Supporting Information

Sulfonyl radical-triggered two/three-component tandem bicyclization of CN-containing 1,6-enynes under transition-metal- and base-free conditions

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(A) General information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. CN-Containing 1,6-enynes was synthesized according to literature reports.[1] The progress of the reactions was monitored by TLC with silica gel plates and the visualization was carried out under UV light (254 nm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker 400 (400, 101, and 376 MHz) or Bruker 500 (500, 126, and 471 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

(B) Typical experimental procedures

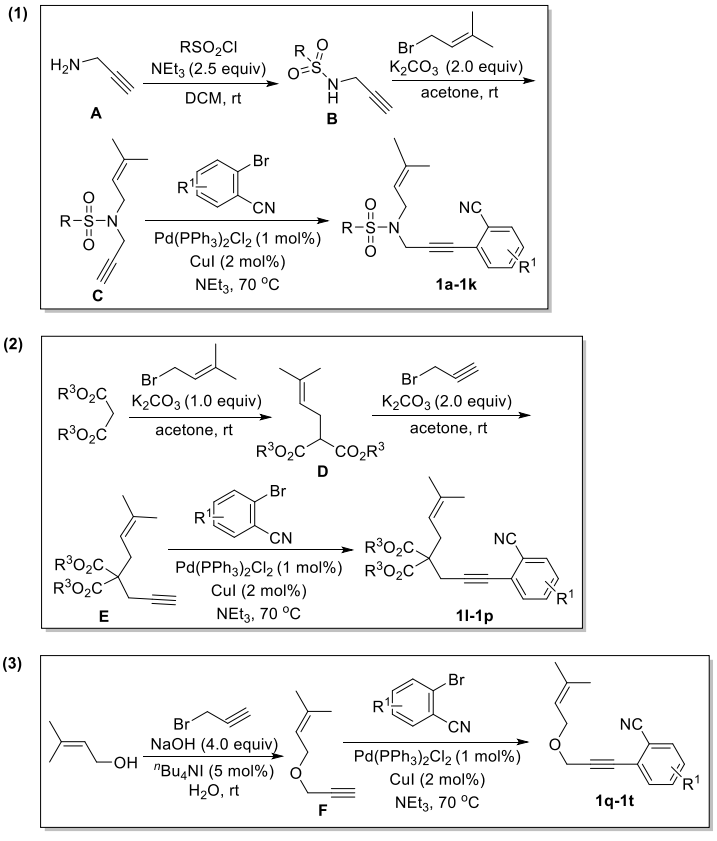
(1) General procedure for the synthesis of substrates 1.[1]

Procedure 1.1: RSO_2Cl (5.0 mmol, 1.0 equiv) and triethylamine (2.5 equiv) were sequentially added to a stirred solution of prop-2-yn-1-amine (**A**, 1.1 equiv) in DCM (15.0 mL). The resulting mixture was stirred overnight at room temperature. The resulting mixture was then extracted with CH_2Cl_2, washed with a saturated aqueous solution of saturated brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl ether) to afford **B**.

Procedure 1.2: K_2CO_3 (2.0 equiv), 1-bromo-3-methylbut-2-ene (2.0 equiv) were sequentially added to a stirred solution of **B** (1.0 equiv) in acetone (15.0 mL). The resulting mixture was stirred at room temperature for 24 h. After completion, K_2CO_3

was removed by filtration though a funnel. The resulting mixture was then extracted with ethyl ether, washed with a saturated aqueous solution of saturated brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford **C**.

Procedure 1.3: $Pd(PPh_3)_2Cl_2$ (1 mol%) and CuI (2 mol%) were sequentially added to a stirred solution of **C** (1.0 equiv) in triethylamine (15.0 mL) under argon at 70 ^oC. The mixture was allowed to stir for 10 min. Then 2-bromobenzonitrile (1.2 equiv) was added, and the mixture was stirred overnight. The resulting mixture was then poured into an aqueous saturated solution of NH_4Cl, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give **1a-1k**.



Procedure 2.1: K_2CO_3 (1.0 equiv), 1-bromo-3-methylbut-2-ene (5.0 mmol, 1.0 equiv) were sequentially added to a stirred solution of dimethyl malonate (1.3 equiv) in acetone (15.0 mL). The resulting mixture was stirred at room temperature for 24 h. After completion, K_2CO_3 was removed by filtration though a funnel. The resulting mixture was then extracted with ethyl ether, washed with a saturated aqueous solution of saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford **D**.

Procedure 2.2: K_2CO_3 (2.0 equiv), 3-bromoprop-1-yne (2.0 equiv) were sequentially added to a stirred solution of **D** (1.0 equiv) in DMF (15.0 mL). The resulting mixture was stirred at room temperature for 24 h. After completion, K_2CO_3 was removed by filtration though a funnel. The resulting mixture was then extracted with ethyl ether, washed with a saturated aqueous solution of saturated brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether /ethyl acetate) to afford **E**.

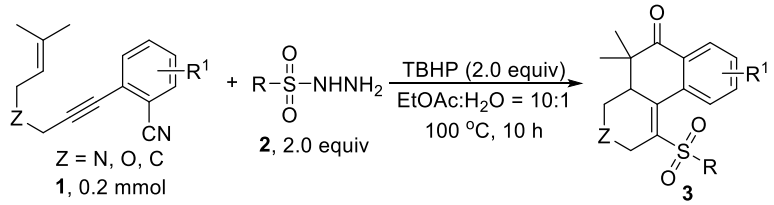
Procedure 2.3: $Pd(PPh_3)_2Cl_2$ (1 mol%) and CuI (2 mol%) were sequentially added to a stirred solution of **E** (1.0 equiv) in triethylamine (15.0 mL) under argon at 70 ^oC. The mixture was allowed to stir for 10 min. Then 2-bromobenzonitrile (1.2 equiv) was added, and the mixture was stirred overnight. After completion, the resulting mixture was poured into an aqueous saturated solution of NH_4Cl, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column

chromatography (petroleum ether/ethyl acetate) to give **1l-1p**.

Procedure 3.1: Sodium hydroxide (4.0 equiv), tetra(*n*-butyl)ammonium hydrogensulfate (1.0 equiv), 3-bromoprop-1-yne (2.0 equiv) were sequentially added to a stirred solution of 3-methylbut-2-en-1-ol (5.0 mmol, 1.0 equiv) in water (15.0 mL). The resulting mixture was stirred at room temperature for 24 h. The resulting mixture was then extracted with ethyl ether, washed with a saturated aqueous solution of saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford **F**.

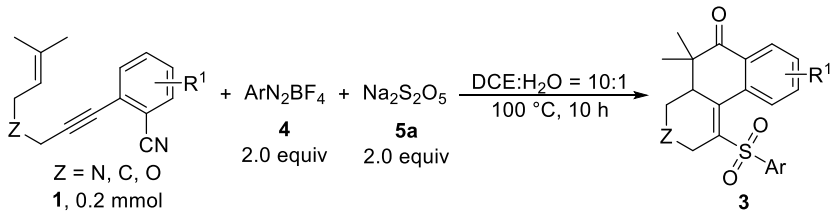
Procedure 3.2: $Pd(PPh_3)_2Cl_2$ (1 mol%) and CuI (2 mol%) were sequentially added to a stirred solution of **F** (1.0 equiv) in triethylamine (15.0 mL) under argon at 70 ^oC. The mixture was allowed to stir for 10 min. Then 2-bromobenzonitrile (1.2 equiv) was added, and the mixture was stirred overnight. The resulting mixture was poured into an aqueous saturated solution of NH_4Cl, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give **1q-1m**.

(2) General procedure for synthesis of compounds 3.



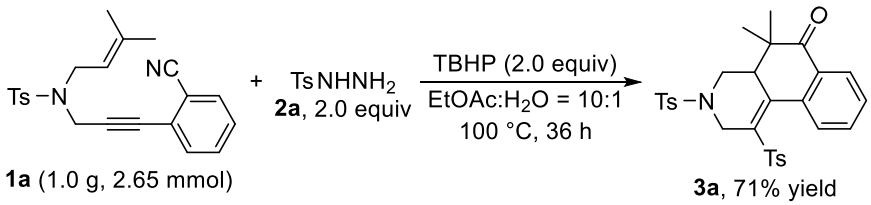
CN-containing 1,6-enynes (**1**, 0.2 mmol), sulfonyl hydrazides (**2**, 2.0 equiv),

EtOAc/H_2O (v/v = 10:1, 2.0 mL), and TBHP (2.0 equiv) were sequentially added to a Schlenk tube (10 mL), and the reaction mixture was heated with stirring in air at 100 ^oC for 10 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature and the solution was concentrated in vacuum. The resulting mixture purified by flash column chromatography (petroleum ether/ethyl acetate (v/v = 5:1~3:1) to give the desired products **3**.



CN-containing 1,6-enynes (**1**, 0.2 mmol), aryldiazonium tetrafluoroborates (**4**, 2.0 equiv), $Na_2S_2O_5$ (**5a**, 2.0 equiv), and DCE/H_2O (v/v = 10:1, 2.0 mL) were sequentially added to a Schlenk tube (10 mL), and the reaction mixture was heated with stirring in air at 100 ^oC for 10 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature and the solution was concentrated in vacuum. The resulting mixture purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1~3:1) to give the desired products **3**.

(3) Experimental procedure for the scale-up reaction.

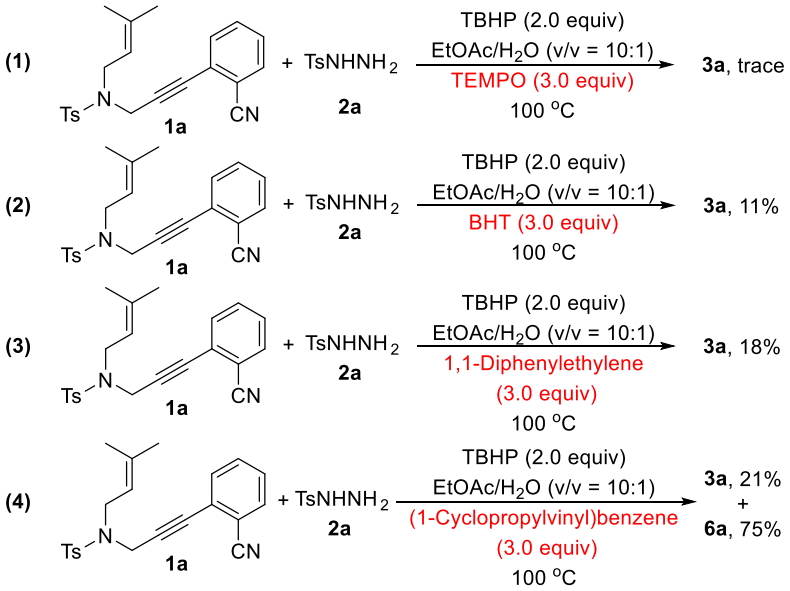


To a Schlenk tube were added CN-containing 1,6- enynes **1a** (1000.0 mg, 2.65 mmol), $TsNHNH_2$ **2a** (987.0 mg, 2.0 equiv), TBHP (522.1 μL, 2.0 equiv) and EtOAc/H_2O (v/v = 10:1, 26.5 mL). Then the tube was placed in in air at 100 ºC for 36 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solvent was removed under reduced pressure. And the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) to obtain the desired product **3a** (1006.6 mg, 71% yield).

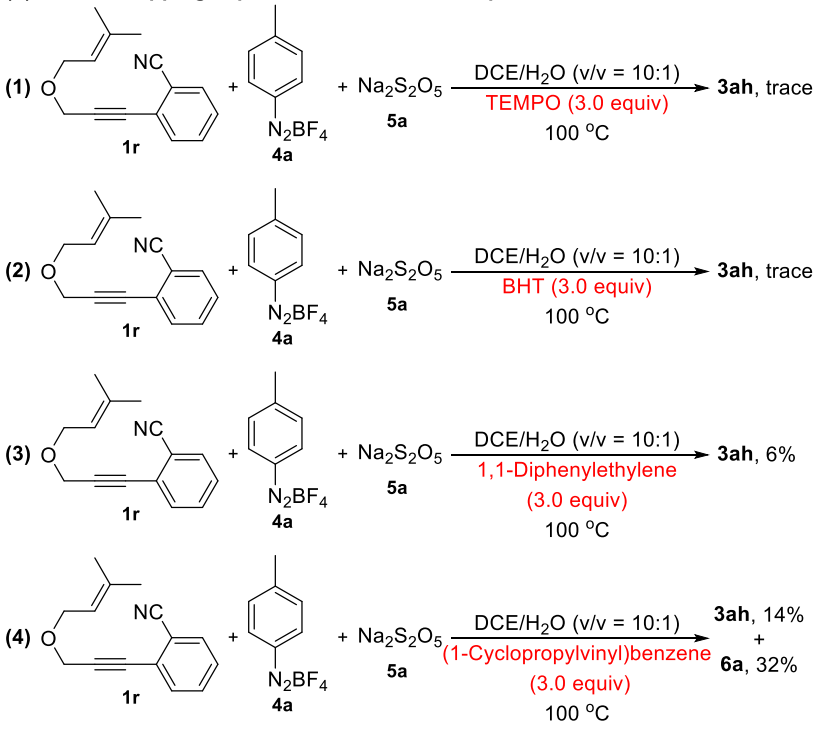
(4) Radical-trapping experiments.

For two-component reaction, CN-containing 1,6-enyne (**1a**, 0.2 mmol), $TsNHNH_2$ (**2a**, 2.0 equiv), TBHP (2.0 equiv, anhydrous), EtOAc/H_2O (v/v = 10:1) and radical scavenger ((2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 3.0 equiv), or 2,6-di(*tert*-butyl)-4-methylphenol (BHT, 3.0 equiv), or 1,1-diphenylethylene (3.0 equiv)) was added to a Schlenk tube (10 mL), and the reaction mixture was heated with stirring under air at 100 ºC for 10 h. After the reaction was completed, the yield of desired product **3a** dropped sharply, indicating that the reaction was inhibited by radical scavenger. Meanwhile, the radical clock experiment with 3.0 equiv of (1-cyclopropylvinyl)benzene as the probe afforded adduct **6a** in 75% yield, and only 21% yield of target product **3a** was detected.

(a) Radical-trapping experimwnts for two-component reaction:



(b) Radical-trapping experimwnts for three-component reaction:

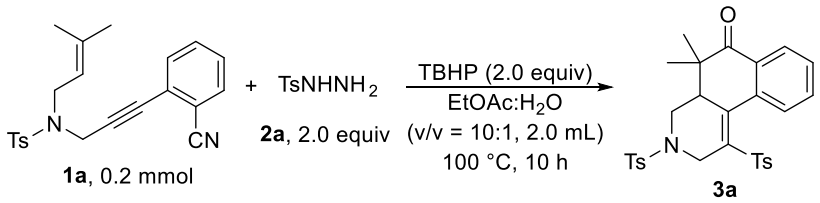


For three-component reaction, CN-containing 1,6-enyne (**1r**, 0.2 mmol), aryldiazonium tetrafluoroborates (**4a**, 2.0 equiv), $Na_2S_2O_5$ (**5a**, 2.0 equiv), DCE/H_2O (v/v = 10:1) and radical scavenger ((2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 3.0 equiv), or 2,6-di(*tert*-butyl)-4-methylphenol (BHT, 3.0 equiv), or 1,1-diphenylethylene (3.0 equiv)) was added to a Schlenk tube (10 mL), and the

reaction mixture was heated with stirring under air at 100 °C for 10 h. After the reaction was completed, the yield of desired product **3ah** dropped sharply, indicating that the reaction was inhibited by radical scavenger. Similarly, when 3.0 equiv of (1-cyclopropylvinyl)benzene was added to the reaction system, the adduct **6a** was obtained in 32% yield.

(C) Sensitivity Assessments

A reaction-condition-based sensitivity assessment, as recently reported, has been undertaken to evaluate the sensitivity of the reaction of CN-containing 1,6-enyne **1a** and $TsNHNH_2$ **2a**. For this analysis, the standard reaction was performed varying different conditions: temperature, concentration, stir rate and content of water and oxygen.



Standard Conditions: n = 0.2 mmol, c = 0.1 M, V = 2.0 mL, in Air, T = 100 °C.

Stock Solution: n = 2.0 mmol, c = 0.111 M, V = 18.0 mL, **1a**: 756.28 mg, **2a**: 744.92 mg, TBHP: 394.0 μL.

Stock Solution ‘big scale’: n = 2.65 mmol, c = 0.1 M, V = 26.5 mL, **1a**: 1002.07 mg, **2a**: 987.02 mg, TBHP: 522.1 μL.

Table 1. Preparation of sensitivity assessment of reaction.

Number	Experiment	Preparation
1	High c	1.8 mL stock sol.
2	Low c	1.8 mL stock sol. + 0.4 mL co-solvent
3	Low O_2	1.8 mL stock sol. + 0.2 mL co-solvent + degassed
4	Medium O_2	1.8 mL stock sol. + 0.2 mL co-solvent + inert atmosphere
5	Low T	1.8 mL stock sol. + 0.2 mL co-solvent, T = 90 °C

6	High *T*	1.8 mL stock sol. + 0.2 mL co-solvent, *T* = 110 °C
7	Low Stir	1.8 mL stock sol. + 0.2 mL co-solvent, stir rate = 720 rmp
8	High Stir	1.8 mL stock sol. + 0.2 mL co-solvent, stir rate = 1350 rmp
9	Control	1.8 mL stock sol. + 0.2 mL co-solvent
10	Big Scale	40.0 mL stock solution 'big scale'

Table 2. Results of sensitivity assessment of reaction.

Number	Experiment	Yield / %	Deviation / %
1	High *c*	87	+1
2	Low *c*	81	-6
3	Medium O_2	85	-1
4	Low O_2	83	-3
5	High *T*	81	-6
6	Low *T*	12	-86
7	Low Stir	85	-1
8	High Stir	87	+1
9	Control	86	0
10	Big Scale	71	-17

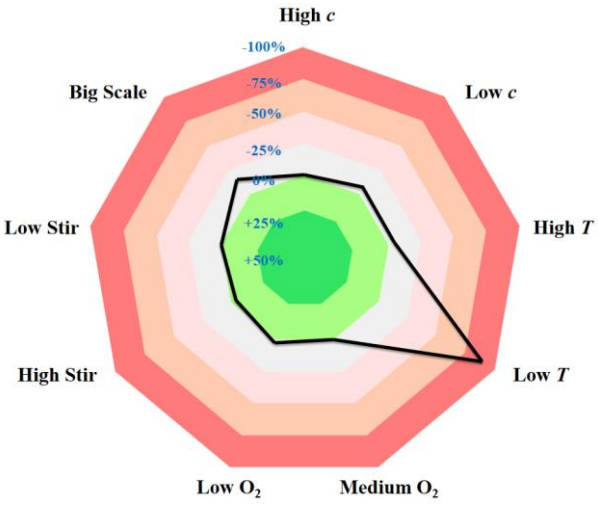
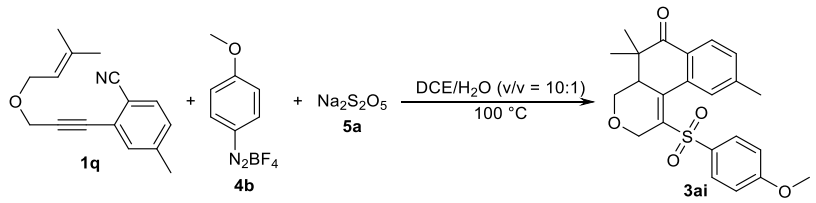


Figure S1. Radar diagram of the sensitivity for this reaction.

(D) Optimization of reaction conditions for the formation of 3ai

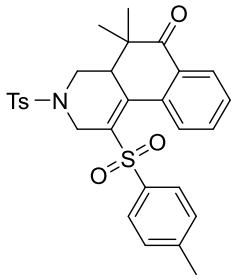
Table 3. Optimization of three-component reaction conditions.[a]



Entry	Variations from standard conditions	Yield of **3ai** (%)[b]
1	None	67
2	EtOAc/H_2O (v/v = 10:1) instead of DCE/H_2O (v/v = 10:1)	52
3	MeCN/H_2O (v/v = 10:1) instead of DCE/H_2O (v/v = 10:1)	46
4	THF/H_2O (v/v = 10:1) instead of DCE/H_2O (v/v = 10:1)	48
5	DCE/H_2O (v/v = 15:1) instead of DCE/H_2O (v/v = 10:1)	24
6	DCE/H_2O (v/v = 5:1) instead of DCE/H_2O (v/v = 10:1)	66
7	H_2O instead of DCE/H_2O (v/v = 10:1)	8
8	80 °C instead of 100 °C	11
9	120 °C instead of 100 °C	61

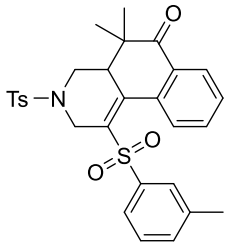
[a] Unless otherwise noted, the reactions were performed with **1q** (0.2 mmol), **4b** (2.0 equiv) and **5a** (2.0 equiv) in solvent sealed in air for 10 h. [b] Isolated yield based on **1q**.

(E) Analytical data

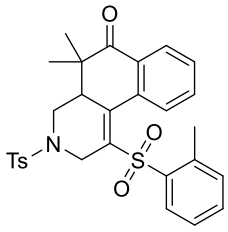


5,5-Dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (92.0 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.90 (m, 1H), 7.74-7.69 (m, 3H), 7.57-7.53 (m, 2H), 7.52-7.47 (m, 2H), 7.29 (s, 1H), 7.27 (s, 1H), 7.20 (d, J = 8.0 Hz, 2H), 4.41-4.37 (m, 1H), 3.70-3.60 (m, 2H), 3.06-3.01 (m, 1H), 2.88-2.82 (m, 1H), 2.37 (s, 6H), 1.25 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.7, 145.1, 144.1, 143.0, 136.3, 136.2, 135.5, 133.9, 131.8, 131.4, 130.9, 130.0, 129.7, 129.5, 128.0, 127.6, 127.5, 47.5, 46.8, 46.3, 43.6,

22.2, 21.6, 21.4, 18.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NNaO_5S_2$ ($[M+Na]^+$) 558.1379, found 558.1381.

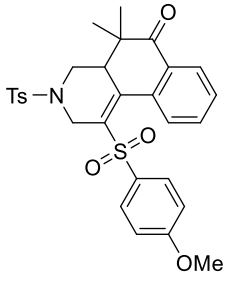


5,5-Dimethyl-1-(*m*-tolylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (86.7 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93-7.91 (m, 1H), 7.77-7.70 (m, 3H), 7.51-7.43 (m, 4H), 7.30-7.26 (m, 4H), 4.43-4.38 (m, 1H), 3.74-3.64 (m, 2H), 3.10-3.04 (m, 1H), 2.85 (t, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 1.25 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.7, 144.2, 143.2, 139.3, 139.2, 136.2, 135.6, 134.6, 133.9, 131.9, 131.4, 130.9, 130.0, 129.6, 128.9, 128.3, 127.7, 127.5, 125.0, 47.6, 46.8, 46.2, 43.6, 22.4, 21.5, 21.1, 18.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NNaO_5S_2$ ($[M+Na]^+$) 558.1379, found 558.1381.

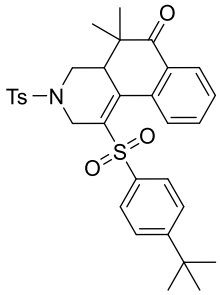


5,5-Dimethyl-1-(*o*-tolylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (70.6 mg, 66% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.45-7.35 (m, 4H), 7.20 (d, *J* = 6.8 Hz, 3H), 7.13 (t, *J* = 3.6 Hz, 1H), 4.12-4.08 (m, 1H), 3.58-3.50 (m, 2H), 3.08-3.02 (m, 1H), 2.76 (t, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 1.20 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.7, 144.2, 142.8, 137.8, 136.7, 135.9, 135.0, 133.9, 133.7, 132.7, 132.0, 131.2, 130.9, 130.1, 130.0, 128.0, 127.7, 127.5, 126.3, 47.3, 46.7,

46.4, 43.5, 22.7, 21.4, 20.3, 19.6; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NNaO_5S_2$ ($[M+Na]^+$) 558.1379, found 558.1381.

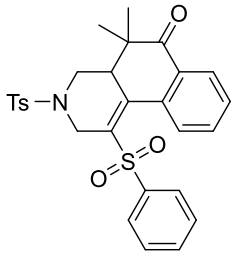


1-((4-Methoxyphenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (95.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.93 (m, 1H), 7.74 (d, J = 6.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.50-7.48 (m, 2H), 7.28 (t, J = 4.0 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.41-4.37 (m, 1H), 3.82 (s, 3H), 3.71-3.59 (m, 2H), 3.05-2.99 (m, 1H), 2.84 (t, J = 7.6 Hz, 1H), 2.36 (s, 3H), 1.24 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.6, 163.8, 144.1, 142.4, 136.2, 135.8, 133.9, 131.8, 131.4, 130.8, 130.5, 130.2, 129.9, 129.4, 127.5, 127.4, 114.2, 55.6, 47.4, 46.6, 46.3, 43.6, 22.2, 21.4, 18.8; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NNaO_6S_2$ ($[M+Na]^+$) 574.1329, found 574.1327.

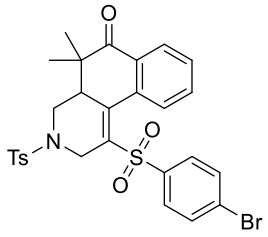


1-((4-(*tert*-Butyl)phenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (94.7 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.92 (m, 1H), 7.70 (t, J = 4.0 Hz, 3H), 7.59 (d, J = 8.4 Hz, 2H), 7.49-7.47 (m, 2H), 7.42-7.40 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 4.43-4.38 (m, 1H), 3.73-3.68 (m, 1H), 3.62-3.58 (m, 1H), 3.04-2.98 (m, 1H), 2.85 (t, J = 7.6 Hz, 1H), 2.36 (s, 3H), 1.28 (s, 9H), 1.24 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101

MHz, $CDCl_3$) δ: 199.6, 158.0, 144.1, 142.9, 136.2, 136.1, 135.6, 134.0, 131.9, 131.4, 130.8, 130.0, 129.5, 127.8, 127.5 (2), 126.1, 47.4, 46.7, 46.3, 43.6, 35.2, 30.9, 22.3, 21.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{32}H_{35}NNaO_5S_2$ ($[M+Na]^+$) 600.1849, found 600.1843.

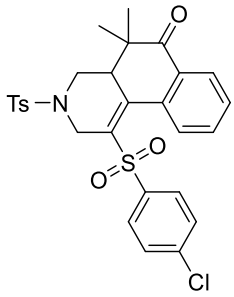


5,5-Dimethyl-1-(phenylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (85.5 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 6.4 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 1H), 7.71-7.66 (m, 4H), 7.54-7.49 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 4.42-4.38 (m, 1H), 3.70-3.64 (m, 2H), 3.08-3.03 (m, 1H), 2.86 (t, *J* = 6.8 Hz, 1H), 2.38 (s, 3H), 1.25 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.6, 144.2, 143.5, 139.3, 136.1, 135.4, 133.9, 133.8, 131.9, 131.3, 131.0, 130.0, 129.5, 129.0, 127.9, 127.7, 127.5, 47.6, 46.8, 46.2, 43.6, 22.3, 21.5, 19.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{27}NNaO_5S_2$ ($[M+Na]^+$) 544.1223, found 544.1229.

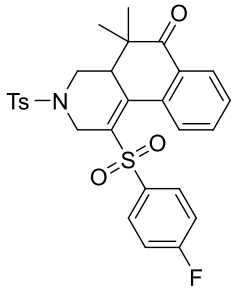


1-((4-Bromophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (94.6 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7,87 (m, 1H), 7.66-7.61 (m, 3H), 7.49-7.41 (m, 6H), 7.23 (d, *J* = 7.6 Hz, 2H), 4.31-4.27 (m, 1H), 3.61-3.53 (m, 2H), 2.99-2.94 (m, 1H), 2.81 (t, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.19 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)

δ: 199.4, 144.3, 144.2, 138.5, 136.0, 134.8, 133.7, 132.4, 132.0, 131.3, 131.2, 130.0, 129.6, 129.4, 129.3, 127.9, 127.6, 47.6, 47.0, 46.2, 43.6, 22.4, 21.5, 19.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}BrNNaO_5S_2$ ($[M+Na]^+$) 622.0328, found 623.0891.

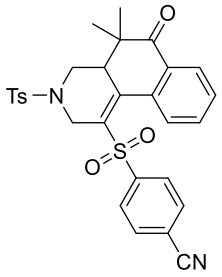


1-((4-Chlorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3h). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (86.6 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.94 (m, 1H), 7.73-7.69 (m, 3H), 7.61-7.58 (m, 2H), 7.52-7.50 (m, 2H), 7.39-7.37 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.39-4.34 (m, 1H), 3.68-3.61 (m, 2H), 3.07-3.02 (m, 1H), 2.88 (t, J = 7.6 Hz, 1H), 2.39 (s, 3H), 1.26 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.4, 144.3, 144.1, 140.7, 137.9, 136.0, 134.9, 133.6, 132.0, 131.3, 131.2, 130.0, 129.6, 129.4, 129.3, 127.8, 127.5, 47.6, 46.9, 46.2, 43.6, 22.4, 21.5, 19.0; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}ClNNaO_5S_2$ ($[M+Na]^+$) 578.0833, found 578.0831.

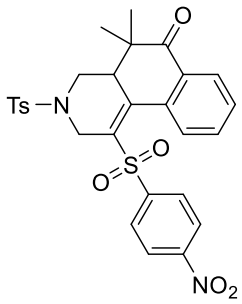


1-((4-Fluorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3i). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (84.1 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.92 (m, 1H), 7.75 (t, J = 4.4 Hz, 1H), 7.71-7.66 (m, 4H), 7.51 (t, J = 3.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.09-7.04 (m, 2H), 4.41-4.35 (m, 1H), 3.70-3.62 (m, 2H), 3.10-3.04 (m, 1H), 2.87 (t, J = 7.6 Hz, 1H), 2.38 (s, 3H), 1.26 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.4, 165.6 (d, J_{C-F} =

258.8 Hz), 144.2, 143.7, 136.0, 135.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 135.2, 133.7, 131.9, 131.2, 131.1, 130.8 (d, $J_{C\text{-}F}$ = 9.7 Hz), 130.0, 129.5, 127.8, 127.5, 116.3 (d, $J_{C\text{-}F}$ = 22.8 Hz), 47.6, 46.9, 46.1, 43.5, 22.3, 21.4, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.1; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}FNNaO_5S_2$ ($[M+Na]^+$) 562.1129, found 562.1125.

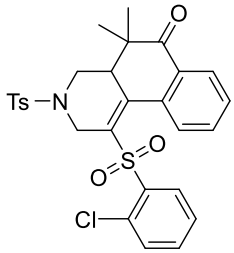


4-((5,5-Dimethyl-6-oxo-3-tosyl-2,3,4,4a,5,6-hexahydrobenzo[*f*]isoquinolin-1-yl)sulfonyl)benzonitrile (3j). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (77.6 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.94 (m, 1H), 7.77-7.69 (m, 7H), 7.53 (t, J = 2.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.36-4.31 (m, 1H), 3.79-3.74 (m, 1H), 3.62-3.57 (m, 1H), 3.16-3.11 (m, 1H), 2.92-2.88 (m, 1H), 2.41 (s, 3H), 1.27 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.2, 145.5, 144.4, 143.7, 135.7, 134.2, 133.5, 132.7, 132.1, 131.4, 131.1, 130.1, 129.7, 128.4, 128.1, 127.6, 117.5, 116.7, 47.8, 47.1, 45.9, 43.5, 22.6, 21.5, 19.3; HRMS *m/z* (ESI) calcd for $C_{29}H_{26}N_2NaO_5S_2$ ($[M+Na]^+$) 569.1175, found 569.1171.

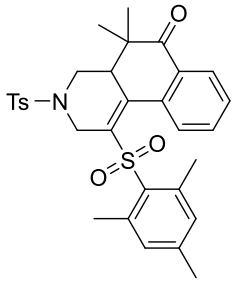


5,5-Dimethyl-1-((4-nitrophenyl)sulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3k). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (70.2 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.20 (m, 2H), 7.96-7.93 (m, 1H), 7.85-7.82 (m, 2H), 7.74-7.69 (m, 3H), 7.54-7.52 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.41-4.34 (m, 1H), 3.80-3.75 (m, 1H), 3.63-3.58 (m, 1H), 3.16-3.11 (m, 1H), 2.91 (t, J = 7.2 Hz,

1H), 2.40 (s, 3H), 1.28 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.2, 150.5, 145.8, 145.2, 144.5, 135.7, 134.1, 133.4, 132.1, 131.5, 131.1, 130.1, 129.7, 129.1, 128.1, 127.6, 124.1, 47.8, 47.2, 46.0, 43.5, 22.6, 21.5, 19.3; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}N_2NaO_7S_2$ ($[M+H]^+$) 589.1074, found 589.1078.

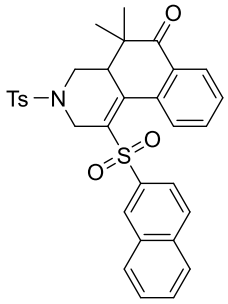


1-((2-Chlorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3l). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (68.8 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-7.96 (m, 2H), 7.90-7.88 (m, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.49-7.43 (m, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 3H), 4.21-4.16 (m, 1H), 3.93-3.91 (m, 1H), 3.59-3.54 (m, 1H), 3.32-3.27 (m, 1H), 2.79 (t, J = 6.8 Hz, 1H), 2.37 (s, 3H), 1.28 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.0, 144.2, 143.1, 136.3, 135.8, 135.0, 134.5, 133.7, 132.6, 132.0 (2), 131.8, 130.9, 130.8, 130.0, 129.9, 127.9, 127.6, 126.9, 47.8, 46.7, 46.0, 43.4, 23.2, 21.5, 20.2; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}ClNNaO_5S_2$ ($[M+Na]^+$) 578.0833, found 578.0837.

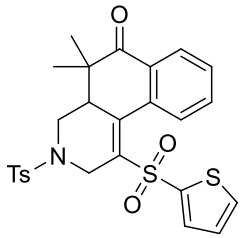


1-(Mesitylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3m). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (80.0 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01-7.95 (m, 2H), 7.74-7.71 (m, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.49-7.47 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 4.15-4.10 (m, 1H), 3.70-3.64 (m, 1H), 3.33-3.28 (m, 1H), 3.15-3.09 (m, 1H), 2.73 (t, J = 8.0 Hz, 1H),

2.58 (s, 6H), 2.31 (d, J = 2.0 Hz, 6H), 1.27 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.0, 144.1 (2), 140.2 (2), 136.5, 136.2, 134.1, 132.4, 131.9, 131.2, 130.8, 129.9, 129.6, 128.8, 127.7, 127.6, 52.7, 47.2, 46.0, 43.4, 22.8, 22.7 (2), 21.4, 21.0, 19.8; HRMS *m/z* (ESI) calcd for $C_{31}H_{33}NNaO_5S_2$ ($[M+Na]^+$) 586.1692, found 586.1698.

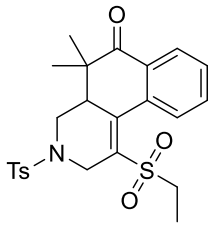


5,5-Dimethyl-1-(naphthalen-2-ylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3n). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (85.7 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 7.89-7.78 (m, 5H), 7.68-7.61 (m, 4H), 7.57-7.51 (m, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 4.49-4.45 (m, 1H), 3.73-3.67 (m, 1H), 3.61-3.57 (m, 1H), 3.01-2.96 (m, 1H), 2.91-2.86 (m, 1H), 2.34 (s, 3H), 1.24 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.5, 144.1, 143.5, 136.1, 135.9, 135.3, 135.1, 133.8, 131.8, 131.7, 131.5, 131.1, 131.0, 130.3, 130.0, 129.6 (2), 129.2, 127.9 (2), 127.6, 127.5, 122.1, 47.5, 46.9, 46.5, 43.7, 22.3, 21.5, 18.9; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}NNaO_5S_2$ ($[M+Na]^+$) 594.1379, found 594.1371.

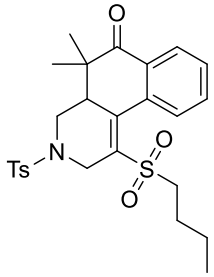


5,5-Dimethyl-1-(thiophen-2-ylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3o). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (64.3 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.90 (m, 1H), 7.62 (d, J = 8.4 Hz, 3H), 7.47-7.43

(m, 3H), 7.20 (d, *J* = 8.4 Hz, 3H), 6.97 (t, *J* = 4.4 Hz, 1H), 4.43-4.38 (m, 1H), 3.67-3.62 (m, 2H), 3.00-2.94 (m, 1H), 2.81 (t, *J* = 7.6 Hz, 1H), 2.30 (s, 3H), 1.19 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 199.6, 144.2, 143.8, 140.4, 136.1, 135.5, 134.9, 134.7, 133.9, 131.8, 131.4, 131.1, 130.0, 129.6, 127.7 (2), 127.5, 47.6, 47.0, 46.1, 43.6, 22.3, 21.5, 18.8; HRMS *m/z* (ESI) calcd for $C_{26}H_{25}NNaO_5S_3$ ($[M+Na]^+$) 550.0787, found 550.0785.

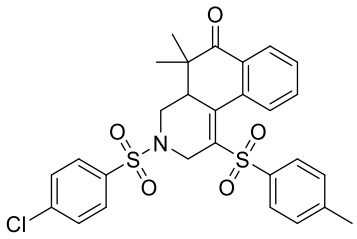


1-(Ethylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3p). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (45.4 mg, 48% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.71-7.69 (m, 2H), 7.56-7.54 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.40-4.36 (m, 1H), 3.69-3.61 (m, 2H), 3.06-3.02 (m, 1H), 2.83 (d, *J* = 7.5 Hz, 1H), 2.48-2.41 (m, 2H), 2.37 (s, 3H), 1.29 (s, 3H), 1.25 (t, *J* = 2.0 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 199.7, 145.1, 144.2, 143.0, 135.6, 134.0, 131.9, 131.4, 130.9, 130.0, 129.7, 128.0, 127.6, 47.6, 46.9, 46.3, 43.6, 22.3, 21.6, 21.5, 18.9, 14.1; HRMS *m/z* (ESI) calcd for $C_{24}H_{27}NNaO_5S_2$ ($[M+Na]^+$) 496.1223, found 496.1225.

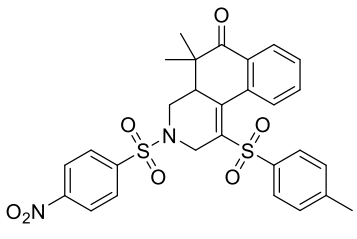


1-(Butylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3q). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Yellow oil (39.1 mg, 39% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.71-7.69 (m, 2H), 7.57-7.54 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.41-4.36 (m, 1H), 3.69-3.61 (m, 2H), 3.06-3.02 (m, 1H), 2.84 (t, *J* = 7.5 Hz,

1H), 2.48-2.42 (m, 2H), 2.37 (s, 3H), 1.67-1.60 (m, 2H), 1.50-1.40 (m, 2H), 1.29 (s, 3H), 1.25 (t, *J* = 3.0 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 199.7, 145.1, 144.2, 143.0, 135.6, 134.0, 131.9, 131.5, 130.9, 130.0, 129.7, 128.0, 127.6, 47.6, 46.9, 46.3, 43.6, 31.5, 30.1, 22.3, 21.6, 21.5, 18.9, 14.1; HRMS *m/z* (ESI) calcd for $C_{26}H_{31}NNaO_5S_2$ ($[M+Na]^+$) 524.1536, found 524.1534.

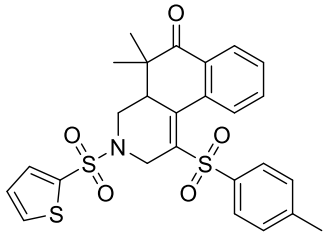


3-((4-Chlorophenyl)sulfonyl)-5,5-dimethyl-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3r). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (91.0 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.95-7.93 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.57-7.53 (m, 3H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.44-4.39 (m, 1H), 3.76-3.70 (m, 1H), 3.67-3.62 (m, 1H), 3.10-3.03 (m, 1H), 2.83 (t, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 1.25 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 199.5, 145.2, 143.0, 139.9, 136.2, 136.0, 135.8, 135.5, 132.1, 131.3, 131.1, 129.7, 129.5, 128.9, 128.0, 127.7, 47.5, 46.7, 46.2, 43.7, 22.3, 21.6, 18.8; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}ClNNaO_5S_2$ ($[M+Na]^+$) 578.0833, found 578.1031.

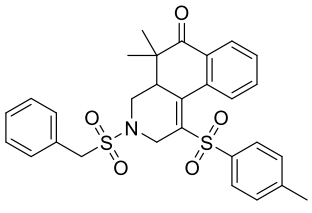


5,5-Dimethyl-3-((4-nitrophenyl)sulfonyl)-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3s). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow solid (69.1 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.34-8.30 (m, 2H), 8.05-8.03 (m, 2H),

7.94-7.92 (m, 1H), 7.64-7.62 (m, 1H), 7.56-7.53 (m, 2H), 7.49-7.44 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 4.53-4.49 (m, 1H), 3.83-3.79 (m, 1H), 3.74-3.70 (m, 1H), 3.16-3.11 (m, 1H), 2.82-2.78 (m, 1H), 2.37 (s, 3H), 1.26 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 199.1, 150.3, 145.4, 143.4, 142.8, 136.0, 135.7, 135.5, 132.1, 131.3, 131.0, 129.8, 129.4, 128.7, 128.1, 127.9, 124.6, 47.4, 46.6, 46.2, 43.8, 22.2, 21.6, 18.7; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}N_2NaO_7S_2$ ($[M+Na]^+$) 589.1074, found 589.1078.

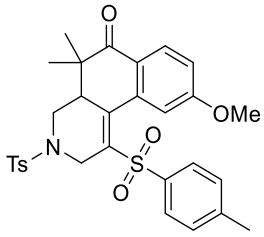


5,5-Dimethyl-3-(thiophen-2-ylsulfonyl)-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3t). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (73.8 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.61-7.58 (m, 2H), 7.54-7.49 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 4.4 Hz 1H), 4.38 (d, *J* = 17.6 Hz, 1H), 3.74-3.63 (m, 2H), 3.13-3.08 (m, 1H), 2.97 (t, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 1.26 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.6, 145.1, 143.1, 136.7, 136.4, 136.3, 135.2, 133.0, 132.8, 132.1, 131.4, 131.0, 129.7, 129.6, 128.0, 127.9, 127.7, 47.6, 47.1, 46.2, 43.7, 22.4, 21.5, 19.0; HRMS *m/z* (ESI) calcd for $C_{26}H_{25}NNaO_5S_3$ ($[M+Na]^+$) 550.0787, found 550.0781.

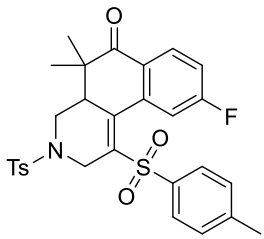


3-(Benzylsulfonyl)-5,5-dimethyl-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3u). The product was purified by silica gel column chromatography with

petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (64.2 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99-7.92 (m, 2H), 7.54-7.45 (m, 5H), 7.33 (t, J = 4.0 Hz, 1H), 7.30 (t, J = 2.4 Hz, 1H), 7.20-7.19 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.29 (d, J = 6.0 Hz, 1H), 4.22 (t, J = 8.8 Hz, 2H), 3.53 (d, J = 17.6 Hz, 1H), 3.42-3.36 (m, 1H), 2.79-2.74 (m, 1H), 2.53 (t, J = 8.0 Hz, 1H), 2.32 (s, 3H), 1.04 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.6, 145.1, 143.9, 136.6 (2), 136.4, 132.3, 131.8, 131.1, 130.6, 129.8, 129.6, 129.0, 128.8, 128.4, 127.9, 127.8, 58.4, 47.7, 47.2, 46.3, 43.9, 21.9, 21.6, 18.7; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NNaO_5S_2$ ($[M+Na]^+$) 558.1379, found 558.1381.

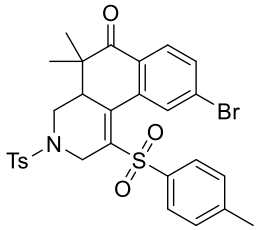


9-Methoxy-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3v). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (98.3 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (t, J = 7.2 Hz, 3H), 7.50 (d, J = 8.0 Hz, 2H), 7.20-7.14 (m, 5H), 6.97-6.94 (m, 1H), 4.36-4.32 (m, 1H), 3.78 (s, 3H), 3.67-3.62 (m, 1H), 3.43 (d, J = 17.2 Hz, 1H), 2.88-2.82 (m, 1H), 2.75 (t, J = 7.6 Hz, 1H), 2.30 (d, J = 6.0 Hz, 6H), 1.16 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.6, 161.6, 144.9, 144.1, 142.8, 136.6, 134.0, 133.6, 133.3, 131.0, 129.9, 129.7, 129.1, 127.9, 127.5, 119.1, 110.2, 55.6, 47.2, 46.9, 46.5, 43.8, 22.0, 21.5, 21.4, 18.8; HRMS *m/z* (ESI) calcd for $C_{30}H_{31}NNaO_6S_2$ ($[M+Na]^+$) 588.1485, found 588.1483.

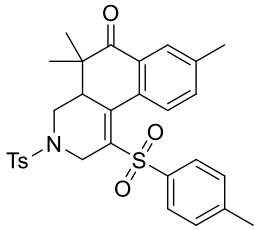


9-Fluoro-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3w). The product was purified by

silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (89.6 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89-7.86 (m, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.32-7.29 (m, 2H), 7.21 (d, J = 10.0 Hz, 3H), 7.08-7.03 (m, 1H), 4.34 (d, J = 18.0 Hz, 1H), 3.64 (t, J = 9.6 Hz, 2H), 3.03-2.98 (m, 1H), 2.74 (t, J = 7.6 Hz, 1H), 2.31 (s, 6H), 1.17 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.3, 163.9 (d, $J_{C\text{-}F}$ = 256.6 Hz), 145.4, 144.3, 141.4, 138.6 (d, $J_{C\text{-}F}$ = 9.9 Hz), 137.0, 136.1, 134.1, 130.7 (d, $J_{C\text{-}F}$ = 9.7 Hz), 130.0, 129.7, 128.0, 127.5, 126.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 118.1, 117.9 (d, $J_{C\text{-}F}$ = 3.6 Hz), 77.3, 77.0, 76.7, 47.5, 46.5, 46.1, 43.6, 22.2, 21.6, 21.3, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.2; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}FNNaO_5S_2$ ([M+Na]$^+$) 576.1285, found 576.1283.

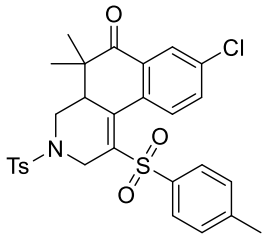


9-Bromo-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3x). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (98.1 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.8 Hz, 4H), 7.22-7.18 (m, 4H), 4.28-4.23 (m, 1H), 3.61-3.45 (m, 2H), 2.97-2.92 (m, 1H), 2.76-2.72 (m, 1H), 2.32 (d, J = 10.0 Hz, 6H), 1.17 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.5, 145.4, 144.2, 141.8, 136.2, 136.1, 135.0, 134.6, 133.9, 133.0, 130.9, 130.5, 130.0, 129.9, 128.0, 127.5, 125.7, 47.6, 46.6, 46.4, 43.5, 22.2, 21.6, 21.5, 18.8; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}BrNNaO_5S_2$ ([M+Na]$^+$) 636.0484, found 636.0480.

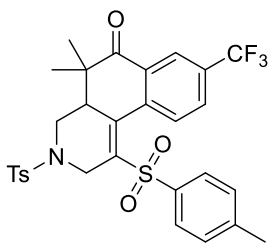


5,5,8-Trimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3y). The product was purified by silica gel

column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (90.1 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.56-7.49 (m, 3H), 7.22-7.14 (m, 5H), 4.33-4.28 (m, 1H), 3.63-3.58 (m, 1H), 3.50-3.44 (m, 1H), 2.93-2.88 (m 1H), 2.77-2.72 (m, 1H), 2.32 (d, J = 4.0 Hz, 6H), 1.16 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.9, 145.0, 144.1, 143.2, 141.5, 136.6, 134.6, 134.0, 133.6, 132.7, 131.5, 130.0, 129.7, 129.4, 128.0, 127.9, 127.5, 47.5, 46.9, 46.4, 43.7, 22.2, 21.6, 21.5, 21.3, 18.9; HRMS *m/z* (ESI) calcd for $C_{30}H_{31}NNaO_5S_2$ ([M+Na]$^+$) 572.1536, found 572.1532.

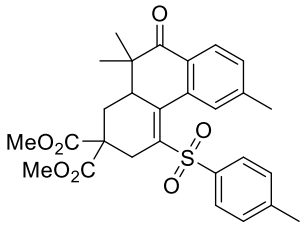


8-Chloro-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3z). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (91.1 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 2.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 3H), 7.54 (d, J = 8.4 Hz, 2H), 7.43-7.40 (m, 1H), 7.24-7.21 (m, 4H), 4.29 (t, J = 13.6 Hz 1H), 3.65-3.60 (m, 1H), 3.54-3.50 (m, 1H), 3.01-2.95 (m, 1H), 2.77 (t, J = 7.6 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.6, 145.4, 144.2, 141.8, 137.5, 136.2, 136.1, 134.6, 133.9, 133.0, 131.7, 130.9, 130.0, 129.9, 128.0, 127.6, 127.5, 47.6, 46.7, 46.4, 43.6, 22.2, 21.6, 21.5, 18.8; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}ClNNaO_5S_2$ ([M+Na]$^+$) 592.0990, found 592.0996.

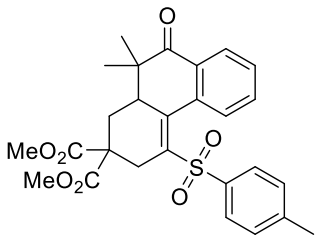


5,5-Dimethyl-1,3-ditosyl-8-(trifluoromethyl)-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3aa). The product was purified by silica gel column chromatography with petroleum

ether/ethyl acetate (3:1, v/v). Yellow oil (91.7 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 6.5 Hz, 3H), 7.59-7.56 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.36-4.32 (m, 1H), 3.66-3.60 (m, 2H), 3.11-3.07 (m, 1H), 2.84-2.81 (m, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 1.28 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.5, 145.6, 144.3, 141.2, 139.3, 137.7, 136.0, 133.9, 132.9, 132.6, 132.2, 130.0, 129.9, 128.0, 127.9 (q, $J_{C\text{-}F}$ = 3.3 Hz), 127.6, 127.3, 124.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 47.8, 46.6, 46.3, 43.4, 22.3, 21.6, 21.4, 18.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -63.2; HRMS *m/z* (ESI) calcd for $C_{30}H_{28}F_3NNaO_5S_2$ ($[M+Na]^+$) 626.1253, found 626.1255.

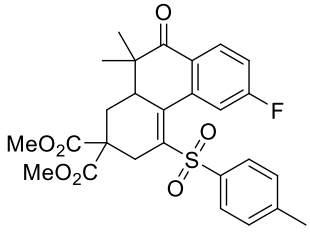


Dimethyl-6,10,10-trimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3ab). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (73.5 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89-7.87 (m, 1H), 7.63 (t, J = 7.6 Hz 3H), 7.29 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 3.77 (d, J = 1.2 Hz, 3H), 3.74 (d, J = 1.2 Hz, 3H), 3.47-3.42 (m, 1H), 3.11 (t, J = 8.8 Hz, 1H), 2.54-2.48 (m, 1H), 2.44 (t, J = 3.2 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 1.74-1.68 (m, 1H), 1.27 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.4, 171.0, 169.5, 144.5, 144.3, 142.8, 137.2, 136.8, 135.7, 131.5 (2), 129.5, 128.0, 127.6, 127.2, 53.4, 53.2, 53.0, 48.0, 47.5, 33.6, 29.7, 22.0, 21.6, 21.5, 18.5; HRMS *m/z* (ESI) calcd for $C_{28}H_{30}NaO_7S$ ($[M+Na]^+$) 533.1604, found 533.1606.

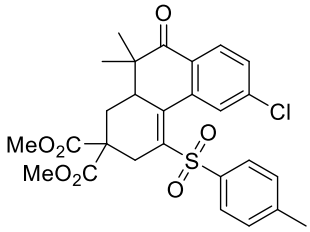


Dimethyl-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3ac). The

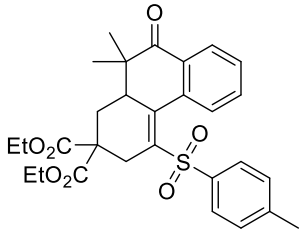
product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (70.5 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01-7.99 (m, 1H), 7.88-7.86 (m, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.53-7.48 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.41-3.36 (m, 1H), 3.12 (t, J = 8.8 Hz, 1H), 2.53-2.47 (m, 1H), 2.39 (s, 3H), 2.34-2.29 (m, 1H), 1.71-1.65 (m, 1H), 1.28 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.7, 171.1, 169.5, 144.7, 144.3, 137.4, 136.7, 135.8, 132.1, 131.4, 130.7, 129.7, 129.6, 128.3, 127.5, 53.5, 53.2, 53.1, 48.1, 47.6, 33.7, 29.8, 22.1, 21.6, 18.5; HRMS *m/z* (ESI) calcd for $C_{27}H_{28}NaO_7S$ ($[M+Na]^+$) 519.1448, found 519.1444.



Dimethyl-6-fluoro-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3ad). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (69.9 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-7.99 (m, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.57-7.55 (m, 1H), 7.24 (s, 2H), 7.17-7.12 (m, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.41 (d, J = 17.6 Hz, 1H), 3.11 (t, J = 8.4 Hz, 1H), 2.53-2.47 (m, 1H), 2.39 (s, 3H), 1.71-1.66 (m, 2H), 1.27 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.3, 170.9, 169.5, 164.2 (d, J_{C-F} = 256.4 Hz), 144.9, 142.7, 139.8 (d, J_{C-F} = 10.0 Hz), 137.4, 136.5, 130.5 (d, J_{C-F} = 9.7 Hz), 129.7, 128.2, 126.2 (d, J_{C-F} = 2.7 Hz), 118.0, 117.8 (d, J_{C-F} = 2.6 Hz), 53.4, 53.3, 53.1, 48.1, 47.5, 33.7, 29.7, 22.0, 21.6, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.4; HRMS *m/z* (ESI) calcd for $C_{27}H_{27}FNaO_7S$ ($[M+Na]^+$) 537.1534, found 537.1530.

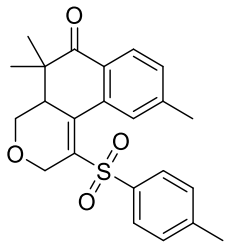


Dimethyl-6-chloro-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3ae). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (71.0 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.45-7.43 (m, 1H), 7.24 (d, J = 2.8 Hz, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.30 (d, J = 17.6 Hz, 1H), 3.05 (t, J = 8.4 Hz, 1H), 2.49-2.43 (m, 1H), 2.38 (s, 3H), 2.22 (d, J = 17.6 Hz, 1H), 1.63 (t, J = 6.4 Hz, 1H), 1.24 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.5, 170.9, 169.4, 144.9, 142.9, 137.2, 136.4, 136.3, 135.7, 132.9, 131.9, 130.8, 129.8, 128.2, 127.2, 53.4, 53.3, 53.1, 48.0, 47.4, 33.8, 29.7, 22.0, 21.6, 18.3; HRMS *m/z* (ESI) calcd for $C_{27}H_{27}ClNaO_7S$ ($[M+Na]^+$) 553.1058, found 553.1056.

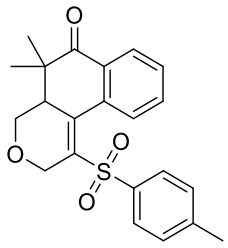


Diethyl-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3af). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (69.2 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 7.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.56-7.49 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.26-4.15 (m, 4H), 3.37 (d, J = 17.6 Hz, 1H), 3.15 (t, J = 8.8 Hz, 1H), 2.53-2.47 (m, 1H), 2.39 (s, 3H), 2.32-2.27 (m, 1H), 1.68-1.63 (m, 1H), 1.28 (s, 3H), 1.25 (t, J = 6.4 Hz, 6H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.8, 170.6, 169.0, 144.6, 144.1, 137.4, 136.5, 135.8, 132.0,

131.3, 130.6, 129.6, 129.5, 128.2, 127.4, 62.2, 61.9, 53.4, 48.0, 47.5, 33.6, 29.6, 22.0, 21.5, 18.4, 14.0, 13.9; HRMS *m/z* (ESI) calcd for $C_{29}H_{32}NaO_7S$ ($[M+Na]^+$) 547.1761, found 547.1763.

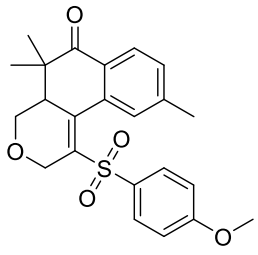


5,5,9-Trimethyl-1-tosyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ag). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow solid (64.2 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 4.67-4.63 (m, 1H), 4.17 (d, J = 16.4 Hz, 1H), 4.05-4.01 (m, 1H), 3.68-3.64 (m, 1H), 2.91 (t, J = 6.0 Hz, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 1.23 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.2, 144.7, 143.1, 142.1, 138.4, 137.0, 136.4, 131.7, 131.5, 129.4, 127.9, 127.7, 127.4, 66.3, 65.4, 47.0, 46.5, 22.3, 21.7, 21.5, 19.5; HRMS *m/z* (ESI) calcd for $C_{23}H_{24}NaO_4S$ ($[M+Na]^+$) 419.1288, found 419.1286.

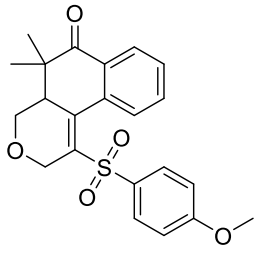


5,5-Dimethyl-1-tosyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ah). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (61.1 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J = 7.6 Hz, 1H), 8.02-8.00 (m, 1H), 7.61-7.57 (m, 3H), 7.54-7.50 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 4.63-4.58 (m, 1H), 4.10-4.01 (m, 2H), 3.68-3.63 (m, 1H), 2.95-2.90 (m, 1H), 2.36 (s, 3H), 1.24 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.4, 144.8, 142.0, 138.5, 136.8, 136.6, 132.2, 131.4, 130.7, 129.8, 129.6,

127.8, 127.7, 66.3, 65.3, 47.1, 46.5, 22.3, 21.5, 19.4; HRMS *m/z* (ESI) calcd for $C_{22}H_{22}NaO_4S$ ($[M+Na]^+$) 405.1131, found 405.1135.

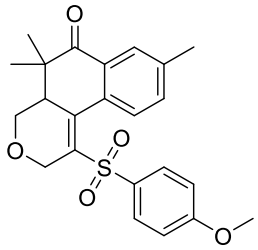


1-((4-Methoxyphenyl)sulfonyl)-5,5,9-trimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ai). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow solid (69.2 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (t, J = 7.0 Hz, 2H), 7.63-7.60 (m, 2H), 7.29 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 4.64 (d, J = 17.5 Hz, 1H), 4.18-4.15 (m, 1H), 4.04-4.01 (m, 1H), 3.81 (s, 3H), 3.65 (t, J = 6.0 Hz, 1H), 2.91-2.89 (m, 1H), 2.47 (s, 3H), 1.22 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.2, 163.6, 143.1, 141.7, 138.9, 136.5, 131.8, 131.5 (2), 130.0, 127.9, 127.6, 114.0, 66.3, 65.4, 55.6, 47.1, 46.6, 22.3, 21.7, 19.5; HRMS *m/z* (ESI) calcd for $C_{23}H_{24}NaO_5S$ ($[M+Na]^+$) 435.1237, found 435.1231.

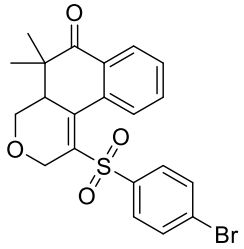


1-((4-Methoxyphenyl)sulfonyl)-5,5-dimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3aj). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (65.3 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.62-7.56 (m, 3H), 7.50 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 4.61-4.56 (m, 1H), 4.10-3.99 (m, 2H), 3.80 (s, 3H), 3.67-3.62 (m, 1H), 2.91 (t, J = 6.8 Hz, 1H), 1.22 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.4, 163.7, 141.6, 139.0, 136.7, 132.2, 131.4, 131.3, 130.6, 130.1, 129.9, 127.7, 114.1, 66.3, 65.3, 55.6, 47.1,

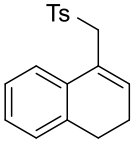
46.5, 22.3, 19.4; HRMS *m/z* (ESI) calcd for $C_{22}H_{22}NaO_5S$ ([M+Na]$^+$) 421.1080, found 421.1266.



1-((4-Methoxyphenyl)sulfonyl)-5,5,8-trimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ak). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Yellow oil (56.1 mg, 68% yield); 1H NMR (500 MHz, $CDCl_3$) δ: 7.90 (t, J = 7.0 Hz, 2H), 7.63-7.60 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 6.85-6.82 (m, 2H), 4.65-4.62 (m, 1H), 4.18-4.15 (m, 1H), 4.04-4.01 (m, 1H), 3.81 (s, 3H), 3.68-3.64 (m, 1H), 2.91-2.88 (m, 1H), 2.47 (s, 3H), 1.22 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.2, 163.6, 143.1, 141.7, 138.9, 136.5, 131.8, 131.5 (2), 130.0, 127.9, 127.5, 114.0, 66.3, 65.4, 55.6, 47.0, 46.6, 22.3, 21.7, 19.5; HRMS *m/z* (ESI) calcd for $C_{23}H_{24}NaO_5S$ ([M+Na]$^+$) 435.1237, found 435.1233.



1-((4-Bromophenyl)sulfonyl)-5,5-dimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3al). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (53.5 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.11-8.09 (m, 1H), 8.04-8.02 (m, 1H), 7.60-7.58 (m, 1H), 7.56-7.52 (m, 5H), 4.63-4.59 (m, 1H), 4.14-4.10 (m, 1H), 4.06-4.02 (m, 1H), 3.70-3.67 (m, 1H), 2.94-2.91 (m, 1H), 1.25 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.1, 143.3, 139.0, 137.9, 136.4, 132.3 (2), 131.3, 131.0, 130.0, 129.2, 129.1, 127.9, 66.2, 65.3, 47.3, 46.7, 22.5, 19.5; HRMS *m/z* (ESI) calcd for $C_{21}H_{19}BrNaO_4S$ ([M+Na]$^+$) 469.0080, found 469.0088.



4-(Tosylmethyl)-1,2-dihydronaphthalene (6a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69-7.66 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.12-7.06 (m, 4H), 5.91 (t, J = 5.0 Hz, 1H), 4.20 (s, 2H), 2.69 (t, J = 8.0 Hz, 2H), 2.38 (s, 3H), 2.25-2.20 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.5, 135.9, 135.4, 134.7, 132.6, 129.4, 128.7, 127.5, 127.2, 126.3, 125.9, 123.2, 60.0, 27.7, 23.3, 21.5; HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_2S$ ($[M+H]^+$) 299.1100, found 299.1104.

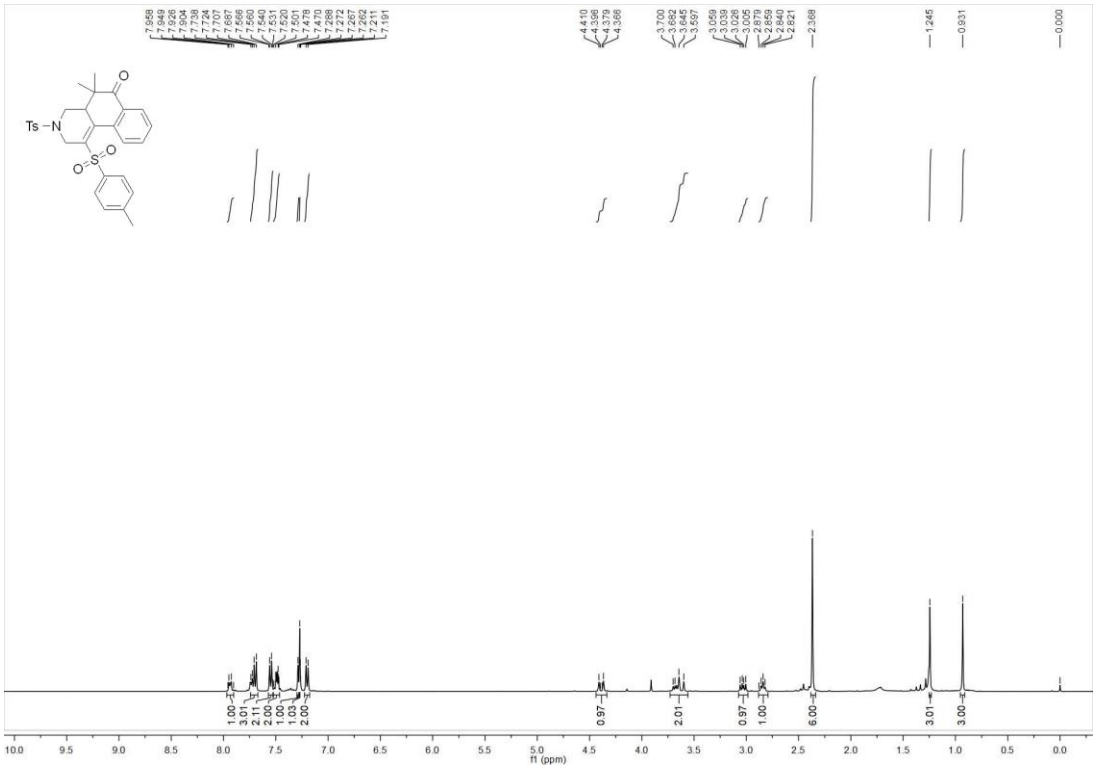
(F) References

1. (a) Shi, S.; Zheng, Z.; Zhang, Y.; Yang, Y.; Ma, D.; Gao, Y.; Liu, Y.; Tang, G.; Zhao, Y., *Org. Lett.* **2021**, *23*, 9348-9352. (b) Zheng, Y.-N.; Cai, X.-E.; Wu, H.-L.; Zhou, Y.; Tian, W.-C.; Ruan, Y.; Liu, H.; Wei, W.-T., *Chem-Asian. J.* **2023**, DOI: 10.1002/asia.202201149.

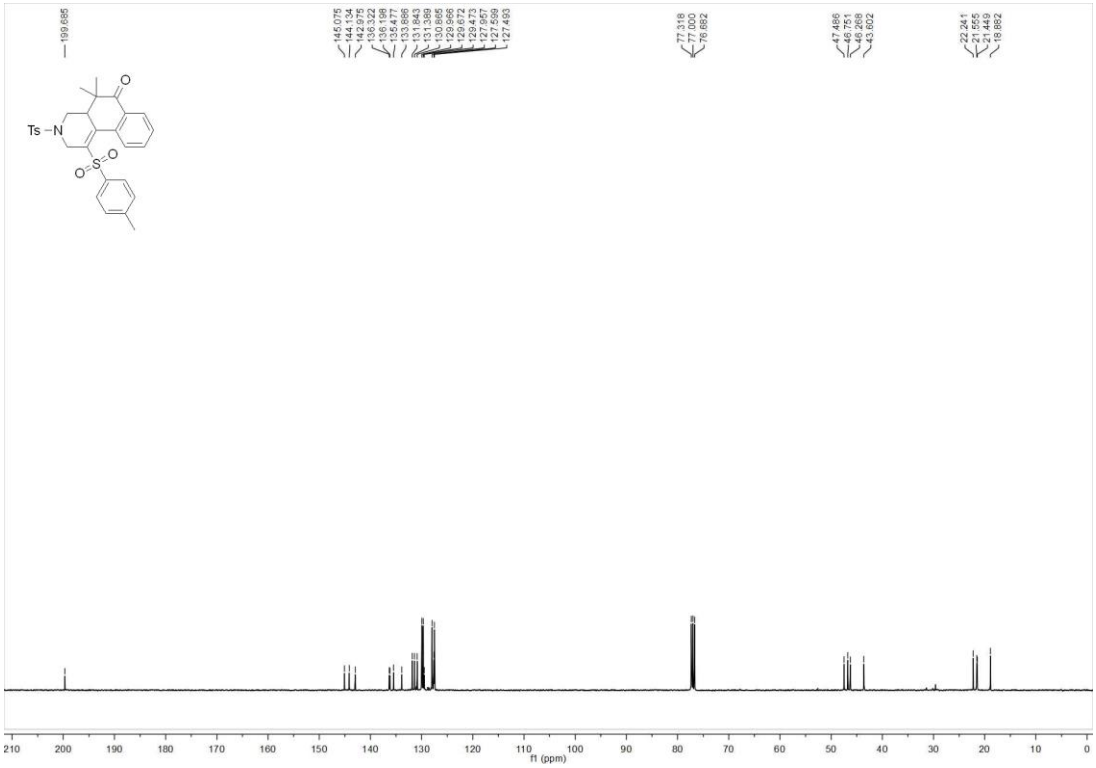
(G) Spectra

5,5-Dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3a)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**

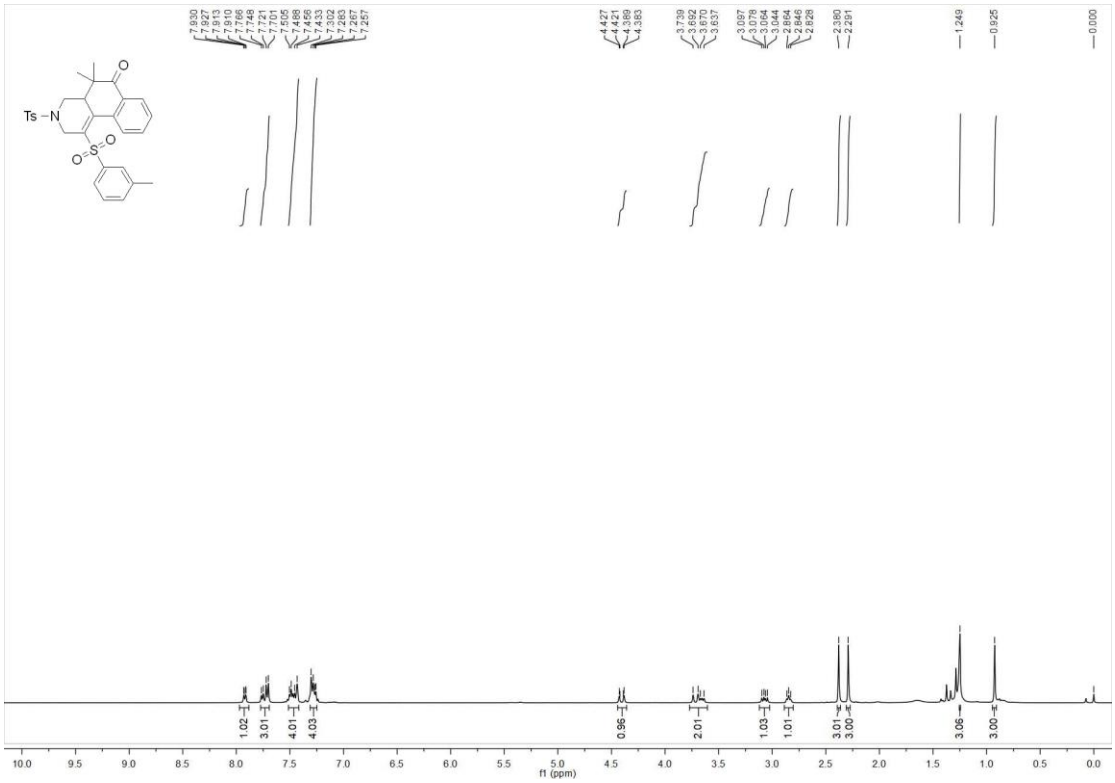


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3a**

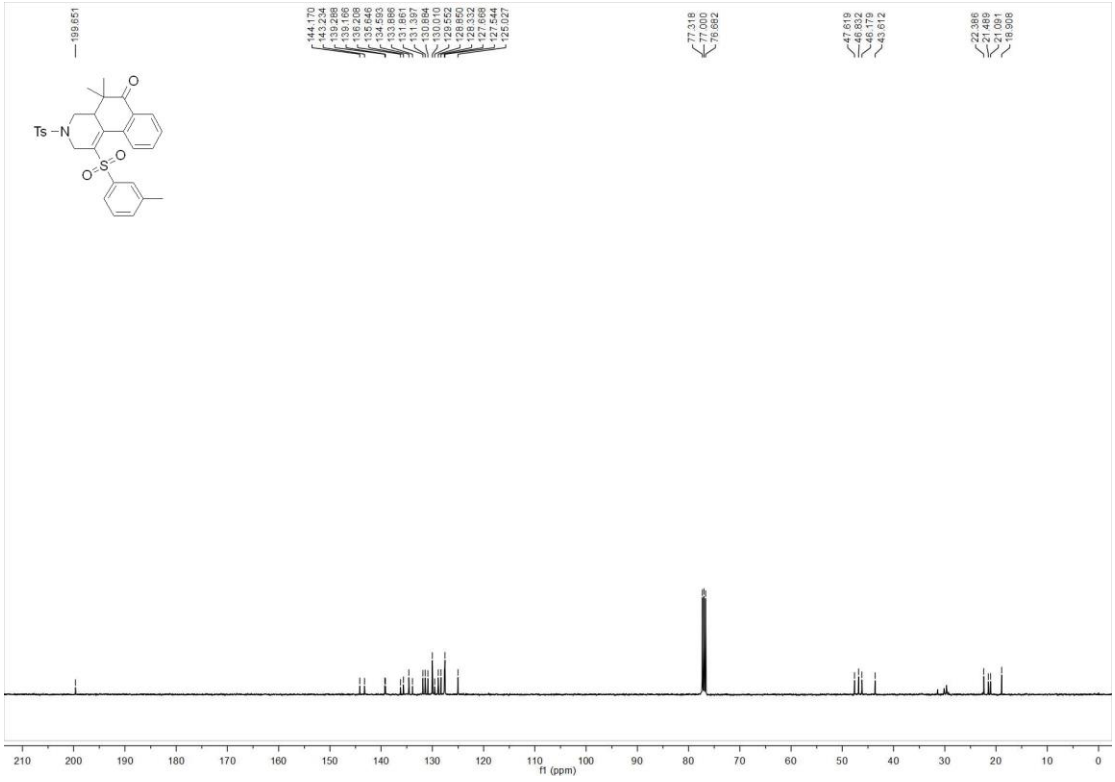


5,5-Dimethyl-1-(*m*-tolylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6 (2*H*)-one (3b)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3b**

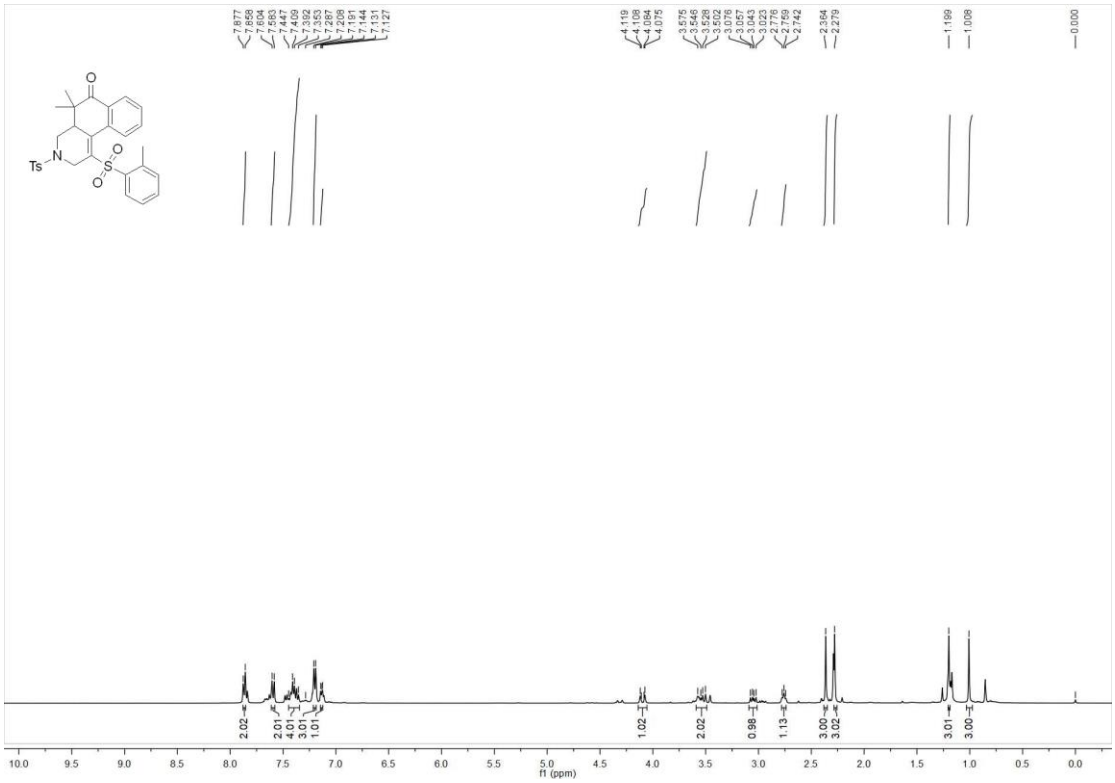


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3b**

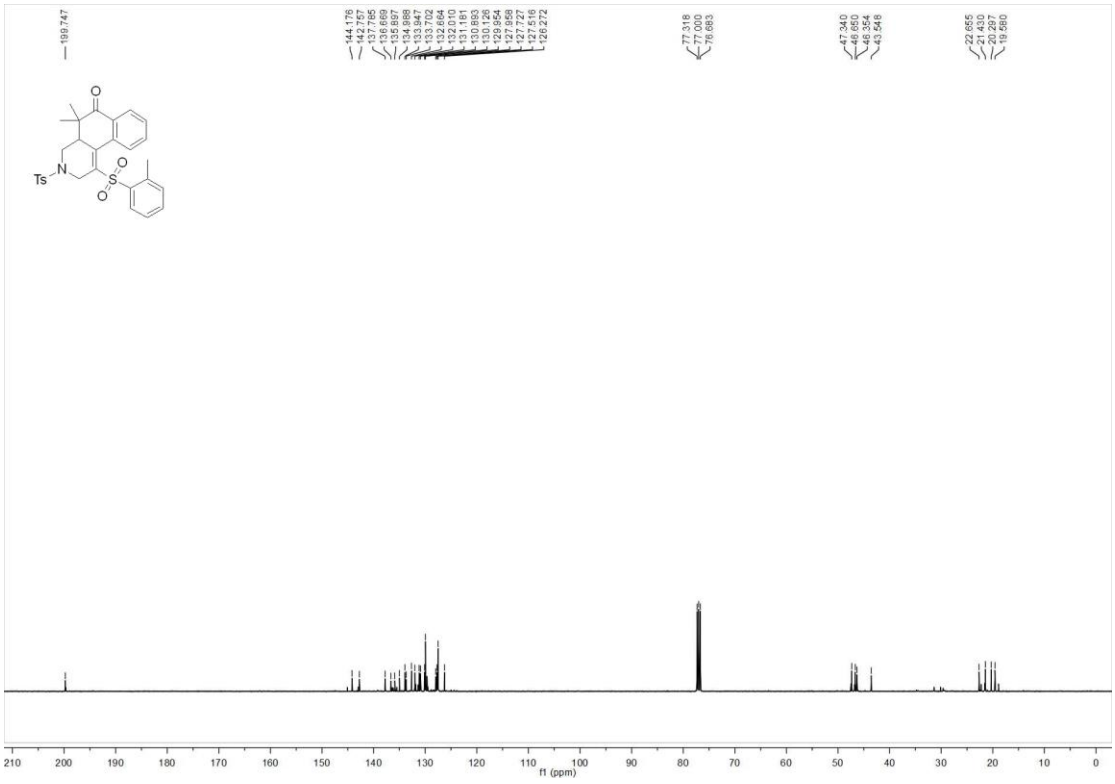


5,5-Dimethyl-1-(*o*-tolylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6 (2*H*)-one (3c)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**

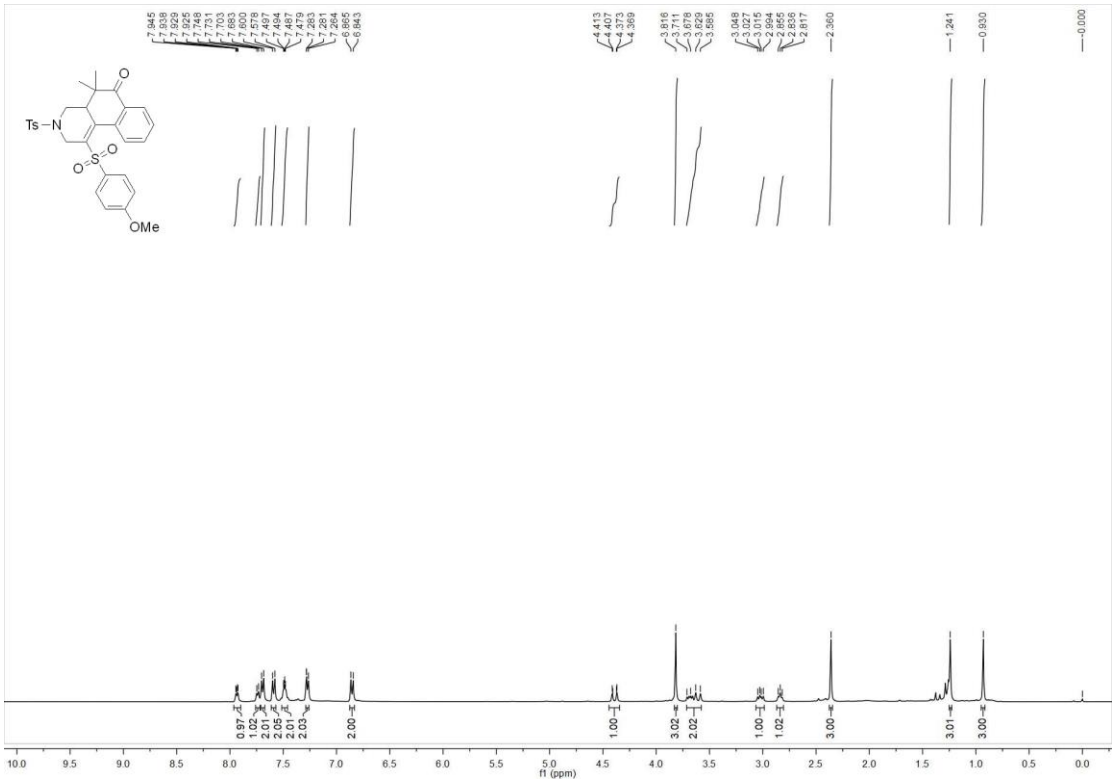


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3c**

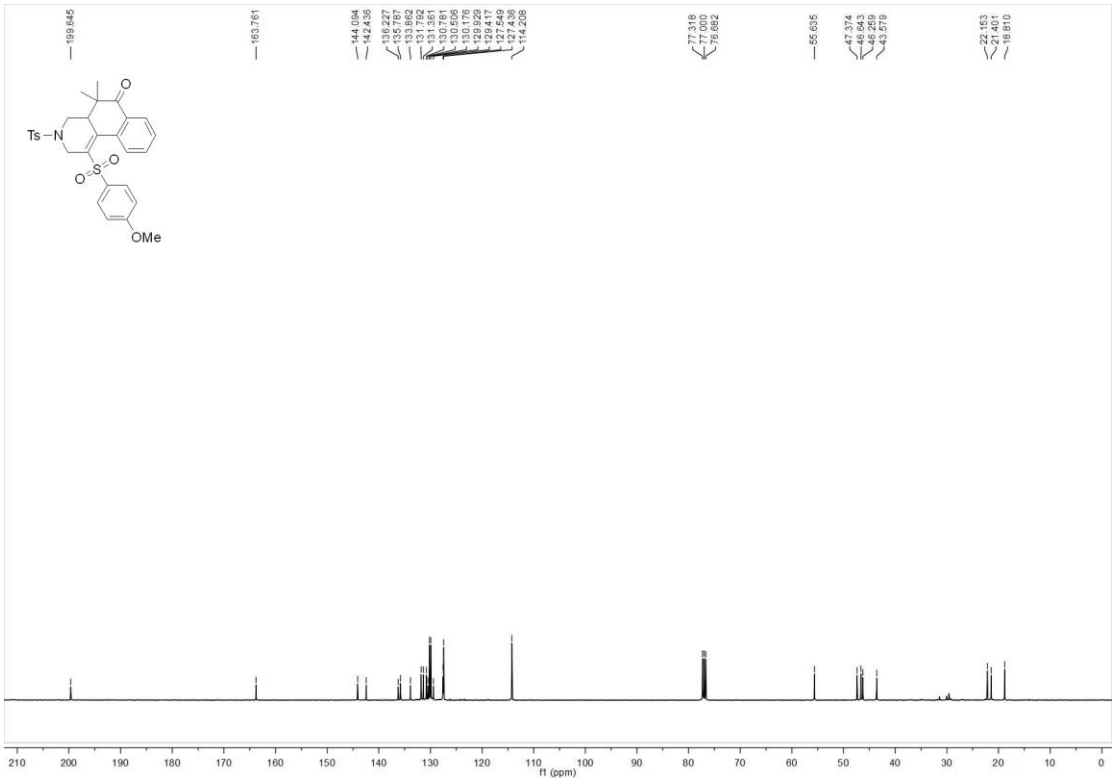


1-((4-Methoxyphenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3d)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d**



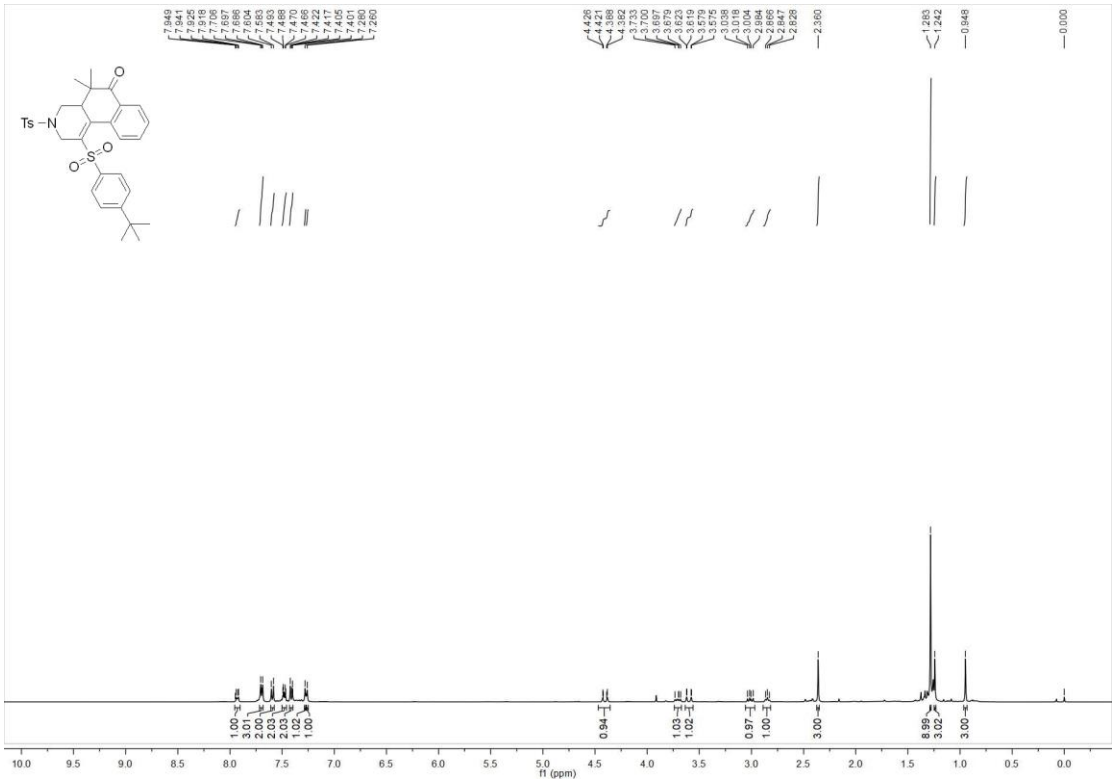
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3d**



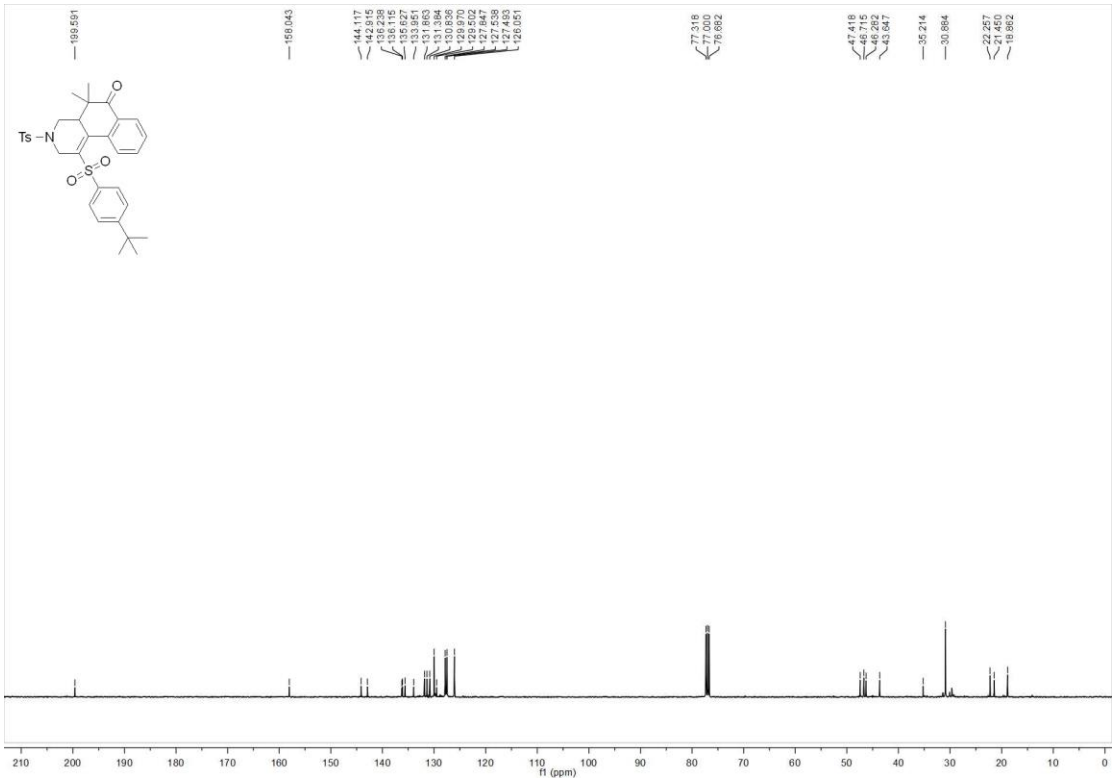
1-((4-(*tert*-Butyl)phenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]

isoquinolin-6(2*H*)-one (3e)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e**

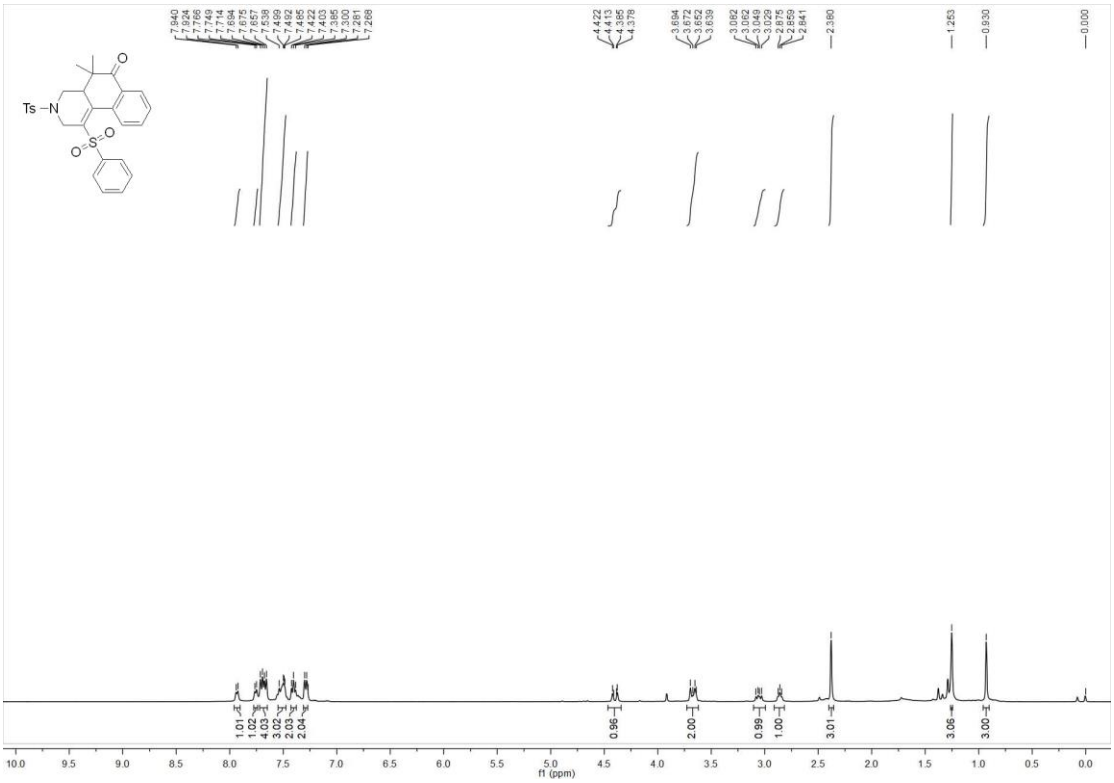


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3e**

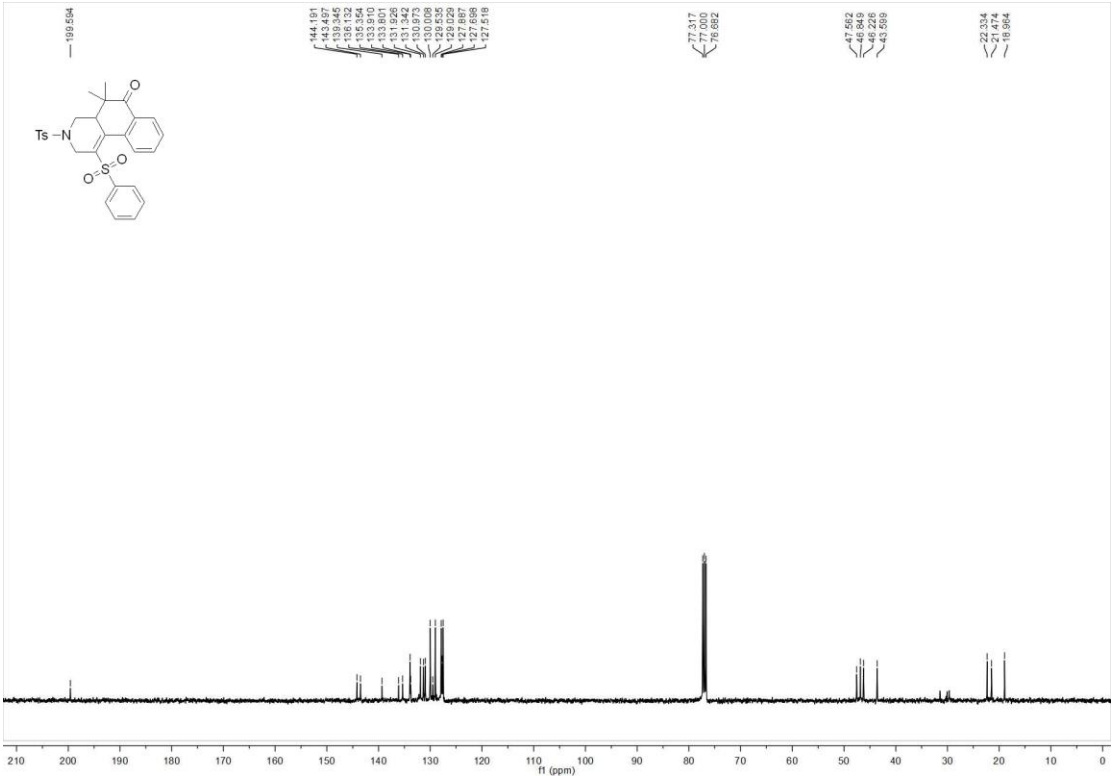


5,5-Dimethyl-1-(phenylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6 (2*H*)-one (3f)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**

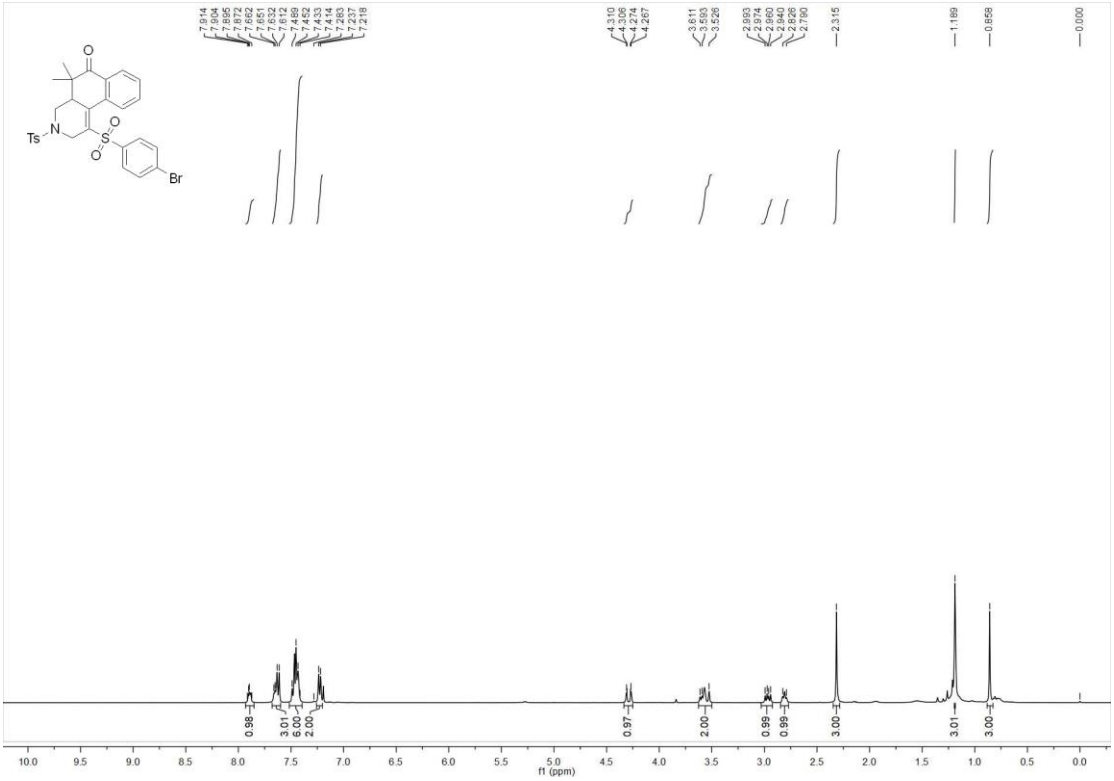


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3f**

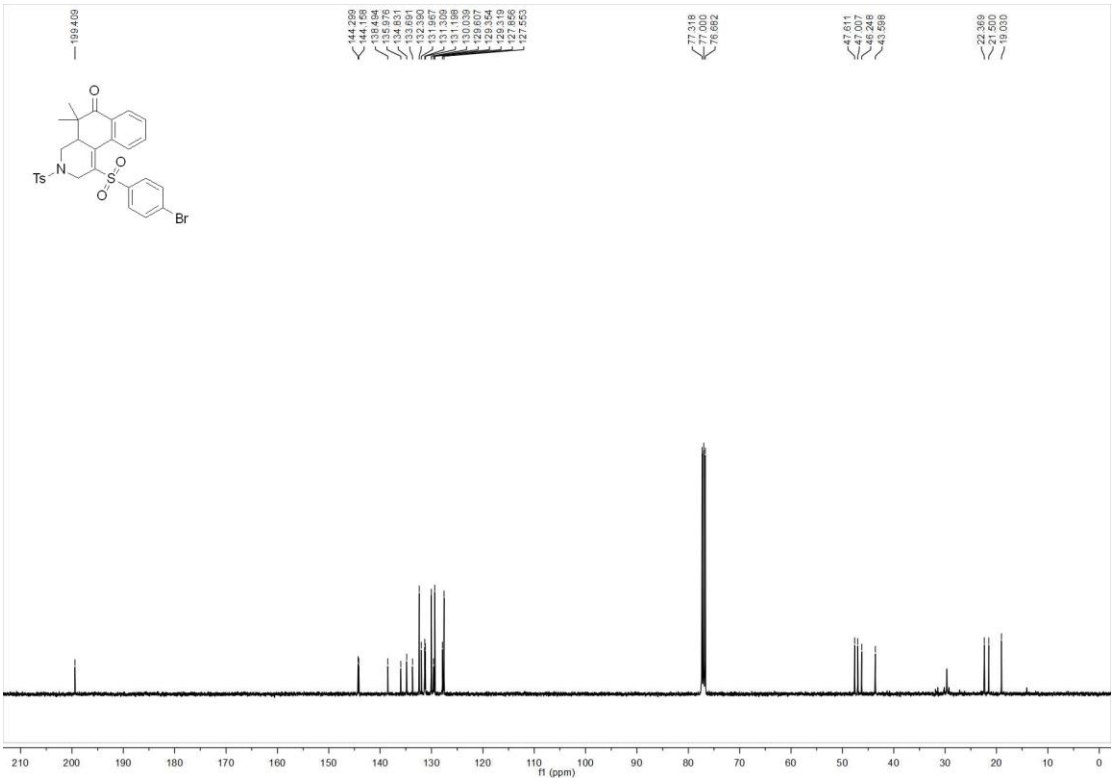


1-((4-Bromophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]iso quinolin-6(2*H*)-one (3g)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3g**

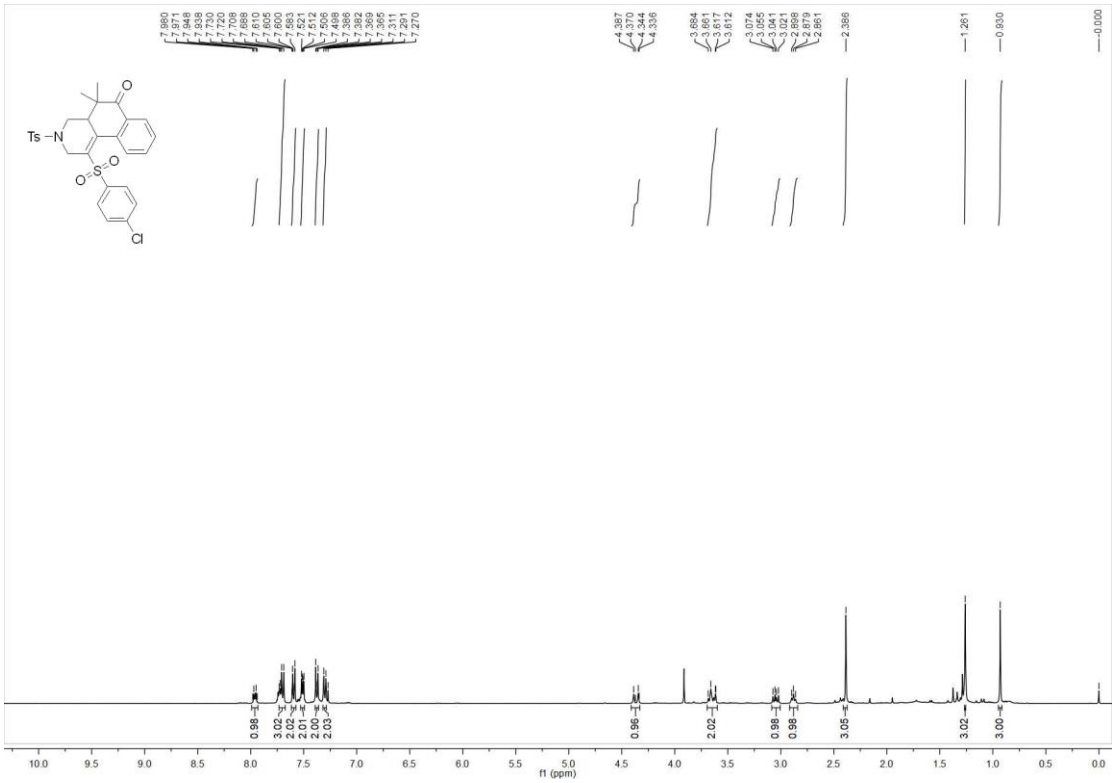


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3g**

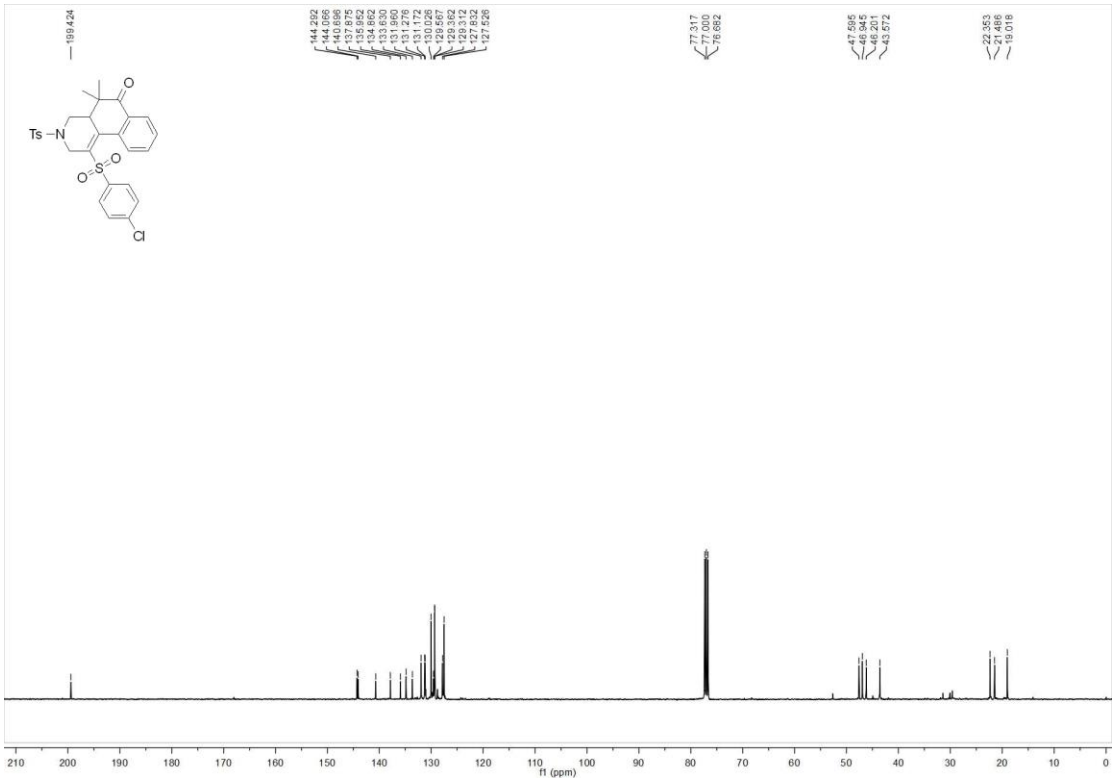


1-((4-Chlorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]iso quinolin-6(2*H*)-one (3h)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



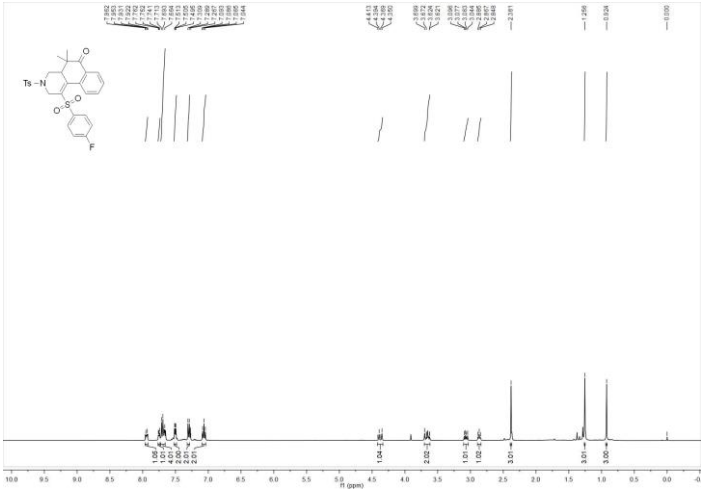
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3h**



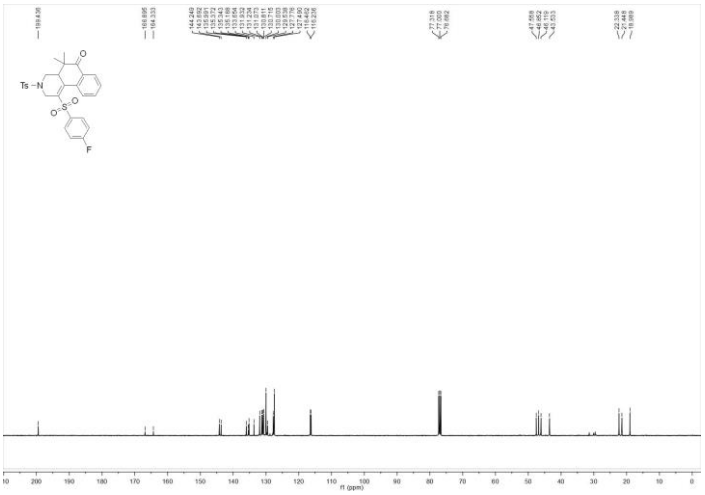
1-((4-Fluorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]iso

quinolin-6(2*H*)-one (3i)

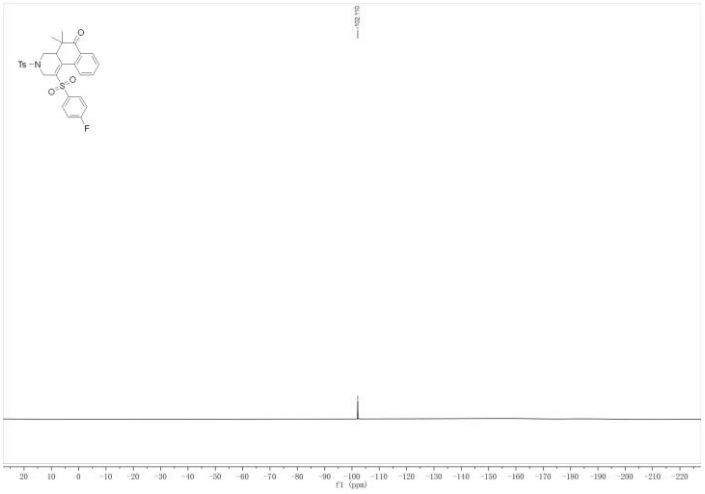
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3i**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3i**

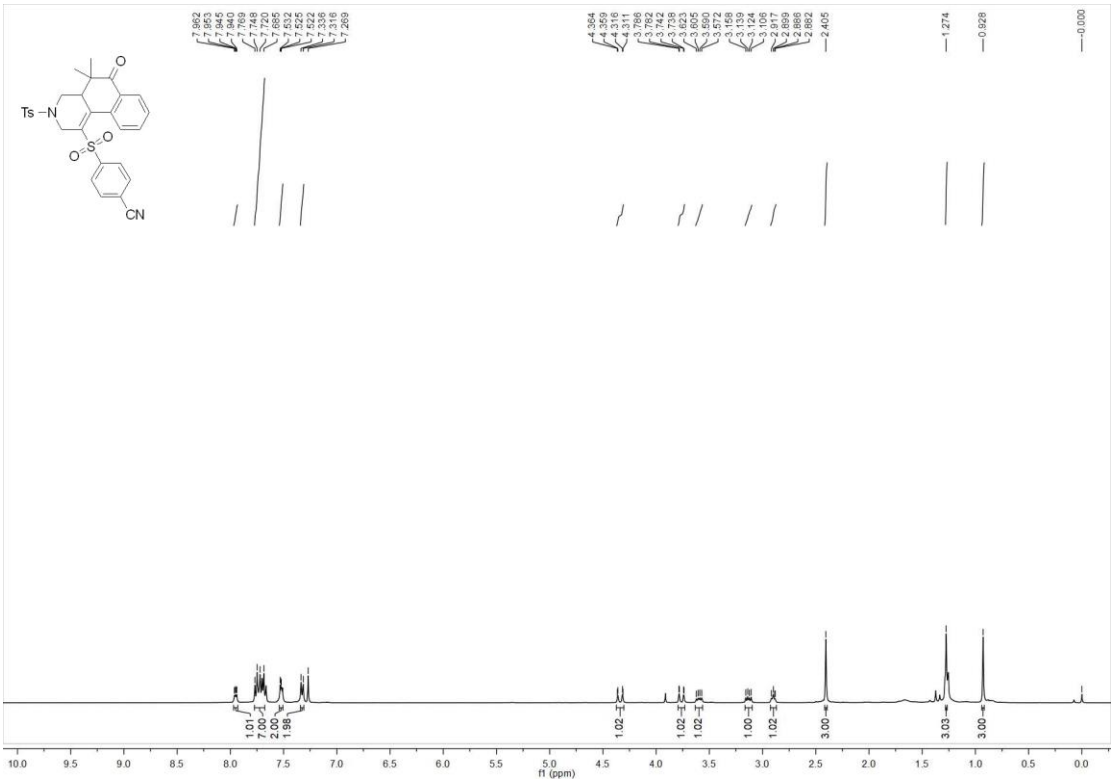


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3i**

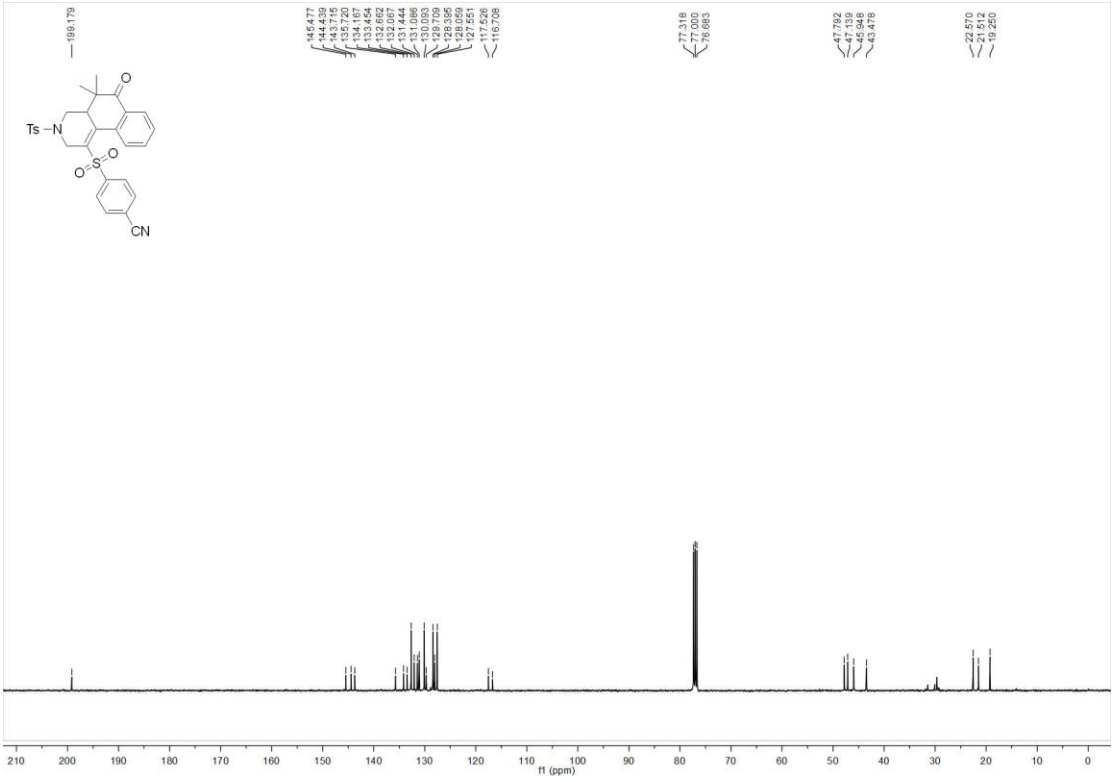


4-((5,5-Dimethyl-6-oxo-3-tosyl-2,3,4,4a,5,6-hexahydrobenzo[*f*]isoquinolin-1-yl)sulfonyl)benzonitrile (3j)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3j**

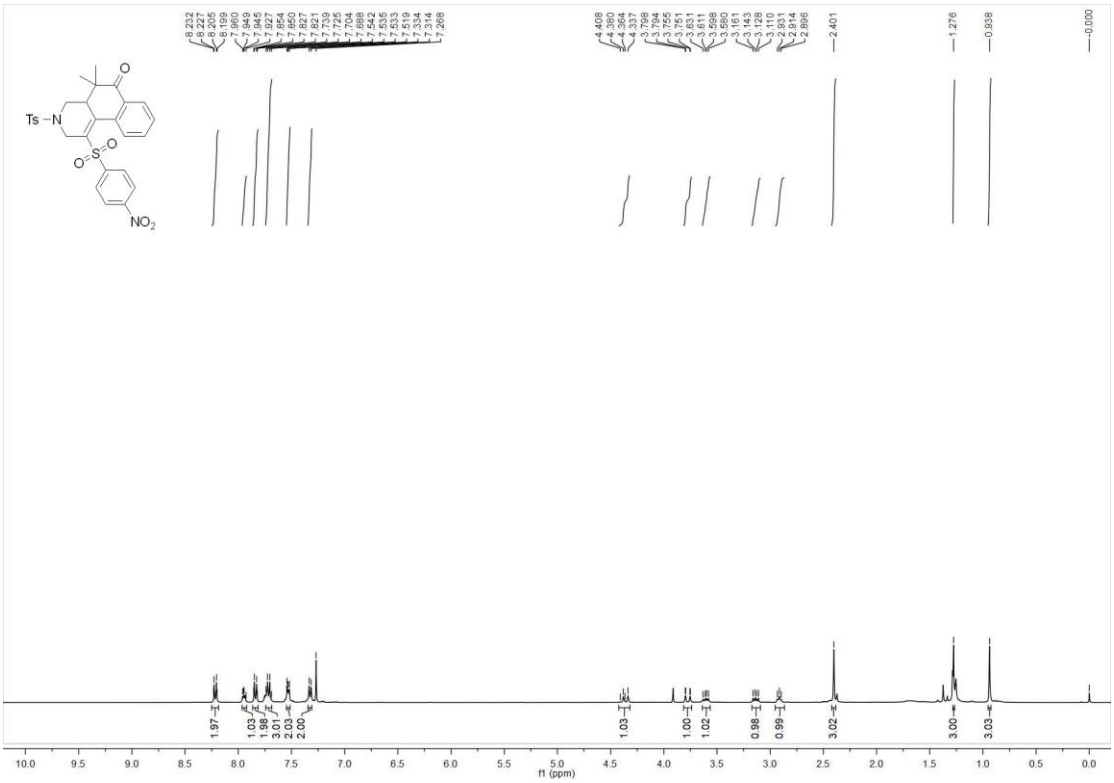


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3j**

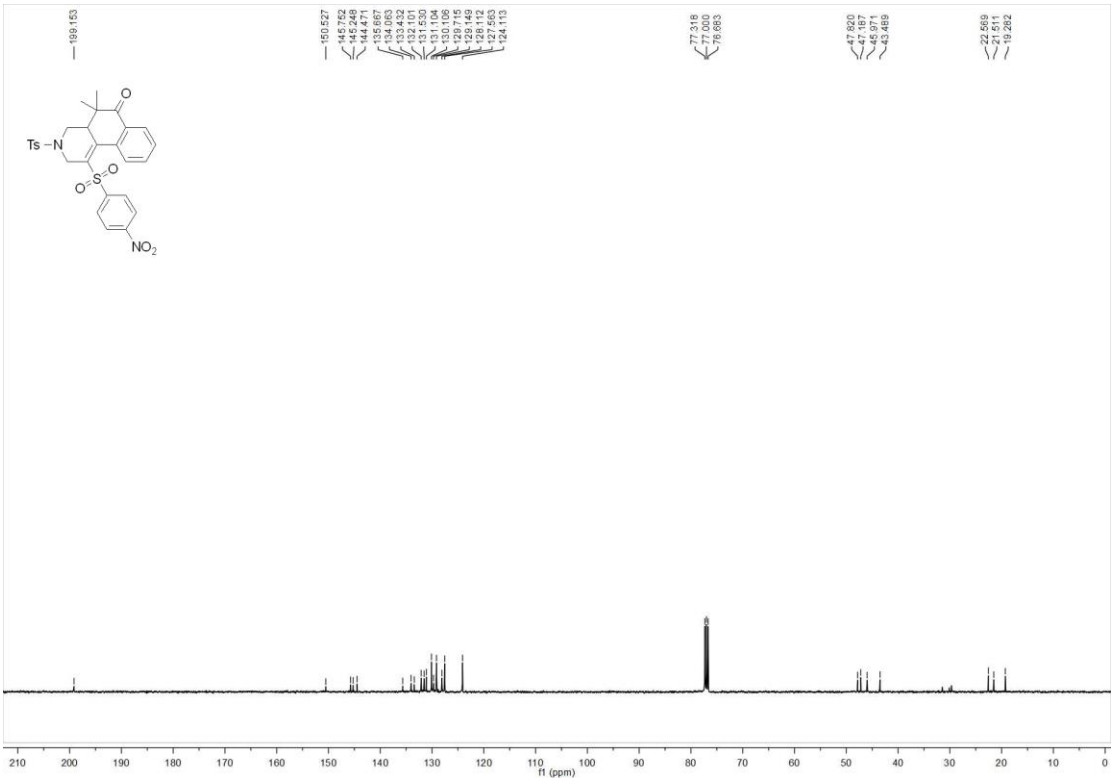


5,5-Dimethyl-1-((4-nitrophenyl)sulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3k)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3k**

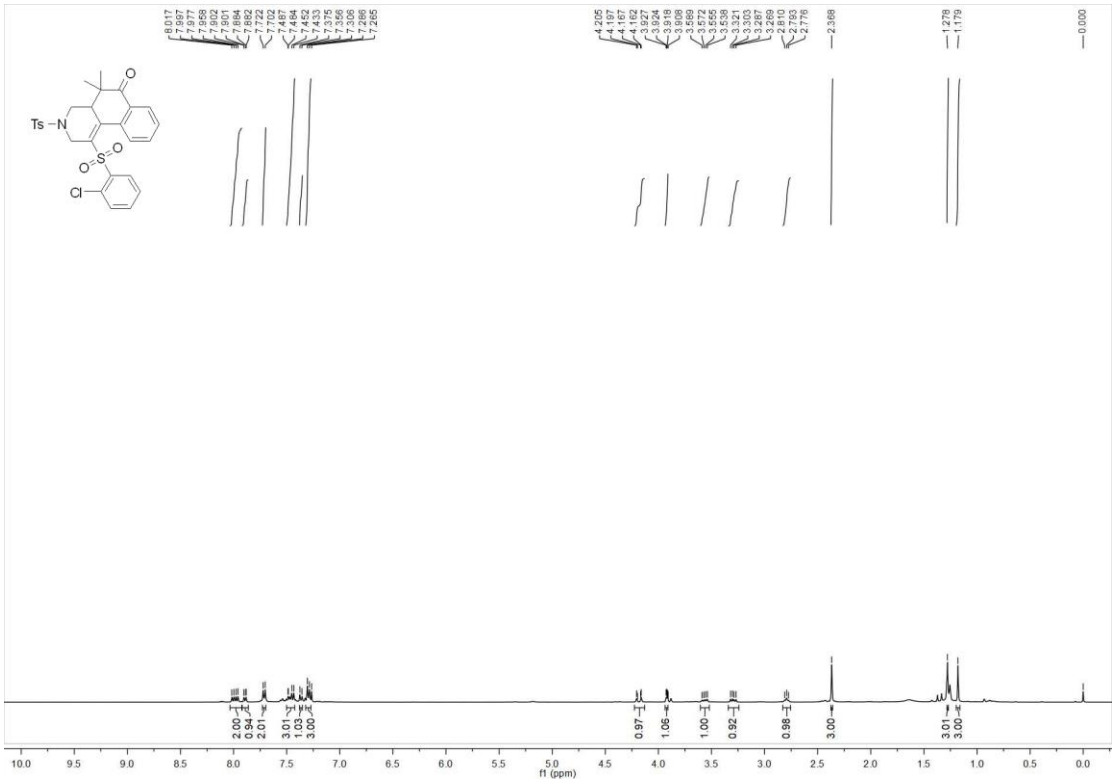


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3k**

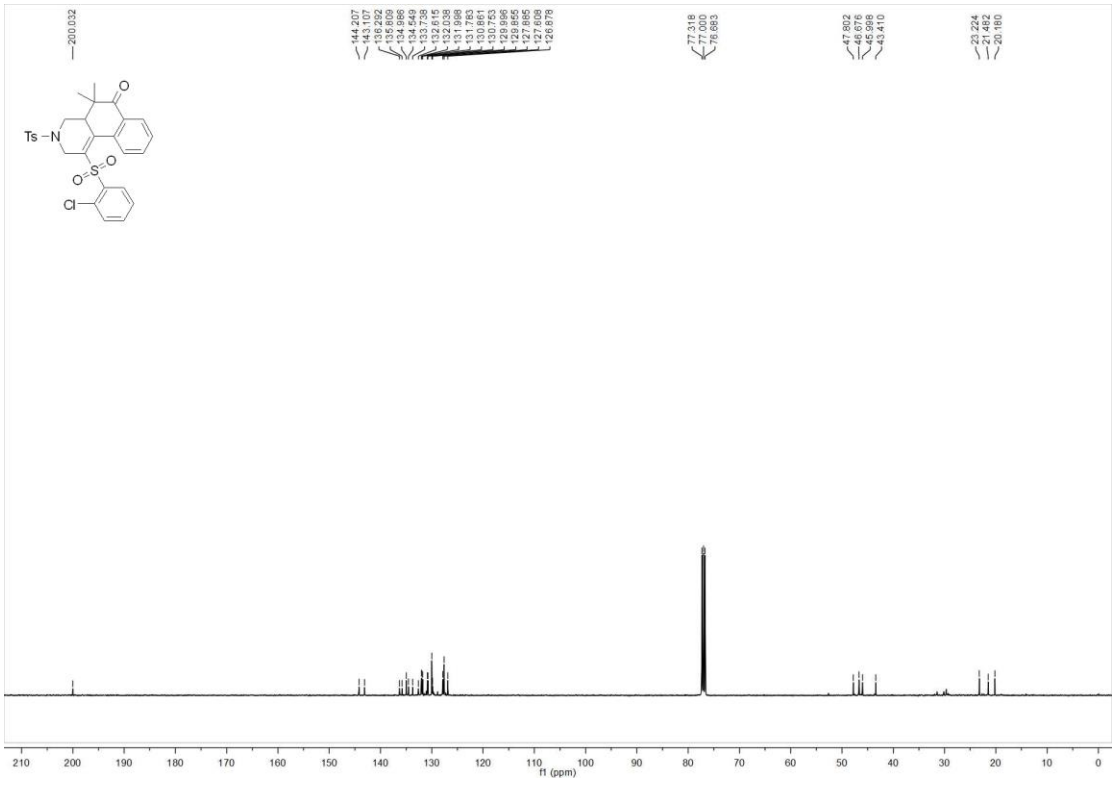


1-((2-Chlorophenyl)sulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]iso quinolin-6(2*H*)-one (3l)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3l**

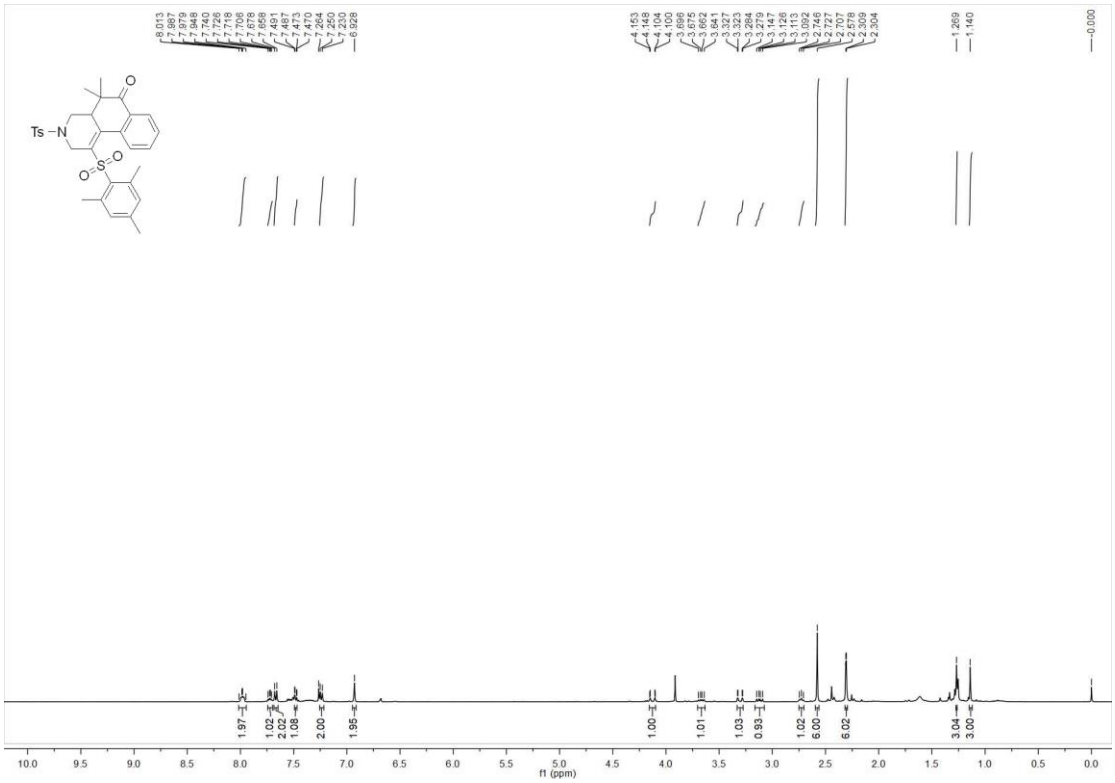


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3l**

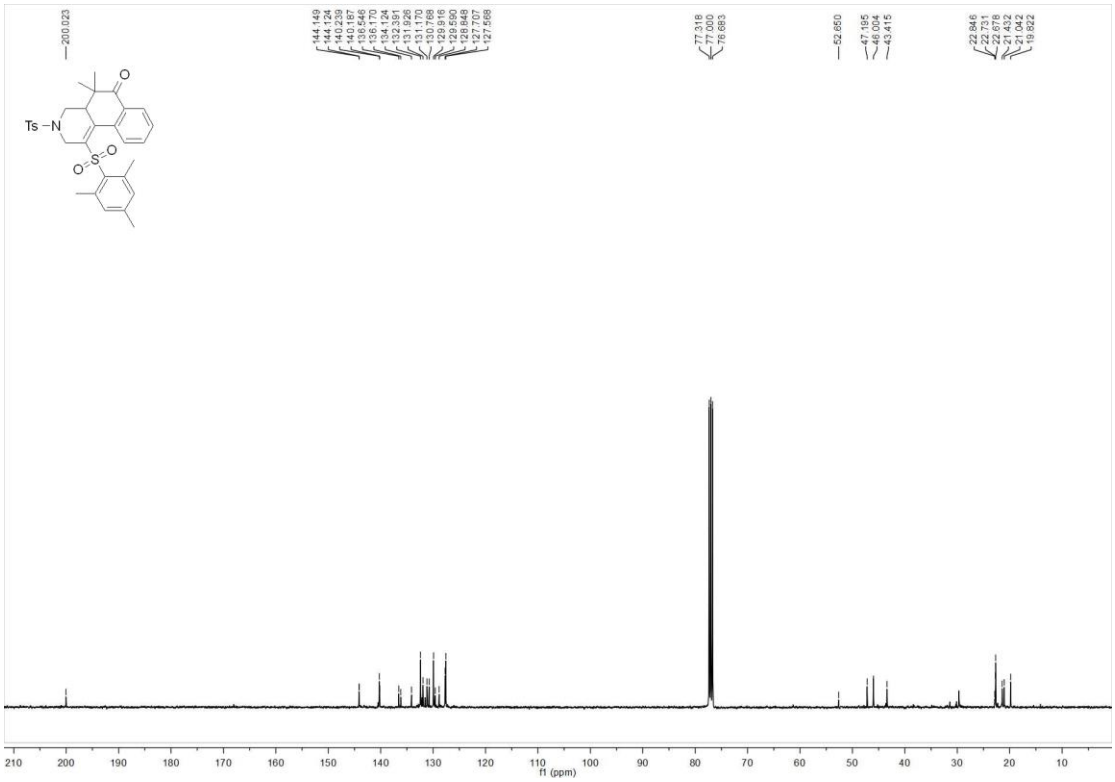


1-(Mesitylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6 (2*H*)-one (3m)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3m**

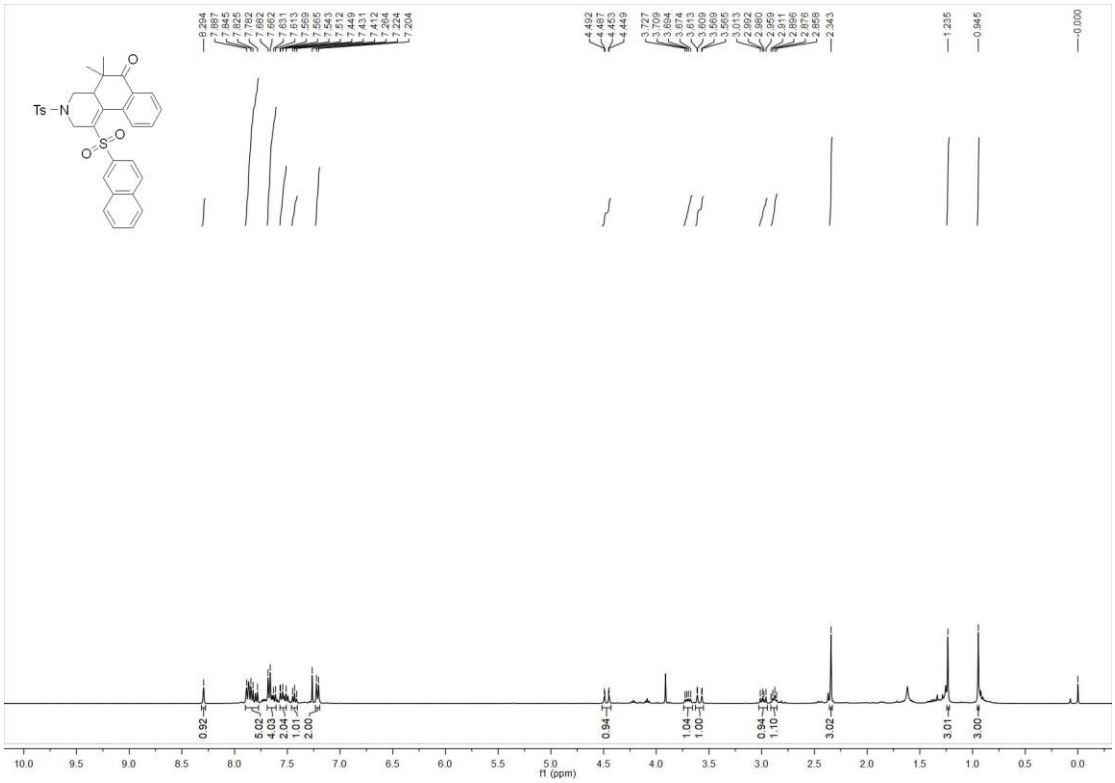


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3m**

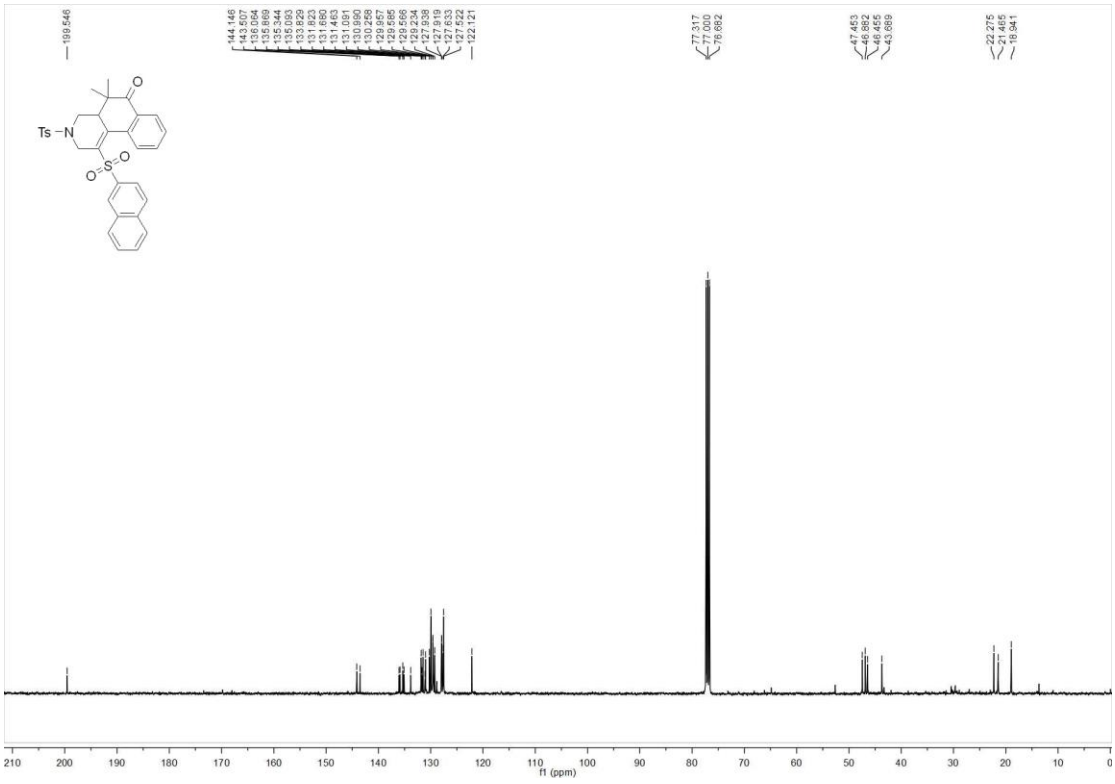


5,5-Dimethyl-1-(naphthalen-2-ylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3n)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3n**

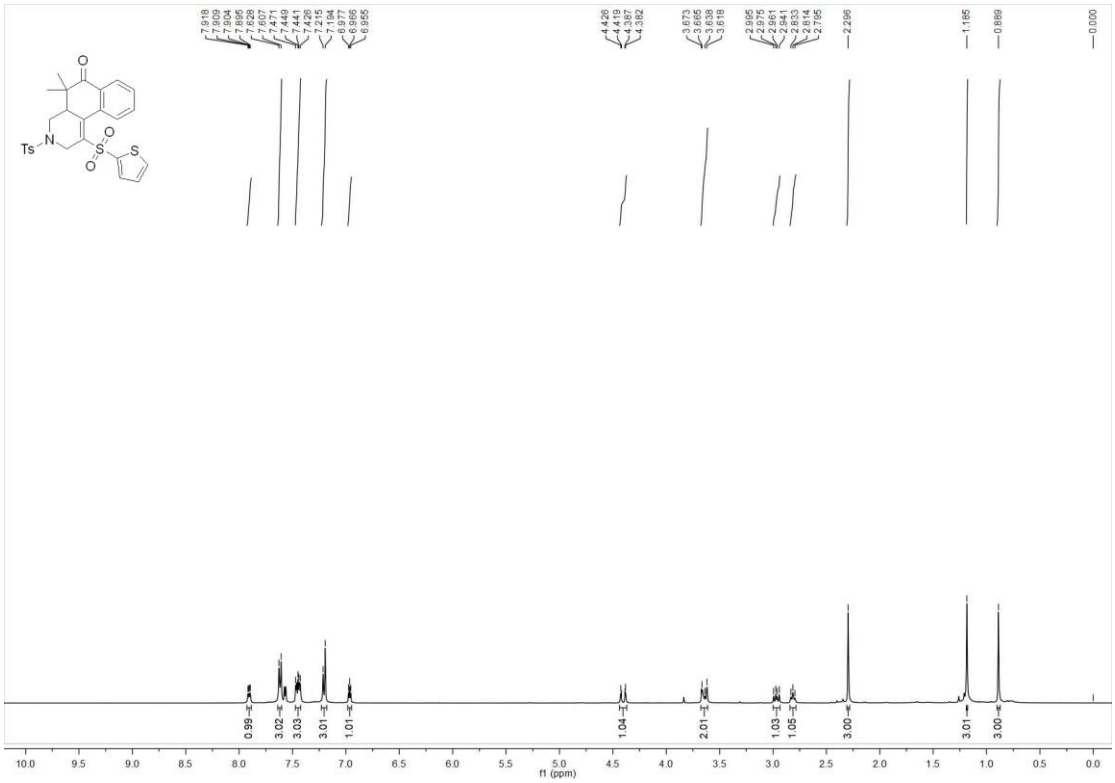


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3n**

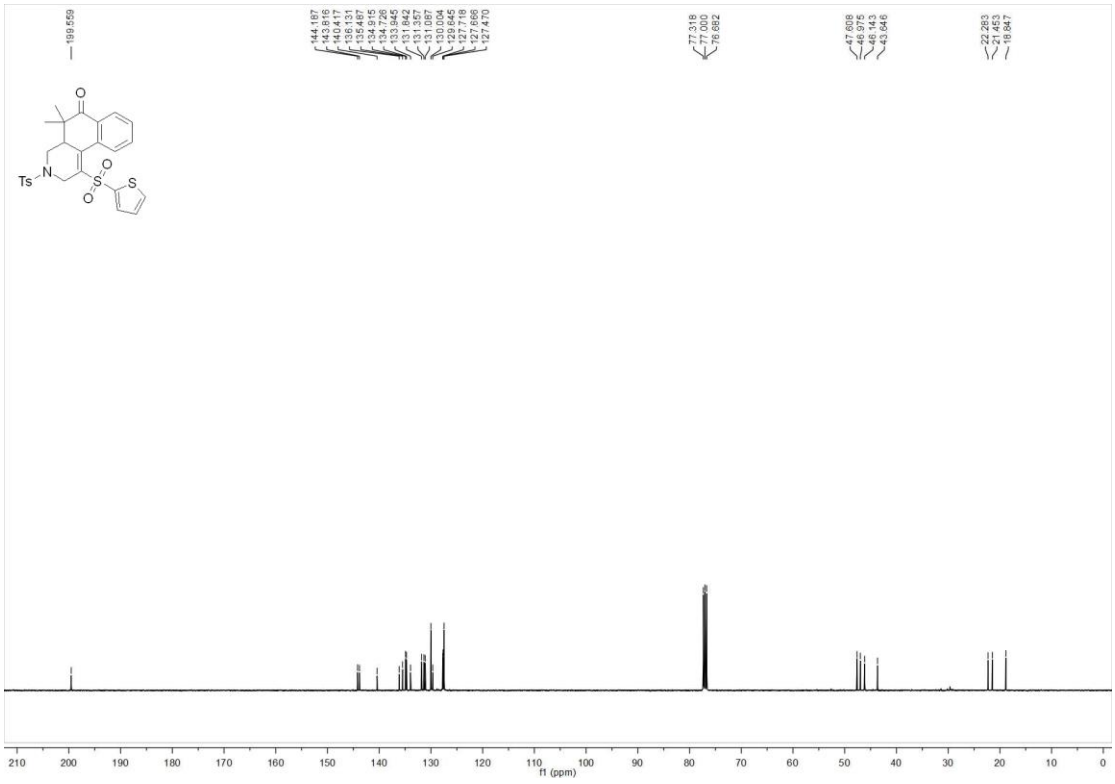


5,5-Dimethyl-1-(thiophen-2-ylsulfonyl)-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3o)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3o**

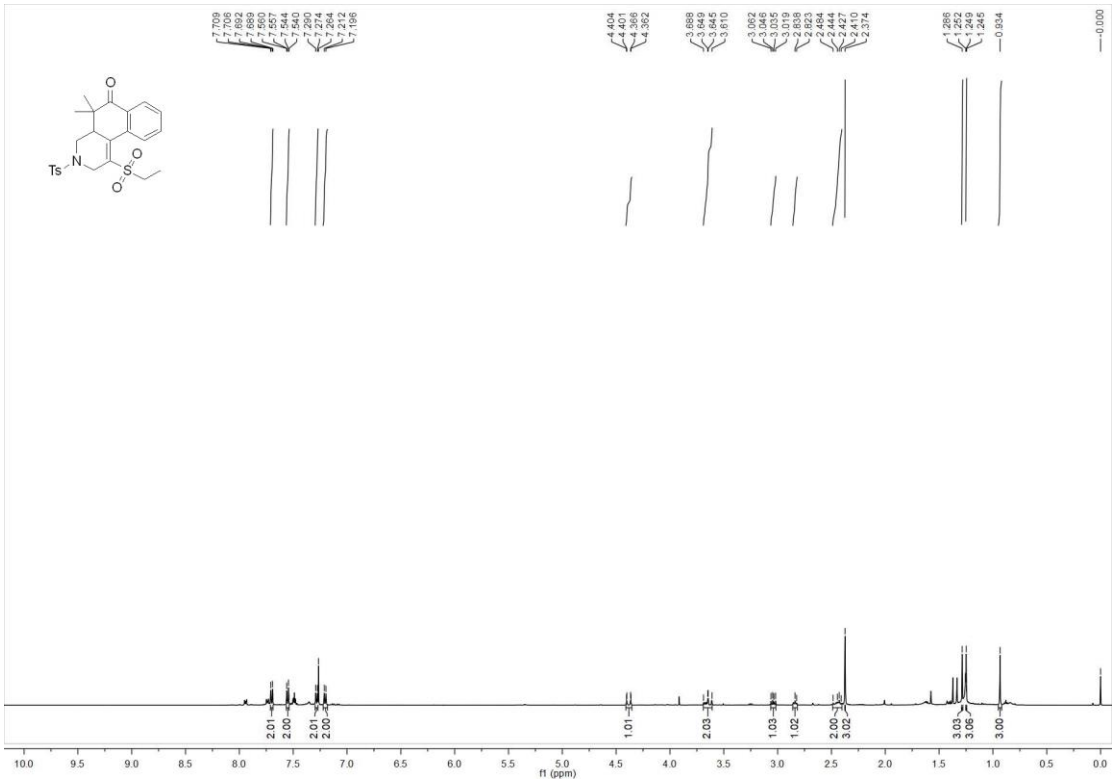


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3o**

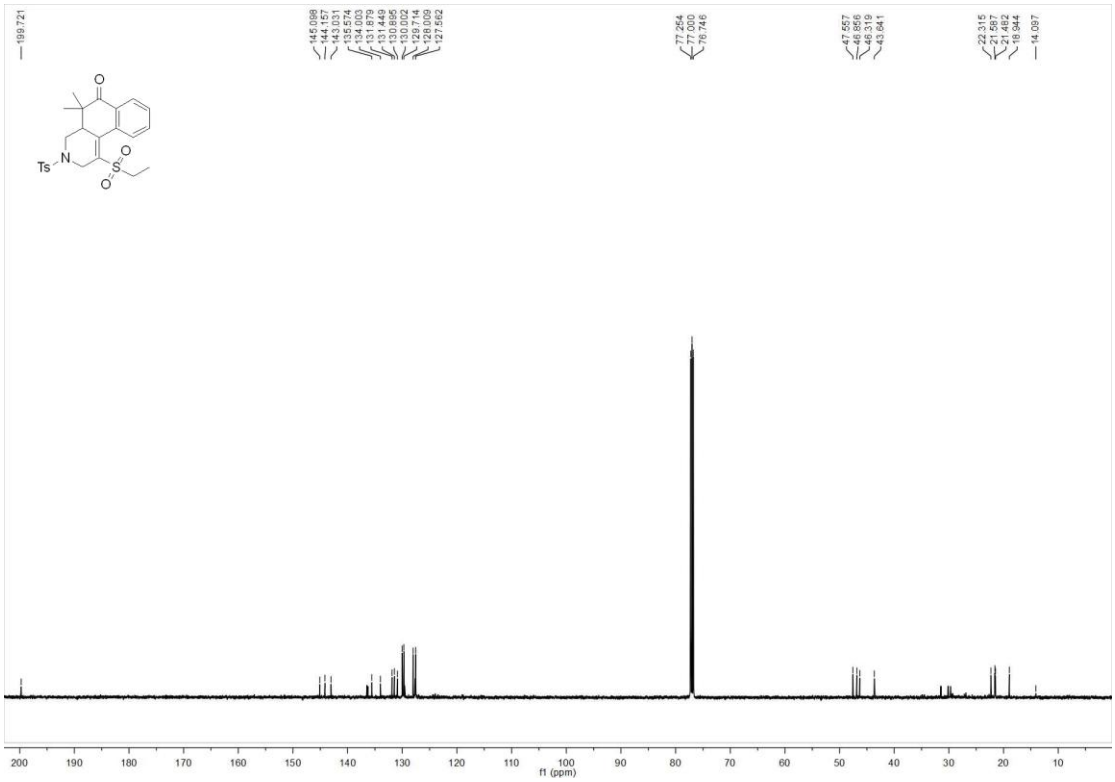


1-(Ethylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3p)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3p**

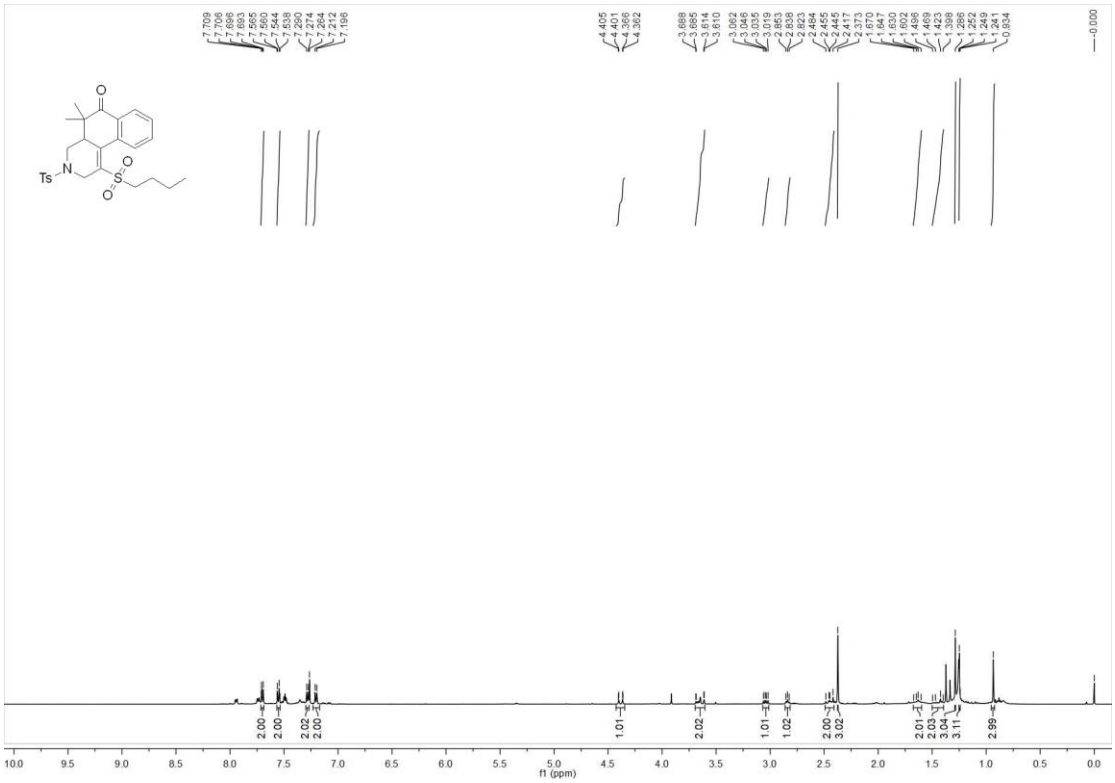


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3p**

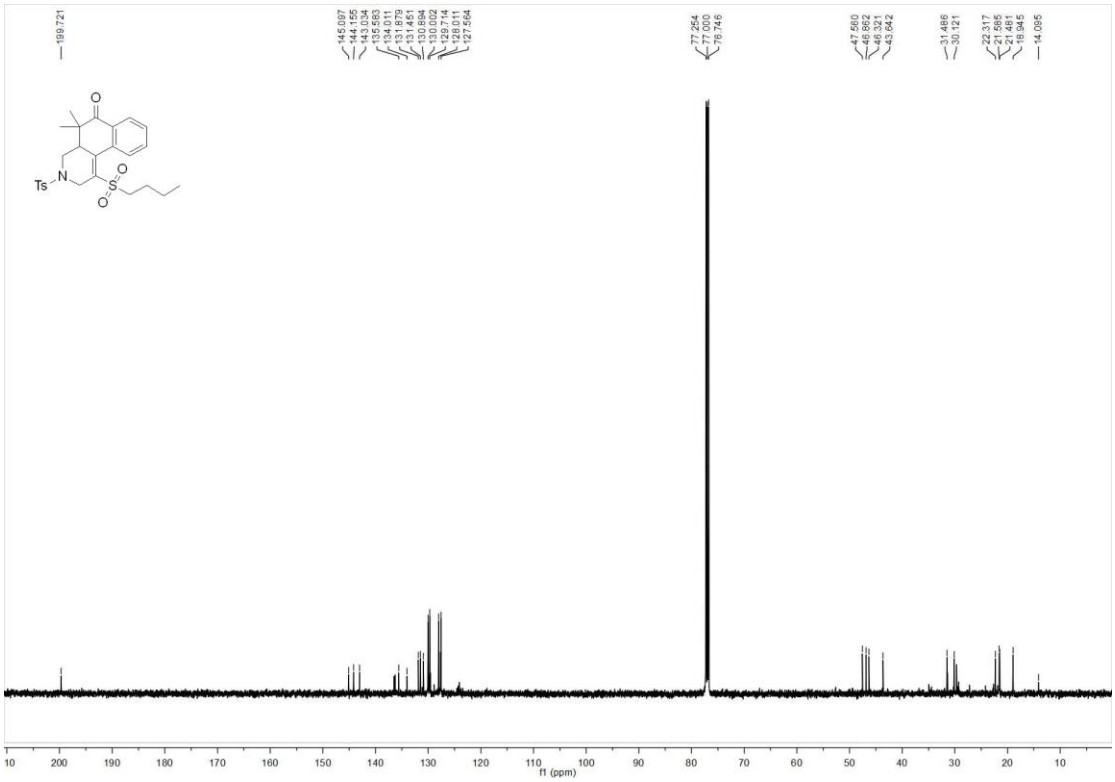


1-(Butylsulfonyl)-5,5-dimethyl-3-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3q)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3q**

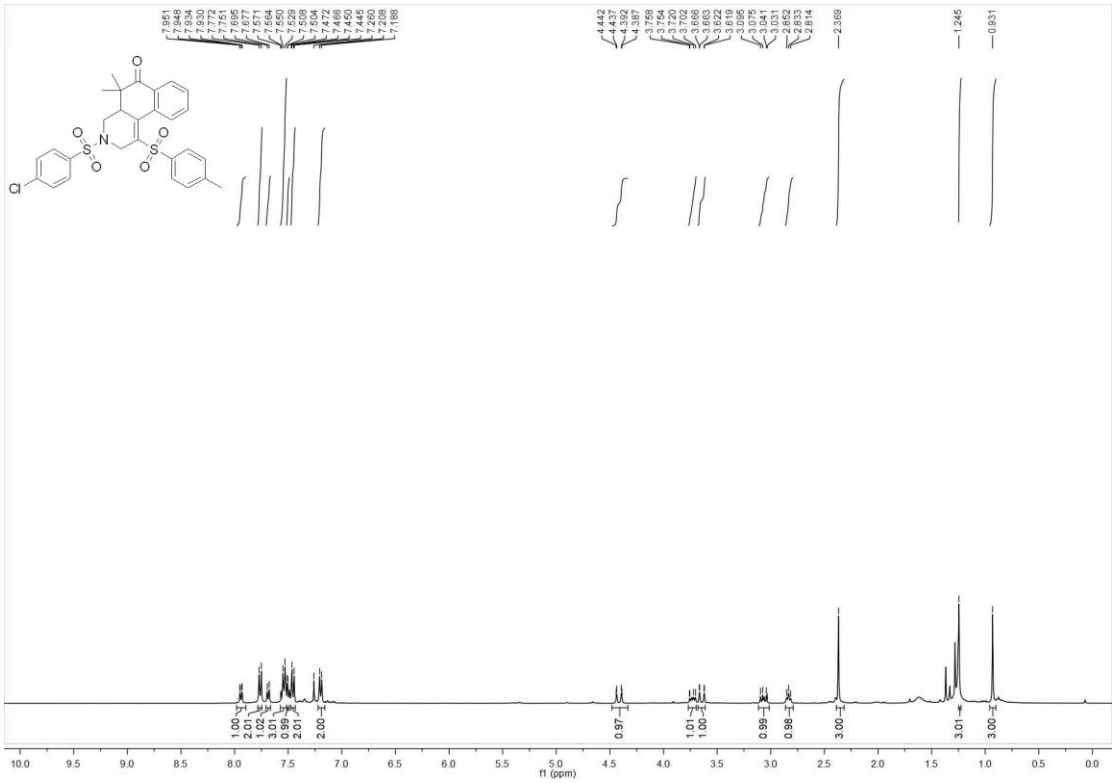


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3q**

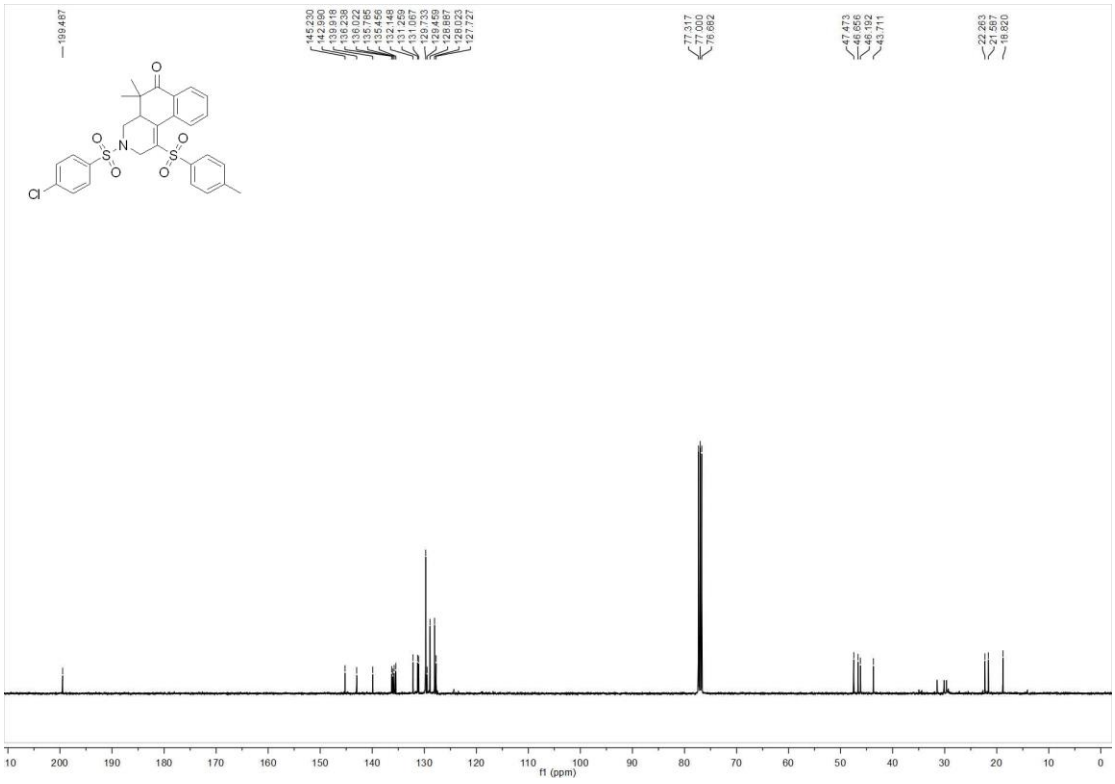


3-((4-Chlorophenyl)sulfonyl)-5,5-dimethyl-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]iso quinolin-6(2*H*)-one (3r)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3r**

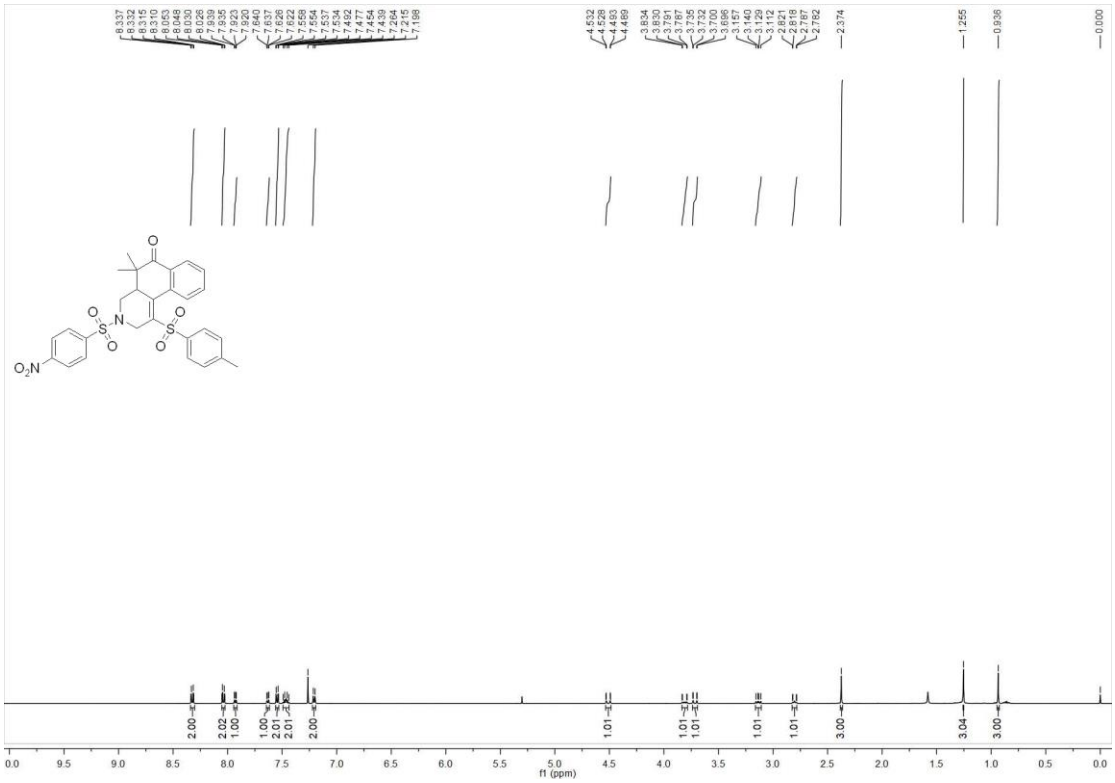


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3r**

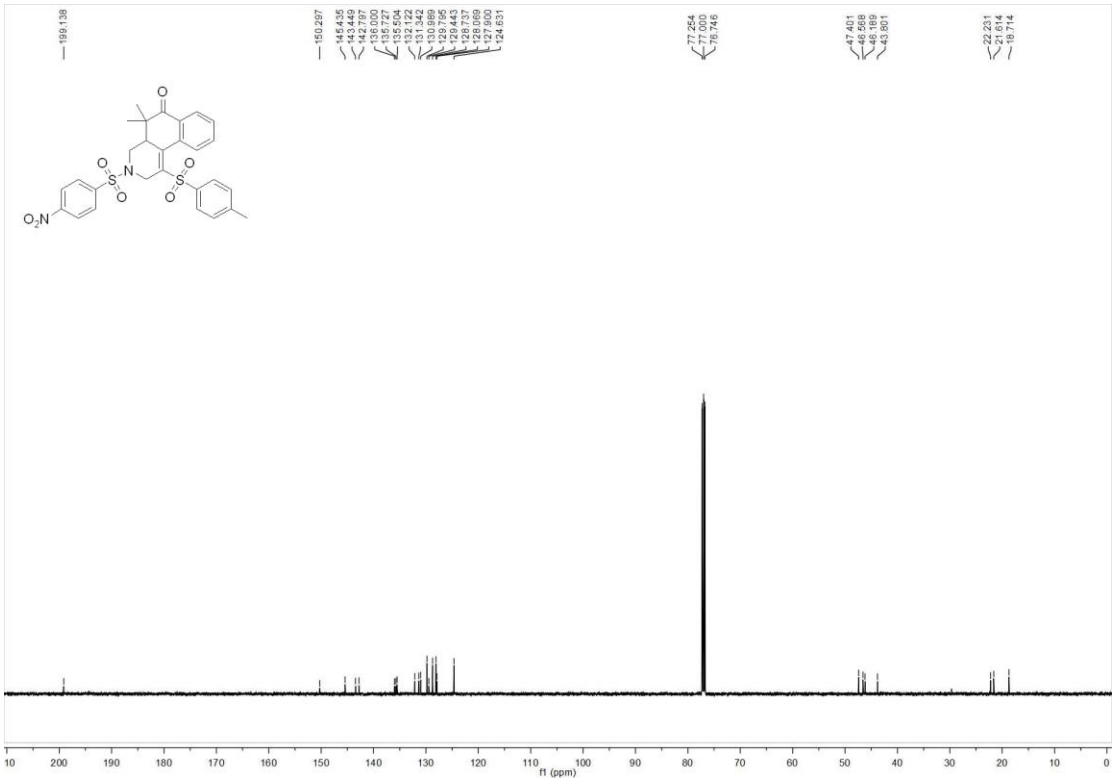


5,5-Dimethyl-3-((4-nitrophenyl)sulfonyl)-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3s)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3s**

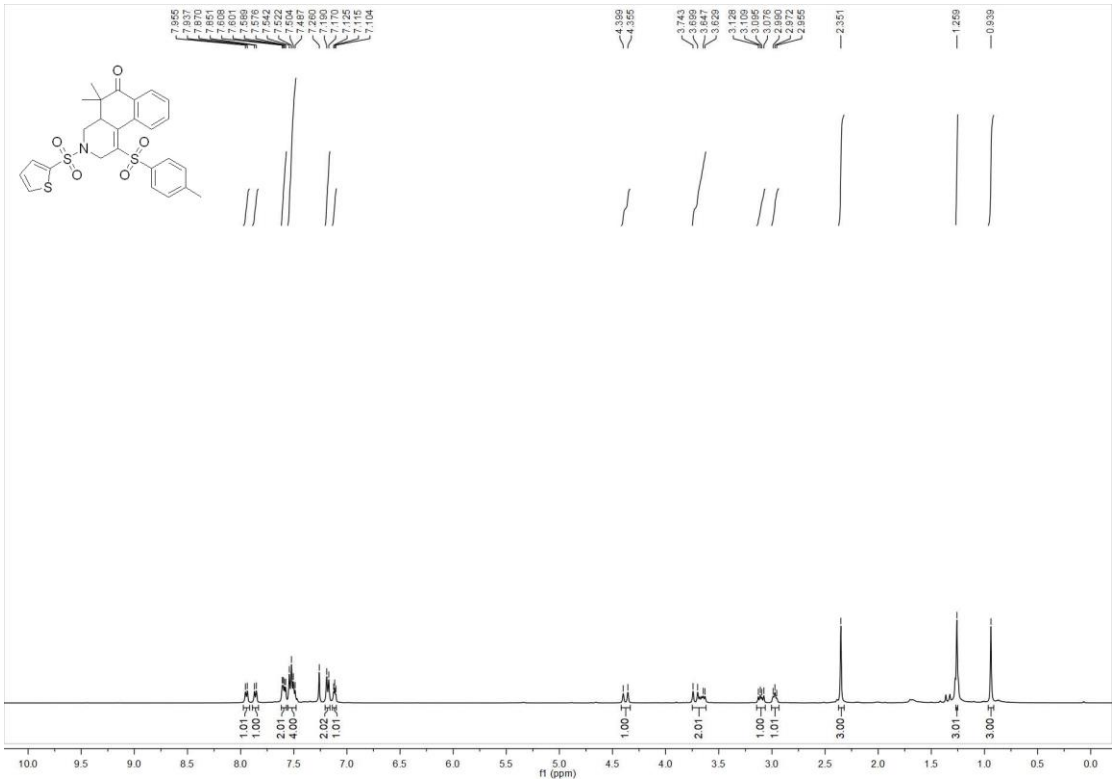


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3s**

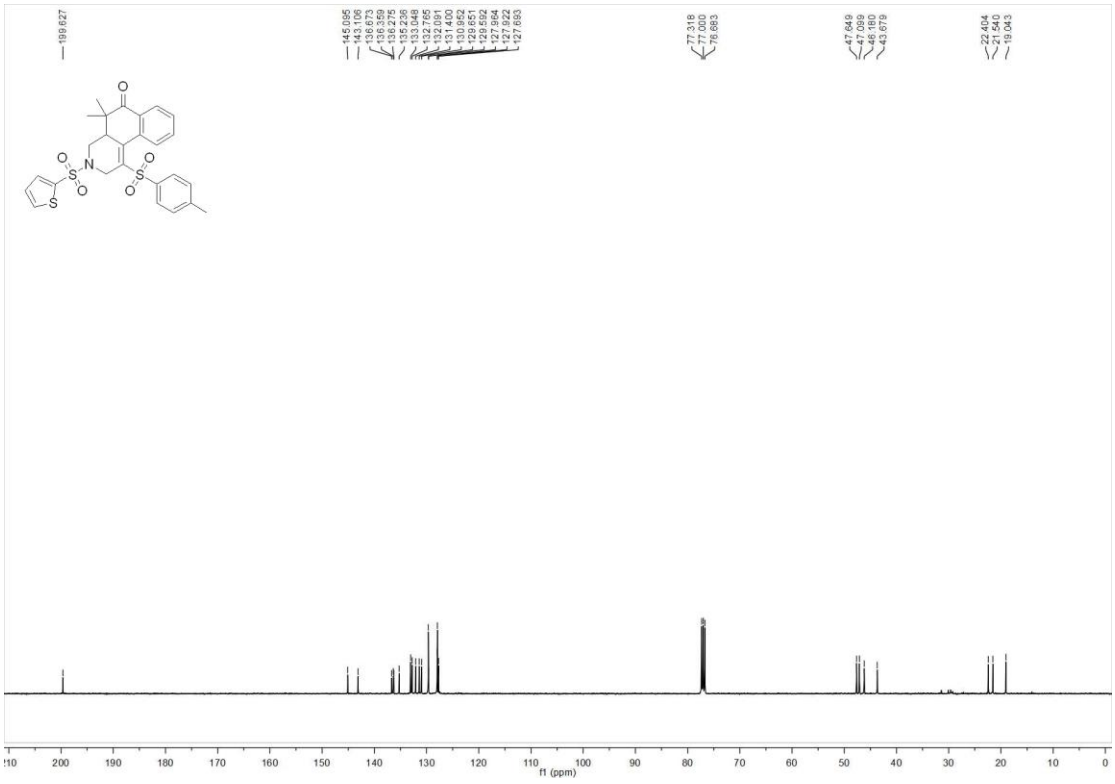


5,5-Dimethyl-3-(thiophen-2-ylsulfonyl)-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3t)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3t**

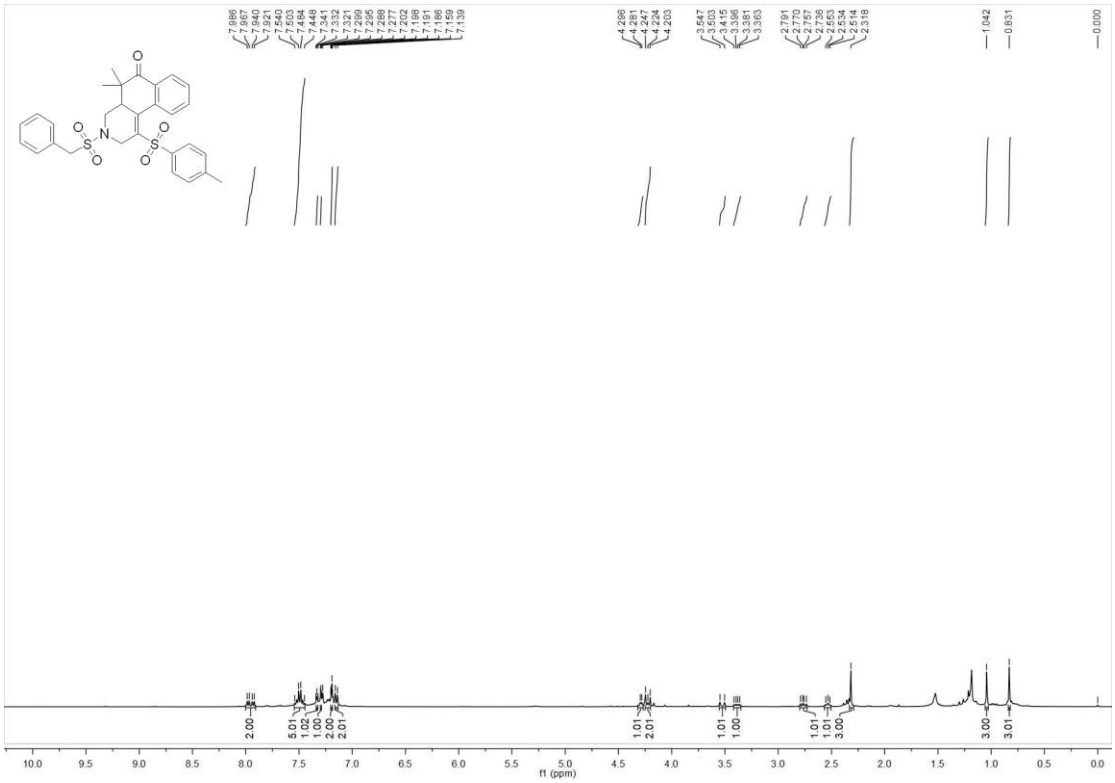


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3t**

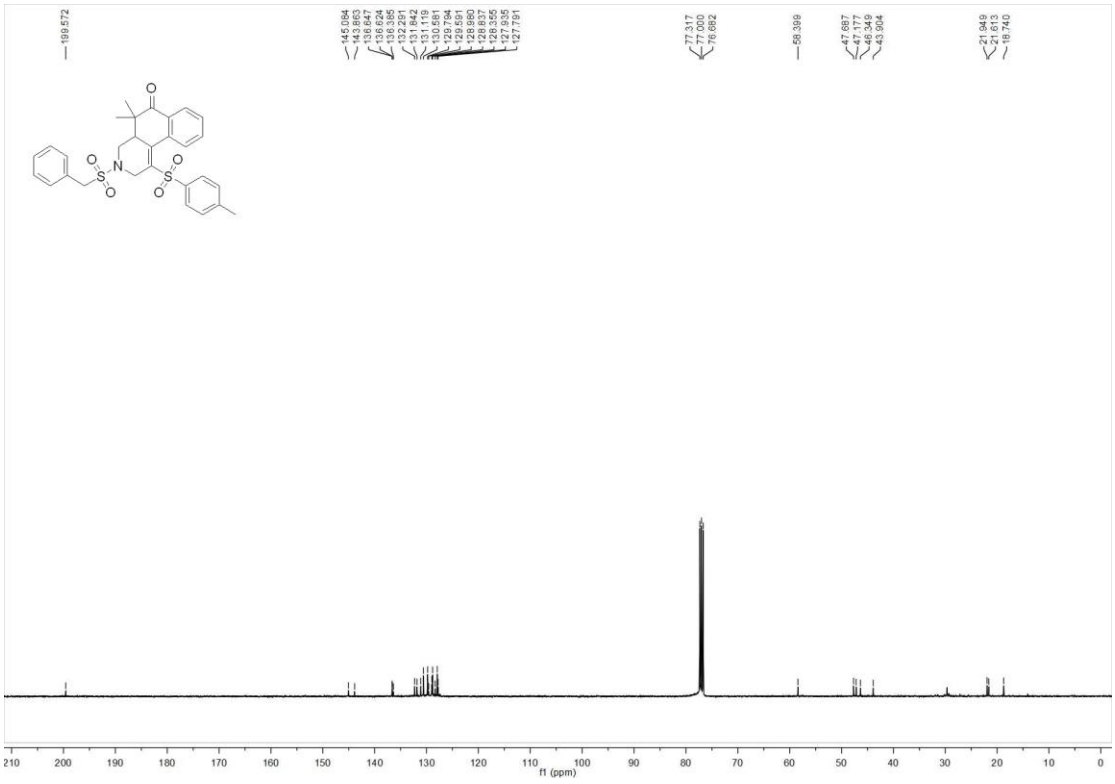


3-(Benzylsulfonyl)-5,5-dimethyl-1-tosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6 (2*H*)-one (3u)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3u**

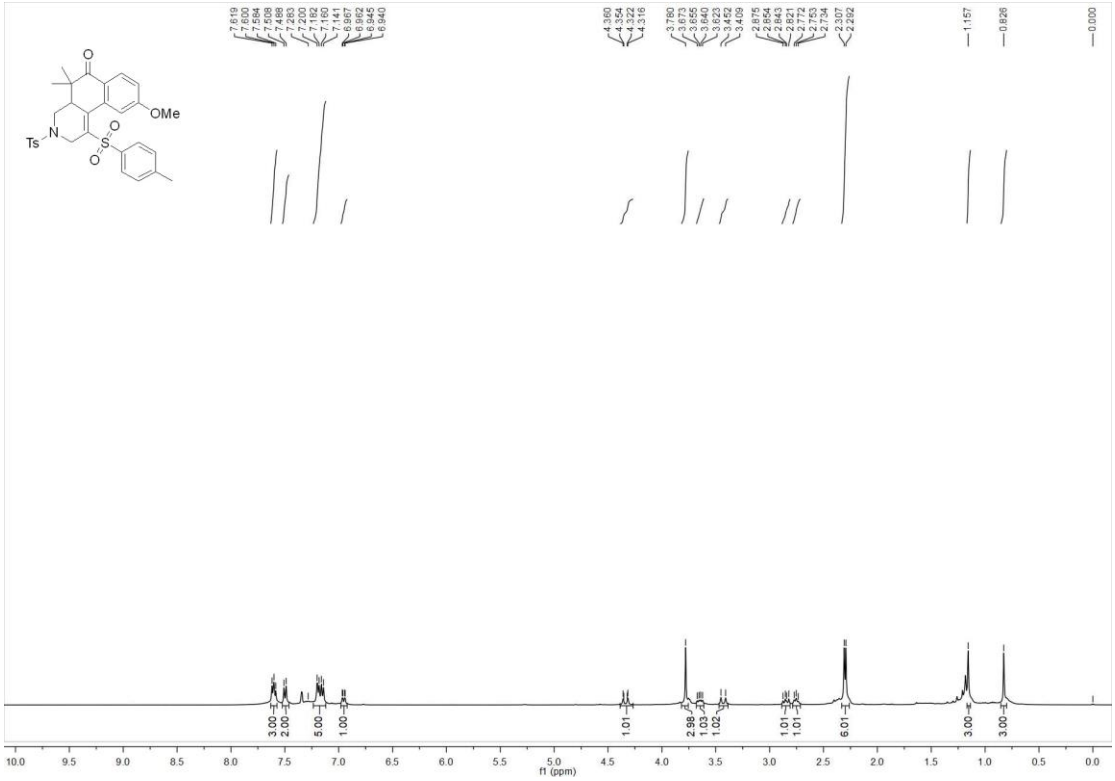


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3u**

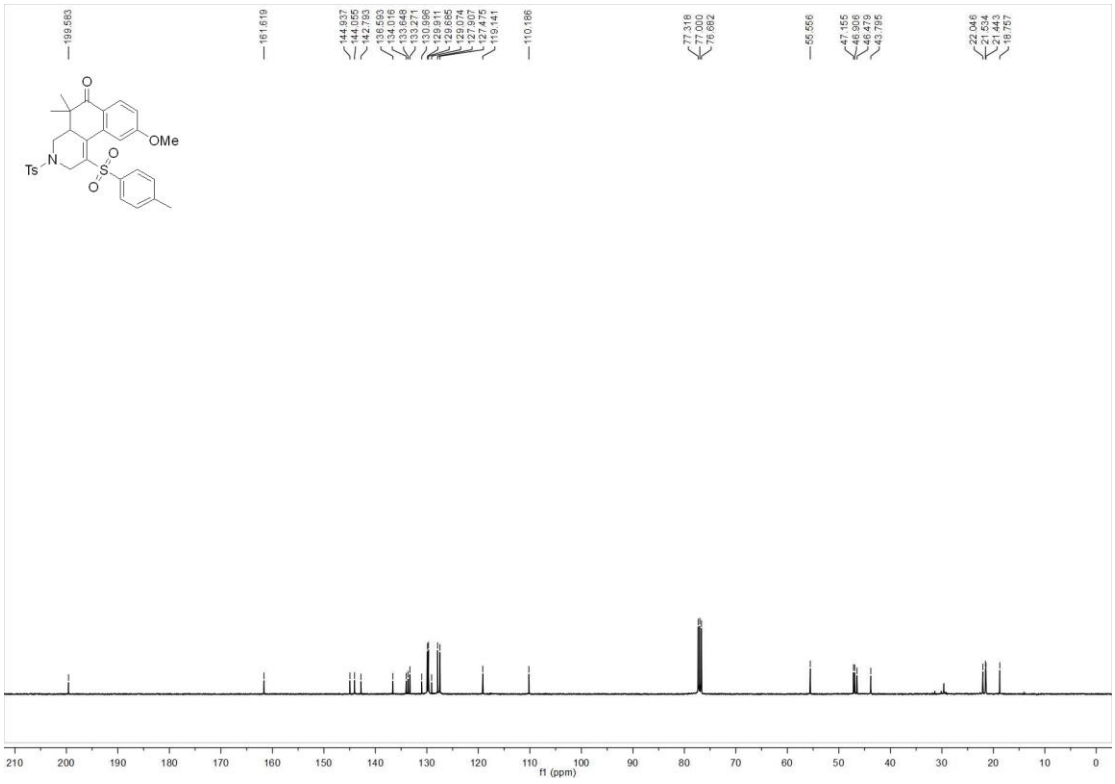


9-Methoxy-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3v)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3v**

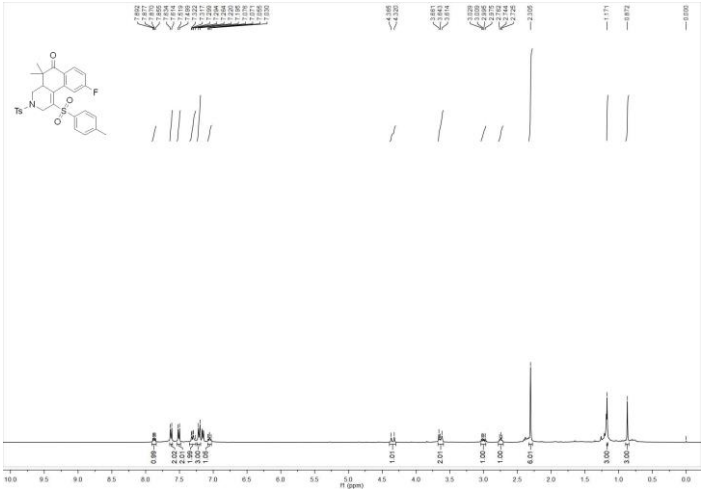


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3v**

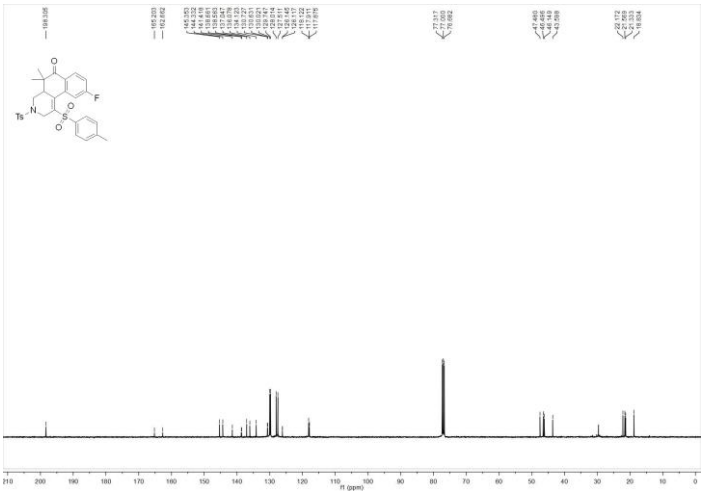


9-Fluoro-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3w)

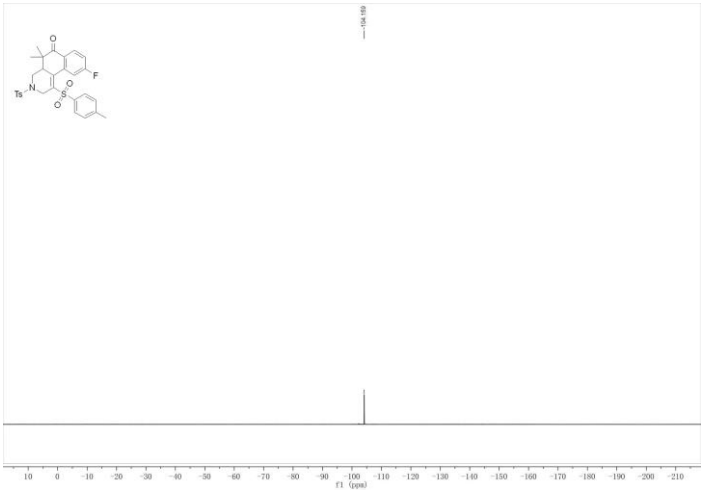
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3w**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3w**

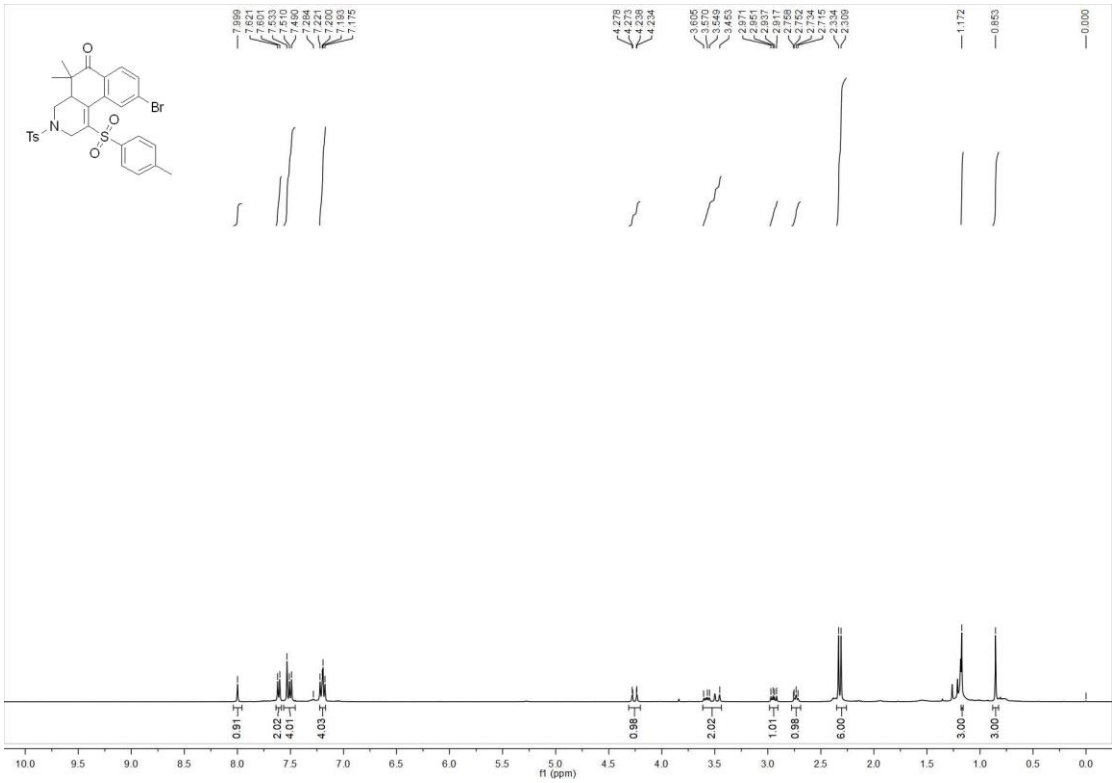


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3w**

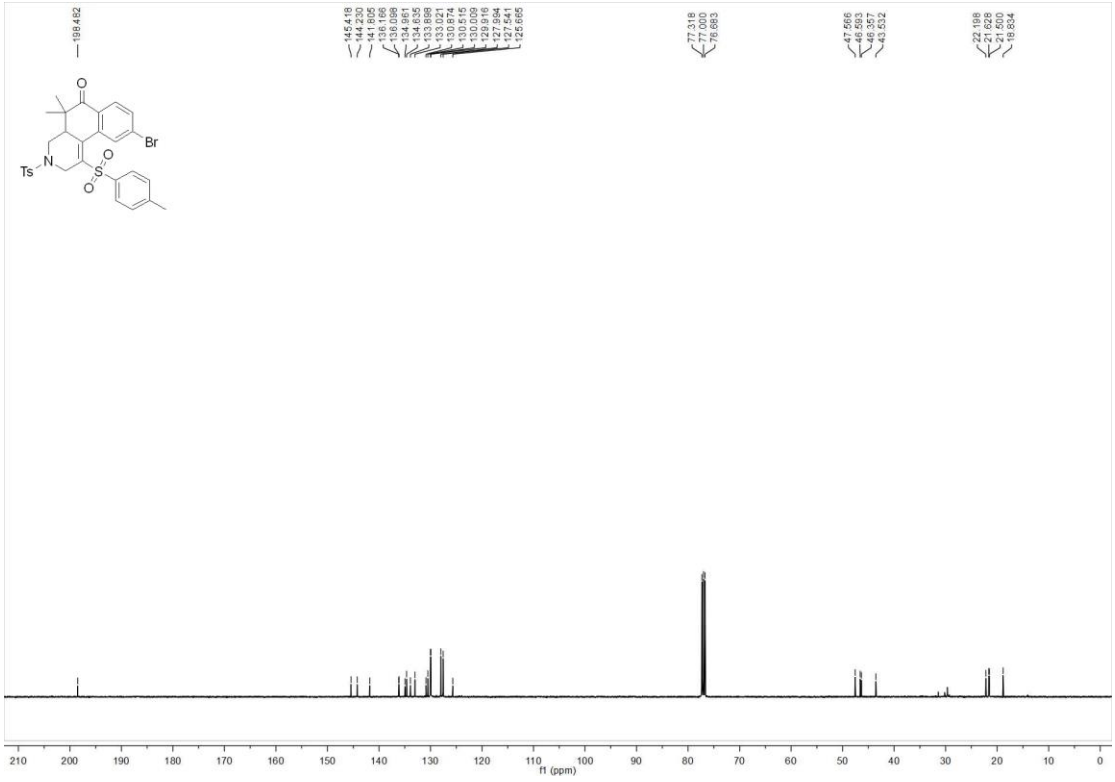


9-Bromo-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3x)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3x**

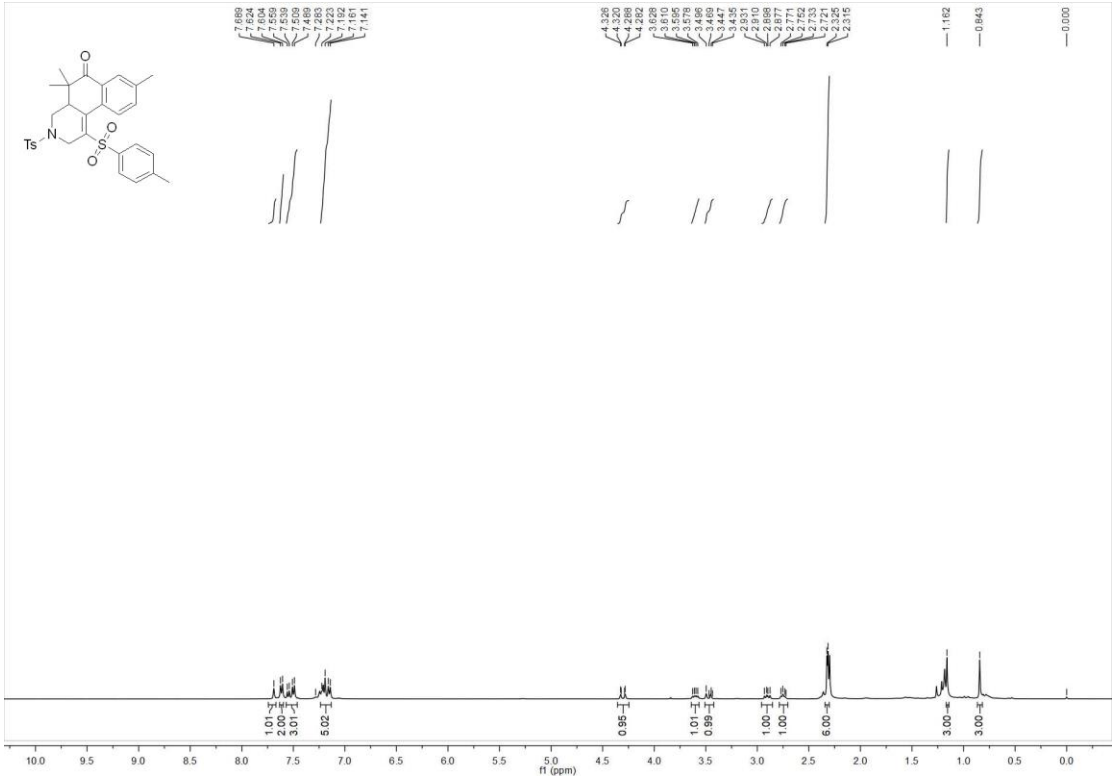


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3x**

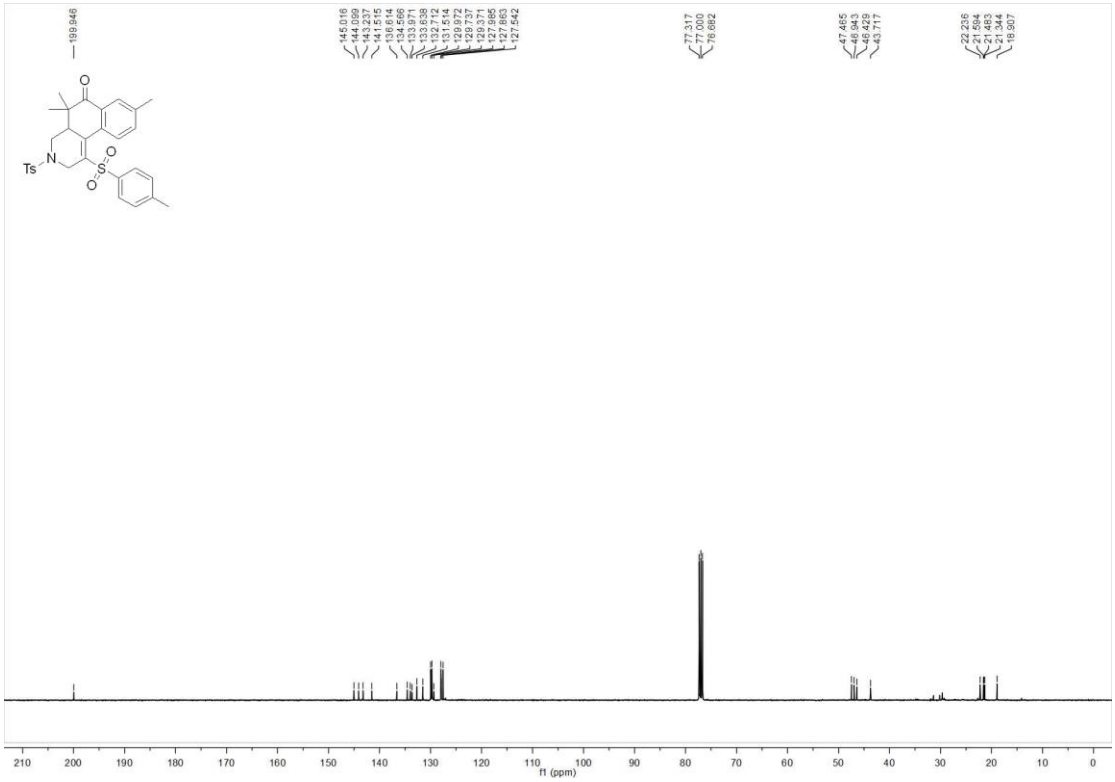


5,5,8-Trimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3y)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3y**

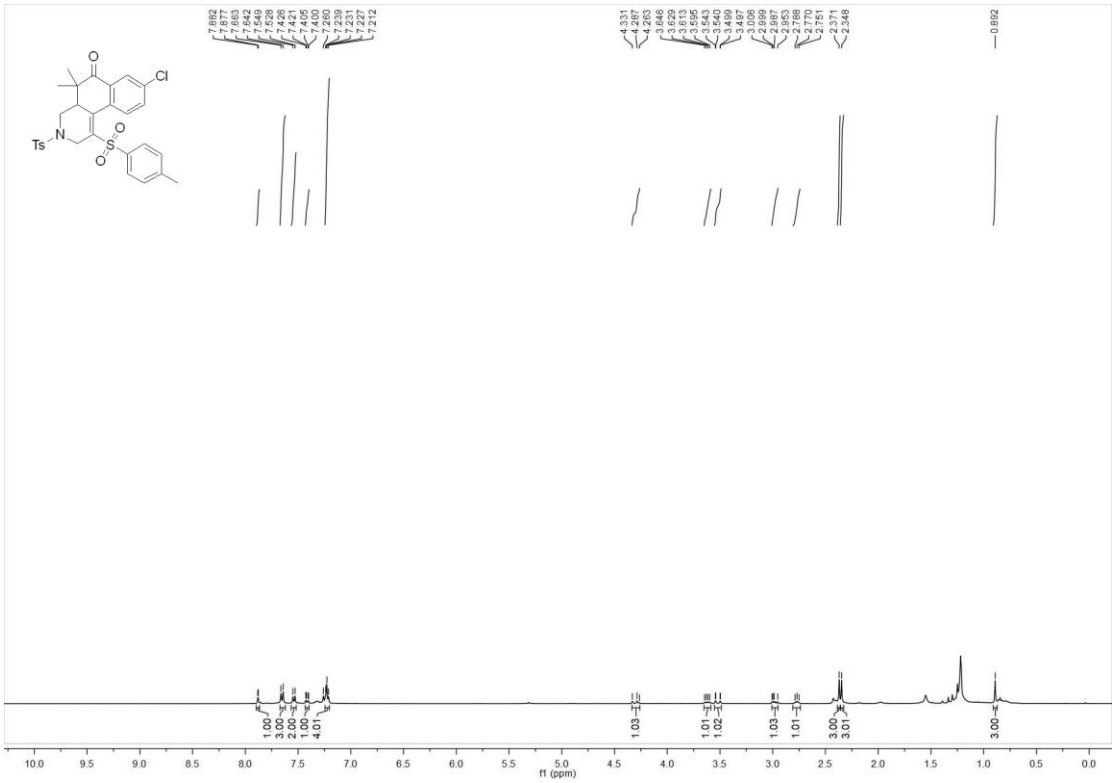


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3y**

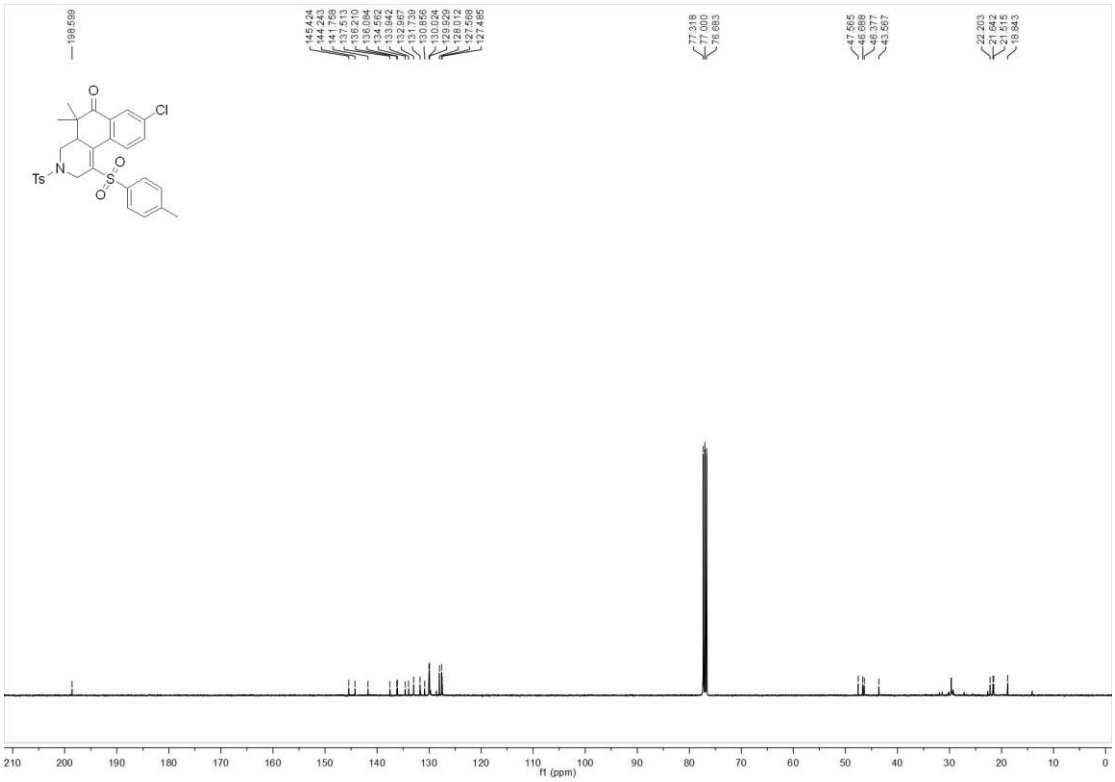


8-Chloro-5,5-dimethyl-1,3-ditosyl-3,4,4a,5-tetrahydrobenzo[*f*]isoquinolin-6(2*H*)-one (3z)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3z**



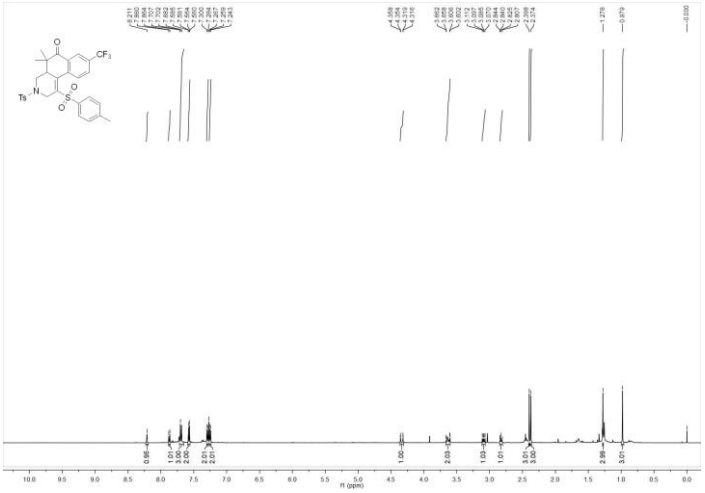
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3z**



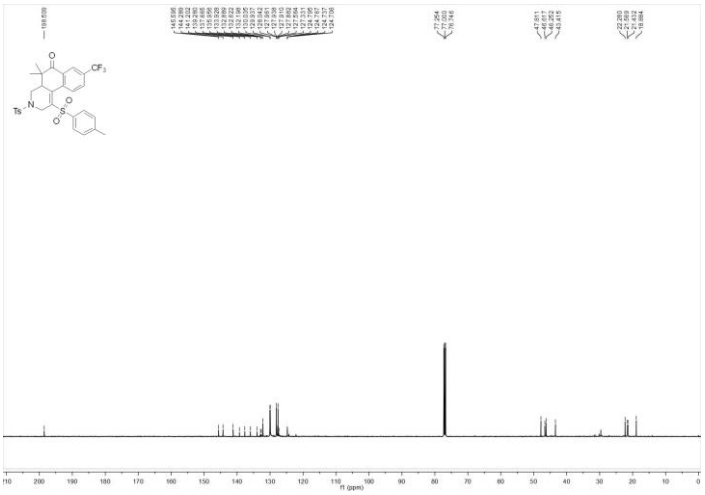
5,5-Dimethyl-1,3-ditosyl-8-(trifluoromethyl)-3,4,4a,5-tetrahydrobenzo[*f*]isoquinol

in-6(2*H*)-one (3aa)

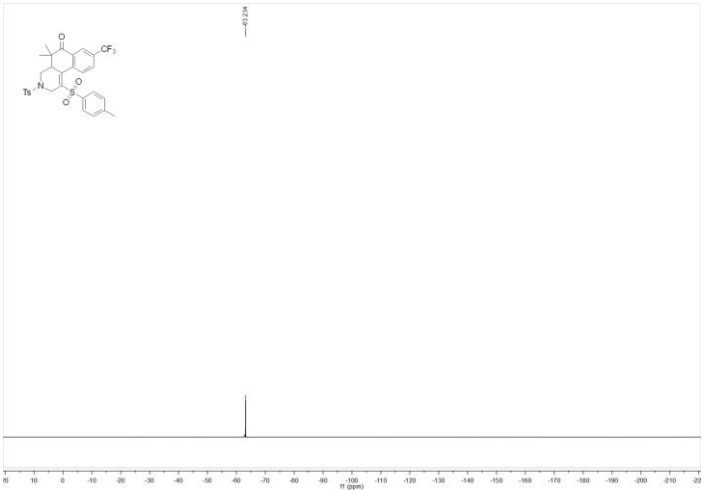
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3aa**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3aa**



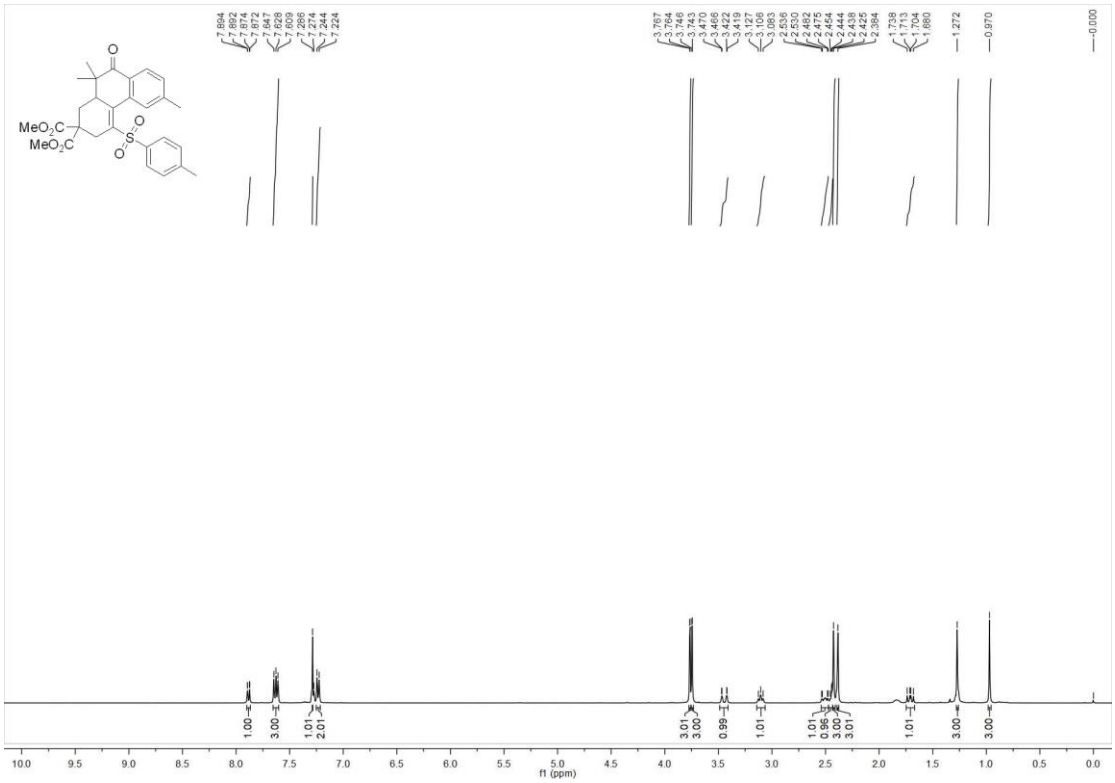
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3aa**



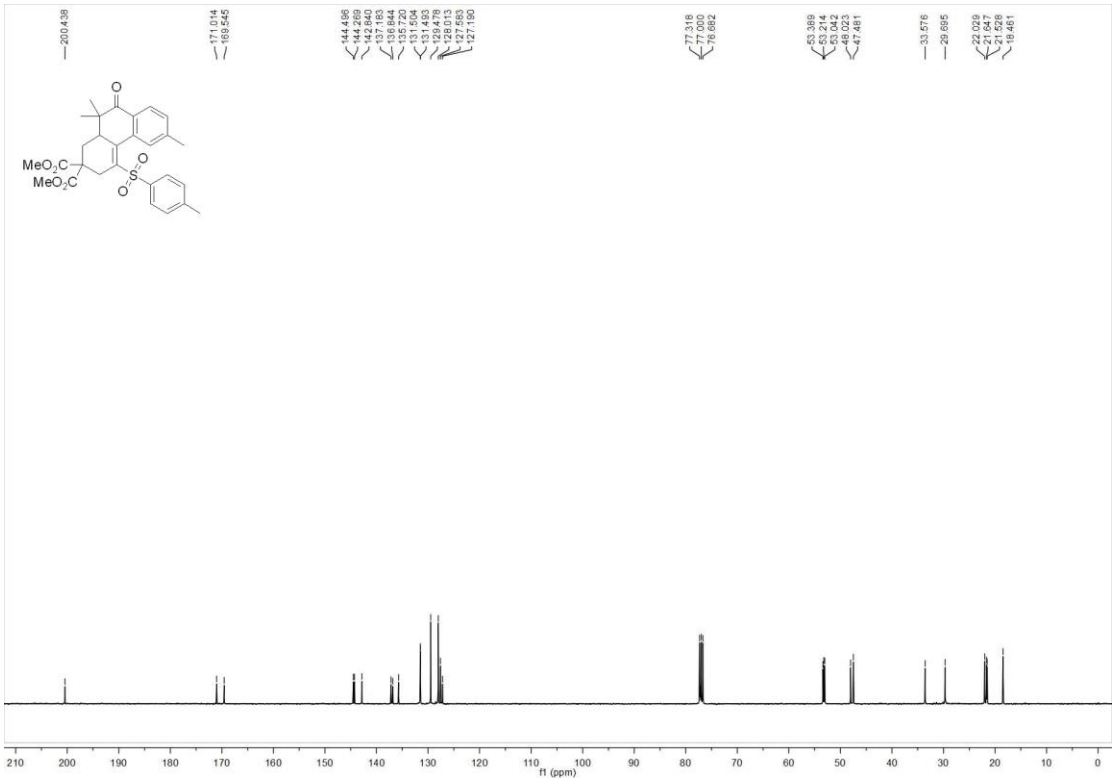
Dimethyl-6,10,10-trimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2

(1*H*)-dicarboxylate (3ab)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ab**

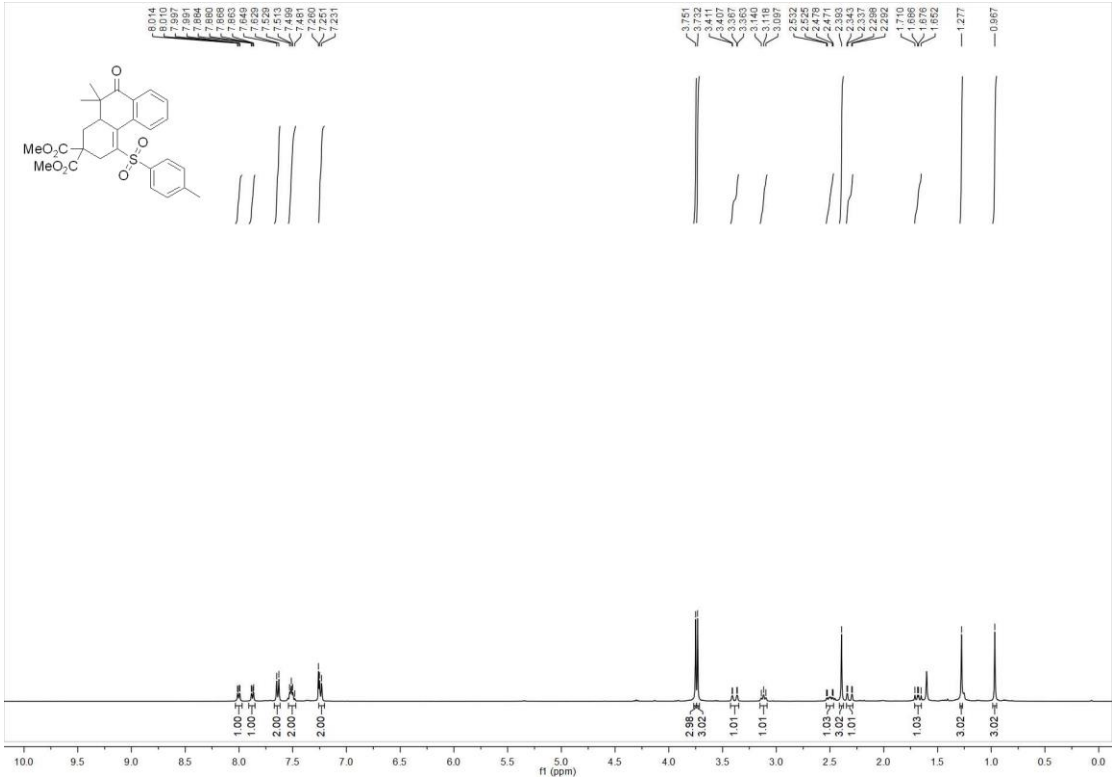


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ab**

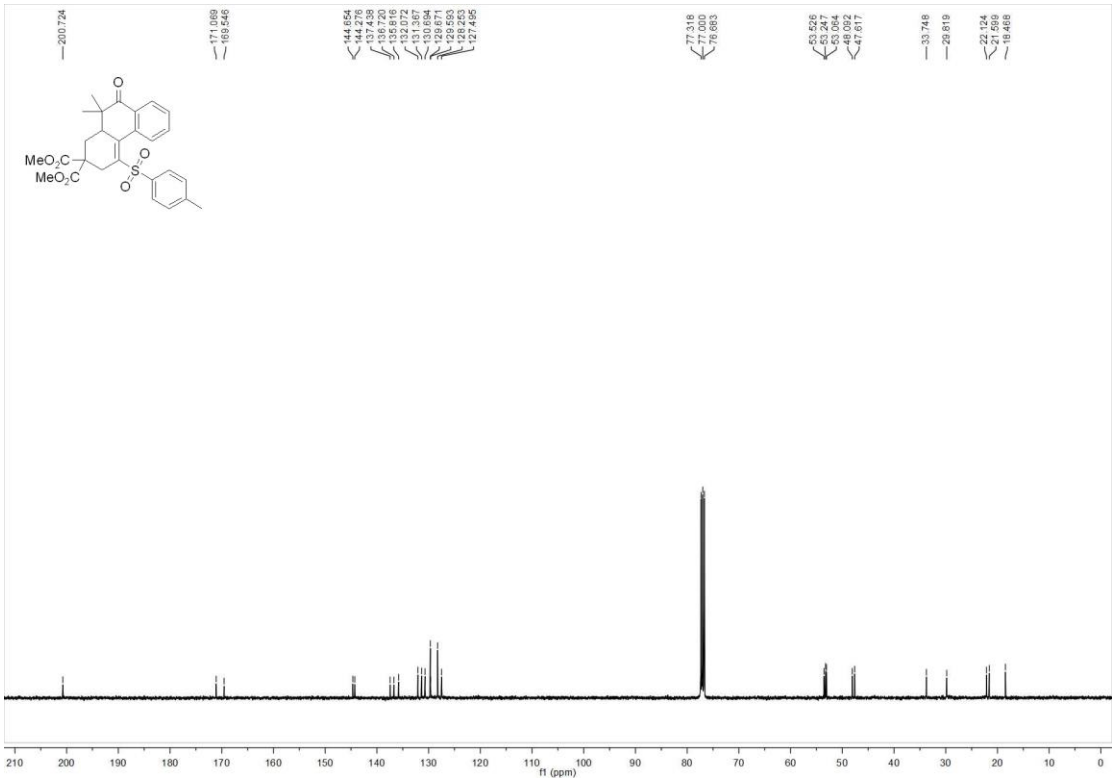


Dimethyl-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)-dicarboxylate (3ac)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ac**



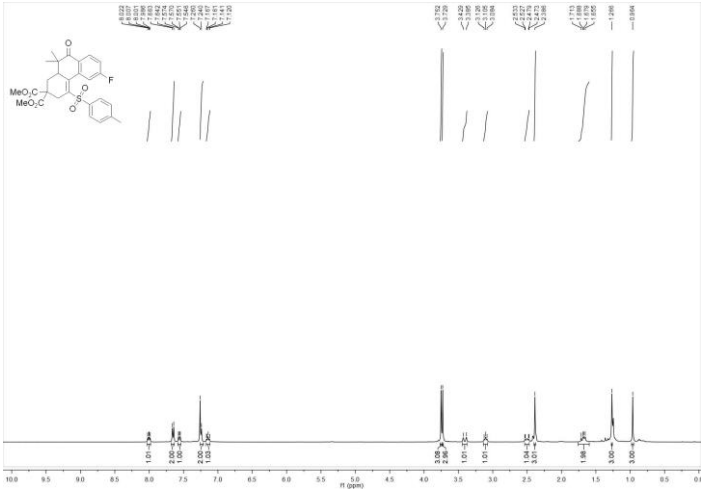
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ac**



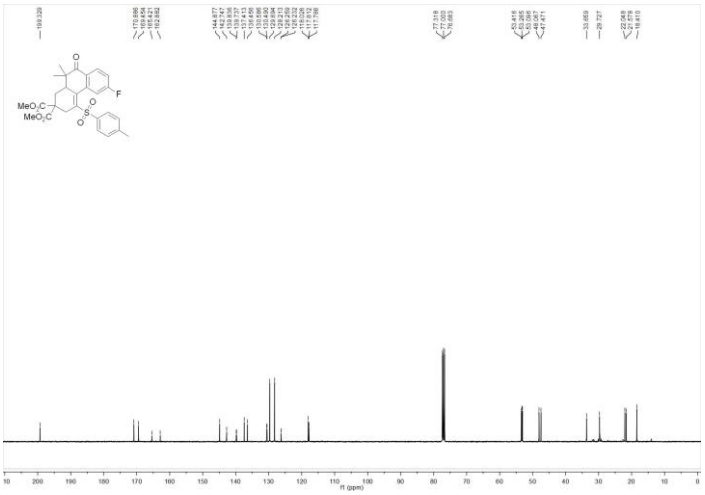
Dimethyl-6-fluoro-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthr

ene-2,2(1*H*)-dicarboxylate (3ad)

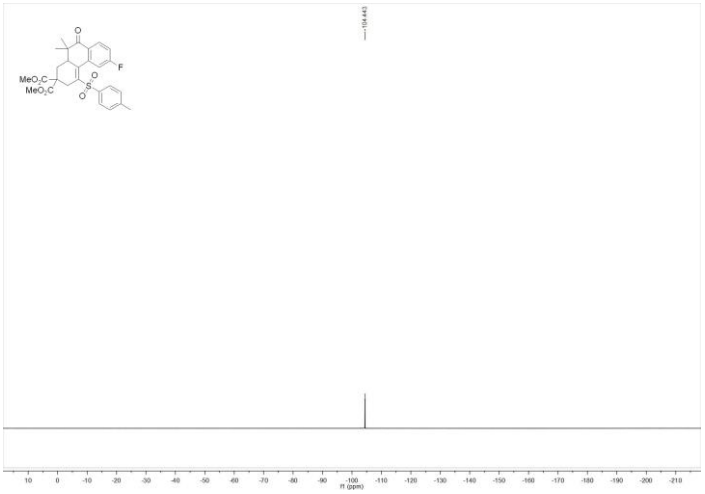
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ad**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ad**



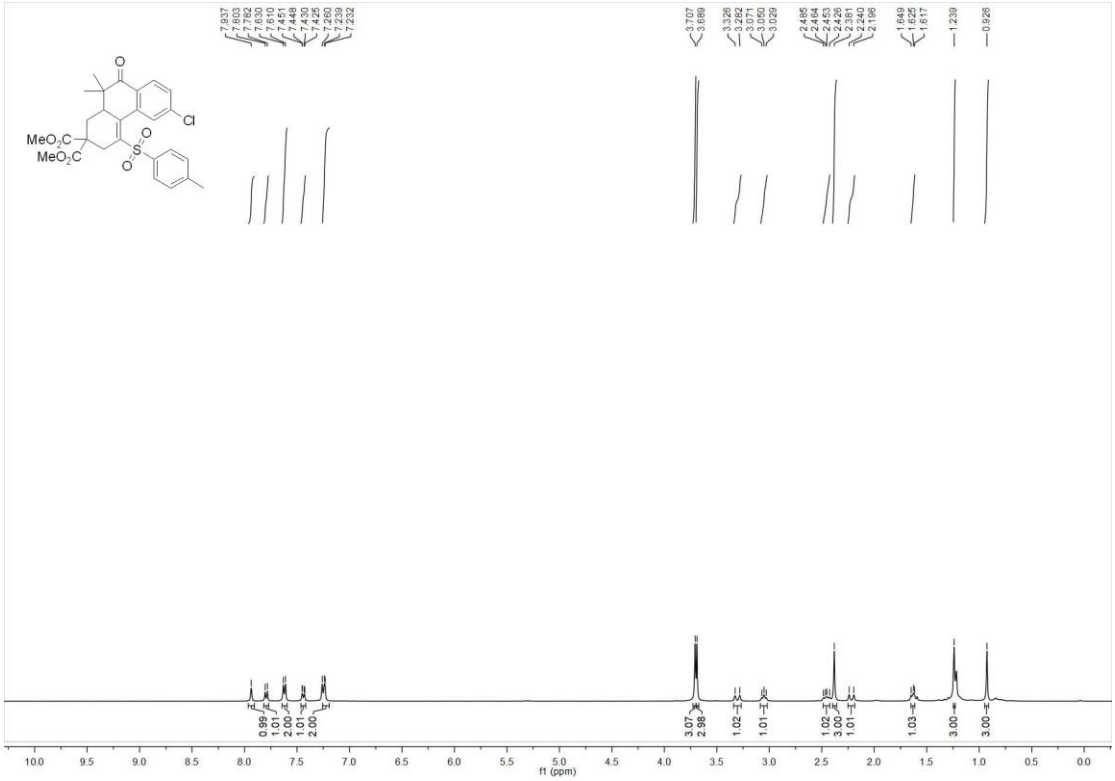
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3ad**



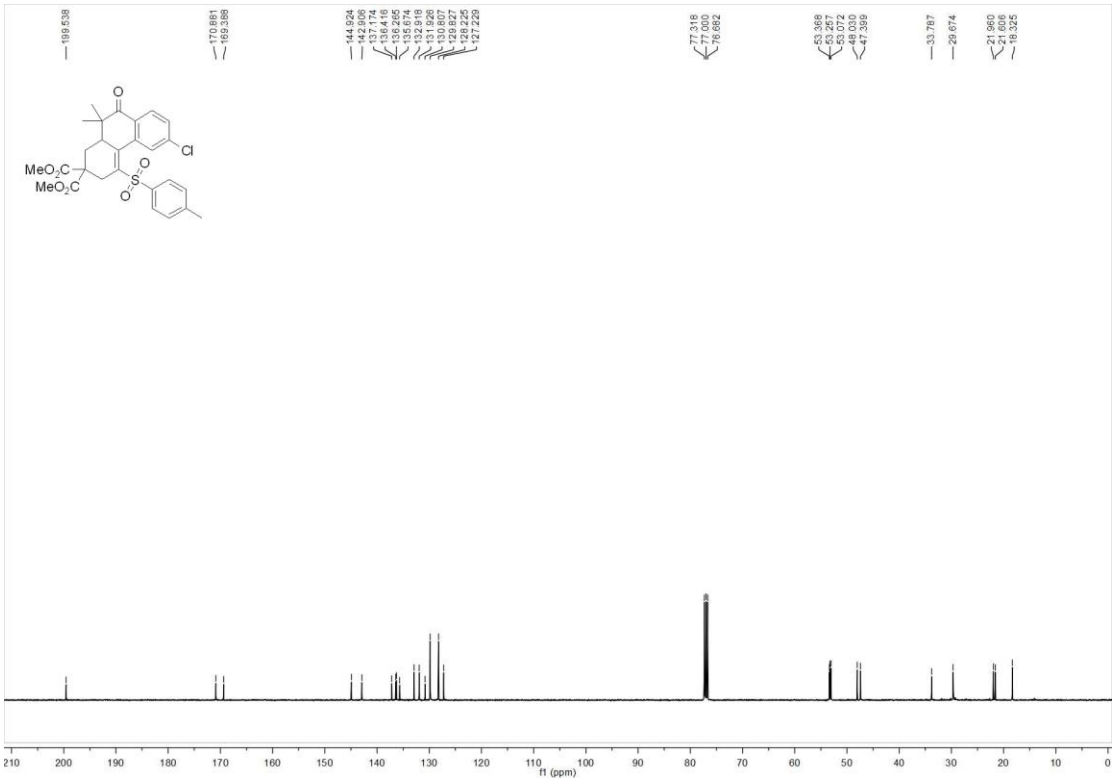
Dimethyl-6-chloro-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthr

ene-2,2(1*H*)-dicarboxylate (3ae)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ae**



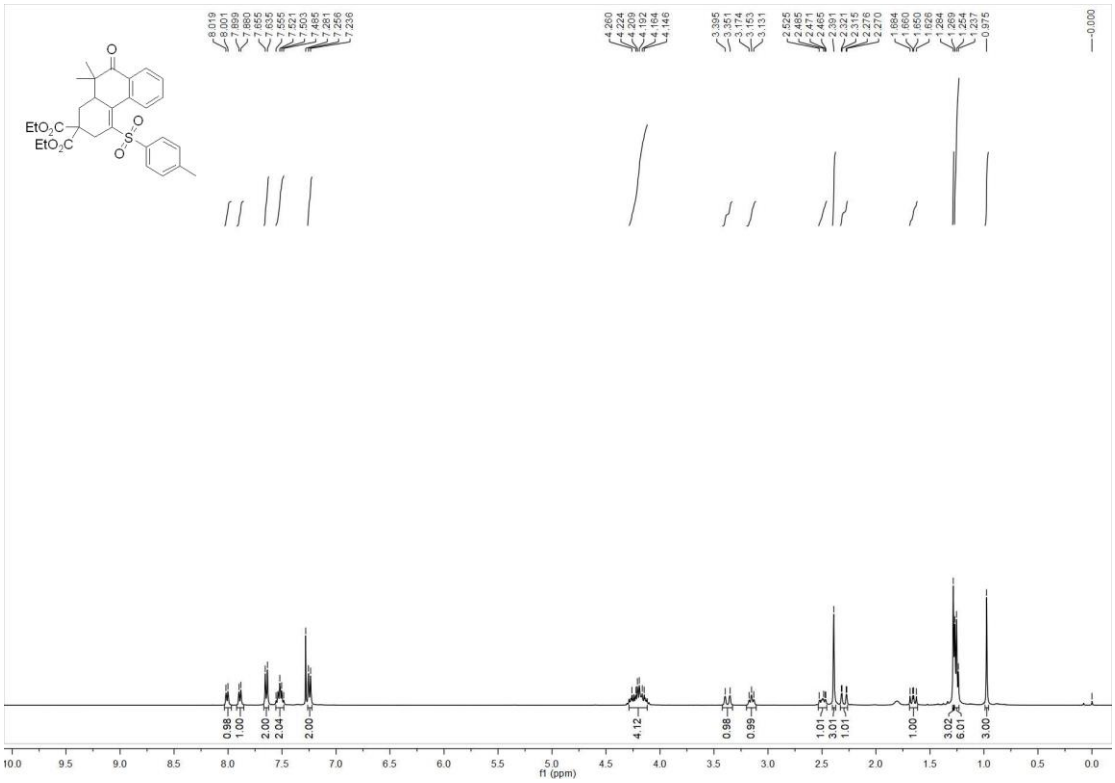
^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ae**



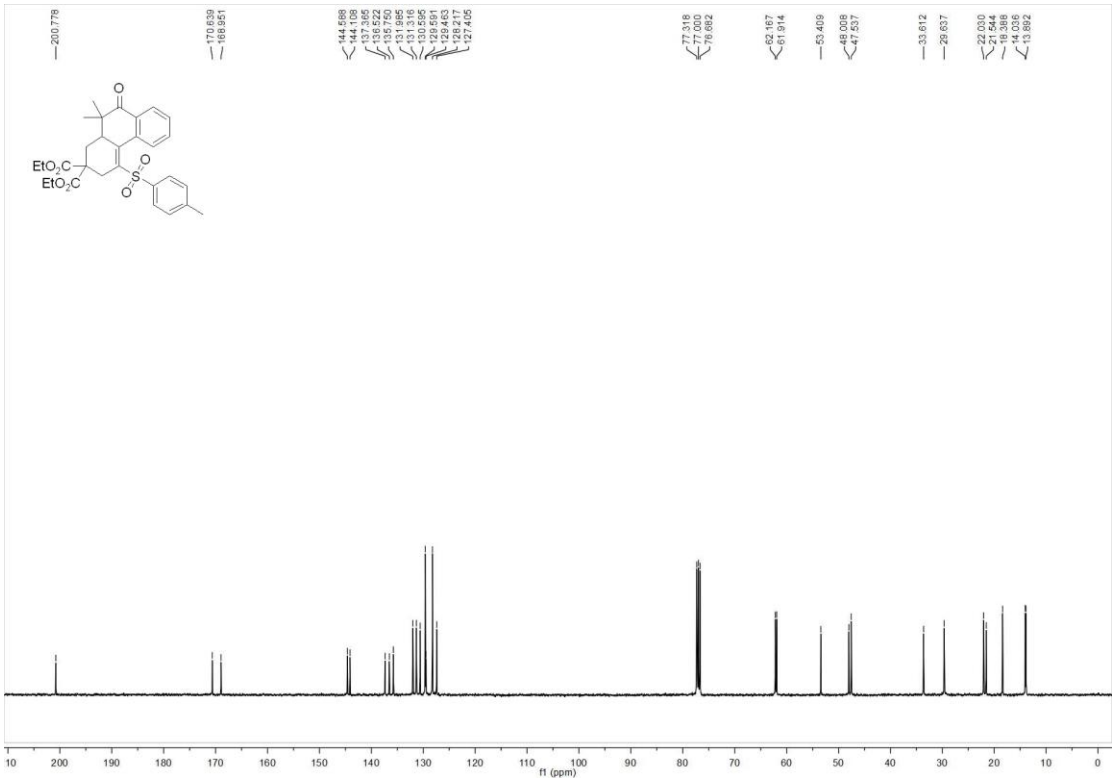
Diethyl-10,10-dimethyl-9-oxo-4-tosyl-3,9,10,10a-tetrahydrophenanthrene-2,2(1*H*)

-dicarboxylate (3af)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3af**

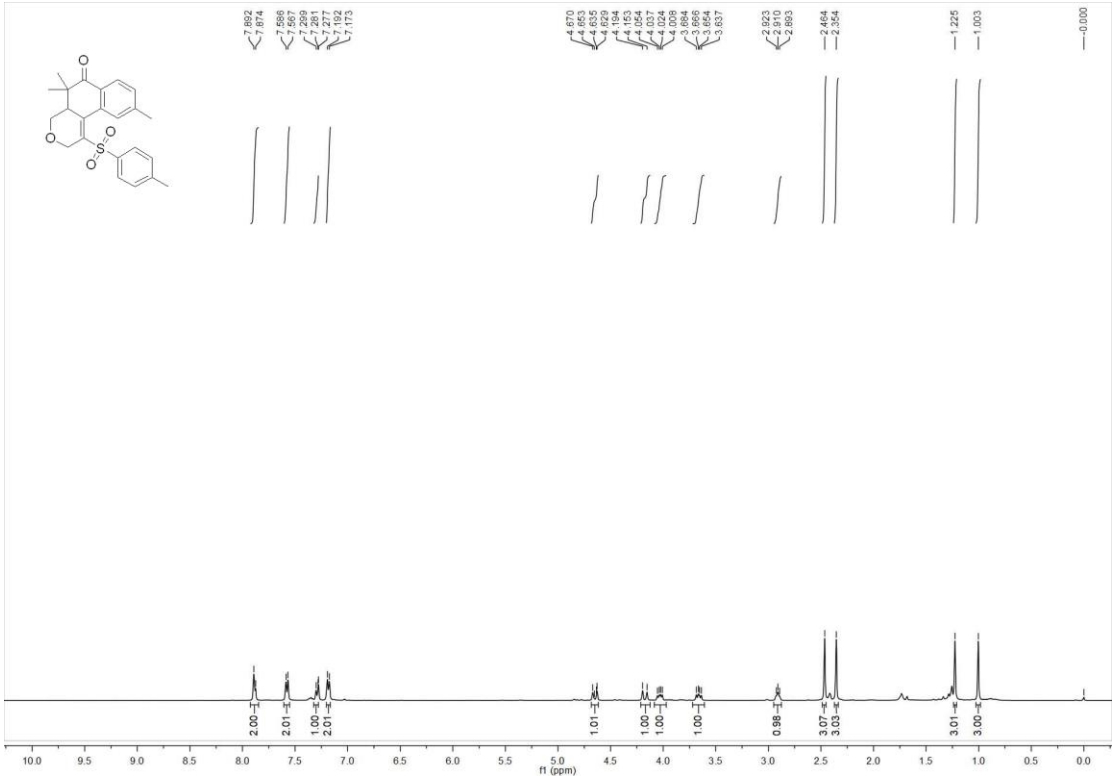


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3af**

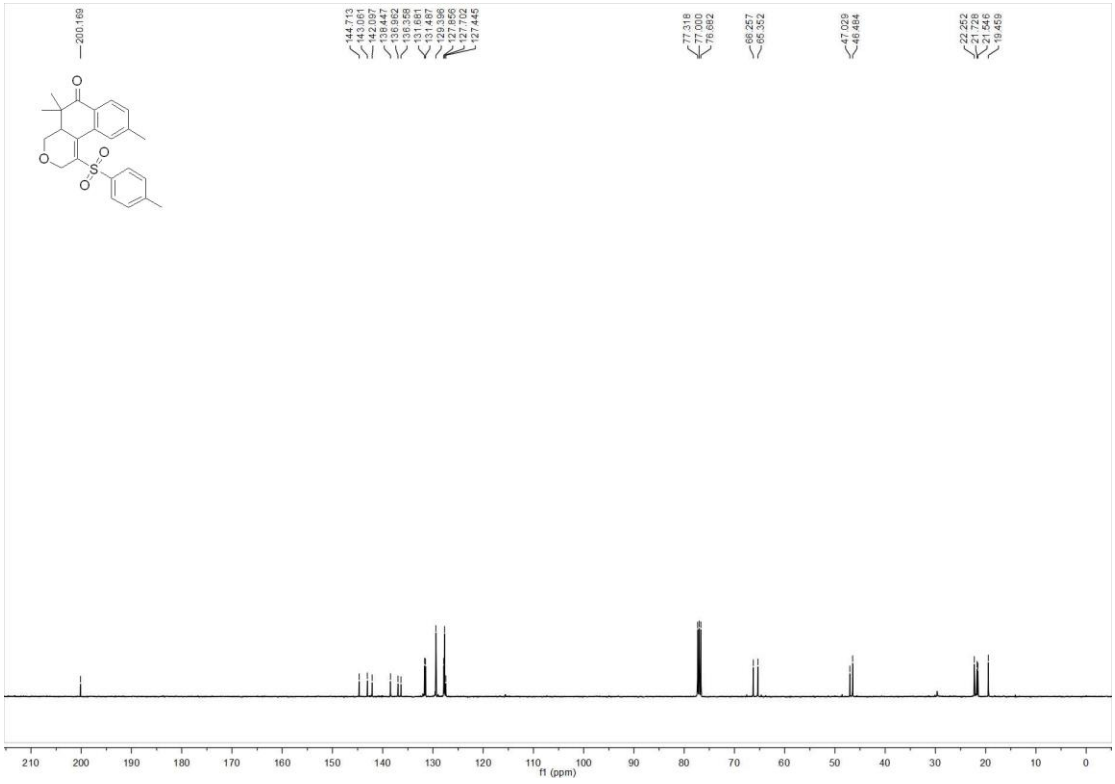


5,5,9-Trimethyl-1-tosyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ag)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ag**

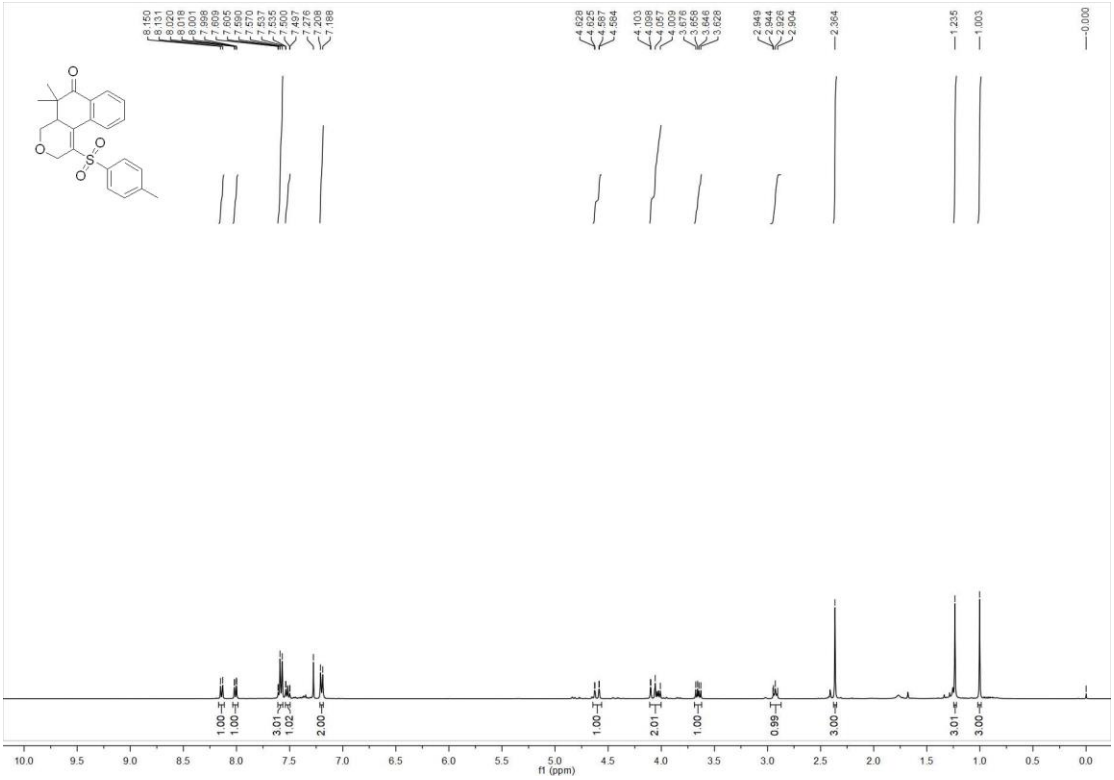


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ag**

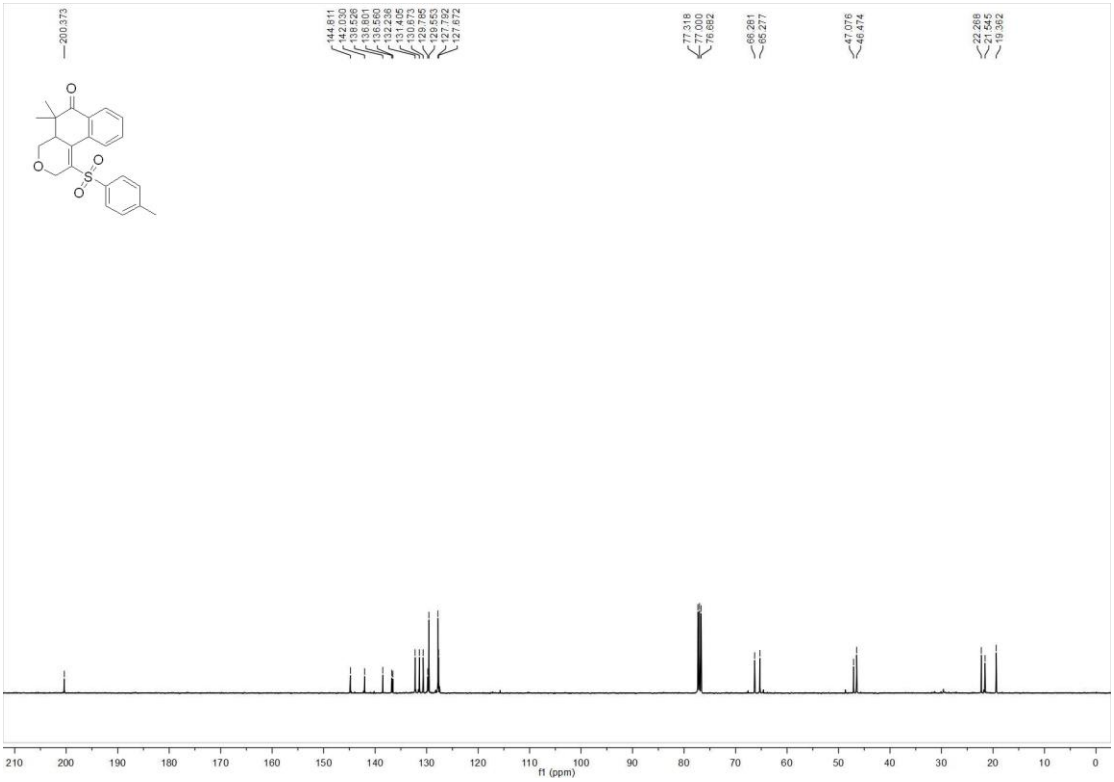


5,5-Dimethyl-1-tosyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ah)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ah**

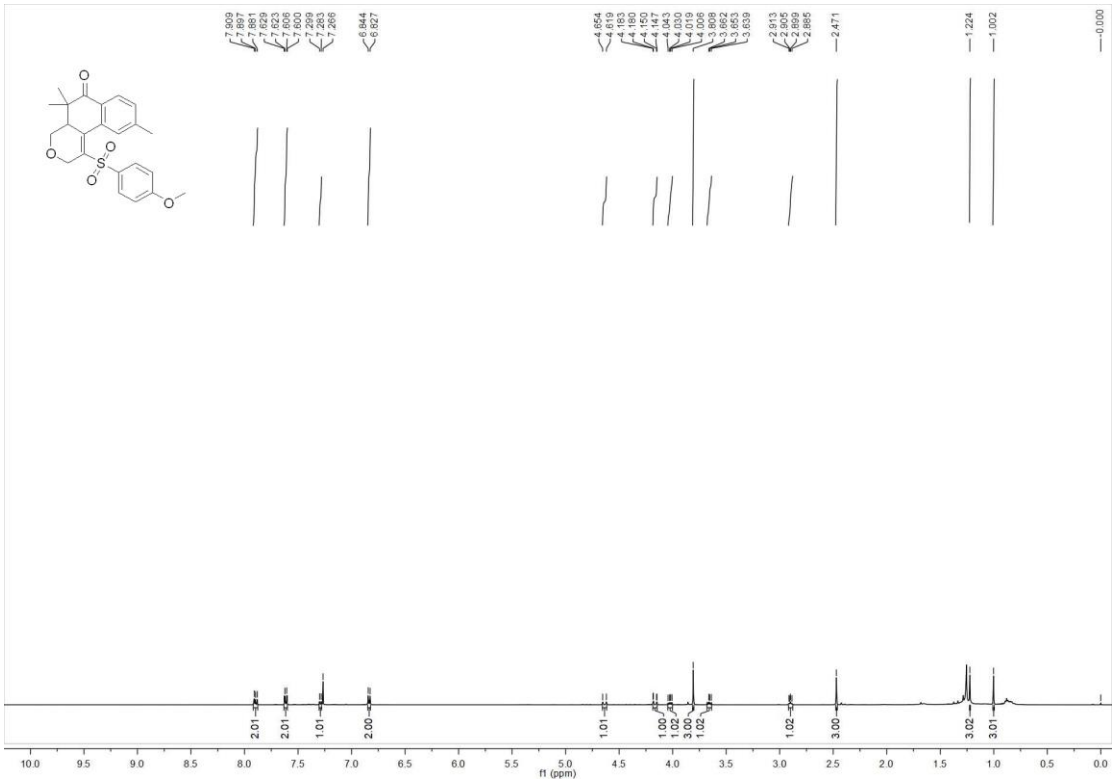


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3ah**

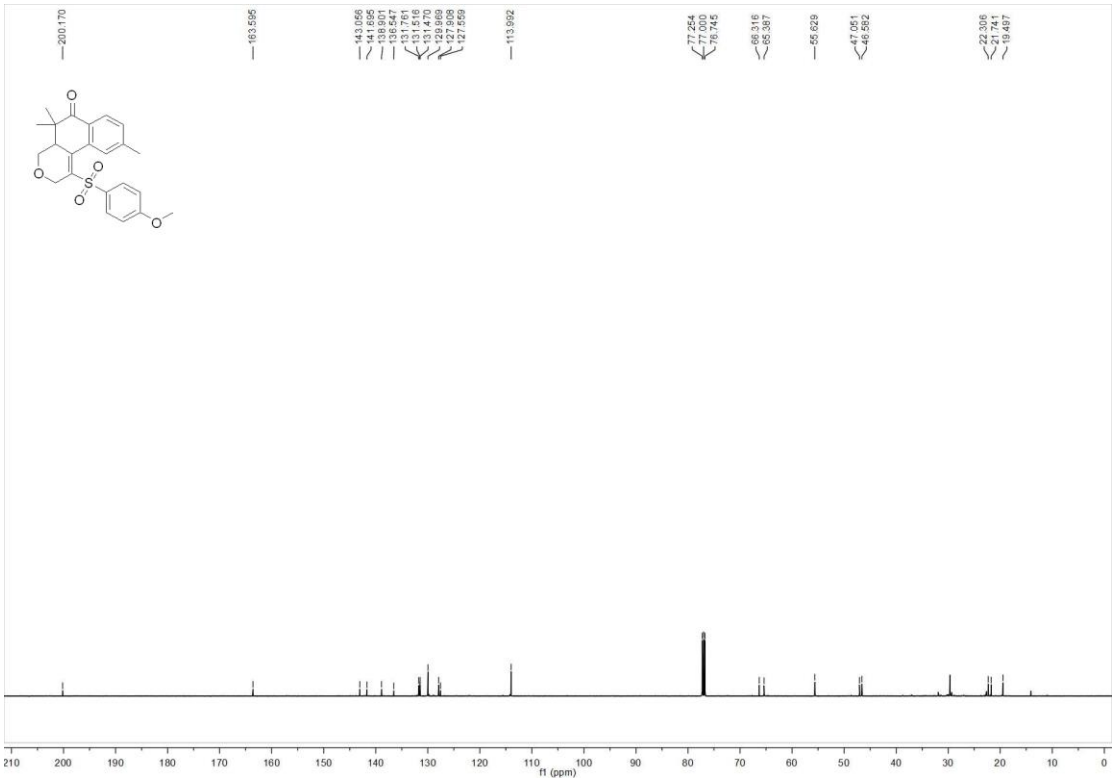


1-((4-Methoxyphenyl)sulfonyl)-5,5,9-trimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3ai)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ai**

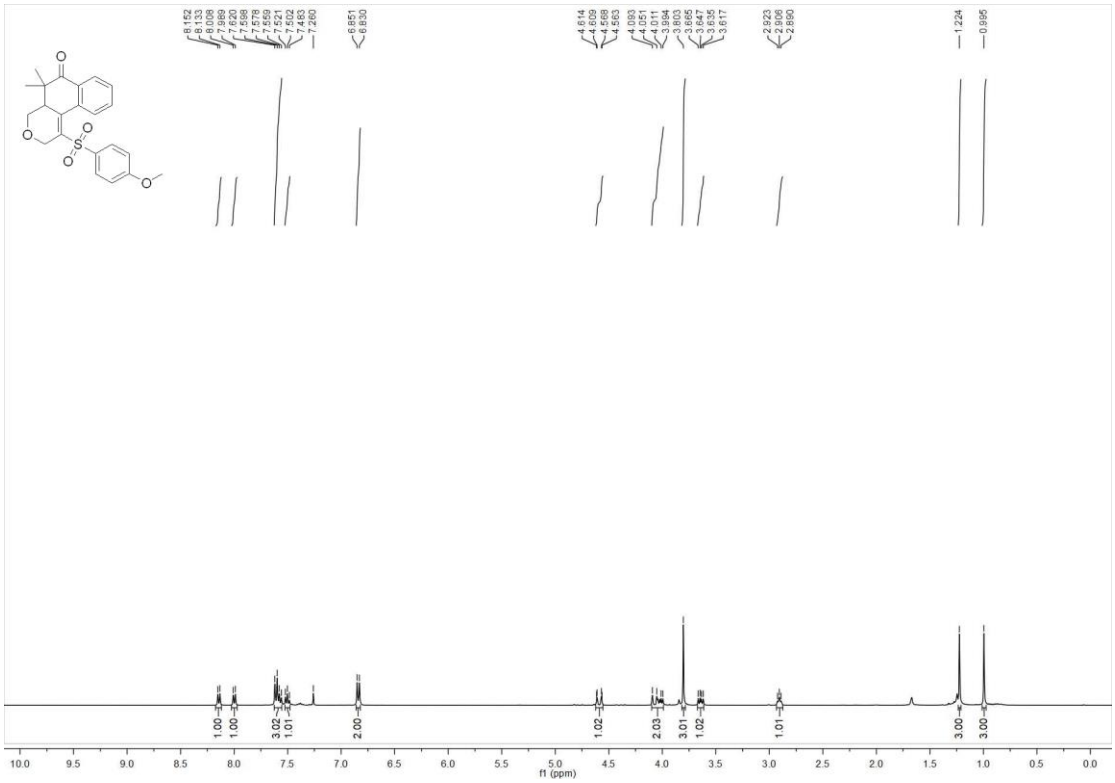


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3ai**

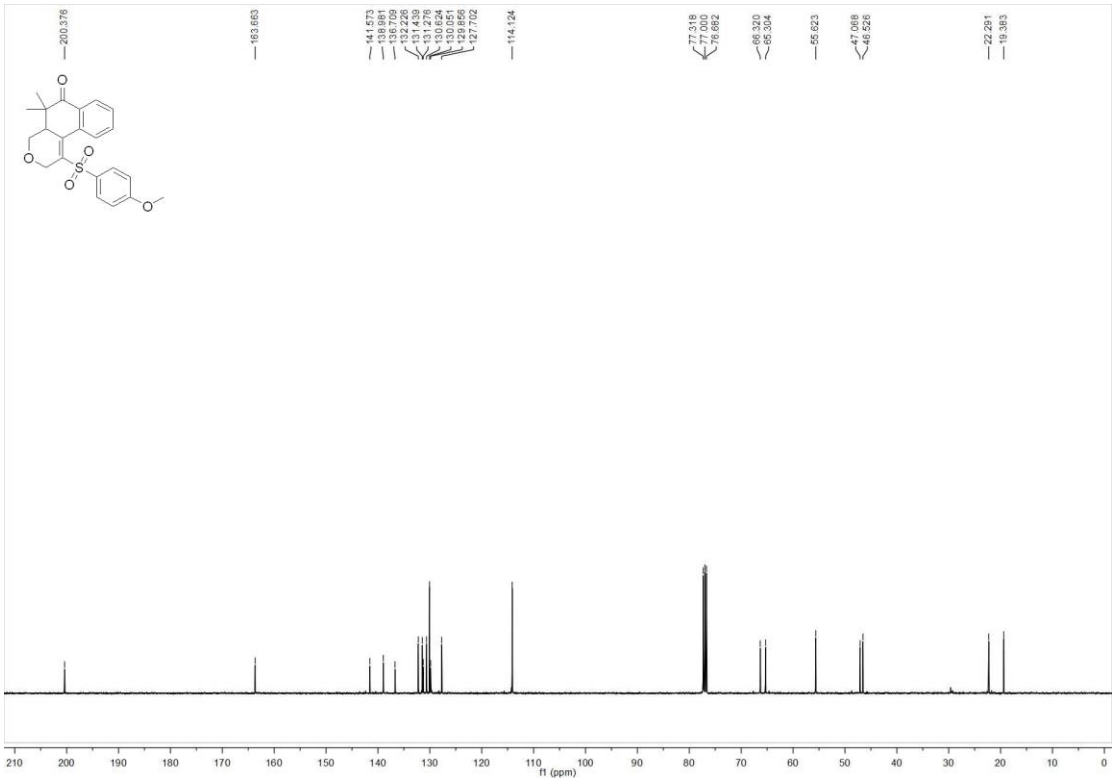


1-((4-Methoxyphenyl)sulfonyl)-5,5-dimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochrome n-6(4*H*)-one (3aj)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3aj**

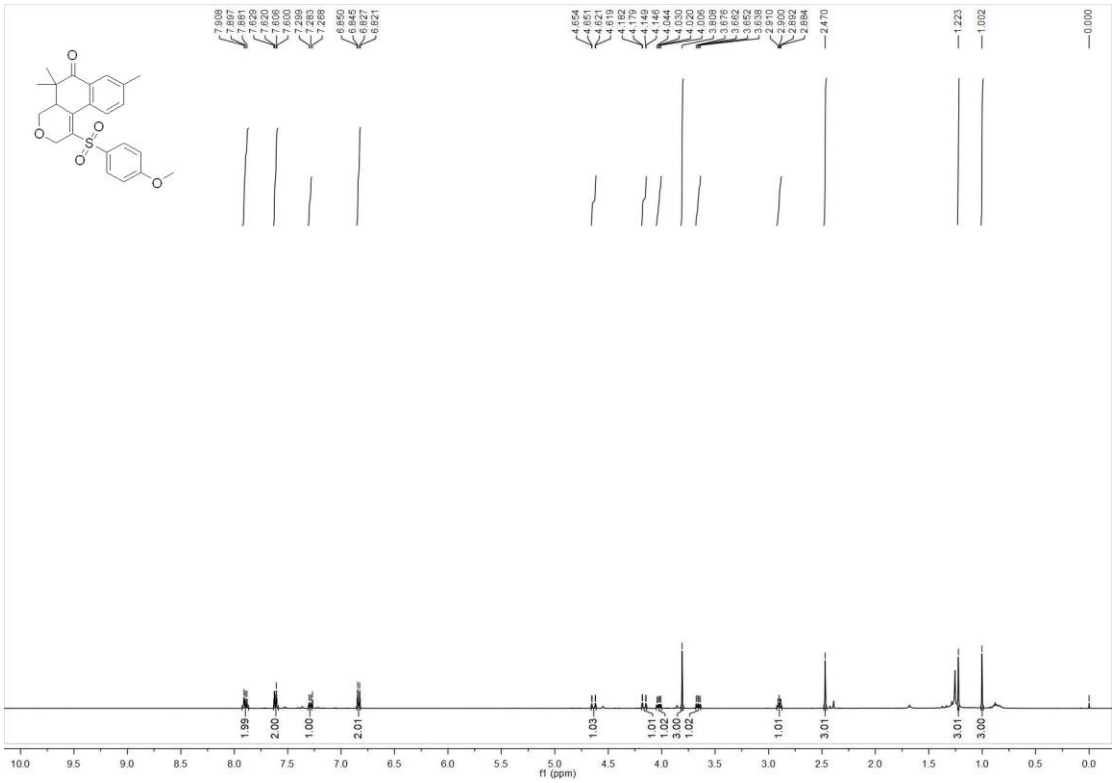


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3aj**

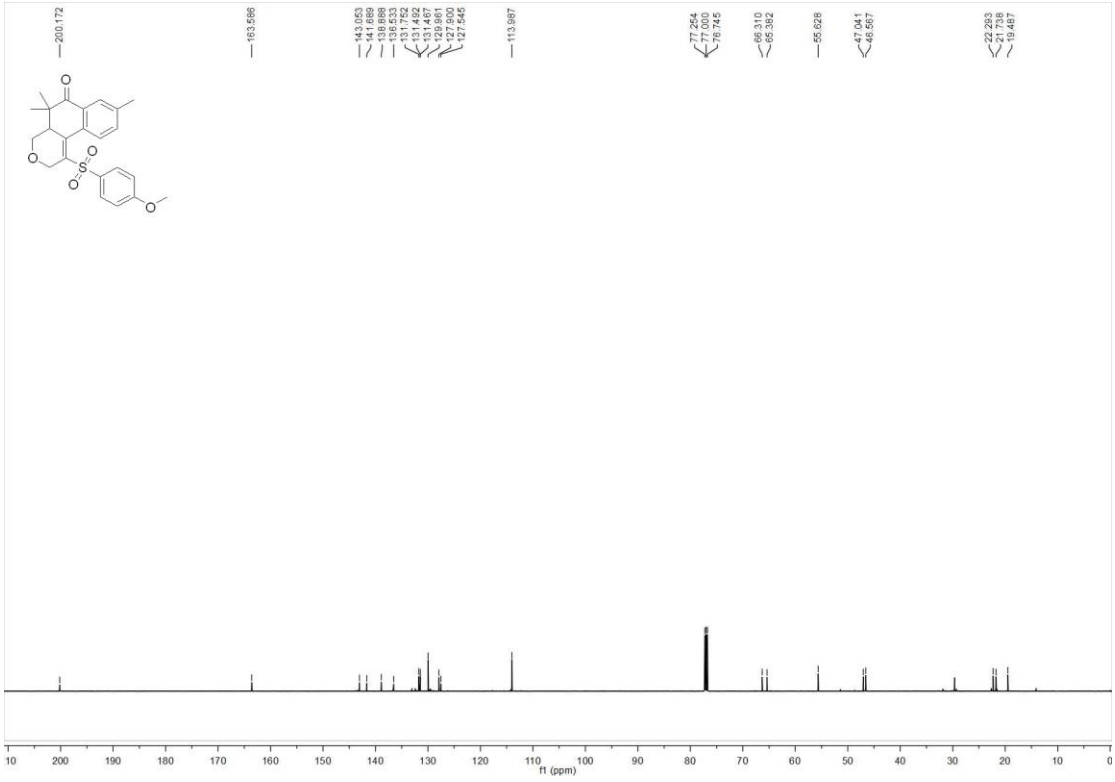


((4-Methoxyphenyl)sulfonyl)-5,5,8-trimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochrome n-6(4*H*)-one (3ak)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3ak**

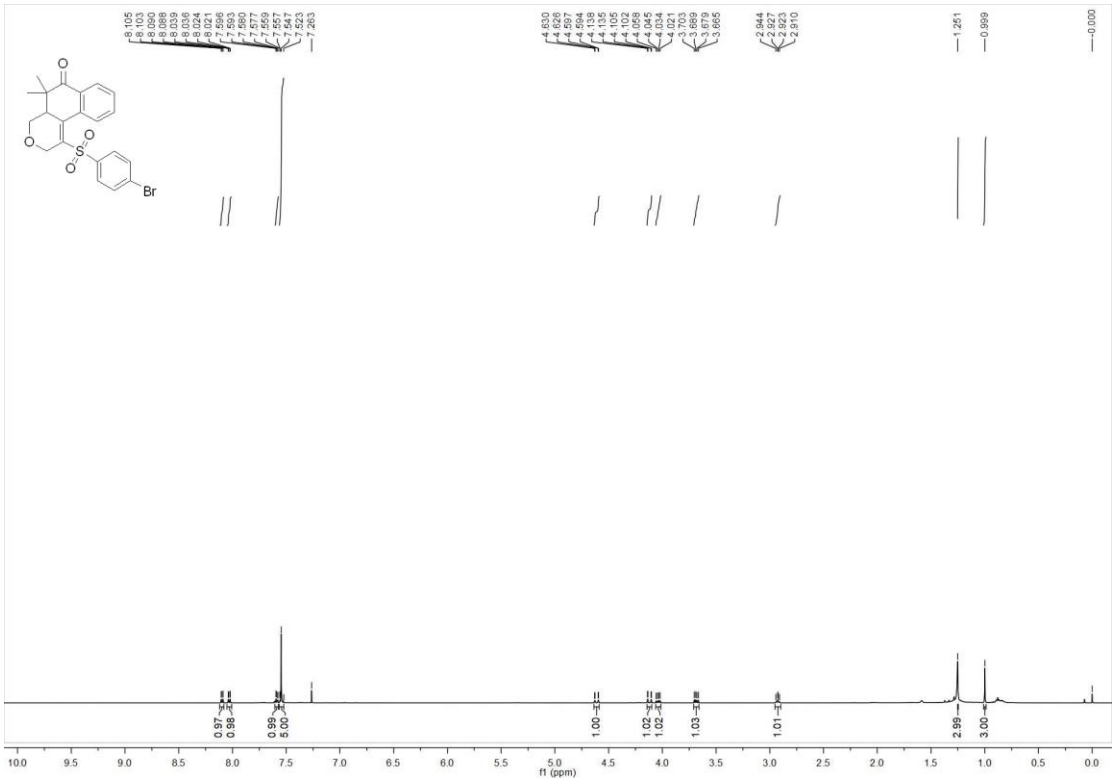


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3ak**

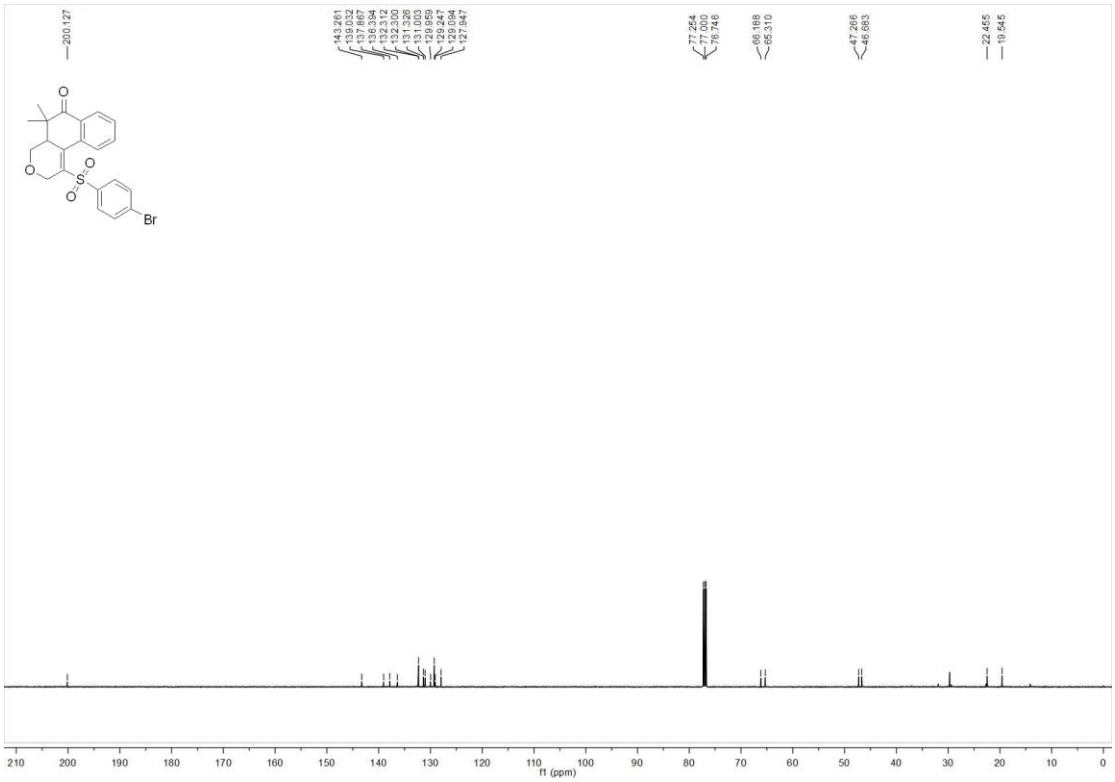


1-((4-Bromophenyl)sulfonyl)-5,5-dimethyl-4a,5-dihydro-2*H*-benzo[*f*]isochromen-6(4*H*)-one (3al)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3al**

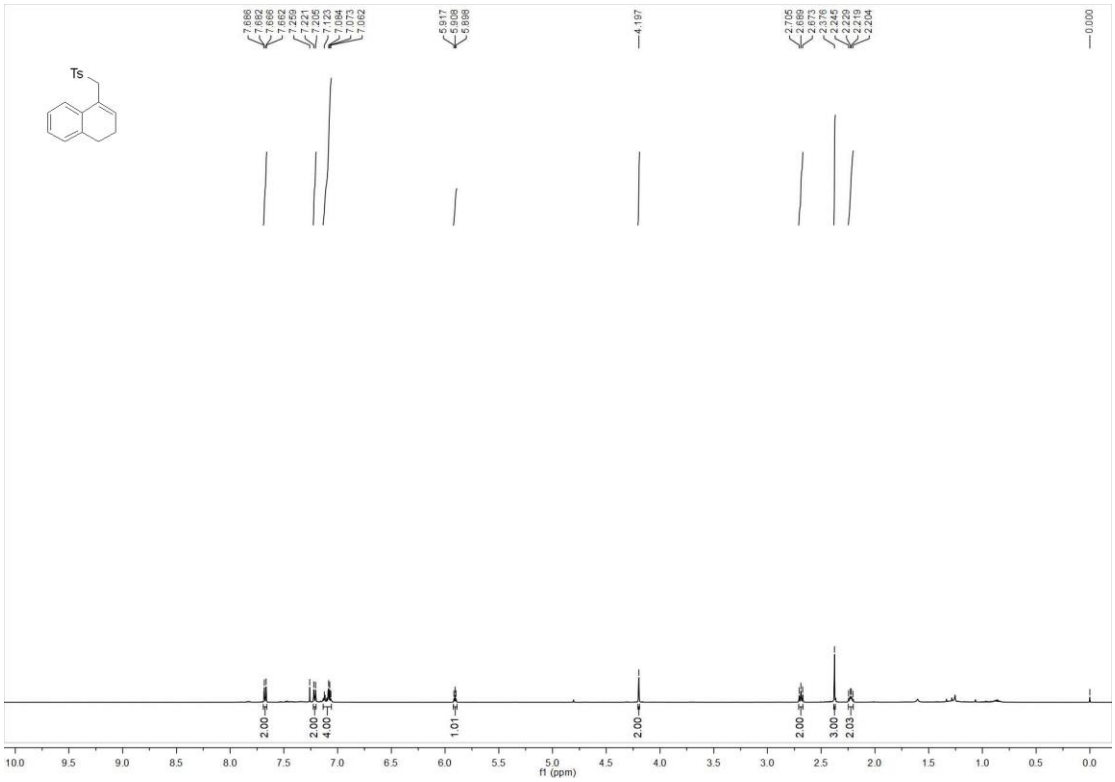


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3al**



4-(Tosylmethyl)-1,2-dihydronaphthalene (6a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6a**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **6a**