Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

for DOI: 10.1055/a-2067-4099

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Contents

1. Procedure for the gram-scale reaction

To a solution of 4-aminocoumarin **1a** (6.2 mmol, 1.0 g), 1,3-diphenylpropene **2a** (13.6 mmol, 2.7 g) in DCE (90 mL), $Cu(OTf)_2$ (0.3 mmol, 0.1122 g) and TBHP (31.0 mmol, 4.25 mL) was added. The resulting mixture was stirred for 12 h at 80 °C at an atmosphere of dioxygen. After completion of the reaction, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and EtOAc (35:1) as the eluent to give the pure product **3a** (1.3441 g, 62% yield).

2. Procedure for the control reaction

Reaction 1: To a solution of 4-aminocoumarin **1a** (0.5 mmol, 0.0801 g), 1,3-dihenylpropene **2a** (1.1 mmol, 0.2137 g) in DCE (6 mL), $Cu(OTf)_2$ (0.025 mmol, 0.0090 g) and TBHP (2.5 mmol, 342 μL) were added. The resulting mixture was stirred at 80 °C at an atmosphere of dioxygen. During the reaction, it was observed by TLC that 4-aminocoumarin **1a** was consumed up within 2 h. Then, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and EtOAc (12:1) as the eluent to give the pure product **4a** (138.0 mg, 79% yield).

Reaction 2: To a solution of 4-aminocoumarin **1a** (0.5 mmol, 0.0801 g), 1,3-dihenylpropene **2a** (1.1 mmol, 0.2137 g) in DCE (6 mL), $Cu(OTf)_2$ (0.025 mmol, 0.0090 g) and TBHP (2.5 mmol, 342 μL) were added. The resulting mixture was stirred at 80 °C at an atmosphere of dioxygen. During the reaction, the mixture was measured by GC-MS, which showed the formation of tert-butylperoxy-linked 1,3-diphenylpropene **5** and chalcone **6** in the reaction.

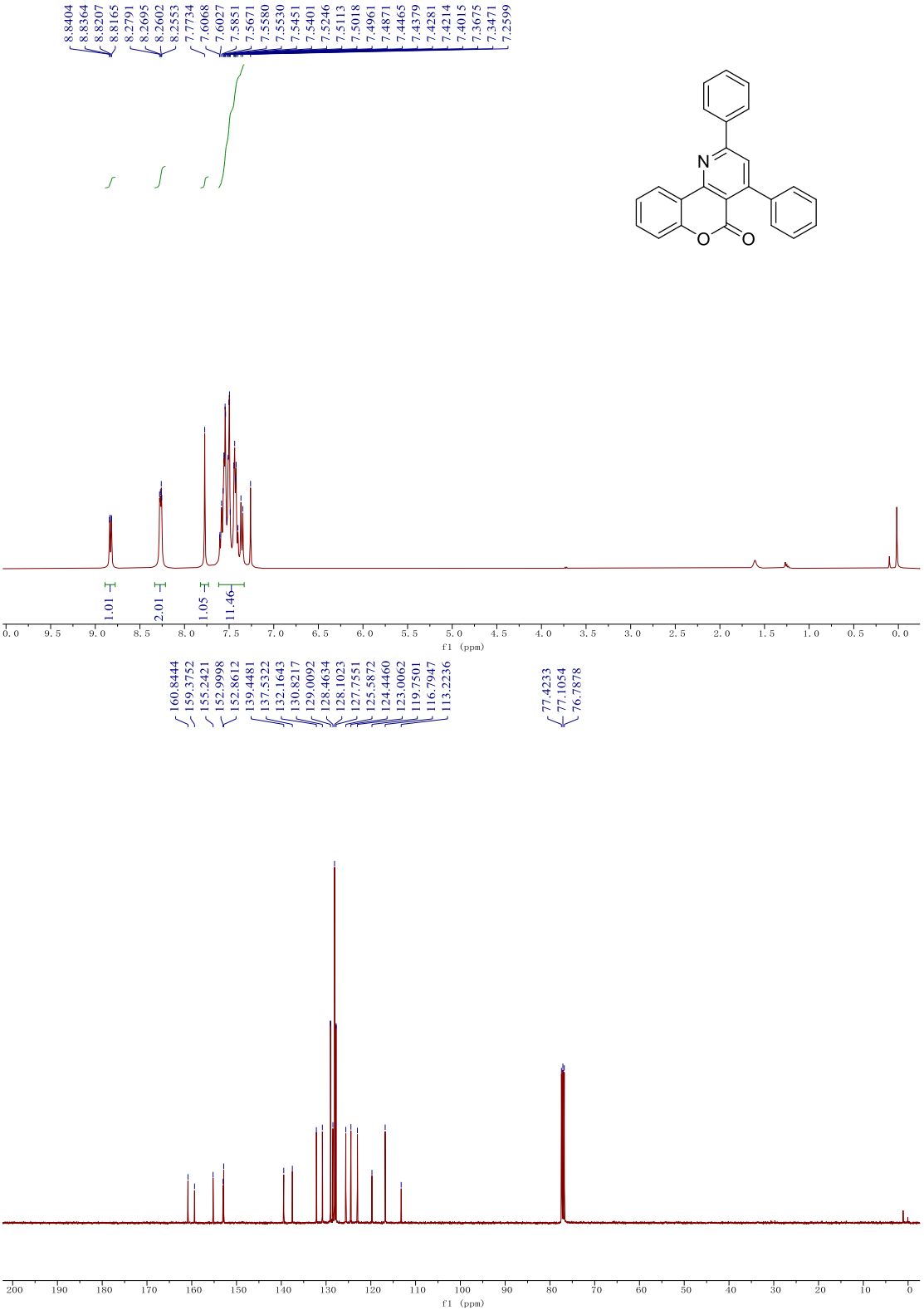
Reaction 3: To a solution of 4-aminocoumarin **1a** (0.2 mmol, 0.0322 g), 1,3-diphenylpropene **2a** (0.44 mmol, 0.0855 g) in DCE (3 mL), $Cu(OTf)_2$ (0.01 mmol, 0.0036 g), TEMPO (2 mmol, 0.3125 g) or BHT (2 mmol,0.4407 g), and TBHP (1.0 mmol, 137 μL) were added sequentially. The resulting mixture was stirred at 80 °C at an atmosphere of dioxygen. The products **3a** and **4a** were not observed by TLC.

Reaction 4: To a 10 mL round bottom flask, the coupling product **4a** (0.2 mmol, 0.0706 g), $Cu(OTf)_2$ (0.01 mmol, 0.0036 g), DCE (3 mL), and TBHP (1.0 mmol, 137 μL) were added sequentially. The resulting mixture was stirred for 10 h at 80 °C at an atmosphere of dioxygen, and **4a** was consumed up. After that, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and EtOAc (35:1) as the eluent to give the pure product **3a** (55.9 mg, 83% yield).

Reaction 5: To a 10 mL round bottom flask, the coupling product **4a** (0.2 mmol, 0.0706 g), $Cu(OTf)_2$ (0.01 mmol, 0.0036 g), DCE (3 mL), TEMPO (2 mmol, 0.3125 g), and TBHP (1.0 mmol, 137 μL) were added sequentially. The resulting mixture was stirred for 10 h at 80 °C at an atmosphere of dioxygen. Then, the reaction mixture was washed with saturated solution of Na_2SO_3 and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and EtOAc (35:1) as the eluent to give the pure product **3a** (42.6 mg, 61% yield).

Reaction 6: To a 10 mL round bottom flask, the coupling product **4a** (0.2 mmol, 0.0706 g), $Cu(OTf)_2$ (0.01 mmol, 0.0036 g), and DCE (3 mL), were added sequentially. The resulting mixture was stirred for 10 h at 80 °C at an atmosphere of dioxygen. The products **3a** was not observed by TLC.

2,4-Diphenyl-5H-chromeno[4,3-b]pyridin-5-one (3a)



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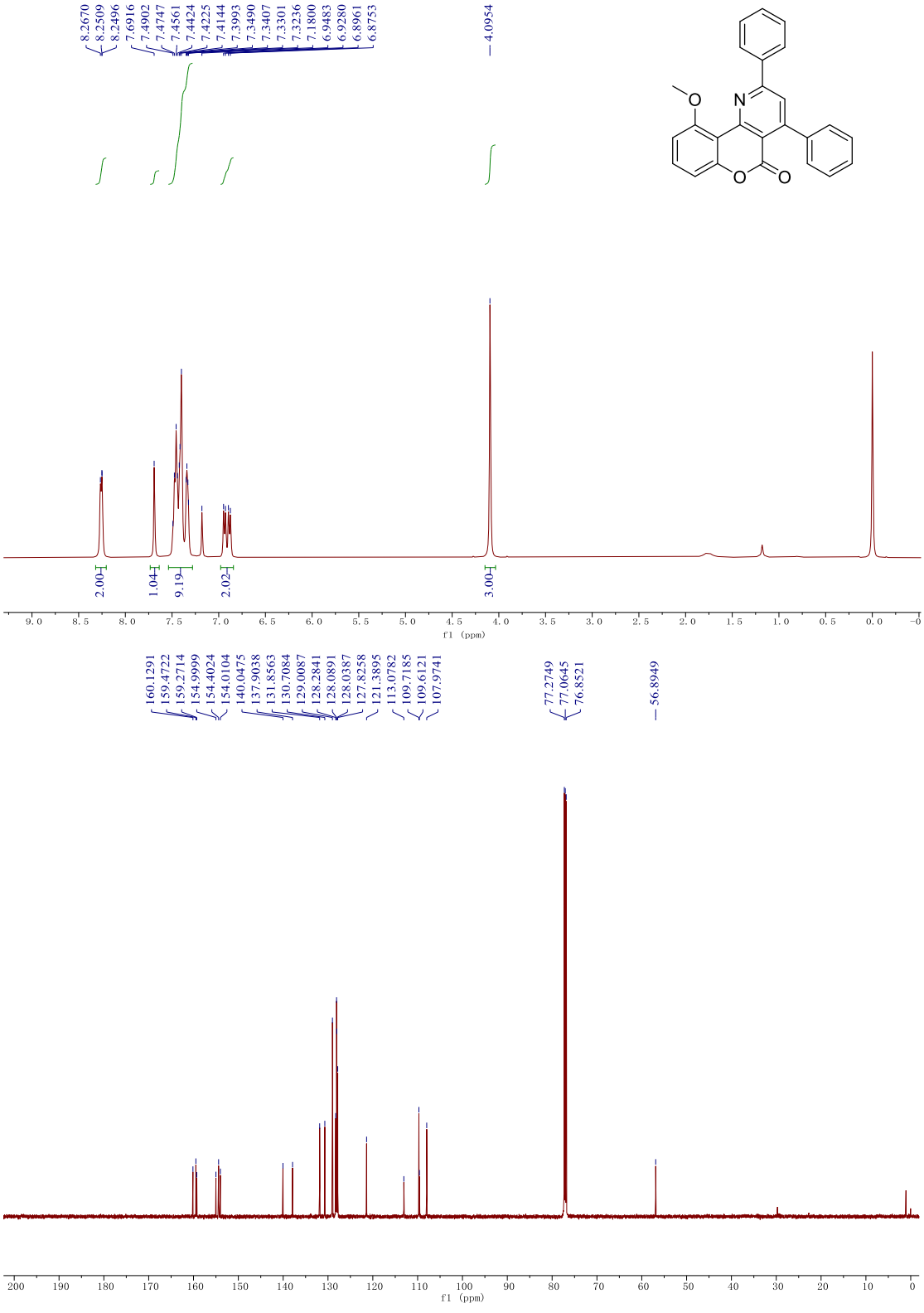

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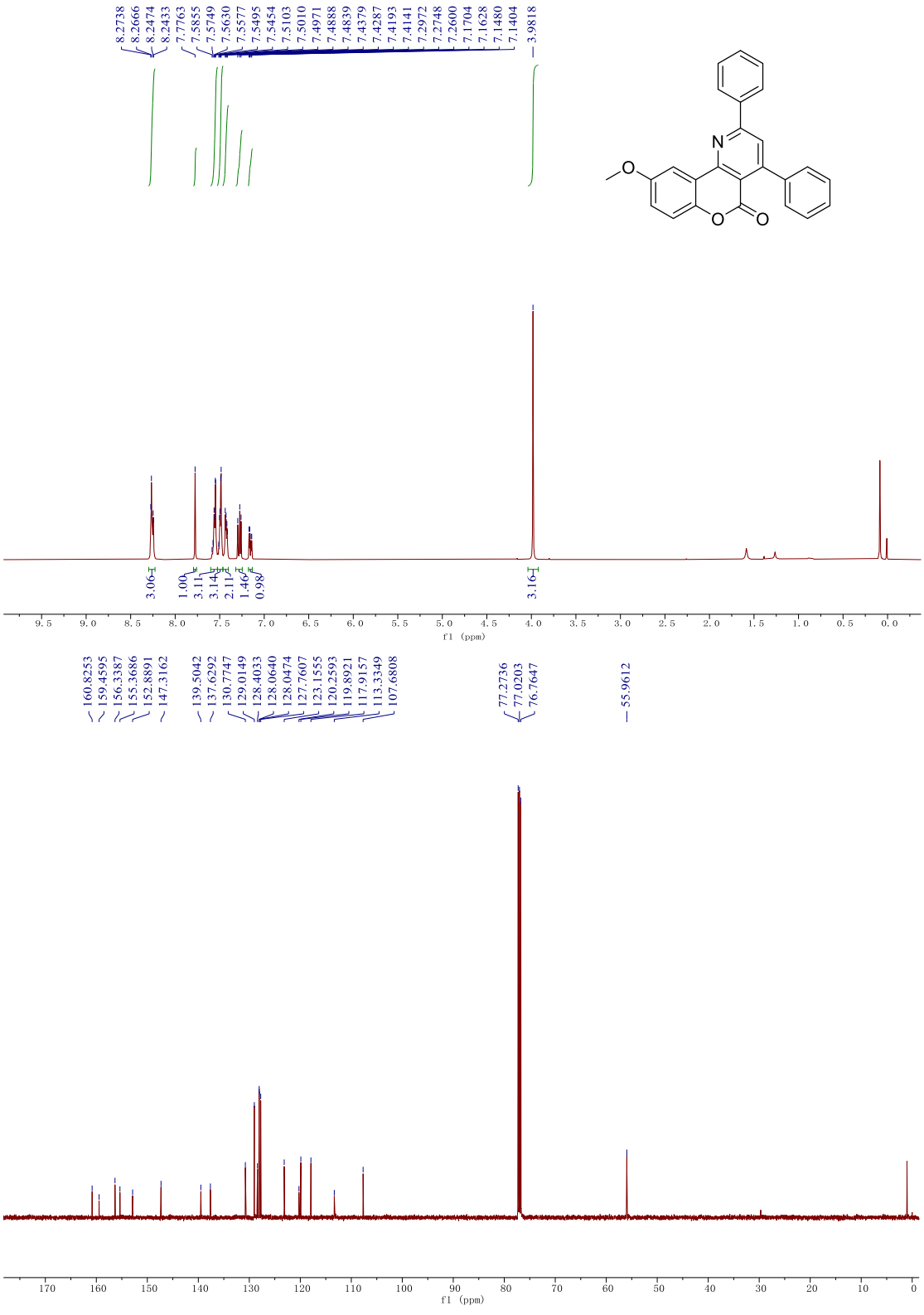

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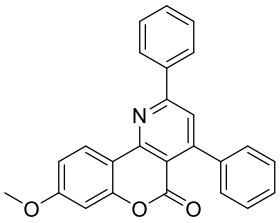

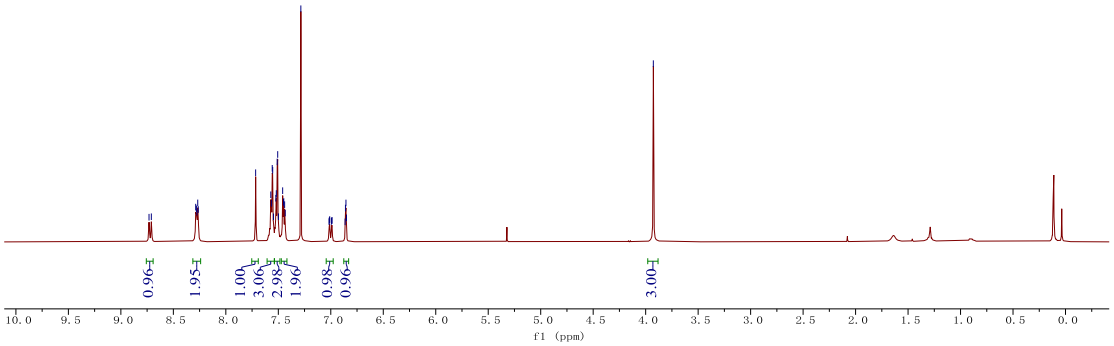

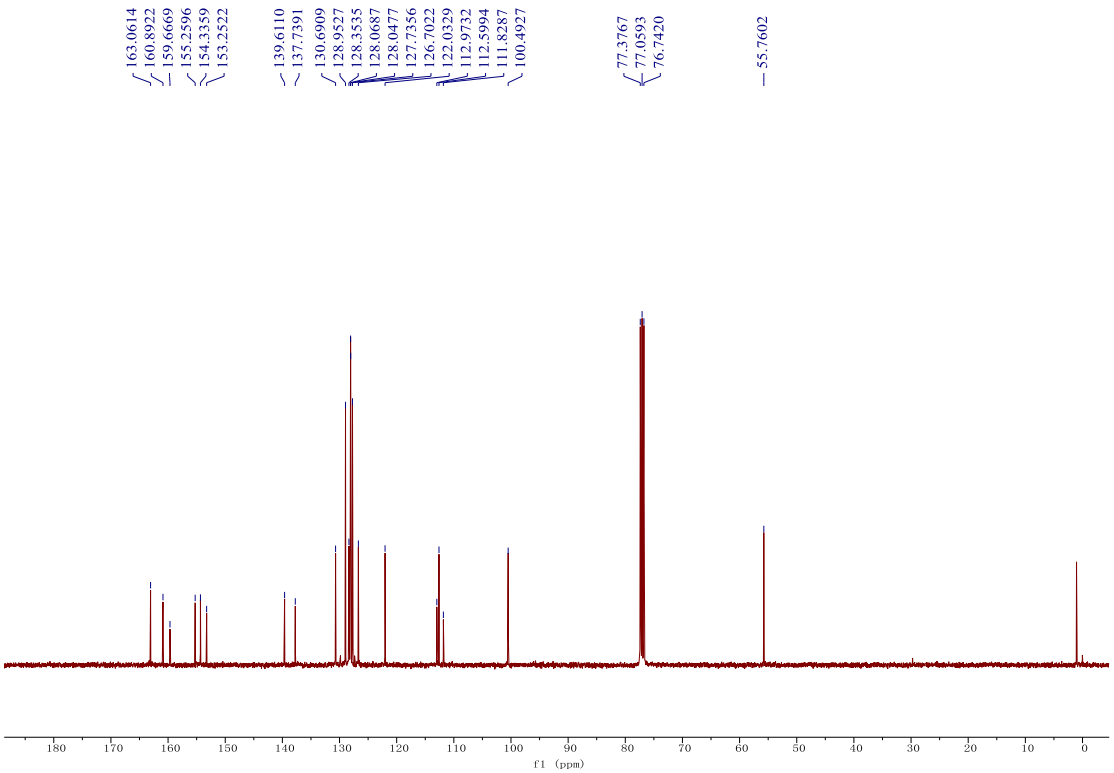

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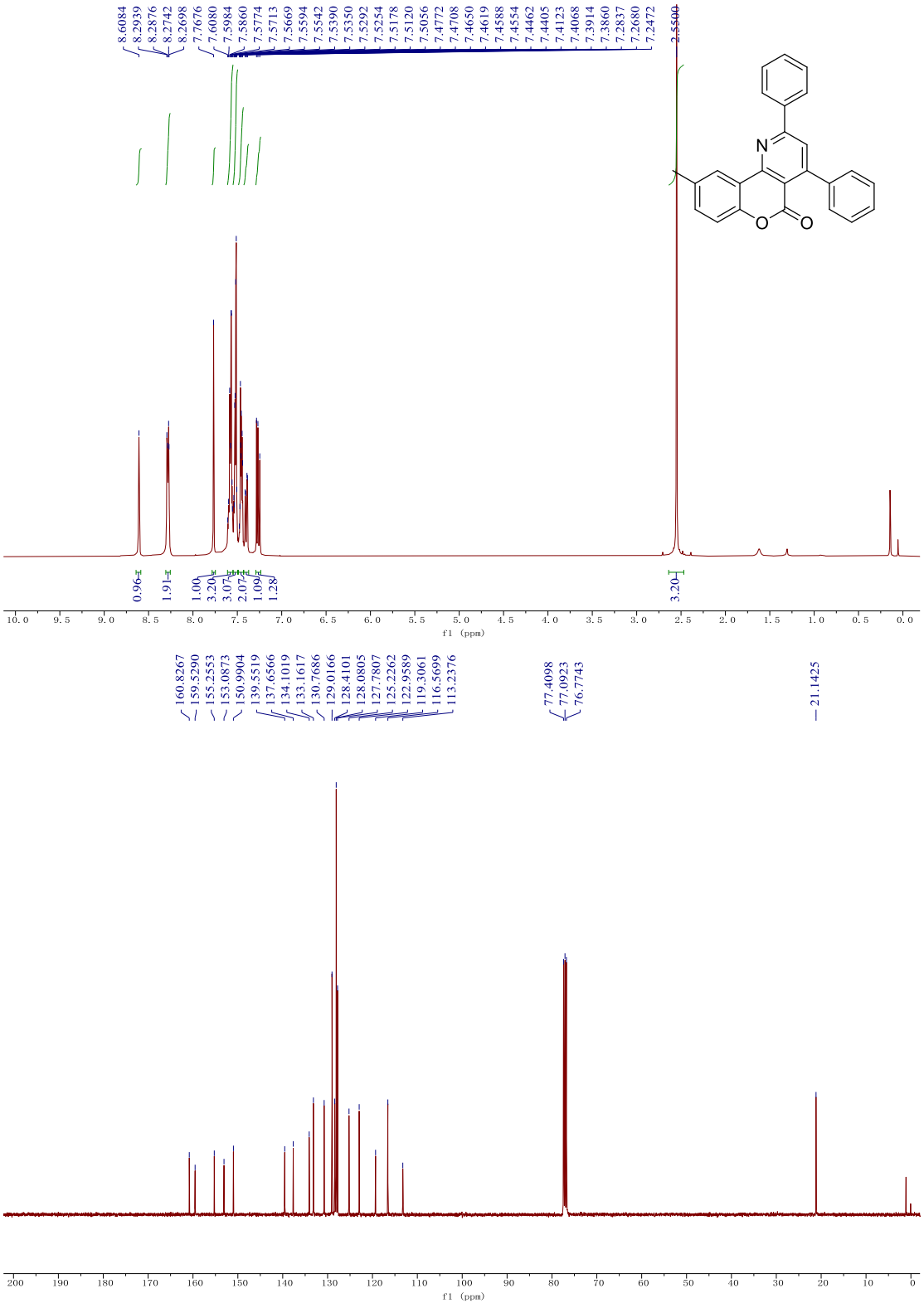

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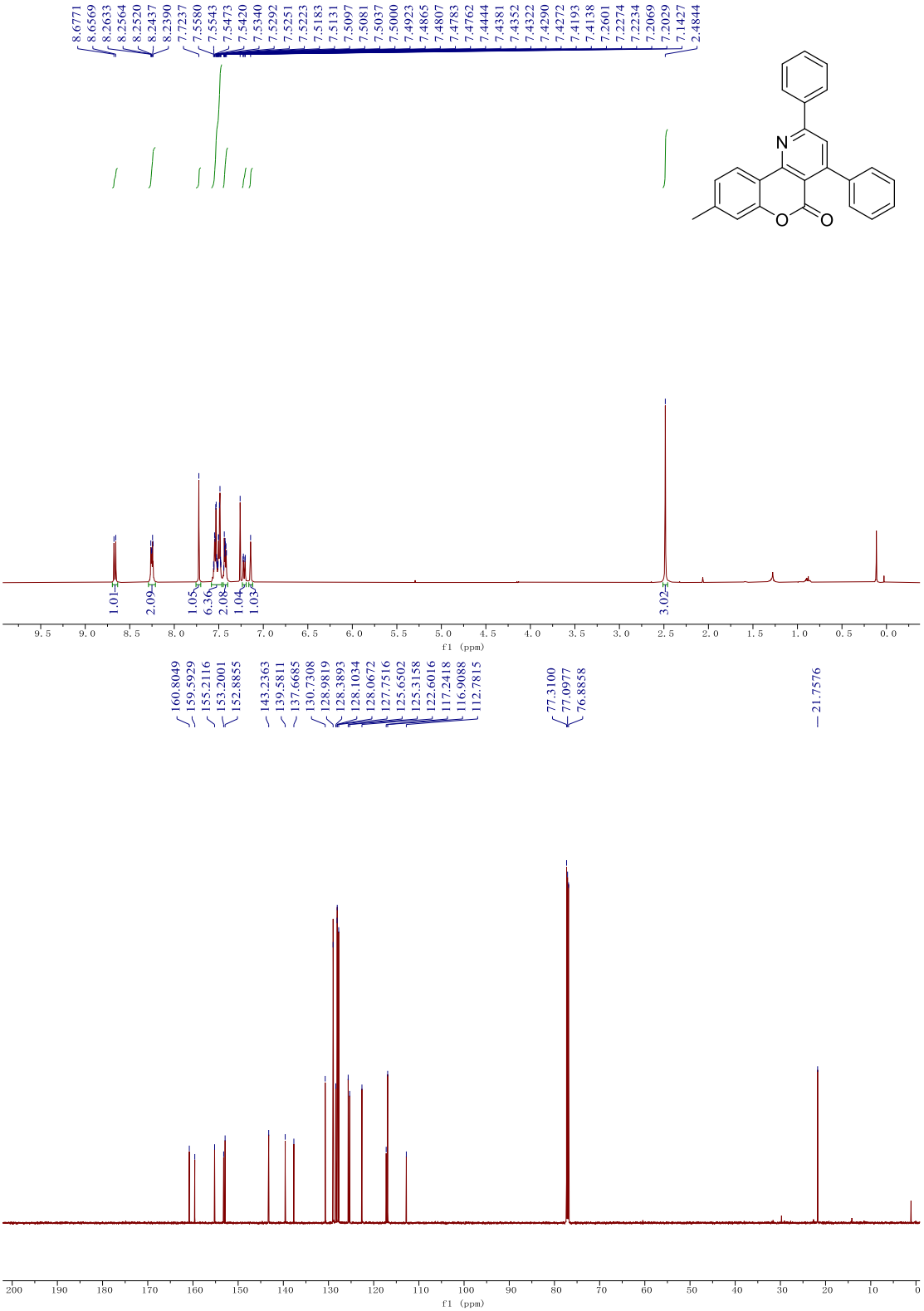
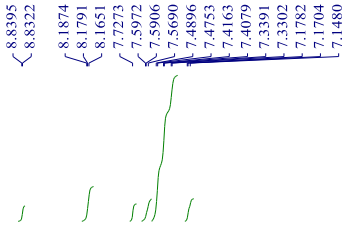
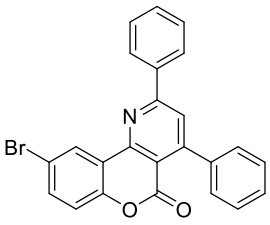
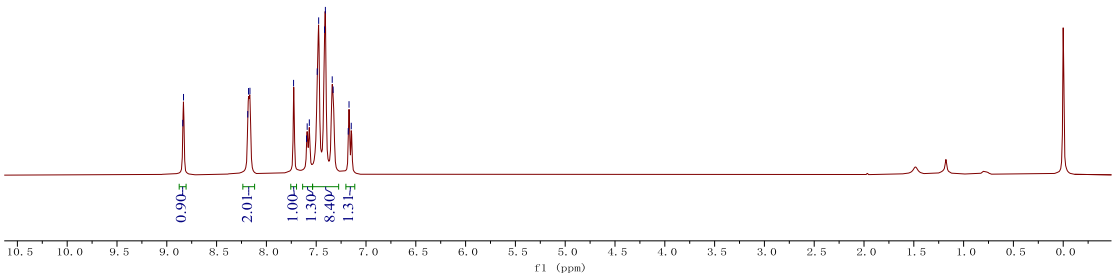
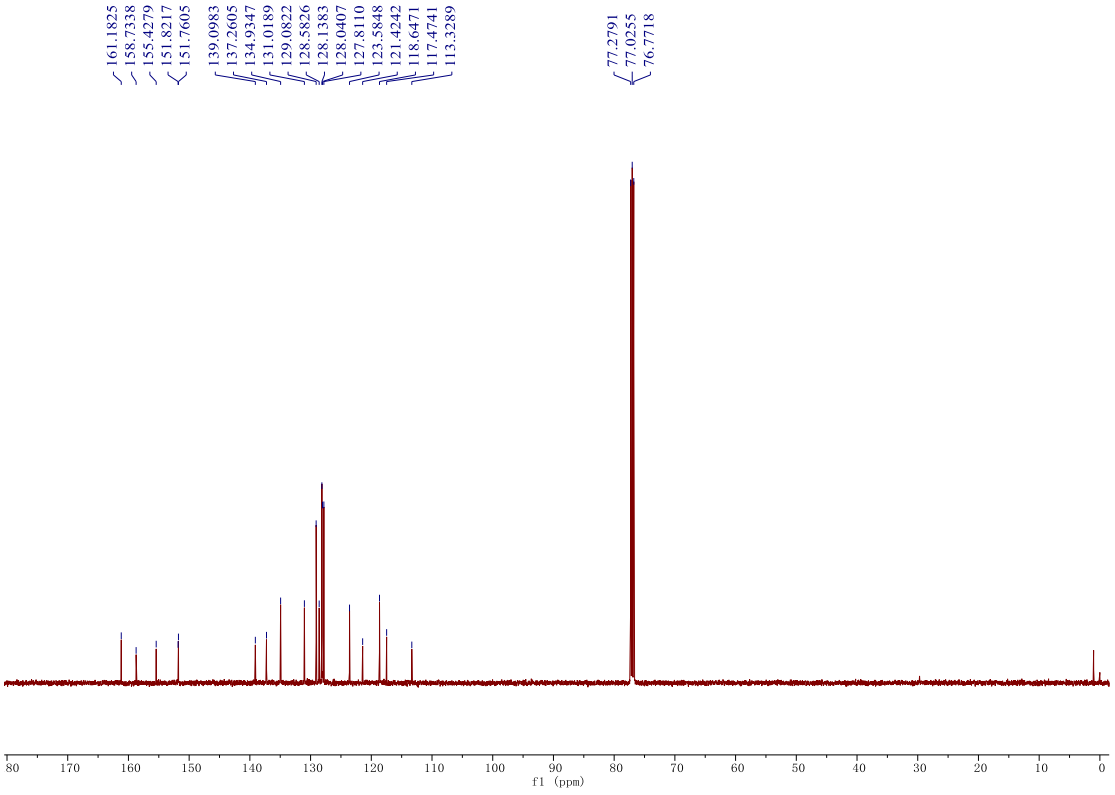


9-Bromo-2,4-diphenyl-5H-chromeno[4,3-b]pyridin-5-one (3g)

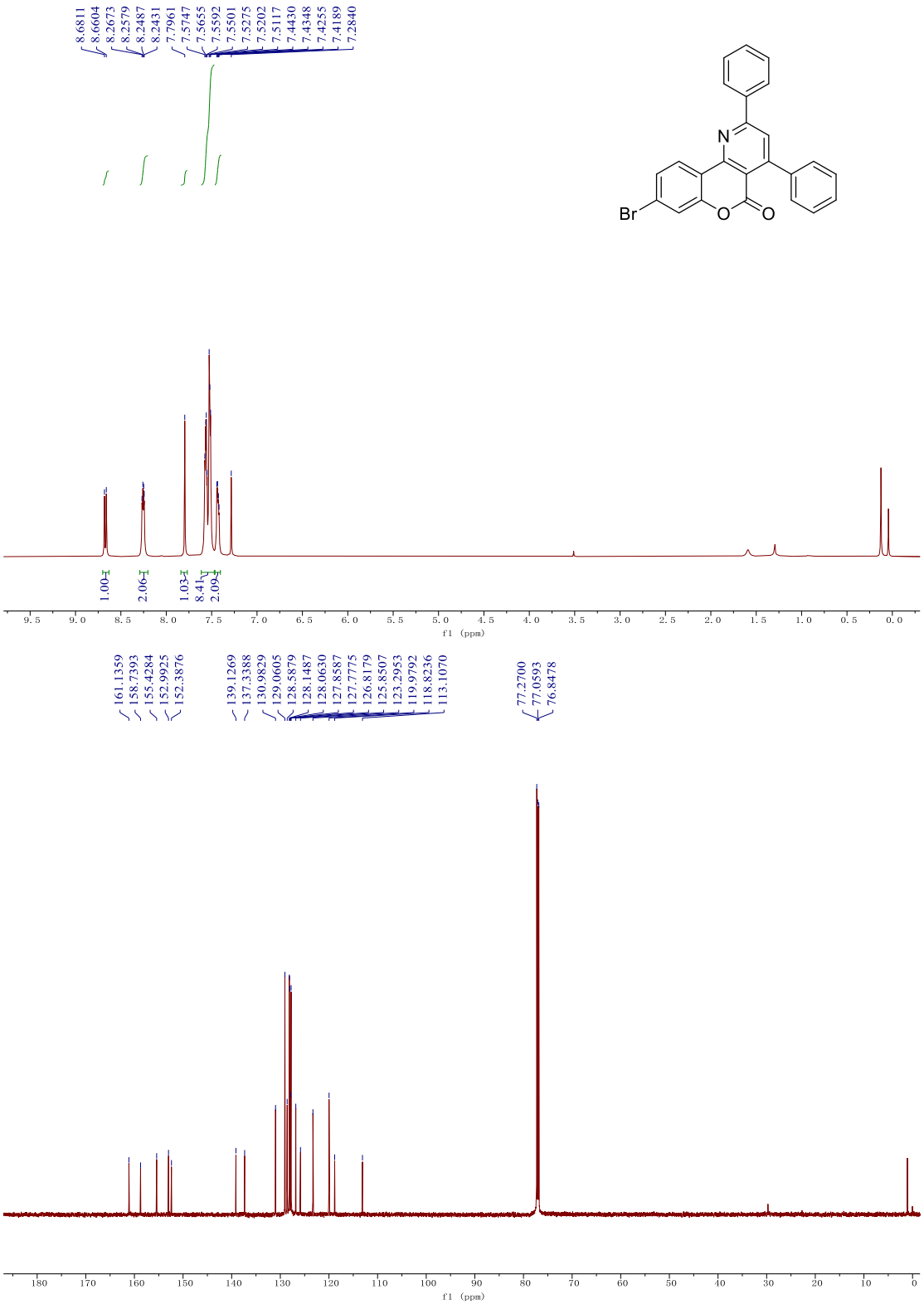








8-Bromo-2,4-diphenyl-5H-chromeno[4,3-b]pyridin-5-one (3h)



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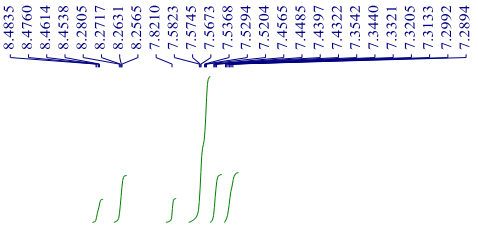

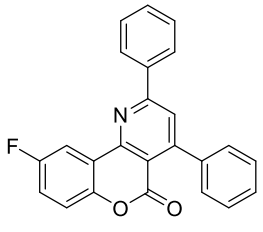

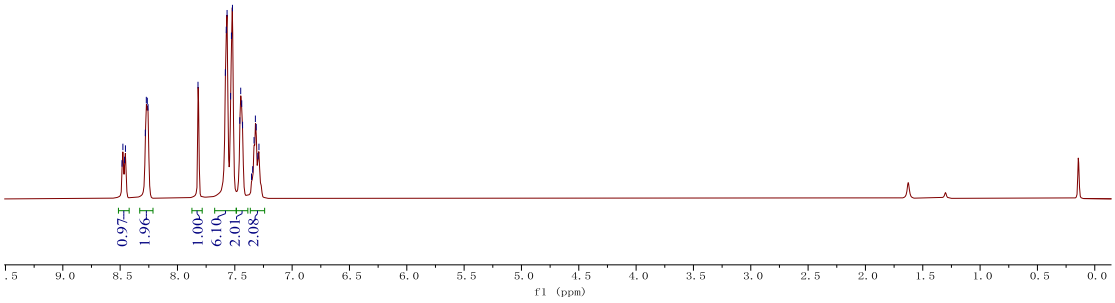

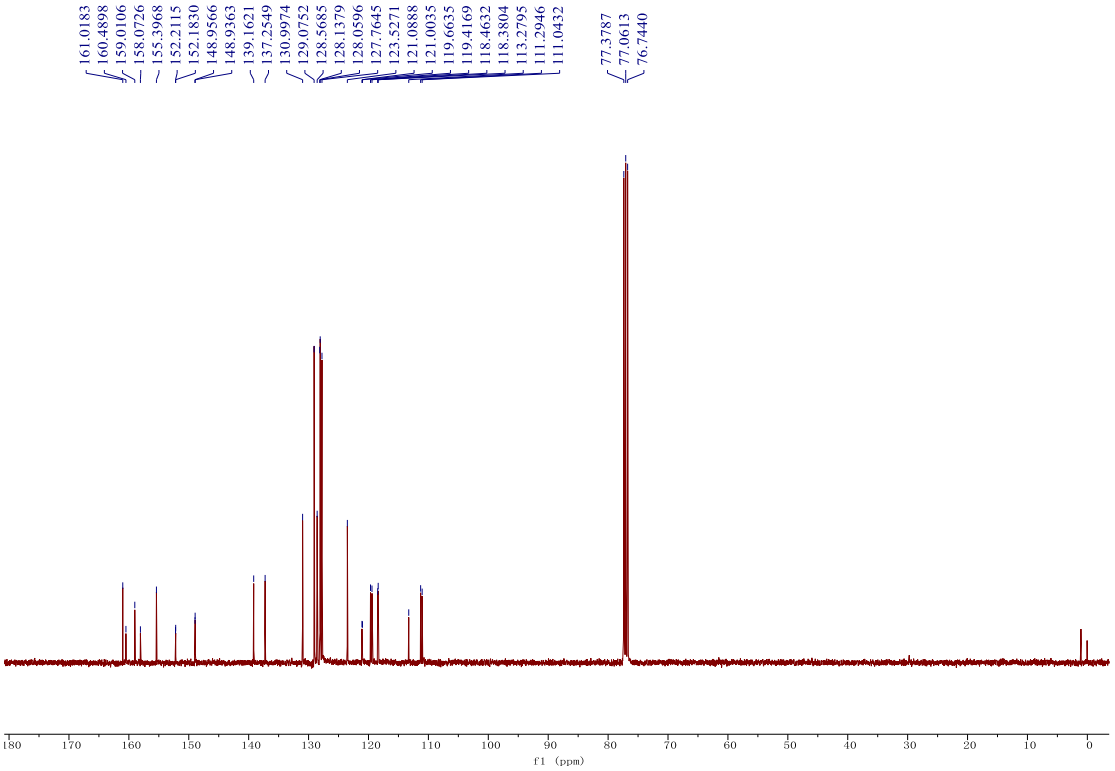

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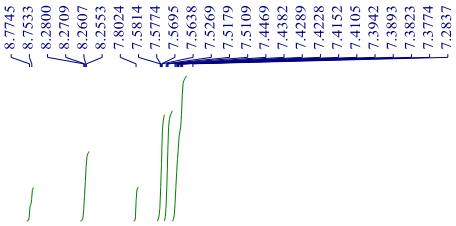
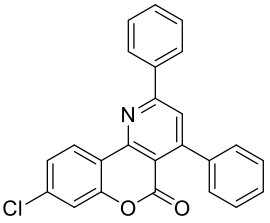
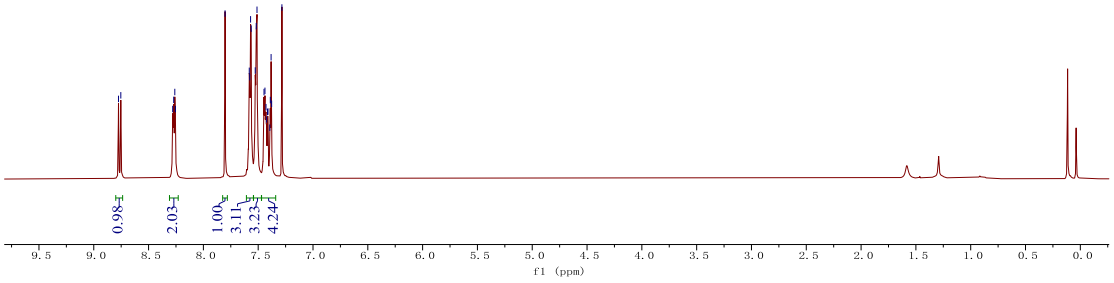
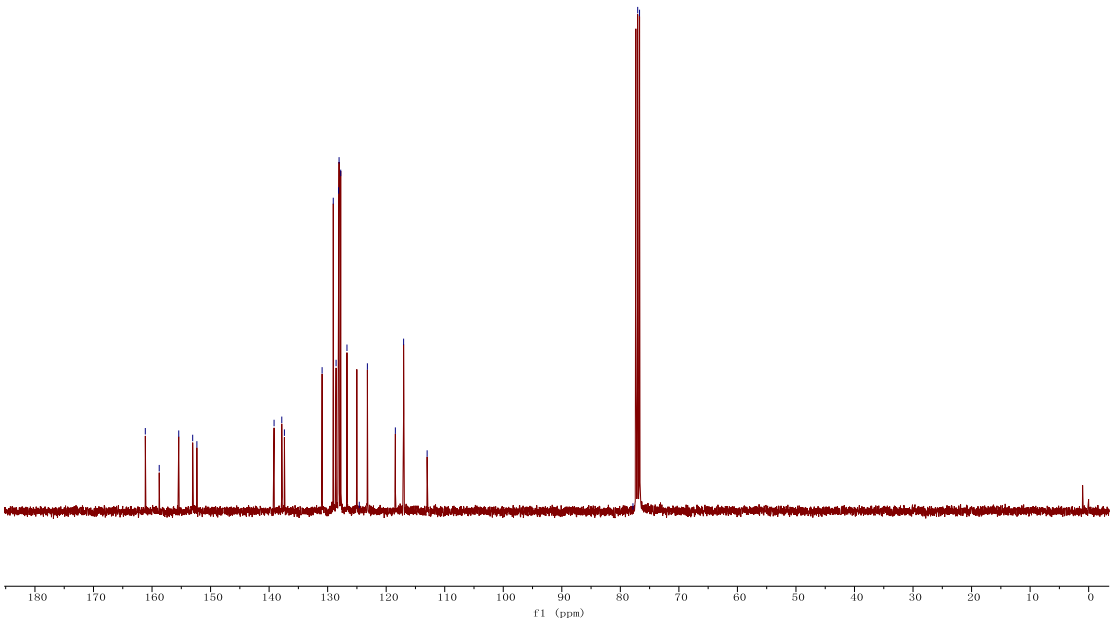
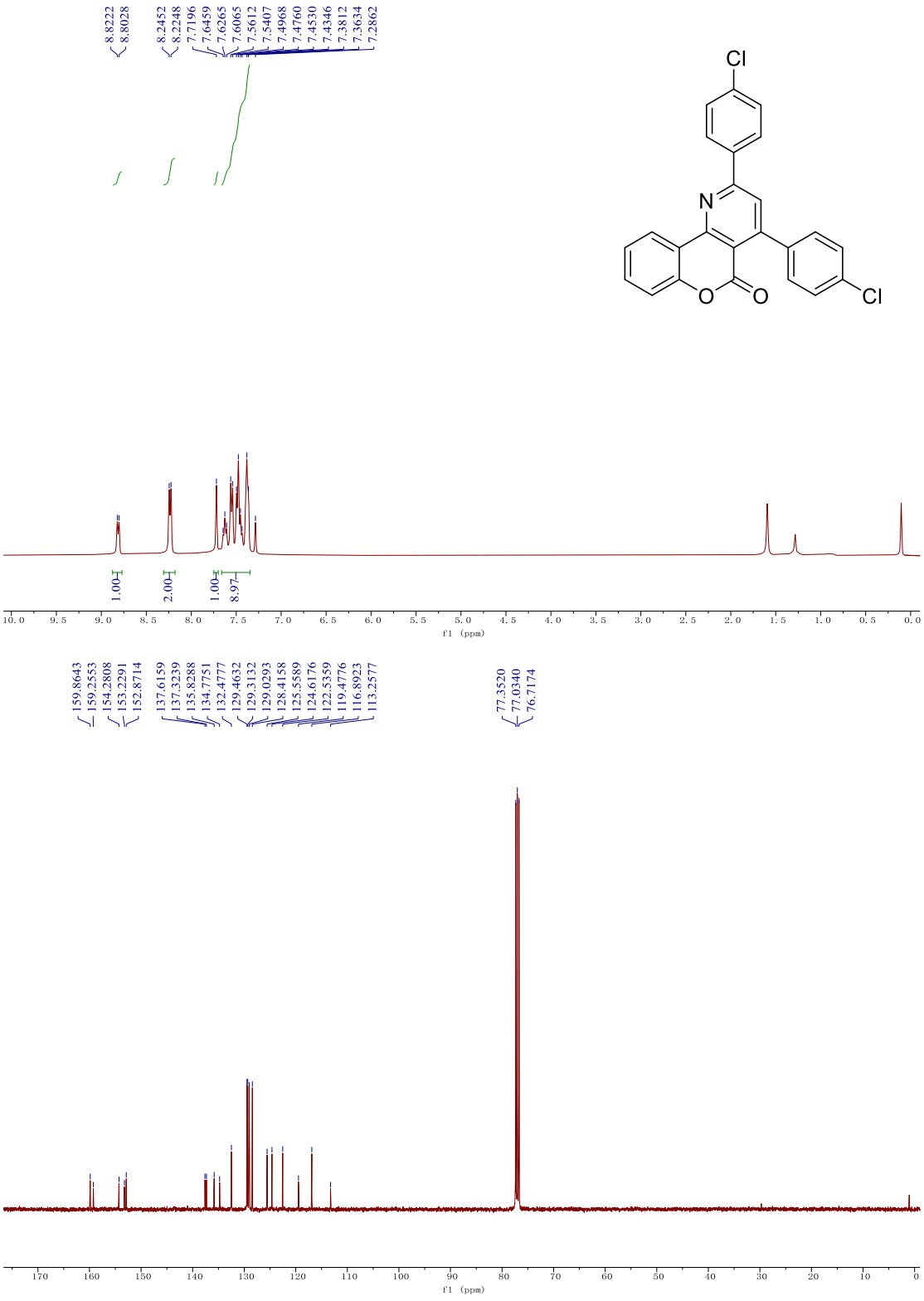




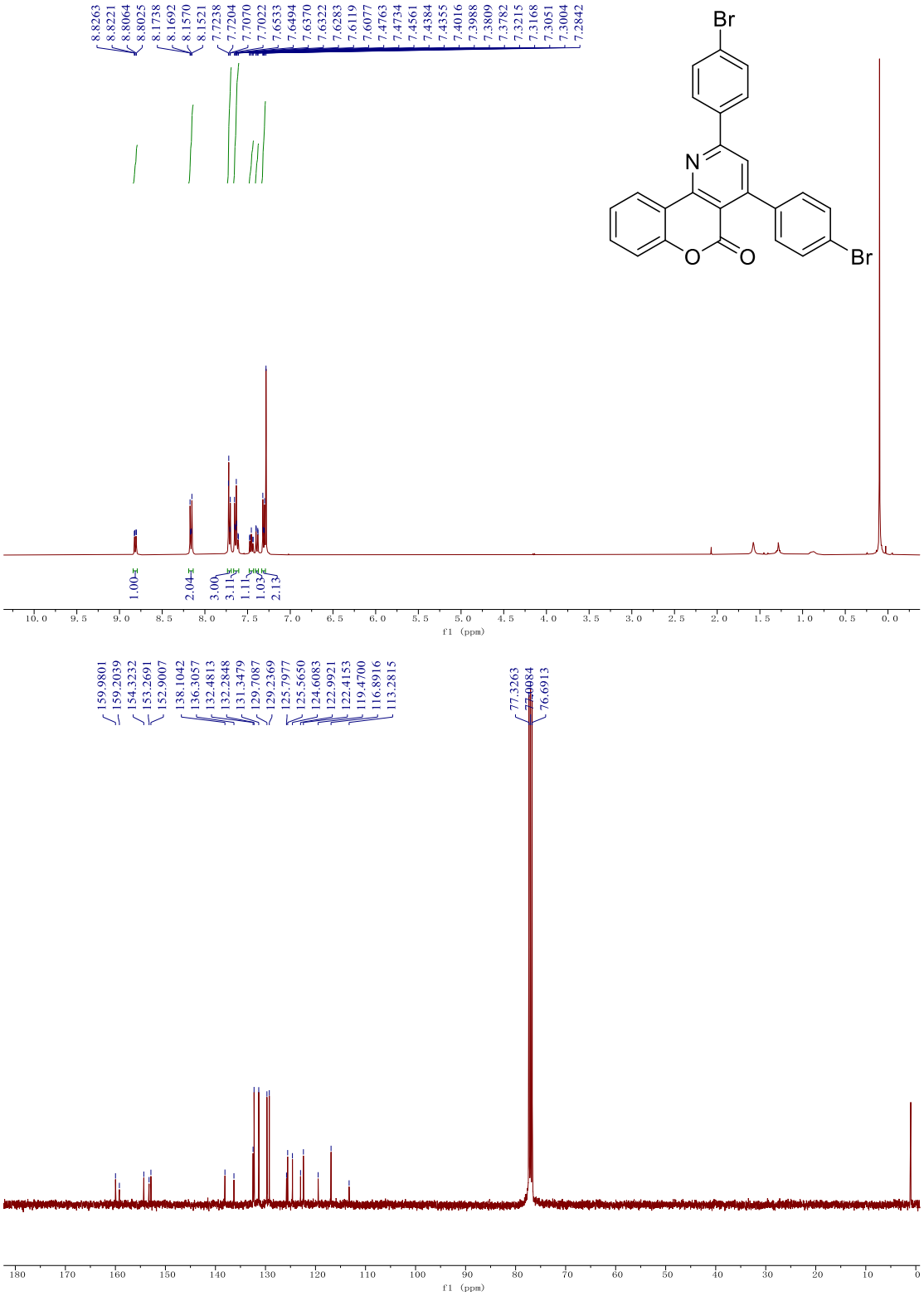




2,4-Bis(4-chlorophenyl)-5H-chromeno[4,3-b]pyridin-5-one (3k)



2,4-Bis(4-bromophenyl)-5H-chromeno[4,3-b]pyridin-5-one (3l)



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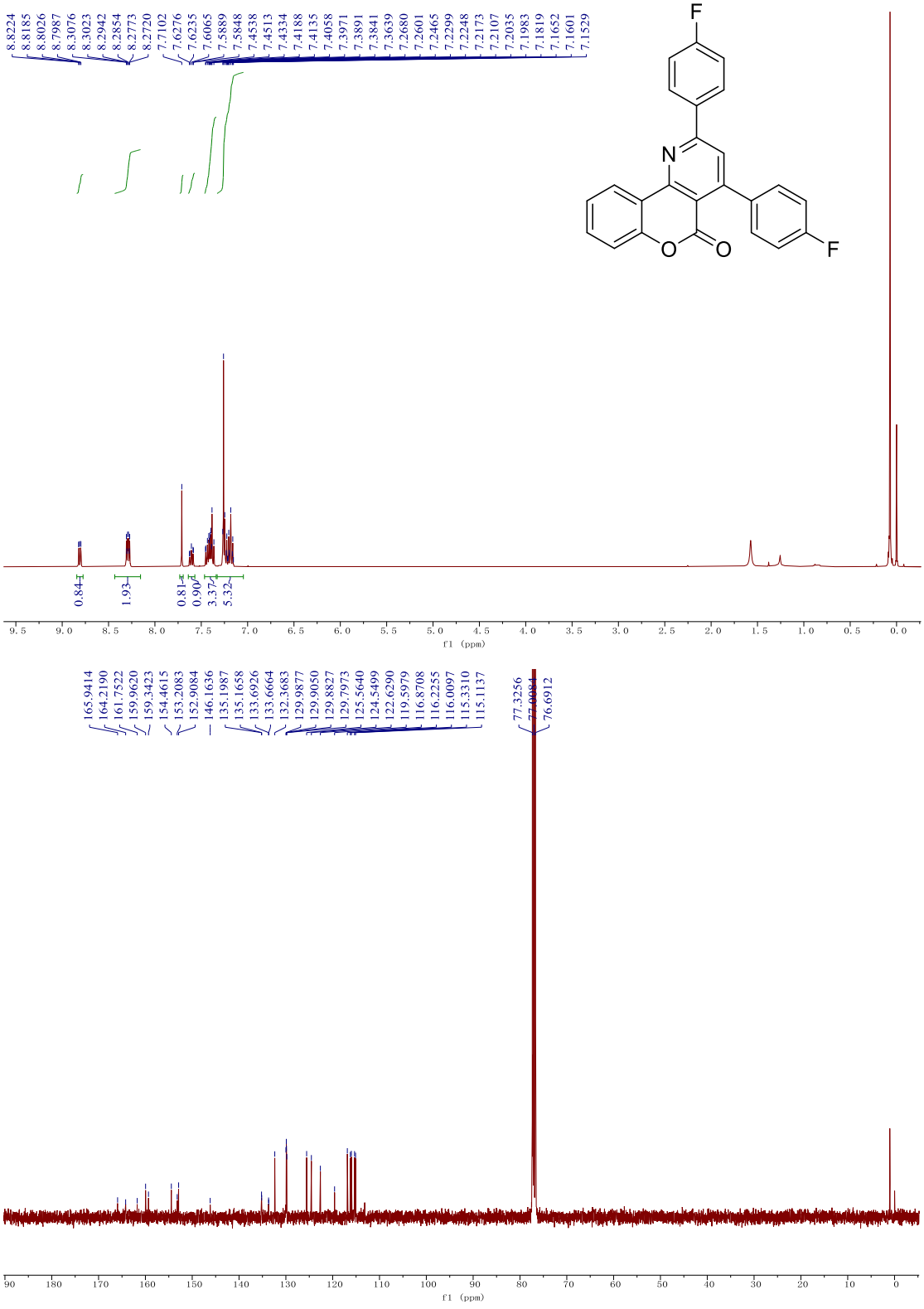
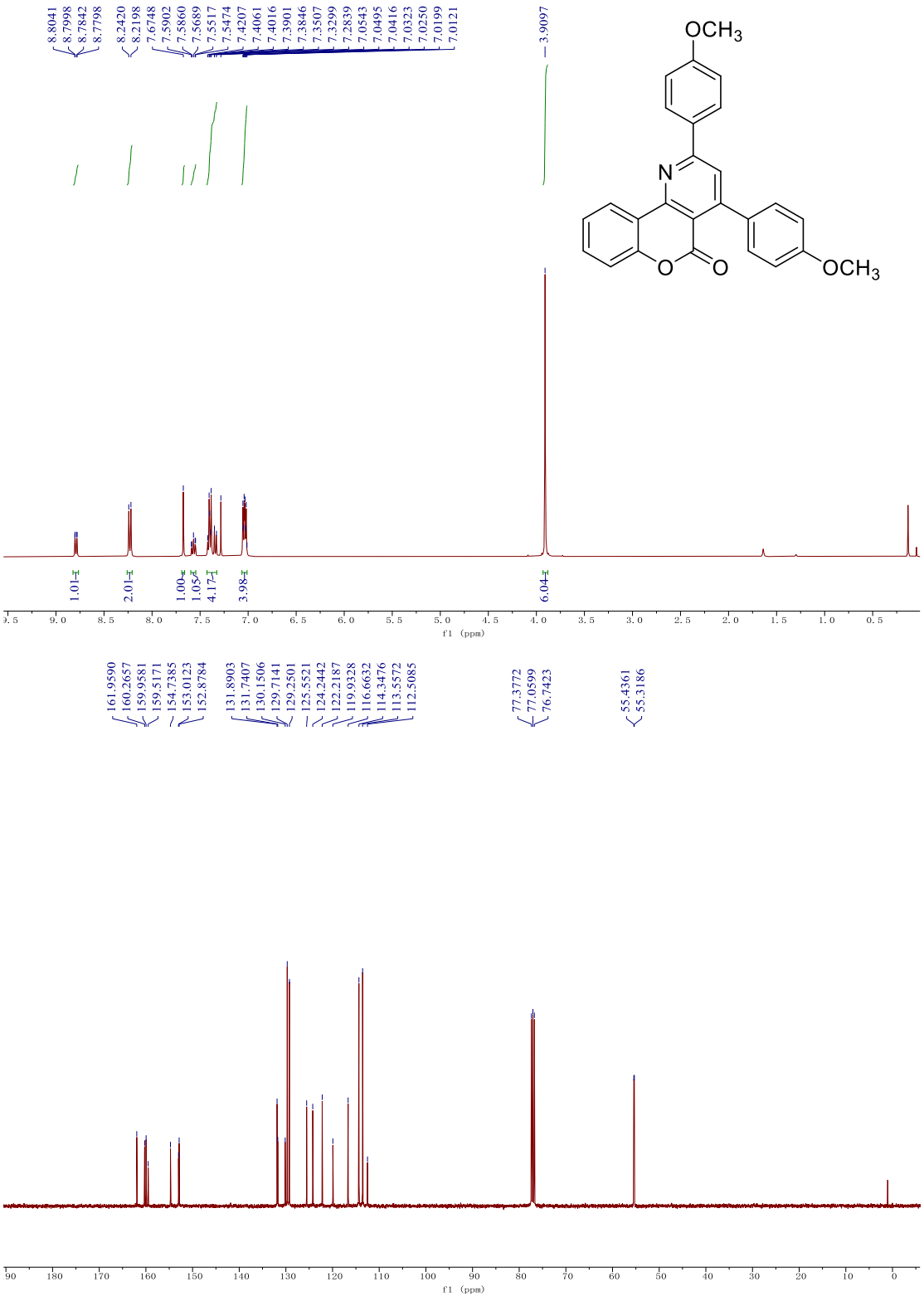


2,4-Bis(4-methoxyphenyl)-5H-chromeno[4,3-b]pyridin-5-one (3n)



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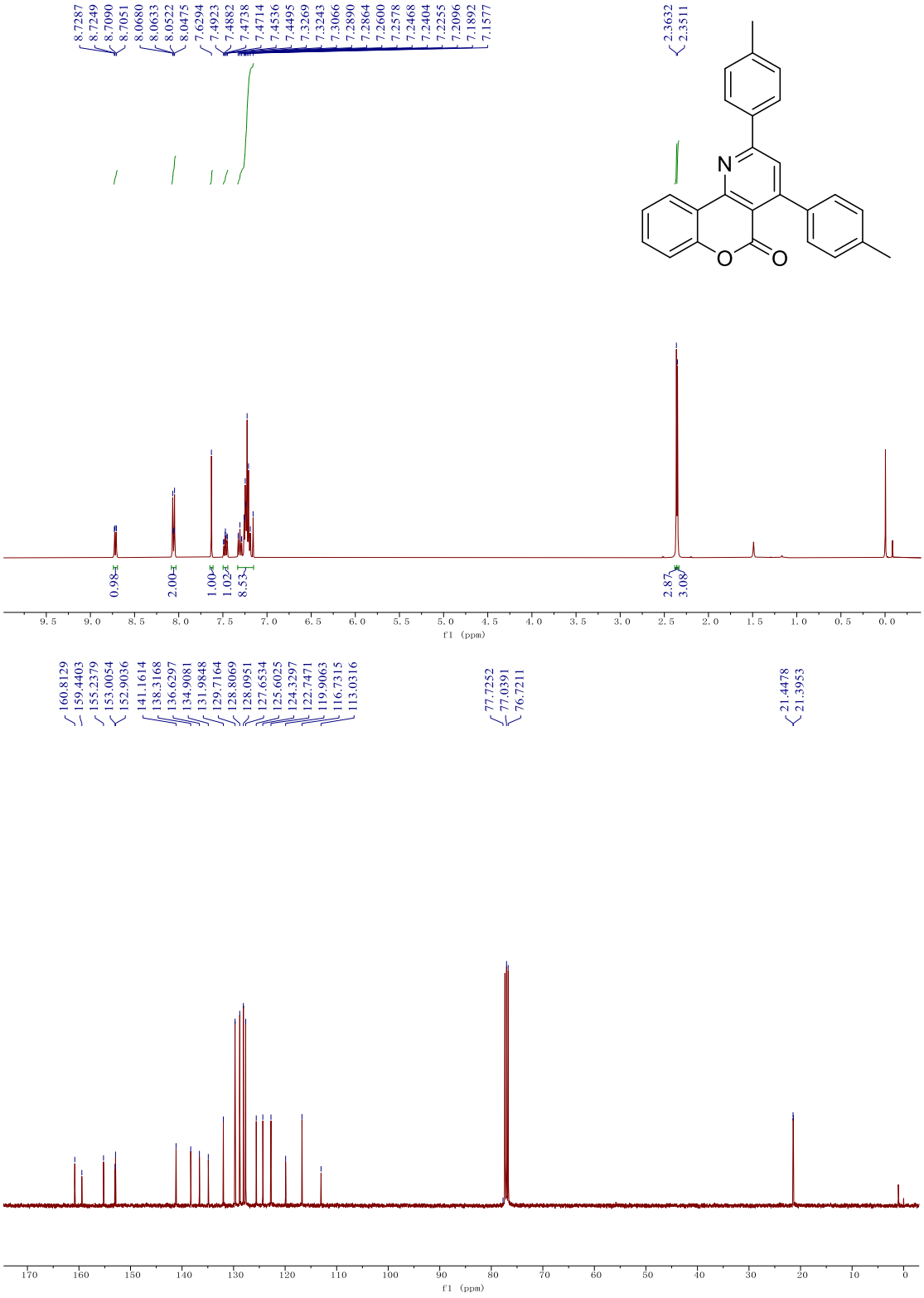
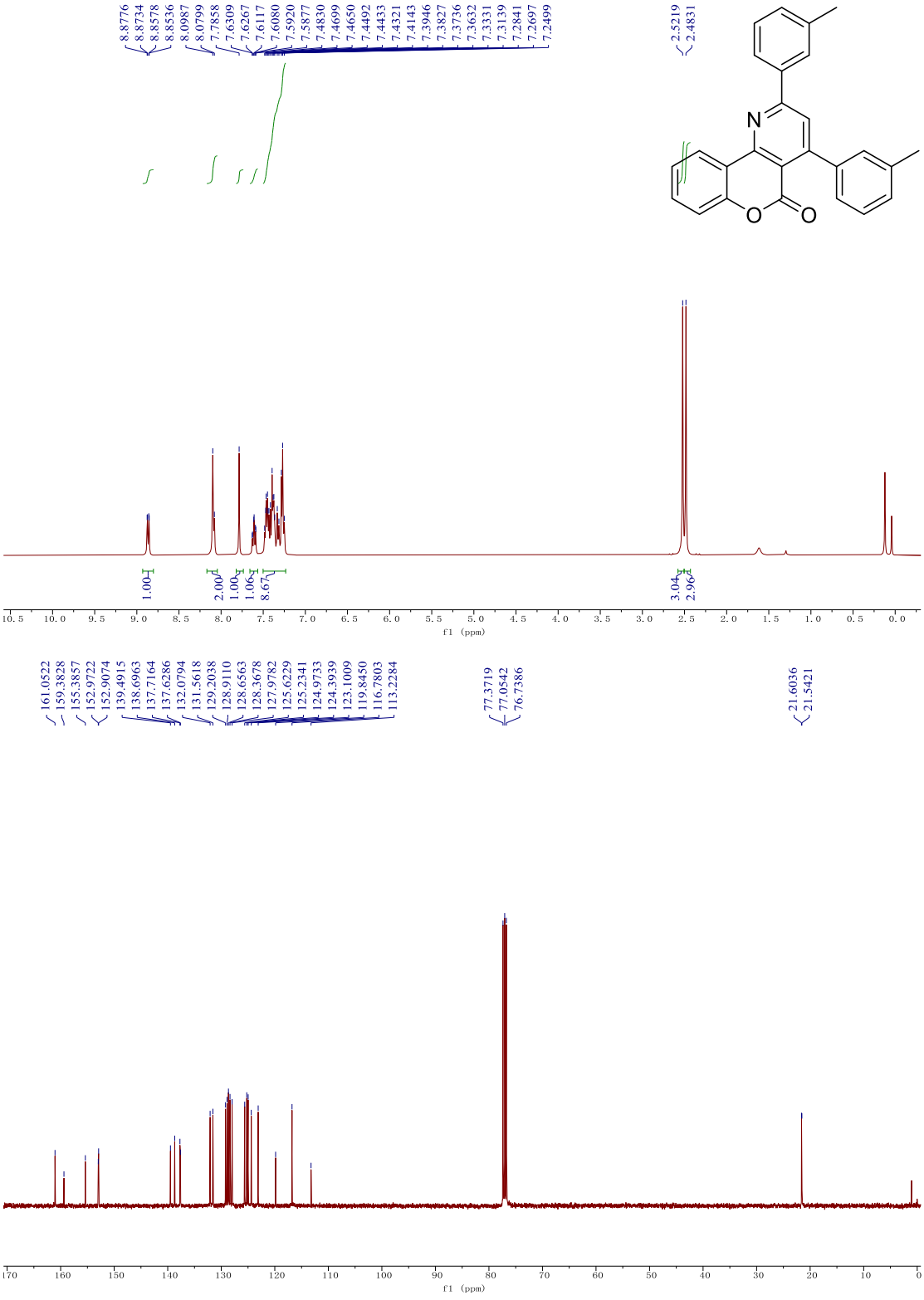


2,4-Di-m-tolyl-5H-chromeno[4,3-b]pyridin-5-one (3p)



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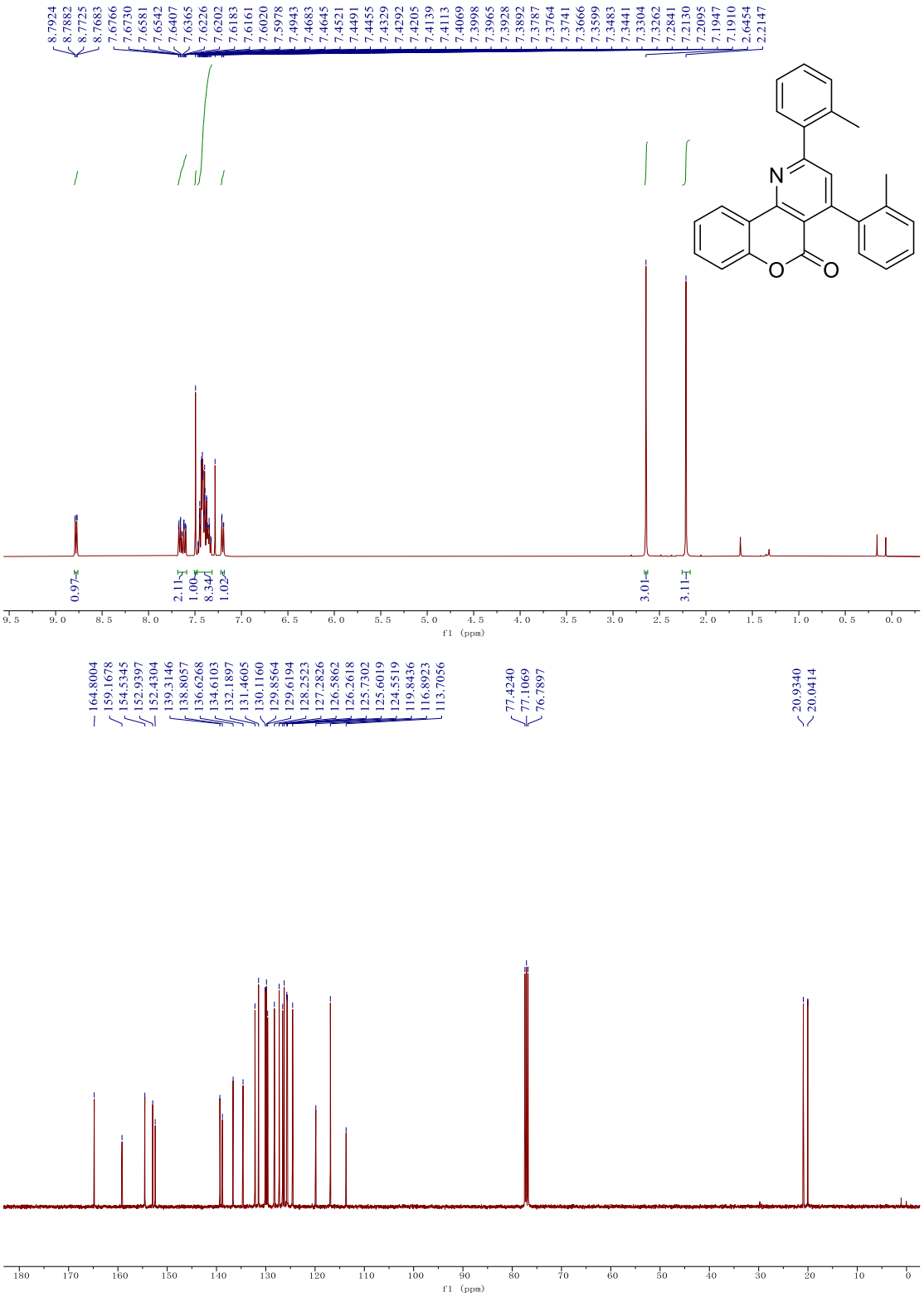
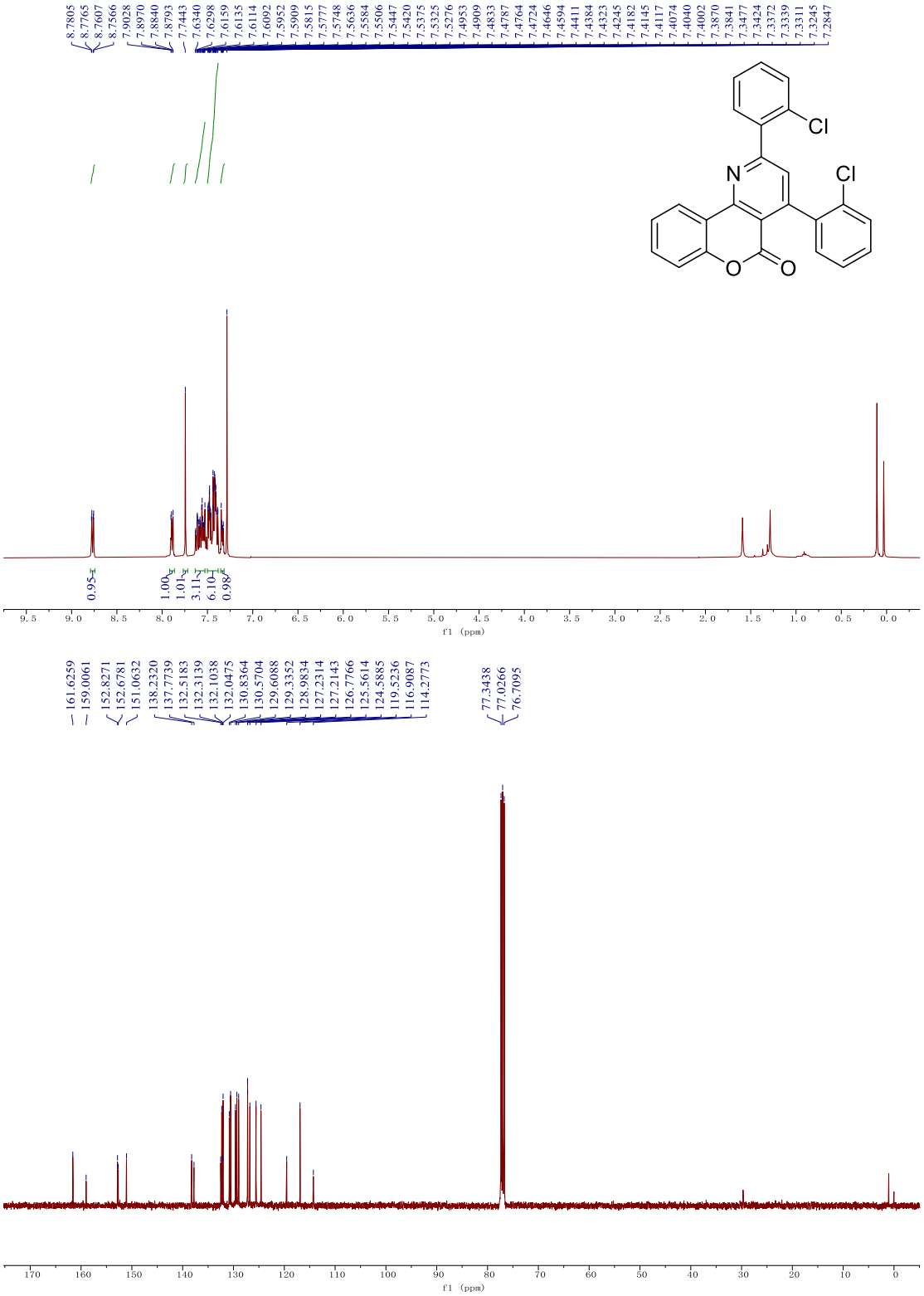
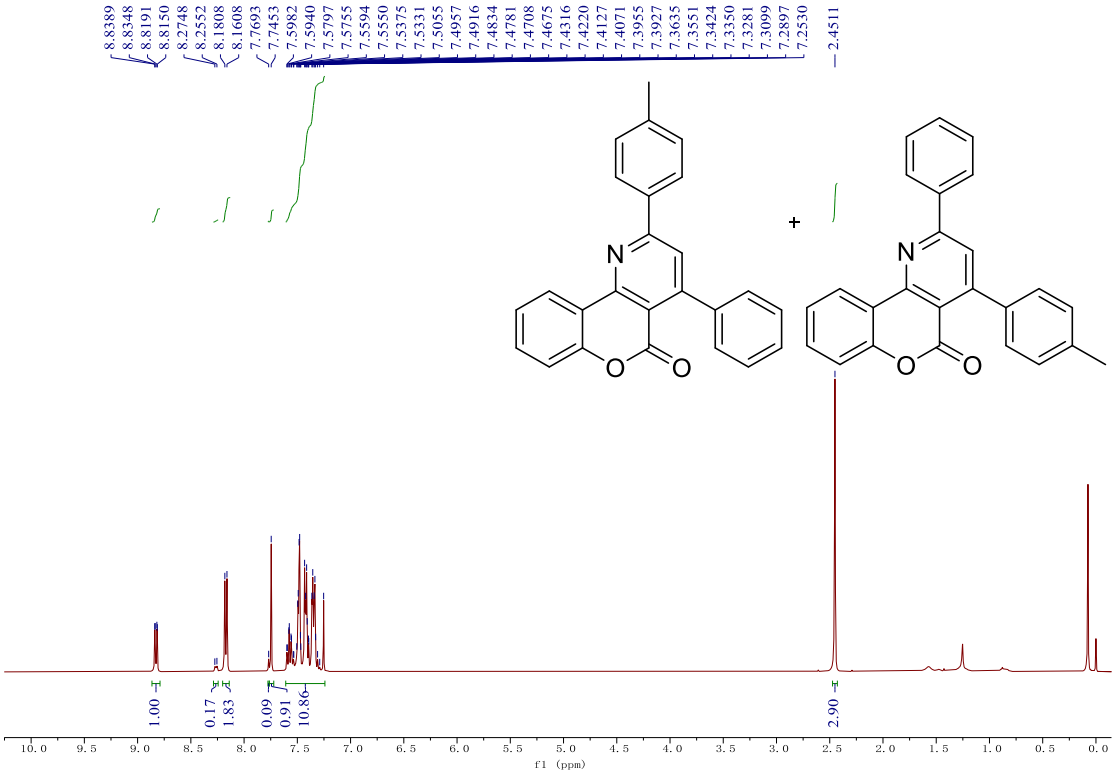
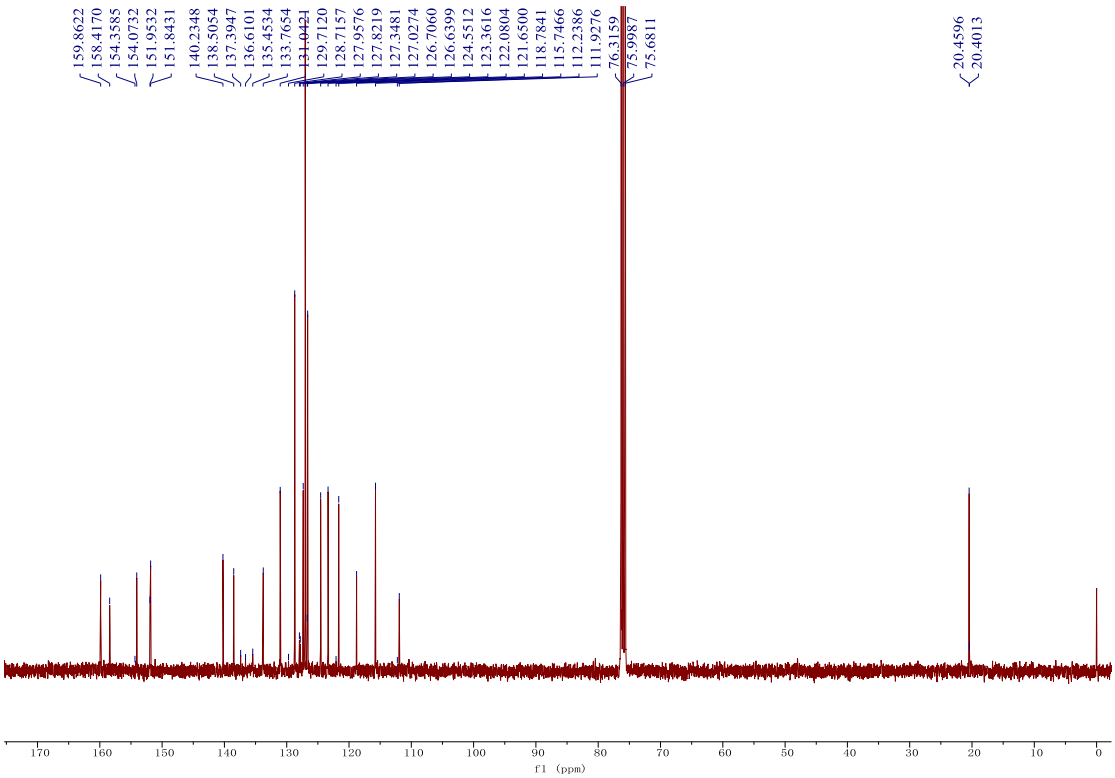


2,4-Bis(2-chlorophenyl)-5H-chromeno[4,3-b]pyridin-5-one (3r)

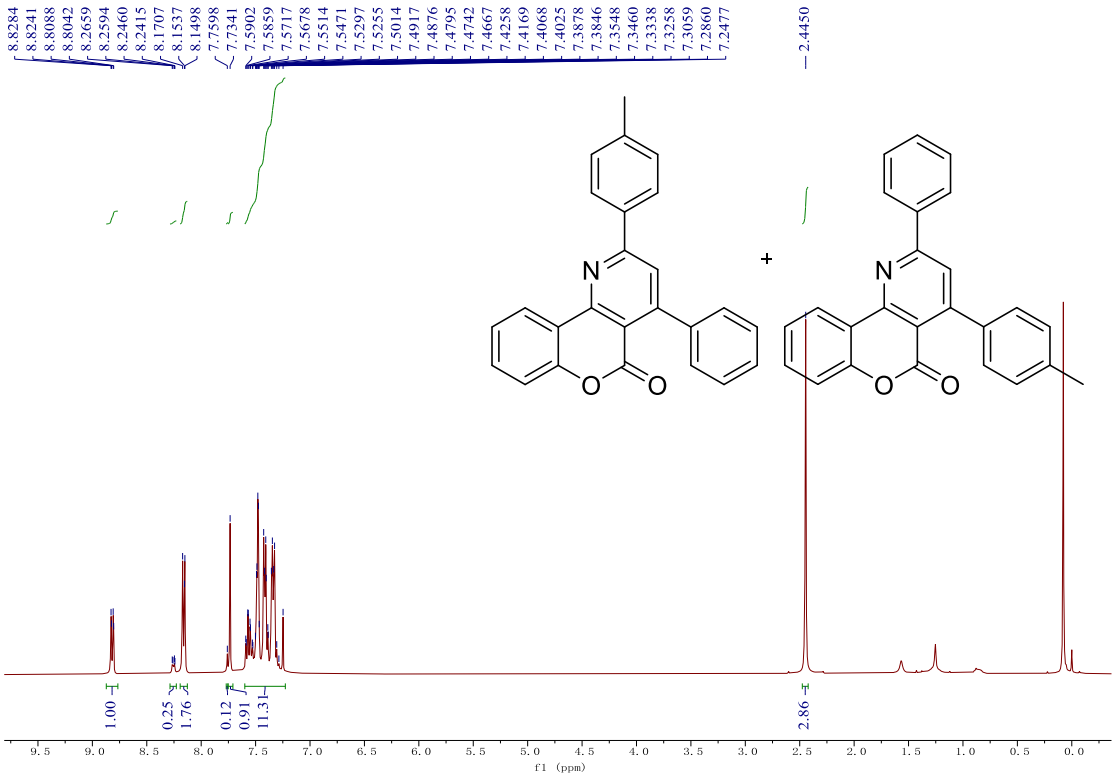


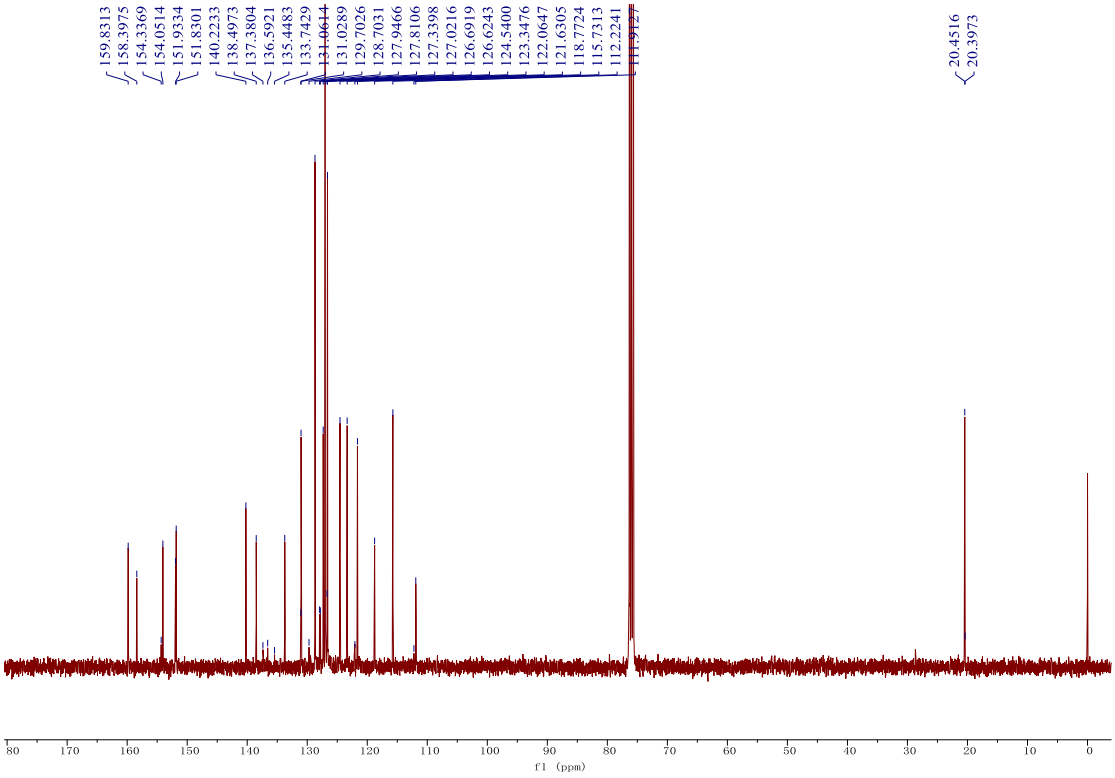
A mixture of 4-phenyl-2-(p-tolyl)-5H-chromeno[4,3-b]pyridin-5-one and 2-phenyl-4-(p-tolyl)-5H-chromeno[4,3-b]pyridin-5-one as 9:91 or 91:9 (3s)





A mixture of 4-phenyl-2-(p-tolyl)-5H-chromeno[4,3-b]pyridin-5-one and 2-phenyl-4-(p-tolyl)-5H-chromeno[4,3-b]pyridin-5-one as 12:88 or 88:12 (3t)





4. GC-MS spectra