# *Supporting Information*

## Palladium-catalyzed [4+3] dearomatizing cycloaddition reaction of *N*-Iminoquinolinium Ylides

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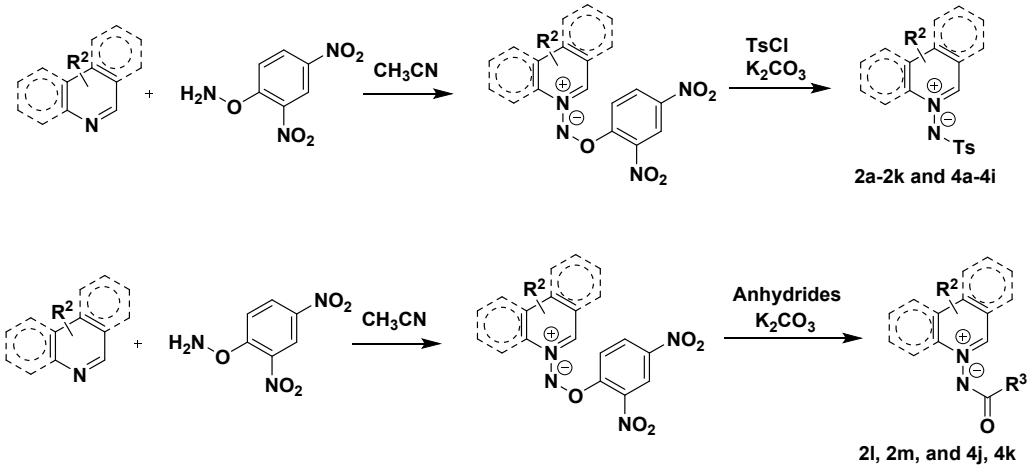
## (A) General Methods

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Preparative thin layer chromatography (PTLC) was HSGF 254(0.4-0.5 mm thickness). The reagents (chemicals) were purchased from commercial sources (J&K, TCI, Sigma-Aldrich, Adamas-beta, TCI, etc.), and used without further purification. Analytical all products were characterized by their NMR and MS spectra. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a 400 MHz, 500 MHz or 600 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet(t), quartet (q), multiplet (m), doublet of doublets (dd) and broad (br). High-resolution mass spectra (HRMS) were measured on Micromass Ultra Q-TOF spectrometer. The substrates **1** were prepared according to previous literature[1].

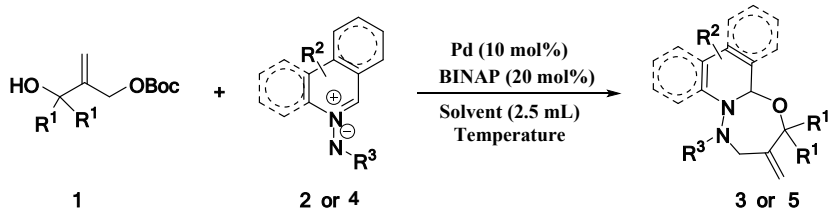
## (B)Typical Synthesis Procedure of 2 and 4




To a solution of quinoline or isoquinoline (0.77 g, 6.0 mmol) in acetonitrile (25 mL) was added *O*-(2,4-dinitrophenyl) hydroxylamine (1.3 g, 6.6 mmol). The reaction flask was sealed with rubber plug, and the reaction mixture was stirred for 24 h at room

temperature. Upon filtering off the solvent, the orange precipitate was dissolved in THF/ $H_2O$ (30 mL, 1/1, v/v). The reaction mixture was added $K_2CO_3$ (2.9 g, 21.0 mmol) at room temperature, and 4-toluenesulfonyl chloride (2.3 g, 12.0 mmol) was slowly added. After 12 h, the reaction was diluted with 20 mL of $H_2O$ and extracted three times with DCM (30 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure, and purified by column chromatography on silica gel (DCM/$CH_3OH$ = 20/1, v/v) to afford corresponding product. The substrates **2a-2k** and **4a-4i** were prepared according typical synthesis procedure.[2] **2l**, **2m**, **4j**, **4k** and **4l** were prepared according to previous literature.[3]

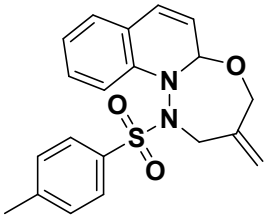
## (C)Typical Synthesis Procedure and Characterization of 3 and 5




1 2 or 4 3 or 5

To a dried reaction tube was added *N*-Iminoquinolinium Ylides **2** or **4** (0.10 mmol), 2-(hydroxy tert-butyl) allylmethyl carbonate **1** (0.20 mmol), $Pd(OAc)_2$ (10 mol%), BINAP (20 mol%) and anhydrous THF (2.5 mL). Then the reaction tube was evacuated and purged with argon three times. The solution was kept at 65 $^oC$ for 24 h. The crude mixture was purified by silica gel column chromatography (PE/EA = 4/1, v/v) to give the corresponding product **3** or **5**.

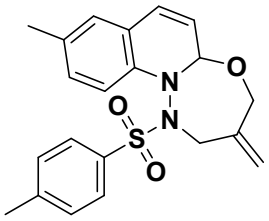
## 1. Characterization of 3 and 5




**(3a)** 3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino [3,2-*a*] quinoline

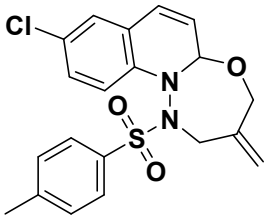
Following general procedure **C**, **3a** was obtained as white solid (29.8 mg, yield 81%): melting point 116.4−118.1 °C. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.09 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.06-7.00 (m, 1H), 6.80 (td, *J* = 7.4, 0.8 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 9.6 Hz, 1H), 5.89 (dd, *J* = 9.5, 5.4 Hz, 1H), 5.35 (s, 1H), 5.16 (d, *J* = 5.4 Hz, 1H), 5.11 (s, 1H), 4.89 (d, *J* = 14.9 Hz, 1H), 4.38 (d, *J* = 14.6 Hz, 1H), 4.31 (d, *J* = 14.9 Hz, 1H), 4.22 (d, *J* = 14.8 Hz, 1H),

2.35 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.10, 143.26, 139.93, 135.57, 129.36, 128.92, 128.22, 127.73, 127.59, 121.32, 120.38, 120.19, 116.26, 112.24, 87.10, 73.14, 53.42, 21.55. HRMS (ESI) m/z: calculated for $C_{20}H_{21}N_2O_3S^+$ $(M+H)^+$: 369.1267, found: 369.1268.



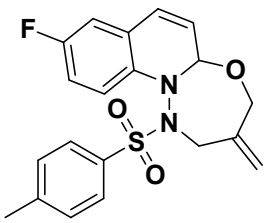
**(3b)** 9-methyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*- [1, 3,4] oxadiazepino [3,2-*a*] quinoline

Following general procedure **C**, **3b** was obtained as white solid (26.0 mg, yield 68%): melting point 115.5−117.6 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, $J$ = 8.3 Hz, 2H), 7.18 (d, $J$ = 8.1 Hz, 2H), 6.91 (s, 1H), 6.87 (d, $J$ = 8.3 Hz, 1H), 6.68 (d, $J$ = 8.3 Hz, 1H), 6.64 (d, $J$ = 9.6 Hz, 1H), 5.85 (dd, $J$ = 9.5, 5.4 Hz, 1H), 5.33 (s, 1H), 5.08 (s, 1H), 5.05 (d, $J$ = 5.4 Hz, 1H), 4.87 (d, $J$ = 14.9 Hz, 1H), 4.32 (dd, $J$ = 33.7, 14.7 Hz, 2H), 4.22 (d, $J$ = 14.9 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (126 MHz, CDCl3) δ 144.03, 143.39, 137.69, 135.66, 129.64, 129.37, 128.22, 128.02, 127.76, 121.30, 120.19, 115.99, 112.31, 87.23, 73.08, 53.30, 21.57, 20.38. HRMS (ESI) m/z: calculated for $C_{21}H_{23}N_2O_3S^+$ $(M+H)^+$: 383.1424, found: 383.1422.



**(3c)** 9-chloro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1, 3,4] oxadiazepino [3,2-*a*] quinoline

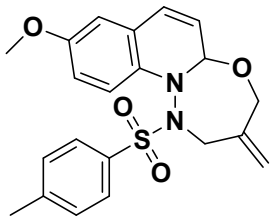
Following general procedure **C**, **3c** was obtained as white solid (32.6 mg, yield 81%): melting point 117.5−118.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, $J$ = 8.3 Hz, 2H), 7.18 (d, $J$ = 8.1 Hz, 2H), 7.06 (d, $J$ = 2.2 Hz, 1H), 6.97 (dd, $J$ = 8.7, 2.3 Hz, 1H), 6.68 (d, $J$ = 8.8 Hz, 1H), 6.61 (d, $J$ = 9.6 Hz, 1H), 5.94 (dd, $J$ = 9.6, 5.4 Hz, 1H), 5.38 (s, 1H), 5.16 (d, $J$ = 5.4 Hz, 1H), 5.13 (s, 1H), 4.87 (d, $J$ = 14.7 Hz, 1H), 4.36 (d, $J$ = 14.6 Hz, 1H), 4.29 (d, $J$ = 14.6 Hz, 1H), 4.16 (d, $J$ = 14.7 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (126 MHz, CDCl3) δ 144.34, 142.64, 138.55, 135.16, 129.41, 128.49, 128.18, 126.90, 126.61, 125.28, 122.55, 121.66, 117.09, 113.67, 86.38, 73.05, 53.38, 21.55. HRMS (ESI) m/z: calculated for $C_{20}H_{20}ClN_2O_3S^+$ $(M+H)^+$: 403.0878, found: 403.0882.



**(3d)** 9-fluoro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1, 3,4] oxadiazepino [3,2-*a*] quinoline

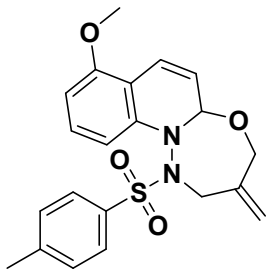
Following general procedure **C**, **3d** was obtained as white solid (28.6 mg, yield 74%): melting point 137.4−139.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J$ = 8.2 Hz, 2H), 7.17 (d, $J$ = 8.2 Hz, 2H), 6.81 (dd, $J$ = 8.6, 2.7 Hz, 1H), 6.74 (td, $J$ = 8.6, 2.7 Hz, 1H), 6.69 (dd, $J$ = 9.0, 4.8 Hz, 1H), 6.62 (d, $J$ = 9.6 Hz, 1H), 5.96 (dd, $J$ = 9.6, 5.5 Hz, 1H), 5.38 (s, 1H), 5.14 – 5.10 (m, 2H), 4.88 (d, $J$ = 14.7 Hz, 1H), 4.33 (q, $J$ = 14.6 Hz, 2H), 4.18 (d, $J$ = 14.7 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (126 MHz, CDCl3) δ 156.67 ($J_{CF}$= 239.4 Hz), 143.81, 142.38, 135.63, 134.84, 128.93, 127.79, 126.44, 121.84 (d,

$J_{CF}$ = 8.0 Hz), 121.40, 116.52, 114.92($J_{CF}$ = 11.34 Hz), 113.08 ($J_{CF}$ = 15.1 Hz), 113.02 ($J_{CF}$ = 16.3 Hz), 86.05, 72.62, 52.84, 21.12. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -124.75 (m). HRMS (ESI) m/z: calculated for $C_{20}H_{20}FN_2O_3S^+$ $(M+H)^+$: 387.1173, found: 387.1174.



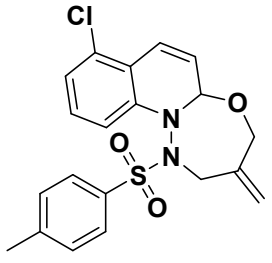
**(3e)** 9-methoxy-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino [3,2-*a*] quinoline

Following general procedure **C**, **3e** was obtained as white solid (23.9 mg, yield 60%): melting point 116.1−118.1 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.66 (ddd, *J* = 11.4, 10.4, 5.7 Hz, 4H), 5.91 (dd, *J* = 9.5, 5.5 Hz, 1H), 5.35 (s, 1H), 5.09 (s, 1H), 5.07 (d, *J* = 5.5 Hz, 1H), 4.87 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.7 Hz, 1H), 4.29 (d, *J* = 14.7 Hz, 1H), 4.21 (d, *J* = 14.8 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.70, 143.02, 142.29, 134.56, 132.90, 128.33, 127.20, 126.56, 121.12, 120.06, 115.14, 114.16, 112.41, 111.31, 86.01, 72.03, 54.70, 52.15, 20.55. HRMS (ESI) m/z: calculated for $C_{21}H_{23}N_2O_4S^+$ $(M+H)^+$: 399.1373, found: 399.1374.



**(3f)** 8-methoxy-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino[3,2-*a*]quinoline

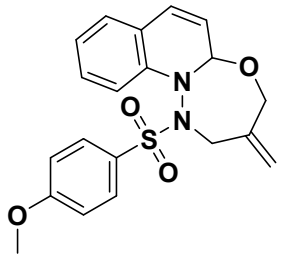
Following general procedure **C**, **3f** was obtained as white solid (22.7 mg, yield 57%): melting point 118.2−120.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13-7.08 (m, 1H), 6.98 (t, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 8.3 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 5.82 (dd, *J* = 9.8, 5.4 Hz, 1H), 5.34 (s, 1H), 5.10 (s, 1H), 5.07 (d, *J* = 5.5 Hz, 1H), 4.87 (d, *J* = 14.8 Hz, 1H), 4.36 (d, *J* = 14.6 Hz, 1H), 4.27 (d, *J* = 14.8 Hz, 1H), 4.22 (d, *J* = 14.8 Hz, 1H), 3.78 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.68, 144.04, 143.22, 141.01, 135.57, 129.37, 129.06, 128.25, 121.79, 118.39, 116.36, 110.65, 105.53, 102.52, 86.85, 73.03, 55.64, 53.63, 21.57. HRMS (ESI) m/z: calculated for $C_{21}H_{23}N_2O_4S^+$ $(M+H)^+$: 399.1373, found: 399.1367.



**(3g)** 8-chloro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino[3,2-*a*] quinoline

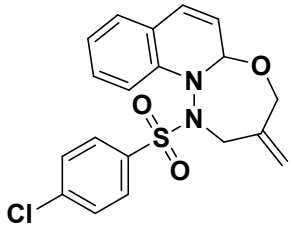
Following general procedure **C**, **3g** was obtained as white solid (26.1 mg, yield 65%): melting point 146.0−148.1 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 9.8 Hz, 1H), 6.94 (t, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.00 (dd, *J* = 9.8, 5.5 Hz, 1H), 5.39 (s, 1H), 5.15 – 5.11 (m, 2H), 4.88 (d, *J* = 14.7 Hz, 1H), 4.36 (d, *J* = 14.5 Hz, 1H), 4.29 (d, *J* = 14.5 Hz, 1H), 4.18 (d, *J* = 14.6 Hz, 1H), 2.36 (s, 3H). $^{13}$C

NMR (151 MHz, CDCl3) δ 144.38, 142.49, 141.39, 135.10, 131.94, 129.47, 128.95, 128.26, 123.73, 121.31, 121.21, 118.98, 117.50, 111.22, 85.83, 73.10, 53.59, 21.62. HRMS (ESI) m/z: calculated for $C_{20}H_{20}ClN_2O_3S^+$ $(M+H)^+$: 403.0878, found: 403.0882.



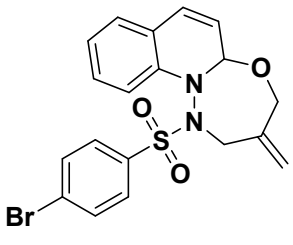
**(3h)** 1-((4-methoxyphenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino[3,2-*a*]quinoline

Following general procedure **C**, **3h** was obtained as white solid (31.1 mg, yield 81%): melting point 95.4−98.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.07-7.02 (m, 1H), 6.86-6.78 (m, 3H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 9.6 Hz, 1H), 5.90 (dd, *J* = 9.5, 5.4 Hz, 1H), 5.36 (s, 1H), 5.19 (d, *J* = 5.4 Hz, 1H), 5.11 (s, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.38 (d, *J* = 14.6 Hz, 1H), 4.32 (d, *J* = 14.7 Hz, 1H), 4.21 (d, *J* = 14.8 Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.26, 143.21, 139.90, 130.34, 129.97, 128.91, 127.67, 127.54, 121.24, 120.34, 120.13, 116.33, 113.85, 112.20, 86.88, 73.06, 55.56, 53.36. HRMS (ESI) m/z: calculated for $C_{20}H_{21}N_2O_4S^+$ $(M+H)^+$: 385.1217, found: 385.1216.



**(3i)** 1-((4-chlorophenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino [3,2-*a*]quinoline

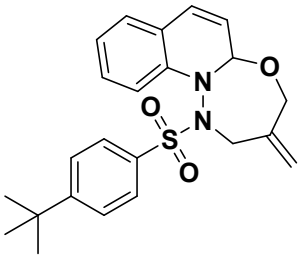
Following general procedure B, **3i** was obtained as white solid (34.1 mg, yield 88%): melting point 146.4−148.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 5.93 (dd, *J* = 9.5, 5.4 Hz, 1H), 5.38 (s, 1H), 5.23 (d, *J* = 5.4 Hz, 1H), 5.14 (s, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.42-4.32 (m, 2H), 4.20 (d, *J* = 14.8 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.97, 139.75, 139.50, 136.83, 129.58, 128.97, 128.91, 127.69, 121.37, 120.67, 120.22, 116.66, 111.93, 86.95, 72.99, 53.29. HRMS (ESI) m/z: calculated for $C_{19}H_{18}ClN_2O_3S^+$ $(M+H)^+$: 389.0721, found: 389.0726.



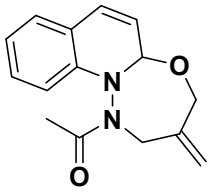
**(3j)** 1-((4-bromophenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino[3,2-*a*]quinoline

Following general procedure **C**, **3j** was obtained as white solid (25.1 mg, yield 58%): melting point 145.9−148.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.68 (dd, *J* = 14.2, 8.9 Hz, 2H), 5.93 (dd, *J* = 9.5, 5.4 Hz, 1H), 5.37 (s, 1H), 5.22 (d, *J* = 5.4 Hz, 1H), 5.13 (s, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.37 (q, *J* = 14.7 Hz, 2H), 4.21 (d, *J* = 14.8 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 142.94, 139.48, 137.36, 131.95, 129.61, 128.91, 128.27, 127.68, 121.35, 120.66, 120.19, 116.61, 111.91, 86.96, 72.97, 53.28. HRMS (ESI) m/z: calculated for $C_{19}H_{18}BrN_2O_3S^+$

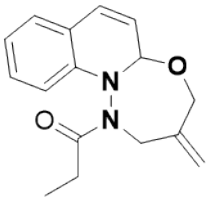
$(M+H)^+$: 433.0216, found: 433.0213.



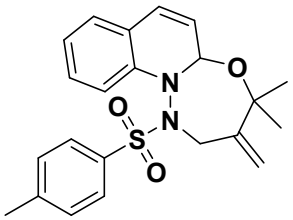
**(3k)** 1-((4-(tert-butyl)phenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino[3,2-*a*]quinoline
Following general procedure **C**, **3k** was obtained as white solid (31.2 mg, yield 76%): melting point 94.0−96.0 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.06 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.74 (dt, *J* = 7.4, 3.7 Hz, 1H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 5.91 (dd, *J* = 9.6, 5.3 Hz, 1H), 5.35 (s, 1H), 5.31 (d, *J* = 5.4 Hz, 1H), 5.12 (s, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.41 – 4.33 (m, 2H), 4.21 (d, *J* = 14.8 Hz, 1H), 1.25 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.17, 143.22, 139.76, 135.33, 128.71, 128.03, 127.71, 127.52, 125.64, 121.16, 120.21, 120.18, 116.62, 111.97, 87.16, 73.18, 53.44, 35.12, 31.02. HRMS (ESI) m/z: calculated for $C_{23}H_{27}N_2O_3S^+$ $(M+H)^+$: 411.1737, found: 411.1741.



**(3l)** 1-(3-methylene-3,4-dihydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinolin-1(2H)-yl)ethan-1-one
Following general procedure **C**, **3l** was obtained as white solid (10.8 mg, yield 42%) by aluminium oxide: melting point 102.4−104.1 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.02 (dd, *J* = 9.6, 5.1 Hz, 1H), 5.29 (d, *J* = 5.1 Hz, 1H), 5.17 (s, 1H), 5.06 (d, *J* = 14.8 Hz, 2H), 4.43 (d, *J* = 14.0 Hz, 1H), 4.34 (d, *J* = 13.9 Hz, 1H), 4.09 (d, *J* = 14.8 Hz, 1H), 2.01 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 173.13, 142.27, 139.82, 129.76, 128.19, 120.64, 120.34, 119.92, 116.24, 110.63, 88.66, 73.42, 51.28, 20.38. HRMS (ESI) m/z: calculated for $C_{15}H_{17}N_2O_2^+$ $(M+H)^+$: 257.1285, found: 257.1286.

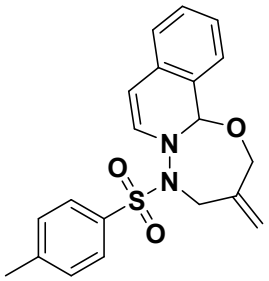


**(3m)** 1-(3-methylene-3,4-dihydro-5a*H*-[1,3,4] oxadiazepino [3,2-*a*] quinolin-1(2H)-yl)propan-1-one
Following general procedure **C**, **3m** was obtained as white solid (10.8 mg, yield 40%) by aluminium oxide: melting point 125.6−127.1 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.24 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.83 (d, *J* = 7.6 Hz, 1H), 5.56 (d, *J* = 1.4 Hz, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 5.04 (d, *J* = 15.0 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.33 (d, *J* = 13.3 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 2.41 – 2.31 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.96, 141.82, 131.28, 130.66, 129.28, 128.17, 127.68, 126.03, 124.78, 117.81, 102.88, 91.33, 73.22, 52.82, 26.01, 8.93. HRMS (ESI) m/z: calculated for $C_{16}H_{19}N_2O_2^+$ $(M+H)^+$: 271.1441, found: 271.1436.



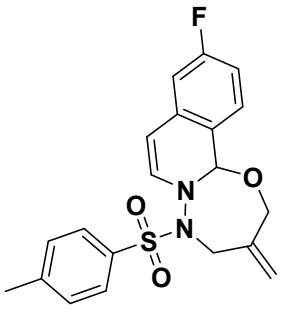
**(3n)** 4,4-dimethyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*- [1,3,4] oxadiazepino [3,2-*a*] quinoline

Following general procedure **C**, **3n** was obtained as white solid (26.9 mg, yield 68%): melting point 121.4−123.2 °C. $^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 9.5 Hz, 1H), 5.80 (dd, *J* = 9.5, 5.6 Hz, 1H), 5.59 (s, 1H), 5.24 (s, 1H), 5.10 (d, *J* = 5.6 Hz, 1H), 4.87 (d, *J* = 14.5 Hz, 1H), 4.07 (d, *J* = 14.5 Hz, 1H), 2.32 (s, 3H), 1.35 (s, 3H), 1.13 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 150.36, 143.98, 140.08, 134.89, 128.99, 128.79, 128.73, 127.42, 127.10, 121.51, 121.09, 120.25, 118.16, 112.48, 80.52, 79.01, 51.54, 30.61, 25.30, 21.56. HRMS (ESI) m/z: calculated for $C_{22}H_{25}N_2O_3S^+$ $(M+H)^+$: 397.158, found: 397.1578.



**(5a)** 3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline

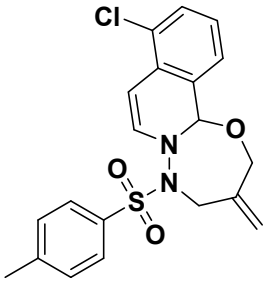
Following general procedure **C**, **5a** was obtained as white solid (32.8 mg, yield 89%): melting point 136.4−138.4 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.32-7.28 (m, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21-7.15 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.83 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.63 (d, *J* = 7.7 Hz, 1H), 5.43 (d, *J* = 1.5 Hz, 1H), 5.27 (s, 1H), 5.21 (s, 1H), 4.85 (d, *J* = 14.5 Hz, 1H), 4.45 (d, *J* = 13.1 Hz, 1H), 4.33 (d, *J* = 13.1 Hz, 1H), 4.12 (d, *J* = 14.5 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.47, 141.57, 134.69, 130.57, 130.50, 129.73, 129.02, 128.59, 128.34, 127.53, 125.86, 124.66, 118.32, 103.20, 90.25, 72.70, 54.24, 21.65. HRMS (ESI) m/z: calculated for $C_{20}H_{21}N_2O_3S^+$ $(M+H)^+$: 369.1267, found: 369.1267.



**(5b)** 10-fluoro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline

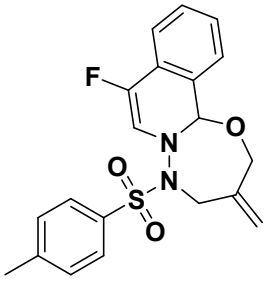
Following general procedure **C**, **5b** was obtained as white solid (31.7 mg, yield 82%): melting point 144.6−147.1 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 2H), 7.13 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.87 (td, *J* = 8.5, 2.5 Hz, 1H), 6.78 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.86 (d, *J* = 7.8 Hz, 1H), 5.57 (d, *J* = 7.7 Hz, 1H), 5.41 (d, *J* = 1.3 Hz, 1H), 5.28 (s, 1H), 5.22 (s, 1H), 4.84 (d, *J* = 14.5 Hz, 1H), 4.42 (d, *J* = 13.0 Hz, 1H), 4.31 (d, *J* = 13.0 Hz, 1H), 4.09 (d, *J* = 14.5 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.06 (d, $J_{CF}$ = 246.96 Hz), 144.63, 141.22, 134.52, 132.66 (d, $J_{CF}$ = 9.1 Hz), 131.59, 129.78, 129.40 (d, $J_{CF}$ = 9.1 Hz), 128.32, 124.58 (d, $J_{CF}$ = 2.4 Hz), 118.75, 112.87 (d, $J_{CF}$ = 22.68), 110.78 (d, $J_{CF}$ = 21.42), 102.32 (d, $J_{CF}$ = 2.0 Hz), 89.58, 72.58, 54.26, 21.65. $^{19}$F NMR (376 MHz, CDCl3) δ -112.81 (m). HRMS (ESI) m/z: calculated for $C_{20}H_{20}FN_2O_3S^+$

$(M+H)^+$: 387.1173, found: 387.1168.



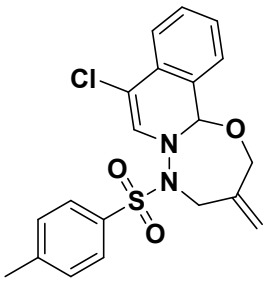
**(5c)** 9-chloro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline

Following general procedure **C**, **5c** was obtained as white solid (36.2 mg, yield 90%): melting point 120.4−122.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.14-7.07 (m, 2H), 5.98 (d, *J* = 7.9 Hz, 1H), 5.91 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.43 (d, *J* = 1.3 Hz, 1H), 5.29 (s, 1H), 5.24 (s, 1H), 4.84 (d, *J* = 14.4 Hz, 1H), 4.44 (d, *J* = 13.0 Hz, 1H), 4.31 (d, *J* = 13.0 Hz, 1H), 4.10 (d, *J* = 14.5 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 144.71, 140.93, 134.37, 131.76, 130.00, 129.86, 129.72, 129.45, 128.63, 128.32, 126.46, 126.25, 119.16, 99.26, 89.59, 72.68, 54.25, 21.68. HRMS (ESI) m/z: calculated for $C_{20}H_{20}ClN_2O_3S^+$ $(M+H)^+$: 403.0878, found: 403.0869.



**(5d)** 8-fluoro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline

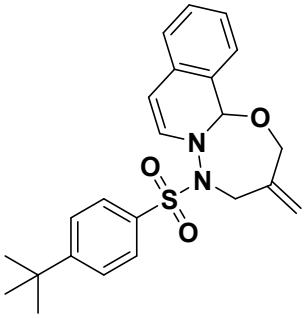
Following general procedure **C**, **5d** was obtained as white solid (18.1 mg, yield 47%): melting point 116.4−118.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.44-7.39 (m, 1H), 7.37 (d, *J* = 6.6 Hz, 1H), 7.32-7.26 (m, 3H), 7.24 (s, 1H), 5.82 (dd, *J* = 7.1, 1.2 Hz, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 5.28 (s, 1H), 5.21 (s, 1H), 4.84 (d, *J* = 14.8 Hz, 1H), 4.46 (d, *J* = 13.1 Hz, 1H), 4.33 (d, *J* = 13.1 Hz, 1H), 4.07 (d, *J* = 14.8 Hz, 1H), 2.43 (s, 3H).$^{13}$C NMR (151 MHz, $CDCl_3$) δ 144.69, 143.44 (d, $J_{CF}$ = 234.05 Hz), 141.24, 134.40, 129.81, 129.26, 128.32, 127.98 (d, $J_{CF}$ = 6.4 Hz), 127.53, 127.42 (d, $J_{CF}$ = 4.5 Hz), 125.67, 125.52, 118.84 (d, $J_{CF}$ = 2.4 Hz), 118.34, 114.00, 113.77, 90.58, 72.86, 53.65, 21.67. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -162.10 (d, J = 7.0 Hz). HRMS (ESI) m/z: calculated for $C_{20}H_{20}FN_2O_3S^+$ $(M+H)^+$: 387.1173, found: 387.1169.



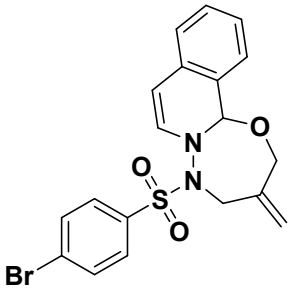
**(5e)** 8-chloro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1, 3, 4] oxadiazepino[2,3-*a*] isoquinoline

Following general procedure **C**, **5e** was obtained as white solid (12.1 mg, yield 30%): melting point 134.4−136.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 11.3, 4.6 Hz, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.02 (d, *J* = 1.4 Hz, 1H), 5.39 (d, *J* = 1.3 Hz, 1H), 5.30 (s, 1H), 5.23 (s, 1H), 4.84 (d, *J* = 14.6 Hz, 1H), 4.43 (d, *J* = 13.1 Hz, 1H), 4.33 (d, *J* = 13.1 Hz, 1H), 4.09 (d, *J* = 14.6 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 144.86, 140.83, 134.12, 129.84, 129.48, 128.90, 128.37, 127.37, 127.28, 122.24, 119.10, 107.82, 90.14, 72.78, 54.23, 21.70. HRMS (ESI) m/z:

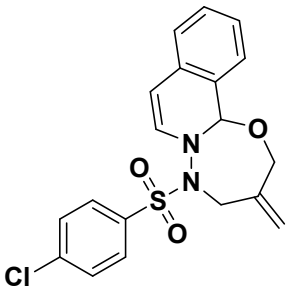
calculated for $C_{20}H_{20}ClN_2O_3S^+$ $(M+H)^+$: 403.0878, found: 403.0879.



**(5f)** 5-((4-(tert-butyl)phenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline
Following general procedure **C**, **5f** was obtained as white solid (37.3 mg, yield 91%): melting point 141.4−143.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.49-7.45 (m, 2H), 7.31-7.27 (m, 1H), 7.17 (td, *J* = 7.4, 1.1 Hz, 1H), 7.10 (t, *J* = 6.4 Hz, 2H), 5.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.65 (d, *J* = 7.7 Hz, 1H), 5.31-5.28 (m, 2H), 5.22 (s, 1H), 4.84 (d, *J* = 14.5 Hz, 1H), 4.42 (d, *J* = 13.0 Hz, 1H), 4.32 (d, *J* = 13.0 Hz, 1H), 4.17-4.12 (m, 1H), 1.34 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.48, 141.33, 134.30, 130.46, 128.97, 128.45, 128.19, 127.40, 126.00, 125.76, 124.61, 118.58, 103.06, 90.11, 72.60, 54.08, 35.22, 31.02. HRMS (ESI) m/z: calculated for $C_{23}H_{27}N_2O_3S^+$ $(M+H)^+$: 411.1737, found: 411.1736.

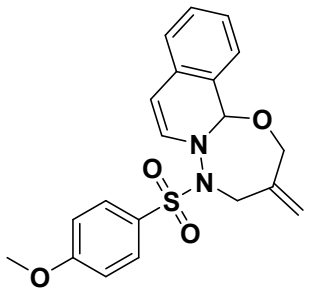


**(5g)** 5-((4-bromophenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinoline
Following general procedure **C**, **5g** was obtained as white solid (35.4 mg, yield 82%): melting point 146.4−148.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2H), 7.64-7.58 (m, 2H), 7.34-7.29 (m, 1H), 7.24-7.17 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 5.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.67 (d, *J* = 7.7 Hz, 1H), 5.44 (d, *J* = 1.4 Hz, 1H), 5.30 (s, 1H), 5.23 (s, 1H), 4.85 (d, *J* = 14.5 Hz, 1H), 4.45 (d, *J* = 13.3 Hz, 1H), 4.35 (d, *J* = 13.3 Hz, 1H), 4.13 (d, *J* = 14.5 Hz, 1H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 141.36, 136.71, 132.36, 130.42, 130.23, 129.74, 129.12, 128.68, 128.49, 127.46, 126.07, 124.73, 118.44, 103.80, 90.24, 72.67, 54.25. HRMS (ESI) m/z: calculated for $C_{19}H_{18}BrN_2O_3S^+$ $(M+H)^+$: 433.0216, found: 433.0208.



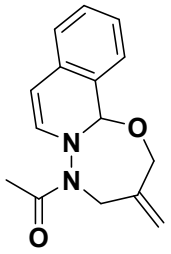
**(5h)** 5-((4-chlorophenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino [2,3-*a*] isoquinoline
Following general procedure **C**, **5h** was obtained as white solid (31.8 mg, yield 82%): melting point 125.3−127.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.34-7.29 (m, 1H), 7.24-7.17 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.67 (d, *J* = 7.7 Hz, 1H), 5.44 (d, *J* = 1.5 Hz, 1H), 5.30 (s, 1H), 5.23 (s, 1H), 4.85 (d, *J* = 14.5 Hz, 1H), 4.45 (d, *J* = 13.3 Hz, 1H), 4.35 (d, *J* = 13.3 Hz, 1H), 4.13 (d, *J* = 14.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 141.47, 140.16, 136.26, 130.52, 130.30, 129.74, 129.42, 128.55, 127.51, 126.11, 124.77, 118.44, 103.82, 90.29,

72.73, 54.30. HRMS (ESI) m/z: calculated for $C_{19}H_{18}ClN_2O_3S^+$ $(M+H)^+$: 389.0721, found: 389.073.



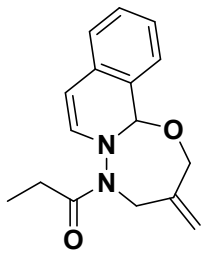
**(5i)** 5-((4-methoxyphenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4] oxadiazepino [2,3-*a*]isoquinoline

Following general procedure **C**, **5i** was obtained as white solid (36.1 mg, yield 94%): melting point 113.8−115.2 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.32-7.27 (m, 1H), 7.21-7.15 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.86 (dd, *J* = 7.7, 1.3 Hz, 1H), 5.64 (d, *J* = 7.7 Hz, 1H), 5.42 (d, *J* = 1.3 Hz, 1H), 5.28 (s, 1H), 5.21 (s, 1H), 4.83 (d, *J* = 14.5 Hz, 1H), 4.44 (d, *J* = 13.1 Hz, 1H), 4.32 (d, *J* = 13.1 Hz, 1H), 4.12 (d, *J* = 14.5 Hz, 1H), 3.85 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.54, 141.46, 130.58, 130.47, 128.97, 128.92, 128.51, 127.49, 125.80, 124.61, 118.41, 114.23, 103.08, 90.09, 72.61, 55.64, 54.14. HRMS (ESI) m/z: calculated for $C_{20}H_{21}N_2O_4S^+$ $(M+H)^+$: 385.1217, found: 385.1209.



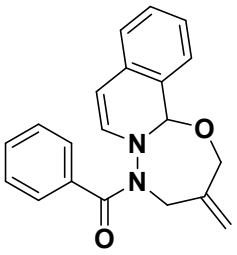
**(5j)** 1-(3-methylene-3,4-dihydro-12b*H*-[1,3,4]oxadiazepino [2,3-*a*] isoquinolin-5(2H)-yl)ethan-1-one

Following general procedure **C**, **5j** was obtained as colorless oil (12.8 mg, yield 50%) by aluminium oxide. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.24 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.83 (d, *J* = 7.6 Hz, 1H), 5.58 (d, *J* = 1.5 Hz, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 5.03 (d, *J* = 15.0 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.34 (d, *J* = 13.3 Hz, 1H), 4.03 (d, *J* = 15.0 Hz, 1H), 2.06 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.26, 143.11, 132.47, 132.03, 130.72, 129.57, 129.12, 127.49, 126.21, 119.26, 104.34, 92.66, 74.64, 54.03, 22.26. HRMS (ESI) m/z: calculated for $C_{15}H_{17}N_2O_2^+$ $(M+H)^+$: 257.1285, found: 257.129.



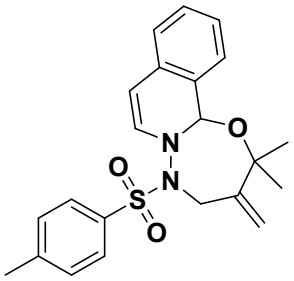
**(5k)** 1-(3-methylene-3,4-dihydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinolin-5(2H)-yl)propan-1-one

Following general procedure **C**, **5k** was obtained as colorless oil (14.0 mg, yield 52%) by aluminium oxide. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.22 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.83 (d, *J* = 7.6 Hz, 1H), 5.56 (d, *J* = 1.2 Hz, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 5.04 (d, *J* = 15.0 Hz, 1H), 4.43 (d, *J* = 13.3 Hz, 1H), 4.33 (d, *J* = 13.3 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 2.40 – 2.31 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.96, 141.82, 131.28, 130.66, 129.28, 128.17, 127.68, 126.03, 124.78, 117.81, 102.88, 91.33, 73.22, 52.83, 26.01, 8.93. HRMS (ESI) m/z: calculated for $C_{16}H_{19}N_2O_2^+$ $(M+H)^+$: 271.1441, found: 271.1445.



**(5l)** (3-methylene-3,4-dihydro-12b*H*-[1,3,4] oxadiazepino[2,3-*a*] isoquinolin-5(2H)yl) (phenyl)methanone

Following general procedure **C**, **5l** was obtained as white solid (13.7 mg, yield 43%) by aluminium oxide: melting point 108.8−110.2 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.22 (dd, *J* = 13.9, 6.2 Hz, 3H), 7.15 – 7.11 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.36 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.78 (d, *J* = 7.6 Hz, 1H), 5.45 (s, 1H), 5.28 (s, 1H), 5.17 (d, *J* = 17.2 Hz, 2H), 4.44 (q, *J* = 13.7 Hz, 2H), 4.25 (d, *J* = 15.2 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl3) δ 171.36, 142.21, 133.92, 131.60, 130.48, 130.36, 129.08, 127.94, 127.90, 127.84, 127.64, 125.91, 124.58, 116.67, 102.91, 92.05, 73.37. HRMS (ESI) m/z: calculated for $C_{20}H_{19}N_2O_2^+$ $(M+H)^+$: 319.1441, found: 319.1447.

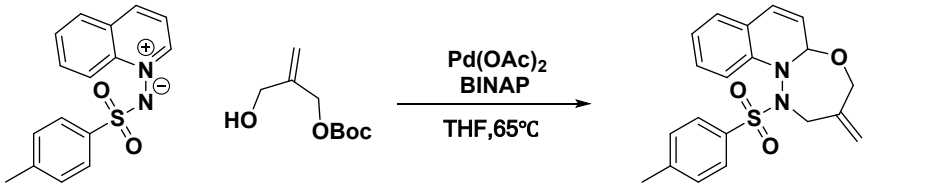


**(5m)** 2,2-dimethyl-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12bH-[1,3,4]oxadiazepino [2,3-a]isoquinoline

Following general procedure **C**, **5m** was obtained as white solid (29.7 mg, yield 75%): melting point 127.8−129.5 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.26 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.20 – 7.14 (m, 3H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.00 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.62 (d, *J* = 7.7 Hz, 1H), 5.56 (s, 1H), 5.48 (d, *J* = 1.1 Hz, 1H), 5.25 (s, 1H), 4.86 (d, *J* = 14.4 Hz, 1H), 4.11 (d, *J* = 14.4 Hz, 1H), 2.40 (s, 3H), 1.46 (s, 3H), 1.18 (s, 3H). $^{13}$C NMR (126 MHz, CDCl3) δ 151.89, 145.46, 136.64, 135.70, 131.94, 130.66, 130.21, 129.91, 128.36, 127.11, 126.03, 119.58, 104.30, 85.15, 80.53, 54.94, 31.82, 26.78, 23.03. HRMS (ESI) m/z: calculated for $C_{22}H_{25}N_2O_3S^+$ $(M+H)^+$: 397.158, found: 397.1577.

## (D) Gram-scale preparation of 3a and synthetic applications of 3a

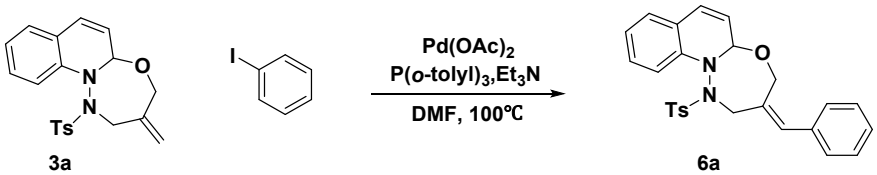
### a) Gram-scale preparation of 3a



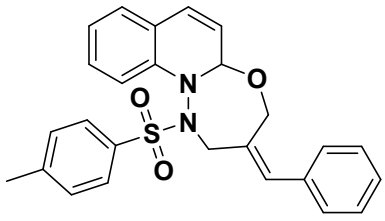

The dried sealed tube was charged with *N*-Iminoquinolinium Ylides **2a** (1.0 g, 2.7 mmol) and 2-(hydroxy tert-butyl) allylmethyl carbonate **1a** (1.0 g, 5.4 mmol), $Pd(OAc)_2$ (0.061 g, 10 mol%), BINAP (0.34 g, 20 mol%) and anhydrous THF (68 mL).

Then the reaction tube was evacuated and purged with argon three times. The solution was kept at 65 ℃ for 24 h. The mixture was extracted with DCM (30 mL×3), and the combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE/EA = 4/1, v/v) to give the desired product **3a** (0.81 g, 66% yield)**.**

**b) The coulping reaction of 3a**




The dry sealed tube was charged with **3a** (100.0 mg, 0.27 mmol), iodobenzene (343.0 mg, 0.30 mmol), $Pd(OAc)_2$ (6.0 mg, 0.027 mmol), P(*o*-tolyl)$_3$ (16.0 mg, 0.054 mmol) and triethylamine (77.0 mg, 0.76 mmol) in anhydrous DMF (4 mL). Then the reaction tube was evacuated and purged with argon three times. And the reaction was heated at 100° C. for 24 h. The mixture was extracted with DCM (3×30 mL), and the combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by preparative TLC (PE/EA = 4/1, v/v) to give **6a** as white solid (54.3 mg, 45%)

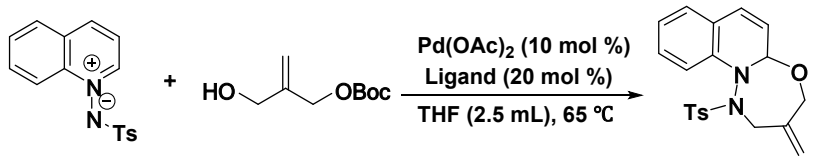


**(6a)** 3-benzylidene-1-tosyl-1,2,3,4-tetrahydro-5aH-[1,3,4] oxadiazepino[3,2-a]quinoline

**6a** was obtained as white solid (54.3 mg, yield 45%): melting point 132.8−134.7 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 6.9 Hz, 1H), 7.19-7.09 (m, 6H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 11.2 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 9.5 Hz, 1H), 5.81 (dd, *J* = 9.5, 5.4 Hz, 1H), 4.99 (d, *J* = 14.5 Hz, 1H), 4.91 (d, *J* = 5.4 Hz, 1H), 4.59 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.45 (d, *J* = 15.5 Hz, 1H), 4.38 (d, *J* = 14.5 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.99, 140.23, 135.89, 135.73, 135.42, 131.67, 129.24, 129.00, 128.76, 128.29, 127.63, 127.47, 127.43, 121.30, 120.49, 119.85, 112.52, 87.07, 69.88, 55.68, 21.47. HRMS (ESI) m/z: calculated for $C_{26}H_{25}N_2O_{3S}^+$ $(M+H)^+$: 445.158, found: 445.1577.

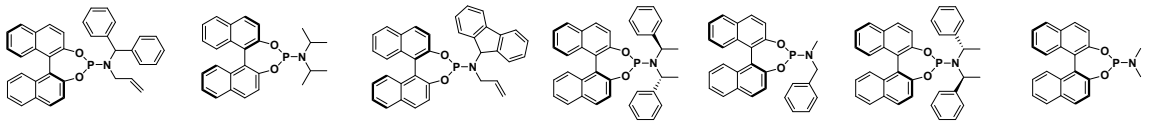
## (E) Screening Asymmetric Reaction Condition

### a) Table S1. Optimization of asymmetric reaction conditions[a].




2a 1a 3a

| entry | catalyst | ligand | solvent | T(°C) | yield (%)[b] | e.e.[d] |
|---|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | L1 | THF | 65 | 20 | - |
| 2 | $Pd(OAc)_2$ | L2 | THF | 65 | 28 | - |
| 3 | $Pd(OAc)_2$ | L3 | THF | 65 | 18 | - |
| 4 | $Pd(OAc)_2$ | L4 | THF | 65 | trace | - |
| 5 | $Pd(OAc)_2$ | L5 | THF | 65 | trace | - |
| 6 | $Pd(OAc)_2$ | L6 | THF | 65 | 18 | - |
| 7 | $Pd(OAc)_2$ | L7 | THF | 65 | trace | - |
| 8 | $Pd(OAc)_2$ | (*R*)-BINAP | THF | 65 | 83[c] | 8.5 |
| 9 | $Pd(OAc)_2$ | (*S*)-BINAP | $CH_2Cl_2$ | 65 | 76[c] | 6.1 |



L1 L2 L3 L4 L5 L6 L7

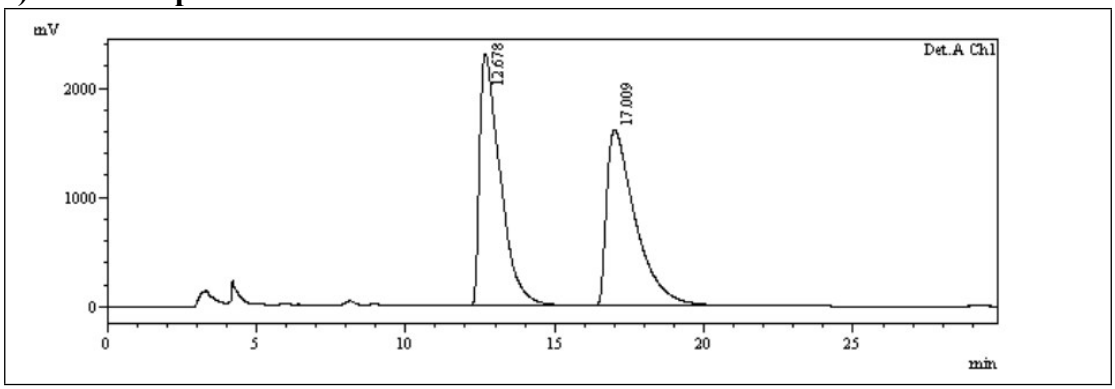
[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.10 mmol), Ligand (20 mol%), $Pd(OAc)_2$ (10 mol%) and 2.5 mL THF in Ar atmosphere for 24h. [b]Determined by $^1H$ NMR yields using $(CH_3)_2SO_2$ as an internal standard. [c]Isolated yields. [d]Determined by HPLC analysis using a chiral stationary phase.

### b) HPLC acquisition parameters :

Chiral column: CHIRALCEL ® OD-H, Wave length: 214 nm,

Mobile phase: *i*PrOH : Hex = 30 : 70, Flow rate: 0.6 mL/min, Temperature: 25 ℃.

### c) HPLC Spectra of racemic 3a:

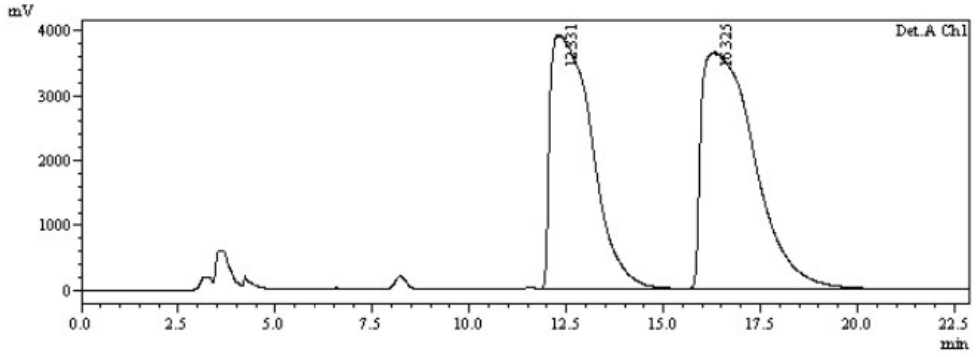


PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.678 | 111337629 | 2300933 | 50.707 | 58.840 |
| 2 | 17.009 | 108234777 | 1609590 | 49.293 | 41.160 |
| Total | | 219572406 | 3910523 | 100.000 | 100.000 |

## HPLC Spectra of 3a (Ligand: (*R*)-BINAP)

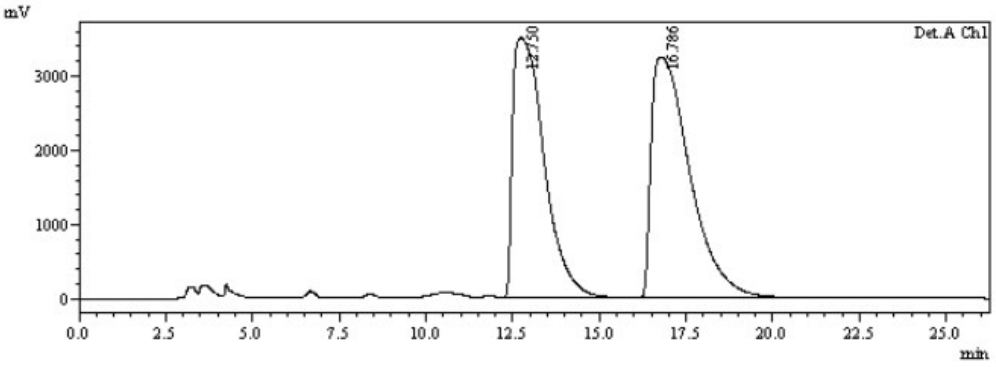



PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.331 | 289942438 | 3901235 | 45.739 | 51.734 |
| 2 | 16.325 | 343968032 | 3639705 | 54.261 | 48.266 |
| Total | | 633910470 | 7540940 | 100.000 | 100.000 |

## HPLC Spectra of 3a (Ligand: (*S*)-BINAP)



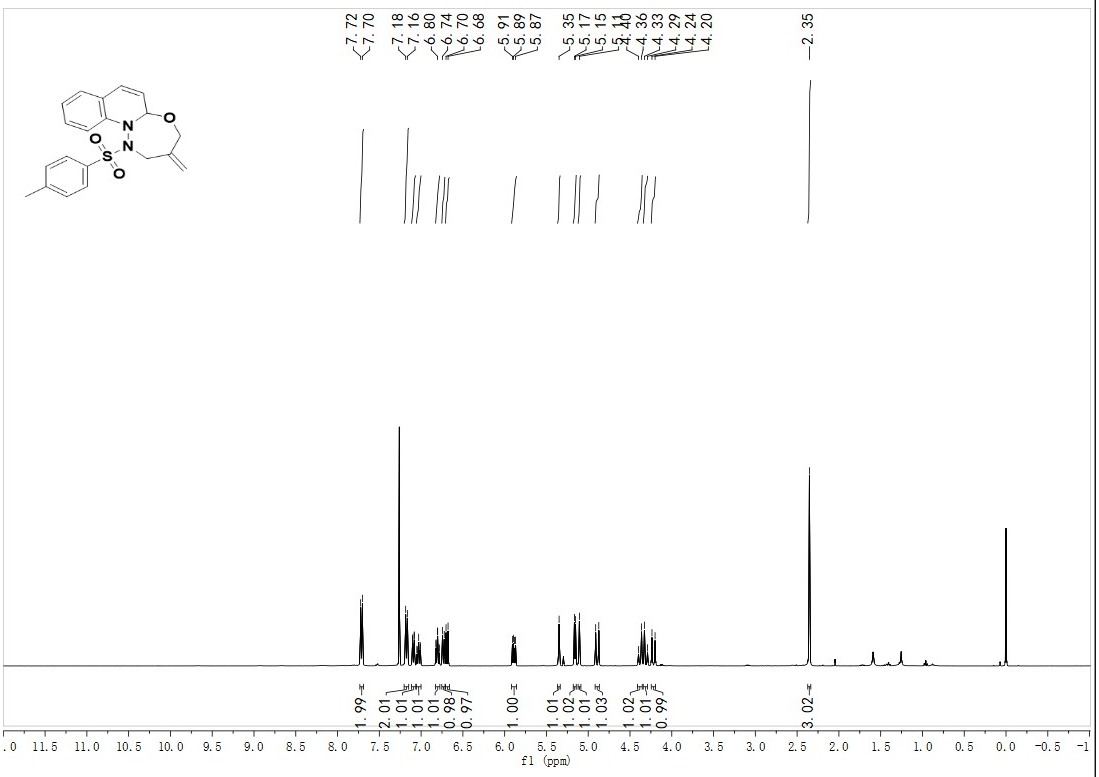

PeakTable

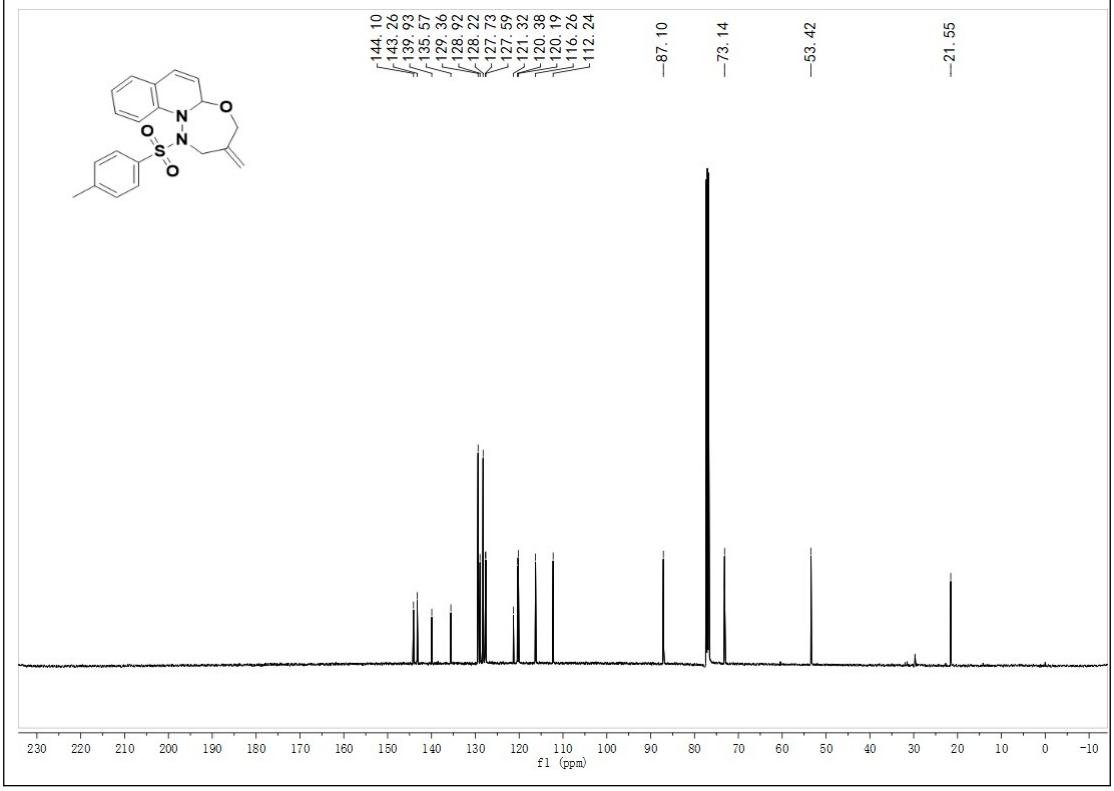
Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.750 | 222592890 | 3512210 | 46.936 | 51.983 |
| 2 | 16.786 | 251654710 | 3244257 | 53.064 | 48.017 |
| Total | | 474247600 | 6756467 | 100.000 | 100.000 |

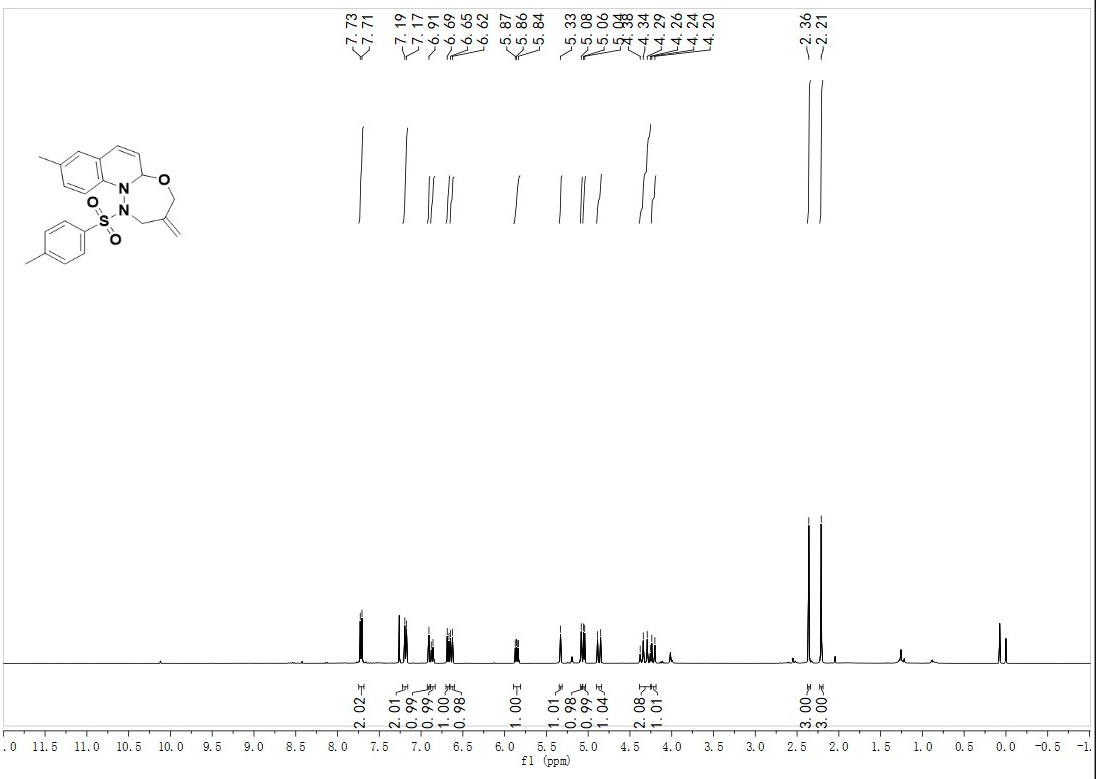
## (F) Copies of $^{1}H$ NMR and $^{13}C$ NMR Spectra for the Products

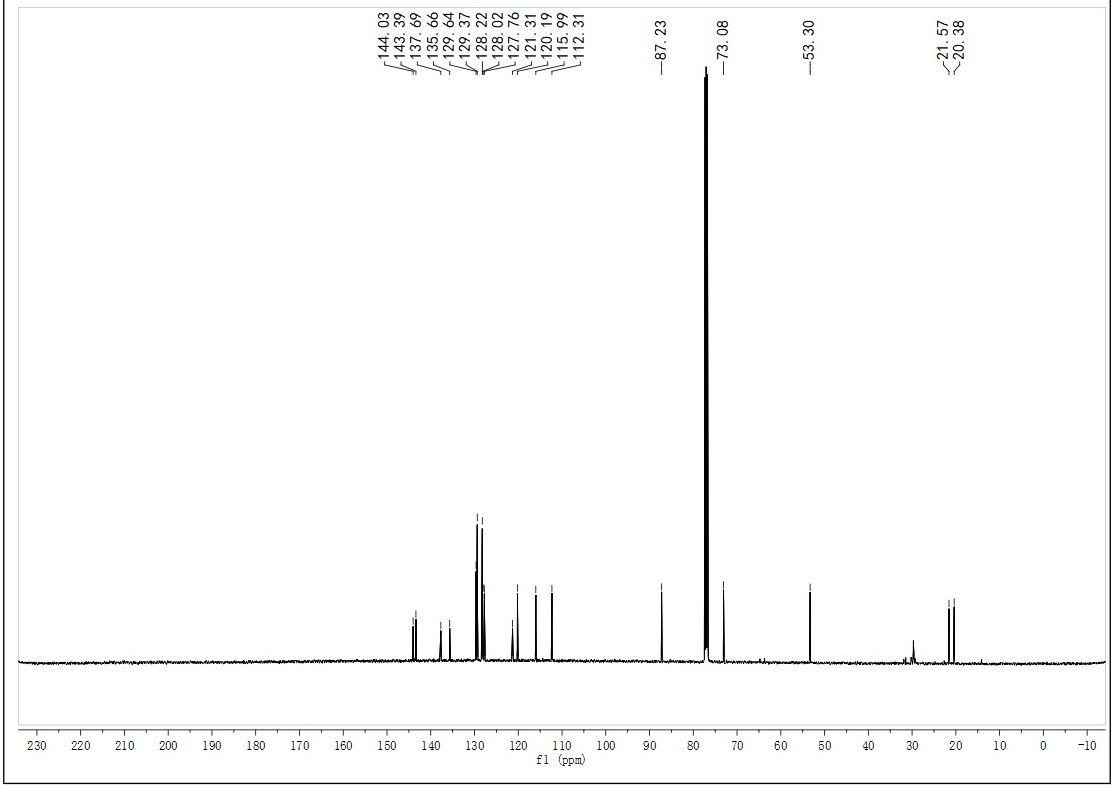
(3a) 3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino [3,2-*a*]quinoline



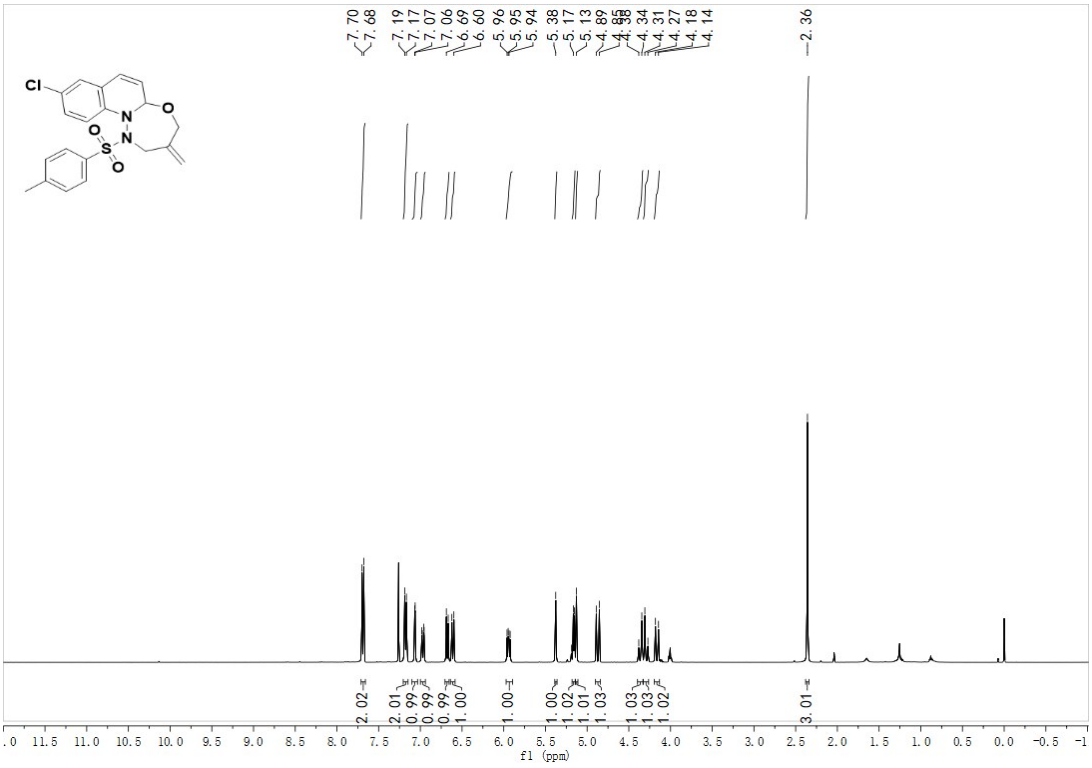



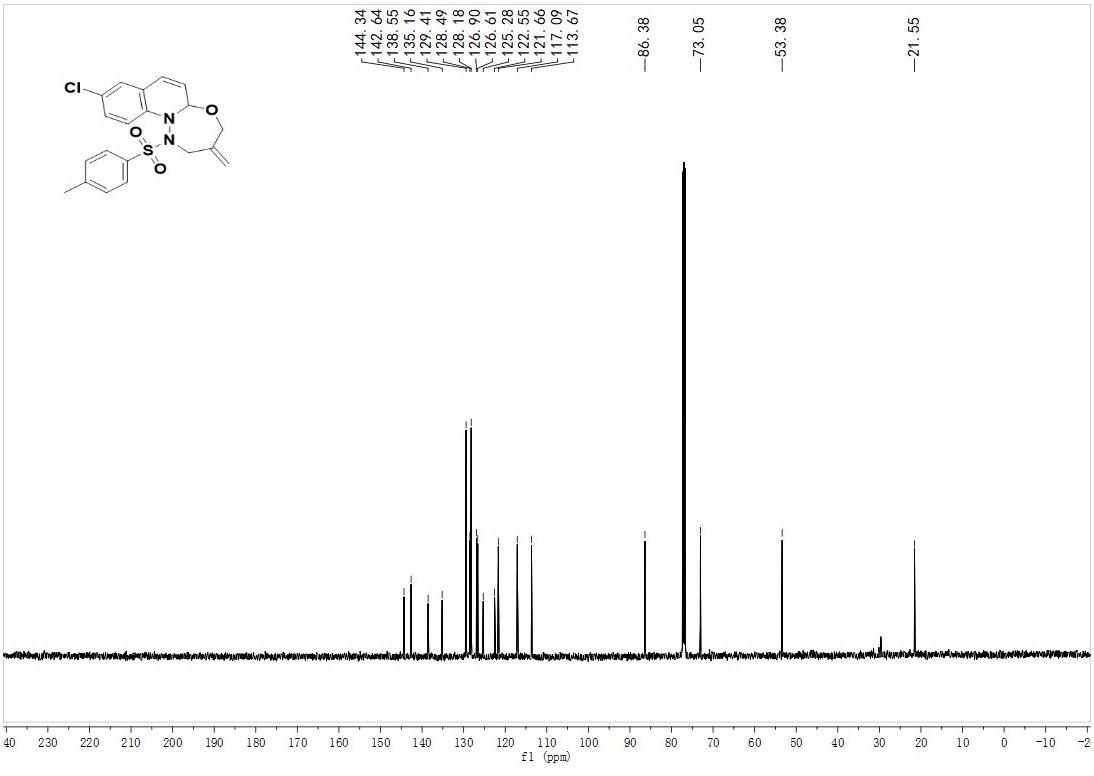
(3b)9-methyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinoline



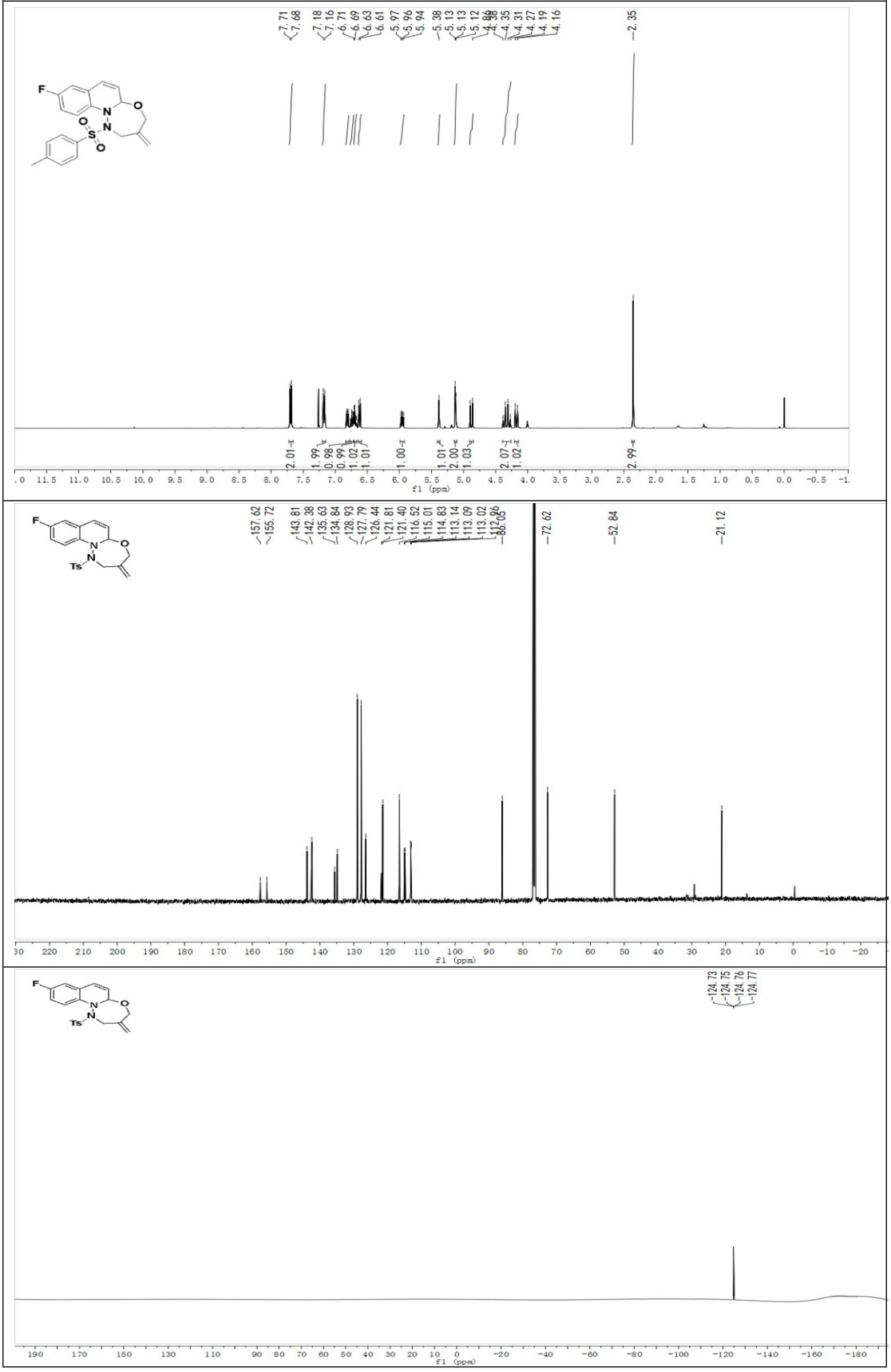



(3c) 9-chloro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinoline

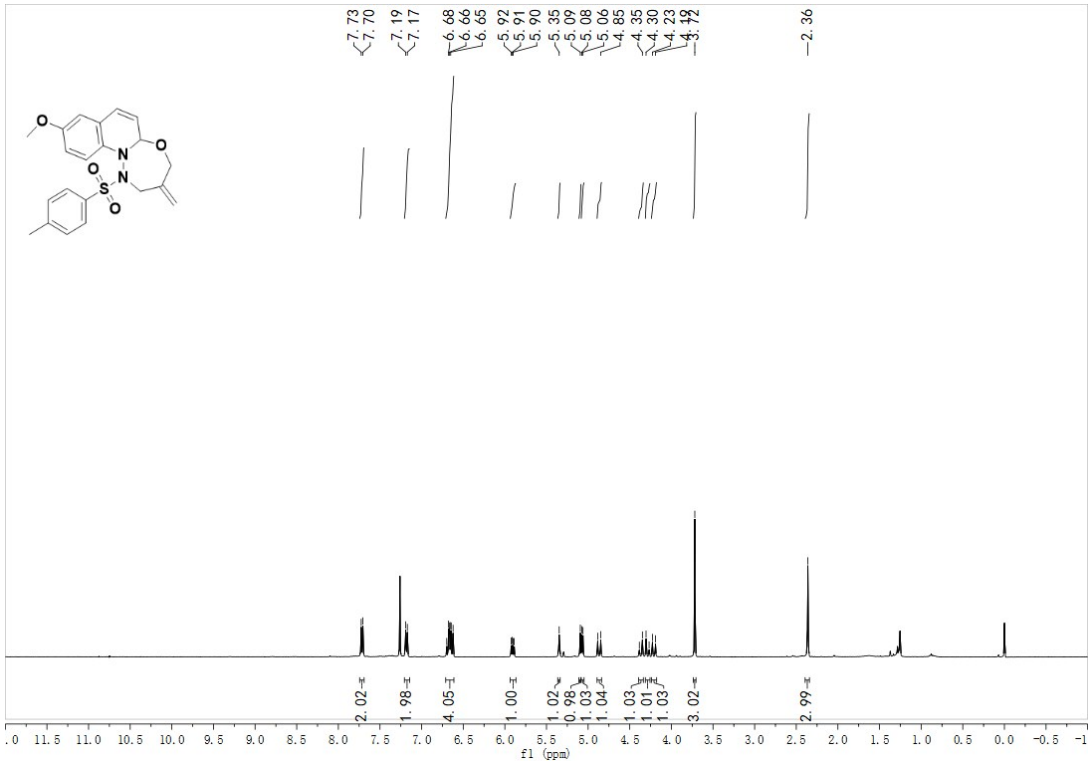


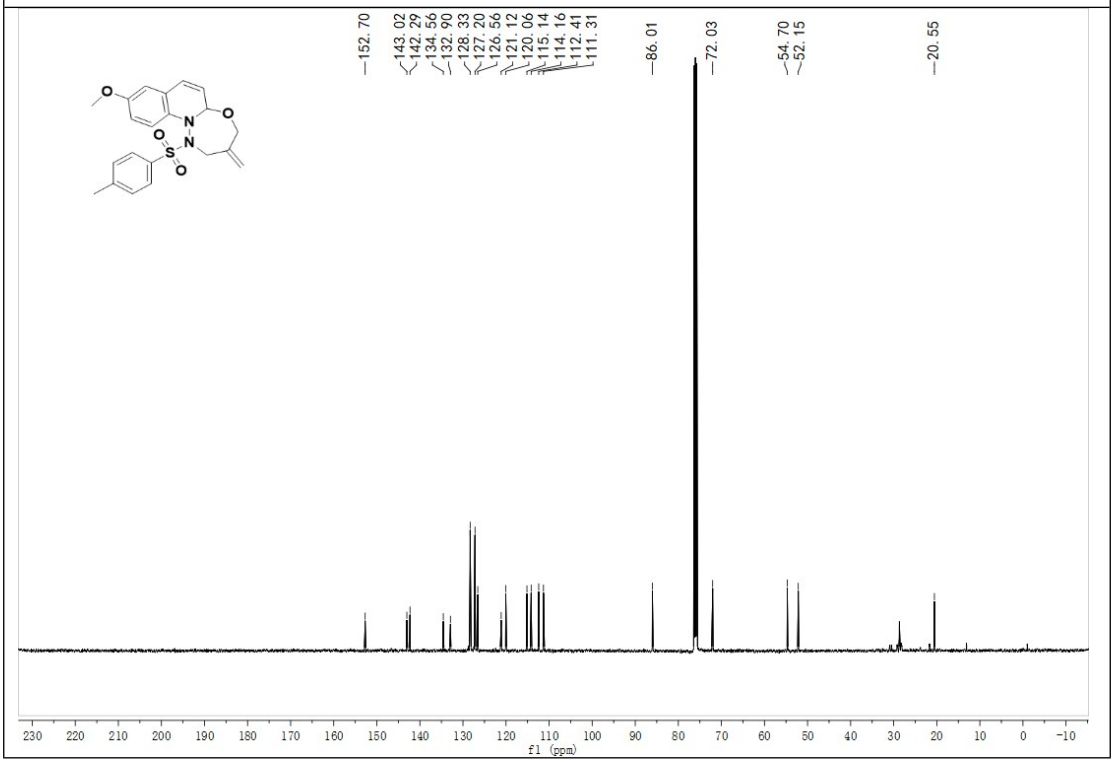



(3d) 9-fluoro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinoline

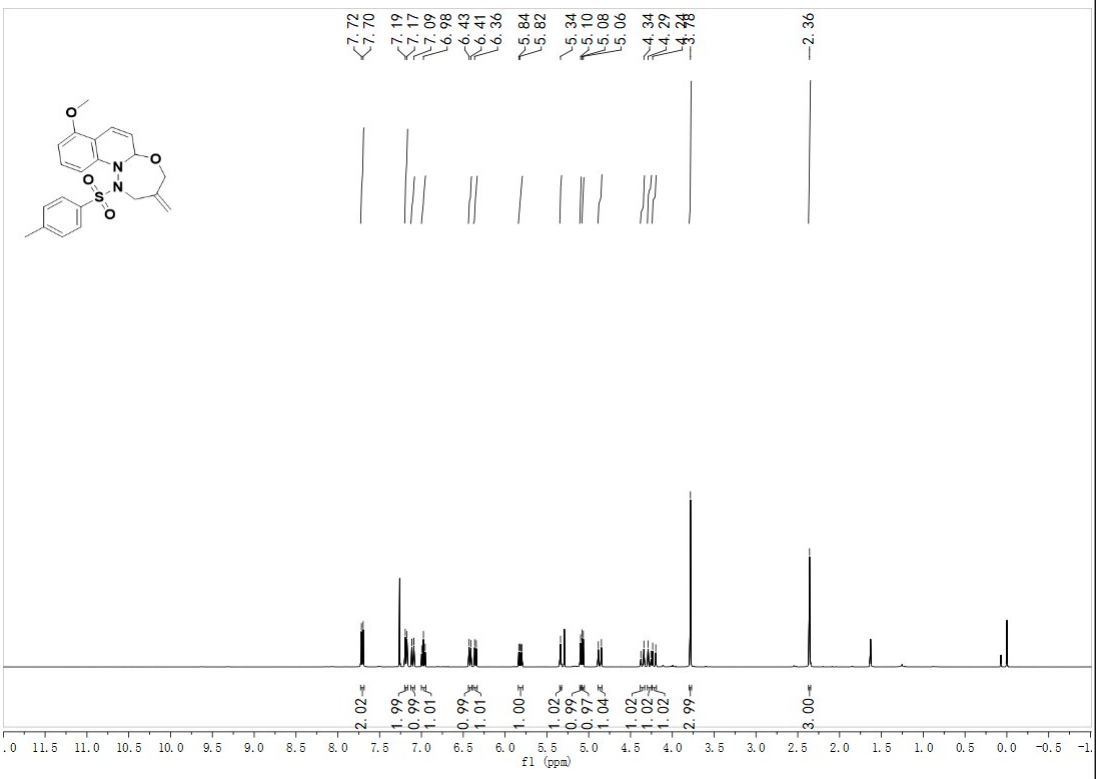


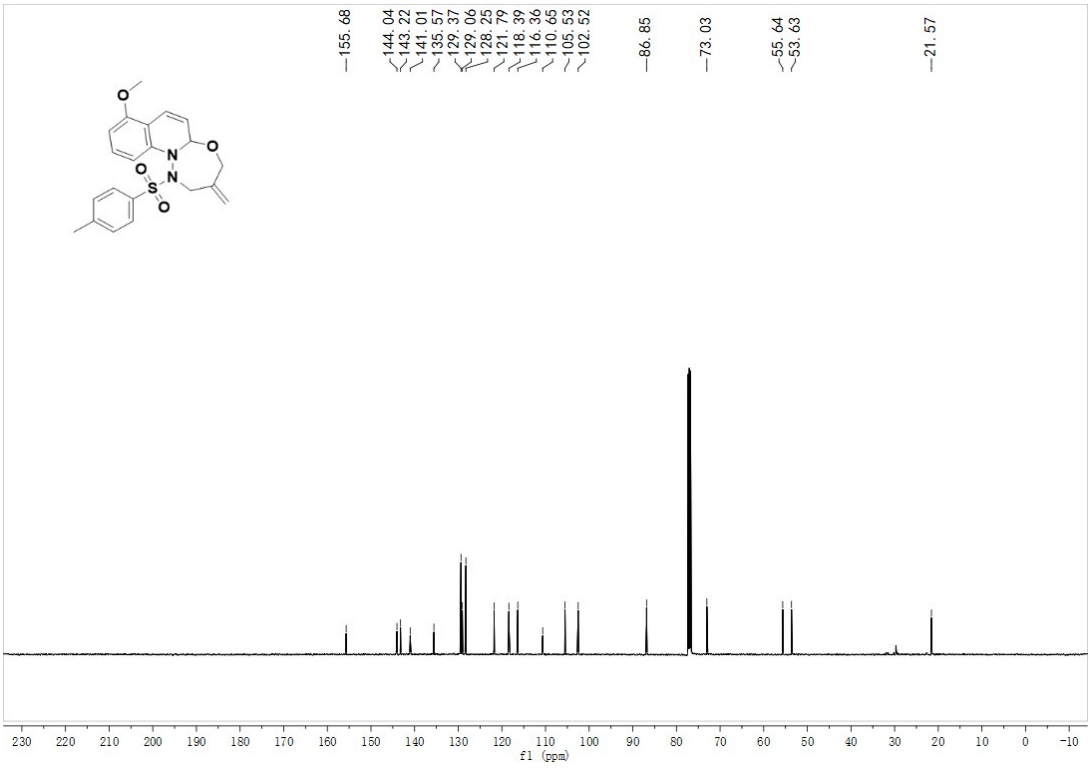
(3e) 9-methoxy-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*[1,3,4]oxadiazepino [3,2-*a*] quinoline



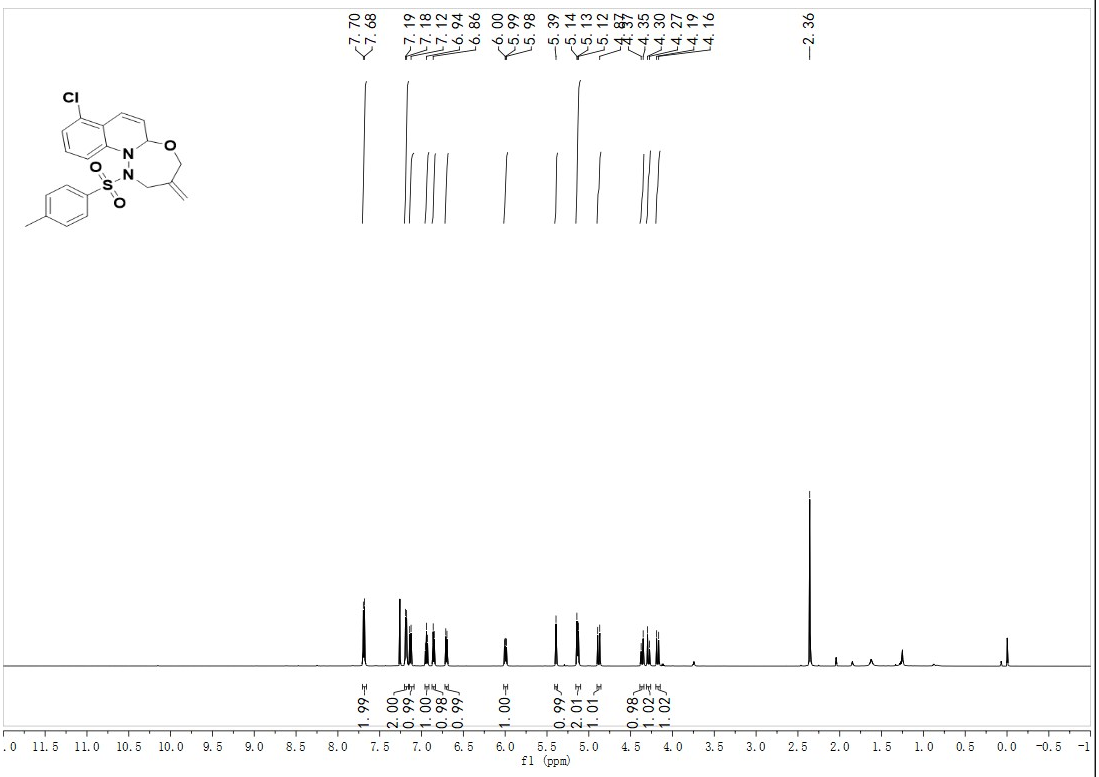



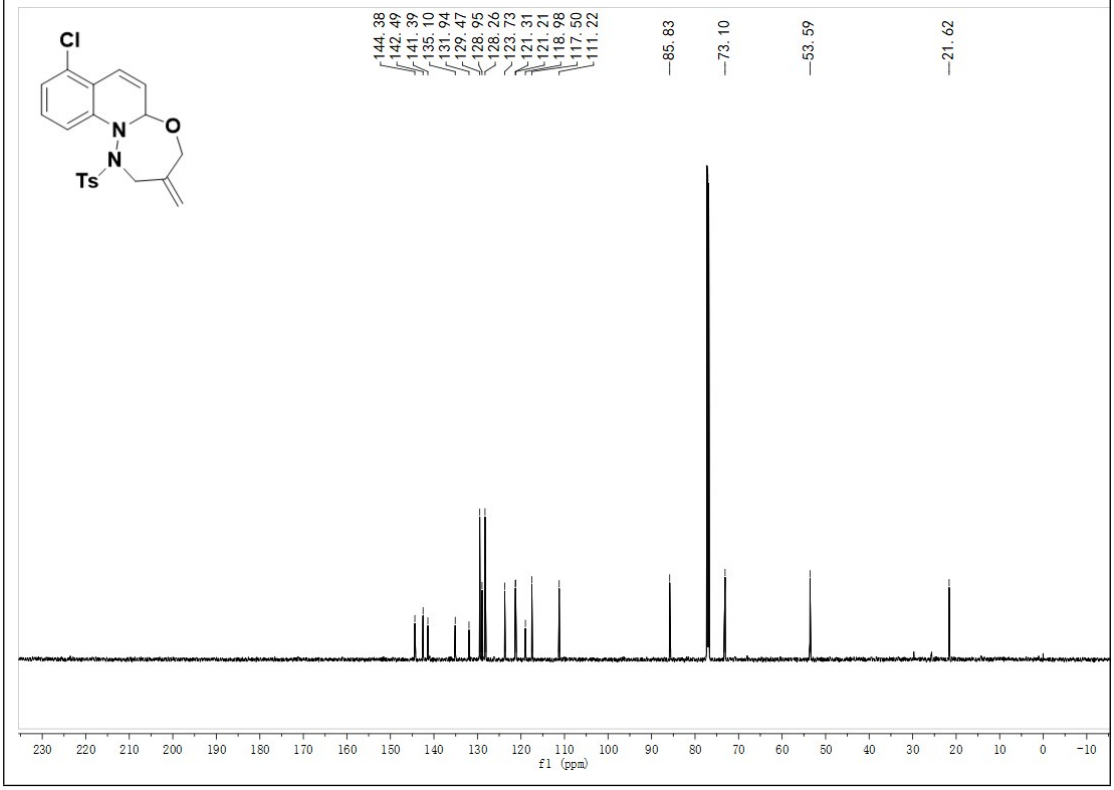
(3f) 8-methoxy-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino [3,2-*a*]quinoline



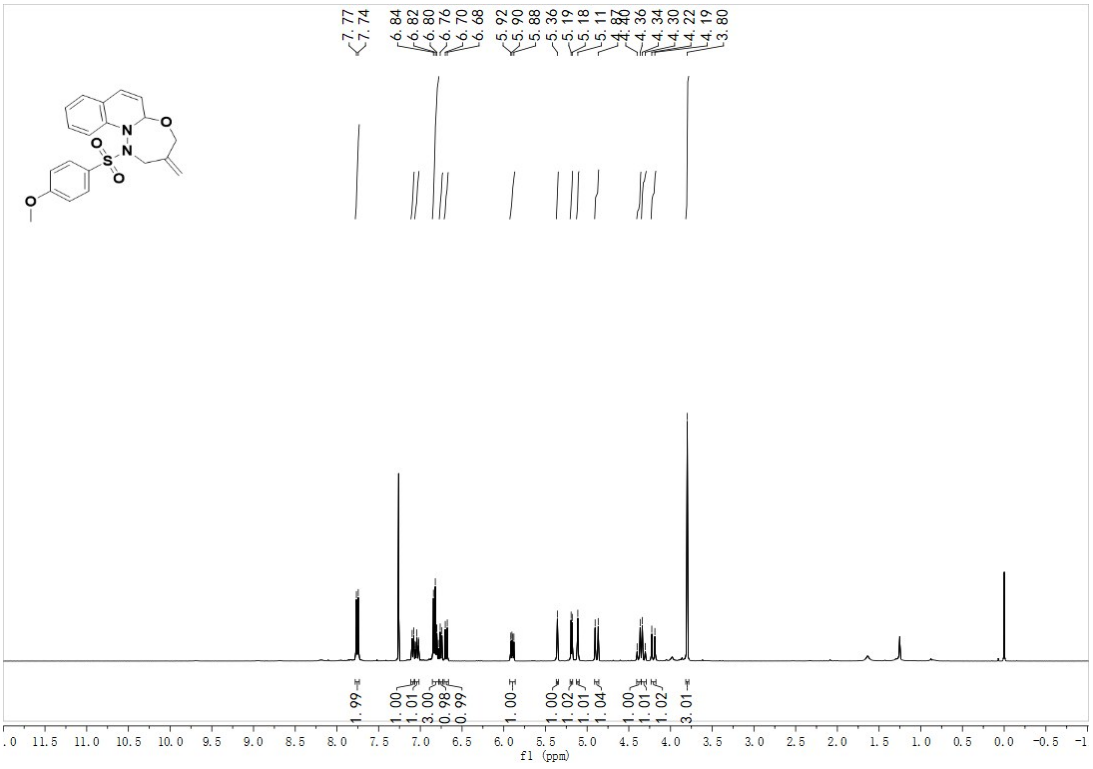



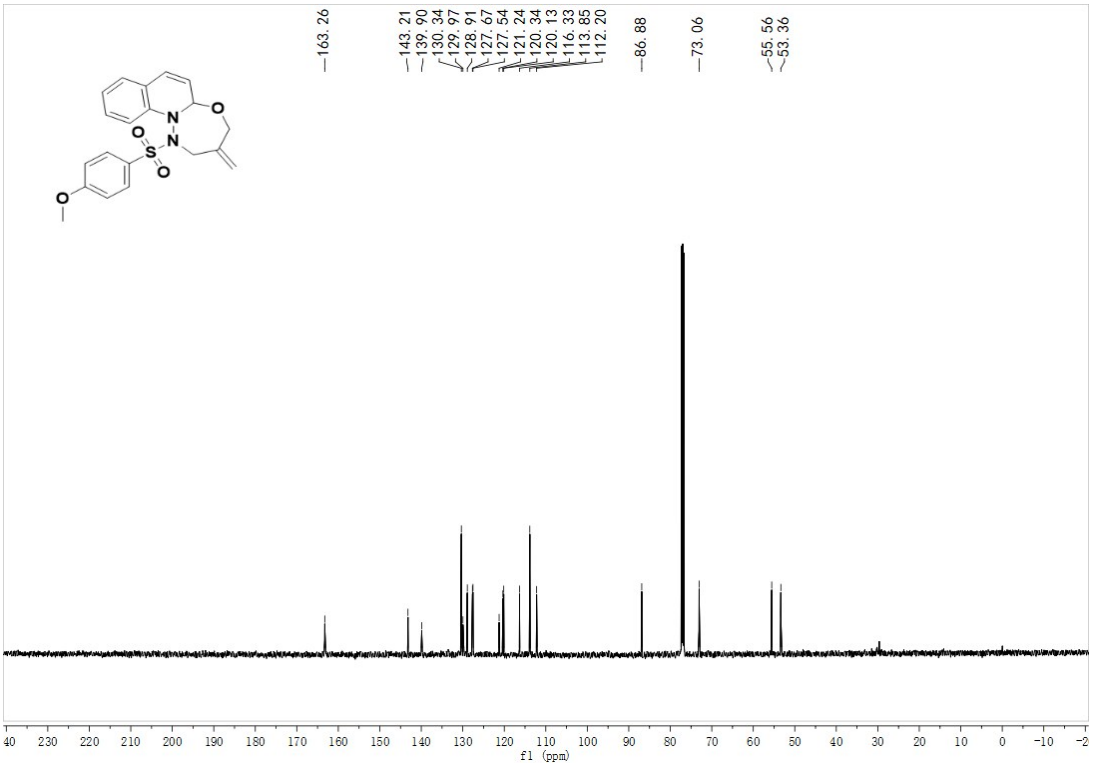
(3g) 8-chloro-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinoline



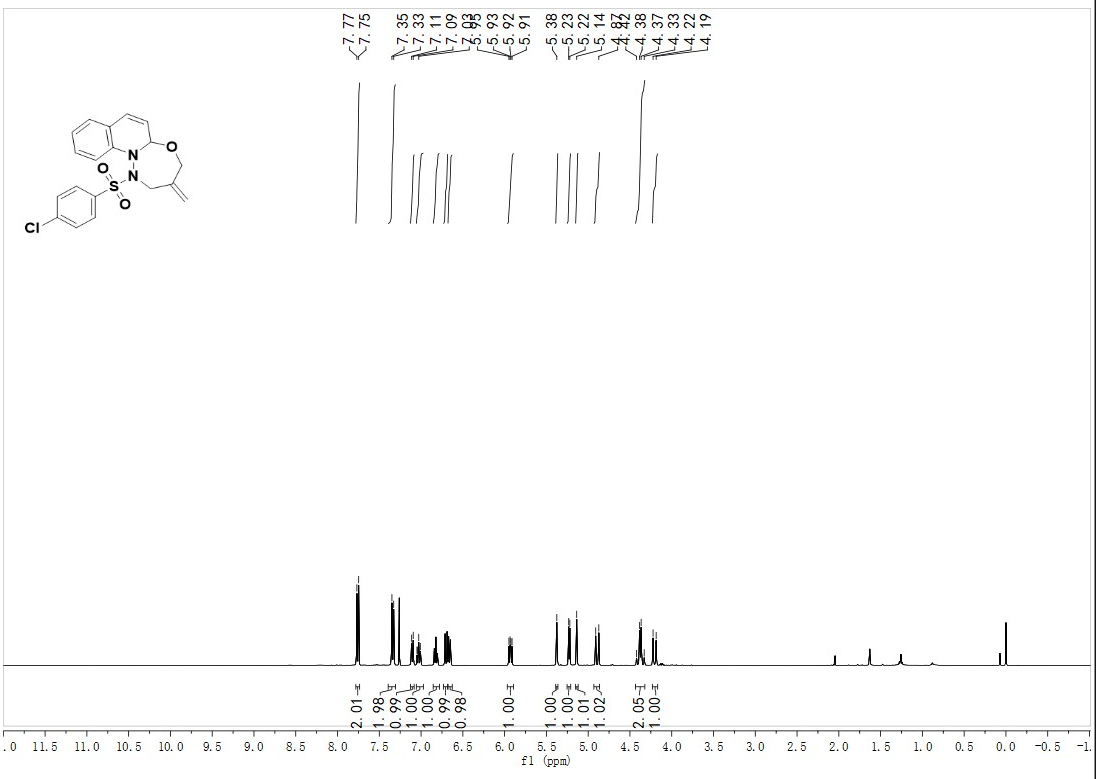



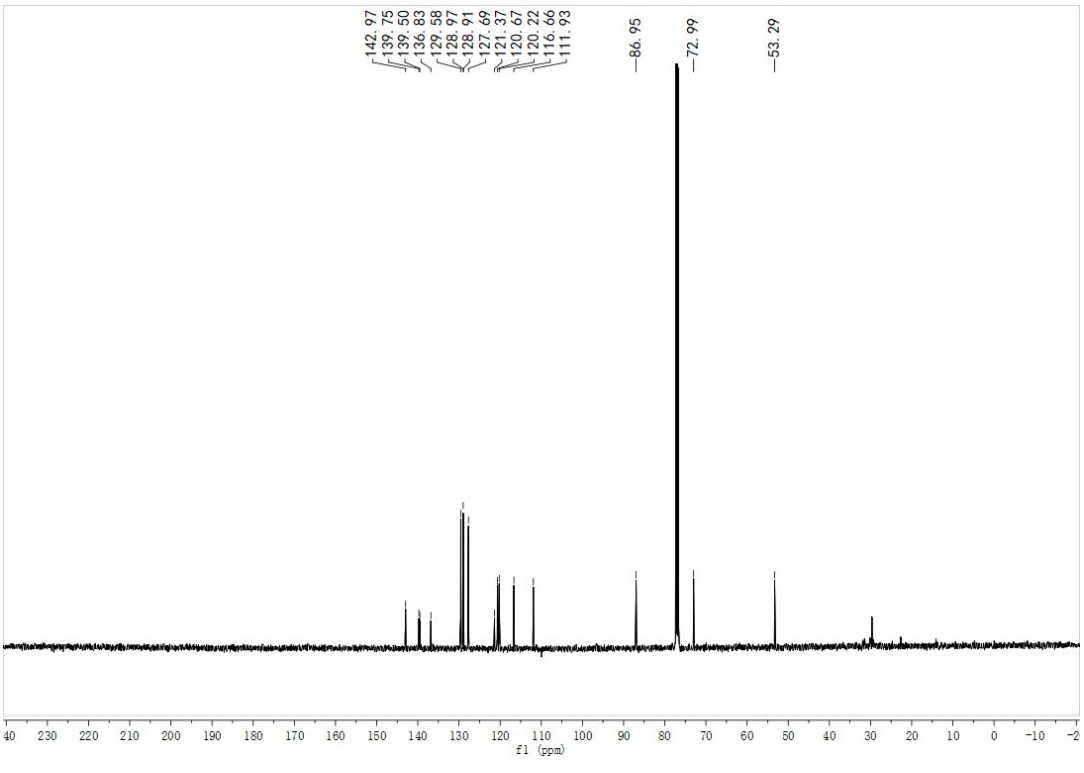
(3h) 1-((4-methoxyphenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4]-oxadiazepino [3,2-*a*]quinoline



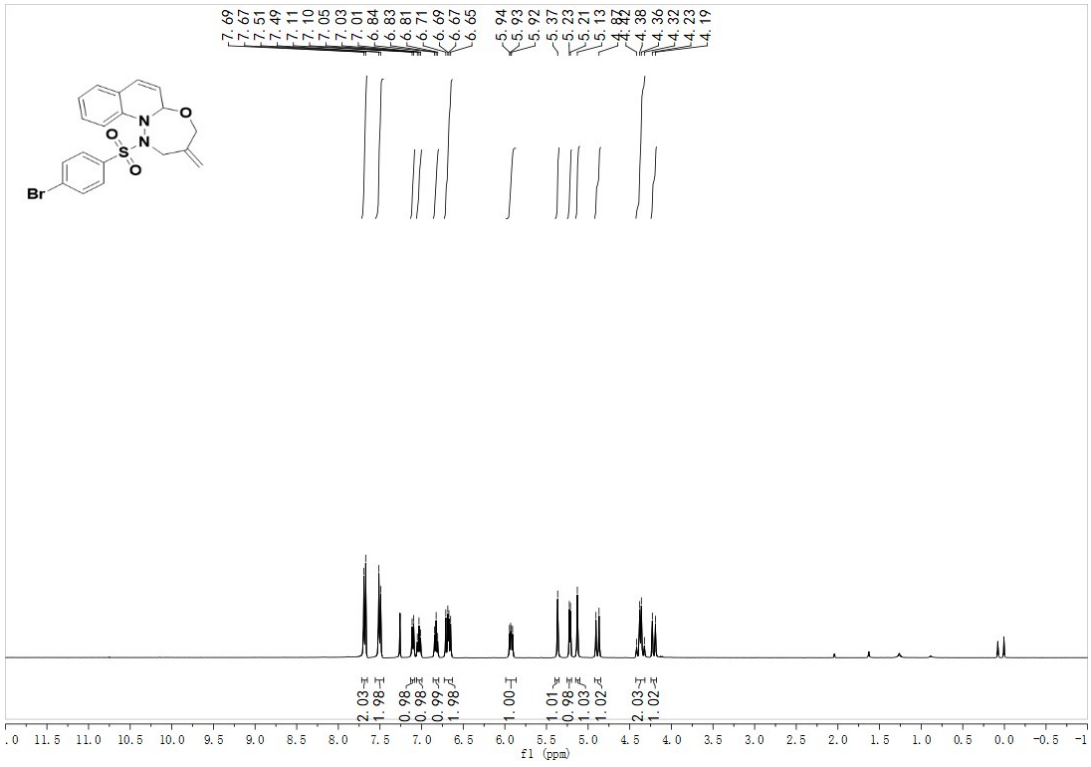



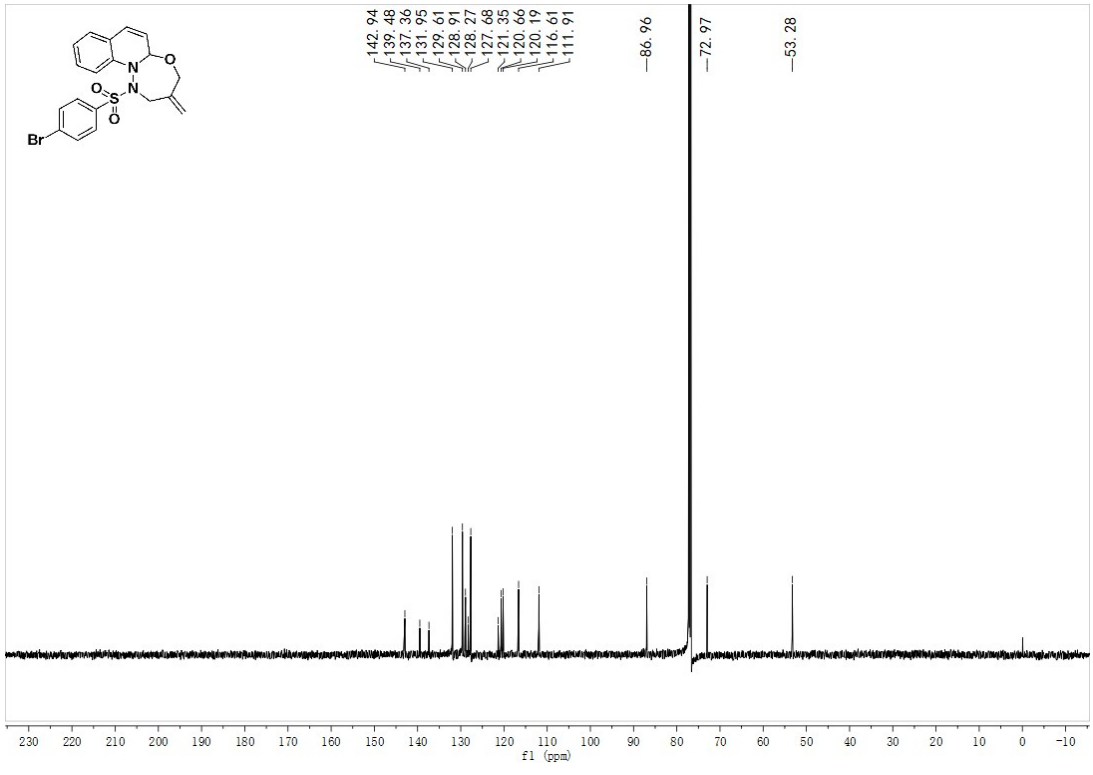
(3i) 1-((4-chlorophenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4]-oxadiazepino [3,2-*a*]quinoline



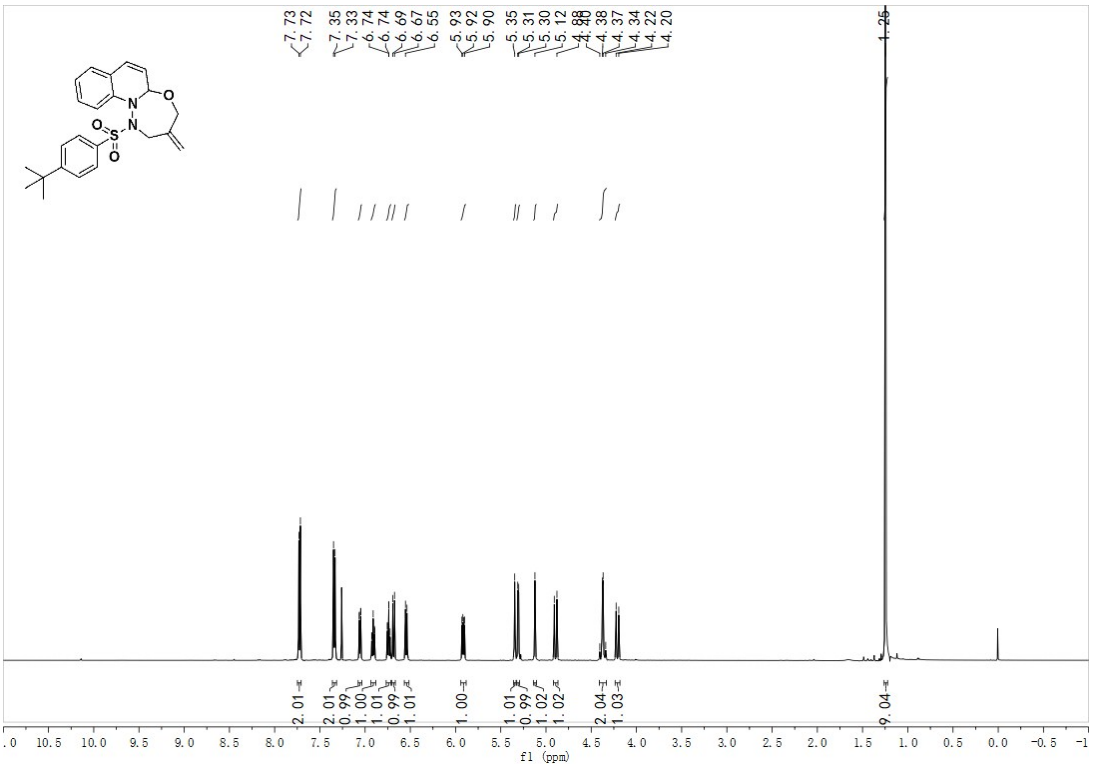



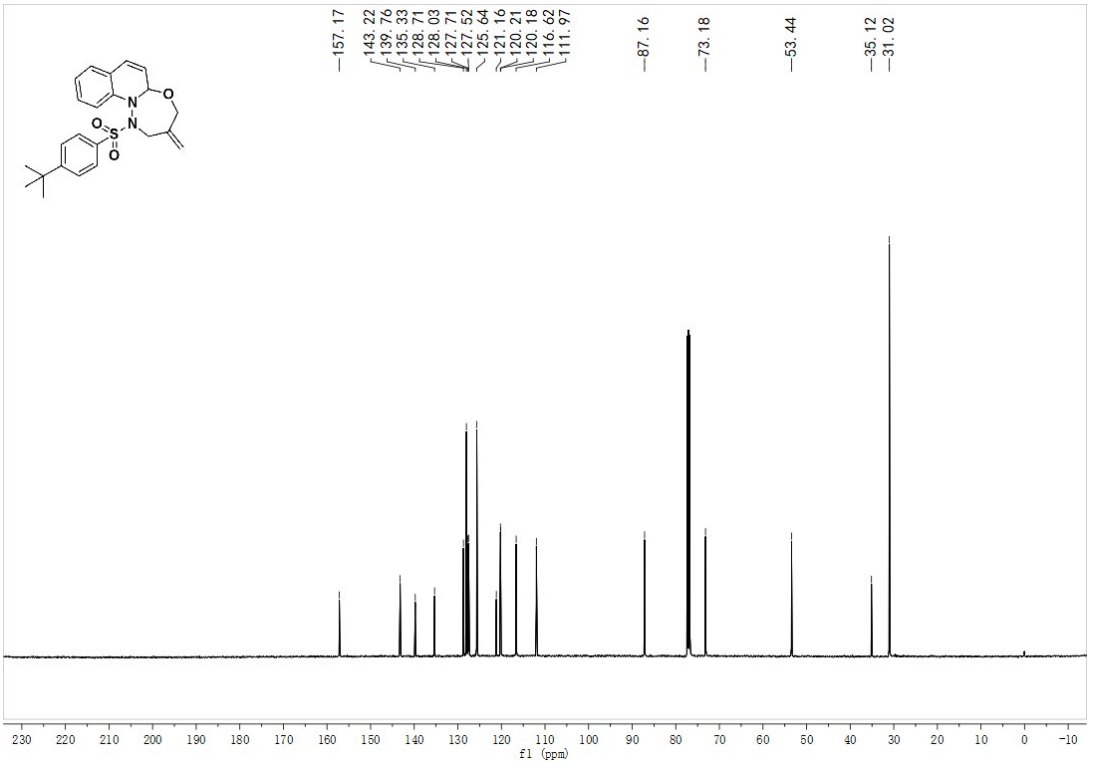
(3j)1-((4-bromophenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*]quinoline



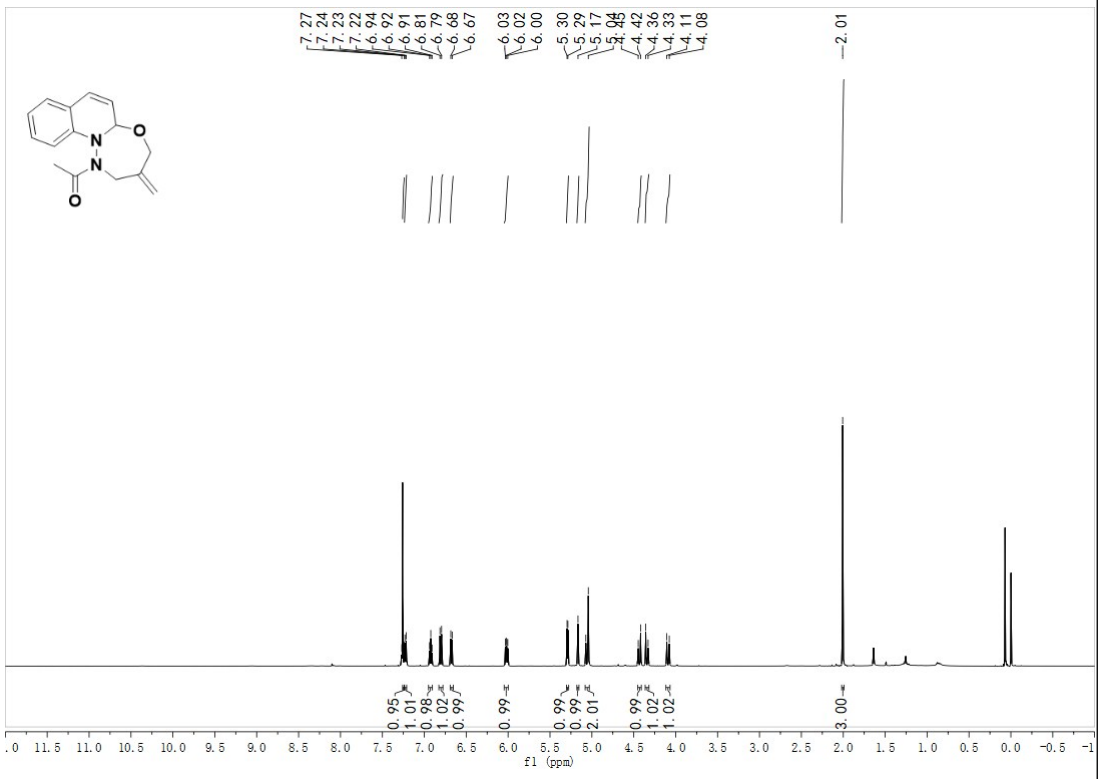



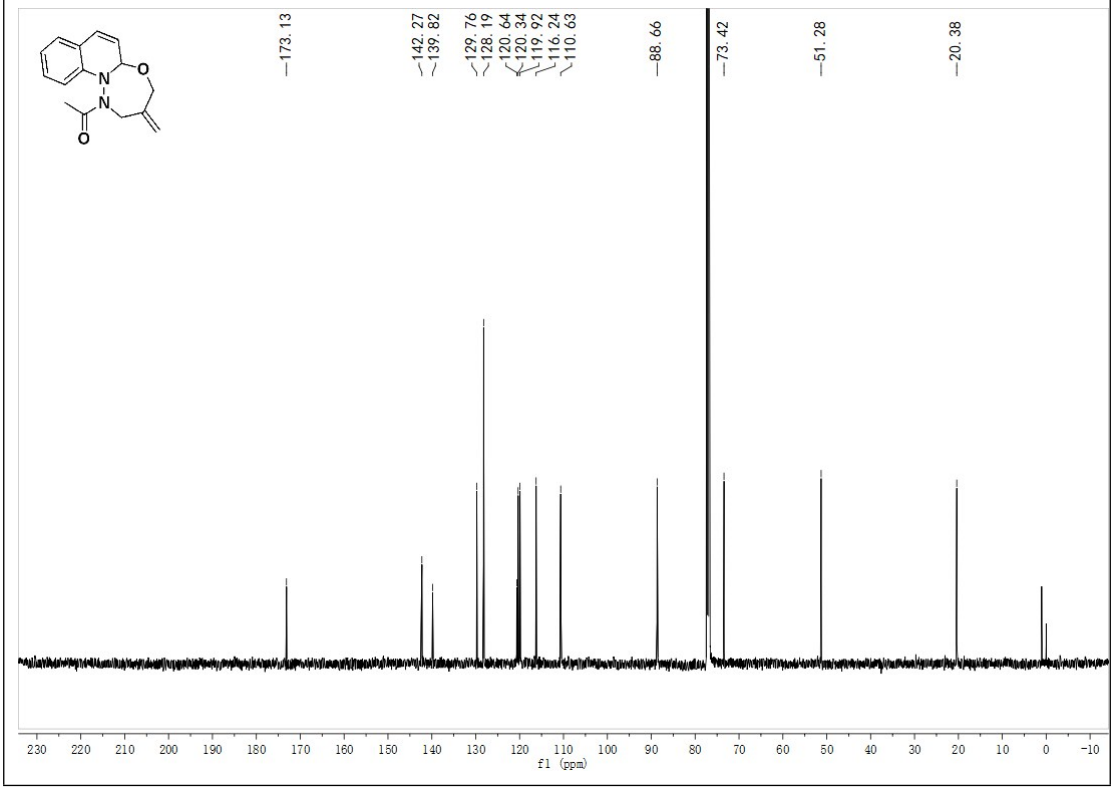
(3k) 1-((4-(tert-butyl)phenyl)sulfonyl)-3-methylene-1,2,3,4-tetrahydro-5a*H*-[1,3,4] oxadiazepino [3,2-*a*]quinoline



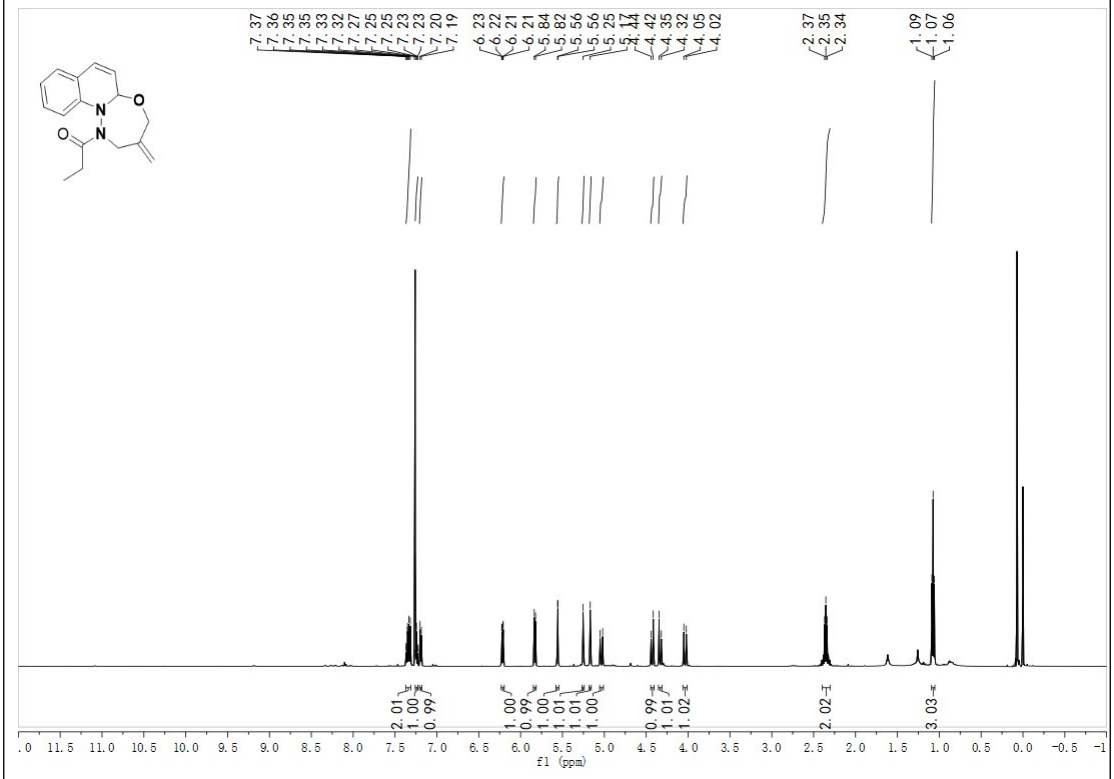



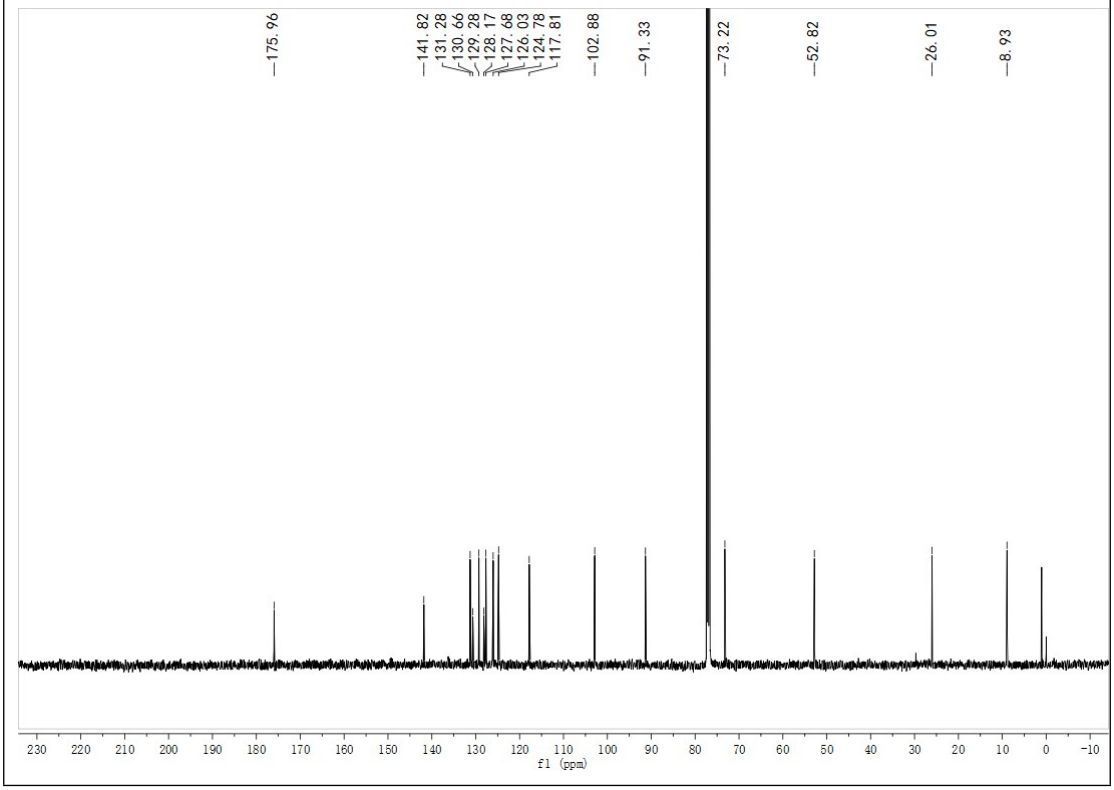
(3l) 1-(3-methylene-3,4-dihydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*]quinolin-1(2H)-yl) ethan-1-one



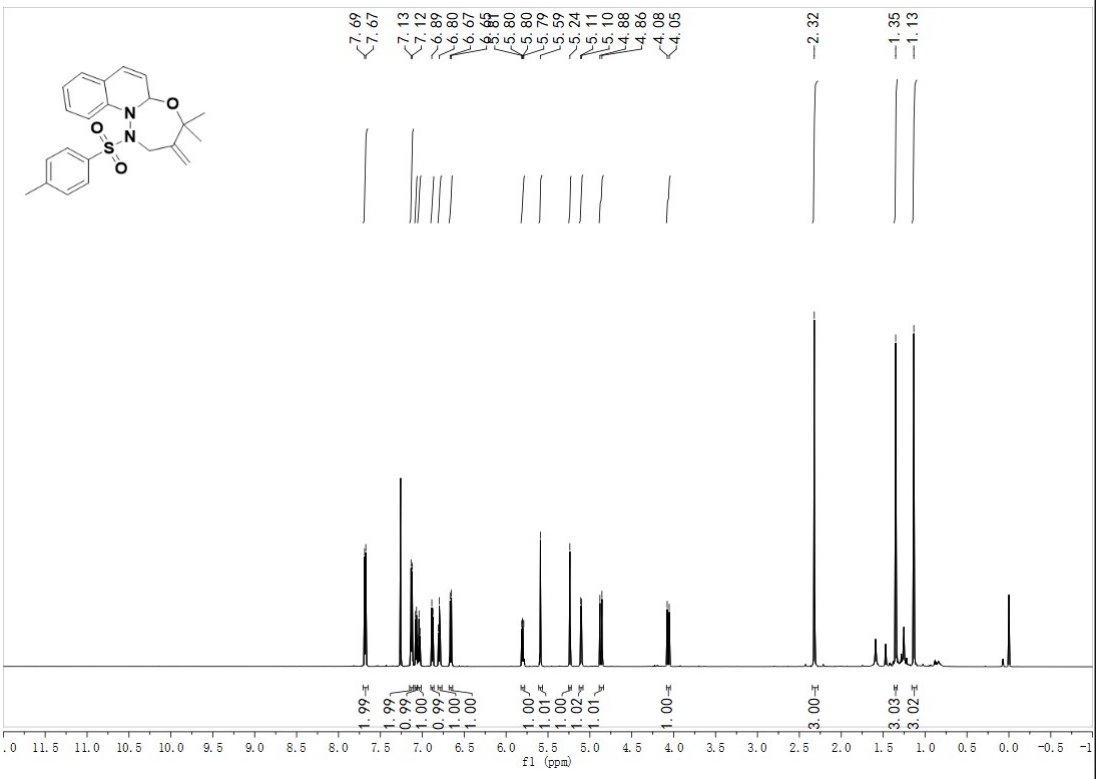



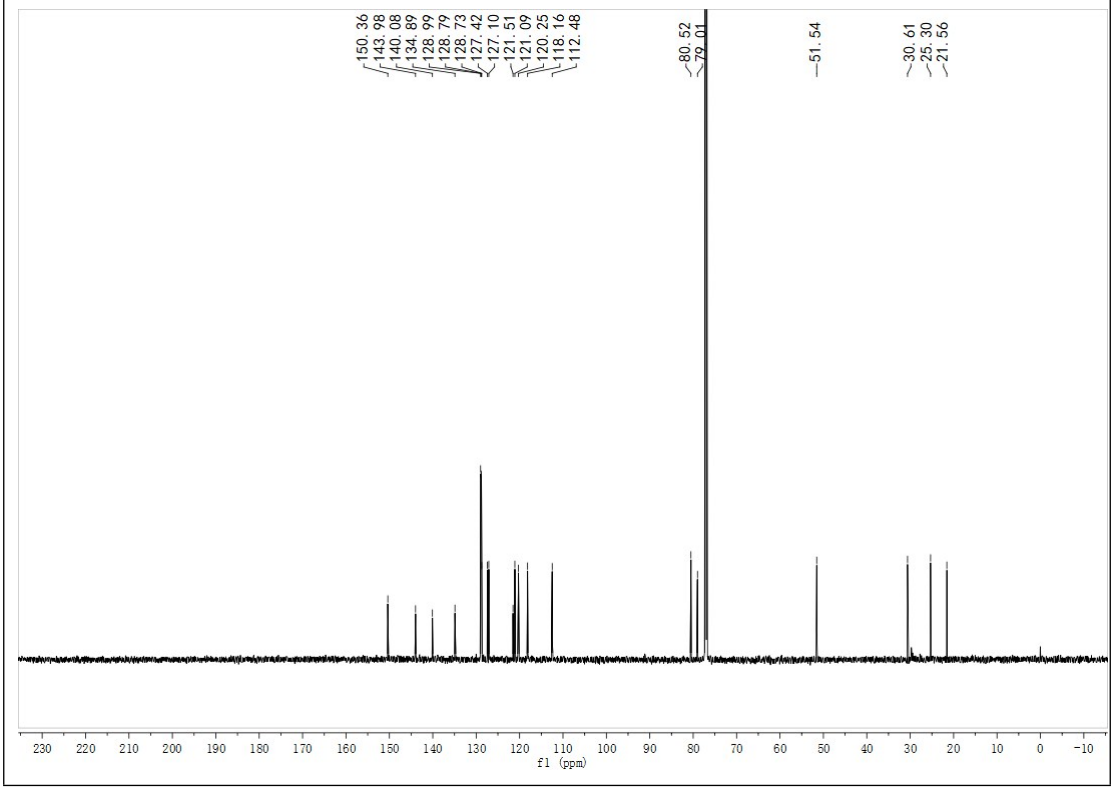
(3m) 1-(3-methylene-3,4-dihydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*]quinolin-1(2H)-yl) propan-1-one



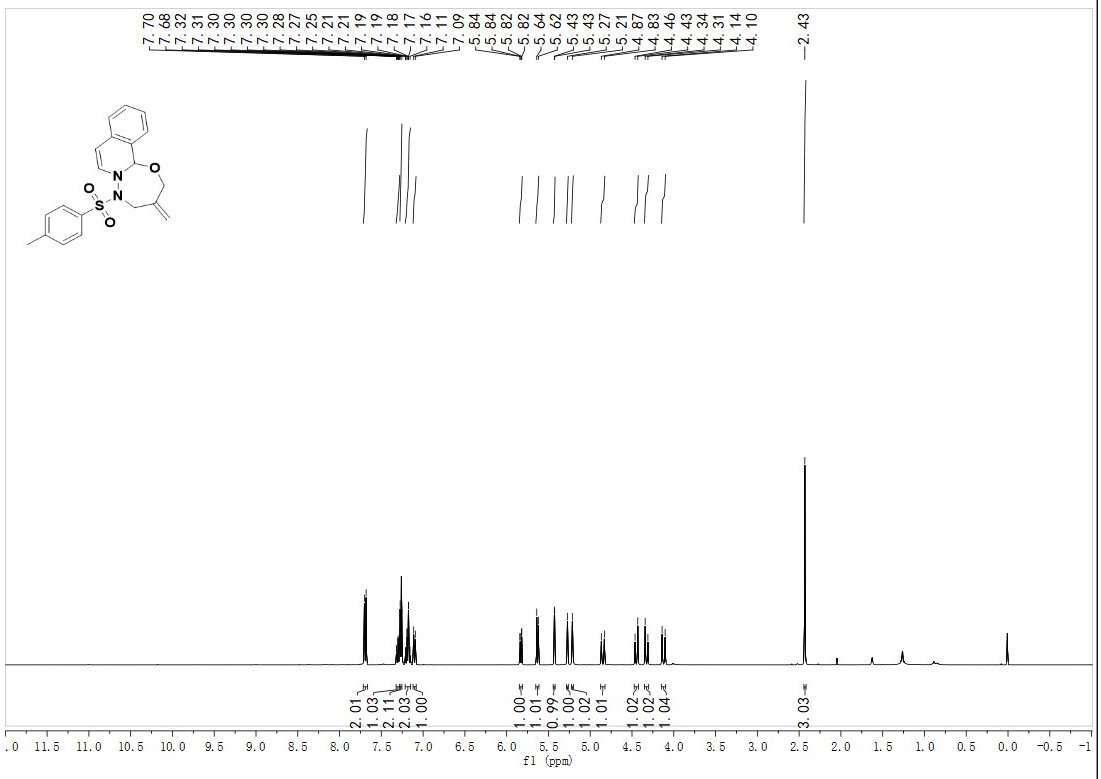



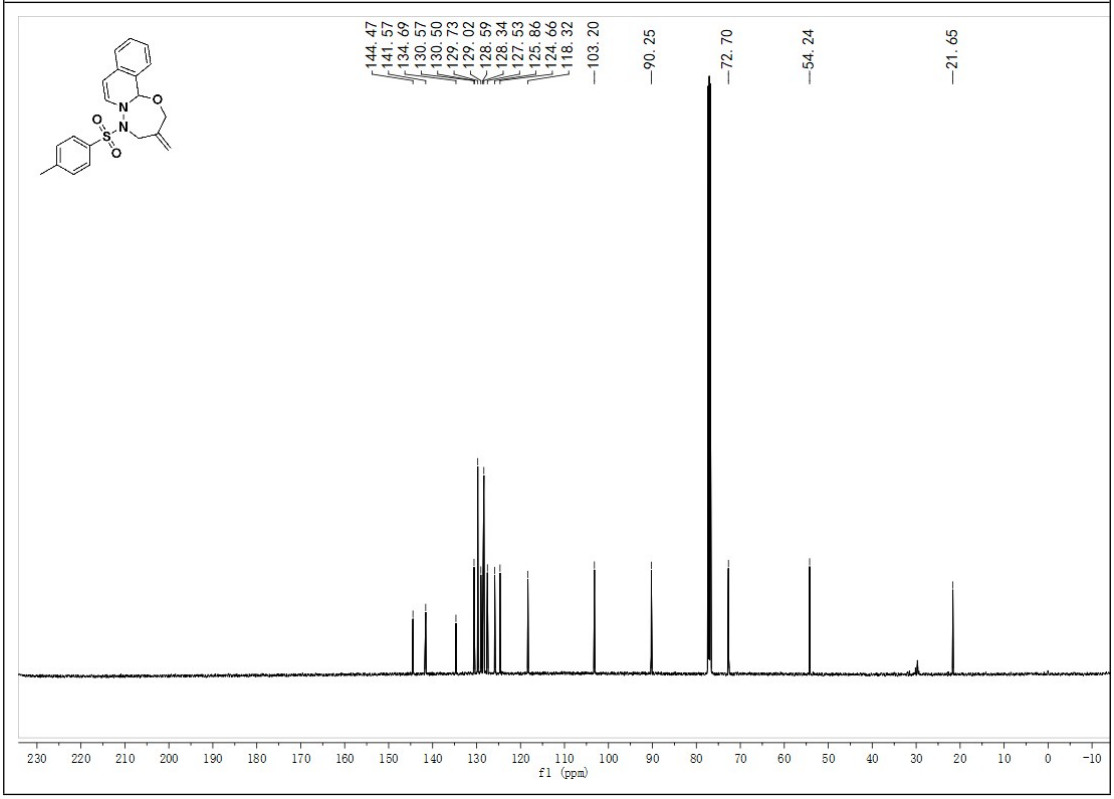
(3n) 4,4-dimethyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5a*H*- [1,3,4] oxadiazepino [3,2-*a*] quinoline



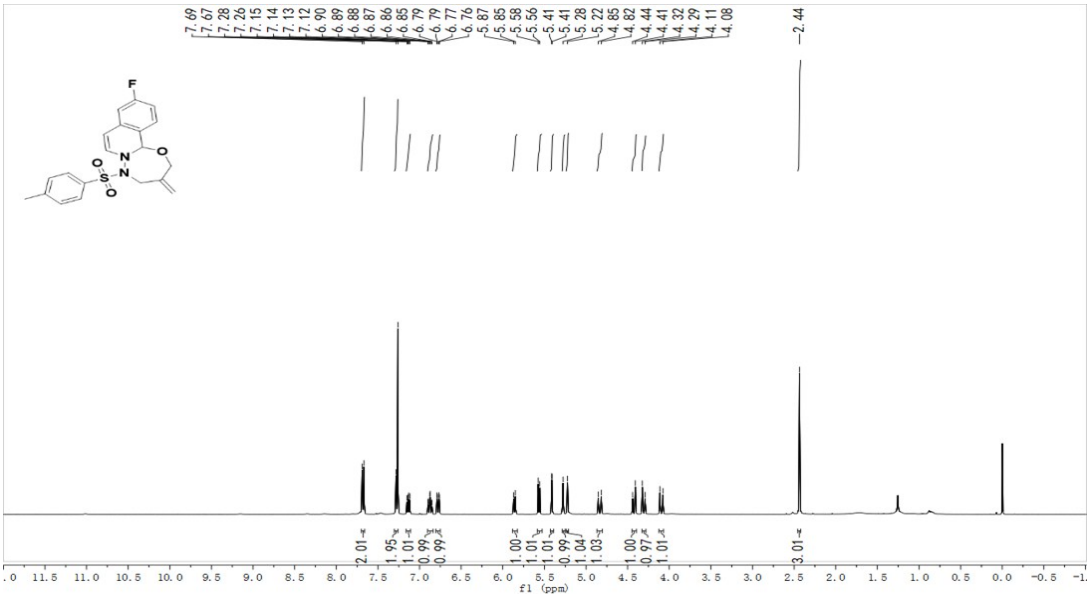



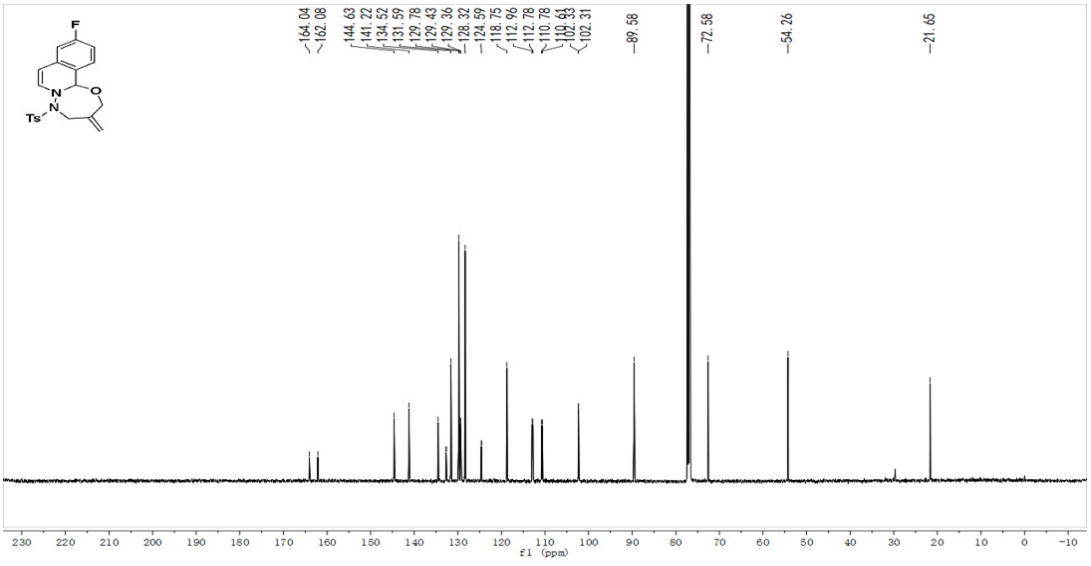
(5a) 3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinoline

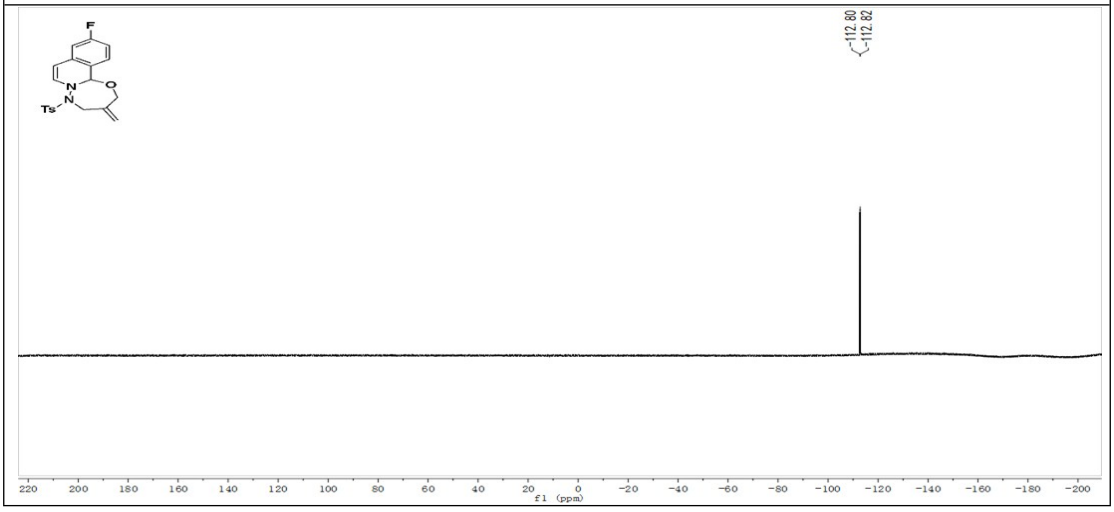


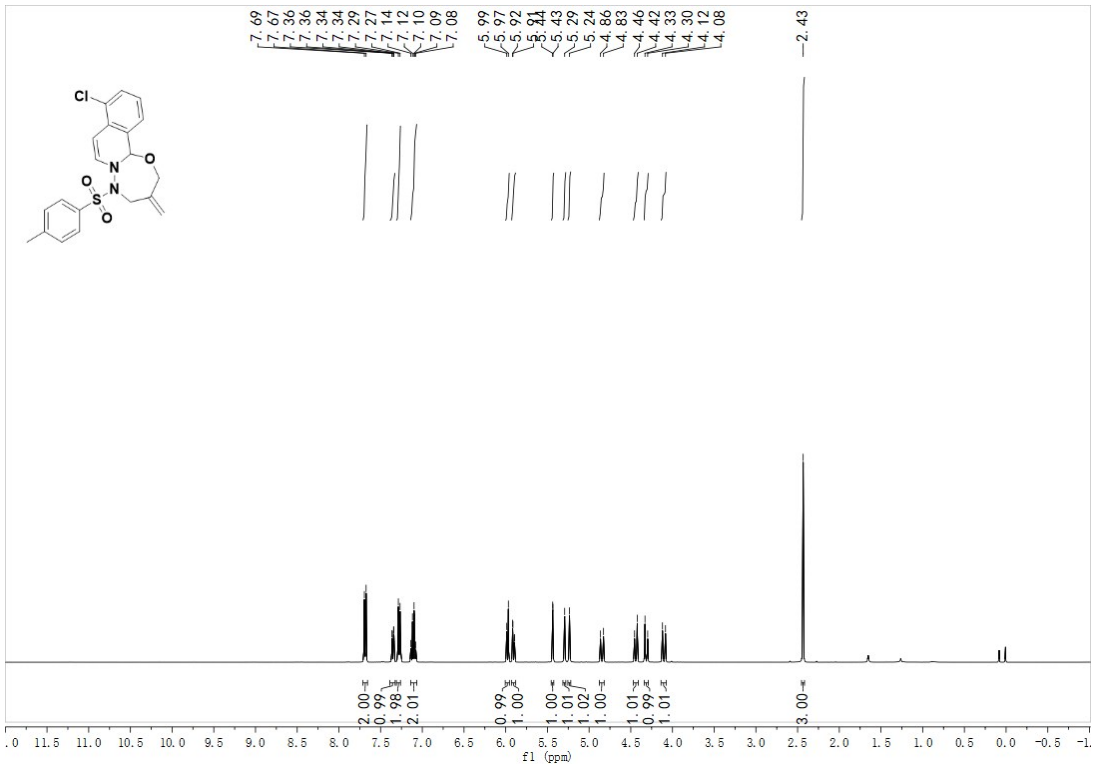
(5b) 10-fluoro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino-[2,3-*a*]isoquinoline

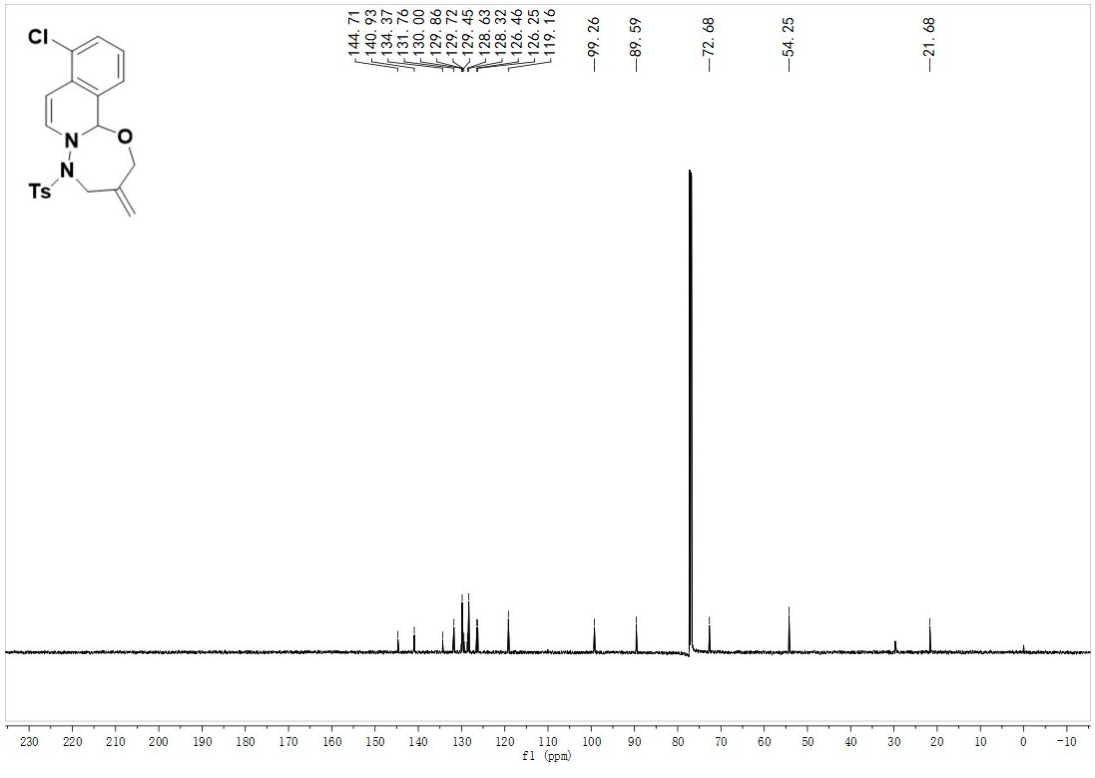


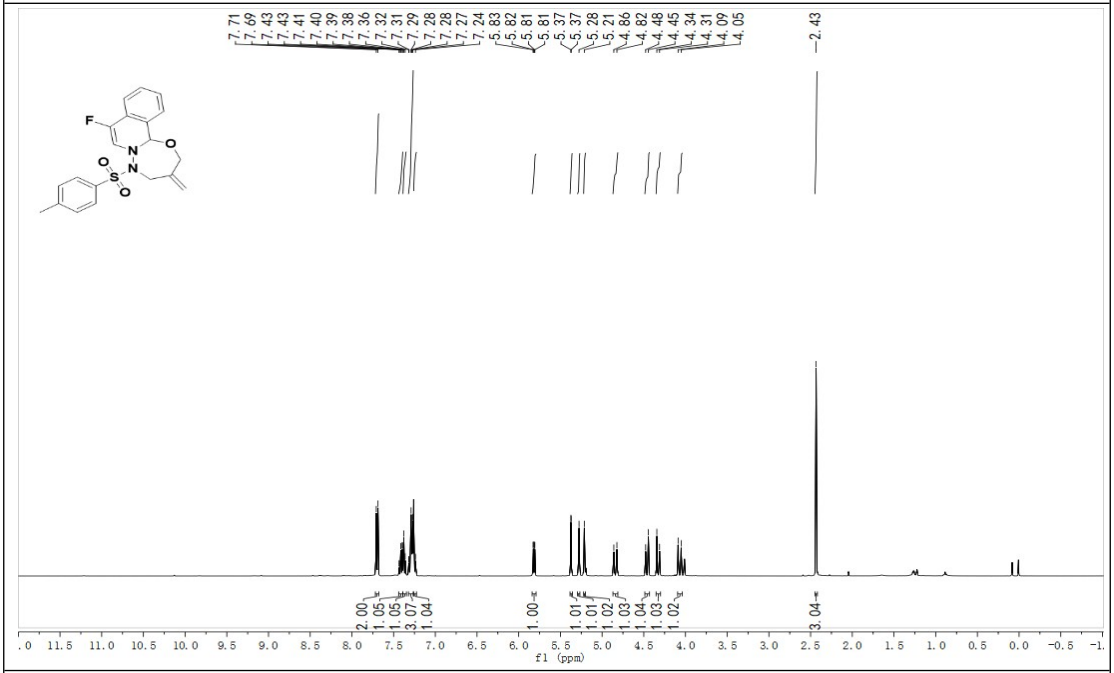



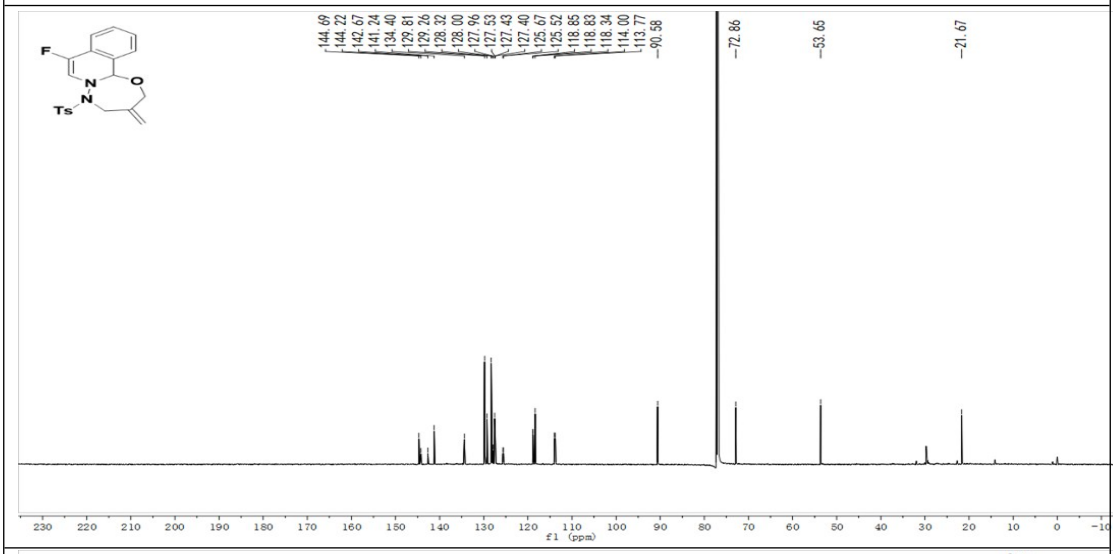
(5c) 9-chloro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino-[2,3-*a*]isoquinoline

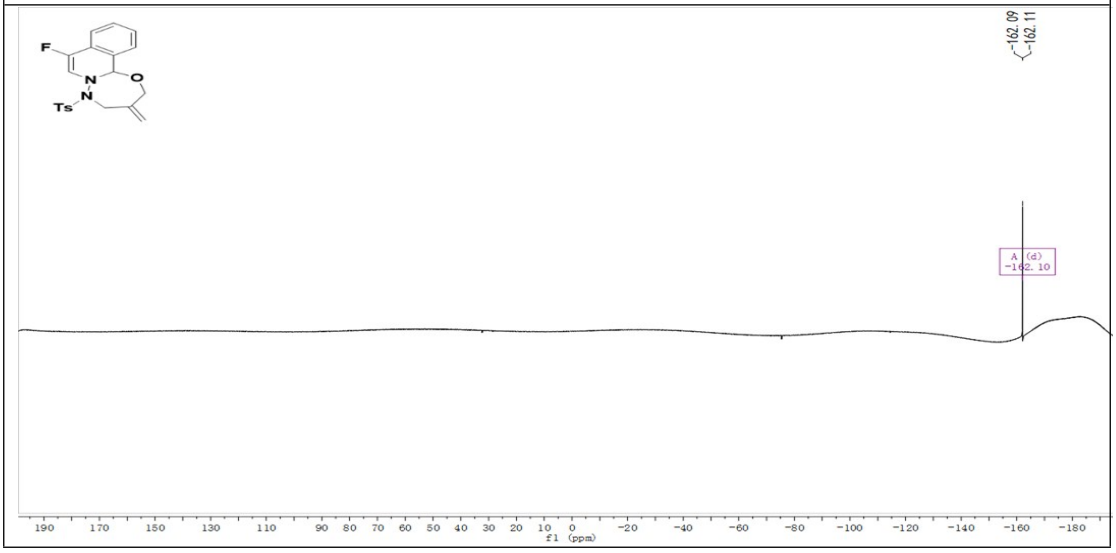


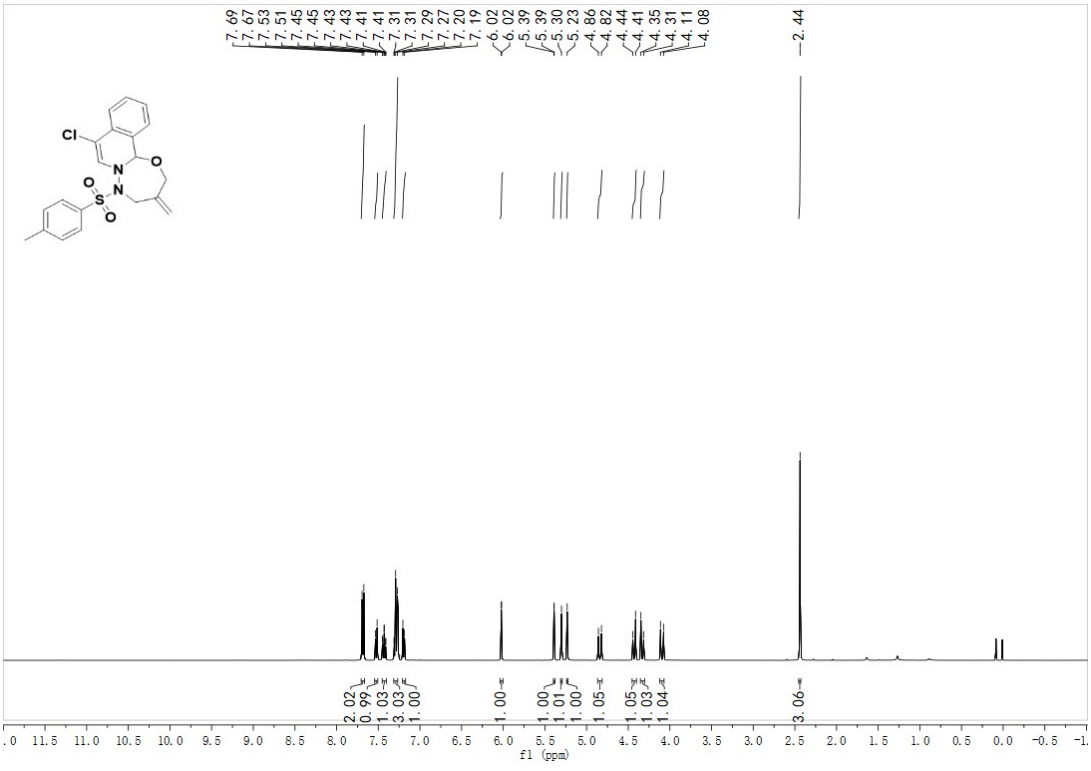
(5d) 8-fluoro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino-[2,3-*a*] isoquinoline

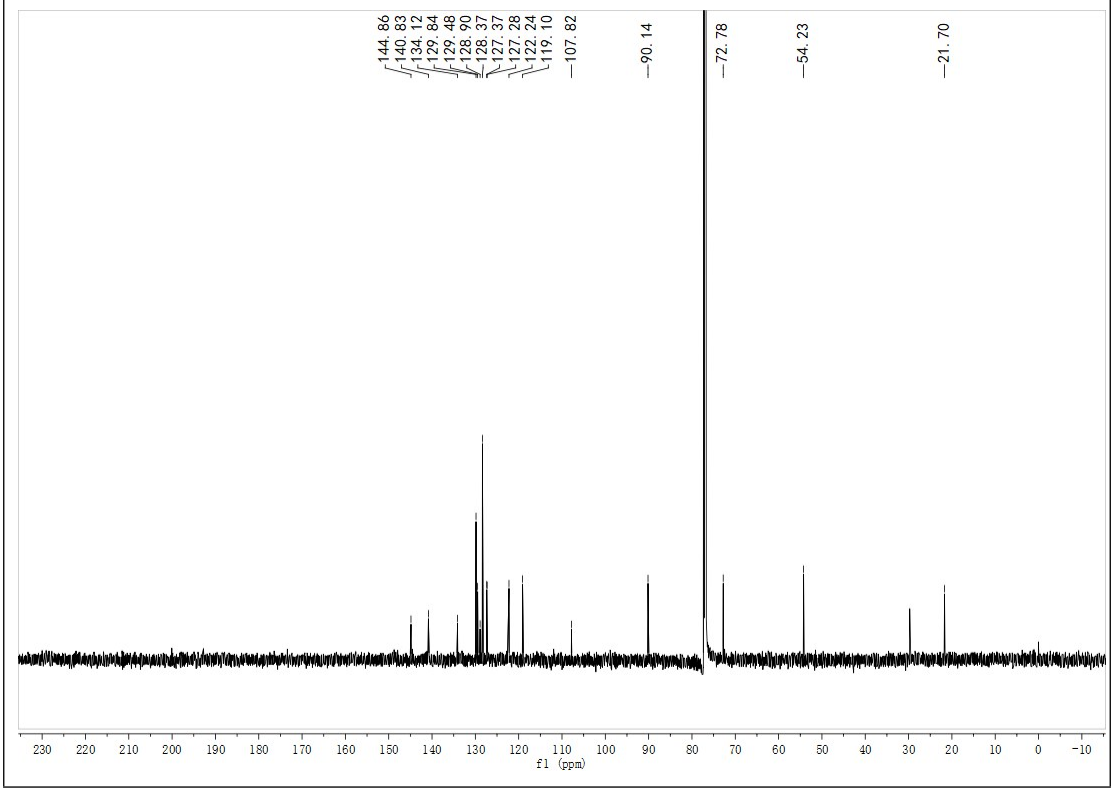




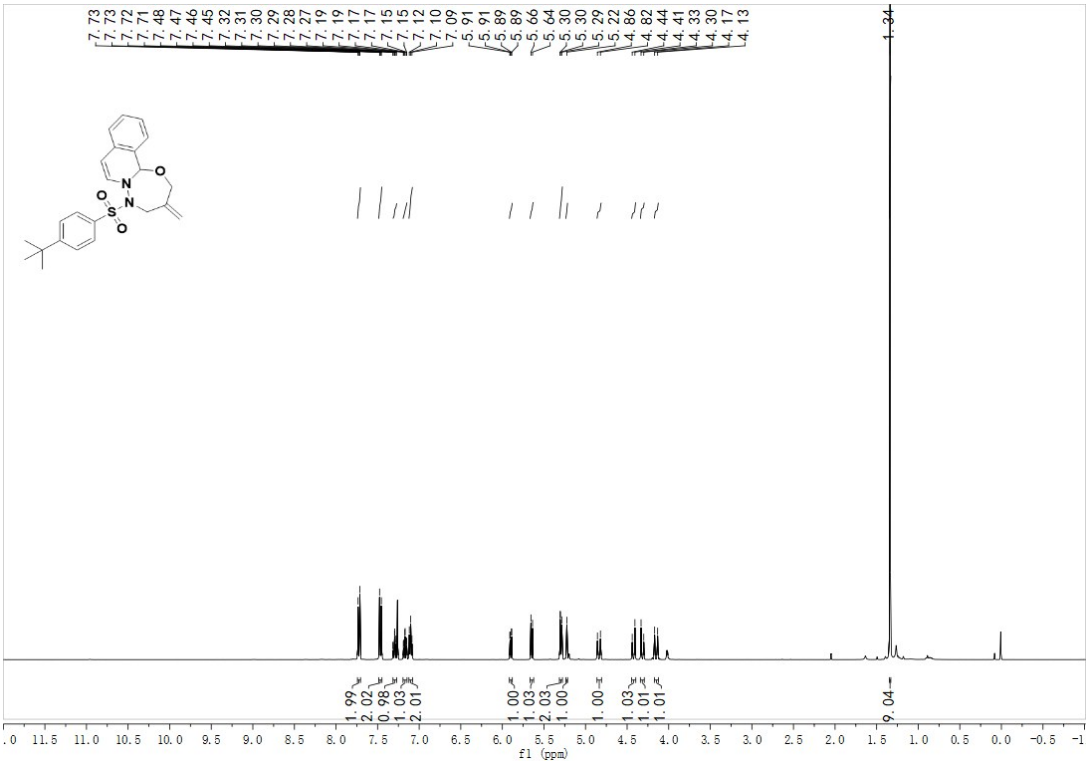


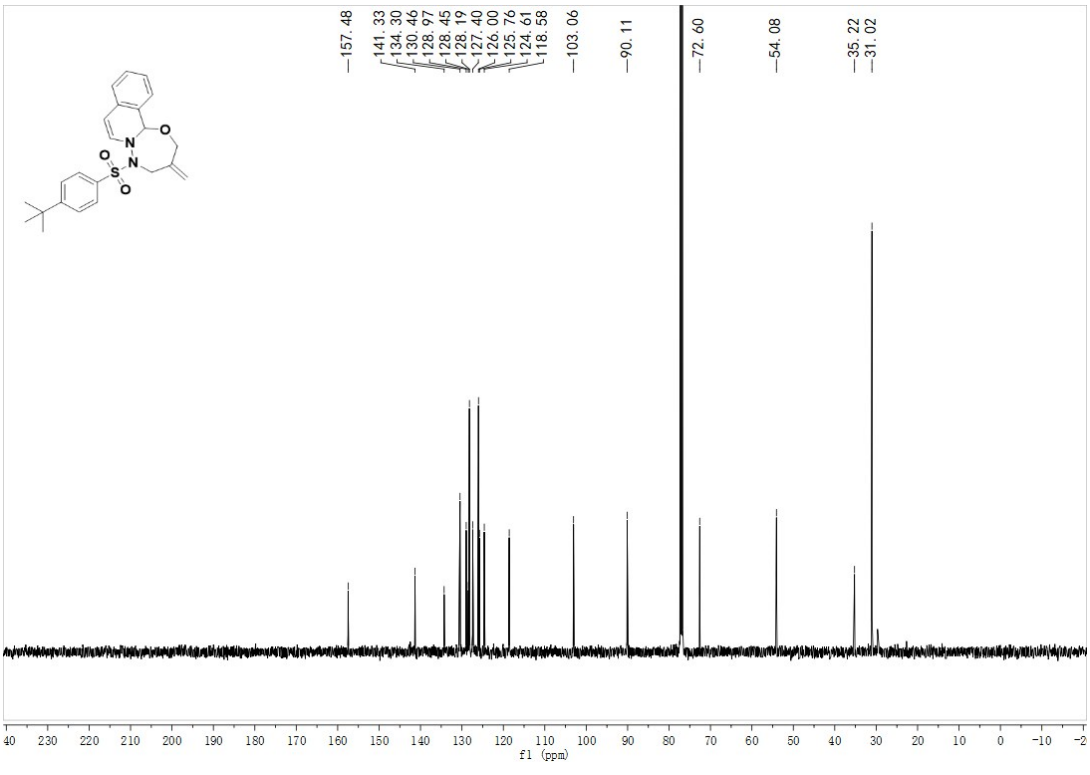
(5e) 8-chloro-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino-[2,3-*a*] isoquinoline



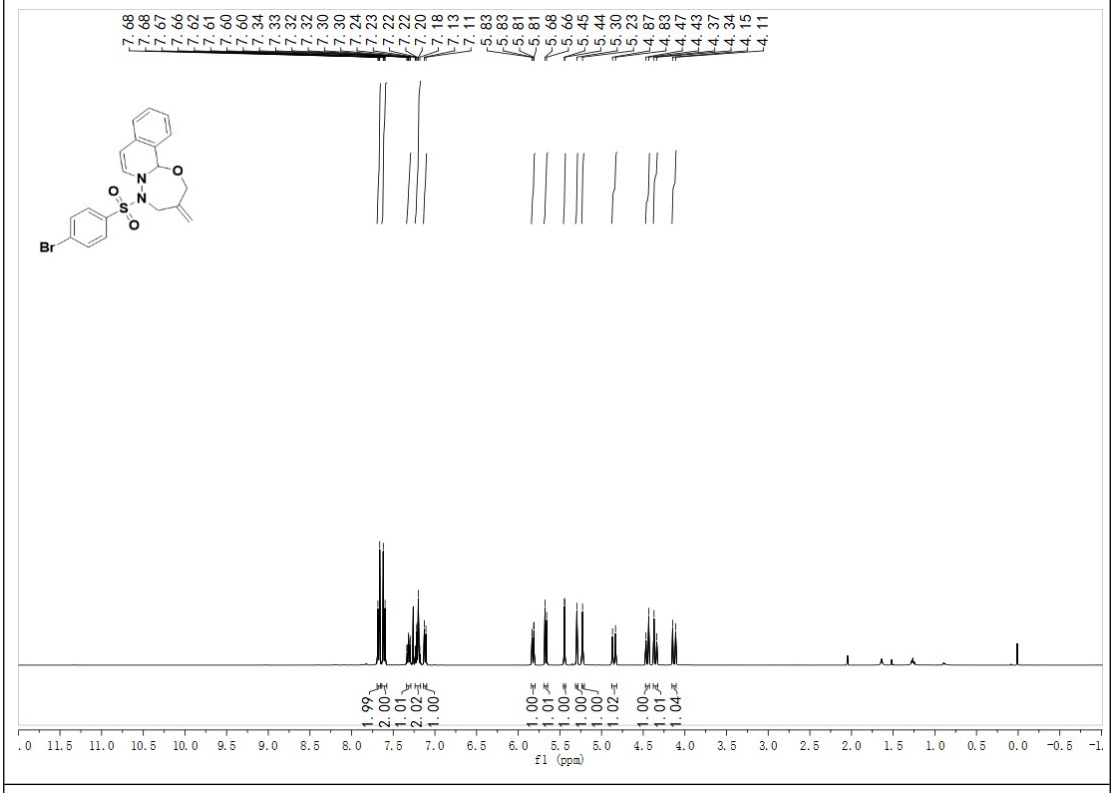



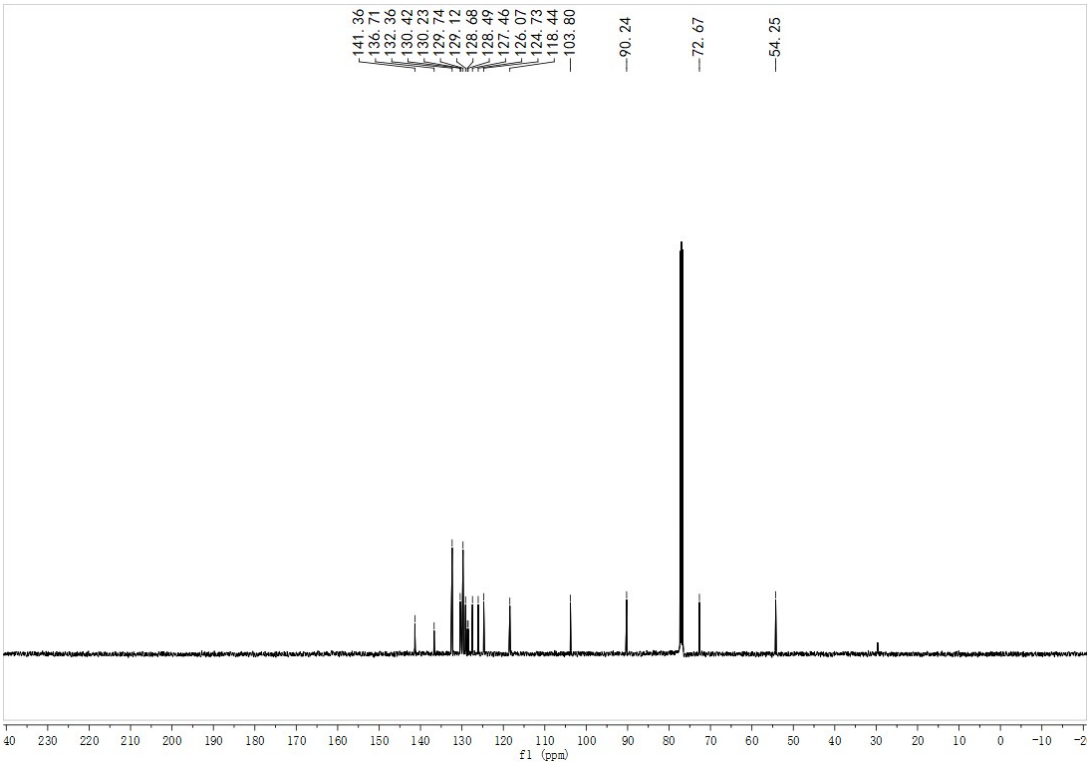
(5f) 5-((4-(tert-butyl)phenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinoline



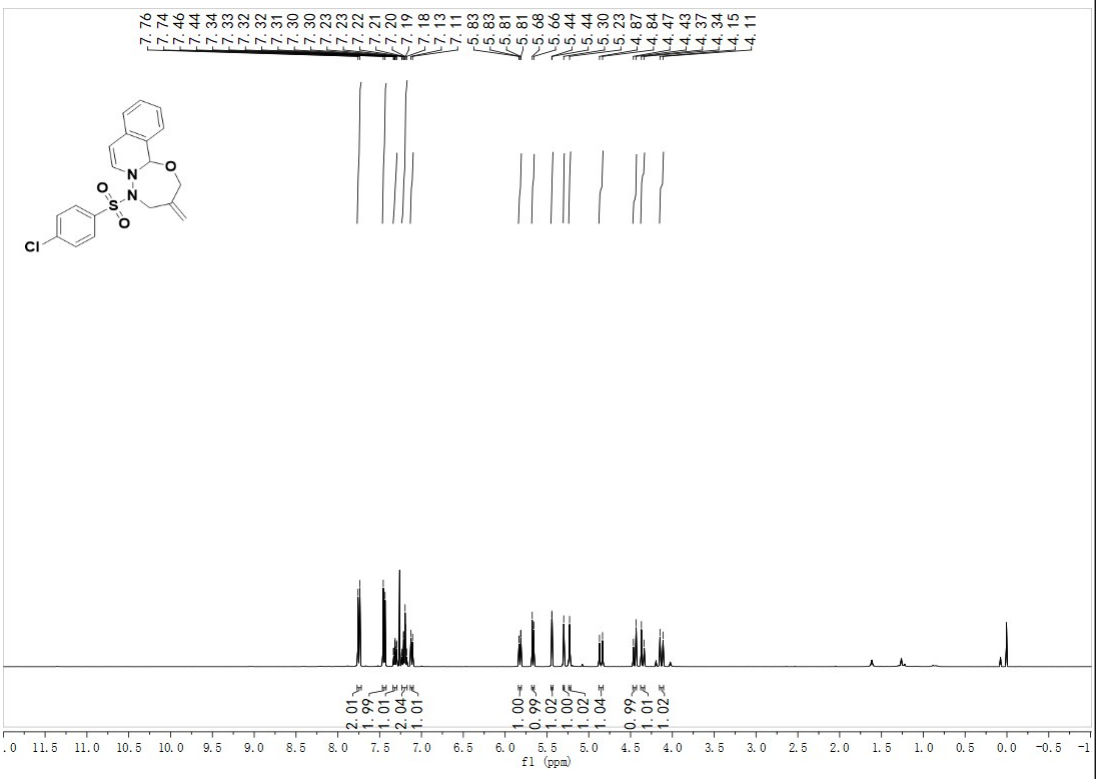



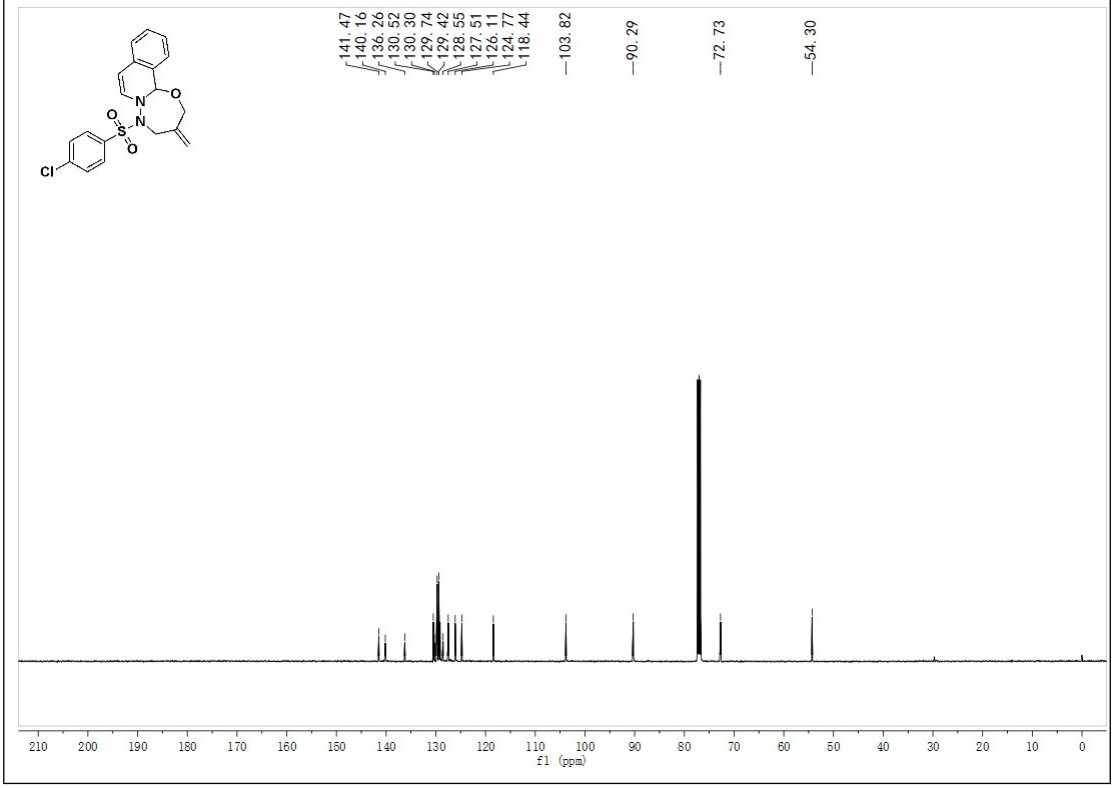
(5g) 5-((4-bromophenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4]-oxadiazepino[2,3-*a*] isoquinoline



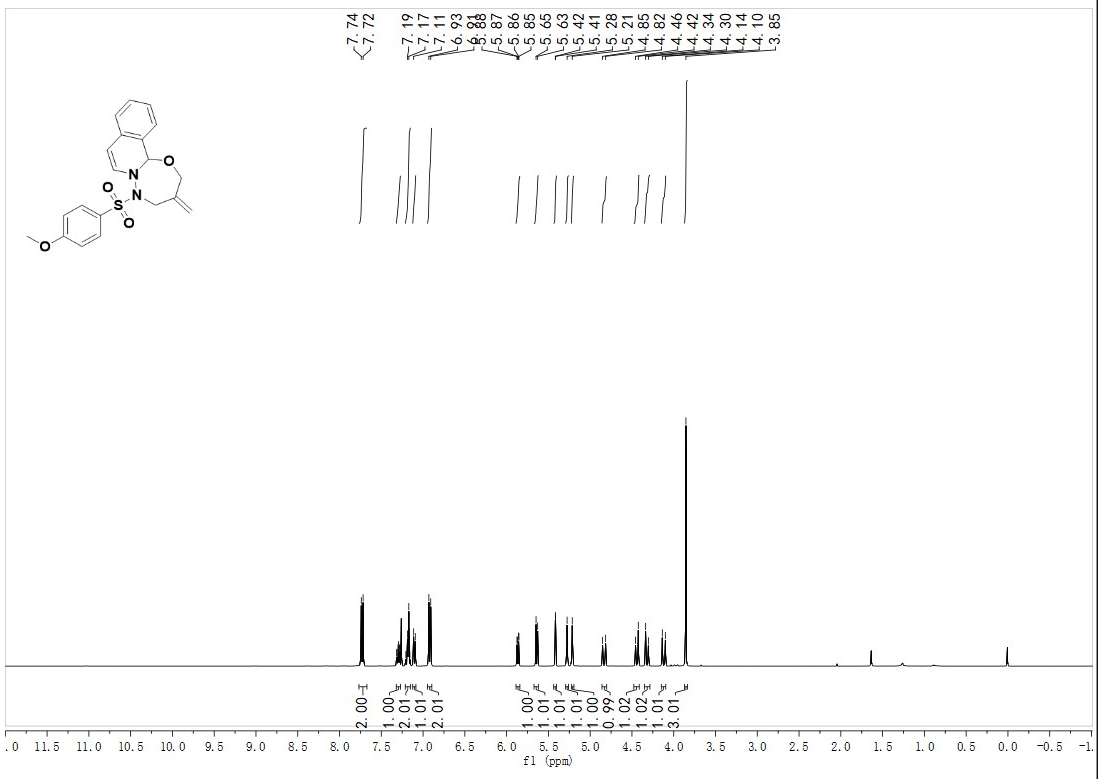



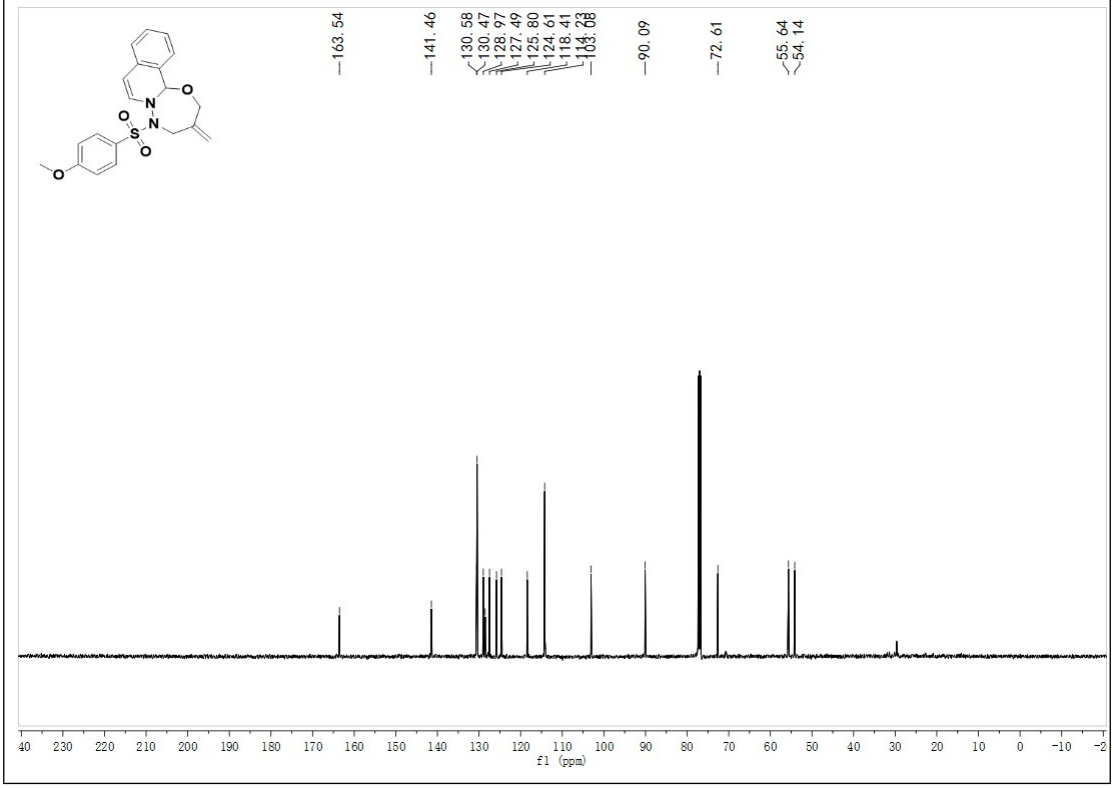
(5h) 5-((4-chlorophenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4]-oxadiazepino[2,3-*a*] isoquinoline



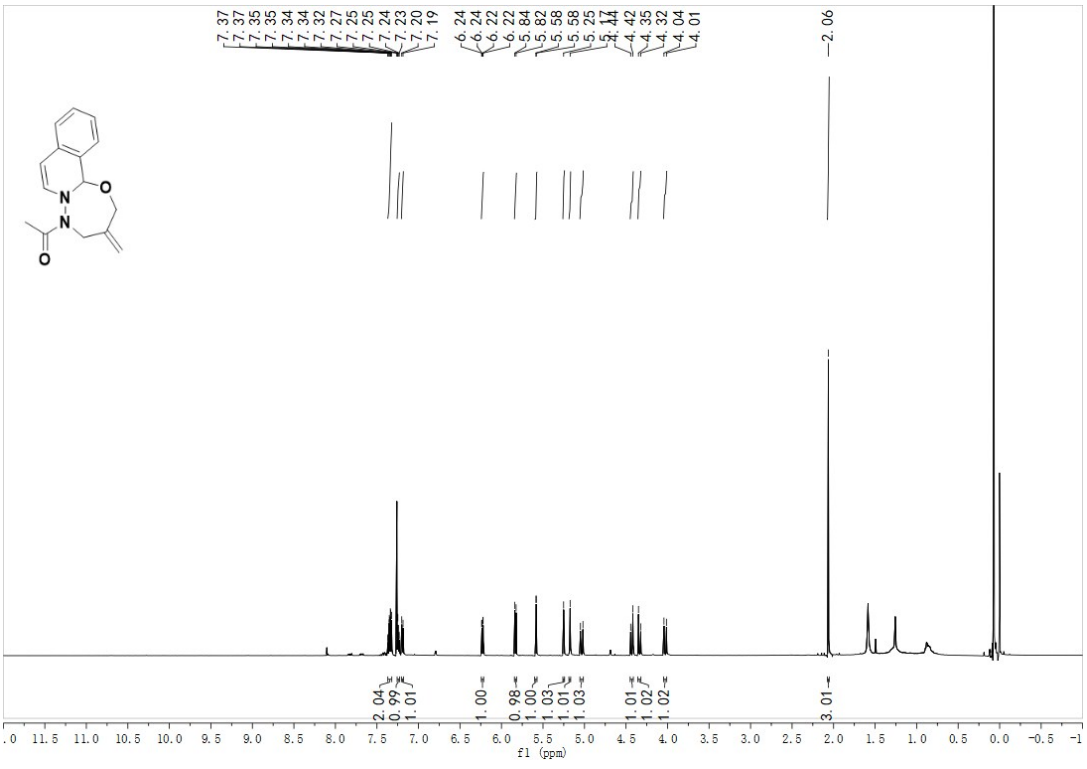



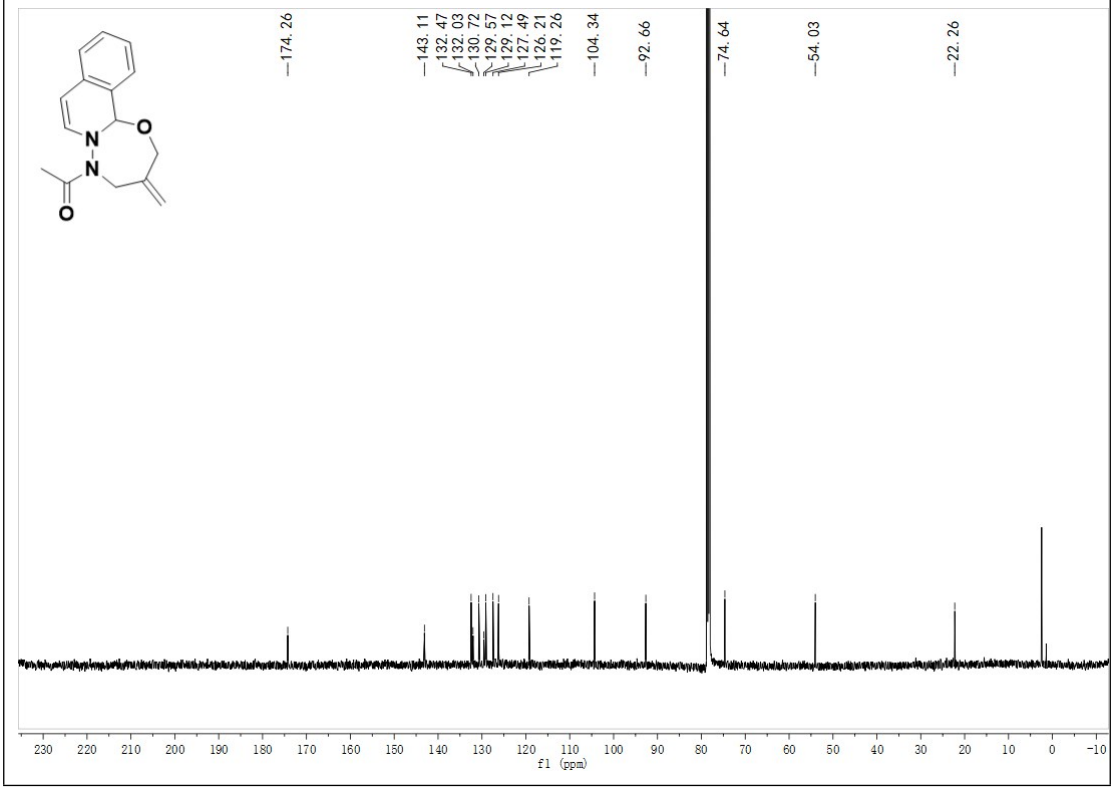
(5i) 5-((4-methoxyphenyl)sulfonyl)-3-methylene-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinoline



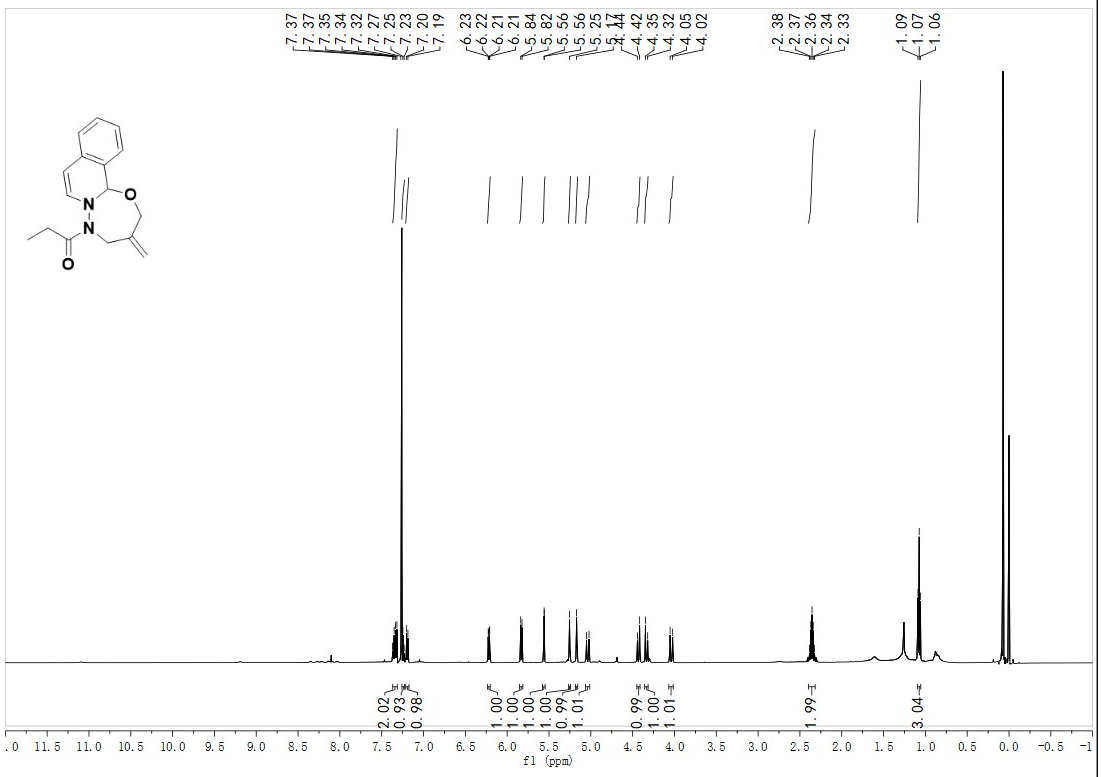



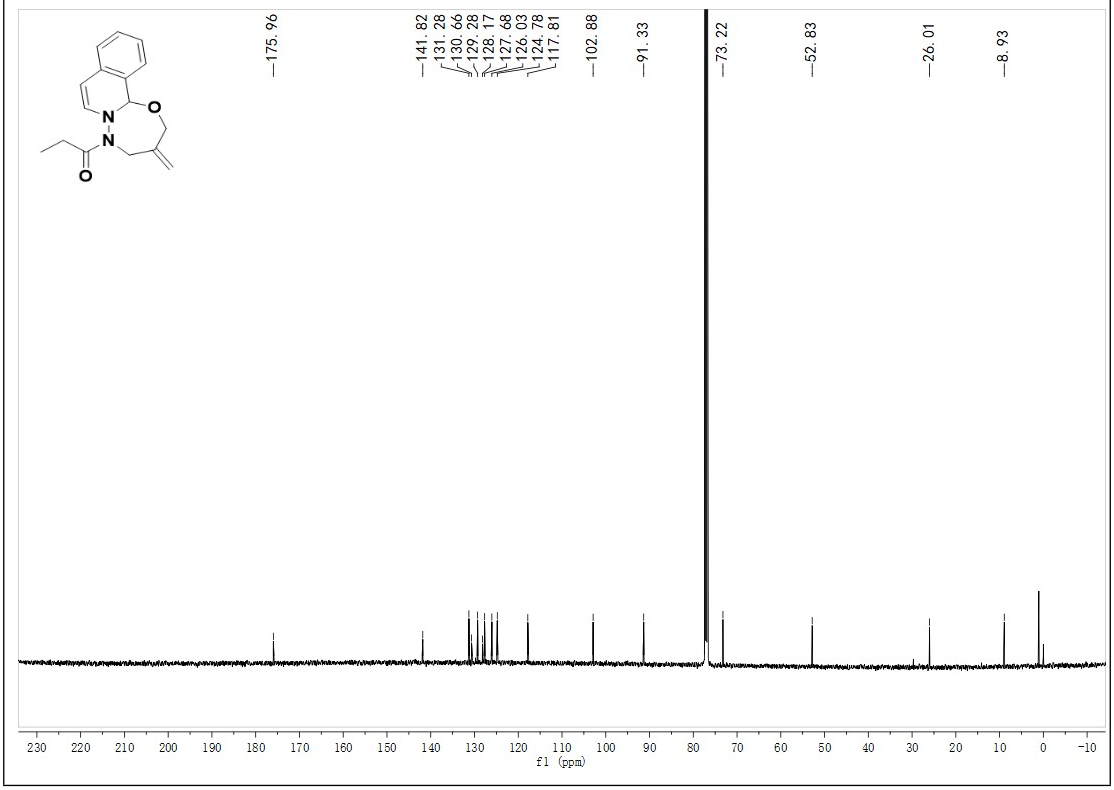
(5j) 1-(3-methylene-3,4-dihydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinolin-5(2H)-yl)ethan-1-one



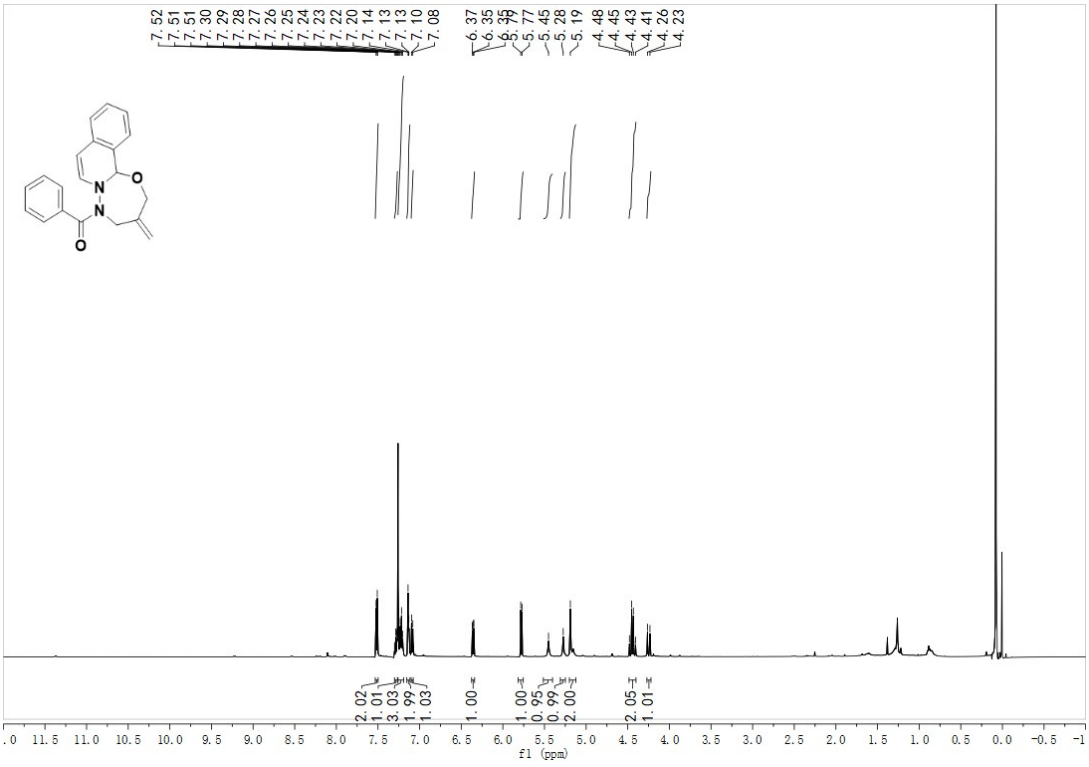



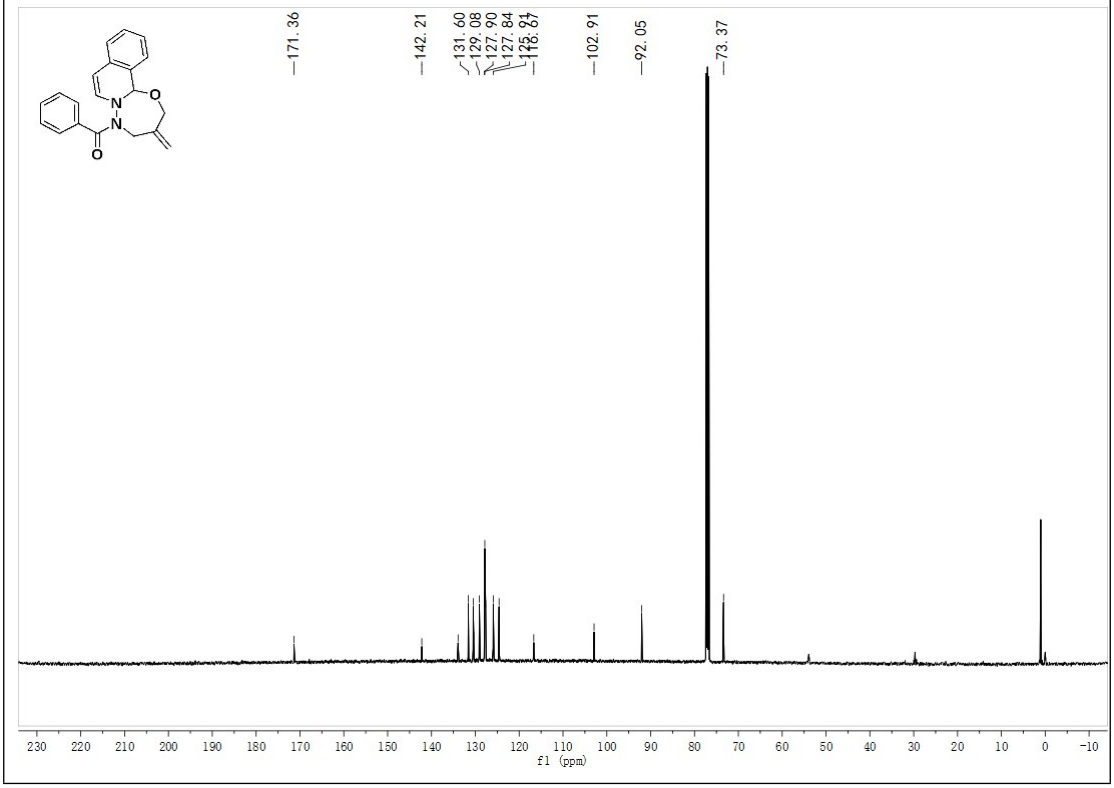
(5k) 1-(3-methylene-3,4-dihydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinolin-5(2H)-yl)propan-1-one



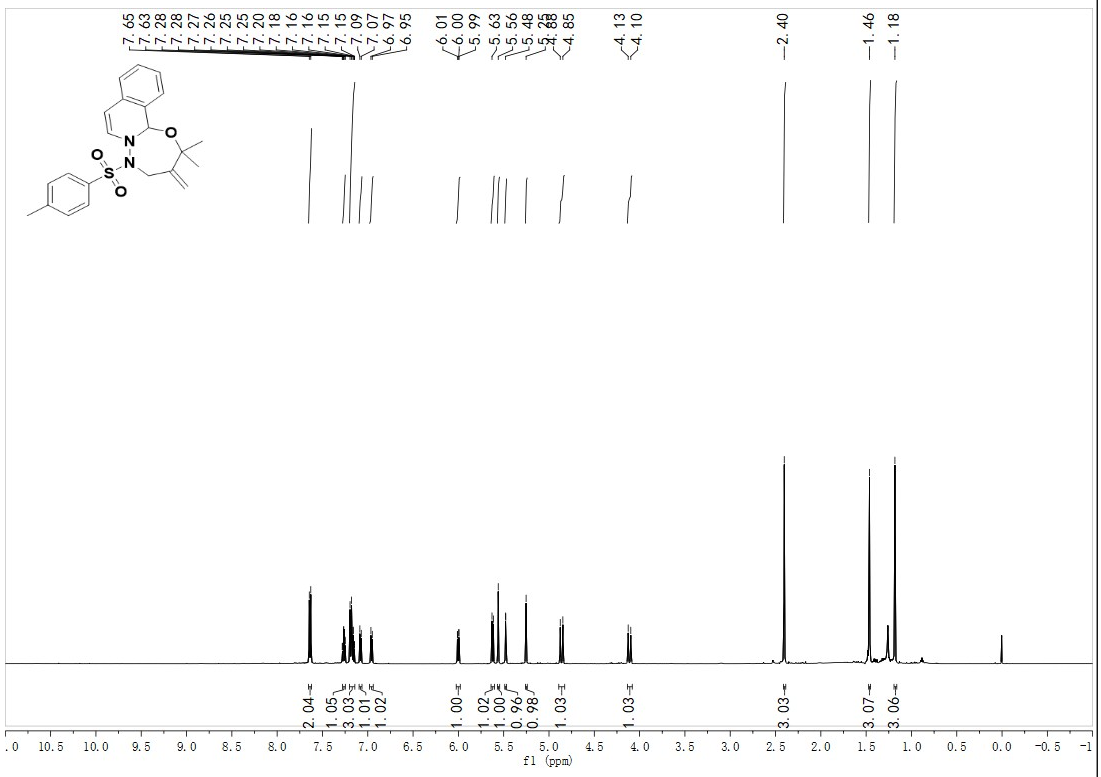



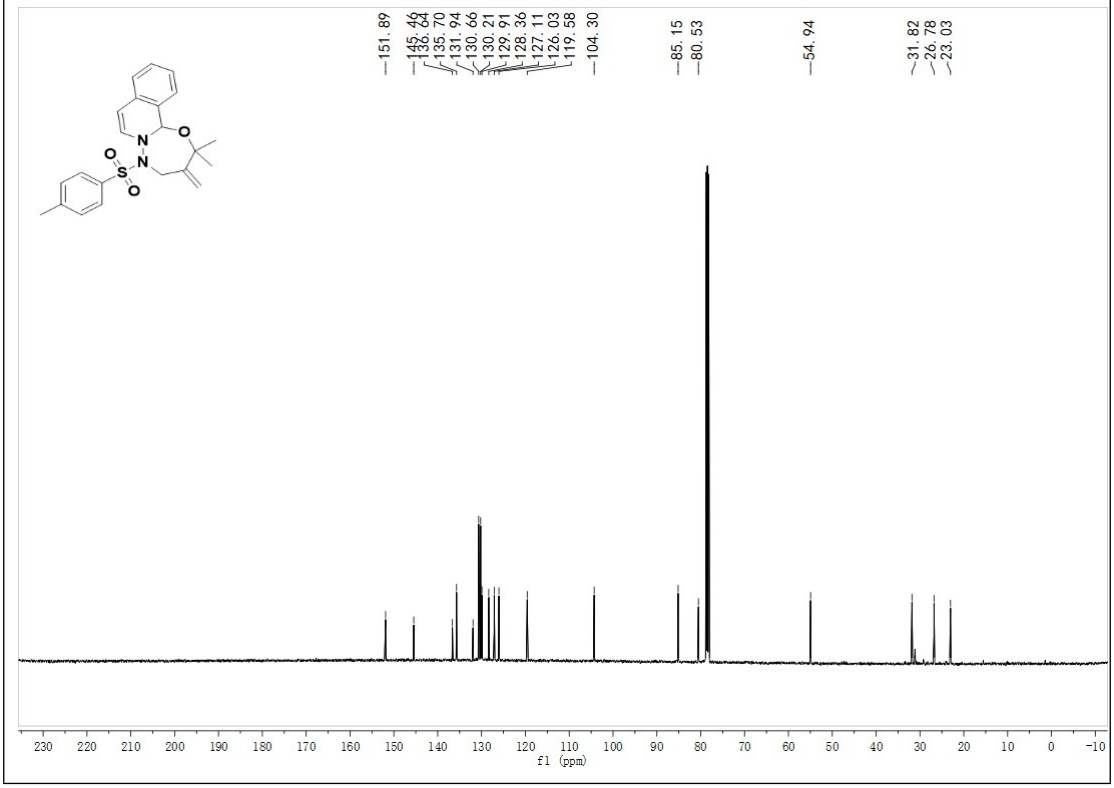
(5l) (3-methylene-3,4-dihydro-12b*H*-[1,3,4]oxadiazepino[2,3-*a*]isoquinolin-5(2H)-yl)(phenyl)methanone



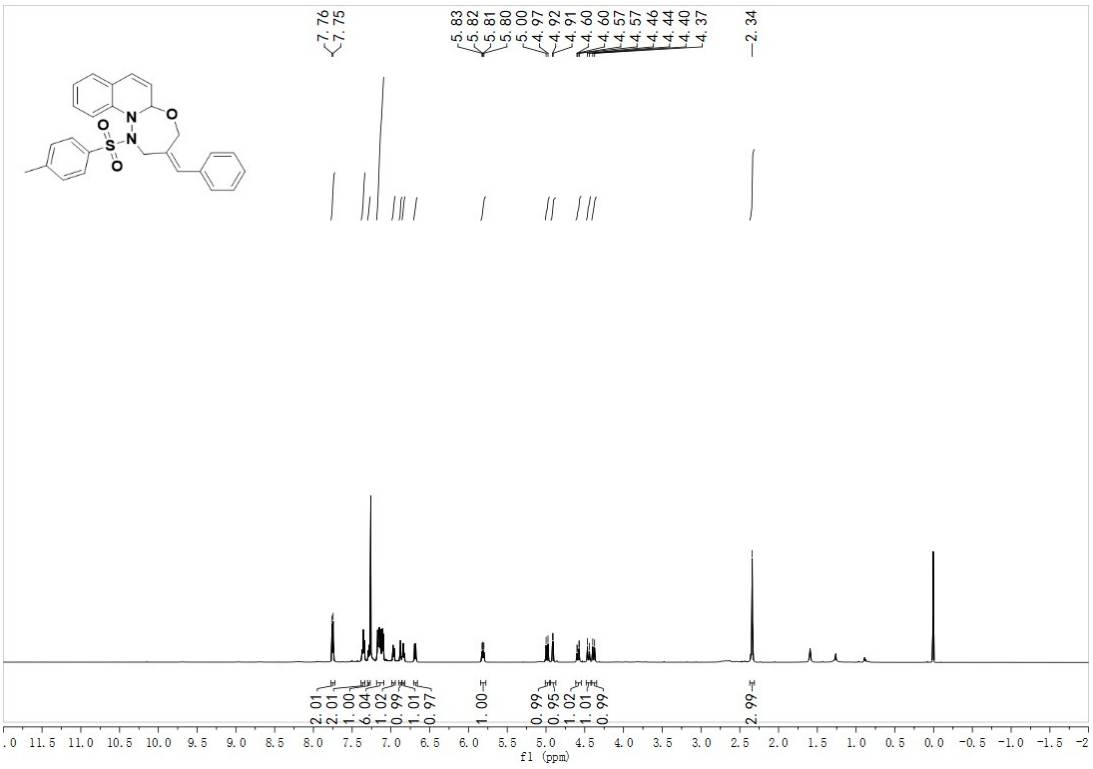



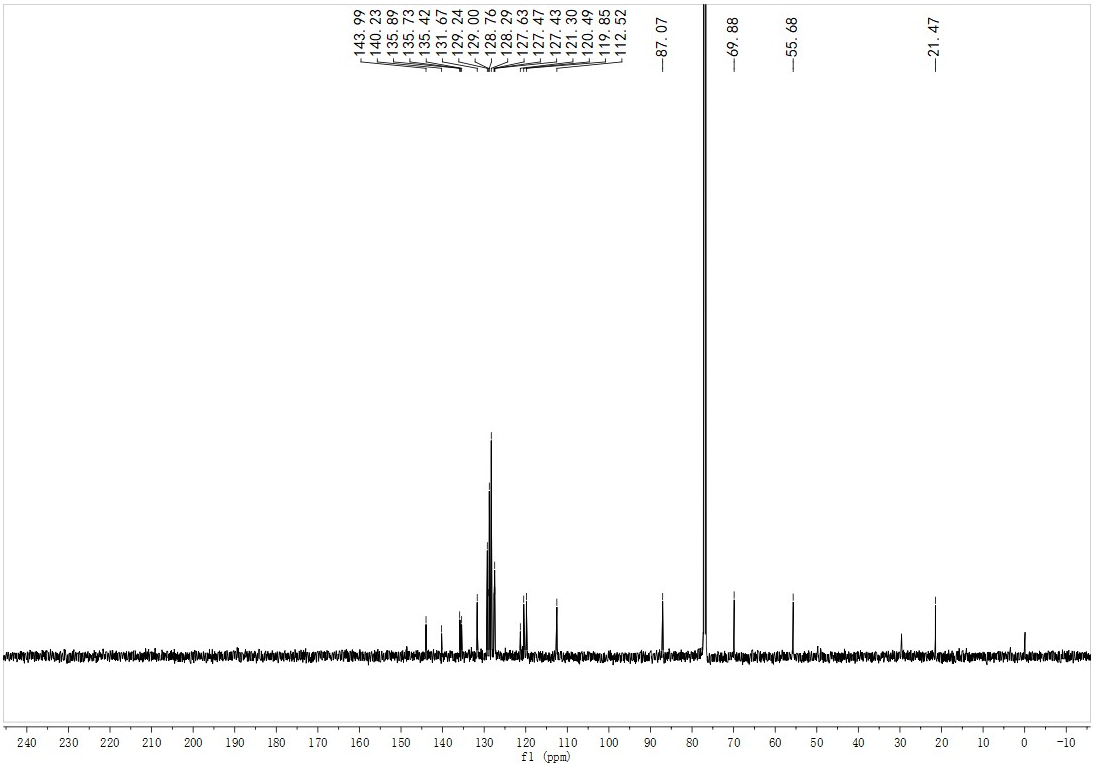
(5m) 2,2-dimethyl-3-methylene-5-tosyl-2,3,4,5-tetrahydro-12b*H*-[1,3,4]oxadiazepino [2,3-*a*]isoquinoline



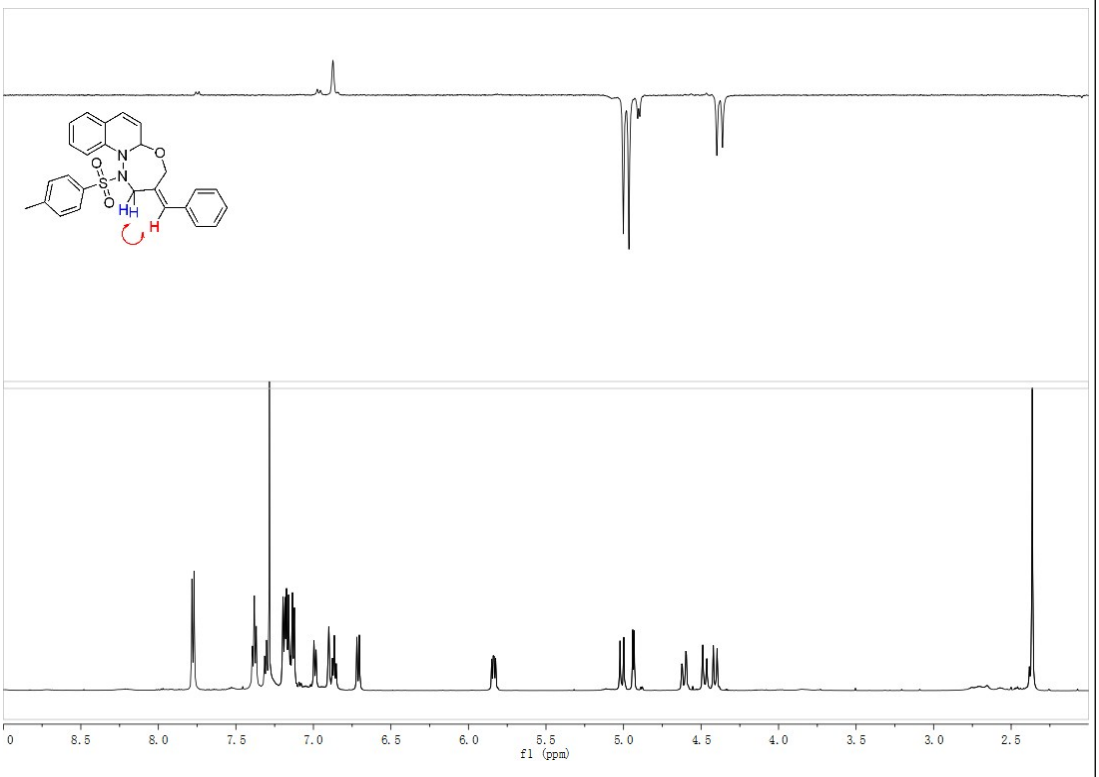



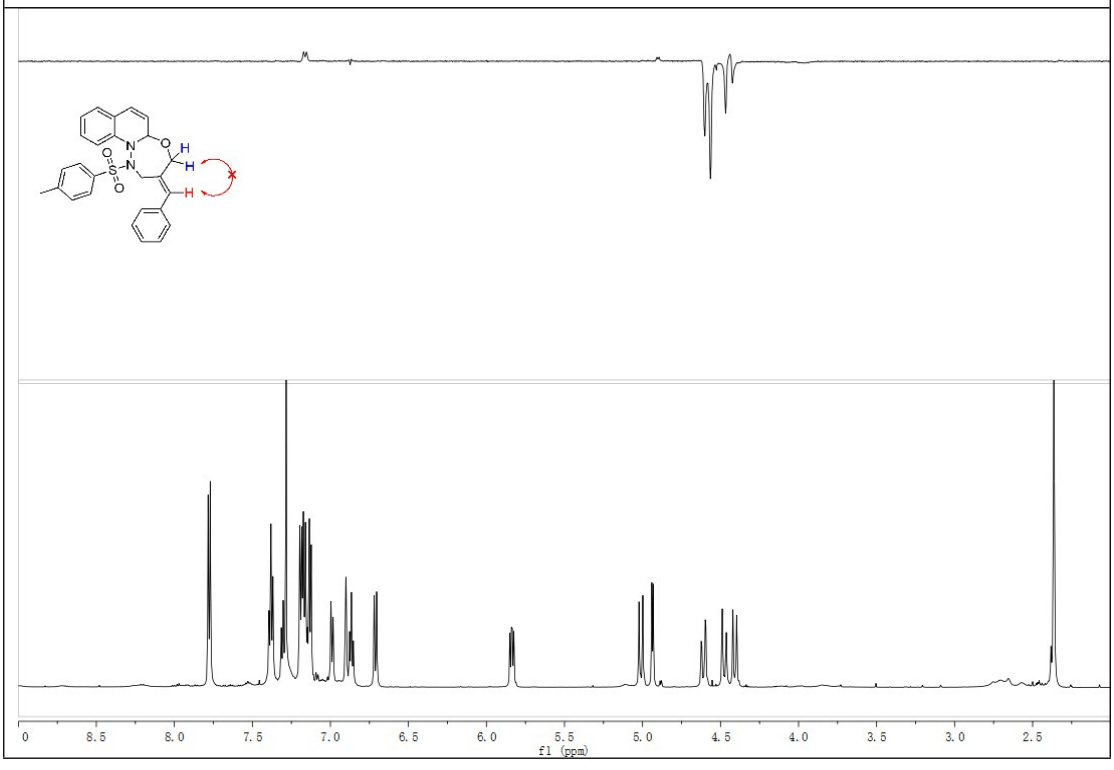
(6a) 3-benzylidene-1-tosyl-1,2,3,4-tetrahydro-5a*H*-[1,3,4]oxadiazepino[3,2-*a*] quinoline



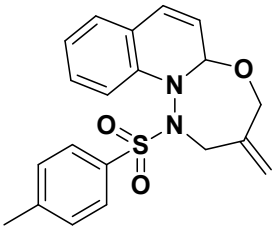
NOE Spectrum of **6a**



**(G) X-ray crystallographic data of 3a and 5a**

**X-ray crystallographic data of 3a (CCDC 1989296)**




3a

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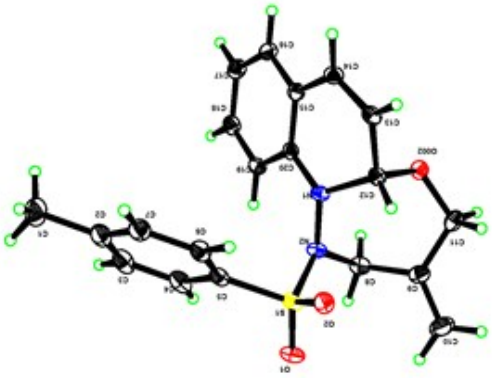
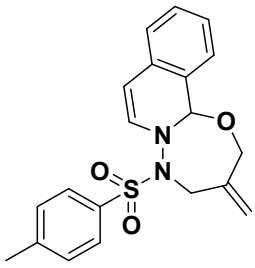


**Crystal structure determination of [22019647_0m]**

Crystal Data for $C_{20}H_{20}N_2O_3S$ (M =368.44 g/mol): orthorhombic, space group Pbca (no. 61), a = 8.8840(5) Å, b = 19.9039(11) Å, c = 20.2479(12) Å, V = 3580.4(4) Å3, Z = 8, T = 100.0 K, μ(MoKα) = 0.204 mm-1, Dcalc = 1.367 g/cm3, 24907 reflections measured (4.56° ≤ 2Θ ≤ 52.836°), 3649 unique (Rint = 0.0983, Rsigma = 0.0672) which were used in all calculations. The final R1 was 0.0577 (I > 2σ(I)) and wR2 was 0.1329 (all data).

| | |
|---|---|
| Identification code | 22019647_0m |
| Empirical formula | $C_{20}H_{20}N_2O_3S$ |
| Formula weight | 368.44 |
| Temperature/K | 100.0 |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 8.8840(5) |
| b/Å | 19.9039(11) |
| c/Å | 20.2479(12) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 3580.4(4) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.367 |
| μ/mm$^{-1}$ | 0.204 |
| F(000) | 1552.0 |
| Crystal size/mm$^3$ | 0.15 × 0.12 × 0.08 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.56 to 52.836 |
| Index ranges | -10 ≤ h ≤ 11, -24 ≤ k ≤ 22, -20 ≤ l ≤ 24 |
| Reflections collected | 24907 |
| Independent reflections | 3649 [$R_{int}$ = 0.0983, $R_{sigma}$ = 0.0672] |
| Data/restraints/parameters | 3649/0/236 |
| Goodness-of-fit on F$^2$ | 1.075 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0577, w$R_2$ = 0.1087 |
| Final R indexes [all data] | $R_1$ = 0.1116, w$R_2$ = 0.1329 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.24/-0.44 |

**X-ray crystallographic data of 5a (CCDC 1989297)**




**5a**

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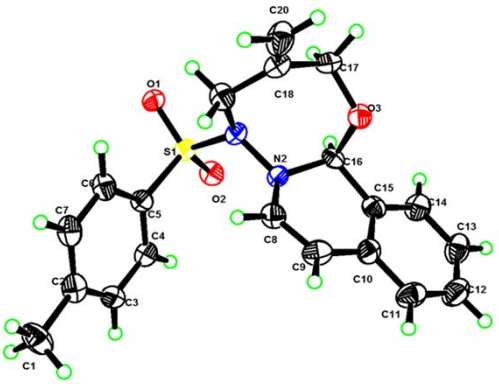

Crystal structure determination of [22019576_0m]

Crystal Data for $C_{20}H_{20}N_2O_3S$ (M =368.44 g/mol): orthorhombic, space group P212121 (no. 19), a = 6.0044(7) Å, b = 10.0276(15) Å, c = 30.040(4) Å, V = 1808.7(4) Å3, Z = 4, T = 100.15 K, μ(MoKα) = 0.202 mm-1, Dcalc = 1.353 g/cm3, 10149 reflections measured (4.884° ≤ 2Θ ≤ 50.64°), 3254 unique (Rint = 0.0961, Rsigma = 0.1089) which were used in all calculations. The final R1 was 0.0595 (I > 2σ(I)) and wR2 was 0.1399 (all data)

| | |
|---|---|
| Identification code | 22019576_0m |
| Empirical formula | $C_{20}H_{20}N_2O_3S$ |
| Formula weight | 368.44 |
| Temperature/K | 100.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 6.0044(7) |
| b/Å | 10.0276(15) |
| c/Å | 30.040(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1808.7(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.353 |
| μ/mm$^{-1}$ | 0.202 |
| F(000) | 776.0 |
| Crystal size/mm$^3$ | 0.08 × 0.05 × 0.02 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.884 to 50.64 |
| Index ranges | -7 ≤ h ≤ 6, -11 ≤ k ≤ 12, -36 ≤ l ≤ 31 |
| Reflections collected | 10149 |
| Independent reflections | 3254 [$R_{int}$ = 0.0961, $R_{sigma}$ = 0.1089] |
| Data/restraints/parameters | 3254/0/236 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0595, $wR_2$ = 0.1177 |
| Final R indexes [all data] | $R_1$ = 0.1063, $wR_2$ = 0.1399 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.32/-0.43 |
| Flack parameter | 0.00(13) |

**(H) References**


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