

**Supporting Information for**  
**Iridium- and Rhodium-Catalyzed C–H Activation and Formyl Arylation of**  
**Benzaldehydes under Chelation-Assistance**

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## General Information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. *N*-Sulfonyl 2-aminobenzaldehyde (**4**), cyclometalated Rh(III) complexes (**11**),<sup>1</sup> and diaryliodonium triflates<sup>2</sup> were prepared according to following literature reports. All reactions were carried out using Schlenk techniques or in an argon-filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvents indicated. The chemical shift is given in dimensionless  $\delta$  values and is frequency referenced relative to TMS in <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. HRMS data were obtained using a TOF mode. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

**General Procedure for Synthesis of 3.** Aldehydes (0.20 mmol), diaryliodonium triflate (0.22 mmol), CsOAc (0.24 mmol), [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (2.5 mol %), CH<sub>3</sub>OH or CH<sub>3</sub>CN (2.0 mL) were charged into the sealed tube. The reaction mixture was stirred at room temperature for 20 h. After the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (50:1) to afford compounds **3**.

**(2-Hydroxyphenyl)(*o*-tolyl)methanone (3aa).**<sup>3</sup> Pale yellow solid (31.8 mg, 75%, 0.15 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.25 (s, 1H), 7.53–7.46 (m, 1H), 7.43–7.37 (m, 1H), 7.33–7.26 (m, 4H), 7.06 (dd,  $J$  = 8.4, 0.8 Hz, 1H), 6.85–6.76 (m, 1H), 2.30 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  204.6, 163.4, 138.0, 136.9, 135.7, 133.8, 131.0, 130.3, 127.6, 125.5, 120.0, 119.0, 118.4, 19.7.

**(2-Hydroxyphenyl)(*m*-tolyl)methanone (3ab).**<sup>4</sup> Pale yellow liquid (42.2 mg, 99%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.06 (s, 1H), 7.60 (dd,  $J$  = 8.0, 1.3 Hz, 1H), 7.54–7.43 (m, 3H), 7.38–7.41 (m, 2H), 7.07 (d,  $J$  = 8.4 Hz, 1H), 6.87–6.91 (m, 1H), 2.43 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.9, 163.2, 138.3, 138.0, 136.3, 133.7, 132.7, 129.6, 128.2, 126.4, 119.2, 118.6, 118.4, 21.4.

**(2-Hydroxyphenyl)(*p*-tolyl)methanone (3ac).**<sup>3</sup> Pale yellow solid (38.1 mg, 90%, 0.18 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.04 (s, 1H), 7.58–7.63 (m, 3H), 7.52–7.44 (m, 1H), 7.30 (d,  $J$  = 7.9 Hz, 2H), 7.06 (d,  $J$  = 8.4 Hz, 1H), 6.86 (m, 1H), 2.44 (s, 3H). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.5, 163.2, 142.9, 136.2, 135.3, 133.6, 129.6, 129.1, 119.4, 118.7, 118.5, 21.7.

**(4-Chlorophenyl)(2-hydroxyphenyl)methanone (3ad).**<sup>3</sup> Yellow solid (44.0 mg, 95%, 0.19 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.88 (s, 1H), 7.66–7.60 (m, 2H), 7.53 (m, 2H), 7.51–7.47 (m, 2H), 7.13–7.02 (m, 1H), 6.94–6.83 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.4, 163.3, 138.5, 136.7, 136.3, 133.3, 130.8, 128.8, 119.1, 118.9, 118.7.

**(4-Bromophenyl)(2-hydroxyphenyl)methanone (3ae).**<sup>3</sup> Yellow solid (50.9 mg, 92%, 0.18 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.87 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.56–7.49 (m, 4H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.91–6.83 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 200.4, 163.3, 136.7, 133.3, 131.8, 130.9, 127.0, 119.0, 118.9, 118.7.

**(2-Hydroxyphenyl)(4-(trifluoromethyl)phenyl)methanone (3af).**<sup>4</sup> Yellow solid (51.6 mg, 97%, 0.19 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.88 (s, 1H), 7.78 (s, 4H), 7.58–7.52 (m, 1H), 7.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.10 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.95–6.85 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.6, 163.5, 141.2, 137.1, 133.6 (q, *J* = 26.4 Hz), 133.4, 129.4, 125.6 (q, *J* = 3.8 Hz), 123.74 (q, *J* = 272.6 Hz), 119.1, 118.9, 118.8. HRMS: [M + H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>O<sub>2</sub><sup>+</sup>: 267.0627, found: 267.0629.

**(2-Hydroxy-3-methylphenyl)(*p*-tolyl)methanone (3ag).**<sup>5</sup> Yellow solid (44.8 mg, 99%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.34 (s, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.7 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.8, 161.7, 142.7, 137.0, 135.6, 131.3, 129.6, 129.1, 127.5, 118.7, 118.0, 21.7, 15.7.

**(2-Hydroxy-4-methylphenyl)(*p*-tolyl)methanone (3ah).**<sup>6</sup> Yellow solid (44.5 mg, 98%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.14 (s, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.87 (s, 1H), 6.67 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.0, 163.5, 147.9, 142.6, 135.5, 133.6, 129.5, 129.1, 120.0, 118.5, 117.2, 22.1, 21.7.

**(2-Hydroxy-5-methoxyphenyl)(*p*-tolyl)methanone (3ai).**<sup>7</sup> Yellow solid (40.8 mg, 84%, 0.17 mmol) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.58 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.13 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.09 (d, *J* = 3.0 Hz, 1H), 7.01 (d, *J* = 9.0 Hz,

1H), 3.71 (s, 3H), 2.45 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 157.5, 151.5, 142.9, 135.3, 129.5, 129.2, 123.9, 119.3, 119.0, 116.4, 56.1, 21.8.

**(2-Hydroxy-3-methoxyphenyl)(*p*-tolyl)methanone (3aj).** Yellow solid (45.6 mg, 94%, 0.19 mmol); mp 76-77 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.21 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 8.1 Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.6, 153.4, 149.1, 143.0, 135.4, 129.7, 129.1, 124.9, 119.7, 118.1, 117.0, 56.4, 21.8. HRMS: [M + H]<sup>+</sup> calculated for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub><sup>+</sup>: 243.1016, found: 243.1016.

**(5-Fluoro-2-hydroxyphenyl)(*p*-tolyl)methanone (3ak).**<sup>8</sup> Yellow solid (41.7 mg, 91%, 0.18 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.74 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 12.3, 5.7 Hz, 3H), 7.27–7.19 (m, 1H), 7.03 (dd, *J* = 9.1, 4.5 Hz, 1H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 159.2, 155.7, 153.3, 143.3, 134.6, 129.4 (d, *J* = 18.0 Hz), 123.7 (d, *J* = 23.6 Hz), 119.8 (d, *J* = 7.3 Hz), 119.0 (d, *J* = 6.3 Hz), 118.4 (d, *J* = 23.7 Hz), 21.8. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.43, 159.35 (d, *J* = 1.4 Hz), 154.65 (d, *J* = 238.3 Hz), 143.38, 134.72, 129.52, 129.34, 123.70 (d, *J* = 23.6 Hz), 119.75 (d, *J* = 7.3 Hz), 118.97 (d, *J* = 6.3 Hz), 118.41 (d, *J* = 23.7 Hz), 21.78.

**(5-Chloro-2-hydroxyphenyl)(*p*-tolyl)methanone (3al).**<sup>9</sup> Yellow solid (49.0 mg, 99%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.90 (s, 1H), 7.58 (t, *J* = 5.8 Hz, 3H), 7.43 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.4, 161.7, 143.5, 136.0, 134.6, 132.5, 129.6, 129.4, 123.4, 120.1, 120.0, 21.8.

**(3-Bromo-2-hydroxyphenyl)(*p*-tolyl)methanone (3am).** Yellow solid (54.7 mg, 94%, 0.19 mmol); mp: 116-117 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.70 (s, 1H), 7.74–7.76 (m, 1H), 7.61–7.58 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 7.9 Hz, 1H), 2.45 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 159.6, 143.5, 139.3, 134.7, 132.9, 129.7, 129.3, 120.3, 119.4, 112.1, 21.8. HRMS: [M + H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>12</sub>BrO<sub>2</sub><sup>+</sup>: 291.0015, found: 291.0017.

**(4-(Diethylamino)-2-hydroxyphenyl)(*p*-tolyl)methanone (3an).**<sup>10</sup> Yellow solid (56.1 mg, 99%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.03 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 6.19–6.09 (m, 2H), 3.40 (q, *J* = 7.1

Hz, 4H), 2.42 (s, 3H), 1.20 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.9, 166.3, 153.8, 141.2, 136.3, 135.6, 129.0, 128.9, 109.2, 103.5, 97.4, 44.8, 21.6, 12.8.

**(2-Hydroxy-5-nitrophenyl)(*p*-tolyl)methanone (3ao).** Yellow solid (38.0 mg, 74%, 0.15 mmol); mp: 107-108;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.70 (s, 1H), 8.62 (d,  $J = 2.7$  Hz, 1H), 8.38 (dd,  $J = 9.2, 2.7$  Hz, 1H), 7.64 (d,  $J = 8.1$  Hz, 2H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 9.2$  Hz, 1H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.3, 168.1, 144.4, 139.5, 133.8, 130.8, 129.7, 129.7, 129.7, 119.6, 118.3, 21.9. HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{12}\text{NO}_4^+$ : 258.0761, found: 258.0762.

**(3,5-Di-*tert*-butyl-2-hydroxyphenyl)(*p*-tolyl)methanone (3ap).**<sup>11</sup> Yellow solid (62.8 mg, 97%, 0.20 mmol);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.70 (s, 1H), 7.59 (d,  $J = 8.0$  Hz, 3H), 7.46 (d,  $J = 1.9$  Hz, 1H), 7.29 (d,  $J = 7.9$  Hz, 2H), 2.44 (s, 3H), 1.47 (s, 9H), 1.25 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.4, 160.7, 142.5, 139.8, 137.9, 136.1, 131.1, 129.7, 129.0, 128.0, 118.5, 35.3, 34.4, 31.5, 29.6, 21.7.

**(3,5-Dichloro-2-hydroxyphenyl)(*p*-tolyl)methanone (3aq).** Yellow solid (55.8 mg, 99%, 0.20 mmol). mp: 99-101 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.42 (s, 1H), 7.61 (s, 1H), 7.59 (d,  $J = 2.8$  Hz, 2H), 7.53 (d,  $J = 2.5$  Hz, 2H), 7.35 (d,  $J = 7.9$  Hz, 1H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 157.5, 144.0, 135.6, 134.2, 131.1, 129.7, 129.5, 124.1, 123.3, 120.6, 21.9. HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{O}_2^+$ : 281.0131, found: 281.0131.

**(3,5-Dibromo-2-hydroxyphenyl)(*p*-tolyl)methanone (3ar).** Yellow solid (67.0 mg, 90%, 0.18 mmol); mp: 134-135 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.57 (s, 1H), 7.88 (s, 1H), 7.71 (d,  $J = 1.7$  Hz, 1H), 7.60 (d,  $J = 7.9$  Hz, 2H), 7.35 (d,  $J = 7.9$  Hz, 2H), 2.48 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 158.8, 144.0, 141.2, 134.8, 134.1, 129.7, 129.5, 121.1, 113.3, 110.3, 21.9. HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{O}_2^+$ : 368.9120, found: 368.9119.

**(3-Bromo-5-chloro-2-hydroxyphenyl)(*p*-tolyl)methanone (3as).** Yellow solid (64.4 mg, 99%, 0.20 mmol); mp: 114-115 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.54 (s, 1H), 7.74 (d,  $J = 1.7$  Hz, 1H), 7.59 (d,  $J = 8.1$  Hz, 2H), 7.57 (d,  $J = 2.5$  Hz, 1H), 7.34 (d,  $J = 8.0$  Hz, 2H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 158.3, 144.0, 138.6, 134.1, 131.8,

129.7, 129.5, 123.7, 120.4, 112.9, 21.8. HRMS:  $[M + H]^+$  calculated for  $C_{14}H_{11}BrClO_2^+$ : 324.9625, found: 324.9627.

**(2-Hydroxynaphthalen-1-yl)(p-tolyl)methanone (3at).** Yellow solid (52.0 mg, 99%, 0.20 mmol); mp: 129-130;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.97 (s, 1H), 7.90 (d,  $J = 9.0$  Hz, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.54 (d,  $J = 8.0$  Hz, 2H), 7.35 (d,  $J = 8.5$  Hz, 1H), 7.29–7.10 (m, 5H), 2.40 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  200.1, 160.9, 143.8, 137.6, 136.0, 132.5, 129.8, 129.3, 128.6, 128.5, 126.7, 126.41, 123.8, 119.2, 114.9, 21.8. HRMS:  $[M + H]^+$  calculated for  $C_{18}H_{15}O_2^+$ : 263.1067, found: 263.1070.

**General Procedure for Synthesis of 5.** *N*-sulfonyl 2-aminobenzaldehyde (0.20 mmol), diaryliodonium salts (0.40 mmol), CsOAc (0.40 mmol),  $[RhCp^*Cl_2]_2$  (4 mol %) and DCM (2.0 mL) were charged into the sealed tube. The reaction mixture was stirred at 80 °C for 20 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (30:1) to afford compounds **5**.

***N*-(2-benzoylphenyl)-4-methylbenzenesulfonamide (5aa).**<sup>12</sup> White solid (58.7 mg, 84%, 0.17 mmol);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.99 (s, 1H), 7.79 (d,  $J = 8.2$  Hz, 1H), 7.60–7.48 (m, 4H), 7.43–7.34 (m, 5H), 7.1–7.07 (m, 1H), 7.02 (d,  $J = 8.1$  Hz, 2H), 2.22 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  198.6, 143.8, 139.0, 137.6, 135.8, 133.8, 133.2, 132.8, 129.9, 129.6, 128.2, 127.3, 126.4, 123.6, 123.2, 21.5.

**4-Methyl-*N*-(2-(2-methylbenzoyl)phenyl)benzenesulfonamide (5ab).** White solid (72.4 mg, 99%, 0.20 mmol); mp: 92-93 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  11.03 (s, 1H), 7.80 (d,  $J = 8.3$  Hz, 1H), 7.72 (d,  $J = 8.3$  Hz, 2H), 7.54–7.43 (m, 1H), 7.37 (m, 1H), 7.25 (dd,  $J = 10.2, 4.3$  Hz, 2H), 7.21–7.16 (m, 3H), 6.98 (m, 1H), 6.88 (d,  $J = 7.6$  Hz, 1H), 2.35 (s, 3H), 2.12 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  202.2, 144.02, 140.4, 138.6, 136.6, 136.2, 134.9, 134.6, 131.0, 130.6, 129.8, 128.1, 127.4, 125.30, 124.4, 123.1, 120.8, 21.6, 19.6.  $[M + H]^+$  calculated for  $C_{21}H_{20}NO_3S^+$ : 366.1158, found: 366.1158.

**4-Methyl-*N*-(2-(3-methylbenzoyl)phenyl)benzenesulfonamide (5ac).** White solid (72.3 mg, 99%, 0.20 mmol) mp: 90-91 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.01 (s, 1H), 7.78 (d,  $J = 8.2$  Hz, 1H), 7.56 (d,  $J = 8.2$  Hz, 2H), 7.53–7.47 (m, 1H), 7.37 (d,  $J = 7.7$  Hz, 2H), 7.26 (t,  $J = 7.6$  Hz, 1H), 7.22 (s, 1H), 7.10 (t,  $J = 7.5$  Hz, 2H), 7.04 (d,  $J = 8.1$  Hz, 2H), 2.38 (s,

3H), 2.23 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 143.8, 139.0, 138.1, 137.72, 136.0, 133.8, 133.5, 133.2, 130.3, 129.6, 128.0, 127.3, 127.2, 126.5, 123.6, 123.2, 21.5, 21.4.  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{21}\text{H}_{20}\text{NO}_3\text{S}^+$ : 366.1158, found: 366.1158.

**4-Methyl-N-(2-(4-methylbenzoyl)phenyl)benzenesulfonamide (5ad).**<sup>13</sup> White solid (70.2 mg, 96%, 0.19 mmol);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.89 (s, 1H), 7.78 (d,  $J = 8.2$  Hz, 1H), 7.53 (d,  $J = 8.3$  Hz, 2H), 7.51–7.46 (m, 1H), 7.37 (d,  $J = 7.8$  Hz, 1H), 7.29 (d,  $J = 8.1$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 7.10 (m, 1H), 7.01 (d,  $J = 8.1$  Hz, 2H), 2.43 (s, 3H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 143.8, 143.7, 138.8, 135.9, 134.9, 133.6, 132.9, 130.2, 129.62, 128.9, 127.3, 126.9, 123.6, 123.4, 21.8, 21.5.

**N-(2-(4-chlorobenzoyl)phenyl)-4-methylbenzenesulfonamide (5ae).** White solid (70.9 mg, 96%, 0.19 mmol); mp: 118–119 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.83 (s, 1H), 7.78 (d,  $J = 8.3$  Hz, 1H), 7.53 (dd,  $J = 11.8, 4.7$  Hz, 3H), 7.41–7.30 (m, 5H), 7.12 (t,  $J = 7.5$  Hz, 1H), 7.03 (d,  $J = 8.2$  Hz, 2H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 143.9, 139.3, 138.9, 135.9, 135.8, 134.0, 132.7, 131.4, 129.7, 128.5, 127.3, 126.3, 123.8, 123.5, 21.5. HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{20}\text{H}_{17}\text{ClNO}_3\text{S}^+$ : 380.0612, found: 380.0611.

**(2-Hydroxyphenyl)(4-(trifluoromethyl)phenyl)methanone (5af).** Pale yellow solid (45.4 mg, 54%, 0.11 mmol); mp: 138–139 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.81 (s, 1H), 7.78 (d,  $J = 8.2$  Hz, 1H), 7.56 (d,  $J = 8.5$  Hz, 2H), 7.54–7.49 (m, 1H), 7.39 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.28 (d,  $J = 8.2$  Hz, 2H), 7.21 (d,  $J = 8.1$  Hz, 2H), 7.16 (dd,  $J = 10.3, 4.7$  Hz, 3H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 144.0, 140.8, 139.4, 135.9, 134.6, 133.9 (q,  $J = 32.7$  Hz), 133.2, 130.0, 129.7, 127.7, 125.2 (q,  $J = 7.2, 3.5$  Hz), 123.7, 123.6 (q,  $J = 272.7$  Hz), 123.0, 21.4. One carbon is not visible due to overlapping peaks HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NO}_3\text{S}^+$ : 420.0876, found: 420.0876.

**4-Methyl-N-(4-methyl-2-(4-methylbenzoyl)phenyl)benzenesulfonamide (5ag).** White solid (75.8 mg, 99%, 0.20 mmol); mp: 118–119 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.57 (s, 1H), 7.67 (d,  $J = 8.3$  Hz, 1H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.31 (d,  $J = 8.2$  Hz, 1H), 7.25 (d,  $J = 8.1$  Hz, 2H), 7.18 (d,  $J = 7.8$  Hz, 2H), 7.12 (s, 1H), 6.97 (d,  $J = 7.9$  Hz, 2H), 2.43 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 143.7, 143.6, 135.9, 135.8, 134.9, 134.2, 133.8, 132.9, 130.3, 129.6, 128.8, 127.7, 127.3, 124.3, 21.8, 21.5, 20.9. HRMS:  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{22}\text{H}_{22}\text{NO}_3\text{S}^+$ : 380.1315, found: 380.1315.

***N*-(4-fluoro-2-(4-methylbenzoyl)phenyl)-4-methylbenzenesulfonamide (5ah).** White solid (67.8 mg, 88%, 0.18 mmol); mp: 136-137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.33 (s, 1H), 7.78 (dd, *J* = 9.0, 4.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.27–7.21 (m, 3H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 2.17 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.30, 158.61 (d, *J* = 247.0 Hz), 144.4, 143.8, 135.4, 134.3, 134.2, 133.9, 130.2, 129.6, 123.0, 127.3, 127.2 (d, *J* = 7.7 Hz) 120.3 (d, *J* = 22.4 Hz), 118.7 (d, *J* = 23.9 Hz). 21.8, 21.4. HRMS: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>FNO<sub>3</sub>S<sup>+</sup>: 384.1064, found: 384.1064.

***N*-(4-bromo-2-(4-methylbenzoyl)phenyl)-4-methylbenzenesulfonamide (5ai).** White solid (80.2 mg, 90%, 0.18 mmol); mp: 112-113 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.63 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.60 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.21 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.6, 144.4, 144.0, 137.7, 136.3, 135.6, 135.0, 134.2, 130.2, 129.8, 129.1, 128.7, 127.3, 125.4, 116.8, 21.8, 21.5. HRMS: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>BrNO<sub>3</sub>S<sup>+</sup>: 444.0264, found: 444.0264.

**4-Methyl-*N*-(2-(4-methylbenzoyl)-5-nitrophenyl)benzenesulfonamide (5aj).** Yellow solid (22.3 mg, 27%, 0.05 mmol); mp: 158-159 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.77 (s, 1H), 8.59 (d, *J* = 2.1 Hz, 1H), 7.90 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 9.3 Hz, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 2H), 2.26 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.6, 149.3, 145.1, 144.6, 140.1, 135.6, 134.1, 133.4, 130.5, 130.44, 130.0, 129.4, 127.5, 117.6, 117.2, 21.9, 21.6. HRMS: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>5</sub>S<sup>+</sup>: 411.1009, found: 411.1008.

***N*-(2-(4-methylbenzoyl)phenyl)-[1,1'-biphenyl]-4-sulfonamide (5ak).** White solid (84.5 mg, 99%, 0.20 mol); mp: 130-131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.83 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.57–7.49 (m, 1H), 7.44–7.32 (m, 8H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.13 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.0, 145.6, 143.9, 138.9, 138.4, 137.3, 134.7, 133.5, 132.7, 130.1, 129.0, 129.0, 128.6, 127.8, 127.7, 127.4, 127.3, 124.3, 124.0, 21.6. HRMS: [M + H]<sup>+</sup> calculated for C<sub>26</sub>H<sub>22</sub>NO<sub>3</sub>S<sup>+</sup>: 428.1315, found: 428.1317.



***N*-(2-(4-methylbenzoyl)phenyl)naphthalene-1-sulfonamide (5al)**. White solid (79.4 mg, 99%, 0.20 mmol) White solid; mp: 130-131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.40 (s, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 7.3 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.46–7.36 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.1, 143.5, 138.8, 134.7, 134.1, 133.8, 133.4, 132.9, 130.4, 129.9, 128.8, 128.5, 127.8, 126.9, 126.1, 124.3, 123.9, 123.0, 121.6, 21.7. HRMS: [M + H]<sup>+</sup> calculated for C<sub>24</sub>H<sub>20</sub>NO<sub>3</sub>S<sup>+</sup>: 402.1158, found: 402.1158.

***N*-(2-(4-methylbenzoyl)phenyl)-3-(trifluoromethyl)benzenesulfonamide (5am)**. White solid (76.4 mg, 91%, 0.18 mmol); mp: 121-122 °C; Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.03 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.53-7.58 (m, 2H), 7.35-7.42 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.14-7.19 (m, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.0, 144.2, 140.1, 138.0, 134.5, 133.8, 133.0, 131.5 (q, *J* = 33.3 Hz), 130.5, 130.1, 129.9, 129.5 (q, *J* = 3.2 Hz), 129.0, 127.0, 124.3 (q, *J* = 36.2 Hz), 124.3, 123.7, 120.3 (q, *J* = 273.7 Hz), 21.7. HRMS: [M + H]<sup>+</sup> calculated for C<sub>21</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>3</sub>S<sup>+</sup>: 420.0876, found: 420.0883.

***N*-(2-(4-methylbenzoyl)phenyl)benzenesulfonamide (5an)**. Colorless liquid (65.9 mg, 94%, 0.19 mmol); mp: 95-96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.16 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.81–7.71 (m, 2H), 7.62–7.53 (m, 1H), 7.50–7.39 (m, 2H), 7.40–7.30 (m, 4H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.20–7.11 (m, 1H), 2.49 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.4, 143.8, 139.1, 138.9, 135.1, 133.7, 133.2, 132.9, 130.2, 129.0, 129.0, 127.3, 126.4, 123.5, 122.8, 21.8.

**4-Chloro-*N*-(2-(4-methylbenzoyl)phenyl)benzenesulfonamide (5ao)**. White solid (70.0 mg, 91%, 0.18 mmol); mp: 118-119 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.81 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.54–7.47 (m, 1H), 7.39 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (m, 3H), 2.44 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.0, 144.3, 139.5, 138.1, 137.3, 134.6, 133.6, 132.8, 130.2, 129.3, 129.1, 128.8, 127.6, 124.2, 124.1, 21.8. HRMS: [M + H]<sup>+</sup> calculated for C<sub>20</sub>H<sub>17</sub>ClNO<sub>3</sub>S<sup>+</sup>: 386.0612, found: 386.0612.

**4-(Tert-butyl)-N-(2-(4-methylbenzoyl)phenyl)benzenesulfonamide (5ap).** White solid (53.7 mg, 66%, 0.13 mmol); mp: 138-139 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.08 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 2.41 (s, 3H), 1.19 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.4, 156.7, 143.7, 139.1, 136.2, 135.2, 133.7, 133.2, 130.1, 129.0, 127.1, 126.4, 126.0, 123.4, 123.1, 35.1, 31.0, 21.7. HRMS: [M + H]<sup>+</sup> calculated for C<sub>24</sub>H<sub>26</sub>NO<sub>3</sub>S<sup>+</sup>: 408.1628, found: 408.1629.

**N-(2-(4-methylbenzoyl)phenyl)-4-nitrobenzenesulfonamide (5aq).** Yellow solid (26.5 mg, 33%, 0.07 mmol); mp: 168-170°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.68 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.58 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.25 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.3, 150.0, 145.0, 144.4, 137.0, 134.0, 133.6, 132.3, 130.3, 129.1, 128.7, 128.3, 125.3, 125.0, 124.2, 21.7. HRMS: [M + H]<sup>+</sup> calculated for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>S<sup>+</sup>: 397.0853, found: 397.0853.

**N-(2-(4-methylbenzoyl)phenyl)methanesulfonamide (5ar).**<sup>13</sup> White solid (53.0 mg, 92%, 0.18 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.13 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.60 (m, 4H), 7.30 (d, *J* = 7.1 Hz, 2H), 7.15 (t, *J* = 6.9 Hz, 1H), 3.05 (s, 3H), 2.45 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8, 143.9, 139.9, 135.4, 134.3, 134.1, 130.2, 129.2, 124.1, 122.7, 119.8, 40.2, 21.8.

**N-(2-(4-methylbenzoyl)phenyl)acetamide (5as).**<sup>14</sup> White solid (21.0 mg, 39%, 0.08 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.73 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.33–7.24 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 2.45 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.5, 169.3, 143.7, 140.4, 136.0, 134.1, 133.4, 130.4, 129.2, 123.8, 122.2, 121.7, 25.4, 21.8.

**General Procedure for Synthesis of 6.** Quinoline-8-carbaldehyde (0.20 mmol), diaryliodonium salts (0.24 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (2 mol %), AgNTf<sub>2</sub> (16 mol %), 200 mg 4 Å MS and, cyclohexane (2.0 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 20 h. After cooled to room temperature, the solvent was removed

under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (25:1-8:1) to afford compounds **6**.

**Phenyl(quinolin-8-yl)methanone (6aa).**<sup>15</sup> White solid (46.4 mg, 99%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (dd,  $J$  = 4.2, 1.7 Hz, 1H), 8.21 (dd,  $J$  = 8.3, 1.6 Hz, 1H), 7.96 (dd,  $J$  = 8.2, 1.2 Hz, 1H), 7.89–7.76 (m, 2H), 7.74 (dd,  $J$  = 7.0, 1.3 Hz, 1H), 7.66–7.59 (m, 1H), 7.55 (t,  $J$  = 7.4 Hz, 1H), 7.45–7.33 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.0, 151.0, 146.3, 139.5, 137.9, 136.1, 133.4, 130.4, 129.8, 128.5, 128.4, 126.0, 121.8.

**Quinolin-8-yl(*o*-tolyl)methanone (6ab).**<sup>15</sup> White solid (41.8 mg, 85%, 0.17 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (dd,  $J$  = 4.1, 1.6 Hz, 1H), 8.17 (dd,  $J$  = 8.3, 1.3 Hz, 1H), 7.93 (d,  $J$  = 8.1 Hz, 1H), 7.72 (dd,  $J$  = 7.0, 1.1 Hz, 1H), 7.64–7.53 (m, 1H), 7.42–7.27 (m, 4H), 7.08 (m, 1H), 2.68 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.0, 151.1, 146.2, 140.7, 139.8, 138.1, 136.0, 132.4, 131.9, 131.8, 130.1, 128.8, 128.4, 125.9, 125.4, 121.6, 21.8.

**Quinolin-8-yl(*m*-tolyl)methanone (6ac).**<sup>15</sup> White solid (45.7 mg, 92%, 0.18 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.83 (d,  $J$  = 2.4 Hz, 1H), 8.19 (d,  $J$  = 8.3 Hz, 1H), 7.94 (d,  $J$  = 8.1 Hz, 1H), 7.75–7.69 (m, 2H), 7.61 (t,  $J$  = 7.6 Hz, 1H), 7.55 (d,  $J$  = 7.7 Hz, 1H), 7.43–7.32 (m, 2H), 7.26 (t,  $J$  = 7.6 Hz, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.2, 150.9, 146.2, 139.6, 138.24, 137.9, 136.1, 134.2, 130.4, 129.7, 128.3, 128.2, 127.9, 125.9, 121.7, 21.4.

**Quinolin-8-yl(*p*-tolyl)methanone (6ad).**<sup>15</sup> White solid (48.4 mg, 98%, 0.20 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (dd,  $J$  = 4.2, 1.7 Hz, 1H), 8.21 (dd,  $J$  = 8.3, 1.7 Hz, 1H), 7.95 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.73 (dd,  $J$  = 10.2, 4.8 Hz, 3H), 7.65–7.54 (m, 1H), 7.41 (dd,  $J$  = 8.3, 4.2 Hz, 1H), 7.21 (d,  $J$  = 8.0 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.7, 151.0, 146.3, 144.3, 136.1, 135.5, 130.5, 129.7, 129.2, 128.4, 128.2, 126.0, 121.7, 21.9.

**(5-Bromoquinolin-8-yl)(phenyl)methanone (6ae).**<sup>15</sup> White solid (53.6 mg, 86%, 0.17 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.86–8.77 (m, 1H), 8.58 (dd,  $J$  = 8.5, 1.5 Hz, 1H), 7.92 (dd,  $J$  = 7.6, 2.8 Hz, 1H), 7.83–7.79 (m, 2H), 7.60 (dd,  $J$  = 7.6, 1.7 Hz, 1H), 7.57–7.47 (m, 2H), 7.40 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.1, 151.5, 146.8, 139.3, 137.63, 135.6, 133.5, 130.2, 129.8, 128.5, 128.4, 127.7, 123.8, 122.9.

**(5-Bromoquinolin-8-yl)(o-tolyl)methanone (6af).** White solid (59.7 mg, 92%, 0.18 mmol); mp: 130-131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.83 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.56 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.40–7.34 (m, 1H), 7.32–7.23 (m, 2H), 7.08 (m, 1H), 2.69 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.1, 151.6, 146.8, 140.6, 40.0, 137.7, 135.5, 132.4, 132.0, 132.0, 129.8, 128.8, 127.8, 125.4, 124.1, 122.8, 21.9. HRMS: [M + H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>13</sub>BrNO<sup>+</sup>: 326.0175, found: 326.0176.

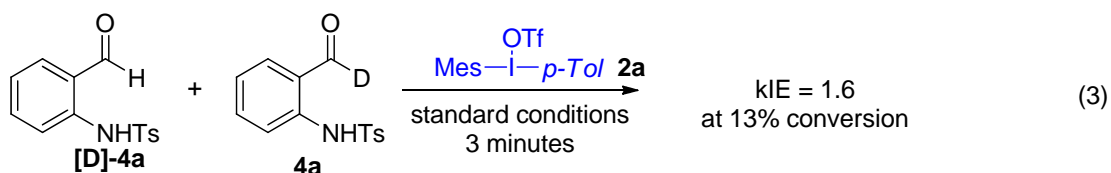
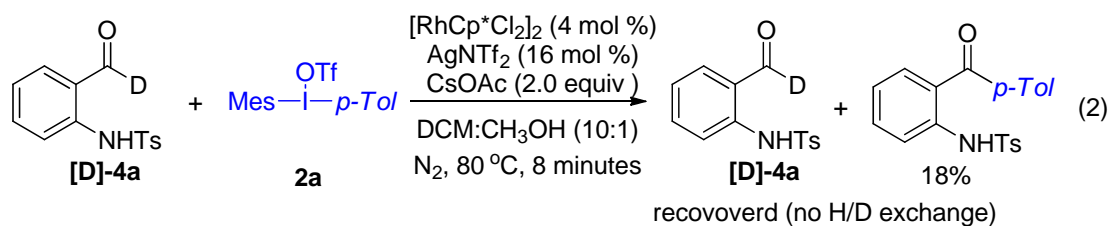
**(5-Bromoquinolin-8-yl)(m-tolyl)methanone (6ag).** White solid (60.4 mg, 93%, 0.19 mmol); mp: 107-108 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.59 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.59 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.55–7.48 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.3, 151.5, 146.9, 139.5, 138.4, 137.6, 135.6, 134.4, 130.4, 129.8, 128.4, 128.3, 127.8, 127.7, 123.7, 122.9 21.4. HRMS: [M + H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>13</sub>BrNO<sup>+</sup>: 326.0175, found: 326.0177.

**(5-Bromoquinolin-8-yl)(p-tolyl)methanone (6ah).** White solid (61.3 mg, 94%, 0.19 mmol); mp: 173-174°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.7, 151.5, 146.8, 144.5, 139.6, 135.5 135.2, 130.4, 129.8, 129.3, 128.3, 127.7, 123.6, 122.8, 21.9. <sup>1</sup>H NMR HRMS: [M + H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>13</sub>BrNO<sup>+</sup>: 326.0175, found: 326.0176.

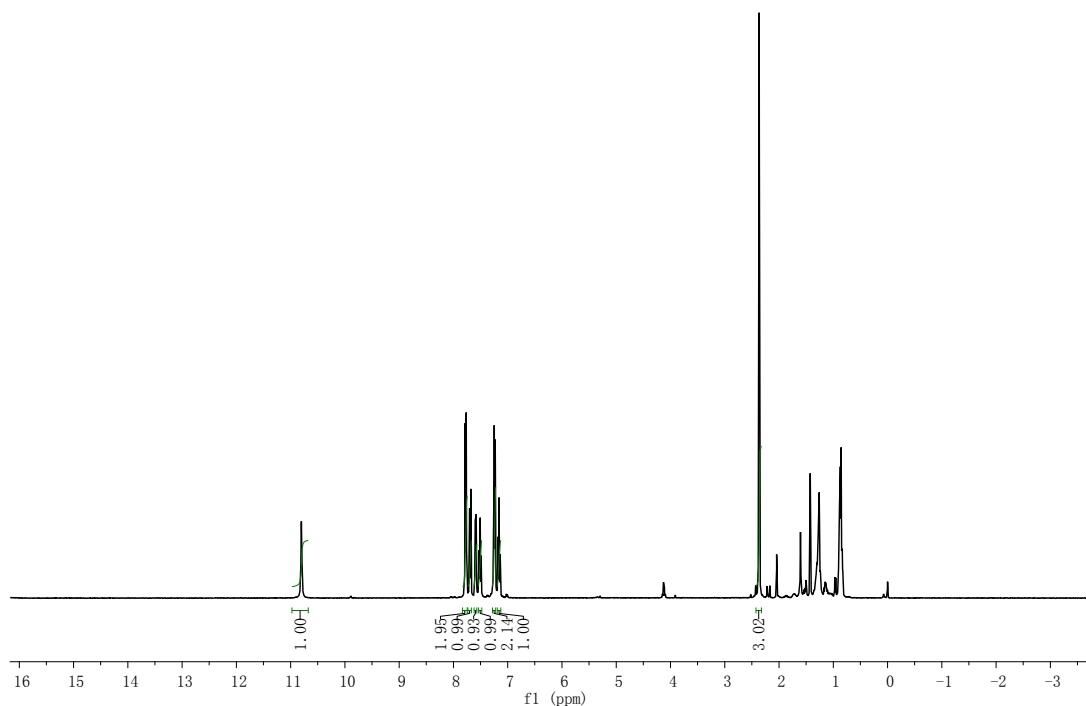
1. T. Zhang, Z. Qi, X. Zhang, L. Wu and X. Li, *Chem. -Eur. J.*, 2014, **20**, 3283.
2. (a) M. Bielawski and B. Olofsson, *Chem. Commun.*, 2007, **24** 2521. (b) M. Bielawski, M. Zhu and B. Olofsson. *Adv. Synth. Catal.*, 2007, **349**, 2610.
3. D. Wang and S. Cui, *Tetrahedron*, 2015, **71**, 8511.
4. F. Weng, C. Wang, B. Xu, *Tetrahedron Lett.*, 2010, **51**, 2593.
5. A. R. Katritzky, K. N. Le, L. Khelashvili and P. P. Mohapatra, *J. Org. Chem.*, 2006, **71**, 9861.
6. P. Y. Choy and F. Y. Kwong, *Org. Lett.*, 2013, **15**, 270.

7. J. Hu, E. A. Adogla, Y. Ju, D. Fan and Q. Wang, *Chem. Commun.*, 2012, **48**, 11256.
8. W. B. Motherwell and S. Vázquez, *Tetrahedron Lett.*, 2000, **41**, 9667.
9. M. Xia and Z. Chen, *Synth. Commun.*, 2000, **30**, 531.
10. S. Kamino, H. Ichikawa, S. I. Wada, Y. Horio, Y. Usami, T. Yamaguchi and M. Doi, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 4380.
11. V. Dhayalan, R. Murakami and M. Hayashi, *Tetrahedron:Asymmetry.*, 2013, **24**, 543.
12. Q. Z. Zheng, Y. F. Liang, C. Qin and N. Jiao, *Chem. Commun.*, 2013, **49**, 5654.
13. G. Dannhardt, B. L. Fiebich and J. Schweppenhäuser, *E. J. Med. Chem.*, 2002, **37**, 147.
14. Z. Yin and P. Sun, *J. Org. Chem.*, 2012, **77**, 11339.
15. J. Wang, S. Zuo, W. Chen, X. Zhang, K. Tan, Y. Tian and J. Wang, *J. Org. Chem.*, 2013, **78**, 8217.

## H/D exchange



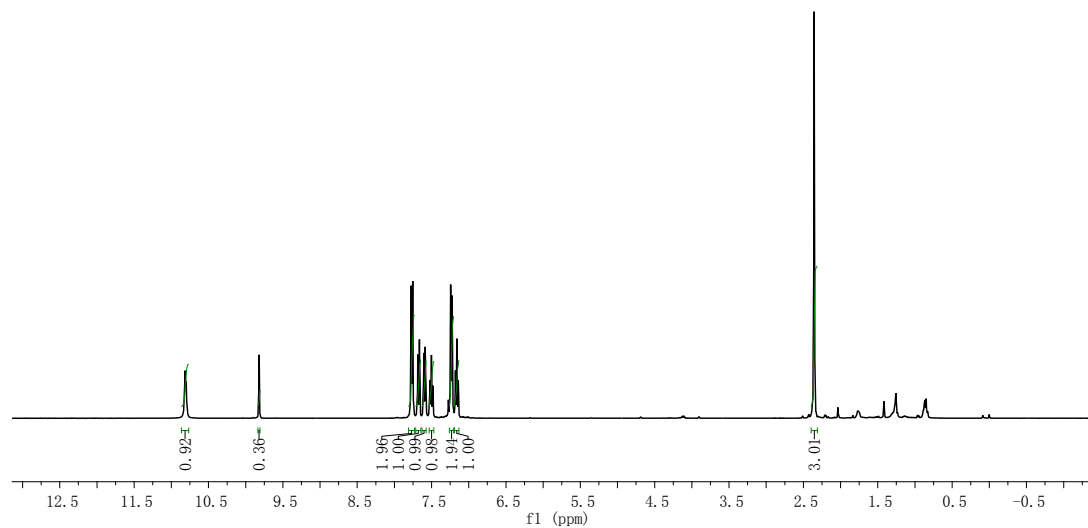
**4a** (0.2 mmol), **2a** (0.4 mmol)  $[\text{RhCp}^*\text{Cl}_2]_2$  (4 mol %),  $\text{AgNTf}_2$  (16 mol %),  $\text{CsOAc}$  (0.4 mmol), and  $\text{DCM}:\text{CH}_3\text{OH}$  (10: 1, 2mL) were charged into an NMR tube, and the mixture was heated at 80 °C for 8 minutes. No H/D exchange was observed on the basis of  $^1\text{H}$  NMR analysis.



## Deuterium-Labeling Experiment

An equimolar mixture of **4a** and  $[\text{D}]-\mathbf{4a}$  (0.4 mmol in total), **2a** (0.40 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.08 mmol),  $\text{AgNTf}_2$  (0.16 mmol),  $\text{CsOAc}$  (0.4 mmol) were charged into a pressure tube, to which was added  $\text{DCM}$  (2.0 mL) The reaction mixture was stirred under  $\text{N}_2$  at 80 °C for 3 minutes. After quenched at 0 °C, the conversion was isolated 13% after chromatography using  $\text{EA/PE}$  (25:1).  $^1\text{H}$  NMR analysis of the level of deuteration of the recovered aldehydes (64% C-D and 36% C-H)

gave  $k_H/k_D = 1.6$



	C-H	C-D
$t = 0$	1	1
conversion	-kx	-x
$t = 3$ minutes	1-kx	1-x

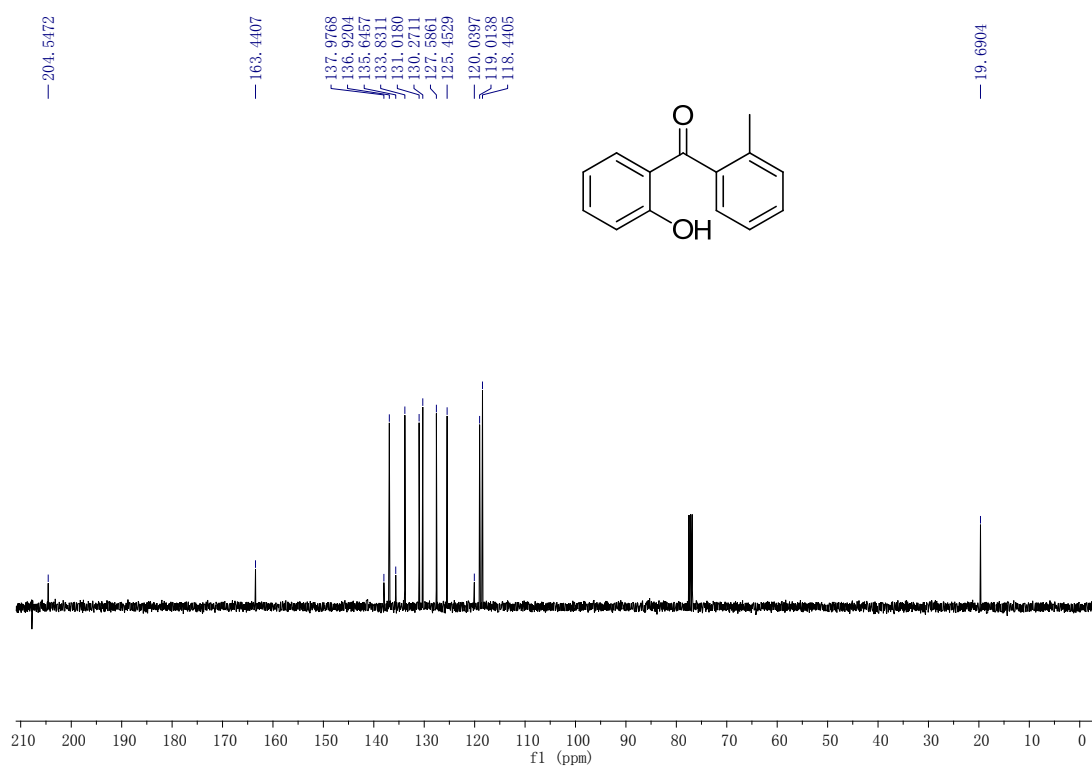
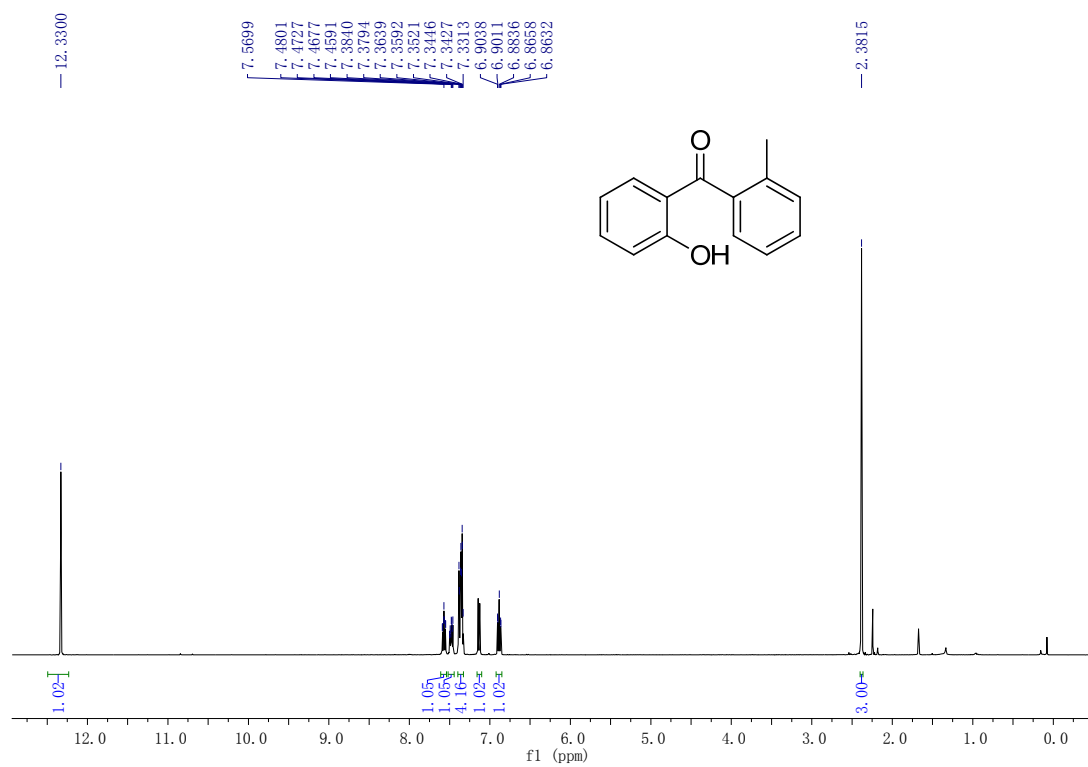
$$(1-x)/(1-kx) = 0.64/0.36$$

$$(kx+x)/2 = 0.13$$

$$k = \text{KIE} = 1.6$$

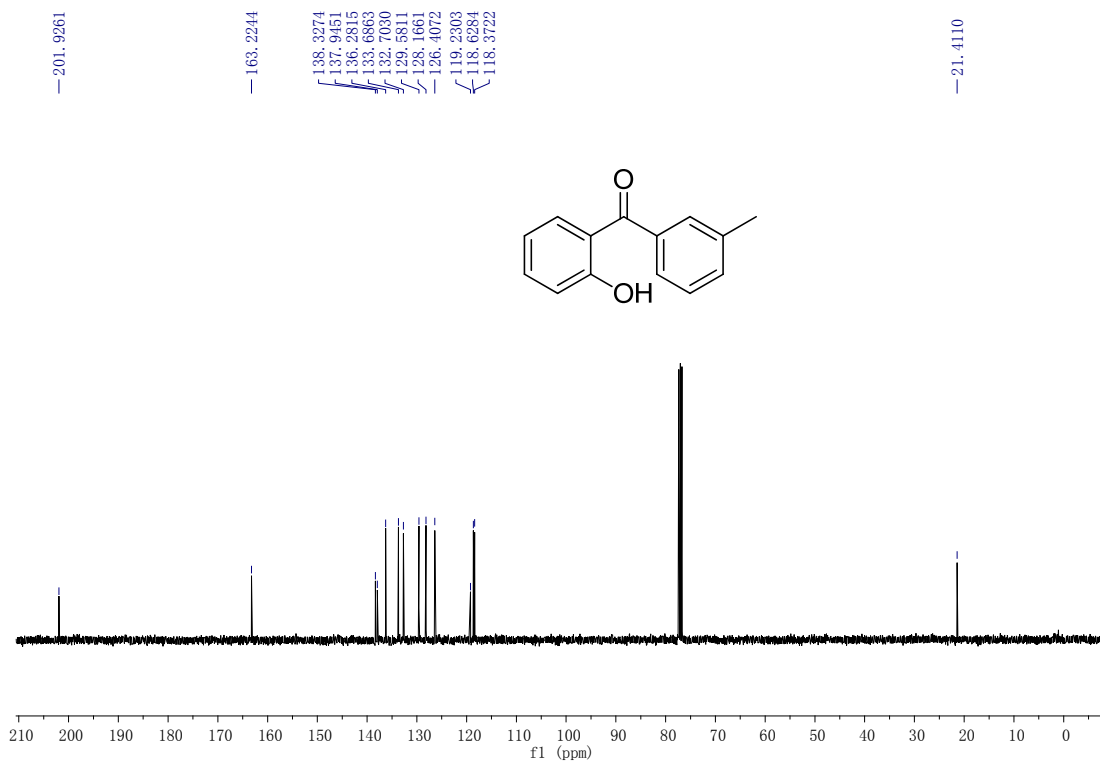
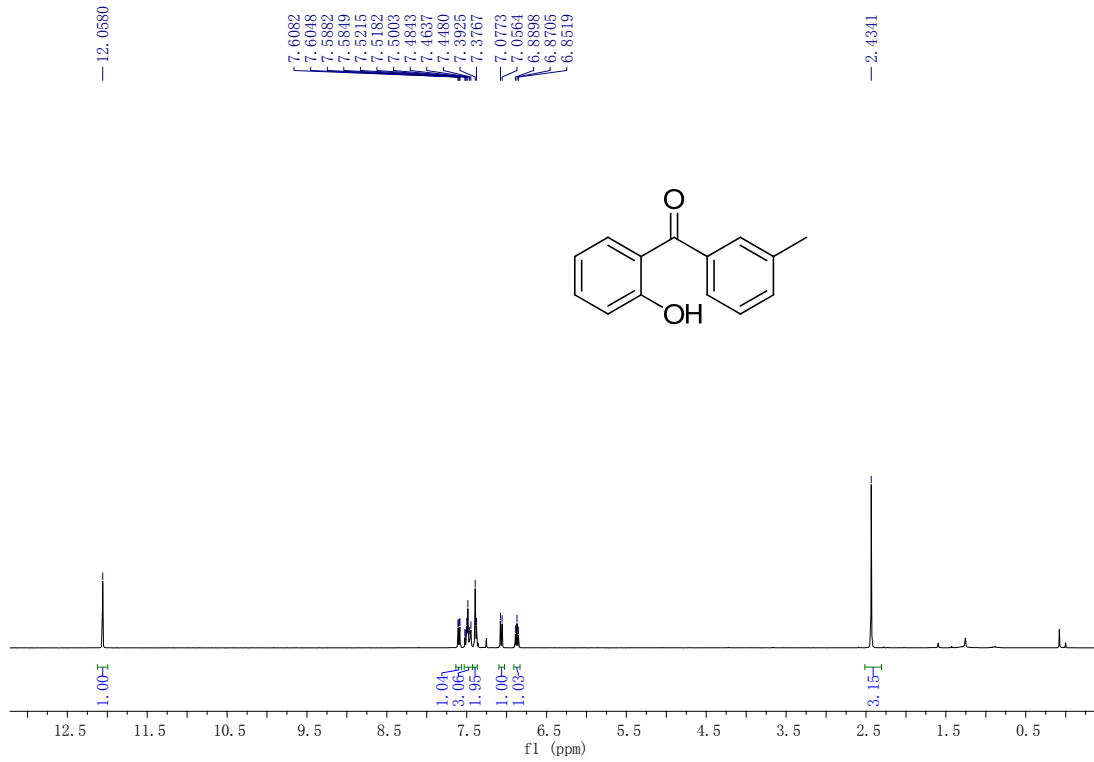
## NMR spectra

### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound **3aa**

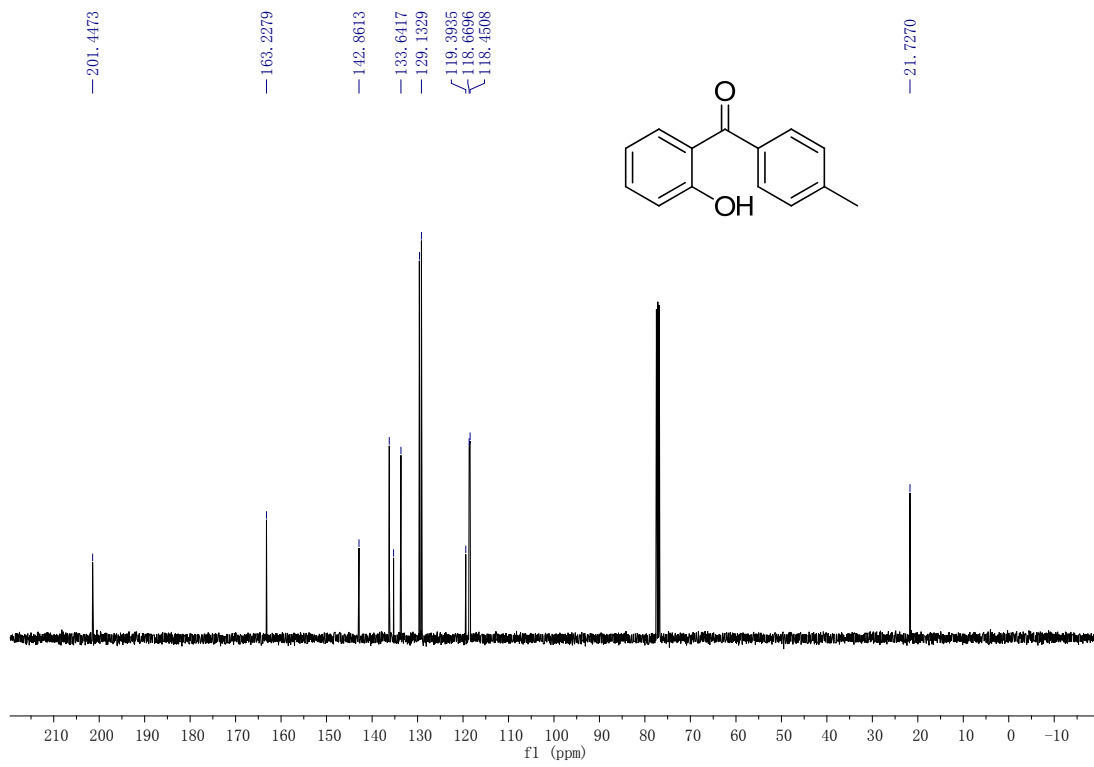
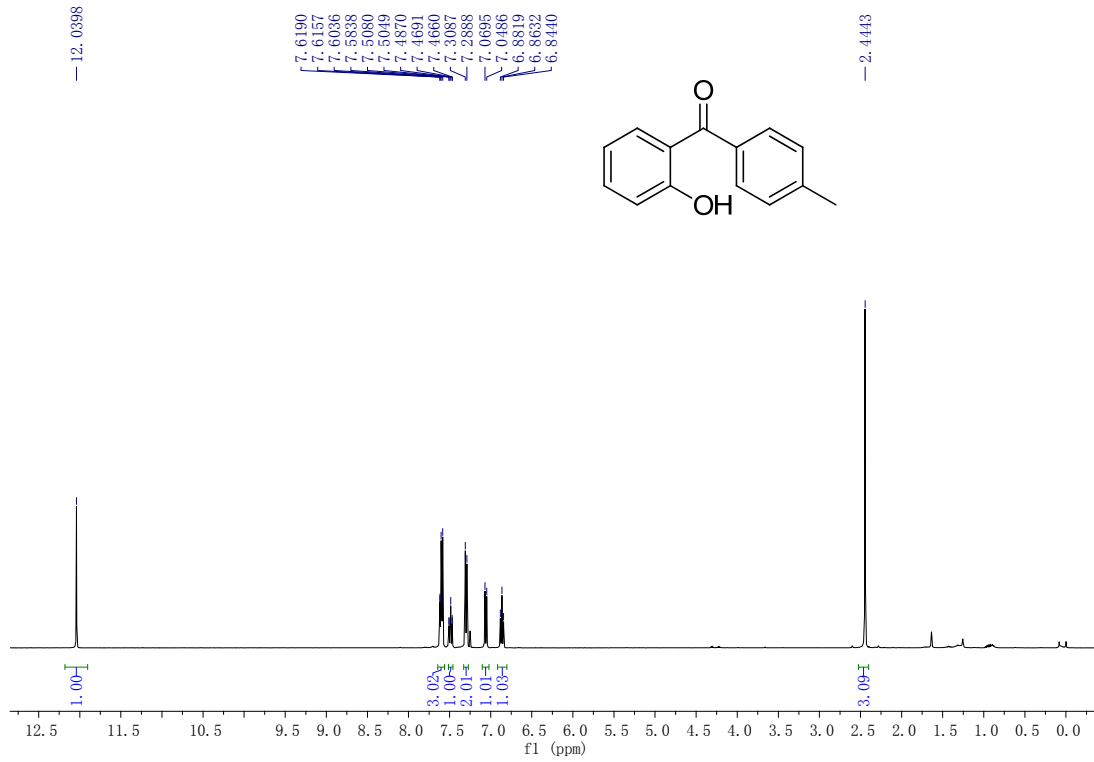


### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound **3ab**

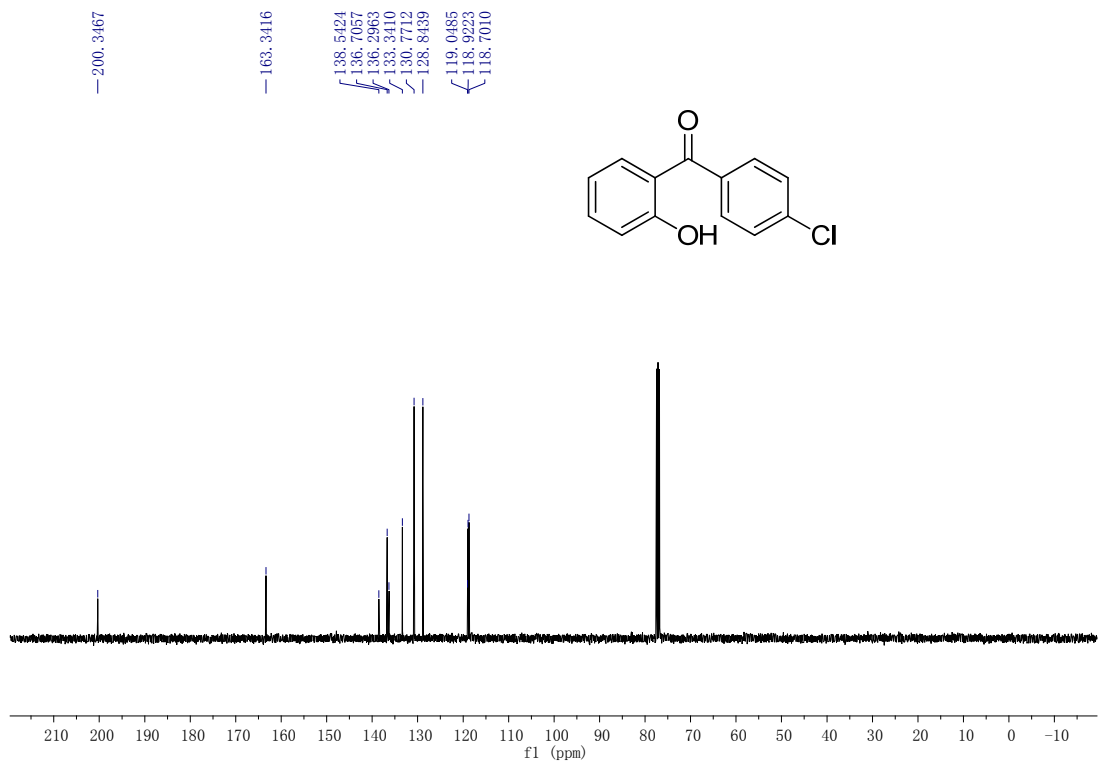
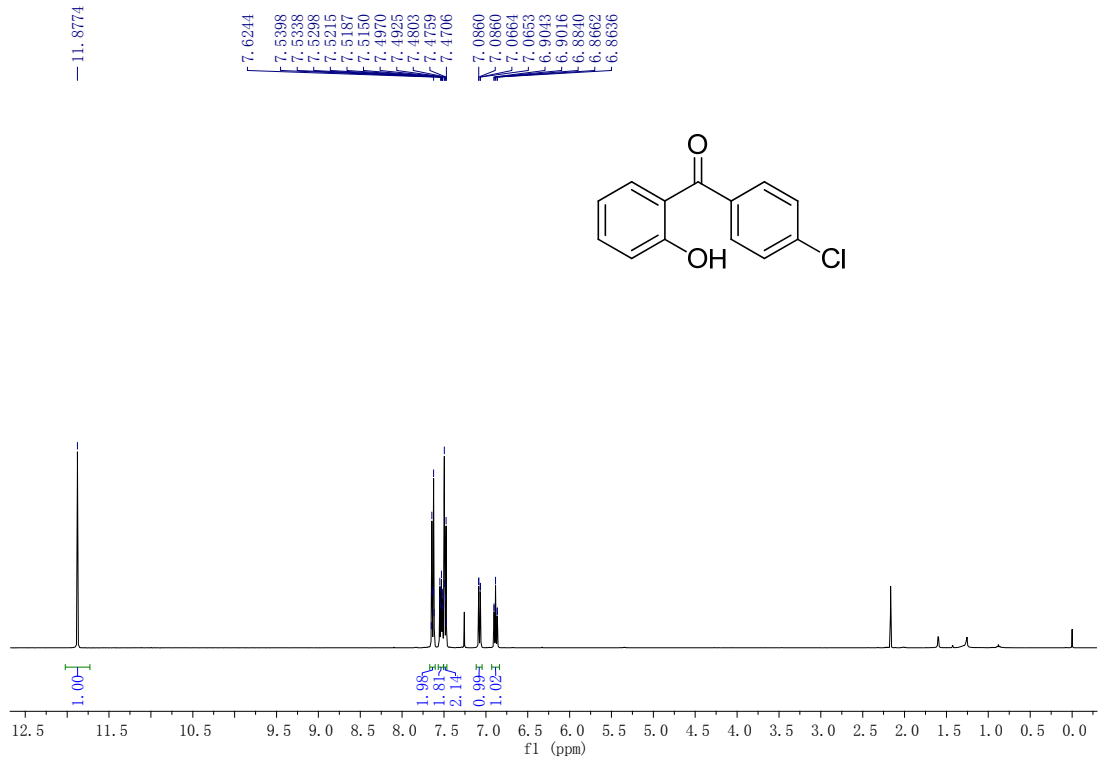




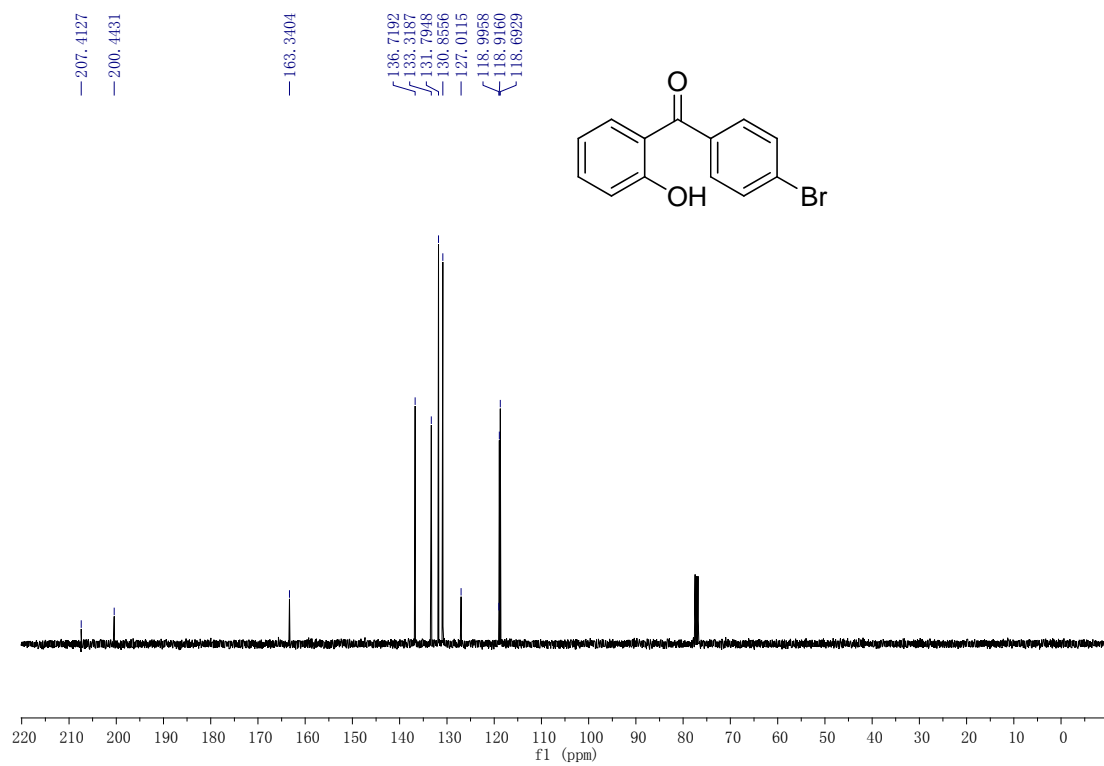
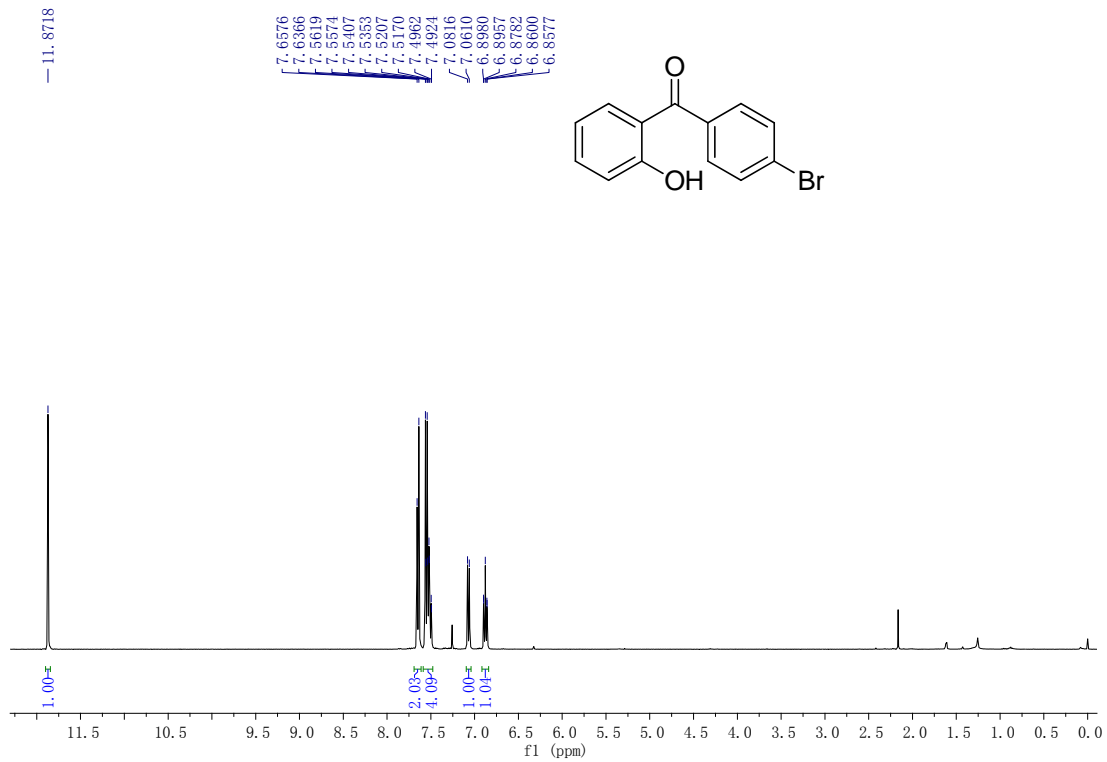
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound 3ac



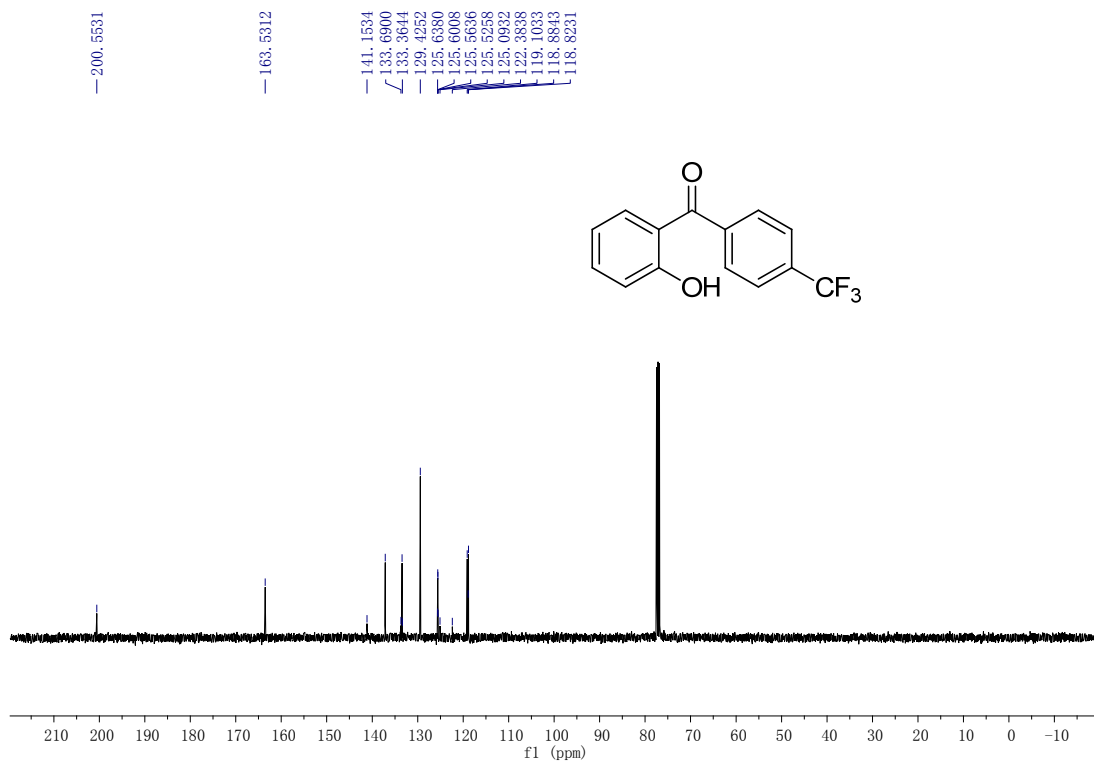
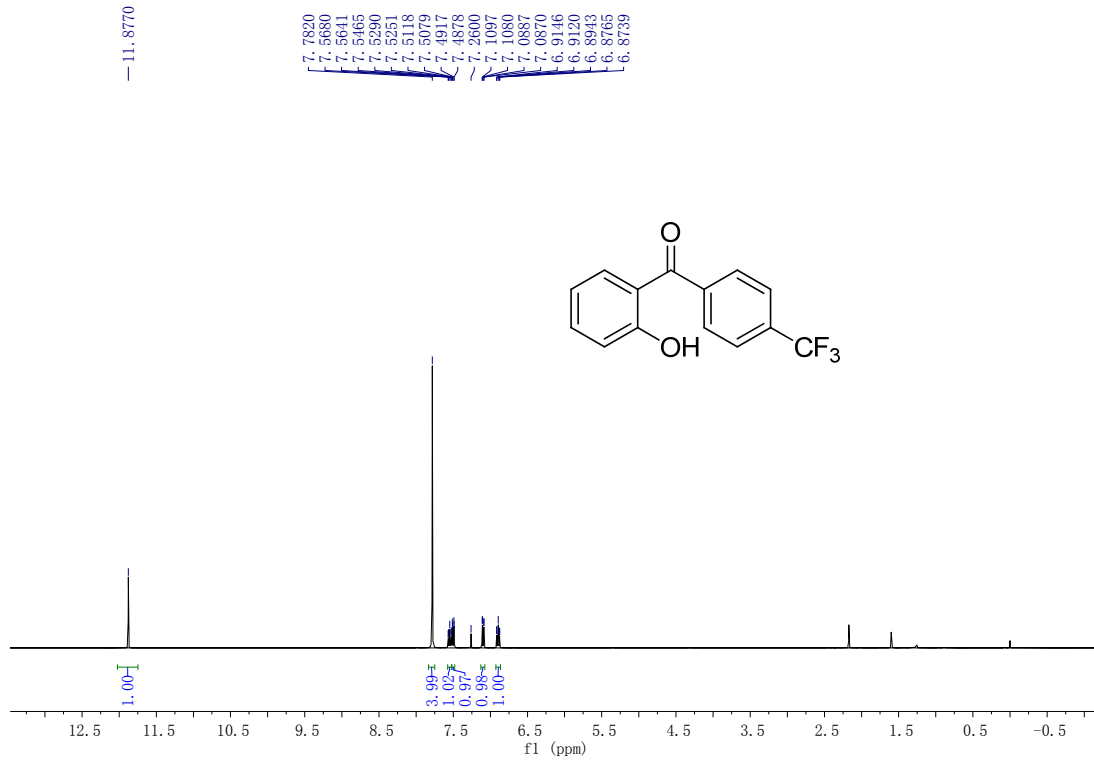
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ad



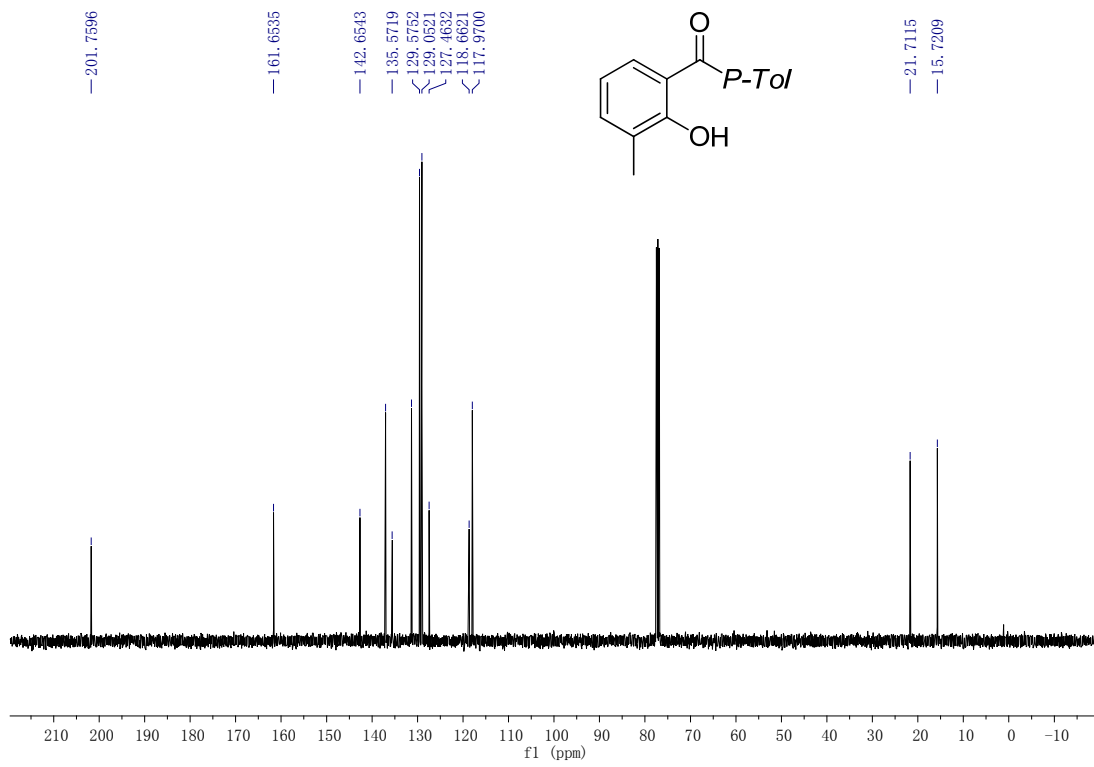
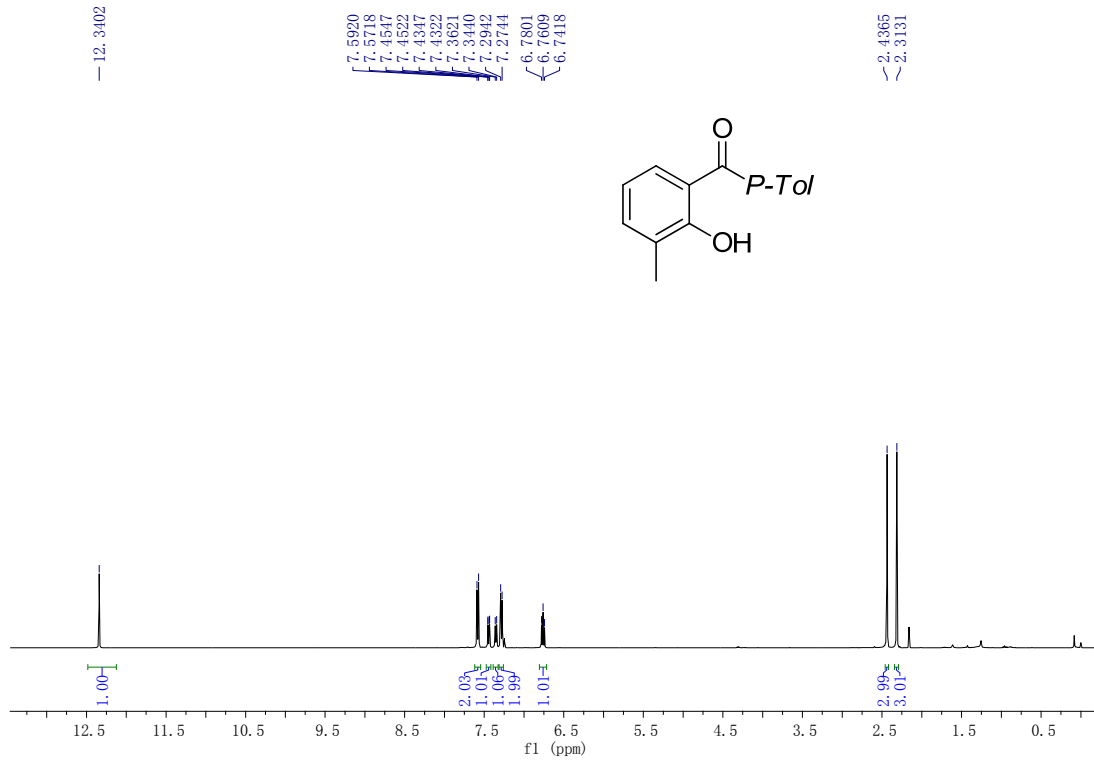
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ae



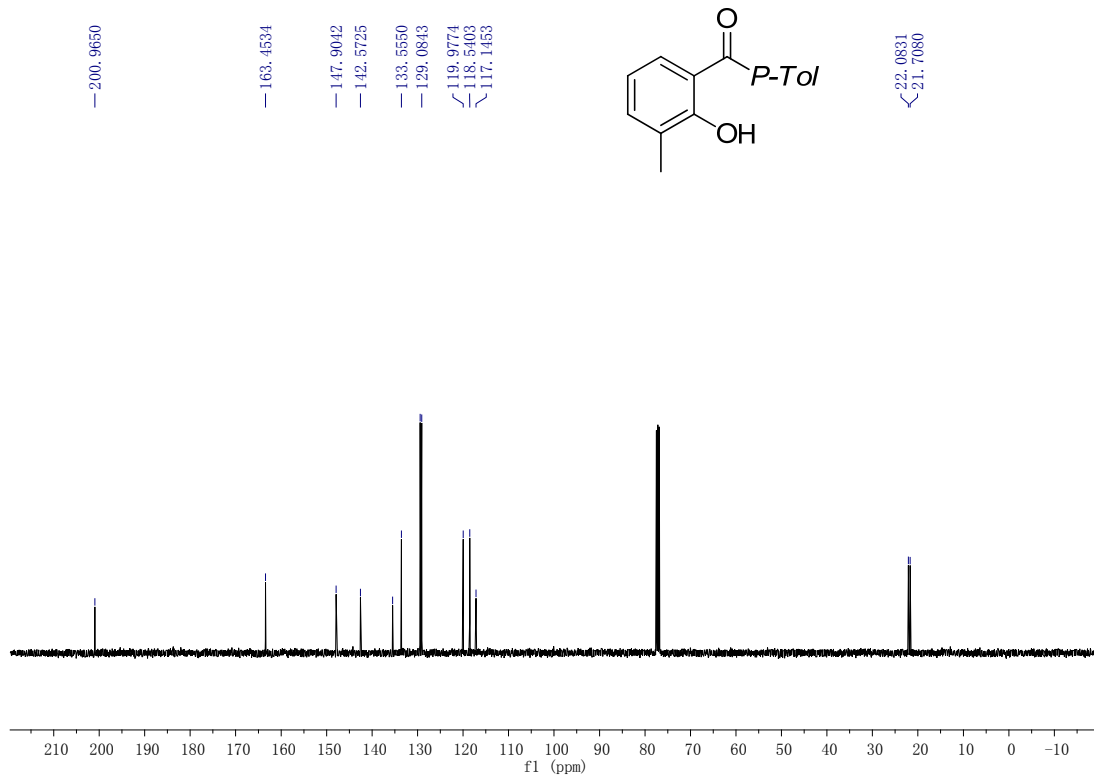
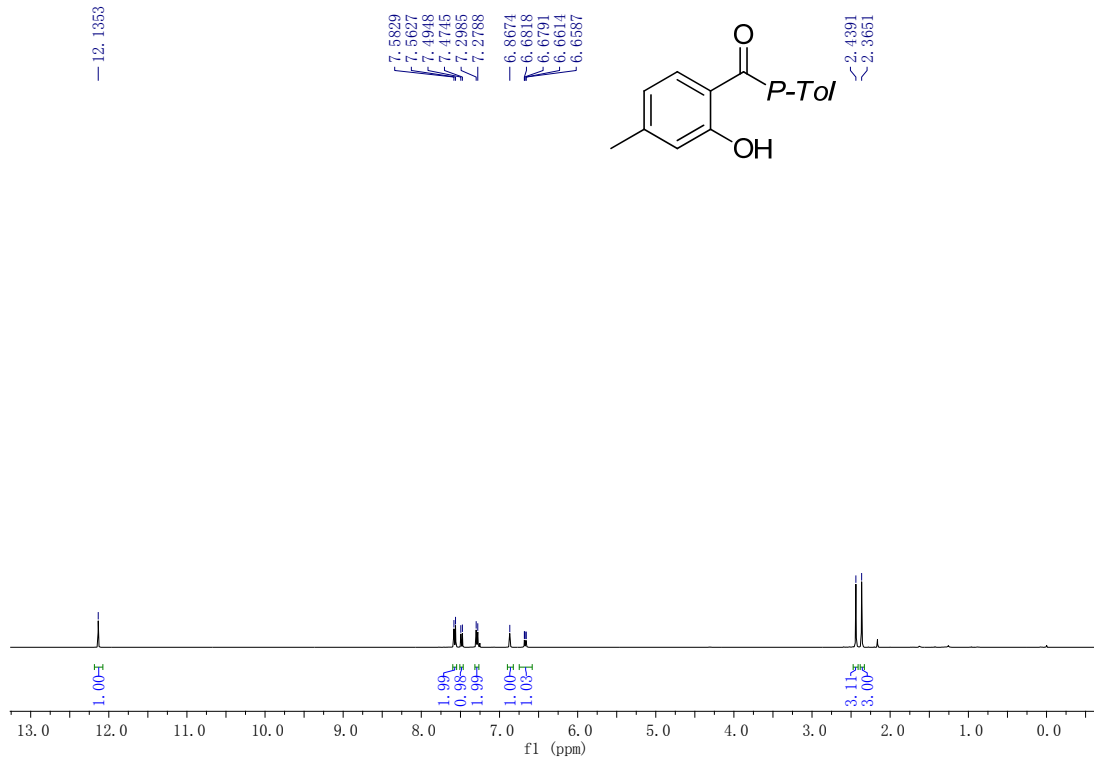
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound 3af



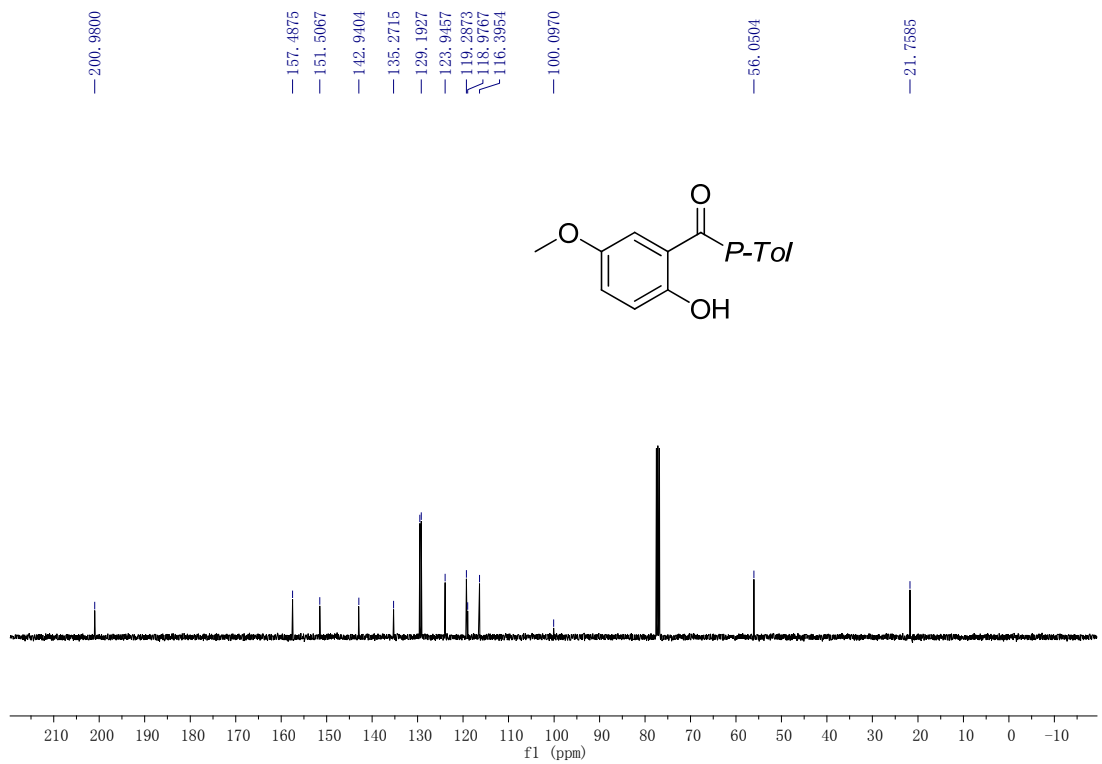
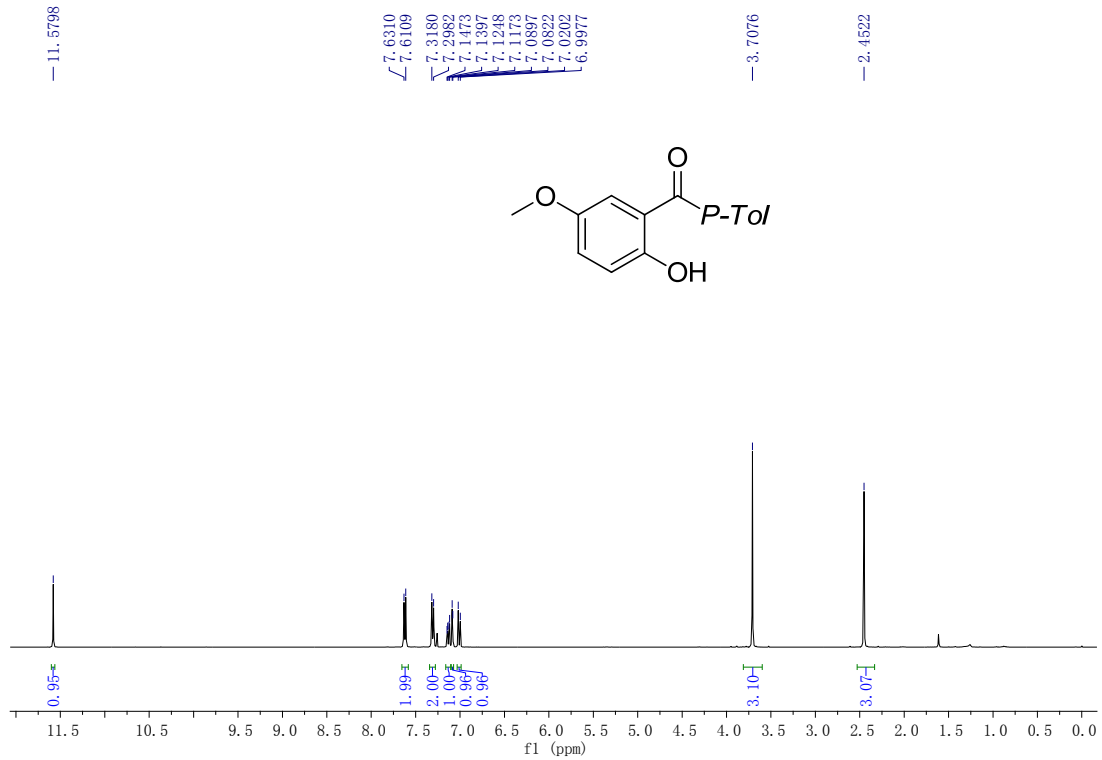
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ag



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ah

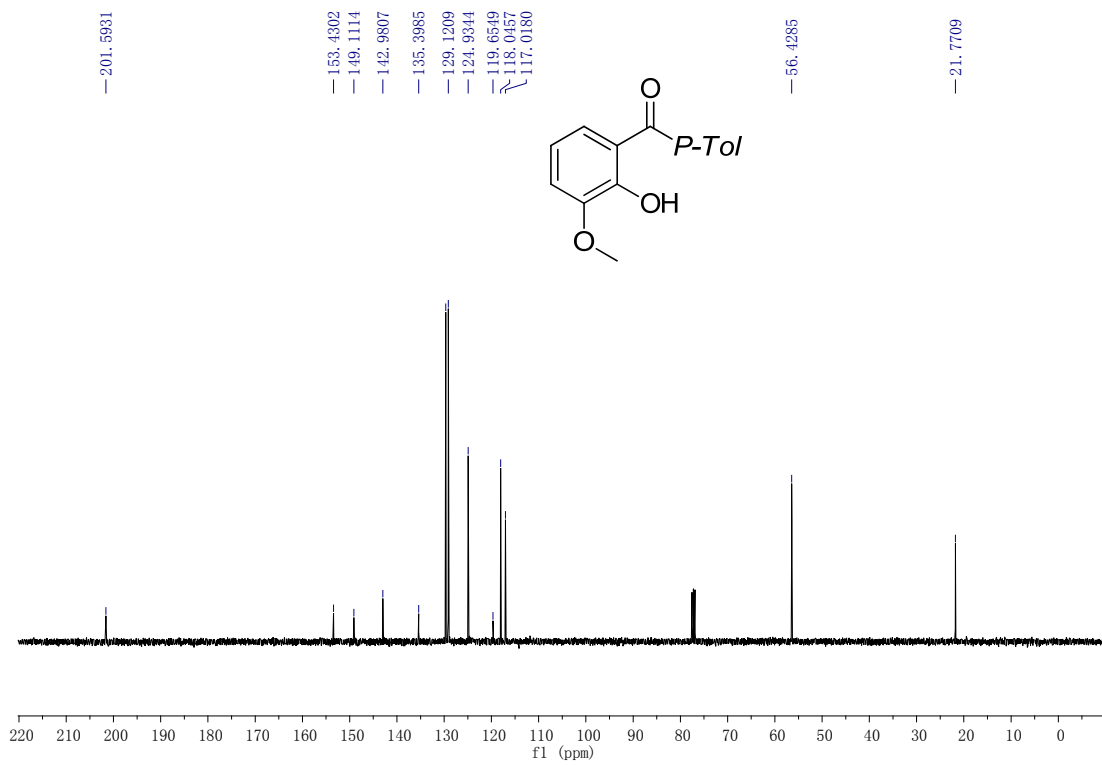
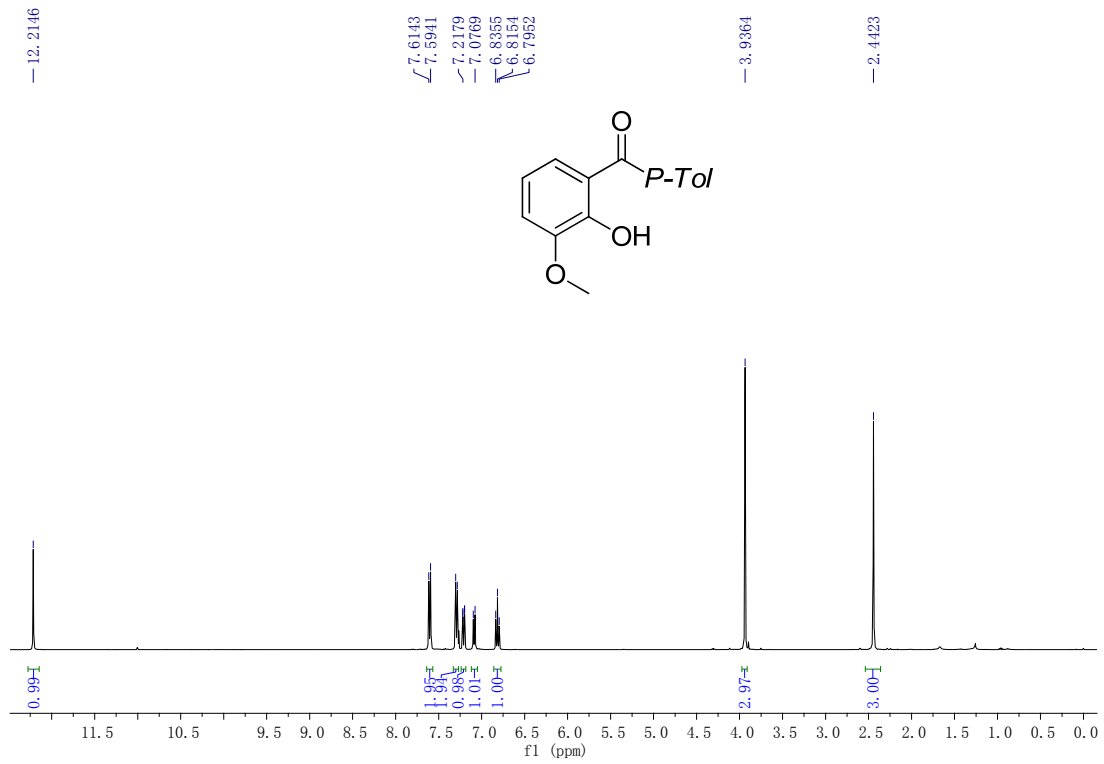


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3ai**

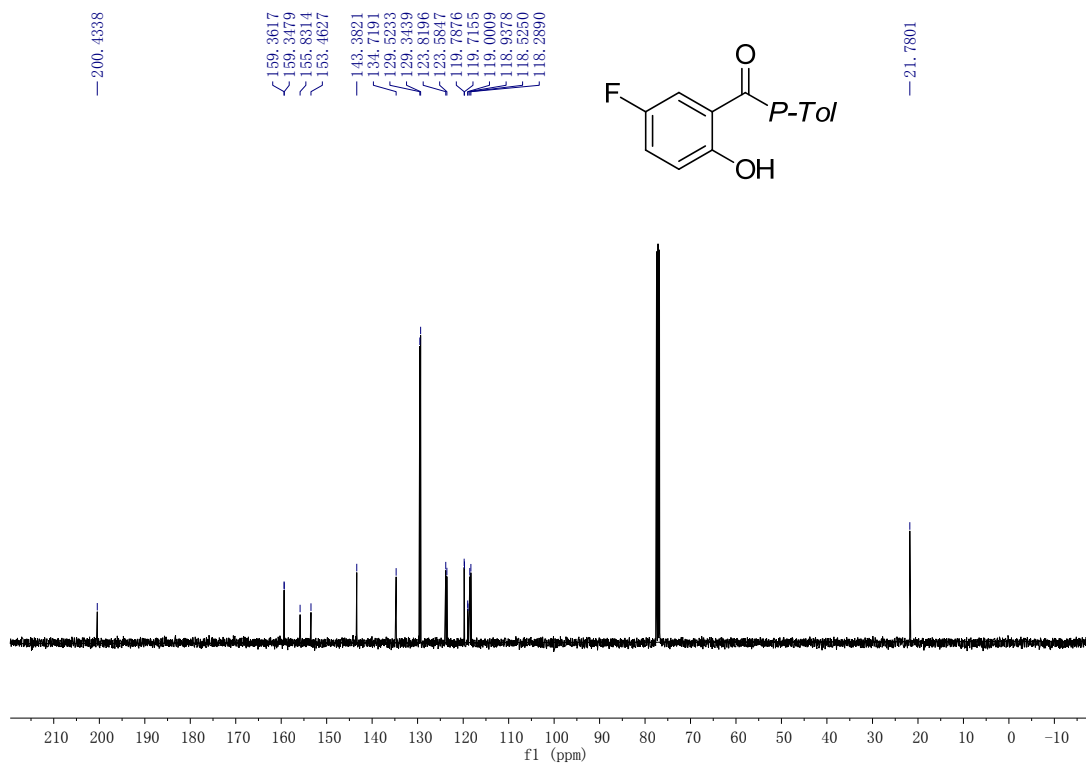
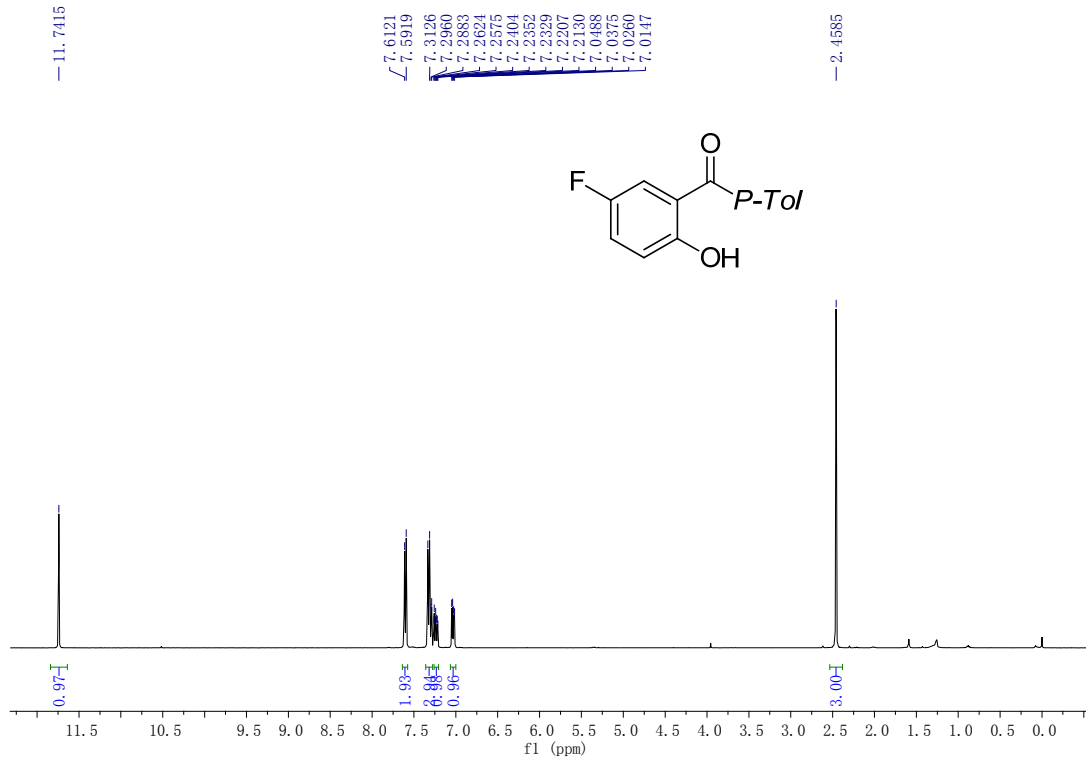


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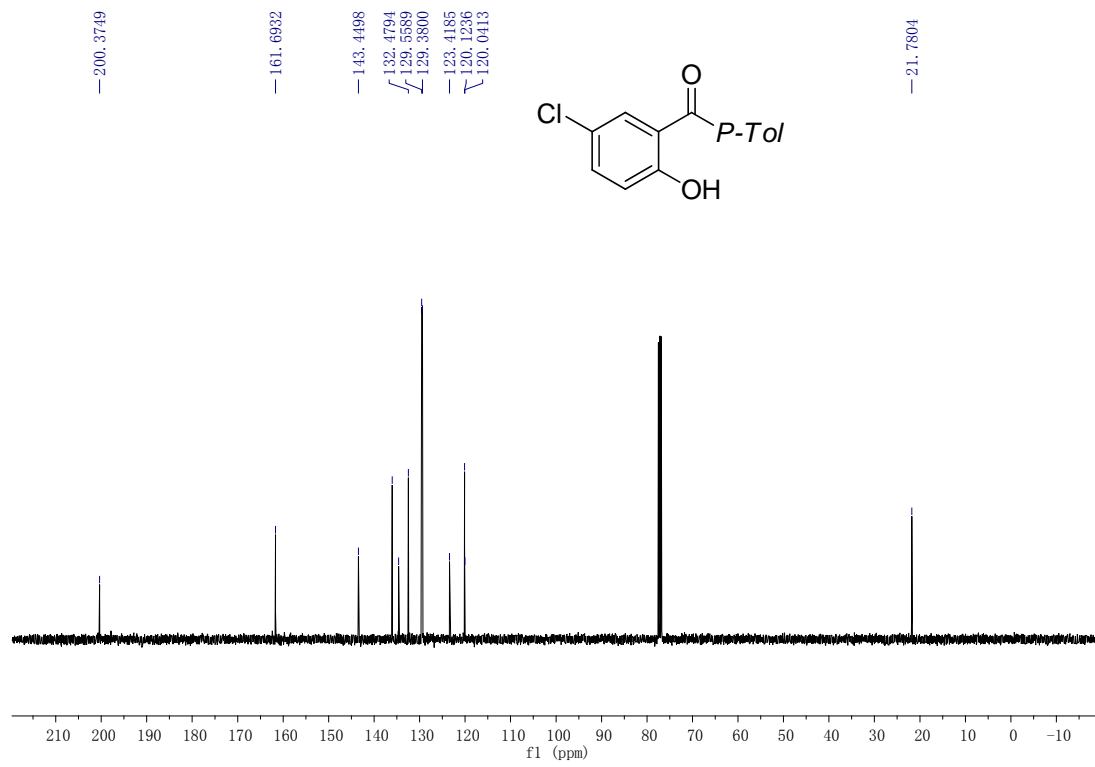
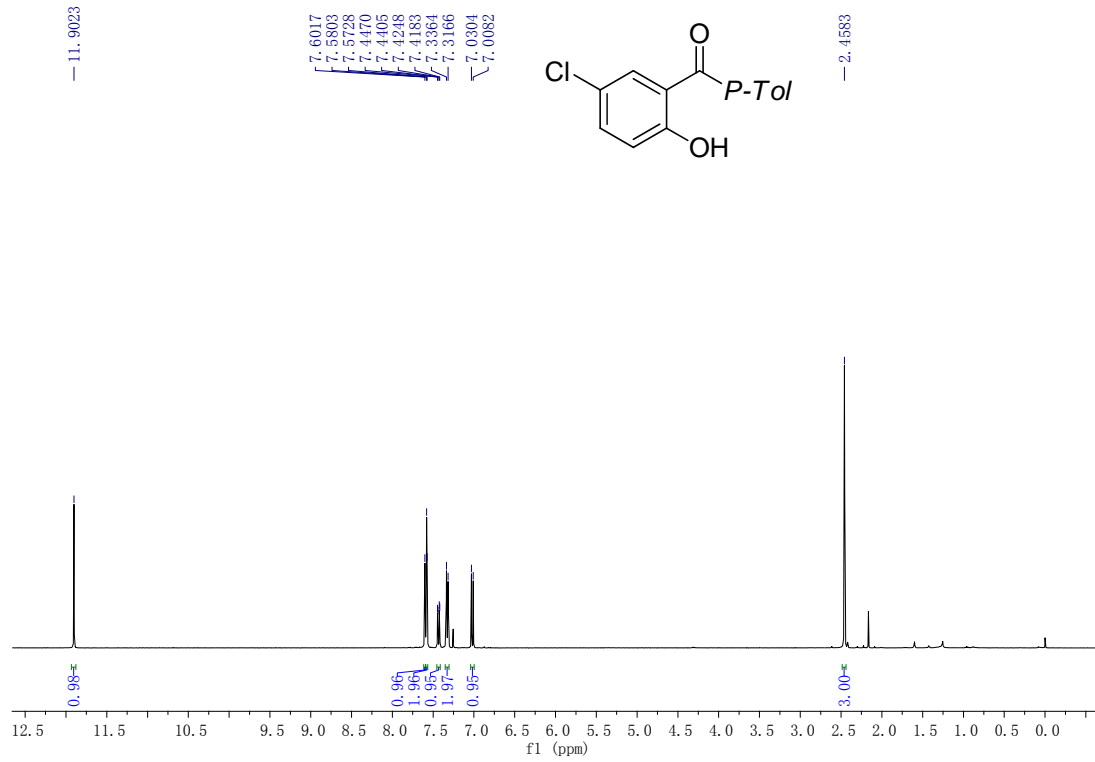




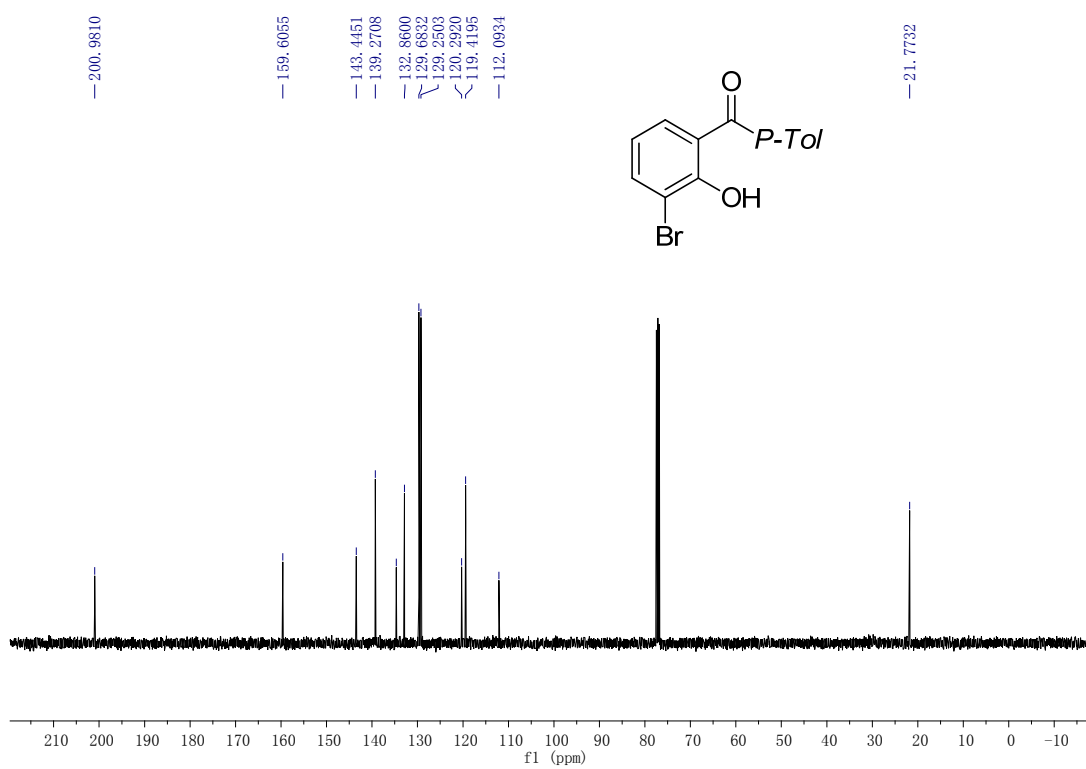
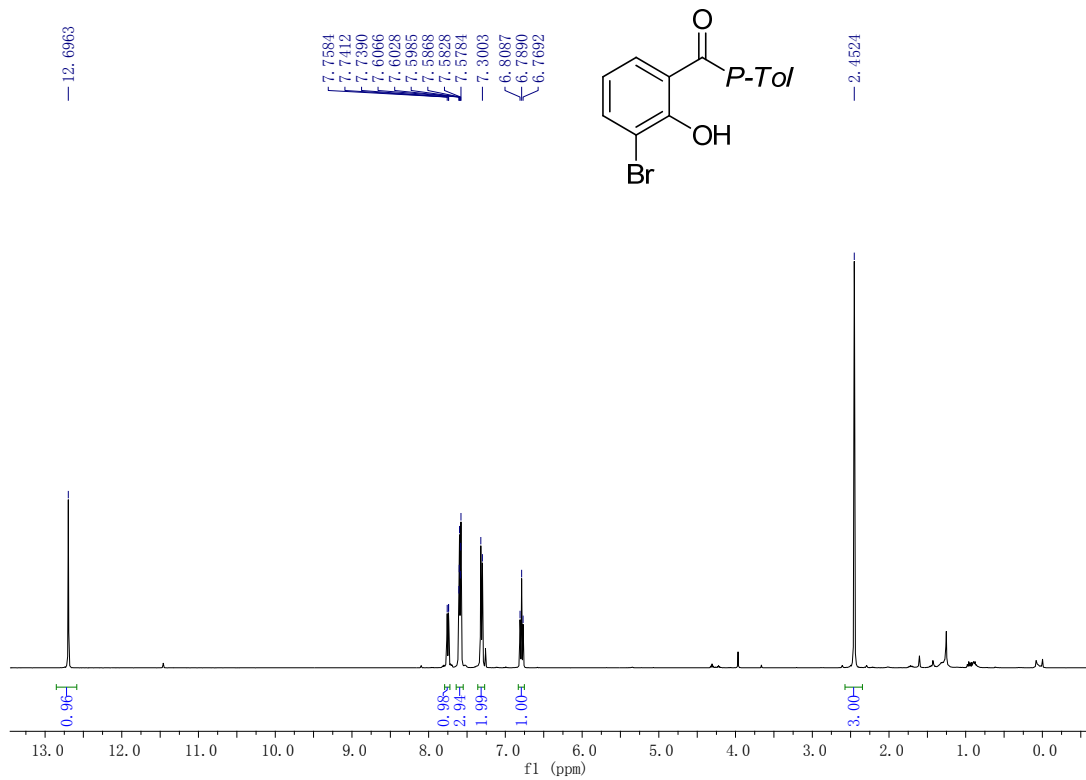
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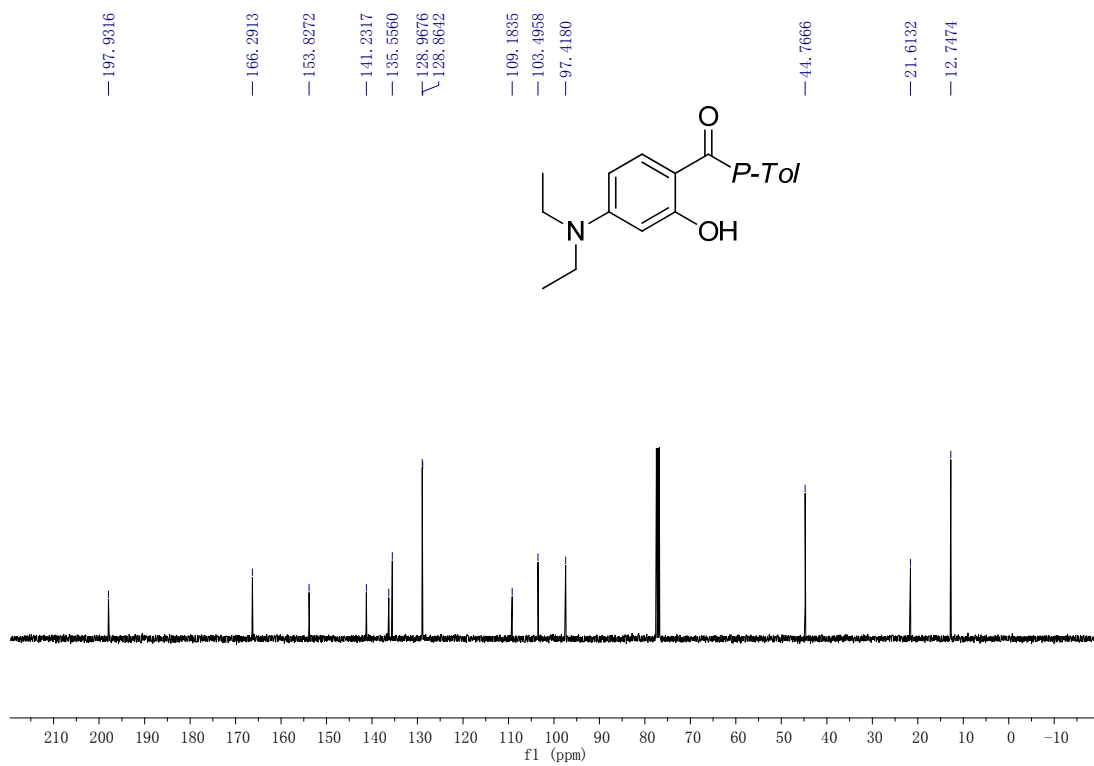
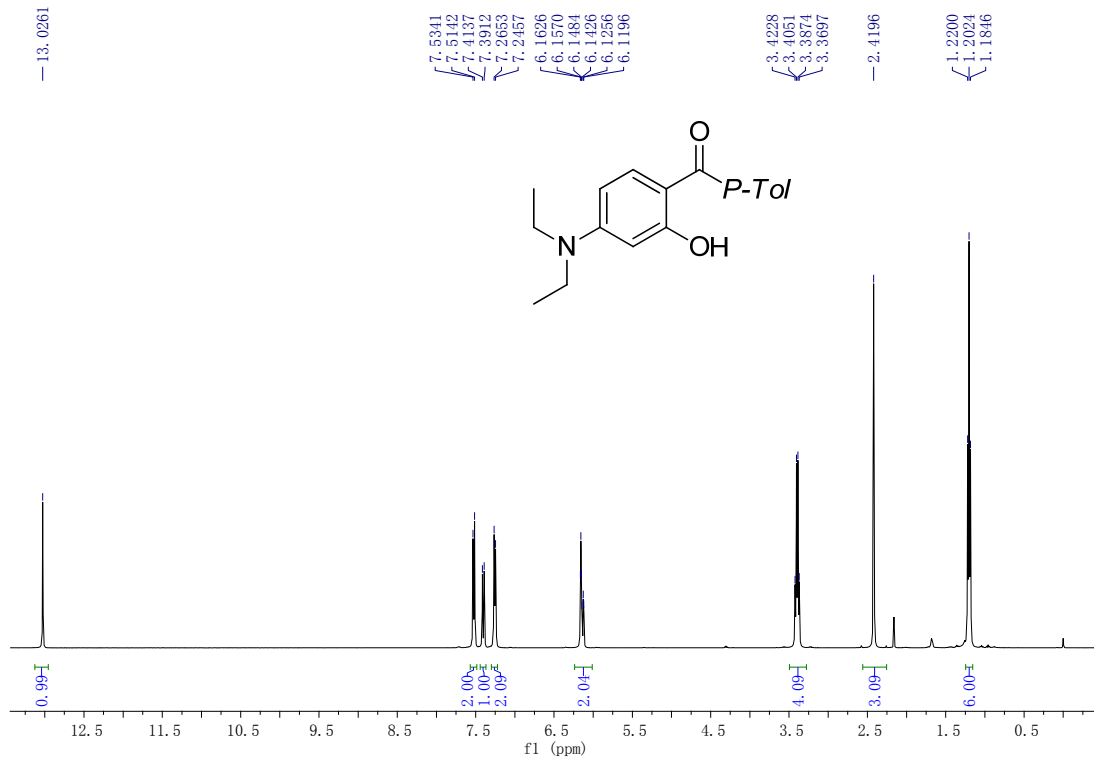
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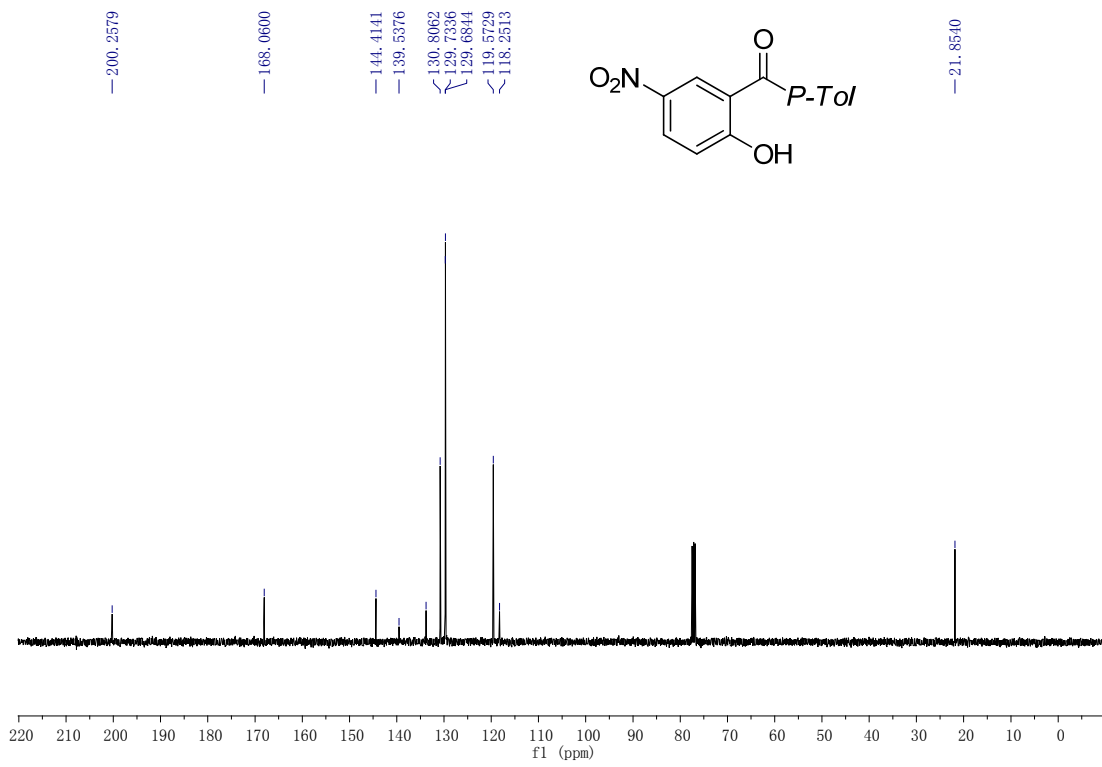
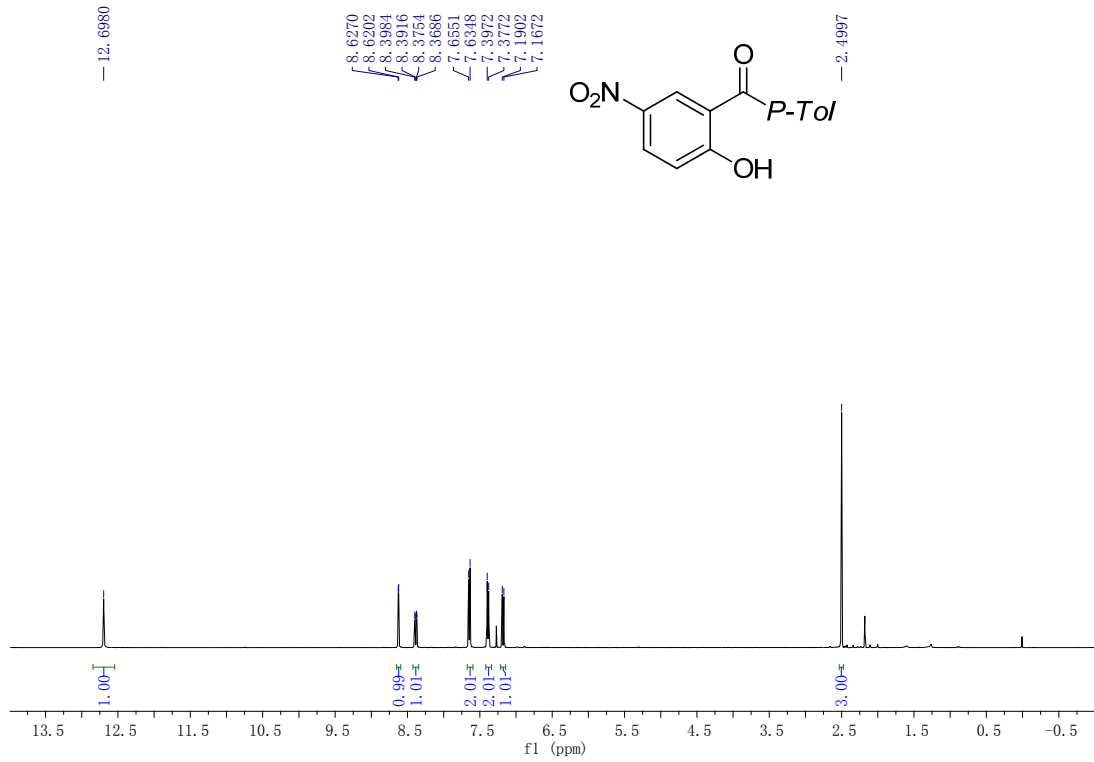
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **3am**



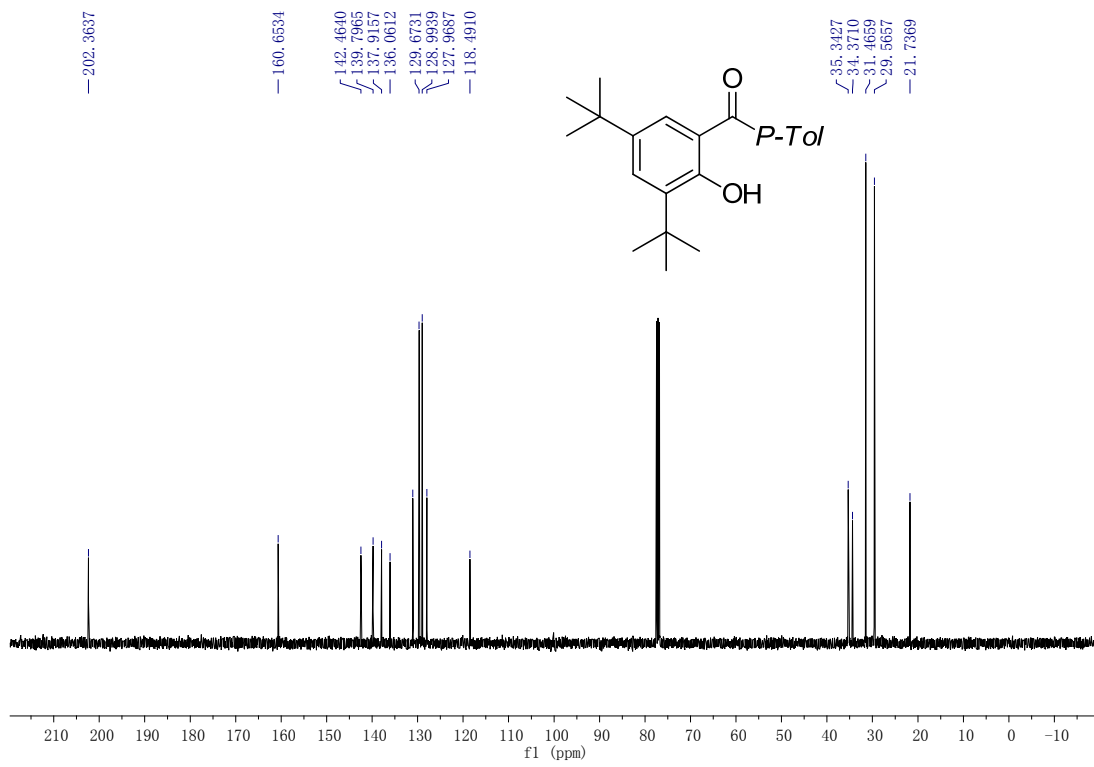
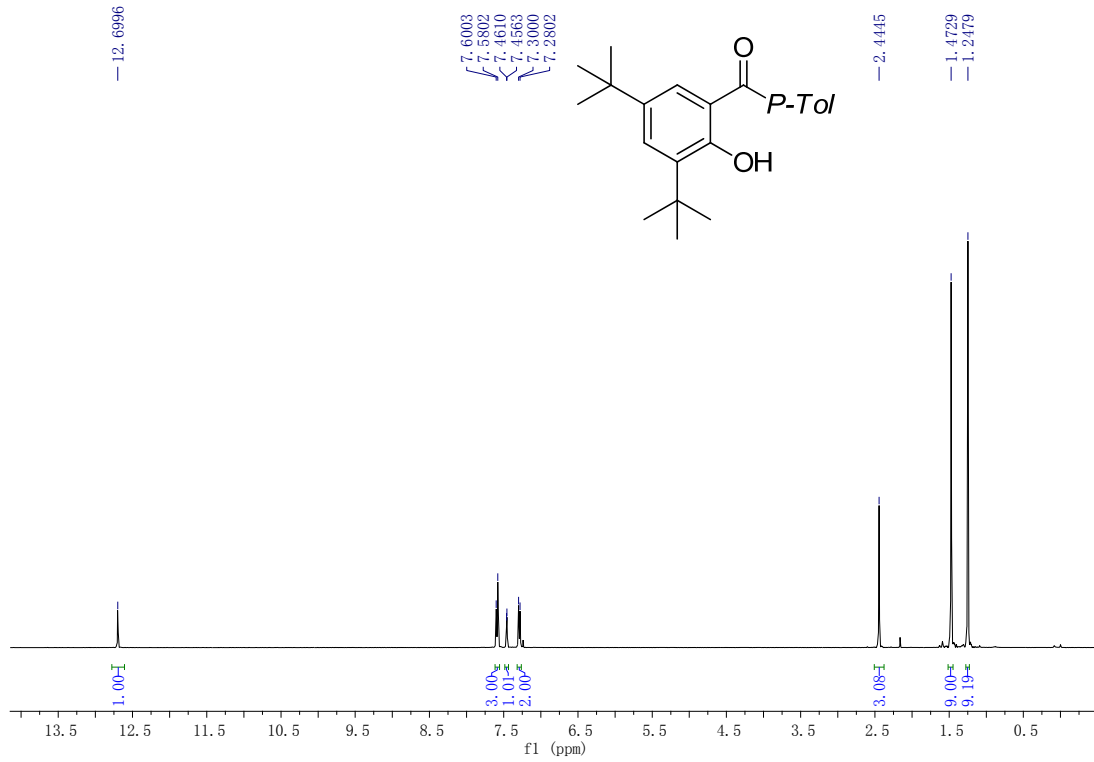
**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3an**



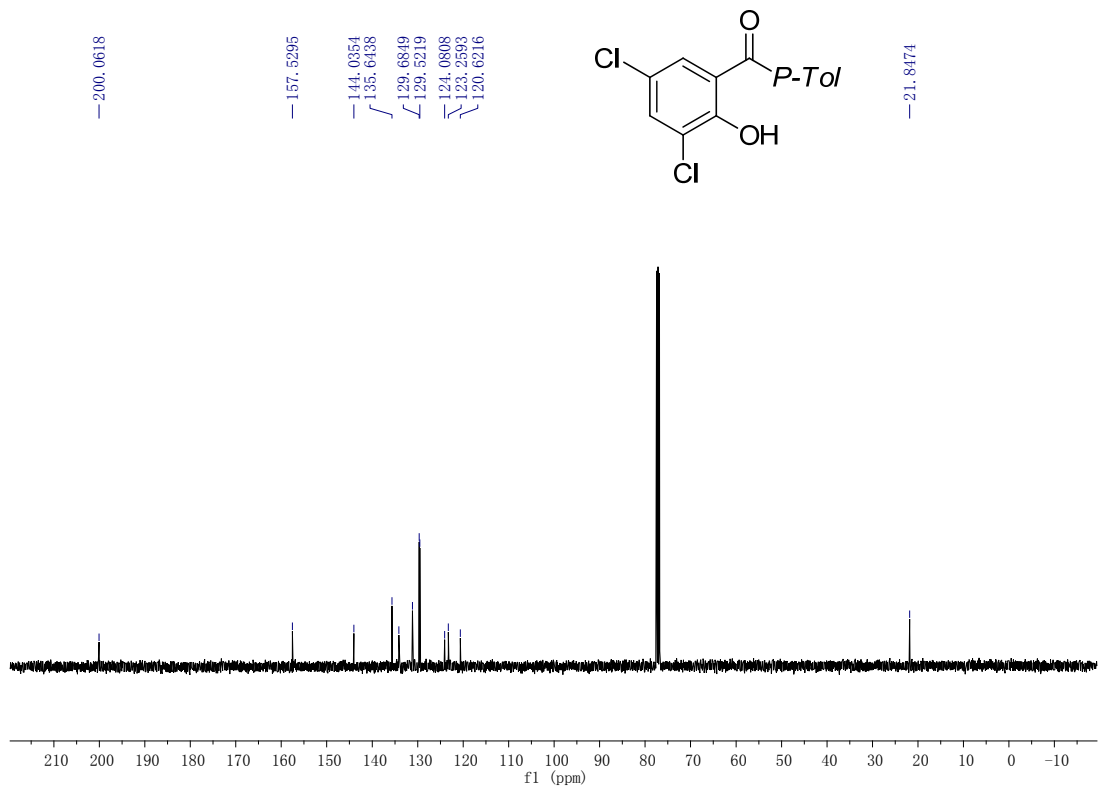
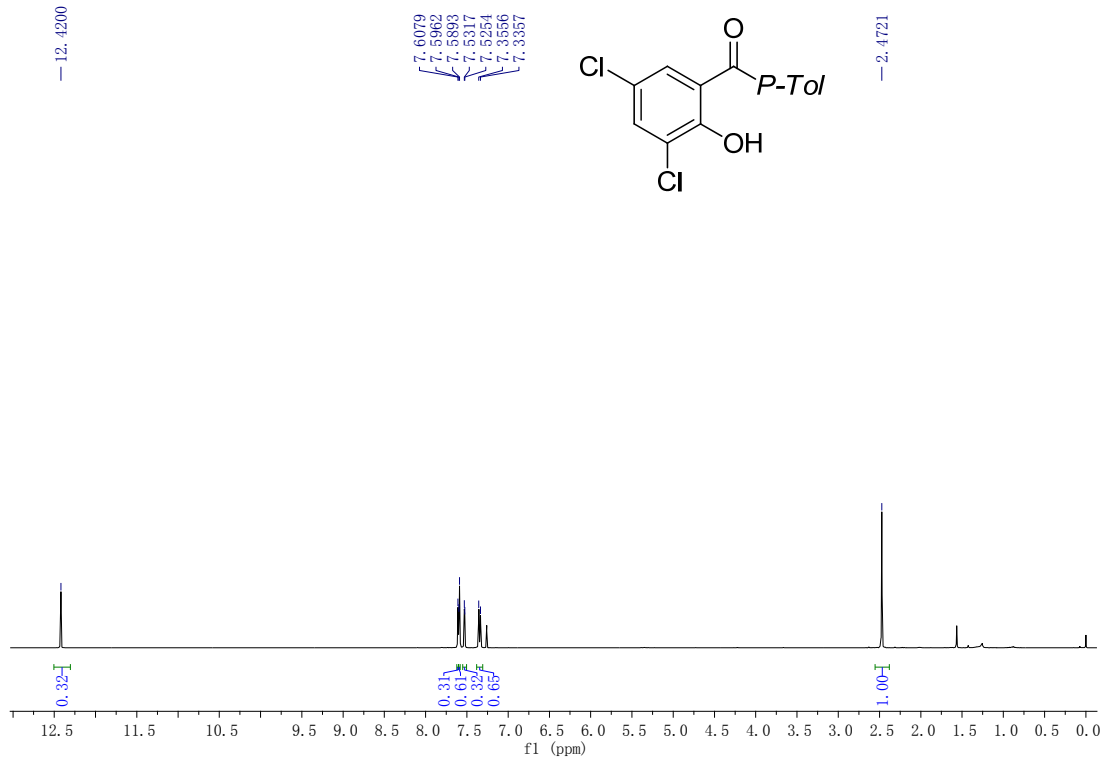
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **3ao**



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ap

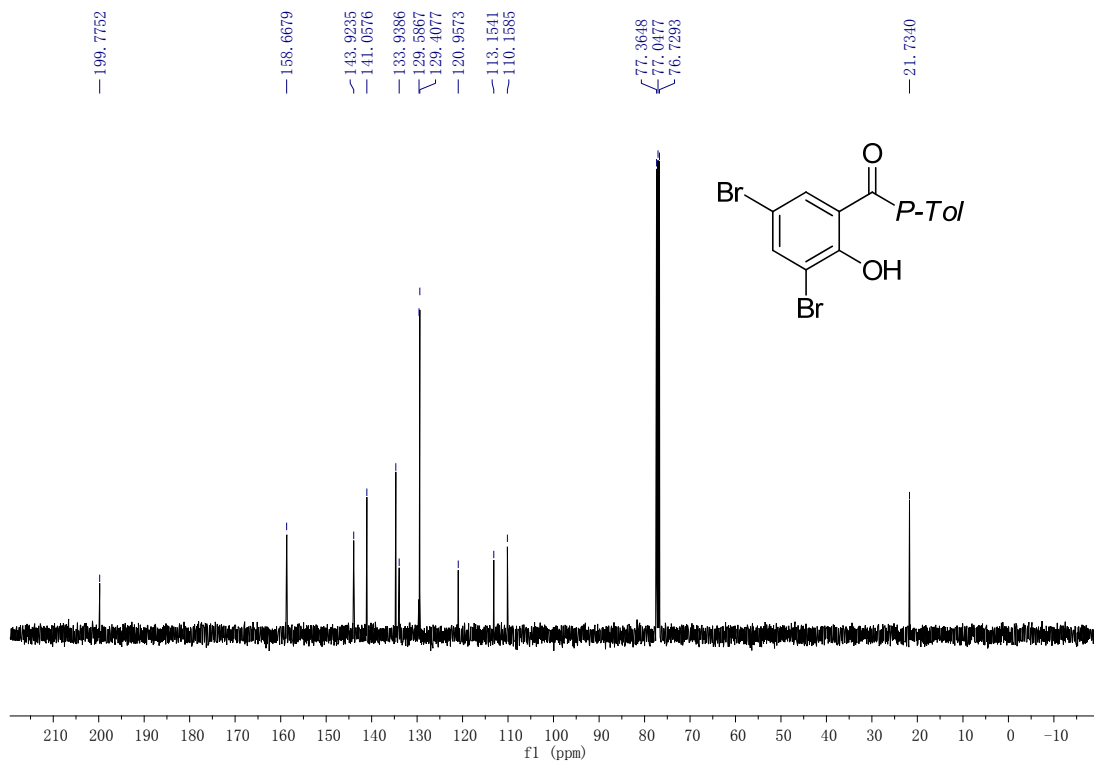
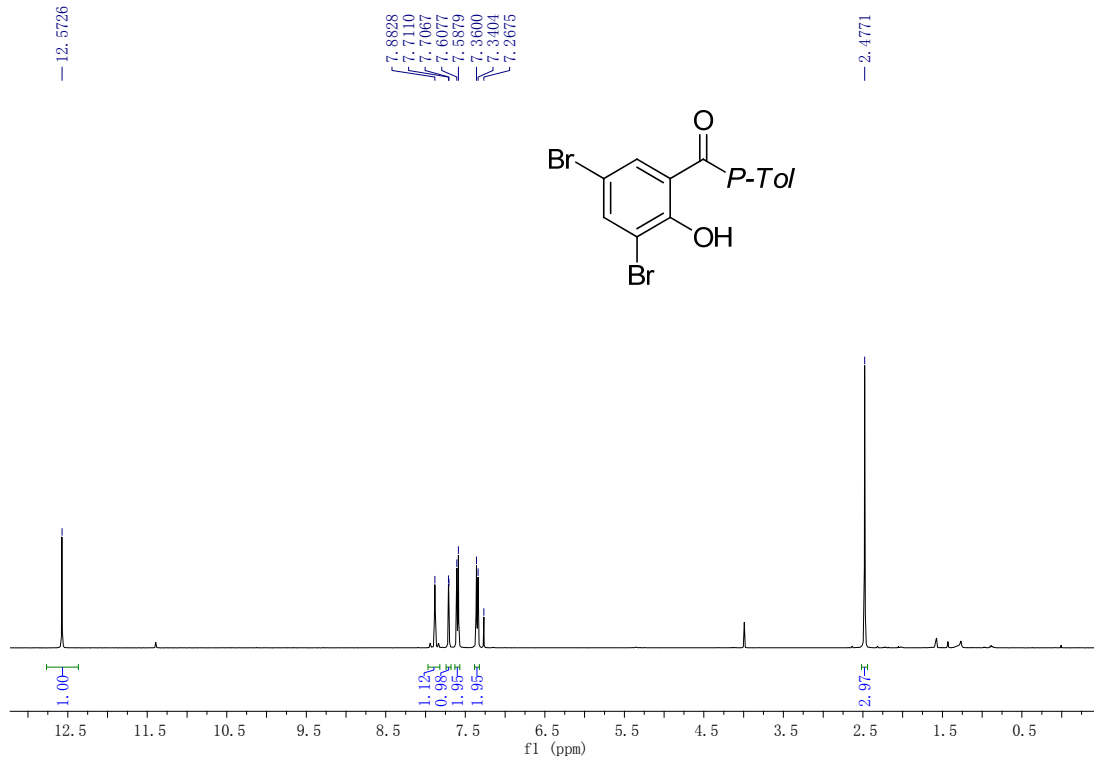


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3aq

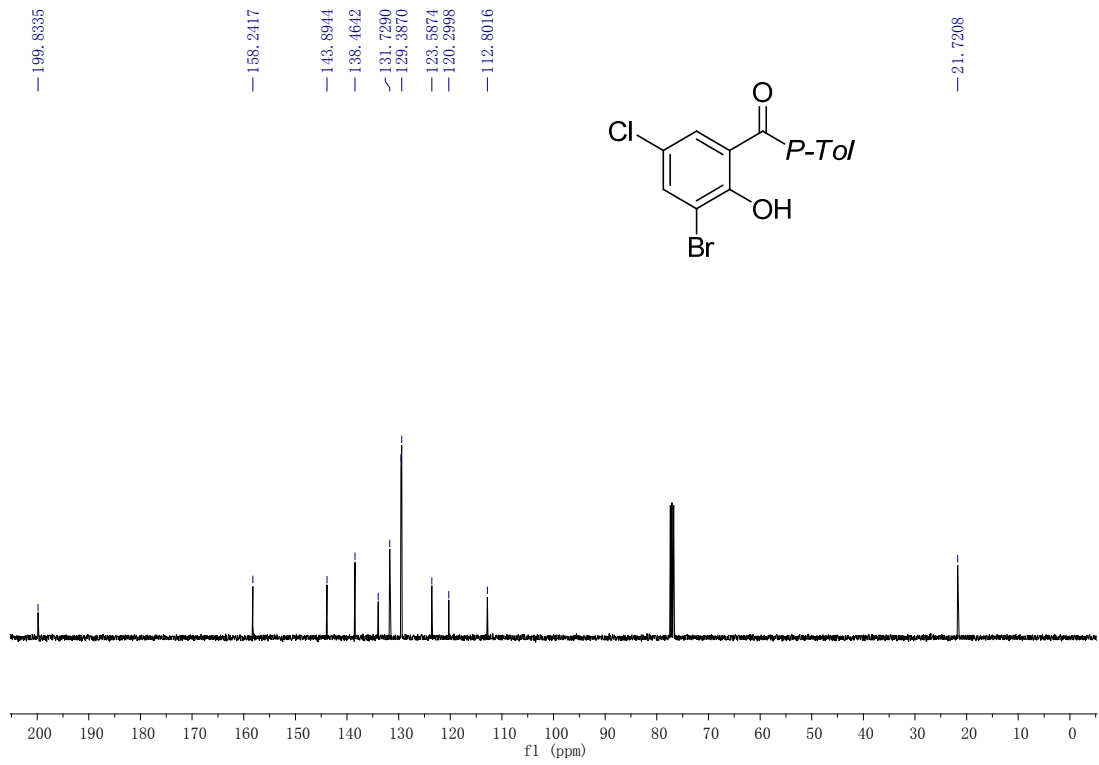
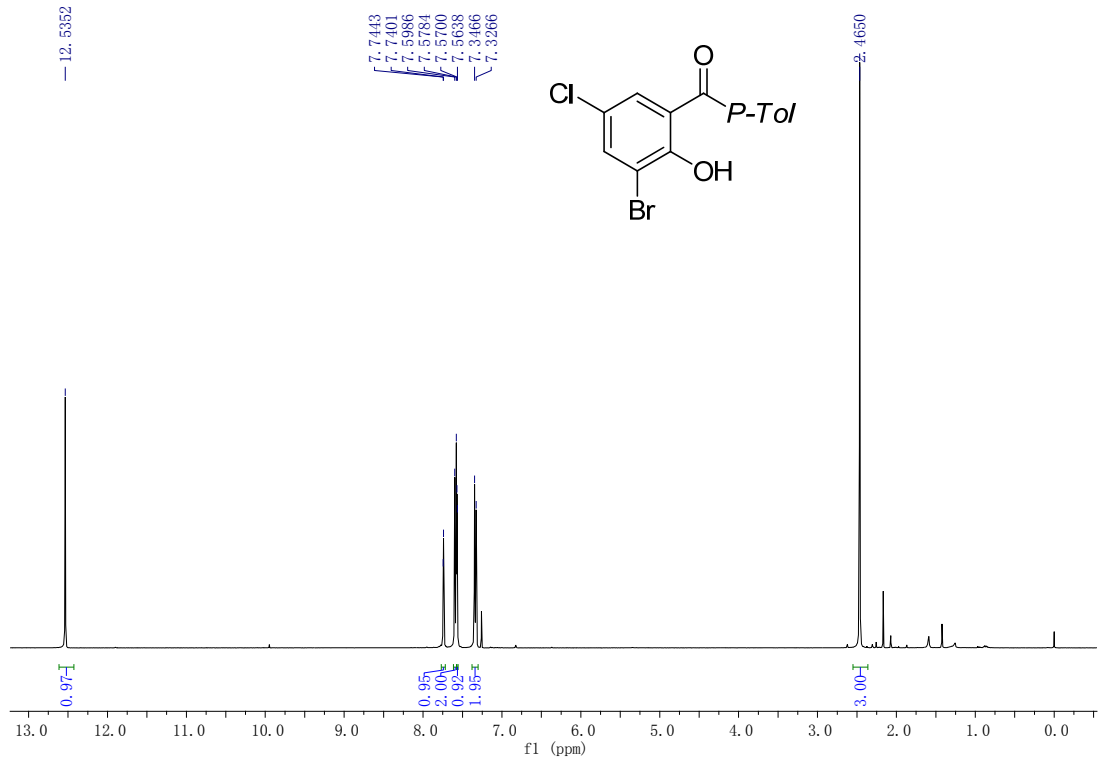


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3ar

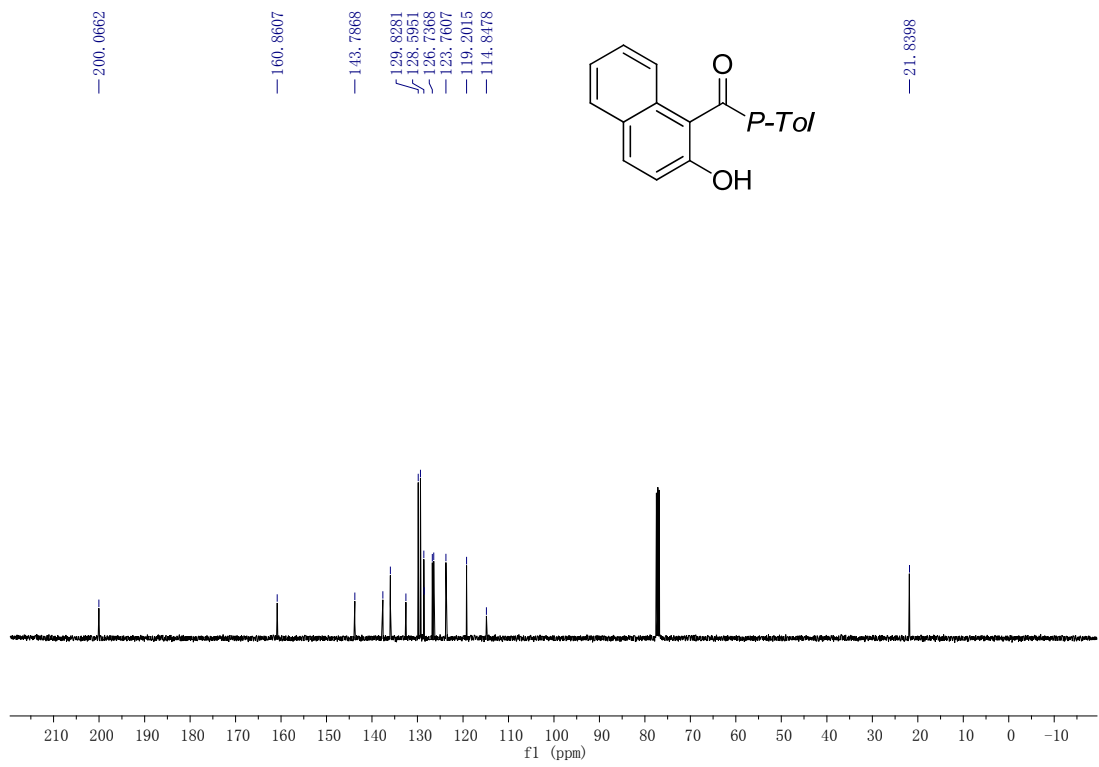
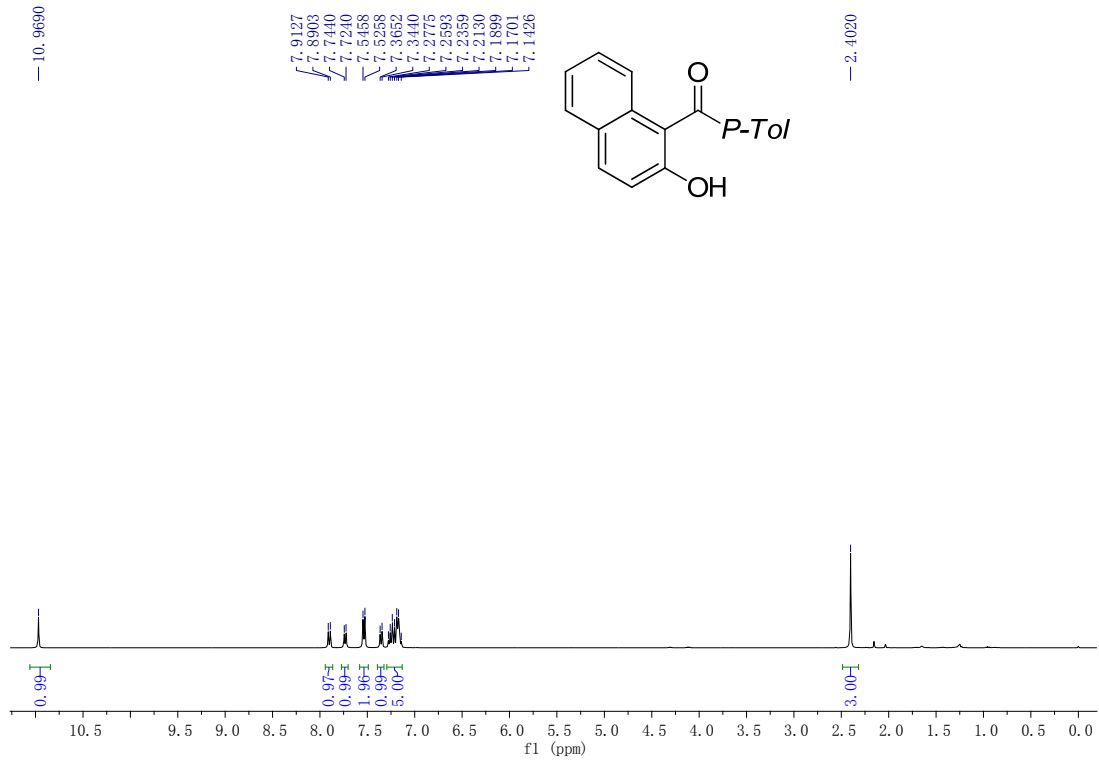




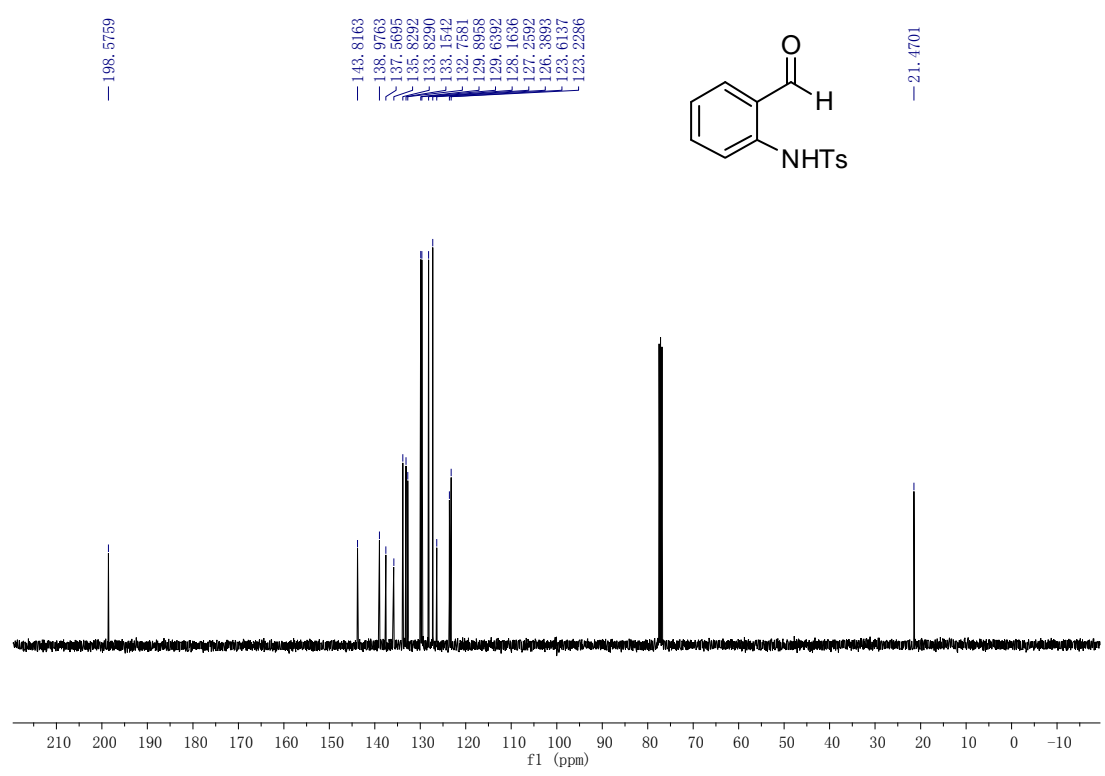
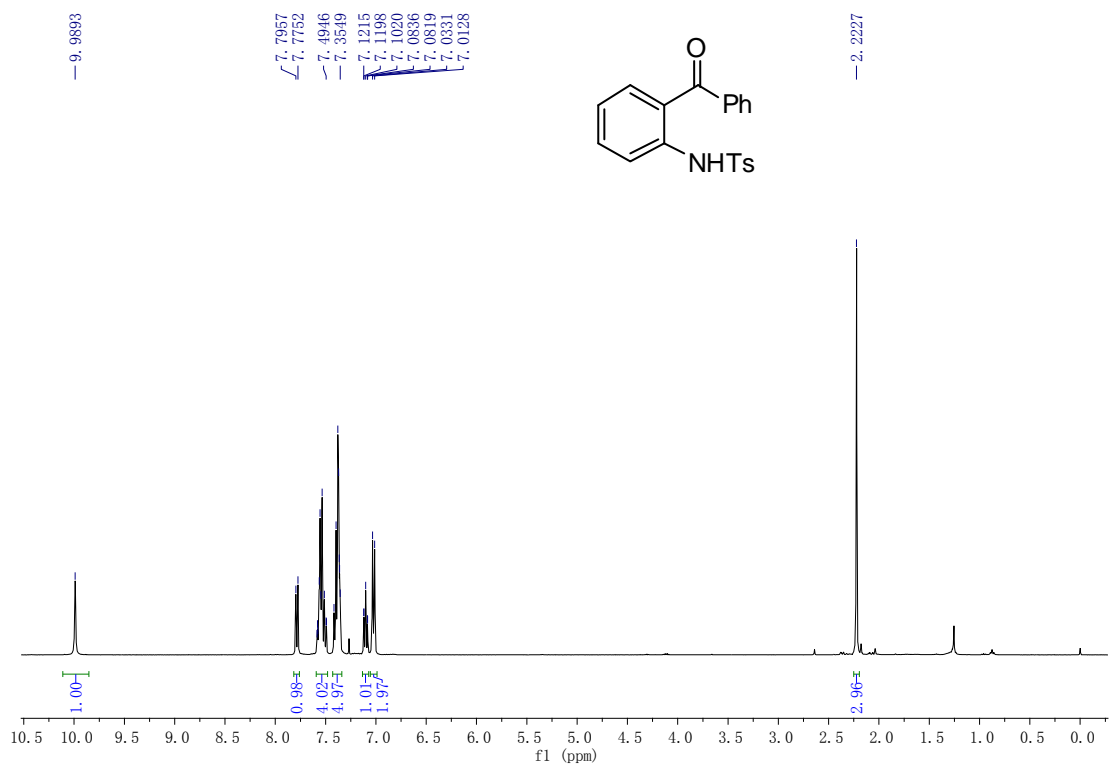
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **3as**



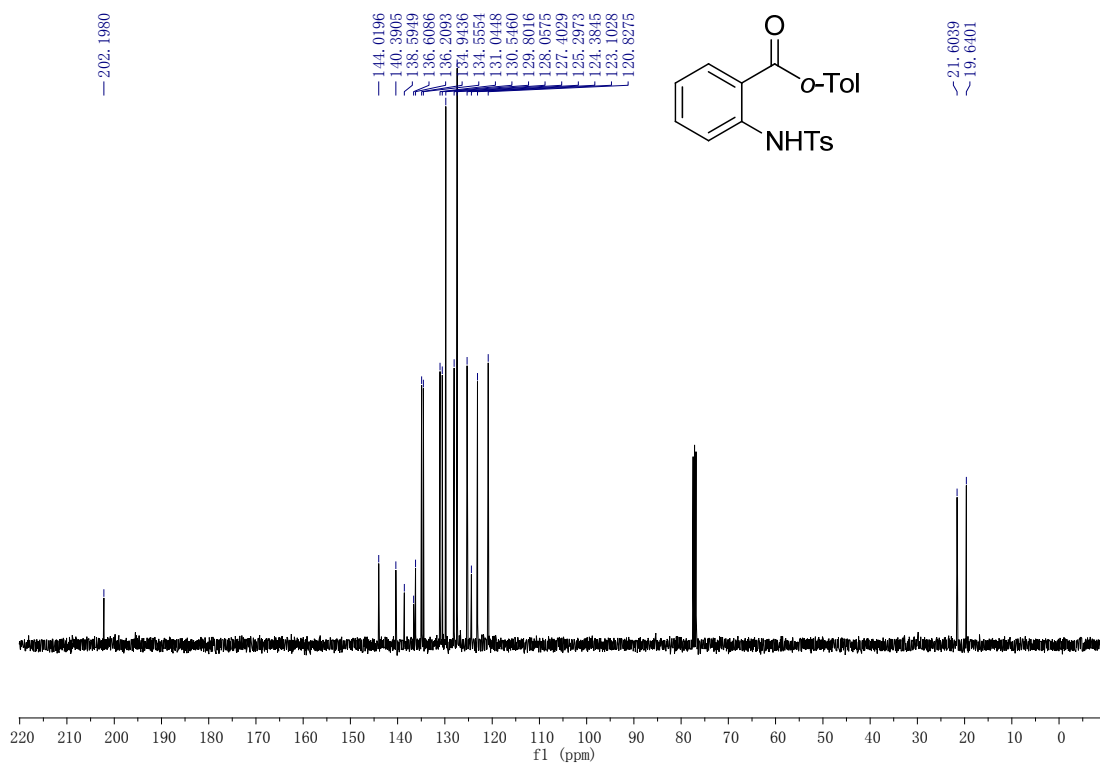
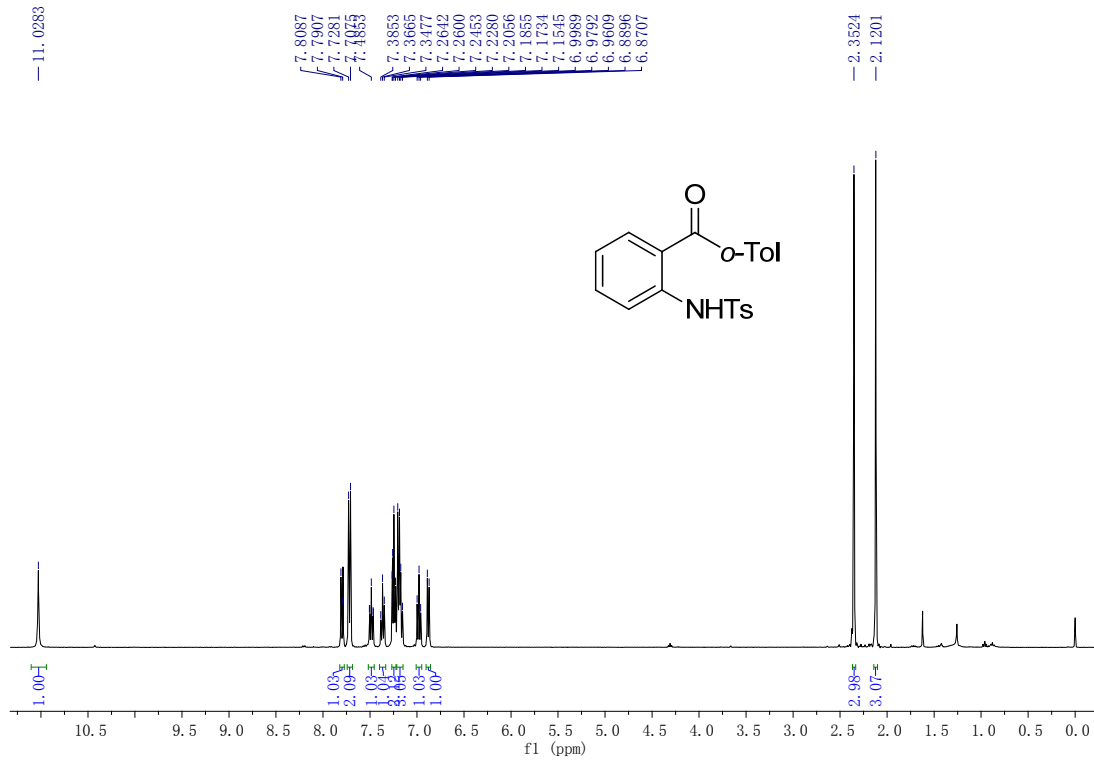
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 3at



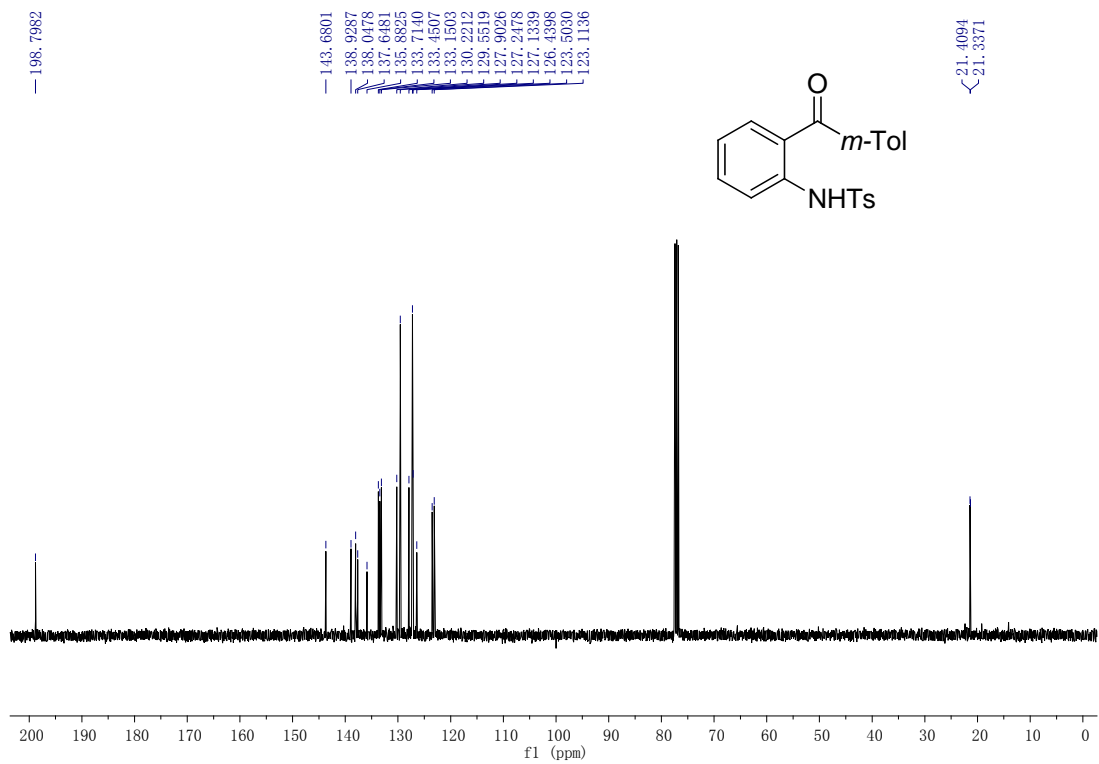
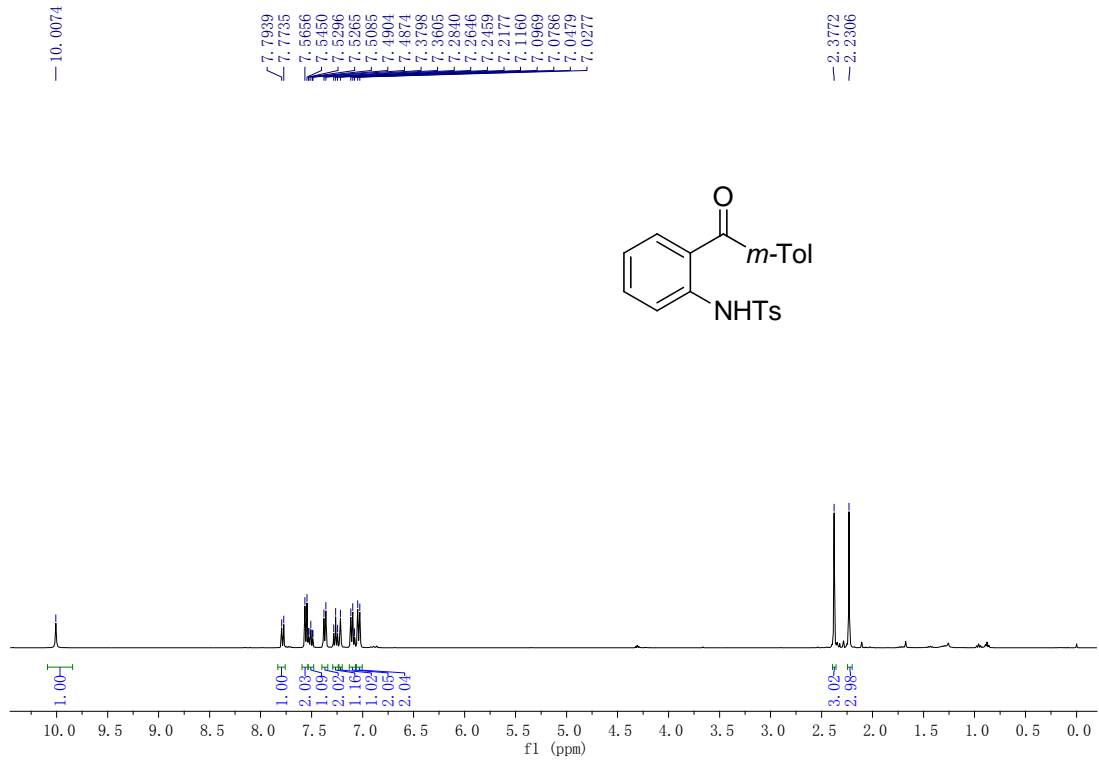
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5aa



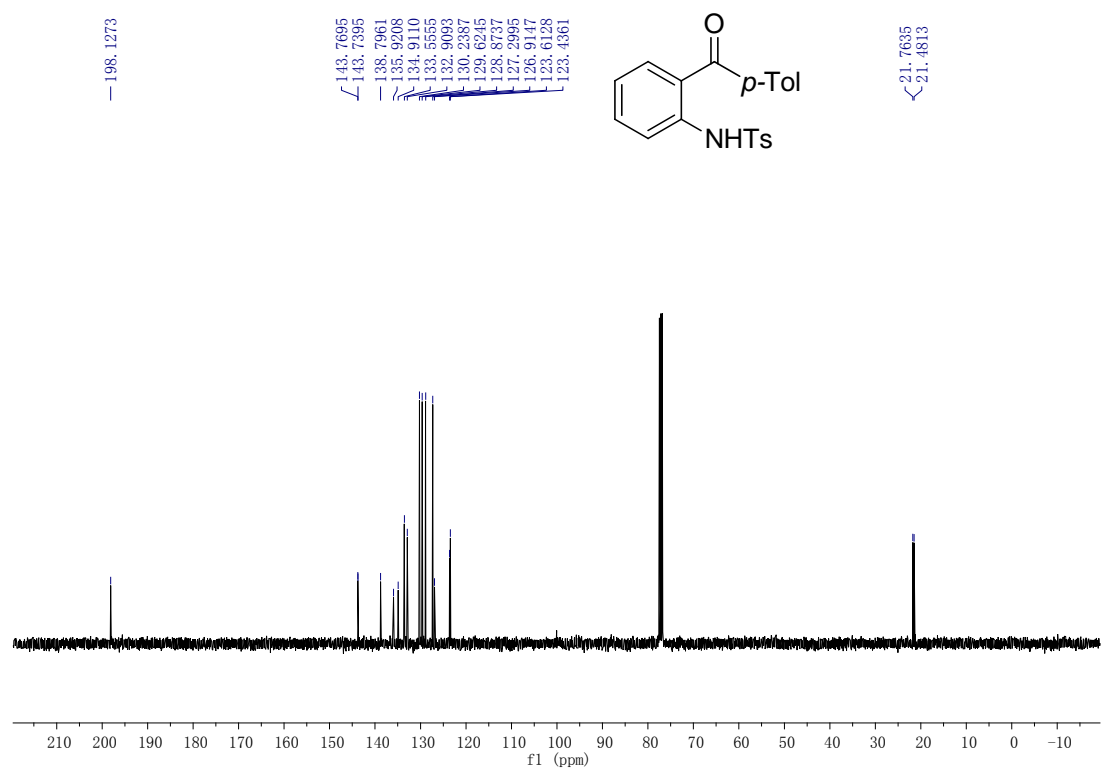
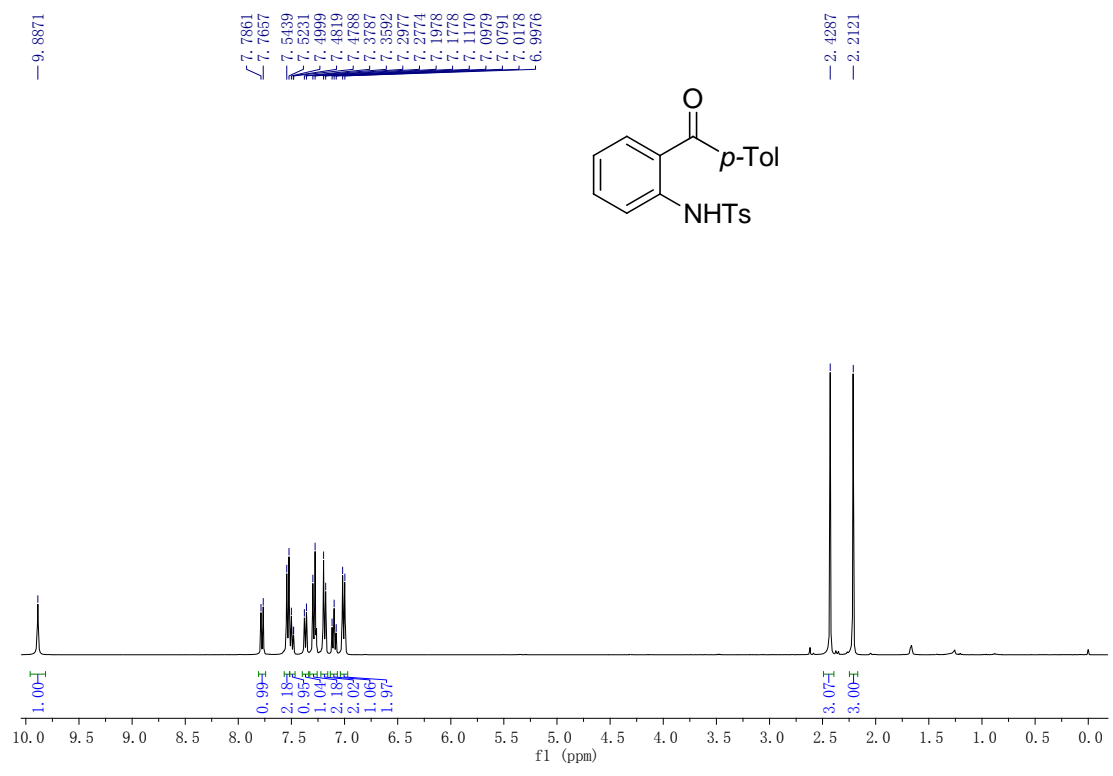
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ab**



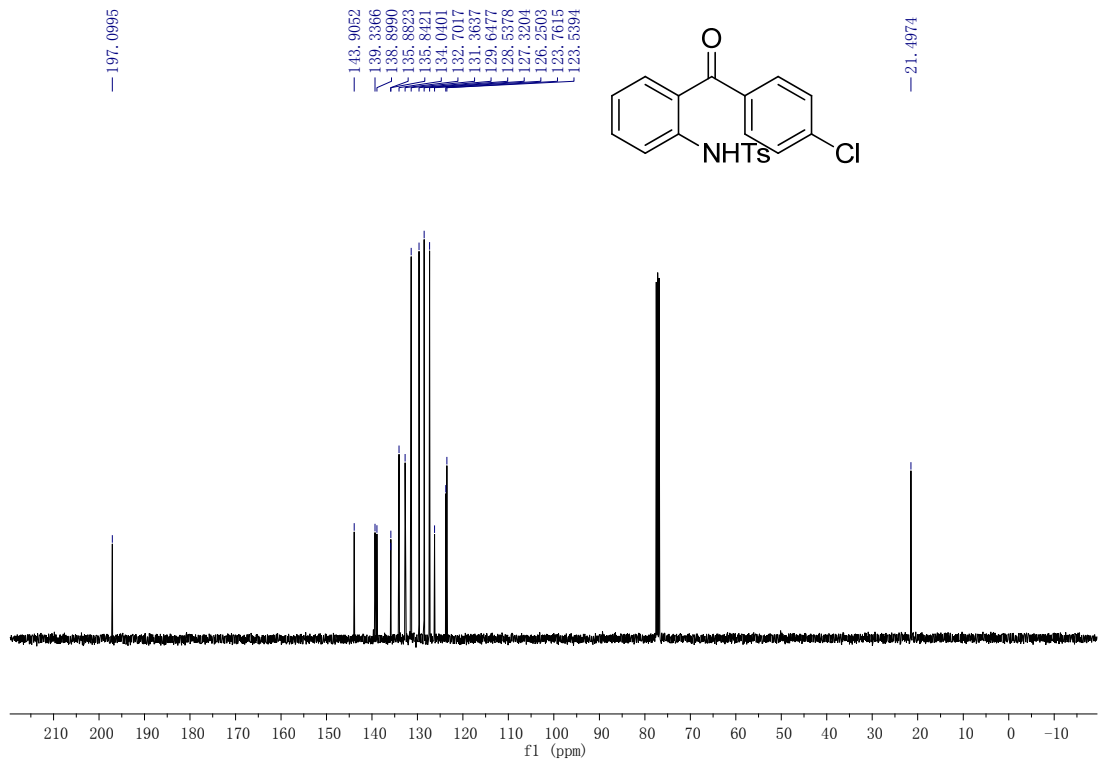
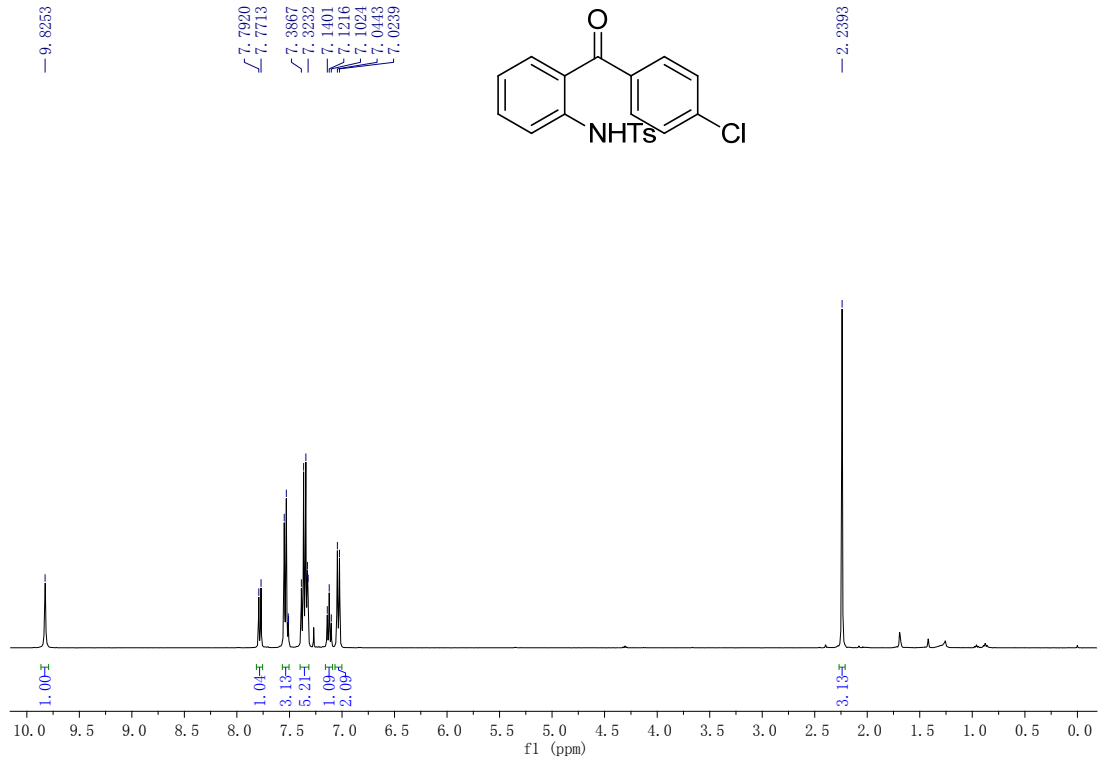
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **5ac**



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5ad

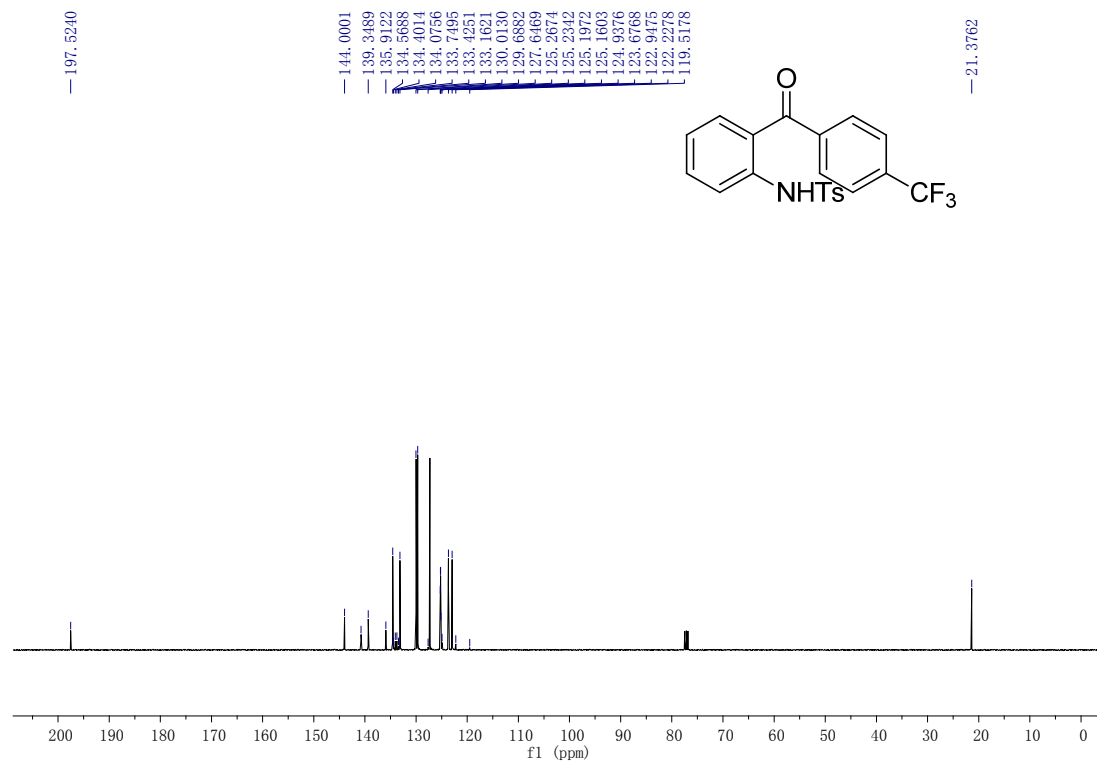
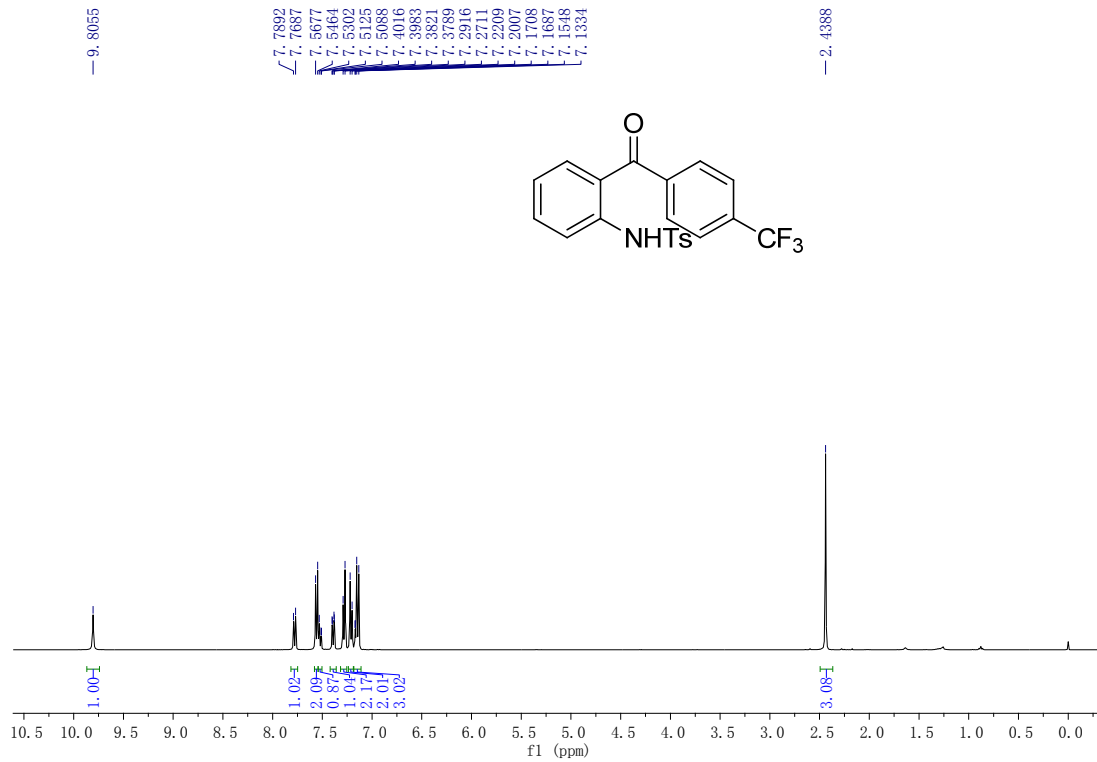


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ae**

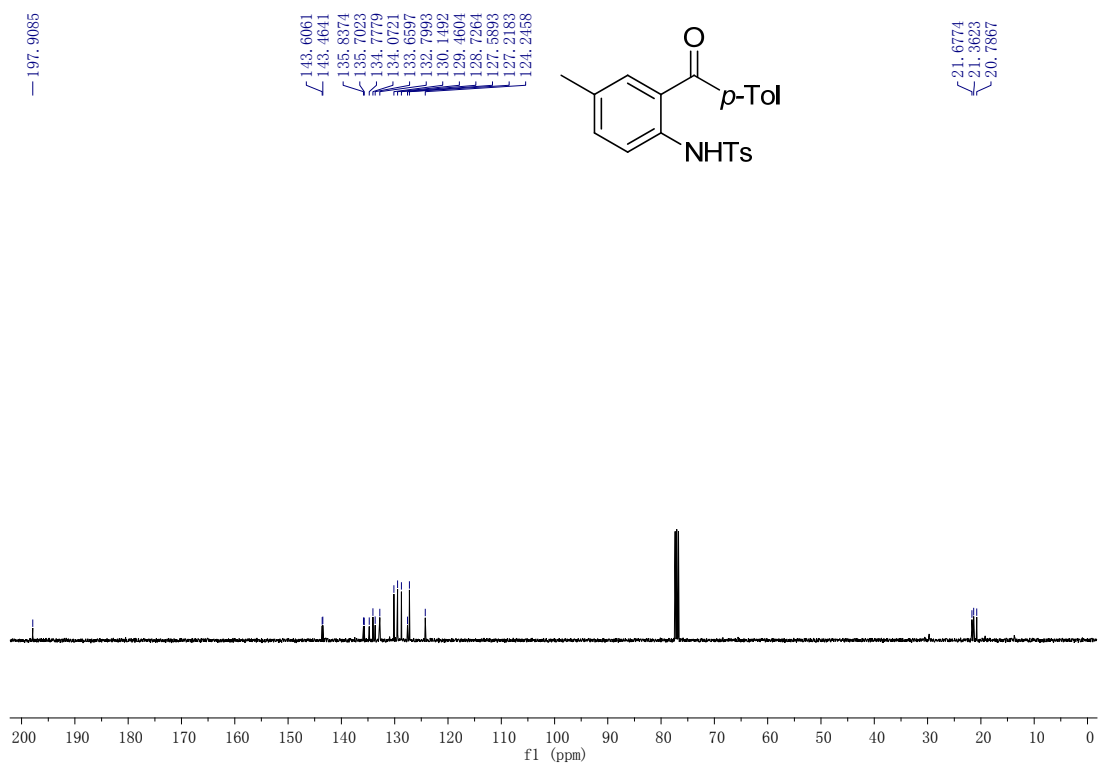
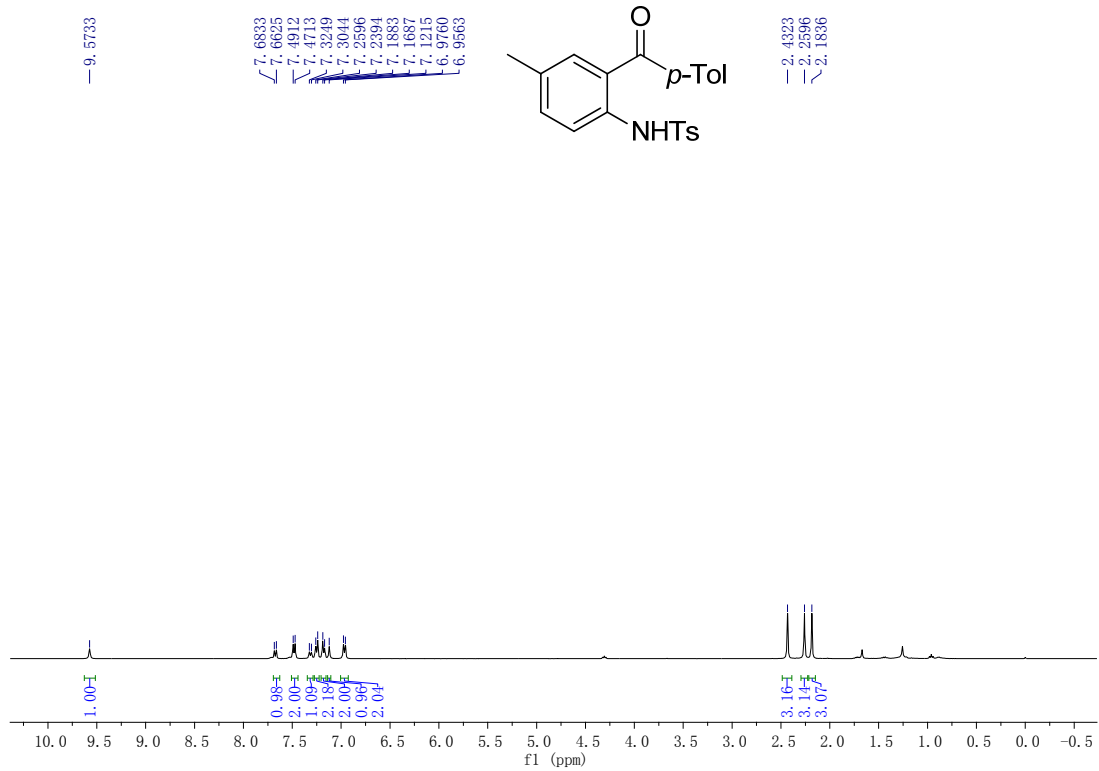


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5af**

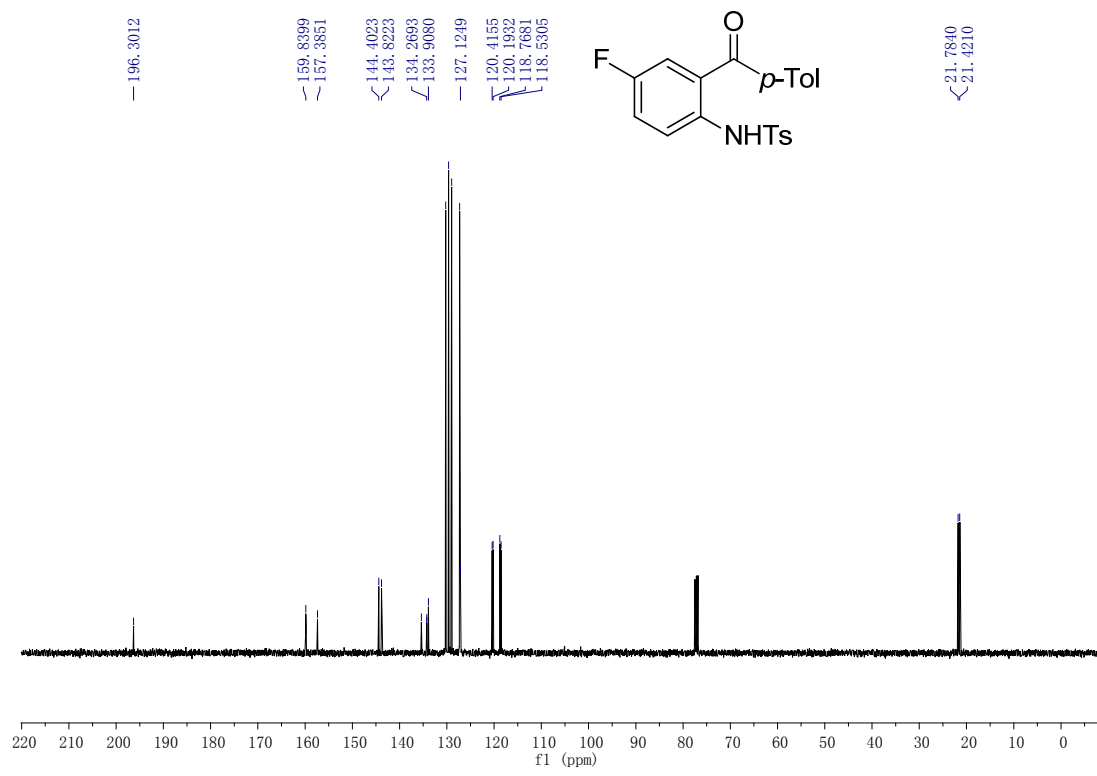
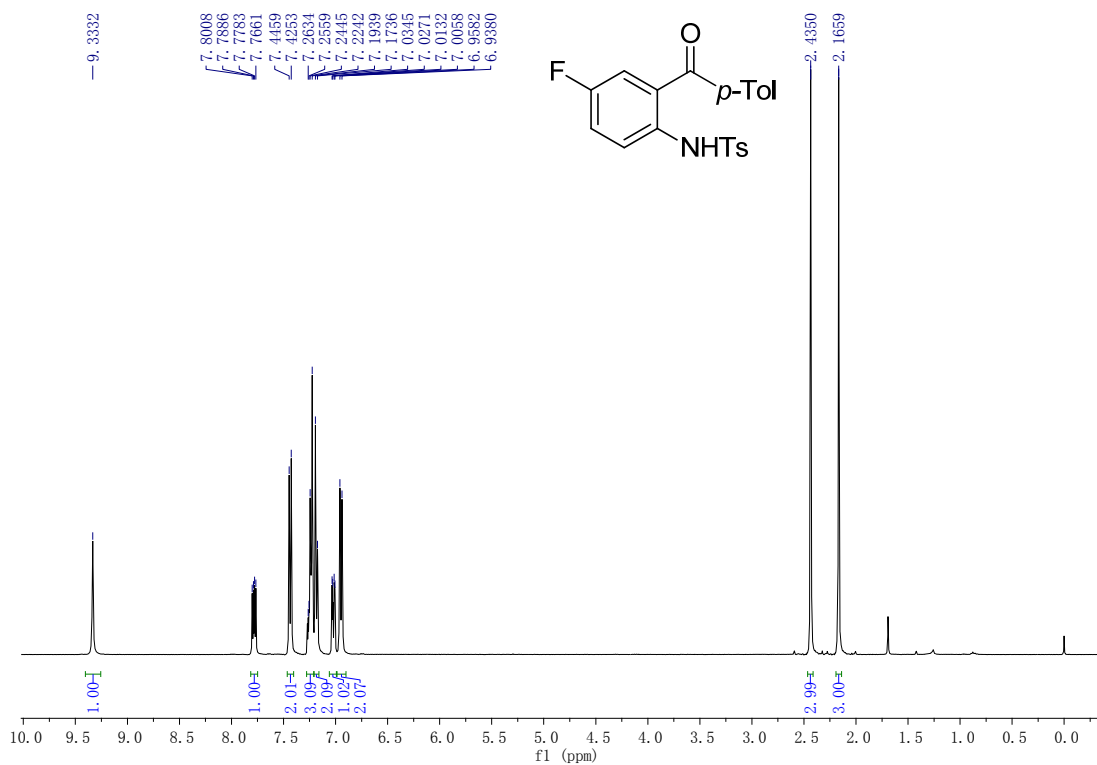




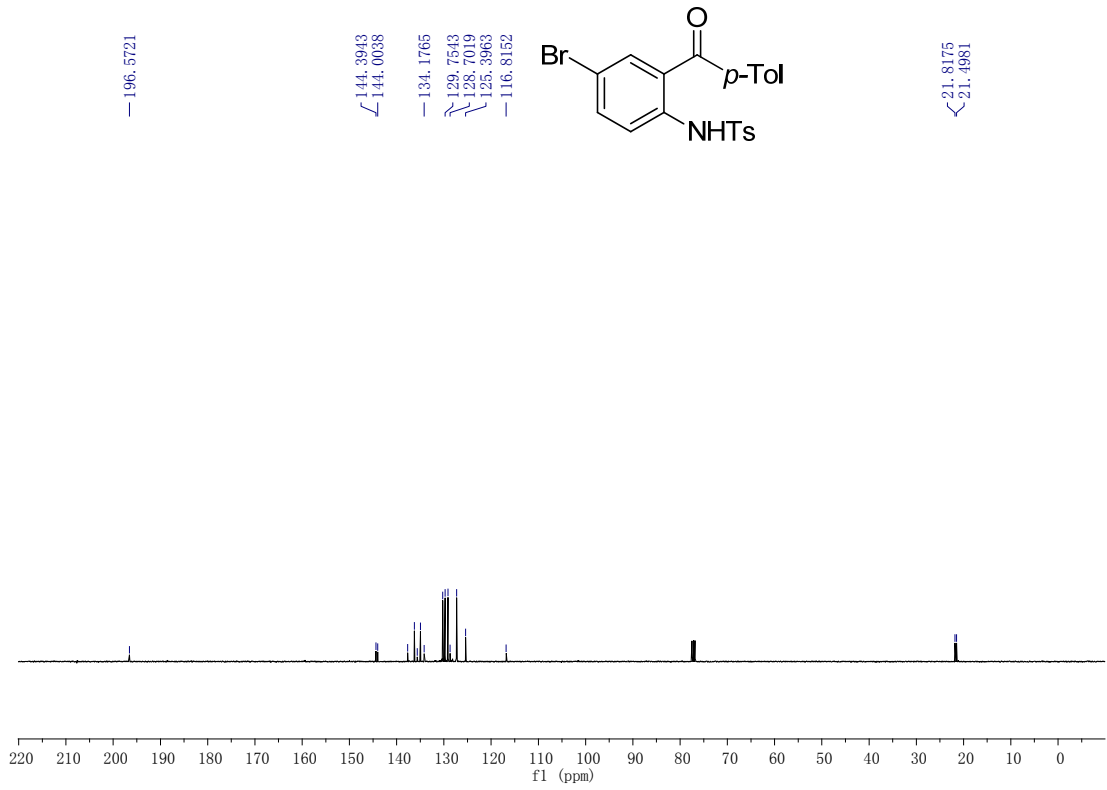
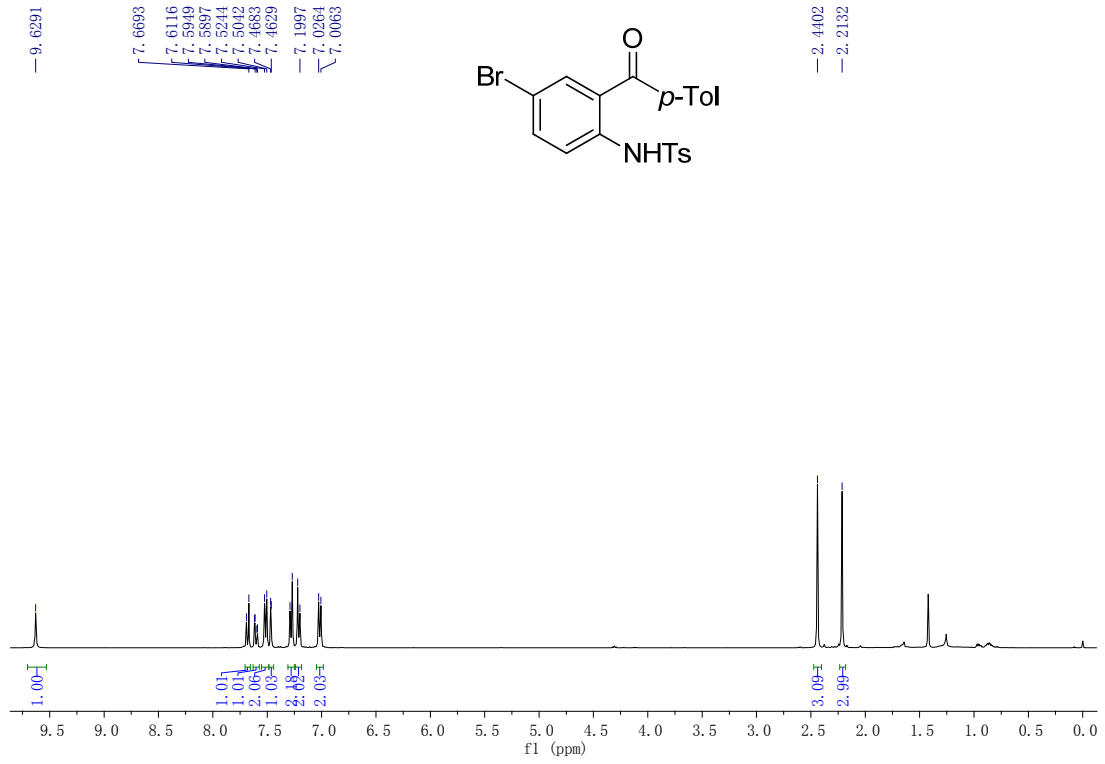
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ag**



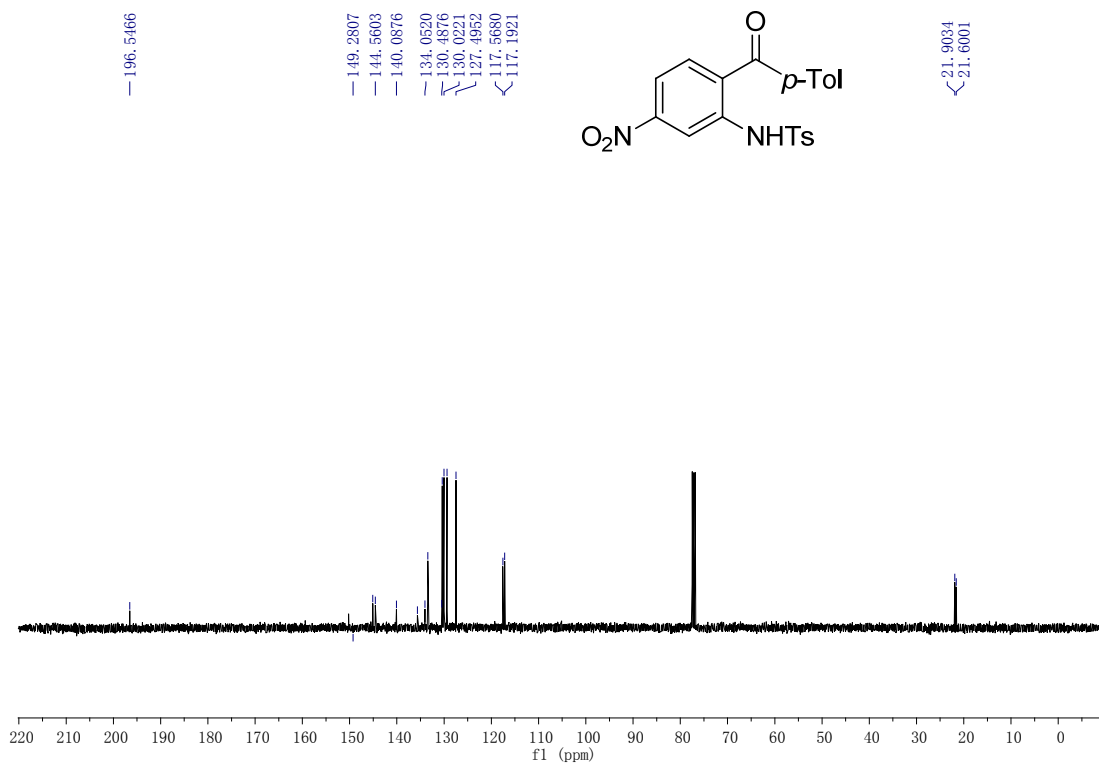
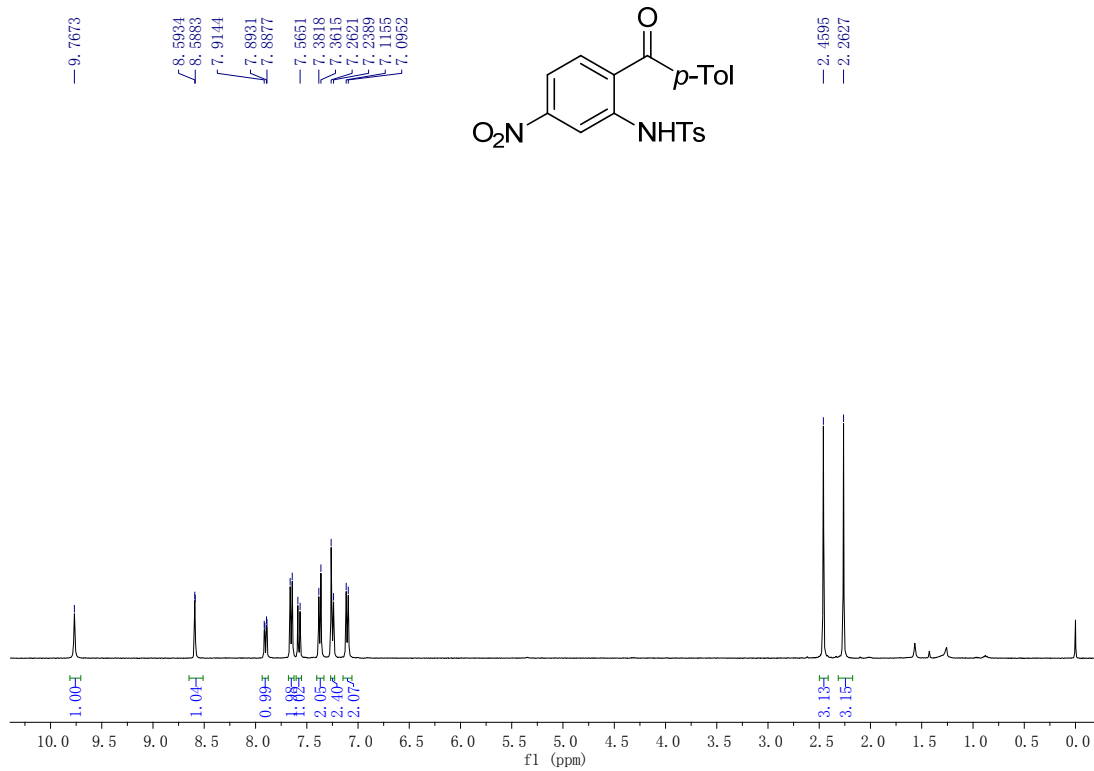
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ah**



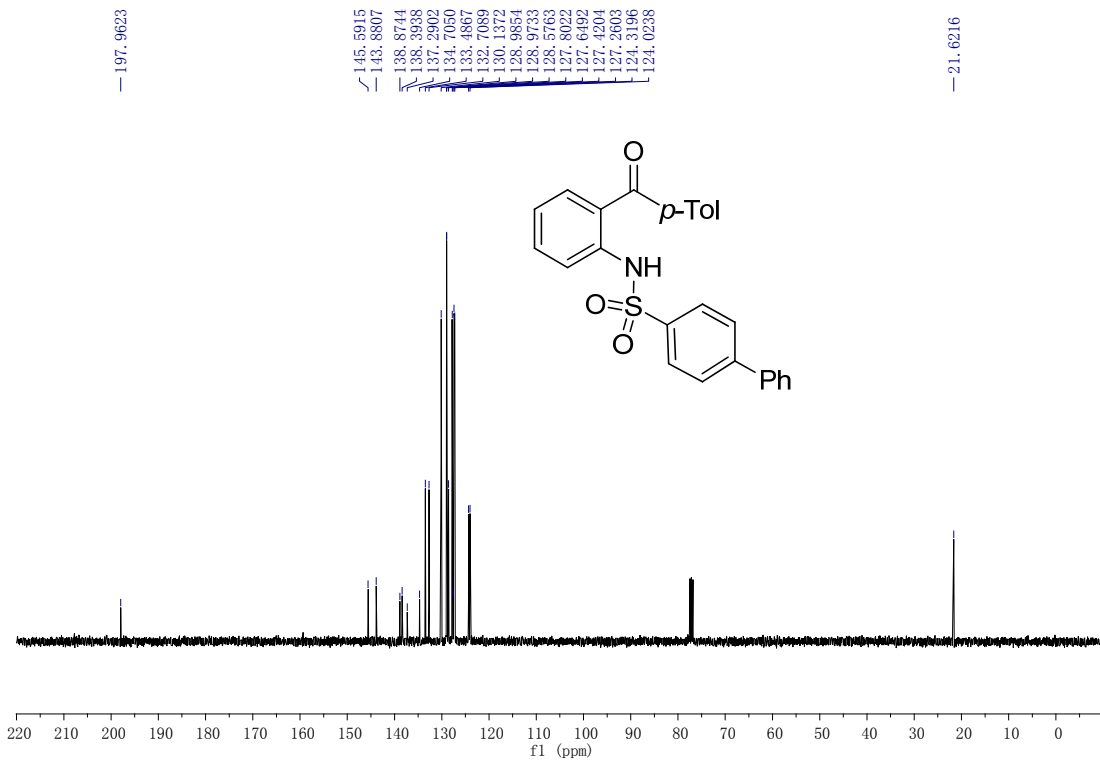
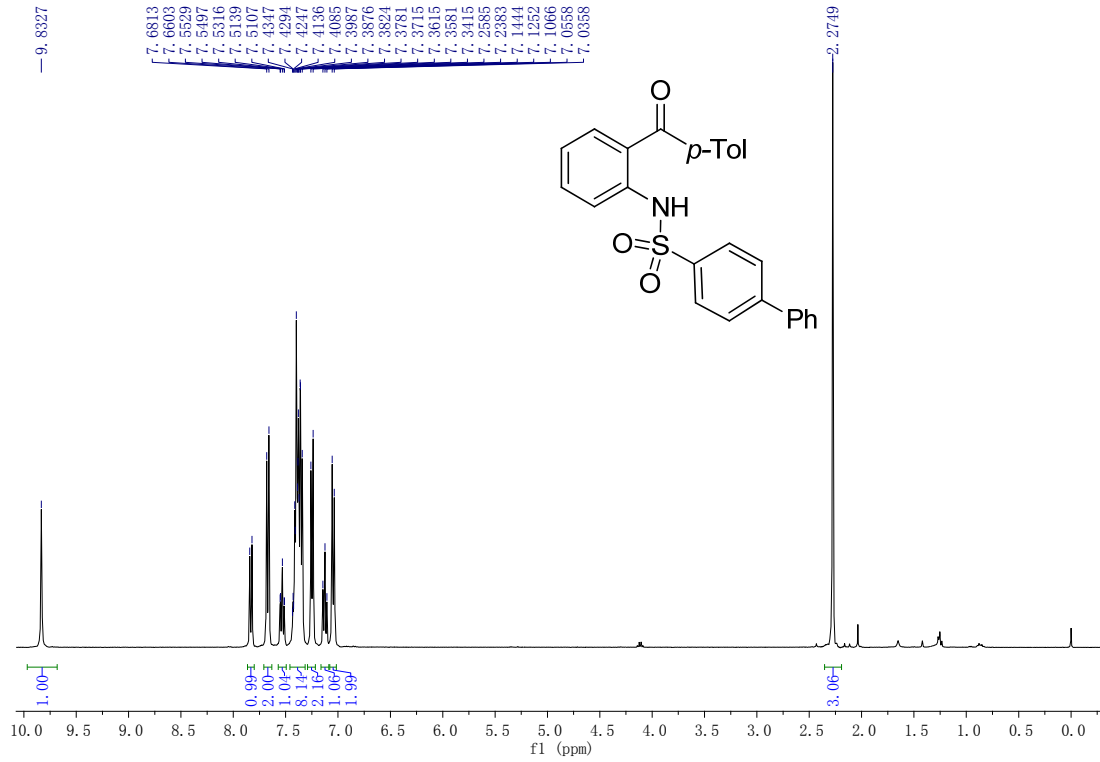
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5ai



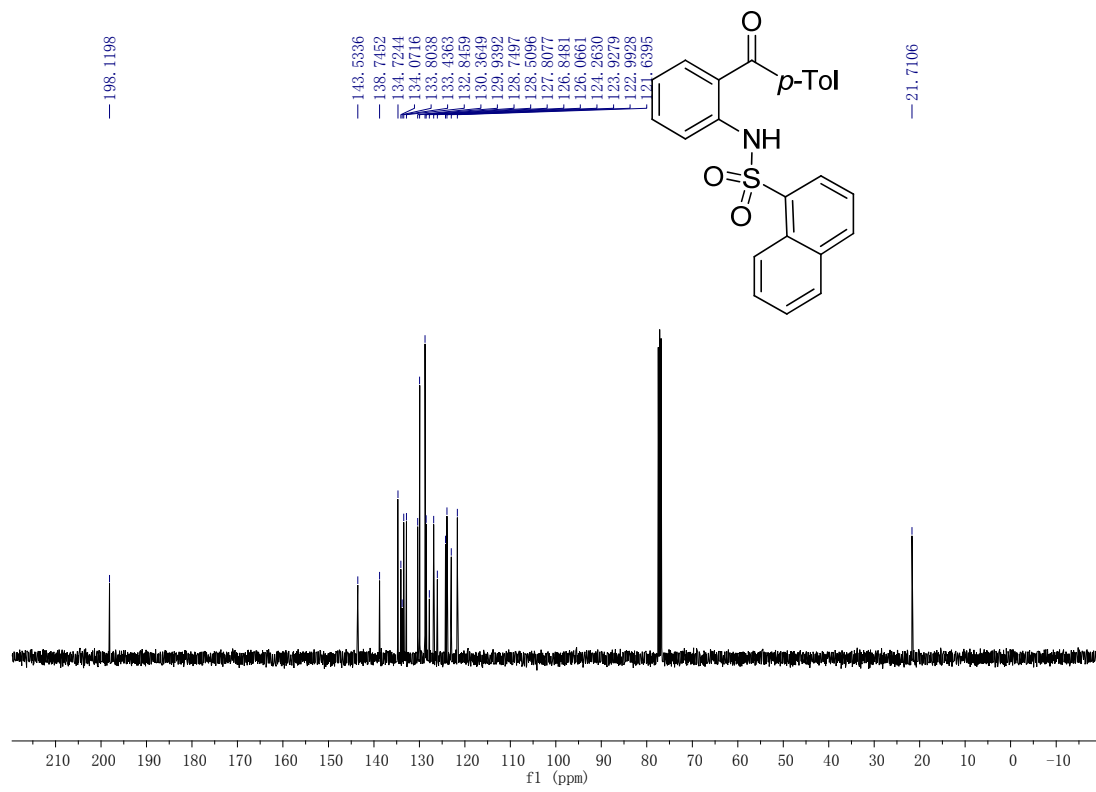
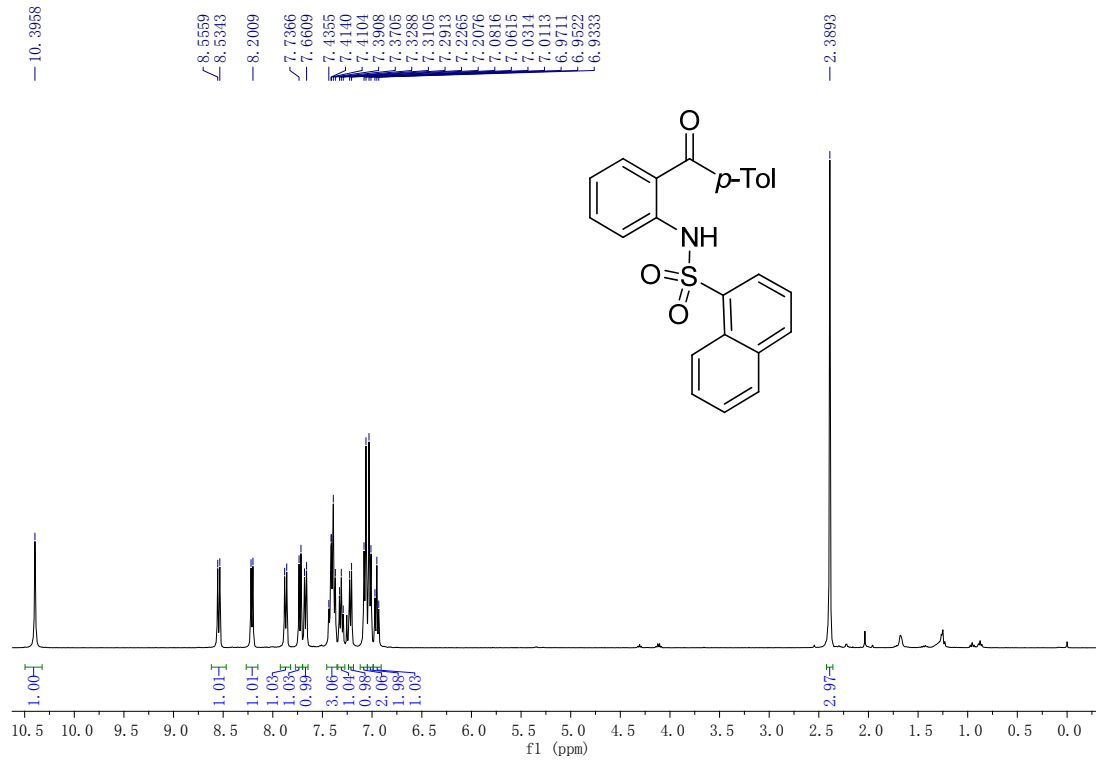
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5aj**



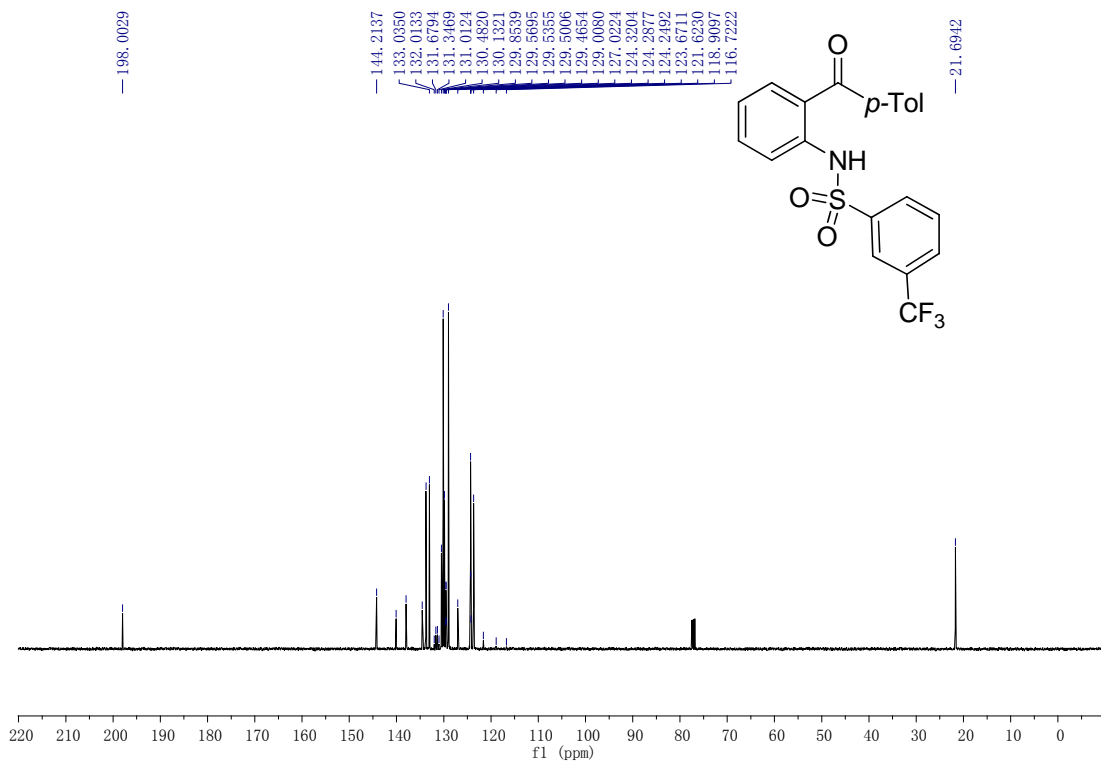
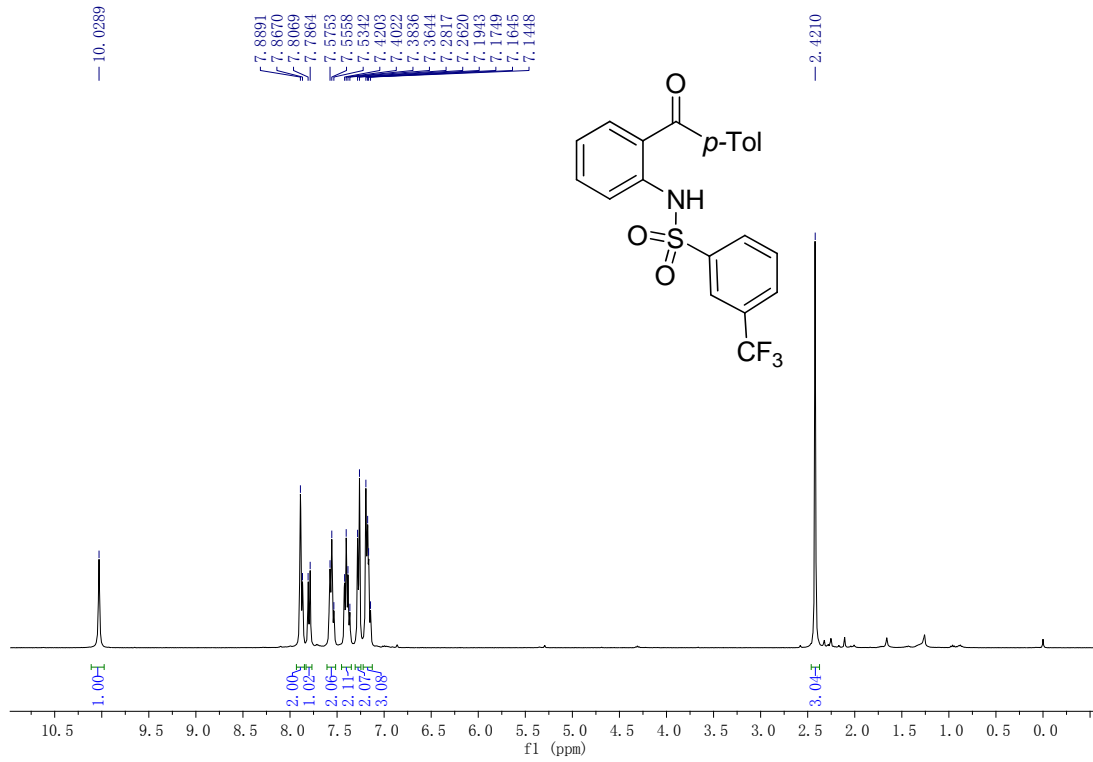
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ak**



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5aI

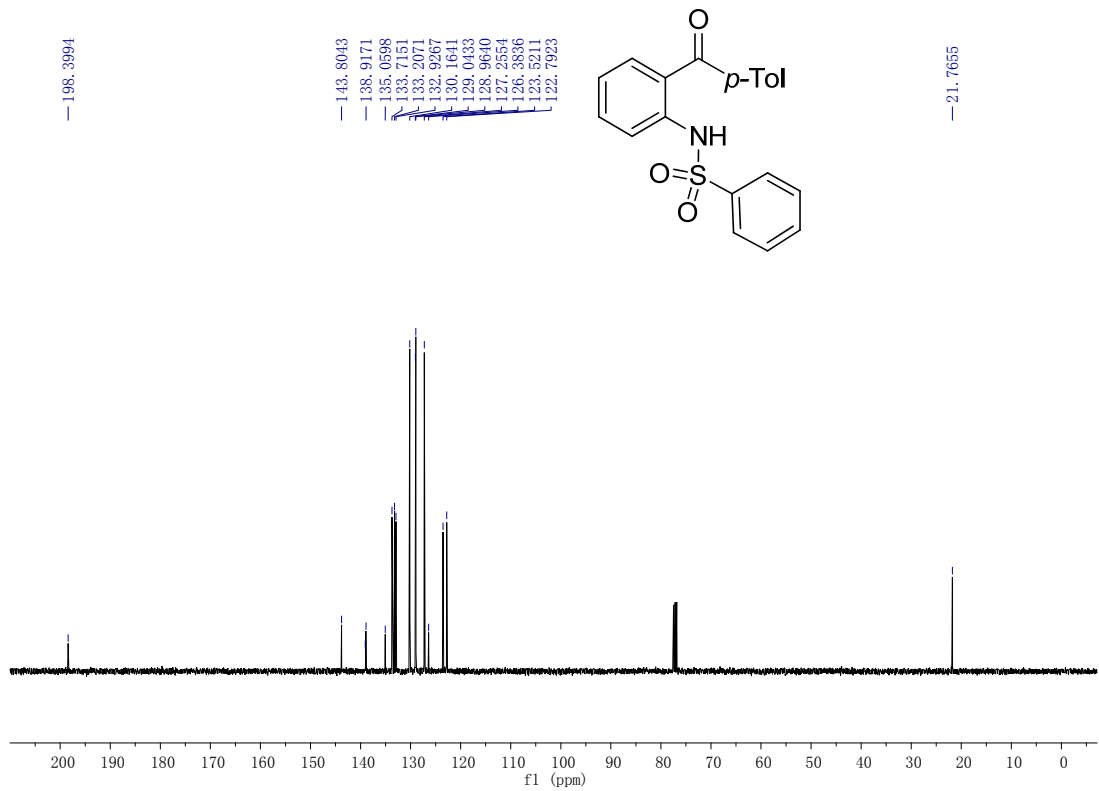
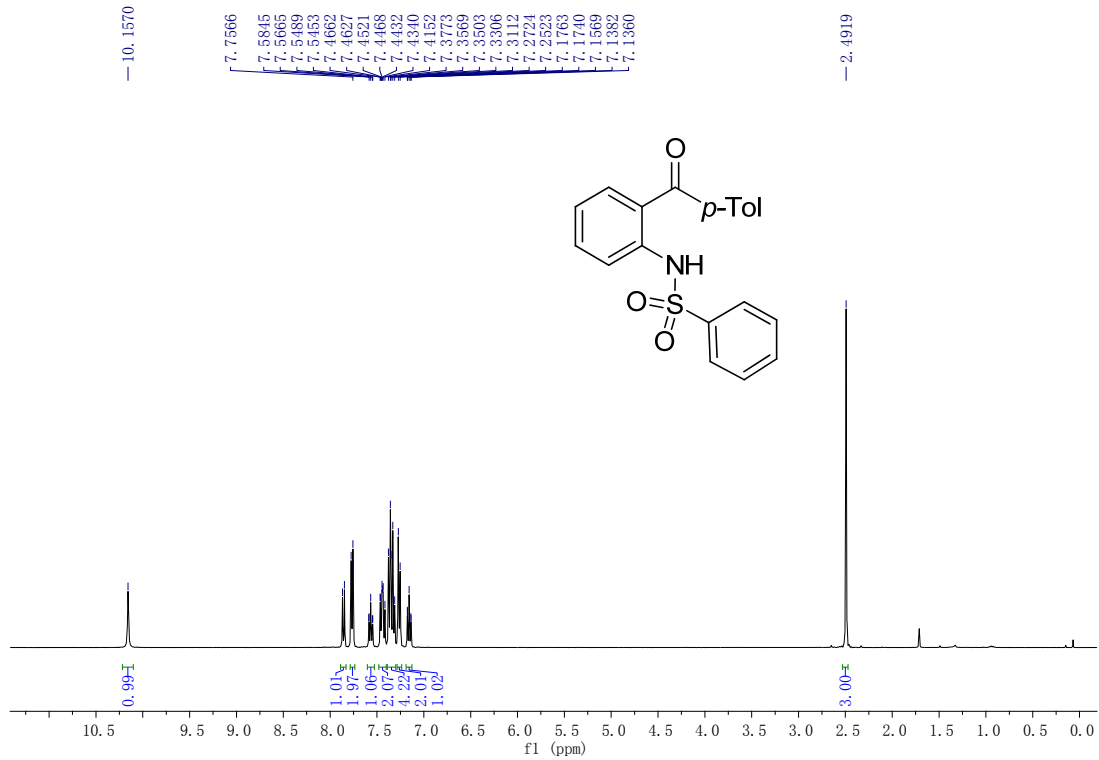


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5am**

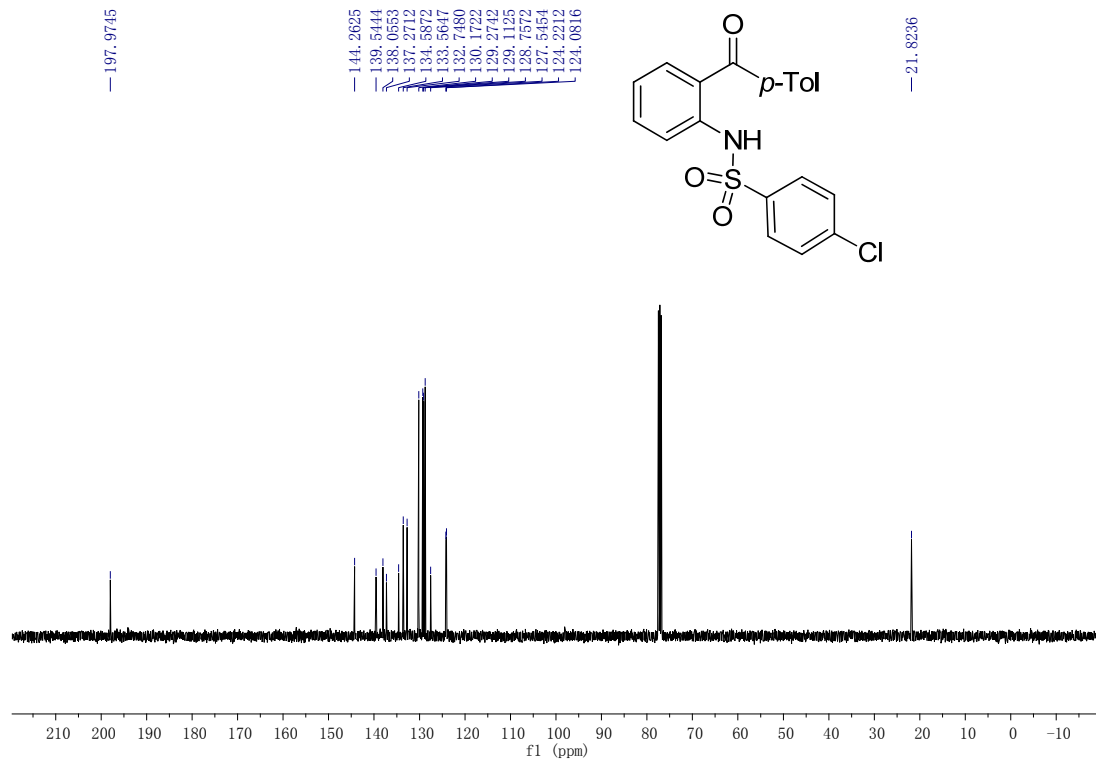
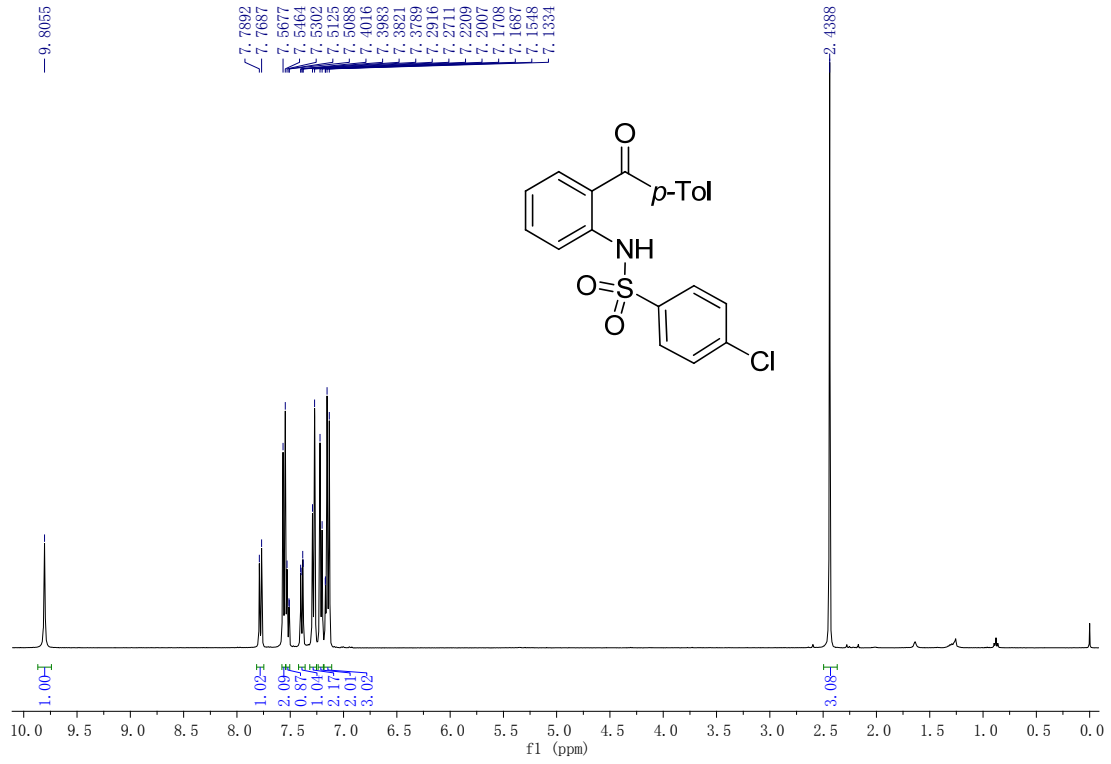


**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5an**

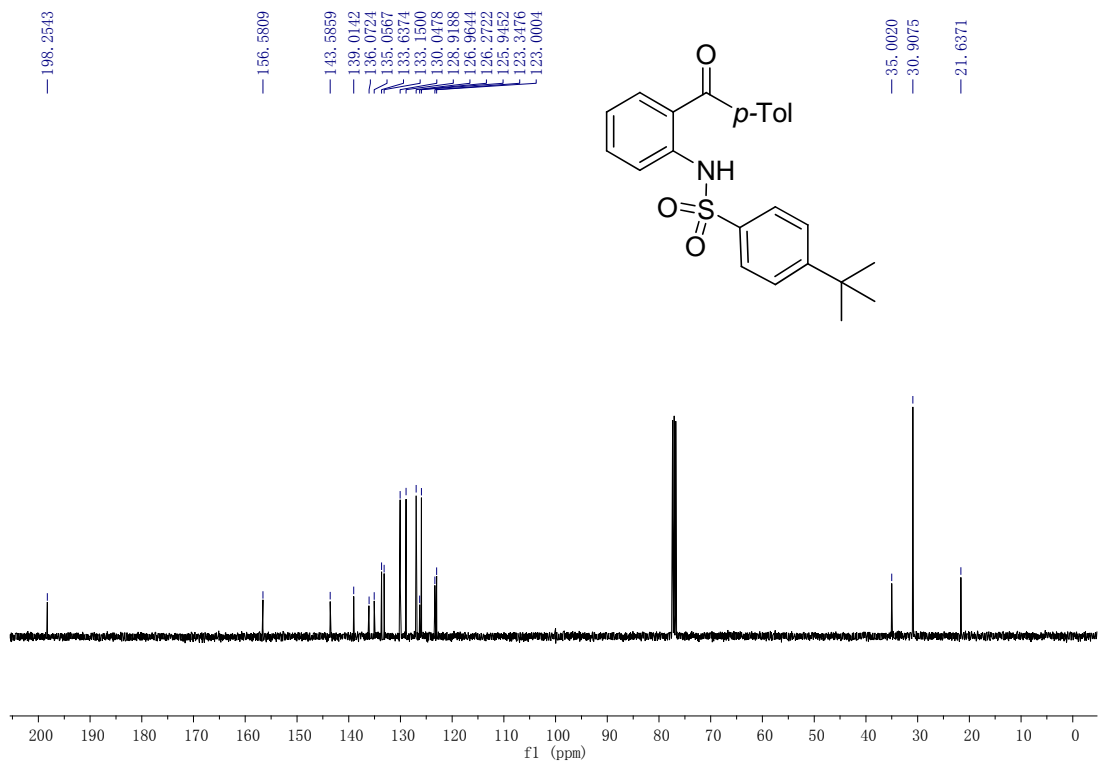
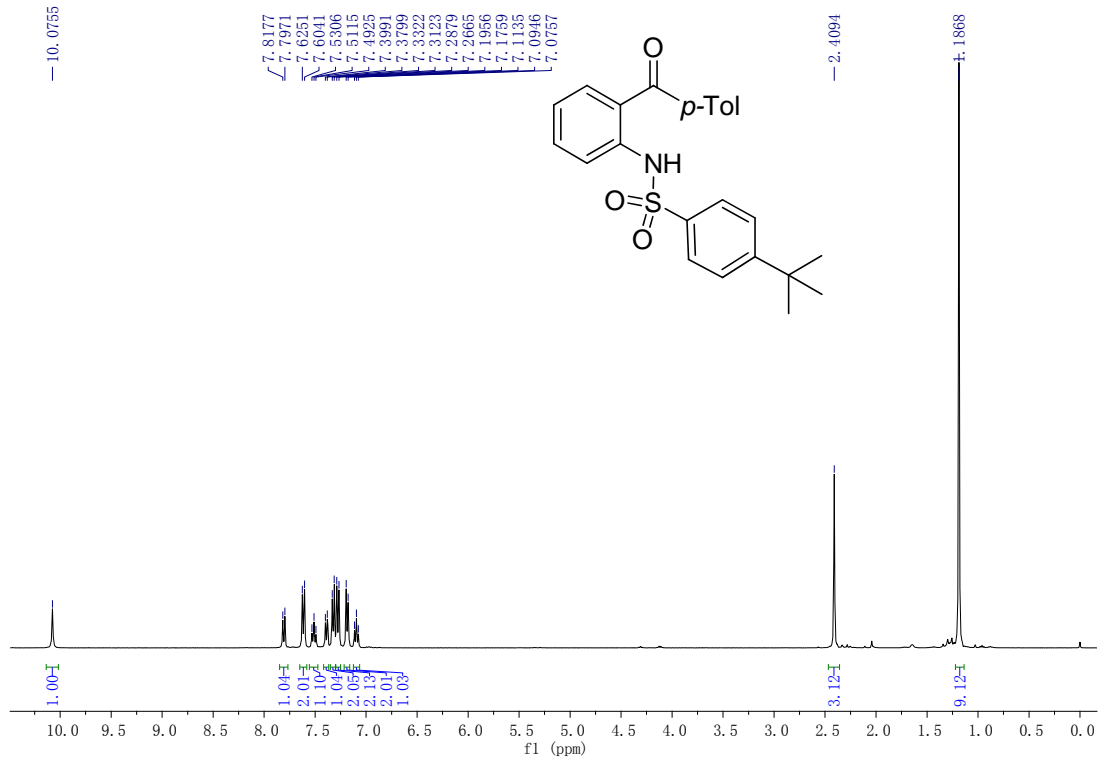




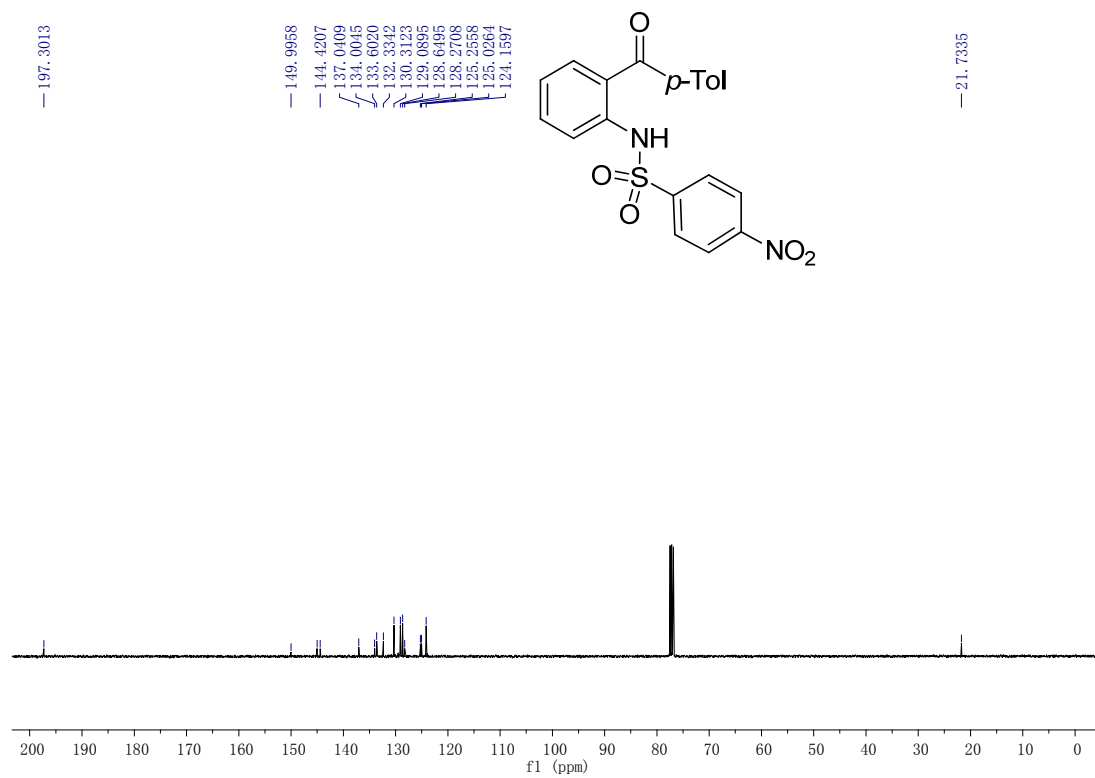
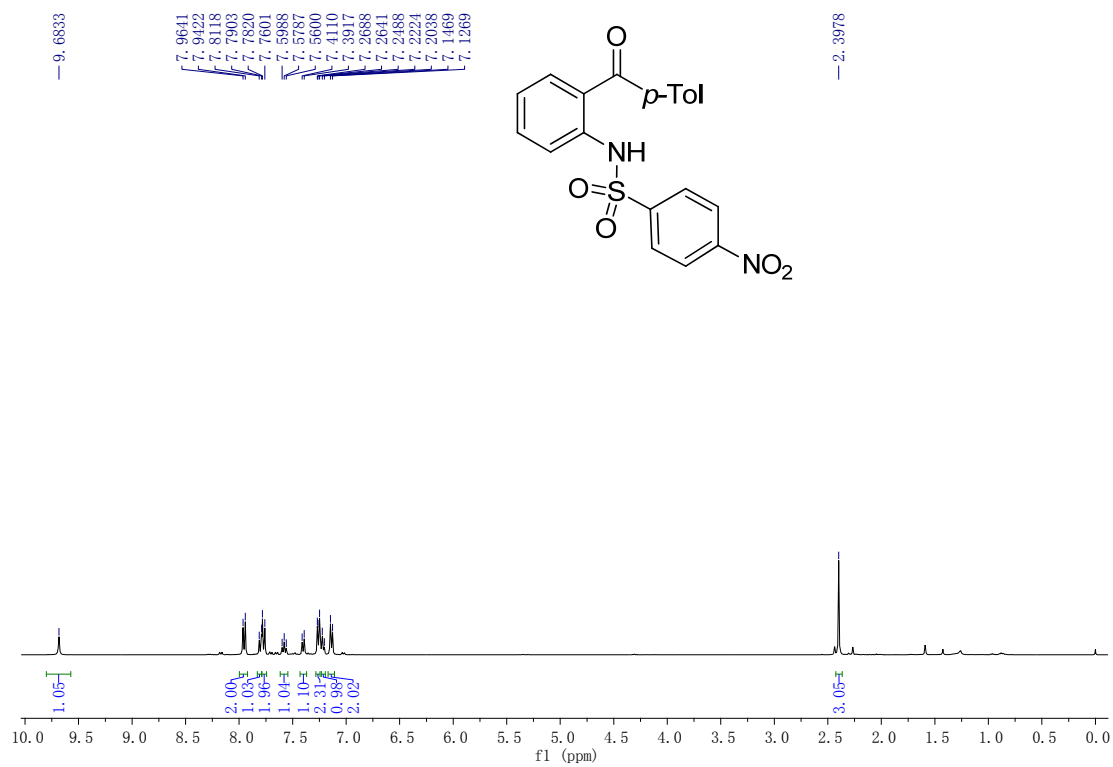
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5ao



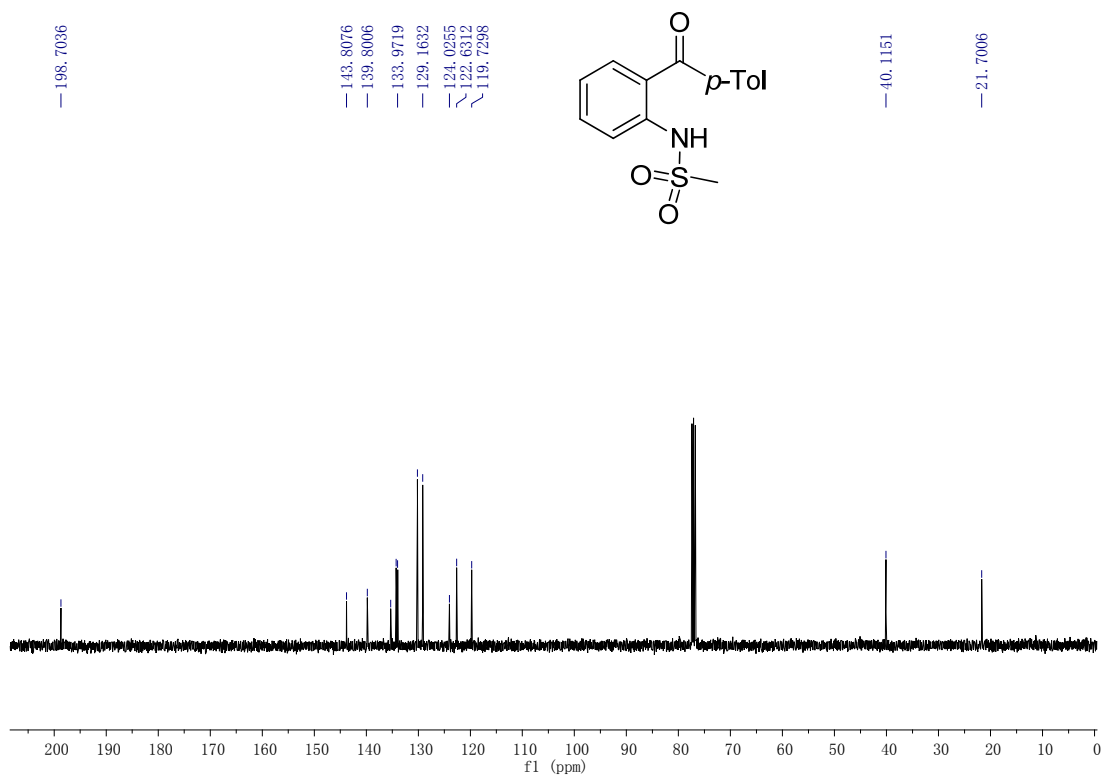
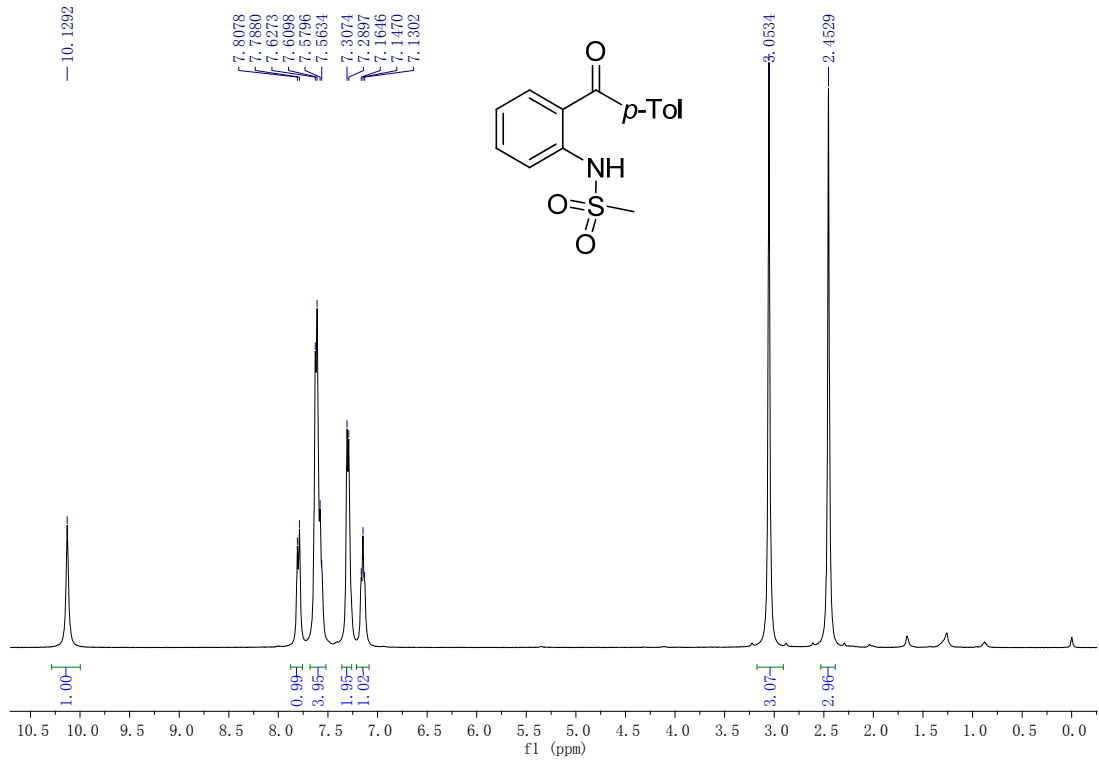
**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5ap**



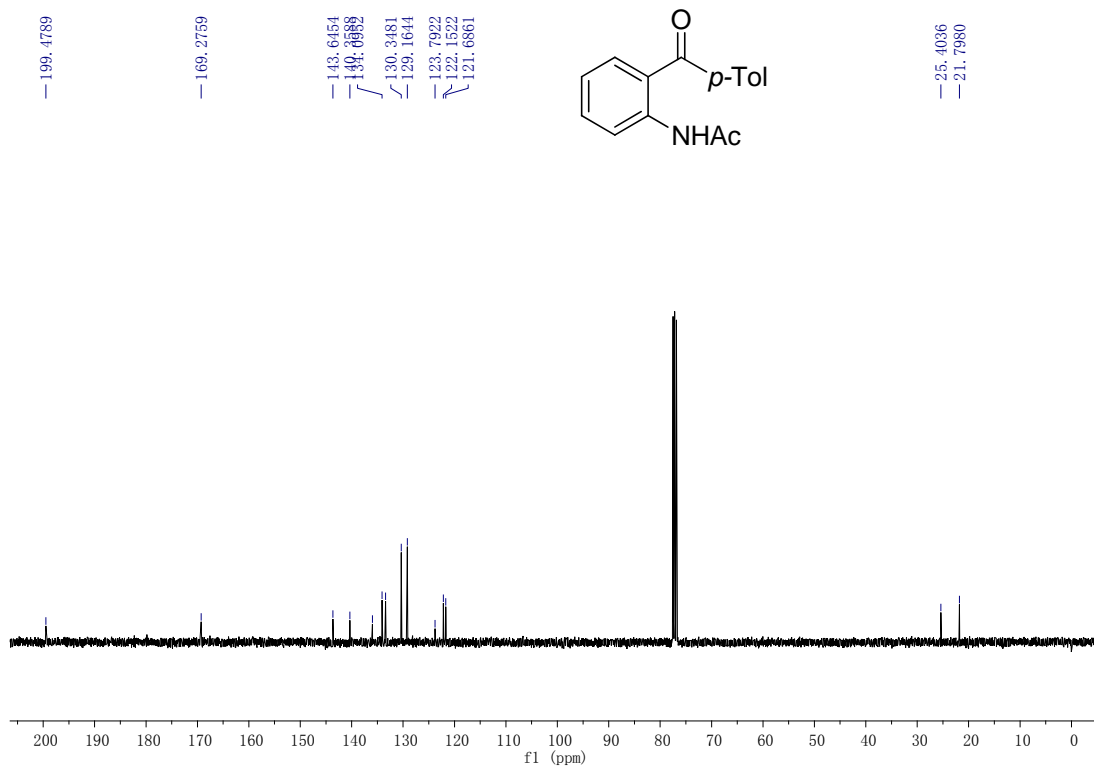
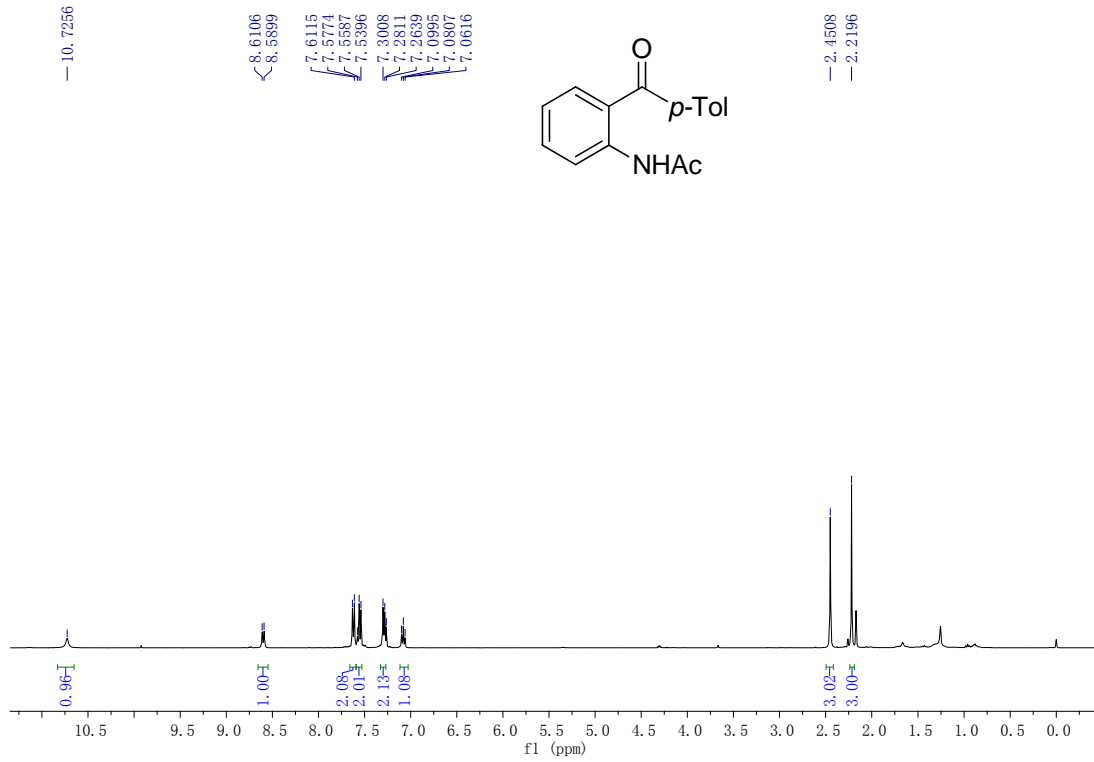
**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5aq**



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 5ar

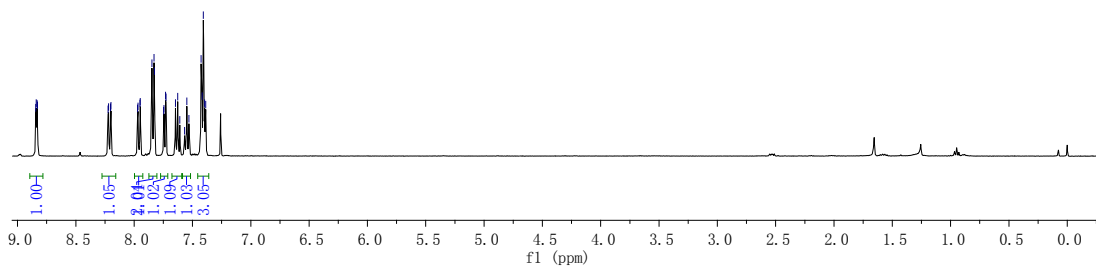
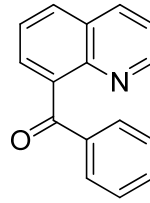


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5as**



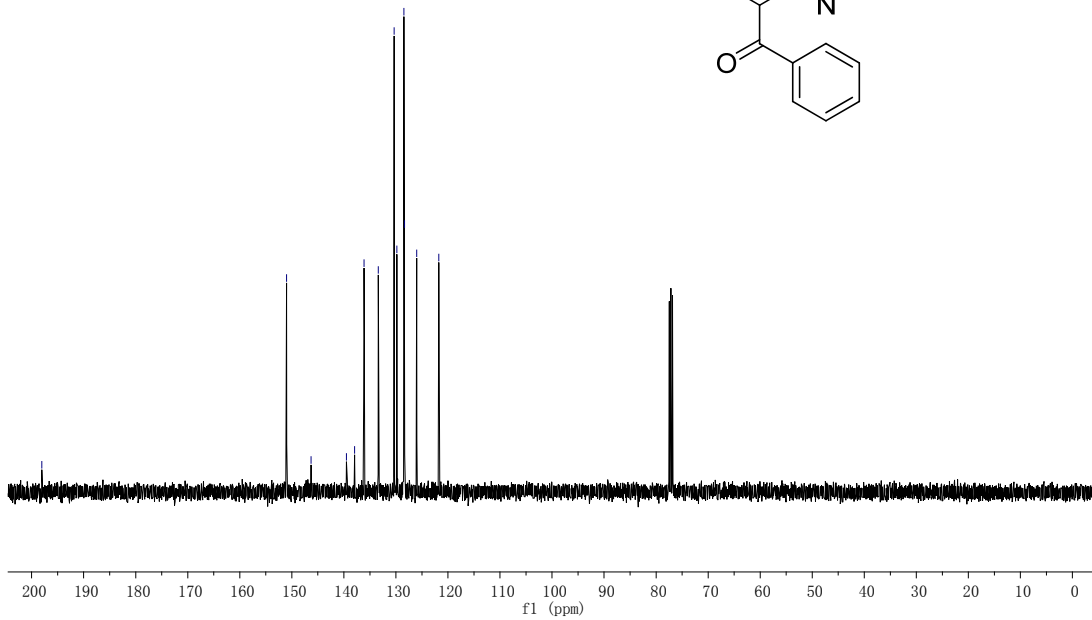
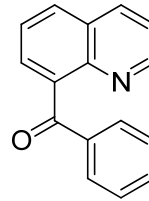
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 6aa

8.8438  
8.8396  
8.8324  
8.8292  
8.2701  
8.2033  
8.1992  
7.9704  
7.9675  
7.9500  
7.9471  
7.8470  
7.8291  
7.8260  
7.7479  
7.7447  
7.7394  
7.7272  
7.6163  
7.6264  
7.6084  
7.5673  
7.5489  
7.5304  
7.4262  
7.4171  
7.4063  
7.3963  
7.3868

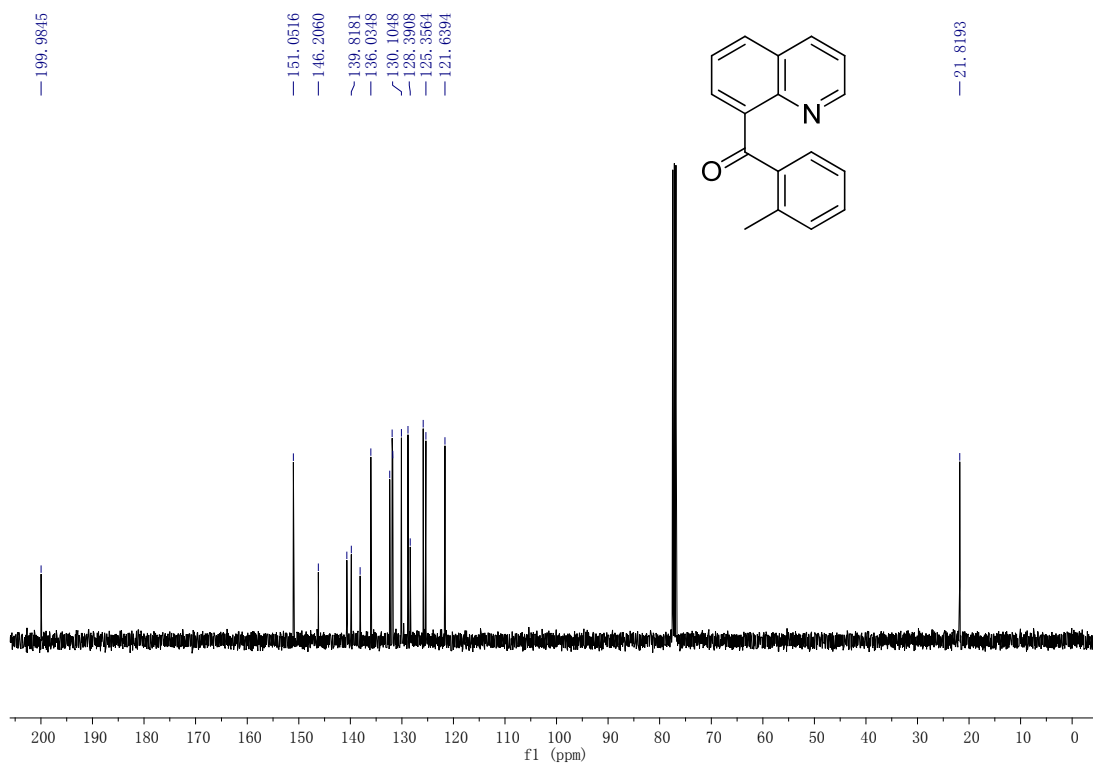
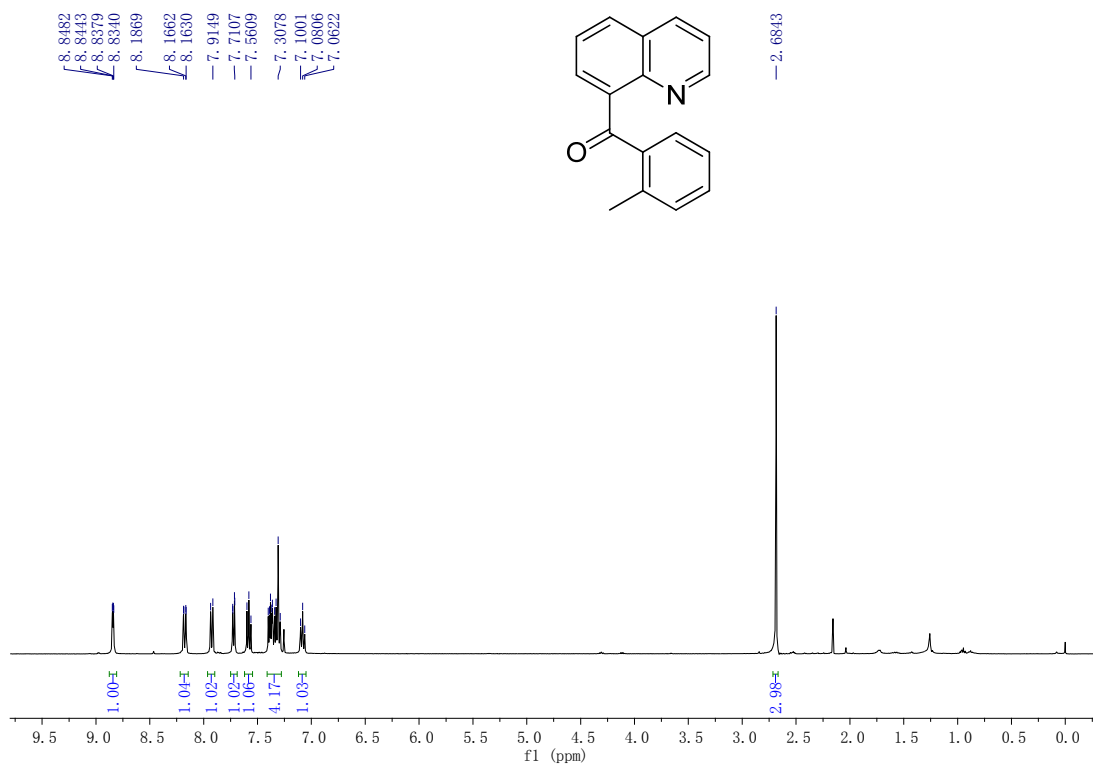


198.0356

150.9987  
146.2326  
130.3479  
129.8228  
128.4652  
128.3536  
125.9982  
121.7664

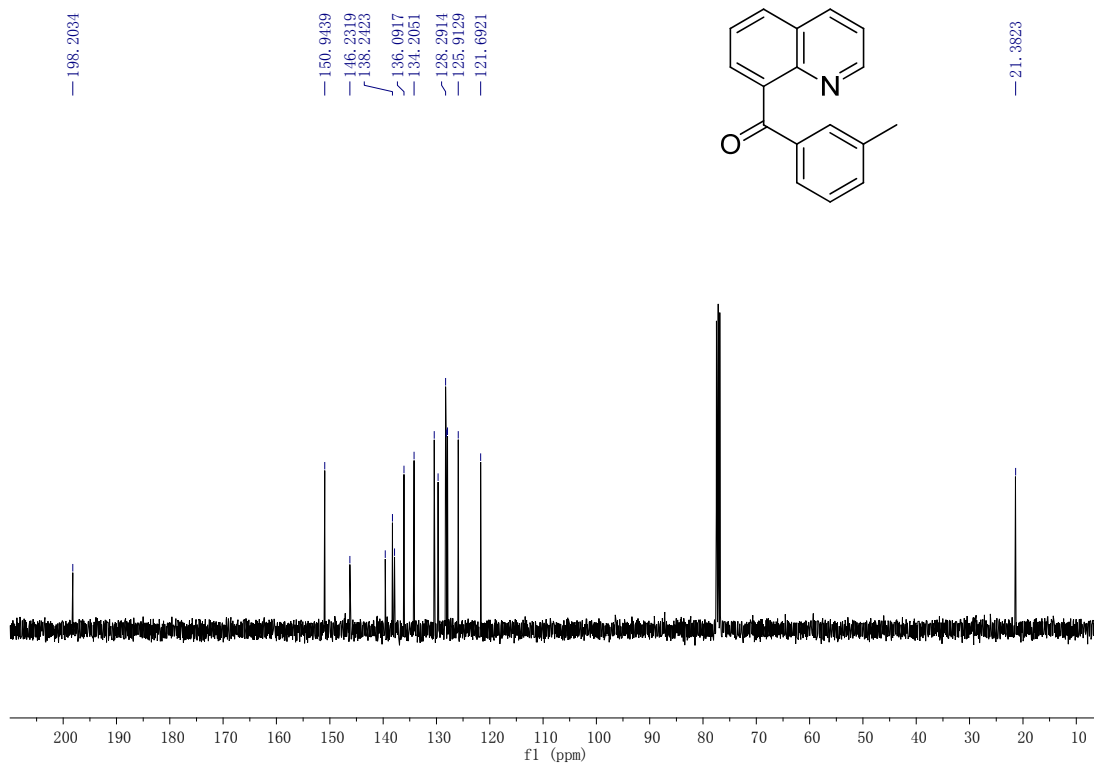
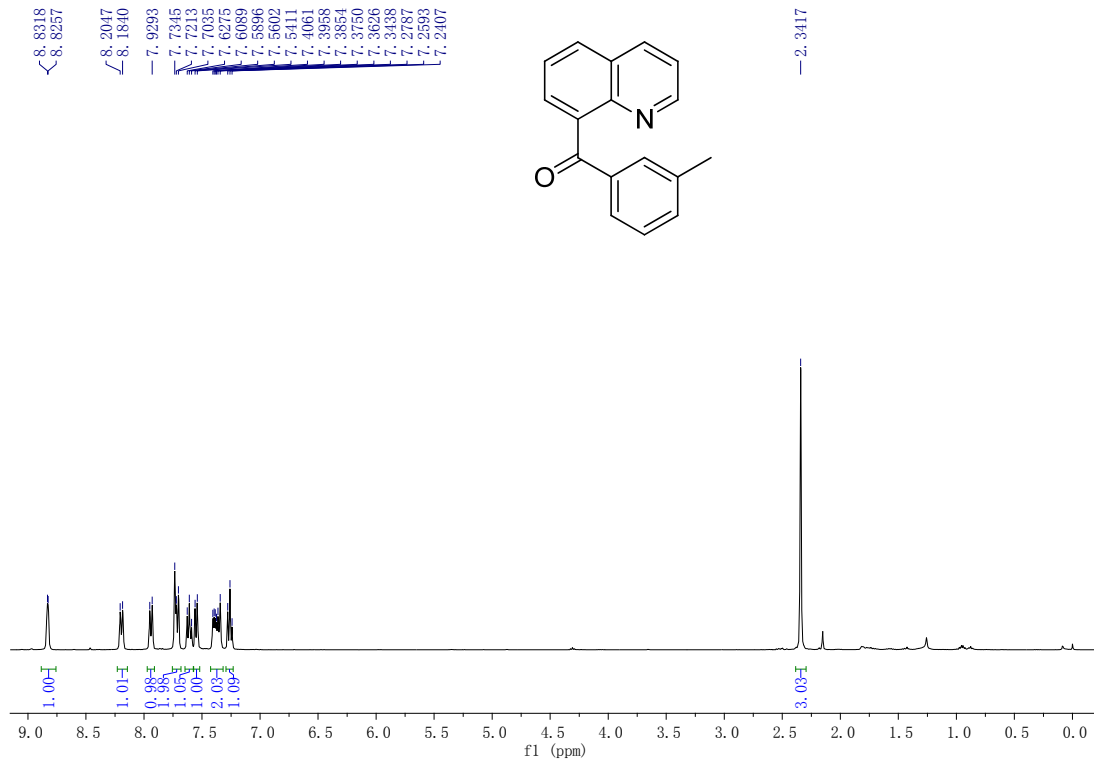


$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **6ab**

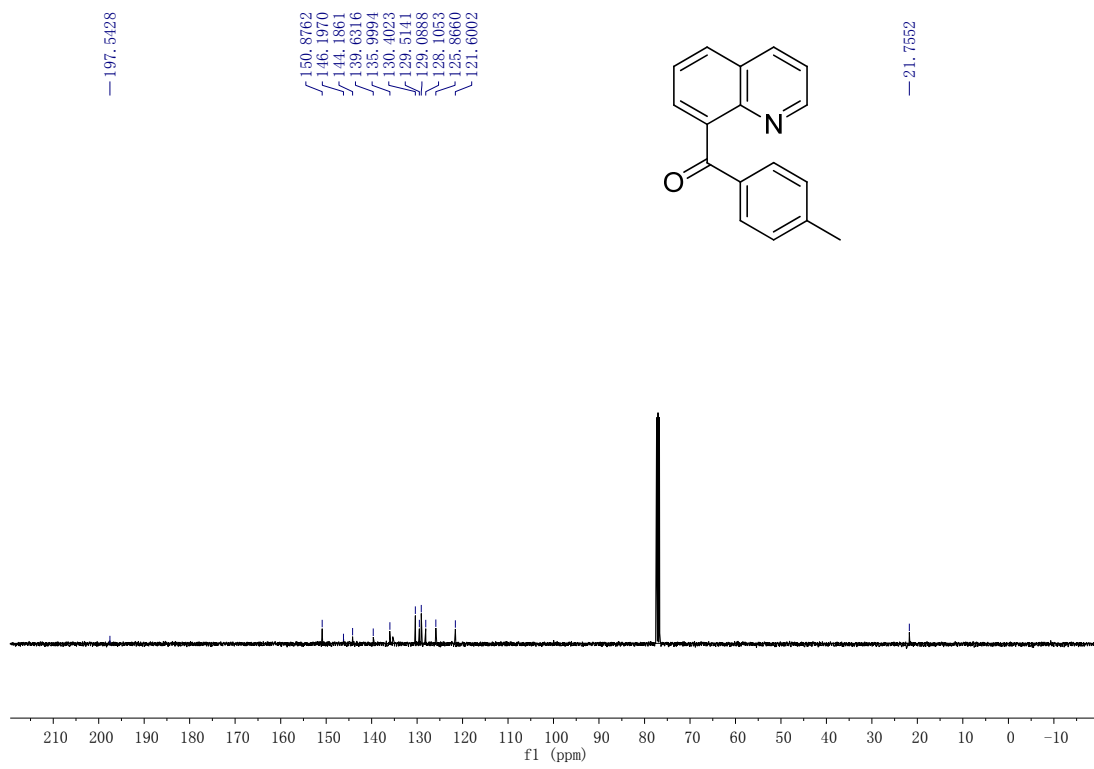
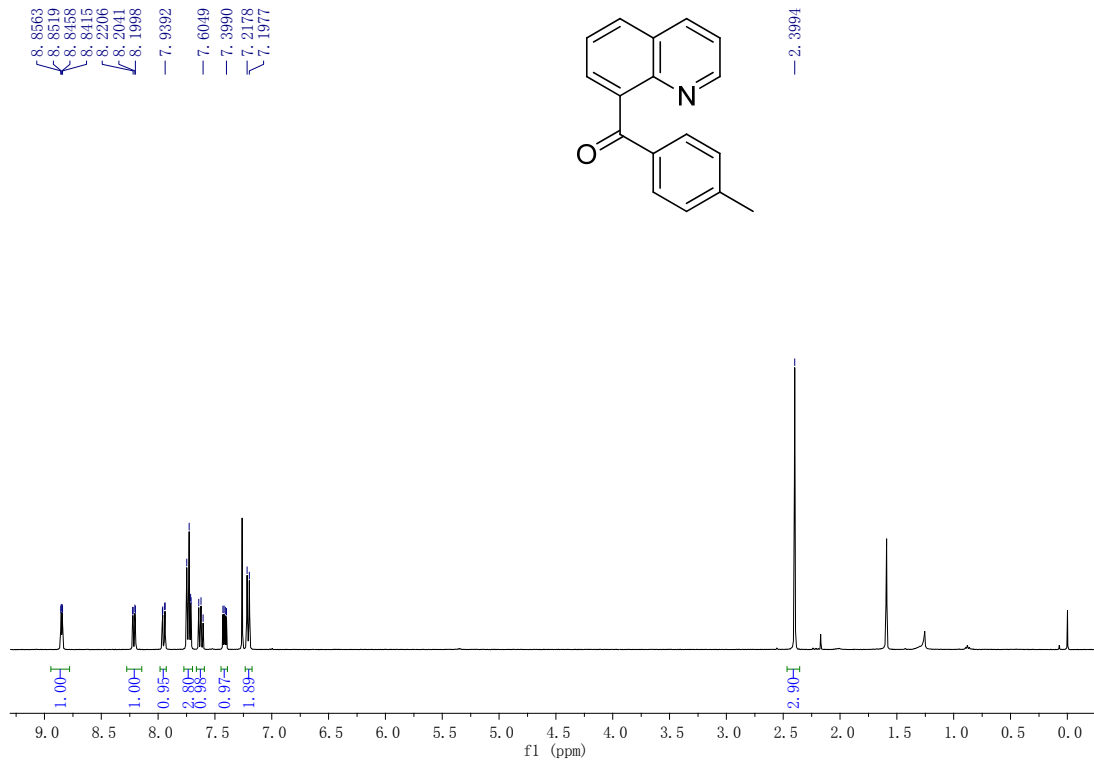


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 6ac



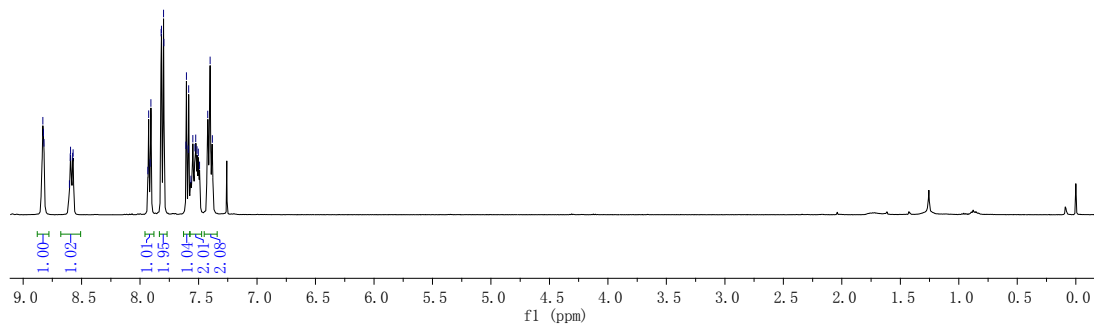
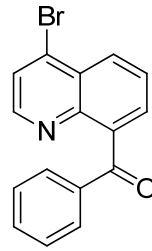


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **6ad**



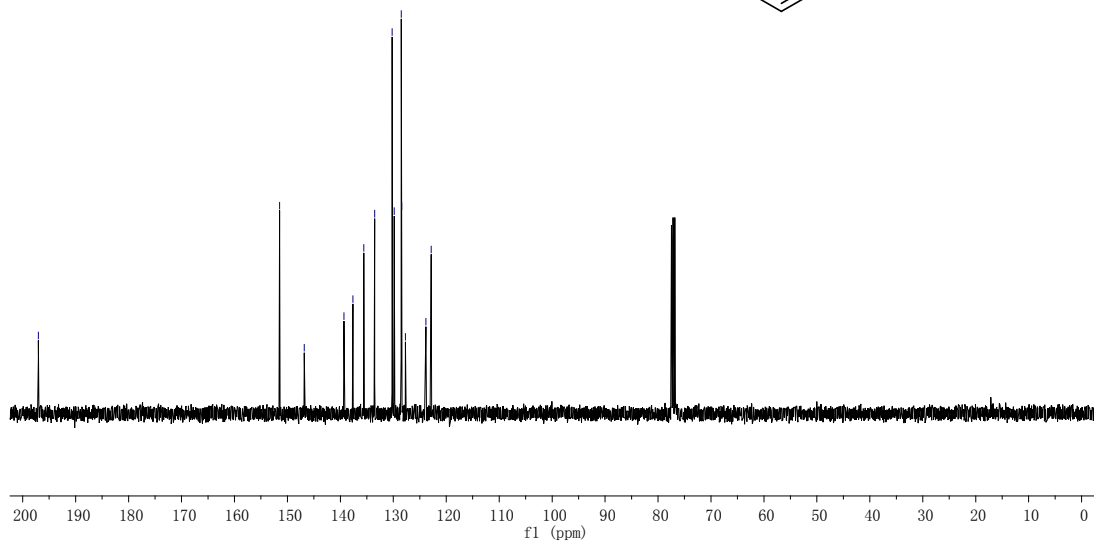
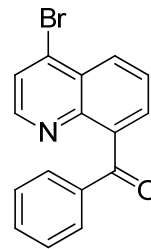
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **6ae**

8.8311  
8.8254  
8.8210  
8.5938  
8.5762  
8.5262  
7.9071  
7.8176  
7.7968  
7.6078  
7.6037  
7.5888  
7.5846  
7.5645  
7.5491  
7.5305  
7.5235  
7.5128  
7.5018  
7.4915  
7.4208  
7.4010  
7.3823

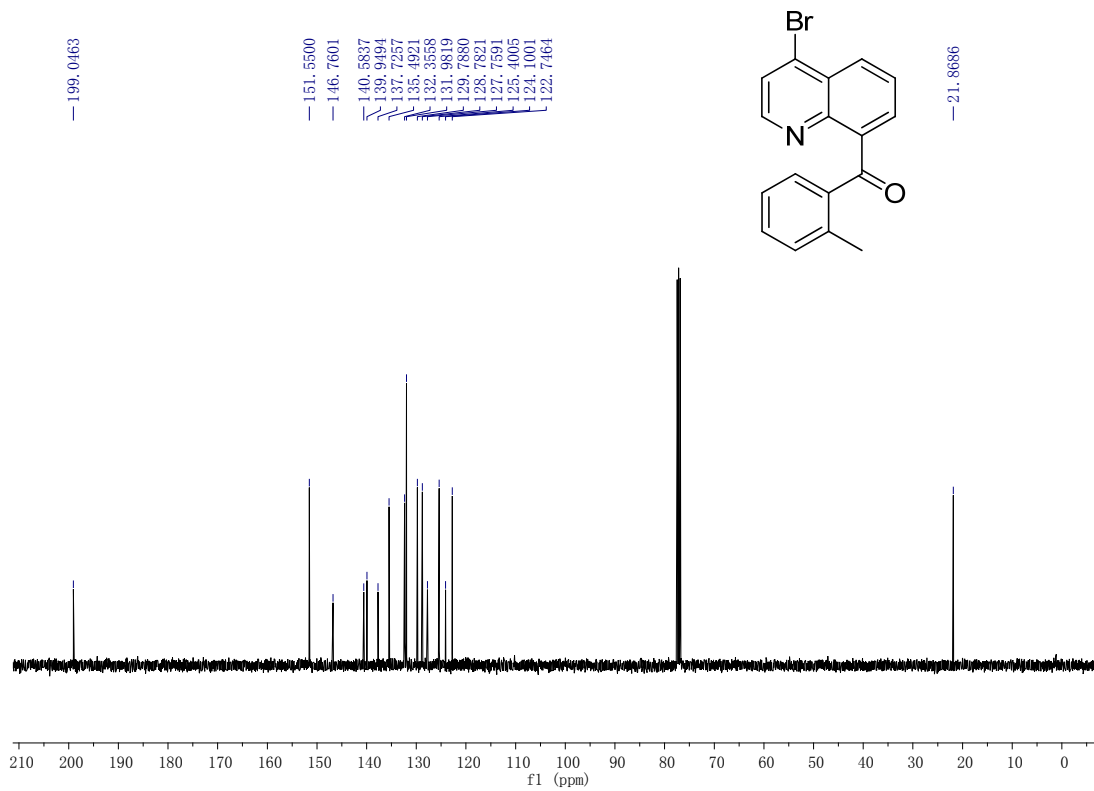
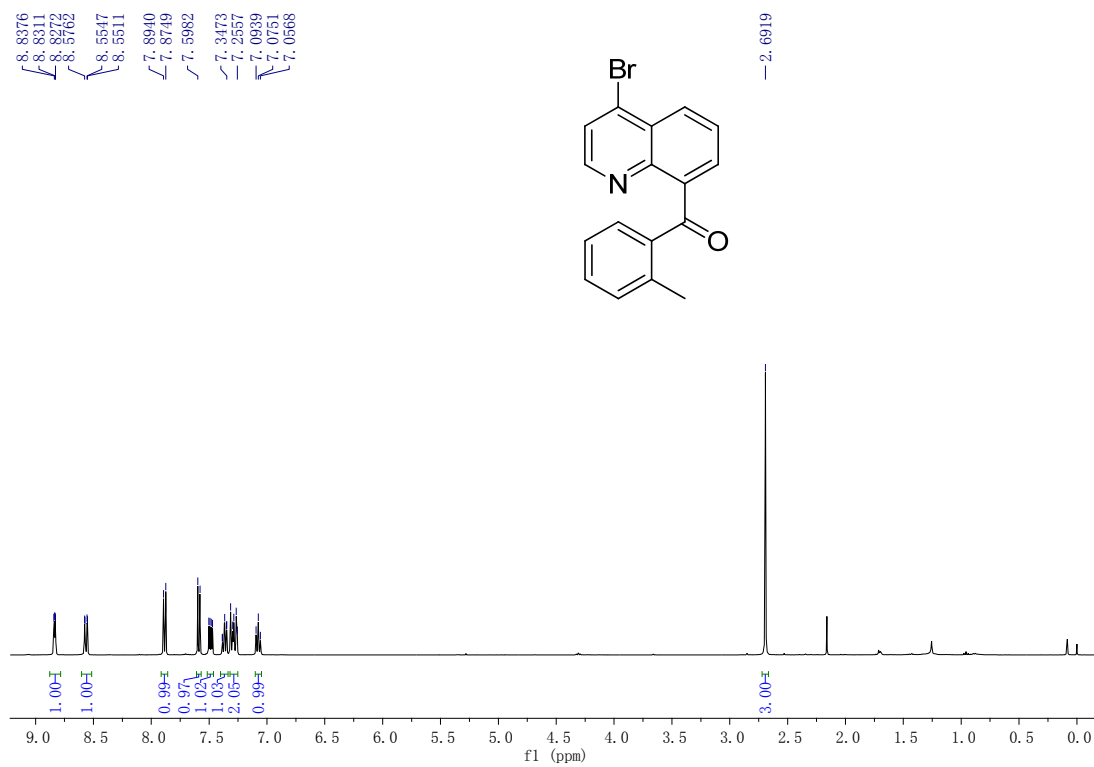


197.0460

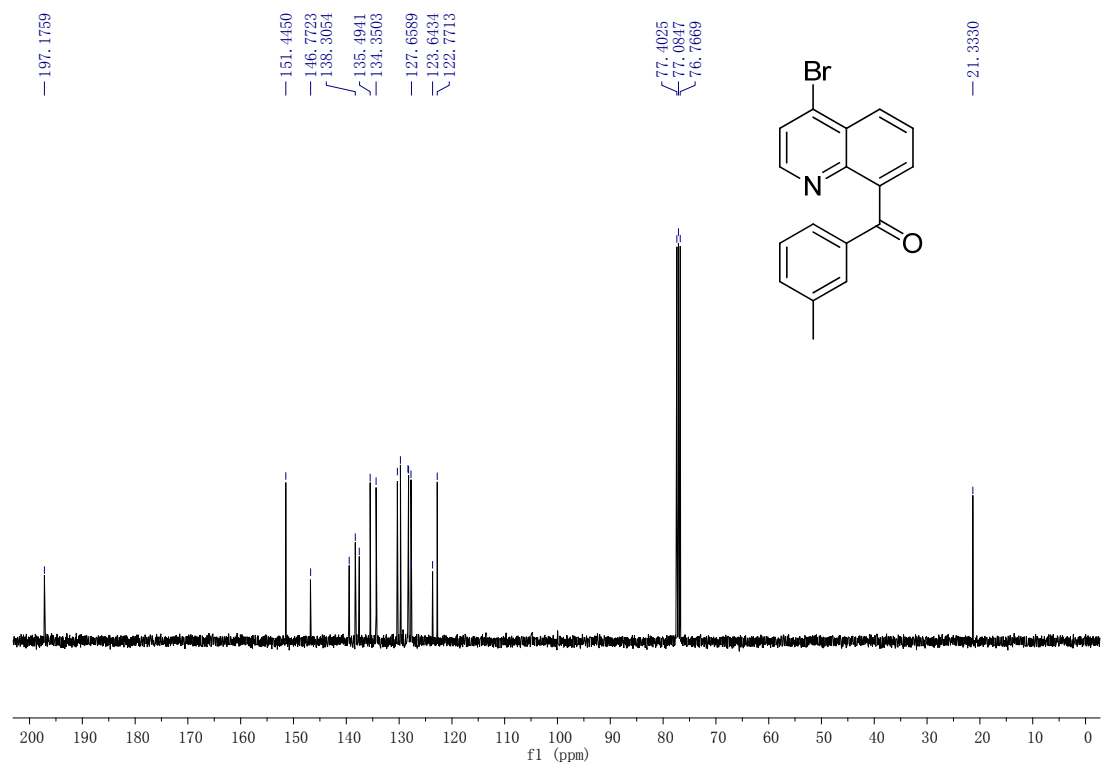
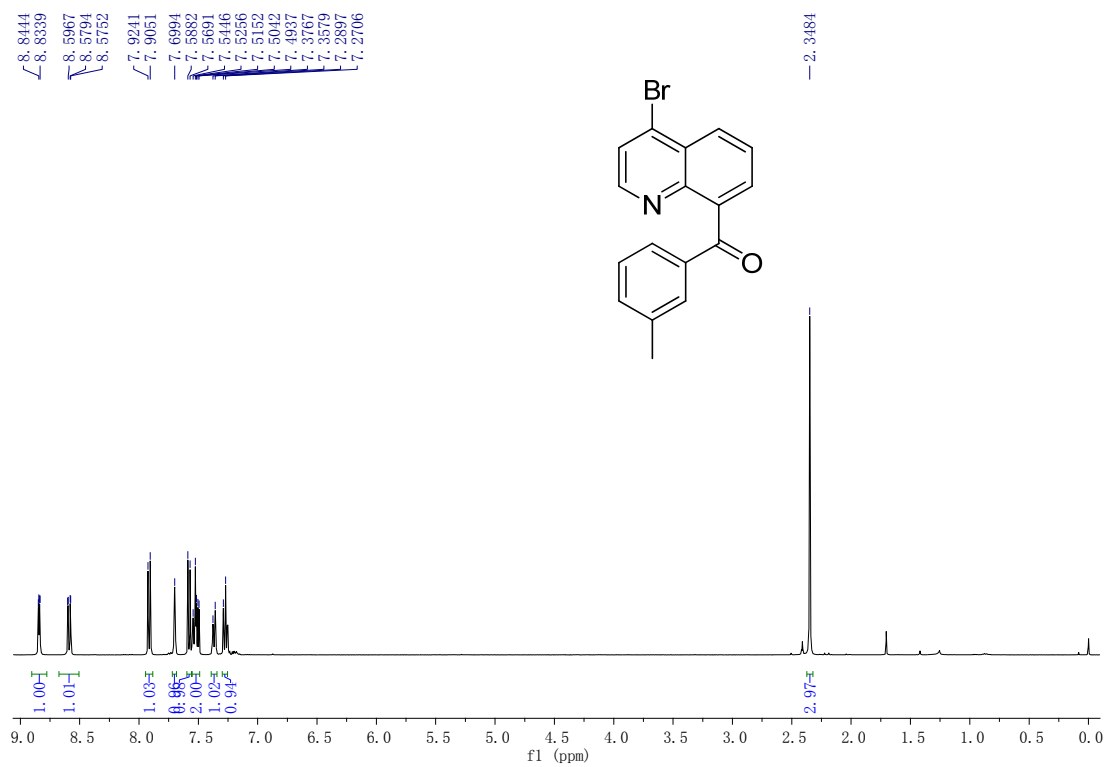
151.4901  
146.8132  
139.3294  
137.6347  
135.5624  
133.5265  
128.5002  
123.8436  
122.8591



$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Compound **6af**



**<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 6ag**



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **6ah**

