Supporting Information

Divergent α-functionalization of cyclic amines via ring construction by molecular O_2 oxidized dearomatization and ring deconstruction by aromatization driven C-C σ-bond cleavage

Fangzhi Hu,[a, §] Liang Wang,[a,b, §] Chunyan Ge,[a] Xinyao Li,[a] Zhanshuai Ding,[a] Lubin Xu,[a] Shuai-Shuai Li*[a,b]

[a] College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, China.

[b] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

[§] These authors contributed equally.

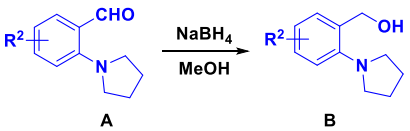
Table of Contents

1. General Information

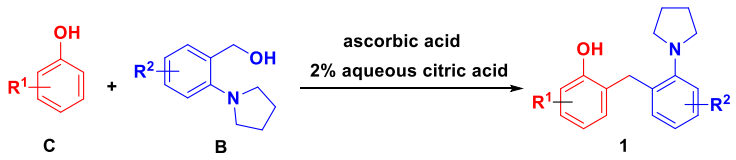
Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d_6 (δ 2.54, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. All substituted 2-fluorobenzaldehydes and phenols were purchased from adamas-beta. All *o*-aminobenzaldehydes were prepared according to literature.[1]

2. General Procedure

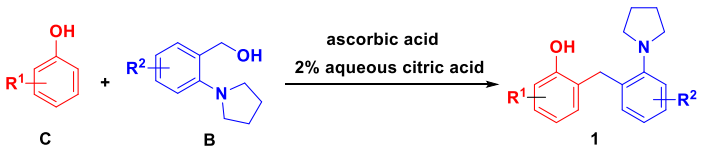
2.1 General Procedure for Preparation of the Starting Materials 1[2]



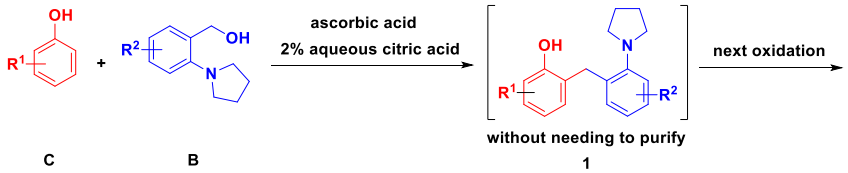
A round-bottom flask was charged with *o*-aminobenzaldehyde **A** (2 mmol) and MeOH (10 mL). $NaBH_4$ (6 mmol) was added slowly to the mixture. The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, H_2O (10 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (20 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue could be used directly in the next step without needing purification.



Method A: A suspension of phenol **C** (2.2 mmol) and alcohol **B** (2.0 mmol) in 2% aqueous citric acid (10 ml) containing ascorbic acid (100 mg, 0.56 mmol) was heated under reflux for over 15 hrs. Upon completion of the reaction as indicated by TLC analysis, the resulting solution was extracted with EtOAc (20 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was recrystallized with ethyl acetate/petroleum ether for three times to obtained the pure diarylmethane **1**.

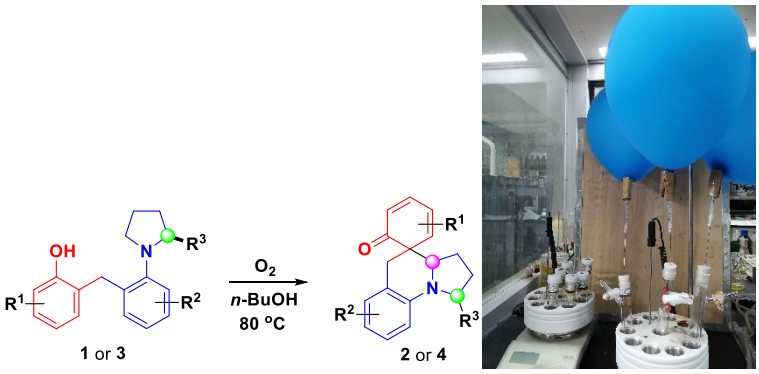


Method B: A suspension of phenol **C** (2.2 mmol) and alcohol **B** (2.0 mmol) in 2% aqueous citric acid (10 ml) containing ascorbic acid (100 mg, 0.56 mmol) was heated under reflux for over 15 hrs. Upon completion of the reaction as indicated by TLC analysis, the resulting solution was extracted with EtOAc (20 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:200) to afford the desired diarylmethane **1**.



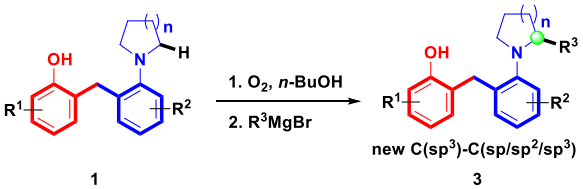
Method C: A suspension of phenol **C** (2.2 mmol) and alcohol **B** (2.0 mmol) in 2% aqueous citric acid (10 ml) containing ascorbic acid (100 mg, 0.56 mmol) was heated under reflux for over 15 hrs. Upon completion of the reaction as indicated by TLC analysis, the resulting solution was washed with $NaHCO_3$ (10 mL×2), and extracted with EtOAc (20 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue could be used directly in the next oxidation without needing purification. However, the product was difficult to isolate which mixed with the impurity from the first step.

2.2 General Procedure for Construction of the α- and α,α'-C(sp^3)-H Bond Functionalized Polycyclic Amines 2 or 4



A Shrek tube was charged with diarylmethane **1** or **3** (0.1 mmol) and *n*-BuOH (2.0 mL) under an O_2 atmosphere with an O_2 balloon. The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:8) to afford the pure product **2** or **4**.

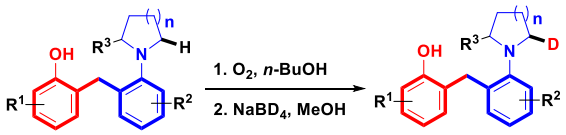
2.3 General Procedure for Synthesis of α-C(sp^3)−H Functionalized Cyclic Anilines 3



A Shrek tube was charged with diarylmethane **1** (0.1 mmol) and *n*-BuOH (2.0 mL) under an O_2

atmosphere with an O_2 balloon. The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added to the system and the resulting solution was extracted with DCM (3 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was directly used for next operation. The Shrek tube with the residue was charged with Et_2O (2 mL) at 0 °C under N_2 atmosphere. Then Grignard reagent (0.4 mmol) was added dropwise in the mixture, and the mixture was stirred at 0 °C continually. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (3 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:200) to afford the pure product **3**.

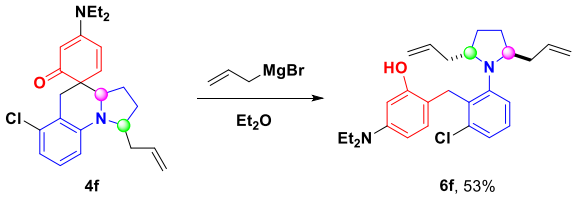
2.4 General Procedure for Synthesis of α-C(sp^3)-H Bond Deuterated Cyclic Anilines 5



1 or 3 5

A Shrek tube was charged with diarylmethane **1** or **3** (0.1 mmol) and *n*-BuOH (2.0 mL) under an O_2 atmosphere with an O_2 balloon. The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added to the system and the resulting solution was extracted with DCM (3 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was directly used for next operation. The reaction tube with the residue was charged with $NaBD_4$ (3 equiv.) and MeOH (2 mL), and stirred at room temperature. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (3 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:200) to afford the pure product **5**.

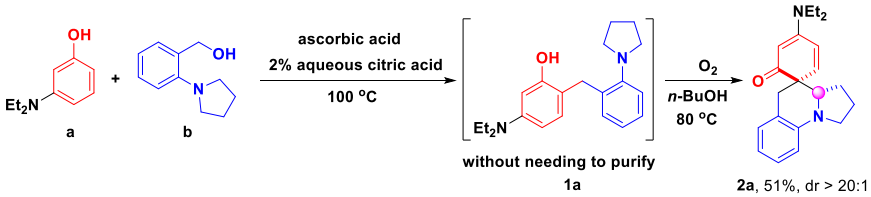
2.5 General Procedure for Synthesis of α, α'-Diallyl Substituted Aniline



4f 6f, 53%

A reaction tube was charged with **4f** (0.05 mmol), Et_2O (2 mL) at 0 °C under N_2 atmosphere. Then allyl magnesium bromide (0.2 mmol) was added in the mixture, and the mixture was stirred at 0 °C continually. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:200) to afford the pure α, α'-diallyl substituted aniline **6f** in 53% yield.

2.6 General Procedure for Sequential Operation for Achieving the α-C(sp^3)-H Bond Functionalized Polycyclic Amine

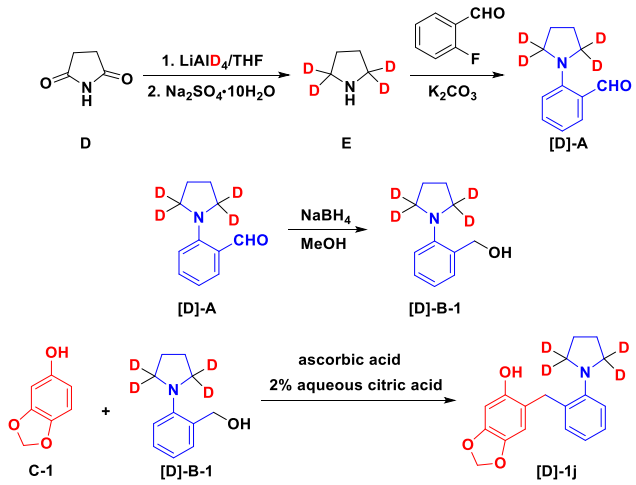


A suspension of phenol **a** (0.11 mmol) and alcohol **b** (0.1 mmol) in 2% aqueous citric acid (1 ml) containing ascorbic acid (5 mg) was heated under reflux for over 15 hrs. Upon completion of the reaction as indicated by TLC analysis, the resulting solution was washed with $NaHCO_3$ (3 mL×2), and extracted with EtOAc (3 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue could be used directly in the next oxidation without needing purification.

Subsequently, a Shrek tube was charged with the residue and *n*-BuOH (2.0 mL) under an O_2 atmosphere with an O_2 balloon. The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:8) to afford the pure product **2a**.

3. Mechanistic studies

3.1. General Procedure for the Preparation of Deuterated Diarylmethane

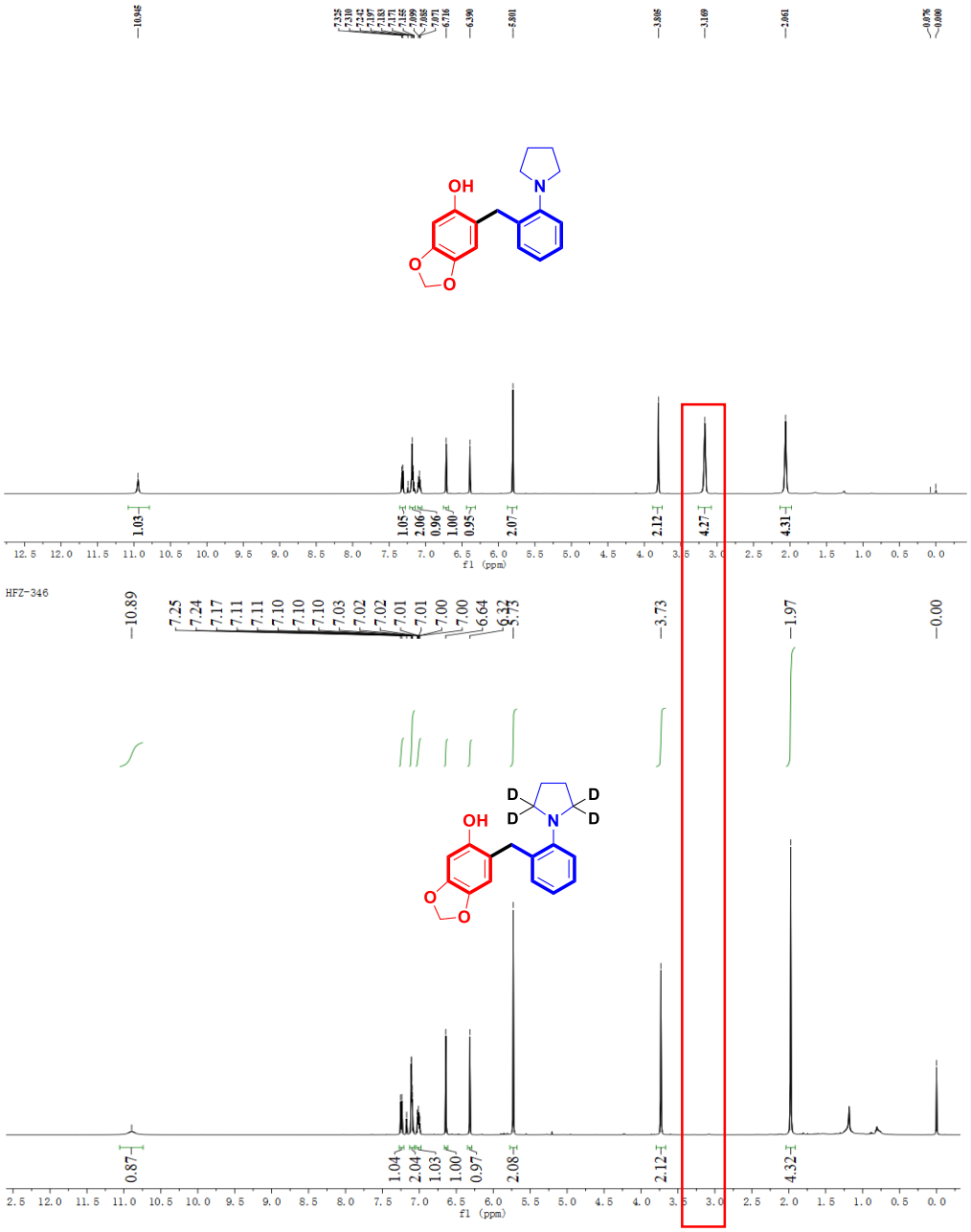


A thick-walled pressure tube was charged with succinimide **D** (0.5 mmol), THF (4 mL), and $LiAlD_4$ (2.0 mmol) at 90 ℃. The reaction was stirred for 12 h at 90 ℃, and was quenched with $Na_2SO_4.10H_2O$ (0.8 mmol). Then *o*-fluorobenzaldehyde (0.4 mmol) and K_2CO_3 (0.6 mmol) were added in the mixture. The mixture was stirred for 12 h at 100 ℃. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The crude mixture purified by flash silica gel chromatography (petroleum ether/ethyl acetate = 100:1) to afford the pure product **[D]-A**.

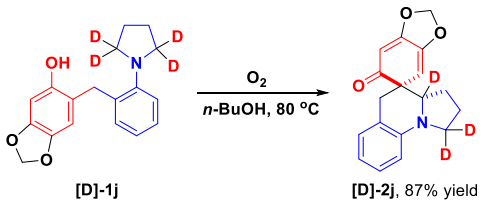
A reaction tube was charged with *o*-aminobenzaldehyde **[D]-A** (0.4 mmol) and MeOH (2 mL). $NaBH_4$ (1.2 mmol) was added slowly to the mixture. The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, H_2O (10

mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (20 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue could be used directly in the next step without needing purifying.

A suspension of sesamol **C-1** (0.44 mmol) and alcohol **[D]-B-1** (0.4 mmol) in 2% aqueous citric acid (2 ml) containing ascorbic acid (20 mg, 0.112 mmol) was heated under reflux for over 15 hrs. Upon completion of the reaction as indicated by TLC analysis, the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:200) to afford the deuterated diarylmethane **[D]-1j** in 55% yield.

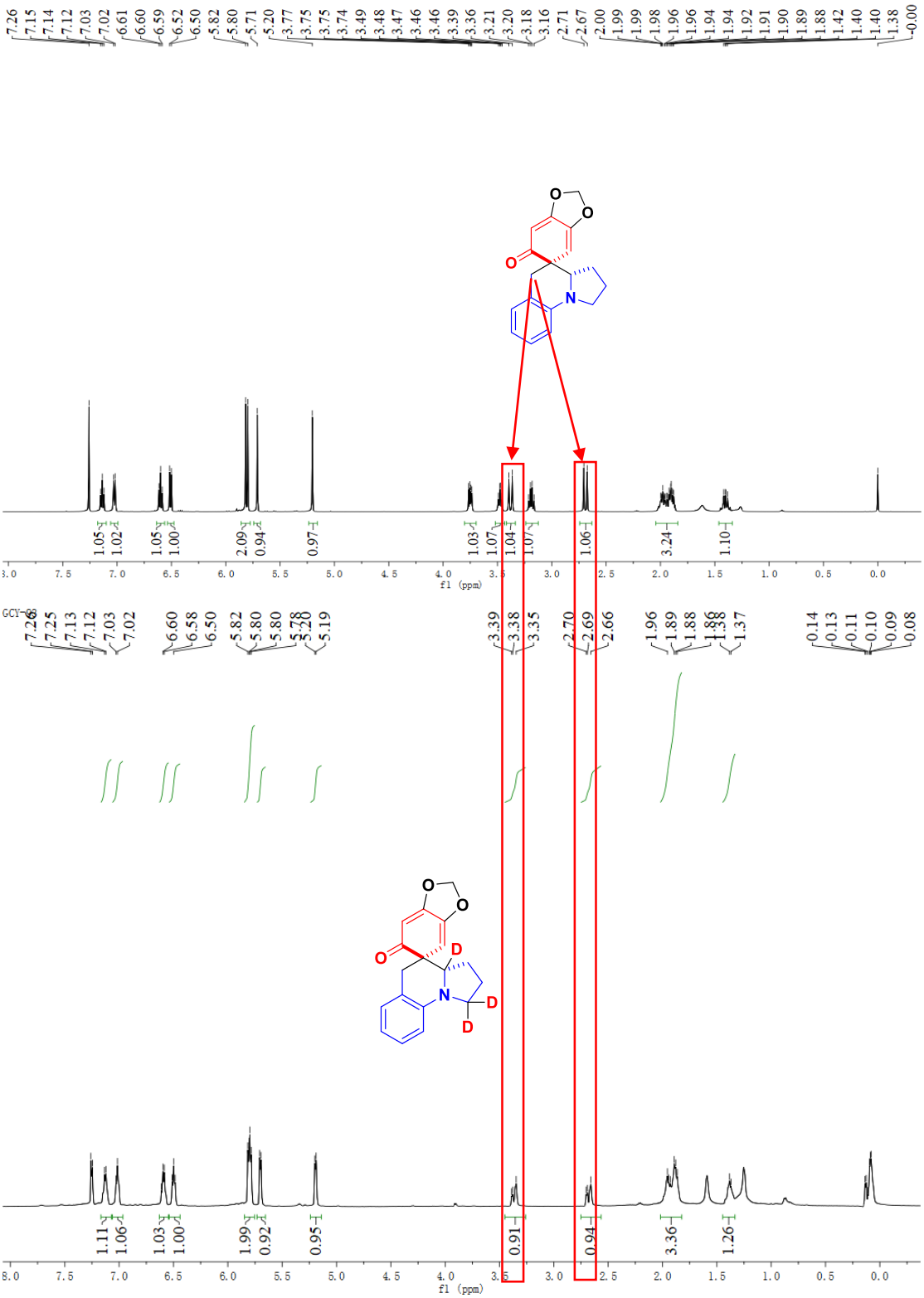


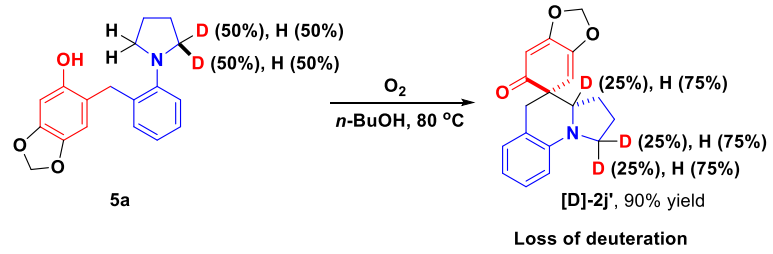
3.2 Spectra Contrast between Deuterated Product and Non-deuterated Product.

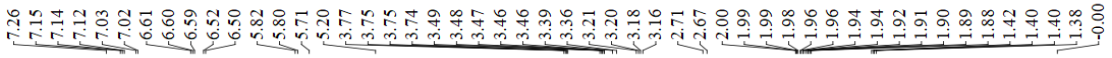


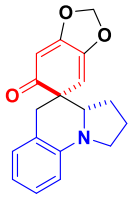
[D]-1j

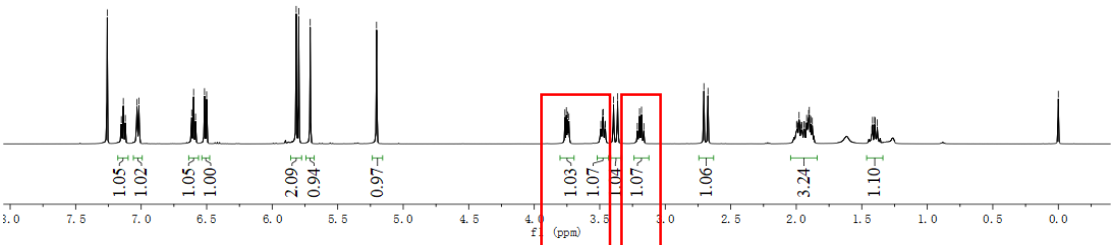
[D]-2j, 87% yield

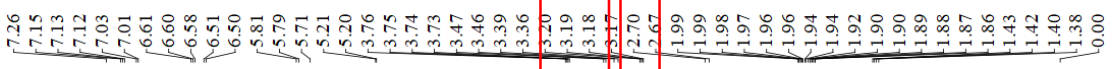


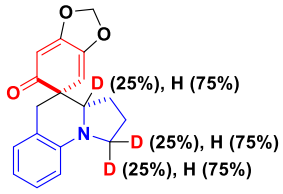

H
H
D (50%), H (50%)
D (50%), H (50%)
OH
N
O
O
5a
O2
n-BuOH, 80 °C
O
O
O
D (25%), H (75%)
N
D (25%), H (75%)
D (25%), H (75%)
[D]-2j', 90% yield
Loss of deuteration

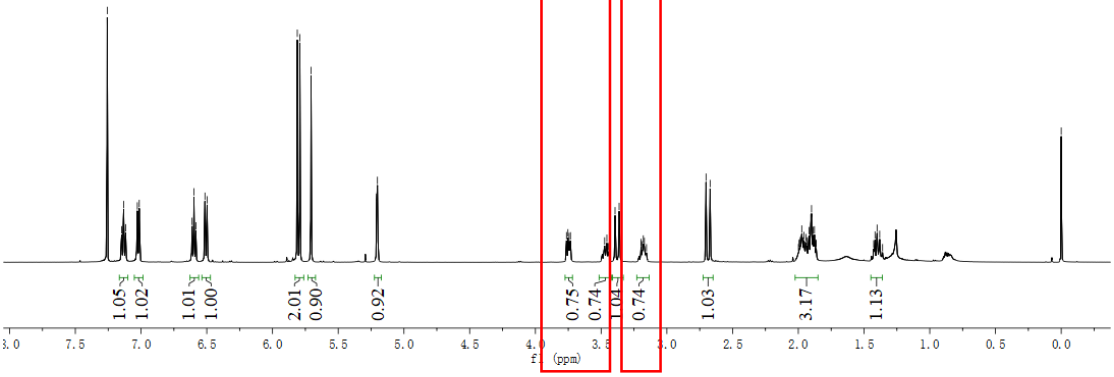




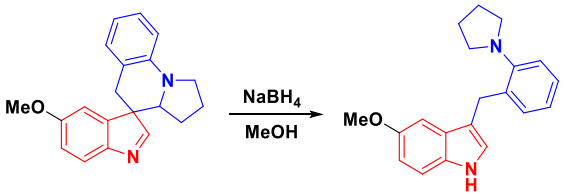





O
O
O
D (25%), H (75%)
N
D (25%), H (75%)
D (25%), H (75%)



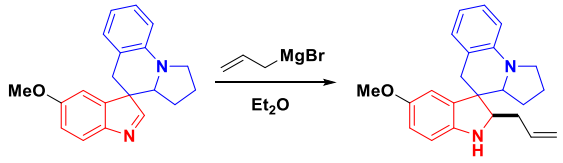
3.3 Aromatization-driven C-C Bond Cleavage of Spiroindolenine.



11 **7**, 68% yield

The reaction tube was charged with spiroindolenine **11** (0.1 mmol), $NaBH_4$ (0.3 mmol, 3 equiv.) and MeOH (2 mL), and stirred at room temperature. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:50) to afford the pure product **7**.

3.4 Nucleophilic Addition between Grignard Reagent and the Imine of Spiroindolenine

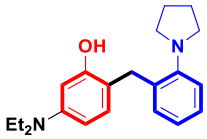


11 **12**, 92% yield, dr 1:1

A reaction tube was charged with spiroindolenine **11** (0.05 mmol), Et_2O (2 mL) at 0 °C under N_2 atmosphere. Then allyl magnesium bromide (0.2 mmol) was added in the mixture, and the mixture was stirred at 0 °C continually. Upon completion of the reaction as indicated by TLC analysis, the H_2O (2 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:50) to afford the pure addition-compound **12** in 92% yield (dr 1:1).

4. Characterization of Products

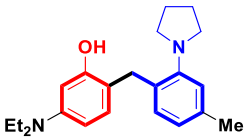
5-(diethylamino)-2-(2-(pyrrolidin-1-yl)benzyl)phenol (1a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (401 mg, 62% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.09 (m, 2H), 7.06 (dd, *J* = 7.5, 4.6 Hz, 2H), 6.18 (s, 1H), 6.15 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 2H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.19 (s, 4H), 2.07 (s, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.3, 146.1, 137.9, 130.9, 130.3, 127.2, 125.8, 119.8, 115.2, 103.8, 100.1, 53.8, 44.3, 33.3, 23.8, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{29}N_2O$ 325.2274, found: 325.2267.

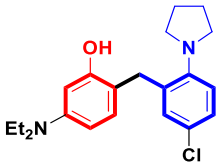
5-(diethylamino)-2-(4-methyl-2-(pyrrolidin-1-yl)benzyl)phenol (1b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (392 mg, 58% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.97 (s, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.18 (d, *J* = 2.2 Hz, 1H), 6.14 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.76 (s, 2H), 3.25 (q, *J* = 7.0 Hz, 4H), 3.17 (t, *J* = 6.0 Hz, 4H), 2.26 (s, 3H), 2.11 – 2.01 (m, 4H), 1.09 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.3, 145.8, 136.9, 134.8, 130.8, 130.3, 126.5, 120.4, 115.6, 103.9, 100.2, 53.8, 44.4, 32.9, 23.8, 21.2, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{31}N_2O$ 339.2431, found: 339.2422.

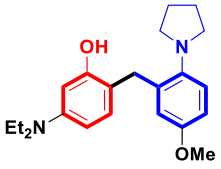
2-(5-chloro-2-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (393 mg, 55% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.29 (s, 1H), 7.09 (s, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.17 (d, *J* = 10.6 Hz, 2H), 3.76 (s, 2H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.15 (t, *J* = 5.7 Hz, 4H), 2.07 (dt, *J* = 6.2, 3.1 Hz, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.5, 144.7, 139.7, 130.8, 130.7, 130.4, 127.2, 121.8, 114.2, 103.9, 99.9, 53.9, 44.3, 33.0, 23.8, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{28}ClN_2O$ 359.1885, found: 359.1877.

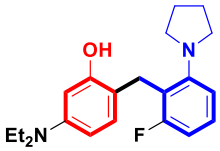
5-(diethylamino)-2-(5-methoxy-2-(pyrrolidin-1-yl)benzyl)phenol (1d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (438 mg, 62% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.67 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.19 (d, *J* = 2.5 Hz, 1H), 6.15 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.76 (s, 2H), 3.75 (s, 3H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.18 – 3.08 (m, 4H), 2.10 – 2.02 (m, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.2, 156.4, 148.4, 139.4, 139.1, 130.3, 120.9, 116.1, 114.9, 112.2, 103.8, 100.1, 55.4, 54.2, 44.4, 33.4, 23.8, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{31}N_2O_2$ 355.2380, found: 355.2369.

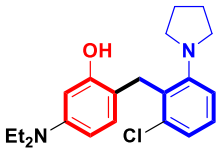
5-(diethylamino)-2-(2-fluoro-6-(pyrrolidin-1-yl)benzyl)phenol (1e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (410 mg, 60% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.18 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.82 (t, *J* = 8.8 Hz, 1H), 6.22 – 6.12 (m, 2H), 3.85 (d, *J* = 2.1 Hz, 2H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.22-3.13 (m, 4H), 2.07 (dt, *J* = 6.1, 3.2 Hz, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.1, 161.1, 156.5, 148.3, 148.2, 148.1, 131.5, 127.5, 127.5, 125.3, 125.2, 115.4, 115.4, 113.2, 112.8, 112.6, 103.7, 99.7, 53.9, 44.3, 25.1, 23.8, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{28}FN_2O$ 343.2180, found: 343.2167.

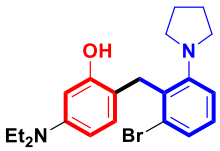
2-(2-chloro-6-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (379 mg, 53% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.11 (d, *J* = 6.9 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.22-6.13 (m, 2H), 4.01 (s, 2H), 3.27 (q, *J* = 7.0 Hz, 4H), 3.22-3.11 (m, 4H), 2.13 – 2.00 (m, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.9, 148.4, 148.3, 135.9, 135.2, 132.4, 127.6, 127.3, 118.5, 112.4, 103.6, 99.5, 54.1, 44.3, 29.1, 23.8, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{28}ClN_2O$ 359.1885, found: 359.1879.

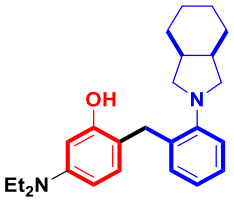
2-(2-bromo-6-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (434 mg, 54% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.16 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.21 – 6.13 (m, 2H), 4.06 (s, 2H), 3.27 (q, *J* = 7.0 Hz, 4H), 3.18 (s, 4H), 2.13 – 2.03 (m, 4H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.9, 148.4, 148.4, 136.7, 132.6, 130.8, 128.0, 126.7, 119.3, 112.4, 103.2, 99.6, 54.1, 44.3, 31.5, 23.8, 12.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{28}BrN_2O$ 403.1380, found: 403.1371.

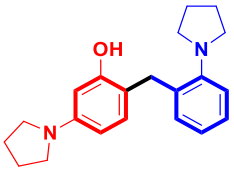
5-(diethylamino)-2-(2-((3aR,7aS)-octahydro-2H-isoindol-2-yl)benzyl)phenol (1h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (378 mg, 50% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (d, *J* = 165.2 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.20 (dd, *J* = 23.8, 8.0 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.08 – 6.98 (m, 2H), 6.24 – 6.18 (m, 1H), 6.14 (d, *J* = 8.3 Hz, 1H), 3.89 (d, *J* = 14.1 Hz, 1H), 3.79 (s, 1H), 3.68 (d, *J* = 14.1 Hz, 1H), 3.42 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.32 – 3.16 (m, 7H), 2.47 – 2.37 (m, 1H), 1.95 (d, *J* = 12.1 Hz, 1H), 1.84 (d, *J* = 8.9 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.69-1.67 (m, 1H), 1.66 – 1.56 (m, 2H), 1.46 – 1.37 (m, 1H), 1.33 (t, *J* = 9.6 Hz, 1H), 1.25 – 1.16 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.5, 148.2, 137.6, 137.3, 131.1, 131.0, 130.4, 130.3, 127.2, 127.2, 125.1, 125.1, 120.2, 119.9, 115.6, 115.4, 103.8, 100.3, 100.1, 59.1, 57.7, 45.2, 44.4, 37.8, 34.1, 33.8, 28.9, 26.3, 25.7, 22.9, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{35}N_2O$ 379.2744, found: 379.2733.

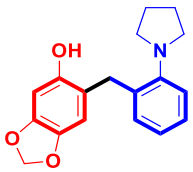
5-(pyrrolidin-1-yl)-2-(2-(pyrrolidin-1-yl)benzyl)phenol (1i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (386 mg, 60% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.10 – 7.01 (m, 2H), 6.08 (s, 1H), 6.05 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 2H), 3.19 (s, 8H), 2.07 (s, 4H), 1.92 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.2, 148.5, 146.0, 137.9, 130.9, 130.2, 127.2, 125.8, 119.8, 115.4, 103.7, 100.1, 53.9, 47.7, 33.3, 25.5, 23.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{27}N_2O$ 323.2118, found: 323.2110.

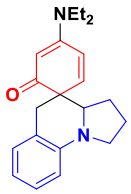
6-(2-(pyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (1j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (326 mg, 55% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 6.4 Hz, 2H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.72 (s, 1H), 6.39 (s, 1H), 5.80 (s, 2H), 3.81 (s, 2H), 3.17 (s, 4H), 2.06 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.3, 146.9, 146.3, 140.4, 137.4, 130.7, 127.6, 125.9, 120.2, 119.3, 108.7, 100.7, 99.1, 54.1, 33.8, 23.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{18}H_{19}NO_3$ 298.1438, found: 298.1430.

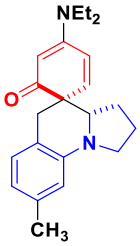
4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2a)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (26.4 mg, 82% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 6.39 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.16 (d, *J* = 10.5 Hz, 1H), 5.33 (d, *J* = 2.1 Hz, 1H), 3.86 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.54 – 3.43 (m, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 3.18 (d, *J* = 7.5 Hz, 1H), 2.62 (d, *J* = 15.8 Hz, 1H), 1.99 – 1.87 (m, 3H), 1.34 – 1.28 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 156.5, 143.9, 143.2, 129.1, 127.3, 119.9, 118.5, 114.9, 110.1, 96.6, 64.4, 47.2, 45.7, 44.9, 39.7, 27.8, 23.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{27}N_2O$ 323.2118, found: 323.2108.

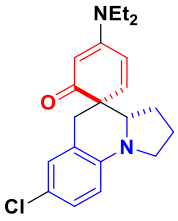
4-(diethylamino)-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (26.9 mg, 80% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 7.5 Hz, 1H), 6.44 – 6.35 (m, 2H), 6.32 (s, 1H), 6.17 (d, *J* = 10.5 Hz, 1H), 5.33 (d, *J* = 2.2 Hz, 1H), 3.84 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.49 – 3.40 (m, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 3.18 (d, *J* = 7.5 Hz, 1H), 2.59 (d, *J* = 15.7 Hz, 1H), 2.31 (s, 3H), 1.99 – 1.88 (m, 3H), 1.34 – 1.25 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.5, 156.5, 144.1, 143.1, 136.9, 129.0, 118.4, 117.0, 115.9, 110.9, 96.6, 64.4, 47.2, 46.0, 44.9, 39.5, 27.8, 23.5, 21.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{29}N_2O$ 337.2274, found: 337.2269.

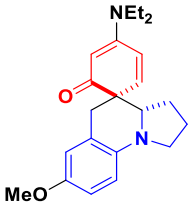
7'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (32.0 mg, 90% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (t, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.42 (dd, *J* = 16.1, 5.3 Hz, 2H), 6.12 (d, *J* = 10.4 Hz, 1H), 5.36 (s, 1H), 3.80 (dd, *J* = 9.8, 5.1 Hz, 1H), 3.45 (t, *J* = 8.2 Hz, 1H), 3.38 (q, *J* = 7.1 Hz, 4H), 3.25 (d, *J* = 16.8 Hz, 1H), 3.20 (d, *J* = 7.8 Hz, 1H), 2.97 (d, *J* = 16.7 Hz, 1H), 2.01 – 1.88 (m, 3H), 1.38-1.28 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.8, 156.6, 144.4, 143.5, 134.7, 127.5, 118.8, 117.8, 115.9, 108.7, 96.6, 63.8, 47.5, 45.6, 44.9, 37.0, 27.8, 23.6, 18.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{26}ClN_2O$ 357.1728, found: 357.1720.

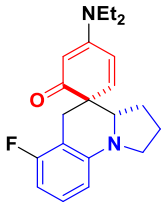
4-(diethylamino)-7'-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (18.3 mg, 52% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 6.37 (d, *J* = 8.7 Hz, 1H), 6.33 (dd, *J* = 10.5, 2.3 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 5.26 (d, *J* = 2.3 Hz, 1H), 3.72 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.68 – 3.60 (m, 3H), 3.42 (d, *J* = 15.9 Hz, 1H), 3.37 – 3.19 (m, 5H), 3.08 (dd, *J* = 16.0, 8.3 Hz, 1H), 2.56 – 2.46 (m, 1H), 1.90 – 1.82 (m, 2H), 1.29 – 1.17 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 6H), 1.05 (dd, *J* = 13.4, 6.6 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 156.6, 150.3, 144.1, 138.1, 121.1, 118.5, 115.4, 112.9, 111.0, 96.6, 64.7, 55.9, 47.7, 46.2, 44.9, 39.7, 27.7, 23.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{29}N_2O_2$ 353.2224, found: 353.2229.

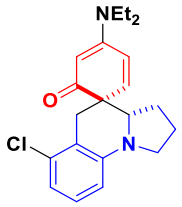
4-(diethylamino)-6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (25.8 mg, 76% yield, dr 2:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 15.0, 7.8 Hz, 1H), 6.44 (ddd, *J* = 36.8, 10.5, 2.0 Hz, 1H), 6.37 – 6.27 (m, 2H), 6.19 (dd, *J* = 47.4, 10.4 Hz, 1H), 5.79 (tdd, *J* = 10.6, 8.7, 5.1 Hz, 1H), 5.35 (dd, *J* = 10.8, 2.0 Hz, 1H), 5.10 (dd, *J* = 15.1, 9.2 Hz, 2H), 3.96 – 3.74 (m, 2H), 3.48 – 3.32 (m, 4H), 3.18 (dd, *J* = 31.4, 16.6 Hz, 1H), 2.83 (dd, *J* = 16.0, 11.6 Hz, 1H), 2.54 (dt, *J* = 18.7, 9.3 Hz, 1H), 2.26 – 1.96 (m, 1H), 1.96 – 1.72 (m, 3H), 1.43 – 1.32 (m, 1H), 1.23 (q, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.10 (s), 196.78 (s), 162.1 (d, *J* = 240.0 Hz), 161.7 (d, *J* = 240.0 Hz), 156.6, 143.5, 143.3, 143.2, 135.3, 134.9, 127.4, 127.3, 118.7, 118.6, 117.5, 117.2, 107.9 (d, *J* = 20.0 Hz), 106.9 (d, *J* = 20.0 Hz), 106.46 (d, *J* = 2.2 Hz), 106.1 (d, *J* = 2.2 Hz), 101.9, 101.7, 96.7, 96.6, 65.1, 62.6, 59.1, 57.0, 45.1, 45.0, 44.9, 37.0, 36.1, 32.1, 31.8, 28.5, 27.7, 26.0, 25.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{26}FN_2O$ 341.2024, found: 341.2016.

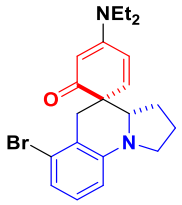
6'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'*H*-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (29.5 mg, 83% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.6 Hz, 1H), 6.99 (s, 1H), 6.41 (t, *J* = 10.7 Hz, 2H), 6.08 (d, *J* = 10.4 Hz, 1H), 5.33 (s, 1H), 3.83 (dd, *J* = 9.4, 4.4 Hz, 1H), 3.41 (dq, *J* = 27.4, 6.9 Hz, 6H), 3.14 (d, *J* = 7.7 Hz, 1H), 2.56 (d, *J* = 16.0 Hz, 1H), 1.94 (dt, *J* = 22.1, 11.2 Hz, 3H), 1.28 (dd, *J* = 16.6, 8.8 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 156.5, 143.3, 141.8, 128.7, 127.0, 121.4, 119.5, 118.9, 111.1, 96.6, 64.4, 47.4, 45.3, 39.4, 27.8, 23.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{26}ClN_2O$ 357.1728, found: 357.1721.

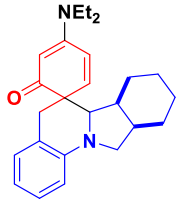
6'-bromo-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (28.0 mg, 90% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.47 – 6.39 (m, 2H), 6.12 (d, *J* = 10.4 Hz, 1H), 5.36 (d, *J* = 2.2 Hz, 1H), 3.80 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.49 – 3.41 (m, 1H), 3.39 (q, *J* = 7.1 Hz, 4H), 3.27 (d, *J* = 16.7 Hz, 1H), 3.20 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.94 (d, *J* = 16.7 Hz, 1H), 2.03 – 1.86 (m, 3H), 1.31 (dd, *J* = 14.5, 6.6 Hz, 1H), 1.27 – 1.19 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.7, 156.6, 144.5, 143.4, 128.0, 125.6, 119.4, 119.1, 118.8, 109.3, 96.6, 63.9, 58.4, 47.4, 45.9, 45.0, 39.9, 27.7, 23.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{26}BrN_2O$ 401.1223, found: 401.1228.

4-(diethylamino)-6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[cyclohexane-1,6'-isoindolo[2,1-a]quinoline]-2,4-dien-6-one (2h)

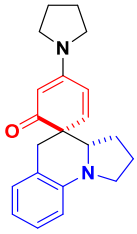


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (29.3 mg, 78% yield, dr 1:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.4 Hz, 2H), 6.99 (t, *J* = 6.9 Hz, 2H), 6.59 – 6.52 (m, 2H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.37 (t, *J* = 2.5 Hz, 1H), 6.35 (t, *J* = 2.5 Hz, 1H), 6.14

(d, *J* = 3.7 Hz, 1H), 6.12 (d, *J* = 3.7 Hz, 1H), 5.35 (dd, *J* = 6.4, 2.2 Hz, 2H), 4.43 (dt, *J* = 12.8, 6.4 Hz, 1H), 4.10 (d, *J* = 9.7 Hz, 1H), 3.74 (d, *J* = 10.0 Hz, 1H), 3.62 – 3.54 (m, 1H), 3.50 – 3.34 (m, 9H), 3.26 – 3.16 (m, 2H), 2.71 (dd, *J* = 10.4, 8.7 Hz, 1H), 2.59 (dd, *J* = 15.7, 5.2 Hz, 2H), 2.08 (dd, *J* = 11.9, 5.5 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.84 – 1.59 (m, 9H), 1.45 – 1.39 (m, 3H), 1.25 – 1.19 (m, 12H), 1.17 – 0.96 (m, 5H), 0.90 – 0.83 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.1, 197.9, 157.2, 156.9, 145.1, 145.0, 143.5, 143.0, 128.8, 127.5, 127.4, 119.3, 119.0, 118.0, 117.9, 114.7, 114.4, 109.9, 109.1, 96.3, 96.2, 69.4, 69.1, 68.8, 64.0, 53.8, 51.9, 48.3, 45.1, 44.9, 43.3, 41.1, 41.0, 40.9, 37.4, 29.6, 29.1, 28.6, 26.6, 25.8, 25.8, 25.2, 21.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{33}N_2O$ 377.2587, found: 377.2576.

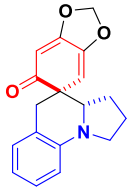
4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2i)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (23.4 mg, 73% yield, dr > 20:1) as a reddish brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.58 (dd, *J* = 10.7, 4.0 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.38 (dd, *J* = 10.3, 2.1 Hz, 1H), 6.16 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 1.9 Hz, 1H), 3.88 (dd, *J* = 9.9, 5.2 Hz, 1H), 3.55 (s, 2H), 3.48 (dd, *J* = 9.2, 6.8 Hz, 2H), 3.33 (s, 2H), 3.20 (t, *J* = 8.1 Hz, 1H), 2.61 (d, *J* = 15.8 Hz, 1H), 2.01 (s, 4H), 1.98 – 1.90 (m, 3H), 1.37 – 1.25 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.0, 155.9, 144.1, 143.2, 129.1, 127.3, 119.9, 115.0, 110.1, 97.0, 64.3, 48.2, 47.9, 47.2, 46.2, 40.0, 27.9, 25.4, 24.8, 23.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{25}N_2O$ 321.1961, found: 321.1955.

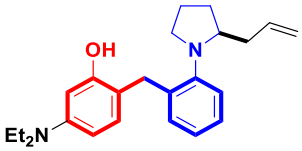
1',2',3',3a'-tetrahydro-5'*H*,6*H*-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (2j)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (27.1 mg, 92% yield, dr > 20:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 5.81 (d, *J* = 9.9 Hz, 2H), 5.71 (s, 1H), 5.20 (s, 1H), 3.75 (dd, *J* = 9.8, 5.4 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.38 (d, *J* = 15.5 Hz, 1H), 3.19 (dd, *J* = 16.3, 8.7 Hz, 1H), 2.69 (d, *J* = 15.6 Hz, 1H), 2.04 – 1.84 (m, 3H), 1.46 – 1.34 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.2, 163.8, 145.2, 142.9, 129.3, 127.6, 119.2, 115.4, 110.4, 104.6, 101.5, 99.3, 65.4, 48.4, 47.1, 41.1, 27.5, 23.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{18}H_{18}NO_3$ 296.1281, found: 296.1271.

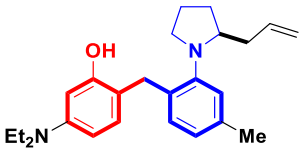
2-(2-(2-allylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (25.7 mg, 71% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.10 – 7.04 (m, 2H), 6.22 (d, *J* = 2.0 Hz, 1H), 6.17 (d, *J* = 8.3 Hz, 1H), 5.70 (ddd, *J* = 14.2, 10.0, 5.1 Hz, 1H), 5.08 – 4.95 (m, 2H), 3.92 (d, *J* = 14.1 Hz, 1H), 3.67 (d, *J* = 14.0 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.42 – 3.36 (m, 1H), 3.32 – 3.22 (m, 4H), 2.82 (dd, *J* = 17.4, 8.6 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.24 – 2.18 (m, 1H), 2.13-2.07 (m, 2H), 2.00 – 1.90 (m, 1H), 1.86 – 1.76 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 148.3, 145.0, 139.2, 135.5, 131.2, 130.3, 127.3, 125.9, 121.0, 116.7, 115.5, 104.1, 100.4, 63.0, 55.8, 44.4, 36.6, 33.2, 29.5, 22.0, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{33}N_2O$ 365.2587, found: 365.2572.

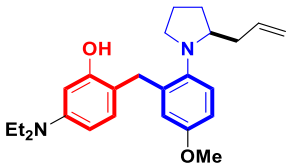
2-(2-(2-allylpyrrolidin-1-yl)-4-methylbenzyl)-5-(diethylamino)phenol (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (22.3 mg, 60% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 6.16 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.76-5.68 (m, 1H), 5.06 – 4.96 (m, 2H), 3.87 (d, *J* = 14.1 Hz, 1H), 3.64 (d, *J* = 14.1 Hz, 1H), 3.57 (ddd, *J* = 9.8, 8.3, 4.4 Hz, 1H), 3.43 – 3.33 (m, 1H), 3.26 (q, *J* = 7.0 Hz, 4H), 2.88 – 2.78 (m, 1H), 2.34 – 2.29 (m, 1H), 2.27 (s, 3H), 2.24-2.18 (m, 1H), 2.16 – 2.06 (m, 2H), 2.02 – 1.90 (m, 1H), 1.86 – 1.74 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.8, 148.2, 144.8, 136.9, 136.2, 135.6, 130.9, 130.3, 126.6, 121.7, 116.7, 115.8, 104.2, 100.5, 63.0, 55.6, 44.4, 36.6, 32.9, 29.5, 22.0, 21.2, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{35}N_2O$ 379.2744, found: 379.2736.

2-(2-(2-allylpyrrolidin-1-yl)-5-methoxybenzyl)-5-(diethylamino)phenol (3c)

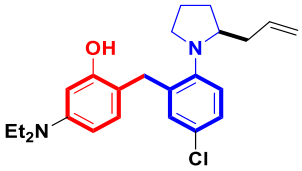


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (16.9 mg, 43% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, 1H), 6.99 (dd, *J* = 11.3, 8.6 Hz, 2H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.64 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.15 (d, *J* = 2.2 Hz, 1H), 6.09 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.66-5.58 (m, 1H), 5.00 – 4.85 (m, 2H), 3.77 (d, *J* = 13.9 Hz, 1H), 3.70 (s, 3H), 3.59 (d, *J* = 14.0 Hz, 1H), 3.43 (ddd, *J* = 9.7, 8.4, 4.0 Hz, 1H), 3.20 (q, *J* = 7.2 Hz, 5H), 2.71 (dd, *J* = 17.9, 8.5 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.16 – 2.09 (m, 1H), 2.09 – 1.96 (m, 2H), 1.92 – 1.82 (m, 1H), 1.76 – 1.68 (m, 1H), 1.03 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.1, 154.8, 147.3, 139.8, 136.9, 134.5, 129.2, 121.2, 115.6, 115.1,

114.2, 111.3, 103.1, 99.4, 62.7, 54.9, 54.3, 43.3, 35.5, 32.4, 28.3, 20.8, 11.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{35}N_2O_2$ 395.2693, found: 395.2700.

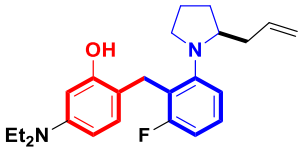
2-(2-(2-allylpyrrolidin-1-yl)-5-chlorobenzyl)-5-(diethylamino)phenol (3d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (33.8 mg, 85% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.05 (dd, *J* = 10.1, 8.6 Hz, 2H), 6.24 – 6.15 (m, 2H), 5.73-5.65 (m, 1H), 5.04-4.98 (m, 2H), 3.88 (d, *J* = 14.1 Hz, 1H), 3.62 (d, *J* = 14.1 Hz, 1H), 3.57 (ddd, *J* = 9.7, 8.3, 4.6 Hz, 1H), 3.34 (dt, *J* = 14.5, 5.2 Hz, 1H), 3.27 (q, *J* = 7.2 Hz, 4H), 2.79 (dd, *J* = 17.2, 8.6 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.15 – 2.06 (m, 2H), 2.01 – 1.89 (m, 1H), 1.87 – 1.74 (m, 1H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.7, 148.5, 143.7, 141.0, 135.2, 130.9, 130.8, 130.4, 127.2, 122.5, 116.9, 114.4, 104.2, 100.2, 63.2, 55.7, 44.4, 36.5, 32.9, 29.5, 22.0, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{32}ClN_2O$ 399.2198, found: 399.2190.

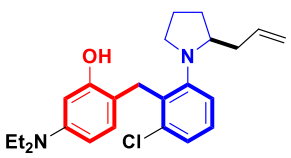
2-(2-(2-allylpyrrolidin-1-yl)-6-fluorobenzyl)-5-(diethylamino)phenol (3e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (24.0 mg, 63% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.15 – 7.07 (m, 1H), 7.05 – 6.97 (m, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.75 (t, *J* = 8.8 Hz, 1H), 6.12 (s, 1H), 6.09 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.67 – 5.55 (m, 1H), 4.96-4.90 (m, 2H), 3.81 (d, *J* = 14.3 Hz, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 3.56 – 3.49 (m, 1H), 3.35 – 3.26 (m, 1H), 3.22 – 3.12 (m, 4H), 2.73 (dd, *J* = 17.1, 8.5 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.15-2.09 (m, 1H), 2.09 – 1.97 (m, 2H), 1.90-1.81 (m, 1H), 1.75-1.68 (m, 1H), 1.02 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.7 Hz), 156.1, 148.3, 147.1 (d, *J* = 6.2 Hz), 135.3, 131.4 (d, *J* = 3.0 Hz), 127.5 (d, *J* = 10.2 Hz), 126.5 (d, *J* = 15.9 Hz), 116.9, 116.6 (d, *J* = 2.5 Hz), 113.6, 112.8, 112.6, 104.0, 99.9, 63.0, 55.7, 44.4, 36.5, 29.5, 24.7 (d, *J* = 3.4 Hz), 22.0, 12.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{32}FN_2O$ 383.2493, found: 383.2484.

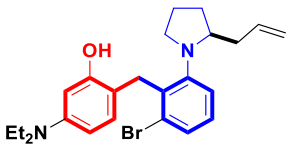
2-(2-(2-allylpyrrolidin-1-yl)-6-chlorobenzyl)-5-(diethylamino)phenol (3f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (27.8 mg, 70% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.21 (d, *J* = 2.3 Hz, 1H), 6.17 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.73-5.64 (m, 1H), 5.04-4.98 (m, 2H), 4.02 (dd, *J* = 56.0, 14.4 Hz, 2H), 3.59 (td, *J* = 9.2, 4.9 Hz, 1H), 3.45 – 3.35 (m, 1H), 3.27 (q, *J* = 7.1 Hz, 4H), 2.81 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.33 – 2.18 (m, 2H), 2.17 – 2.06 (m, 2H), 2.02 – 1.91 (m, 1H), 1.90 – 1.78 (m, 1H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.4, 148.3, 147.3, 136.6, 135.9, 135.2, 132.0, 127.5, 127.3, 119.9, 116.9, 113.1, 103.7, 99.9, 63.4, 55.6, 44.3, 36.3, 29.3, 28.7, 21.9, 12.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{32}ClN_2O$ 399.2198, found: 399.2191.

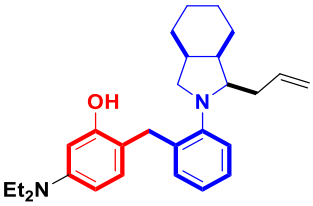
2-(2-(2-allylpyrrolidin-1-yl)-6-bromobenzyl)-5-(diethylamino)phenol (3g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (27.4 mg, 62% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.21 (d, *J* = 2.2 Hz, 1H), 6.17 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.74 – 5.62 (m, 1H), 5.01 (t, *J* = 13.9 Hz, 2H), 4.07 (dd, *J* = 36.4, 14.5 Hz, 2H), 3.56 (td, *J* = 9.1, 4.8 Hz, 1H), 3.46 – 3.34 (m, 1H), 3.27 (q, *J* = 7.0 Hz, 4H), 2.80 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.26-2.17 (m, 2H), 2.16 – 2.06 (m, 2H), 2.01 – 1.92 (m, 1H), 1.88 – 1.78 (m, 1H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.3, 147.5, 138.3, 135.2, 132.1, 130.9, 127.9, 126.7, 120.7, 116.9, 113.2, 103.6, 99.9, 63.6, 55.7, 44.3, 36.3, 31.1, 29.3, 21.9, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{32}BrN_2O$ 443.1693, found: 443.1684.

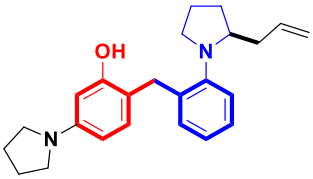
2-(2-(1-allyloctahydro-2H-isoindol-2-yl)benzyl)-5-(diethylamino)phenol (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (25.0 mg, 60% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.31 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.08-7.05 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.26 (d, *J* = 2.5 Hz, 1H), 6.18 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.66 (ddd, *J* = 17.1, 6.7, 3.6 Hz, 1H), 5.03 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.92 (dd, *J* = 10.3, 1.6 Hz, 1H), 4.04 (d, *J* = 14.2 Hz, 1H), 3.70-3.65 (m, 2H), 3.36 (dd, *J* = 9.6, 5.9 Hz, 1H), 3.27 (q, *J* = 7.1 Hz, 4H), 2.61 (t, *J* = 9.9 Hz, 1H), 2.39 (t, *J* = 6.7 Hz, 2H), 2.01-1.95 (m, 2H), 1.92-1.77 (m, 4H), 1.39 – 1.21 (m, 4H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.6, 149.9, 148.2, 139.6, 136.6, 130.9, 130.4, 127.6, 125.8, 125.0, 116.5, 115.5, 104.4, 100.5, 69.8, 62.2, 49.1, 44.4, 42.7, 36.5, 33.5, 29.6, 27.6, 26.4, 25.6, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{39}N_2O$ 419.3057, found: 419.3048.

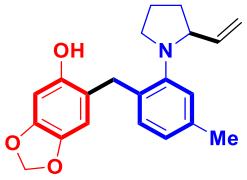
2-(2-(2-allylpyrrolidin-1-yl)benzyl)-5-(pyrrolidin-1-yl)phenol (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (18.1 mg, 50% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.36 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.08-7.05 (m, 2H), 6.12 (d, *J* = 2.0 Hz, 1H), 6.07 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.71 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.06 – 4.95 (m, 2H), 3.94 (d, *J* = 14.0 Hz, 1H), 3.68 (d, *J* = 14.1 Hz, 1H), 3.60 (ddd, *J* = 9.8, 8.3, 4.3 Hz, 1H), 3.43 – 3.35 (m, 1H), 3.20 (t, *J* = 6.5 Hz, 4H), 2.82 (dd, *J* = 17.5, 8.6 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.25-2.18 (m, 1H), 2.16-2.06 (m, 2H), 2.03 – 1.86 (m, 5H), 1.85-1.77 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.6, 148.5, 144.9, 139.3, 135.5, 131.1, 130.2, 127.2, 125.8, 120.9, 116.7, 115.6, 104.0, 100.3, 62.9, 55.8, 47.7, 36.5, 33.2, 29.5, 25.5, 21.9. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{31}N_2O$ 363.2431, found: 363.2423.

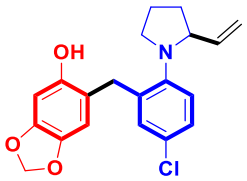
6-(4-methyl-2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (21.9 mg, 65% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 6.42 (s, 1H), 5.80 (d, *J* = 15.4 Hz, 2H), 5.78 – 5.70 (m, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 3.92 – 3.82 (m, 2H), 3.63 (d, *J* = 14.0 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.27 (s, 3H), 2.23 – 2.09 (m, 2H), 2.05 – 1.92 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.5, 146.8, 144.8, 140.7, 137.2, 137.1, 135.4, 130.5, 126.7, 122.5, 120.0, 118.2, 108.7, 100.7, 99.4, 67.0, 55.9, 33.4, 30.9, 22.3, 21.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{24}NO_3$ 338.1751, found: 338.1754.

6-(5-chloro-2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3k)

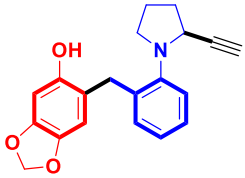


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (22.8 mg, 64% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.28 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 6.43 (s, 1H), 5.84 (d, *J* = 13.3 Hz, 2H), 5.77 – 5.63 (m, 1H), 5.04 (dd, *J* = 24.9, 13.6 Hz, 2H), 3.88 (d, *J* = 14.0 Hz, 1H), 3.81 (dd, *J* = 15.3, 7.6 Hz, 1H), 3.62 (d, *J* = 14.0 Hz, 1H), 3.57 (d, *J* = 8.3 Hz, 1H), 2.83 (dd, *J* = 16.6, 8.3 Hz, 1H), 2.21 (dd, *J* = 10.8, 6.1 Hz, 1H), 2.17 – 2.07 (m, 1H), 2.07

– 1.90 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.5, 147.1, 143.7, 140.9, 140.2, 136.8, 130.9, 130.5, 127.4, 123.3, 118.7, 118.6, 108.7, 100.9, 99.4, 67.4, 55.9, 33.5, 30.9, 22.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{21}ClNO_3$ 358.1204, found: 358.1193.

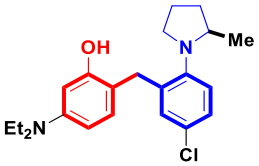
6-(2-(2-ethynylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3l)[3]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (19.9 mg, 62% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 6.41 (s, 1H), 5.81 (d, *J* = 14.0 Hz, 2H), 4.21 (s, 1H), 3.87 (d, *J* = 14.1 Hz, 1H), 3.79 (d, *J* = 14.1 Hz, 1H), 3.58 – 3.47 (m, 1H), 3.03 (t, *J* = 9.9 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.23 (s, 1H), 2.22 – 2.13 (m, 2H), 2.12 – 2.04 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.8, 146.9, 143.7, 140.6, 137.9, 130.7, 127.3, 126.5, 122.2, 119.1, 108.7, 100.8, 99.0, 81.8, 73.7, 55.8, 51.7, 33.5, 31.8, 22.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$ 322.1438, found: 322.1426.

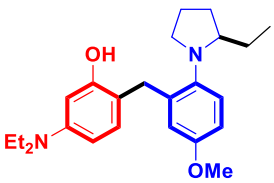
2-(5-chloro-2-(2-methylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (26.7 mg, 72% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.03 (t, *J* = 8.2 Hz, 2H), 6.21 (d, *J* = 2.0 Hz, 1H), 6.17 (d, *J* = 8.3 Hz, 1H), 3.91 (d, *J* = 14.1 Hz, 1H), 3.64 – 3.54 (m, 2H), 3.42 (dt, *J* = 8.4, 6.4 Hz, 1H), 3.26 (q, *J* = 7.4 Hz, 4H), 2.76 (dd, *J* = 17.1, 9.0 Hz, 1H), 2.24 – 2.14 (m, 1H), 2.13 – 2.03 (m, 1H), 2.00 – 1.87 (m, 1H), 1.84 – 1.70 (m, 1H), 1.10 (t, *J* = 7.1 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.9, 148.5, 143.7, 140.9, 130.9, 130.6, 130.4, 127.2, 122.4, 114.5, 104.1, 100.3, 58.8, 55.7, 44.4, 33.0, 31.8, 21.9, 17.0, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{30}ClN_2O$ 373.2041, found: 373.2033.

5-(diethylamino)-2-(2-(2-ethylpyrrolidin-1-yl)-5-methoxybenzyl)phenol (3n)

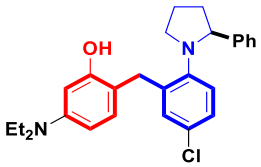


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (16.4 mg, 43% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 6.22 (s, 1H), 6.16 (d, *J* = 8.1 Hz, 1H), 3.83 (d, *J* = 13.9 Hz, 1H), 3.76 (s, 3H), 3.68 (d, *J* = 13.9 Hz,

1H), 3.48 (s, 1H), 3.35 – 3.20 (m, 4H), 3.10 (d, *J* = 7.4 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.21 (d, *J* = 5.6 Hz, 1H), 2.07 (d, *J* = 8.1 Hz, 1H), 1.93 (s, 1H), 1.78 – 1.67 (m, 1H), 1.54 (s, 1H), 1.38 (dd, *J* = 9.7, 7.0 Hz, 1H), 1.10 (t, *J* = 6.5 Hz, 6H), 0.85 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.1, 155.9, 148.3, 140.94, 138.3, 130.3, 122.2, 116.0, 115.4, 112.3, 104.1, 100.5, 66.2, 56.3, 55.4, 44.4, 33.5, 29.3, 24.9, 21.8, 12.7, 11.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{35}N_2O_2$ 383.2693, found: 383.2697.

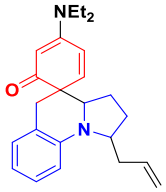
2-(5-chloro-2-(2-phenylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (26.0 mg, 60% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.22 – 7.15 (m, 5H), 7.13 (d, *J* = 2.2 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.23 (d, *J* = 2.1 Hz, 1H), 6.16 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.29 (t, *J* = 7.6 Hz, 1H), 3.66 – 3.54 (m, 1H), 3.41 (s, 2H), 3.34 – 3.21 (m, 4H), 3.14 – 3.03 (m, 1H), 2.52 – 2.41 (m, 1H), 2.35 – 2.22 (m, 2H), 2.20 – 2.07 (m, 1H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.5, 148.4, 144.6, 140.7, 139.9, 130.5, 130.5, 130.4, 128.4, 128.1, 127.7, 127.1, 123.6, 114.3, 104.4, 100.2, 70.2, 55.4, 44.4, 33.1, 32.5, 23.5, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{32}ClN_2O$ 435.2198, found: 435.2188.

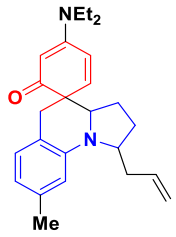
1'-allyl-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (27.1 mg, 75% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 29.2, 7.5 Hz, 1H), 6.56 (ddd, *J* = 32.1, 18.0, 4.4 Hz, 2H), 6.42 (ddd, *J* = 40.3, 10.5, 2.3 Hz, 1H), 6.23 (dd, *J* = 60.0, 10.4 Hz, 1H), 5.80 (ddt, *J* = 17.0, 10.3, 7.1 Hz, 1H), 5.33 (dd, *J* = 10.4, 2.3 Hz, 1H), 5.15 – 5.04 (m, 2H), 4.02 – 3.78 (m, 2H), 3.48 (t, *J* = 16.4 Hz, 1H), 3.43 – 3.32 (m, 4H), 2.66 – 2.51 (m, 2H), 2.23 – 1.67 (m, 4H), 1.43 – 1.32 (m, 1H), 1.29 – 1.15 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 197.1, 156.6, 156.5, 144.1, 144.0, 142.1, 141.7, 135.6, 135.2, 129.8, 129.4, 127.2, 127.0, 120.7, 119.8, 118.5, 118.3, 117.3, 117.0, 115.0, 114.9, 110.9, 110.3, 96.6, 96.5, 65.6, 63.3, 58.6, 56.5, 45.9, 45.8, 44.9, 39.8, 39.4, 37.2, 36.0, 28.7, 27.8, 26.2, 25.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{31}N_2O$ 363.2431, found: 363.2439.

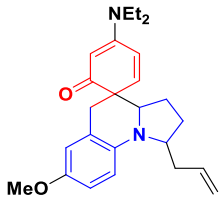
1'-allyl-4-(diethylamino)-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (26.3 mg, 70% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 30.3, 7.4 Hz, 1H), 6.45-6.36 (m, 2H), 6.36 – 6.15 (m, 2H), 5.89 – 5.75 (m, 1H), 5.32 (dd, *J* = 10.6, 2.0 Hz, 1H), 5.10 (dd, *J* = 16.4, 11.2 Hz, 2H), 4.00 – 3.77 (m, 2H), 3.52 – 3.25 (m, 5H), 2.66 – 2.50 (m, 2H), 2.31 (s, 3H), 2.23 – 1.72 (m, 4H), 1.39-1.30 (m, 1H), 1.25-1.19 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.6, 197.3, 156.6, 156.5, 144.2, 144.1, 142.0, 141.6, 136.8, 136.6, 135.7, 135.3, 129.7, 129.2, 118.3, 118.2, 117.8, 117.2, 116.9, 115.9, 115.9, 111.5, 110.9, 96.7, 96.6, 65.7, 63.3, 58.5, 56.5, 46.2, 46.0, 44.9, 39.6, 39.2, 37.2, 36.1, 29.7, 29.3, 28.7, 27.8, 26.2, 25.2, 21.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{33}N_2O$ 377.2587, found: 377.2578.

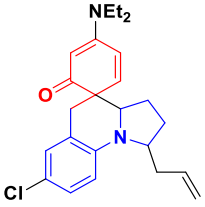
1'-allyl-4-(diethylamino)-7'-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (21.1 mg, 54% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74-6.64 (m, 2H), 6.52 – 6.35 (m, 2H), 6.25 (dd, *J* = 63.0, 10.4 Hz, 1H), 5.86 – 5.73 (m, 1H), 5.33 (dd, *J* = 12.0, 2.2 Hz, 1H), 5.11-5.05 (m, 2H), 3.96 – 3.76 (m, 2H), 3.76 – 3.73 (m, 3H), 3.50 (dd, *J* = 16.0, 12.3 Hz, 1H), 3.44 – 3.33 (m, 4H), 2.56 (dd, *J* = 27.3, 16.2 Hz, 2H), 1.97-1.68 (m, 4H), 1.40 – 1.31 (m, 1H), 1.26 – 1.19 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.5, 197.1, 156.6, 156.5, 150.1, 150.0, 144.3, 144.2, 136.8, 136.4, 135.8, 135.4, 121.8, 120.9, 118.3, 118.2, 117.2, 116.9, 115.9, 115.6, 112.9, 112.8, 111.3, 110.9, 96.7, 96.6, 65.9, 63.6, 59.0, 56.7, 55.9, 46.4, 46.2, 44.9, 39.9, 39.5, 37.3, 36.3, 28.7, 27.9, 26.2, 25.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{33}N_2O_2$ 393.2537, found: 393.2528.

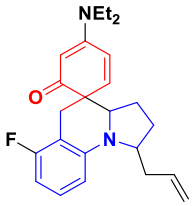
1'-allyl-7'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (28.5 mg, 72% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 6.95 (m, 2H), 6.52 – 6.45 (m, 1H), 6.44 – 6.36 (m, 1H), 6.21 (d, *J* = 10.4 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 5.85 – 5.72 (m, 1H), 5.33 (dd, *J* = 9.5, 2.0 Hz, 1H), 5.11-5.07 (m, 2H), 3.94 (t, *J* = 7.0 Hz, 1H), 3.87 – 3.75 (m, 2H), 3.51 – 3.33 (m, 5H), 2.61 – 2.46 (m, 2H), 2.23 – 2.13 (m, 1H), 2.02 – 1.69 (m, 4H), 1.41 – 1.32 (m, 1H), 1.27 – 1.19 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 196.6, 156.7, 156.5, 143.5, 143.4, 140.6, 140.2, 135.3, 134.7, 129.3, 128.9, 126.9, 126.7, 122.3, 121.4, 119.6, 119.4, 118.7, 118.6, 117.5, 117.2, 111.8, 111.1, 96.6, 96.6, 65.6, 63.3, 58.6, 56.7, 45.5, 45.4, 45.0, 39.4, 39.1, 37.0, 35.7, 28.7, 27.7, 26.1, 25.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{30}ClN_2O$ 397.2041, found: 397.2037.

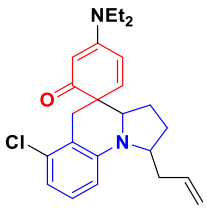
1'-allyl-4-(diethylamino)-6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (31.2 mg, 82% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 15.0, 7.8 Hz, 1H), 6.44 (ddd, *J* = 36.8, 10.5, 2.0 Hz, 1H), 6.37 – 6.27 (m, 2H), 6.19 (dd, *J* = 47.4, 10.4 Hz, 1H), 5.83-5.74 m, 1H), 5.35 (dd, *J* = 10.8, 2.0 Hz, 1H), 5.10 (dd, *J* = 15.1, 9.2 Hz, 2H), 3.96 – 3.74 (m, 2H), 3.48 – 3.32 (m, 4H), 3.18 (dd, *J* = 31.4, 16.6 Hz, 1H), 2.83 (dd, J = 16.0, 11.6 Hz, 1H), 2.56-2.50 (m, 1H), 2.26 – 1.96 (m, 1H), 1.96 – 1.72 (m, 3H), 1.43 – 1.32 (m, 1H), 1.23 (q, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.1, 196.8, 163.1, 162.6, 161.2, 160.7, 156.6, 143.5, 143.4, 143.3, 135.3, 134.9, 127.5, 127.4, 127.3, 118.7, 118.6, 117.5, 117.2, 107.9, 107.8, 106.9, 106.5, 106.5, 106.1, 101.9, 101.7, 96.7, 96.6, 65.1, 62.6, 59.1, 57.0, 45.1, 45.0, 44.9, 37.0, 36.1, 32.2, 32.1, 31.9, 28.5, 27.7, 26.0, 25.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{30}FN_2O$ 381.2337, found: 381.2330.

1'-allyl-6'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4f)

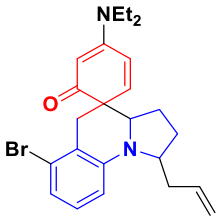


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (30.8 mg, 78% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.1 Hz, 1H), 6.72 – 6.62 (m, 1H), 6.47 (dd, *J* = 10.3, 2.0 Hz, 1H), 6.44 – 6.37 (m, 1H), 6.19 (dd, *J* = 51.4, 10.4 Hz, 1H), 5.83-5.73 (m, 1H), 5.36 (dd, *J* = 11.4, 2.2 Hz, 1H), 5.16 – 5.04 (m, 2H), 3.95 – 3.73 (m, 2H), 3.50 – 3.33 (m, 4H), 3.26 (dd, *J* = 22.9, 16.9 Hz, 1H), 2.97-2.89 (t, *J* = 18.1 Hz, 1H), 2.55-2.48 (m, 1H), 2.20 – 1.70 (m, 5H), 1.43 – 1.33 (m, 1H), 1.23 (q, *J* = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 196.6, 156.6, 143.7, 143.6, 143.3, 143.1, 135.4, 135.3, 134.85, 127.4, 127.3, 118.7, 118.6, 118.6, 117.7, 117.6, 117.3, 116.0, 115.9, 109.2, 108.9, 96.8, 96.6,

65.0, 62.5, 59.0, 56.9, 45.9, 45.7, 45.0, 37.1, 36.8, 36.7, 36.1, 28.5, 27.9, 25.9, 25.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{30}ClN_2O$ 397.2041, found: 397.2034.

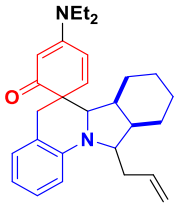
1'-allyl-6'-bromo-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (27.3 mg, 62% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 8.0 Hz, 1H), 6.86-6.82 (m, 1H), 6.54 – 6.38 (m, 2H), 6.19 (dd, *J* = 51.6, 10.4 Hz, 1H), 5.83-5.73 (m, 1H), 5.36 (dd, *J* = 11.4, 2.2 Hz, 1H), 5.15 – 5.05 (m, 2H), 3.94 – 3.74 (m, 2H), 3.48 – 3.34 (m, 4H), 3.30-3.24 (m, 1H), 2.94-2.86 (m, 1H), 2.53 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.23 – 1.88 (m, 2H), 1.88 – 1.69 (m, 3H), 1.43 – 1.33 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.8, 196.5, 156.6, 143.6, 143.5, 143.4, 143.2, 135.3, 134.8, 127.9, 127.8, 126.3, 125.9, 120.3, 119.2, 119.2, 118.6, 118.6, 117.6, 117.3, 109.9, 109.6, 96.8, 96.6, 65.1, 62.6, 59.0, 56.9, 46.2, 46.0, 45.0, 40.1, 39.8, 36.7, 36.0, 28.6, 27.9, 25.9, 25.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{30}BrN_2O$ 441.1536, found: 441.1527.

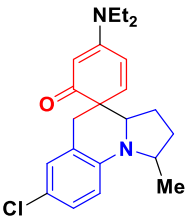
11'-allyl-4-(diethylamino)-6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[cyclohexane-1,6'-isoindolo[2,1-a]quinoline]-2,4-dien-6-one (4h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (22.0 mg, 53% yield, dr 7:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.56 (dd, *J* = 13.0, 5.7 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 6.42 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.23 (d, *J* = 10.4 Hz, 1H), 5.86 – 5.75 (m, 1H), 5.32 (d, *J* = 2.2 Hz, 1H), 5.09 (d, *J* = 5.3 Hz, 1H), 5.07 (s, 1H), 4.05 (d, *J* = 10.3 Hz, 1H), 3.52 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.46 – 3.32 (m, 4H), 2.61 (d, *J* = 16.2 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.02 – 1.89 (m, 2H), 1.89 – 1.82 (m, 1H), 1.78 – 1.70 (m, 2H), 1.69 – 1.57 (m, 2H), 1.46 – 1.37 (m, 3H), 1.33 – 1.25 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.2, 156.4, 144.3, 142.0, 135.8, 129.5, 126.9, 120.5, 118.2, 116.7, 114.7, 110.9, 97.2, 64.2, 62.9, 45.4, 44.9, 41.6, 40.5, 37.6, 34.9, 29.0, 26.2, 25.6, 21.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{37}N_2O$ 417.2900, found: 417.2888.

7'-chloro-4-(diethylamino)-1'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4i)

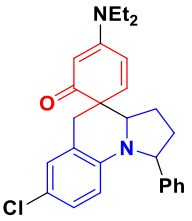


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (22.6 mg, 61% yield, dr 2:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95-6.88 (m, 2H), 6.44 – 6.37 (m, 1H), 6.33 (dd, *J* = 15.4, 5.2 Hz, 1H), 6.08 (dd, *J* = 42.9, 10.4 Hz, 1H), 5.25 (dd, *J* = 9.0, 1.7 Hz, 1H), 3.90-3.85 (m, 1H), 3.85 – 3.68 (m, 1H), 3.43 – 3.24 (m, 5H), 2.46 (dd, *J* = 22.1, 16.1 Hz, 1H), 2.02 – 1.70 (m, 2H), 1.53-1.46 (m, 1H), 1.36-1.26 (m, 1H), 1.19 – 1.09 (m, 7H), 0.98 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 196.7, 156.6, 156.5, 143.6, 143.4, 140.8, 140.4, 129.2, 128.8, 126.9, 126.7, 121.9, 121.5, 119.2, 119.1, 118.7, 118.5, 111.9, 111.1, 96.5, 65.7, 62.8, 54.3, 52.2, 45.4, 45.1, 44.9, 39.5, 39.2, 31.8, 31.0, 26.1, 25.2, 19.0, 17.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{28}ClN_2O$ 371.1885, found: 371.1875.

DEPT 90 ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 143.4, 129.2, 128.8, 126.9, 126.7, 118.7, 118.5, 111.9, 111.1, 96.5, 65.7, 62.8, 54.3, 52.2.

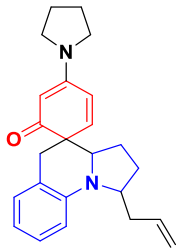
7'-chloro-4-(diethylamino)-1'-phenyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (25.9 mg, 60% yield, dr 2:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.04-6.98 (m, 1H), 6.87 – 6.80 (m, 1H), 6.71 (d, *J* = 10.4 Hz, 1H), 6.61-6.41 (m, 1H), 6.13 (dd, *J* = 26.3, 9.6 Hz, 2H), 5.37 (dd, *J* = 11.4, 2.2 Hz, 1H), 4.73 – 4.54 (m, 1H), 4.33 (t, *J* = 7.1 Hz, 1H), 3.86 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.58 (dd, *J* = 24.5, 16.1 Hz, 1H), 3.41-3.37 (m, 4H), 2.63 (t, *J* = 16.6 Hz, 1H), 2.48 – 2.29 (m, 1H), 2.04-1.96 (m, 1H), 1.88 – 1.74 (m, 2H), 1.58 – 1.40 (m, 1H), 1.26-1.22 (m, 6H), 0.91 – 0.82 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 196.2, 156.5, 145.0, 144.2, 143.8, 143.4, 141.5, 140.8, 128.9, 128.8, 128.7, 126.9, 126.9, 126.6, 125.9, 125.5, 123.0, 121.5, 120.8, 120.0, 118.8, 118.8, 113.4, 112.4, 96.6, 96.4, 66.8, 65.7, 64.6, 61.9, 46.9, 45.5, 45.0, 39.7, 38.9, 35.6, 34.1, 26.9, 25.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{30}ClN_2O$ 433.2041, found: 433.2029.

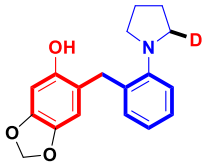
1'-allyl-4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (21.6 mg, 60% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 1H), 7.03 (dd, *J* = 30.5, 7.5 Hz, 1H), 6.61 – 6.48 (m, 2H), 6.39 (ddd, *J* = 39.1, 10.3, 2.1 Hz, 1H), 6.22 (dd, *J* = 60.2, 10.3 Hz, 1H), 5.86 – 5.75 (m, 1H), 5.21 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.02 – 3.79 (m, 2H), 3.63 – 3.44 (m, 3H), 3.33 (s, 2H), 2.62-2.52 (m, 2H), 2.11-1.98 (m, 4H), 1.98 – 1.67 (m, 4H), 1.44 – 1.32 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.1, 196.7, 155.9, 155.9, 144.1, 144.1, 142.1, 141.7, 135.6, 135.2, 129.8, 129.4, 127.2, 127.1, 120.7, 119.9, 119.8, 119.7, 117.3, 117.0, 115.0, 114.9, 110.9, 110.3, 97.0, 96.9, 65.6, 63.2, 58.6, 56.6, 48.2, 47.9, 46.4, 46.2, 40.0, 39.6, 37.2, 36.0, 28.7, 27.8, 26.2, 25.4, 25.3, 24.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{29}N_2O$ 361.2274, found: 361.2266.

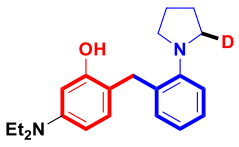
6-(2-(pyrrolidin-1-yl-2-d)benzyl)benzo[d][1,3]dioxol-5-ol (5a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) gave the product (24.4 mg, 82% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.12 – 7.06 (m, 1H), 6.72 (s, 1H), 6.39 (s, 1H), 5.80 (s, 2H), 3.81 (s, 2H), 3.17 (d, *J* = 6.1 Hz, 3H), 2.09 – 2.04 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.3, 146.9, 146.4, 140.5, 137.4, 130.8, 127.6, 125.9, 120.2, 119.3, 108.7, 100.7, 99.1, 54.1, 53.9, 53.7, 53.6, 33.8, 23.9, 23.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{18}H_{19}DNO_3$ 299.1500, found: 299.1487.

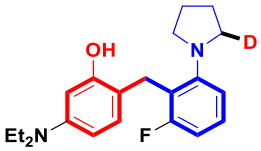
5-(diethylamino)-2-(2-(pyrrolidin-1-yl-2-d)benzyl)phenol (5b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (20.4 mg, 63% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.89 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 9.0 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.19 (d, *J* = 2.1 Hz, 1H), 6.15 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.80 (s, 2H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.21 – 3.12 (m, 3H), 2.07 (d, *J* = 2.9 Hz, 4H), 1.09 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 148.4, 146.1, 137.9, 130.9, 130.3, 127.3, 125.8, 119.8, 115.3, 103.8, 100.1, 53.8, 44.4, 33.3, 29.7, 23.8, 23.7, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{28}DN_2O$ 326.2337, found: 326.2330.

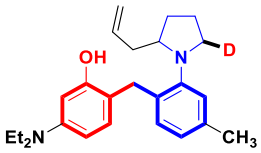
5-(diethylamino)-2-(3-fluoro-2-(pyrrolidin-1-yl-2-d)benzyl)phenol (5c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (18.5 mg, 54% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.18 (dd, *J* = 8.3, 2.8 Hz, 1H), 7.08 (dt, *J* = 8.1, 4.1 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.79 (m, 1H), 6.17 (dt, *J* = 8.3, 2.6 Hz, 2H), 3.84 (d, *J* = 2.5 Hz, 2H), 3.26 (q, *J* = 7.0 Hz, 4H), 3.18 (dd, *J* = 11.4, 4.8 Hz, 3H), 2.06 (dd, *J* = 6.4, 3.1 Hz, 4H), 1.10 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.1 (d, *J* = 242.5 Hz), 161.1, 156.5, 148.3, 148.1 (d, *J* = 6.3 Hz), 131.5 (d, *J* = 2.9 Hz), 127.5 (d, *J* = 10.2 Hz), 125.2 (d, *J* = 16.0 Hz), 115.4 (d, *J* = 2.9 Hz), 113.2, 112.8, 112.6, 103.7, 99.7, 53.9, 44.3, 25.1, 25.0, 23.8, 23.7, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{27}DFN_2O$ 344.2243, found: 344.2236.

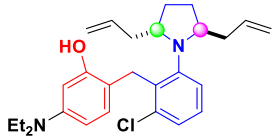
2-(2-(2-allylpyrrolidin-1-yl-5-d)-4-methylbenzyl)-5-(diethylamino)phenol (5d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (23.8 mg, 63% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 1.8 Hz, 1H), 6.16 (d, *J* = 8.3 Hz, 1H), 5.80 – 5.65 (m, 1H), 5.08 – 4.95 (m, 2H), 3.86 (d, *J* = 14.1 Hz, 1H), 3.64 (d, *J* = 14.1 Hz, 1H), 3.55 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.43 – 3.34 (m, 1H), 3.32 – 3.20 (m, 4H), 2.81 (t, *J* = 8.0 Hz, 1H), 2.31 (s, 1H), 2.28 (d, *J* = 9.5 Hz, 3H), 2.24 – 2.16 (m, 1H), 2.10 (tdd, *J* = 12.1, 9.2, 6.0 Hz, 2H), 1.95 (dt, *J* = 9.9, 6.8 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 6H), 0.90 – 0.79 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.7, 147.2, 143.7, 135.8, 135.1, 134.5, 129.8, 129.2, 125.5, 120.6, 115.6, 114.7, 103.1, 99.4, 62.0, 43.3, 35.5, 31.8, 28.4, 20.9, 20.2, 11.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{34}DN_2O$ 380.2807, found: 380.2800.

2-(3-chloro-2-(2,5-diallylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (6f)

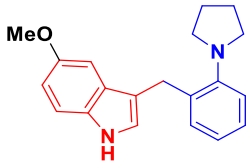


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (23.2 mg, 53% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 6.17 (d, *J* = 8.5 Hz, 1H), 5.80-5.72 (m, 1H), 5.56 – 5.48 (m, 1H), 5.08 – 4.91 (m, 4H), 4.10 (d, *J* = 14.5 Hz, 1H), 4.04-3.98 (m, 1H), 3.87 (d, *J* =

14.5 Hz, 1H), 3.65 – 3.56 (m, 1H), 3.33 – 3.22 (m, 4H), 2.38 – 2.16 (m, 4H), 1.88 – 1.70 (m, 4H), 1.11 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.2, 148.3, 143.9, 136.3, 135.5, 134.7, 132.1, 126.8, 126.7, 121.9, 117.5, 116.7, 113.0, 103.6, 99.8, 62.0, 59.2, 44.3, 36.3, 36.0, 29.7, 29.0, 28.8, 27.9, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{36}ClN_2O$ 439.2511, found: 439.2500.

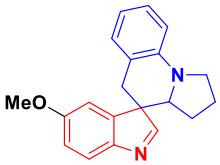
5-methoxy-3-(2-(pyrrolidin-1-yl)benzyl)-1H-indole (7)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the product (20.8 mg, 68% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.10 (dd, *J* = 15.5, 8.7 Hz, 3H), 6.99 (d, *J* = 4.1 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 5.6, 2.0 Hz, 2H), 6.69 (s, 1H), 4.08 (s, 2H), 3.76 (d, *J* = 2.4 Hz, 3H), 3.15 (s, 4H), 1.84 (d, *J* = 2.7 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.9, 149.2, 132.4, 131.7, 131.2, 128.3, 126.7, 123.6, 121.1, 116.9, 116.1, 112.1, 111.9, 101.1, 56.0, 51.9, 28.3, 25.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{23}N_2O$ 307.1805, found: 307.1796.

5-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[indole-3,4'-pyrrolo[1,2-a]quinoline] (11)[4]

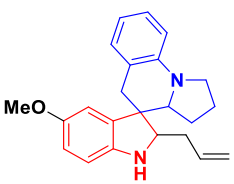


Prepared According to the Literature.[4]

Flash column chromatography on a neutral alumina (ethyl acetate: petroleum ether, 1:15) gave the product as inseparable diastereomers (dr = 1:1) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.6 Hz, 1H), 7.80 (d, *J* = 2.6 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.19 (dd, *J* = 15.1, 7.3 Hz, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.92 – 6.86 (m, 1H), 6.83 – 6.77 (m, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.67 – 6.60 (m, 2H), 6.57 (d, *J* = 3.0 Hz, 2H), 6.12 (d, *J* = 2.1 Hz, 1H), 4.18 – 4.07 (m, 1H), 3.96 – 3.87 (m, 1H), 3.87 – 3.77 (m, 3H), 3.58-3.55 (m, 4H), 3.49 (dd, *J* = 18.8, 9.8 Hz, 2H), 3.40 (d, *J* = 16.2 Hz, 1H), 3.33 – 3.25 (m, 1H), 3.24 – 3.15 (m, 1H), 2.61 (d, *J* = 16.1 Hz, 1H), 2.42 (d, *J* = 15.5 Hz, 1H), 1.98 (d, *J* = 5.2 Hz, 1H), 1.92 – 1.80 (m, 3H), 1.78-1.66 (m, 1H), 1.58-1.48 (m, 1H), 1.05 – 0.92 (m, 1H), 0.75-0.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 173.2, 159.0, 158.4, 149.8, 149.4, 144.0, 143.8, 142.8, 140.2, 129.7, 128.7, 128.3, 128.0, 121.7, 121.2, 119.8, 117.2, 115.9, 115.8, 112.6, 112.5, 110.9, 110.6, 110.1, 108.4, 62.9, 60.2, 57.0, 56.8, 55.8, 55.4, 47.4, 36.1, 34.2, 27.6, 27.1, 23.5, 23.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{21}N_2O$ 305.1648, found: 305.1651.

2-allyl-5-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline] (12)



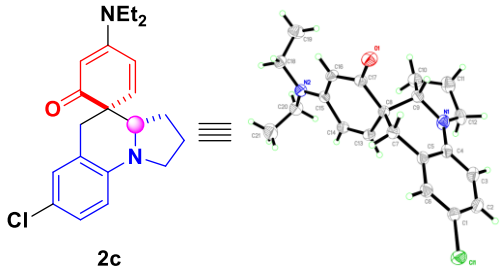
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave the separable diastereomers (31.8 mg, 92% yield, dr 1:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.60 – 6.49 (m, 3H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.96 (d, *J* = 1.8 Hz, 1H), 5.90 – 5.77 (m, 1H), 5.25-5.13 (m, 2H), 3.62-3.54 (m, 2H), 3.47-3.44 (m, 1H), 3.43 (s, 3H), 3.20 (dd, *J* = 16.6, 9.2 Hz, 1H), 3.07 (d, *J* = 15.2 Hz, 1H), 2.77 (d, *J* = 15.3 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.35 – 2.25 (m, 1H), 2.04-1.97 (m, 1H), 1.97 – 1.86 (m, 2H), 1.40-1.30 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.2, 144.3, 144.0, 135.9, 132.6, 129.5, 127.7, 119.3, 118.1, 115.4, 112.7, 112.2, 109.3, 109.1, 65.5, 64.4, 55.5, 47.3, 46.2, 35.5, 35.0, 28.8, 23.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{27}N_2O$ 347.2118, found: 347.2106.

Reference

1. Jurberg, I. D.; Peng, B.; W çstefeld, E.; Wasserloos, M.; Maulide, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 1950.
2. Adili, A.; Tao, Z.-L.; Chen, D.-F.; Han, Z.-Y. *Org. Biomol. Chem.* **2015**, *13*, 2247.
3. Li, S.-S.; Lv, X.; Ren, D.; Shao, C.-L.; Liu, Q.; Xiao, J. *Chem. Sci.* **2018**, *9*, 8253.
4. Bai, G.; Dong, F.; Xu, L.; Liu, Y.; Wang, L.; Li, S.-S. *Org. Lett.* **2019**, *21*, 6225.

5. Crystal Structures and Data

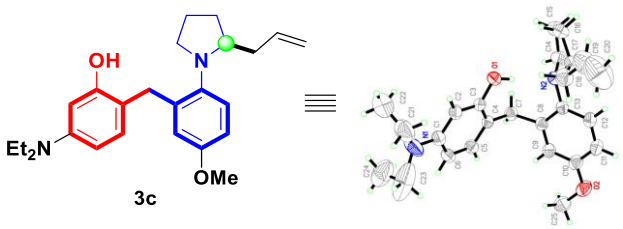


2c

CCDC (2061370)

Table 1. Crystal data and structure refinement for **2c**.

Identification code	**2c**
Empirical formula	$C_{21}H_{25}ClN_2O$
Formula weight	356.88
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 15.3242(6) A alpha = 90 deg.
	b = 13.8242(5) A beta = 104.165(4) deg.
	c = 9.0303(4) A gamma = 90 deg.
Volume	1854.85(13) A^3
Z, Calculated density	4, 1.278 Mg/m^3
Absorption coefficient	1.896 mm^-1
F(000)	760
Crystal size	0.230 x 0.220 x 0.210 mm
Theta range for data collection	4.368 to 67.243 deg.
Limiting indices	-18<=h<=17, -16<=k<=12, -10<=l<=10
Reflections collected / unique	6379 / 3327 [R(int) = 0.0208]
Completeness to theta = 67.243	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3327 / 0 / 229
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1046
R indices (all data)	R1 = 0.0502, wR2 = 0.1108
Extinction coefficient	0.0041(3)
Largest diff. peak and hole	0.182 and -0.168 e.A^-3



CCDC (2057763)

Table S2. Crystal data and structure refinement for **3c**.

Identification code	**3c**	
Empirical formula	$C_{25}H_{34}N_2O_2$	
Formula weight	394.54	
Temperature	293(2) K	
Wavelength	1.54184 A	
Crystal system, space group	Trigonal, R-3	
Unit cell dimensions	a = 34.3408(11) A	alpha = 90 deg.
	b = 34.3408(11) A	beta = 90 deg.
	c = 10.4316(3) A	gamma = 120 deg.
Volume	10653.8(6) A^3	
Z, Calculated density	18, 1.107 Mg/m^3	
Absorption coefficient	0.545 mm^-1	
F(000)	3852	
Crystal size	0.12 x 0.12 x 0.11 mm	
Theta range for data collection	2.57 to 67.19 deg.	
Limiting indices	-40<=h<=41, -27<=k<=41, -12<=l<=12	
Reflections collected / unique	23249 / 4238 [R(int) = 0.0452]	
Completeness to theta = 67.19	100.0 %	
Max. and min. transmission	0.9425 and 0.9375	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4238 / 6 / 287	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0732, wR2 = 0.2217	
R indices (all data)	R1 = 0.1047, wR2 = 0.2539	
Extinction coefficient	0.00032(7)	
Largest diff. peak and hole	0.464 and -0.221 e.A^-3	

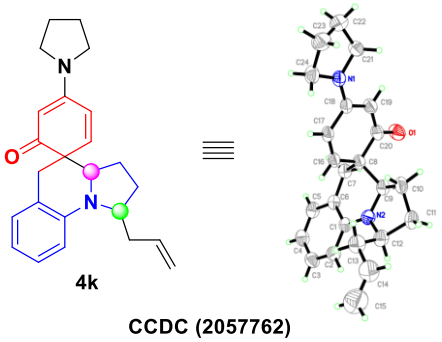
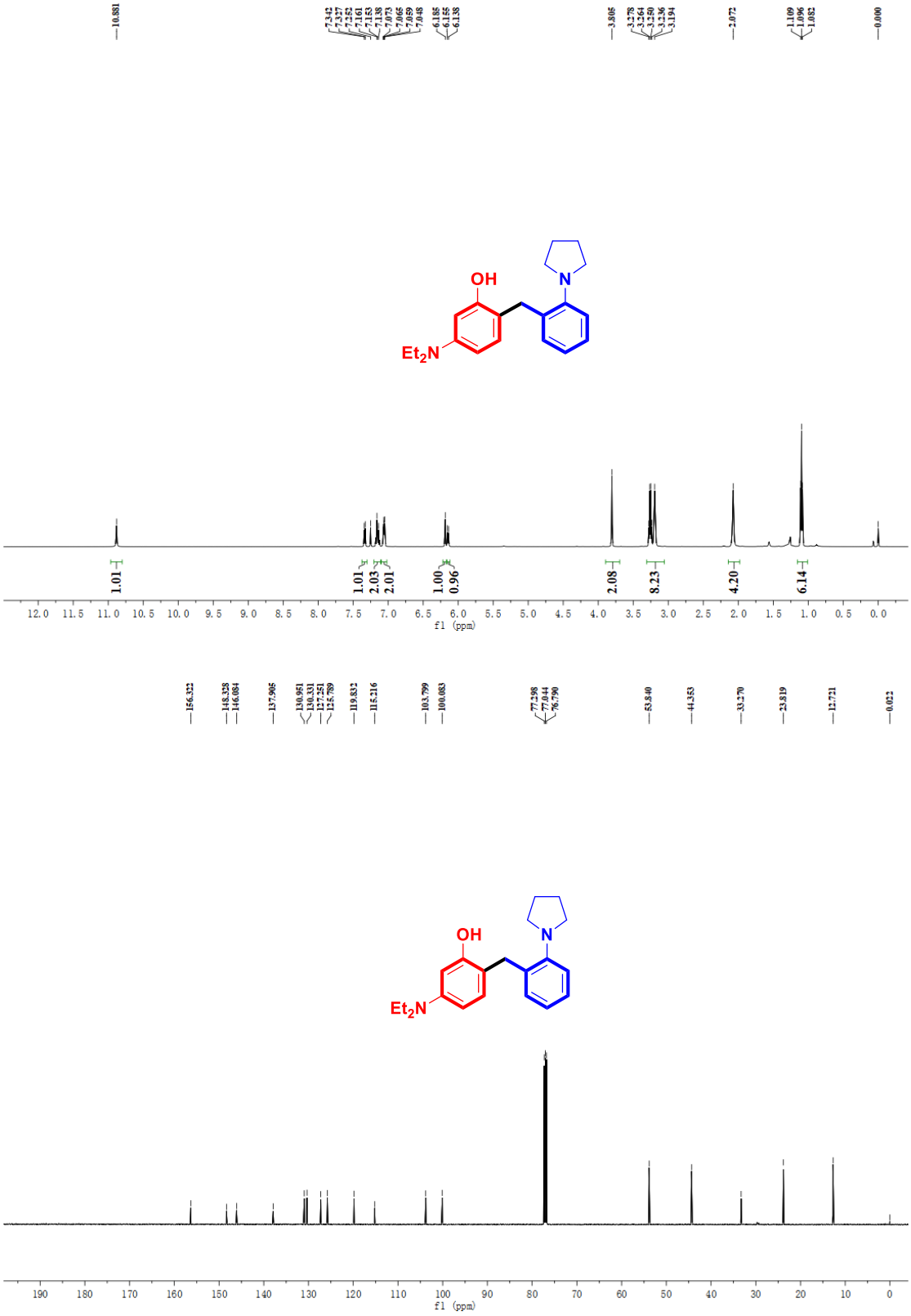


Table S3. Crystal data and structure refinement for **4k**.

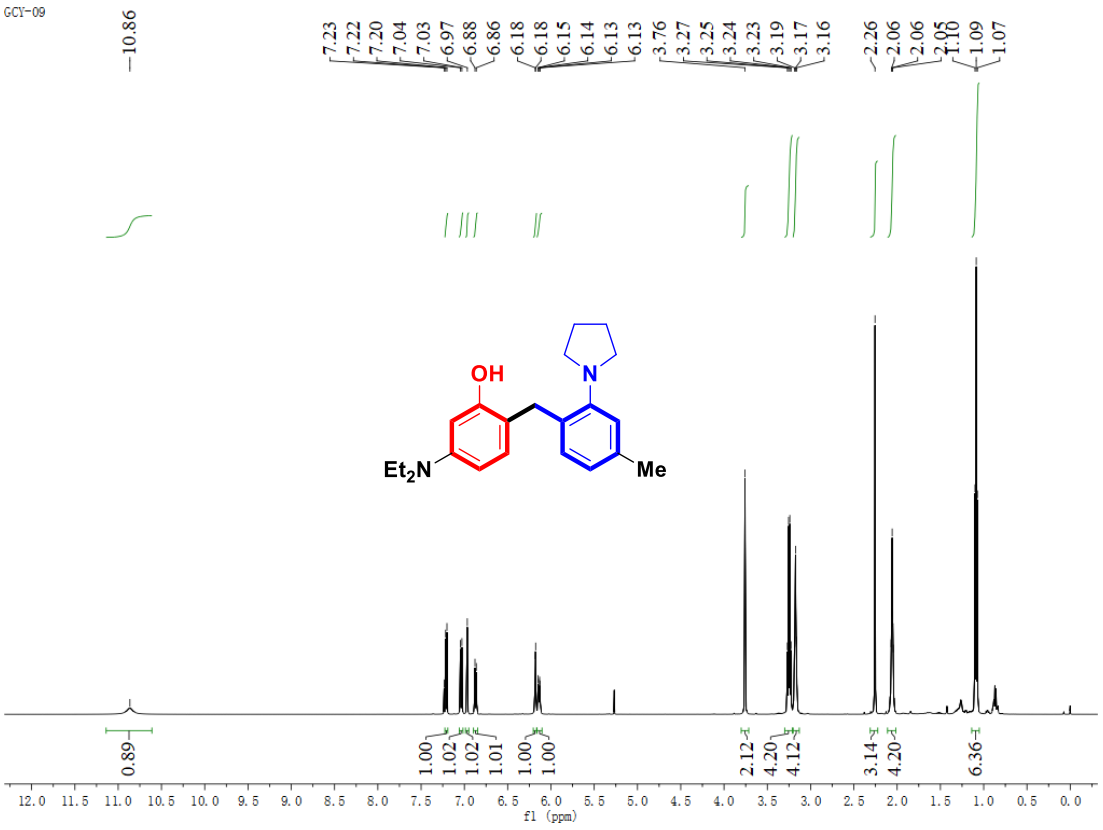
Identification code	**4k**
Empirical formula	$C_{24}H_{28}N_2O$
Formula weight	360.22
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 11.9297(10) A alpha = 75.136(9) deg.
	b = 12.9240(9) A beta = 78.644(10) deg.
	c = 13.666(2) A gamma = 89.902(6) deg.
Volume	1994.0(4) A^3
Z, Calculated density	2, 1.199 Mg/m^3
Absorption coefficient	0.567 mm^-1
F(000)	774
Crystal size	0.08 x 0.08 x 0.07 mm
Theta range for data collection	3.42 to 67.24 deg.
Limiting indices	-14<=h<=13, -10<=k<=15, -15<=l<=16
Reflections collected / unique	13345 / 7100 [R(int) = 0.0415]
Completeness to theta = 67.24	99.3 %
Max. and min. transmission	0.9614 and 0.9561
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7100 / 6 / 487
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.1157, wR2 = 0.2884
R indices (all data)	R1 = 0.1753, wR2 = 0.3647
Largest diff. peak and hole	0.612 and -0.477 e.A^-3

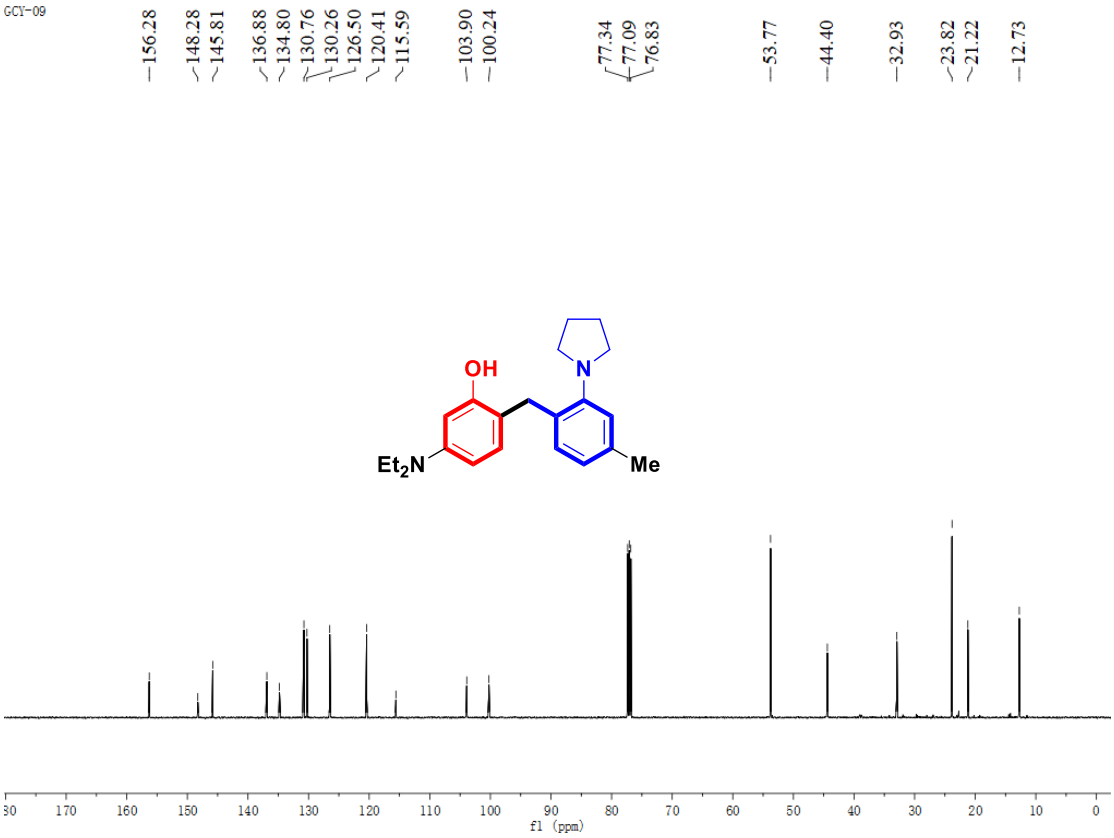
6. ^{1}H and ^{13}C NMR Spectra

5-(diethylamino)-2-(2-(pyrrolidin-1-yl)benzyl)phenol (1a)

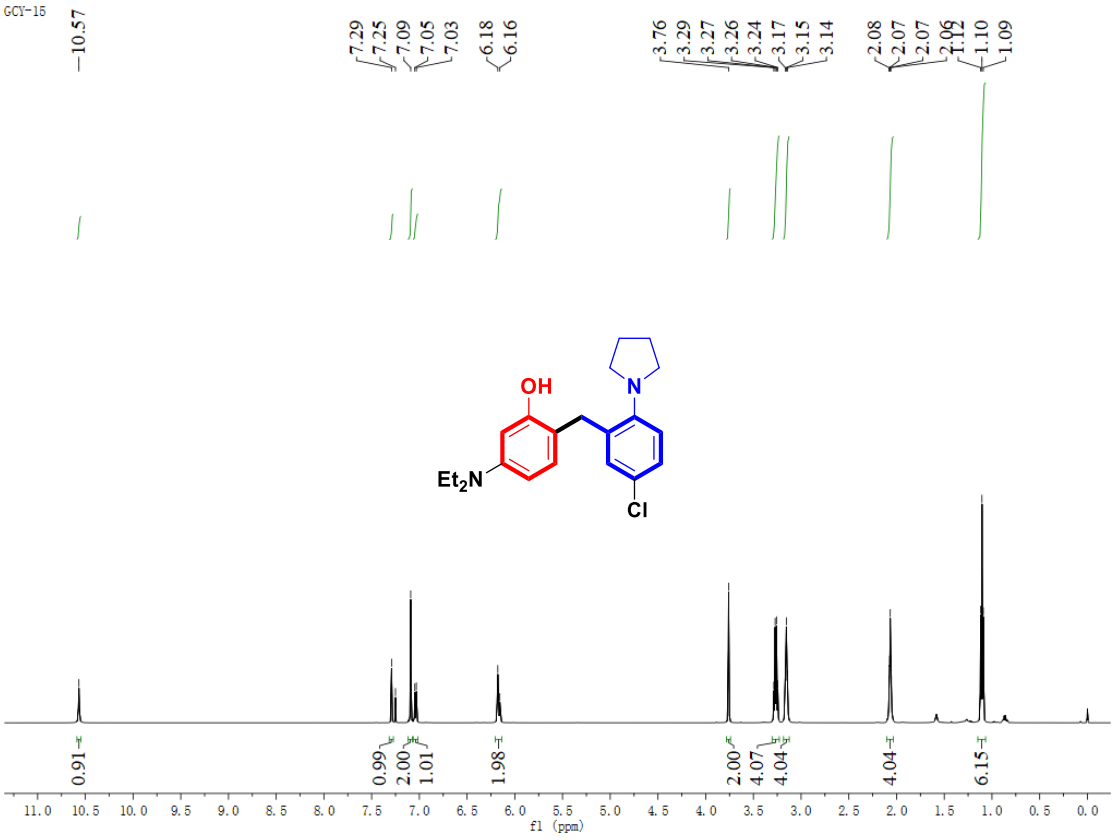


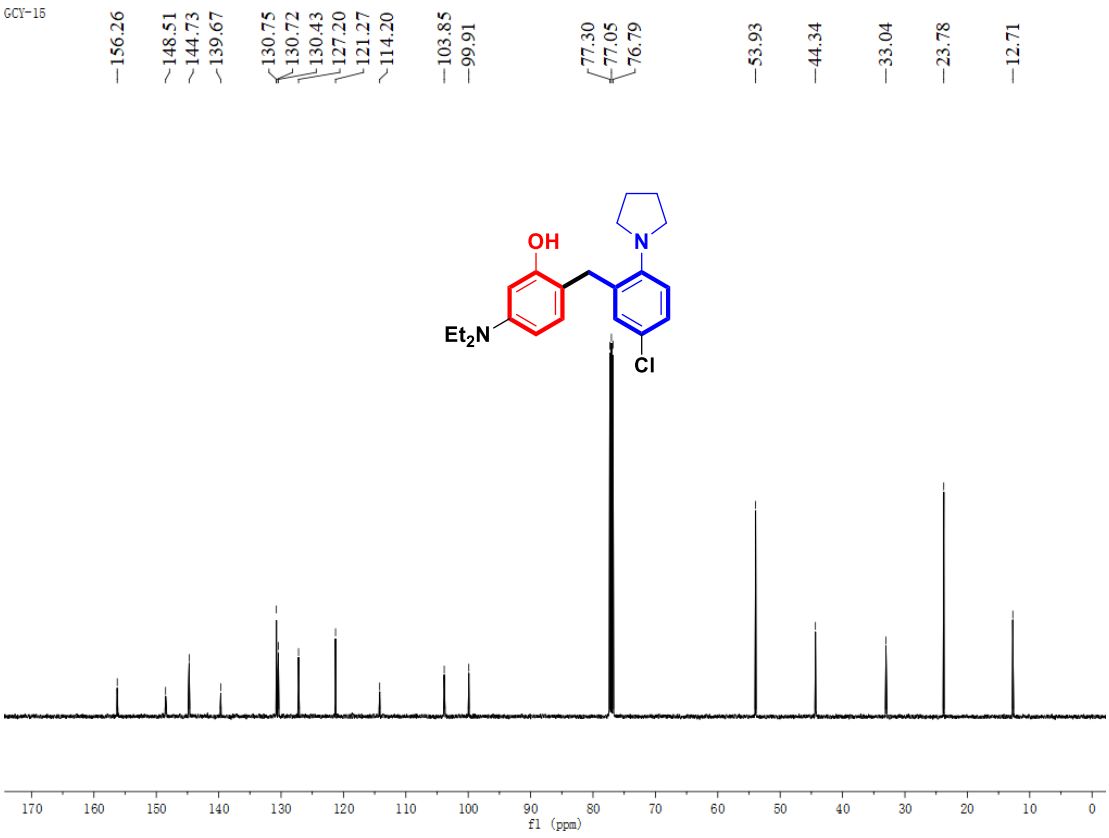
5-(diethylamino)-2-(4-methyl-2-(pyrrolidin-1-yl)benzyl)phenol (1b)



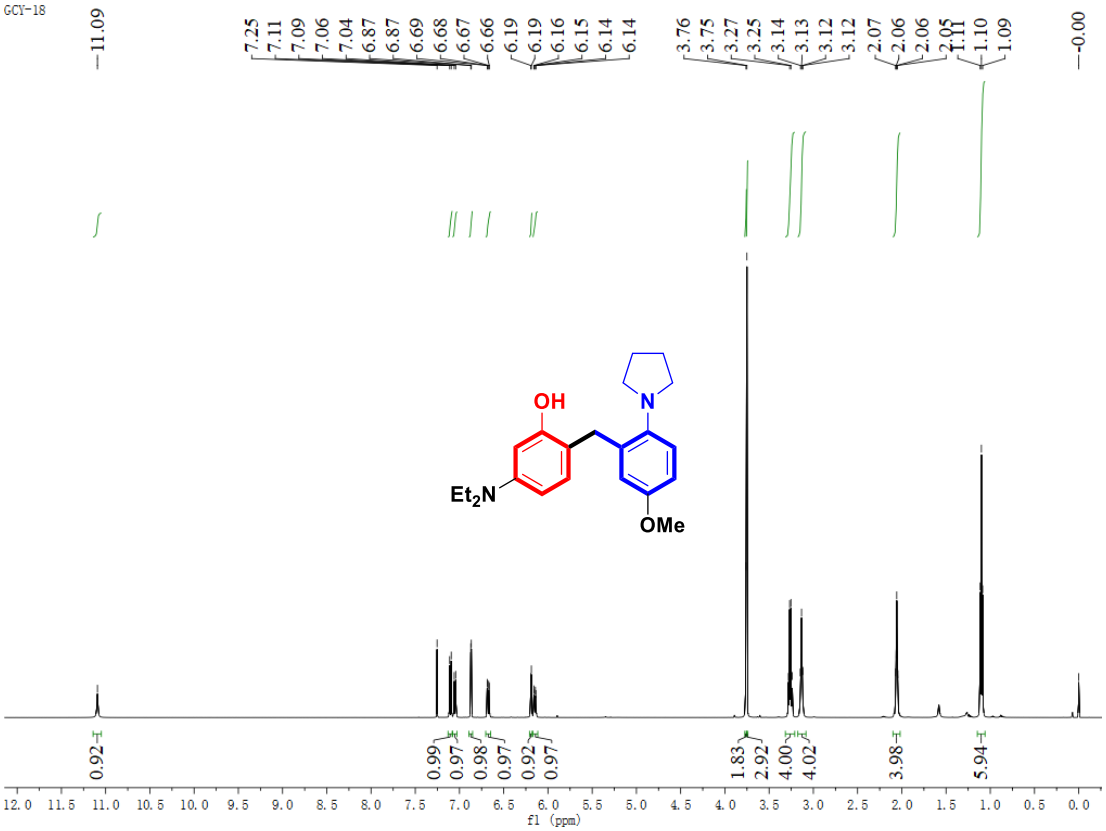


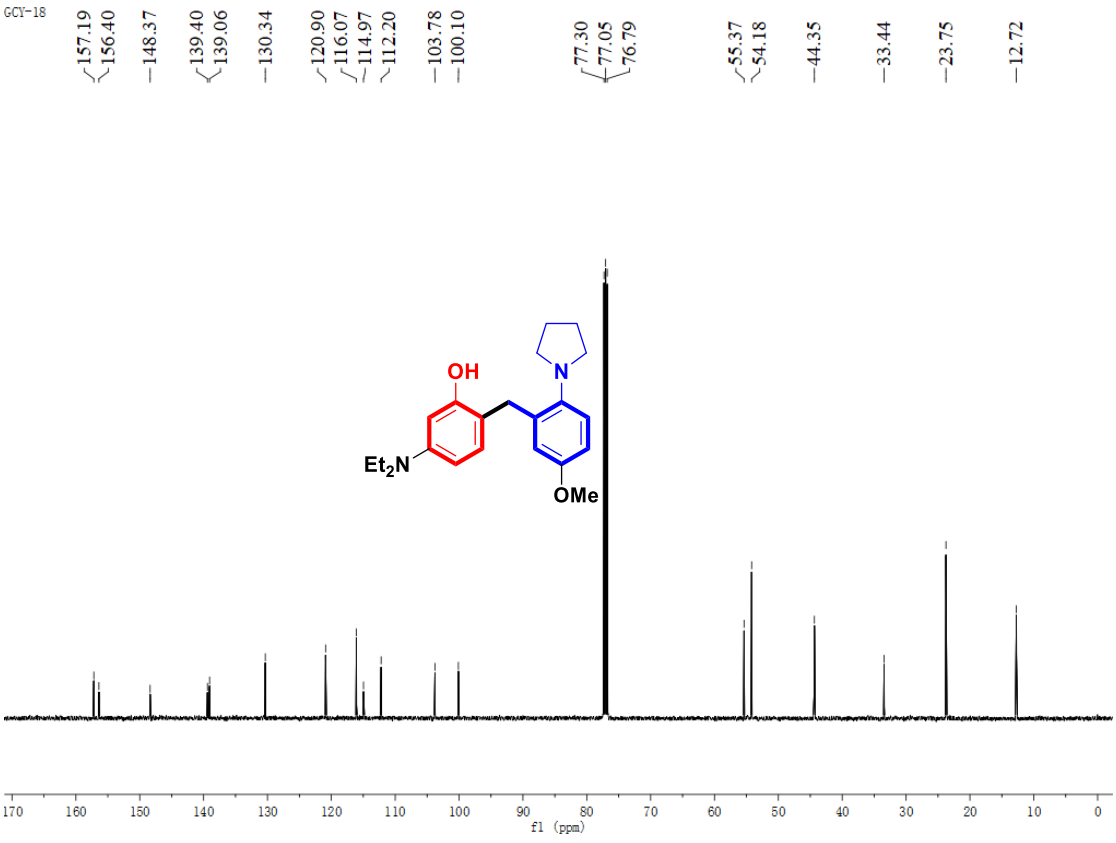
2-(5-chloro-2-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1c)



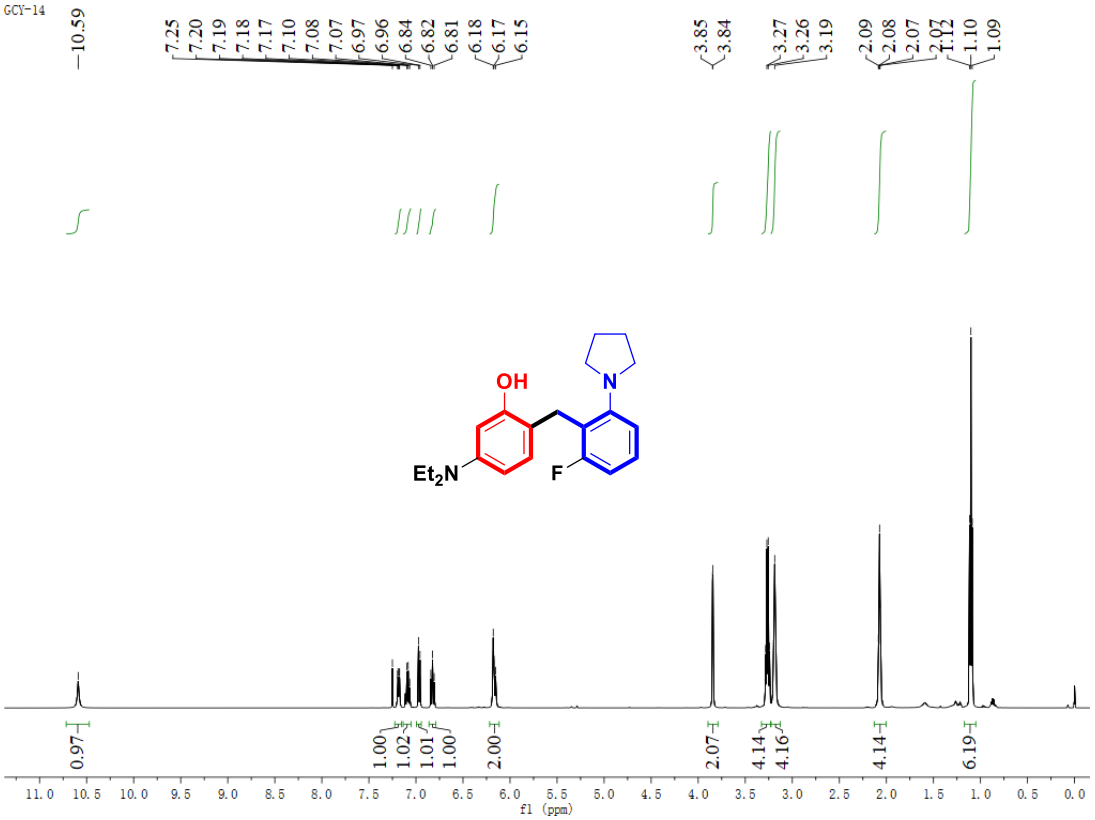


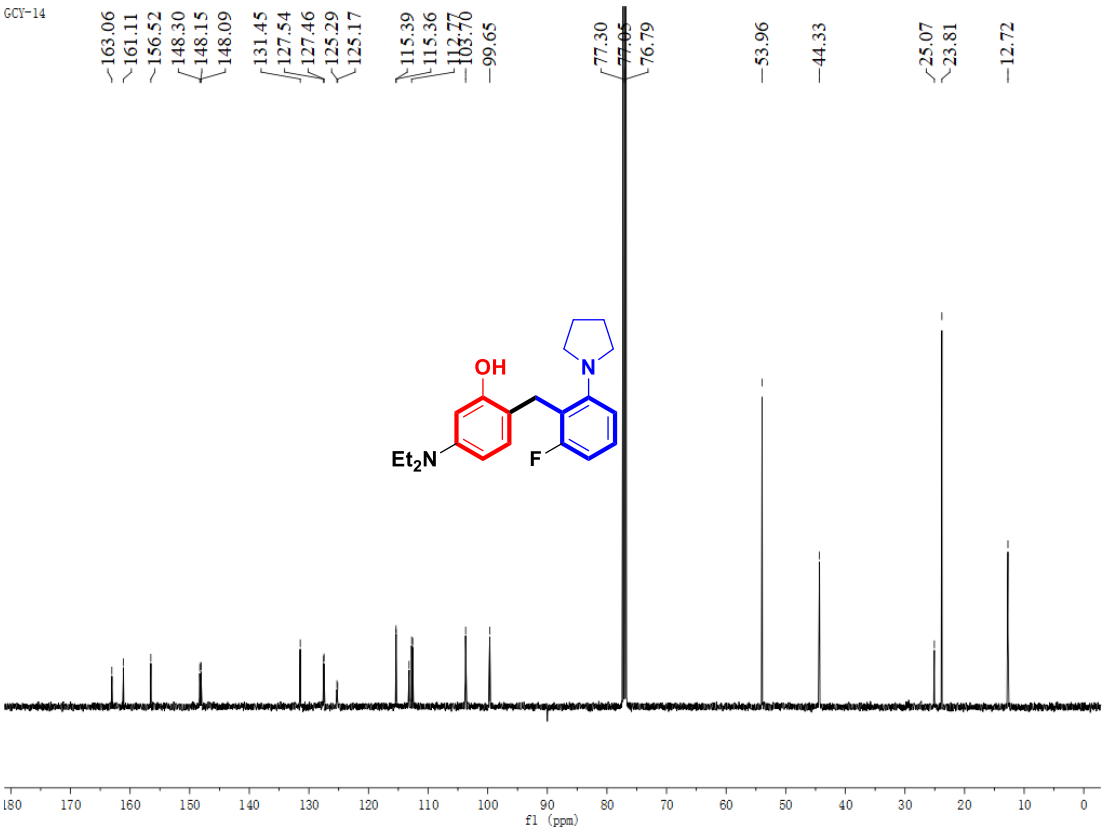
5-(diethylamino)-2-(5-methoxy-2-(pyrrolidin-1-yl)benzyl)phenol (1d)



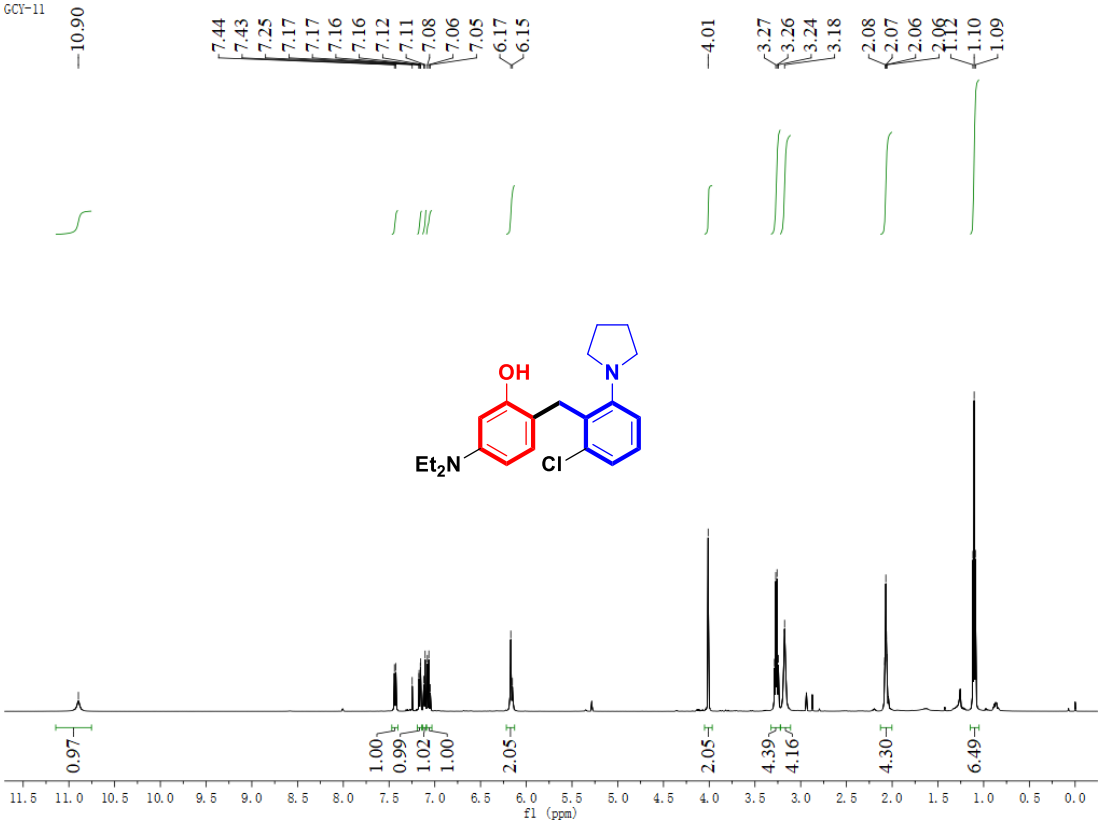


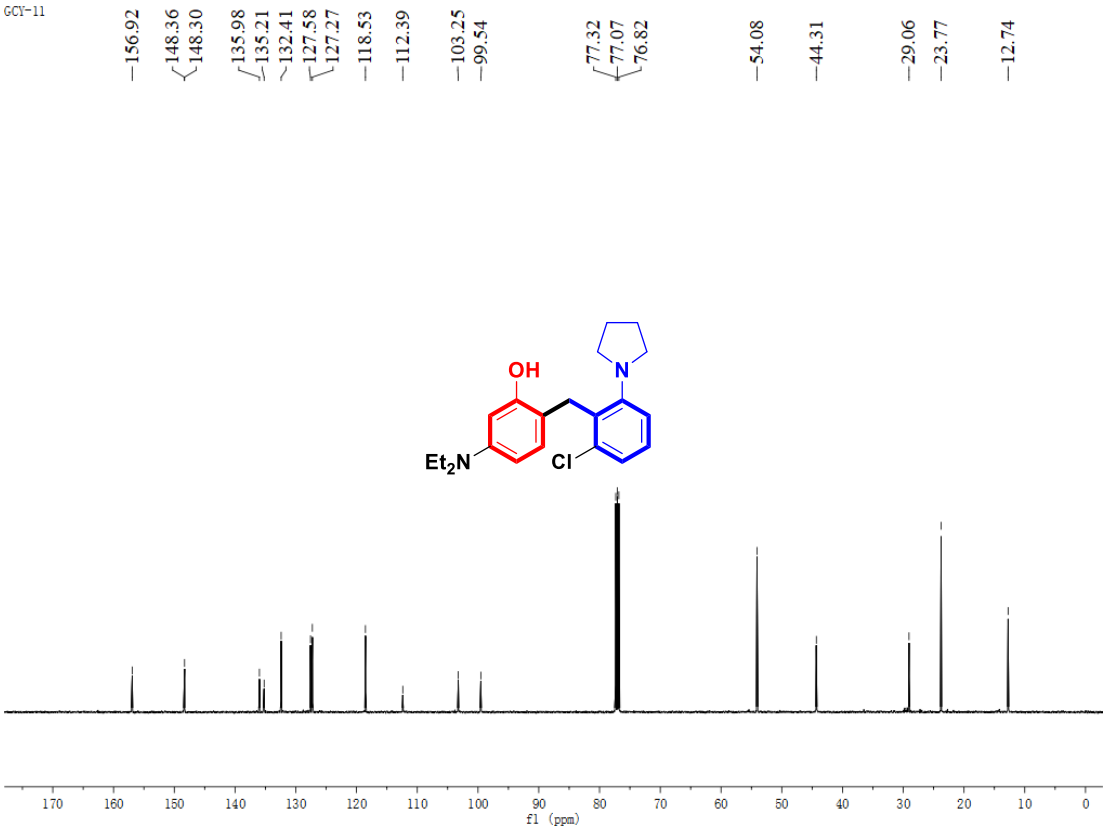
5-(diethylamino)-2-(2-fluoro-6-(pyrrolidin-1-yl)benzyl)phenol (1e)



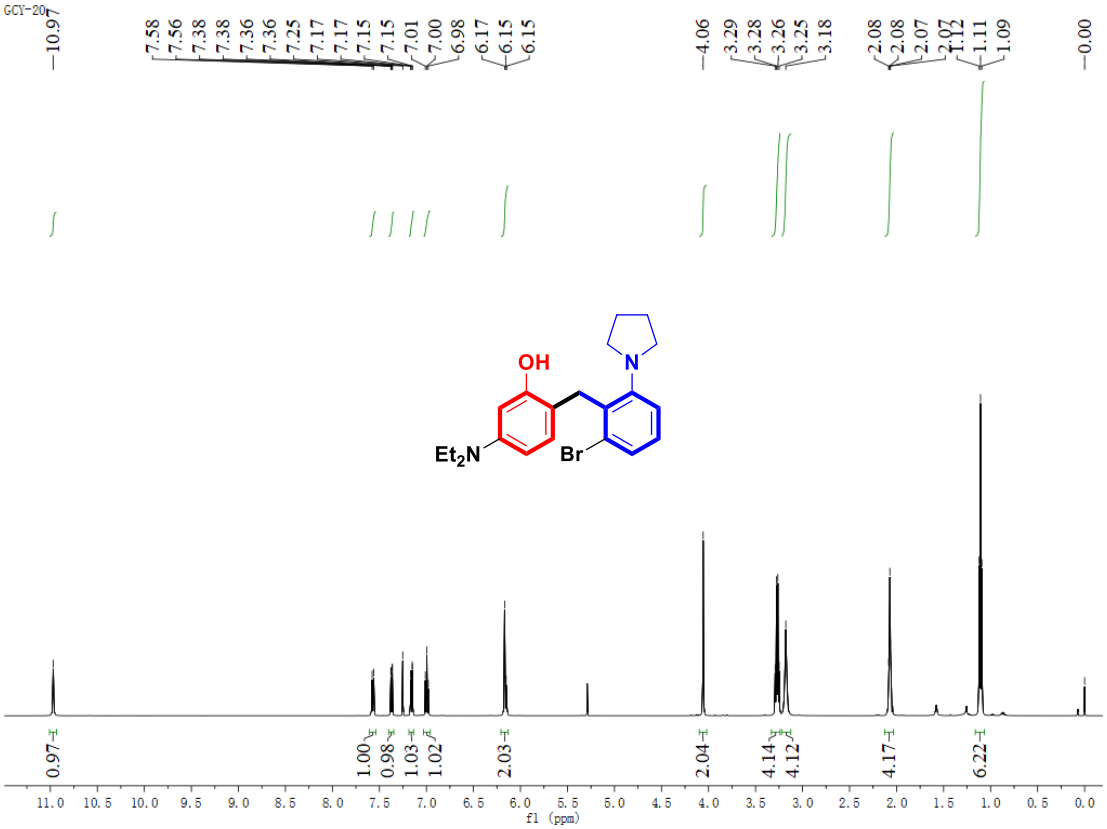


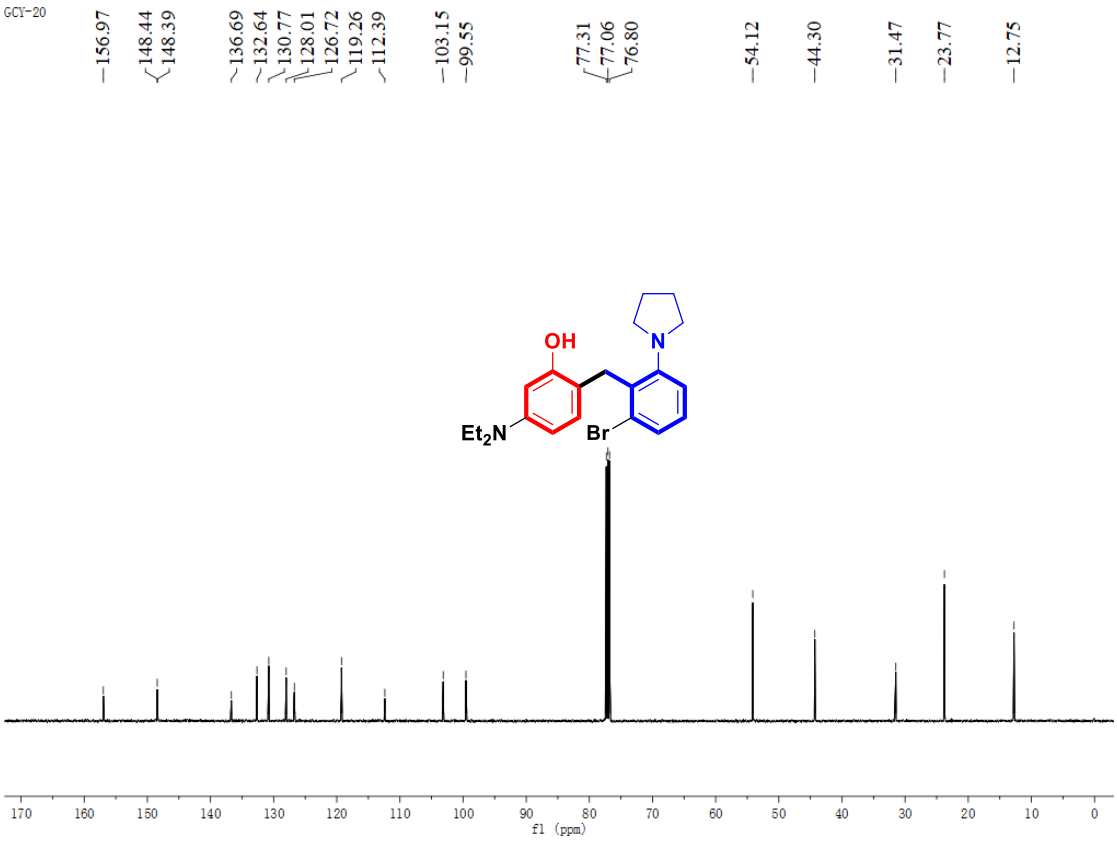
2-(2-chloro-6-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1f)



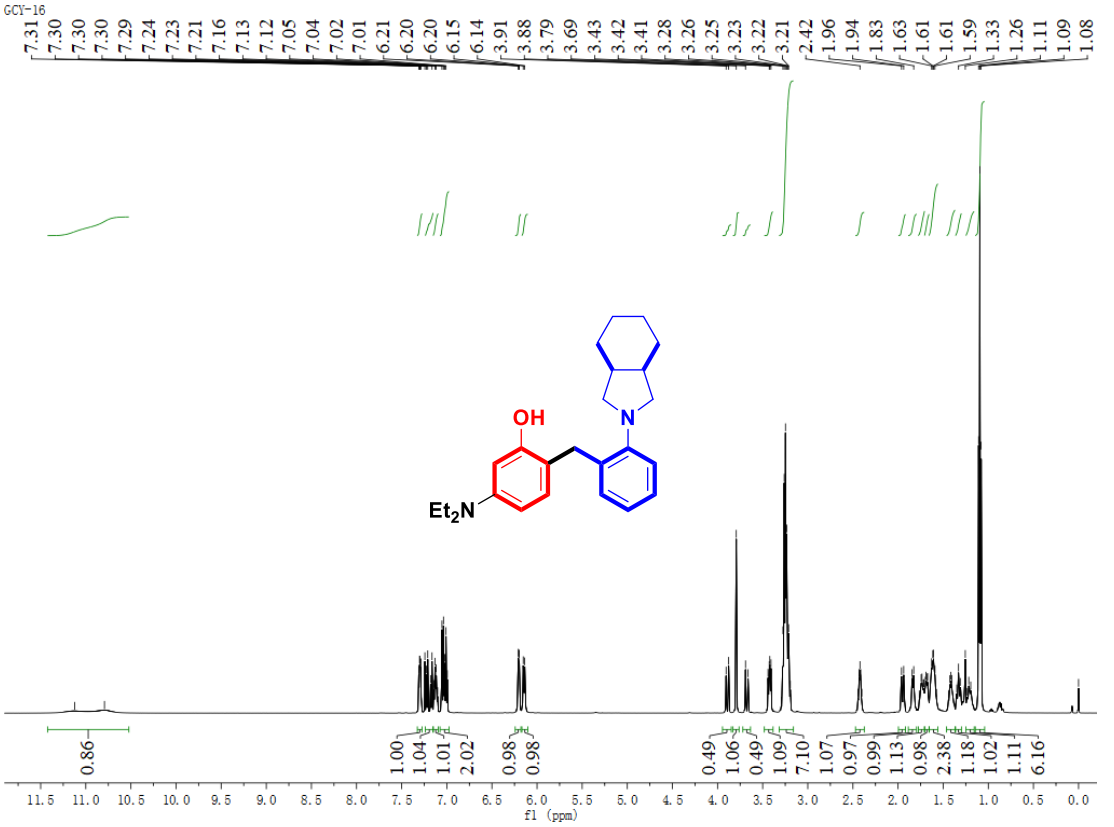


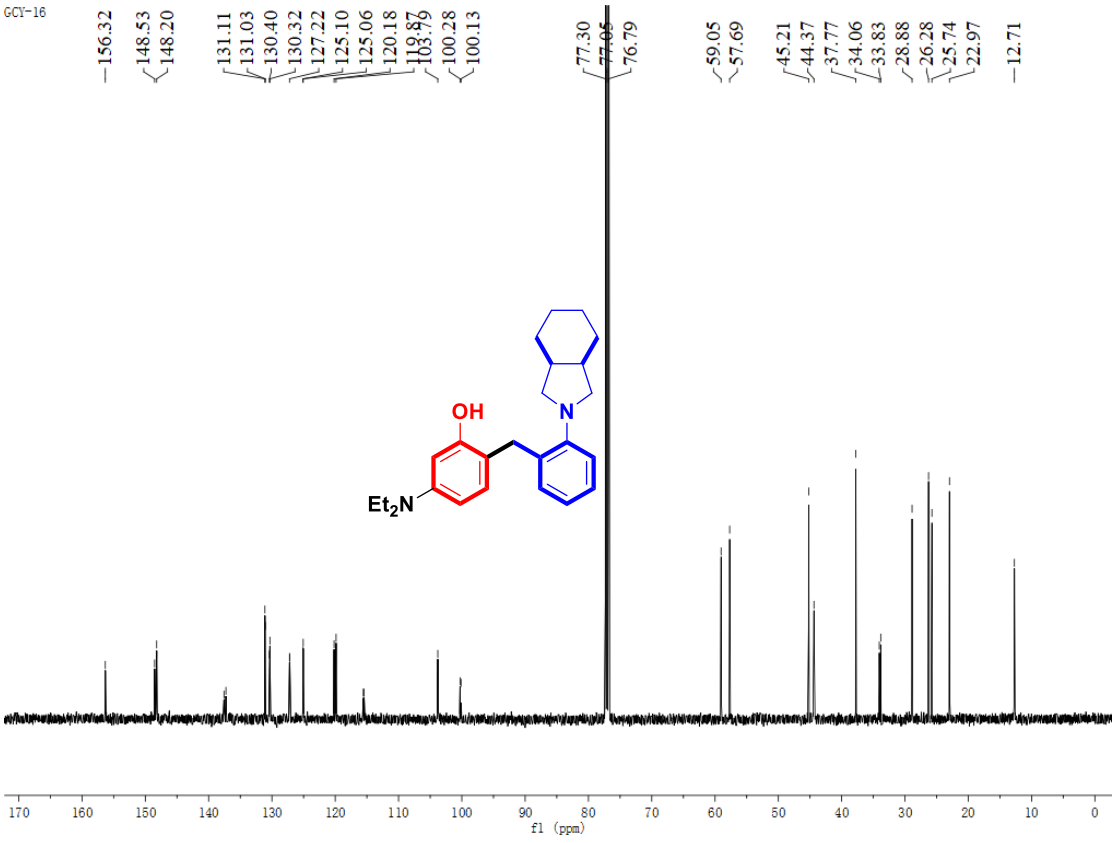
2-(2-bromo-6-(pyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (1g)



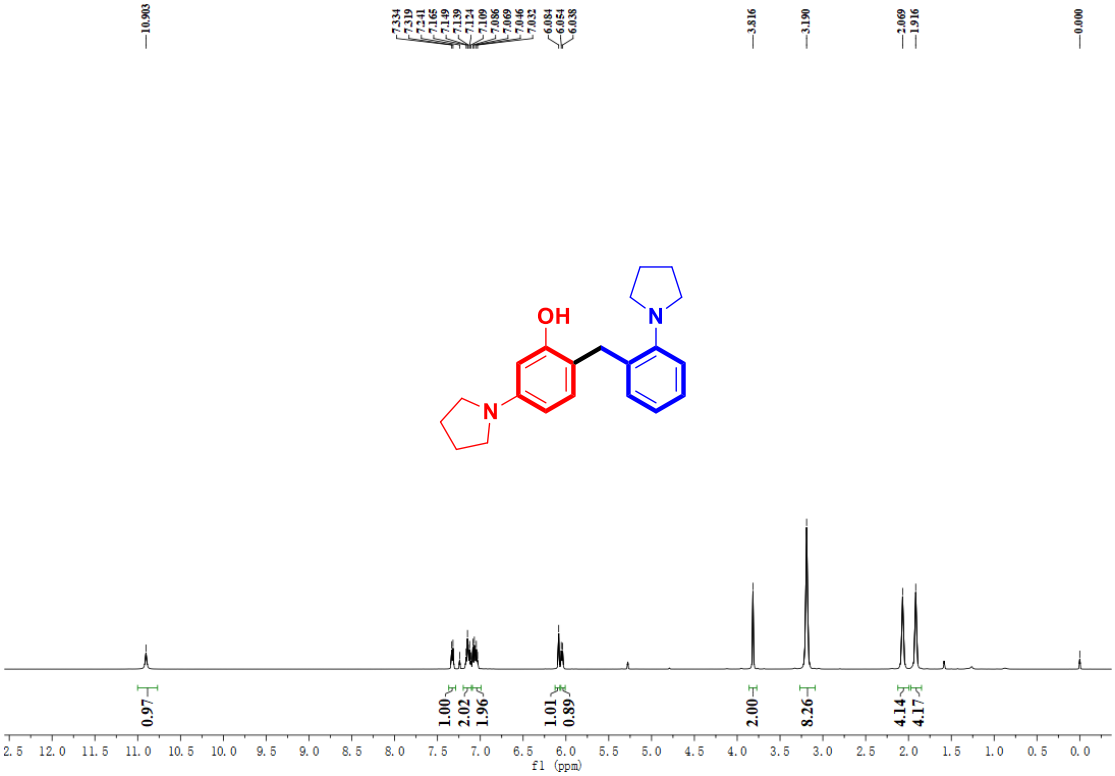


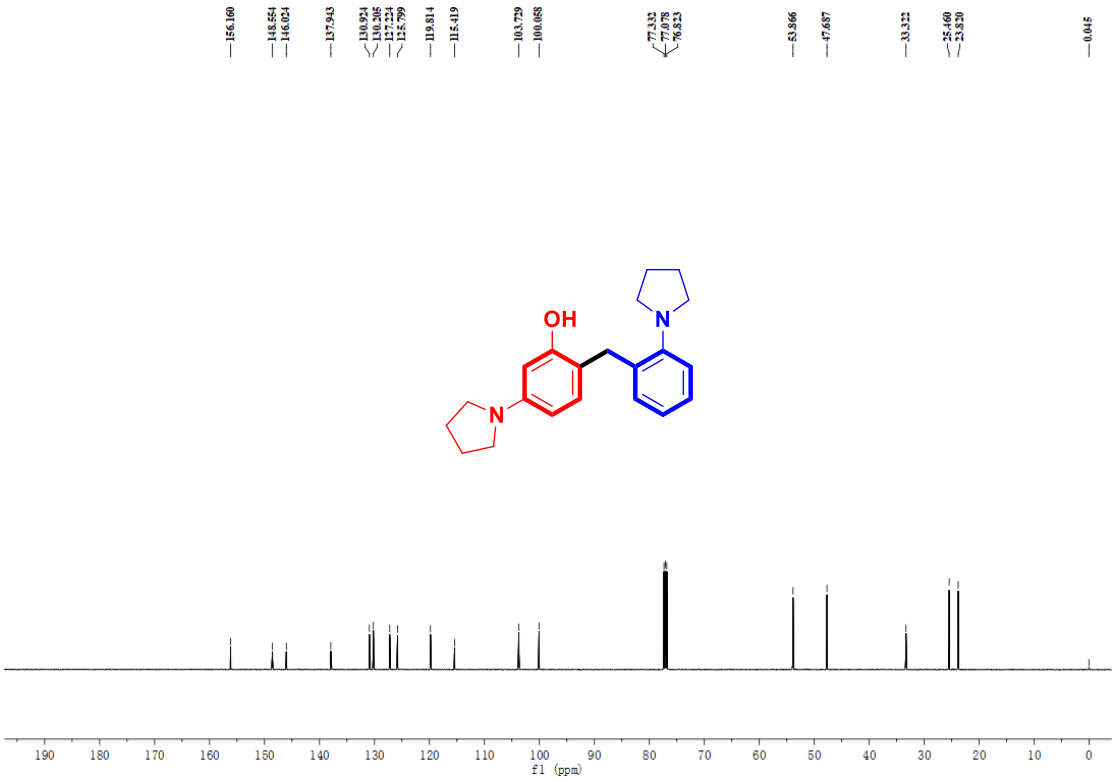
5-(diethylamino)-2-(2-((3aR,7aS)-octahydro-2H-isoindol-2-yl)benzyl)phenol (1h)



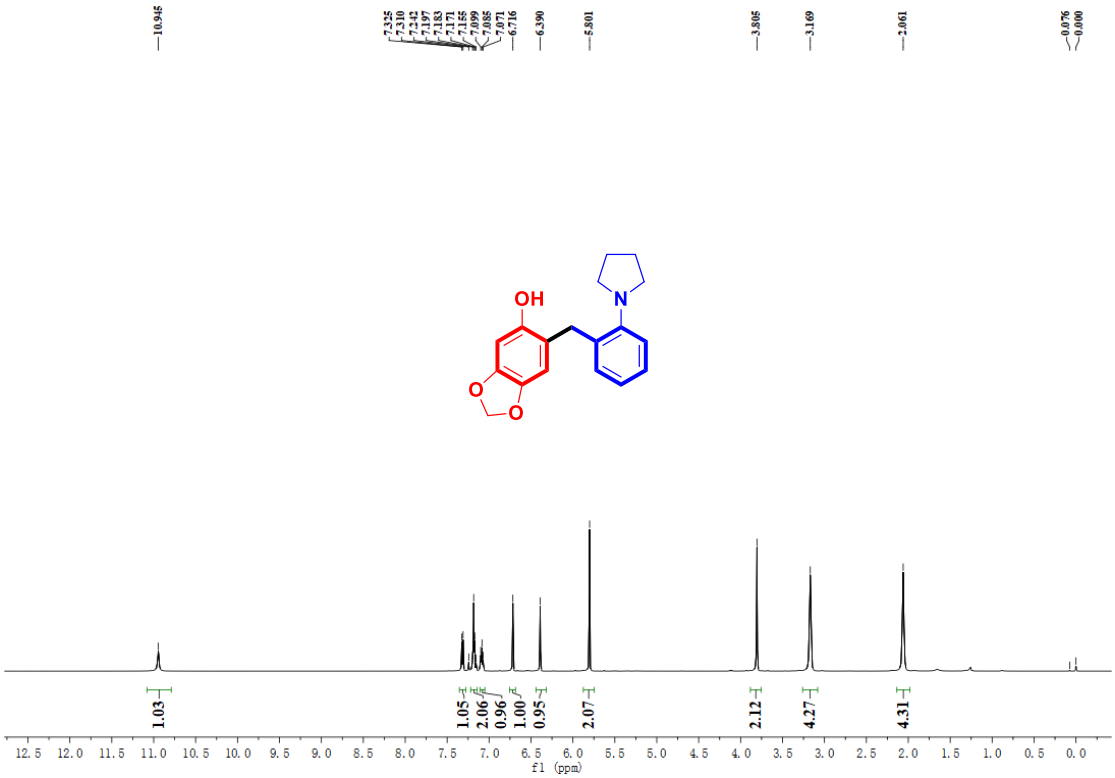


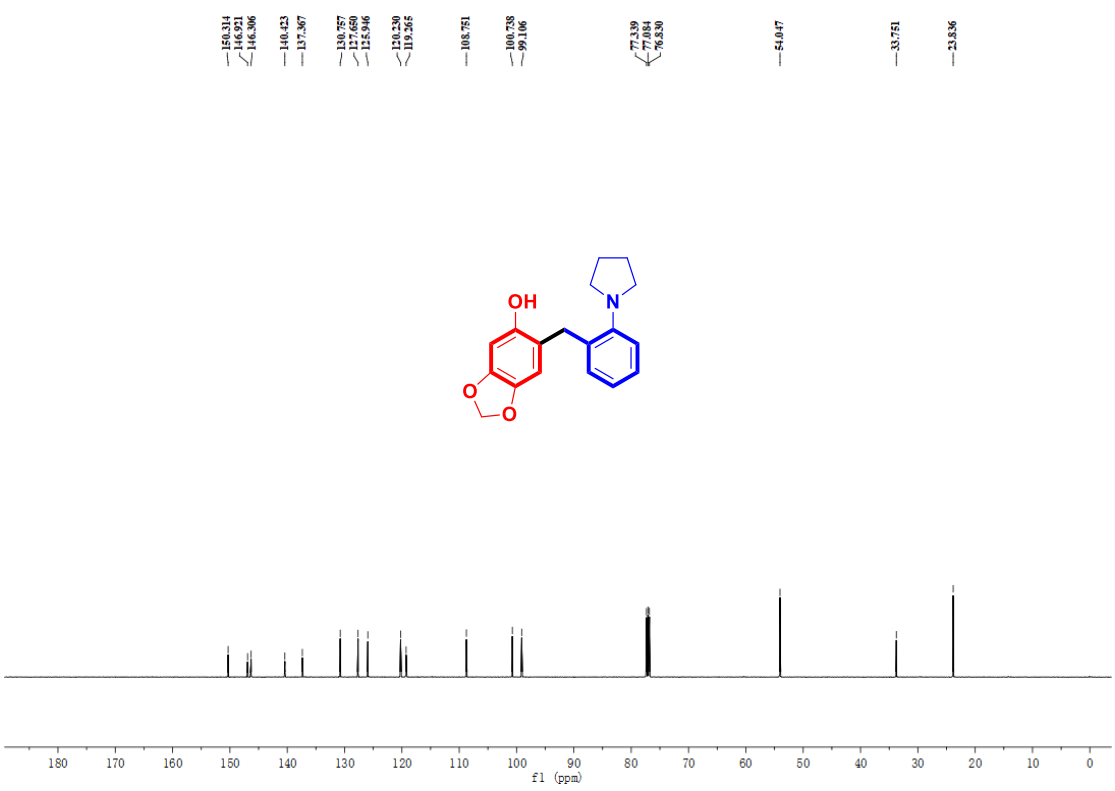
5-(pyrrolidin-1-yl)-2-(2-(pyrrolidin-1-yl)benzyl)phenol (1i)



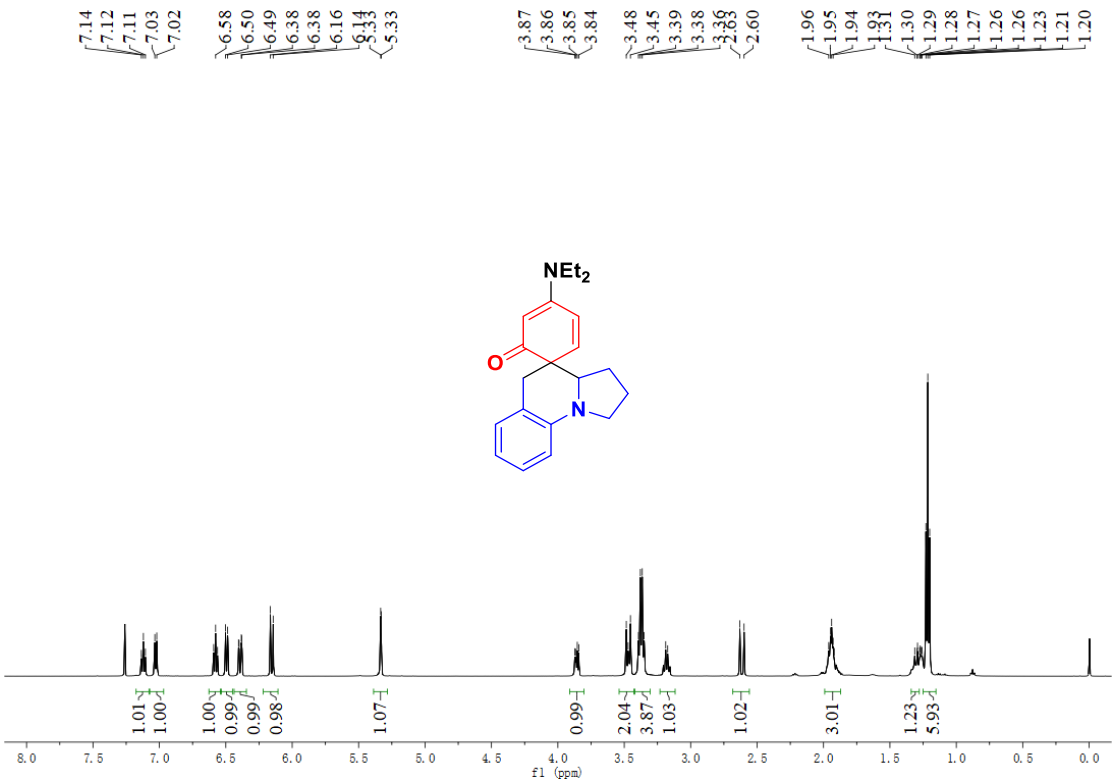


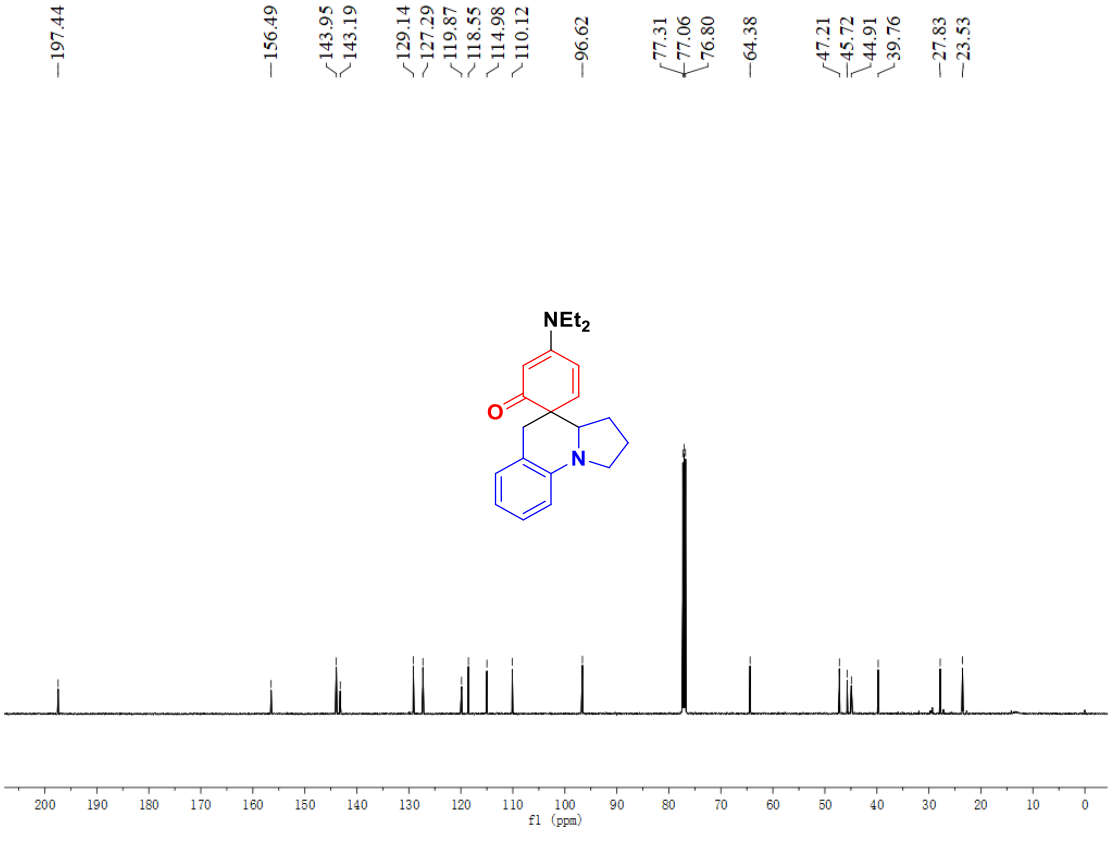
6-(2-(pyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (1j)



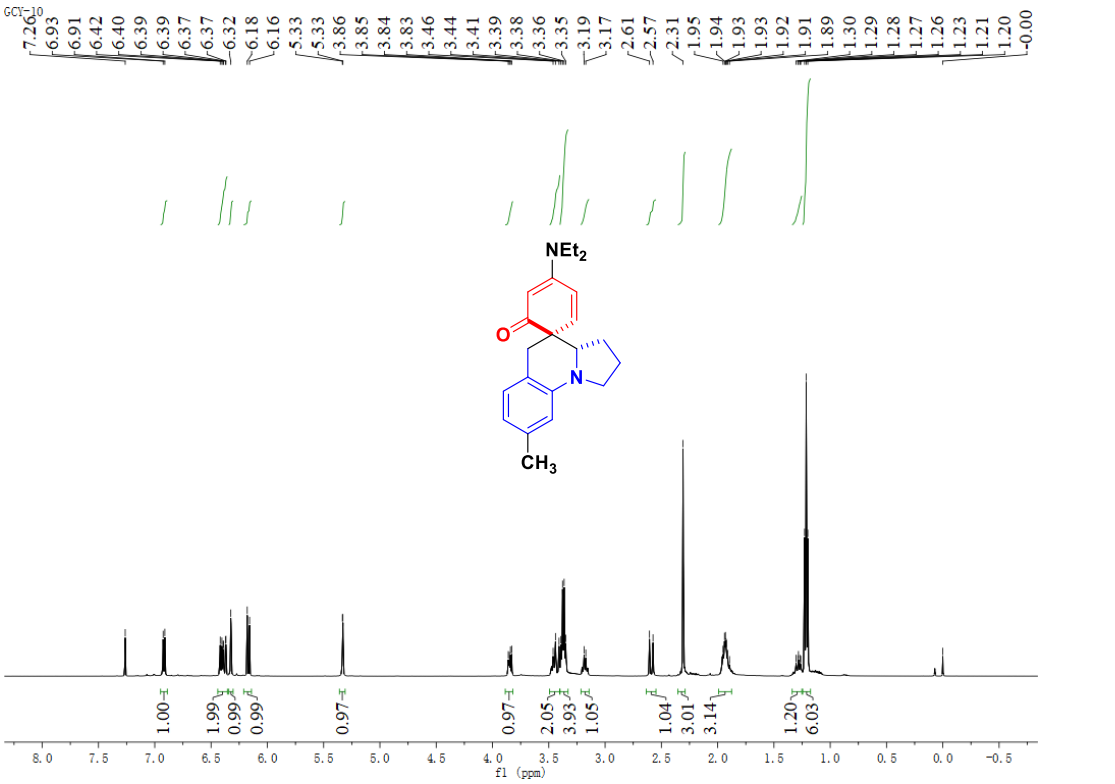


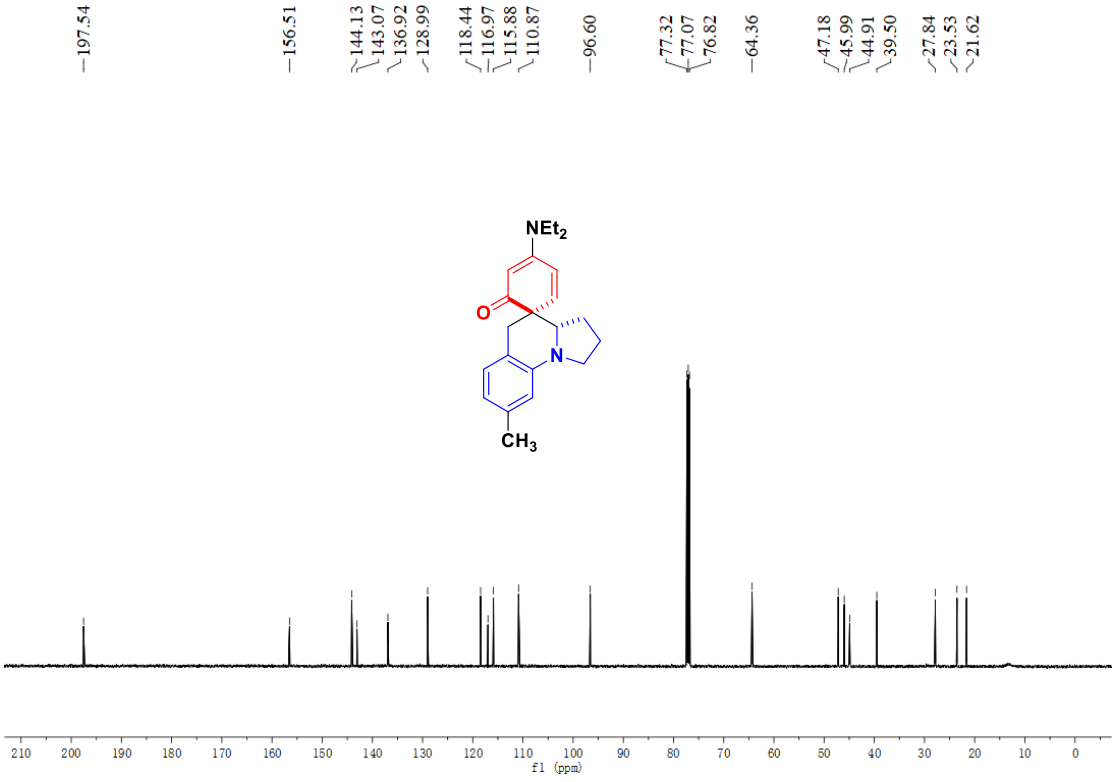
4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2a)[3]



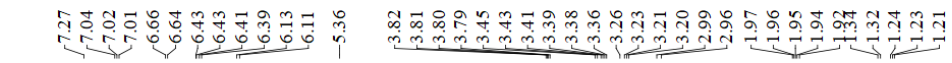


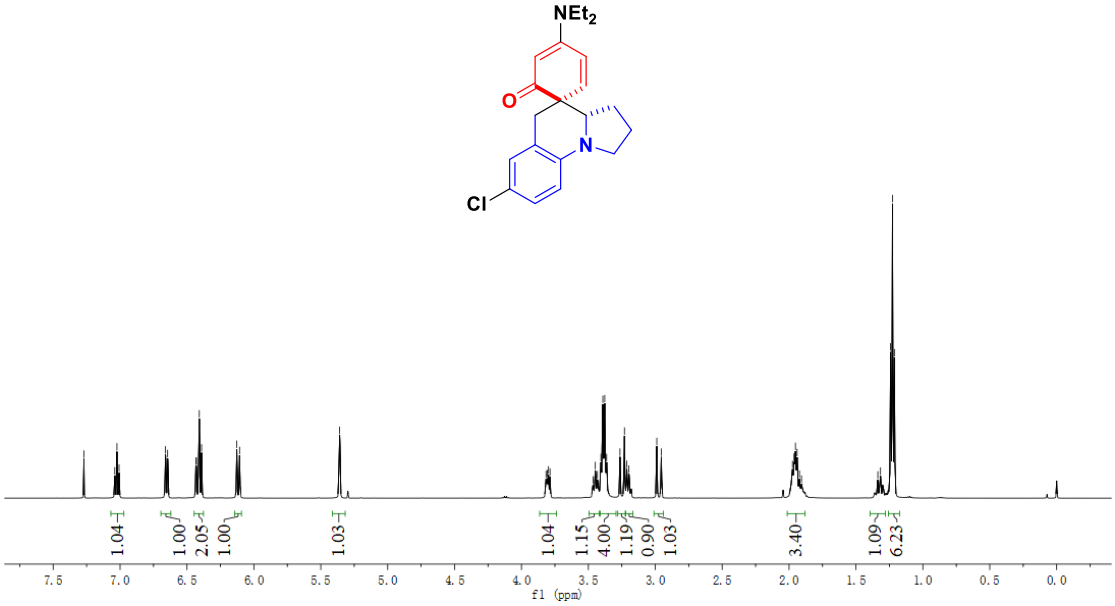
4-(diethylamino)-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2b)

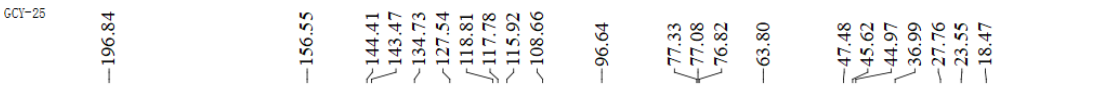


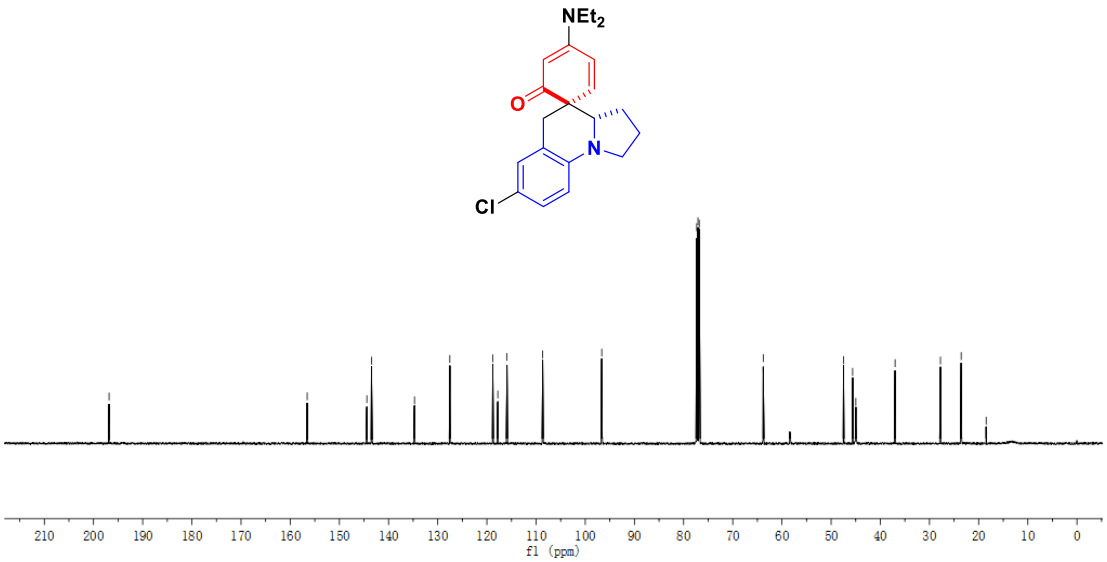


7'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2c)

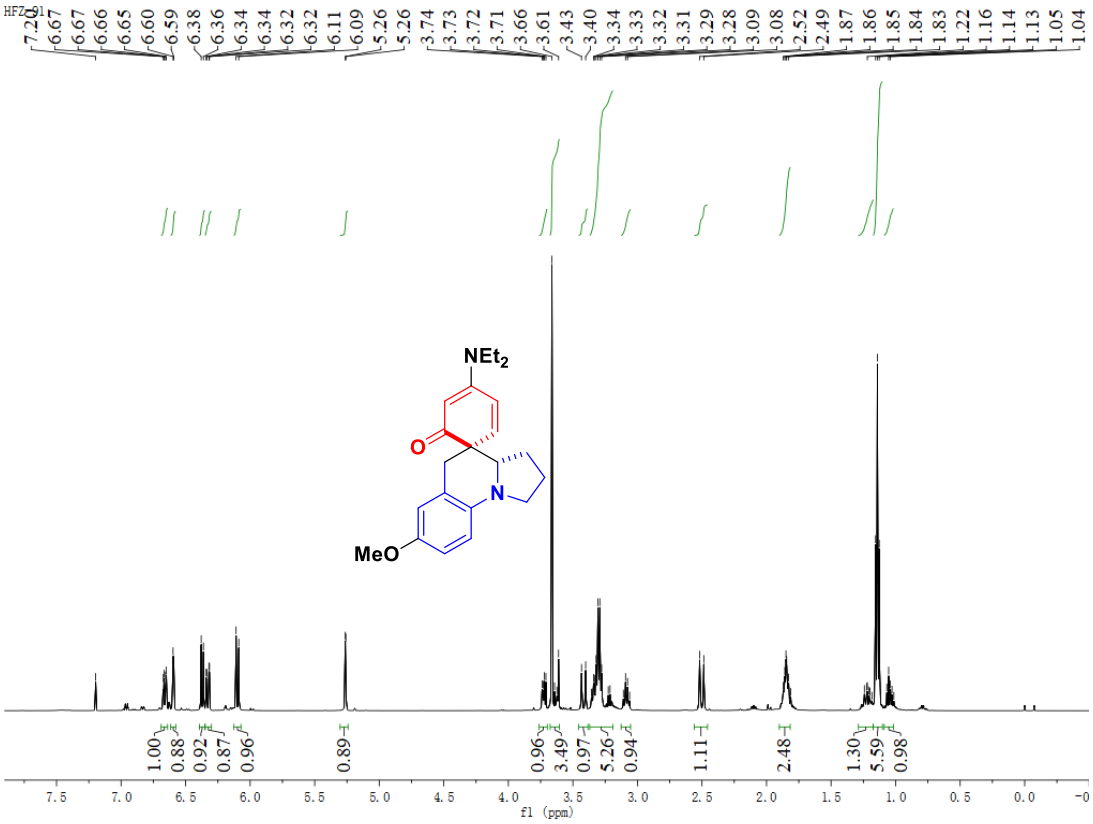


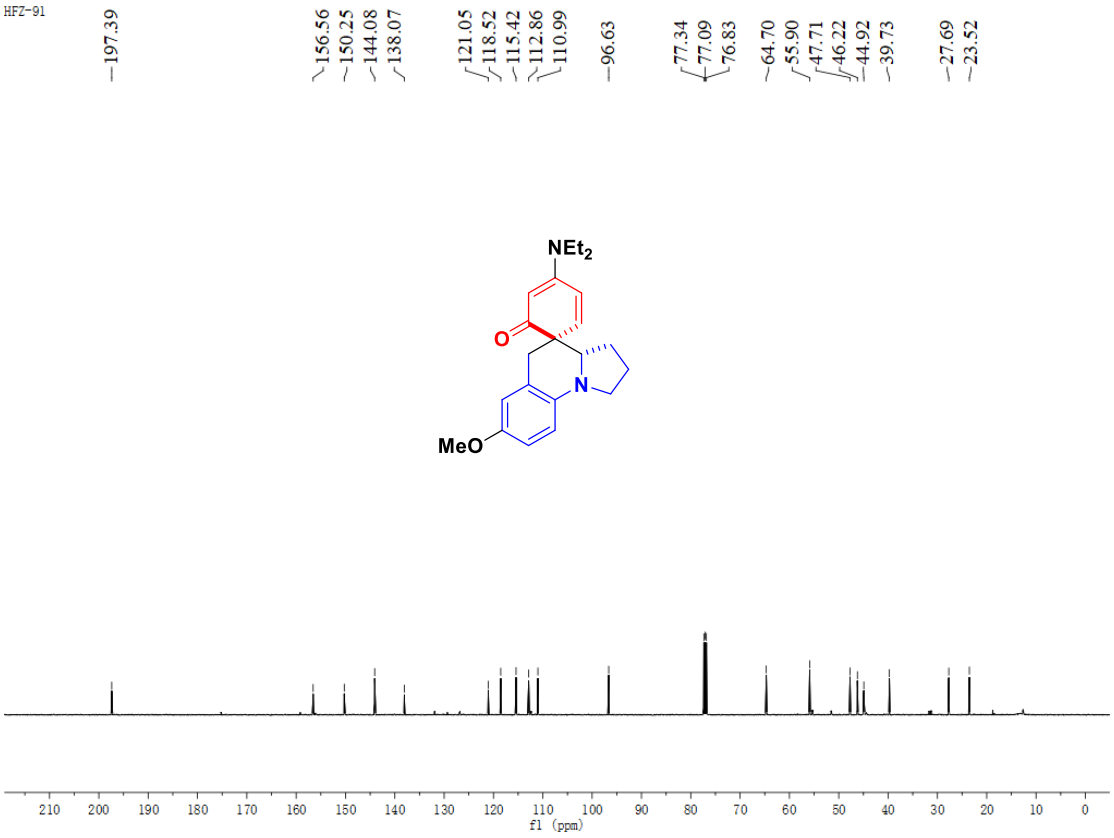




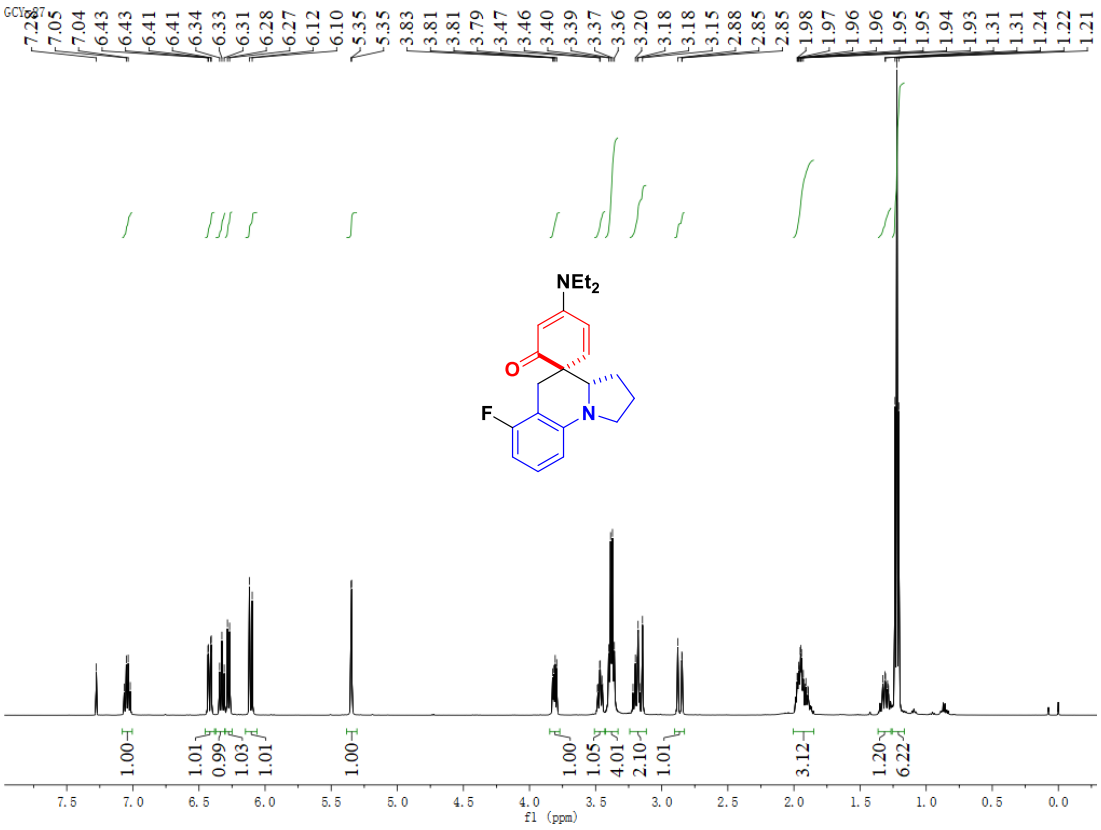


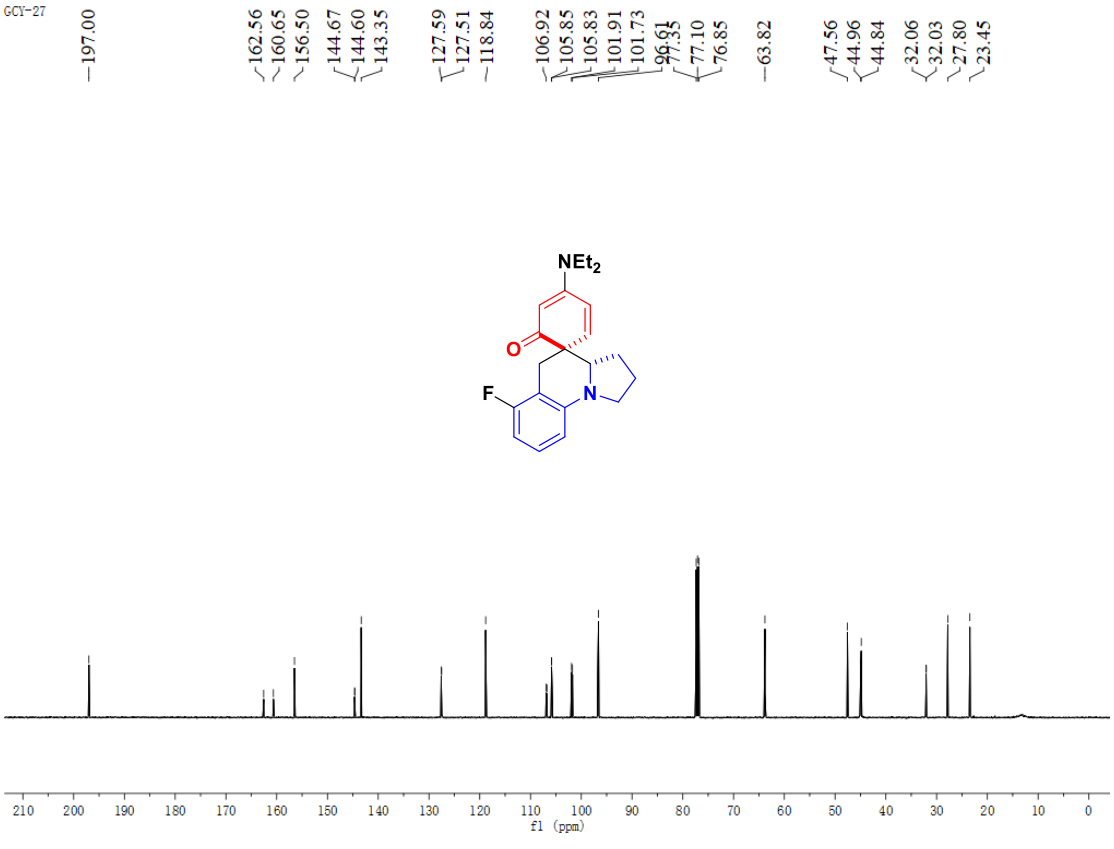
4-(diethylamino)-7'-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2d)



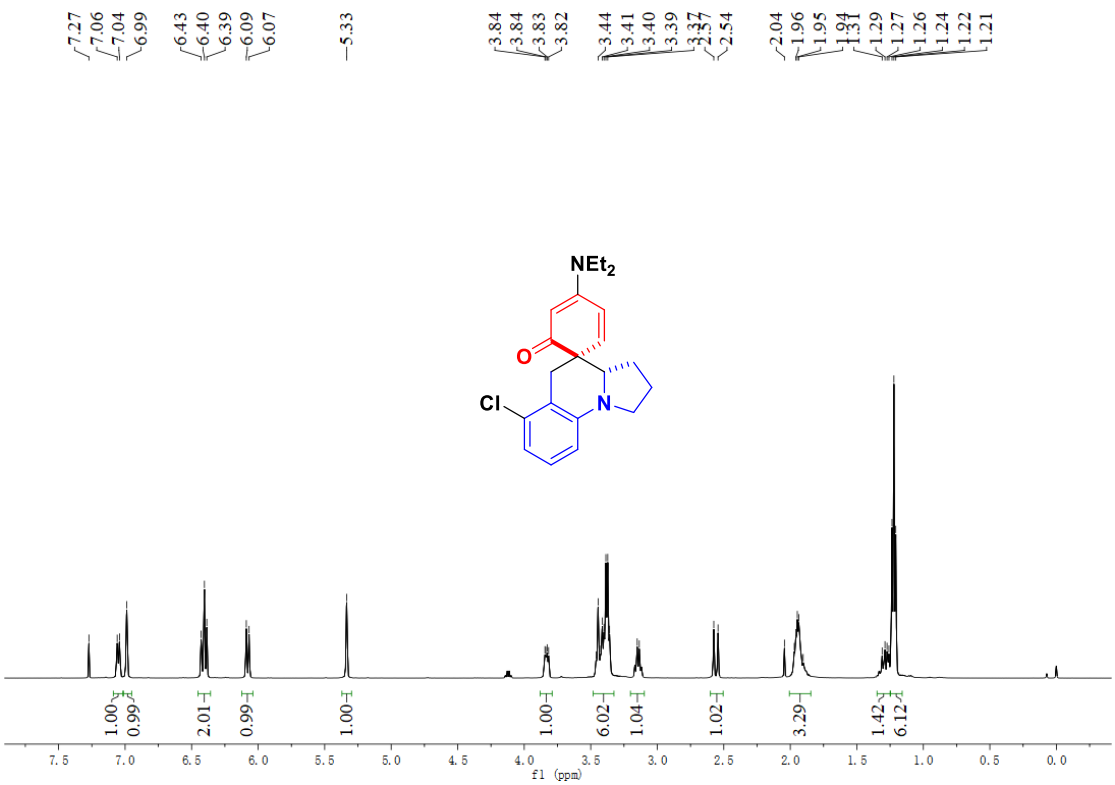


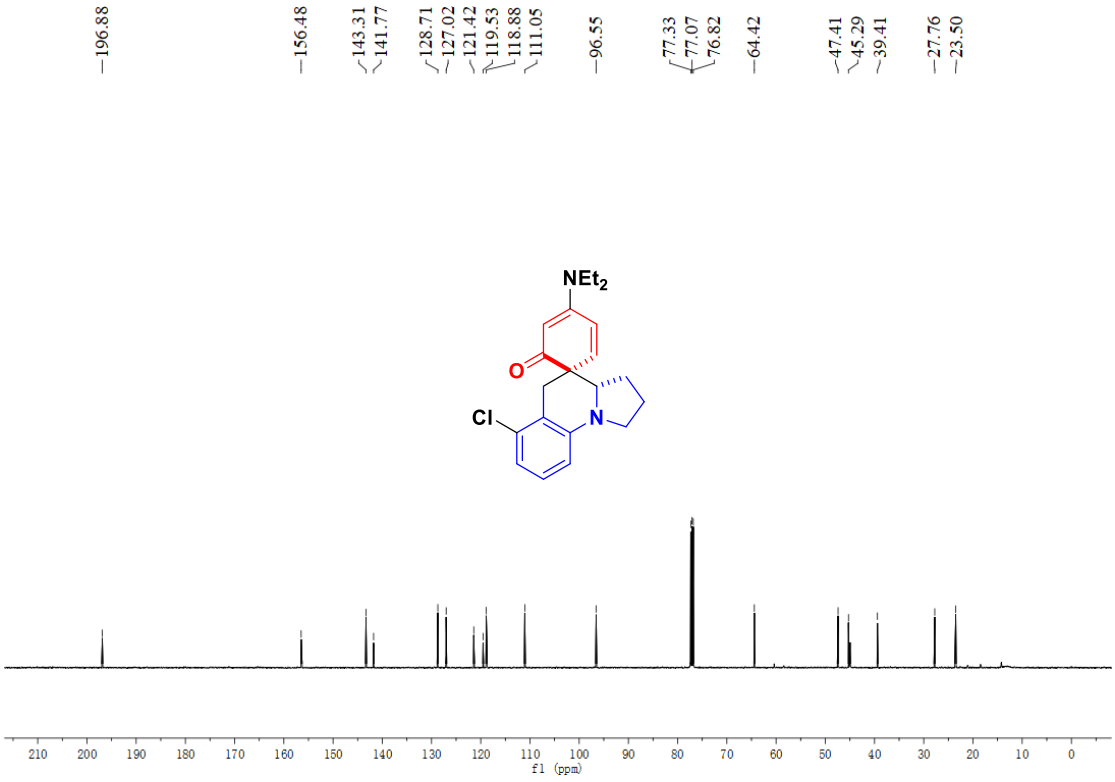
4-(diethylamino)-6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2e)



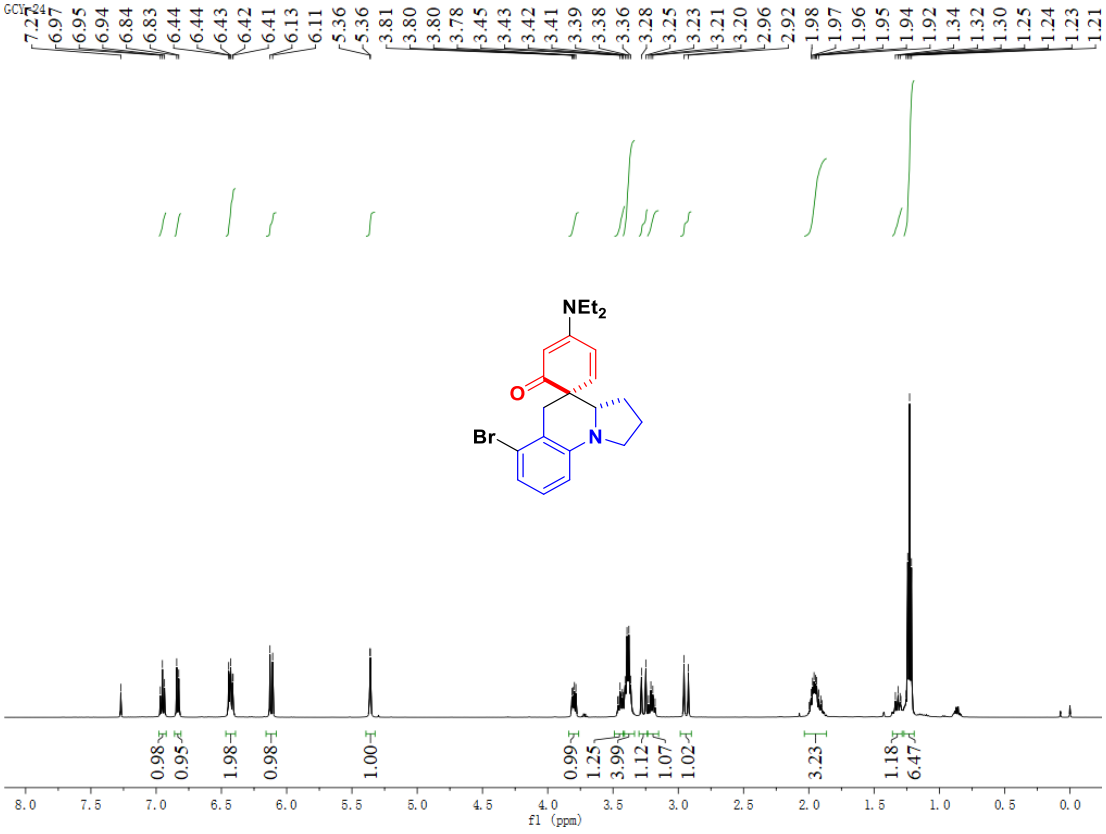


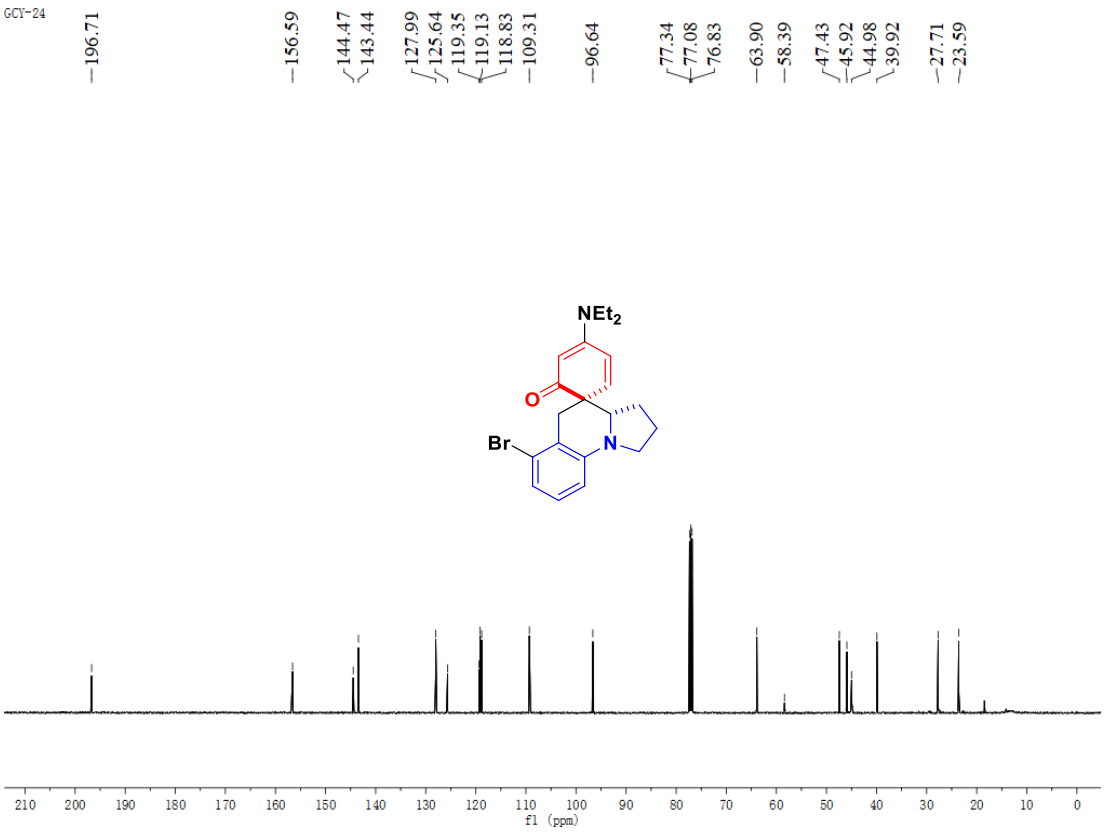
6'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2f)



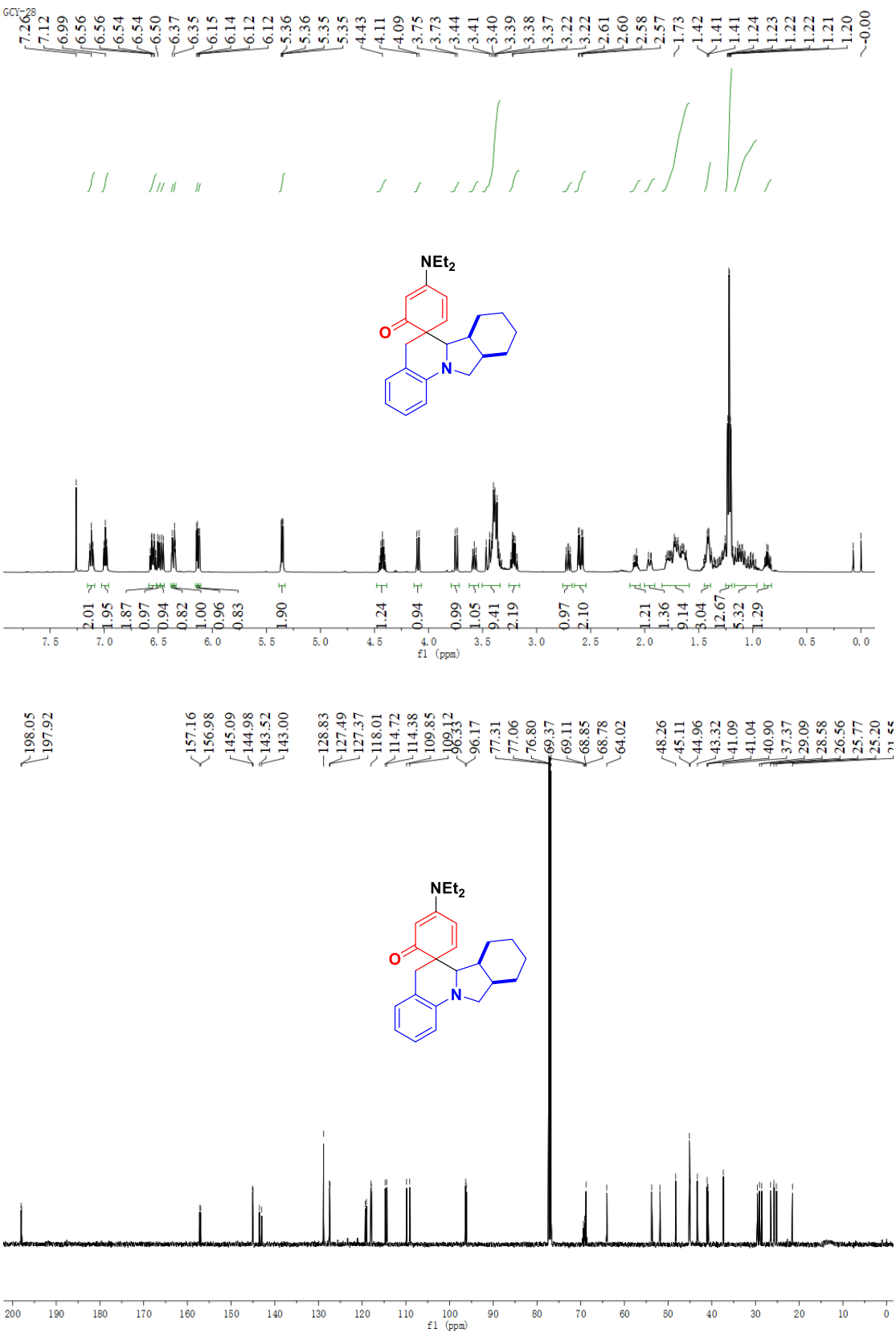


6'-bromo-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2g)

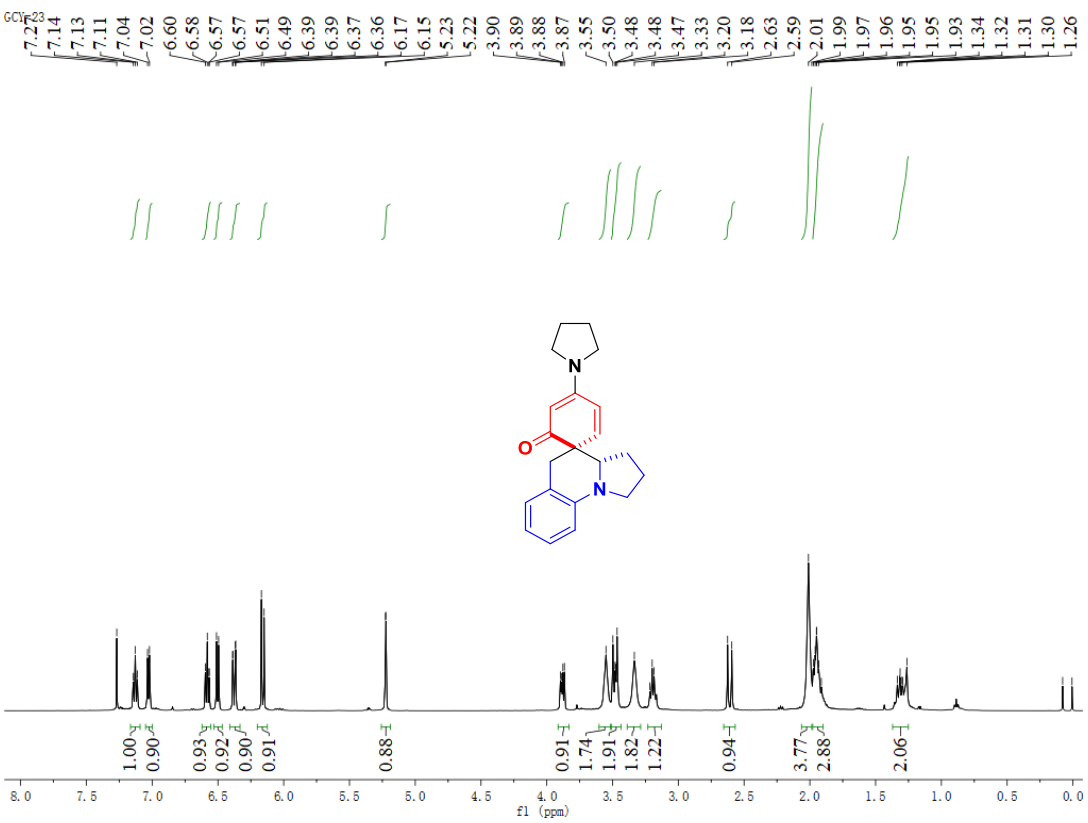


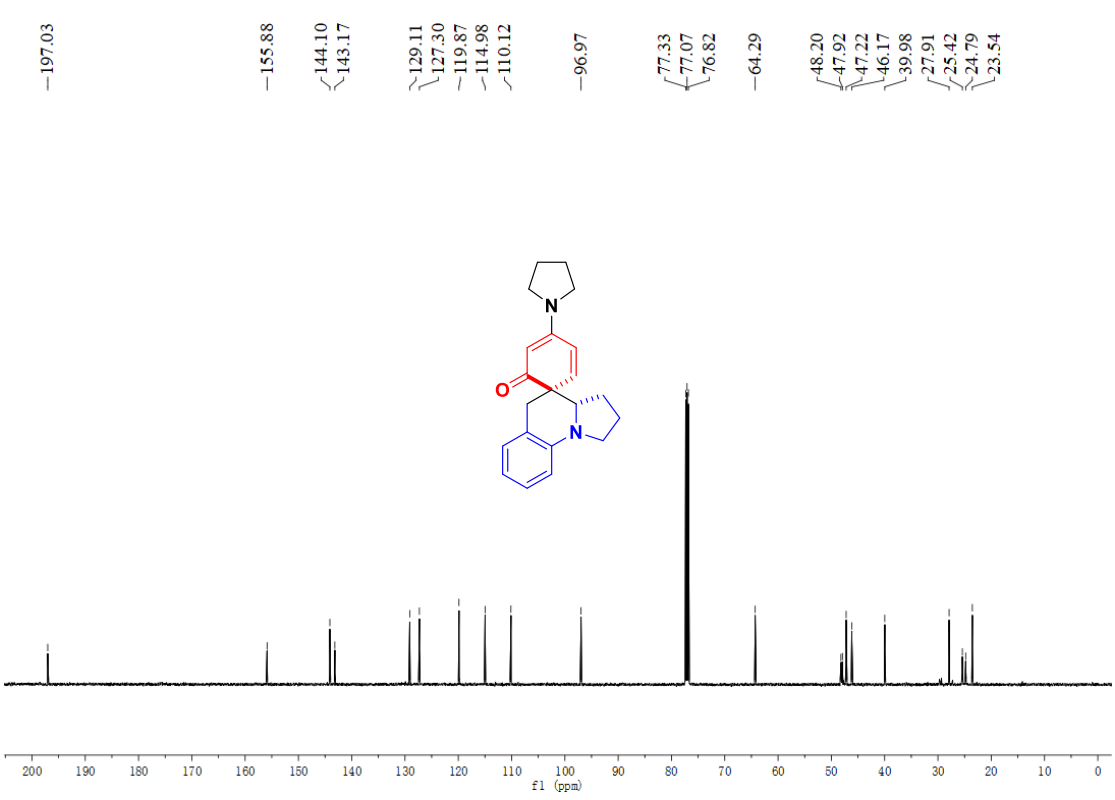


4-(diethylamino)-6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[cyclohexane-1,6'-isoindolo[2,1-a]quinoline]-2,4-dien-6-one (2h)

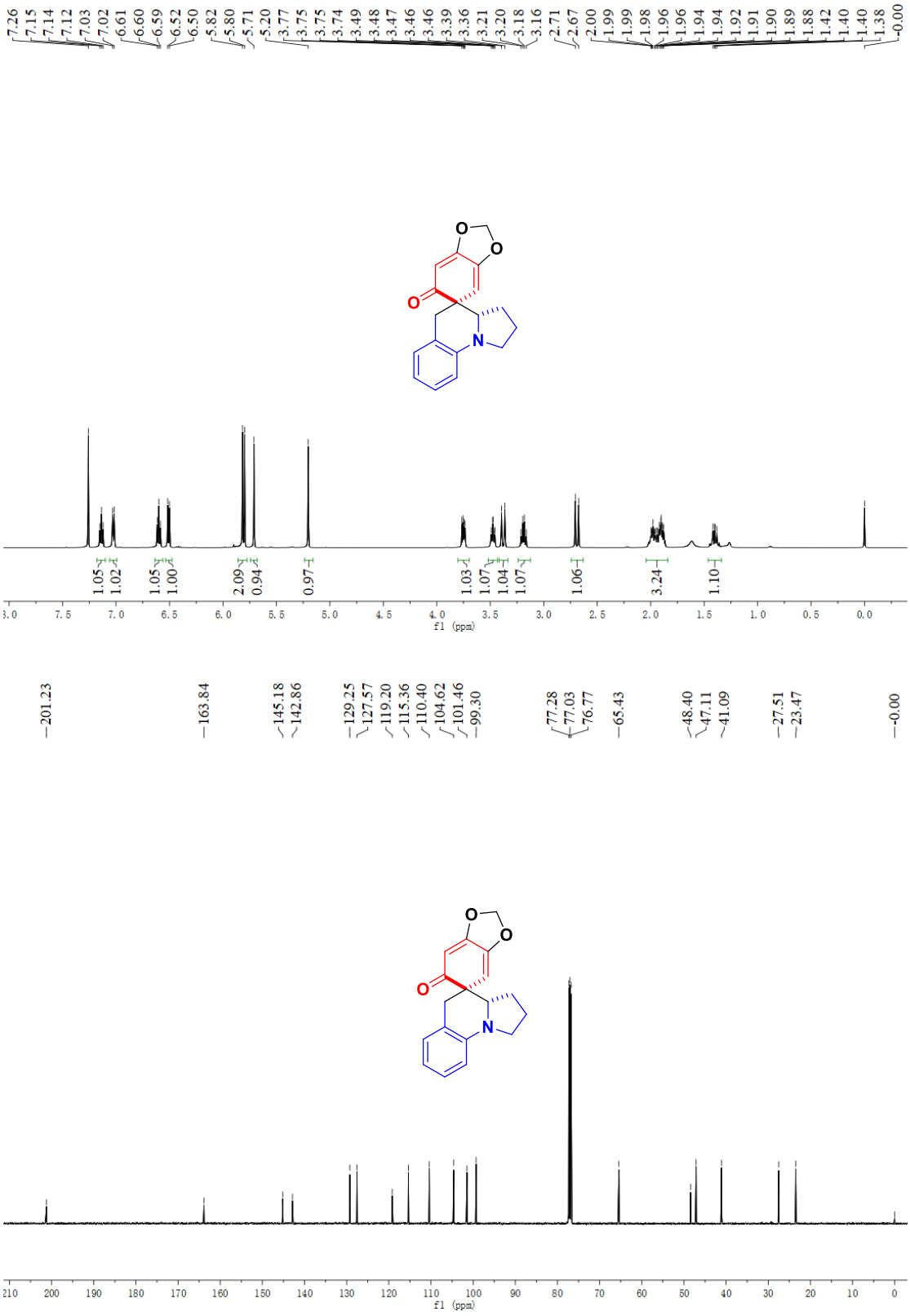


4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (2i)[3]

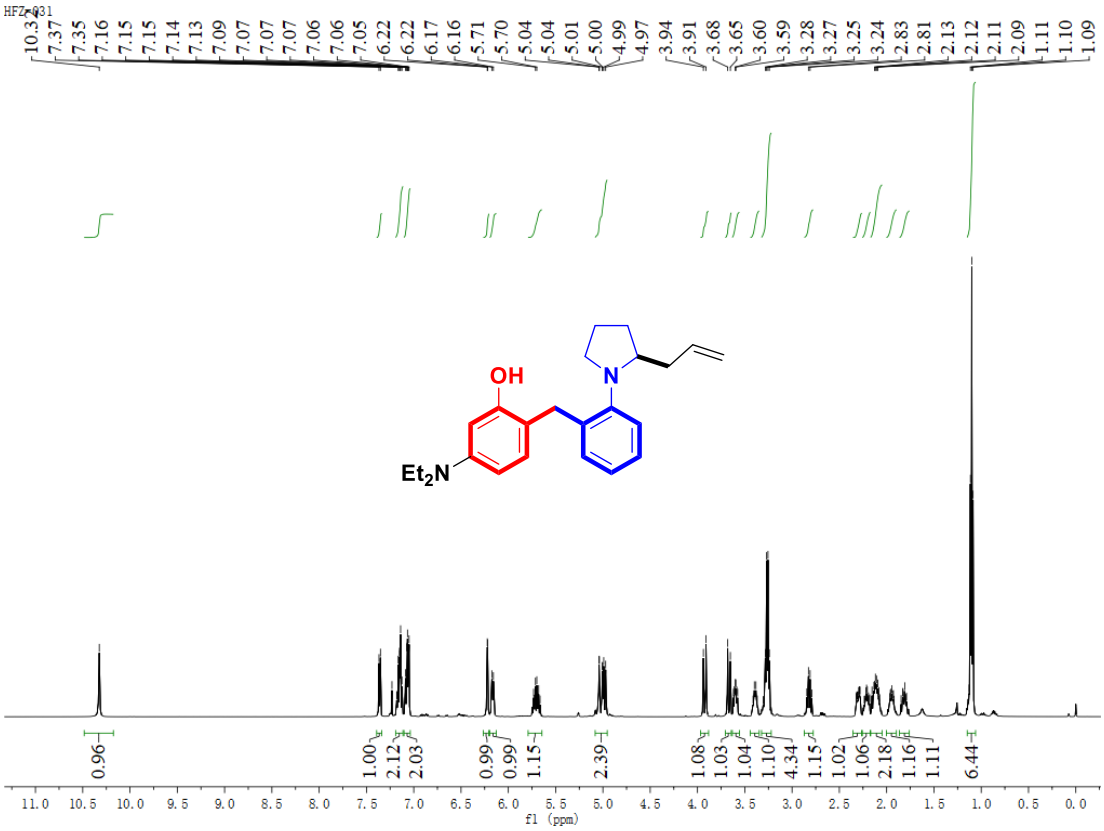


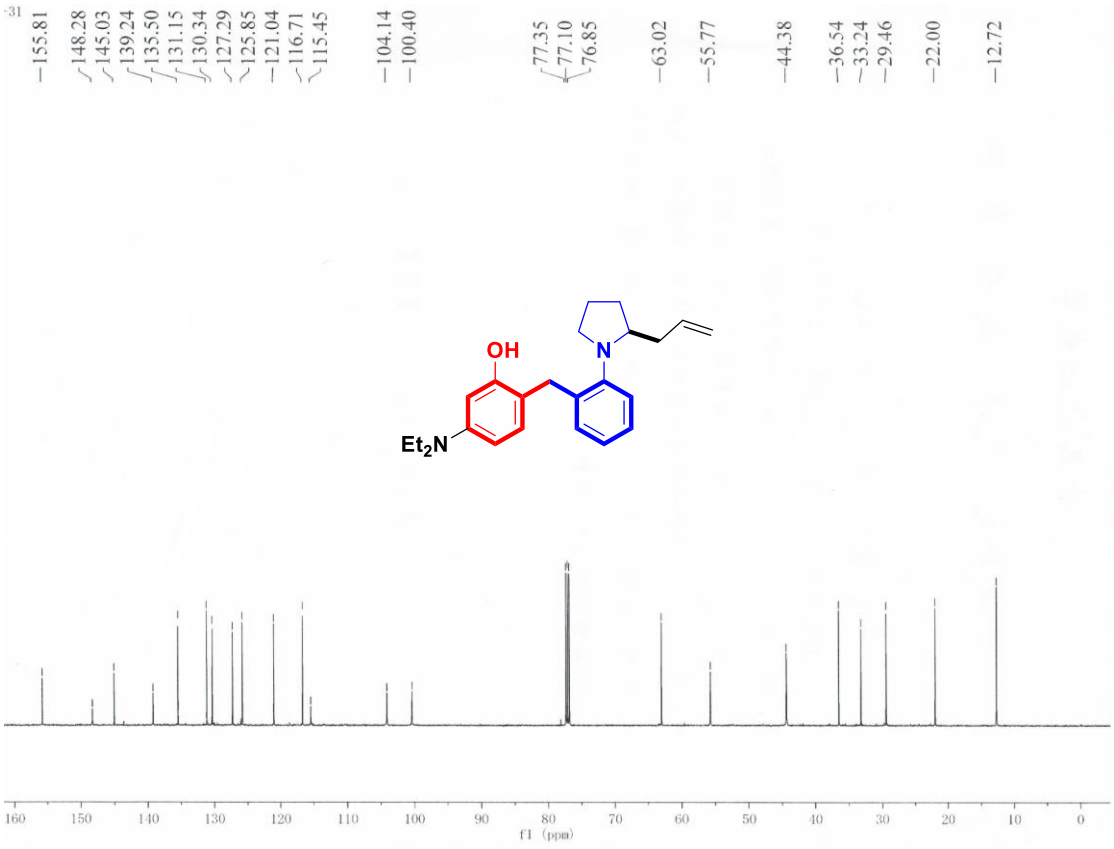


1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (2j)[3]

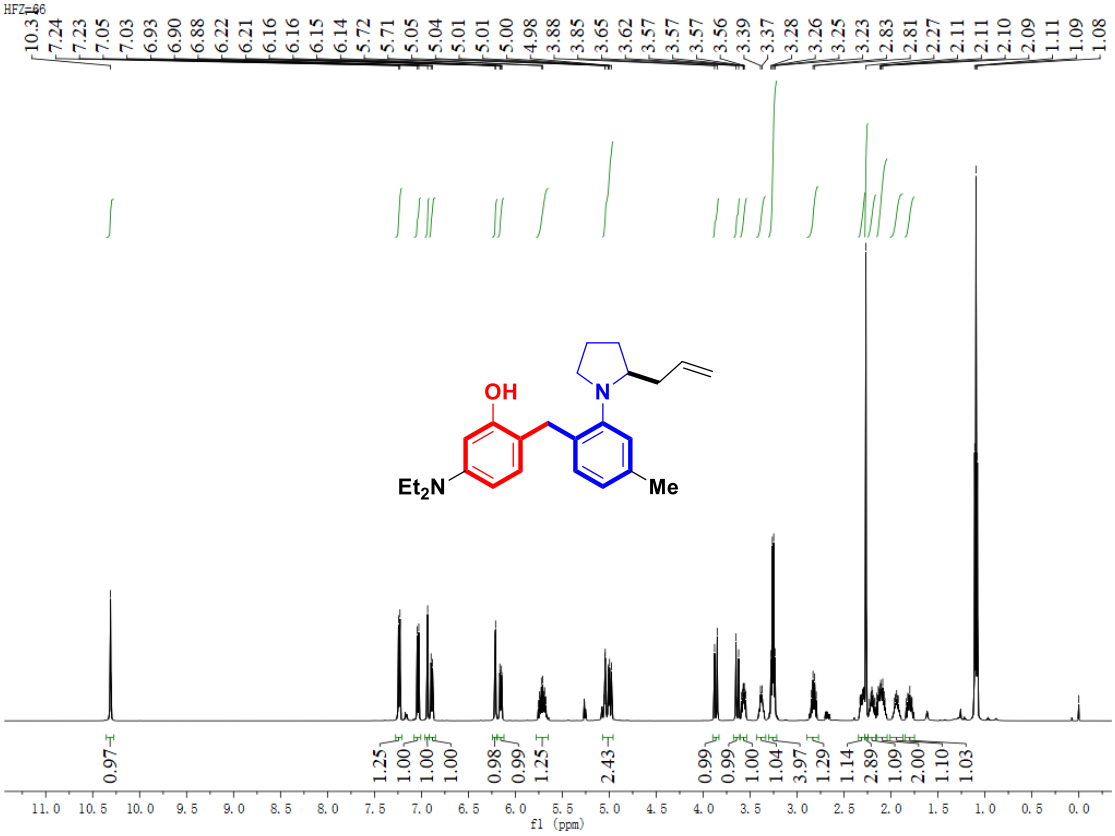


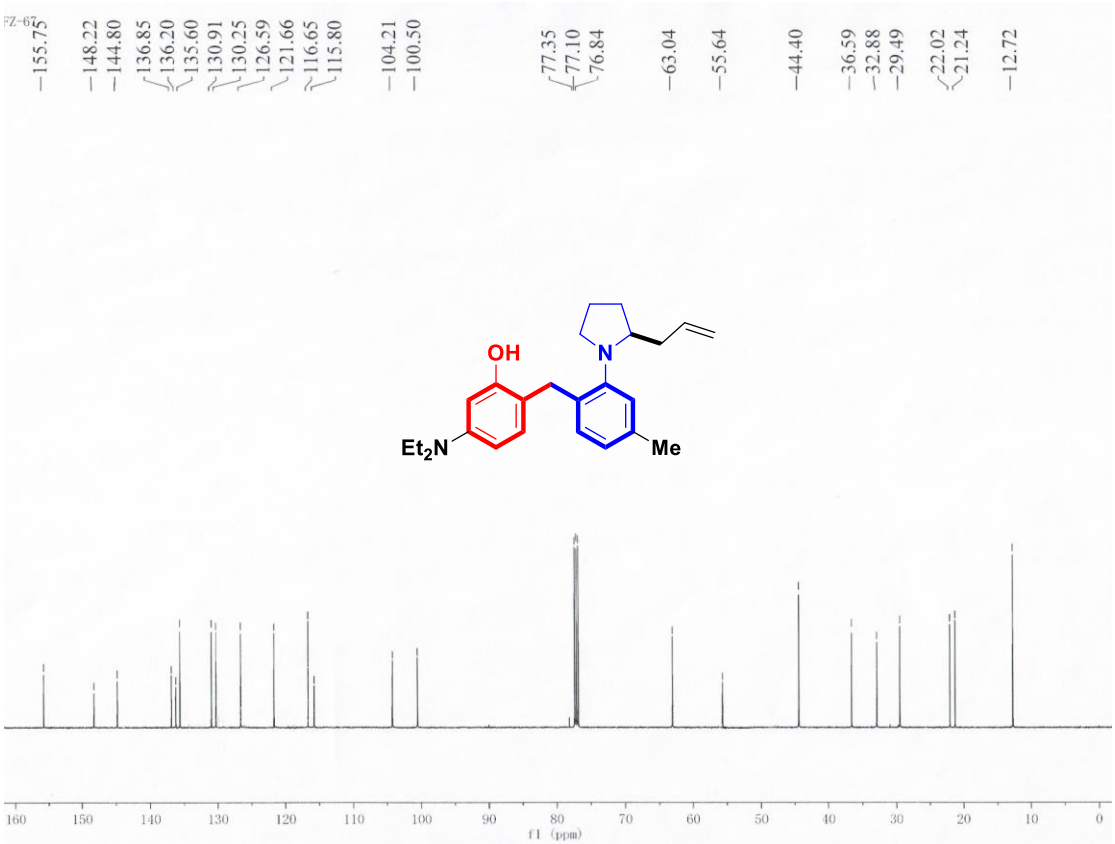
2-(2-(2-allylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3a)



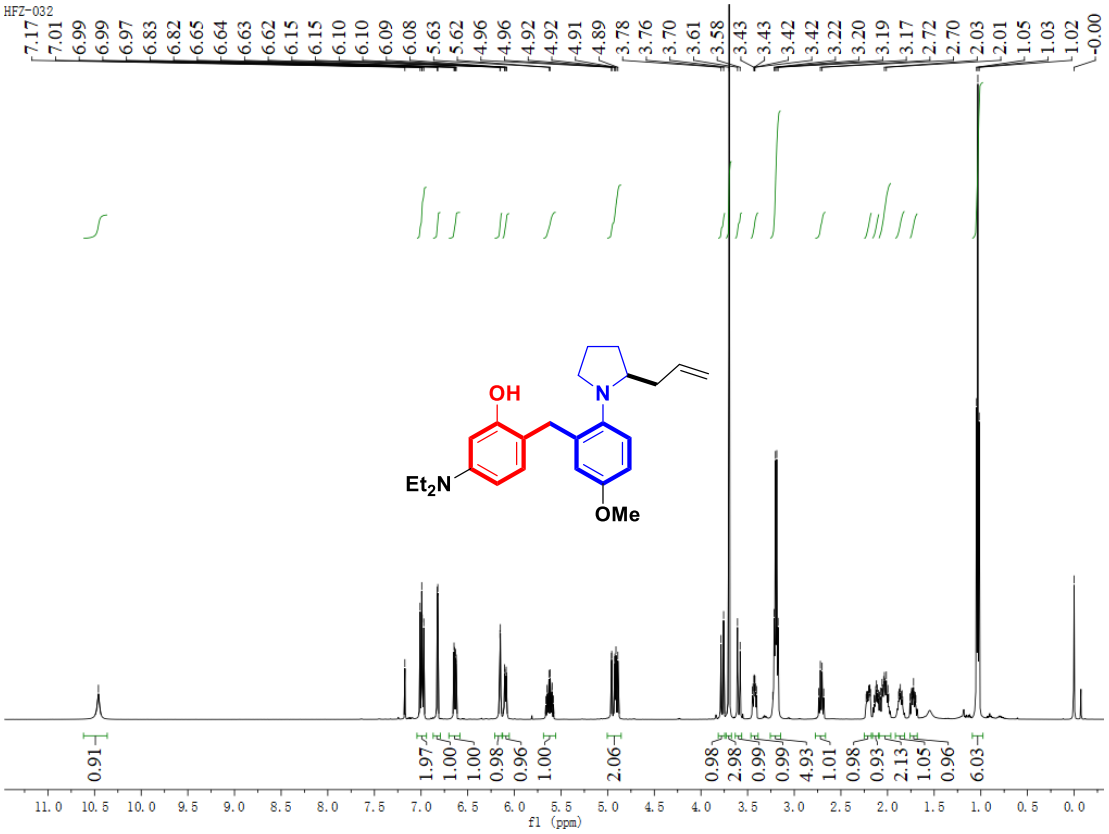


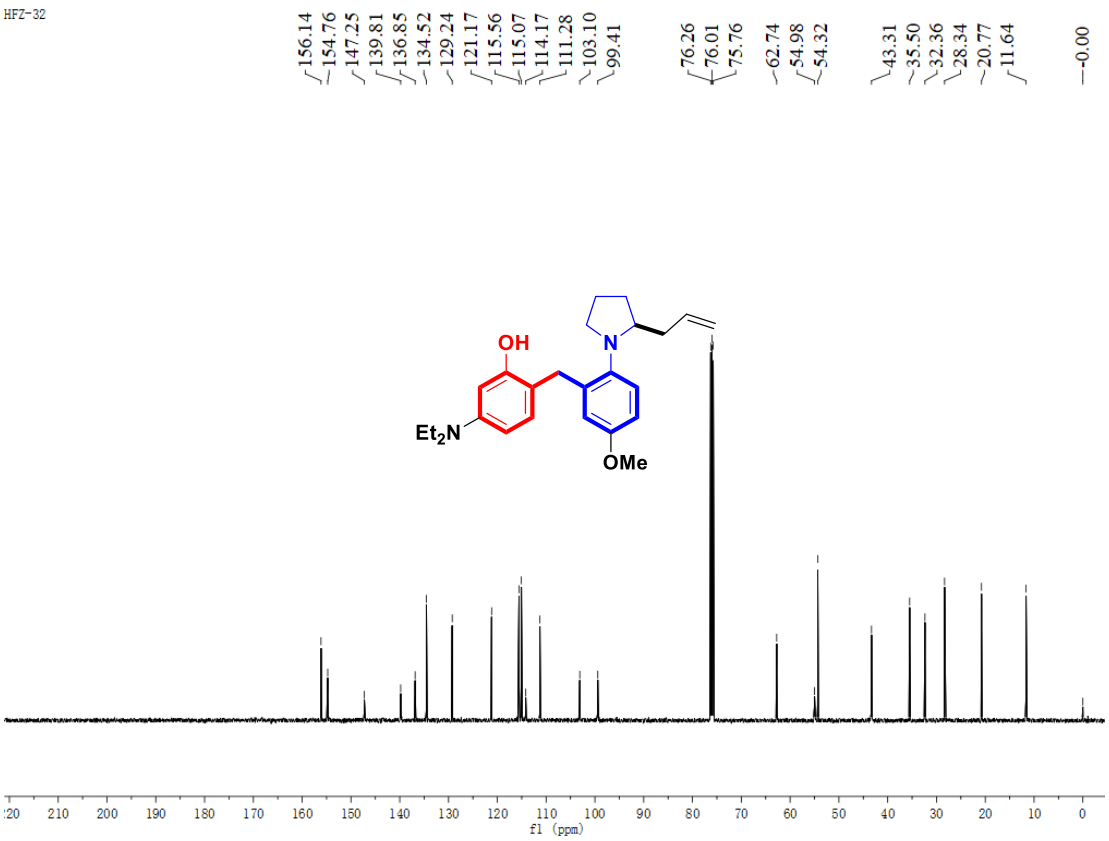
2-(2-(2-allylpyrrolidin-1-yl)-4-methylbenzyl)-5-(diethylamino)phenol (3b)



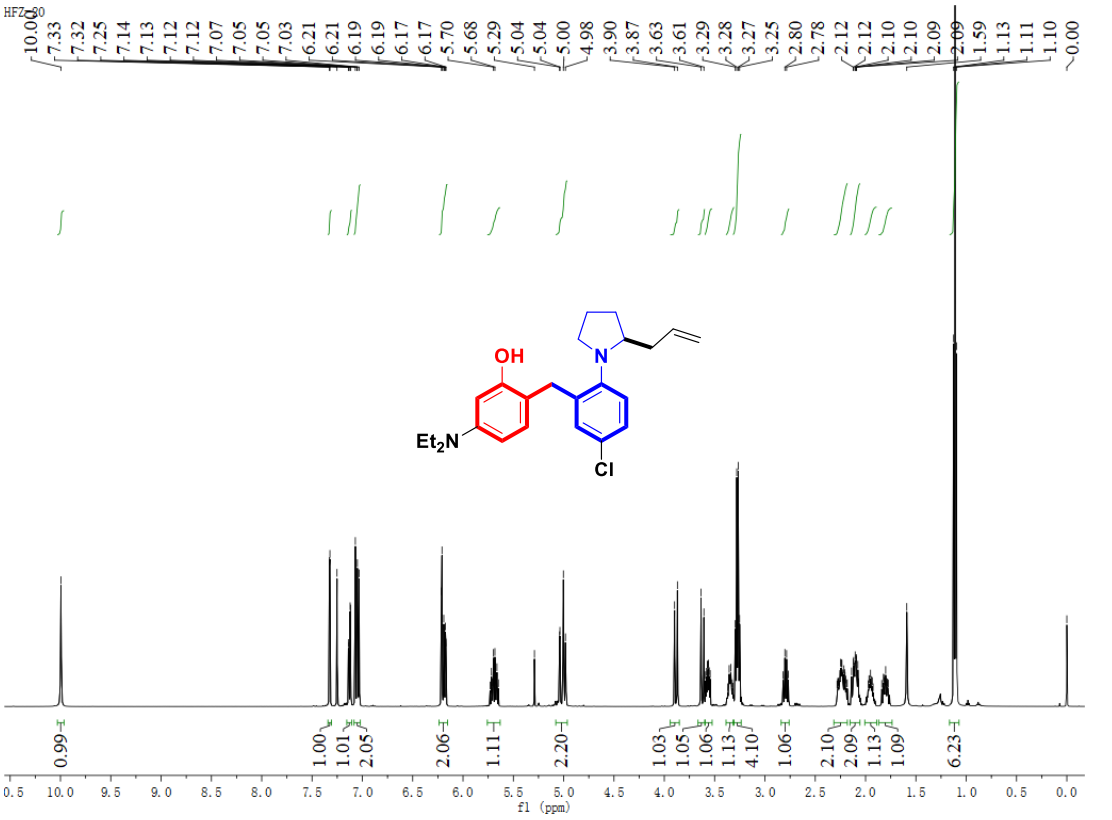


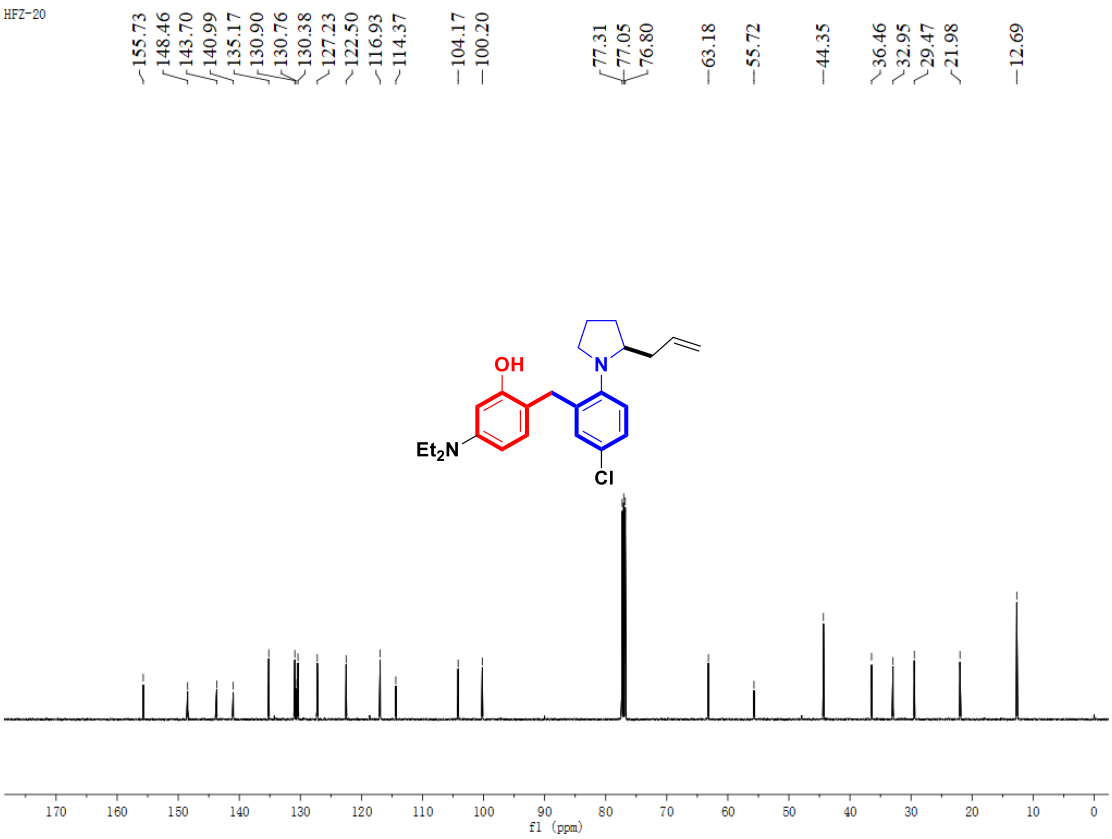
2-(2-(2-allylpyrrolidin-1-yl)-5-methoxybenzyl)-5-(diethylamino)phenol (3c)



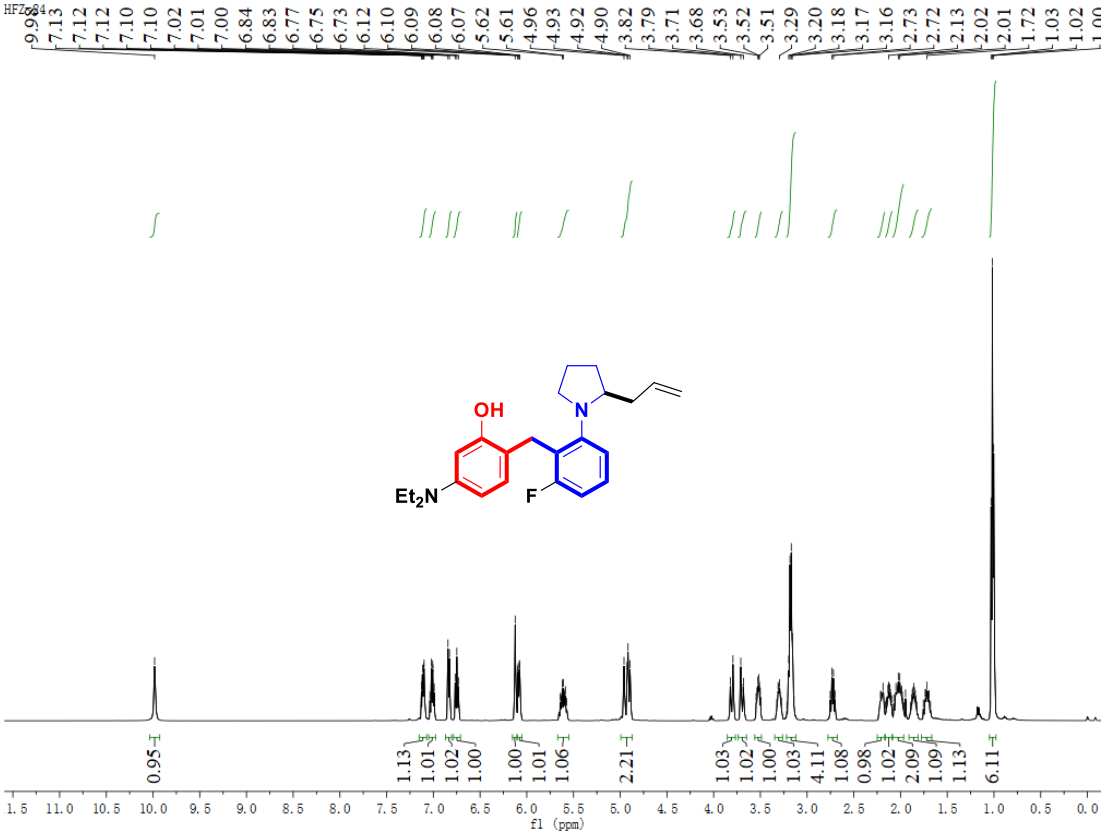


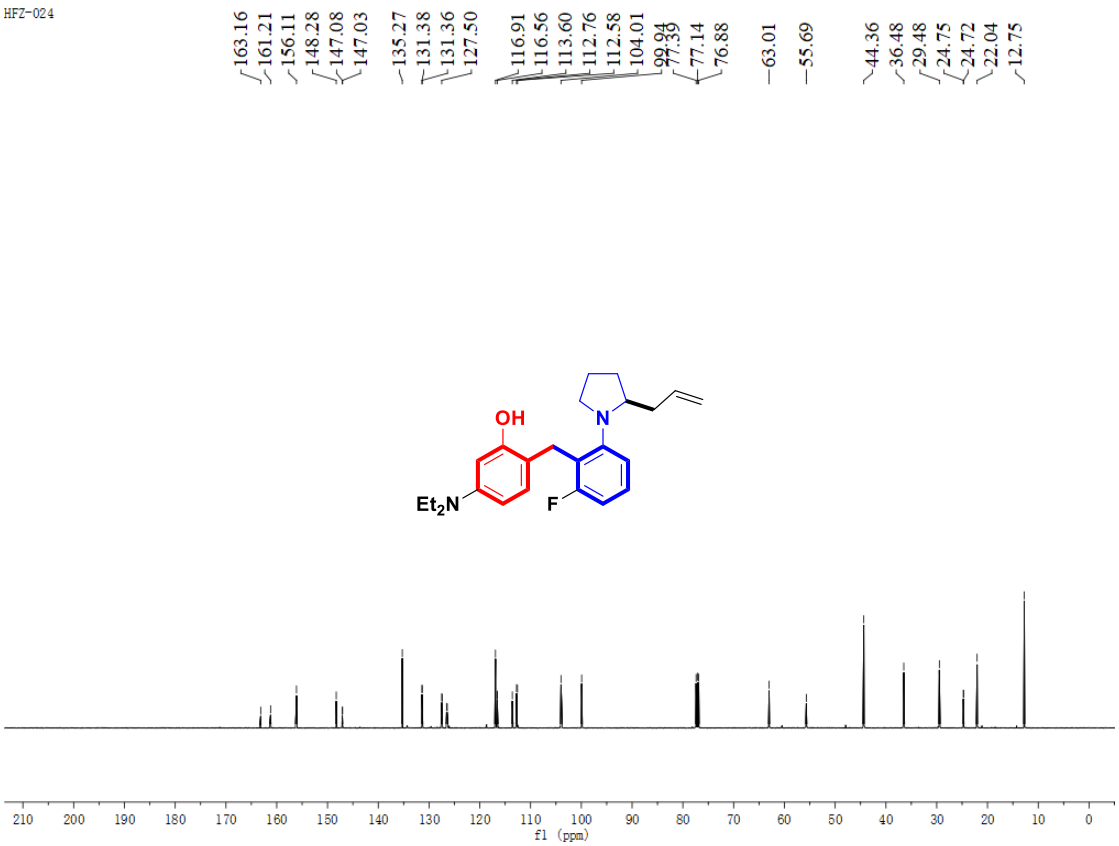
2-(2-(2-allylpyrrolidin-1-yl)-5-chlorobenzyl)-5-(diethylamino)phenol (3d)



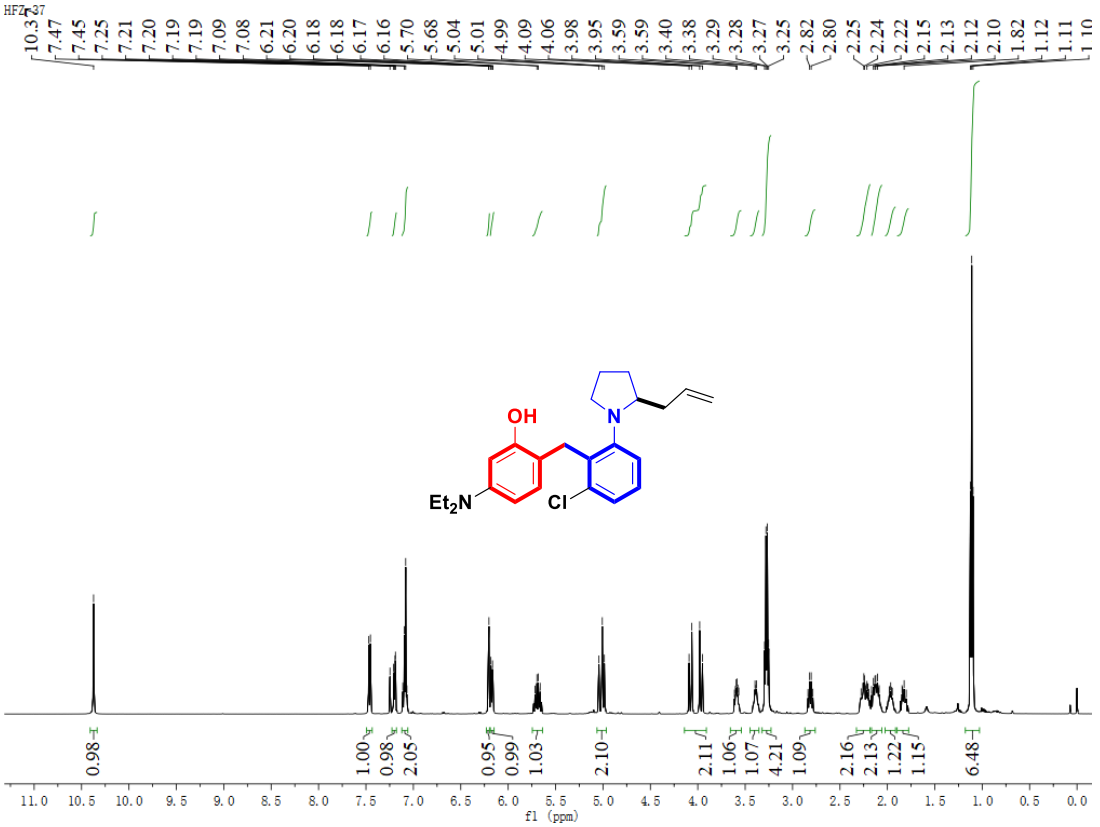


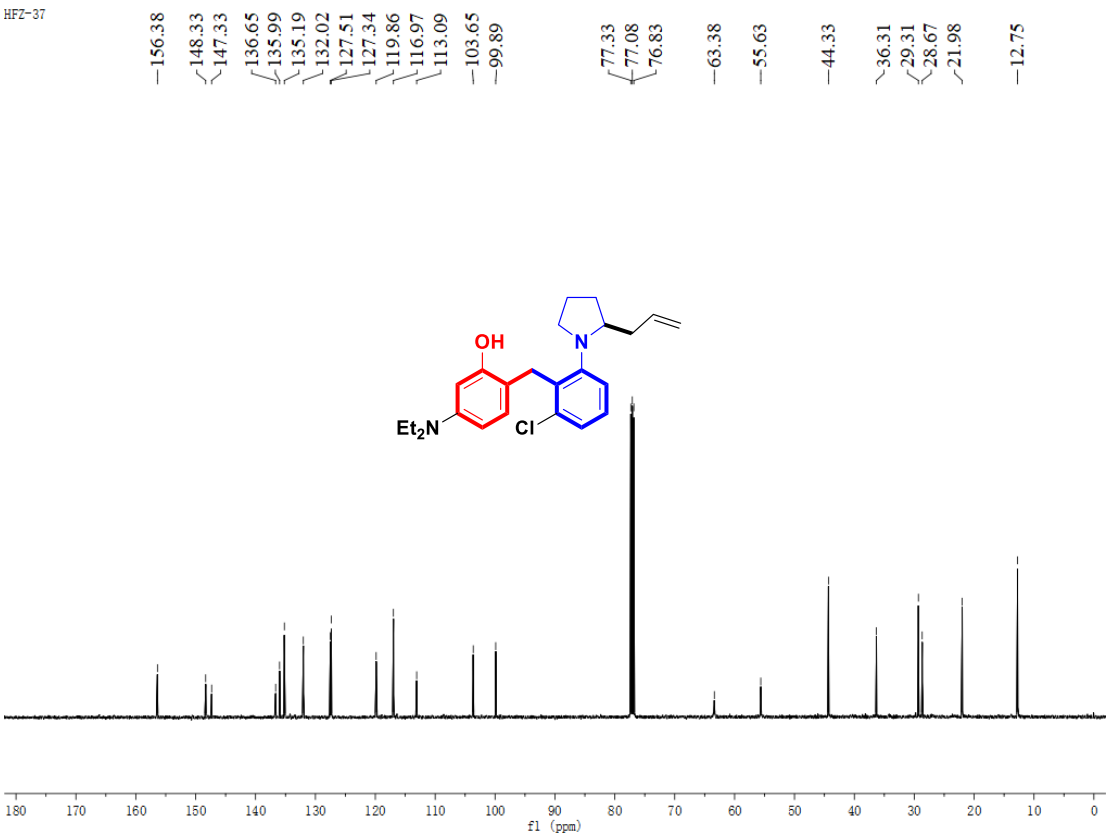
2-(2-(2-allylpyrrolidin-1-yl)-6-fluorobenzyl)-5-(diethylamino)phenol (3e)



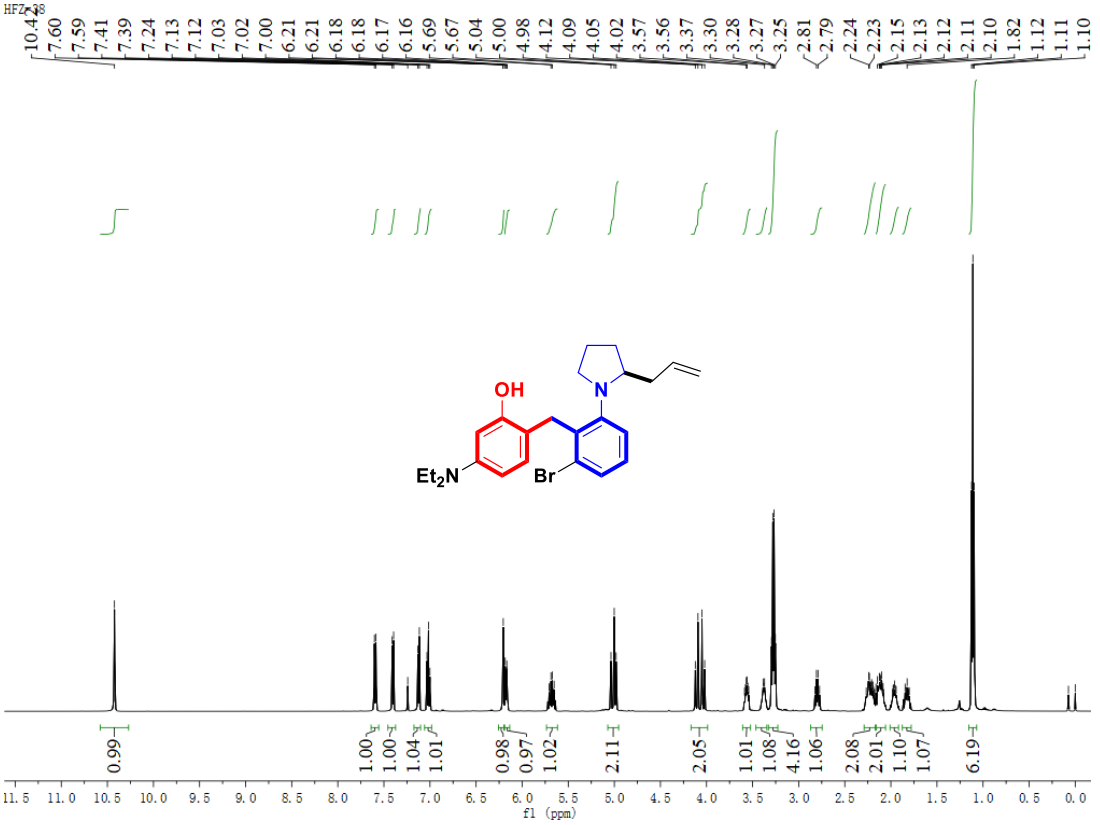


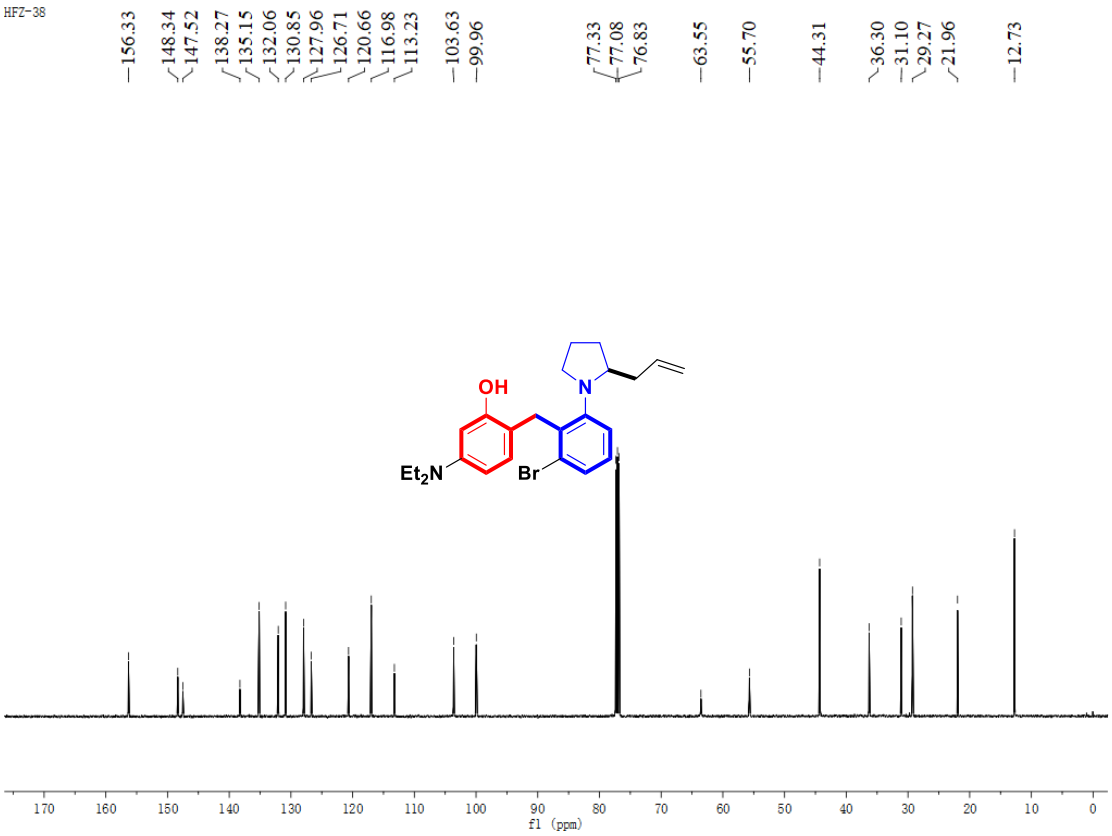
2-(2-(2-allylpyrrolidin-1-yl)-6-chlorobenzyl)-5-(diethylamino)phenol (3f)



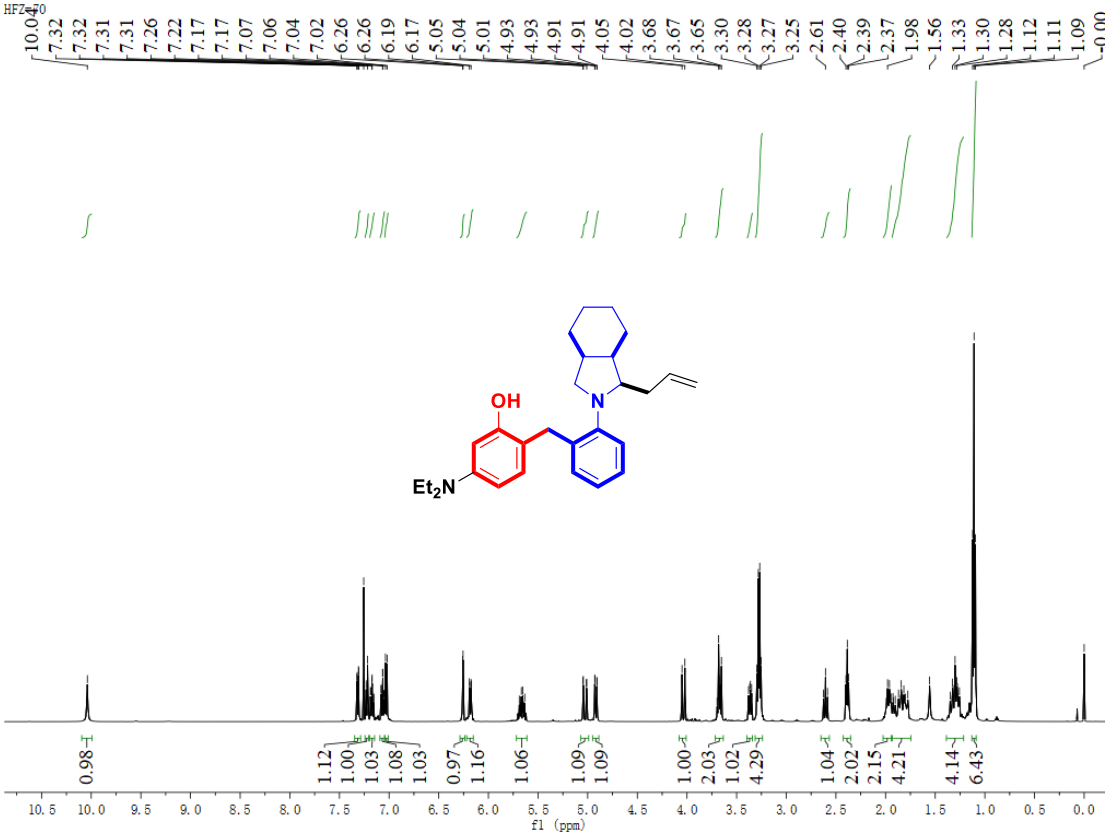


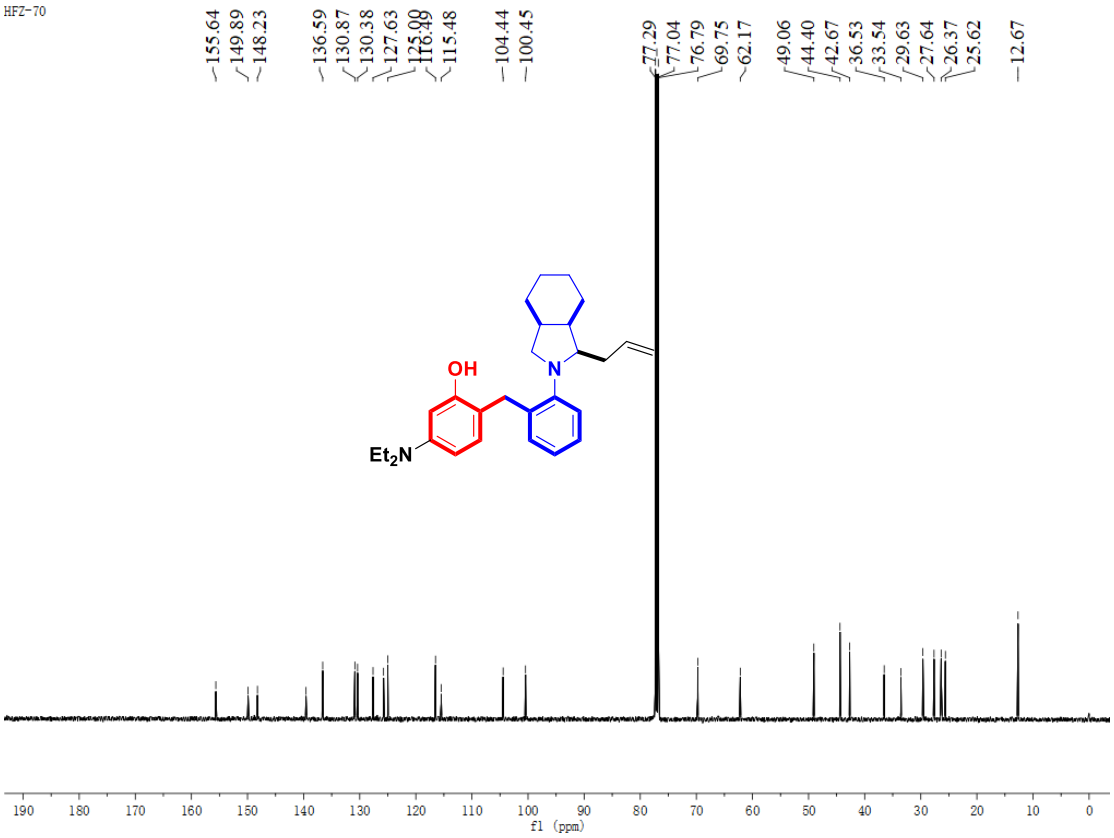
2-(2-(2-allylpyrrolidin-1-yl)-6-bromobenzyl)-5-(diethylamino)phenol (3g)



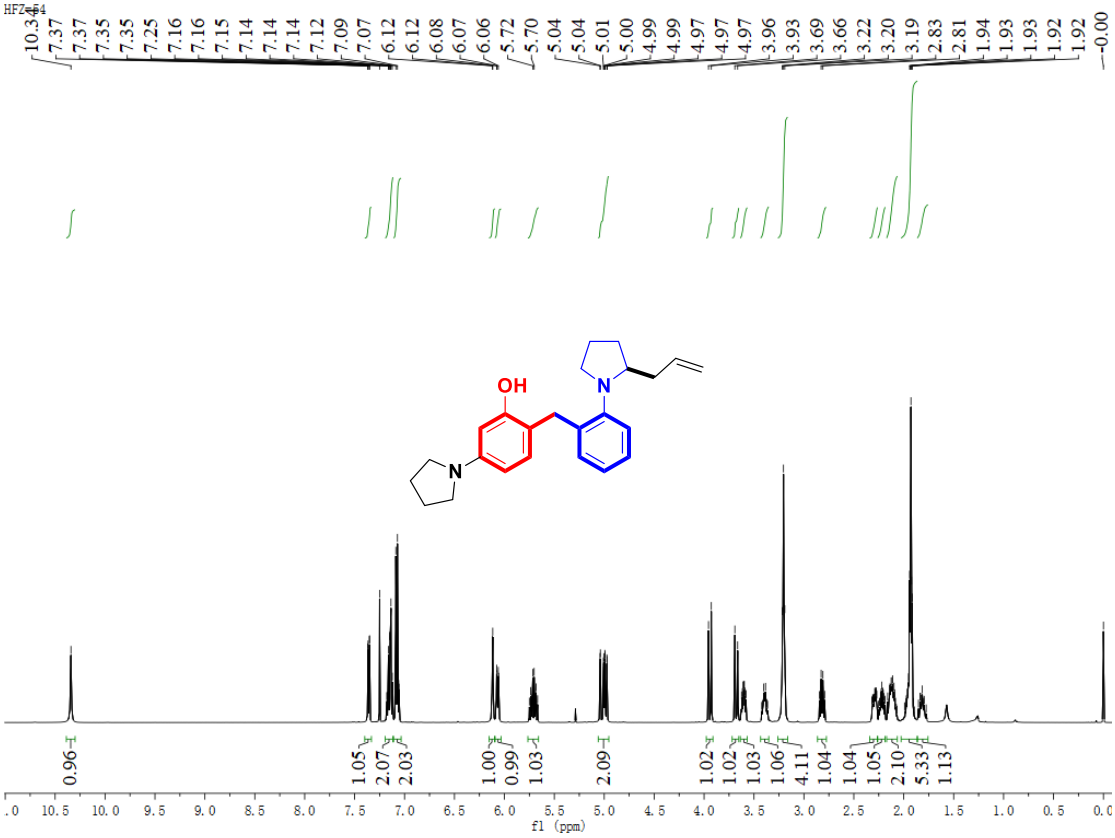


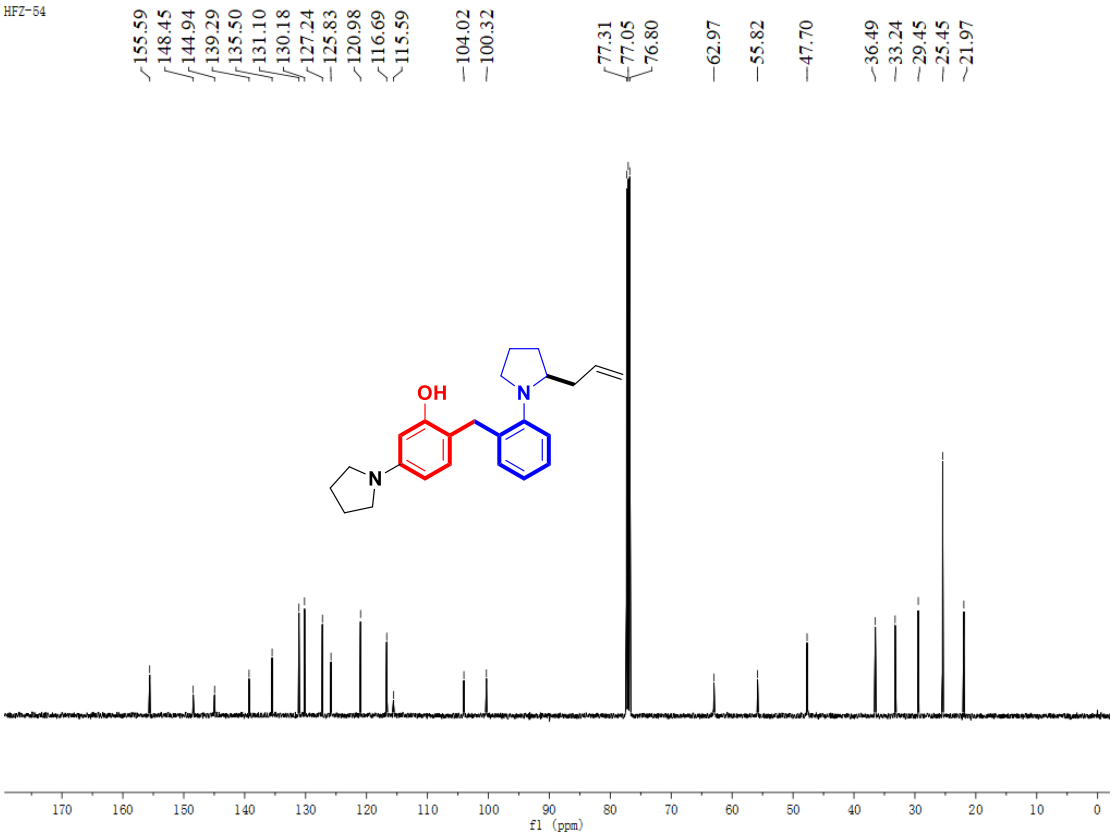
2-(2-(1-allyloctahydro-2H-isoindol-2-yl)benzyl)-5-(diethylamino)phenol (3h)



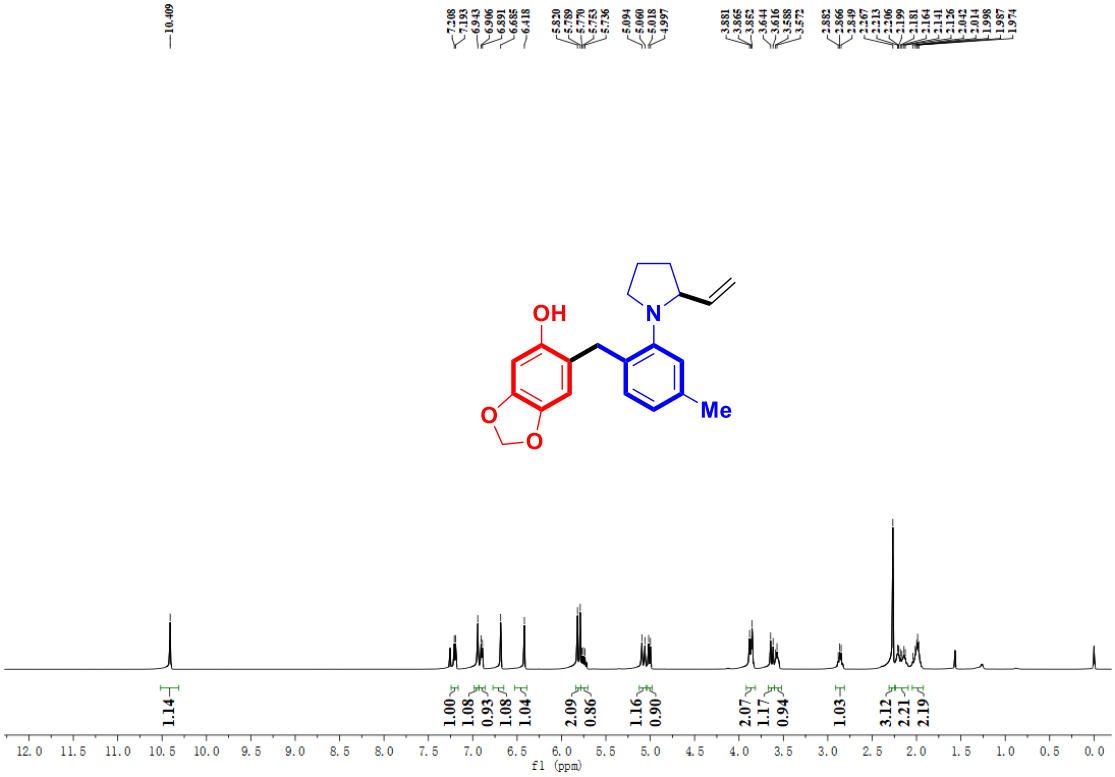


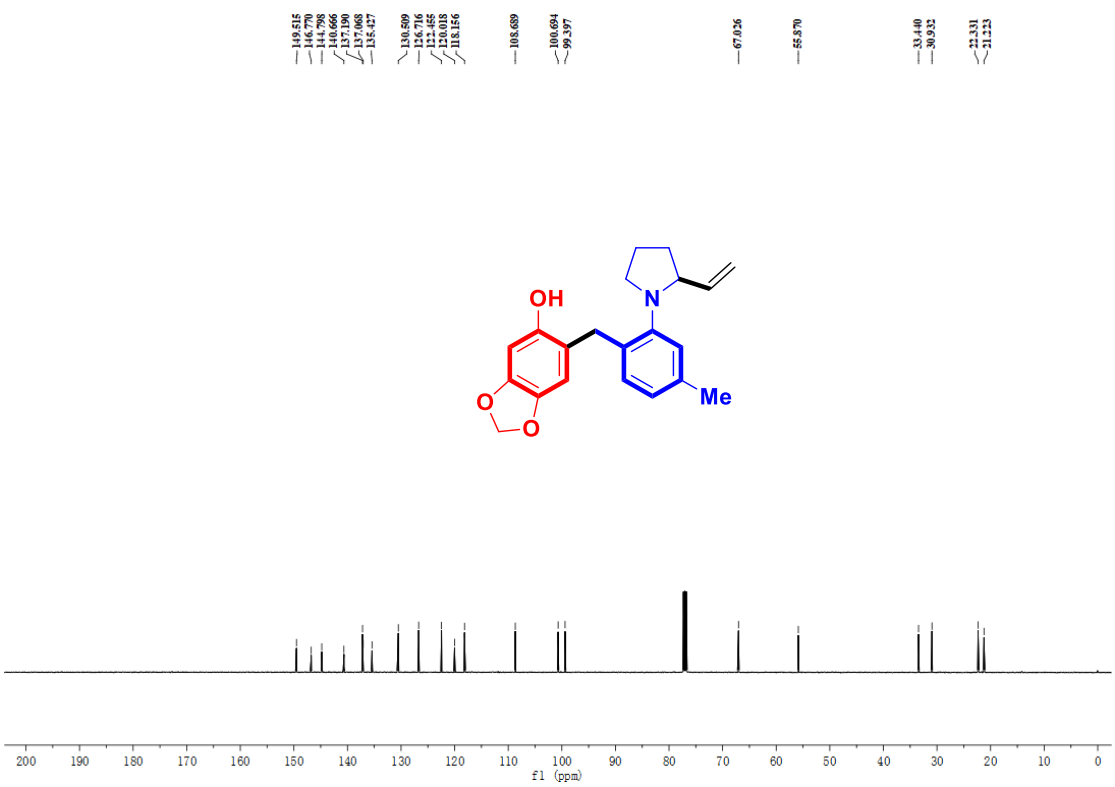
2-(2-(2-allylpyrrolidin-1-yl)benzyl)-5-(pyrrolidin-1-yl)phenol (3i)



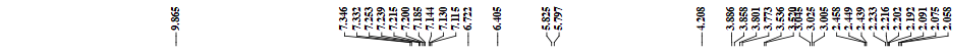


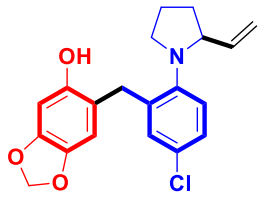
6-(4-methyl-2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3j)

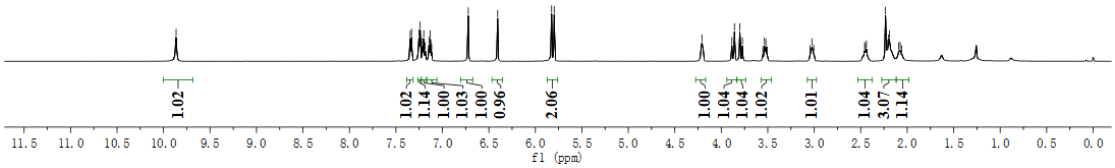


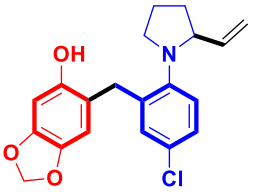


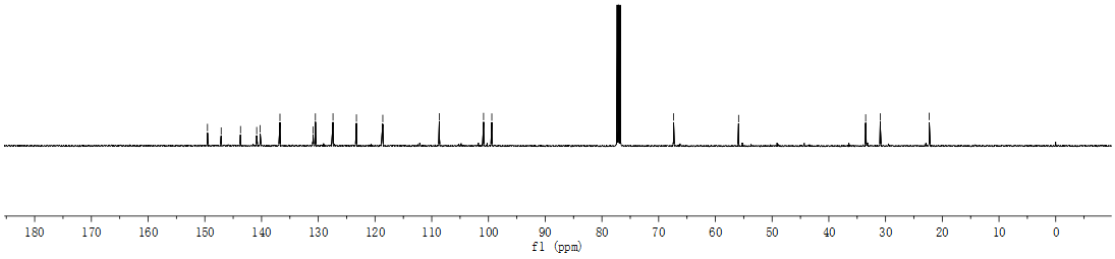
6-(5-chloro-2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3k)



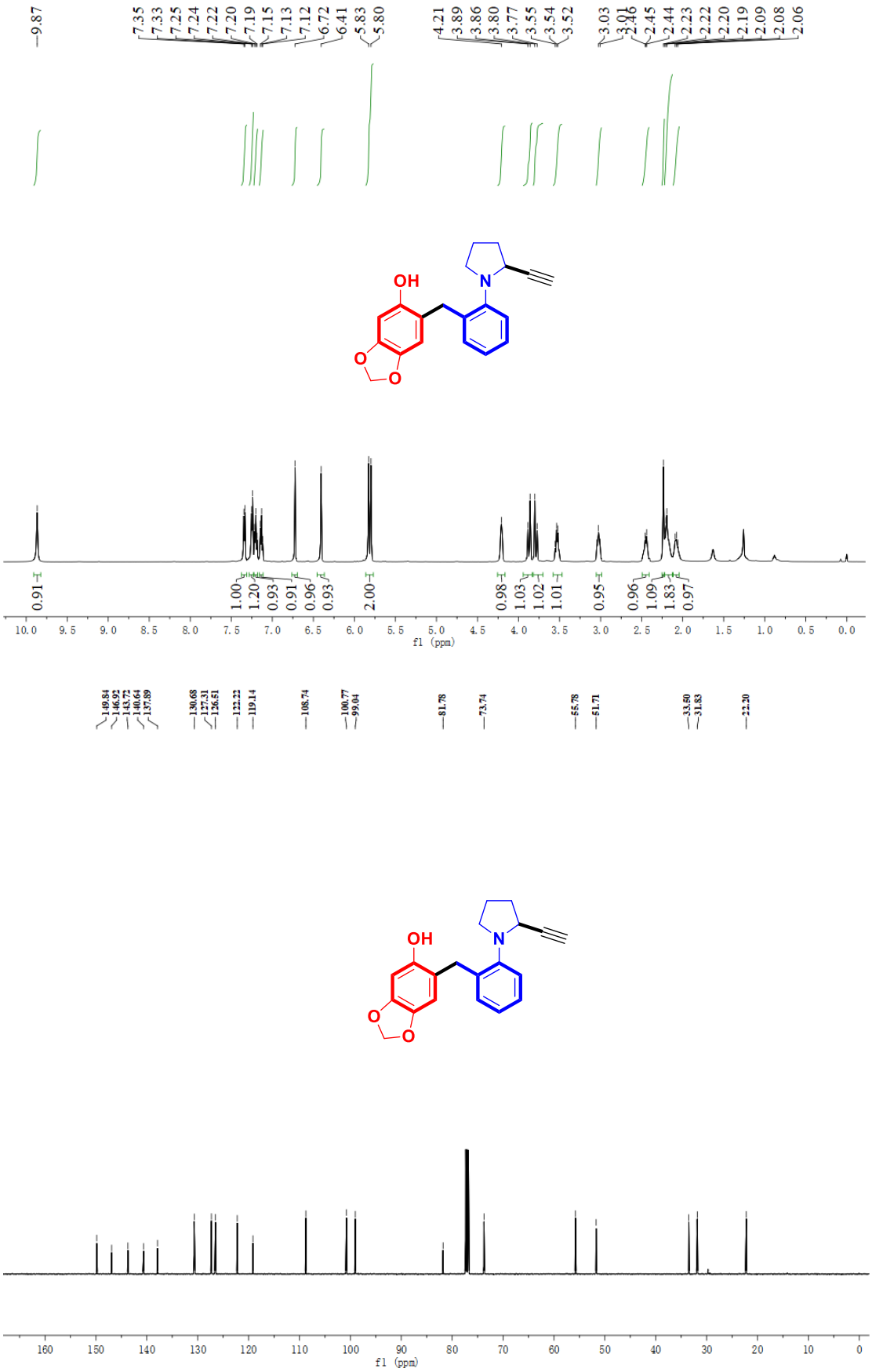




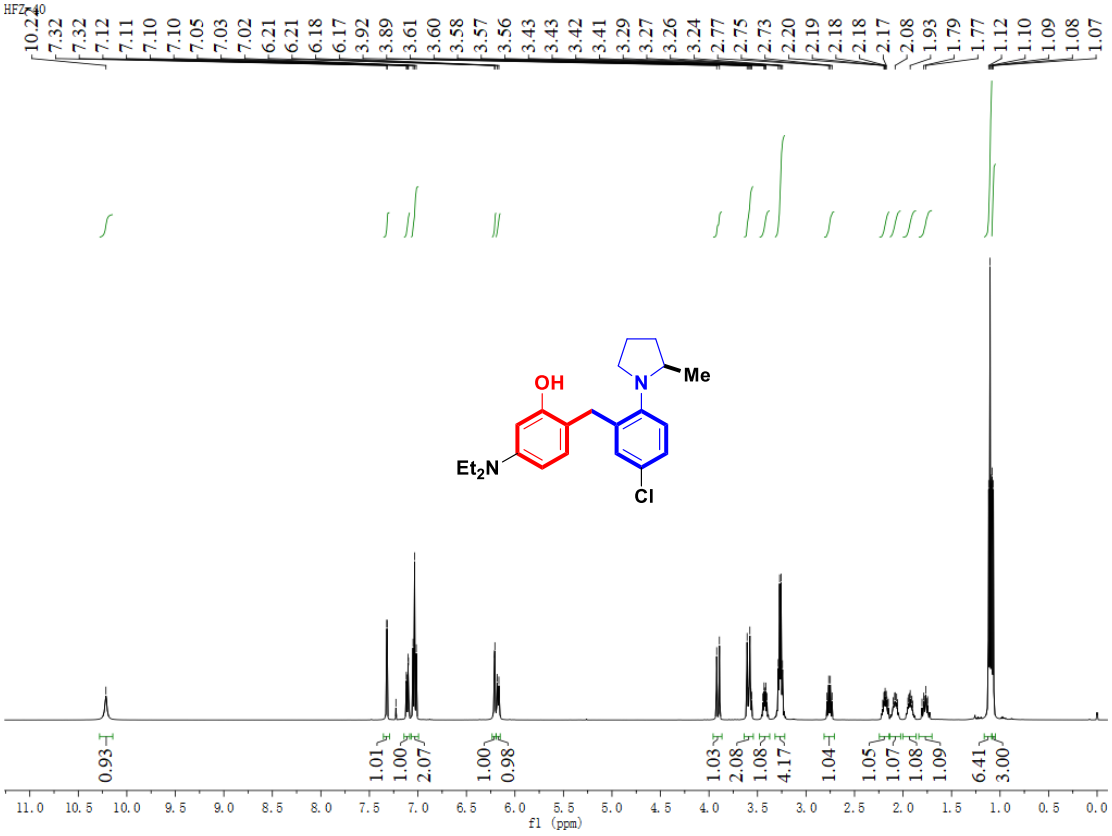


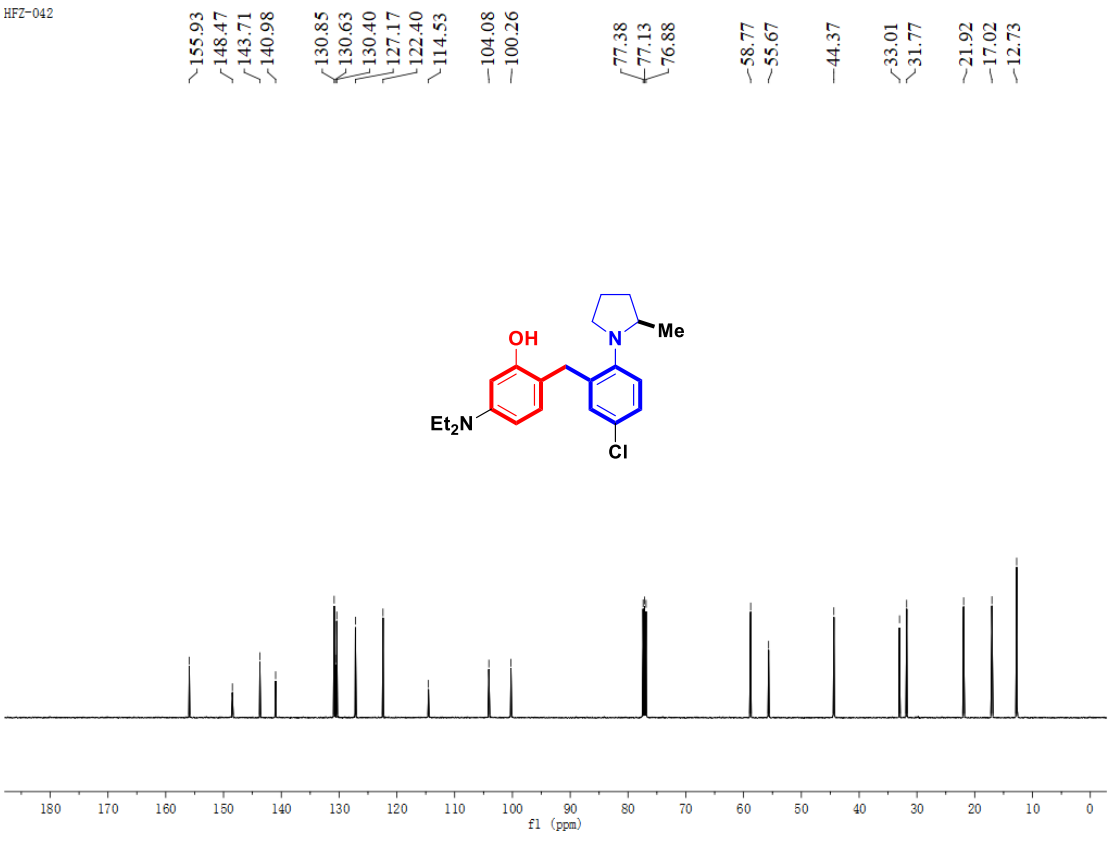


6-(2-(2-ethynylpyrrolidin-1-yl)benzyl)benzo[*d*][1,3]dioxol-5-ol (3l)[3]

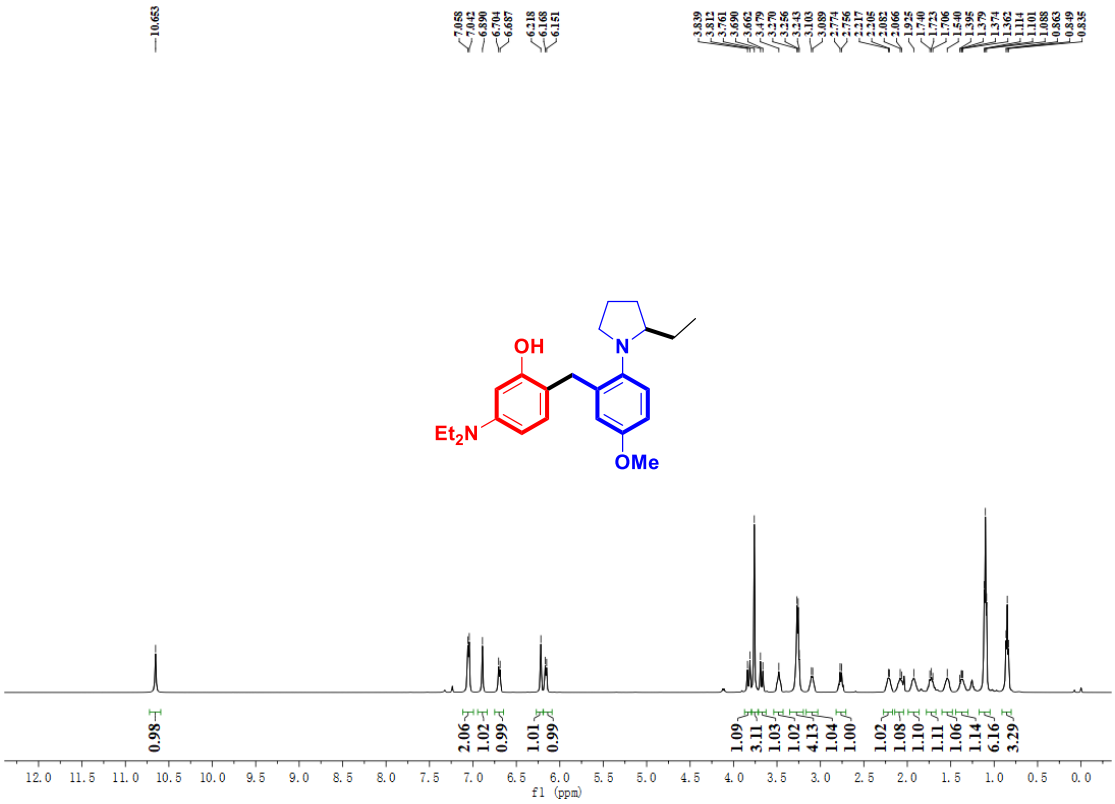


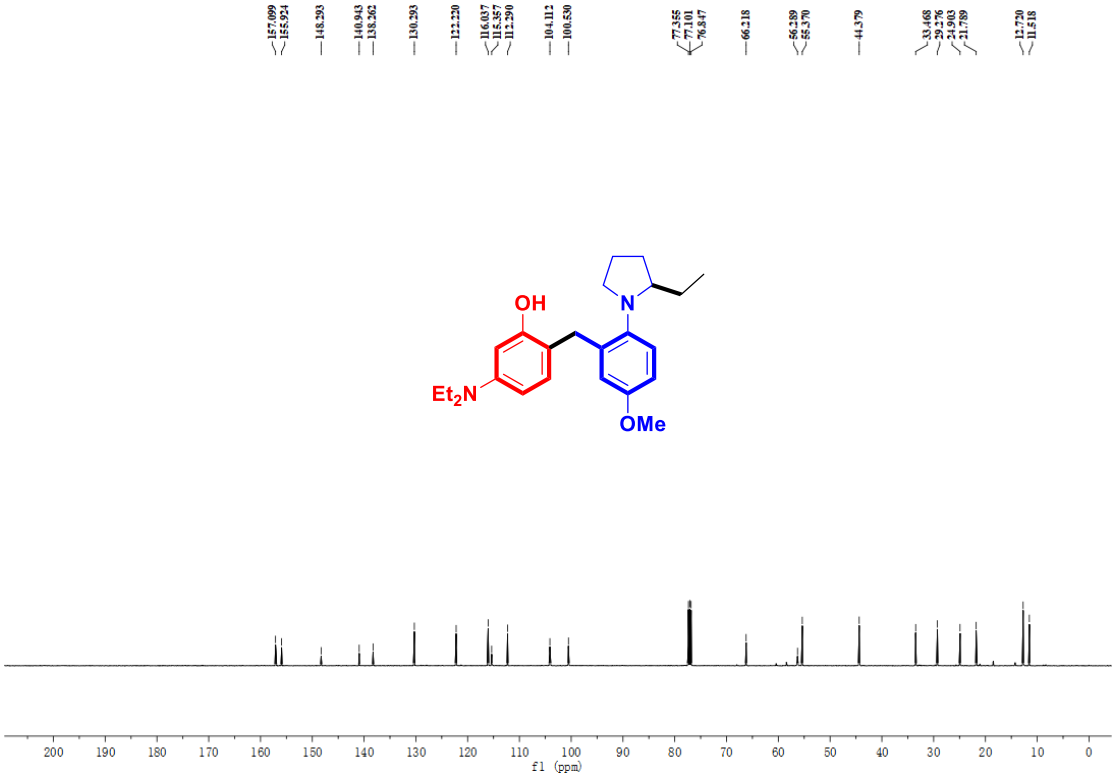
2-(5-chloro-2-(2-methylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3m)



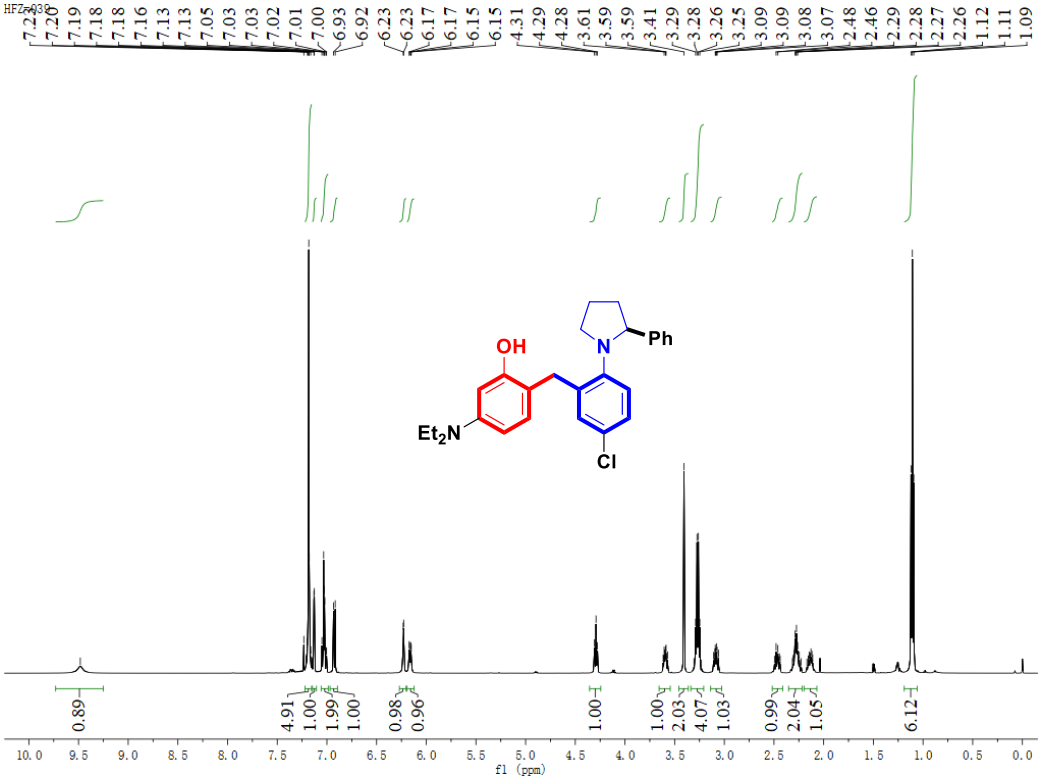


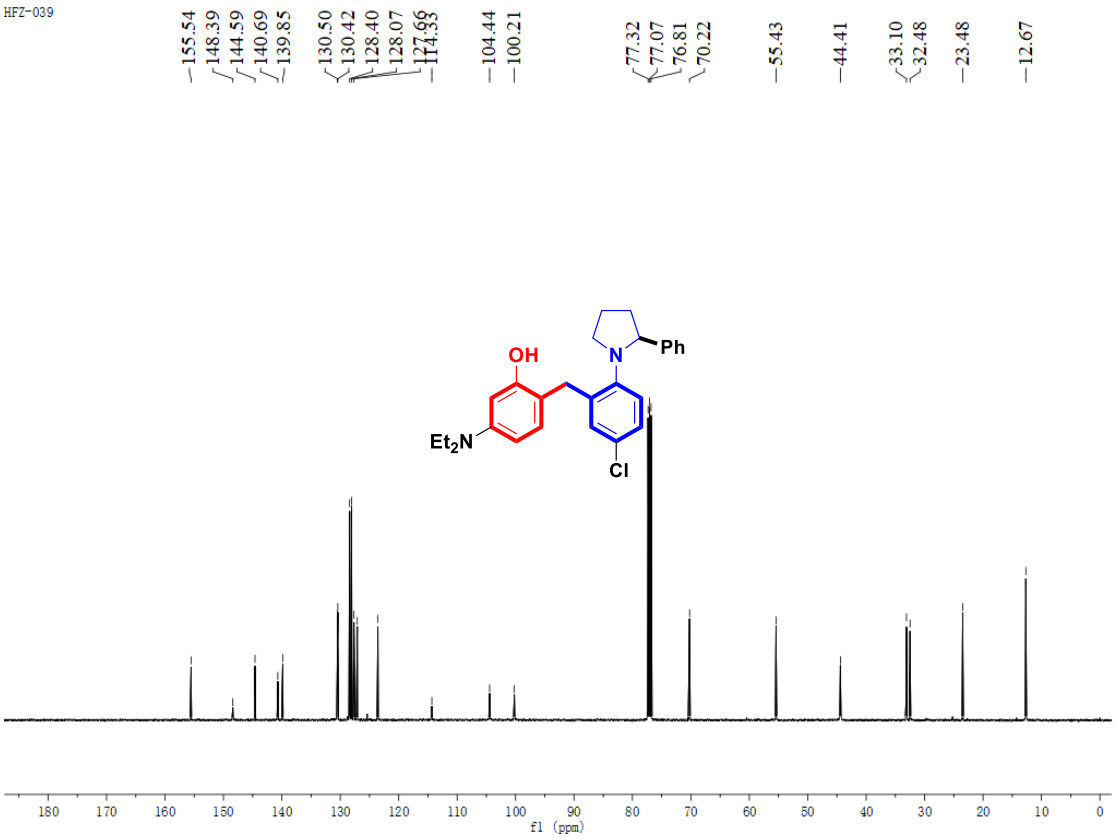
5-(diethylamino)-2-(2-(2-ethylpyrrolidin-1-yl)-5-methoxybenzyl)phenol (3n)



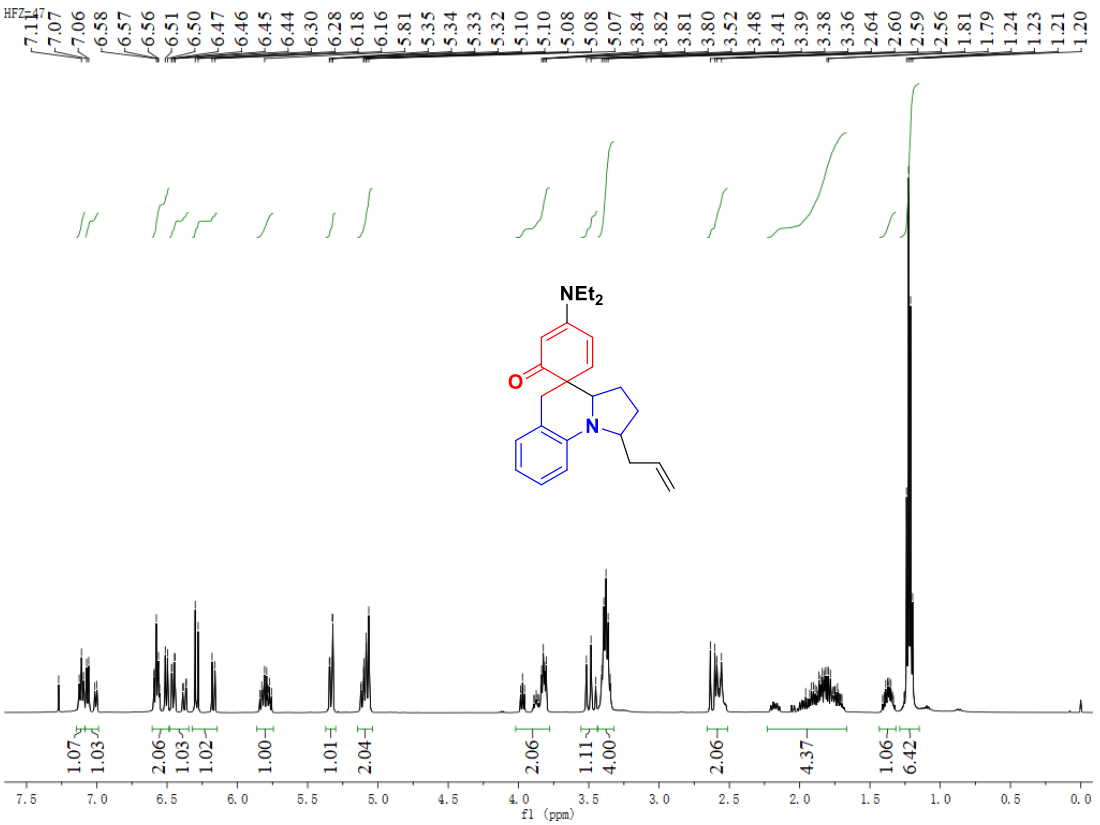


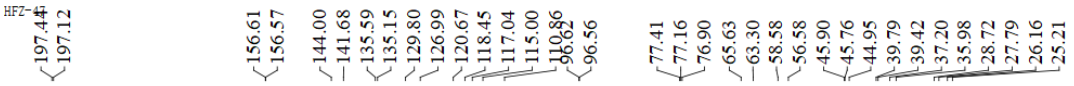
2-(5-chloro-2-(2-phenylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (3o)

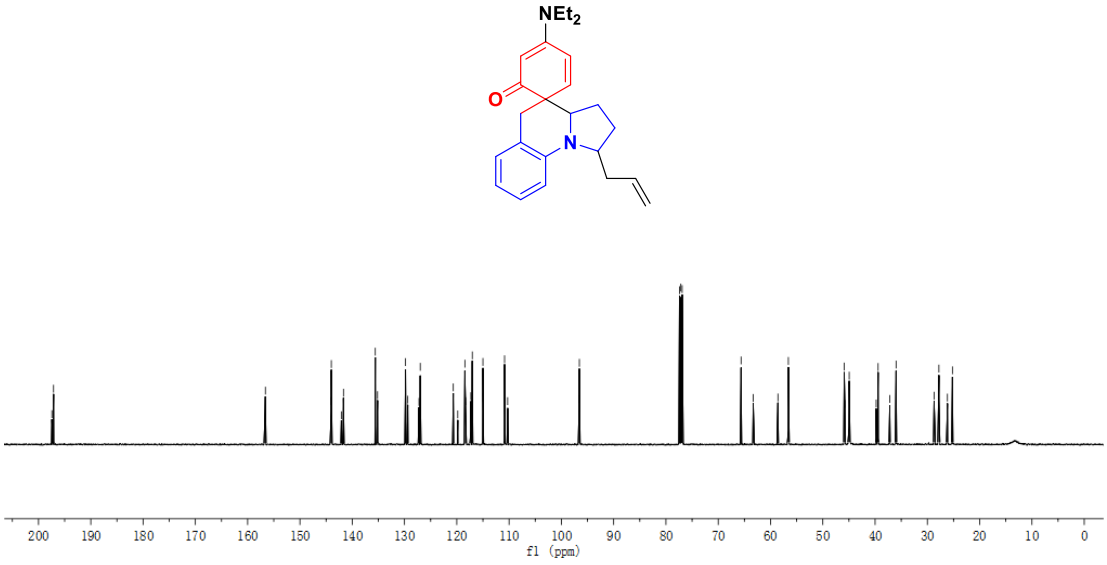




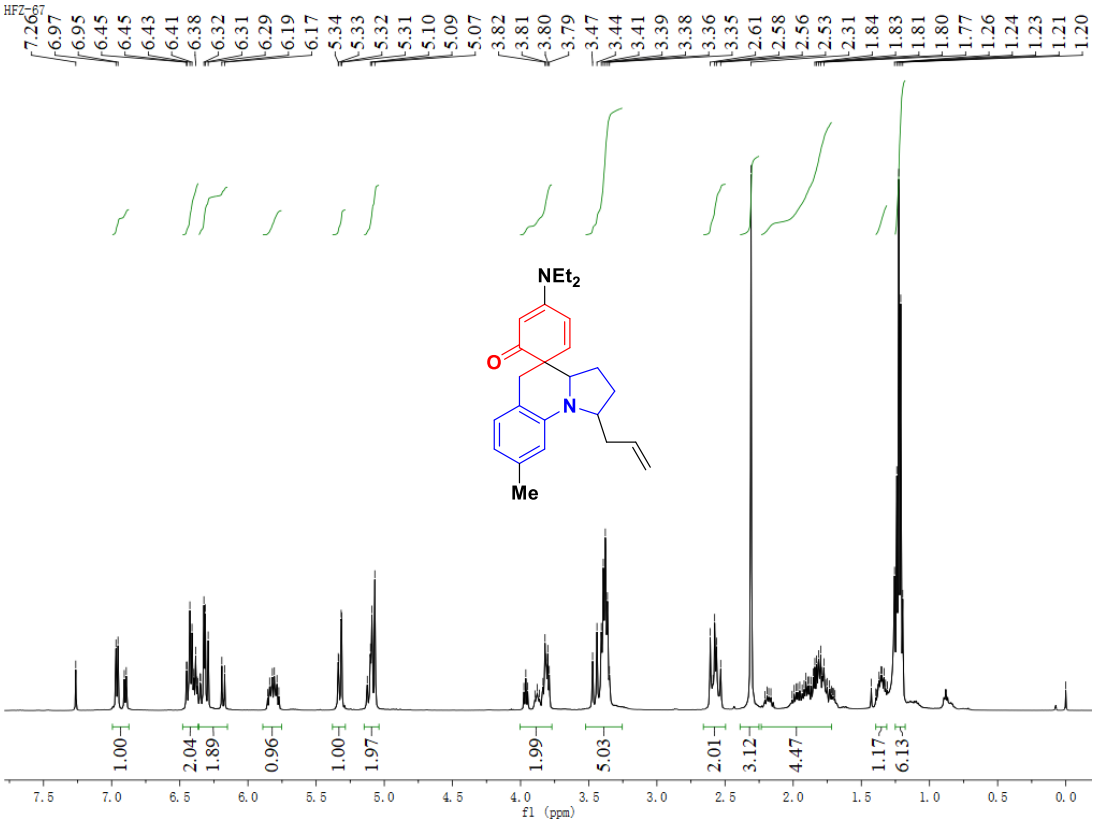
1'-allyl-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4a)

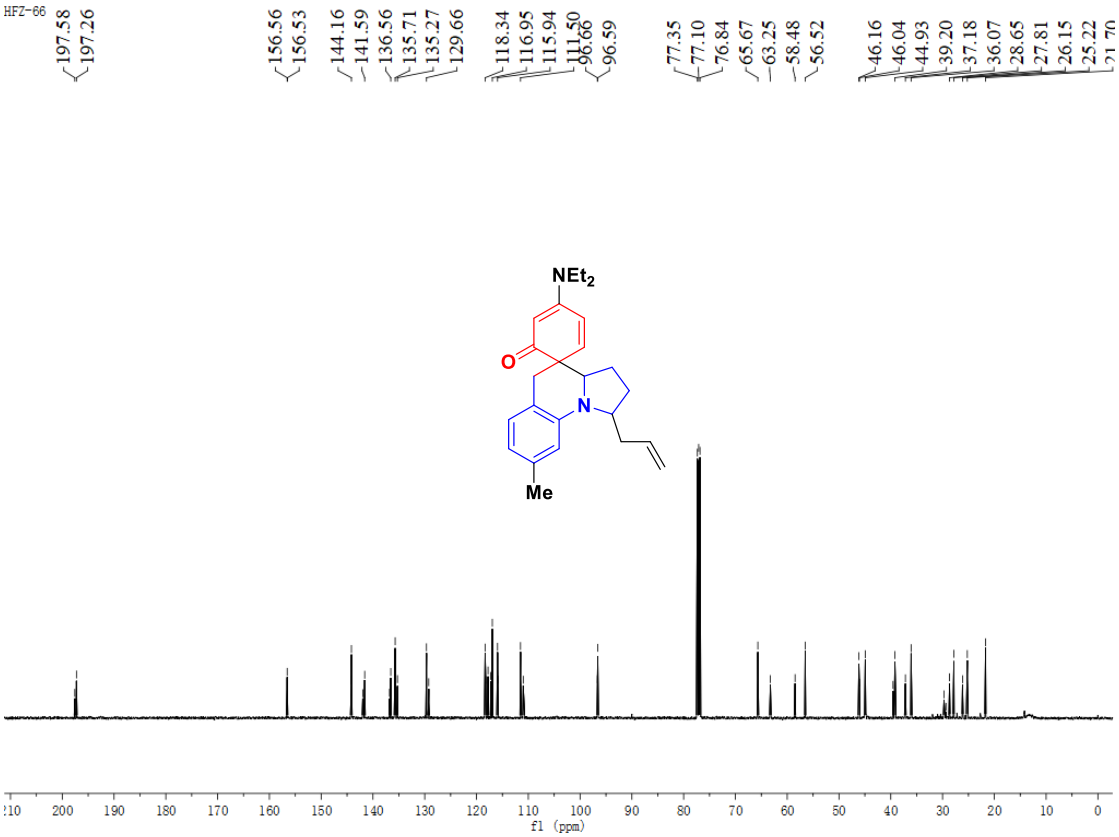




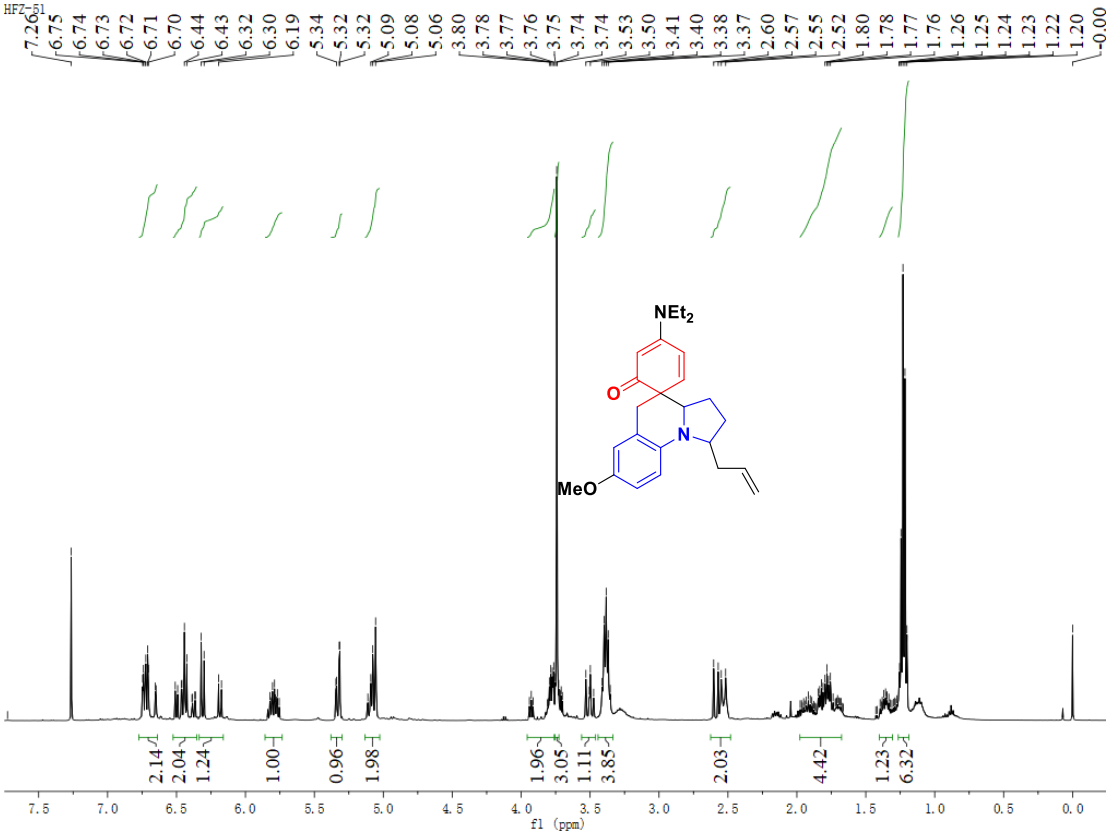


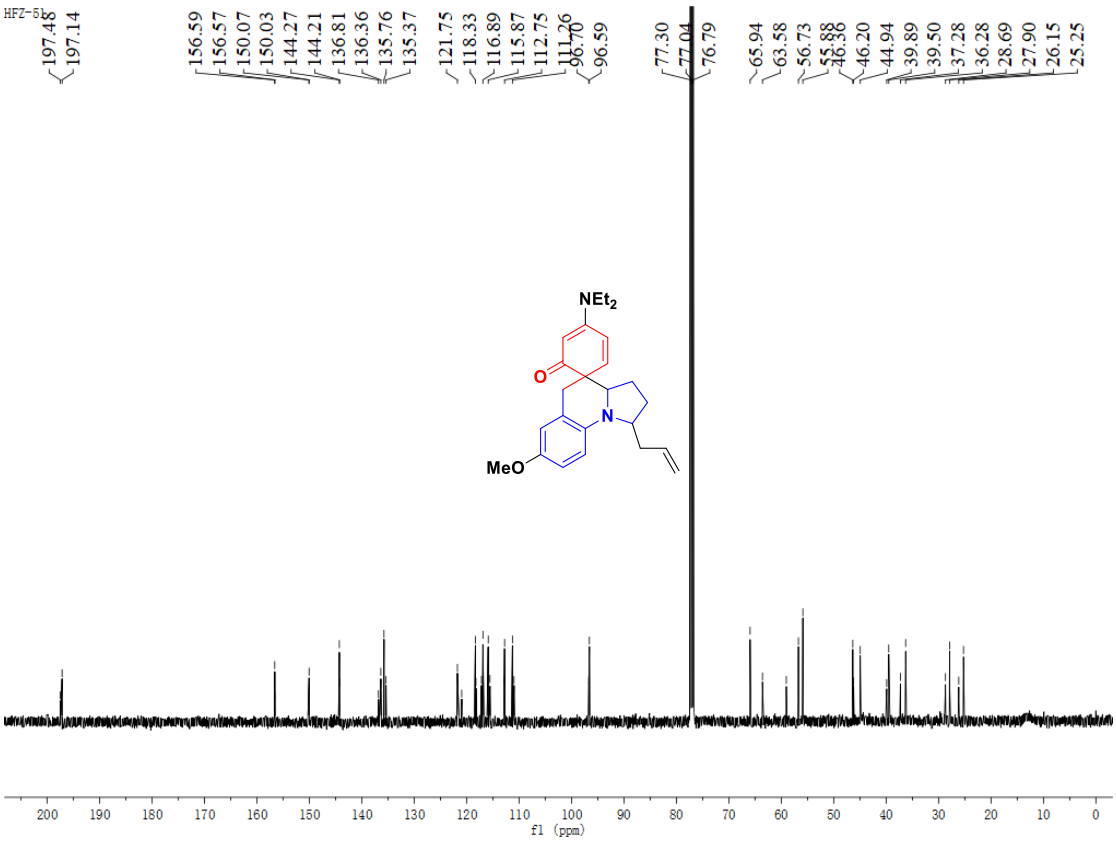
1'-allyl-4-(diethylamino)-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4b)



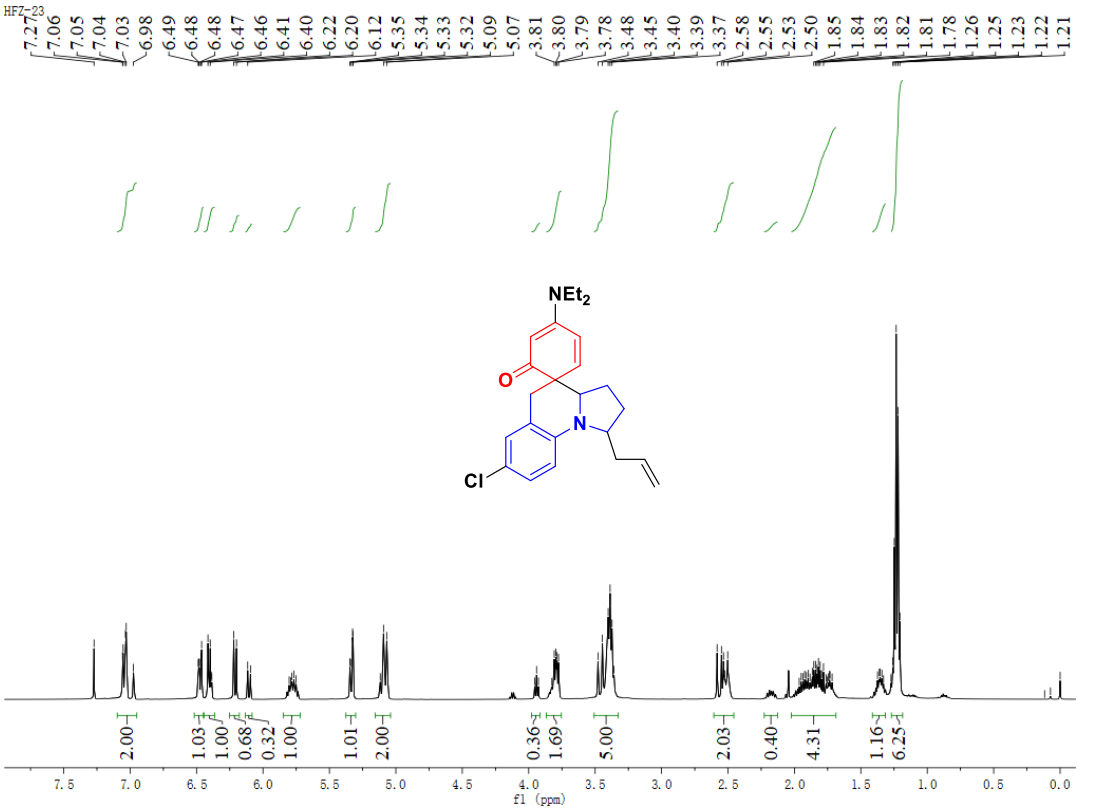


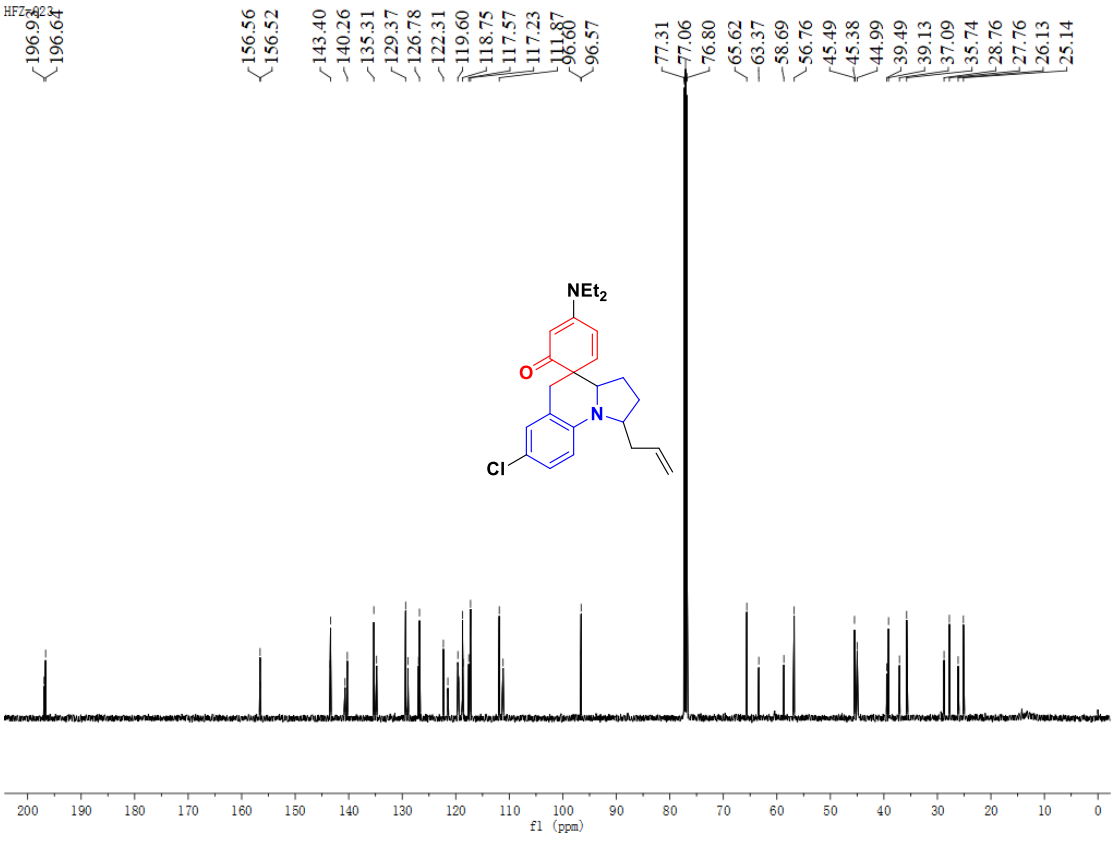
1'-allyl-4-(diethylamino)-7'-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4c)



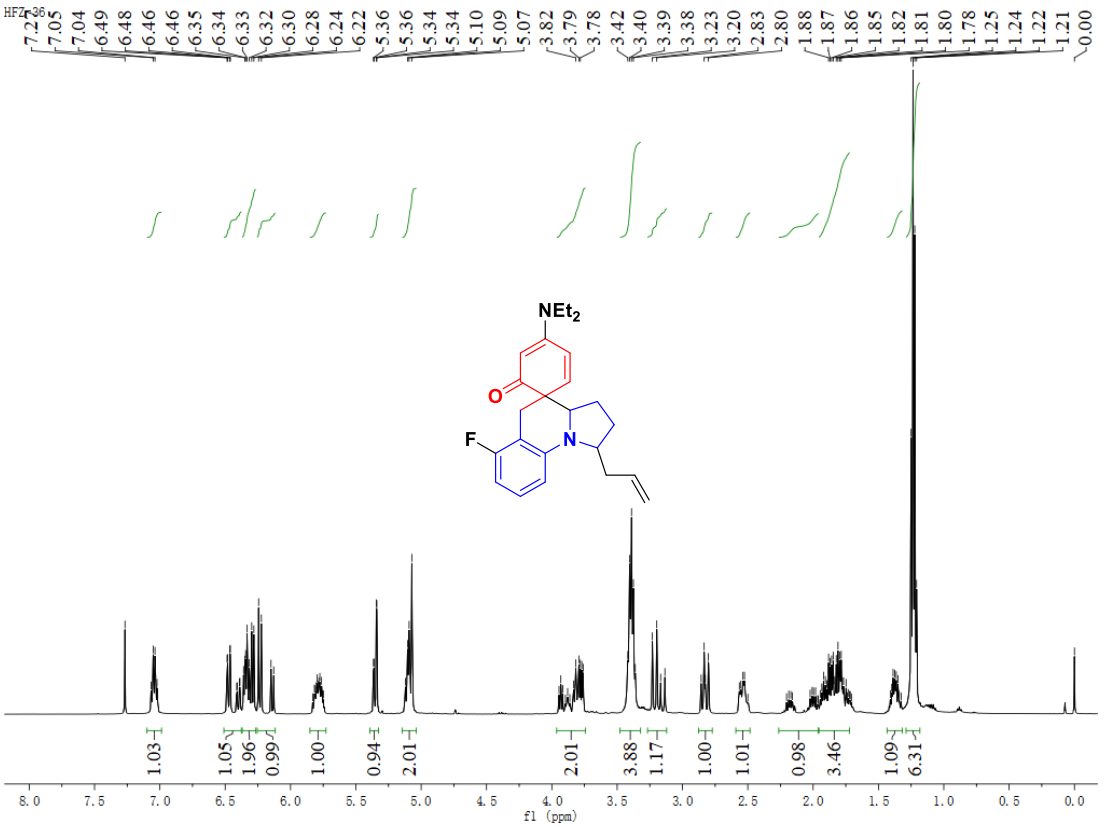


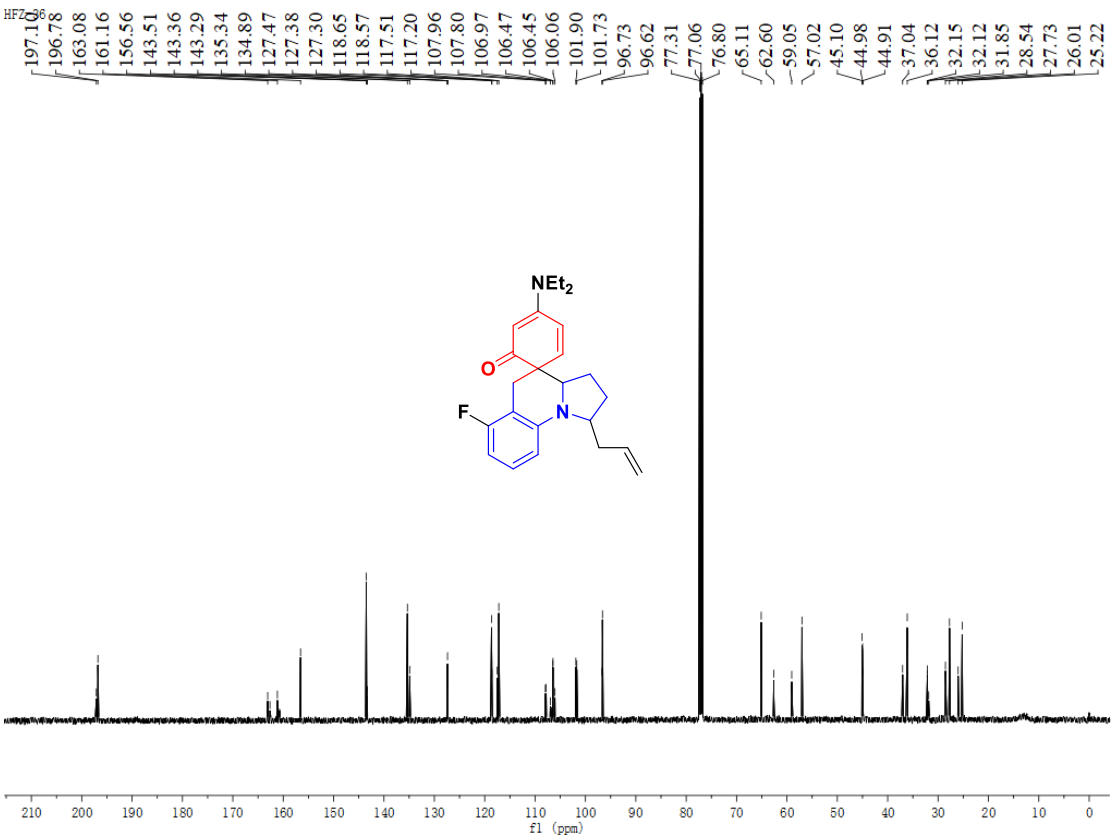
1'-allyl-7'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4d)



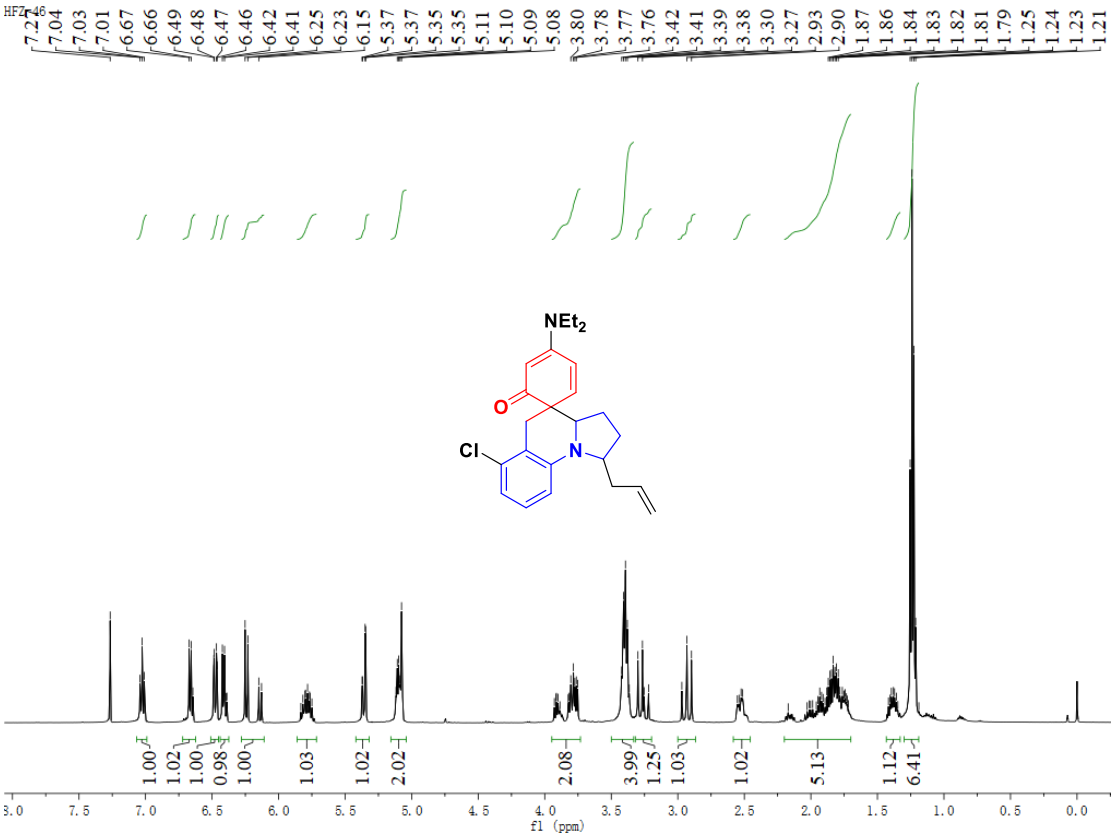


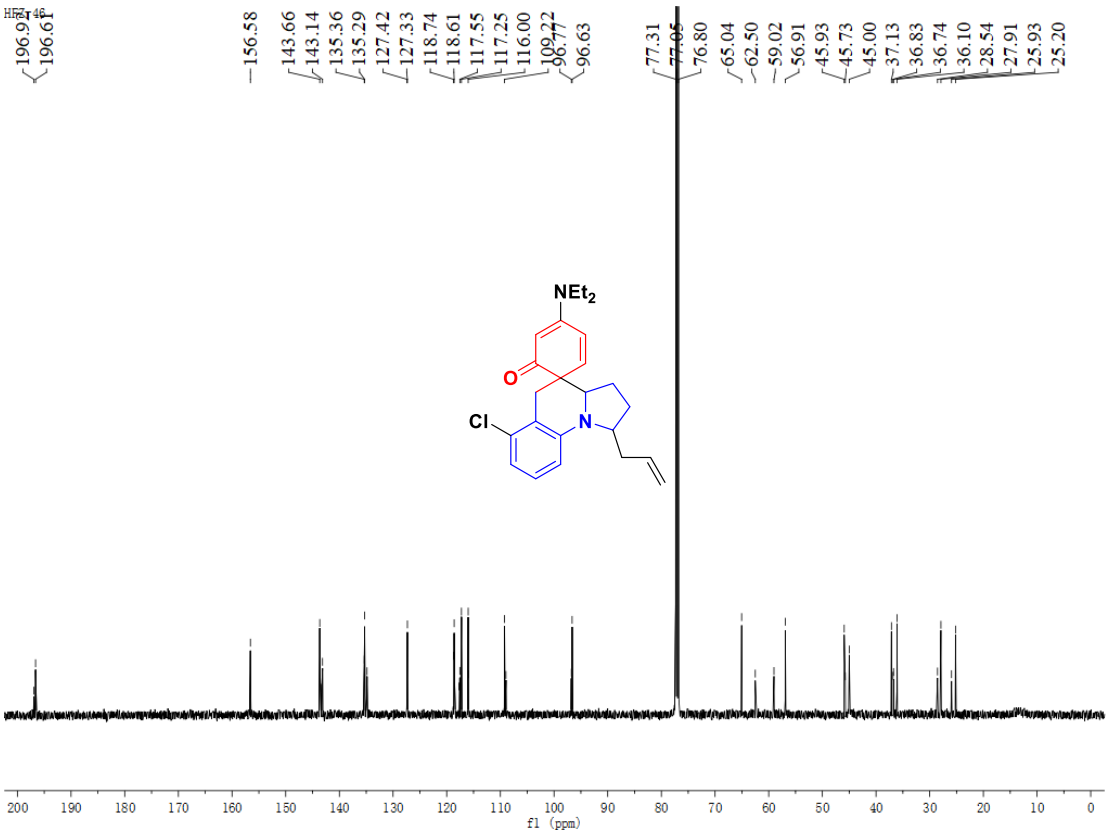
1'-allyl-4-(diethylamino)-6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4e)



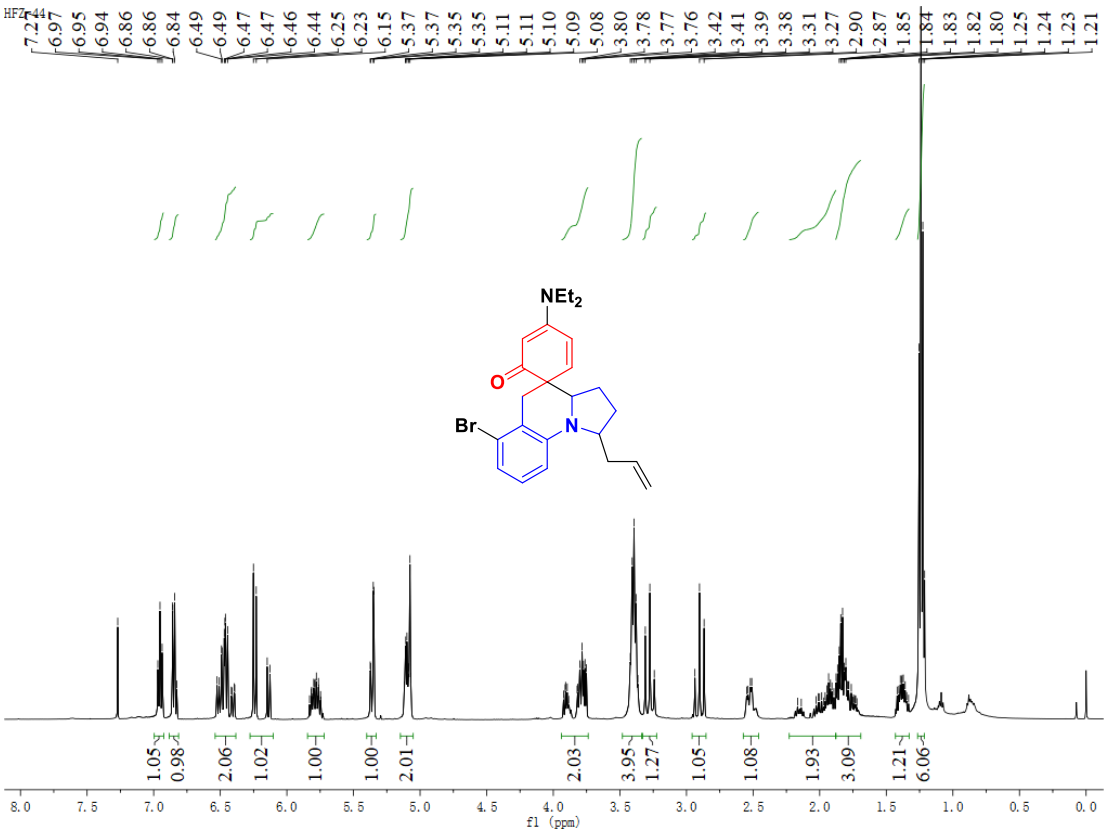


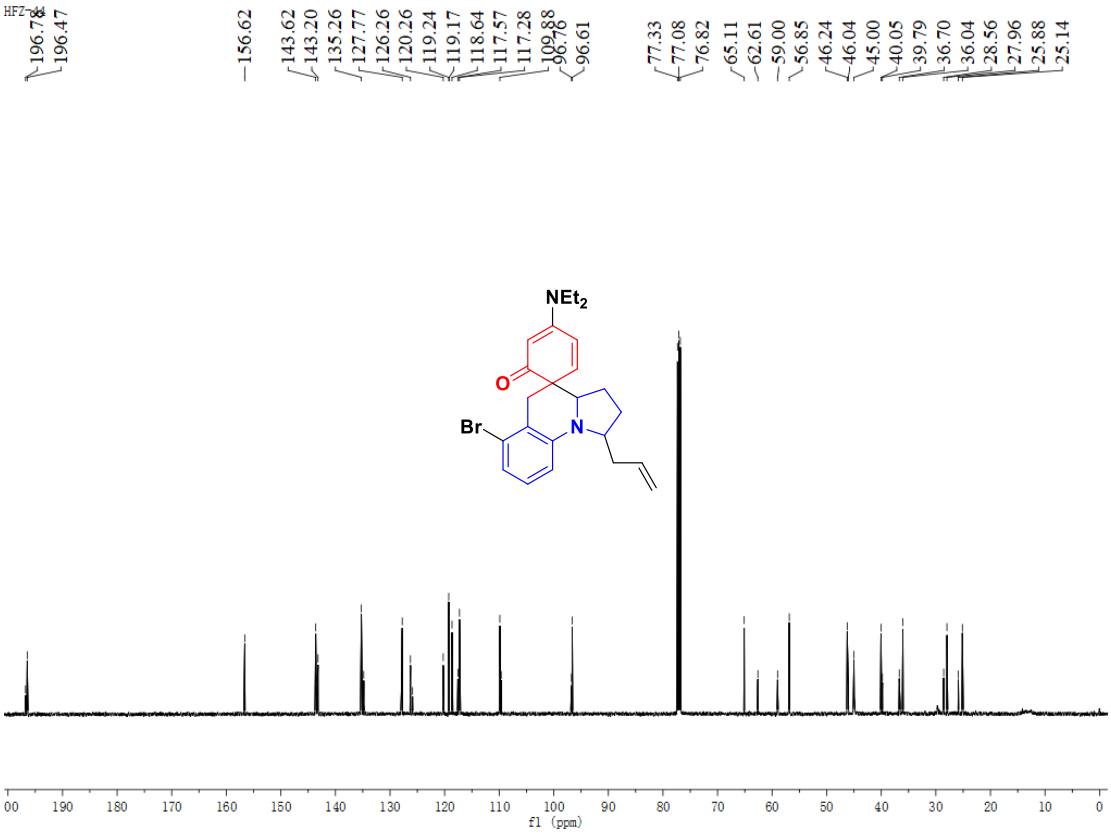
1'-allyl-6'-chloro-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4f)



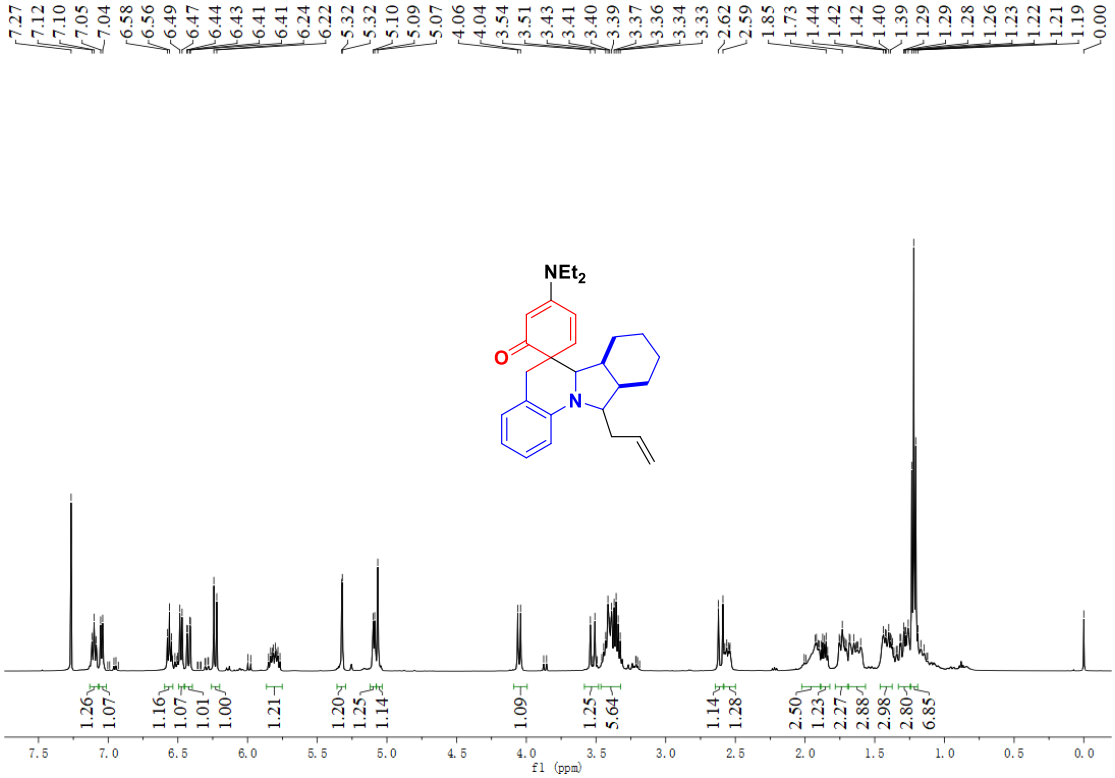


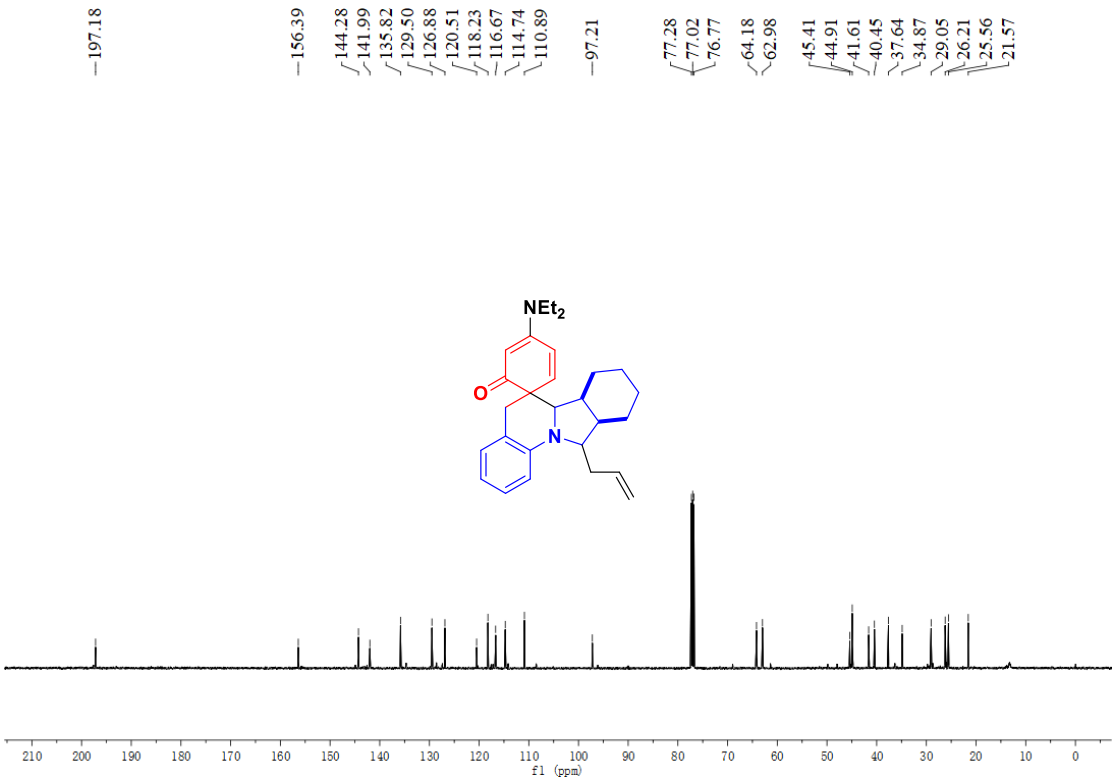
1'-allyl-6'-bromo-4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4g)



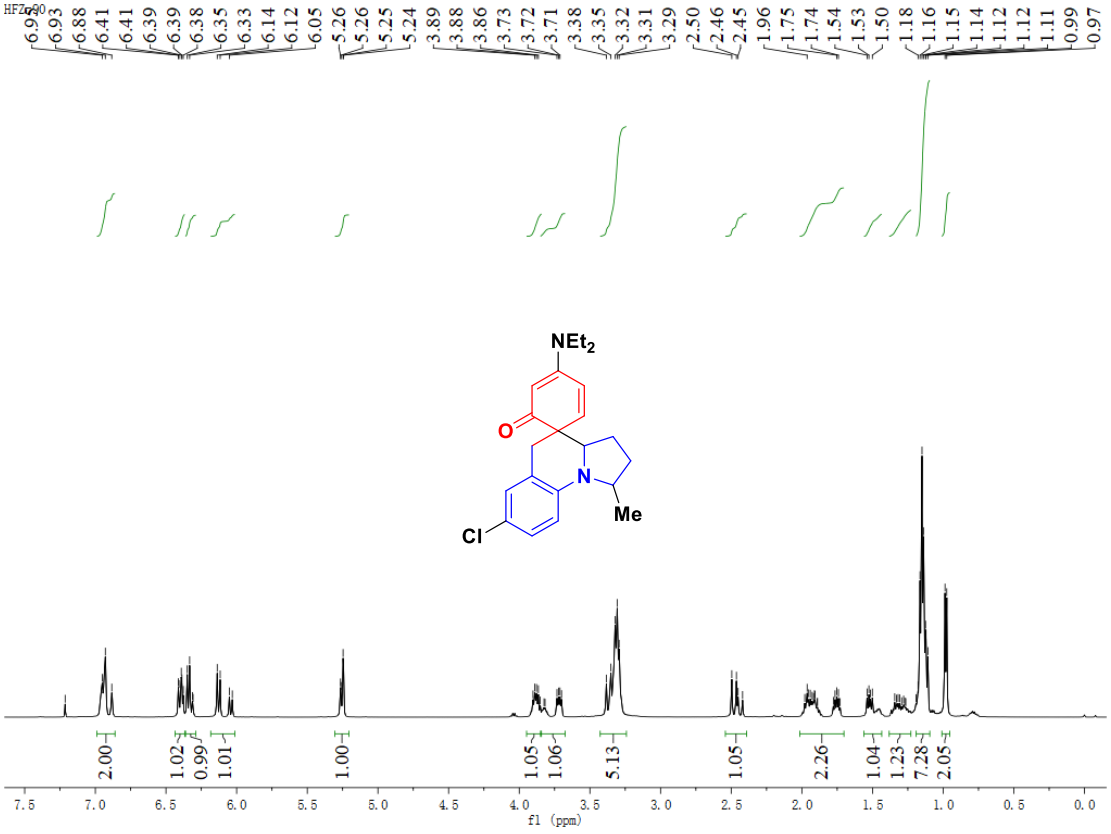


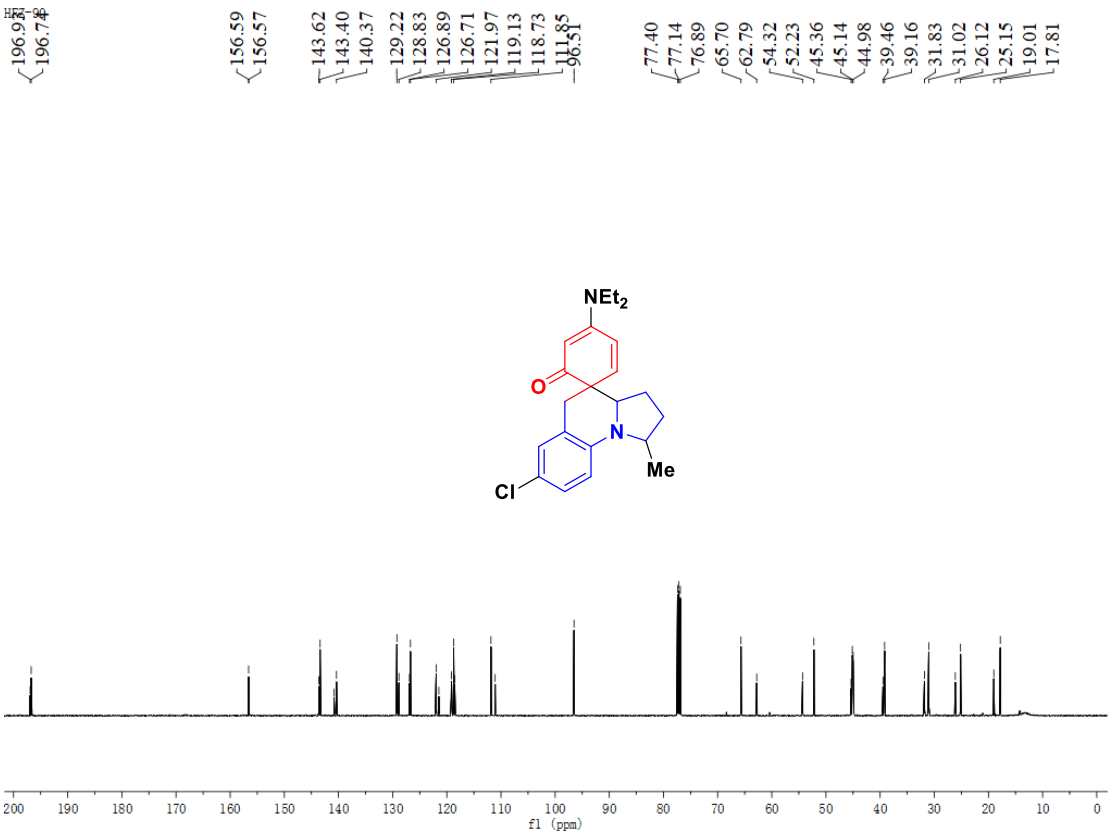
11'-allyl-4-(diethylamino)-6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[cyclohexane-1,6'-isoindolo[2,1-a]quinoline]-2,4-dien-6-one (4h)

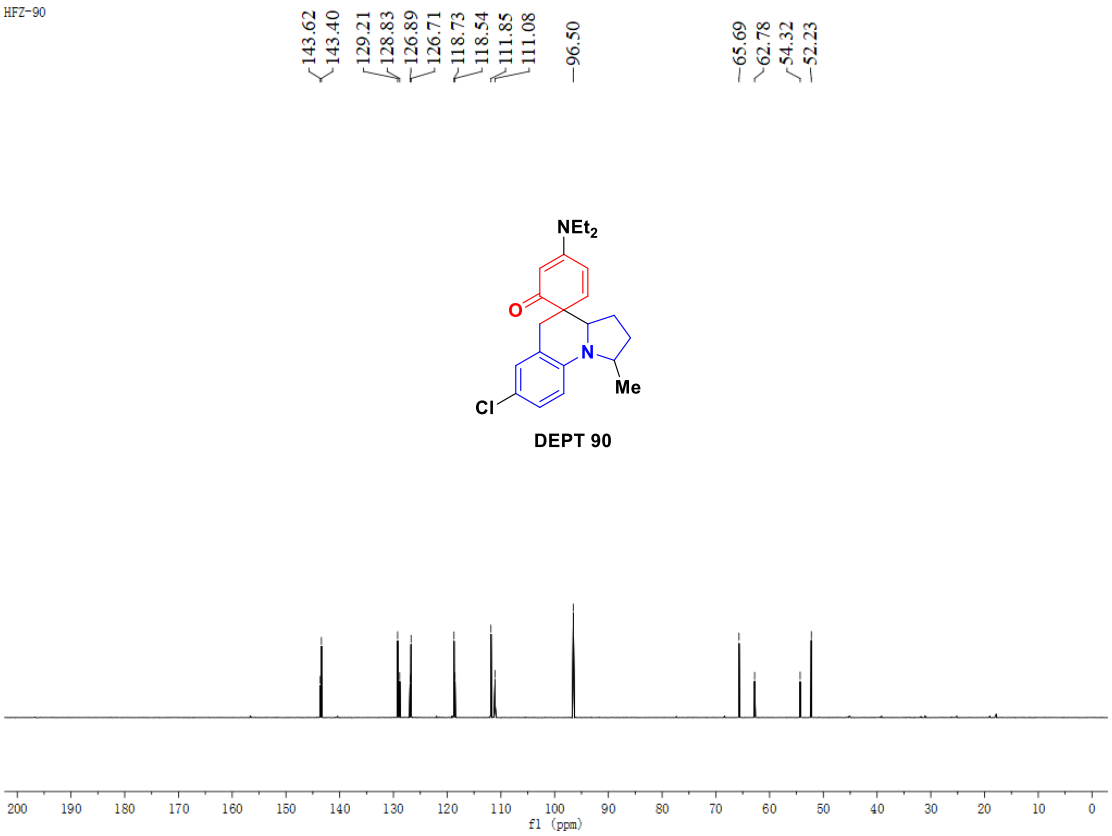




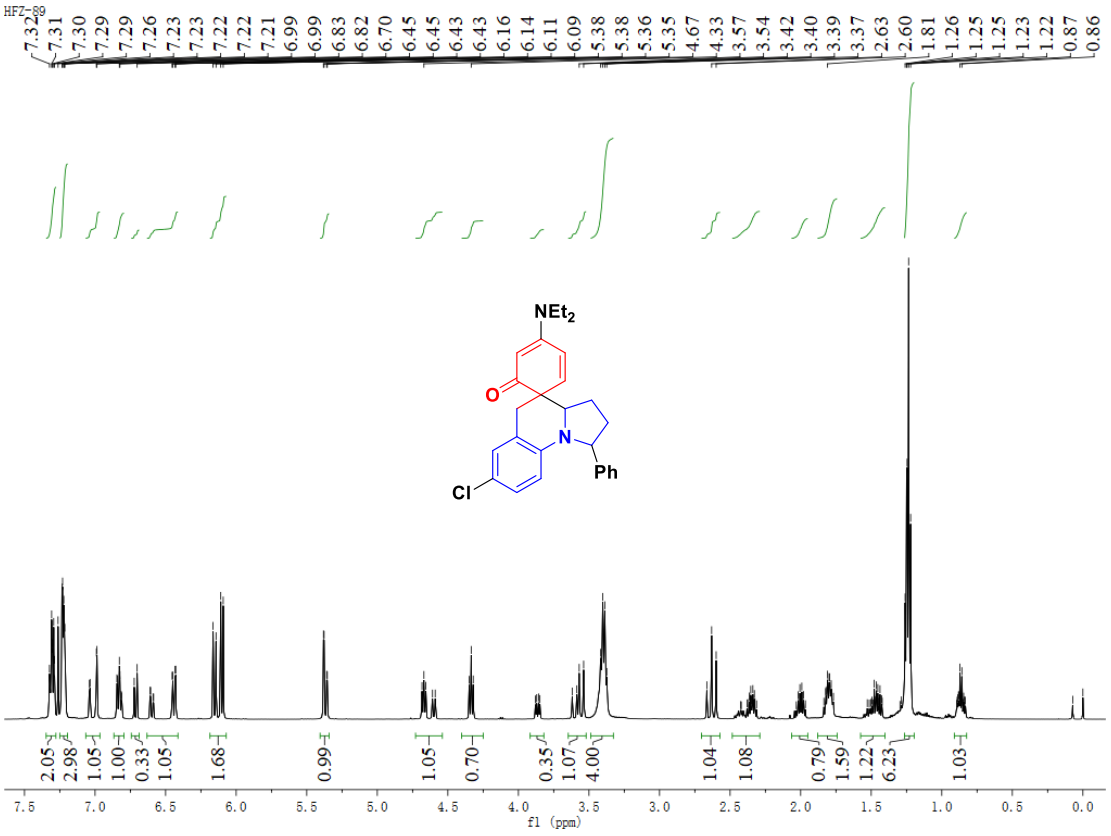
7'-chloro-4-(diethylamino)-1'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4i)

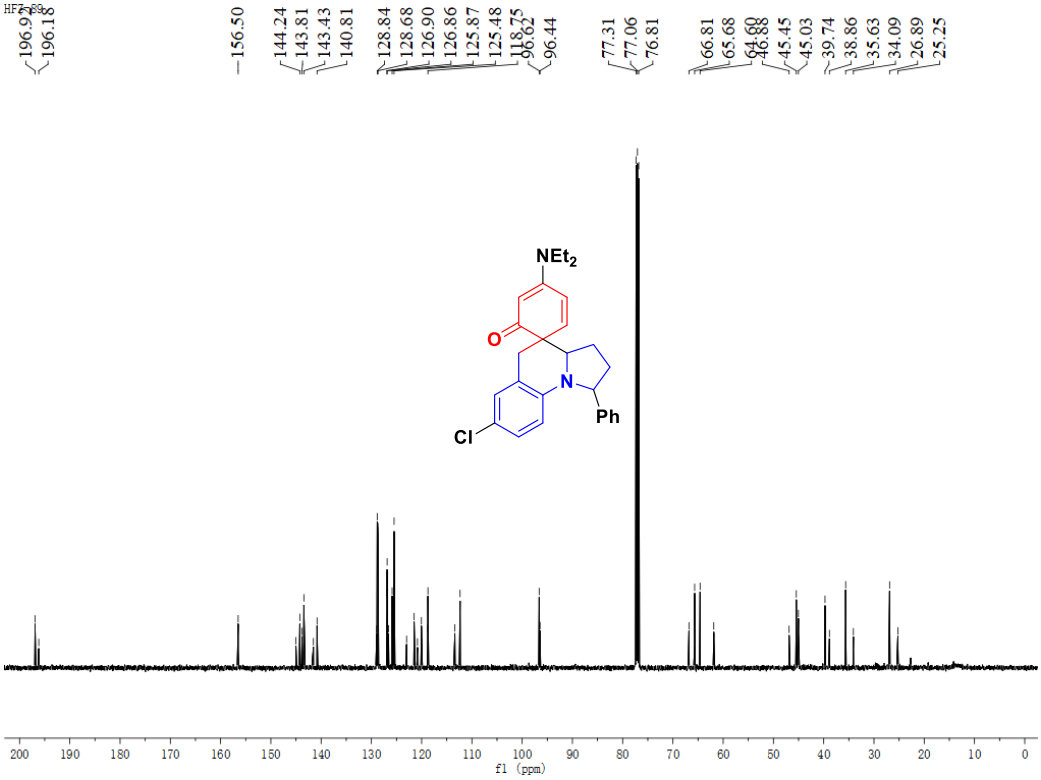


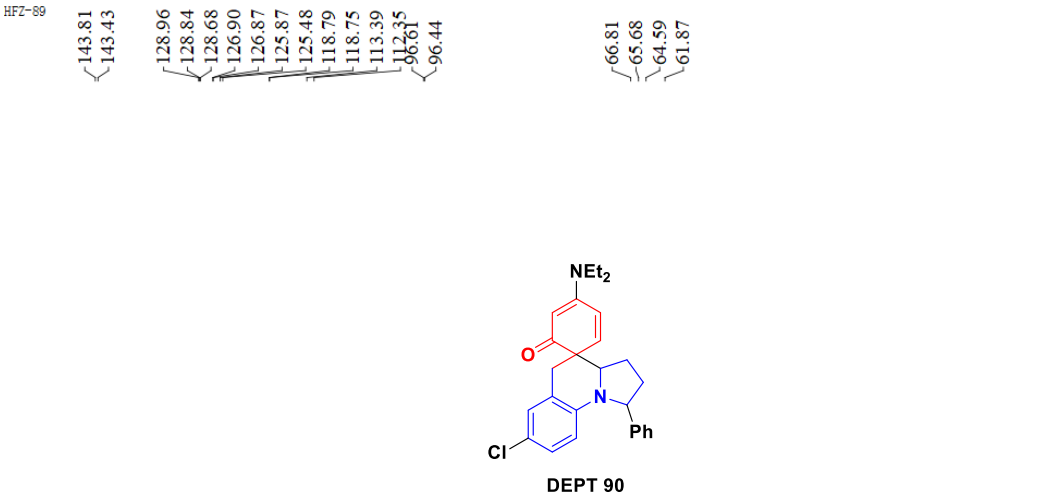




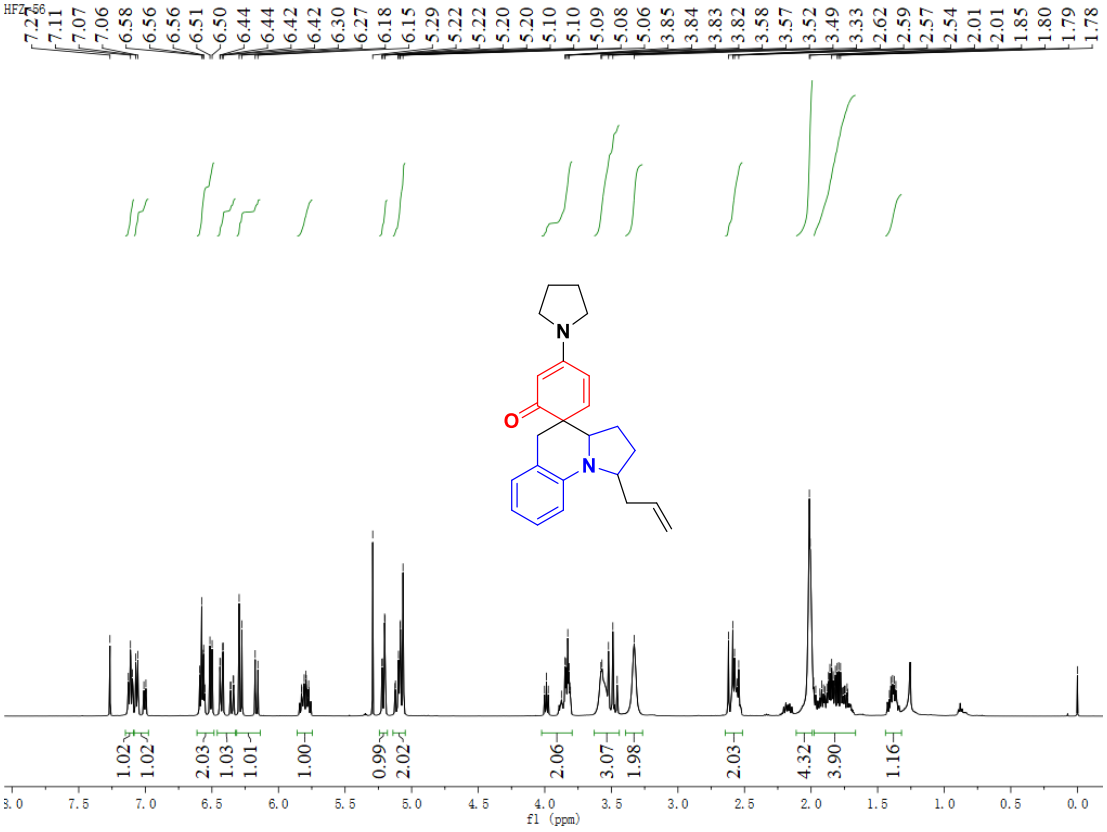
7'-chloro-4-(diethylamino)-1'-phenyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4j)

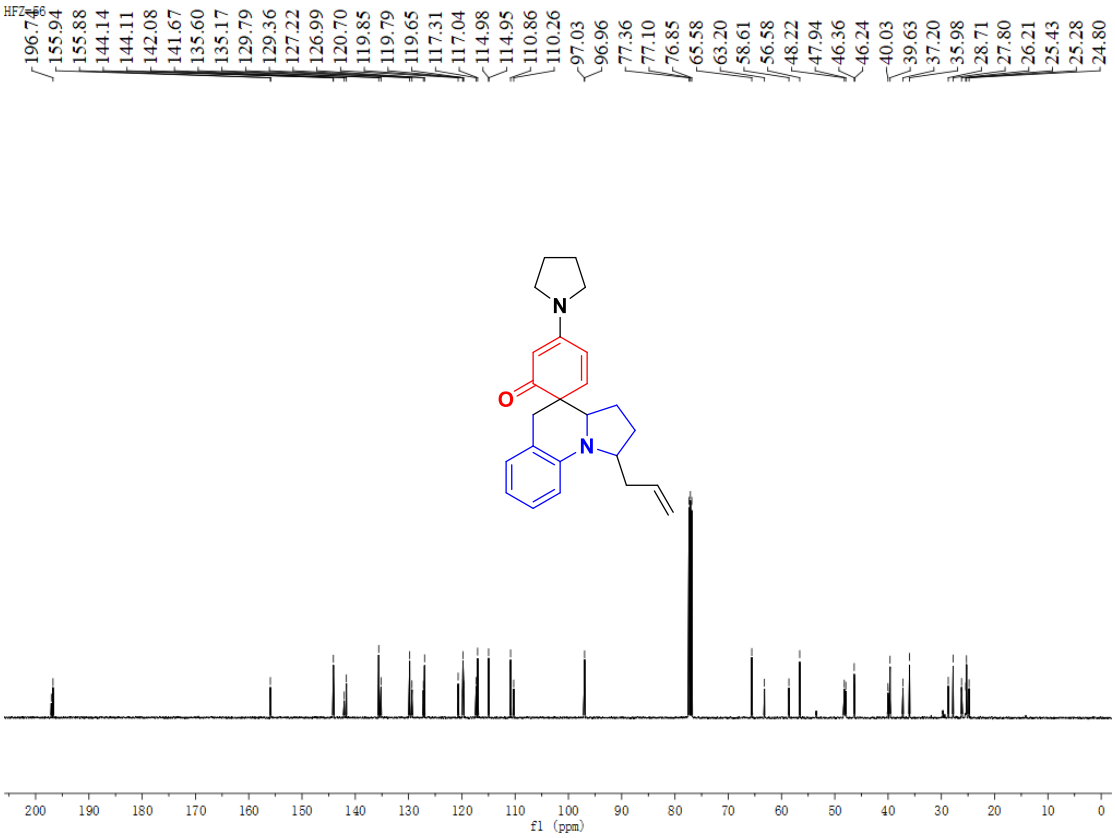



HFZ-89
196.92
196.18
156.50
144.24
143.81
143.43
140.81
128.84
128.68
126.90
126.86
125.87
125.48
118.75
96.62
96.44
77.31
77.06
76.81
66.81
65.68
64.60
46.88
45.45
45.03
39.74
38.86
35.63
34.09
26.89
25.25
NEt2
O
N
Ph
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

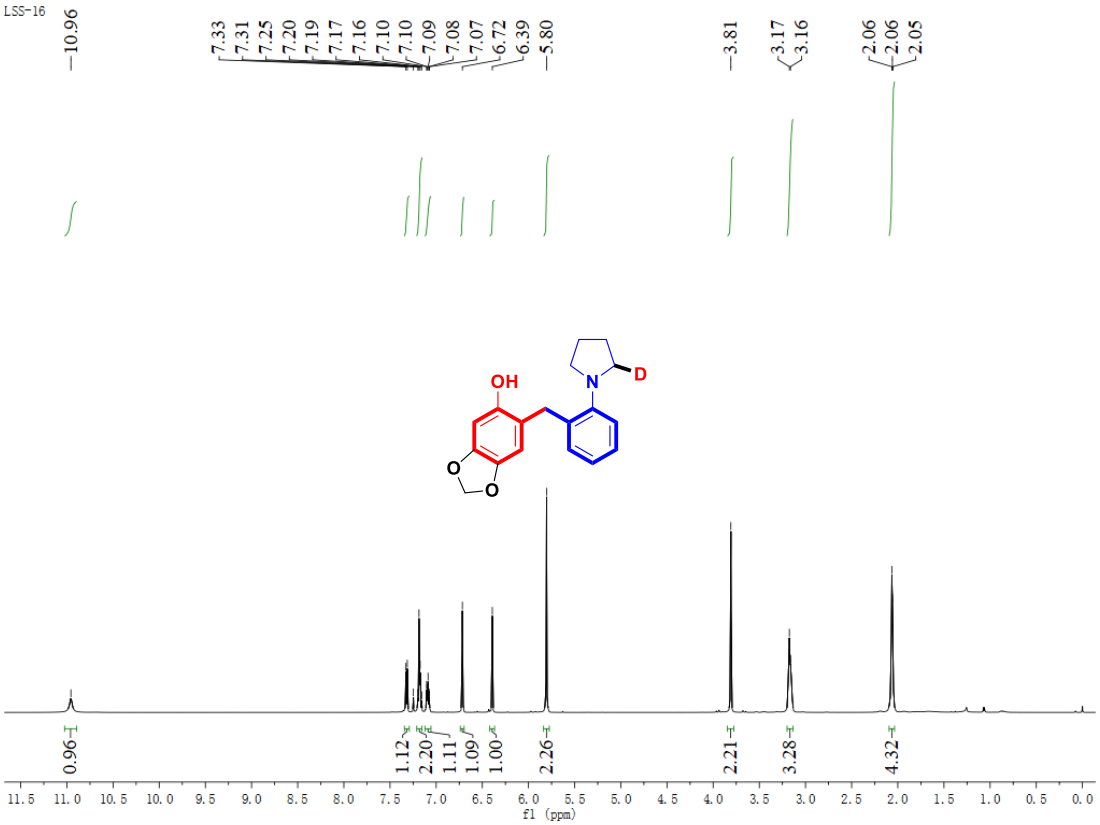

HFZ-89
143.81
143.43
128.96
128.84
128.68
126.90
126.87
125.87
125.48
118.79
118.75
113.39
112.35
96.61
96.44
66.81
65.68
64.59
61.87
NEt2
O
N
Ph
Cl
DEPT 90
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

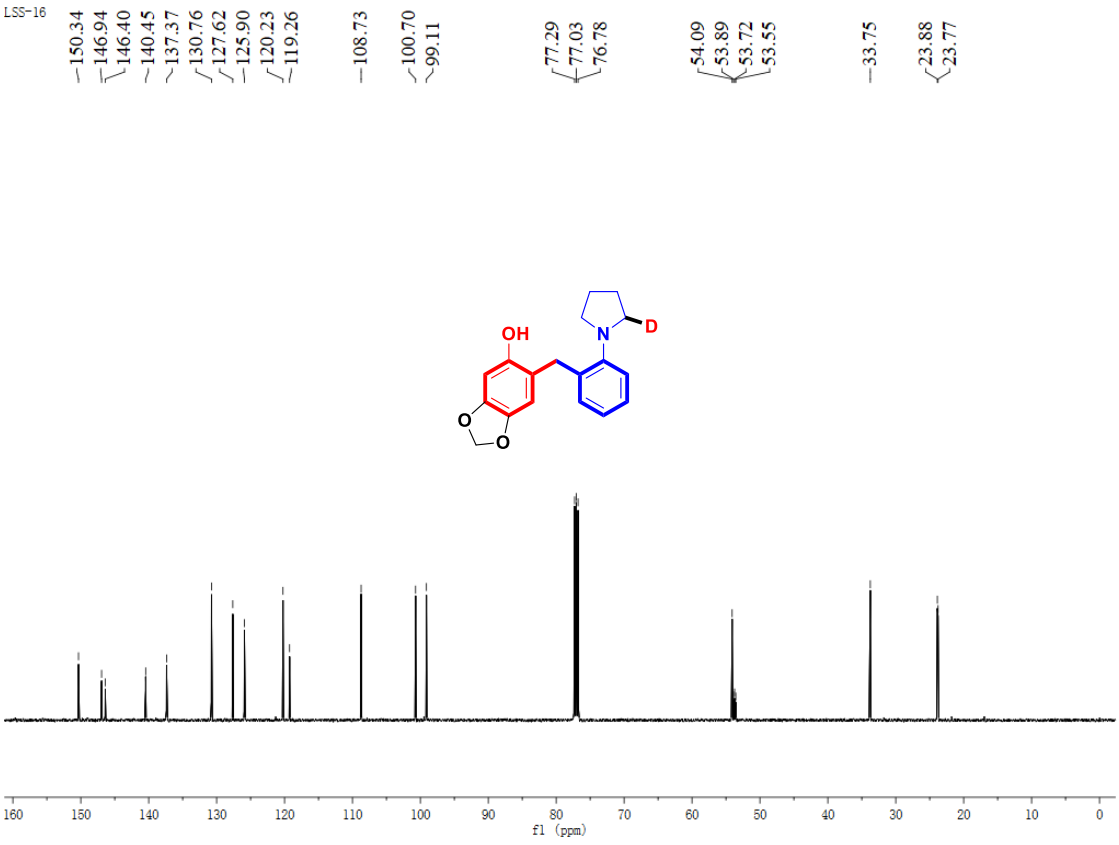
1'-allyl-4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (4k)



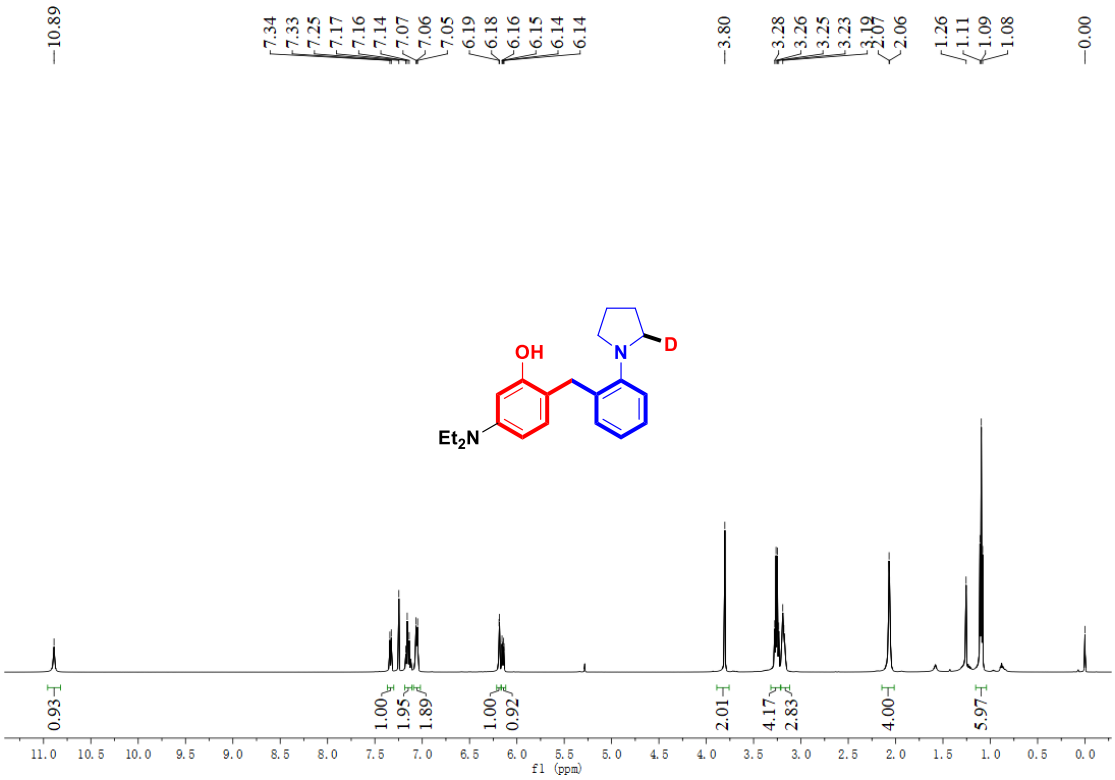


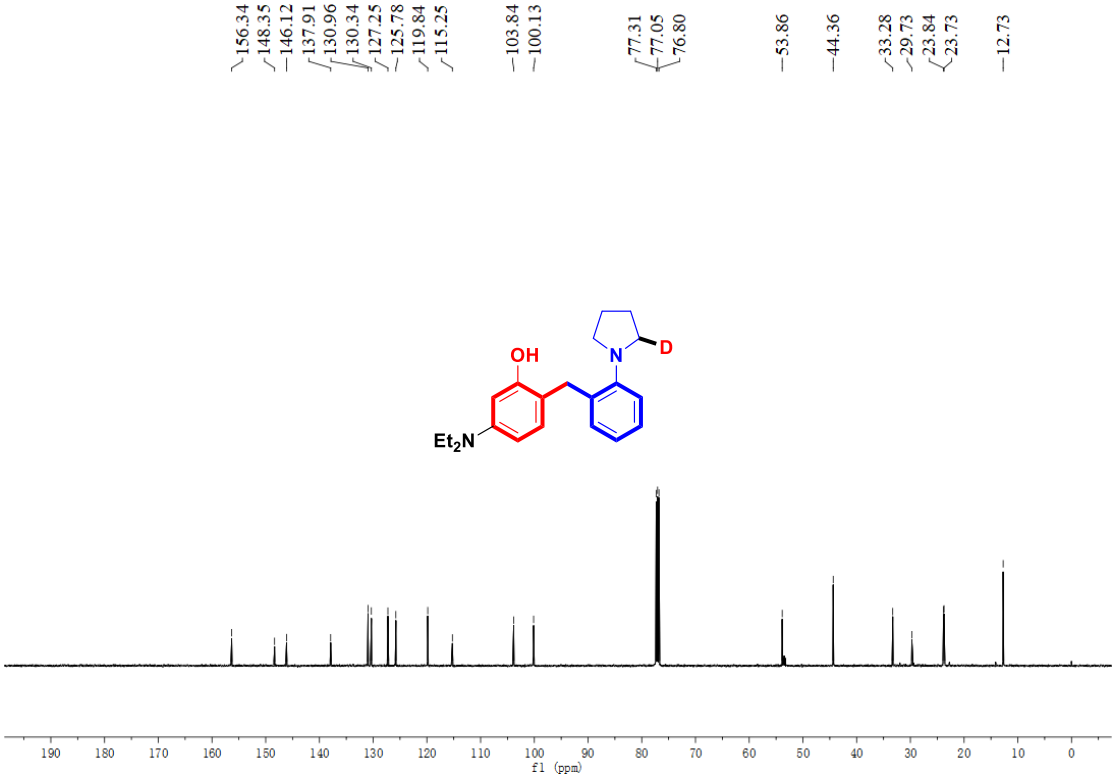
6-(2-(pyrrolidin-1-yl-2-d)benzyl)benzo[d][1,3]dioxol-5-ol (5a)



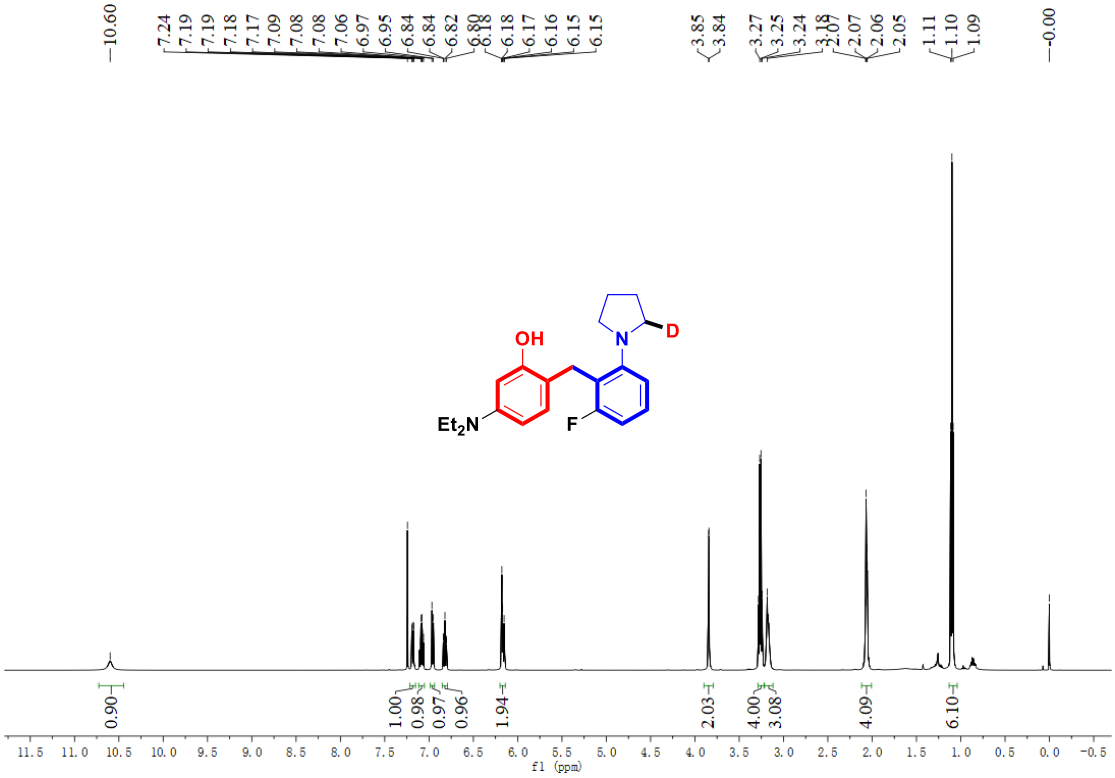


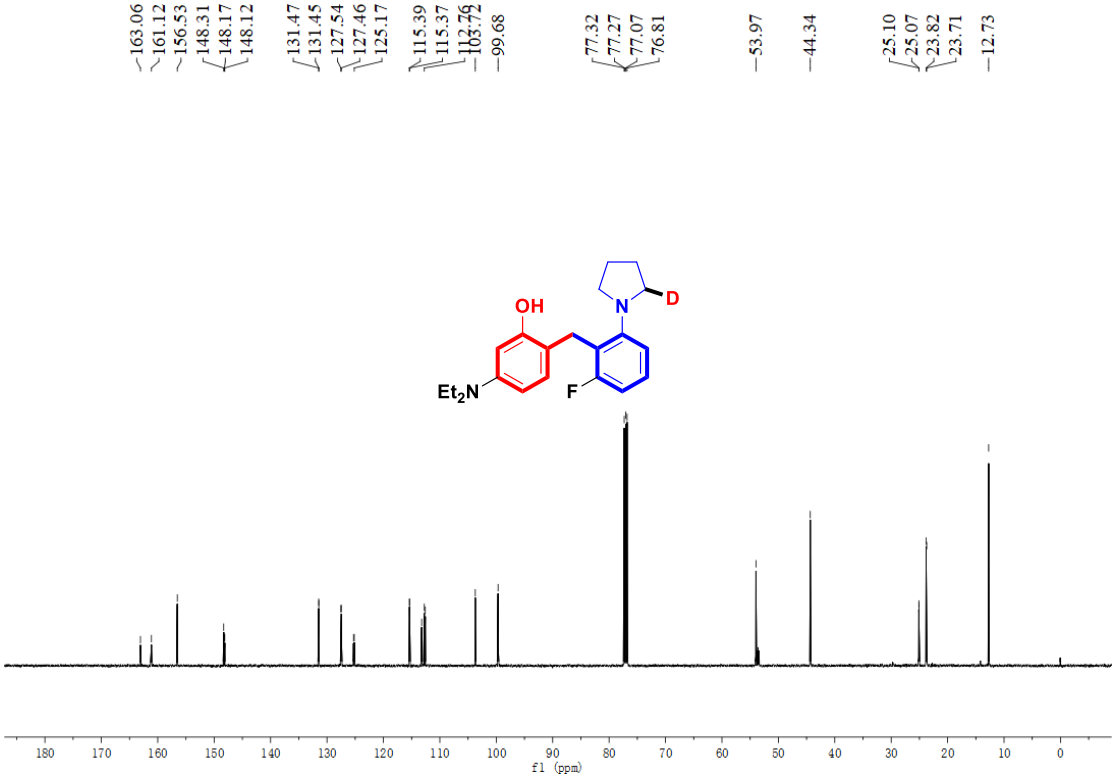
5-(diethylamino)-2-(2-(pyrrolidin-1-yl-2-d)benzyl)phenol (5b)



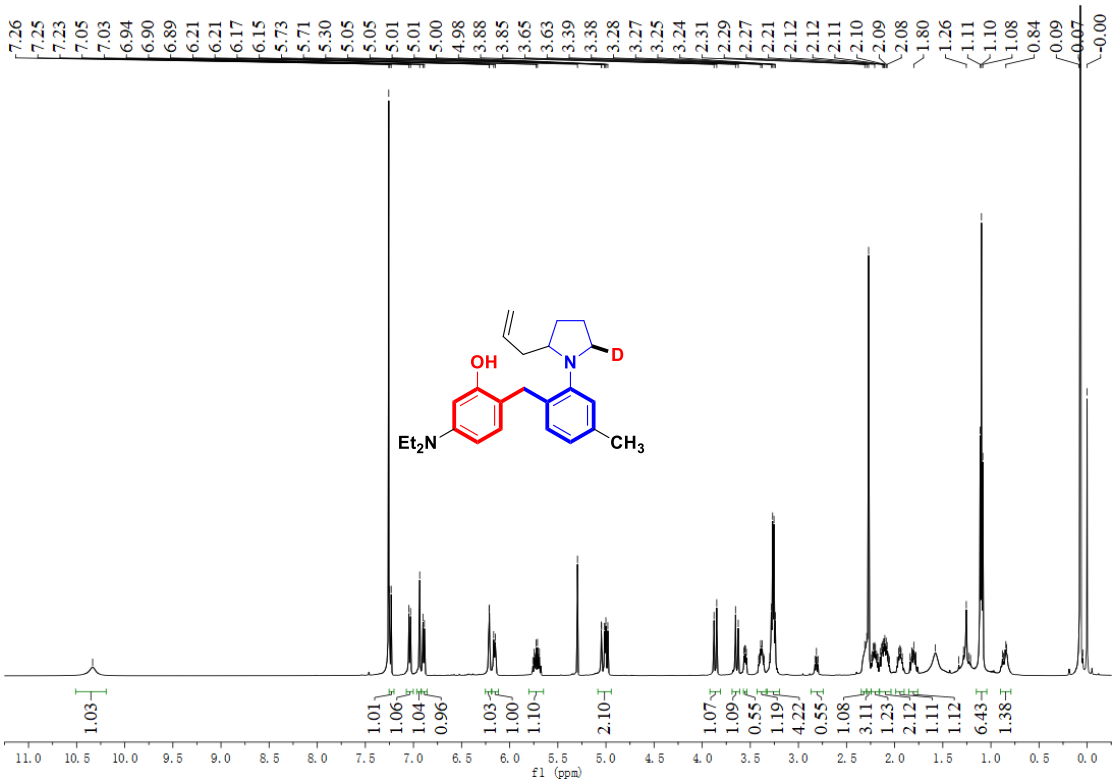


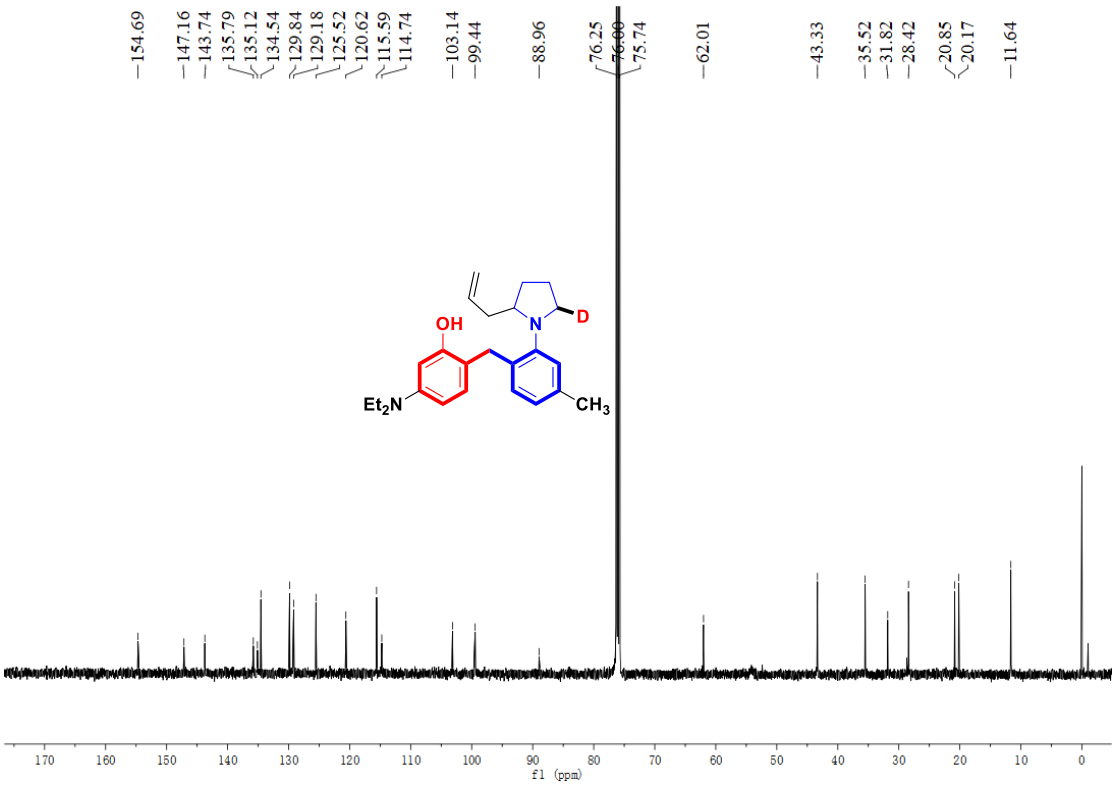
5-(diethylamino)-2-(3-fluoro-2-(pyrrolidin-1-yl-2-d)benzyl)phenol (5c)



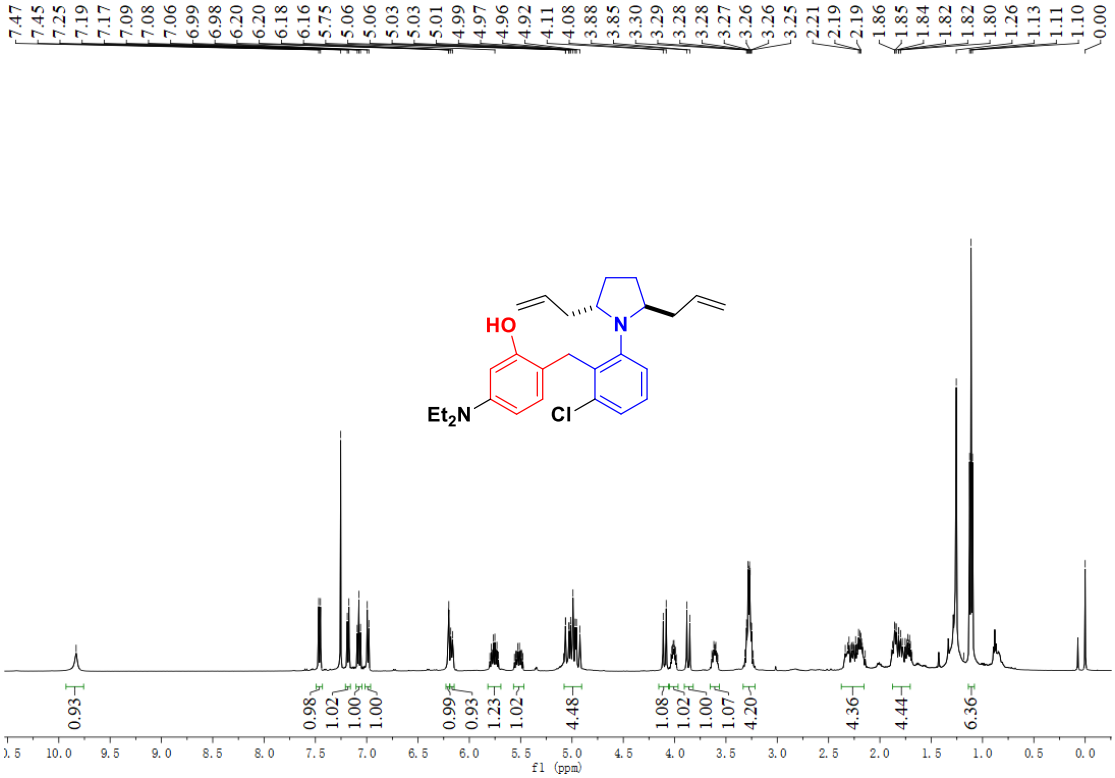


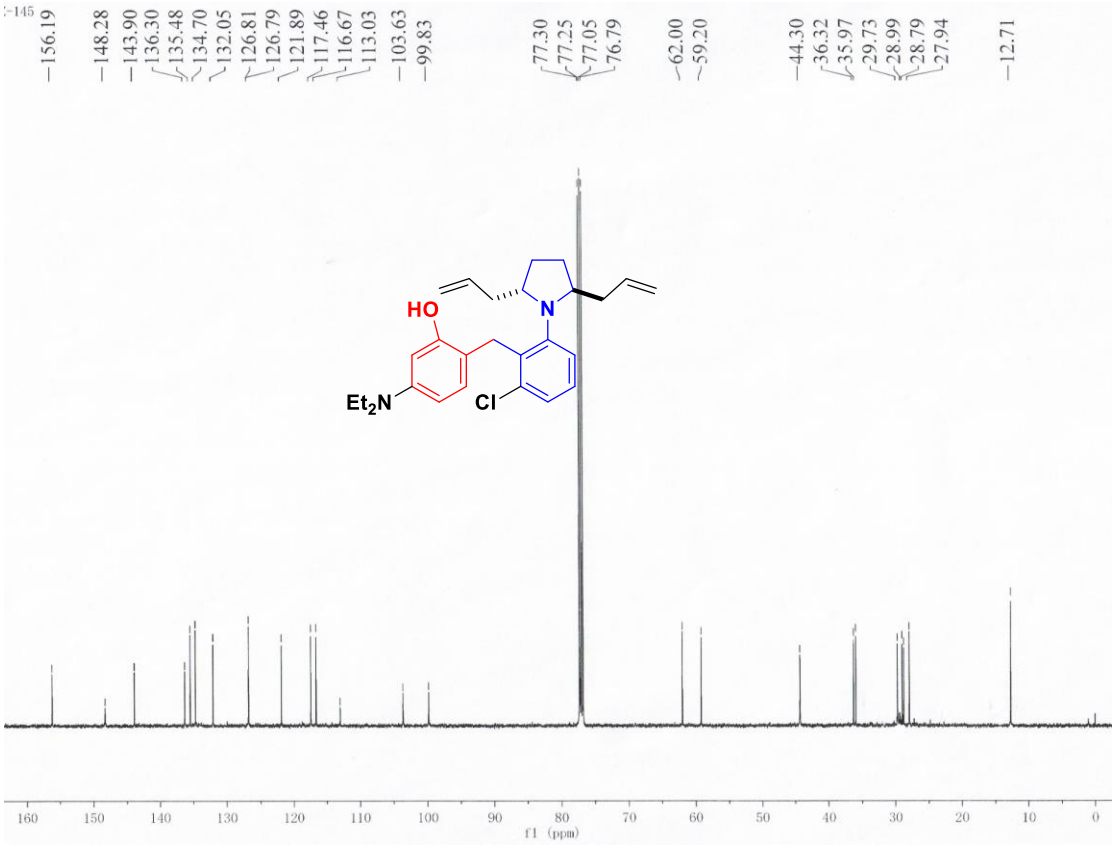
2-(2-(2-allylpyrrolidin-1-yl-5-d)-4-methylbenzyl)-5-(diethylamino)phenol (5d)



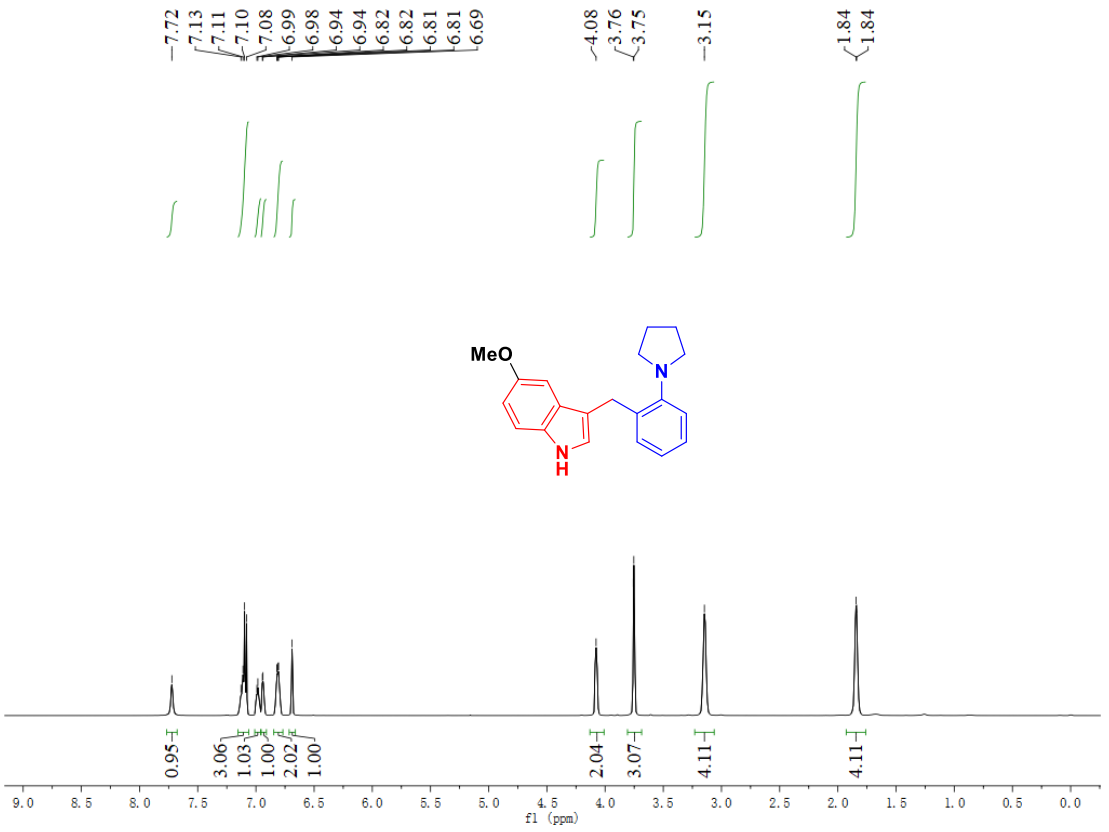


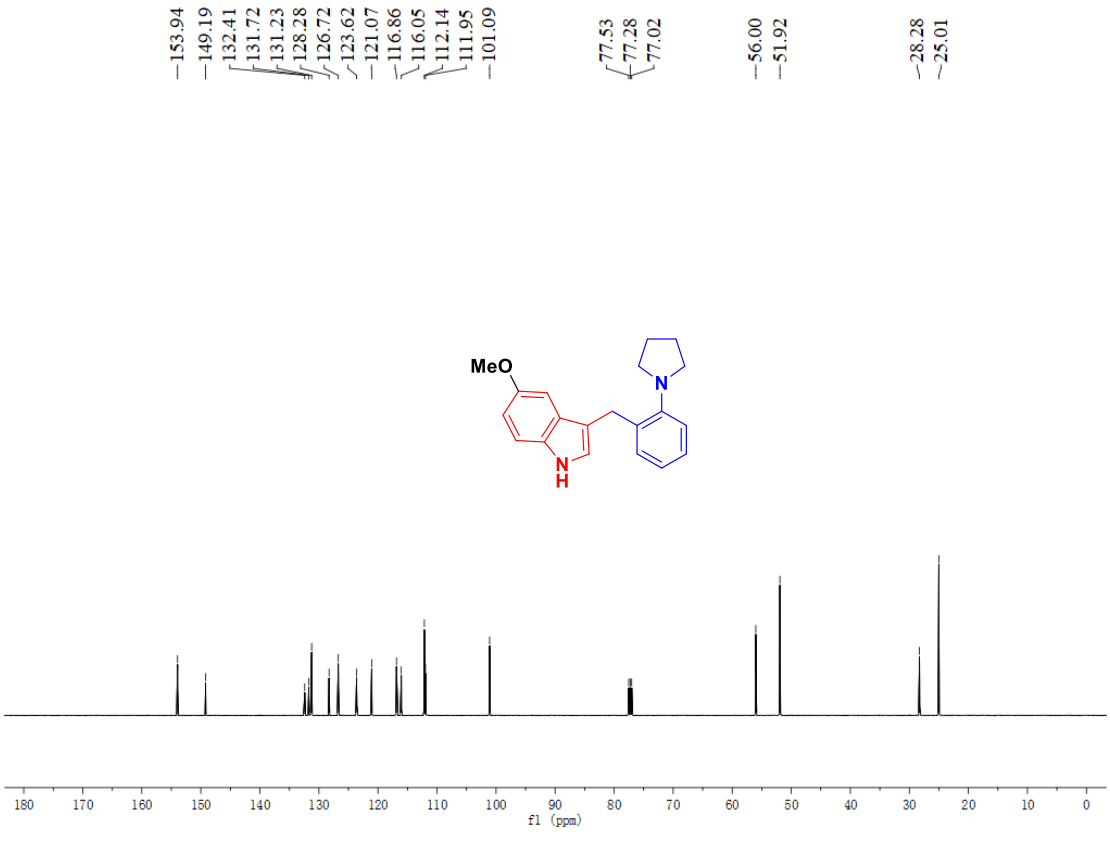
2-(3-chloro-2-(2,5-diallylpyrrolidin-1-yl)benzyl)-5-(diethylamino)phenol (6f)



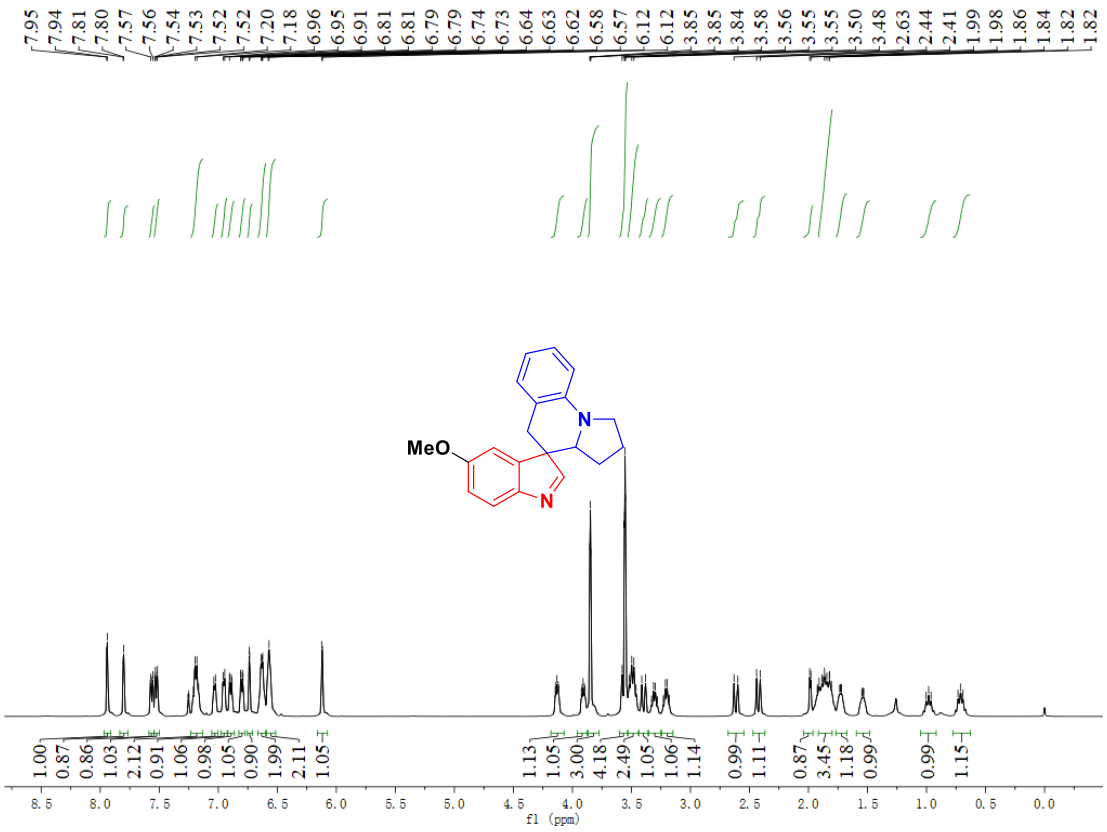


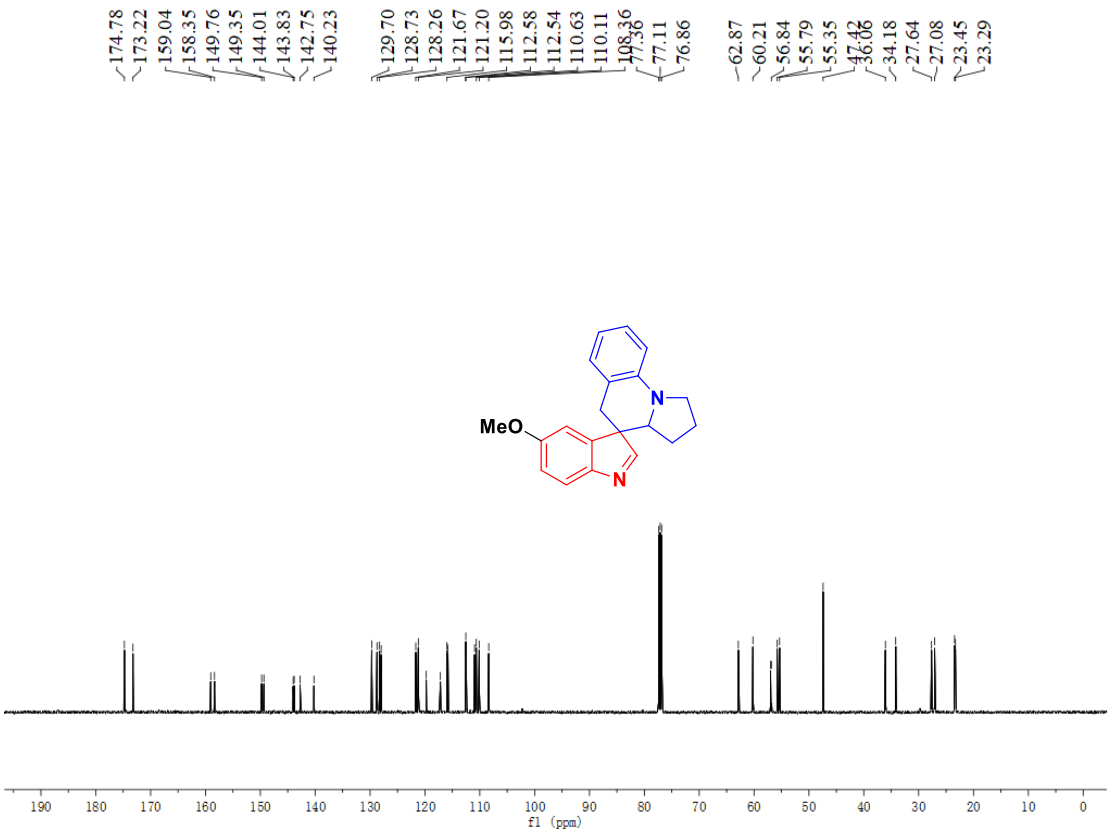
5-methoxy-3-(2-(pyrrolidin-1-yl)benzyl)-1H-indole (7)





5-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[indole-3,4'-pyrrolo[1,2-a]quinoline] (11)[4]





2-allyl-5-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline] (12)