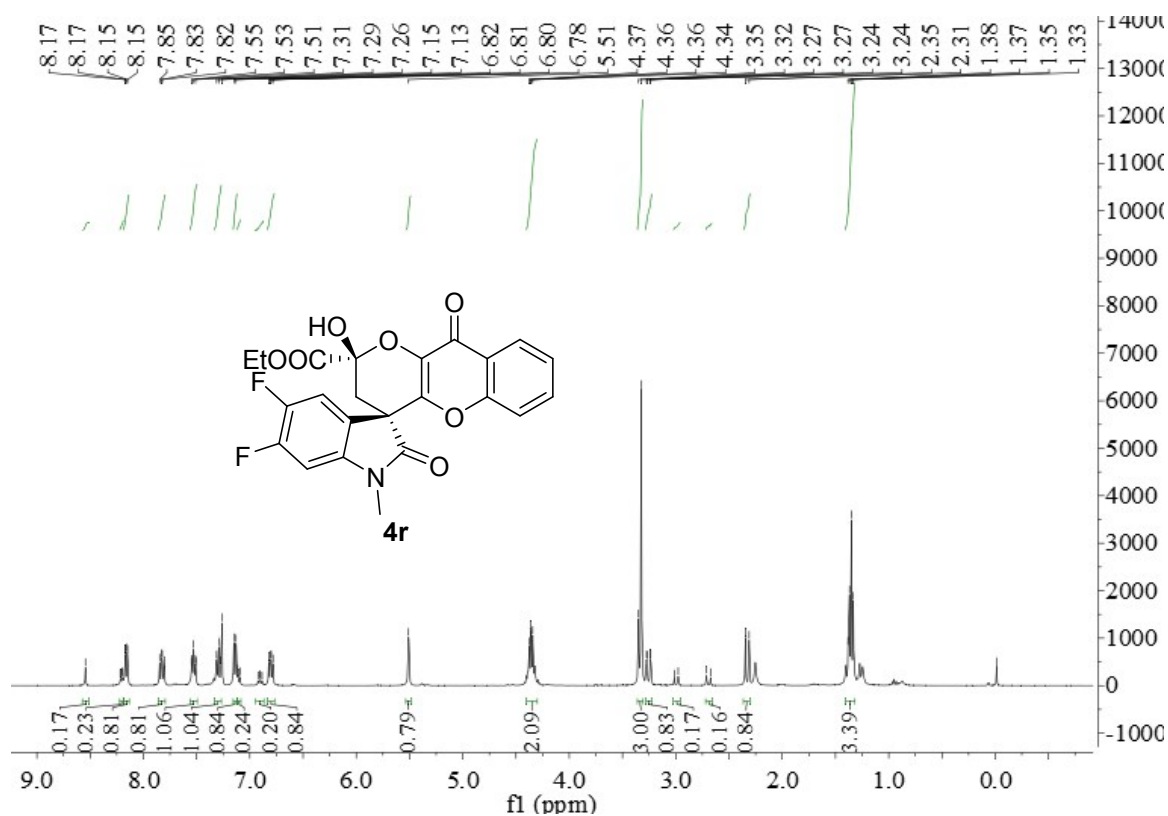
**Ethyl 2'-hydroxy-1,5,7-trimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4q**



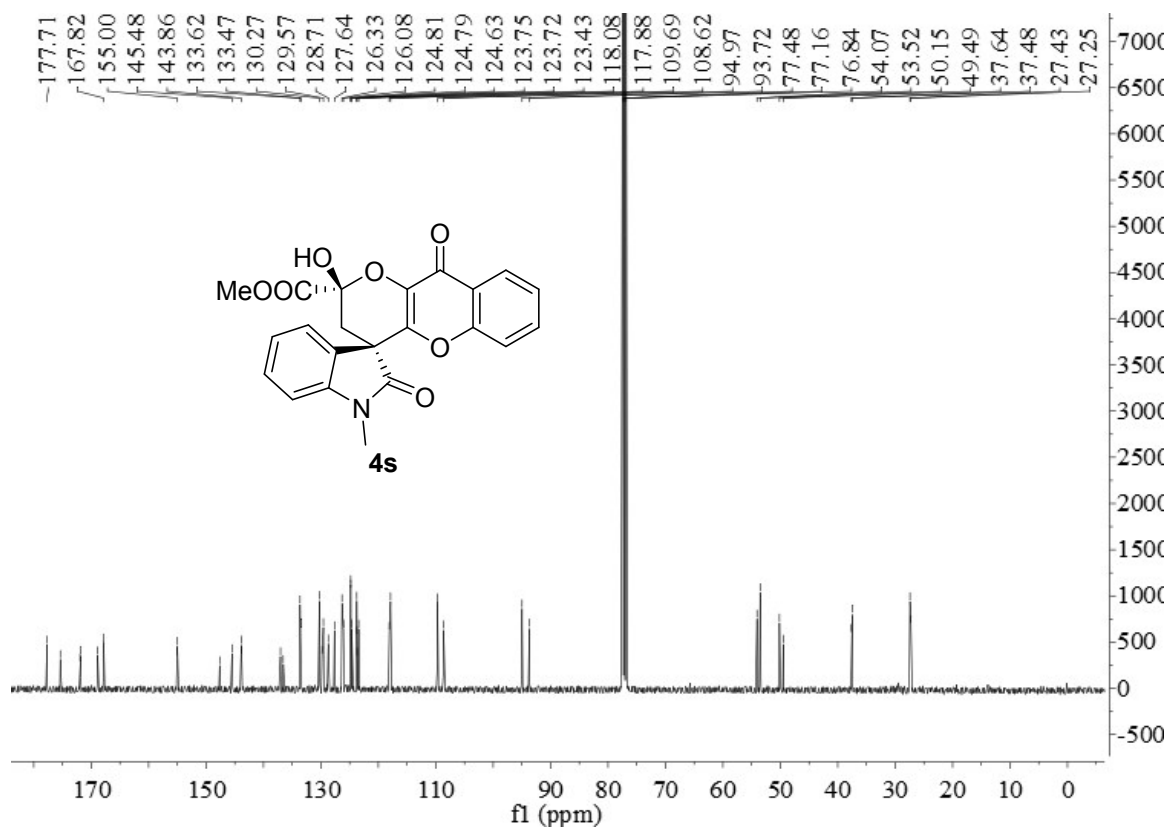
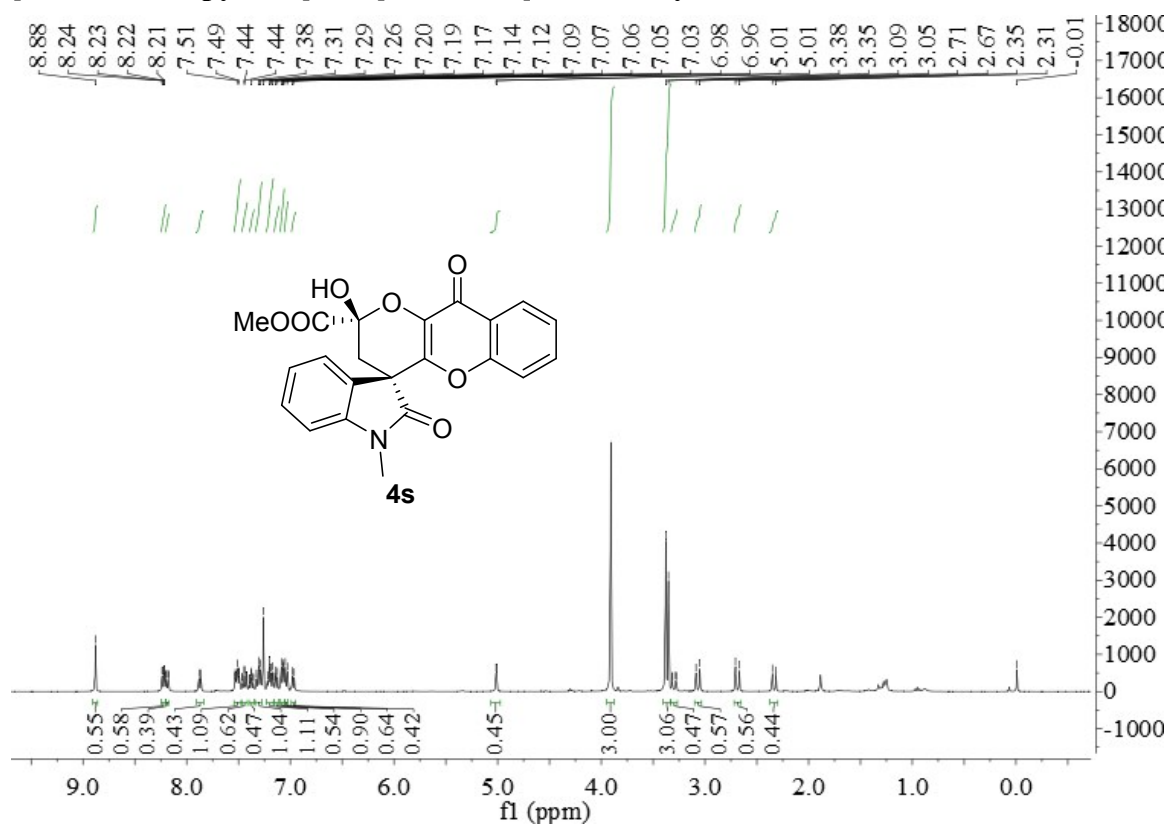
**Ethyl 5,6-difluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4r**



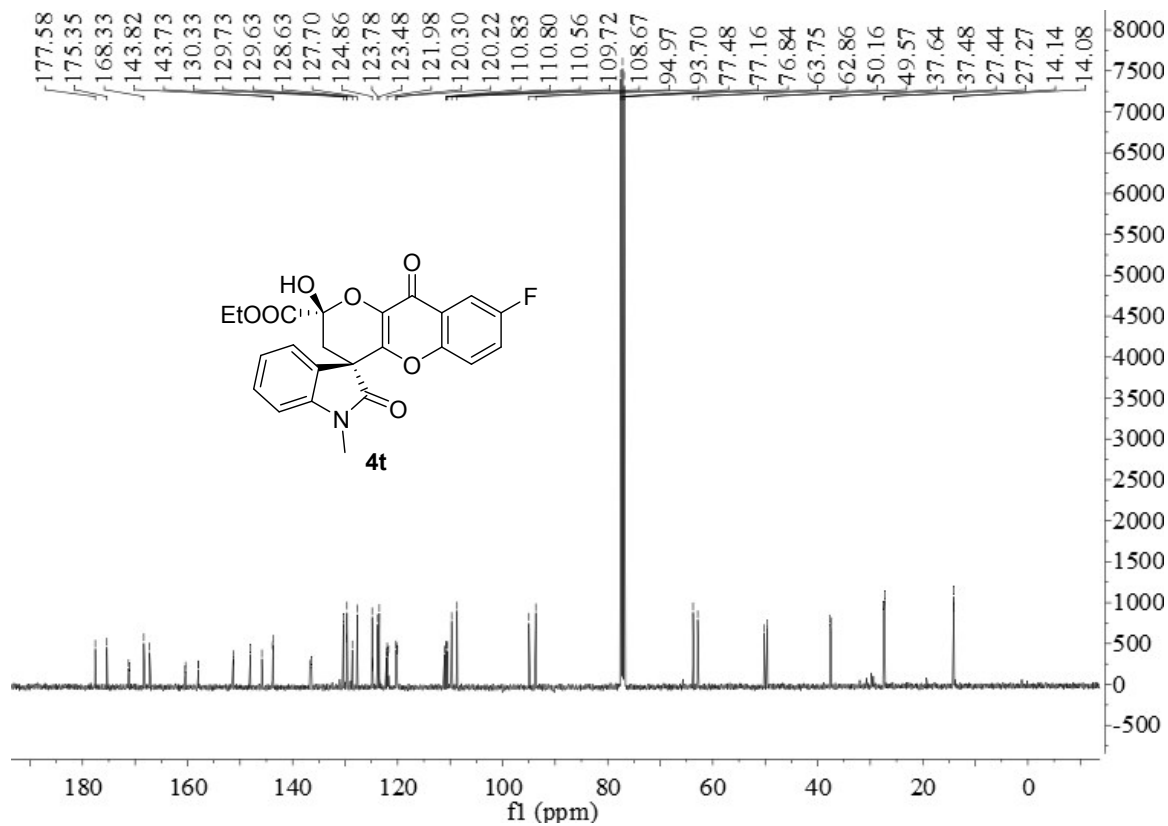
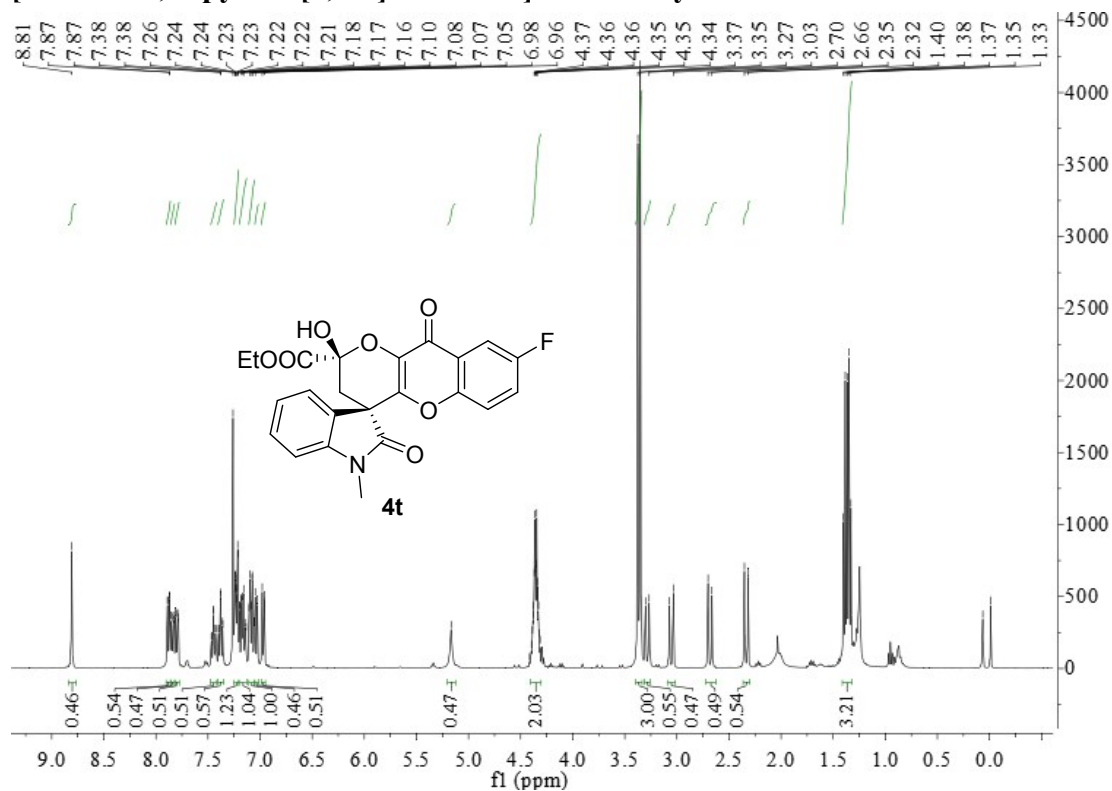
**Methyl 2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4s**



**Ethyl 8'-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

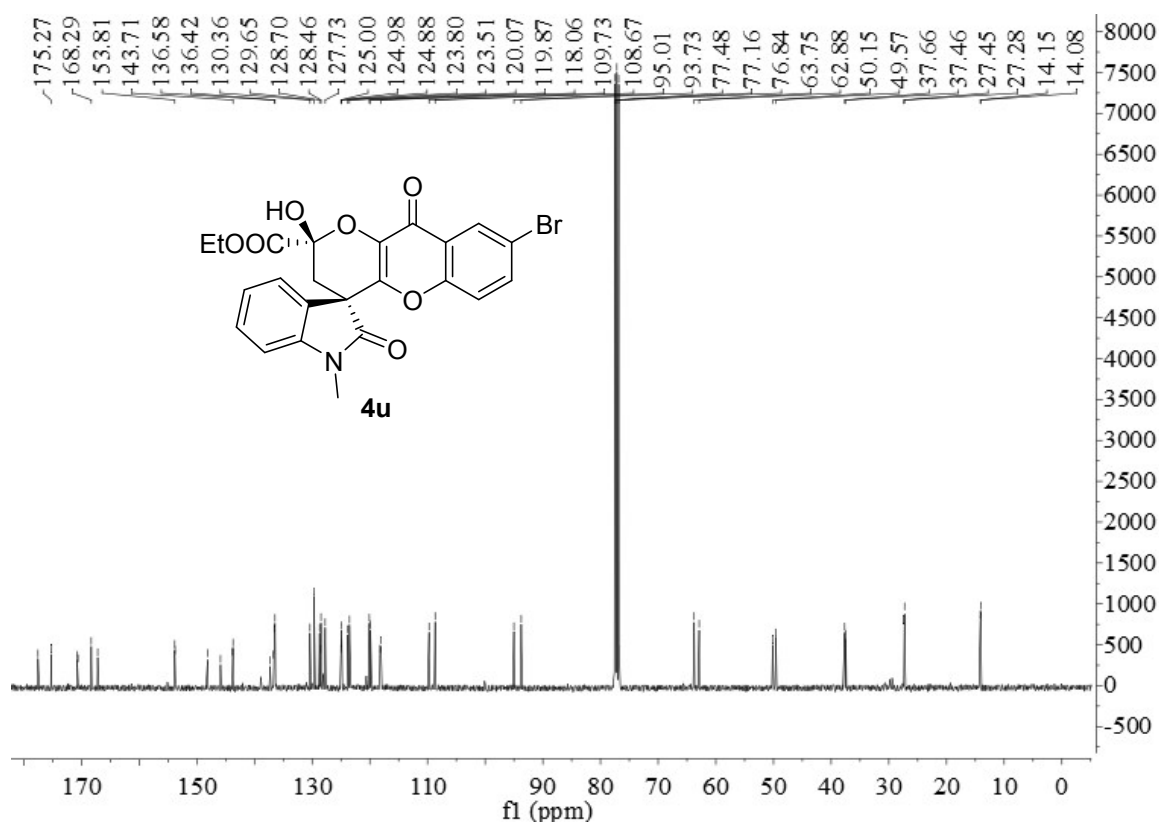
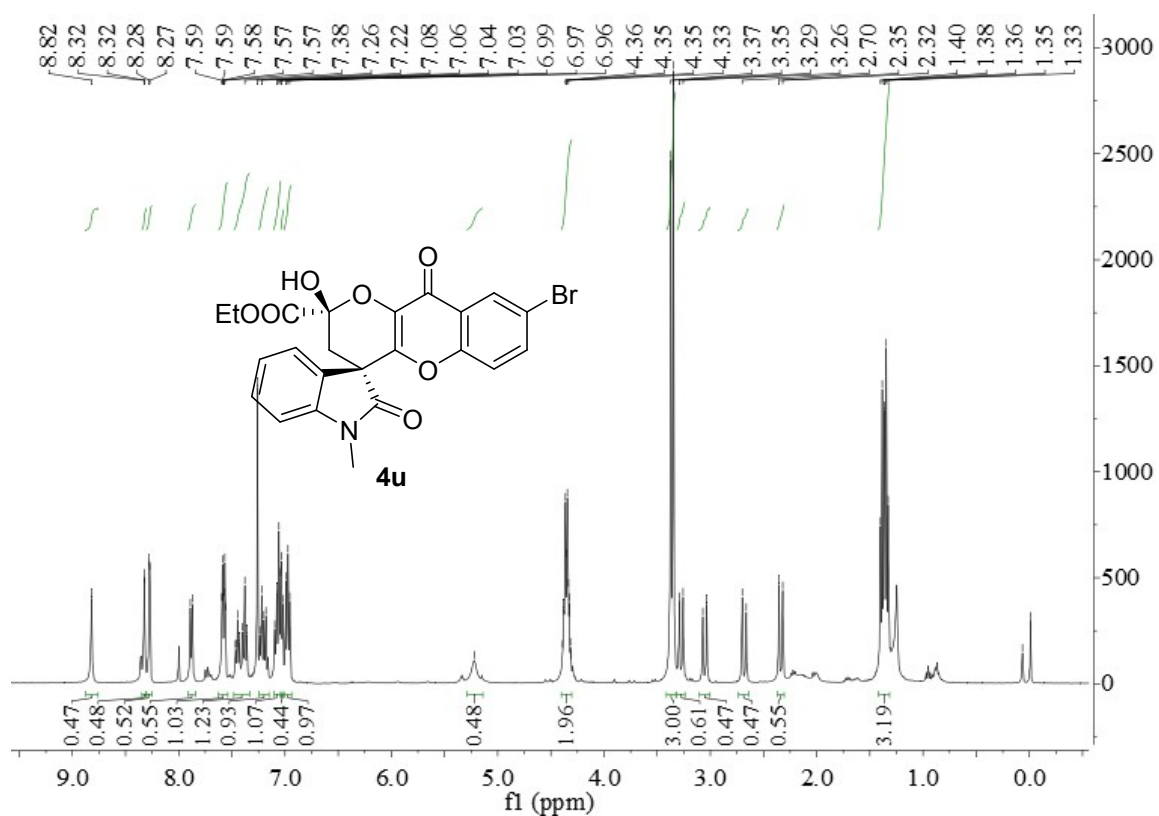
**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4t**



**Ethyl 8'-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

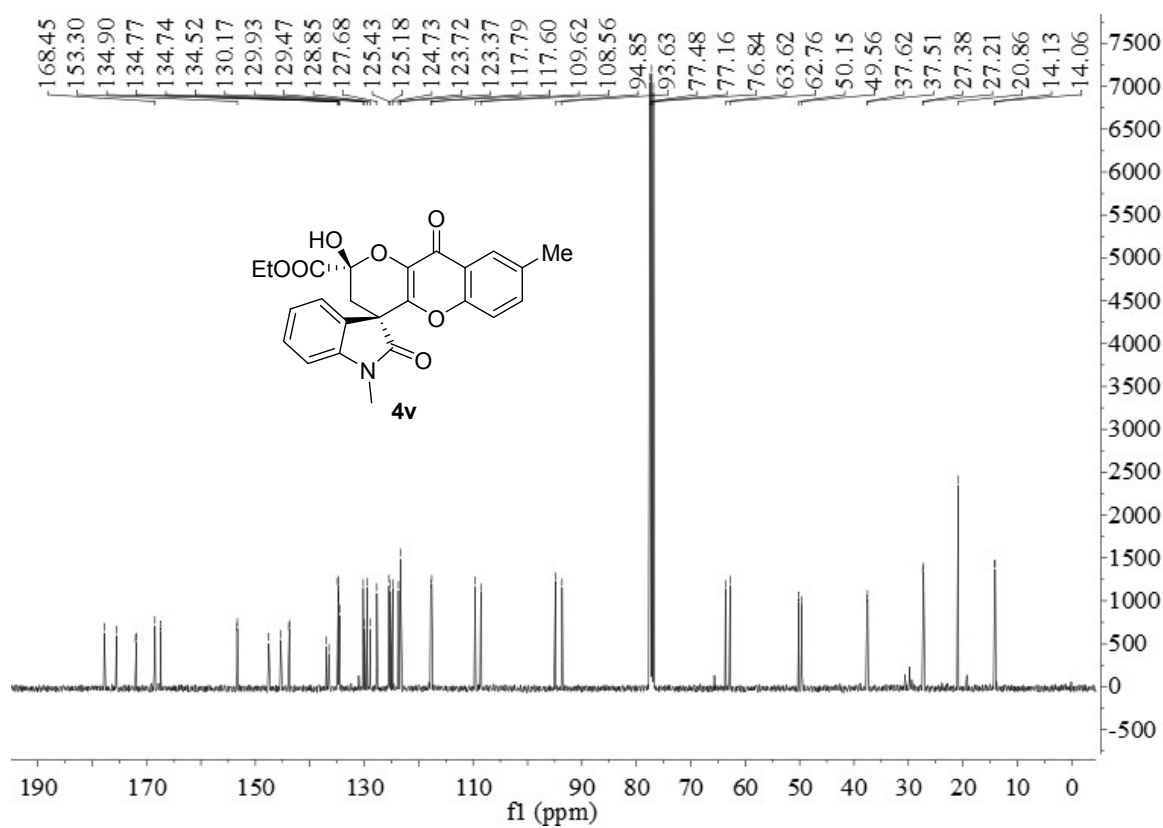
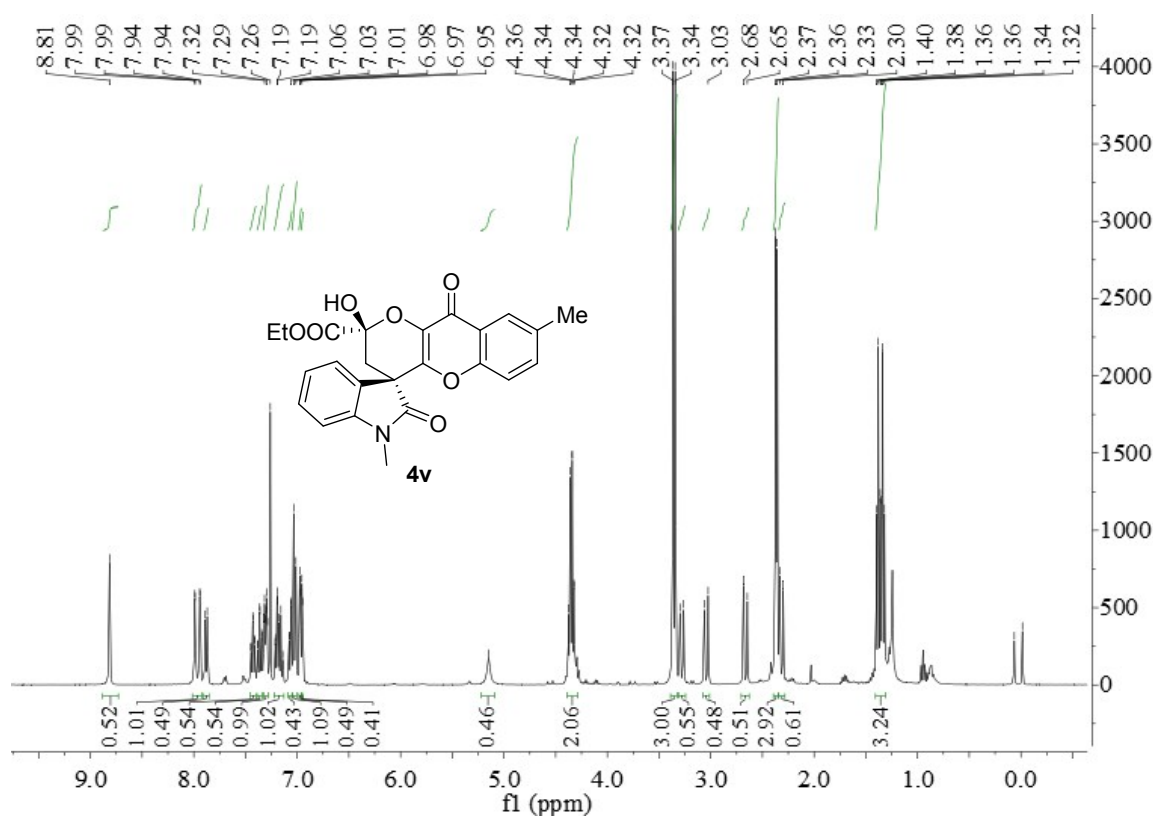


**[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4u**



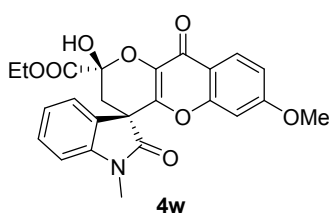
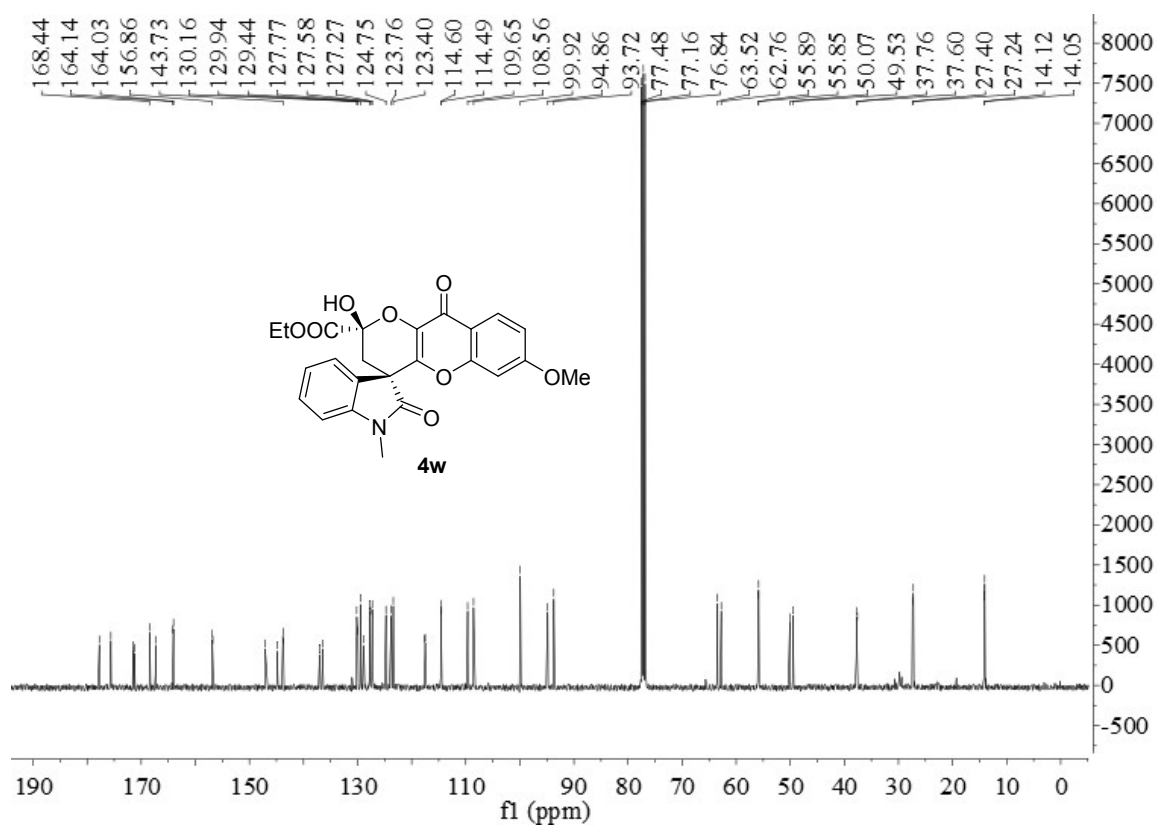
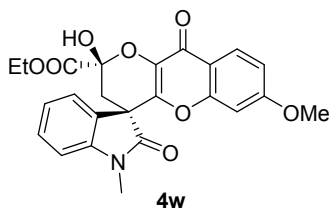
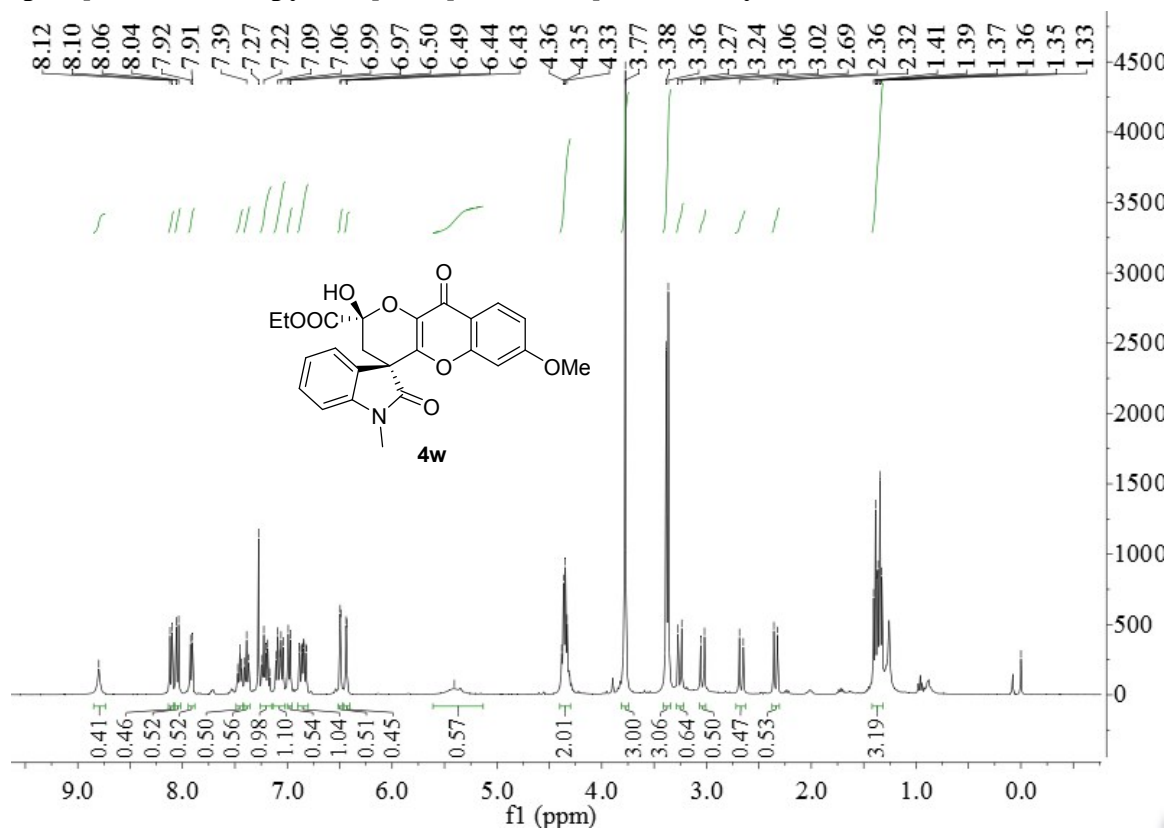
**Ethyl 2'-hydroxy-1,8'-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro**

**[indoline-3,4'-pyrano[3,2-*b*]-chromene]-2'-carboxylate 4v**

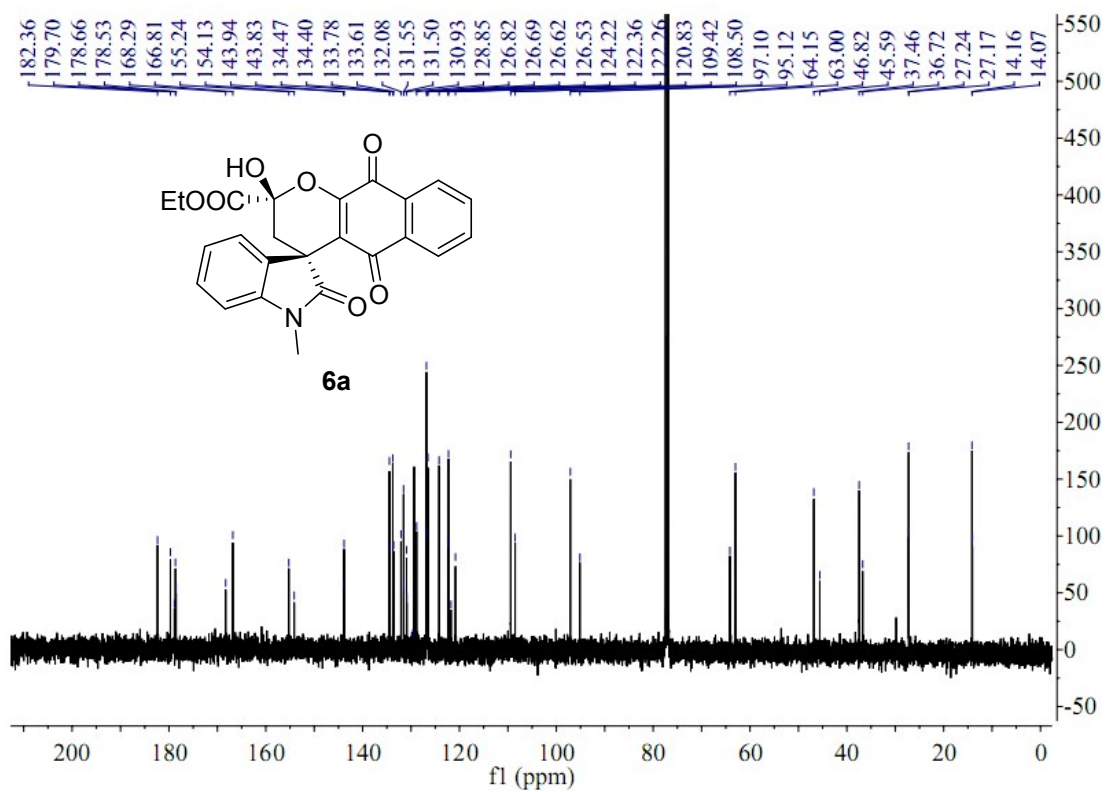
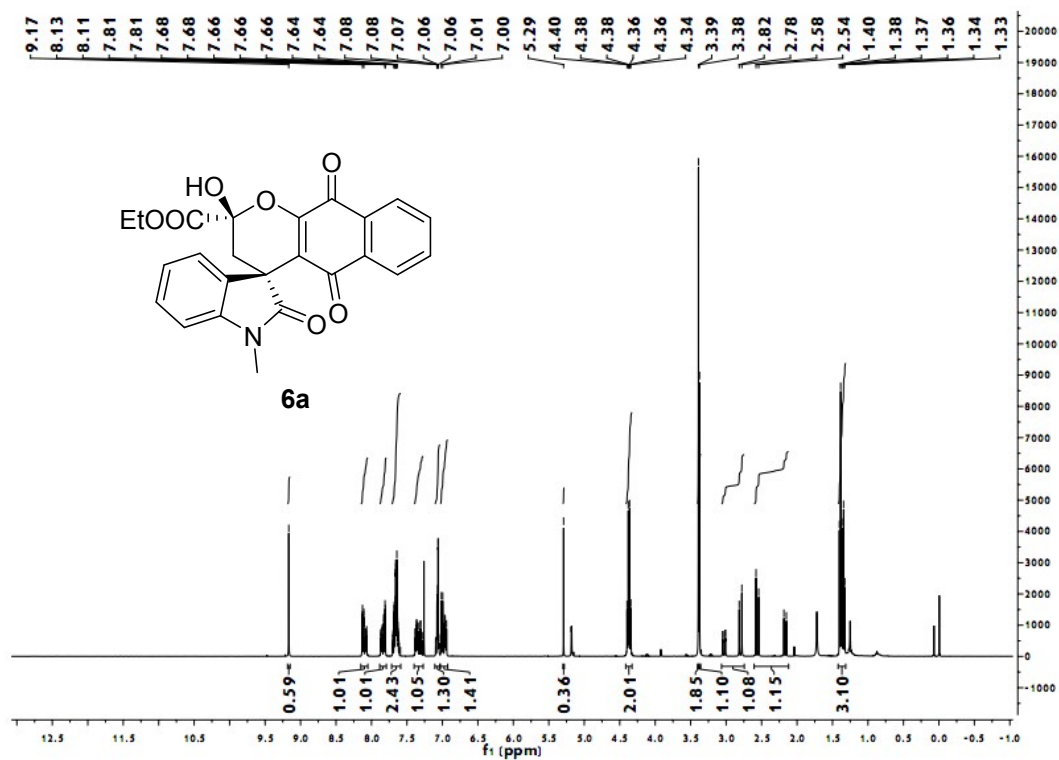


**Ethyl2'-hydroxy-7'-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-**

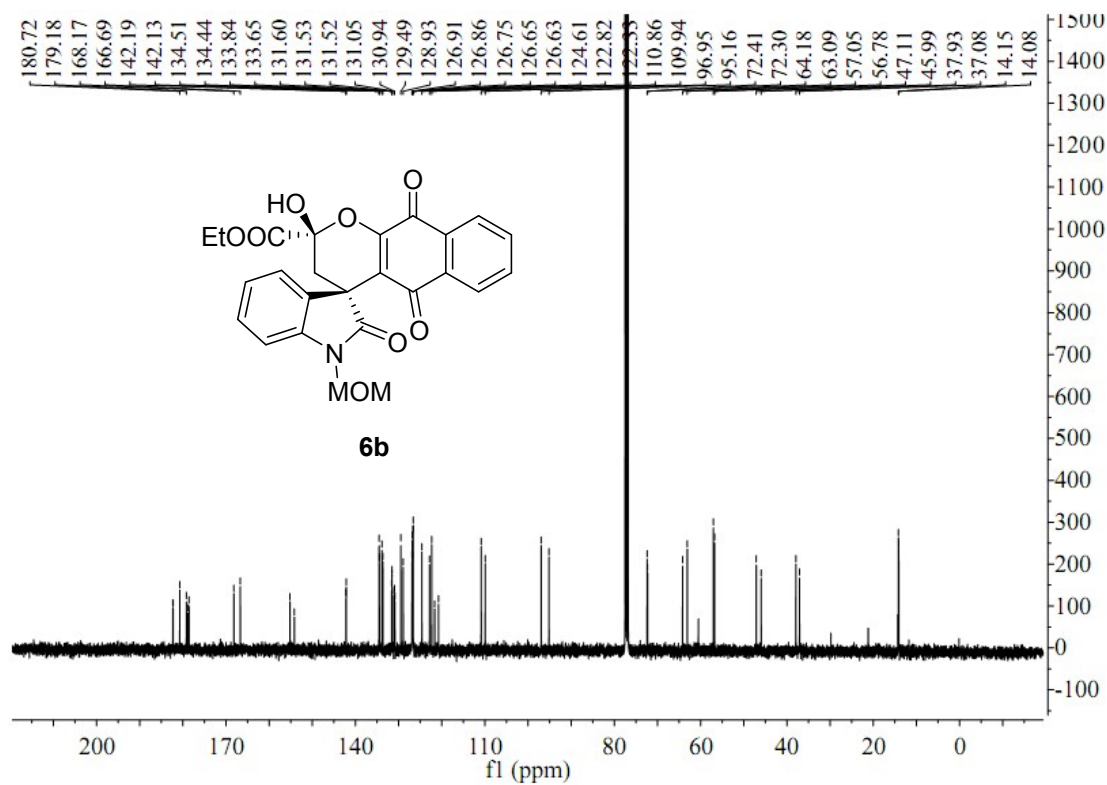
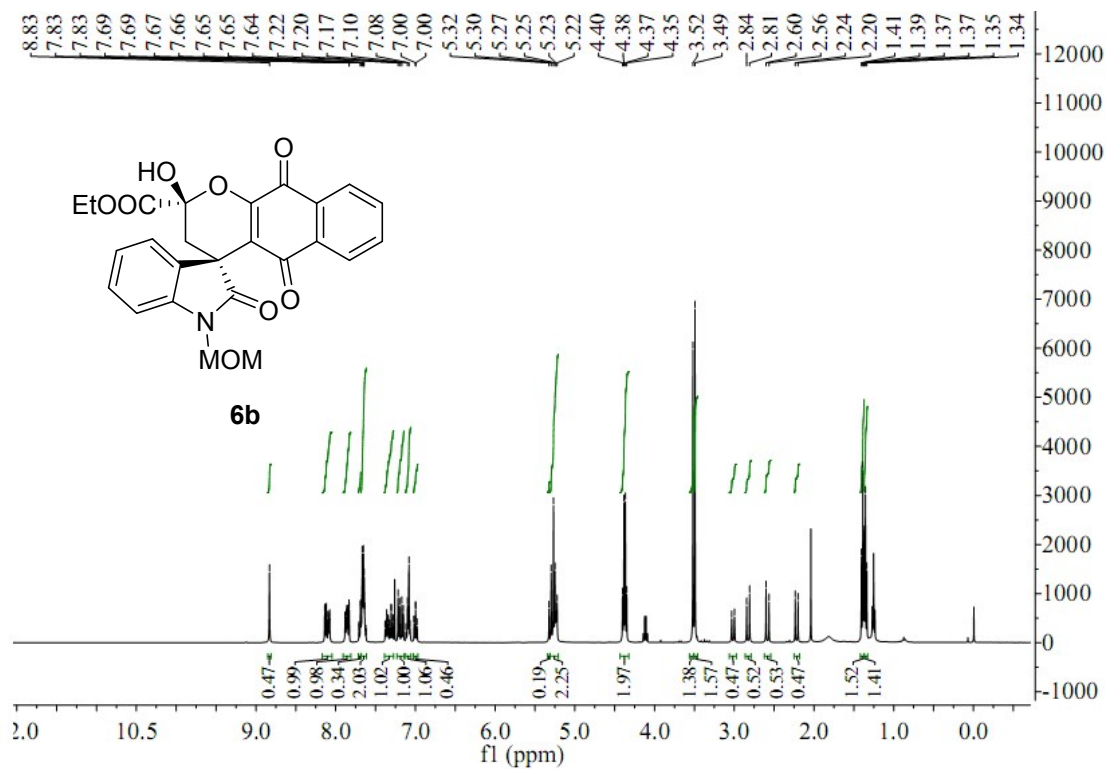
spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4w



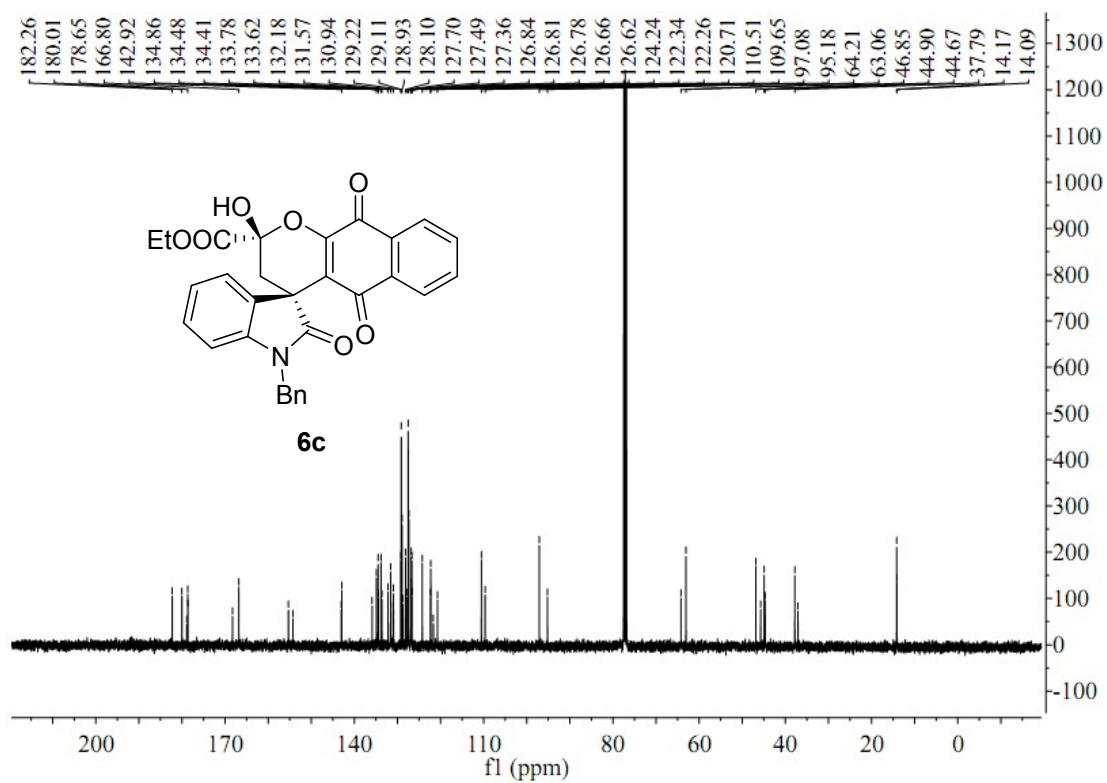
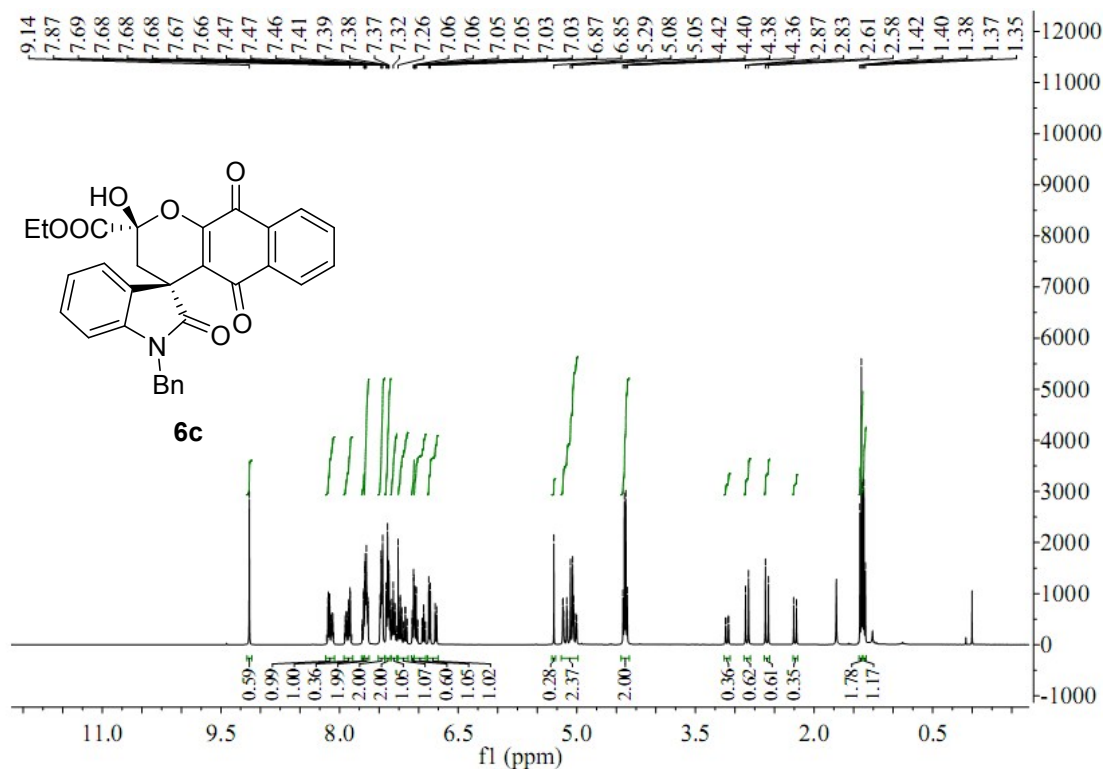
**Ethyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6a**



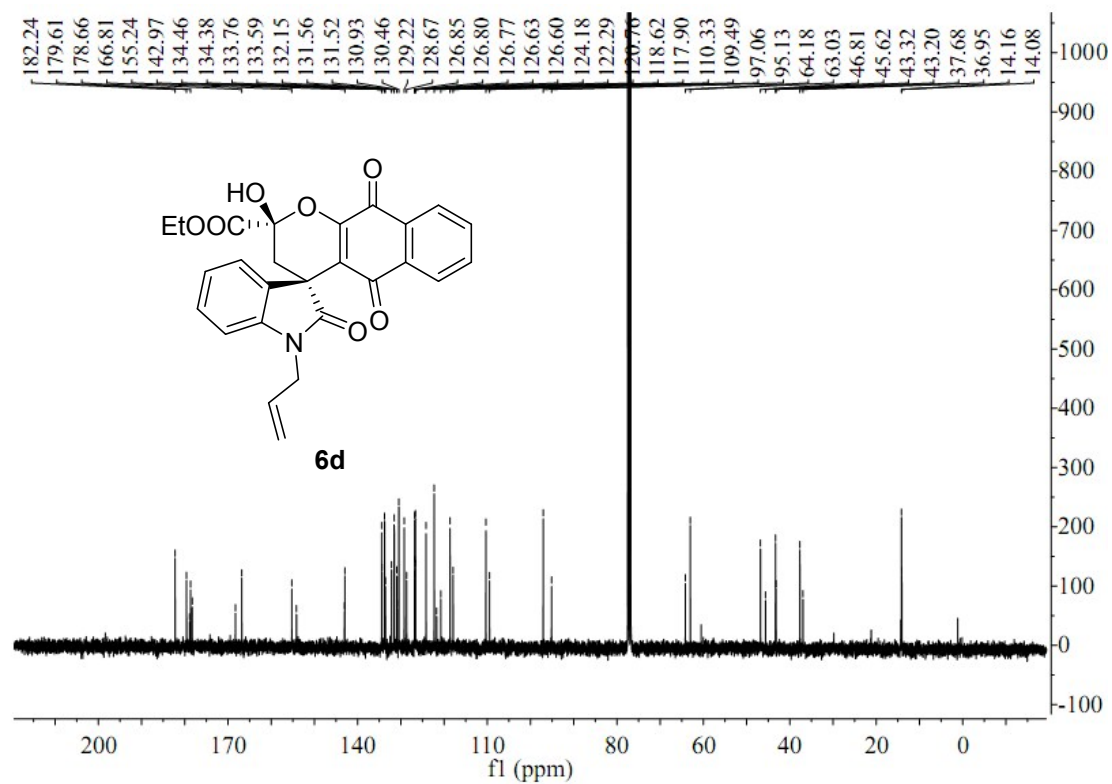
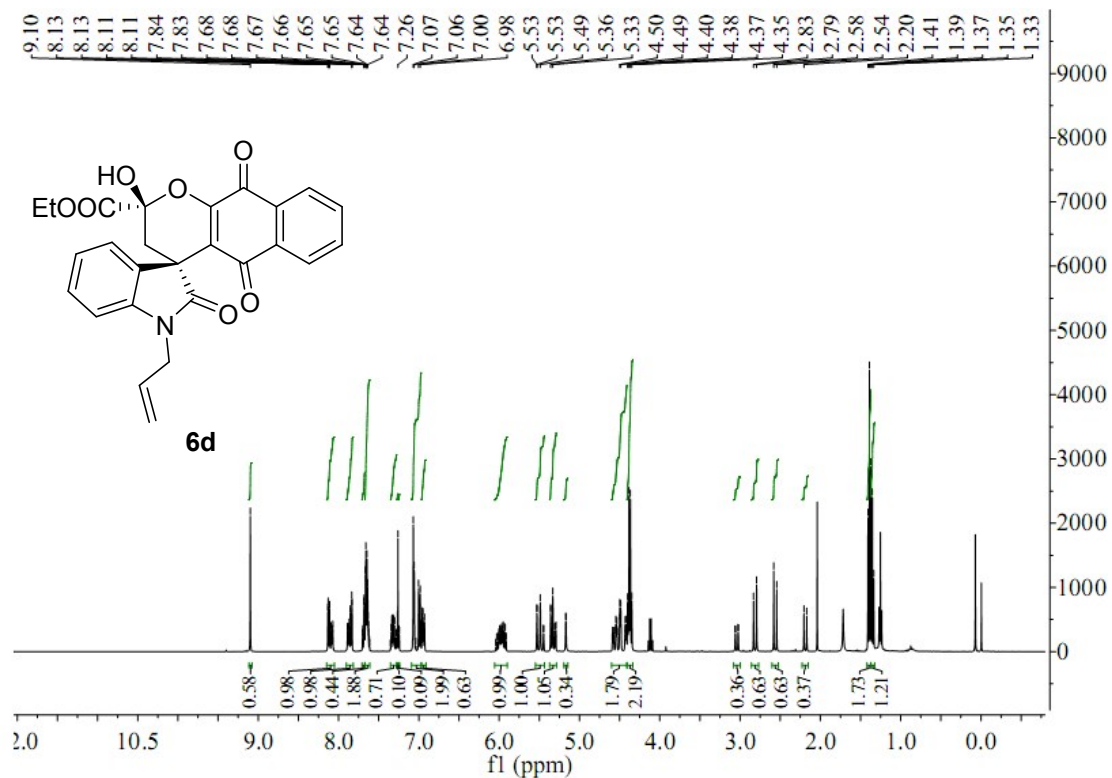
**Ethyl-2-hydroxy-1'-(methoxymethyl)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6b**



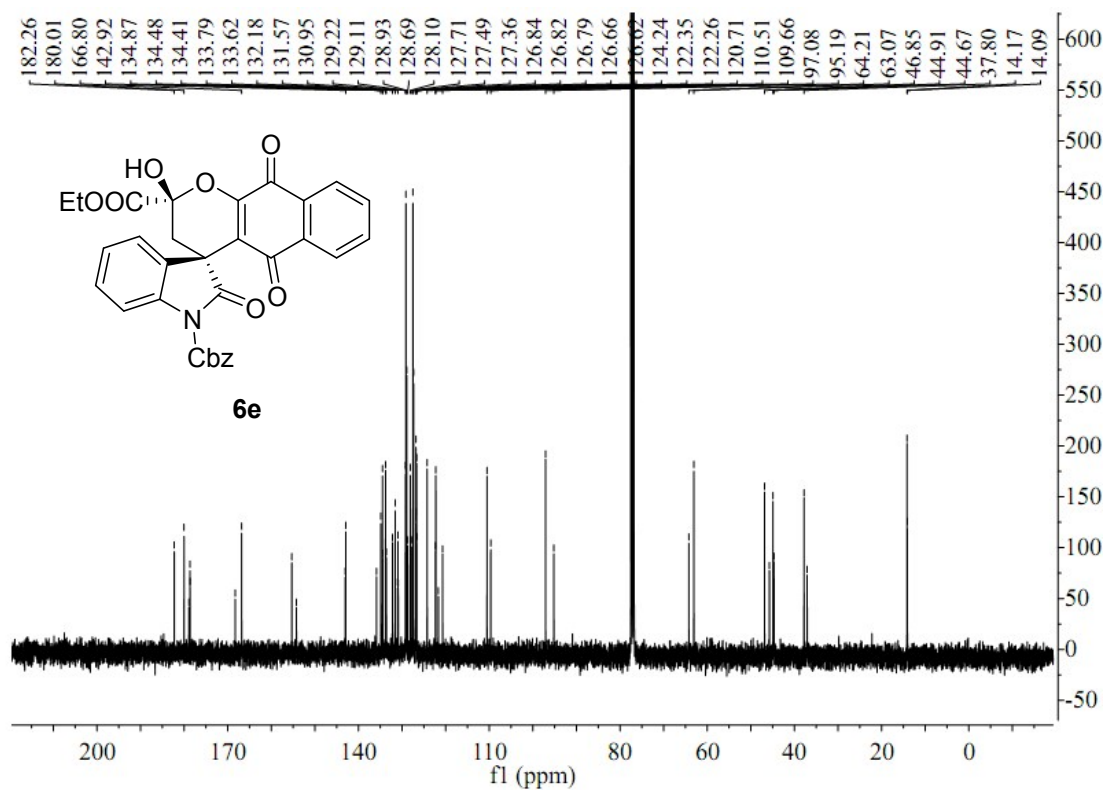
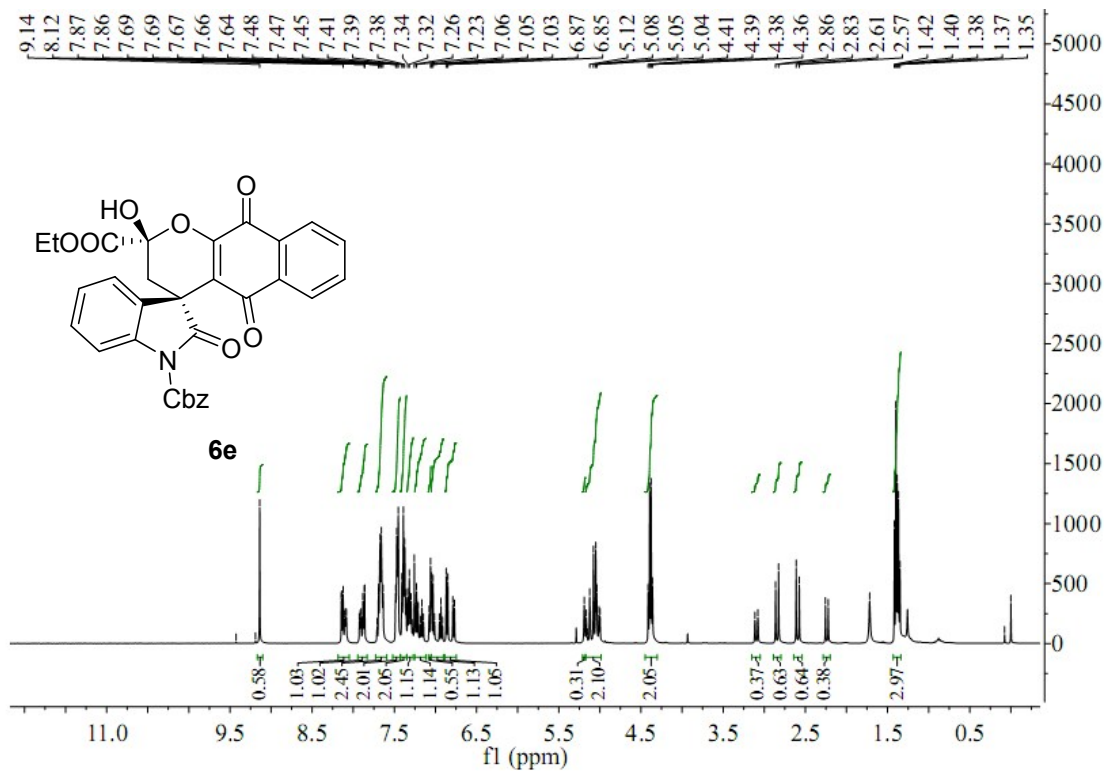
**Ethyl-1'-benzyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6c**



**Ethyl-1'-allyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6d**

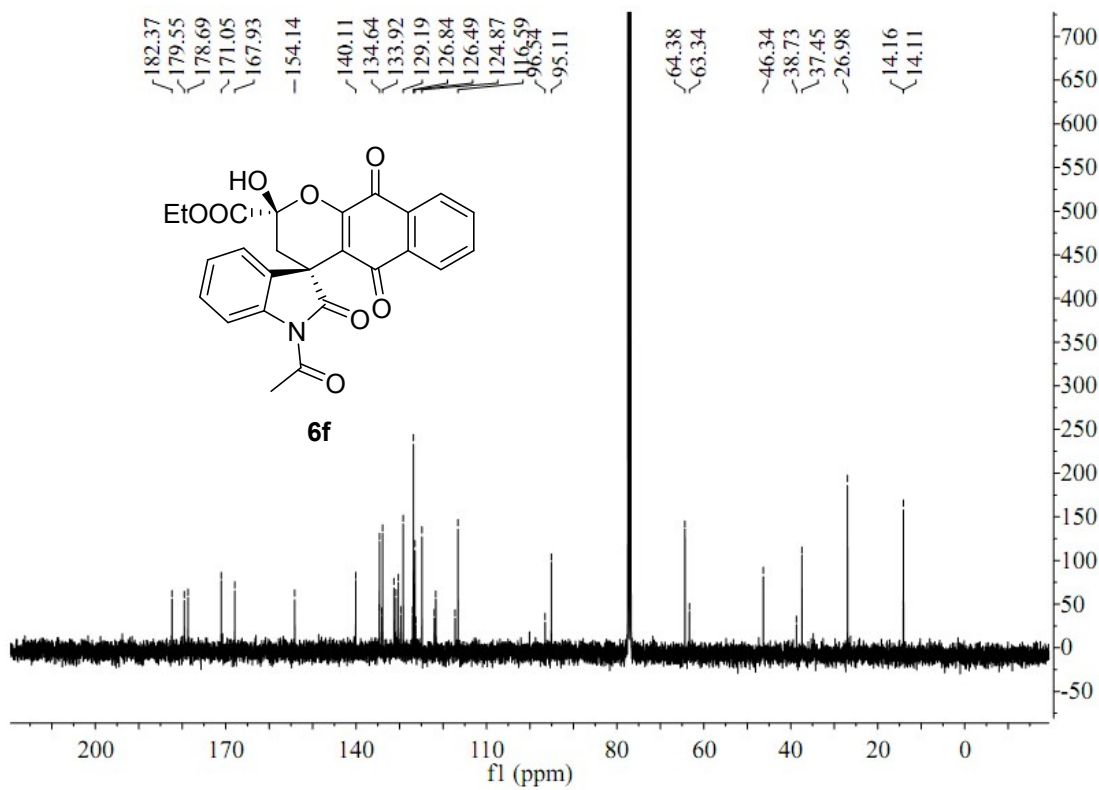
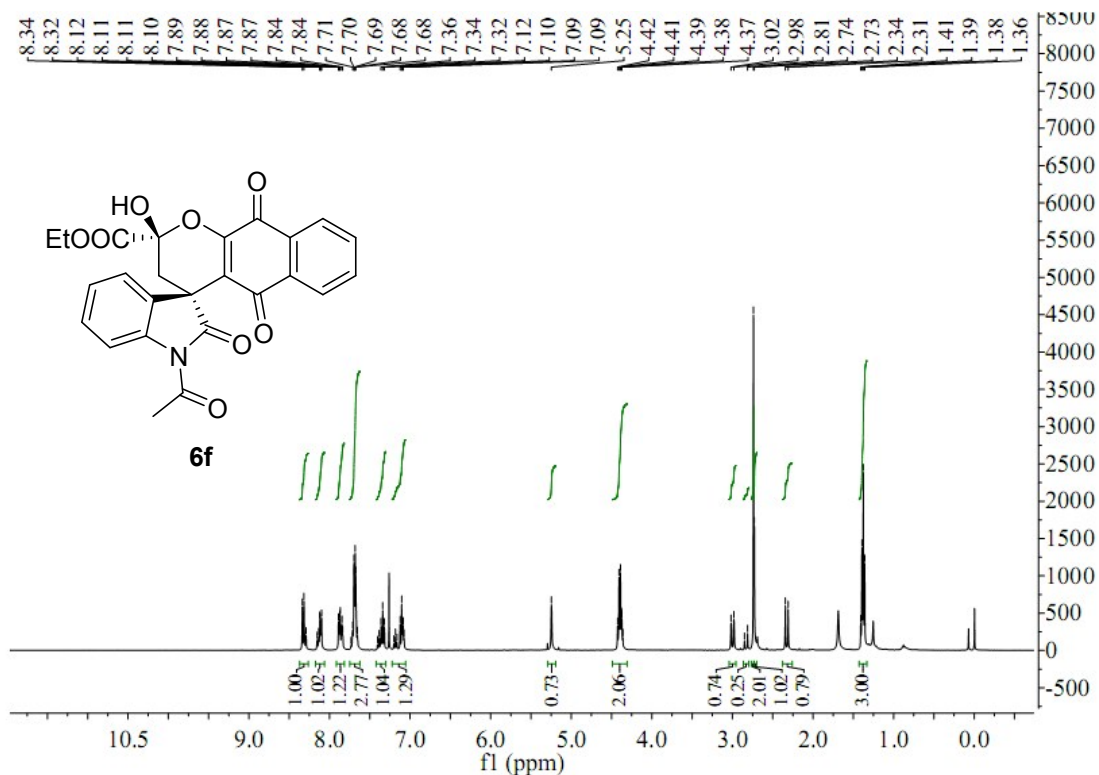


**1'-benzyl-2-ethyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-1',2-dicarboxylate 6e**

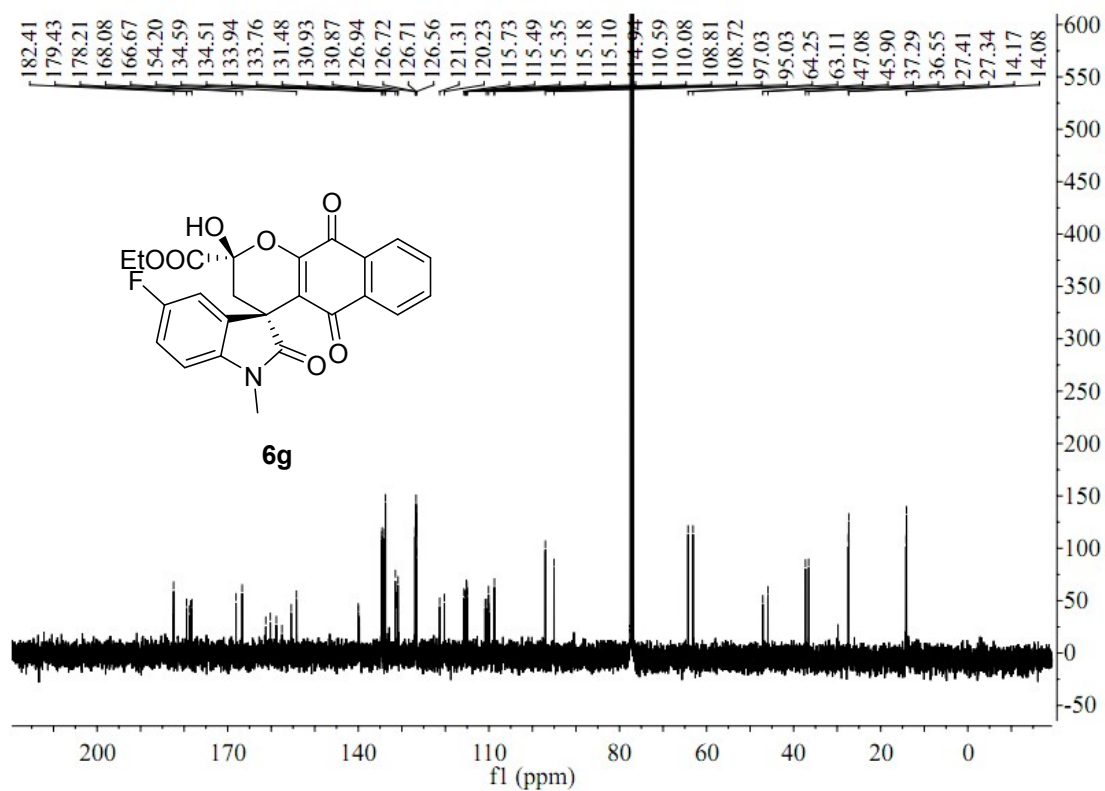
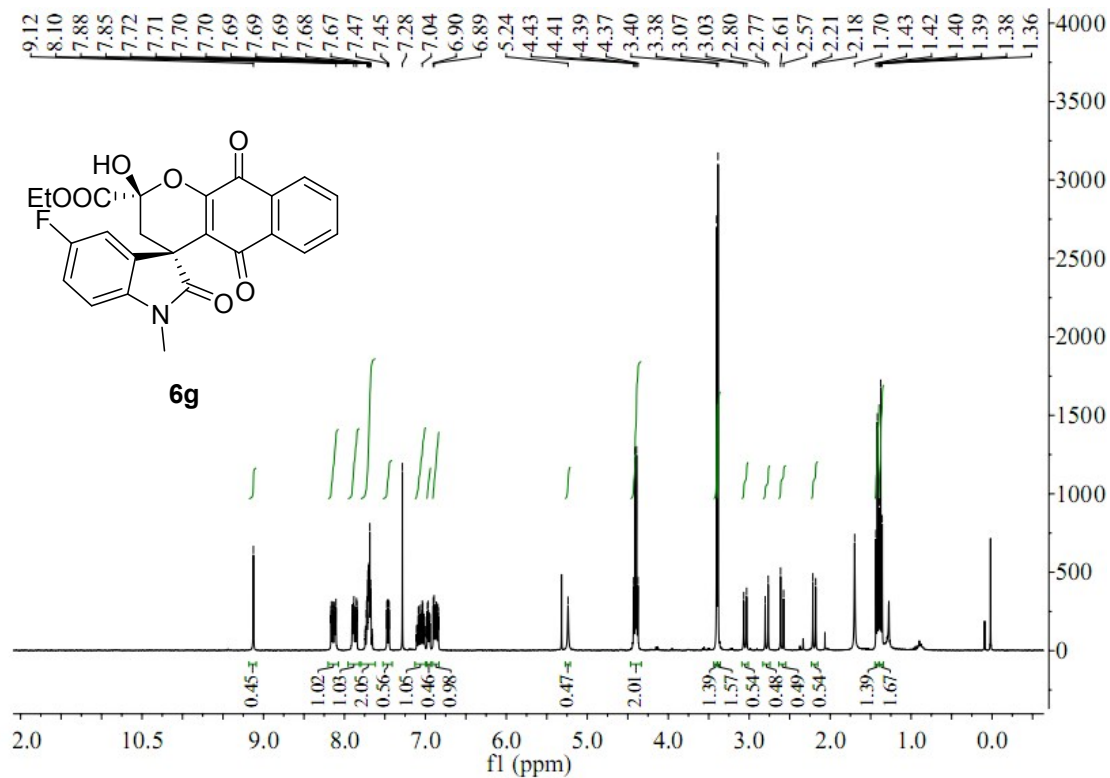




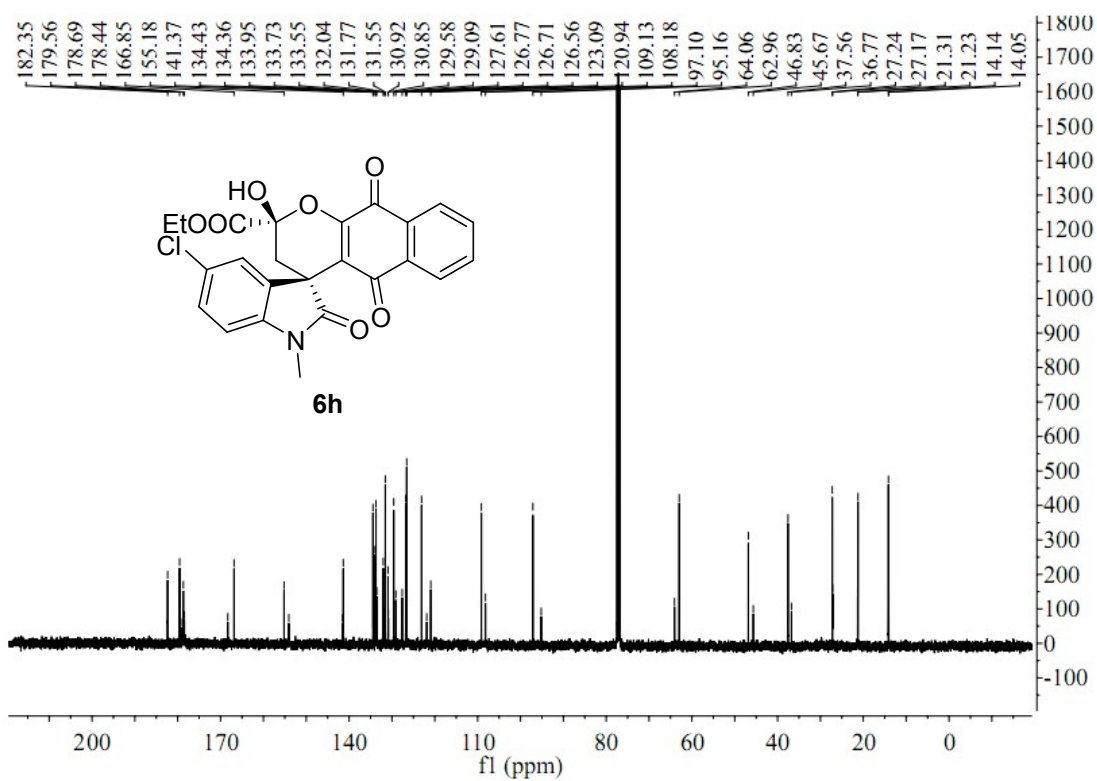
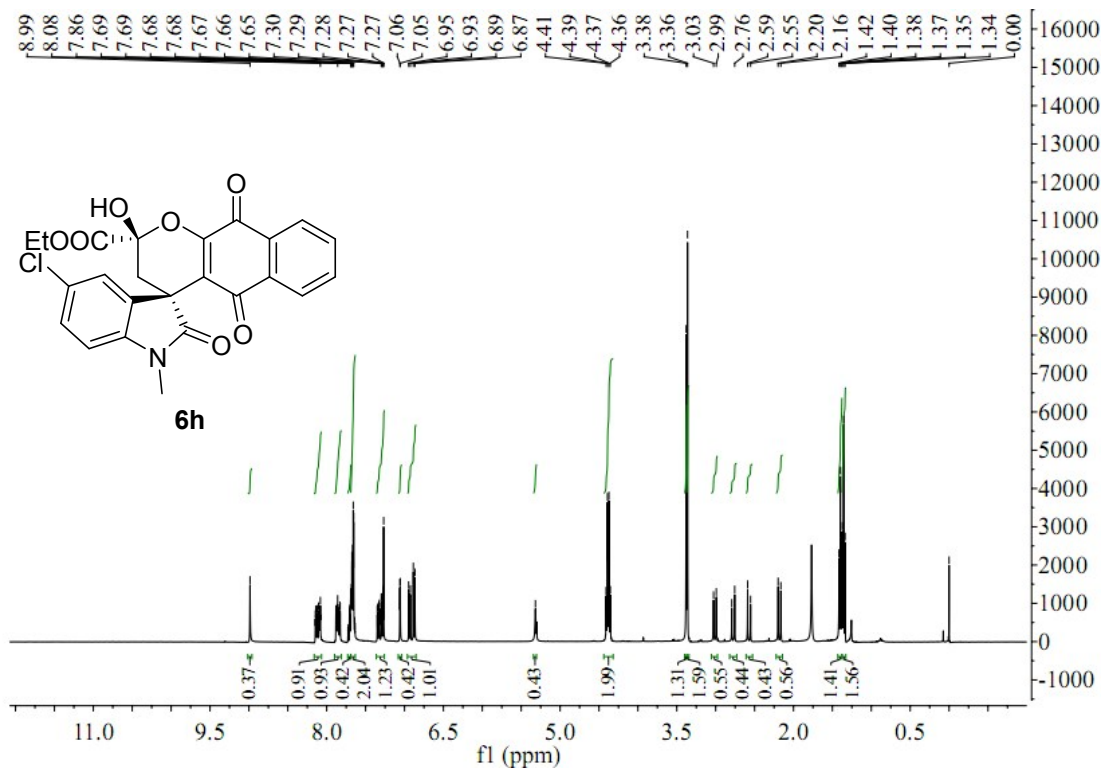
**Ethyl-1'-acetyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6f**



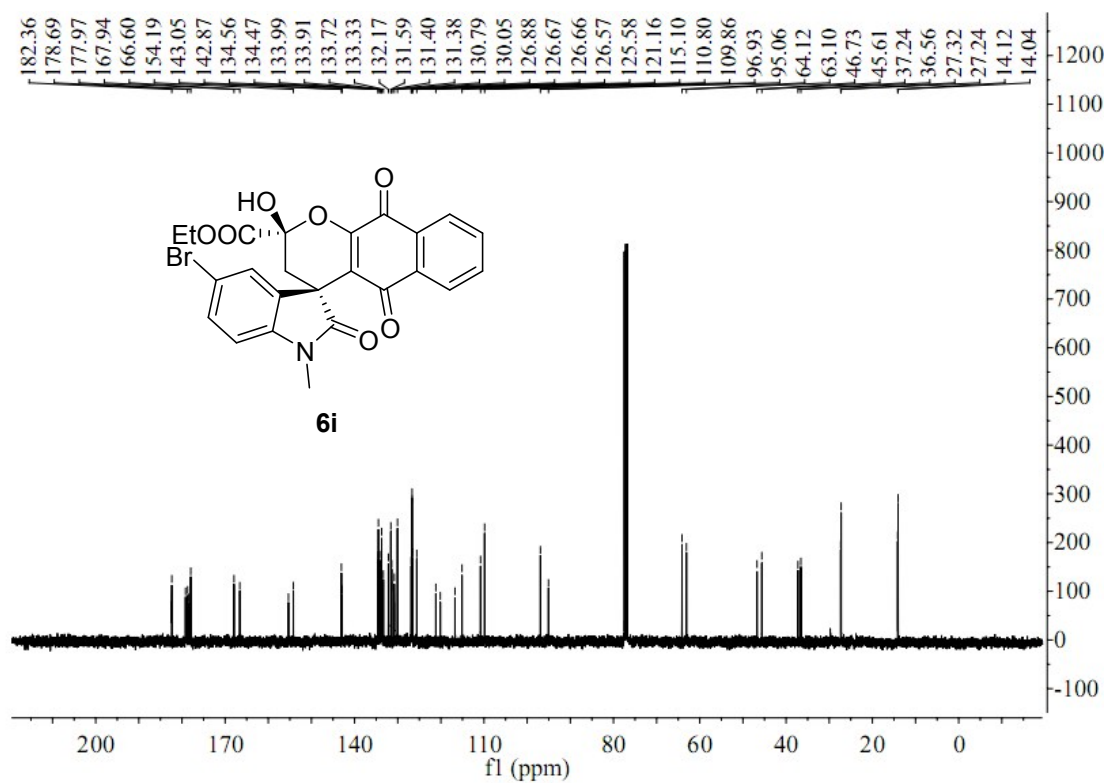
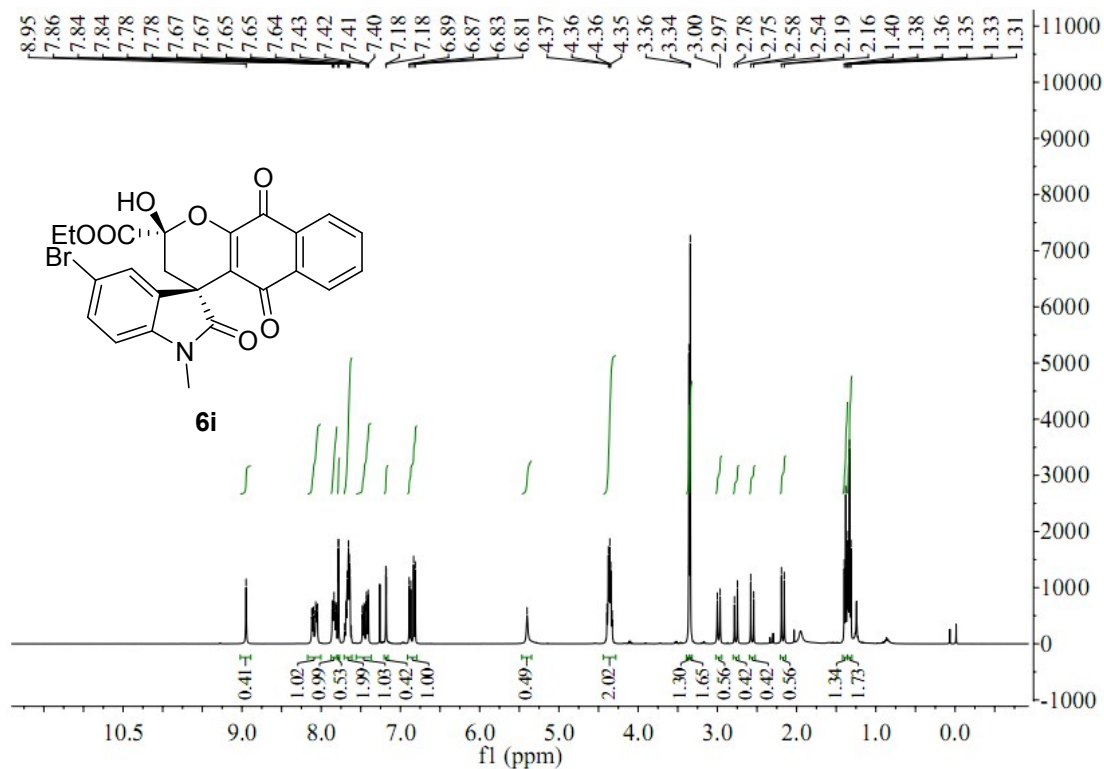
**Ethyl-5'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6g**



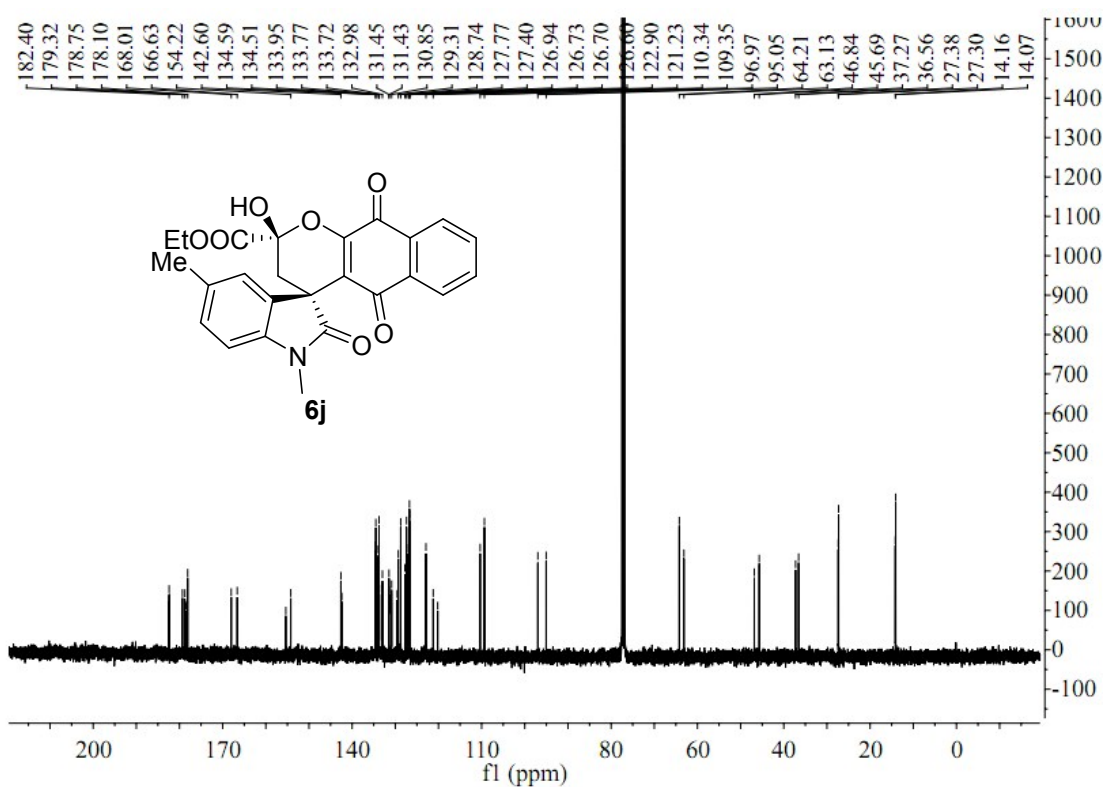
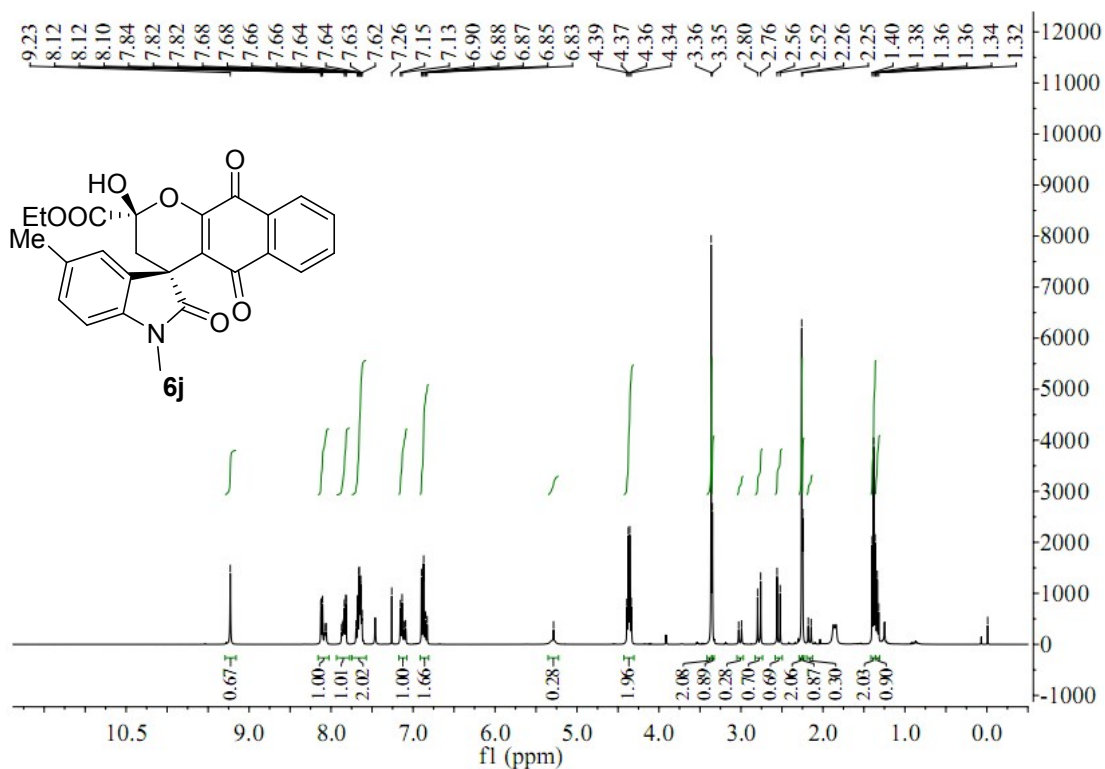
**Ethyl-5'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6h**



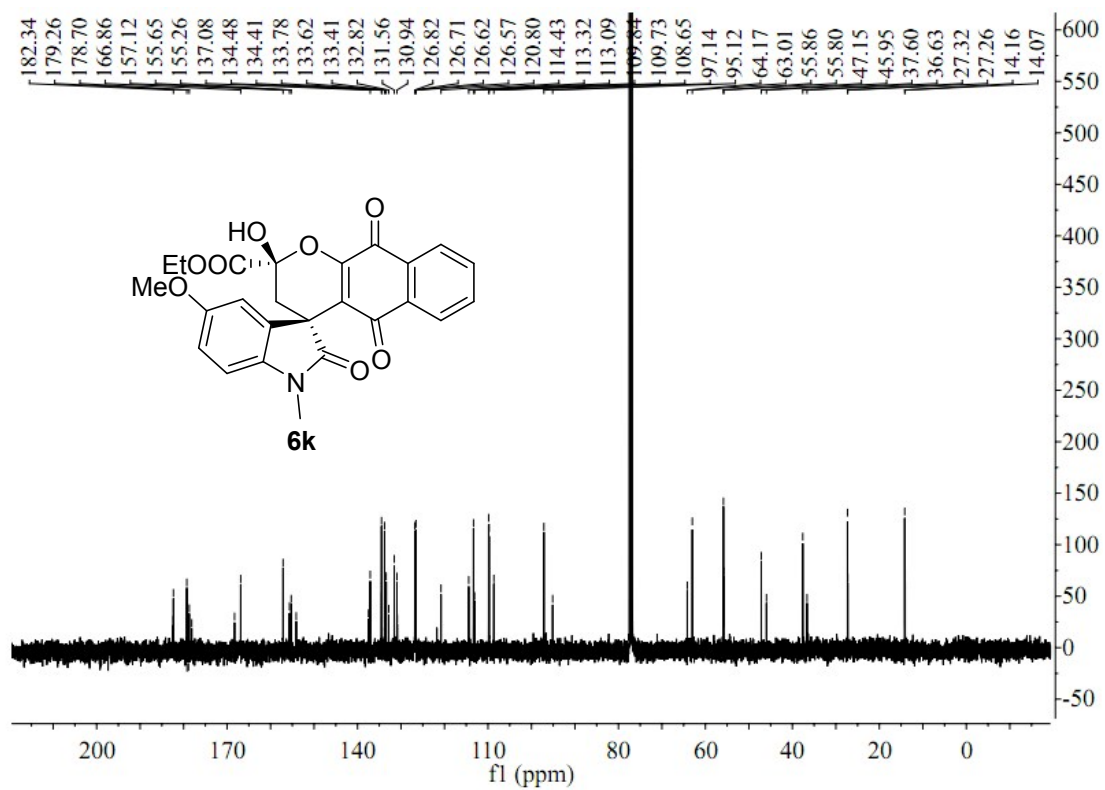
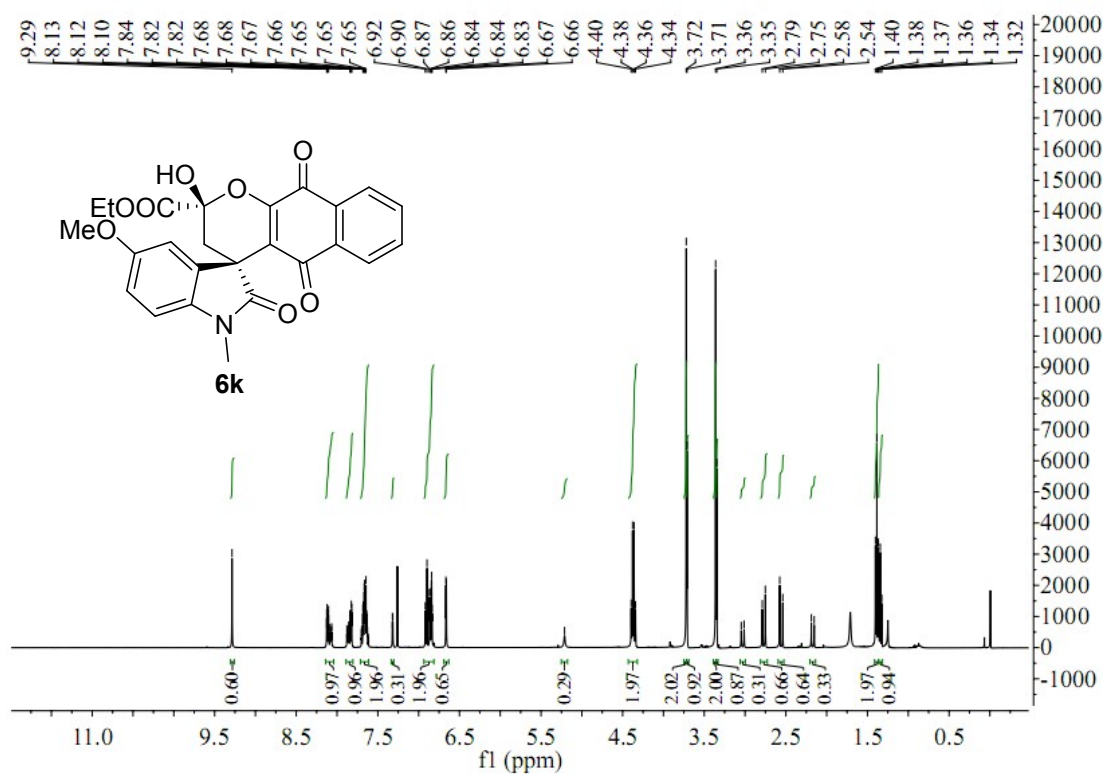
**Ethyl-5'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate **6i****



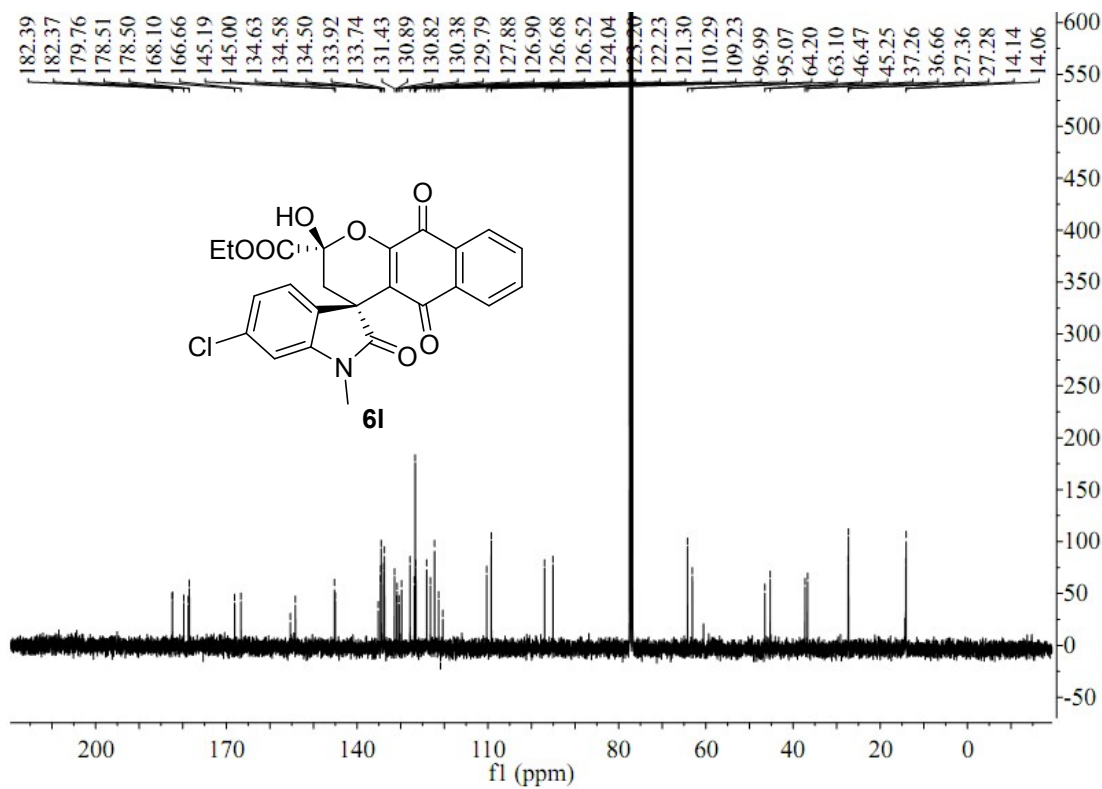
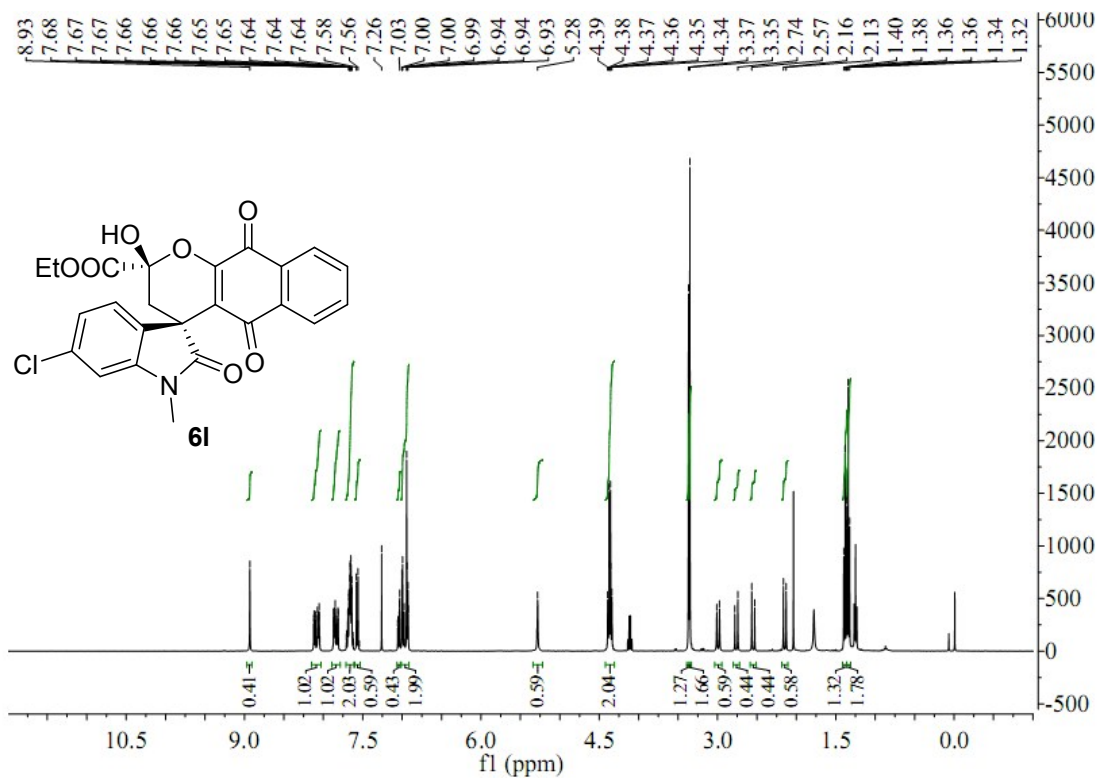
**Ethyl-2-hydroxy-1',5'-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6j**



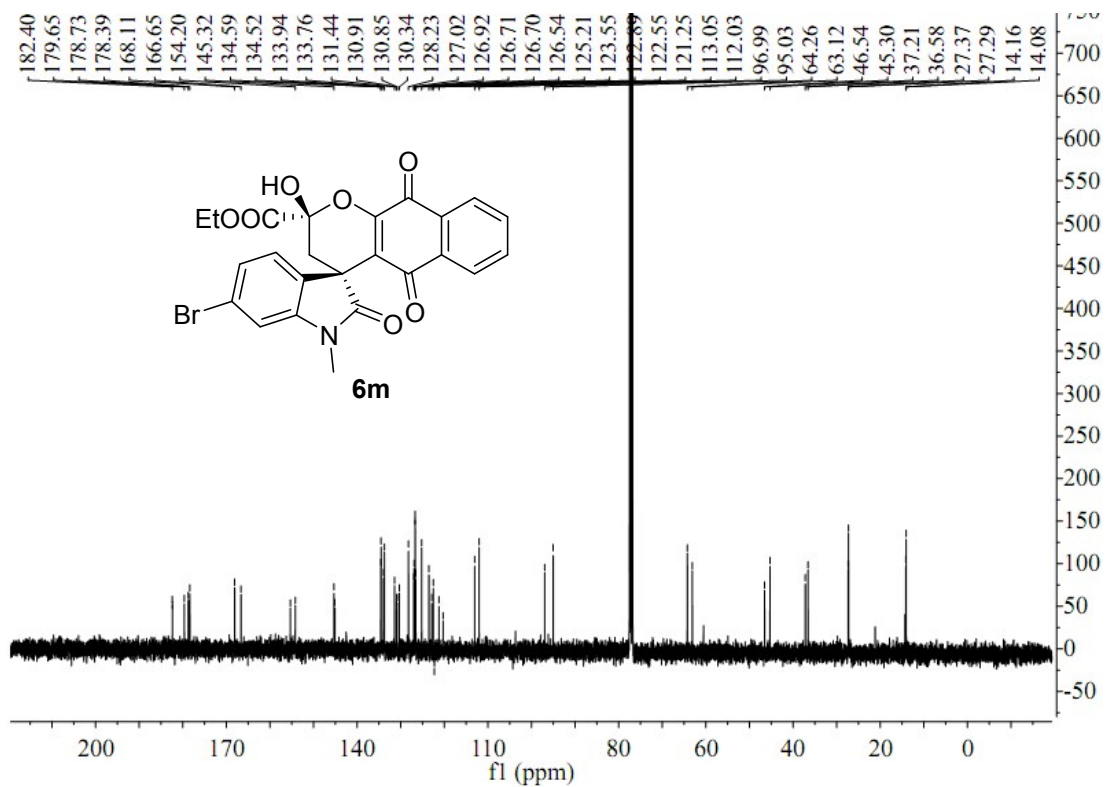
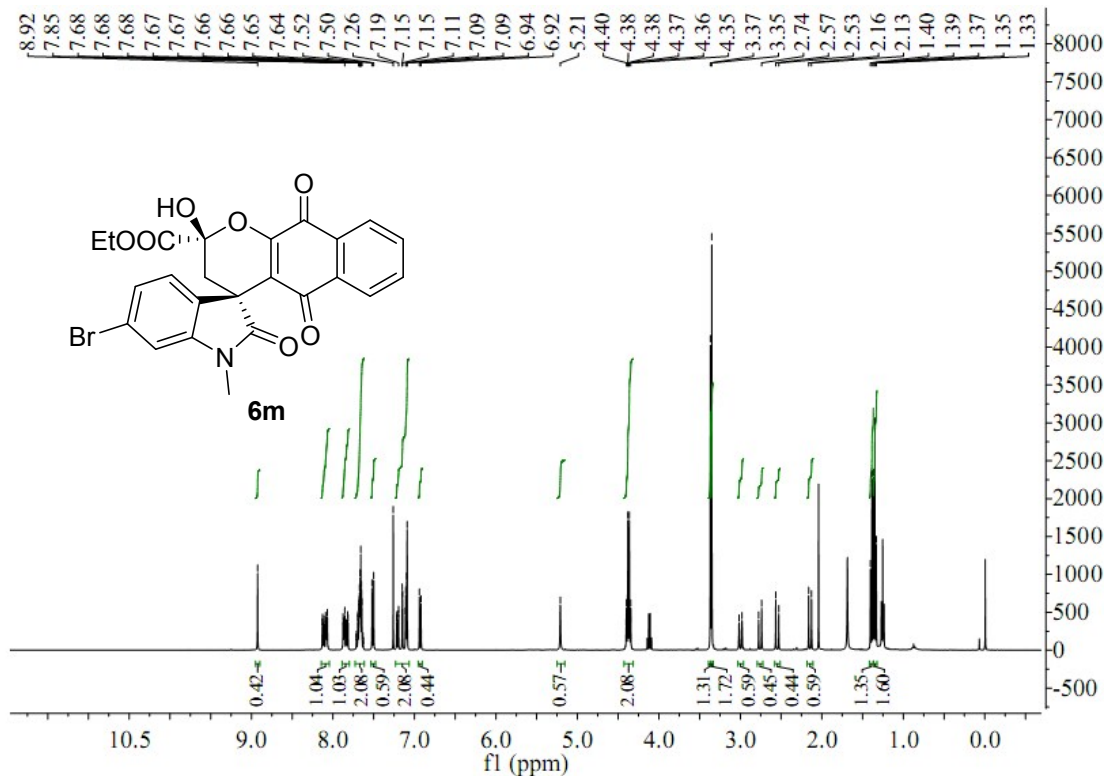
**Ethyl-2-hydroxy-5'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6k**



**Ethyl-6'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6l**

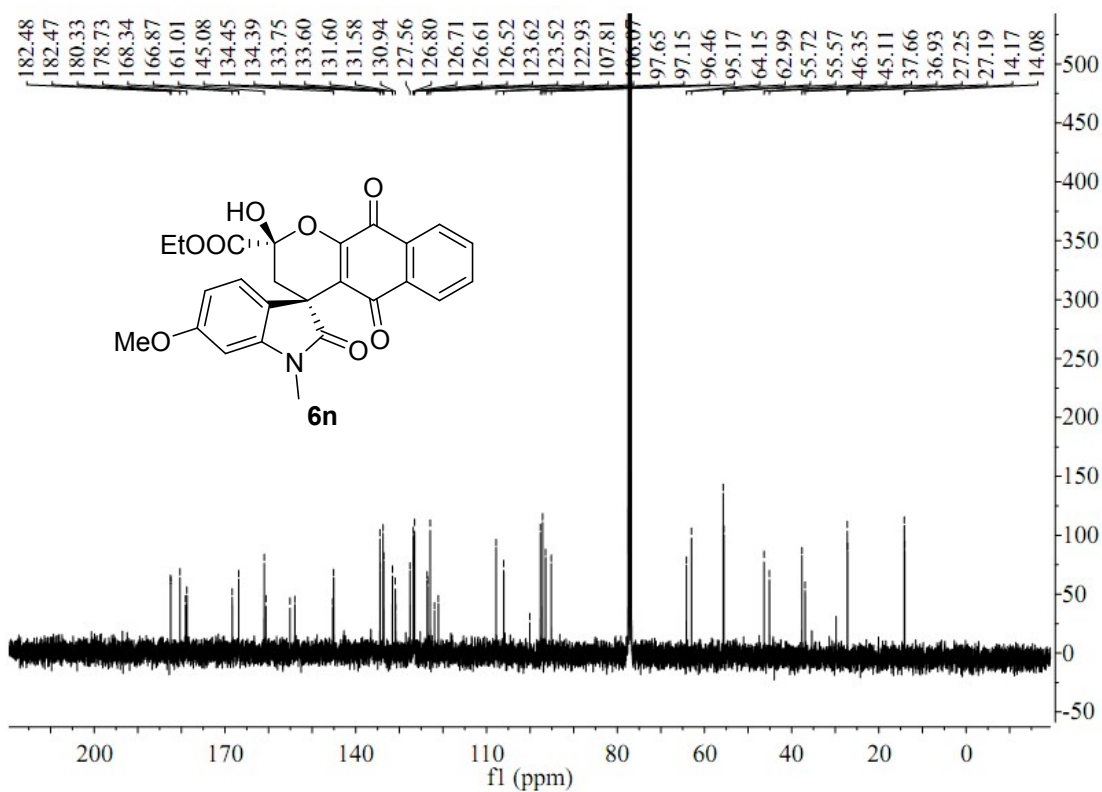
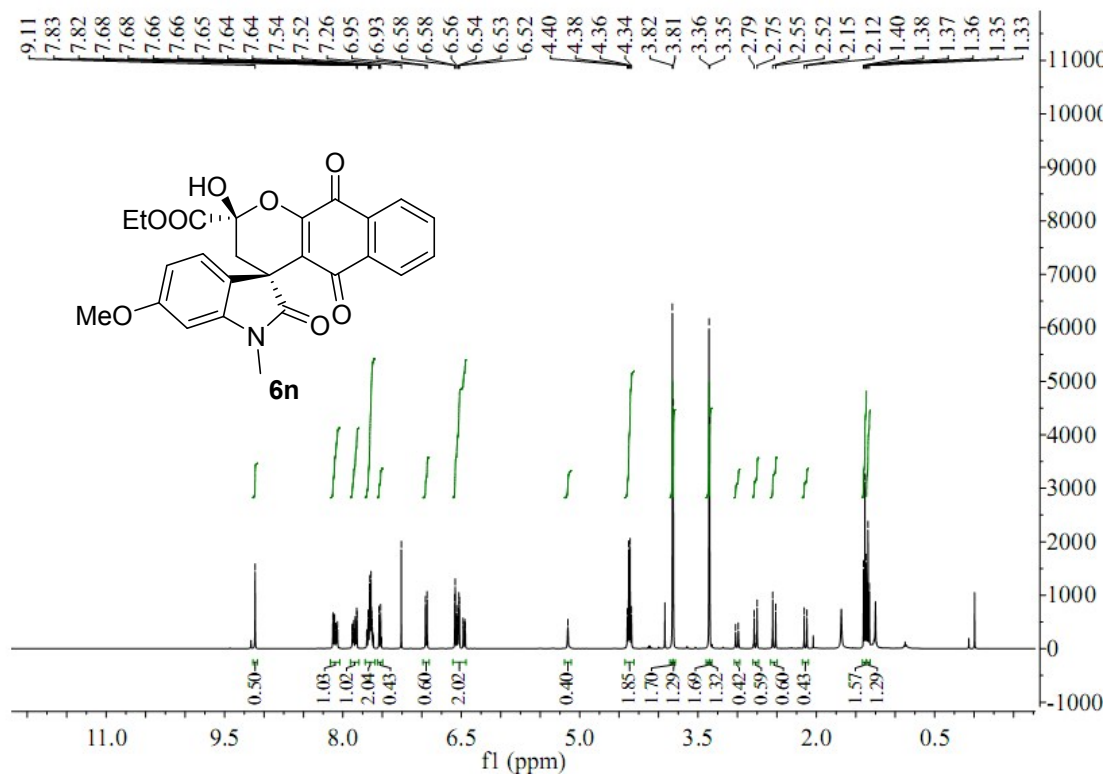


**Ethyl-6'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6m**

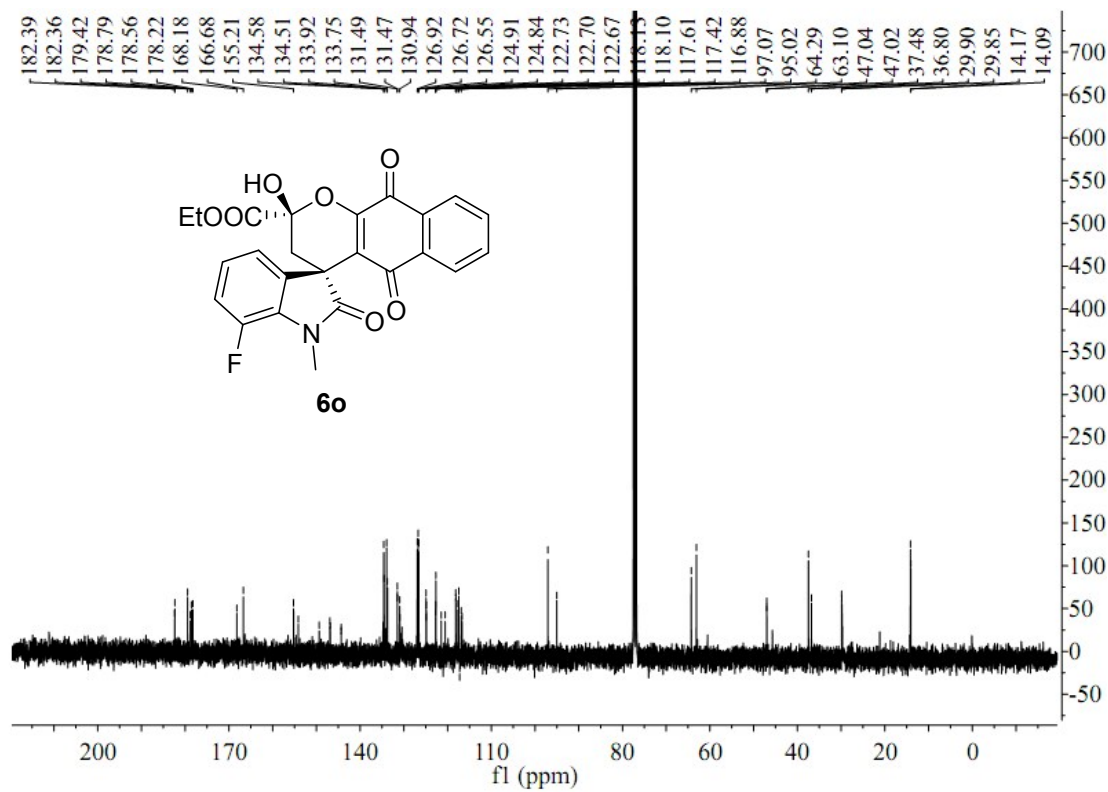
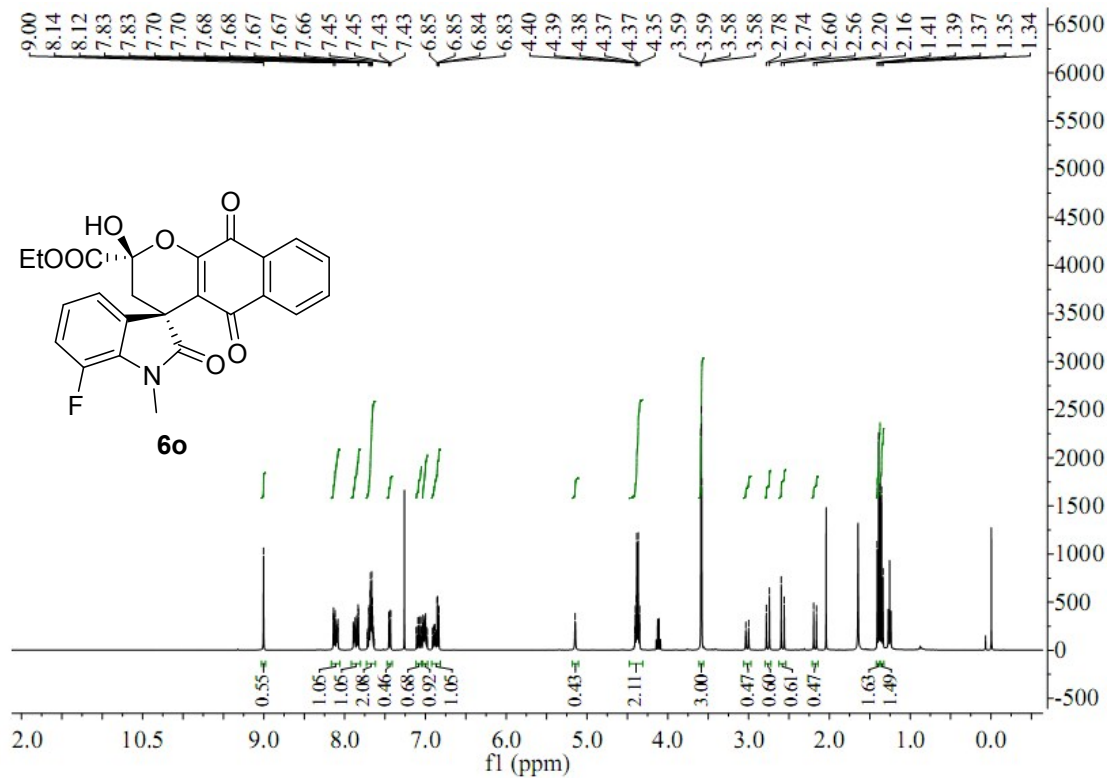




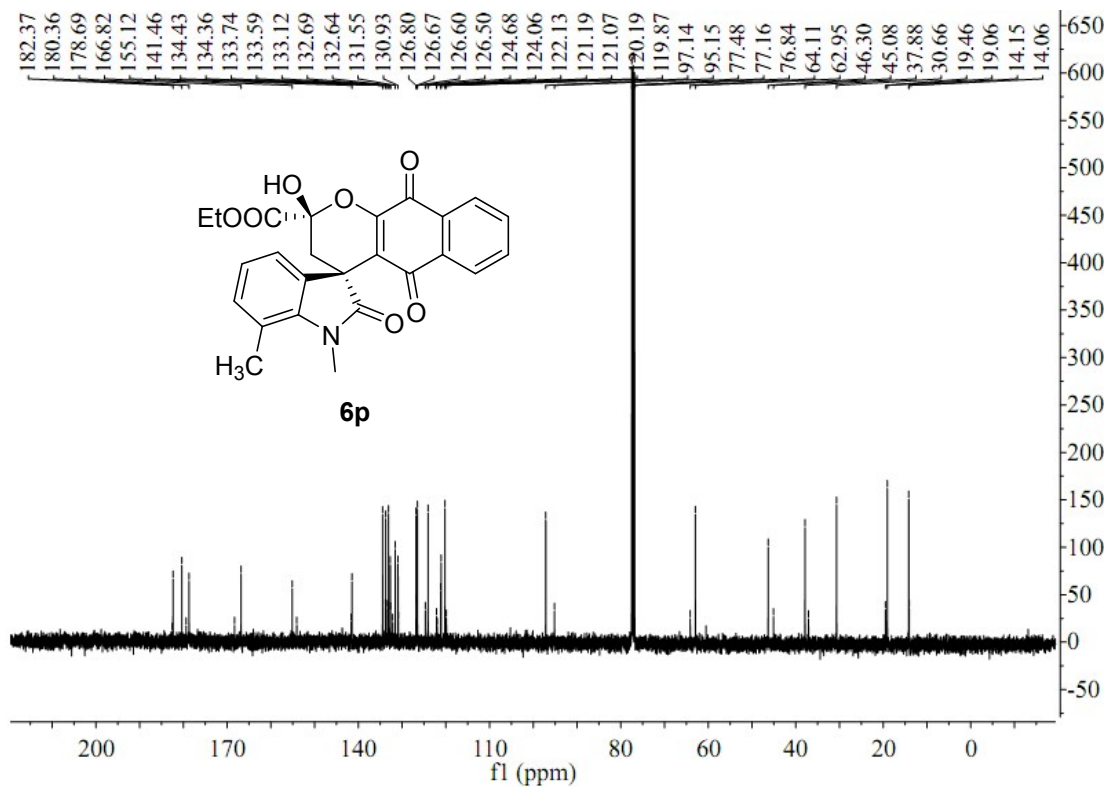
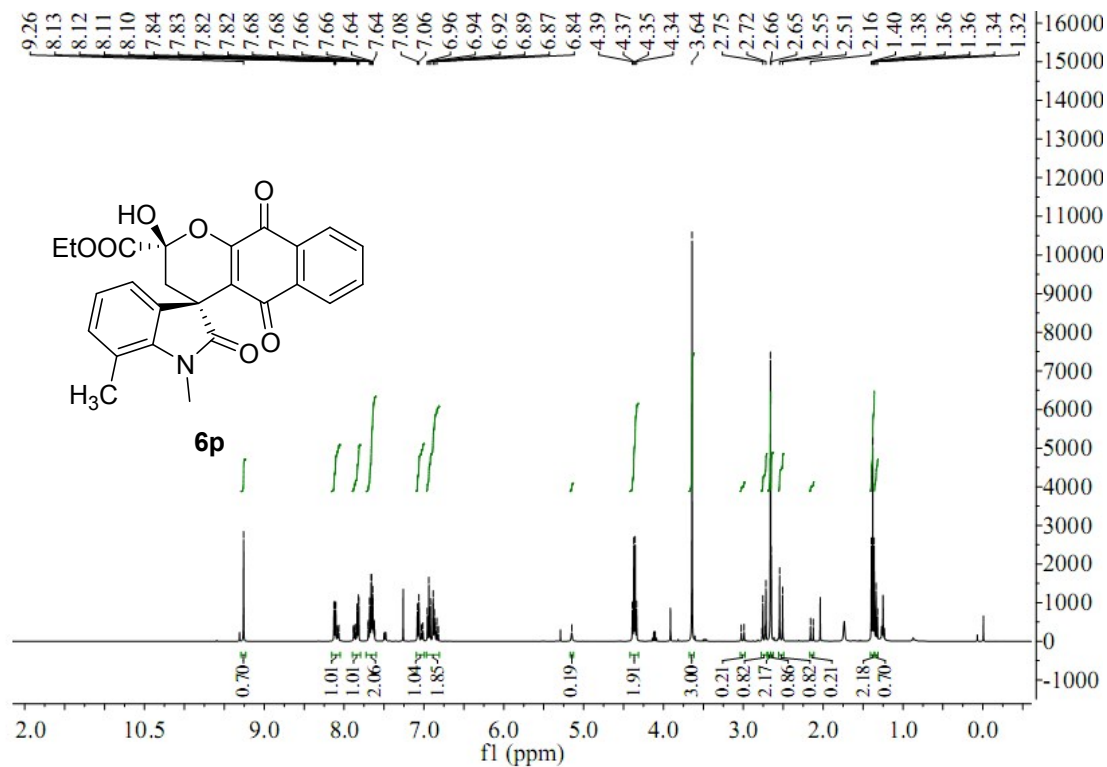
**Ethyl-2-hydroxy-6'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6n**



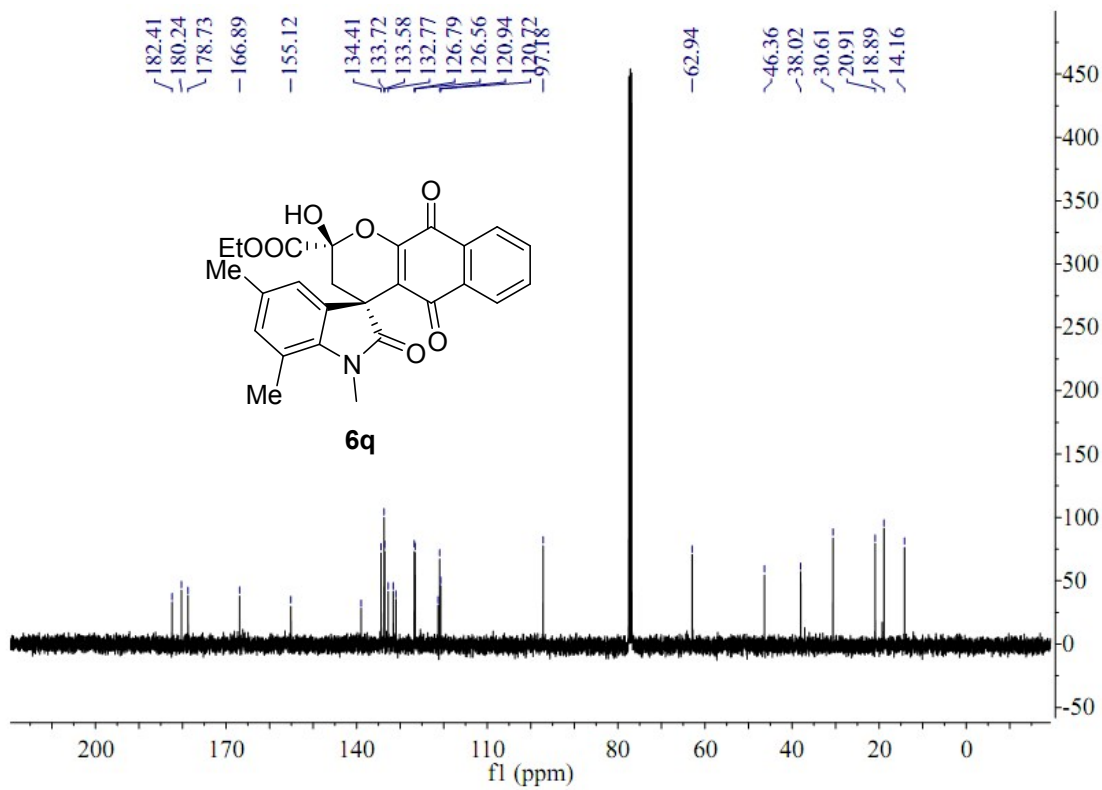
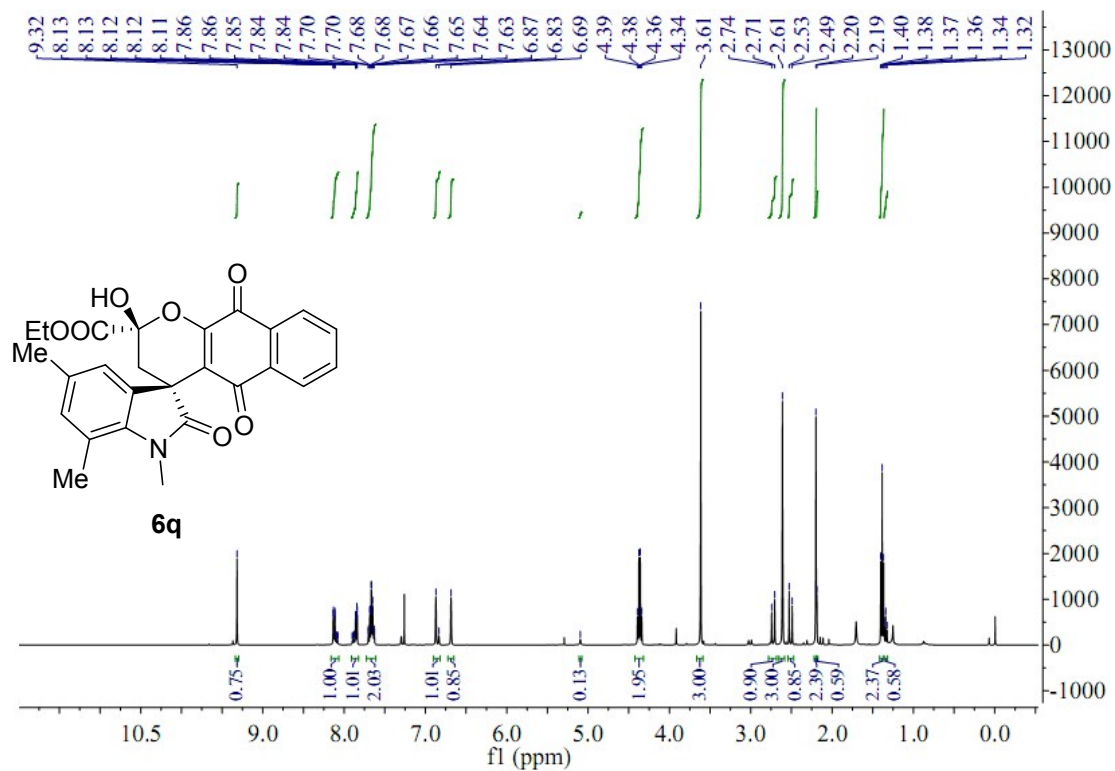
**Ethyl-7'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6o**



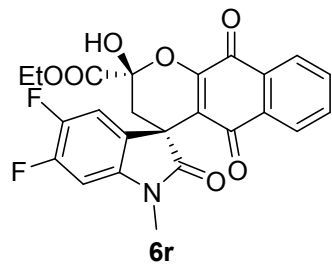
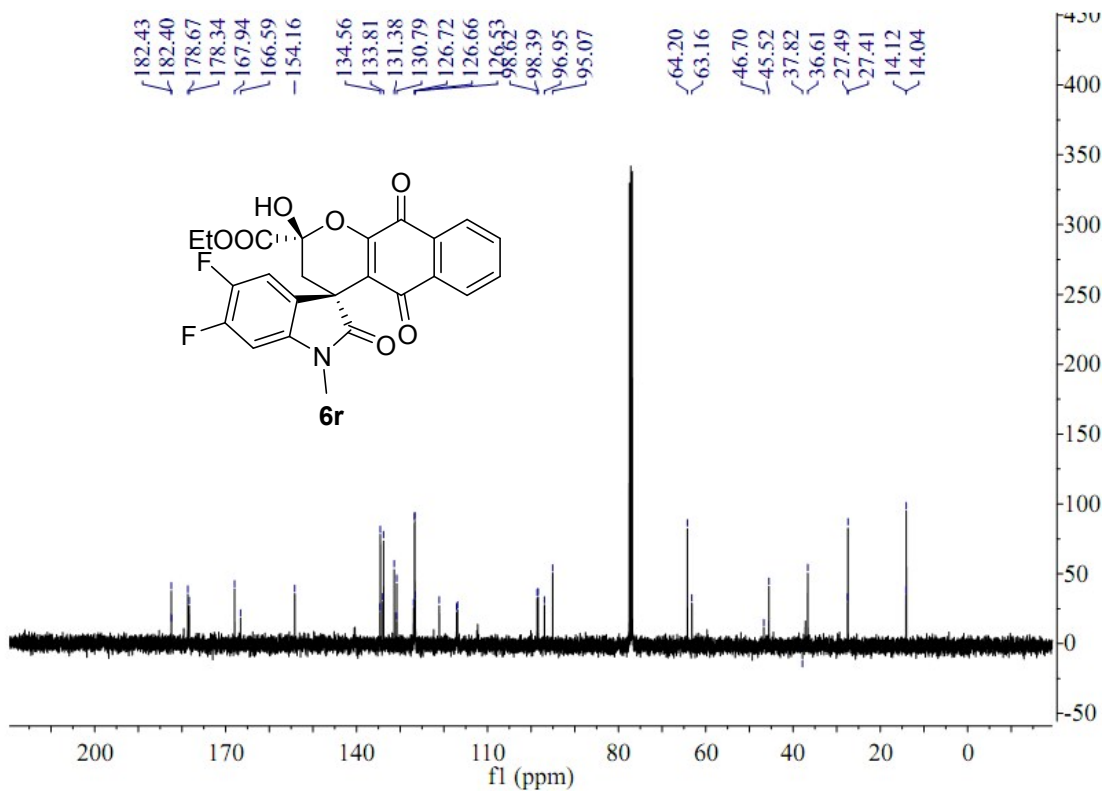
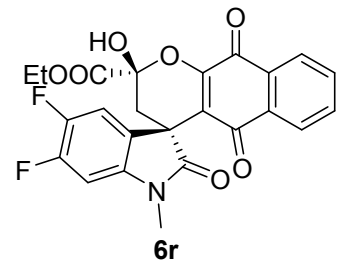
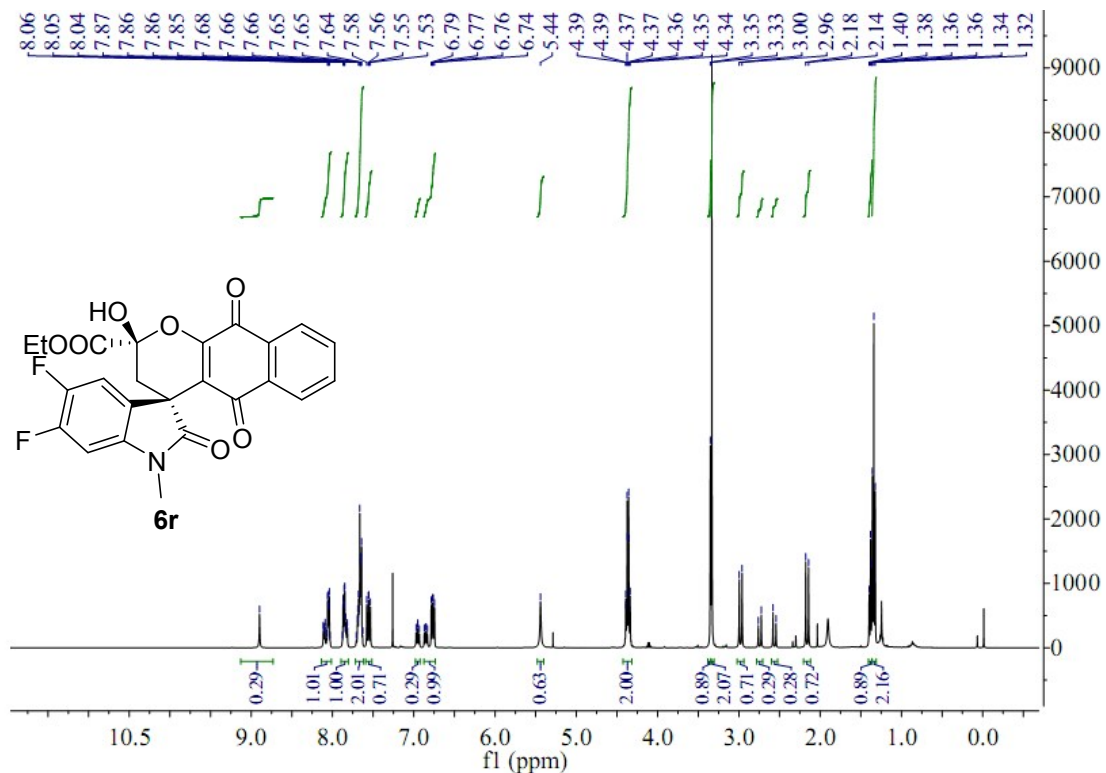
**Ethyl-2-hydroxy-1',7'-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6p**



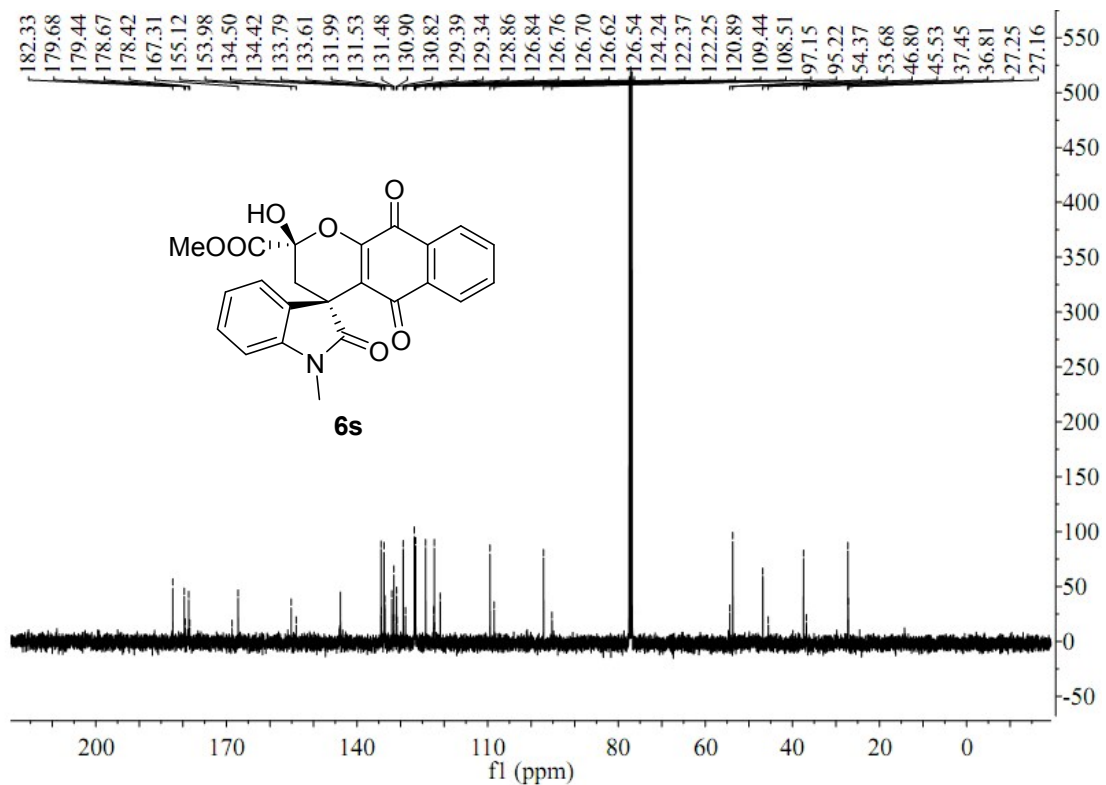
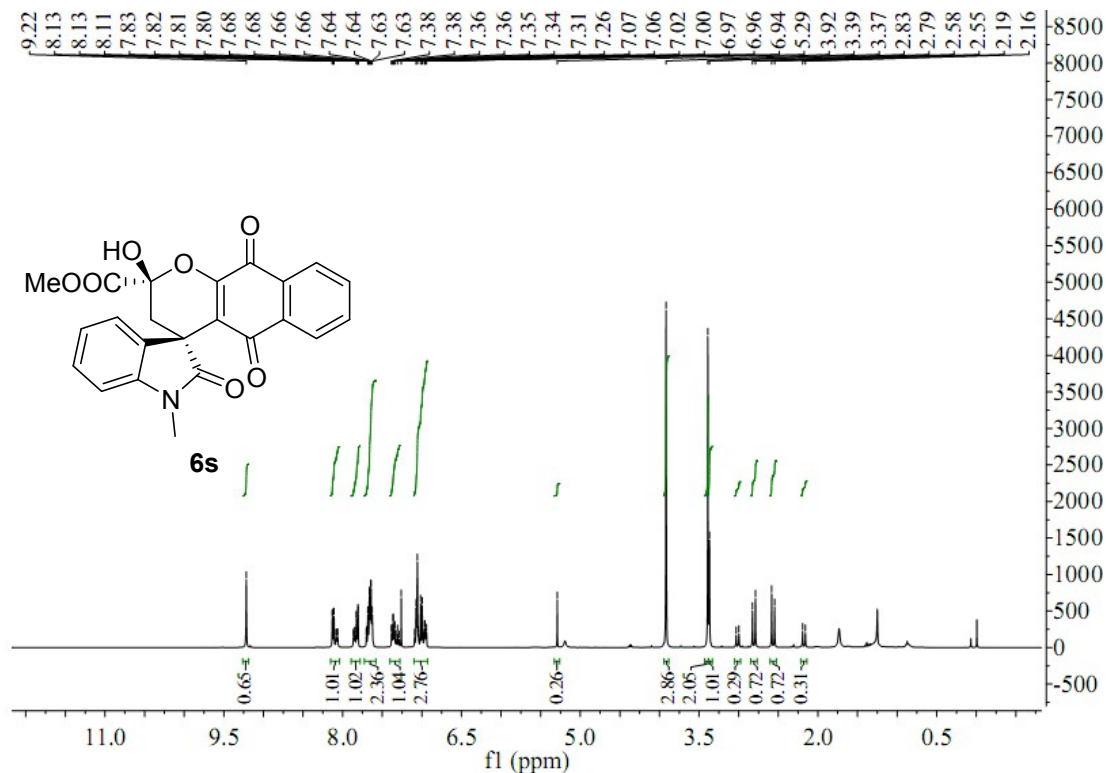
**Ethyl-2-hydroxy-1',5',7'-trimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6q**



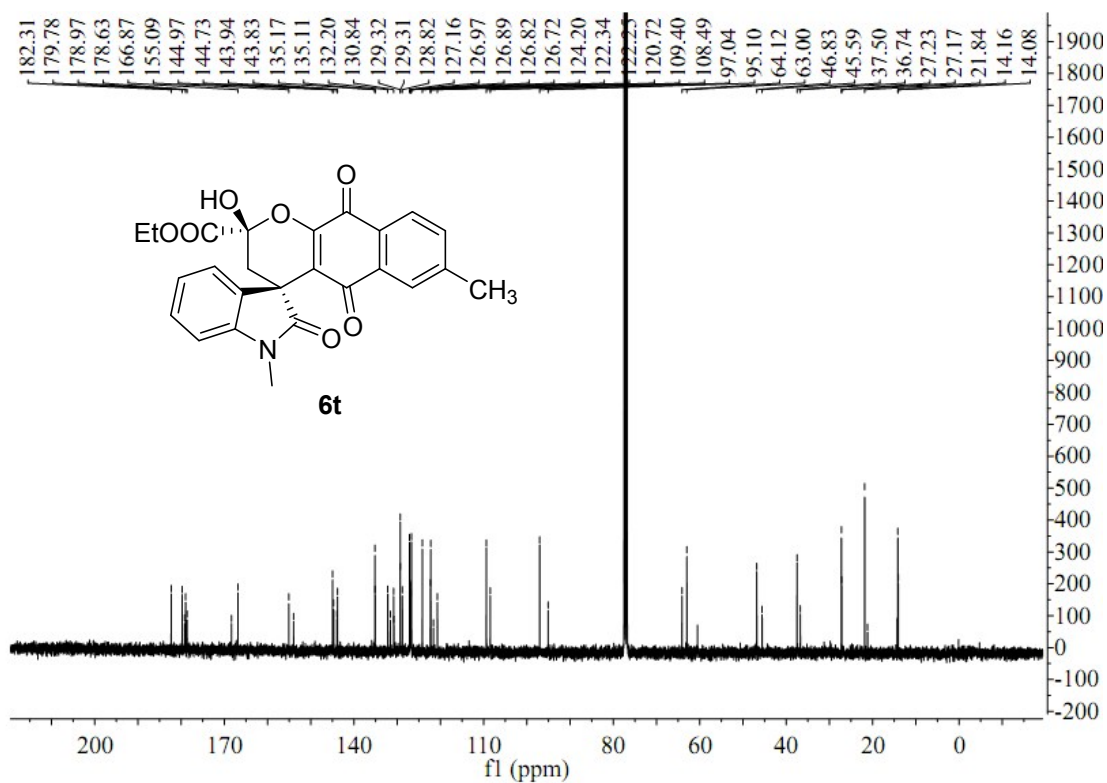
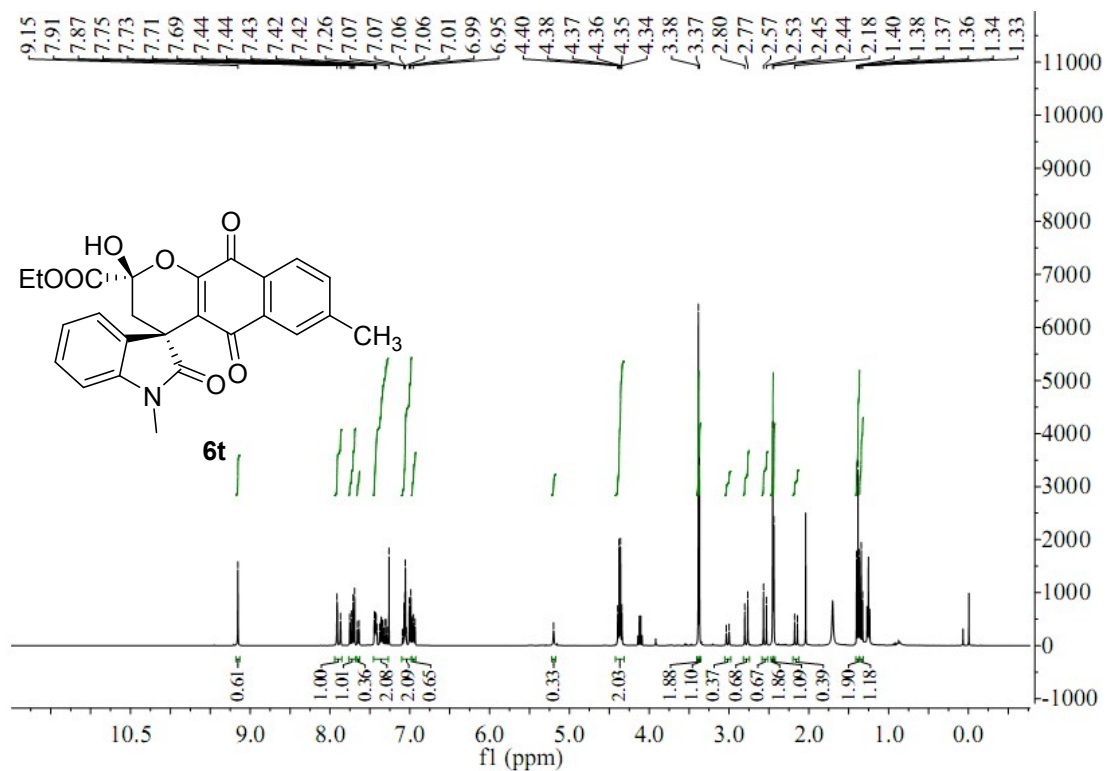
**Ethyl-5',6'-difluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6r**



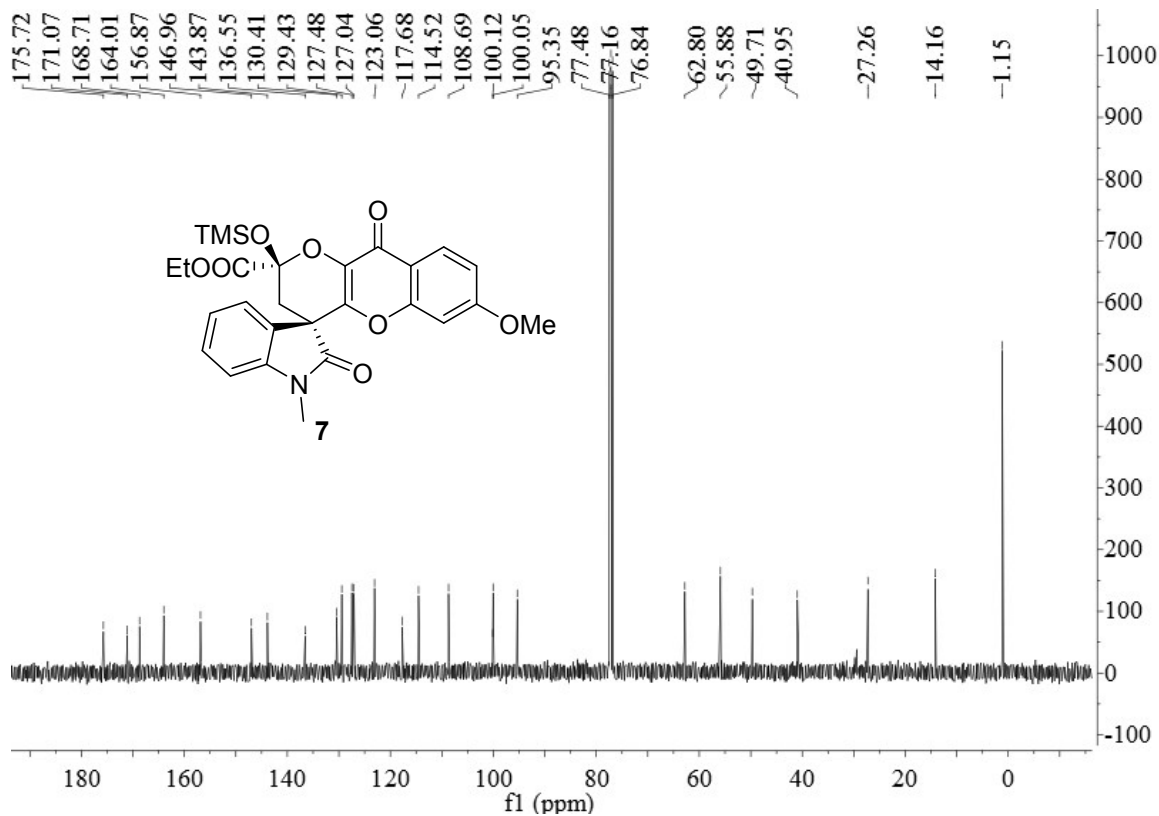
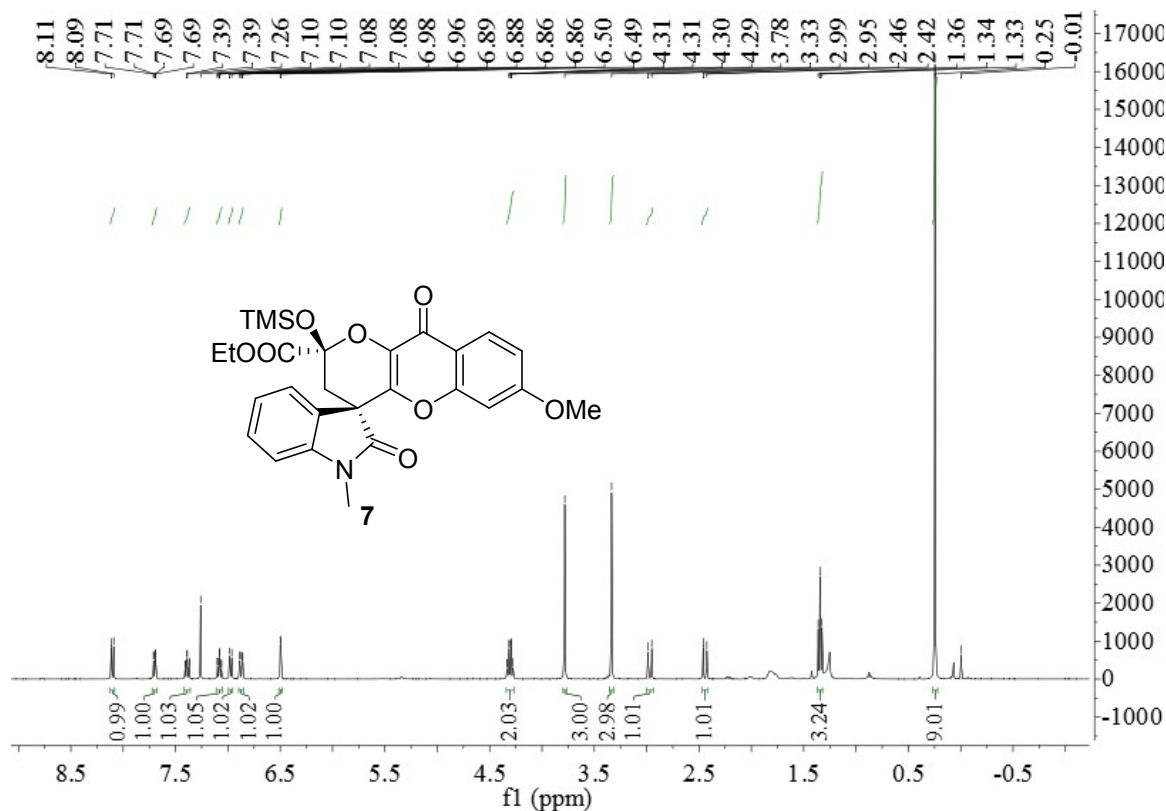
**Methyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6s**



**Ethyl-2-hydroxy-1',7-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6t**

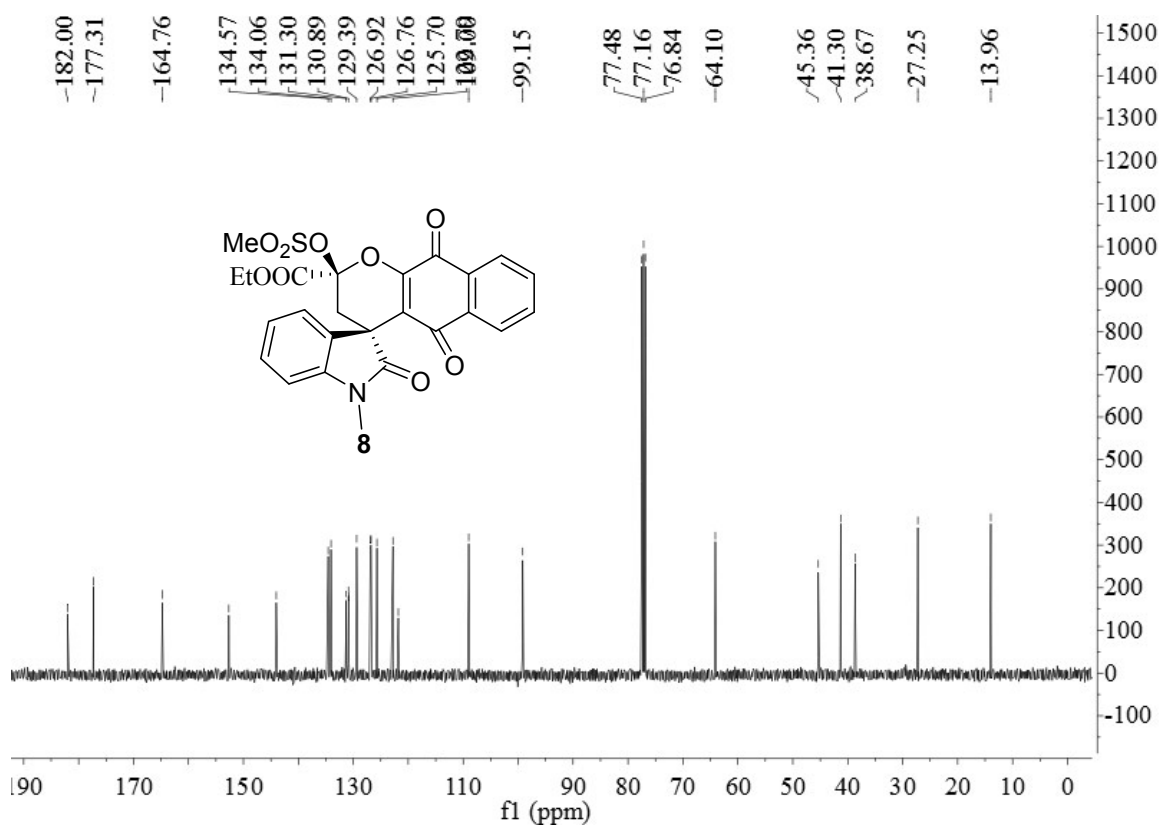
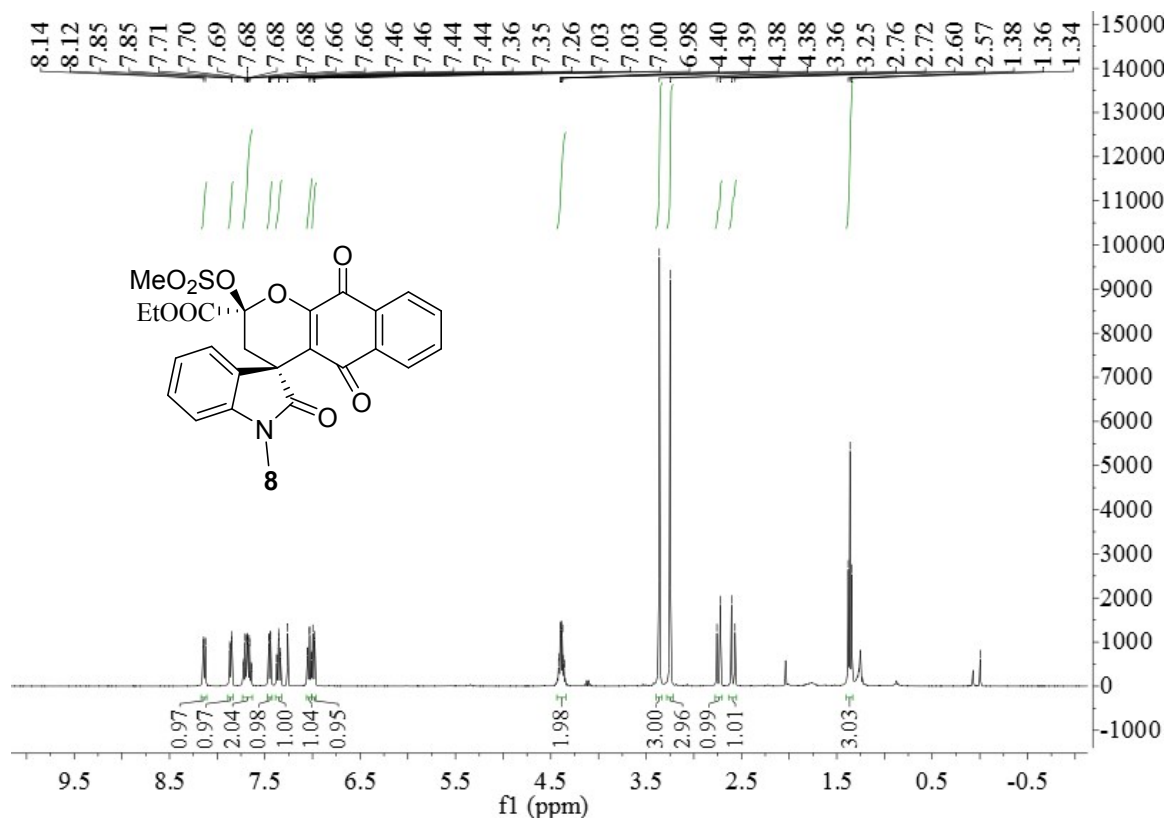


**Ethyl-1-methyl-2,10'-dioxo-2'-((trimethylsilyl)oxy)-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 7**



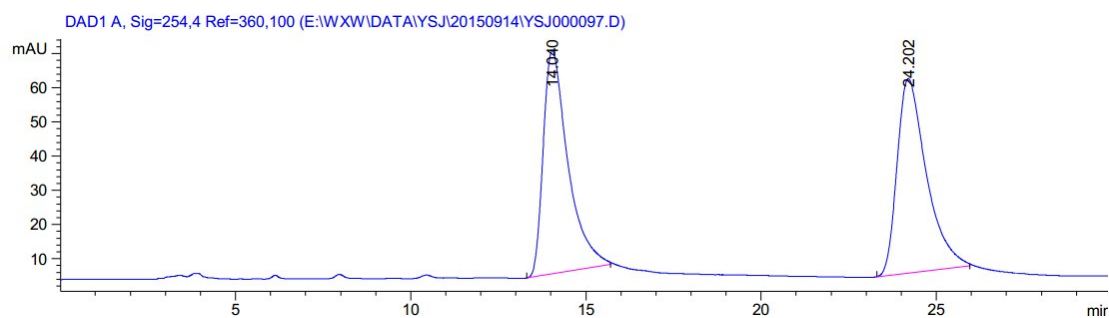


**Ethyl-1'-methyl-2-((methylsulfonyl)oxy)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 8**



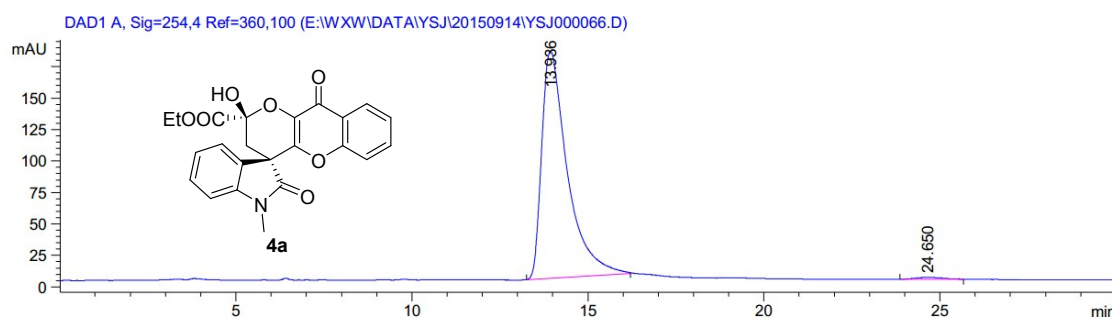
**5. HPLC spectra**

**Ethyl 2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4a**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.040	BB	0.7338	3217.62280	65.42322	49.3172
2	24.202	BB	0.8686	3306.72314	56.84908	50.6828

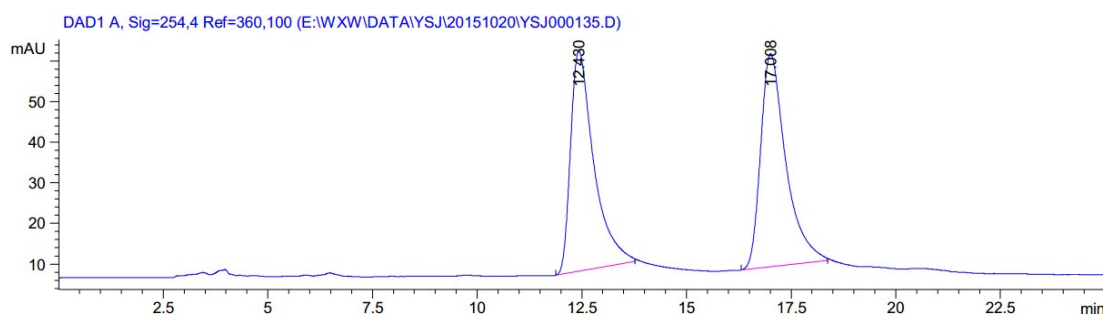
Totals : 6524.34595 122.27230



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.936	BB	0.7537	9152.50684	180.44893	99.1264
2	24.650	MM R	0.8756	80.65916	1.53531	0.8736

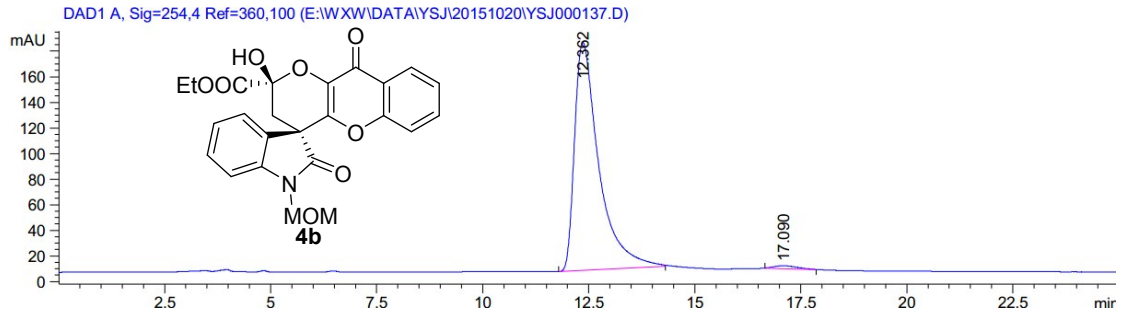
Totals : 9233.16600 181.98424

**Ethyl 2'-hydroxy-1-(methoxymethyl)-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4b**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.430	BB	0.5780	2102.57446	54.26806	48.8232
2	17.008	BB	0.6257	2203.93457	52.50396	51.1768

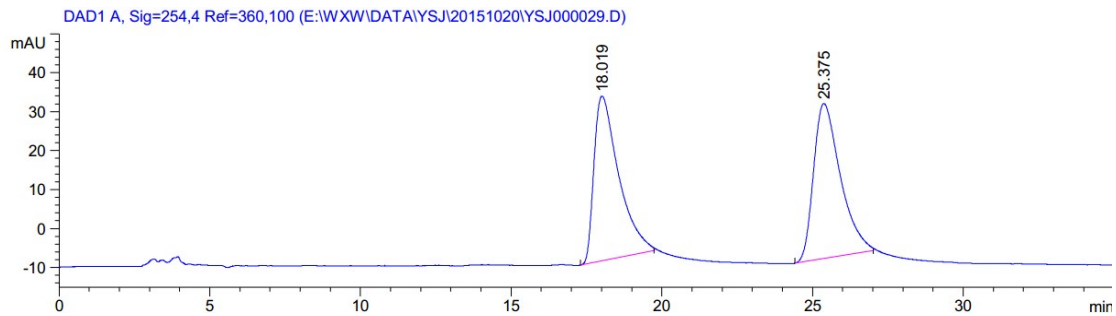
Totals : 4306.50903 106.77202



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.362	BB	0.5892	7103.74316	178.13443	98.7620
2	17.090	BB	0.4822	89.04506	2.30777	1.2380

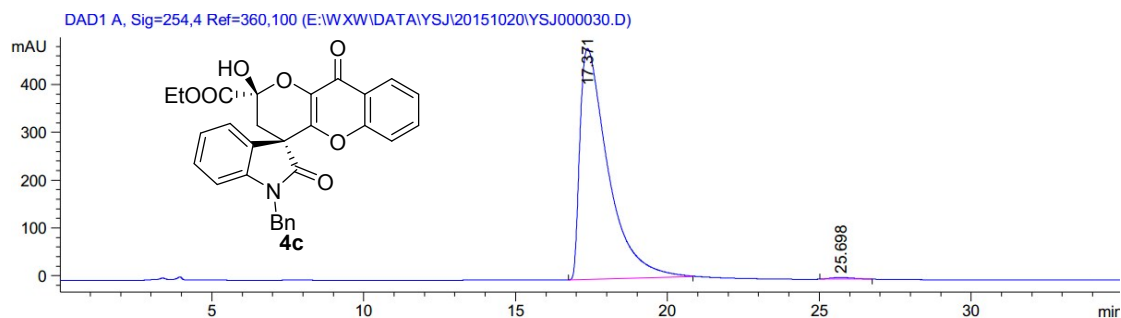
Totals : 7192.78822 180.44220

**Ethyl 1-benzyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4c**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.019	BB	0.8315	2409.38428	42.23662	49.4604
2	25.375	BB	0.8960	2461.95923	39.78049	50.5396

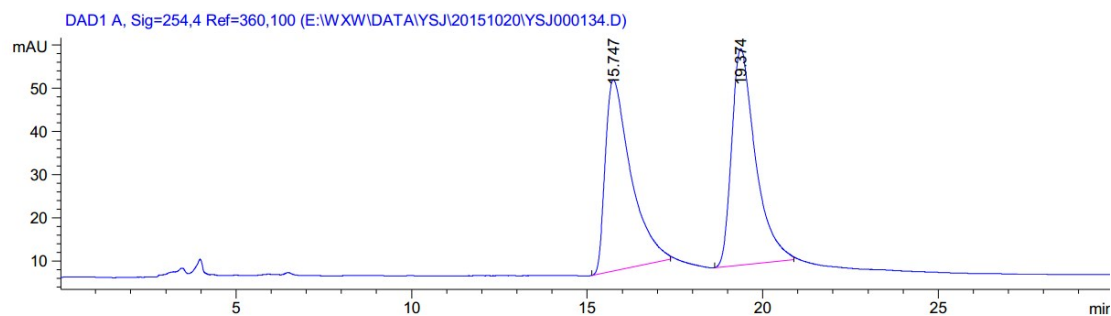
Totals : 4871.34351 82.01712



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.371	BB	0.9486	3.11348e4	482.64487	99.3749
2	25.698	BB	0.6619	195.85359	3.51567	0.6251

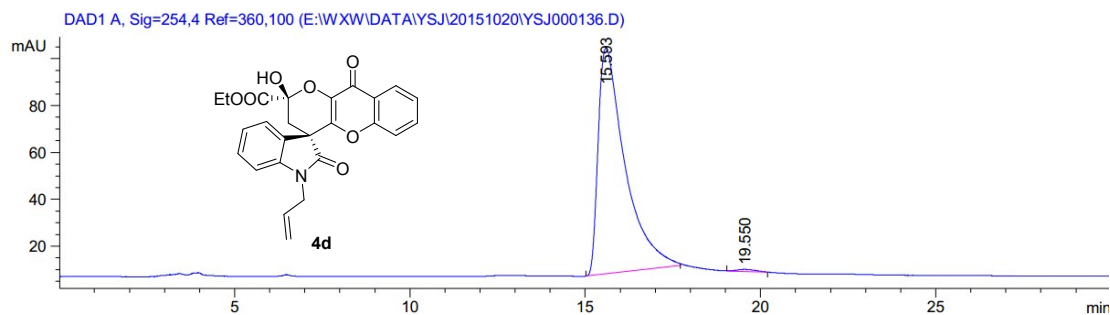
Totals : 3.13307e4 486.16054

**Ethyl 1-allyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4d**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.747	BB	0.7234	2243.50708	44.25544	48.7150
2	19.374	BB	0.7012	2361.86865	49.99260	51.2850

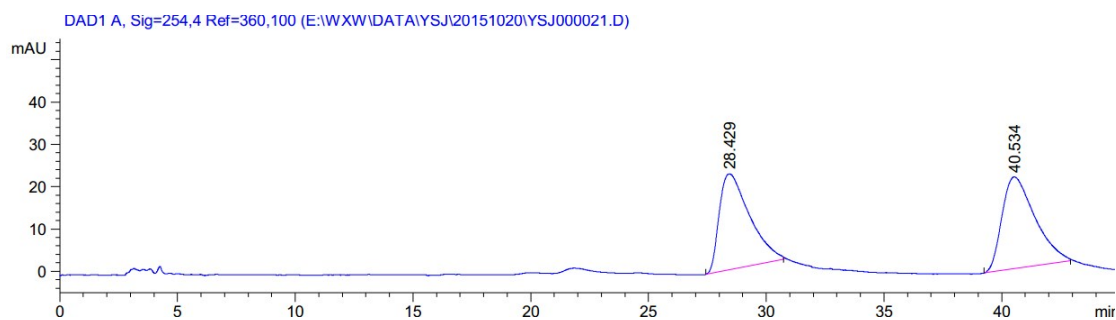
Totals : 4605.37573 94.24804



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.593	BB	0.7702	5119.03760	96.28848	99.3525
2	19.550	MM R	0.6286	33.36403	8.84553e-1	0.6475

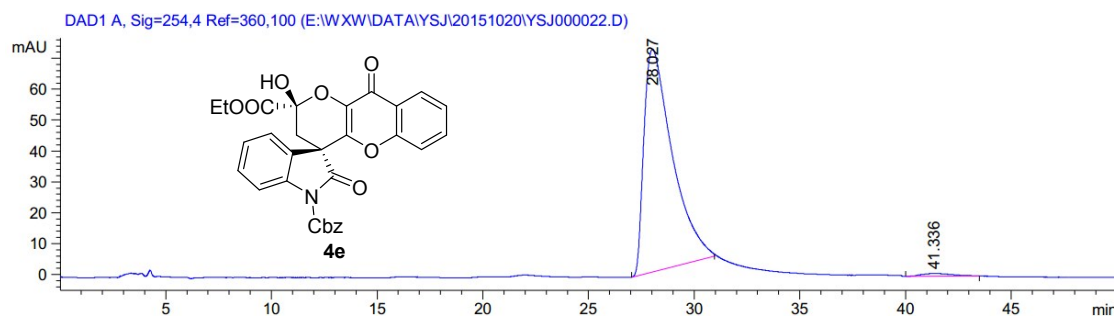
Totals : 5152.40163 97.17303

**1-benzyl 2'-ethyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-1,2'-dicarboxylate4e**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.429	BB	1.1894	2021.06787	22.68575	48.9735
2	40.534	BB	1.1878	2105.78833	21.66875	51.0265

Totals : 4126.85620 44.35450

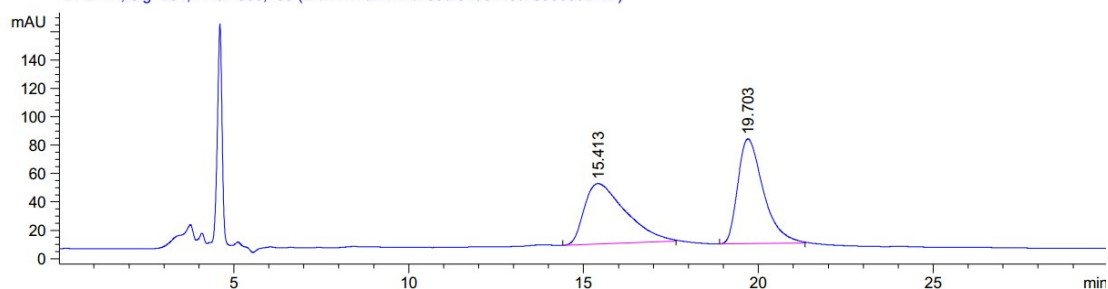


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.027	BB	1.3364	6737.96045	72.09135	98.7080
2	41.336	MM R	1.6883	88.19569	8.70631e-1	1.2920

Totals : 6826.15614 72.96198

**Ethyl 1-acetyl-2'-hydroxy-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate4f**

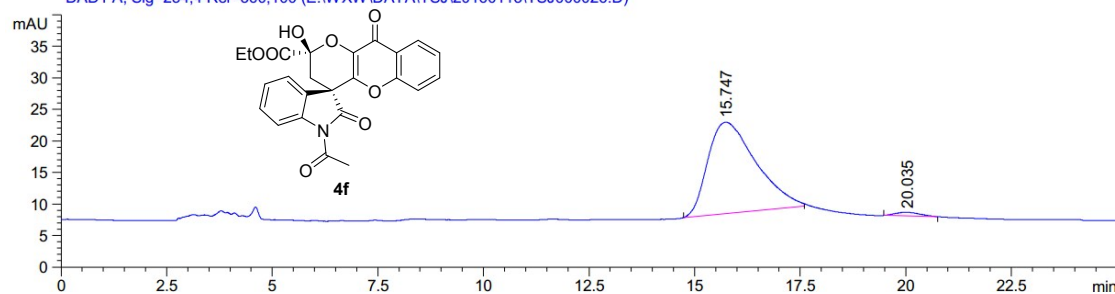
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20160113\YSJ000024.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.413	BB	1.1217	3484.34009	42.62595	48.1464
2	19.703	BB	0.7818	3752.62231	73.97834	51.8536

Totals : 7236.96240 116.60429

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20160113\YSJ000026.D)

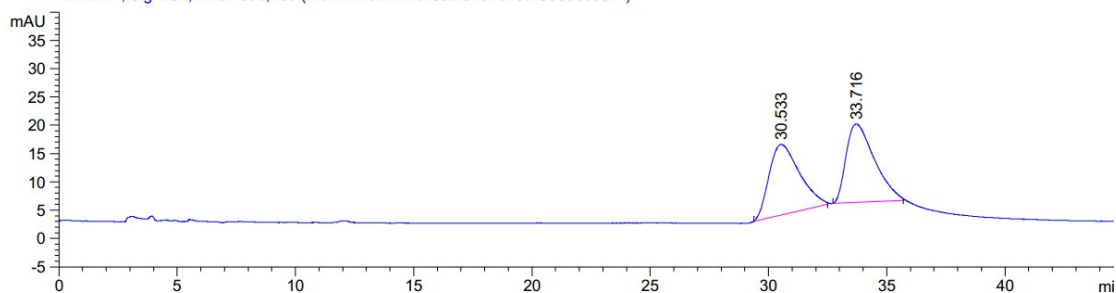


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.747	BB	0.9784	1146.07373	14.49519	97.9738
2	20.035	MM R	0.6677	23.70196	5.91638e-1	2.0262

Totals : 1169.77569 15.08683

**Ethyl 5-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4g**

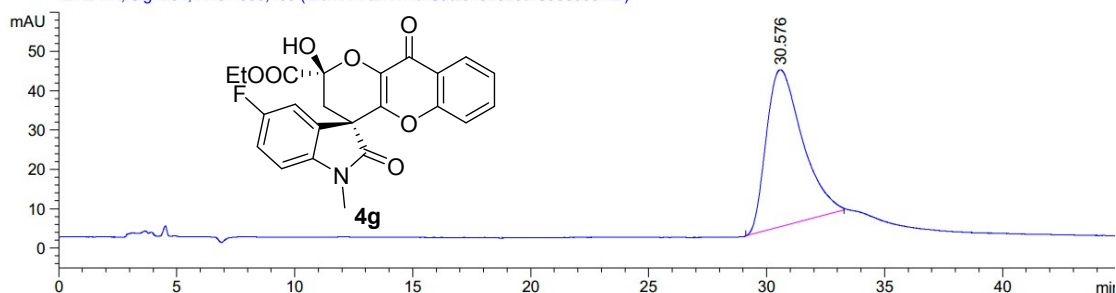
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000003.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.533	BB	1.0605	1111.14148	12.45931	49.0738
2	33.716	BB	1.0111	1153.08521	13.85361	50.9262

Totals : 2264.22668 26.31292

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000004.D)

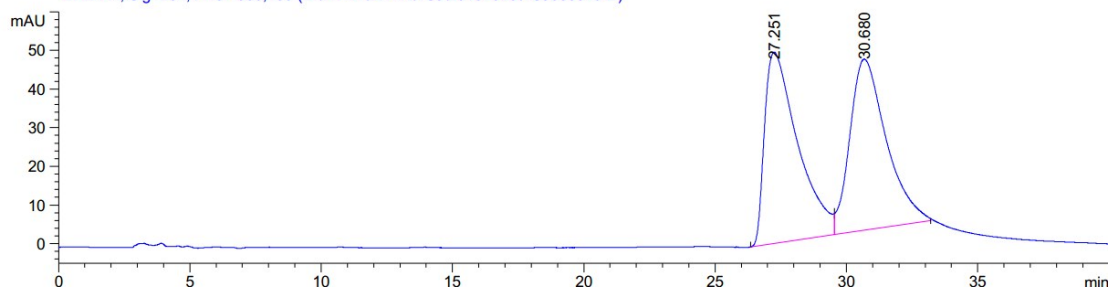


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.576	BB	1.5023	4242.28662	39.96831	100.0000

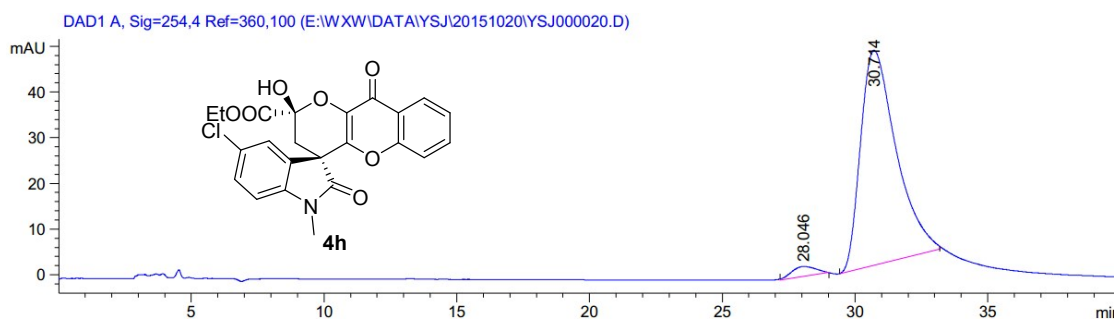
Totals : 4242.28662 39.96831

**Ethyl 5-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4h**

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000019.D)

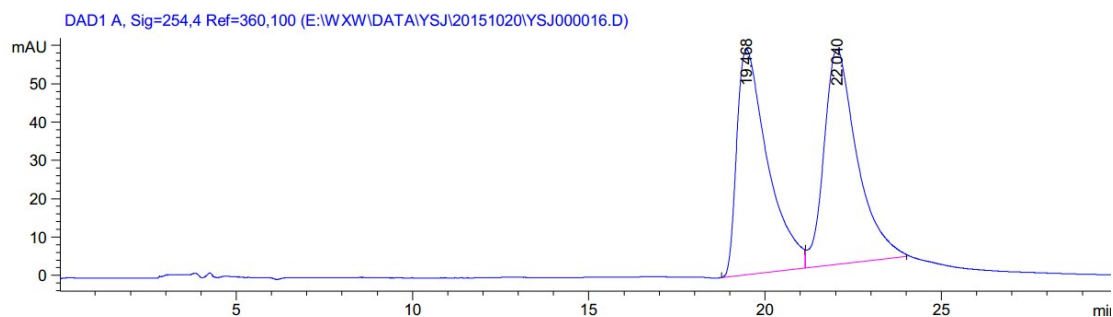


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.251	BB	1.2416	4336.33936	49.52062	50.3223
2	30.680	BB	1.4080	4280.78809	44.27415	49.6777
Totals :				8617.12744	93.79477	



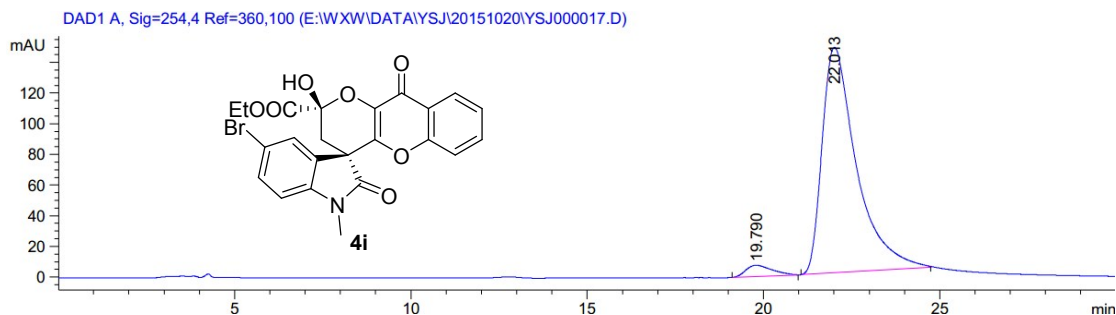
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.046	MM R	0.7436	138.00710	2.20083	3.0503
2	30.714	BB	1.3623	4386.33057	47.02105	96.9497
Totals :				4524.33766	49.22188	

**Ethyl 5-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4i**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.468	BB	0.8774	3567.27368	58.83055	49.2951
2	22.040	BB	0.9594	3669.30151	56.07469	50.7049
Totals :				7236.57520	114.90524	

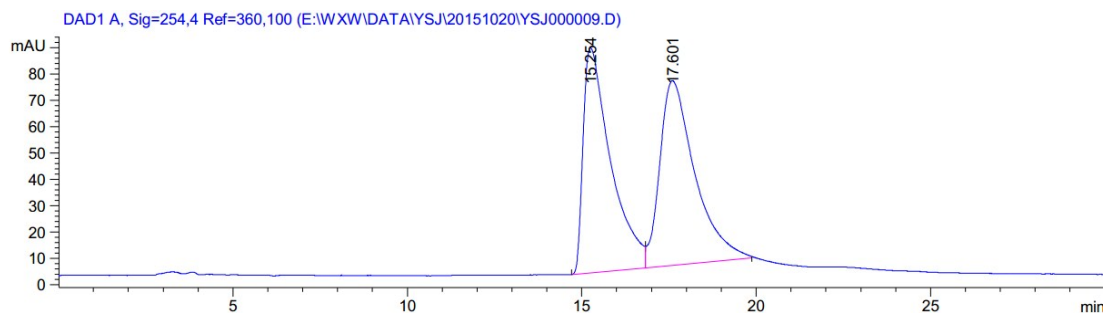




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.790	BB	0.6976	378.29303	7.33628	3.6523
2	22.013	BB	1.0081	9979.23340	146.97752	96.3477

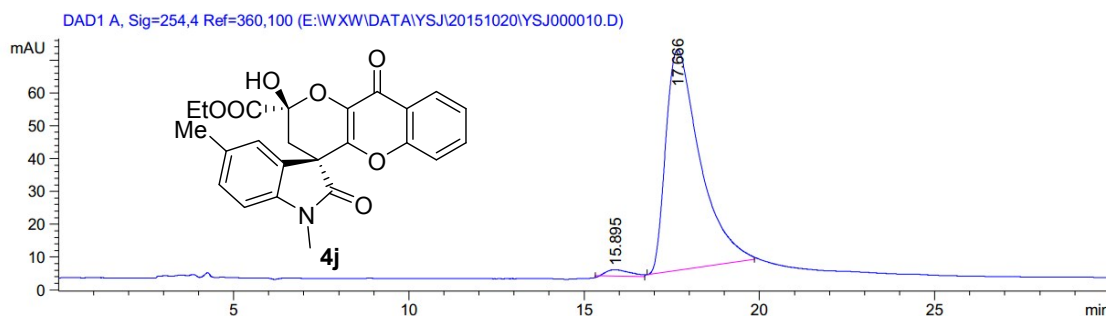
Totals : 1.03575e4 154.31380

**Ethyl 2'-hydroxy-1,5-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4j**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.254	BB	0.7923	4678.19775	85.51177	48.7580
2	17.601	BB	1.0291	4916.53760	70.19901	51.2420

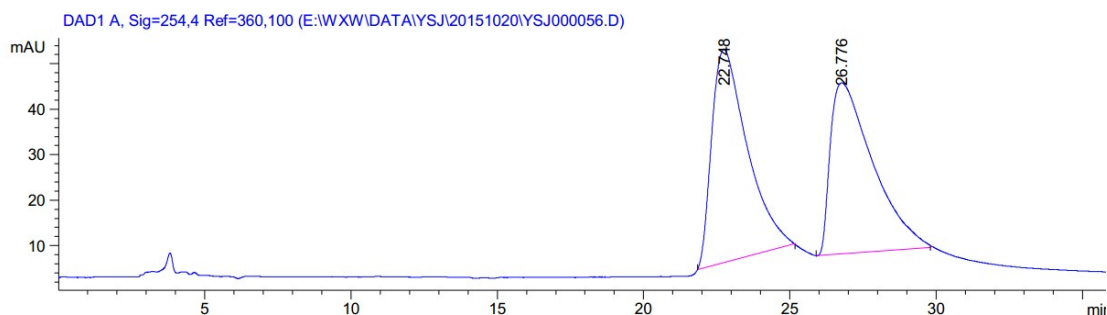
Totals : 9594.73535 155.71078



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.895	MM R	0.8109	92.14249	1.89384	1.9821
2	17.666	BB	1.0054	4556.61621	67.17547	98.0179

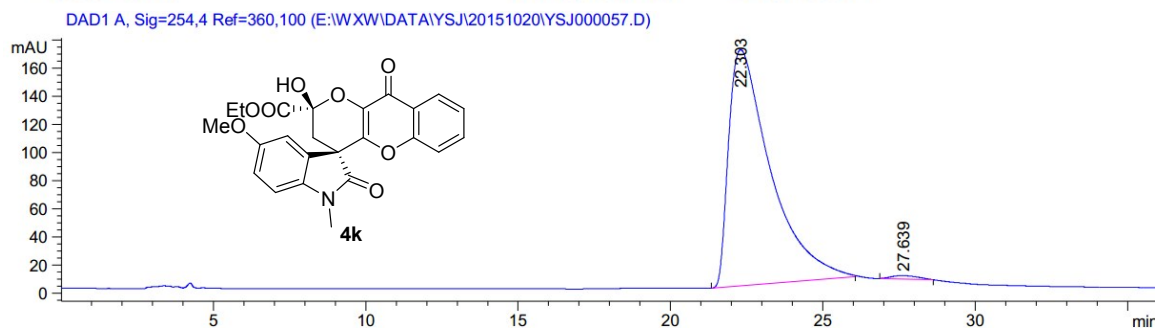
Totals : 4648.75871 69.06931

**Ethyl 2'-hydroxy-5-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4k**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.748	MM R	1.4036	3946.73608	46.86358	50.9388
2	26.776	BB	1.3745	3801.26660	37.62954	49.0612

Totals : 7748.00269 84.49311

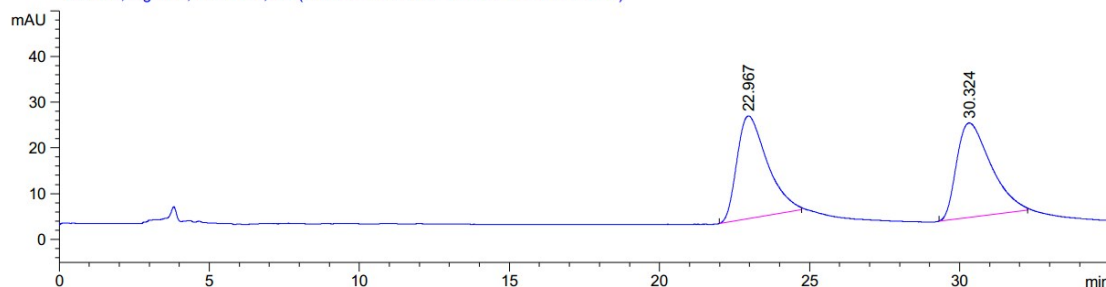


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.303	BB	1.3751	1.60207e4	167.60925	99.0847
2	27.639	MM R	1.0050	147.99214	2.45422	0.9153

Totals : 1.61687e4 170.06347

**Ethyl 6-chloro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4I**

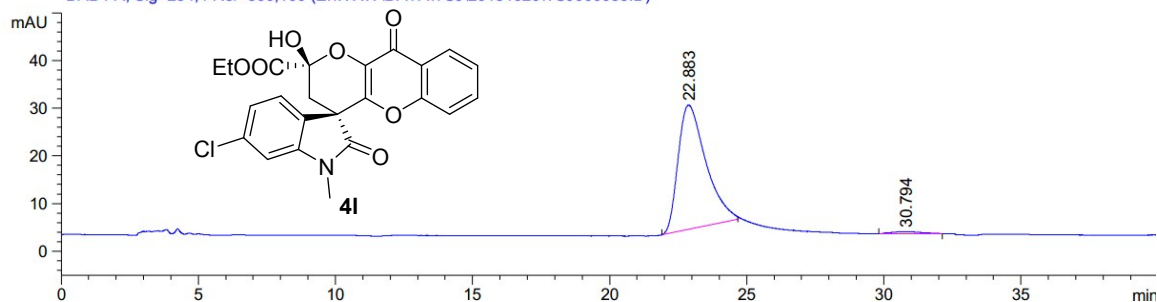
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000052.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.967	BB	0.9890	1571.45581	22.43939	49.0396
2	30.324	BB	1.1269	1633.00806	20.64290	50.9604

Totals : 3204.46387 43.08228

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000053.D)

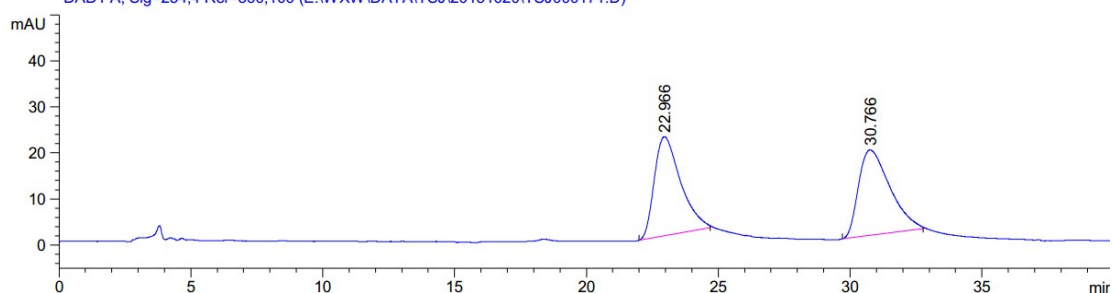


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.883	BB	1.0257	1828.51318	26.02448	98.2637
2	30.794	MM R	1.1908	32.30936	4.52210e-1	1.7363

Totals : 1860.82255 26.47669

**Ethyl 6-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4m**

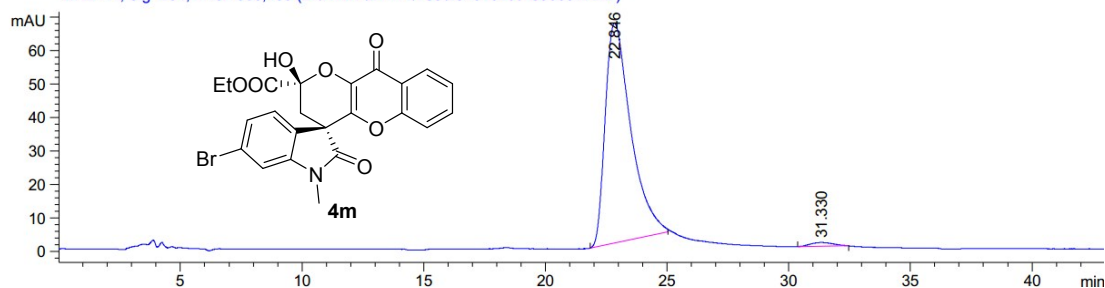
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000171.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.966	BB	0.9657	1494.78760	21.53656	49.2990
2	30.766	BB	1.1229	1537.30017	18.54871	50.7010

Totals : 3032.08777 40.08527

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000172.D)

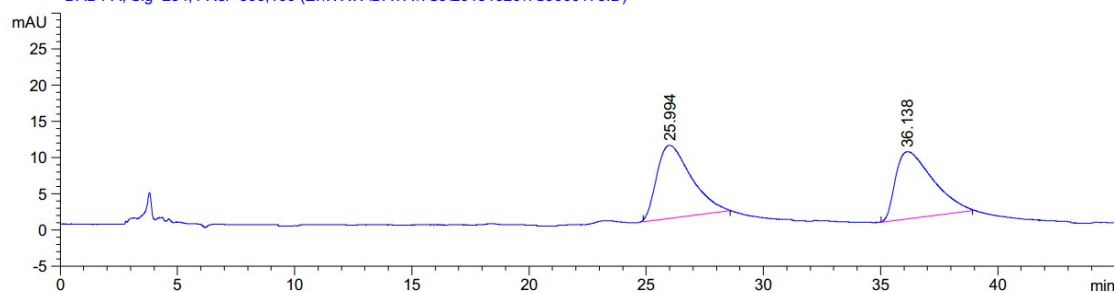


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.846	BB	1.0894	4810.16650	65.75564	98.4816
2	31.330	MM R	1.0880	74.16244	1.13608	1.5184

Totals : 4884.32894 66.89172

**Ethyl 2'-hydroxy-6-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4n**

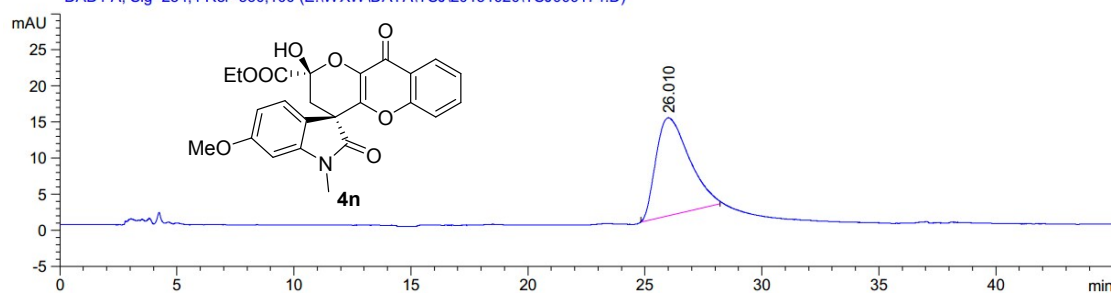
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000173.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.994	MM R	1.7062	1034.94873	10.10994	50.1373
2	36.138	MM R	1.8427	1029.28235	9.30976	49.8627

Totals : 2064.23108 19.41970

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000174.D)

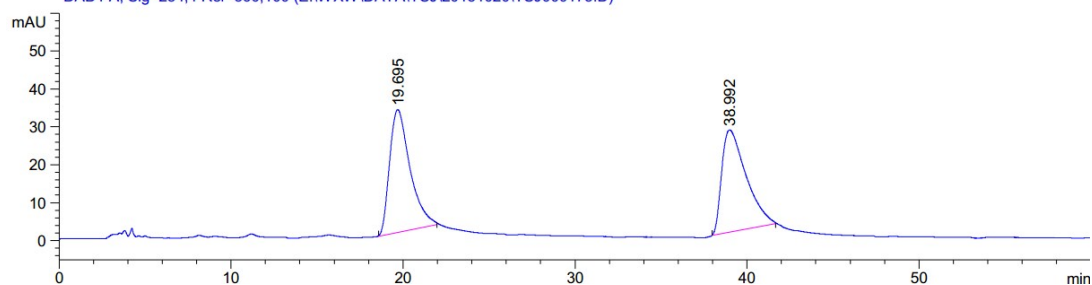


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.010	BB	1.1677	1338.87024	13.58643	100.0000

Totals : 1338.87024 13.58643

## Ethyl 7-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4o

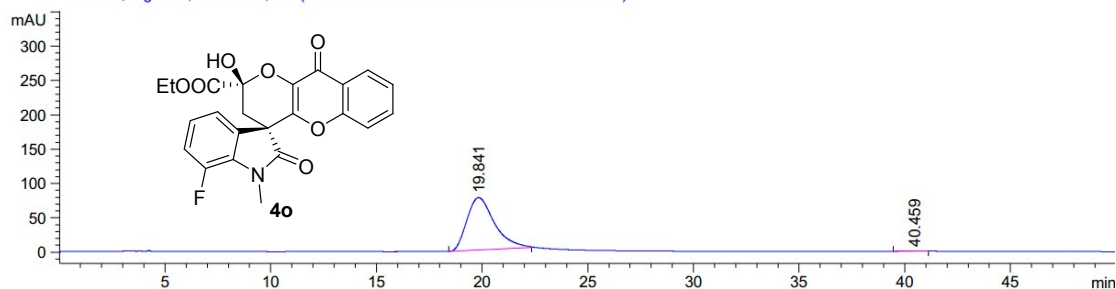
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000175.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.695	MM R	1.3759	2670.78442	32.35140	50.1927
2	38.992	MM R	1.6375	2650.27881	26.97417	49.8073

Totals : 5321.06323 59.32557

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000176.D)

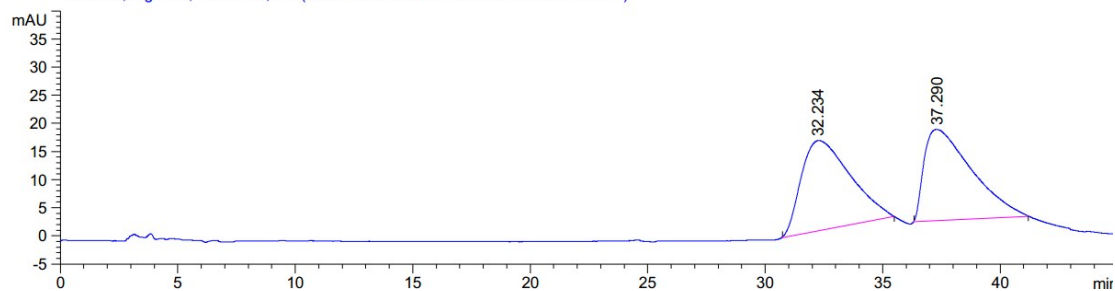


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.841	BB	1.3625	6898.83057	76.18313	99.5597
2	40.459	MM R	0.9463	30.50644	5.37286e-1	0.4403

Totals : 6929.33700 76.72041

**Ethyl 2'-hydroxy-1,7-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4p**

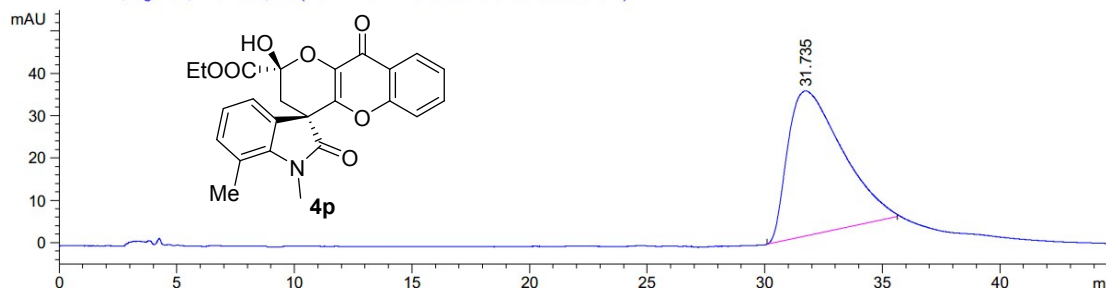
DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000024.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.234	MM R	2.4028	2318.36230	16.08074	50.4078
2	37.290	MM R	2.3472	2280.85034	16.19520	49.5922

Totals : 4599.21265 32.27595

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000025.D)

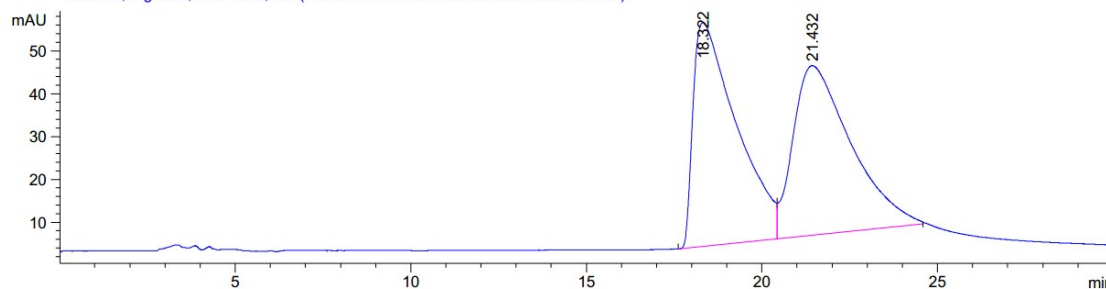


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.735	BB	1.8955	5495.75195	34.29660	100.0000

Totals : 5495.75195 34.29660

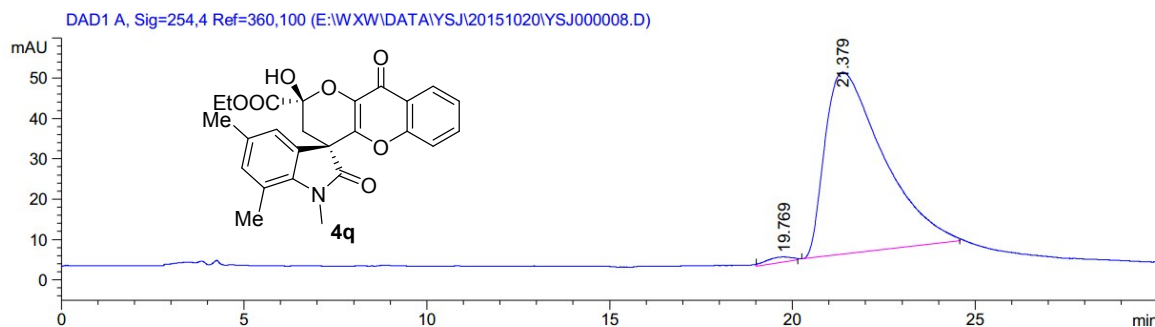
**Ethyl 2'-hydroxy-1,5,7-trimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4q**

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000006.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.322	BV	1.1735	4480.33936	52.29545	49.6593
2	21.432	VB	1.5225	4541.81445	39.58774	50.3407

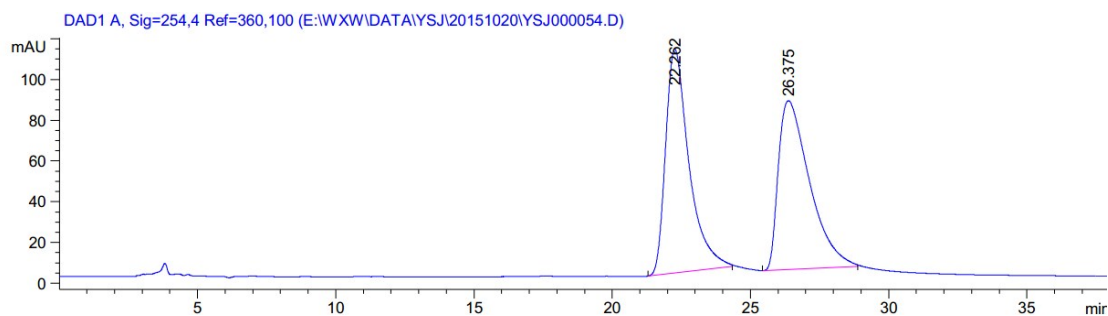
Totals : 9022.15381 91.88319



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.769	MM R	0.6400	64.79082	1.22321	1.2766
2	21.379	BB	1.5345	5010.36963	45.08607	98.7234

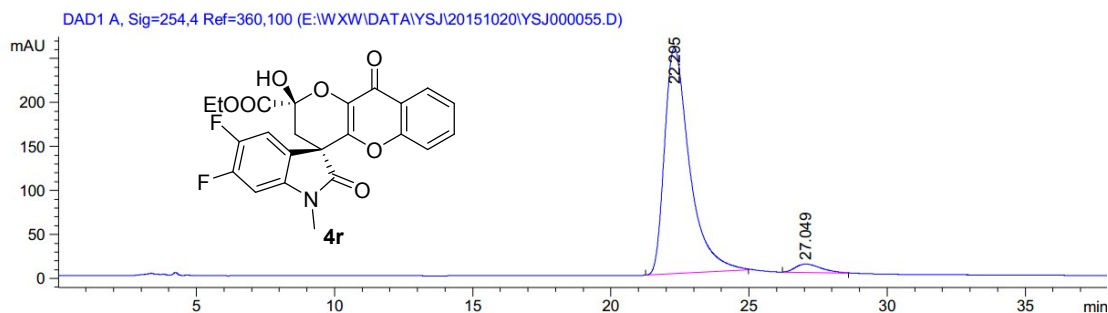
Totals : 5075.16045 46.30928

**Ethyl 5,6-difluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4r**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.262	BB	0.8865	6490.21143	109.97916	50.0013
2	26.375	BB	1.1830	6489.86816	82.92921	49.9987

Totals : 1.29801e4 192.90836

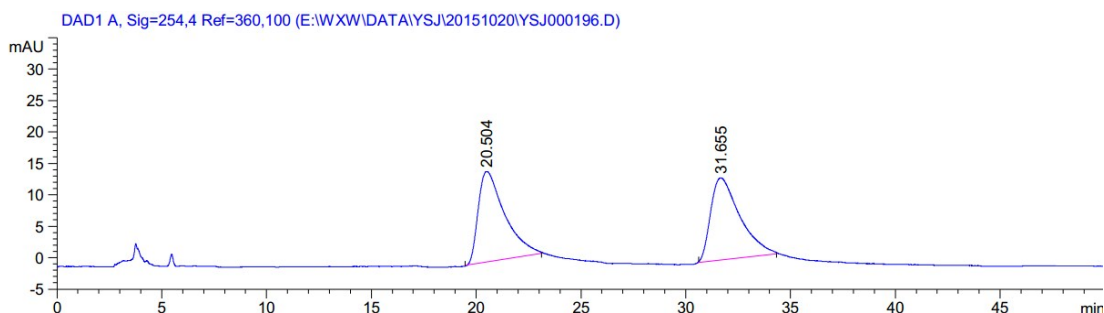




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.295	BB	0.9528	1.61579e4	256.55420	96.3889
2	27.049	BB	0.8077	605.34357	9.42067	3.6111

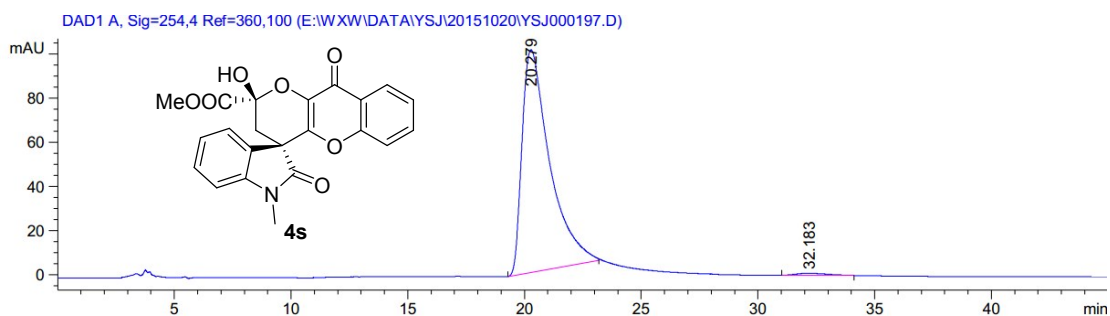
Totals : 1.67632e4 265.97487

**Methyl-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4s**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.504	MM R	1.4593	1260.40442	14.39524	49.9723
2	31.655	MM R	1.6140	1261.79944	13.02959	50.0277

Totals : 2522.20386 27.42484

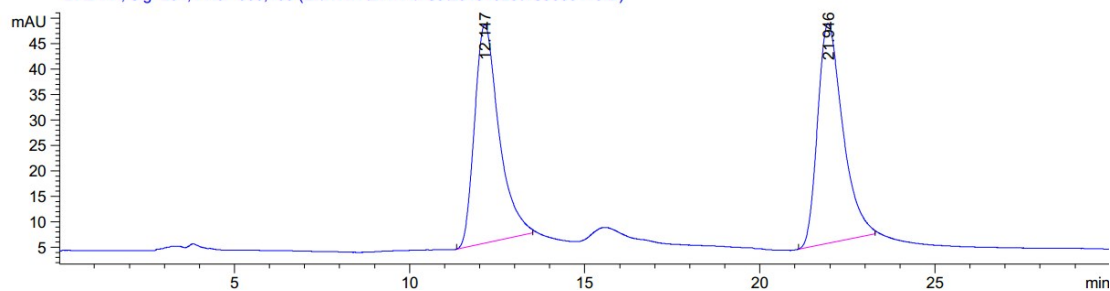


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.279	BB	1.1899	8348.59961	101.04670	98.9346
2	32.183	MM R	1.5266	89.90571	9.81533e-1	1.0654

Totals : 8438.50532 102.02823

**Ethyl 8'-fluoro-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4t**

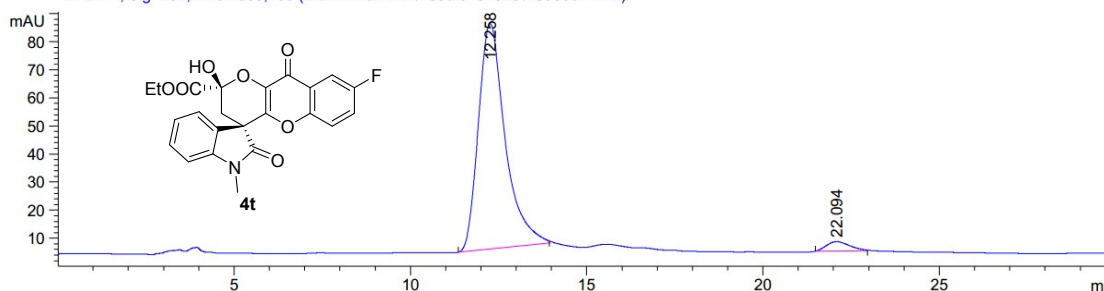
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000110.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.147	BB	0.7248	2082.40625	43.01824	49.1594
2	21.946	BB	0.7544	2153.62573	43.14286	50.8406

Totals : 4236.03198 86.16110

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000111.D)

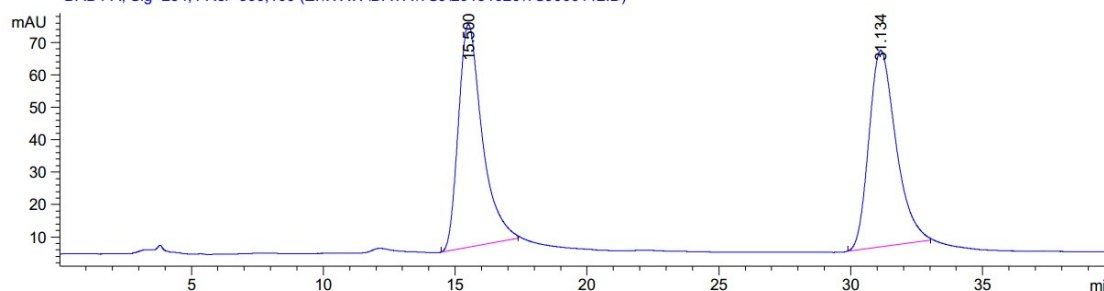


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.258	BB	0.7933	4220.74707	80.29678	96.5261
2	22.094	BB	0.6110	151.90244	3.32475	3.4739

Totals : 4372.64951 83.62153

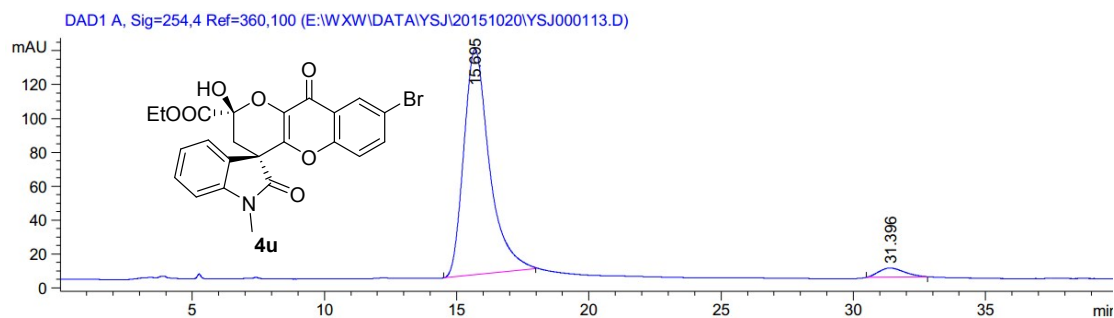
**Ethyl 8'-bromo-2'-hydroxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4u**

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\YSJ\20151020\YSJ000112.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.500	BB	0.9360	4312.88428	68.74043	49.8998
2	31.134	BB	1.0639	4330.20850	60.58333	50.1002

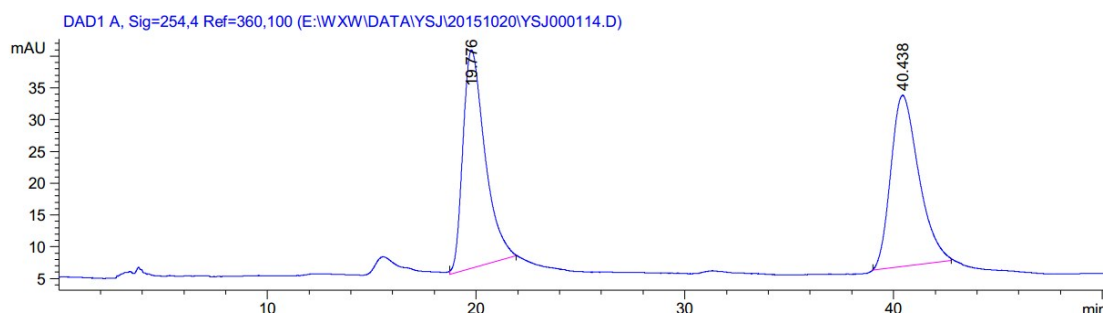
Totals : 8643.09277 129.32376



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.695	BB	1.0187	9002.20996	133.16742	95.9956
2	31.396	BB	0.8082	375.52078	5.47481	4.0044

Totals : 9377.73074 138.64223

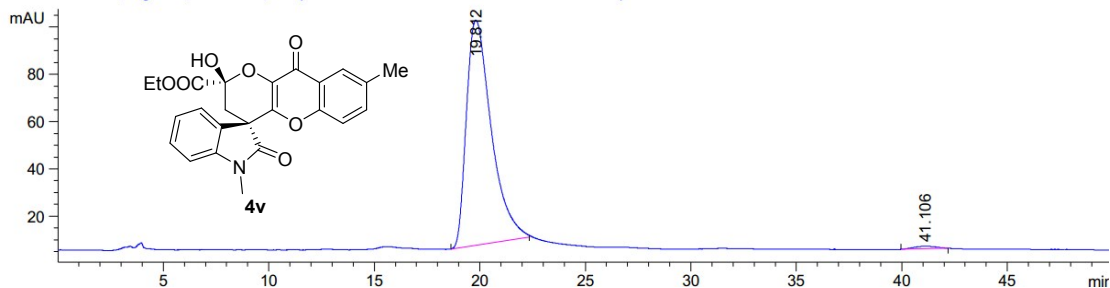
### Ethyl 2'-hydroxy-1,8'-dimethyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 4v



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.776	MM R	1.2252	2524.61938	34.34168	50.0575
2	40.438	BB	1.3200	2518.82397	26.95934	49.9425

Totals : 5043.44336 61.30102

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\YSJ20151020\YSJ000115.D)

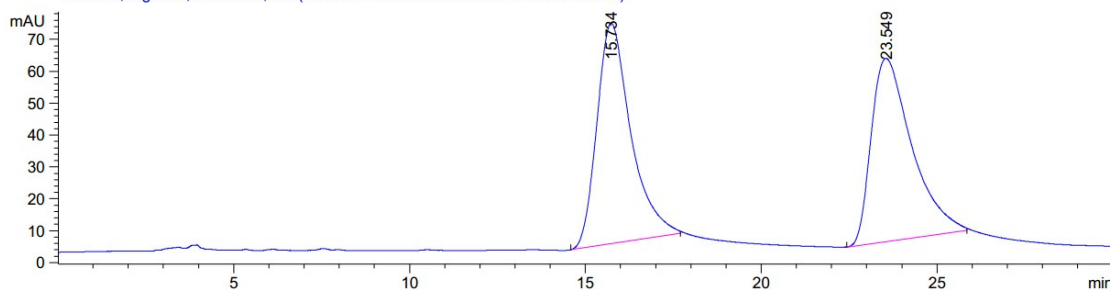


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.812	BB	1.2437	7788.38867	95.07392	98.9898
2	41.106	MM R	1.2343	79.48289	1.07323	1.0102

Totals : 7867.87157 96.14715

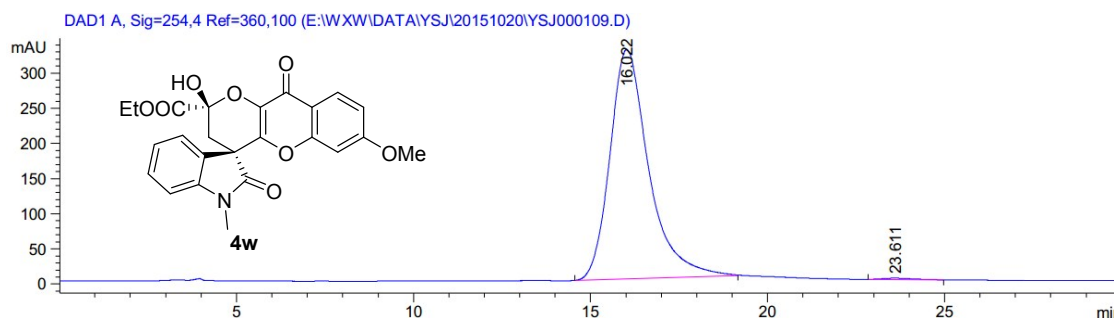
**Ethyl 2'-hydroxy-7'-methoxy-1-methyl-2,10'-dioxo-2',3'-dihydro-10'H-spiro [indoline-3,4'-pyrano[3,2-*b*]chromene]-2'-carboxylate 4w**

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\YSJ20151020\YSJ000108.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.734	BB	0.9958	4638.27930	69.21696	50.1448
2	23.549	BB	1.1932	4611.49463	57.53107	49.8552

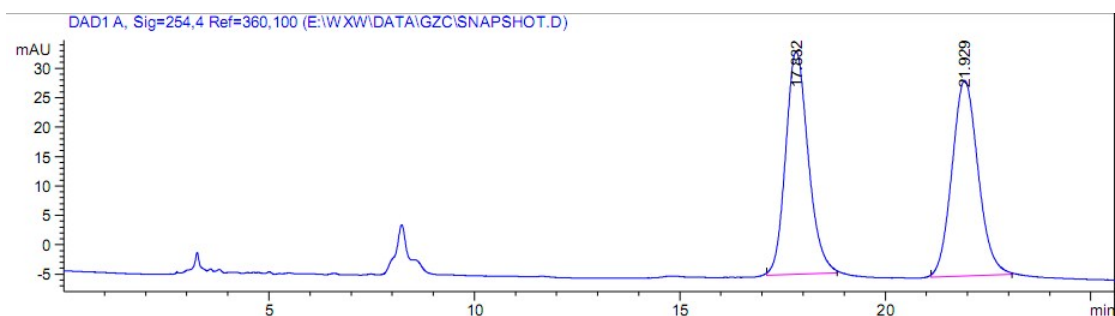
Totals : 9249.77393 126.74802



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.022	BB	1.1426	2.49009e4	326.20676	99.5273
2	23.611	MM R	1.0072	118.26797	1.95712	0.4727

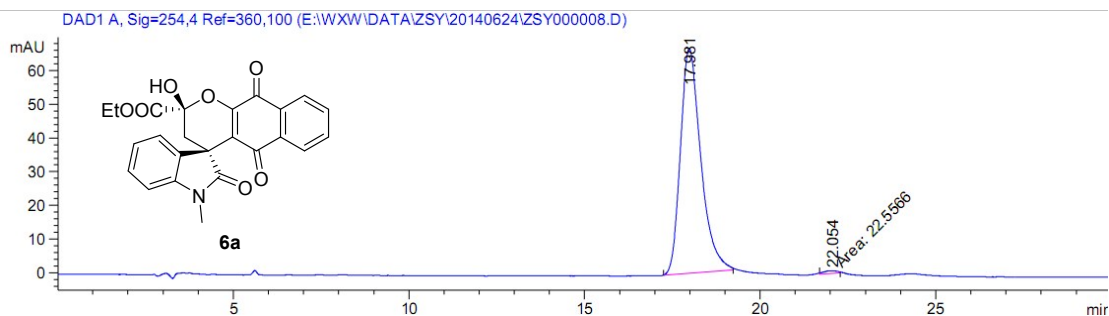
Totals : 2.50192e4 328.16388

**Ethyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6a**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.832	BB	0.5838	1448.11353	37.89828	49.6325
2	21.929	BB	0.6798	1469.55640	33.23857	50.3675

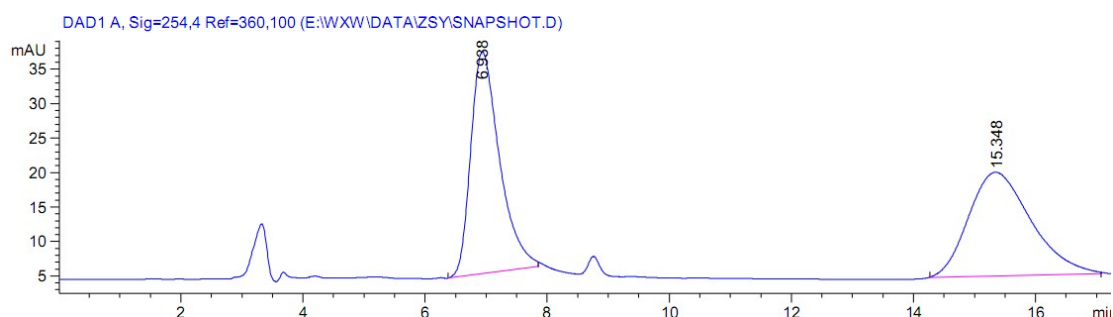
Totals : 2917.66992 71.13685



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.981	BB	0.6157	2696.38379	66.69093	99.1704
2	22.054	MM	0.3451	22.55664	8.12515e-1	0.8296

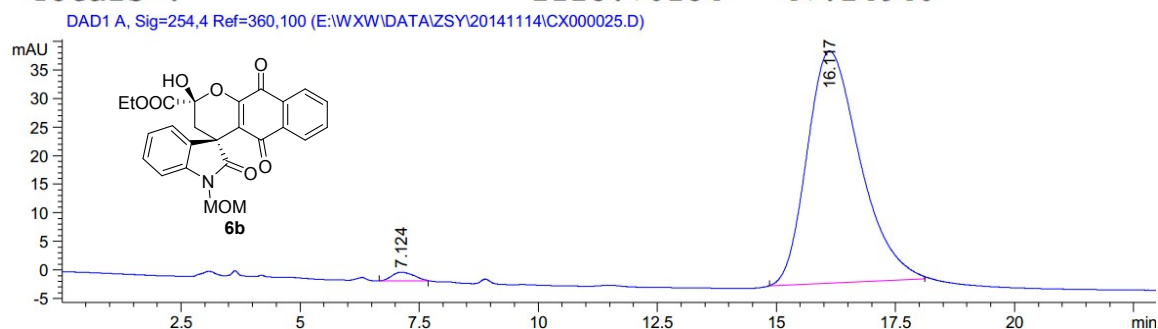
Totals : 2718.94043 67.50345

**Ethyl-2-hydroxy-1'-(methoxymethyl)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6b**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.938	BB	0.4949	1056.68359	32.19254	49.7099
2	15.348	BB	1.0463	1069.01794	15.05686	50.2901

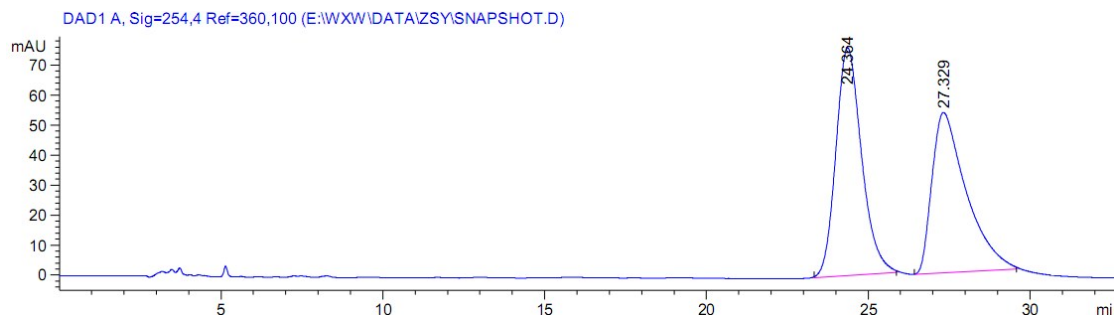
Totals : 2125.70154 47.24940



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.124	MM R	0.5240	47.47104	1.50998	1.4911
2	16.117	BB	1.1544	3136.22583	40.63460	98.5089

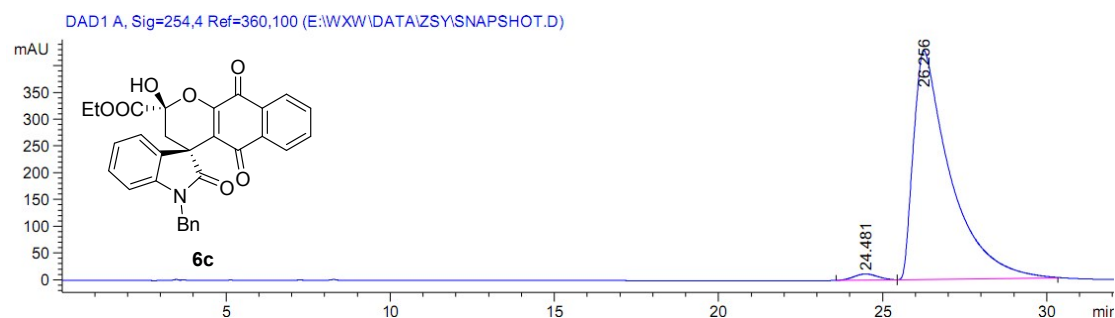
Totals : 3183.69687 42.14458

**Ethyl-1'-benzyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6c**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.364	BB	0.8469	4197.37402	75.93567	51.5773
2	27.329	BB	1.0733	3940.64893	53.50246	48.4227

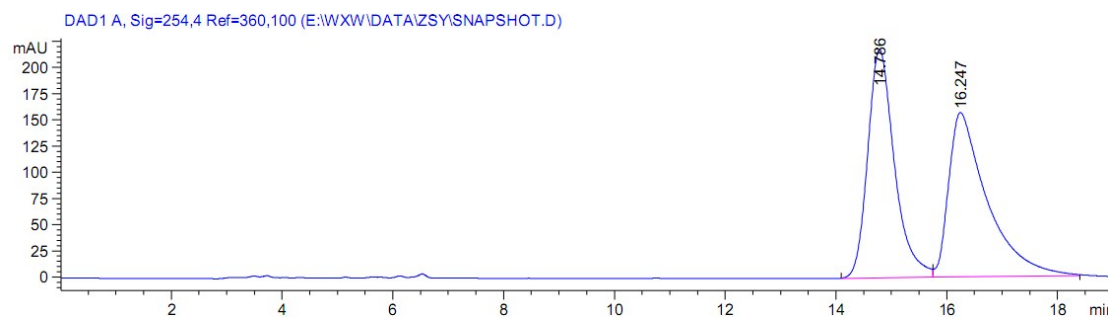
Totals : 8138.02295 129.43813



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.481	BV	0.7807	583.87915	11.53107	1.7213
2	26.256	VB	1.1262	3.33361e4	427.31015	98.2787

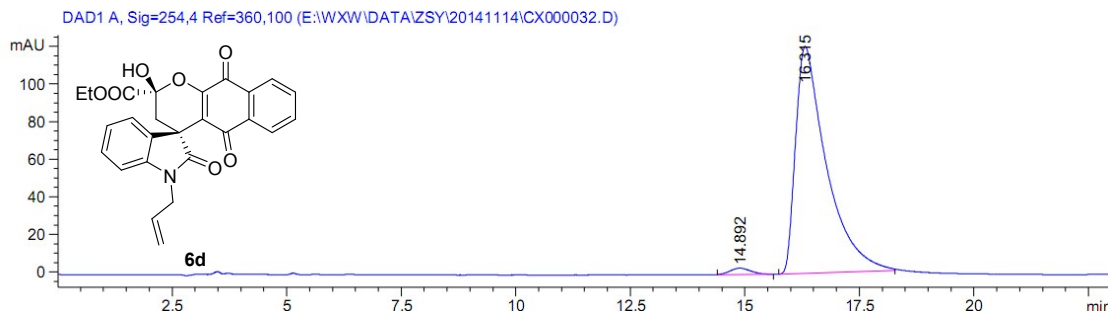
Totals : 3.39200e4 438.84122

**Ethyl-1'-allyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6d**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.786	BV	0.5107	7334.21973	217.90457	49.1801
2	16.247	VB	0.6968	7578.76611	157.10030	50.8199

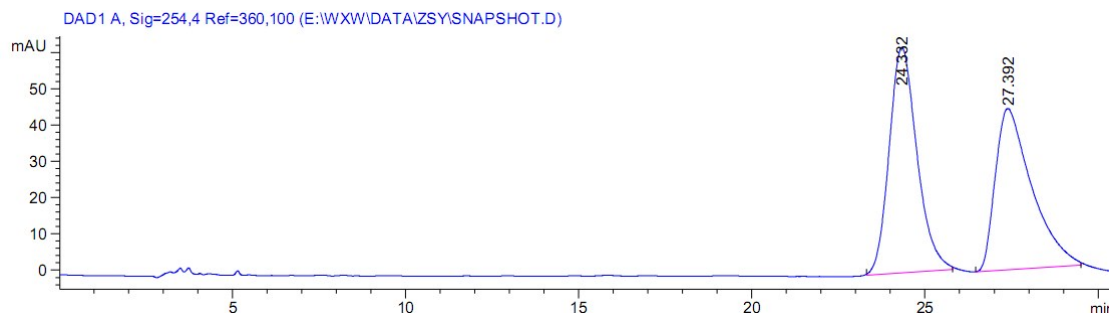
Totals : 1.49130e4 375.00487



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.892	BB	0.4700	107.36703	3.40346	1.8652
2	16.315	BB	0.6798	5648.83252	120.75301	98.1348

Totals : 5756.19955 124.15646

**1'-benzyl-2-ethyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-1',2-dicarboxylate 6e**

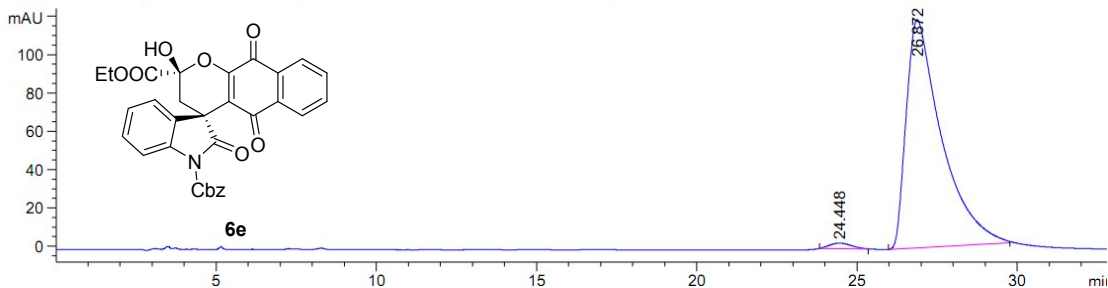


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.332	BB	0.8458	3473.16821	62.16756	51.6697
2	27.392	BB	1.0721	3248.69531	44.48141	48.3303

Totals : 6721.86353 106.64897



DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\ZSY\20141114\CX000034.D)

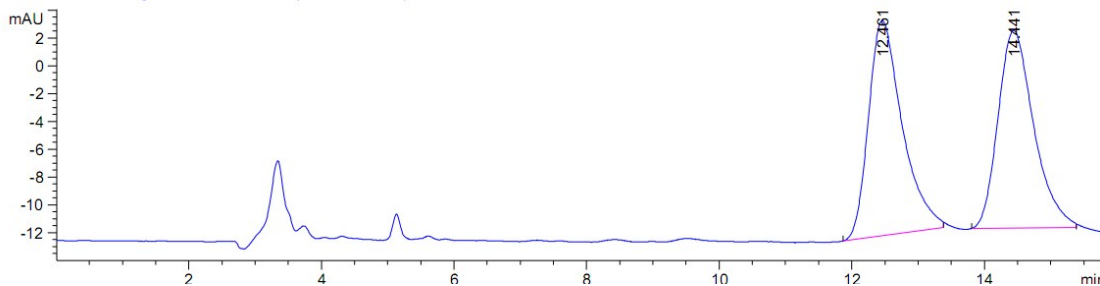


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.448	BB	0.5933	146.48157	3.00159	1.5821
2	26.872	BB	1.1189	9111.98145	119.05298	98.4179

Totals : 9258.46301 122.05457

**Ethyl-1'-acetyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6f**

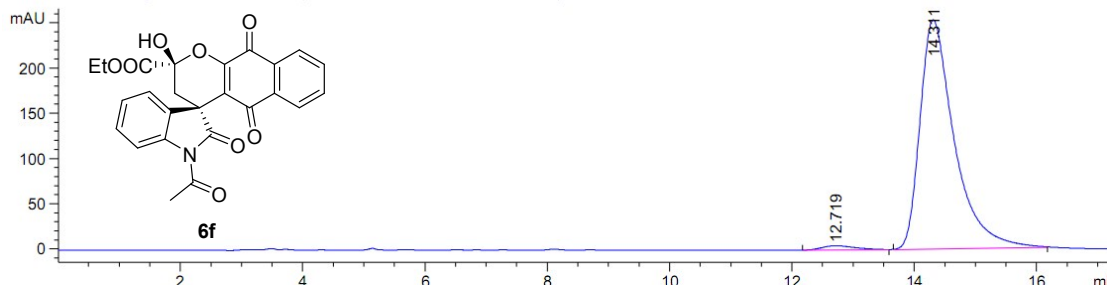
DAD1 A, Sig=254.4 Ref=360,100 (SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.461	BB	0.5252	545.09662	15.46523	50.6342
2	14.441	BB	0.5704	531.44202	14.20676	49.3658

Totals : 1076.53864 29.67199

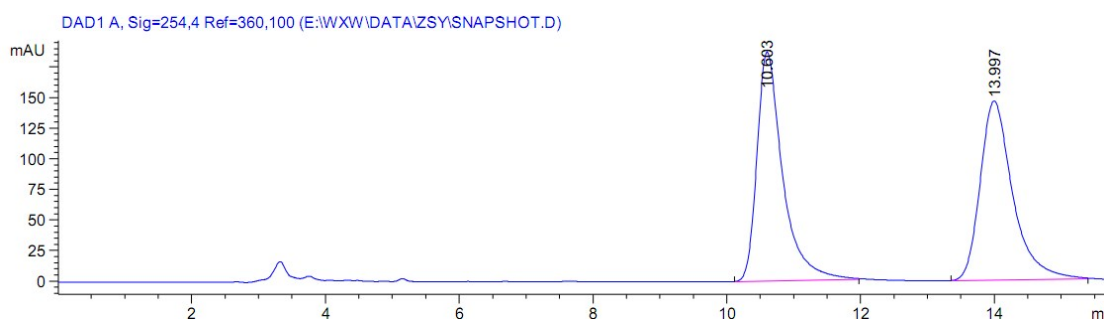
DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\ZSY\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.719	BB	0.5367	169.73434	4.64057	1.6889
2	14.311	BB	0.5813	9880.06836	253.14079	98.3111

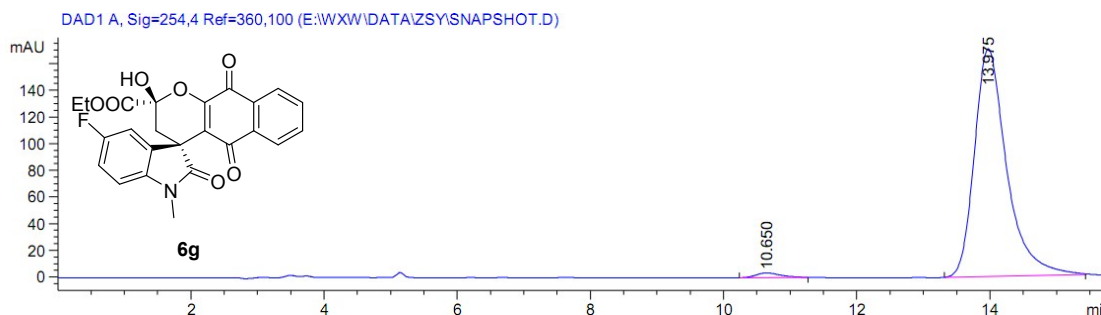
Totals : 1.00498e4 257.78137

**Ethyl-5'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6g**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.603	BB	0.3962	5012.96289	187.33189	50.2219
2	13.997	BB	0.5097	4968.66504	146.50003	49.7781

Totals : 9981.62793 333.83192

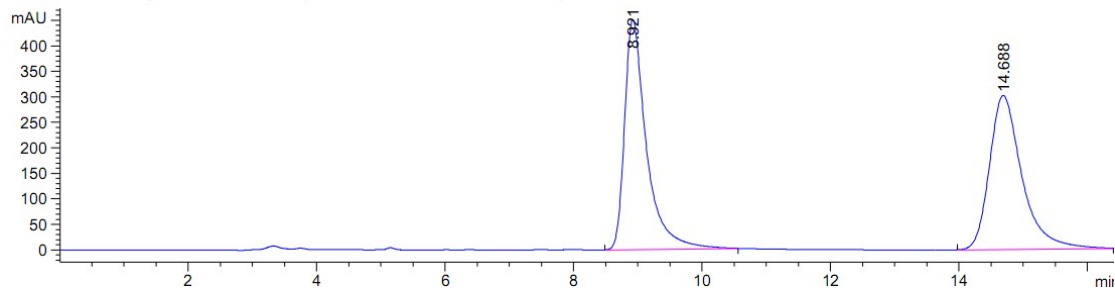


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.650	BB	0.3819	93.46729	3.56514	1.5989
2	13.975	BB	0.5070	5752.07910	170.75229	98.4011

Totals : 5845.54639 174.31743

**Ethyl-5'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6h**

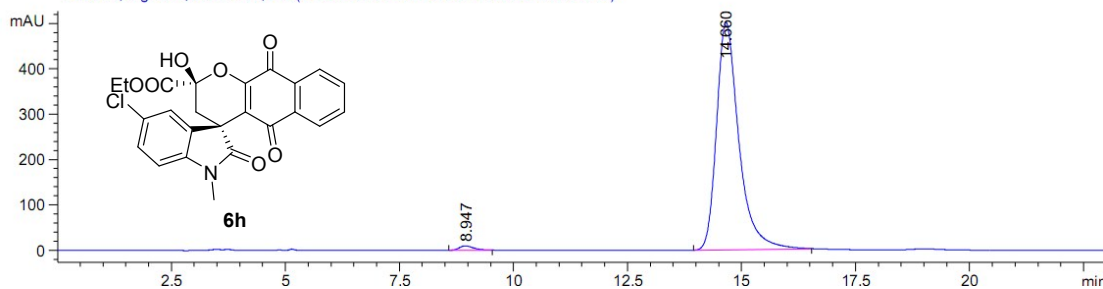
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZSY\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.921	BB	0.3486	1.06937e4	450.99490	50.2570
2	14.688	BB	0.5250	1.05844e4	301.91107	49.7430

Totals : 2.12781e4 752.90598

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZSY\20141029\CX000029.D)

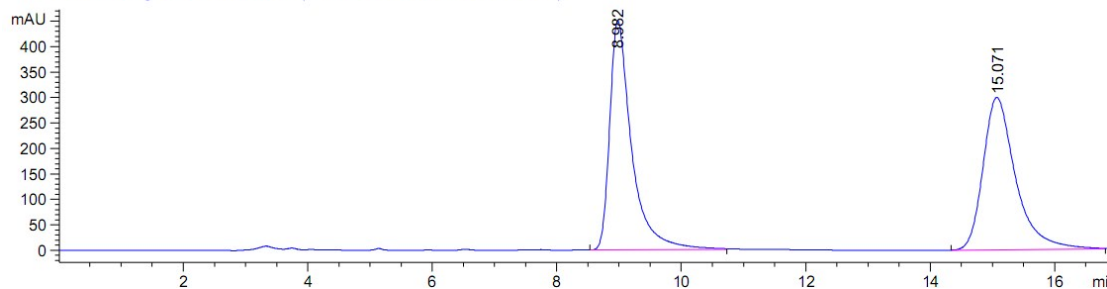


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.947	BB	0.3389	222.97485	9.81894	1.2845
2	14.660	BB	0.5122	1.71357e4	502.06799	98.7155

Totals : 1.73587e4 511.88693

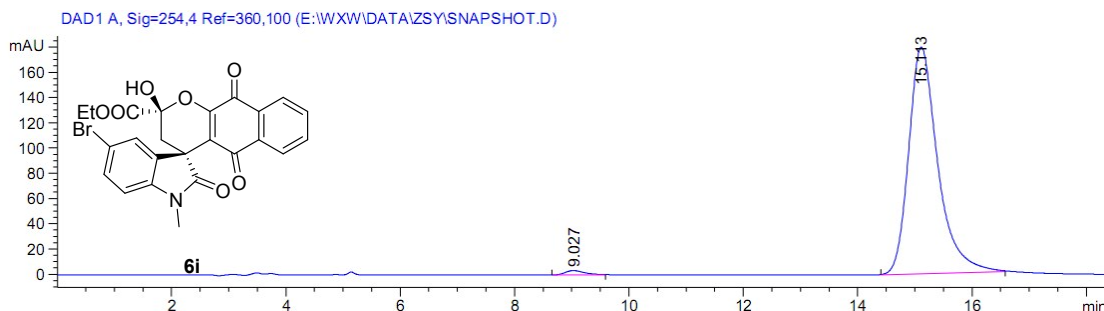
**Ethyl-5'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6i**

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZSY\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.982	VB	0.3620	1.10359e4	450.25565	50.3668
2	15.071	BB	0.5459	1.08751e4	299.31036	49.6332

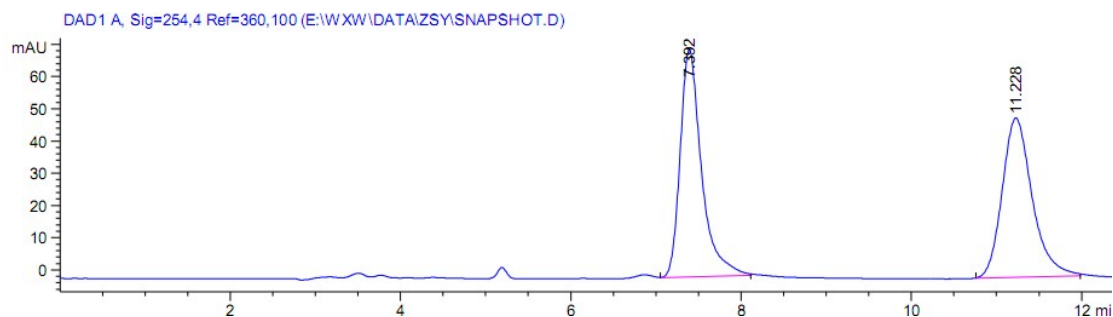
Totals : 2.19110e4 749.56601



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.027	BB	0.3549	81.02819	3.43909	1.2582
2	15.113	BB	0.5333	6359.01563	179.48303	98.7418

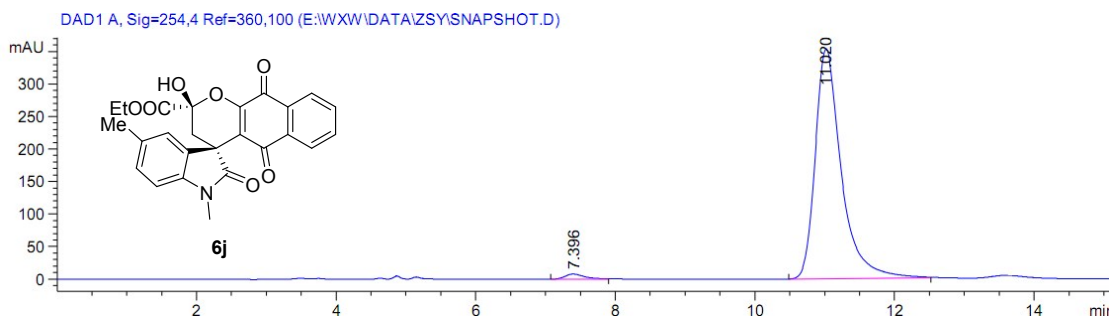
Totals : 6440.04382 182.92212

**Ethyl-2-hydroxy-1',5'-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6j**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.392	VB	0.2611	1228.95825	70.58884	50.3530
2	11.228	BB	0.3719	1211.72485	49.44472	49.6470

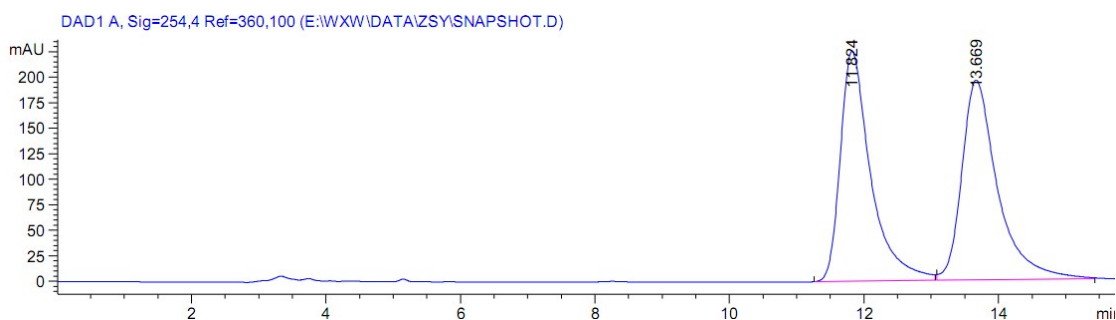
Totals : 2440.68311 120.03355



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.396	BB	0.2856	148.39984	7.81373	1.5917
2	11.020	BB	0.3887	9174.66406	353.66498	98.4083

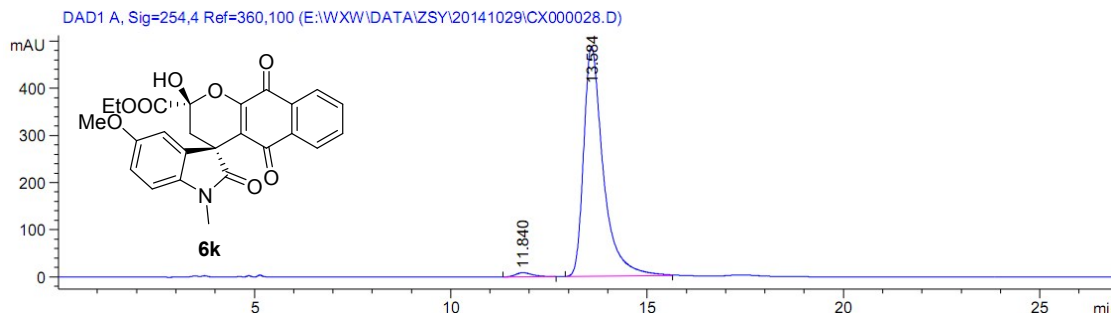
Totals : 9323.06390 361.47870

**Ethyl-2-hydroxy-5'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6k**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.824	BB	0.4654	7111.09766	225.82668	49.5036
2	13.669	BB	0.5480	7253.70947	195.89703	50.4964

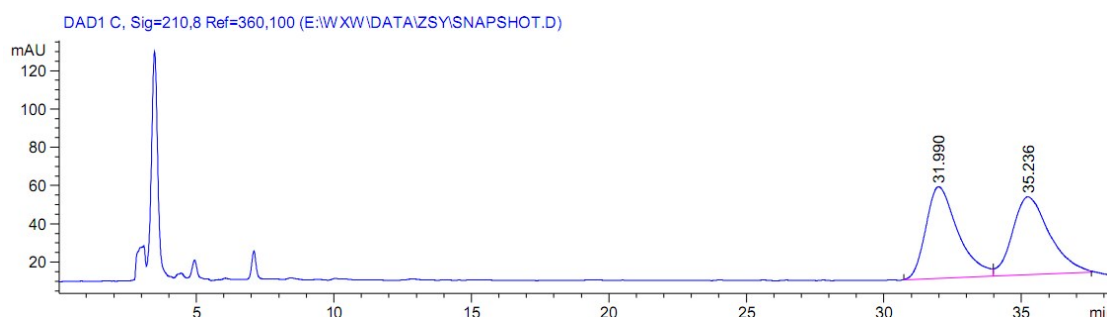
Totals : 1.43648e4 421.72371



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.840	BB	0.4464	264.84549	8.91912	1.5432
2	13.584	BB	0.5146	1.68968e4	487.22214	98.4568

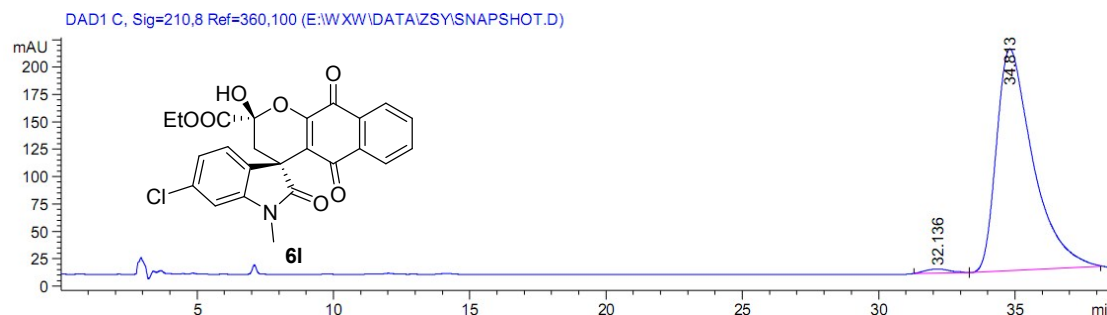
Totals : 1.71617e4 496.14126

**Ethyl-6'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6l**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.990	BB	1.1777	3894.71045	47.84369	50.6530
2	35.236	BB	1.2792	3794.28589	40.64005	49.3470

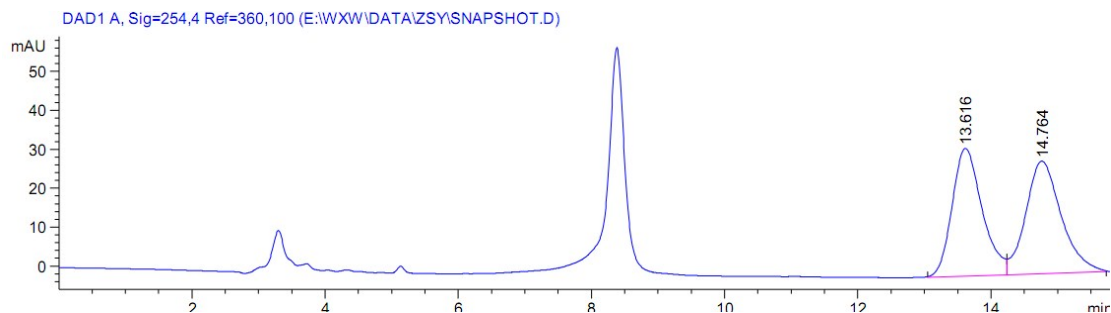
Totals : 7688.99634 88.48373



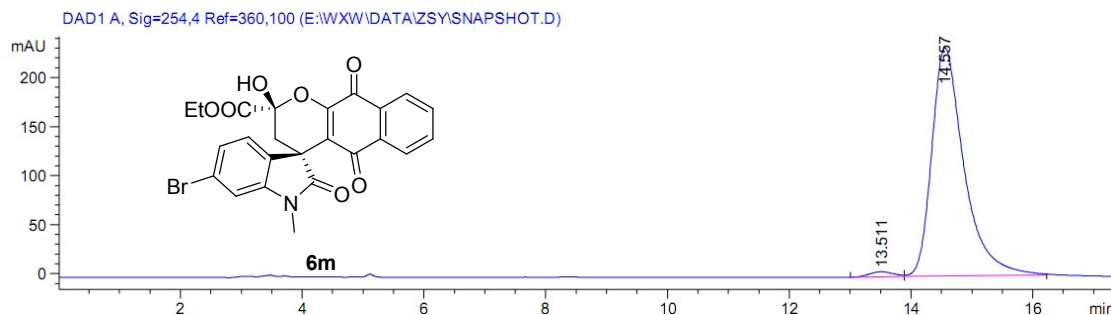
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.136	BV	0.7702	253.28360	3.87711	1.3232
2	34.813	VB	1.3462	1.88884e4	202.87770	98.6768

Totals : 1.91417e4 206.75481

**Ethyl-6'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6m**



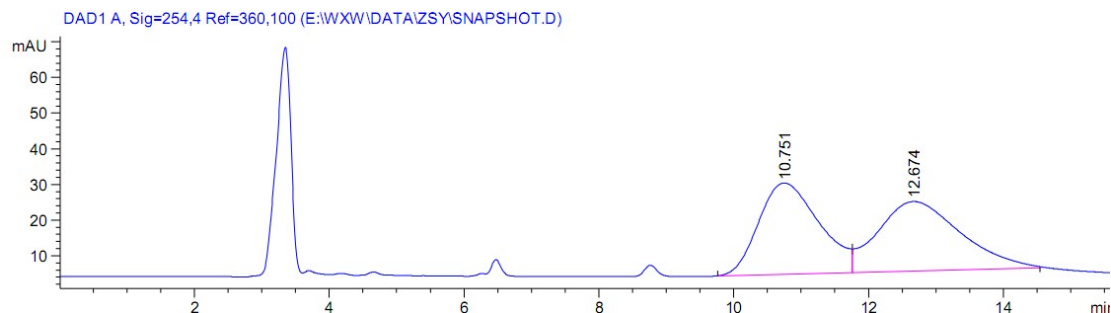
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.616	BV	0.4757	1028.76245	32.82059	48.9957
2	14.764	VB	0.5560	1070.93665	28.92279	51.0043



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.511	BV	0.4278	142.38757	5.16267	1.6358
2	14.557	VB	0.5513	8562.33496	232.69293	98.3642

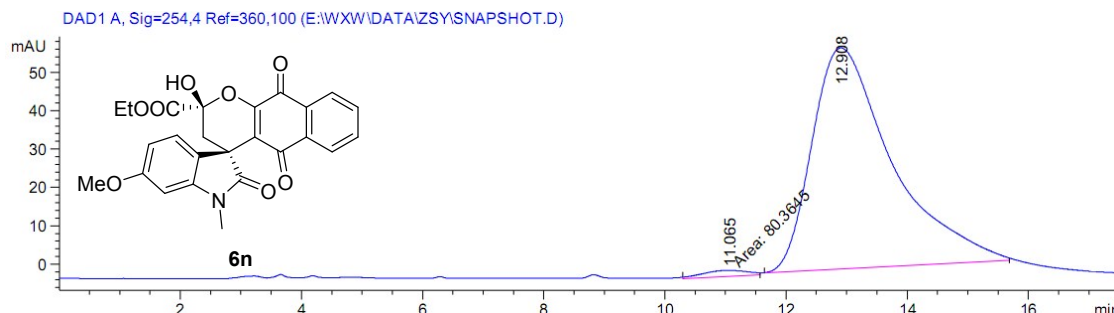
Totals : 8704.72253 237.85561

**Ethyl-2-hydroxy-6'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6n**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.751	BV	0.9416	1595.52100	25.58156	48.9236
2	12.674	VB	1.2125	1665.72729	19.50119	51.0764

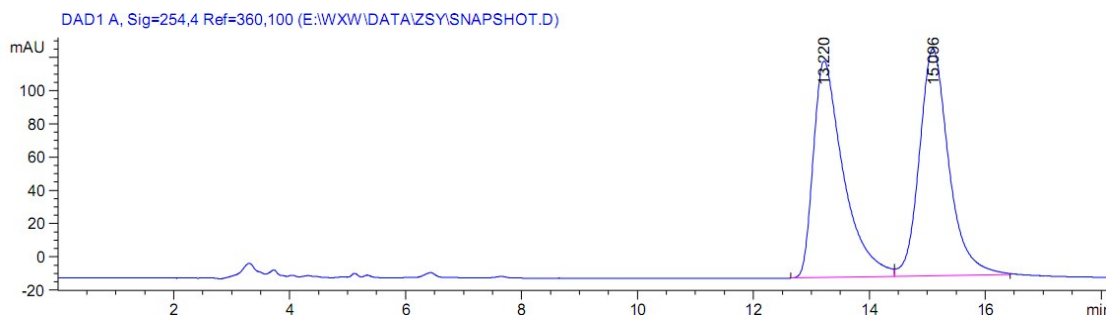
Totals : 3261.24829 45.08275



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.065	MM	0.6468	80.36452	1.50776	1.5007
2	12.908	BB	1.3614	5274.90186	57.54477	98.4993

Totals : 5355.26637 59.05252

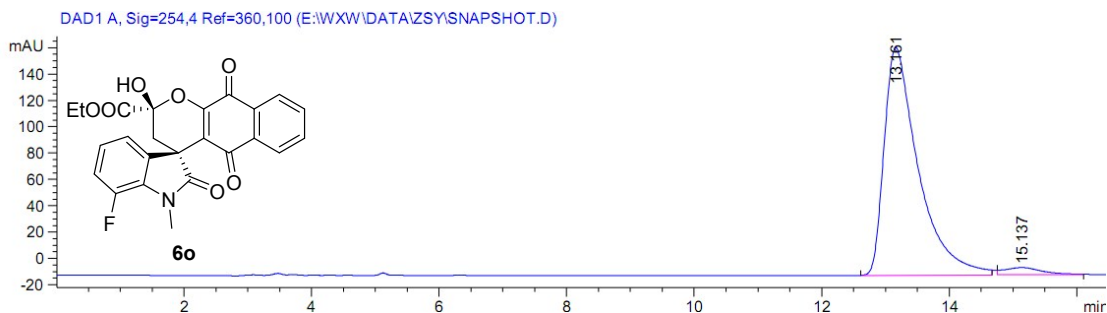
**Ethyl-7'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6o**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.220	BV	0.5366	4698.39893	130.33797	49.2694
2	15.096	VB	0.5351	4837.74072	136.62614	50.7306

Totals : 9536.13965 266.96411

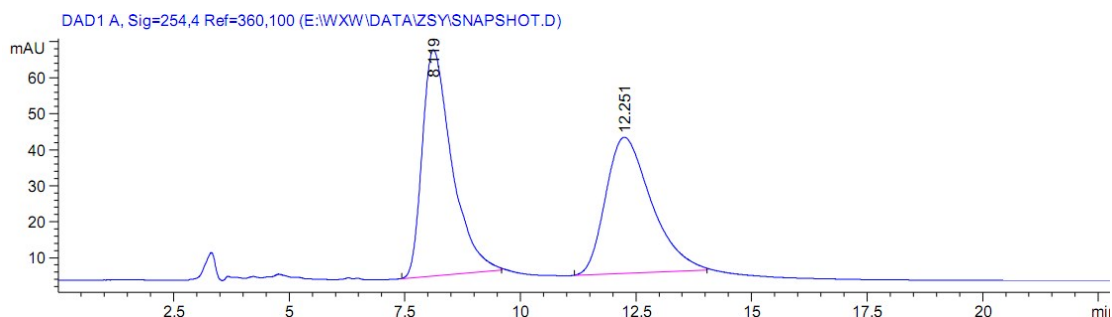




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.161	BB	0.5479	6432.60205	172.94328	96.6316
2	15.137	BB	0.5768	224.22606	5.44093	3.3684

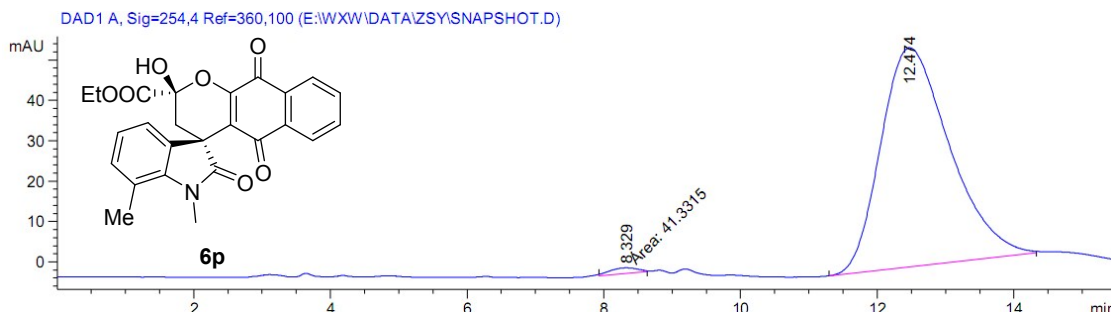
Totals : 6656.82811 178.38422

**Ethyl-2-hydroxy-1',7'-dimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6p**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.119	BB	0.6721	2809.10767	62.77014	51.9935
2	12.251	BB	1.0397	2593.69434	37.74561	48.0065

Totals : 5402.80200 100.51575

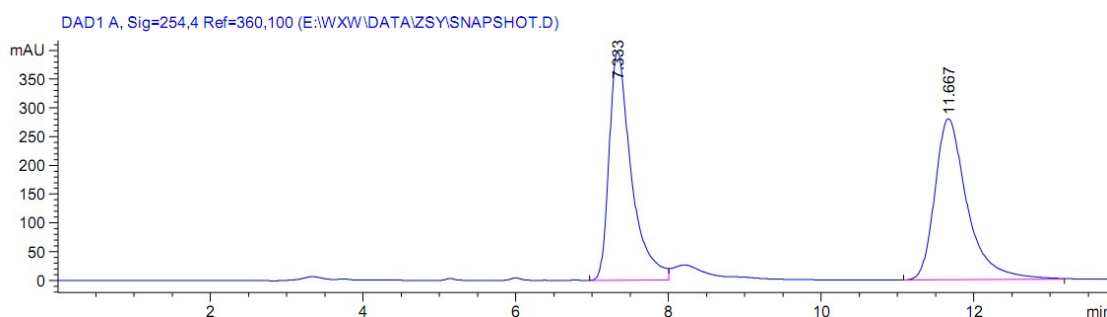


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.329	MM	0.4899	41.33153	1.40609	1.0764
2	12.474	BB	1.0530	3798.54053	54.24078	98.9236

Totals : 3839.87206 55.64687

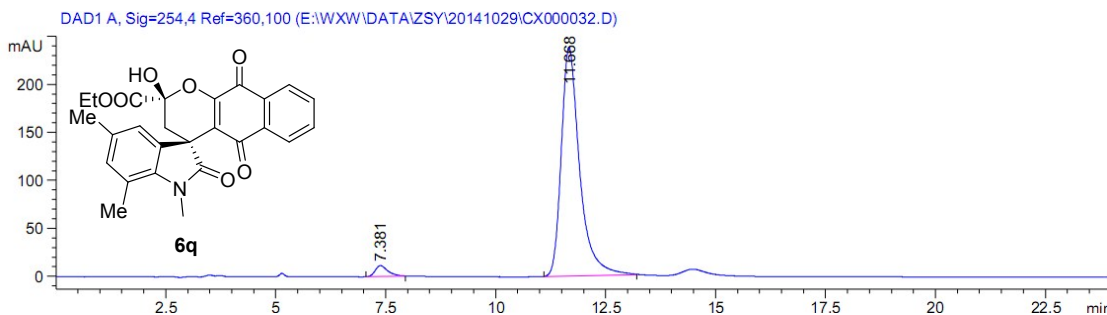
**Ethyl-2-hydroxy-1',5',7'-trimethyl-2',5,10-trioxo-2,3,5,10-**

**tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6q**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.333	BV	0.2993	8018.89600	397.64301	49.2899
2	11.667	BB	0.4415	8249.94434	280.24136	50.7101

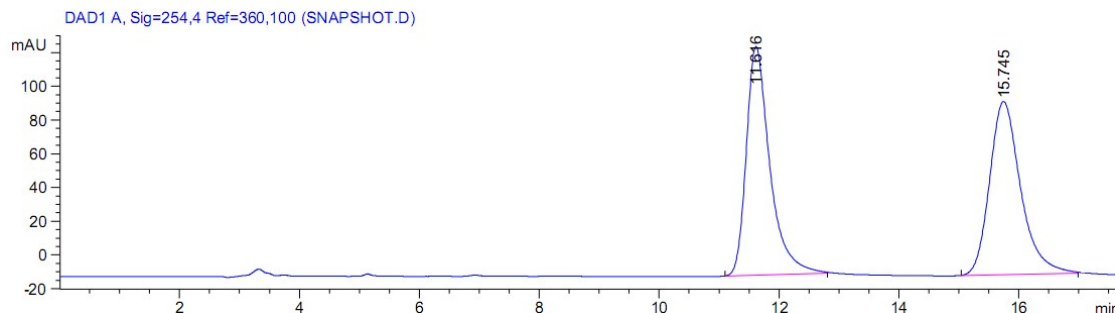
Totals : 1.62688e4 677.88437



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.381	BB	0.3033	231.95744	11.40619	3.2345
2	11.668	BB	0.4358	6939.35742	238.27428	96.7655

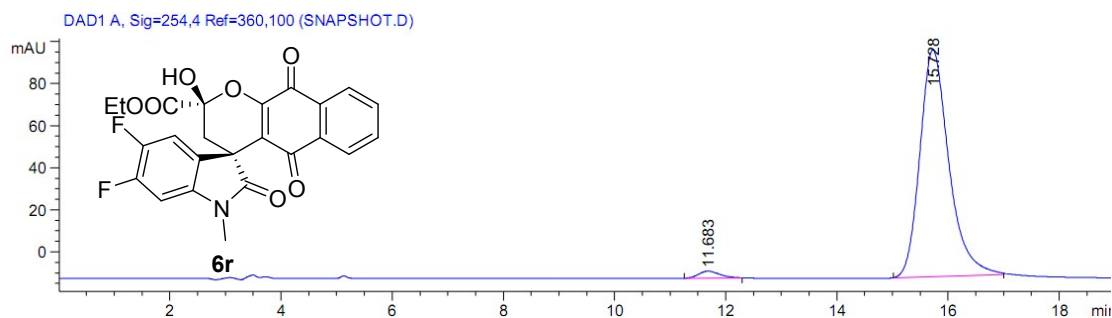
Totals : 7171.31487 249.68047

**Ethyl-5',6'-difluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6r**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.616	BB	0.4090	3706.02222	135.51880	50.0802
2	15.745	BB	0.5478	3694.14624	102.66139	49.9198

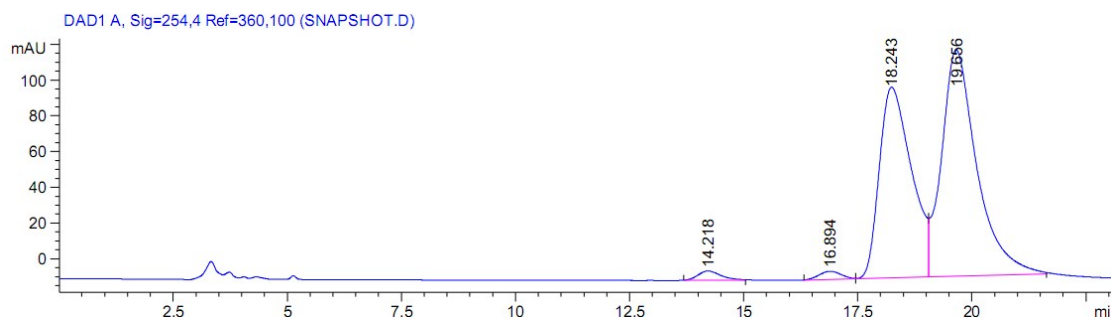
Totals : 7400.16846 238.18019



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.683	BB	0.4022	91.15219	3.38452	2.2733
2	15.728	BB	0.5496	3918.56079	107.91299	97.7267

Totals : 4009.71298 111.29751

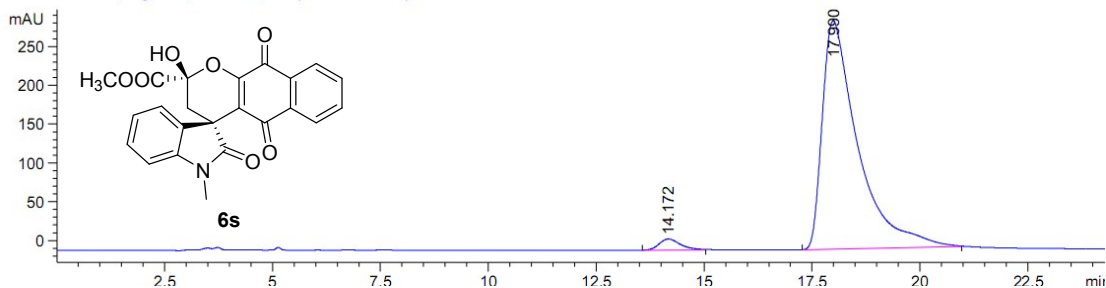
**Methyl-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6s**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.218	BB	0.5257	178.67189	5.16410	1.4451
2	16.894	BV	0.5209	151.20691	4.53598	1.2230
3	18.243	VV	0.7458	5228.24170	106.67732	42.2871
4	19.656	VB	0.7871	6805.55029	126.60309	55.0447

Totals : 1.23637e4 242.98049

DAD1 A, Sig=254,4 Ref=360,100 (SNAPSHOT.D)



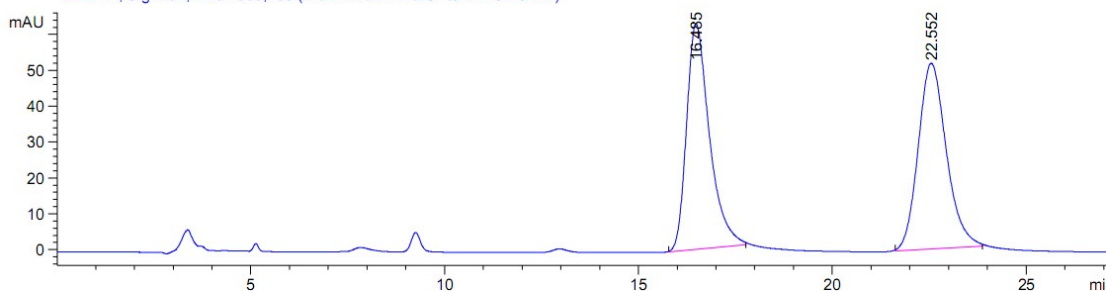
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.172	BB	0.5142	477.73090	14.13994	2.7595
2	17.990	BB	0.8292	1.68343e4	294.38358	97.2405

Totals : 1.73121e4 308.52352

**Ethyl-2-hydroxy-1',7-dimethyl-2',5,10-trioxo-2,3,5,10-**

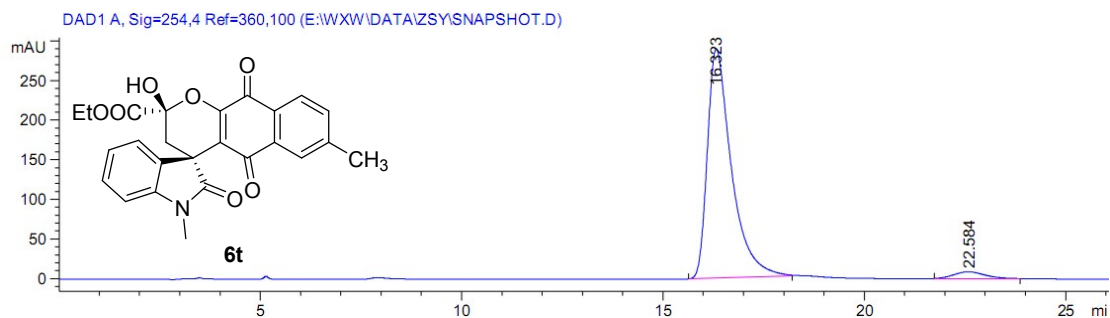
**tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 6t**

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\ZSY\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.485	BB	0.6187	2578.53394	62.84503	49.7469
2	22.552	BB	0.7692	2604.76709	51.74819	50.2531

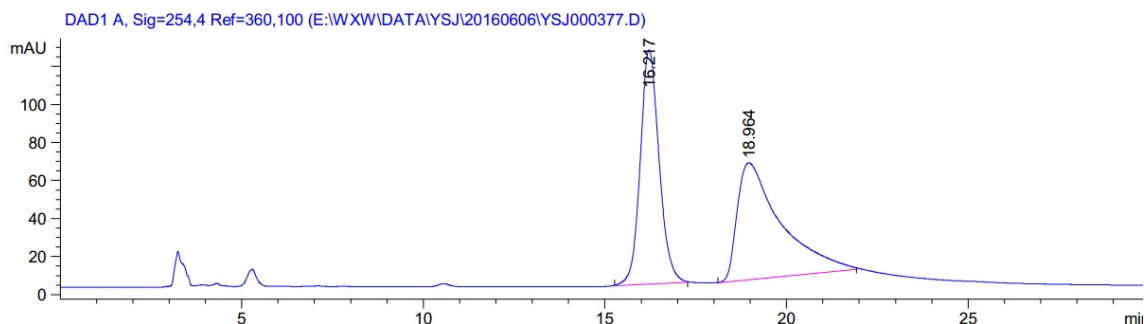
Totals : 5183.30103 114.59322



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.323	BB	0.6164	1.20090e4	289.21008	96.2763
2	22.584	BB	0.7949	464.47089	8.58945	3.7237

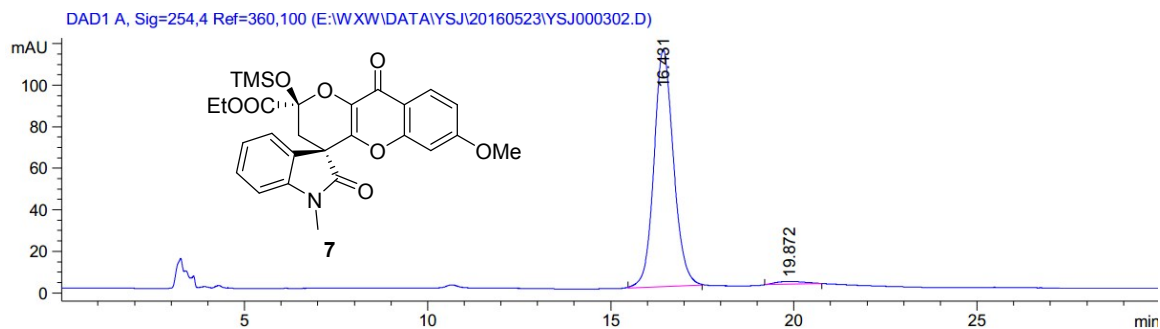
Totals : 1.24734e4 297.79954

**Ethyl-7'-methoxy-1-methyl-2,10'-dioxo-2'-((trimethylsilyl)oxy)-2',3'-dihydro-10'H-spiro[indoline-3,4'-pyrano[3,2-b]chromene]-2'-carboxylate 7**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.217	BB	0.5539	4451.29248	123.10169	46.5760
2	18.964	BB	1.1594	5105.75879	61.44842	53.4240

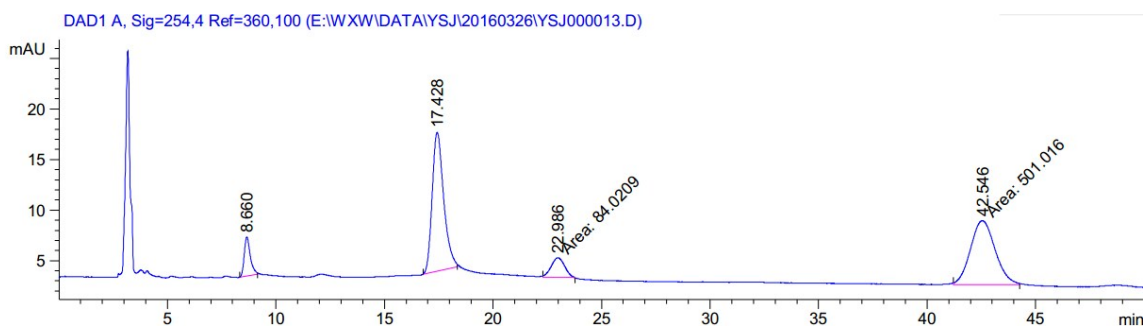
Totals : 9557.05127 184.55011



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.431	BB	0.5693	4237.82959	114.11116	98.2993
2	19.872	MM R	0.9135	73.32010	1.33773	1.7007

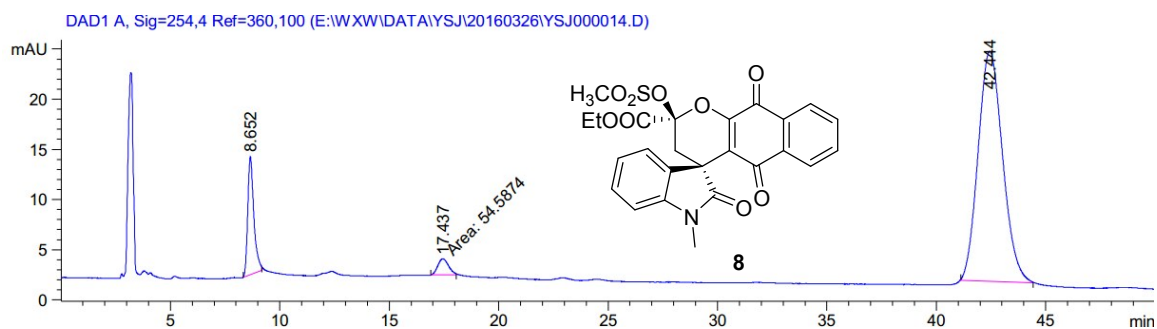
Totals : 4311.14969 115.44889

**Ethyl 1'-methyl-2-((methylthio)trioxidanyl)-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 8**



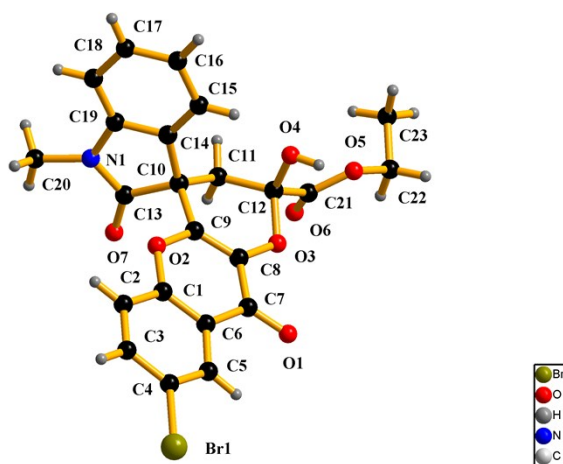
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.660	BB	0.2940	75.03631	3.87430	6.4299
2	17.428	BB	0.5564	506.91077	13.74205	43.4377
3	22.986	MM	0.7184	84.02094	1.94938	7.1998
4	42.546	MM	1.3177	501.01611	6.33699	42.9326

Totals : 1166.98413 25.90272



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.652	BB	0.2911	226.63710	11.74415	10.9727
2	17.437	MM	0.5693	54.58736	1.59797	2.6429
3	42.444	BB	1.1079	1784.23010	22.92797	86.3844
Totals :				2065.45457	36.27010	

## 6. Single-Crystal X-ray Crystallography of rac-4u



Identification code	g160108a
Empirical formula	C <sub>49</sub> H <sub>36</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>14</sub>
Formula weight	1036.62
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.7894(8)
b/Å	17.4413(12)
c/Å	10.9644(7)
α/°	90.00
β/°	96.421(6)
γ/°	90.00
Volume/Å <sup>3</sup>	2430.4(3)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.417
μ/mm <sup>-1</sup>	2.685
F(000)	1052.0
Crystal size/mm <sup>3</sup>	0.3 × 0.15 × 0.1



Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^{\circ}$	8.6 to 146.74
Index ranges	$-15 \leq h \leq 15, -17 \leq k \leq 21, -13 \leq l \leq 11$
Reflections collected	9219
Independent reflections	4746 [ $R_{\text{int}} = 0.0478, R_{\text{sigma}} = 0.0698$ ]
Data/restraints/parameters	4746/17/319
Goodness-of-fit on $F^2$	1.083
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0653, wR_2 = 0.1966$
Final R indexes [all data]	$R_1 = 0.0942, wR_2 = 0.2246$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.88/-0.40

The crystal was prepared from the solution of **4u** in ethyl acetate and n-hexane. CCDC 1446846 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).