

## Supporting Information

### Metal-free synthesis of sulfonylated indolo[2,1-*a*]isoquinolines from sulfur dioxide

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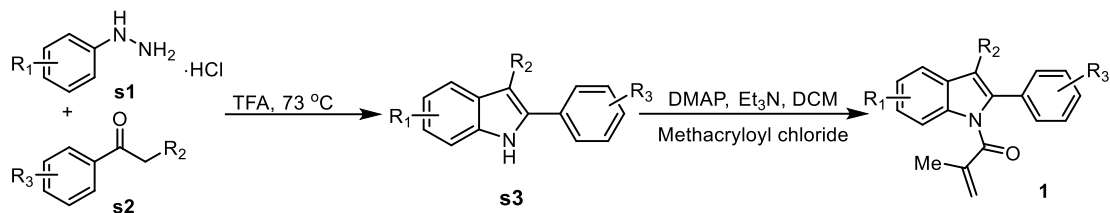
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## 1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200–300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuteriochloroform ( $\text{CDCl}_3$ ) as solvent at room temperature,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.0$  ppm). Data for  $^1\text{H}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for  $^{13}\text{C}$  NMR are reported as chemical shift. Mass spectra were measured on Shimadzu GCMS-QP2010 instrument (EI). Electrospray-ionisation HRMS data were acquired on a Q-TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF.

## 2. General experimental procedure

### 1. General procedure for the synthesis of substrates 1a-1g and 1i-1o.<sup>1</sup>

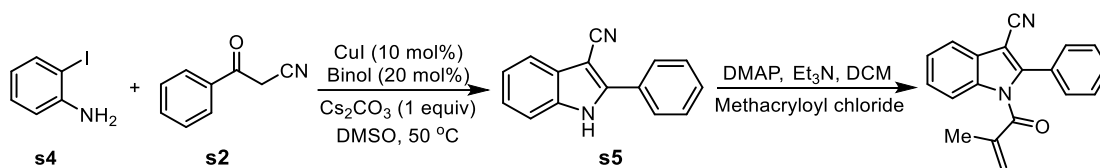


Fischer indole synthesis and the following acylation reaction.

In a 100 mL flask with a stir-bar was charged with substituted phenylhydrazine hydrochloride **s1** (22.0 mmol, 1.1 equiv), ketone **s2** (20.0 mmol, 1.0 equiv) and trifluoroacetic acid (20.0 mL, 1.0 M). After stirring for 12-24 h at 73 °C (oil bath) in a 100 mL round-bottomed flask under N<sub>2</sub> atmosphere, TFA was removed and the residue was portioned between saturated sodium chloride solution (100 mL) and EtOAc (50 mL). The aqueous layer was extracted with EtOAc (50 mL x 3), and the combined organic phase was washed with a saturated solution of brine (50 mL), the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated to afford the residue. The crude product was purified by column chromatography to afford the desired product indole **s3**.

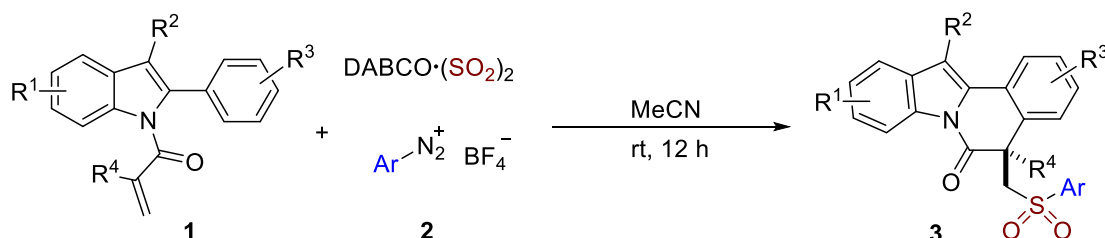
In a 100 mL flask with a stir-bar was charged with indole **s3** (10 mmol, 1.0 equiv) and DMAP (2.0 mmol, 0.2 equiv) in DCM (0.5 M). The solution was stirred at 0 °C, triethylamine (20 mmol, 2.0 equiv) and methacryloyl chloride (20 mmol, 2.0 equiv) was added. The solution was warmed up to room temperature and stirred for 2-3 days under N<sub>2</sub> atmosphere. The mixture was diluted with DCM (50 mL) and saturated NH<sub>4</sub>Cl solution (50 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (50 mL x 3). The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from PE/EtOAc to afford the products **1**.

## 2. General procedure for the synthesis of substrates **1h**.<sup>2</sup>



2-Iodoaniline (9.1 mmol, 1.0 equiv), ketone **s2** (10 mmol, 1.1 equiv), CuI (173 mg, 0.91 mmol, 0.1 equiv), (*rac*)-binol (521 mg, 1.8 mmol, 0.2 equiv), and Cs<sub>2</sub>CO<sub>3</sub> (3.0 g, 9.1 mmol, 1.0 equiv) were placed in a round-bottomed flask under N<sub>2</sub> atmosphere. DMSO (20 mL) was added to the mixture, and the solution was stirred at 50 °C (oil bath) for 2 days. Saturated NH<sub>4</sub>Cl solution was added to the mixture and the resulting mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was subjected to column chromatography on silica gel with PE/EtOAc (8:1) to give **s5**. The following acylation procedure will deliver substrates **1h**.

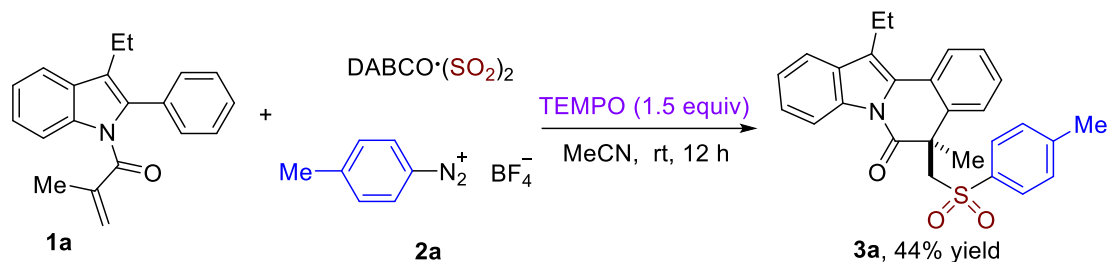
## 3. General procedure for sulfonylated indolo[2,1-*a*]isoquinoline.



All optimization reactions were set up in a glove box under N<sub>2</sub> atmosphere. Substrate **1** (0.2 mmol, 1.0 equiv), DABCO·(SO<sub>2</sub>)<sub>2</sub> (0.2 mmol, 1.0 equiv) and aryldiazonium tetrafluoroborate **2** (0.3 mmol, 1.5 equiv) were added to dry MeCN (4 mL) at room temperature. The resulting mixture was stirred at rt for 12 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate (30 mL), washed with brine (10 mL x 3), dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude product was purified by column chromatography on silica gel to afford the desired product **3**.

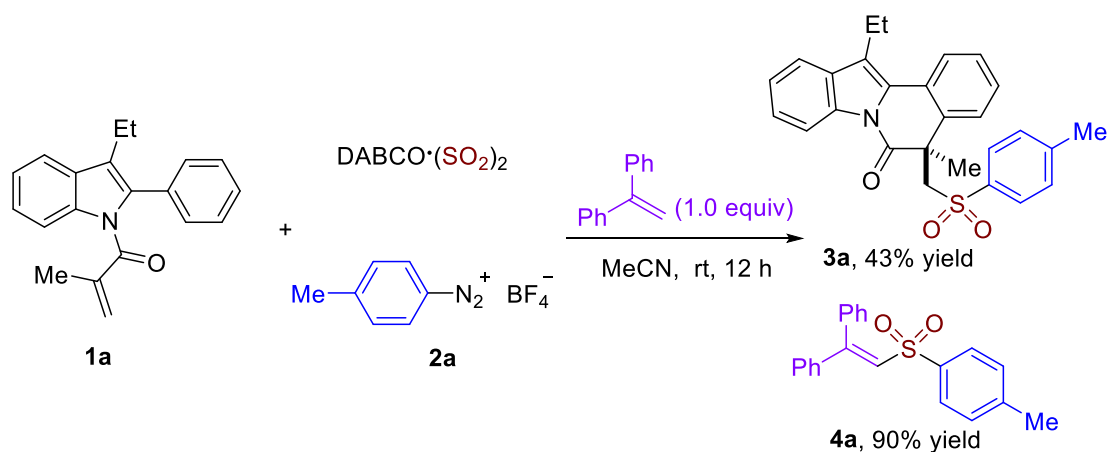
## 4. Radical trapping experiments

### 1. TEMPO trapping experiment



Substrate **1** (0.2 mmol, 1.0 equiv), DABCO·(SO<sub>2</sub>)<sub>2</sub> (0.2 mmol, 1.0 equiv), aryldiazonium tetrafluoroborate **2** (0.3 mmol, 1.5 equiv) and TEMPO (0.3 mmol, 1.5 equiv) were added to dry MeCN (4 mL) at room temperature under N<sub>2</sub> atmosphere for 12 h. The yield of **3a** decreased remarkably.

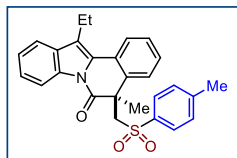
### 2. 1,1-Diphenylethylene trapping experiment



Substrate **1** (0.2 mmol, 1.0 equiv), DABCO·(SO<sub>2</sub>)<sub>2</sub> (0.2 mmol, 1.0 equiv), aryldiazonium tetrafluoroborate **2** (0.3 mmol, 1.5 equiv) and 1,1-diphenylethylene (0.2 mmol, 1.0 equiv) were added to dry MeCN (4 mL) at room temperature under N<sub>2</sub> atmosphere for 12 h. The yield of **3a** decreased remarkably along with the 90% yield of sulfonated alkene **4a**.

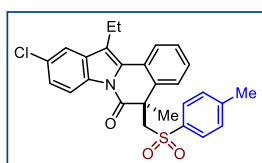
## 5. Characterization of new substrates and all products

### 12-Ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3a)



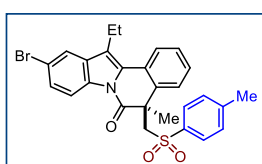
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 154-156 °C; 84.2 mg, 95% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.47–8.41 (m, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.61–7.54 (m, 1H), 7.42–7.32 (m, 6H), 7.27–7.22 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.56 (d, *J* = 14.6 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 1.61 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.9, 144.4, 136.3, 134.4, 134.2, 131.6, 129.2, 128.6, 127.9, 127.9, 127.6, 127.5, 125.9, 125.7, 124.6, 124.3, 121.5, 118.1, 117.0, 64.3, 46.3, 31.9, 21.2, 18.6, 13.3; HRMS (ESI) for C<sub>27</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 444.1628, found 444.1634.

### 10-Chloro-12-ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3b)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 193-195°C; 83.2 mg, 87% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.38 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.35–7.29 (m, 4H), 7.25 (td, *J* = 7.5, 0.8 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 14.6 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 2.16 (s, 3H), 1.62 (s, 3H), 1.42 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 170.0, 144.4, 136.5, 134.5, 133.1, 132.7, 130.0, 130.0, 129.2, 128.0, 127.8, 127.4, 125.6, 125.5, 124.8, 120.6, 118.0, 117.8, 64.4, 46.2, 31.7, 21.3, 18.5, 13.2; HRMS (ESI) for C<sub>27</sub>H<sub>25</sub>ClNO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 478.1238, found 478.1243.

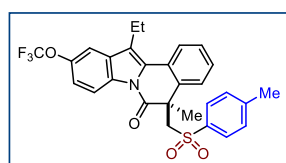
### 10-bromo-12-ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3c)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 222-224°C; 76.5 mg, 73% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.33 (d, *J* = 8.7 Hz, 1H), 7.97 (d,

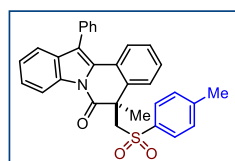
$J = 7.8$  Hz, 1H), 7.70 (d,  $J = 2.0$  Hz, 1H), 7.46–7.39 (m, 2H), 7.35–7.30 (m, 3H), 7.28–7.23 (m, 1H), 6.96 (d,  $J = 8.0$  Hz, 2H), 4.52 (d,  $J = 14.6$  Hz, 1H), 3.92 (d,  $J = 14.6$  Hz, 1H), 3.10 (q,  $J = 7.6$  Hz, 2H), 2.16 (s, 3H), 1.62 (s, 3H), 1.42 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 170.0, 144.4, 136.5, 134.5, 133.5, 133.0, 129.8, 129.2, 128.3, 128.0, 127.8, 127.4, 125.4, 124.8, 120.9, 120.5, 118.4, 117.8, 64.4, 46.3, 31.7, 21.3, 18.5, 13.3; HRMS (ESI) for  $\text{C}_{27}\text{H}_{25}\text{BrNO}_3\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 522.0733, found 522.0739.

### 12-Ethyl-5-methyl-5-(tosylmethyl)-10-(trifluoromethoxy)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (3d)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 162-164°C; 96.2 mg, 91% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.48 (d,  $J = 8.9$  Hz, 1H), 7.99 (d,  $J = 7.9$  Hz, 1H), 7.44–7.39 (m, 2H), 7.35–7.31 (m, 3H), 7.28–7.21 (m, 2H), 6.96 (d,  $J = 8.0$  Hz, 2H), 4.54 (d,  $J = 14.6$  Hz, 1H), 3.94 (d,  $J = 14.6$  Hz, 1H), 3.12 (q,  $J = 7.6$  Hz, 2H), 2.13 (s, 3H), 1.62 (s, 3H), 1.43 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 170.1, 146.1 (q,  $J = 1.5$  Hz), 144.4, 136.4, 134.5, 132.7, 132.5, 130.4, 129.2, 128.1, 128.0, 127.9, 127.5, 125.4, 124.8, 121.6 (q,  $J = 255.1$  Hz), 120.8, 118.7, 117.9, 110.6, 64.3, 46.2, 31.7, 21.1, 18.6, 13.2; HRMS (ESI) for  $\text{C}_{28}\text{H}_{25}\text{F}_3\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 528.1451, found 528.1461.

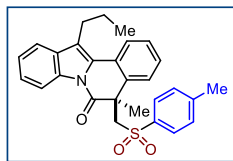
### 5-Methyl-12-phenyl-5-(tosylmethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (3e)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 196-197°C; 79.6 mg, 81% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.48 (d,  $J = 8.2$  Hz, 1H), 7.61–7.35 (m, 9H), 7.30–7.25 (m, 3H), 7.17–7.13 (m, 1H), 7.04–6.97 (m, 3H), 4.59 (d,  $J = 14.6$  Hz, 1H), 3.95 (d,  $J = 14.6$  Hz, 1H), 2.12 (s, 3H), 1.68 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 170.3, 144.5, 136.4, 134.4, 134.2, 134.0, 132.3, 130.1, 129.3, 129.3, 129.1, 128.2, 128.0, 127.9, 127.3, 127.1, 125.9, 125.3, 125.0, 124.7, 120.8, 119.4, 116.8, 64.3, 46.5, 31.8, 21.3; HRMS (ESI) for  $\text{C}_{31}\text{H}_{26}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 492.1628, found

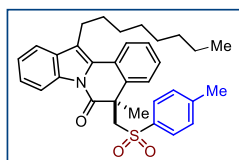
492.1629.

**5-Methyl-12-propyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3f)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 186-187°C; 68.5 mg, 75% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.37–8.34 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.50–7.47 (m, 1H), 7.31–7.20 (m, 6H), 7.15–7.10 (m, 1H), 6.82(d, *J* = 8.1 Hz, 2H), 4.46 (d, *J* = 14.6 Hz, 1H), 3.83 (d, *J* = 14.6 Hz, 1H), 2.99 (t, *J* = 7.9 Hz, 2H), 1.99 (s, 3H), 1.80–1.70 (m, 2H), 1.51 (s, 3H), 1.07 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.9, 144.3, 136.3, 134.2, 134.2, 132.0, 129.1, 128.7, 127.8, 127.8, 127.5, 127.4, 125.8, 125.6, 124.6, 124.2, 120.2, 118.3, 116.9, 64.2, 46.2, 31.8, 27.3, 22.2, 21.2, 14.5; HRMS (ESI) for C<sub>28</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 458.1784, found 458.1793.

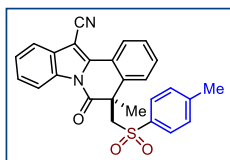
**5-Methyl-12-octyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3g)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 118-120°C; 50.5 mg, 48% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.44–8.41 (m, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.60–7.54 (m, 1H), 7.42–7.32 (m, 6H), 7.25 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.55 (d, *J* = 14.6 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.09 (t, *J* = 8.1 Hz, 2H), 2.09 (s, 3H), 1.85–1.76 (m, 2H), 1.61–1.54 (m, 5H), 1.47–1.30 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.9, 144.4, 136.3, 134.3, 134.2, 132.0, 129.2, 128.7, 127.9, 127.8, 127.5, 127.5, 125.9, 125.7, 124.6, 124.3, 120.5, 118.3, 116.9, 64.3, 46.3, 31.9, 31.9, 30.0, 29.4, 29.3, 28.9, 25.4, 22.6, 21.2, 14.1; HRMS (ESI) for C<sub>33</sub>H<sub>38</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 528.2567, found 528.2577.

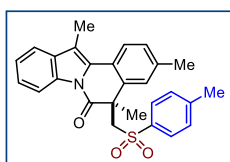
**5-methyl-6-oxo-5-(tosylmethyl)-5,6-dihydroindolo[2,1-a]isoquinoline-12-carbonitrile (3h)**





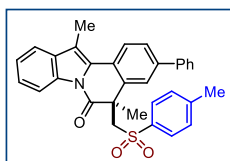
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 224-226°C; 44.7 mg, 51% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.75 (dd, *J* = 8.0, 0.5 Hz, 1H), 8.56–8.51 (m, 1H), 7.79–7.74 (m, 1H), 7.52–7.44 (m, 3H), 7.36–7.27 (m, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 14.7 Hz, 1H), 3.99 (d, *J* = 14.7 Hz, 1H), 2.22 (s, 3H), 1.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 170.6, 144.8, 140.3, 136.5, 135.6, 133.8, 130.8, 129.5, 128.8, 128.6, 127.7, 127.3, 127.2, 126.0, 125.4, 122.4, 119.1, 117.2, 115.4, 88.1, 64.7, 46.7, 31.5, 21.4; HRMS (ESI) for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> calcd. 441.1267, found 441.1271.

### 3,5,12-trimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3i)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 186-188°C; 40.5 mg, 46% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.50–8.45 (m, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.58–7.53 (m, 1H), 7.38–7.27 (m, 4H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.96–6.93 (m, 3H), 4.56 (d, *J* = 14.7 Hz, 1H), 3.92 (d, *J* = 14.7 Hz, 1H), 2.64 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H), 1.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 170.0, 144.1, 137.3, 136.8, 134.2, 134.0, 132.4, 129.4, 129.1, 128.6, 127.8, 127.7, 125.4, 124.9, 124.2, 123.6, 118.1, 116.8, 114.0, 64.4, 46.2, 31.8, 21.3, 21.2, 11.5; HRMS (ESI) for C<sub>27</sub>H<sub>26</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 444.1628, found 444.1635.

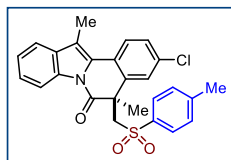
### 5,12-dimethyl-3-phenyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3j)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 203-204°C; 97.8 mg, 97% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.55–8.49 (m, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.63–7.58 (m, 2H), 7.50–7.32 (m, 10H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 14.8 Hz, 1H), 4.03 (d, *J* = 14.8 Hz, 1H), 2.70 (s, 3H), 2.04 (s, 3H), 1.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 170.0, 144.5, 140.0, 139.8, 136.9, 134.7, 134.4, 132.4, 129.2, 129.1, 128.8, 127.8, 127.7, 126.9, 126.4, 126.1, 125.8, 125.5, 125.3, 124.4, 118.3, 116.9, 115.0, 64.4, 46.7, 31.9, 21.2, 11.6; HRMS (ESI) for C<sub>32</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>

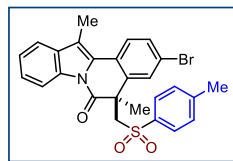
calcd. 506.1784, found 506.1791.

### 3-chloro-5,12-dimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3k)



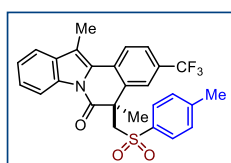
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 236-238°C; 71.1 mg, 77% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.52–8.49 (m, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.60–7.57 (m, 1H), 7.42–7.28 (m, 5H), 7.08 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.56 (d, *J* = 14.8 Hz, 1H), 3.86 (d, *J* = 14.8 Hz, 1H), 2.64 (s, 3H), 2.23 (s, 3H), 1.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.3, 144.6, 136.7, 135.9, 134.3, 133.2, 132.2, 129.4, 128.3, 128.0, 127.5, 127.4, 126.2, 126.0, 124.9, 124.5, 118.4, 116.9, 115.5, 64.2, 46.3, 31.5, 21.4, 11.6; HRMS (ESI) for C<sub>26</sub>H<sub>23</sub>ClNO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 464.1082, found 464.1078.

### 3-bromo-5,12-dimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3l)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 240-241°C; 69.7 mg, 69% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.53–8.50 (m, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.61–7.58 (m, 1H), 7.47–7.30 (m, 5H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.57 (d, *J* = 14.8 Hz, 1H), 3.86 (d, *J* = 14.8 Hz, 1H), 2.65 (s, 3H), 2.26 (s, 3H), 1.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.3, 144.6, 136.8, 136.1, 134.4, 132.2, 130.9, 130.4, 129.5, 128.4, 127.5, 126.4, 126.1, 125.4, 124.5, 121.3, 118.5, 117.0, 115.7, 64.3, 46.2, 31.5, 21.5, 11.6; HRMS (ESI) for C<sub>26</sub>H<sub>22</sub>BrNO<sub>3</sub>SNa [M+Na]<sup>+</sup> calcd. 530.0396, found 530.0406.

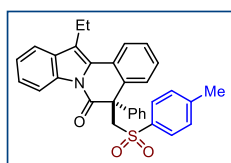
### 5,12-dimethyl-5-(tosylmethyl)-3-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3m)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 222-224°C; 58.8 mg, 59% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.47 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.37–7.27

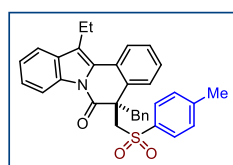
(m, 3H), 7.20 (d,  $J = 8.3$  Hz, 2H), 6.91 (d,  $J = 8.0$  Hz, 2H), 4.51 (d,  $J = 14.9$  Hz, 1H), 3.86 (d,  $J = 14.9$  Hz, 1H), 2.60 (s, 3H), 2.13 (s, 3H), 1.55 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 169.3, 144.7, 136.8, 134.8, 134.5, 132.0, 131.4, 130.3, 129.6 (q,  $J = 1.0$  Hz), 129.4, 128.8 (q,  $J = 32.7$  Hz), 127.9, 127.4, 126.6, 125.3, 124.6, 124.5 (q,  $J = 3.6$  Hz), 124.2 (q,  $J = 3.8$  Hz), 123.5 (q,  $J = 302.2$  Hz), 118.8, 117.3, 117.0, 64.3, 46.4, 31.4, 21.3, 11.7; HRMS (ESI) for  $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 498.1345, found 498.1354.

### 12-ethyl-5-phenyl-5-(tosylmethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (3n)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 92-94°C; 42.7 mg, 42% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.34–8.28 (m, 1H), 7.98 (d,  $J = 8.1$  Hz, 1H), 7.51–7.36 (m, 3H), 7.26–7.20 (m, 2H), 7.14–7.06 (m, 5H), 7.00–6.96 (m, 4H), 5.11 (d,  $J = 14.2$  Hz, 1H), 4.21 (d,  $J = 14.2$  Hz, 1H), 3.16–3.02 (m, 2H), 2.10 (s, 3H), 1.39 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 168.1, 144.4, 142.1, 137.2, 134.7, 133.4, 131.6, 129.7, 129.3, 128.9, 128.7, 128.3, 128.0, 127.9, 127.5, 127.3, 126.6, 125.7, 124.6, 124.3, 121.9, 118.2, 116.9, 63.5, 54.1, 21.3, 18.6, 13.4; HRMS (ESI) for  $\text{C}_{32}\text{H}_{28}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 506.1784, found 506.1792.

### 5-benzyl-12-ethyl-5-(tosylmethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (3o)

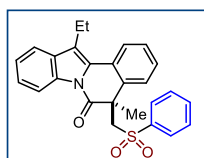


Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; mp 217-219°C; 60.7 mg, 58% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.45 (dd,  $J = 7.9, 0.6$  Hz, 1H), 7.74 (d,  $J = 7.6$  Hz, 1H), 7.43–7.24 (m, 8H), 6.97 (d,  $J = 8.0$  Hz, 2H), 6.82 (t,  $J = 7.4$  Hz, 1H), 6.66 (t,  $J = 7.8$  Hz, 2H), 6.35 (d,  $J = 7.3$  Hz, 2H), 4.78 (d,  $J = 14.5$  Hz, 1H), 4.11 (d,  $J = 14.5$  Hz, 1H), 3.30 (d,  $J = 12.4$  Hz, 1H), 2.96 (d,  $J = 12.4$  Hz, 1H), 2.92–2.78 (m, 2H), 2.10 (s, 3H), 1.18 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 168.7, 144.5, 136.8, 134.0, 133.0, 131.6, 131.3, 129.3, 129.2, 128.2, 128.1, 127.9, 127.9, 127.8, 127.3, 127.1, 127.0, 125.4, 124.2, 124.1, 121.1, 117.9, 116.7, 63.1, 52.4, 51.0, 21.2, 18.2, 13.2; HRMS (ESI) for  $\text{C}_{33}\text{H}_{30}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 520.1941, found

520.1948.

**12-ethyl-5-methyl-5-((phenylsulfonyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one**

**(3p)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1);

White solid; 151-154°C; 56.3 mg, 66% yield; <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>) δ (ppm) = 8.56–8.51 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H),

7.61–7.58 (m, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.40–7.33 (m, 4H), 7.28–7.21 (m, 3H),

7.16 (t, *J* = 7.7 Hz, 1H), 4.58 (d, *J* = 14.6 Hz, 1H), 3.96 (d, *J* = 14.6 Hz, 1H), 3.15 (q, *J*

= 7.6 Hz, 2H), 1.62 (s, 3H), 1.42 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

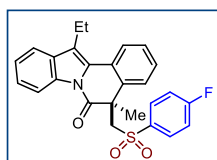
(ppm) = 170.1, 140.1, 134.4, 134.2, 133.1, 131.6, 128.7, 128.5, 127.9, 127.7, 127.5,

127.1, 126.0, 125.8, 124.7, 124.4, 121.6, 118.2, 117.0, 64.2, 46.4, 31.5, 18.6, 13.3;

HRMS (ESI) for C<sub>26</sub>H<sub>24</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 430.1471, found 430.1474.

**12-ethyl-5-(((4-fluorophenyl)sulfonyl)methyl)-5-methylindolo[2,1-a]isoquinolin-**

**6(5H)-one (3q)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1);

White solid; 149-151°C; 58.4 mg, 65% yield; <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>) δ (ppm) = 8.52–8.49 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H),

7.62–7.59 (m, 1H), 7.52–7.47 (m, 2H), 7.43–7.34 (m, 3H), 7.30–7.20 (m, 2H),

6.90–6.85 (m, 2H), 4.58 (d, *J* = 14.7 Hz, 1H), 3.96 (d, *J* = 14.7 Hz, 1H), 3.16 (q, *J*

= 7.6 Hz, 2H), 1.63 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

(ppm) = 170.0, 165.4 (d, *J* = 254.7 Hz), 135.9 (d, *J* = 3.0 Hz), 134.3 (d, *J* = 18.9 Hz),

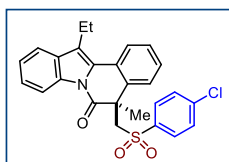
131.6, 130.7, 130.6, 128.0, 127.6, 127.2 (d, *J* = 231.3 Hz), 127.1, 125.9, 124.8, 124.5,

121.8, 118.3, 116.9, 116.0, 115.8, 64.4, 46.4, 31.6, 18.6, 13.3; HRMS (ESI) for

C<sub>26</sub>H<sub>23</sub>FNO<sub>3</sub>S [M+Na]<sup>+</sup> calcd. 448.1377, found 448.1384.

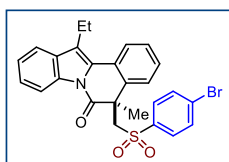
**5-(((4-chlorophenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-**

**6(5H)-one (3r)**



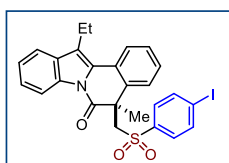
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; 153-154°C; 60.0 mg, 73% yield; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ (ppm) = 8.50–8.47 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.62–7.59 (m, 1H), 7.42–7.34 (m, 5H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 4.57 (d, *J* = 14.7 Hz, 1H), 3.95 (d, *J* = 14.7 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 1.62 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ (ppm) = 169.9, 140.1, 138.1, 134.3, 134.1, 131.6, 129.3, 128.9, 128.3, 128.0, 127.6, 127.2, 126.0, 126.0, 124.7, 124.5, 121.9, 118.3, 116.9, 64.4, 46.4, 31.6, 18.6, 13.3; HRMS (ESI) for C<sub>26</sub>H<sub>23</sub>ClNO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 464.1082, found 464.1077.

### 5-(((4-bromophenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3s)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 5/1); White solid; 166-168°C; 92.4 mg, 91% yield; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ (ppm) = 8.48 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.60–7.58 (m, 1H), 7.43–7.34 (m, 3H), 7.30–7.24 (m, 5H), 7.22–7.17 (m, 1H), 4.56 (d, *J* = 14.7 Hz, 1H), 3.94 (d, *J* = 14.7 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 1.61 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ (ppm) = 169.8, 138.6, 134.3, 134.0, 131.9, 131.5, 129.3, 128.7, 128.3, 128.0, 127.6, 127.2, 126.0, 125.9, 124.7, 124.5, 121.8, 118.3, 116.9, 64.3, 46.3, 31.6, 18.6, 13.3; HRMS (ESI) for C<sub>23</sub>BrH<sub>23</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 508.0577, found 508.0576.

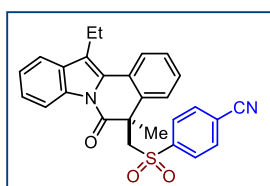
### 12-ethyl-5-(((4-iodophenyl)sulfonyl)methyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3t)



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 5/1); White solid; 184-186°C; 91.6 mg, 82% yield; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ (ppm) = 8.47 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.62–7.59 (m, 1H), 7.53–7.49 (m, 2H), 7.44–7.34 (m, 3H), 7.25 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.22–7.17 (m, 1H), 7.15–7.12 (m, 2H), 4.55 (d, *J* = 14.7 Hz, 1H), 3.93 (d, *J* = 14.7 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 1.61 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C**

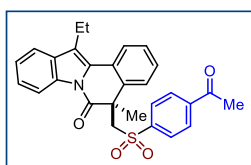
**NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  (ppm) = 169.8, 139.1, 137.9, 134.3, 134.0, 131.5, 129.1, 128.3, 128.0, 127.6, 127.2, 126.1, 125.9, 124.7, 124.6, 121.8, 118.3, 116.9, 101.5, 64.3, 46.3, 31.6, 18.6, 13.3; HRMS (ESI) for C<sub>26</sub>H<sub>23</sub>INO<sub>3</sub>S [M+H]<sup>+</sup> calcd. 556.0438, found 556.0446.

**4-(((12-ethyl-5-methyl-6-oxo-5,6-dihydroindolo[2,1-*a*]isoquinolin-5-yl)methyl)sulfonyl)benzonitrile (3u)**



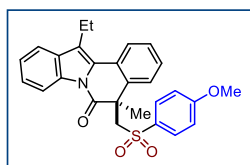
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; 189-191°C; 69.4 mg, 76% yield; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  (ppm) = 8.45–8.40 (m, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.64–7.55 (m, 3H), 7.47–7.37 (m, 5H), 7.28–7.18 (m, 2H), 4.59 (d, *J* = 14.8 Hz, 1H), 3.98 (d, *J* = 14.8 Hz, 1H), 3.16 (q, *J* = 7.6 Hz, 2H), 1.64 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  (ppm) = 169.7, 143.7, 134.2, 133.9, 132.3, 131.5, 128.5, 128.2, 127.7, 127.1, 126.2, 126.0, 124.9, 124.8, 122.2, 118.4, 116.9, 116.8, 116.8, 64.3, 46.3, 31.5, 18.6, 13.3; HRMS (ESI) for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> calcd. 455.1424, found 455.1425.

**5-(((4-acetylphenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (3v)**



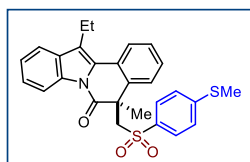
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; 202-204°C; 84.8 mg, 90% yield; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  (ppm) = 8.41–8.38 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.59–7.52 (m, 3H), 7.43–7.31 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.61 (d, *J* = 14.7 Hz, 1H), 3.98 (d, *J* = 14.7 Hz, 1H), 3.14 (q, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.63 (s, 3H), 1.43 (t, *J* = 7.5 Hz, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  (ppm) = 196.3, 169.7, 142.8, 139.9, 134.2, 133.9, 131.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 125.8, 124.7, 124.6, 121.8, 118.3, 116.9, 64.2, 46.2, 31.8, 26.6, 18.5, 13.3; HRMS (ESI) for C<sub>28</sub>H<sub>26</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 472.1577, found 472.1583.

**12-ethyl-5-(((4-methoxyphenyl)sulfonyl)methyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3w)**



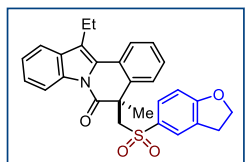
Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; 138-140°C; 74.2 mg, 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.48–8.43 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.59–7.56 (m, 1H), 7.43–7.32 (m, 6H), 7.27 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.9 Hz, 2H), 4.57 (d, *J* = 14.6 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.54 (s, 3H), 3.14 (q, *J* = 7.6 Hz, 2H), 1.61 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.9, 163.2, 134.3, 134.2, 131.5, 130.7, 130.1, 128.5, 127.9, 127.6, 127.5, 125.8, 125.7, 124.6, 124.3, 121.5, 118.1, 117.0, 113.7, 64.4, 55.3, 46.3, 31.9, 18.6, 13.3; HRMS (ESI) for C<sub>27</sub>H<sub>26</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 460.1577, found 460.1581.

**12-ethyl-5-methyl-5-(((4-(methylthio)phenyl)sulfonyl)methyl)indolo[2,1-a]isoquinolin-6(5H)-one (3x)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1); White solid; 146-148°C; 59.7 mg, 63% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.47–8.43 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.60–7.57 (m, 1H), 7.44–7.24 (m, 7H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.58 (d, *J* = 14.6 Hz, 1H), 3.93 (d, *J* = 14.6 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.61 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 169.9, 146.9, 134.8, 134.3, 134.2, 131.6, 128.5, 128.1, 127.9, 127.6, 127.4, 125.9, 125.8, 124.7, 124.6, 124.4, 121.6, 118.2, 116.9, 64.4, 46.3, 31.9, 18.6, 14.4, 13.3; HRMS (ESI) for C<sub>27</sub>H<sub>26</sub>NO<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> calcd. 476.1349, found 476.1357.

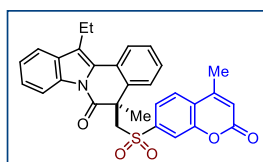
**5-(((2,3-dihydrobenzofuran-5-yl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3y)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 2/1); White solid; 184-186°C; 90.1mg, 95% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 8.48–8.43 (m, 1H), 7.97 (d, *J* = 8.0 Hz,

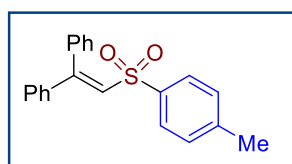
1H), 7.59–7.55 (m, 1H), 7.43–7.33 (m, 4H), 7.31–7.25 (m, 1H), 7.18–7.14 (m, 2H), 6.48–6.45 (m, 1H), 4.57 (d,  $J = 14.6$  Hz, 1H), 4.33–4.21 (m, 2H), 3.93 (d,  $J = 14.6$  Hz, 1H), 3.13 (q,  $J = 7.6$  Hz, 2H), 2.88–2.68 (m, 2H), 1.61 (s, 3H), 1.42 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 169.9, 164.3, 134.2, 131.5, 130.2, 129.9, 128.5, 127.8, 127.7, 127.6, 127.5, 125.8, 125.7, 125.3, 124.5, 124.4, 121.3, 118.1, 116.9, 109.0, 72.1, 64.6, 46.2, 32.1, 28.5, 18.5, 13.2; HRMS (ESI) for  $\text{C}_{28}\text{H}_{26}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 472.1577, found 472.1585.

**12-ethyl-5-methyl-5-(((4-methyl-2-oxo-2H-chromen-7-yl)sulfonyl)methyl)indolo [2,1-a]isoquinolin-6(5H)-one (3z)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 2/1); White solid; 188–190°C; 72.8 mg, 71% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.30–8.24 (m, 1H), 8.00 (d,  $J = 8.0$  Hz, 1H), 7.52–7.37 (m, 4H), 7.32–7.26 (m, 4H), 7.17 (d,  $J = 1.4$  Hz, 1H), 6.16 (d,  $J = 0.6$  Hz, 1H), 4.64 (d,  $J = 14.7$  Hz, 1H), 3.98 (d,  $J = 14.7$  Hz, 1H), 3.21–3.05 (m, 2H), 2.14 (s, 3H), 1.63 (s, 3H), 1.41 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 169.4, 159.1, 152.2, 150.5, 140.6, 134.0, 133.5, 131.4, 128.3, 128.2, 127.8, 127.7, 125.7, 125.6, 125.0, 124.8, 124.7, 123.5, 123.5, 122.1, 118.4, 117.6, 117.4, 116.7, 64.3, 46.0, 32.3, 18.5, 18.4, 13.3; HRMS (ESI) for  $\text{C}_{30}\text{H}_{26}\text{NO}_5\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 512.1526, found 512.1534.

**(2-tosylethene-1,1-diyl)dibenzene (4a)**



Purification by flash chromatography (*n*-hexane/ ethyl acetate = 3/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.47 (d,  $J = 8.3$  Hz, 2H), 7.39–7.34 (m, 2H), 7.32–7.27 (m, 4H), 7.21–7.18 (m, 2H), 7.15 (d,  $J = 8.2$  Hz, 2H), 7.11–7.08 (m, 2H), 6.99 (s, 1H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 154.7, 143.7, 139.2, 138.5, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.6, 21.5; HRMS (ESI) for  $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 335.1100, found 335.1108.

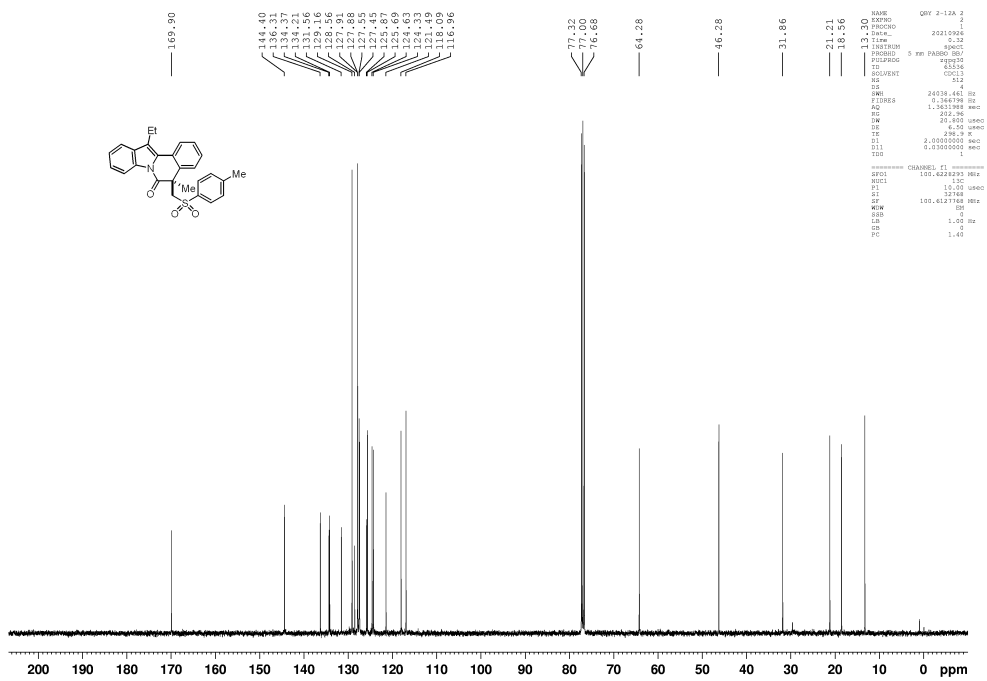
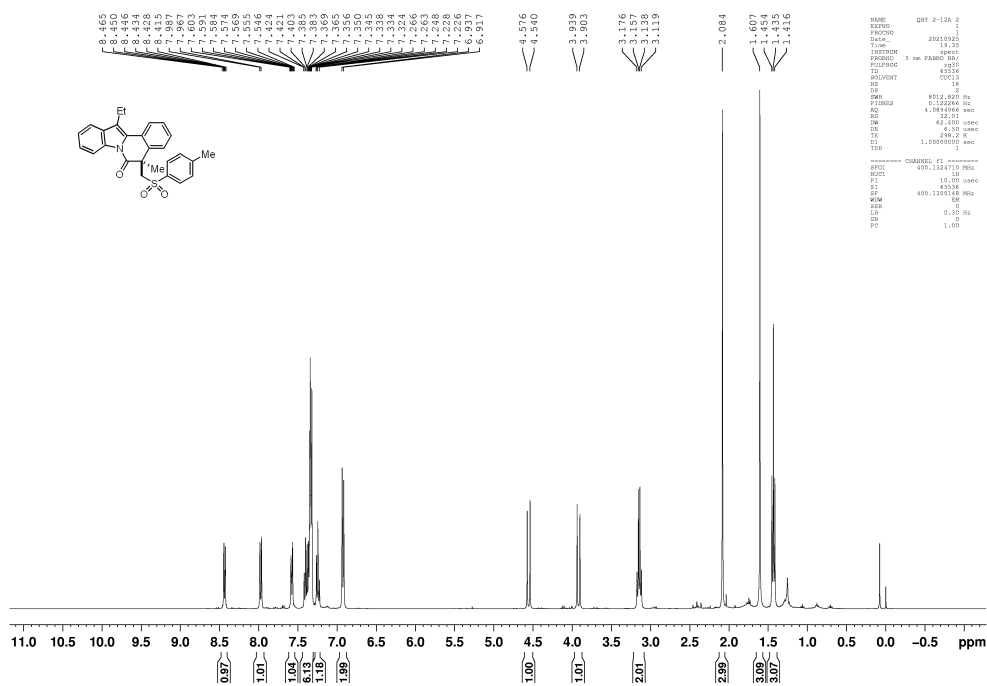


## 6. References

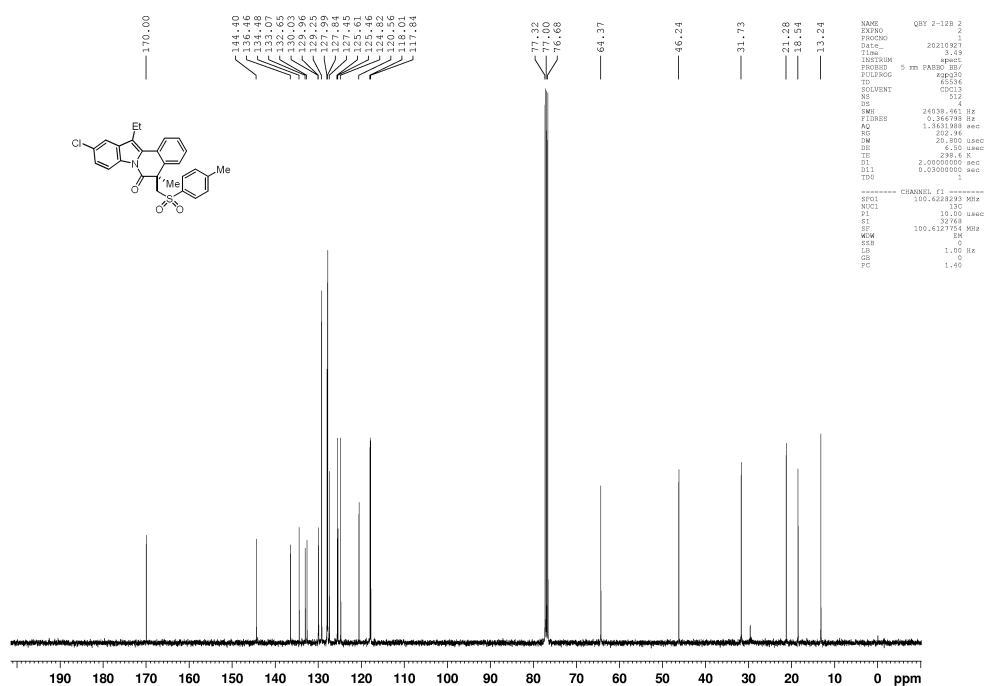
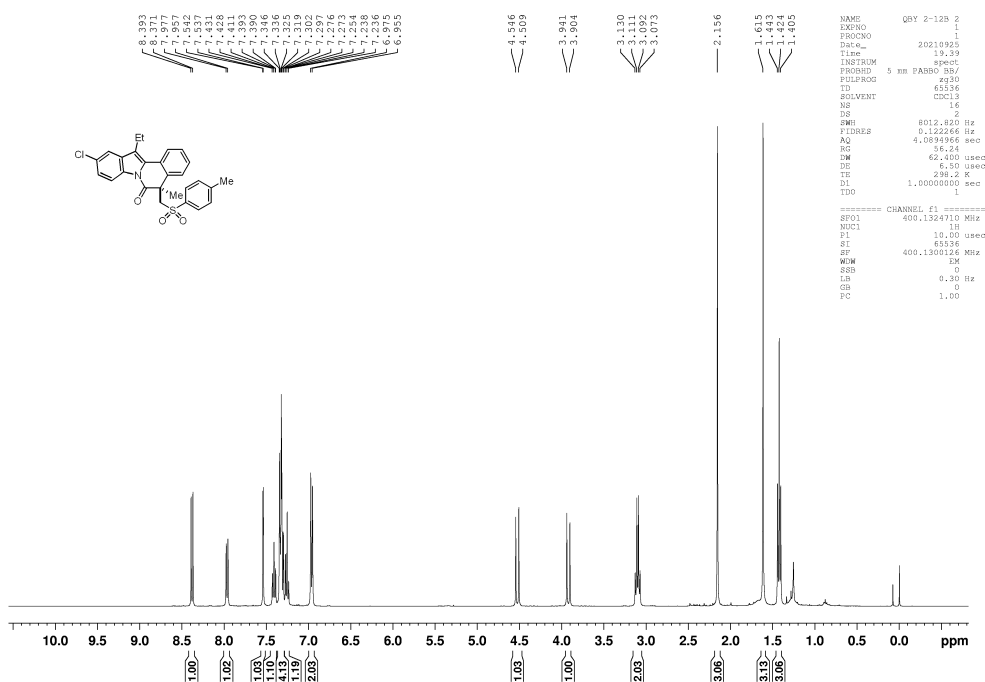
- (1) (a) Yuan, X.; Duan, X.; Cui, Y.-S.; Sun, Q.; Qin, L.-Z.; Zhang, X.-P.; Liu, J.; Wu, M.-Y.; Qiu, J.-K.; Guo, K. *Org. Lett.* **2021**, *23*, 1950–1954. (b) Yuan, Y.; Zheng, Y.; Xu, B.; Liao, J.; Bu, F.; Wang, S.; Hu, J.-G.; Lei, A. *ACS Catal.* **2020**, *10*, 6676–6681. (c) Wei, Y.-L.; Chen, J.-Q.; Sun, B.; Xu, P.-F. *Chem. Commun.* **2019**, *55*, 5922–5925.
- (2) Yamauchi, D.; Nishimura, T.; Yorimitsu, H. *Chem. Commun.* **2017**, *53*, 2760–2763.

# 7. NMR spectra of compounds

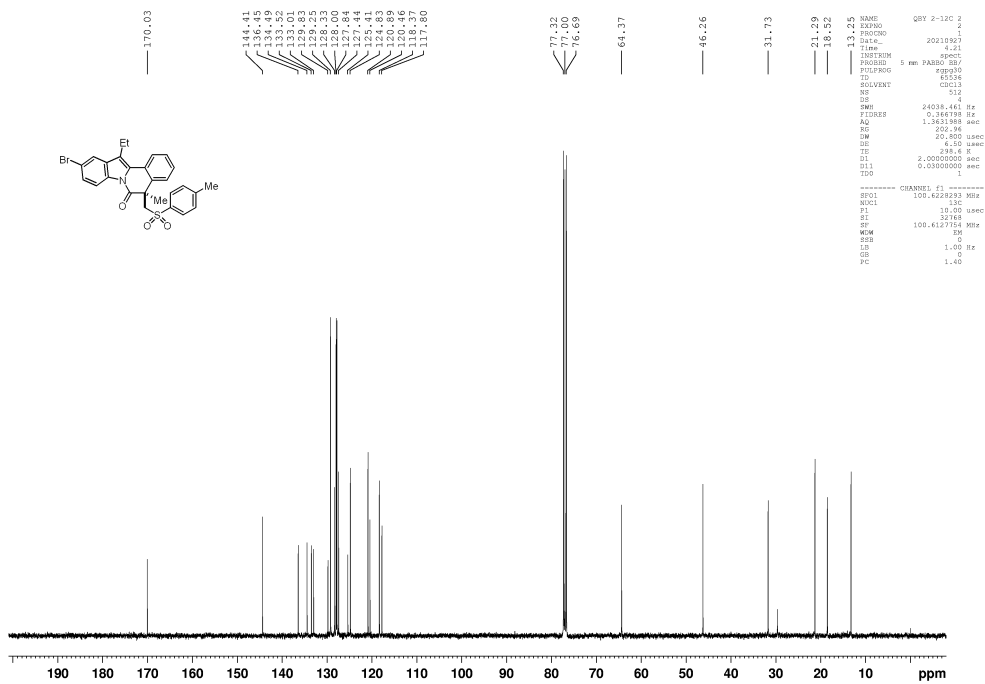
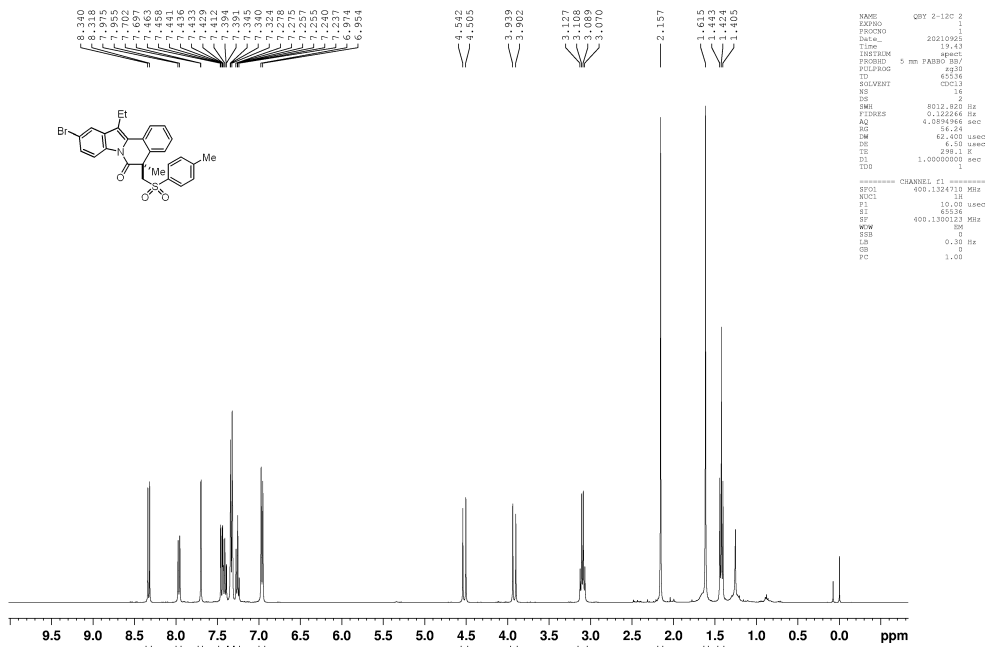
## 12-Ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3a)



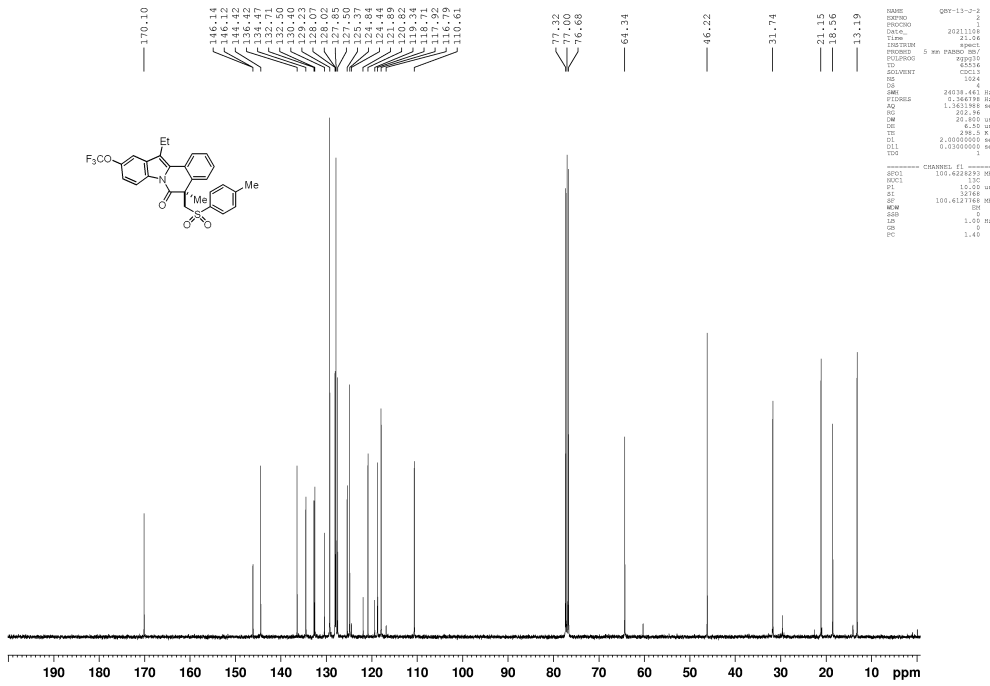
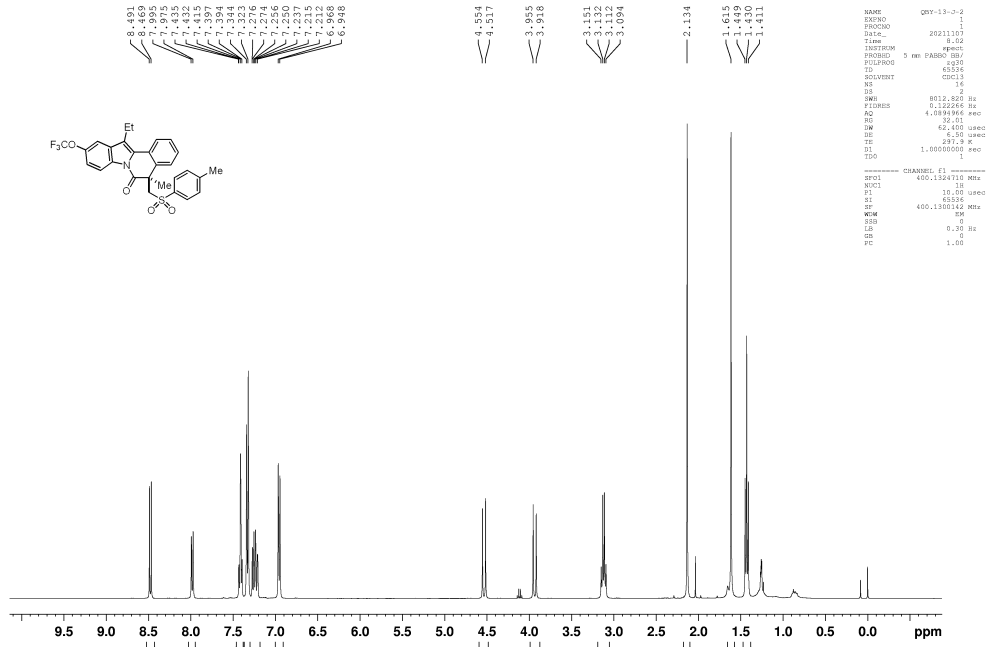
# 10-Chloro-12-ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3b)



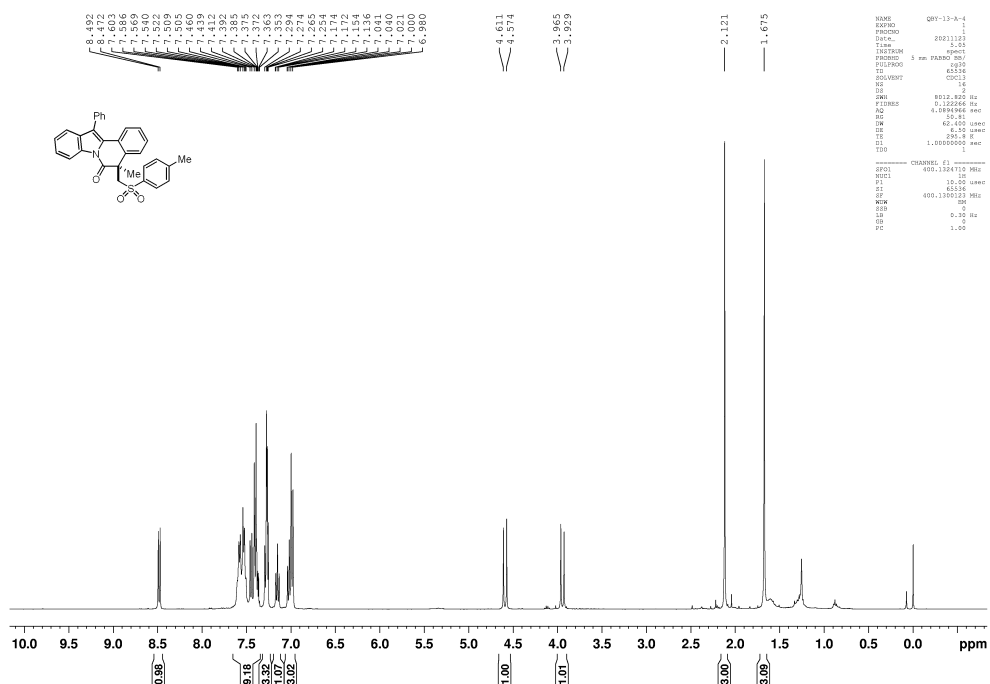
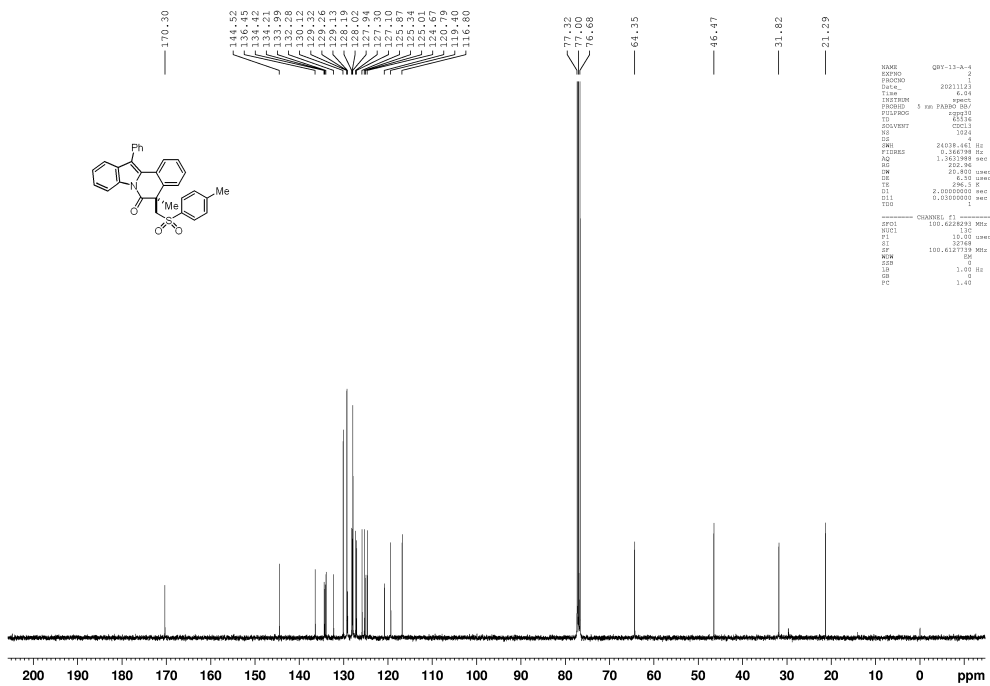
# 10-bromo-12-ethyl-5-methyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3c)



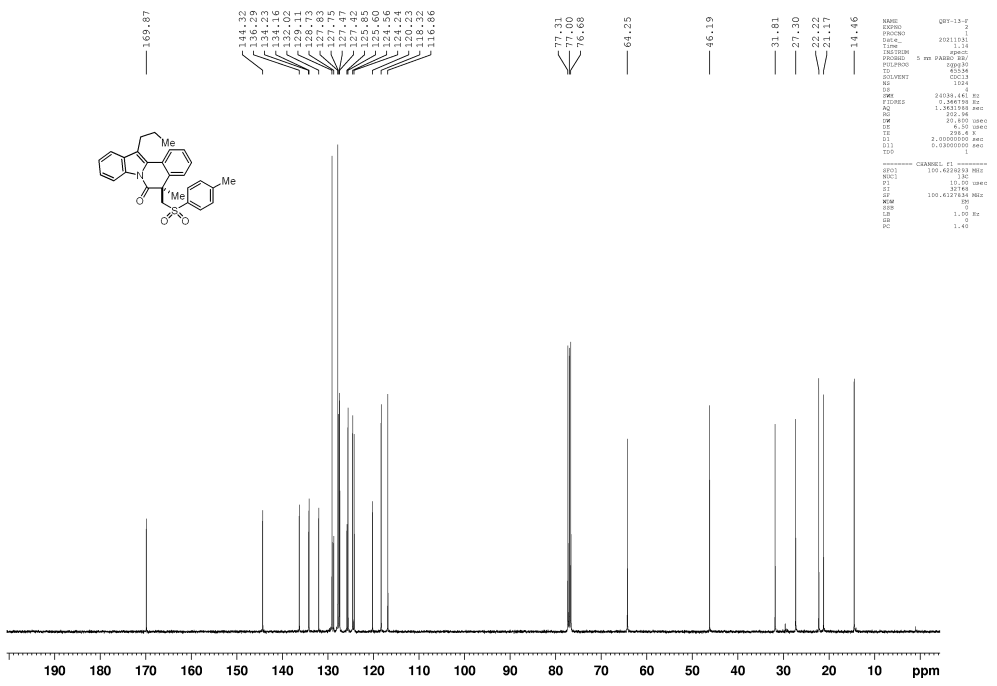
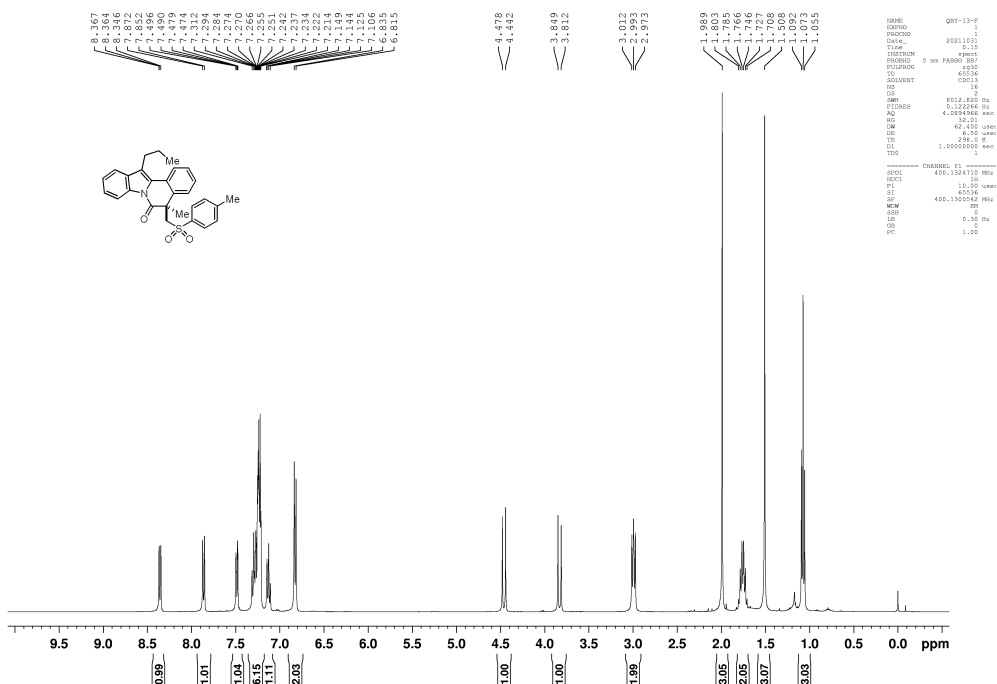
12-Ethyl-5-methyl-5-(tosylmethyl)-10-(trifluoromethoxy)indolo[2,1-a]isoquinolin-6(5H)-one (3d)



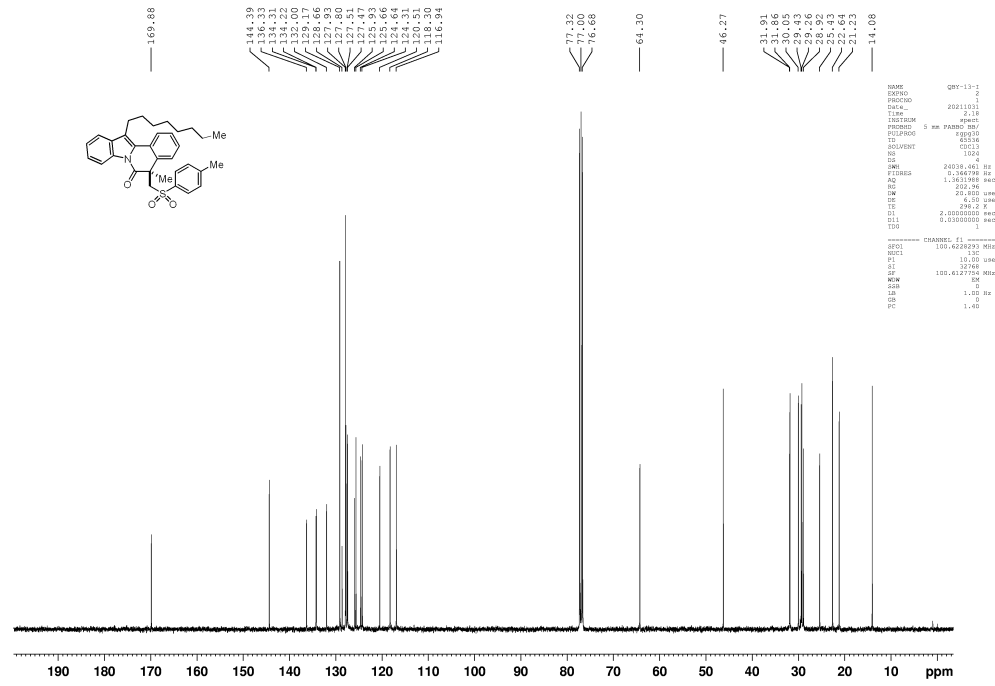
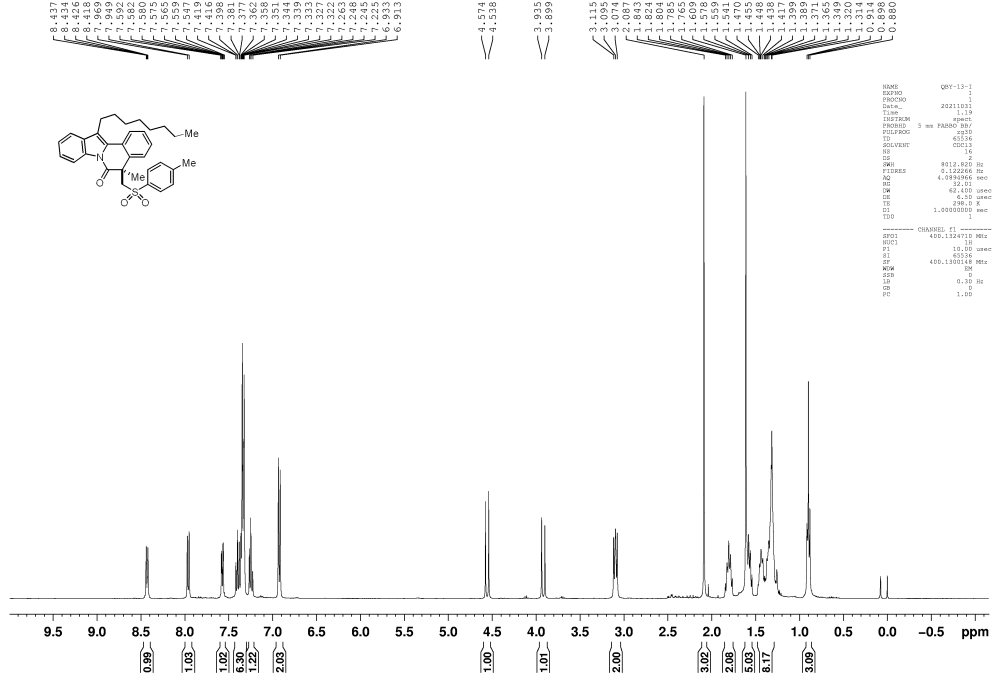
# 5-Methyl-12-phenyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3e)



# 5-Methyl-12-propyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3f)

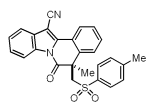
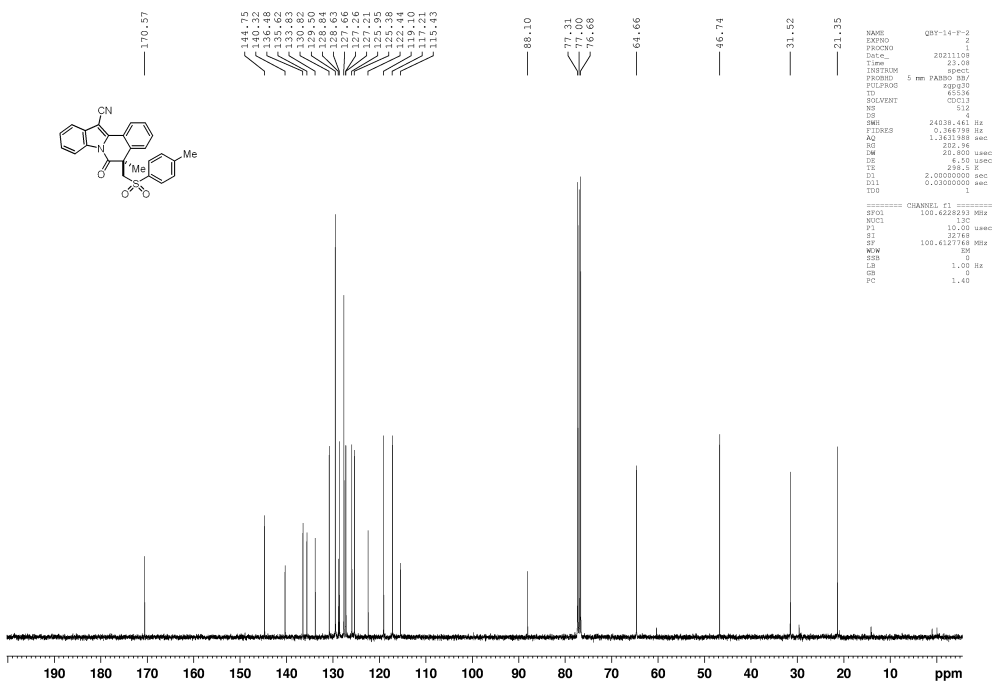
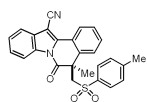
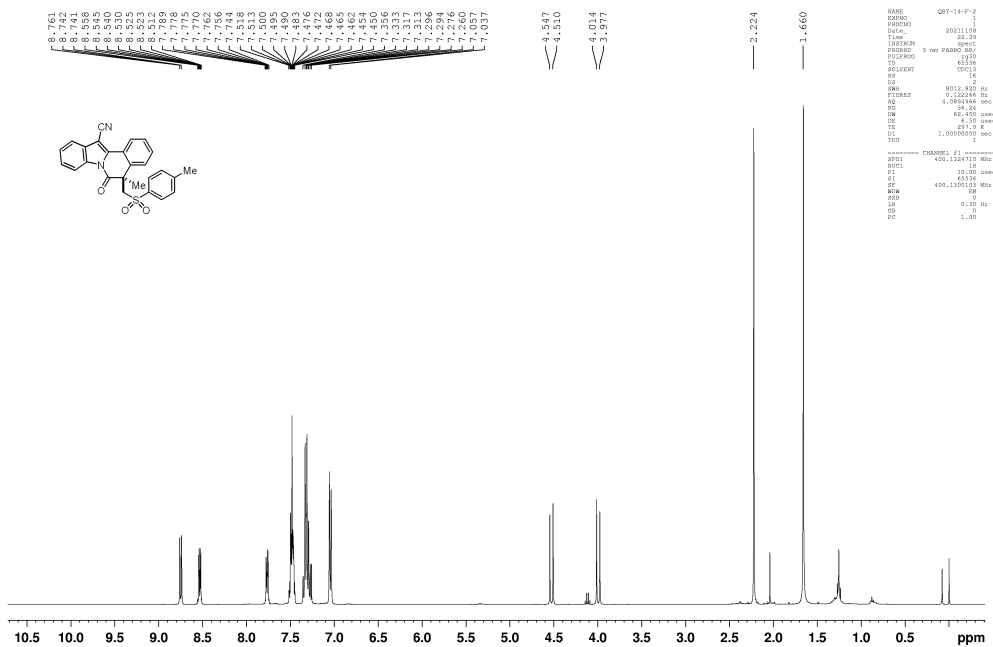


# 5-Methyl-12-octyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3g)

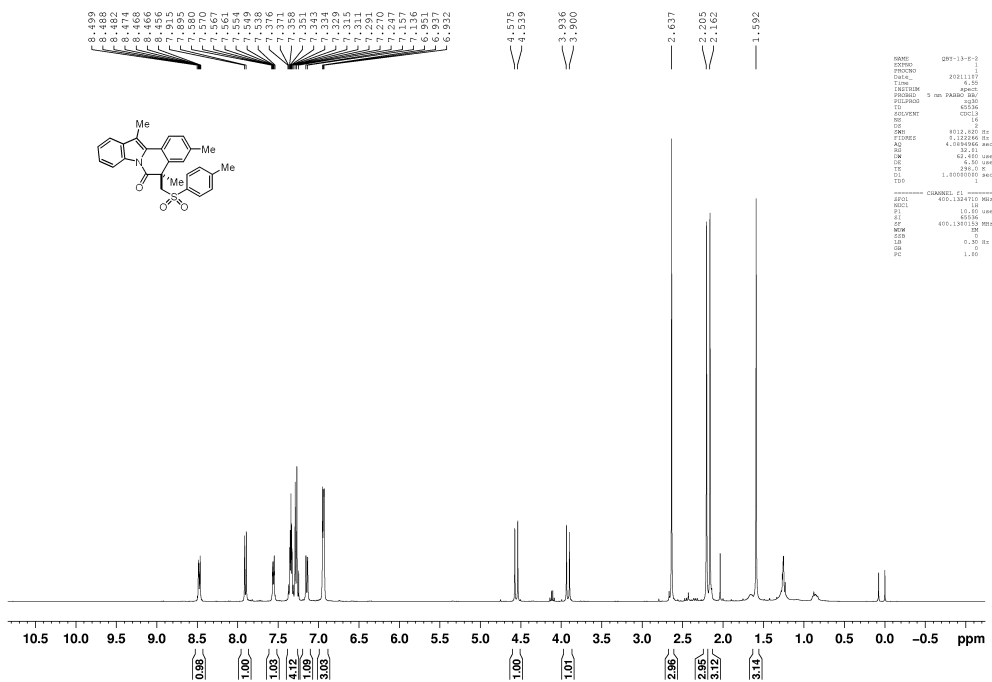




# 5-methyl-6-oxo-5-(tosylmethyl)-5,6-dihydroindolo[2,1-a]isoquinoline-12-carbonitrile (3h)

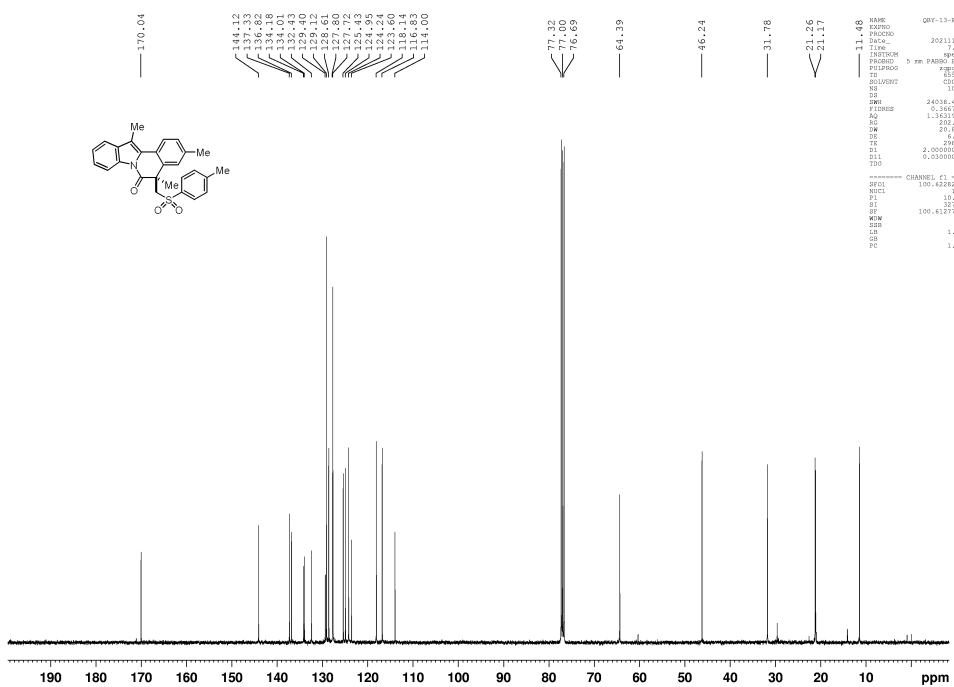


### 3,5,12-trimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3i)



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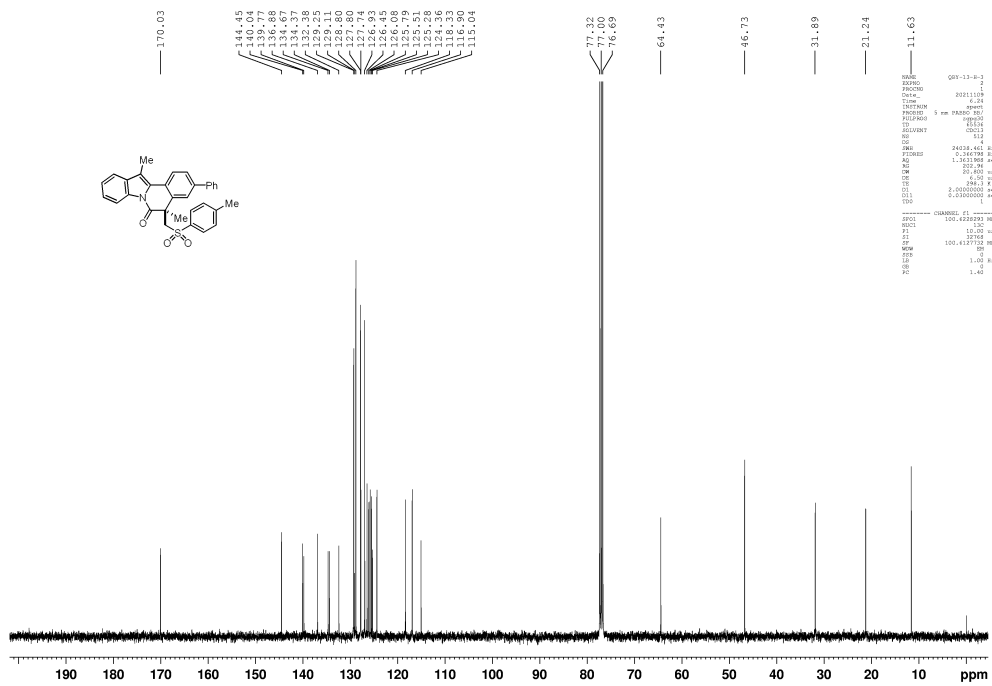
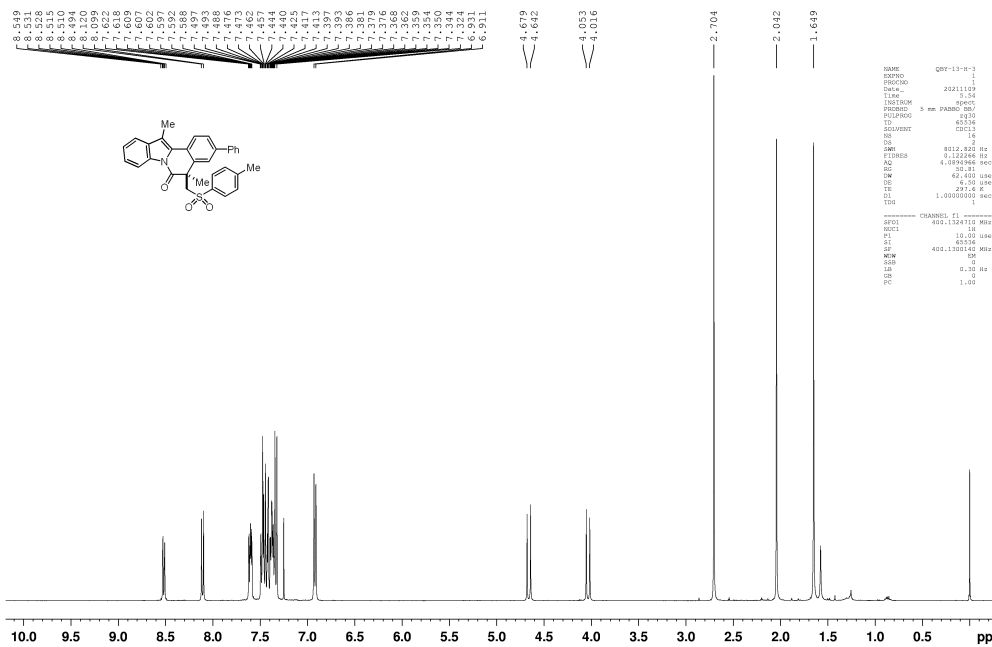
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PROCNO   1
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RG       60.480 usec
OR       4.10 usec
TE       298.2 K
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TD       1
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NUC2     13C
PC       1.00
  
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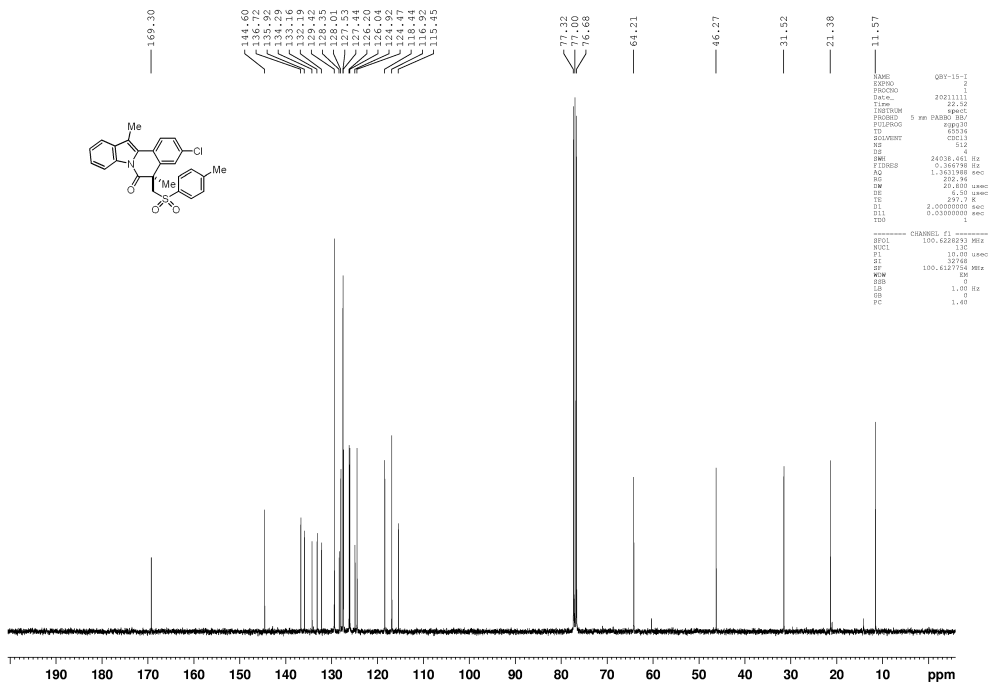
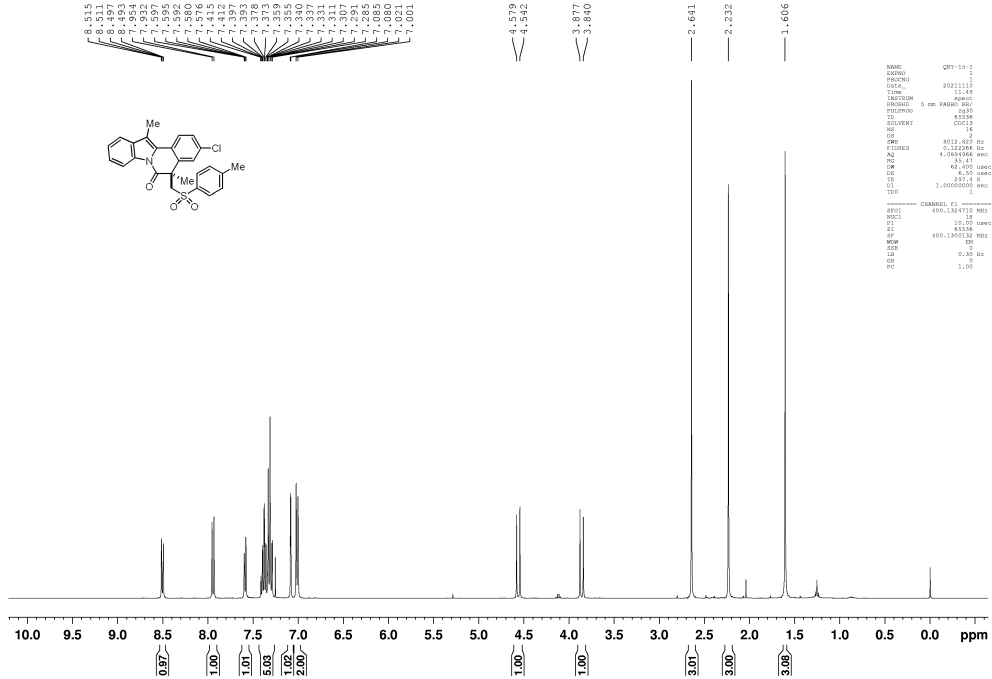
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PROCNO   1
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PROCNO   1
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RG       202.56
OR       20.850 usec
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NUC2     13C
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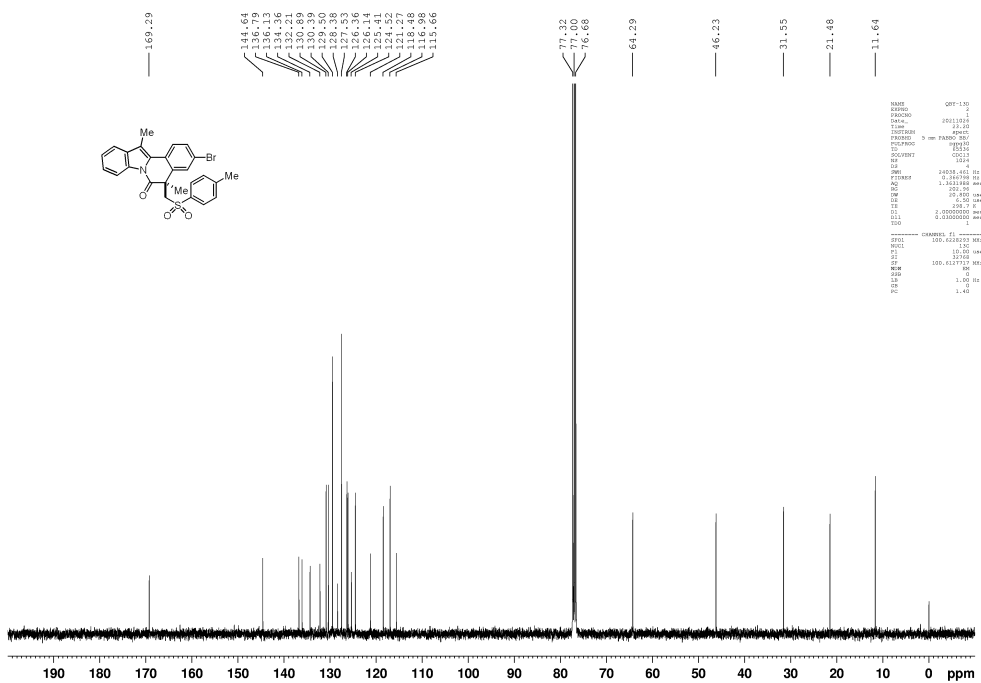
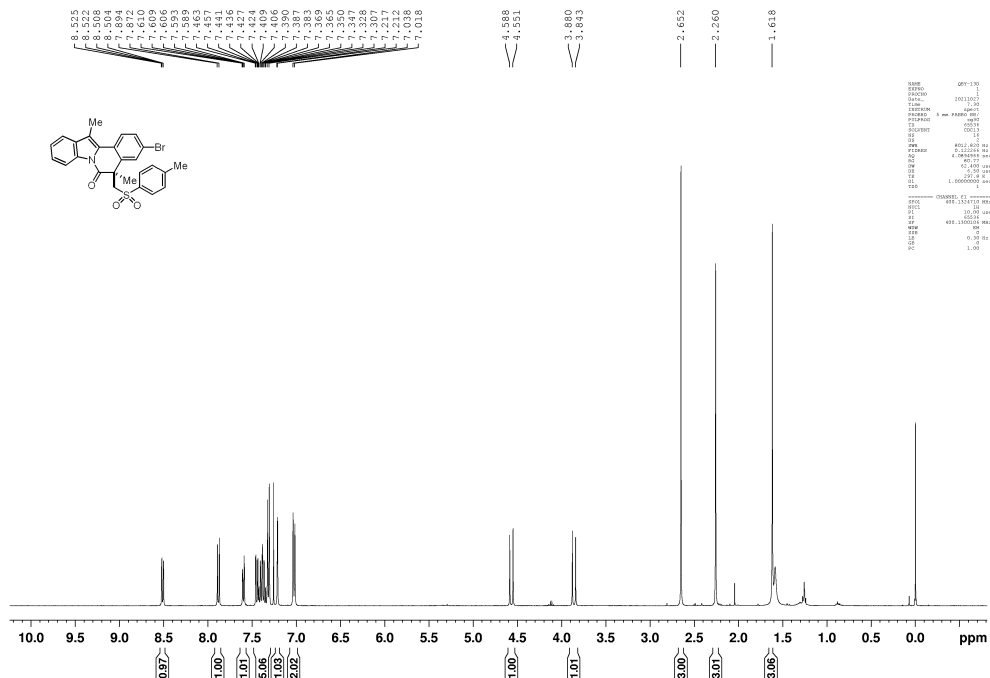
**5,12-dimethyl-3-phenyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3j)**



**3-chloro-5,12-dimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3k)**

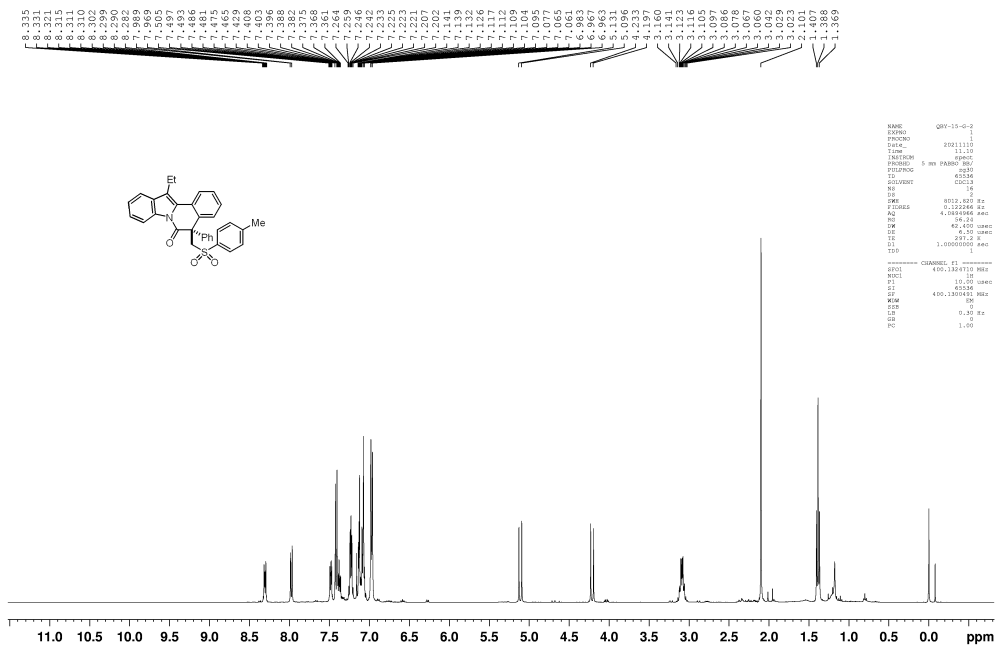


### 3-bromo-5,12-dimethyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3l)



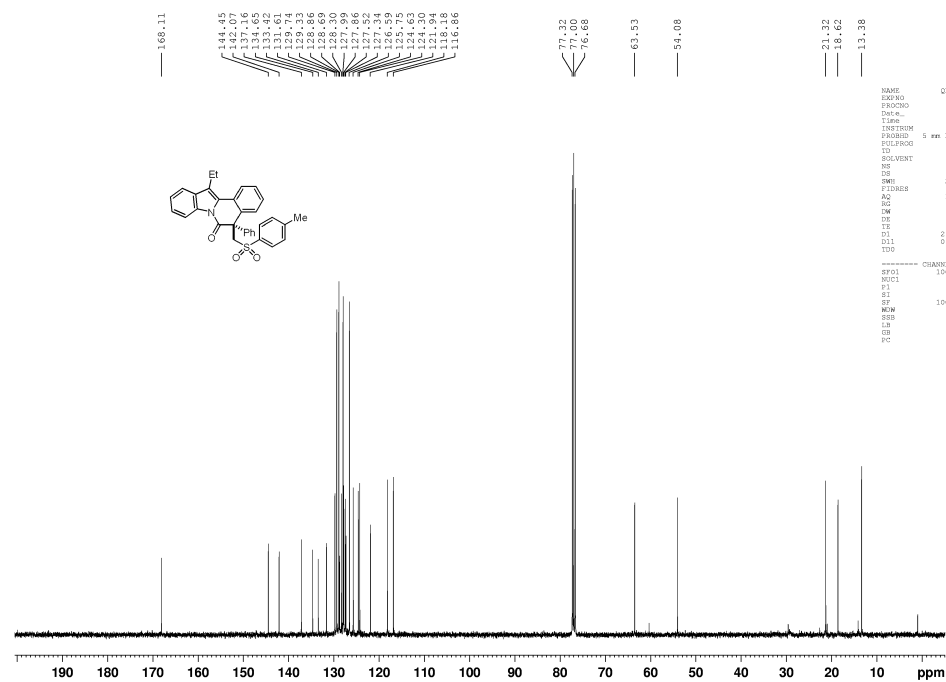


12-ethyl-5-phenyl-5-(tosylmethyl)indolo[2,1-a]isoquinolin-6(5H)-one (3n)



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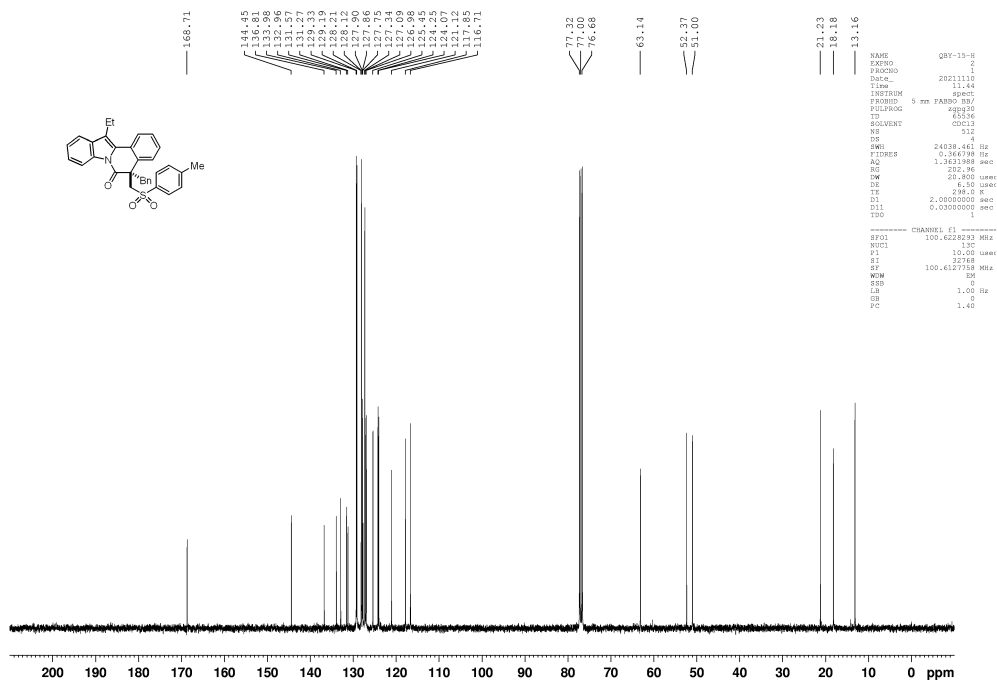
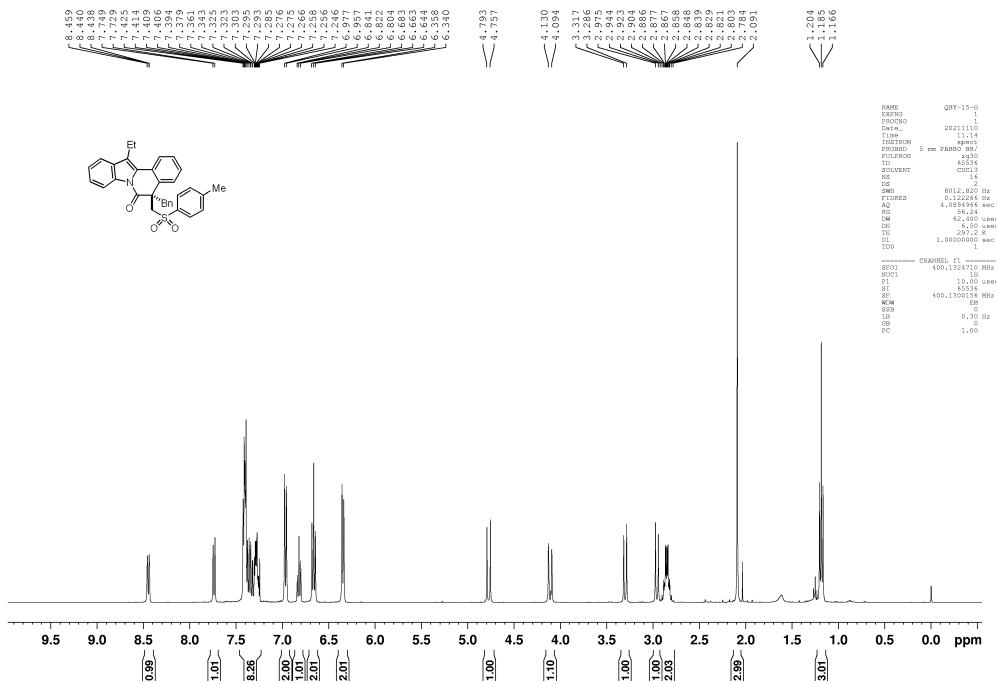
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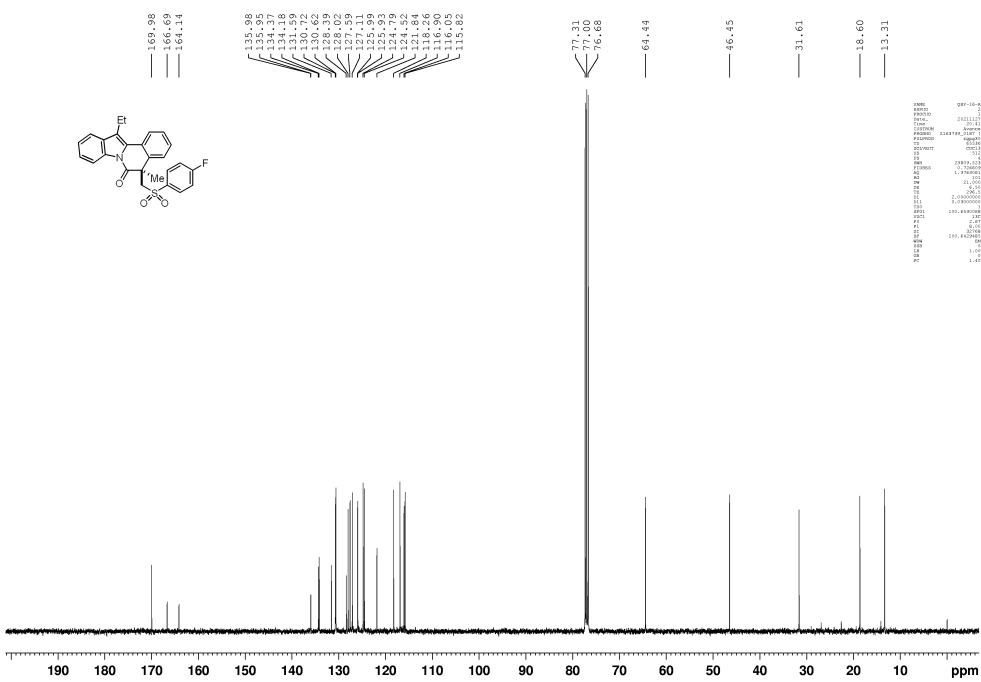
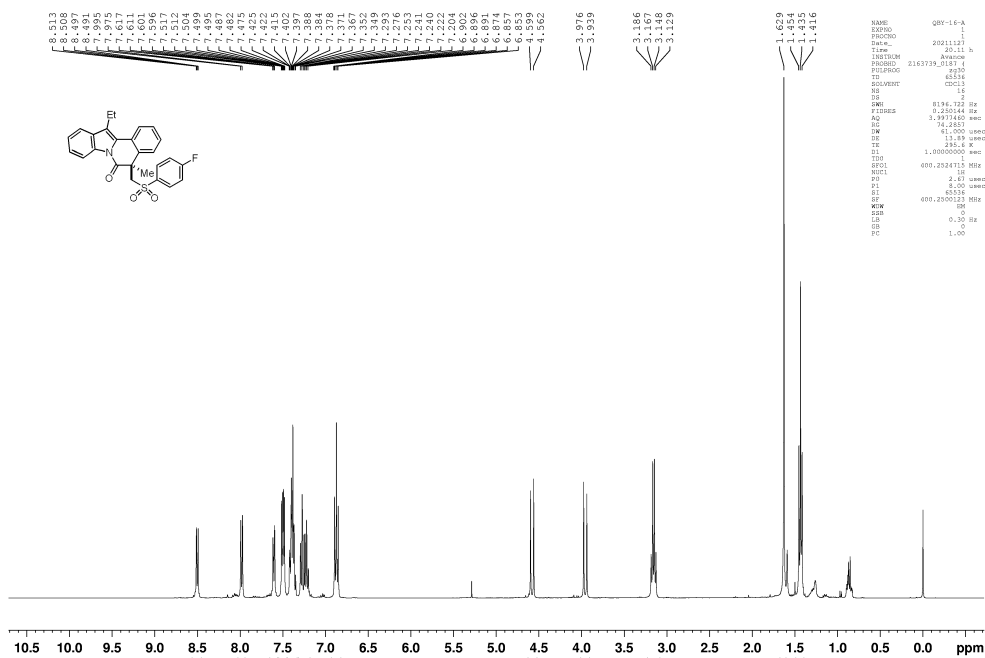
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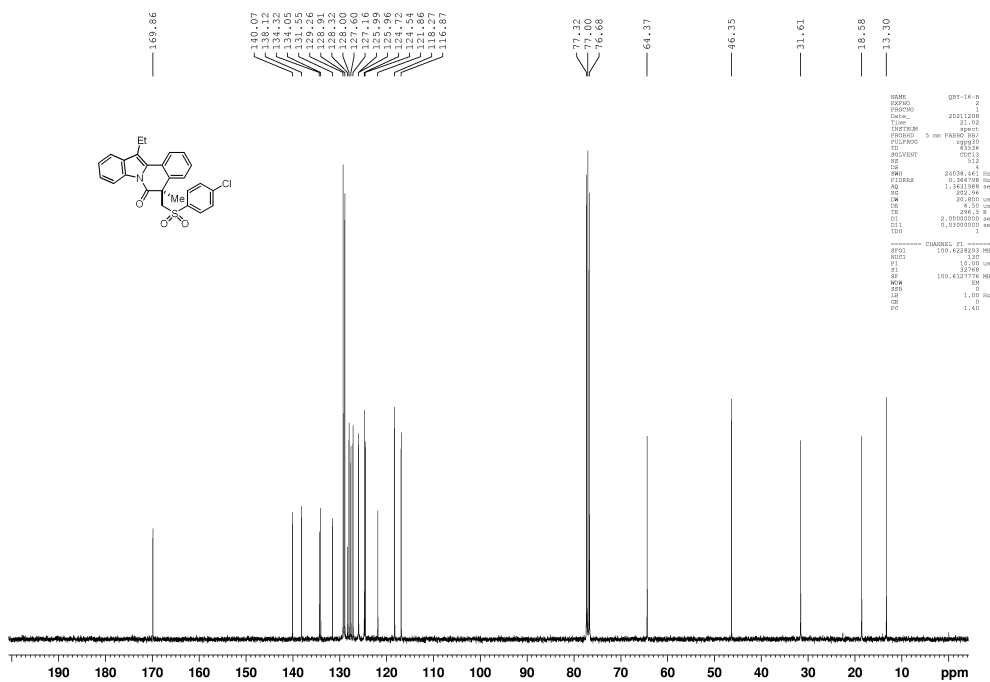
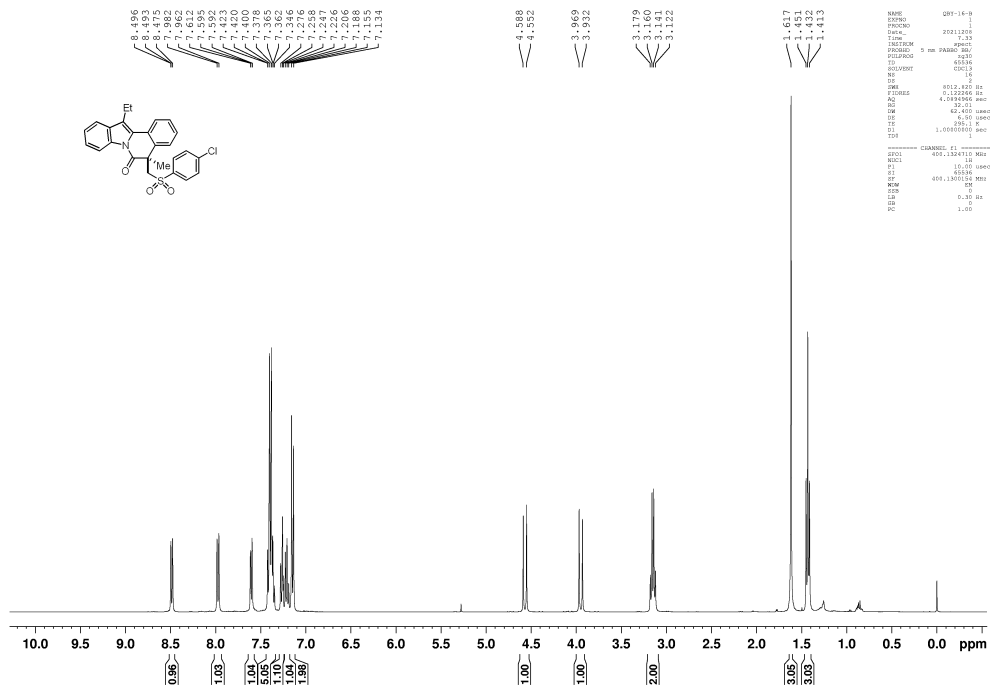




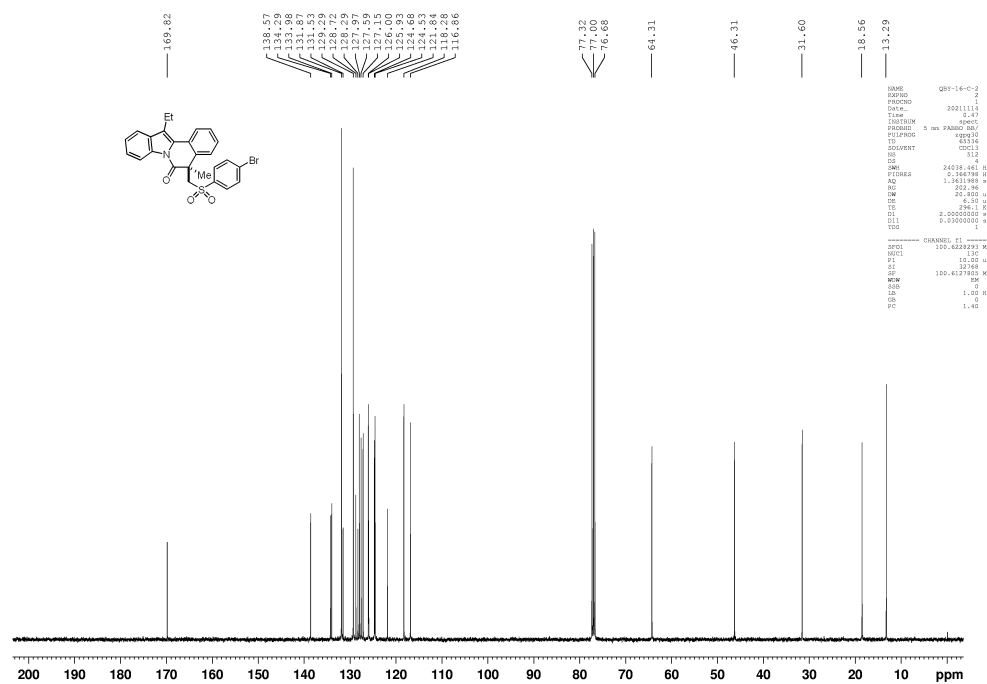
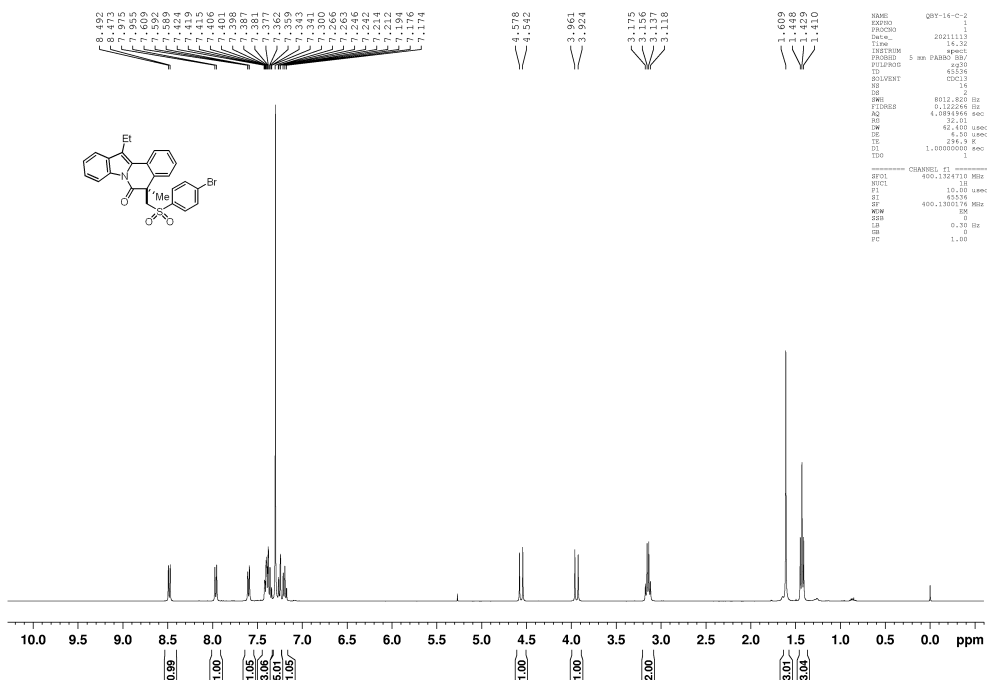
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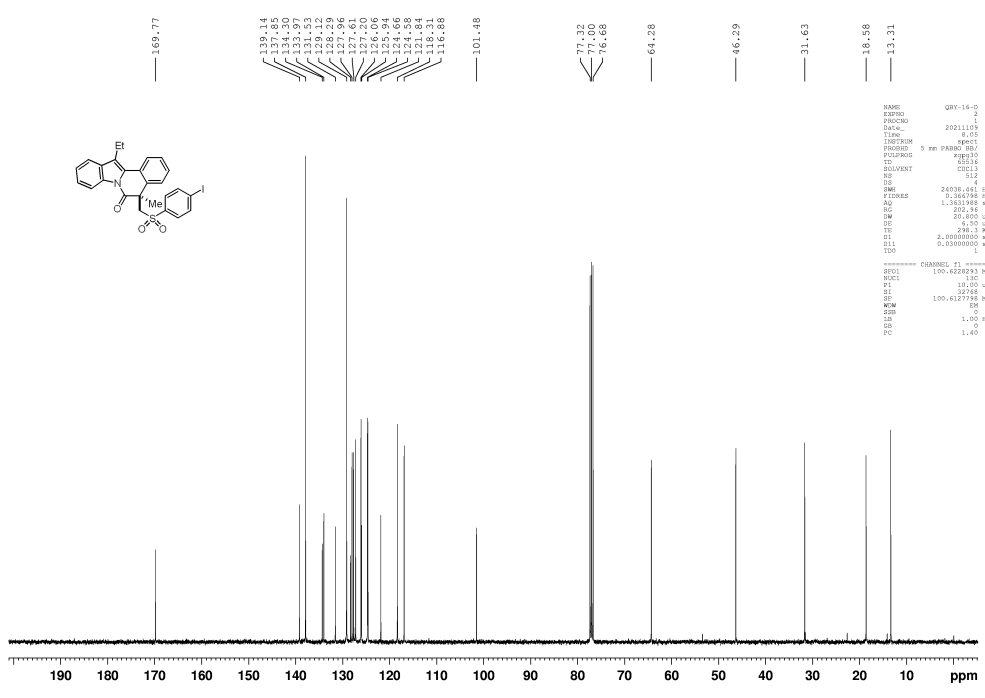
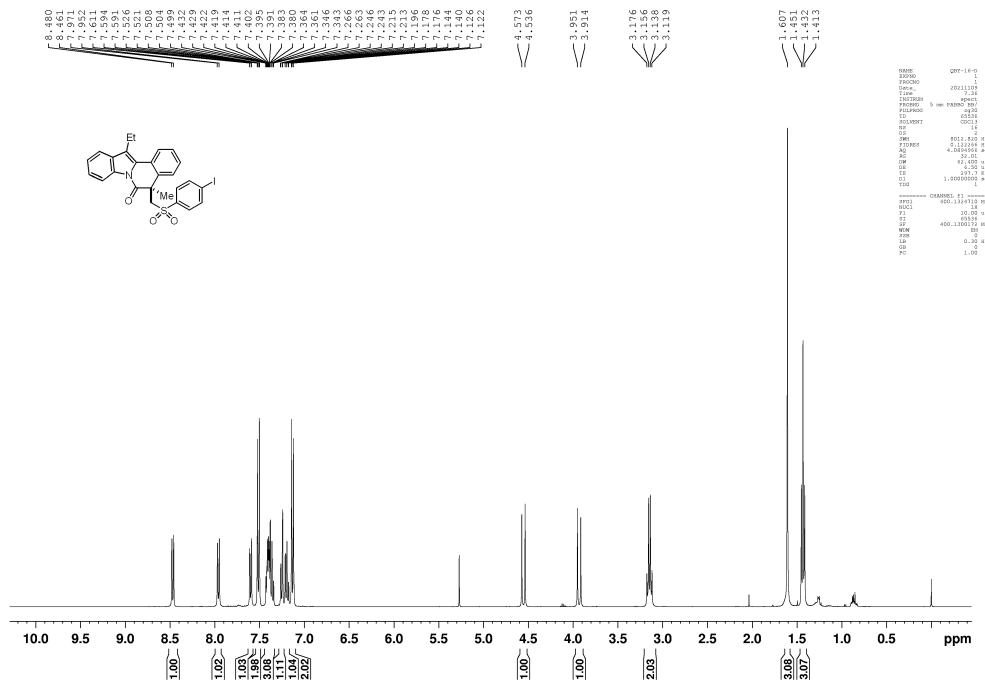
**5-(((4-chlorophenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3r)**



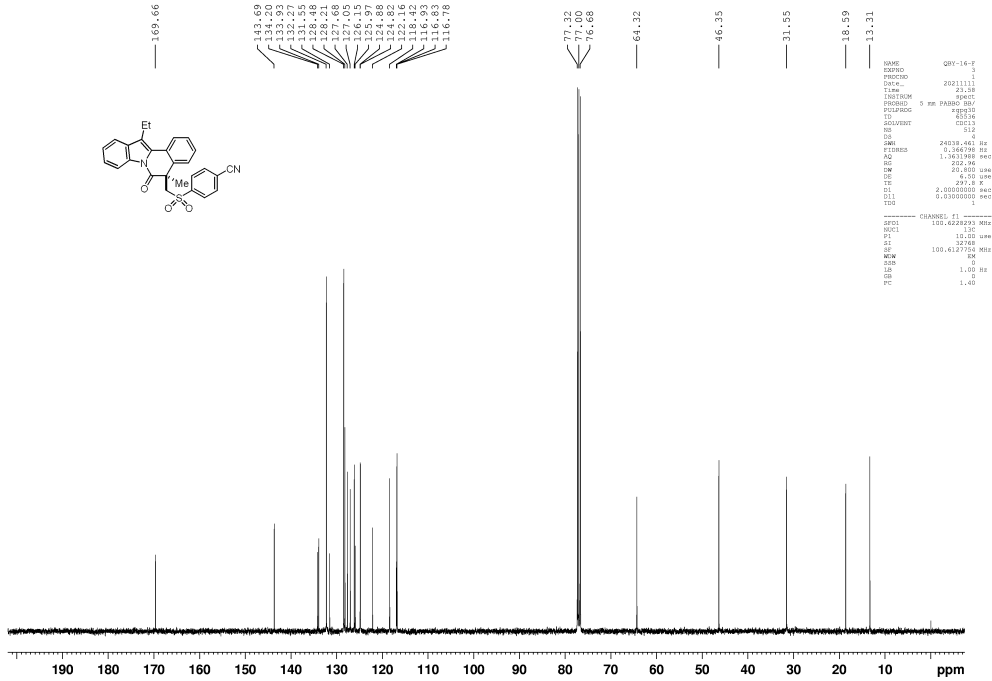
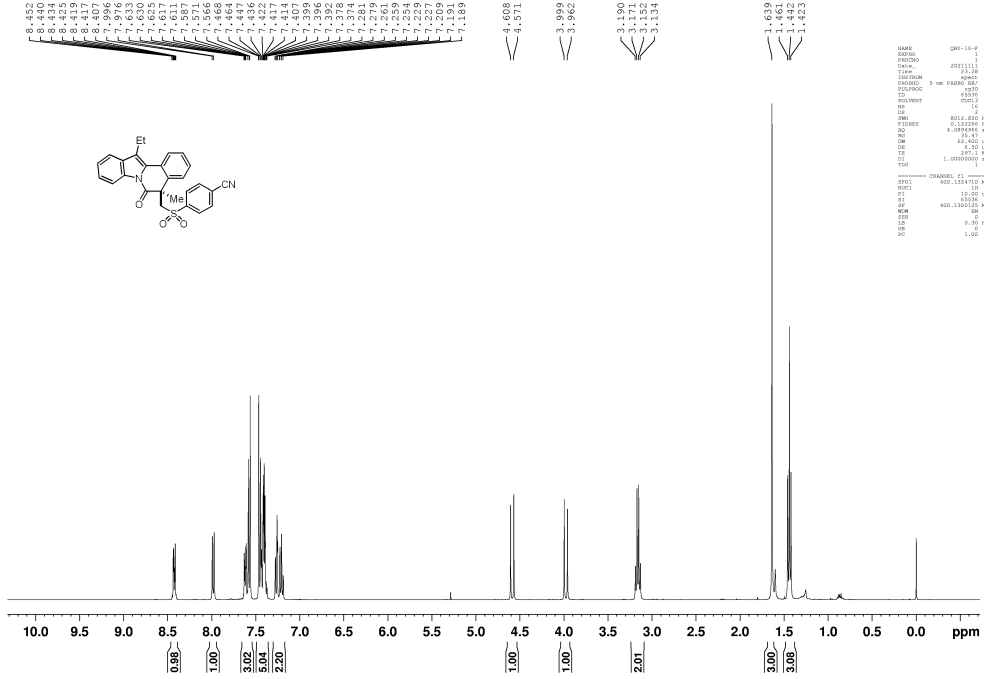
**5-(((4-bromophenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3s)**



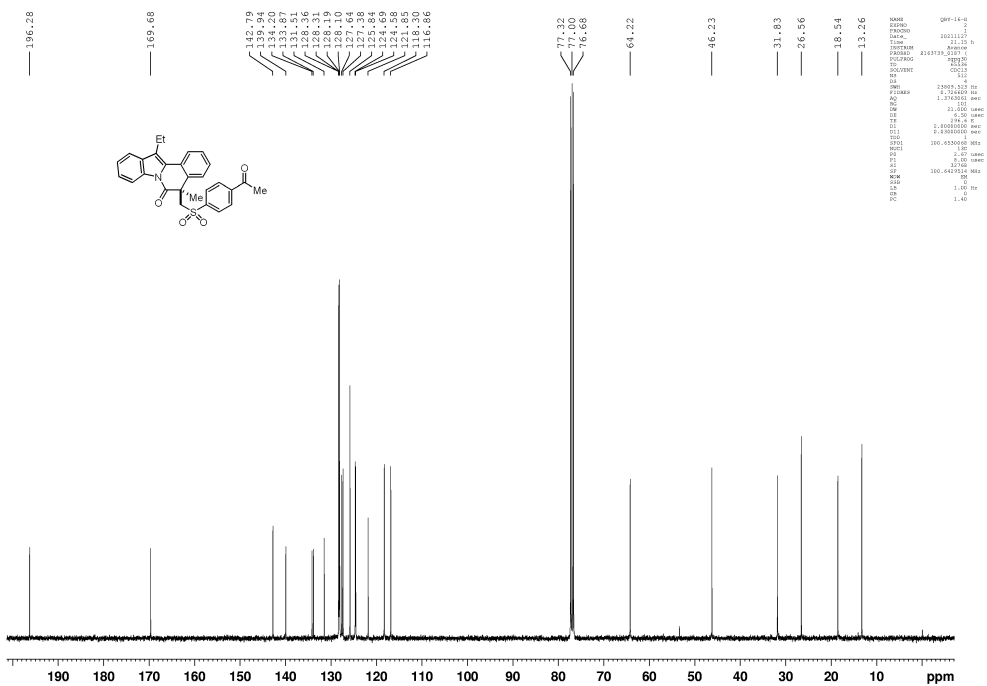
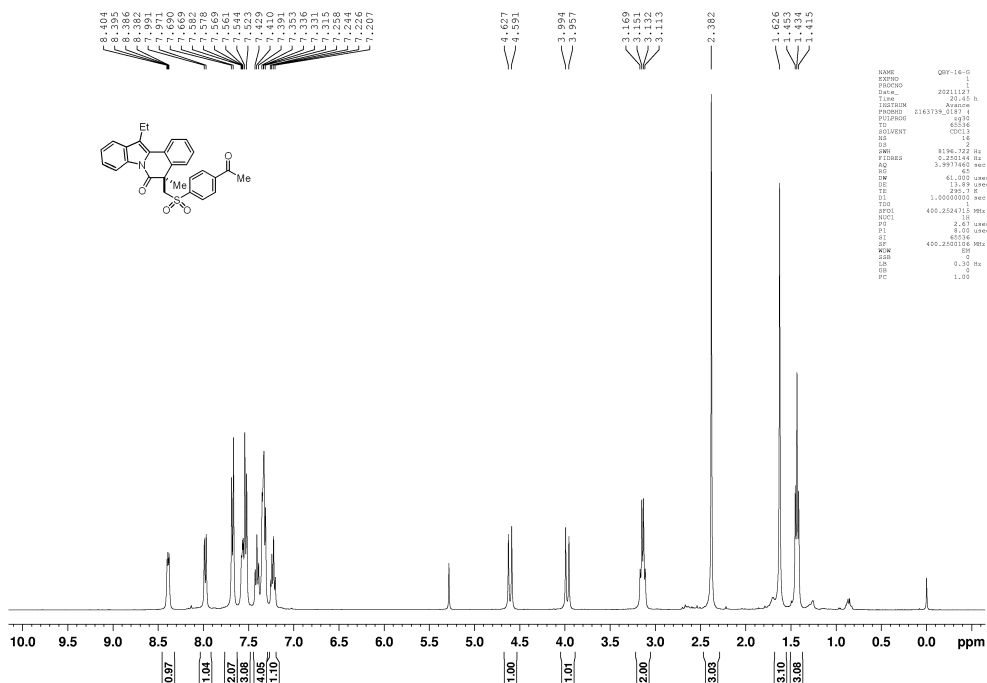
**12-ethyl-5-(((4-iodophenyl)sulfonyl)methyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3t)**



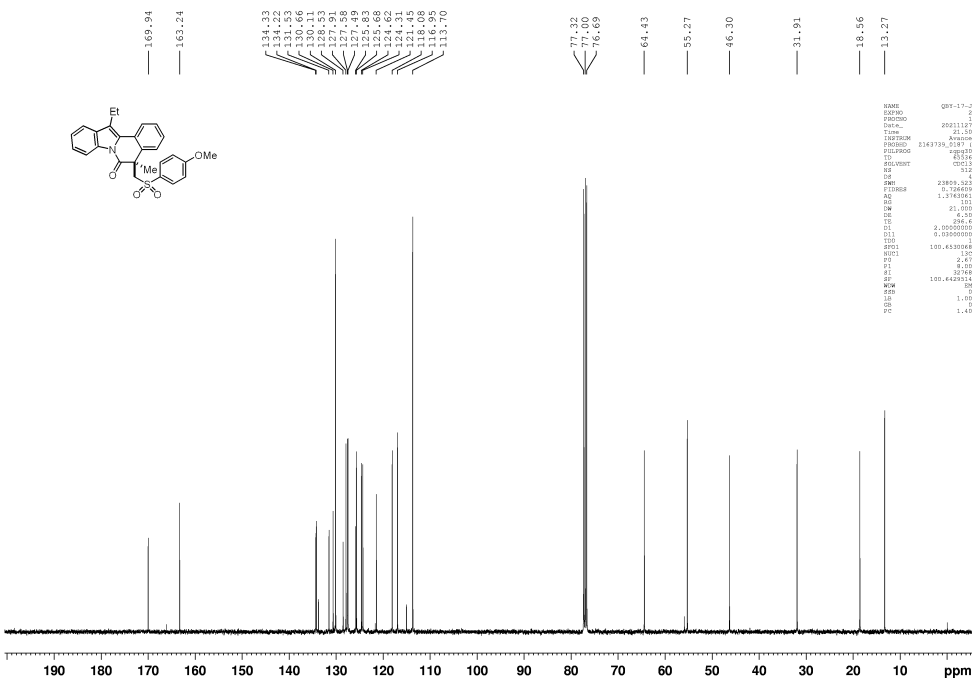
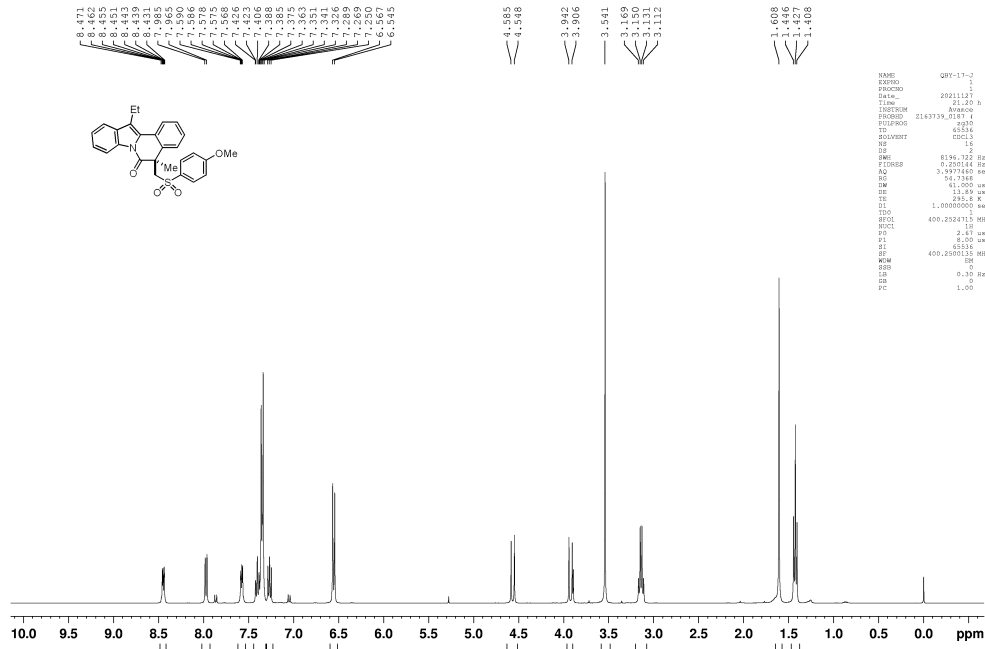
4-(((12-ethyl-5-methyl-6-oxo-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)sulfonyl)benzonitrile (3u)



**5-(((4-acetylphenyl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3v)**

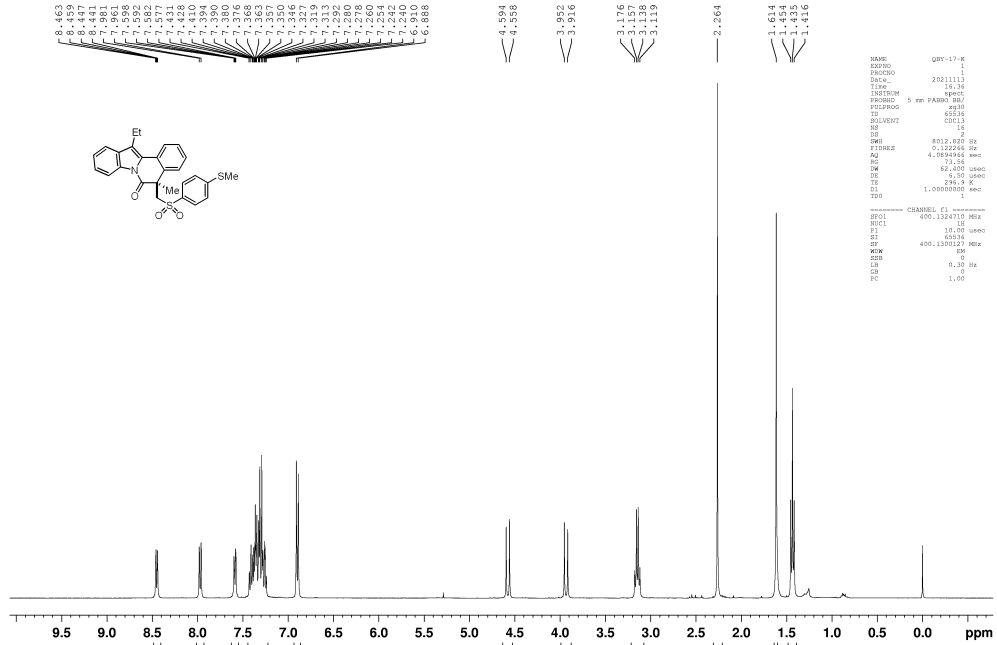


**12-ethyl-5-(((4-methoxyphenyl)sulfonyl)methyl)-5-methylindolo[2,1-a]isoquinolin-6(5H)-one (3w)**

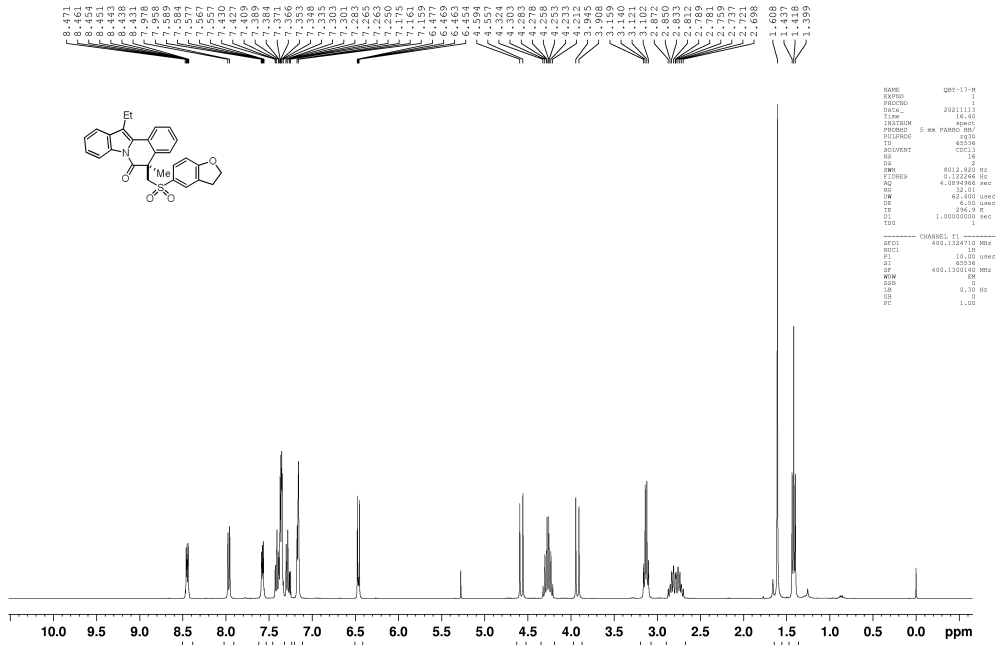




**12-ethyl-5-methyl-5-(((4-(methylthio)phenyl)sulfonyl)methyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (3x)**



5-(((2,3-dihydrobenzofuran-5-yl)sulfonyl)methyl)-12-ethyl-5-methylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (3y)





# (2-tosylethene-1,1-diyl)dibenzene (4a)

