

Supporting Information

Visible light-photocatalysed carbazole synthesis via formal (4+2) cycloaddition of indole-derived bromides and alkynes

Zhi-Guang Yuan,^a Qiang Wang,^a Ang Zheng,^a Kai Zhang,^a Liang-Qiu Lu,^{*a} Zilong Tang^b
and Wen-Jing Xiao^{a,b}

^aKey Laboratory of Pesticide & Chemical Biology, Ministry of Education; College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China.

^bSchool of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

E-mail: luliangqiu@mail.ccnu.edu.cn; Fax: +86 27 67862041;

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1. General Information

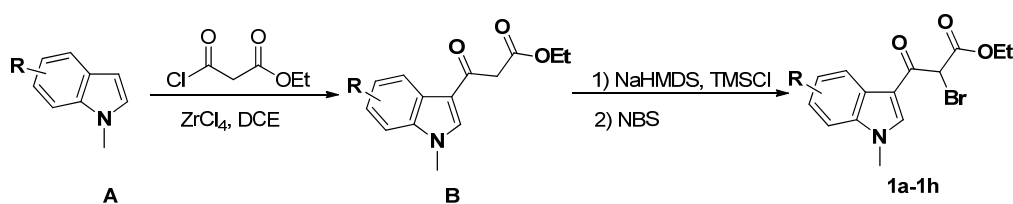
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel.

^1H NMR spectra were recorded on 400 and 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity ((s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 and 150 MHz with complete proton decoupling spectrophotometers. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for CDCl_3 or 39.6.0 ppm for DMSO-d_6 . Mass spectra were measured on a MS spectrometer. The high-resolution mass spectroscopic (HRMS) data were obtained on a Shimadazu LCMS-IT-TOF spectrometer.

2. Preparation and Spectral Data of Substrates

2.1 Preparation of Substrates 1a – 1h

2.1.1 Substrates 1a-1h were prepared according to the following general procedures A:^{1,2,3}



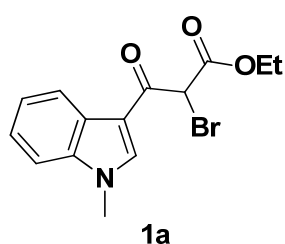
To a solution of 1-methylindole (A, 26 mmol) in anhydrous DCE (30 mL) taken in a round-bottom flask at 0 °C under nitrogen was added ethyl 3-chloro-3-oxopropanoate (20 mmol) in anhydrous DCE (30 mL) by a syringe under nitrogen. Zirconiumtetrachloride (30 mmol) was added under a flow of nitrogen. The reaction temperature was then gradually increased to room temperature, and the

reaction was stirred overnight at room temperature. After the completion of the reaction as indicated by TLC, the resultant mixture was quenched with water (100 mL) and extracted with EtOAc. The combined organic phase was washed with water (100 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. Purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/CH₂Cl₂ (20:1:2) providing the acylation product **B** which was used to next step.

A flame dried round bottom flask equipped with a magnetic stir bar was charged with **B** (1.0 equiv) from above procedure and anhydrous THF (0.1 M), and then cooled to -78 °C. A solution of NaHMDS in THF (1.1 eq., 2.0 M) was then added dropwise and the mixture was allowed to be stirred for 30 min. TMSCl (1.1 eq.) was then added and the mixture continued to be stirred for 1 h. NBS (1.1 eq.) was then added and the reaction was allowed to be stirred at -78 °C. When the reaction finished as judged by TLC analysis, the mixture was poured into a separatory funnel containing Et₂O and H₂O. The layers were separated and the aqueous layer was extracted with Et₂O. The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel eluting with petroleum ether/CH₂Cl₂ (1:2) to afford the desired products **1a-1h**.

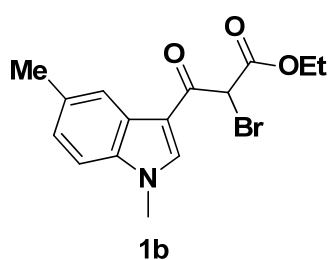
2.1.2 Spectral Data of Substrates

Ethyl 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxopropanoate (**1a**)



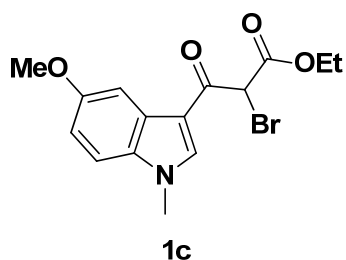
White solid, mp. 126 - 127 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.67 – 8.26 (m, 1H), 7.93 (s, 1H), 7.53 – 7.27 (m, 3H), 5.42 (s, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 1.27 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 182.0, 165.7, 137.3, 136.8, 126.5, 123.9, 123.2, 122.4, 112.4, 109.8, 63.0, 47.8, 33.7, 13.8; IR (in KBr): 3526, 3437, 3099, 1768, 1754, 1626, 1522, 1455, 1360, 1238, 1145, 1082, 834, 793 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₄NO₃Br: 324.0230; found: 324.0238; MS (EI): *m/z* = 323.04.

Ethyl 2-bromo-3-(1,5-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1b)



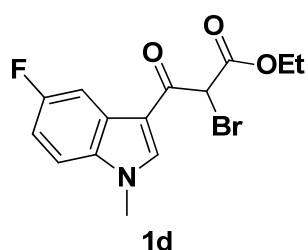
White solid, mp. 161 - 162 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.18 (s, 1H), 7.88 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 5.42 (s, 1H), 4.40 – 4.17 (m, 2H), 3.85 (s, 3H), 2.49 (s, 3H), 1.27 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 181.8, 165.4, 136.7, 135.6, 132.7, 126.6, 125.2, 121.9, 111.9, 109.5, 63.0, 47.8, 33.8, 21.6, 14.0; IR (in KBr): 3526, 3437, 3103, 1755, 1664, 1636, 1526, 1484, 1268, 1237, 1140, 1087, 836, 803, 702 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₆NO₃Br: 338.0386; found: 338.0396; MS (EI): *m/z* = 337.03.

Ethyl 2-bromo-3-(5-methoxy-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1c)



White solid, mp. 122 - 123 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.95 – 7.72 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 6.94 (dd, *J*₁ = 8.9 Hz, *J*₂ = 2.5 Hz, 1H), 5.40 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 182.0, 165.5, 156.6, 136.7, 132.1, 127.3, 114.0, 111.9, 110.7, 103.4, 62.9, 55.4, 47.5, 33.7, 13.7; IR (in KBr): 3526, 3437, 3103, 2967, 1755, 1664, 1636, 1526, 1484, 1268, 1237, 1140, 1087, 836, 803, 702 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₆NO₄Br: 354.0335; found: 354.0345; MS (EI): *m/z* = 353.07.

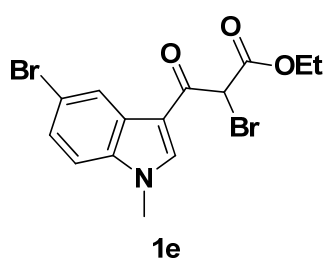
Ethyl 2-bromo-3-(5-fluoro-1-methyl-1H-indol-3-yl)-3-oxopropanoate(1d)



White solid, mp. 127 - 128 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.96 (dd, *J*₁ = 9.5 Hz, *J*₂ = 2.4 Hz, 1H), 7.90 (s, 1H), 7.27 – 7.16 (m, 1H), 7.00 (td, *J*₁ = 8.9 Hz, *J*₂ = 2.4 Hz, 1H), 5.41 (s, 1H), 4.25 (dd, *J*₁ = 14.1 Hz, *J*₂ = 7.0 Hz, 2H), 3.83 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 181.7, 165.4, 160.9, 158.5, 137.7, 133.7, 127.2 (d, *J* = 11.2 Hz), 112.2 (d, *J* = 26.4 Hz), 110.8 (d, *J* = 9.8 Hz), 107.8 (d, *J* = 25.1 Hz), 63.2, 47.7, 34.2,

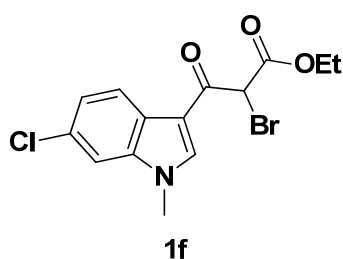
14.1; IR (in KBr): 3525, 3438, 3116, 1768, 1754, 1634, 1586, 1534, 1477, 1263, 1111, 1078, 837, 804 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{FBr}$: 342.0145; found: 342.0136; MS (EI): m/z = 341.00.

Ethyl 2-bromo-3-(5-bromo-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1e)



White solid, mp. 155 - 156 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.52 (s, 1H), 7.91 (s, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 5.38 (s, 1H), 4.28 (m, 2H), 3.86 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 181.7, 165.2, 137.2, 135.7, 127.8, 126.6, 124.6, 116.6, 111.6, 111.2, 63.1, 47.6, 34.0, 14.0; IR (in KBr): 3525, 3437, 3101, 1754, 1662, 1636, 1526, 1457, 1361, 1276, 1235, 1122, 1088, 793, 702 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{Br}_2$: 401.9345; found: 401.9335; MS (EI): m/z = 400.93.

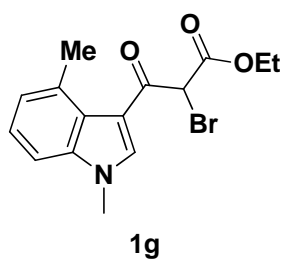
Ethyl 2-bromo-3-(6-chloro-1-methyl-1H-indol-3-yl)-3-oxopropanoate (1f)



White solid, mp. 138 - 139 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.27 (d, J = 8.5 Hz, 1H), 7.93 (s, 1H), 7.36 (s, 1H), 7.30 (d, J = 10.0 Hz, 1H), 5.39 (s, 1H), 4.28 (m, 2H), 3.85 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 181.8, 165.3, 137.5, 137.2, 129.6, 124.8, 123.5, 123.1, 112.3, 109.9, 63.2, 47.7, 33.9, 14.1; IR (in KBr): 3414, 3108, 2997, 1758, 1652, 1531, 1467, 1368, 1302, 1214, 1130, 1017, 920, 823, 707 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{ClBr}$: 357.9840; found: 357.9853; MS (EI): m/z = 357.00.

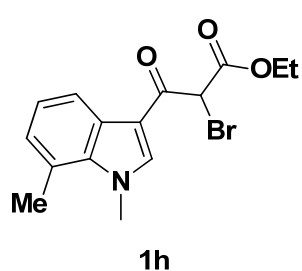
Ethyl 2-bromo-3-(1,4-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1g)

Light yellow solid, mp. 93 - 95 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.83 (s, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 7.1 Hz, 1H), 5.50 (s, 1H), 4.25 (dd, J_1 = 12.7 Hz, J_2 = 6.6 Hz, 2H), 3.81 (s, 3H), 2.81 (s, 3H), 1.25 (t, J =



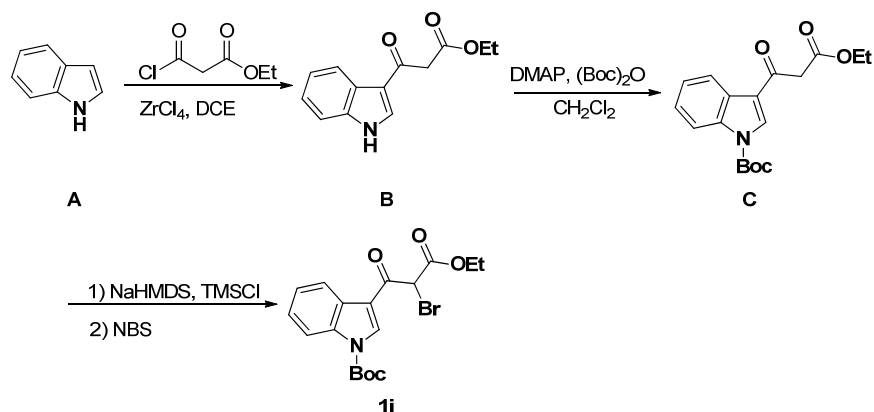
7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 181.3, 165.6, 138.1, 137.5, 133.1, 124.9, 124.7, 123.9, 113.8, 107.3, 62.7, 48.9, 33.5, 22.5, 13.7; IR (in KBr): 3524, 3438, 3117, 1764, 1752, 1662, 1497, 1434, 1360, 1276, 1112, 832, 743 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{Br}$: 338.0386; found: 338.0394; MS (EI): m/z = 337.03.

Ethyl 2-bromo-3-(1,7-dimethyl-1H-indol-3-yl)-3-oxopropanoate (1h)



White solid, mp. 137 - 138 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.21 (d, J = 7.9 Hz, 1H), 7.77 (s, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 5.39 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 4.09 (s, 3H), 2.73 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 181.5, 165.4, 138.2, 135.8, 127.4, 126.4, 123.1, 121.7, 120.2, 111.7, 63.0, 47.8, 38.0, 19.4, 14.0; IR (in KBr): 3526, 3437, 3102, 1761, 1663, 1631, 1536, 1456, 1365, 1315, 1151, 1101, 832, 724 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{Br}$: 338.0386; found: 338.0395; MS (EI): m/z = 337.03.

2.2 Tert-butyl 3-(2-bromo-3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (1i) could be prepared with the following procedures B.⁴



To a solution of indole (**A**, 26 mmol) in anhydrous DCE (30 mL) taken in a round-bottom flask at 0 °C under nitrogen was added ethyl 3-chloro-3-oxopropanoate (20 mmol) in anhydrous DCE (30 mL) by a syringe under nitrogen.

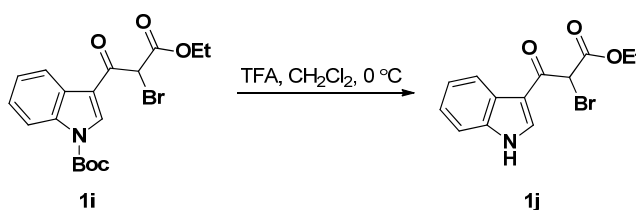
Zirconiumtetrachloride (30 mmol) was added under a flow of nitrogen. The reaction was then gradually increased to room temperature, and stirred overnight at room temperature. After completion of the reaction as indicated by TLC, the resultant mixture was quenched with water (100 mL) and extracted with EtOAc. The combined organic layer was washed with water (100 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. Purified by flash column chromatography eluting with petroleum ether/EtOAc/dichloromethane provided the acylation product **B** which was used to next step.

To a solution of ethyl 3-(1H-indol-3-yl)-3-oxopropanoate (**B**, 1.0 eq.) and DMAP (0.33 eq.) in dry CH₂Cl₂ (0.4 M) was added di-tert-butyl dicarbonate (1.0 eq.). The resulting mixture was stirred at 0 °C for 1 h and then warmed to 25 °C for 12 h. Solvent was removed in vacuo and the residue was triturated with ether (2 x 25 ml) to afford the N-Boc- protected indole product **C** as a light yellow solid. **C** was used to the next step without further purification.

1i could be obtained with the same bromination method in **procedures A** from tert-butyl 3-(3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (**C**).

1i, white solid, mp. 119 - 121 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.39 (s, 1 H), 8.36 – 8.25 (m, 1 H), 8.09 (d, *J* = 7.6 Hz, 1 H), 7.37 (dd, *J*₁ = 9.4 Hz, *J*₂ = 3.8 Hz, 2 H), 5.48 (s, 1 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 1.71 (s, 9 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 183.1, 164.8, 148.4, 135.1, 133.2, 127.2, 125.8, 124.5, 122.4, 116.3, 114.9, 85.9, 63.3, 47.4, 28.1, 14.1; IR (in KBr): 3526, 3437, 3137, 2984, 1764, 1732, 1643, 1548, 1377, 1261, 1238, 1162, 1122, 1026, 836, 687, 591 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₈H₂₀NO₅Br: 410.0598; found: 410.0608; MS (EI): *m/z* = 409.05.

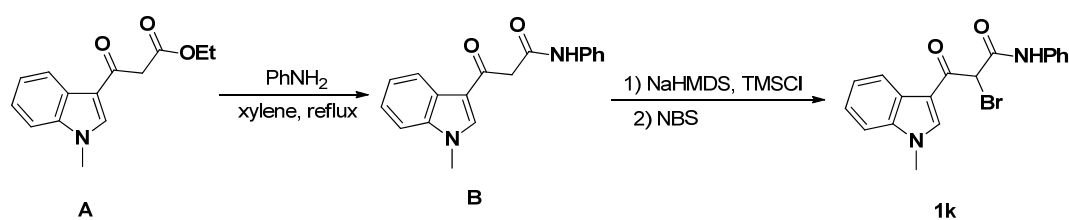
2.3 Preparation of ethyl 2-bromo-3-(1H-indol-3-yl)-3-oxopropanoate (**1j**)⁵



To a solution of tert-butyl 3-(2-bromo-3-ethoxy-3-oxopropanoyl)-1H-indole-1-carboxylate (**1i**) in DCM (0.2 M), TFA (40 eq.) was added at 0 °C, after stirred for 2.5 h, TFA and DCM was removed under vacuo, the residue was purified by flash column chromatography (DCM/PE=2:1) to give the desired product as white solid.

1j, white solid, mp. 138 - 139 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 10.06 (s, 1H), 8.34 (d, *J* = 6.4 Hz, 1H), 8.12 (d, *J* = 3.0 Hz, 1H), 7.71 – 7.41 (m, 1H), 7.41 – 7.08 (m, 2H), 5.59 (s, 1H), 4.24 (dd, *J*₁ = 7.0 Hz, *J*₂ = 2.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 183.1, 165.9, 136.5, 134.2, 125.6, 124.2, 123.3, 122.0, 113.9, 112.2, 63.5, 47.6, 14.1; IR (in KBr): 3524, 3438, 3120, 1772, 1736, 1631, 1517, 1430, 1239, 1146, 833, 755 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₃H₁₂NO₃Br: 310.0073; found: 310.0075; MS (EI): *m/z* = 309.15.

2.4 Preparation of 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxo-N-phenylpropanamide (**1k**).⁶



The xylene (0.5 M) solution of aniline (1.0 eq.) and the keto ester (**A**, 1.0 eq.) was heated at 165 °C overnight. After cooled to below 100 °C, toluene was then added. Upon cooling the crystals of α -keto amide was precipitated. After filtration, the α -keto amide was used to next step without further purification.

With the amide product **B** in hand, substrates 2-bromo-3-(1-methyl-1H-indol-3-yl)-3-oxo-N-phenylpropanamide (**1k**) could be obtained with the same bromination procedure in the **procedures A**.

1k, white solid, mp. 187 - 189 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.18 (s, 1H), 8.40 – 8.26 (m, 1H), 7.95 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.25 (m, 5H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.41 (s, 1H), 3.87 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ (ppm) 182.9, 162.3, 138.4, 138.2, 137.1, 128.6, 125.9, 123.9, 123.3, 122.6, 121.2, 119.3, 111.9, 110.8, 50.8, 33.6; IR (in KBr): 3422, 3109, 1686, 1593, 1550, 1530,

1463, 1448, 1373, 1128, 1085, 750, 690 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_2\text{Br}$: 371.0390; found: 371.0405; MS (EI): m/z = 370.10.

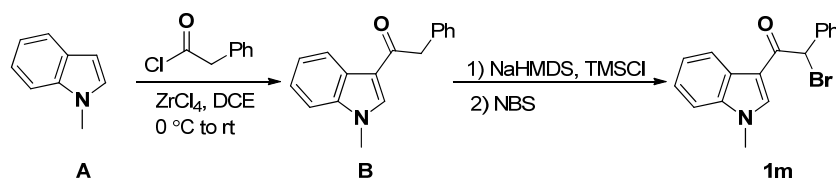
2.5 Preparation of 2-bromo-1-(1-methyl-1H-indol-3-yl)butane-1,3-dione (**1l**)



1-(1-methyl-1H-indol-3-yl)butane-1,3-dione (**A**) could be prepared according to the literature reported⁷. Then substrate 2-bromo-1-(1-methyl-1H-indol-3-yl)-butane-1,3-dione (**1l**) could be obtained with the same bromination procedure in the **procedures A**. The substrate **1l** was the mixture of ketone and enol form (about 3:1).

1l, white solid, mp. 156 - 157 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.38 (d, J = 5.2 Hz, 1H), 7.88 (d, J = 23.7 Hz, 1H), 7.37 (s, 3H), 5.42 (s, 1H), 5.37 (s, 1H), 3.87 (s, 3H), 2.44 (s, 2H), 2.37 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 199.2, 198.7, 182.3, 137.4, 137.2, 137.1, 126.4, 126.4, 124.1, 123.4, 122.5, 113.1, 112.8, 109.9, 67.5, 56.6, 34.0, 26.5, 26.5; IR (in KBr): 3525, 3437, 3099, 1769, 1732, 1626, 1527, 1349, 1262, 1148, 1034, 832, 760 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{Br}$: 294.0124; found: 294.0126.

2.6 Preparation of 2-bromo-1-(1-methyl-1H-indol-3-yl)-2-phenylethanone (**1m**)

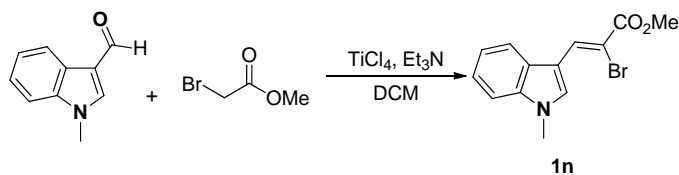


Substrates 2-bromo-1-(1-methyl-1H-indol-3-yl)-2-phenylethanone (**1m**) could also be prepared through the same procedure in procedures **A** from 1-methylindole and phenylacetyl chloride.

1m, light yellow solid; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.42 (d, J = 5.8 Hz, 1H), 7.67 (s, 1H), 7.58 (d, J = 7.3 Hz, 2H), 7.43 – 7.14 (m, 6H), 6.13 (s, 1H), 3.73 (s,

3H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 185.8, 137.4, 137.1, 135.8, 128.8, 128.8, 126.7, 123.8, 123.1, 122.6, 112.9, 109.8, 52.5, 33.7, 33.6; MS (EI): $m/z = 292.94$.

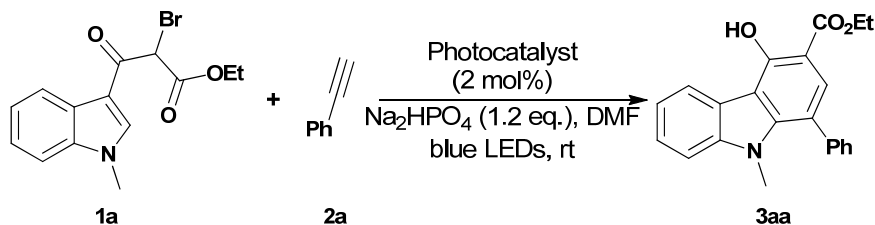
2.7 Preparation of (Z)-methyl 2-bromo-3-(1-methyl-1H-indol-3-yl)acrylate (**1n**)



(Z)-methyl 2-bromo-3-(1-methyl-1H-indol-3-yl)acrylate (**1n**) could be prepared according to the literature.⁸ ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.60 (s, 1H), 8.38 (s, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.42 – 7.28 (m, 2H), 7.28 – 7.21 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 164.3, 136.3, 132.6, 132.2, 128.6, 123.1, 121.1, 118.4, 109.9, 109.8, 106.2, 53.2, 33.6; MS (EI): $m/z = 327.00$.

3. Details for Condition Optimization

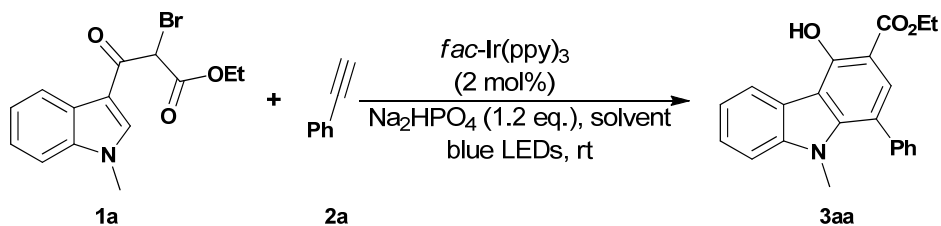
Table S1. Photocatalyst effects for the visible light photocatalyzed formal (4+2) cycloaddition reaction.^a



Entry	Photocatalyst	Time (h)	Yield (%) ^b
1	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	20	39
2	Ru(bpy) ₃ (PF ₆) ₂	20	12
3	Ru(bpz) ₃ (PF ₆) ₂	20	trace
4	<i>fac</i> -Ir(ppy) ₃	20	76
5	Ir(ppy) ₂ (dtbbpy)PF ₆	20	25
6	Ir[(dF(CF ₃)ppy)] ₂ (dtbbpy)PF ₆	20	42
7	Ir(ppy) ₂ (bpy)PF ₆	20	trace
8	Eosin Y	20	NR

^a The reactions were carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), photocatalyst (2 mol%) and Na₂HPO₄ (0.12 mmol) in dry DMF (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. ^b Isolated yields.

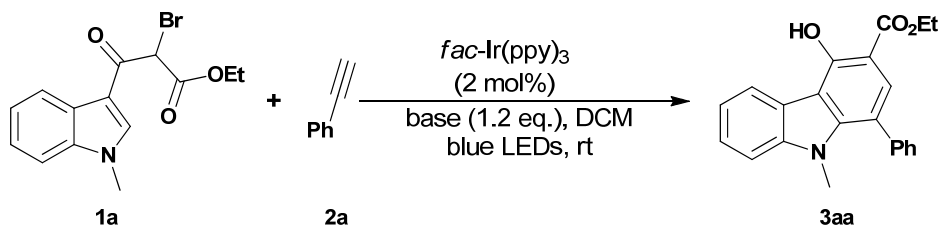
Table S2. Solvent effects for the visible light photocatalyzed formal (4+2) cycloaddition reaction.^a



Entry	Solvent	Time (h)	Yield (%) ^b
1	DMF	20	76
2	DMA	20	76
3	DMSO	20	75
4	THF	20	65
5	CH ₃ CN	20	83
6	CH ₂ Cl ₂	20	83
7	DCE	20	59
8	CHCl ₃	20	82

^a The reactions were carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), *fac*-Ir(ppy)₃ (2 mol%) and Na₂HPO₄ (0.12 mmol) in dry solvent (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. ^b Isolated yields.

Table S3. Base effects for visible light photocatalyzed formal (4+2) cycloaddition reaction.^a

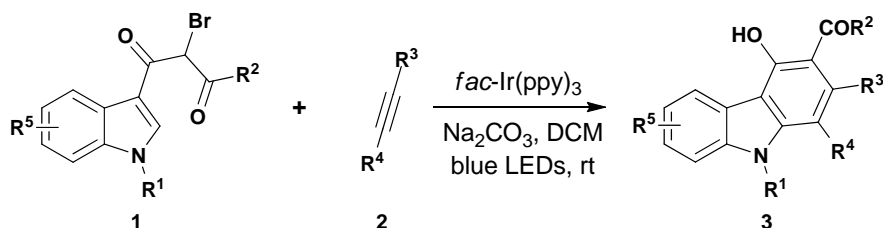


Entry	Base	Time (h)	Yield (%) ^b
1	Na ₂ HPO ₄	20	83
2	NaHCO ₃	20	82
3	Na ₂ CO ₃	20	95
4	K ₂ CO ₃	20	89
5 ^c	--	20	7

^a The reactions were carried out with **1a** (0.1 mmol), **2a** (0.1 mmol), *fac*-Ir(ppy)₃ (2 mol%) and base (0.12 mmol) in dry DCM (1.0 mL) under Ar, and irradiated under 3 W blue LEDs at room temperature. ^b Isolated yield. ^c Without base.

4. General Procedure and Spectral Data of Products

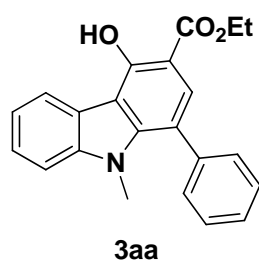
4.1 General procedure for the synthesis of product 3



To a 10 mL schlenk tube equipped with a magnetic stirrer bar was added **1** (0.3 mmol, 1.0 eq.), **2** (0.3 mmol, 1.0 eq.), Na₂CO₃ (0.36 mmol, 1.2 eq.), *fac*-Ir(ppy)₃ (2 mol%, 0.006 mmol) and 3 mL dry CH₂Cl₂. The resulting mixture was degassed through ‘freeze-pump-thaw’ procedure three times, and then the solution was stirred at room temperature under the irradiation of 3W blue LEDs for 20 hours. Upon the completion of the cycloaddition reaction as monitored by TLC, the solvent was evaporated under reduced pressure, the residue was purified by flash chromatography on silica gel to give the desired product **3**.

4.2 Spectral Data of Products

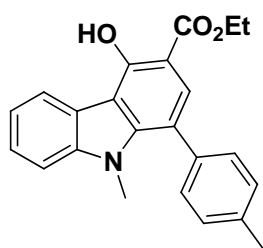
Ethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (**3aa**)



84% yield, white solid, mp. 180 - 181 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.81 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.49 – 7.38 (m, 5H), 7.37 – 7.26 (m, 2H), 4.42 (dd, *J*₁ = 14.2 Hz, *J*₂ = 7.1 Hz, 2H), 3.36 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 170.9, 158.8, 142.8, 141.2, 139.6, 130.21, 129.2, 128.1, 127.3, 125.2, 123.1, 122.4, 120.6, 118.0, 111.5, 108.6, 102.7, 60.9, 32.6, 14.3; IR (in KBr): 2980, 1652, 1627, 1602, 1467, 1372, 1330, 1258, 1195, 1062, 1017, 906, 796, 753, 702 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₂H₁₉NO₃: 345.1365; found: 345.1345.

Ethyl 4-hydroxy-9-methyl-1-(*p*-tolyl)-9H-carbazole-3-carboxylate (**3ab**)

85% yield, white solid, mp. 154 - 156 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.79



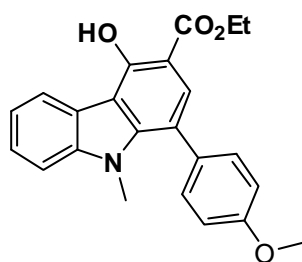
3ab

(s, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 7.70 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.32 (dt, *J*₁ = 12.7 Hz, *J*₂ = 6.3 Hz, 4H), 7.27 – 7.22 (m, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.37 (s, 3H), 2.44 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.4, 142.6, 141.0, 136.8, 136.4, 129.9, 129.1, 128.5,

124.9, 122.8, 122.2, 120.3, 117.8, 111.3, 108.4, 102.5, 60.8, 32.6, 21.3, 14.4; IR (in KBr): 3117, 2993, 1770, 1747, 1605, 1515, 1488, 1465, 1374, 1329, 1248, 1189, 1143, 1059, 795, 734 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₃H₂₁NO₄: 359.1521; found: 359.1515.

Ethyl 4-hydroxy-1-(4-methoxyphenyl)-9-methyl-9H-carbazole-3-carboxylate

(**3ac**)

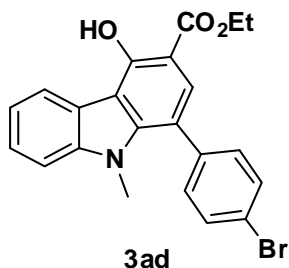


3ac

55% yield; white solid, mp. 136 - 137 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.80 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 4.42 (q, *J* = 7.0 Hz, 2H), 3.90 (s, 3H), 3.39 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6,

158.6, 158.3, 142.7, 140.9, 131.5, 131.0, 129.1, 124.9, 122.8, 122.2, 120.3, 117.4, 113.2, 111.2, 108.4, 102.4, 60.8, 55.3, 32.5, 14.4; IR (in KBr): 3118, 3099, 1765, 1665, 1628, 1605, 1517, 1378, 1245, 1180, 1144, 1030, 832, 797, 730 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₃H₂₁NO₄: 375.1471; found: 375.1466.

Ethyl 1-(4-bromophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (**3ad**)

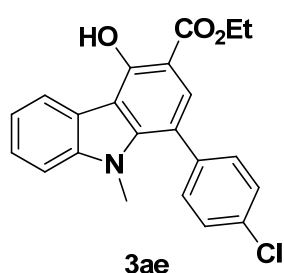


3ad

90% yield, white solid, mp. 183 – 185 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.75 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 7.61 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24 (dd, *J*₁ = 21.8 Hz, *J*₂ = 12.8 Hz, 4H), 4.37 (q, *J* = 7.0 Hz,

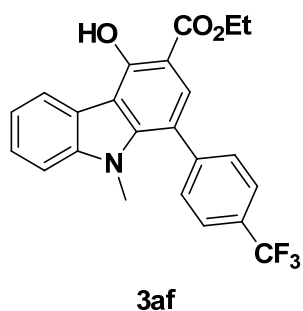
2H), 3.31 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.6, 158.8, 142.4, 141.1, 138.5, 131.7, 131.1, 129.1, 125.3, 123.1, 122.3, 121.5, 120.7, 116.5, 111.7, 108.6, 102.8, 61.1, 33.1, 14.6; IR (in KBr): 3046, 2977, 1764, 1748, 1658, 1603, 1371, 1298, 1192, 1142, 1098, 797, 696, 554 cm^{-1} ; HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{BrNO}_3$: 423.0470; found: 423.0465.

Ethyl 1-(4-chlorophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ae)



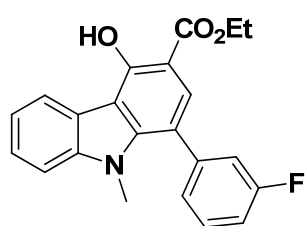
90% yield, white solid, mp. 188 - 190 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.82 (s, 1H), 8.47 (d, $J = 7.8$ Hz, 1H), 7.68 (s, 1H), 7.46 (dd, $J_1 = 20.5$ Hz, $J_2 = 7.7$ Hz, 3H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.0$ Hz, 2H), 4.42 (q, $J = 7.2$ Hz, 2H), 3.38 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.5, 158.6, 142.4, 141.0, 137.9, 133.2, 131.3, 129.1, 128.1, 125.16, 122.9, 122.2, 120.5, 116.4, 111.5, 108.5, 102.7, 61.0, 32.9, 14.5; IR (in KBr): 3046, 2977, 1656, 1604, 1465, 1372, 1331, 1252, 1192, 1062, 1015, 798, 729, cm^{-1} ; HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{ClNO}_3$: 379.0975; found: 379.0974.

Ethyl 4-hydroxy-9-methyl-1-(4-(trifluoromethyl)phenyl)-9H-carbazole-3-carboxylate (3af)



83% yield, white solid, mp. 176 - 177 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.86 (s, 1H), 8.48 (d, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.71 (s, 1H), 7.60 (d, $J = 7.9$ Hz, 2H), 7.49 (t, $J = 7.7$ Hz, 1H), 7.41 - 7.29 (m, 2H), 4.43 (q, $J = 7.1$ Hz, 2H), 3.38 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 170.5, 158.8, 143.3, 142.2, 141.0, 130.3, 129.3 (q, $J_1 = 31.9$ Hz), 129.2, 125.2, 124.9 (q, $J = 3.4$ Hz), 124.1 (q, $J = 269.6$ Hz), 122.9, 122.1, 120.6, 116.2, 111.6, 108.5, 102.8, 61.1, 33.1, 14.5; IR (in KBr): 3059, 2957, 1661, 1608, 1470, 1375, 1327, 1252, 1162, 1106, 1069, 794, 747, 733 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{18}\text{NO}_3\text{F}_3$: 414.1312; found: 414.1315.

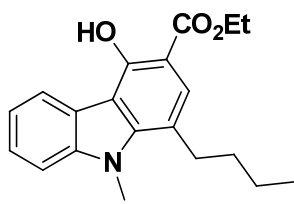
Ethyl 1-(3-fluorophenyl)-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (**3ag**)



3ag

78% yield, white solid, mp. 181 - 182 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.84 (s, 1H), 8.48 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J*₁ = 14.4 Hz, *J*₂ = 7.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.24 (s, 1H), 7.19 (d, *J* = 9.8 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.40 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 170.5, 162.1 (d, *J* = 246.5 Hz), 158.7, 142.3, 141.6 (d, *J* = 7.7 Hz), 141.0, 129.3 (d, *J* = 8.4 Hz), 129.0, 125.9 (d, *J* = 2.7 Hz), 125.2, 122.9, 122.2, 120.5, 117.0 (d, *J* = 21.0 Hz), 116.5 (d, *J* = 1.9 Hz), 114.1 (d, *J* = 20.9 Hz), 111.5, 108.5, 102.7, 61.0, 32.8, 14.5; IR (in KBr): 3076, 2983, 1656, 1609, 1584, 1469, 1373, 1329, 1268, 1210, 1063, 789, 730 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₂H₁₈FNO₃: 363.1271; found: 363.1263.

Ethyl 1-butyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (**3ah**)

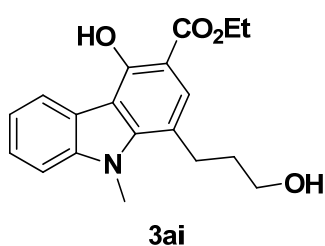


3ah

67% yield, white solid, mp. 112 - 113 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 11.64 (s, 1H), 8.44 (d, *J* = 7.7 Hz, 1H), 7.61 (s, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 3.09 - 3.00 (m, 2H), 1.74 - 1.66 (m, 2H), 1.47 (dt, *J*₁ = 19.3 Hz, *J*₂ = 7.3 Hz, 5H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 157.8, 143.4, 140.8, 128.11, 124.8, 122.9, 122.5, 120.2, 116.9, 111.6, 108.2, 102.6, 60.8, 34.7, 32.6, 32.1, 22.6, 14.6, 14.2; IR (in KBr): 3525, 3438, 3118, 2961, 2927, 1771, 1735, 1629, 1604, 1506, 1337, 1265, 1169, 1047, 932, 795, 748 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₀H₂₃NO₃: 325.1678; found: 325.1672.

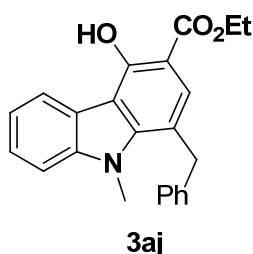
Ethyl 4-hydroxy-1-(3-hydroxypropyl)-9-methyl-9H-carbazole-3-carboxylate (**3ai**)

81% yield, light yellow solid, mp. 113 - 114 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.58 (s, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 - 7.11 (m, 2H), 4.39 (dd, *J*₁ = 14.2 Hz, *J*₂ = 7.1 Hz, 2H), 3.97 (s, 3H), 3.73 (t, *J* = 6.1 Hz,



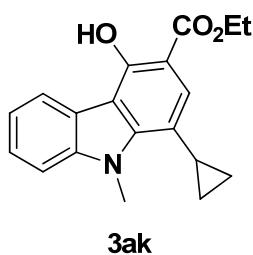
2H), 3.25 – 2.83 (m, 2H), 2.06 – 1.73 (m, 2H), 1.43 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.6, 158.0, 143.4, 140.9, 128.2, 125.0, 122.9, 122.5, 120.4, 116.0, 111.8, 108.4, 102.7, 62.1, 61.0, 35.1, 32.2, 29.0, 14.7; IR (in KBr): 3419, 2990, 2980, 2903, 1708, 1663, 1629, 1602, 1467, 1400, 1363, 1329, 1244, 1216, 1076, 1017, 807, 777, 734 cm^{-1} ; HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: 327.1471; found: 327.1464.

Ethyl 1-benzyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3aj)



60% yield, white solid, mp. 176 - 177 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.75 (s, 1H), 8.46 (d, $J = 7.8$ Hz, 1H), 7.68 (s, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.33 – 7.23 (m, 4H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 2H), 4.47 (s, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 3.76 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.6, 158.4, 143.8, 141.0, 140.5, 130.3, 128.5, 127.7, 126.0, 124.9, 122.8, 122.3, 120.3, 113.0, 111.7, 108.2, 102.7, 60.8, 38.5, 31.6, 14.4; IR (in KBr): 3421, 3394, 3062, 2908, 2844, 1655, 1626, 1508, 1463, 1373, 1323, 1254, 1226, 1125, 797, 733, 696 cm^{-1} ; HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$: 359.1521; found: 359.1513

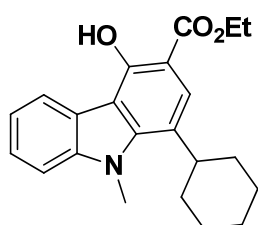
Ethyl 1-cyclopropyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3ak)



86% yield, white solid, mp. 148 - 150 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.72 (s, 1H), 8.43 (d, $J = 7.7$ Hz, 1H), 7.66 (s, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.41 (d, $J = 8.2$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 4.31 (s, 3H), 2.41 – 2.25 (m, 1H), 1.45 (t, $J = 7.1$ Hz, 3H), 1.12 – 1.01 (m, 2H), 0.94 – 0.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.6, 158.4, 144.9, 140.8, 127.3, 124.9, 122.9, 122.5, 120.4, 117.0, 111.2, 108.4, 102.3, 60.9, 32.4, 14.7, 13.9, 8.3; IR (in KBr): 3421, 3394, 3062, 2908, 2844, 1655, 1626, 1508, 1463, 1373, 1323, 1254, 1226, 1125, 797, 733, 696 cm^{-1} ; HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$:

309.1365; found: 309.1355.

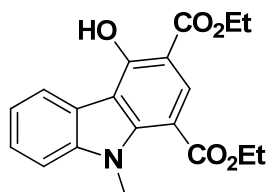
Ethyl 1-cyclohexyl-4-hydroxy-9-methyl-9H-carbazole-3-carboxylate (3al)



3al

73% yield, white solid, mp. 157 - 158 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.60 (s, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.17 (m, 2H), 4.41 (dd, *J*₁ = 13.6 Hz, *J*₂ = 6.7 Hz, 2H), 4.01 (s, 3H), 3.28 (t, *J* = 10.3 Hz, 1H), 2.01 (d, *J* = 11.5 Hz, 2H), 1.92 (d, *J* = 12.0 Hz, 2H), 1.82 (d, *J* = 12.0 Hz, 1H), 1.59 – 1.29 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.7, 157.6, 143.2, 141.1, 124.8, 123.9, 122.9, 122.8, 122.5, 120.2, 111.8, 108.3, 102.8, 60.8, 38.5, 35.1, 32.8, 27.2, 26.4, 14.6; IR (in KBr): 3421, 3395, 2932, 2851, 1656, 1608, 1508, 1468, 1324, 1257, 1224, 1139, 793, 731, 685 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₂H₂₅NO₃: 351.1834; found: 351.1837.

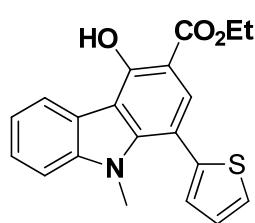
Diethyl 4-hydroxy-9-methyl-9H-carbazole-1,3-dicarboxylate (3am)



3am

64% yield, white solid; mp. 146 - 148 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 12.09 (s, 1H), 8.43 (s, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 4.47 (qd, *J*₁ = 7.1 Hz, *J*₂ = 3.3 Hz, 4H), 3.93 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.2, 166.4, 161.2, 143.3, 141.4, 131.4, 125.6, 122.9, 122.0, 121.1, 112.4, 109.1, 108.1, 102.9, 61.4, 61.25, 34.0, 14.6, 14.6; IR (in KBr): 3424, 3392, 2845, 2815, 1654, 1606, 1508, 1463, 1375, 1313, 1259, 1226, 1196, 1127, 719, 680, 643 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₁₉H₁₉NO₅: 341.1263; found: 341.1258.

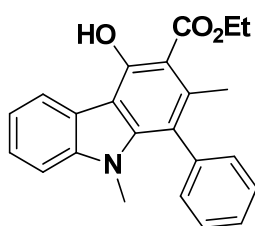
Ethyl 4-hydroxy-9-methyl-1-(thiophen-2-yl)-9H-carbazole-3-carboxylate (3an)



3an

46% yield, light yellow solid, mp. 212 - 213 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.81 (s, 1H), 8.41 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.61 – 7.34 (m, 2H), 7.27 (dd, *J*₁ = 22.8 Hz, *J*₂ = 16.8 Hz, 2H), 7.19 – 6.74 (m, 2H), 4.39 (dd, *J*₁ = 14.0 Hz, *J*₂ = 7.0 Hz, 2H), 3.44 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 159.3, 143.3, 141.0, 140.0, 130.9, 128.5, 126.8, 125.9, 125.3, 123.1, 122.2, 120.7, 111.5, 109.2, 108.6, 102.7, 61.1, 31.9, 14.6; IR (in KBr): 3525, 3438, 3119, 3099, 2988, 1772, 1733, 1627, 1603, 1507, 1427, 1404, 1327, 1264, 1246, 1141, 1055, 834, 795, 738 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₀H₁₇NO₃S: 351.0929; found: 351.0923

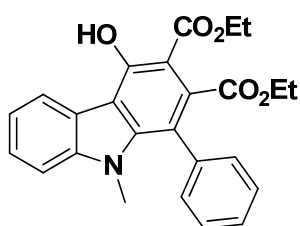
Ethyl 4-hydroxy-2,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ao)



3ao

64% yield; white solid, mp : 149 - 151 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 12.39 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 7.35 (dd, *J*₁ = 19.1 Hz, *J*₂ = 11.2 Hz, 4H), 7.20 (dd, *J*₁ = 32.4 Hz, *J*₂ = 7.8 Hz, 4H), 4.41 (dd, *J*₁ = 14.1 Hz, *J*₂ = 7.0 Hz, 2H), 3.00 (s, 3H), 2.32 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.4, 159.5, 142.3, 141.0, 139.0, 136.5, 131.3, 128.2, 127.4, 124.6, 122.7, 122.3, 120.2, 118.6, 109.5, 108.3, 103.5, 61.2, 31.9, 20.9, 14.4; IR (in KBr): 3525, 3438, 3119, 2986, 1772, 1734, 1597, 1507, 142, 1398, 1298, 1247, 1077, 901, 832, 811, 752 cm⁻¹; HRMS (ESI): *m/z* [M]⁺ calcd for C₂₃H₂₁NO₃: 359.1521; found: 359.1513.

Diethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-2,3-dicarboxylate (3ap)

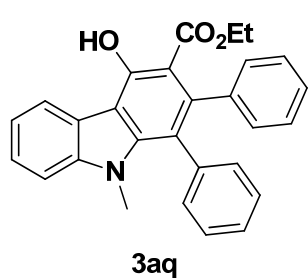


3ap

36 h, 46% yield, yellow solid, mp. 149 - 150 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 12.23 (s, 1H), 8.44 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.30 (m, 6H), 7.30 – 7.15 (m, 2H), 4.37 (dd, *J*₁ = 14.1 Hz, *J*₂ = 7.0 Hz, 2H), 3.91 (dd, *J*₁ = 14.1 Hz, *J*₂ = 7.1 Hz, 2H), 3.14 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 169.8, 168.3, 159.0, 141.7, 141.3, 135.7,

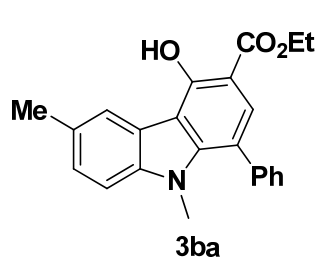
133.5, 131.7, 128.1, 127.7, 125.6, 123.4, 121.9, 120.8, 116.2, 111.6, 108.6, 99.3, 61.7, 61.0, 32.1, 14.2, 13.92; IR (in KBr): 3429, 3055, 2982, 2903, 1725, 1656, 1600, 1371, 1309, 1232, 1191, 1064, 950, 803, 735, 689 cm^{-1} ; HRMS (ESI): m/z $[M]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_5$: 417.1576; found: 417.1577.

Ethyl 4-hydroxy-9-methyl-1,2-diphenyl-9H-carbazole-3-carboxylate (3aq)



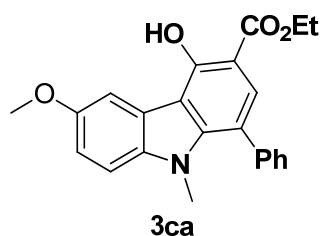
27% yield, white solid, mp. 181 - 183 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 12.37 (s, 1H), 8.50 (d, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.36 - 7.21 (m, 2H), 7.19 - 6.77 (m, 10H), 3.89 (q, $J = 7.1$ Hz, 2H), 3.09 (s, 3H), 0.64 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.7, 158.8, 141.8, 141.6, 141.2, 141.1, 137.5, 132.0, 129.7, 127.1, 126.6, 126.3, 125.3, 125.0, 123.0, 122.1, 120.4, 118.5, 110.5, 108.4, 103.1, 60.4, 32.0, 13.1.; IR (in KBr): 2981, 1656, 1501, 1478, 1396, 1656, 1334, 1308, 1242, 1199, 1001, 860, 818, 722, 692 cm^{-1} ; HRMS (ESI): m/z $[M+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{23}\text{NO}_3$: 444.1570; found: 444.1583.

Ethyl 4-hydroxy-6,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ba)



84% yield, white solid, mp. 173 - 175 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.85 (s, 1H), 8.28 (s, 1H), 7.70 (s, 1H), 7.62 - 7.34 (m, 5H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.22 (d, $J = 8.3$ Hz, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 3.33 (s, 3H), 2.56 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.7, 158.5, 142.7, 139.5, 139.4, 130.1, 129.8, 128.9, 127.9, 127.1, 126.3, 122.9, 122.4, 117.9, 111.2, 108.2, 102.4, 60.9, 32.7, 21.6, 14.5; IR (in KBr): 3307, 2977, 2924, 1652, 1629, 1474, 1370, 1301, 1258, 1168, 1058, 795, 726, 700 cm^{-1} ; HRMS (ESI): m/z $[M+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$: 360.1594; found: 360.1597.

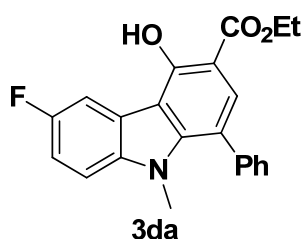
Ethyl 4-hydroxy-6-methoxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3ca)



74% yield, white solid, mp. 177 - 178 $^{\circ}\text{C}$; ^1H NMR (600

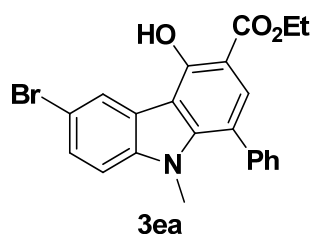
MHz, CDCl₃) δ (ppm) 11.87 (s, 1H), 7.99 (s, 1H), 7.69 (s, 1H), 7.49 – 7.41 (m, 4H), 7.32 – 7.18 (m, 2H), 7.10 (d, $J = 8.8$ Hz, 1H), 4.41 (q, $J = 7.0$ Hz, 2H), 3.97 (s, 3H), 3.33 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.7, 158.6, 154.4, 142.9, 139.4, 135.9, 130.0, 128.8, 127.9, 127.1, 122.7, 117.9, 114.5, 111.3, 109.2, 105.4, 102.1, 60.9, 56.01, 32.8, 14.5; IR (in KBr): 3421, 2983, 1658, 1625, 1474, 1432, 1373, 1263, 1227, 1057, 862, 793, 728 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₃H₂₁NO₄: 376.1543; found: 376.1541.

Ethyl 6-fluoro-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3da)



84% yield, white solid, mp. 185 - 187 °C; ¹H NMR (400 MHz, CDCl₃) 11.72 (s, 1H), 8.01 (d, $J = 8.8$ Hz, 1H), 7.65 (s, 1H), 7.29 (d, $J = 81.5$ Hz, 5H), 7.07 (dd, $J_1 = 12.1$ Hz, $J_2 = 5.0$ Hz, 2H), 4.36 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.0$ Hz, 2H), 3.25 (s, 3H), 1.38 (t, $J = 7.0$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.6, 157.8 (d, $J = 235.5$ Hz), 143.3, 139.2, 137.5, 130.1, 129.6, 128.0, 127.4, 122.7 (d, $J = 10.0$ Hz), 118.1, 112.8 (d, $J = 25.5$ Hz), 111.2 (d, $J = 3.3$ Hz), 109.0 (d, $J = 9.1$ Hz), 108.7 (d, $J = 24.7$ Hz), 102.5, 61.1, 33.0, 14.6; IR (in KBr): 2988, 2940, 1656, 1632, 1470, 1373, 1330, 1311, 1247, 1154, 1051, 875, 764, 707 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₂H₁₈NO₃F: 364.1343; found: 364.1346.

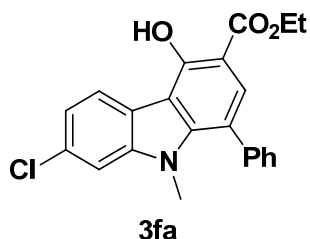
Ethyl 6-bromo-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3ea)



82% yield, white solid, mp : 175 - 177 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 11.69 (s, 1H), 8.43 (s, 1H), 7.65 (s, 1H), 7.30 (d, $J = 81.4$ Hz, 6H), 7.03 (d, $J = 8.5$ Hz, 1H), 4.36 (dd, $J_1 = 13.7$ Hz, $J_2 = 6.8$ Hz, 2H), 3.23 (s, 3H), 1.38 (t, $J = 6.9$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 170.6, 158.5, 142.7, 139.7, 139.1, 130.2, 129.7, 128.1, 127.7, 127.4, 125.3, 123.8, 118.0, 113.3, 110.6, 109.9, 102.9, 61.1, 33.0, 14.6; IR (in KBr): 3118, 3098, 2928, 1771, 1663, 1628, 1595, 1507, 1427, 1427, 1328, 1291, 1254, 1192, 1121, 1050, 875,

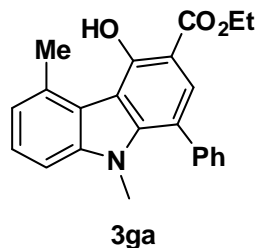
773, 711 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_3\text{Br}$: 424.0543; found: 424.0537.

Ethyl 7-chloro-4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate (3fa)



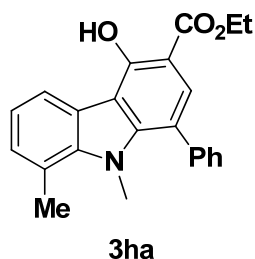
87% yield, white solid, mp. 175 - 177 °C; ^1H NMR (CDCl_3 , 600 MHz), δ (ppm) 11.80 (s, 1H), 8.35 (d, $J = 8.3$ Hz, 1H), 7.73 (s, 1H), 7.46 (dd, $J_1 = 12.6$ Hz, $J_2 = 6.7$ Hz, 5H), 7.34 - 7.26 (m, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 3.32 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.5, 158.2, 142.7, 141.6, 139.1, 130.8, 130.0, 129.3, 127.9, 127.3, 123.6, 120.7, 117.9, 110.9, 108.6, 103.0, 61.0, 32.8, 14.5; IR (in KBr): 2983, 1663, 1602, 1466, 1421, 1375, 1248, 1190, 1147, 1057, 911, 769, 711 cm^{-1} ; HRMS (EI): m/z $[M+H]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_3\text{Cl}$: 380.1048; found: 380.1058.

Ethyl 4-hydroxy-5,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ga)



88% yield, white solid, mp. 135 - 137 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 12.30 (s, 1H), 7.73 (d, $J = 0.6$ Hz, 1H), 7.53 - 7.34 (m, 5H), 7.28 (m, 1H), 7.20 (s, 1H), 7.11 (d, $J = 8.1$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 3.26 (s, 3H), 3.11 (s, 3H), 1.38 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 171.6, 158.5, 143.4, 142.2, 140.3, 134.2, 130.2, 129.7, 128.19, 127.3, 125.6, 123.7, 121.8, 117.7, 112.2, 106.5, 102.4, 61.0, 33.3, 24.6, 14.4; IR (in KBr): 3523, 3438, 3120, 2985, 1773, 1735, 1645, 1597, 1495, 1442, 1404, 1323, 1250, 1184, 1081, 1037, 893, 800, 780 cm^{-1} ; HRMS (ESI): m/z $[M-H]^-$ calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$: 358.1446; found: 358.1449.

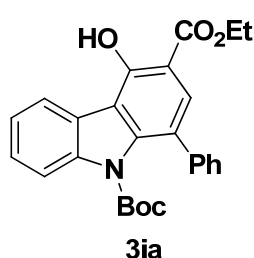
Ethyl 4-hydroxy-8,9-dimethyl-1-phenyl-9H-carbazole-3-carboxylate (3ha)



84% yield, white solid, mp. 200 - 201 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.81 (s, 1H), 8.35 (d, $J = 7.4$ Hz, 1H), 7.74

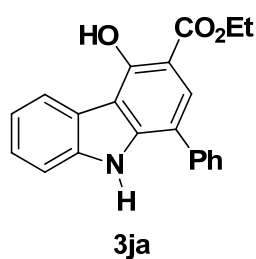
(s, 1H), 7.53 – 7.44 (m, 3H), 7.40 (t, $J = 6.7$ Hz, 1H), 7.33 – 7.06 (m, 3H), 4.42 (dd, $J_1 = 14.1$ Hz, $J_2 = 7.1$ Hz, 2H), 3.56 (s, 3H), 2.75 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.7, 158.4, 144.5, 140.8, 139.9, 129.5, 129.3, 128.5, 128.1, 126.9, 123.5, 121.0, 120.8, 120.5, 118.0, 112.0, 103.0, 60.9, 36.8, 20.5, 14.5; IR (in KBr): 3523, 3440, 3120, 2983, 1773, 1735, 1627, 1595, 1469, 1398, 1328, 1251, 1145, 1032, 880, 800, 713 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$: 360.1594; found: 360.1596.

9-tert-butyl 3-ethyl 4-hydroxy-1-phenyl-9H-carbazole-3,9-dicarboxylate (3ia)



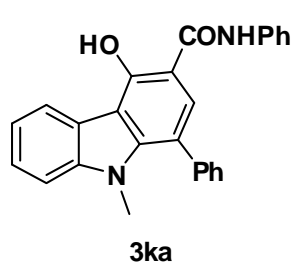
82% yield, white solid, mp. 183 - 184 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 11.71 (s, 1H), 8.44 (d, $J = 7.7$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.88 (s, 1H), 7.57 (d, $J = 7.6$ Hz, 2H), 7.45 (qd, $J_1 = 15.2$ Hz, $J_2 = 7.5$ Hz, 4H), 7.33 (t, $J = 7.4$ Hz, 1H), 4.46 (q, $J = 6.9$ Hz, 2H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.4, 157.7, 149.8, 141.2, 141.0, 139.3, 130.2, 128.9, 127.1, 126.7, 126.5, 124.5, 123.4, 123.1, 122.0, 115.7, 113.6, 107.3, 84.5, 61.5, 27.7, 14.6; IR (in KBr): 3441, 3043, 2983, 1731, 1672, 1626, 1444, 1369, 1326, 1220, 1187, 1111, 785, 749, 700 cm^{-1} ; HRMS (ESI): m/z $[\text{M}-\text{H}]^-$ calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_5$: 430.1668; found: 430.1660.

Ethyl 4-hydroxy-1-phenyl-9H-carbazole-3-carboxylate (3ja)



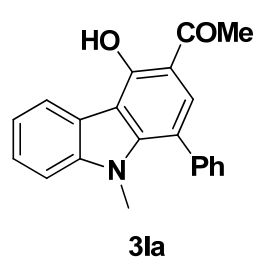
76% yield, white solid, mp. 136 - 137 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 11.85 (s, 1H), 8.44 (s, 1H), 8.38 (d, $J = 7.7$ Hz, 1H), 7.84 (s, 1H), 7.59 (d, $J = 7.3$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.43 – 7.20 (m, 4H), 4.42 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.9, 159.0, 142.0, 138.3, 137.9, 129.2, 128.2, 127.4, 126.8, 125.4, 123.1, 120.8, 117.2, 111.5, 110.4, 103.9, 61.1, 14.6; IR (in KBr): 3420, 3397, 1646, 1506, 1450, 1375, 1344, 1249, 1180, 1130, 797, 765, 645 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_3$: 332.1281; found: 332.1277.

4-hydroxy-9-methyl-N,1-diphenyl-9H-carbazole-3-carboxamide (3ka)



61% yield, white solid, mp. 230 - 231 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 13.19 (s, 1 H), 8.53 (d, $J = 7.8$ Hz, 1 H), 7.84 (s, 1 H), 7.58 (d, $J = 7.9$ Hz, 2 H), 7.51 (d, $J = 3.6$ Hz, 3 H), 7.49 – 7.45 (m, 2 H), 7.38 (t, $J = 7.8$ Hz, 2 H), 7.33 (dd, $J_1 = 14.4$ Hz, $J_2 = 6.4$ Hz, 3 H), 7.17 (t, $J = 7.4$ Hz, 1 H), 3.37 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 169.0, 159.1, 141.8, 141.1, 139.4, 136.9, 130.2, 128.9, 128.1, 127.5, 125.2, 125.0, 124.7, 123.2, 122.3, 121.0, 120.4, 117.6, 112.3, 108.5, 104.1, 32.7; IR (in KBr): 3404, 3060, 3024, 1645, 1587, 1509, 1465, 1346, 1257, 842, 738, 709 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$: 393.1598; found: 393.1604.

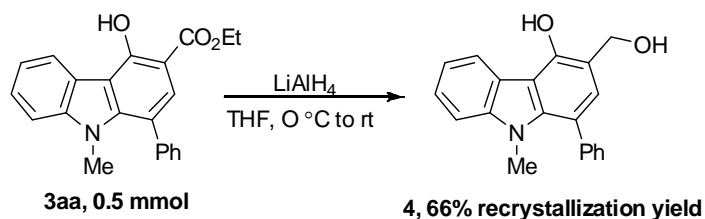
1-(4-hydroxy-9-methyl-1-phenyl-9H-carbazol-3-yl)ethanone (3la)



89% yield, light yellow solid, mp. 191 - 192 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.56 (s, 1H), 8.41 (d, $J = 7.7$ Hz, 1H), 7.42 (dd, $J_1 = 20.4$ Hz, $J_2 = 11.4$ Hz, 7H), 7.27 (dd, $J_1 = 13.6$ Hz, $J_2 = 7.7$ Hz, 2H), 3.30 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 202.9, 159.9, 143.0, 141.1, 139.3, 130.3, 130.1, 128.1, 127.4, 125.2, 123.0, 122.5, 120.7, 117.8, 111.4, 111.2, 108.7, 32.7, 26.7; IR (in KBr): 3524, 3438, 3118, 1765, 1733, 1593, 1517, 1324, 1255, 1186, 1103, 986, 838, 740 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_2$: 316.1332; found: 316.1328.

5. Synthetic Transformation

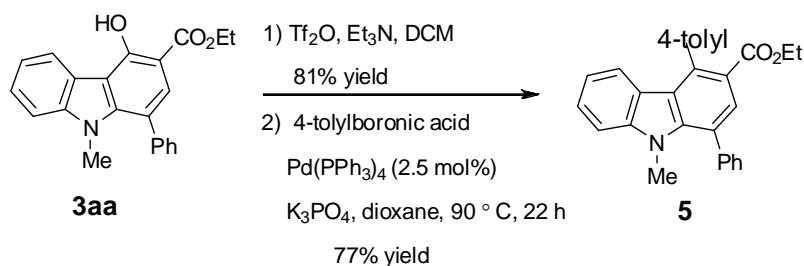
5.1 Reduction reaction of the product



A THF solution containing 0.1727 g (0.5 mmol) of ethyl 4-hydroxy-9-methyl-1-phenyl-9H-carbazole-3-carboxylate was added slowly to stirred suspension of 0.038 g (1.0 mmol) of lithium aluminum hydride in THF (2 mL) at 0 °C, and the resultant mixture was then stirred at room temperature for one hour. After completion, the reaction was quenched sequentially with water (0.04 mL), 15% sodium hydroxide (0.08 mL), water (0.04 mL), then added anhydrous magnesium sulfate. After filtering out insoluble matter, the filtrate was concentrated to dryness under reduced pressure. Recrystallized from CH_2Cl_2 /petroleum ether at -20 °C can obtain the desired product.

4, 66% yield, white solid, mp. 116 - 117 °C; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.44 (d, $J = 7.7$ Hz, 1H), 8.12 (s, 1H), 7.48 – 7.38 (m, 5H), 7.37 – 7.15 (m, 3H), 6.93 (s, 1H), 5.07 (d, $J = 5.3$ Hz, 2H), 3.35 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 152.1, 141.8, 140.1, 139.7, 130.2, 127.9, 126.9, 125.1, 123.1, 122.0, 119.5, 117.5, 113.6, 112.8, 108.2, 65.1, 32.7; IR (in KBr): 3535, 1671, 1604, 1458, 1403, 1272, 1209, 1170, 1119, 999, 876, 731 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_2$: 326.1160; found: 326.1152

5.2 Cross-coupling reaction of the product



To a solution of 3aa (0.3 mmol, 103.6 mg) and Et₃N (0.9 mmol, 0.12 mL) in CH₂Cl₂ (1 mL), Tf₂O (0.72 mmol, 203.2 mg) was added slowly to the stirred suspension at 0 °C, and the resultant mixture was then stirred at room temperature overnight. After completion, the reaction was quenched with saturated sodium bicarbonate, extracted with CH₂Cl₂, combined the organic phase and washed with brine, dried over anhydrous Na₂SO₄, the solvent was evaporated under reduced pressure, the residue was purified by flash chromatography on silica gel to give the desired product as white solid in a 81% yield. And the product was used to the cross-coupling reaction⁹.

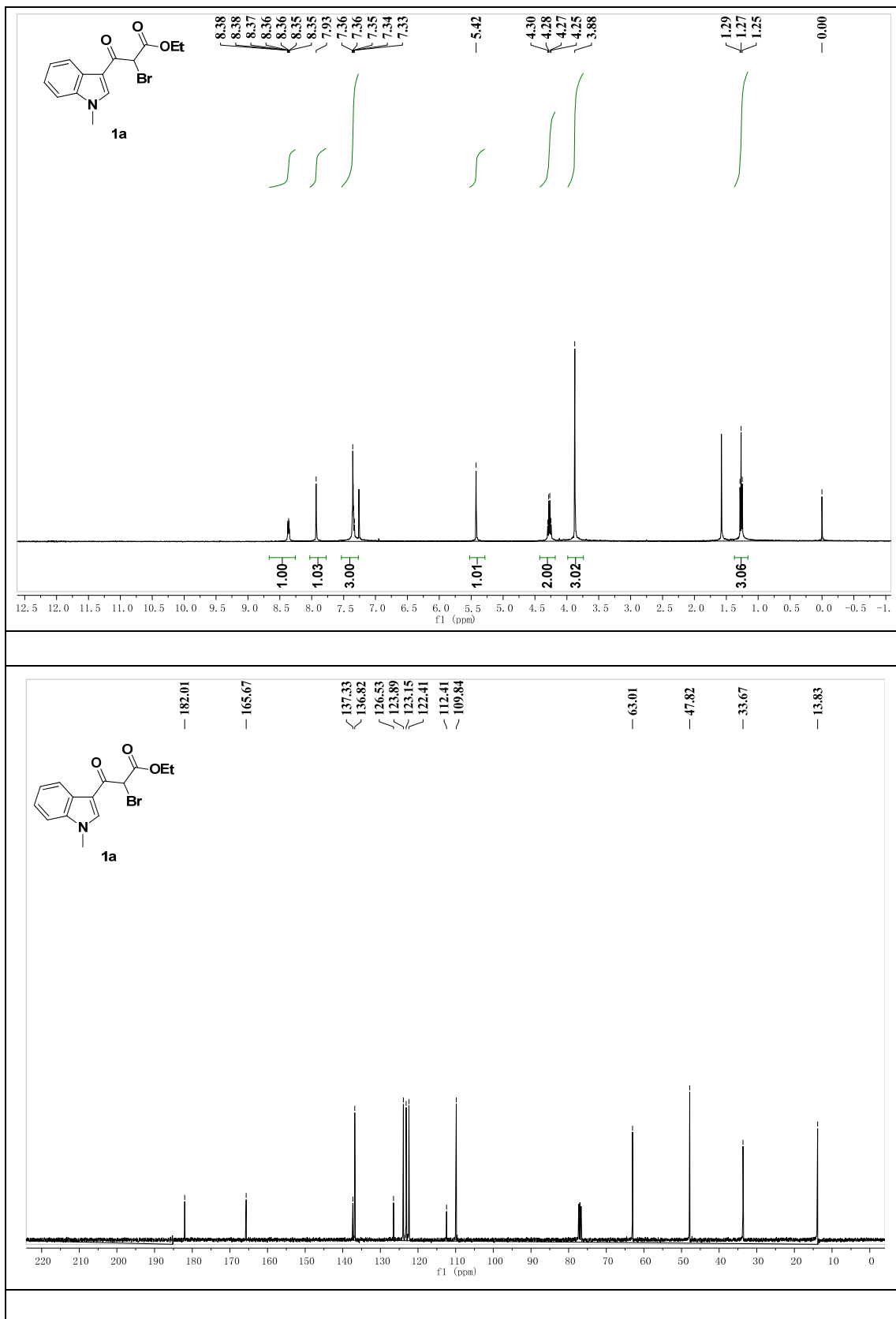
A mixture of 4-tolylboronic acid (0.11 mmol), ethyl 9-methyl-1-phenyl-4-(((trifluoromethyl)sulfonyl)oxy)-9H-carbazole-3-carboxylate (0.1 mmol), Pd(PPh₃)₄ (0.0025 mmol), and K₃PO₄ (0.15 mmol) in dioxane (1 mL) was heated to 90 °C for 22 h. The mixture was diluted with toluene (2 mL) and treated with aqueous 3 M NaOH (0.05 mL) and 30% H₂O₂ (0.05 mL) for 1 h at room temperature to oxidize the residual borane. The product was extracted with ethyl acetate, washed with brine, and dried over MgSO₄. Isolation by column chromatography over silica gel gave the desired compound in a 77% yield (average yield of two parallel reactions).

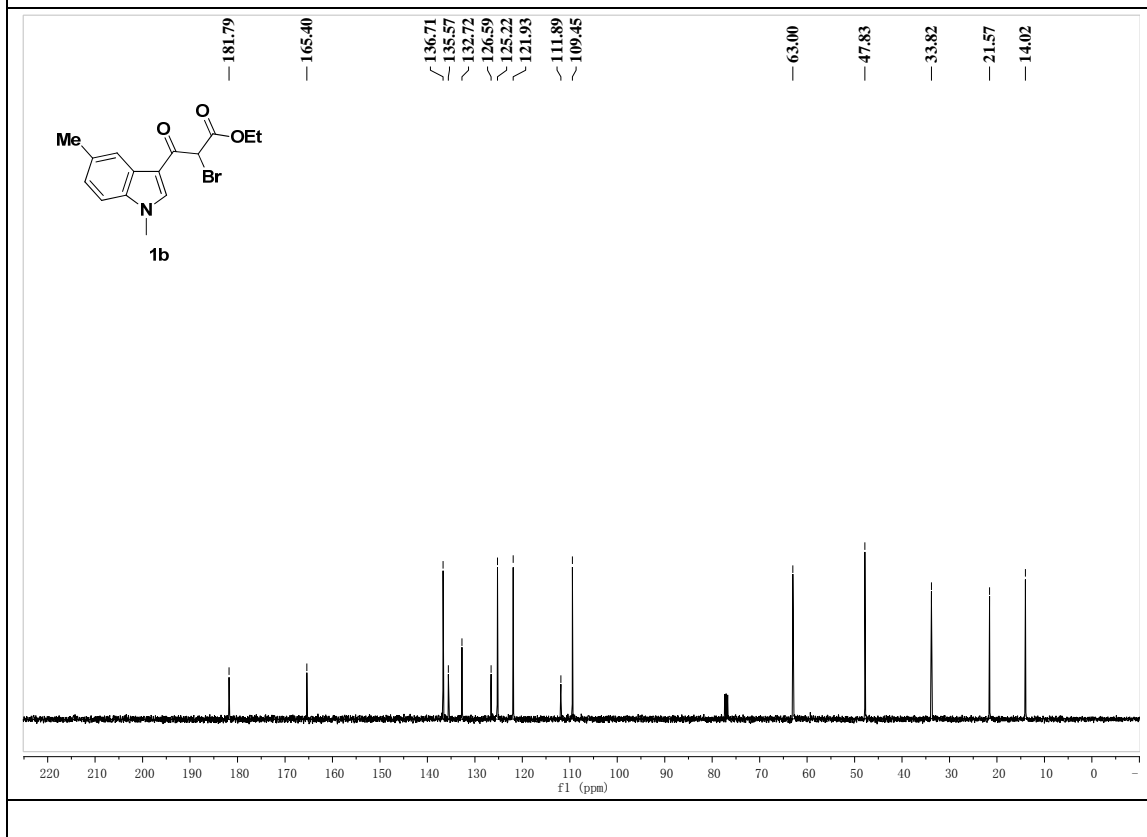
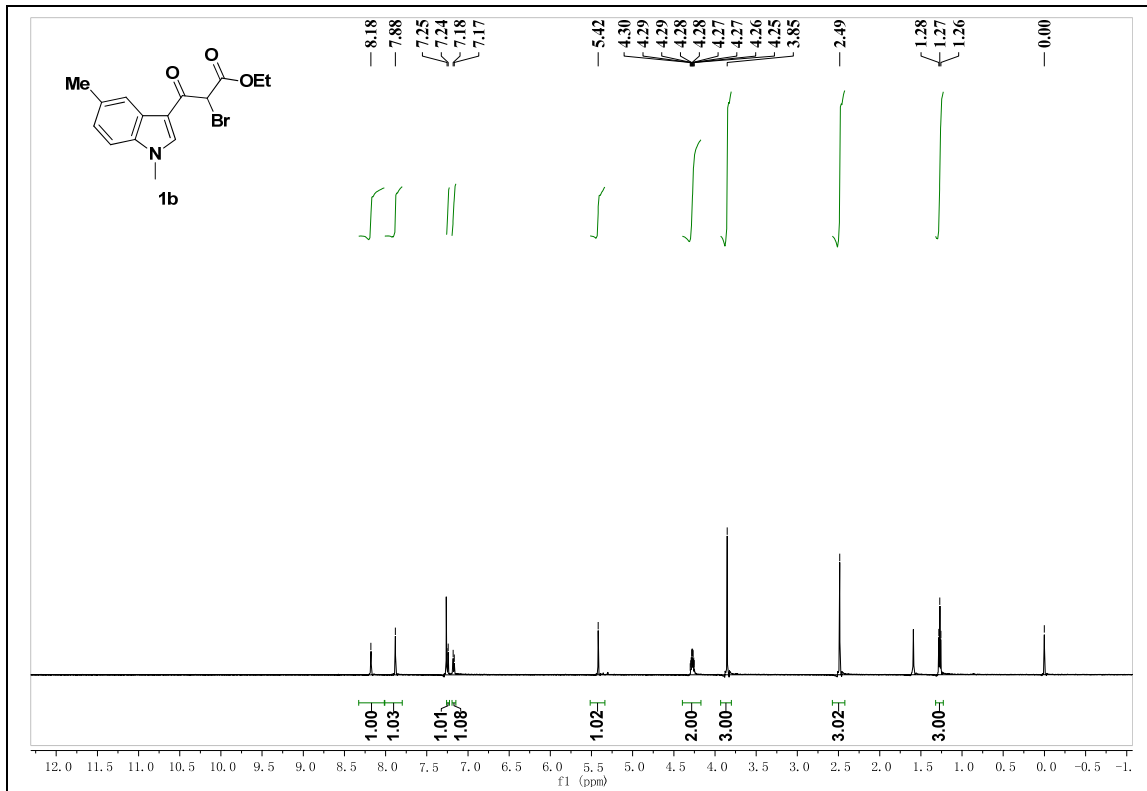
5, 77% yield, white solid, mp. 154 - 156 °C; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.98 (s, 1H), 7.77 – 7.42 (m, 6H), 7.35 (ddd, *J*₁ = 26.7 Hz, *J*₂ = 13.5 Hz, *J*₃ = 7.4 Hz, 5H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.10 (q, *J* = 6.9 Hz, 2H), 3.40 (s, 3H), 2.52 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 167.8, 142.6, 139.9, 139.7, 138.6, 137.3, 136.7, 130.4, 130.0, 129.0, 128.3, 128.1, 127.6, 125.9, 124.3, 123.1, 122.7, 120.8, 119.6, 108.7, 60.4, 32.9, 21.5, 13.9; IR (in KBr): 2985, 1703, 1555, 1447, 1398, 1339, 1240, 1185, 1013, 860, 821, 738 cm⁻¹; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₉H₂₅NO₂: 420.1958; found: 420.1957.

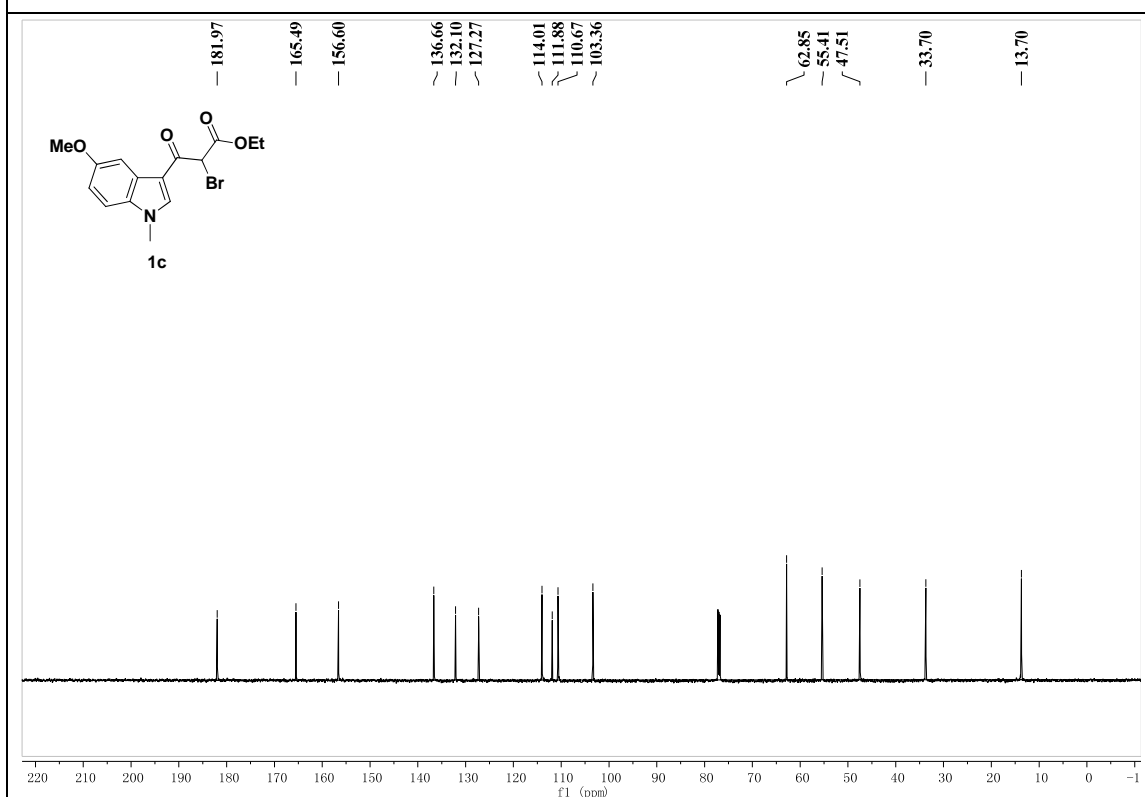
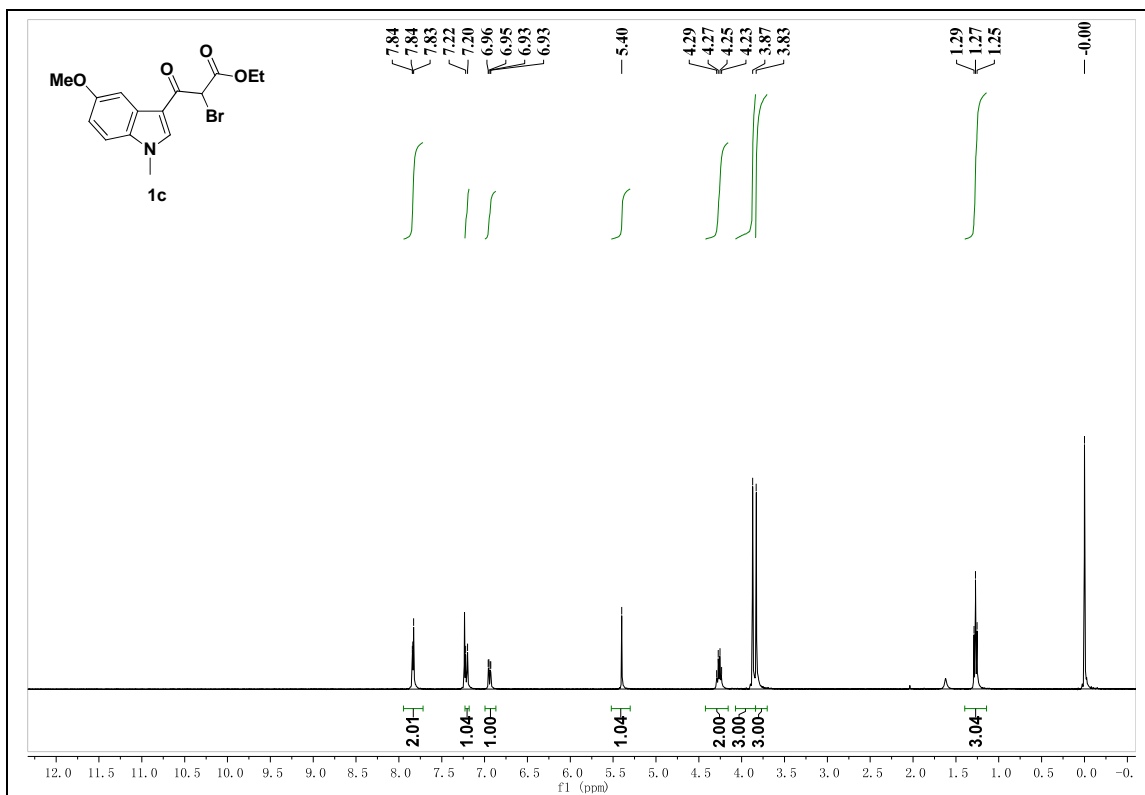
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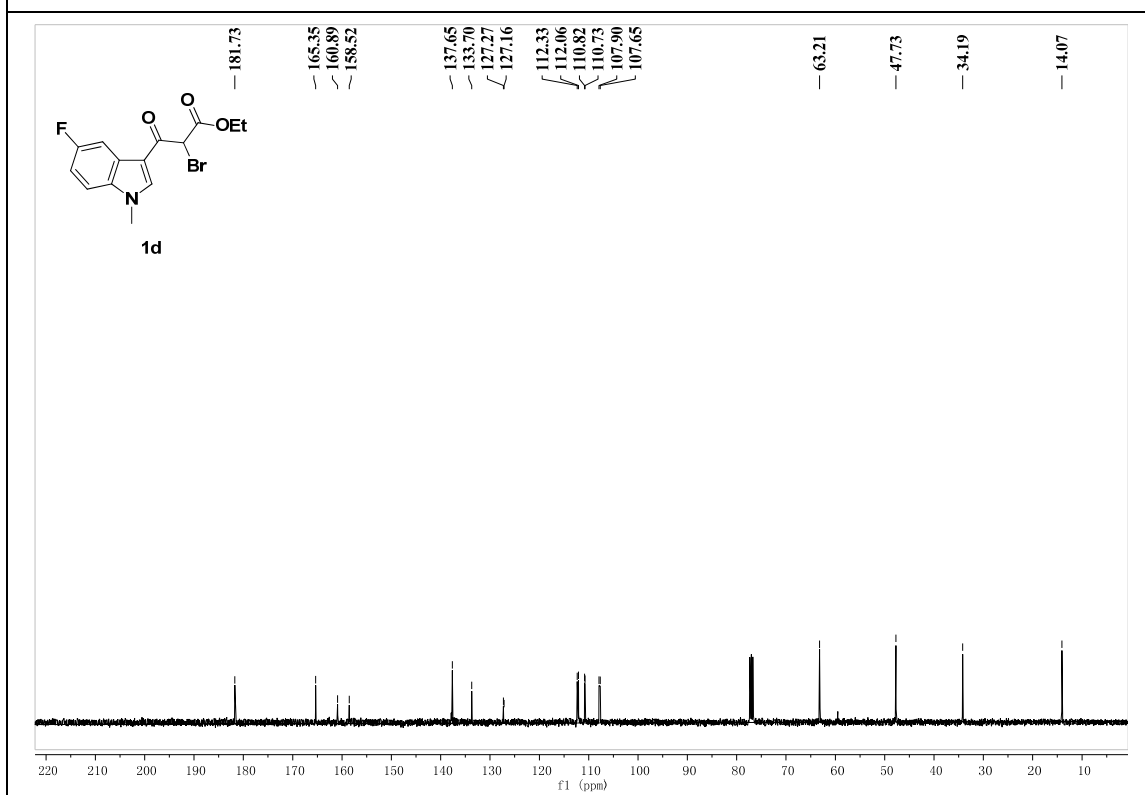
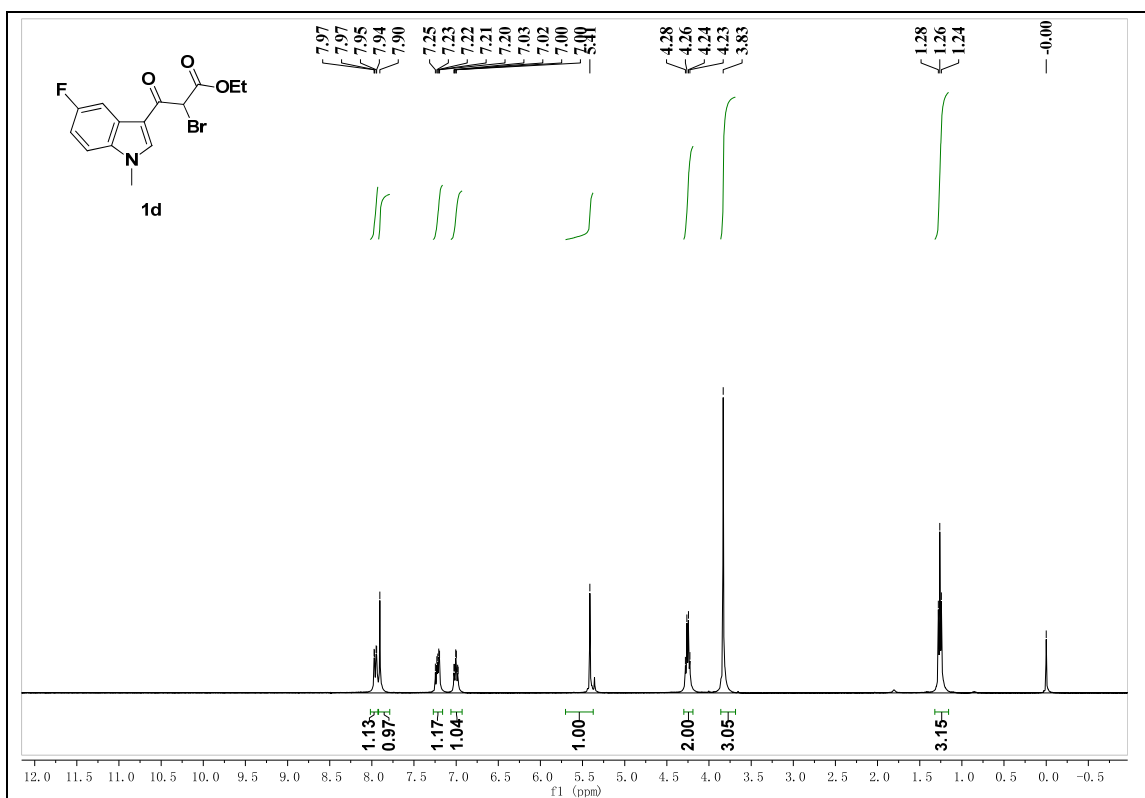
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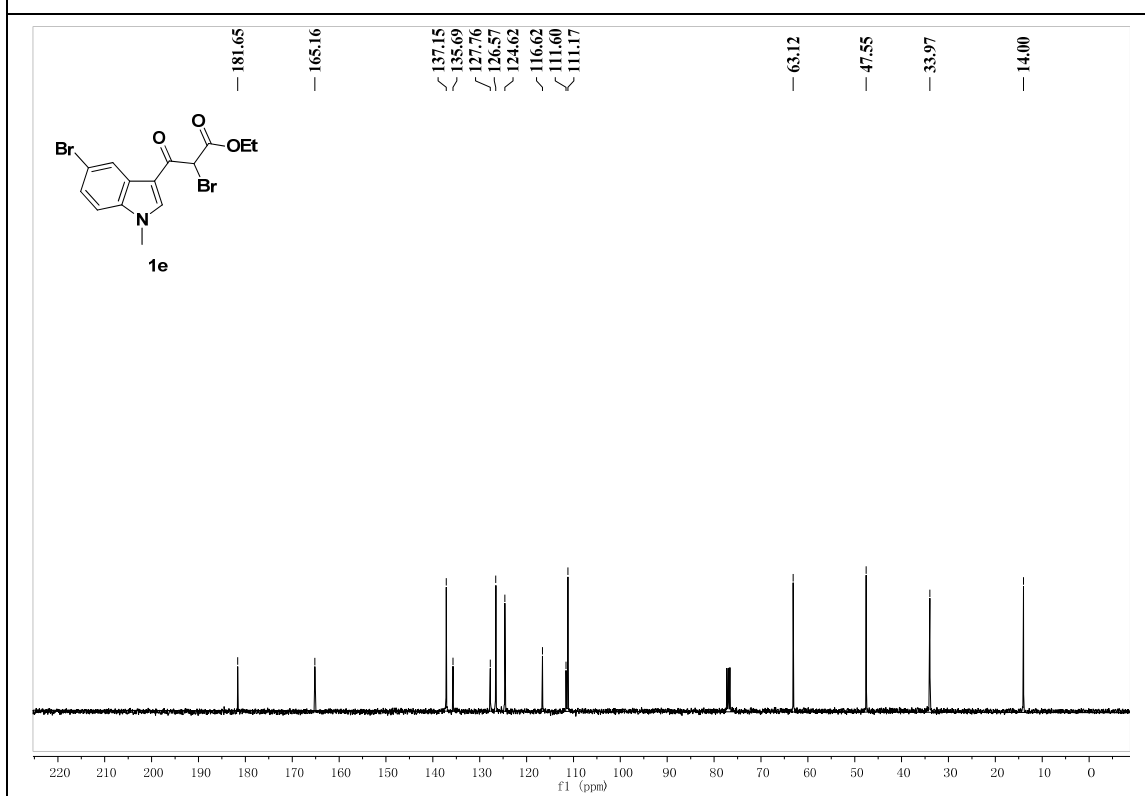
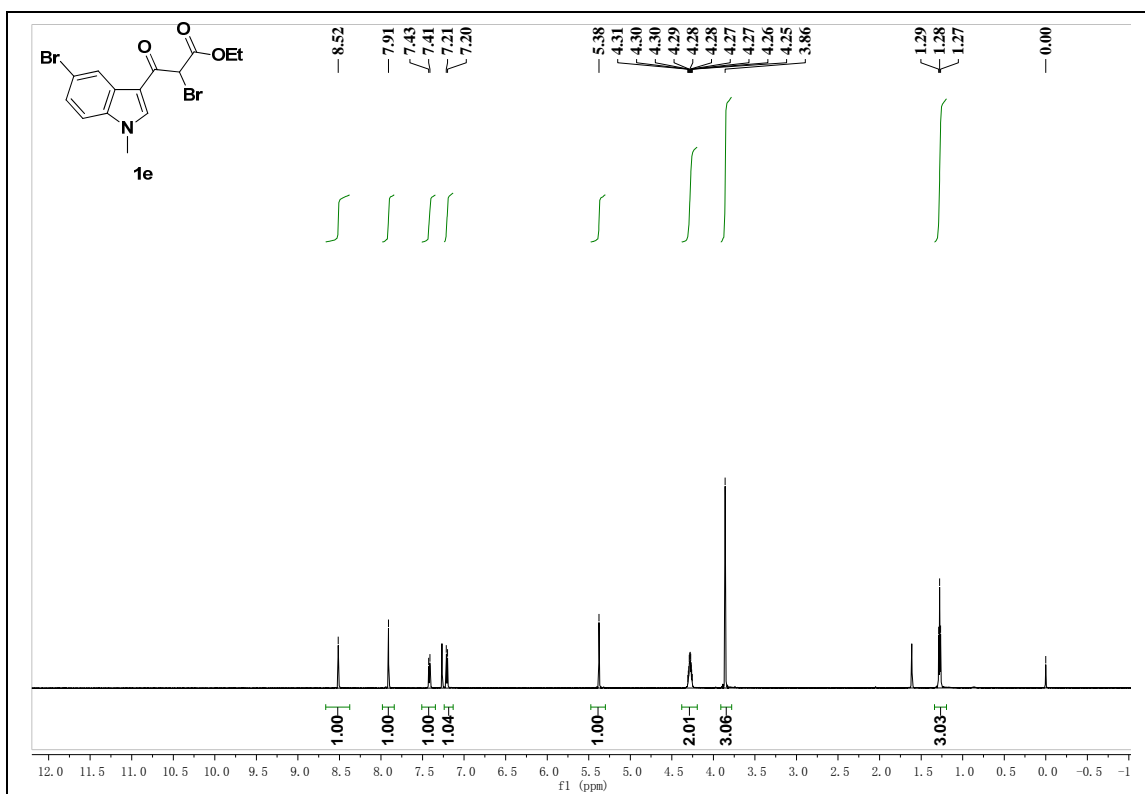
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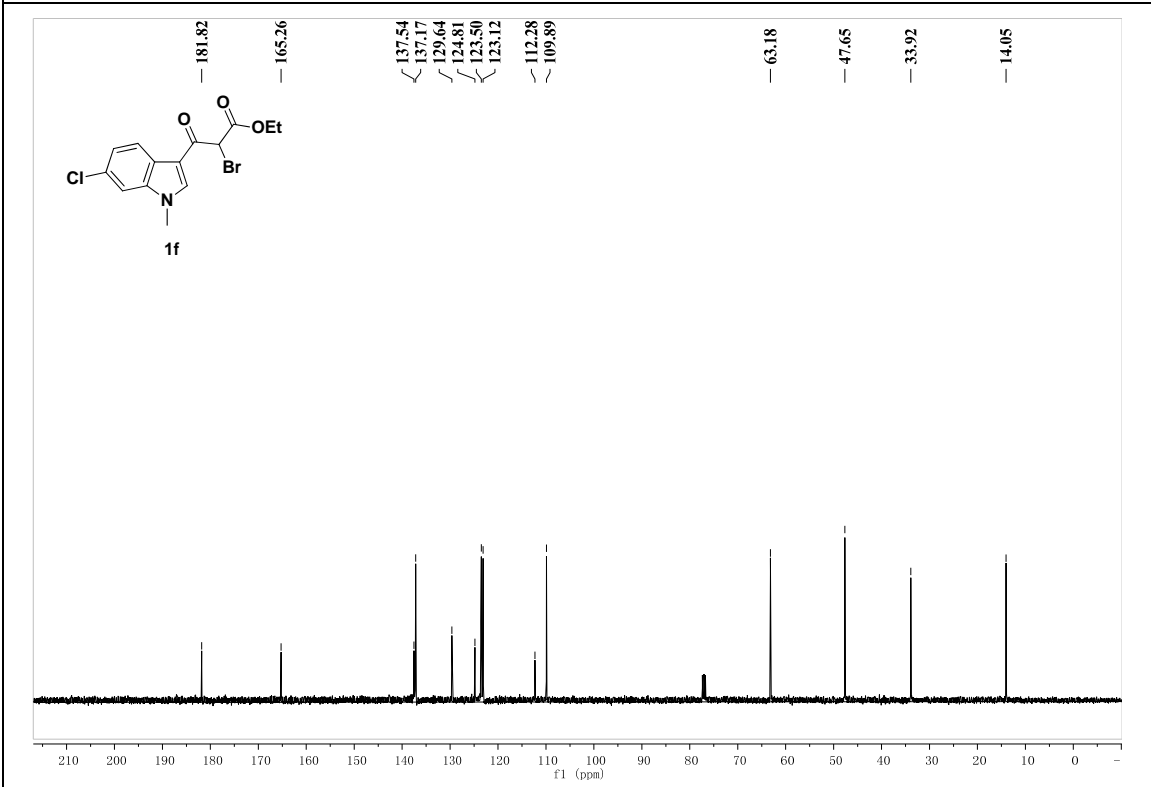
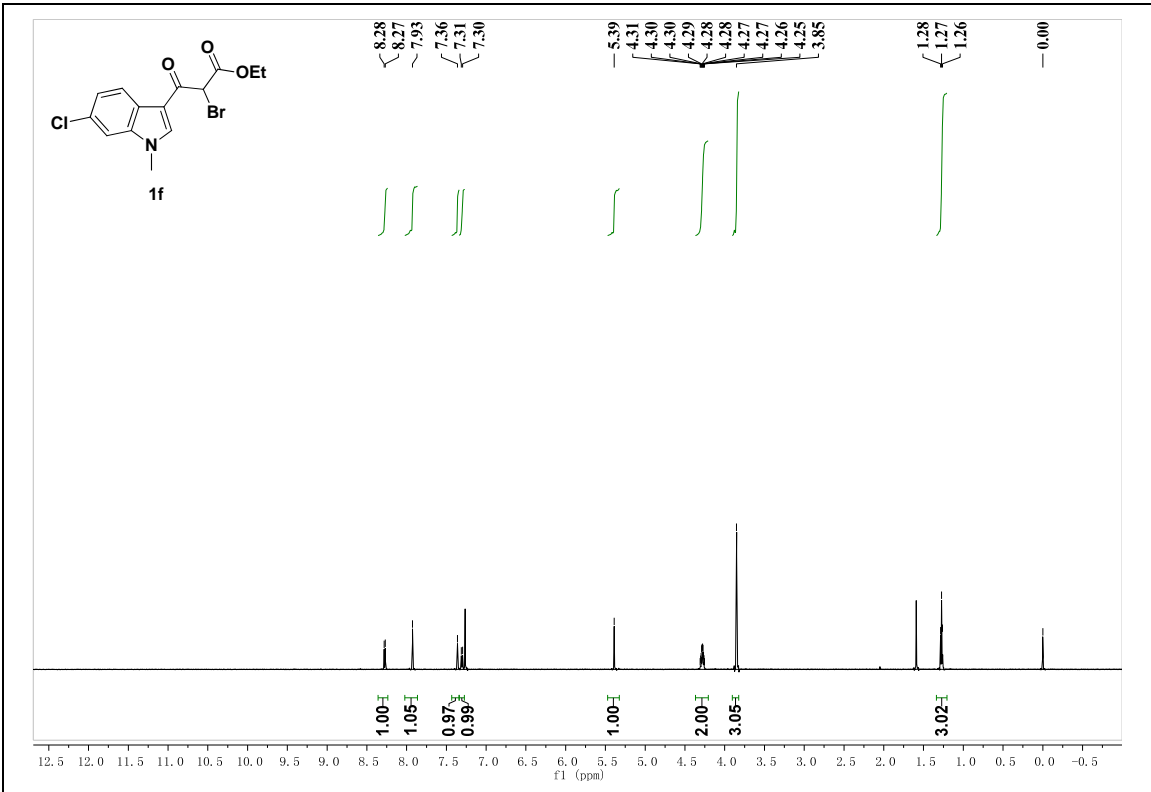


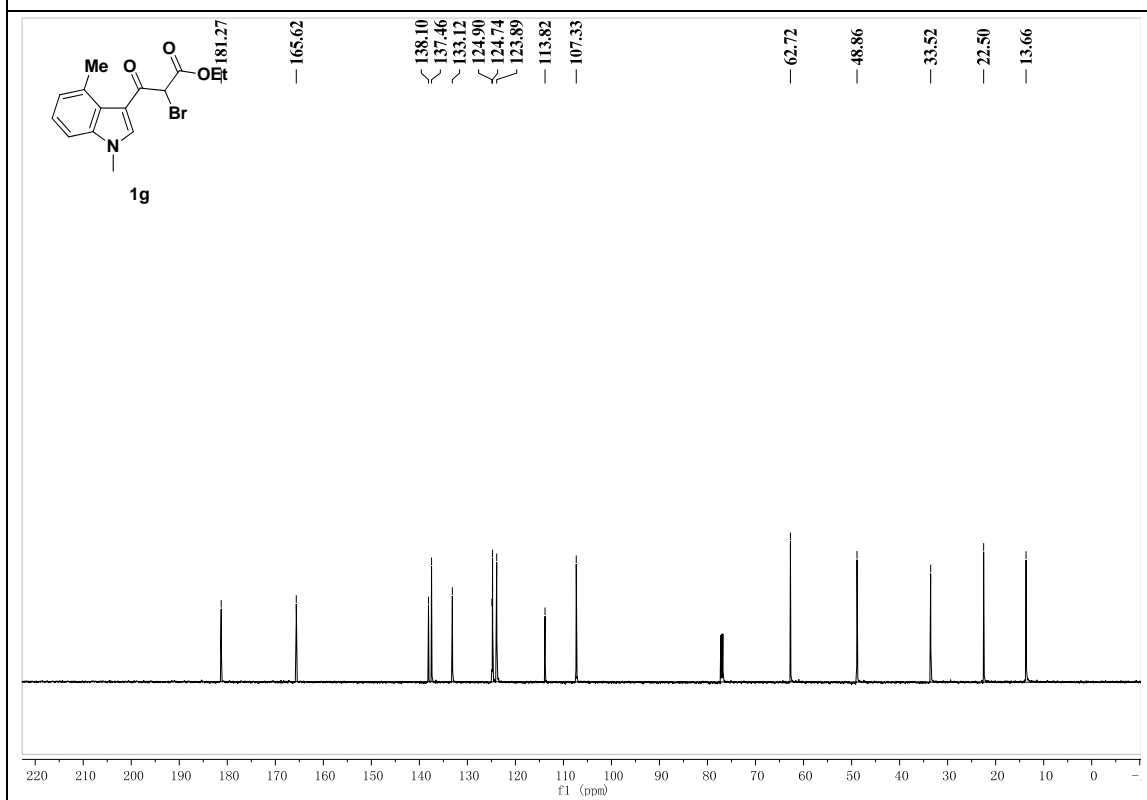
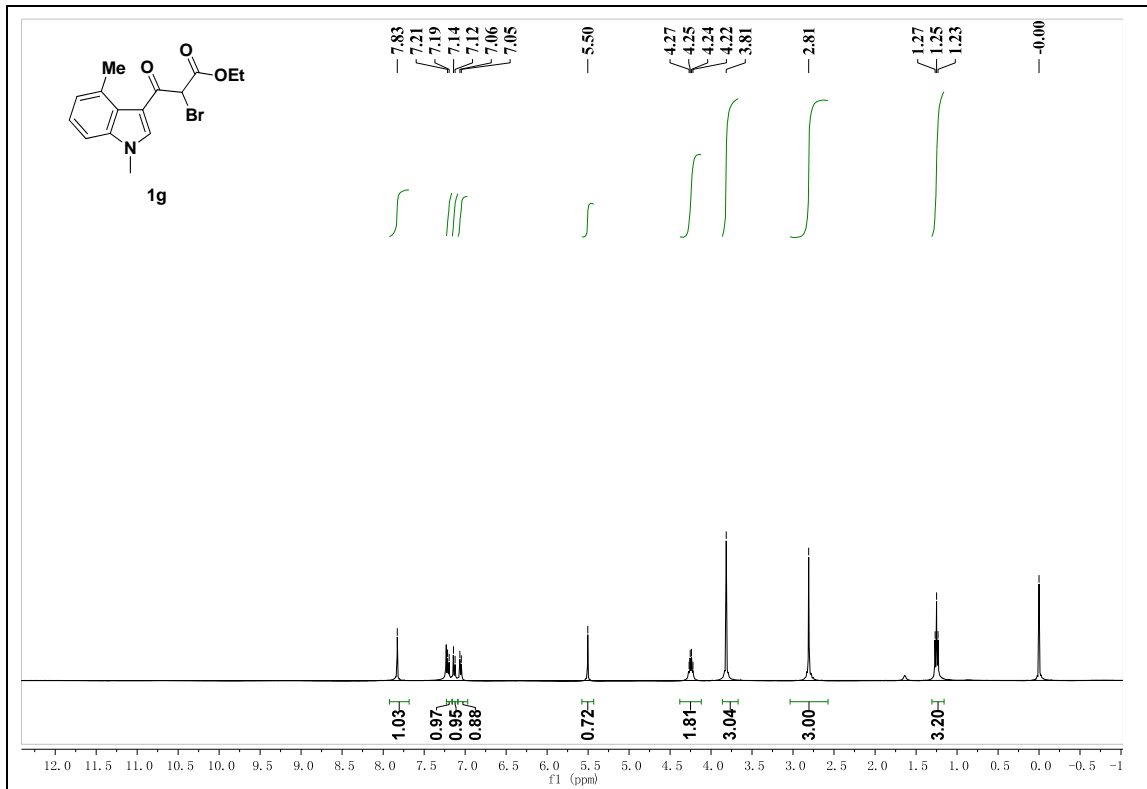


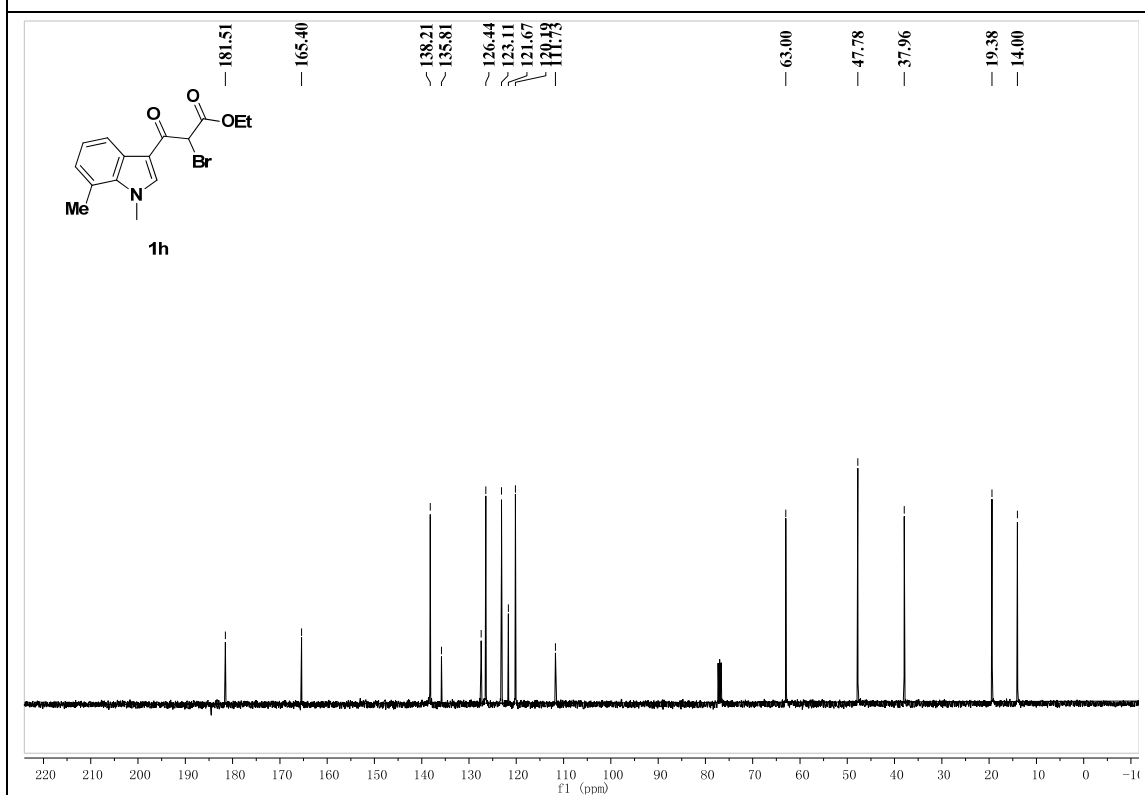
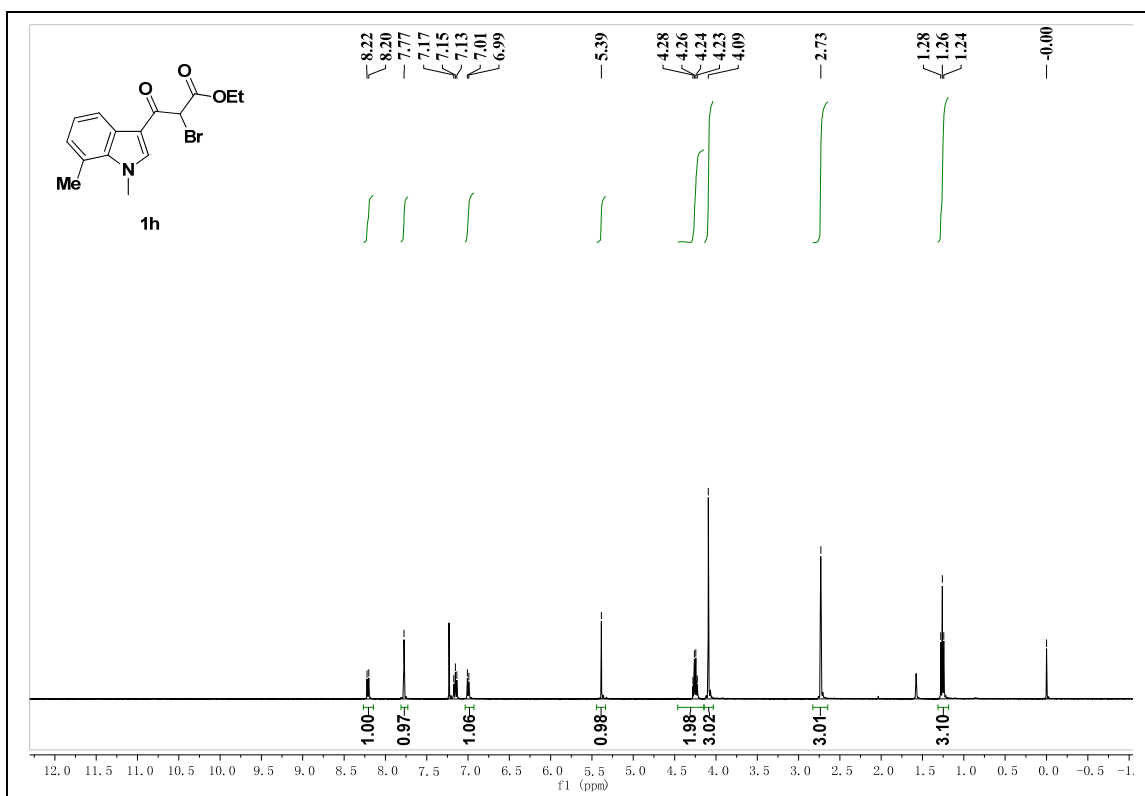


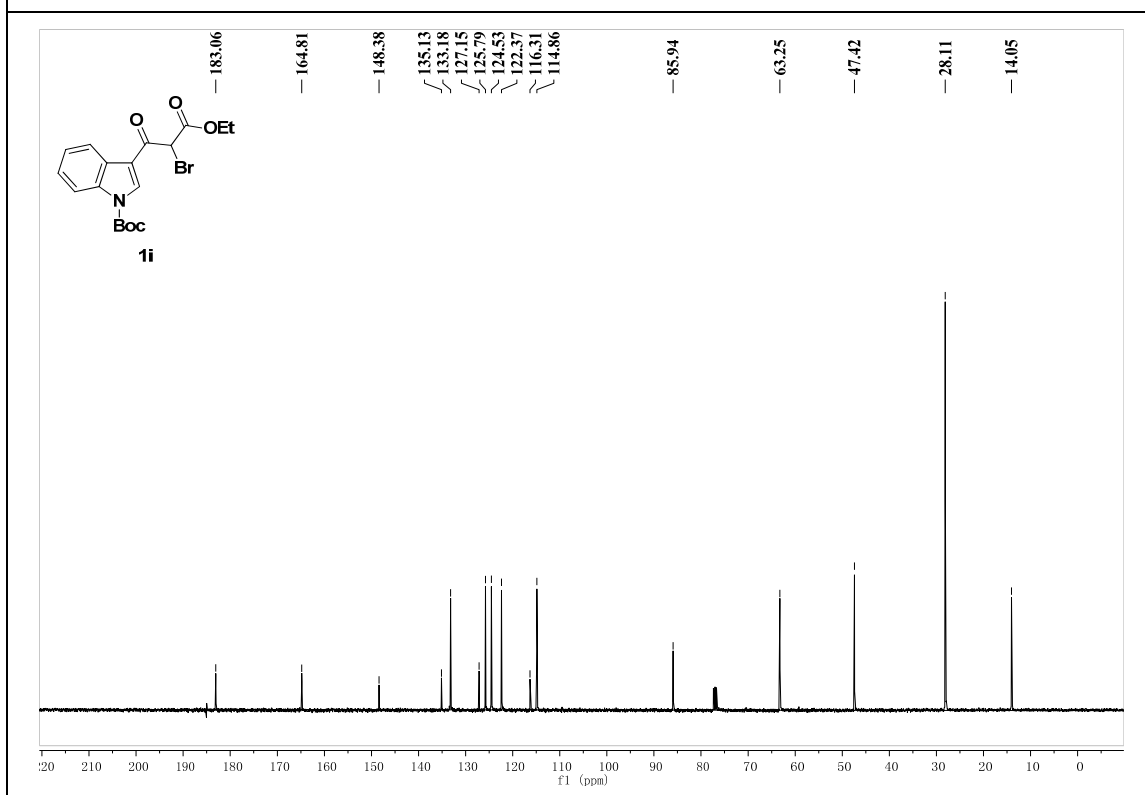
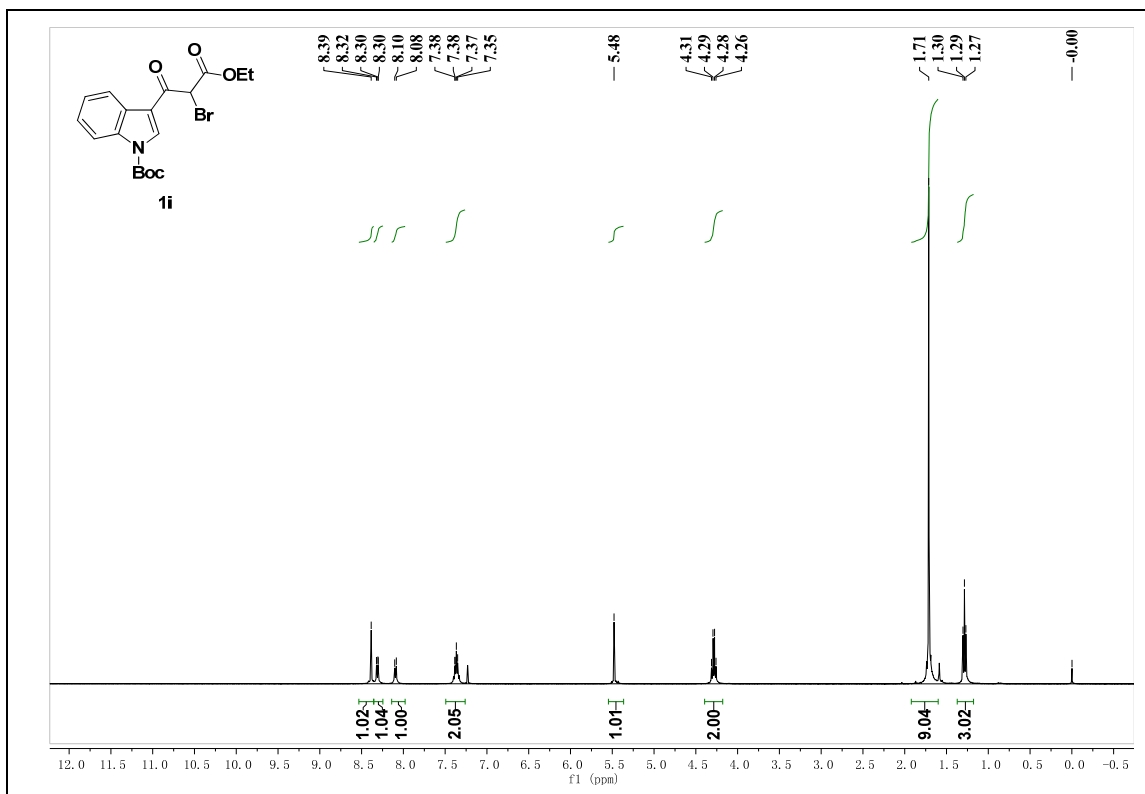


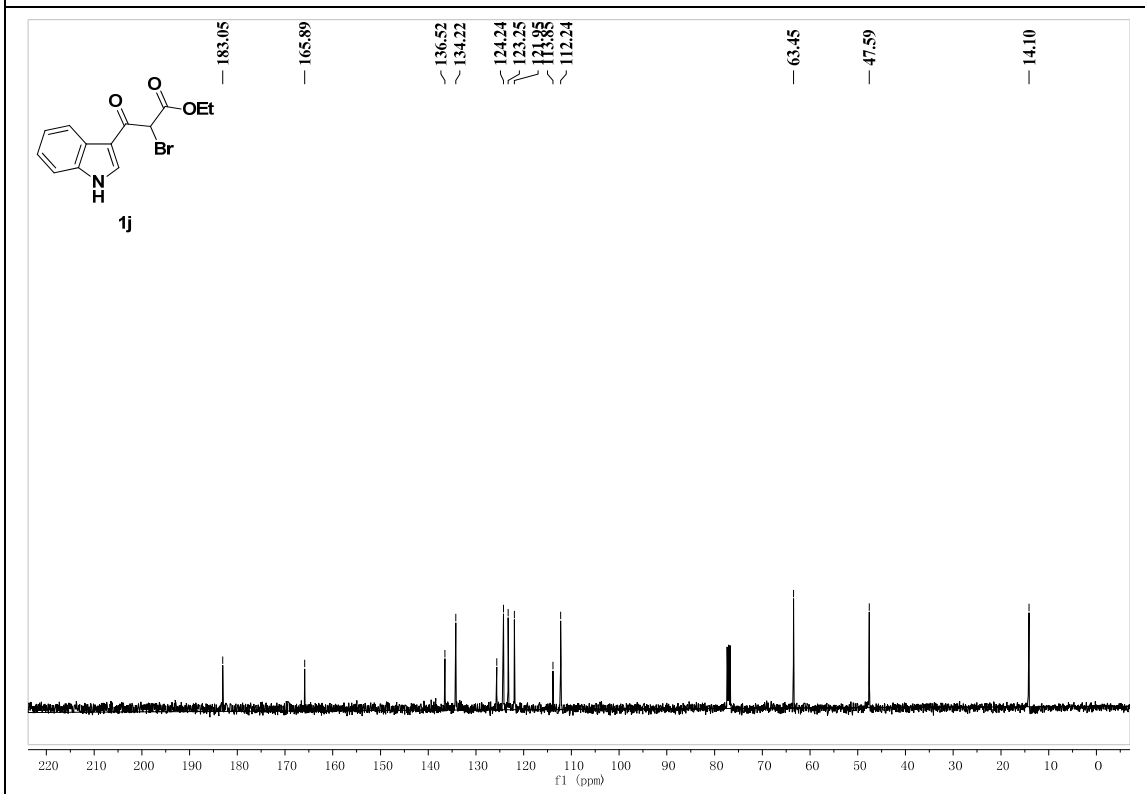
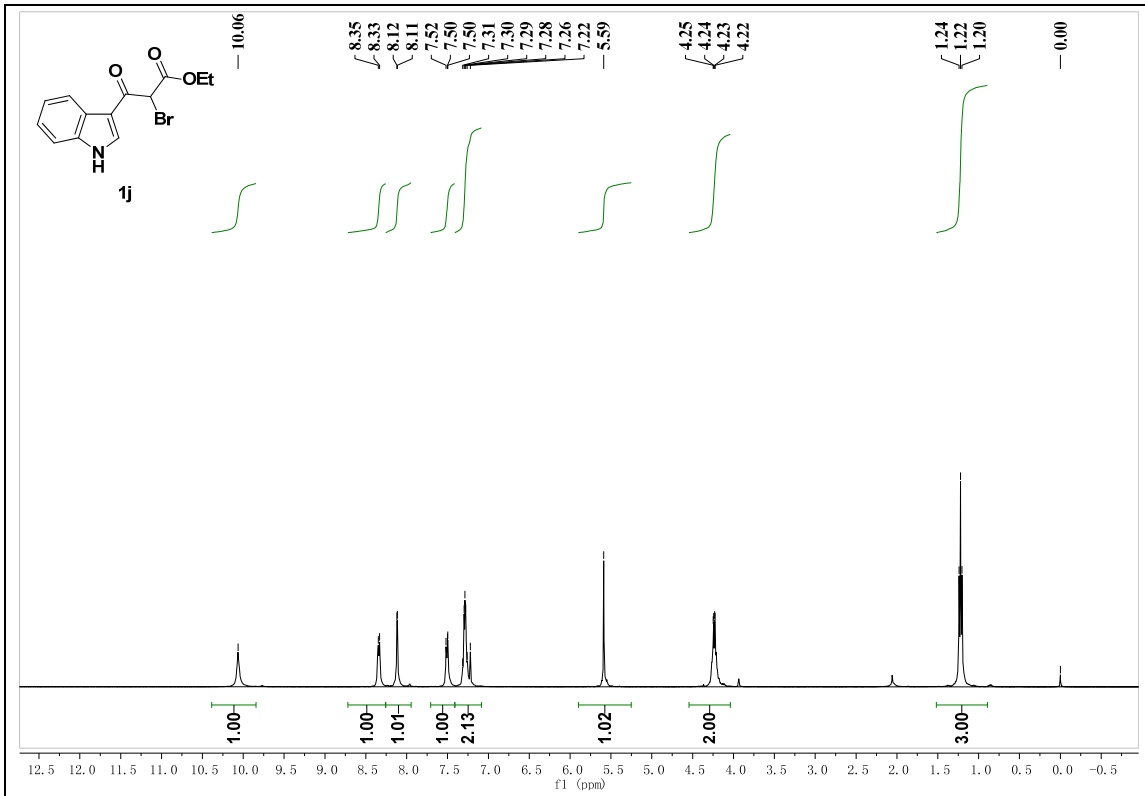


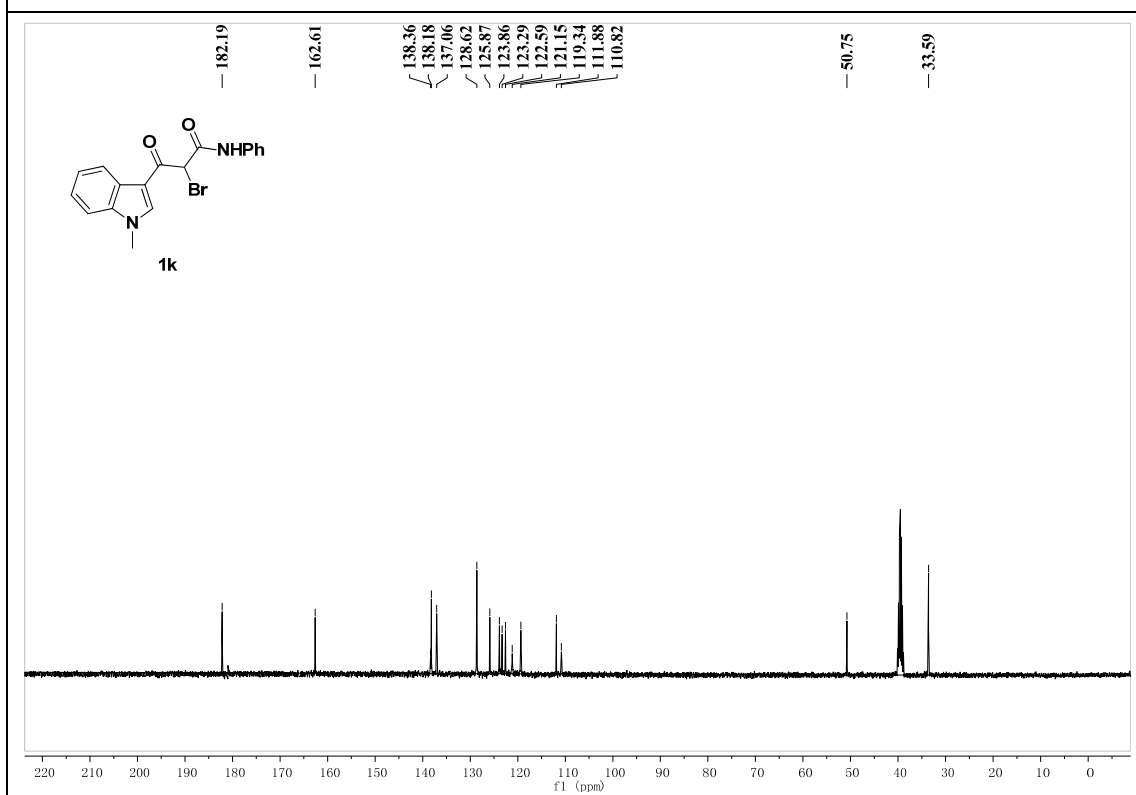
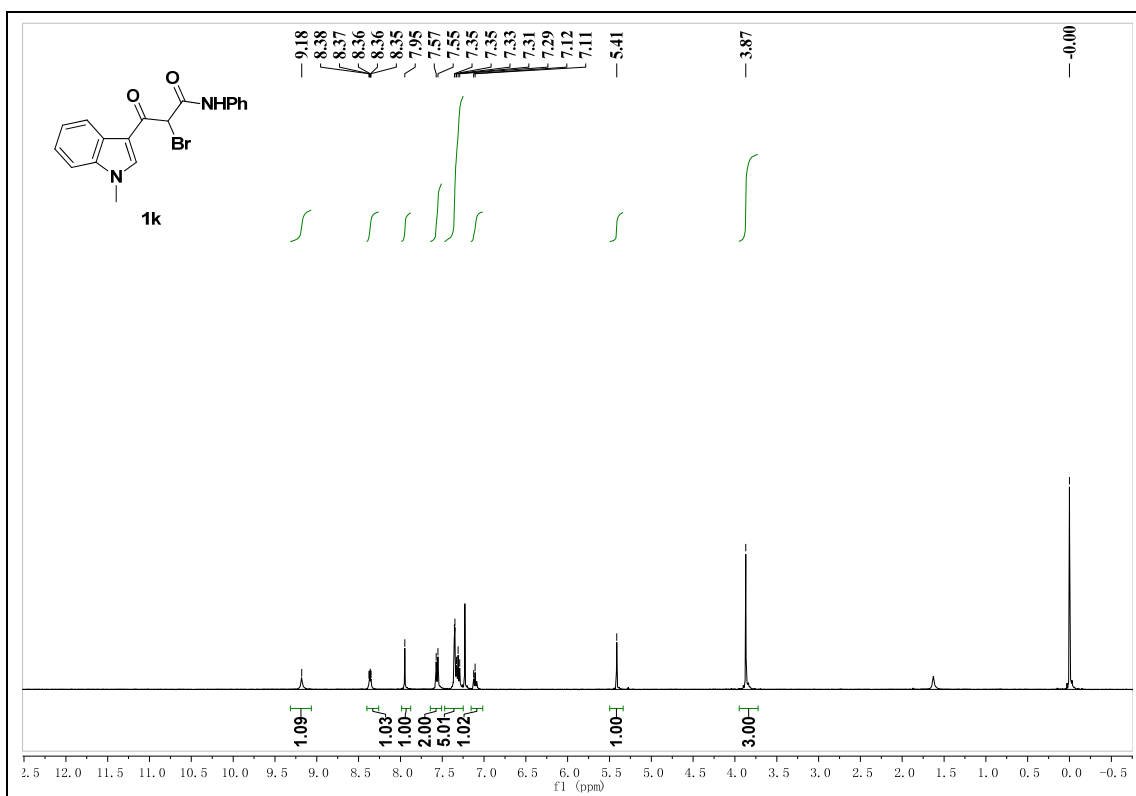


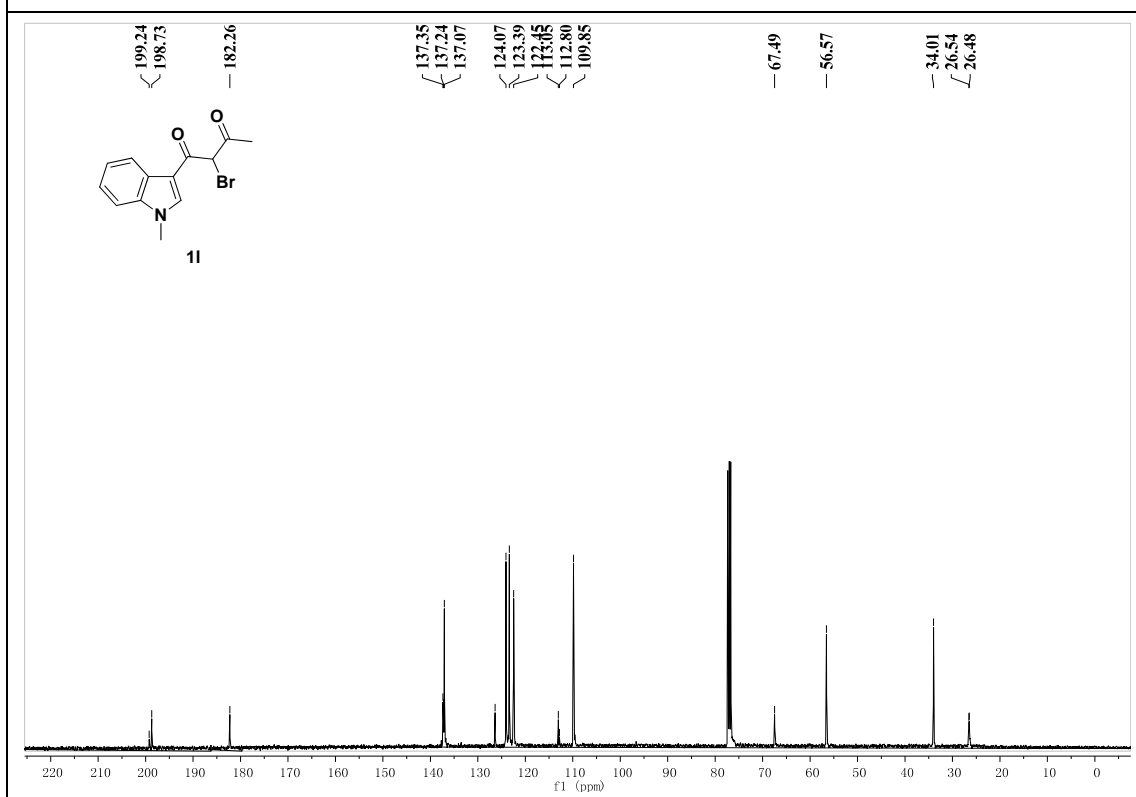
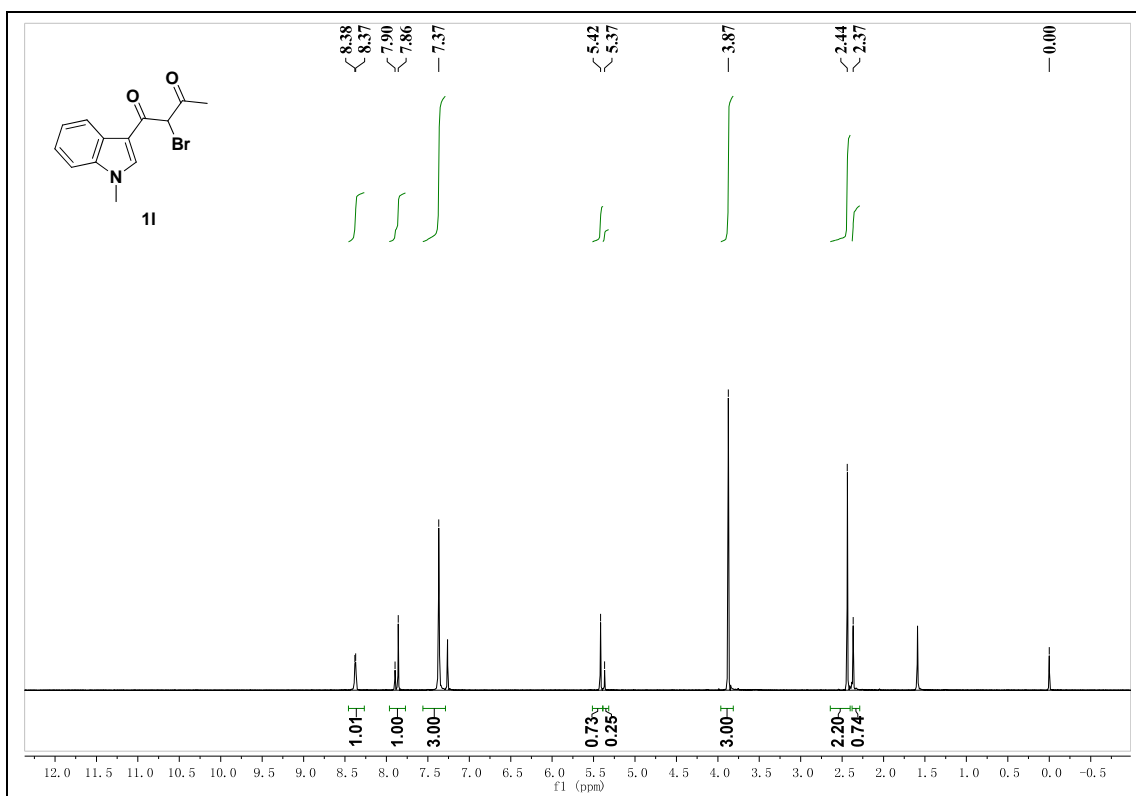


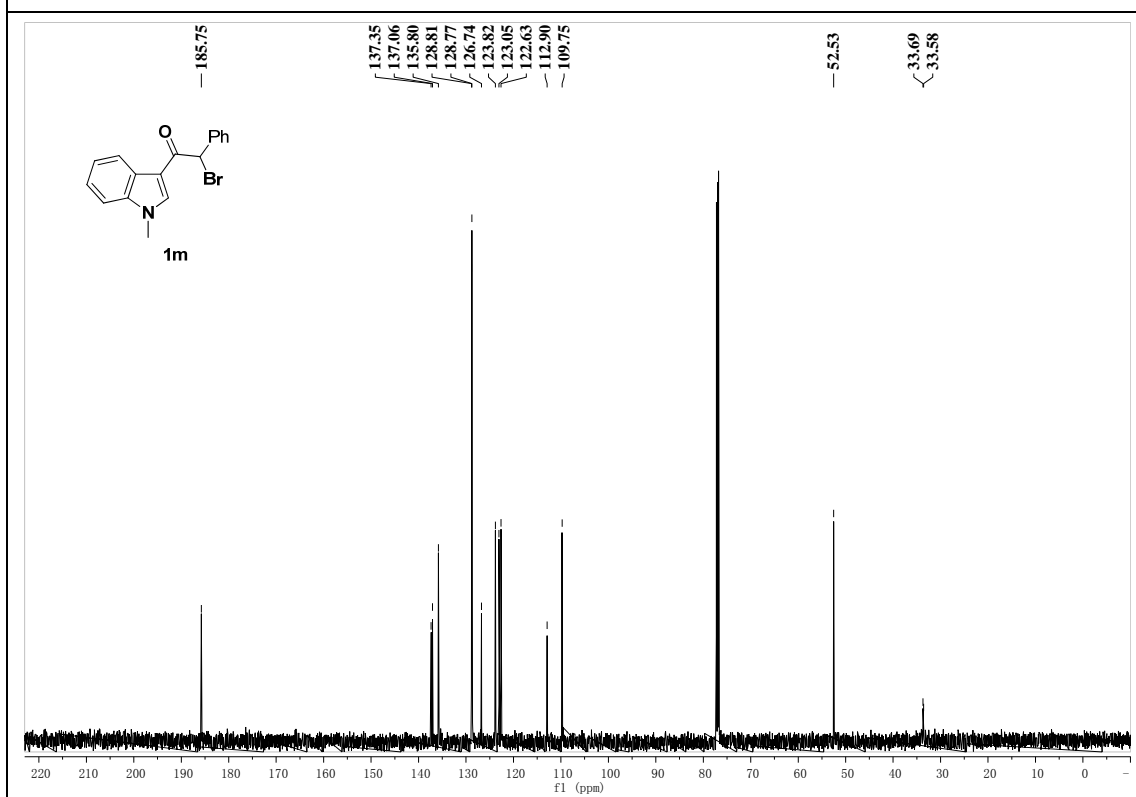
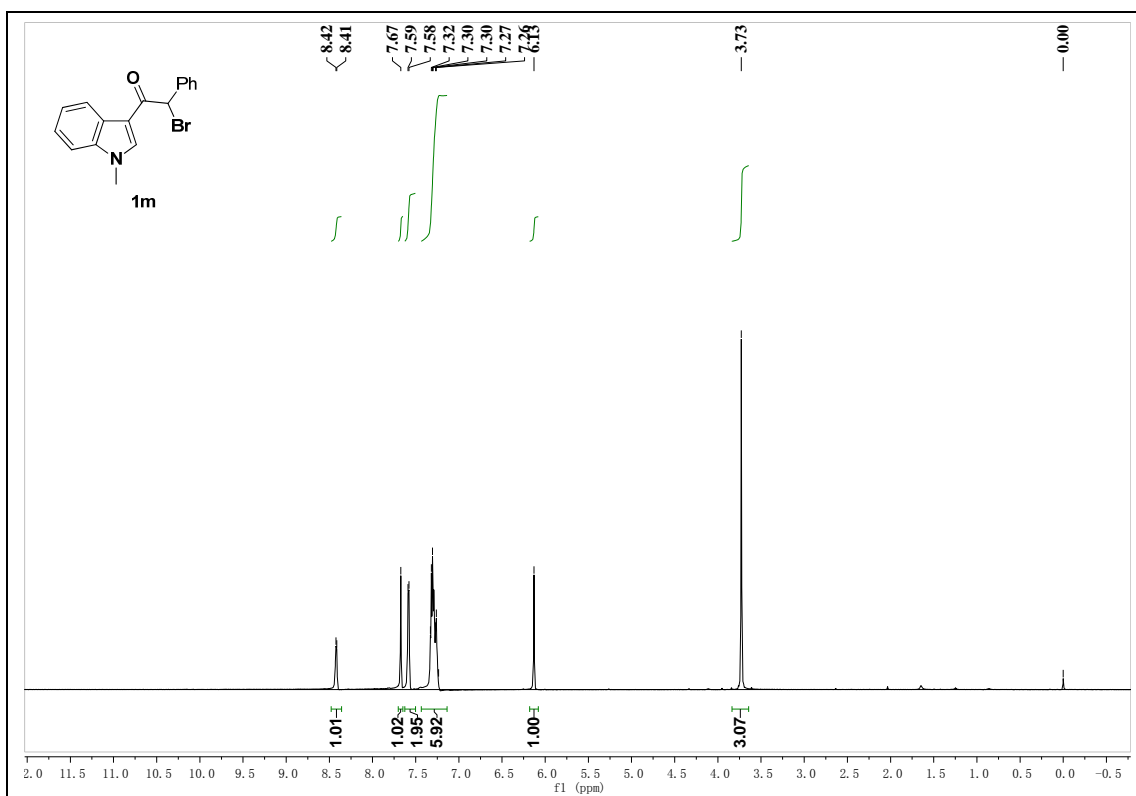


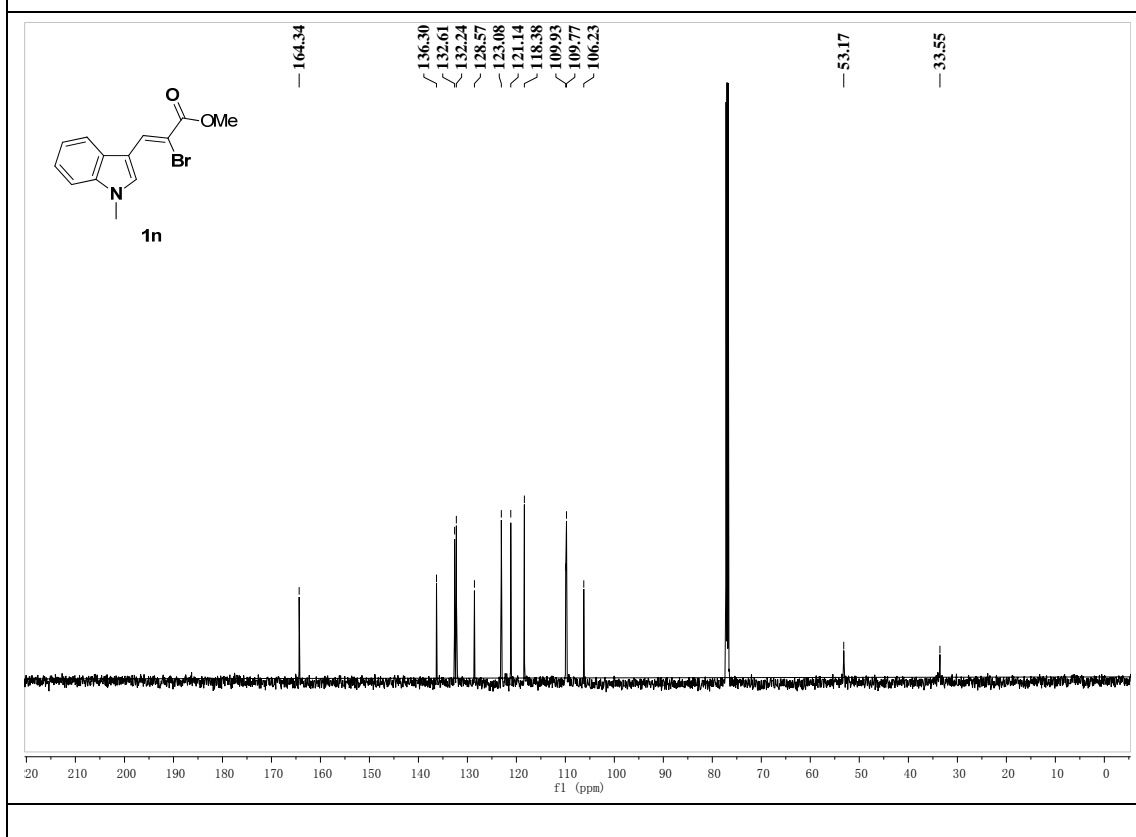
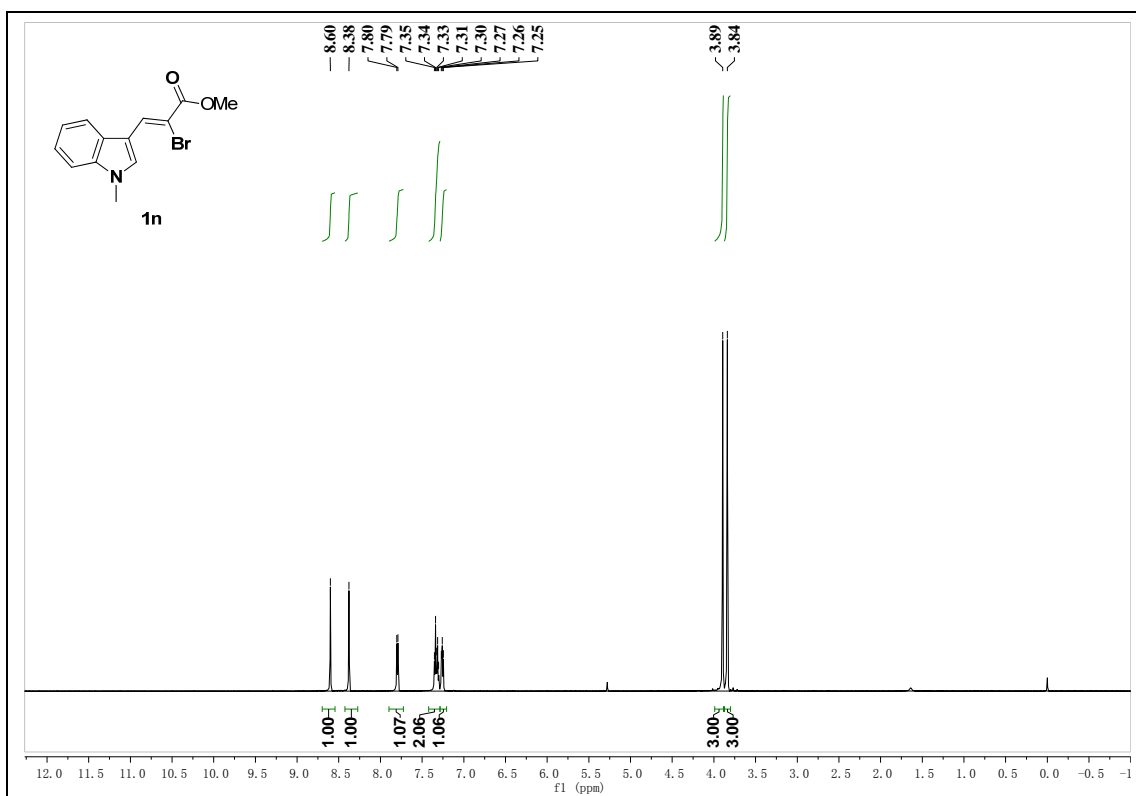




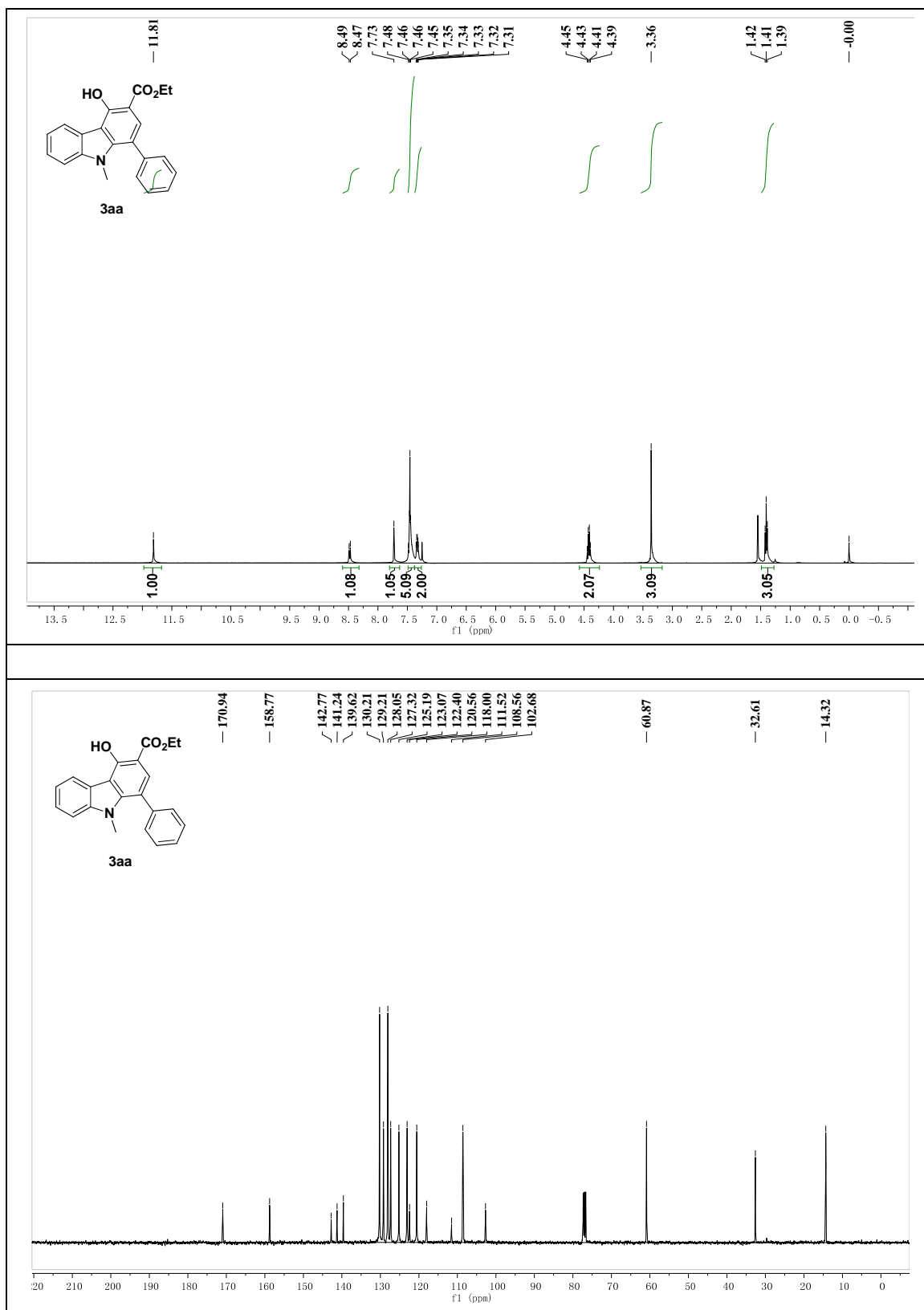


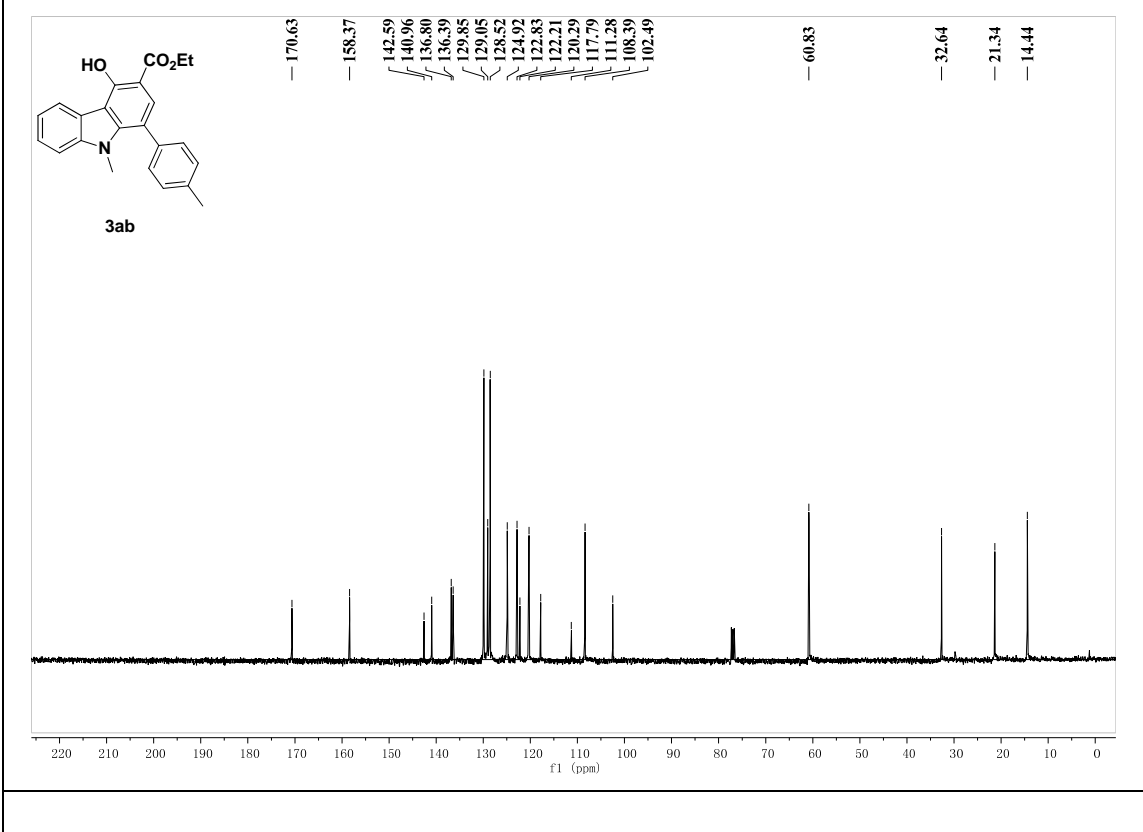
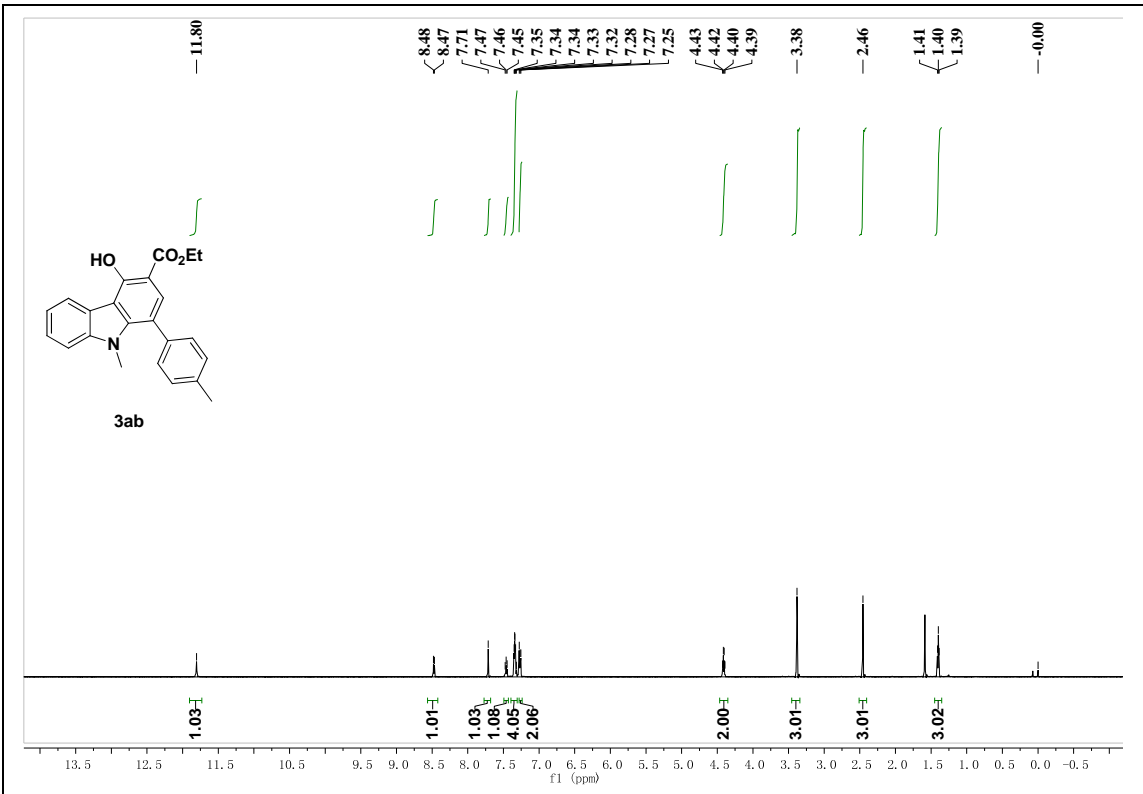


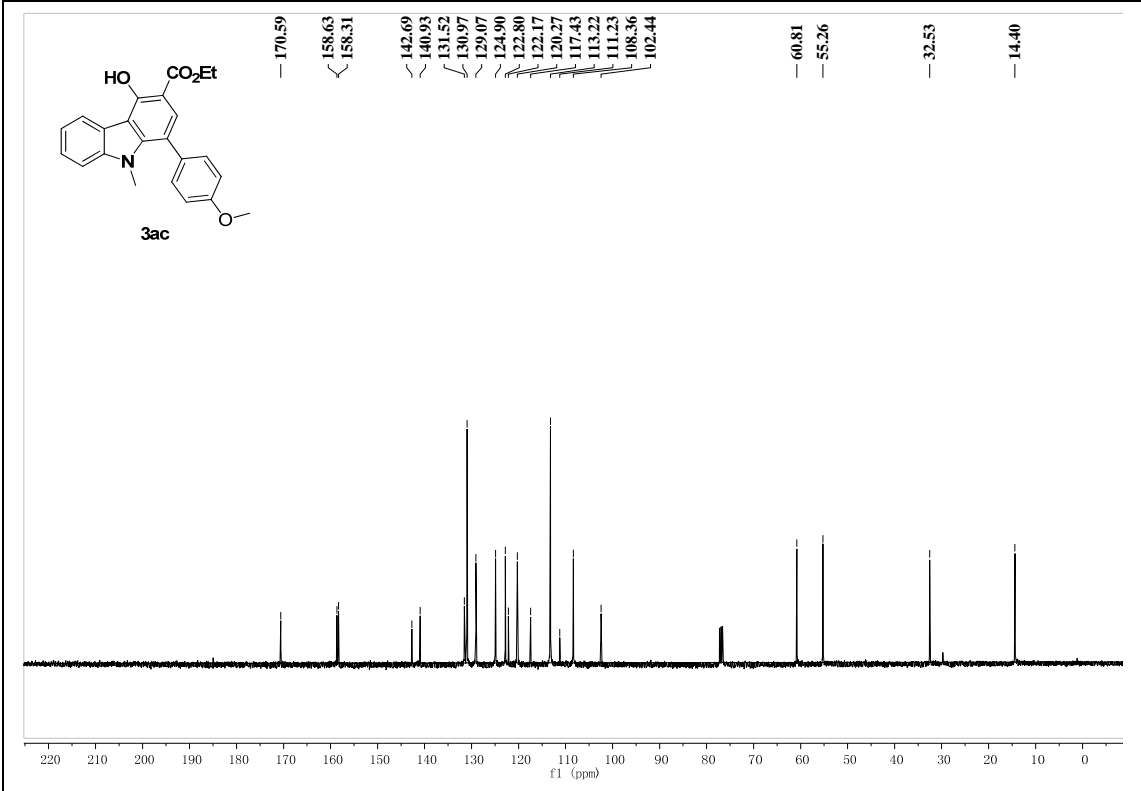
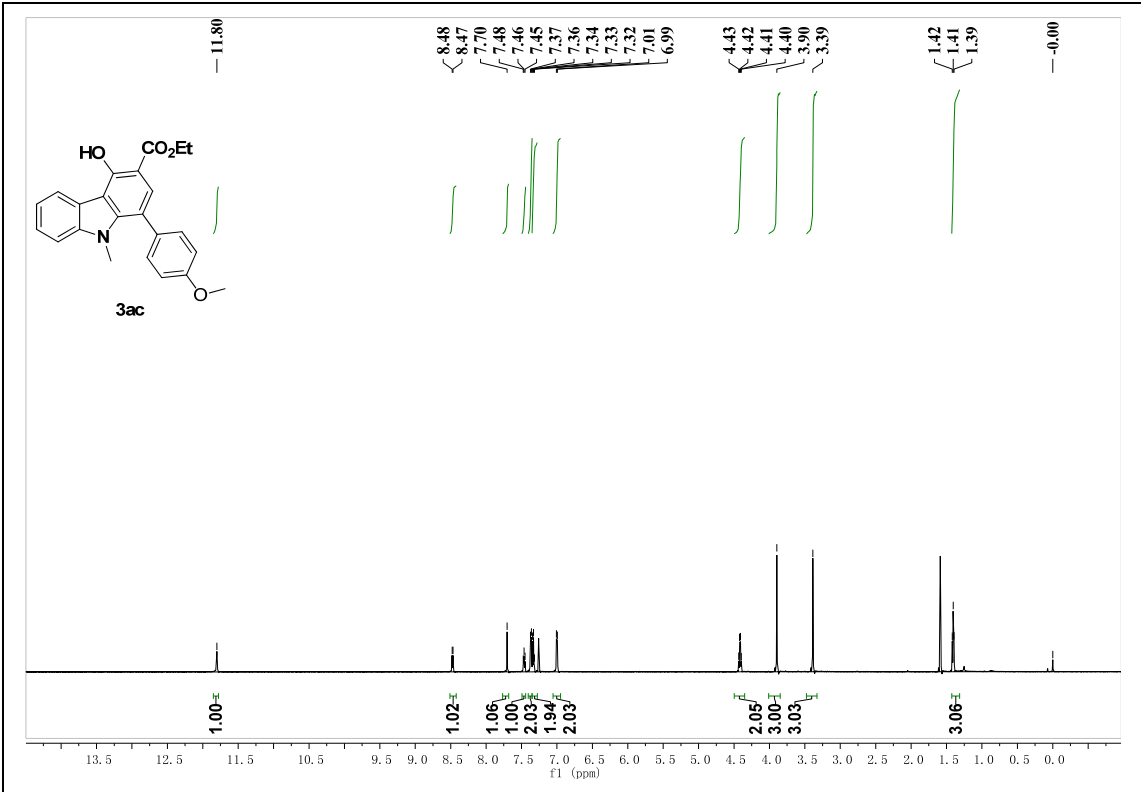


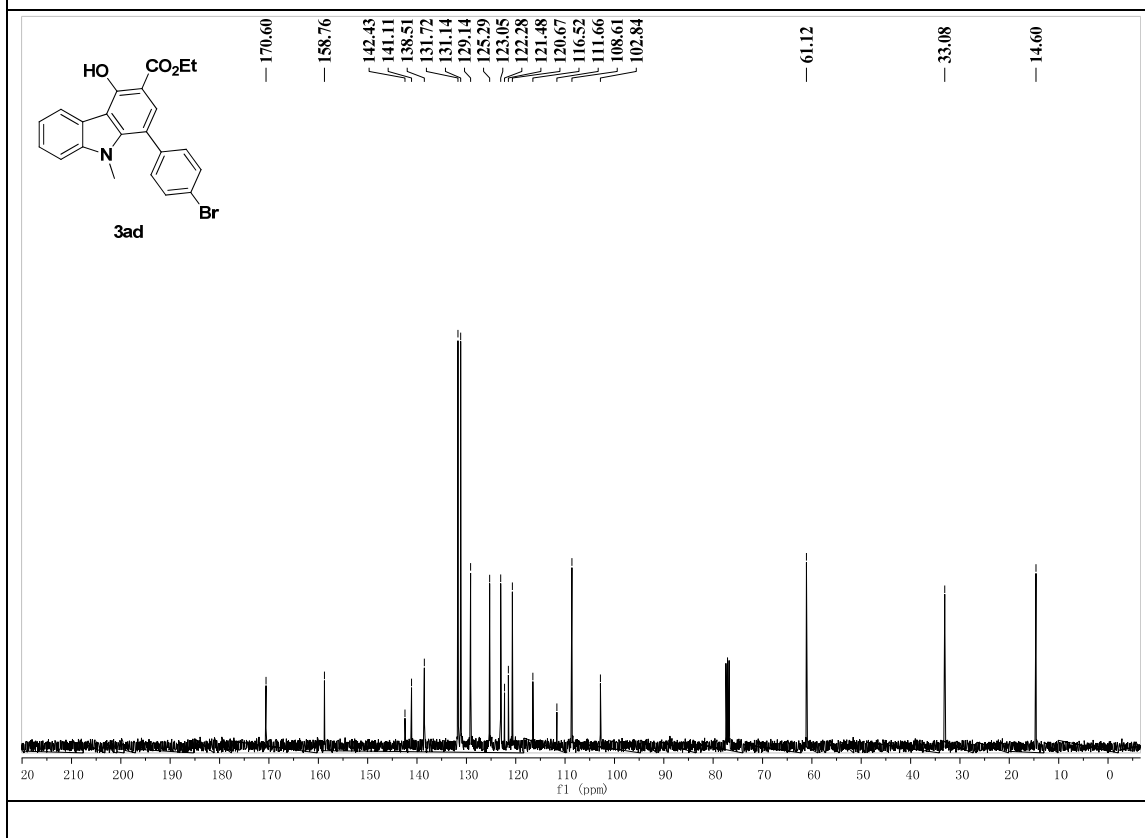
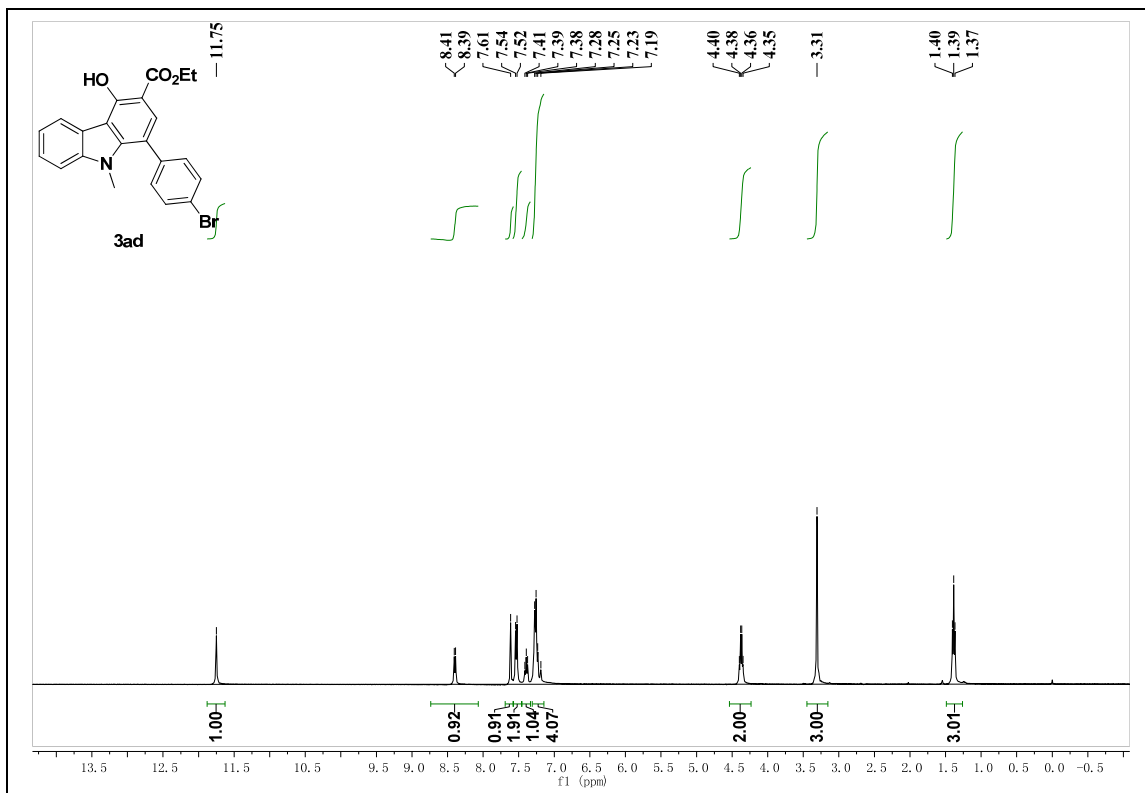


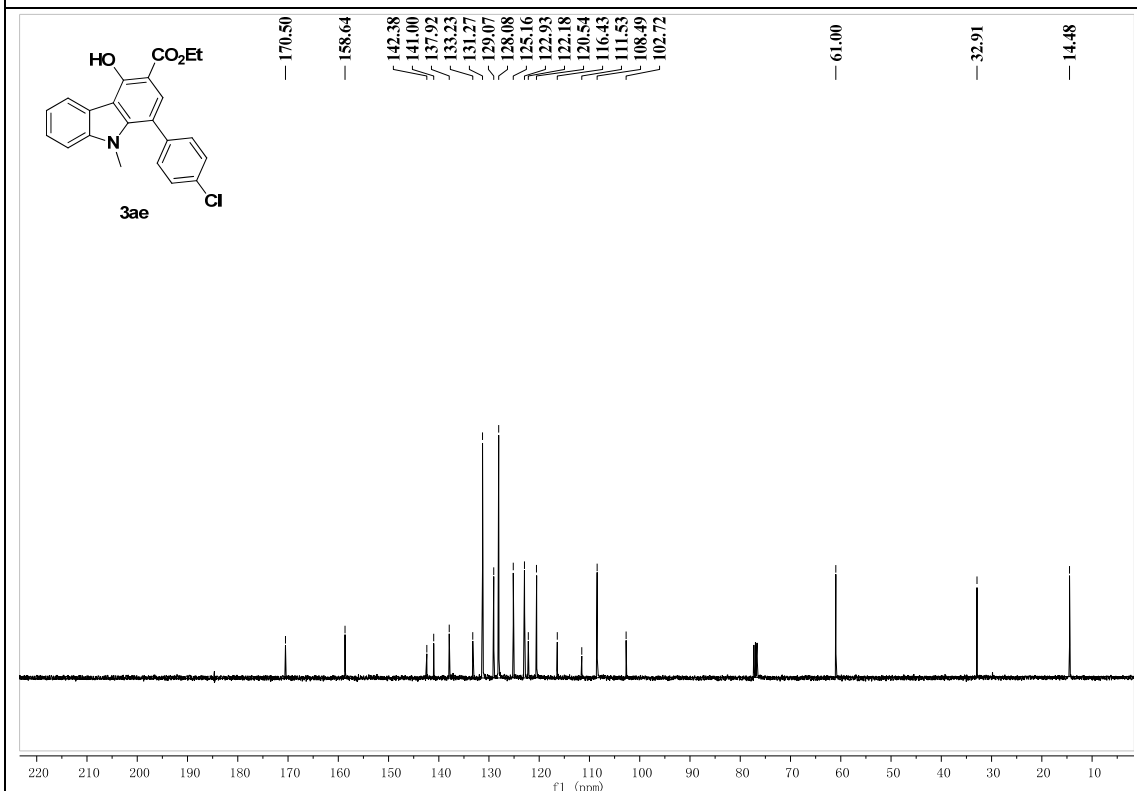
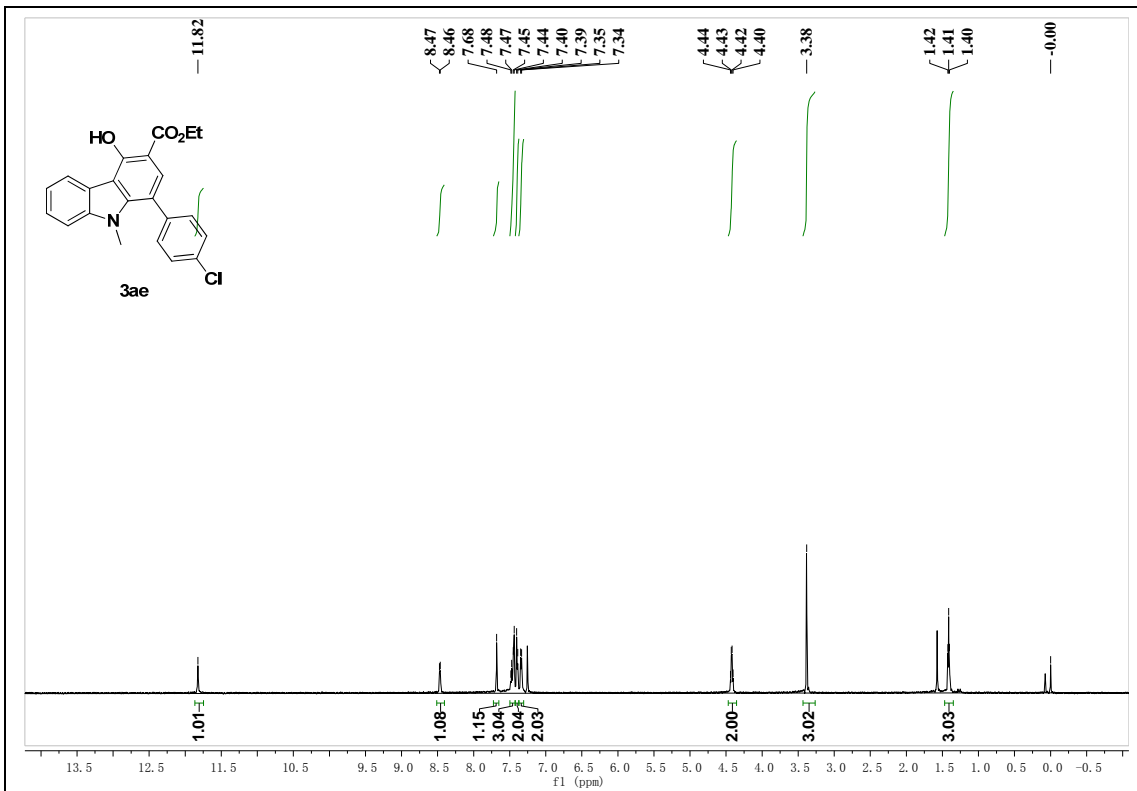
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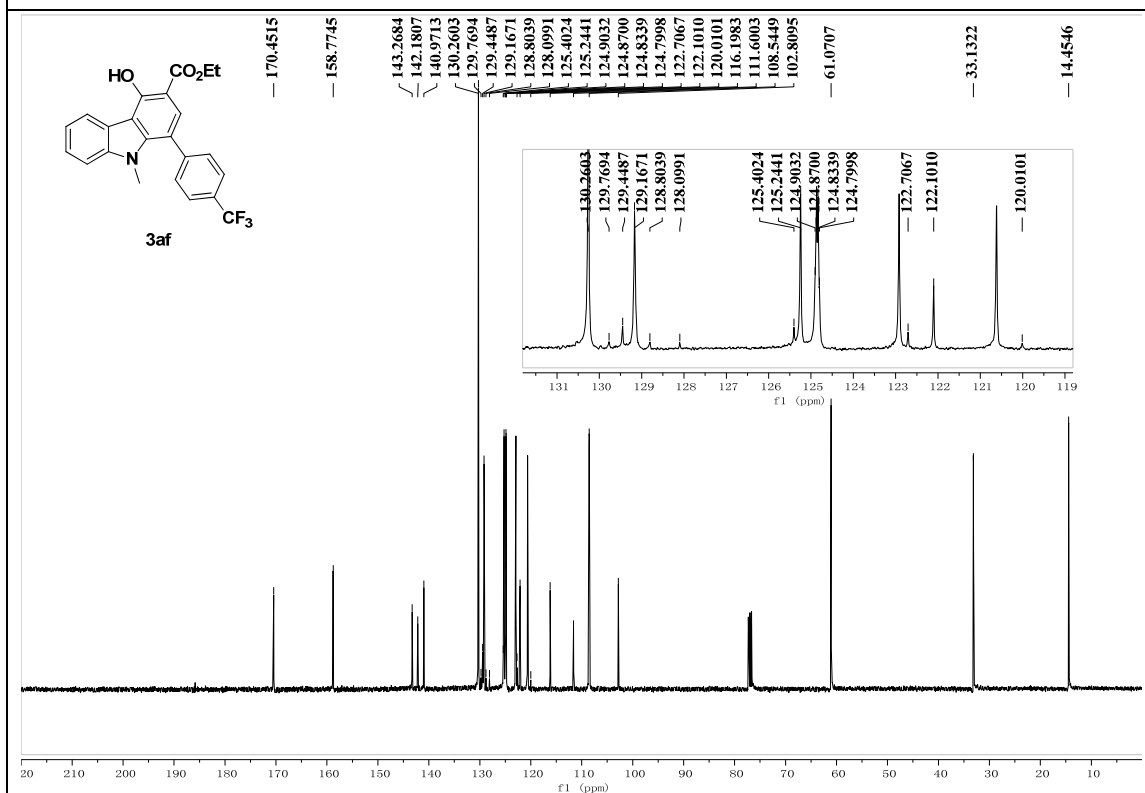
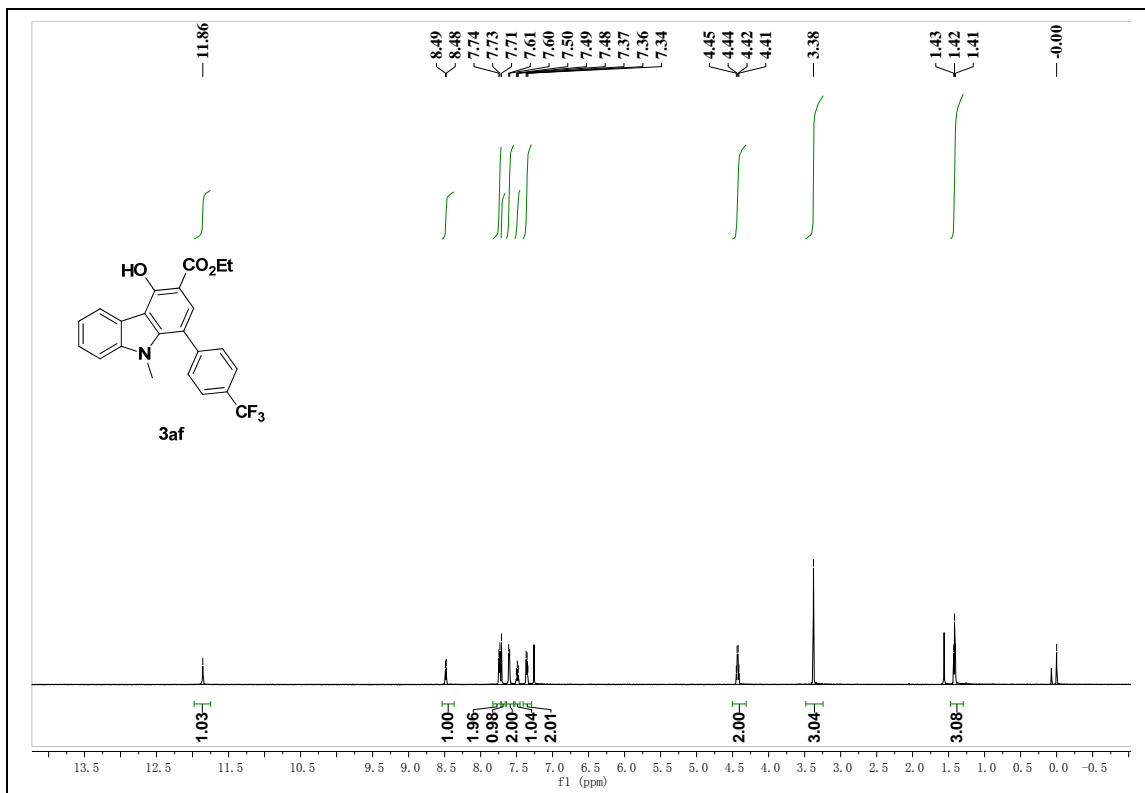


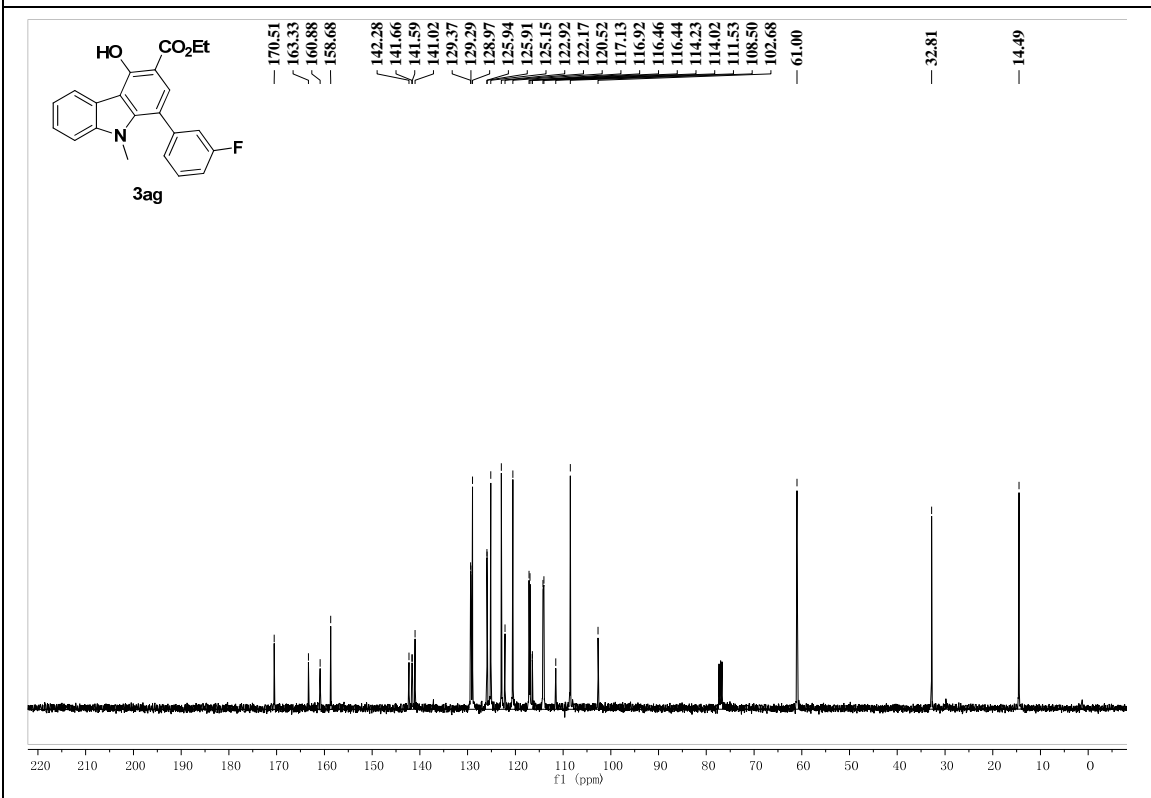
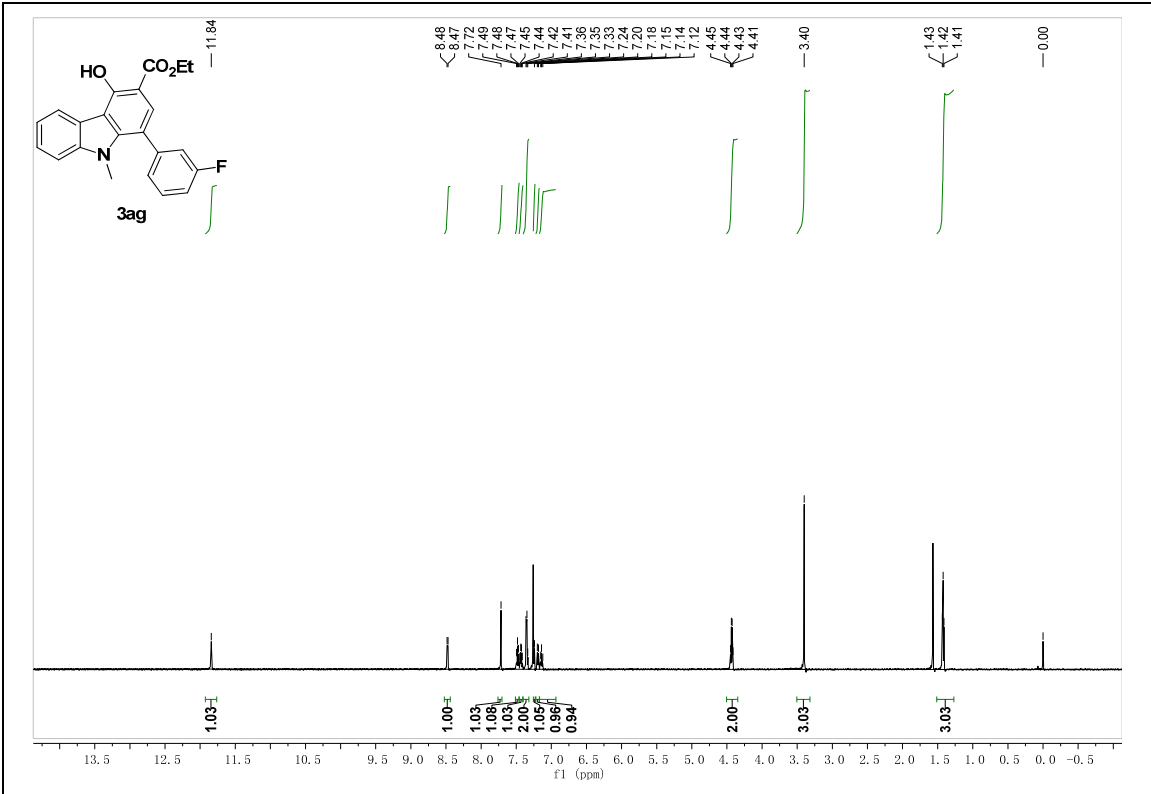


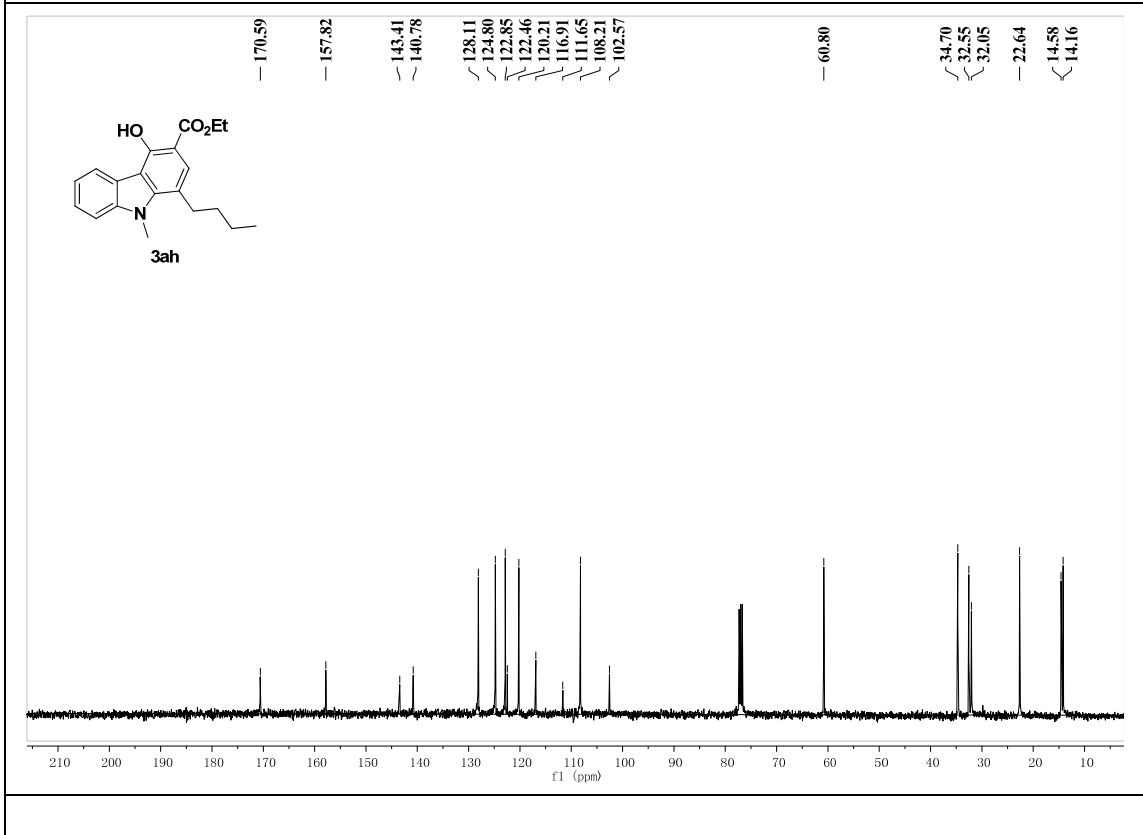
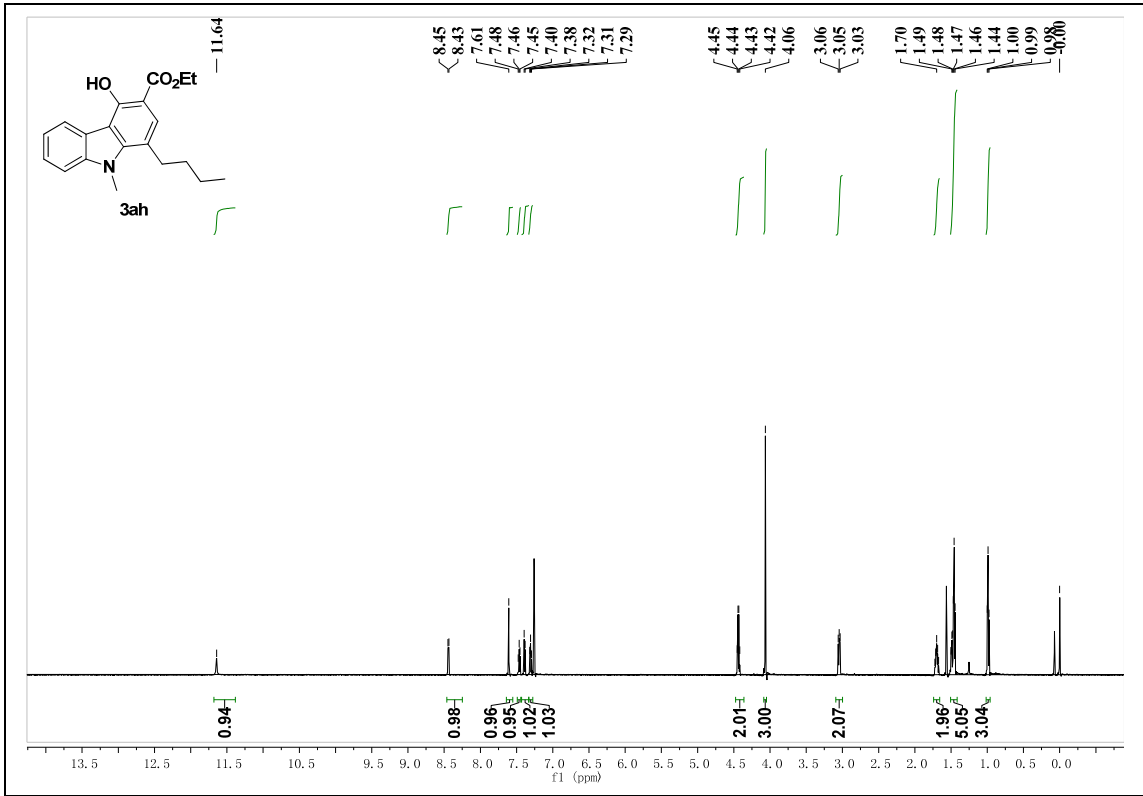


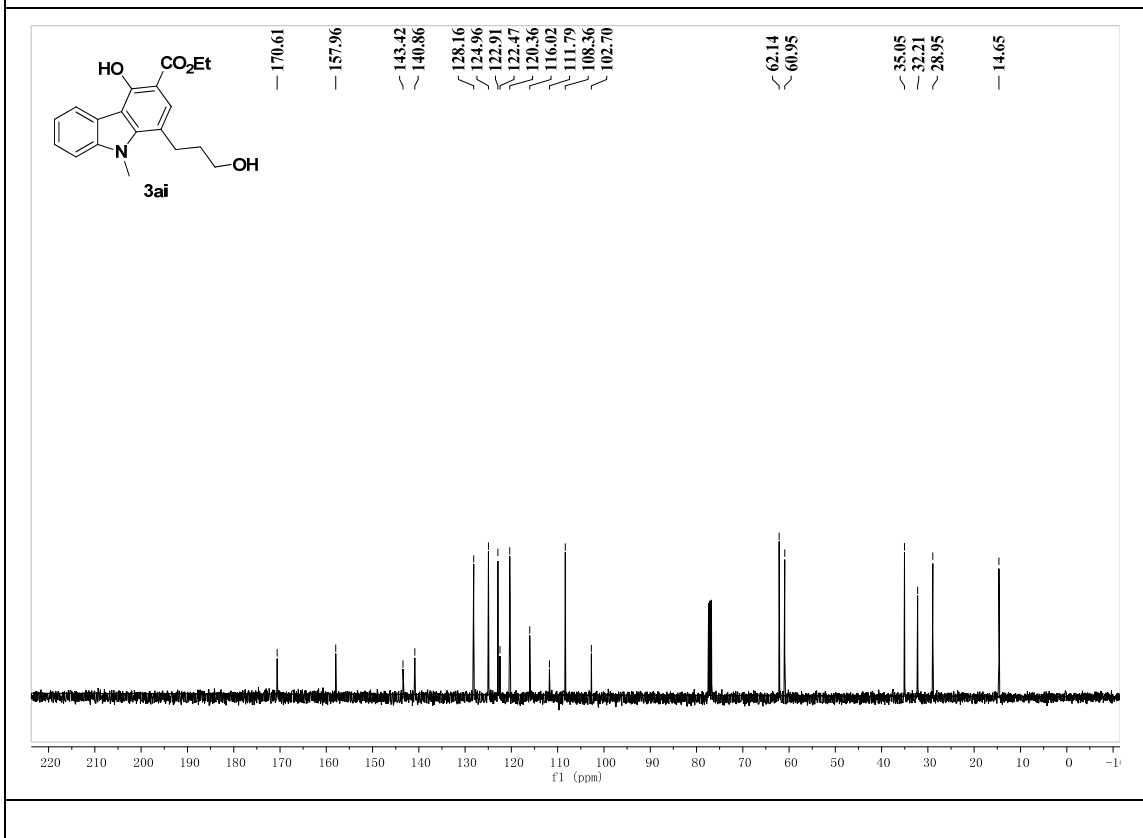
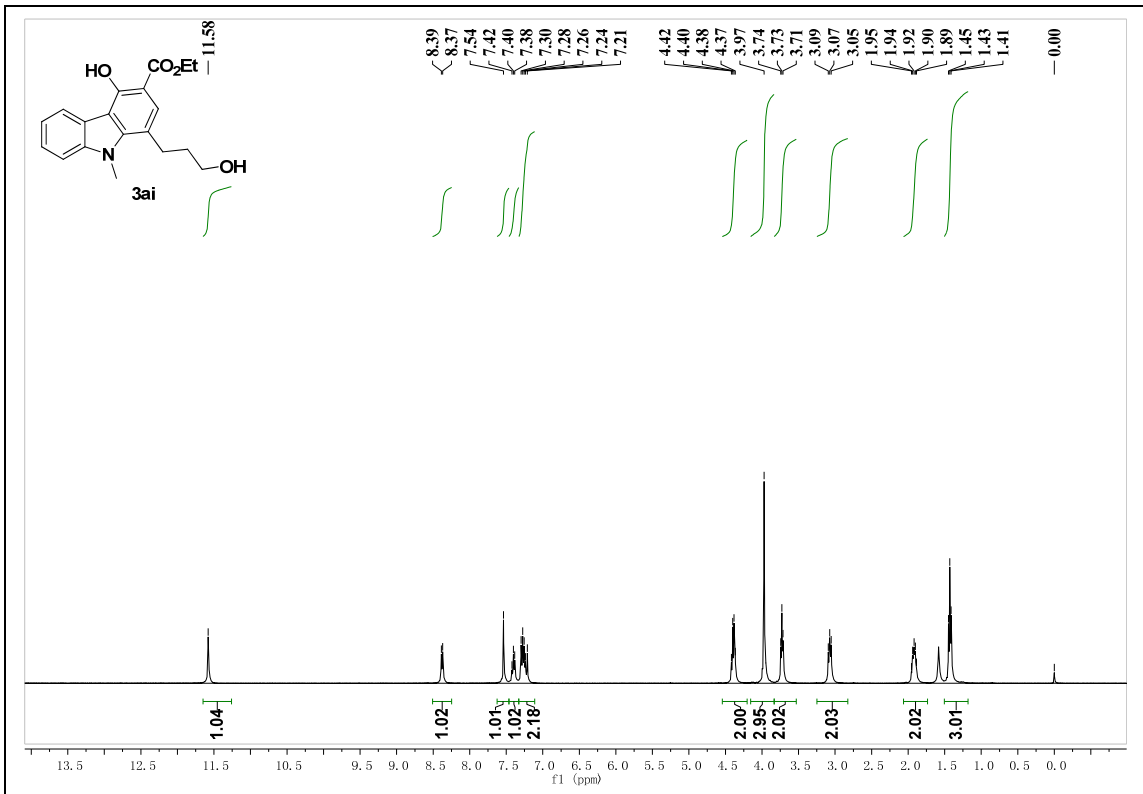


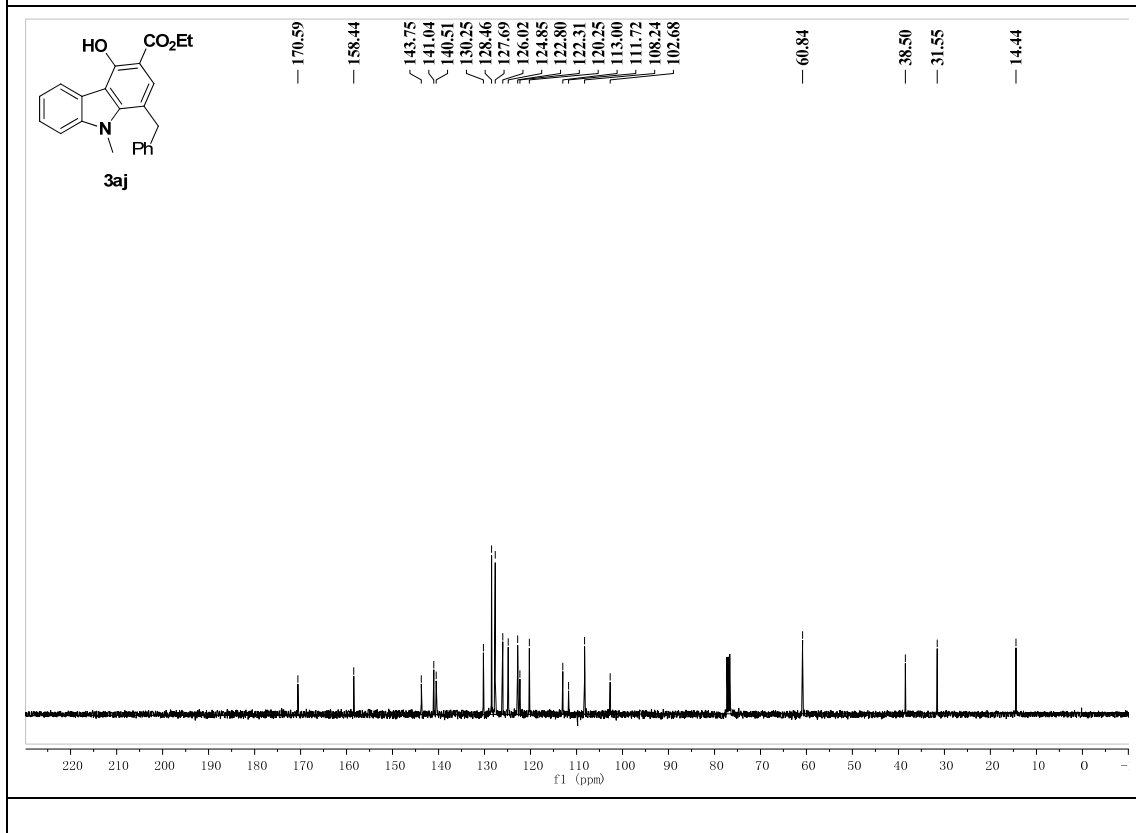
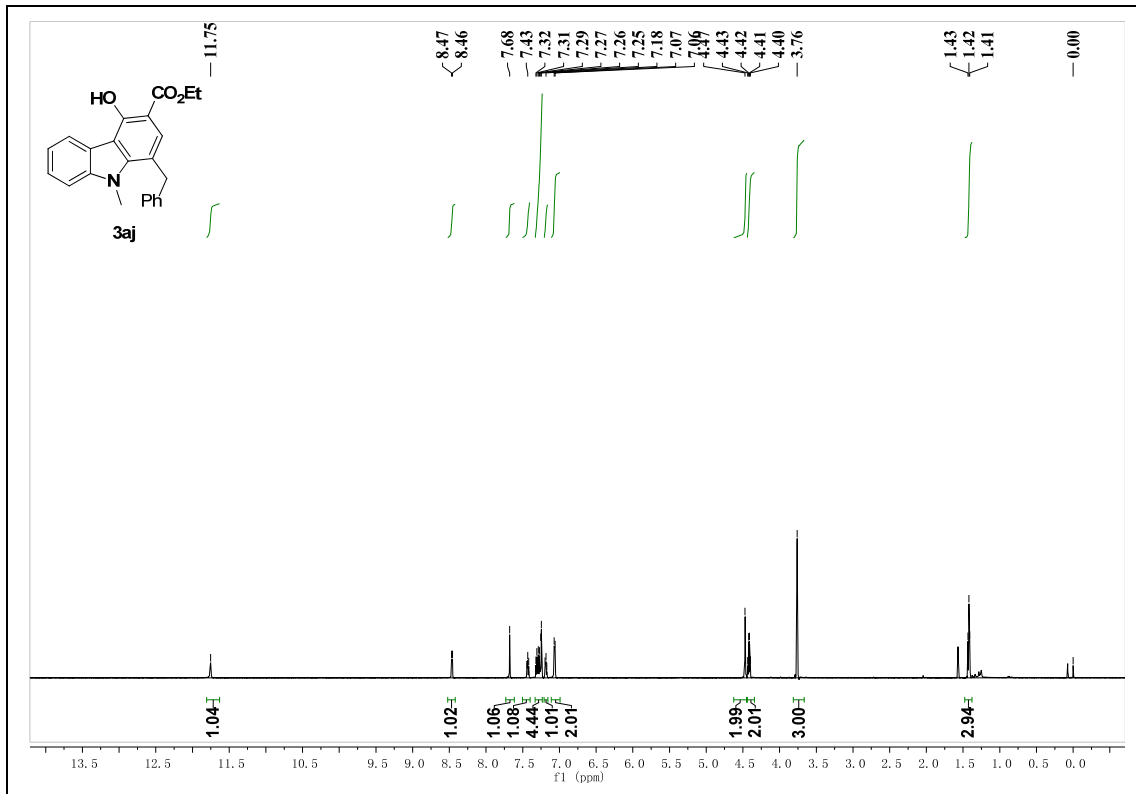


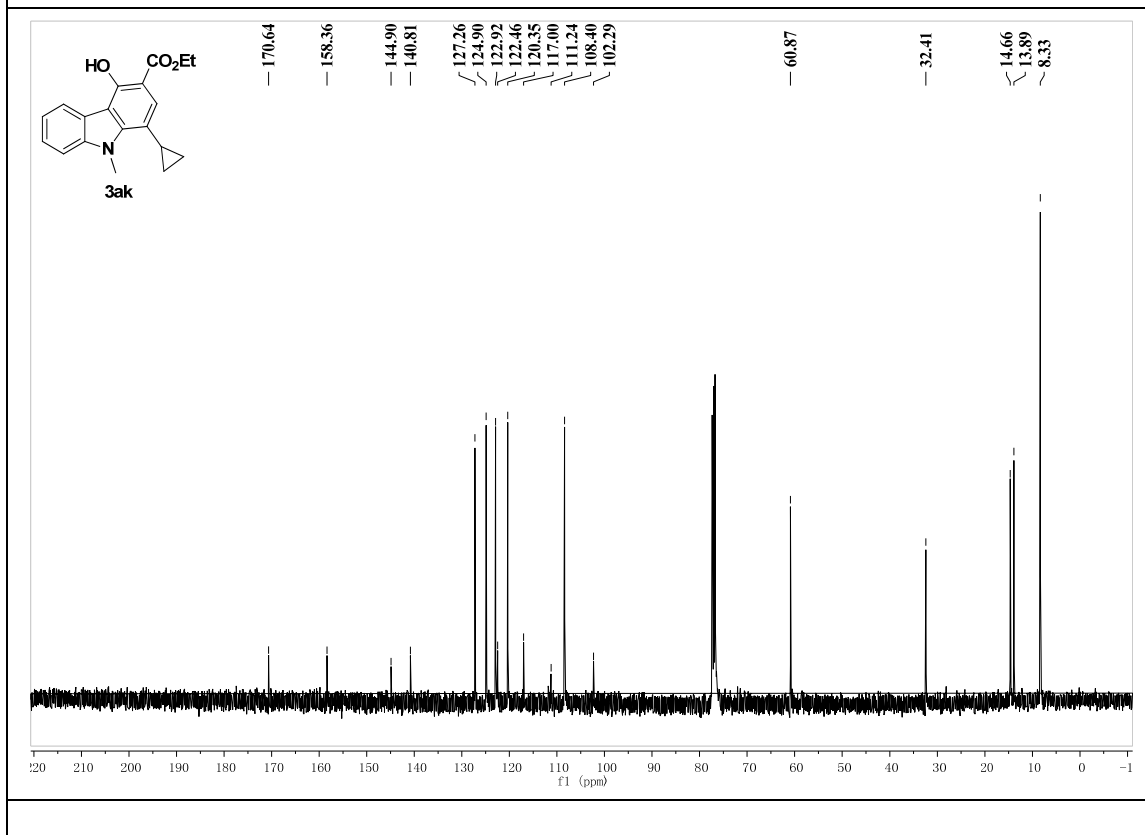
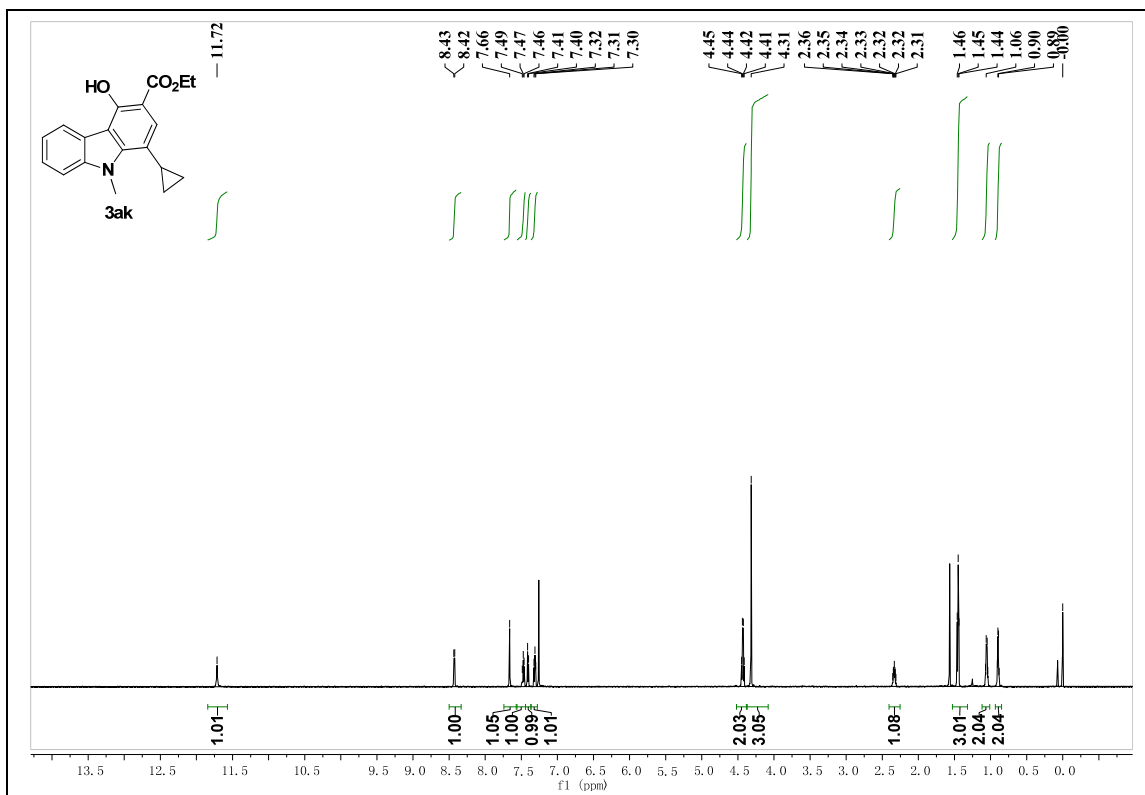


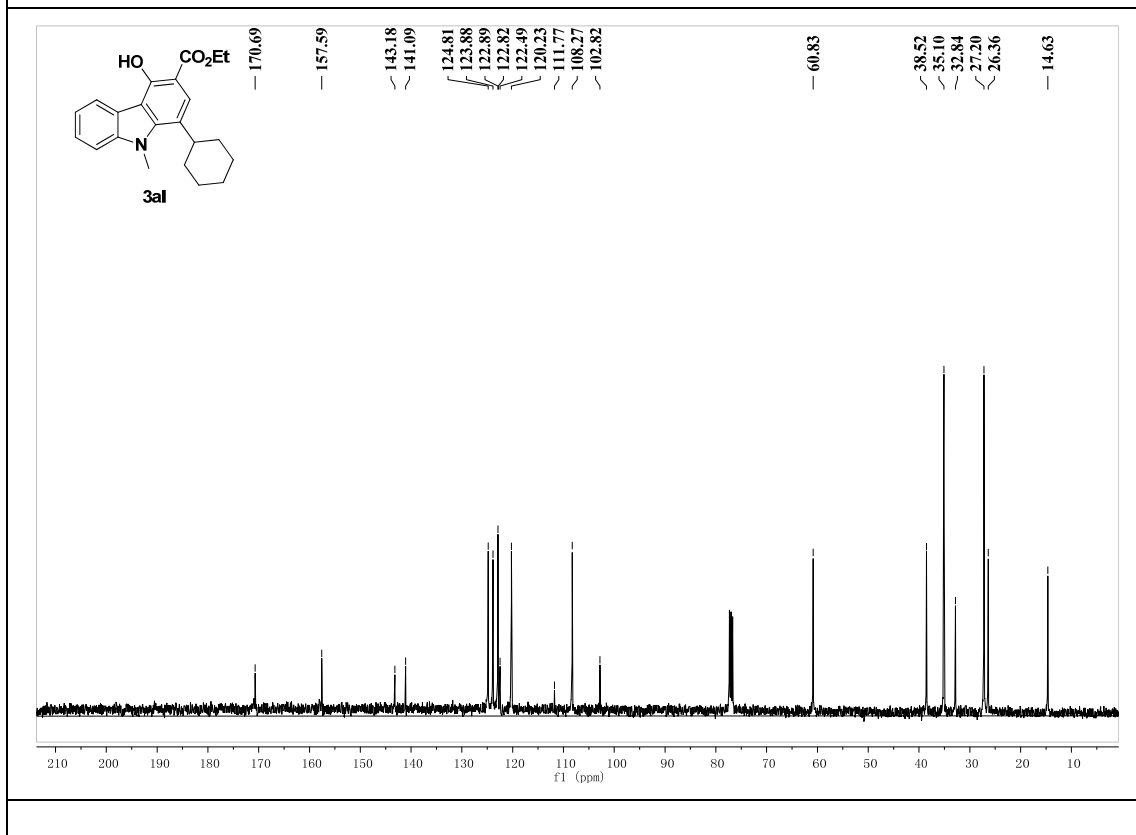
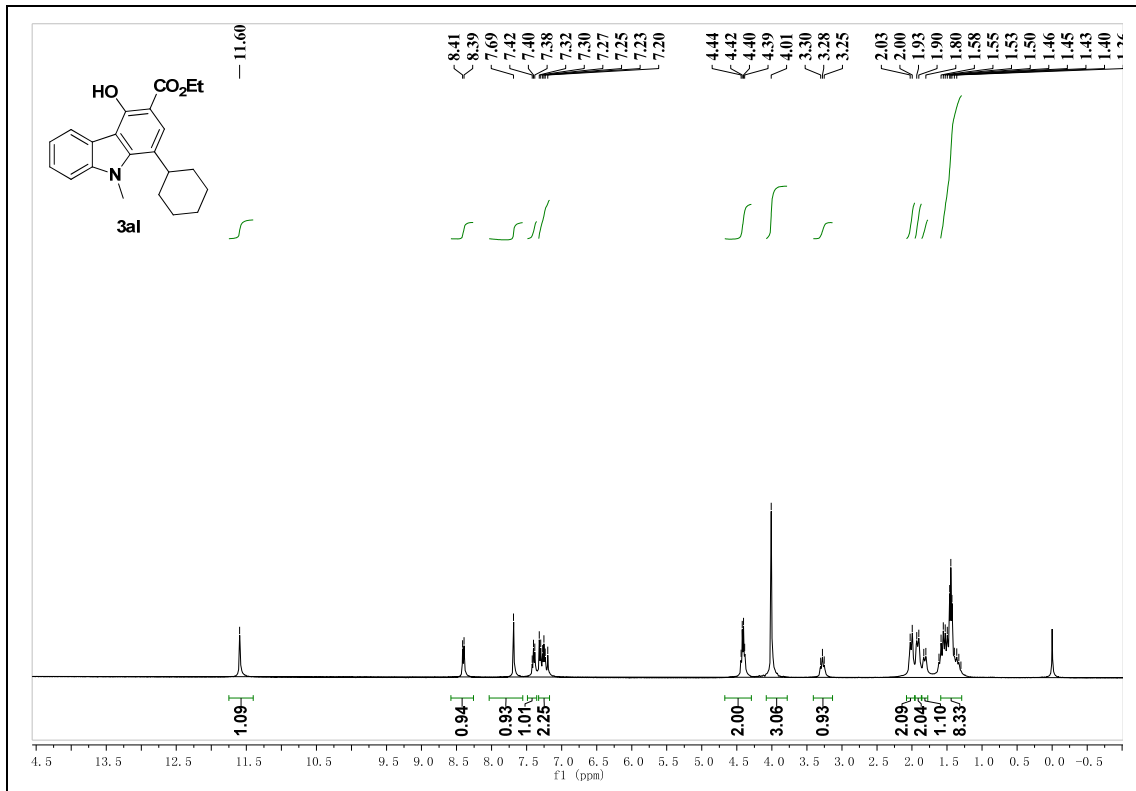


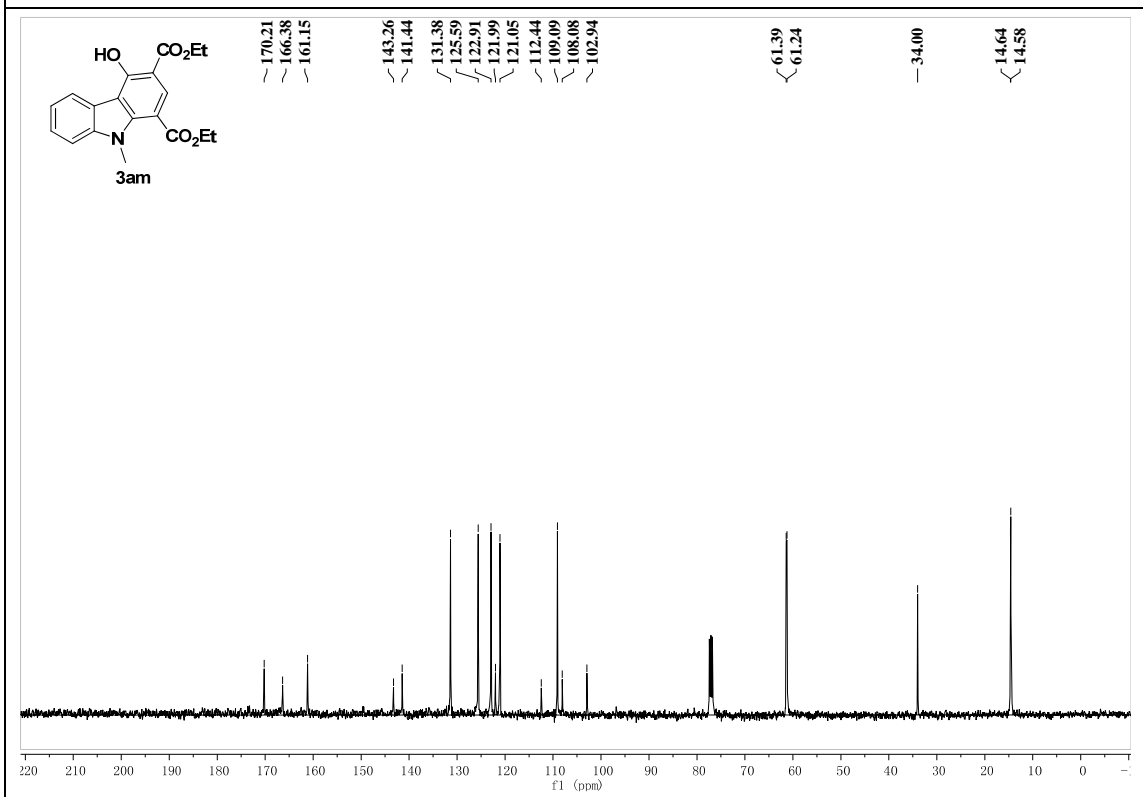
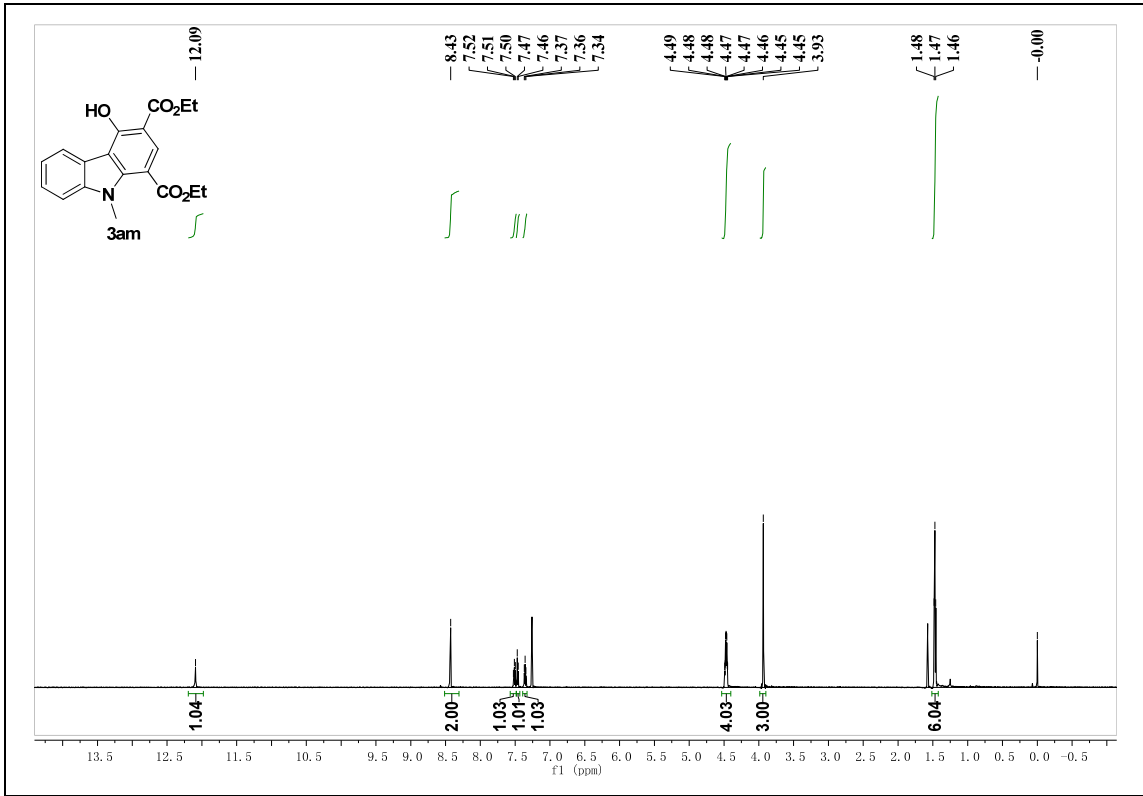


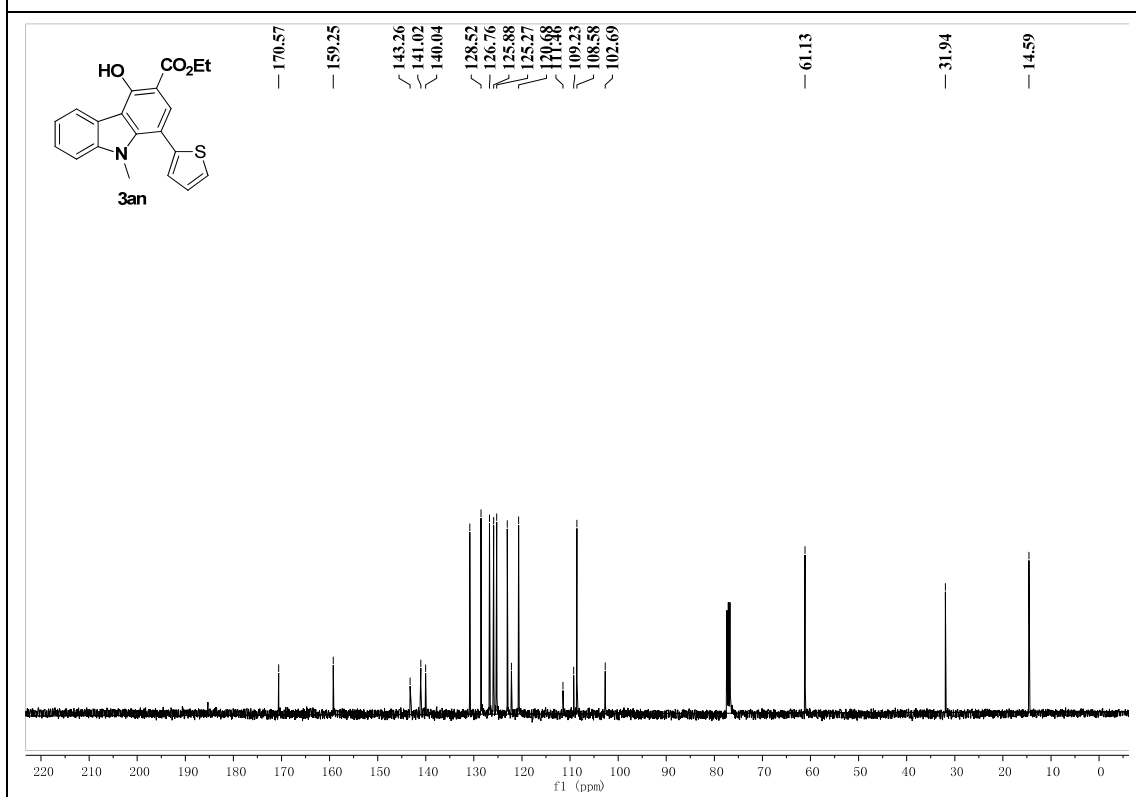
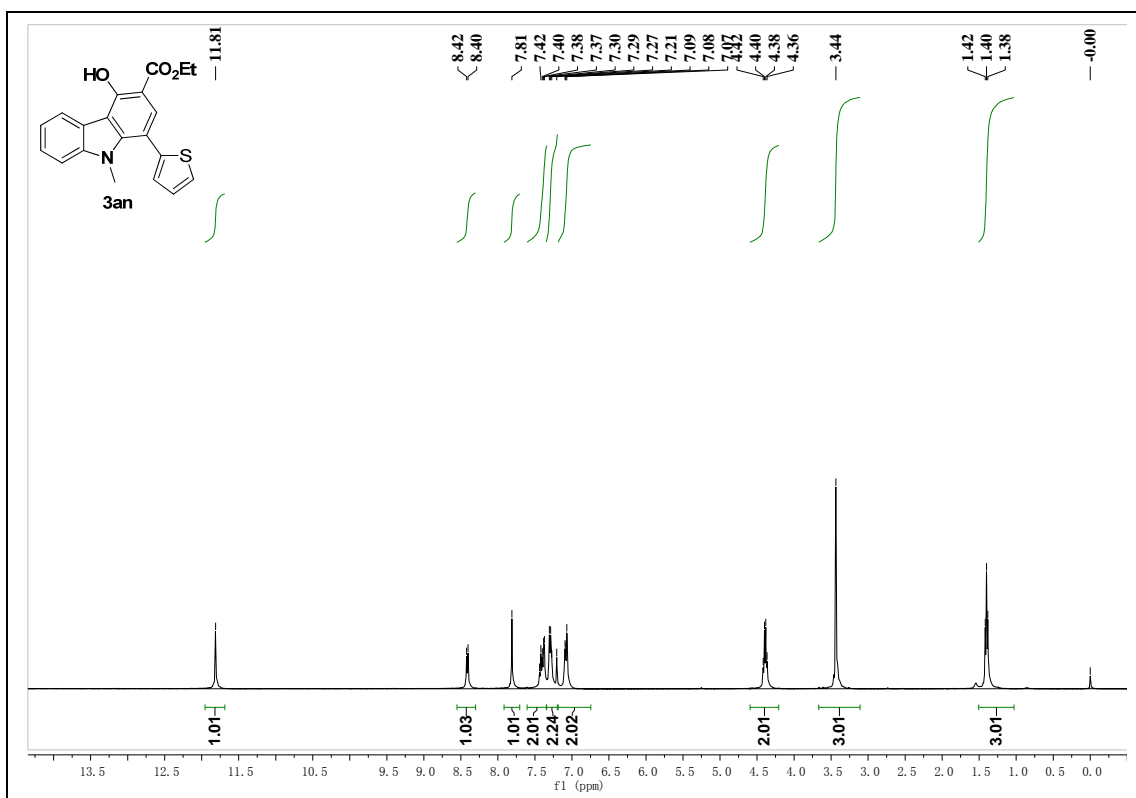


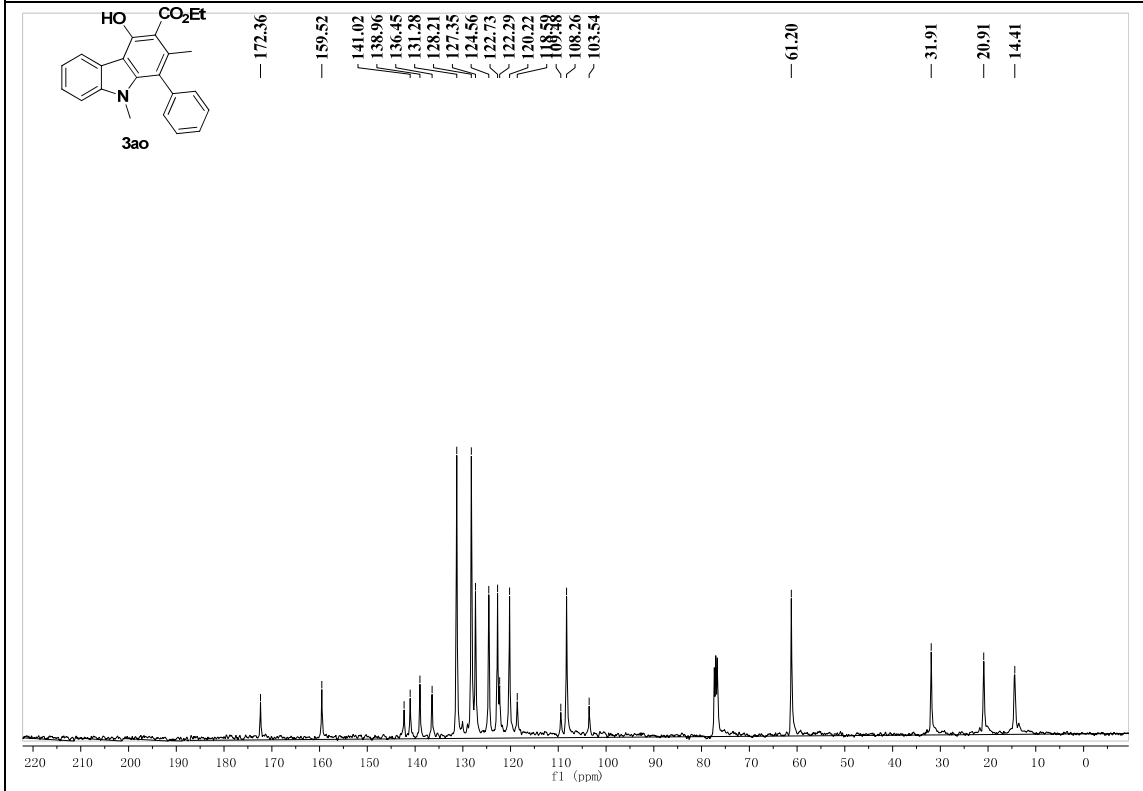
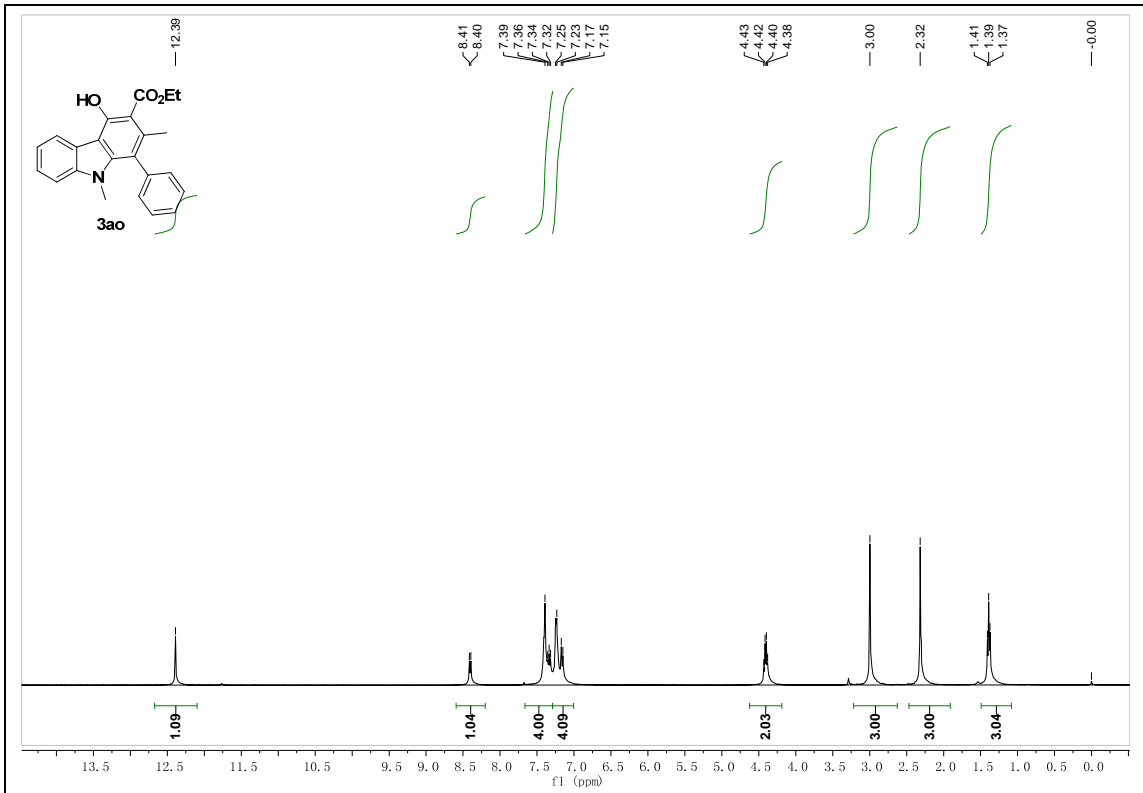


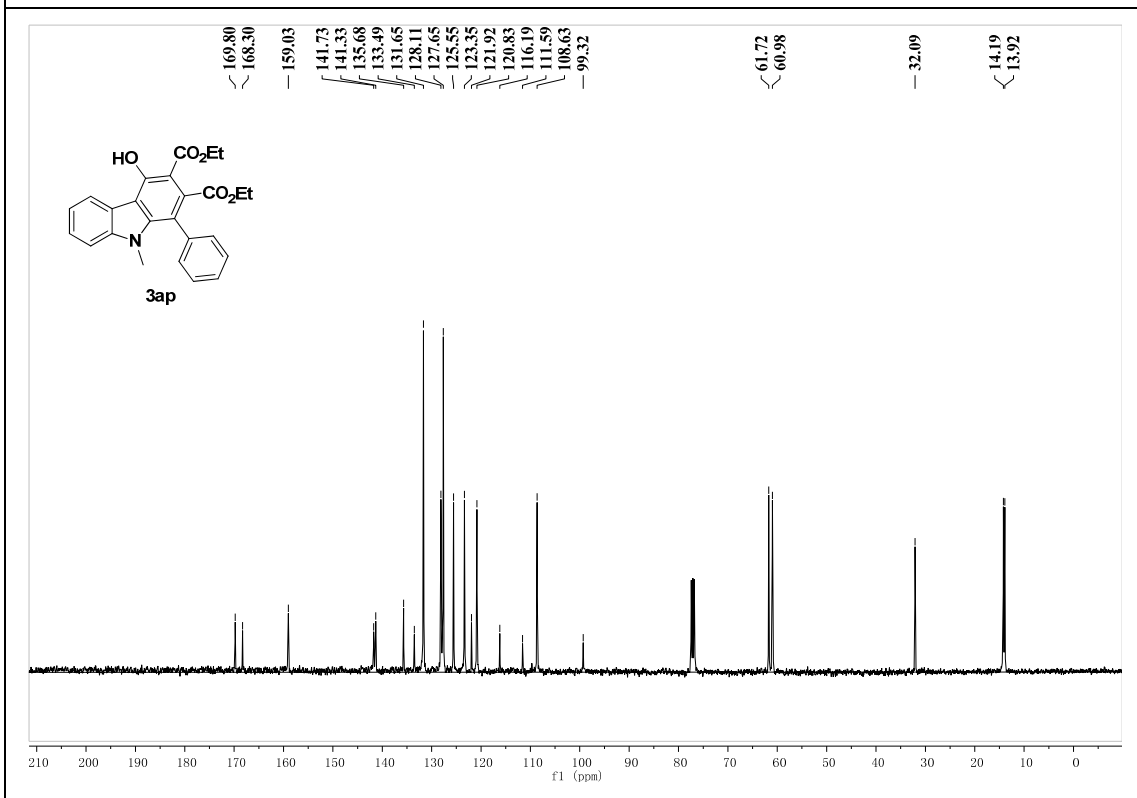
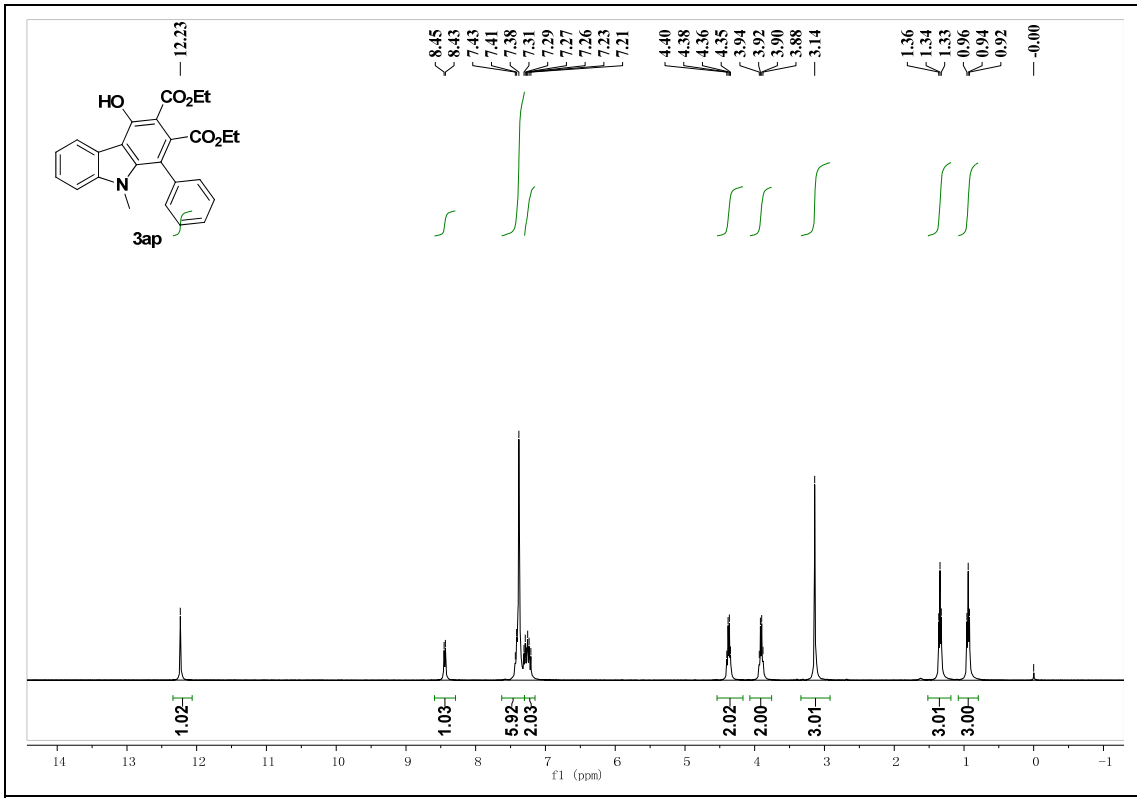


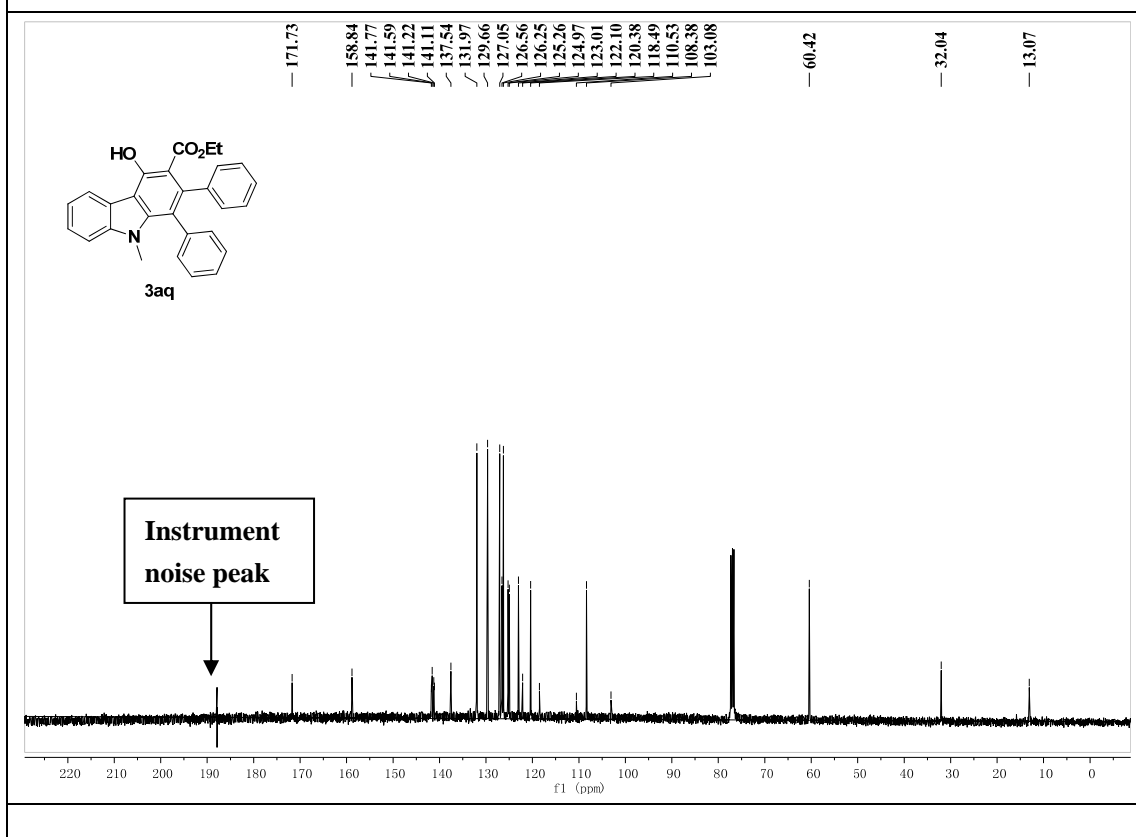
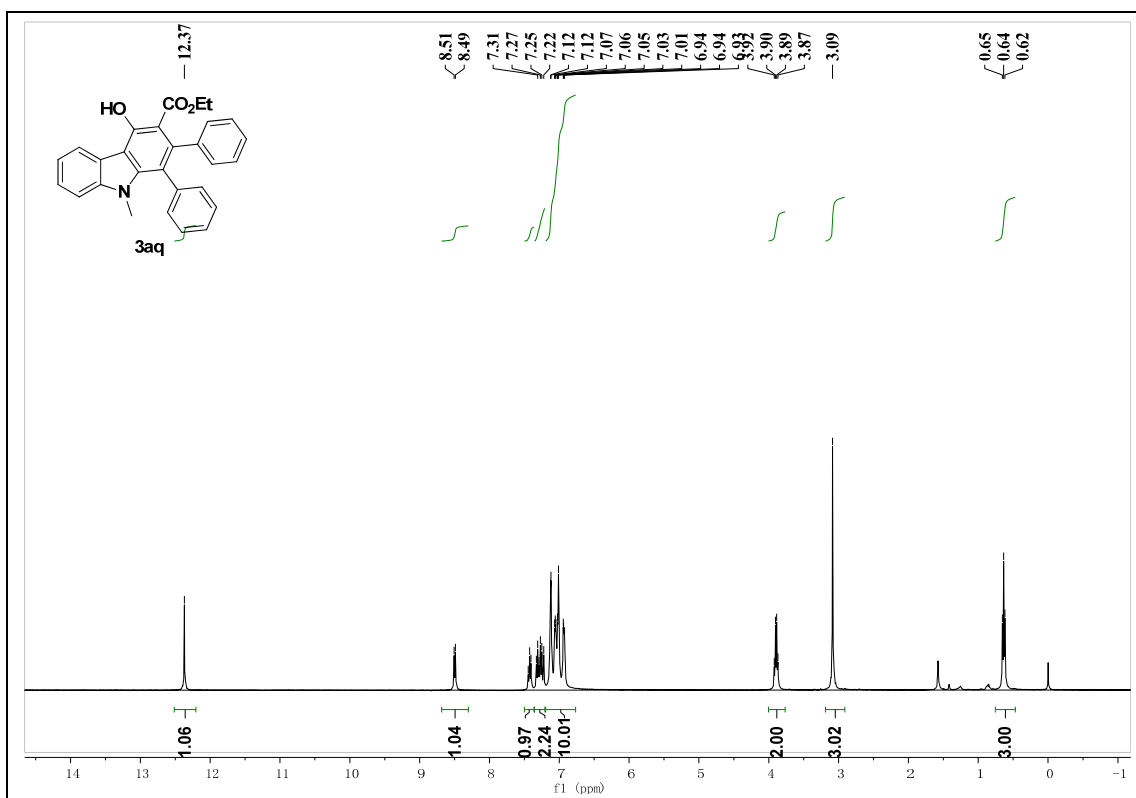


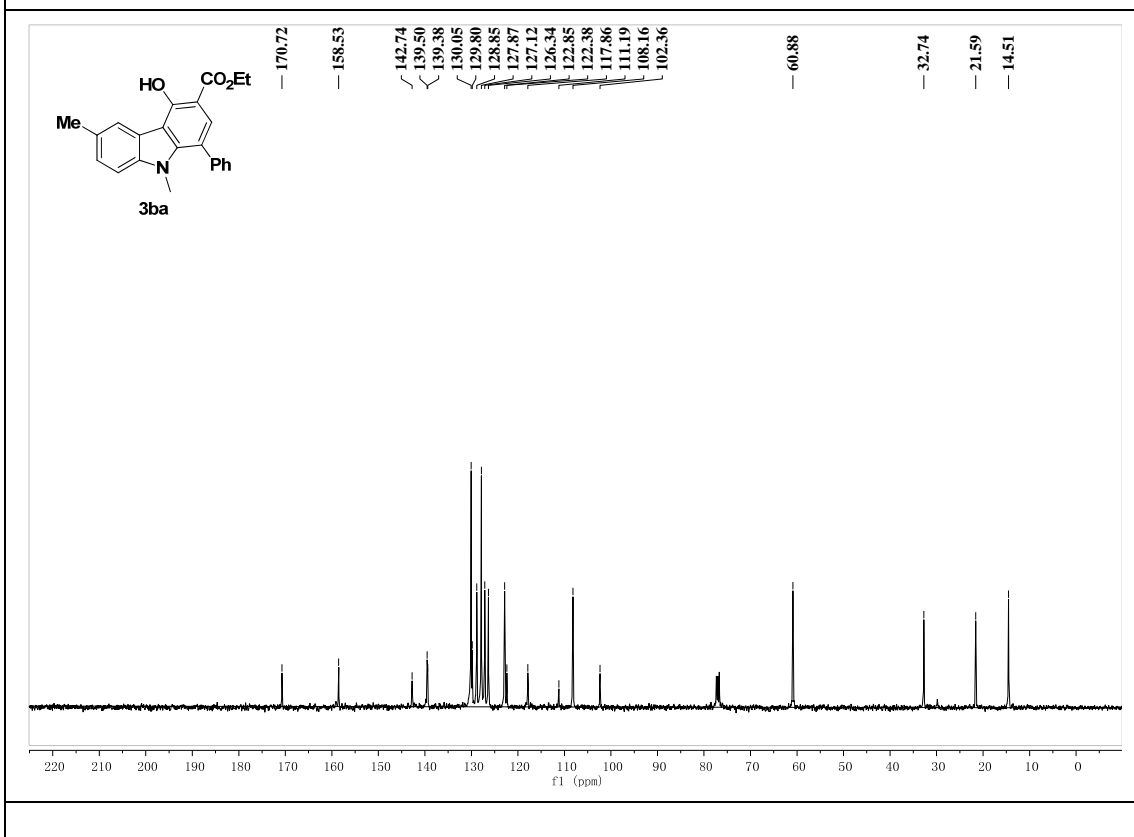
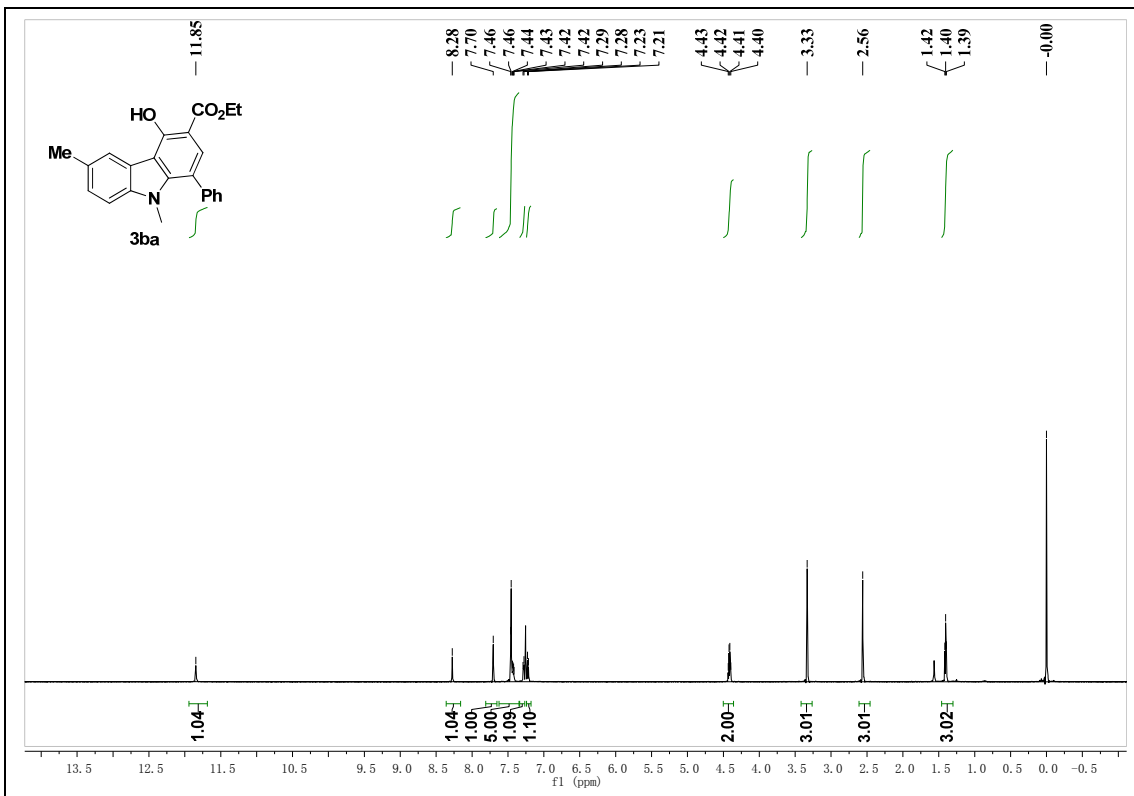


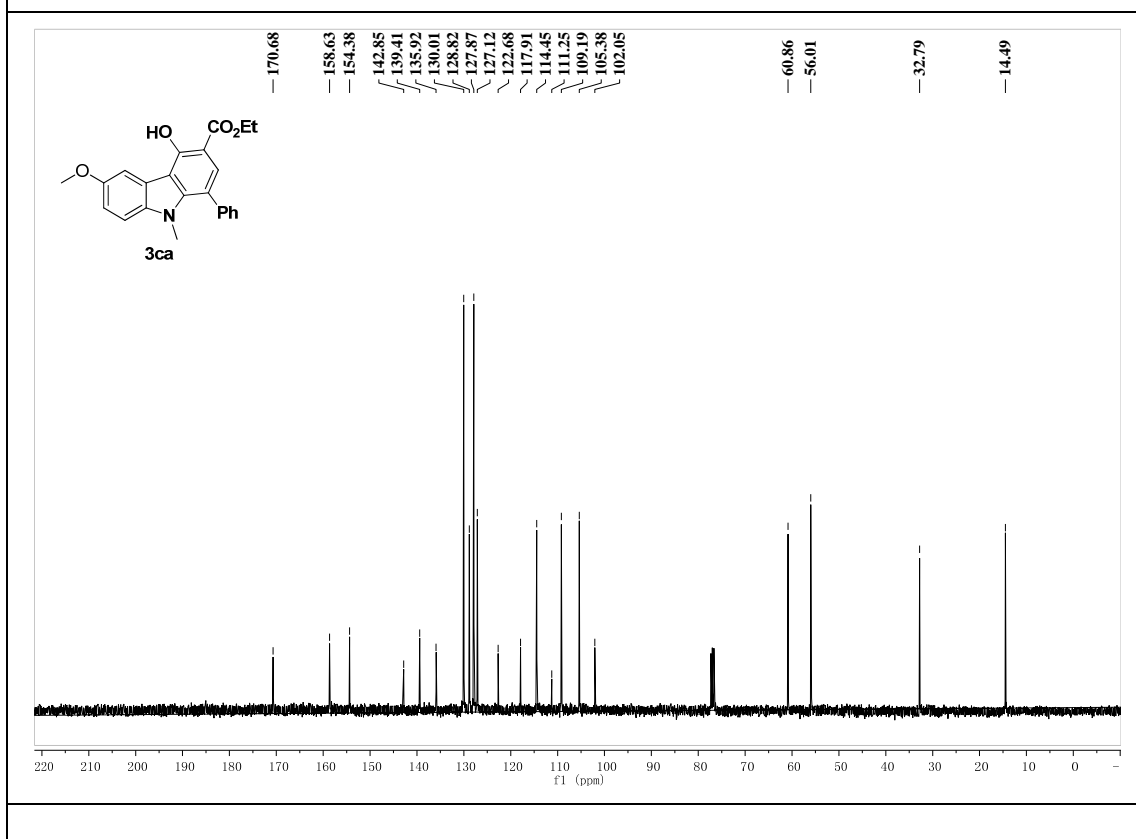
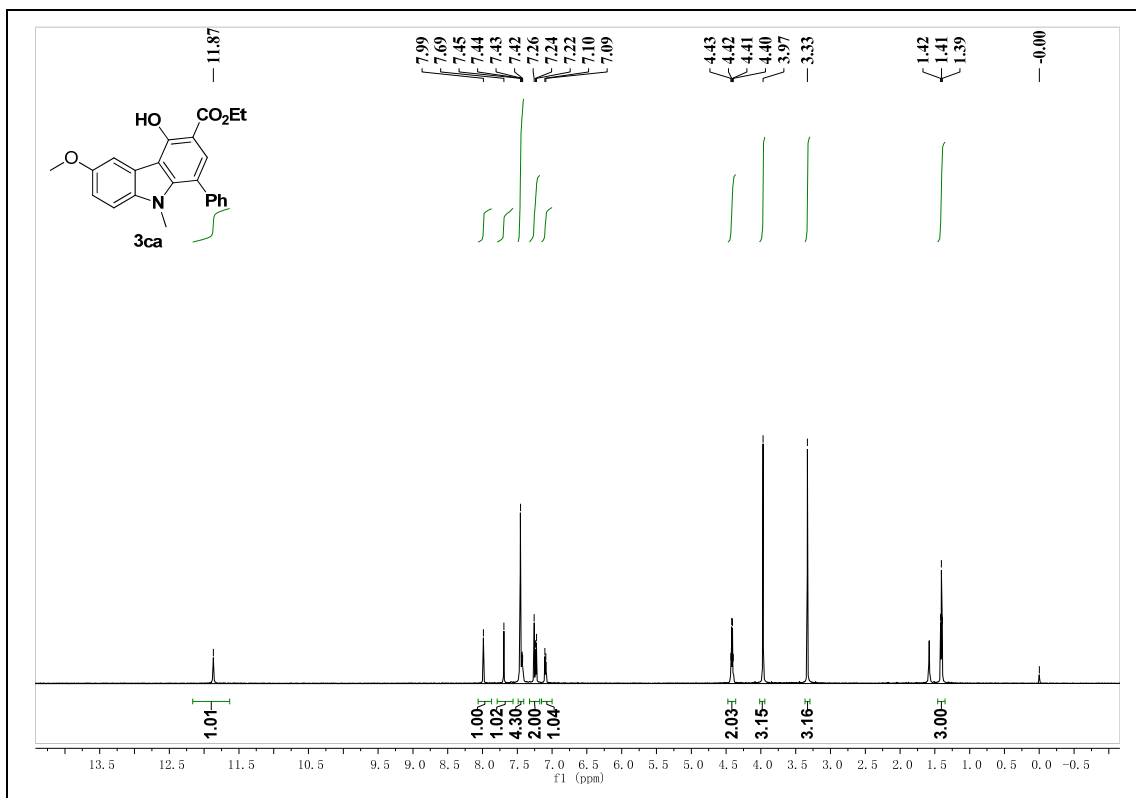


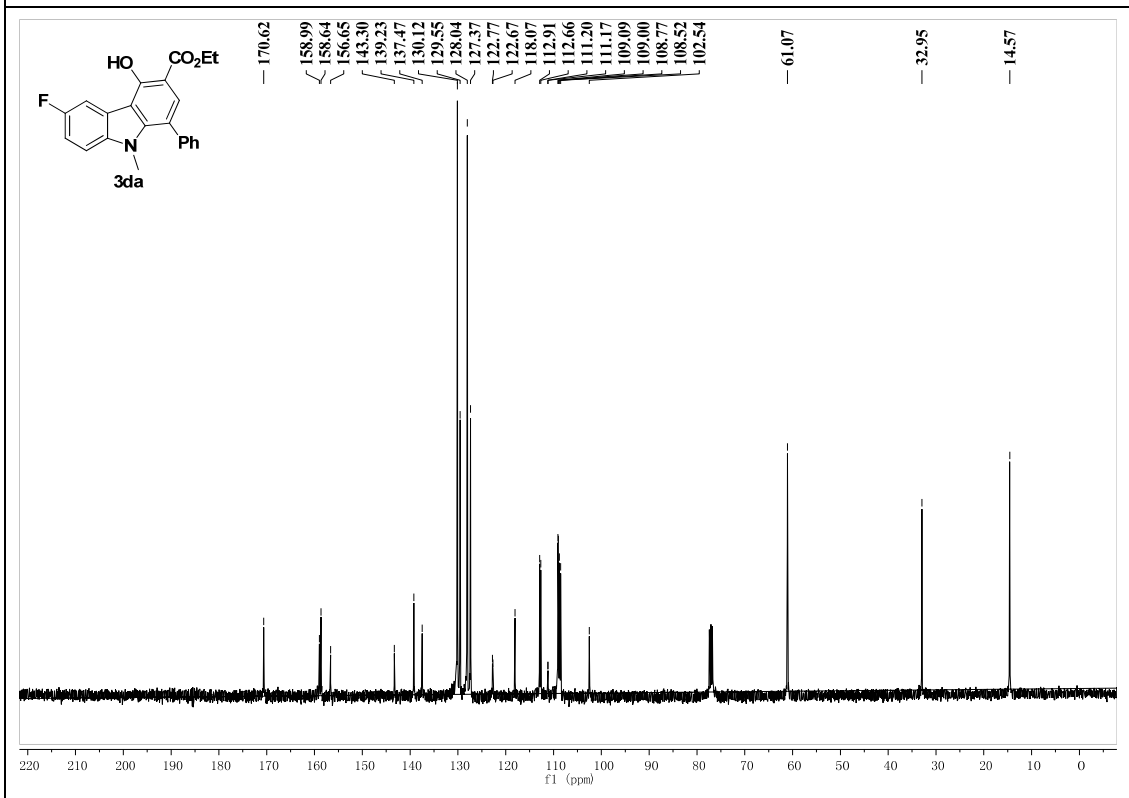
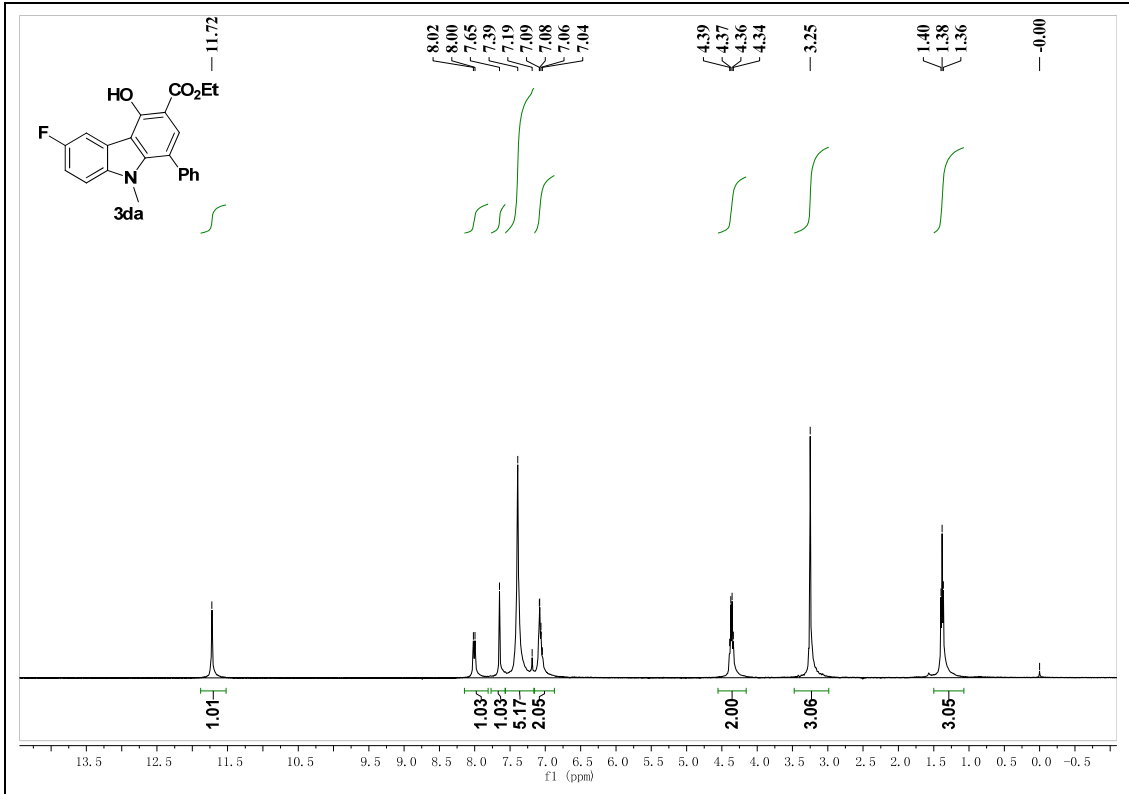


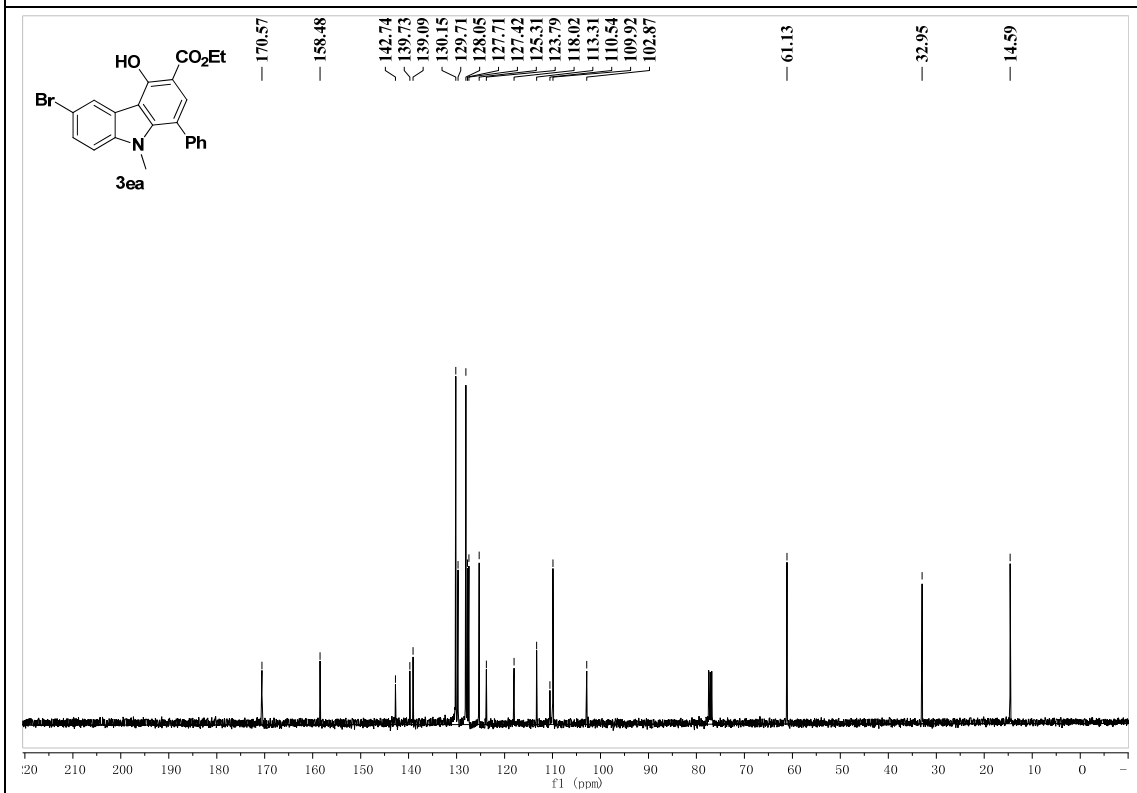
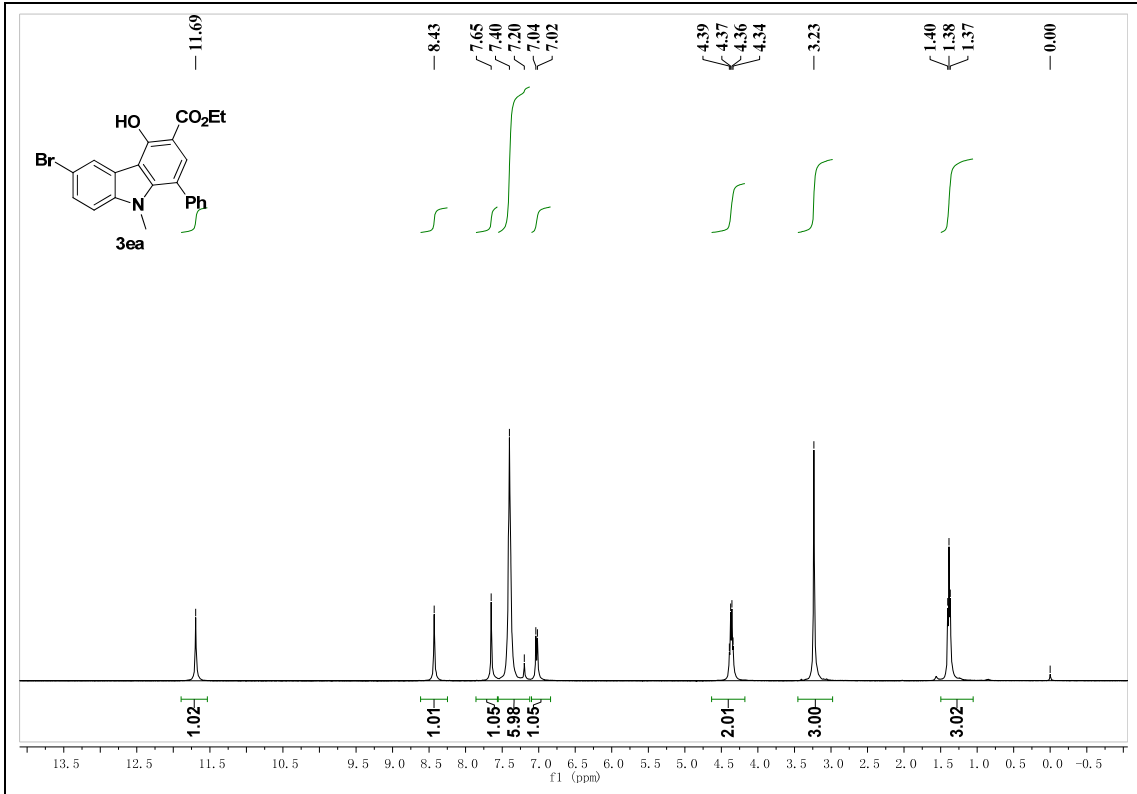


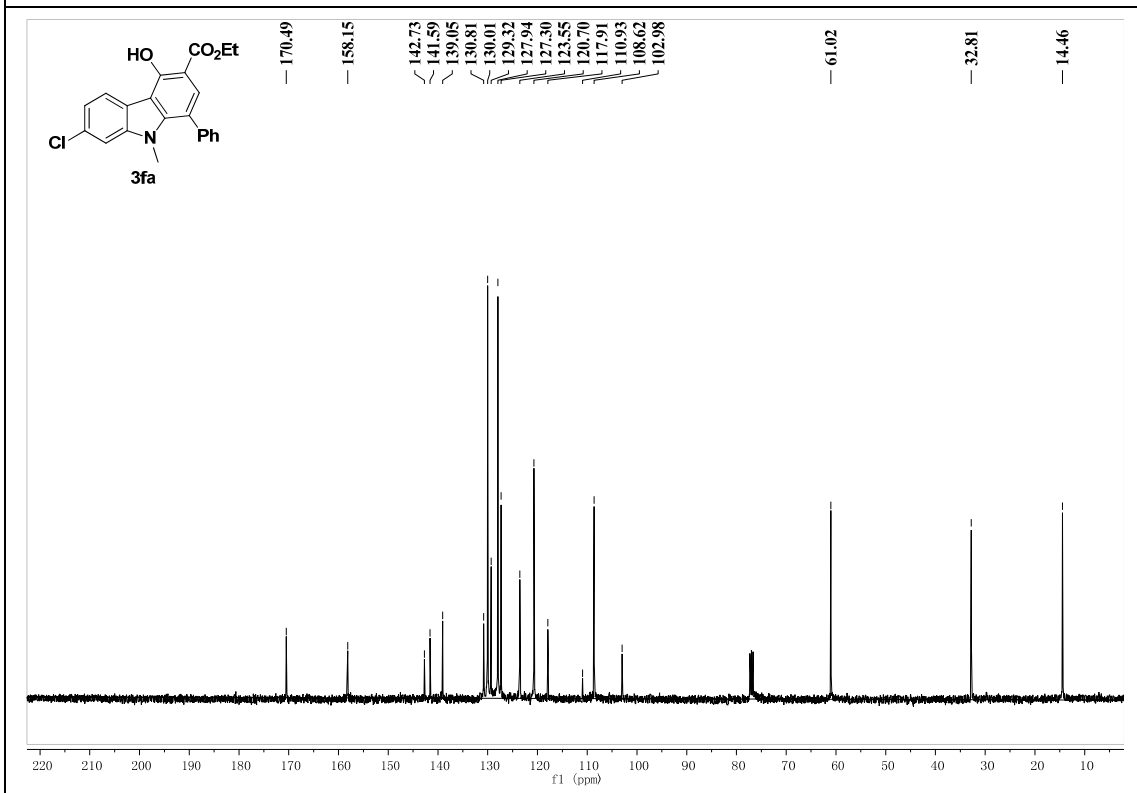
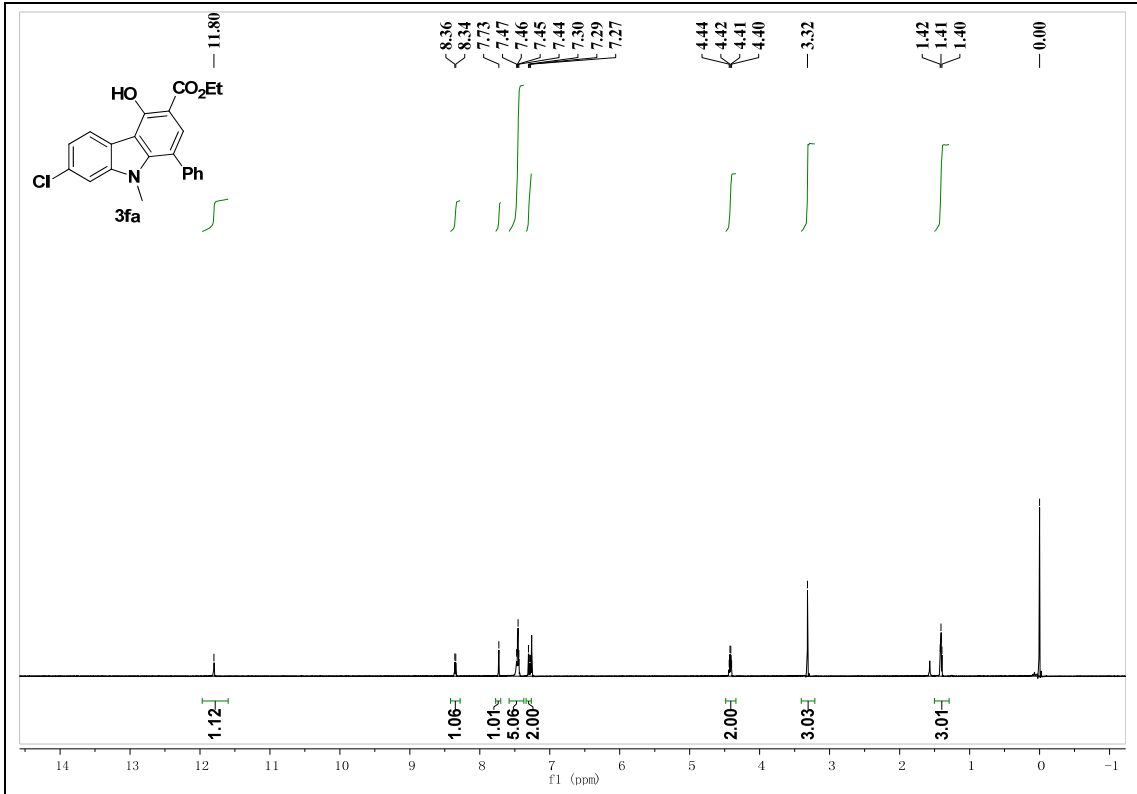


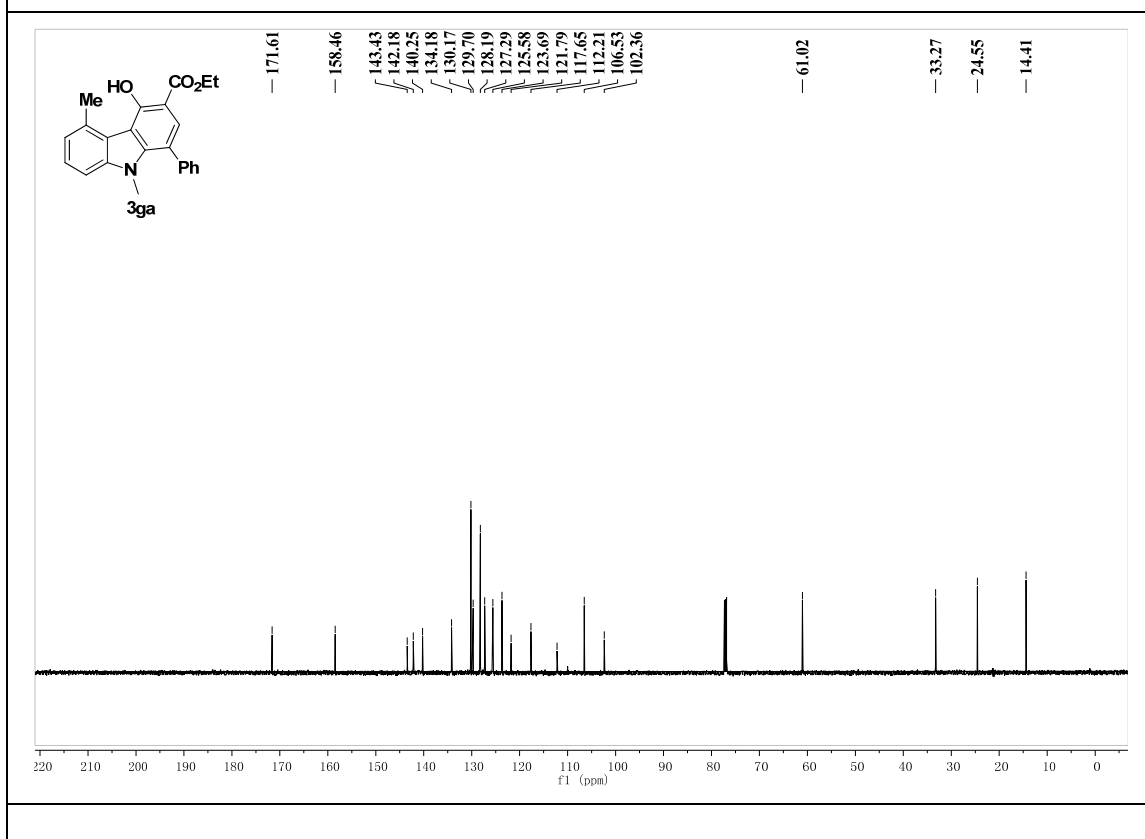
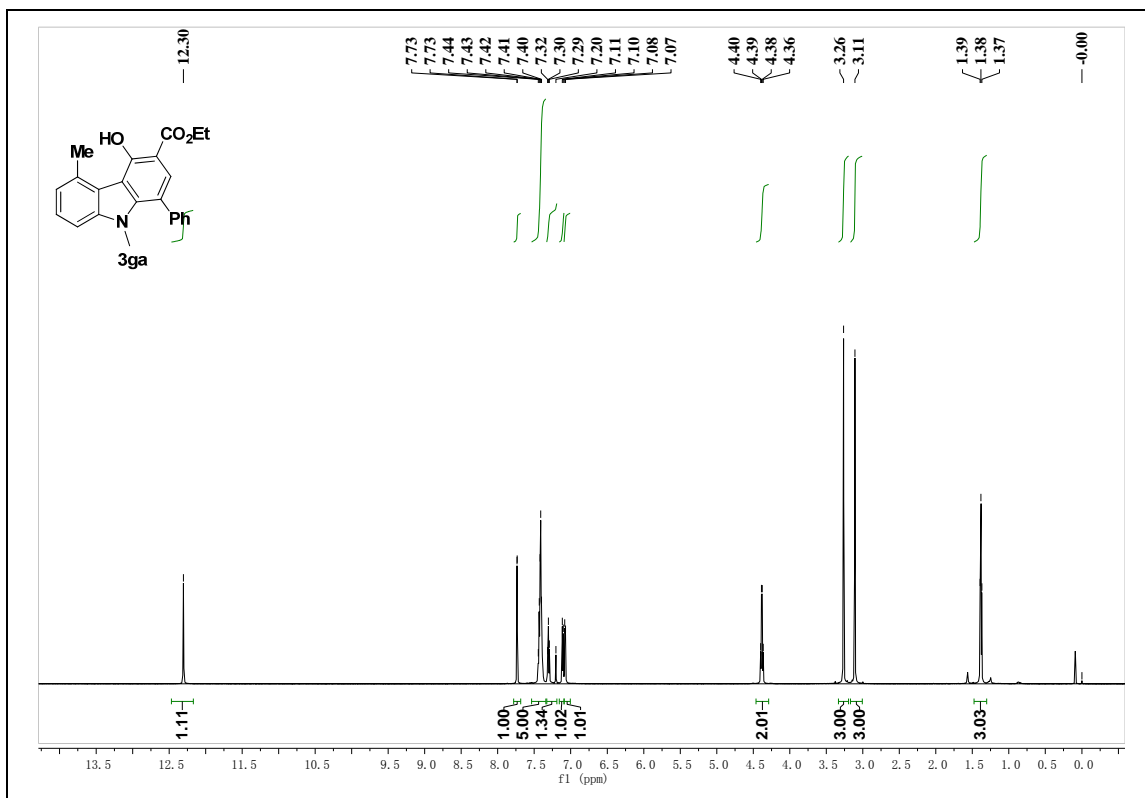


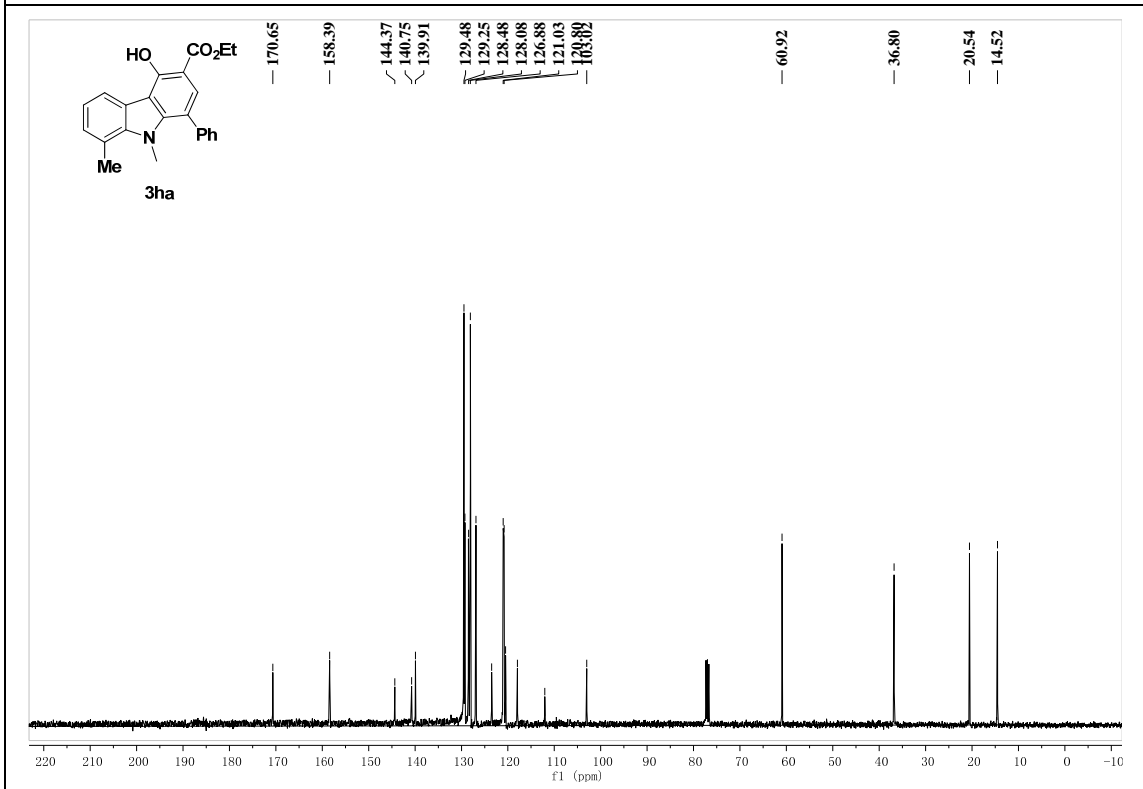
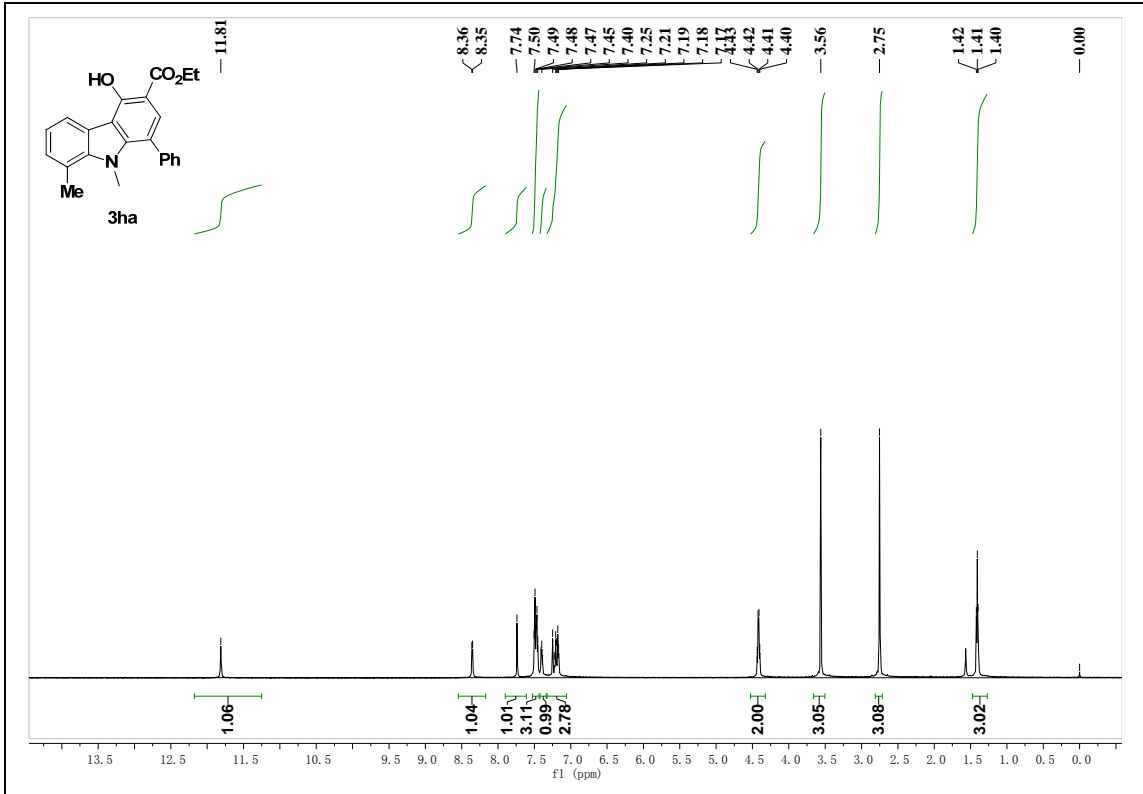


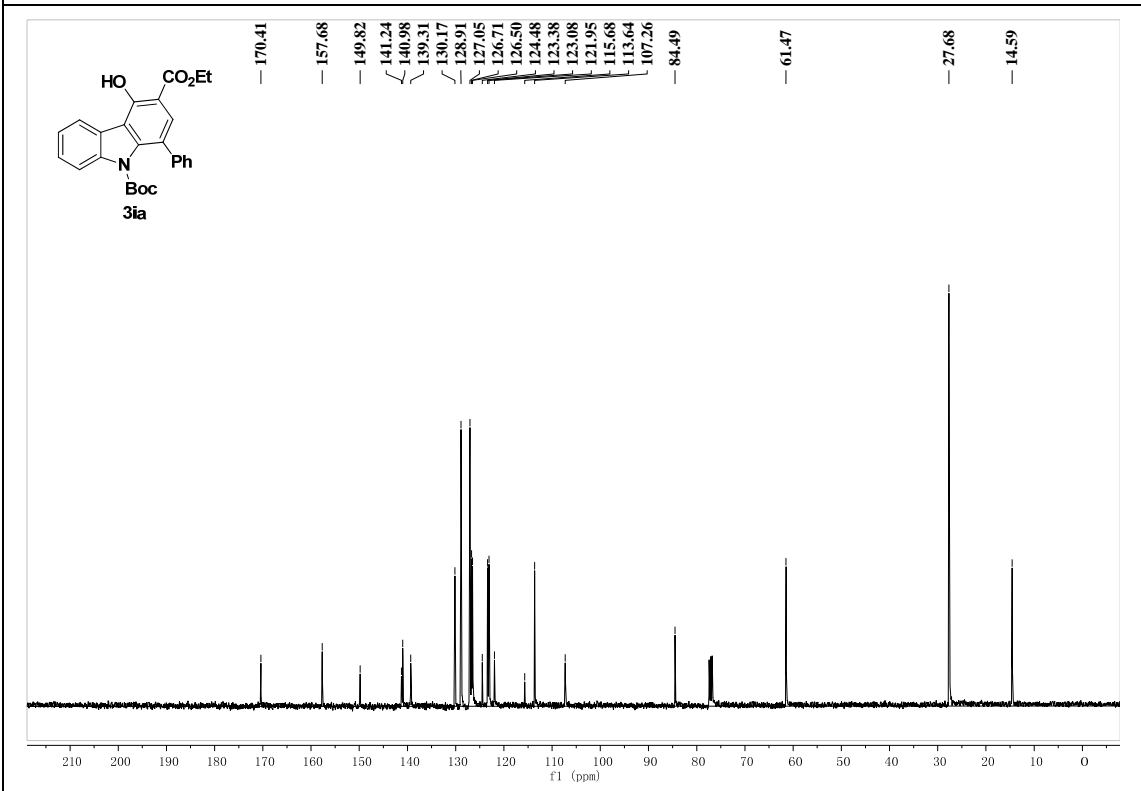
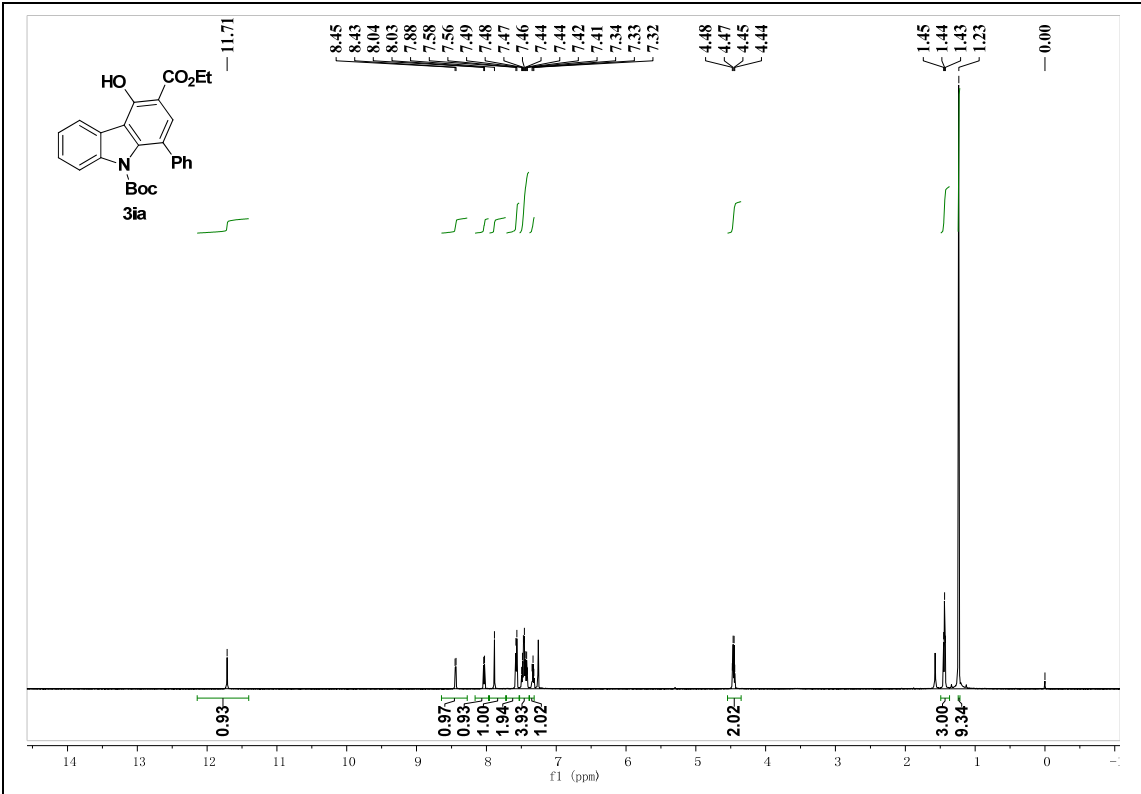


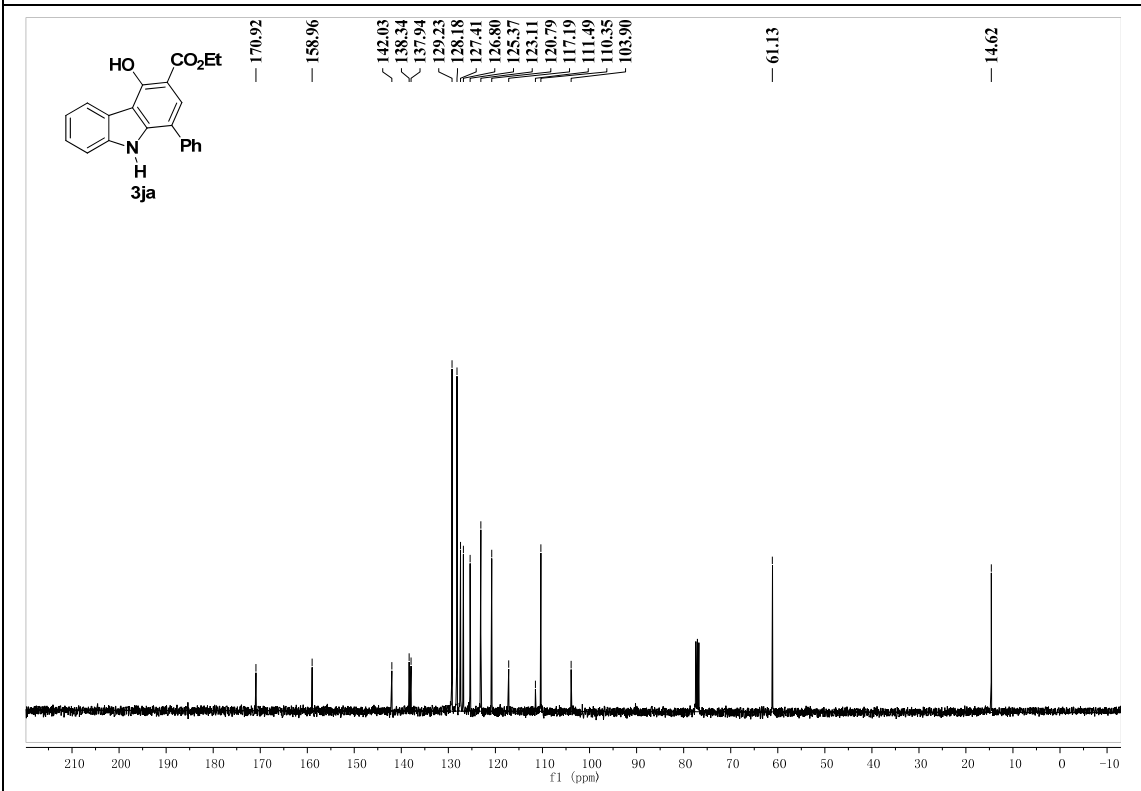
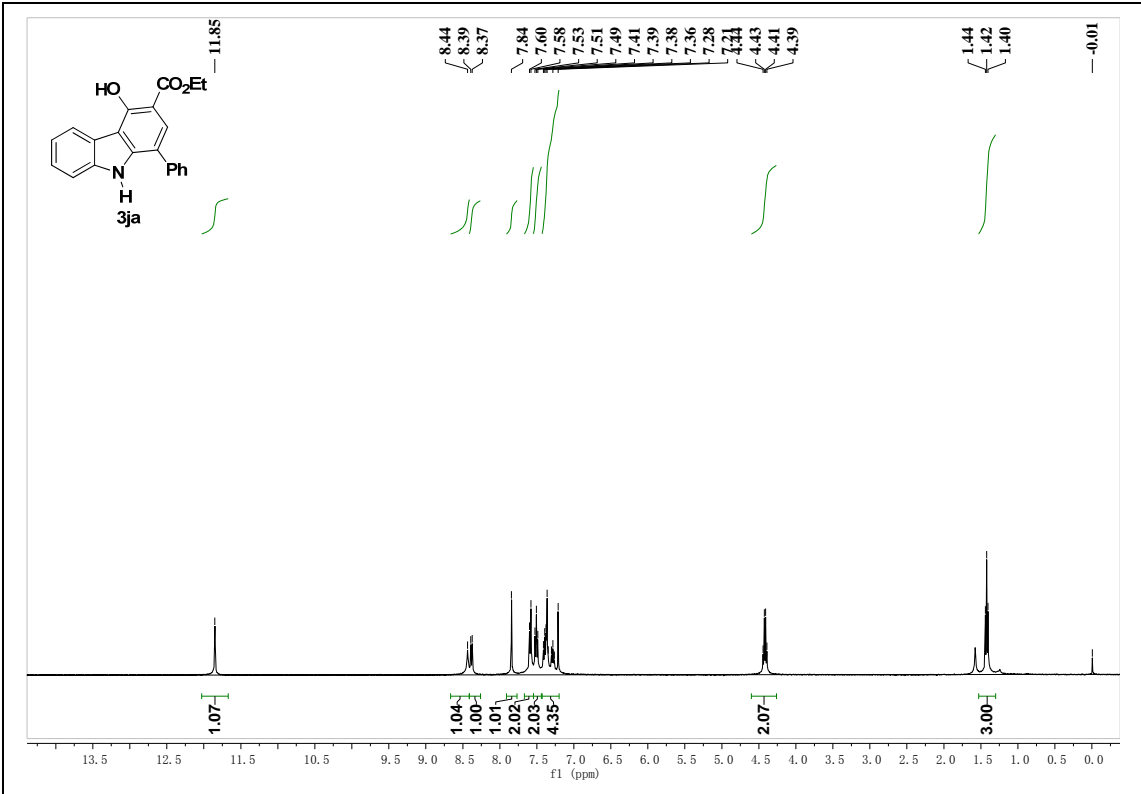


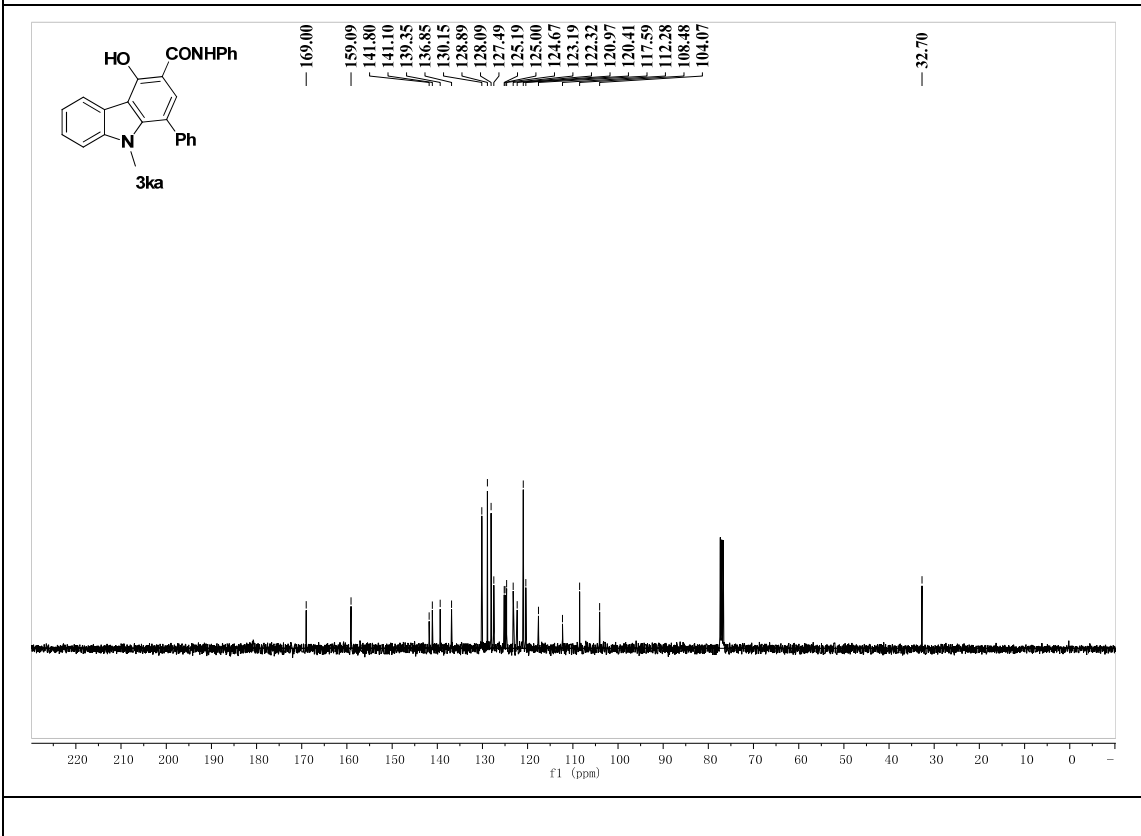
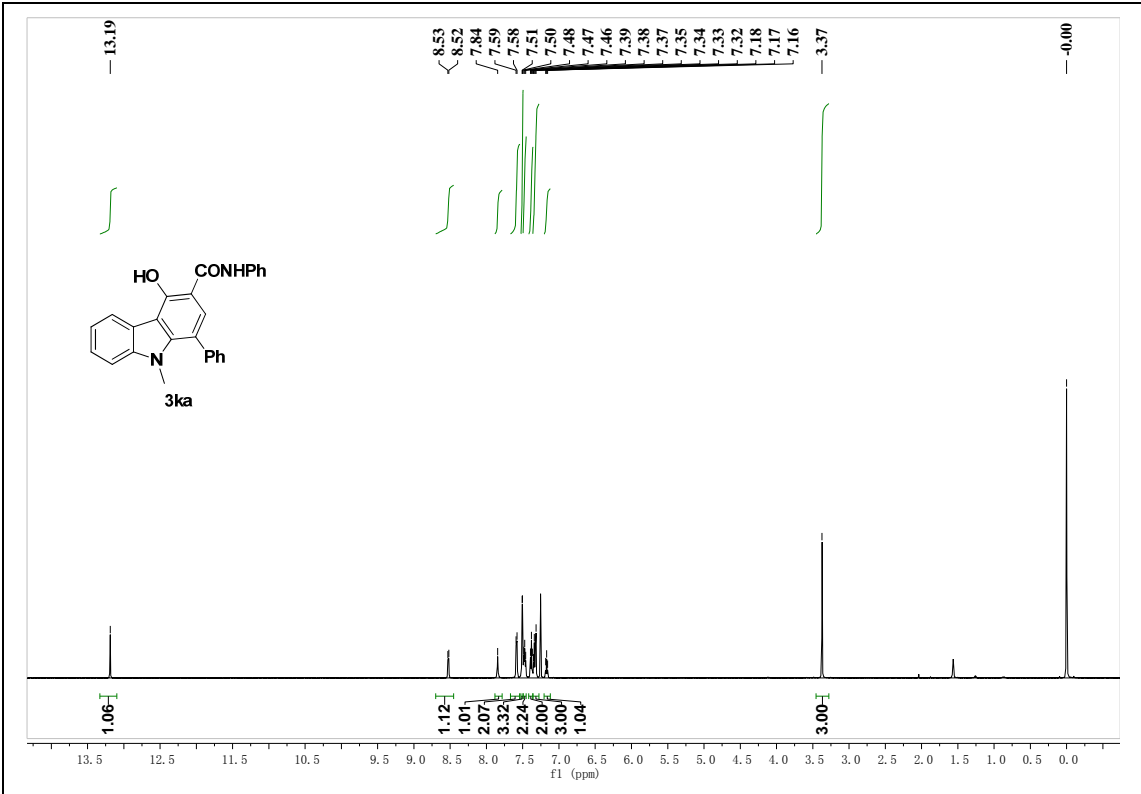


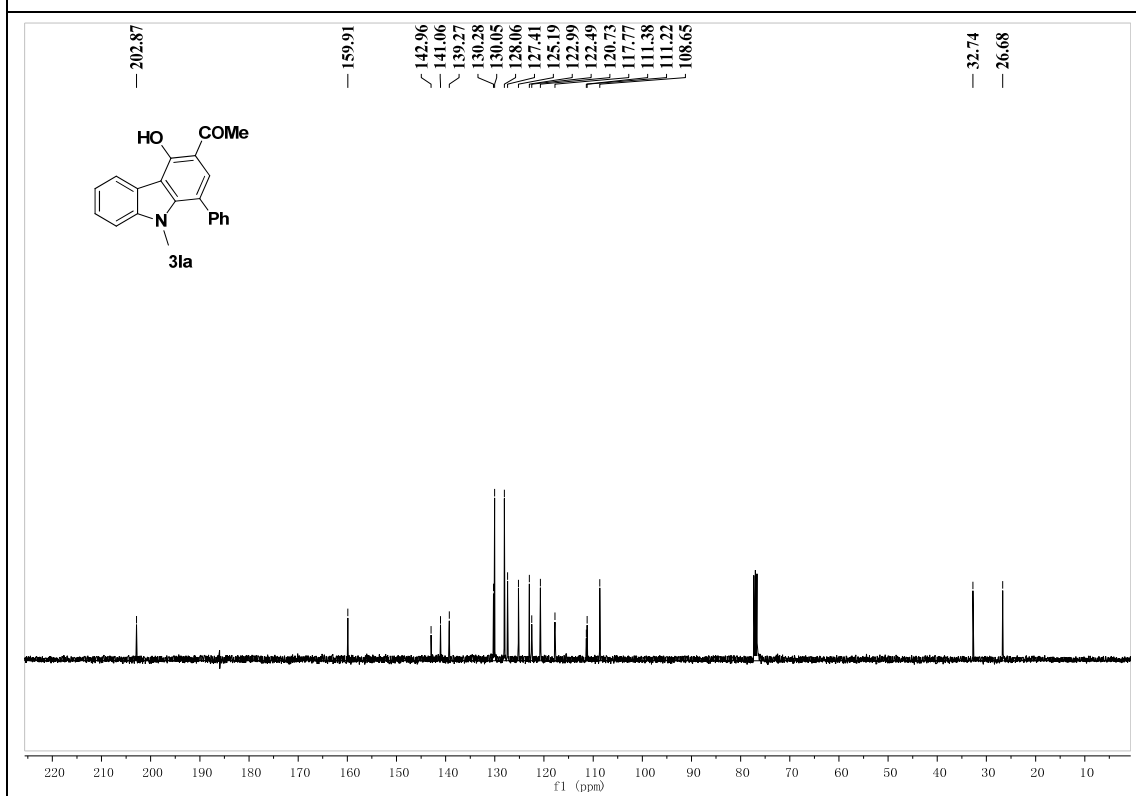
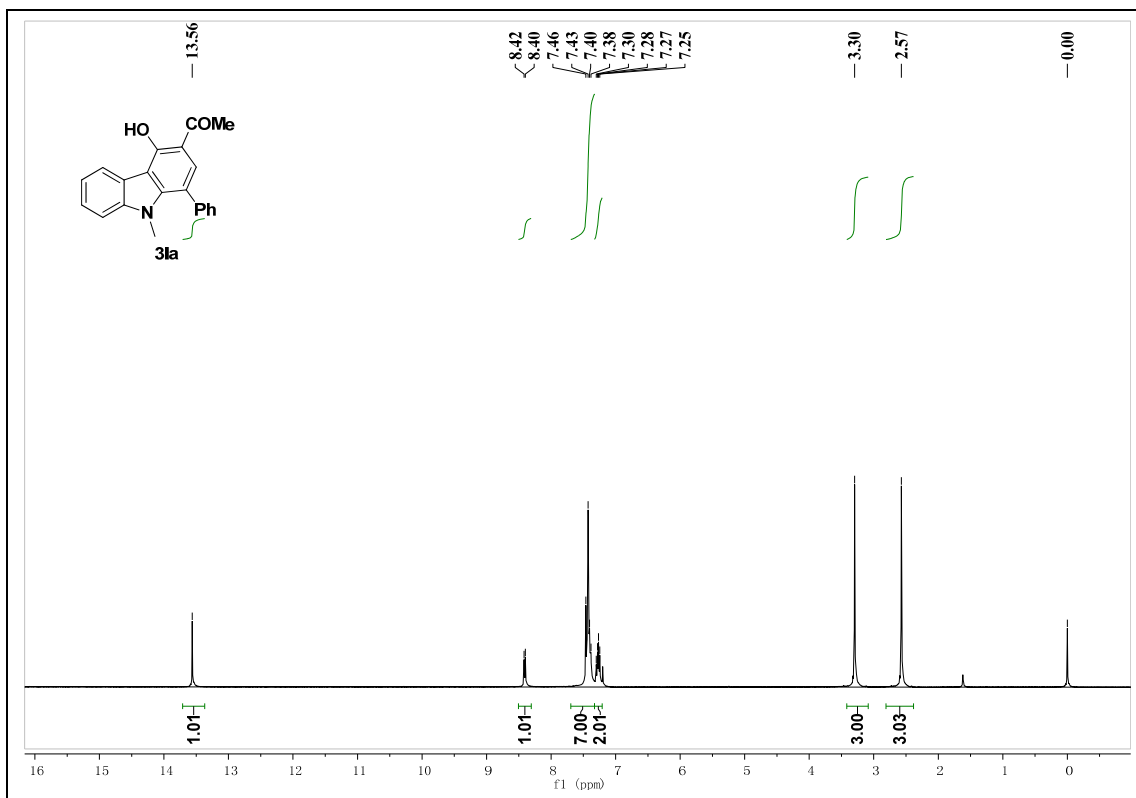












8. Copies of NMR Spectrums of Synthetic Transformation Prducts

