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# Enantioselective N-Heterocyclic Carbene-Catalyzed Cascade Reaction for the Synthesis of Pyrroloquinolines *via* N-H Functionalization of Indoles

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## Supporting Information

1. General Information	S2
2. General Procedure for the Optimization of the Reaction Conditions	S3
3. General Procedure for the Enantioselective Synthesis of Pyrroloquinolines	S6
4. X-ray data of <b>3h</b>	S7
5. Synthesis and Characterization of Indole Derivatives	S9
6. Synthesis and Characterization of Pyrroloquinoline Derivatives	S12
7. Functionalization of Pyrroloquinolines	S29
8. <sup>1</sup> H and <sup>13</sup> C NMR Spectra of Indole derivative	S33
9. <sup>1</sup> H and <sup>13</sup> C NMR Spectra of Pyrroloquinoline Derivatives	S38
10. HPLC data of Pyrroloquinoline Derivatives	S65

## 1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry DMSO was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The  $\alpha,\beta$ -unsaturated aldehydes **2a**, **2e**, **2f**, **2m**, **2t** were purchased from commercial sources and were used without further purification, and others were synthesized following the literature procedure.<sup>1</sup> Indole derivative **1d** were synthesized by following the literature procedure.<sup>2</sup> The triazolium salt **4** was synthesized following the literature procedure.<sup>3</sup> 25 °C corresponds to the room temperature of the lab when the experiments were carried out.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F<sub>254</sub>. Visualization was accomplished with short wave UV light or KMnO<sub>4</sub> staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Ultrashield spectrometer in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent. Chemical shifts ( $\delta$ ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>:  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.16$  ppm and DMSO-*d*<sub>6</sub>:  $\delta_{\text{H}} = 2.50$  ppm,  $\delta_{\text{C}} = 39.50$  ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer,  $\nu$ -max in cm<sup>-1</sup>. Optical rotations were measured on JASCO P-2000 polarimeter. HRMS (ESI) data were recorded on a Micromass Q-TOF Micro instrument. HPLC analysis was performed on Agilent Technologies 1260 Infinity II with UV detector.

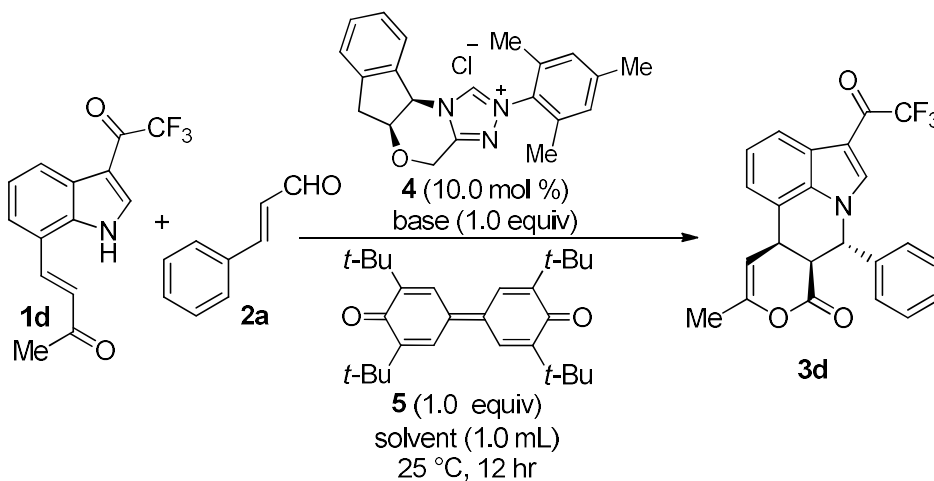
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<sup>1</sup> A. A. Wubea, A. Hüfner, C. Thomaschitz, M. Blunder, M. Kollroser, R. Bauer, F. Bucar, *Bioorg. Med. Chem.* **2011**, *19*, 567.

<sup>2</sup> Giardinetti, M.; Moreau, X.; Coeffard, V.; Greck, C. *Adv. Synth. Catal.* **2015**, *357*, 3501.

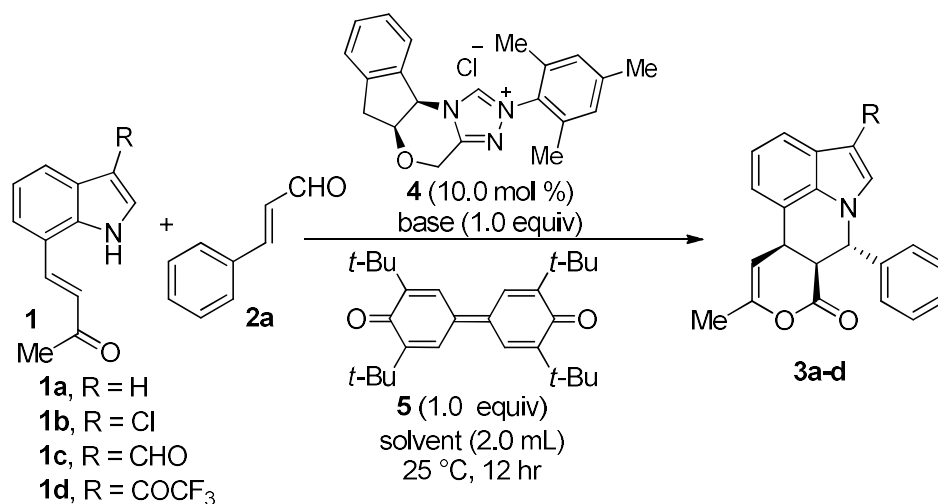
<sup>3</sup> J. R. Struble, and J. W. Bode, *Org. Synth.* **2010**, *87*, 362.

## 2. General Procedure for the Optimization of Reaction Conditions<sup>a</sup>



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.015 g, 0.0375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (0.125 mmol), and enal **2a** (0.125 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added solvent (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture base (0.125 mmol) was successively added. After 12 h, the reaction is quenched and the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) and filtered through a short pad of silica gel and eluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solvent was removed to obtain the crude product, which was analyzed using <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> (9.0 μL, 0.125 mmol) as the internal standard. The enantiomeric ratio was determined by HPLC analysis on a chiral column.

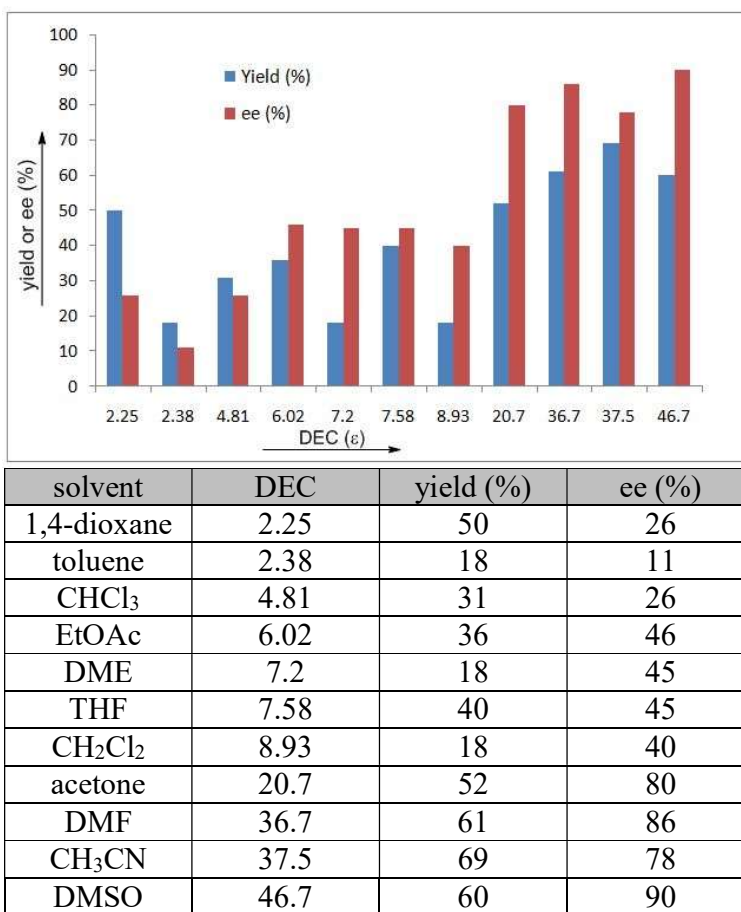
## Optimization Studies



Entry	(1)	Base	Solvent	Yield (%) <sup>b</sup>	dr <sup>c</sup>	er <sup>d</sup>
1	1a	DABCO	DMSO	<5	-nd-	-nd-
2	1b	DABCO	DMSO	<5	-nd-	-nd-
3	1c	DABCO	DMSO	42	>20:1	77:23
4	1d	DABCO	DMSO	60	>20:1	95:5
5	1d	DABCO	toluene	18	>20:1	56:44
6	1d	DABCO	CH <sub>2</sub> Cl <sub>2</sub>	18	>20:1	70:30
7	1d	DABCO	THF	40	>20:1	73:27
8	1d	DABCO	DMF	61	>20:1	93:7
9	1d	DABCO	CHCl <sub>3</sub>	31	>20:1	75:25
10	1d	DABCO	EtOAc	36	>20:1	74:26
11	1d	DABCO	CH <sub>3</sub> CN	69	>20:1	89:11
12	1d	DABCO	Acetone	52	>20:1	90:10
13	1d	DABCO	DME	18	>20:1	77:23
14	1d	DBU	DMSO	<5	-nd-	-nd-
15	1d	K <sub>2</sub> CO <sub>3</sub>	DMSO	49	>20:1	95:5
16	1d	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	47	>20:1	95:5
17	1d	DMAP	DMSO	37	>20:1	95:5
<b>18<sup>d</sup></b>	1d	<b>DABCO</b>	<b>DMSO</b>	<b>84</b>	<b>&gt;20:1</b>	<b>95:5</b>

<sup>a</sup> Conditions: **1** (0.125 mmol), **2a** (0.125 mmol), **4** (10 mol%), **5** (1.0 equiv), base (1.0 equiv), solvent (1.0 mL), 25 °C and 12 h. <sup>b</sup> The yields were determined by <sup>1</sup>H NMR analysis of crude product using CH<sub>2</sub>Br<sub>2</sub> as the internal standard. <sup>c</sup> Diastereomeric ratio was determined by <sup>1</sup>H NMR spectroscopy prior to purification. <sup>d</sup> Enantiomer ratio was determined by HPLC analysis on a chiral column. <sup>e</sup> 1.5 equiv each of **2a** and **5**, and 15 mol % of **4** was used.

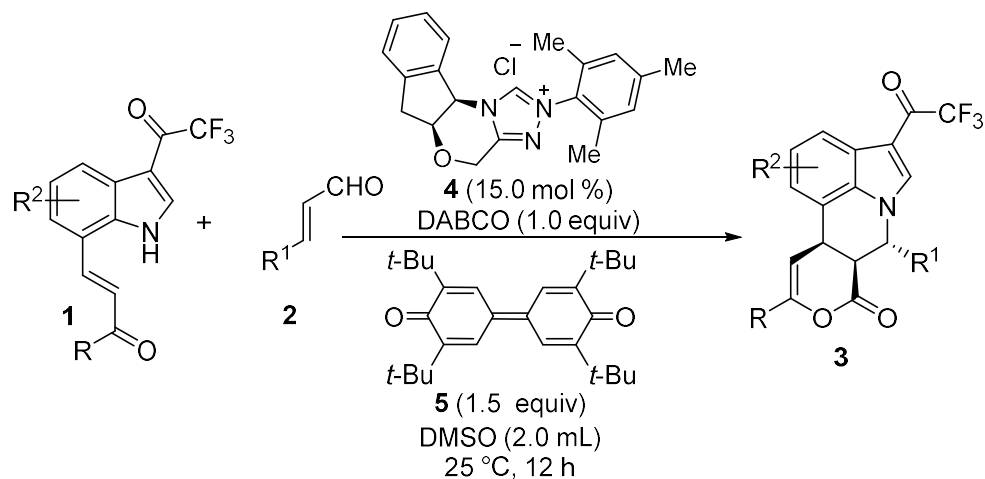
The enhancement in reactivity and selectivity was observed while performing the reaction in polar aprotic solvents, such as CH<sub>3</sub>CN, DMF, DMSO etc. To validate this, the reaction was performed in various solvents and the dielectric constant (DEC) of the solvent was plotted against the yield/ee of **3d** obtained (Figure S1).<sup>4</sup> For instance, the reaction afforded poor yield/ee when performed in toluene (DEC: 2.38), moderate yield/ee in THF (DEC: 7.58), and high yield/ee in DMF (DEC: 36.7). Although a general linear relationship was not observed, the overall trend observed was that the reactivity/selectivity was improved in polar aprotic solvents.



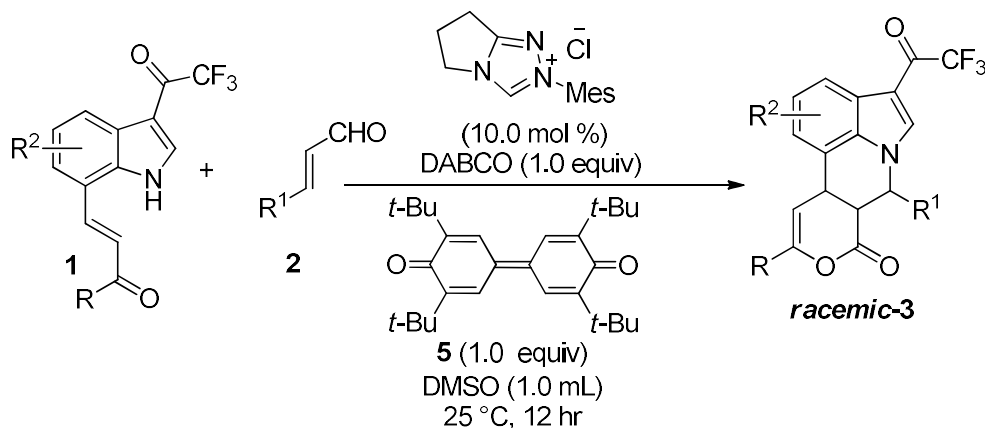
**Figure S1.** Variation of yield/ee of **3d** with polarity of solvent (dielectric constant)

<sup>4</sup> Gorman, W. G.; Hall, G. D. *J. Pharm. Sci.* **1964**, *53*, 1017.

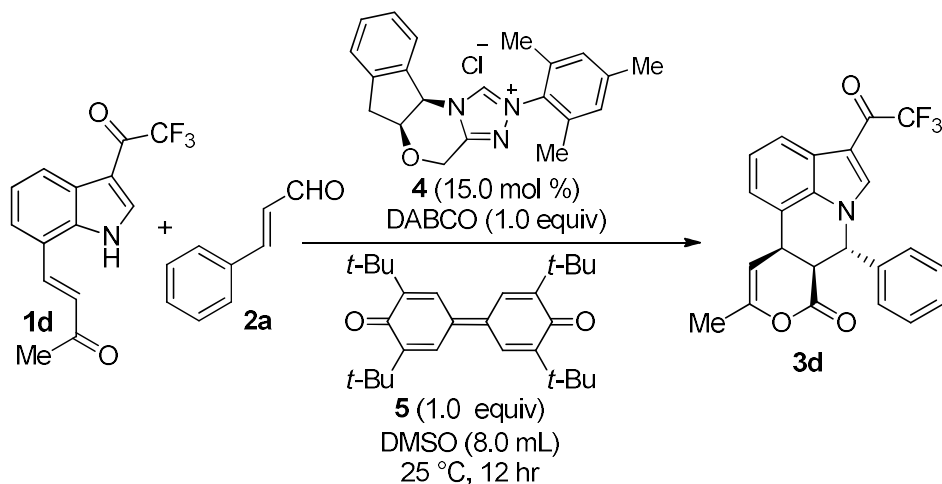
### 3. General Procedure for the Enantioselective Synthesis of Pyrroloquinolines



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.015 g, 0.037 mmol) and N-H indole derivative bearing a Michael acceptor moiety at the 7-position **1** (0.25 mmol), and enal **2** (0.375 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added DMSO (2.0 mL) under argon atmosphere. To this mixture DABCO (0.25 mmol) was successively added, and the resulting mixture was stirred at 25 °C for 12 h. When the reaction is complete, standard work-up of the reaction mixture was done using EtOAc and organic fractions were dried with Na<sub>2</sub>SO<sub>4</sub>, and solvent was evaporated. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding pyrroloquinoline derivatives **3**. All racemic pyrroloquinoline derivatives were prepared using NHC generated from the *N*-mesityl triazolium salt using DABCO.



### Procedure for 1.0 mmol scale experiment



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (56.0 mg, 0.15 mmol, 15 mol %) and N-H indole derivative bearing a Michael acceptor moiety at the 7-position **1d** (281.0 mg, 1.0 mmol, 1.0 equiv) and enal **2a** (198.0 mg, 1.5 mmol, 1.5 equiv) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added DMSO (8.0 mL) under argon atmosphere. To this mixture DABCO (112 mg, 1.0 mmol, 1.0 equiv) was successively added, and the resulting mixture was stirred at 25 °C for 12 h. When the reaction is complete, standard work-up of the reaction mixture was done using EtOAc and organic fractions were dried with Na<sub>2</sub>SO<sub>4</sub>, solvent was evaporated. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding pyrroloquinoline derivative **3d** as white solid (353 mg, 86% yield, >20:1 dr, 95:5 er).

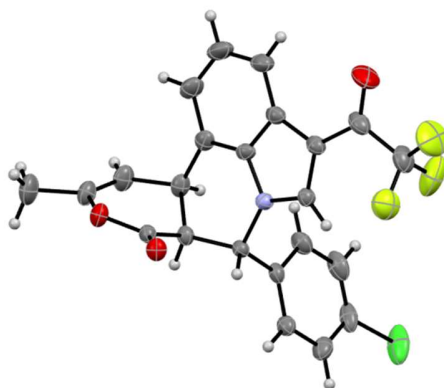
### 4. X-ray Data of **3h**

Single crystal of **3h** (recrystallized from 1:4 CHCl<sub>3</sub>/*n*-Hexane at 25 °C) was mounted and the diffraction data was collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Kα radiation (71.073 pm). The structure was solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F<sub>2</sub>. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were



included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

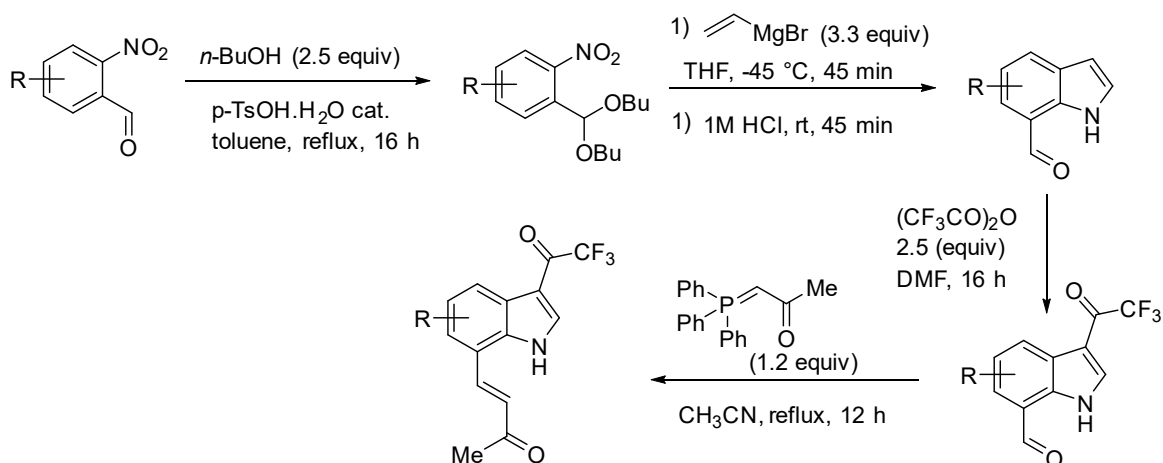
Identification code	<b>3h</b>
CCDC	CCDC 1863110
Empirical formula	C <sub>23</sub> H <sub>15</sub> ClF <sub>3</sub> NO <sub>3</sub>
Formula weight	445.81
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	10.3570(8)
b/Å	17.0723(13)
c/Å	23.2760(18)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	4115.6(5)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.439
μ/mm <sup>-1</sup>	0.238
F(000)	1824.0
Crystal size/mm <sup>3</sup>	0.25 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.768 to 55.19
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -30 ≤ l ≤ 30
Reflections collected	131106
Independent reflections	9493 [R <sub>int</sub> = 0.0680, R <sub>sigma</sub> = 0.0336]
Data/restraints/parameters	9493/0/561
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0489, wR <sub>2</sub> = 0.1313
Final R indexes [all data]	R <sub>1</sub> = 0.0803, wR <sub>2</sub> = 0.1523
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.30
Flack parameter	0.00(2)



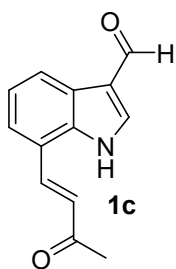
**Figure S2.** ORTEP representation of the X-ray structure of **3h** (thermal ellipsoids at 30% probability)

## 5. Synthesis and Characterization of Indole Derivatives

The *1H*-indole-7-carbaldehyde derivatives were prepared from following the known synthetic route depicted below.<sup>2</sup> Next, 3-(2,2,2-trifluoroacetyl)-*1H*-indole-7-carbaldehyde derivatives and 1-(triphenylphosphoranylidene)propan-2-one were added to CH<sub>3</sub>CN. The reaction mixture was reflux for overnight. The reaction mixture cooled and the solvent was evaporated under reduced pressure. This was followed by purification using column chromatography to provide *N*-unsubstituted indole derivative bearing a Michael acceptor at the 7-position as a light green solid.



**(E)-7-(3-Oxobut-1-en-1-yl)-1H-indole-3-carbaldehyde (1c)**

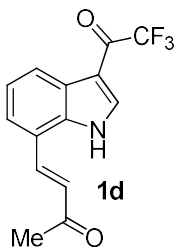


Following the general procedure,<sup>2</sup> treatment of (*E*)-4-(1*H*-indol-7-yl)but-3-en-2-one (348 mg, 1.878 mmol) and phosphoryl trichloride (317 mg, 2.066 mmol) in DMF (2.0 mL) and stirring the reaction mixture at 25 °C for 16 h followed by flash column chromatography (Pet. ether- EtOAc: 7:3) to afford (*E*)-7-(3-oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde **1c** as a white solid (151.0 mg, 37% yield).

$R_f$  (Pet. ether /EtOAc = 70/30): 0.2;

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.68 (s, 1H), 10.02 (s, 1H), 8.47 (s, 1H), 8.23-8.17 (m, 2H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 2.45 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 198.17, 185.22, 139.00, 137.88, 135.91, 128.01, 125.12, 123.28, 122.68, 121.67, 119.36, 118.40, 27.37. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub>: 214.0863, found: 214.0868. FTIR (cm<sup>-1</sup>) 3428, 2923, 2853, 2131, 1529, 1462, 1374, 1231, 1179, 990.

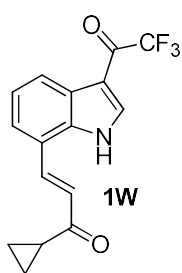
**(E)-4-(3-(2,2,2-Trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1d)**



Following the known procedure,<sup>5</sup> 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (1.0 g, 4.14 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (1.58 g, 4.9 mmol) were added to CH<sub>3</sub>CN. The reaction mixture was reflux for overnight and concentrated followed by purified by column chromatography to provide (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one (**1d**) as a light green solid (0.91 g, 78% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.2; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.18 (s, 1H), 8.59 (s, 1H), 8.26-8.19 (m, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 198.14, 174.11 (q, *J* = 34.3 Hz), 138.07 (q, *J* = 4.3 Hz), 137.27, 135.54, 128.53, 126.68, 123.89, 123.34, 122.04, 120.03, 116.78 (q, *J* = 290.0 Hz), 109.17, 27.34. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>N<sub>1</sub>F<sub>3</sub>: 282.0736, found: 282.0745. FTIR (cm<sup>-1</sup>) 3157, 2912, 1667, 1580, 1522, 1463, 1271, 1232, 1125, 956, 889.

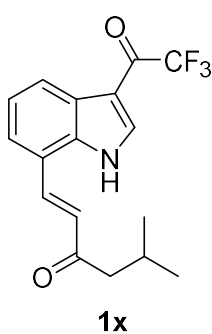
### (*E*)-1-Cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one (**1w**)



Following the known procedure,<sup>5</sup> 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (0.2 g, 0.82 mmol) and 1-cyclopropyl-2-(triphenylphosphoranylidene)ethanone (0.36 g, 1.0 mmol) were added to CH<sub>3</sub>CN. The reaction mixture was reflux for over night and concentrated followed by purified by column chromatography to provide (*E*)-1-cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one (**1w**) as a white solid (0.21 g, 83% yield).

*R<sub>f</sub>* (Pet. ether /EtOAc = 80/20): 0.4; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.84 (s, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.21 – 8.13 (m, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 15.7 Hz, 1H), 2.28-2.25 (m, 1H), 1.24-1.12 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.36, 175.62 (q, *J* = 35.2 Hz), 136.97, 135.60, 135.20 (q, *J* = 5.2 Hz), 127.19, 126.76, 125.11, 124.24, 123.37, 119.68, 117.07 (q, *J* = 291.0 Hz), 111.32, 21.53, 12.33. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>N<sub>1</sub>F<sub>3</sub>: 308.0893, found: 308.0895. FTIR (cm<sup>-1</sup>) 3361, 2913, 1664, 1591, 1447, 1390, 1272, 1181, 1130, 973, 888.

### (*E*)-5-Methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one (**1x**)



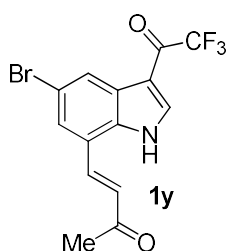
Following the known procedure,<sup>5</sup> treatment of 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (250 mg, 1.036 mmol) and 4-methyl-1-(triphenyl-15-phosphaneylidene)pentan-2-one (448 mg, 1.244 mmol) in acetonitrile (5.0 mL) and stirring the reaction mixture in reflux for 12 h, followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*E*)-5-methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one **1x** as a green solid (291.0 mg, 87% yield).

*R<sub>f</sub>* (Pet. ether /EtOAc = 90/10): 0.45; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.20 (s, 1H), 8.58 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 16.1 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 2.66 (d, *J* = 6.9 Hz, 2H), 2.16 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 199.75, 174.10 (q, *J* = 34.3 Hz), 137.96 (q, *J* = 4.89 Hz), 136.01, 135.58, 128.18, 126.69, 123.88, 123.29, 122.05, 120.12, 117.18, 109.16, 48.69,

<sup>5</sup> Mukherjee, S.; Ghosh, A.; Marelli, U. K.; Biju, A. T. *Org. Lett.* **2018**, *20*, 2952.

24.53, 22.48. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{17}H_{17}F_3NO_2$ : 324.1206, found: 324.1209. **FTIR (cm<sup>-1</sup>)** 3359, 2956, 1658, 1528, 1461, 1369, 1297, 1264, 1180, 1130, 976.

**(E)-4-(5-Bromo-3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1y)**



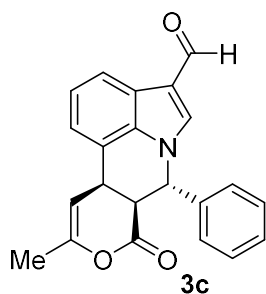
Following the known procedure,<sup>5</sup> 5-bromo-3-(2,2,2-trifluoroacetyl)-1H-indole-7-carbaldehyde (0.44 g, 1.38 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (0.52 g, 1.65 mmol) were added to  $CH_3CN$ . The reaction mixture was reflux for overnight and concentrated followed by purified by column chromatography to provide (E)-4-(5-bromo-3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (**1y**) as a light

green solid (0.4 g, 80% yield).

**R<sub>f</sub>** (Pet. ether /EtOAc = 80/20): 0.35; **<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  13.31 (s, 1H), 8.60 (s, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 8.08 (d, *J* = 16.2 Hz, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H). **<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  198.00, 174.07 (q, *J* = 35.1 Hz), 138.81 (q, *J* = 4.5 Hz), 135.46, 134.37, 129.75, 128.20, 124.86, 124.05, 121.94, 116.65, 116.60 (q, *J* = 292.0 Hz), 108.58, 27.60. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{14}H_{10}O_2N_1F_3Br$ : 359.9842, found: 359.9847. **FTIR (cm<sup>-1</sup>)** 3398, 3135, 2912, 1662, 1589, 1516, 1451, 1356, 1124, 976, 869.

## 6. Synthesis and Characterization of Pyrroloquinoline Derivatives

**(7*S*,7*aS*,11*aR*)-10-Methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde (3c)**



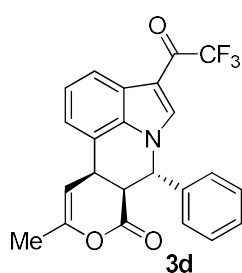
Following the general procedure, treatment of cinnamaldehyde **2a** (37.0 mg, 35  $\mu$ L, 0.280 mmol) and (E)-7-(3-oxobut-1-en-1-yl)-1H-indole-3-carbaldehyde **1c** (40.0 mg, 0.187 mmol) with triazolium salt **4** (10.3 mg, 0.0280 mmol), oxidant **5** (114.4 mg, 0.280 mmol) and DABCO (20.9 mg, 0.187 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether-

EtOAc: 7:3) to afford (7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde **3c** as a brown solid (27.0 mg, 42% yield).

$R_f$  (Pet. ether /EtOAc = 70/30): 0.30; er = 77:23,  $[\alpha]_D^{25} = +118.7$  (c 0.2, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 11.6 min, *Major*: 13.6 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.00 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.33-7.31 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 6.30 (s, 1H), 5.64 (d, *J* = 6.7 Hz, 1H), 3.70 (t, *J* = 6.1 Hz, 1H), 3.37 (d, *J* = 6.3 Hz, 1H), 1.94 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 184.02, 166.66, 149.21, 138.36, 136.09, 133.00, 128.44, 127.77, 124.50, 122.87, 122.14, 120.09, 119.98, 119.92, 118.77, 101.17, 55.94, 44.85, 26.33, 17.76. HRMS (ESI) calculated  $[M+H]^+$  for C<sub>22</sub>H<sub>18</sub>O<sub>3</sub>N: 344.1281, found: 344.1290. FTIR (cm<sup>-1</sup>) 3406, 3103, 2923, 2807, 1761, 1659, 1522, 1451, 1150, 1075, 935.

#### (7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (**3d**)



Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47 μL, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc:

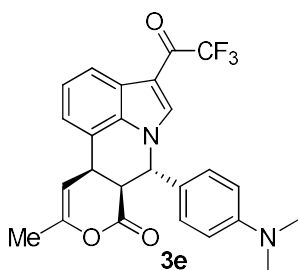
9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3d** as a white solid (86.0 mg, 84% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.50; er = 95:5,  $[\alpha]_D^{25} = +156.6$  (c 0.1, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 7.7 min, *Major*: 9.9 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.40-7.33 (m, 4H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 4.0 Hz, 2H), 6.36 (s, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 3.71 (t, *J* = 6.1 Hz, 1H), 3.40 (d, *J* = 6.2 Hz, 1H), 1.95 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.35 (q, *J* = 35.1 Hz), 167.52, 150.41, 138.85, 136.08 (q, *J* = 4.8 Hz), 133.37, 129.52, 128.90, 125.32, 124.84, 121.64, 121.48, 121.39, 116.99 (q, *J* = 291.0 Hz), 111.22, 101.92, 57.26, 45.81, 27.11,

18.69. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{23}H_{17}O_3N_1F_3$ : 412.1155, found: 412.1161. **FTIR** ( $cm^{-1}$ ) 3412, 2923, 1763, 1672, 1517, 1393, 1146, 1048, 906.

**(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)**



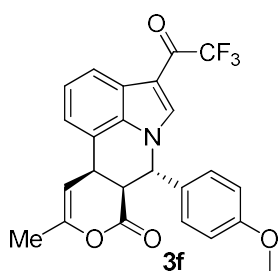
Following the general procedure, treatment of (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde **2e** (66.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S*,7*aS*,11*aR*)-7-(4-(dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3a** as a black solid (70.0 mg, 63% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 98:2,  $[\alpha]_D^{25} = +276.1$  (c 0.1,  $CHCl_3$ ). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 14.6 min, *Major*: 11.3 min.

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.24 (d,  $J = 7.9$  Hz, 1H), 8.0 (s, 1H), 7.36 (t,  $J = 7.7$  Hz, 1H), 7.17 (d,  $J = 7.2$  Hz, 1H), 6.72-6.65 (m, 4H), 6.23 (s, 1H), 5.64 (d,  $J = 6.7$  Hz, 1H), 3.78 (t,  $J = 6.3$  Hz, 1H), 3.34 (d,  $J = 6.3$  Hz, 1H), 2.93 (s, 6H), 1.94 (s, 3H).  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**  $\delta$  175.32 (q,  $J = 35.6$  Hz), 167.76, 150.42, 150.25, 136.21 (q,  $J = 5.3$  Hz), 133.46, 126.31, 124.88, 124.71, 121.51, 121.36, 118.47, 115.58, 112.93, 110.96, 102.11, 56.85, 45.99, 40.54, 27.30, 18.73. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{25}H_{22}O_3N_2F_3$ : 455.1577, found: 455.1586. **FTIR** ( $cm^{-1}$ ) 3428, 1763, 1670, 1615, 1519, 1451, 1391, 1143, 1047, 905.

**(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3f)**



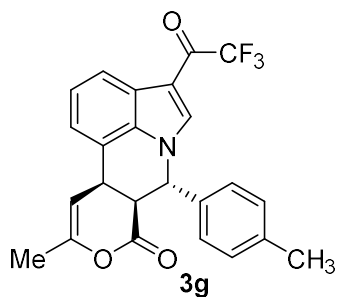
Following the general procedure, treatment of (*E*)-3-(4-methoxyphenyl)acrylaldehyde **2f** (61.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0

mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3f** as a white solid (93.0 mg, 84% yield).

*R<sub>f</sub>*(Pet. ether /EtOAc = 80/20): 0.35; er = 98:2, [α]<sub>D</sub><sup>25</sup> = +159.6 (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 12.7 min, *Major*: 14.0 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 1.1 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.29 (s, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 3.76-3.72 (m, 4H), 3.37 (dd, *J*<sub>1</sub> = 6.4, *J*<sub>2</sub> = 2.2 Hz, 1H), 1.94 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.30 (q, *J* = 36.1 Hz), 167.57, 159.96, 150.33, 136.06 (q, *J* = 4.9 Hz), 133.34, 130.63, 126.61, 124.84, 121.60, 121.41, 117.0 (q, *J* = 290.0 Hz), 114.83, 111.10, 101.98, 56.77, 56.41, 45.87, 27.17, 18.66. **HRMS (ESI)** calculated [M+H]<sup>+</sup> for C<sub>24</sub>H<sub>19</sub>O<sub>4</sub>N<sub>1</sub>F<sub>3</sub>: 442.1261, found: 442.1267. **FTIR (cm<sup>-1</sup>)** 3444, 2927, 1763, 1672, 1515, 1391, 1254, 1177, 1047, 906.

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3g)**



Following the general procedure, treatment of (*E*)-3-(*p*-tolyl)acrylaldehyde **2g** (54.8 mg, 0.375mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3g** as a brown solid (100.0 mg, 93% yield).

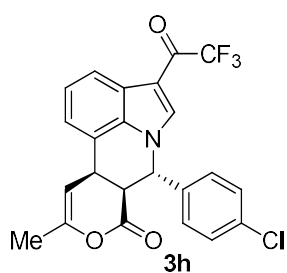
*R<sub>f</sub>*(Pet. Ether /EtOAc = 80/20): 0.46; er = 96:4, [α]<sub>D</sub><sup>25</sup> = 138.88 (c 1.0, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.9 min, *Major*: 10.1 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8 Hz, 2H), 6.32 (s, 1H), 5.66 (d, *J* = 7 Hz, 1H), 3.73 (t, *J* = 6.6 Hz, 1H), 3.39 (dd, *J*<sub>1</sub> = 6.4, *J*<sub>2</sub> = 2.0 Hz, 1H), 2.32 (s, 3H), 1.95 (s,



3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.31 (q,  $J = 35.1$  Hz), 166.58, 149.36, 137.88, 135.09 (q,  $J = 4.9$  Hz), 134.82, 132.28, 129.13, 124.25, 123.81 (d,  $J = 3.5$  Hz), 120.59, 120.42 (d,  $J = 2.0$  Hz), 116.23 (q,  $J = 290.7$  Hz), 110.12, 100.96, 56.06, 44.84, 26.13, 20.08, 17.68. HRMS (ESI) calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{24}\text{H}_{19}\text{O}_3\text{NF}_3$ : 426.1312, found: 426.1313. FTIR ( $\text{cm}^{-1}$ ) 3442, 3024, 2924, 1763, 1672, 1516, 1452, 1390, 1146, 1049, 906.

**(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*h*)**



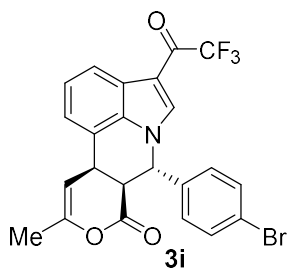
Following the general procedure, treatment of (*E*)-3-(4-chlorophenyl)acrylaldehyde **2h** (63.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by

flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3h** as a white solid (90.0 mg, 81% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.45; er = 93:7,  $[\alpha]_D^{25} = +168.6$  (c 0.1,  $\text{CHCl}_3$ ). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 11.0 min, *Major*: 12.6 min.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J = 8.0$  Hz, 1H), 8.0 (s, 1H), 7.37 (t,  $J = 7.7$  Hz, 1H), 7.30-7.26 (m, 2H), 7.18 (d,  $J = 7.4$  Hz, 1H), 6.76 (d,  $J = 8.1$  Hz, 2H), 6.33 (s, 1H), 5.66 (d,  $J = 6.9$  Hz, 1H), 3.69 (t,  $J = 6.4$  Hz, 1H), 3.37 (d,  $J = 6.3$  Hz, 1H), 1.94 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.36 (q,  $J = 35.5$  Hz), 167.126, 150.50, 137.34, 135.83 (q,  $J = 5.0$  Hz), 134.94, 133.17, 129.73, 126.80, 124.98, 124.84, 124.82, 121.77, 121.56, 121.16, 116.95 (q,  $J = 291.0$  Hz), 111.37, 101.79, 56.72, 45.65, 27.07, 18.69. HRMS (ESI) calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{23}\text{H}_{16}\text{O}_3\text{N}_1\text{F}_3\text{Cl}$ : 446.0765, found: 446.0772. FTIR ( $\text{cm}^{-1}$ ) 3129, 2924, 1762, 1673, 1517, 1493, 1388, 1147, 1013, 906.

**(7*S*,7*aS*,11*aR*)-7-(4-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*i*)**



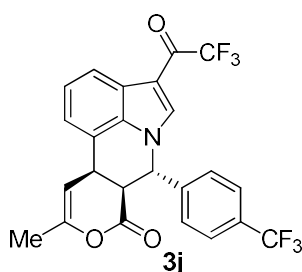
Following the general procedure, treatment of (*E*)-3-(4-bromophenyl)acrylaldehyde **2i** (79.1 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S*,7*aS*,11*aR*)-7-(4-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3i** as a brown solid (107.0 mg, 87% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.46; er = 93:7,  $[\alpha]_D^{25} = 159.40$  (c 1.0, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 11.3 min, *Major*: 13.2 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 5.66 (d, *J* = 7.0 Hz, 1H), 3.68 (t, *J* = 6.6 Hz, 1H), 3.35 (dd, *J*<sub>1</sub> = 6.4 Hz, *J*<sub>2</sub> = 2.1 Hz, 1H), 1.95 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.33 (q, *J* = 35.2 Hz), 166.23, 149.49, 136.86, 134.38, 132.14, 126.08, 123.98, 123.80, 121.98, 120.78, 120.55, 120.16, 115.93 (q, *J* = 290.88 Hz), 110.36, 100.77, 55.76, 44.57, 26.05, 17.70. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>23</sub>H<sub>16</sub>BrF<sub>3</sub>NO<sub>3</sub>: 490.0260, found: 490.0267. FTIR (cm<sup>-1</sup>) 3437, 3130, 3024, 2924, 1762, 1672, 1517, 1452, 1146, 1048, 905, 833.

**(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*j*)**



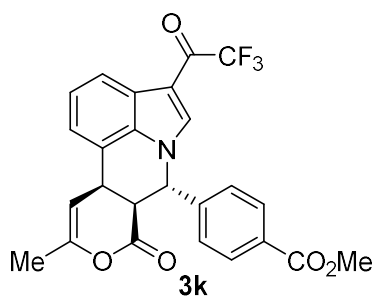
Following the general procedure, treatment of (*E*)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde **2j** (75.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford

(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3j** as a white solid (108.0 mg, 90% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.45; er = 92:8,  $[\alpha]_D^{25} = +130.7$  (c 0.1, CHCl<sub>3</sub>). HPLC (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.7 min, *Major*: 11.6 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 1.4 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.44 (s, 1H), 5.68 (d, *J* = 7.0 Hz, 1H), 3.67 (t, *J* = 6.6 Hz, 1H), 3.43 (dd, *J*<sub>1</sub> = 6.4 Hz, *J*<sub>2</sub> = 1.9 Hz, 1H), 1.95 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.42 (q, *J* = 34.9 Hz), 167.14, 150.62, 142.86, 135.76 (q, *J* = 5.0 Hz), 133.16, 131.29 (q, *J* = 33.1 Hz), 126.59 (q, *J* = 3.8 Hz), 125.95, 125.09, 124.85, 122.36, 121.89, 121.66, 121.11, 116.95 (q, *J* = 292.0 Hz), 111.53, 101.70, 56.95, 45.57, 27.07, 18.68. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>24</sub>H<sub>16</sub>O<sub>3</sub>N<sub>1</sub>F<sub>6</sub>: 480.1029, found: 480.1039. FTIR (cm<sup>-1</sup>) 3445, 2926, 1763, 1674, 1518, 1452, 1390, 1326, 1147, 1015, 906.

**Methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*, 8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (**3k**)**



Following the general procedure, treatment of methyl (*E*)-4-(3-oxoprop-1-en-1-yl)benzoate **2k** (95mg, 0.5mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture

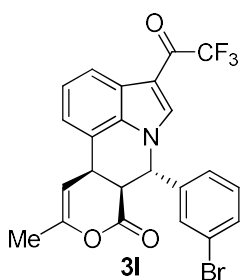
at 25 °C for 12h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3k** as a black solid (84.5 mg, 72% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.42; er = 87:13,  $[\alpha]_D^{25} = 121.28$  (c 1.0, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 18.4 min, *Major*: 20.4 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.99 (t, *J* = 7.97 Hz, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.41 (s, 1H), 5.66 (d, *J* = 6.7 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 1H), 3.42 (d, *J* = 5.9 Hz, 1H), 1.94 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.39 (q, *J* = 35.2 Hz), 167.20, 166.23, 150.54, 143.66, 135.85 (q, *J* = 5.0 Hz),

133.18, 130.86, 130.78, 125.51, 125.01, 124.84, 121.79, 121.63, 121.12, 116.94 (q,  $J = 291$  Hz), 111.44, 101.76, 57.07, 52.46, 45.57, 27.10, 18.72. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{23}H_{17}O_3N_1F_3$ : 412.1155, found: 412.1161. **FTIR (cm<sup>-1</sup>)** 3441, 3023, 2954, 1763, 1722, 1672, 1518, 1390, 1285, 1146, 906.

**(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (31)**

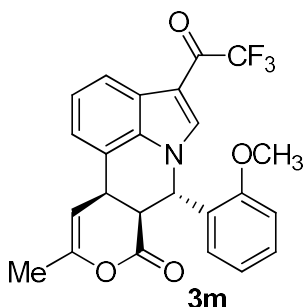


Following the general procedure, treatment of (*E*)-3-(3-bromophenyl)acrylaldehyde **21** (79.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S*,7*aS*,11*aR*)-7-(3-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **31** as a white solid (112.0 mg, 91% yield).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.45; er = 95:5,  $[\alpha]_D^{25} = +152.7$  (c 0.1,  $CHCl_3$ ). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 9.3 min, *Major*: 10.1 min.

**<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.24 (d,  $J = 7.9$  Hz, 1H), 8.01 (s, 1H), 7.46 (d,  $J = 7.9$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 1H), 7.19-7.15 (m, 2H), 7.10 (s, 1H), 6.64 (d,  $J = 7.7$  Hz, 1H), 6.33 (s, 1H), 5.67 (d,  $J = 7.0$  Hz, 1H), 3.70 (t,  $J = 6.4$  Hz, 1H), 3.40 (d,  $J = 6.3$  Hz, 1H), 1.94 (s, 3H). **<sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )**  $\delta$  175.37 (q,  $J = 35.3$  Hz), 167.19, 150.53, 141.17, 135.80, 133.12, 132.15, 131.12, 128.53, 124.98, 124.80, 123.99, 123.67, 121.81, 121.60, 121.10, 116.94 (q,  $J = 291.0$  Hz), 111.45, 101.77, 56.68, 45.66, 27.04, 18.70. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{23}H_{16}O_3N_1F_3Br$ : 490.0260, found: 490.0265. **FTIR (cm<sup>-1</sup>)** 3440, 2924, 1762, 1672, 1517, 1389, 1147, 1048, 1015, 906.

**(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3m)**



Following the general procedure, treatment of 2-methoxy cinnamaldehyde **2m** (121.6 mg, 0.75 mmol) and (*E*)-4-(3-(2,2,2-

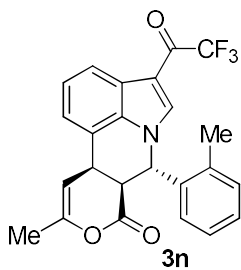
trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (140.6 mg, 0.5 mmol) with triazolium salt **4** (27.6 mg, 0.075 mmol), oxidant **5** (306.0 mg, 0.75 mmol) and DABCO (56.0 mg, 0.5 mmol) in DMSO (4.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3m** as a yellow solid (200.0 mg, 90% yield).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.42; er = 98:2,  $[\alpha]_D^{25} = 181.52$  (c 1.0, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.5 min, *Major*: 7.8 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32-7.28 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 6.01 (d, *J* = 7.5 Hz, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 3.94 (s, 3H) 3.65-3.58 (m, 2H) 1.95 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 174.35 (q, *J* = 35.1 Hz), 166.85, 154.26, 149.42, 135.17 (q, *J* = 4.9 Hz), 132.75, 129.03, 127.44, 125.79, 125.01, 123.82, 120.60, 120.50, 120.41, 120.26, 116.05 (q, *J* = 290.9 Hz), 110.14, 109.85, 100.98, 54.71, 51

.97, 41.83, 26.50, 17.76. **HRMS (ESI)** calculated  $[M+H]^+$  for C<sub>24</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>4</sub>: 442.1261, found: 442.1265. **FTIR (cm<sup>-1</sup>)** 3130, 3022, 2961, 1763, 1672, 1597, 1518, 1458, 1391, 1145, 906.

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3n)**

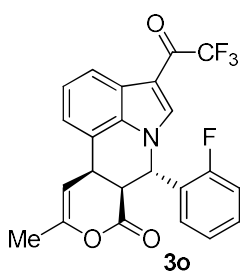


Following the general procedure, treatment of (*E*)-3-(*o*-tolyl)acrylaldehyde **2n** (55.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3n** as a white solid (98.0 mg, 92% yield).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.50; er = 96:4,  $[\alpha]_D^{25} = +263.2$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.0 min, *Major*: 6.0 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.30-7.19 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.68 (d, *J* = 7.0 Hz, 1H), 3.73 (t, *J* = 6.5 Hz, 1H), 3.29 (d, *J* = 6.3 Hz, 1H), 2.52 (s, 3H), 1.96 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 175.37 (q, *J* = 35.4 Hz), 167.57, 150.43, 136.94, 136.06 (q, *J* = 5.1 Hz), 133.83, 133.78, 131.57, 128.83, 127.15, 125.14, 124.83, 124.72, 121.54, 121.23, 116.98 (q, *J* = 291.0 Hz), 111.27, 102.00, 54.53, 43.55, 27.10, 19.00, 18.73. **HRMS (ESI)** calculated [M+H]<sup>+</sup> for C<sub>24</sub>H<sub>19</sub>O<sub>3</sub>N<sub>1</sub>F<sub>3</sub>: 426.1312, found: 426.1317. **FTIR (cm<sup>-1</sup>)** 3424, 1759, 1671, 1517, 1454, 1397, 1346, 1145, 907.

**(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)**



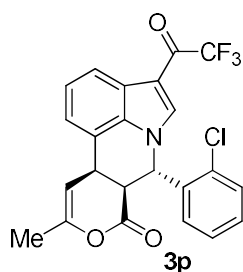
Following the general procedure, treatment of (*E*)-3-(2-fluorophenyl)acrylaldehyde **2o** (56.0 mg, 0.375mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12h followed by flash column

chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8 (11*aH*)-one **3o** as a white solid (79.0 mg, 74% yield).

**R<sub>f</sub>**(Pet. ether /EtOAc = 80/20): 0.40; er = 93:7, [α]<sub>D</sub><sup>25</sup> = +130.2 (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.7 min, *Major*: 8.0 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.40-7.31(m, 2H), 7.20-7.15 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 6.12 (t, *J* = 7.5 Hz, 1H), 5.67 (d, *J* = 6.8 Hz, 1H), 3.67 (t, *J* = 6.4 Hz, 1H), 3.51-3.49 (m, 1H), 1.95 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 175.40 (q, *J* = 35.2 Hz), 167.12, 158.83 (d, *J* = 247.0 Hz), 150.61, 135.83 (q, *J* = 4.9 Hz), 133.43, 130.78 (d, *J* = 8.1 Hz), 126.84 (d, *J* = 3.0 Hz), 126.10, 125.97, 125.25 (d, *J* = 3.0 Hz), 125.01, 124.84, 121.75, 121.62, 121.19, 116.97 (q, *J* = 291.0 Hz), 116.34, 116.13, 111.42, 101.74, 52.13 (d, *J* = 3.2 Hz), 43.69, 27.40, 18.76. **HRMS (ESI)** calculated [M+H]<sup>+</sup> for C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>N<sub>1</sub>F<sub>4</sub>: 430.1061, found: 430.1065. **FTIR (cm<sup>-1</sup>)** 2925, 2125, 1763, 1673, 1519, 1454, 1394, 1147, 1048, 907.

**(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*p*)**



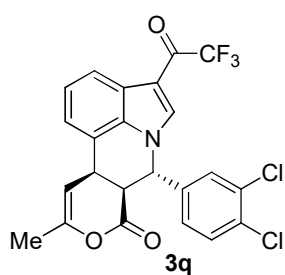
Following the general procedure, treatment of (*E*)-3-(2-chlorophenyl)acrylaldehyde **2p** (63.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column

chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3p** as a white solid (106.0 mg, 95% yield).

*R<sub>f</sub>* (Pet. ether /EtOAc = 80/20): 0.50; er = 94:6, [α]<sub>D</sub><sup>25</sup> = +213.4 (c 0.1, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.2 min, *Major*: 6.2 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31-7.26 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.33 (s, 1H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 3.64 (t, *J* = 6.3 Hz, 1H), 3.57 (d, *J* = 6.4 Hz, 1H), 1.95 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.36 (q, *J* = 35.4 Hz), 167.17, 150.59, 136.12, 135.88, 133.53, 131.26, 130.56, 130.25, 127.96, 126.83, 124.98, 124.71, 121.72, 121.53, 121.24, 116.92 (q, *J* = 291.0 Hz), 111.47, 101.68, 77.48, 77.16, 76.84, 54.95, 54.91, 42.84, 27.20, 18.72, 18.70. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>23</sub>H<sub>16</sub>O<sub>3</sub>N<sub>1</sub>F<sub>3</sub>Cl: 446.0765, found: 446.0771. FTIR (cm<sup>-1</sup>) 3440, 2959, 1762, 1675, 1518, 1447, 1391, 1147, 1042, 907.

**(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*q*)**



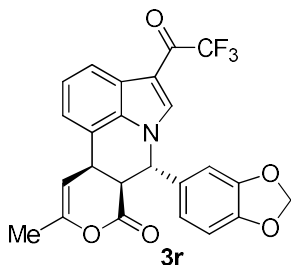
Following the general procedure, treatment of (*E*)-3-(3,4-dichlorophenyl)acrylaldehyde **2q** (75.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by

flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(3,4-dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3q** as a white solid (100.0 mg, 83% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.50; er = 93:7,  $[\alpha]_D^{25} = +149.5$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak IB, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 12.2 min, *Major*: 13.8 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.24 (d,  $J = 8.0$  Hz, 1H), 7.99 (s, 1H), 7.40-7.36 (m, 2H), 7.19 (d,  $J = 7.2$  Hz, 1H), 7.01 (s, 1H), 6.58 (d,  $J = 8.3$  Hz, 1H), 6.32 (s, 1H), 5.67 (d,  $J = 7.0$  Hz, 1H), 3.69 (t,  $J = 6.3$  Hz, 1H), 3.37 (d,  $J = 6.3$  Hz, 1H), 1.94 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  175.40 (q,  $J = 35.2$  Hz), 167.0, 150.61, 139.09, 135.64 (q,  $J = 4.9$  Hz), 133.96, 133.36, 133.0, 131.56, 127.52, 125.09, 124.84, 124.75, 121.92, 121.68, 120.96, 116.91 (q,  $J = 291.0$  Hz), 111.58, 101.68, 56.36, 45.54, 27.07, 18.69. **HRMS (ESI)** calculated  $[M+H]^+$  for C<sub>23</sub>H<sub>15</sub>O<sub>3</sub>N<sub>1</sub>F<sub>3</sub>Cl<sub>2</sub>: 480.0376, found: 480.0380. **FTIR (cm<sup>-1</sup>)** 3430, 2924, 1764, 1673, 1518, 1146, 1049, 907.

**(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (**3r**)**



Following the general procedure, treatment of (*E*)-3-(benzo[d][1,3]dioxol-4-yl)acrylaldehyde **2r** (66.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3r** as a white solid (94.0 mg, 82% yield).

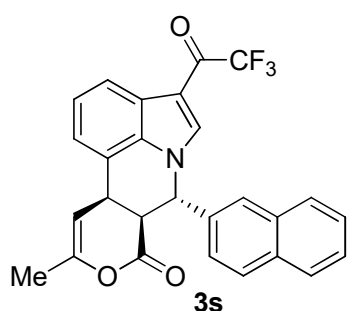
$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3,  $[\alpha]_D^{25} = +186.92$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 16.9 min, *Major*: 18.8 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.23 (d,  $J = 8.0$  Hz, 1H), 8.00 (s, 1H), 7.36 (t,  $J = 7.7$  Hz, 1H), 7.17 (d,  $J = 7.1$  Hz, 1H), 6.71 (d,  $J = 7.8$  Hz, 1H), 6.29-6.23 (m, 3H), 5.93 (s, 2H), 5.66 (d,  $J = 6.8$  Hz, 1H), 3.76 (t,  $J = 6.3$  Hz, 1H), 3.34 (d,  $J = 6.3$  Hz, 1H), 1.94 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  175.35 (q,  $J = 35.1$  Hz), 167.47, 150.38, 148.73, 148.11, 135.97 (q,  $J = 5.0$  Hz),



133.25, 132.53, 124.83, 124.80, 121.65, 121.47, 121.26, 118.94, 116.98 (q,  $J = 290.0$  Hz), 111.21, 108.98, 105.83, 101.93, 101.66, 56.97, 45.90, 27.21, 18.67. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{24}H_{17}O_5N_1F_3$ : 456.1053, found: 456.1056. **FTIR (cm<sup>-1</sup>)** 3499, 3022, 1761, 1672, 1516, 1446, 1395, 1147, 1042, 862.

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*s*)**



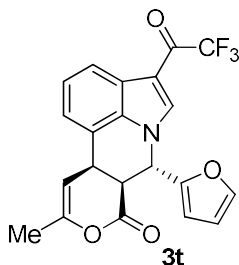
Following the general procedure, treatment of (*E*)-3-(naphthalen-2-yl)acrylaldehyde **2s** (68.3 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (13.8 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc:

9:1) to afford (*7S*,7*aS*,11*aR*)-10-methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3s** as a brown solid (88.0 mg, 77% yield).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.42; er = 95:5,  $[\alpha]_D^{25} = 166.48$  (c 1.0,  $CHCl_3$ ). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 18.8 min, *Major*: 20.5 min.

**<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.31 (d,  $J = 7.8$  Hz, 1H), 8.08 (s, 1H), 7.85 (t,  $J = 7.5$  Hz, 2H), 7.65 (d,  $J = 7.8$  Hz, 1H), 7.49 (m, 2H), 7.41 (t,  $J = 7.7$  Hz, 1H), 7.20 (d,  $J = 7.2$  Hz, 1H), 7.10 (d,  $J = 10.1$  Hz, 2H), 6.53 (s, 1H), 5.64 (d,  $J = 6.9$  Hz, 1H), 3.74 (t,  $J = 6.4$  Hz, 1H), 3.52 (d,  $J = 6.3$  Hz, 1H), 1.96 (s, 3H). **<sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )**  $\delta$  174.44 (q,  $J = 35.19$  Hz), 166.51, 149.45, 135.17, 132.43, 132.23, 132.20, 128.72, 127.06, 126.85, 126.14, 126.01, 123.90, 123.59, 121.74, 120.71, 121.72, 120.56, 120.40, 120.34, 116.0 (q,  $J = 290.92$  Hz), 110.33, 100.93, 56.42, 44.77, 26.23, 17.72. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{27}H_{19}O_3NF_3$ : 462.1312, found: 462.1316. **FTIR (cm<sup>-1</sup>)** 3127, 3057, 2924, 1762, 1672, 1516, 1452, 1146, 1049, 906.

**(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*t*)**

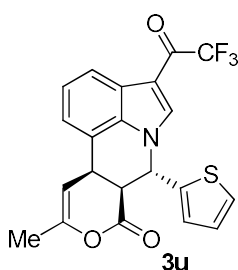


Following the general procedure, treatment of (*E*)-3-(furan-2-yl)acrylaldehyde **2t** (46.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S,7aS,11aR*)-7-(furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3t** as a white solid (67.0 mg, 67% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 96:4,  $[\alpha]_D^{25} = +152.7$  (c 0.1, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.0 min, *Major*: 9.5 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 6.30 (dd, *J*<sub>1</sub> = 3.2 Hz, *J*<sub>2</sub> = 1.9 Hz, 1H), 5.95 (d, *J* = 3.2 Hz, 1H), 5.72 (d, *J* = 7.0 Hz, 1H), 3.99 (t, *J* = 6.7 Hz, 1H), 3.68 (dd, *J*<sub>1</sub> = 6.6 Hz, *J*<sub>2</sub> = 2.1 Hz, 1H), 1.96 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.36 (q, *J* = 35.3 Hz), 167.06, 150.44, 150.41, 143.63, 135.93 (q, *J* = 5.0 Hz), 132.65, 124.92, 124.83, 121.55, 121.38, 120.98, 115.50 (q, *J* = 290.0 Hz), 111.23, 110.83, 108.24, 101.88, 51.85, 42.63, 28.25, 18.75. HRMS (ESI) calculated [M+H]<sup>+</sup> for C<sub>23</sub>H<sub>17</sub>O<sub>3</sub>N<sub>1</sub>F<sub>3</sub>: 402.0948, found: 402.0951. FTIR (cm<sup>-1</sup>) 2926, 1762, 1669, 1517, 1389, 1286, 1147, 1046, 996.

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*u*)**



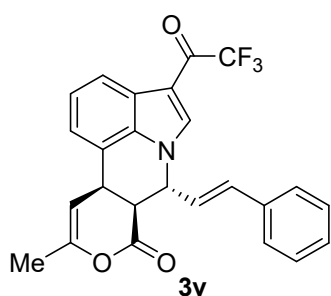
Following the general procedure, treatment of (*E*)-3-(thiophen-2-yl)acrylaldehyde **2u** (52.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S,7aS,11aR*)-10-methyl-7-(thiophen-2-yl)-

4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8(1*laH*)-one **3u** as a white solid (84.0 mg, 81% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 90:10,  $[\alpha]_D^{25} = +150.1$  (c 0.1, CHCl<sub>3</sub>). HPLC (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 9.0 min, *Major*: 11.9 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.22 (d,  $J = 7.9$  Hz, 1H), 8.09 (s, 1H), 7.36 (t,  $J = 7.7$  Hz, 1H), 7.27 (d,  $J = 4.4$  Hz, 1H), 7.17 (d,  $J = 7.2$  Hz, 1H), 6.91 (s, 1H), 6.56 (s, 2H), 5.71 (d,  $J = 6.8$  Hz, 1H), 3.94 (t,  $J = 6.3$  Hz, 1H), 3.51 (d,  $J = 6.1$  Hz, 1H), 1.95 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  175.36 (q,  $J = 35.1$  Hz), 167.00, 150.40, 141.27, 135.90, 135.85, 132.58, 127.60, 126.11, 125.38, 124.92, 121.66, 121.45, 121.25, 120.92, 116.98 (q,  $J = 291.0$  Hz), 111.26, 101.87, 53.76, 45.87, 27.57, 18.71, 18.68. HRMS (ESI) calculated  $[M+H]^+$  for C<sub>21</sub>H<sub>15</sub>O<sub>4</sub>N<sub>1</sub>F<sub>3</sub>S: 418.0719, found: 418.0724. FTIR (cm<sup>-1</sup>) 3440, 2924, 1761, 1672, 1517, 1451, 1391, 1147, 1077, 1047, 1012, 905.

**(7*R*,7*aS*,11*aR*)-10-Methyl-7-((*E*)-styryl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3v)**



Following the general procedure, treatment of (*2E,4E*)-5-phenylpenta-2,4-dienal **2v** (59.3 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

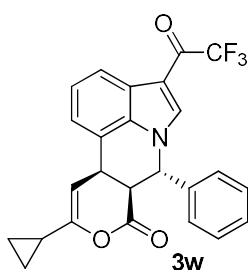
followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7R,7aS,11aR*)-10-methyl-7-((*E*)-styryl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3v** as a white solid (101.0 mg, 93% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.35; er = 96:4,  $[\alpha]_D^{25} = 155.16$  (c 1.0, CHCl<sub>3</sub>). HPLC (ChiralpakAD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 10.6 min, *Major*: 13.0 min.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23(d,  $J = 8.0$  Hz, 1H), 8.06 (s, 1H), 7.36 (t,  $J = 7.7$  Hz, 1H), 7.29(s, 5H), 6.32 (dd,  $J_1 = 5.8$  Hz,  $J_2 = 15.8$  Hz, 2H), 6.16 (d,  $J = 15.6$  Hz, 1H), 5.85 (s, 1H), 5.70 (d,  $J = 6.6$  Hz, 1H), 4.03 (t,  $J = 6.2$  Hz, 1H), 3.37 (d,  $J = 6.3$  Hz, 1H), 1.97(s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.53 (q,  $J = 35.2$  Hz), 166.14, 149.39, 134.87 (q,  $J = 4.9$  Hz), 133.96, 132.88, 131.66, 127.89, 125.88, 124.16, 124.14, 123.85, 120.53, 120.50, 120.18, 120.41, 116.08

(q,  $J = 290.9$  Hz), 110.04, 101.05, 54.67, 42.55, 27.02, 17.76. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{25}H_{19}O_3NF_3$ : 438.1312, found: 438.1315. **FTIR (cm<sup>-1</sup>)** 3435, 3027, 2924, 1762, 1670, 1516, 1451, 1392, 1148, 838.

**(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*w*)**

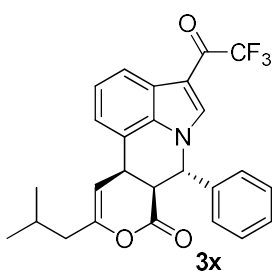


Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47  $\mu$ L, 0.375 mmol) and (*E*)-1-cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one **1w** (76.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7S*,7*aS*,11*aR*)-10-cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3w** as a white solid (104.0 mg, 95% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.50; er = 99:1,  $[\alpha]_D^{25} = +146.6$  (c 0.1,  $CHCl_3$ ). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.6 min, *Major*: 11.3 min.

**<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.25 (d,  $J = 7.7$  Hz, 1H), 8.02 (s, 1H), 7.40-7.33 (m, 4H), 7.19 (d,  $J = 7.2$  Hz, 1H), 6.84-6.82 (m, 2H), 6.34 (s, 1H), 5.69 (d,  $J = 7.1$  Hz, 1H), 3.71 (t,  $J = 6.5$  Hz, 1H), 3.41-3.39 (m, 1H), 1.57-1.52 (m, 1H), 0.74-0.72 (m, 1H). **<sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )**  $\delta$  175.29 (q,  $J = 35.3$  Hz), 167.41, 153.91, 138.79, 136.06, 133.36, 129.48, 128.86, 125.28, 124.86, 124.79, 121.69, 121.56, 121.35, 116.97 (q,  $J = 291.0$  Hz), 111.15, 99.55, 57.30, 46.05, 27.03, 12.67, 5.13, 4.81. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{25}H_{19}O_3N_1F_3$ : 438.1312, found: 438.1318. **FTIR (cm<sup>-1</sup>)** 2078, 1761, 1668, 1517, 1452, 1392, 1349, 1143, 1076, 967.

**(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*x*)**



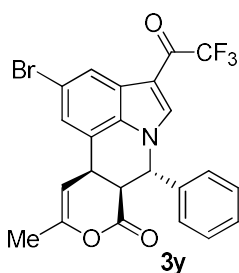
Following the general procedure, treatment of cinnamaldehyde **2a** (40.0 mg, 38  $\mu$ L, 0.3 mmol) and (*E*)-5-methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one **1x** (65.0 mg, 0.20 mmol) with triazolium salt **4** (11.0 mg, 0.03 mmol), oxidant **5** (123.0 mg, 0.3 mmol) and DABCO

(23.0 mg, 0.2 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3x** as a white solid (69.0 mg, 76% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.60; er = 96:4,  $[\alpha]_D^{25} = +113.5$  (c 0.2, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 7.7 min, *Major*: 9.9 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.26 (d,  $J = 8.0$  Hz, 1H), 8.02 (d,  $J = 1.1$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 1H), 7.35-7.33 (m, 3H), 7.19 (d,  $J = 7.4$  Hz, 1H), 6.84 (dd,  $J_1 = 6.6$ ,  $J_2 = 2.7$  Hz, 1H), 6.36 (s, 1H), 5.67 (d,  $J = 7.1$  Hz, 1H), 3.73 (t,  $J = 6.7$  Hz, 1H), 3.38 (dd,  $J_1 = 6.3$ ,  $J_2 = 1.8$  Hz, 1H), 2.13-2.02 (m, 2H), 1.95-1.85 (m, 1H), 0.91 (dd,  $J_1 = 13.4$ ,  $J_2 = 6.6$  Hz, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 175.37 (q,  $J = 35.4$  Hz), 167.64, 153.08, 138.93, 136.06 (q,  $J = 5.0$  Hz), 133.42, 129.57, 128.93, 125.39, 124.89, 121.61, 121.54, 121.45, 117.0 (q,  $J = 291.0$  Hz), 111.26, 102.70, 57.31, 45.99, 41.83, 27.08, 25.68, 22.41, 22.02. **HRMS (ESI)** calculated  $[M+H]^+$  for C<sub>26</sub>H<sub>23</sub>O<sub>3</sub>F<sub>3</sub>N<sub>1</sub>: 454.1625, found: 454.1630. **FTIR (cm<sup>-1</sup>)** 3439, 2960, 1761, 1671, 1518, 1454, 1394, 1145, 1041, 907.

**(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)**



Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47 μL, 0.375 mmol) and (*E*)-4-(5-bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1y** (90.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford

(7*S*,7*aS*,11*aR*)-2-bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3y** as a white solid (93.0 mg, 76% yield).

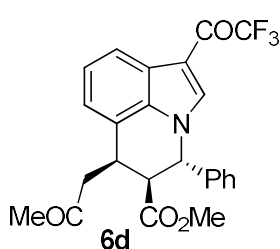
$R_f$  (Pet. ether /EtOAc = 80/20): 0.45; er = 99:1,  $[\alpha]_D^{25} = +82.8$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 10.4 min, *Major*: 8.5 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.50 (s, 1H), 8.09 (s, 1H), 7.42-7.34 (m, 5H), 6.87-6.85 (m, 2H), 6.43 (s, 1H), 5.71 (d,  $J = 7.1$  Hz, 1H), 3.77 (t,  $J = 6.6$  Hz, 1H), 3.49 (dd,  $J_1 = 6.4$ ,  $J_2 = 1.8$  Hz, 1H), 2.04 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 175.21 (q,  $J = 35.4$  Hz), 167.13, 138.41,

136.48 (q,  $J = 4.8$  Hz), 132.05, 129.63, 129.08, 126.16, 125.19, 124.92, 124.20, 123.09, 118.47, 116.82 (q,  $J = 291.0$  Hz), 110.70, 101.17, 57.28, 45.70, 26.99, 18.78. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{23}H_{16}O_3N_1F_3Br$ : 490.0260, found: 490.0266. **FTIR (cm<sup>-1</sup>)** 3436, 2924, 1764, 1674, 1516, 1451, 1394, 1306, 1147, 1045, 912.

## 7. Functionalization of Pyrroloquinolines

### (4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (**6a**)

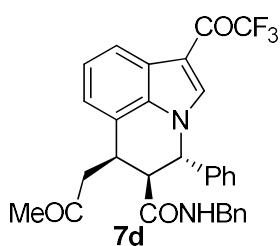


To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol) MeOH (2.0 mL) was added. The resulting mixture was allowed to stir overnight at 60 °C. Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (5:1) to afford the (4*S*,5*S*,6*R*)-methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate **6a** (42.0 mg, 76% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 95:5,  $[\alpha]_D^{25} = +20.8$  (c 0.1,  $CHCl_3$ ). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.4 min, *Major*: 8.0 min.

**<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.19 (d,  $J = 7.9$  Hz, 1H), 7.56 (s, 1H), 7.42-7.41 (m, 3H), 7.34 (t,  $J = 7.7$  Hz, 1H), 7.18-7.16 (m, 3H), 5.64 (d,  $J = 8.1$  Hz, 1H), 4.11 (s, 1H), 3.59 (dd,  $J_1 = 8.6$ ,  $J_2 = 4.3$  Hz, 1H), 3.52 (s, 3H), 3.16 (dd,  $J_1 = 18.2$ ,  $J_2 = 7.4$  Hz, 1H), 2.85 (d,  $J = 15.0$  Hz, 1H), 2.15 (s, 3H). **<sup>13</sup>C NMR (100 MHz,  $CDCl_3$ )**  $\delta$  205.82, 175.18 (q,  $J = 35.3$  Hz), 171.36, 135.15 (q,  $J = 5.0$  Hz), 133.78, 129.57, 129.46, 125.09, 124.72, 124.29, 121.38, 121.30, 121.01, 116.96 (q,  $J = 291.0$  Hz), 110.98, 58.90, 58.87, 52.39, 49.84, 49.79, 30.51, 29.87, 29.80. **HRMS (ESI)** calculated  $[M+H]^+$  for  $C_{24}H_{21}O_4N_1F_3$ : 444.1417, found: 444.1427. **FTIR (cm<sup>-1</sup>)** 3435, 2921, 1730, 1669, 1517, 1453, 1170, 997, 963.

### (4*S*,5*S*,6*R*)-*N*-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxamide (**7d**)



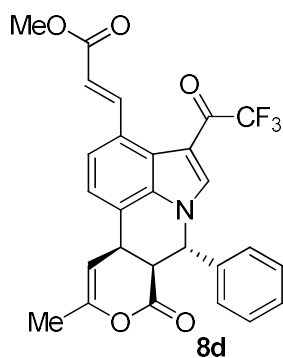
To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol) in THF (2.0 mL) was added benzylamine (28.0  $\mu$ L, 0.25 mmol) at room temperature. The resulting mixture was allowed to stir 48 h. Then the

solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the (4*S*,5*S*,6*R*)-*N*-benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxamide **7d** (52.0 mg, 81% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3,  $[\alpha]_D^{25} = +28.7$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 24.3 min, *Major*: 32.3 min.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.15 (d,  $J = 7.8$  Hz, 1H), 7.48-7.13 (m, 10H), 6.67 (d,  $J = 5.6$  Hz, 2H), 6.34 (s, 1H), 5.54 (t,  $J = 10.2$  Hz, 1H), 4.37-4.23 (m, 2H), 3.94 (d,  $J = 12.8$  Hz, 1H), 3.44 (dd,  $J_1 = 17.6$ ,  $J_2 = 5.7$  Hz, 1H), 3.26 (d,  $J = 6.7$  Hz, 1H), 2.69-2.64 (m, 1H), 2.11 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  206.18, 169.97, 137.45, 136.47, 135.34, 135.30, 133.74, 129.62, 129.44, 128.60, 127.34, 127.07, 125.21, 124.72, 121.96, 120.86, 118.37, 115.48, 58.69, 51.90, 46.93, 43.20, 33.05, 30.57. **HRMS (ESI)** calculated  $[M+H]^+$  for C<sub>30</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>F<sub>3</sub>: 519.1890, found: 519.1898. **FTIR (cm<sup>-1</sup>)** 3428, 2923, 1715, 1515, 1193, 1140, 1034, 996, 935.

**(*E*)-Methyl 3-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)acrylate (**8d**)<sup>6</sup>**



To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (2.5 mol%), AgSbF<sub>6</sub> (10 mol%), acrylate derivative (0.5 mmol, 4 equiv) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.125 mmol, 1equiv) and dichloroethane (1 mL). The Schlenk tube was placed in a pre-heated (100 °C) oil bath. After 6 h, the reaction mixture was cooled to room temperature, and diluted with diethyl ether and passed through a short silica gel (230-400 mesh size) bed, and repeatedly washed with diethyl ether (5 mL x 3 times). Then the solution was concentrated under

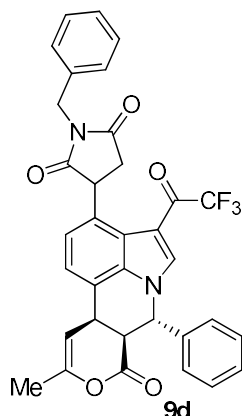
reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (5:1) to afford the (*E*)-methyl 3-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)acrylate **8d** (49.0 mg, 79% yield).

$R_f$  (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3,  $[\alpha]_D^{25} = -41.0$  (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralcel OD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 34.3 min, *Major*: 38.3 min.

<sup>6</sup> Lanke, V.; Bettadapur, K. R.; Prabhu, K. R. *Org. Lett.* **2016**, *18*, 5496.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.21 (d, *J* = 15.9 Hz, 1H), 8.12 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 2H), 6.35 (d, *J* = 14.2 Hz, 2H), 5.66 (d, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.68 (t, *J* = 6.3 Hz, 1H), 3.41 (d, *J* = 6.3 Hz, 1H), 1.95 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 174.46 (q, *J* = 34.4 Hz), 167.54, 167.25, 150.79, 145.85, 138.75 (q, *J* = 5.4 Hz), 134.28, 129.63, 129.59, 125.22, 123.47, 123.30, 123.09, 122.32, 119.14, 117.48 (q, *J* = 291.0 Hz), 112.04, 101.57, 57.37, 51.85, 45.35, 27.09, 18.74. **HRMS (ESI)** calculated [M+Na]<sup>+</sup> for C<sub>27</sub>H<sub>20</sub>O<sub>5</sub>N<sub>1</sub>F<sub>3</sub>Na: 518.1186, found: 518.1194. **FTIR (cm<sup>-1</sup>)** 3442, 3140, 2924, 1765, 1633, 1404, 1349, 1286, 1187, 1147, 981, 955.

**1-Benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione (9d)<sup>7</sup>**



To a dry Schlenk tube containing compound **3d** (51.0 mg, 0.125 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (5.0 mol%), AgSbF<sub>6</sub> (20 mol%), *N*-benzyl maleimide (0.25 mmol, 2 equiv), AcOH (23 mg, 3 equiv) and AgOAc (63 mg, 3 equiv) and dichloroethane (1 mL). The Schlenk tube was placed in a pre-heated (120 °C) oil bath. After 12 h, the reaction mixture was cooled to room temperature, and diluted with diethyl ether and passed through a short silica gel (230-400 mesh size) bed, and repeatedly washed with diethyl ether (5 mL x 3 times). Then the solution was concentrated under reduced

pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the 1-benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione **9d** (61.0 mg, 81% yield) in 2:1 diastereomeric ratio (dr was determined by HPLC analysis).

*R<sub>f</sub>*(Pet. ether /EtOAc = 70/30): 0.20; er = 95:5, [α]<sub>D</sub><sup>25</sup> = +116.4 (c 0.1, CHCl<sub>3</sub>). **HPLC** (Chiralpak AD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 12.2 min, *Major*: 31.7 min, for another dr *Minor*: 21.4 min, *Major*: 25.2 min

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.12 (s, 1H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.37-7.29 (m, 6H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.91-6.89 (m, 1H), 6.81-6.80 (m, 2H), 6.35 (s, 1H), 5.84 (bs, 1H), 5.63-5.59

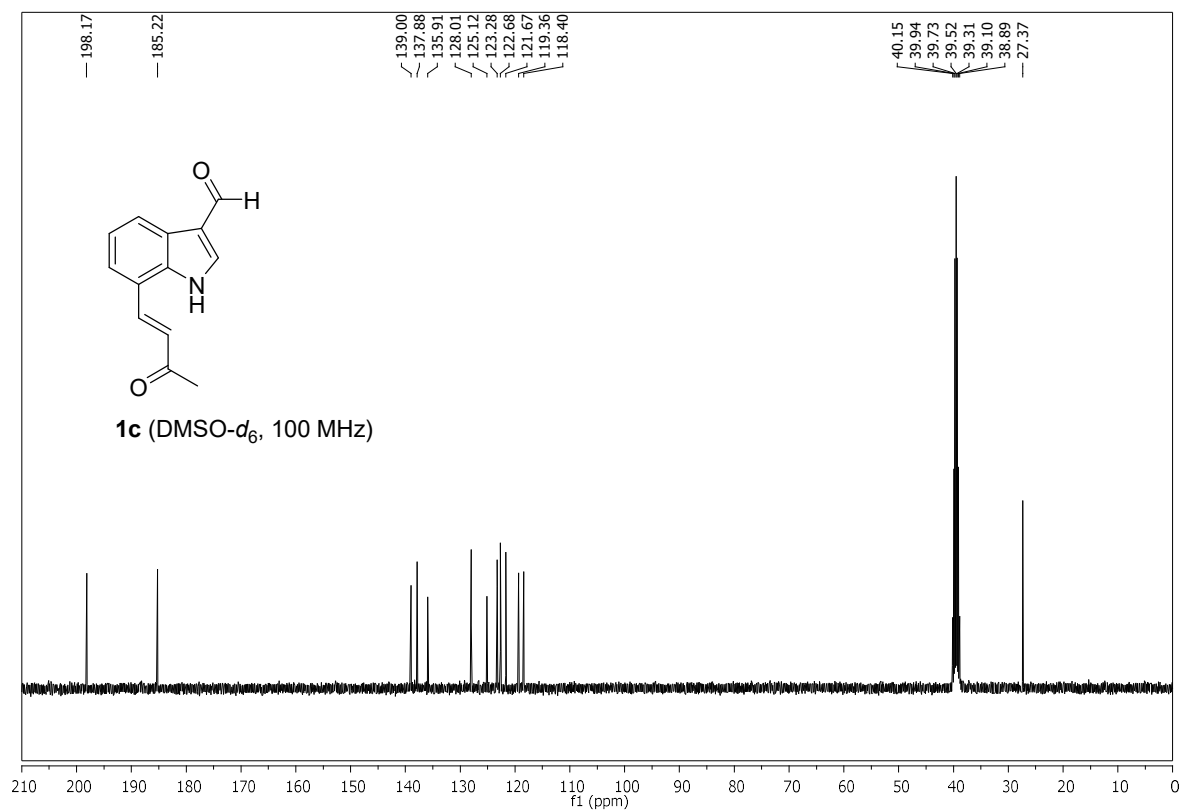
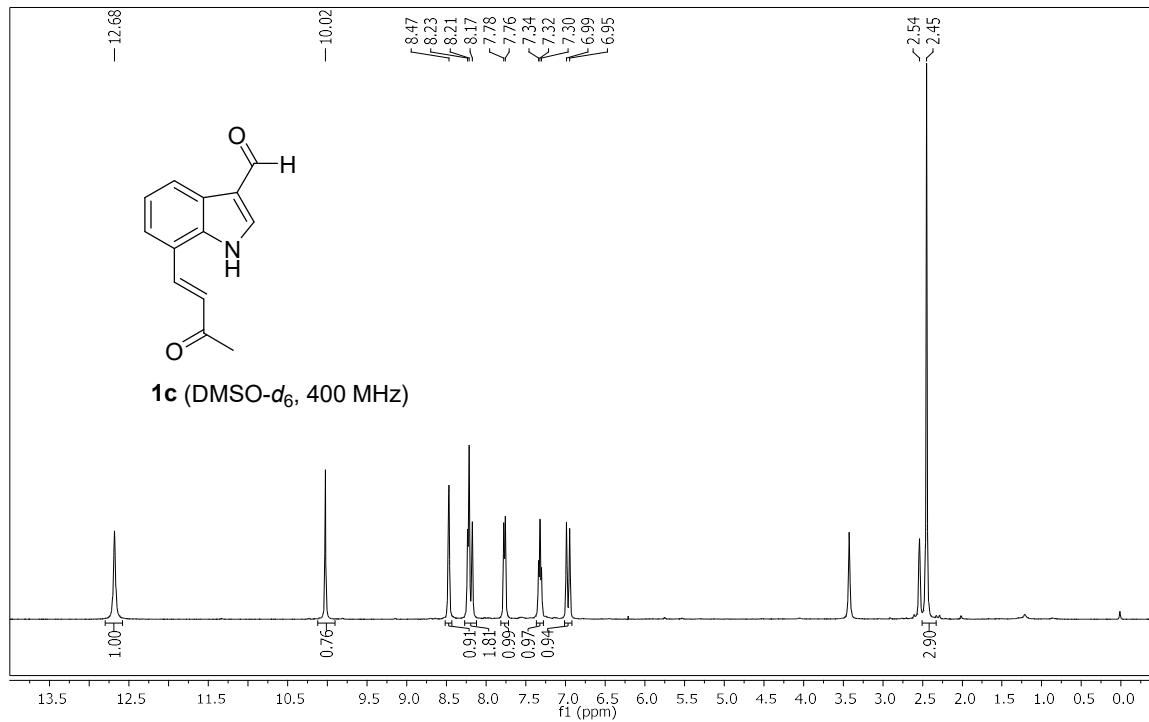
<sup>7</sup> Sherikar, M.S.; Kapanaiyah, R.; Lanke, V.; Prabhu, K. R. *Chem. Commun.* **2018**, *54*, 11200.



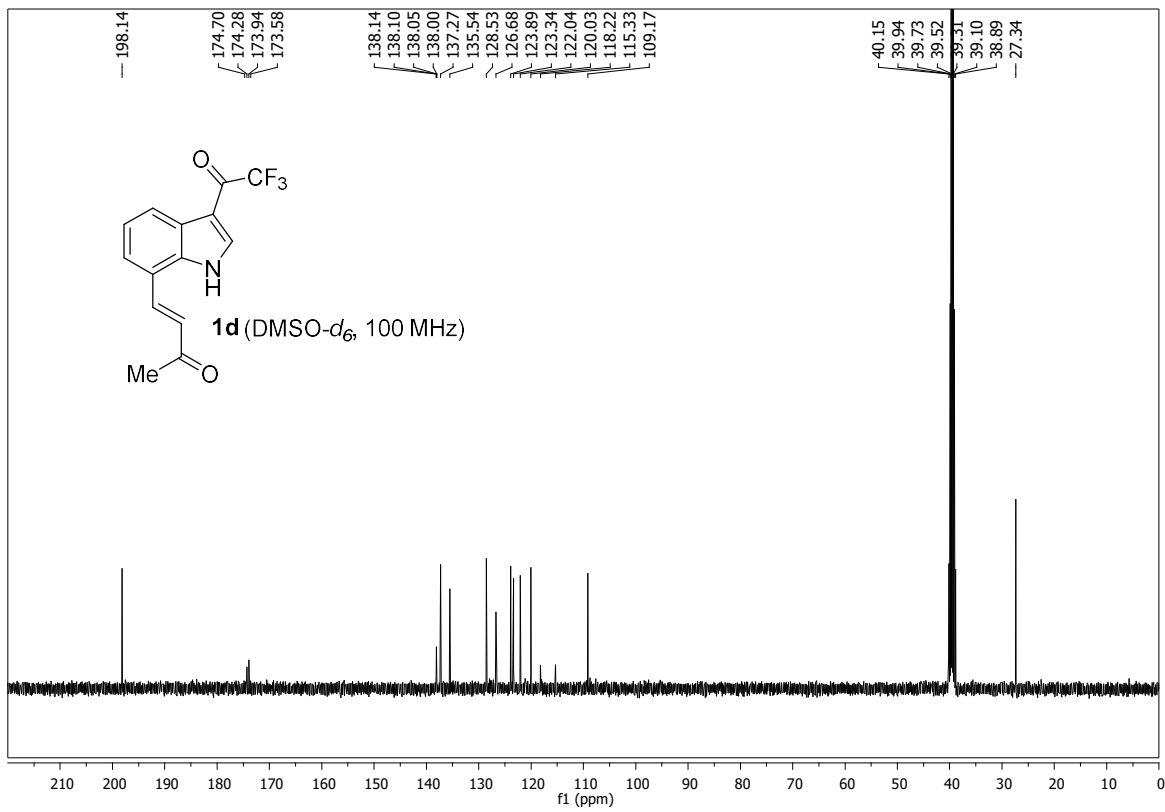
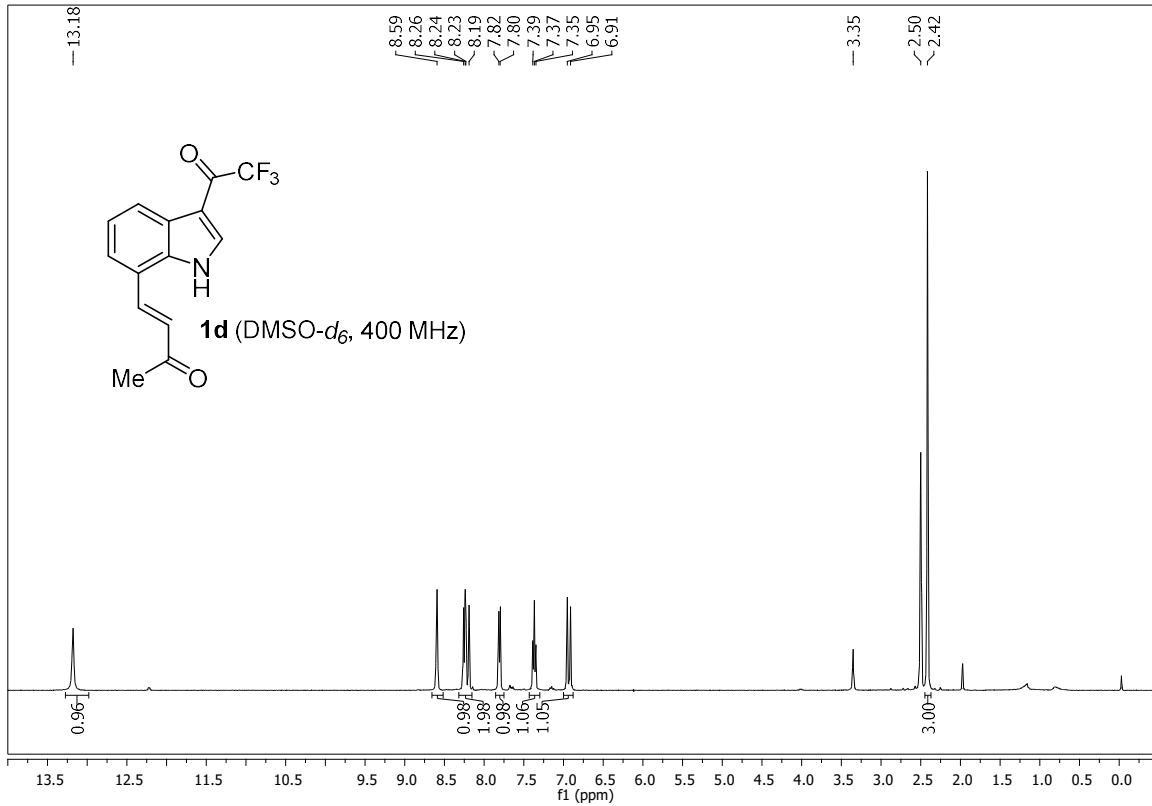
(m,1H), 4.79 (s, 1H), 3.66-3.61 (m, 1H), 3.48-3.36 (m, 2H), 2.70 (dd,  $J_1 = 30.6$  Hz,  $J_2 = 11.8$  Hz, 1H), 1.93 (s, 3H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  178.72, 176.26, 175.16 (q,  $J = 34.4$  Hz), 167.04, 150.70, 138.99, 138.52, 136.18, 134.41, 132.74, 129.64, 129.07, 128.92, 128.86, 128.82, 128.81, 128.03, 125.27, 122.92, 121.12, 117.43 (q,  $J = 291.0$  Hz), 111.65, 111.68, 101.53, 57.44, 45.32, 42.80, 39.69, 26.91, 18.72. Representative Peaks of Minor Isomer:  **$^{13}\text{C}$  NMR**  $\delta$  178.98, 176.20, 175.09 (q,  $J = 34.3$  Hz), 167.36, 138.42, 136.17, 134.35, 101.73, 57.47, 44.95, 30.80, 26.83. **HRMS (ESI)** calculated  $[\text{M}+\text{H}]^+$  for  $\text{C}_{34}\text{H}_{26}\text{O}_5\text{N}_2\text{F}_3$ : 599.1788, found: 599.1767. **FTIR ( $\text{cm}^{-1}$ )** 1957, 1766, 1703, 1588, 1513, 1401, 1340, 1309, 1149, 1077, 970, 935, 755, 701, 630.

## 8. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Indole Derivatives

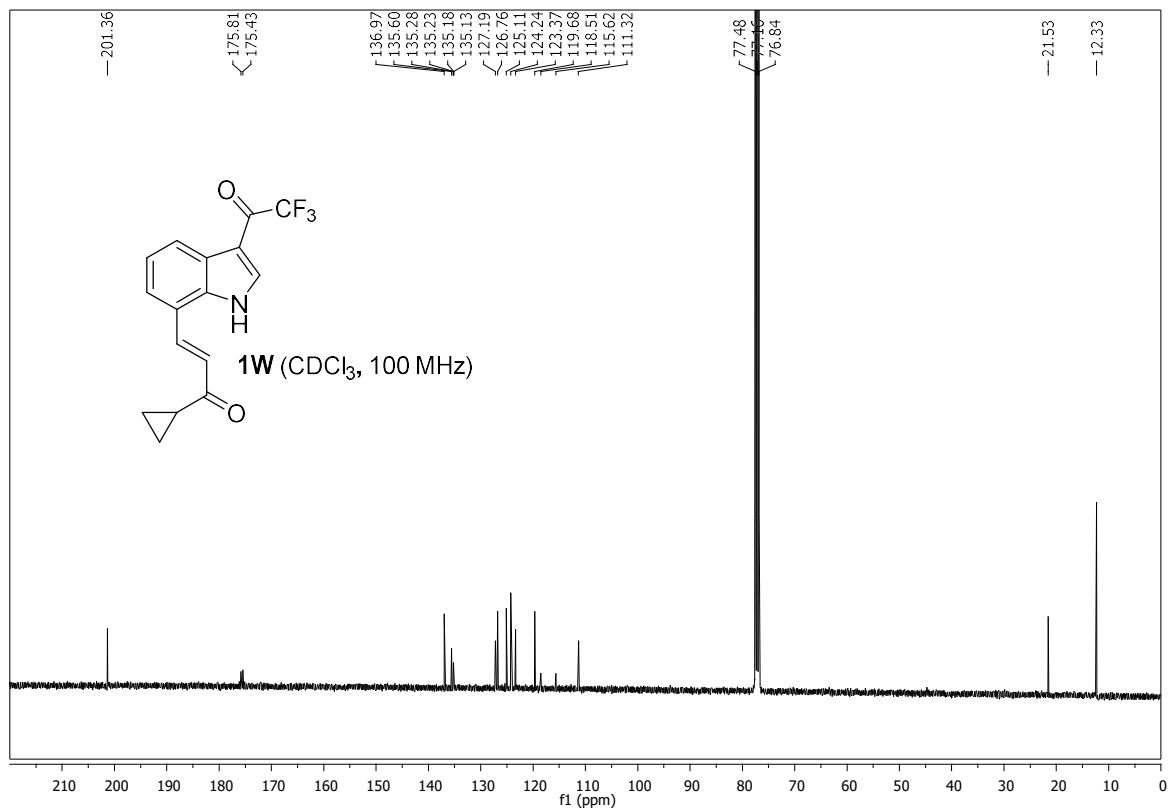
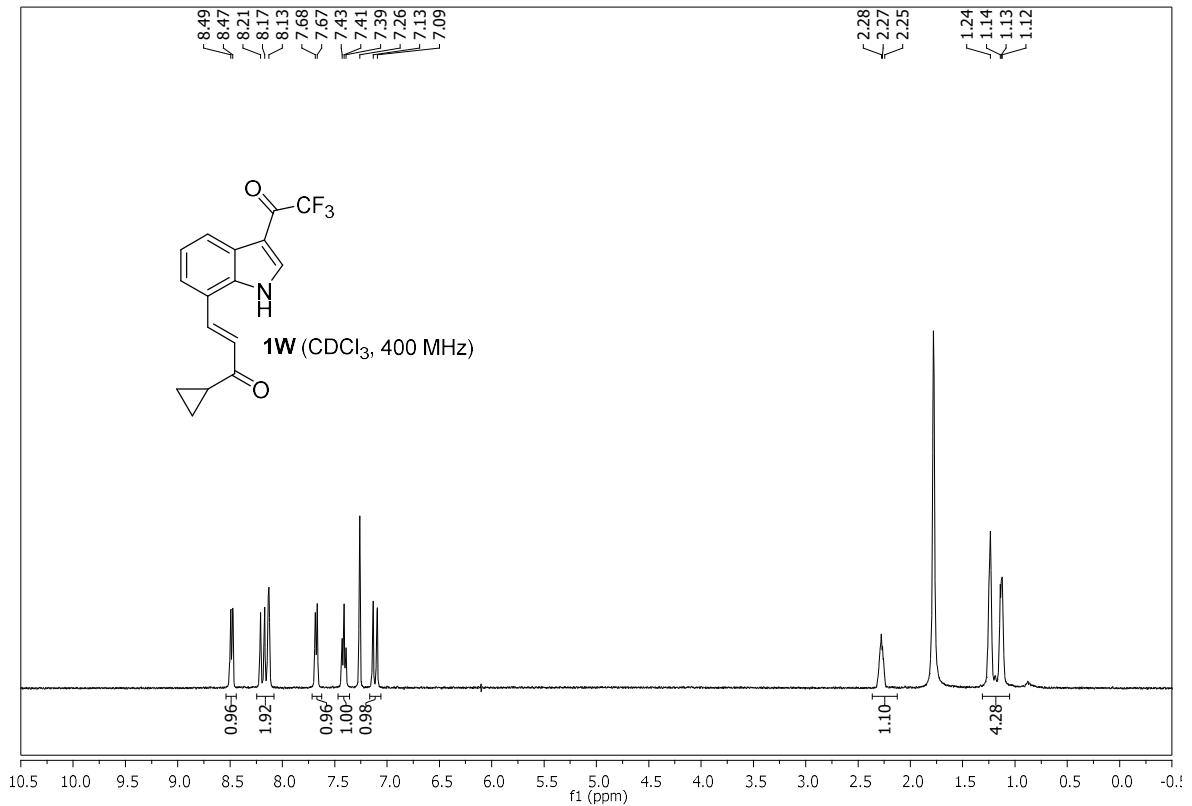
### (*E*)-7-(3-Oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde (**1c**)



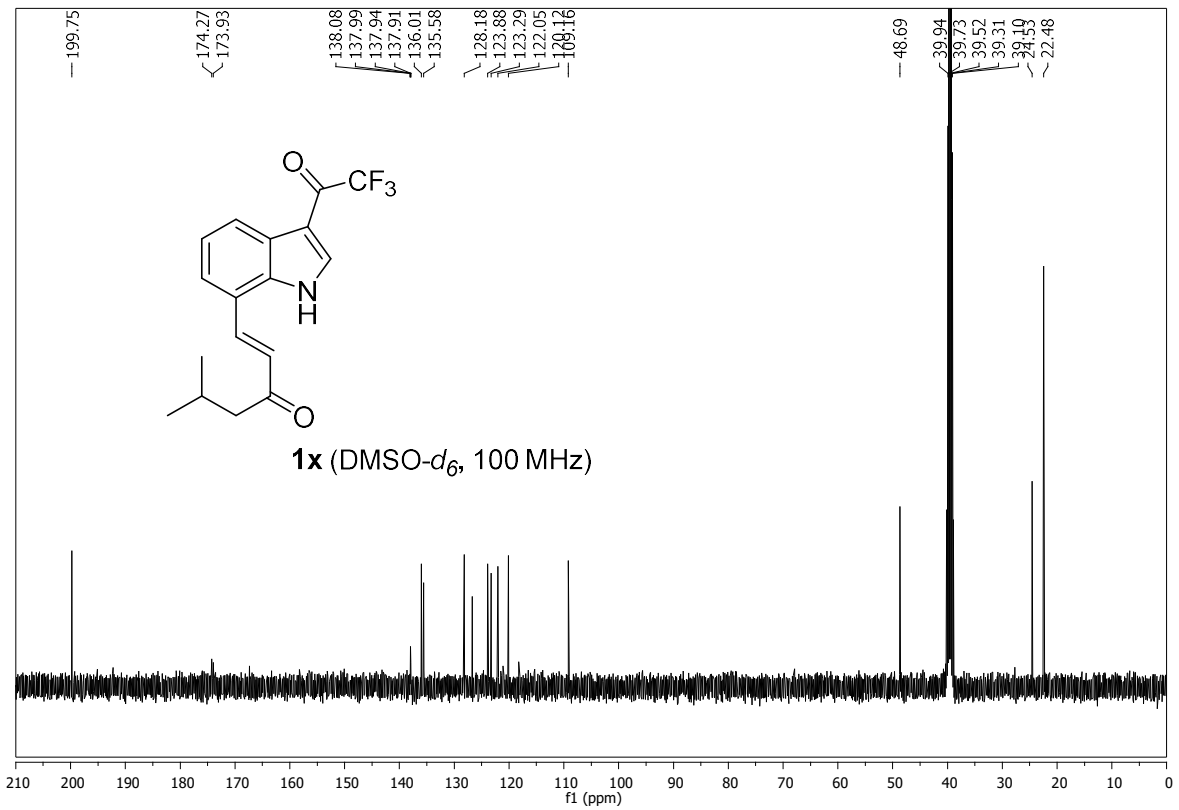
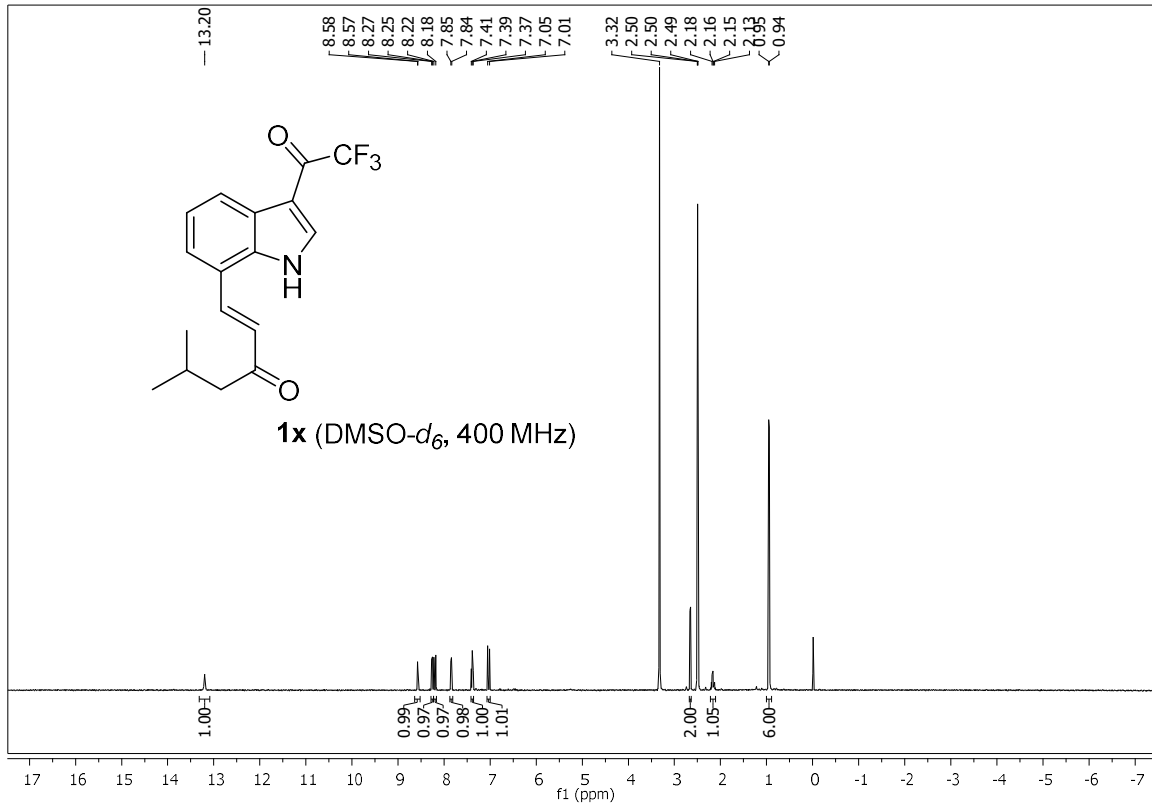
**(E)-4-(3-(2,2,2-Trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1d)**



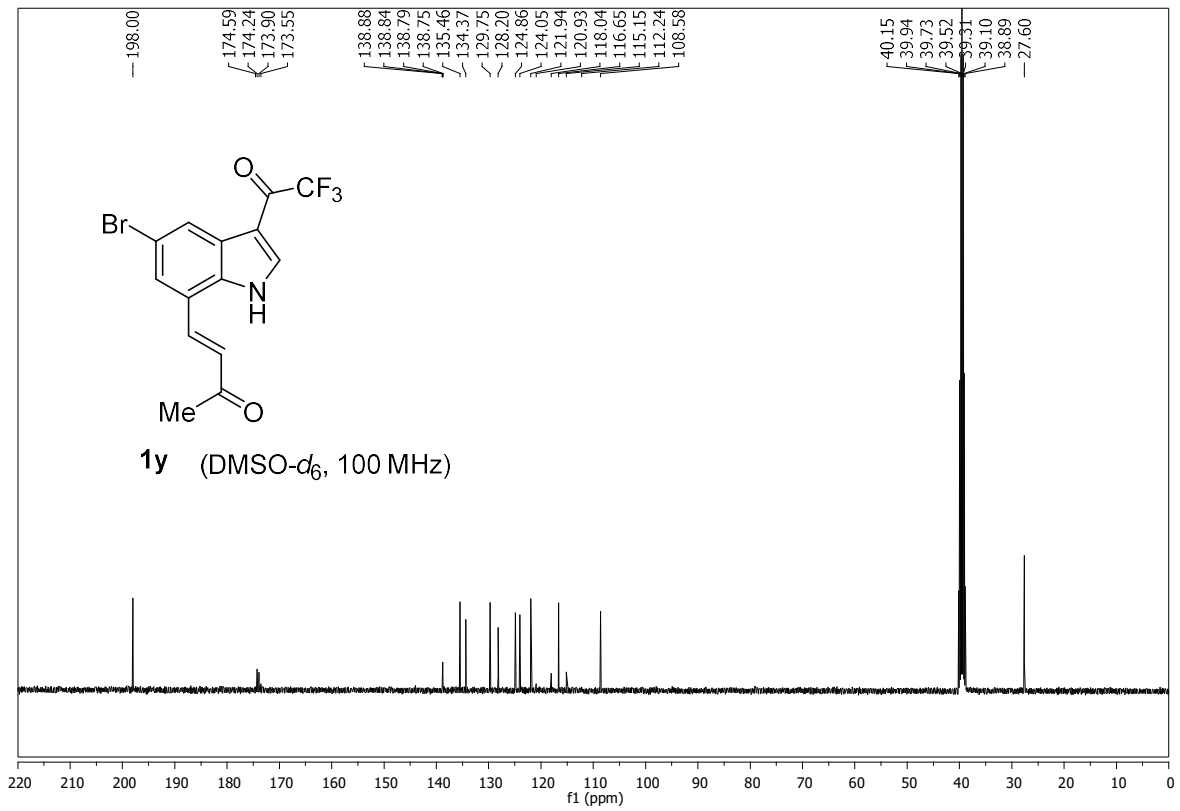
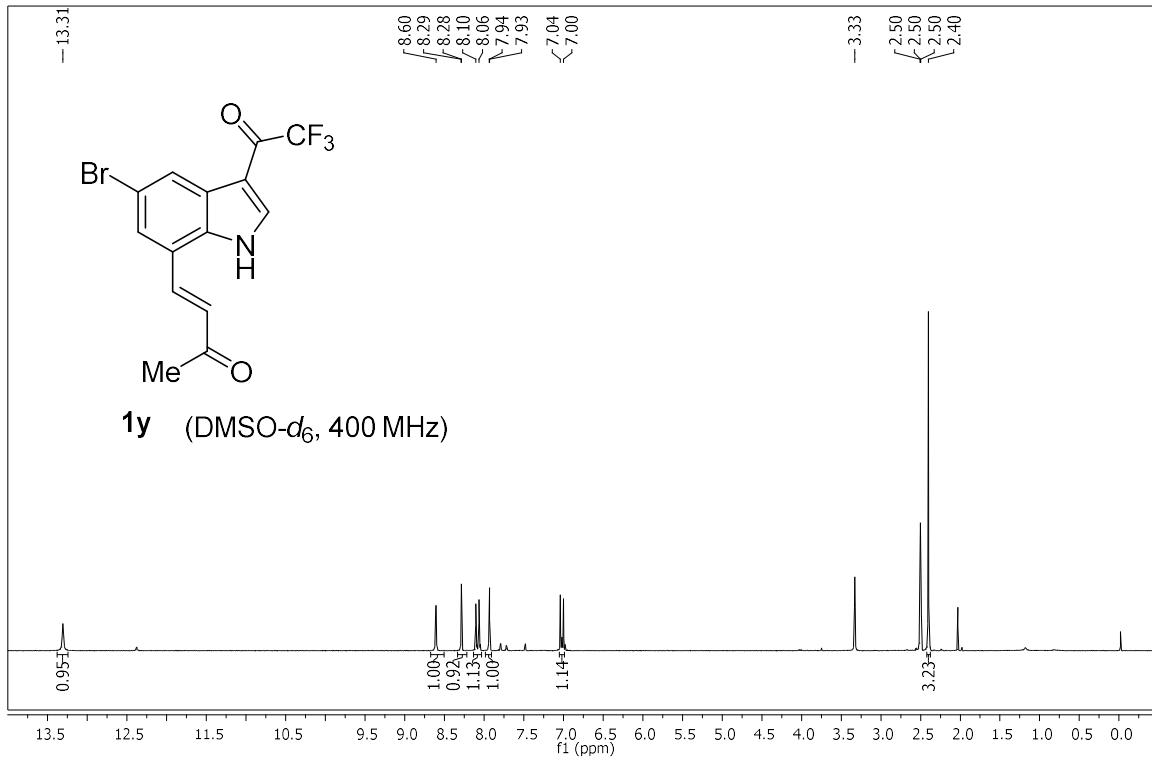
**(E)-1-Cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)prop-2-en-1-one (1w)**



**(E)-5-Methyl-1-(3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)hex-1-en-3-one (1x)**

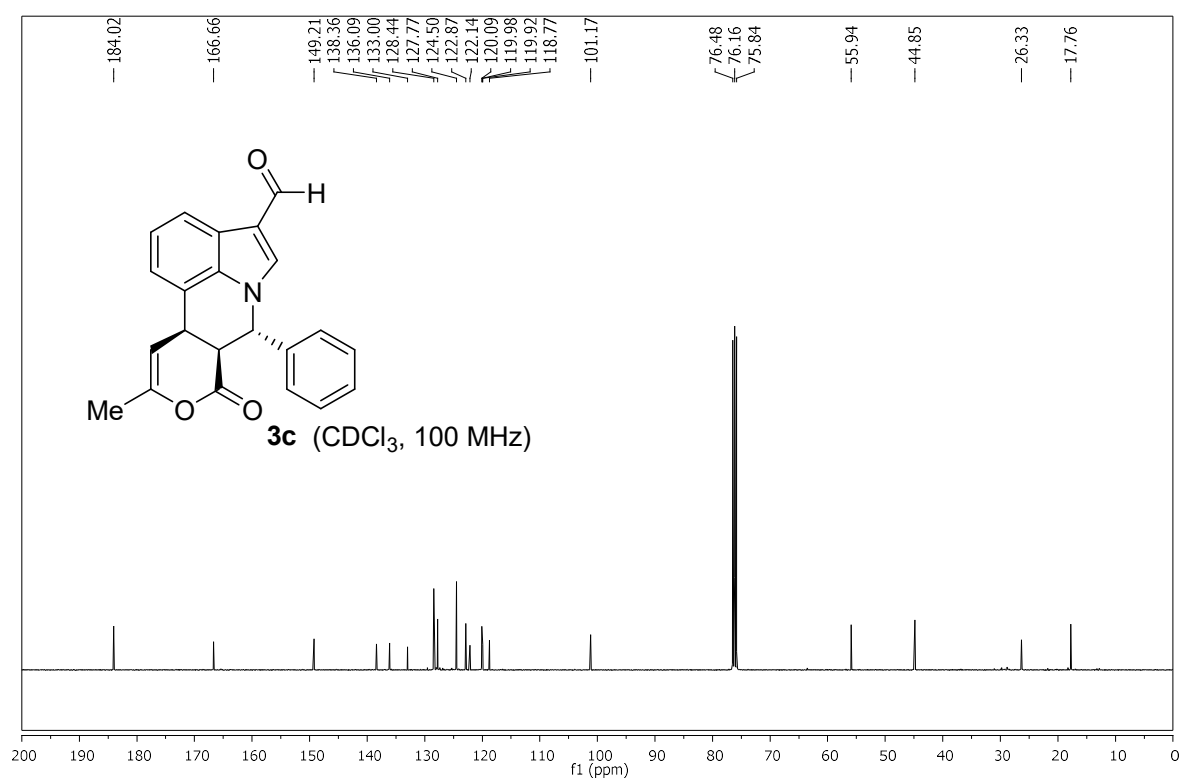
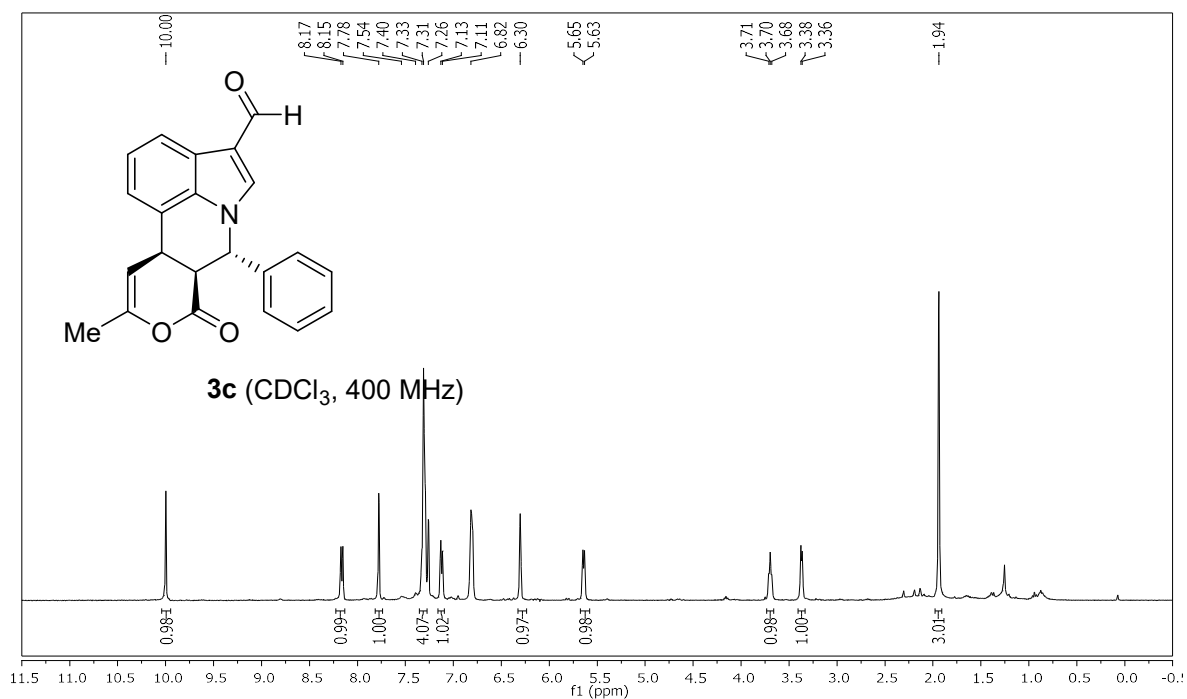


**(E)-4-(5-Bromo-3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1y)**

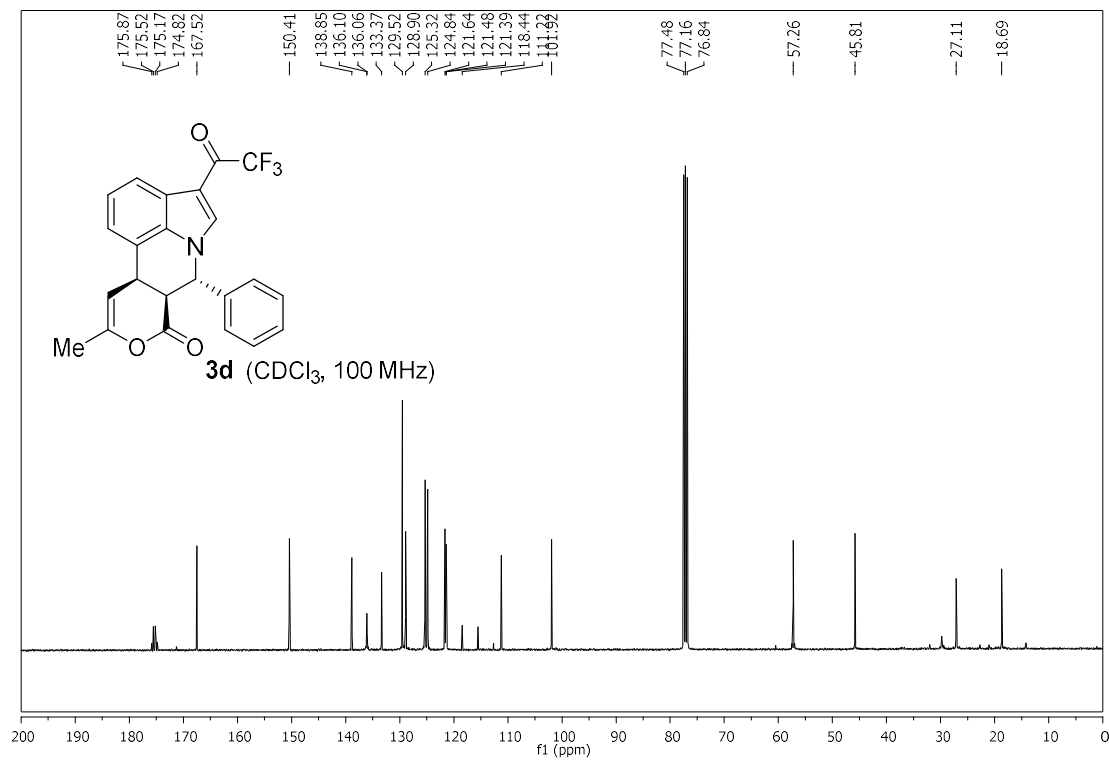
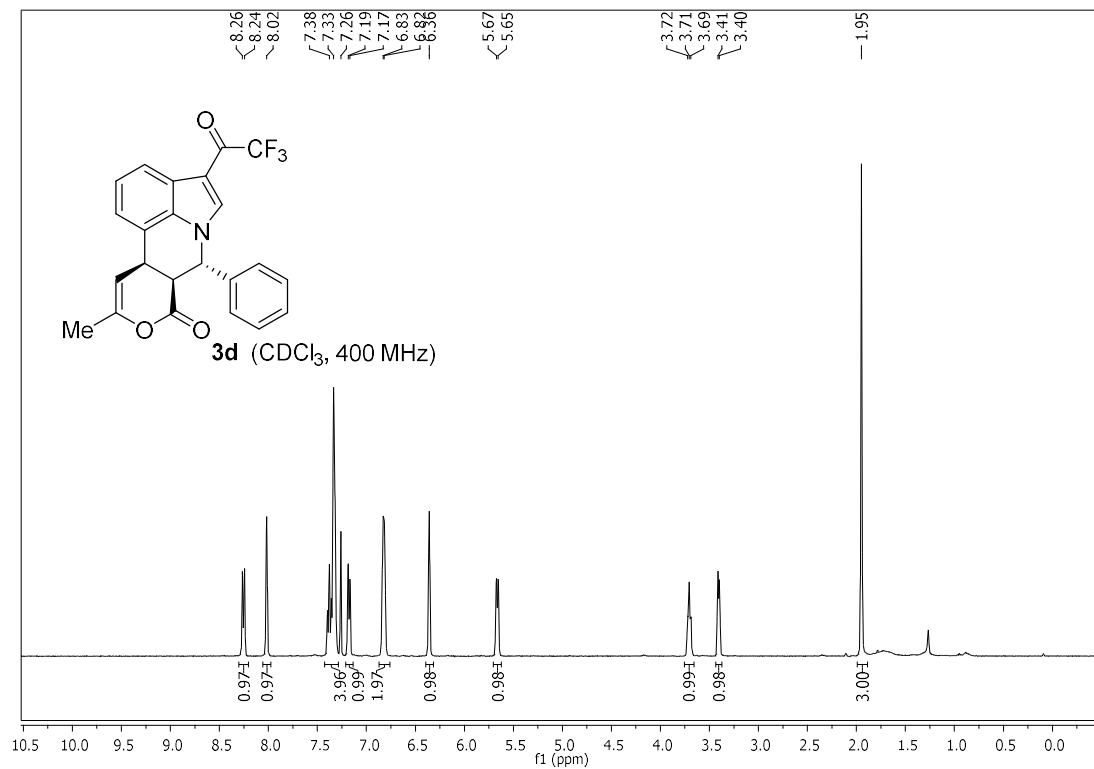


## 9. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Pyrroloquinoline Derivatives

### (7*S*,7*aS*,11*aR*)-10-Methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde (**3c**)

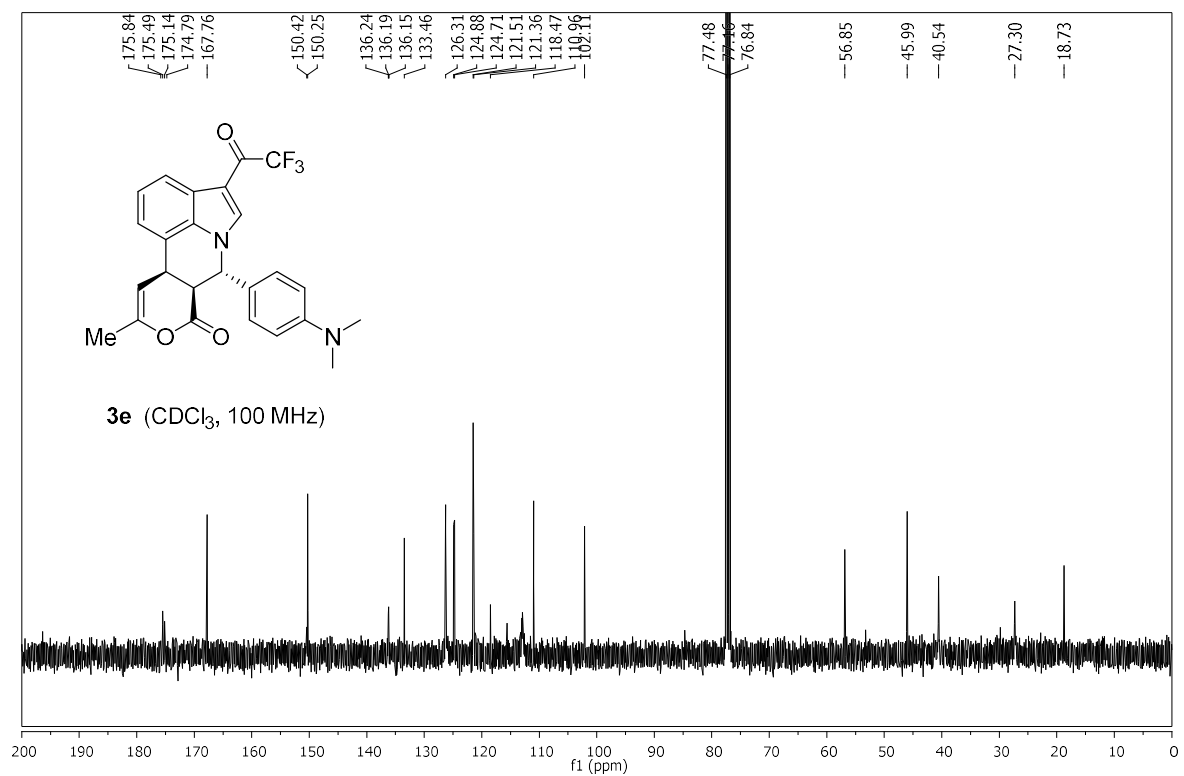
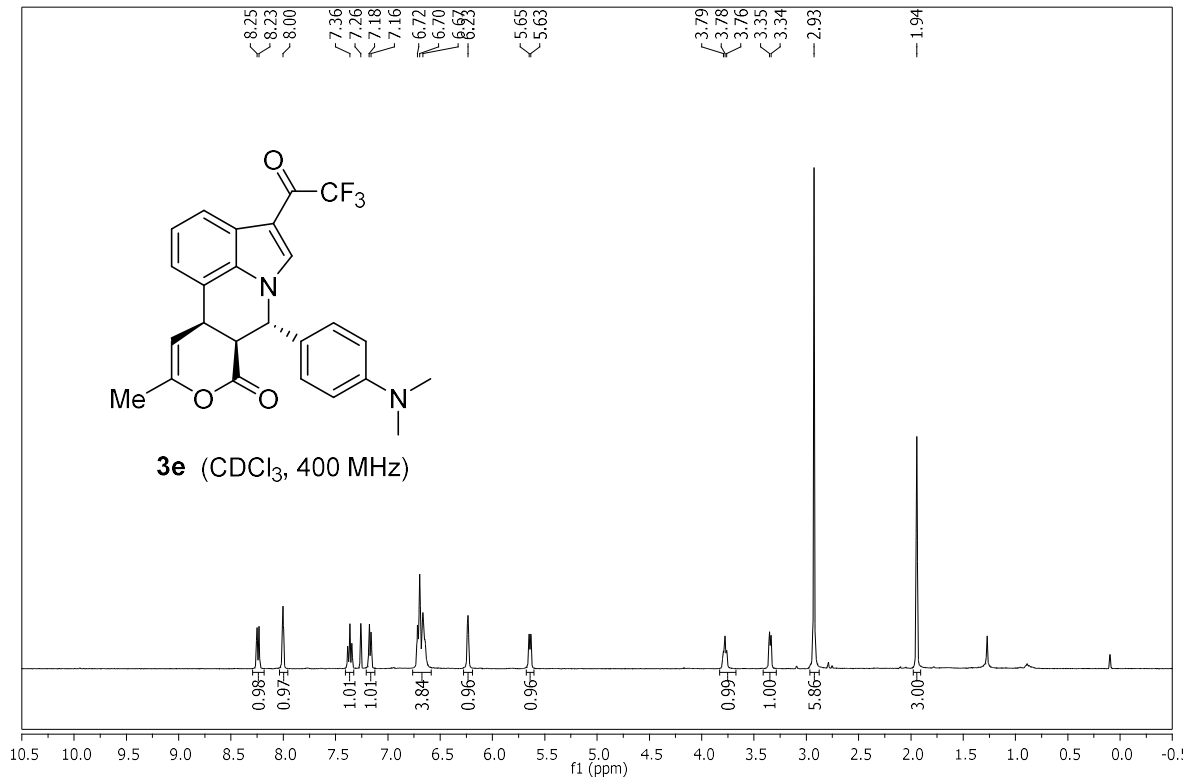


**(7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3d)**

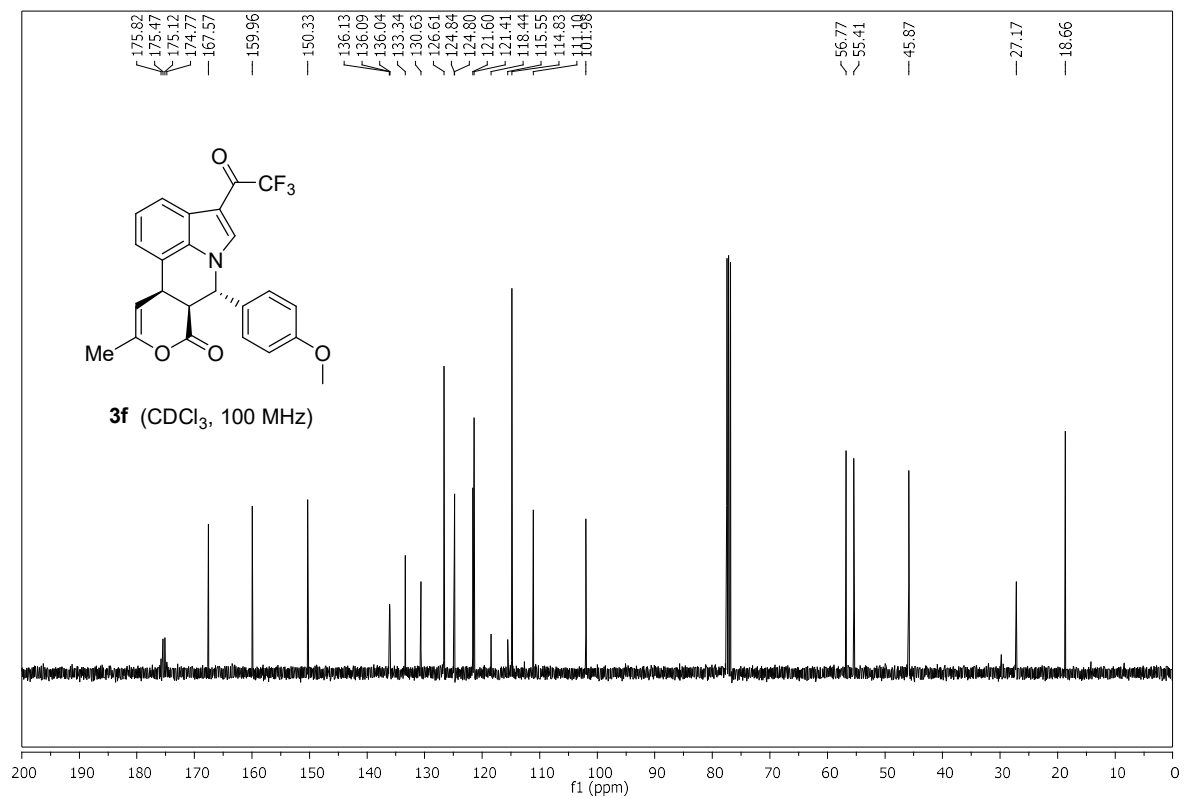
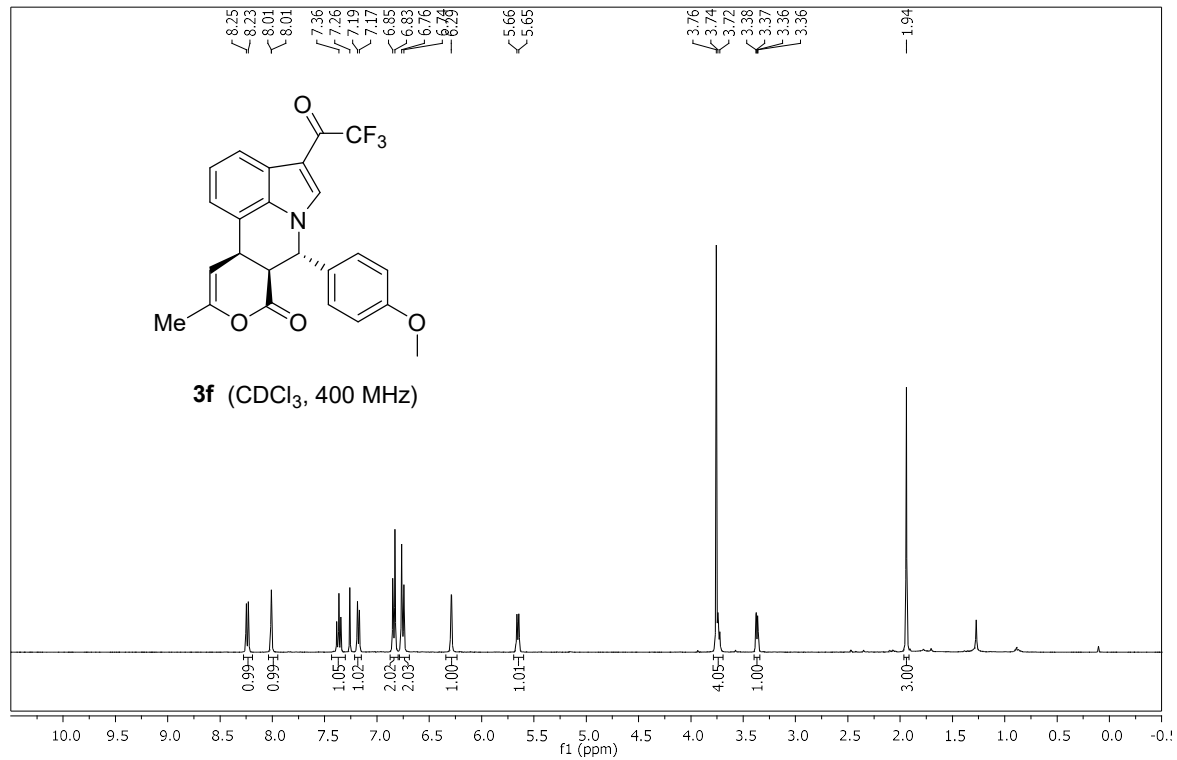




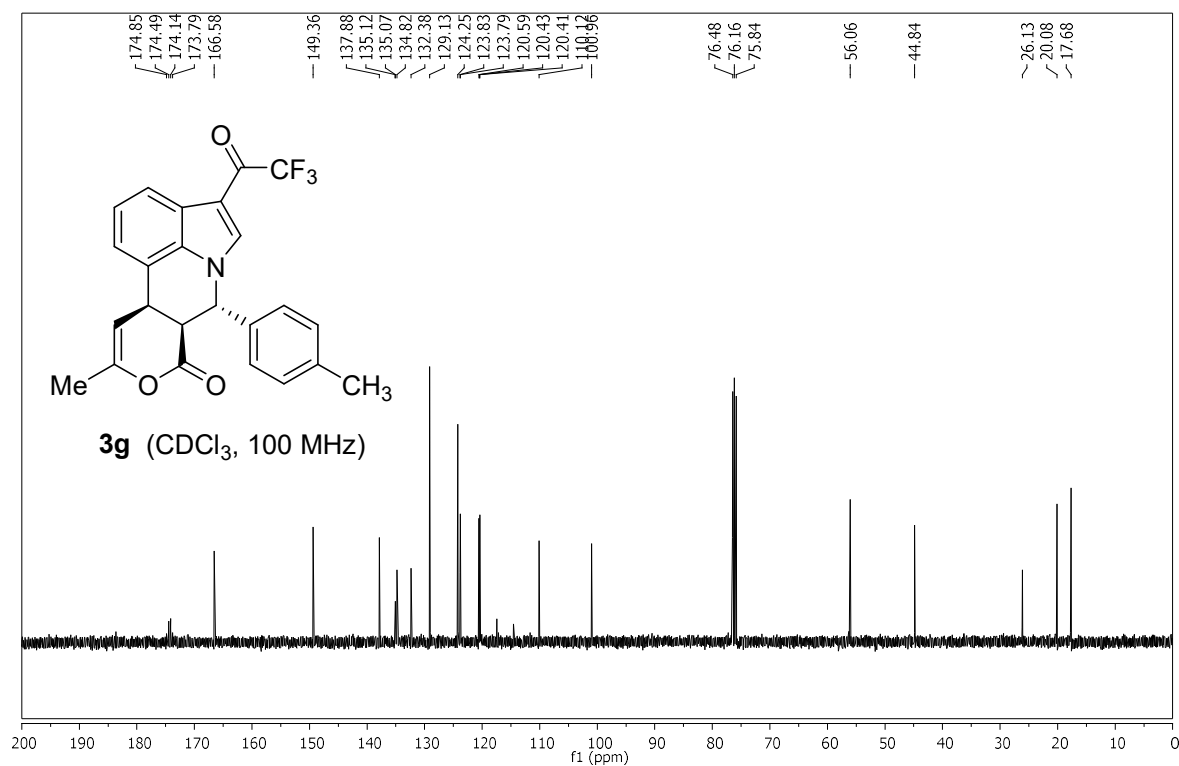
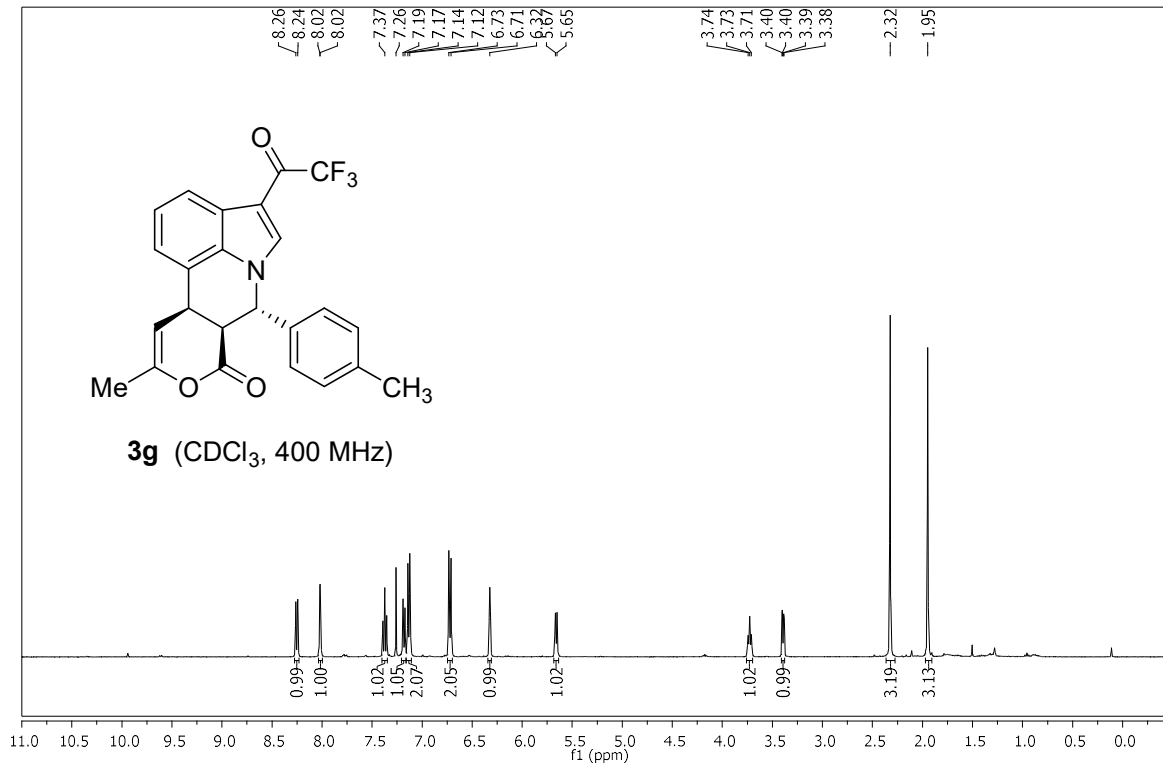
**(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)**



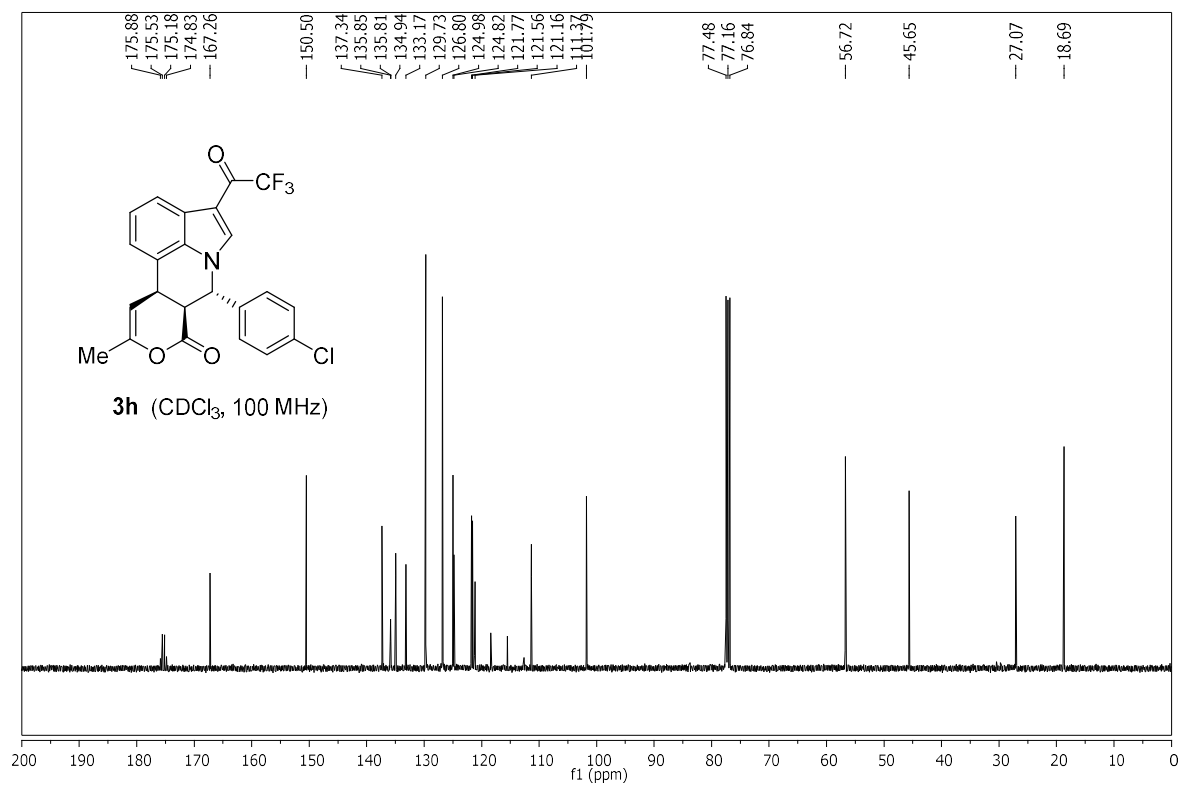
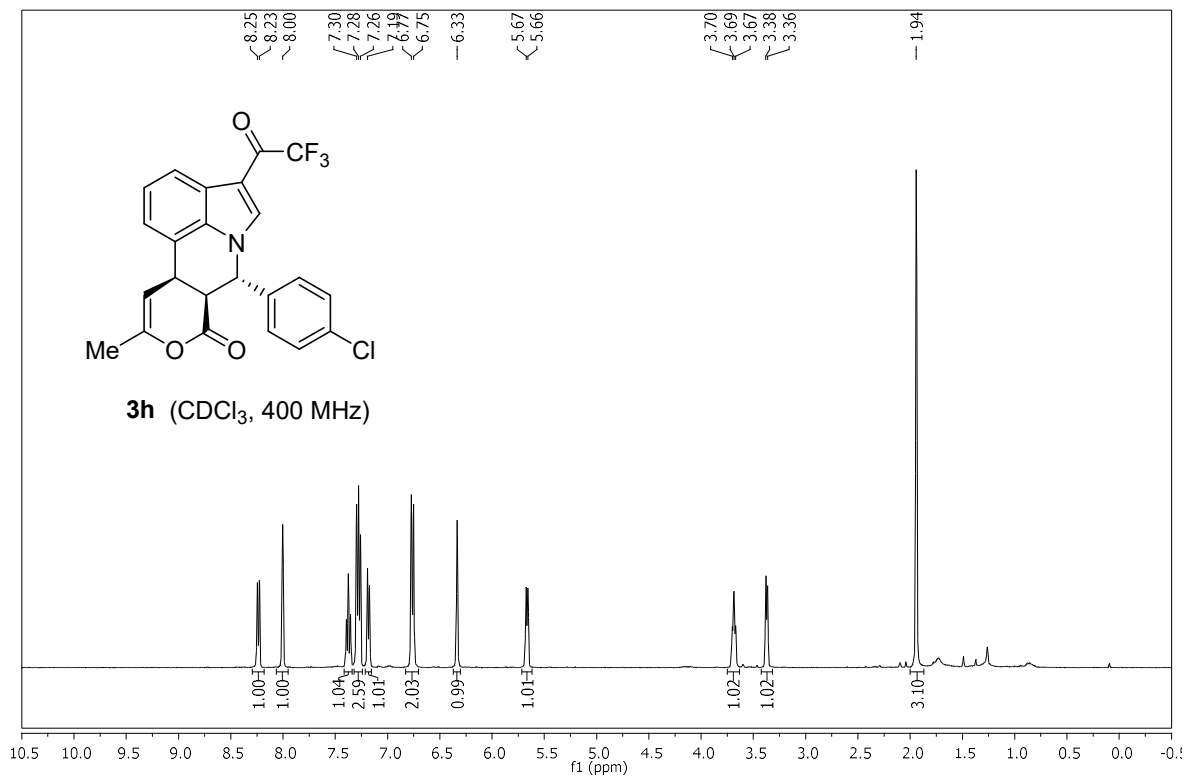
**(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one(3f)**



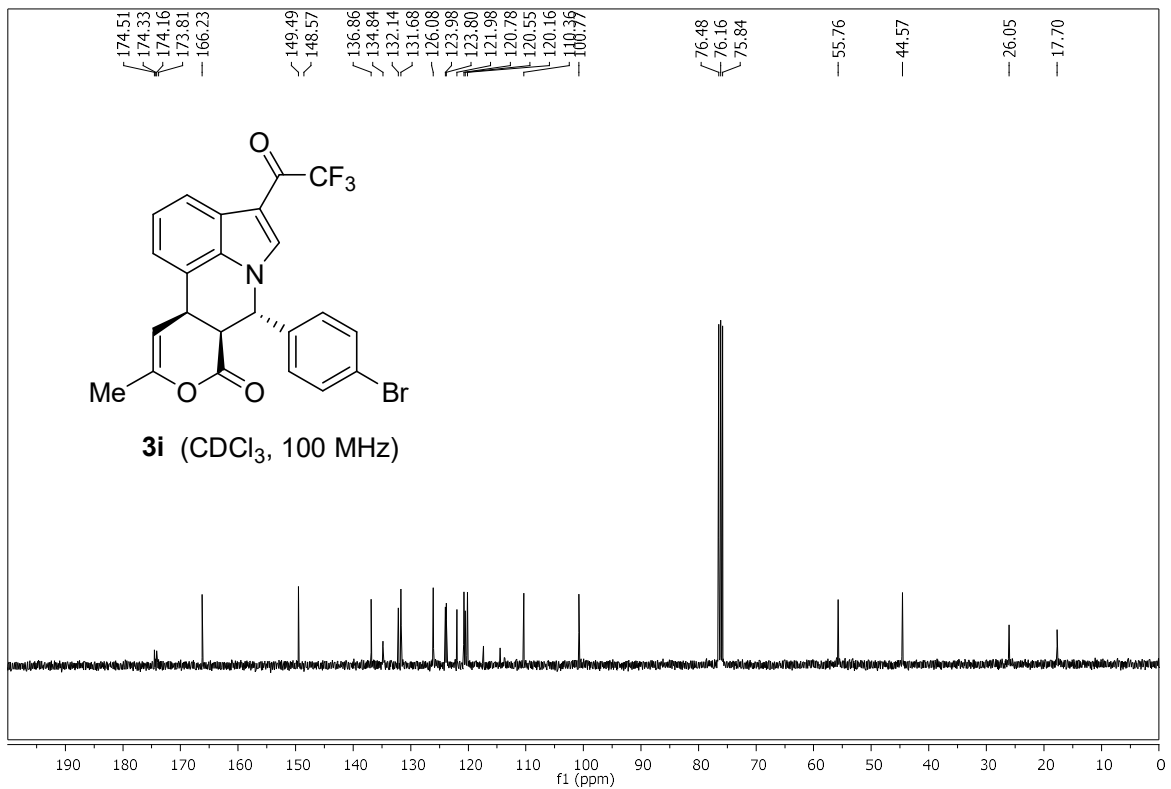
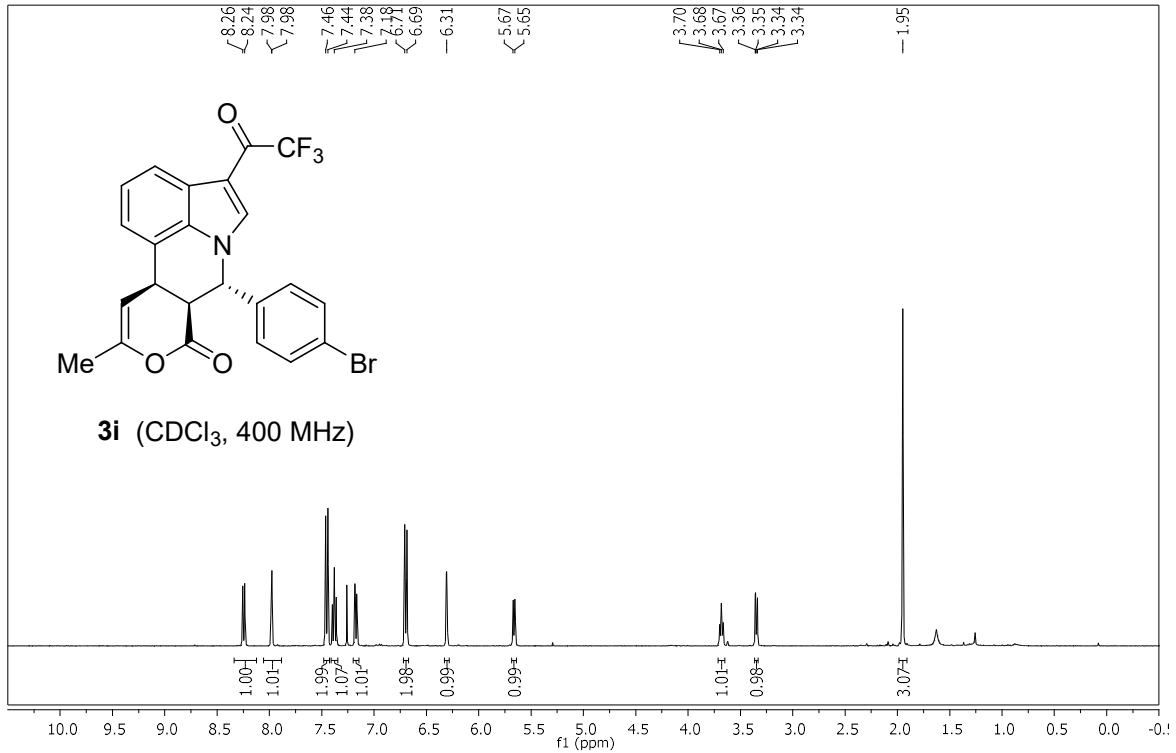
**7*S*,7*aS*,11*aR*)-10-methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3g)**



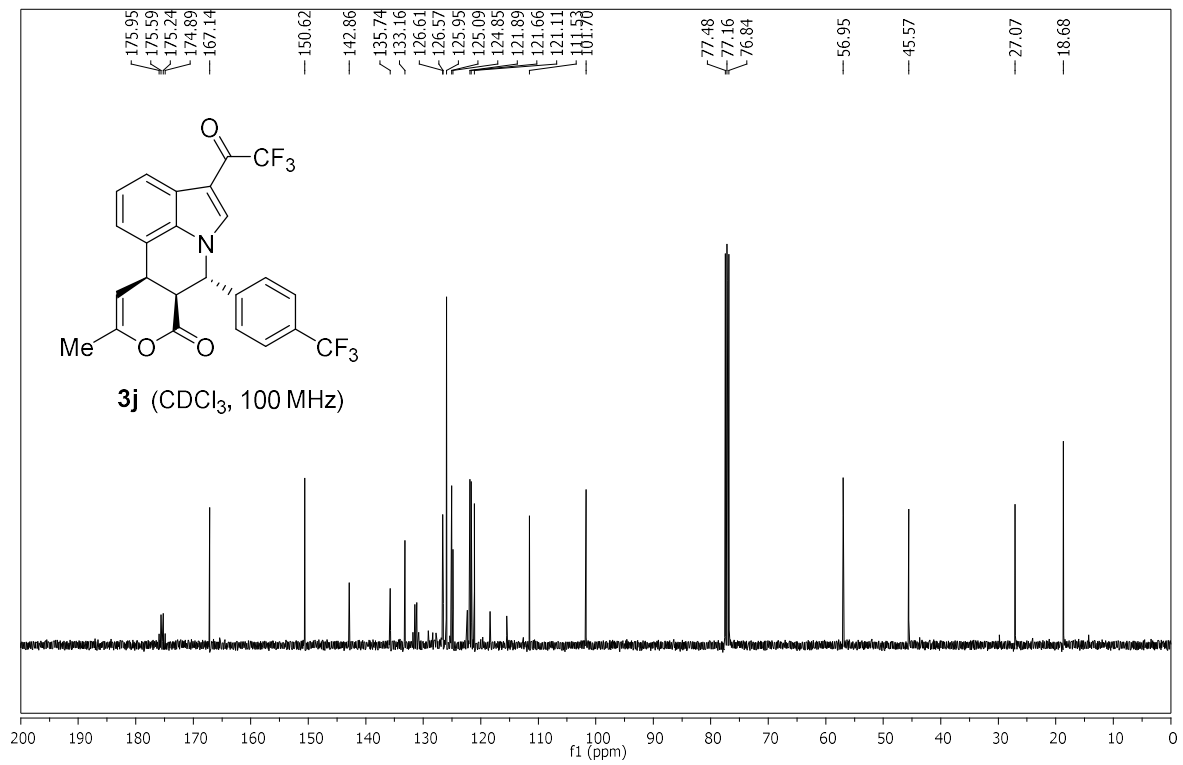
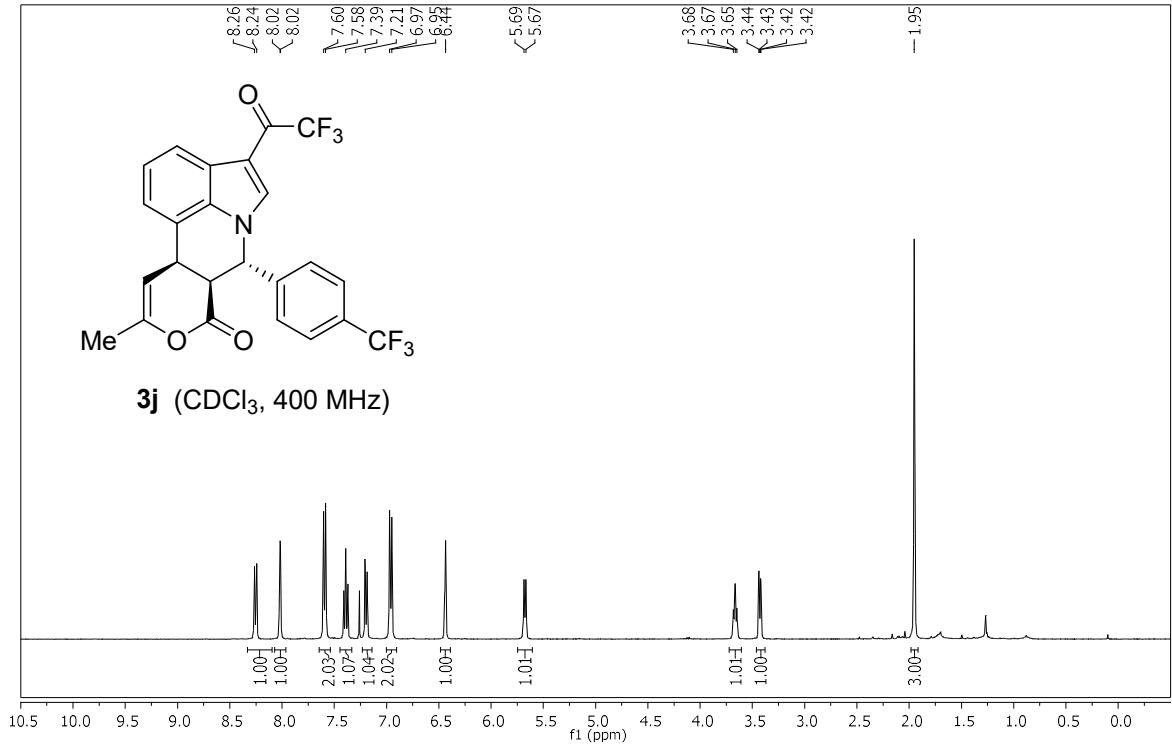
**(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3h)**



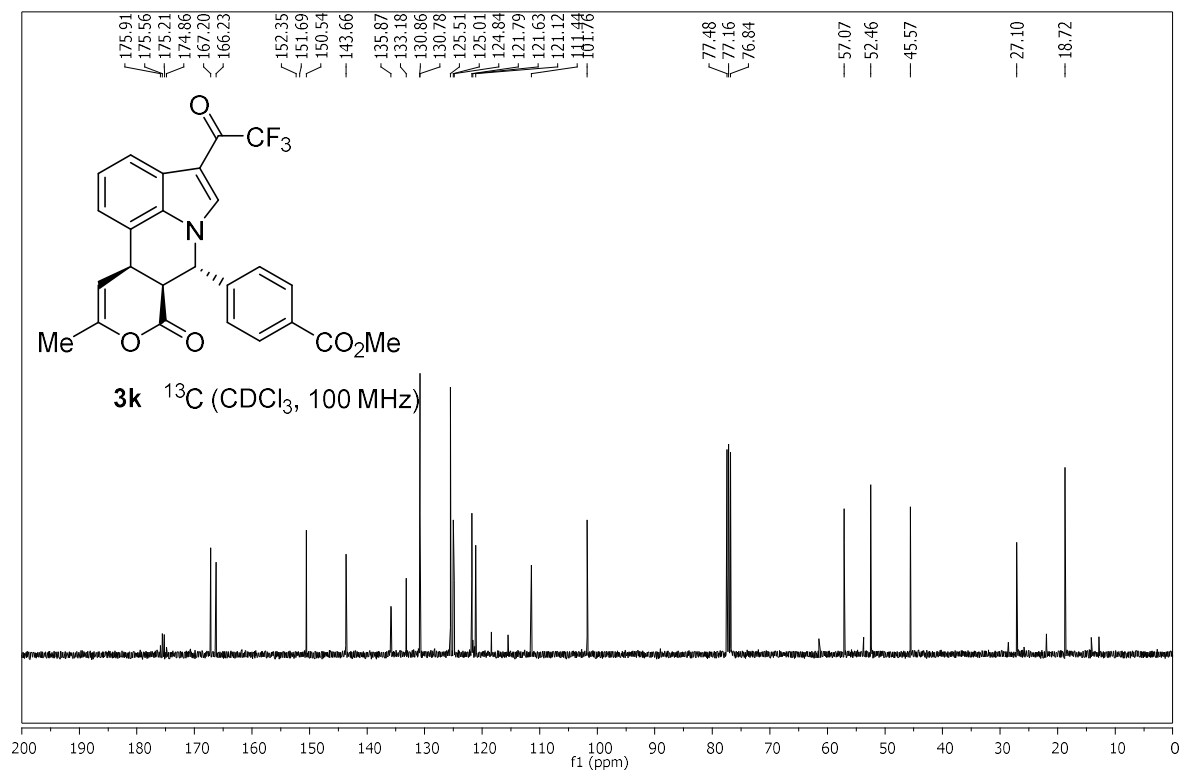
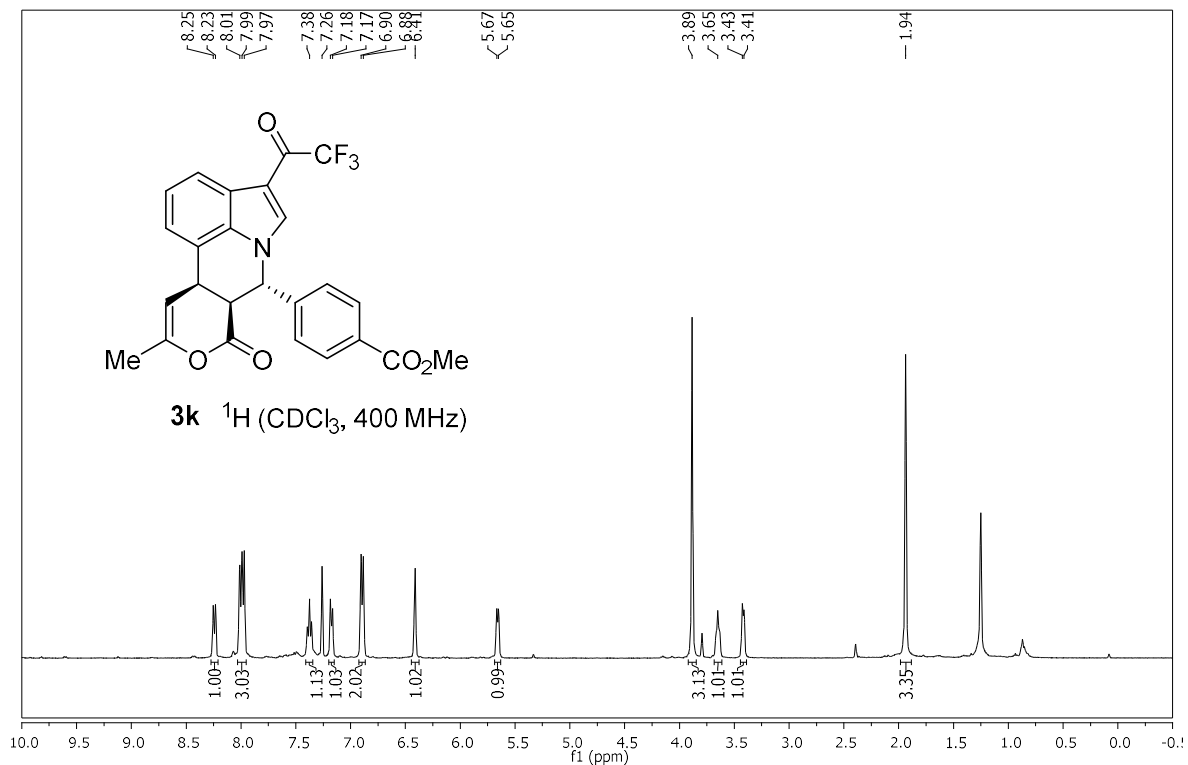
**(7*S*,7*aS*,11*aR*)-7-(4-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3i)**



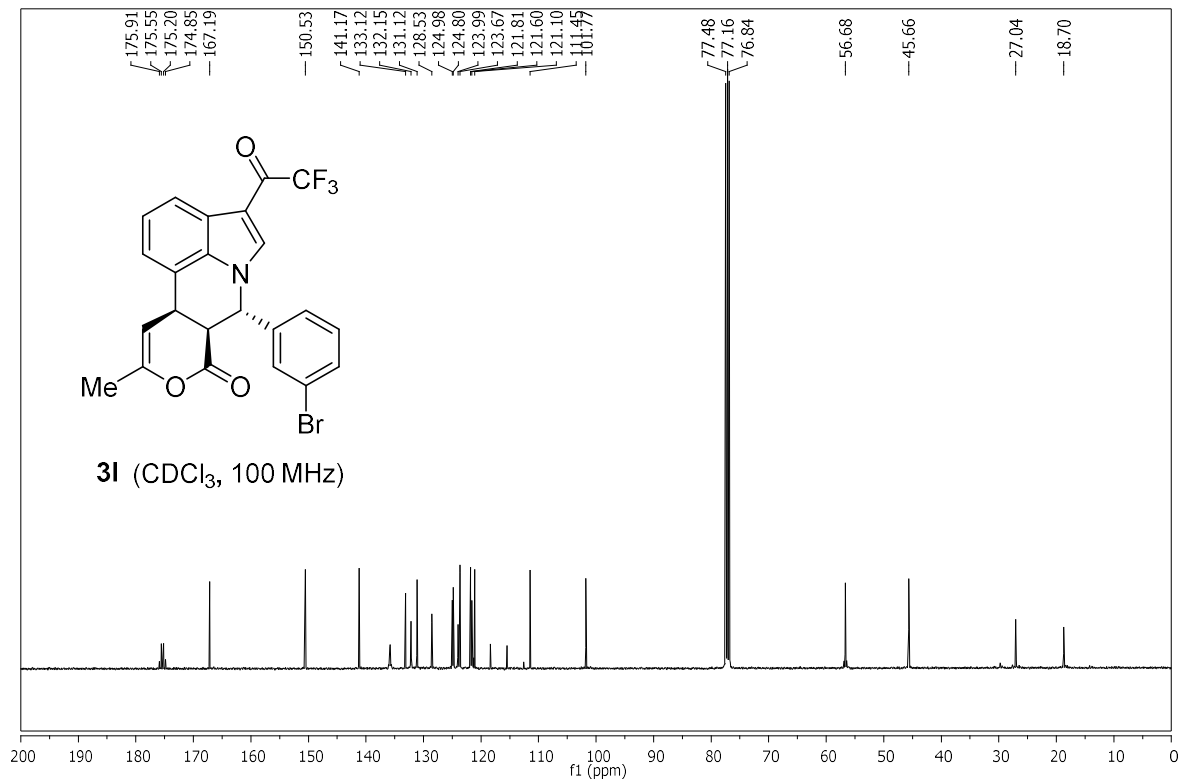
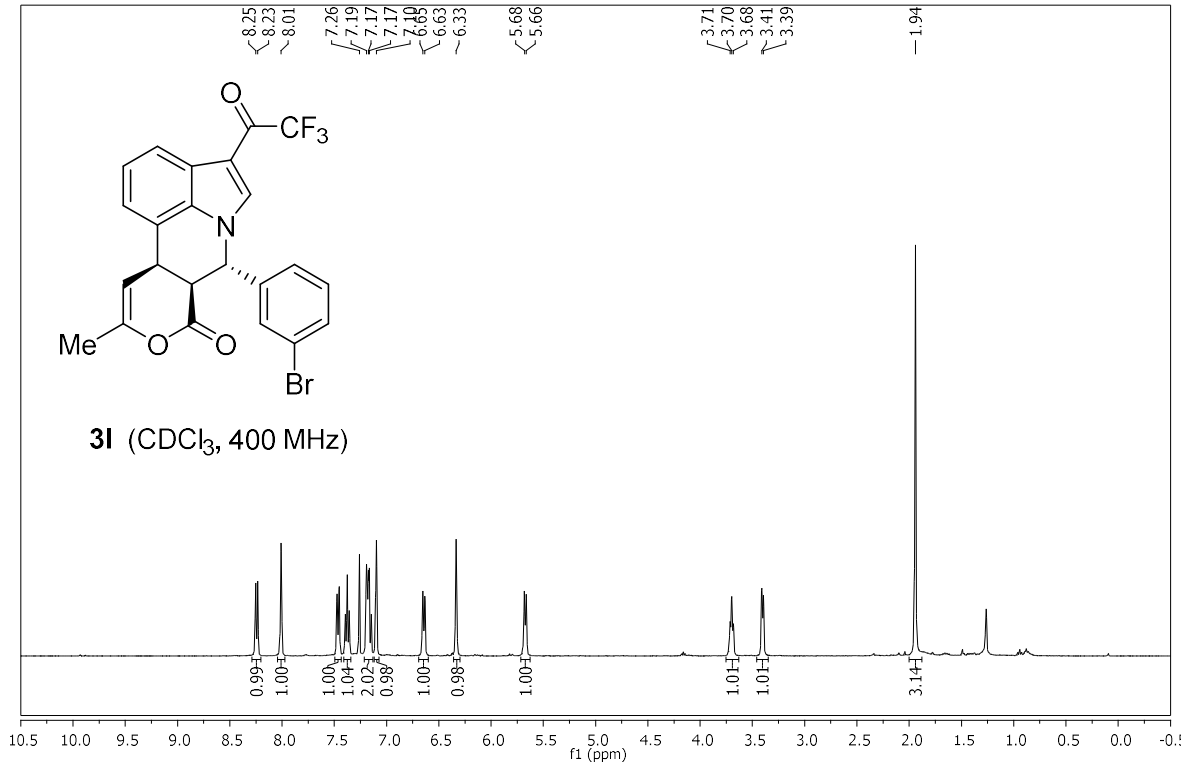
**(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3j)**



**Methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*, 8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (**3k**)**

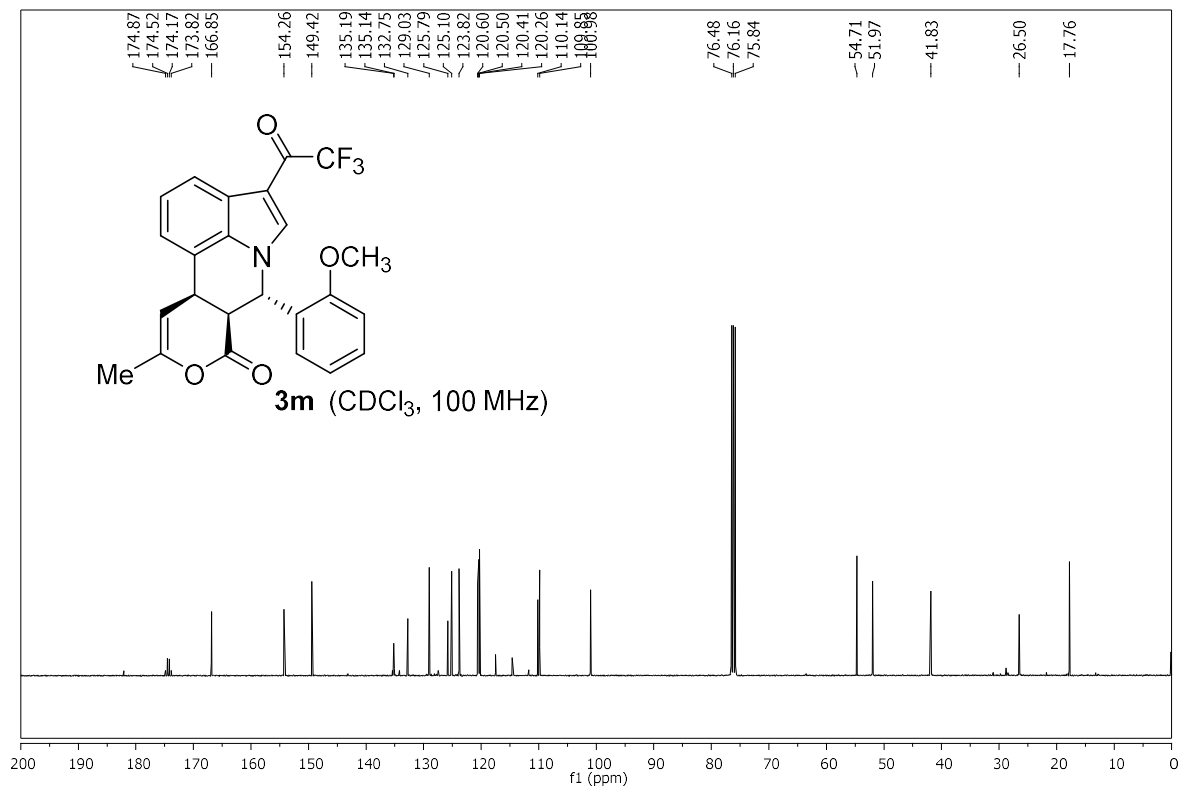
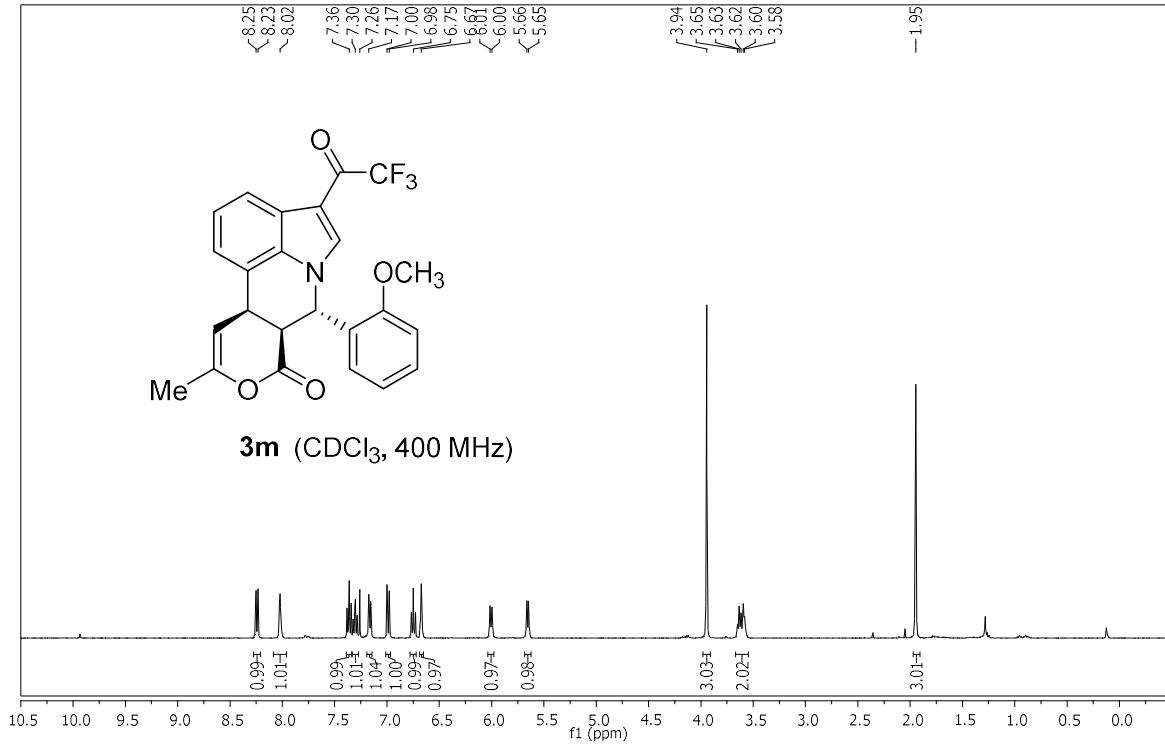


**(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3I)**

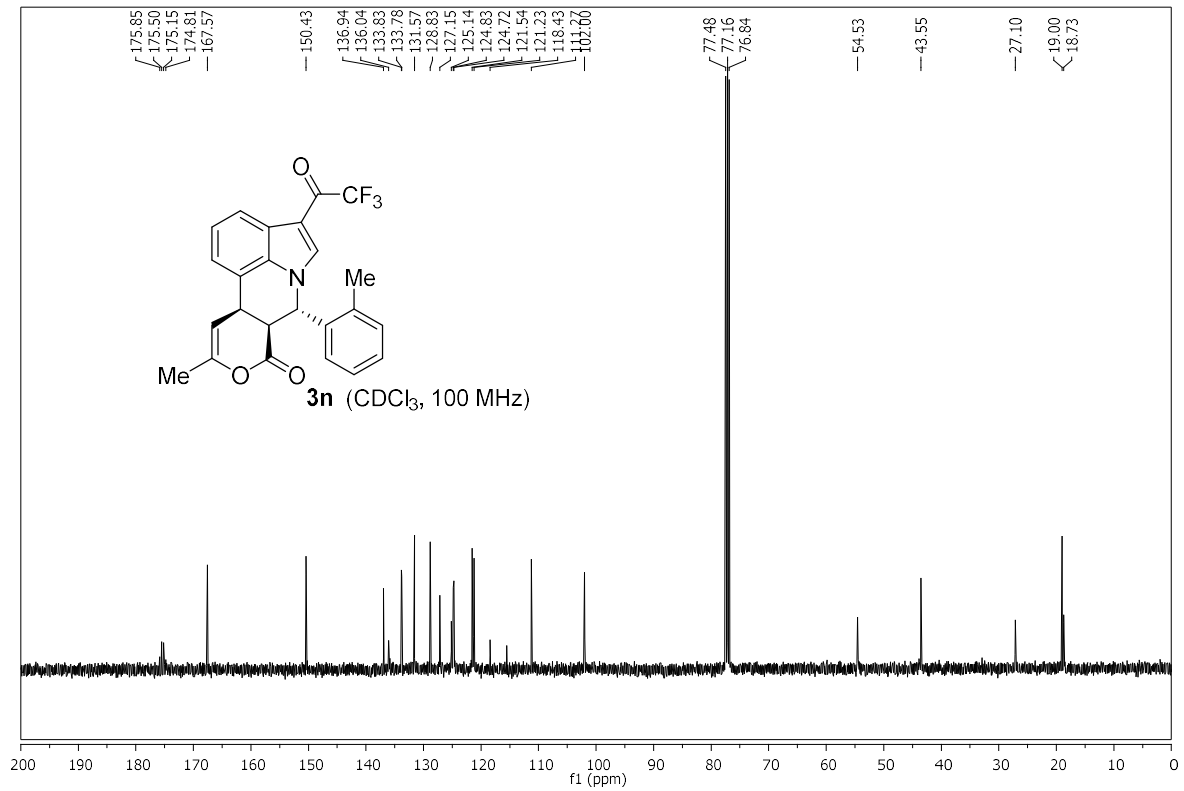
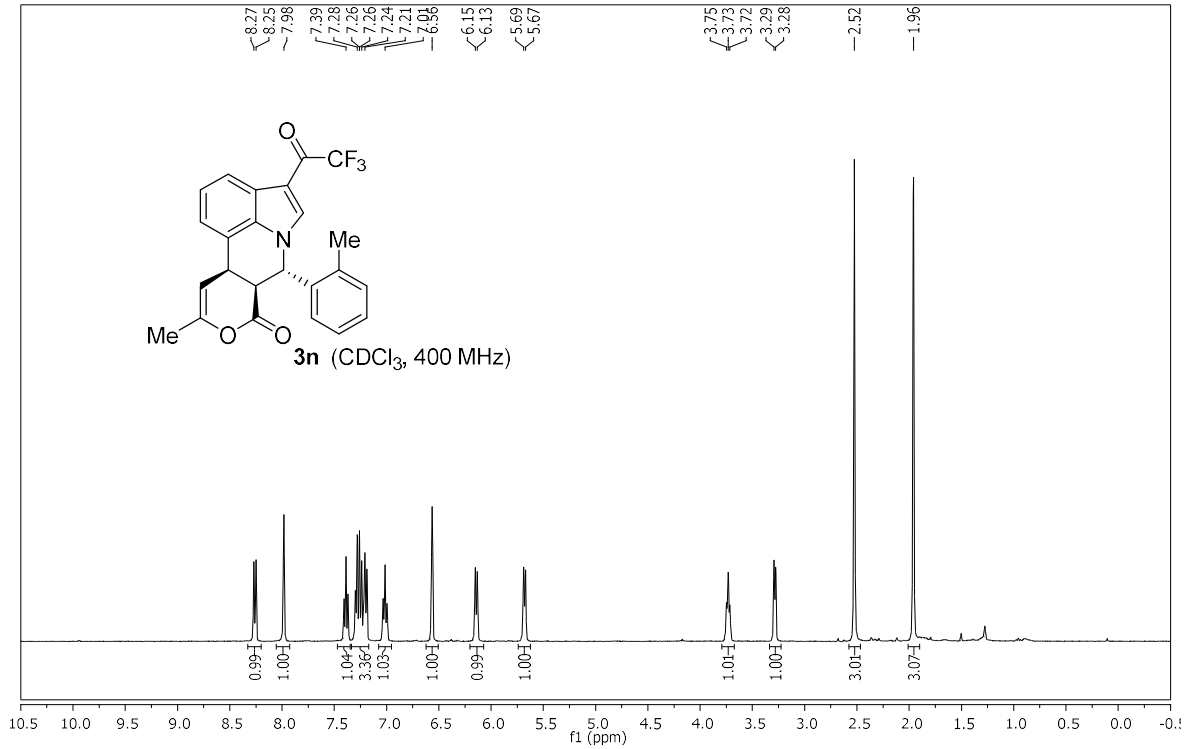




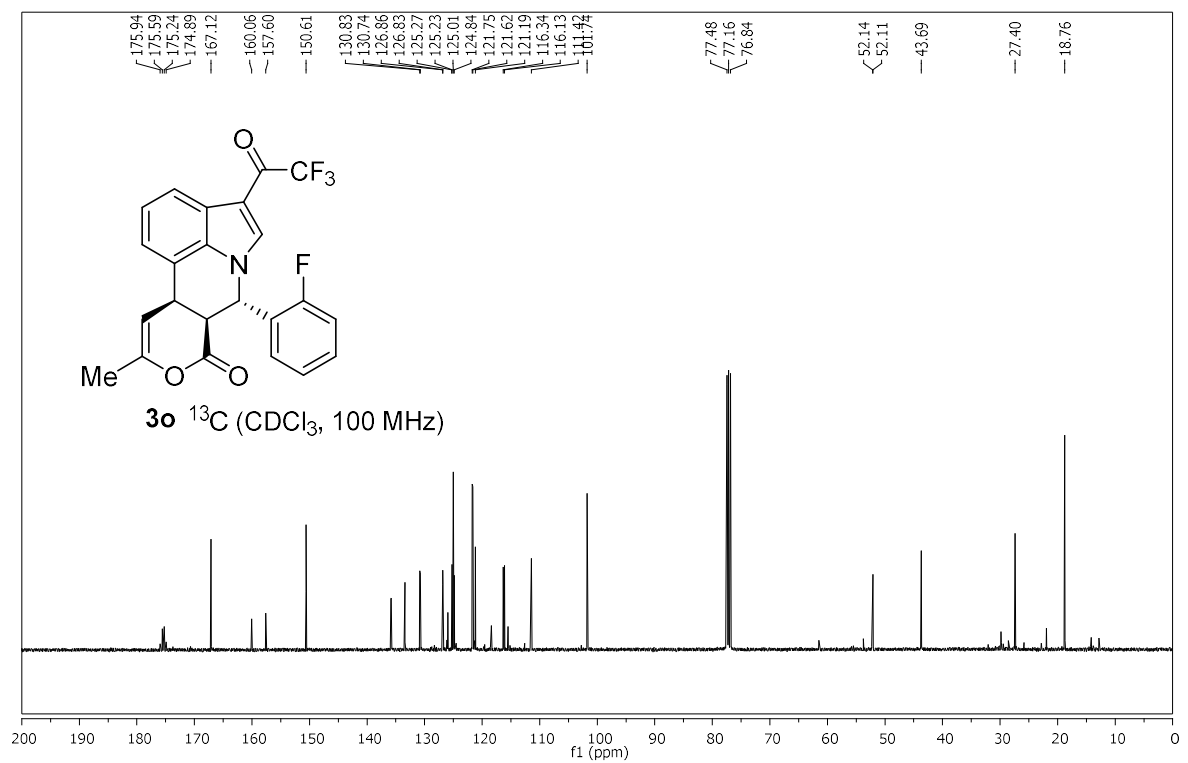
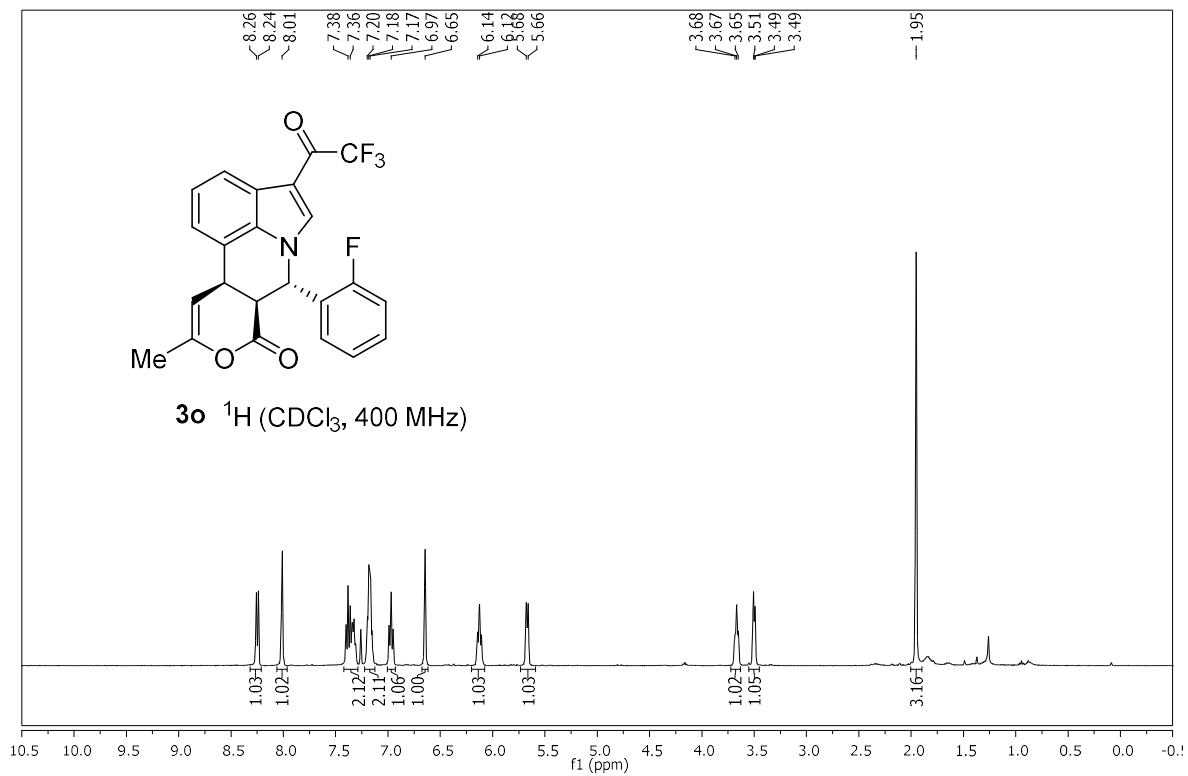
**(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*m*)**



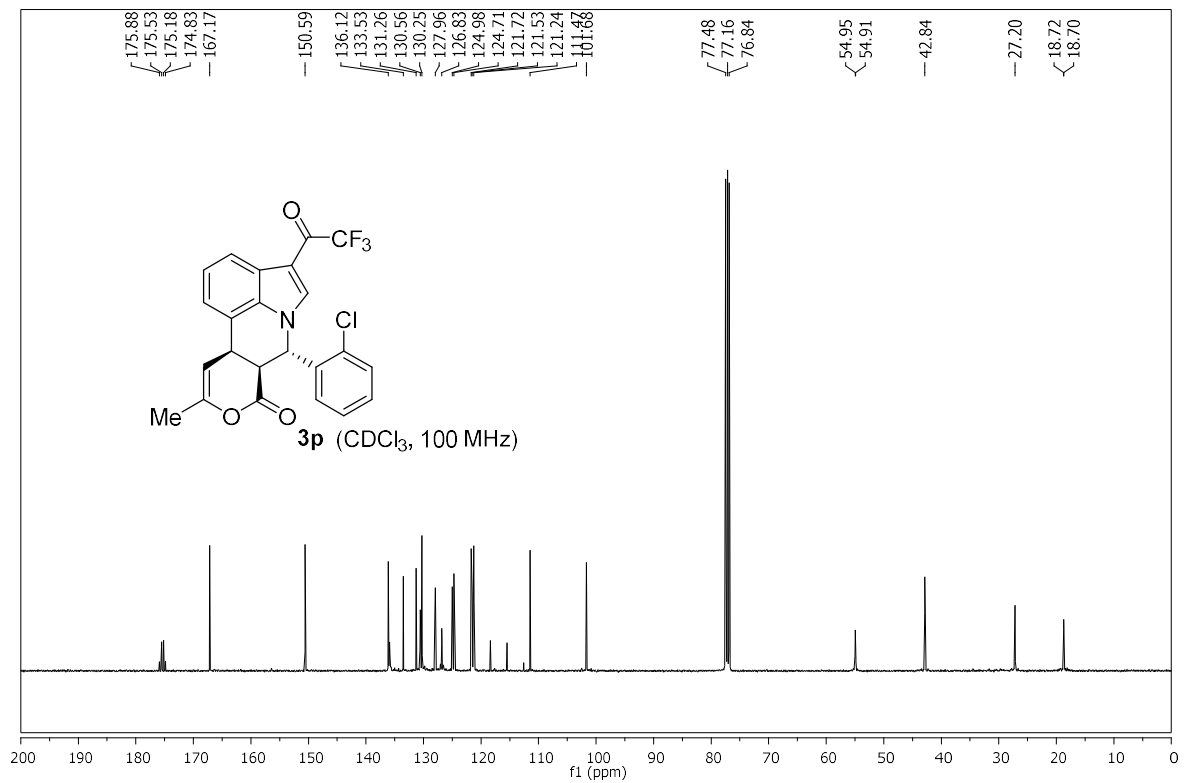
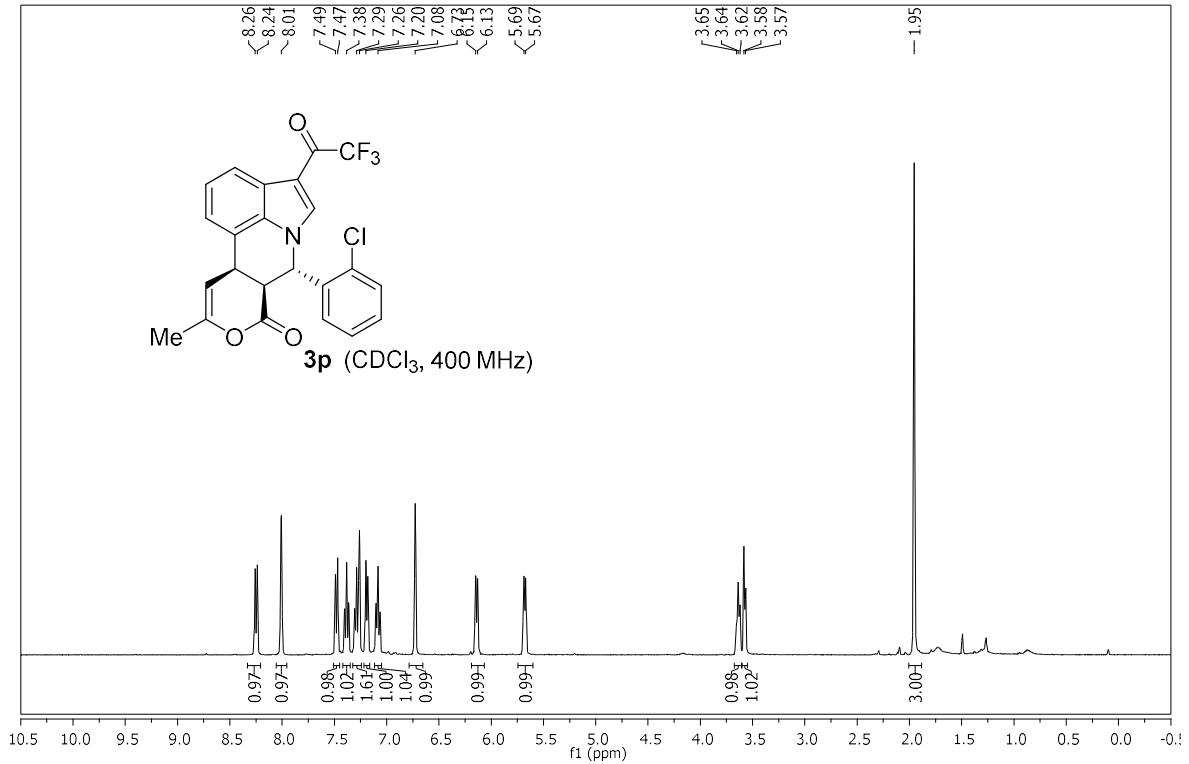
**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3n)**



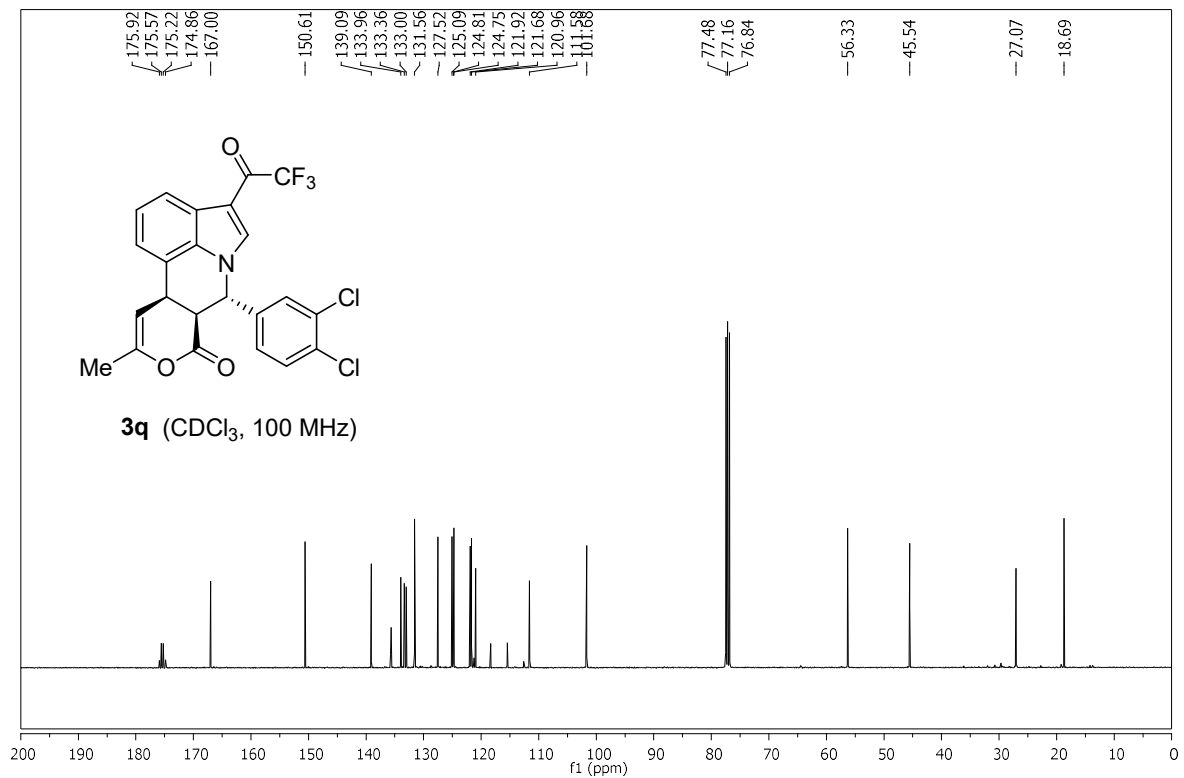
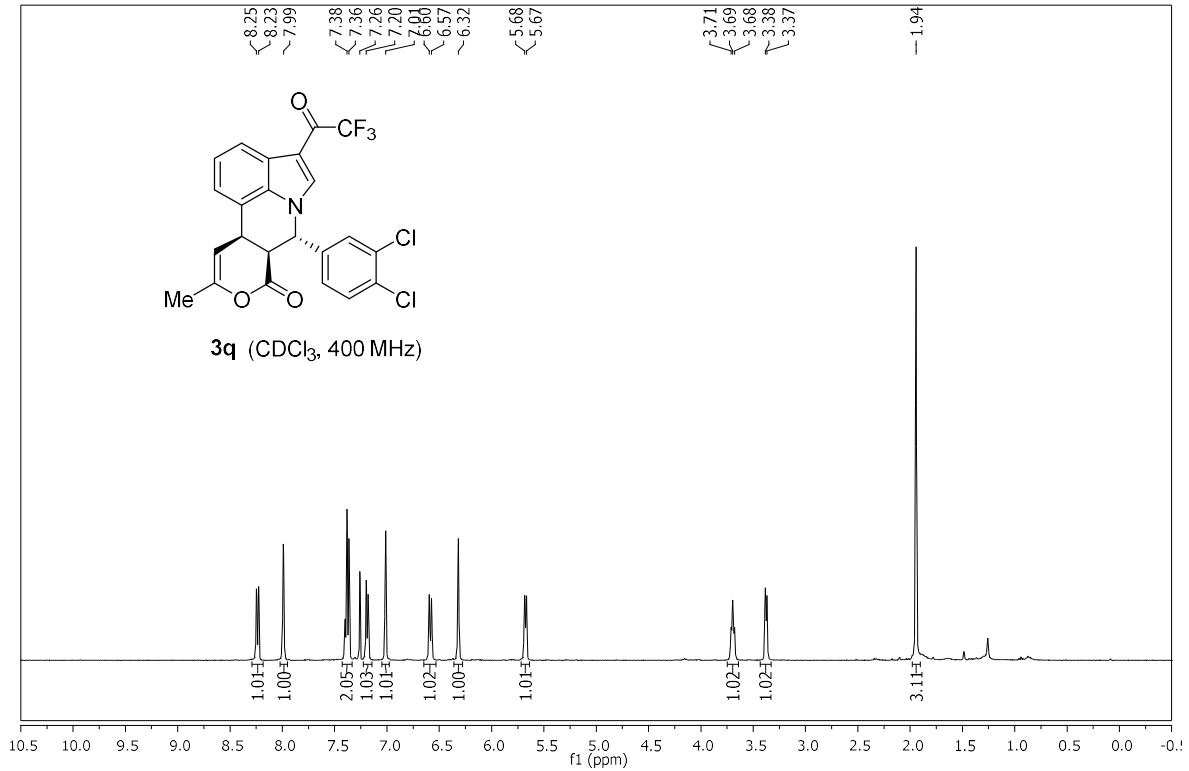
**(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)**



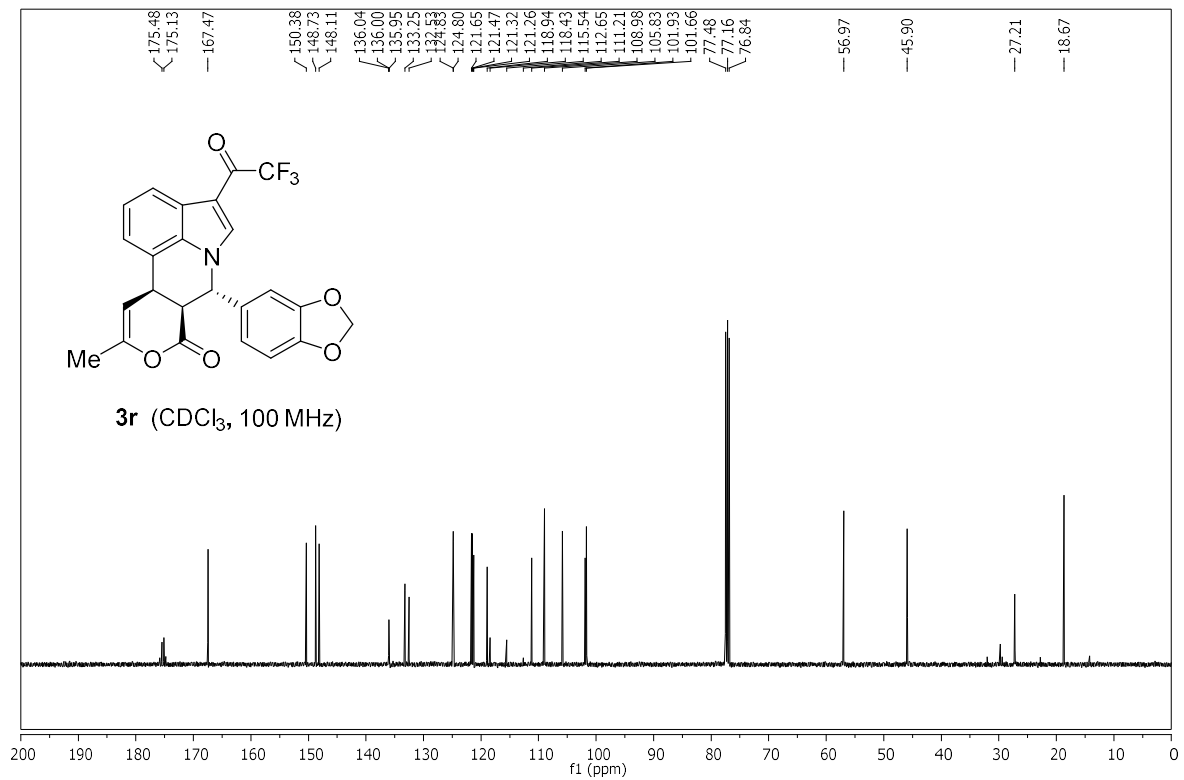
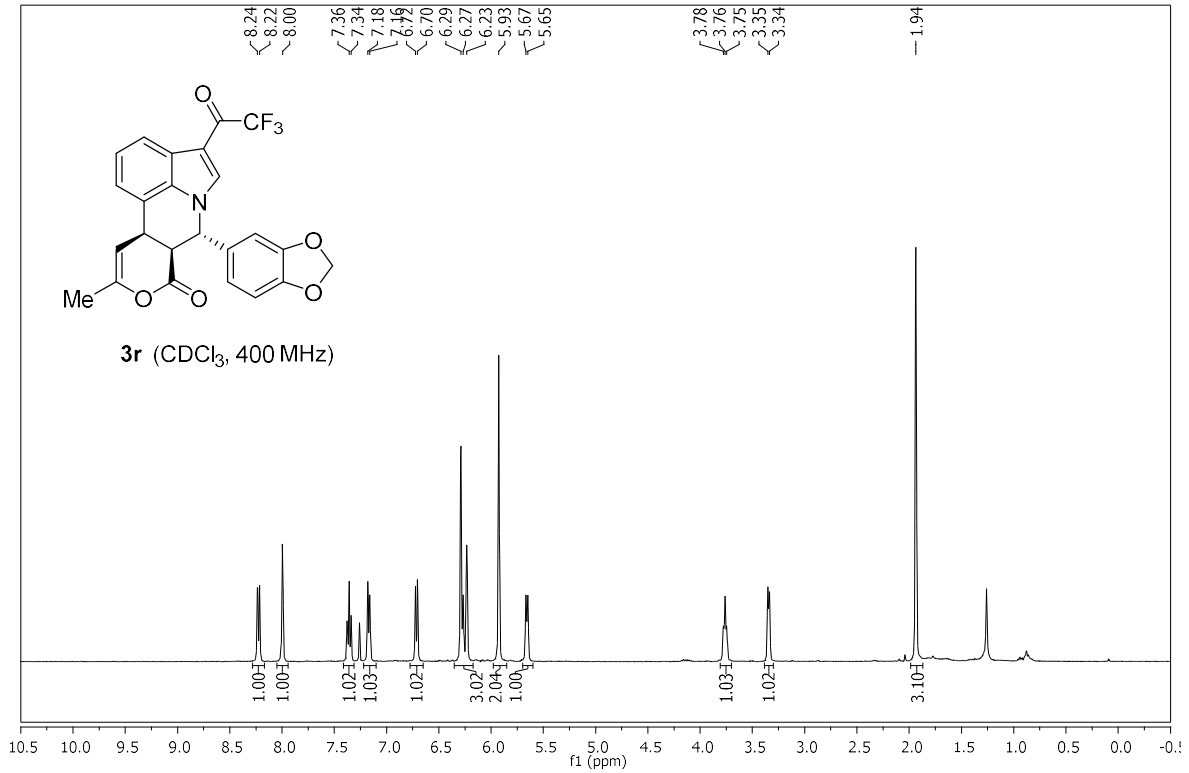
**(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3p)**



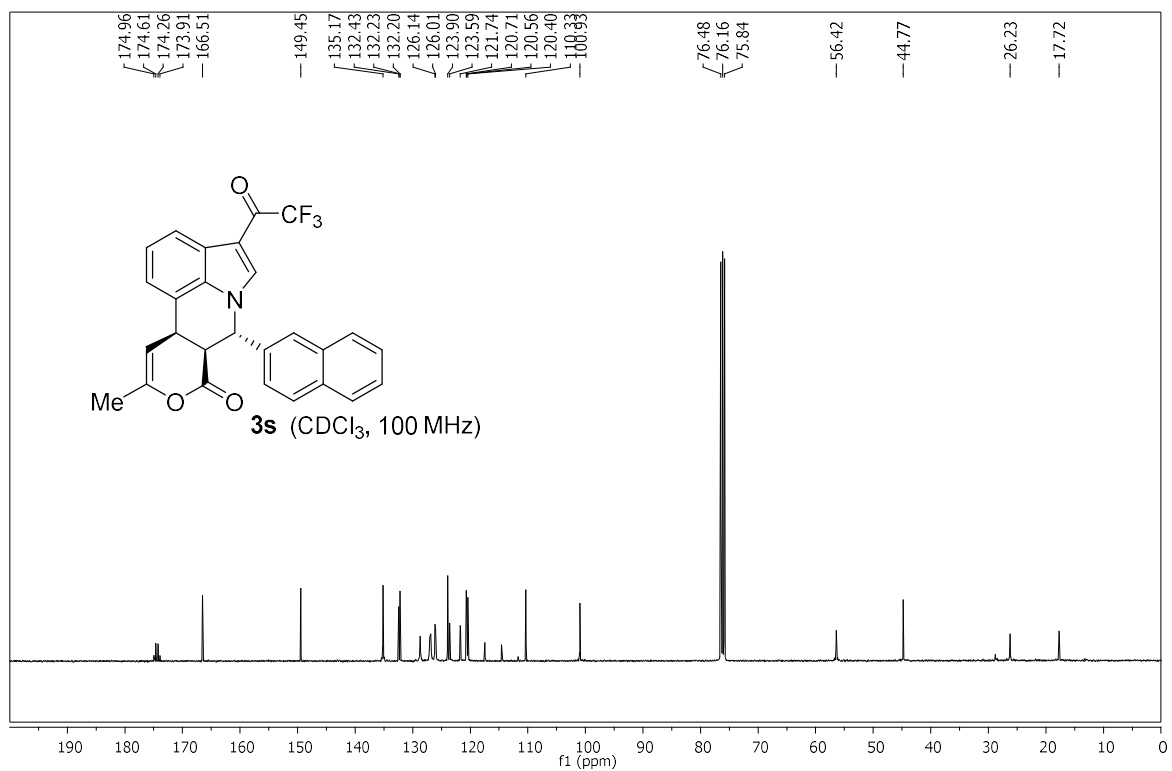
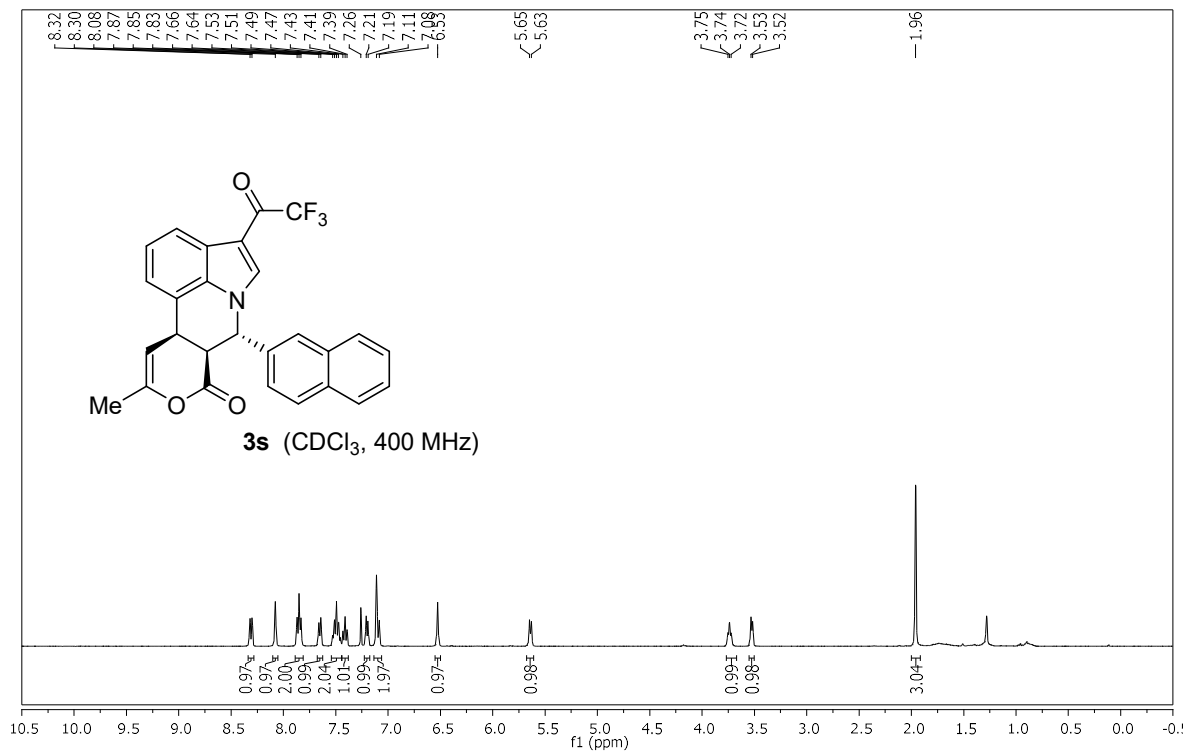
**(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3q)**



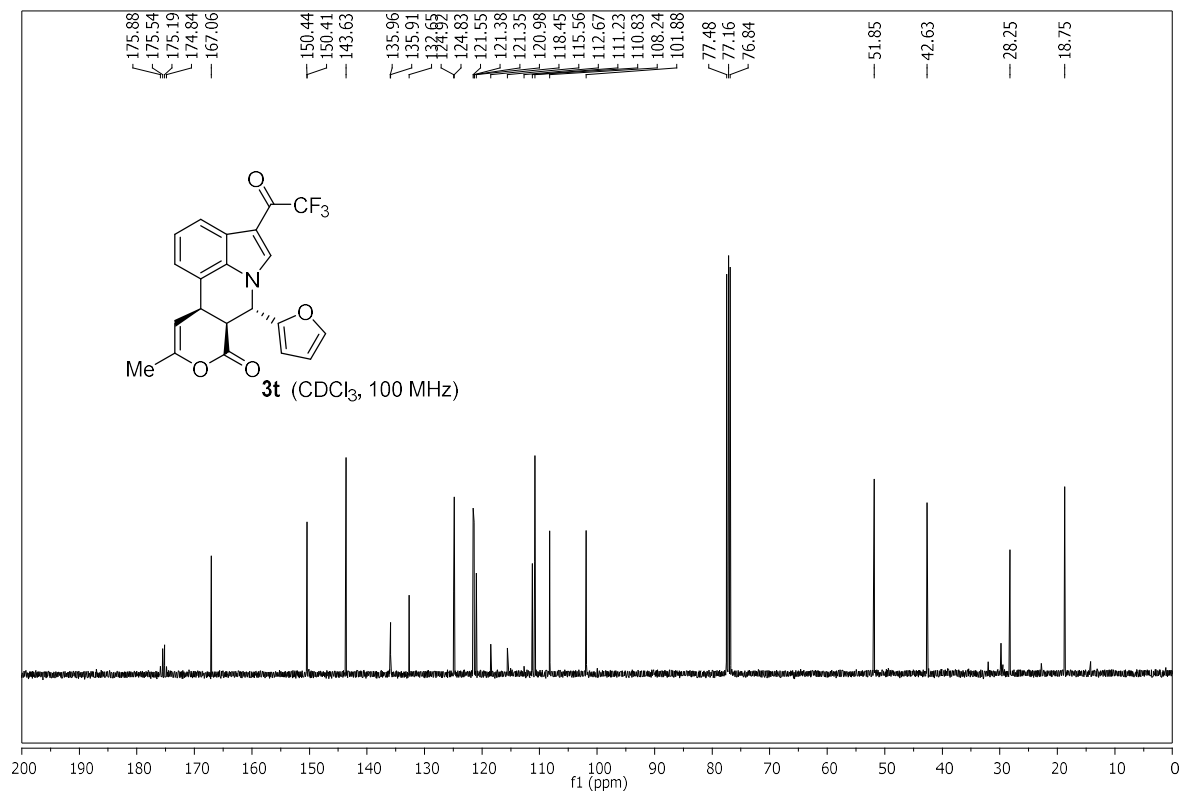
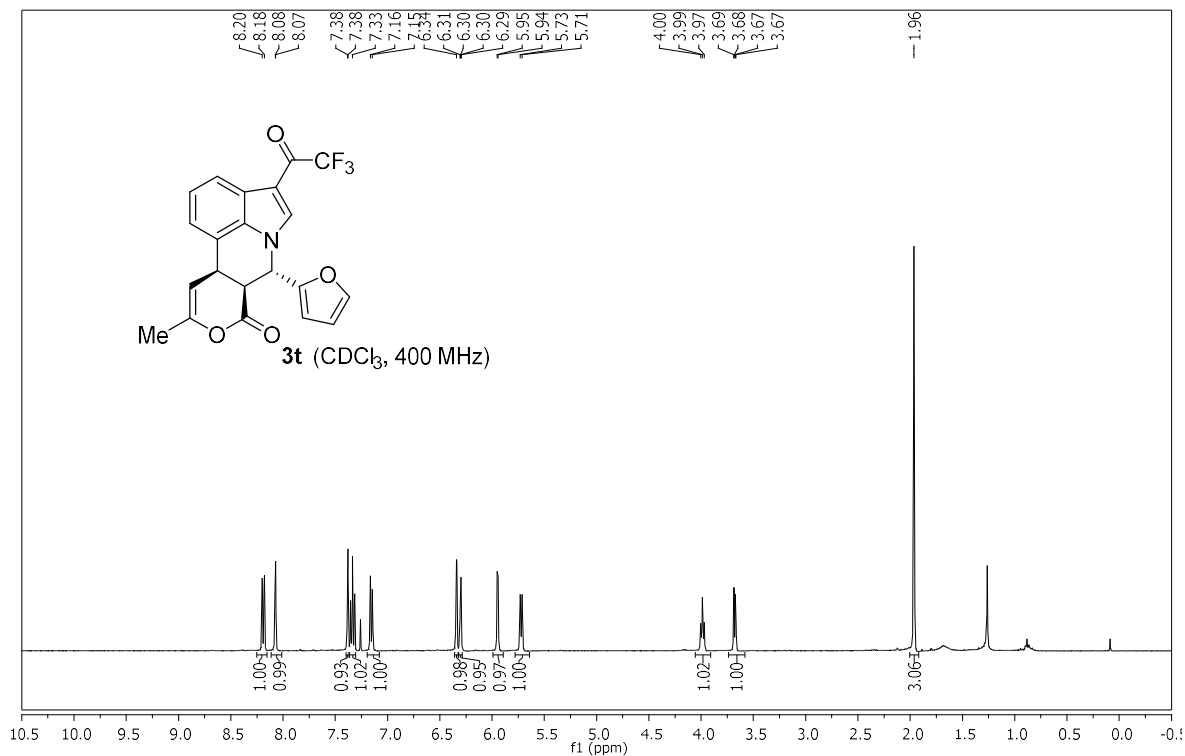
**(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3r)**



**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*s*)**

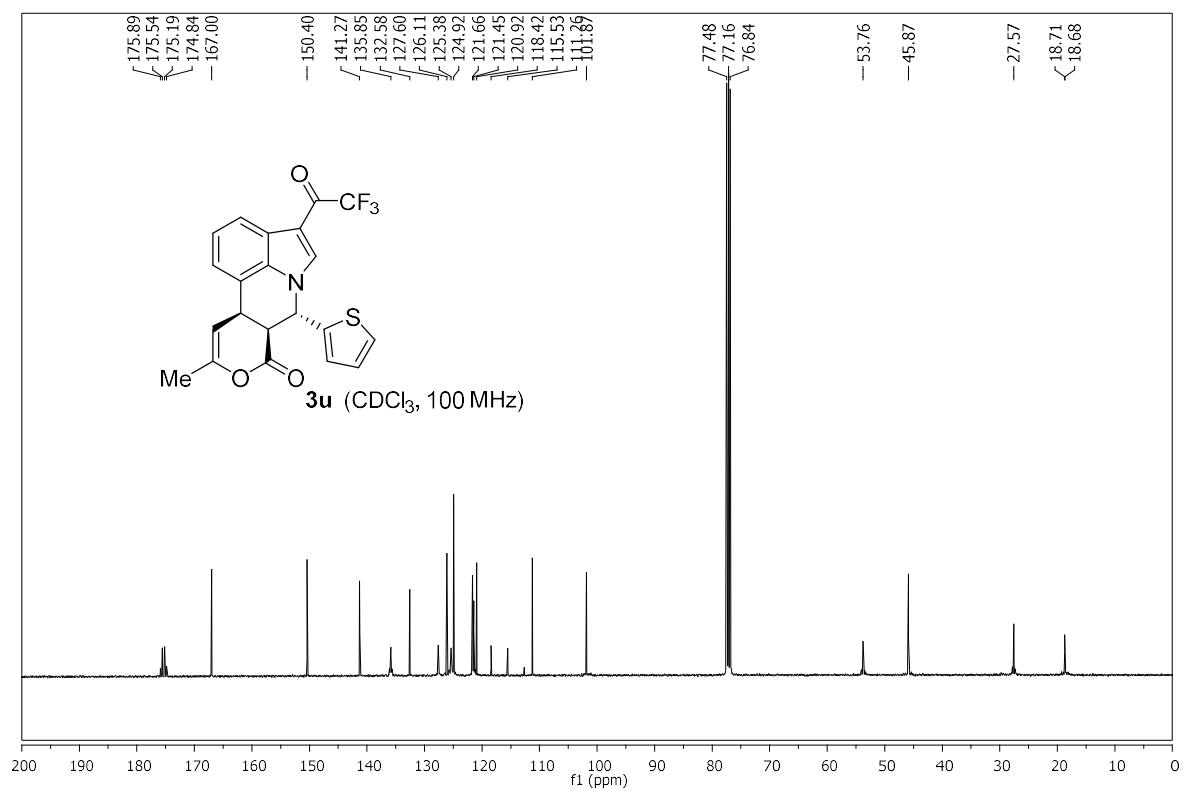
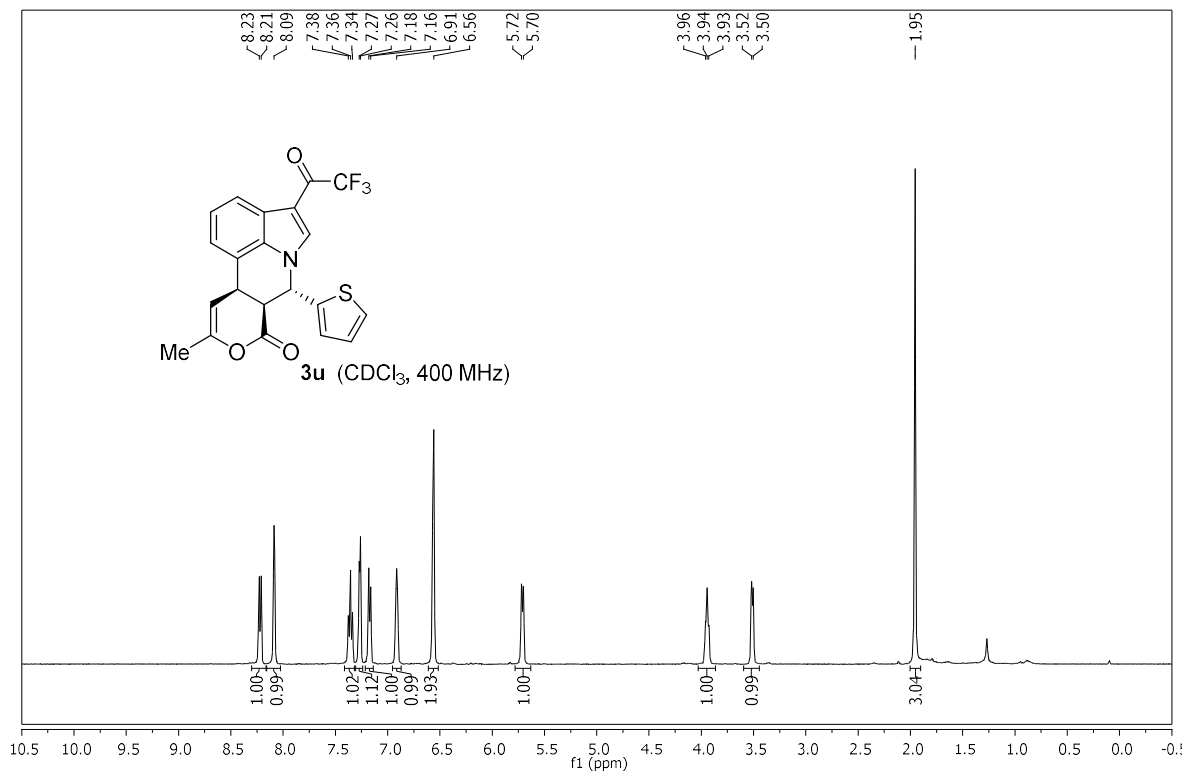


**(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3t)**

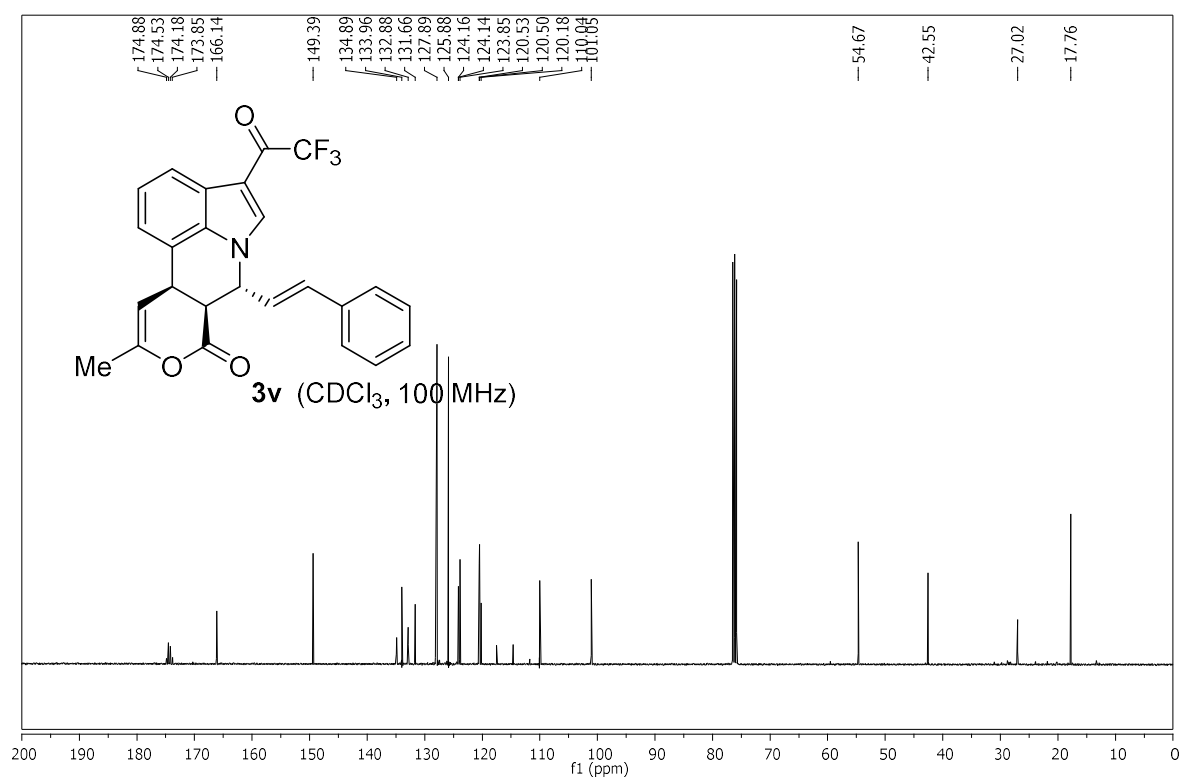
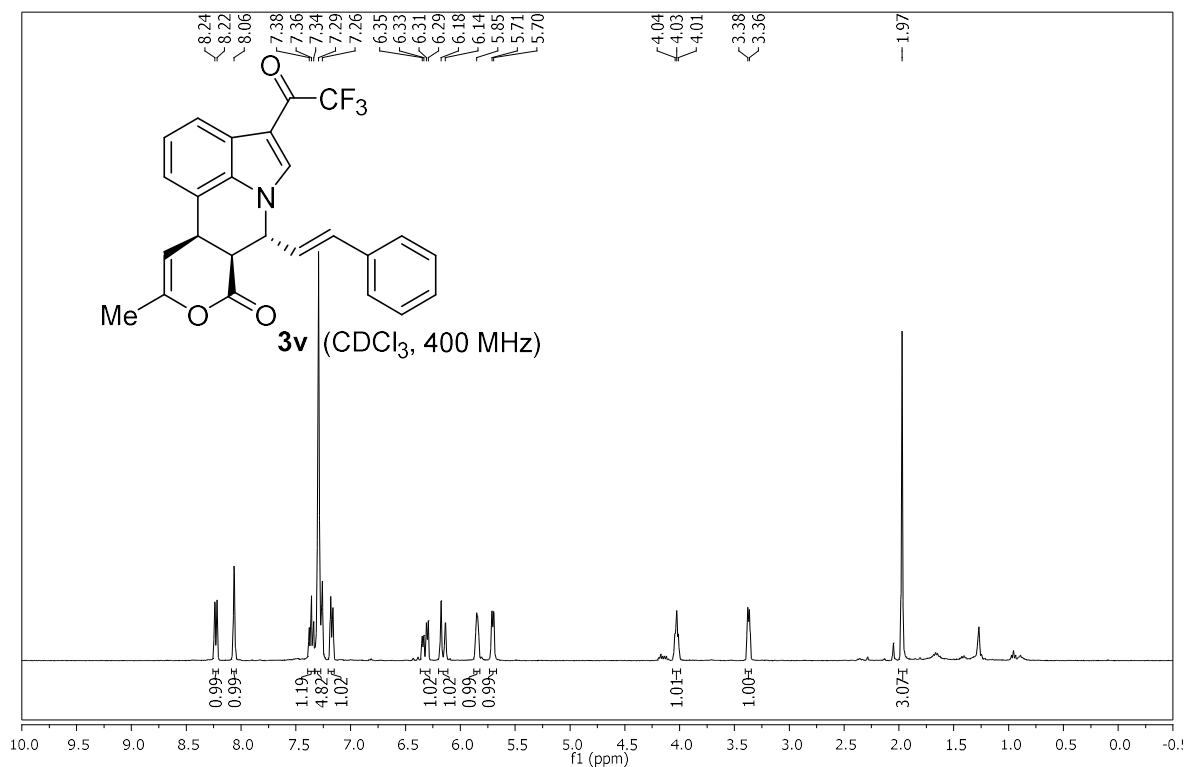




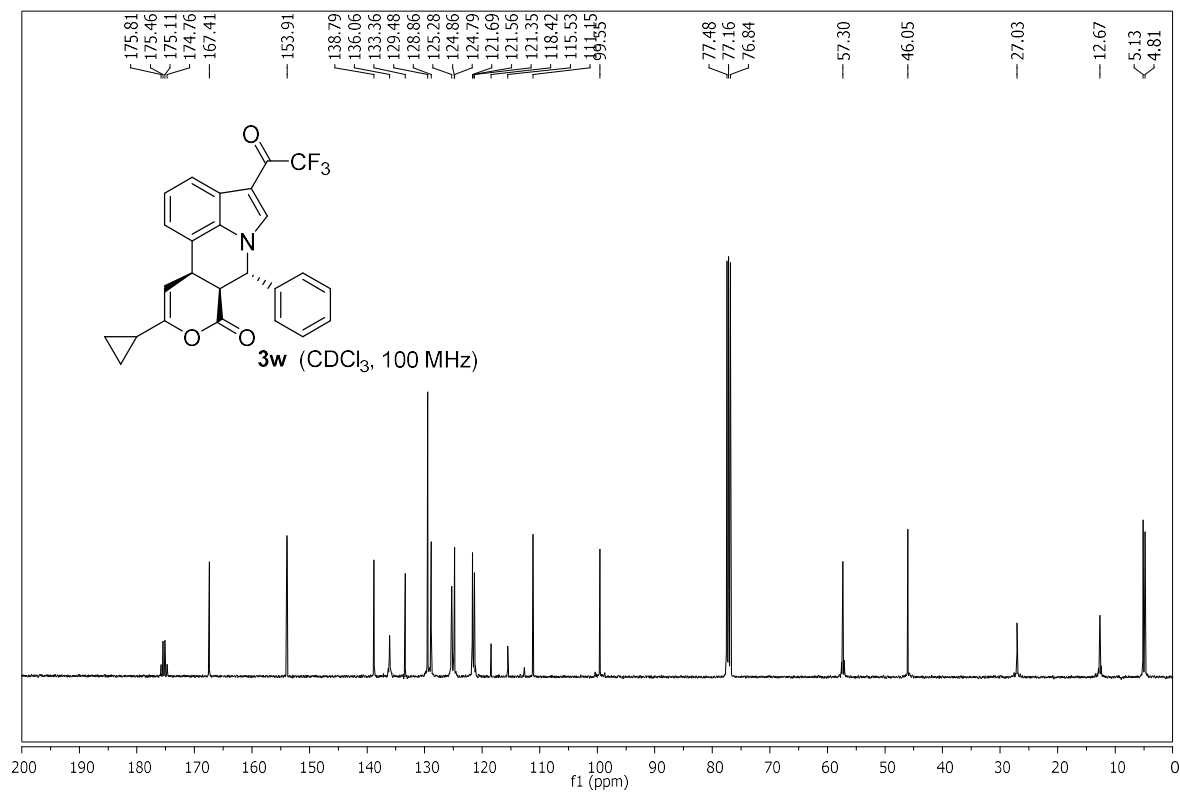
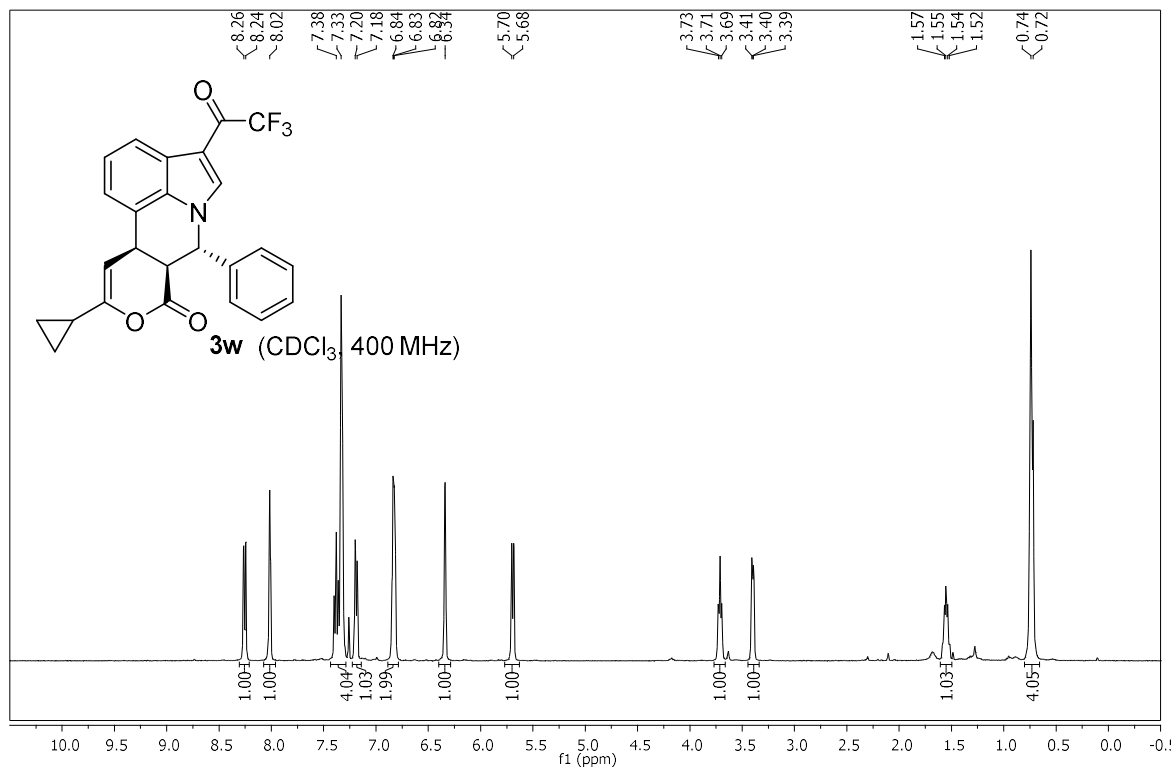
**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3u)**



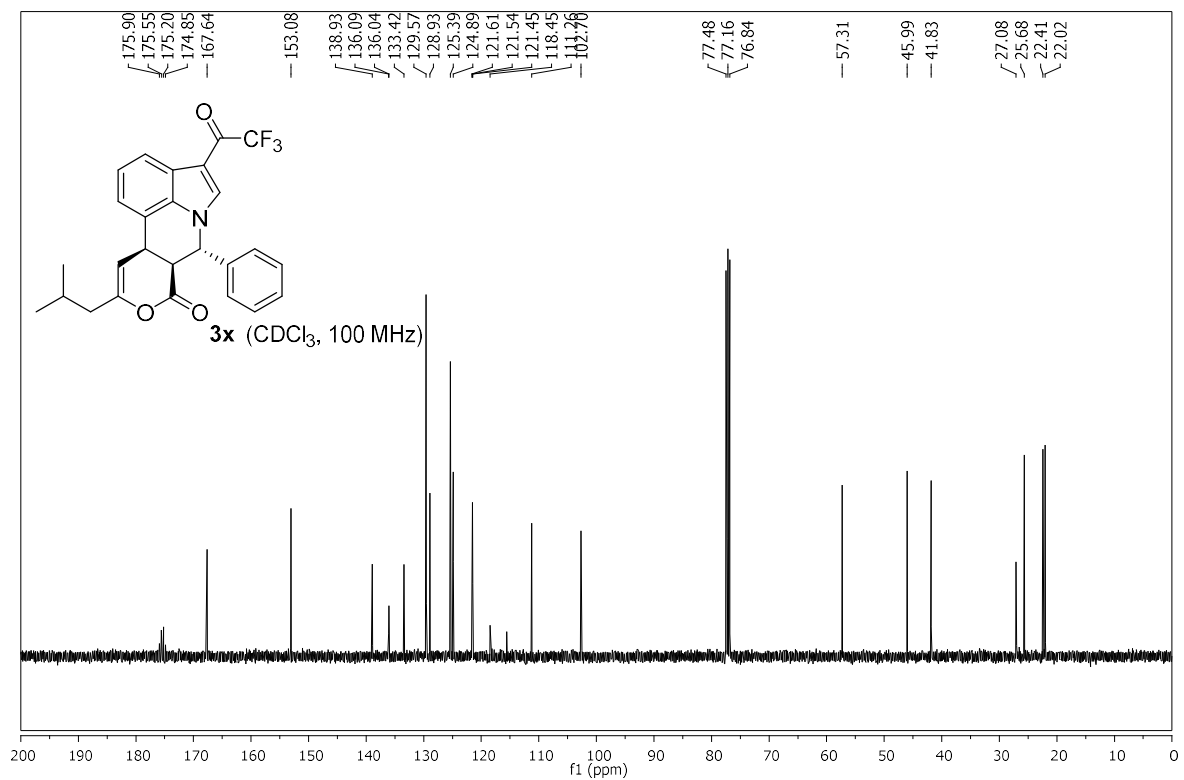
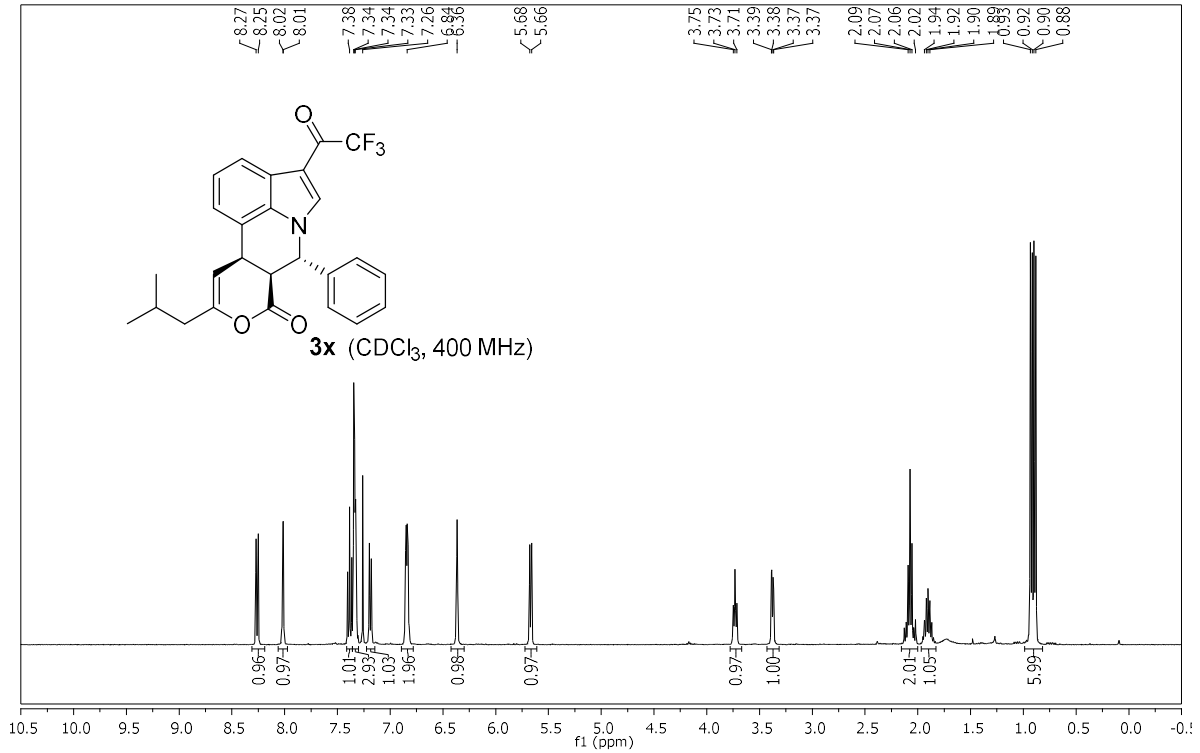
**(7R,7aS,11aR)-10-Methyl-7-((E)-styryl)-4-(2,2,2-trifluoroacetyl)-7a,11a-dihydro-7H,8H-pyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8-one (3v)**



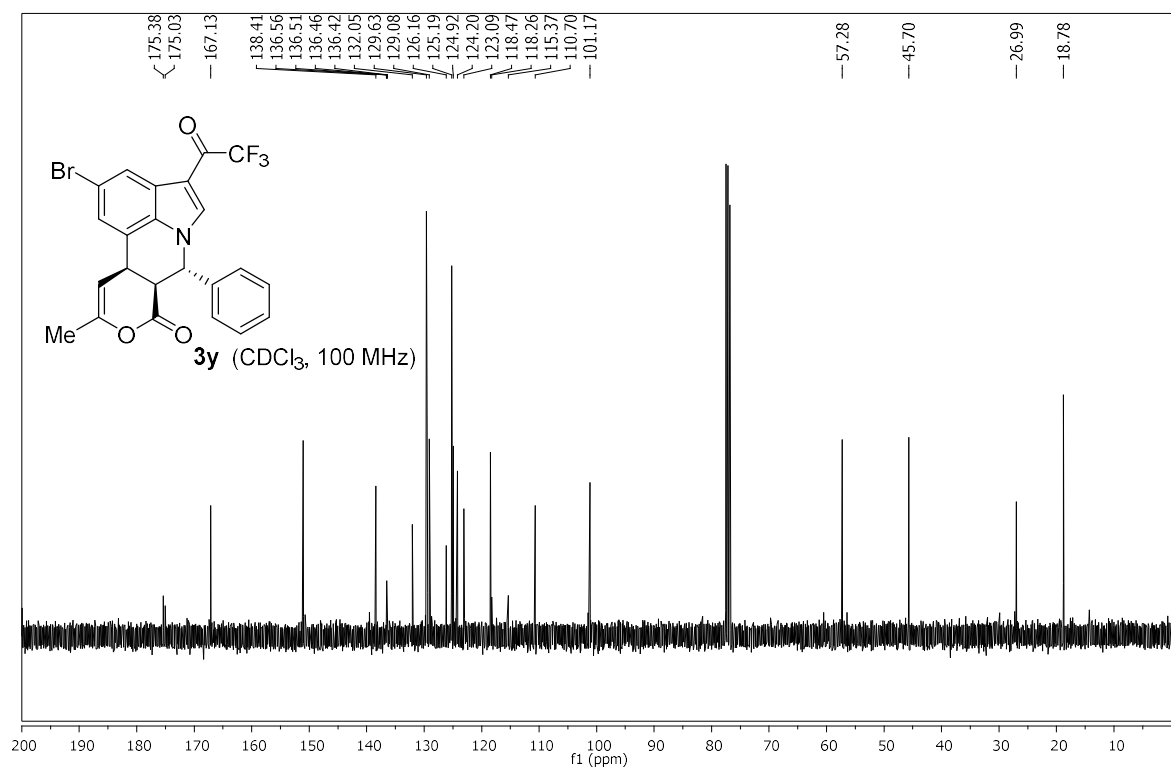
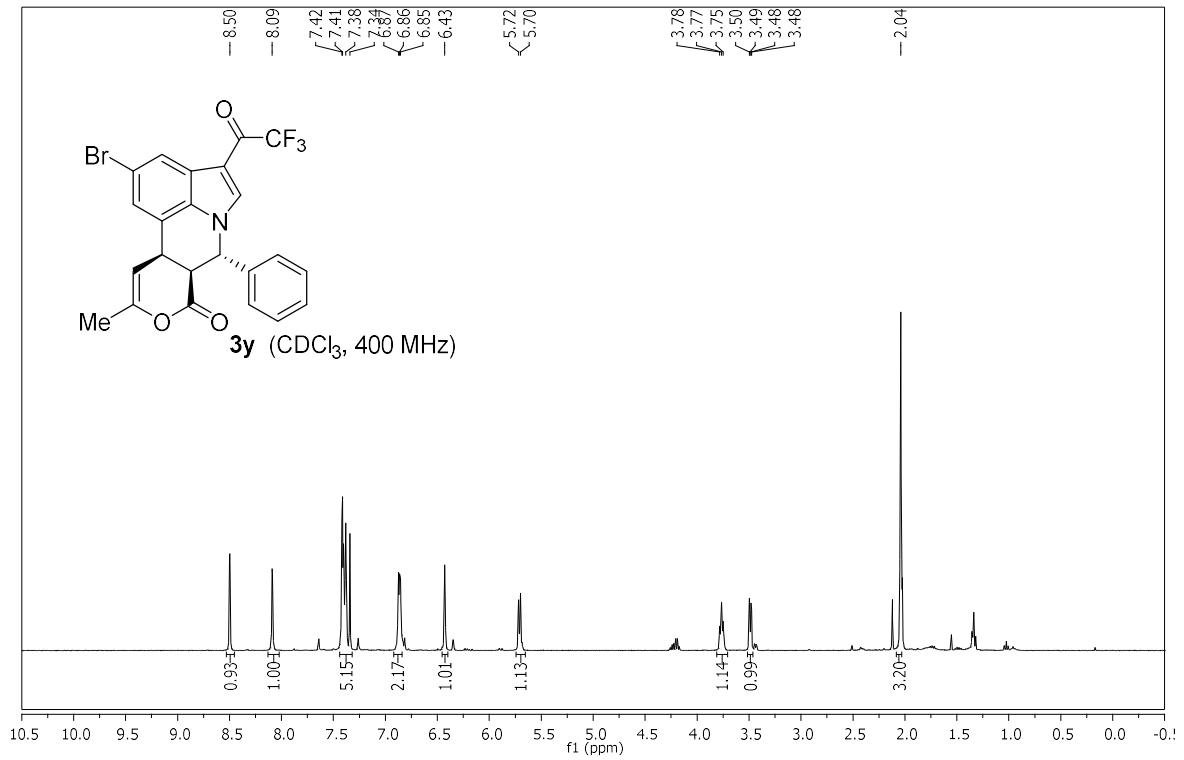
**(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3w)**



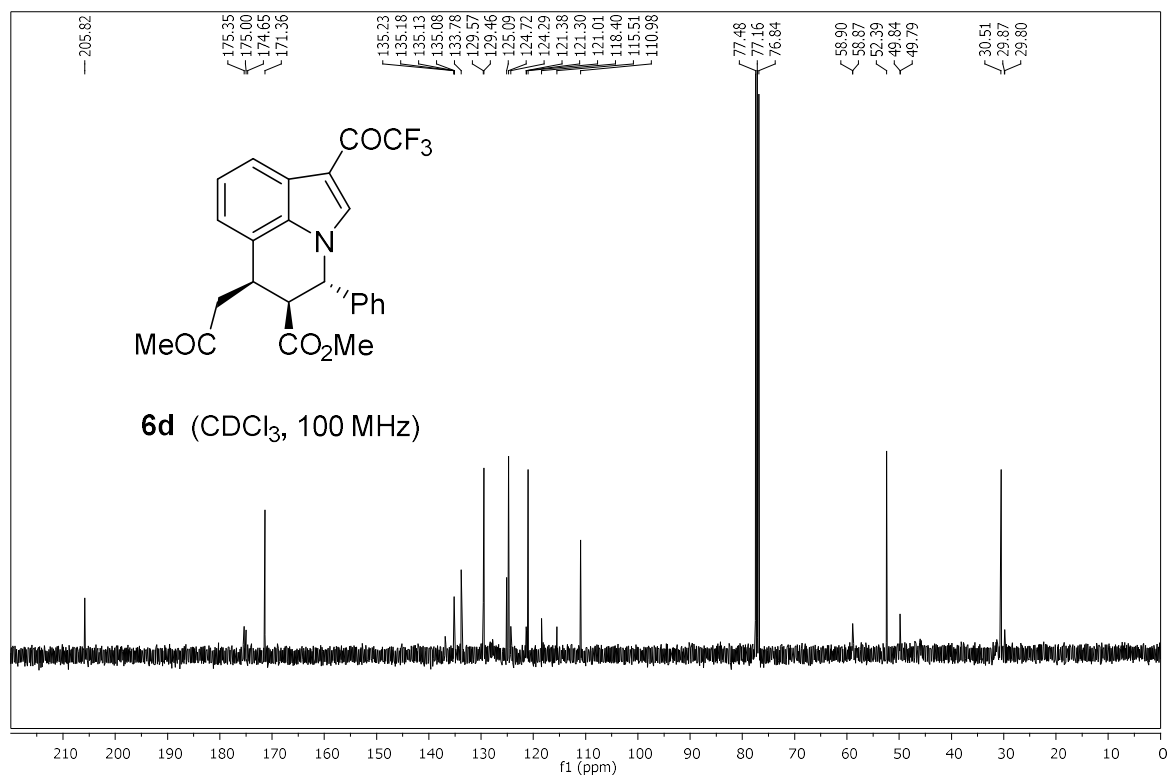
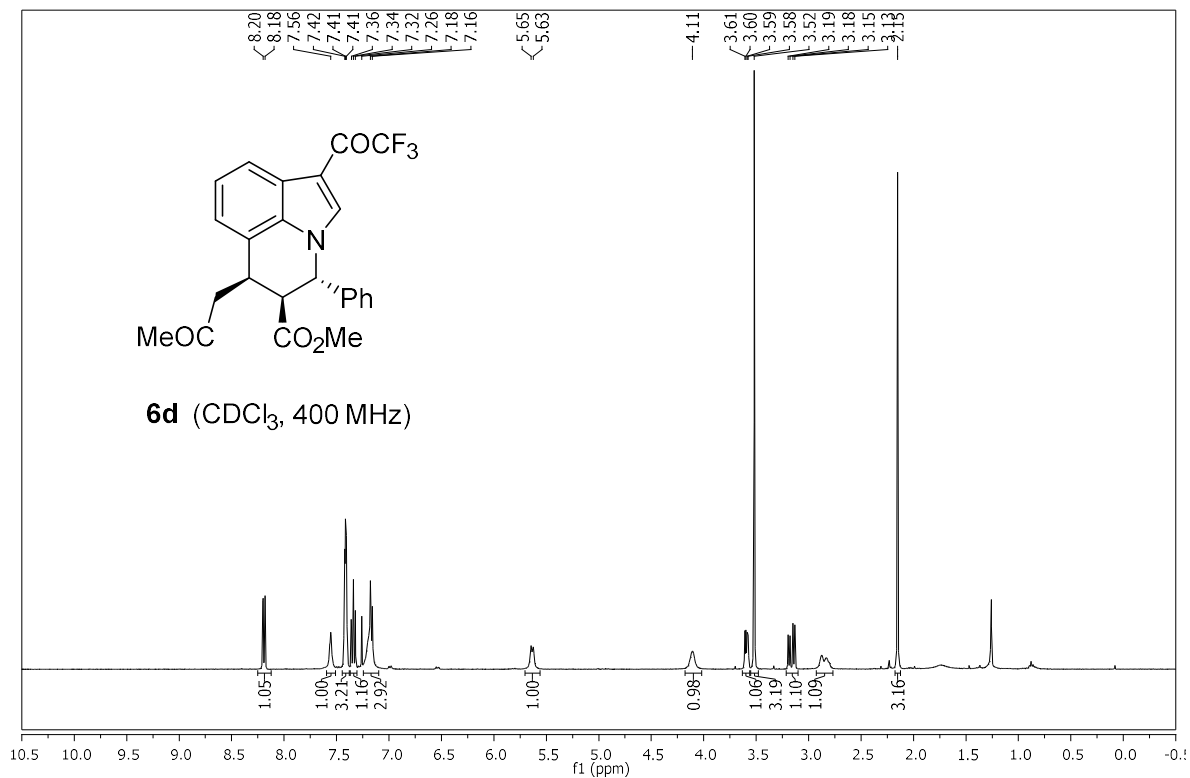
**(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*x*)**



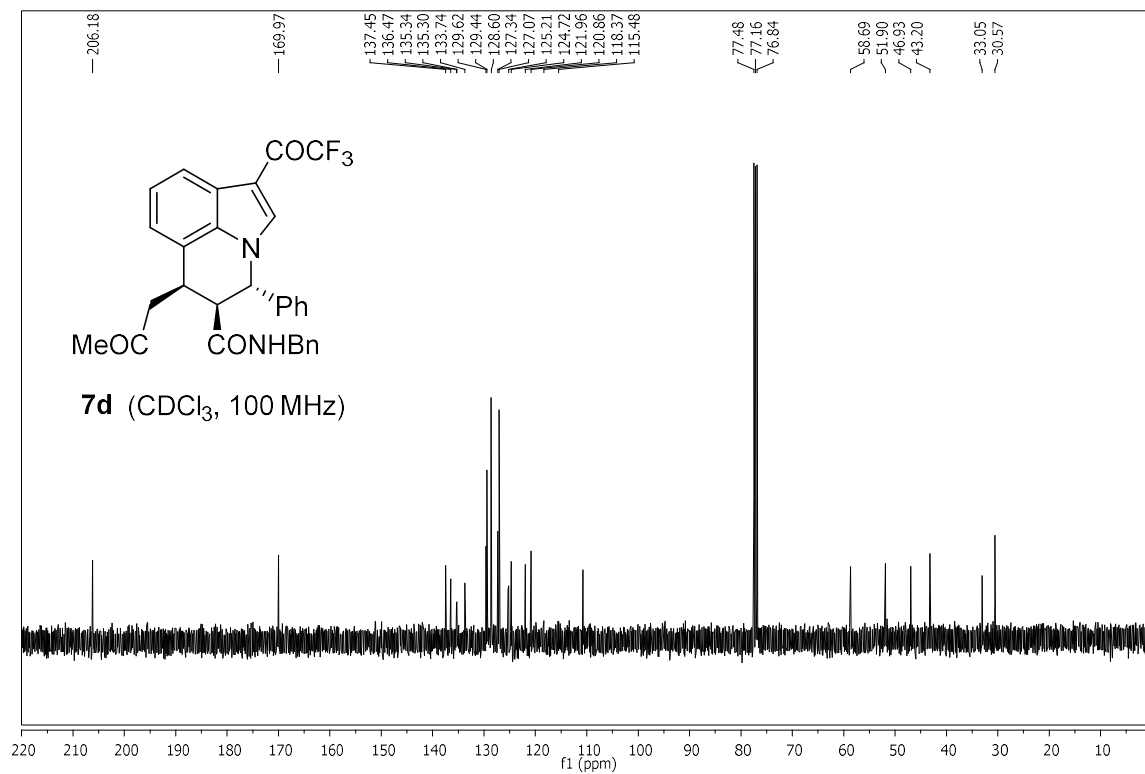
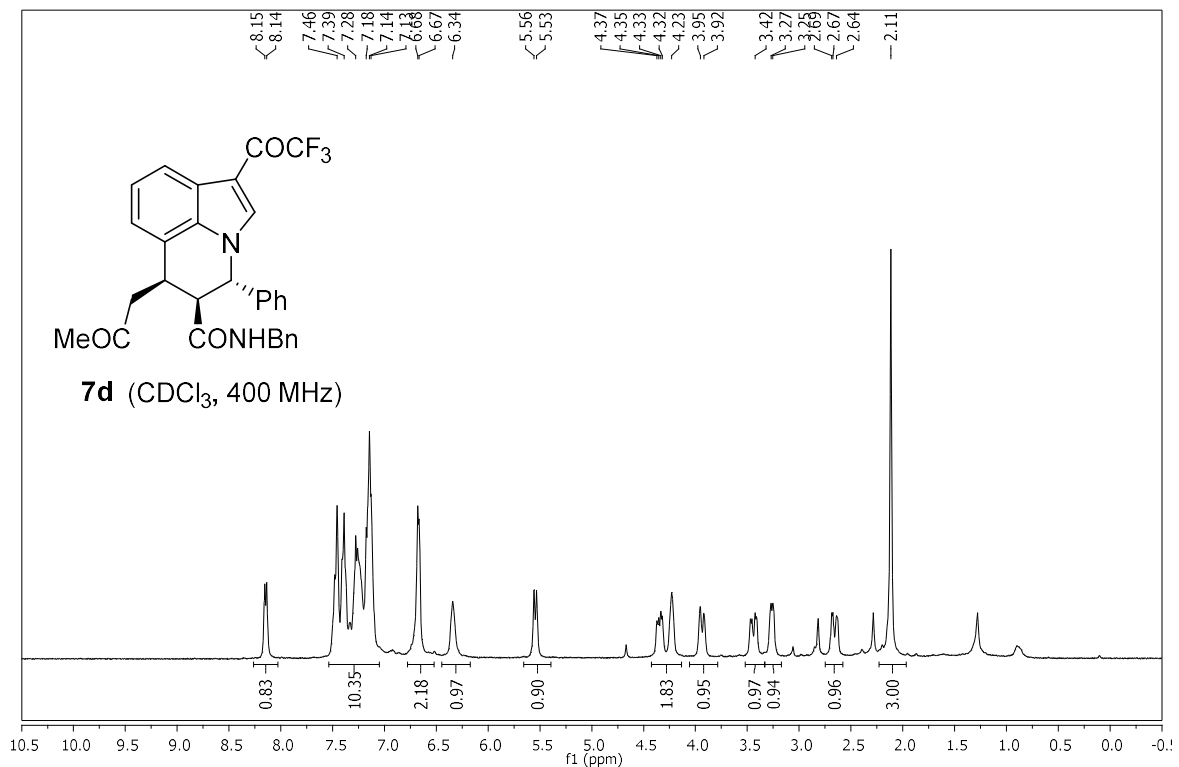
**(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)**



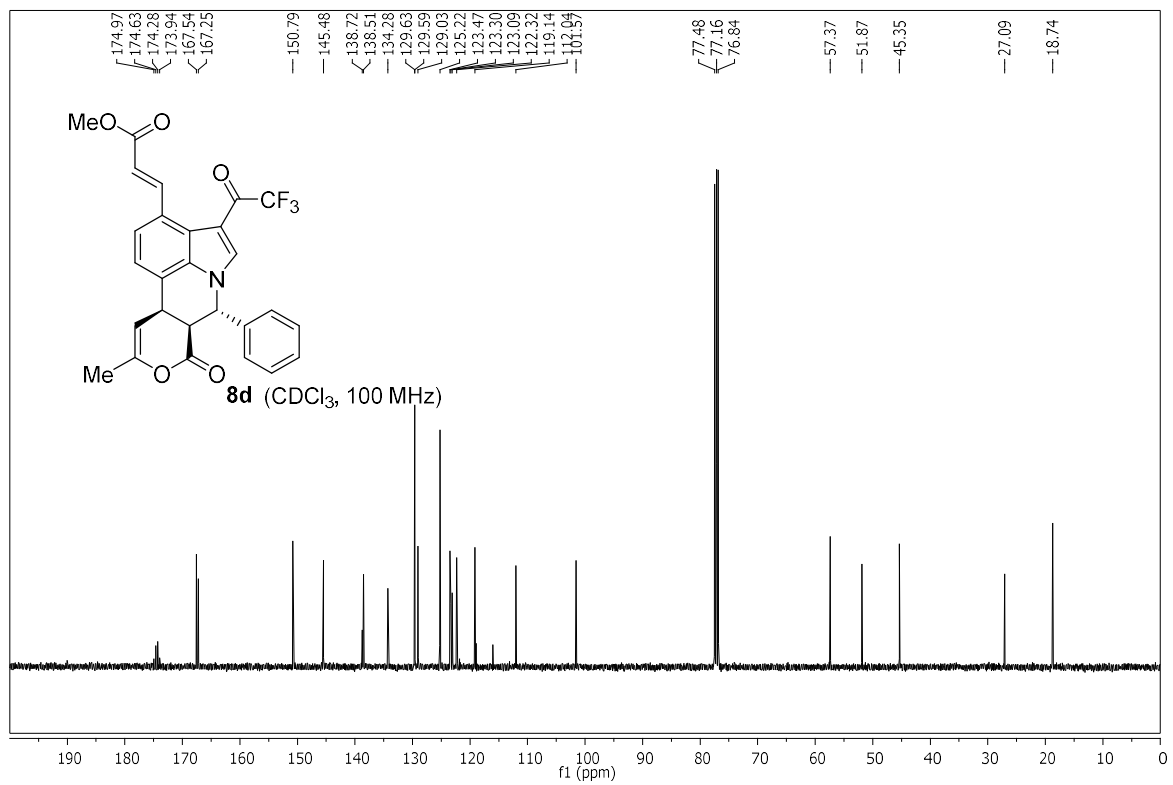
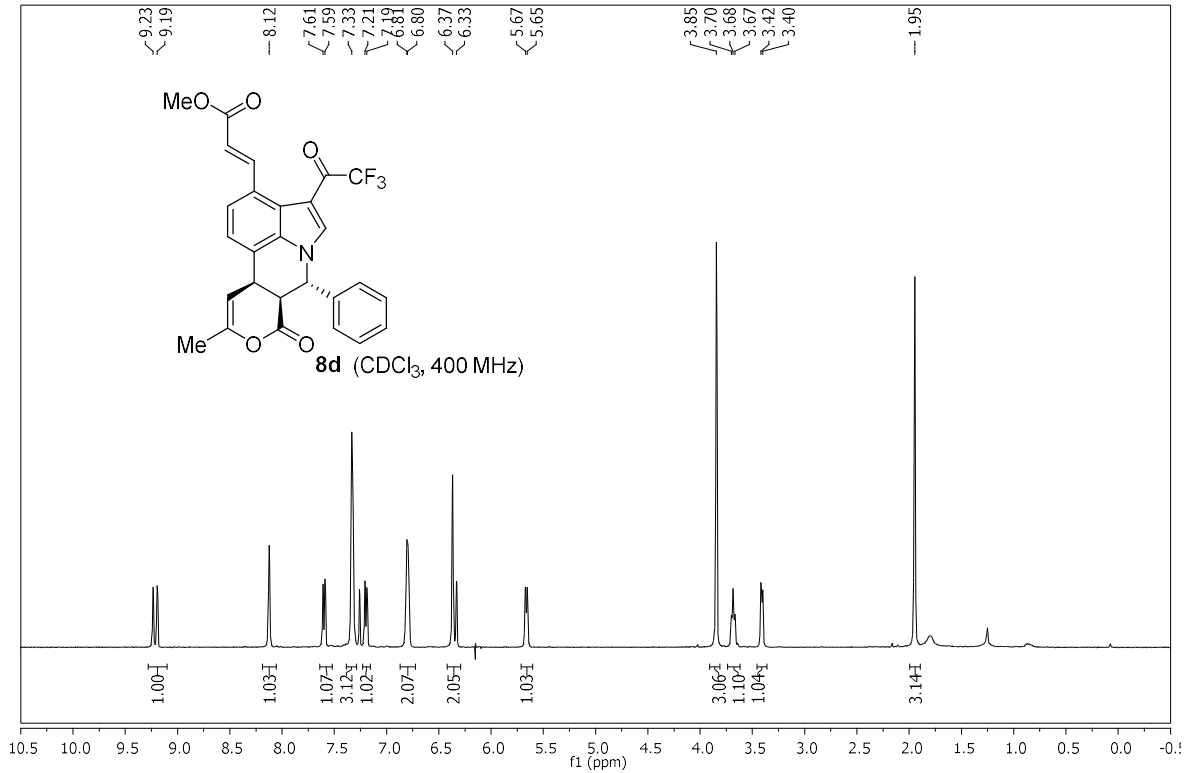
**(4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxylate (**6d**)**



**(4*S*,5*S*,6*R*)-N-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxamide (7d)**

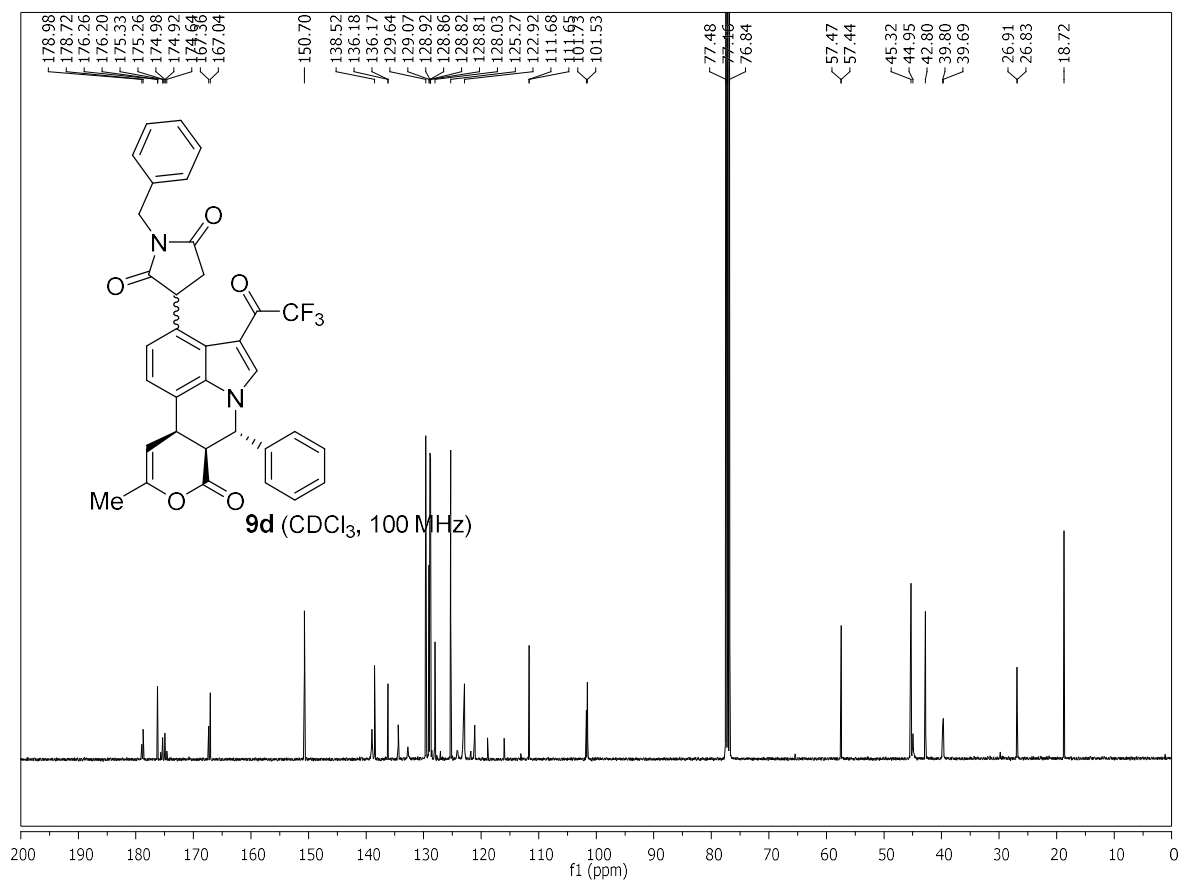
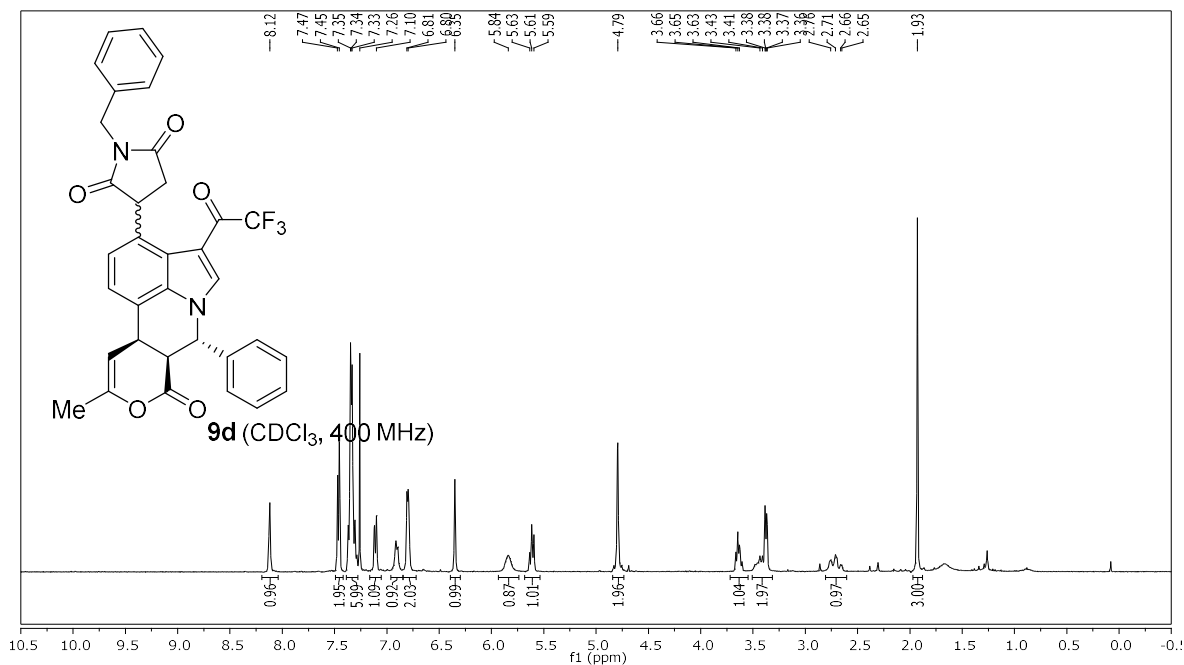


**(E)-Methyl 3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)acrylate (8d)**



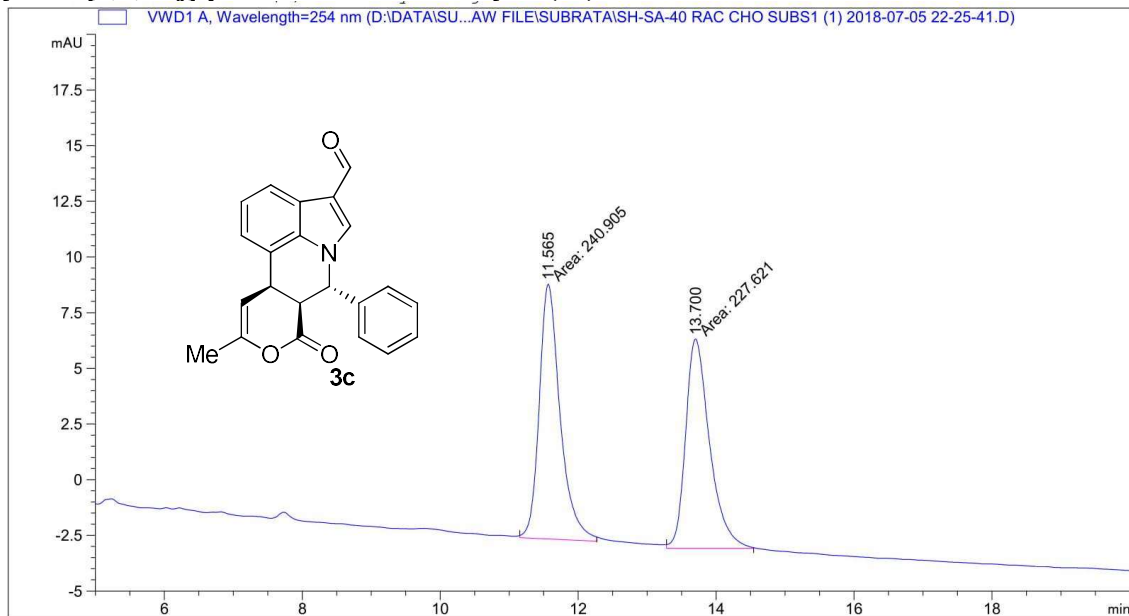


**1-Benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione (9d)**

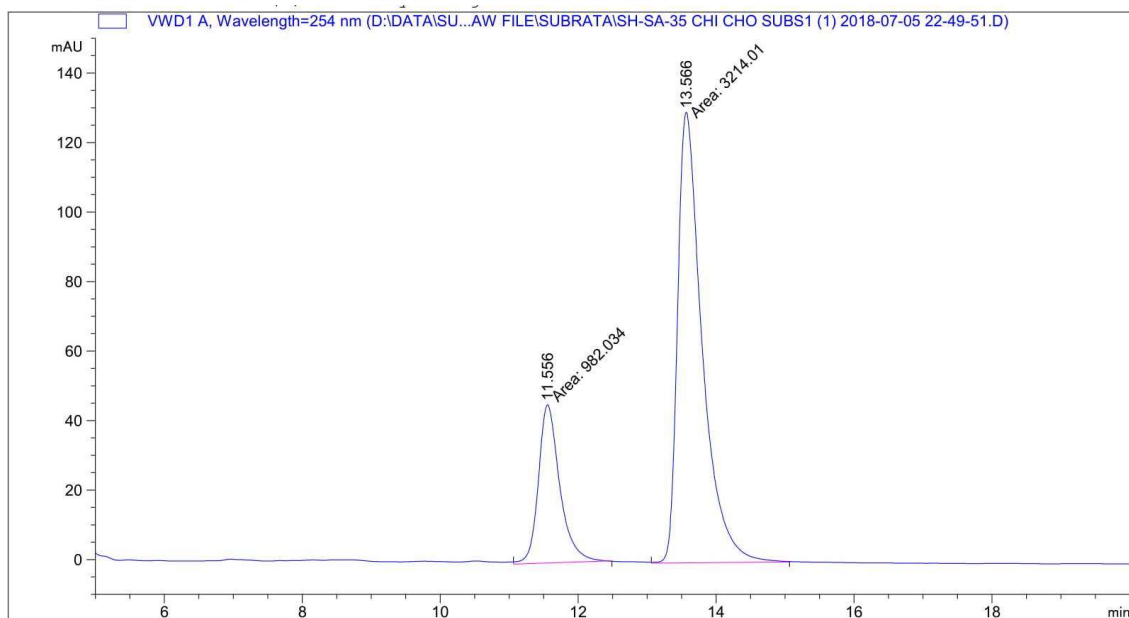


## 10. HPLC data of Pyrroloquinoline Derivatives

### (7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2-*ij*]quinoline-4-carbaldehyde (**3c**)



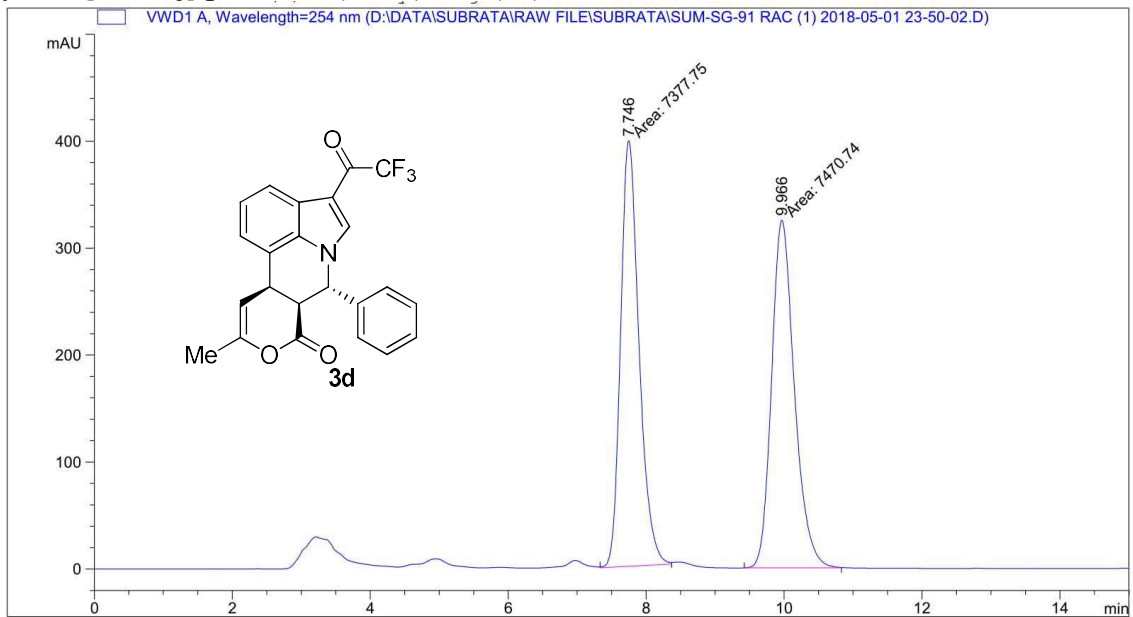
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.565	MM	0.3507	240.90524	11.45041	51.4177
2	13.700	MM	0.4037	227.62073	9.39836	48.5823



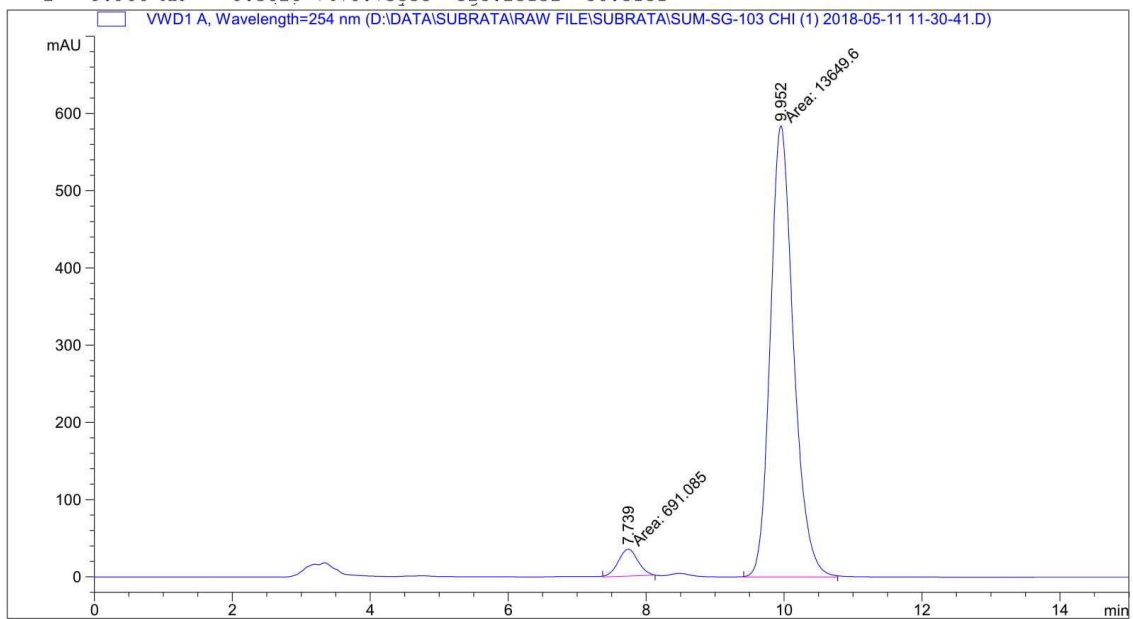
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.556	MM	0.3594	982.03436	45.53738	23.4038
2	13.566	MM	0.4132	3214.00879	129.64984	76.5962

Sample Info : CHIRALPAK-AD, 20% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3d)**



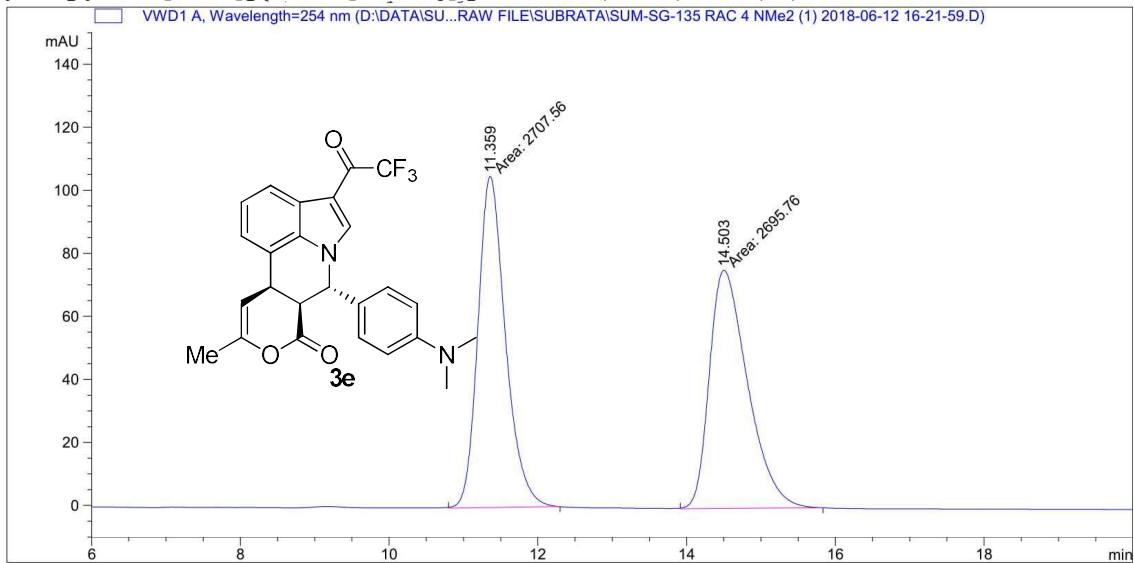
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.746	MM	0.3090	7377.74951	397.90634	49.6869
2	9.966	MM	0.3828	7470.73535	325.23132	50.3131



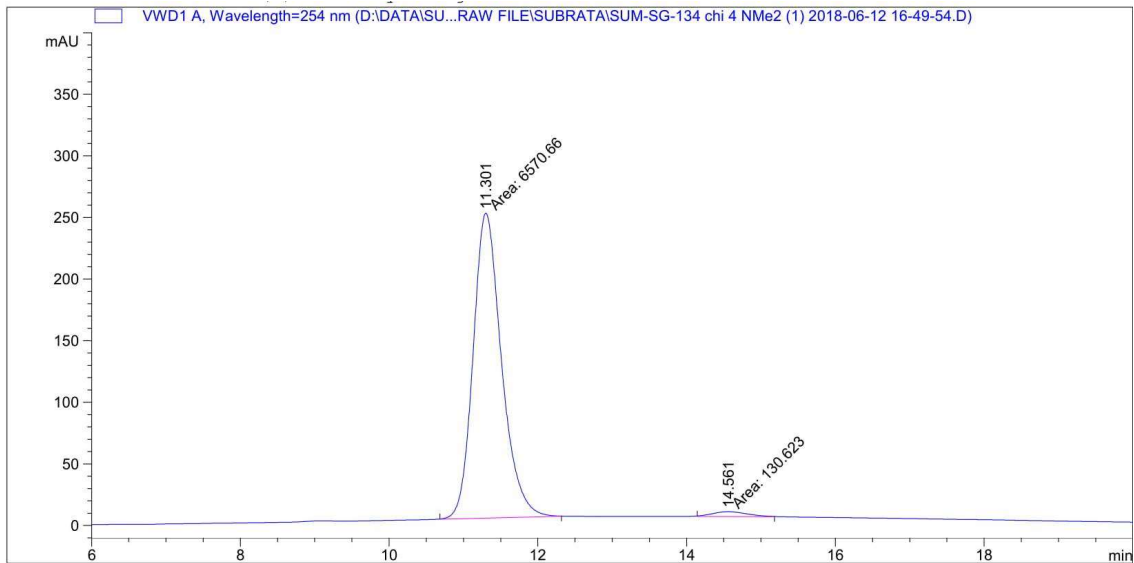
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.739	MM	0.3311	691.08453	34.78994	4.8191
2	9.952	MM	0.3895	1.36496e4	584.12219	95.1809

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)**



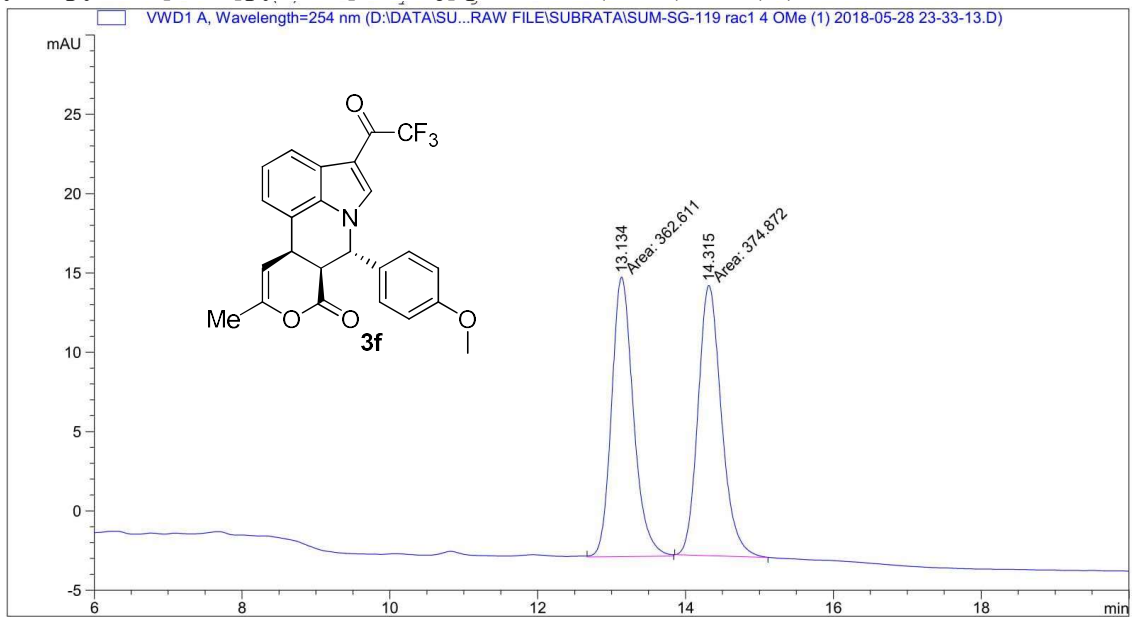
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.359	MM	0.4296	2707.55664	105.05225	50.1092
2	14.503	MM	0.5947	2695.75757	75.55278	49.8908



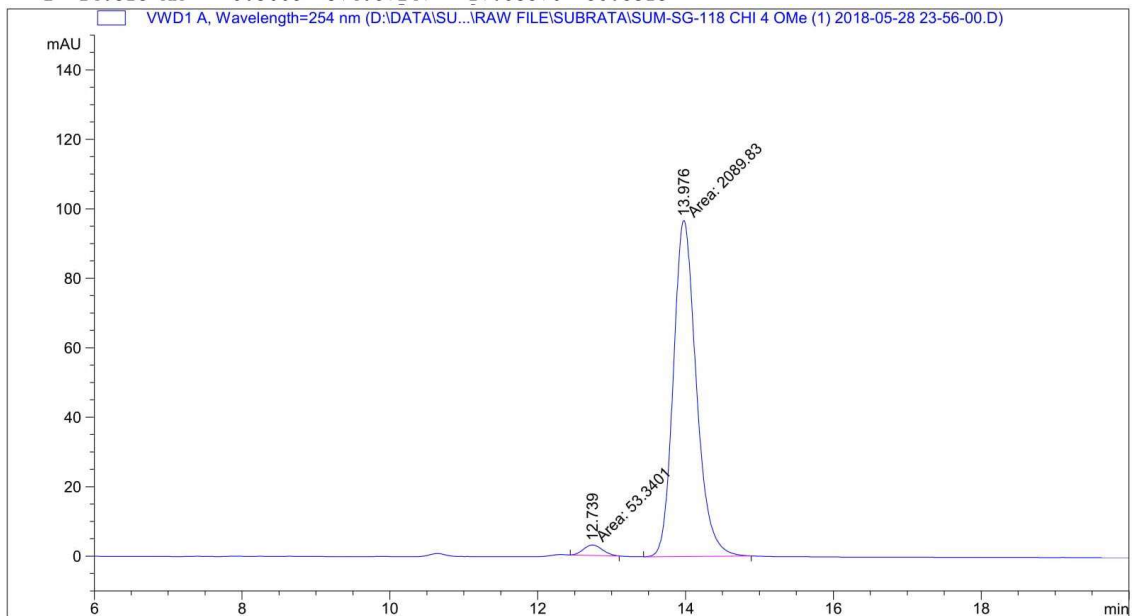
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.301	MM	0.4424	6570.66162	247.52592	98.0508
2	14.561	MM	0.5431	130.62265	4.00854	1.9492

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3f)**



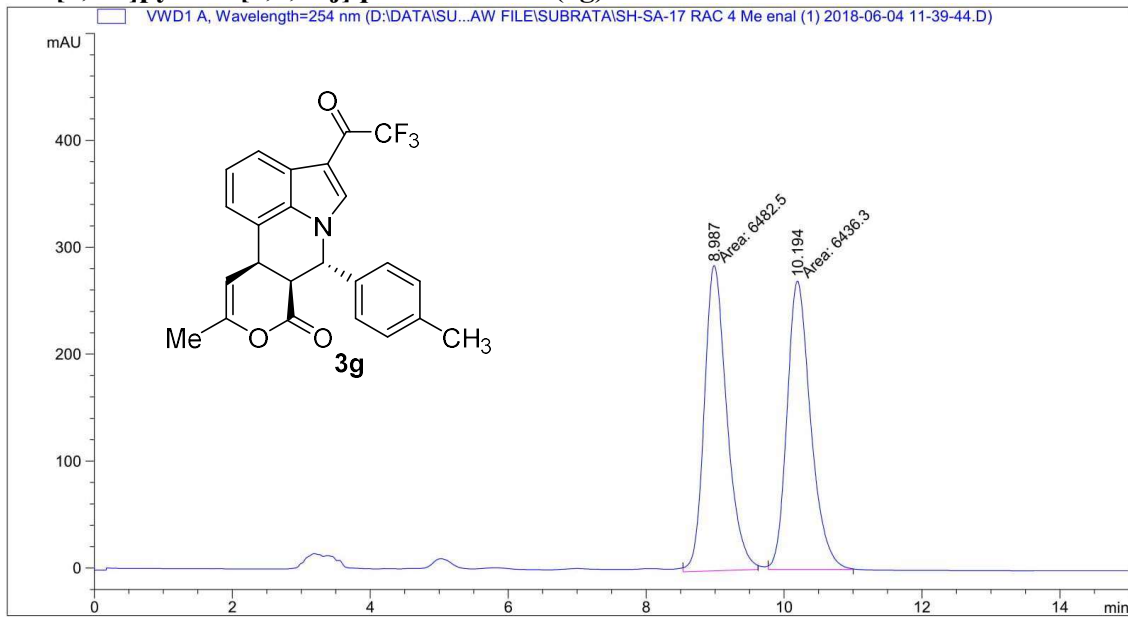
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.134	MM	0.3429	362.61053	17.62497	49.1687
2	14.315	MM	0.3668	374.87247	17.03576	50.8313



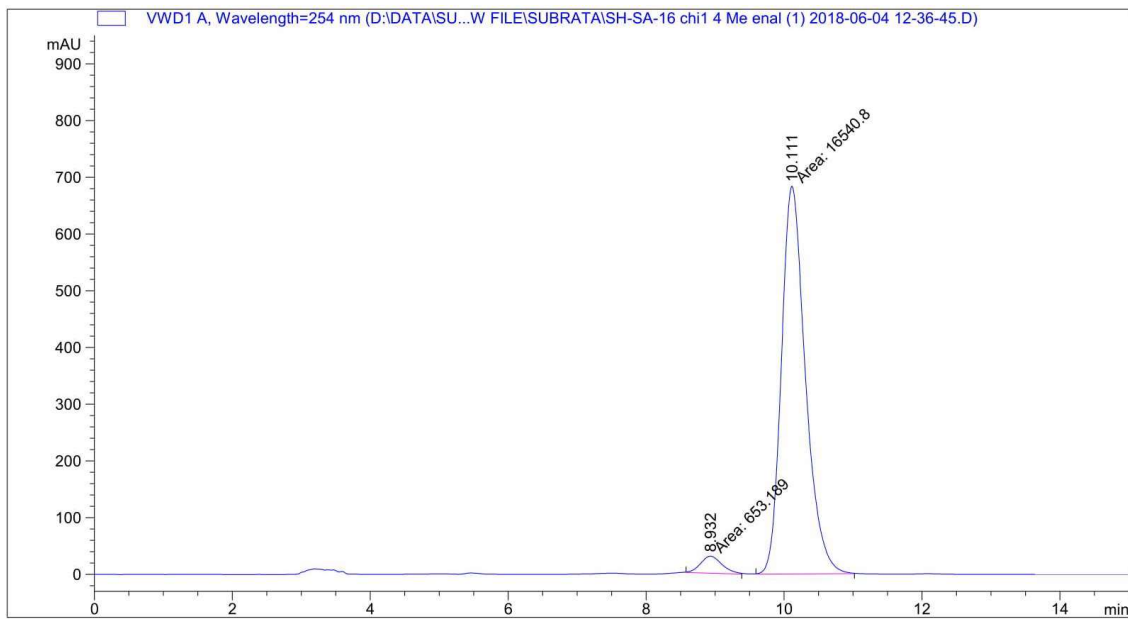
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.739	MM	0.2960	53.34007	3.00358	2.4888
2	13.976	MM	0.3600	2089.82959	96.76202	97.5112

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*g*)**



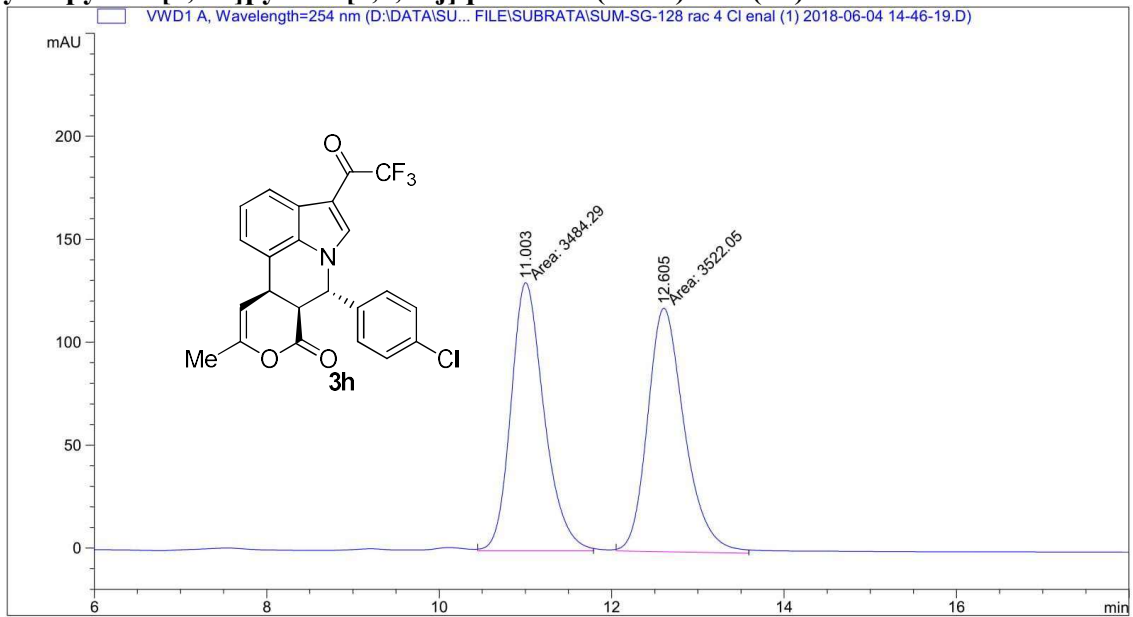
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.987	MM	0.3785	6482.49805	285.48145	50.1788
2	10.194	MM	0.3977	6436.30127	269.70953	49.8212



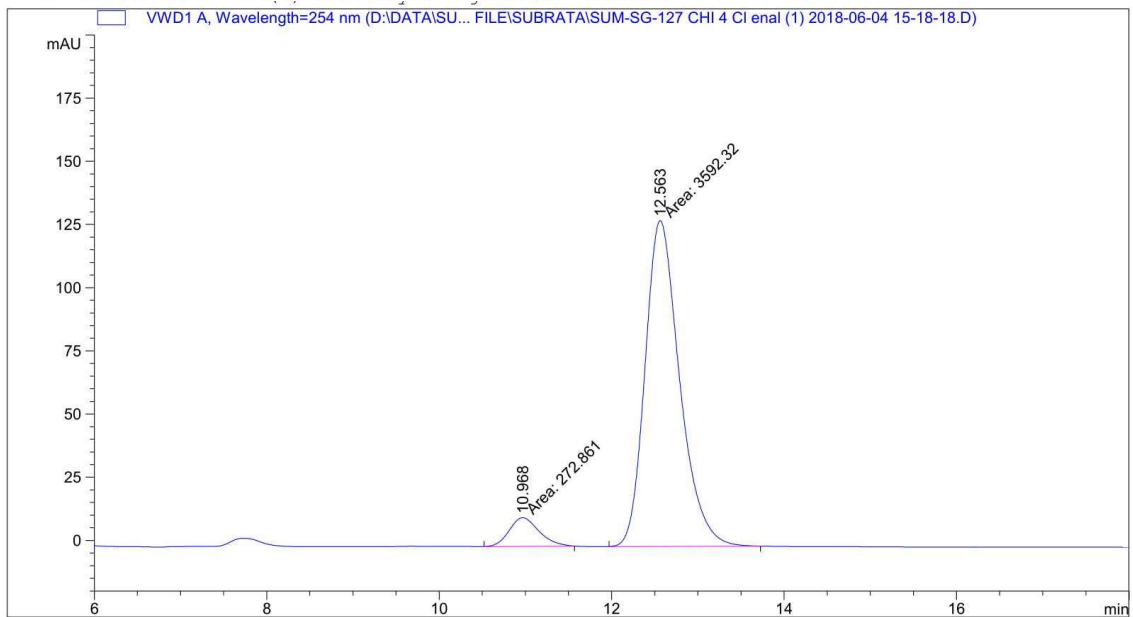
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.932	MM	0.3629	653.18878	29.99679	3.7989
2	10.111	MM	0.4032	1.65408e4	683.73535	96.2011

Sample Info : CHIRALPAK-AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3h)**



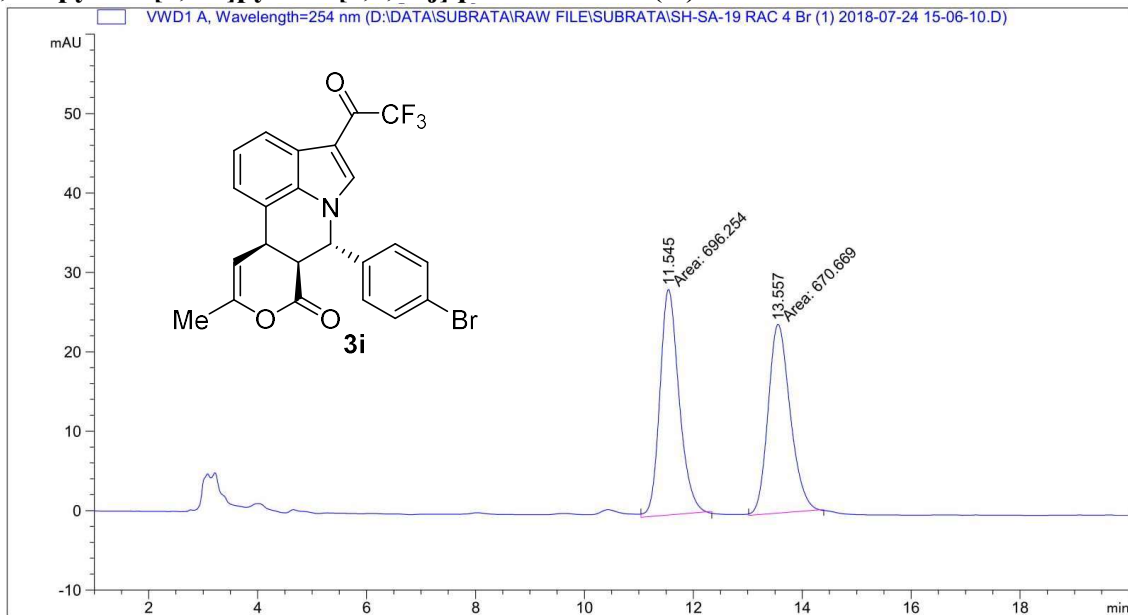
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.003	MM	0.4461	3484.28833	130.18623	49.7305
2	12.605	MM	0.4965	3522.04736	118.23128	50.2695



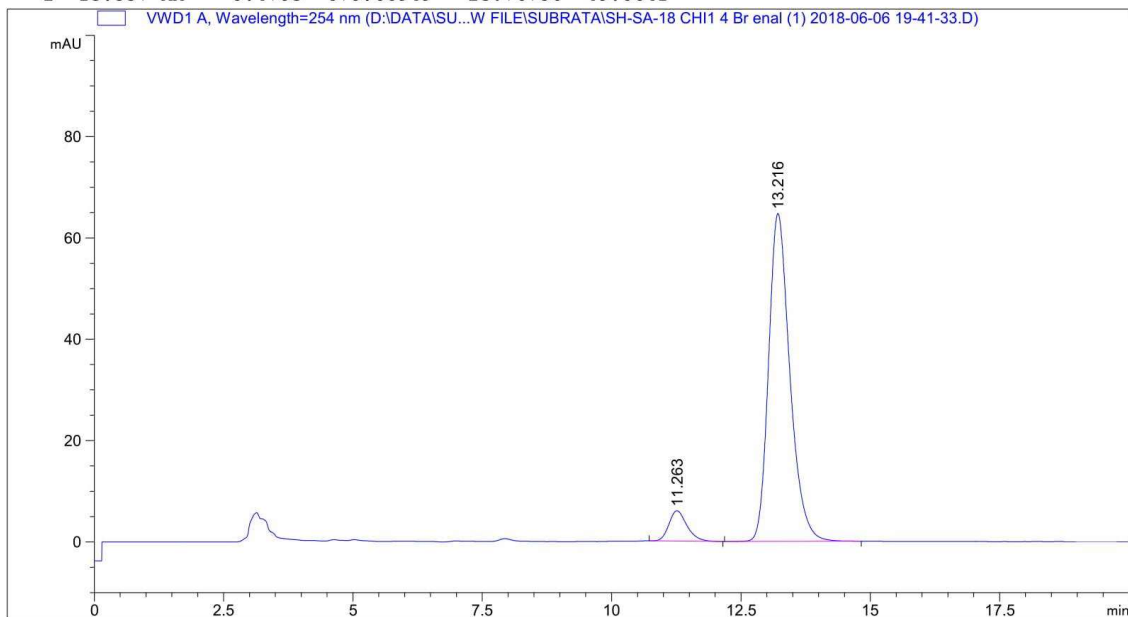
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.968	MM	0.4002	272.86102	11.36379	7.0595
2	12.563	MM	0.4644	3592.31592	128.93359	92.9405

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(4-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (**3i**)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.545	MM	0.4086	696.25433	28.40251	50.9359
2	13.557	MM	0.4703	670.66949	23.76786	49.0641

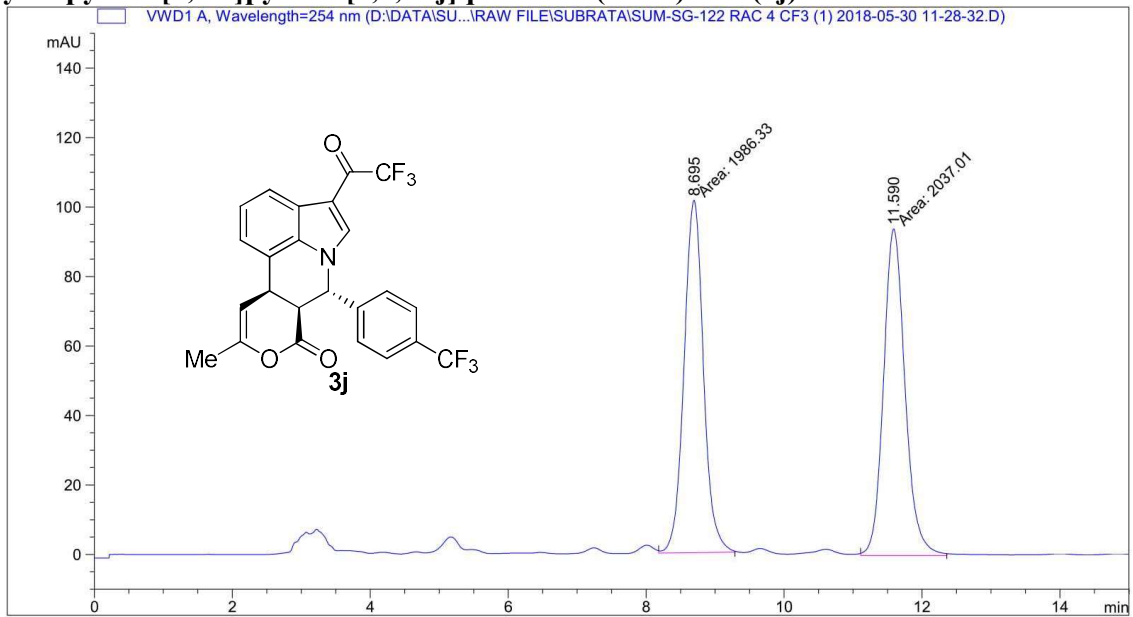


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.263	BB	0.3661	145.01529	5.99775	7.2636
2	13.216	BB	0.4346	1851.43799	64.74017	92.7364

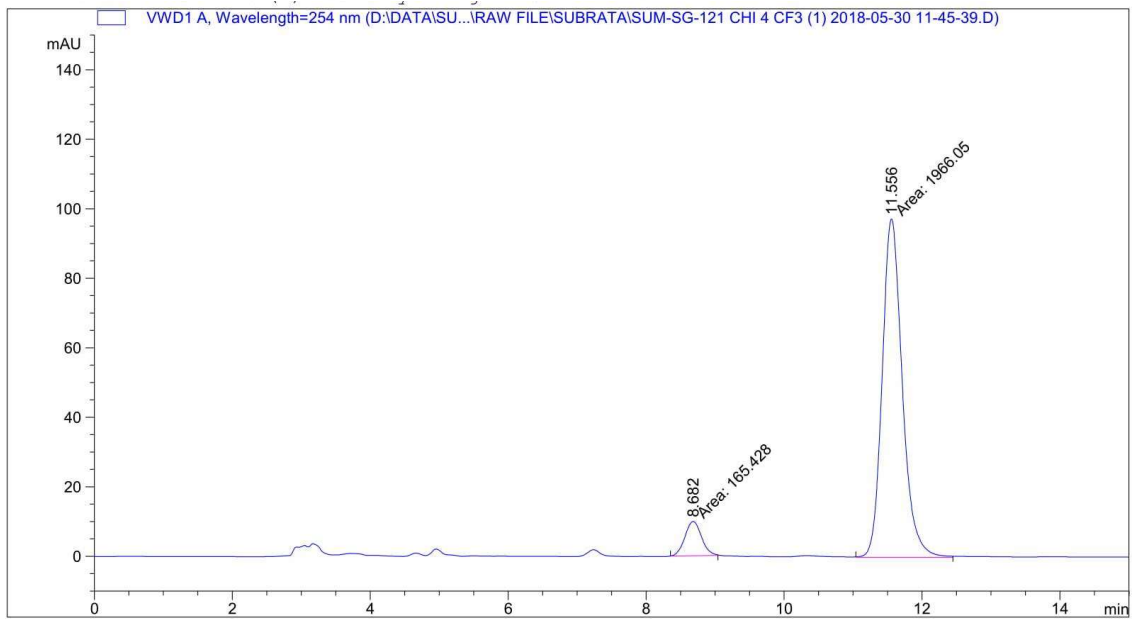
Sample Info : CHIRALPAK-AD, 10% IPA-Hexane, 1.0 ml/min, 254nm



**(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3j)**



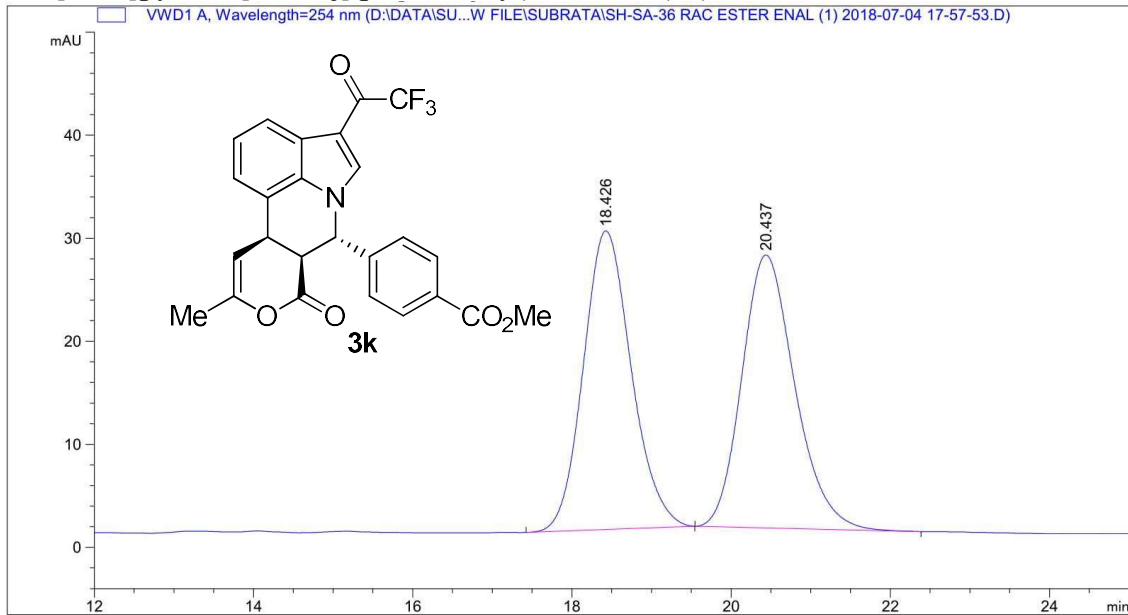
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.695	MM	0.3263	1986.32874	101.45470	49.3702
2	11.590	MM	0.3612	2037.00647	93.99446	50.6298



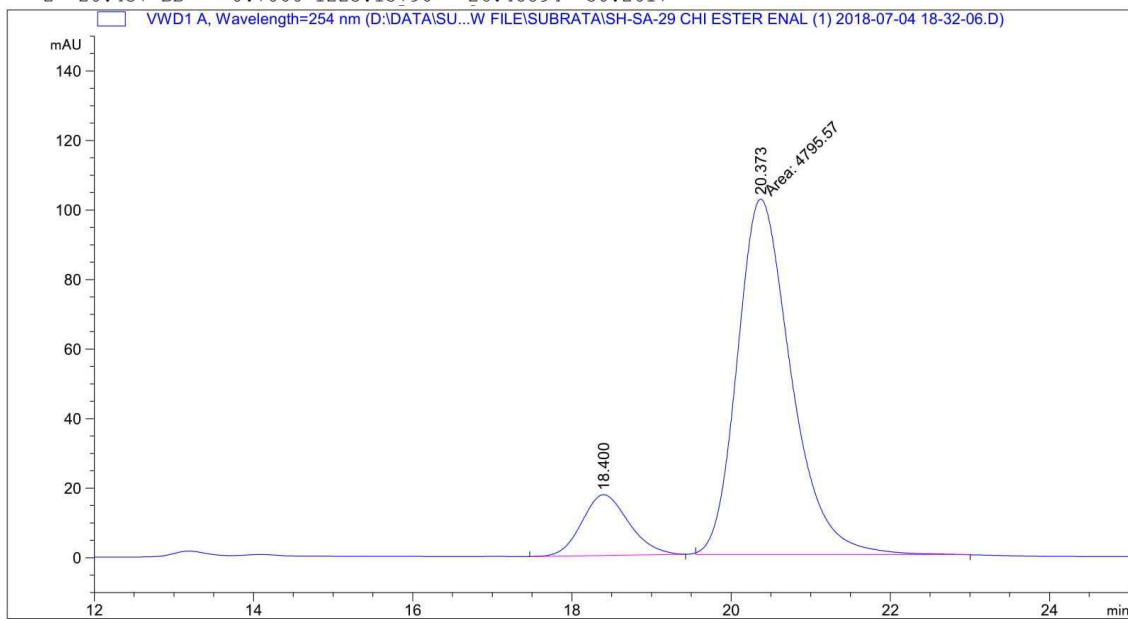
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.682	MM	0.2788	165.42751	9.88865	7.7612
2	11.556	MM	0.3366	1966.04858	97.34234	92.2388

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

**Methyl4-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (3k)**



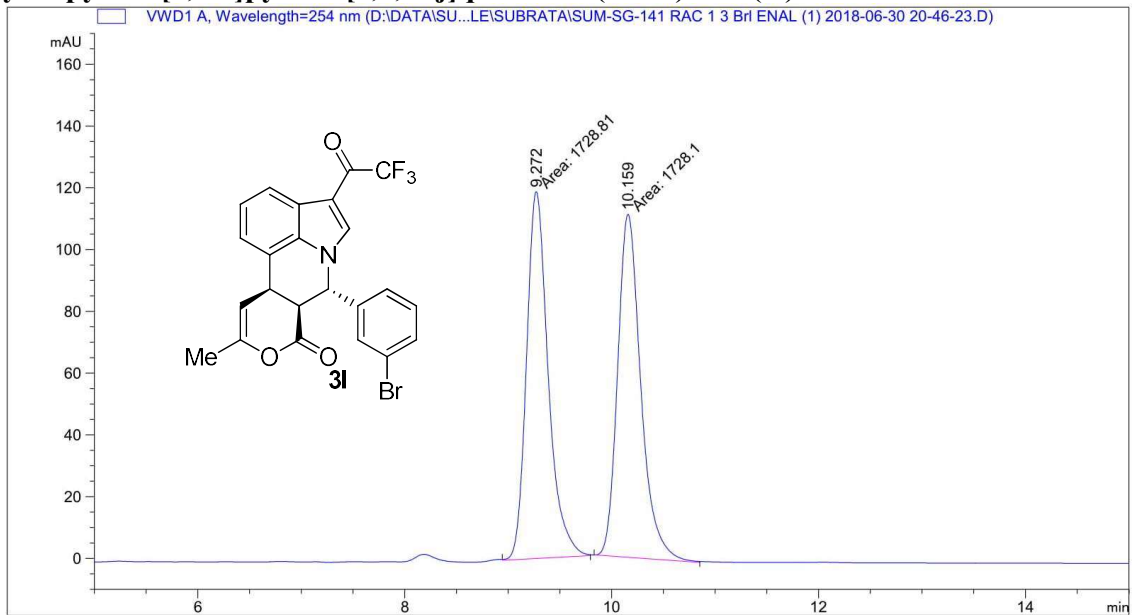
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.426	BB	0.6441	1212.39832	28.98144	49.7383
2	20.437	BB	0.7066	1225.15796	26.48894	50.2617



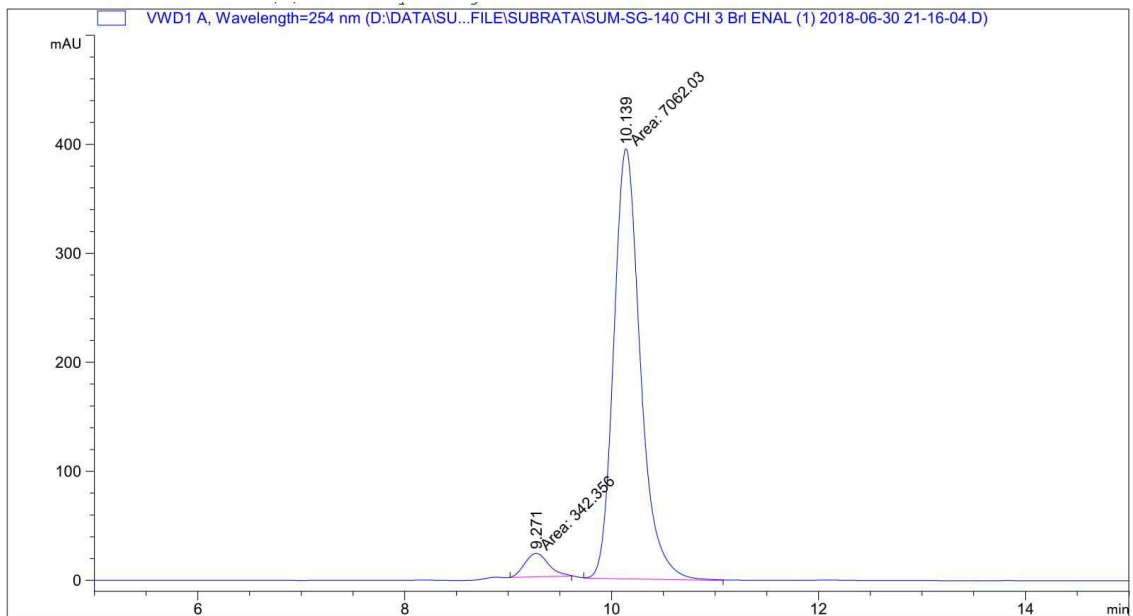
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.400	BB	0.6283	715.22528	17.48192	12.9786
2	20.373	MM	0.7821	4795.57080	102.19435	87.0214

Sample Info : CHIRALPAK -AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3I)**



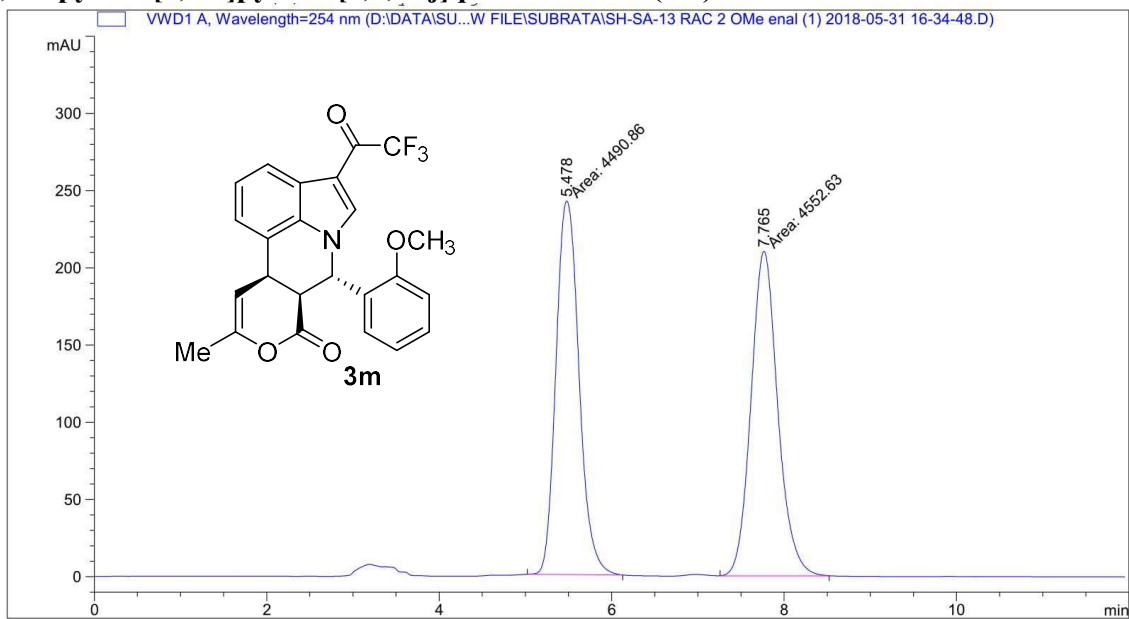
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.272	MM	0.2426	1728.80713	118.79083	50.0102
2	10.159	MM	0.2593	1728.10388	111.09288	49.9898



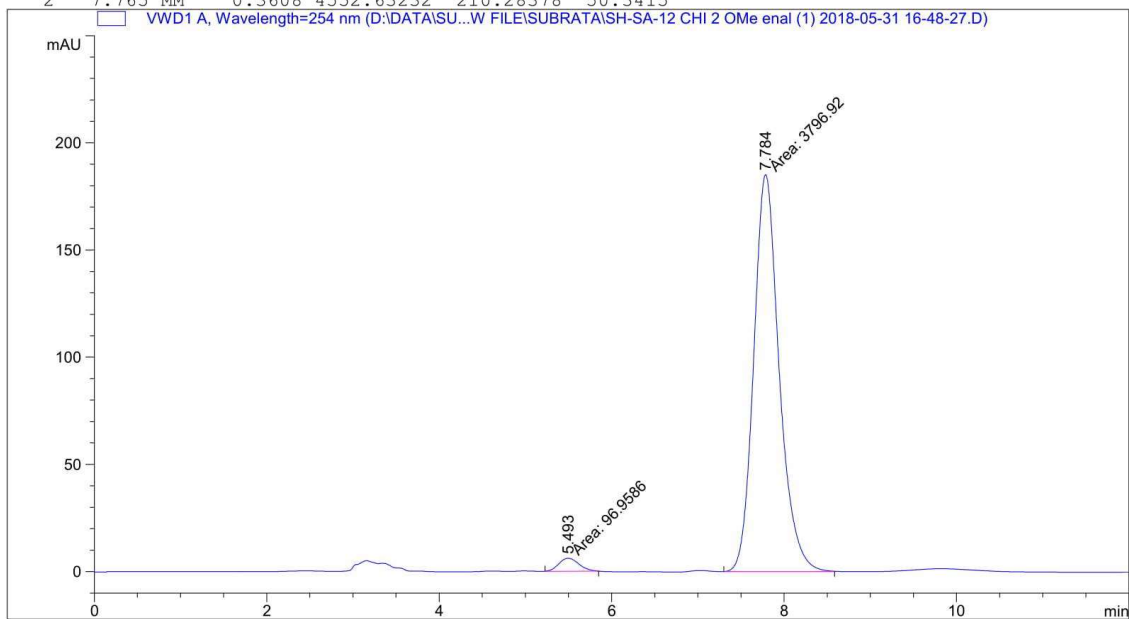
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.271	MM	0.2654	342.35580	21.49758	4.6237
2	10.139	MM	0.2983	7062.02637	394.60016	95.3763

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*m*)**



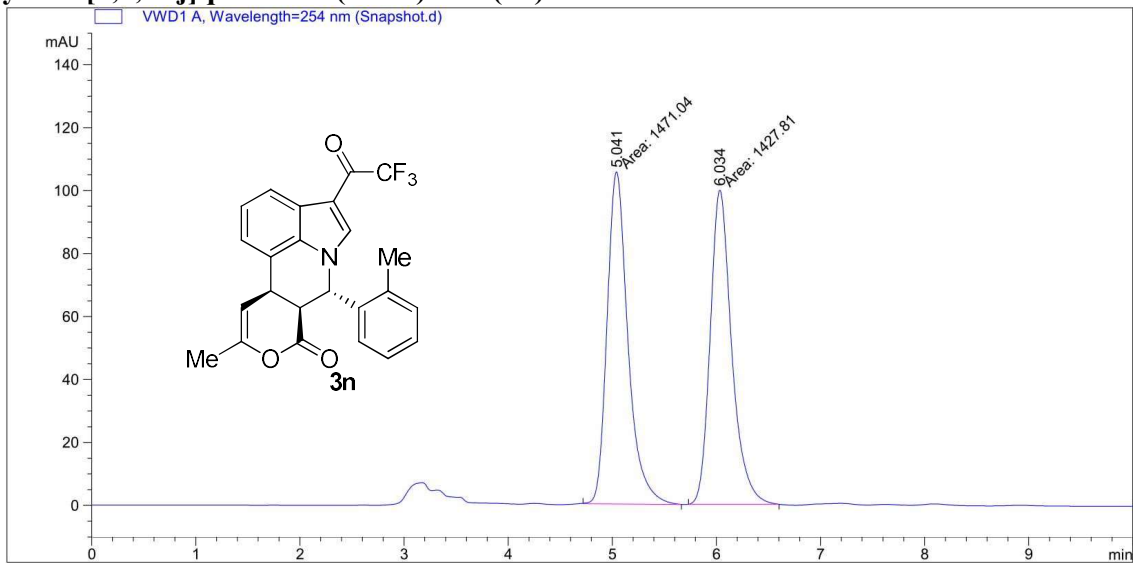
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.478	MM	0.3094	4490.86475	241.92430	49.6585
2	7.765	MM	0.3608	4552.63232	210.28378	50.3415



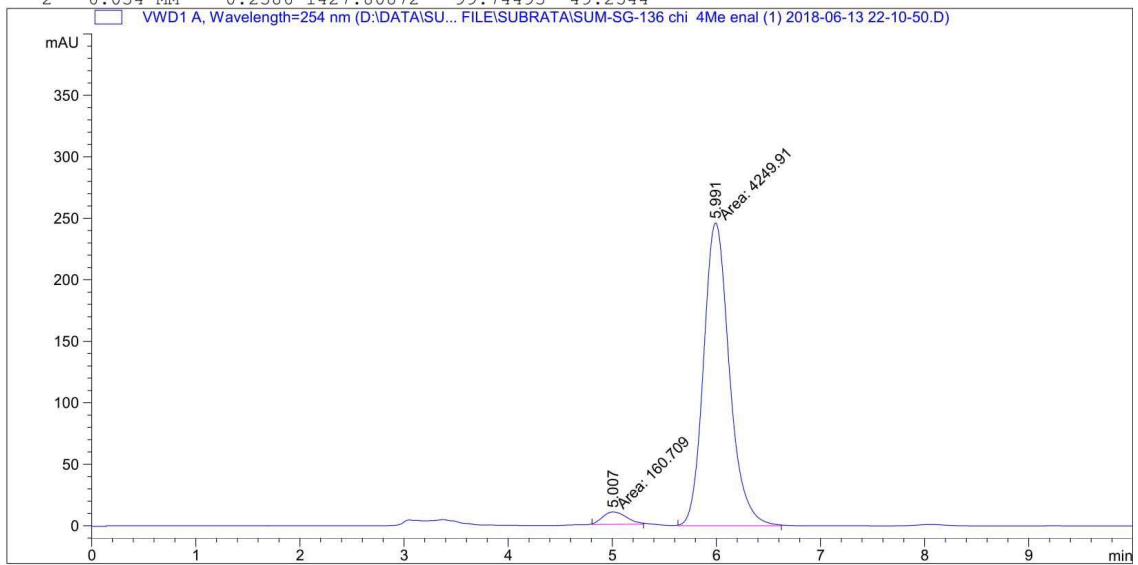
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.493	MM	0.2682	96.95860	6.02567	2.4900
2	7.784	MM	0.3419	3796.91577	185.10767	97.5100

Sample Info : CHIRALPAK-AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2-*ij*]quinolin-8(11*aH*)-one (3n)**



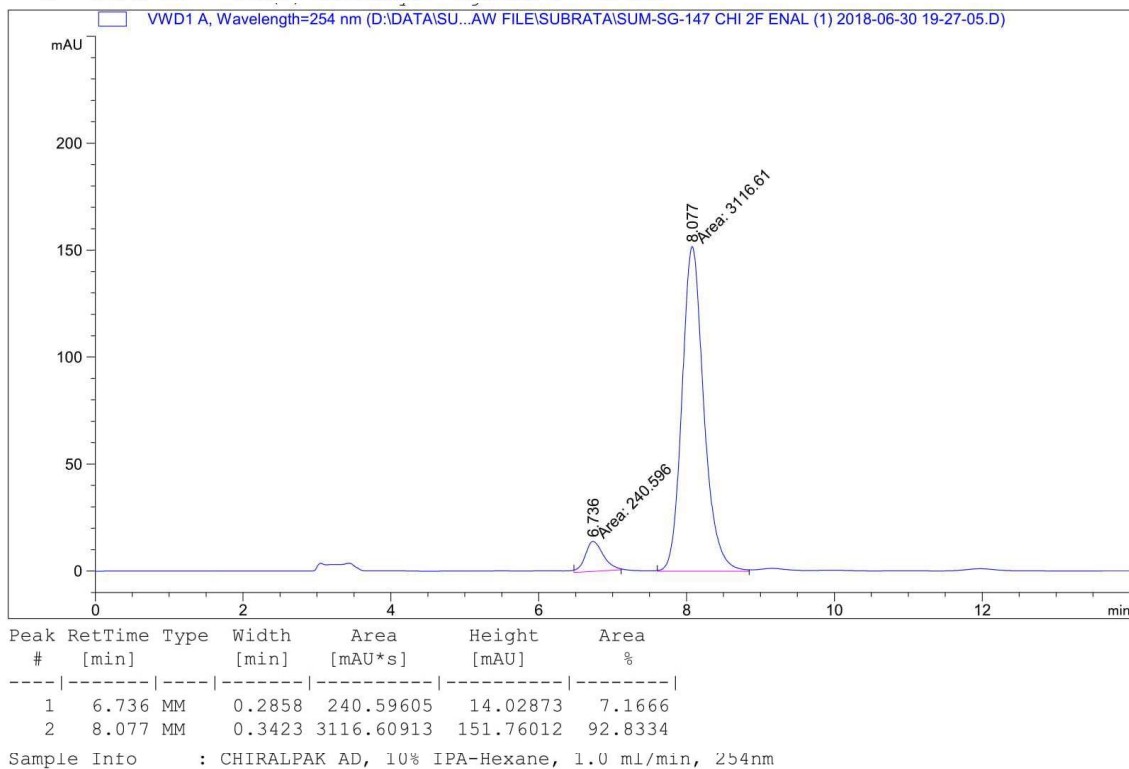
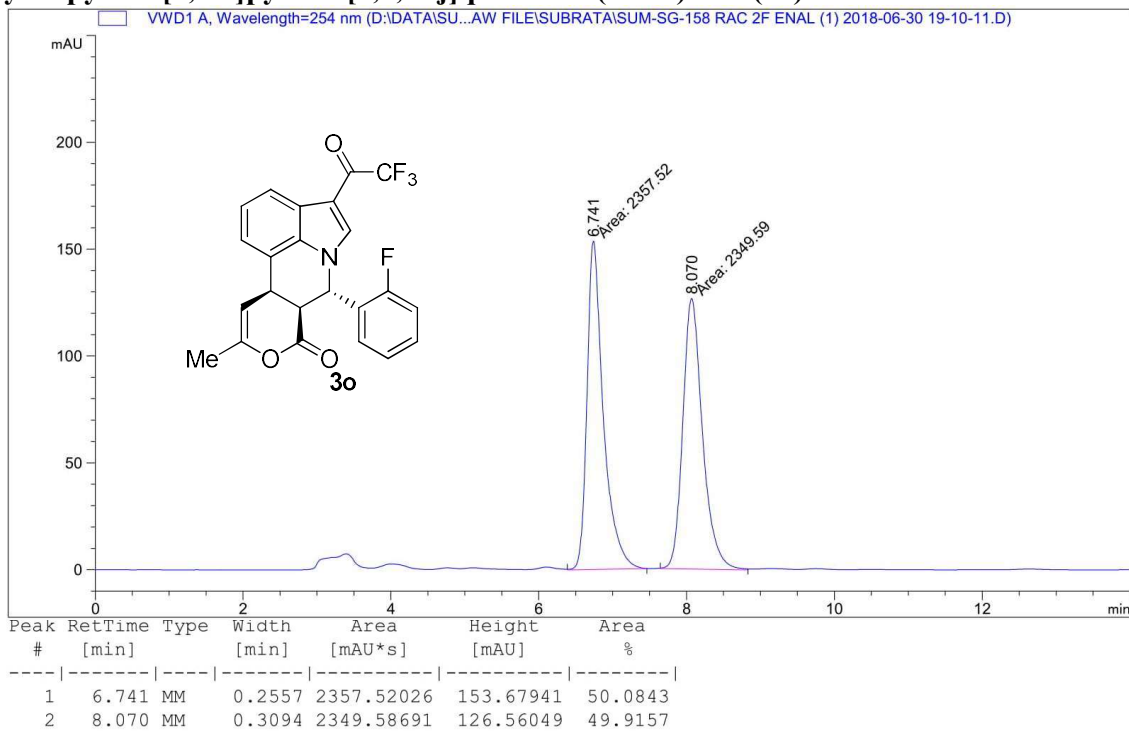
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.041	MM	0.2325	1471.03870	105.46463	50.7456
2	6.034	MM	0.2386	1427.80872	99.74493	49.2544



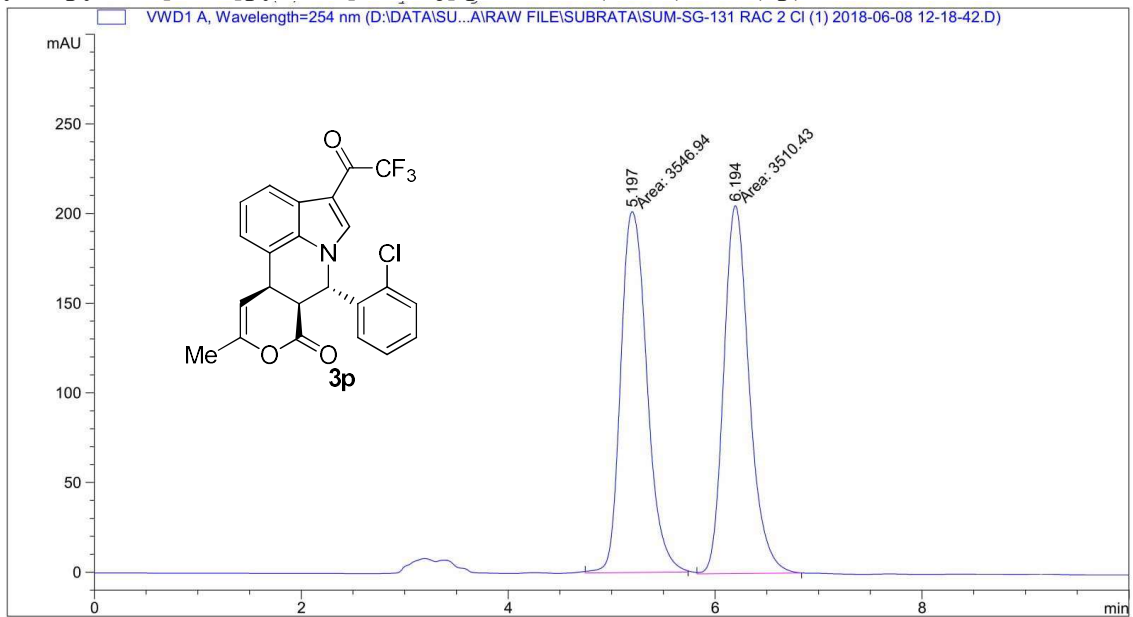
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.007	MM	0.2658	160.70891	10.07840	3.6437
2	5.991	MM	0.2876	4249.90820	246.26048	96.3563

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

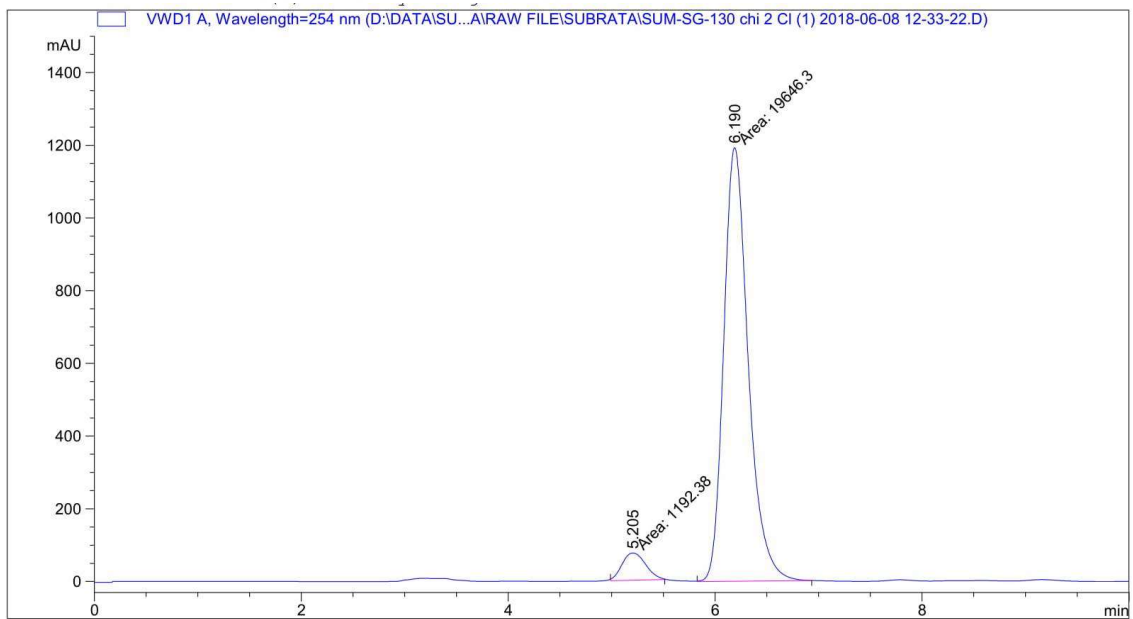
**(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)**



**(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3p)**



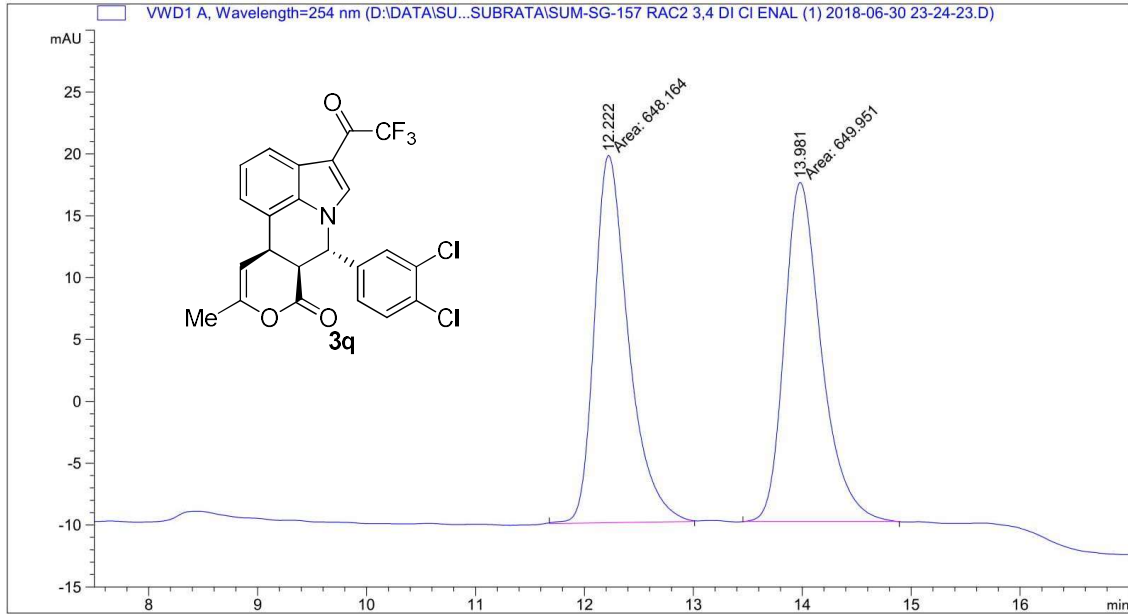
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.197	MM	0.2937	3546.93848	201.28427	50.2586
2	6.194	MM	0.2852	3510.43359	205.16528	49.7414



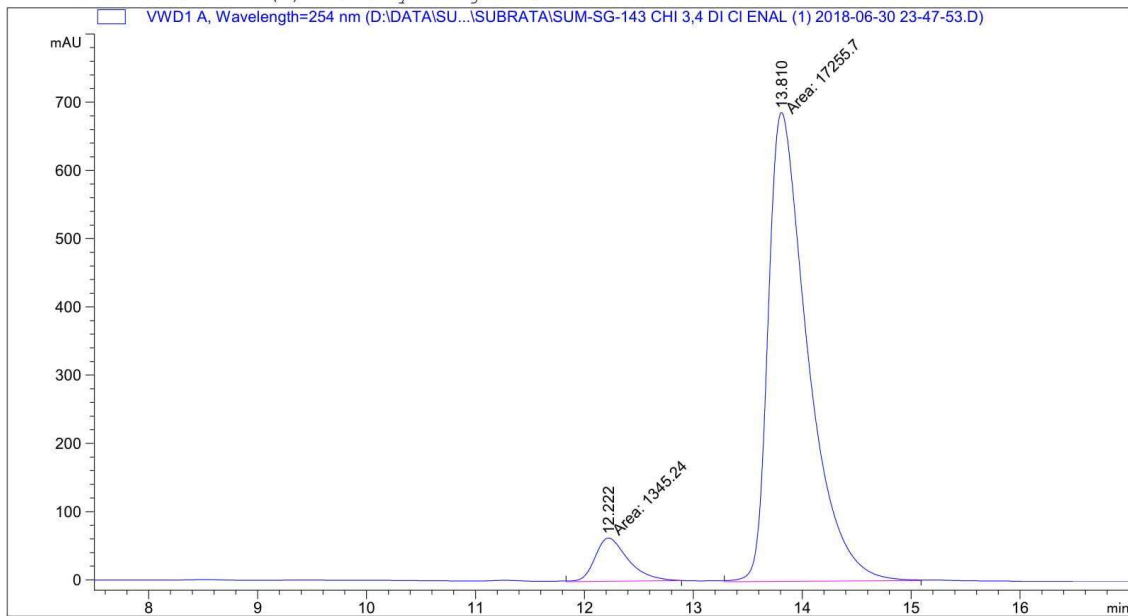
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.205	MM	0.2648	1192.37561	75.04144	5.7219
2	6.190	MM	0.2744	1.96463e4	1193.08789	94.2781

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3q)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.222	MM	0.3640	648.16394	29.68172	49.9312
2	13.981	MM	0.3953	649.95050	27.40337	50.0688

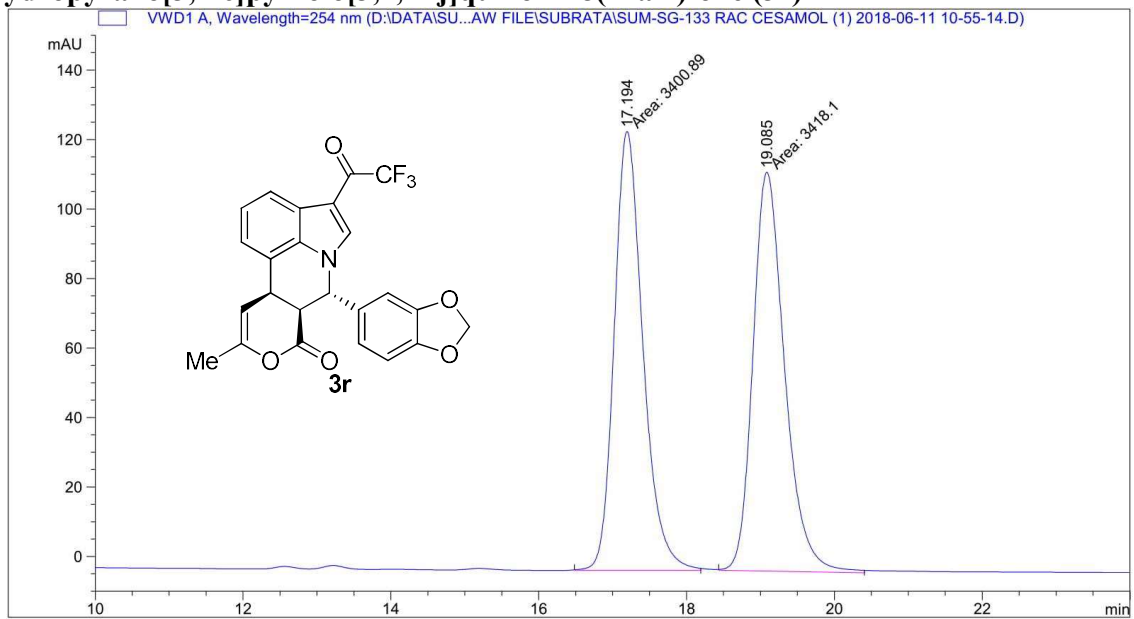


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.222	MM	0.3537	1345.23877	63.39055	7.2321
2	13.810	MM	0.4185	1.72557e4	687.17780	92.7679

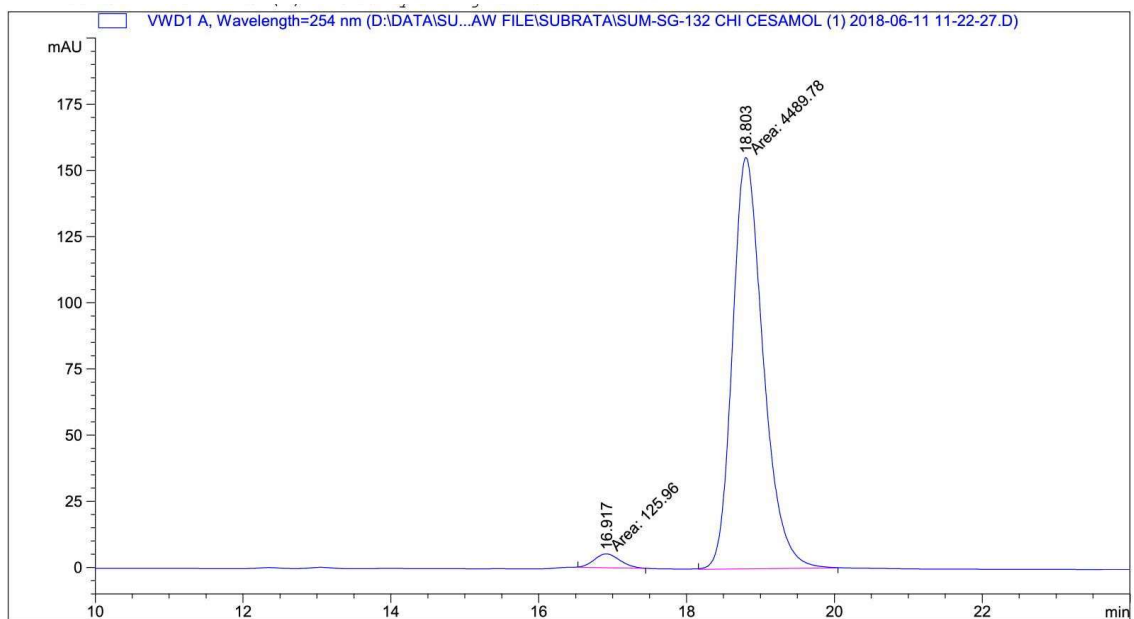
Sample Info : CHIRALPAK-IB, 10% IPA-Hexane, 1.0 ml/min, 254nm



**(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2-*ij*]quinolin-8(11*aH*)-one (3r)**



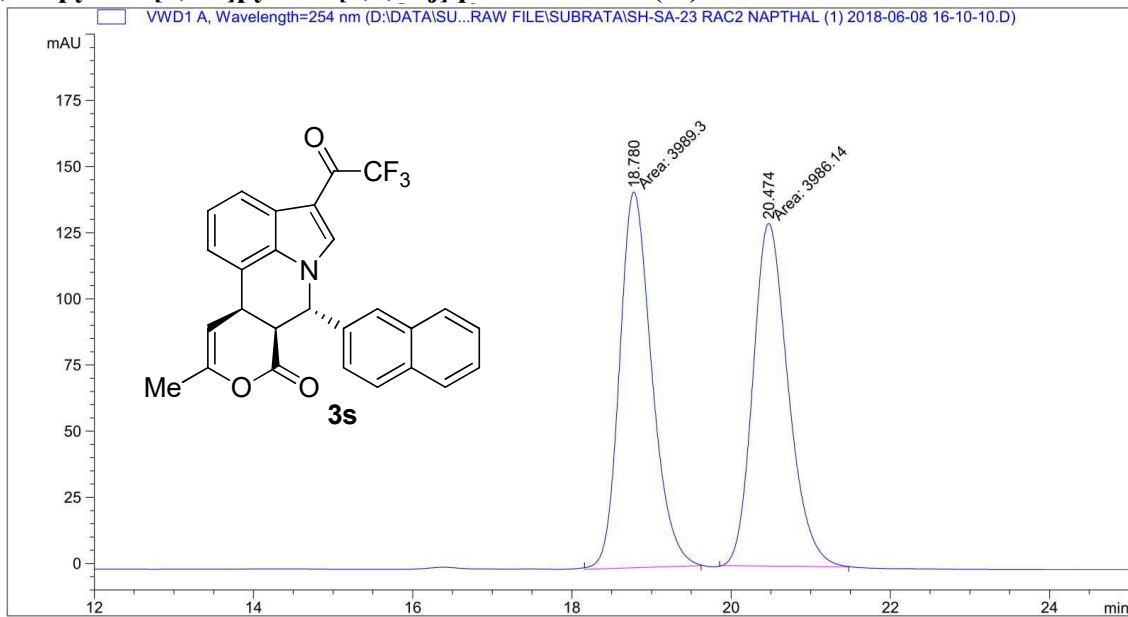
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.194	MM	0.4489	3400.89185	126.27410	49.8738
2	19.085	MM	0.4963	3418.10474	114.79146	50.1262



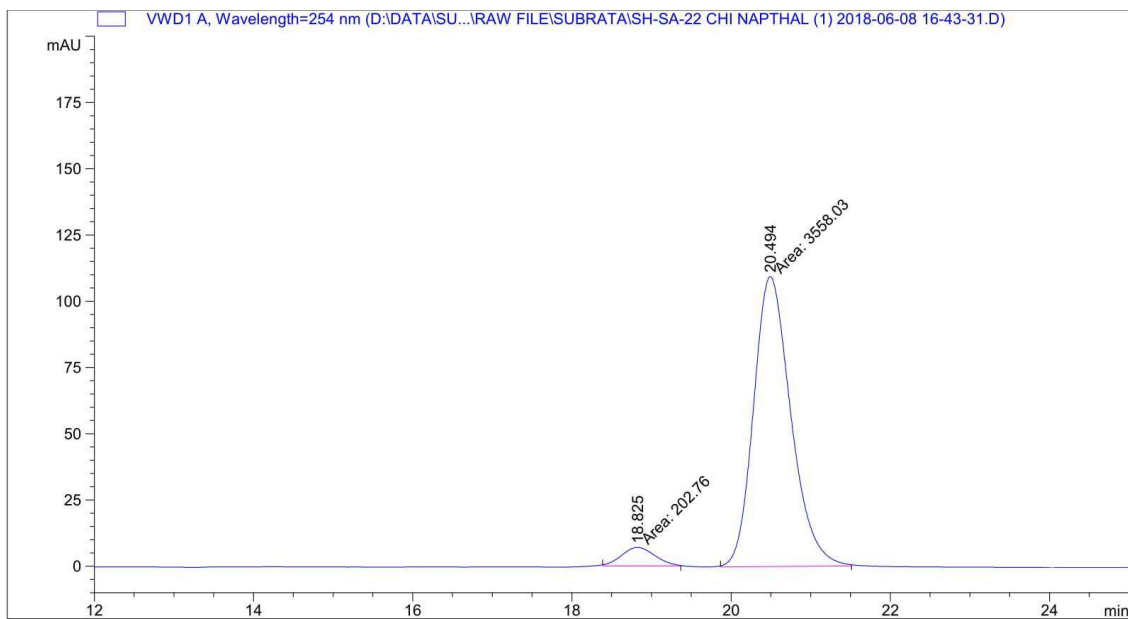
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.917	MM	0.4022	125.95990	5.21926	2.7289
2	18.803	MM	0.4815	4489.77637	155.39536	97.2711

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3s)**



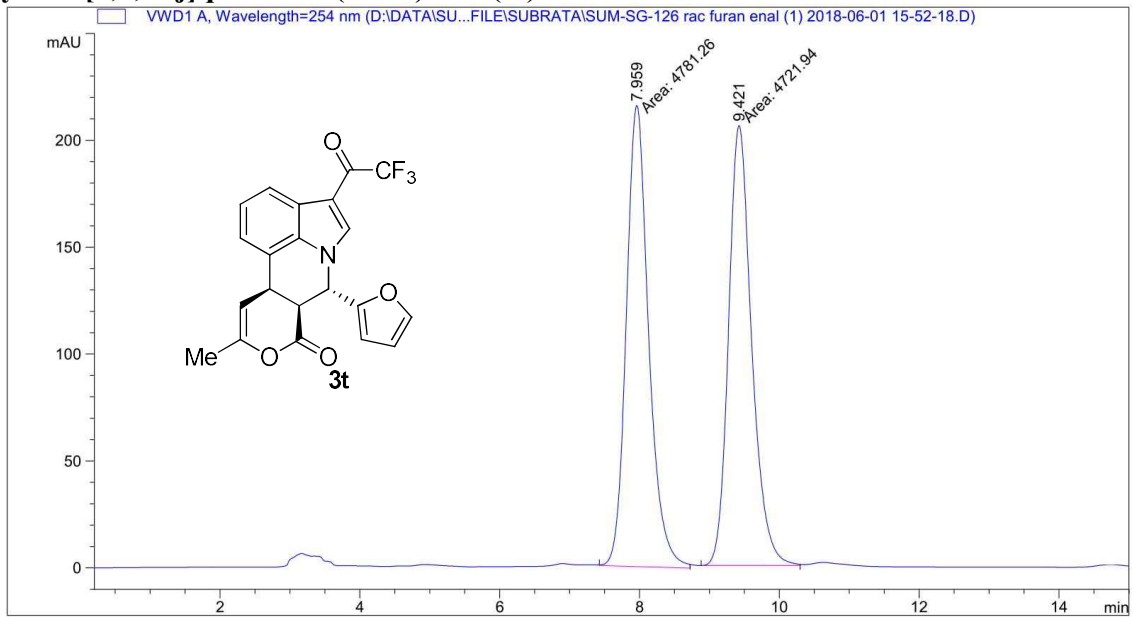
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.780	MM	0.4684	3989.29541	141.96040	50.0198
2	20.474	MM	0.5130	3986.14429	129.51402	49.9802



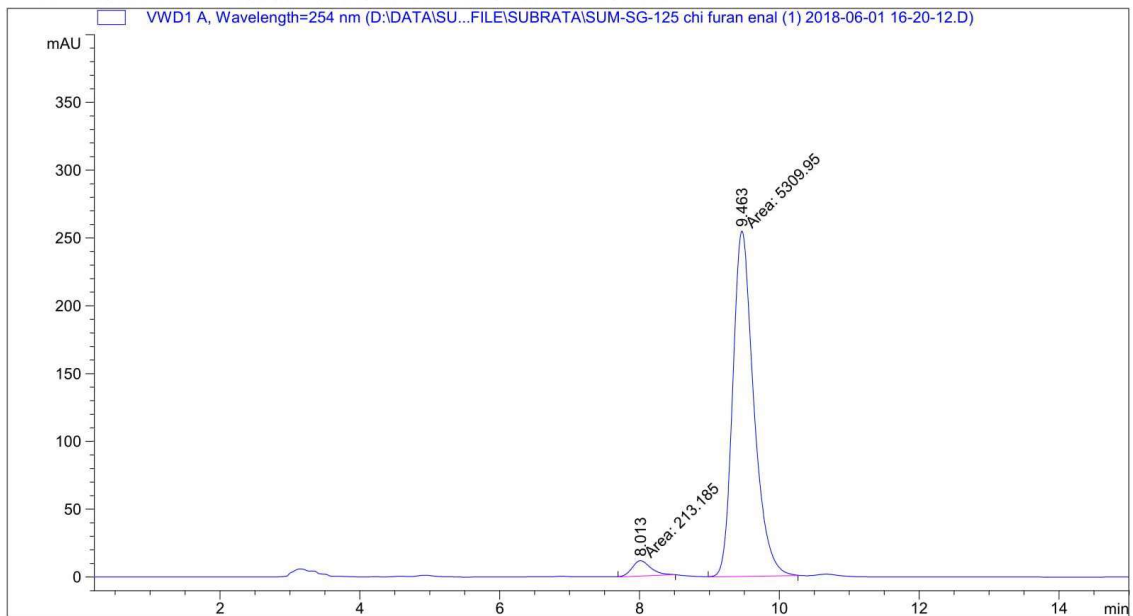
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.825	MM	0.4845	202.75995	6.97453	5.3914
2	20.494	MM	0.5420	3558.03345	109.40266	94.6086

Sample Info : CHIRALPAK-IA, 5% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3t)**



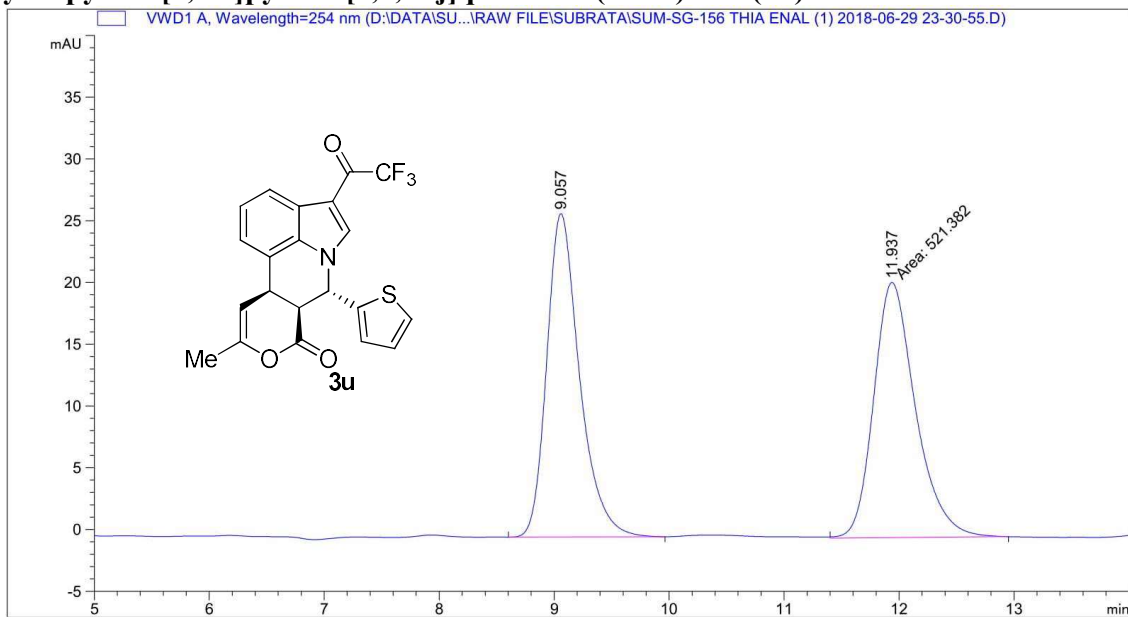
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.959	MM	0.3696	4781.26465	215.60083	50.3121
2	9.421	MM	0.3825	4721.94141	205.76492	49.6879



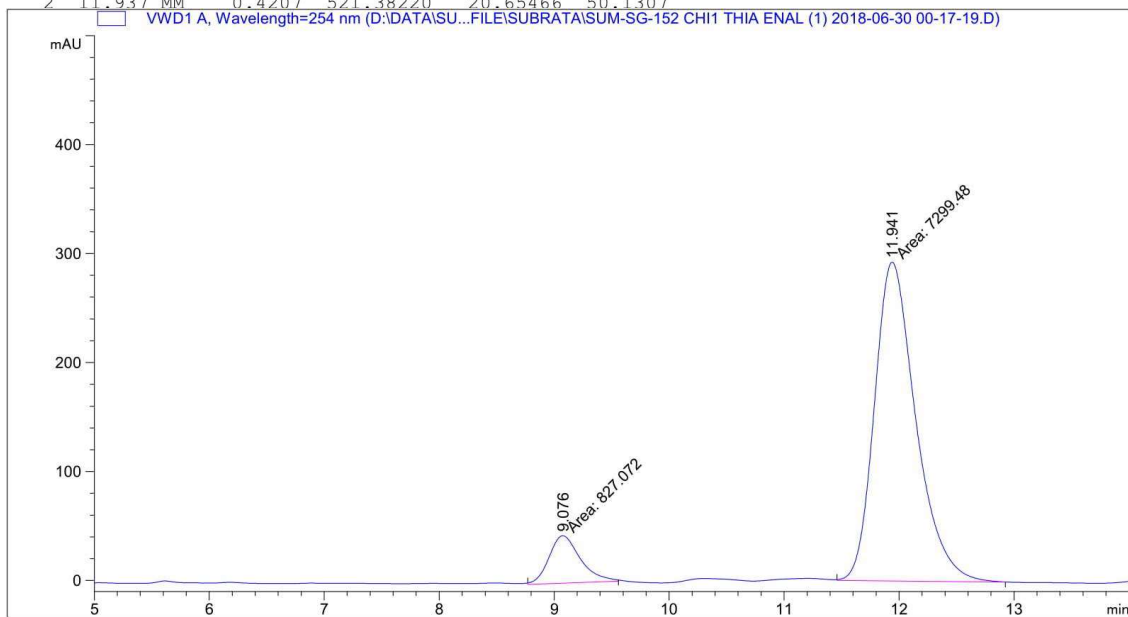
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.013	MM	0.3108	213.18469	11.43056	3.8599
2	9.463	MM	0.3474	5309.94531	254.71782	96.1401

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3u)**



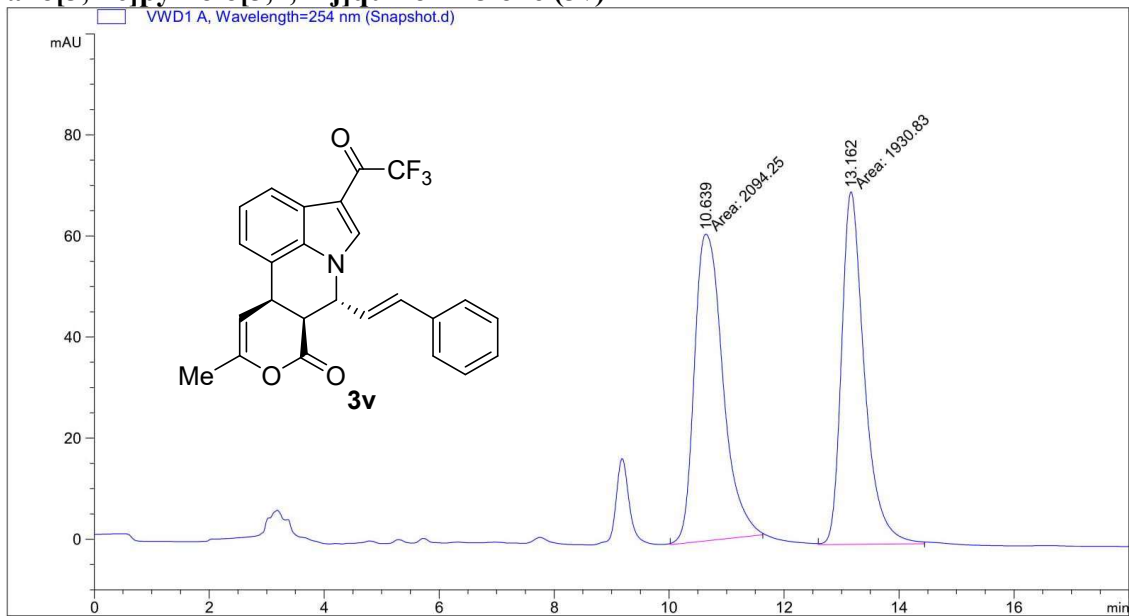
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.057	BB	0.2992	518.66455	26.17386	49.8693
2	11.937	MM	0.4207	521.38220	20.65466	50.1307



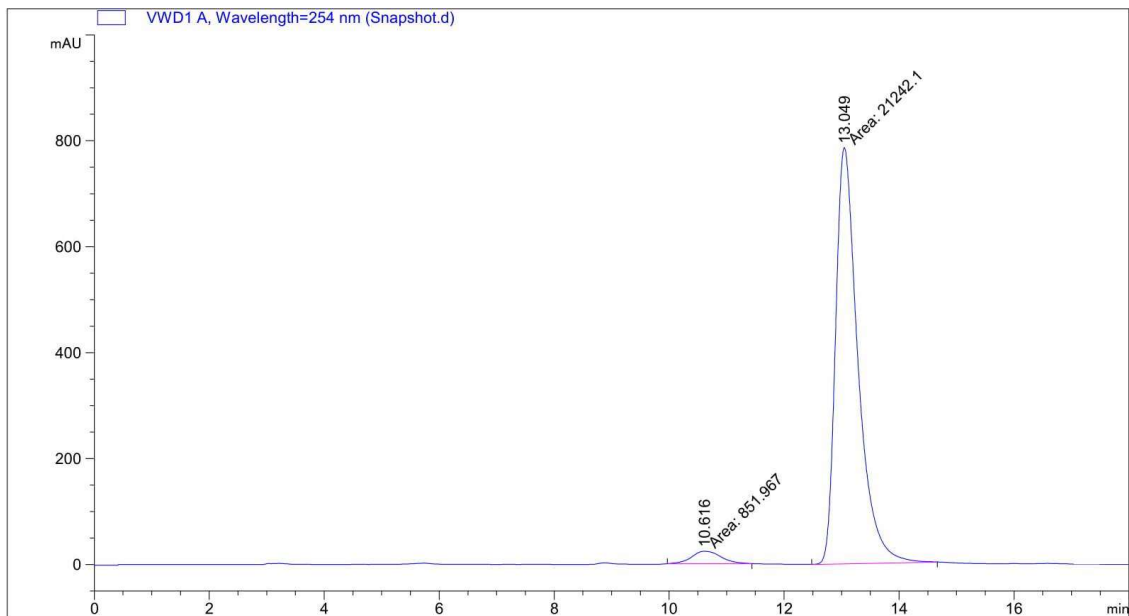
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.076	MM	0.3168	827.07208	43.51102	10.1774
2	11.941	MM	0.4160	7299.48438	292.46518	89.8226

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7R,7aS,11aR)-10-Methyl-7-((E)-styryl)-4-(2,2,2-trifluoroacetyl)-7a,11a-dihydro-7H,8H-pyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8-one (3v)**



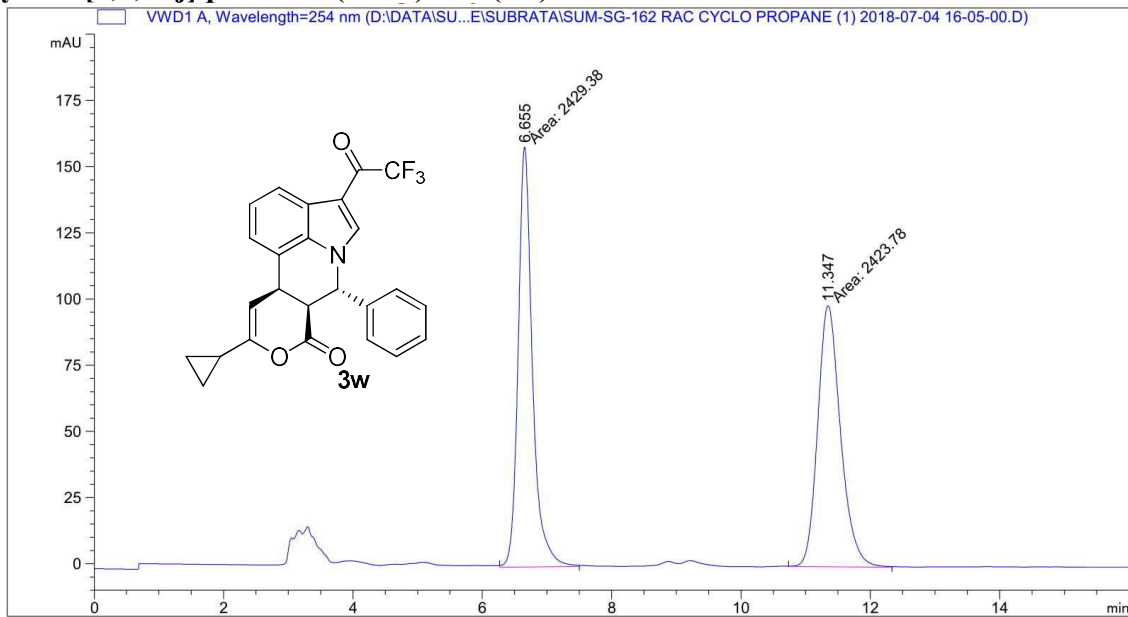
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.639	MM	0.5750	2094.24707	60.70765	52.0300
2	13.162	MM	0.4612	1930.82776	69.76952	47.9700



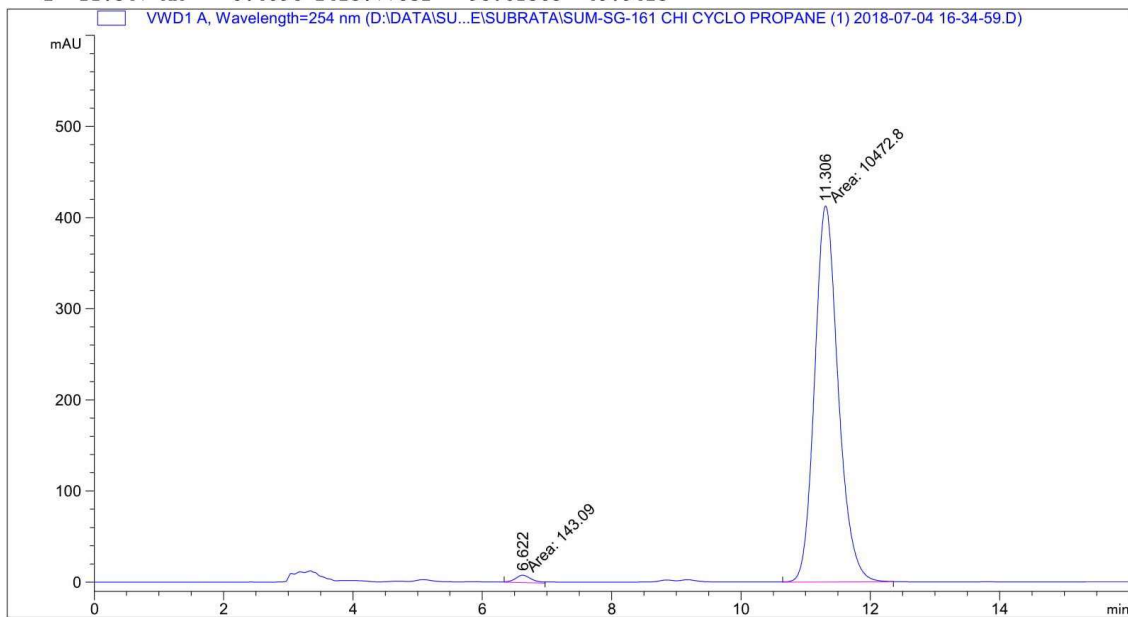
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.616	MM	0.6017	851.96692	23.59889	3.8561
2	13.049	MM	0.4505	2.12421e4	785.88135	96.1439

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3w)**



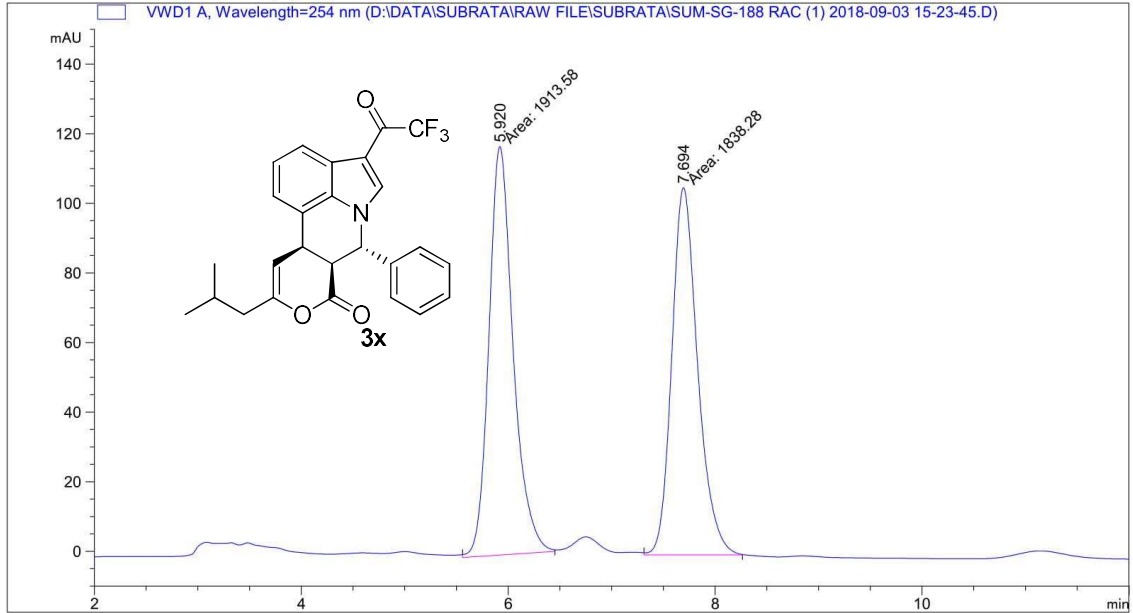
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.655	MM	0.2551	2429.37573	158.69545	50.0577
2	11.347	MM	0.4096	2423.77832	98.61365	49.9423



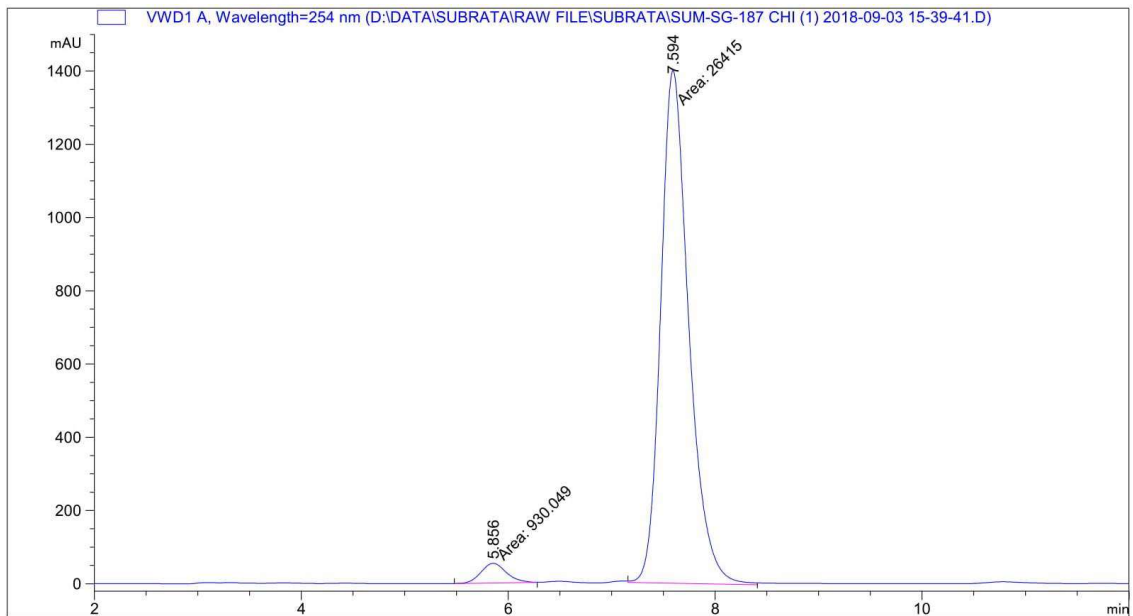
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.622	MM	0.2920	143.08952	8.16610	1.3479
2	11.306	MM	0.4229	1.04728e4	412.72995	98.6521

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*x*)**



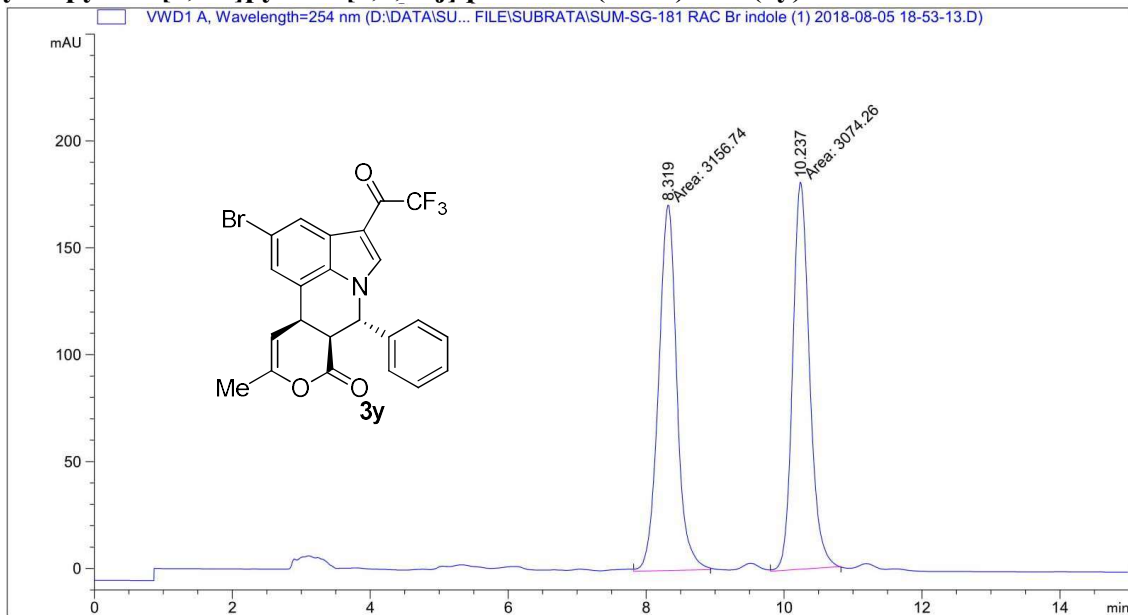
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.920	MM	0.2717	1913.57861	117.38689	51.0034
2	7.694	MM	0.2903	1838.28418	105.52666	48.9966



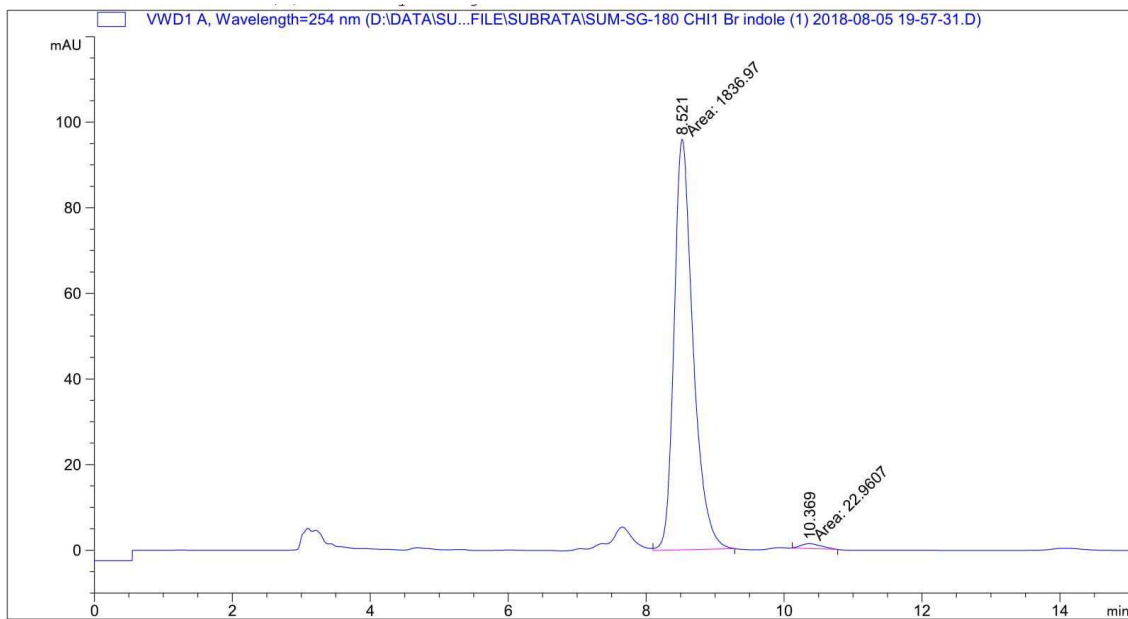
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.856	MM	0.2868	930.04877	54.04660	3.4012
2	7.594	MM	0.3144	2.64150e4	1400.24341	96.5988

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 01.0 ml/min, 254nm

**(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.319	MM	0.3076	3156.73779	171.02858	50.6618
2	10.237	MM	0.2830	3074.26343	181.08357	49.3382

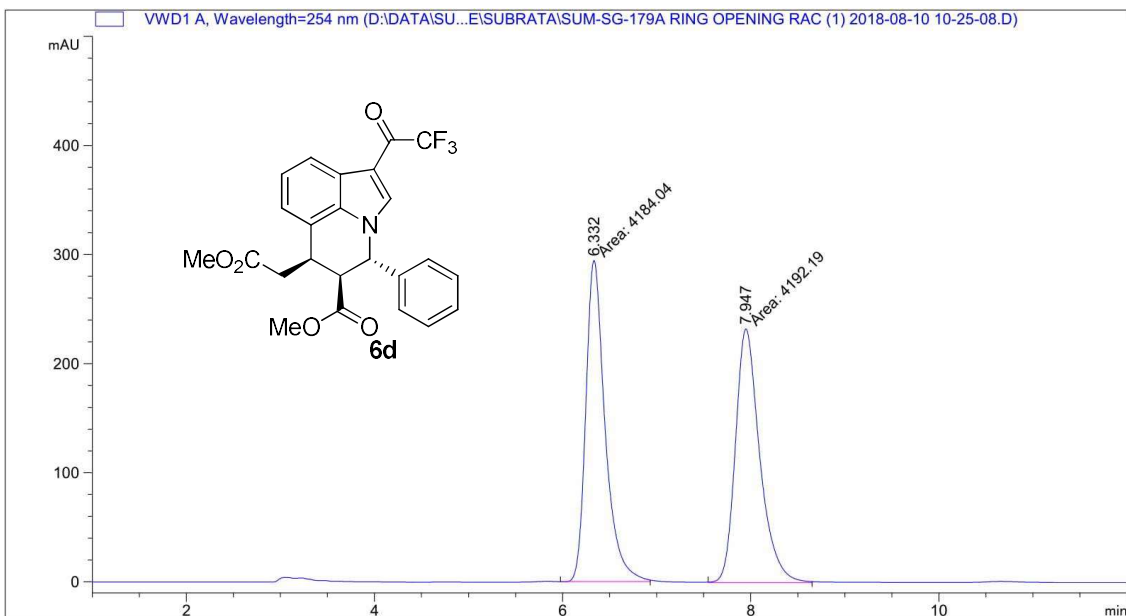


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.521	MM	0.3192	1836.97498	95.91038	98.7655
2	10.369	MM	0.3401	22.96069	1.12525	1.2345

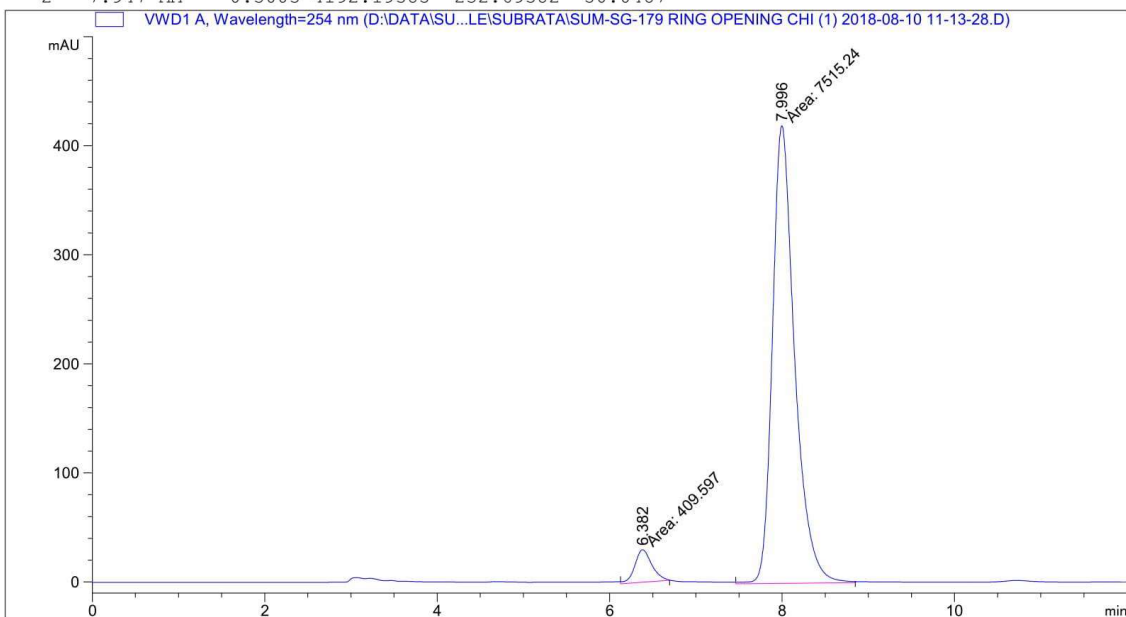
Sample Info : CHIRALPAK IA 10% ipa-Hexane, 1.0 ml/min, 254nm



**(4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxylate (6d)**



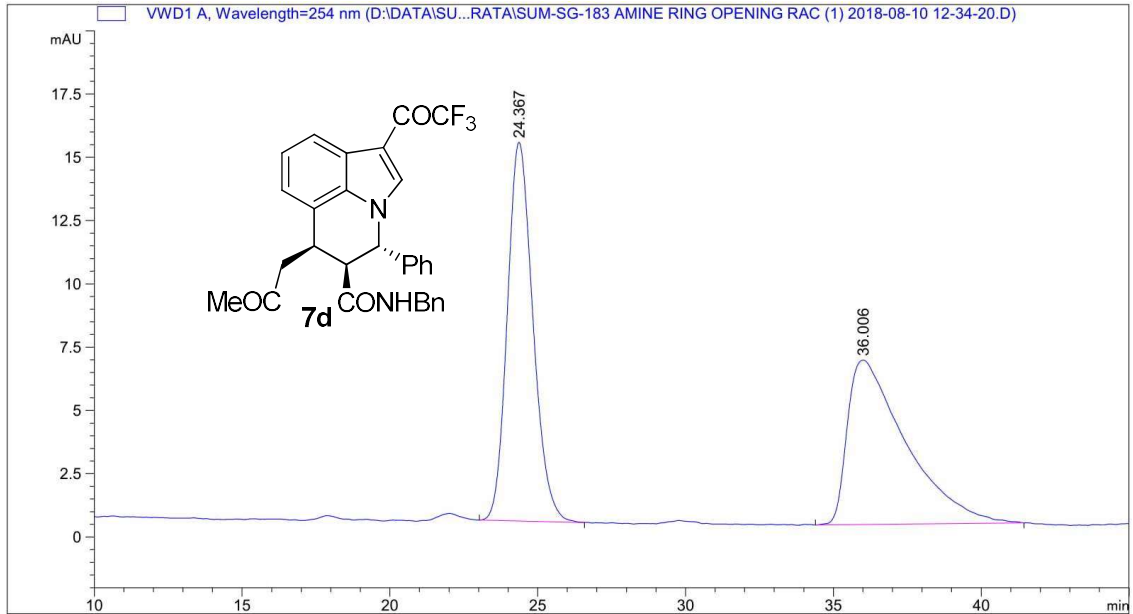
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.332	MM	0.2369	4184.03613	294.34180	49.9513
2	7.947	MM	0.3003	4192.19385	232.69382	50.0487



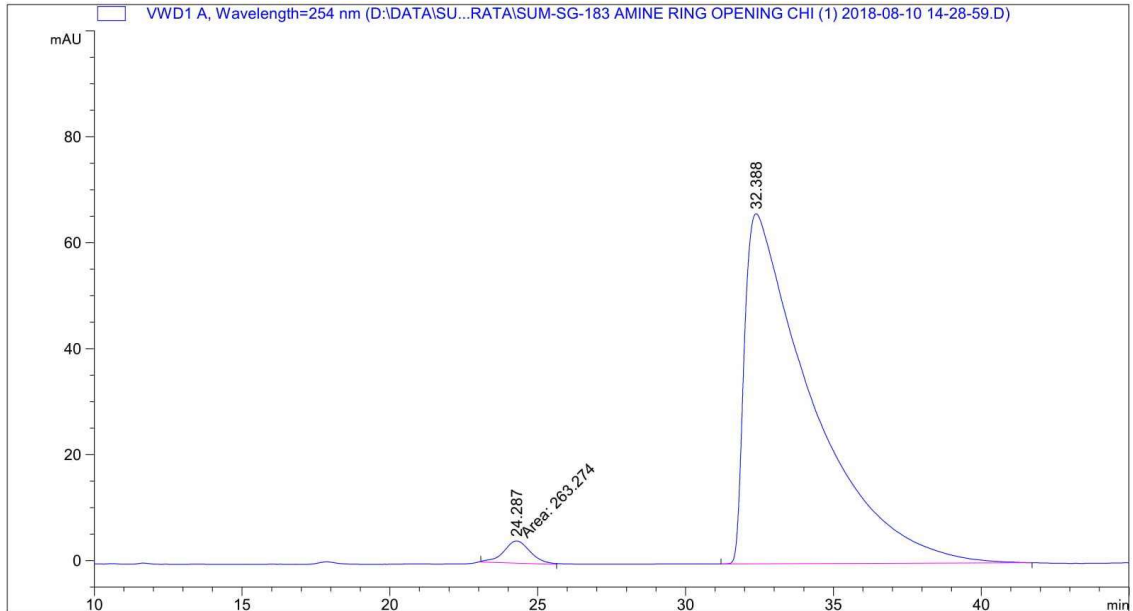
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.382	MM	0.2290	409.59683	29.80632	5.1685
2	7.996	MM	0.2985	7515.24072	419.56036	94.8315

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 1.0 ml/min, 254nm

**(4*S*,5*S*,6*R*)-*N*-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxamide (7d)**



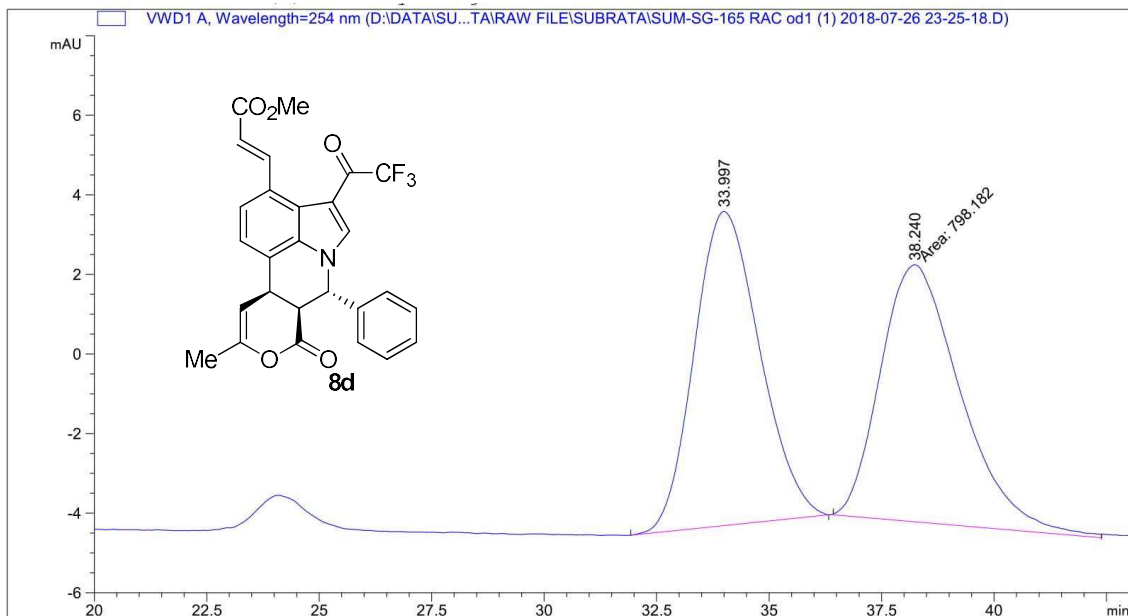
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.367	BB	0.9234	902.17737	14.96303	50.3240
2	36.006	BB	1.8065	890.56012	6.49168	49.6760



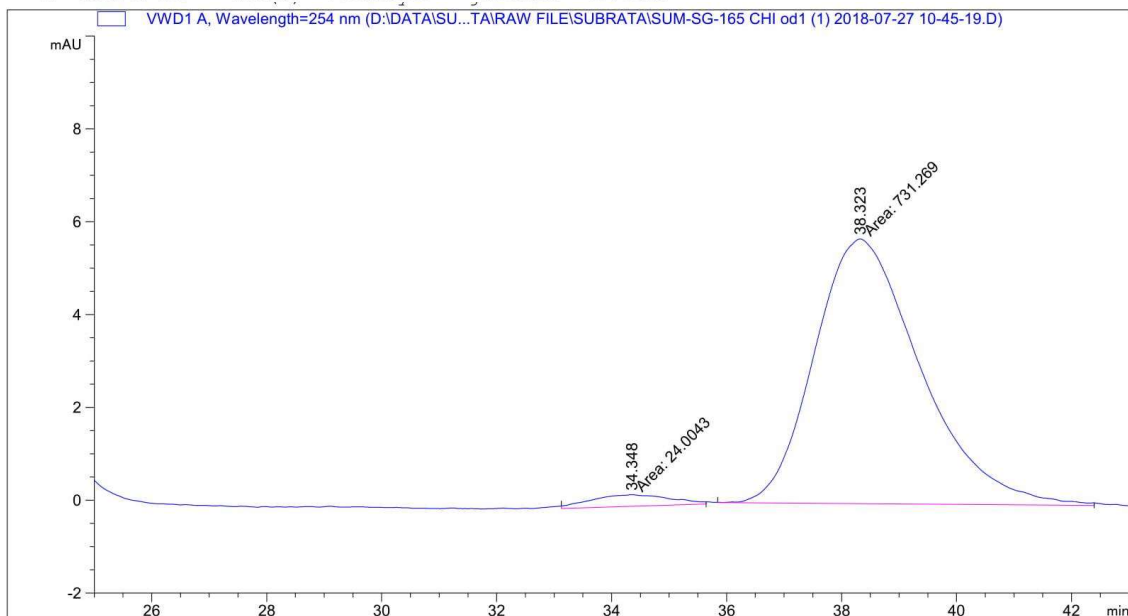
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.287	MM	1.0483	263.27377	4.18583	2.4661
2	32.388	BB	2.0575	1.04124e4	66.07457	97.5339

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 1.0 ml/min, 254nm

**(E)-Methyl 3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)acrylate (8d)**



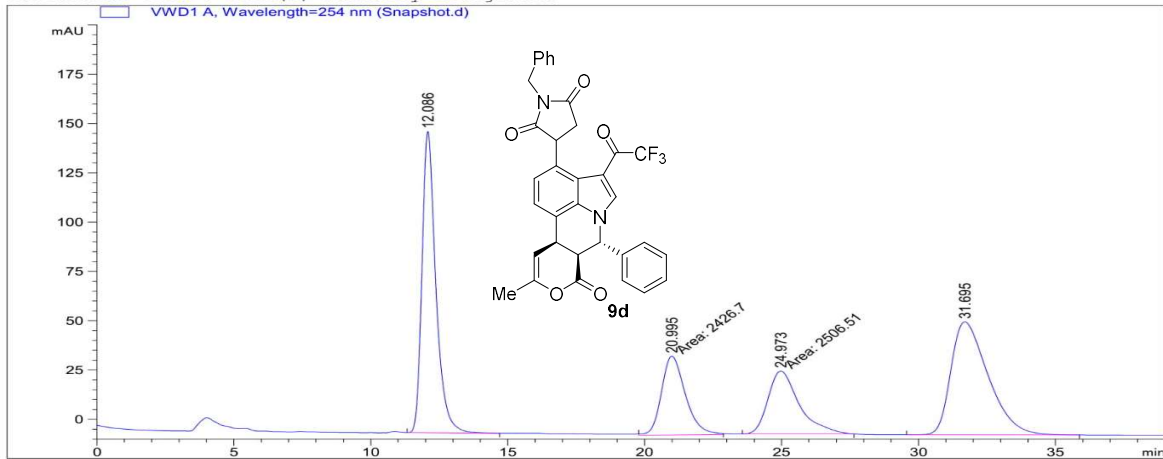
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.997	BB	1.4197	798.42291	7.89624	50.0075
2	38.240	MM	2.0593	798.18188	6.45996	49.9925



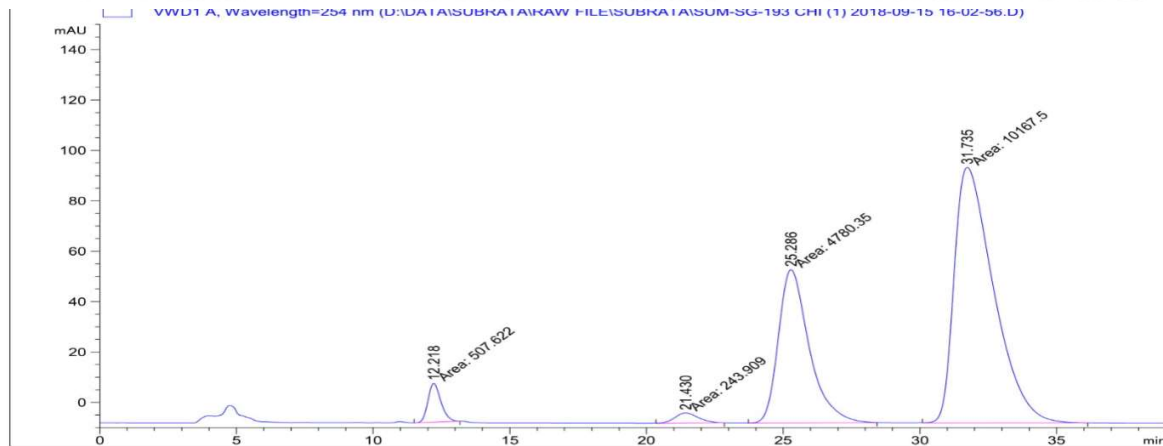
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.348	MM	1.6028	24.00431	2.49612e-1	3.1782
2	38.323	MM	2.1371	731.26868	5.70291	96.8218

Sample Info : Chiralpakcel OD, 20% IPA-Hexane, 1.0 ml/min, 254nm

**1-Benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione (9d)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.086	BB	0.5280	5368.25928	152.76215	34.1754
2	20.995	MM	1.0116	2426.69727	39.98044	15.4489
3	24.973	MM	1.3115	2506.51416	31.85380	15.9570
4	31.695	BB	1.4347	5406.47070	57.30295	34.4187



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.218	MM	0.5485	507.62158	15.42547	3.2334
2	21.430	MM	1.0052	243.90909	4.04396	1.5536
3	25.286	MM	1.3092	4780.35254	60.85360	30.4493
4	31.735	MM	1.6709	1.01675e4	101.41505	64.7637

Sample Info : CHIRALPAK AD 20% ipa-Hexane, 1.0 ml/min, 254nm