

## Table of Contents

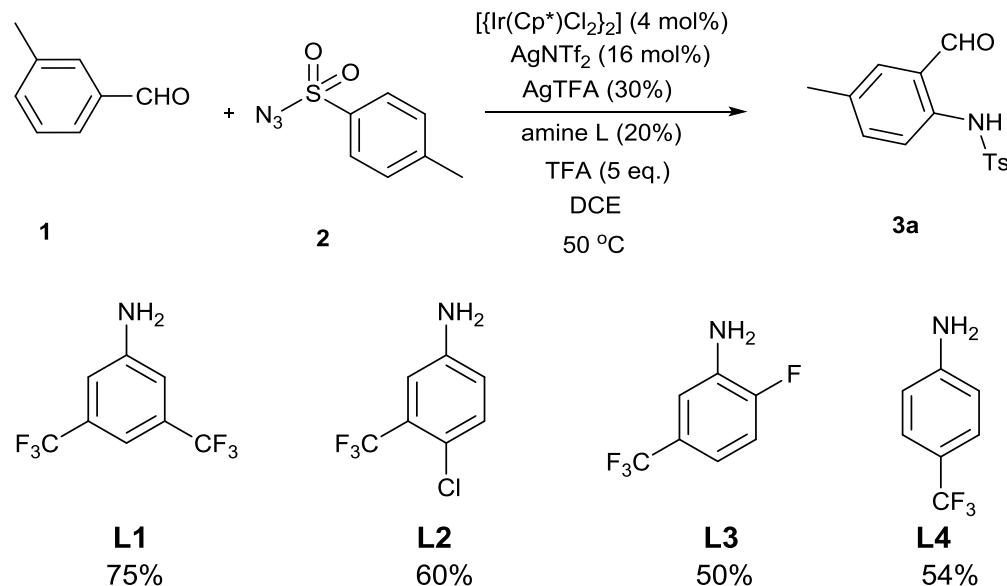
1. General information-----	2
2. Experimental Section-----	2
2.1 General Procedure for the <i>ortho</i> -C(sp <sup>2</sup> )-H Amination of Various Benzaldehyde---	2
2.2 Typical Procedure for the Synthesis of 5-----	9
3. NMR spectra for all compounds-----	19
4. X-ray structure of 5aa-----	60

## 1. General information

Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates. Flash column chromatography was performed on silica gel 60 Å, 10-40 µm. <sup>1</sup>H NMR spectra were recorded on a Bruker instrument (400 MHz and 500 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet), coupling constants (Hz) and integration. <sup>13</sup>C NMR spectra were recorded on a Bruker instrument (101 MHz and 126 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Coupling constants are reported in hertz. IR spectra were recorded on a Bruker FT-IR spectrometer. HRMS was measured on a TOF-Q mass spectrometer equipped with an ESI source.

## 2. Experimental Section

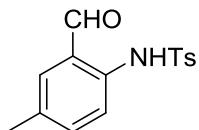
Table 1. Optimization of Ir(III)-catalyzed *ortho*-amidation of aldehydes<sup>a,b</sup>



<sup>a</sup> Conditions: 0.2 mmol **1**, 0.30 mmol **2**, 4% [ $\{\text{Ir}(\text{Cp}^*)\text{Cl}_2\}_2$ ], 16% AgNTf<sub>2</sub>, 30% AgTFA, amine **L**, 5 eq. TFA, 2 mL of DCE, 50 °C, 24 h. <sup>b</sup> Isolated yields given.

### 2.1 General Procedure for the *ortho*-C(sp<sup>2</sup>)–H amination of Various benzaldehyde.

To a solution of aldehyde substrate **1** (0.2 mmol) and tosyl azide **2** (0.3 mmol) in 2.0 mL of DCE was added [ $\{\text{Ir}(\text{Cp}^*)\text{Cl}_2\}_2$ ] (6.4 mg, 0.008 mmol), AgNTf<sub>2</sub> (14 mg, 0.032 mmol), silver trifluoroacetate (13.5 mg, 0.06 mmol), 3,5-bis(trifluoromethyl)aniline (9.6 mg, 0.004 mmol), trifluoroacetic acid (118 mg, 1 mmol), and the mixture was stirred at 50 °C. The reaction was followed by TLC until all the starting material disappeared. After reaction completed, the reaction mixture was cooled to room temperature and concentrated *in vacuo*, and then the residue was purified by column chromatography to give the corresponding product **3**. Unless otherwise specified, all other products **3** were synthesized according to this typical procedure.



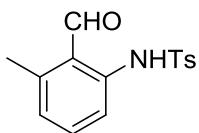
**N-(2-formyl-4-methylphenyl)-4-methylbenzenesulfonamide (3a).**

(white solid, 43 mg, 75% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  10.37 (s, 1H), 9.98 (s, 1H), 7.61 (s, 1H), 7.57 (d,  $J$  = 7.5 Hz, 2H), 7.40 (d,  $J$  = 8.0 Hz, 1H), 7.35 (d,  $J$  = 7.3 Hz, 2H), 7.05 (d,  $J$  = 7.8 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.89, 144.26, 136.82, 136.26, 136.23, 135.72, 131.49, 130.27, 128.49, 127.33, 123.99, 21.44, 20.59.

IR (film):  $\nu$  = 3133, 2861, 1667, 1496, 1341, 1171, 1156 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{SNa}$  [M + Na] $^+$  312.0670, found 312.0666.



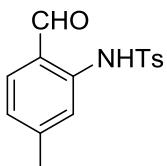
**N-(2-formyl-3-methylphenyl)-4-methylbenzenesulfonamide (3b).**

(white solid, 43 mg, 75% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  10.98 (s, 1H), 10.27 (s, 1H), 7.64 (d,  $J$  = 7.3 Hz, 2H), 7.43 (t,  $J$  = 7.3 Hz, 1H), 7.37 (d,  $J$  = 7.4 Hz, 2H), 7.04-7.09 (m, 2H), 2.55 (s, 3H), 2.35 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-d6)  $\delta$  194.72, 144.44, 143.27, 140.32, 136.27, 135.39, 130.36, 128.09, 127.41, 124.20, 119.43, 21.45, 19.87.

IR (film):  $\nu$  = 3135, 2912, 1647, 1598, 1469, 1195, 1160 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{SNa}$  [M + Na] $^+$  312.0670, found 312.0668.



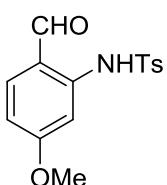
**N-(2-formyl-5-methylphenyl)-4-methylbenzenesulfonamide (3c).**

(white solid, 50 mg, 88% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  10.62 (s, 1H), 9.89 (s, 1H), 7.71 (d,  $J$  = 7.9 Hz, 1H), 7.65 (d,  $J$  = 8.2 Hz, 2H), 7.37 (d,  $J$  = 8.1 Hz, 2H), 7.14 (d,  $J$  = 7.9 Hz, 1H), 7.10 (s, 1H), 2.34 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-d6)  $\delta$  193.50, 146.91, 144.48, 139.34, 136.15, 133.07, 130.35, 127.36, 126.34, 124.52, 122.27, 22.00, 21.44.

IR (film):  $\nu$  = 3202, 2924, 1667, 1630, 1510, 1404, 1325, 1157, 1088 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{SNa}$  [M + Na] $^+$  312.0670, found 312.0672.



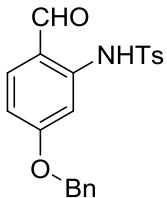
**N-(2-formyl-5-methoxyphenyl)-4-methylbenzenesulfonamide (3d).**

(white solid, 35 mg, 58% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  10.91 (s, 1H), 9.80 (s, 1H), 7.78 (d,  $J$  = 8.7 Hz, 1H), 7.71 (d,  $J$  = 8.3 Hz, 2H), 7.39 (d,  $J$  = 8.1 Hz, 2H), 6.86 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 6.80 (d,  $J$  = 2.2 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-d6)  $\delta$  193.40, 165.06, 144.75, 141.57, 136.91, 136.01, 130.50, 127.47, 118.86, 110.49, 105.29, 56.34, 21.45.

IR (film):  $\nu$  = 3166, 2838, 1670, 1612, 1560, 1389, 1342, 1161, 1091 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{SNa}$  [M + Na] $^+$  328.0619, found 328.0612.



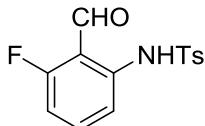
**N-(5-(benzyloxy)-2-formylphenyl)-4-methylbenzenesulfonamide (3e).**

(white solid, 65 mg, 86% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  10.92 (s, 1H), 9.78 (s, 1H), 7.77 (d,  $J$  = 8.3 Hz, 1H), 7.64 (d,  $J$  = 7.0 Hz, 2H), 7.45 – 7.32 (m, 7H), 6.97 – 6.89 (m, 2H), 5.17 (s, 2H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.51, 164.15, 144.72, 141.56, 137.00, 136.37, 135.97, 130.49, 129.05, 128.65, 128.20, 127.38, 118.85, 111.49, 105.93, 70.34, 21.46.

IR (film):  $\nu$  = 3100, 2924, 1670, 1620, 1469, 1395, 1183, 1155 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{SNa}$  [M + Na] $^+$  404.0932, found 404.0930.



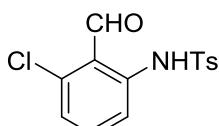
**N-(3-fluoro-2-formylphenyl)-4-methylbenzenesulfonamide (3f).**

(white solid, 46 mg, 78% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  10.94 (s, 1H), 10.16 (s, 1H), 7.74 (d,  $J$  = 7.3 Hz, 2H), 7.63 (dd,  $J$  = 13.8, 6.5 Hz, 1H), 7.40 (d,  $J$  = 7.2 Hz, 2H), 7.15 (d,  $J$  = 8.0 Hz, 1H), 7.08 (t,  $J$  = 9.2 Hz, 1H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  190.62 (d,  $J$  = 8.6 Hz), 164.56 (d,  $J$  = 259.0 Hz), 144.90, 147.71, 138.05 (d,  $J$  = 11.5 Hz), 135.90, 130.53, 127.53, 115.68 (d,  $J$  = 3.1 Hz), 113.47 (d,  $J$  = 9.7 Hz), 111.62 (d,  $J$  = 20.8 Hz), 21.47.

IR (film):  $\nu$  = 3152, 2842, 2360, 2342, 1672, 1615, 1508, 1397, 1342, 1157 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{FNO}_3\text{SNa}$  [M + Na] $^+$  316.0420, found 316.0426.



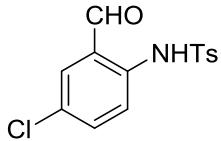
**N-(3-chloro-2-formylphenyl)-4-methylbenzenesulfonamide (3g).**

(white solid, 43 mg, 70% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  11.12 (s, 1H), 10.30 (s, 1H), 7.74 (d,  $J$  = 7.4 Hz, 2H), 7.58 (t,  $J$  = 7.8 Hz, 1H), 7.40 (d,  $J$  = 7.4 Hz, 2H), 7.29–7.35 (m, 2H), 2.36 (s, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 193.42, 144.94, 141.43, 138.45, 136.90, 135.90, 130.55, 127.55, 126.18, 120.34, 118.62, 21.48.

IR (film):  $\nu$  = 3102, 2861, 1644, 1610, 1510, 1440, 1348, 1113 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>12</sub>ClNO<sub>3</sub>SNa [M + Na]<sup>+</sup> 332.0124, found 332.0107.



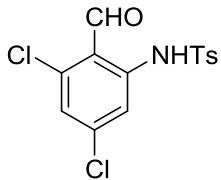
**N-(4-chloro-2-formylphenyl)-4-methylbenzenesulfonamide (3h).**

(white solid, 49 mg, 79% yield); <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 10.53 (s, 1H), 9.96 (s, 1H), 7.80 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 2.36 (s, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO-d6) δ 191.39, 144.54, 138.05, 135.92, 135.20, 130.64, 130.40, 130.20, 127.34, 126.10, 21.47.

IR (film):  $\nu$  = 3358, 3047, 1651, 1597, 1526, 1304, 1159, 1096 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>12</sub>ClNO<sub>3</sub>SNa [M + Na]<sup>+</sup> 332.0124, found 332.0116.



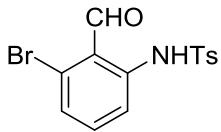
**N-(3,5-dichloro-2-formylphenyl)-4-methylbenzenesulfonamide (3i).**

(white solid, 66 mg, 97% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.25 (s, 1H), 10.20 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 2.35 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.29, 150.04, 146.88, 145.28, 144.59, 140.33, 135.45, 132.27, 130.45, 123.90, 122.68, 26.24.

IR (film):  $\nu$  = 3128, 2922, 1671, 1595, 1480, 1339, 1277, 1162, 1088 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>3</sub>SNa [M + Na]<sup>+</sup> 365.9734, found 365.9722.



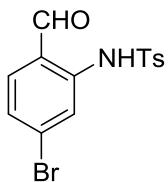
**N-(3-bromo-2-formylphenyl)-4-methylbenzenesulfonamide (3j).**

(white solid, 63 mg, 89% yield); <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 11.11 (s, 1H), 10.20 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.45–7.52 (m, 2H), 7.42 – 7.35 (m, 3H), 2.36 (s, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 195.35, 144.92, 141.43, 136.93, 135.93, 130.55, 129.66, 128.10, 127.55, 121.31, 119.33, 21.48.

IR (film):  $\nu$  = 3131, 2846, 1654, 1610, 1512, 1399, 1347, 1293, 1157 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>12</sub>BrNO<sub>3</sub>SNa [M + Na]<sup>+</sup> 375.9619, found 375.9617.



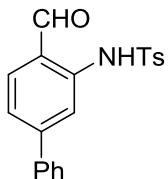
**N-(5-bromo-2-formylphenyl)-4-methylbenzenesulfonamide (3k).**

(white solid, 40 mg, 57% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  10.68 (s, 1H), 9.95 (s, 1H), 7.74 (d,  $J$  = 8.3 Hz, 1H), 7.62 (d,  $J$  = 8.2 Hz, 2H), 7.56 (dd,  $J$  = 8.3, 1.6 Hz, 1H), 7.40 (d,  $J$  = 8.1 Hz, 2H), 7.31 (d,  $J$  = 1.5 Hz, 1H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-d6)  $\delta$  192.26, 144.79, 140.31, 135.78, 133.58, 130.48, 129.00, 127.33, 127.02, 125.66, 21.47.

IR (film):  $\nu$  = 3175, 2858, 1670, 1595, 1484, 1394, 1338, 1303, 1190, 1161 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{BrNO}_3\text{SNa} [\text{M} + \text{Na}]^+$  375.9619, found 375.9623.



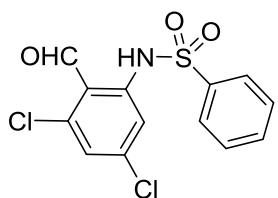
**N-(4-formyl-[1,1'-biphenyl]-3-yl)-4-methylbenzenesulfonamide (3l).**

(white solid, 60 mg, 86% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  10.63 (s, 1H), 10.05 (s, 1H), 7.90 (d,  $J$  = 7.8 Hz, 1H), 7.62-7.67 (m, 3H), 7.49-7.52 (m, 4H), 7.43-7.47 (m, 1H), 7.36-7.40 (m, 3H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.93, 146.96, 144.62, 139.81, 138.57, 136.00, 132.82, 130.40, 129.77, 129.51, 127.49, 127.35, 126.72, 124.24, 121.02, 21.43.

IR (film):  $\nu$  = 3151, 2912, 1664, 1595, 1473, 1381, 1278, 1194, 1167 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  374.0827, found 374.0826.



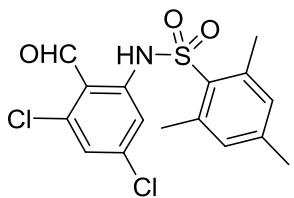
**N-(3,5-dichloro-2-formylphenyl)benzenesulfonamide (3m).**

(white solid, 54 mg, 83% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  11.25 (s, 1H), 10.21 (s, 1H), 7.87 (d,  $J$  = 7.3 Hz, 2H), 7.73 (t,  $J$  = 6.9 Hz, 1H), 7.64 (t,  $J$  = 7.0 Hz, 2H), 7.54 (s, 1H), 7.27 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.26, 142.11, 140.33, 139.48, 138.56, 134.55, 130.26, 127.43, 125.98, 119.91, 118.54.

IR (film):  $\nu$  = 3080, 2923, 1661, 1584, 1555, 1382, 1167, 1089 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_9\text{Cl}_2\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  351.9578, found 351.9586.



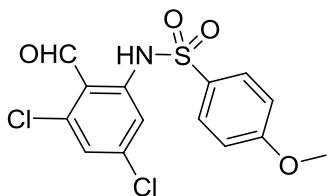
**N-(3,5-dichloro-2-formylphenyl)-2,4,6-trimethylbenzenesulfonamide (3n).**

(white solid, 69 mg, 93% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  11.52 (s, 1H), 10.26 (s, 1H), 7.47 (d,  $J = 1.8$  Hz, 1H), 7.13 (s, 2H), 7.08 (d,  $J = 1.6$  Hz, 1H), 2.58 (s, 6H), 2.26 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.53, 144.26, 142.28, 140.88, 140.78, 139.35, 132.81, 132.61, 132.14, 124.57, 117.11, 115.71, 22.48, 20.92.

IR (film):  $\nu = 3079, 2938, 1666, 1584, 1554, 1367, 1334, 1189, 1155 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{Cl}_2\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  394.0047, found 394.0055.



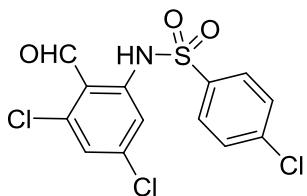
**N-(3,5-dichloro-2-formylphenyl)-4-methoxybenzenesulfonamide (3o).**

(white solid, 68 mg, 95% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  11.20 (s, 1H), 10.23 (s, 1H), 7.82 (d,  $J = 7.3$  Hz, 2H), 7.52 (s, 1H), 7.31 (s, 1H), 7.13 (d,  $J = 7.4$  Hz, 2H), 3.83 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.58, 163.83, 142.24, 140.55, 139.87, 129.87, 129.84, 125.57, 119.05, 117.85, 115.41, 56.30.

IR (film):  $\nu = 3100, 2926, 1668, 1584, 1556, 1254, 1159, 1090 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NO}_4\text{SNa} [\text{M} + \text{Na}]^+$  381.9684, found 381.9681.



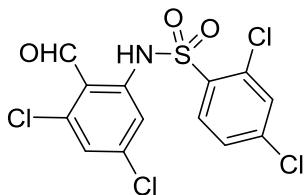
**4-chloro-N-(3,5-dichloro-2-formylphenyl)benzenesulfonamide (3p).**

(white solid, 63 mg, 88% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  11.24 (s, 1H), 10.20 (s, 1H), 7.88 (d,  $J = 7.6$  Hz, 2H), 7.70 (d,  $J = 7.5$  Hz, 2H), 7.58 (s, 1H), 7.27 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  191.99, 141.63, 140.26, 139.46, 139.32, 137.45, 130.39, 129.43, 126.44, 120.56, 119.10.

IR (film):  $\nu = 3098, 2921, 1665, 1583, 1556, 1467, 1381, 1182, 1165 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{Cl}_3\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  385.9188, found 385.9190.



**2,4-dichloro-N-(3,5-dichloro-2-formylphenyl)benzenesulfonamide (3q).**

(white solid, 75 mg, 95% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  12.13 (s, 1H), 10.30 (s, 1H), 7.79 –

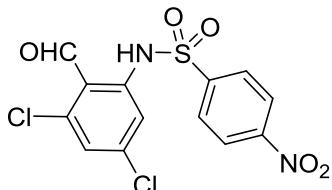
7.72 (m, 2H), 7.67 (dd,  $J$  = 9.0, 7.1 Hz, 1H), 7.54 (d,  $J$  = 1.6 Hz, 1H), 7.42 (d,  $J$  = 1.4 Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.51, 141.14, 141.06, 141.03, 135.84, 134.97, 132.86, 130.20,

125.21, 117.31, 115.70, 99.98.

IR (film):  $\nu$  = 3076, 2909, 1657, 1586, 1557, 1430, 1390, 1169, 1129 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_7\text{Cl}_4\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  419.8798, found 419.8784.



**N-(3,5-dichloro-2-formylphenyl)-4-nitrobenzenesulfonamide (3r).**

(white solid, 63 mg, 85% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  11.37 (s, 1H), 10.18 (s, 1H), 8.40

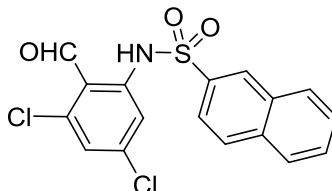
(d,  $J$  = 8.8 Hz, 2H), 8.11 (d,  $J$  = 8.8 Hz, 2H), 7.63 (d,  $J$  = 1.8 Hz, 1H), 7.26 (d,  $J$  = 1.8 Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  191.63, 150.84, 144.13, 141.25, 140.12, 138.95, 129.13, 126.95,

125.44, 121.56, 120.03.

IR (film):  $\nu$  = 3095, 2926, 1653, 1588, 1563, 1533, 1401, 1165, 1087 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_5\text{SNa} [\text{M} + \text{Na}]^+$  396.9429, found 396.9430.



**N-(3,5-dichloro-2-formylphenyl)naphthalene-2-sulfonamide (3s).**

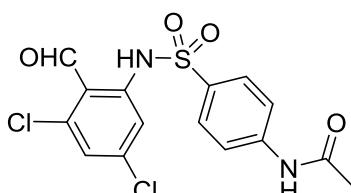
(white solid, 59 mg, 79% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  11.39 (s, 1H), 10.21 (s, 1H), 8.66 (s, 1H), 8.22 (d,  $J$  = 8.0 Hz, 1H), 8.15 (d,  $J$  = 8.7 Hz, 1H), 8.04 (d,  $J$  = 8.0 Hz, 1H), 7.83 (dd,  $J$  = 8.7, 1.8 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.49 (d,  $J$  = 1.7 Hz, 1H), 7.33 (d,  $J$  = 1.7 Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.41, 141.97, 140.43, 139.67, 135.43, 135.13, 132.05, 130.55,

130.09, 129.96, 129.29, 128.48, 128.37, 125.89, 122.18, 119.57, 118.25.

IR (film):  $\nu$  = 3083, 2915, 1659, 1588, 1560, 1465, 1376, 1161, 1154 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{11}\text{Cl}_2\text{NO}_3\text{SNa} [\text{M} + \text{Na}]^+$  401.9734, found 401.9731.



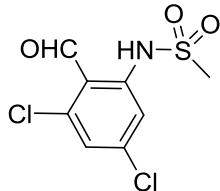
**N-(4-(N-(3,5-dichloro-2-formylphenyl)sulfamoyl)phenyl)acetamide (3t).**

(white solid, 74 mg, 97% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  11.21 (s, 1H), 10.39 (s, 1H), 10.22 (s, 1H), 7.82 (d,  $J$  = 8.0 Hz, 2H), 7.78 (d,  $J$  = 7.7 Hz, 2H), 7.52 (s, 1H), 7.29 (s, 1H), 2.08 (s, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 192.55, 169.68, 144.65, 142.22, 140.52, 139.82, 131.60, 129.40, 128.94, 125.65, 119.34, 117.98, 24.62.

IR (film):  $\nu$  = 3363, 3105, 2924, 1666, 1589, 1558, 1530, 1375, 1317, 1189, 1161 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SNa [M + Na]<sup>+</sup> 408.9793, found 408.9770.



**N-(3,5-dichloro-2-formylphenyl)methanesulfonamide (3u).**

(white solid, 38 mg, 73% yield); <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 10.91 (s, 1H), 10.32 (s, 1H), 7.57 (s, 2H), 3.34 (s, 3H).

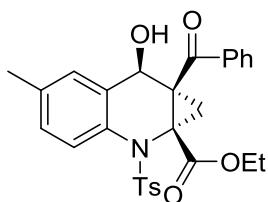
<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 192.85, 142.89, 141.04, 140.18, 124.91, 118.10, 117.55, 41.09.

IR (film):  $\nu$  = 3098, 2934, 1660, 1587, 1560, 1377, 1328, 1153 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>8</sub>H<sub>7</sub>Cl<sub>2</sub>NO<sub>3</sub>SNa [M + Na]<sup>+</sup> 289.9421, found 289.9436.

## 2.2 Typical Procedure for the Synthesis of 5

To a solution of **3** (0.10 mmol) and **4** (0.11 mmol) in 1.00 mL of DMF was added Cs<sub>2</sub>CO<sub>3</sub> (0.20 mmol), and the mixture was stirred at room temperature. The reaction was followed by TLC until all the starting material disappeared. After reaction completed, DCM (20.00 ml) was added, mixture washed with water three times and brine successively. Then the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated under vacuum, the crude product was analyzed by <sup>1</sup>H NMR to determine the *cis* / *trans* ratio, and then the residue was purified by column chromatography to give the corresponding product **5**.



**ethyl**

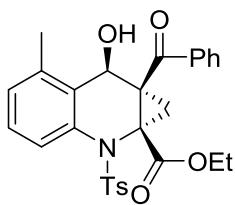
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-5-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5aa).**

(white solid, 42 mg, 84% yield); <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.60-7.70 (m, 2H), 7.54-7.59 (m, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.34-7.42 (m, 4H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 6.34 (s, 1H), 3.91 (s, 1H), 3.78-3.87 (m, 2H), 2.42 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.14 (s, 1H), 0.89-0.95 (m, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 193.40, 169.36, 144.48, 137.59, 137.48, 136.49, 135.42, 134.55, 133.61, 130.51, 129.23, 128.63, 128.37, 126.80, 124.96, 124.10, 72.10, 61.87, 51.67, 47.05, 27.48, 21.46, 21.26, 14.01.

IR (film):  $\nu$  = 3395, 2923, 1726, 1670, 1598, 1358, 1315, 1197, 1166, 1086 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>28</sub>H<sub>27</sub>NO<sub>6</sub>SNa [M + Na]<sup>+</sup> 528.1457, found 528.1421.



**ethyl**

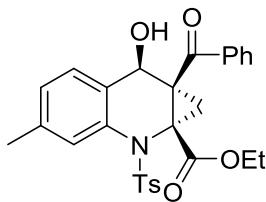
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-6-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ba).**

(white solid, 46 mg, 92% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.81 – 7.76 (m, 3H), 7.66 (t,  $J$  = 7.4 Hz, 1H), 7.61 (d,  $J$  = 8.3 Hz, 2H), 7.48 (t,  $J$  = 7.7 Hz, 2H), 7.32 (d,  $J$  = 8.2 Hz, 2H), 7.24 (t,  $J$  = 7.9 Hz, 1H), 6.96 (d,  $J$  = 7.6 Hz, 1H), 5.76 (d,  $J$  = 3.6 Hz, 1H), 4.96 (d,  $J$  = 3.1 Hz, 1H), 3.91 (qd,  $J$  = 7.0, 3.1 Hz, 2H), 2.56 (d,  $J$  = 5.6 Hz, 1H), 2.38 – 2.30 (m, 4H), 2.04 (s, 3H), 0.98 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  194.47, 169.42, 144.02, 137.74, 136.95, 136.73, 134.52, 134.37, 133.01, 129.90, 129.30, 129.16, 128.50, 127.87, 127.47, 121.36, 61.73, 59.78, 51.21, 49.00, 22.33, 21.46, 18.62, 14.09.

IR (film):  $\nu$  = 3454, 2982, 1734, 1714, 1671, 1596, 1471, 1344, 1191, 1160, 1090 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for C<sub>28</sub>H<sub>27</sub>NO<sub>6</sub>SNa [M + Na] $^+$  528.1457, found 528.1436.



**ethyl**

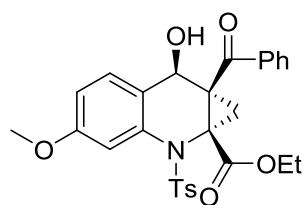
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-4-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ca).**

(white solid, 45 mg, 90% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.60-7.70 (m, 3H), 7.57-7.53 (m, 1H), 7.51 (d,  $J$  = 8.3 Hz, 2H), 7.33-7.40 (m, 4H), 7.16 (d,  $J$  = 7.7 Hz, 1H), 7.05 (d,  $J$  = 7.6 Hz, 1H), 6.34 (d,  $J$  = 5.9 Hz, 1H), 3.89 (d,  $J$  = 5.7 Hz, 1H), 3.82 (dd,  $J$  = 13.4, 6.5 Hz, 2H), 2.39-2.43 (m, 4H), 2.35 (s, 3H), 2.12 (d,  $J$  = 5.6 Hz, 1H), 0.90 (t,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.34, 169.33, 144.50, 137.59, 137.26, 136.91, 136.47, 134.74, 133.56, 130.49, 129.20, 128.63, 126.80, 126.75, 124.79, 124.25, 72.00, 61.86, 51.73, 46.97, 27.40, 21.50, 21.46, 13.98.

IR (film):  $\nu$  = 3420, 2922, 1725, 1670, 1596, 1451, 1357, 1315, 1197, 1168, 1087, 983 cm $^{-1}$ .

HRMS (ESI)  $m/z$  calcd for C<sub>28</sub>H<sub>27</sub>NO<sub>6</sub>SNa [M + Na] $^+$  528.1457, found 528.1447.



**ethyl**

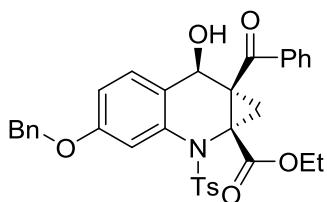
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-4-methoxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5da).**

(white solid, 38 mg, 73% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.60-7.70 (m, 2H), 7.56 (d,  $J$  = 8.2 Hz, 3H), 7.33-7.41 (m, 5H), 7.18 (d,  $J$  = 8.4 Hz, 1H), 6.82 (dd,  $J$  = 8.5, 2.3 Hz, 1H), 6.35 (d,  $J$  = 5.9 Hz, 1H), 3.95 (d,  $J$  = 6.0 Hz, 1H), 3.79-3.85 (m, 5H), 2.43 (d,  $J$  = 6.4 Hz, 1H), 2.35 (s, 3H), 2.14 (d,  $J$  = 4.7 Hz, 1H), 0.91 (t,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.33, 169.34, 159.03, 144.65, 137.77, 137.40, 136.47, 133.57, 130.54, 129.54, 129.18, 128.64, 127.82, 126.97, 125.23, 110.96, 110.59, 71.80, 61.92, 55.85, 51.75, 47.07, 27.57, 21.46, 13.98.

IR (film):  $\nu$  = 3491, 2923, 1726, 1685, 1670, 1610, 1448, 1352, 1205, 1167  $\text{cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{28}\text{H}_{27}\text{NO}_7\text{SNa}$  [M + Na] $^+$  544.1406, found 544.1420.



**ethyl**

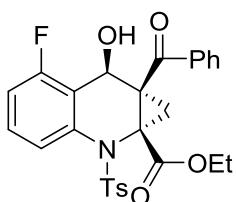
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-4-(benzyloxy)-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ea).**

(white solid, 46 mg, 79% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.58-7.72 (m, 2H), 7.42-7.56 (m, 8H), 7.41 – 7.27 (m, 5H), 7.17 (d,  $J$  = 7.9 Hz, 1H), 6.91 (d,  $J$  = 8.1 Hz, 1H), 6.32 (s, 1H), 5.18 (s, 2H), 3.94 (s, 1H), 3.76-3.85 (s, 2H), 2.43 (s, 1H), 2.36 (s, 3H), 2.13 (s, 1H), 0.86-0.94 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.31, 169.32, 158.02, 144.61, 137.71, 137.36, 137.30, 136.46, 133.55, 130.50, 129.78, 129.18, 128.95, 128.62, 128.36, 128.14, 126.98, 125.23, 112.21, 111.36, 71.78, 69.98, 61.91, 51.74, 47.09, 27.60, 21.46, 13.99.

IR (film):  $\nu$  = 3525, 2925, 1735, 1681, 1608, 1499, 1348, 1267, 1238, 1198, 1171, 1088, 1055  $\text{cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{34}\text{H}_{31}\text{NO}_7\text{SNa}$  [M + Na] $^+$  620.1719, found 620.1734.

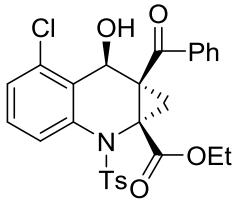


**ethyl**

**(1aS\*,7S\*,7aS\*)-7a-benzoyl-6-fluoro-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5fa).**

(white solid, 47 mg, 93% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.71-7.77 (m, 2H), 7.69 (d,  $J$  = 7.9 Hz, 1H), 7.54-7.63 (m, 3H), 7.47 – 7.36 (m, 5H), 7.01 (t,  $J$  = 9.3 Hz, 1H), 6.25 (s, 1H), 4.18 (s, 1H), 3.87 (d,  $J$  = 6.2 Hz, 2H), 2.44 (s, 1H), 2.38 (s, 3H), 2.25 (s, 1H), 0.92-0.97 (s, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 193.63, 169.08, 159.75 (d, *J* = 248.9 Hz), 144.85, 137.03, 136.60, 133.68, 130.62, 130.59, 129.28, 129.13 (d, *J* = 10.3 Hz), 128.70, 127.03, 124.38 (d, *J* = 9.7 Hz), 120.44 (d, *J* = 3.2 Hz), 115.08 (d, *J* = 22.2 Hz), 73.15, 62.04, 51.30, 47.06, 27.56, 21.49, 14.01.  
 IR (film):  $\nu$  = 3408, 2986, 1744, 1661, 1610, 1595, 1474, 1361, 1240, 1175, 1162, 1092 cm<sup>-1</sup>.  
 HRMS (ESI) *m/z* calcd for C<sub>27</sub>H<sub>24</sub>FNO<sub>6</sub>SNa [M + Na]<sup>+</sup> 532.1206, found 532.1216.



**ethyl**

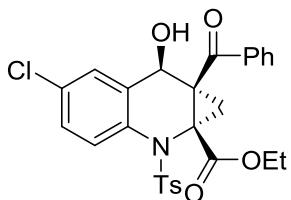
**(1aS\*,7S\*,7aS\*)-7a-benzoyl-6-chloro-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ga).**

(white solid, 39 mg, 75% yield); <sup>1</sup>H NMR (400 MHz, DMSO-d6) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 5.19 (d, *J* = 3.9 Hz, 1H), 3.93 (qd, *J* = 7.1, 3.1 Hz, 2H), 2.61 (d, *J* = 5.8 Hz, 1H), 2.38 (d, *J* = 5.4 Hz, 1H), 2.35 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 194.22, 169.13, 144.39, 139.81, 136.50, 134.65, 134.18, 133.00, 132.55, 130.21, 130.02, 129.46, 129.24, 127.90, 126.34, 122.62, 61.90, 60.69, 51.16, 48.99, 22.38, 21.48, 14.08.

IR (film):  $\nu$  = 3489, 2982, 1732, 1667, 1596, 1450, 1359, 1319, 1249, 1166, 1090, 1002 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>27</sub>H<sub>24</sub>ClNO<sub>6</sub>SNa [M + Na]<sup>+</sup> 548.0911, found 548.0913.



**ethyl**

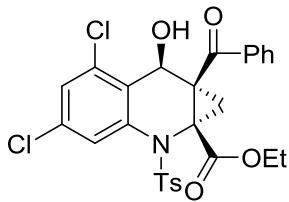
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-5-chloro-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ha).**

(white solid, 38 mg, 73% yield); <sup>1</sup>H NMR (500 MHz, DMSO-d6) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.66-7.76 (m, 2H), 7.58-7.63 (m, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.41-7.46 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.25 (s, 1H), 6.54 (s, 1H), 3.93 (s, 1H), 3.86 (d, *J* = 6.1 Hz, 2H), 2.47 (d, *J* = 4.6 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 1H), 0.91-0.96 (m, 3H).

<sup>13</sup>C NMR (126 MHz, DMSO-d6) δ 193.35, 169.07, 144.84, 140.17, 137.16, 136.38, 133.82, 130.77, 130.67, 129.28, 128.75, 127.98, 126.91, 125.82, 124.37, 71.81, 62.05, 51.30, 47.10, 27.59, 21.48, 14.01.

IR (film):  $\nu$  = 3386, 2923, 1726, 1667, 1597, 1468, 1364, 1317, 1244, 1189, 1168, 1088 cm<sup>-1</sup>.

HRMS (ESI) *m/z* calcd for C<sub>27</sub>H<sub>24</sub>ClNO<sub>6</sub>SNa [M + Na]<sup>+</sup> 548.0911, found 548.0906.



**ethyl**

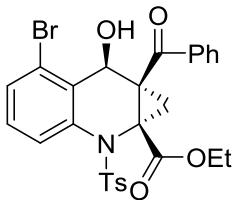
**(1aS\*,7S\*,7aS\*)-7a-benzoyl-4,6-dichloro-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ia).**

(white solid, 30 mg, 54% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.92 (s, 1H), 7.87 (d,  $J$  = 7.1 Hz, 2H), 7.72 (t,  $J$  = 6.9 Hz, 1H), 7.64 (d,  $J$  = 7.5 Hz, 2H), 7.56 (d,  $J$  = 6.8 Hz, 2H), 7.49 (s, 1H), 7.38 (d,  $J$  = 7.5 Hz, 2H), 6.23 (s, 1H), 5.15 (s, 1H), 4.01 – 3.92 (m, 2H), 2.59 (s, 1H), 2.34–2.40 (m, 4H), 0.99–1.05 (m, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  194.10, 184.14, 168.90, 144.79, 140.72, 136.06, 134.80, 134.03, 133.89, 133.80, 131.98, 130.21, 129.54, 129.26, 127.91, 125.88, 122.48, 62.06, 60.41, 51.01, 48.84, 22.19, 21.52, 14.09.

IR (film):  $\nu$  = 3478, 2924, 1732, 1678, 1584, 1565, 1449, 1363, 1248, 1166, 1090, 1022 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{23}\text{Cl}_2\text{NO}_6\text{SNa} [\text{M} + \text{Na}]^+$  582.0521, found 582.0515.



**ethyl**

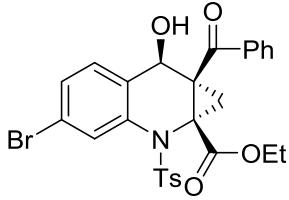
**(1aS\*,7S\*,7aS\*)-7a-benzoyl-6-bromo-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ja).**

(white solid, 44 mg, 78% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.95 (d,  $J$  = 7.9 Hz, 1H), 7.85 (d,  $J$  = 7.3 Hz, 2H), 7.70 (t,  $J$  = 7.4 Hz, 1H), 7.63 (d,  $J$  = 8.3 Hz, 2H), 7.53 (t,  $J$  = 7.7 Hz, 2H), 7.40 (dd,  $J$  = 8.0, 0.7 Hz, 1H), 7.34 (d,  $J$  = 8.1 Hz, 3H), 6.14 (d,  $J$  = 3.9 Hz, 1H), 5.17 (d,  $J$  = 3.8 Hz, 1H), 3.97 – 3.87 (m, 2H), 2.61 (d,  $J$  = 5.8 Hz, 1H), 2.37 (d,  $J$  = 5.8 Hz, 1H), 2.35 (s, 3H), 0.99 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  194.17, 169.11, 144.38, 139.97, 136.52, 134.64, 134.26, 134.21, 130.62, 130.02, 129.54, 129.46, 129.24, 127.93, 123.69, 123.26, 63.70, 61.90, 51.45, 49.02, 22.42, 21.49, 14.08.

IR (film):  $\nu$  = 3447, 2924, 1730, 1699, 1674, 1597, 1450, 1370, 1354, 1264, 1165, 1089 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{24}\text{BrNO}_6\text{SNa} [\text{M} + \text{Na}]^+$  592.0405, found 528.0413.



**ethyl**

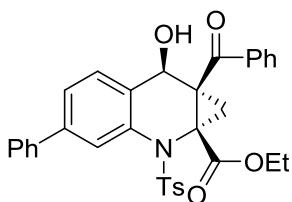
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-4-bromo-7-hydroxy-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropan[b]quinoline-1a-carboxylate (5ka).**

(white solid, 32 mg, 57% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.97 (d,  $J = 1.5$  Hz, 1H), 7.66–7.78 (m, 2H), 7.54–7.62 (m, 3H), 7.48 – 7.36 (m, 5H), 7.23 (d,  $J = 8.2$  Hz, 1H), 6.52 (d,  $J = 6.0$  Hz, 1H), 3.92 – 3.82 (m, 3H), 2.44 (d,  $J = 6.6$  Hz, 1H), 2.36 (s, 3H), 2.20 (d,  $J = 5.7$  Hz, 1H), 0.93 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.31, 169.04, 144.98, 138.52, 137.39, 137.07, 136.34, 133.79, 130.72, 129.28, 129.02, 128.75, 126.90, 126.49, 126.43, 120.28, 71.90, 62.07, 51.38, 47.07, 27.40, 21.49, 14.00.

IR (film):  $\nu = 3425, 2989, 1730, 1669, 1595, 1450, 1357, 1316, 1228, 1168, 1050 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{24}\text{BrNO}_6\text{SNa} [\text{M} + \text{Na}]^+$  592.0405, found 528.0413.



**ethyl**

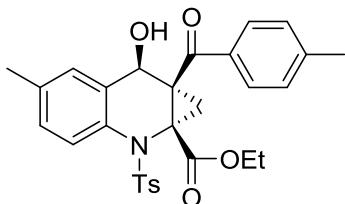
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-4-phenyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropan[b]quinoline-1a-carboxylate (5la).**

(white solid, 43 mg, 77% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  8.02 (s, 1H), 7.69–7.77 (m, 2H), 7.67 (d,  $J = 7.7$  Hz, 2H), 7.62 (d,  $J = 8.3$  Hz, 2H), 7.53–7.59 (m, 4H), 7.35–7.47 (m, 6H), 6.49 (d,  $J = 6.0$  Hz, 1H), 4.06 (d,  $J = 5.8$  Hz, 1H), 3.91 – 3.80 (m, 2H), 2.48 (d,  $J = 6.5$  Hz, 1H), 2.36 (s, 3H), 2.24 (d,  $J = 5.6$  Hz, 1H), 0.93 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  193.44, 169.32, 144.78, 140.00, 139.93, 137.41, 136.95, 136.47, 133.67, 130.61, 129.65, 129.26, 128.69, 128.29, 127.13, 127.09, 125.09, 124.44, 122.27, 72.08, 61.98, 51.60, 47.03, 27.72, 21.48, 14.04.

IR (film):  $\nu = 3474, 2924, 1724, 1676, 1609, 1596, 1480, 1318, 1108, 1164, 1051 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{NO}_6\text{SNa} [\text{M} + \text{Na}]^+$  590.1613, found 590.1620.



**ethyl**

**(1aS\*,7R\*,7aS\*)-7-hydroxy-5-methyl-7a-(4-methylbenzoyl)-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropan[b]quinoline-1a-carboxylate (5ab).**

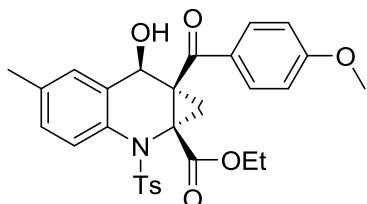
(white solid, 44 mg, 86% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.72 (d,  $J = 7.6$  Hz, 1H), 7.64–7.52 (m, 2H), 7.52 (d,  $J = 7.0$  Hz, 2H), 7.36 (d,  $J = 7.3$  Hz, 2H), 7.22–7.14 (m, 3H), 7.11 (s, 1H), 6.29 (s,

1H), 3.89 (s, 1H), 3.86-3.77 (m, 2H), 2.42 (d,  $J$  = 4.7 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 2.12 (s, 1H), 0.96-0.88 (m, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.88, 169.35, 144.45, 144.05, 137.61, 137.51, 135.38, 134.56, 134.11, 130.50, 129.39, 129.19, 128.33, 126.78, 124.94, 124.07, 72.15, 61.81, 51.67, 46.97, 27.49, 21.58, 21.45, 21.27, 14.01.

IR (film):  $\nu$  = 3498, 2924, 1733, 1681, 1606, 1488, 1351, 1319, 1245, 1176, 1156, 1086 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{29}\text{H}_{29}\text{NO}_6\text{SNa}$  [M + Na]<sup>+</sup> 542.1613, found 542.1607.



ethyl

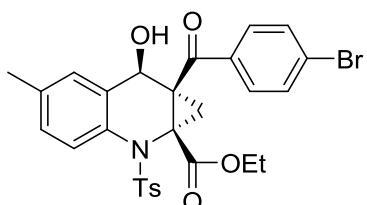
**(1aS\*,7R\*,7aS\*)-7a-(4-methoxybenzoyl)-5-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ac).**

(white solid, 44 mg, 83% yield);  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.72 (d,  $J$  = 6.6 Hz, 2H), 7.52 (d,  $J$  = 7.3 Hz, 2H), 7.38-7.29 (m, 3H), 7.20 (d,  $J$  = 4.9 Hz, 1H), 7.12 (s, 1H), 7.00-6.82 (m, 2H), 6.27 (s, 1H), 3.88 (s, 1H), 3.86-3.76 (m, 5H), 2.42 (s, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 2.12 (s, 1H), 0.98-0.88 (m, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  191.75, 169.38, 163.53, 144.44, 137.65, 137.54, 135.35, 134.66, 131.64, 130.49, 129.67, 128.30, 126.78, 124.89, 124.02, 113.86, 72.16, 61.77, 56.00, 51.65, 46.96, 27.68, 21.45, 21.26, 14.02.

IR (film):  $\nu$  = 3475, 2927, 1729, 1664, 1599, 1487, 1356, 1256, 1167, 1089 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{29}\text{H}_{29}\text{NO}_7\text{SNa}$  [M + Na]<sup>+</sup> 558.1562, found 558.1525.



ethyl

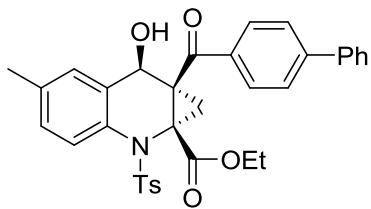
**(1aS\*,7R\*,7aS\*)-7a-(4-bromobenzoyl)-5-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ad).**

(white solid, 47 mg, 81% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-d6)  $\delta$  7.70 (d,  $J$  = 8.1 Hz, 1H), 7.66-7.59 (m, 4H), 7.50 (d,  $J$  = 8.3 Hz, 2H), 7.35 (d,  $J$  = 8.1 Hz, 2H), 7.19 (d,  $J$  = 8.1 Hz, 1H), 7.09 (s, 1H), 6.40 (d,  $J$  = 5.9 Hz, 1H), 3.90-3.81 (m, 3H), 2.42 (d,  $J$  = 6.4 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.16 (d,  $J$  = 5.9 Hz, 1H), 0.94 (t,  $J$  = 7.0 Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.76, 169.32, 144.49, 137.55, 137.32, 135.55, 135.46, 134.57, 131.81, 131.16, 130.50, 128.42, 127.85, 126.78, 124.91, 124.09, 72.10, 61.96, 51.52, 47.09, 27.52, 21.45, 21.25, 14.06.

IR (film):  $\nu$  = 3485, 2922, 1728, 1686, 1587, 1488, 1397, 1350, 1226, 1194, 1159, 1084 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $C_{28}H_{26}BrNO_6SNa$  [M + Na]<sup>+</sup> 606.0562, found 606.0560.



**ethyl**

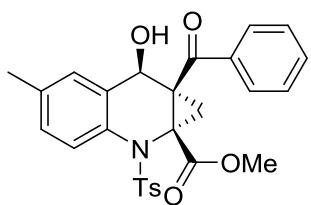
**(1aS\*,7R\*,7aS\*)-7a-((1,1'-biphenyl)-4-carbonyl)-7-hydroxy-5-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5ae).**

(white solid, 51 mg, 88% yield);  $^1H$  NMR (400 MHz, DMSO-d6)  $\delta$  7.77-7.66 (m, 6H), 7.55-7.51 (m, 3H), 7.49 (d,  $J$  = 7.7 Hz, 2H), 7.43 (t,  $J$  = 7.3 Hz, 1H), 7.36 (d,  $J$  = 8.2 Hz, 2H), 7.21 (d,  $J$  = 7.8 Hz, 1H), 7.13 (s, 1H), 6.41 (d,  $J$  = 5.4 Hz, 1H), 3.93 (d,  $J$  = 5.9 Hz, 1H), 3.89-3.80 (m, 2H), 2.48 (d,  $J$  = 6.4 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.20 (d,  $J$  = 6.1 Hz, 1H), 1.00-0.90 (m, 3H).

$^{13}C$  NMR (126 MHz, DMSO-d6)  $\delta$  192.99, 169.41, 145.00, 144.47, 139.30, 137.61, 137.49, 135.43, 134.63, 130.49, 130.00, 129.54, 128.87, 128.37, 127.54, 127.46, 126.84, 126.81, 124.96, 124.09, 72.22, 61.91, 51.75, 47.09, 27.58, 21.46, 21.27, 14.06.

IR (film):  $\nu$  = 3475, 2925, 1727, 1665, 1601, 1486, 1356, 1317, 1252, 1188, 1164, 1089 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $C_{34}H_{31}NO_6SNa$  [M + Na]<sup>+</sup> 604.1770, found 604.1776.



**methyl**

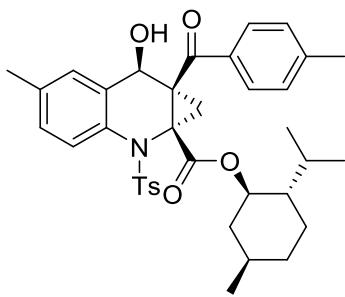
**(1aS\*,7R\*,7aS\*)-7a-benzoyl-7-hydroxy-5-methyl-2-tosyl-1,2,7,7a-tetrahydro-1aH-cyclopropa[b]quinoline-1a-carboxylate (5af).**

(white solid, 45 mg, 93% yield);  $^1H$  NMR (400 MHz, DMSO-d6)  $\delta$  7.76-7.66 (m, 3H), 7.61 – 7.56 (m, 1H), 7.51 (d,  $J$  = 8.2 Hz, 2H), 7.41 (t,  $J$  = 7.3 Hz, 2H), 7.36 (d,  $J$  = 8.2 Hz, 2H), 7.21 (d,  $J$  = 8.0 Hz, 1H), 7.11 (s, 1H), 6.39 (d,  $J$  = 5.9 Hz, 1H), 3.89 (d,  $J$  = 5.7 Hz, 1H), 3.41 (s, 3H), 2.43 (d,  $J$  = 6.4 Hz, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.17 (d,  $J$  = 5.8 Hz, 1H).

$^{13}C$  NMR (126 MHz, DMSO-d6)  $\delta$  193.62, 170.01, 144.51, 137.51, 137.38, 136.50, 135.47, 134.51, 133.59, 130.51, 129.19, 128.67, 128.39, 126.77, 124.94, 124.14, 72.08, 53.00, 51.83, 47.09, 27.61, 21.46, 21.26.

IR (film):  $\nu$  = 3429, 2949, 1733, 1675, 1598, 1487, 1448, 1357, 1325, 1238, 1164, 1068 cm<sup>-1</sup>.

HRMS (ESI)  $m/z$  calcd for  $C_{27}H_{25}NO_6SNa$  [M + Na]<sup>+</sup> 514.1300, found 514.1312.



**(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl**

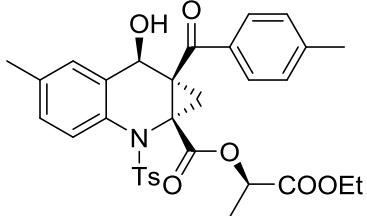
**(1aS,7R,7aS)-7-hydroxy-5-methyl-7a-(4-methylbenzoyl)-2-tosyl-1,2,7,7a-tetrahydro-1aH-cycl opropa[b]quinoline-1a-carboxylate (5ag).**

(white solid, 44 mg, 70% yield);  $[\alpha]_{D}^{23} = -37.38$  ( $c = 1.0$  in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.79-7.68 (m, 1H), 7.61-7.55 (m, 1H), 7.52 (d,  $J = 7.6$  Hz, 2H), 7.46 (d,  $J = 7.6$  Hz, 1H), 7.36-7.31 (m, 2H), 7.30-7.23 (m, 1H), 7.19 (d,  $J = 7.2$  Hz, 1H), 7.09 (s, 3H), 6.28 (s, 1H), 4.42-4.25 (m, 1H), 3.90-3.77 (m, 1H), 2.39-2.27 (m, 10H), 2.19-2.07 (m, 1H), 1.63-1.50 (m, 3H), 1.36-1.23 (m, 2H), 1.21-1.12 (m, 1H), 0.86 (d,  $J = 6.1$  Hz, 2H), 0.78 (s, 3H), 0.74 (s, 3H), 0.62 (d,  $J = 4.6$  Hz, 2H), 0.52 (d,  $J = 4.9$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.45, 168.86, 144.35, 143.83, 137.76, 137.74, 135.29, 134.52, 134.25, 130.46, 129.82, 129.34, 129.09, 128.06, 126.80, 125.00, 124.14, 75.87, 72.25, 60.22, 51.57, 47.29, 46.76, 34.06, 31.00, 27.61, 25.70, 23.17, 22.28, 21.54, 21.44, 21.28, 20.98, 16.51.

IR (film):  $\nu = 3484, 2954, 2926, 2868, 1725, 1675, 1606, 1488, 1450, 1357, 1251, 1164, 1090 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{43}\text{NO}_6\text{SNa} [\text{M} + \text{Na}]^+$  652.2709, found 652.2692.



**(R)-1-ethoxy-1-oxopropan-2-yl**

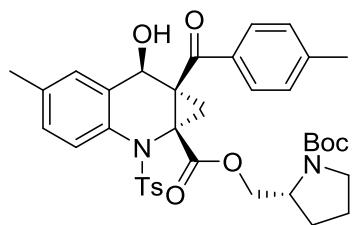
**(1aS,7R,7aS)-7-hydroxy-5-methyl-7a-(4-methylbenzoyl)-2-tosyl-1,2,7,7a-tetrahydro-1aH-cycl opropa[b]quinoline-1a-carboxylate (5ah).**

(white solid, 51 mg, 87% yield);  $[\alpha]_{D}^{23} = -3.24$  ( $c = 1.0$  in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.69 (d,  $J = 8.0$  Hz, 1H), 7.58 (d,  $J = 7.8$  Hz, 1H), 7.56 – 7.47 (m, 3H), 7.35 (d,  $J = 6.4$  Hz, 2H), 7.24-7.14 (m, 3H), 7.10 (d,  $J = 9.6$  Hz, 1H), 6.31 (s, 1H), 4.63 (s, 1H), 4.10 – 3.99 (m, 2H), 3.89 (dd,  $J = 16.6, 5.5$  Hz, 1H), 2.45 – 2.40 (m, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H), 2.24 (d,  $J = 10.0$  Hz, 1H), 1.22 (d,  $J = 6.5$  Hz, 1H), 1.17 (t,  $J = 7.0$  Hz, 1H), 1.12 (t,  $J = 7.0$  Hz, 2H), 1.03 (d,  $J = 6.4$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.55, 169.75, 168.72, 144.46, 144.14, 137.56, 133.93, 130.49, 130.47, 129.46, 129.23, 129.14, 128.33, 126.98, 126.83, 124.93, 124.26, 69.90, 61.36, 51.91, 46.75, 21.59, 21.46, 21.27, 16.90, 16.62, 14.28, 14.20.

IR (film):  $\nu = 3413, 2923, 1743, 1666, 1606, 1488, 1448, 1356, 1254, 1191, 1165, 1088, 1050, 980 \text{ cm}^{-1}$ .

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{33}\text{NO}_8\text{SNa} [\text{M} + \text{Na}]^+$  614.1825, found 614.1823.



**((R)-1-(tert-butoxycarbonyl)pyrrolidin-2-yl)methyl  
(1aS,7R,7aS)-7-hydroxy-5-methyl-7a-(4-methylbenzoyl)-2-tosyl-1,2,7,7a-tetrahydro-1aH-cycl  
opropo[b]quinoline-1a-carboxylate (5ai).**

(white solid, 40 mg, 61% yield);  $[\alpha]_{D}^{25} = -21.49$  ( $c = 1.0$  in  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz, DMSO-d6)  $\delta$  7.74 (d,  $J = 7.2$  Hz, 1H), 7.66 – 7.51 (m, 2H), 7.50 (d,  $J = 7.5$  Hz, 2H), 7.36 (d,  $J = 7.4$  Hz, 2H), 7.24 – 7.13 (m, 3H), 7.10 (s, 1H), 6.29 (s, 1H), 4.08–3.92 (m, 1H), 3.85 (s, 1H), 3.76–3.55 (m, 2H), 3.26–3.10 (m, 2H), 2.40 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.12 (s, 1H), 1.84 – 1.59 (m, 4H), 1.41 – 1.30 (m, 9H).

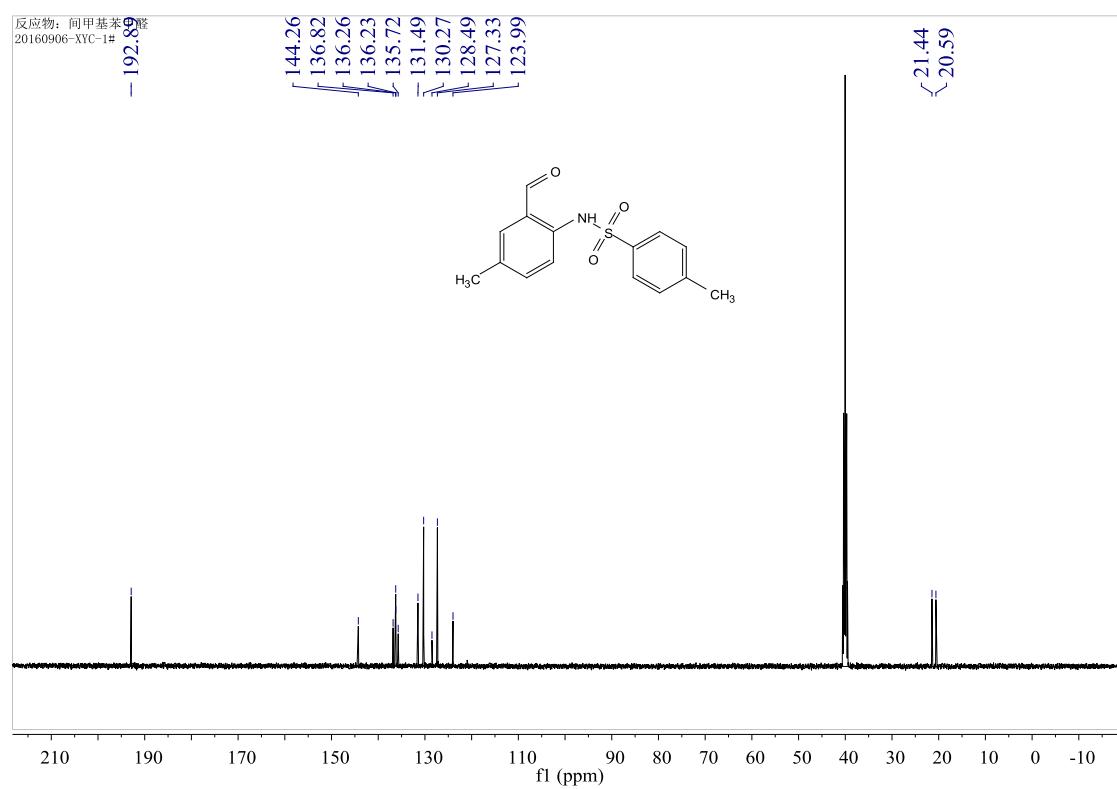
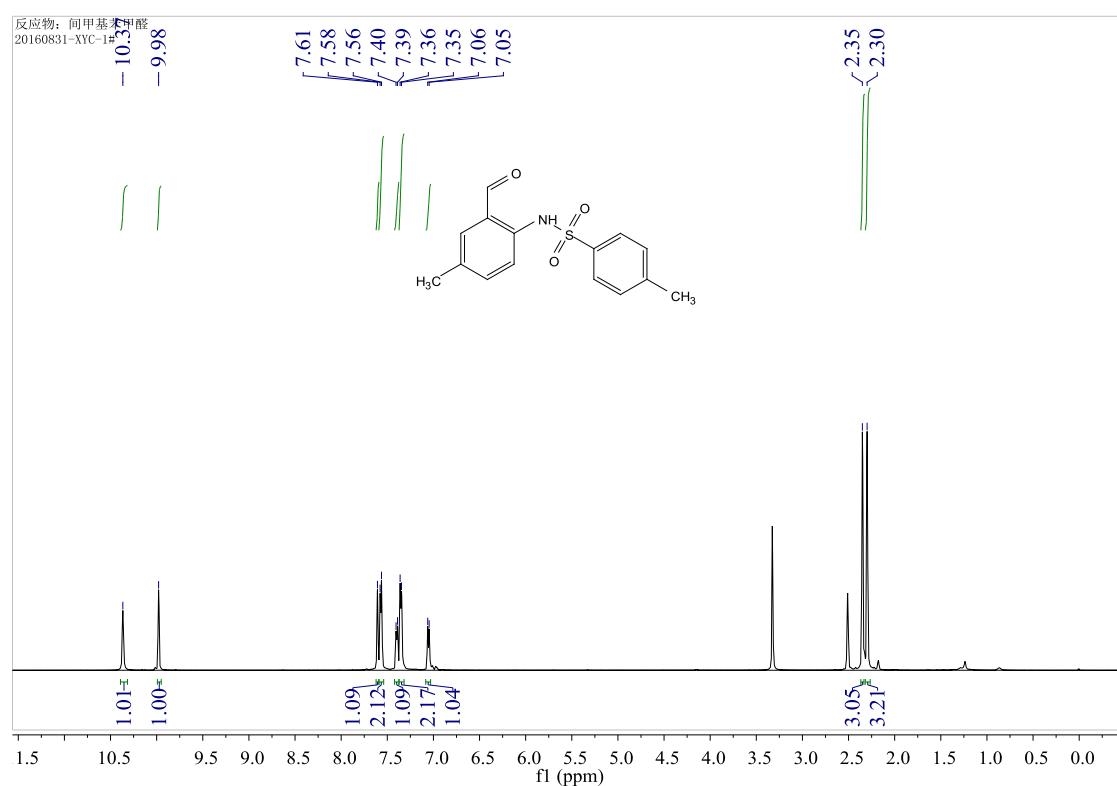
$^{13}\text{C}$  NMR (126 MHz, DMSO-d6)  $\delta$  192.73, 170.77, 169.50, 169.34, 144.48, 144.02, 137.59, 137.47, 135.48, 134.51, 134.08, 130.52, 129.34, 129.16, 128.32, 126.70, 125.01, 124.14, 79.02, 72.11, 65.15, 60.21, 55.40, 52.06, 47.06, 28.57, 27.58, 23.54, 22.78, 21.57, 21.45, 21.27, 21.21, 14.55.

IR (film):  $\nu = 3434, 2975, 1736, 1673, 1606, 1487, 1454, 1395, 1359, 1252, 1165 \text{ cm}^{-1}$ .

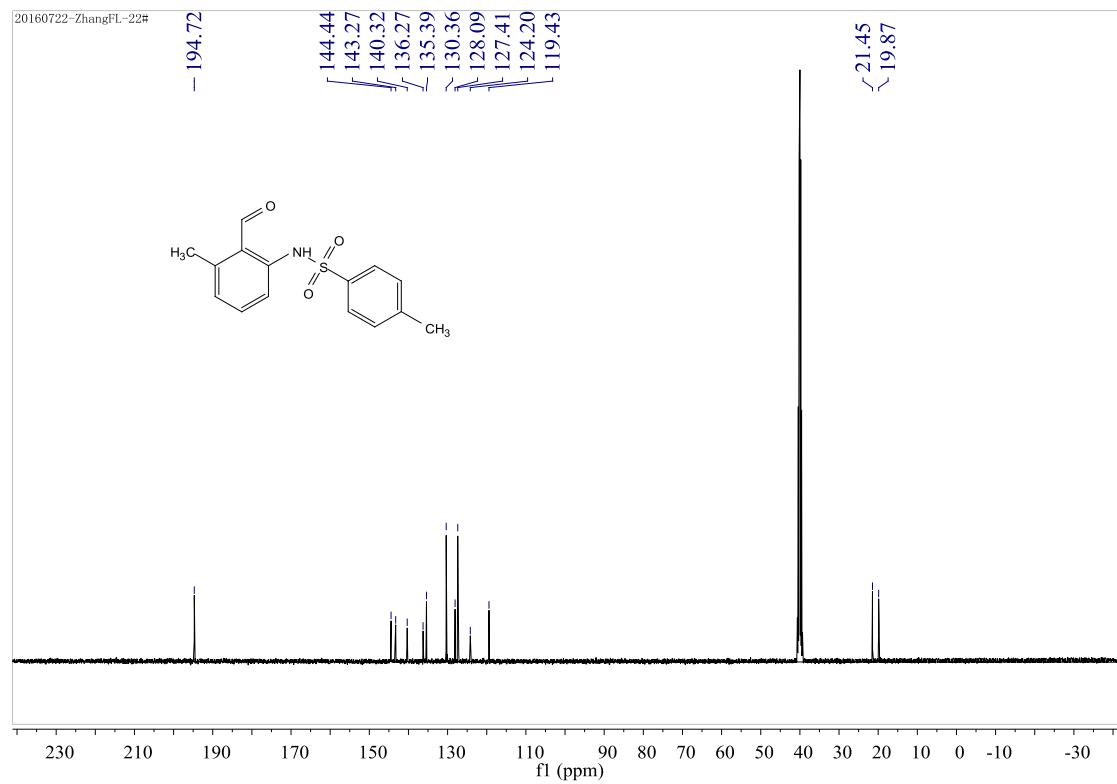
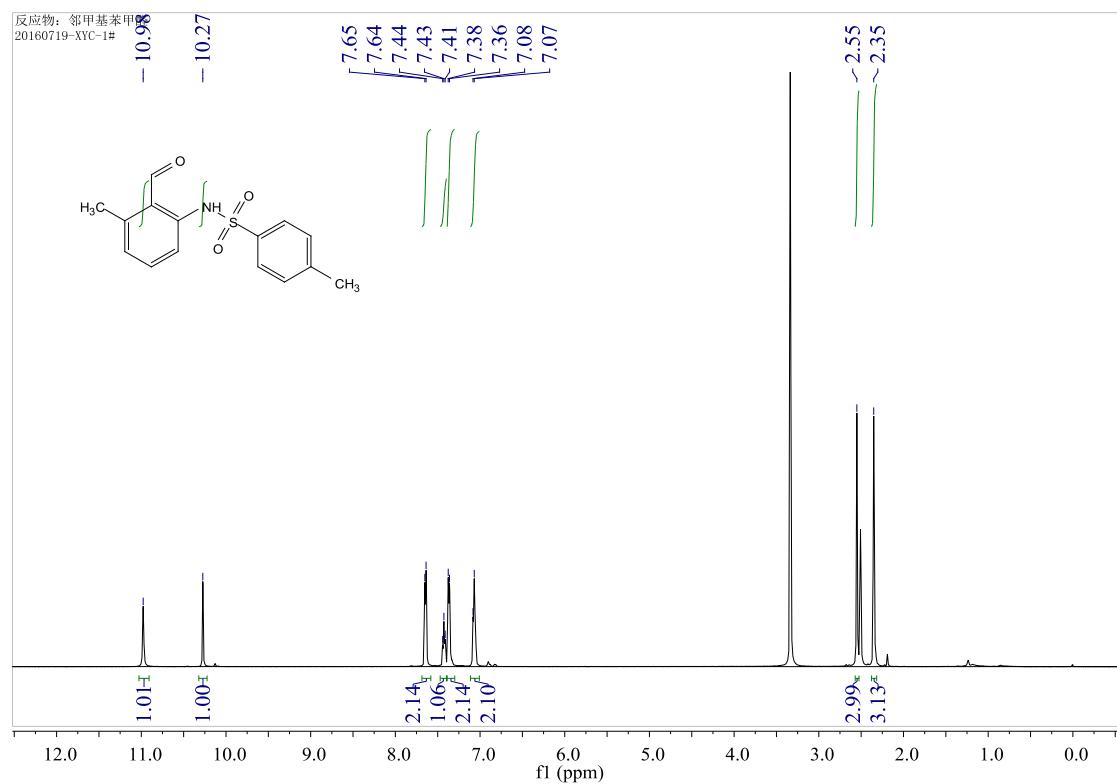
HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_8\text{SNa} [\text{M} + \text{Na}]^+$  697.2560, found 697.2532.

#### 4. NMR spectra for all compounds

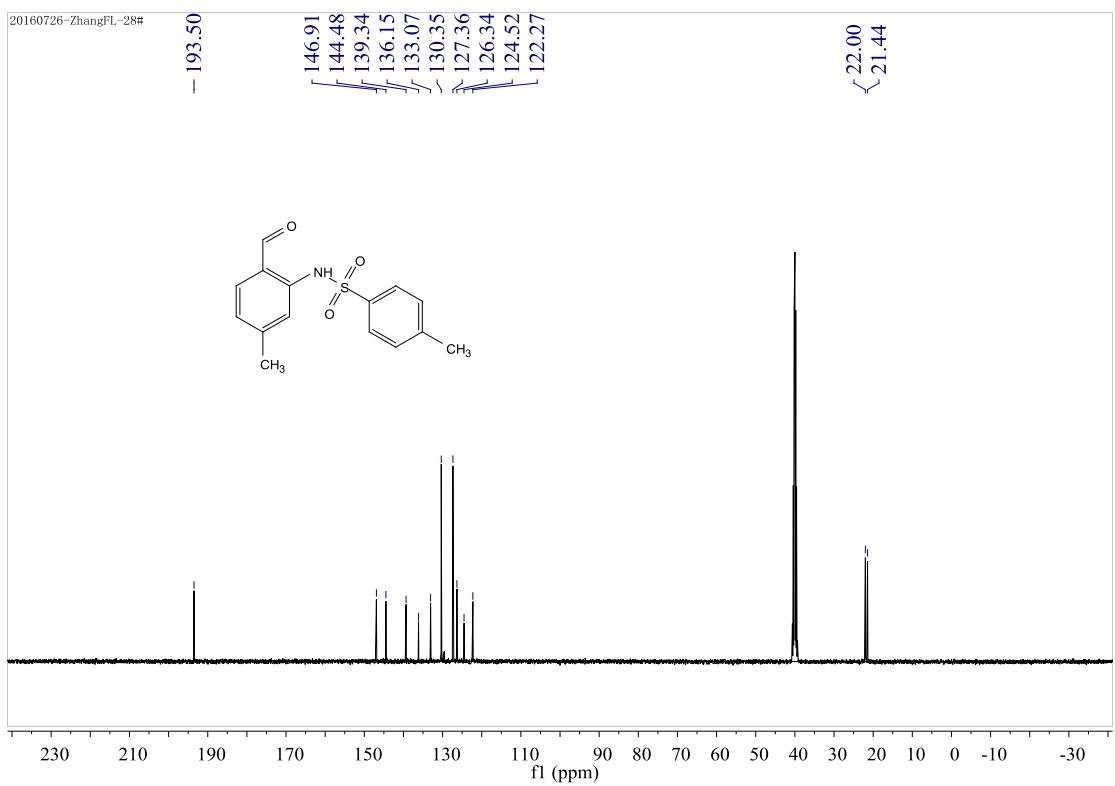
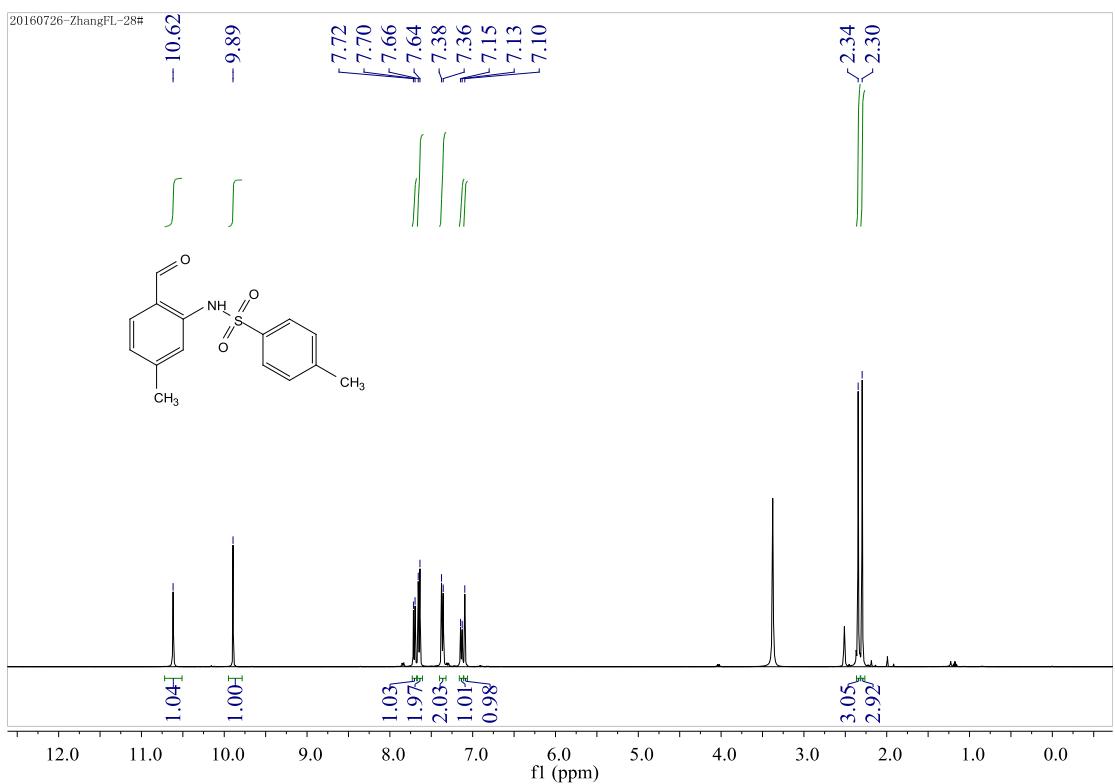
##### 1. 3a



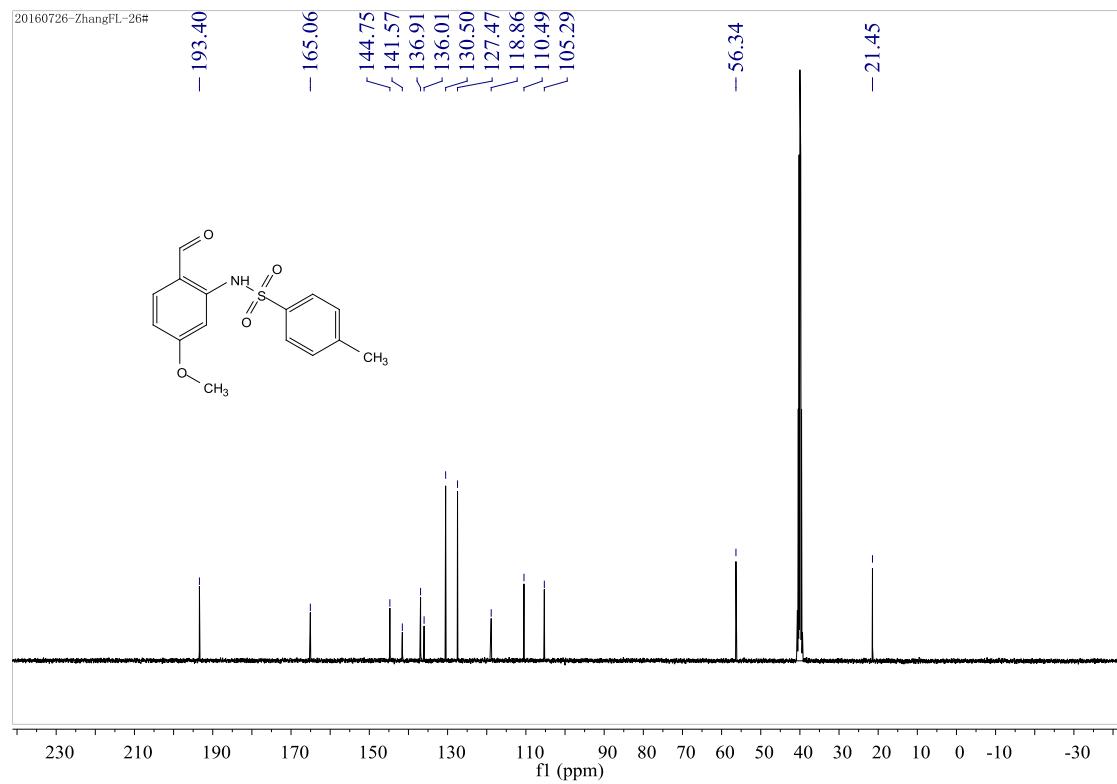
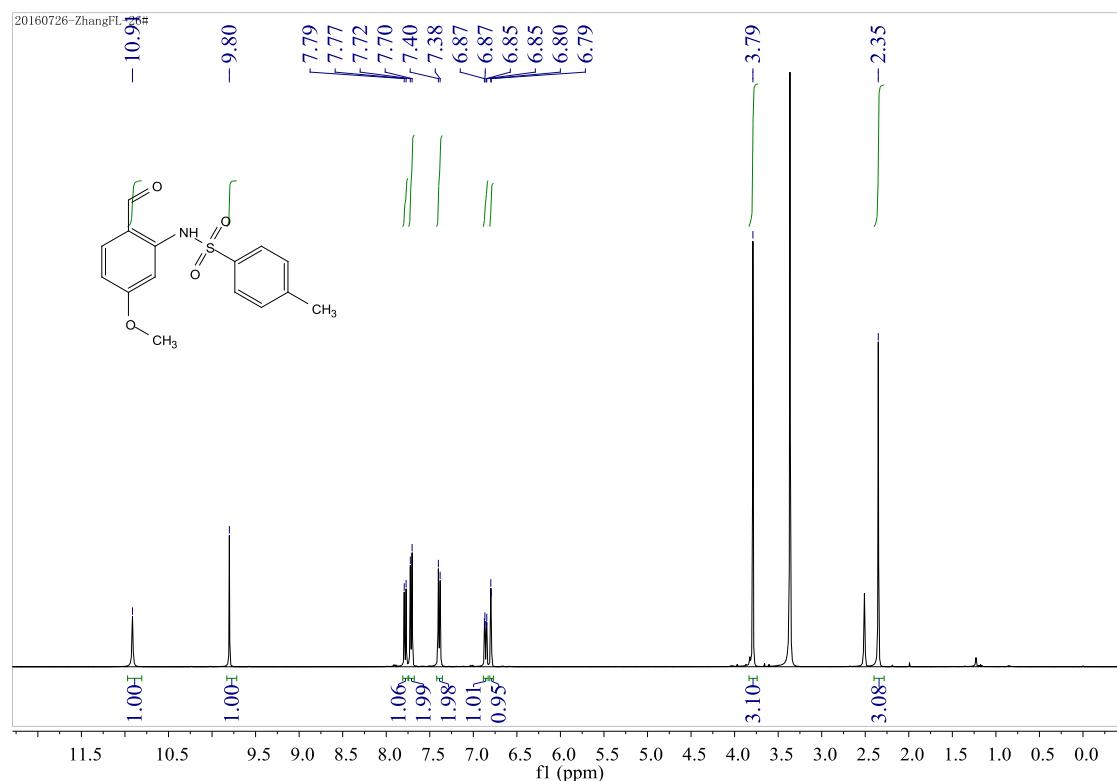
## 2. 3b



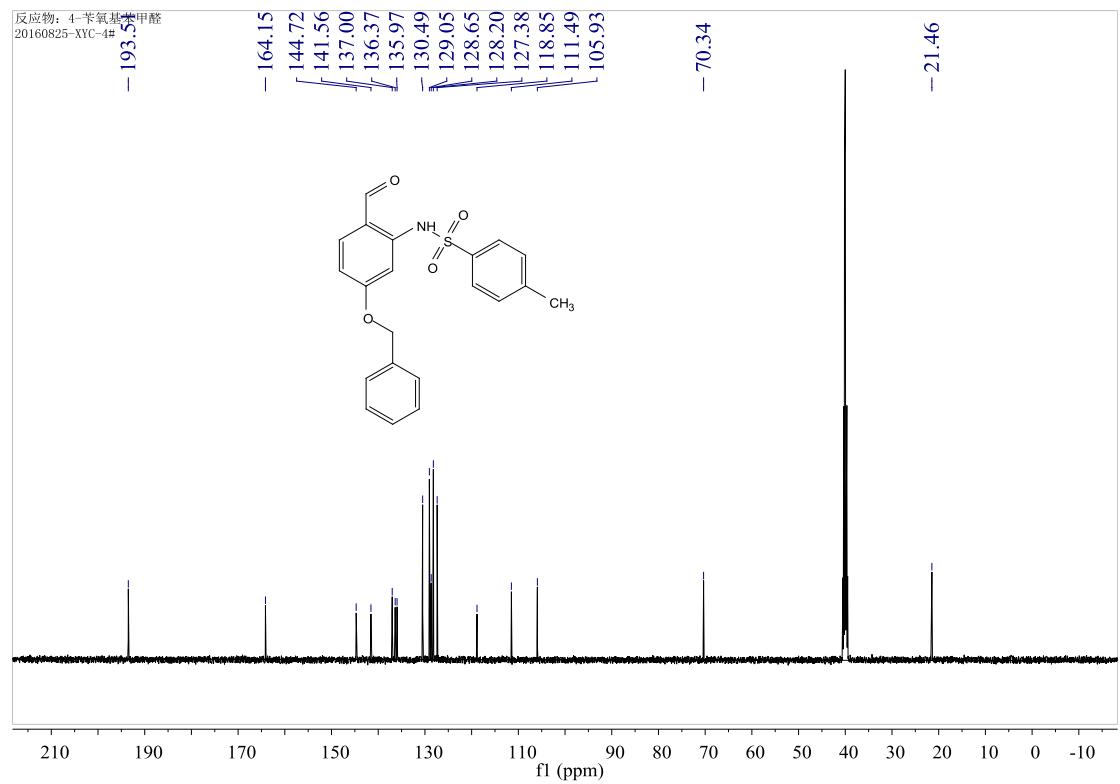
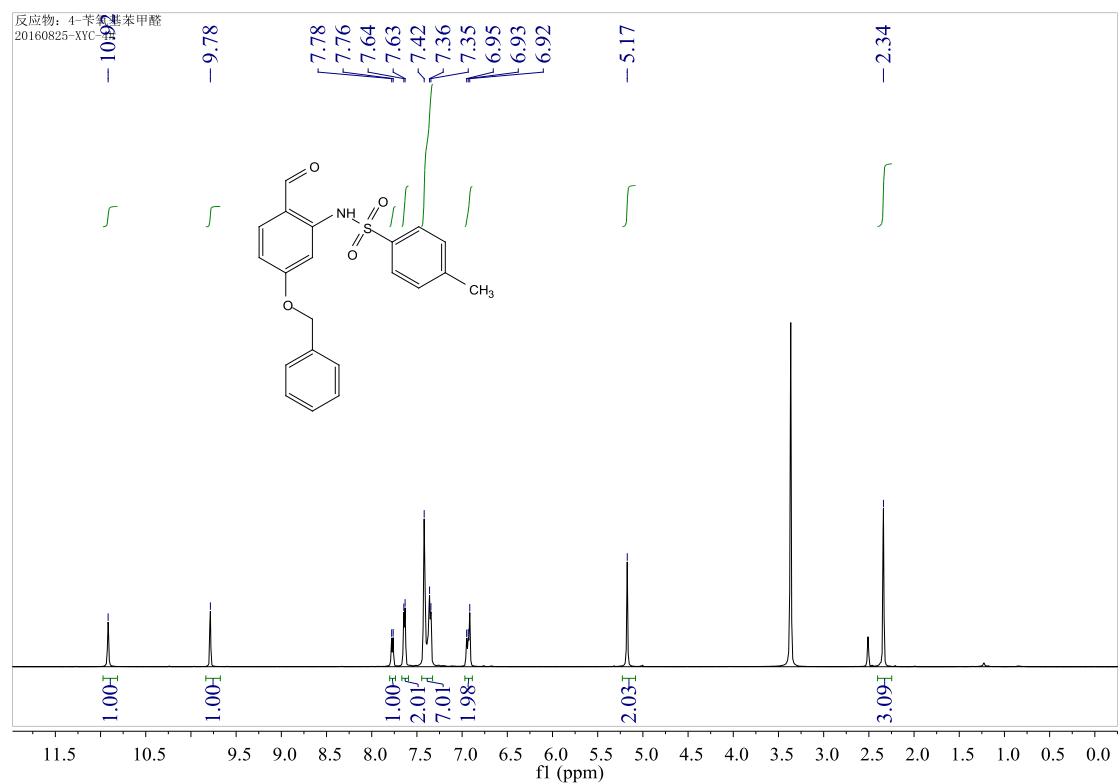
3. 3c



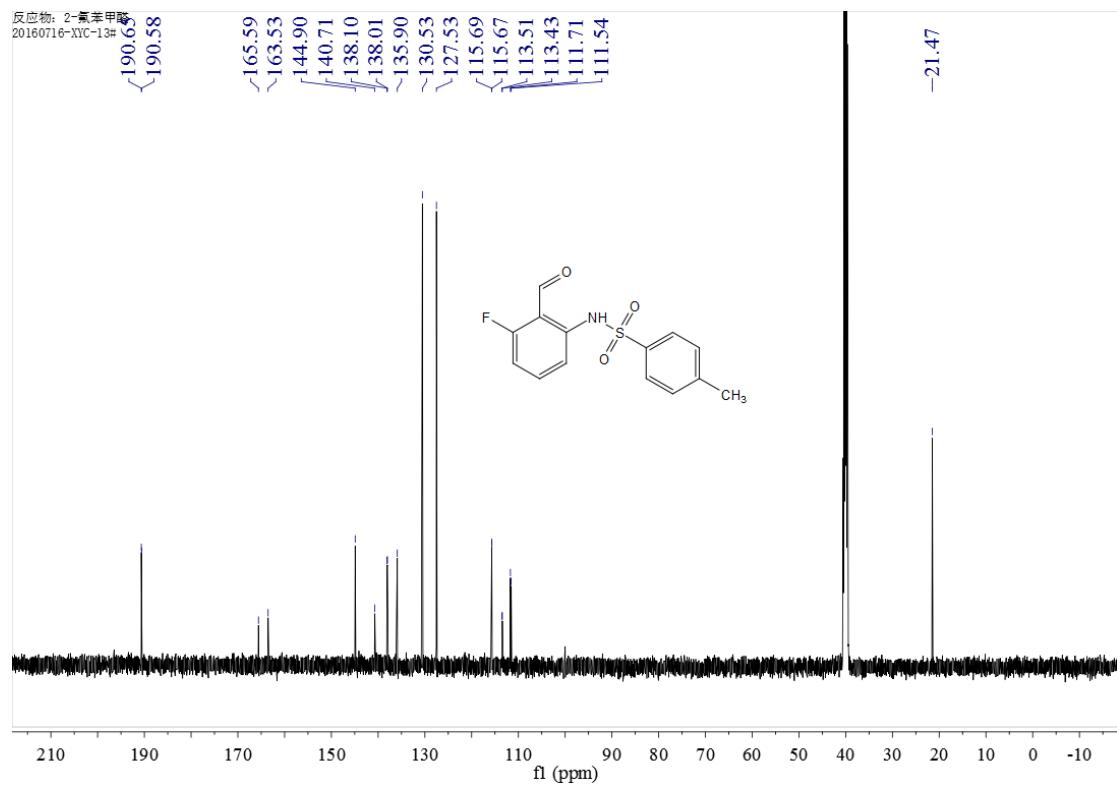
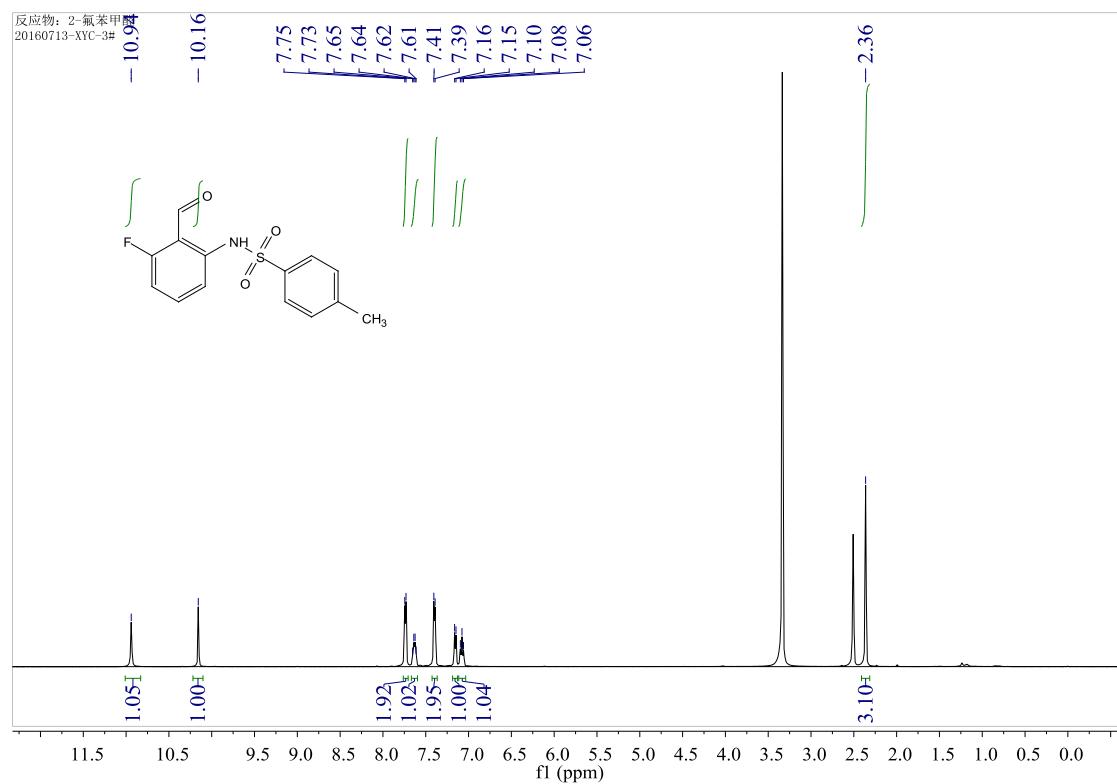
**4. 3d**



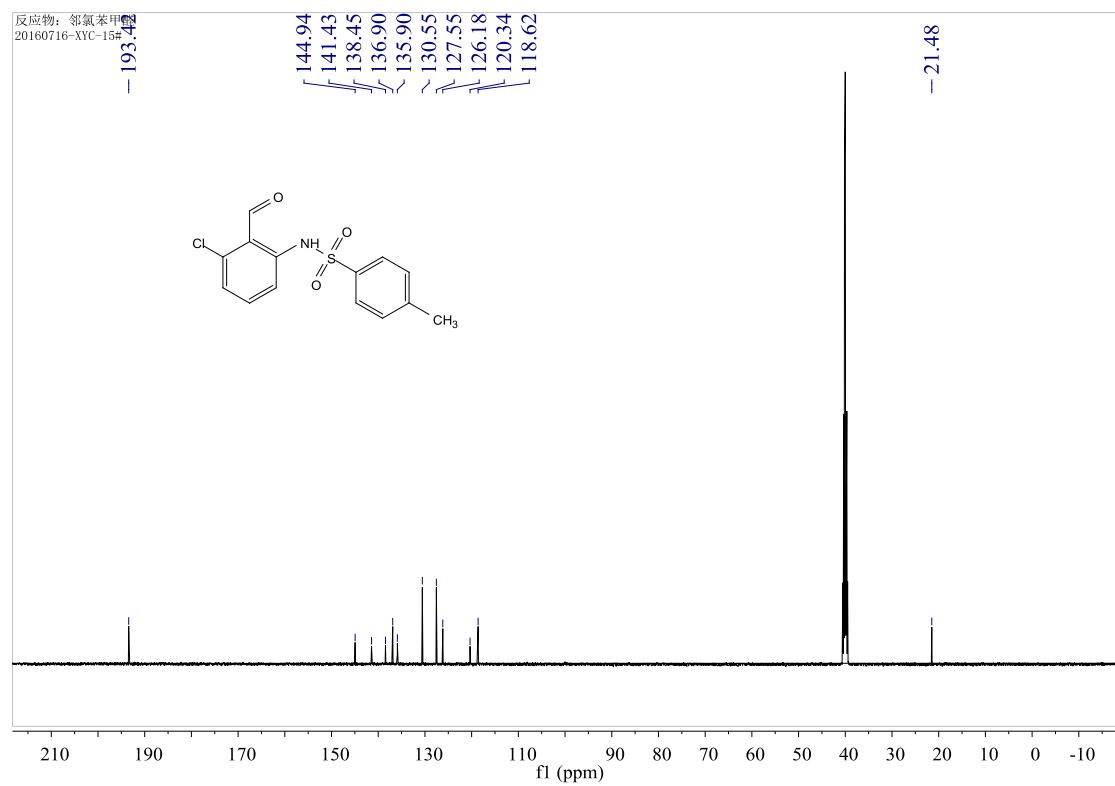
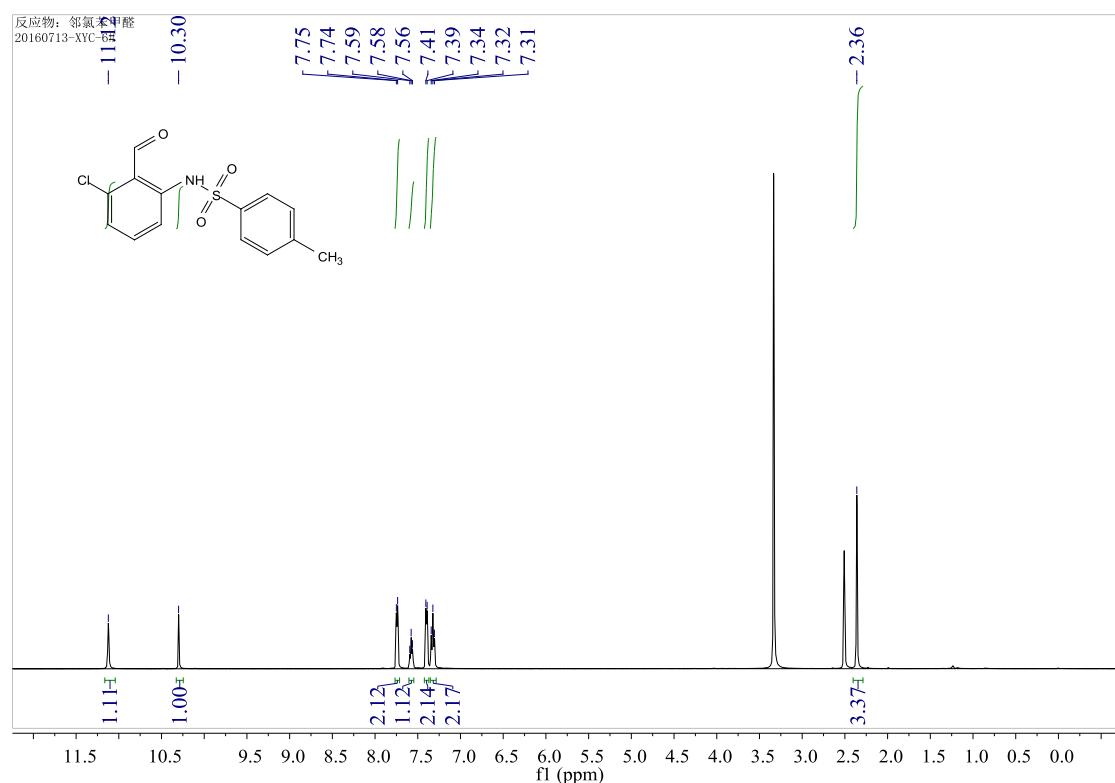
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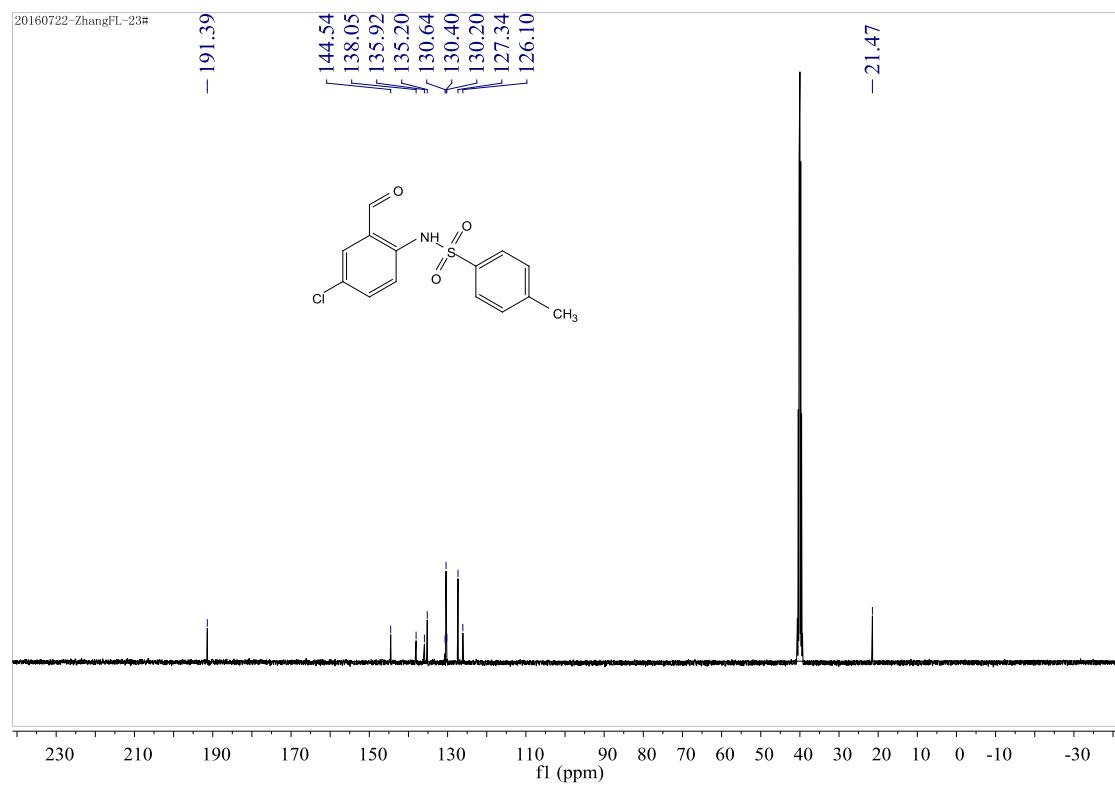
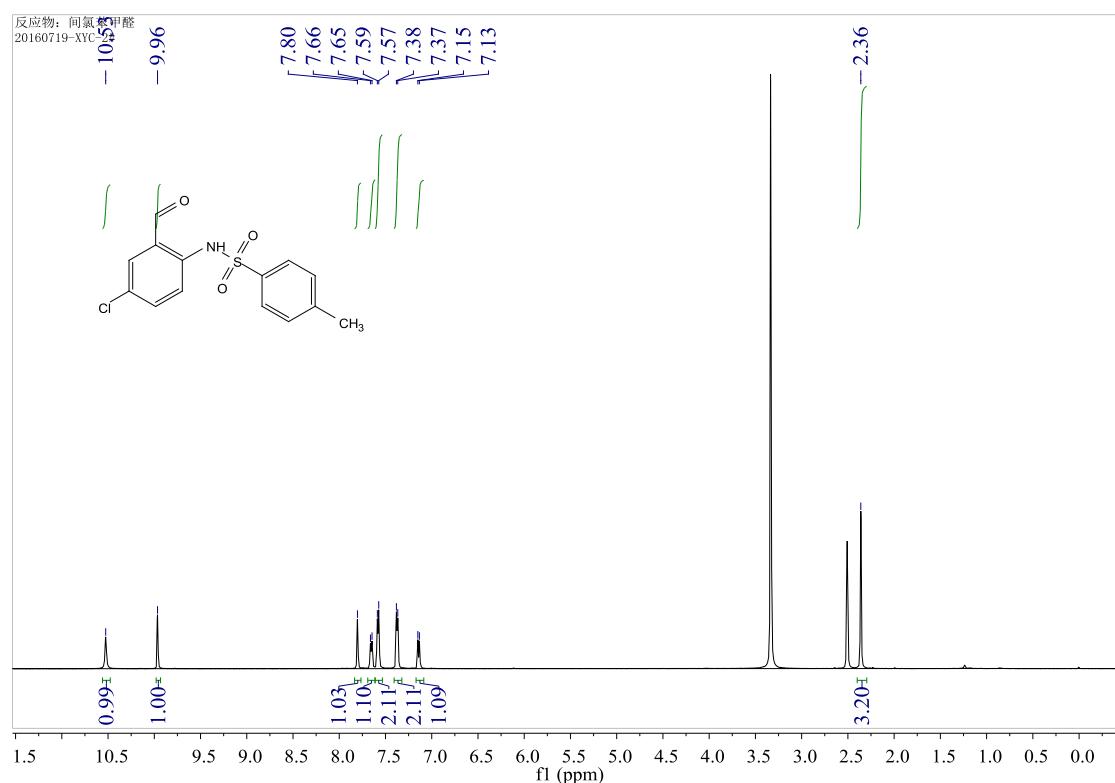
## 6. 3f



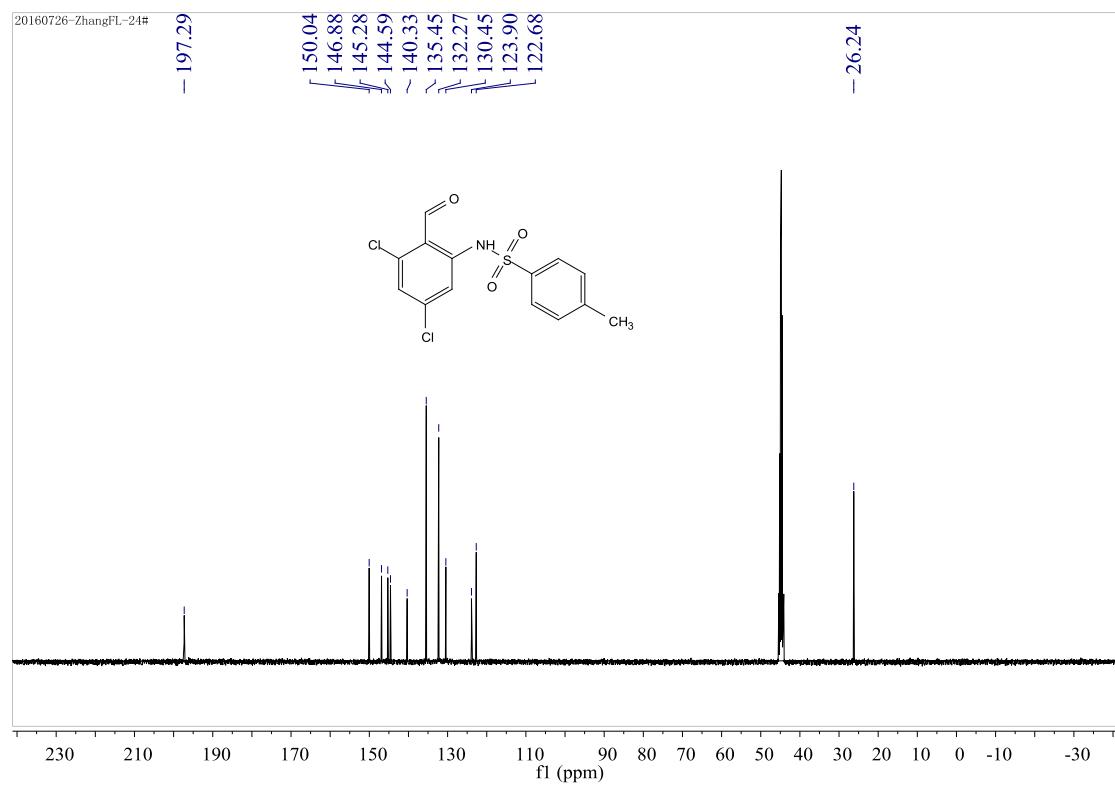
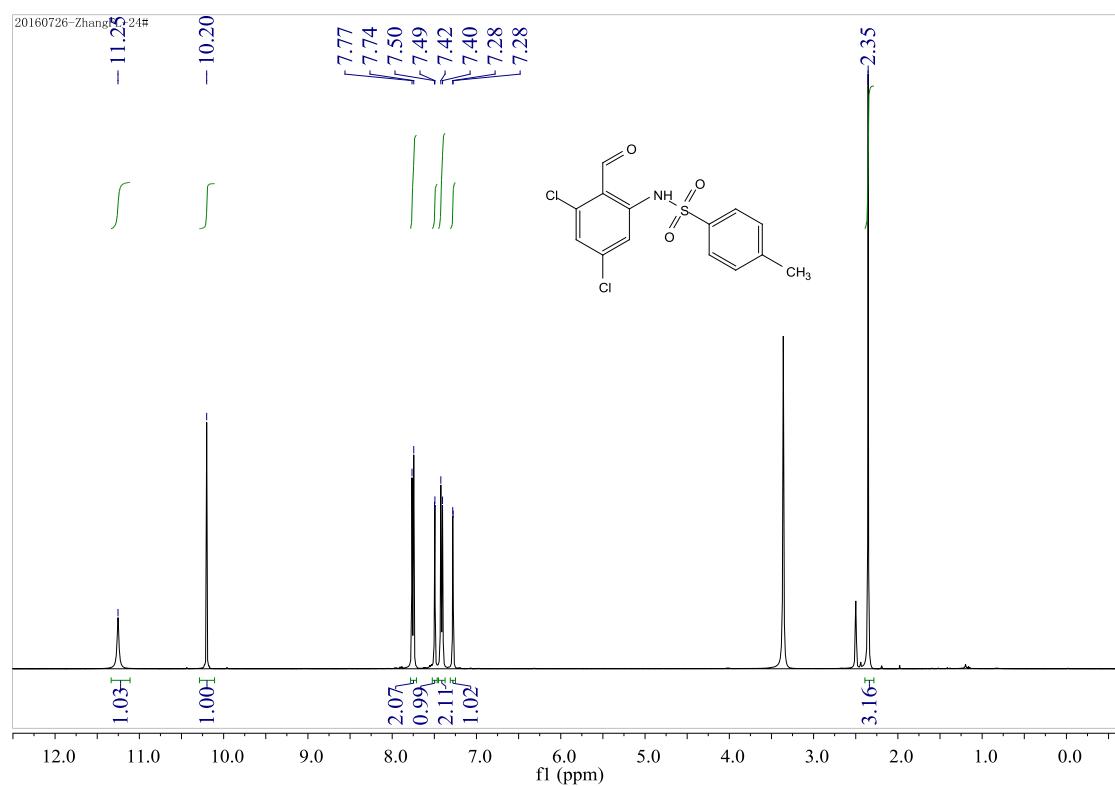
## 7. 3g



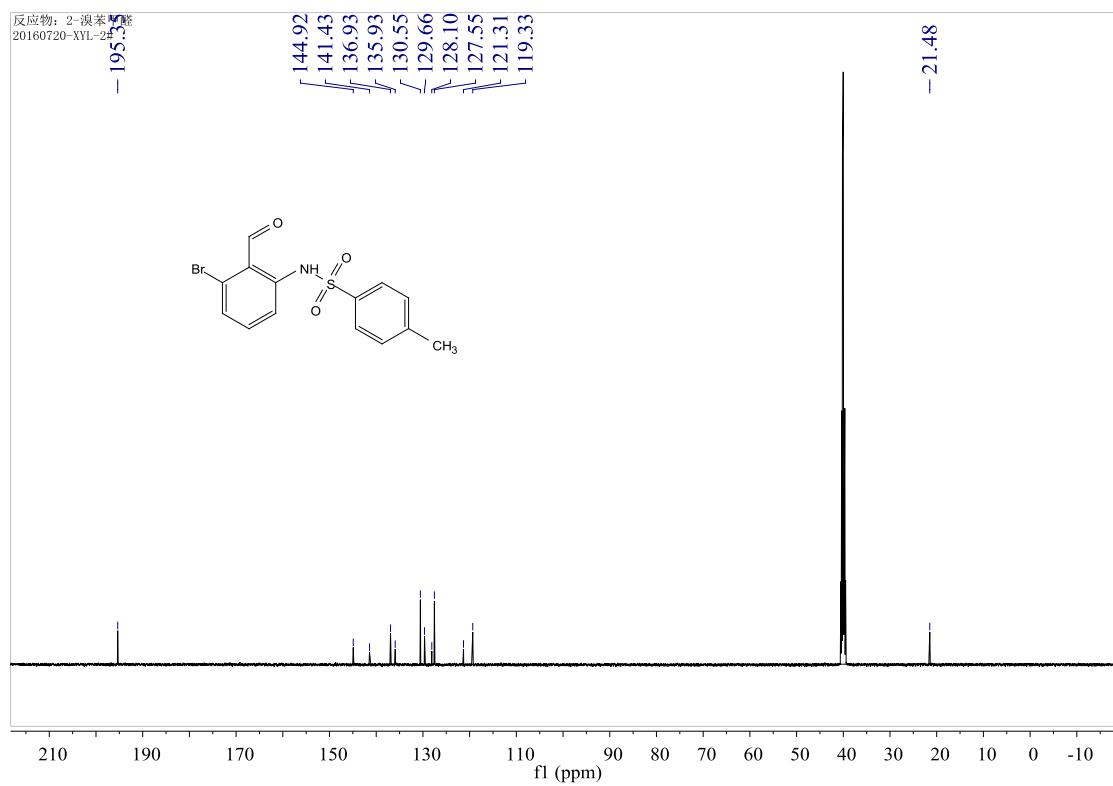
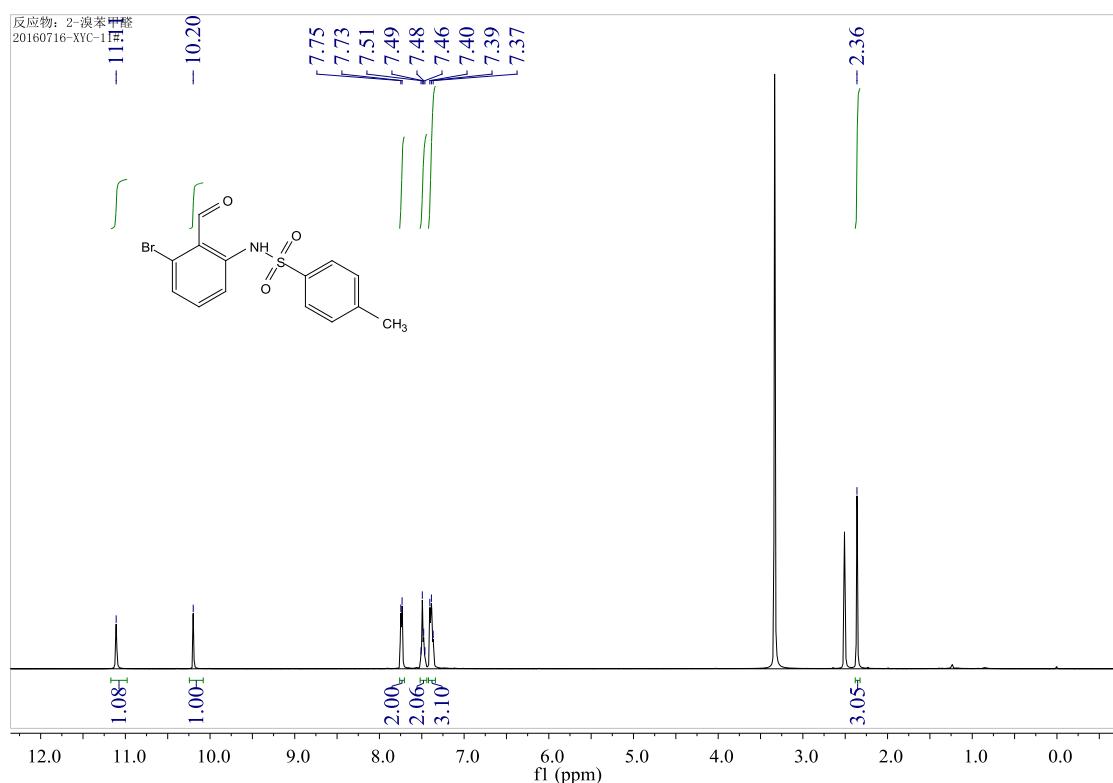
### 8. 3h



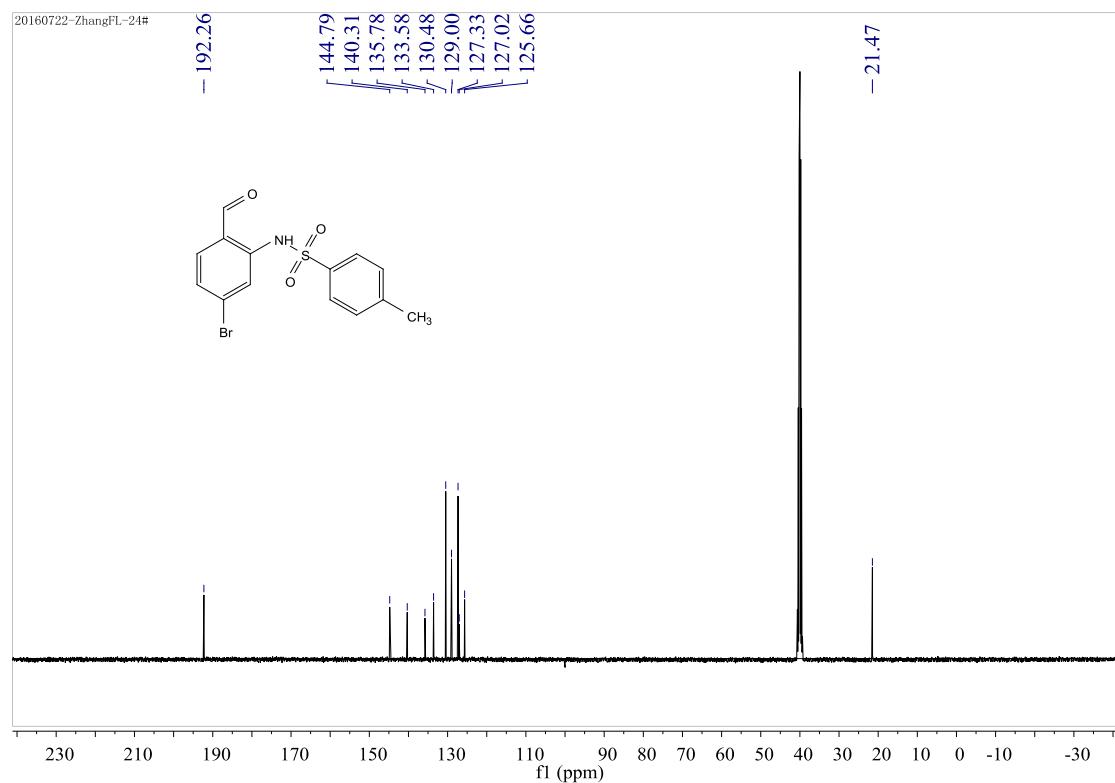
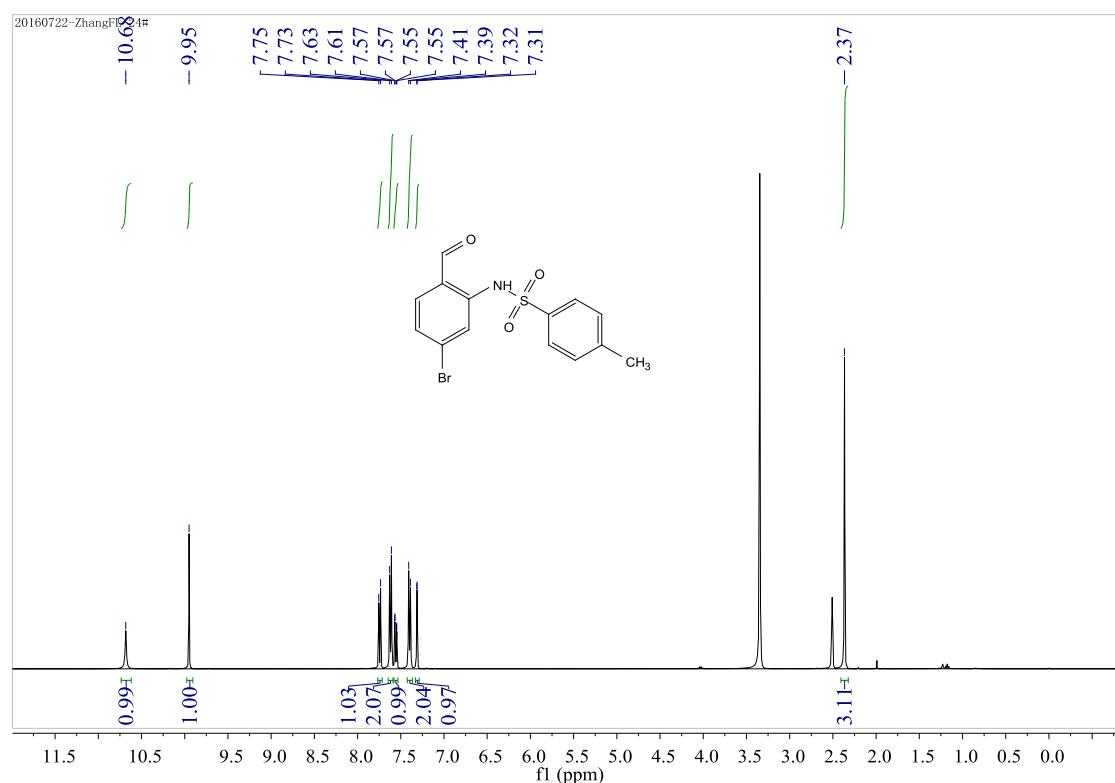
**9. 3i**



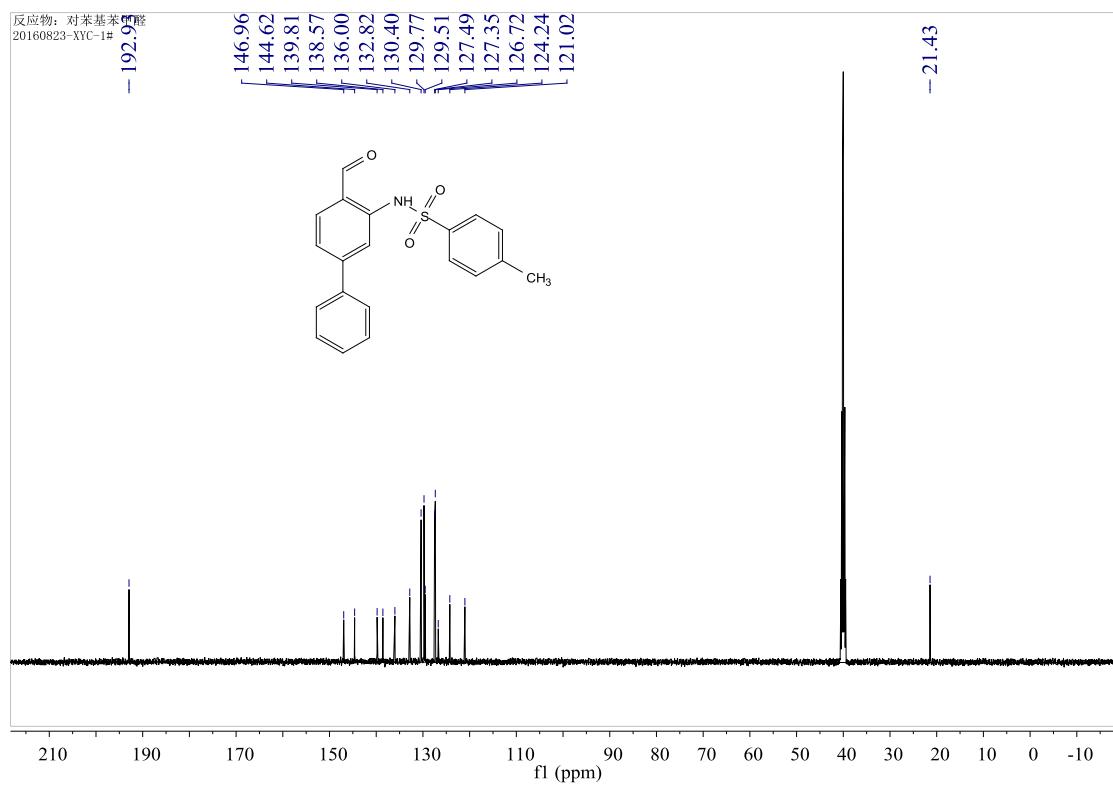
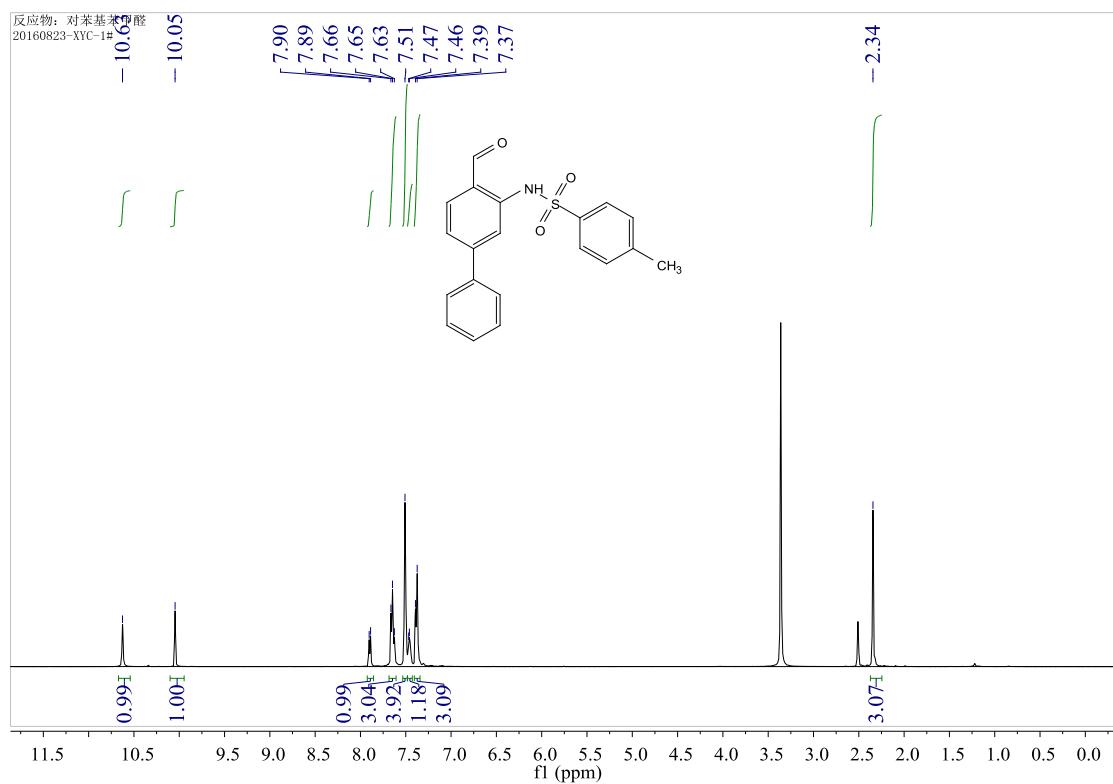
**10. 3j**



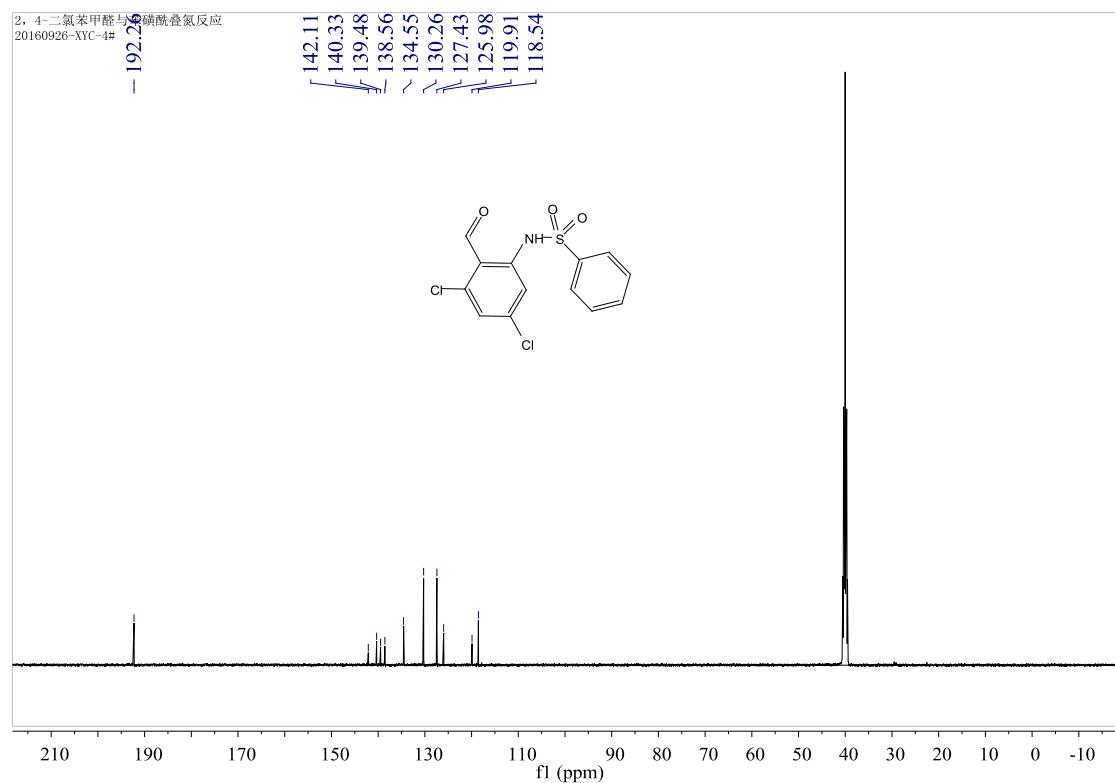
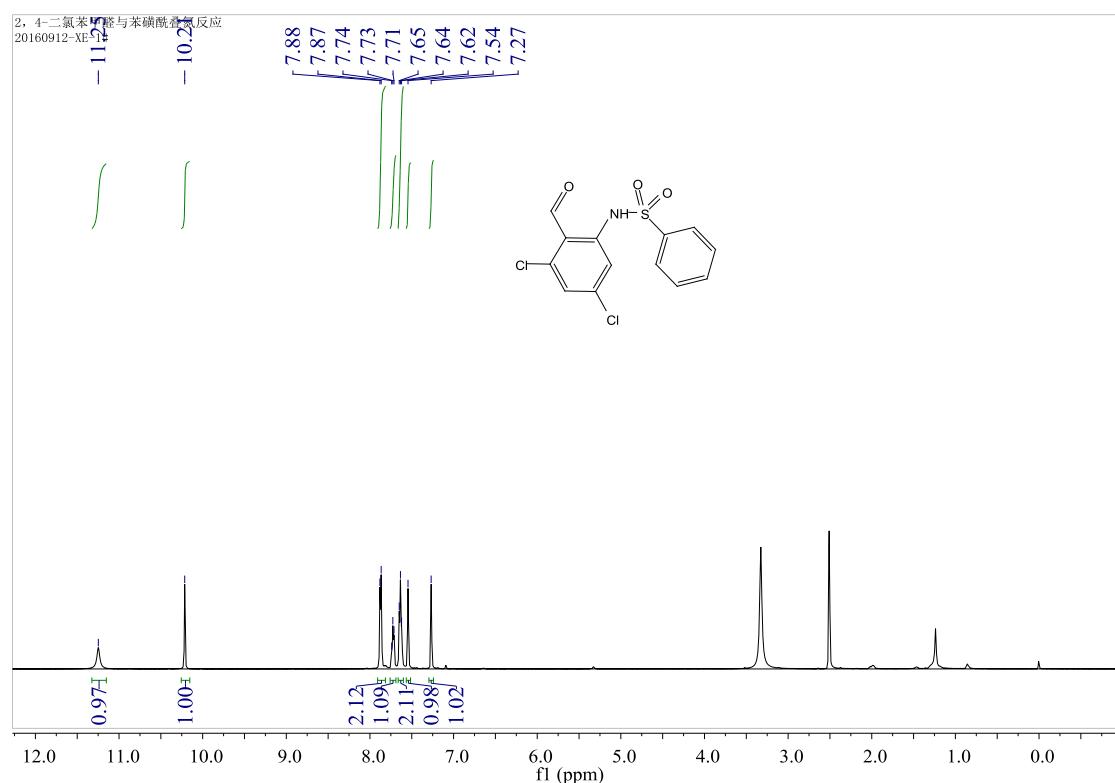
**11. 3k**



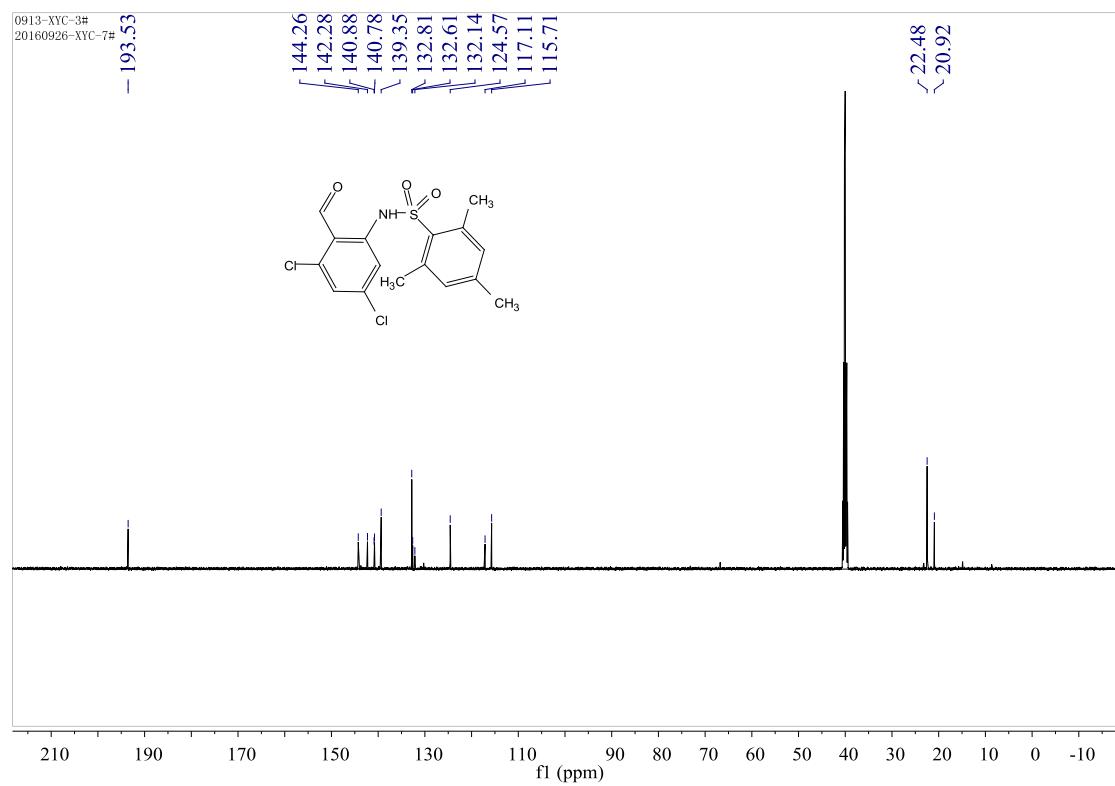
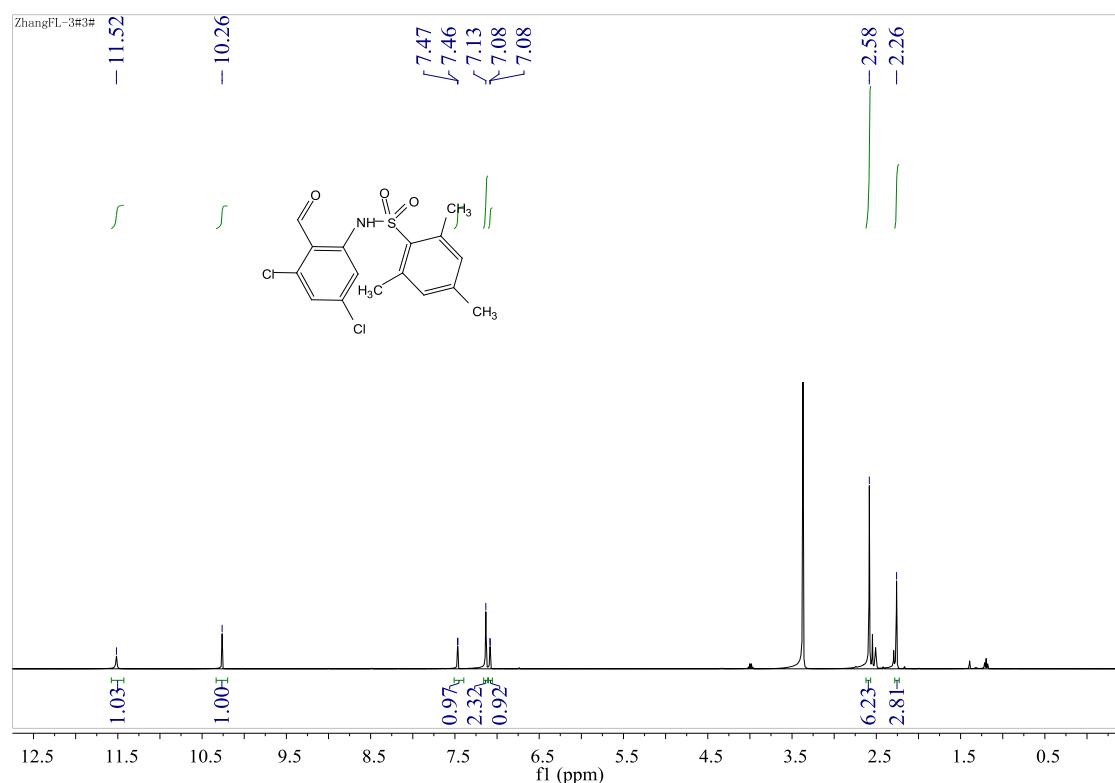
12. 3l



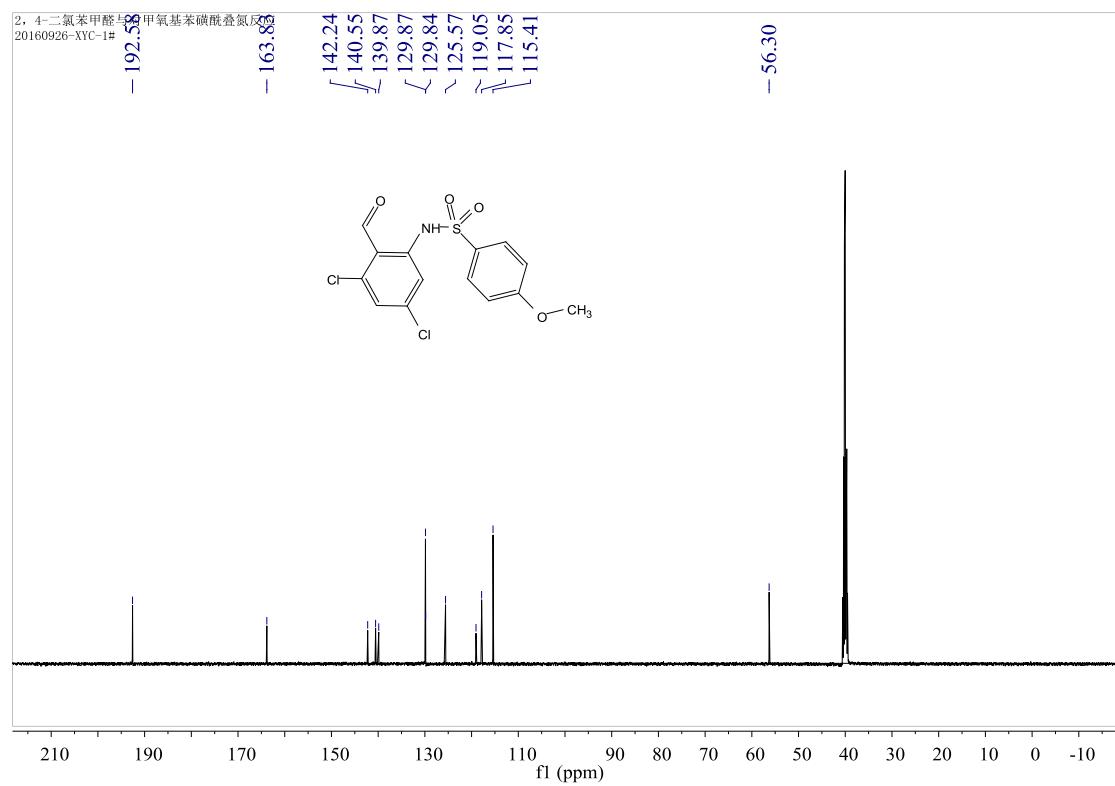
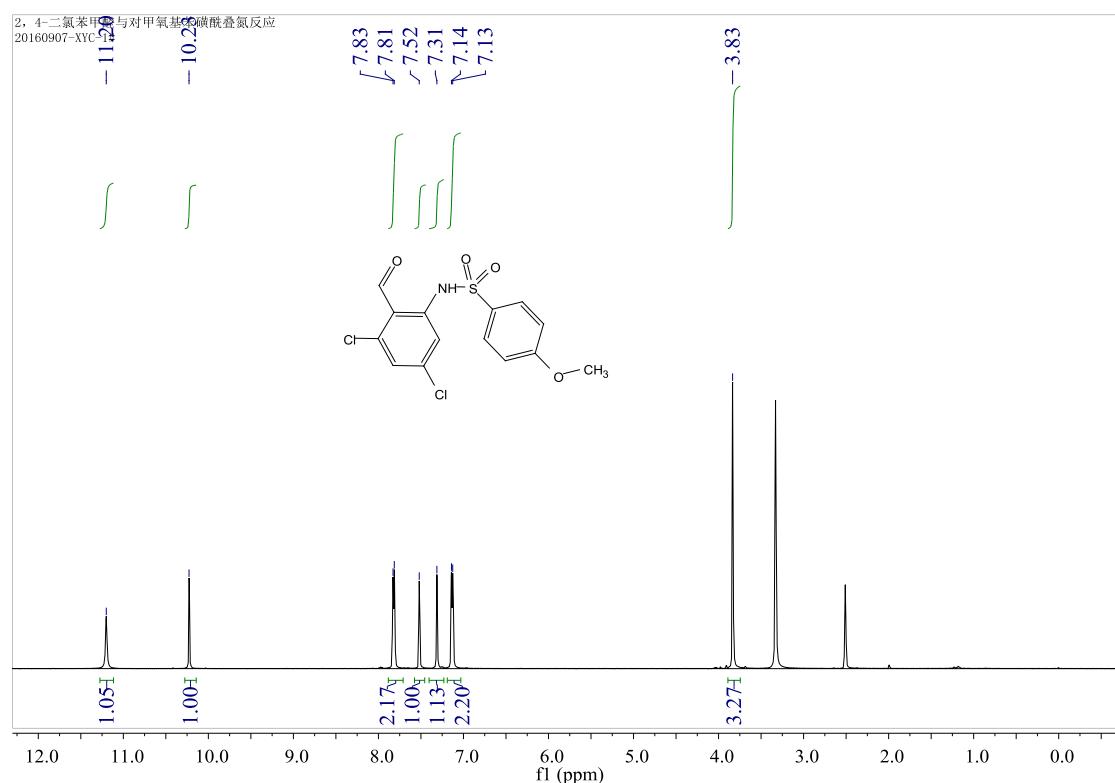
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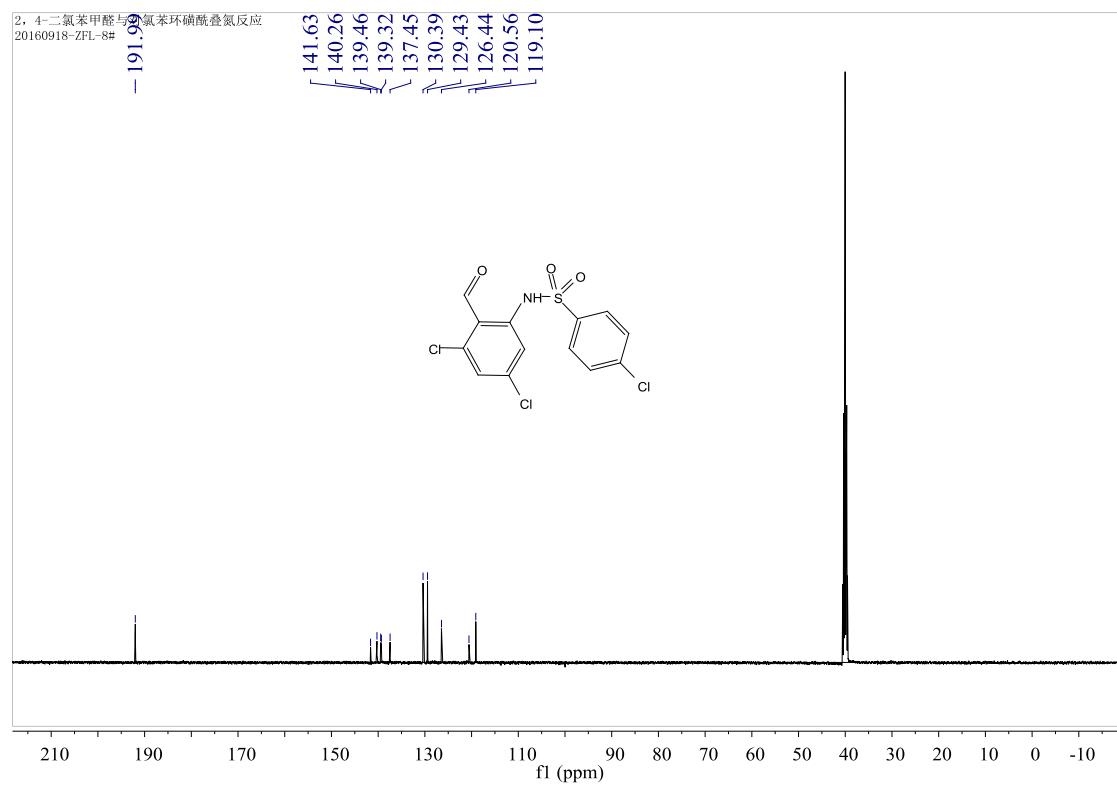
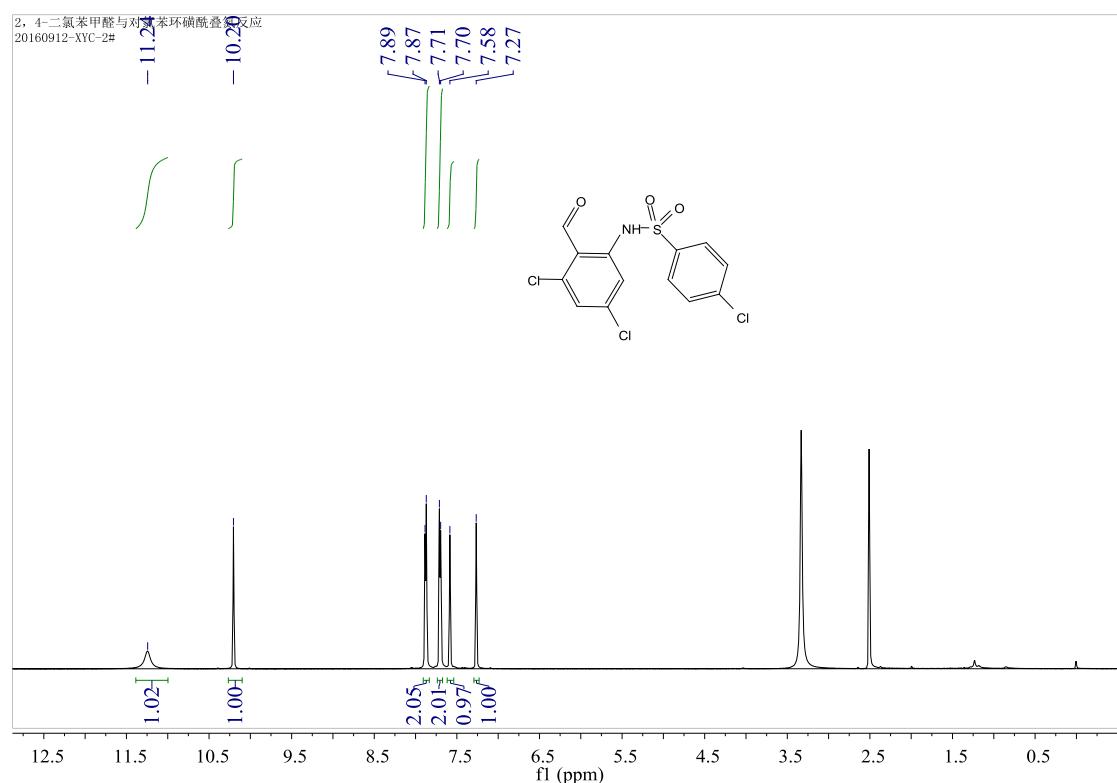
**14. 3n**



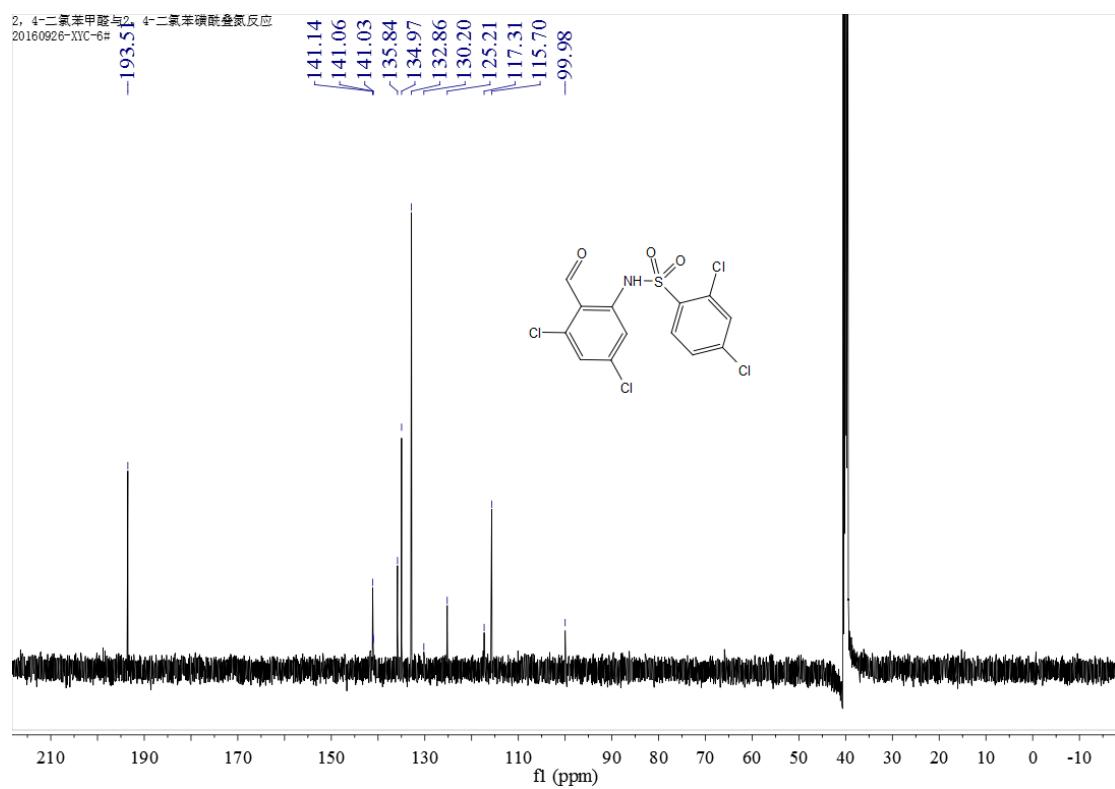
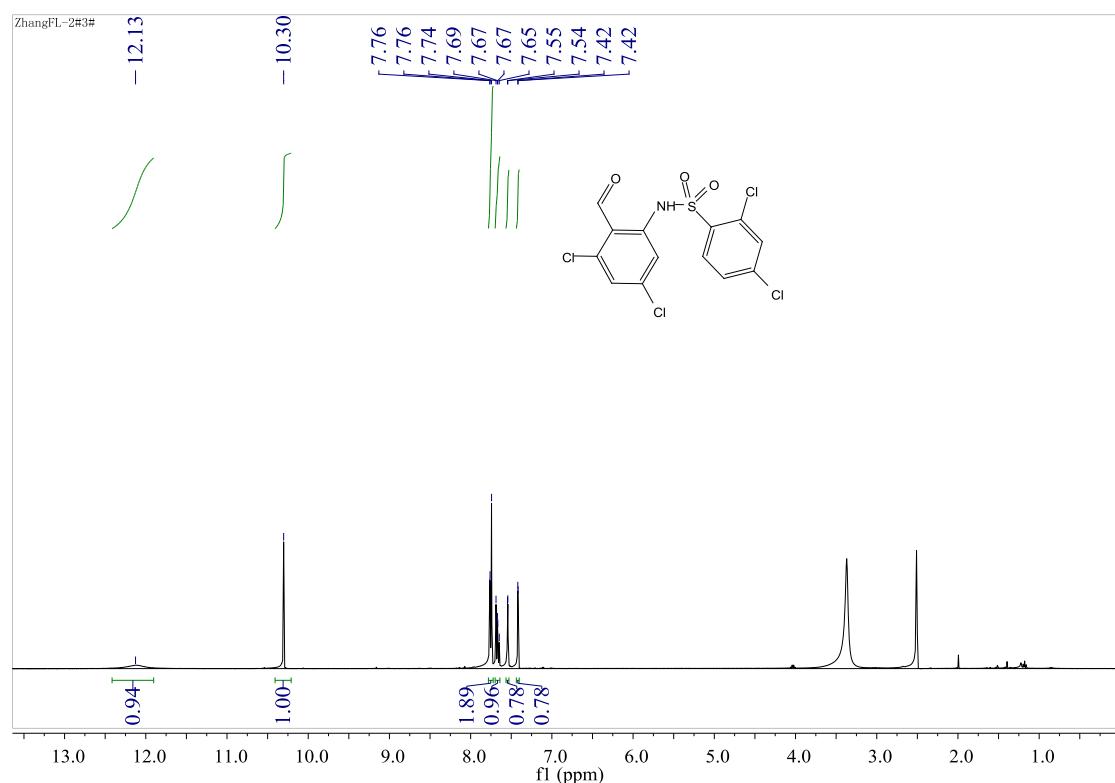
**15. 3o**



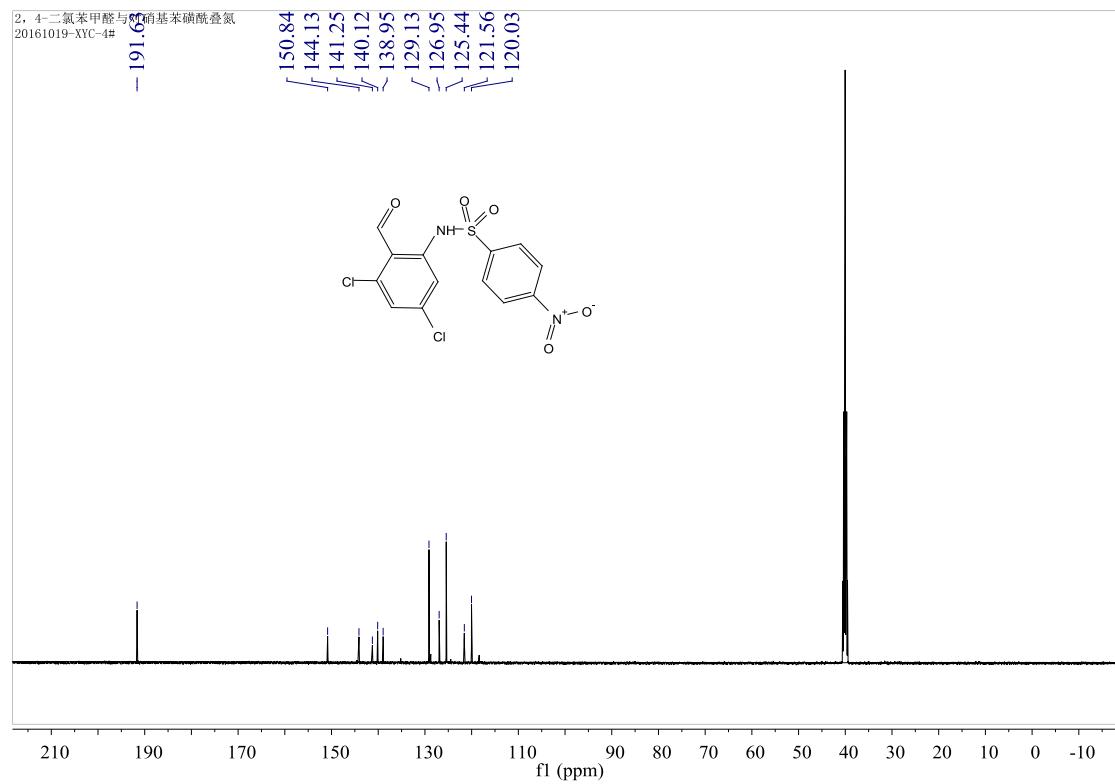
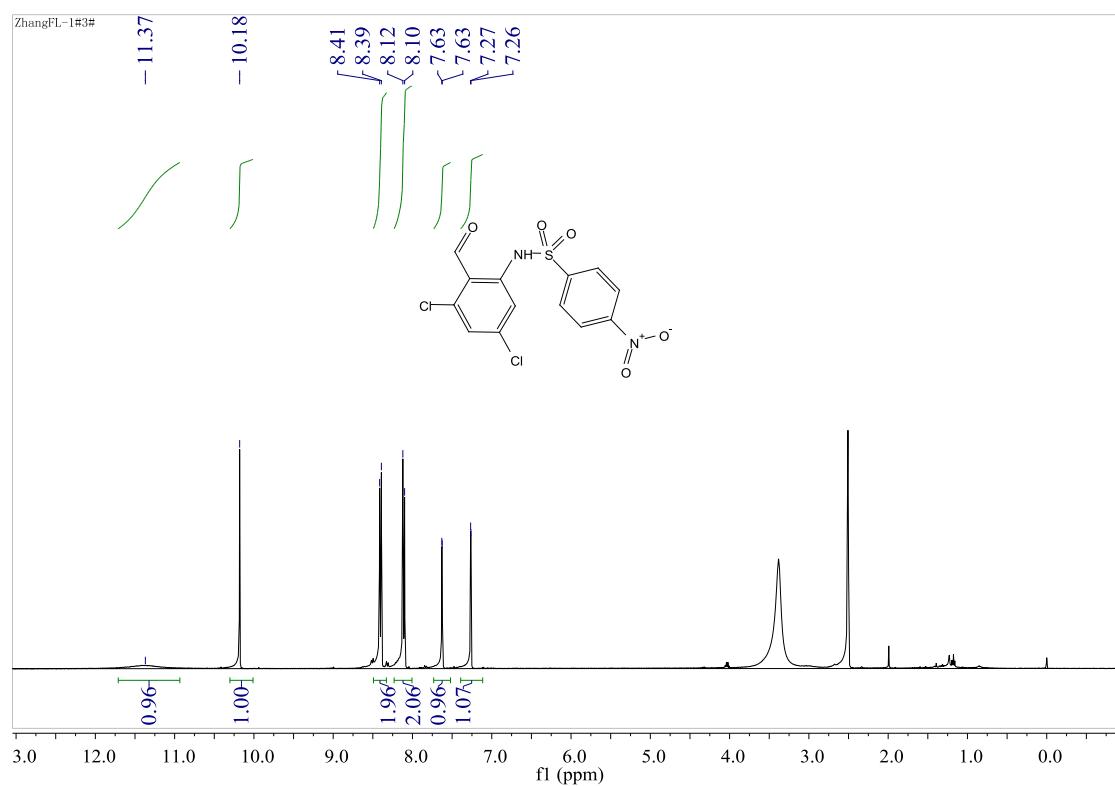
**16. 3p**



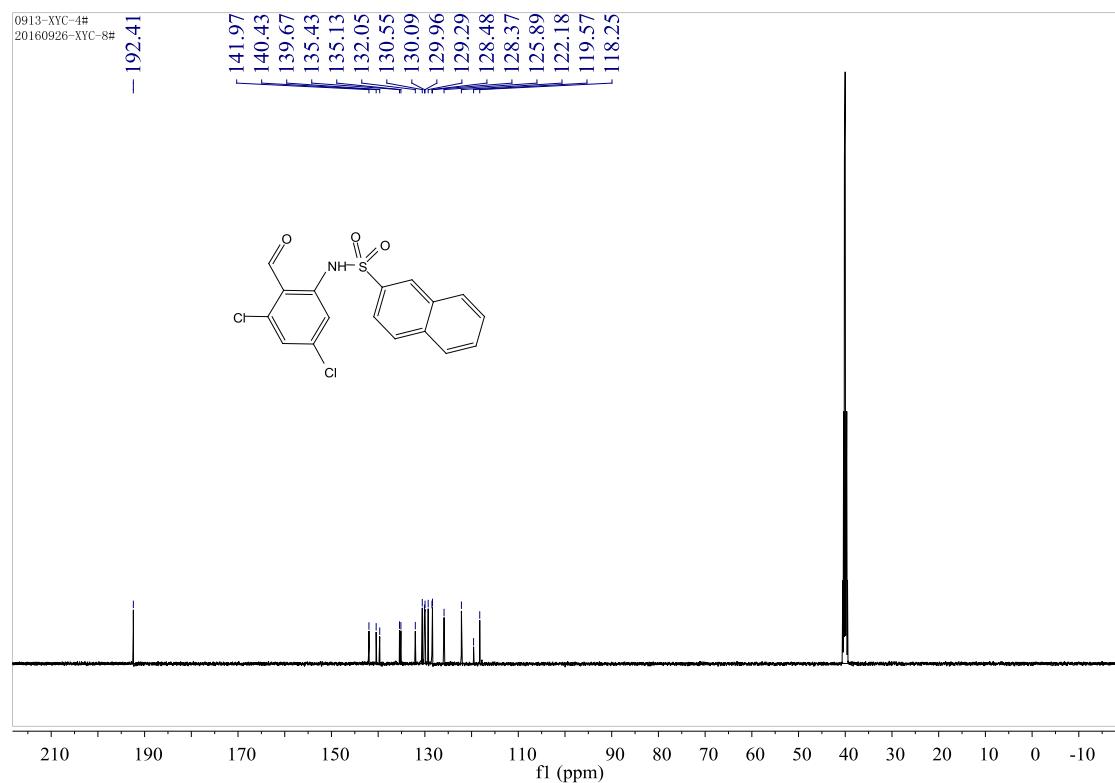
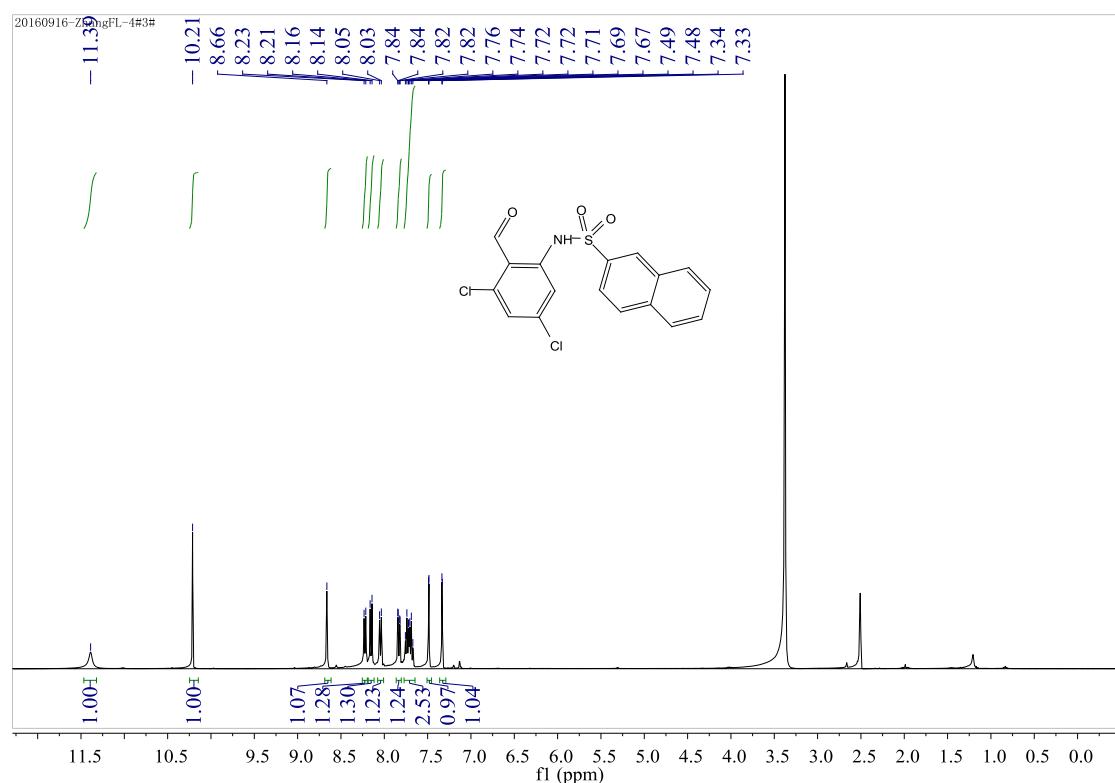
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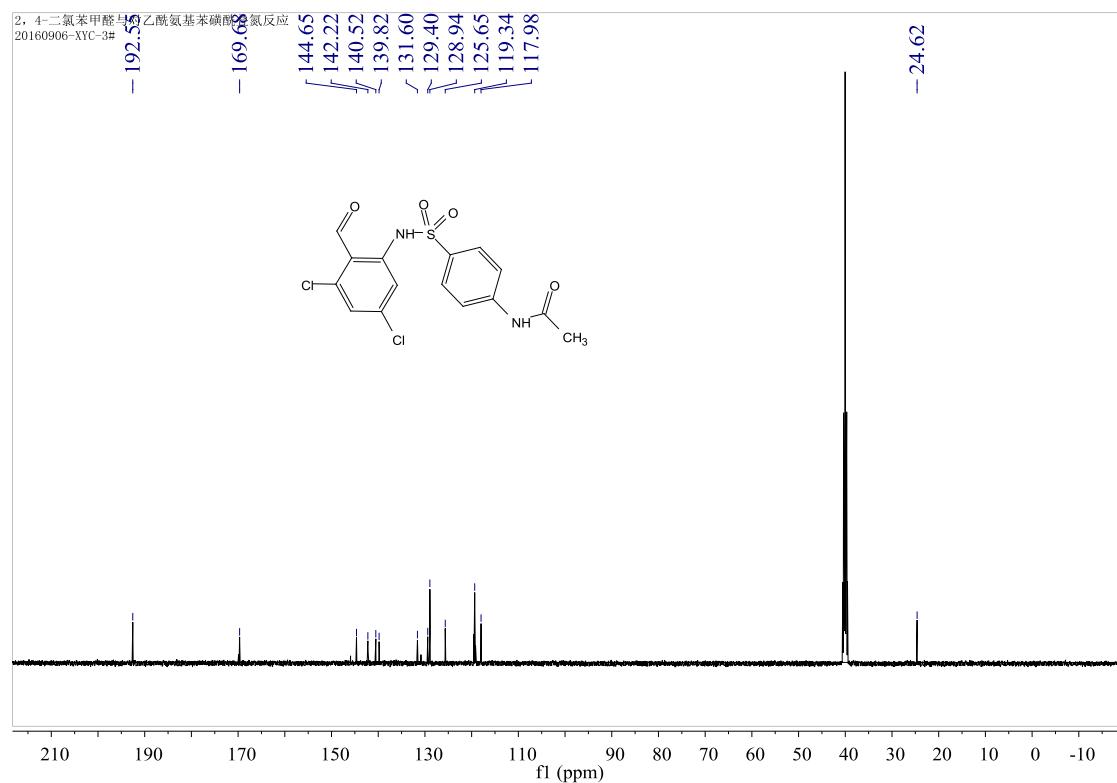
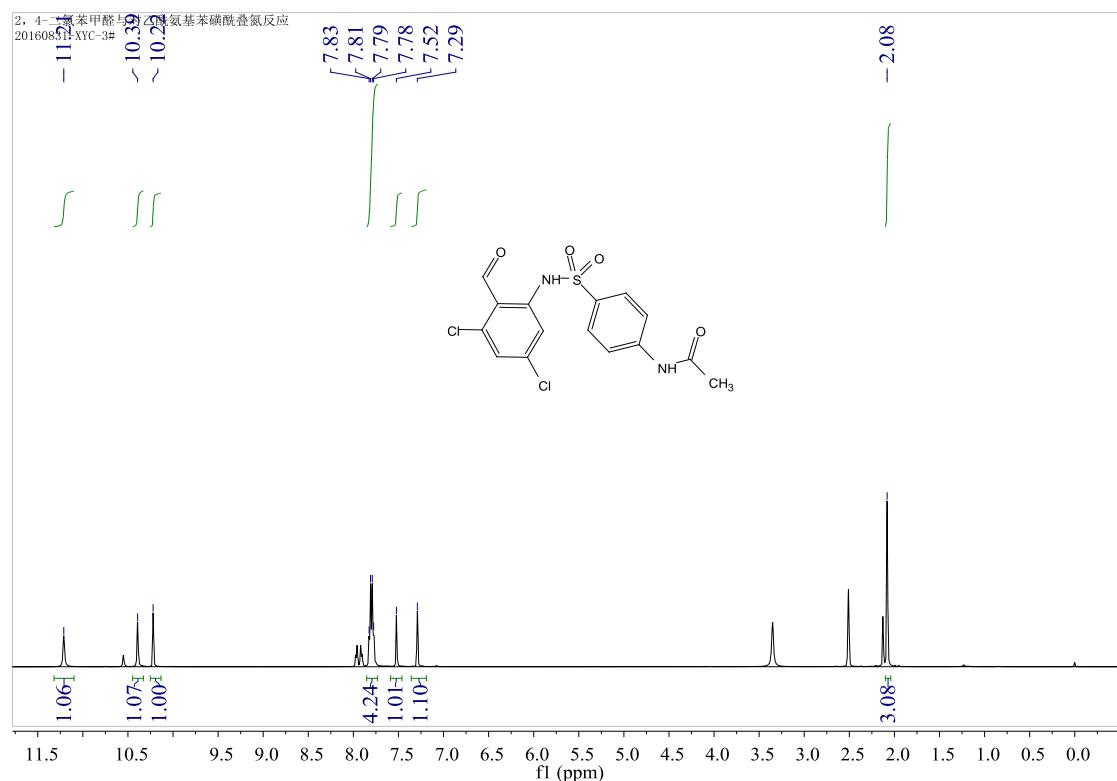
**18. 3r**



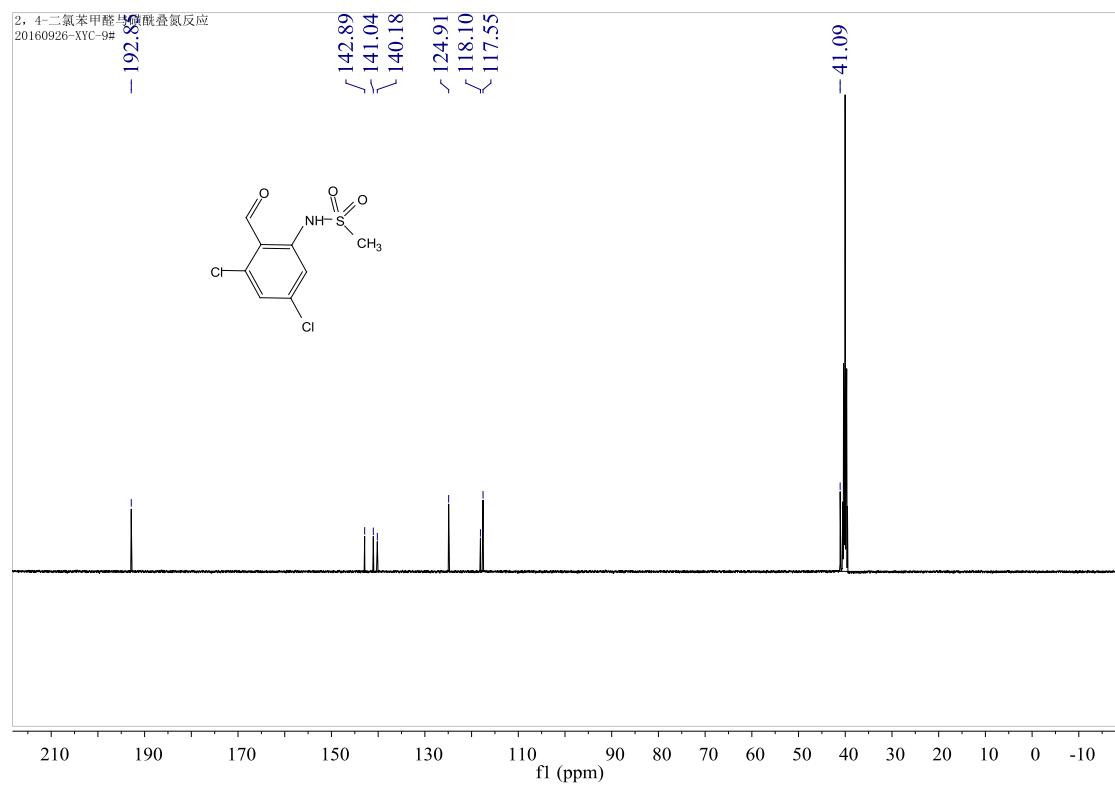
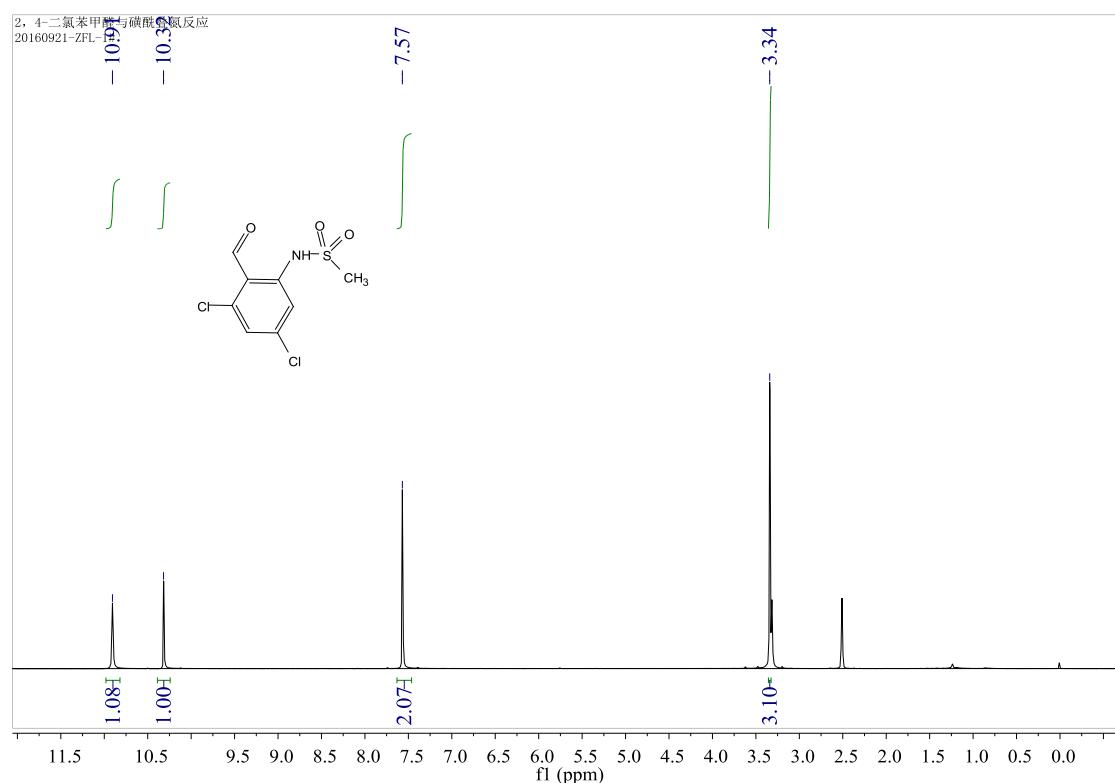
**19. 3s**



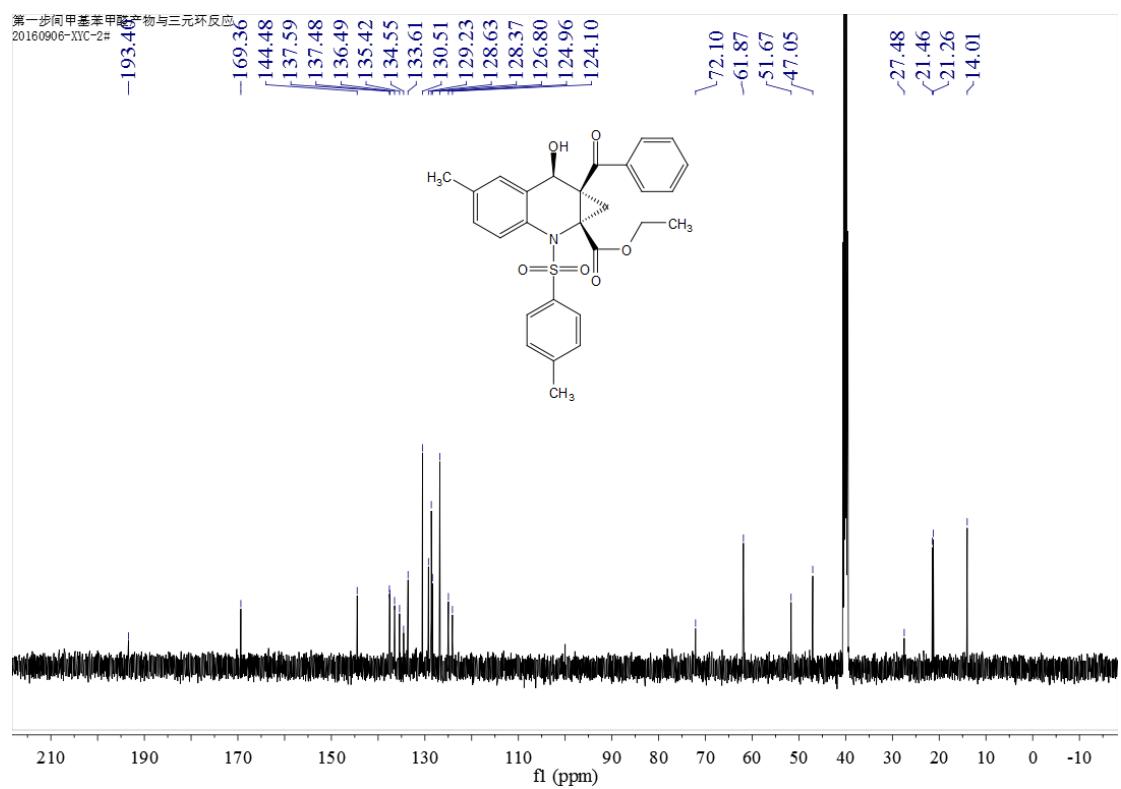
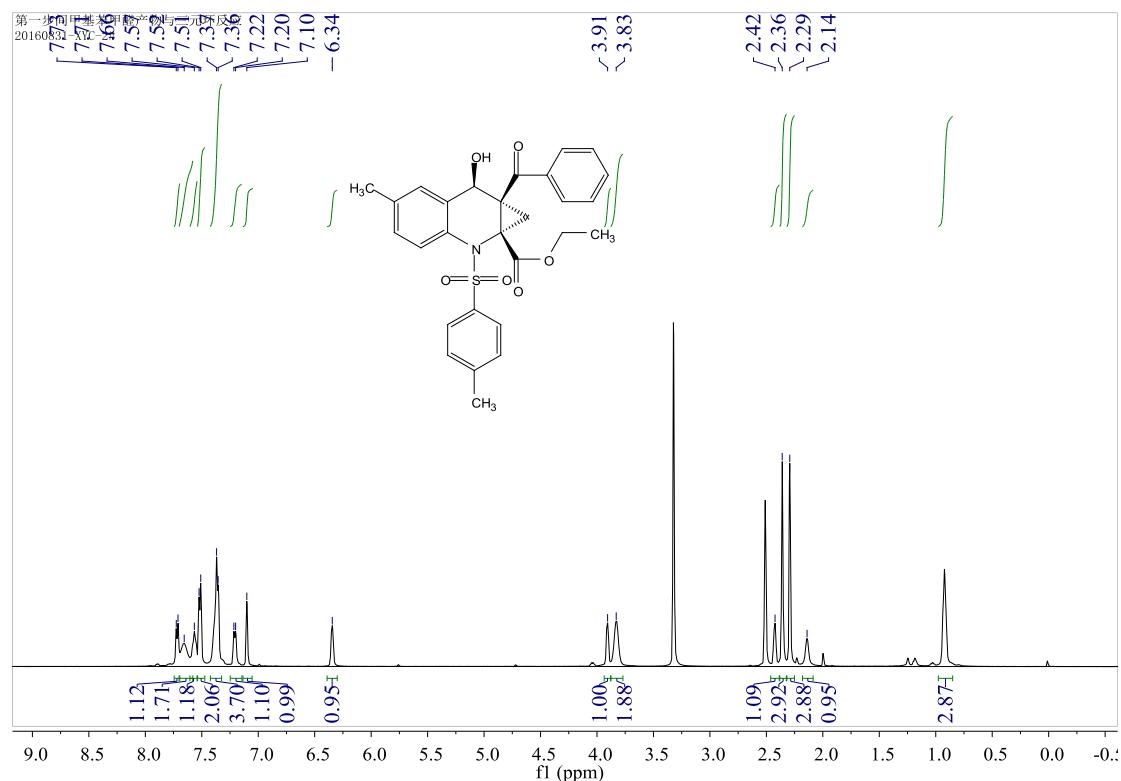
**20. 3t**



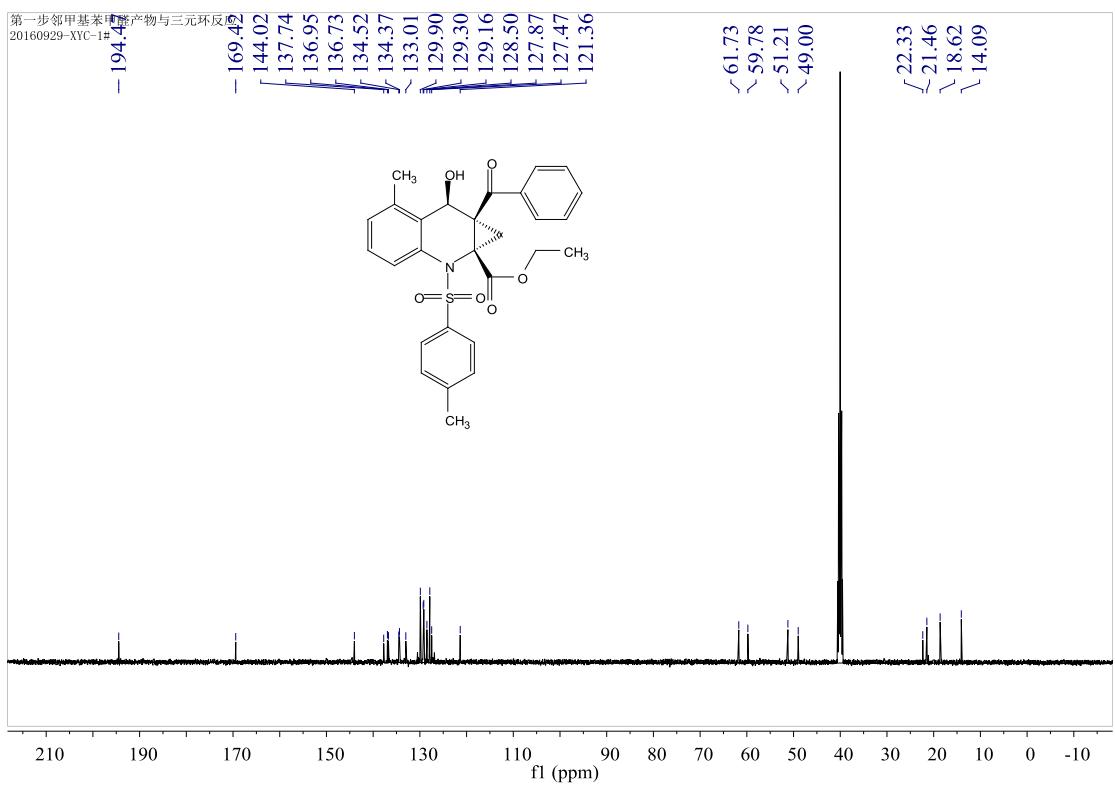
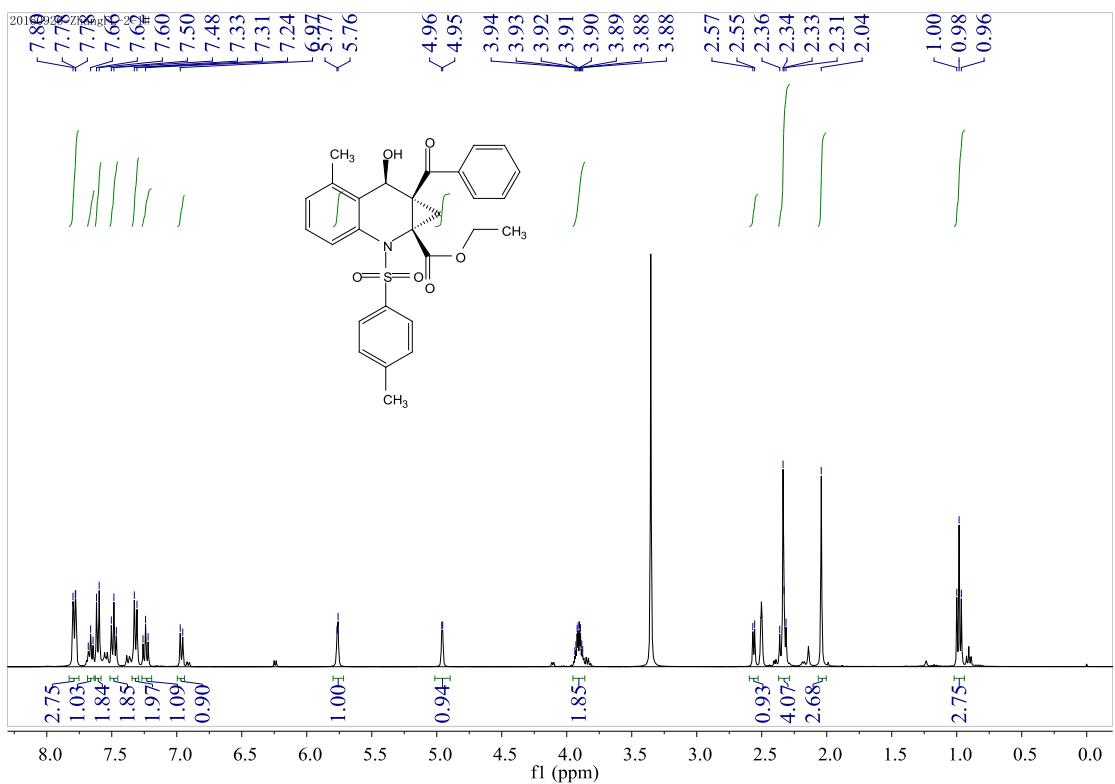
**21. 3u**



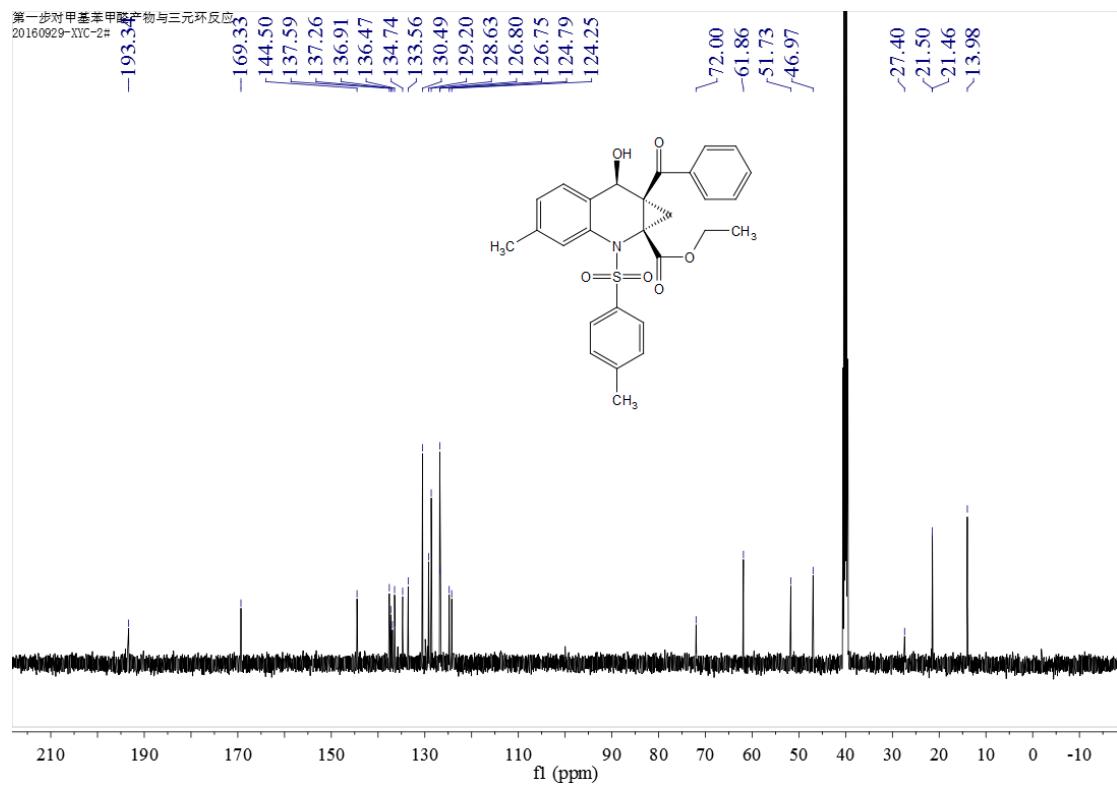
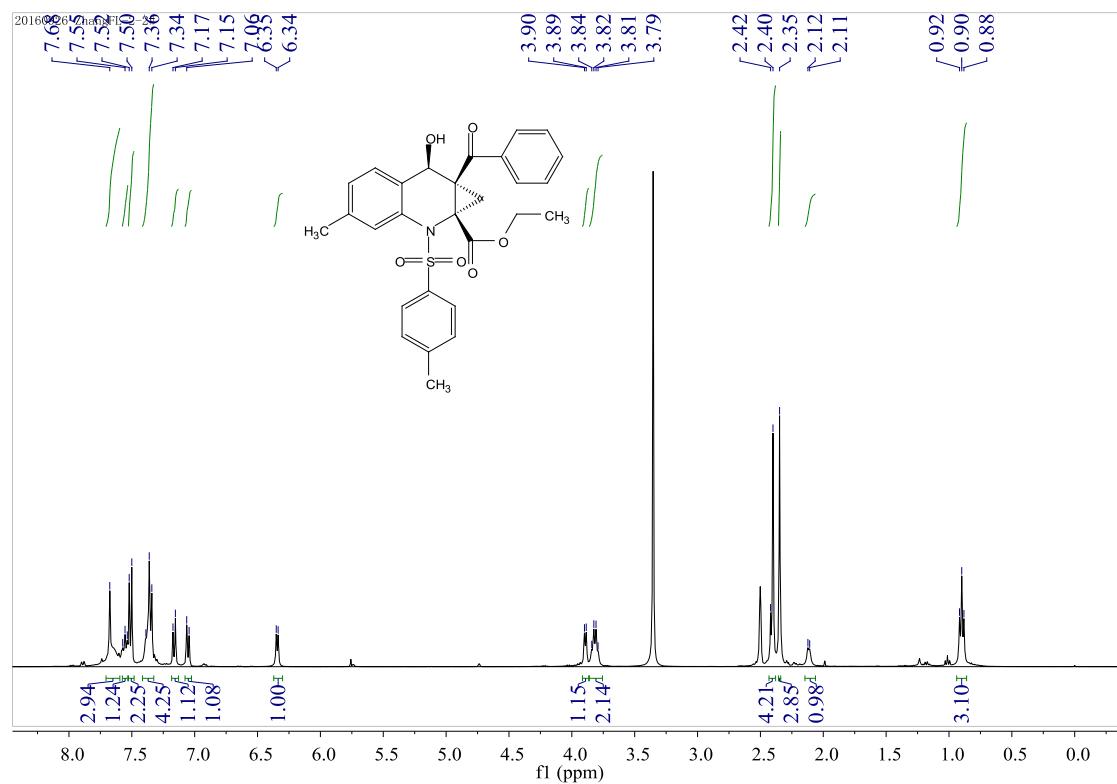
**22. 5aa**



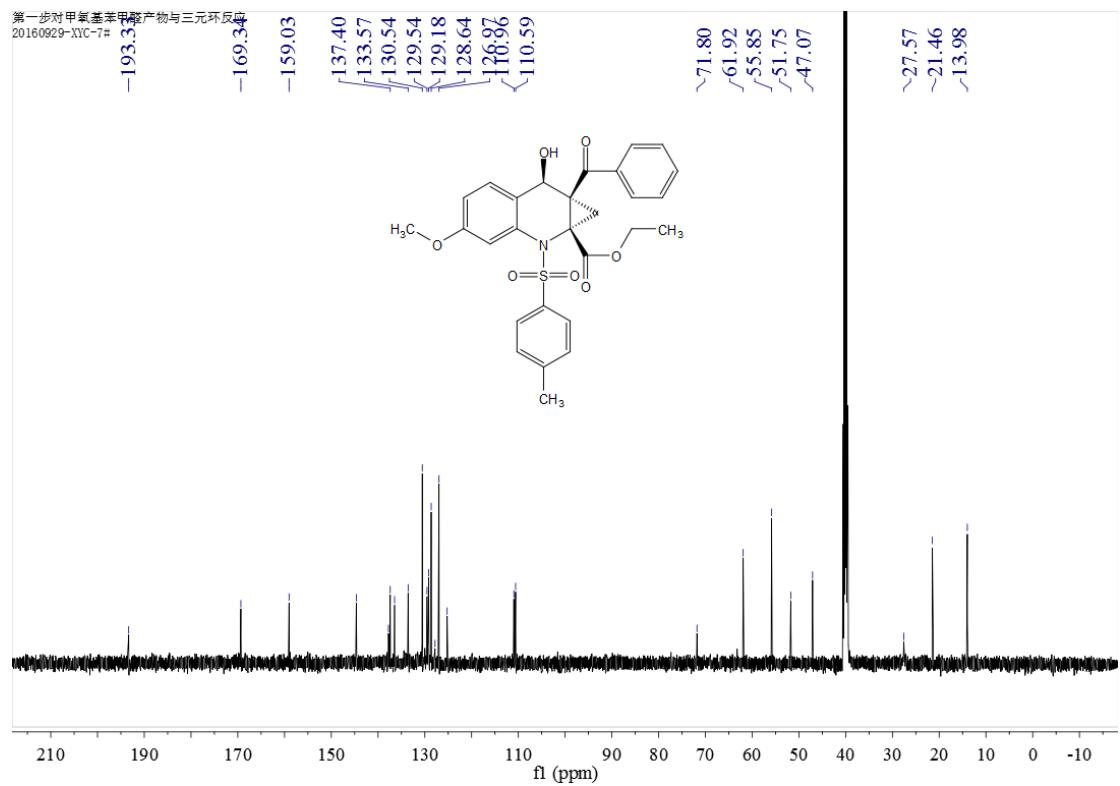
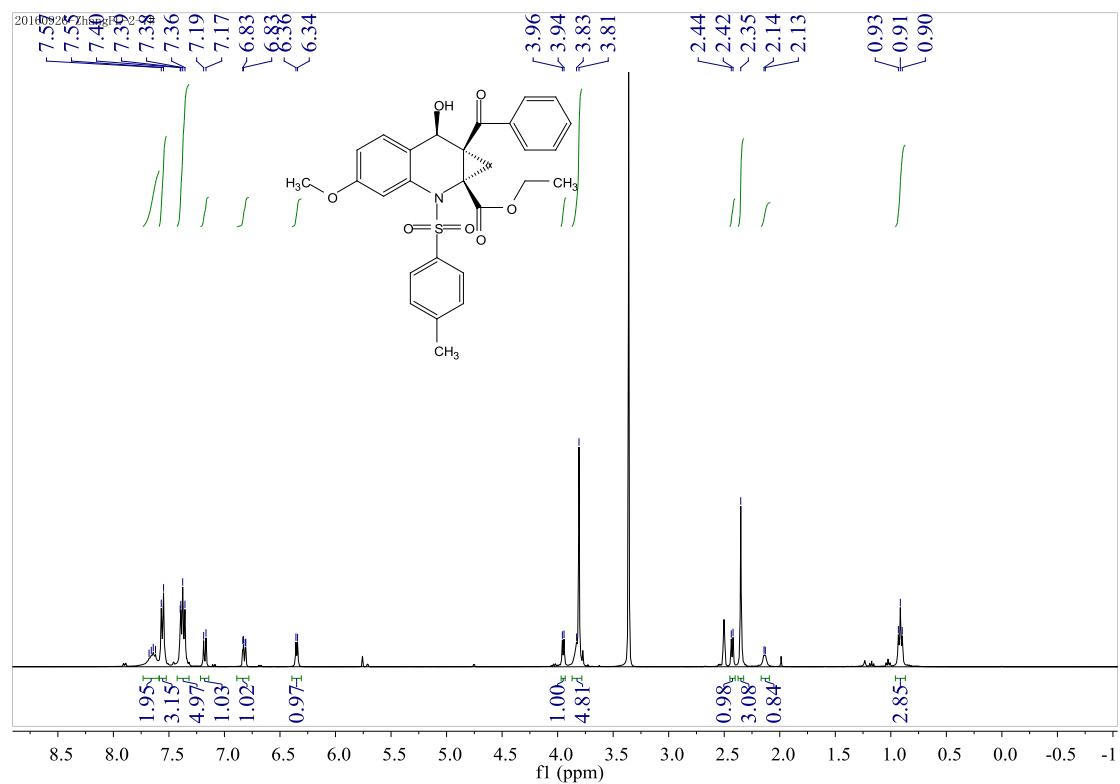
23. 5ba



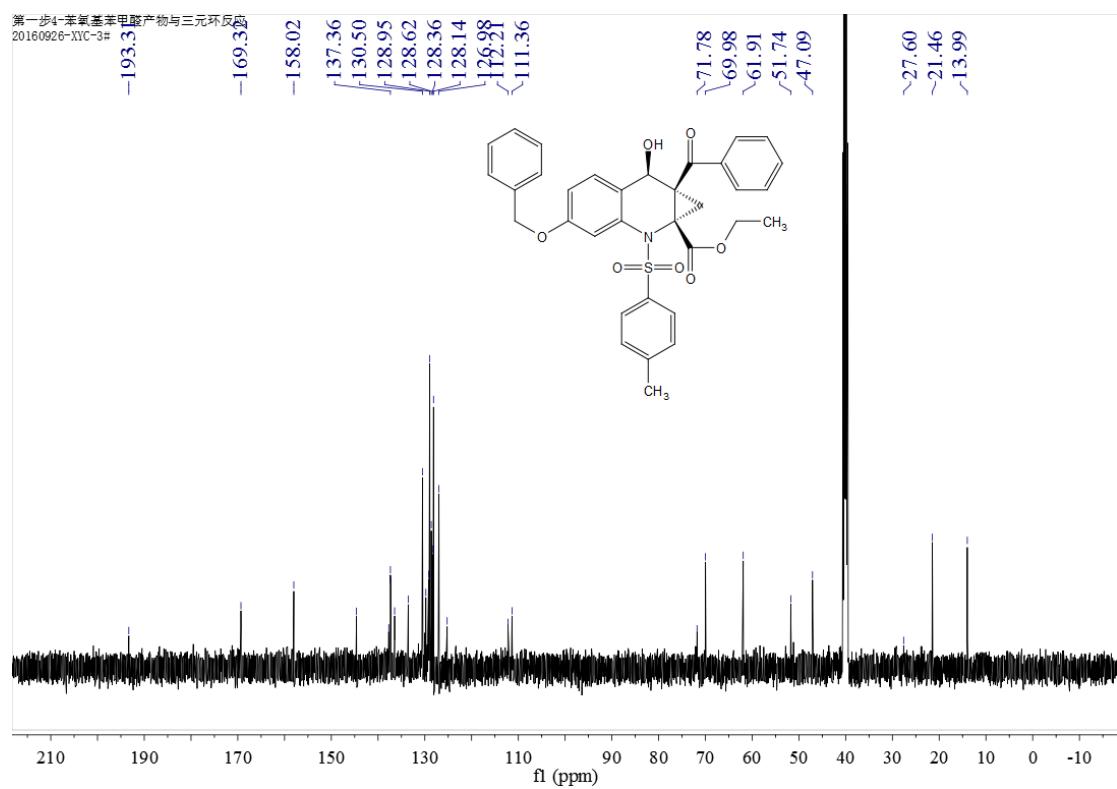
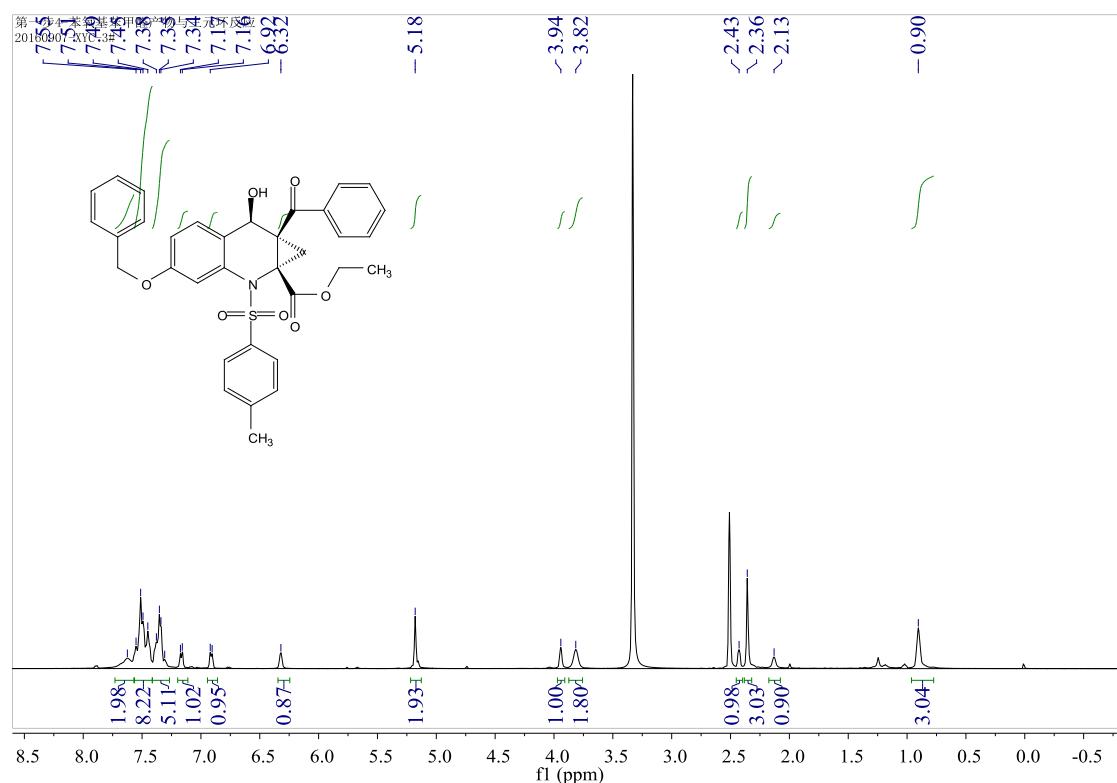
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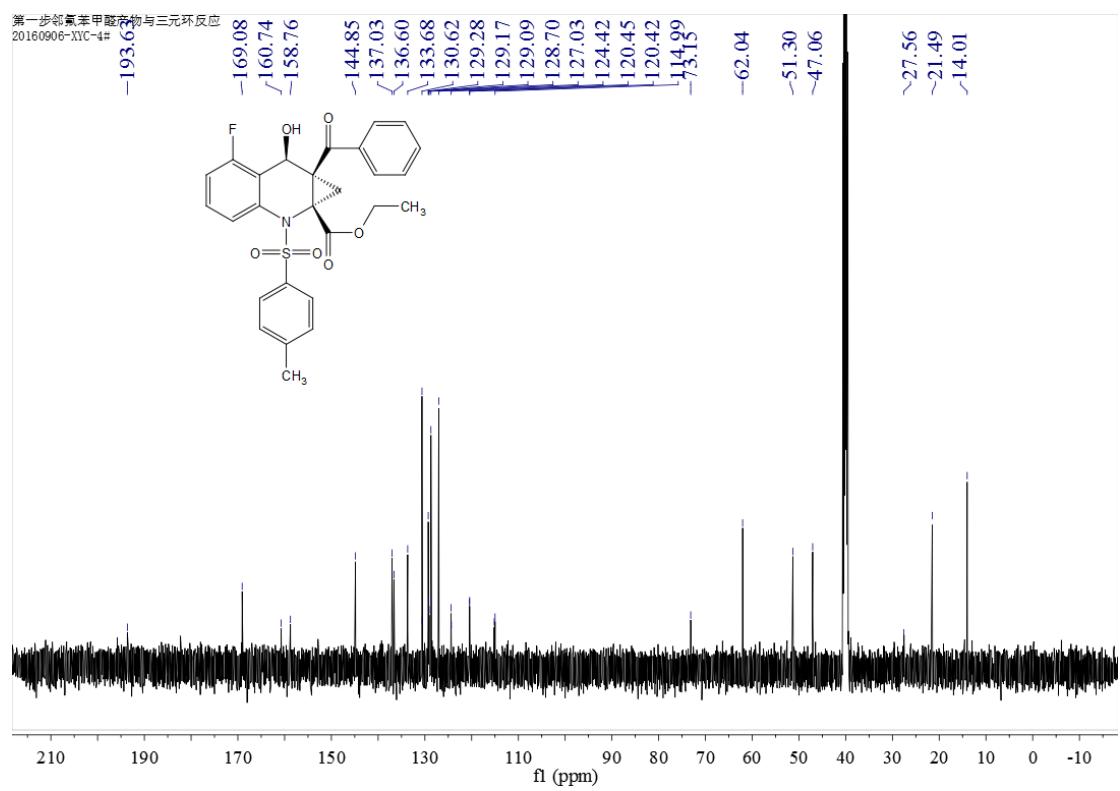
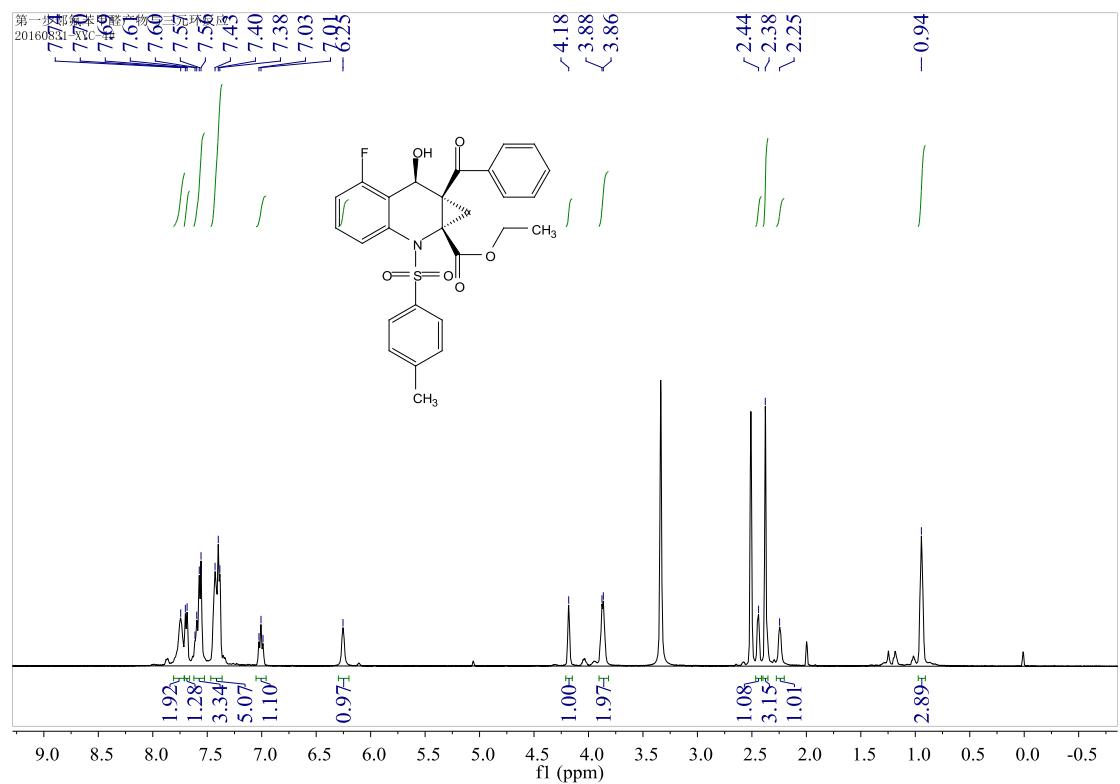
**25. 5da**



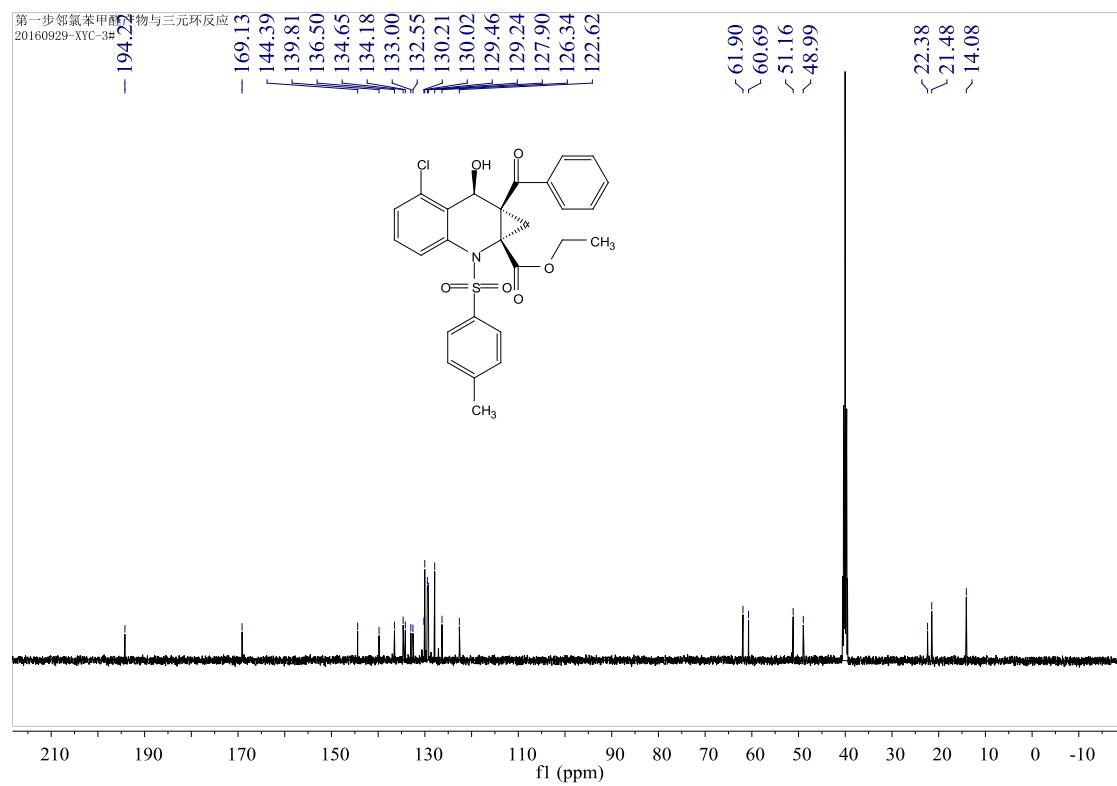
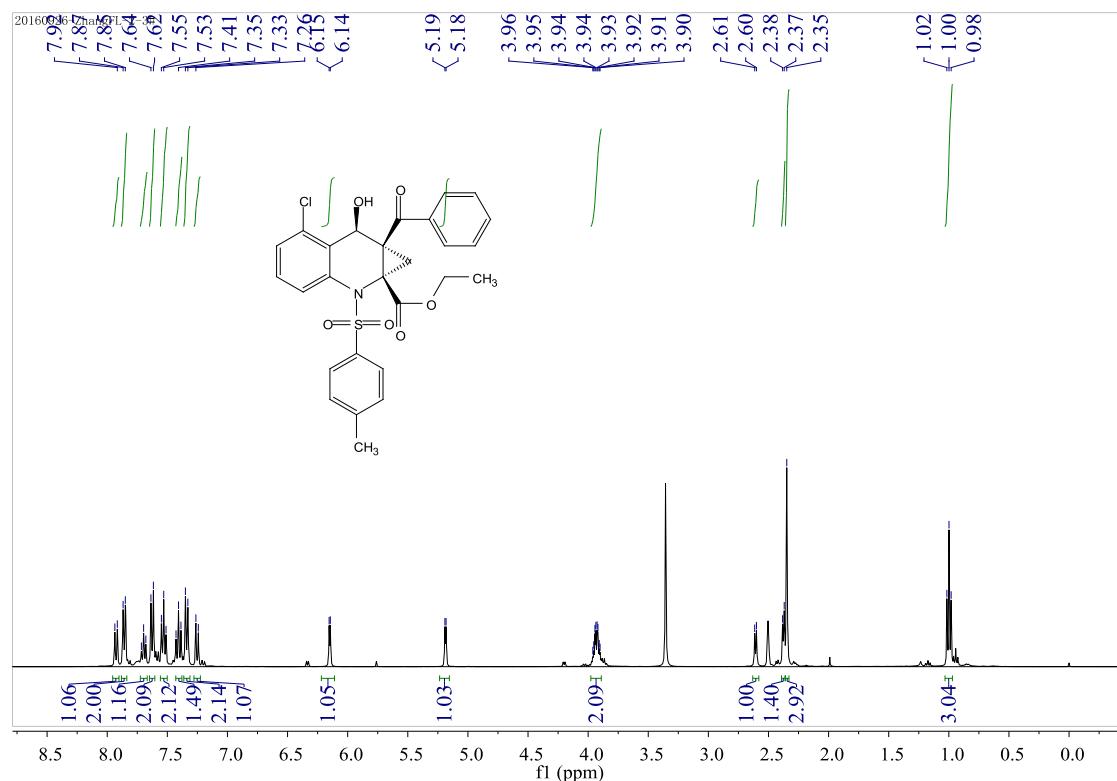
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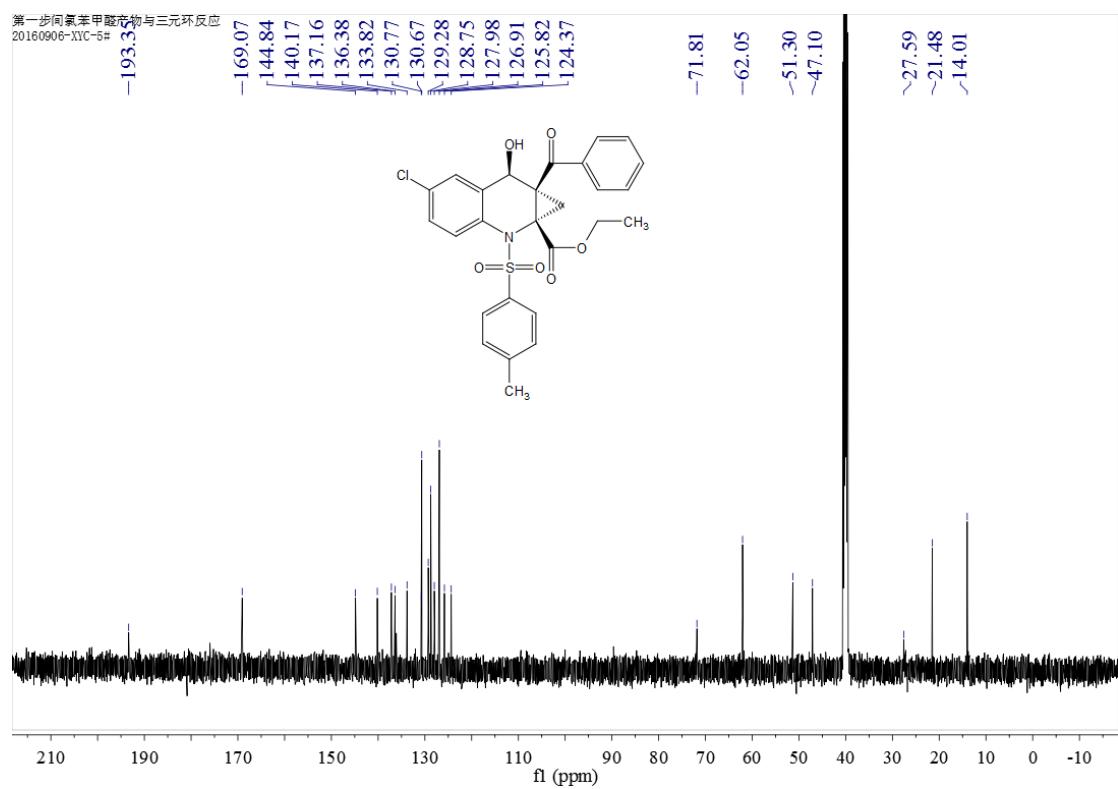
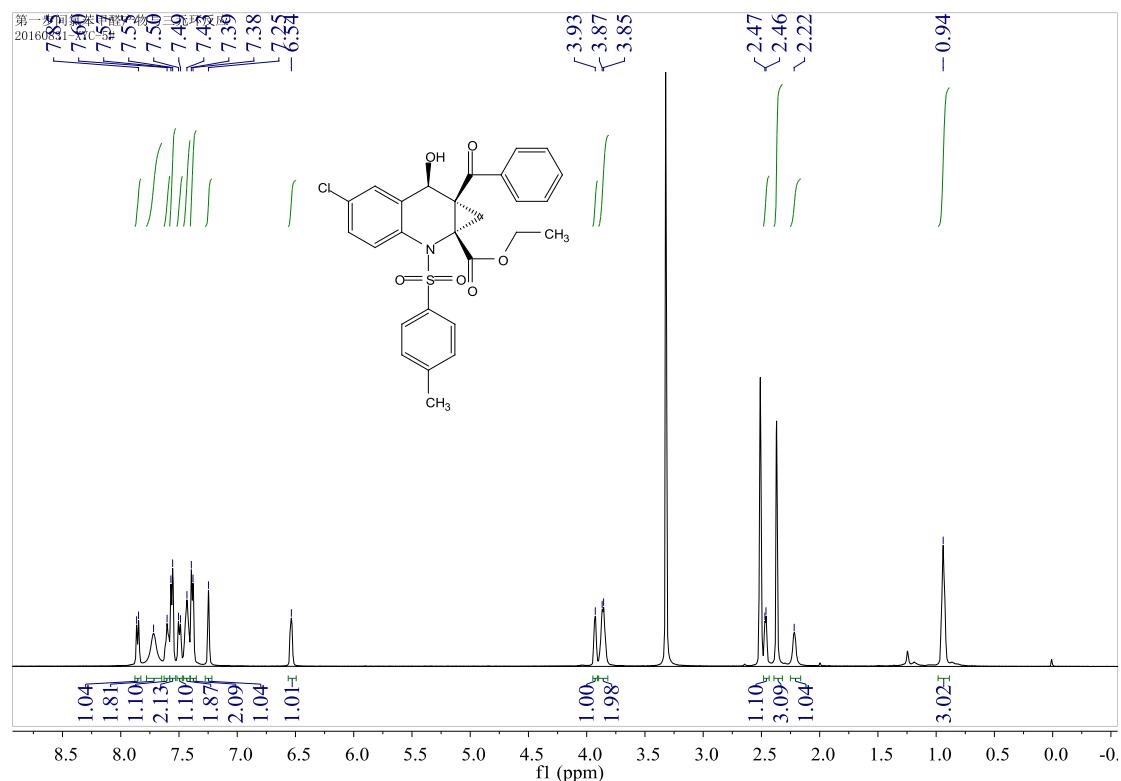
**27. 5fa**



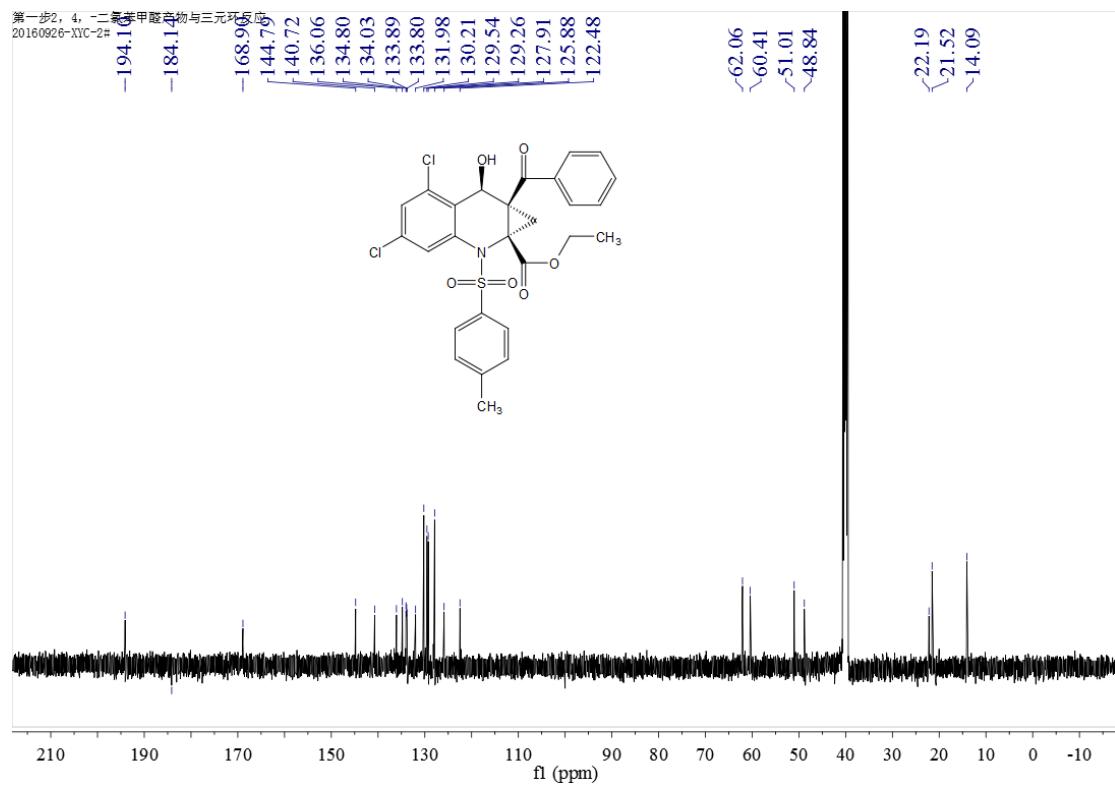
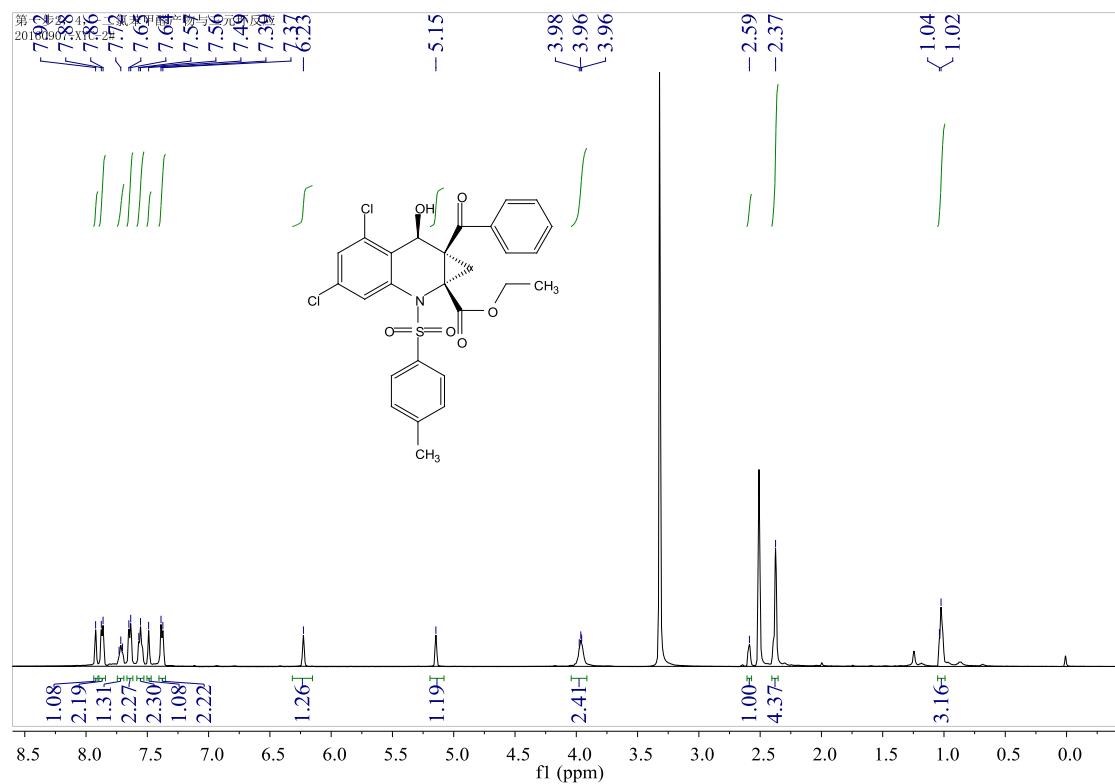
**28. 5ga**



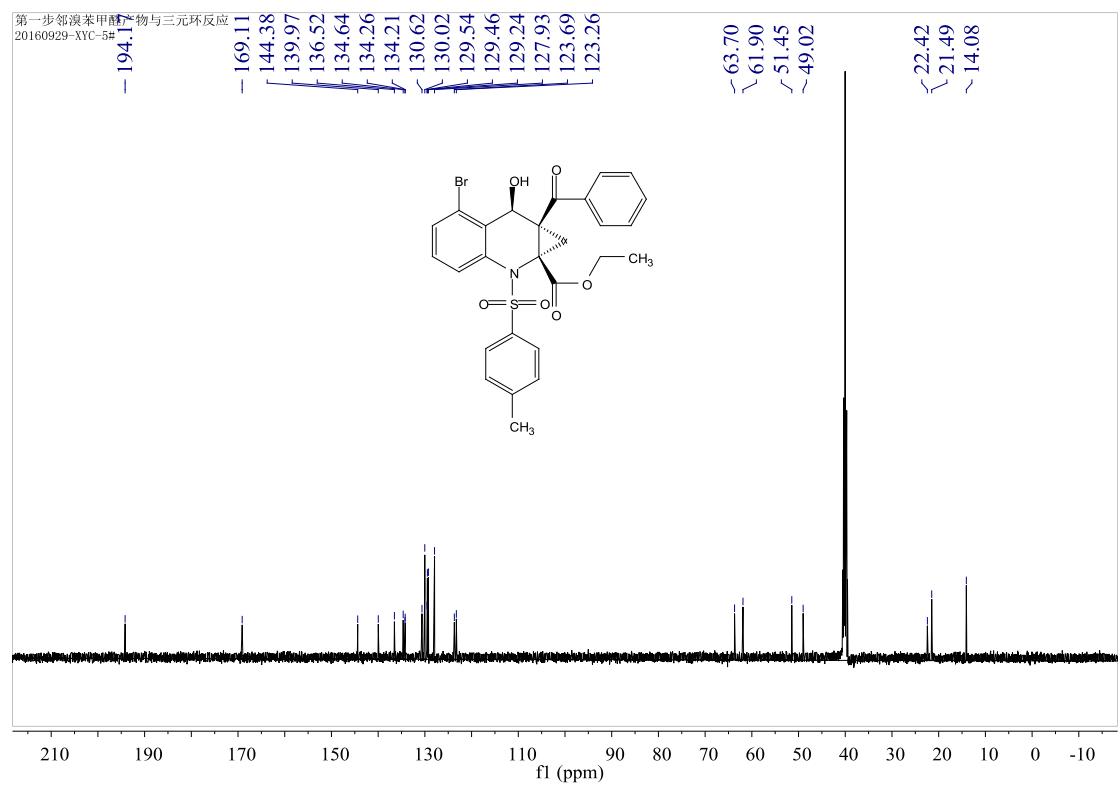
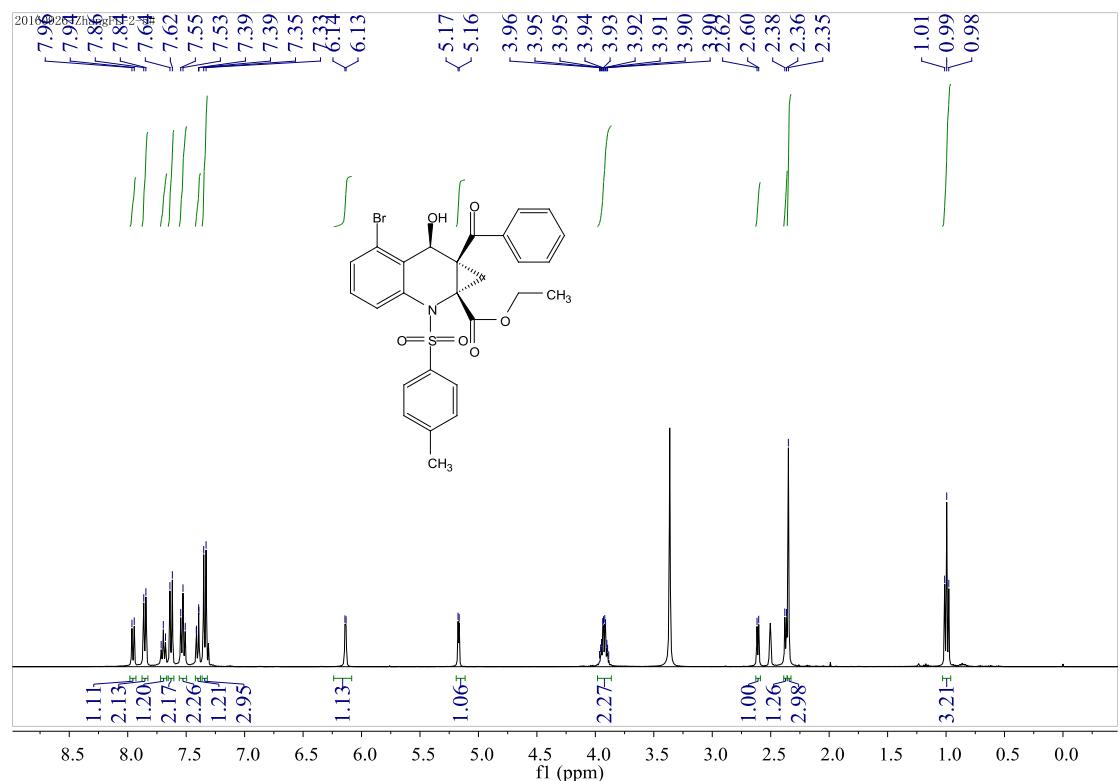
**29. 5ha**



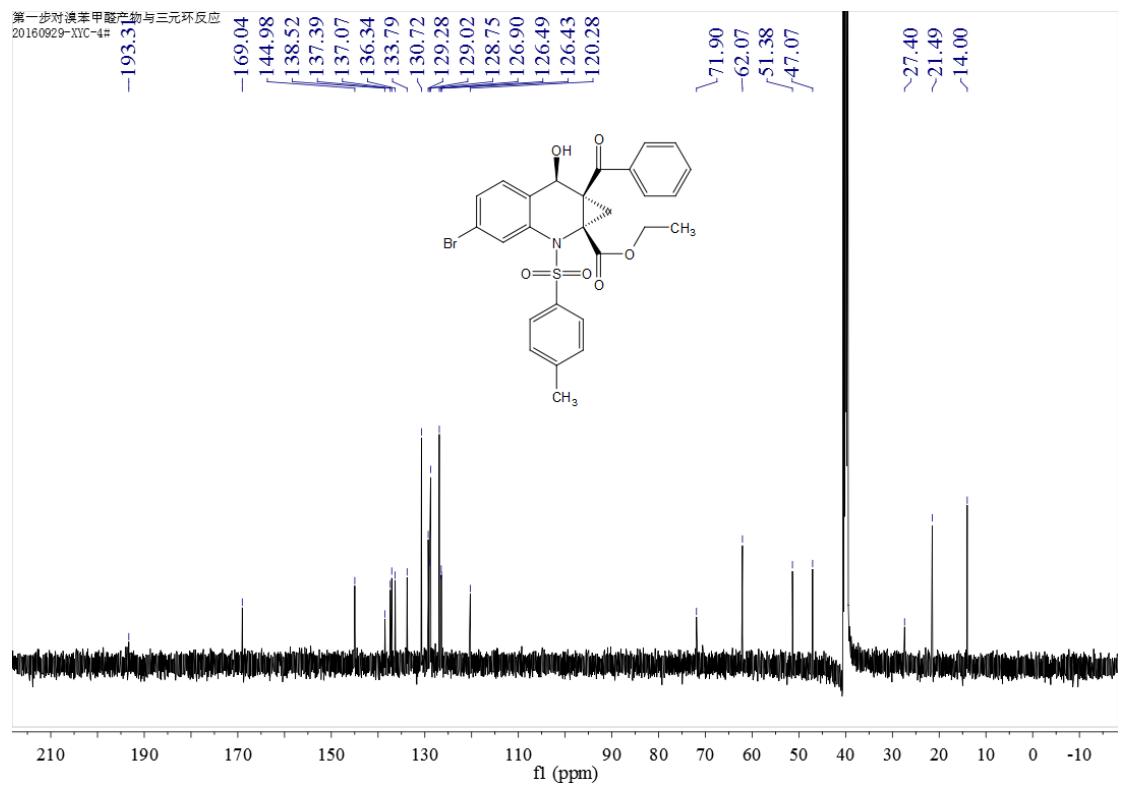
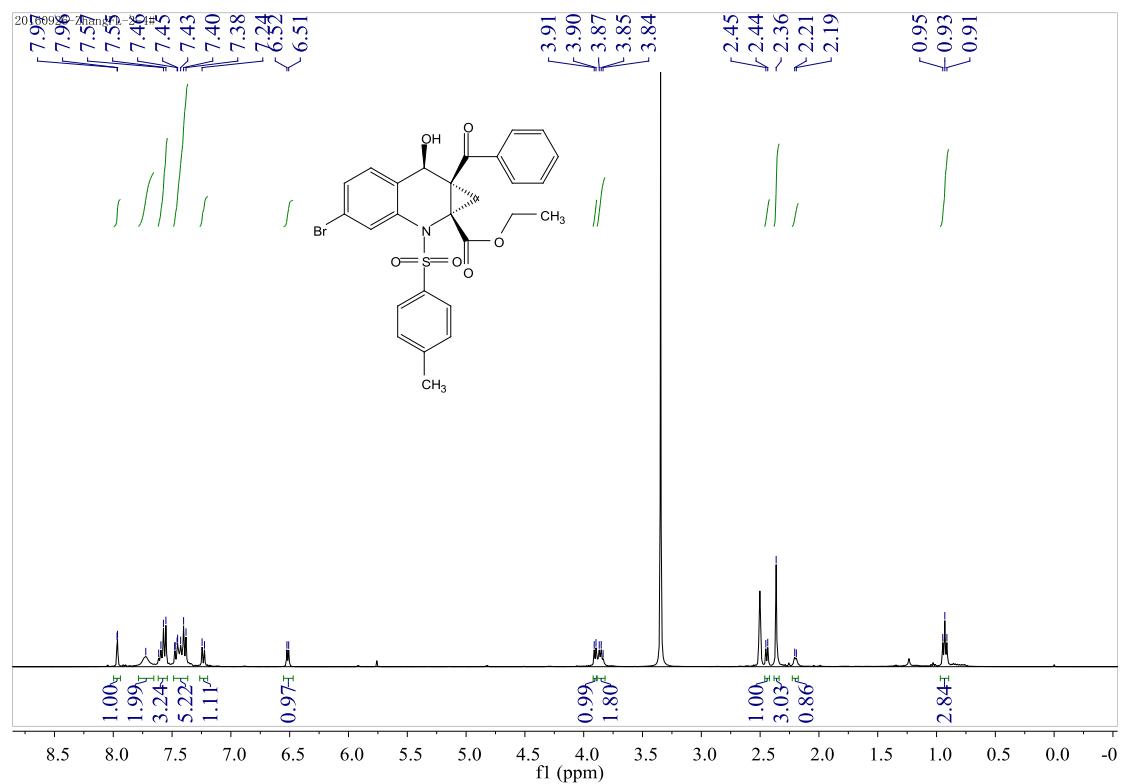
**30. 5ia**



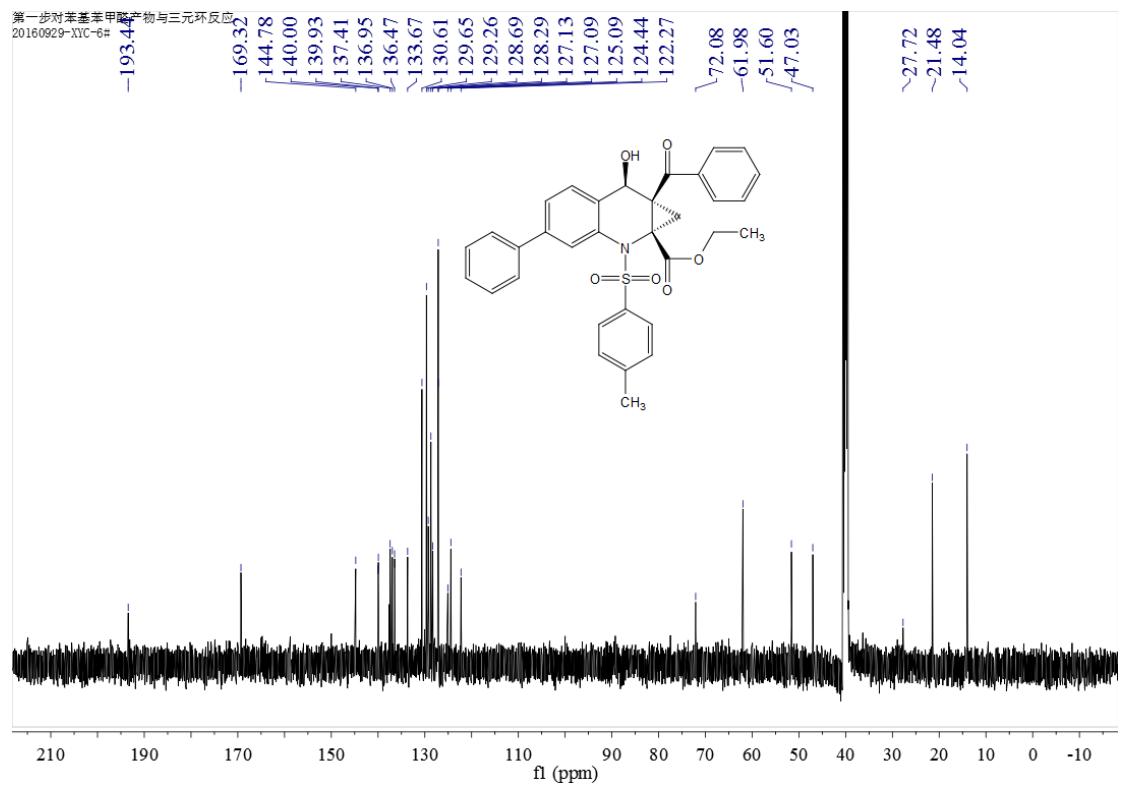
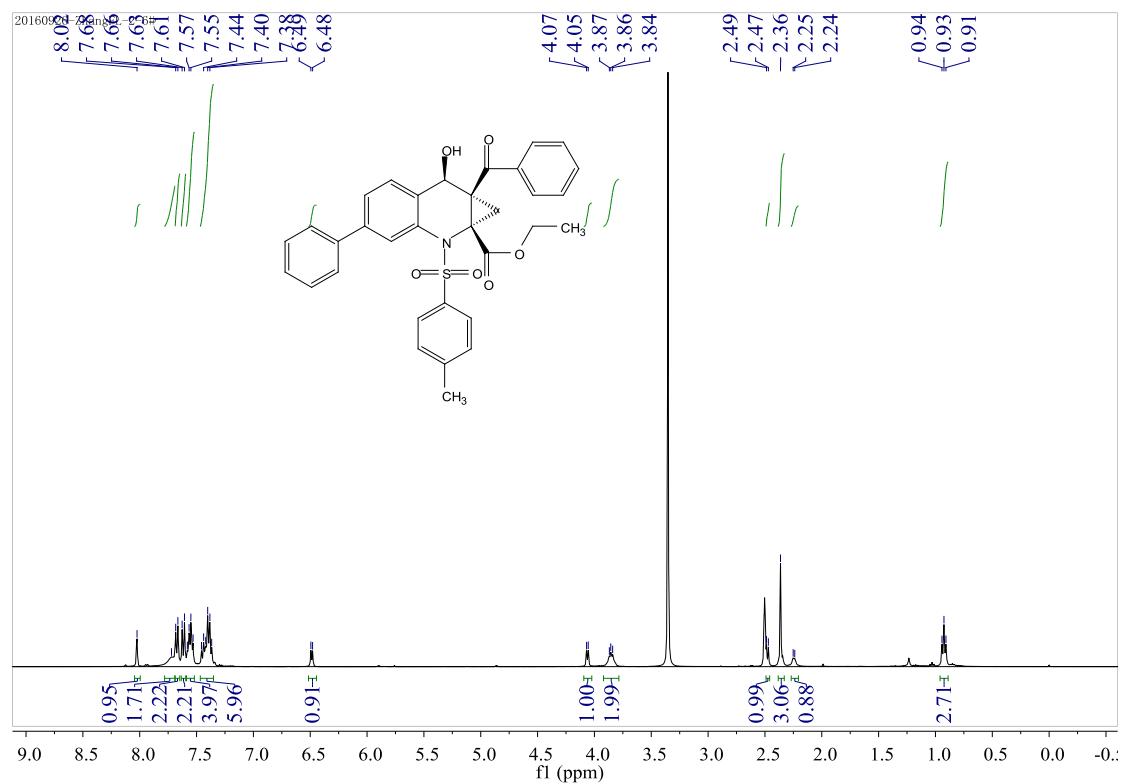
**31. 5ja**



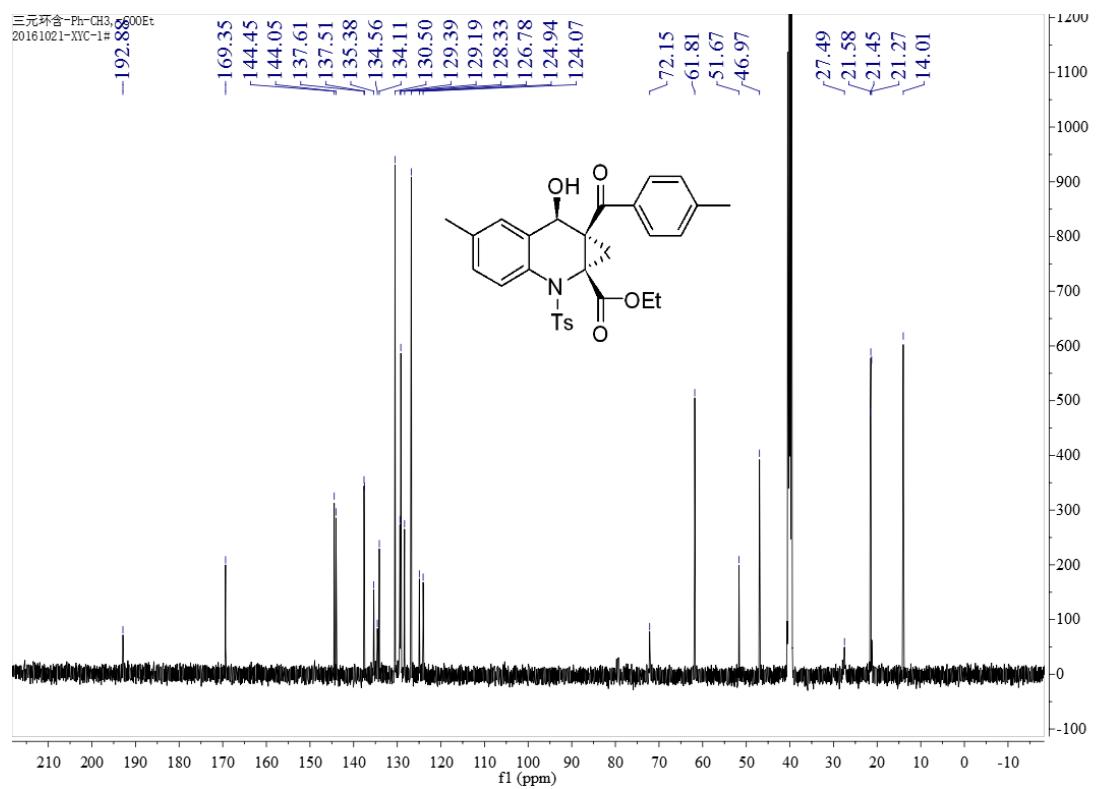
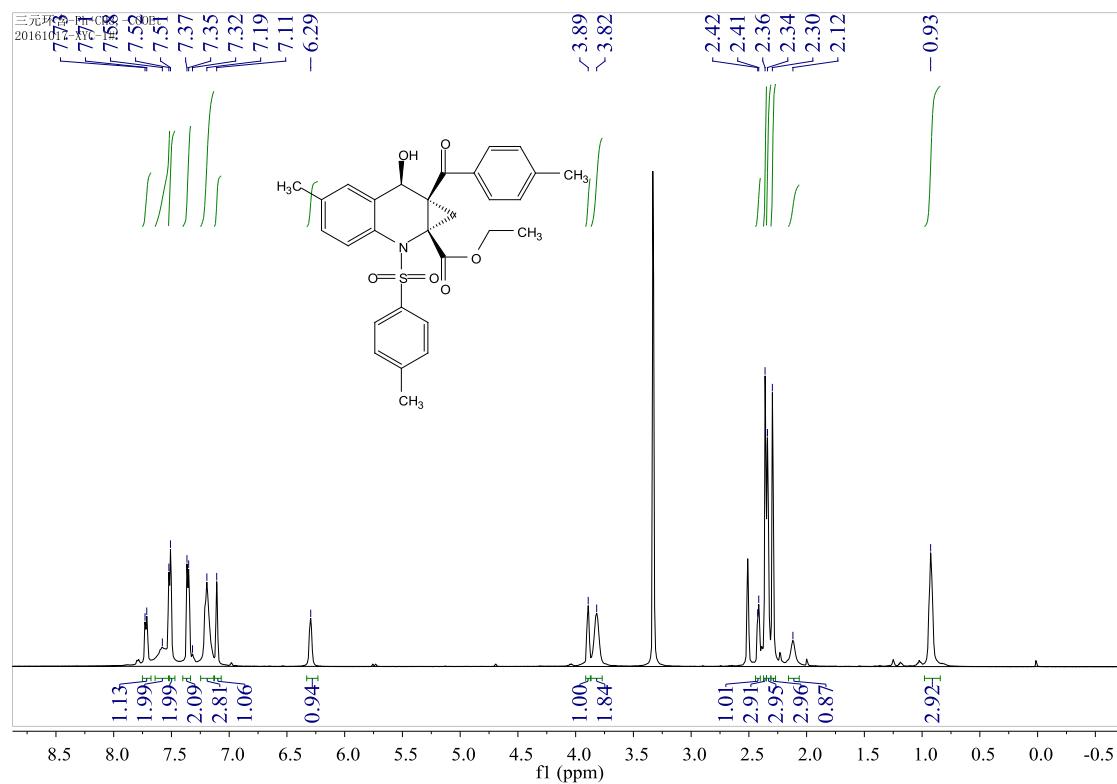
**32. 5ka**



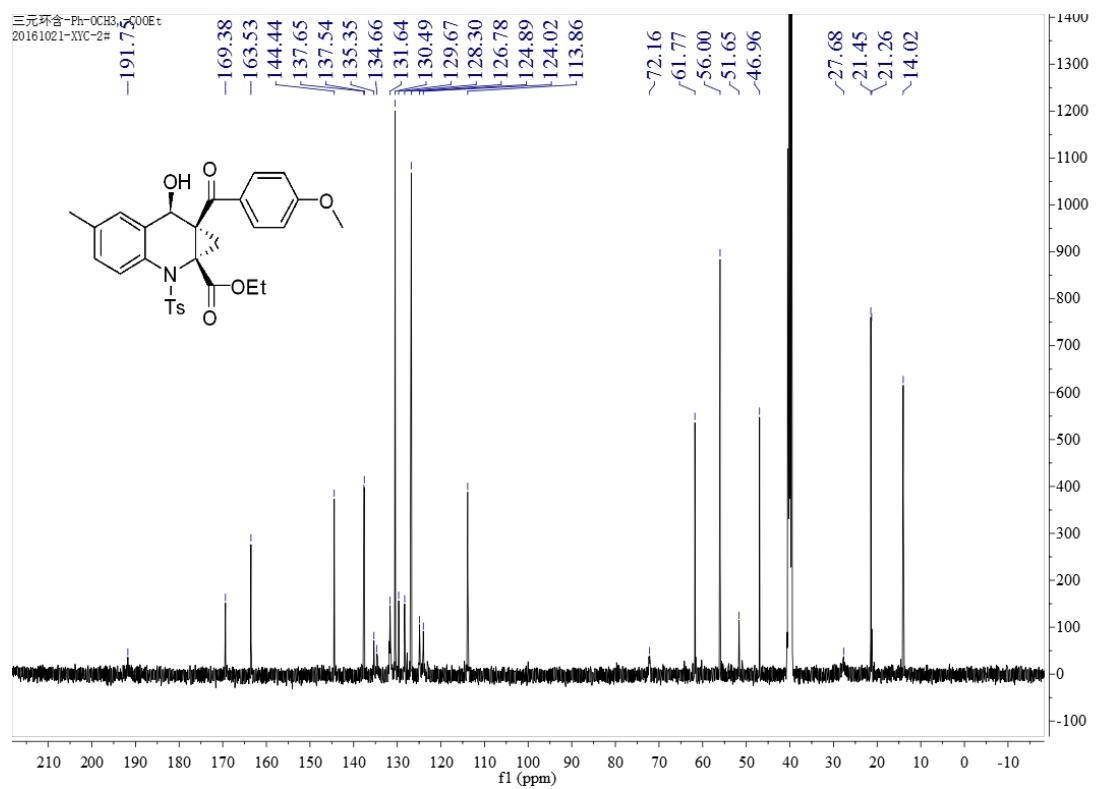
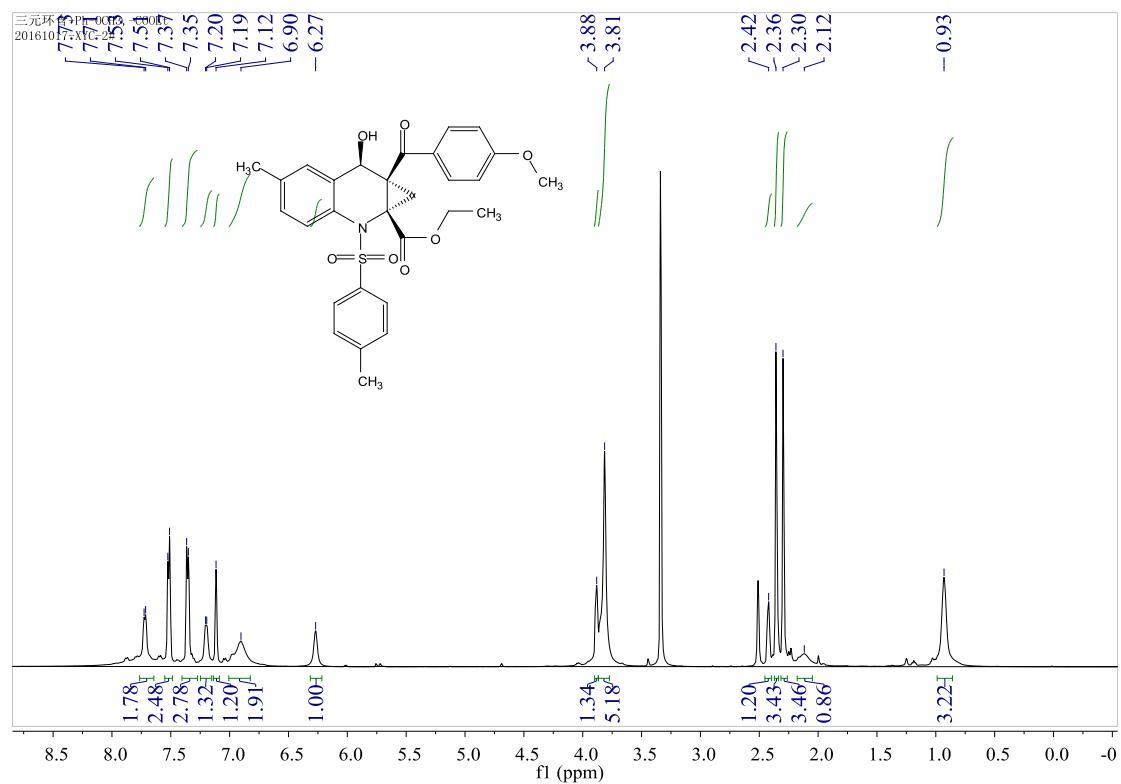
**33. 5la**



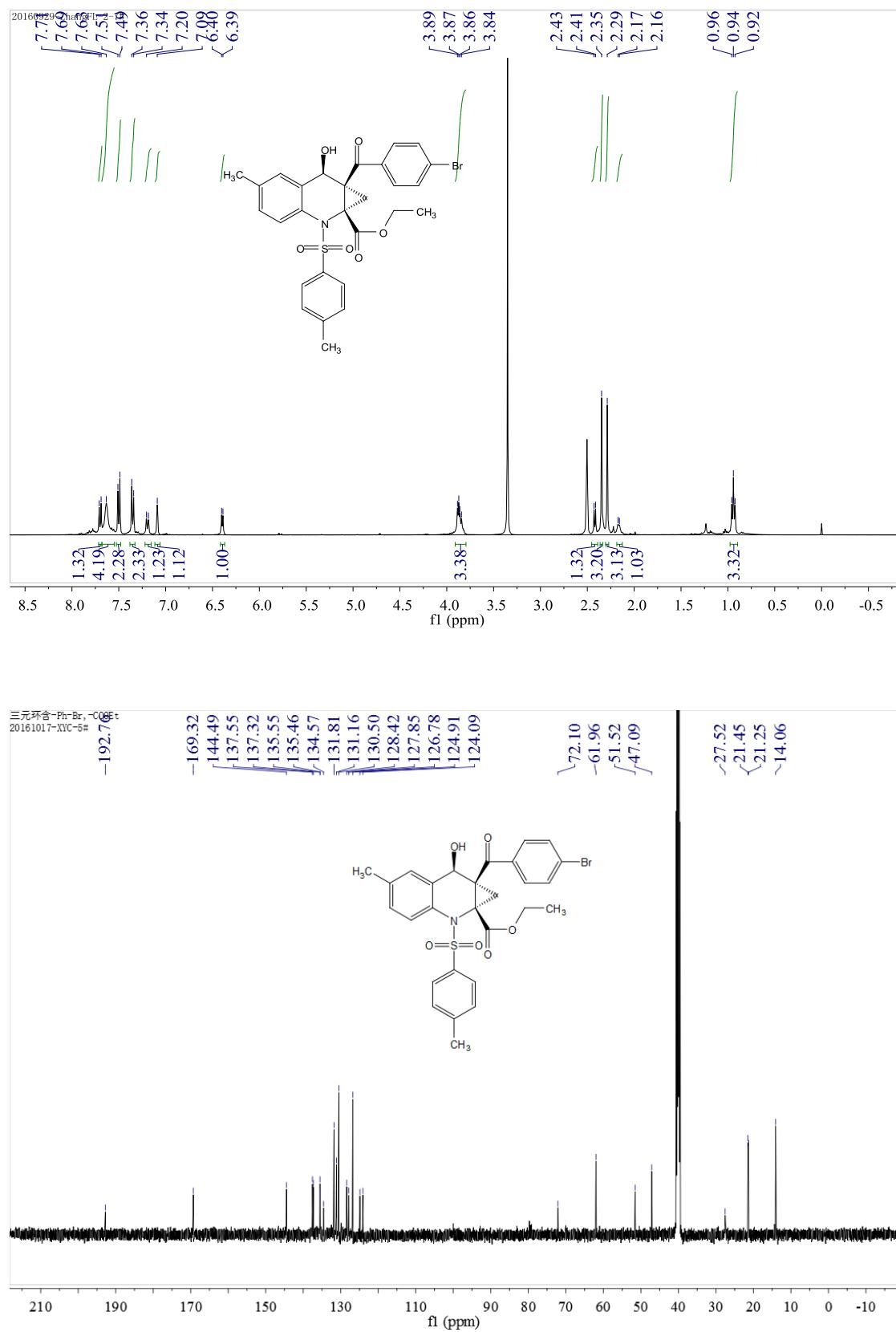
**34. 5ab**



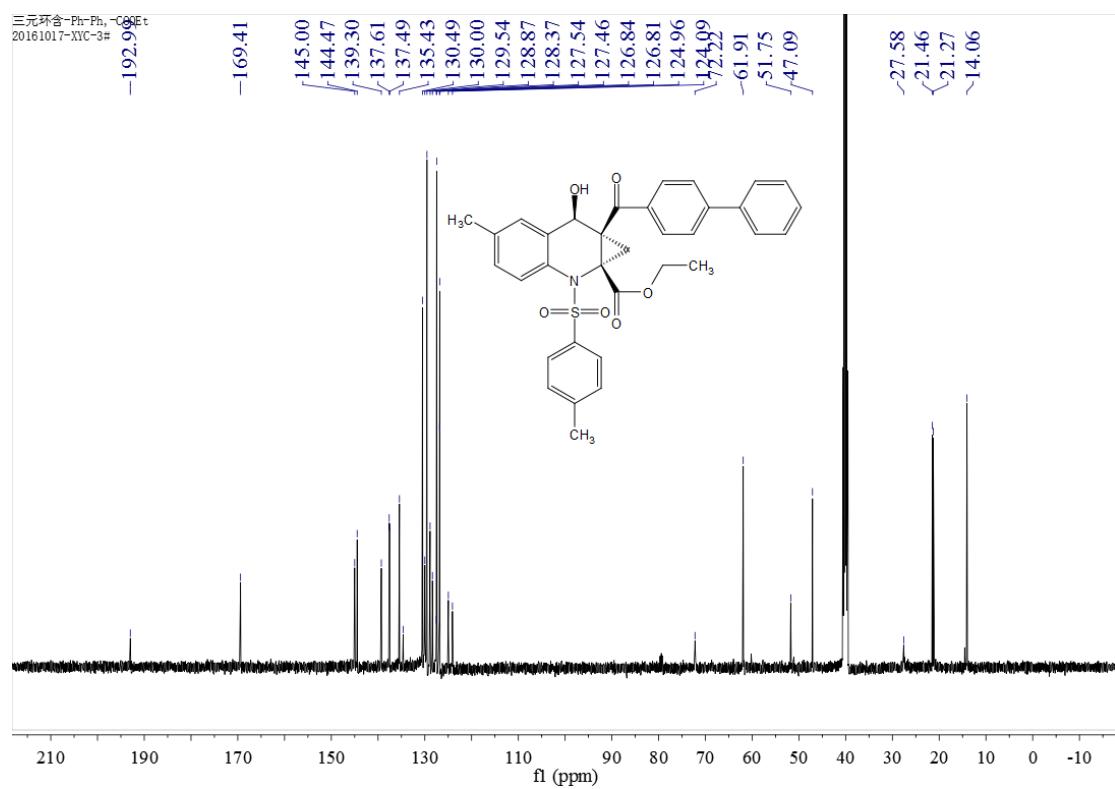
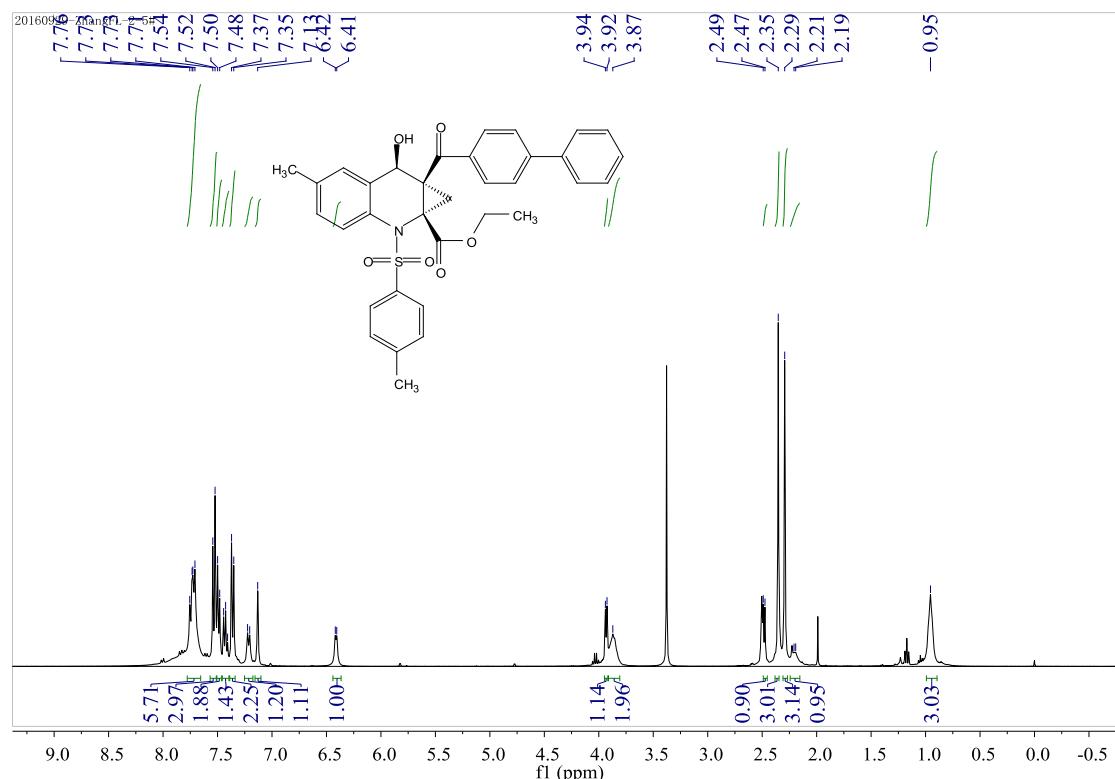
**35. 5ac**



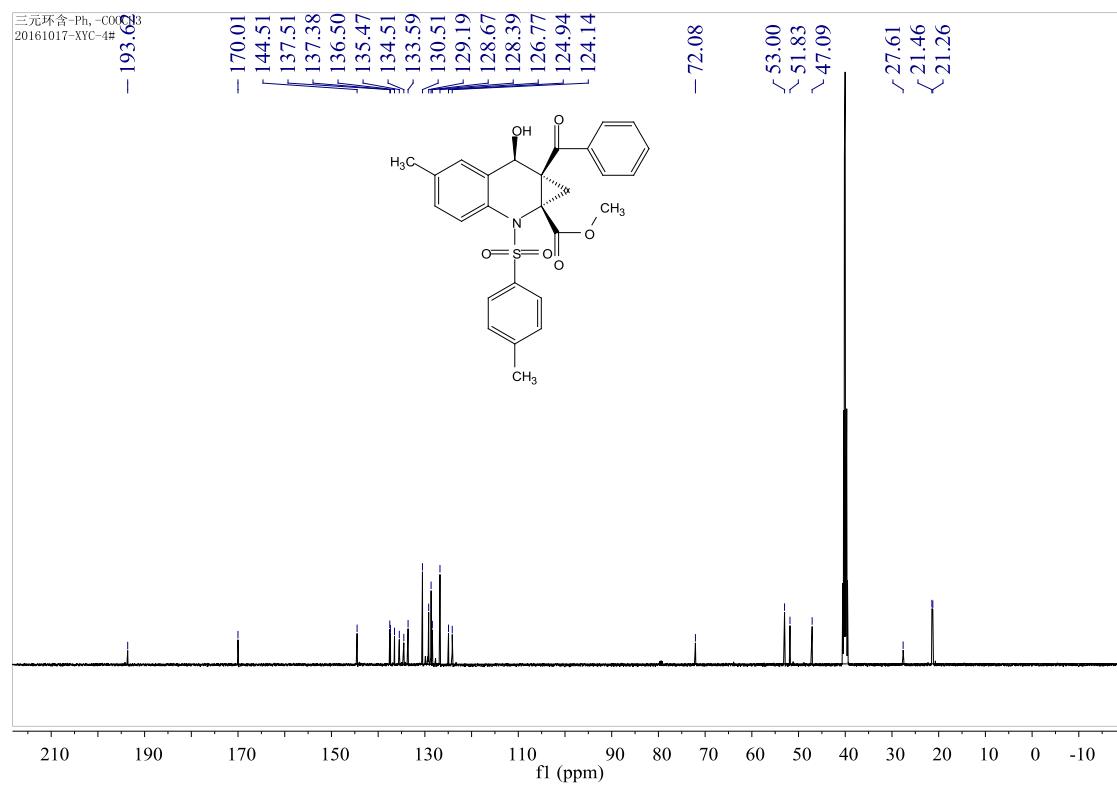
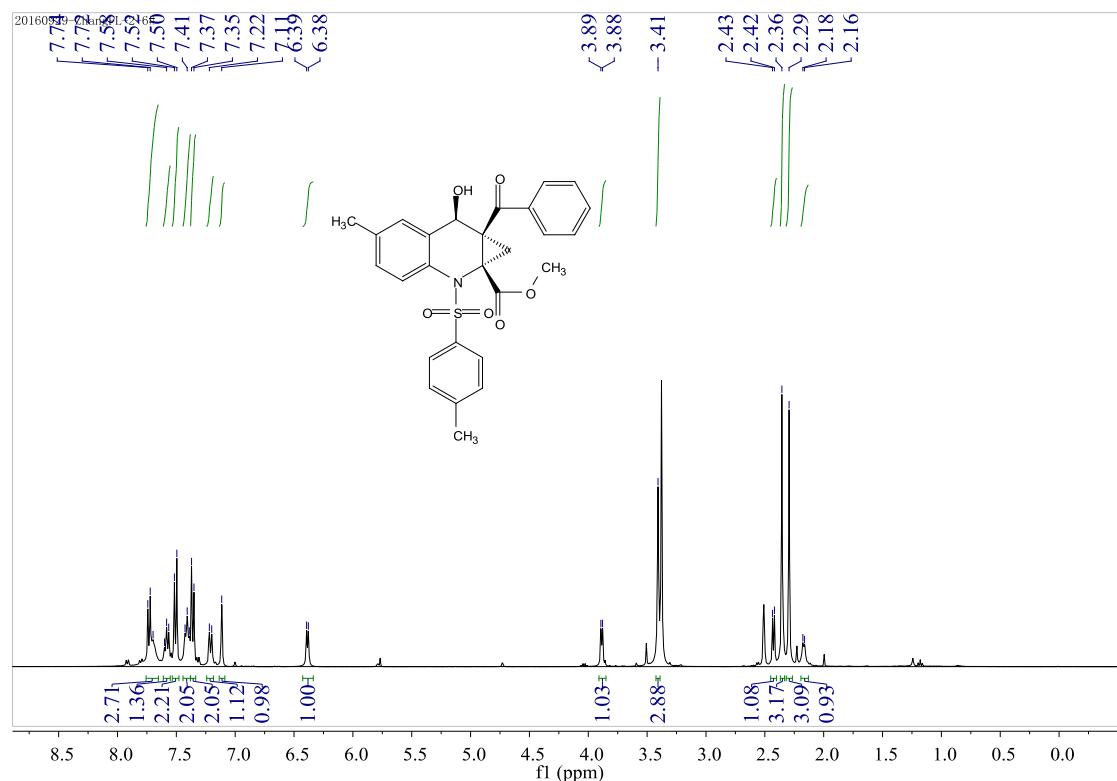
**36. 5ad**



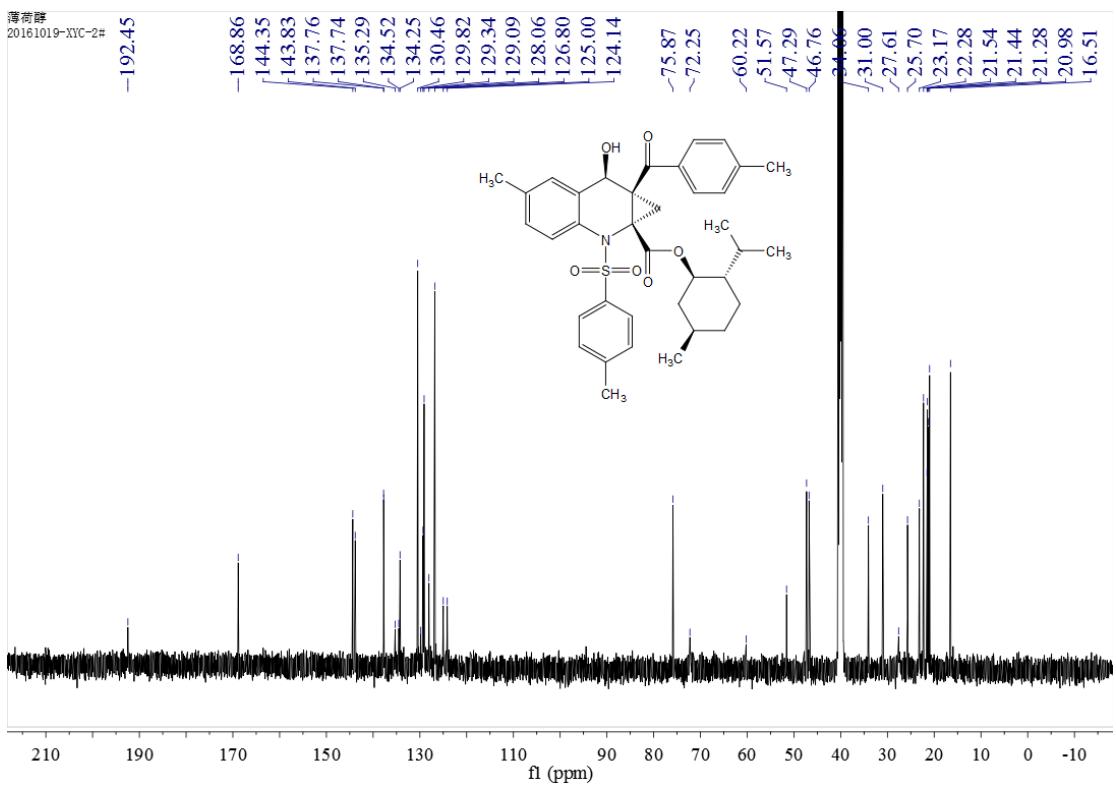
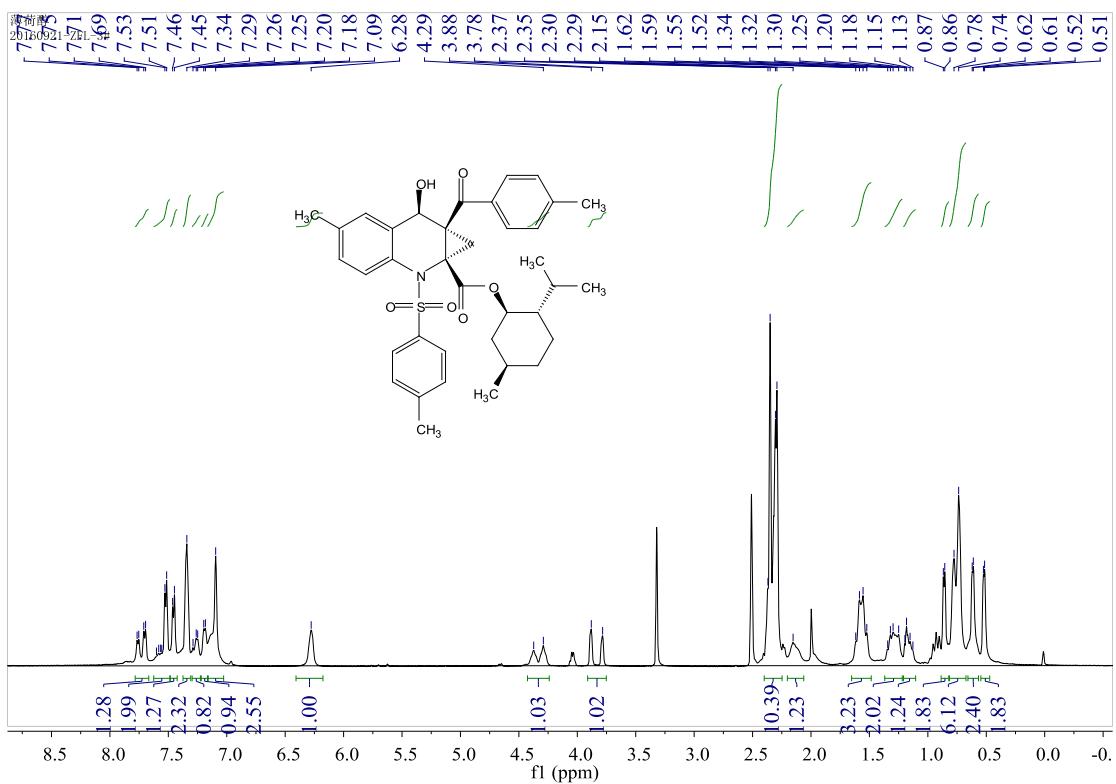
**37. 5ae**



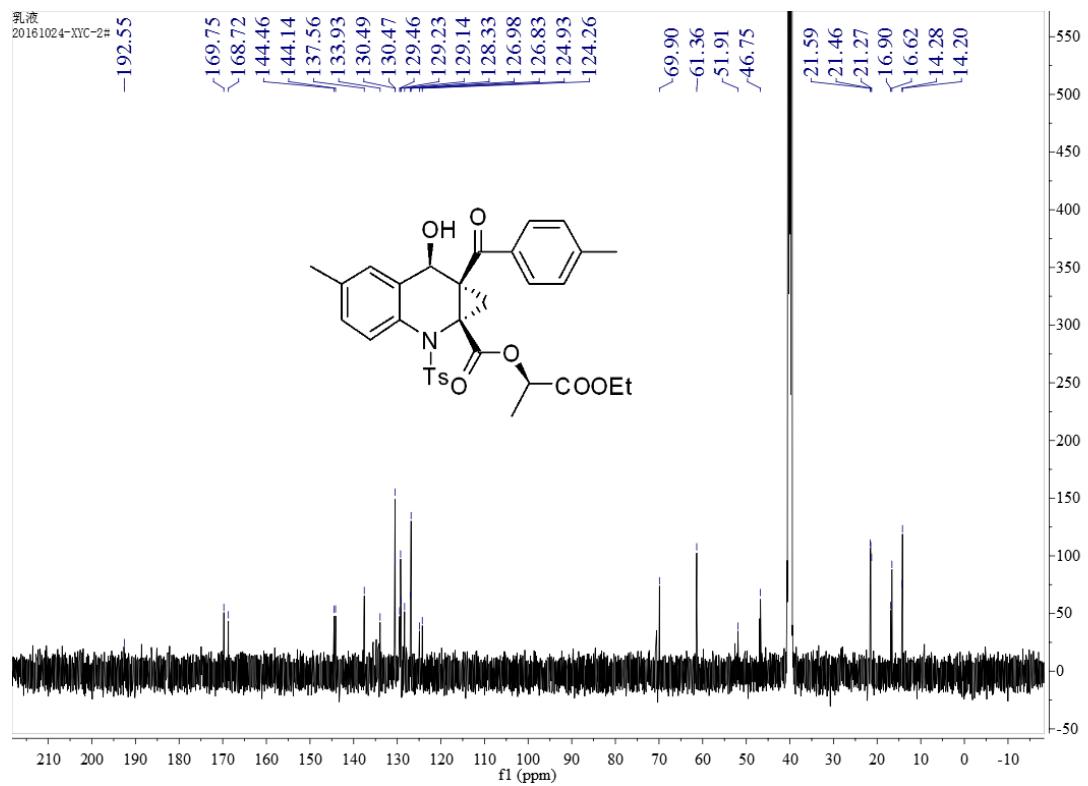
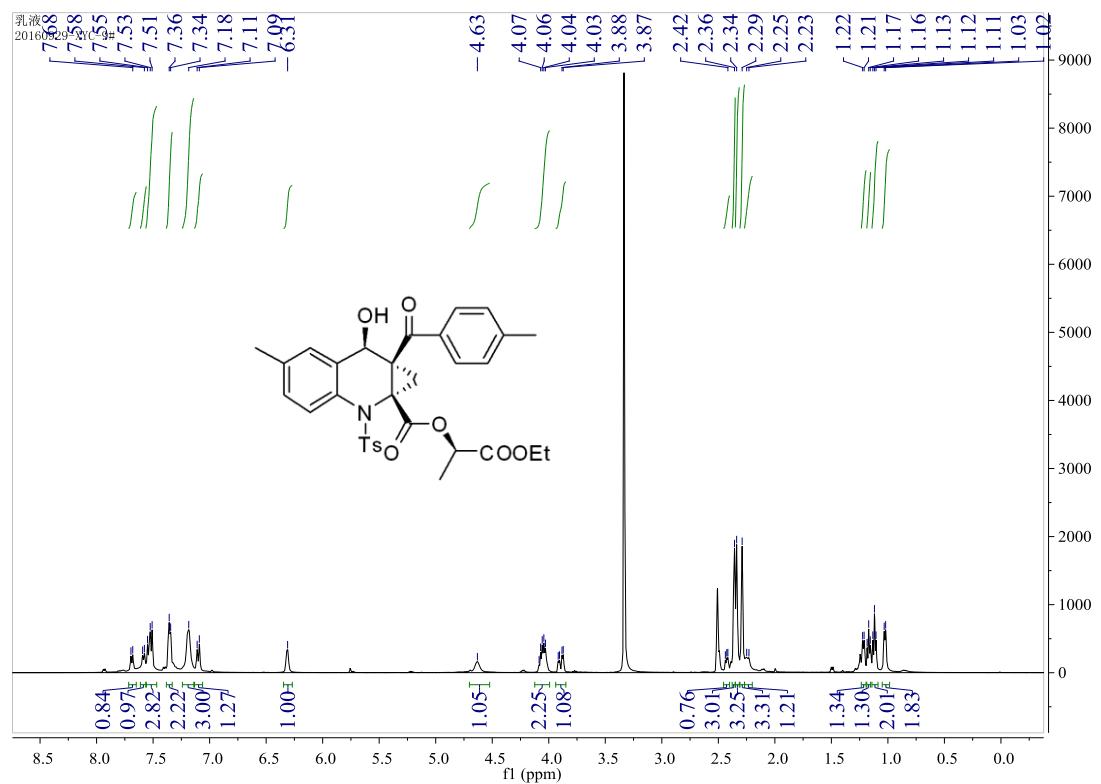
**38. 5af**



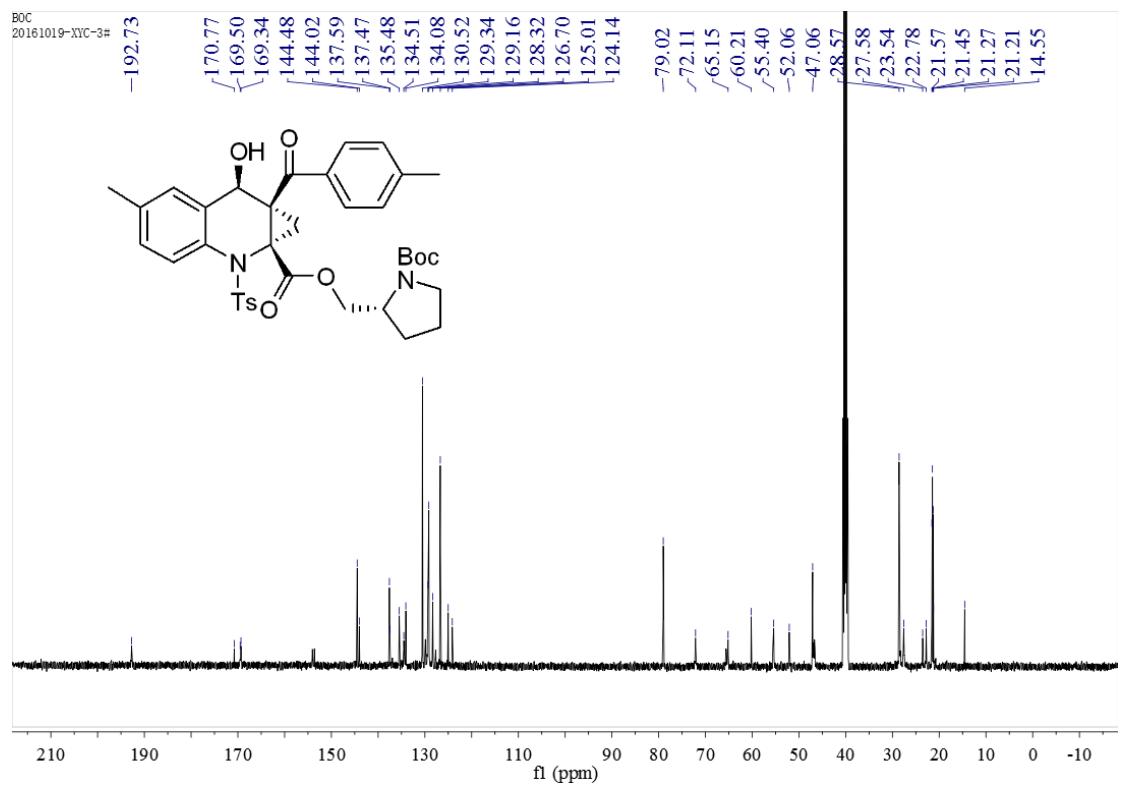
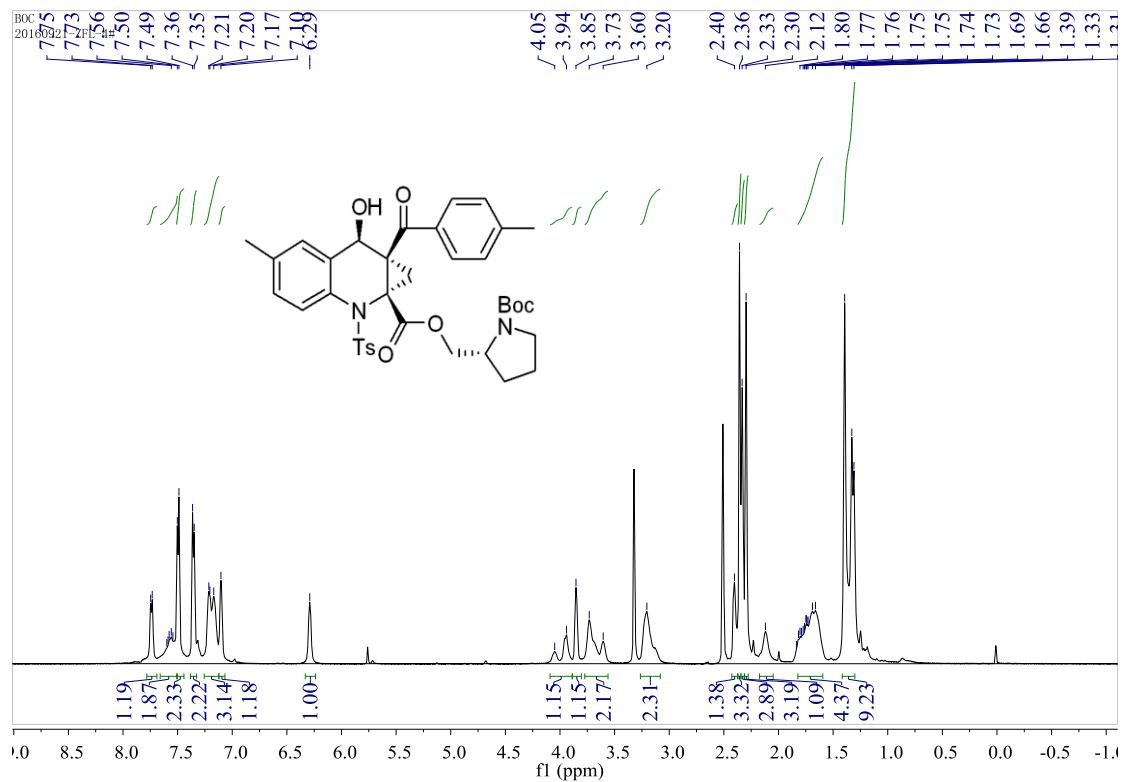
39. 5ag



**40. 5ah**



**41. 5ai**



#### 4. X-ray structure of **5aa**

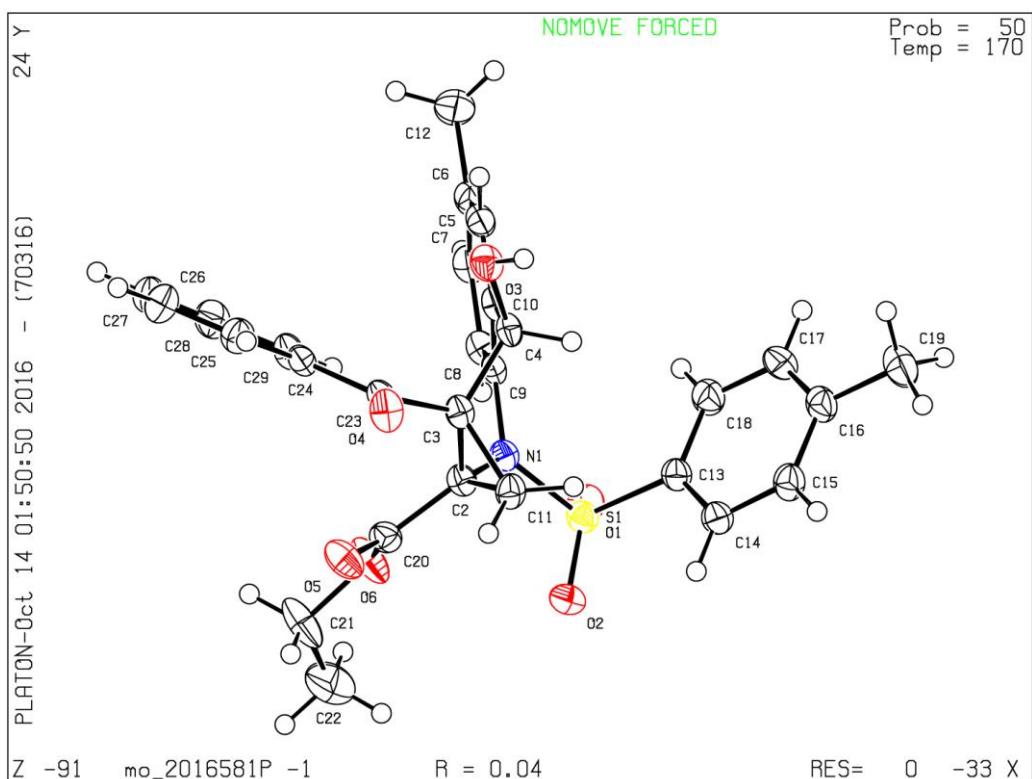


Figure 1. Crystal structure of **5aa**

CCDC-1525861 contains the supplementary crystallographic data for **5aa**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).