

Cp*Rh(III) and Cp*Ir(III)-Catalysed Redox-Neutral C-H Arylation with Quinone Diazides: Quick and Facile Synthesis of Arylated Phenols

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Supporting Information

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1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH₂), dichloromethane (CaH₂). Anhydrous CF₃CH₂OH, CH₃CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (¹H) were recorded at 400 MHz, and Carbon NMR (¹³C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV₂₅₄ plates. Visualization was accomplished with short wave UV light, or KMnO₄ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

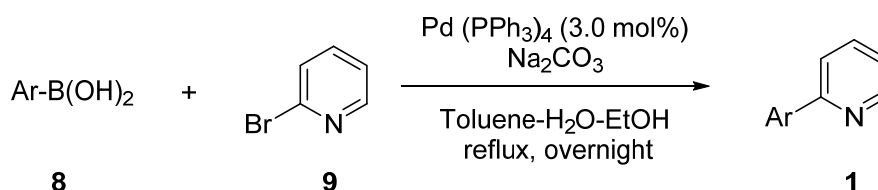
No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1, 2 and 6

The substrates of arylpyridines, heteroarylpyridines, arylpyrimidines and heteroarylpyrimidines were prepared according to the procedure reported by Iwasawa.^[1] Quinone diazides derivatives **2** were prepared following the procedure reported by Baran.^[2] Phenylpyrazoles derivatives were commercially available. 1-(Pyrimidin-2-yl)-1*H*-indole derivatives **6** were prepared following the procedure reported by Lygin.^[3] All the characteristic data are consistent with the data reported before.^[4-10]

Preparation and characterization of arylpyridines and heteroarylpyridines

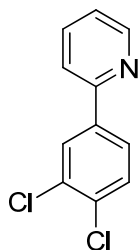
General procedure A:



To a stirred solution of 2-bromopyridine **9** (0.5 g, 3.2 mmol) in toluene (12 mL), ethanol (2.3 mL) and H_2O (12 mL) was added Na_2CO_3 (2.5 g, 23.6 mmol) followed by $\text{Pd}(\text{PPh}_3)_4$ (0.1 g, 0.1 mmol) and arylboronic acid **8** (4.2 mmol) under N_2 in 100 mL two-necked flask. The mixture was refluxed overnight, and then cooled to room temperature. To the reaction mixture were added H_2O and CH_2Cl_2 , then extracted with CH_2Cl_2 three times, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography to give the compound **1**.

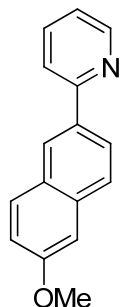
Characterization of substrates 1

2-(3,4-dichlorophenyl)pyridine (**1g**)



Following general procedure A, compound **1g** was obtained in 84% yield (0.6 g, 2.7 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). **R_F** (Petroleum ether/EtOAc 16:1): 0.22. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.74 (td, *J* = 7.7, 1.7 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.24 (dd, *J* = 3.9, 2.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 150.0, 139.4, 137.1, 133.2, 133.2, 130.8, 128.9, 126.0, 123.0, 120.5. **ESI-MS**: calculated C₁₁H₈Cl₂N [M+H]⁺, 224.0028; Found 224.0017.

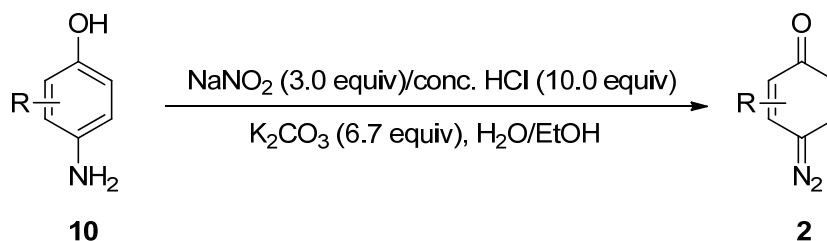
2-(6-methoxynaphthalen-2-yl)pyridine (**1o**)



Following general procedure A, compound **1o** was obtained in 63% yield (0.48 g, 2.0 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). **R_F** (Petroleum ether/EtOAc 16:1): 0.23. ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.42 (d, *J* = 1.2 Hz, 1H), 8.11 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.88 – 7.81 (m, 3H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (ddd, *J* = 7.3, 4.8, 1.1 Hz, 1H), 7.20 – 7.15 (m, 2H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.2, 157.4, 149.7, 136.8, 134.9, 134.5, 130.2, 129.0, 127.2, 126.1, 125.0, 121.8, 120.5, 119.2, 105.6, 55.3. **ESI-MS**: calculated C₁₆H₁₄NO [M+H]⁺, 236.1070; Found 236.1067.

Preparation and characterization of quinone diazides **2**

General procedure B:



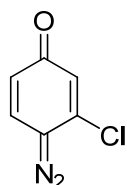
Caution: Quinone diazides are potential explosives. Many of these compounds are sensitive to heat, light, shock and metal catalysts. Therefore, precaution should be

taken in preparation, storage and use.

To a stirred solution of aminophenol **10** (10.0 mmol, 1.0 equiv) in EtOH (60 mL) was slowly added HCl (8.4 mL, 12 N, 100 mmol, 10.0 equiv) at 0 °C. This mixture was stirred at 0 °C for 10 min, then an ice-cold solution of NaNO₂ (2.07 g, 30 mmol, 3.0 equiv) in H₂O (4 mL) was added dropwise over 10 min. The resulting mixture was stirred for another 2 h at 0 °C, then diluted with cold CH₂Cl₂ (200 mL) followed by addition 30 g of ice. The mixture was stirred vigorously while a cold solution of K₂CO₃ (9.2 g, 67 mmol, 6.7 equiv) in H₂O (10 mL) was added. The organic layers were then separated, and the aqueous layer was extracted with CH₂Cl₂ (100 mL). The combined organic layer was washed with brine (100 mL), and dried over Na₂SO₄. Evaporation *in vacuo* resulted in a black solid. This solid was kept anhydrous at -25 °C and used without further purification.

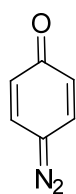
Characterization of substrates 2

3-chloro-4-diazocyclohexa-2,5-dienone(2a)



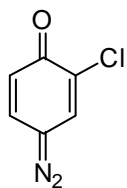
Following general procedure B, compound **2a** was obtained in 91% yield (1.40 g, 9.1 mmol) as a gray solid. ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 9.3 Hz, 1H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.25 (dd, *J* = 9.3, 1.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 147.1, 124.6, 124.1, 117.0, 84.5. **EI-MS**: calculated C₆H₃ClN₂O, 153.9928; Found 153.9929.

4-diazocyclohexa-2,5-dienone (2b)



Following general procedure B, compound **2b** was obtained in 16% yield (0.19 g, 1.6 mmol) as a gray solid. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 9.7 Hz, 2H), 6.47 (d, *J* = 9.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 182.6, 130.3, 129.6, 127.2. **EI-MS**: calculated C₆H₄N₂O, 120.0318; Found 120.0319.

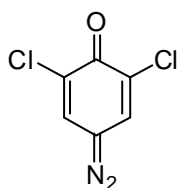
2-chloro-4-diazocyclohexa-2,5-dienone (2c)



Following general procedure B, compound **2c** was obtained in 31% yield (0.48 g, 3.1 mmol) as a black solid. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 2.8$ Hz, 1H), 7.45 (dd, $J = 9.7, 2.8$ Hz, 1H), 6.47 (d, $J = 9.7$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.1, 129.7, 129.3, 127.3, 125.8, 74.9.

EI-MS: calculated $\text{C}_6\text{H}_3\text{ClN}_2\text{O}$, 153.9928; Found 153.9926.

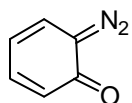
2,6-dichloro-4-diazocyclohexa-2,5-dienone (**2d**)



Following general procedure B, compound **2d** was obtained in 45% yield (0.85 g, 4.5 mmol) as a gray solid. ^1H NMR (400 MHz, DMSO-d_6) δ 8.25 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 129.8, 124.9, 78.4. **EI-MS**: calculated $\text{C}_6\text{H}_2\text{Cl}_2\text{N}_2\text{O}$, 187.9539; Found

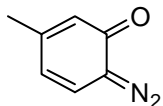
187.9538.

6-diazocyclohexa-2,4-dienone (**2e**)



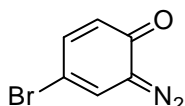
Following general procedure B, compound **2e** was obtained in 67% yield (0.8 g, 6.7 mmol) as a gray solid. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.26 (m, 1H), 7.22 (d, $J = 8.7$ Hz, 1H), 6.69 (d, $J = 9.4$ Hz, 1H), 6.37 – 6.24 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.6, 138.8, 124.0, 123.7, 115.7, 88.1. **EI-MS**: calculated $\text{C}_6\text{H}_4\text{N}_2\text{O}$, 120.0318; Found 120.0316.

6-diazo-3-methylcyclohexa-2,4-dienone (**2f**)



Following general procedure B, compound **2f** was obtained in 82% yield (1.10 g, 8.2 mmol) as a black solid. ^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, $J = 8.9$ Hz, 1H), 6.43 (s, 1H), 6.08 (d, $J = 8.9$ Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 178.6, 150.9, 123.4, 122.9, 118.3, 83.2, 22.8. **EI-MS**: calculated $\text{C}_7\text{H}_6\text{N}_2\text{O}$, 134.0475; Found 134.0474.

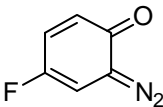
4-bromo-6-diazocyclohexa-2,4-dienone (**2g**)



Following general procedure B, compound **2g** was obtained in 80% yield (1.60 g, 8.0 mmol) as a gray solid. ^1H NMR (400 MHz, CDCl_3)

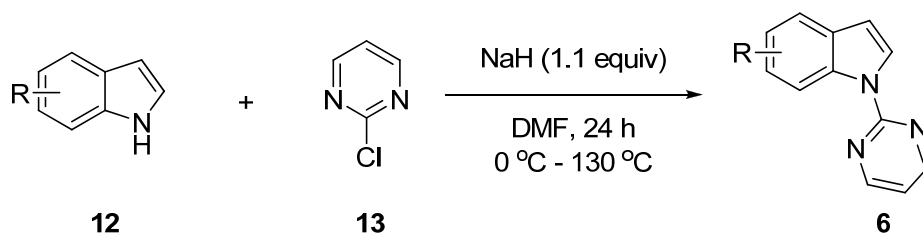
δ 7.35 (d, J = 2.1 Hz, 1H), 7.31 (dd, J = 9.8, 2.3 Hz, 1H), 6.62 (d, J = 9.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.4, 142.2, 125.6, 123.7, 104.9, 90.2. **EI-MS**: calculated $\text{C}_6\text{H}_3\text{BrN}_2\text{O}$, 197.9423; Found 197.9420.

6-diazo-4-fluorocyclohexa-2,4-dienone (2h)

 Following general procedure B, compound **2h** was obtained in 43% yield (0.60 g, 4.3 mmol) as a black solid. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (ddd, J = 9.7, 8.3, 3.0 Hz, 1H), 7.07 (dd, J = 7.2, 3.0 Hz, 1H), 6.97 (dd, J = 9.8, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 152.8 (J = 242.7 Hz), 128.2 (J = 28.0 Hz), 120.8 (J = 8.5 Hz), 104.8 (J = 27.9 Hz), 101.7 (J = 14.1 Hz). **EI-MS**: calculated $\text{C}_6\text{H}_3\text{FN}_2\text{O}$, 138.0224; Found 138.0227.

Preparation and characterization of 1-(pyrimidin-2-yl)-1*H*-indole derivatives **6**

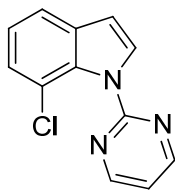
General procedure C:



To a stirred solution of indole **12** (10.0 mmol) in DMF (25 mL) was added NaH (60% dispersion in mineral oil, 440 mg, 11.0 mmol) in portions at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine **13** (1.37 g, 12.0 mmol) was added and the mixture was stirred at 130 °C for 24 h. Then, the reaction mixture was cooled to ambient temperature, poured into H_2O (300 mL) and extracted with EtOAc (4×75 mL). The combined organic phase was dried over Na_2SO_4 . After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to give the target compound **6**.

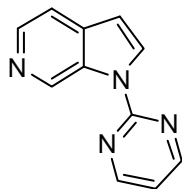
Characterization of substrates **6**

7-chloro-1-(pyrimidin-2-yl)-1*H*-indole (6h)



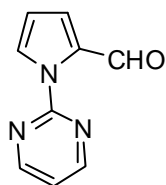
Following general procedure C, compound **6h** was obtained in 31% yield (0.71 g, 3.1 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). **R_F** (Petroleum ether/EtOAc 8:1): 0.26. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (d, *J* = 4.8 Hz, 2H), 7.72 (d, *J* = 3.5 Hz, 1H), 7.55 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.30 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.16 (m, 2H), 6.71 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.2, 157.4, 133.6, 132.1, 130.7, 125.4, 122.7, 119.8, 119.2, 118.2, 106.4. **ESI-MS**: calculated C₁₂H₉ClN₃ [M+H]⁺, 230.0480; Found 230.0478.

1-(pyrimidin-2-yl)-1H-pyrrolo[2,3-c]pyridine (**6j**)



Following general procedure C, compound **6j** was obtained in 76% yield (1.5 g, 7.6 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.28. ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H), 8.75 (d, *J* = 4.8 Hz, 2H), 8.56 – 8.28 (m, 2H), 7.54 (d, *J* = 5.3 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 157.1, 141.4, 138.8, 136.4, 132.5, 128.8, 117.0, 115.3, 105.8. **ESI-MS**: calculated C₁₁H₉N₄ [M+H]⁺, 197.0822; Found 197.0828.

1-(pyrimidin-2-yl)-1H-pyrrole-2-carbaldehyde (**7b**)



Following general procedure C, compound **7b** was obtained in 52% yield (0.91 g, 5.2 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). **R_F** (Petroleum ether/EtOAc 6:1): 0.25. ¹H NMR (400 MHz, CDCl₃) δ 10.58 (s, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 7.94 (s, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.21 (t, *J* = 4.8 Hz, 1H), 6.38 (t, *J* = 3.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 183.2, 158.5, 156.4, 134.4, 127.3, 121.2, 118.5, 111.7. **ESI-MS**: calculated C₉H₇N₃ONa [M+Na]⁺, 196.0481; Found 196.0484.

3. General procedure and characterization of products

General procedure D

To a 15 mL-schlenk tube charged with a stirring bar, was added substrates **1** (0.2 mmol, 1.0 equiv), 3-chloro-4-diazocyclohexa-2,5-dienone **2a** (46.2 mg, 0.3 mmol, 1.5 equiv), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol%), AgSbF₆ (13.7 mg, 0.04 mmol, 0.2 equiv), PivOH (2.0 mg, 0.02 mmol, 0.1 equiv) and DCM (1.0 mL). No special precautions were taken to exclude moisture and air. The reaction was allowed to stir at 50 °C until the complete consumption of **1** as monitored by TLC analysis (typically 12 h). The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product .

General procedure E

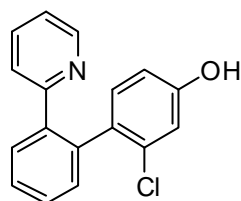
To a 15 mL-schlenk tube charged with a stirring bar, was added substrates **1** (0.2 mmol, 1.0 equiv), 3-chloro-4-diazocyclohexa-2,5-dienone **2a** (77.0 mg, 0.5 mmol, 2.5 equiv), [Cp*IrCl₂]₂ (4.0 mg, 0.005 mmol, 2.5 mol%), AgSbF₆ (6.9 mg, 0.02 mmol, 0.1 equiv), PivOH (2.0 mg, 0.02 mmol, 0.1 equiv) and DCE (1.0 mL). No special precautions were taken to exclude moisture and air. The reaction was allowed to stir at 50 °C until the complete consumption of **1** as monitored by TLC analysis (typically 12 h). The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product .

General procedure F

To a 15 mL-schlenk tube charged with a stirring bar, was added 1-(pyrimidin-2-yl)-1*H*-indole derivatives **6** (0.2 mmol, 1.0 equiv), 3-chloro-4-diazocyclohexa-2,5-dienone **2a** (46.2 mg, 0.3 mmol, 1.5 equiv), [Cp*IrCl₂]₂ (4.0 mg, 0.005 mmol, 2.5 mol%), AgSbF₆ (10.3 mg, 0.03 mmol, 0.15 equiv), PivOH (20.4 mg, 0.2 mmol, 1.0 equiv) and nitromethane (1.0 mL). No special precautions were taken to exclude moisture and air. The reaction was allowed to stir at 40 °C until the complete consumption of **6** as monitored by TLC analysis (typically 12 h). The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product .

Characterization of products

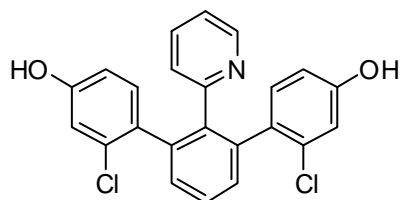
2-chloro-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3aa**)



Following general procedure D, the product **3aa** was obtained in 73% yield (41.5 mg, 0.147 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.21. ¹H NMR (400 MHz, CDCl₃)

δ 8.44 (d, *J* = 4.7 Hz, 1H), 7.74 (td, *J* = 7.8, 1.7 Hz, 1H), 7.47 (dd, *J* = 5.5, 3.8 Hz, 3H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.24 (dd, *J* = 5.0, 1.9 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 156.0, 147.0, 139.1, 138.0, 136.9, 134.1, 132.7, 132.2, 130.8, 130.0, 129.2, 128.2, 124.3, 122.8, 120.7, 119.9. **ESI-MS**: calculated C₁₇H₁₃ClNO [M+H]⁺, 282.0680; Found 282.0682.

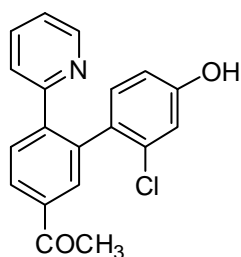
2,2''-dichloro-2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**3aa'**)



Following general procedure D, the product **3aa'**

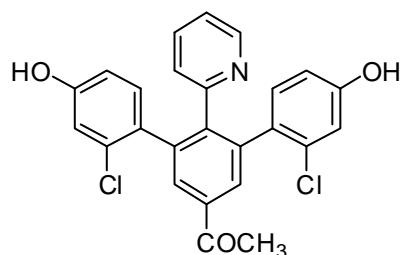
was obtained in 17% yield (14.2 mg, 0.034 mmol), Following general procedure E, The product **3aa'** was obtained in 80% yield (65.3 mg, 0.160 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). R_F (Petroleum ether/EtOAc 4:1): 0.23. 1H NMR (400 MHz, MeOD- d_4) δ 8.14 (d, J = 4.6 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.02 (dd, J = 7.0, 5.4 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.68 – 6.61 (m, 4H), 3.35 (s, 2H). ^{13}C NMR (101 MHz, MeOD- d_4) δ 159.7, 156.2, 147.8, 141.0, 138.8, 136.8, 134.3, 133.5, 131.3, 129.0, 128.7, 127.4, 122.8, 120.0, 116.5. **ESI-MS**: calculated $C_{23}H_{16}Cl_2NO_2$ $[M+H]^+$, 408.0553; Found 408.0535.

1-(2'-chloro-4'-hydroxy-6-(pyridin-2-yl)-[1,1'-biphenyl]-3-yl)ethanone (**3ba**)



Following general procedure D, the product **3ba** was obtained in 52% yield (33.6 mg, 0.104 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). R_F (Petroleum ether/EtOAc 2:1): 0.17. 1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 5.0 Hz, 1H), 8.06 (dd, J = 8.0, 1.8 Hz, 1H), 7.80 (ddd, J = 9.5, 5.9, 1.7 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.31 (ddd, J = 7.6, 5.0, 1.0 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 6.86 (dd, J = 8.2, 2.1 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 158.0, 155.9, 147.4, 143.3, 138.2, 137.6, 137.3, 134.7, 132.8, 132.0, 130.4, 130.0, 127.7, 124.3, 123.4, 121.0, 120.1, 26.9. **ESI-MS**: calculated $C_{19}H_{15}ClNO_2$ $[M+H]^+$, 324.0786; Found 324.0774.

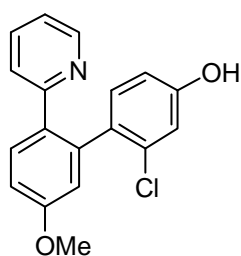
1-(2,2''-dichloro-4,4''-dihydroxy-2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-5'-yl)ethanone (**3ba'**)



Following general procedure D, the product **3ba'** was obtained in 27% yield (24.3 mg, 0.054 mmol), Following general procedure E, The product **3ba'** was obtained in 60% yield (53.9 mg, 0.120 mmol) as

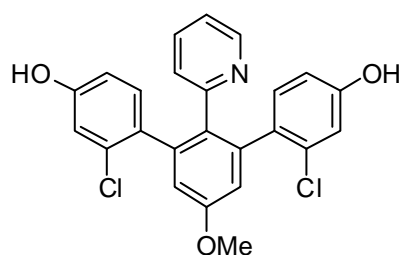
a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.31. ¹H NMR (400 MHz, MeOD-d₄) δ 8.17 (d, *J* = 4.8 Hz, 1H), 7.95 (s, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 6.4 Hz, 4H), 2.64 (s, 3H). ¹³C NMR (101 MHz, MeOD-d₄) δ 199.9, 158.9, 156.3, 148.1, 145.5, 139.6, 137.6, 136.9, 134.8, 133.5, 131.1, 127.8, 127.3, 123.1, 120.1, 116.5, 26.9. **ESI-MS**: calculated C₂₅H₁₈Cl₂NO₃ [M+H]⁺, 450.0658; Found 450.0645.

2-chloro-5'-methoxy-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ca**)



Following general procedure D, the product **3ca** was obtained in 77% yield (48.3 mg, 0.155 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.32. ¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 5.0 Hz, 1H), 7.72 (td, *J* = 7.8, 1.8 Hz, 1H), 7.37 (dd, *J* = 15.9, 8.2 Hz, 2H), 7.22 (ddd, *J* = 7.5, 5.1, 1.0 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.77 (d, *J* = 2.7 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 158.8, 156.1, 146.9, 138.4, 137.9, 134.2, 132.1, 131.9, 131.4, 131.0, 124.2, 122.3, 120.7, 120.1, 117.6, 114.2, 55.5. **ESI-MS**: calculated C₁₈H₁₅ClNO₂ [M+H]⁺, 312.0786; Found 312.0777.

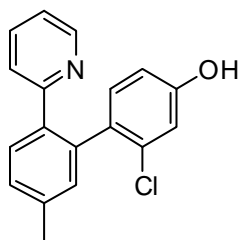
2,2''-dichloro-5'-methoxy-2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**3ca'**)



Following general procedure D, the product **3ca'** was obtained in 22% yield (19.3 mg, 0.044 mmol). Following general procedure E, The product **3ca'** was obtained in 57% yield (50.3 mg, 0.114 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.22. ¹H NMR (400 MHz, MeOD-d₄) δ 8.12 (d, *J* = 4.8 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.95 (m, 1H), 6.90 (d, *J* = 5.6 Hz, 4H), 6.68 – 6.60 (m, 4H), 3.83 (s, 3H). ¹³C NMR (101 MHz, MeOD-d₄) δ 160.3, 159.6, 156.2, 147.8, 140.2, 136.8,

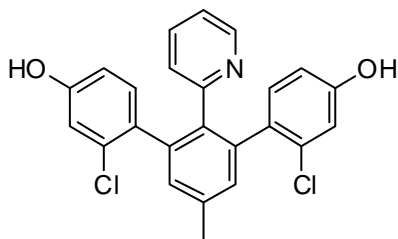
134.4, 133.9, 133.5, 128.7, 127.7, 122.6, 120.0, 116.7, 116.6, 55.8. **ESI-MS**: calculated $C_{24}H_{18}Cl_2NO_3$ $[M+H]^+$, 438.0658; Found 438.0653.

2-chloro-5'-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3da**)



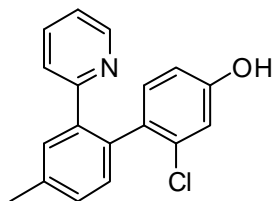
Following general procedure D, the product **3da** was obtained in 47% yield (27.9 mg, 0.094 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.25. 1H NMR (400 MHz, MeOD- d_4) δ 8.44 (dd, J = 4.9, 0.6 Hz, 1H), 7.52 (td, J = 7.8, 1.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.27 (dd, J = 7.8, 1.1 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.06 (d, J = 7.9 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.74 (dd, J = 8.1, 2.1 Hz, 1H), 6.70 (d, J = 2.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, MeOD- d_4) δ 160.6, 156.5, 149.2, 139.5, 138.3, 137.8, 137.5, 134.6, 133.5, 132.8, 130.7, 129.4, 128.7, 125.8, 122.8, 120.4, 116.6, 21.2. **ESI-MS**: calculated $C_{18}H_{15}ClNO$ $[M+H]^+$, 296.0837; Found 296.0827.

2,2''-dichloro-5'-methyl-2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**3da'**)



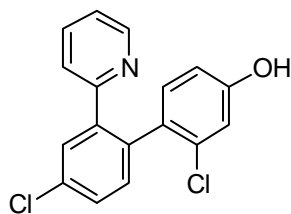
Following general procedure D, the product **3da'** was obtained in 25% yield (21.5 mg, 0.050 mmol). Following general procedure E, The product **3da'** was obtained in 91% yield (76.5 mg, 0.182 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.28. 1H NMR (400 MHz, MeOD- d_4) δ 8.12 (d, J = 4.6 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.17 (s, 2H), 7.09 (d, J = 7.8 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.88 (d, J = 8.1 Hz, 2H), 6.69 – 6.60 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, MeOD- d_4) δ 159.7, 156.2, 147.8, 139.0, 138.7, 138.2, 136.8, 134.2, 133.5, 131.9, 128.8, 127.5, 122.6, 120.0, 116.5, 21.2. **ESI-MS**: calculated $C_{24}H_{18}Cl_2NO_2$ $[M+H]^+$, 422.0709; Found 422.0696.

2-chloro-4'-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ea**)



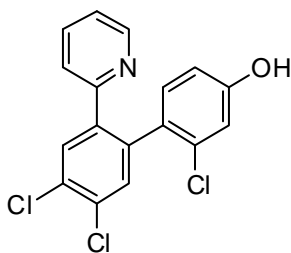
Following general procedure D, the product **3ea** was obtained in 69% yield (40.7 mg, 0.138 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.30. 1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 4.5 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.27 (q, J = 8.7 Hz, 3H), 7.13 (d, J = 7.6 Hz, 1H), 6.99 (s, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.0, 147.0, 139.0, 138.0, 137.9, 134.0, 133.9, 132.6, 132.3, 130.7, 130.6, 129.9, 124.3, 122.7, 120.6, 119.8, 21.2. **ESI-MS**: calculated $C_{18}H_{15}ClNO$ $[M+H]^+$, 296.0837; Found 296.0829.

2,4'-dichloro-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3fa**)



Following general procedure D, the product **3fa** was obtained in 58% yield (37.0 mg, 0.116 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.39. 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 4.7 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 7.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.19 (d, J = 7.9 Hz, 1H), 6.99 (s, 1H), 6.85 (dd, J = 17.9, 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 155.9, 147.3, 140.6, 138.2, 135.5, 134.5, 134.0, 134.0, 132.0, 129.8, 129.6, 129.1, 124.3, 123.2, 120.9, 120.0. **ESI-MS**: calculated $C_{17}H_{12}Cl_2NO$ $[M+H]^+$, 316.0290; Found 316.0280.

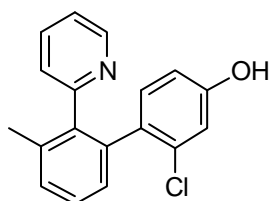
2,4',5'-trichloro-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ga**)



Following general procedure D, the product **3ga** was obtained in 83% yield (58.2 mg, 0.166 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.36. 1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 4.8 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.56 (s, 1H), 7.36 (t, J = 3.6 Hz, 2H), 7.33 – 7.28 (m, 1H), 6.98 (s,

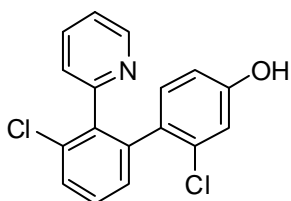
1H), 6.86 (dd, $J = 18.4, 8.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.8, 155.8, 147.4, 138.9, 138.3, 136.9, 134.9, 134.3, 133.2, 132.2, 131.9, 131.5, 128.5, 124.2, 123.4, 121.0, 120.2. **ESI-MS**: calculated $\text{C}_{17}\text{H}_9\text{Cl}_3\text{NO}$ $[\text{M}-\text{H}]^-$, 347.9755; Found 347.9745.

2-chloro-3'-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ha**)



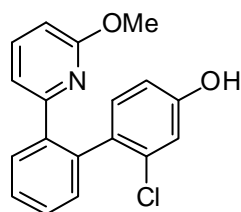
Following general procedure D, the product **3ha** was obtained in 63% yield (37.0 mg, 0.126 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.32. ^1H NMR (400 MHz, CDCl_3) δ 8.49 (d, $J = 4.3$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.24 – 7.19 (m, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 7.09 (d, $J = 7.3$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.86 (s, 1H), 6.77 (d, $J = 7.9$ Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 154.8, 148.0, 139.3, 139.3, 137.1, 136.9, 136.1, 133.9, 131.5, 130.1, 129.0, 128.8, 125.15, 122.8, 120.6, 119.3, 20.6. **ESI-MS**: calculated $\text{C}_{18}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$, 296.0837; Found 296.0830.

2,3'-dichloro-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ia**)



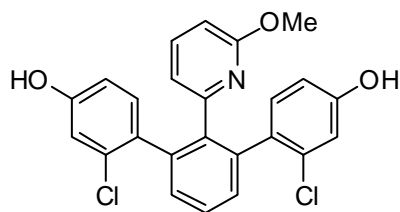
Following general procedure D, the product **3ia** was obtained in 95% yield (60.0 mg, 0.190 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.38. ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, $J = 4.3$ Hz, 1H), 7.70 (t, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 7.9$ Hz, 1H), 7.33 (d, $J = 7.4$ Hz, 1H), 7.25 (s, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.94 – 6.82 (m, 2H), 6.78 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.0, 155.0, 147.6, 139.5, 137.8, 137.2, 134.4, 133.2, 131.3, 130.3, 129.9, 129.4, 126.0, 123.5, 120.8, 120.0. **ESI-MS**: calculated $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{NO}$ $[\text{M}+\text{H}]^+$, 316.0290; Found 316.0278.

2-chloro-2'-(6-methoxypyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ja**)



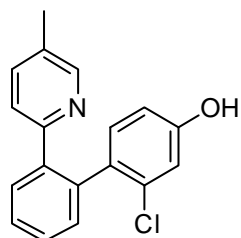
Following general procedure D, the product **3ja** was obtained in 89% yield (55.4 mg, 0.178 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.31. ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.43 (m, 4H), 7.33 – 7.27 (m, 1H), 7.12 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.1 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.3, 156.5, 154.1, 140.1, 139.3, 135.2, 133.9, 131.8, 131.4, 130.4, 129.1, 129.0, 128.5, 120.9, 117.7, 116.8, 109.6, 53.8. **ESI-MS**: calculated C₁₈H₁₃ClNO₂ [M-H]⁻, 310.0640; Found 310.0632.

2,2''-dichloro-2'-(6-methoxypyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**3ja'**)



Following general procedure D, the product **3ja'** was obtained in 9% yield (7.9 mg, 0.018 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.27. ¹H NMR (400 MHz, MeOD-d₄) δ 7.49 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.69 (s, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 6.54 (d, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 8.3 Hz, 1H), 3.56 (s, 3H). ¹³C NMR (101 MHz, MeOD-d₄) δ 164.1, 157.1, 156.4, 141.4, 138.8, 138.7, 134.1, 133.3, 131.5, 129.3, 128.6, 119.9, 119.8, 116.4, 108.9, 53.6. **ESI-MS**: calculated C₂₄H₁₆Cl₂NO₃ [M-H]⁻, 436.0513; Found 436.0506.

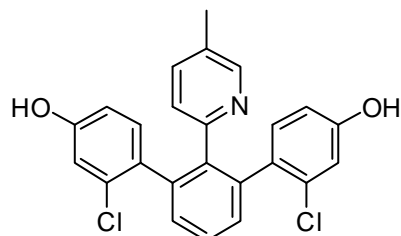
2-chloro-2'-(5-methylpyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ka**)



Following general procedure D, the product **3ka** was obtained in 83% yield (49.0 mg, 0.166 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.24. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.2, 156.1, 147.2,

139.1, 138.7, 137.0, 134.1, 132.7, 132.6, 132.2, 131.1, 129.9, 129.0, 128.1, 123.8, 120.6, 120.1, 18.2. **ESI-MS**: calculated $C_{18}H_{15}ClNO$ $[M+H]^+$, 296.0837; Found 296.0828.

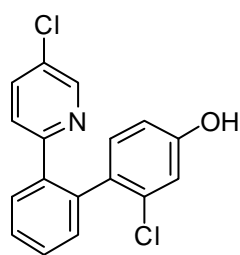
2,2''-dichloro-2'-(5-methylpyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (3ka')



Following general procedure E, the product **3ka'** was obtained in 66% yield (55.6 mg, 0.132 mmol) as a brown solid after column chromatography (eluent = dichloromethane v/v). **R_F** (dichloromethane): 0.23.

1H NMR (400 MHz, MeOD- d_4) δ 8.00 (s, 1H), 7.51 – 7.44 (m, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.26 (dd, J = 8.0, 1.5 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 6.88 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 1.9 Hz, 2H), 6.64 (dd, J = 8.1, 1.9 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, MeOD- d_4) δ 156.7, 156.3, 148.0, 140.8, 139.0, 137.6, 134.3, 133.5, 132.8, 131.3, 128.9, 126.8, 120.0, 116.6, 18.0. **ESI-MS**: calculated $C_{24}H_{18}Cl_2NO_2$ $[M+H]^+$, 422.0709; Found 422.0705.

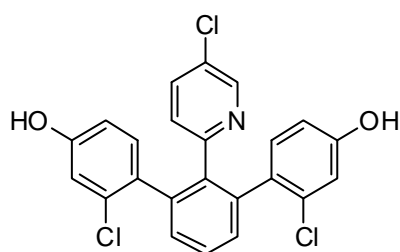
2-chloro-2'-(5-chloropyridin-2-yl)-[1,1'-biphenyl]-4-ol (3la)



Following general procedure D, the product **3la** was obtained in 60% yield (38.0 mg, 0.120 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.35. 1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 2.7 Hz, 3H),

7.26 (t, J = 8.3 Hz, 2H), 6.97 (s, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 146.8, 146.8, 138.5, 137.3, 136.2, 134.4, 132.4, 132.0, 131.3, 130.0, 129.5, 128.5, 124.9, 121.0, 119.1, 119.0. **ESI-MS**: calculated $C_{17}H_{12}Cl_2NO$ $[M+H]^+$, 316.0290; Found 316.0282.

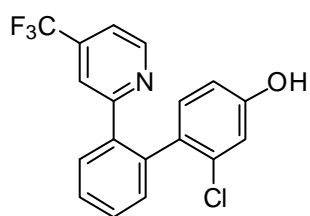
2,2''-dichloro-2'-(5-chloropyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (3la')



Following general procedure D, the product **3la'** was

obtained in 30% yield (26.7 mg, 0.060 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.20. ¹H NMR (400 MHz, MeOD-d₄) δ 8.12 (d, *J* = 2.2 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.46 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 8.1, 1.9 Hz, 2H), 6.66 (d, *J* = 1.8 Hz, 2H). ¹³C NMR (101 MHz, MeOD-d₄) δ 158.5, 156.2, 146.8, 140.1, 138.9, 136.3, 134.5, 133.6, 131.3, 131.0, 129.3, 128.5, 128.4, 120.1, 116.3. **ESI-MS**: calculated C₂₃H₁₅Cl₃NO₂ [M+H]⁺, 442.0163; Found 442.0169.

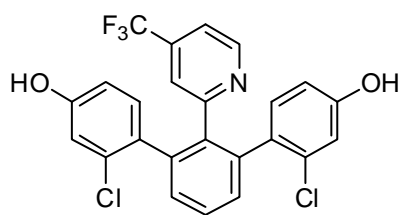
2-chloro-2'-(4-(trifluoromethyl)pyridin-2-yl)-[1,1'-biphenyl]-4-ol (**3ma**)



Following general procedure D, the product **3ma** was obtained in 76% yield (53.1 mg, 0.152 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.28.

¹H NMR (400 MHz, MeOD-d₄) δ 8.71 (d, *J* = 5.1 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.53 – 7.44 (m, 3H), 7.39 (ddd, *J* = 6.4, 3.4, 1.6 Hz, 1H), 7.32 (s, 1H), 7.02 (dt, *J* = 8.1, 1.7 Hz, 1H), 6.81 (ddd, *J* = 8.1, 3.6, 1.7 Hz, 1H), 6.69 (dd, *J* = 3.5, 1.7 Hz, 1H). ¹⁹F NMR (376 MHz, MeOD-d₄) δ -66.6. ¹³C NMR (101 MHz, MeOD-d₄) δ 162.2, 156.2, 151.0, 140.0, 139.1 (q, *J* = 33.9 Hz), 138.3, 135.1, 133.4, 132.2, 130.5, 130.3, 128.9, 128.0, 124.1 (q, *J* = 272.4 Hz), 121.1 (q, *J* = 3.5 Hz), 120.6, 118.2 (q, *J* = 3.3 Hz), 116.3. **ESI-MS**: calculated C₁₈H₁₂ClF₃NO [M+H]⁺, 350.0554; Found 350.0543.

2,2''-dichloro-2'-(4-(trifluoromethyl)pyridin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**3ma'**)

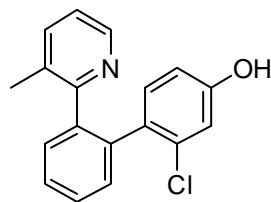


Following general procedure D, the product **3ma'** was obtained in 22% yield (21.5 mg, 0.044 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.25.

¹H NMR (400 MHz, MeOD-d₄) δ 8.34 (d, *J* = 5.2 Hz, 1H), 7.55 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 3H), 7.28 (dd, *J* = 5.2, 1.1 Hz, 1H),

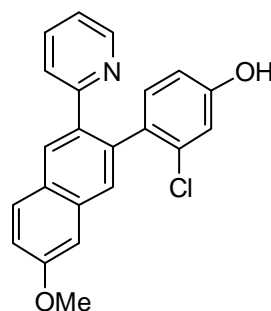
6.97 (d, $J = 7.7$ Hz, 2H), 6.71 (dd, $J = 8.1, 1.8$ Hz, 2H), 6.62 (d, $J = 1.8$ Hz, 2H). ^{19}F NMR (376 MHz, MeOD- d_4) δ -66.5. ^{13}C NMR (101 MHz, MeOD- d_4) δ 161.8, 156.1, 149.3, 140.1, 138.9, 138.2 (q, $J = 33.7$ Hz), 134.7, 133.6, 131.3, 129.7, 128.2, 124.1 (q, $J = 272.6$ Hz), 123.4 (q, $J = 3.6$ Hz), 120.1, 117.8 (q, $J = 3.3$ Hz), 116.1. **ESI-MS**: calculated $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{F}_3\text{NO}_2$ $[\text{M}-\text{H}]^-$, 474.0281; Found 474.0270.

2-chloro-2'-(3-methylpyridin-2-yl)-[1,1'-biphenyl]-4-ol (3na)



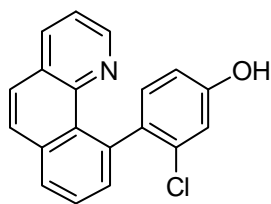
Following general procedure D, the product **3na** was obtained in 58% yield (34.1 mg, 0.116 mmol) as a brown solid after column chromatography (eluent = dichloromethane/EtOAc 20:1 v/v). R_F (dichloromethane/EtOAc 20:1): 0.24. ^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.55 (m, 1H), 7.53 – 7.44 (m, 3H), 7.32 – 7.27 (m, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 6.92 (d, $J = 2.0$ Hz, 1H), 6.88 – 6.79 (m, 2H), 6.63 (d, $J = 8.3$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.3, 155.2, 144.7, 139.4, 138.7, 136.9, 134.1, 132.1, 131.9, 131.3, 130.4, 129.2, 128.8, 127.8, 123.3, 120.7, 119.9, 19.4. **ESI-MS**: calculated $\text{C}_{18}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$, 296.0837; Found 296.0830.

3-chloro-4-(7-methoxy-3-(pyridin-2-yl)naphthalen-2-yl)phenol (3oa)



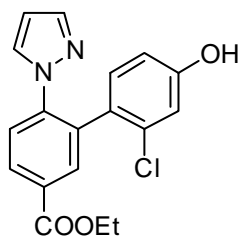
Following general procedure D, the product **3oa** was obtained in 86% yield (62.2 mg, 0.172 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 3:1 v/v). R_F (Petroleum ether /EtOAc 2:1): 0.44. ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, $J = 4.6$ Hz, 1H), 7.86 (s, 1H), 7.79 (d, $J = 8.9$ Hz, 1H), 7.73 (t, $J = 7.7$ Hz, 1H), 7.62 (s, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.25 (t, $J = 6.2$ Hz, 1H), 7.20 (d, $J = 9.0$ Hz, 1H), 7.12 (s, 1H), 7.02 (s, 1H), 6.99 (d, $J = 8.1$ Hz, 1H), 6.85 (d, $J = 8.1$ Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.0, 158.7, 156.1, 147.1, 138.0, 135.1, 135.1, 134.6, 134.2, 132.4, 130.8, 130.6, 129.5, 128.2, 124.4, 122.5, 120.6, 120.0, 119.8, 105.5, 55.5. **ESI-MS**: calculated $\text{C}_{22}\text{H}_{17}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$, 362.0942; Found 362.0932.

4-(benzo[*h*]quinolin-10-yl)-3-chlorophenol (3pa)



Following general procedure D, the product **3pa** was obtained in 88% yield (53.9 mg, 0.176 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 8:1 v/v). **R_F** (Petroleum ether /EtOAc 6:1): 0.31. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (d, *J* = 4.1 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 6.2 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.13 (s, 1H), 7.02 – 6.90 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.6, 147.6, 146.3, 136.2, 135.5, 134.8, 133.7, 133.4, 133.2, 131.4, 129.6, 129.1, 128.9, 127.9, 127.5, 125.8, 121.7, 120.6, 117.5. **ESI-MS**: calculated C₁₉H₁₃ClNO [M+H]⁺, 306.0680; Found 306.0669.

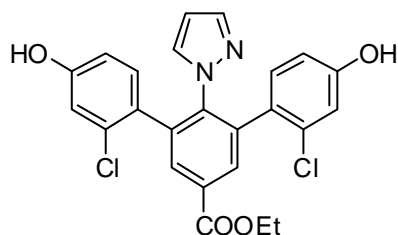
Ethyl 2'-chloro-4'-hydroxy-6-(1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-3-carboxylate (4ca)



Following general procedure D, the product **4ca** was obtained in 37% yield (25.3 mg, 0.074 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.37. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.3 Hz, 1H), 8.02 (s, 1H), 7.65 – 7.49 (m, 2H), 7.35 (s, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 9.6 Hz, 2H), 6.30 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.7, 154.9, 142.3, 140.8, 135.1, 134.2, 132.4, 131.6, 130.8, 130.3, 125.6, 125.3, 121.2, 118.3, 107.5, 61.6, 14.4. **ESI-MS**: calculated C₁₈H₁₄ClN₂O₃ [M-H]⁻, 341.0698; Found 341.0685.

ethyl

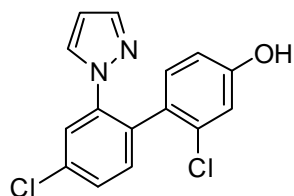
2,2''-dichloro-4,4''-dihydroxy-2'-(1*H*-pyrazol-1-yl)-[1,1':3,1''-terphenyl]-5'-carboxylate (4ca')



Following general procedure D, the product **4ca'** was obtained in 22% yield (20.3 mg, 0.044 mmol),
Following general procedure E, The product **4ca'**

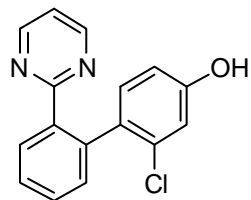
was obtained in 91% yield (85.0mg, 0.182 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.22. ¹H NMR (400 MHz, MeOD-d₄) δ 8.05 (s, 2H), 7.34 (s, 1H), 7.28 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.06 (s, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, MeOD-d₄) δ 166.9, 156.6, 142.9, 140.3, 138.1, 135.2, 133.8, 132.9, 132.4, 131.4, 125.0, 120.1, 116.3, 106.4, 62.5, 14.5. **ESI-MS**: calculated C₂₄H₁₉Cl₂N₂O₄ [M+H]⁺, 469.0716; Found 469.0703.

2,4'-dichloro-2'-(1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-4-ol (**4da**)



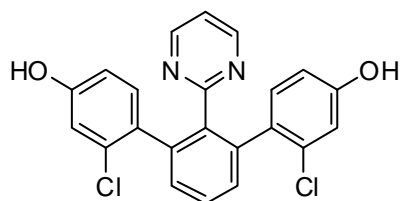
Following general procedure D, the product **4da** was obtained in 32% yield (19.7 mg, 0.064 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 8:1 v/v). **R_F** (Petroleum ether /EtOAc 8:1): 0.28. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 1H), 7.47 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.35 (s, 1H), 7.25 (d, *J* = 10.2 Hz, 1H), 6.88 (d, *J* = 12.6 Hz, 3H), 6.30 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 140.6, 139.8, 135.1, 134.7, 133.9, 131.5, 131.5, 130.8, 129.0, 126.2, 125.6, 121.3, 119.1, 107.6. **ESI-MS**: calculated C₁₅H₉Cl₂N₂O [M-H]⁻, 303.0097; Found 303.0092.

2-chloro-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5aa**)



Following general procedure D, the product **5aa** was obtained in 38% yield (21.5 mg, 0.076 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.25. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 5.0 Hz, 2H), 7.93 – 7.77 (m, 1H), 7.57 – 7.50 (m, 2H), 7.26 (dt, *J* = 7.4, 4.2 Hz, 2H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.86 (dd, *J* = 8.2, 2.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 157.0, 155.4, 138.0, 136.9, 134.2, 132.7, 132.3, 130.5, 130.3, 130.2, 128.4, 120.9, 119.4, 119.3. **ESI-MS**: calculated C₁₆H₁₂ClN₂O [M+H]⁺, 283.0633; Found 283.0621.

2,2''-dichloro-2'-(pyrimidin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**5aa'**)



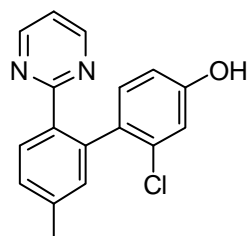
Following general procedure D, the product **5aa'** was obtained in 37% yield (30.6 mg, 0.074 mmol),

Following general procedure E, the product **5aa'** was obtained in 99% yield (80.9 mg, 0.198 mmol) as a

brown solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v).

R_F (Petroleum ether/EtOAc 2:1): 0.33. ¹H NMR (400 MHz, MeOD-d₄) δ 8.43 (d, *J* = 4.8 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 4.8 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 6.65 (s, 2H). ¹³C NMR (101 MHz, MeOD-d₄) δ 168.3, 157.0, 156.3, 139.7, 138.8, 134.4, 133.5, 131.4, 129.7, 128.3, 120.1, 119.9, 116.3. **ESI-MS**: calculated C₂₂H₁₅Cl₂N₂O₂ [M+H]⁺, 409.0505; Found 409.0501.

2-chloro-5'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5ba**)

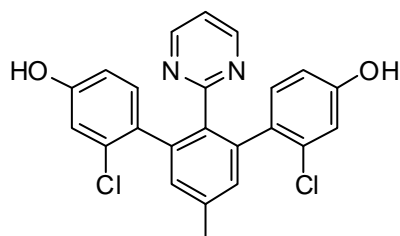


Following general procedure D, the product **5ba** was obtained in 71% yield (42.0 mg, 0.142 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F**

(Petroleum ether /EtOAc 2:1): 0.22. ¹H NMR (400 MHz, CDCl₃)

δ 8.71 (d, *J* = 4.9 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 4.9 Hz, 1H), 7.06 (s, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 156.9, 155.5, 140.4, 136.8, 135.3, 134.1, 133.3, 132.3, 130.6, 129.1, 120.9, 119.3, 119.1, 21.3. **ESI-MS**: calculated C₁₇H₁₄ClN₂O [M+H]⁺, 297.0789; Found 297.0776.

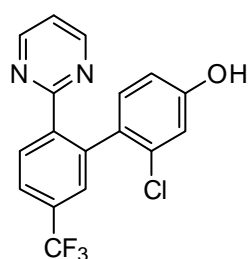
2,2''-dichloro-5'-methyl-2'-(pyrimidin-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**5ba'**)



Following general procedure D, the product **5ba'** was obtained in 25% yield (21.2 mg, 0.050 mmol),

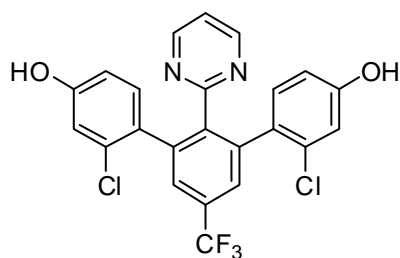
Following general procedure E, the product **5ba'** was obtained in 83% yield (70.3 mg, 0.166 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.40. ¹H NMR (400 MHz, MeOD-d₄) δ 8.40 (d, *J* = 4.9 Hz, 2H), 7.22 (s, 2H), 7.09 (t, *J* = 5.0 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, MeOD-d₄) δ 168.4, 157.0, 156.2, 139.8, 138.7, 137.0, 134.3, 133.5, 132.0, 128.5, 120.1, 119.7, 116.4, 21.3. **ESI-MS**: calculated C₂₃H₁₇Cl₂N₂O₂ [M+H]⁺, 423.0662; Found 423.0649.

2-chloro-2'-(pyrimidin-2-yl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (**5ca**)



Following general procedure D, the product **5ca** was obtained in 56% yield (39.2 mg, 0.112 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.26. ¹H NMR (400 MHz, MeOD-d₄) δ 8.68 (d, *J* = 4.9 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.67 (s, 1H), 7.34 (t, *J* = 4.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.64 (s, 1H). ¹⁹F NMR (376 MHz, MeOD-d₄) δ -64.1. ¹³C NMR (101 MHz, MeOD-d₄) δ 167.7, 158.2, 156.1, 143.4, 139.8, 135.1, 133.0, 132.3 (q, *J* = 32.4 Hz), 131.8, 129.1 (q, *J* = 3.8 Hz), 127.5, 125.5 (q, *J* = 271.6 Hz), 125.1 (q, *J* = 3.8 Hz), 120.7, 120.7, 116.0. **ESI-MS**: calculated C₁₇H₁₁ClF₃N₂O [M+H]⁺, 351.0507; Found 351.0492.

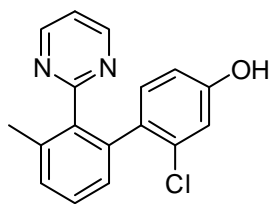
2,2''-dichloro-2'-(pyrimidin-2-yl)-5'-(trifluoromethyl)-[1,1':3',1''-terphenyl]-4,4''-diol (**5ca'**)



Following general procedure D, the product **5ca'** was obtained in 19% yield (18.4 mg, 0.038 mmol). Following general procedure E, the product **5ca'** was obtained in 28% yield (27.2 mg, 0.056 mmol) as a brown solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.34. ¹H NMR

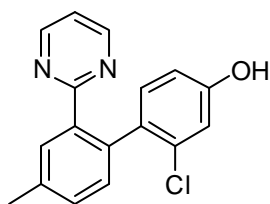
(400 MHz, MeOD- d_4) δ 8.47 (d, J = 4.9 Hz, 2H), 7.69 (s, 2H), 7.16 (t, J = 4.9 Hz, 1H), 6.95 (d, J = 7.9 Hz, 2H), 6.69 (d, J = 9.2 Hz, 4H). ^{19}F NMR (376 MHz, MeOD- d_4) δ -64.0. ^{13}C NMR (101 MHz, MeOD- d_4) δ 167.3, 157.2, 156.3, 143.1, 140.1, 135.1, 133.4, 131.4 (q, J = 32.6 Hz), 127.9 (q, J = 3.2 Hz), 126.9, 125.4 (q, J = 271.8 Hz), 120.3, 120.2, 116.4. **ESI-MS**: calculated $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}_2\text{F}_3\text{Cl}_2$ $[\text{M}+\text{H}]^+$, 477.0379; Found 477.0360.

2-chloro-3'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5da**)



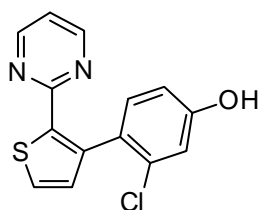
Following general procedure D, the product **5da** was obtained in 98% yield (58.1 mg, 0.196 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 2:1): 0.31. ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, J = 4.9 Hz, 2H), 7.98 (s, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 4.9 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.76 (d, J = 8.1 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.2, 156.7, 154.3, 138.4, 136.4, 136.1, 133.9, 131.8, 130.4, 129.3, 129.1, 128.9, 120.8, 119.5, 118.5, 20.2. **ESI-MS**: calculated $\text{C}_{17}\text{H}_{14}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$, 297.0789; Found 297.0783.

2-chloro-4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5ea**)



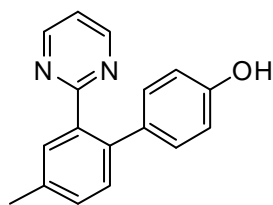
Following general procedure D, the product **5ea** was obtained in 86% yield (51.2 mg, 0.172 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 2:1): 0.31. ^1H NMR (400 MHz, CDCl_3) δ 9.15 (s, 1H), 8.70 (d, J = 4.9 Hz, 2H), 7.65 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.21 (t, J = 4.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 156.9, 155.4, 138.2, 137.7, 134.0, 133.9, 132.6, 132.4, 131.0, 130.9, 130.1, 120.8, 119.3, 119.1, 21.1. **ESI-MS**: calculated $\text{C}_{17}\text{H}_{12}\text{ClN}_2\text{O}$ $[\text{M}-\text{H}]^-$, 295.0644; Found 295.0641.

3-chloro-4-(2-(pyrimidin-2-yl)thiophen-3-yl)phenol (**5fa**)



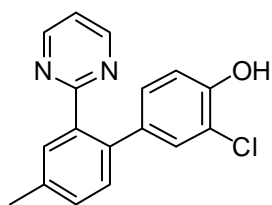
Following general procedure D, the product **5fa** was obtained in 80% yield (46.1 mg, 0.160 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.29. ¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 8.73 (d, *J* = 4.1 Hz, 2H), 7.56 (d, *J* = 4.3 Hz, 1H), 7.18 (d, *J* = 3.9 Hz, 1H), 7.15 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 4.3 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 161.5, 157.4, 155.9, 139.0, 137.1, 134.8, 134.2, 132.5, 129.3, 125.7, 121.1, 120.7, 118.5. **ESI-MS**: calculated C₁₄H₈ClN₂OS [M-H]⁻, 287.0051; Found 287.0044.

4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5eb**)



Following general procedure D, the product **5eb** was obtained in 58% yield (30.4mg, 0.116 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 4.9 Hz, 2H), 7.51 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 156.9, 155.2, 138.3, 137.3, 136.8, 132.9, 131.1, 130.6, 130.5, 130.3, 118.7, 115.3, 21.1. **ESI-MS**: calculated C₁₇H₁₅N₂O [M+H]⁺, 263.1179; Found 263.1170.

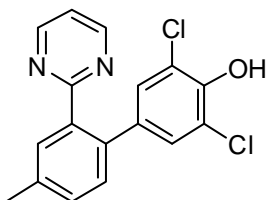
3-chloro-4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5ec**)



Following general procedure D, the product **5ec** was obtained in 75% yield (44.7mg, 0.150 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.26. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 4.9 Hz, 2H), 7.59 (s, 1H), 7.31 (s, 2H), 7.14 (dd, *J* = 5.2, 3.6 Hz, 2H), 6.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.1, 157.0, 150.1, 137.8, 137.5, 136.9, 135.0, 131.3,

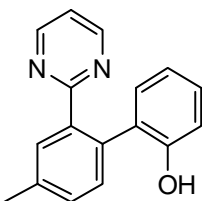
130.6, 130.4, 129.5, 129.3, 119.6, 118.6, 115.7, 21.1. **ESI-MS**: calculated $C_{17}H_{12}ClN_2O$ $[M-H]^-$, 295.0644; Found 295.0641.

3,5-dichloro-4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-4-ol (**5ed**)



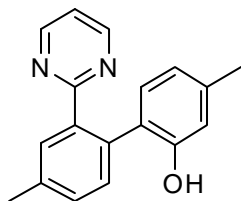
Following general procedure D, the product **5ed** was obtained in 85% yield (56.6mg, 0.170 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.23. 1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.9 Hz, 2H), 7.62 (s, 1H), 7.29 (q, J = 8.1 Hz, 2H), 7.16 (t, J = 4.9 Hz, 1H), 7.00 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 157.0, 146.5, 138.0, 137.8, 135.8, 135.2, 131.4, 130.5, 130.5, 128.9, 120.6, 118.8, 21.2. **ESI-MS**: calculated $C_{17}H_{11}Cl_2N_2O$ $[M-H]^-$, 329.0254; Found 329.0249.

4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-2-ol (**5ee**)



Following general procedure D, the product **5ee** was obtained in 43% yield (22.4mg, 0.086 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.26. 1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.9 Hz, 2H), 7.63 (d, J = 10.5 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.01 – 6.95 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 156.8, 154.4, 137.9, 137.8, 135.0, 132.6, 131.6, 131.5, 130.9, 130.8, 128.9, 120.7, 119.2, 118.7, 21.1. **ESI-MS**: calculated $C_{17}H_{15}N_2O$ $[M+H]^+$, 263.1179; Found 263.1173.

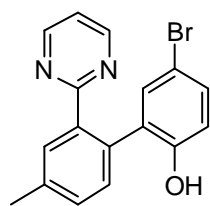
4,4'-dimethyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-2-ol (**5ef**)



Following general procedure D, the product **5ef** was obtained in 98% yield (54.4mg, 0.196 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.29. 1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 5.0 Hz, 2H), 7.63 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.22 – 7.12 (m, 2H),

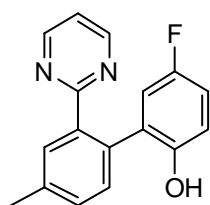
6.87 (d, $J = 7.7$ Hz, 1H), 6.81 (s, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 156.8, 154.2, 138.9, 137.9, 137.6, 135.1, 132.8, 131.4, 130.8, 130.7, 128.4, 121.5, 119.3, 119.1, 21.1, 21.1. **ESI-MS**: calculated $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}$ $[\text{M}-\text{H}]^-$, 275.1190; Found 275.1183.

5-bromo-4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-2-ol (**5eg**)



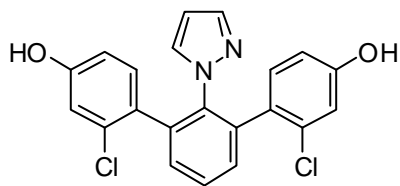
Following general procedure D, the product **5eg** was obtained in 53% yield (36.1mg, 0.106 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 5:2 v/v). R_F (Petroleum ether /EtOAc 2:1): 0.29. ^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, $J = 5.0$ Hz, 2H), 7.66 (s, 1H), 7.35 (d, $J = 7.8$ Hz, 1H), 7.29 (dd, $J = 8.6$, 2.5 Hz, 1H), 7.23 (t, $J = 5.0$ Hz, 1H), 7.16 (d, $J = 7.8$ Hz, 1H), 7.11 (d, $J = 2.5$ Hz, 1H), 6.87 (d, $J = 8.6$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 156.9, 154.0, 138.4, 137.6, 134.0, 133.7, 133.7, 132.5, 131.8, 131.0, 131.0, 120.8, 119.4, 112.7, 21.2. **ESI-MS**: calculated $\text{C}_{17}\text{H}_{12}\text{BrN}_2\text{O}$ $[\text{M}-\text{H}]^-$, 339.0138; Found 339.0128.

5-fluoro-4'-methyl-2'-(pyrimidin-2-yl)-[1,1'-biphenyl]-2-ol (**5eh**)



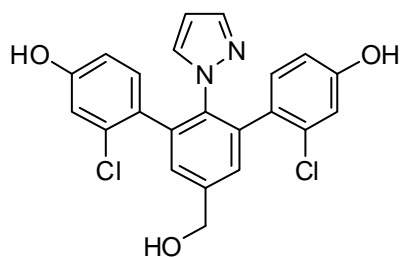
Following general procedure D, the product **5eh** was obtained in 65% yield (36.7mg, 0.130 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). R_F (Petroleum ether /EtOAc 4:1): 0.26. ^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, $J = 5.0$ Hz, 2H), 7.65 (s, 1H), 7.34 (dd, $J = 7.8$, 1.1 Hz, 1H), 7.22 (t, $J = 5.0$ Hz, 1H), 7.18 (d, $J = 7.8$ Hz, 1H), 6.96 – 6.83 (m, 2H), 6.70 (dd, $J = 9.0$, 2.9 Hz, 1H), 2.46 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -124.2. ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 156.9, 156.8 (d, $J = 239.6$ Hz), 150.7 (d, $J = 2.3$ Hz), 138.3, 137.6, 134.1, 132.7 (d, $J = 7.8$ Hz), 132.3, 131.0, 130.9, 119.8 (d, $J = 8.4$ Hz), 119.3, 117.7 (d, $J = 22.9$ Hz), 115.2 (d, $J = 22.5$ Hz), 21.1. **ESI-MS**: calculated $\text{C}_{17}\text{H}_{14}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$, 281.1085; Found 281.1077.

2,2''-dichloro-2'-(1H-pyrazol-1-yl)-[1,1':3',1''-terphenyl]-4,4''-diol (**4aa'**)



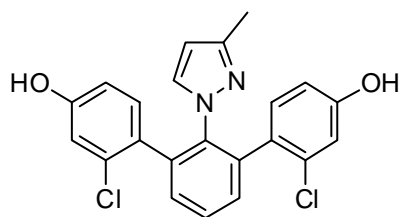
Following general procedure E, the product **4aa'** was obtained in 76% yield (60.5 mg, 0.152 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.21. ¹H NMR (400 MHz, MeOD-d₄) δ 7.54 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.35 (s, 1H), 7.24 (s, 1H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 6.01 (d, *J* = 1.3 Hz, 1H). ¹³C NMR (101 MHz, MeOD-d₄) δ 156.6, 139.9, 139.4, 137.9, 134.8, 134.0, 132.6, 132.1, 129.7, 125.9, 120.1, 116.4, 106.1. **ESI-MS**: calculated C₂₁H₁₃Cl₂N₂O₂ [M-H]⁻, 395.0360; Found 395.0364.

2,2''-dichloro-5'-(hydroxymethyl)-2''-(1H-pyrazol-1-yl)-[1,1':3,1''-terphenyl]-4,4''-diol (4ba')



Following general procedure E, the product **4ba'** was obtained in 92% yield (78.4 mg, 0.184 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 1:1 v/v). **R_F** (Petroleum ether /EtOAc 1:1): 0.22. ¹H NMR (400 MHz, MeOD-d₄) δ 7.42 (s, 2H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.24 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 2H), 6.66 (d, *J* = 8.1 Hz, 2H), 6.01 (s, 1H), 4.73 (s, 2H). ¹³C NMR (101 MHz, MeOD-d₄) δ 156.5, 143.4, 139.8, 138.3, 137.8, 134.8, 134.0, 132.6, 130.1, 125.9, 120.0, 116.3, 105.9, 64.4. **ESI-MS**: calculated C₂₁H₁₂Cl₂N₂O₂ [M-H]⁻, 425.0465; Found 425.0460.

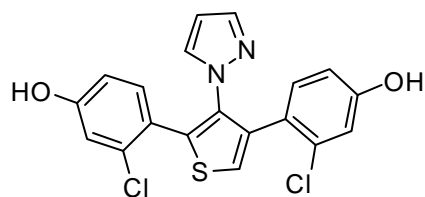
2,2''-dichloro-2''-(3-methyl-1H-pyrazol-1-yl)-[1,1':3,1''-terphenyl]-4,4''-diol (4ea')



Following general procedure E, the product **4ea'** was obtained in 75% yield (61.6mg, 0.150 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.21. ¹H NMR (400 MHz, MeOD-d₄) δ 7.52 (t, *J* = 7.6 Hz, 1H),

7.40 (d, $J = 7.7$ Hz, 2H), 7.21 (s, 1H), 6.89 (d, $J = 8.1$ Hz, 2H), 6.75 (s, 2H), 6.67 (d, $J = 8.1$ Hz, 2H), 5.79 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, MeOD- d_4) δ 156.5, 149.4, 139.4, 137.9, 134.7, 134.7, 132.6, 132.0, 129.4, 126.0, 119.9, 116.4, 105.8, 12.9. **ESI-MS**: calculated $\text{C}_{22}\text{H}_{15}\text{Cl}_2\text{N}_2\text{O}_2$ $[\text{M}-\text{H}]^-$, 409.0516; Found 409.0507.

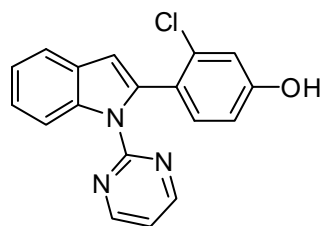
4,4'-(3-(1H-pyrazol-1-yl)thiophene-2,4-diyl)bis(3-chlorophenol) (4fa')



Following general procedure E, the product **4fa'** was obtained in 91% yield (73.4mg, 0.182 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F**

(Petroleum ether /EtOAc 4:1): 0.19. ^1H NMR (400 MHz, DMSO- d_6) δ 10.51 (s, 1H), 9.99 (s, 1H), 7.69 (s, 1H), 7.49 (s, 2H), 6.90 (s, 1H), 6.83 (s, 1H), 6.79 – 6.57 (m, 4H), 6.24 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.0, 155.8, 139.8, 134.8, 133.6, 133.1, 132.3, 132.0, 131.9, 131.1, 131.1, 124.4, 120.6, 118.8, 118.4, 117.7, 115.4, 115.1, 106.1. **ESI-MS**: calculated $\text{C}_{19}\text{H}_{11}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$ $[\text{M}-\text{H}]^-$, 400.9924; Found 400.9911.

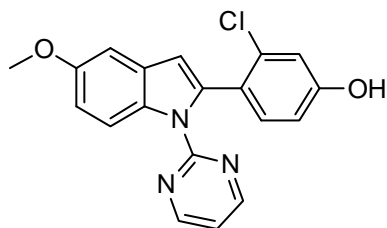
3-chloro-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (6aa)



Following general procedure F, the product **6aa** was obtained in 66% yield (42.7mg, 0.132 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 8:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1):

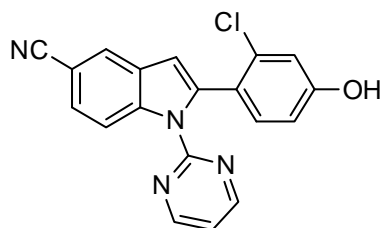
0.44. ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 4.8$ Hz, 2H), 8.16 (d, $J = 8.3$ Hz, 1H), 7.99 (s, 1H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 4.8$ Hz, 1H), 7.08 – 7.03 (m, 2H), 6.88 (dd, $J = 8.1, 1.7$ Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 157.1, 155.9, 137.2, 135.5, 135.0, 133.1, 129.0, 124.1, 122.6, 121.4, 120.9, 120.8, 118.4, 118.0, 113.3, 110.8. **ESI-MS**: calculated $\text{C}_{18}\text{H}_{11}\text{ClN}_3\text{O}$ $[\text{M}-\text{H}]^-$, 320.0596; Found 320.0589.

3-chloro-4-(5-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (6ba)



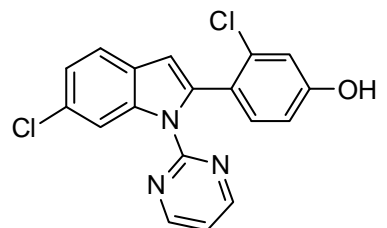
Following general procedure F, the product **6ba** was obtained in 32% yield (22.4mg, 0.064 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 6:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.39. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 4.9 Hz, 2H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.99 (s, 1H), 7.13 (t, *J* = 4.9 Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 7.05 (dd, *J* = 6.1, 5.2 Hz, 2H), 6.96 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.61 (s, 1H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 157.2, 156.0, 155.9, 135.5, 133.1, 132.1, 129.8, 121.6, 120.8, 118.4, 117.7, 114.6, 113.6, 110.9, 102.7, 55.9. **ESI-MS**: calculated C₁₉H₁₃ClN₃O₂ [M-H]⁻, 350.0702; Found 350.0691.

2-(2-chloro-4-hydroxyphenyl)-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (**6ca**)



Following general procedure F, the product **6ca** was obtained in 22% yield (15.6mg, 0.044 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.27. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 4.9 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.99 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.28 (t, *J* = 5.3 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.02 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.75 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 156.6, 155.5, 138.7, 137.8, 136.1, 132.9, 128.8, 126.9, 125.9, 121.2, 120.4, 120.1, 118.9, 118.5, 114.3, 110.1, 105.6. **ESI-MS**: calculated C₁₉H₁₀ClN₄O [M-H]⁻, 345.0549; Found 345.0535.

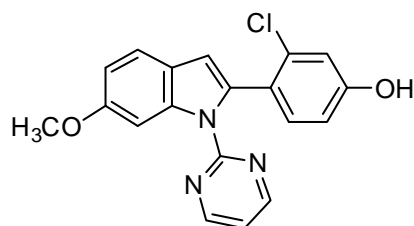
3-chloro-4-(6-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (**6da**)



Following general procedure F, the product **6da** was obtained in 87% yield (62.3mg, 0.174 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.29. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 4.8 Hz, 2H), 8.20 (s, 1H), 7.79 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 9.8, 4.9 Hz, 2H), 7.07 – 7.02

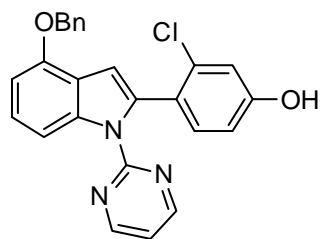
(m, 2H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.66 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 157.8, 156.9, 155.7, 137.5, 135.8, 132.9, 130.0, 127.5, 123.2, 121.6, 121.0, 120.9, 118.4, 118.3, 113.7, 110.5. **ESI-MS**: calculated $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{N}_3\text{O}$ $[\text{M-H}]^-$, 354.0206; Found 354.0199.

3-chloro-4-(6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (**6ea**)



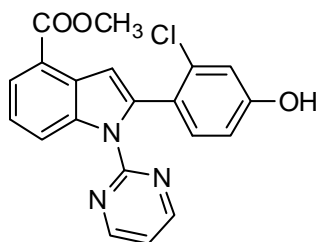
Following general procedure F, the product **6ea** was obtained in 58% yield (40.7mg, 0.116 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 2:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.36. ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 4.9$ Hz, 2H), 7.79 – 7.71 (m, 2H), 7.52 (d, $J = 8.6$ Hz, 1H), 7.16 (t, $J = 4.9$ Hz, 1H), 7.03 (d, $J = 2.4$ Hz, 1H), 7.01 (s, 1H), 6.93 (dd, $J = 8.6, 2.2$ Hz, 1H), 6.86 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.63 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 157.8, 157.3, 155.9, 138.2, 135.3, 133.7, 132.9, 123.1, 121.5, 121.3, 120.6, 118.1, 117.8, 111.8, 110.8, 97.6, 55.8. **ESI-MS**: calculated $\text{C}_{19}\text{H}_{13}\text{ClN}_3\text{O}_2$ $[\text{M-H}]^-$, 350.0702; Found 350.0693.

4-(4-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)-3-chlorophenol (**6fa**)



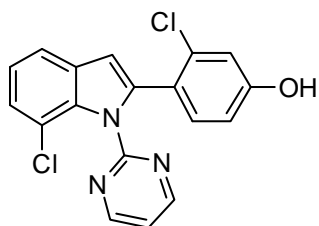
Following general procedure F, the product **6fa** was obtained in 57% yield (49.2mg, 0.114 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 6:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.43. ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 2.9$ Hz, 2H), 7.88 (s, 1H), 7.76 (d, $J = 8.3$ Hz, 1H), 7.51 (d, $J = 7.3$ Hz, 2H), 7.40 (t, $J = 7.1$ Hz, 2H), 7.37 – 7.32 (m, 1H), 7.28 – 7.20 (m, 1H), 7.14 (d, $J = 2.8$ Hz, 1H), 7.08 – 7.00 (m, 2H), 6.92 – 6.84 (m, 2H), 6.76 (d, $J = 7.7$ Hz, 1H), 5.25 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 157.2, 155.8, 152.3, 138.6, 137.3, 135.3, 133.5, 133.1, 128.6, 128.0, 127.4, 125.0, 121.3, 120.7, 120.0, 118.2, 118.0, 108.0, 106.7, 104.1, 70.1. **ESI-MS**: calculated $\text{C}_{25}\text{H}_{17}\text{ClN}_3\text{O}_2$ $[\text{M-H}]^-$, 426.1015; Found 426.1005.

methyl 2-(2-chloro-4-hydroxyphenyl)-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (6ga)



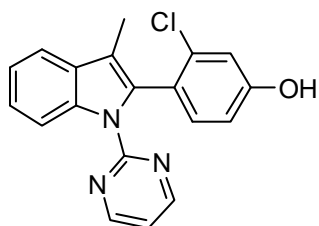
Following general procedure F, the product **6ga** was obtained in 36% yield (27.3 mg, 0.072 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.30. ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.44 – 7.32 (m, 2H), 7.18 (t, *J* = 4.8 Hz, 1H), 7.14 (s, 1H), 7.00 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 158.5, 156.9, 155.6, 137.9, 137.2, 135.7, 132.8, 128.7, 125.6, 123.3, 121.7, 120.9, 120.91, 118.4, 118.2, 118.0, 111.0, 52.0. **ESI-MS**: calculated C₂₀H₁₃ClN₃O₃ [M-H]⁻, 378.0651; Found 378.0642.

3-chloro-4-(7-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (6ha)



Following general procedure F, the product **6ha** was obtained in 59% yield (42.1mg, 0.118 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 4:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.32. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.60 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 4.8 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.16 (dd, *J* = 7.8, 4.7 Hz, 2H), 7.03 (s, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.65 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 157.8, 155.8, 138.6, 136.3, 134.8, 133.0, 132.0, 124.9, 122.9, 121.4, 120.2, 119.8, 119.7, 119.6, 118.0, 108.1. **ESI-MS**: calculated C₁₈H₁₀Cl₂N₃O [M-H]⁻, 354.0206; Found 354.0201.

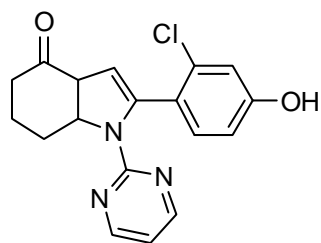
3-chloro-4-(3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)phenol (6ia)



Following general procedure F, the product **6ia** was obtained in 53% yield (35.8 mg, 0.106 mmol) as a brown solid after column chromatography (eluent = Petroleum

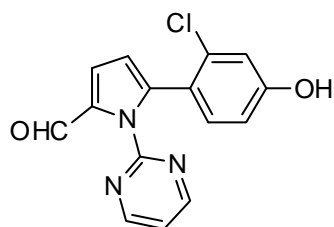
ether /EtOAc 6:1 v/v). **R_F** (Petroleum ether /EtOAc 4:1): 0.45. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 4.9 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.71 (s, 1H), 7.64 – 7.61 (m, 1H), 7.39 – 7.34 (m, 1H), 7.30 (td, *J* = 7.5, 1.1 Hz, 1H), 7.09 (dd, *J* = 7.6, 3.4 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.14 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.3, 157.2, 156.5, 136.8, 135.4, 133.3, 130.5, 130.1, 124.4, 122.2, 120.8, 120.6, 119.1, 118.3, 118.2, 117.4, 113.22, 9.47. **ESI-MS**: calculated C₁₉H₁₃ClN₃O [M-H]⁻, 334.0753; Found 334.0744.

3-chloro-4-(1-(pyrimidin-2-yl)-3a,4,5,6,7,7a-hexahydro-1*H*-indol-2-yl)phenol
(**7aa**)



Following general procedure F, the product **7aa** was obtained in 84% yield (57.6 mg, 0.168 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 1:3 v/v). **R_F** (Petroleum ether /EtOAc 1:3): 0.37. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.77 (d, *J* = 4.8 Hz, 2H), 7.47 (t, *J* = 4.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.61 (s, 0H), 6.47 (s, 1H), 2.98 (t, *J* = 5.6 Hz, 2H), 2.43 (t, *J* = 5.8 Hz, 2H), 2.08 – 2.02 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 193.3, 158.5, 156.6, 154.9, 145.2, 132.3, 132.1, 131.2, 120.9, 119.8, 119.8, 119.0, 114.5, 107.2, 37.4, 23.6, 23.4. **ESI-MS**: calculated C₁₈H₁₃ClN₃O₂ [M-H]⁻, 338.0702; Found 338.0694.

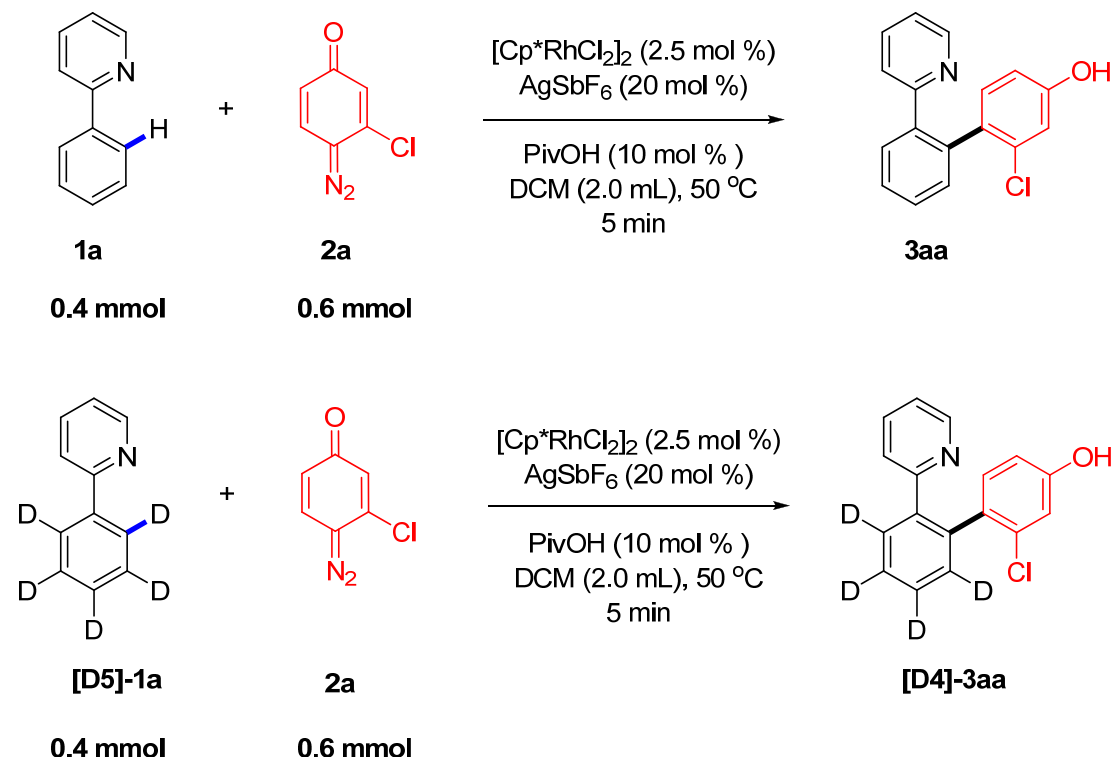
5-(2-chloro-4-hydroxyphenyl)-1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carbaldehyde
(**7ba**)



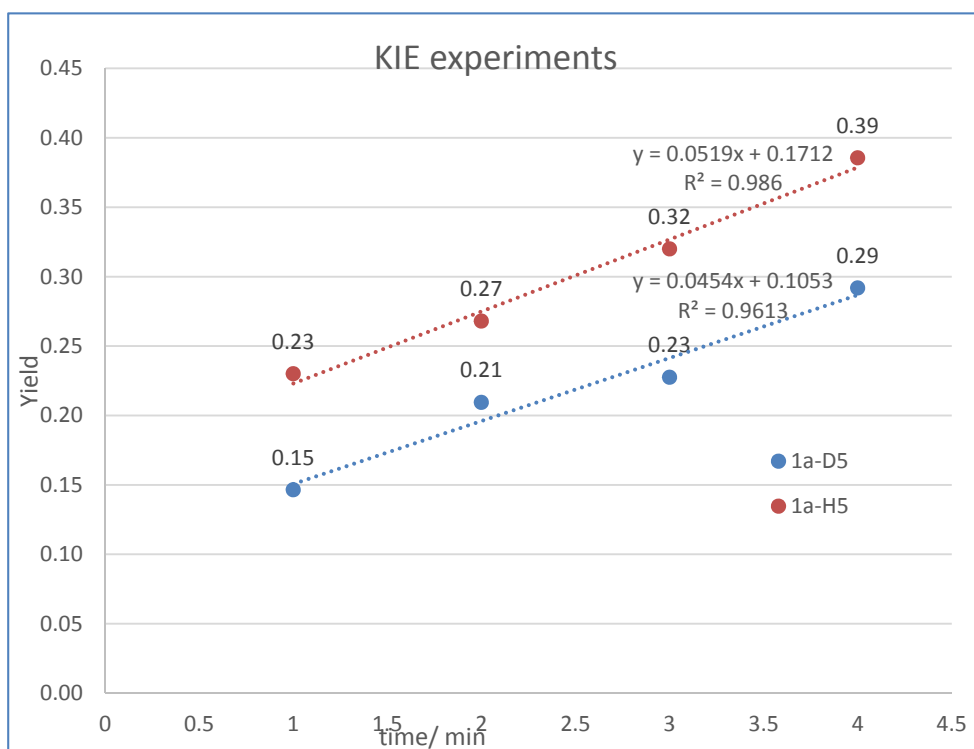
Following general procedure F, the product **7ba** was obtained in 27% yield (16.1 mg, 0.054 mmol) as a brown solid after column chromatography (eluent = Petroleum ether /EtOAc 3:1 v/v). **R_F** (Petroleum ether /EtOAc 2:1): 0.26. ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H), 9.47 (s, 1H), 8.56 (d, *J* = 4.6 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 4.6 Hz, 1H), 6.92 (s, 1H), 6.67 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.9, 164.3, 160.1, 149.6, 134.7,

134.4, 133.4, 129.3, 126.6, 124.2, 122.3, 121.4, 117.3, 111.2. **ESI-MS:** calculated $\text{C}_{15}\text{H}_9\text{ClN}_3\text{O}_2$ $[\text{M}-\text{H}]^-$, 298.0389; Found 298.0384.

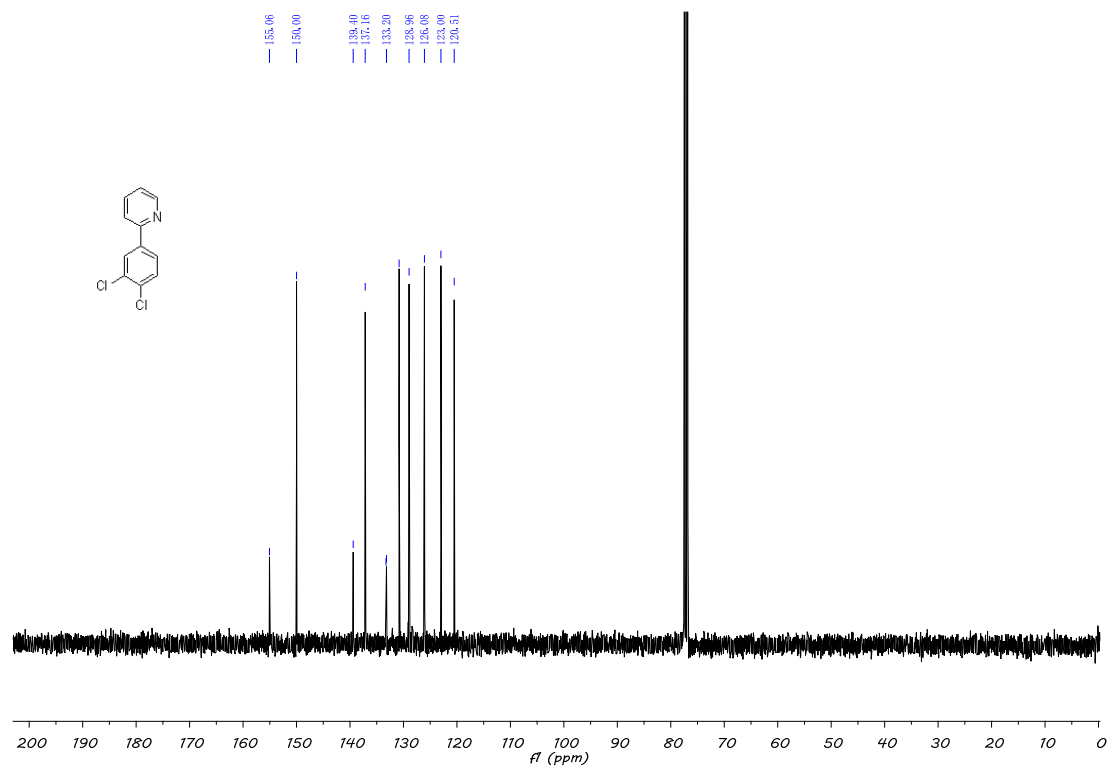
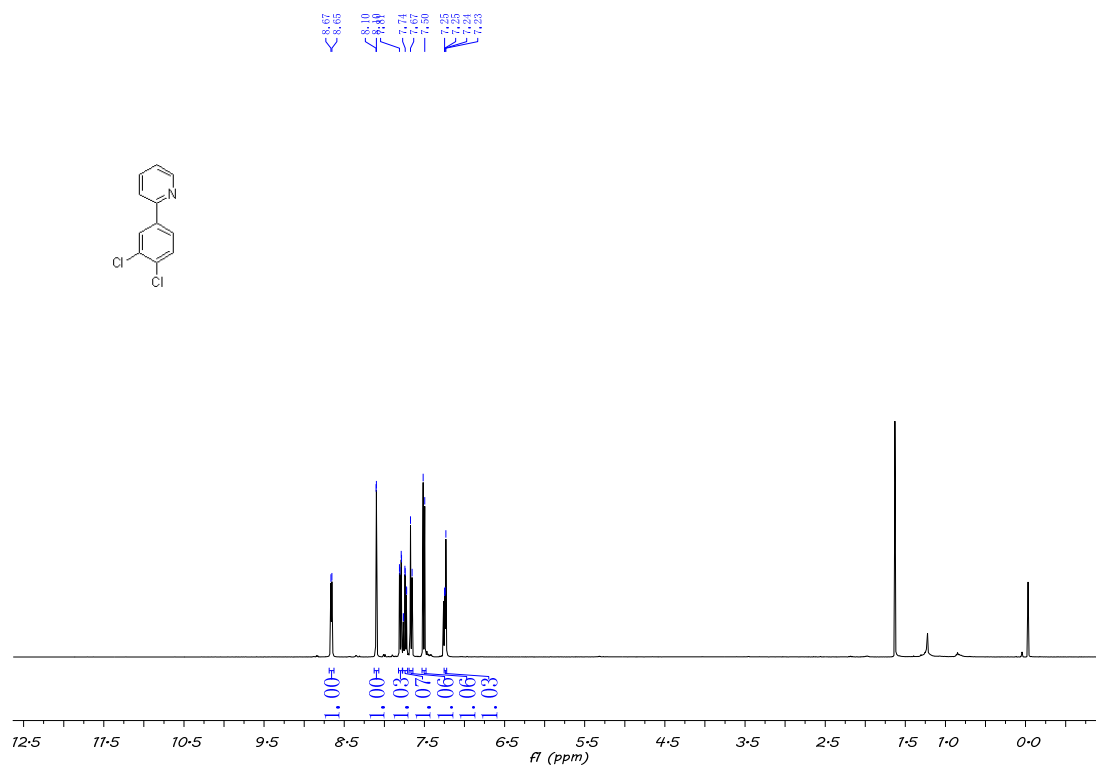
4. Kinetic isotope effect experiments

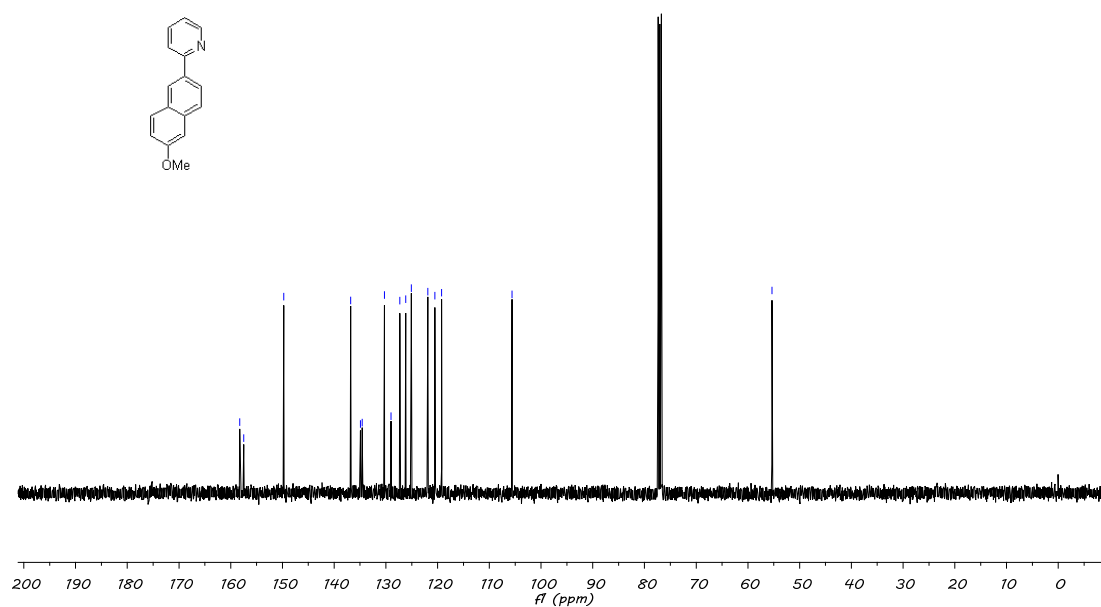
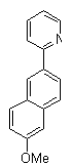
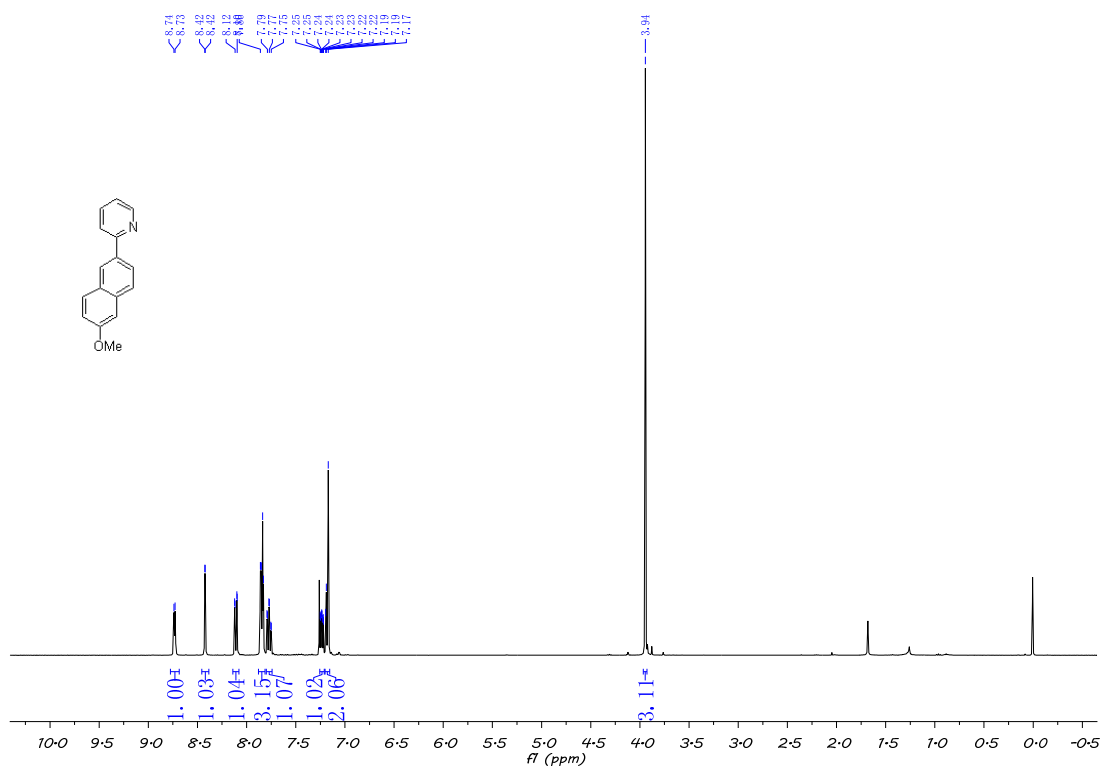
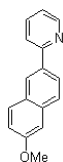


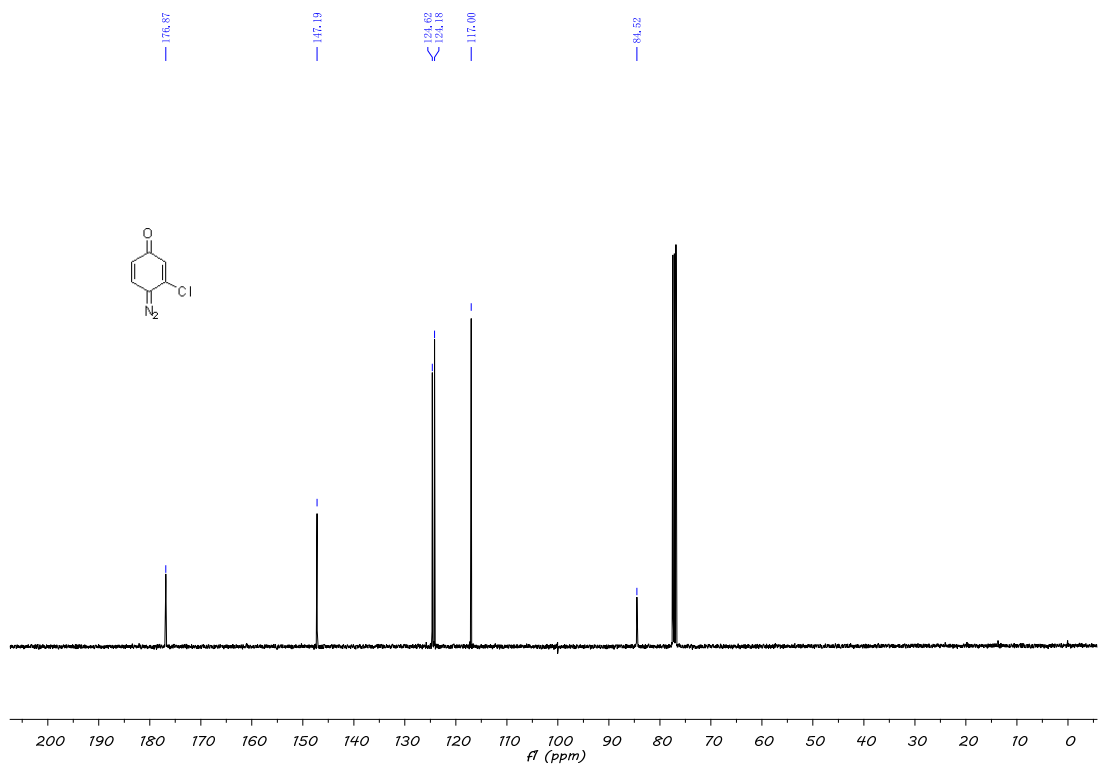
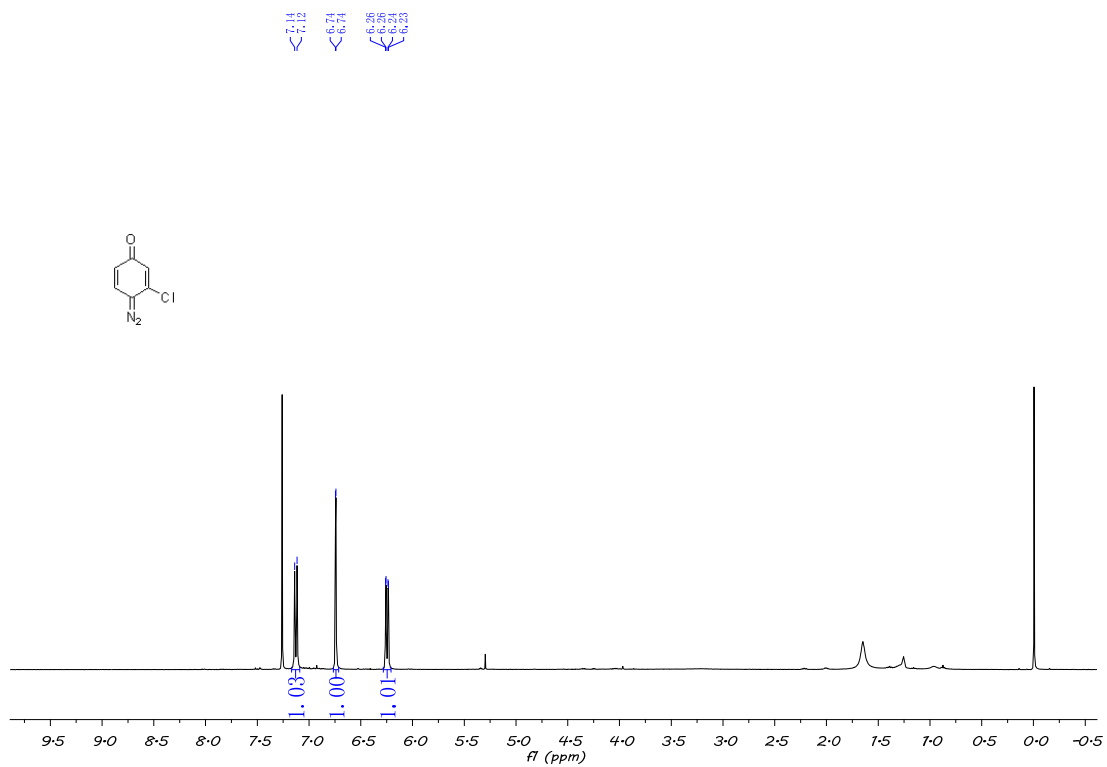
Following general procedure D, to a 15 mL-schlenk tube charged with a stirring bar, were added 2-phenylpyridine **1a** (62.1 mg, 0.4 mmol, 1.0 equiv), 3-chloro-4-diazocyclohexa-2,5-dienone **2a** (92.7 mg, 0.6 mmol, 1.5 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (6.2 mg, 0.01 mmol, 2.5 mol%), AgSbF_6 (27.4 mg, 0.08 mmol, 0.2 equiv), PivOH (4.0 mg, 0.04 mmol, 0.1 equiv), 1-iodo-4-methoxybenzene (93.6 mg, 0.4 mmol, 1.0 equiv, internal standard) and DCM (2.0 mL). No special precautions were taken to exclude moisture and air. In another reaction vessel, $[\text{D}_5]$ -**1a** (64.1 mg, 0.4 mmol, 1.0 equiv) was used instead of **1a**. The two reactions were allowed to stir at 50 °C. An aliquot of each reaction mixture was taken at the time of 1 min, 2 min, 3 min, and 4 min. The corresponding yield of each product was determined by ^1H NMR. A kinetic isotope effect value $K_H/K_D = 1.1$ was obtained

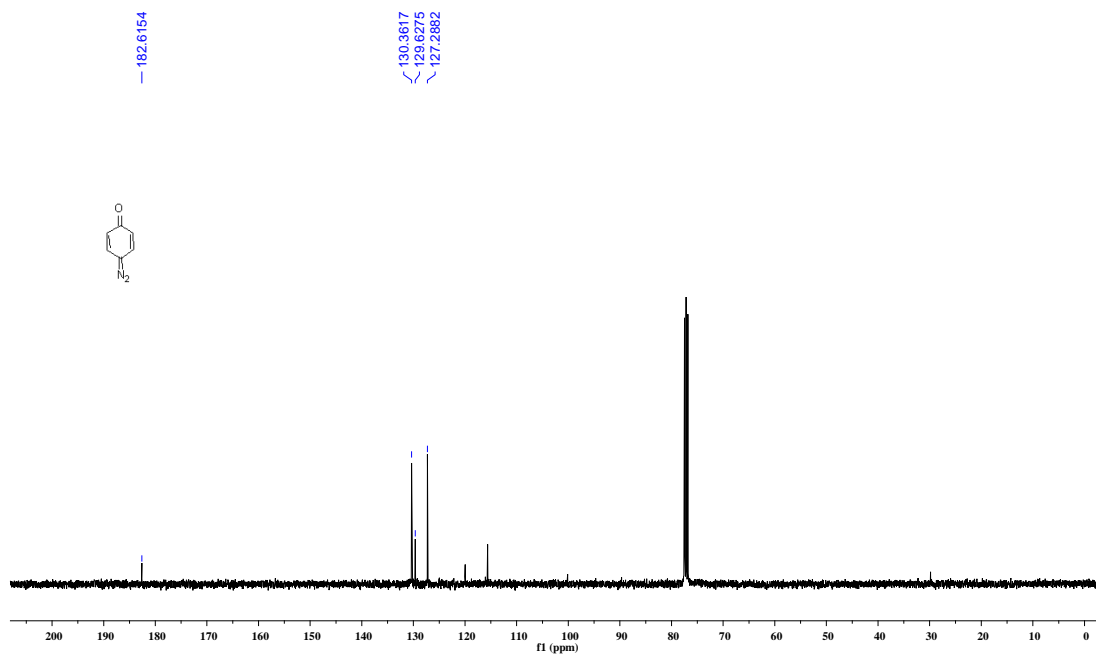
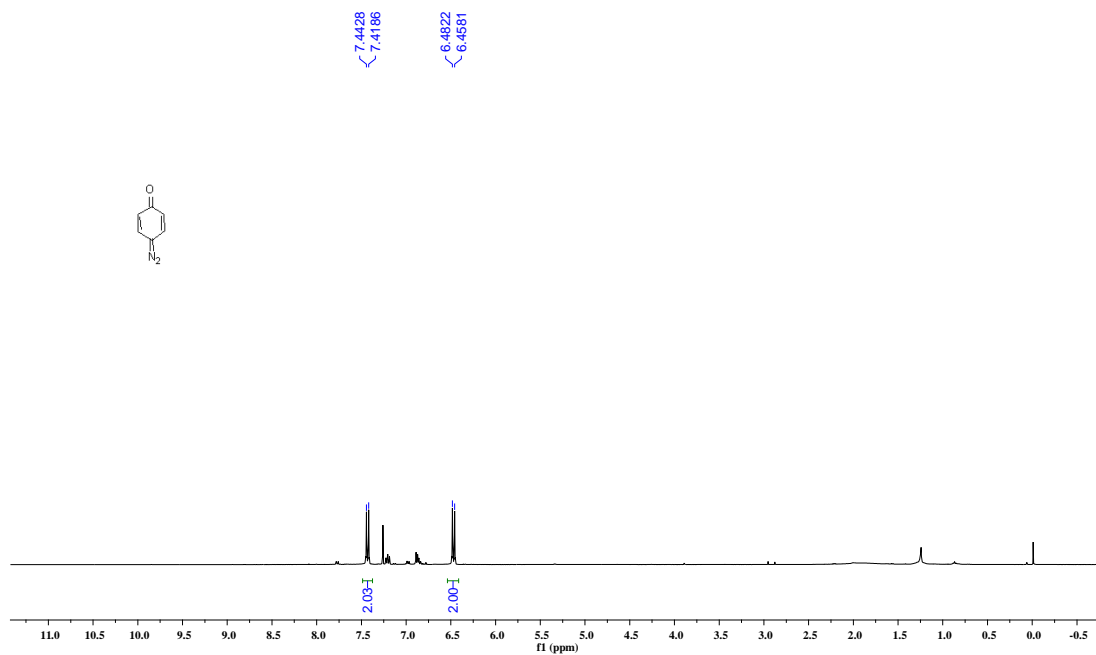


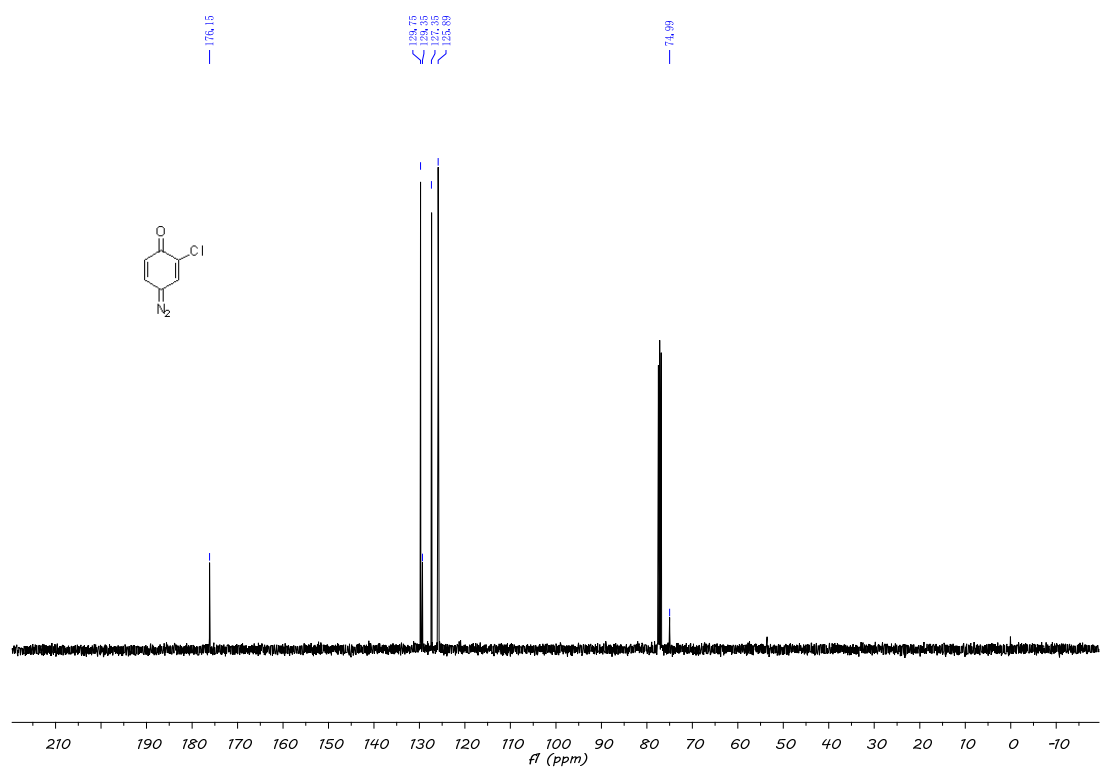
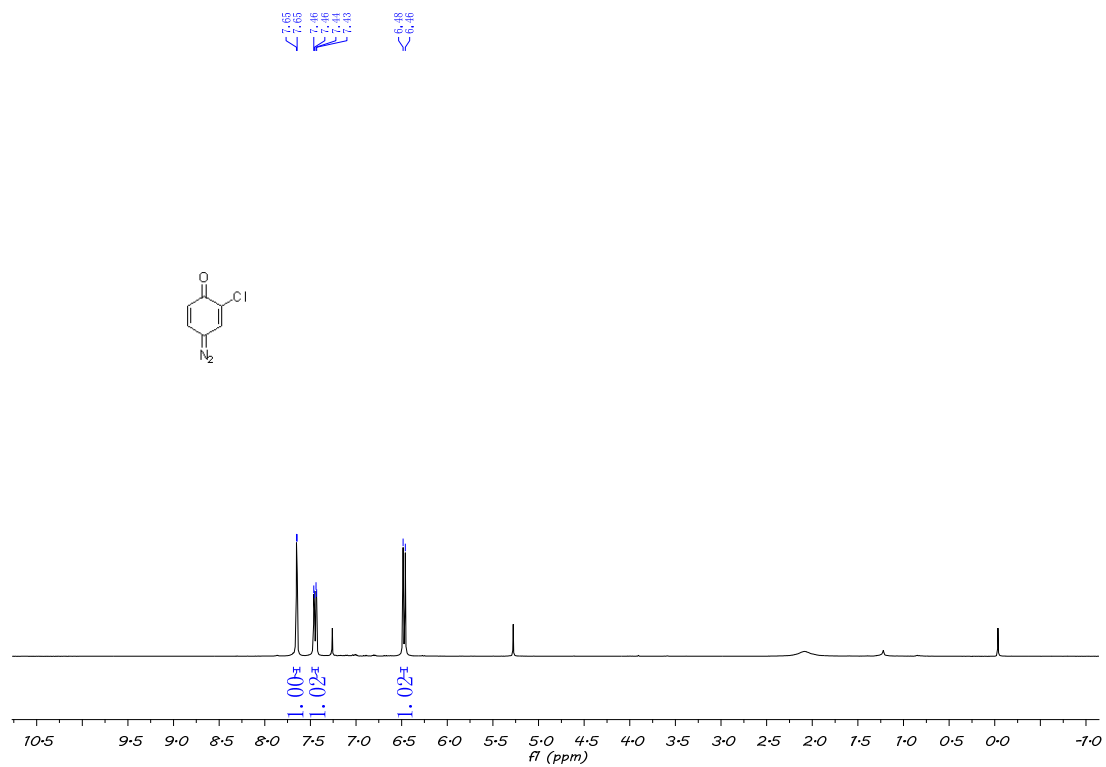
5. Characteristic spectra

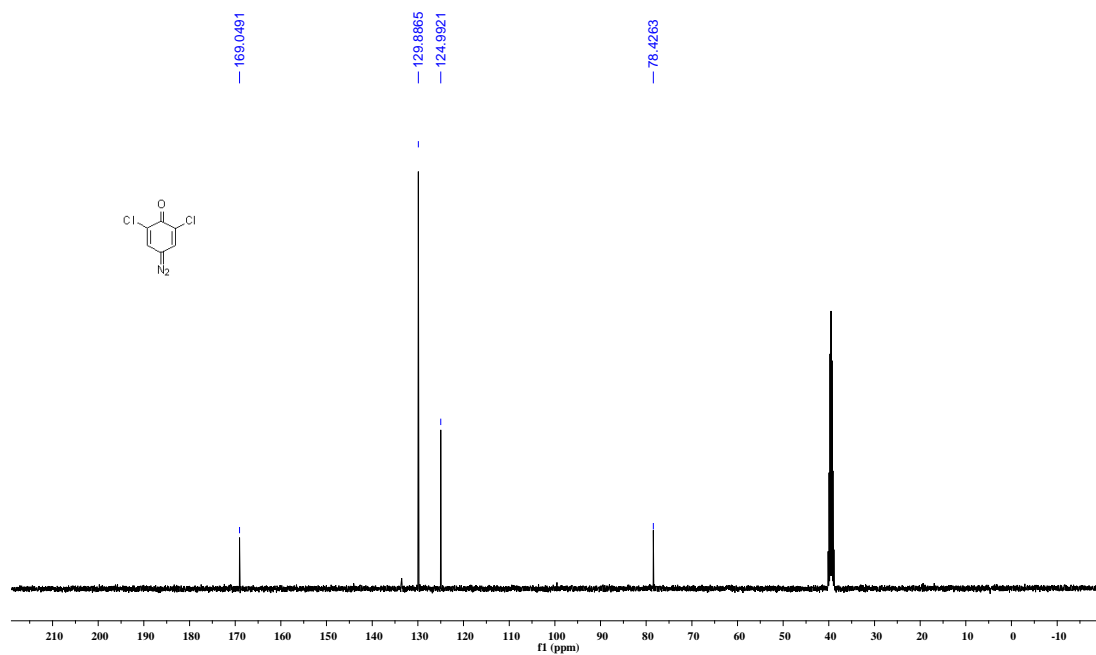
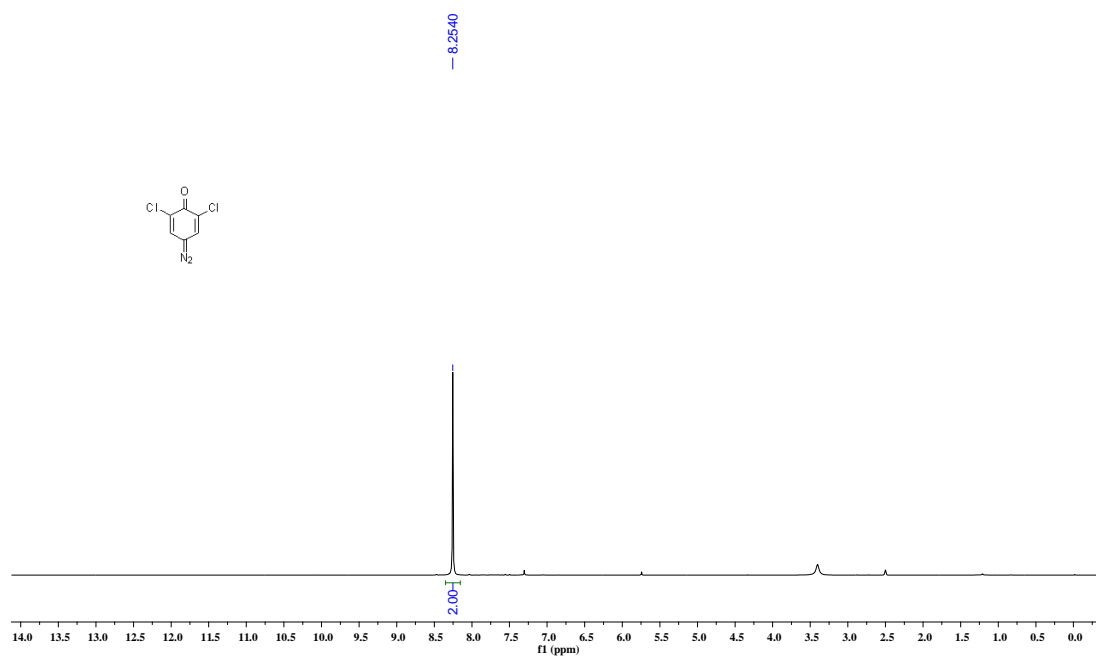


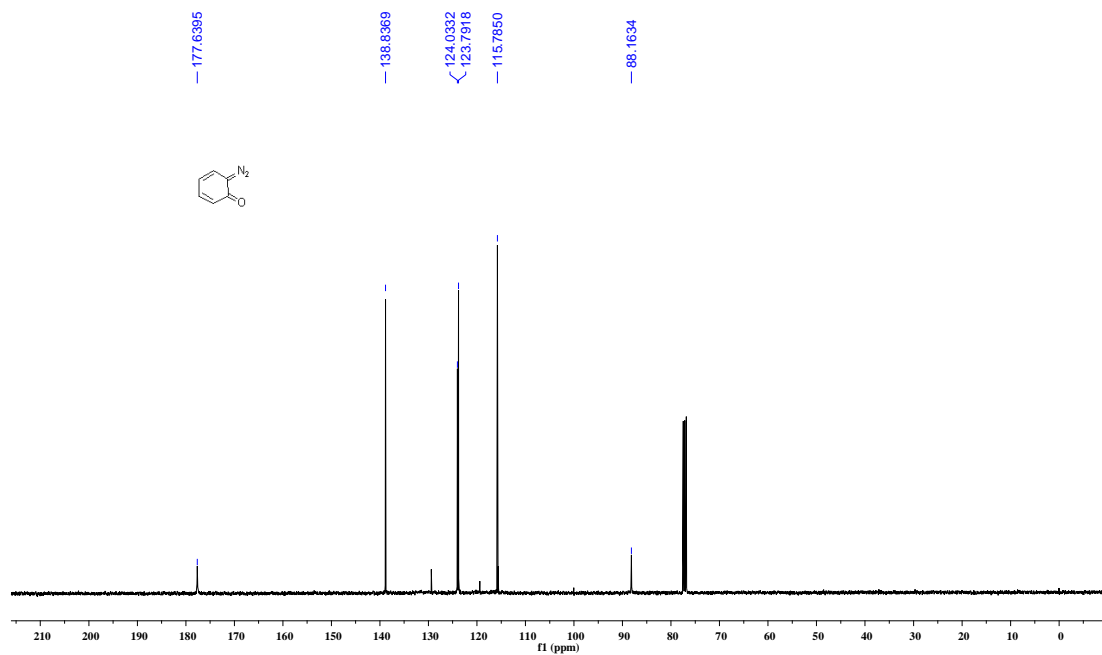
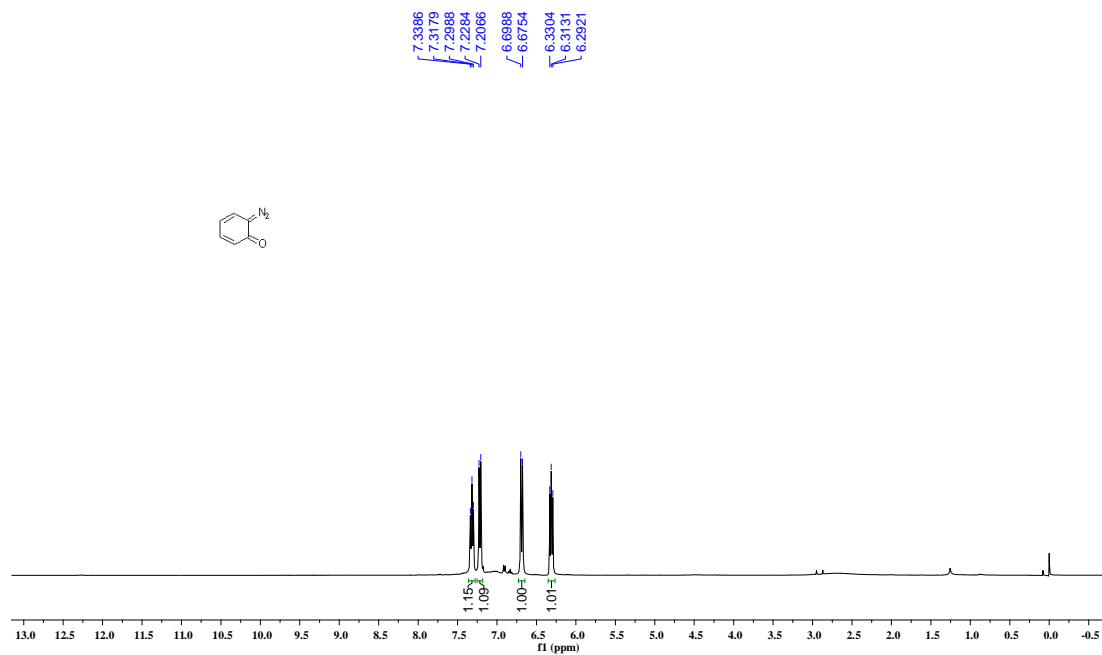


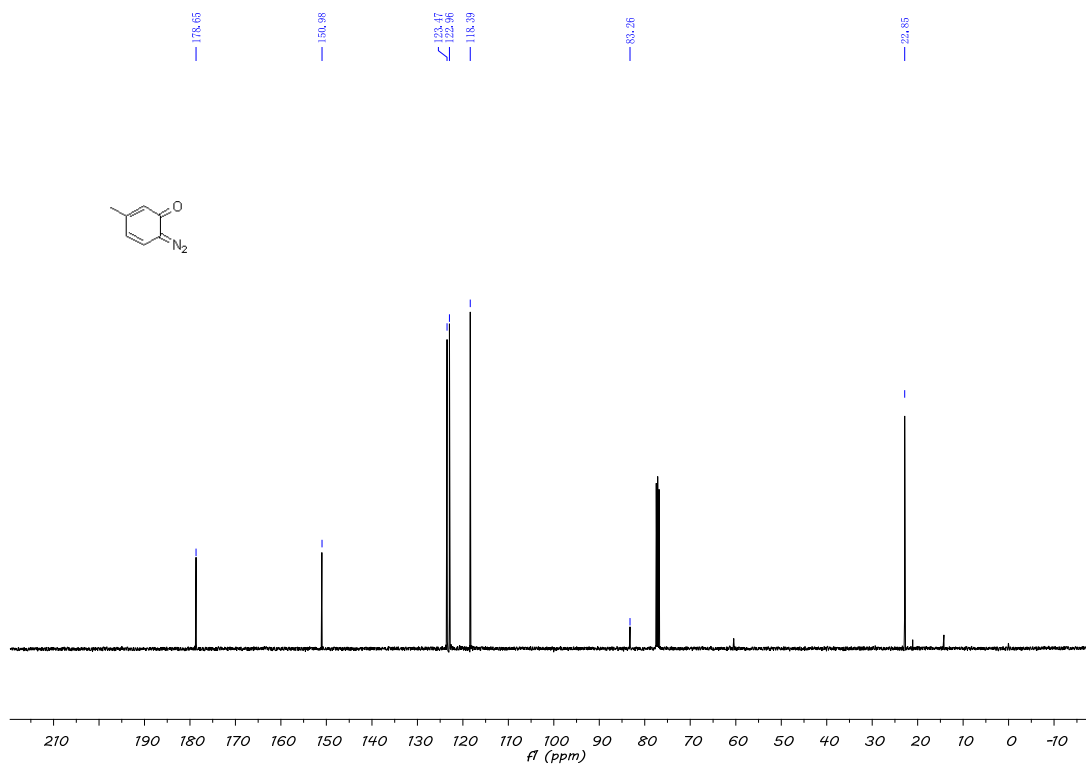
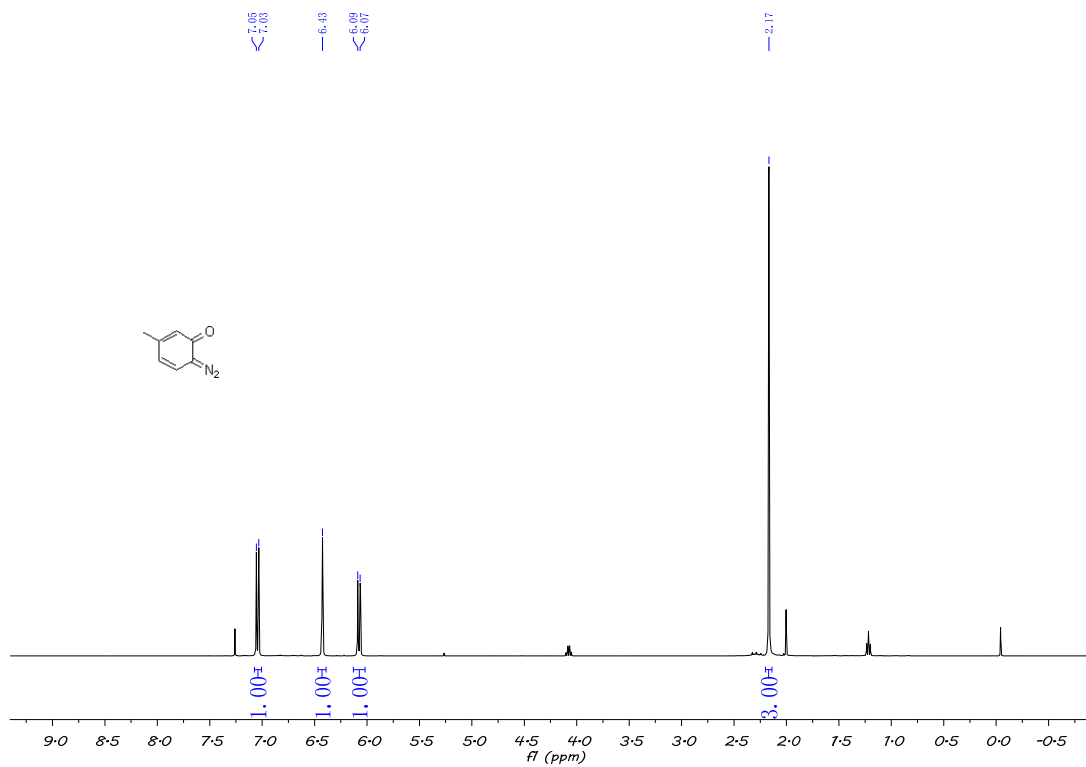


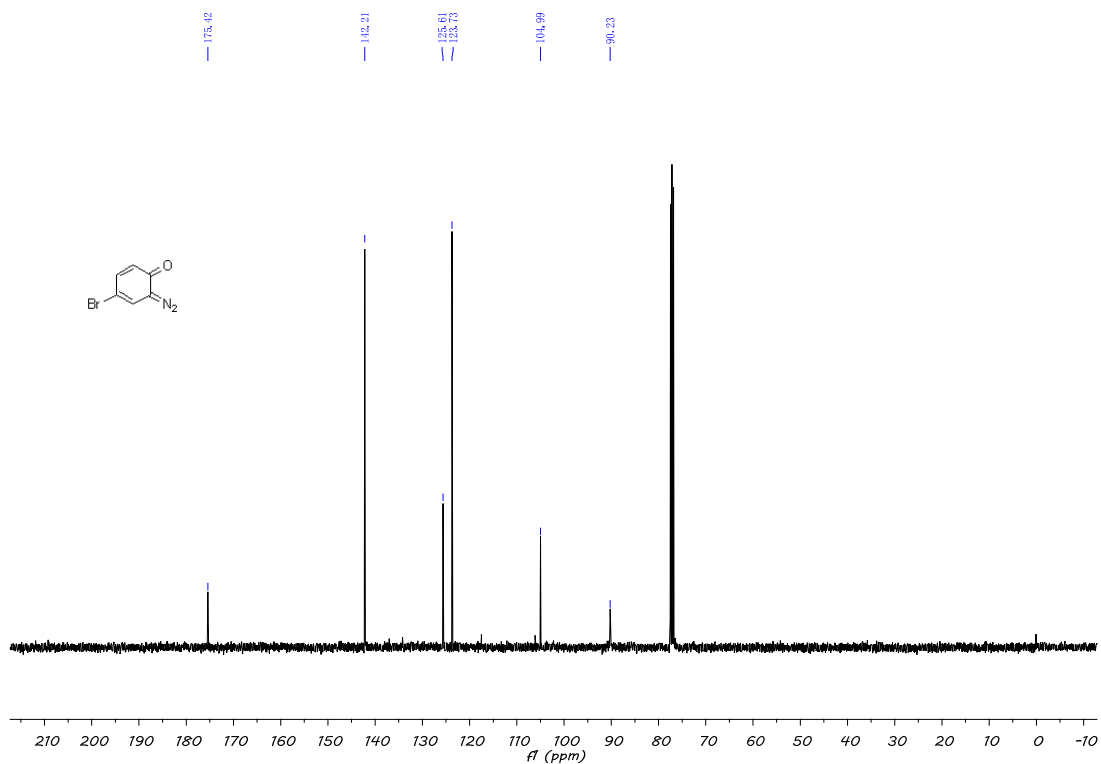
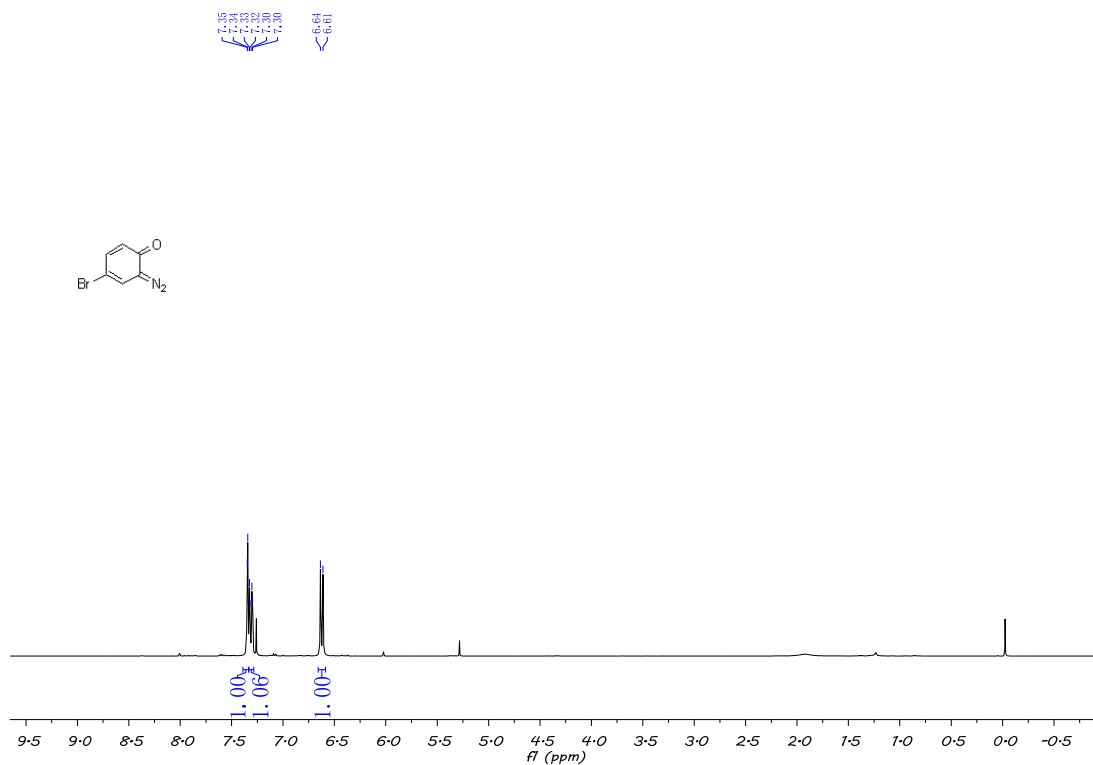


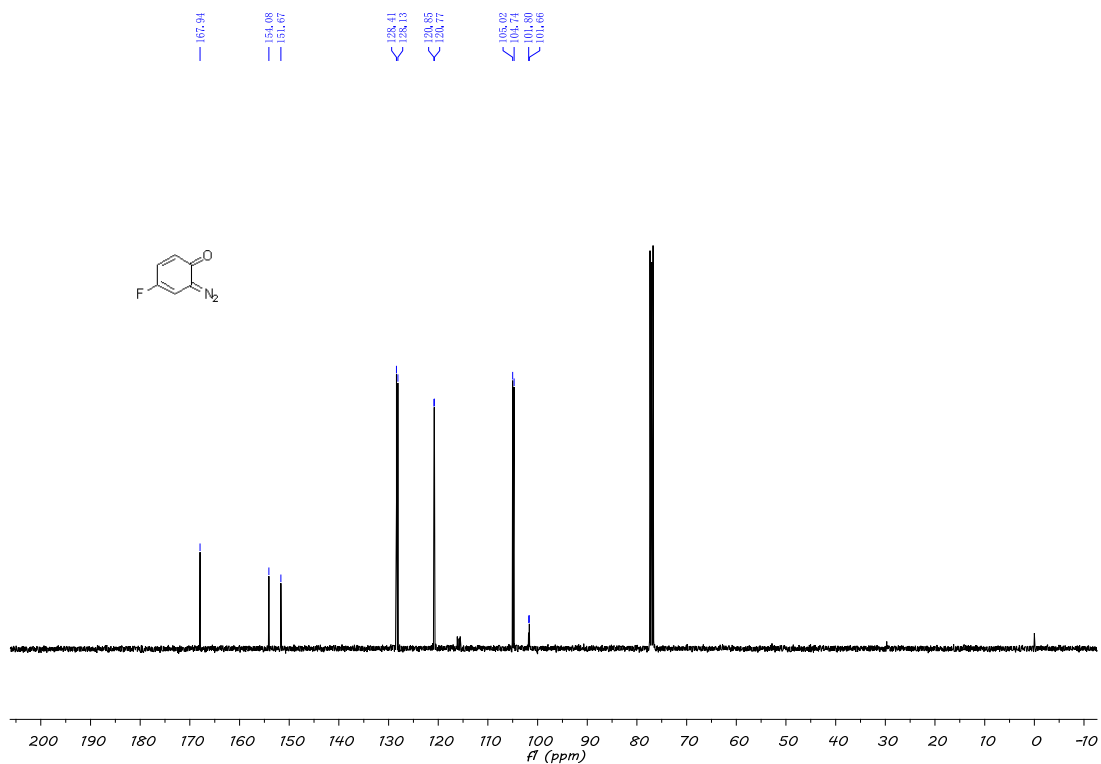
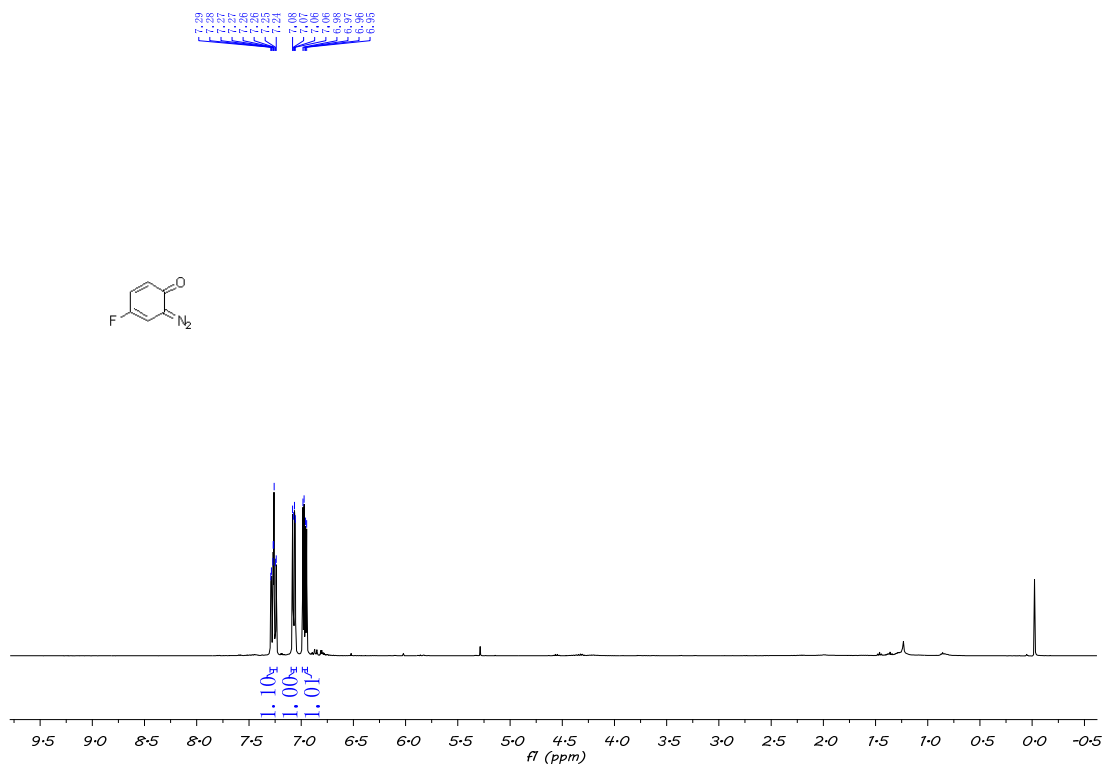


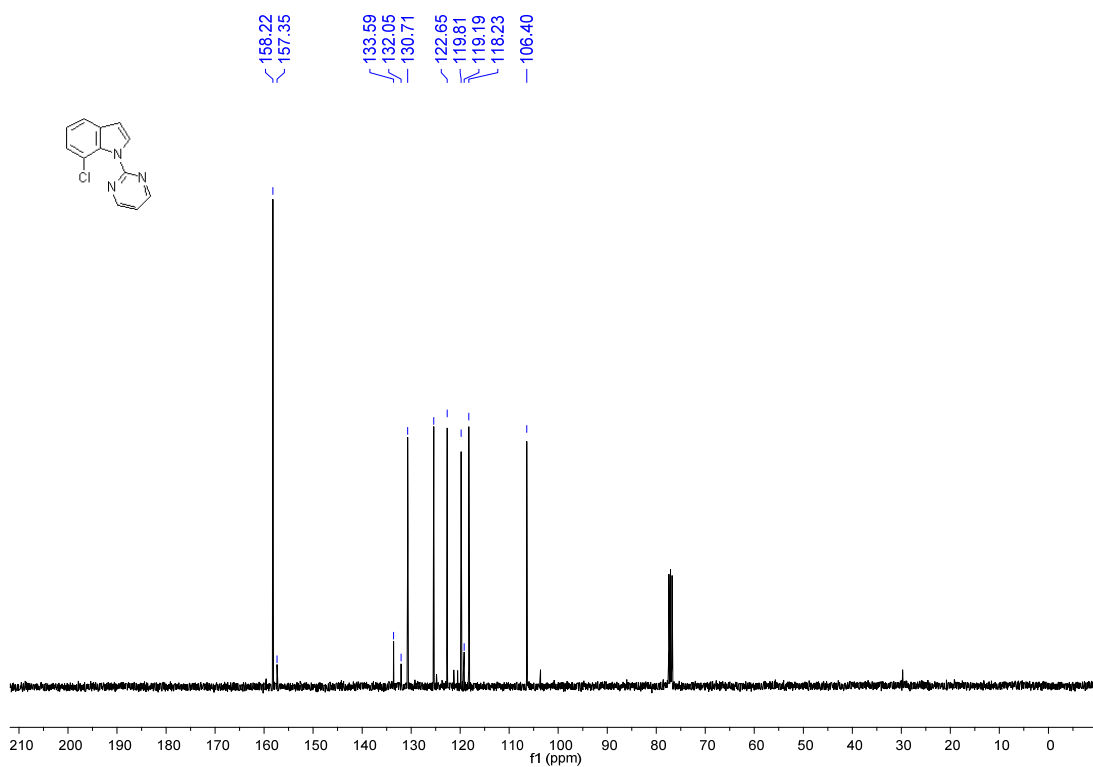
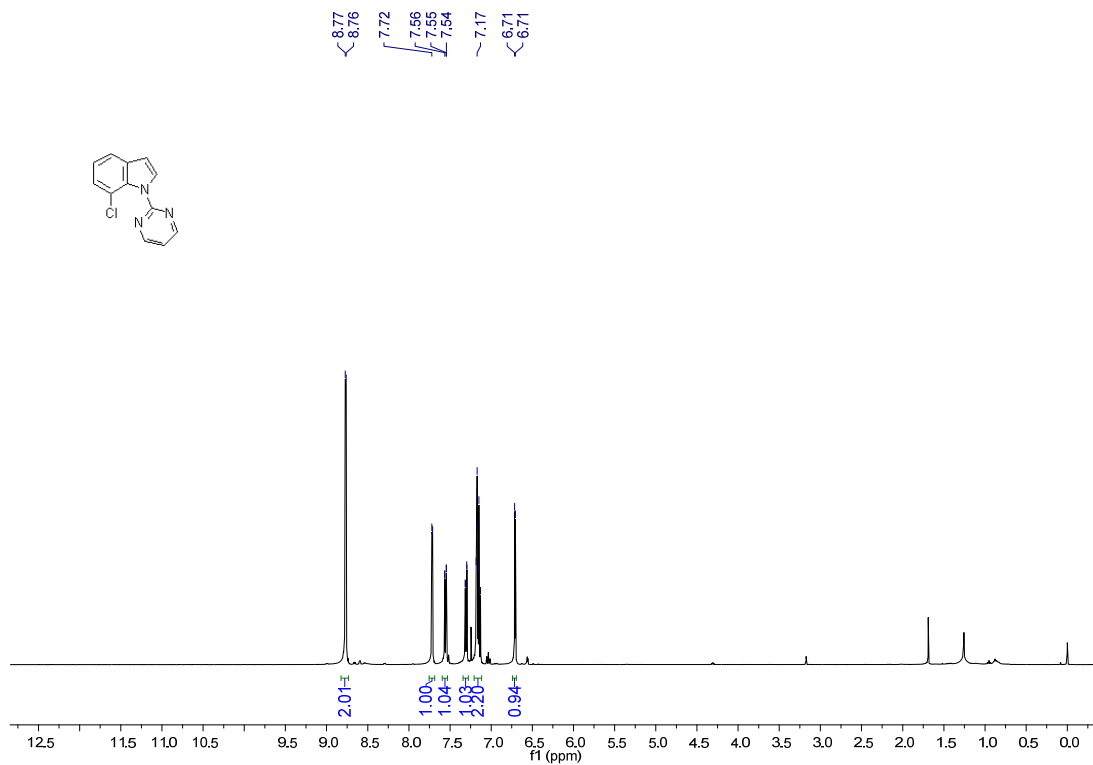


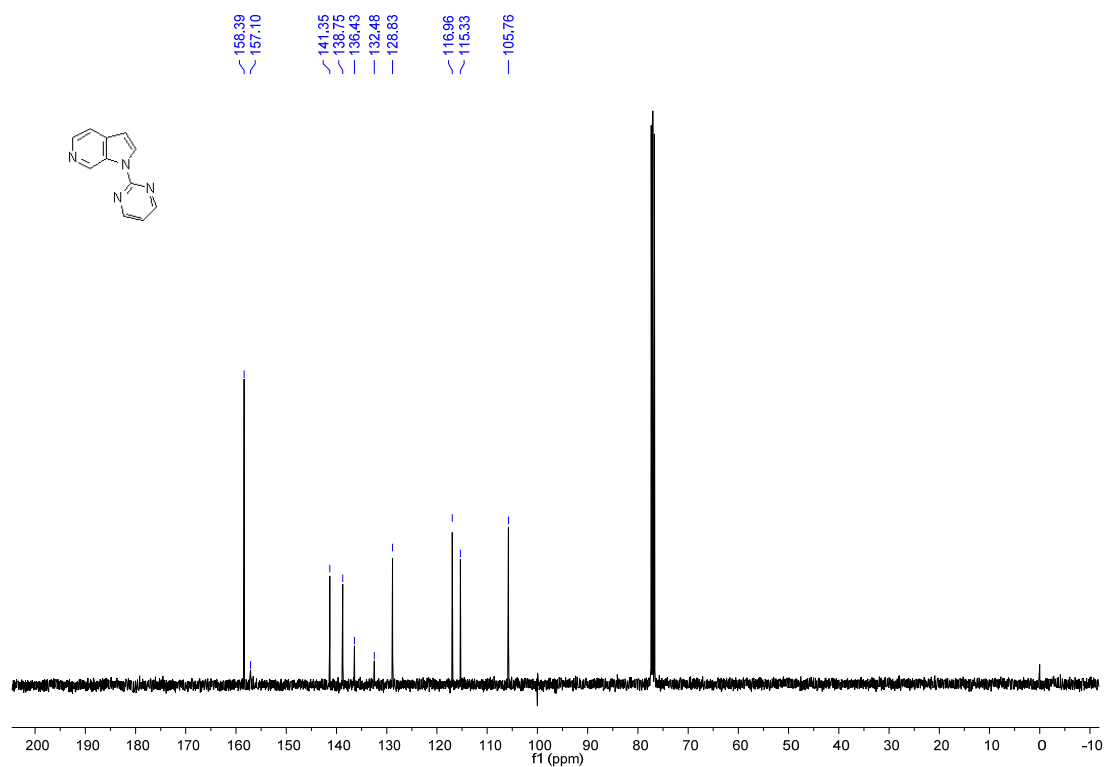
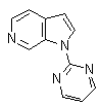
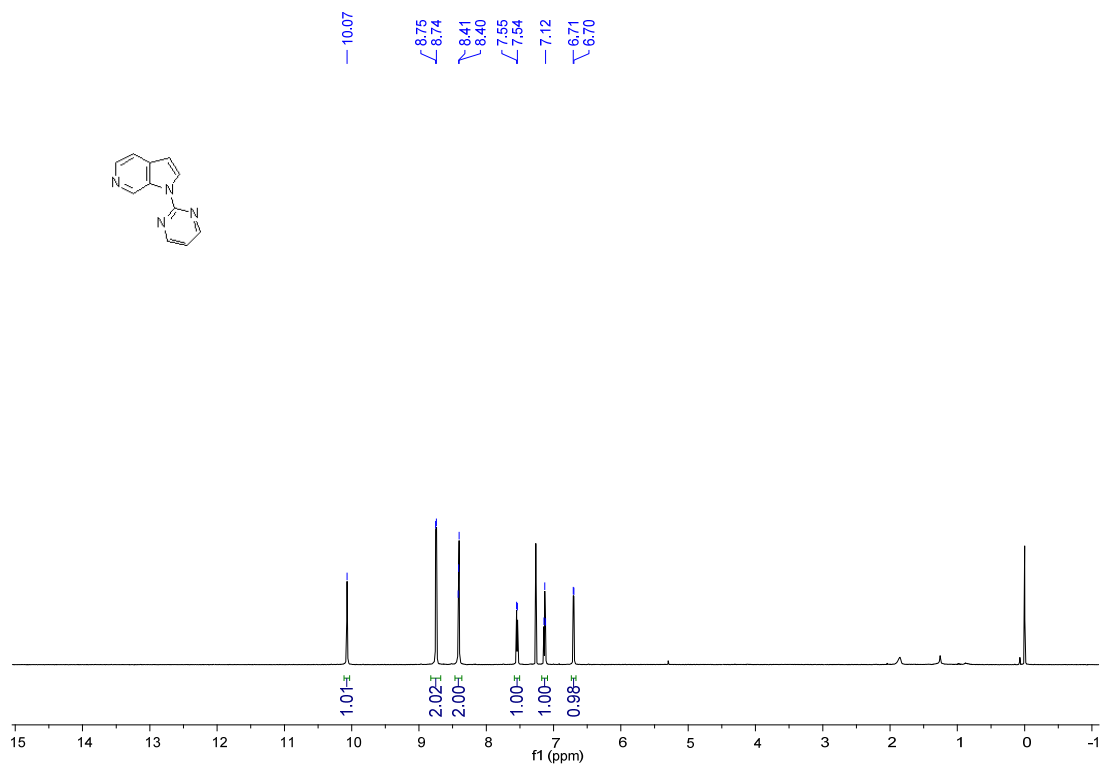
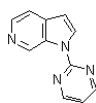


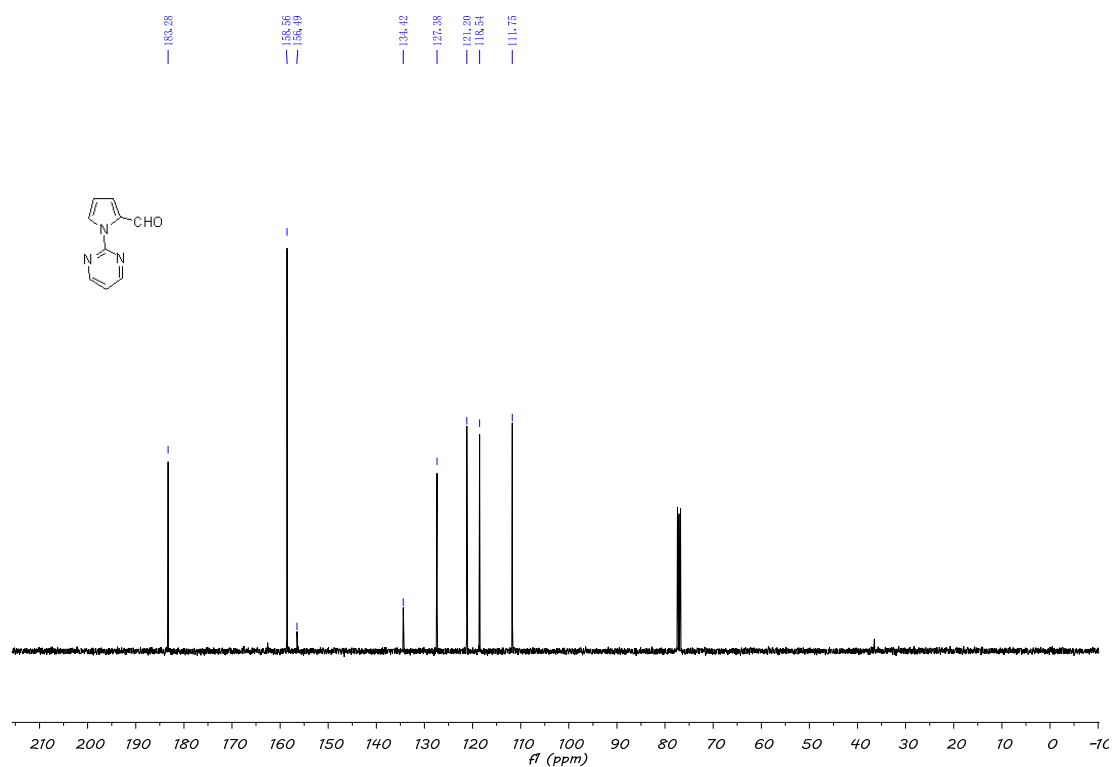
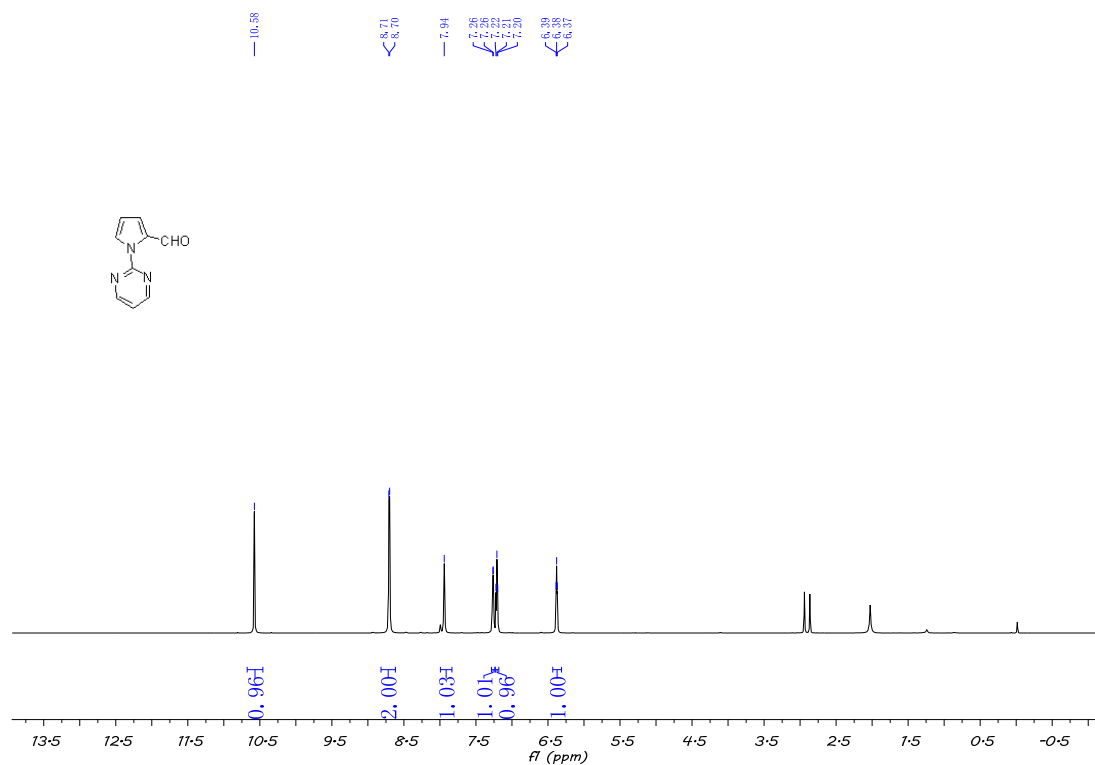


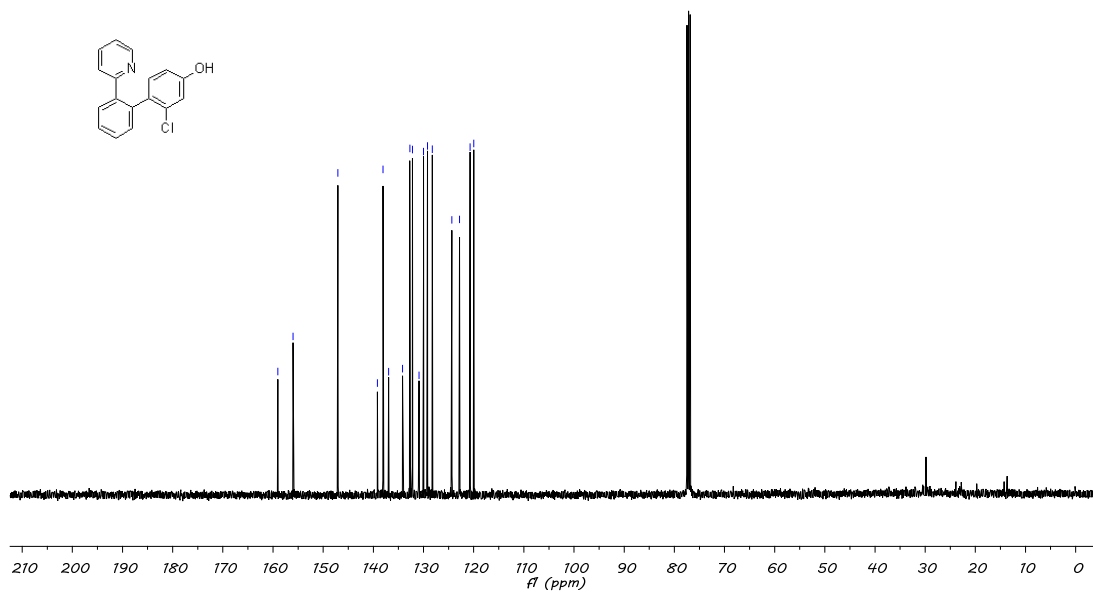
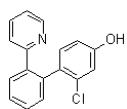
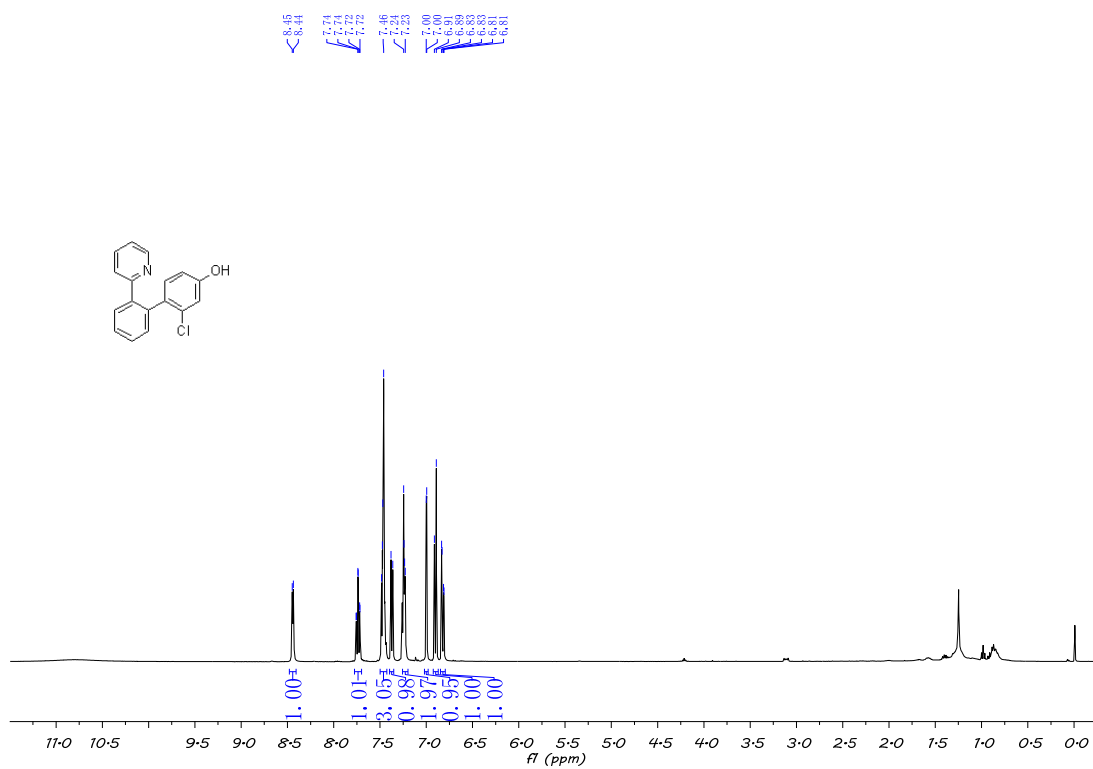
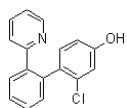


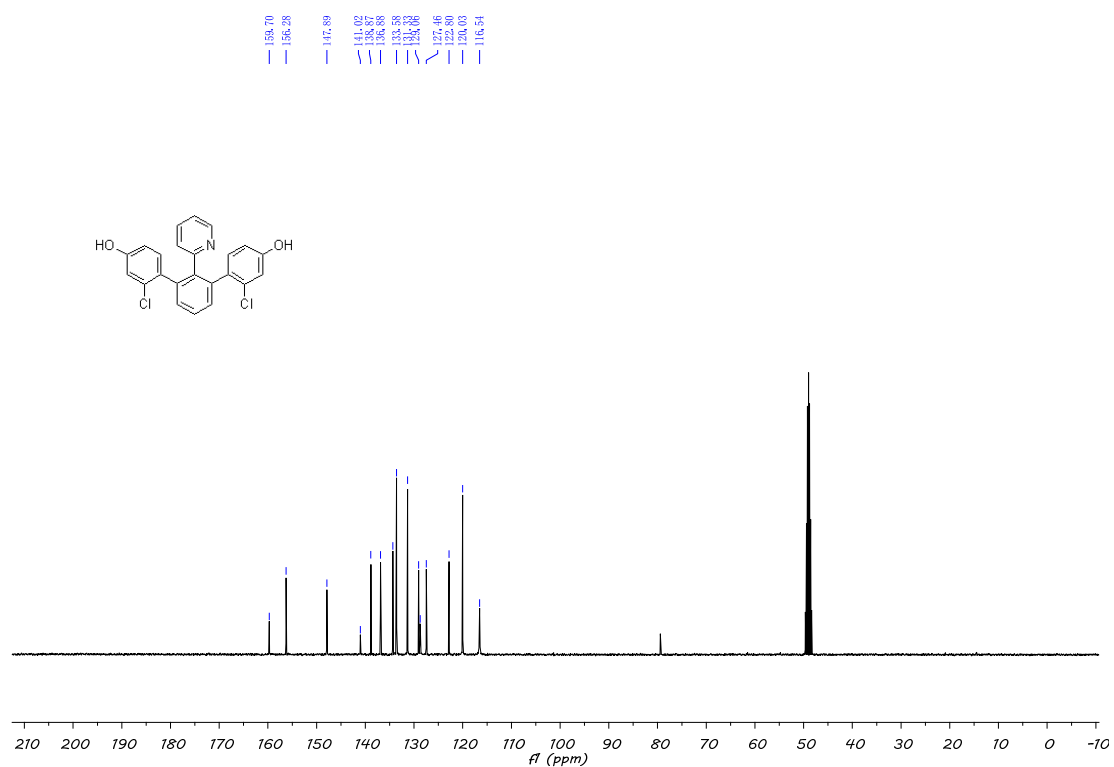
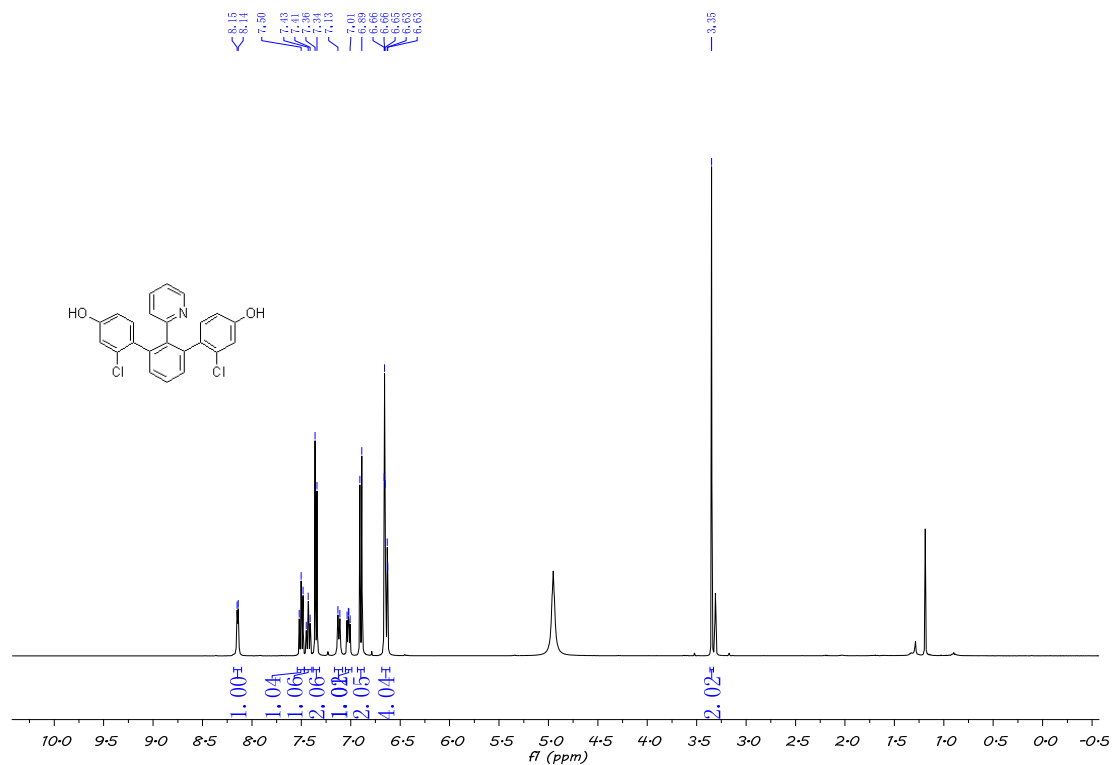


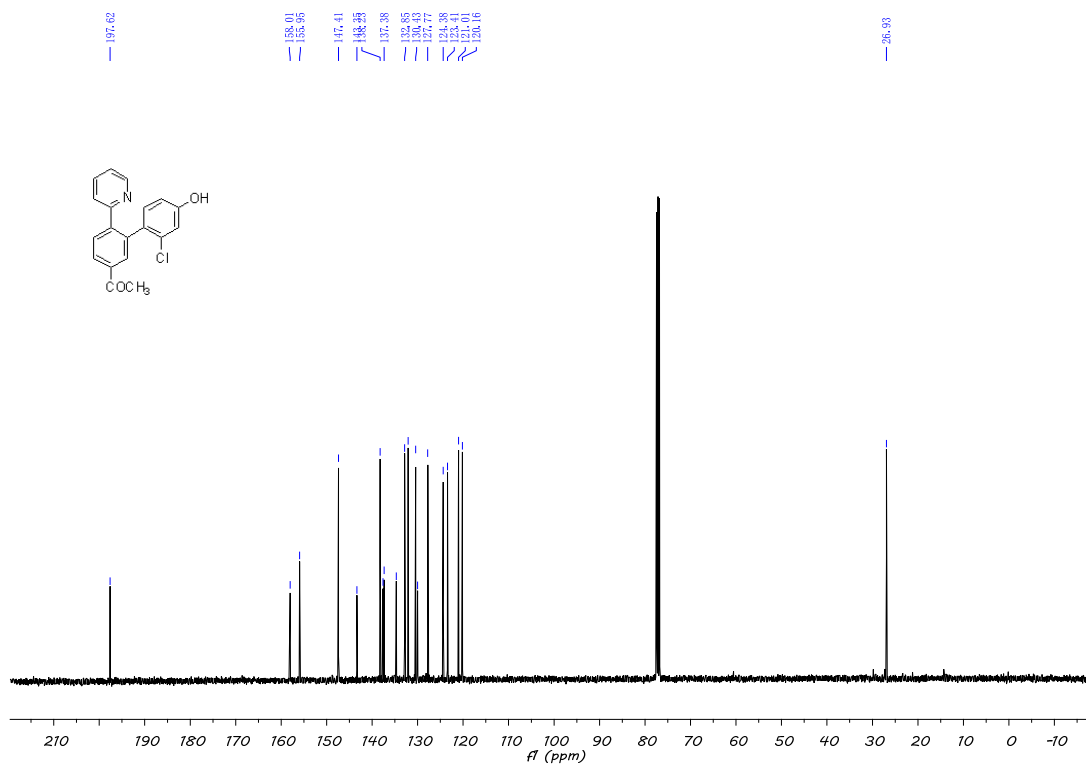
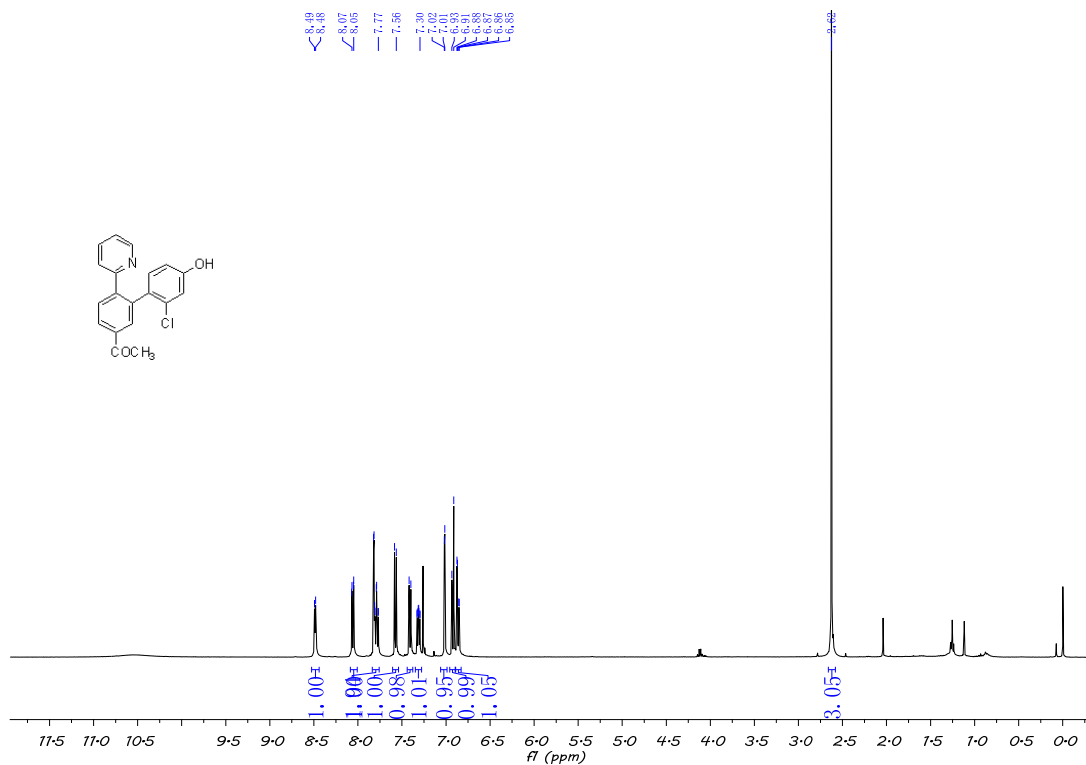


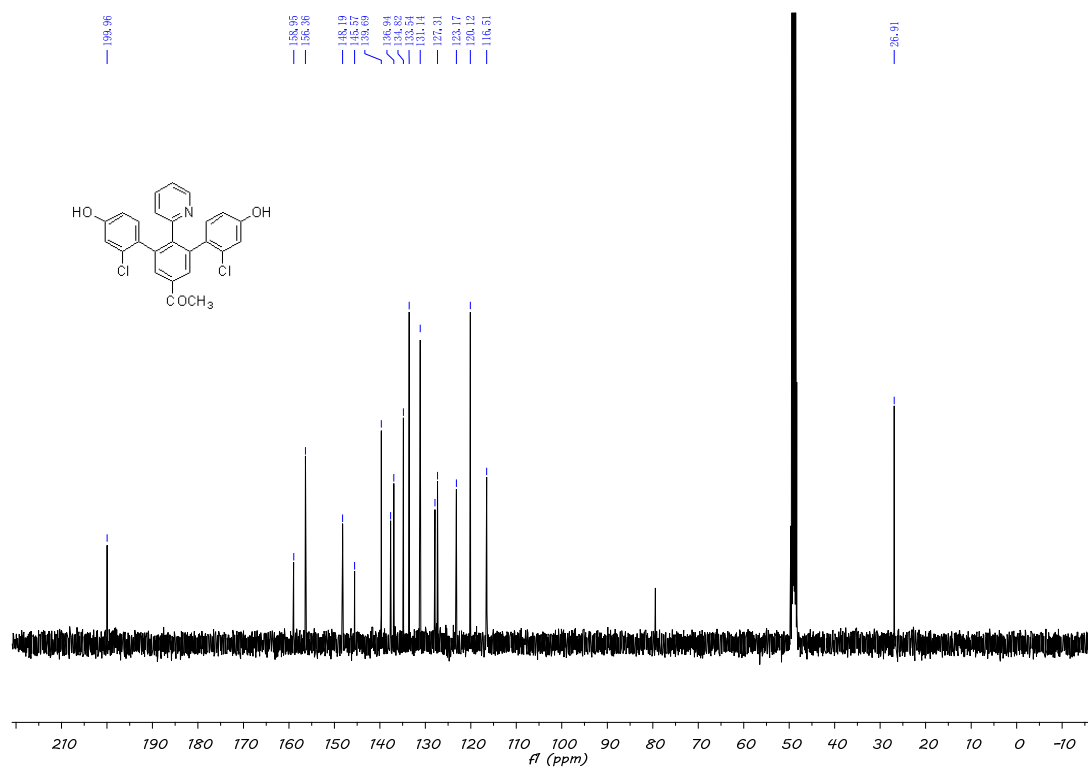
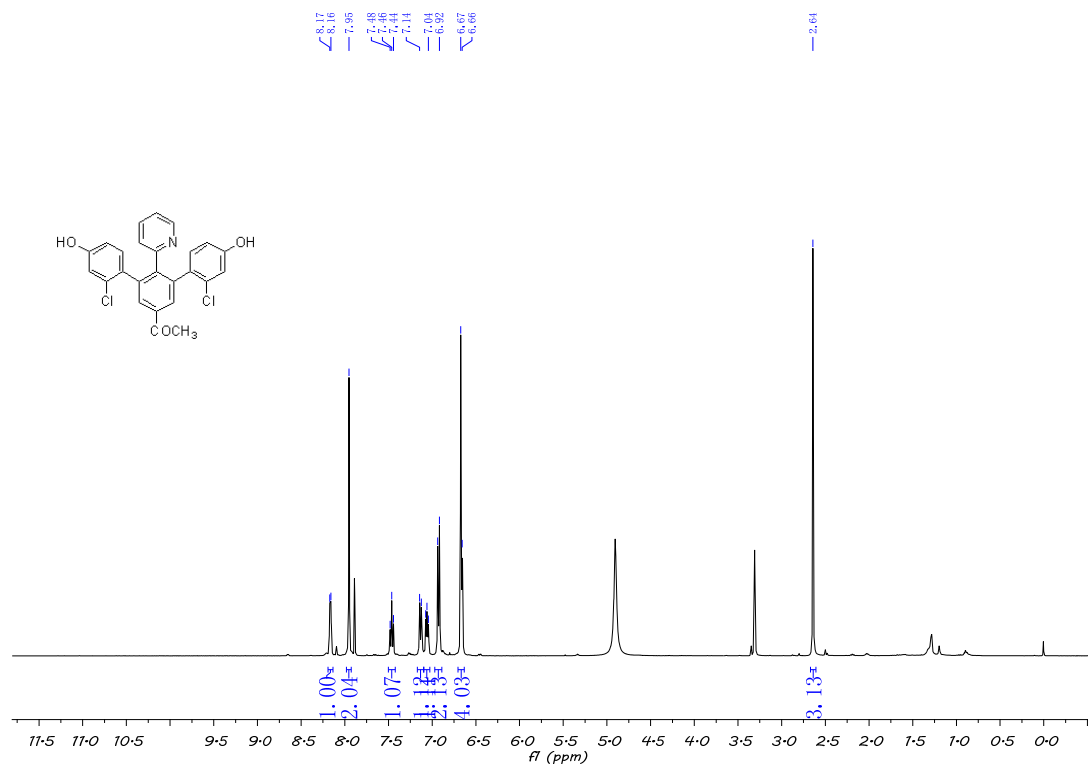


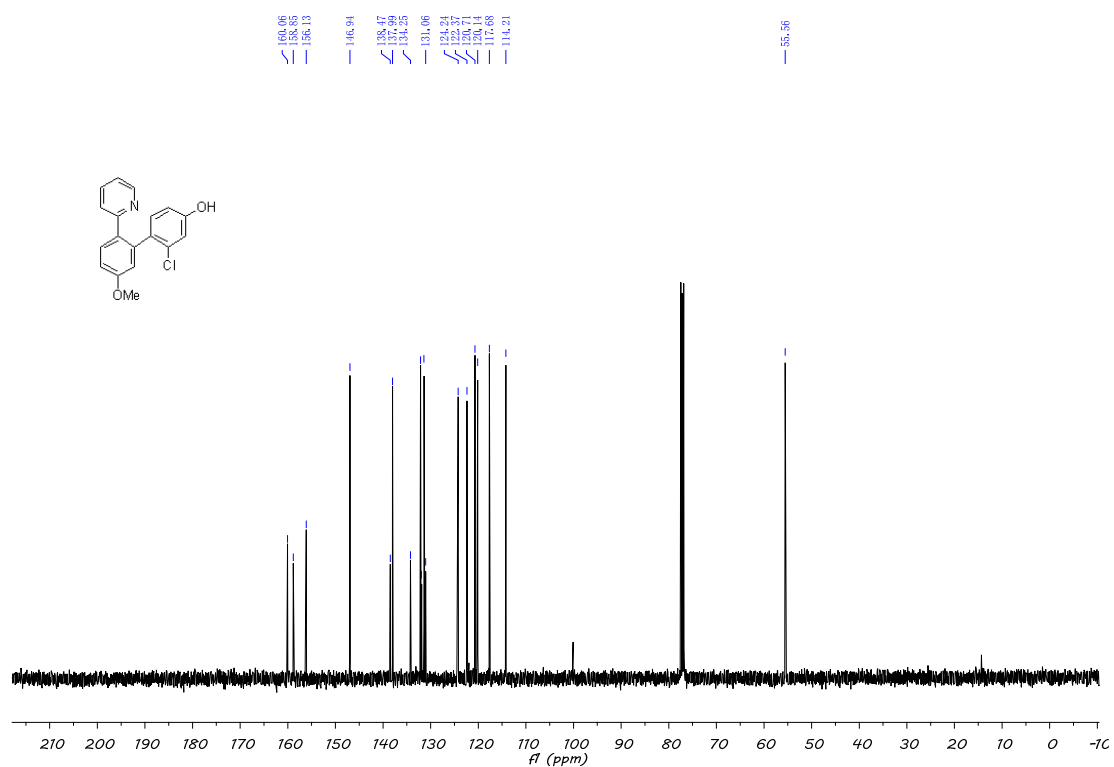
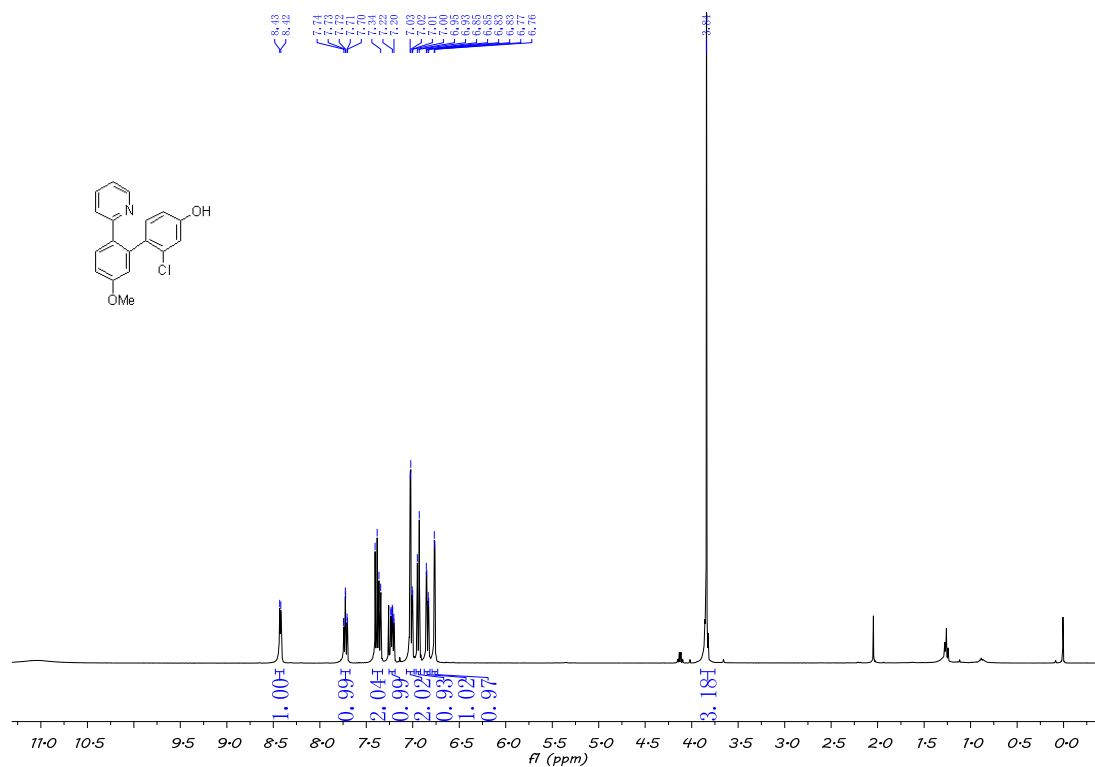


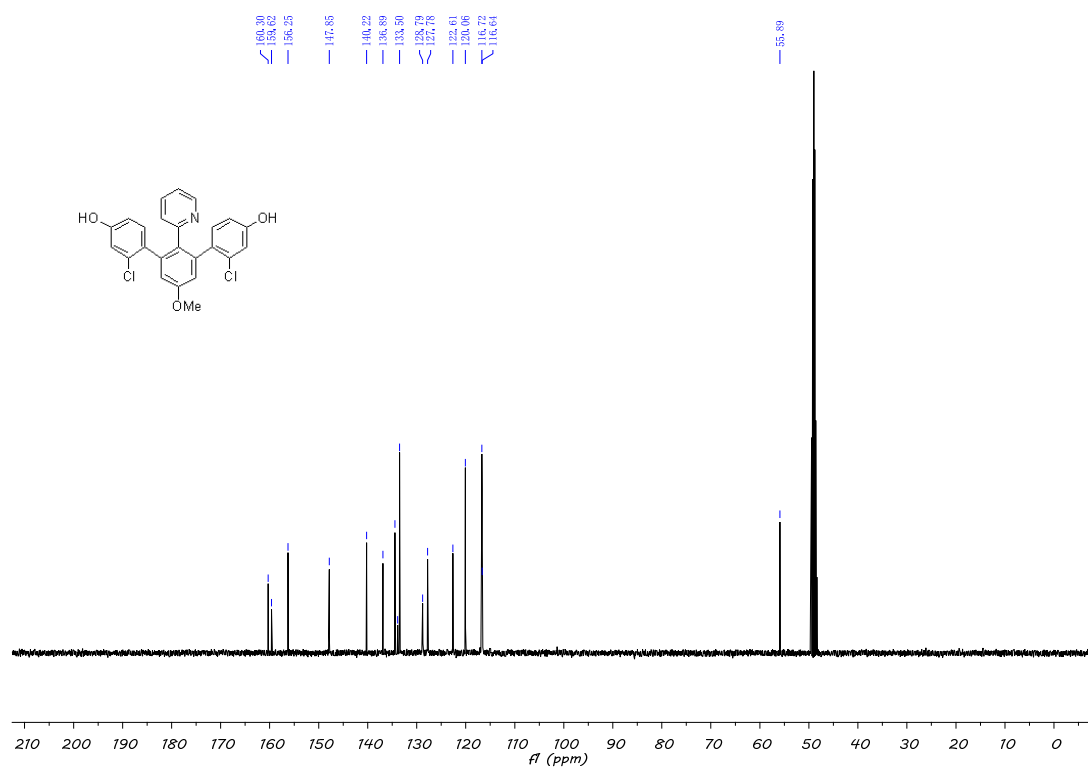
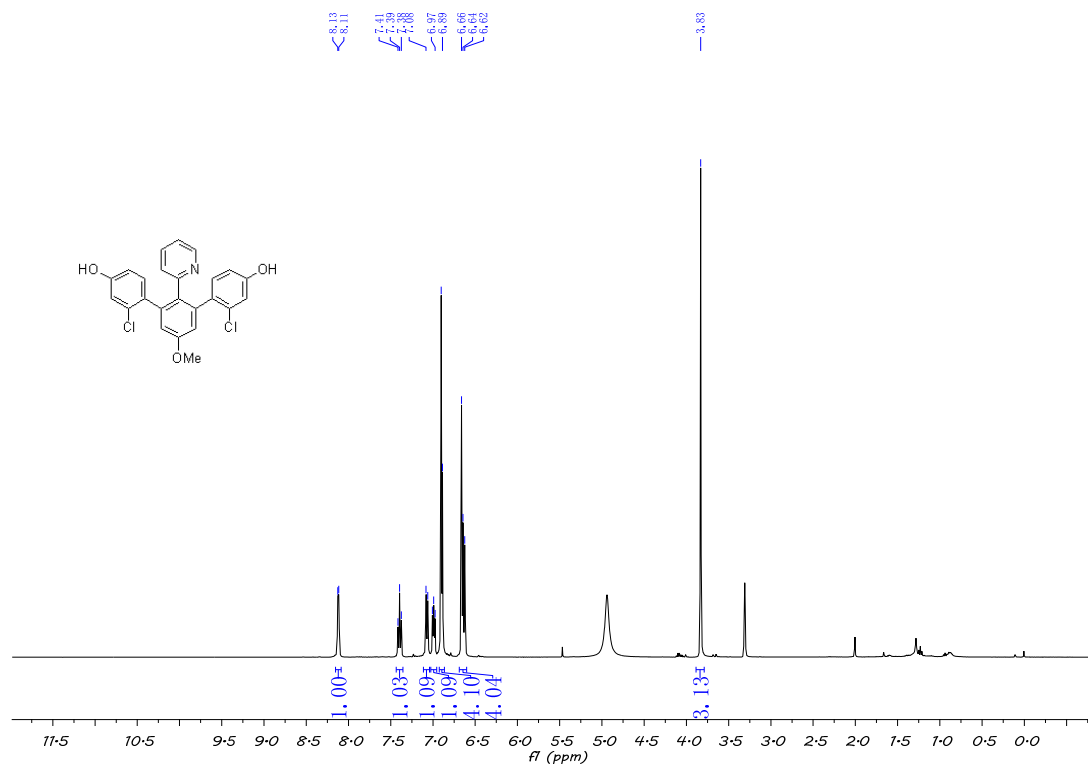


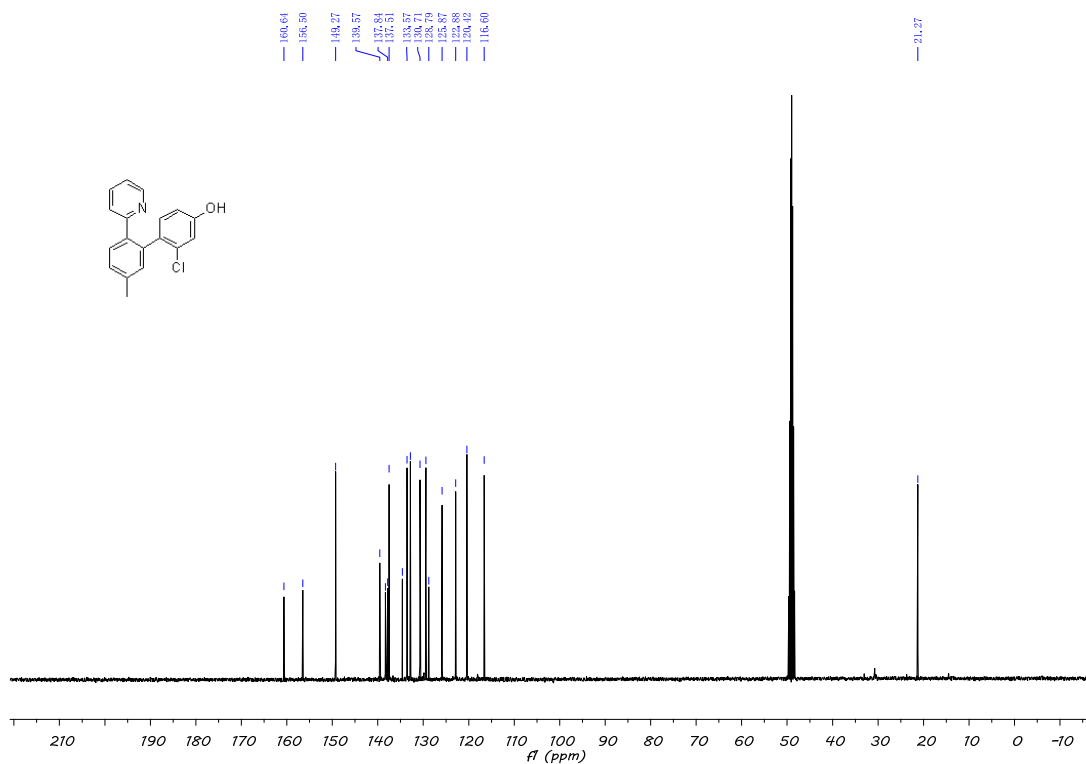
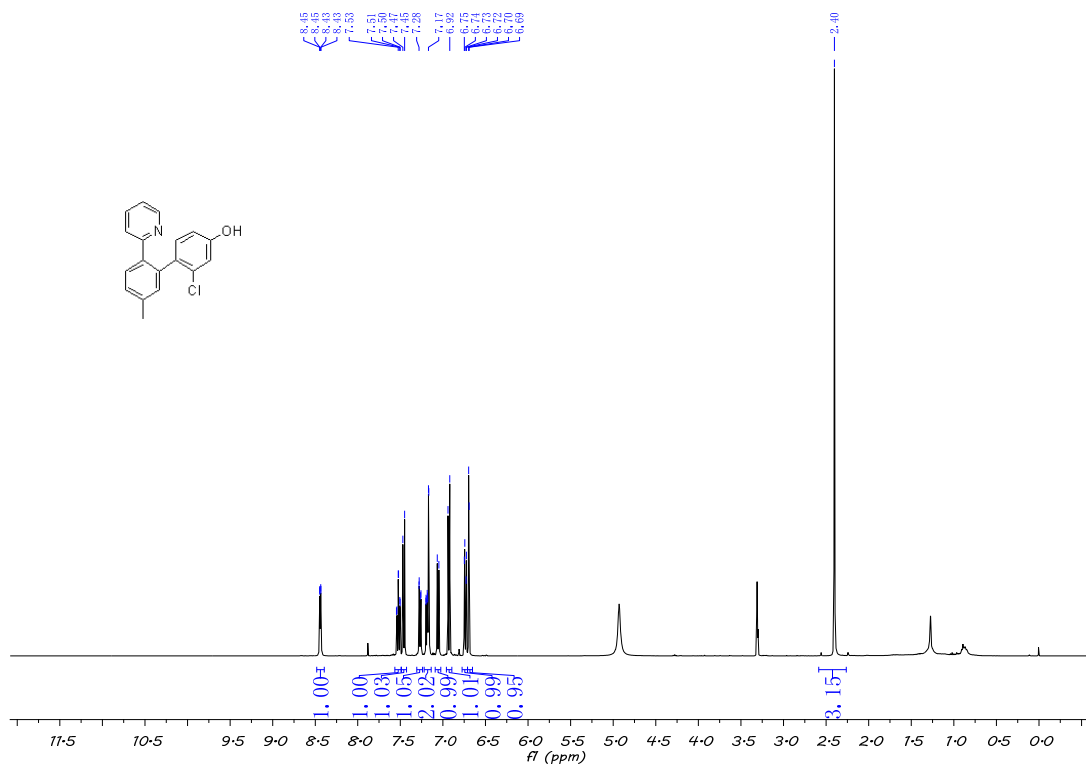


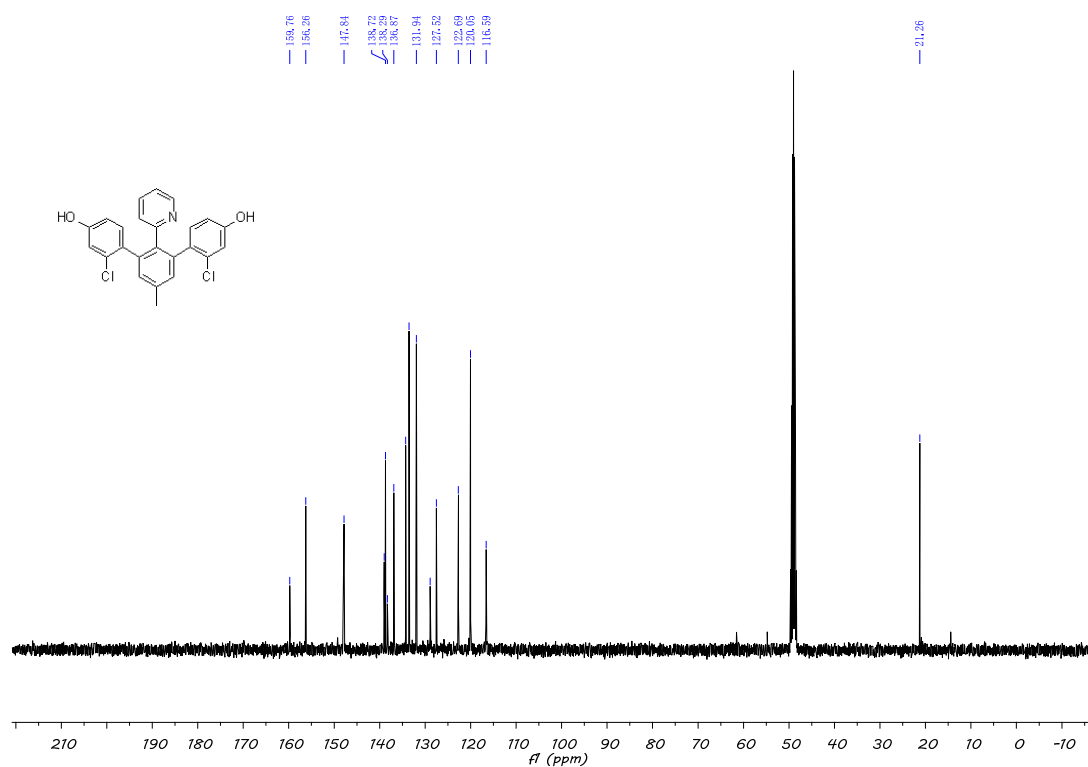
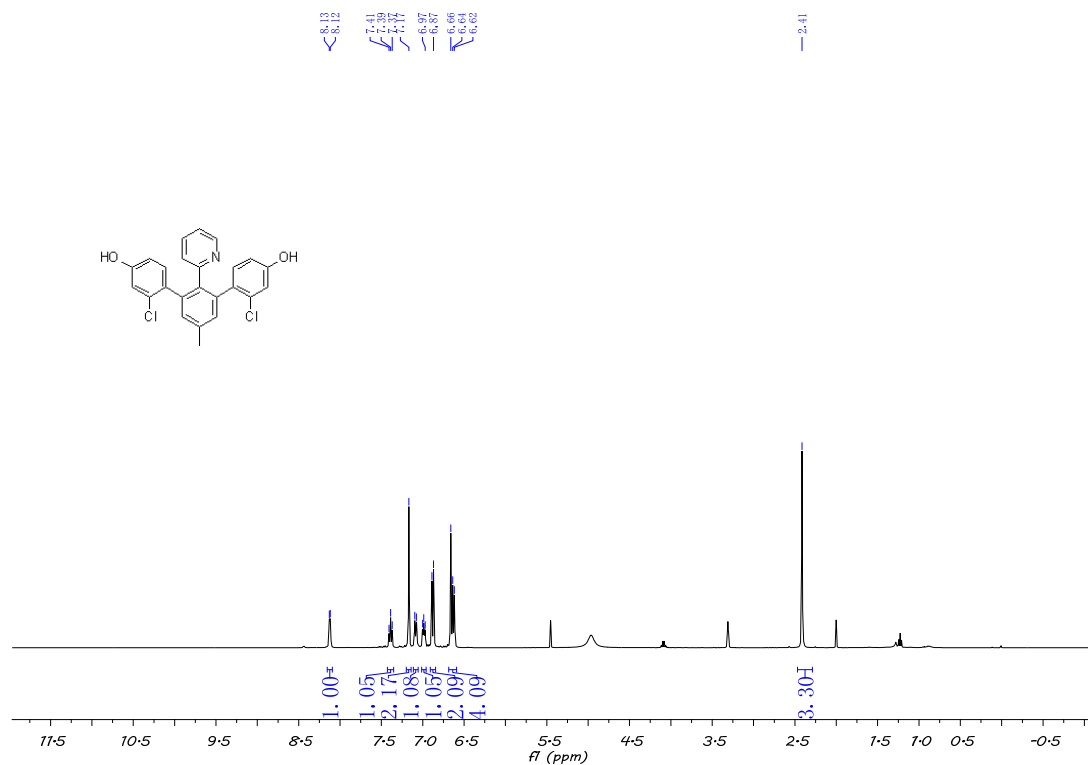


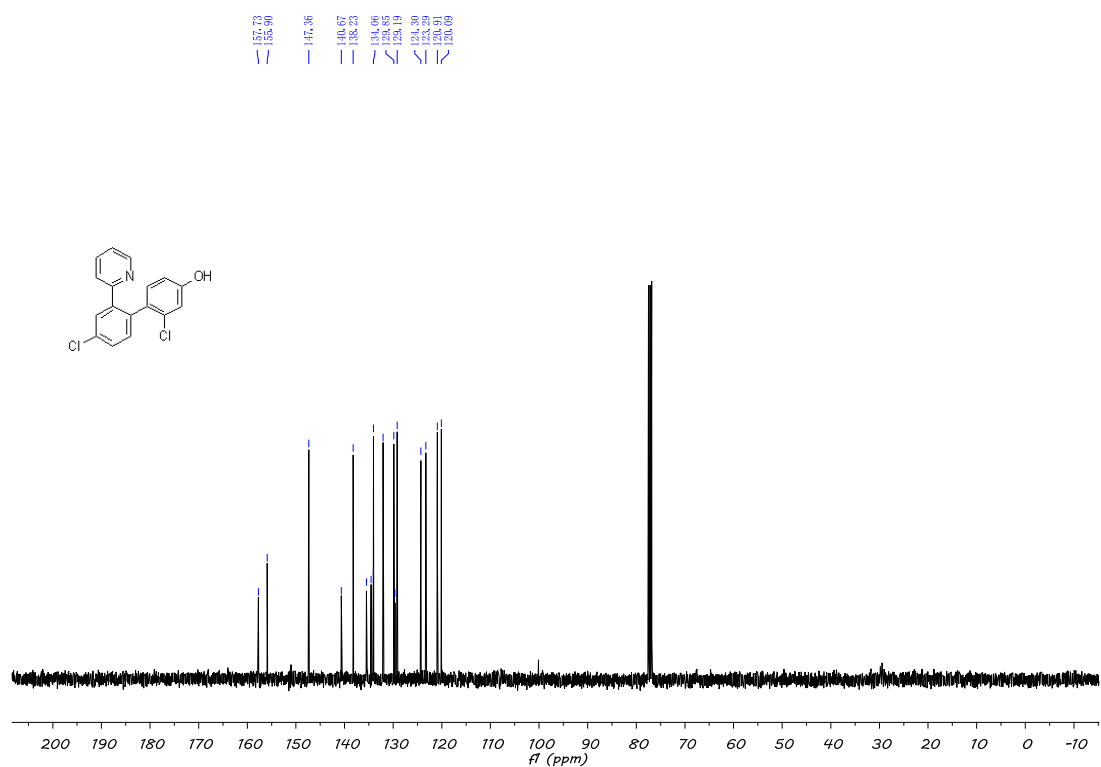
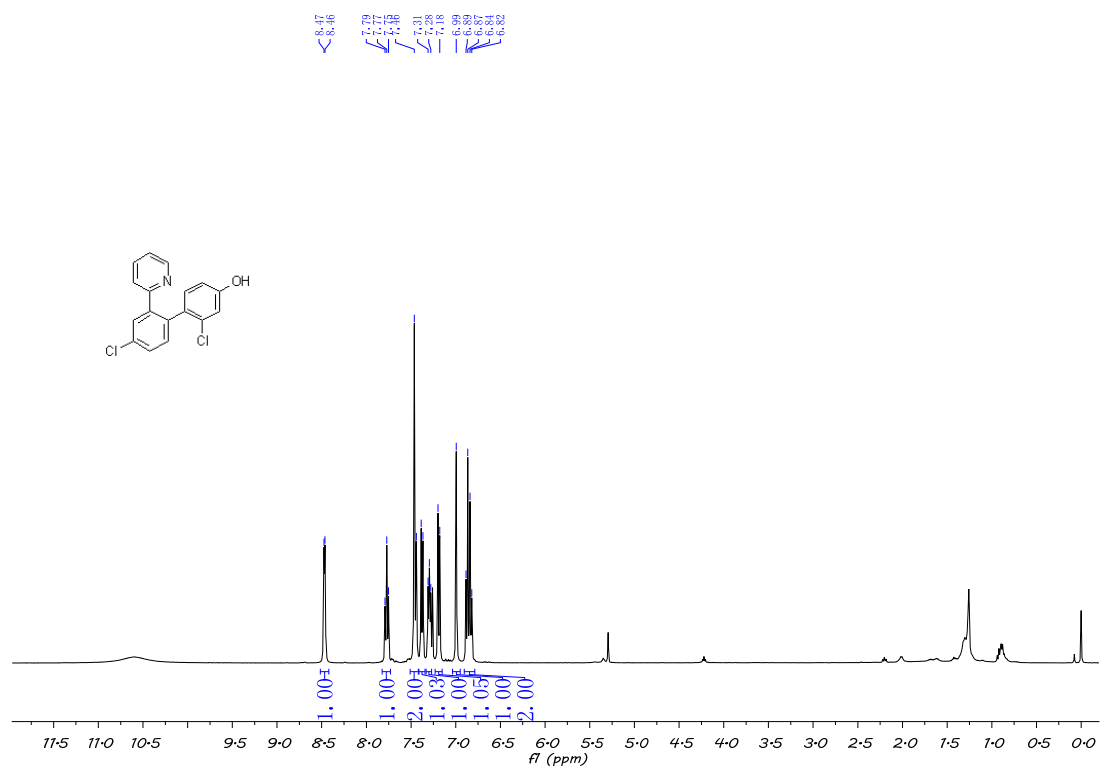


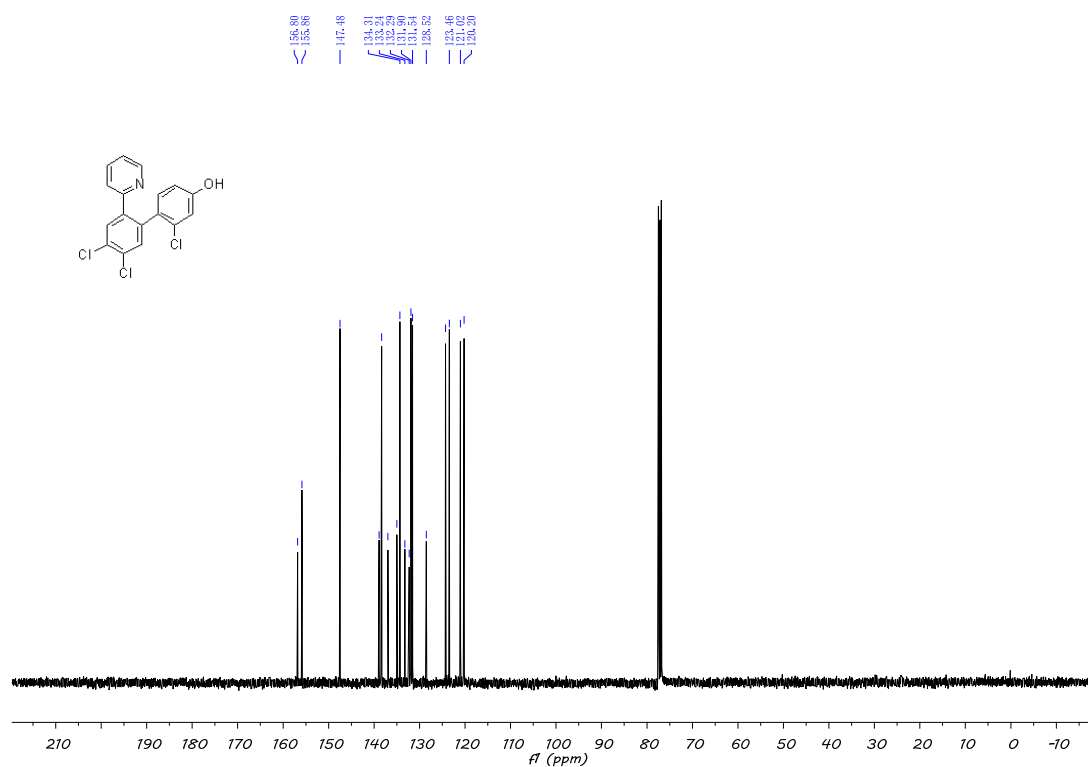
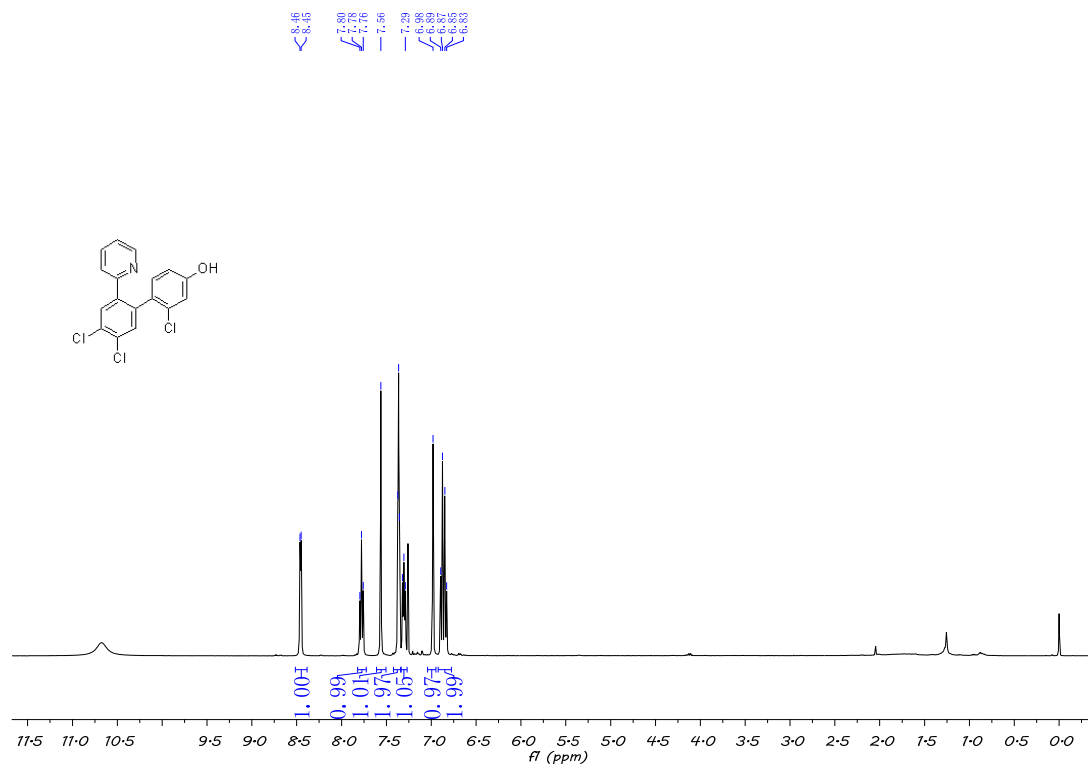


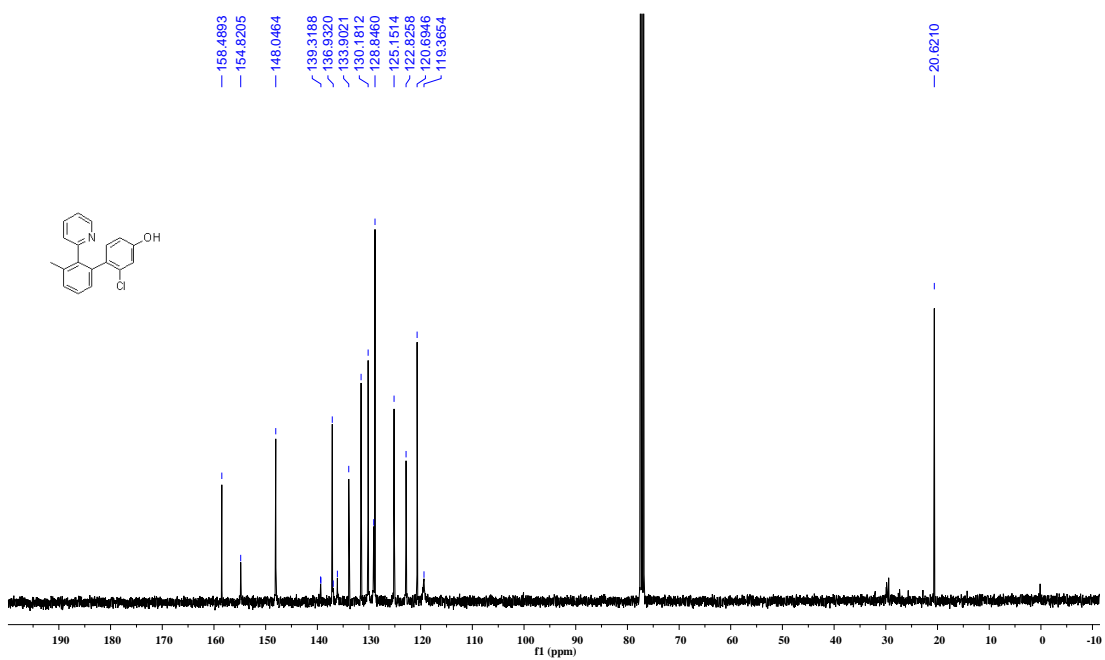
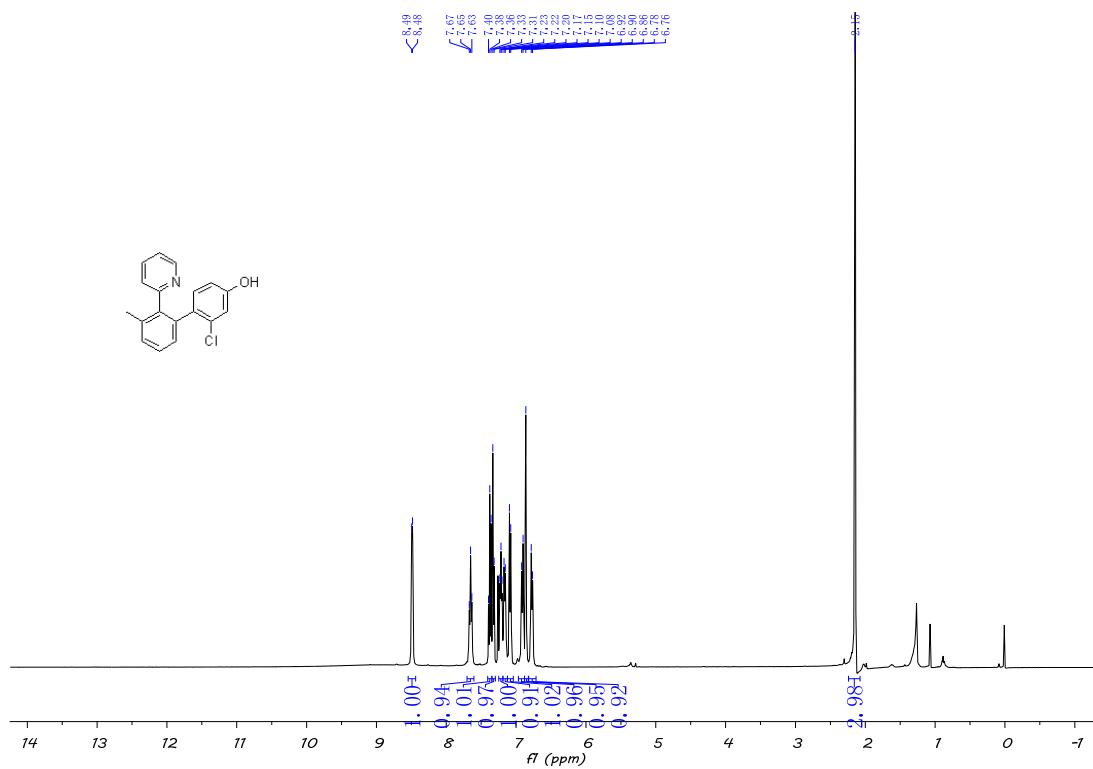


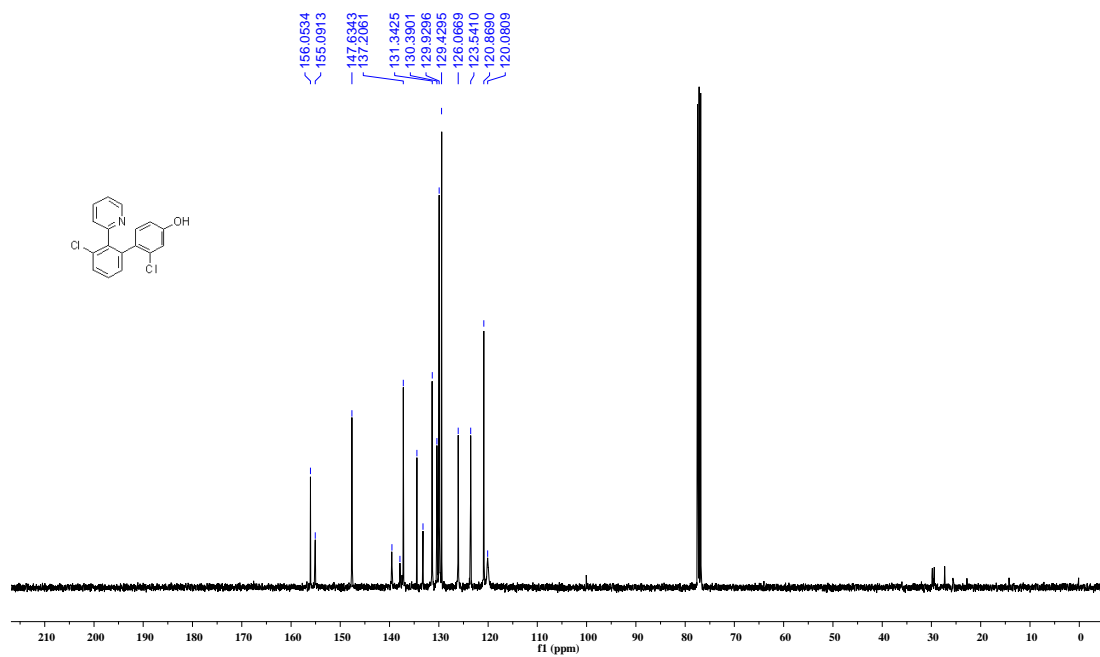
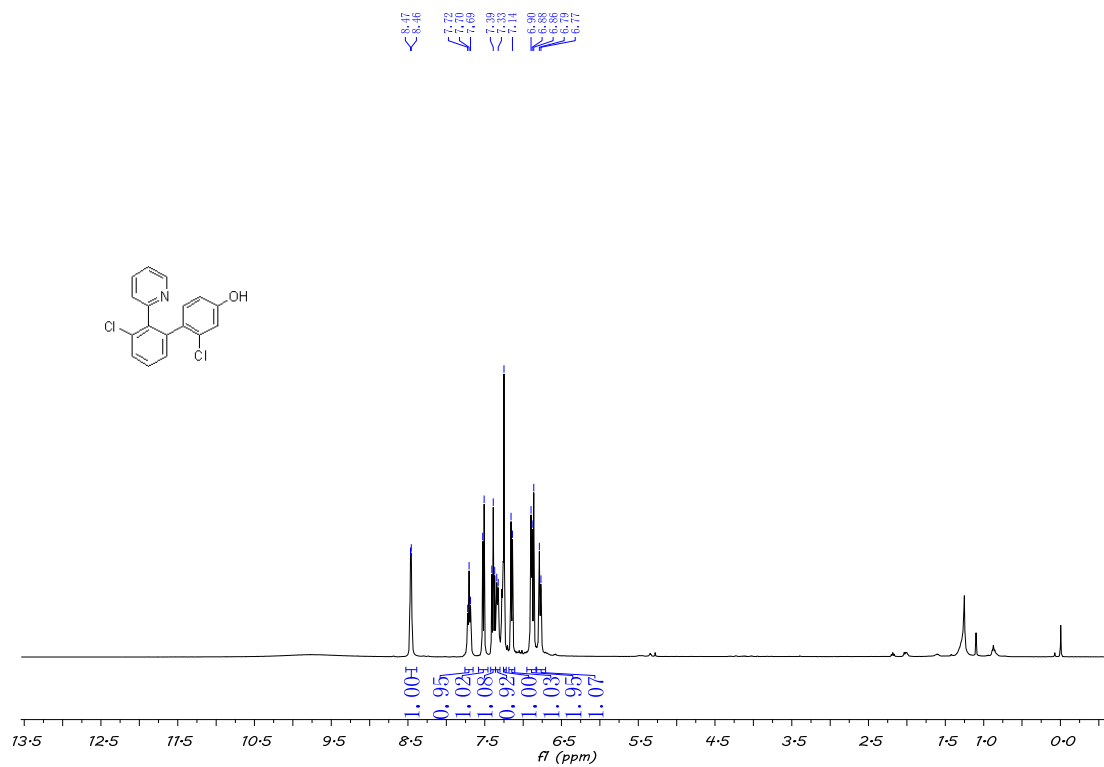


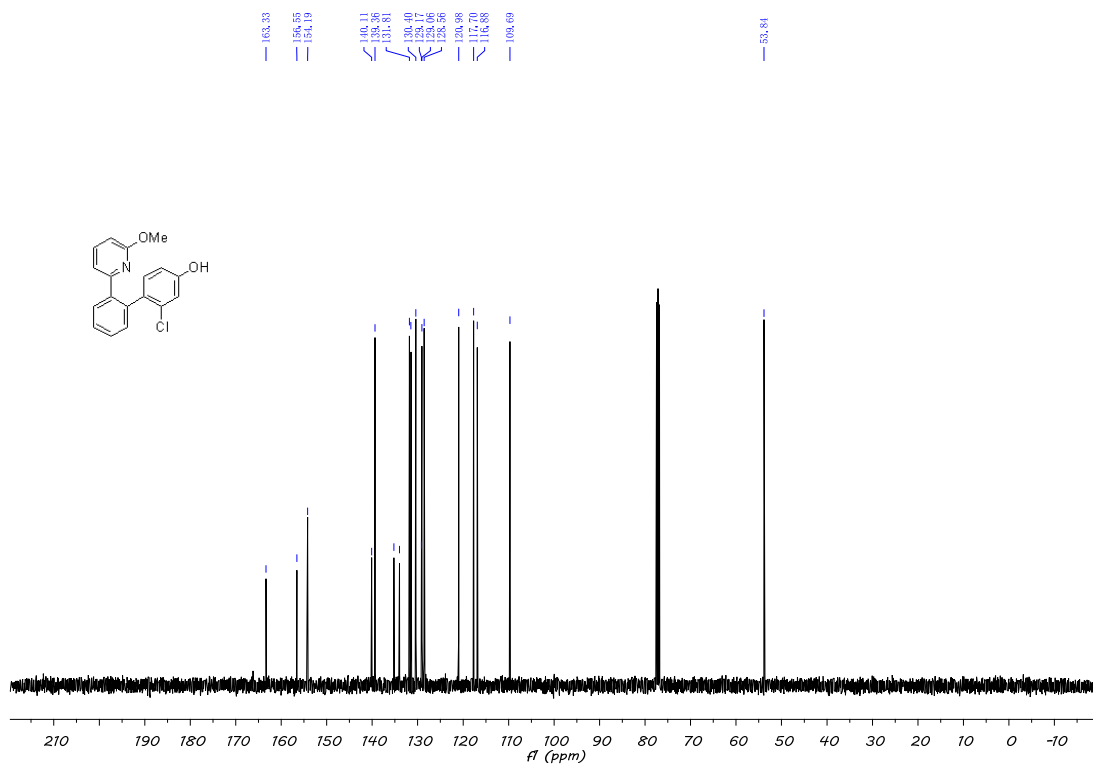
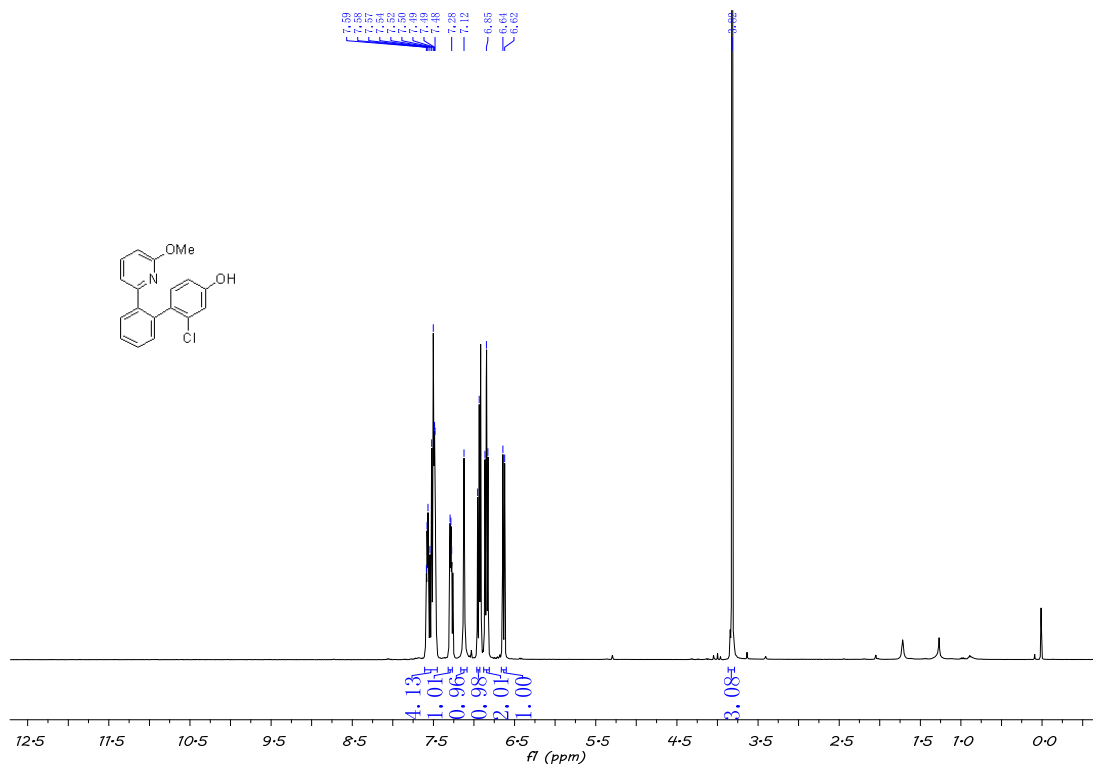


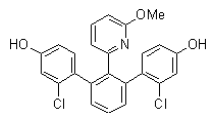
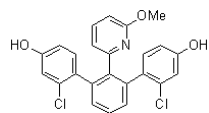


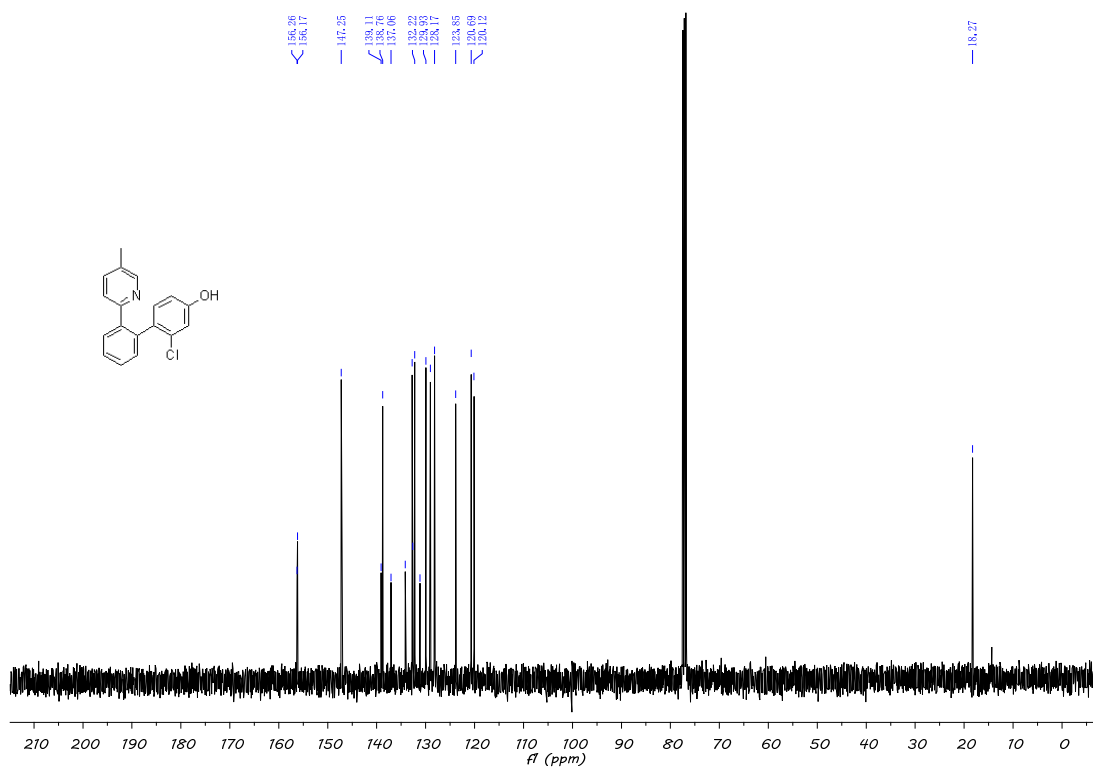
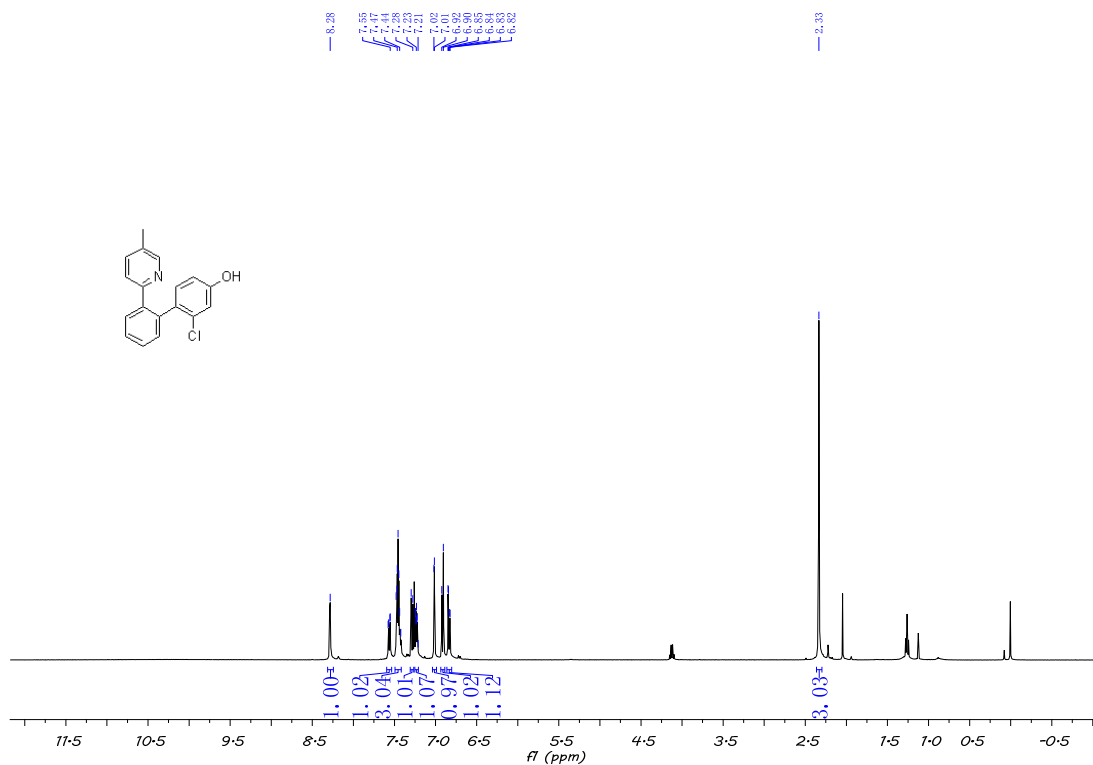


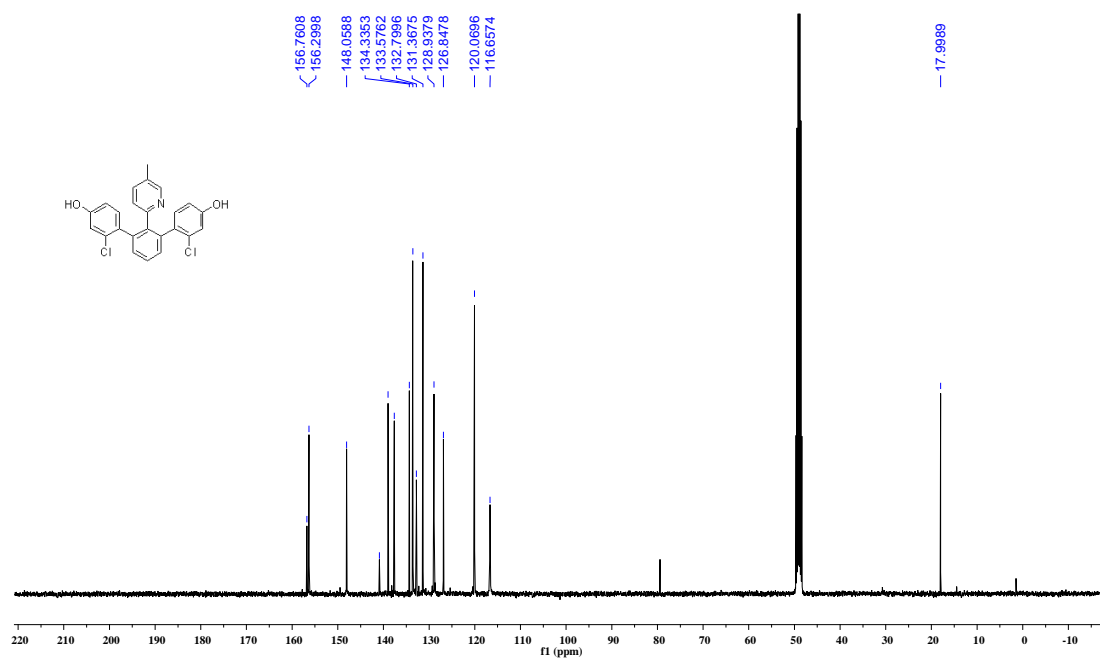
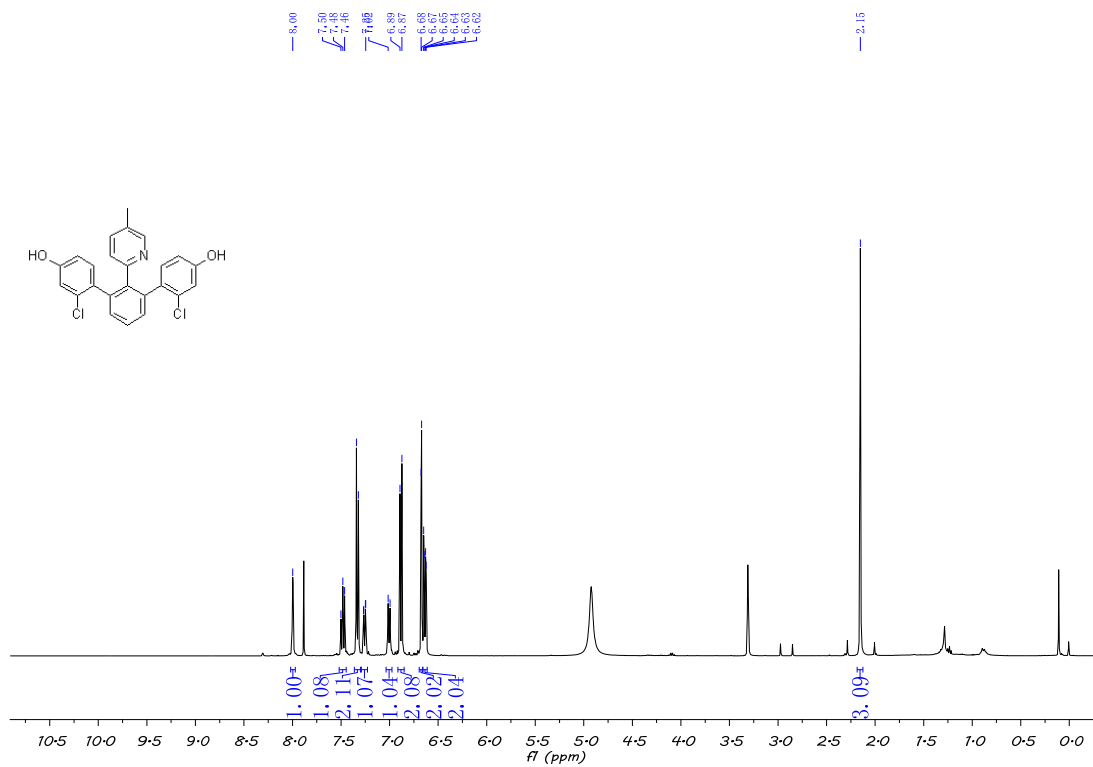


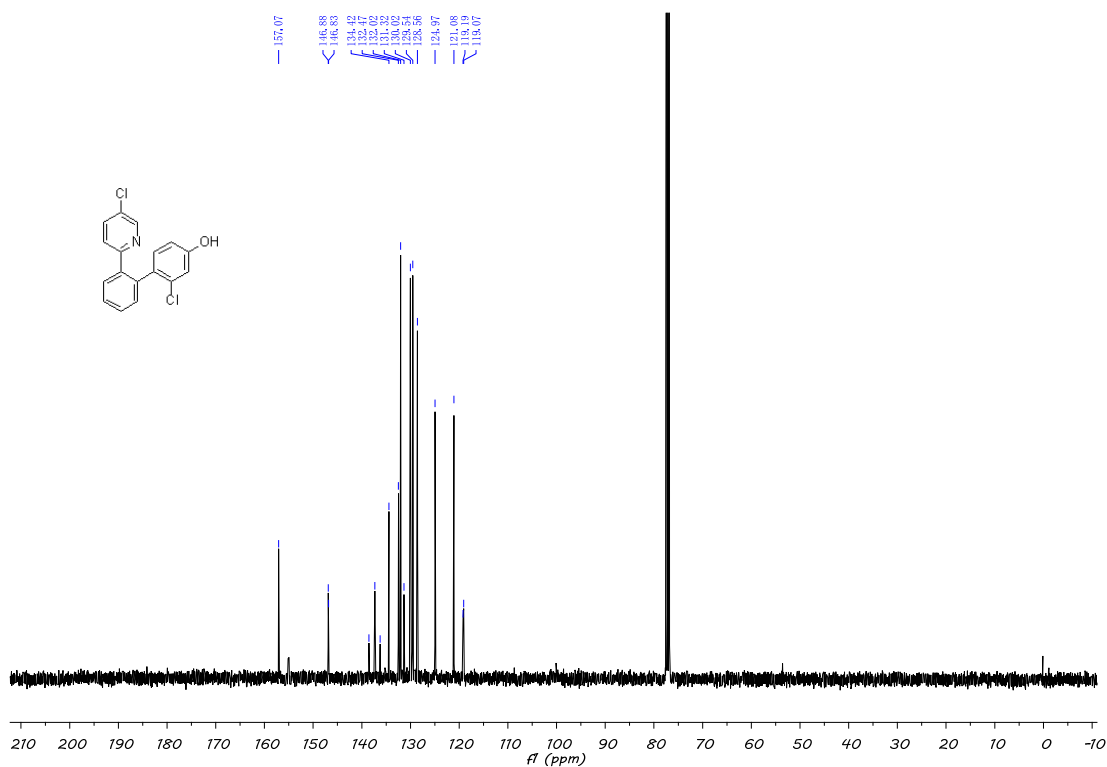
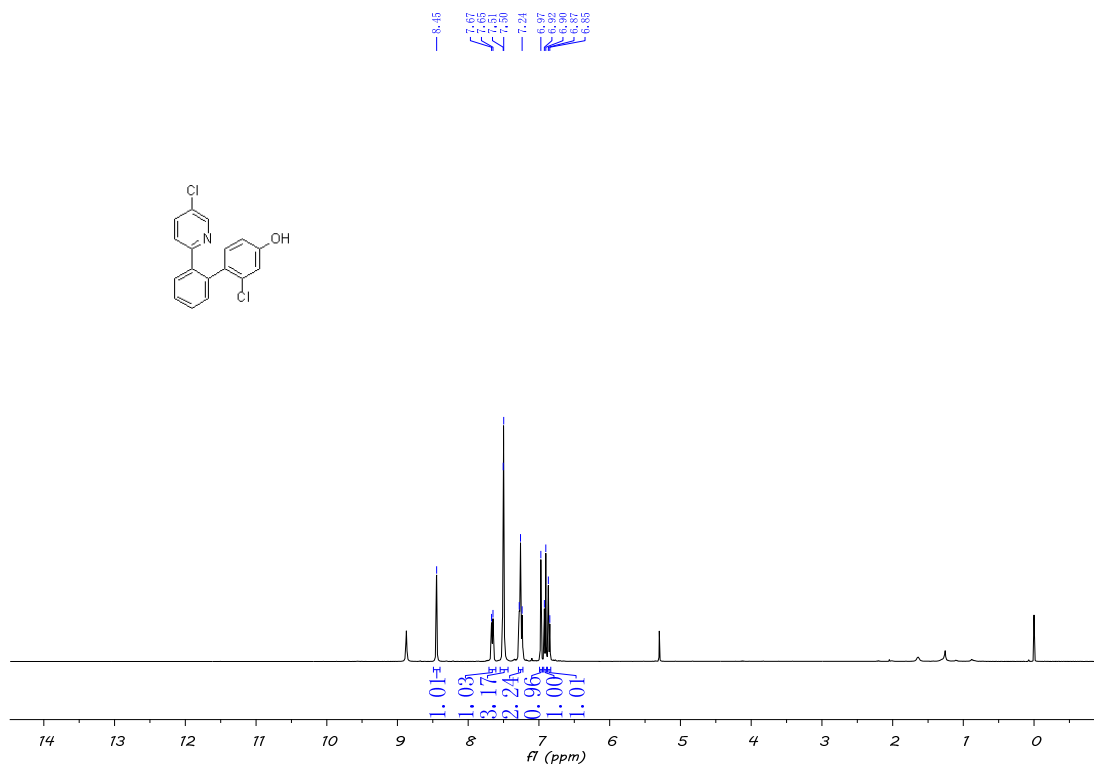


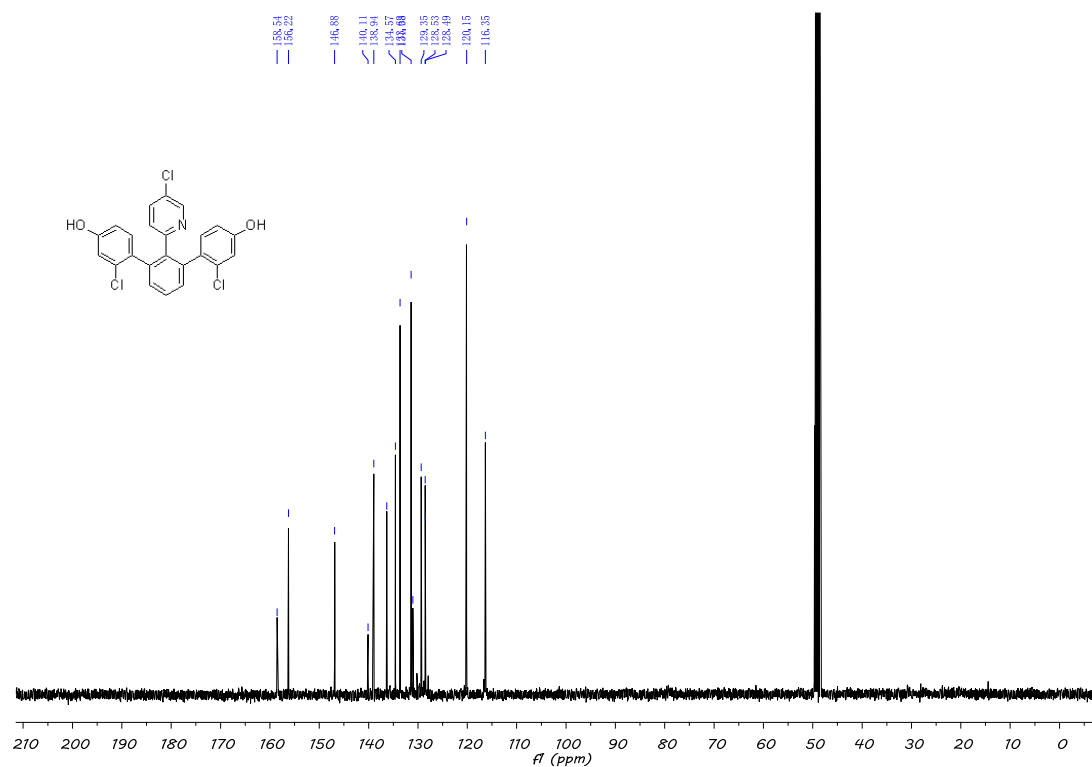
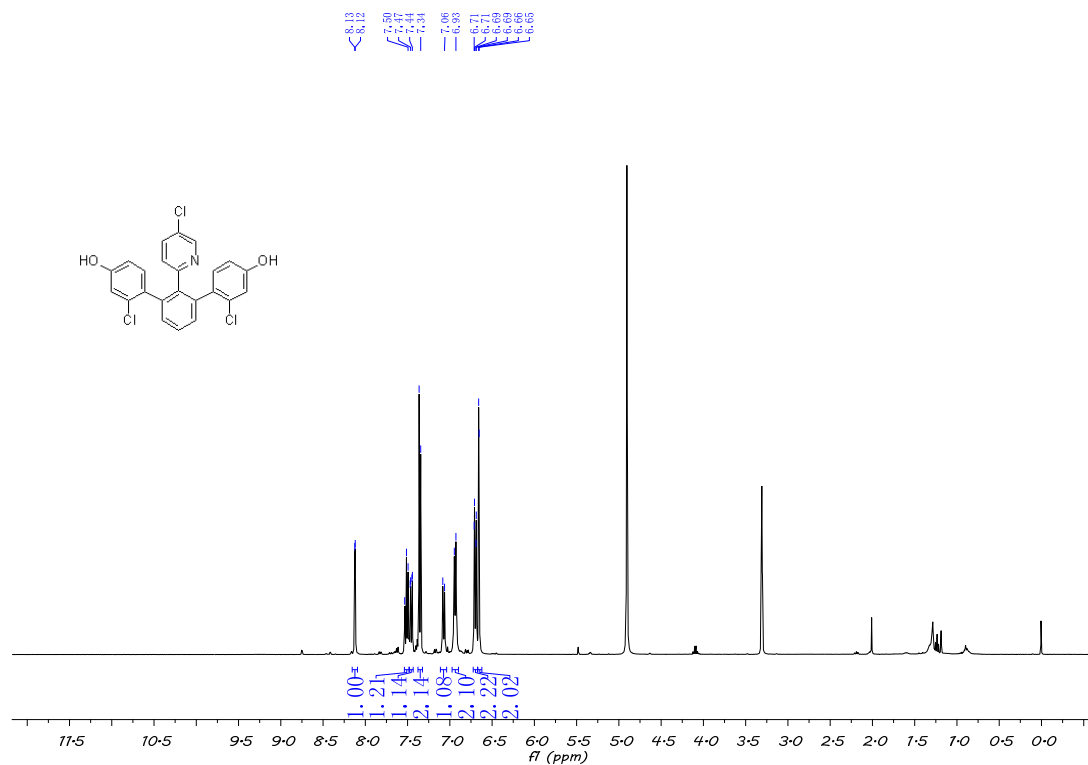


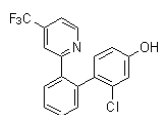
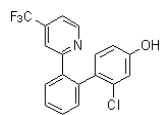


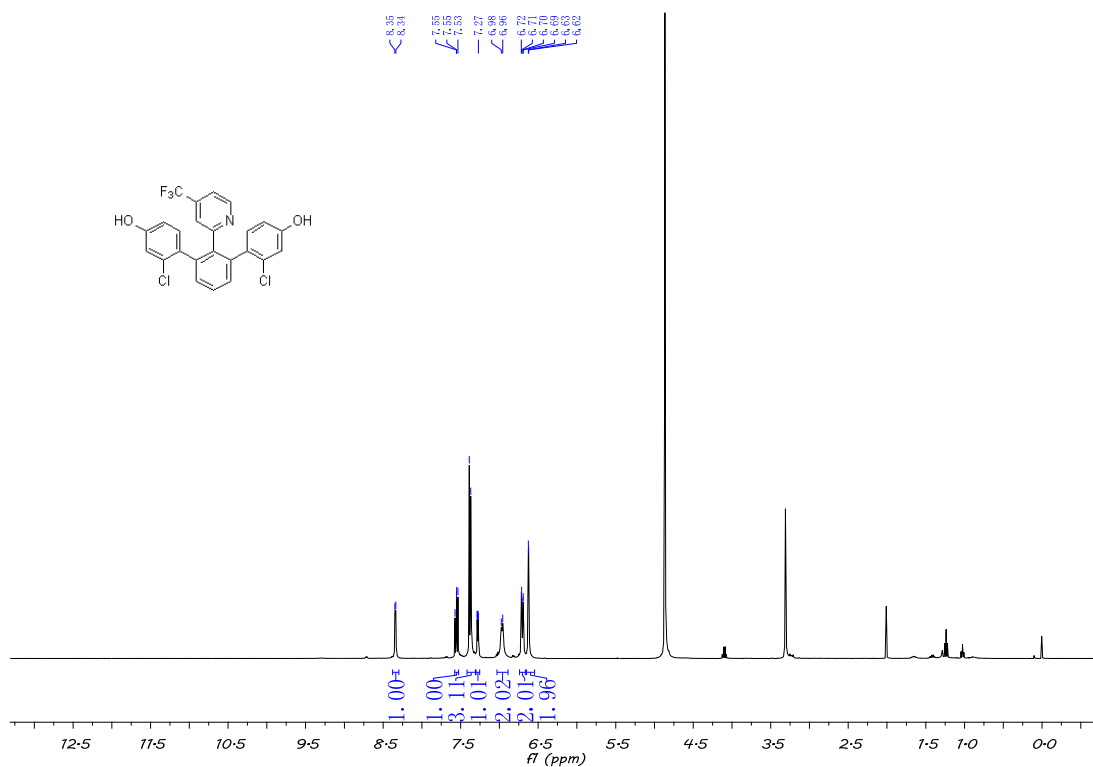
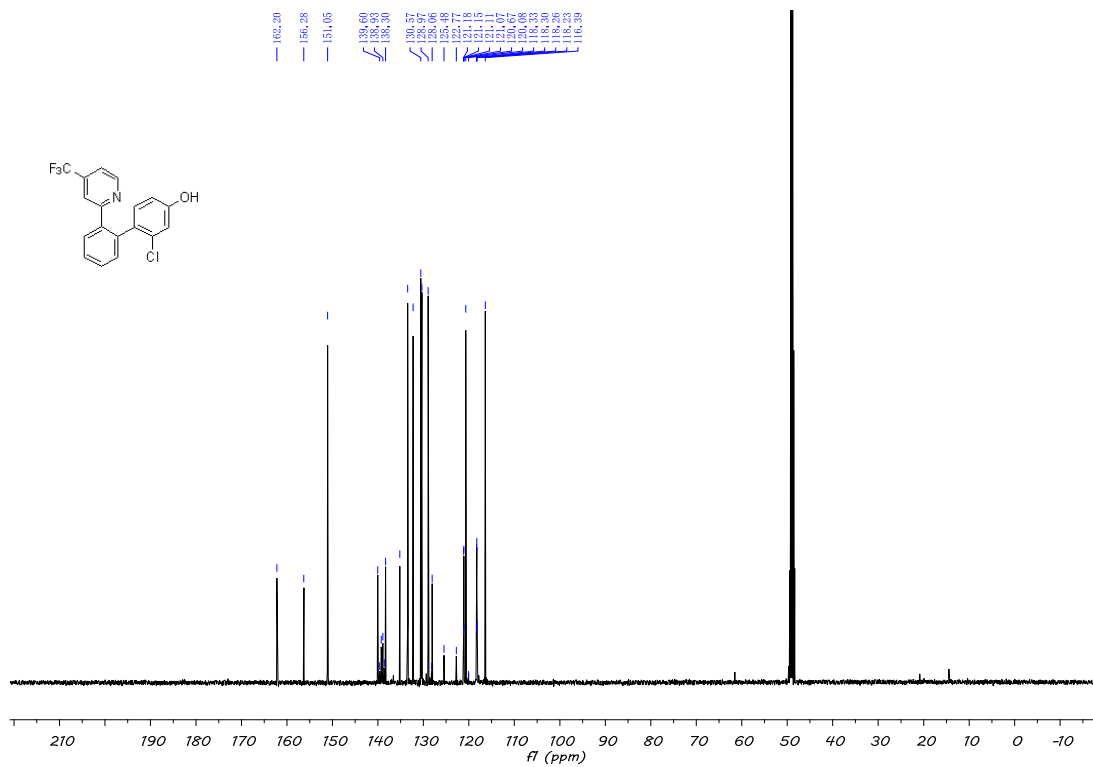


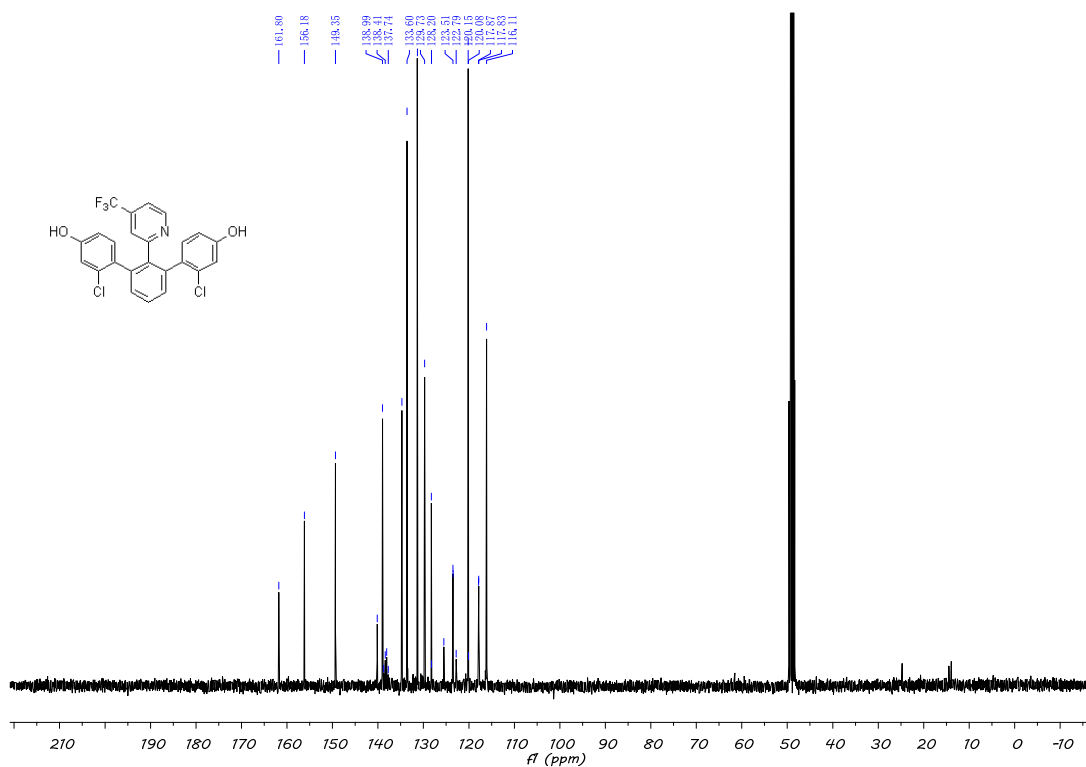
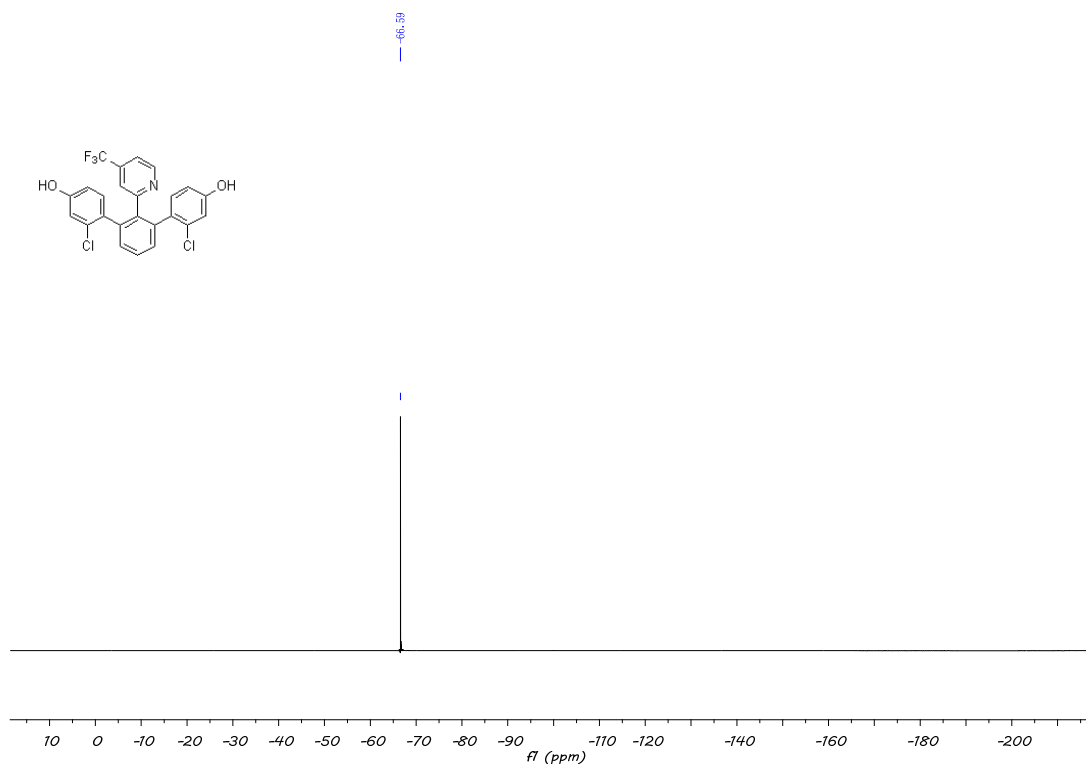


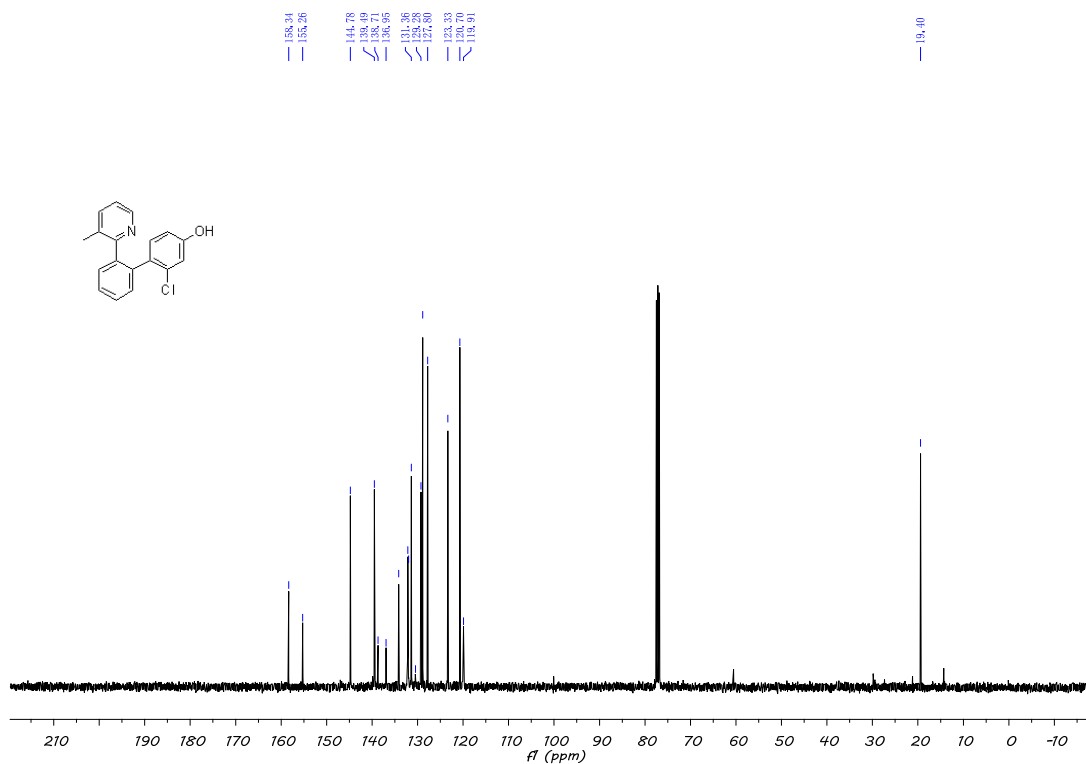
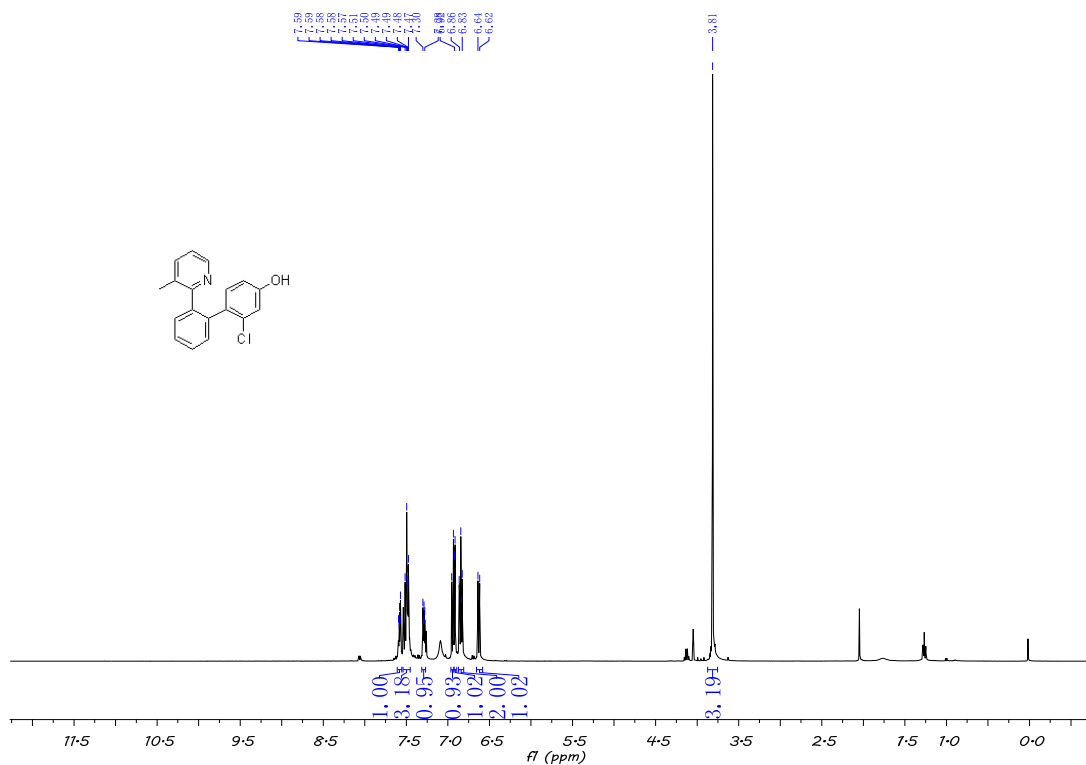


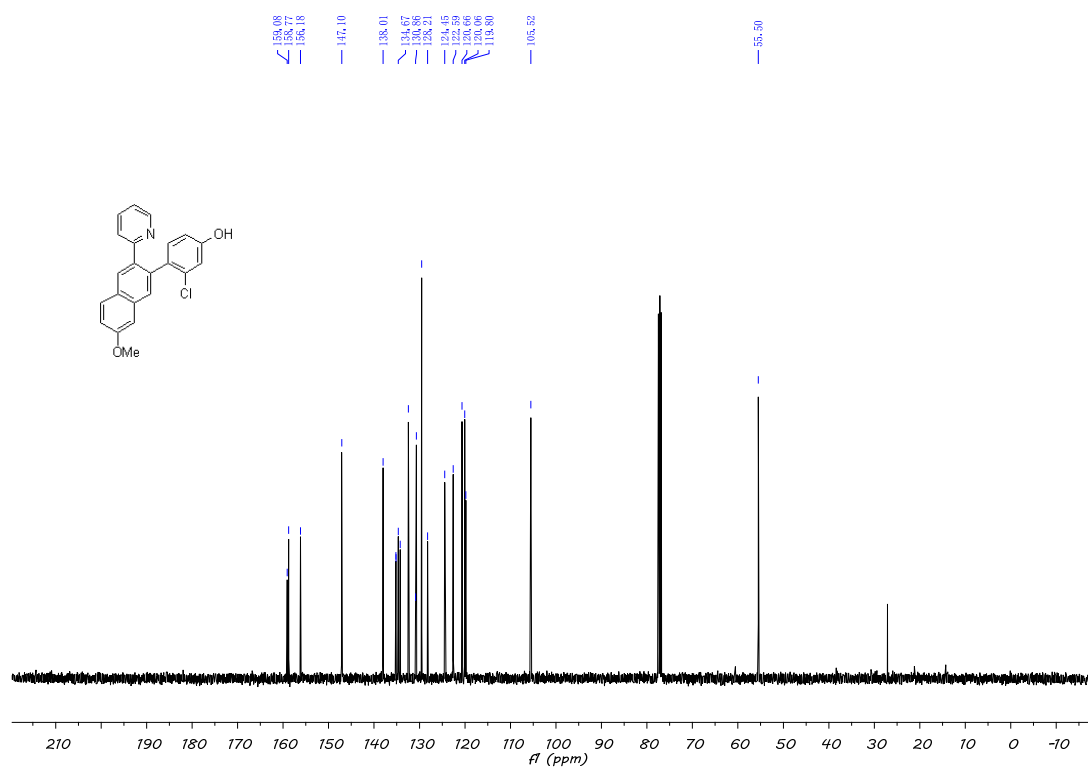
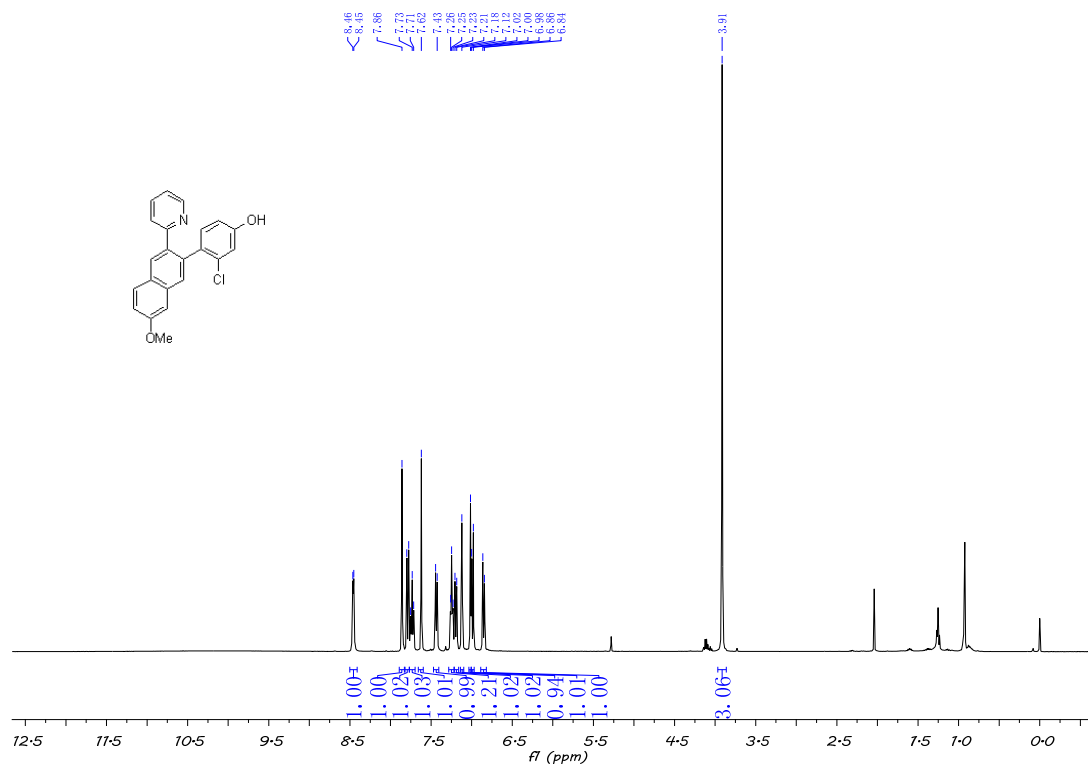


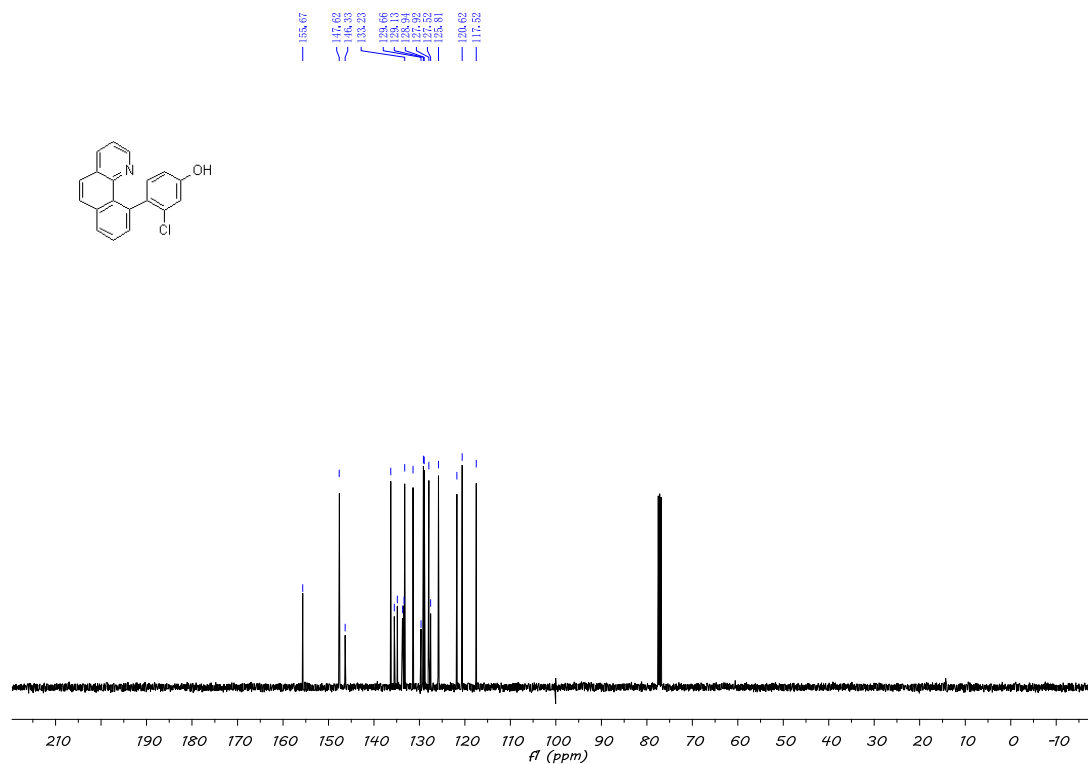
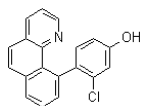
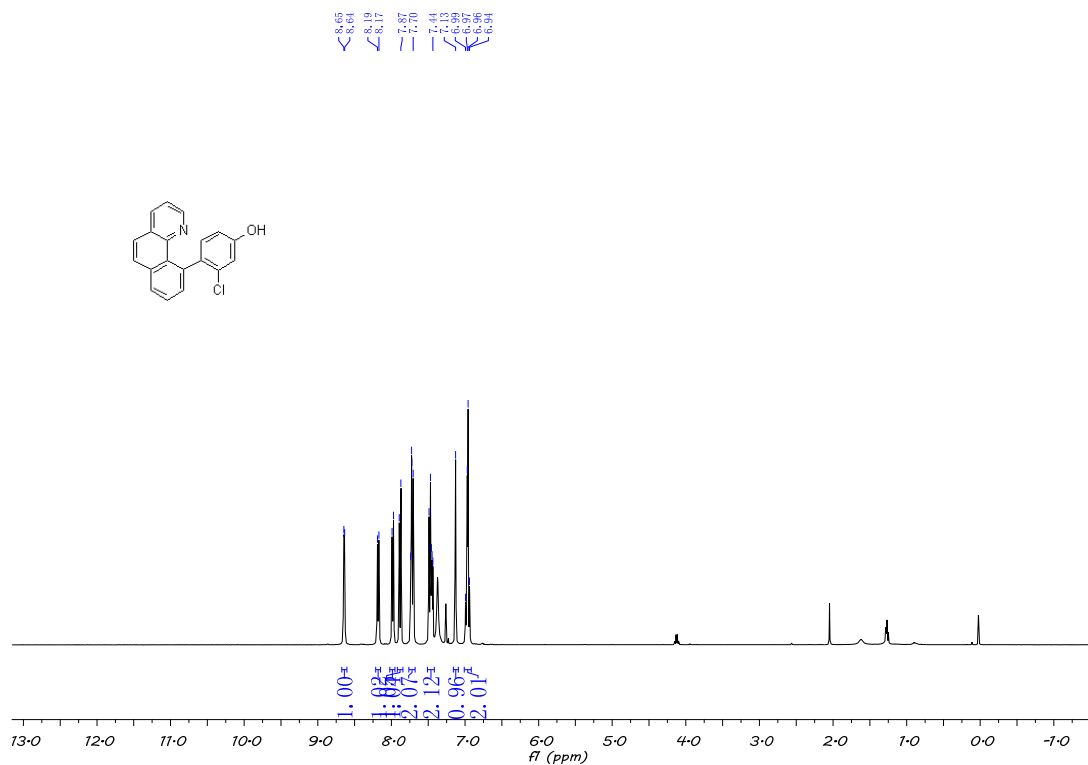
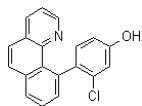


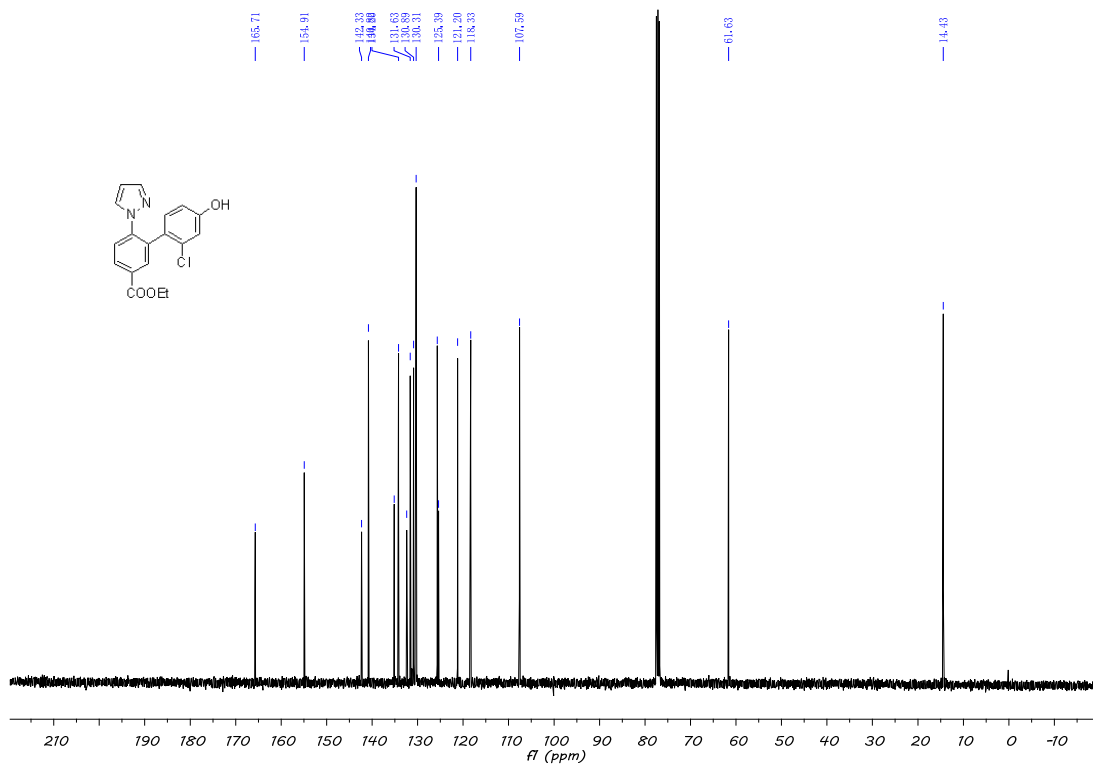
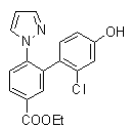
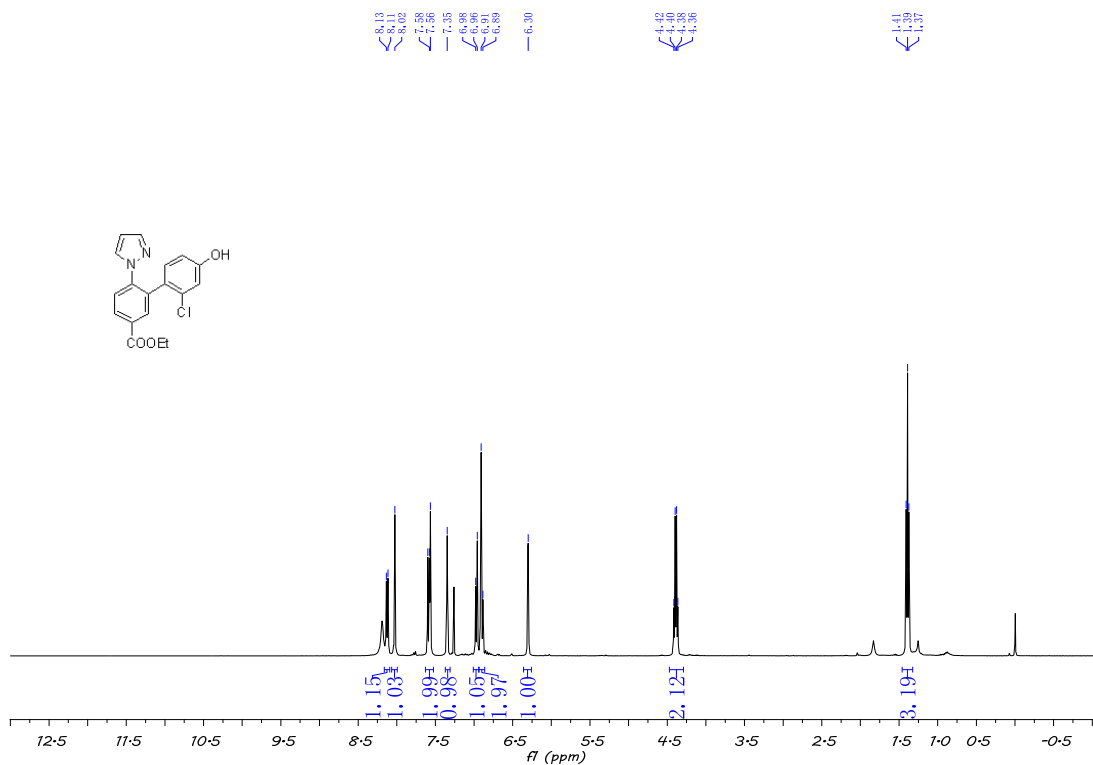
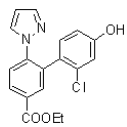


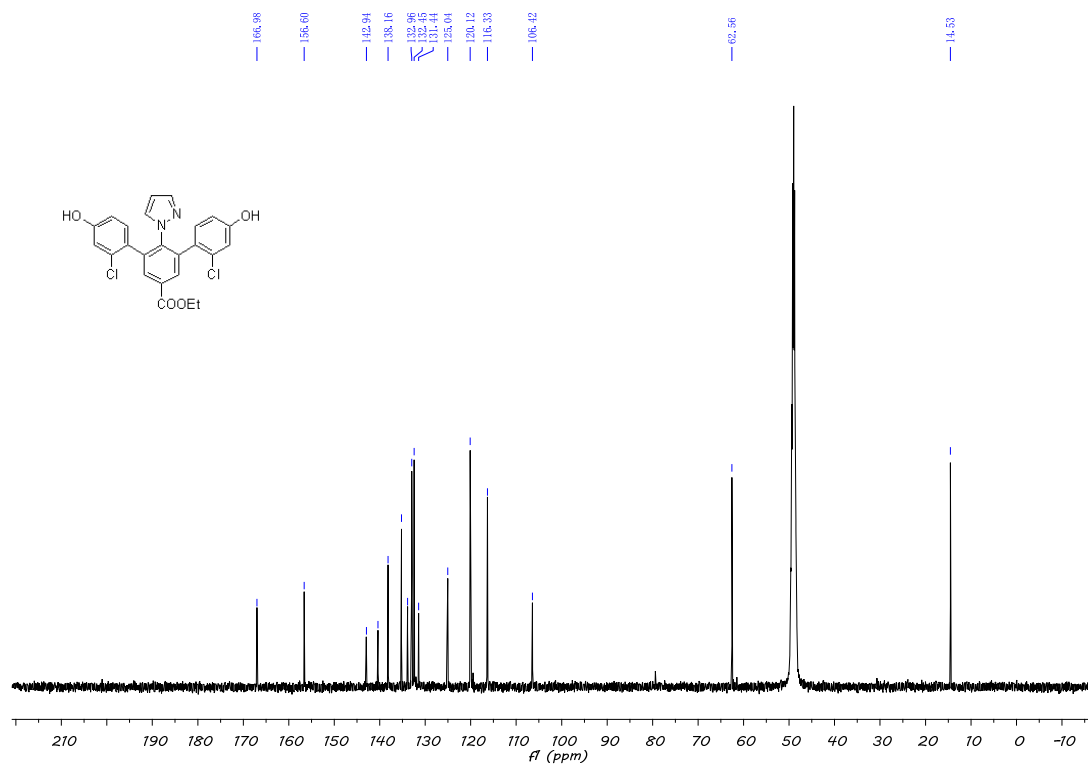
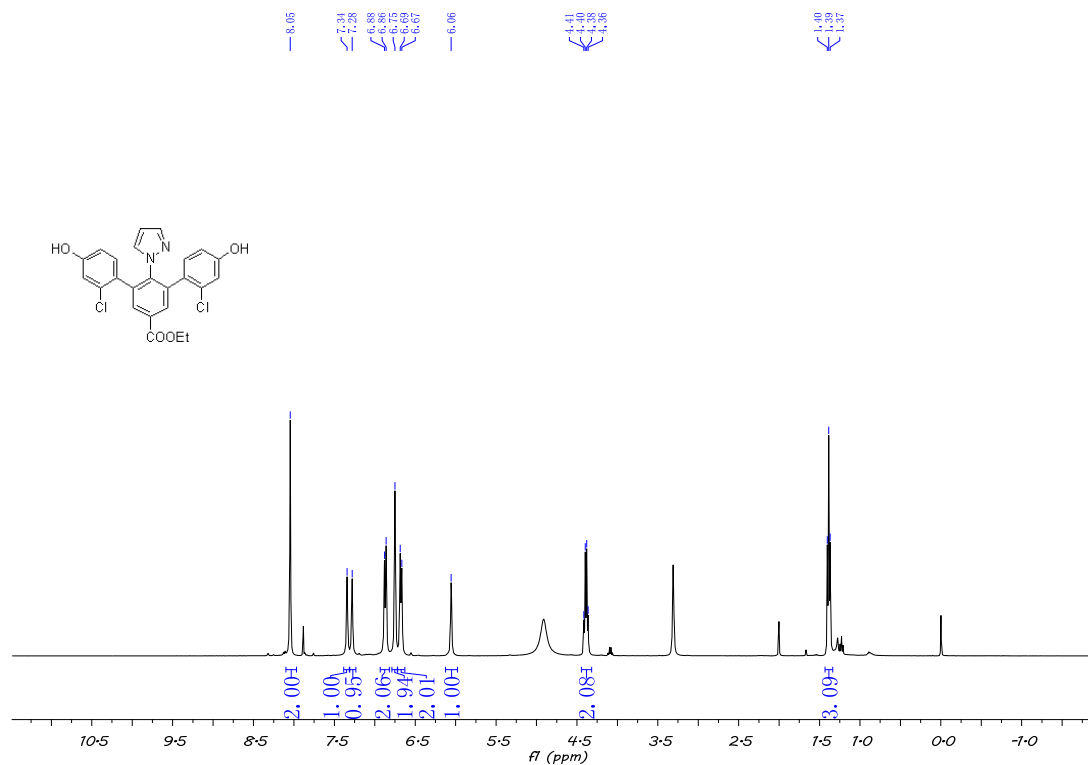


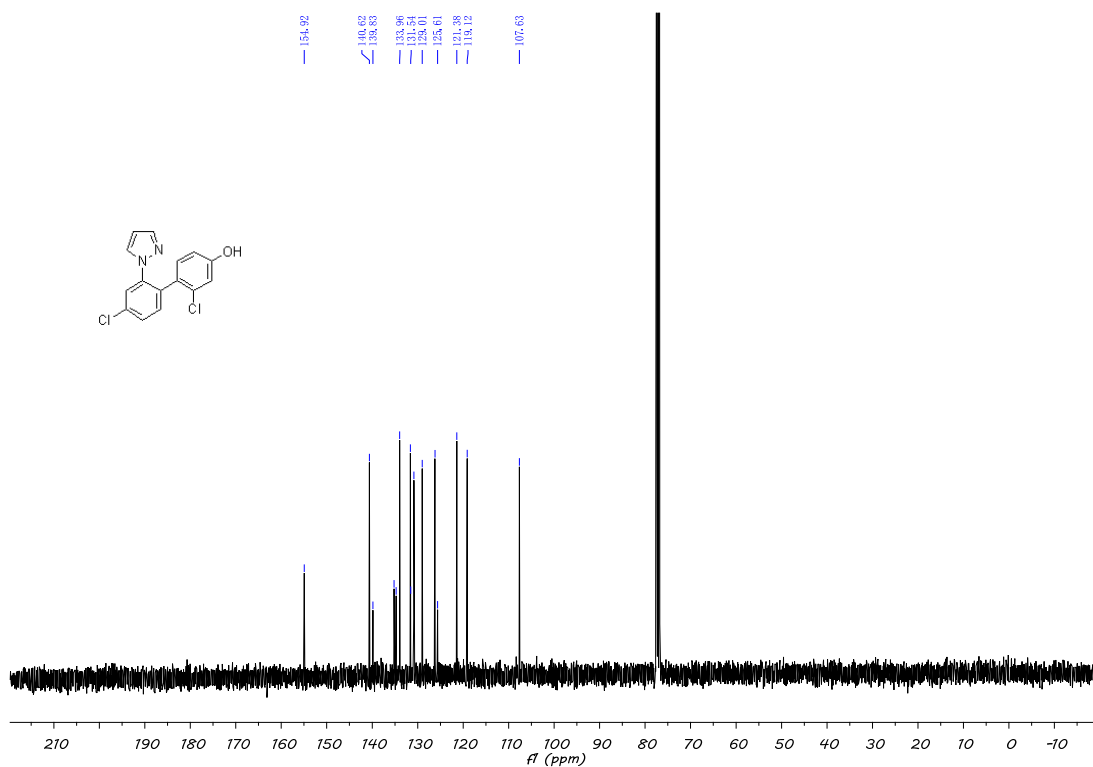
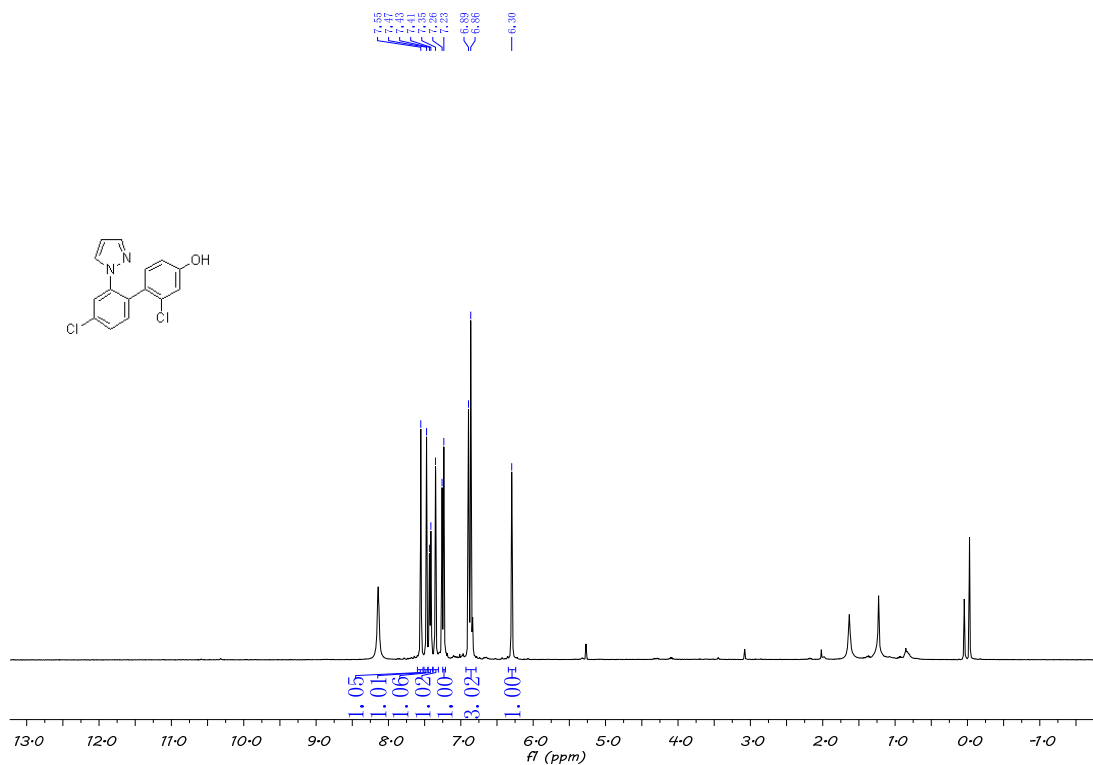


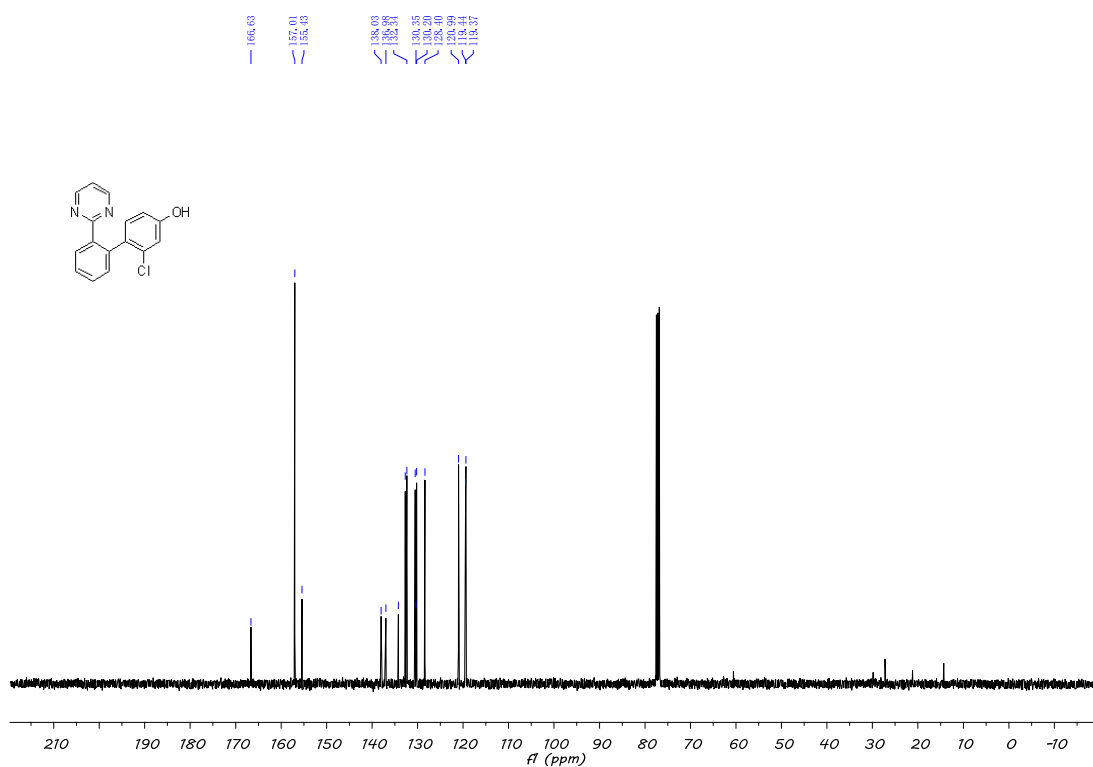
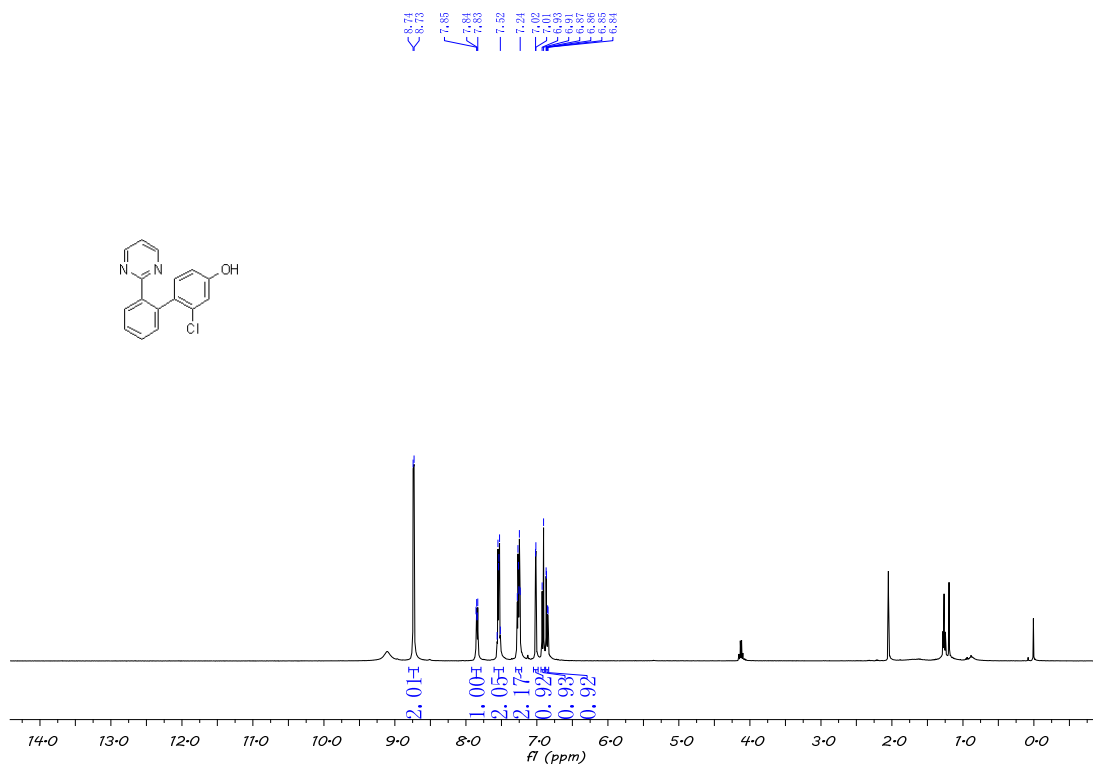


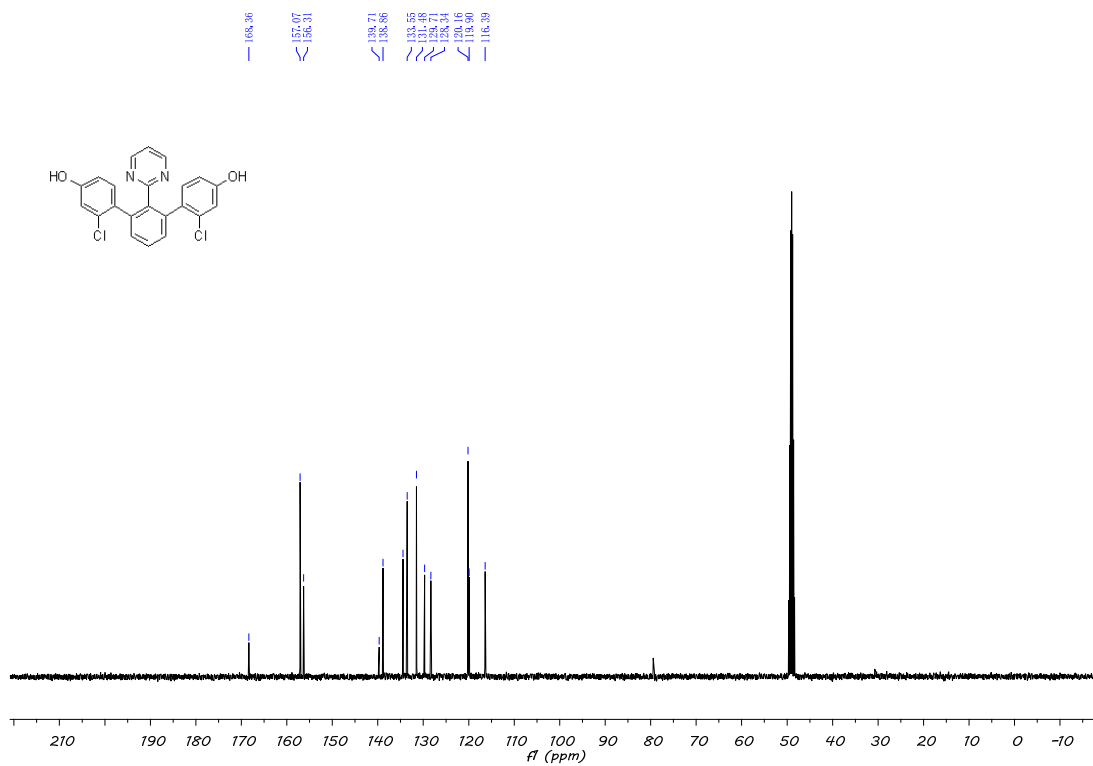
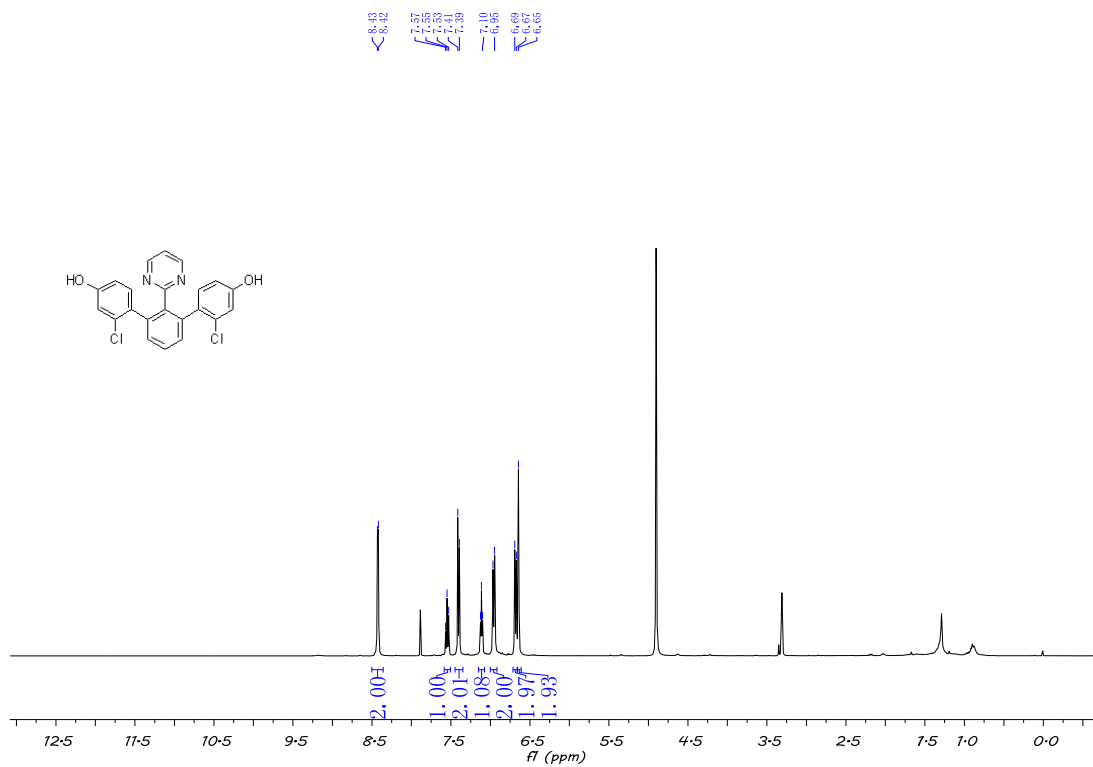


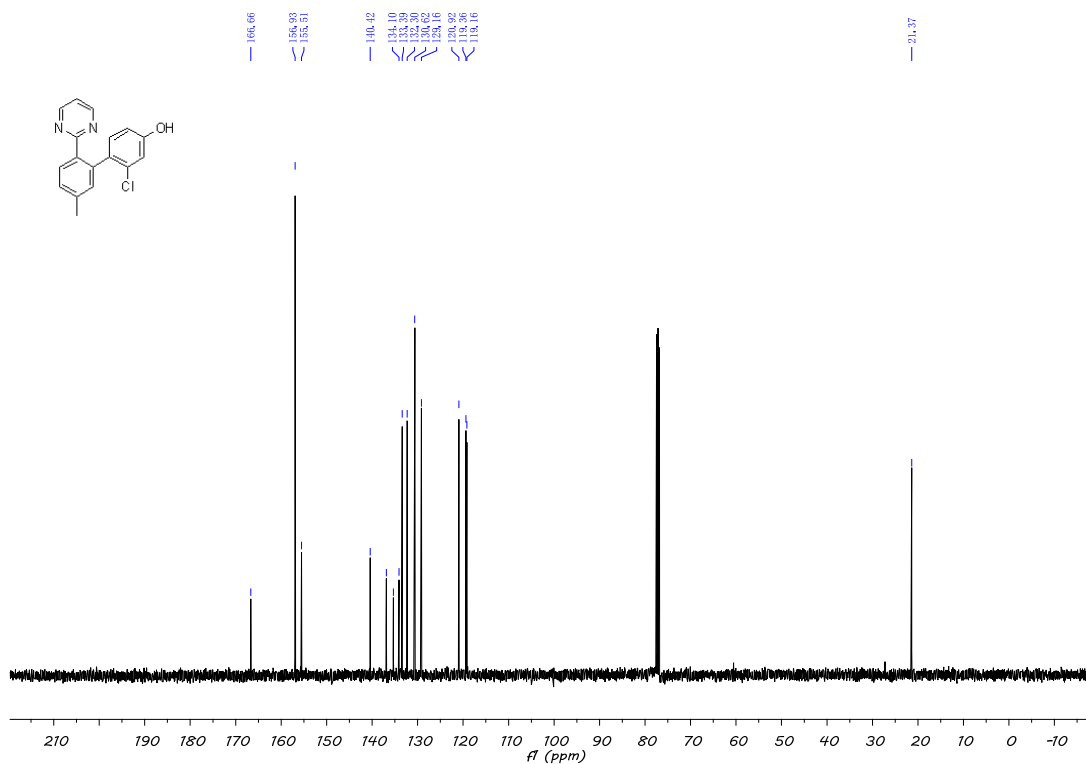
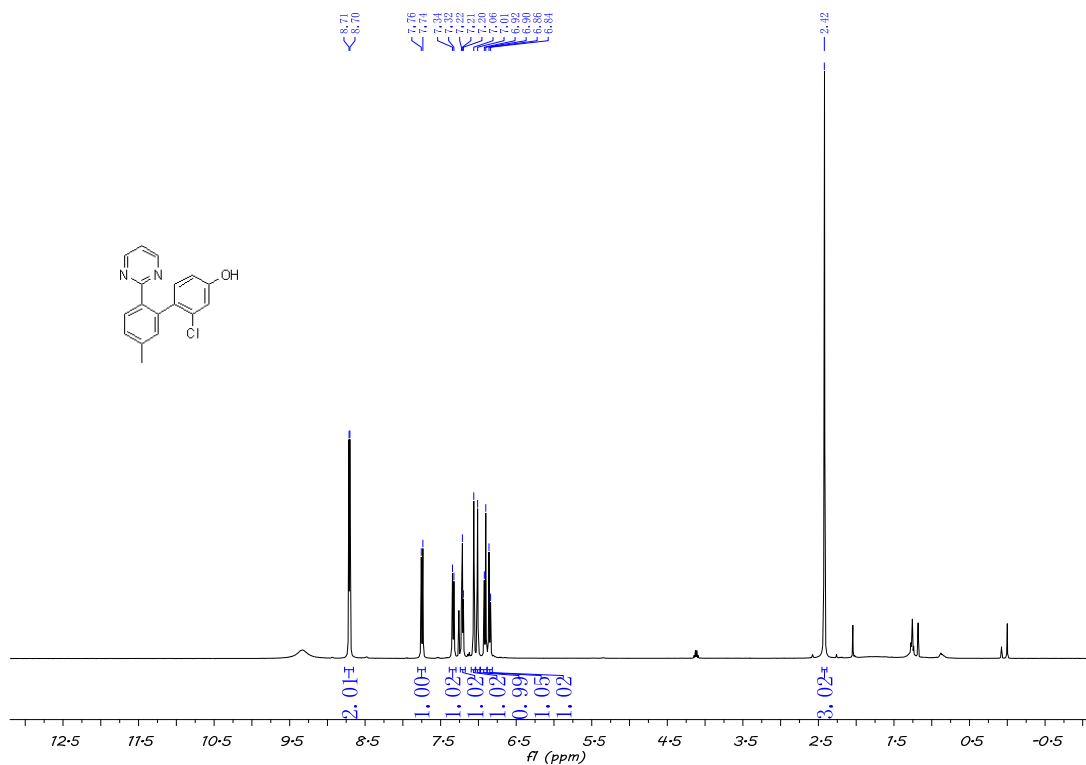


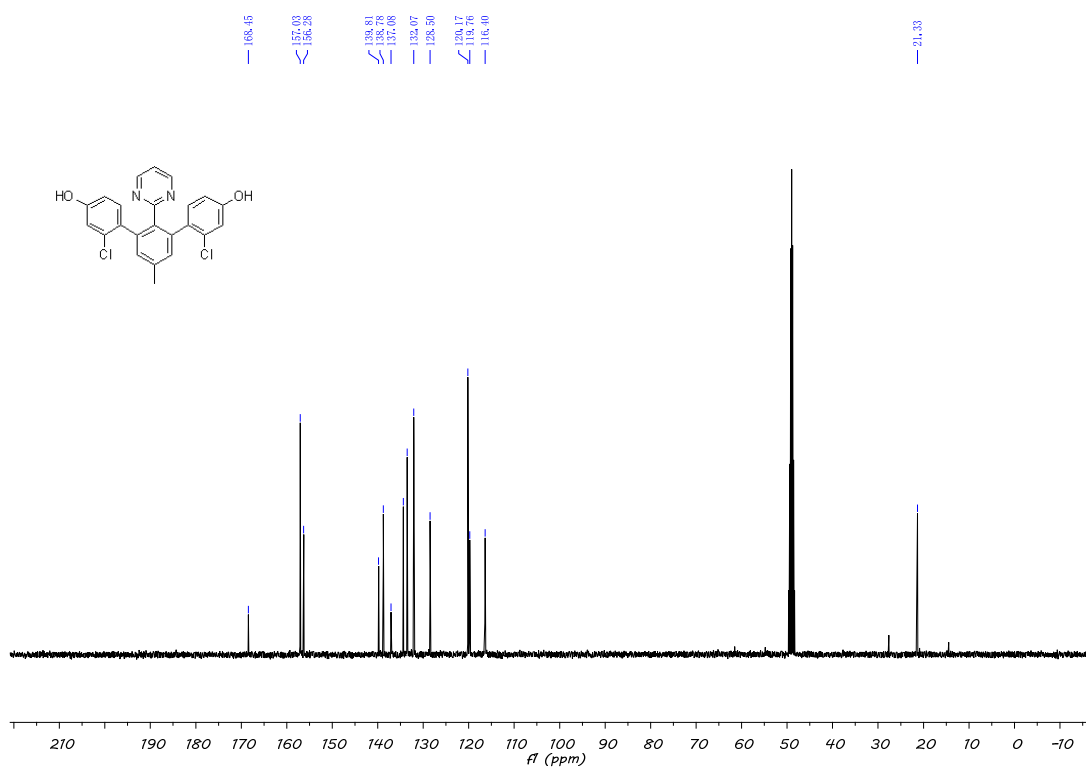
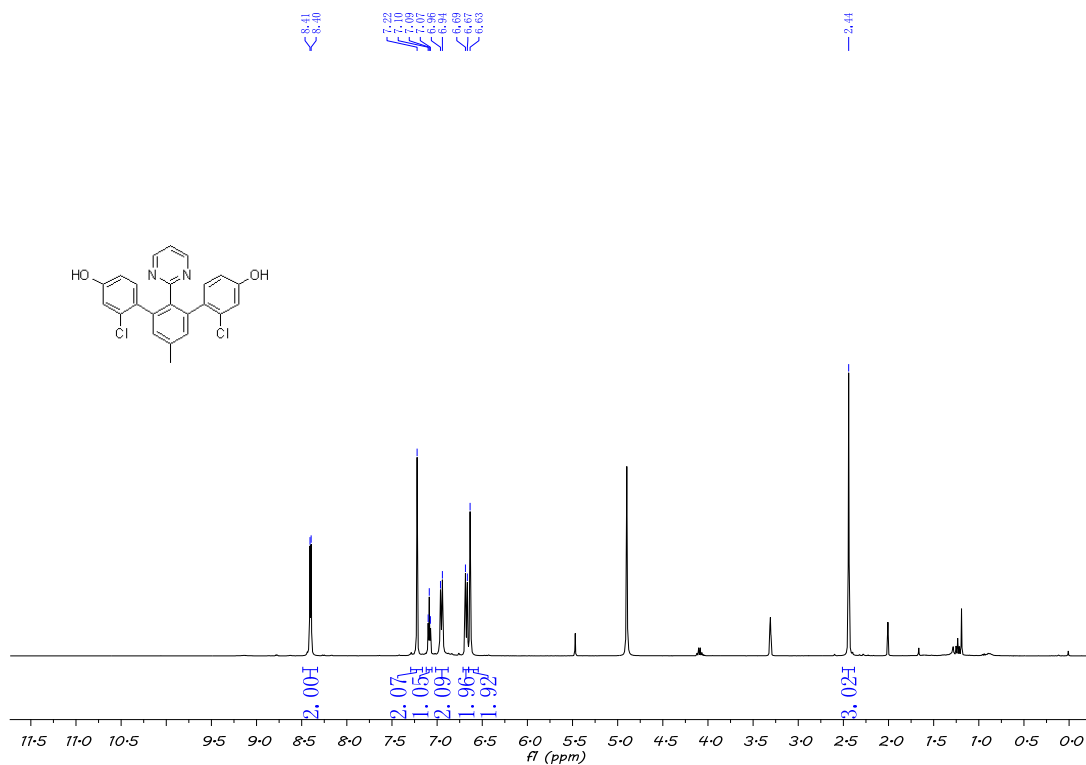


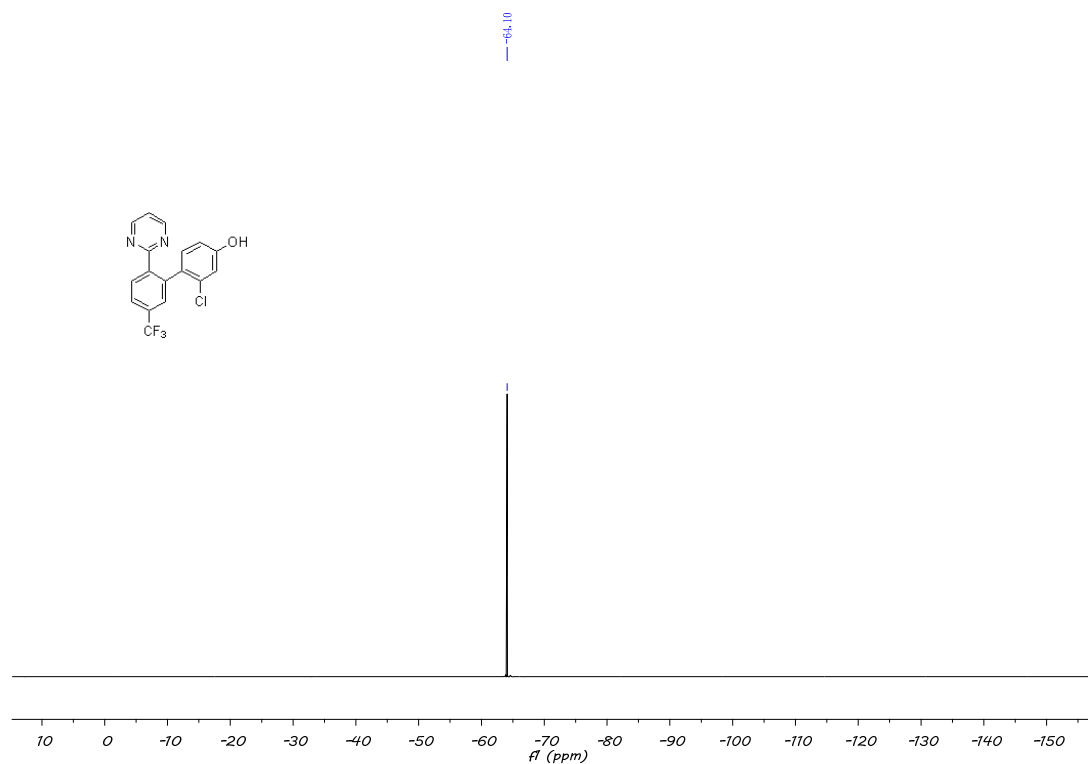
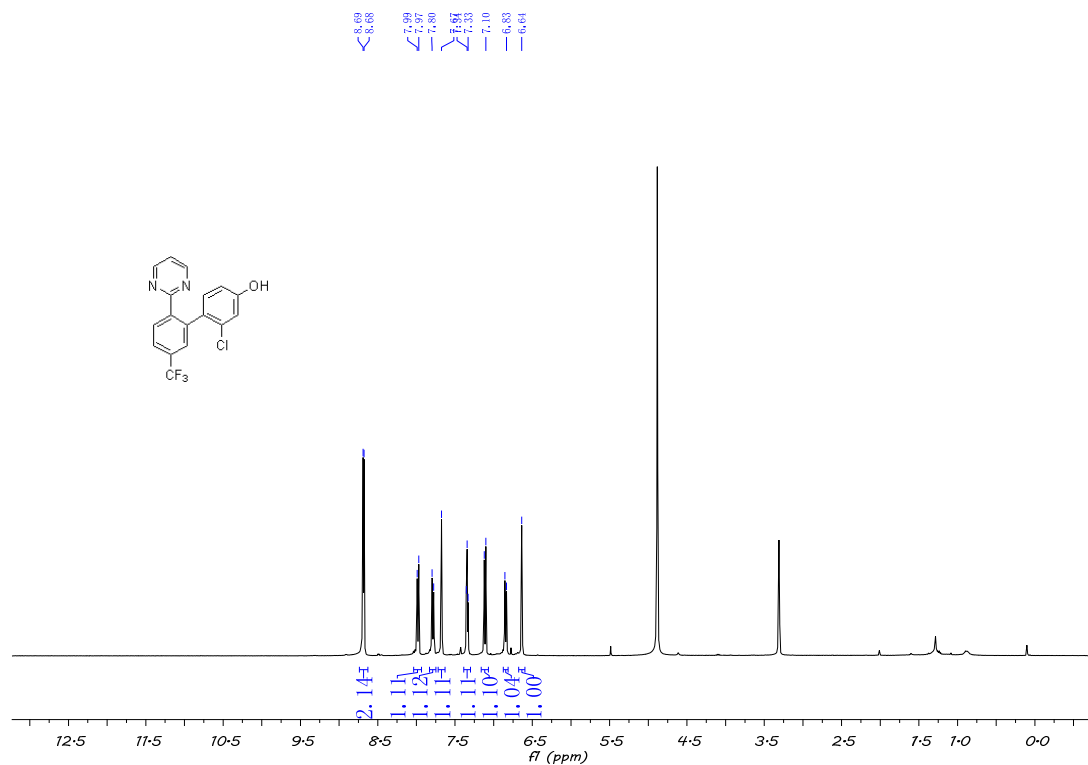


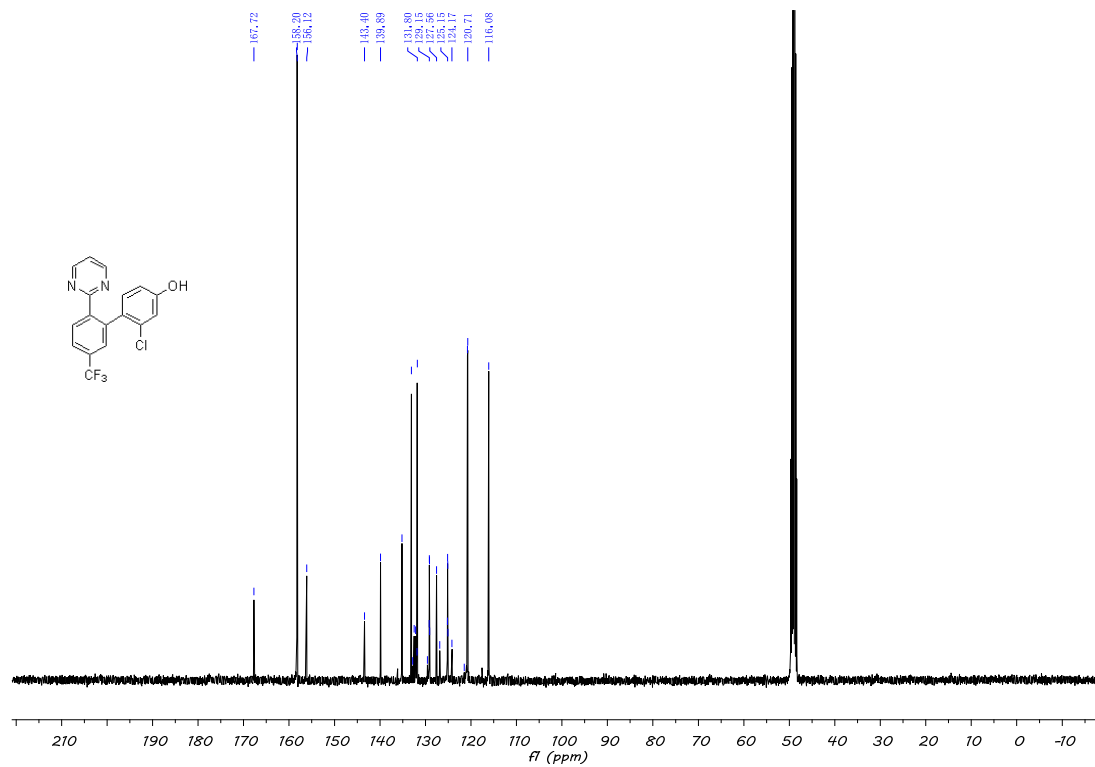


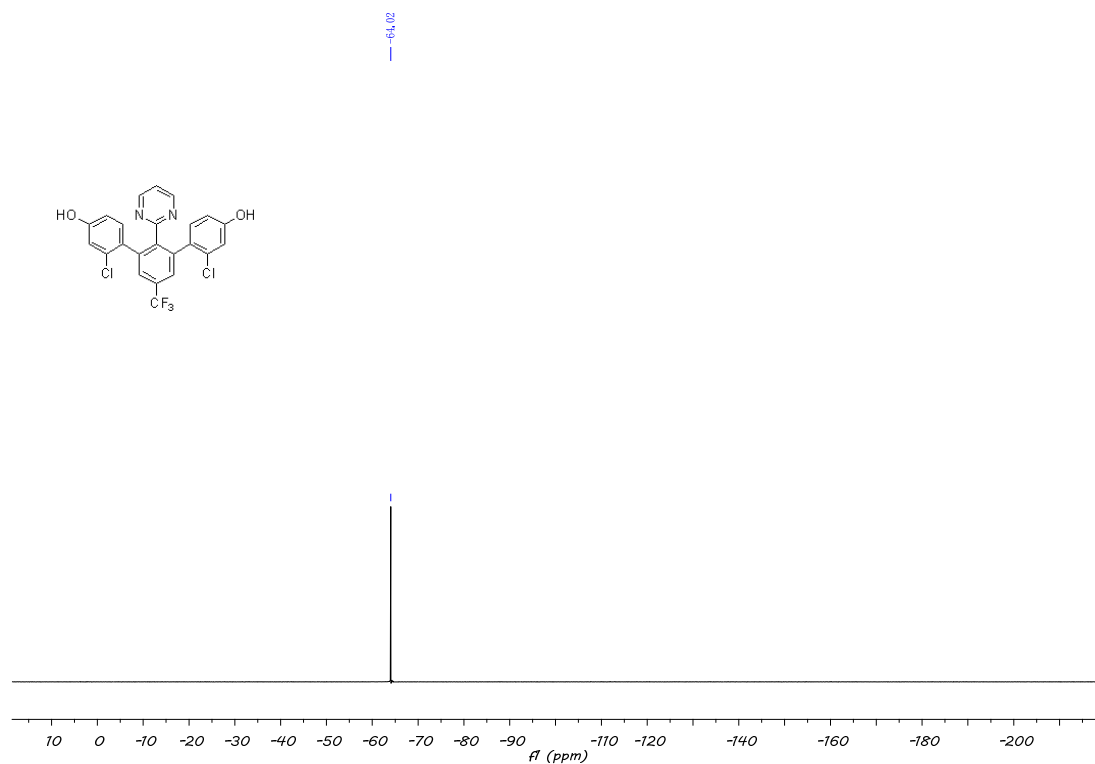
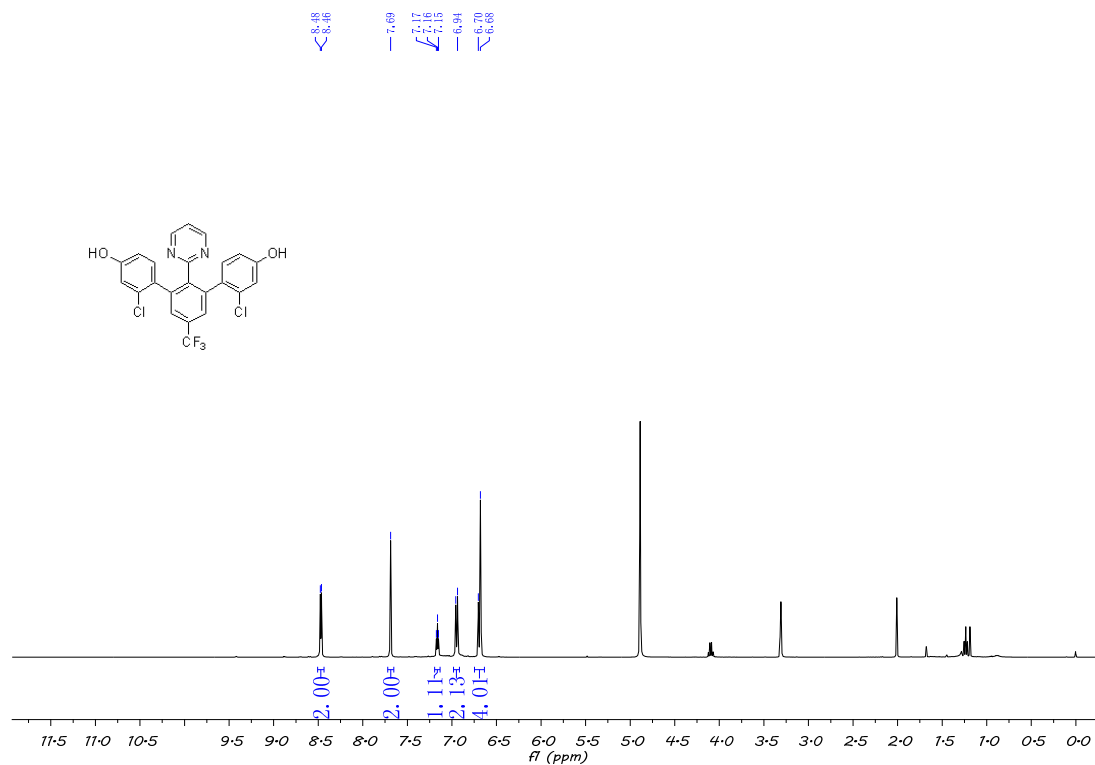


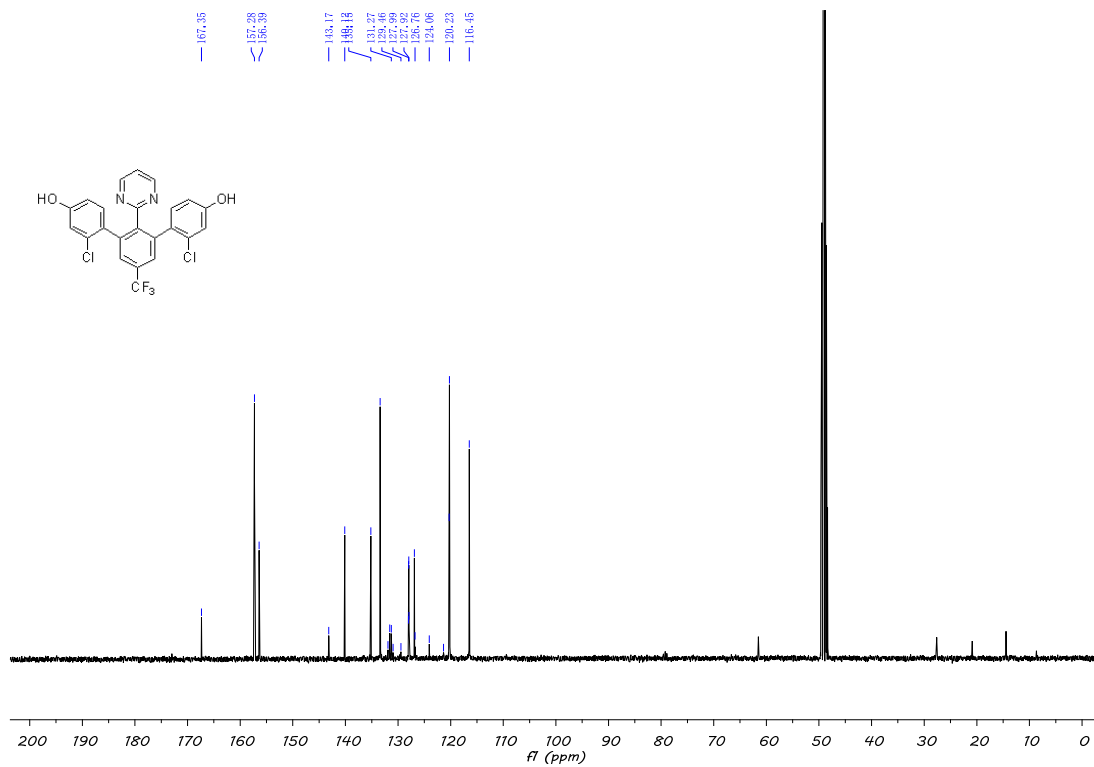


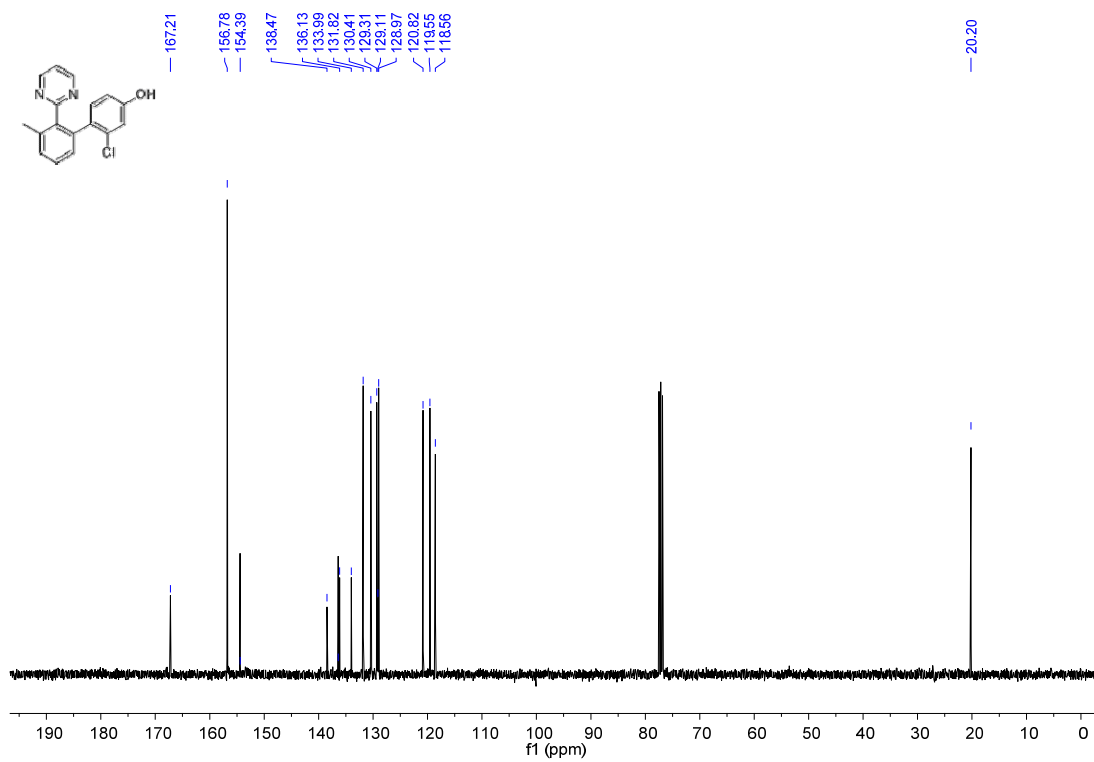
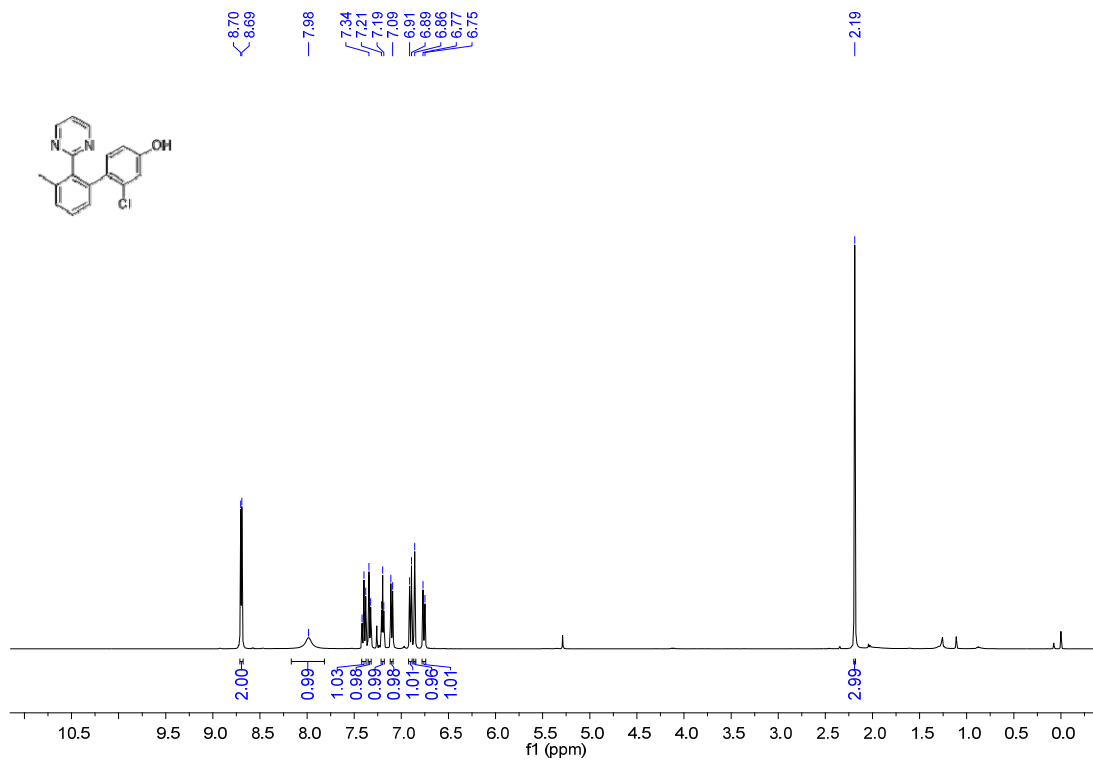


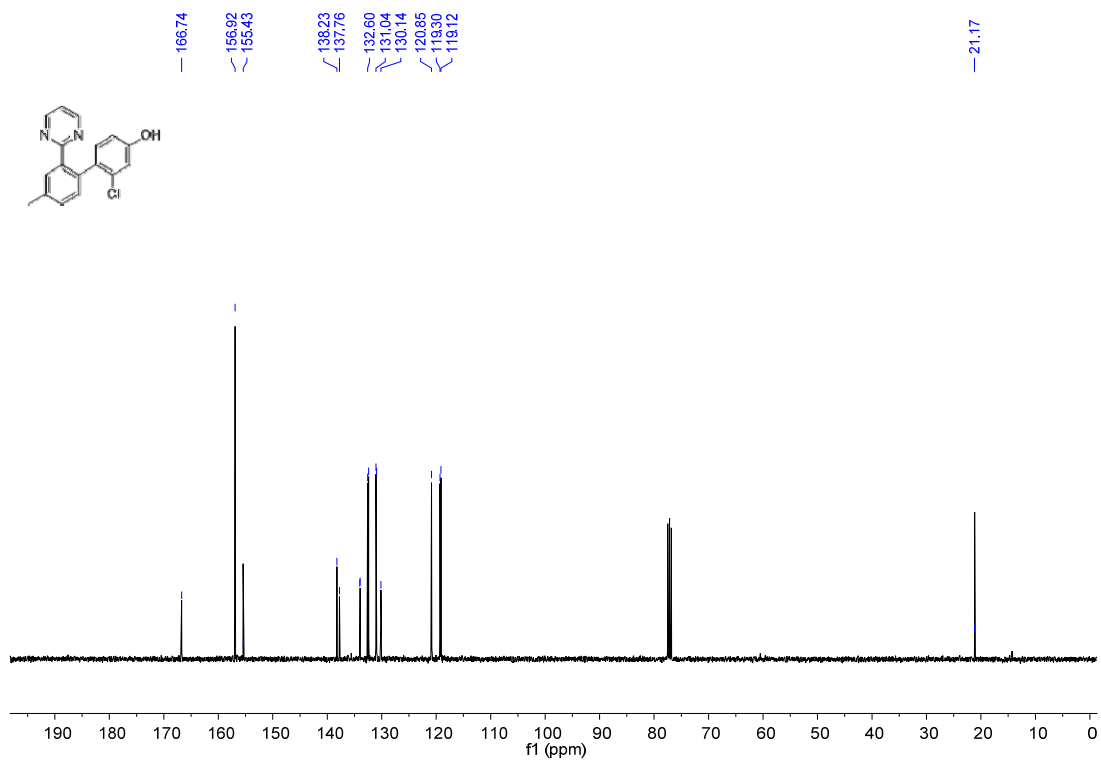
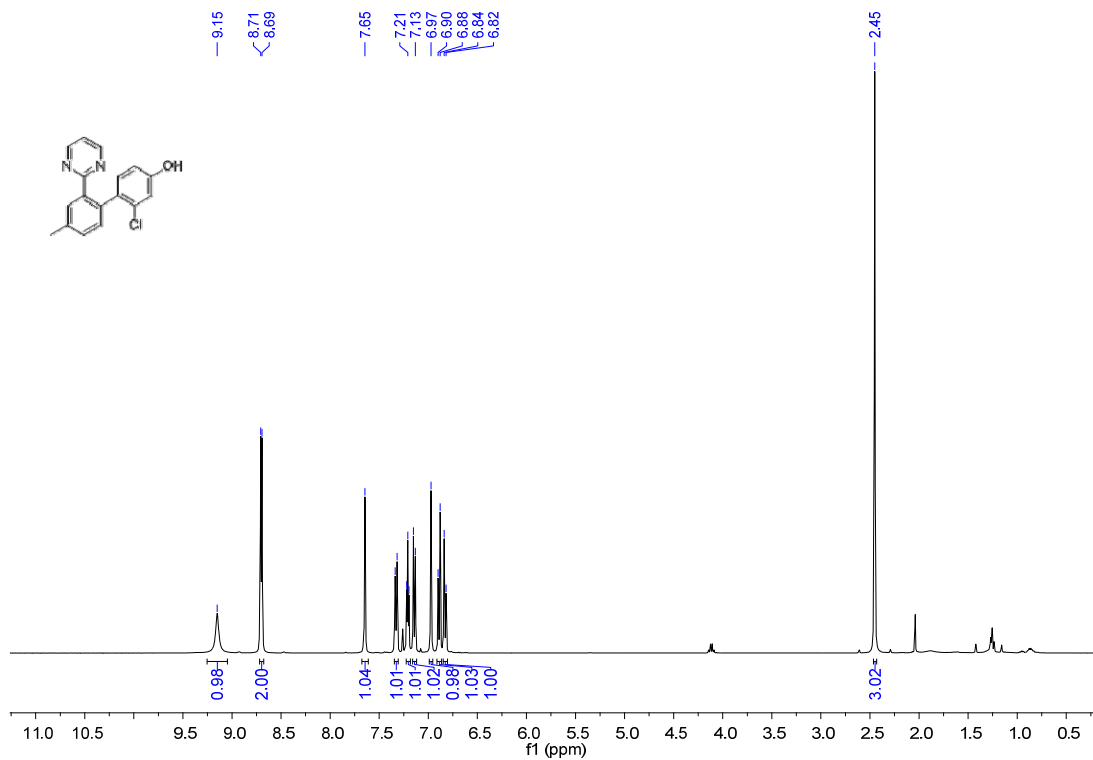


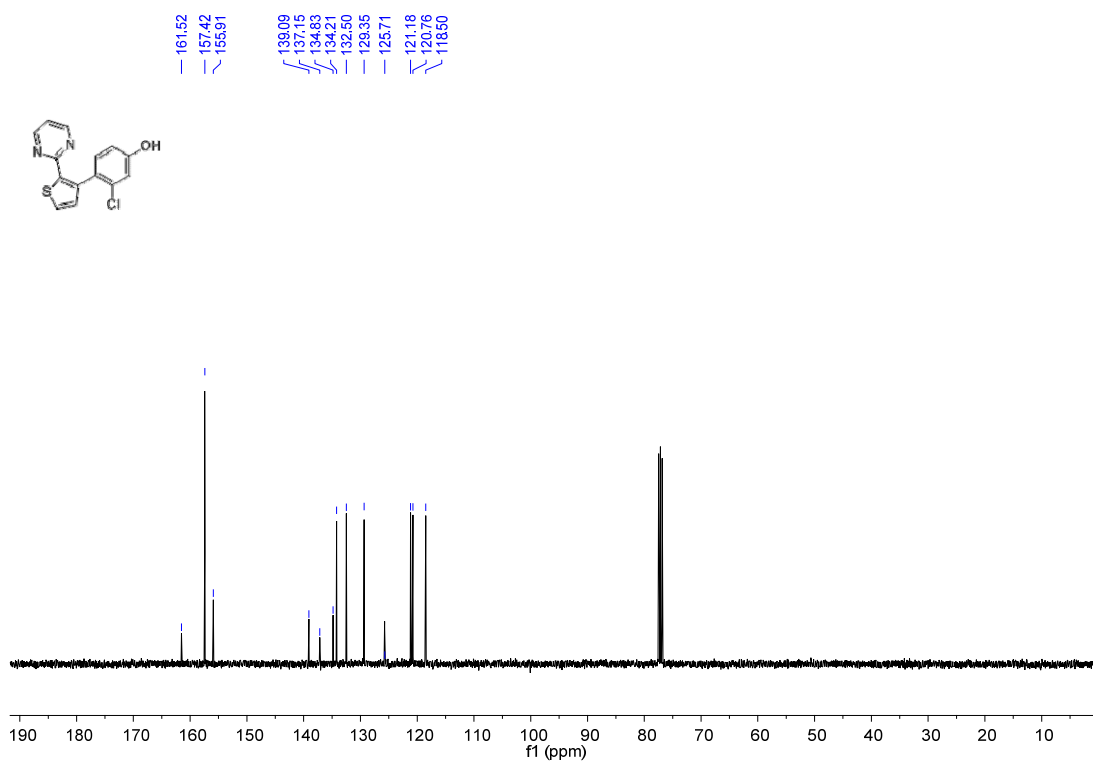
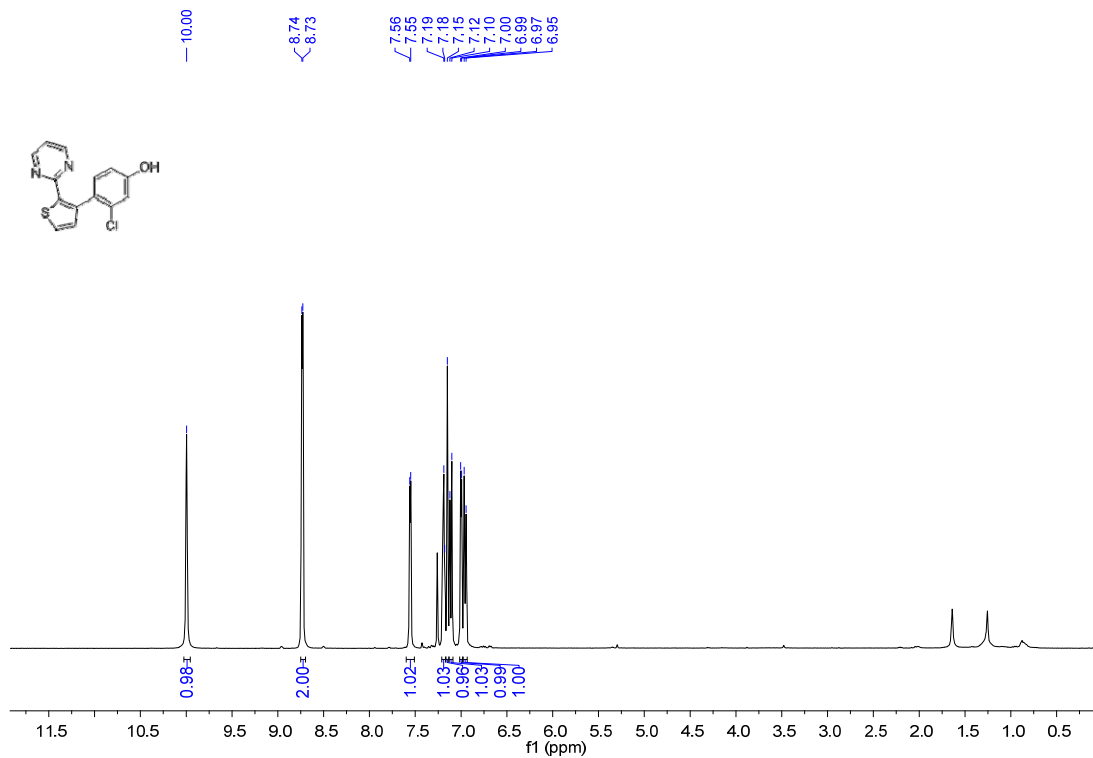


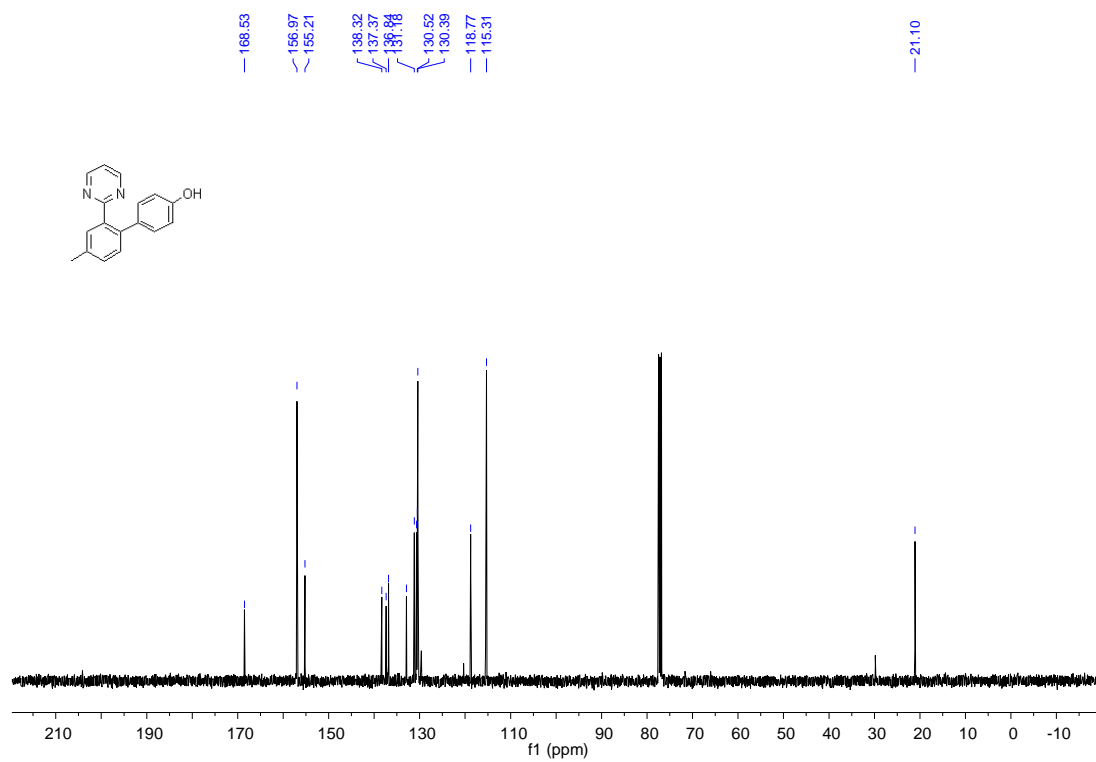
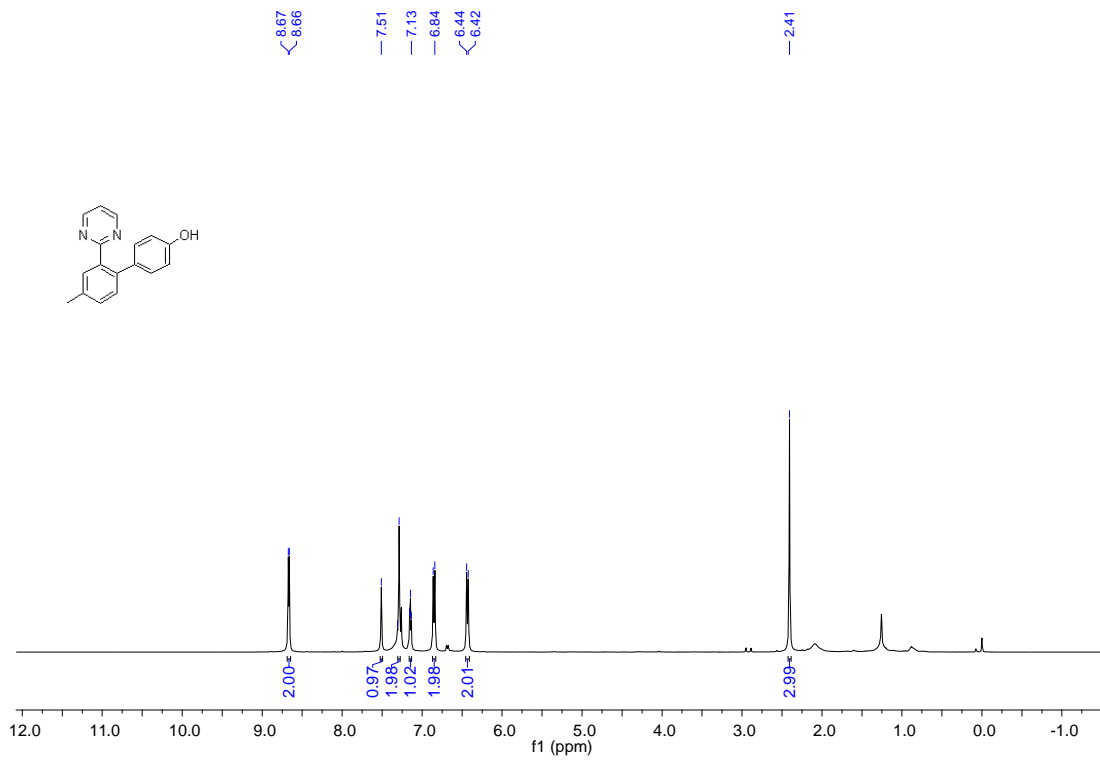


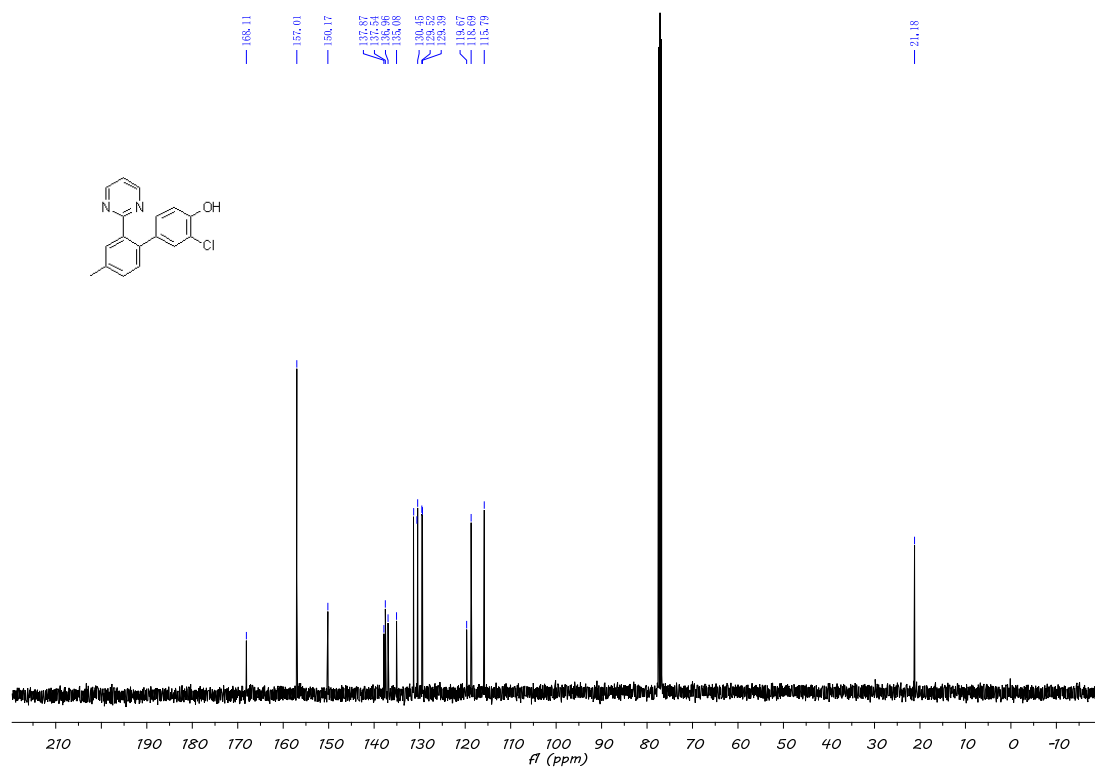
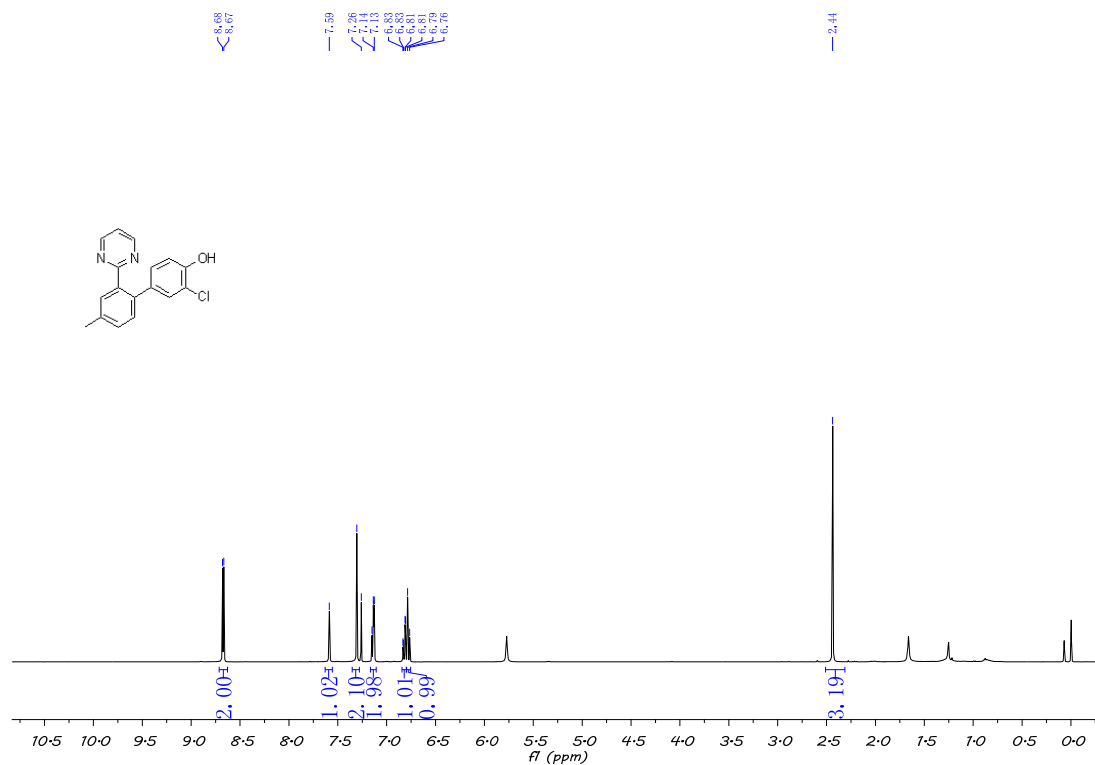


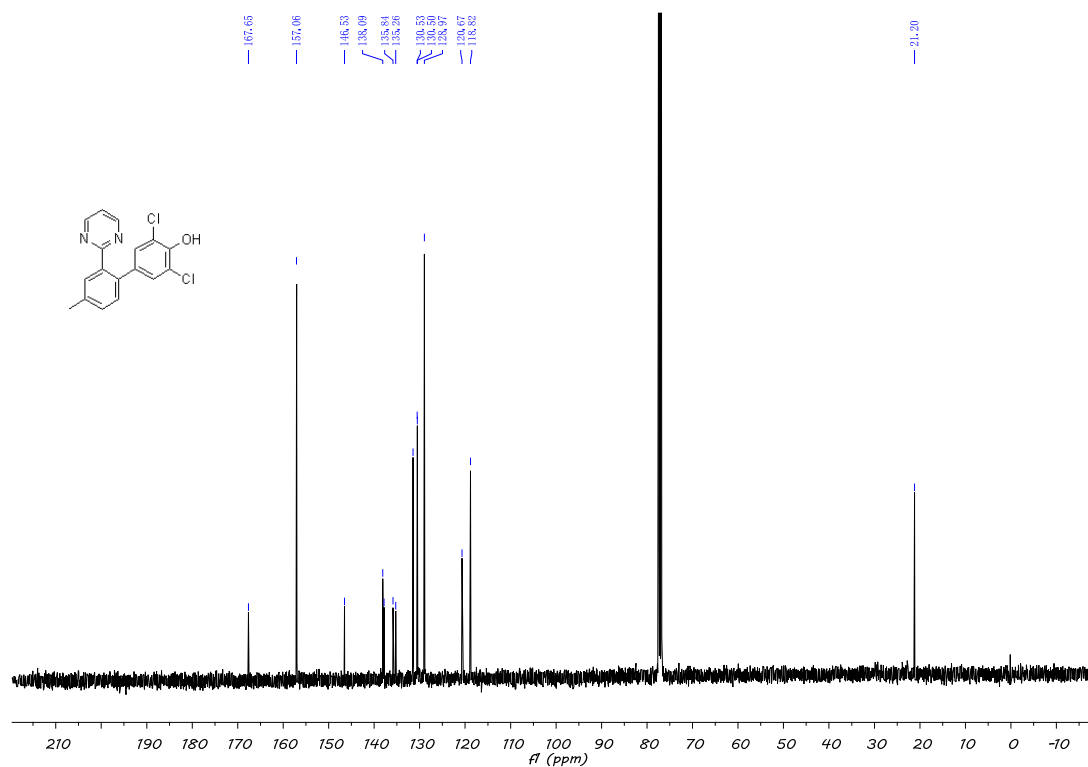
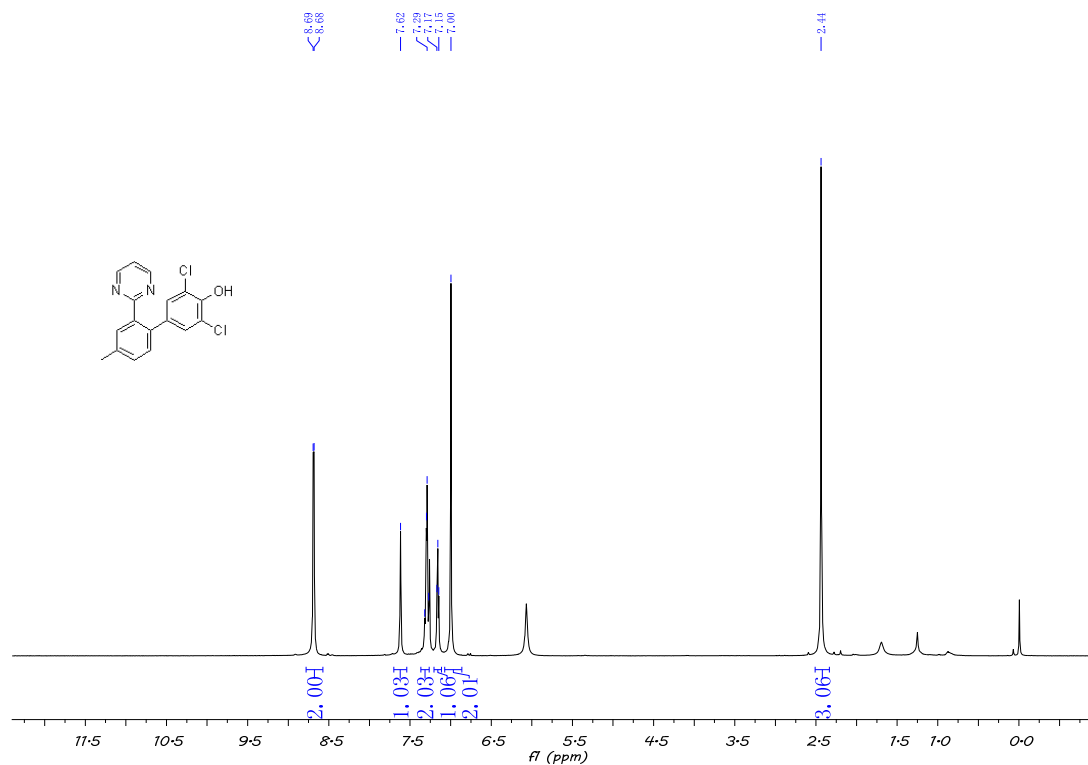


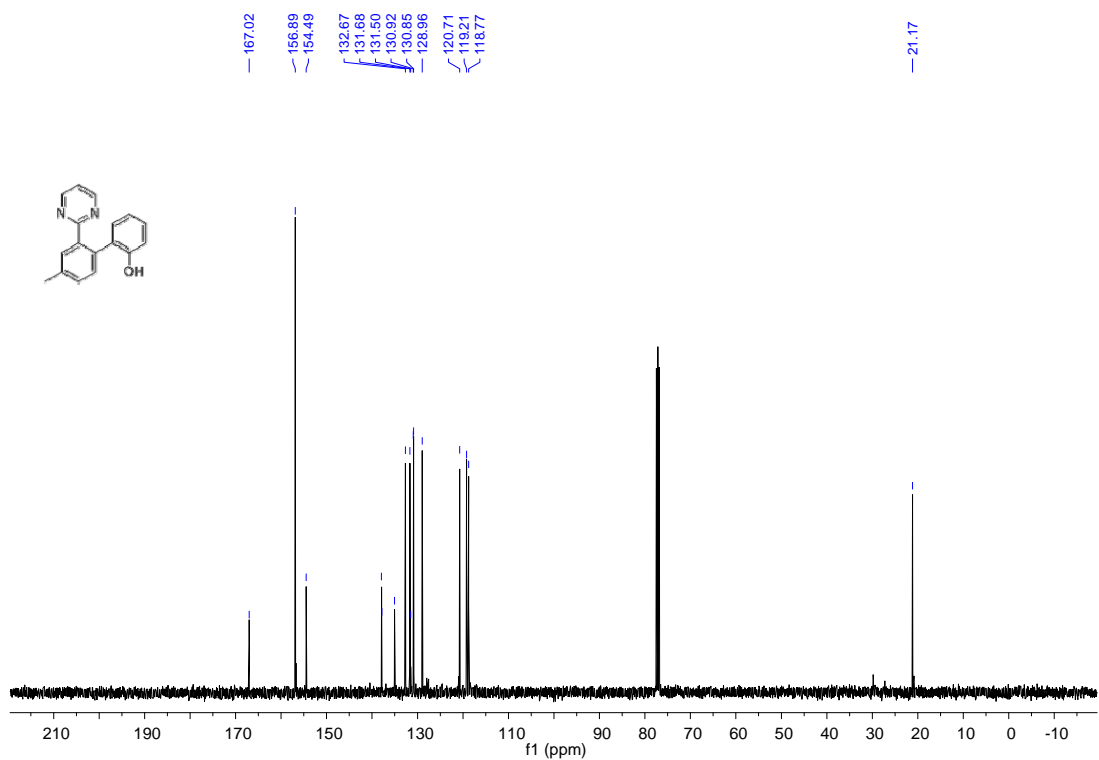
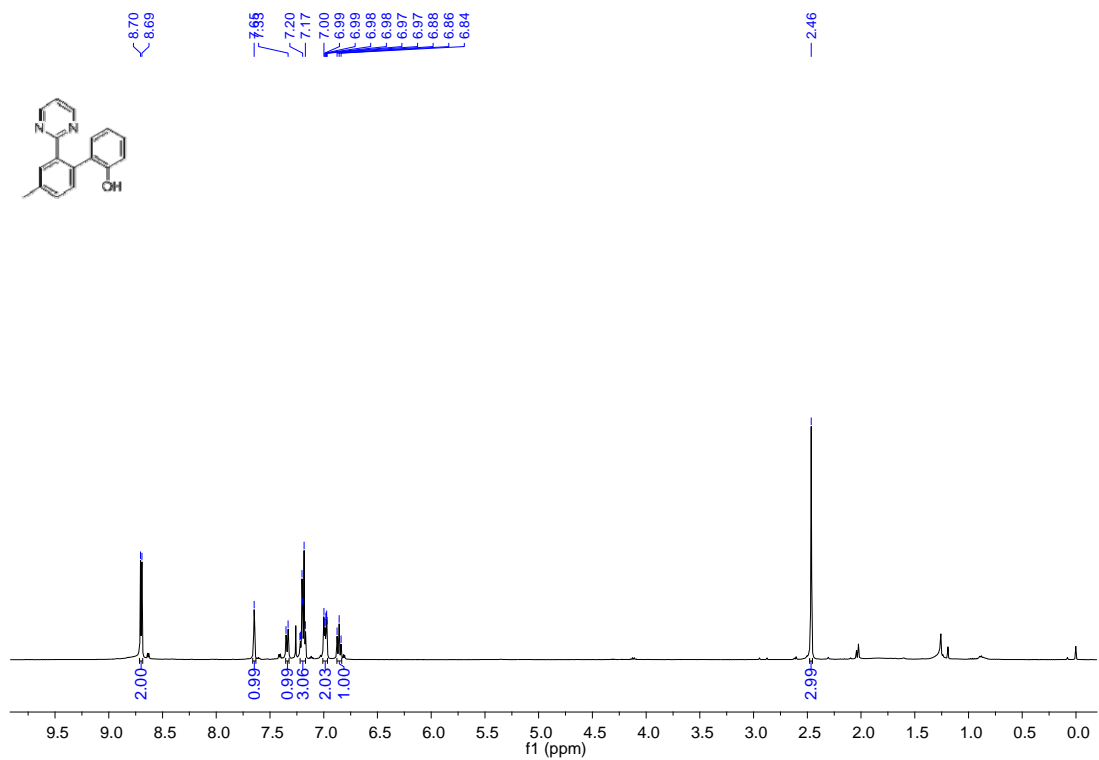


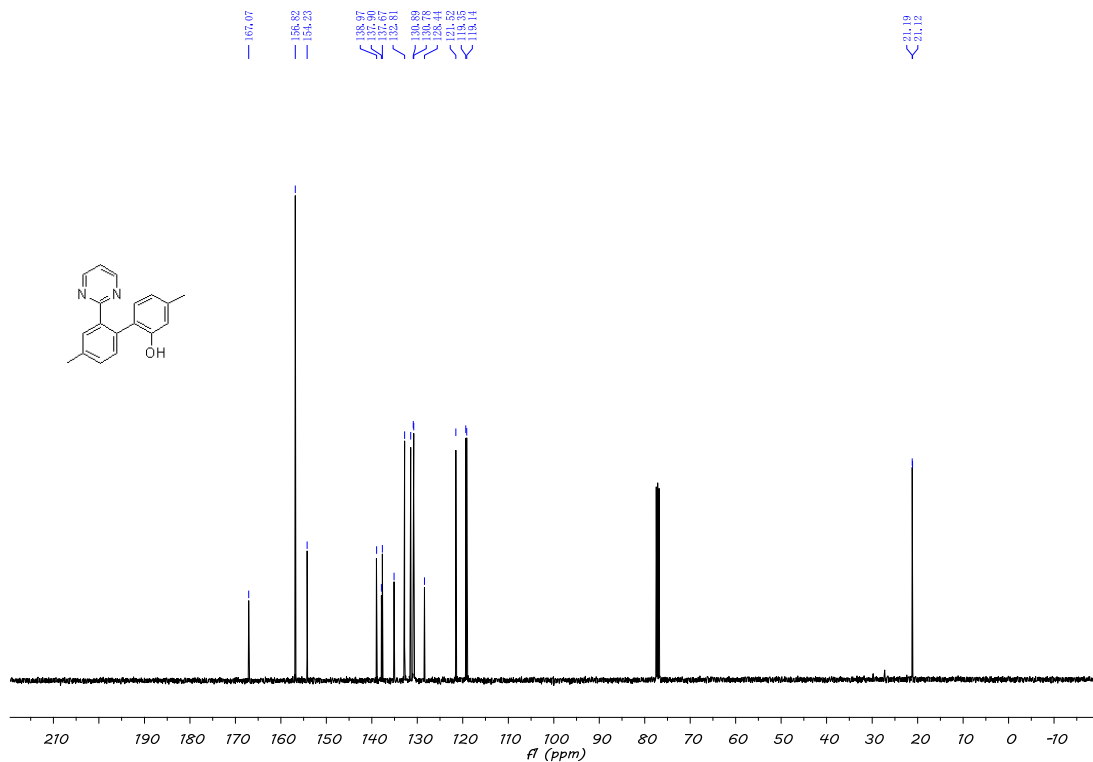
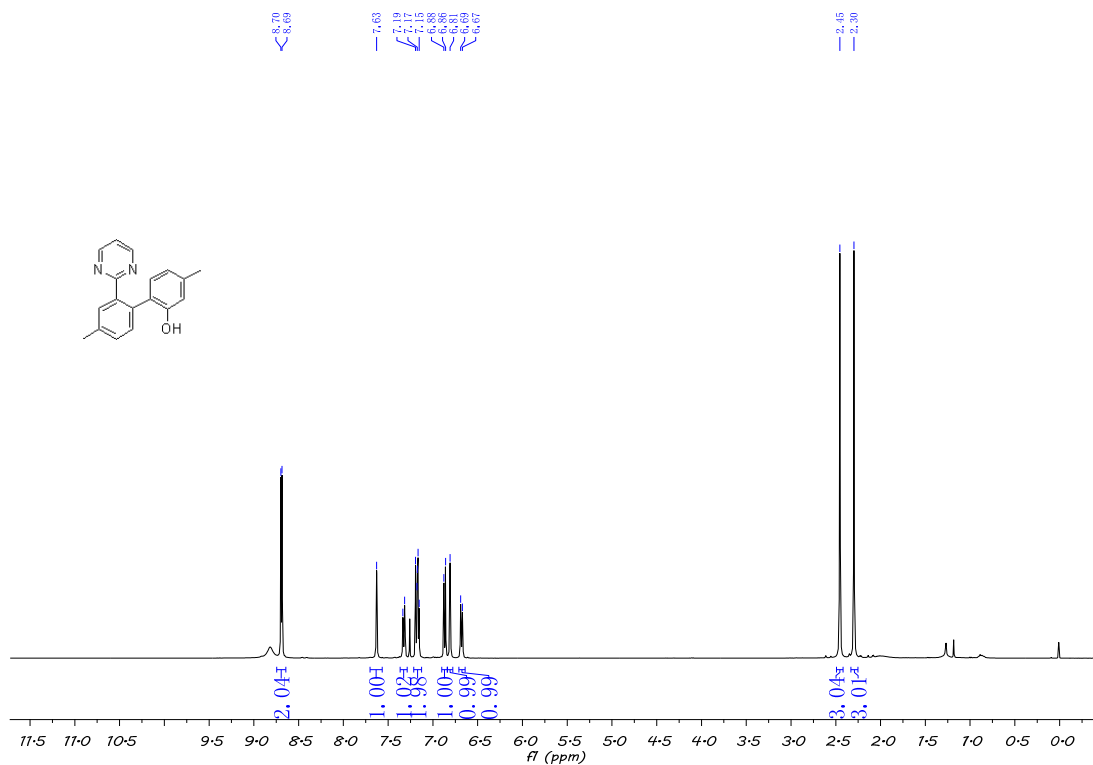


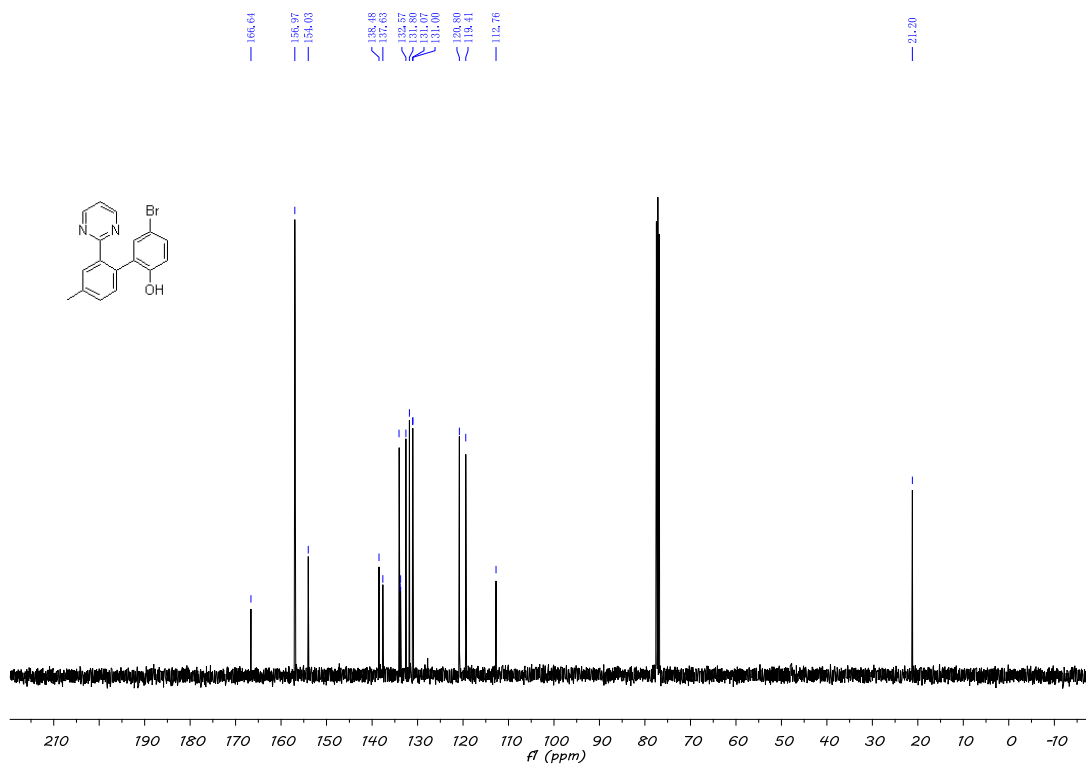
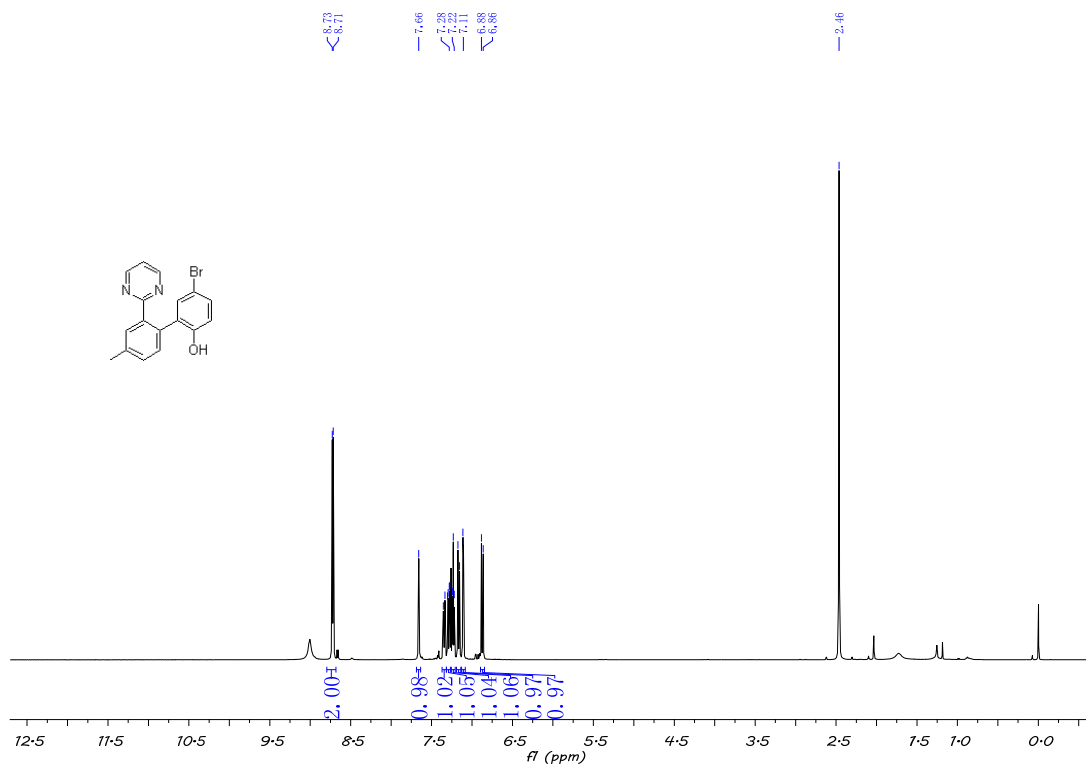


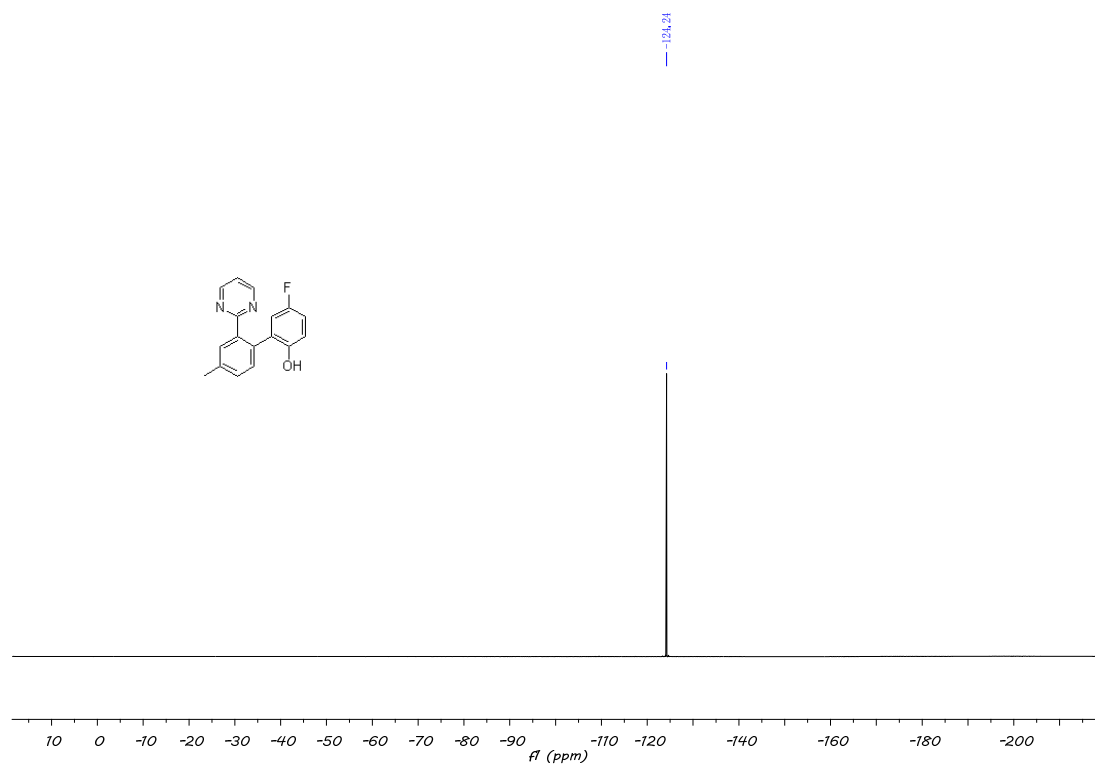
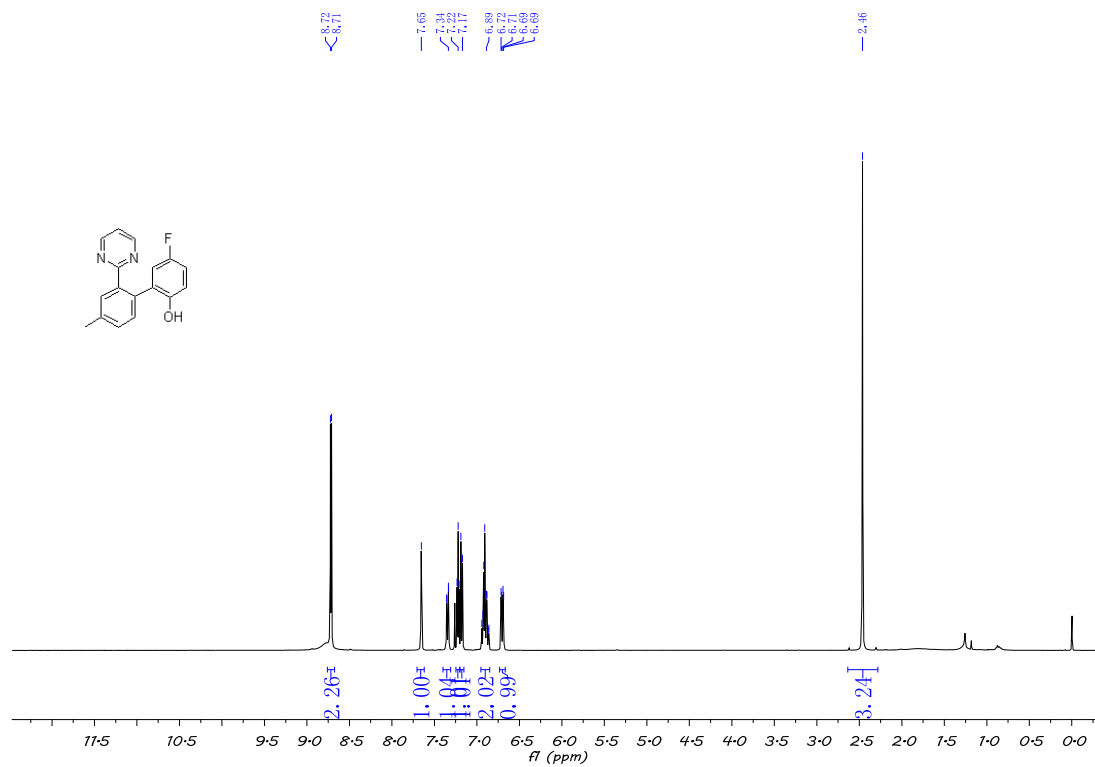


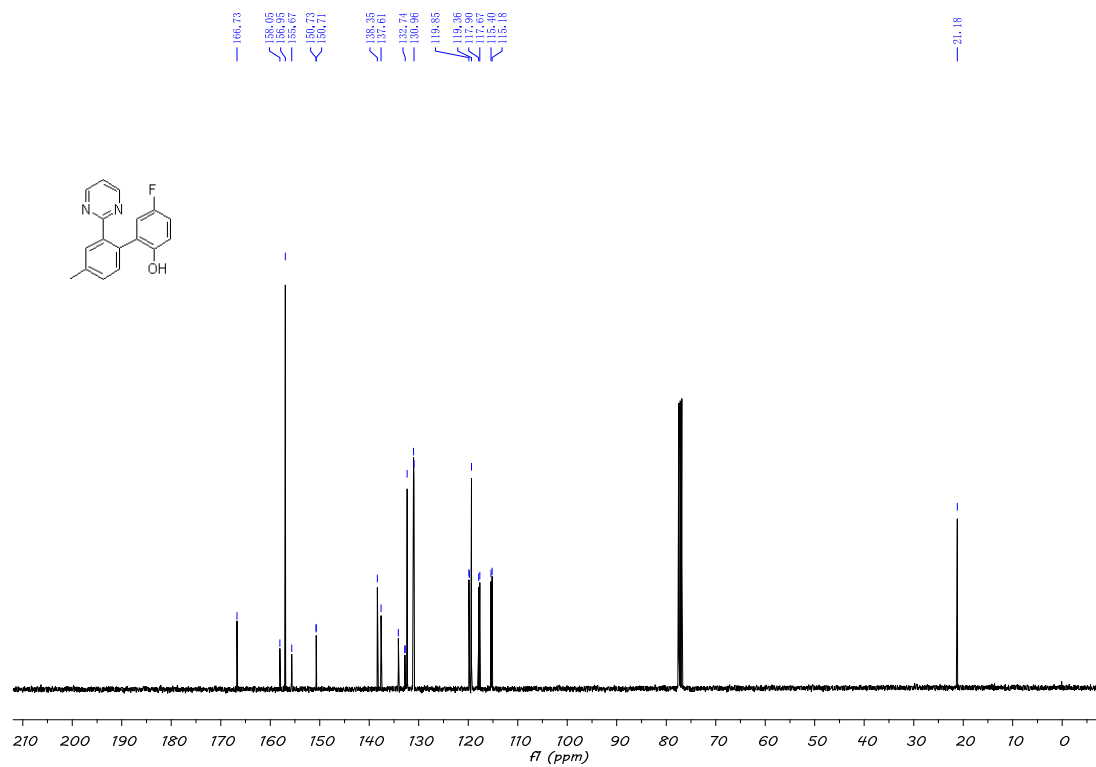


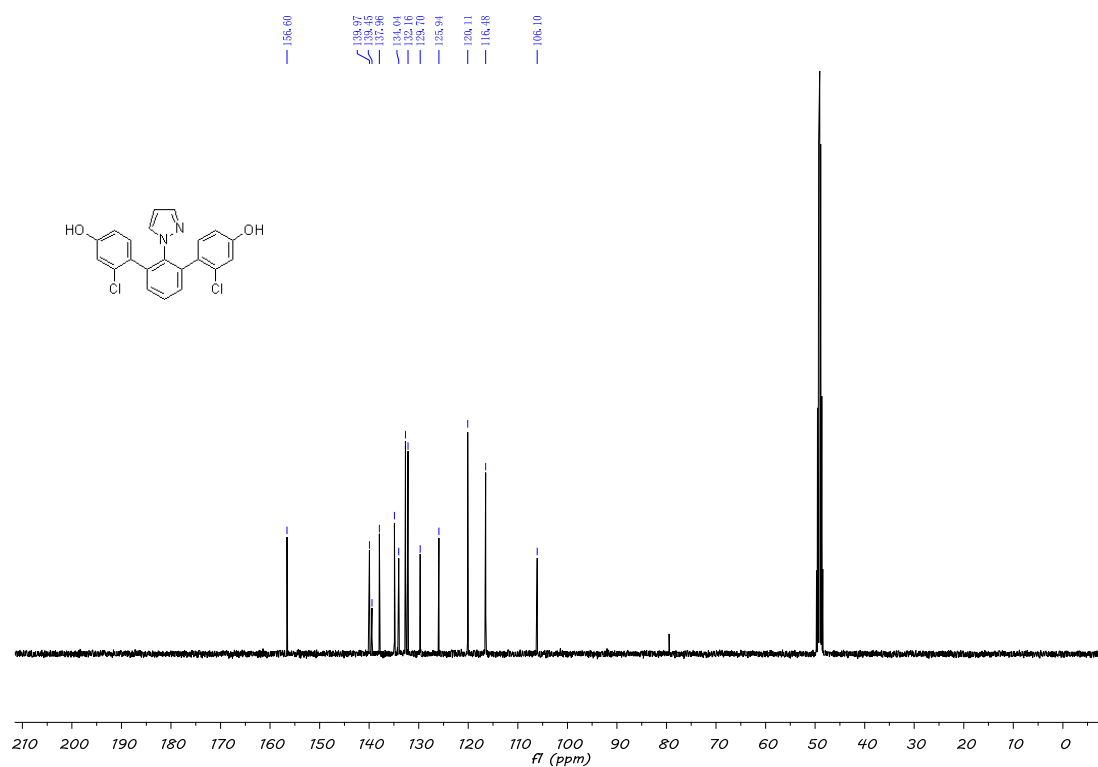
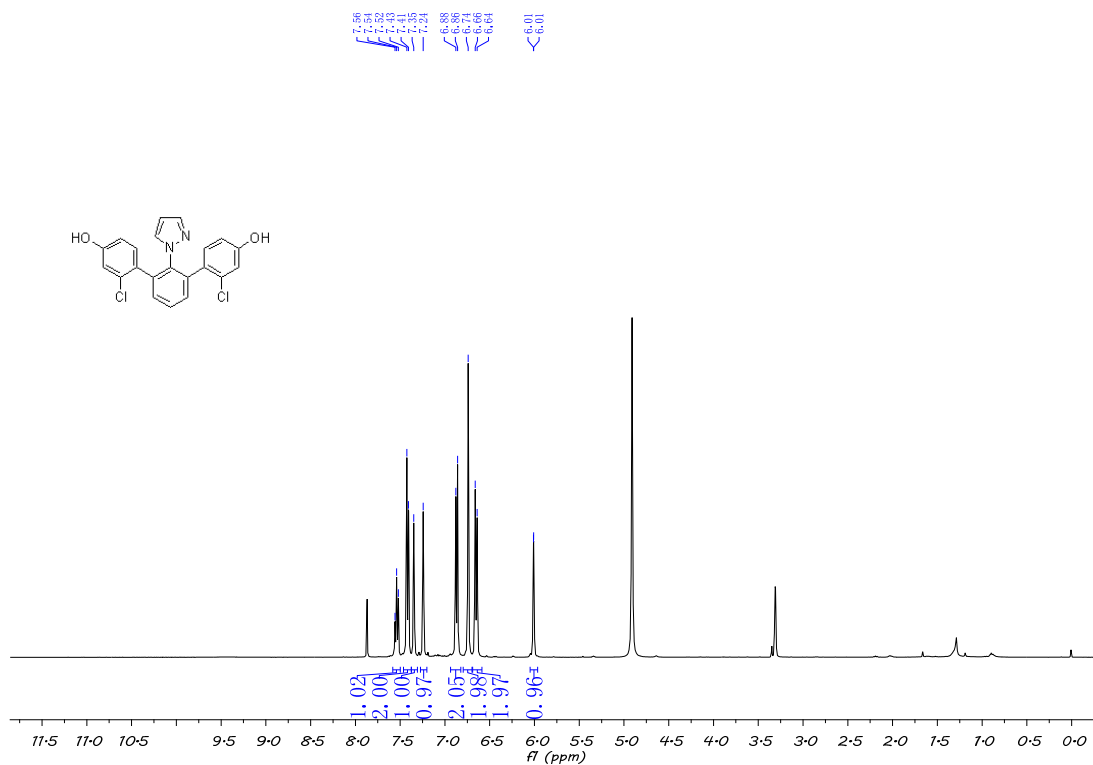


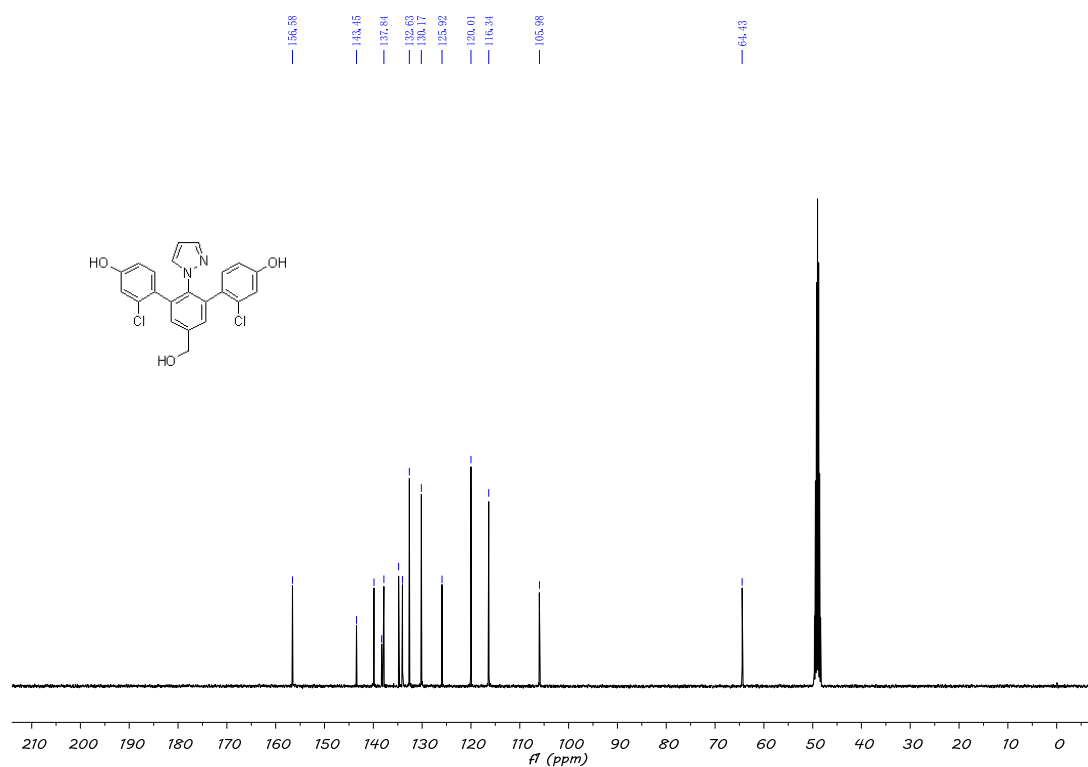
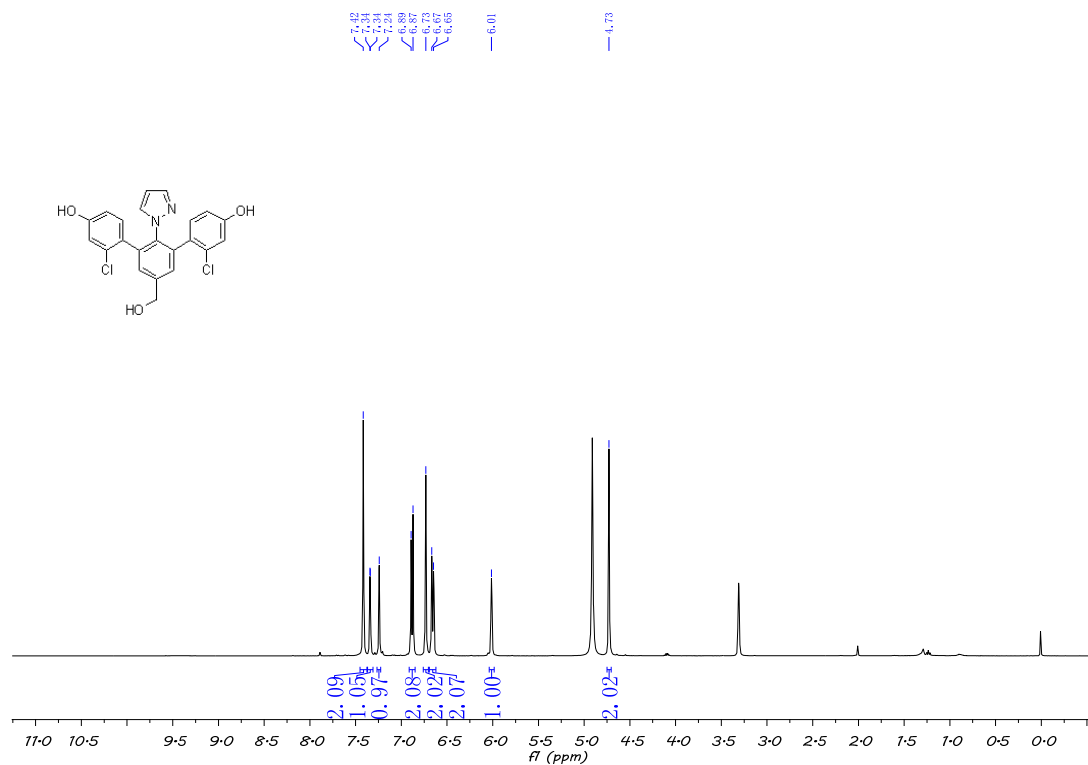


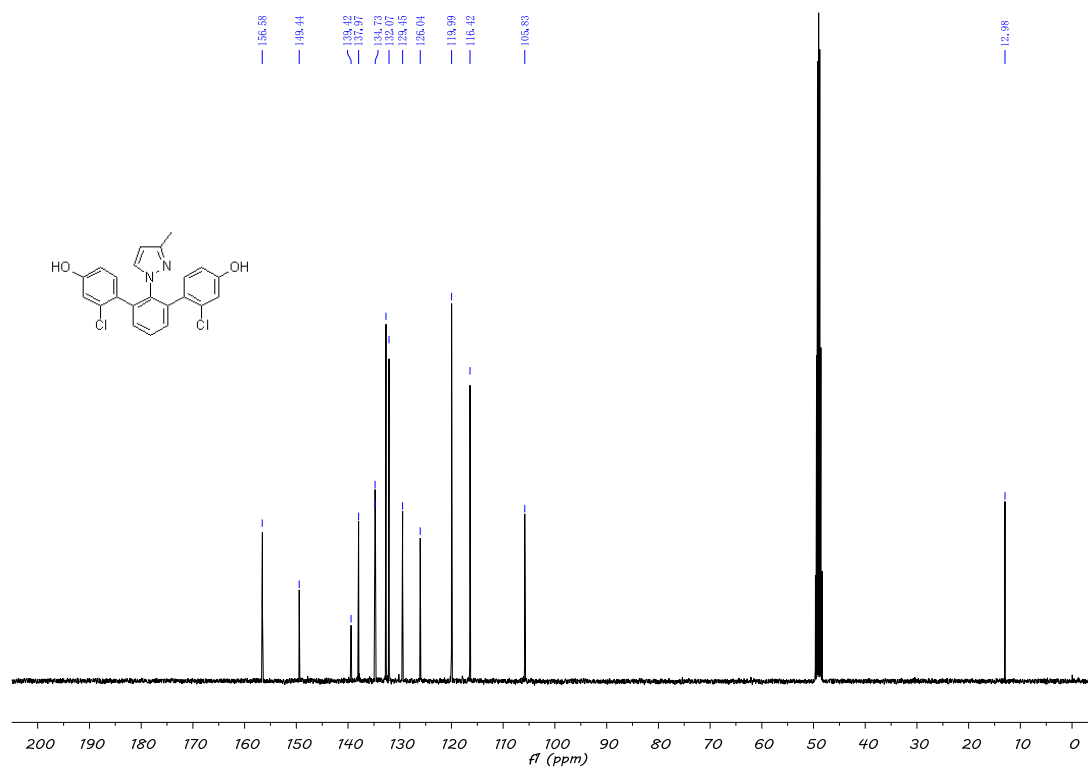
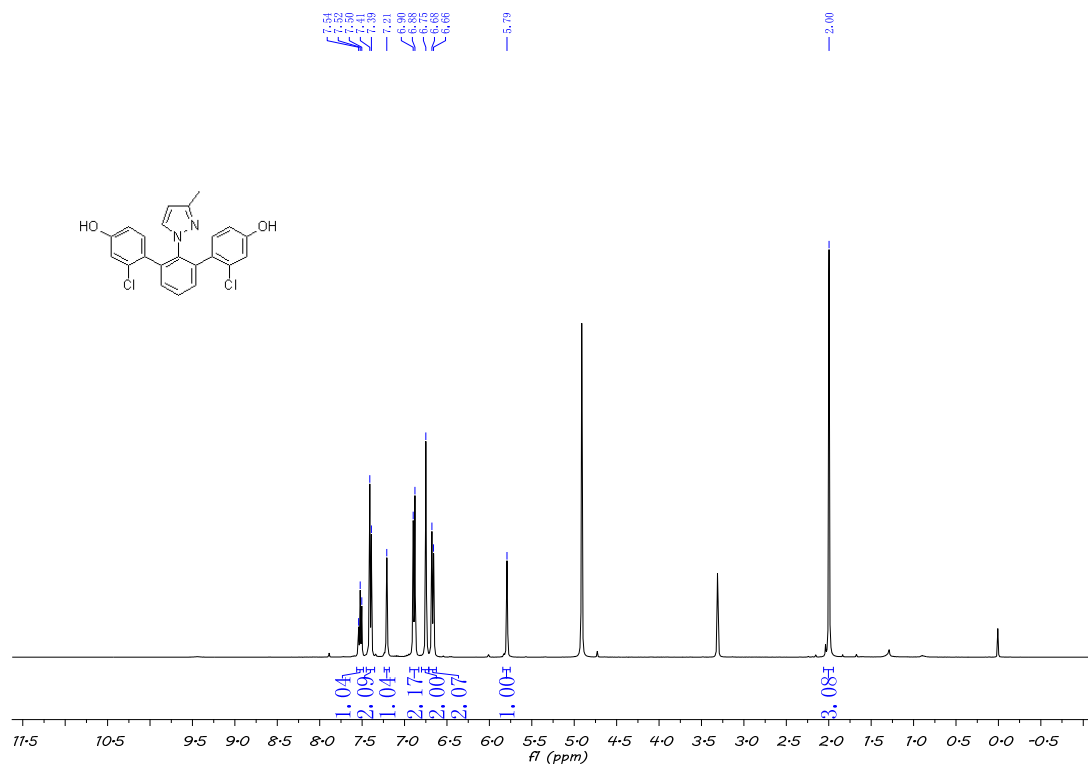


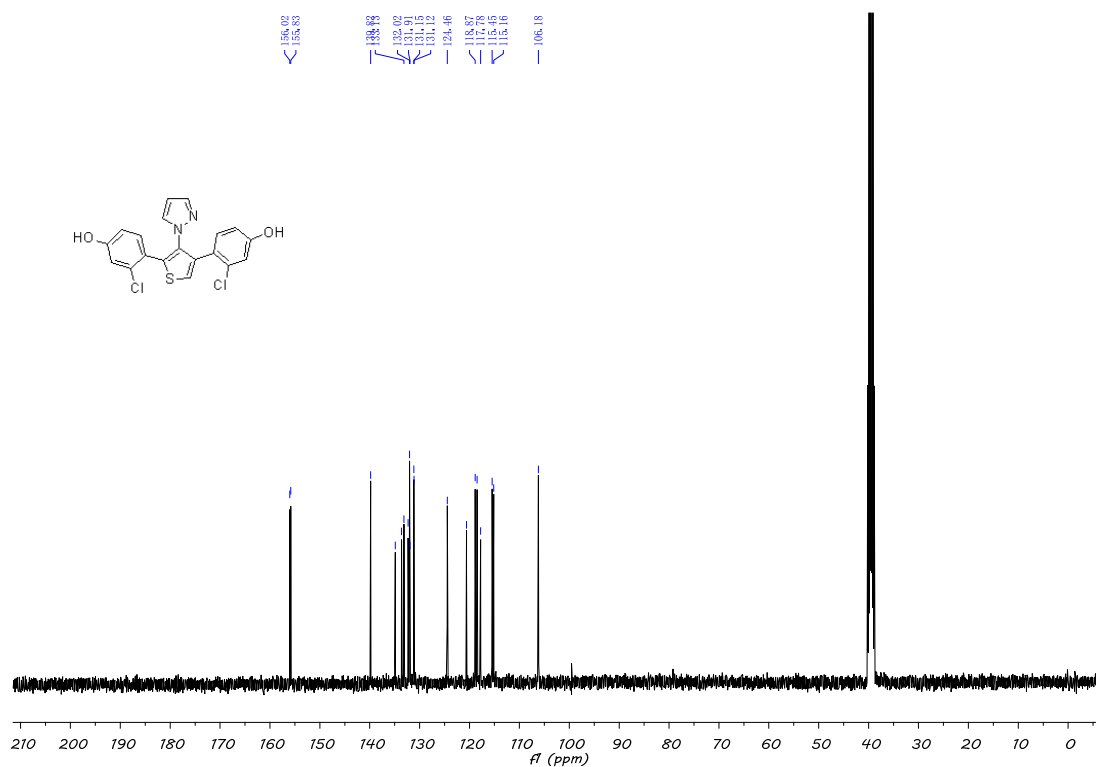
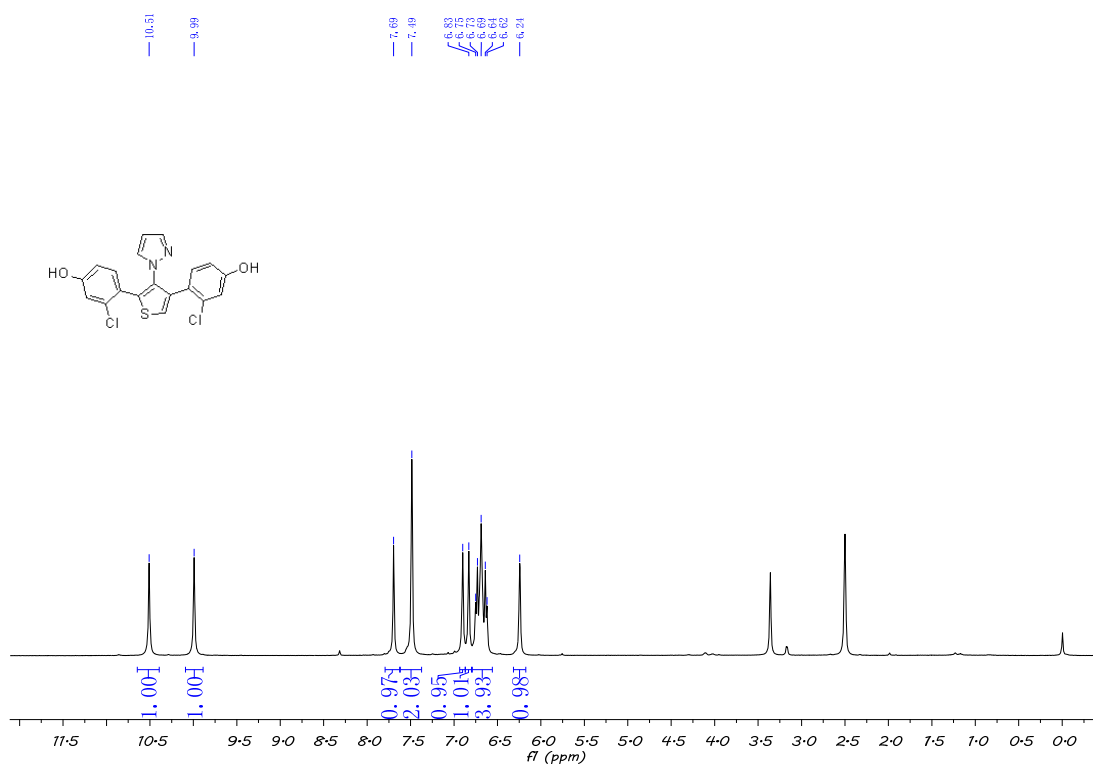


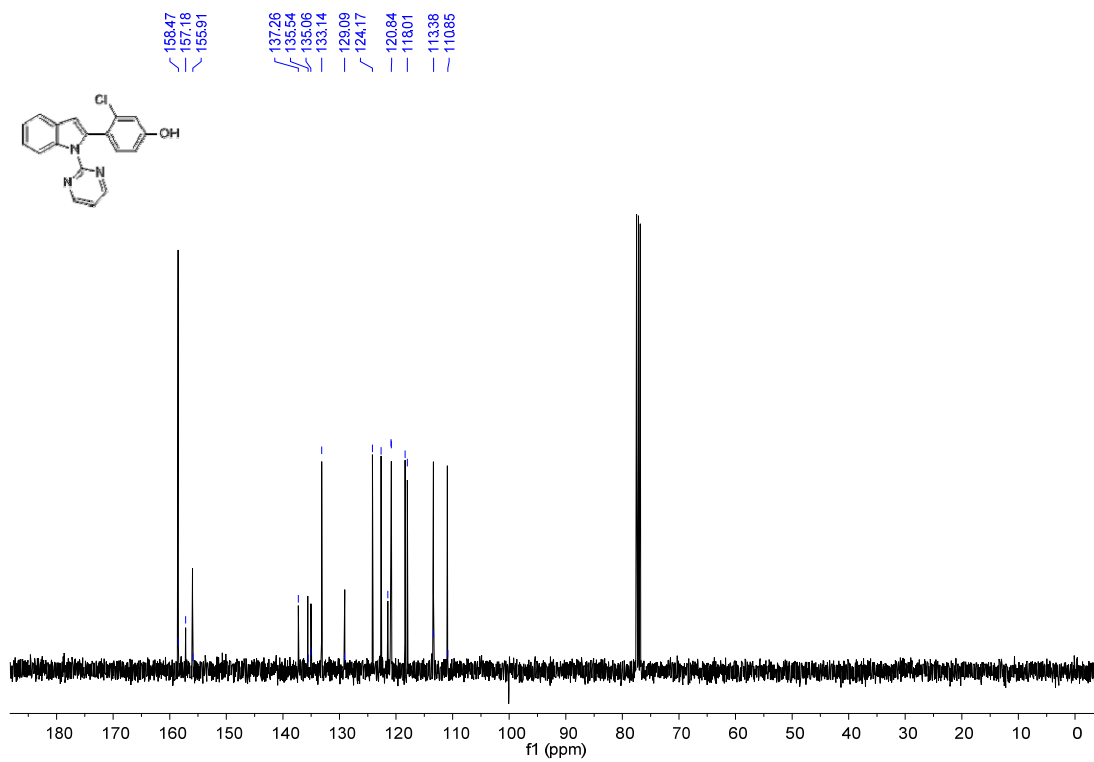
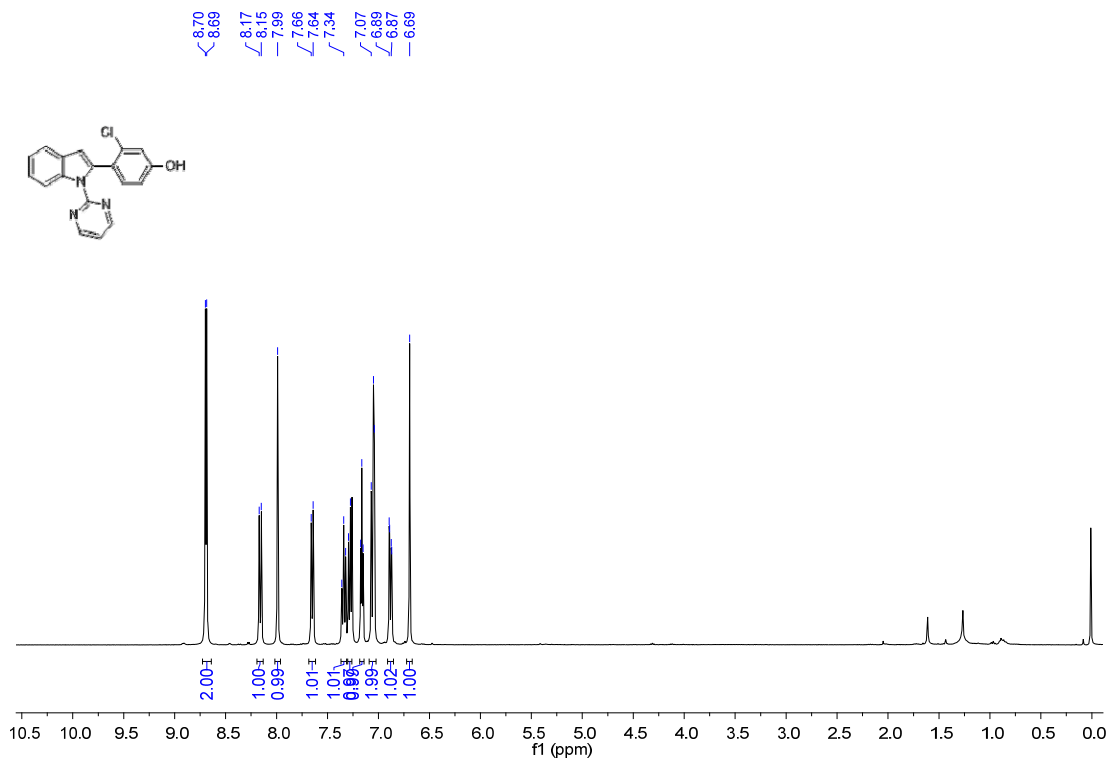


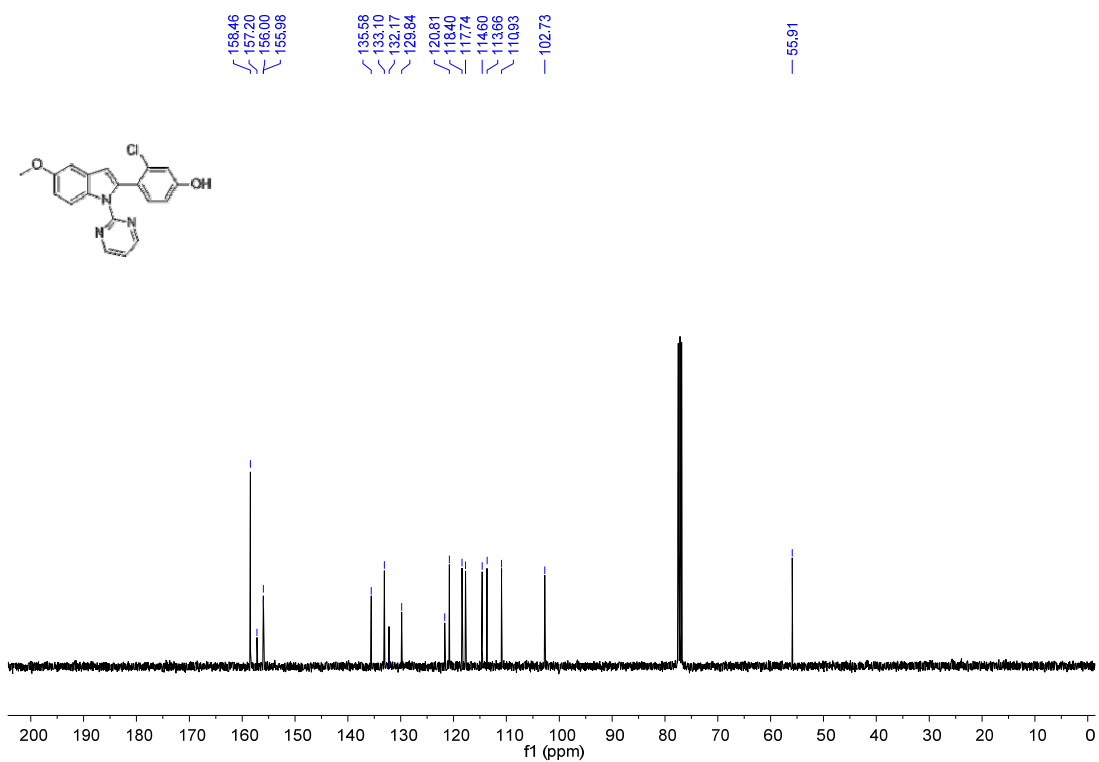
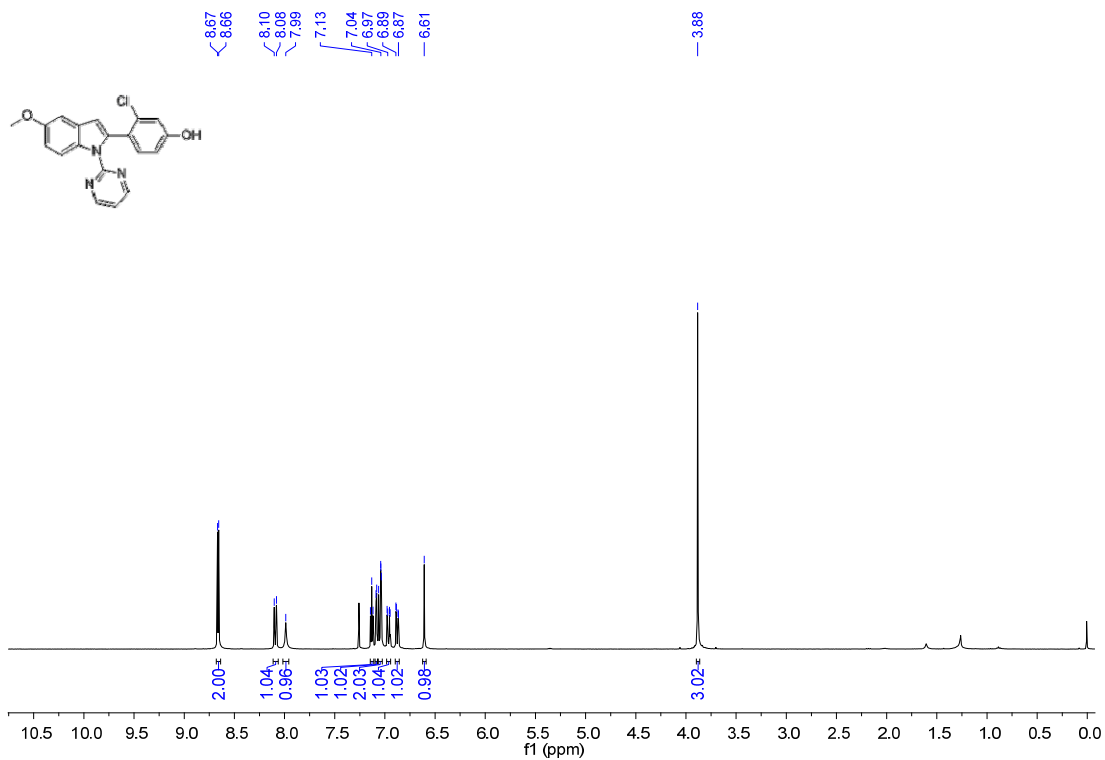


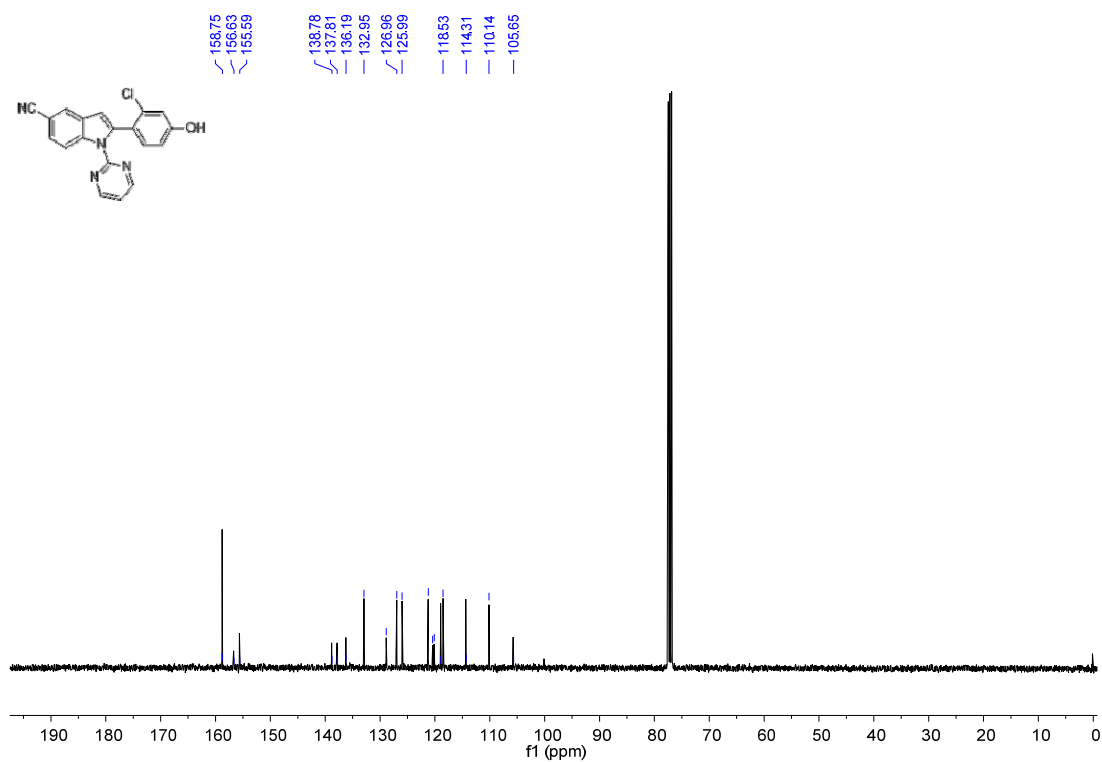
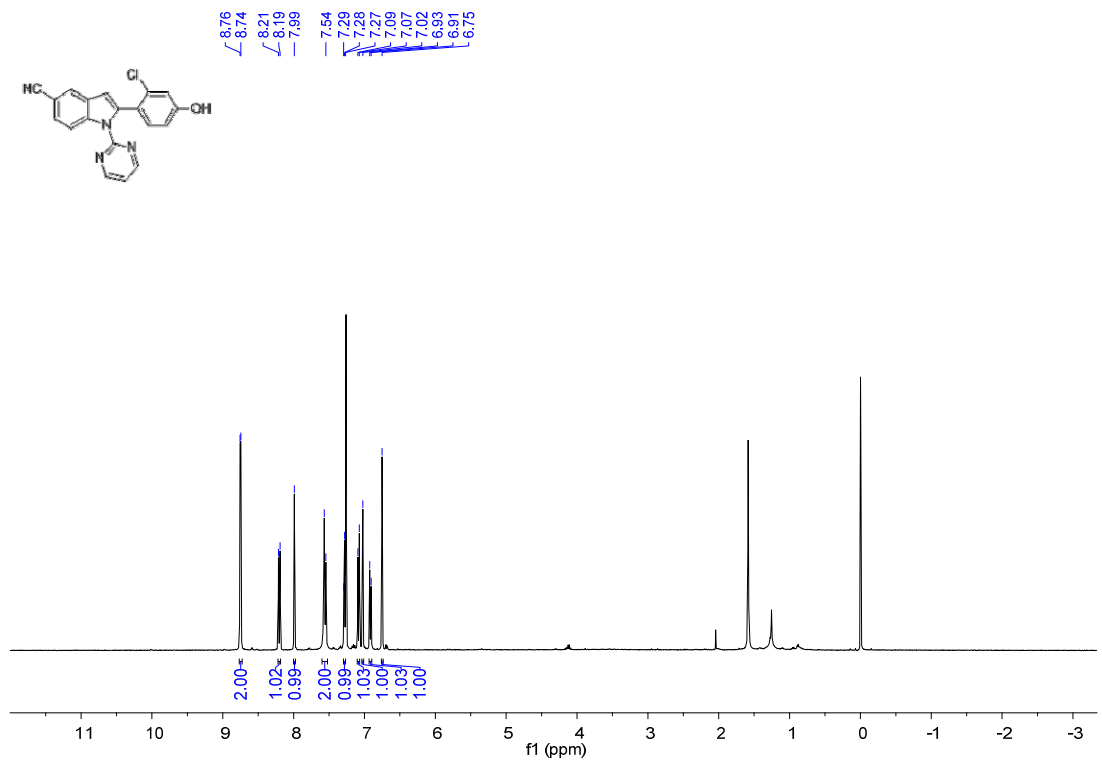


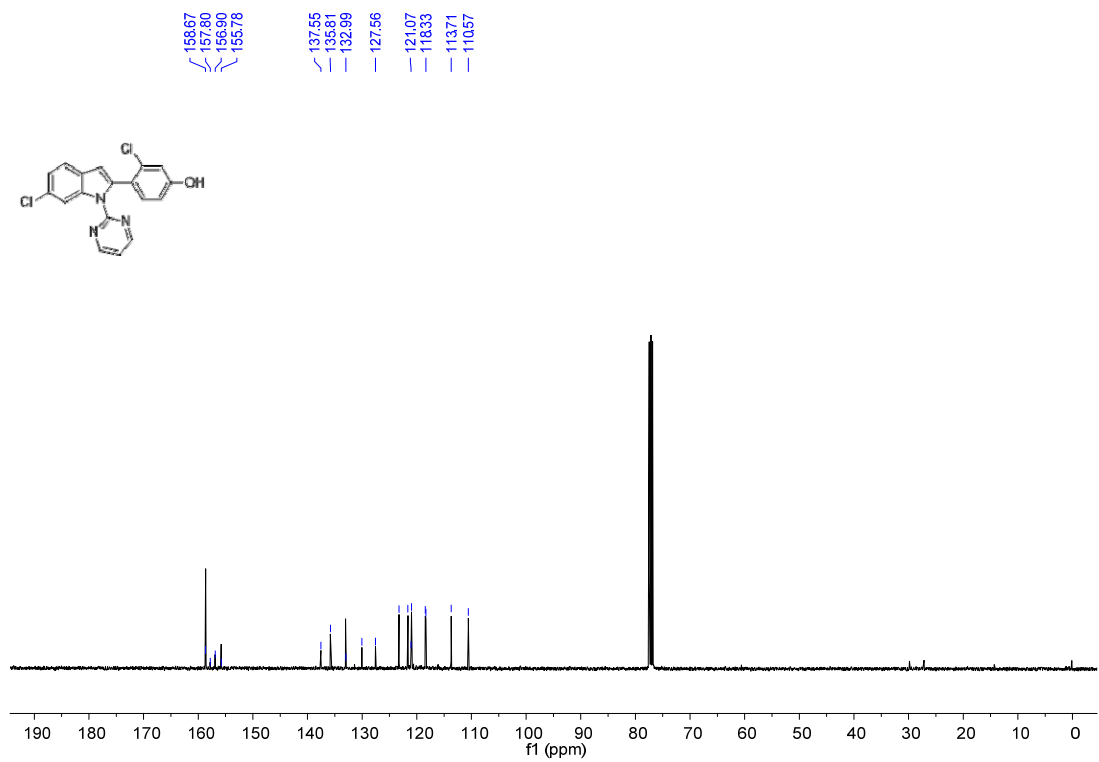
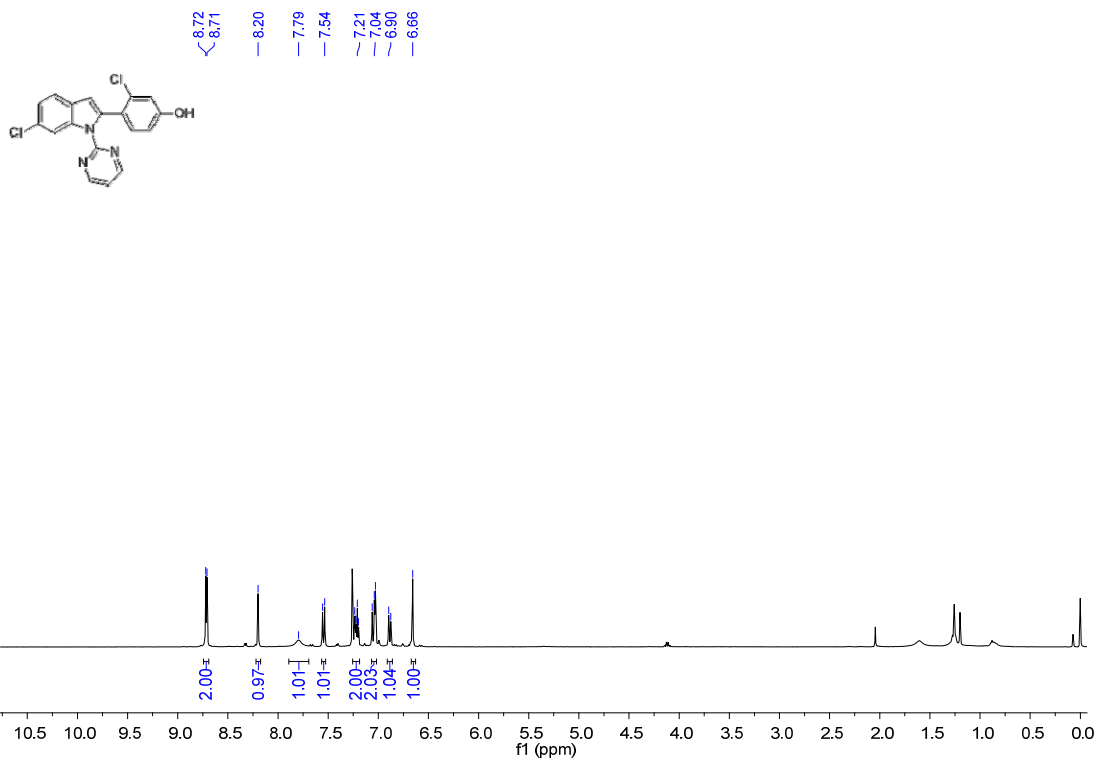


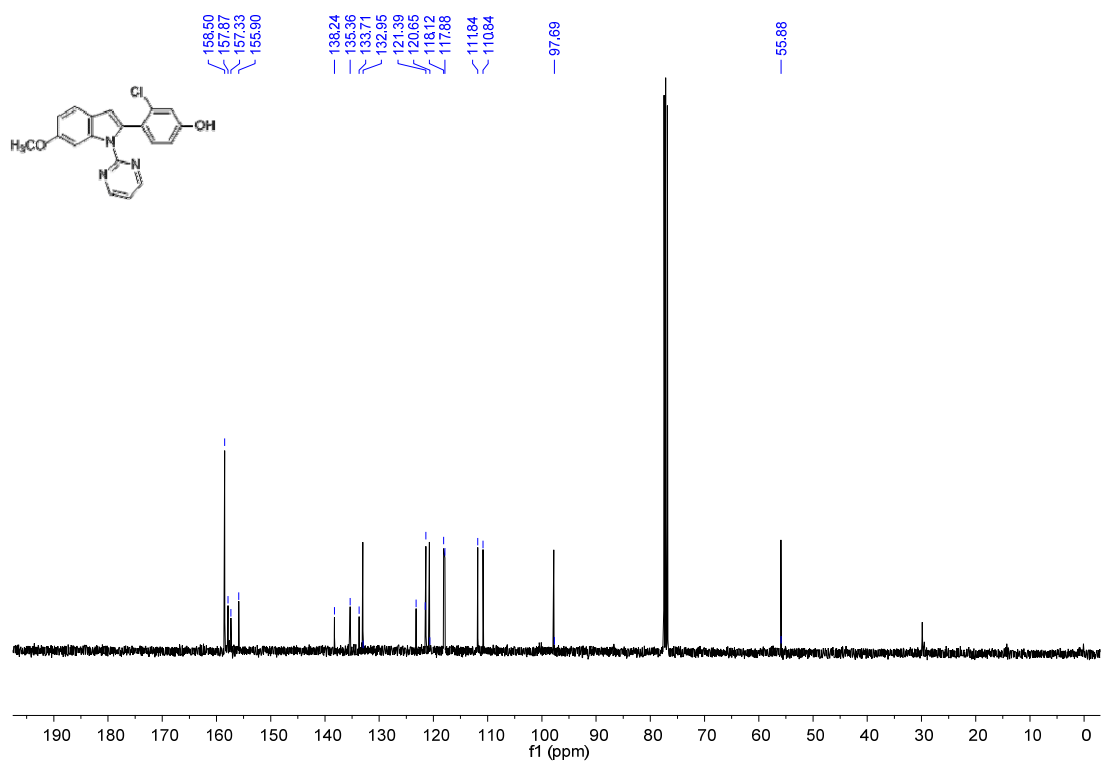
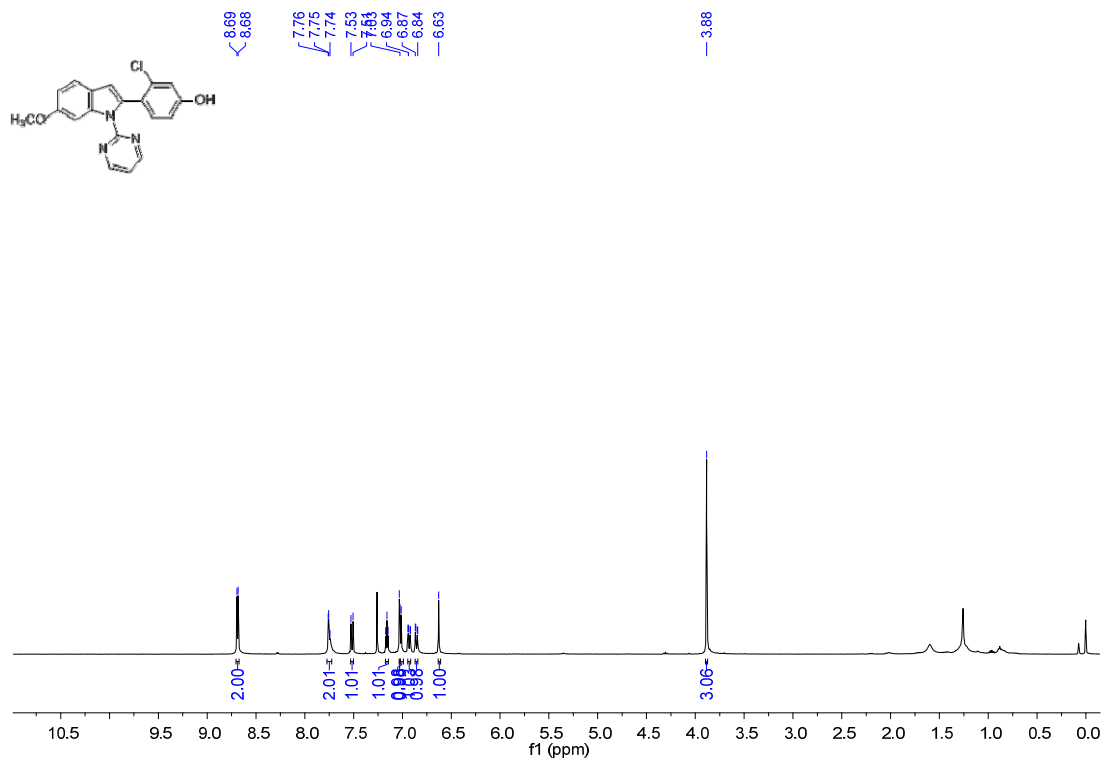


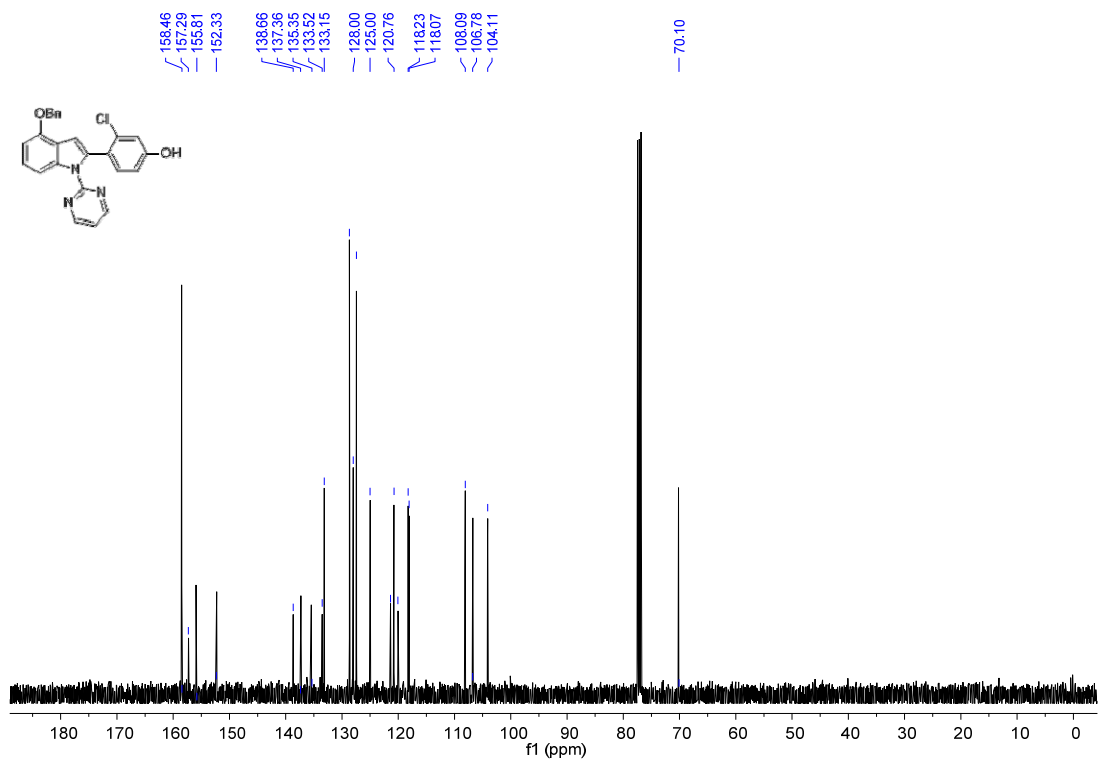
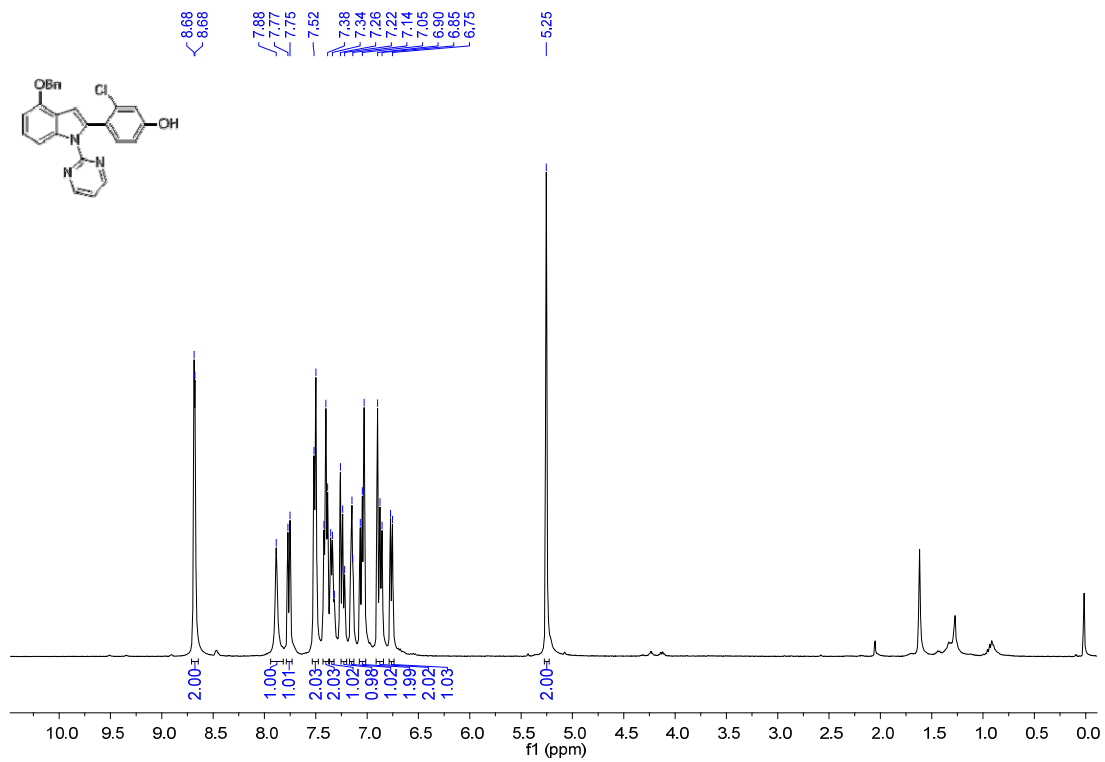


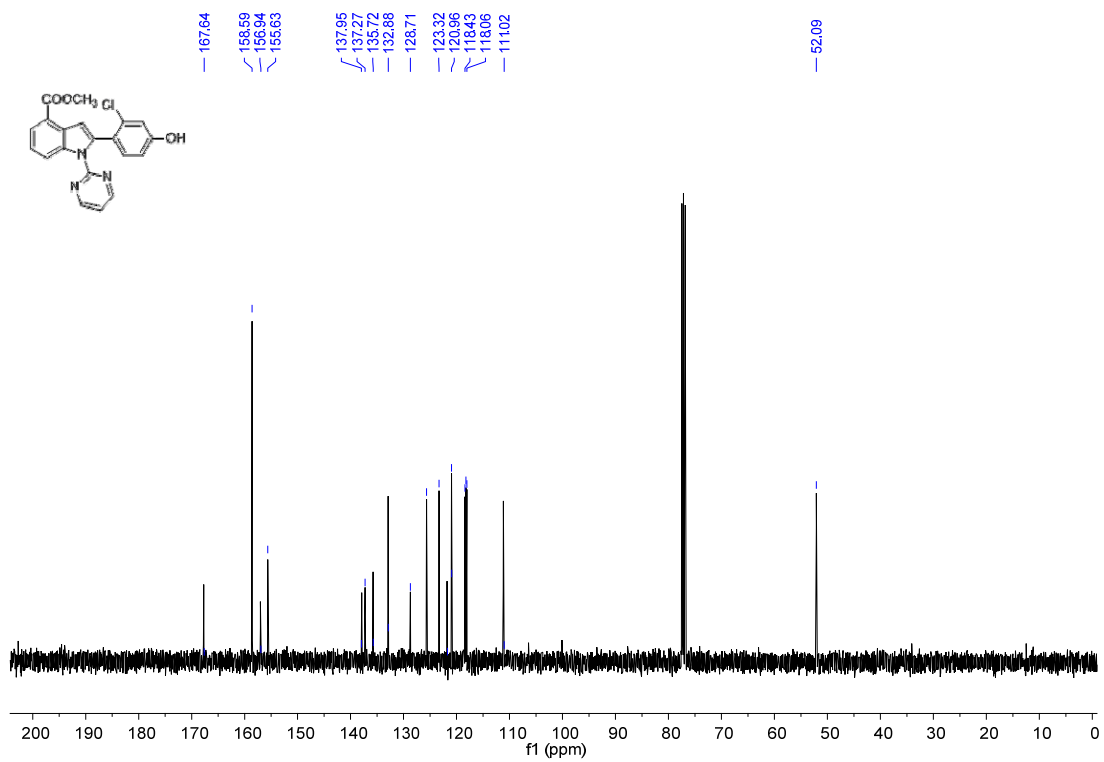
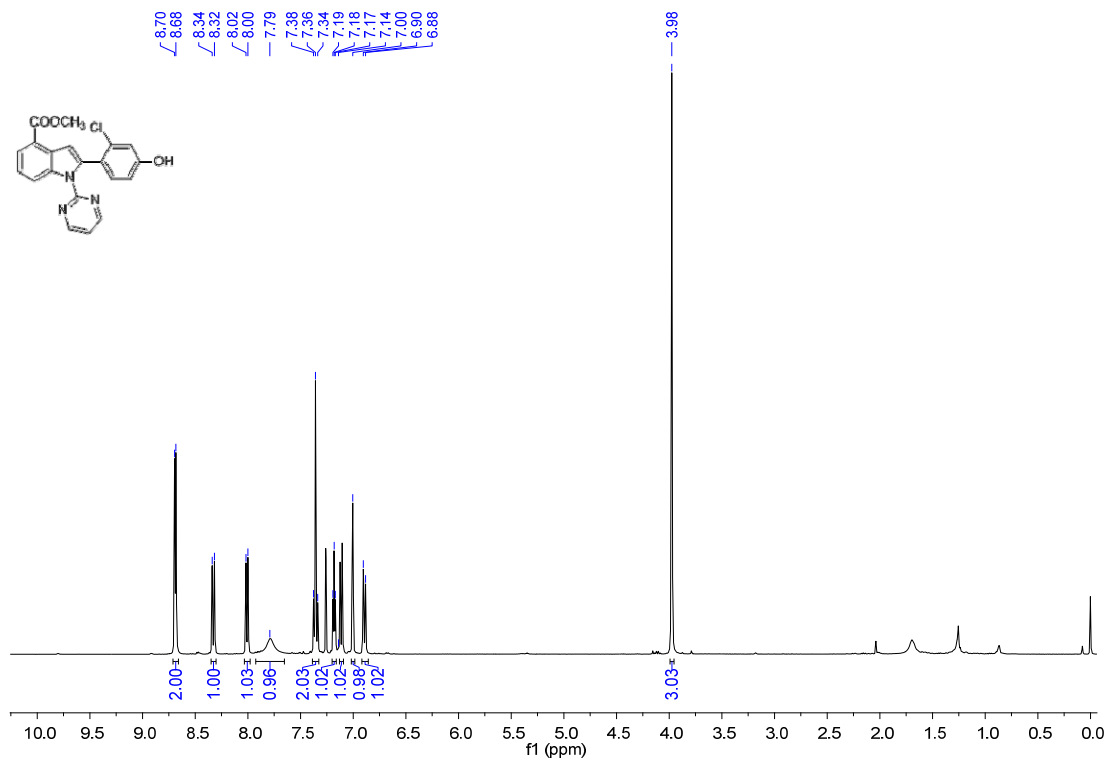


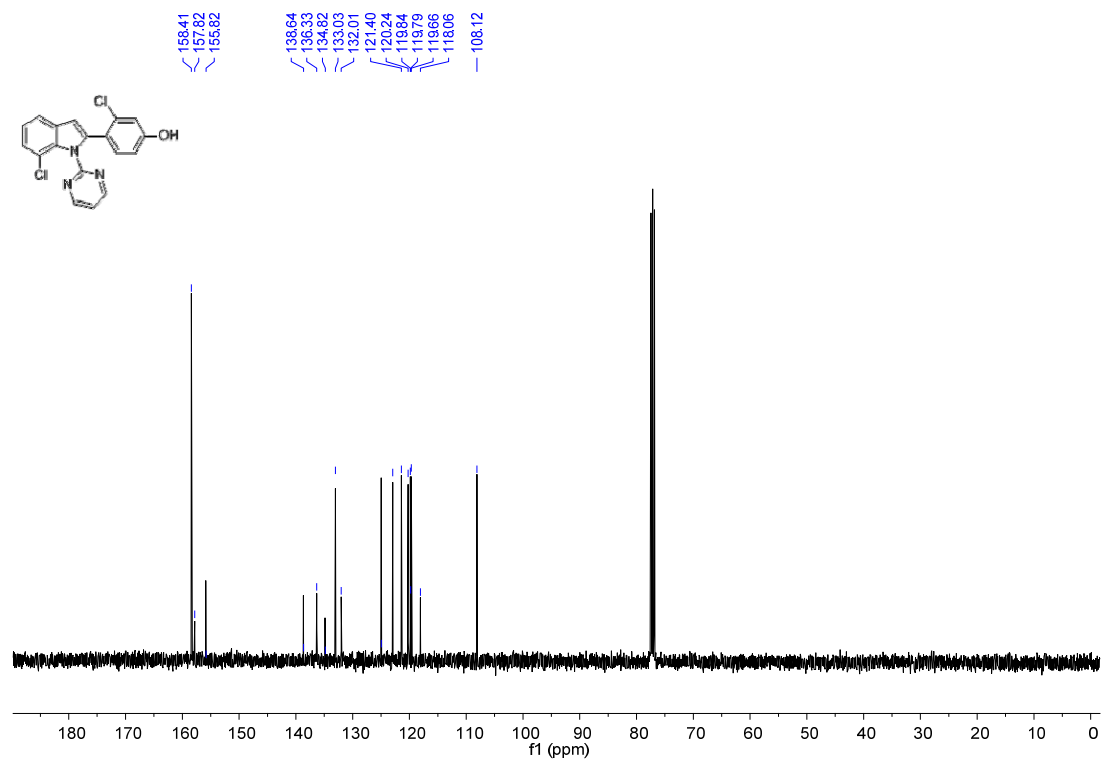
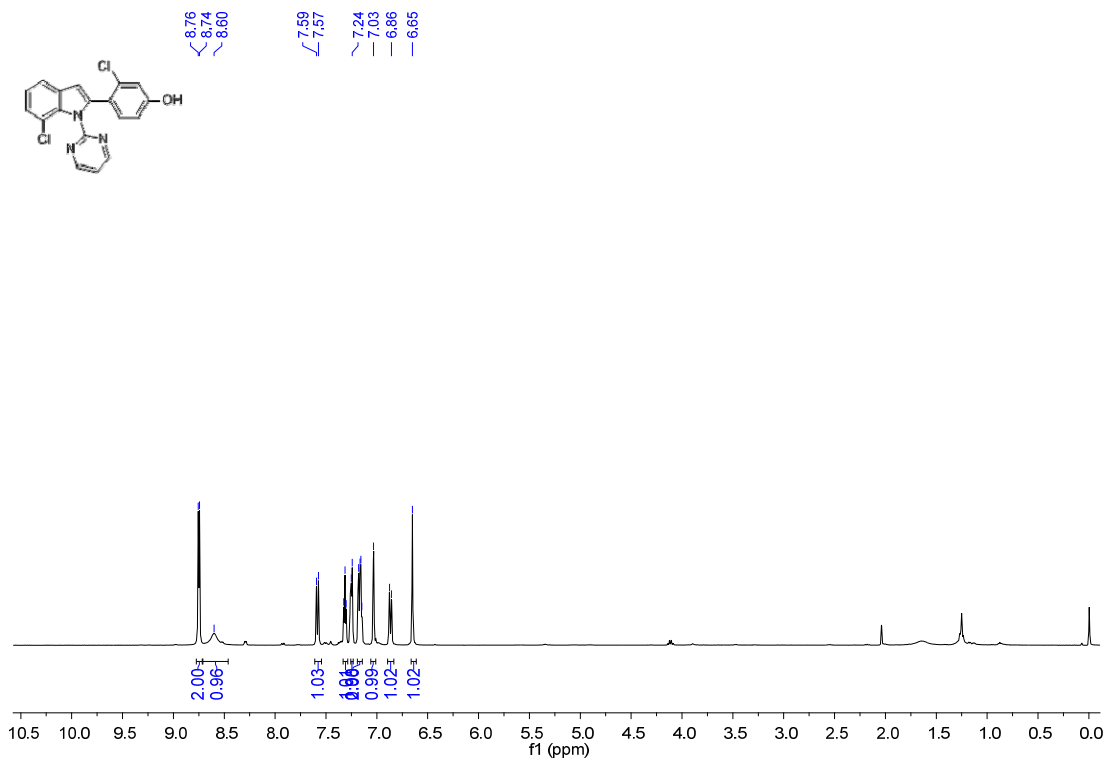


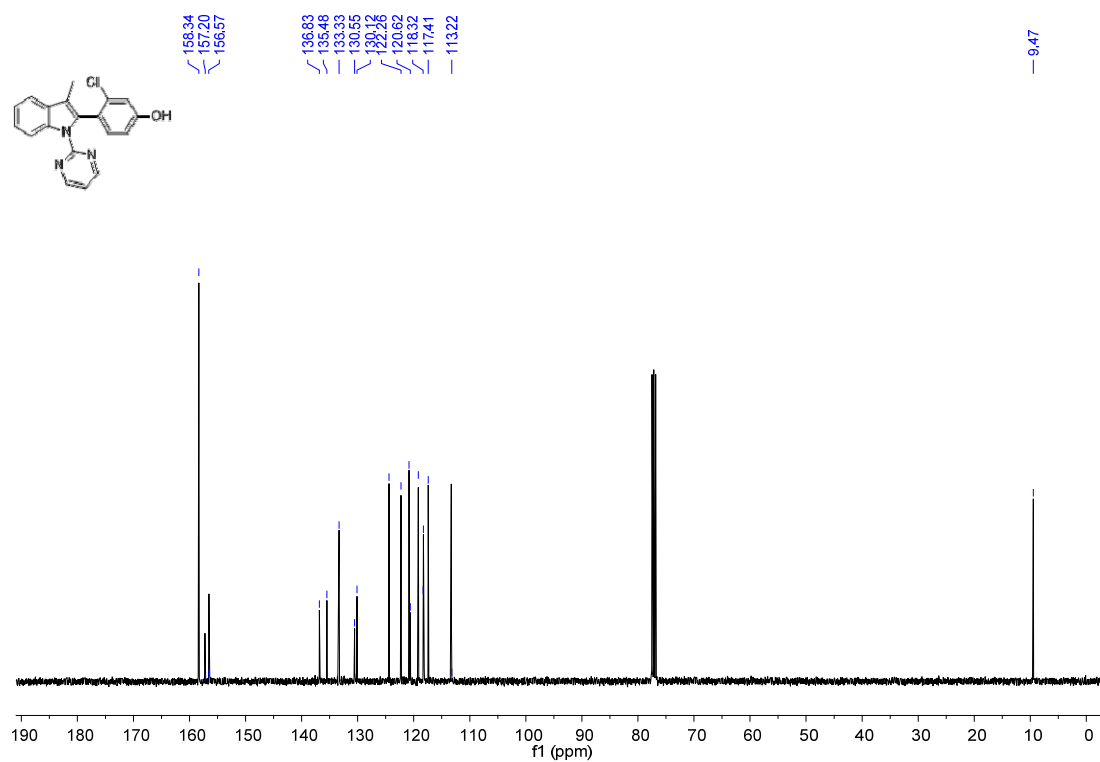
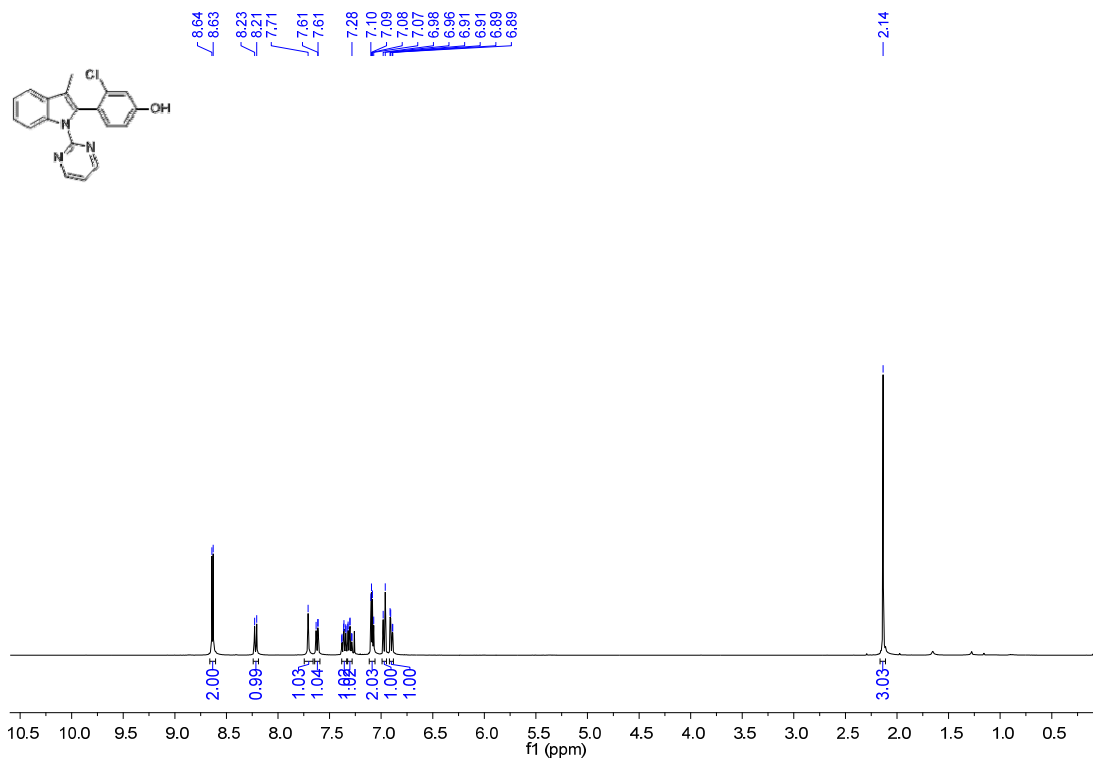


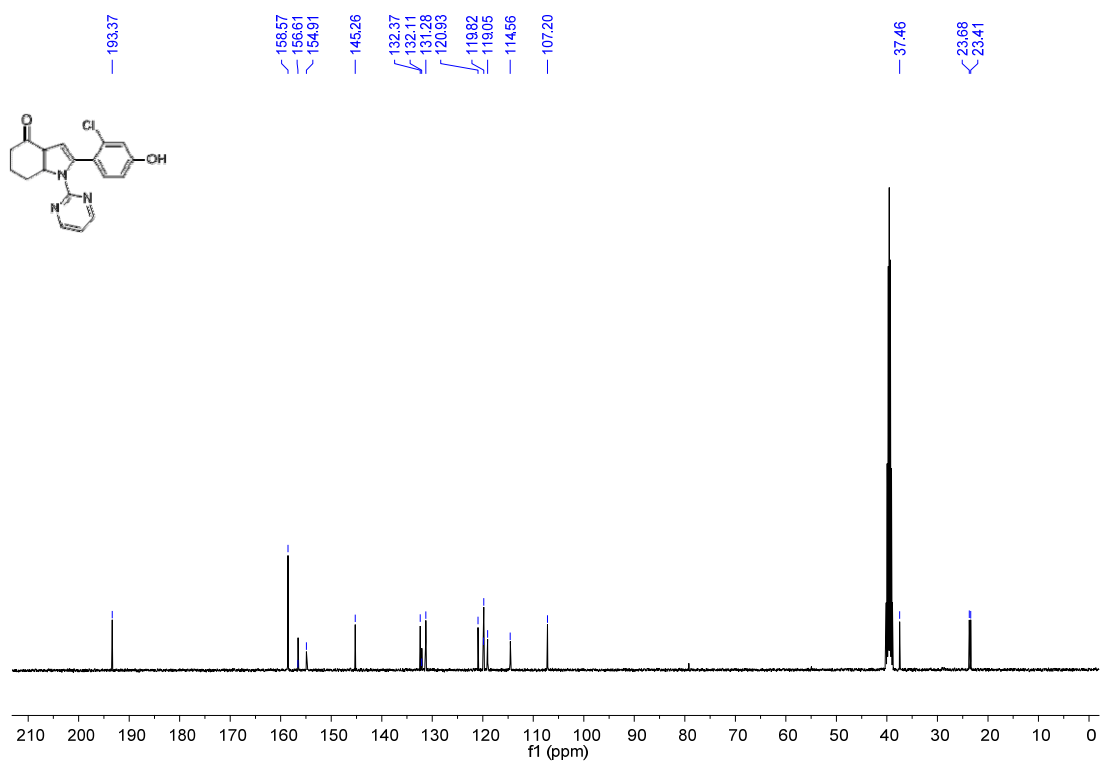
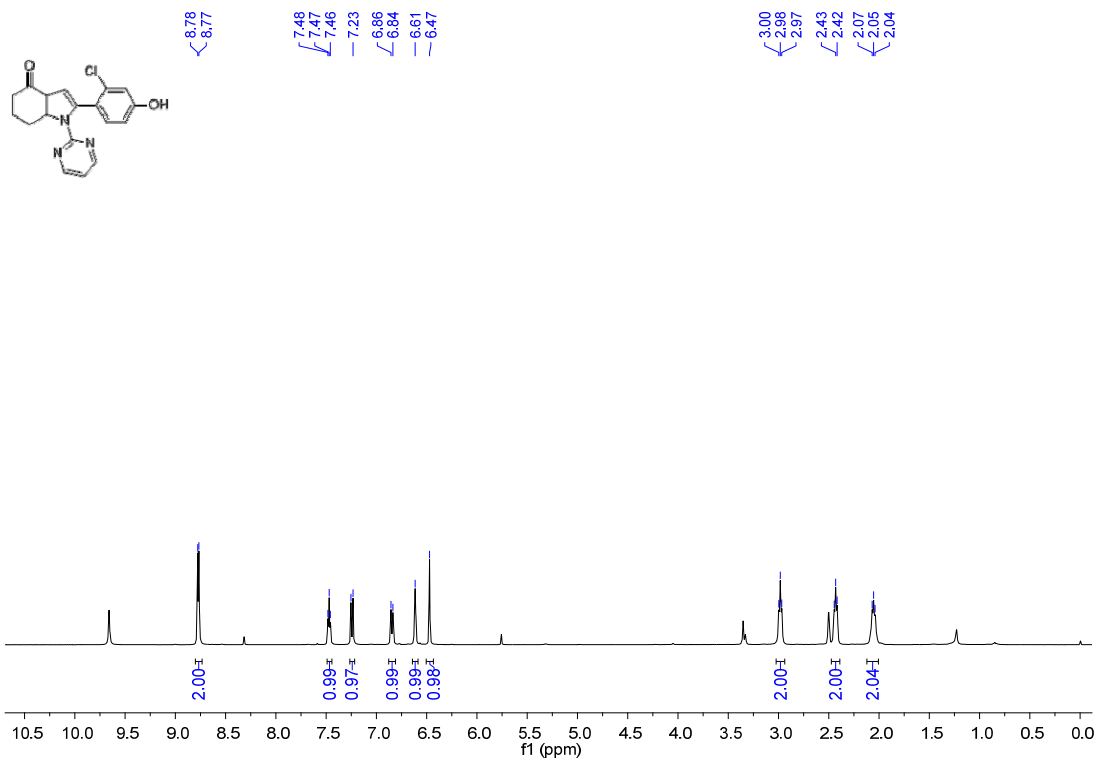


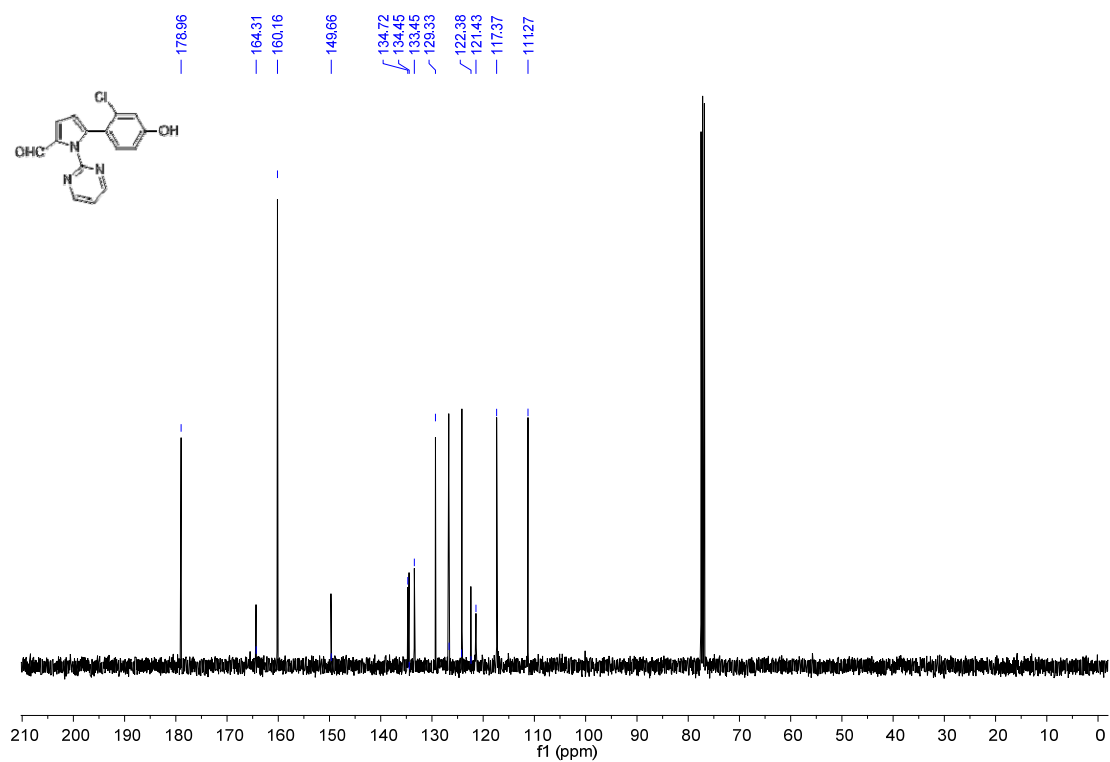
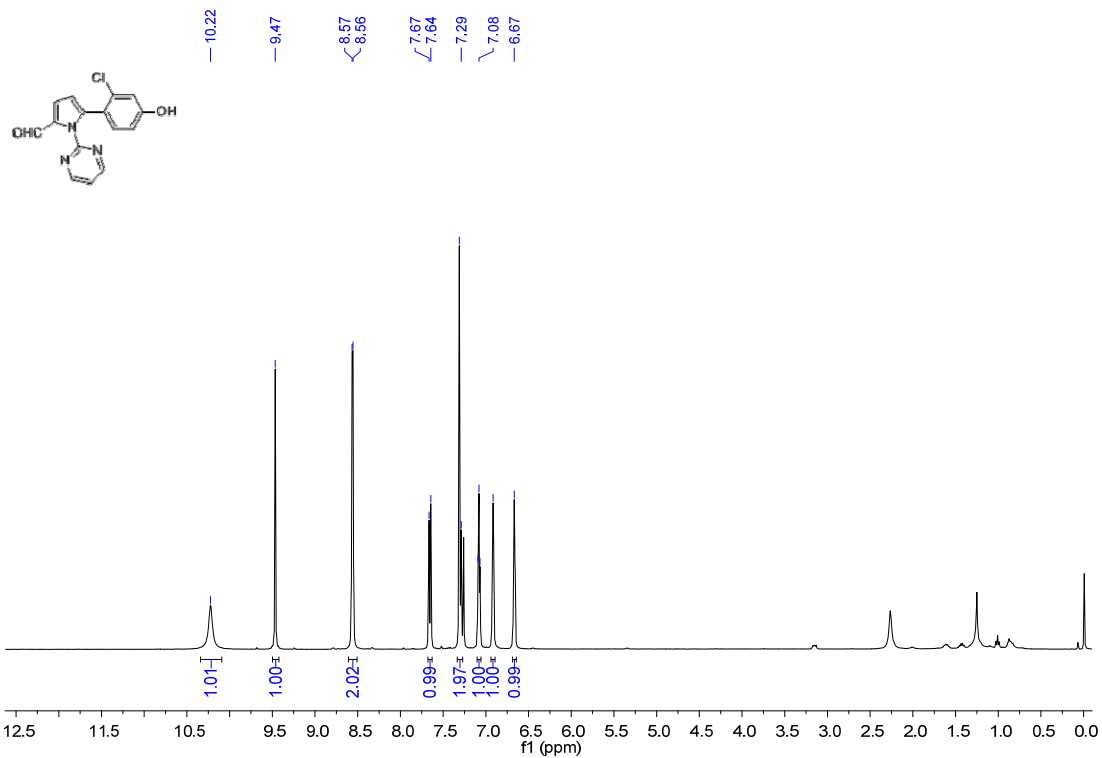












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