Supplementary Information

Rh(III)-Catalyzed dual C-H functionalization of 3-(1*H*-indol-3-yl)-3-oxopropanenitriles with Sulfoxonium Ylides or Diazo Compounds toward Polysubstituted Carbazoles

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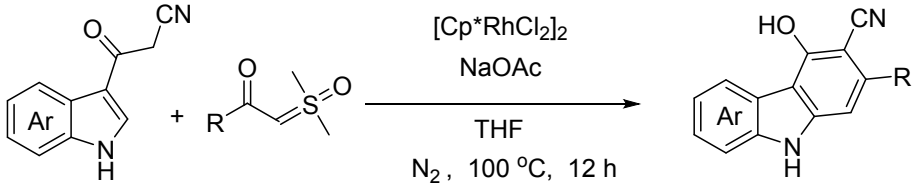
1. General Information

Unless otherwise noted, all the reactions were carried out under nitrogen atmosphere using standard Schlenk technique，and all chemicals were purchased from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to DMSO-d^6 (δ 2.50 or 39.52 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using a 6200 TOF focus spectrometer (APCI-TOF). Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA). All melting points were tested after recrystallization with CH_2Cl_2.

3. Screening of the reaction conditions

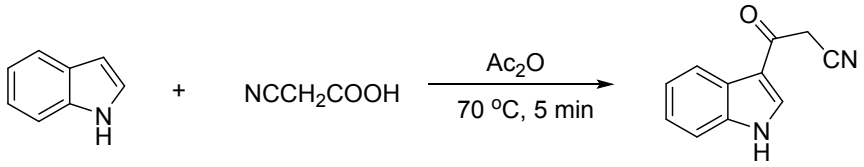


entry	catalyst	additive	solvent	yield[b] (%)
1	[Cp*Rh(MeCN)$_3$] (SbF_6)$_2$	NaOAc	DCE	31
2	[Cp*Co(CO)I_2]	NaOAc	DCE	n.r.
3	$Pd(OAc)_2$	NaOAc	DCE	n.r.
4	[Cp*$IrCl_2$]$_2$	NaOAc	DCE	46
5	[Cp*Rh$(OAc)_2$]$_2$	NaOAc	DCE	49
6	[Cp*$RhCl_2$]$_2$	NaOAc	DCE	55
7	[Cp*$RhCl_2$]$_2$	NaOAc	MeCN	69
8	[Cp*$RhCl_2$]$_2$	NaOAc	DMF	73
9	[Cp*$RhCl_2$]$_2$	NaOAc	EtOH	41
10	[Cp*$RhCl_2$]$_2$	NaOAc	THF	70[c], 83,77[d]
11	[Cp*$RhCl_2$]$_2$	LiOAc	THF	72
12	[Cp*$RhCl_2$]$_2$	CsOAc	THF	78
13	[Cp*$RhCl_2$]$_2$	HOAc	THF	n.r.
14	[Cp*$RhCl_2$]$_2$	Cu$(OAc)_2$	THF	<10
15	[Cp*$RhCl_2$]$_2$	AgOAc	THF	n.r.

[a] Reaction conditions: 3-(1*H*-indol-3-yl)-3-oxopropanenitriles **1a** (0.1 mmol), sulfoxonium ylide **2a** (0.12 mmol), [Cp*$RhCl_2$]$_2$ (5 mol %), additive (0.2 mmol), solvent (2.0 mL), N_2 (1.0 atm.), at 100 °C for 12 h, in a sealed Schlenk tube. [b] Isolated yield. [c] **1a** (0.1 mmol), **2a** (0.1 mmol). [d] **1a** (0.1 mmol), **2a** (0.15 mmol).

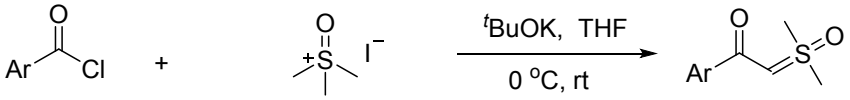
3. Synthesis and Reaction

3.1 Preparation of substituted 3-cyanoacetylindole[1]



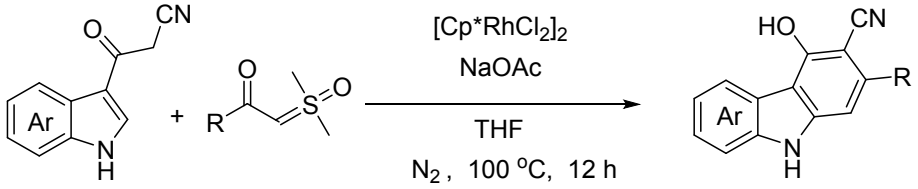
3-cyanoacetylindoles were prepared according to the reported procedures. Indole (5.85 g, 50 mmol) was added to a solution prepared by dissolution of cyanoacetic acid (5.0 g, 50 mmol) in Ac_2O (50 mL) at 50 ℃. The solution was heated at 85 °C for 5 minutes. During that period 3-cyanoacetylindole started to crystallize. After 5 more minutes, the mixture was allowed to cool and the solid was collected, washed with MeOH and dried.

3.2 Preparation of substituted sulfoxonium ylides



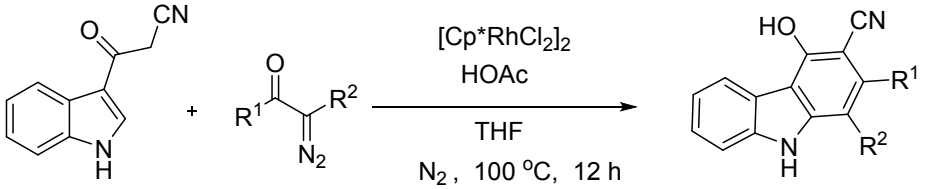
Ylides were prepared according to the reported procedures.[2] To a stirred solution of potassium *tert*-butoxide (3.0 g, 27.2 mmol) in THF (30 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture is refluxed for 2 h. Then reaction mixture is cooled to 0 °C, followed by addition of acyl chlorides (7 mmol) in THF (5 mL). The reaction was allowed to room temperature and stirred for 3 h. Next, the solvent was evaporated and water (15 mL) and ethyl acetate (20 mL) were added to the resulting slurry. The layers were separated and the aqueous layer was washed with ethyl acetate (2 × 30 mL) and the organic layers were combined. The organic solution was dried over anhydrous sodium sulphate (Na_2SO_4), filtered over a sintered funnel, and evaporated to dryness. The crude product was purified by recrystallization with MTBE.

3.3 General procedure for the synthesis of 3



A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted 3-cyanoacetylindole (0.1 mmol, 1.0 eq.), sulfoxonium ylide (0.12 mmol, 1.2 equiv.), $[Cp^*RhCl_2]_2$ (3.0 mg, 5 mol %), NaOAc (0.2 mmol, 2.0 equiv.) and THF (2.0 mL). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 12 h under N_2 in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The water (2.0 mL) and ethyl acetate (2.0 mL) were added, the layers were separated and the aqueous layer was washed with ethyl acetate (2 × 30 mL) and the organic layers were combined, washed with brine (5 mL) and dried over Na_2SO_4, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V1/V2, 5:1) as the eluent to give the desired products.

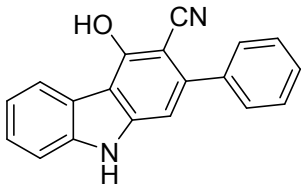
3.4 General procedure for the synthesis of 5



A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted 3-cyanoacetylindole (0.1 mmol, 1.0 eq.), diazo compound (0.12 mmol, 1.2 equiv.), $[Cp^*RhCl_2]_2$ (3.0 mg, 5 mol %), HOAc (0.2 mmol, 2.0 equiv.) and THF (2.0 mL). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 12 h under N_2 in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The water (2.0 mL) and ethyl acetate (2.0 mL) were added, the layers were separated and the aqueous layer was washed with ethyl acetate (2 × 30 mL) and the organic layers were combined, washed with brine (5 mL) and dried over Na_2SO_4, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V1/V2, 5:1) as the eluent to give the desired products.

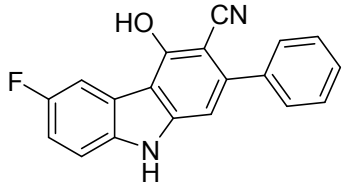
4. Characterization Data for the Products

4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3aa)[3]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3aa** as a brown solid (23.5 mg, 83% yield). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.82 (s, 1H), 11.05 (s, 1H), 8.30-8.28 (m, 1H), 7.62-7.60 (m, 2H), 7.56-7.41 (m, 5H), 7.28-7.24 (s, 1H), 7.11 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.2, 143.4, 142.5, 139.7, 139.5, 129.0, 128.5, 128.1, 125.7, 122.5, 121.2, 120.0, 118.2, 111.3, 111.2, 105.4, 89.9.

6-fluoro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ba)

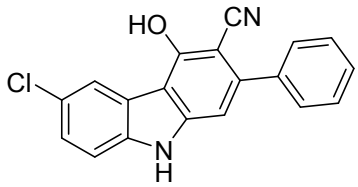


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ba** (18.7 mg, 62% yield) as a yellow solid. m.p. 156-157 ^{o}C ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.88 (s, 1H), 11.23 (s, 1H), 8.04-8.01 (m, 1H), 7.62-7.44 (m, 6H), 7.31-7.26 (m, 1H), 7.13 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.8, 157.4 (d, $J_{C\text{-}F}$ = 232.5 Hz), 144.7, 143.5, 139.8, 136.5, 129.4, 128.9, 128.6, 121.9 (d, $J_{C\text{-}F}$ = 10.5 Hz), 118.4, 113.8 (d, $J_{C\text{-}F}$ = 24.8 Hz), 112.6 (d, $J_{C\text{-}F}$ = 9.8 Hz), 111.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 108.1 (d, $J_{C\text{-}F}$ = 24.8 Hz), 105.9, 90.2.

MS (m/z): 302.3 $[M]^{+}$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}FN_2O$ $[M-H]^{-}$ 301.0783, found: 301.0804.

6-chloro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ca)

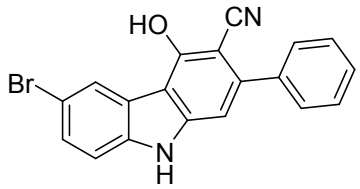


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ca** (22.9 mg, 72% yield) as a yellow solid. m.p. 187-188 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.98 (s, 1H), 11.28 (s, 1H), 8.31-8.28 (m, 1H), 7.63-7.42 (m, 7H), 7.13 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.9, 144.3, 143.7, 139.7, 138.5, 129.4, 128.9, 128.7, 126.0, 124.6, 122.8, 121.9, 118.3, 113.1, 110.8, 105.9, 90.6.

MS (m/z): 318.1 $[M]^{+}$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}ClN_2O$ $[M-H]^{-}$ 317.0487, found: 317.0493.

6-bromo-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3da)

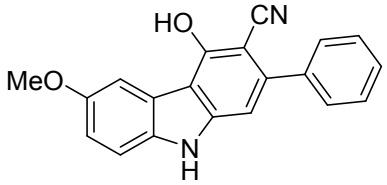


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3da** (27.2 mg, 75% yield) as a yellow solid. m.p. 218-219 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.98 (s, 1H), 11.27 (s, 1H), 8.41-8.31 (m, 1H), 7.62-7.45 (m, 7H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.1, 144.3, 143.9, 139.8, 138.9, 129.5, 129.1, 128.9, 128.7, 124.9, 123.5, 118.5, 113.7, 112.5, 110.9, 105.9, 90.8.

MS (m/z): 362.0 [M] $^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}BrN_2O$ $[M-H]^-$ 360.9982, found: 360.9980.

4-hydroxy-6-methoxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ea)

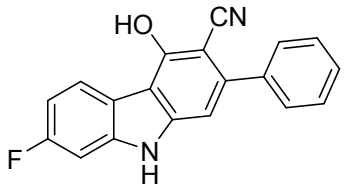


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ea** (25.1 mg, 80% yield) as a yellow solid. m.p. 265-266 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.66 (s, 1H), 11.03 (s, 1H), 7.84-7.83 (m, 1H), 7.62-7.58 (m, 2H), 7.55-7.43 (m, 4H), 7.10-7.06 (m, 2H), 3.86 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.7, 154.2, 144.2, 142.6, 139.9, 134.7, 129.4, 128.9, 128.5, 122.0, 118.6, 115.2, 112.3, 111.5, 105.8, 105.6, 89.7, 56.0.

MS (m/z): 314.1 [M] $^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O_2$ $[M-H]^-$ 313.0983, found: 313.1010.

7-fluoro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3fa)



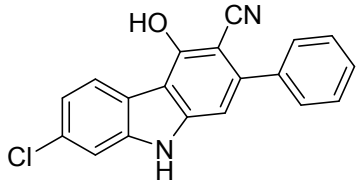
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3fa** (19.9 mg, 66% yield) as a yellow solid. m.p. 293-294 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.92 (s, 1H), 11.13 (s, 1H), 8.28-8.24 (m, 1H), 7.61-7.58 (m, 2H), 7.54-7.44 (m, 3H), 7.36-7.33 (m, 1H), 7.12-7.07 (m, 2H); ^{13}C NMR (100 MHz,

DMSO-d_6) δ 161.6 (d, J_{C-F} = 238.0 Hz), 157.4, 144.6, 143.0, 141.0, 140.9, 139.9, 129.6, 129.0, 128.7, 124.1 (d, J_{C-F} = 11 Hz), 111.5 (d, J_{C-F} = 9 Hz), 108.5 (d, J_{C-F} = 24.0 Hz), 106.0, 98.4 (d, J_{C-F} = 26.0 Hz), 91.0.

MS (m/z): 302.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}FN_2O$ $[M-H]^-$ 301.0783, found: 301.0804.

7-chloro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ga)

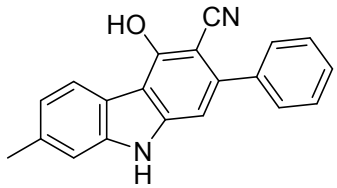


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ga** (23.2 mg, 73% yield) as a yellow solid. m.p. 268-269 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.93 (s, 1H), 11.22 (s, 1H), 8.27-8.25 (m, 1H), 7.62-7.59 (m, 3H), 7.55-7.45 (m, 3H), 7.30-7.27 (m, 1H), 7.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.6, 144.2, 143.5, 140.7, 139.7, 130.6, 129.4, 128.9, 128.7, 124.0, 120.6, 120.5, 118.3, 111.4, 111.2, 105.9, 90.9.

MS (m/z): 318.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}ClN_2O$ $[M-H]^-$ 317.0487, found: 317.0493.

4-hydroxy-7-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ha)

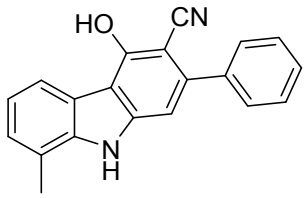


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ha** (23.2 mg, 78% yield) as a yellow solid. m.p. 130-131 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.70 (s, 1H), 10.95 (s, 1H), 8.18-8.15 (m, 1H), 7.62-7.58 (m, 2H), 7.55-7.43 (m, 3H), 7.35-7.34 (m, 1H), 7.10-7.06 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.2, 143.8, 142.4, 140.5, 139.9, 135.8, 129.4, 128.9, 128.5, 122.5, 121.9, 119.3, 118.6, 111.7, 111.6, 105.7, 90.2, 22.1.

MS (m/z): 298.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^-$ 297.1033, found: 297.1053.

4-hydroxy-8-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ia)

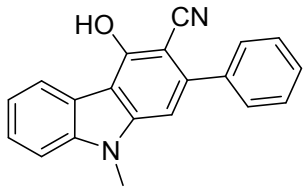


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ia** (23.5 mg, 79% yield) as a yellow solid. m.p. 140-141 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.76 (s, 1H), 11.03 (s, 1H), 8.16-8.14 (m, 1H), 7.64-7.60 (m, 2H), 7.56-7.44 (m, 3H), 7.25-7.12 (m, 3H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.6, 143.8, 142.7, 139.9, 139.3, 129.4, 129.1, 128.6, 126.7, 121.2, 120.7, 120.6, 120.4, 118.6, 112.0, 105.8, 90.1, 17.4.

MS (m/z): 298.1 $[M]^{+}$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^{-}$ 297.1033, found: 297.1053.

4-hydroxy-9-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ja)

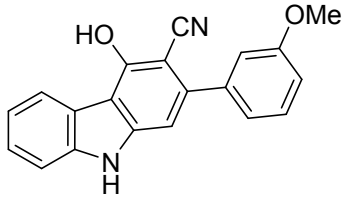


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ja** (24.1 mg, 81% yield) as a yellow solid. m.p. 280-281 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.09 (s, 1H), 8.33-8.30 (m, 1H), 7.66-7.62 (m, 3H), 7.56-7.45 (m, 4H), 7.33-7.27 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.5, 144.4, 143.1, 141.0, 139.9, 129.6, 128.9, 128.6, 126.2, 122.8, 121.2, 120.7, 118.5, 111.0, 109.9, 104.3, 90.6, 29.9.

MS (m/z): 298.1 $[M]^{+}$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^{-}$ 297.1033, found: 297.1053.

4-hydroxy-2-(3-methoxyphenyl)-9*H*-carbazole-3-carbonitrile (3ab)



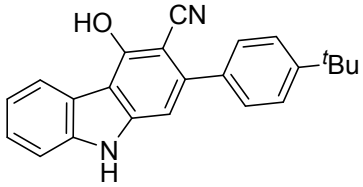
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ab** (20.4 mg, 65% yield) as a yellow solid. m.p. 258-259 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.82 (s, 1H), 11.05 (s, 1H), 8.31-8.28 (m, 1H), 7.56-7.41 (m, 3H), 7.27-7.14 (m, 4H), 7.04-7.02 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5, 157.6, 143.7, 142.7, 141.2, 140.0, 130.0, 126.2, 122.8, 121.8, 121.6, 120.4,

118.5, 115.0, 114.1, 111.7, 111.6, 105.7, 90.3, 55.7.

MS (m/z): 314.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O_2$ $[M-H]^-$ 313.0983, found: 313.1010.

2-(4-(*tert*-butyl)phenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ac)

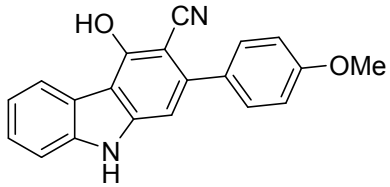


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ac** (25.2 mg, 74% yield) as a yellow solid. m.p. 209-210 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.84 (s, 1H), 11.04 (m, 1H), 8.35-8.32 (m, 1H), 7.57-7.41 (m, 6H), 7.28-7.24 (m, 1H), 7.13 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9, 151.1, 144.0, 142.9, 140.2, 137.1, 129.2, 126.2, 125.8, 123.0, 121.8, 120.5, 118.9, 111.7, 111.7, 105.8, 90.3, 34.9, 31.7.

MS (m/z): 340.2 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{23}H_{19}N_2O$ $[M-H]^-$ 339.1503, found: 339.1516.

4-hydroxy-2-(4-methoxyphenyl)-9*H*-carbazole-3-carbonitrile (3ad)

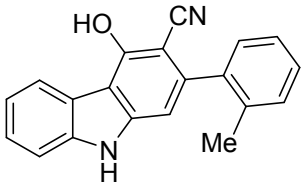


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ad** (23.0 mg, 71% yield) as a yellow solid. m.p. 255-256 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.78 (s, 1H), 10.98 (s, 1H), 8.29-8.27 (m, 1H), 7.55-7.52 (m, 3H), 7.44-7.40 (m, 1H), 7.26-7.22 (m, 1H), 7.08-7.06 (m, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 157.6, 143.8, 142.7, 140.0, 132.1, 130.6, 126.1, 122.8, 121.6, 120.3, 118.7, 114.3, 111.5, 111.3, 105.4, 90.3, 55.7.

MS (m/z): 314.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O_2$ $[M-H]^-$ 313.0983, found: 313.1010.

4-hydroxy-2-(*o*-tolyl)-9*H*-carbazole-3-carbonitrile (3ae)

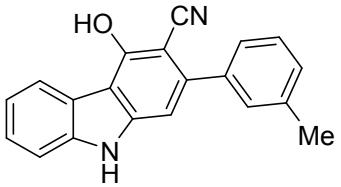


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ae** (22.6 mg, 76% yield) as a yellow solid. m.p. 226-227 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.82 (m, 1H), 11.09 (m, 1H), 8.34-8.31 (m, 1H), 7.58-7.55 (m, 1H), 7.46-7.41 (m, 1H), 7.35-7.24 (m, 5H), 6.98 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.0, 143.7, 143.0, 140.0, 139.9, 136.0, 130.4, 130.0, 128.6, 126.1, 126.1, 122.8, 121.7, 120.4, 118.1, 111.6, 111.5, 105.8, 91.5, 20.0.

MS (m/z): 298.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^-$ 297.1033, found: 297.1053.

4-hydroxy-2-(*m*-tolyl)-9*H*-carbazole-3-carbonitrile (3af)

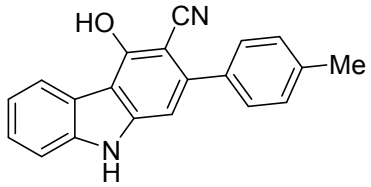


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3af** (23.2 mg, 78% yield) as a yellow solid. m.p. 225-226 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.82 (s, 1H), 11.07 (s, 1H), 8.36-8.33 (m, 1H), 7.59-7.56 (m, 1H), 7.46-7.37 (m, 4H), 7.28-7.24 (m, 2H), 7.15-7.14 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.8, 143.9, 143.2, 140.2, 140.0, 138.2, 130.1, 129.3, 128.9, 126.7, 126.3, 123.0, 121.8, 120.5, 118.7, 111.8, 111.7, 105.8, 90.5, 21.6.

MS (m/z): 298.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^-$ 297.1033, found: 297.1053.

4-hydroxy-2-(*p*-tolyl)-9*H*-carbazole-3-carbonitrile (3ag)



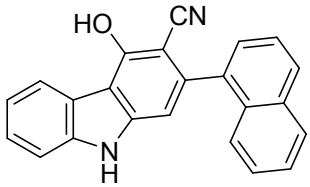
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ag** (22.4 mg, 75% yield) as a yellow solid. m.p. 230-231 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.82 (s, 1H), 11.07 (s, 1H), 8.35-8.31 (m, 1H), 7.58-7.41 (m, 4H), 7.31-7.24 (m, 3H), 7.12 (s, 1H) 2.36 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.7, 143.9, 143.0, 140.0, 138.0, 137.0, 129.5, 129.3, 126.1, 122.8, 121.6, 120.4, 118.7,

111.6, 111.5, 105.6, 90.3.

MS (m/z): 298.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{20}H_{13}N_2O$ $[M-H]^-$ 297.1033, found: 297.1053.

4-hydroxy-2-(naphthalen-1-yl)-9*H*-carbazole-3-carbonitrile (3ah)

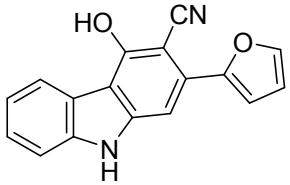


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ah** (19.4 mg, 58% yield) as a yellow solid. m.p. 277-278 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.90 (s, 1H), 11.22 (s, 1H), 8.43-8.40 (m, 1H), 8.02-8.00 (m, 2H), 7.65-7.45 (m, 7H), 7.33-7.29 (m, 1H), 7.20-7.18 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.3, 143.8, 141.6, 140.2, 137.9, 133.8, 132.1, 129.0, 128.9, 128.0, 127.2, 126.7, 126.4, 125.9, 123.1, 121.9, 120.6, 118.2, 112.0, 111.8, 107.2, 92.4.

MS (m/z): 334.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{23}H_{13}N_2O$ $[M-H]^-$ 333.1033, found: 333.1057.

2-(furan-2-yl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ai)

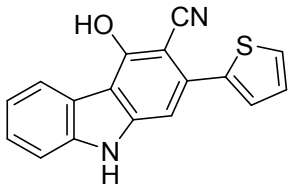


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3ai** (18.1 mg, 66% yield) as a brown solid. m.p. 270-271 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.87 (s, 1H), 11.16 (s, 1H), 8.33-8.30 (m, 1H), 7.87 (s, 1H), 7.57-7.52 (m, 2H), 7.45-7.41 (m, 1H), 7.28-7.24 (m, 2H), 6.71-6.69 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.2, 151.2, 144.1, 144.0, 140.4, 130.4, 126.5, 123.0, 121.8, 120.7, 118.9, 112.8, 112.0, 111.7, 109.9, 102.2, 87.0.

MS (m/z): 274.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{17}H_9N_2O_2$ $[M-H]^-$ 273.0670, found: 273.0689.

4-hydroxy-2-(thiophen-2-yl)-9*H*-carbazole-3-carbonitrile (3aj)

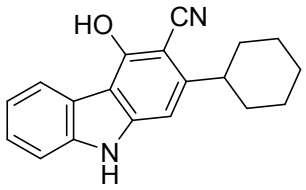


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3aj** (20.0 mg, 69% yield) as a brown solid. m.p. 185-186 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.84 (s, 1H), 11.19 (s, 1H), 8.35-8.33 (m, 1H), 7.67-7.66 (m, 1H), 7.60-7.56 (m, 2H), 7.46-7.42 (m, 1H), 7.29-7.21(m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.2, 143.9, 141.2, 140.3, 134.7, 128.7, 127.8, 127.7, 126.5, 123.0, 121.7, 120.7, 118.7, 112.2, 111.8, 105.7, 89.8.

MS (m/z): 290.0 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{17}H_9N_2OS$ $[M-H]^-$ 289.0441, found: 289.0454.

2-cyclohexyl-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ak)

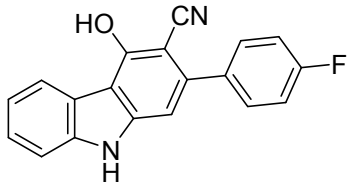


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 11) give **3ak** (18.0 mg, 62% yield) as a yellow solid. m.p. 244-245 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.61 (s, 1H), 10.76 (s, 1H), 8.22-8.20 (m, 1H), 7.50-7.18 (m, 3H), 7.00 (s, 1H), 2,90-2.84 (m, 1H), 1.93-1.72 (m, 5H), 1.55-1.26 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 13C NMR (100 MHz, DMSO) δ 157.0, 148.8, 144.3, 139.8, 125.7, 122.5, 121.7, 120.1, 118.1, 111.4, 110.7, 101.8, 90.9, 43.0, 34.0, 27.0, 26.1.

MS (m/z): 290.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{17}N_2O$ $[M-H]^-$ 289.1346, found: 289.1362.

2-(4-fluorophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3al)



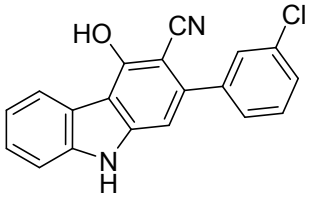
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3al** (16.9 mg, 56% yield) as a yellow solid. m.p. 225-226 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.83 (s, 1H), 11.09 (s, 1H), 8.31-8.29 (m, 1H), 7.68-7.63 (m, 2H), 7.56-7.54 (m, 1H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 2H), 7.27-7.23 (m, 1H), 7.11 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.7 (d, J_{C-F} = 244.0 Hz), 157.8, 143.9, 142.0,

140.2, 136.4 (d, J_{C-F} = 3.0 Hz),131.6 (d, J_{C-F} = 8.0 Hz), 126.3, 123.0, 121.7, 120.6, 118.7, 115.9 (d, J_{C-F} = 21.0 Hz), 111.8, 111.7, 106.0, 90.5.

MS (m/z): 302.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}FN_2O$ $[M-H]^-$ 301.0783, found: 301.0804.

2-(3-chlorophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3am)

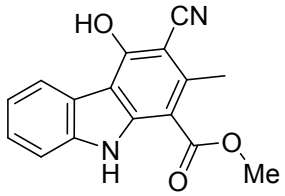


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3am** (19.7 mg, 62% yield) as a yellow solid. m.p. 218-219 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.86 (s, 1H), 11.14 (s, 1H), 8.31-8.28 (m, 1H), 7.67-7.65 (m, 1H), 7.58-7.52 (m, 4H), 7.47-7.41 (m, 1H), 7.28-7.23 (m, 1H), 7.14 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.1, 143.8, 142.0, 141.3, 140.2, 133.6, 130.9, 129.2, 128.6, 128.4, 126.4, 123.0, 121.7, 120.6, 118.6, 112.1, 111.8, 105.9, 90.2.

MS (m/z): 318.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{10}ClN_2O$ $[M-H]^-$ 317.0487, found: 317.0493.

methyl 3-cyano-4-hydroxy-2-methyl-9*H*-carbazole-1-carboxylate (5aa)

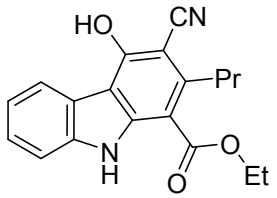


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5aa** (22.4 mg, 80% yield) as a yellow solid. m.p. 281-282 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.48 (s, 1H), 8.32-8.22 (m, 1H), 7.71-7.68 (m, 1H), 7.46-7.40 (m, 1H), 7.28-7.22 (m, 1H), 3.97 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.6, 159.1, 143.4, 143.4, 139.8, 126.4, 122.6, 121.4, 121.0, 117.7, 112.5, 111.5, 107.0, 94.5, 52.7, 20.7.

MS (m/z): 280.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{16}H_{11}N_2O_3$ $[M-H]^-$ 279.0775, found: 279.0803.

ethyl 3-cyano-4-hydroxy-2-propyl-9*H*-carbazole-1-carboxylate (5ab)

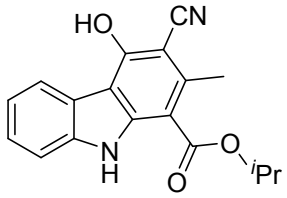


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5ab** (23.2 mg, 72% yield) as a yellow solid. m.p. 226-227 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.51 (s, 1H), 8.25-8.23 (m, 1H), 7.71-7.68 (m, 1H), 7.44-7.39 (m, 1H), 7.27-7.21 (m, 1H), 4.49-4.42 (m, 2H), 3.17-3.11 (m, 2H), 1.70-1.63 (m, 2H), 1.41-1.36 (m, 3H), 1.03-0.98 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 147.1, 143. 4, 139.9, 126.3, 122.6, 121.3, 121.0, 117.6, 112.6, 111.6, 107.1, 93.9, 61.6, 35.6, 25.1, 14.7, 14.7.

MS (m/z): 322.1 [M] $^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{17}N_2O_3$ [M−H]$^-$ 321.1245, found: 321.1243.

isopropyl 3-cyano-4-hydroxy-2-methyl-9*H*-carbazole-1-carboxylate (5ac)

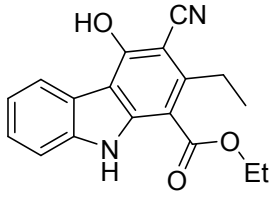


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5ac** (25.3 mg, 82% yield) as a yellow solid. m.p. 314-315 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.49 (s, 1H), 8.31-8.22 (m, 1H), 7.74-7.65 (m, 1H), 7.44-7.39 (m, 1H), 7.27-7.22 (m, 1H), 5.31-5.23 (m, 1H), 2.78 (s, 3H), 1.44-1.40 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 158.9, 143.7, 142.2, 134.0, 126.3, 122.5, 121.3, 121.0, 117.8, 112.8, 111.5, 107.7, 94.4, 69.5, 22.3, 21.0.

MS (m/z): 308.1 [M] $^+$.

HRMS (APCI-TOF): Calcd for $C_{18}H_{15}N_2O_3$ [M−H]$^-$ 307.1088, found: 307.1084.

ethyl 3-cyano-2-ethyl-4-hydroxy-9*H*-carbazole-1-carboxylate (5ad)



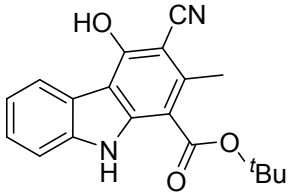
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5ad** (22.3 mg, 76% yield) as a yellow solid. m.p. 251-252 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.51 (s, 1H), 8.30-8.23 (m, 1H), 7.71-7.69 (m, 1H), 7.44-7.40 (m, 1H), 7.27-7.23 (m, 1H), 4.49-4.44 (q, 2H), 3.20-3.14 (q, 2H), 1.41-1.37 (t, 3H), 1.30-

1.26 (t, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 159.2, 148.7, 143.4, 139.9, 126.4, 122.6, 121.3, 121.0, 117.5, 112.6, 111.6, 107.1, 93.4, 61.6, 27.1, 16.2, 14.7.

MS (m/z): 308.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{18}H_{15}N_2O_3$ $[M-H]^-$ 307.1088, found: 307.1084.

tert-butyl 3-cyano-4-hydroxy-2-methyl-9_H_-carbazole-1-carboxylate (5ae)



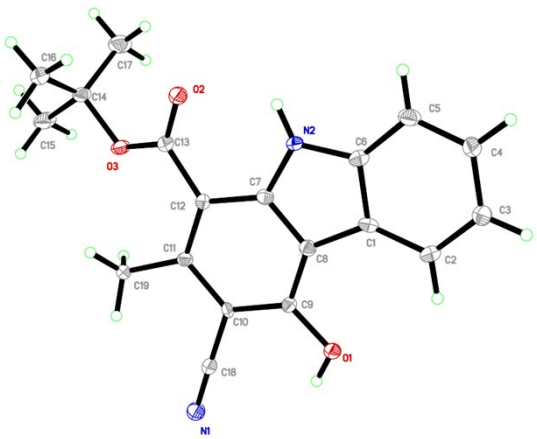
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5ae** (28.6 mg, 85% yield) as a yellow solid. m.p. 206-207 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 11.46 (s, 1H), 7.74-7.71 (m, 1H), 7.43-7.37 (m, 1H), 7.26-7.20 (m, 1H), 2.77 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 159.09, 143.7, 141.9, 139.8, 126.0, 122.3, 121.2, 120.8, 117.9, 112.6, 111.3, 108.2, 94.3, 82.4, 28.5, 21.2.

MS (m/z): 322.1 $[M]^+$.

HRMS (APCI-TOF): Calcd for $C_{19}H_{17}N_2O_3$ $[M-H]^-$ 321.1245, found: 321.1243.

5. Single Crystal Data of 5ae

CCDC 1848812
Summary of Data CCDC 1848812
Formula: $C_{19}H_{18}N_2O_3$
Unit Cell Parameters: a 6.8817(10) b 9.3770(11) c 13.0597(15) P-1



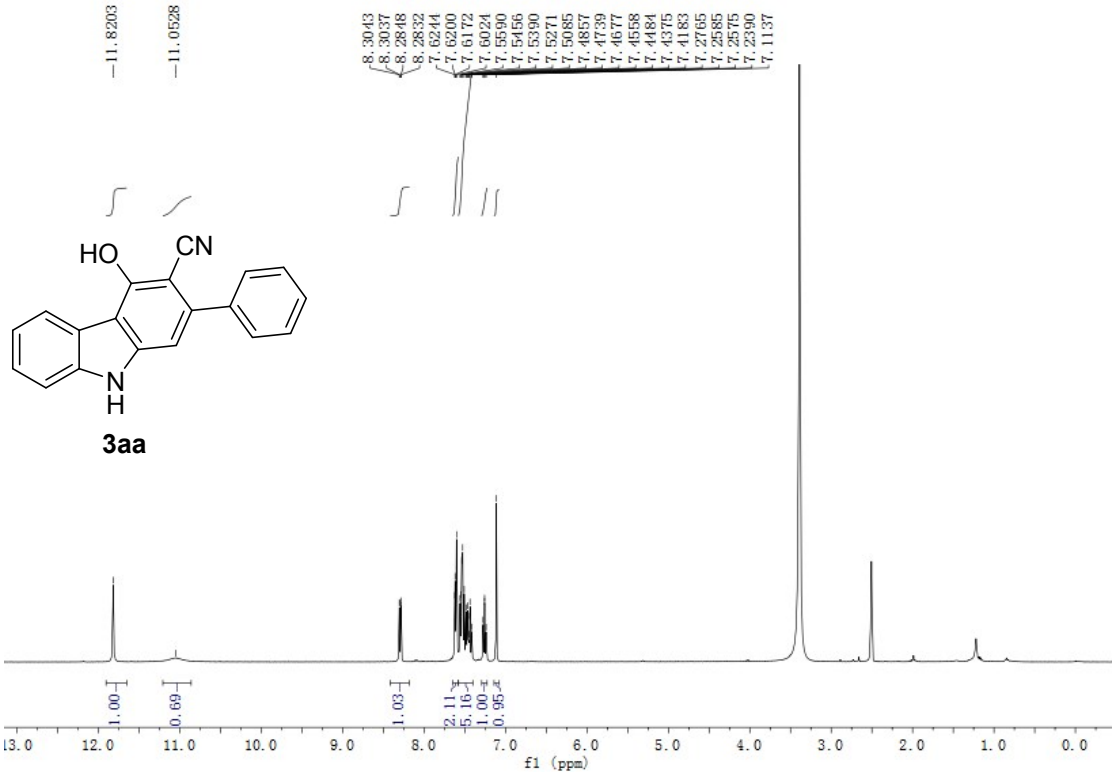
Crystal structure of 5ae

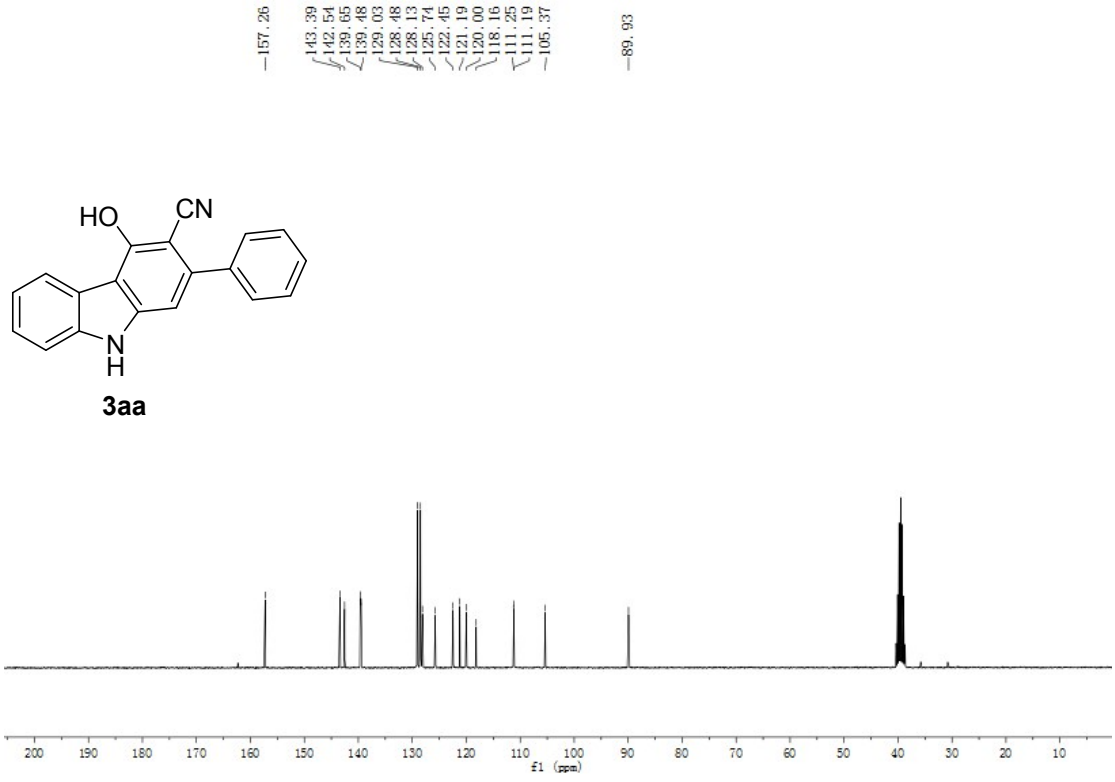
6. Reference.

1. J. Slätt, I. Romero and J. Bergman, *Synthesis.,* 2004, **16**, 2760.
2. J. Vaitla, A. Bayer and K. H. Hopmann, *Angew. Chem. Int. Ed*., 2017, **56**, 4277.
3. T. Shigeo, C. Tominari, M. Kohji, Y. Akira, H. Yuhzo, N. Junko and H. Satoshi, *Heterocycles.,* 2010, **82**, 397.

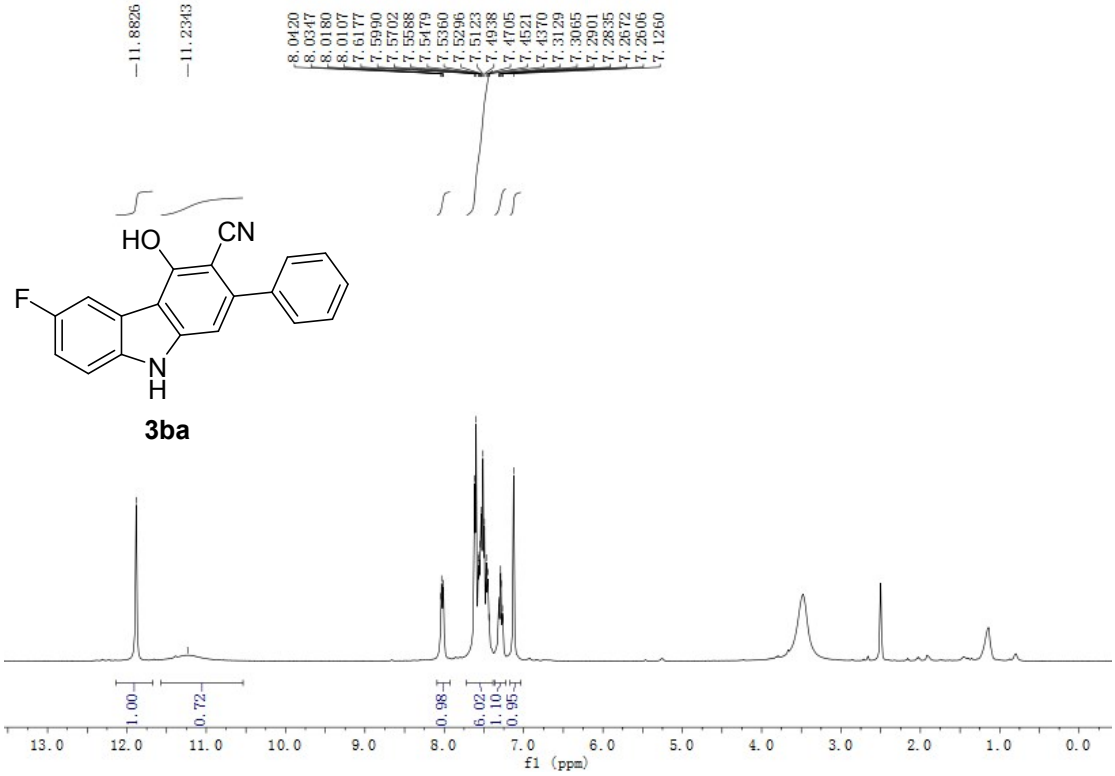
7. ^{1}H NMR, ^{13}C NMR Spectra

4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3aa):

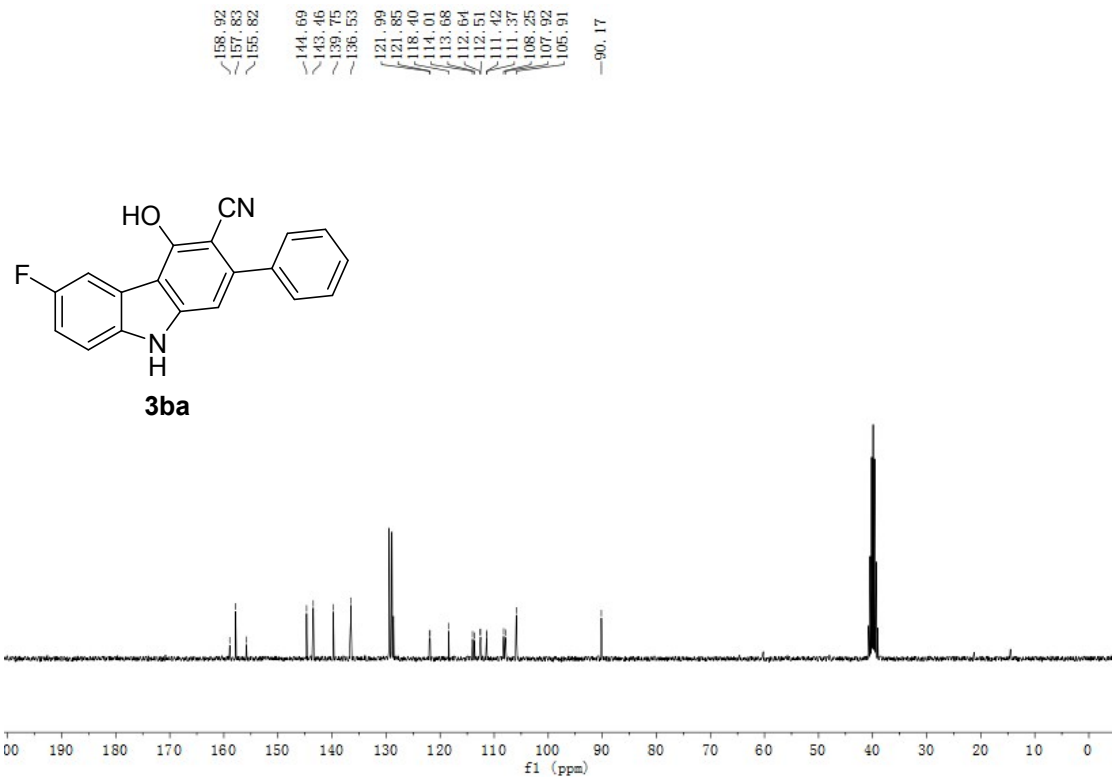




6-fluoro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ba):

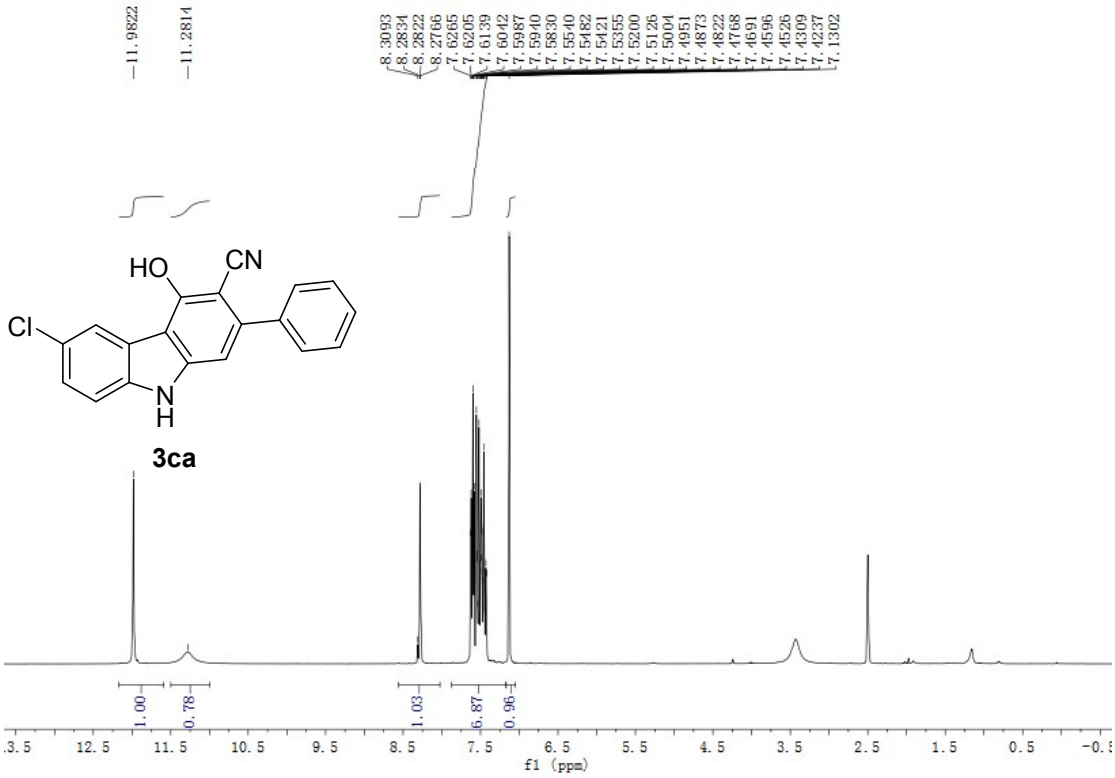


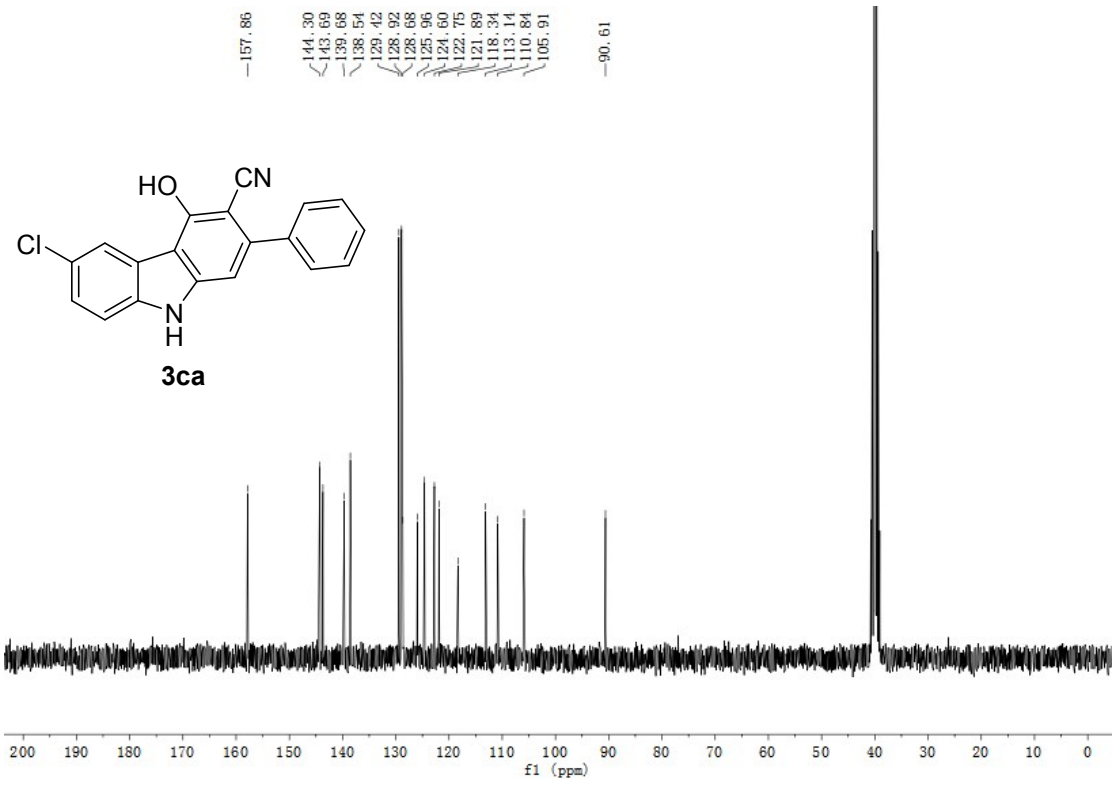
3ba



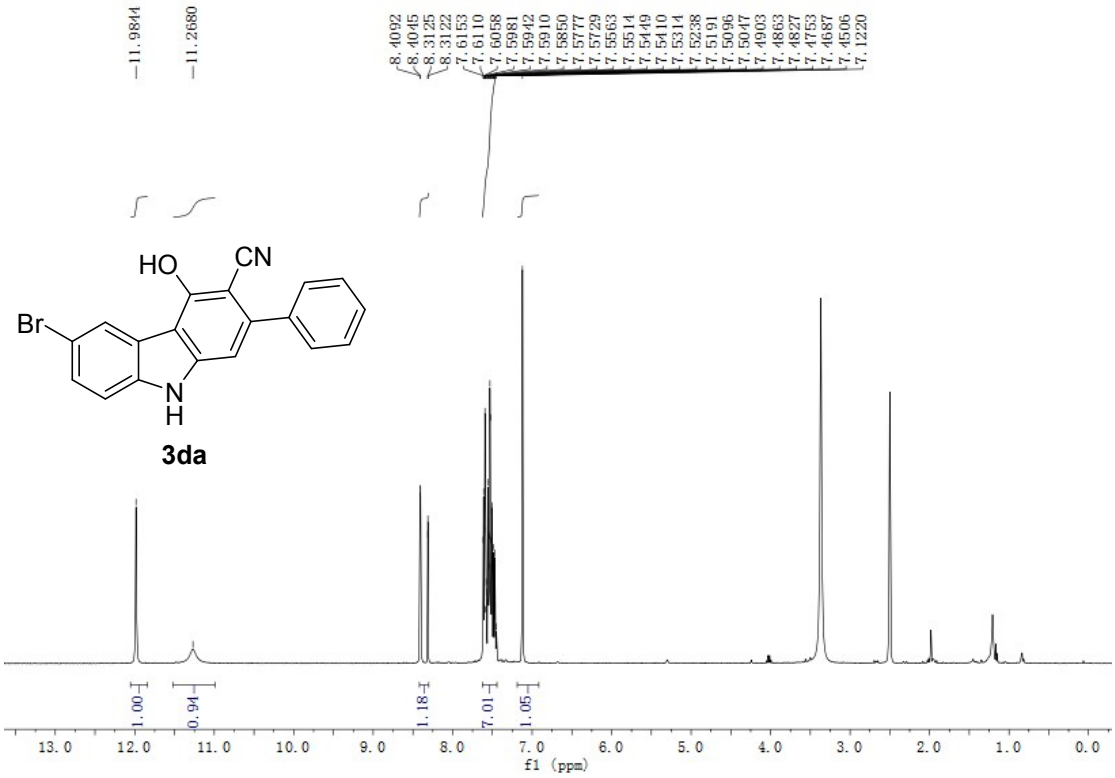
3ba

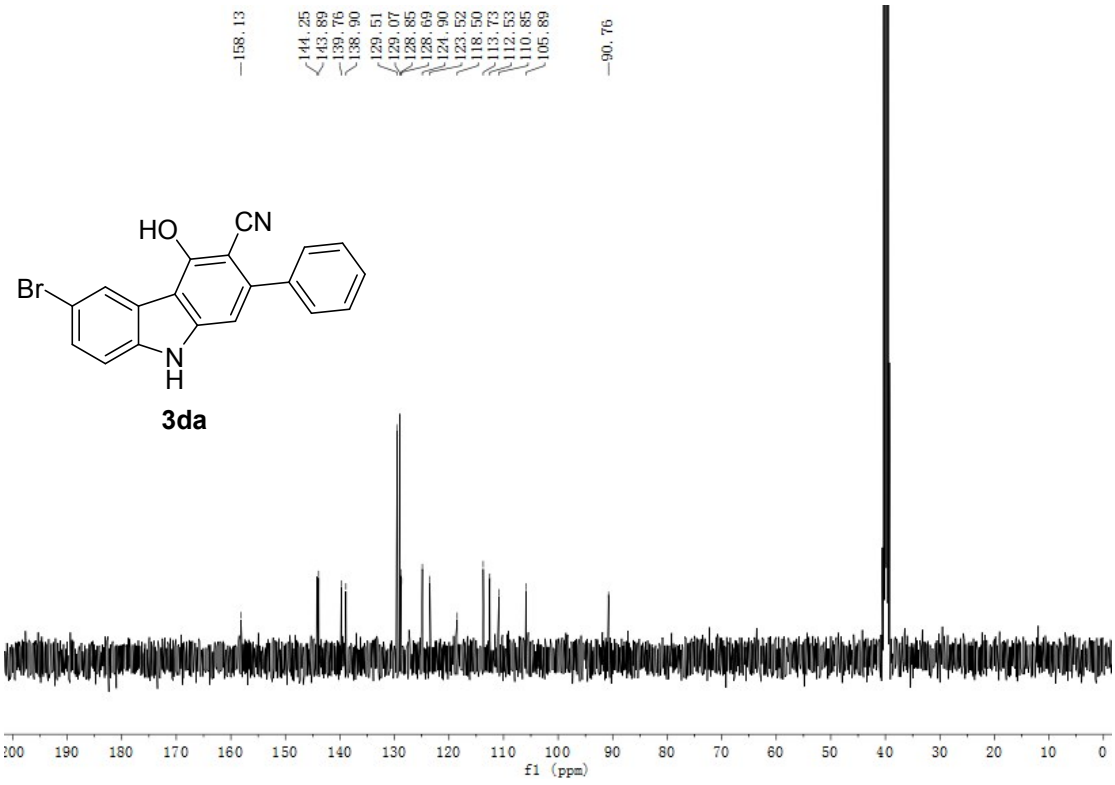
6-chloro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ca):



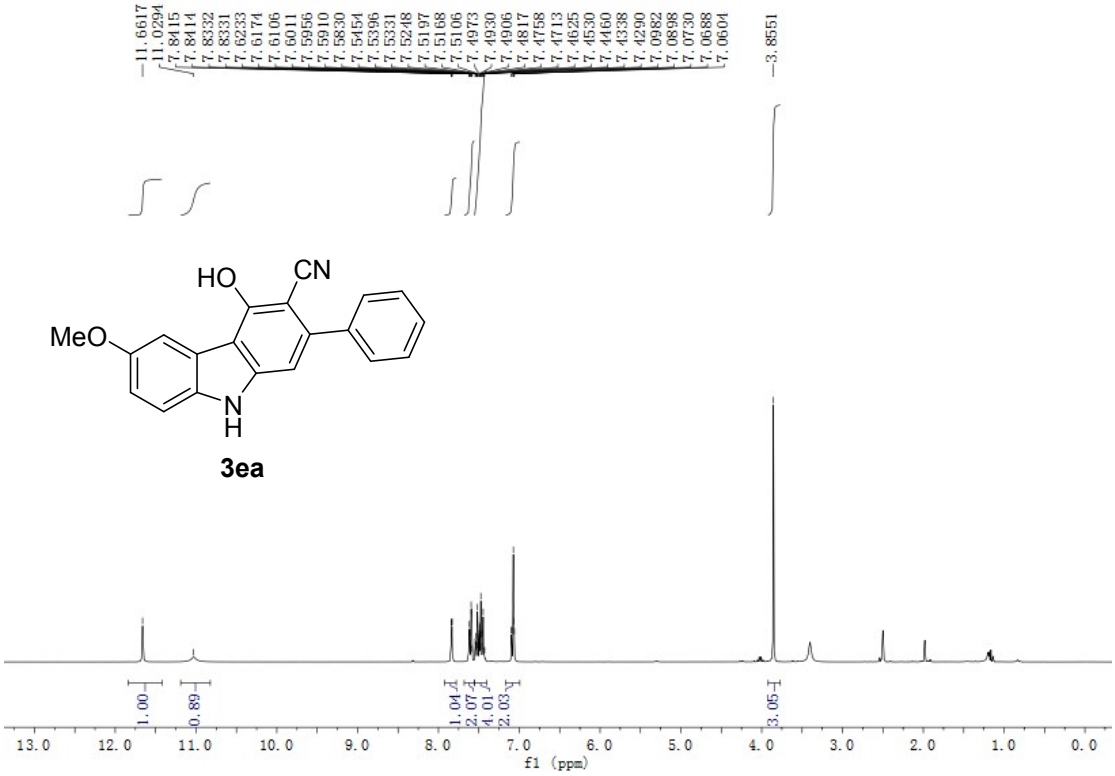


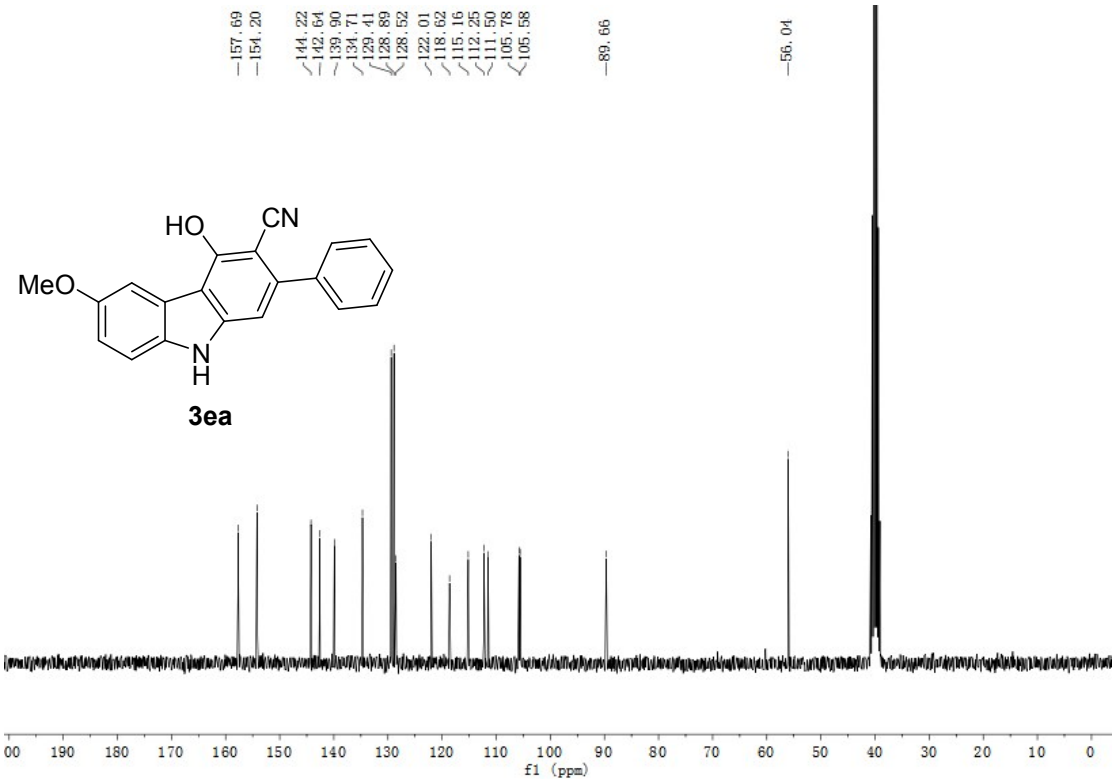
6-bromo-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3da):



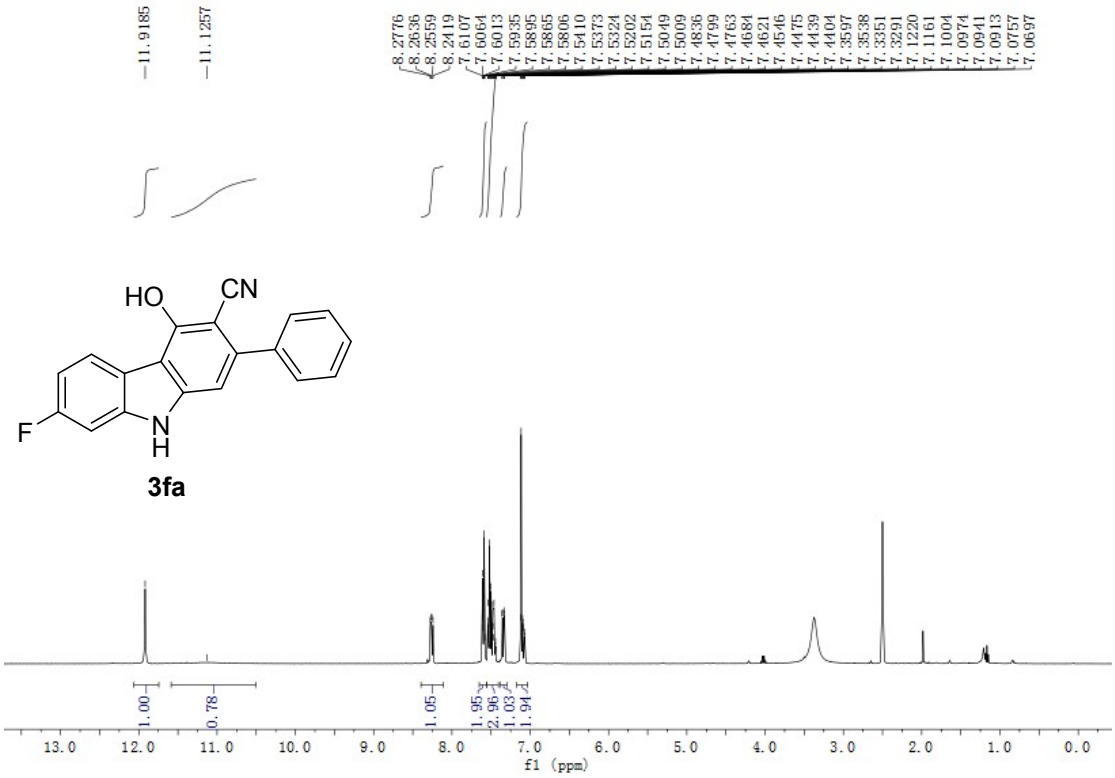


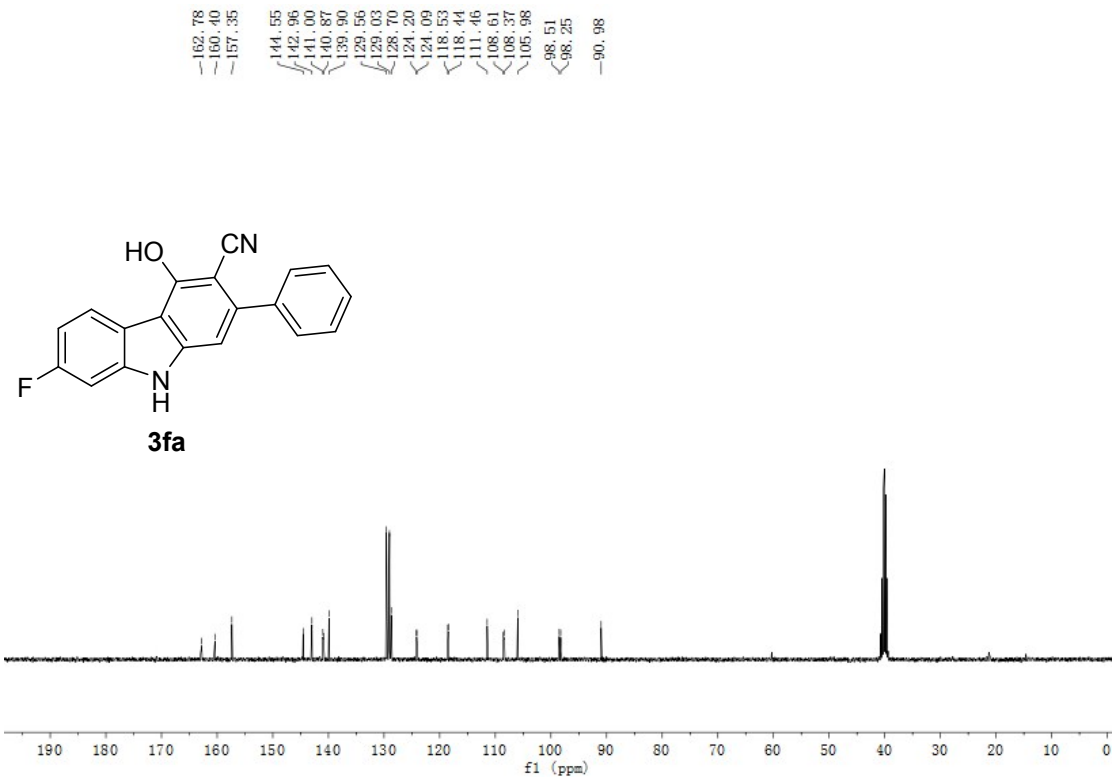
4-hydroxy-6-methoxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ea):



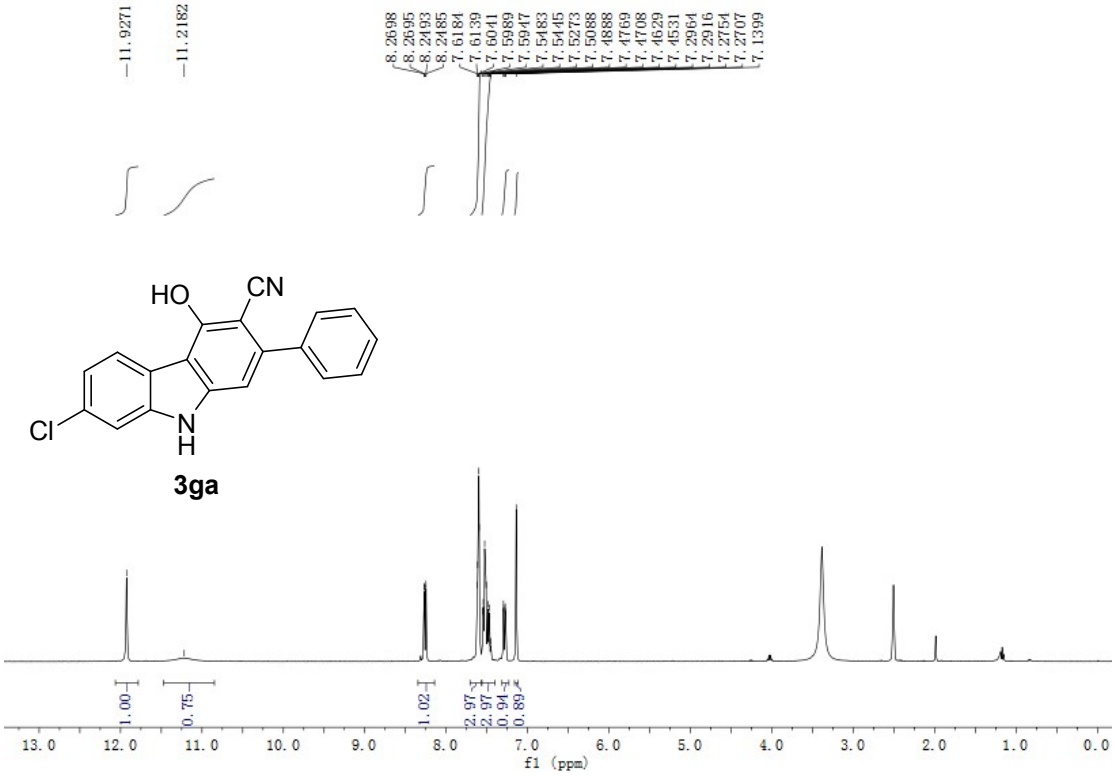


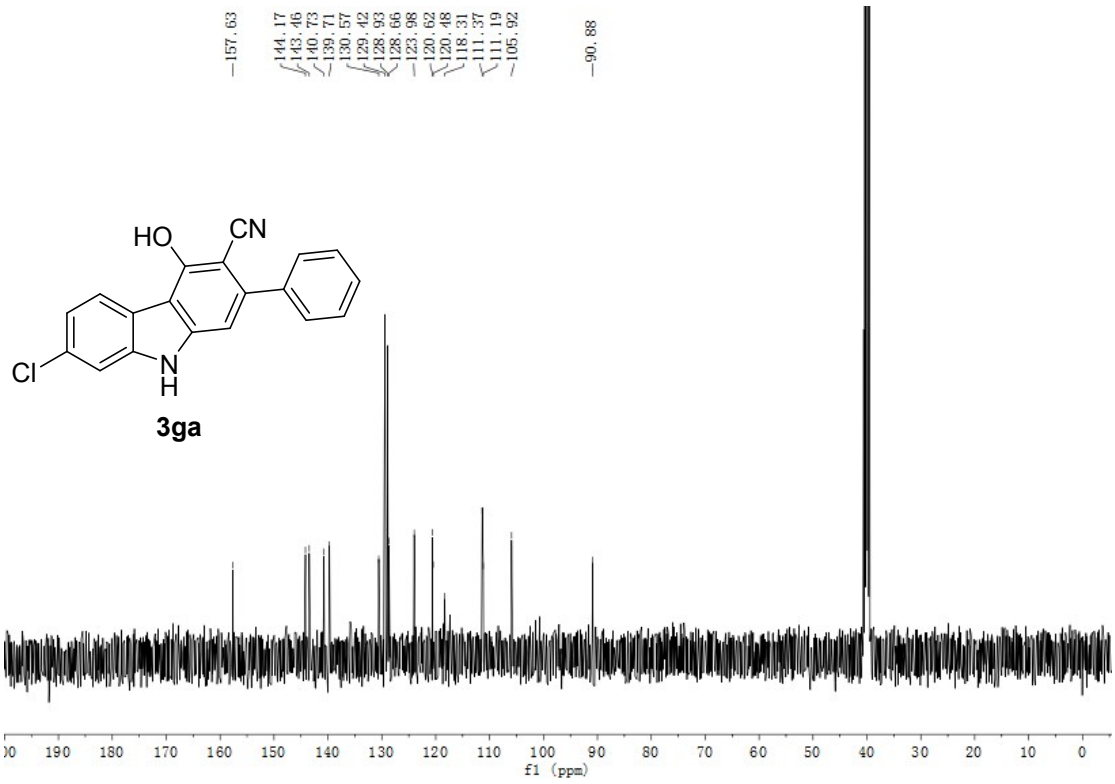
7-fluoro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3fa):



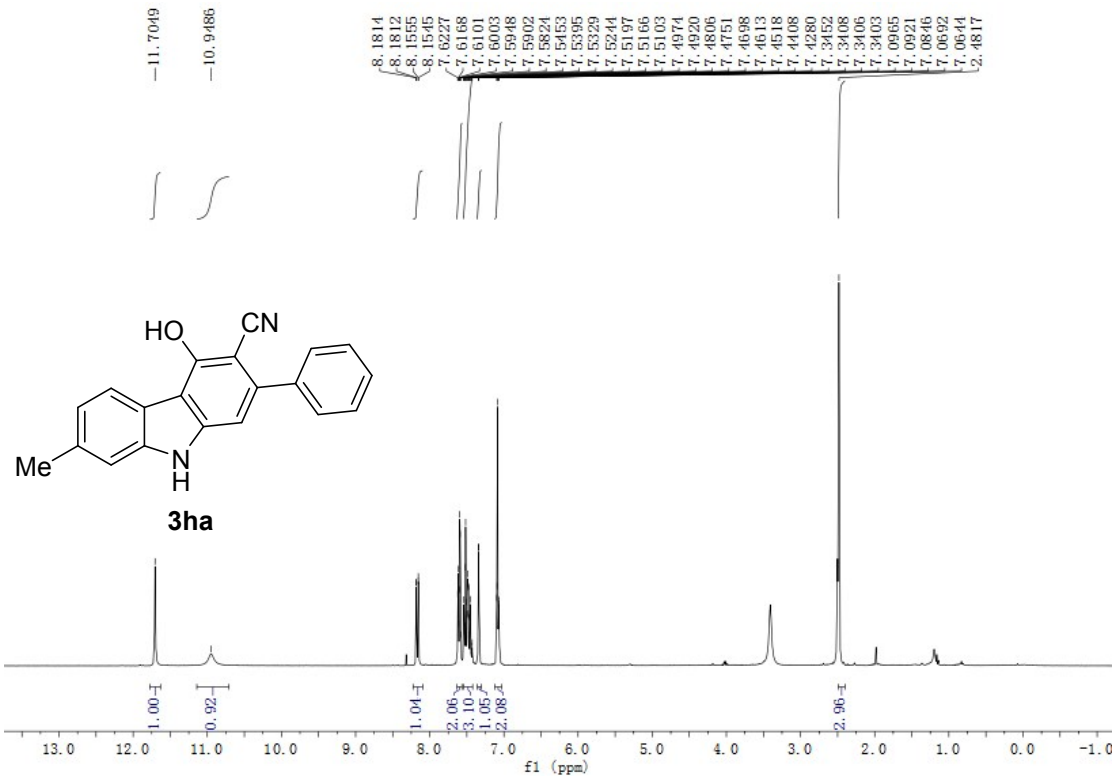


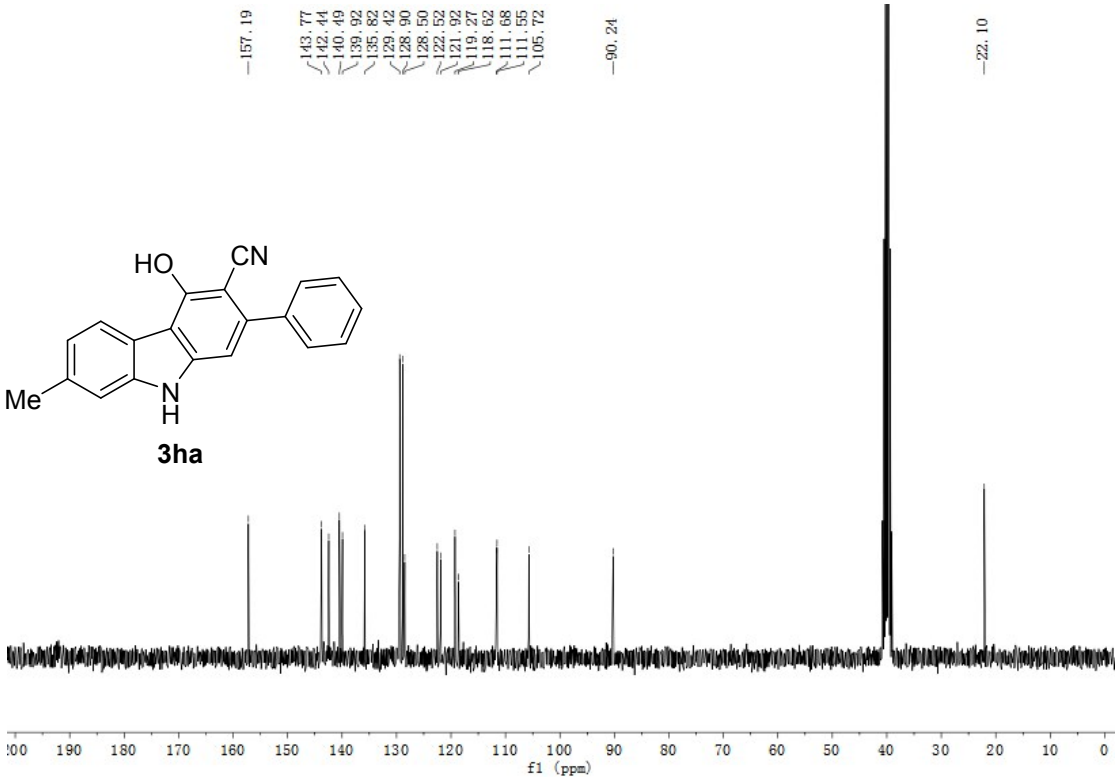
7-chloro-4-hydroxy-2-phenyl-9*H*-carbazole-3-carbonitrile (3ga):



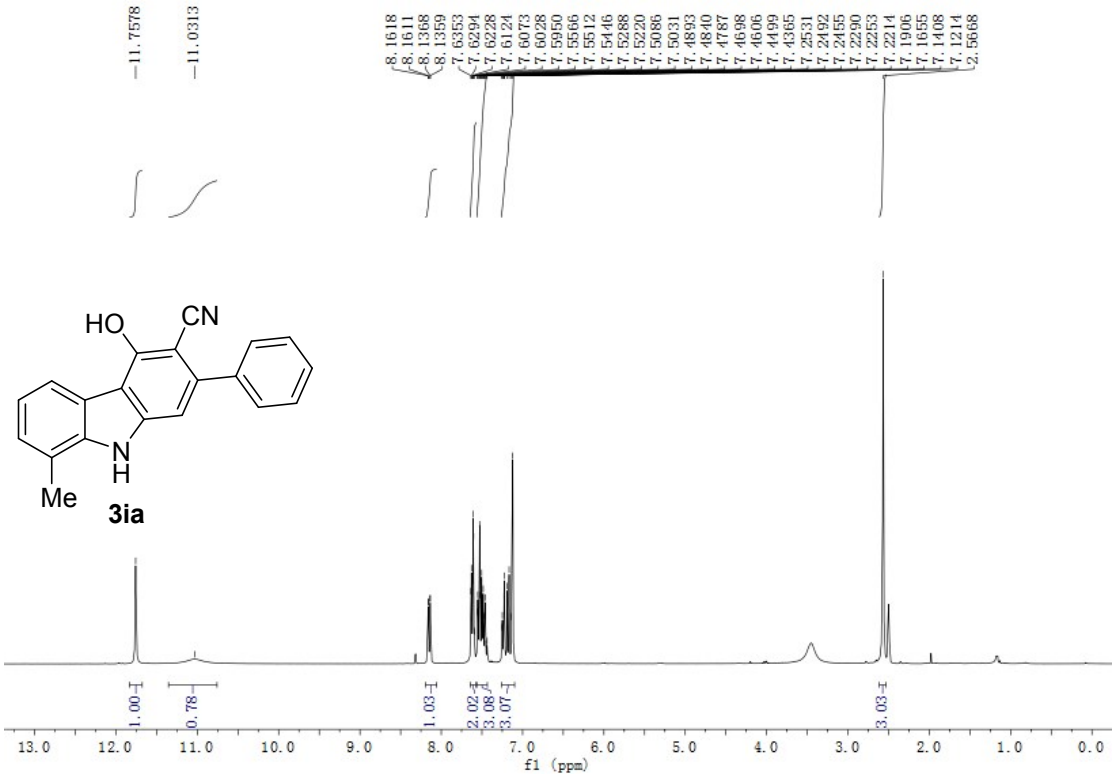


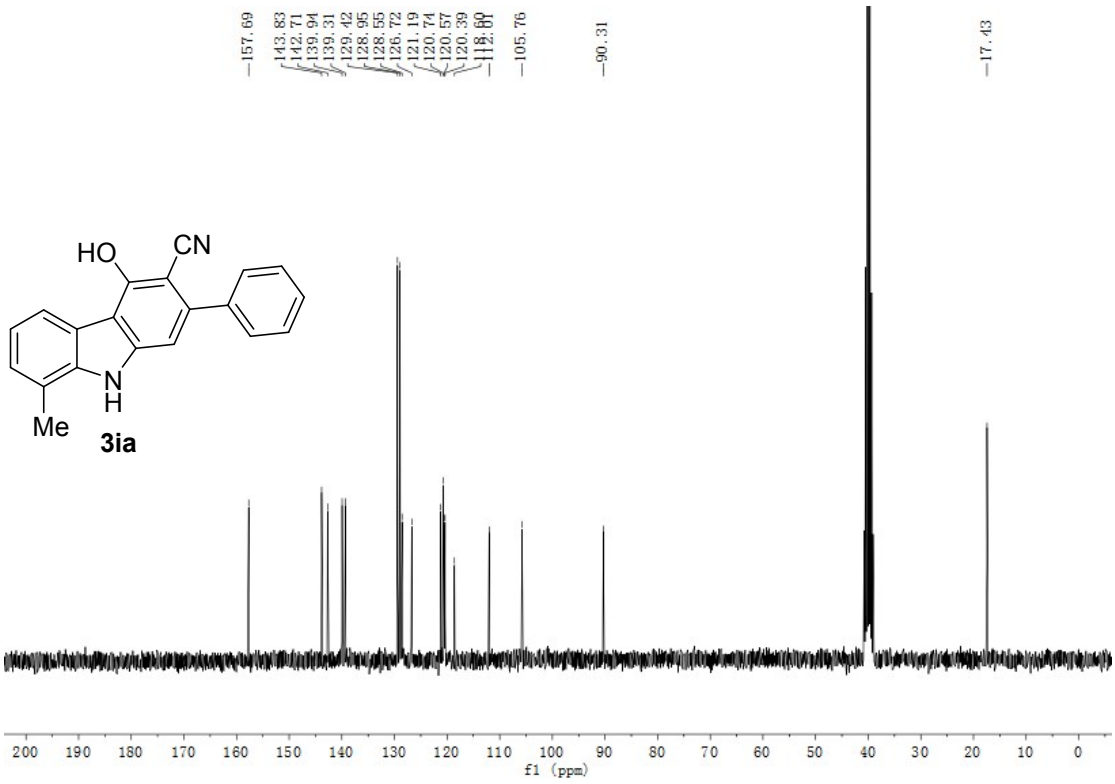
4-hydroxy-7-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ha):



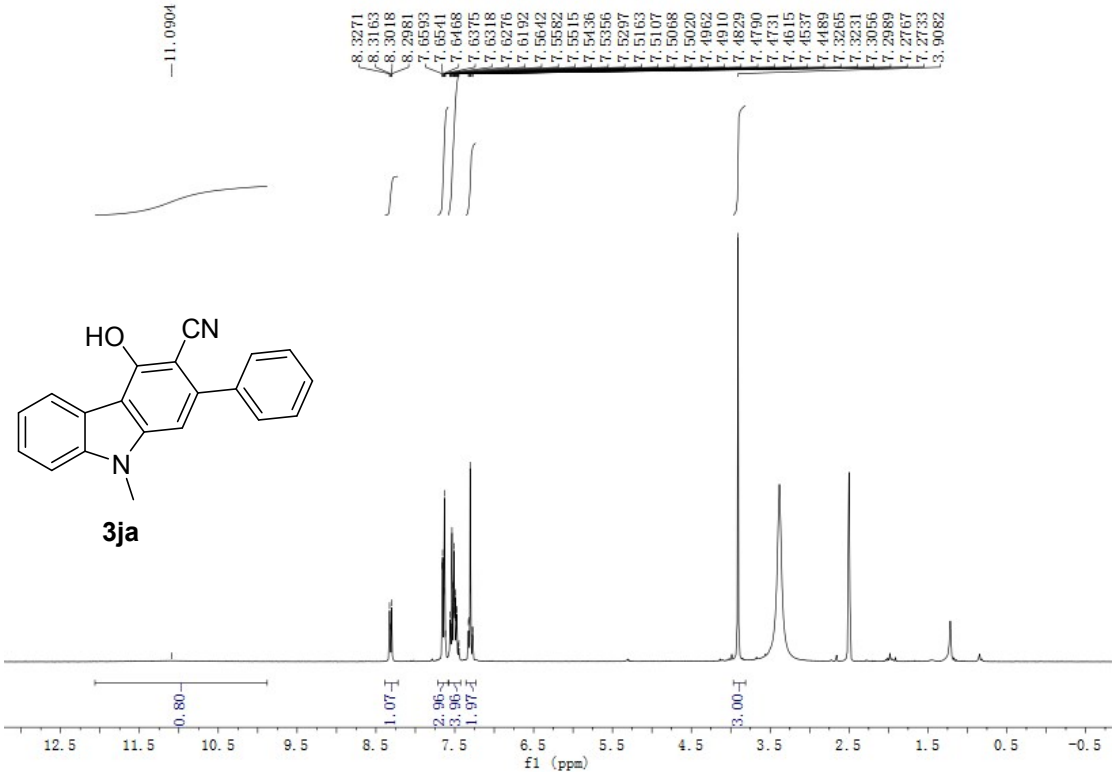


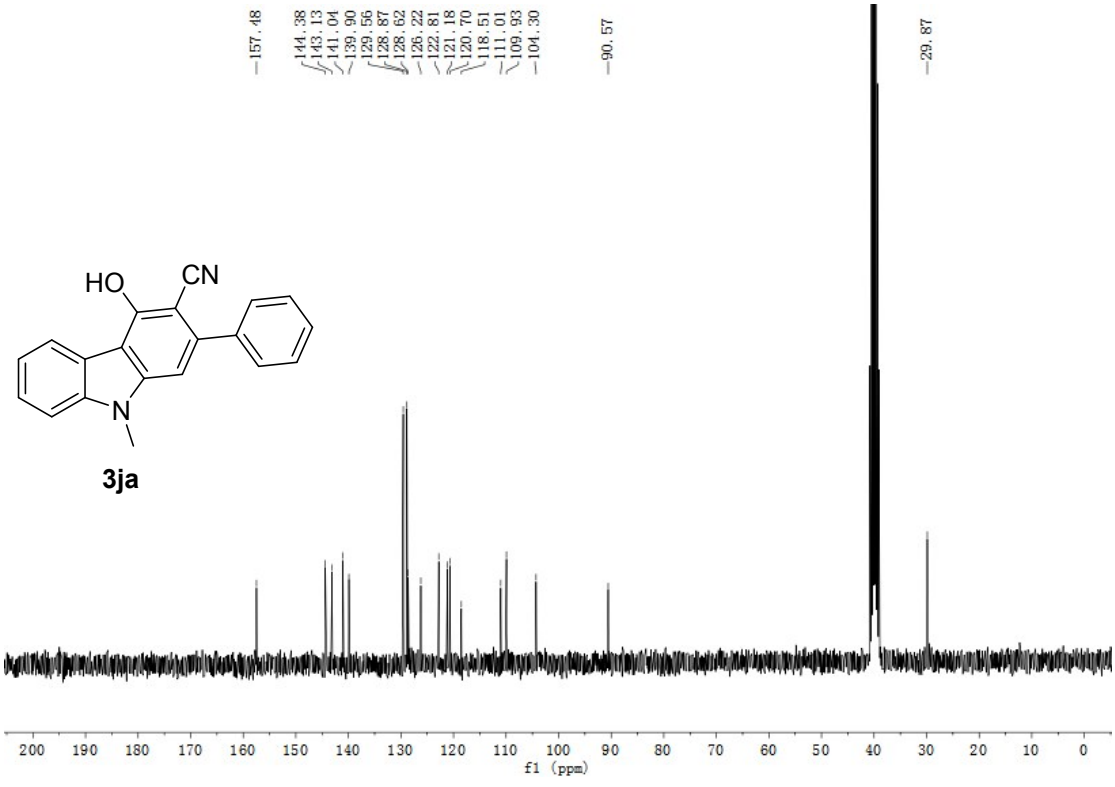
4-hydroxy-8-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ia):



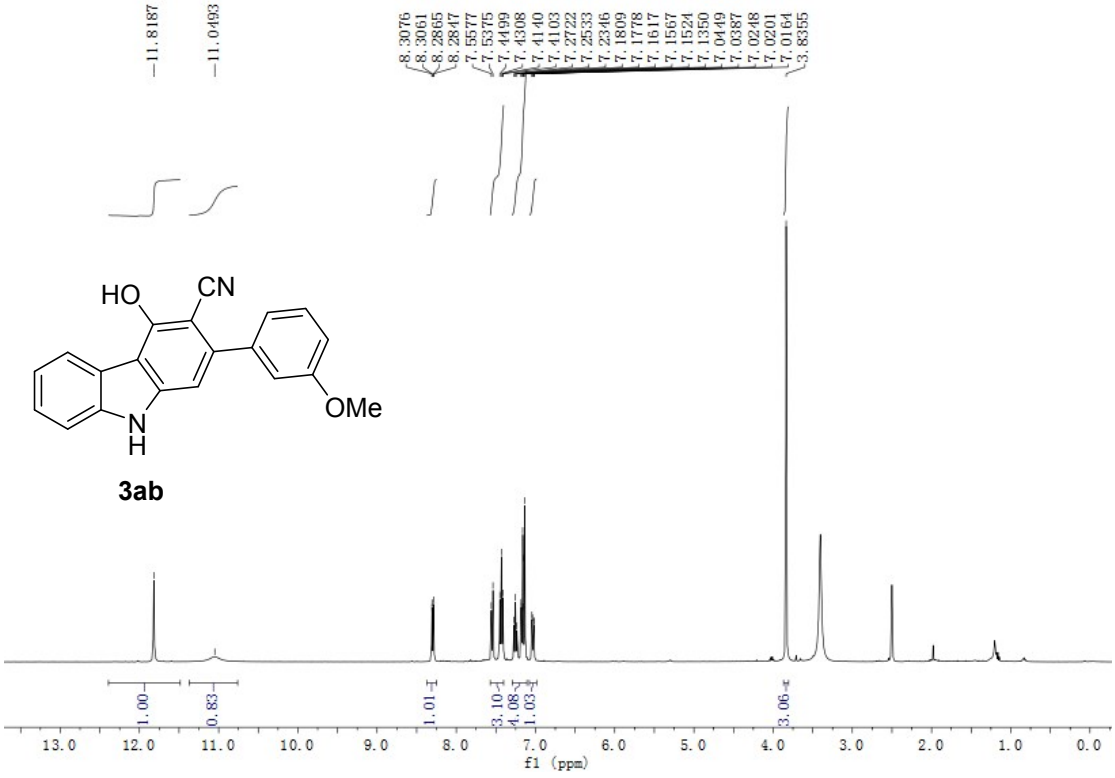


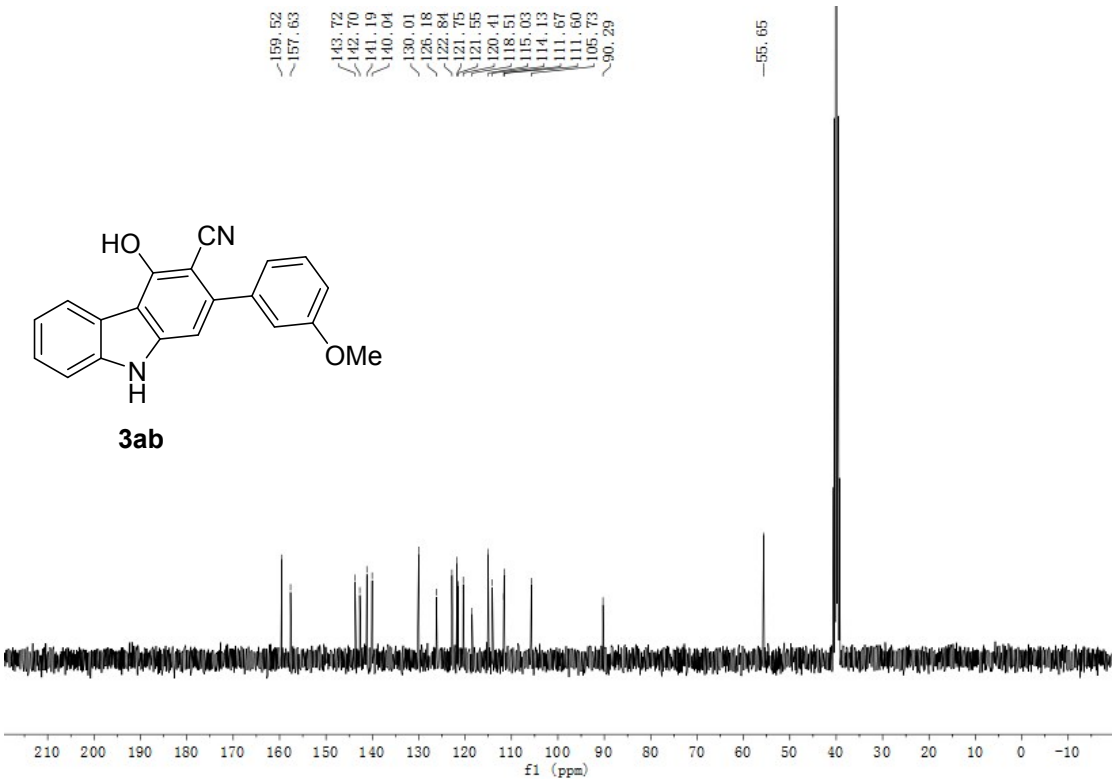
4-hydroxy-9-methyl-2-phenyl-9*H*-carbazole-3-carbonitrile (3ja):



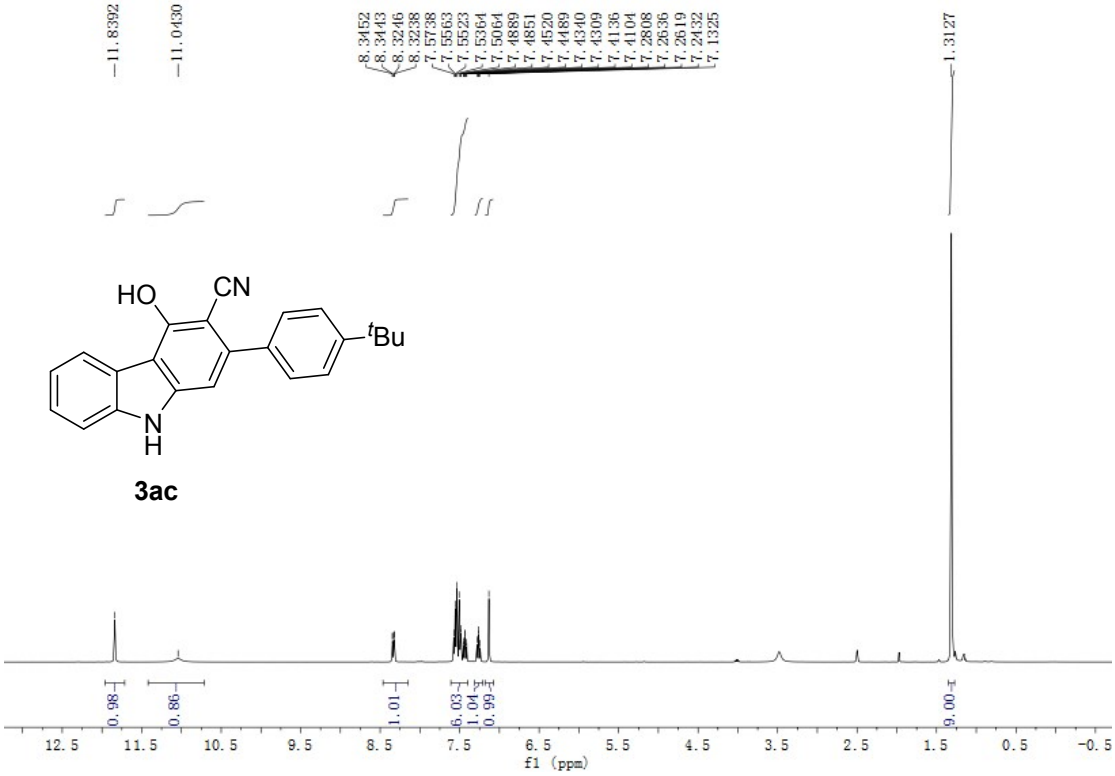


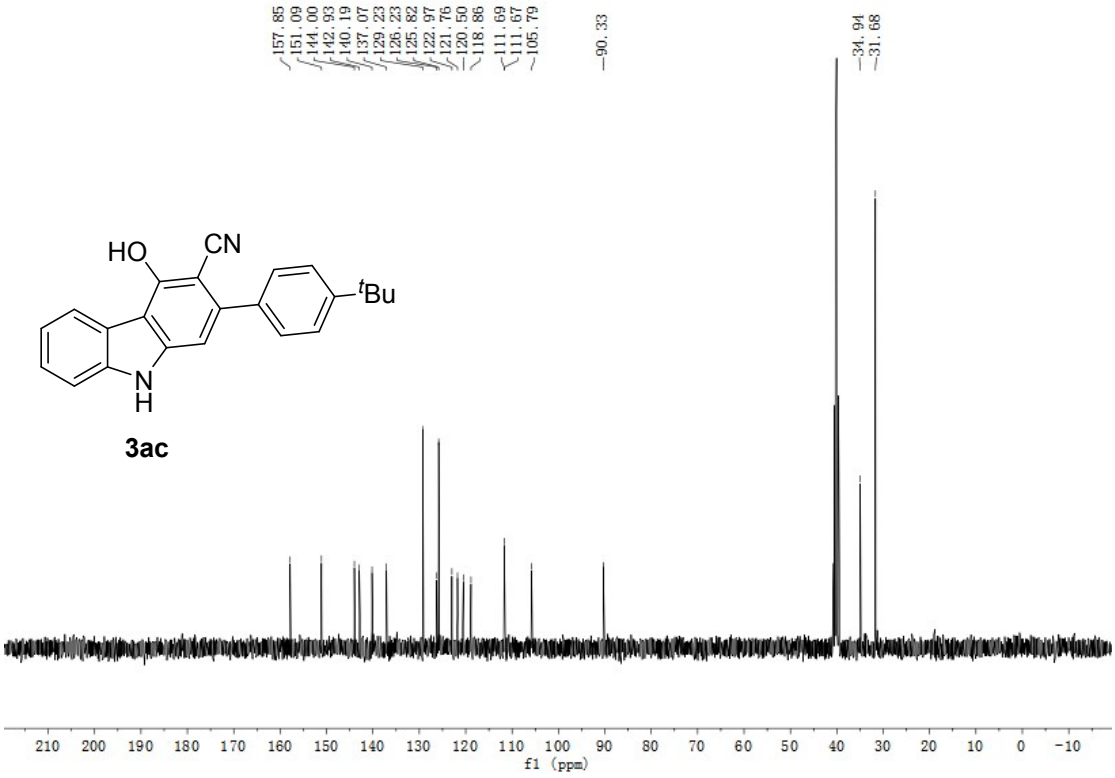
4-hydroxy-2-(3-methoxyphenyl)-9*H*-carbazole-3-carbonitrile (3ab):



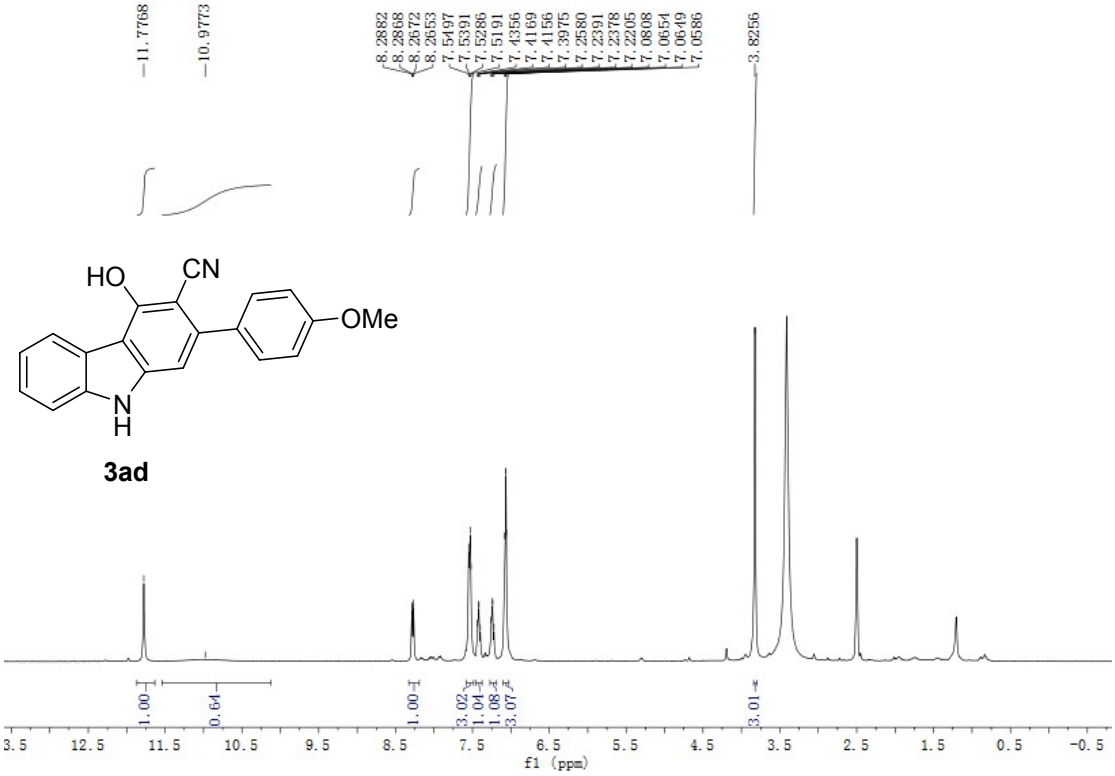


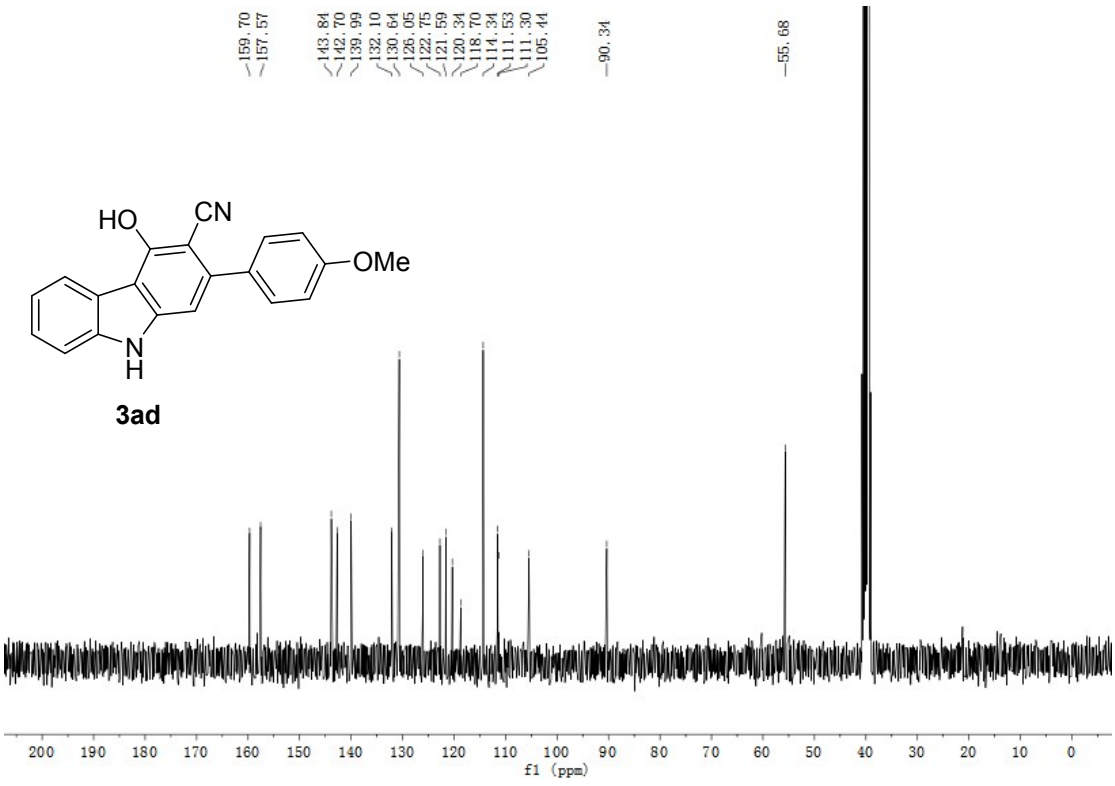
2-(4-(*tert*-butyl)phenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ac):



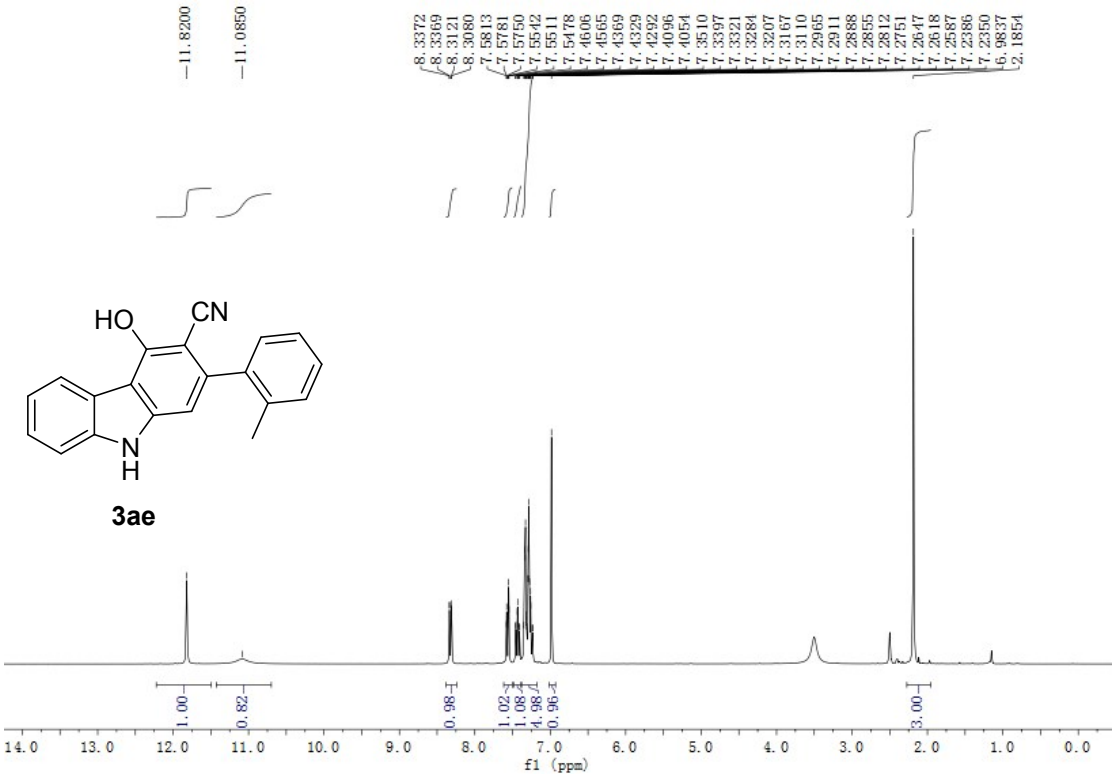


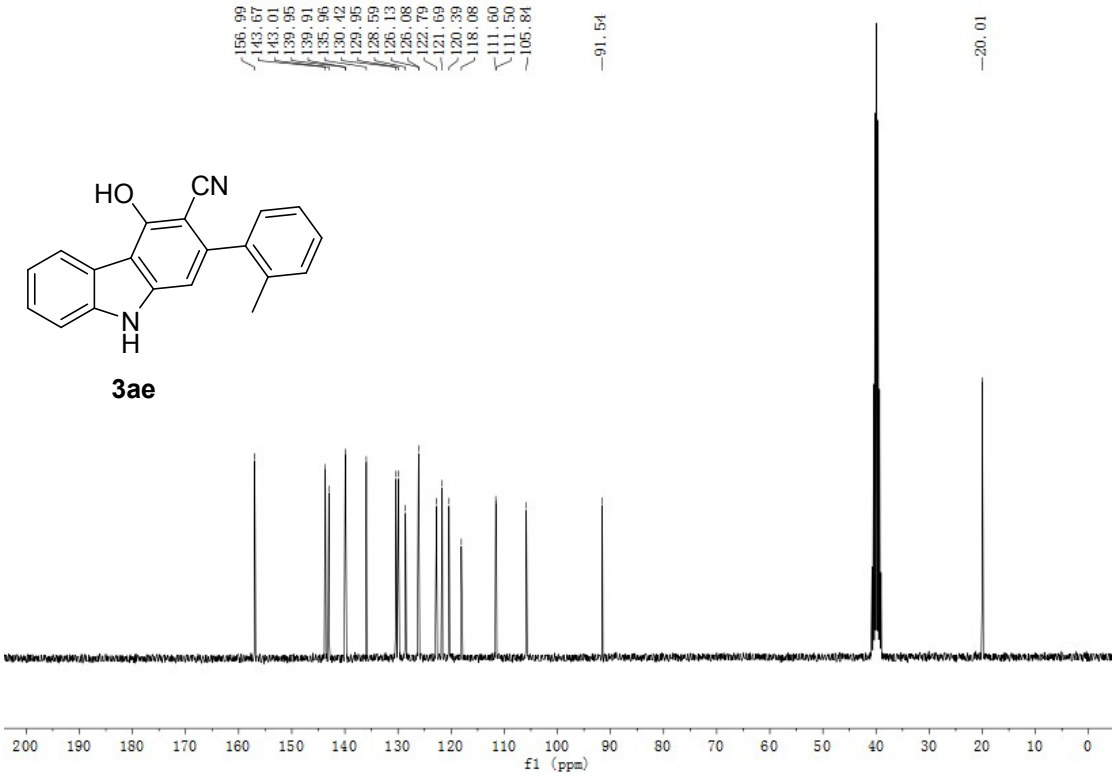
4-hydroxy-2-(4-methoxyphenyl)-9*H*-carbazole-3-carbonitrile (3ad):



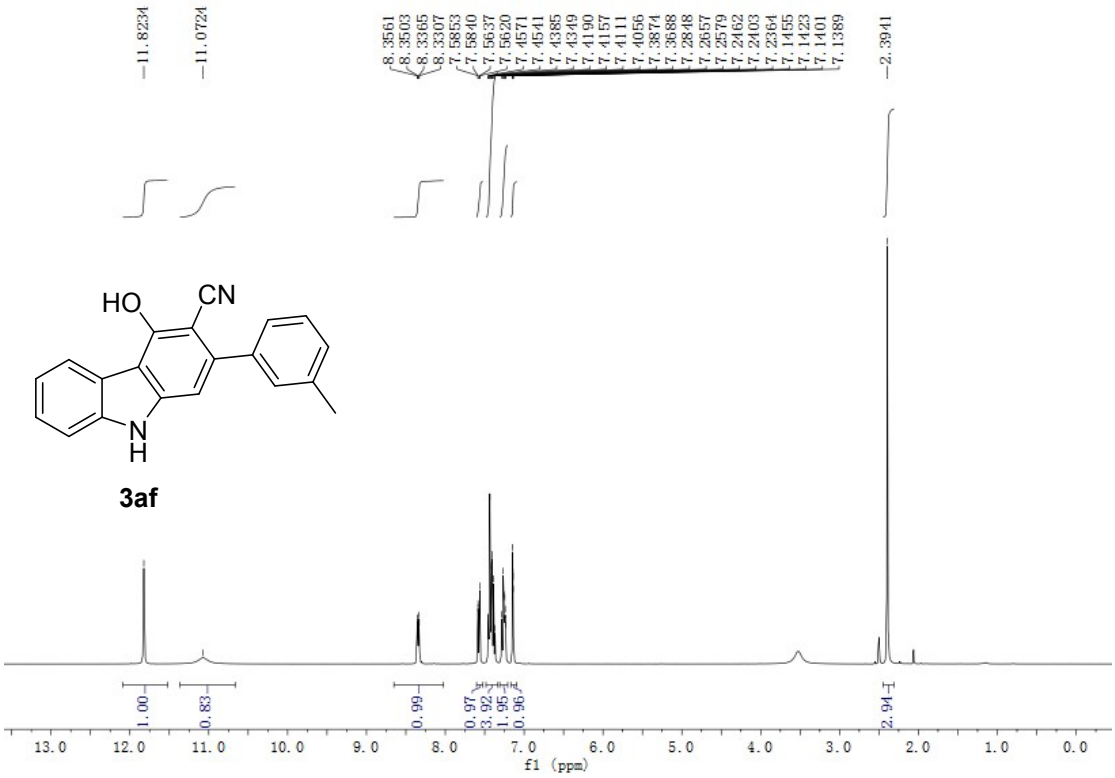


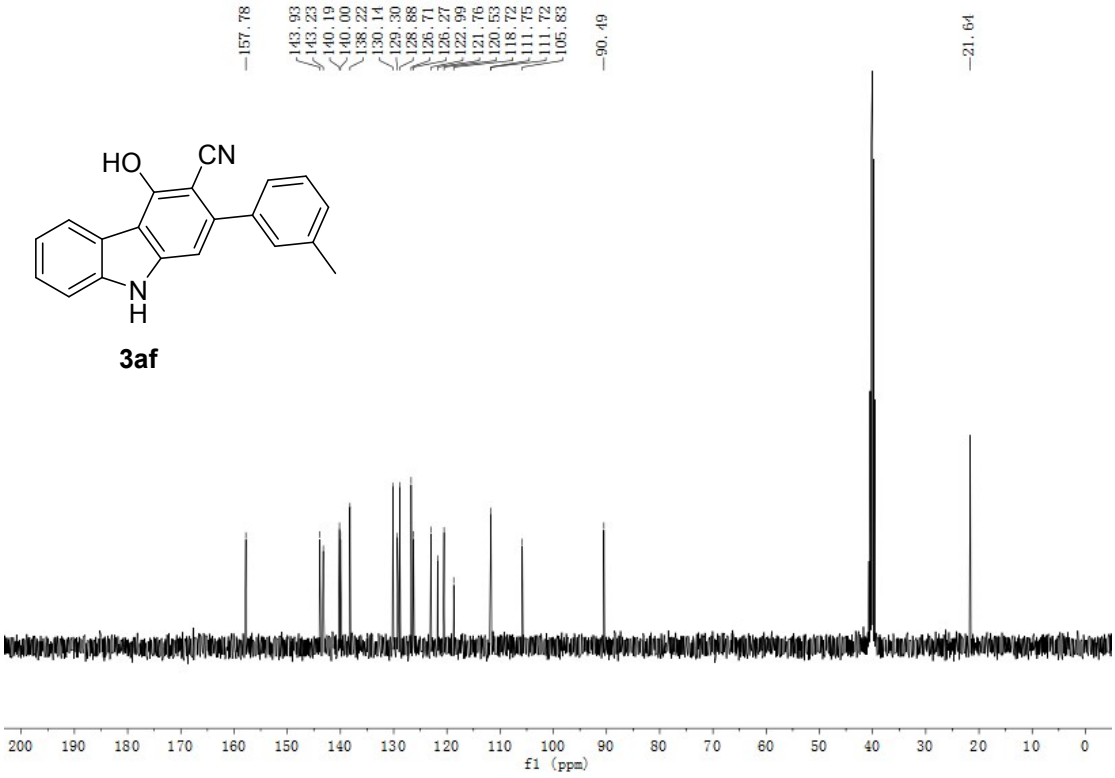
4-hydroxy-2-(o-tolyl)-9*H*-carbazole-3-carbonitrile (3ae):



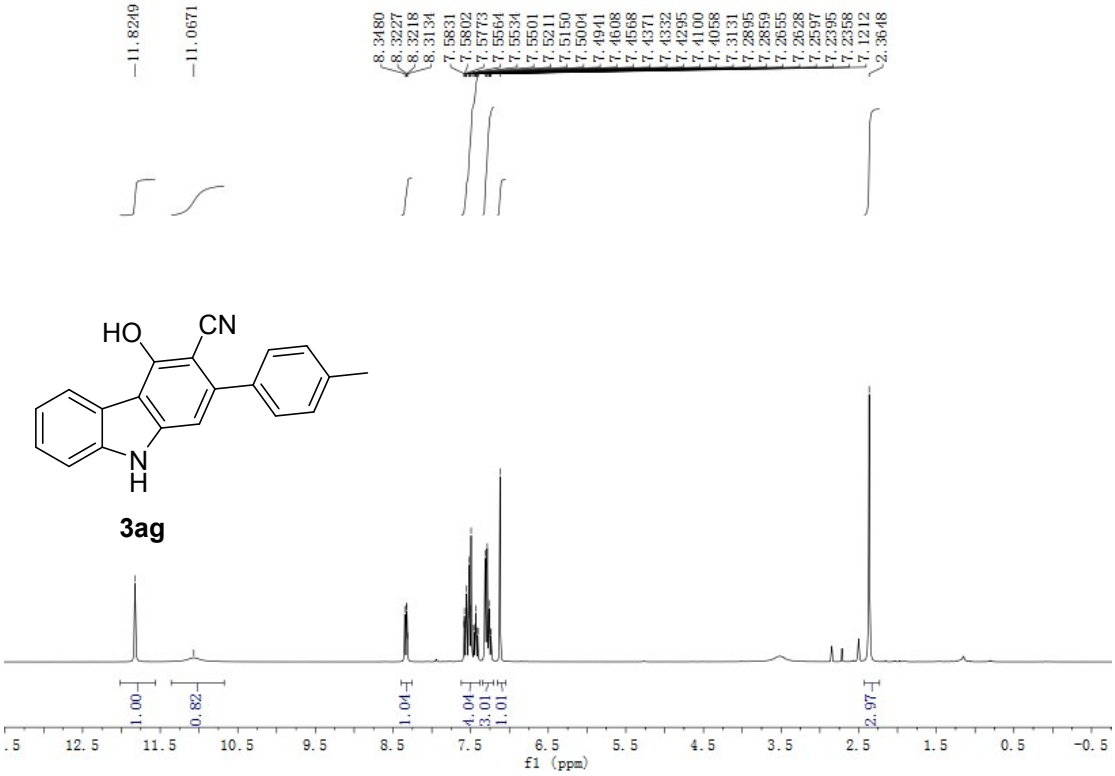


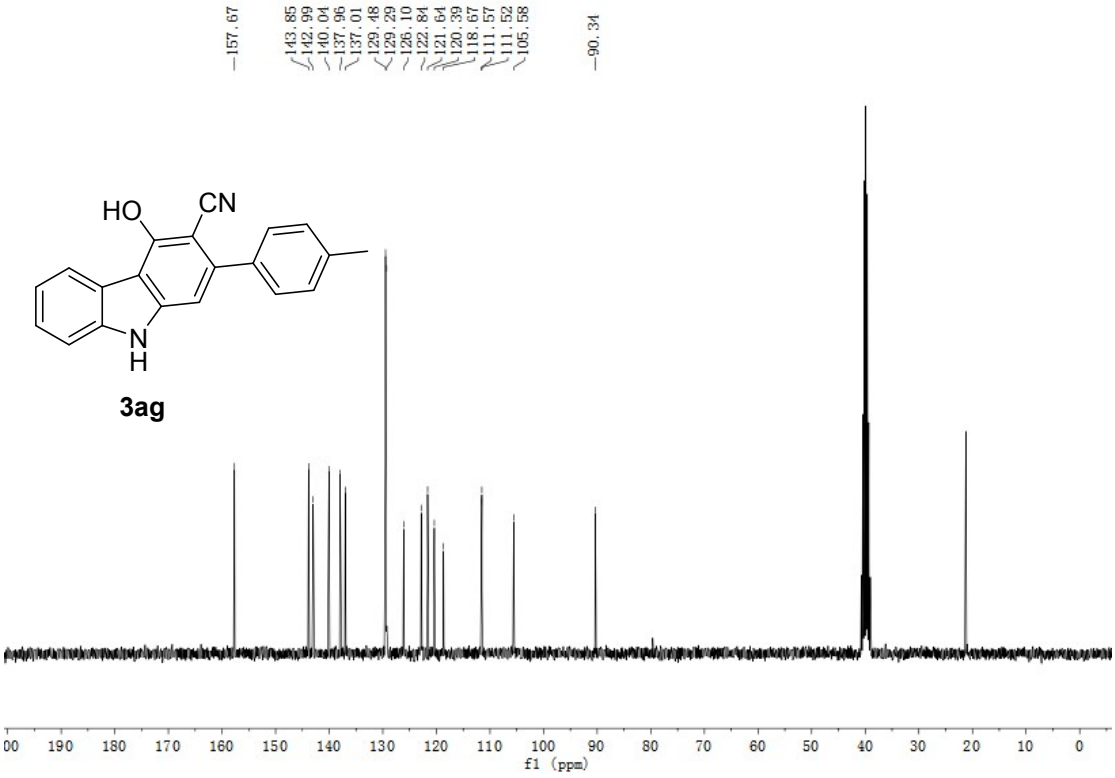
4-hydroxy-2-(m-tolyl)-9*H*-carbazole-3-carbonitrile (3af):



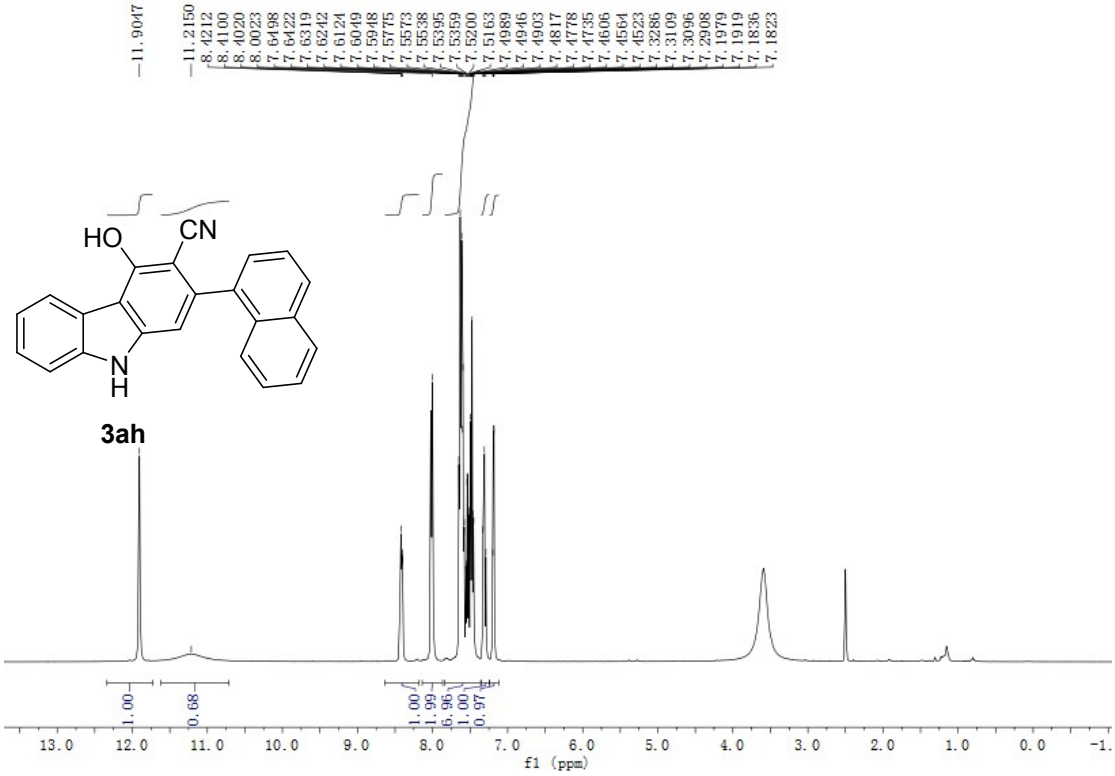


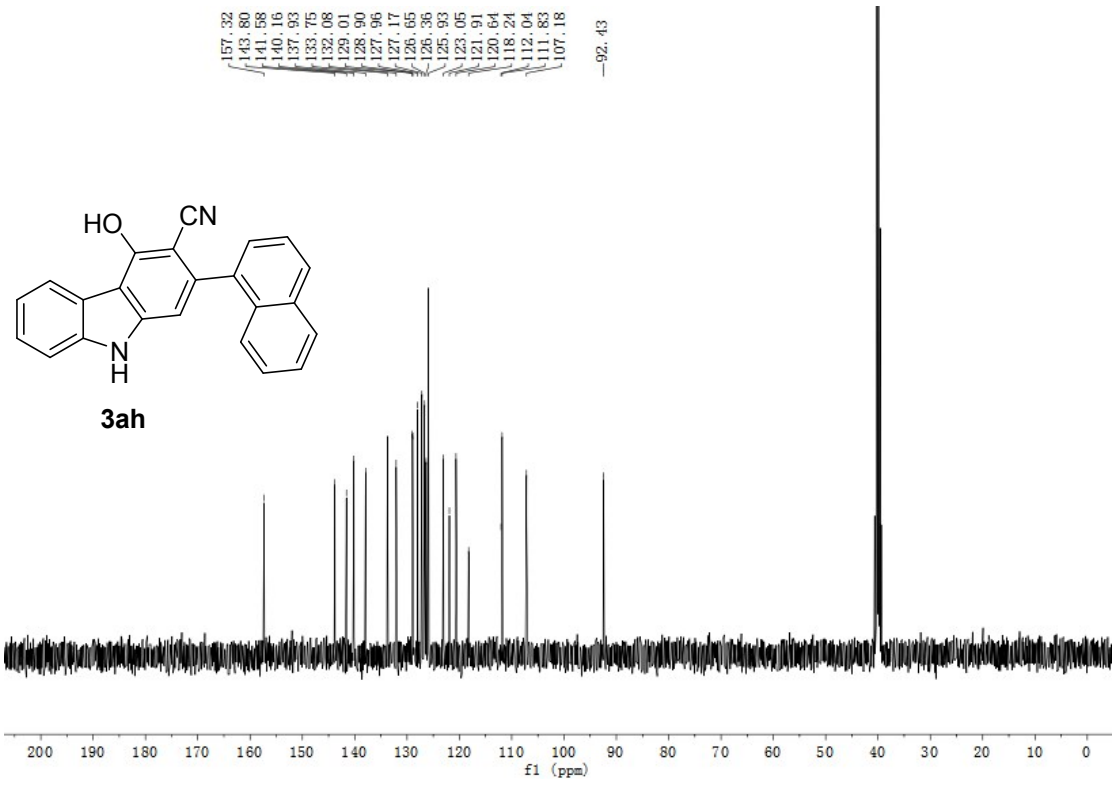
4-hydroxy-2-(p-tolyl)-9*H*-carbazole-3-carbonitrile (3ag):



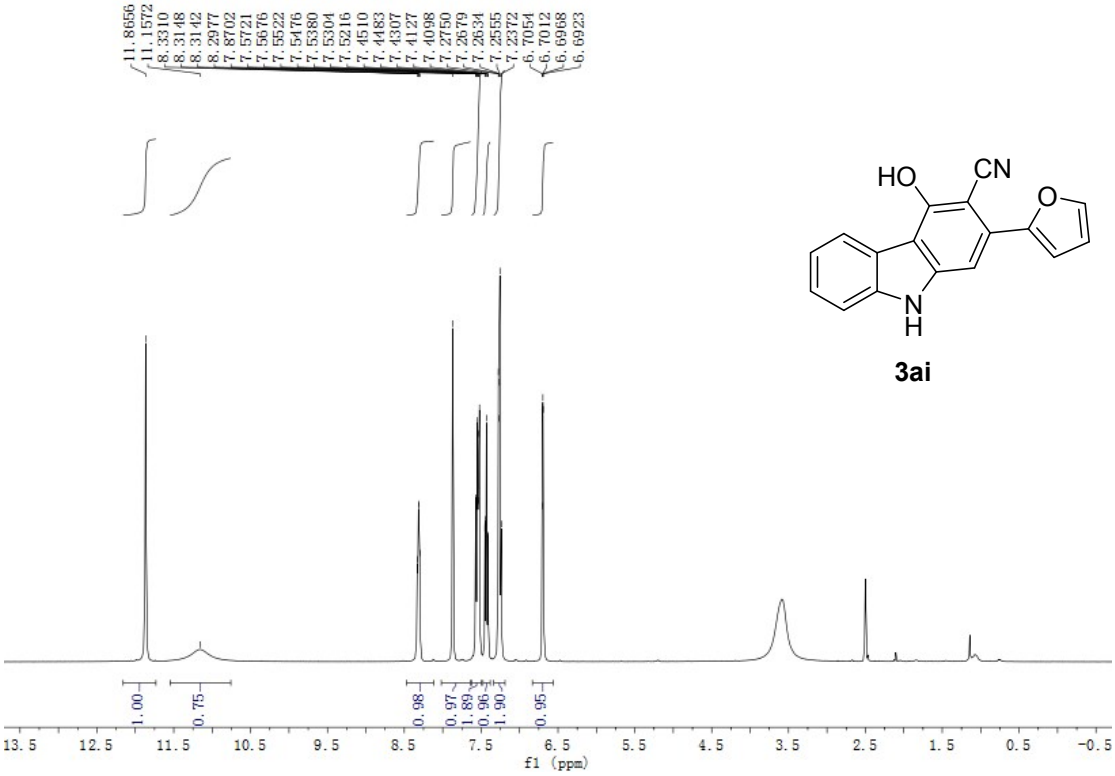


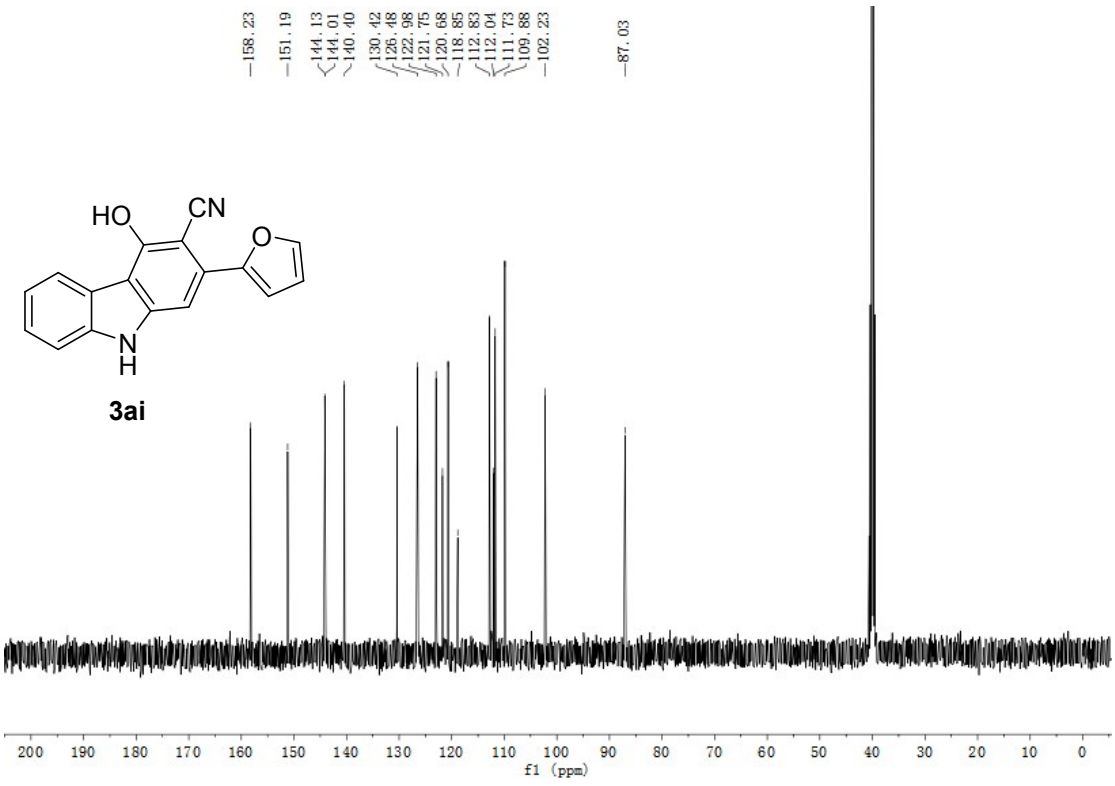
4-hydroxy-2-(naphthalen-1-yl)-9*H*-carbazole-3-carbonitrile (3ah):



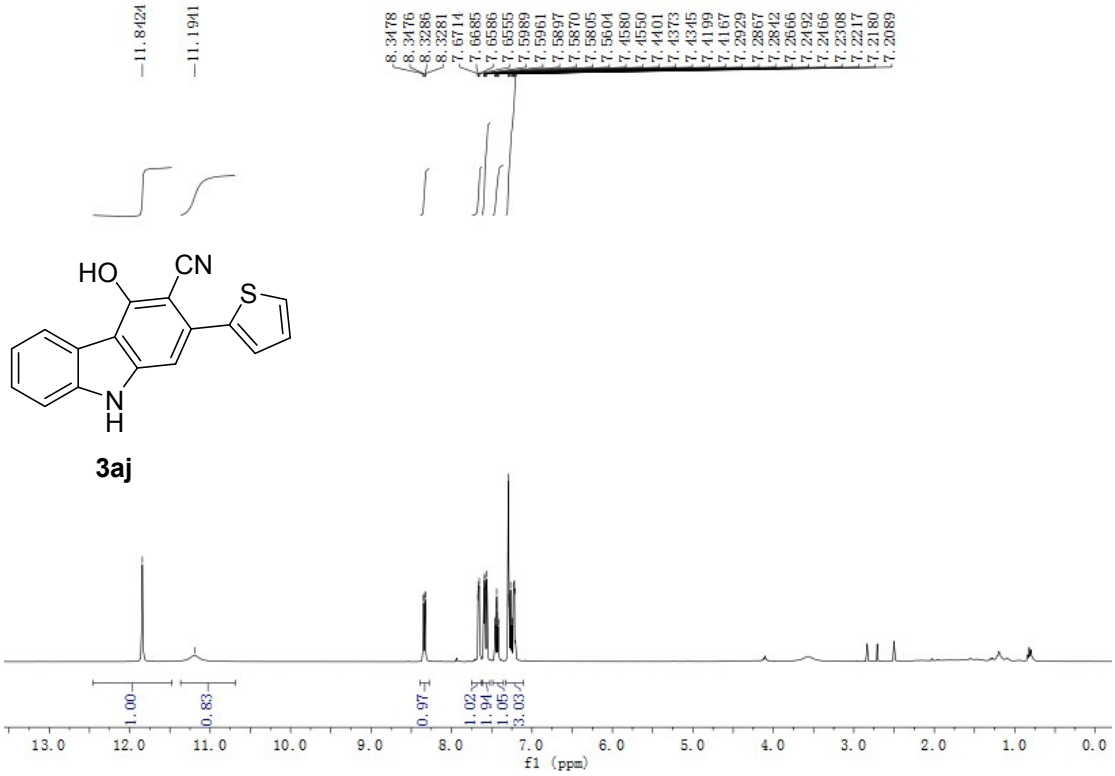


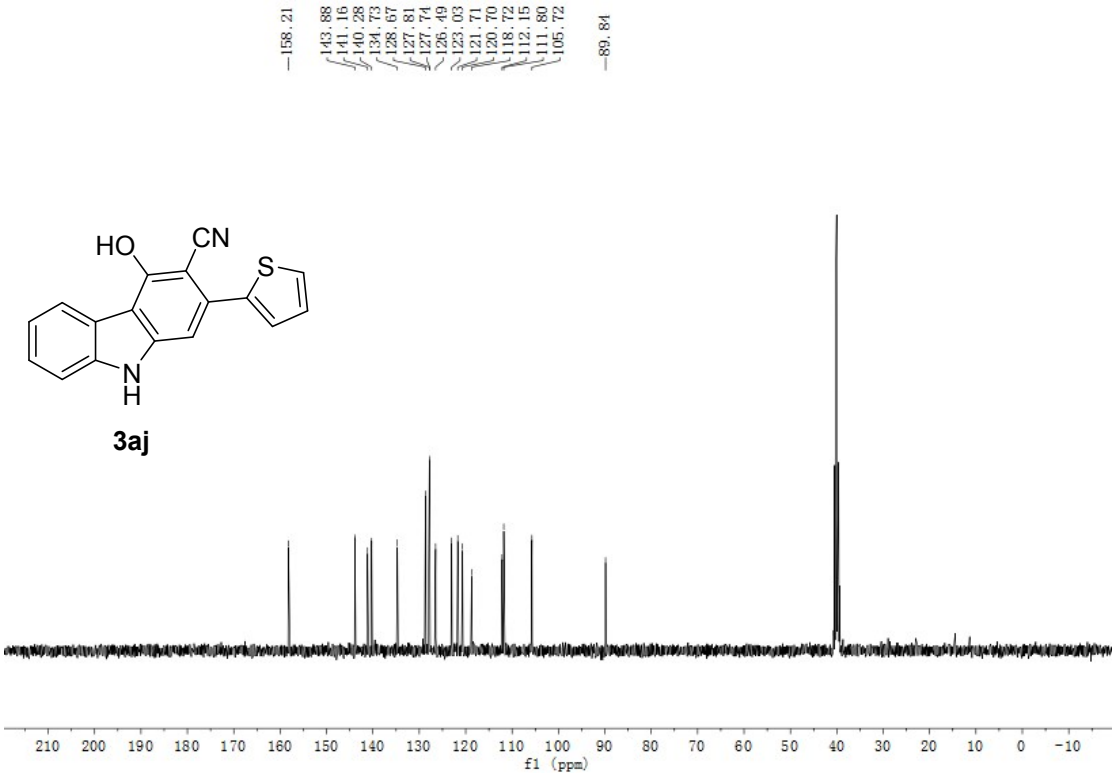
2-(furan-2-yl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ai):



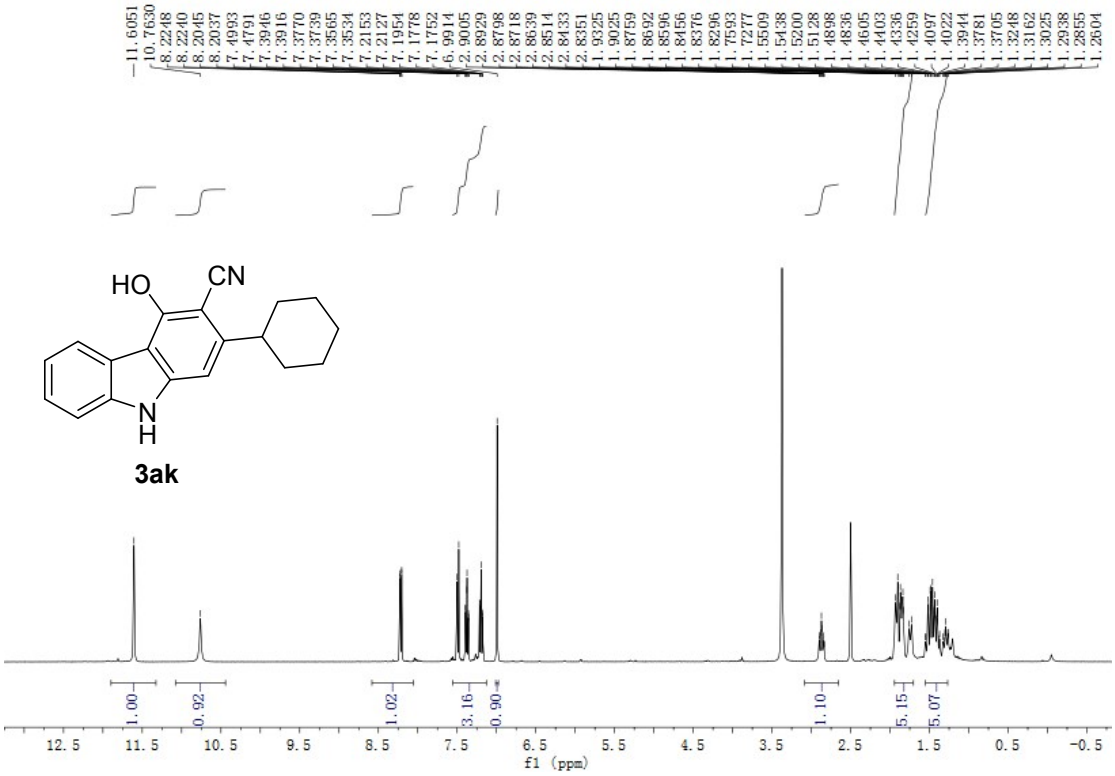


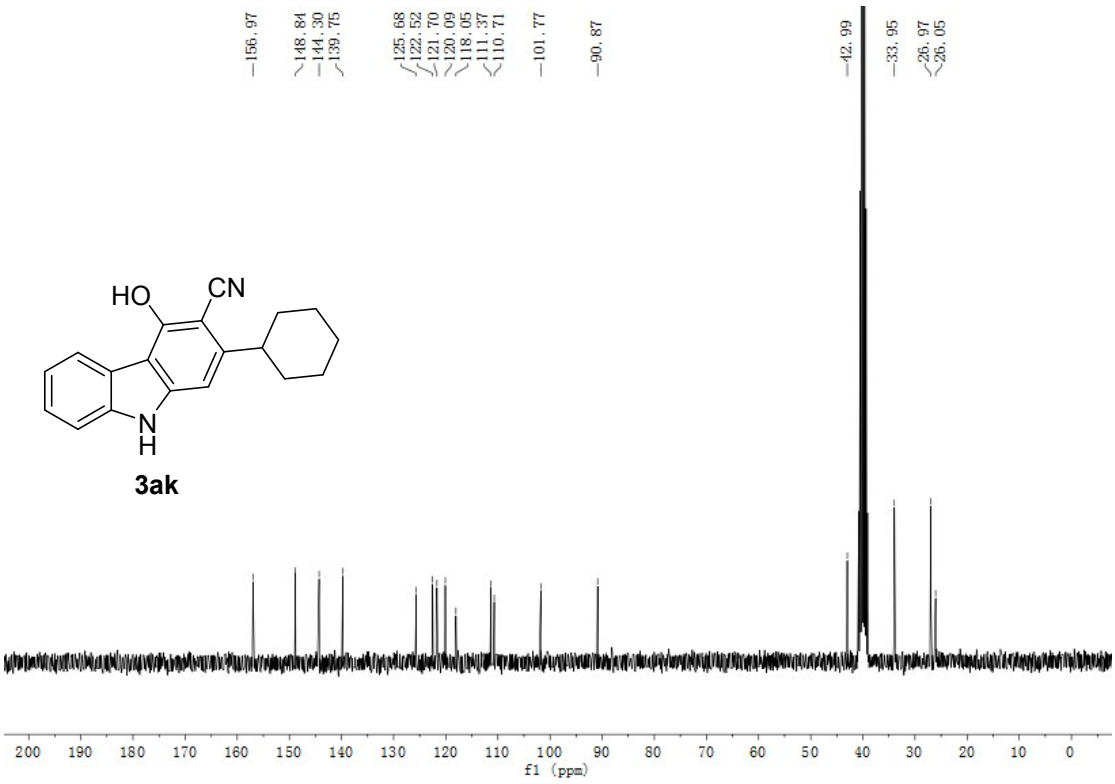
4-hydroxy-2-(thiophen-2-yl)-9*H*-carbazole-3-carbonitrile (3aj):



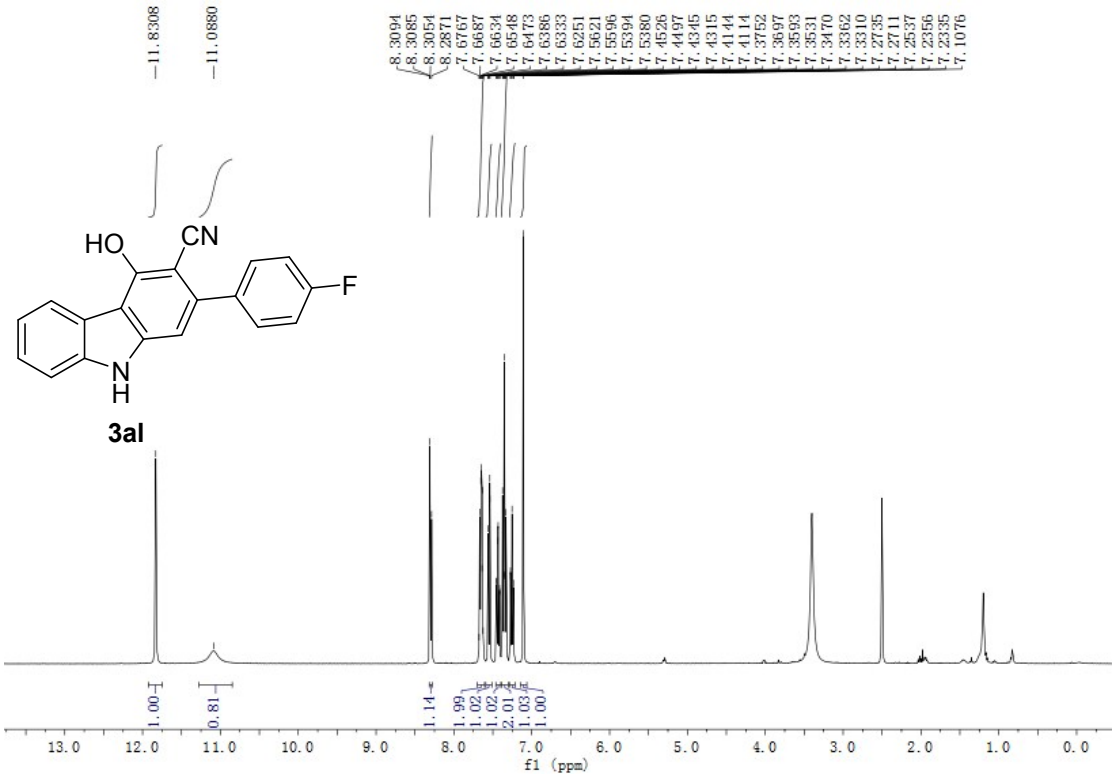


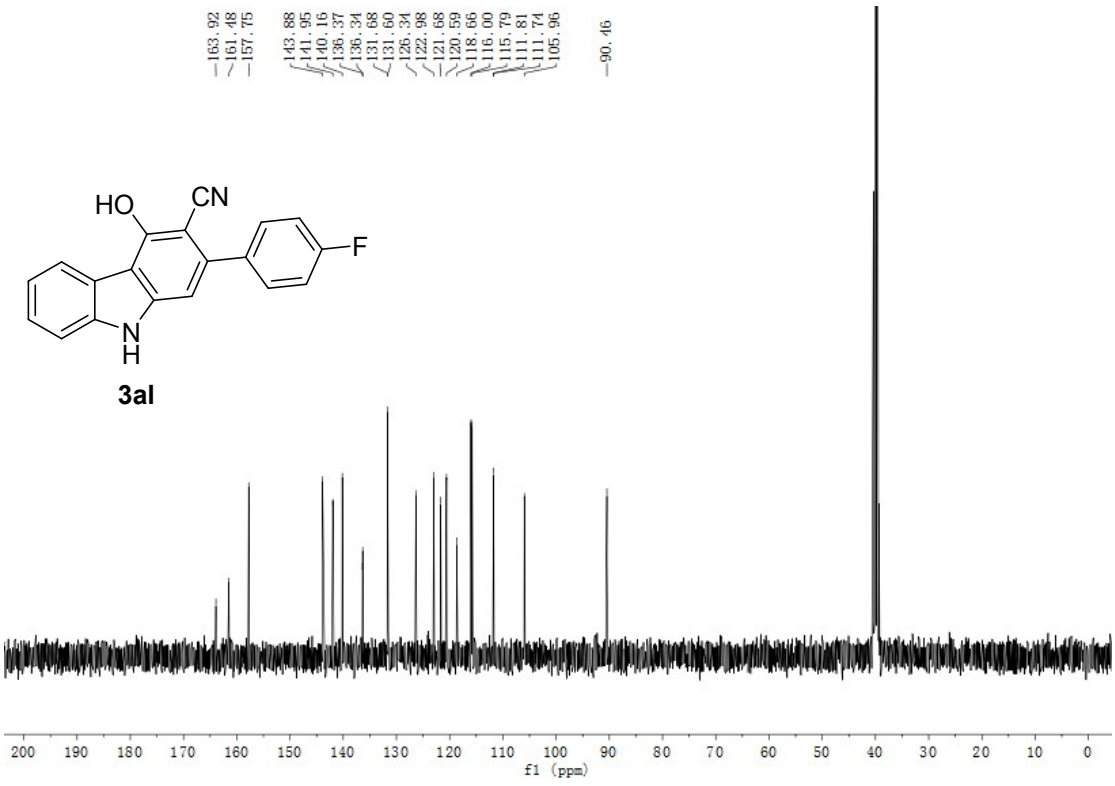
2-cyclohexyl-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ak):



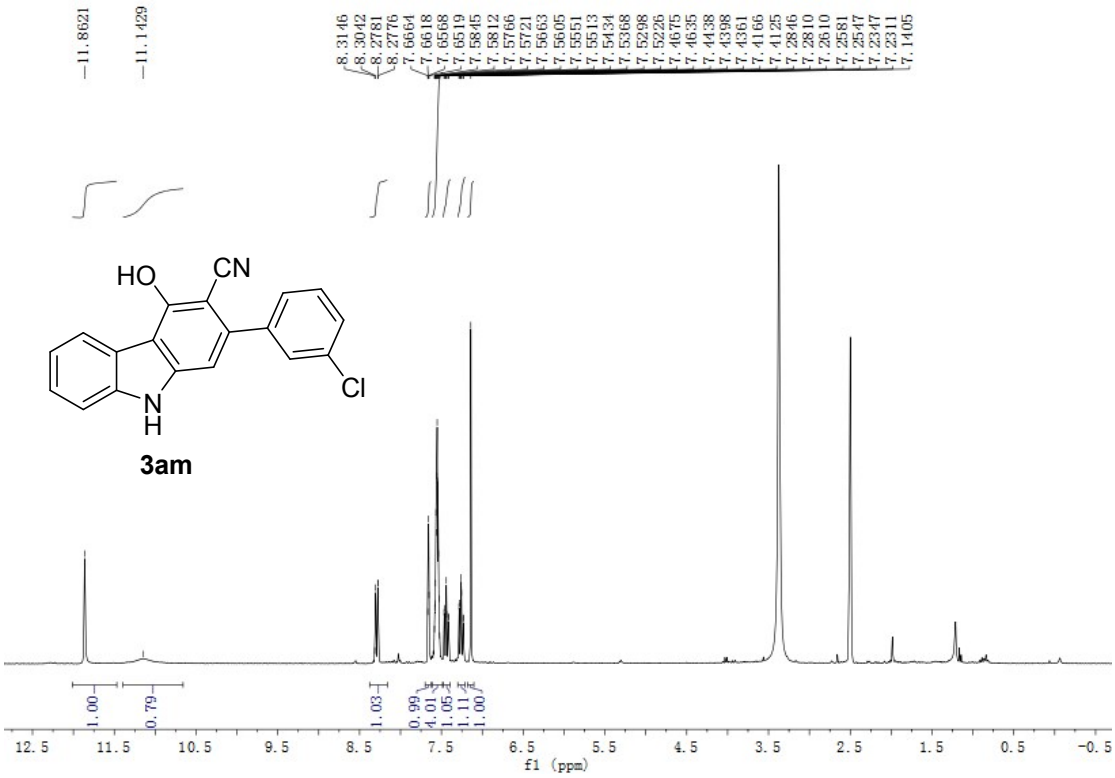


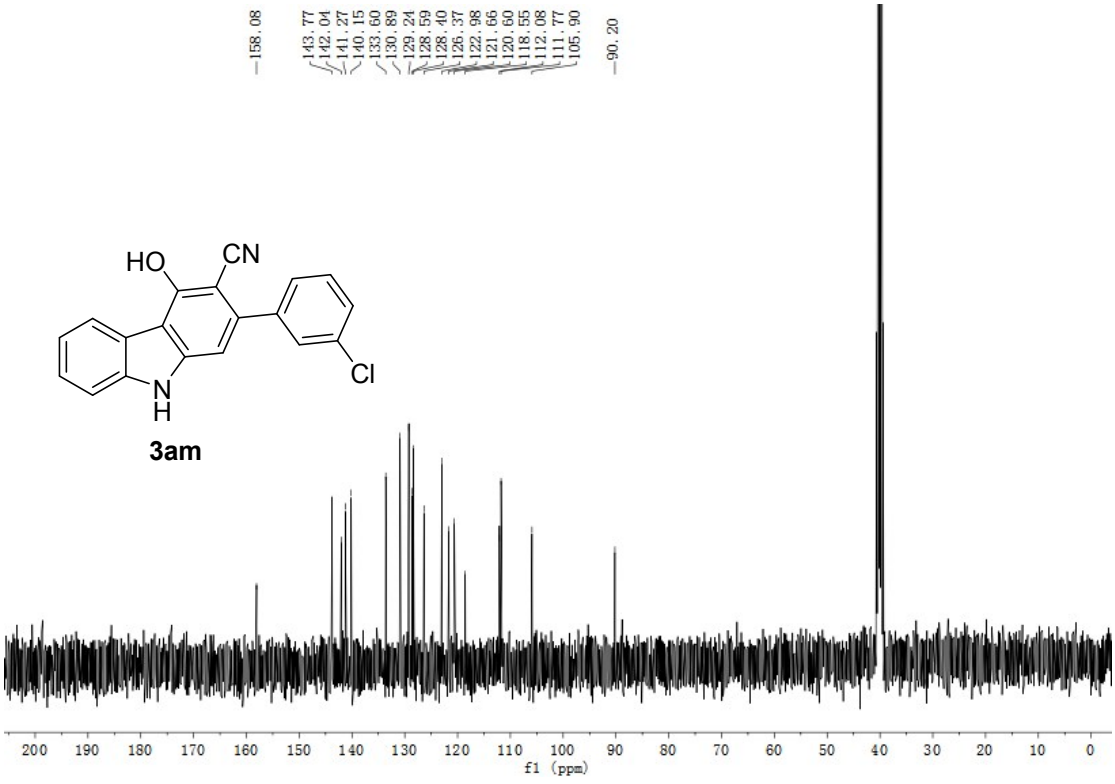
2-(4-fluorophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3al):



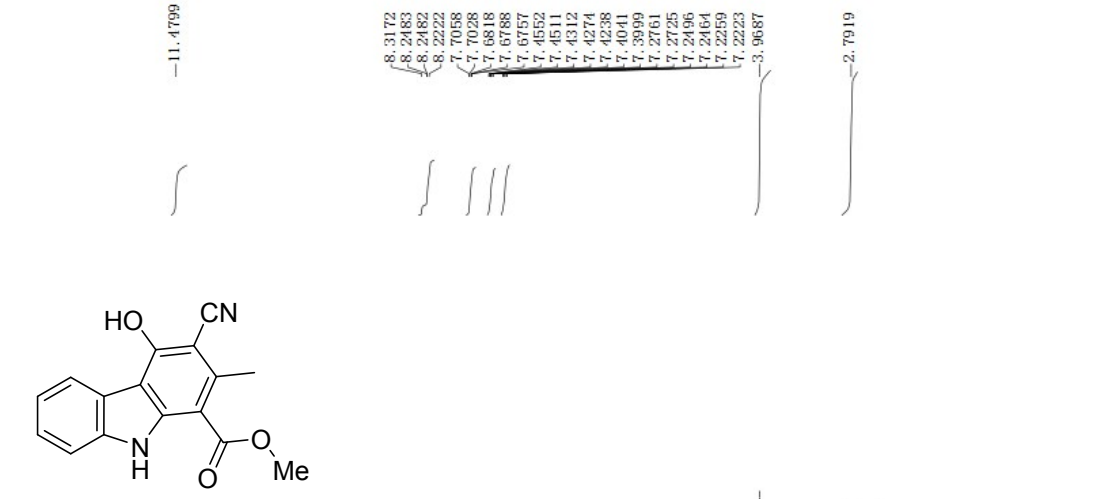


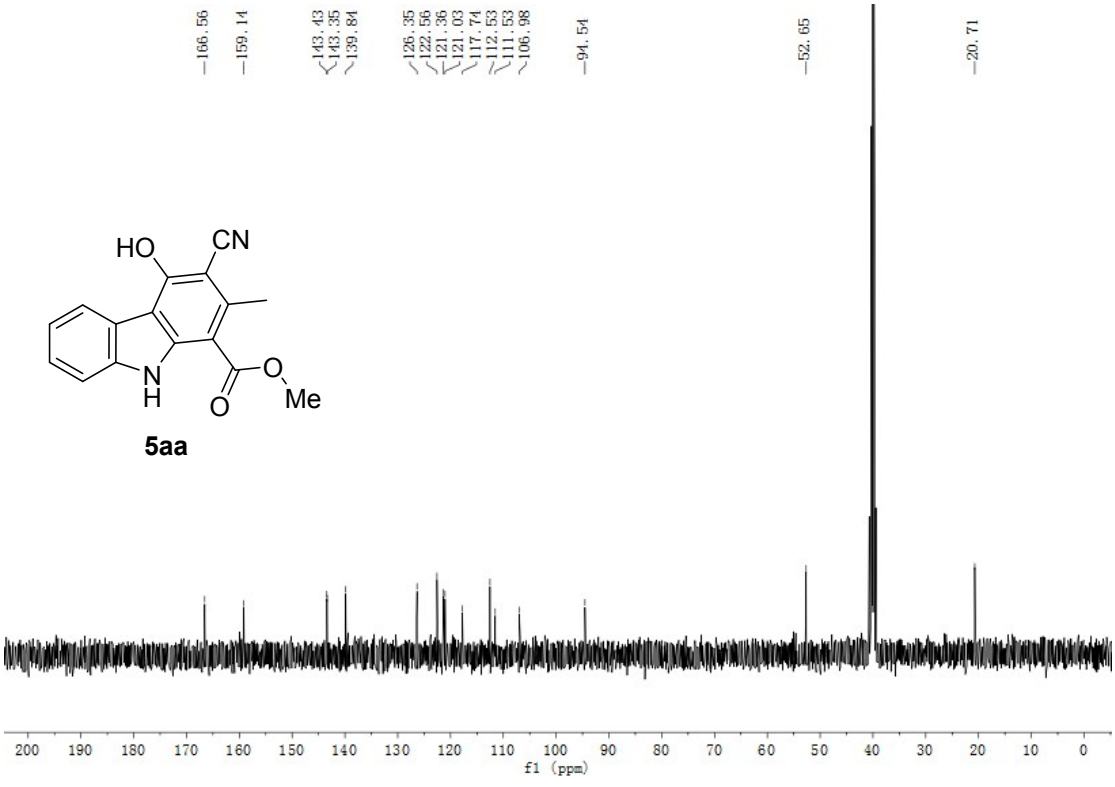
2-(3-chlorophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3am):



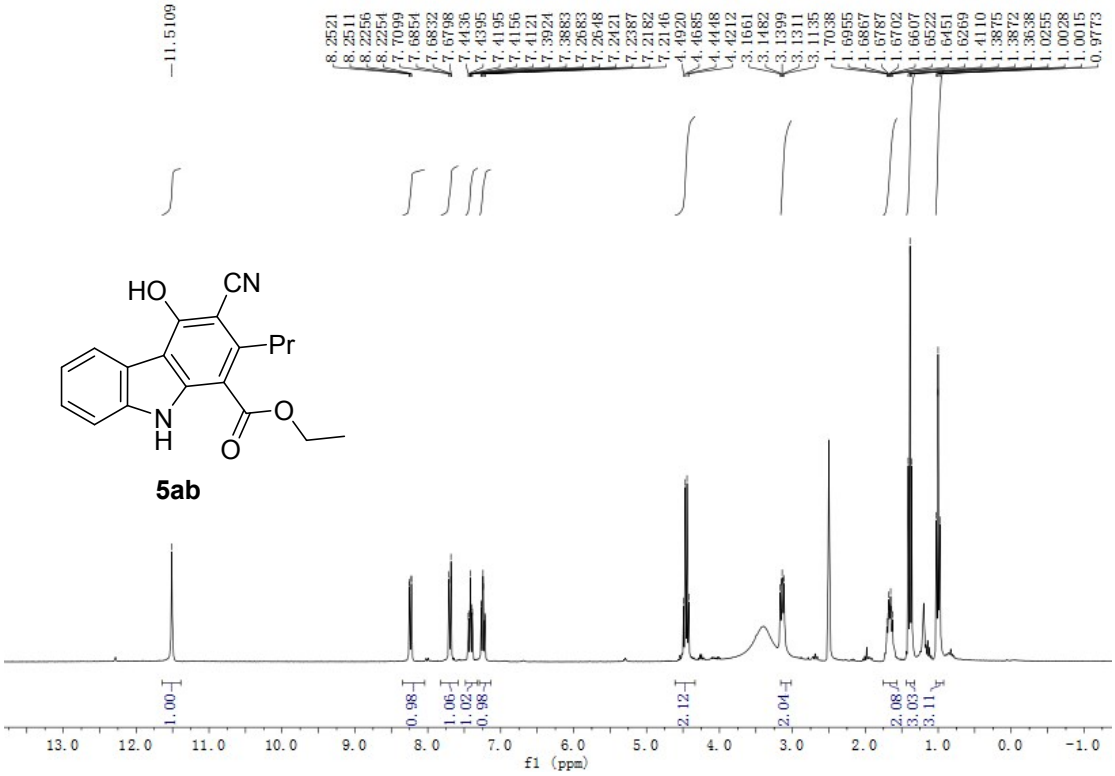


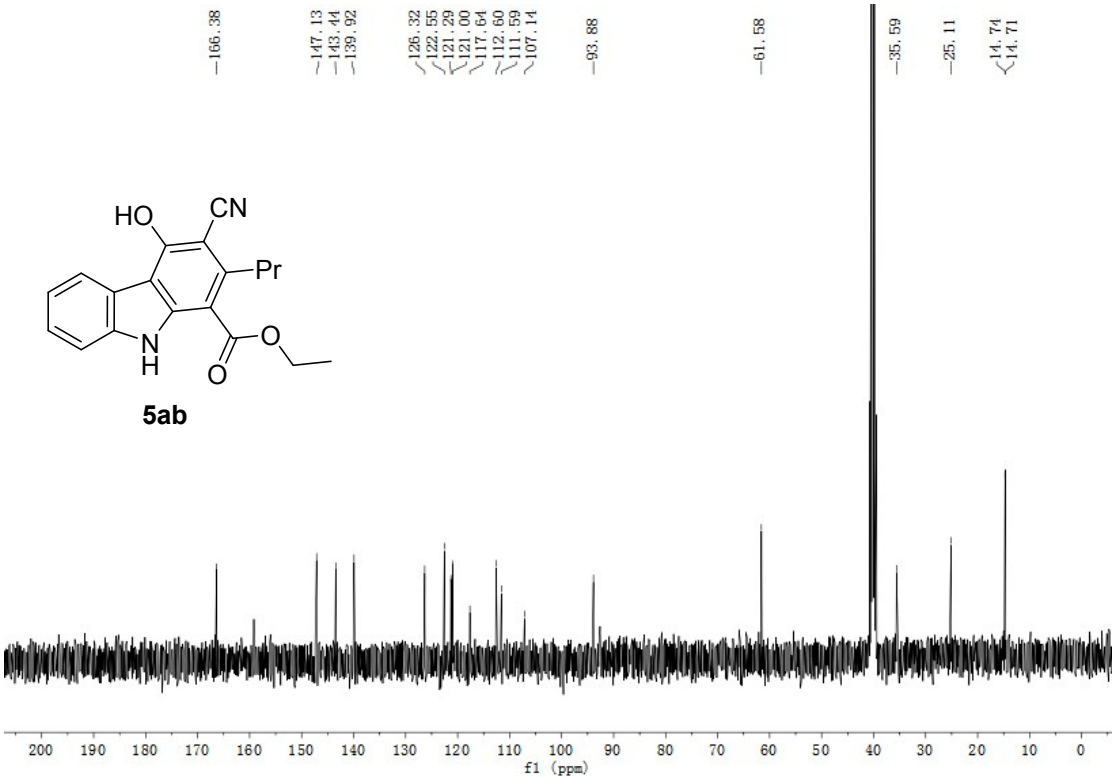
methyl 3-cyano-4-hydroxy-2-methyl-9*H*-carbazole-1-carboxylate (5aa):



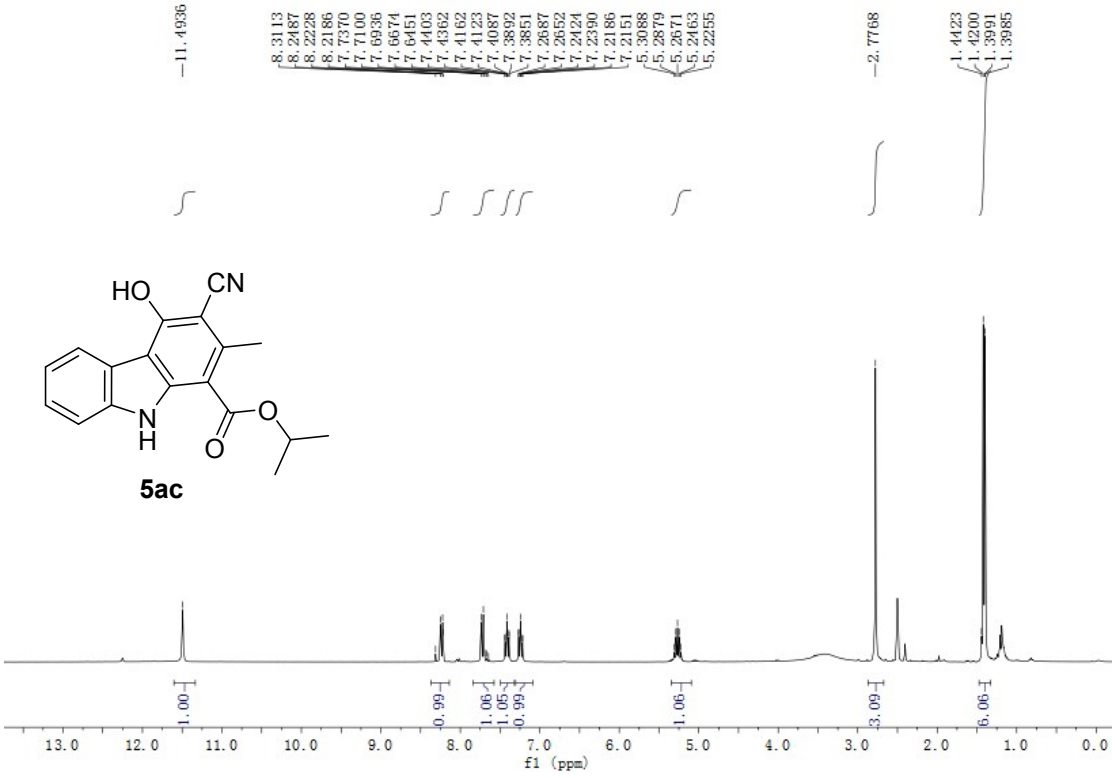


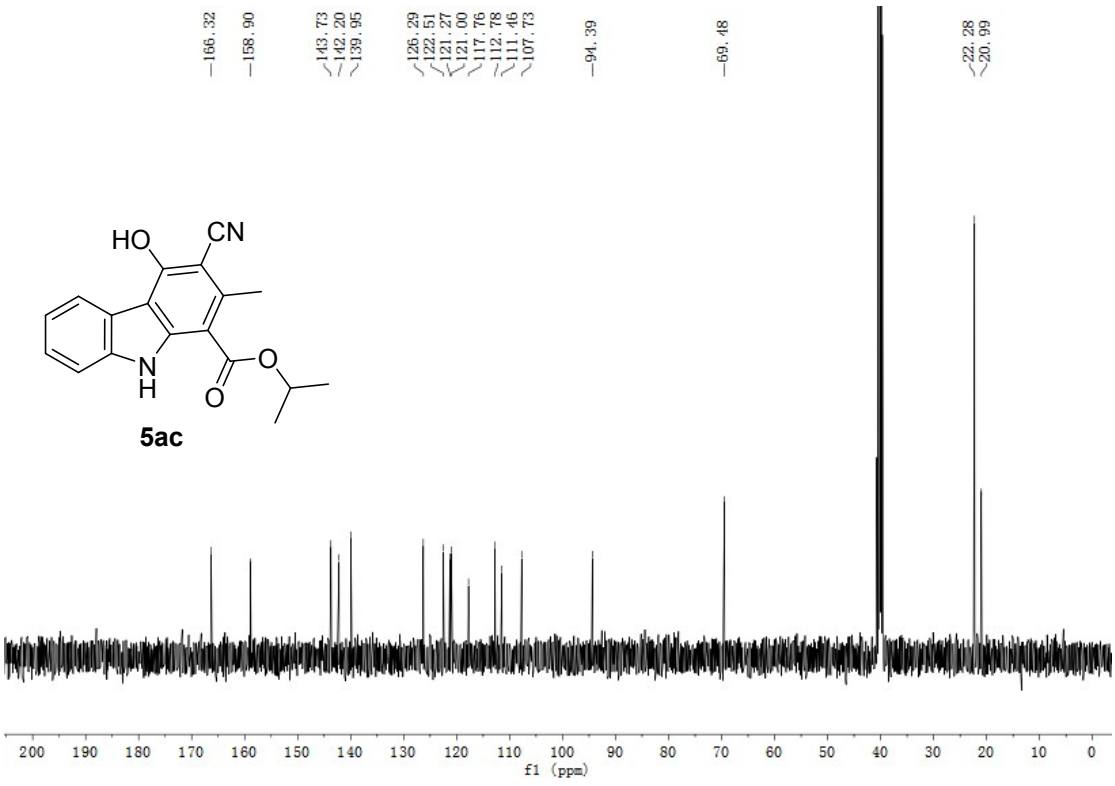
ethyl 3-cyano-4-hydroxy-2-propyl-9*H*-carbazole-1-carboxylate (5ab):



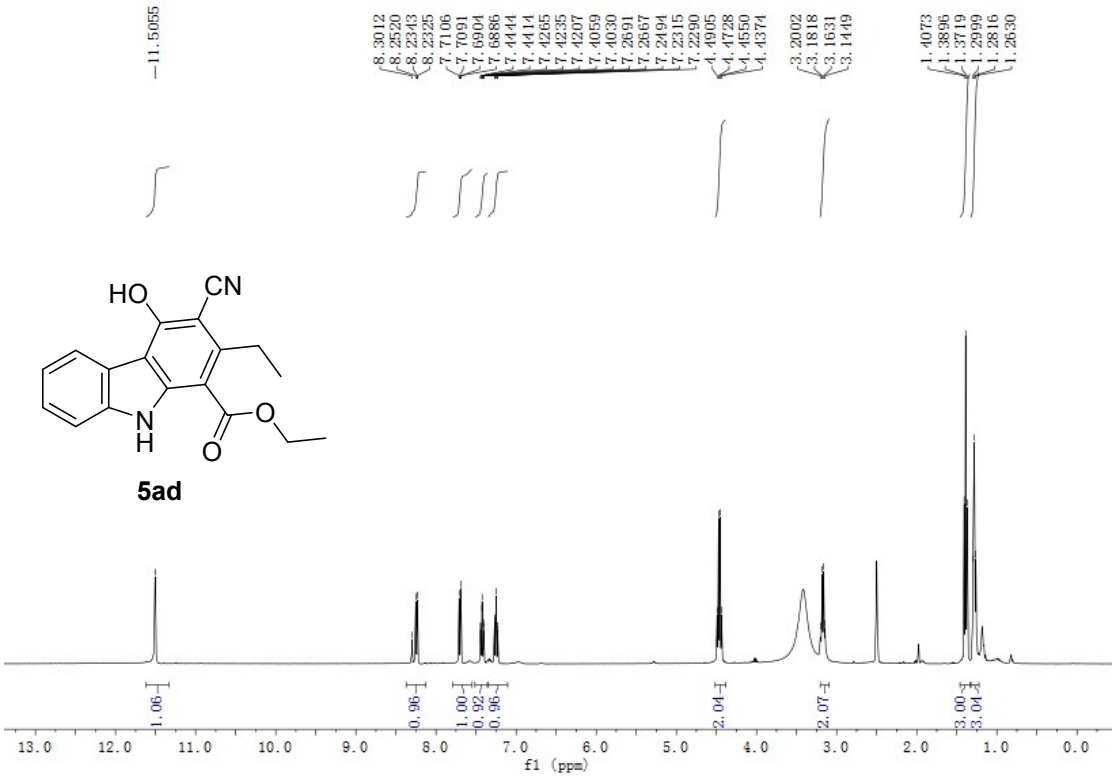


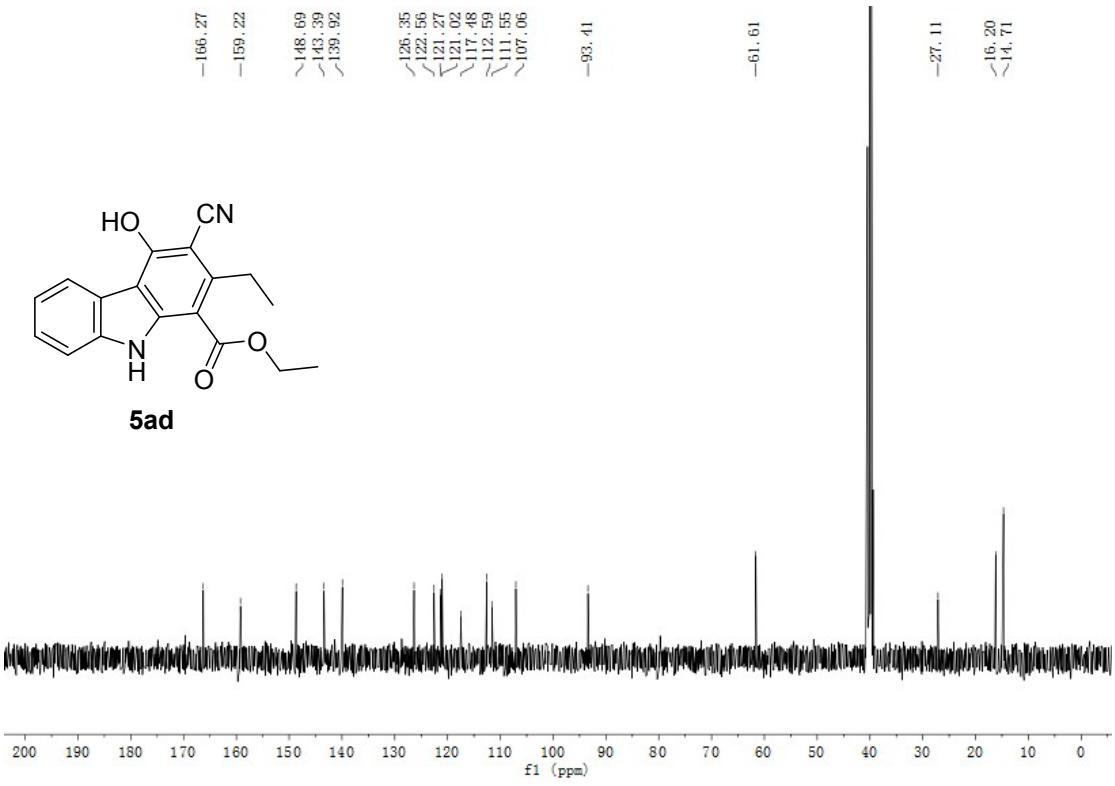
isopropyl 3-cyano-4-hydroxy-2-methyl-9*H*-carbazole-1-carboxylate (5ac):





ethyl 3-cyano-2-ethyl-4-hydroxy-9*H*-carbazole-1-carboxylate (5ad):





***tert*-butyl 3-cyano-2-methyl-4-hydroxy-9*H*-carbazole-1-carboxylate (5ae):**