Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium/Copper-Cocatalyzed Coupling-Cyclization of *o*-Alkenyl Arylisocyanides with Vinyl Azides: One-Pot Synthesis of α-Carbolines

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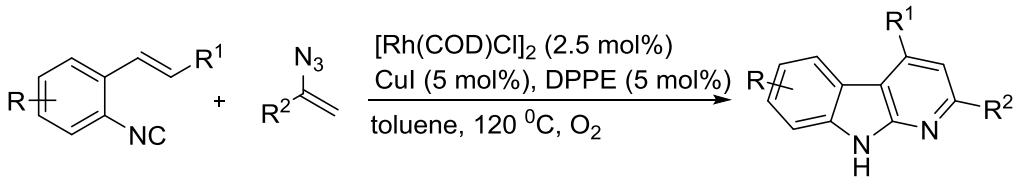
Table of contents

I. General Information:

All reagents were commercial and were used without further purification. The substrates were prepared according to the previous method reported.[1,2] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz, 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 470 MHz, 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3aa** was glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo Kradiation ($\lambda = 0.71073$Å) and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 3 (3aa as example):



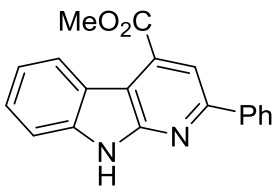
1 **2** **3**

A sealed tube equipped with a magnetic stir bar was charged with **1a** (37.4 mg, 0.2 mmol), **2a** (58.1 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), DPPE (4.1 mg, 0.01 mmol), then toluene (2.0 mL) was added. Subsequently, the reaction mixture was stirred under an oxygen atmosphere (oxygen balloon) at 120 ℃ for 3.5 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10, V/V) to afford pure product **3aa** (42.3 mg, 70%) as a yellow solid.

A gram-scale synthesis of compound 3aa:

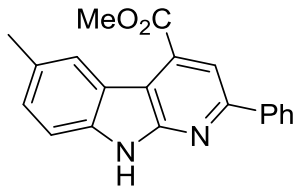
An oven-dried vial equipped with a magnetic stir bar was charged with **1a** (1.12 g, 6 mmol), **2a** (1.74 g, 12 mmol), $[Rh(COD)Cl]_2$ (73.9 mg, 0.15 mmol), CuI (57.1 mg, 0.3 mmol), DPPE (122.0 mg, 0.3 mmol), and toluene (60.0 mL) was added. Subsequently, the reaction mixture was stirred under an oxygen atmosphere (oxygen balloon) at 120 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10, V/V) to afford pure product **3aa** (1.14 g, 62%) as a yellow solid.

Methyl 2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3aa):



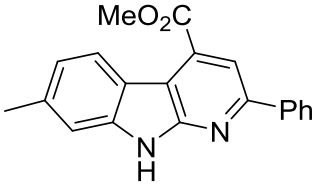
Yellow solid, mp: 182 – 183 ℃, 42.3 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.55 (s, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.21 – 8.15 (m, 3H), 7.57 – 7.53 (m, 2H), 7.52 – 7.49 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.13 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.06, 154.06, 153.81, 140.08, 139.38, 132.77, 129.23, 129.14, 127.69, 127.66, 125.80, 120.31, 119.72, 113.76, 113.55, 111.12, 52.66. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{15}N_2O_2^+$: 303.1128, found: 303.1121.

Methyl 6-methyl-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ba):



Yellow solid, mp: 191 – 192 ℃, 45.6 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.56 (s, 1H), 8.17 (d, *J* = 7.3 Hz, 2H), 8.15 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 4.14 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.14, 153.84, 139.38, 138.12, 132.58, 129.64, 129.16, 129.10, 129.05, 127.52, 125.60, 119.91, 113.52, 113.30, 110.66, 52.63, 21.72. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2^+$: 317.1285, found: 317.1290.

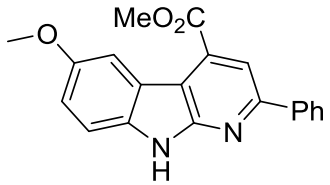
Methyl 7-methyl-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ca):



Yellow solid, mp: 183 – 184 ℃, 44.3 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.78 (d, *J* = 4.0 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.20 – 8.15 (m, 2H), 8.12 (s, 1H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.02 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.12 (s, 1H), 4.11 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.11, 154.01, 153.42, 140.67, 139.76, 138.14, 132.01, 129.22, 128.87, 127.91, 125.47, 121.83, 117.30,

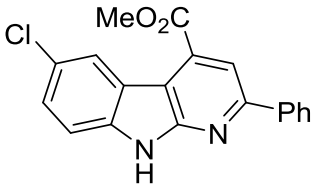
113.93, 113.67, 111.40, 52.56, 21.94. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2^+$: 317.1285, found: 317.1288.

Methyl 6-methoxy-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3da):



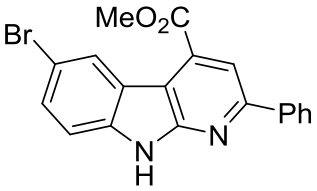
Yellow solid, mp: 154 – 155 ℃, 41.2 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.35 (d, *J* = 2.5 Hz, 1H), 8.17 (dd, *J* = 9.9, 2.6 Hz, 3H), 7.56 – 7.52 (m, 2H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 4.13 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.03, 154.08, 154.04, 153.96, 139.36, 134.82, 132.62, 129.13, 129.10, 127.55, 120.16, 117.47, 113.50, 113.46, 111.67, 108.23, 55.94, 52.66. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO_3^+$: 355.1053, found: 355.1051.

Methyl 6-chloro-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ea):



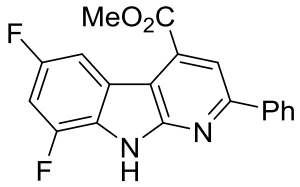
Yellow solid, mp. 192 – 193 ℃, 43.1 mg, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.51 (s, 1H), 8.77 (d, *J* = 2.1 Hz, 1H), 8.18 – 8.08 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 3H), 7.23 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.40 (d, *J* = 8.6 Hz, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.57, 154.83, 153.93, 139.08, 138.19, 133.10, 129.36, 129.26, 127.79, 127.70, 125.75, 125.53, 120.75, 114.21, 112.75, 112.02, 52.78. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{14}ClN_2O_2^+$: 337.0738, found: 337.0732.

Methyl 6-bromo-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3fa):



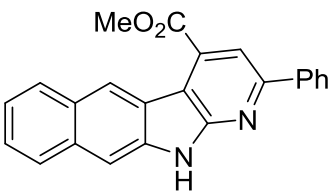
Yellow solid, mp: 192 – 193 ℃, 43.5 mg, 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.92 (s, 1H), 8.12 (s, 1H), 8.11 – 8.09 (m, 2H), 7.53 (d, *J* = 5.0 Hz, 3H), 7.32 (d, *J* = 8.7 Hz, 1H), 6.21 (d, *J* = 8.6 Hz, 1H), 4.15 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.51, 154.80, 153.76, 139.04, 138.51, 133.08, 130.34, 129.35, 129.27, 128.50, 127.73, 121.27, 114.26, 113.18, 112.61, 112.49, 52.78. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{14}BrN_2O_2^+$: 381.0233, found: 381.0227.

Methyl 6,8-difluoro-2-phenyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ga):



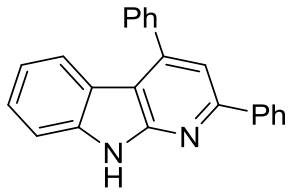
Yellow solid, mp: 197 – 198 ℃, 33.8 mg, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.34 (dd, *J* = 9.9, 2.3 Hz, 1H), 8.20 (s, 1H), 8.12 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.02 – 7.06 (m, 1H), 4.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.40, 156.64 (dd, *J* = 237.07 Hz, 9.8 Hz), 155.66, 153.52, 147.81 (dd, *J* = 247.64 Hz, 13.6Hz), 138.54, 133.27, 129.52, 128.91, 127.25, 124.47 (d, *J* = 15.0 Hz), 122.33 (d, *J* = 6.2 Hz), 114.20, 112.61, 107.63 (dd, *J* = 25.67 Hz, 4.53 Hz), 102.71 (dd, *J* = 29.7, 19.9 Hz), 52.78. ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.64 (t, *J* = 9.7 Hz), -131.74 (d, *J* = 10.4 Hz). HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{13}F_2N_2O_2^+$: 339.0940, found: 339.0941.

Methyl 2-phenyl-11*H*-benzo[*f*]pyrido[2,3-*b*]indole-4-carboxylate (3ha):



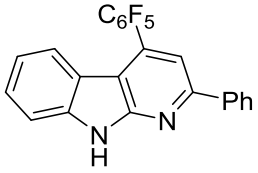
Yellow solid, mp: >250 ℃, 38.1 mg, 54% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.81 (s, 1H), 8.26 (d, *J* = 7.4 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.04 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 4.06 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 170.19, 151.97, 151.68, 139.14, 138.78, 135.48, 130.04, 129.64, 129.62, 129.41, 129.02, 127.28, 127.20, 124.22, 123.80, 113.78, 112.17, 111.39, 110.34, 53.23. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{16}N_2NaO_2^+$: 375.1104, found: 375.1098.

2,4-Diphenyl-9*H*-pyrido[2,3-*b*]indole (3ia):



Yellow solid, mp: 220 – 222 ℃, 46.8 mg, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.29 (s, 1H), 8.17 – 8.11 (m, 2H), 7.68 – 7.63 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.42 (m, 6H), 7.39 (dd, *J* = 8.3, 6.1 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.31, 153.45, 146.27, 140.24, 139.52, 139.30, 129.23, 128.85, 128.79, 128.78, 128.70, 127.92, 126.37, 122.32, 120.53, 119.44, 114.45, 112.99, 111.48. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{23}H_{17}N_2^+$: 321.1386, found: 321.1379.

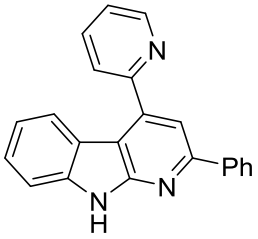
4-(Perfluorophenyl)-2-phenyl-9*H*-pyrido[2,3-*b*]indole (3ja):



Brown solid, mp: 193 – 194 ℃, 55.8 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.19 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.55 (m, 3H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.61 – 6.55 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.54, 152.97, 145.16, 143.50, 139.51,

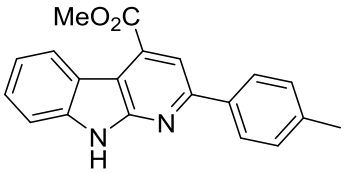
139.45, 137.21, 129.25, 129.20, 128.91, 127.77, 127.28, 121.07, 120.42, 119.79, 115.03, 114.01, 113.25, 111.67. ^{19}F NMR (470 MHz, $CDCl_3$) δ -139.41 (dd, *J* = 22.8, 8.3 Hz), -152.71 (t, *J* = 20.8 Hz), -160.60 (td, *J* = 22.2, 8.3 Hz). HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{23}H_{12}F_5N_2^+$: 411.0915, found: 411.0921.

2-Phenyl-4-(pyridin-2-yl)-9*H*-pyrido[2,3-*b*]indole (3ka):



Brown solid, mp: 192 – 193 ℃, 47.6 mg, 74% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.23 (d, *J* = 4.8 Hz, 1H), 8.91 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.23 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.90 – 7.86 (m, 2H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.49 – 7.46 (m, 1H), 7.45 – 7.42 (m, 1H), 7.14 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.42 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.44, 154.40, 153.68, 150.07, 144.29, 140.07, 139.75, 136.77, 129.14, 128.83, 127.86, 126.65, 124.13, 123.49, 122.99, 120.22, 119.54, 114.05, 112.71, 111.48. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{22}H_{16}N_3^+$: 322.1339, found: 322.1342.

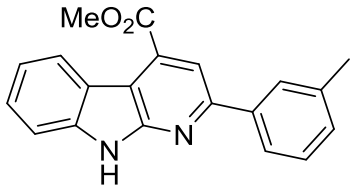
Methyl 2-(p-tolyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ab):



Yellow solid, mp: 193 – 194 ℃, 44.3 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.50 (s, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 4.12 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.13, 154.19, 153.78, 140.01, 139.21, 136.60, 132.72, 129.89, 127.56, 127.41, 125.70, 120.23, 119.80,

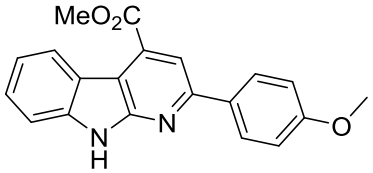
113.50, 113.23, 111.18, 52.62, 21.34. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2^+$: 317.1285, found: 317.1293.

Methyl 2-(m-tolyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ac):



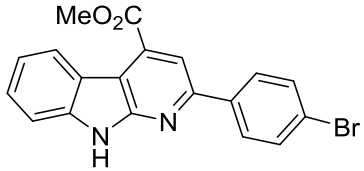
Yellow solid, mp: 160 – 162 ℃, 41.1 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 8.16 (s, 1H), 8.00 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.66 – 6.60 (m, 1H), 4.13 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.14, 154.27, 153.76, 140.04, 139.29, 138.93, 132.72, 129.89, 129.12, 128.31, 127.63, 125.73, 124.83, 120.31, 119.75, 113.80, 113.44, 111.08, 52.66, 21.60. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO_2^+$: 339.1104, found: 339.1104.

Methyl 2-(4-methoxyphenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ad):



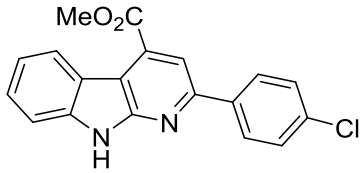
Yellow solid, mp: 174 – 176 ℃, 38.5 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.15 – 8.08 (m, 3H), 7.32 – 7.28 (m, 1H), 7.24 – 7.20 (m, 1H), 7.06 – 7.02 (m, 2H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.12 (d, *J* = 1.3 Hz, 3H), 3.87 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.14, 160.68, 153.85, 153.76, 139.90, 132.73, 131.92, 128.88, 127.37, 125.64, 120.27, 119.88, 114.59, 113.14, 112.85, 111.13, 55.50, 52.60. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO_3^+$: 355.1053, found: 355.1056.

Methyl 2-(4-bromophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ae):



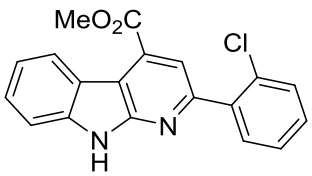
Yellow solid, mp: 199 – 200 ℃, 41.2 mg, 54% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.78 (d, *J* = 8.1 Hz, 1H), 8.13 (s, 1H), 8.05 – 7.99 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.89, 153.43, 152.72, 139.87, 138.06, 132.77, 132.16, 128.89, 128.02, 126.09, 123.61, 120.69, 119.86, 113.66, 113.41, 110.92, 52.72. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{14}BrN_2O_2^+$: 381.0233, found: 381.0223.

Methyl 2-(4-chlorophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3af):



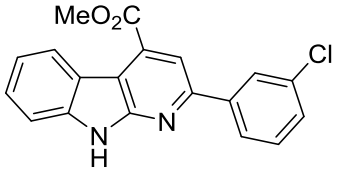
Yellow solid, mp: 197 – 198 ℃, 43.8 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.78 (d, *J* = 8.1 Hz, 1H), 8.14 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.85, 153.54, 152.59, 139.96, 137.62, 135.29, 132.74, 129.25, 128.70, 127.93, 127.07, 126.04, 120.58, 119.75, 113.70, 113.42, 110.97, 52.69. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{14}ClN_2O_2^+$: 337.0738, found: 337.0739.

Methyl 2-(2-chlorophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ag):



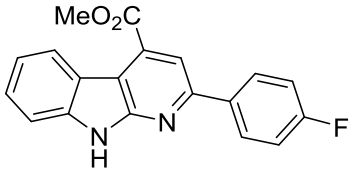
Yellow solid, mp: 194 – 195 ℃, 45.8 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (s, 1H), 8.79 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.05 (s, 1H), 7.77 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.48 (td, *J* = 7.8, 1.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 6.30 (d, *J* = 8.1 Hz, 1H), 4.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.91, 153.42, 152.52, 140.32, 139.03, 133.05, 132.07, 131.96, 130.50, 129.92, 127.86, 127.42, 125.98, 120.30, 119.46, 117.13, 113.98, 111.00, 52.67. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{14}ClN_2O_2^+$: 337.0738, found: 337.0730.

Methyl 2-(3-chlorophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ah):



Yellow solid, mp: 168 – 170 ℃, 48.5 mg, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 7.99 (m, 1H), 7.95 (d, *J* = 1.0 Hz, 1H), 7.87 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.02 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.76, 153.51, 152.13, 140.96, 140.06, 135.15, 132.66, 130.33, 128.99, 128.02, 127.54, 126.08, 125.55, 120.53, 119.65, 114.03, 113.59, 110.95, 52.69. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{13}ClN_2NaO_2^+$: 359.0558, found: 359.0551.

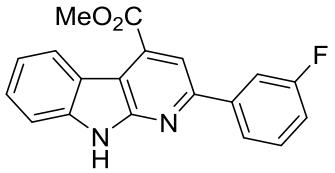
Methyl 2-(4-fluorophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ai):



Yellow solid, mp: 166 – 169 ℃, 42.9 mg, 67% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.75 (d, *J* = 8.1 Hz, 1H), 8.16 – 8.11 (m, 2H), 8.09 (d, *J* = 1.0 Hz, 1H), 7.37 (td, *J* = 7.6, 7.0, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.20 (t, *J* = 8.6 Hz, 2H), 6.80 –

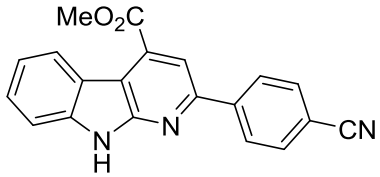
6.76 (m, 1H), 4.13 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.93, 164.43, 162.78, 153.25 (d, *J* = 102.68 Hz), 139.91, 135.39 (d, *J* = 3.02), 132.79, 129.30 (d, *J* = 9.06 Hz), 127.82, 125.95, 120.52, 119.77, 116.06 (d, J = 21.14), 113.42 (d, *J* = 4.53), 110.92, 77.25, 52.69. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.53 – -112.59 (m). HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{13}FN_2NaO_2^+$: 343.0853, found: 343.0856.

Methyl 2-(3-fluorophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3aj):



Yellow solid, mp: 164 – 165 ℃, 41.6 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.75 (d, *J* = 7.8 Hz, 1H), 8.08 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 10.0 Hz, 1H), 7.45 (q, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.81, 163.45 (d, *J* = 246.13), 153.54, 152.35 (d, *J* = 3.12 Hz), 141.50 (d, *J* = 7.55 Hz), 140.09, 132.71, 130.64 (d, *J* = 7.55), 127.99, 126.06, 123.09 (d, *J* = 3.02), 120.52, 119.68, 115.90 (d, *J* = 21.14 Hz), 114.40 (d, *J* = 24.16 Hz), 114.02, 113.64, 110.92, 52.68. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.20 (q, *J* = 8.4 Hz). HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{13}FN_2NaO_2^+$: 343.0853, found: 343.0854.

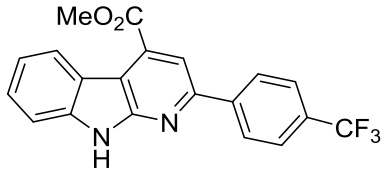
Methyl 2-(4-cyanophenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ak):



Yellow solid, mp: 168 – 169 ℃, 34.0 mg, 52% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.38 (s, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 2H), 8.24 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 5.9 Hz, 2H), 7.28 (td, *J* = 7.1, 6.1, 2.1 Hz, 1H), 4.08

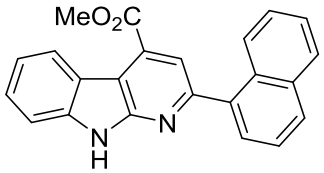
(s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.89, 153.48, 150.88, 143.06, 141.26, 133.26, 132.71, 128.71, 127.85, 125.97, 120.51, 119.27, 119.16, 113.30, 112.98, 111.87, 111.78, 53.27. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{14}N_3O_2^+$: 328.1081, found: 328.1089.

Methyl 2-(4-(trifluoromethyl)phenyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3al):



Green solid, mp: 173 – 175 ℃, 37.0 mg, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 2H), 8.09 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 (s, 1H), 7.25 (s, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.70, 153.57, 152.08, 142.54, 140.07, 132.75, 130.85 (d, *J* = 33.22 Hz), 128.12, 127.79, 126.18, 126 (d, *J* = 3.02 Hz), 124.17 (d, *J*= 271.8 Hz), 120.69, 119.59, 114.28, 113.84, 110.93, 52.72. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.54 (s). HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{14}F_3N_2O_2^+$: 371.1002, found: 371.0976.

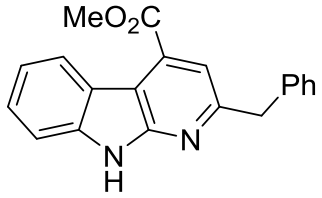
Methyl 2-(naphthalen-2-yl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3am):



Yellow solid, mp: 175 – 177 ℃, 45.8 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.77 (d, *J* = 7.9 Hz, 1H), 8.62 (d, *J* = 1.8 Hz, 1H), 8.30 (d, *J* = 9.9 Hz, 2H), 7.99 – 7.94 (m, 2H), 7.92 – 7.89 (m, 1H), 7.53 (ddd, *J* = 6.6, 3.9, 1.8 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.95 (s, 1H), 4.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.09, 153.93, 153.58, 139.86, 136.49, 133.68, 133.63, 132.72, 128.77, 127.73, 126.85, 126.71, 126.48, 125.93, 124.90, 120.51, 119.94, 113.97,

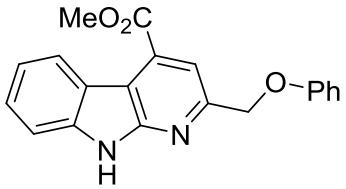
113.37, 110.95, 52.66. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{23}H_{17}N_2O_2^+$: 353.1285, found: 353.1285.

Methyl 2-benzyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3an):



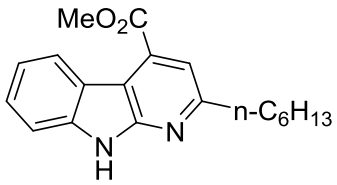
Yellow solid, mp: 160 – 161 ℃, 31.6 mg, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 7.59 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 8.6, 4.3 Hz, 1H), 4.34 (s, 2H), 4.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.06, 157.53, 153.05, 139.48, 139.26, 132.56, 129.06, 128.66, 127.63, 126.51, 125.89, 120.55, 120.08, 115.97, 112.47, 110.75, 52.53, 44.53. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{20}H_{17}N_2O_2^+$: 317.1285, found: 317.1287.

Methyl 2-(phenoxymethyl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ao):



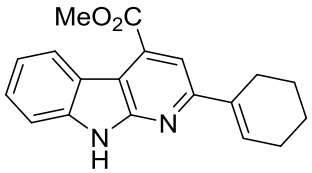
White solid, mp: 185 ℃, 26.6 mg, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.80 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.94 (s, 1H), 7.54 – 7.50 (m, 2H), 7.33 – 7.29 (m, 3H), 7.07 – 7.04 (m, 2H), 6.99 (td, *J* = 7.3, 1.0 Hz, 1H), 5.36 (s, 2H), 4.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 158.48, 153.38, 152.84, 139.57, 132.72, 129.56, 128.09, 126.21, 121.30, 120.73, 119.92, 114.97, 114.27, 114.07, 110.87, 70.77, 52.65. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{16}N_2NaO_3^+$: 355.1053, found: 355.1045.

Methyl 2-hexyl-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3ap):



White solid, mp: 158 – 159 ℃, 26.7 mg, 43% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.76 (d, *J* = 8.1 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.48 (m, 2H), 7.30 (td, *J* = 7.5, 6.9, 1.4 Hz, 1H), 4.11 (s, 3H), 3.07 – 3.03 (m, 2H), 1.85 (m, 2H), 1.42 (q, *J* = 7.2 Hz, 2H), 1.31 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.25, 159.31, 153.36, 139.43, 132.33, 127.37, 125.76, 120.35, 120.14, 115.29, 112.31, 110.78, 52.53, 38.45, 31.71, 30.35, 29.14, 22.58, 14.06. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{22}N_2NaO_2^+$: 333.1573, found: 333.1572.

Methyl 2-(cyclohex-1-en-1-yl)-9*H*-pyrido[2,3-*b*]indole-4-carboxylate (3aq):



Yellow solid, mp: 147 – 148 ℃, 38.0 mg, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.73 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.95 (q, *J* = 2.0 Hz, 1H), 4.11 (d, *J* = 1.5 Hz, 3H), 2.72 (q, *J* = 5.6, 4.4 Hz, 2H), 2.33 – 2.28 (m, 2H), 1.91 – 1.85 (m, 2H), 1.75 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.31, 155.73, 153.25, 139.99, 136.30, 132.34, 129.86, 127.40, 125.73, 120.23, 120.04, 112.94, 112.21, 111.02, 52.55, 26.61, 26.17, 22.96, 22.14. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_2^+$: 329.1260, found: 329.1268.

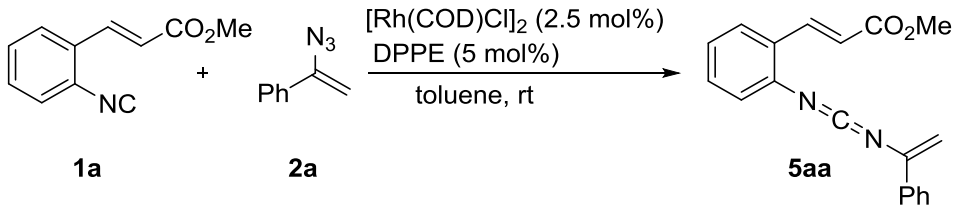
Reference:

1. (a) A. Li, E. Ahmed, X. Chen, M. Cox, A. P. Crew, H. Q. Dong, M. Jin, L. Ma, B. Panciker, K. W. Siu, A. G. Steinig, K. M. Stolz, P. A. R. Tavares, B. Volk, Q. Weng, D. Werner, M. J. Mulvihill, *Org. Biomol. Chem.*, **2007**, *5*, 61; (b) M. Tobisu, H. Fujihara, K. Koh and N. Chatani, *J. Org. Chem.*, **2010**, *75*, 4841; (c) Z. Hu, H. Yuan, Y. Men,

Q. Liu, J. Zhang, X. Xu, *Angew. Chem.*, *Int. Ed.*, **2016**, *55*, 7077. (d) T. Mitamura, K. Iwata and A. Ogawa, *J. Org. Chem.*, **2011**, *76*, 3880.

2. Y. Ning, Q. Ji, P. Liao, E. A. Anderson, X. Bi, *Angew. Chem.*, *Int. Ed.*, **2017**, *56*, 13805.

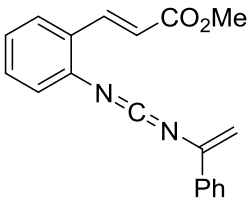
III. General Procedure for the Preparation of 5aa:



1a **2a** **5aa**

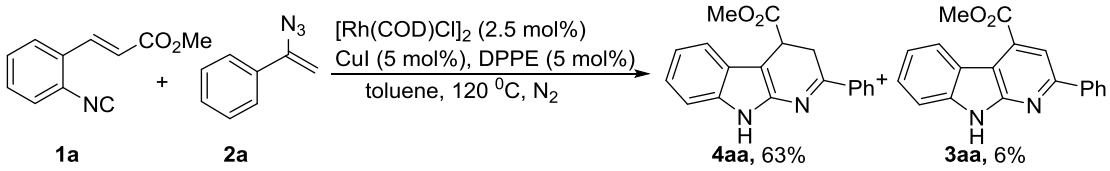
An oven-dried vial equipped with a magnetic stir bar was charged with **1a** (37.4 mg, 0.2 mmol), **2a** (58.1 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), DPPE (4.0 mg, 0.01 mmol), and toluene (2.0 mL) were added. The reaction was then stirred at room temperature for 3.5 h until arylisocyanide disappeared, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/15, V/V) to afford pure product **5aa** (29.2 mg, 48%) as a yellow liquid.

(*E*)-Methyl 3-(2-((((1-phenylvinyl)imino)methylene)amino)phenyl)acrylate (5aa):



Yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 16.1 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.55 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 (td, *J* = 7.7, 1.5 Hz, 1H), 7.20 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.48 (d, *J* = 16.1 Hz, 1H), 5.38 (s, 1H), 5.19 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.35, 141.80, 140.34, 138.25, 136.40, 132.69, 131.09, 128.94, 128.62, 128.60, 127.53, 125.69, 125.60, 125.54, 119.21, 106.30, 51.75. HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{19}H_{16}N_2NaO_2^+$: 327.1104, found: 327.1094.

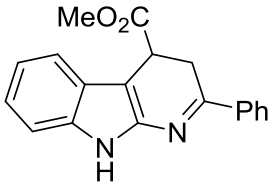
IV. General Procedure for the Preparation of 4aa:



1a **2a** **4aa,** 63% **3aa,** 6%

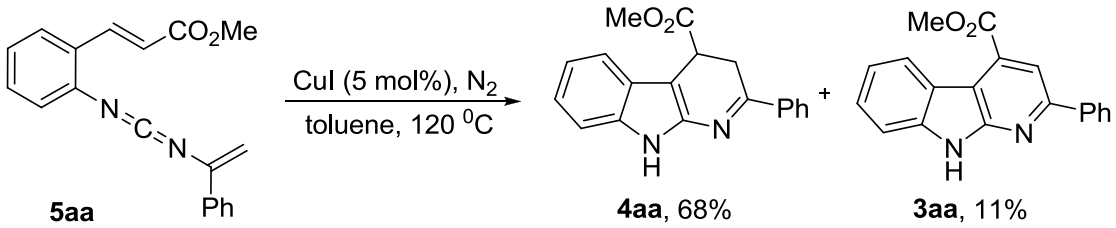
A Schlenck tube charged with **1a** (37.4 mg, 0.2 mmol), **2a** (58.1 mg, 0.4 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), DPPE (4.1 mg, 0.01 mmol) and a magnetic stir bar was evacuated three times under high vacuum and backfilled with N_2. Then toluene (2.0 mL) was added under N_2 atmosphere via syringe and the reaction mixture was heated and stirred for 2.5 h at 120 ℃. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford the mixture of product **4aa** and **3aa** in 69% yield (According to ^{1}H NMR of mixture **4aa** and **3aa**, **4aa**: **3aa** = 11: 1).

Methyl 2-phenyl-4,9-dihydro-3*H*-pyrido[2,3-*b*]indole-4-carboxylate (4aa):



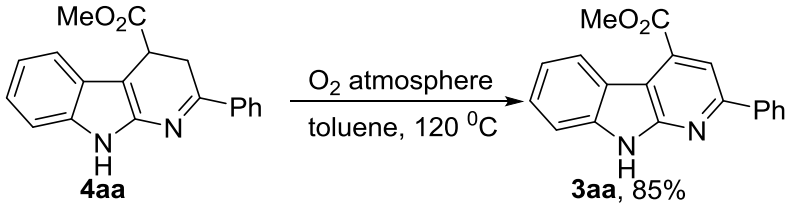
Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.07 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.12 – 7.07 (m, 1H), 7.05 – 6.99 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 4.21 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.70 – 3.73 (m, 1H), 3.66 (s, 3H), 3.07 – 3.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.52, 165.88, 142.52, 138.51, 134.60, 130.84, 128.87, 127.20, 125.32, 122.00, 120.38, 119.17, 111.59, 93.94, 52.25, 35.60, 28.97. HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{17}N_2O_2^+$: 305.1285, found: 305.1286.

V. General Procedure from 5aa to 4aa:



A Schlenck tube charged with **5aa** (60.9 mg, 0.2 mmol), CuI (1.9 mg, 0.01 mmol), and a magnetic stir bar was evacuated three times under high vacuum and backfilled with N_2. Then toluene (2.0 mL) was added under N_2 atmosphere via syringe and the reaction mixture was heated and stirred for 1.5 h at 120 ℃. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford the mixture of product **4aa** and **3aa** in 79% yield (According to ^{1}H NMR of mixture **4aa** and **3aa**, **4aa**: **3aa** = 6: 1).

VI. General Procedure from 4aa to 3aa:



An oven-dried vial equipped with a magnetic stir bar was charged with the mixture **4aa** (48.7 mg, 0.16 mmol) and **3aa** (12.2 mg, 0.04 mmol) under an O_2 atmosphere, then toluene (2.0 mL) was added. The reaction was stirred at 120 ℃ for 1.5 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure with rotary evaporator. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to afford pure product **3aa** generated from **4aa** (41.1 mg, 85%) as a yellow solid.

VII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 3-5：

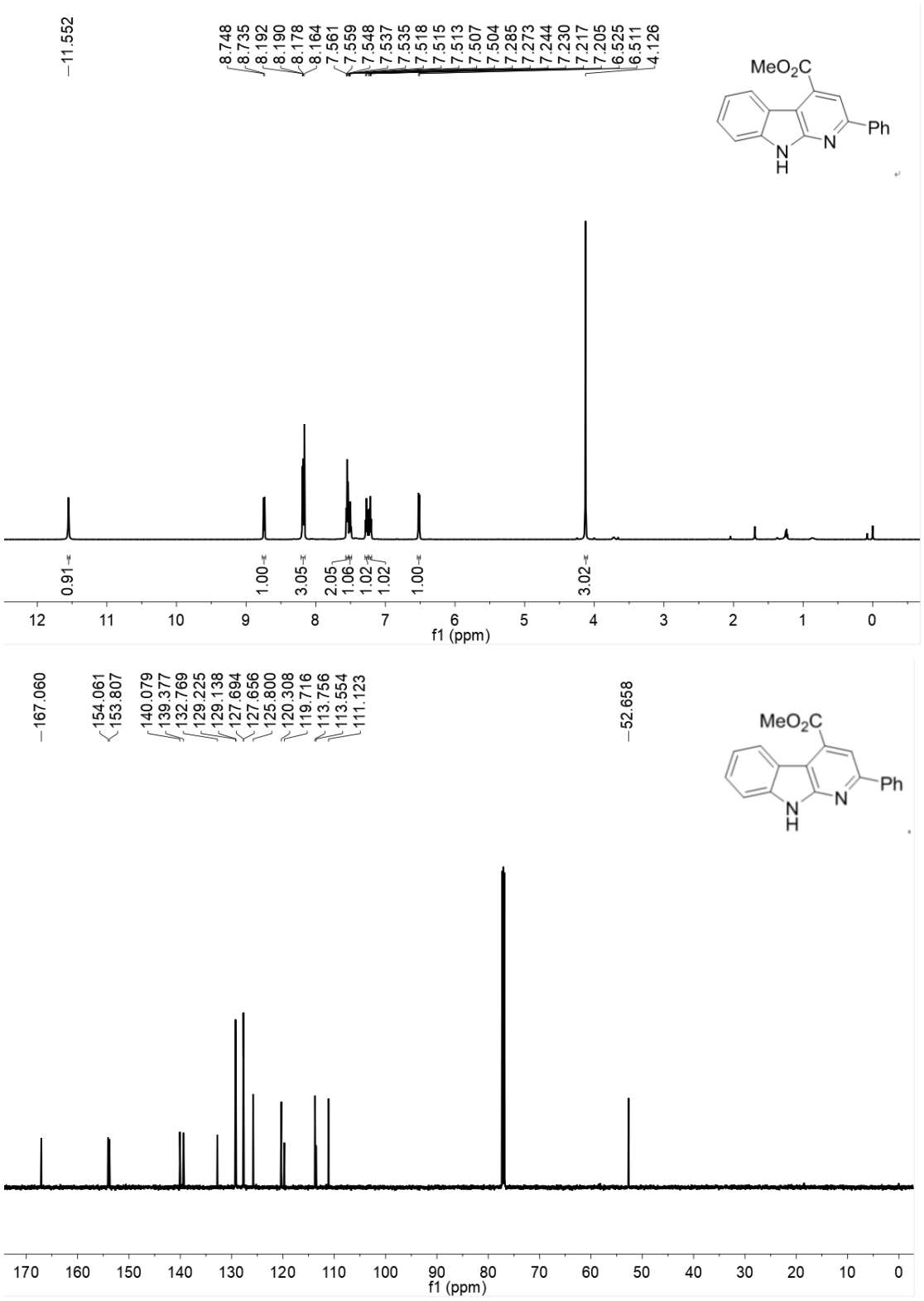


Figure 1. ^{1}H NMR, ^{13}C NMR spectra of compound **3aa**

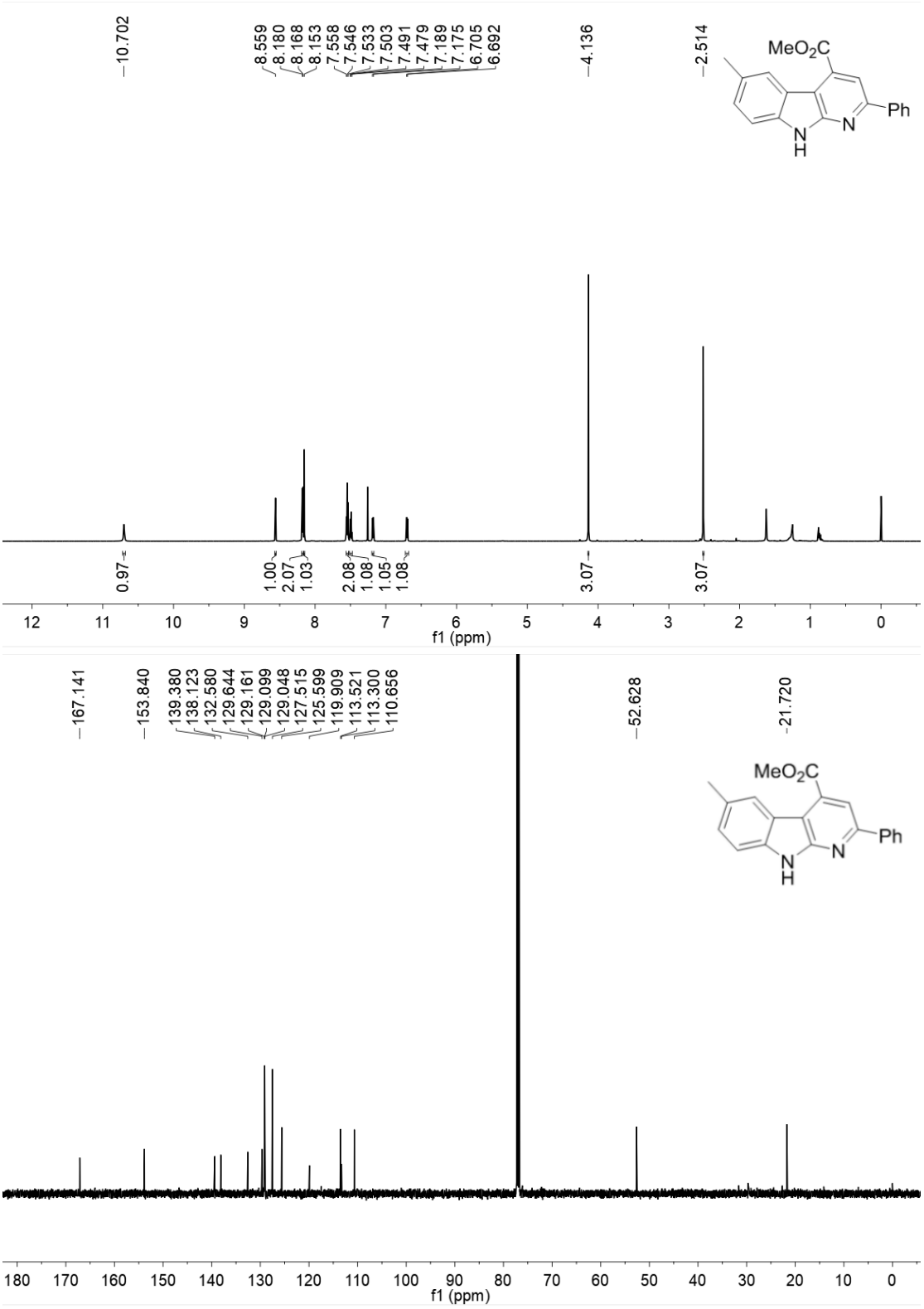


Figure 2. ^{1}H NMR, ^{13}C NMR spectra of compound **3ba**

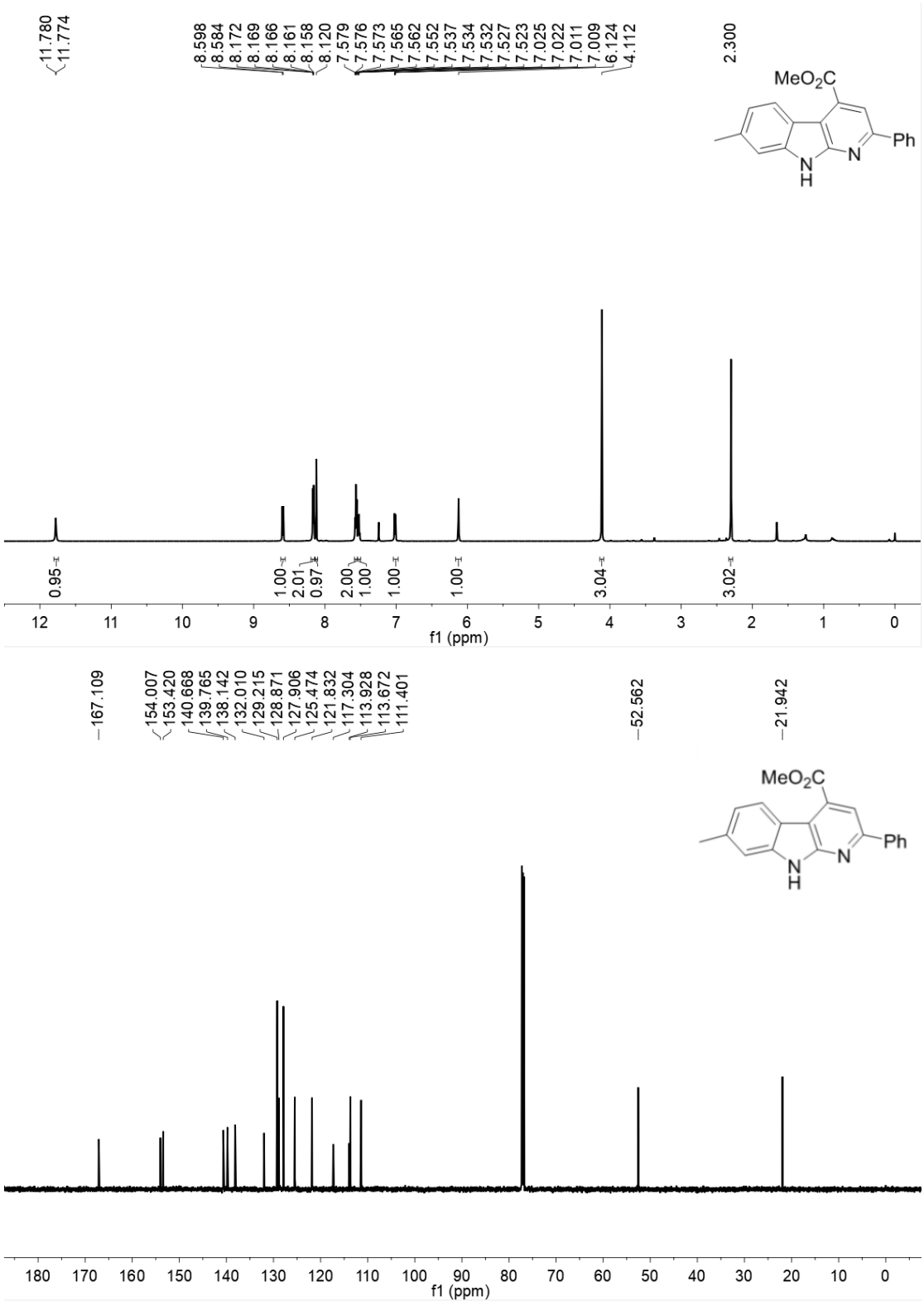


Figure 3. ^{1}H NMR, ^{13}C NMR spectra of compound **3ca**

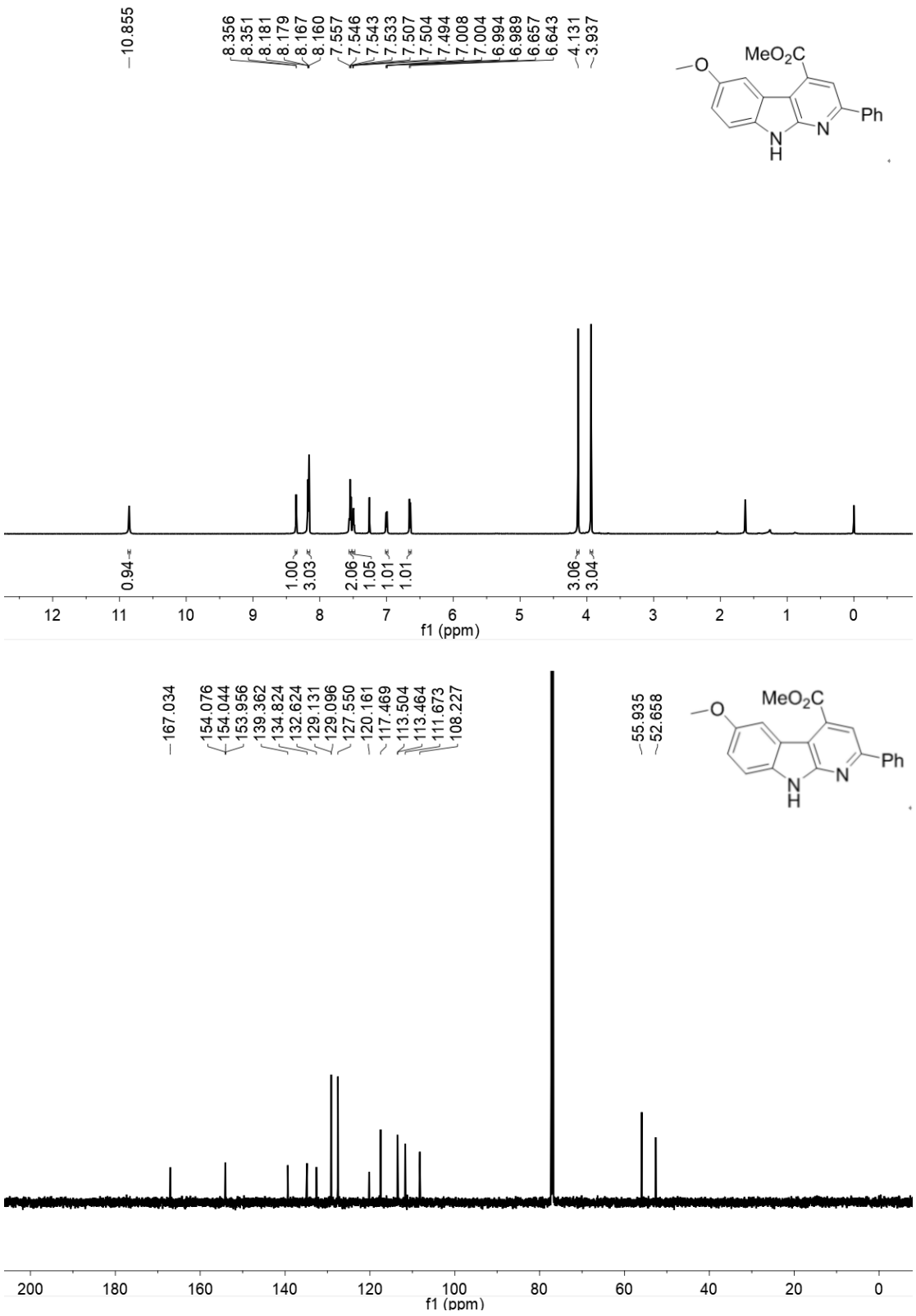


Figure 4. ^{1}H NMR, ^{13}C NMR spectra of compound **3da**

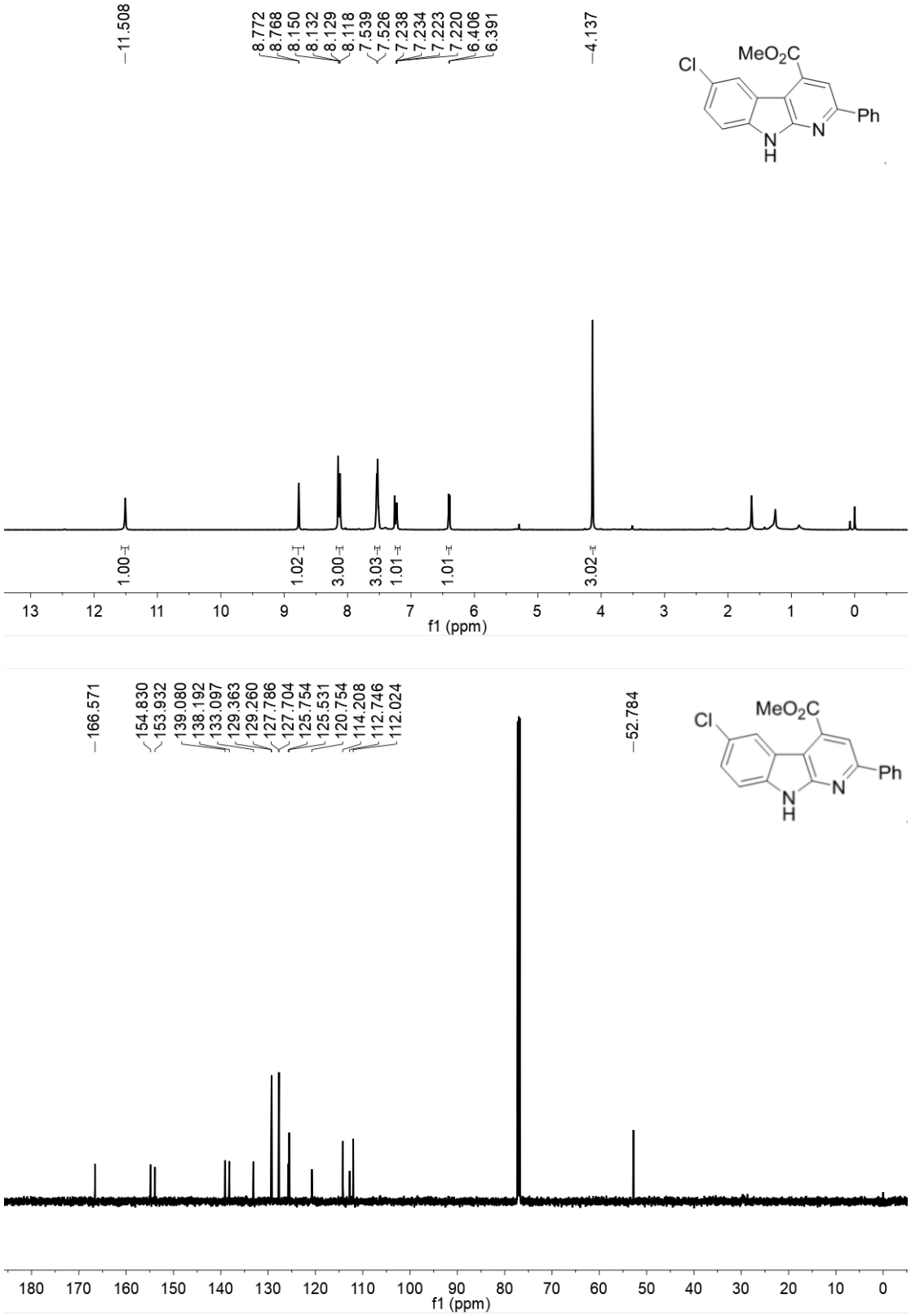


Figure 5. ^{1}H NMR, ^{13}C NMR spectra of compound **3ea**

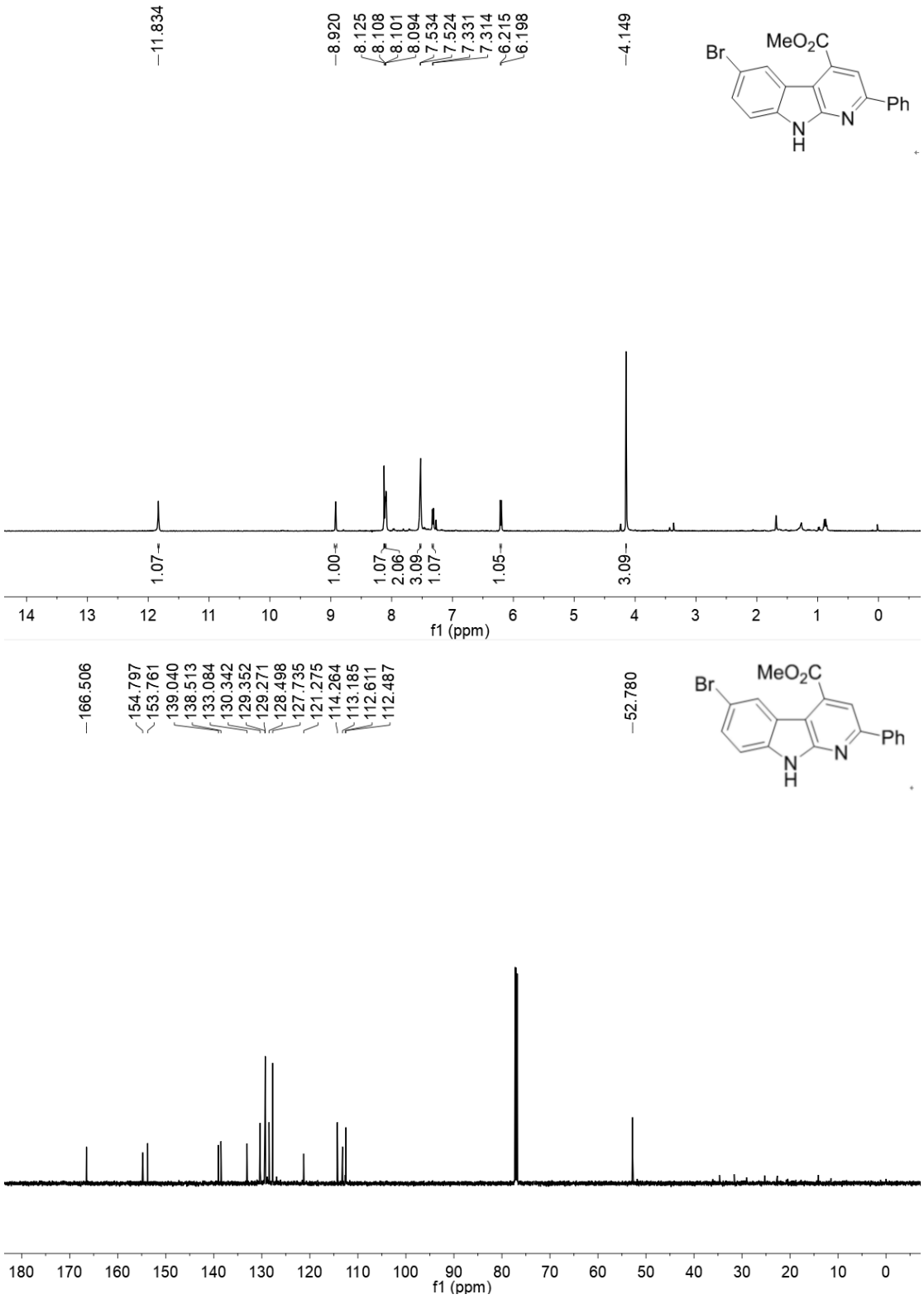
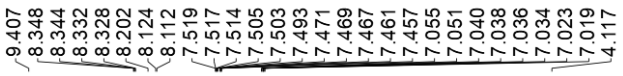
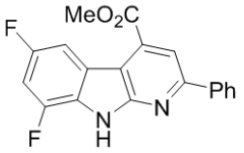
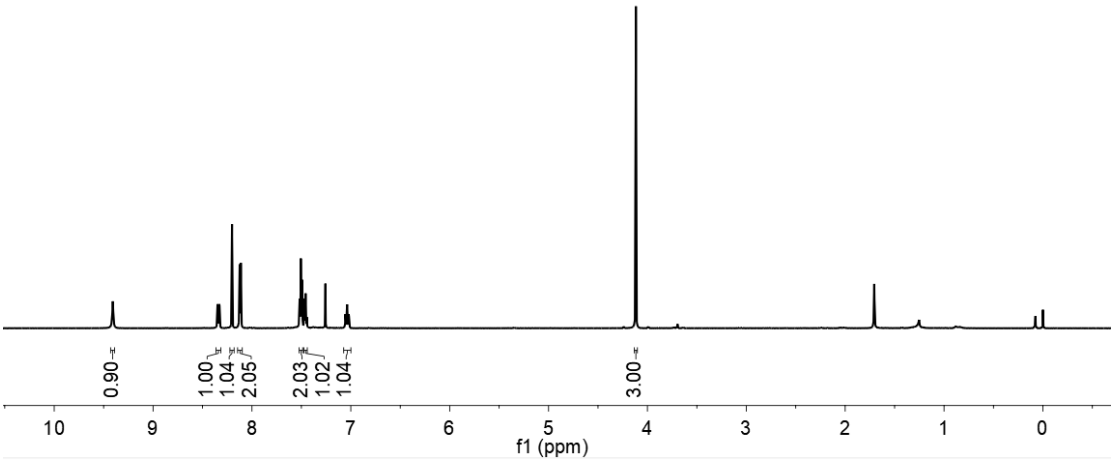
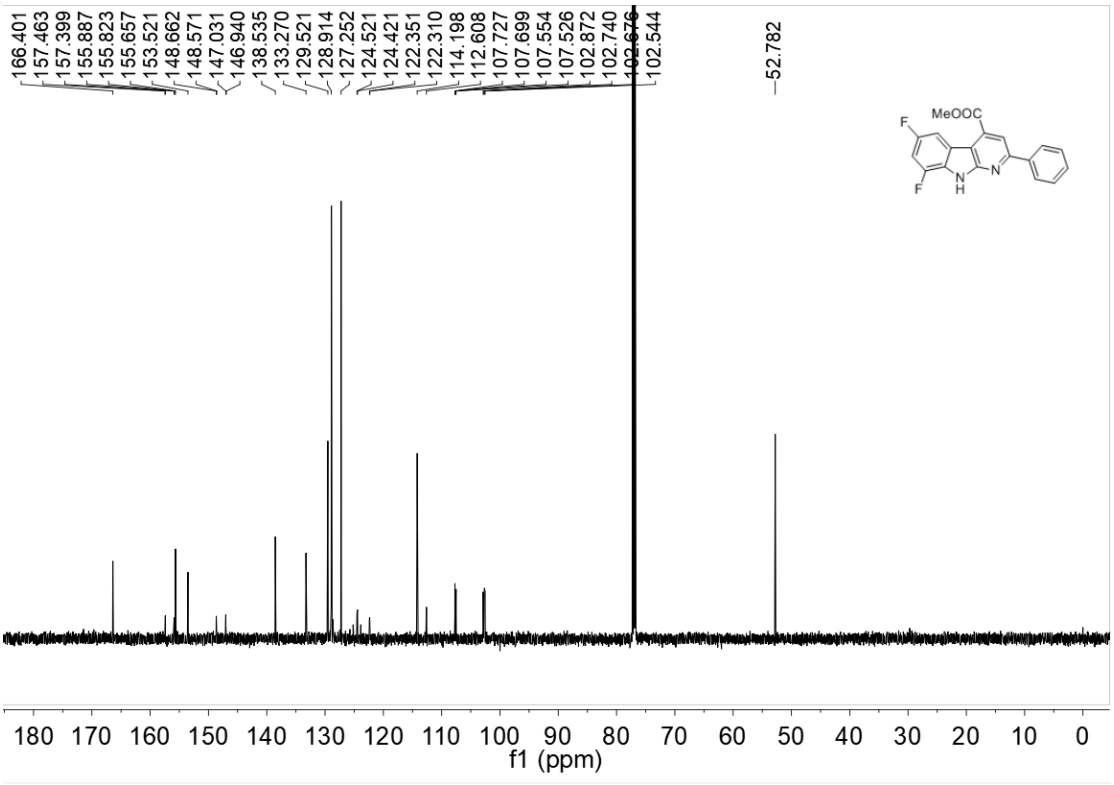


Figure 6. ^{1}H NMR, ^{13}C NMR spectra of compound **3fa**


9.407
8.348
8.344
8.332
8.328
8.202
8.124
8.112
7.519
7.517
7.514
7.505
7.503
7.493
7.471
7.469
7.467
7.461
7.457
7.055
7.051
7.040
7.038
7.036
7.034
7.023
7.019
4.117


MeO2C
F
Ph
N
N
H
F


0.90
1.00
1.04
2.05
2.03
1.02
1.04
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.401
157.463
157.399
155.887
155.823
155.657
153.521
148.662
148.571
147.031
146.940
138.535
133.270
129.521
128.914
127.252
124.521
124.421
122.351
122.310
114.198
112.608
107.727
107.699
107.554
107.526
102.872
102.740
102.676
102.544
52.782
MeOOC
F
N
H
N
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

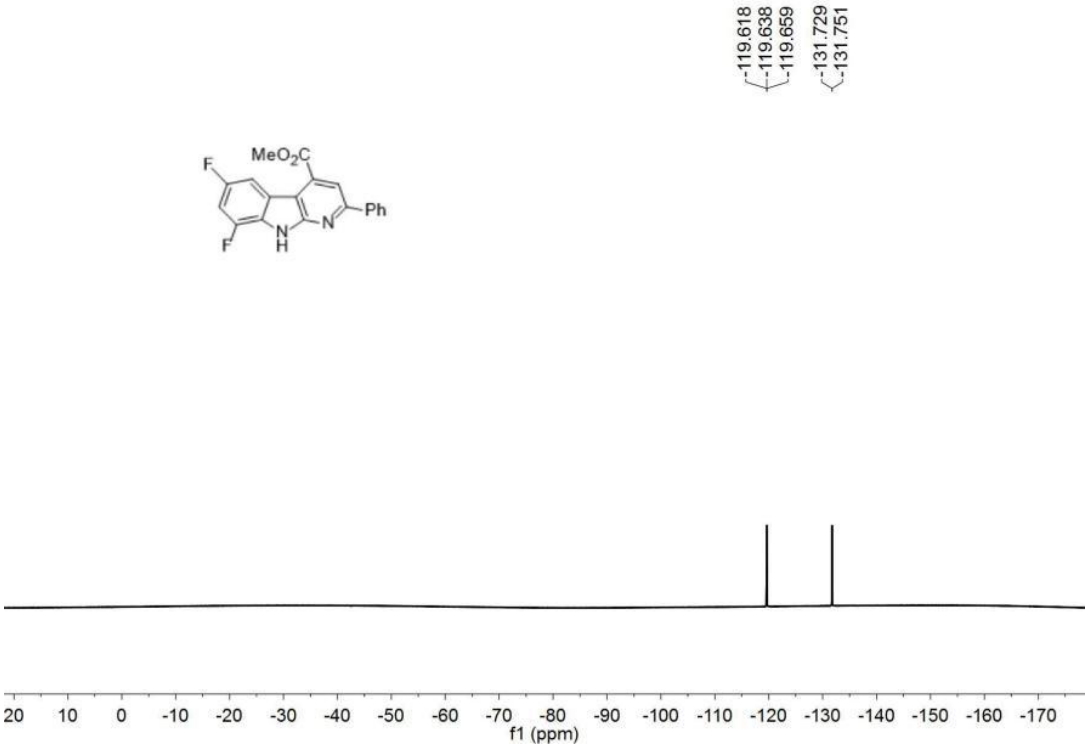
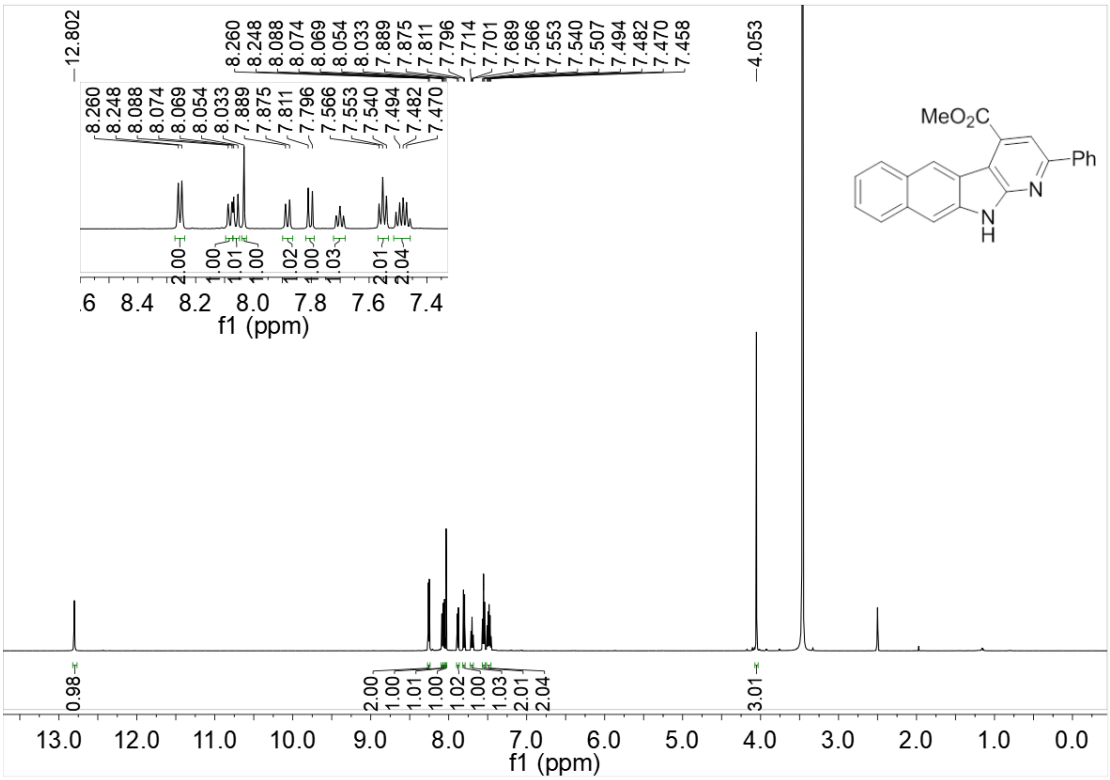


Figure 7. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3ga**



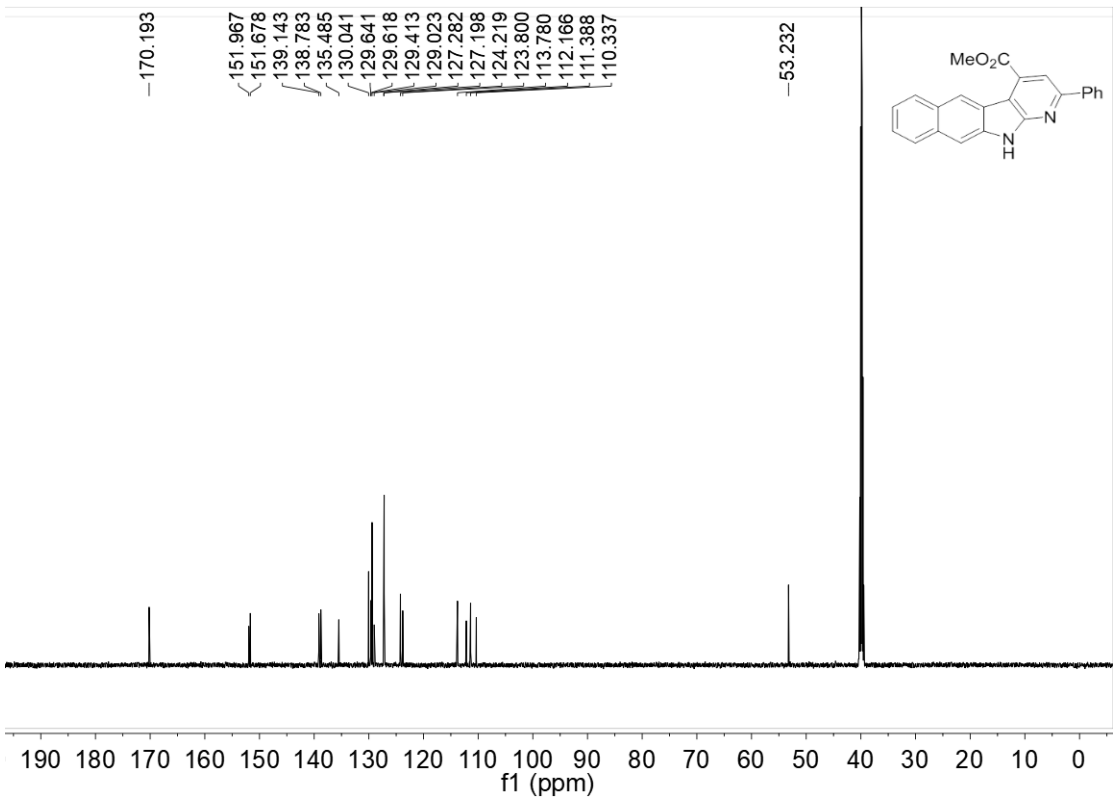
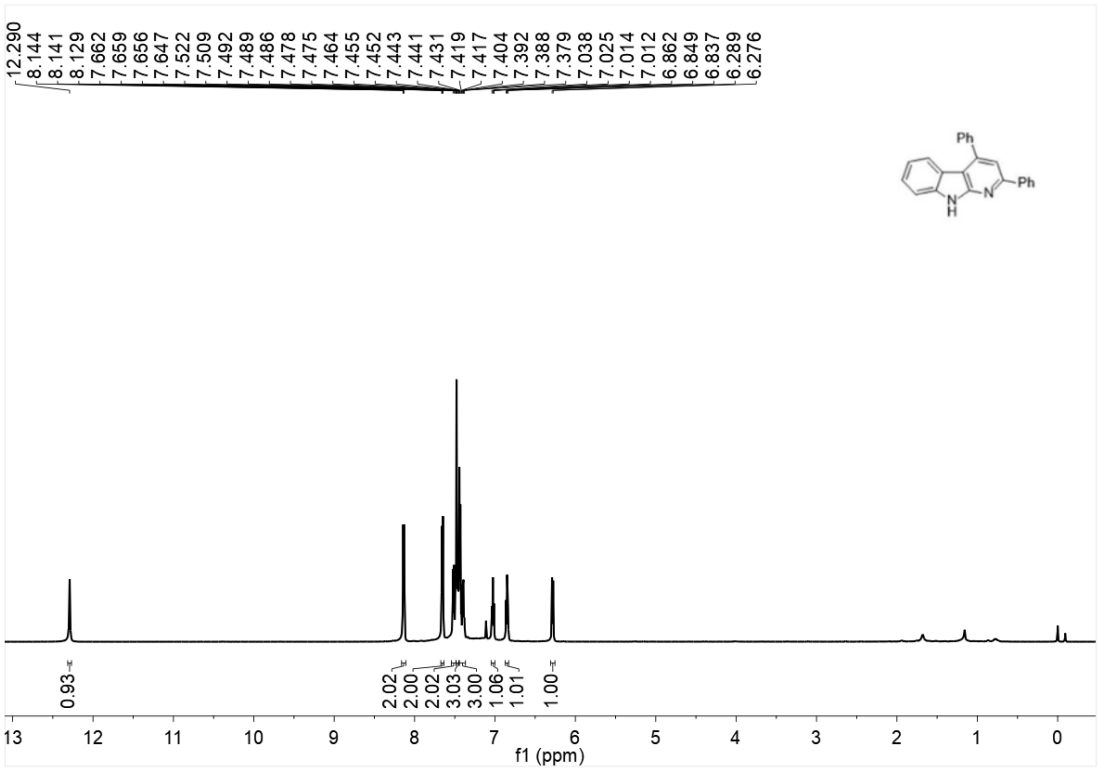


Figure 8. ^{1}H NMR, ^{13}C NMR spectra of compound **3ha**



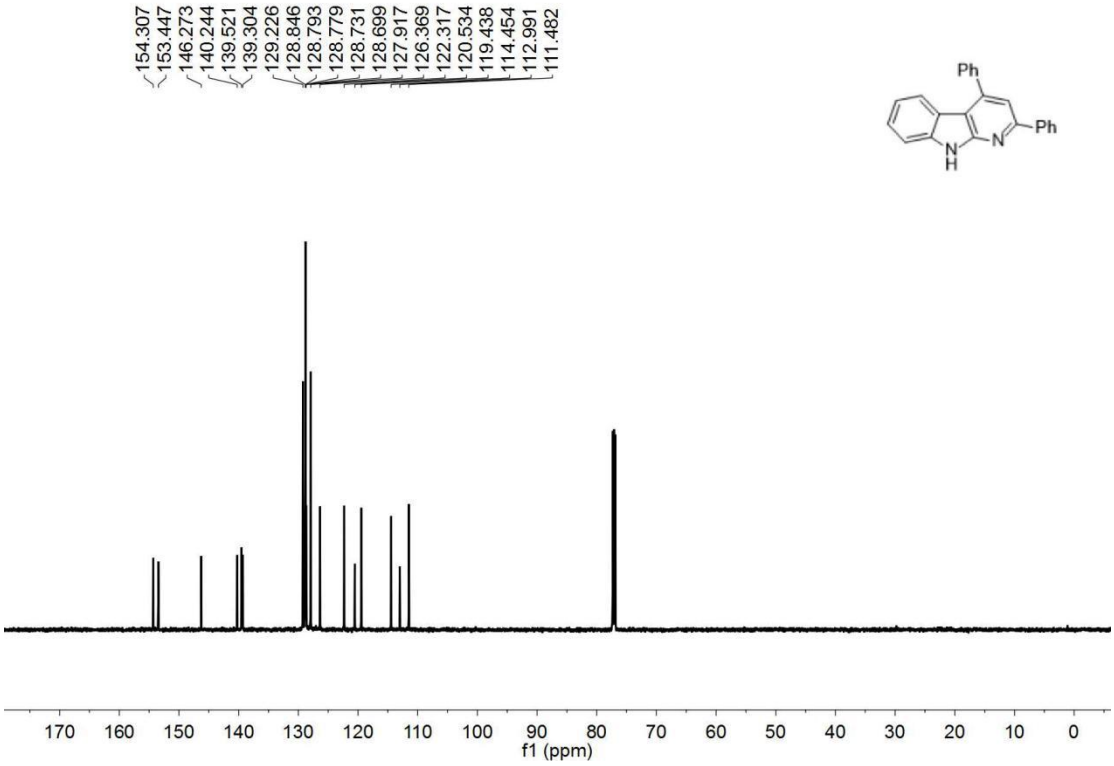
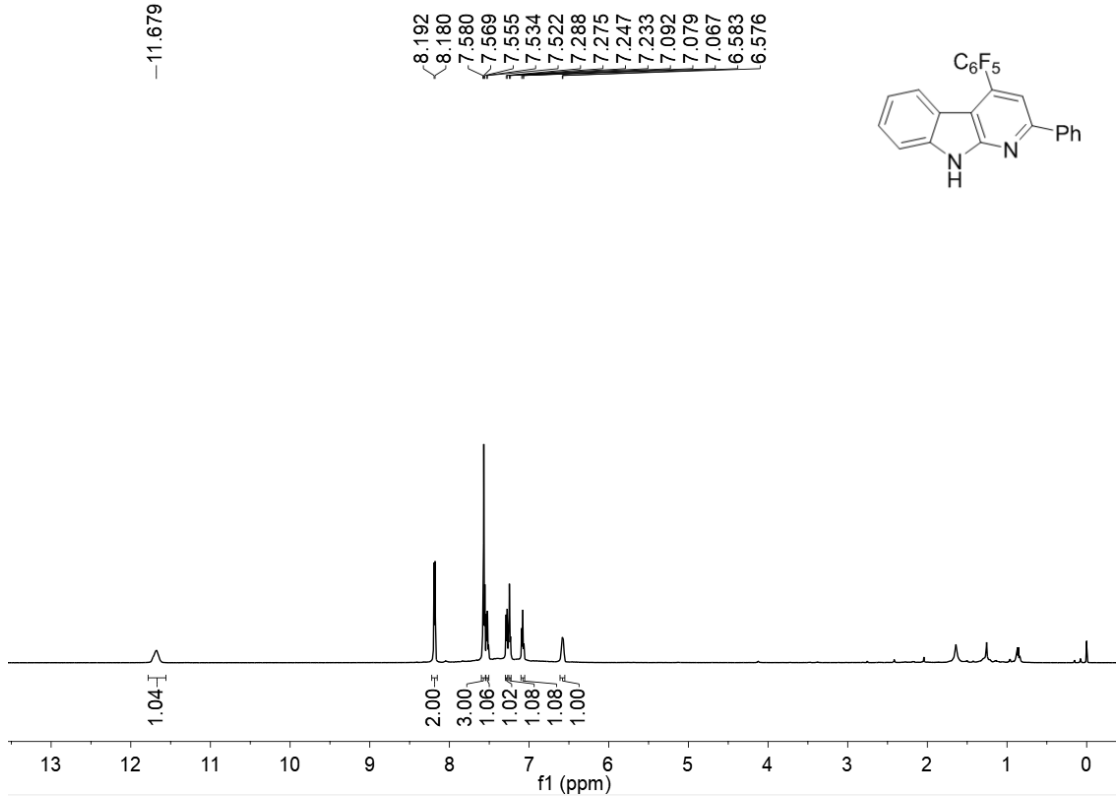


Figure 9. ^{1}H NMR, ^{13}C NMR spectra of compound **3ia**



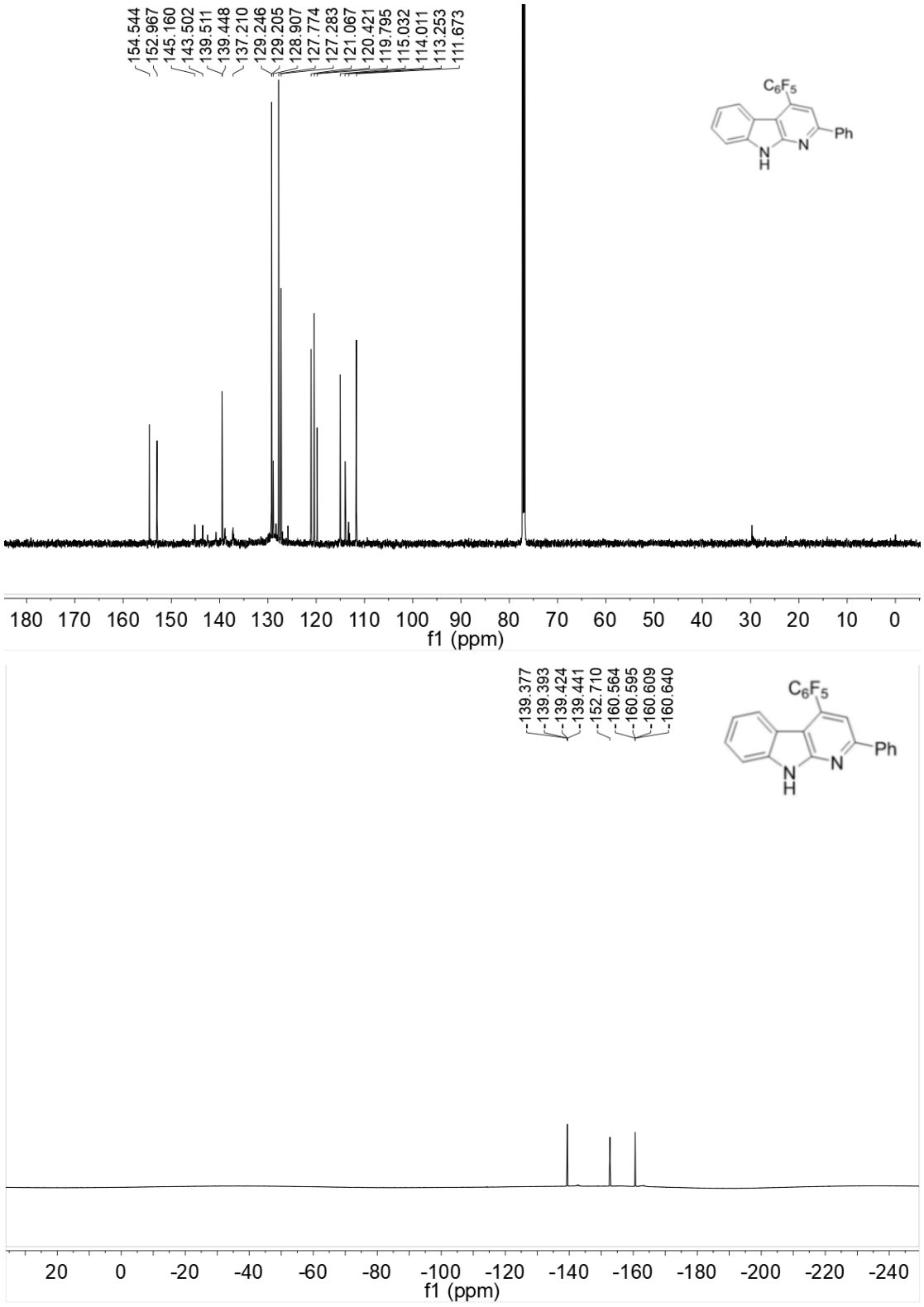


Figure 10. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3ja**

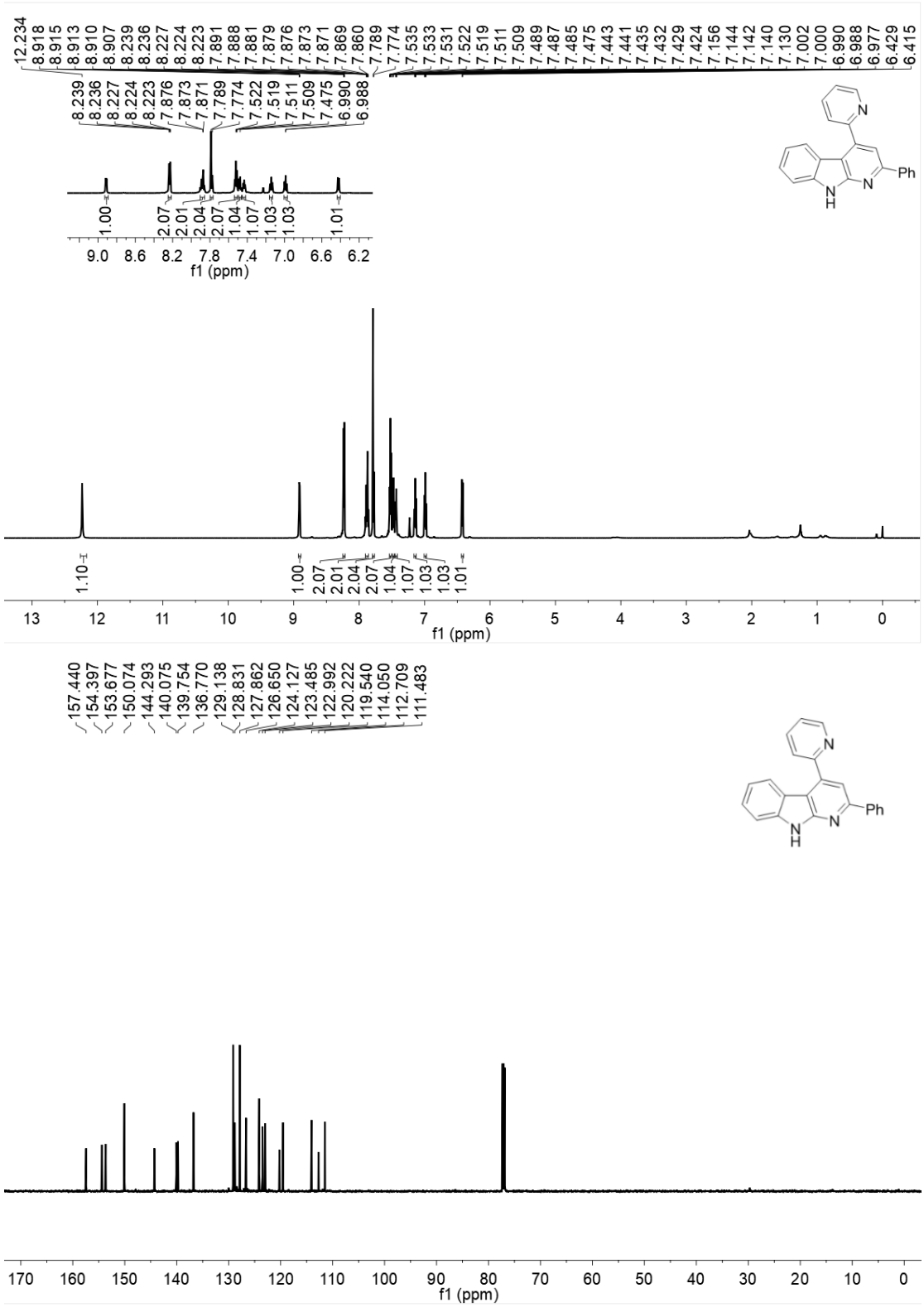


Figure 11. ^{1}H NMR, ^{13}C NMR spectra of compound **3ka**

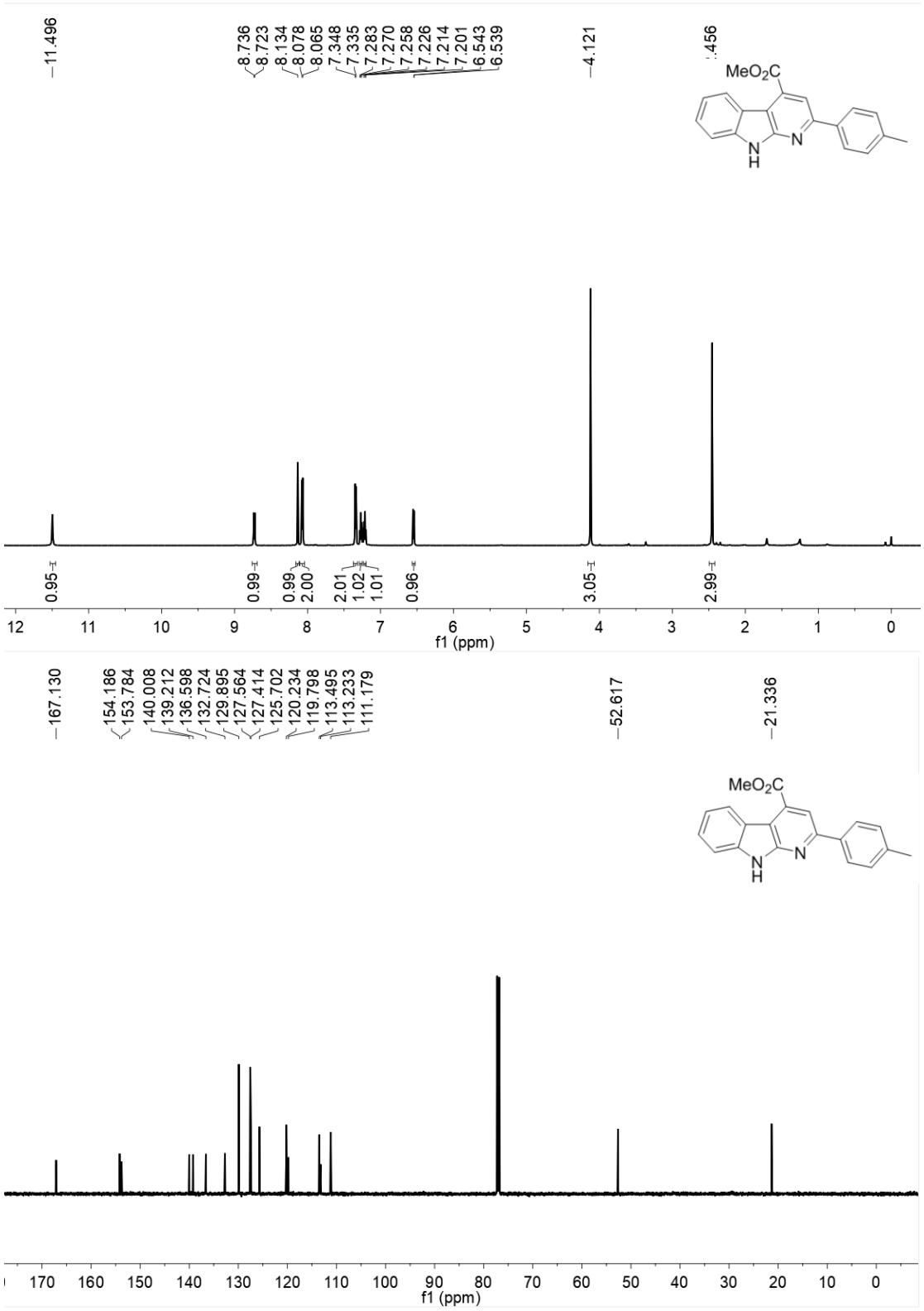


Figure 12. ^{1}H NMR, ^{13}C NMR spectra of compound **3ab**

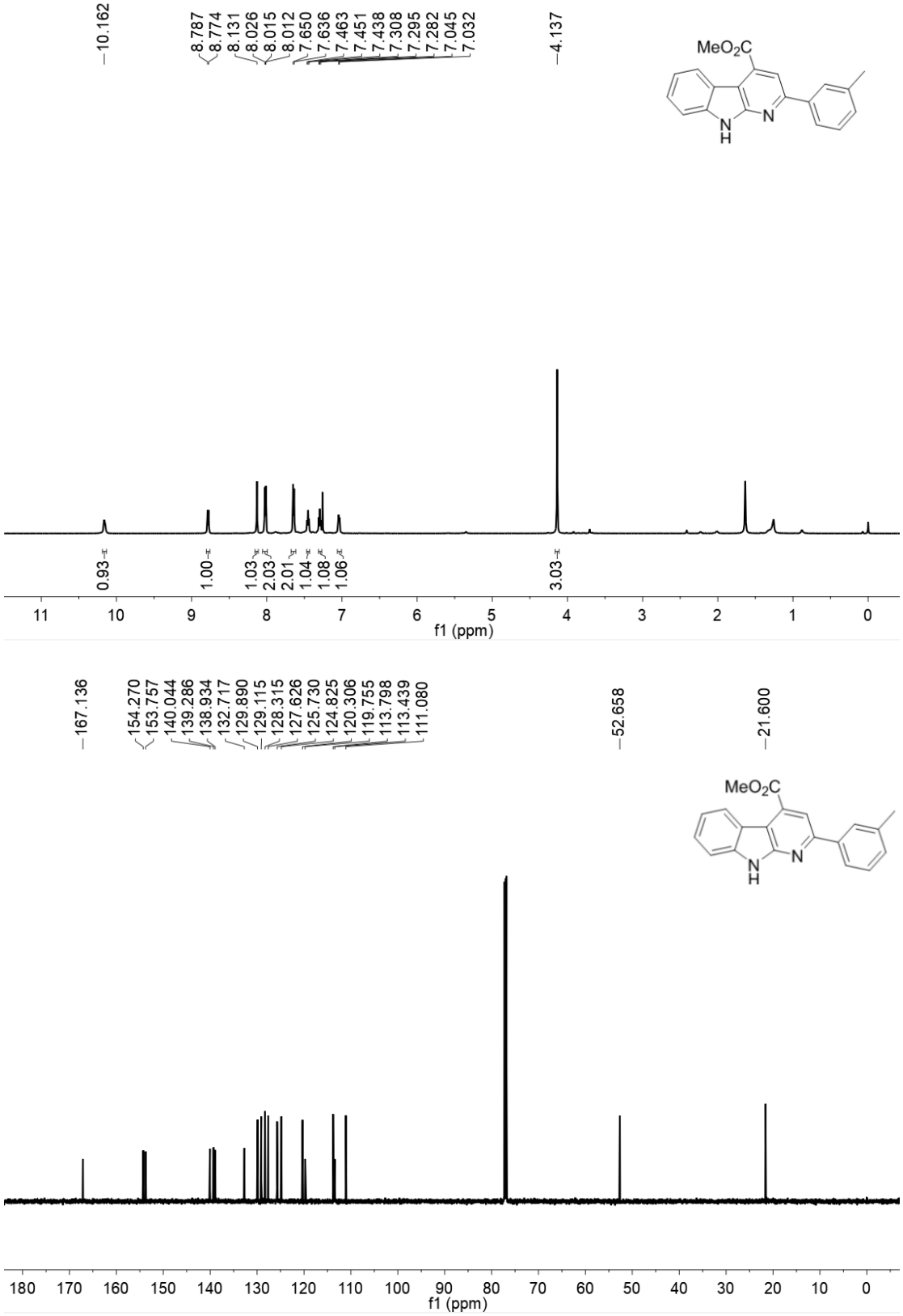


Figure 13. ^{1}H NMR, ^{13}C NMR spectra of compound **3ac**

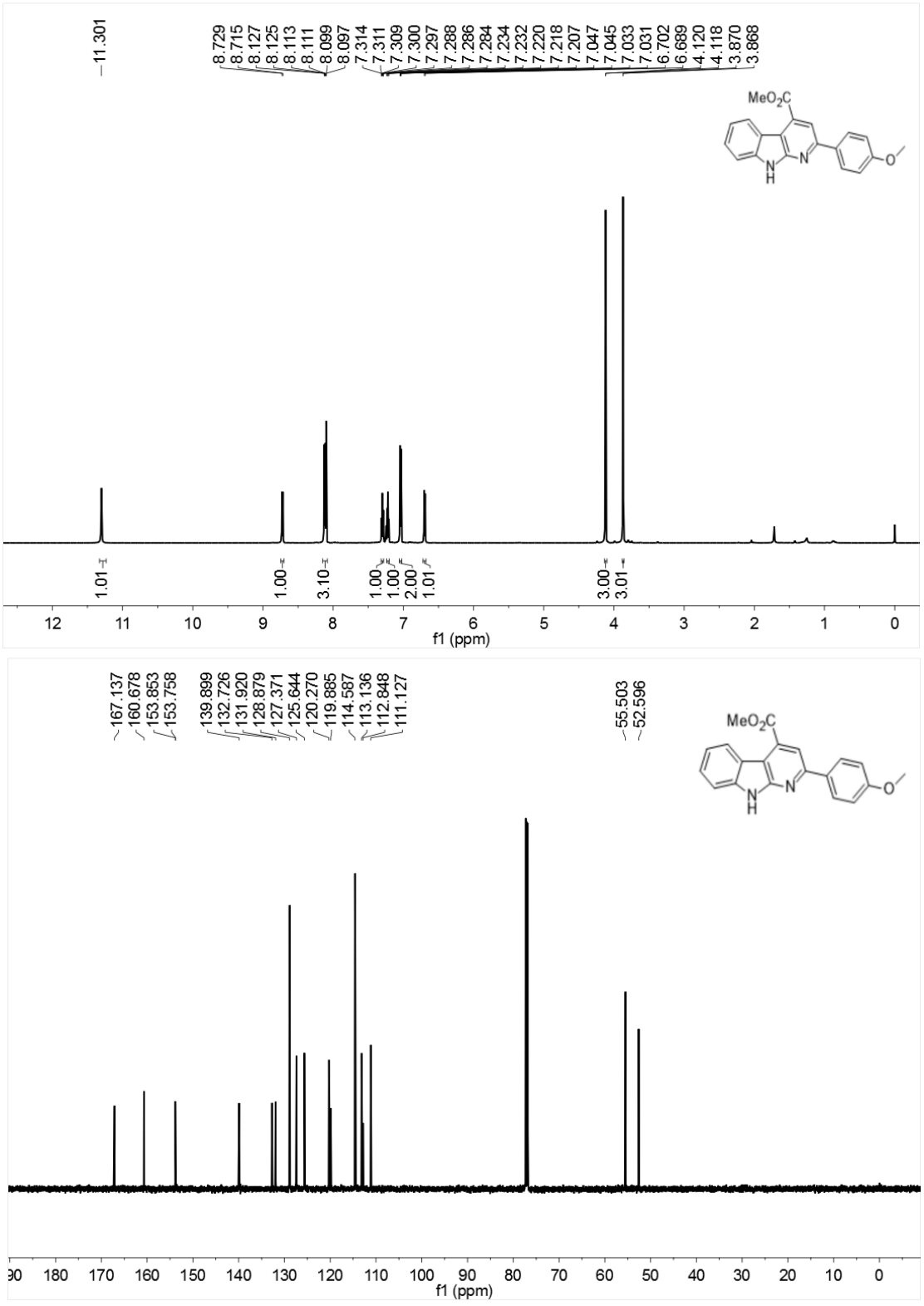


Figure 14. ^{1}H NMR, ^{13}C NMR spectra of compound **3ad**

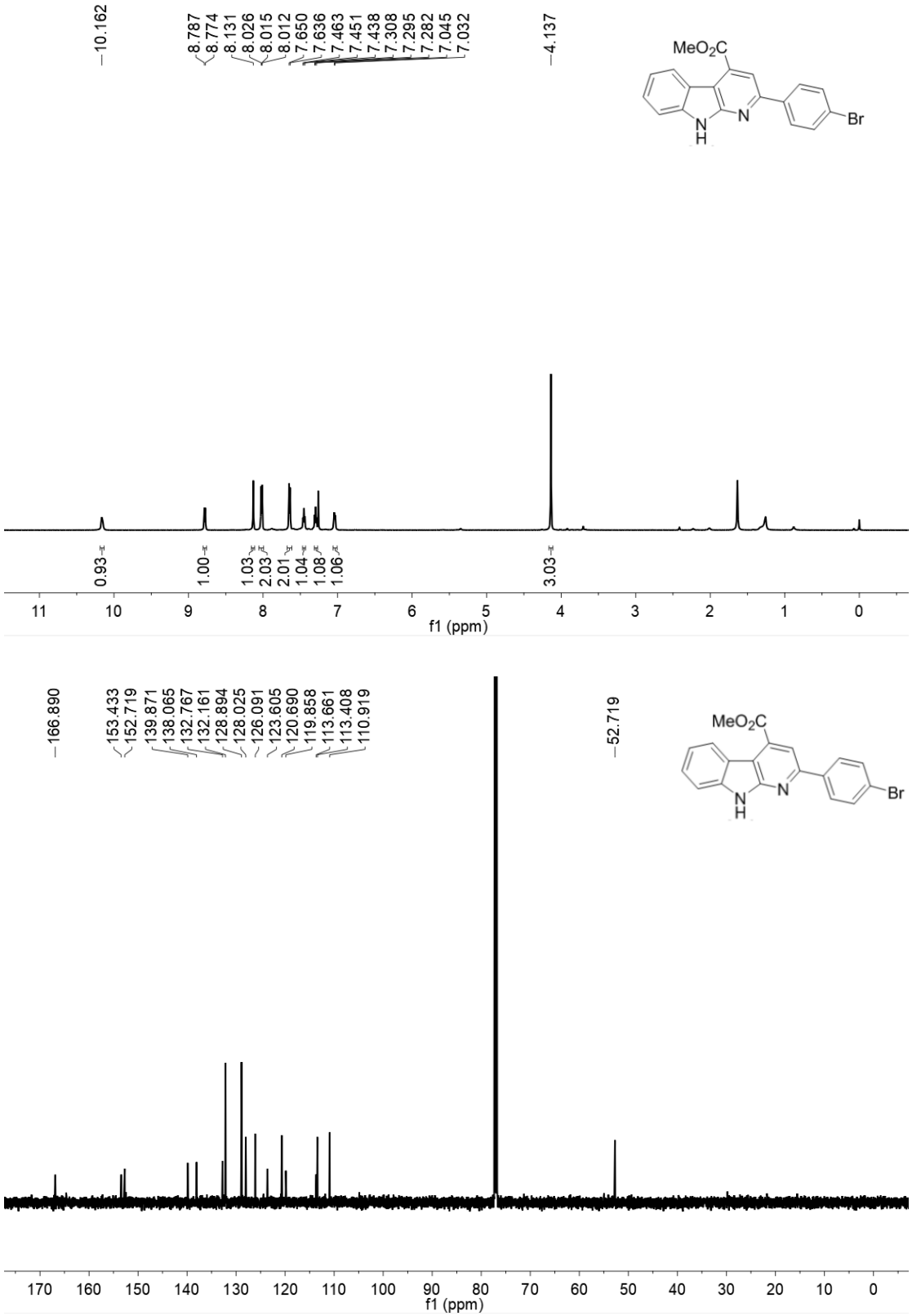


Figure 15. ^{1}H NMR, ^{13}C NMR spectra of compound **3ae**

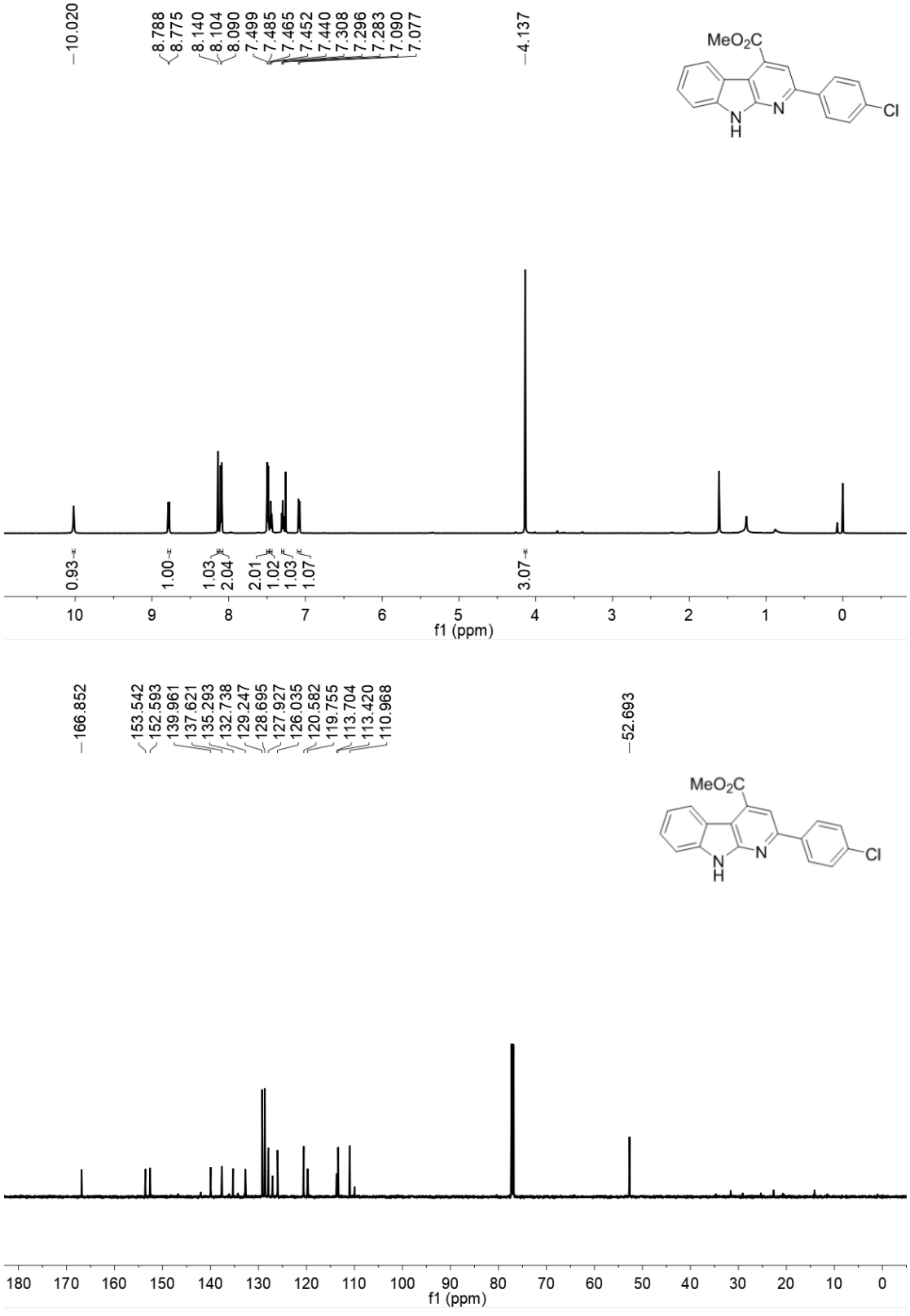


Figure 16. ^{1}H NMR, ^{13}C NMR spectra of compound **3af**

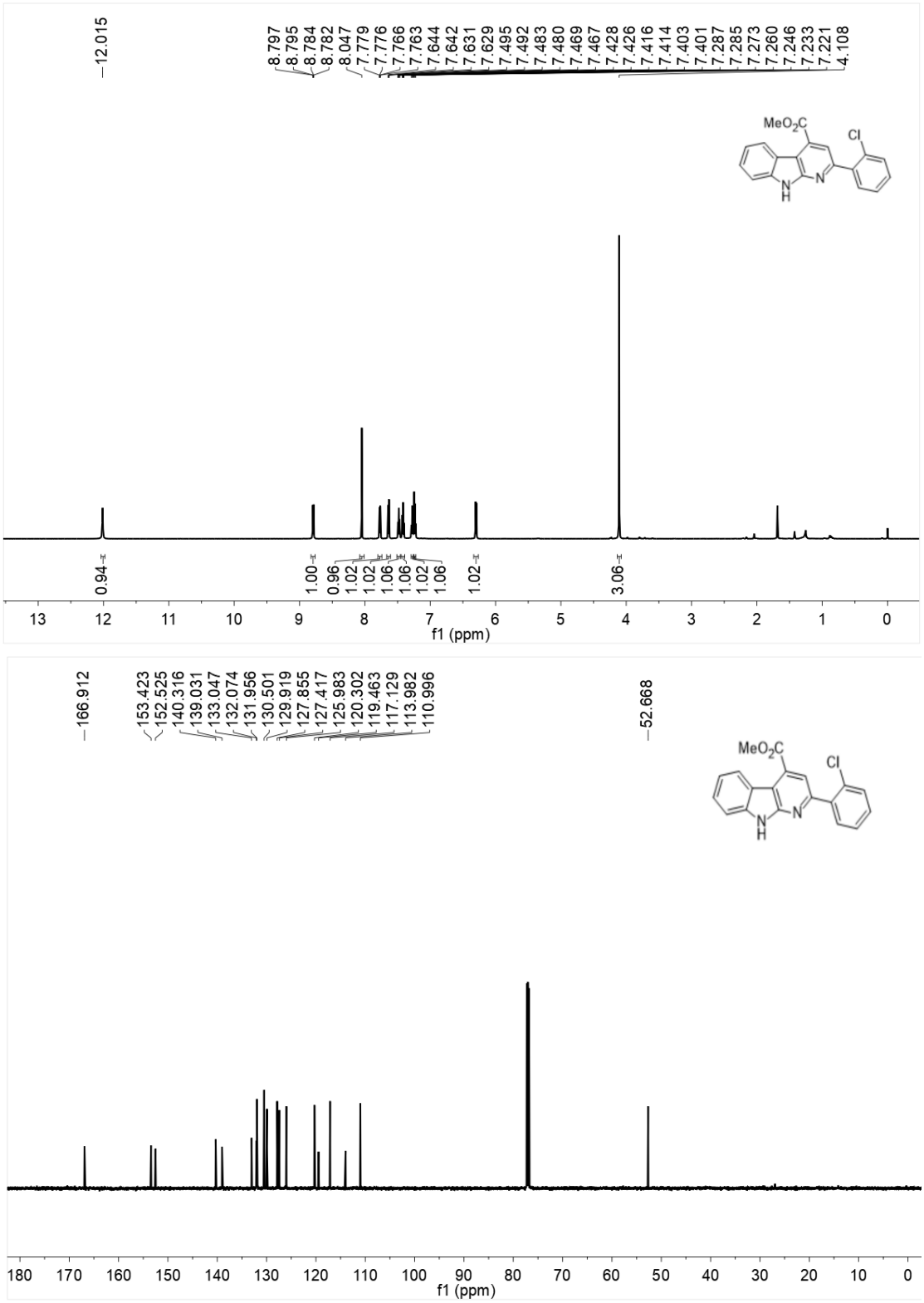


Figure 17. ^{1}H NMR, ^{13}C NMR spectra of compound **3ag**

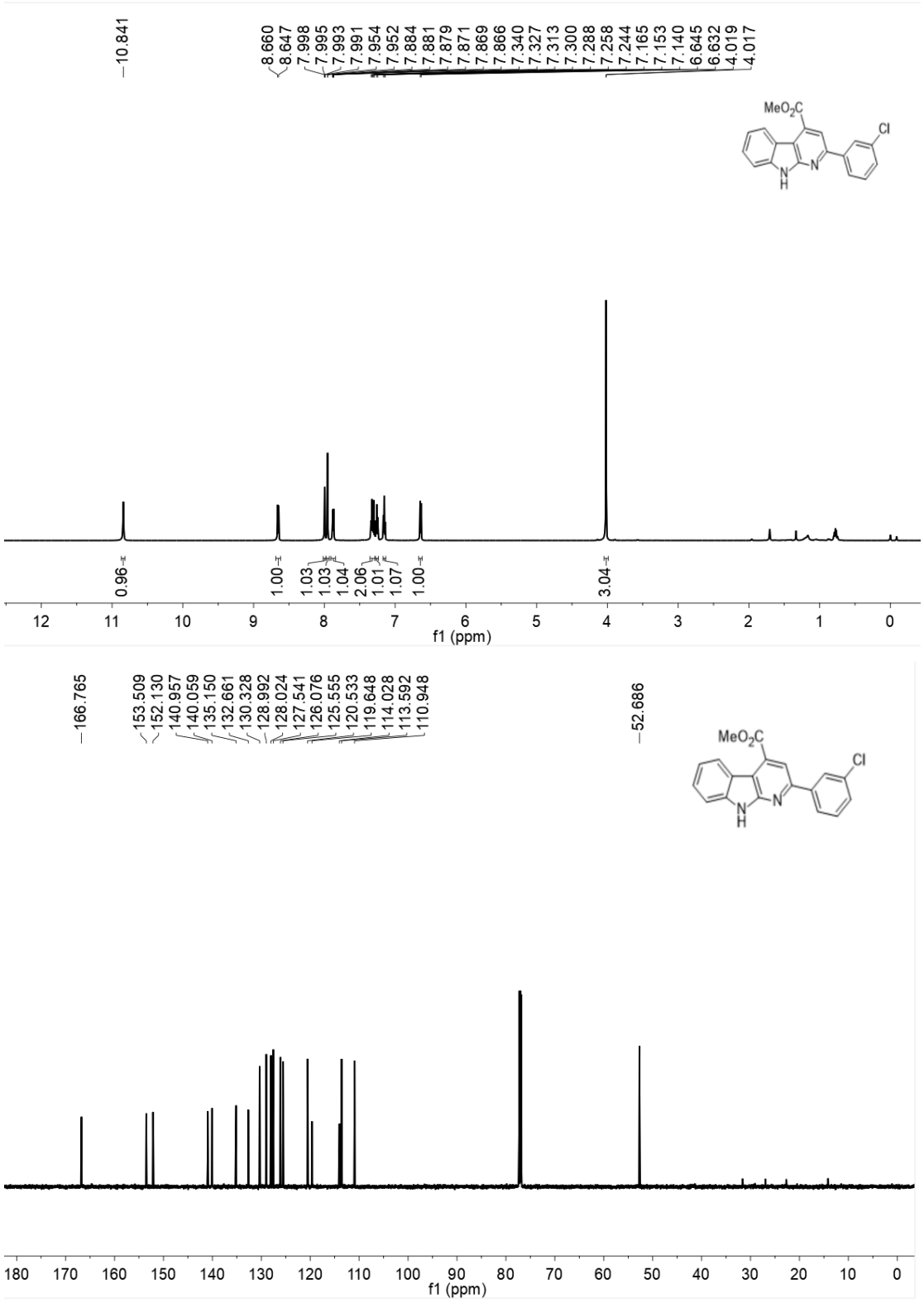
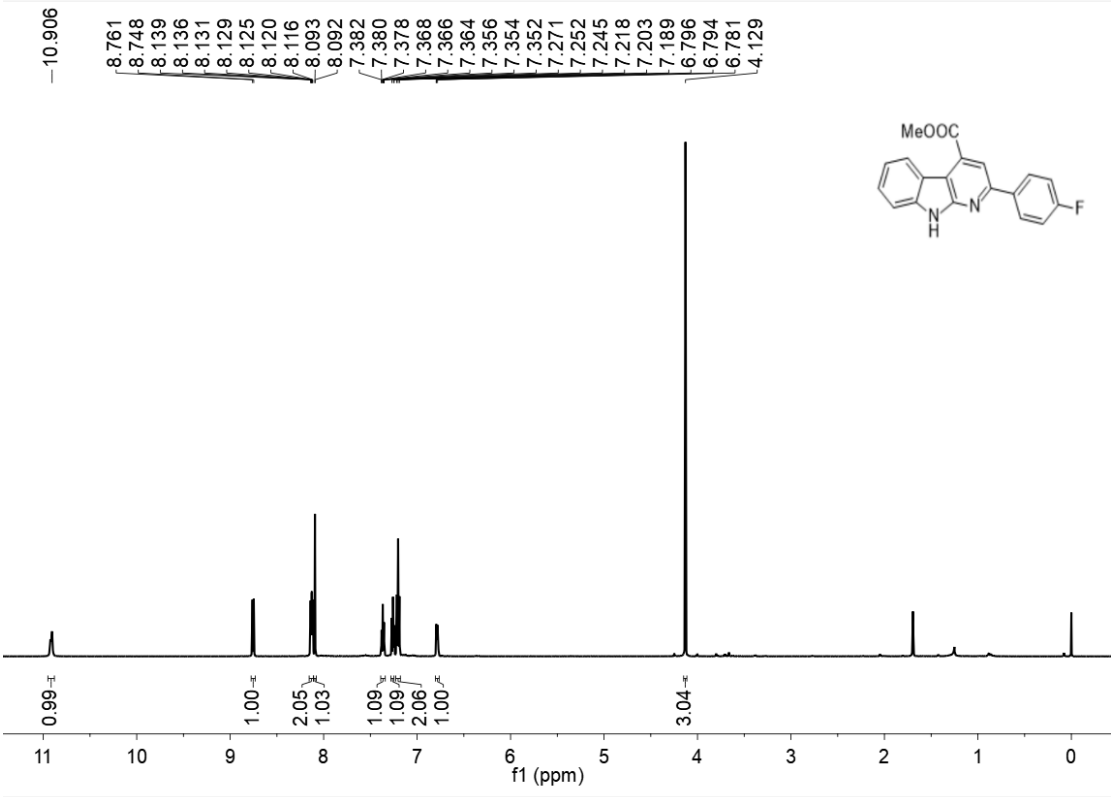
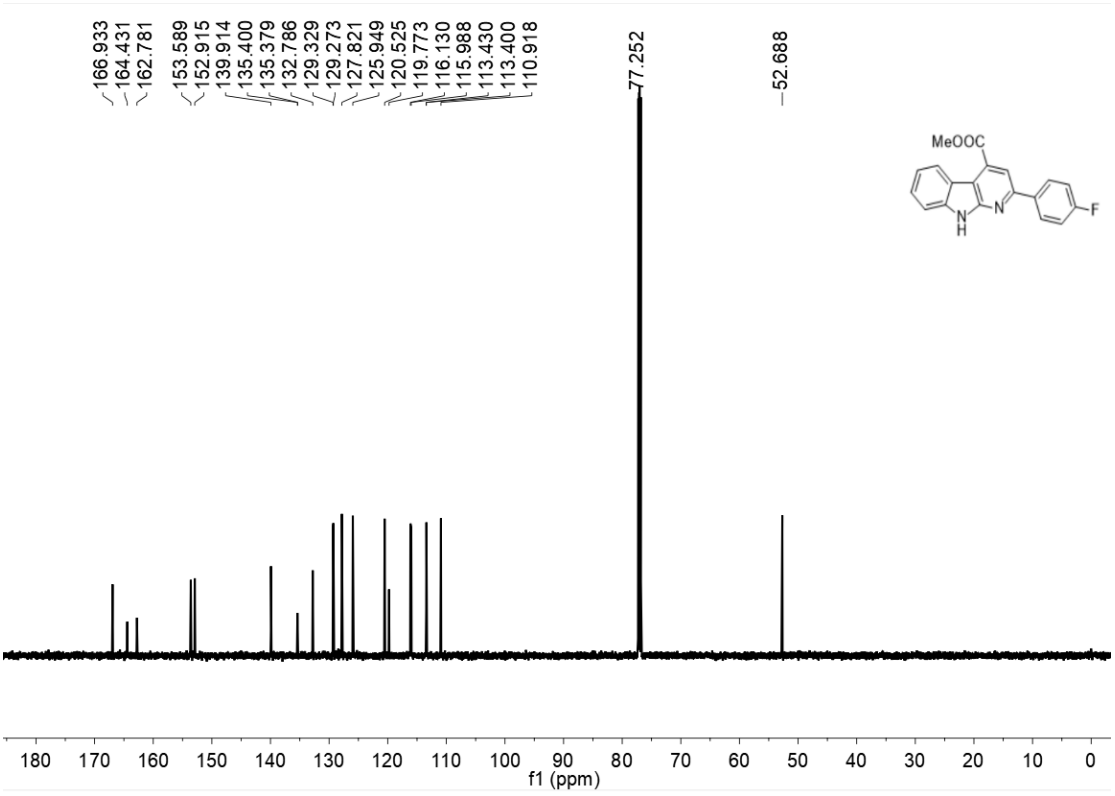


Figure 18. ^{1}H NMR, ^{13}C NMR spectra of compound **3ah**


10.906
8.761
8.748
8.139
8.136
8.131
8.129
8.125
8.120
8.116
8.093
8.092
7.382
7.380
7.378
7.368
7.366
7.364
7.356
7.354
7.352
7.271
7.252
7.245
7.218
7.203
7.189
6.796
6.794
6.781
4.129
MeOOC
N
H
N
F
0.99
1.00
2.05
1.03
1.09
1.09
2.06
1.00
3.04
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.933
164.431
162.781
153.589
152.915
139.914
135.400
135.379
132.786
129.329
129.273
127.821
125.949
120.525
119.773
116.130
115.988
113.430
113.400
110.918
77.252
52.688
MeOOC
N
H
N
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

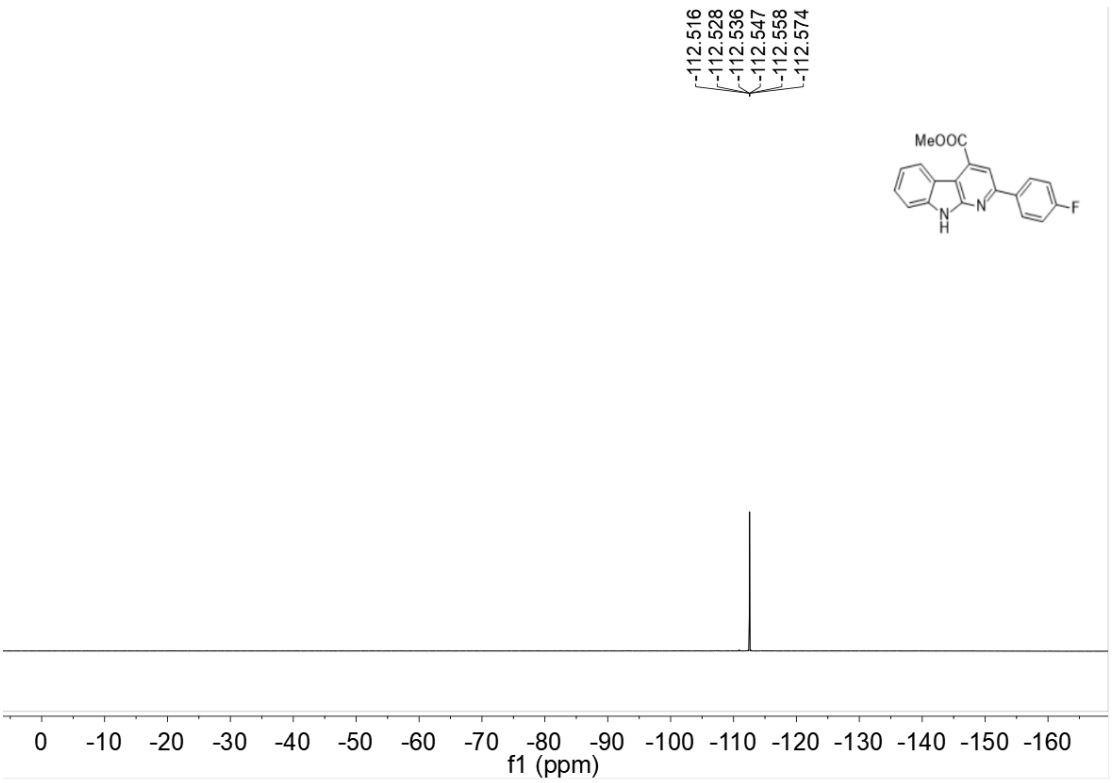
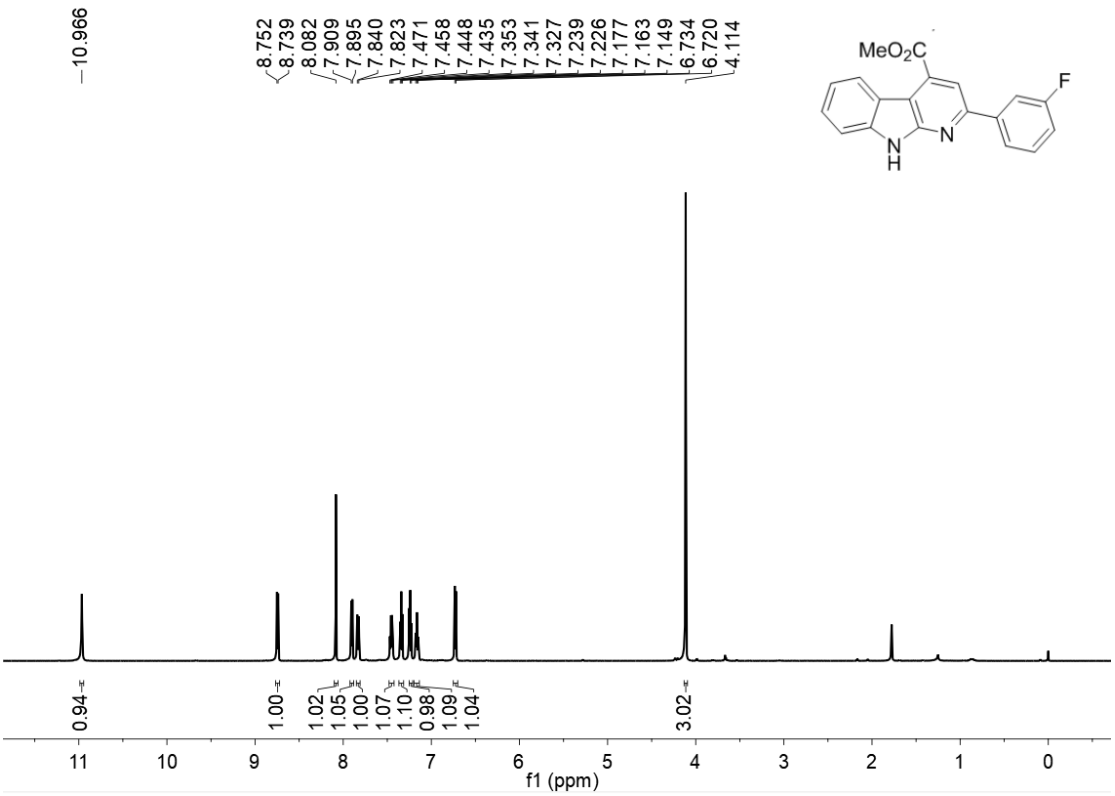


Figure 19. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3ai**



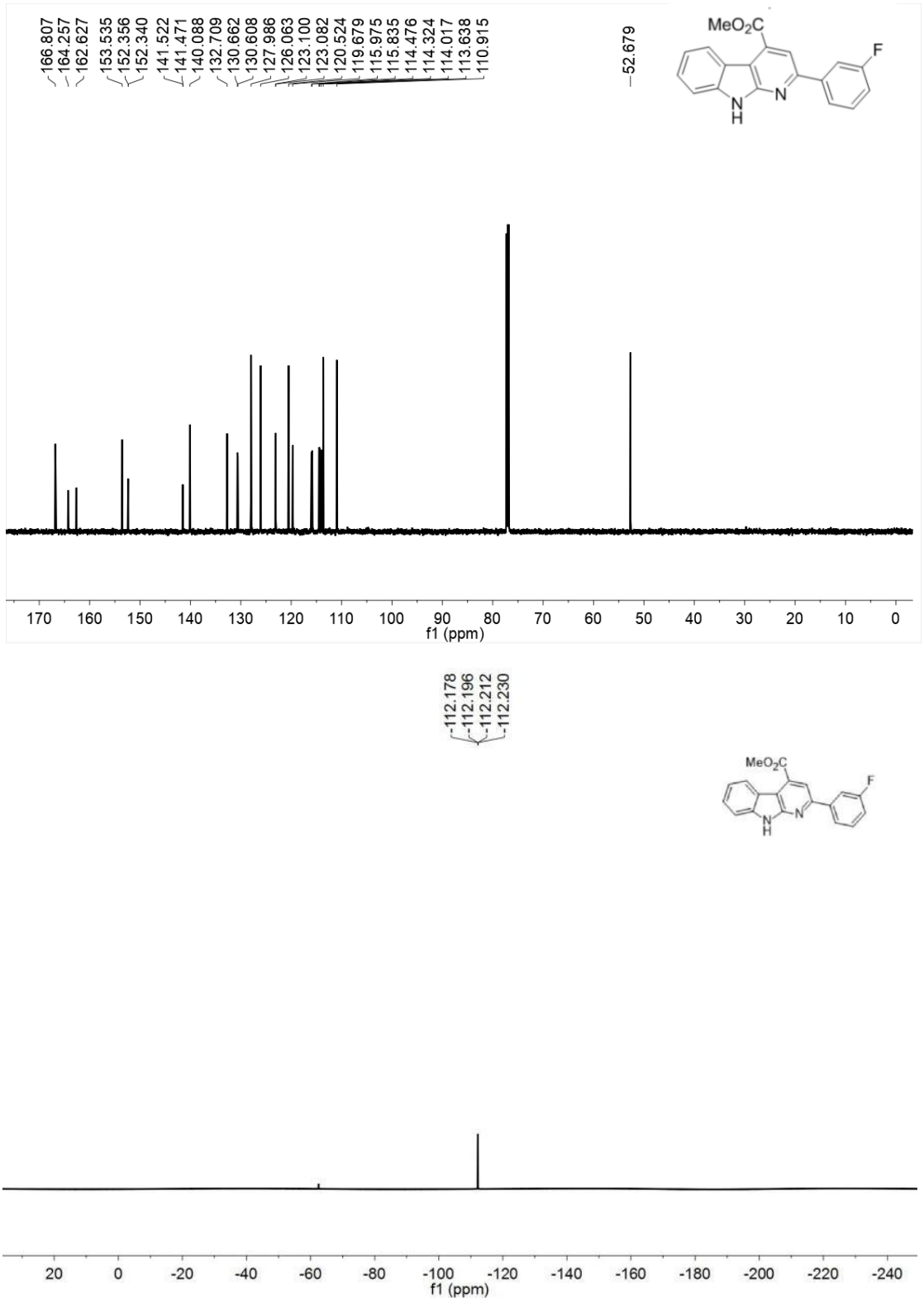


Figure 20. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3aj**

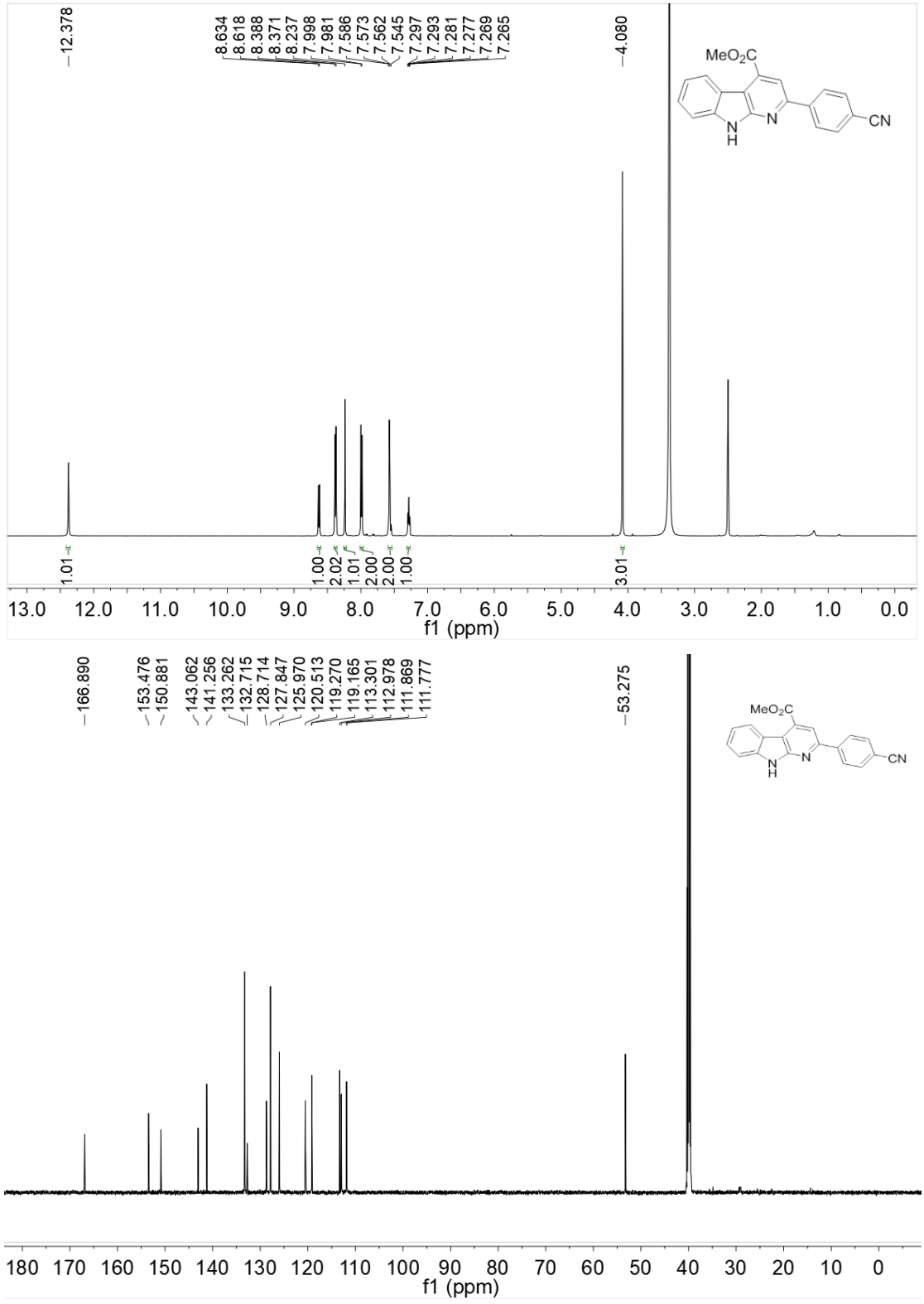
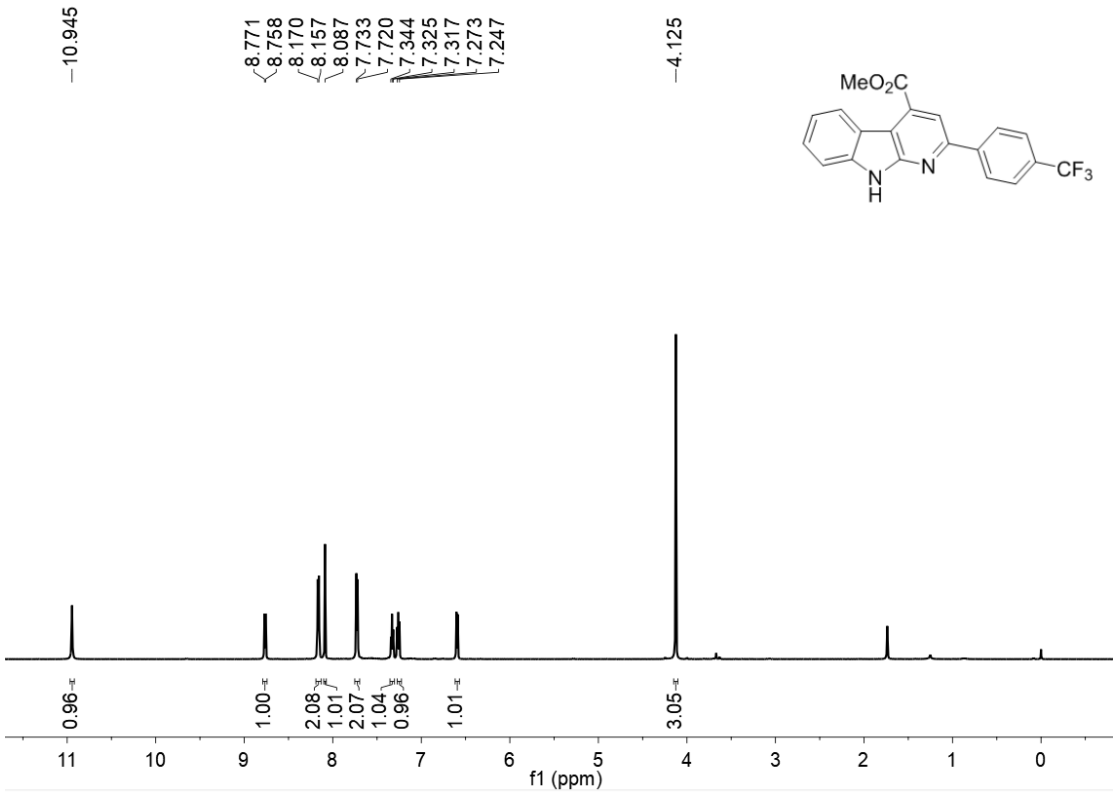
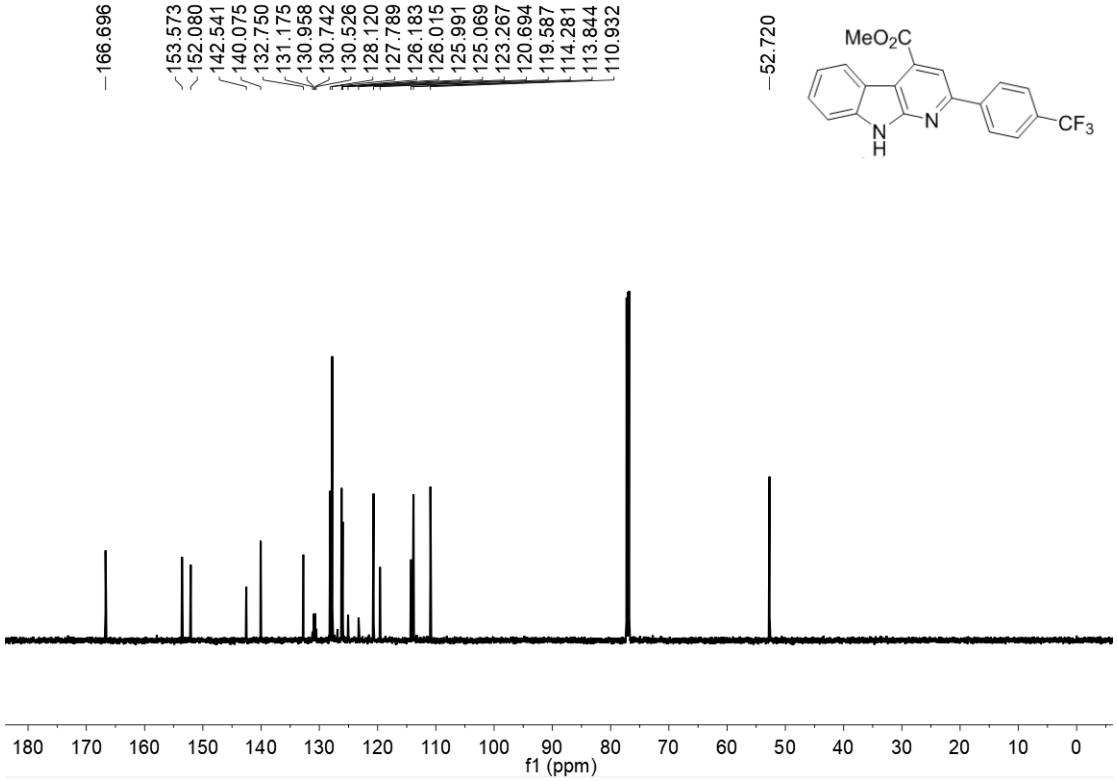


Figure 21. ^{1}H NMR, ^{13}C NMR spectra of compound **3ak**


10.945
8.771
8.758
8.170
8.157
8.087
7.733
7.720
7.344
7.325
7.317
7.273
7.247
4.125
MeO2C
CF3
N
H
0.96
1.00
2.08
1.01
2.07
1.04
0.96
1.01
3.05
f1 (ppm)


166.696
153.573
152.080
142.541
140.075
132.750
131.175
130.958
130.742
130.526
128.120
127.789
126.183
126.015
125.991
125.069
123.267
120.694
119.587
114.281
113.844
110.932
52.720
MeO2C
CF3
N
H
f1 (ppm)

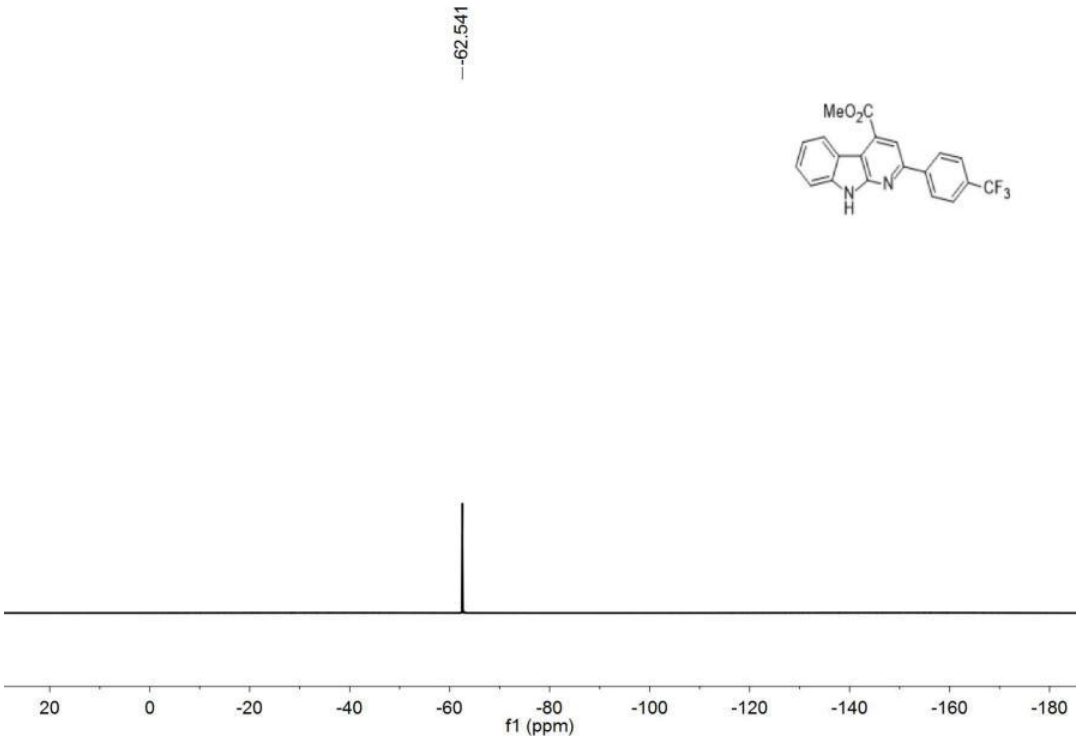
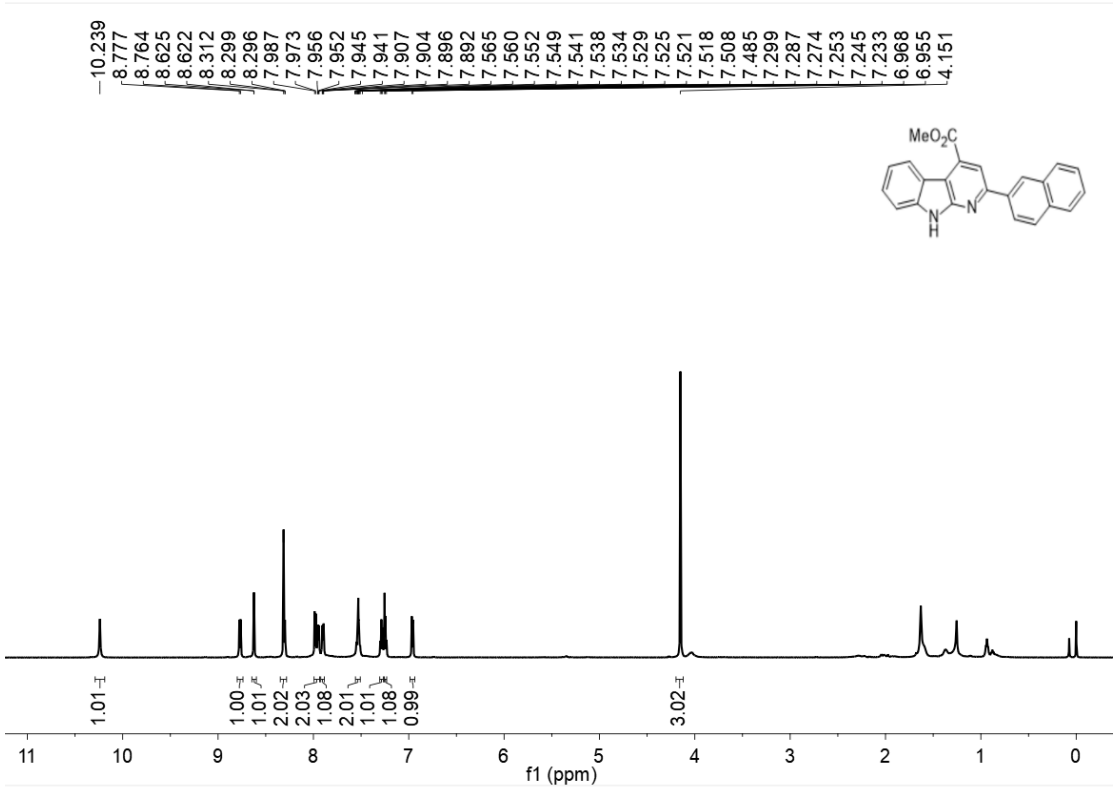


Figure 22. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3al**



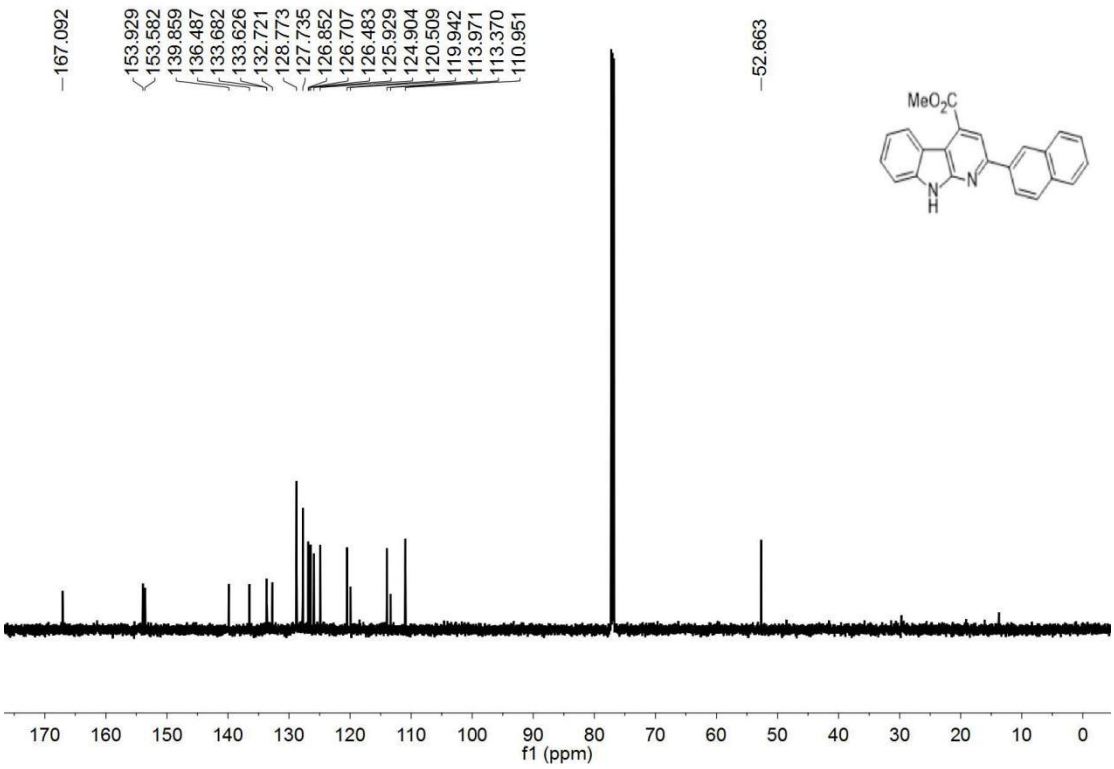
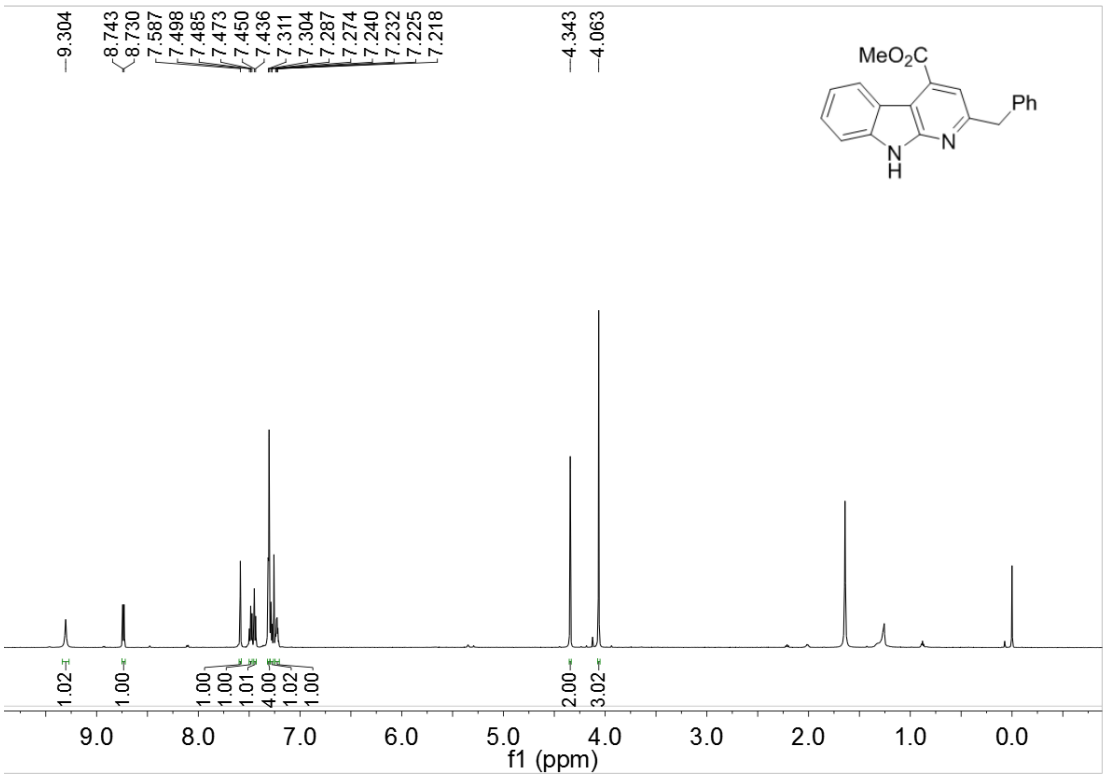


Figure 23. ^{1}H NMR, ^{13}C NMR spectra of compound **3am**



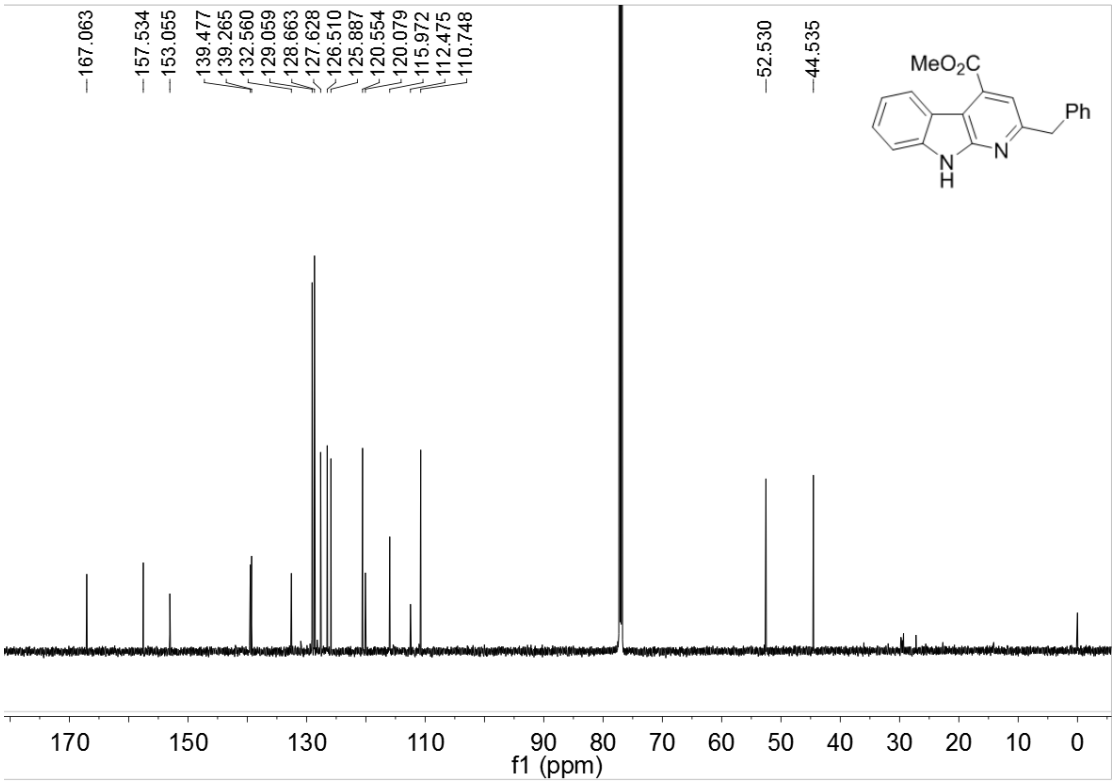
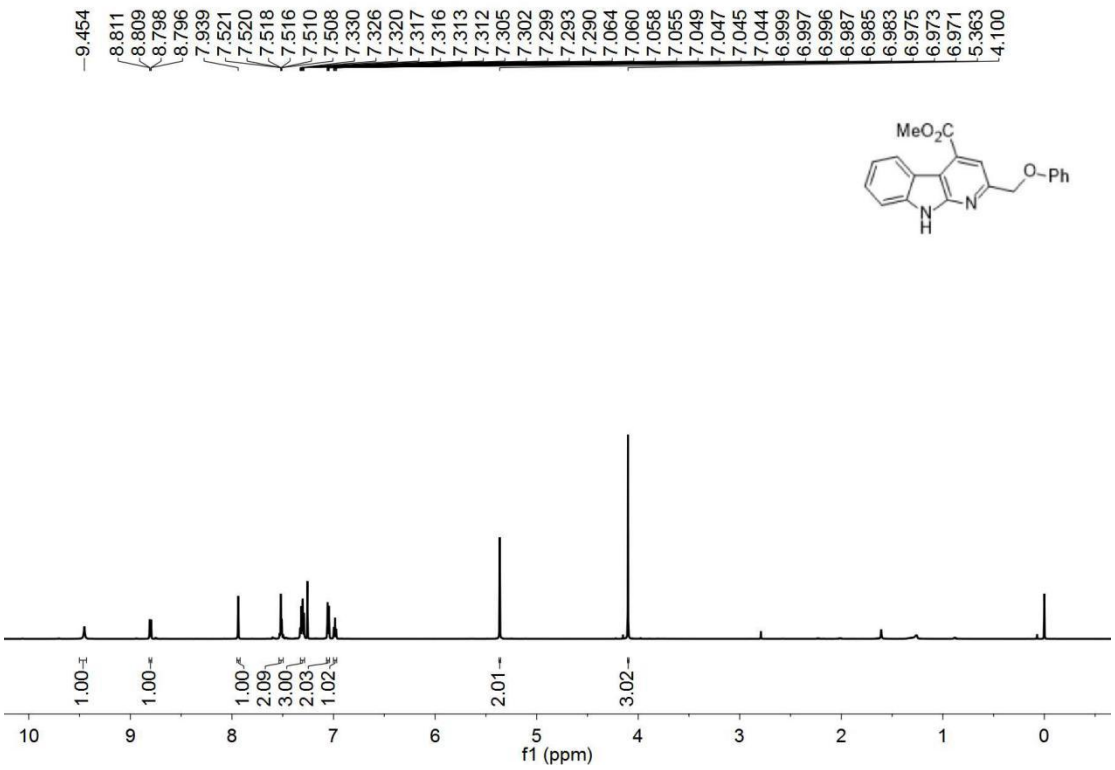


Figure 24. ^{1}H NMR, ^{13}C NMR spectra of compound **3an**



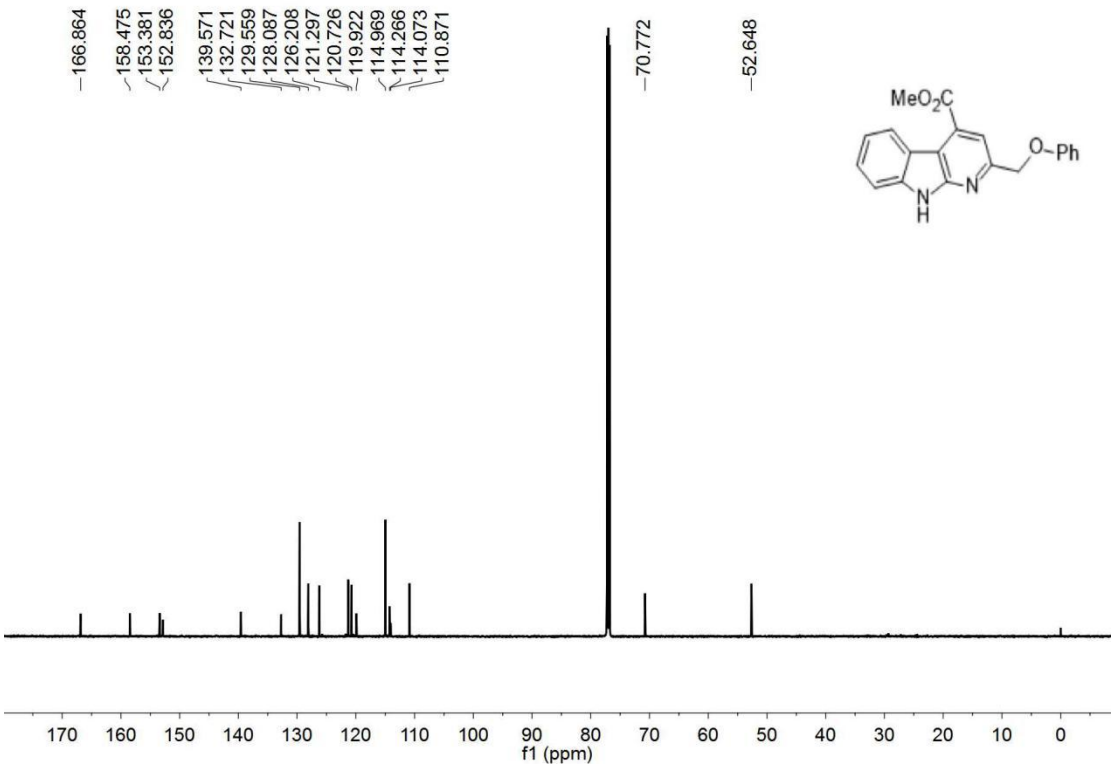
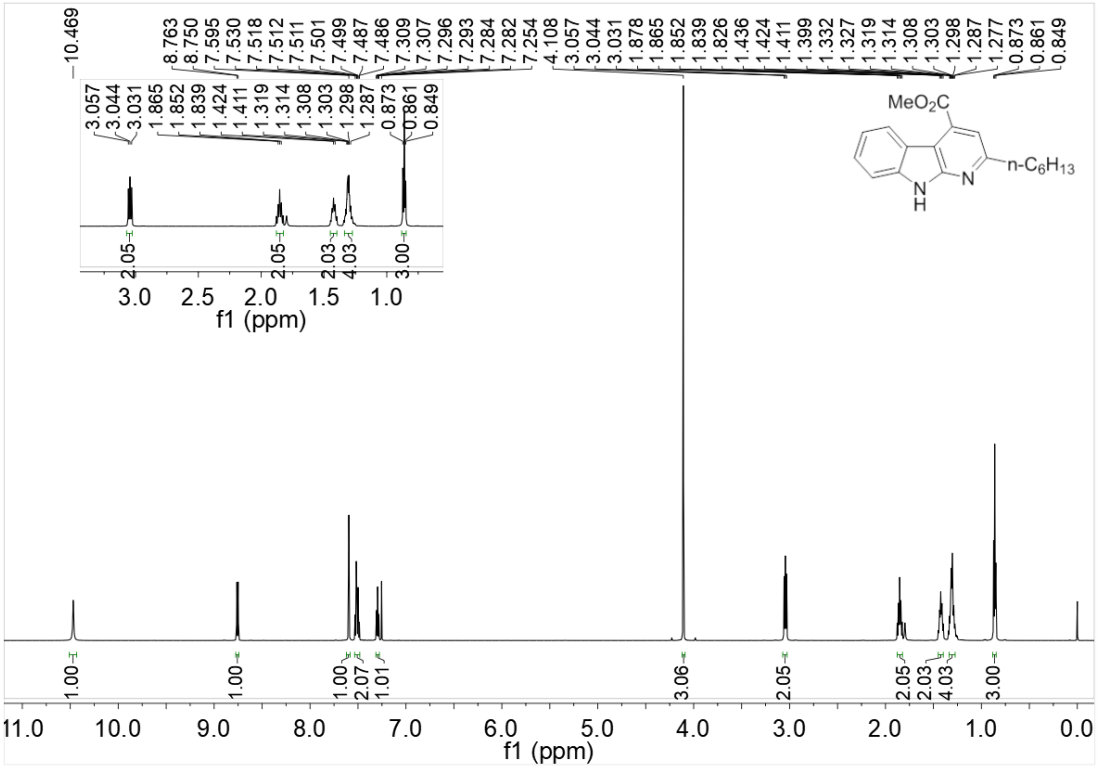


Figure 25. ^{1}H NMR, ^{13}C NMR spectra of compound **3ao**



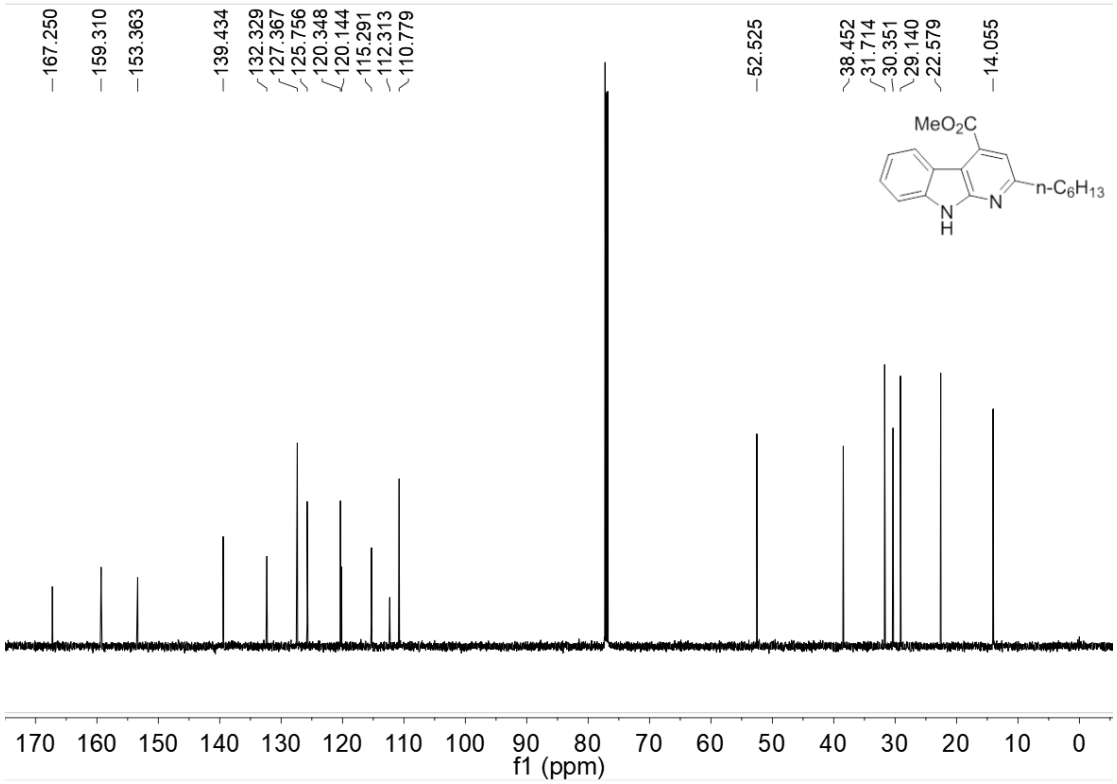
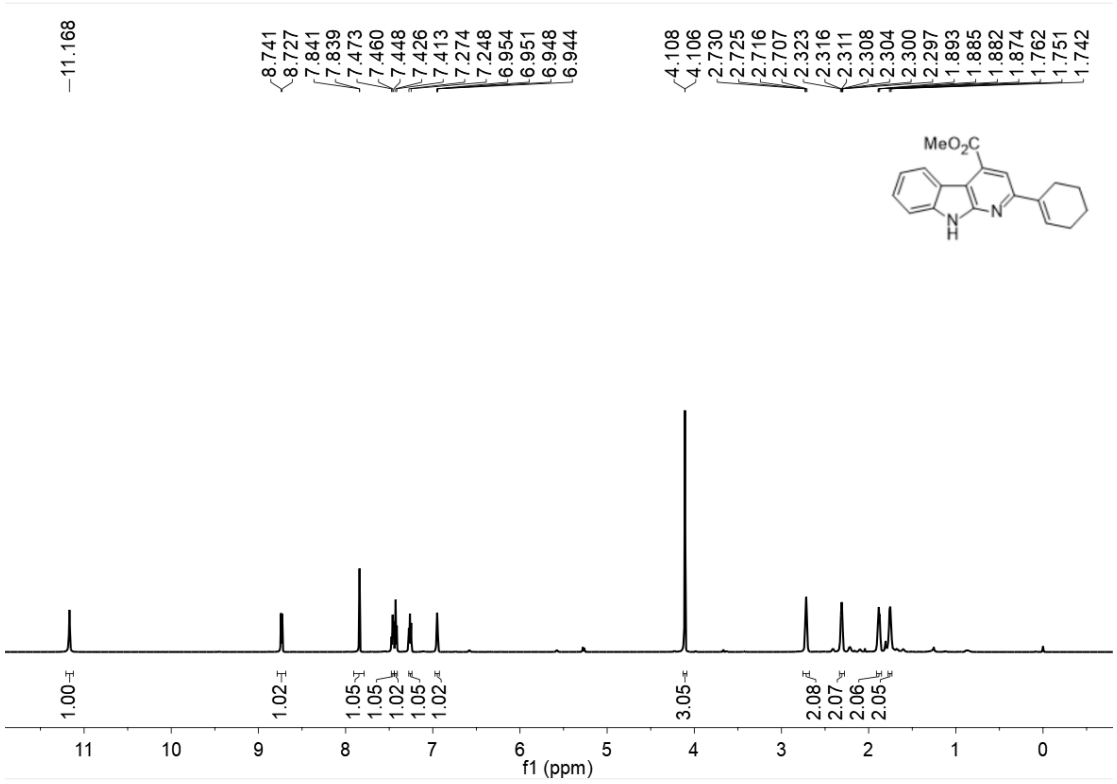


Figure 26. ^{1}H NMR, ^{13}C NMR spectra of compound **3ap**



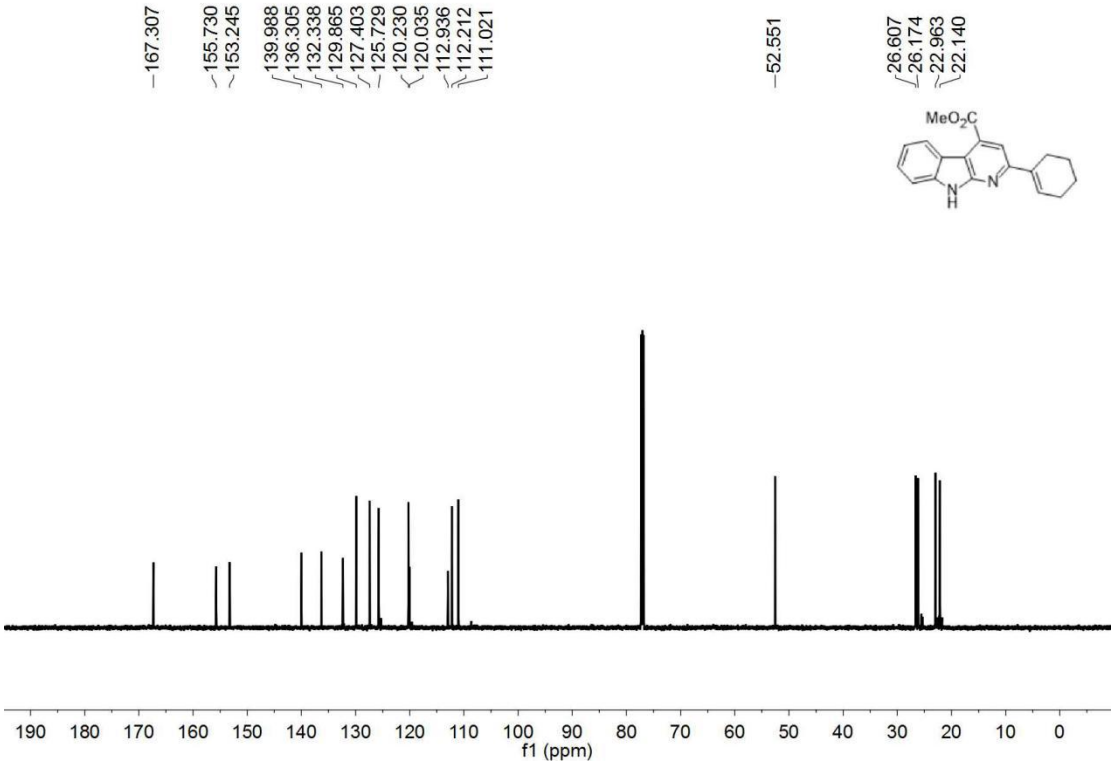
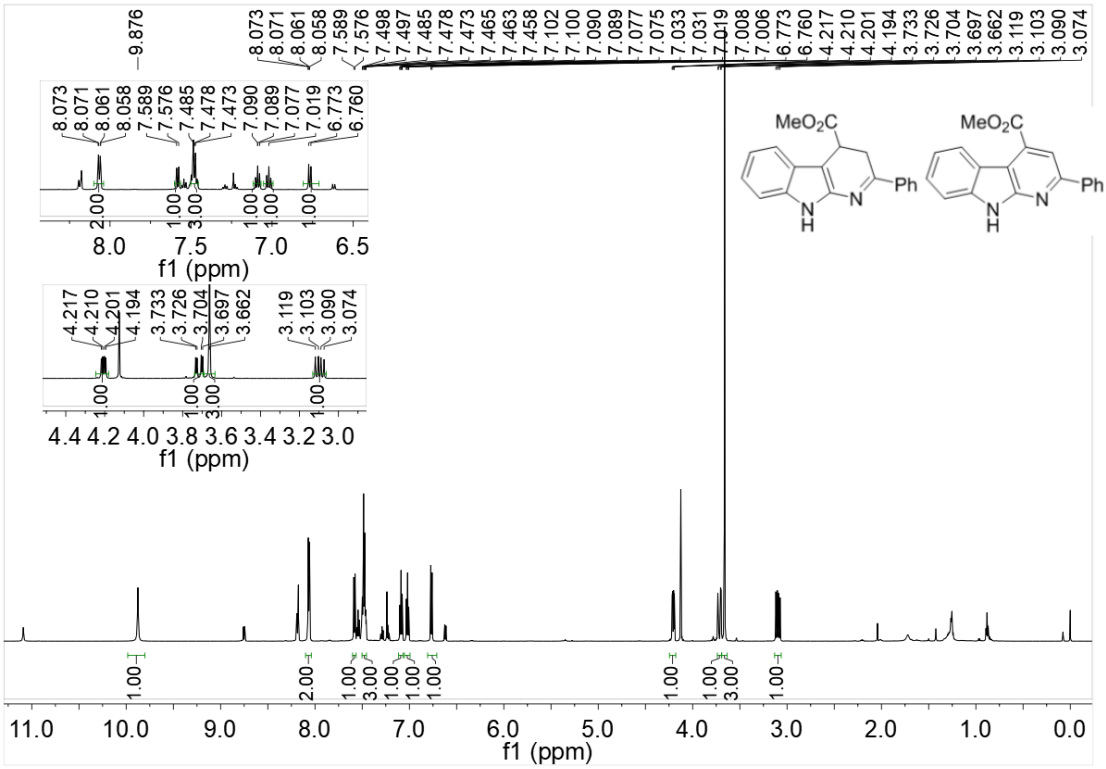


Figure 27. ^{1}H NMR, ^{13}C NMR spectra of compound **3aq**



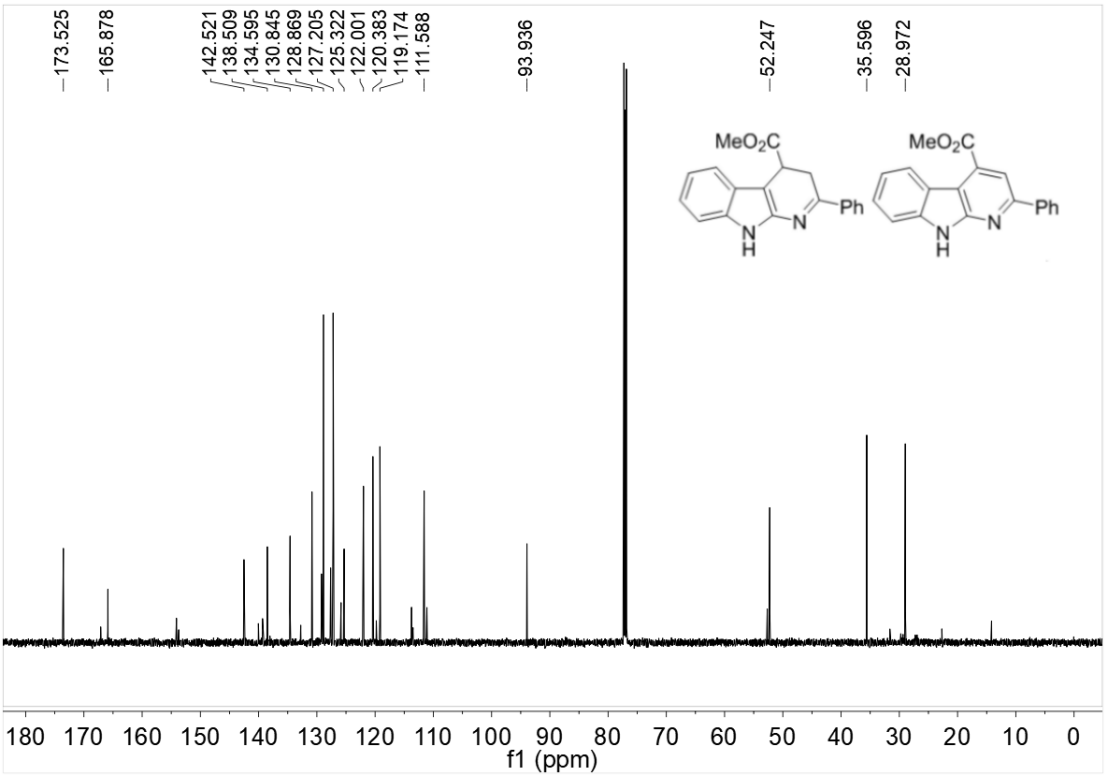
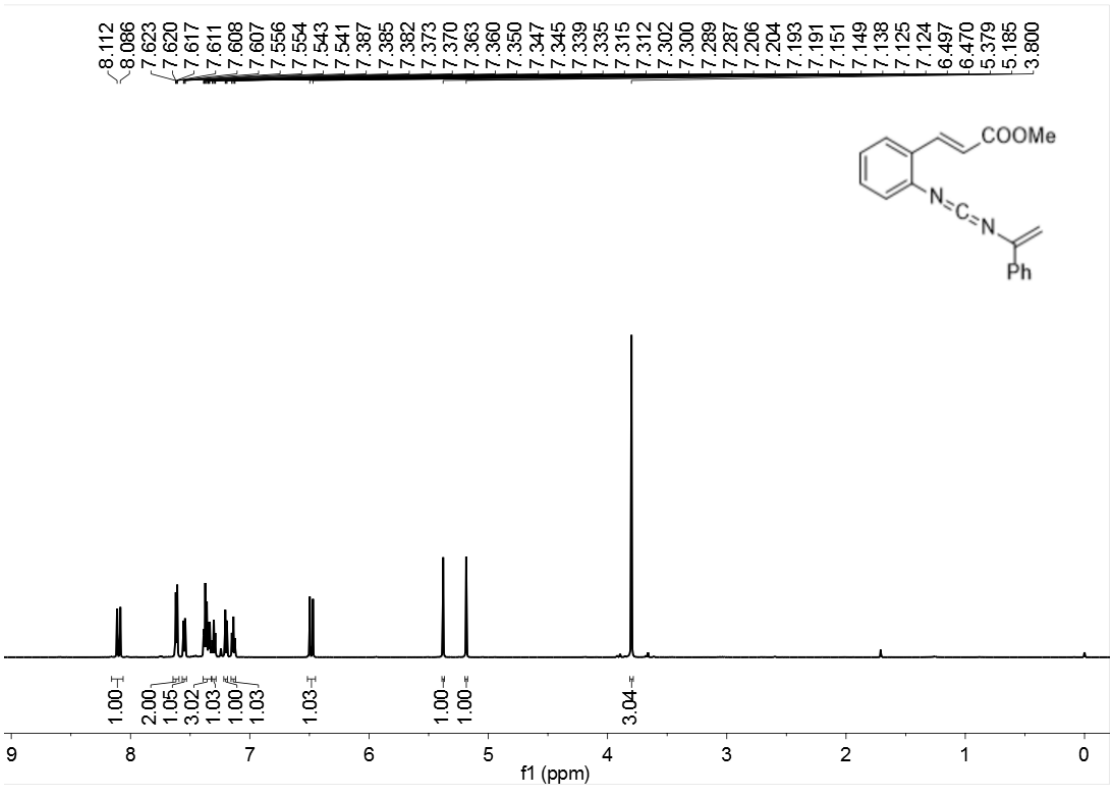


Figure 28. ^{1}H NMR, ^{13}C NMR spectra of compound **4aa**



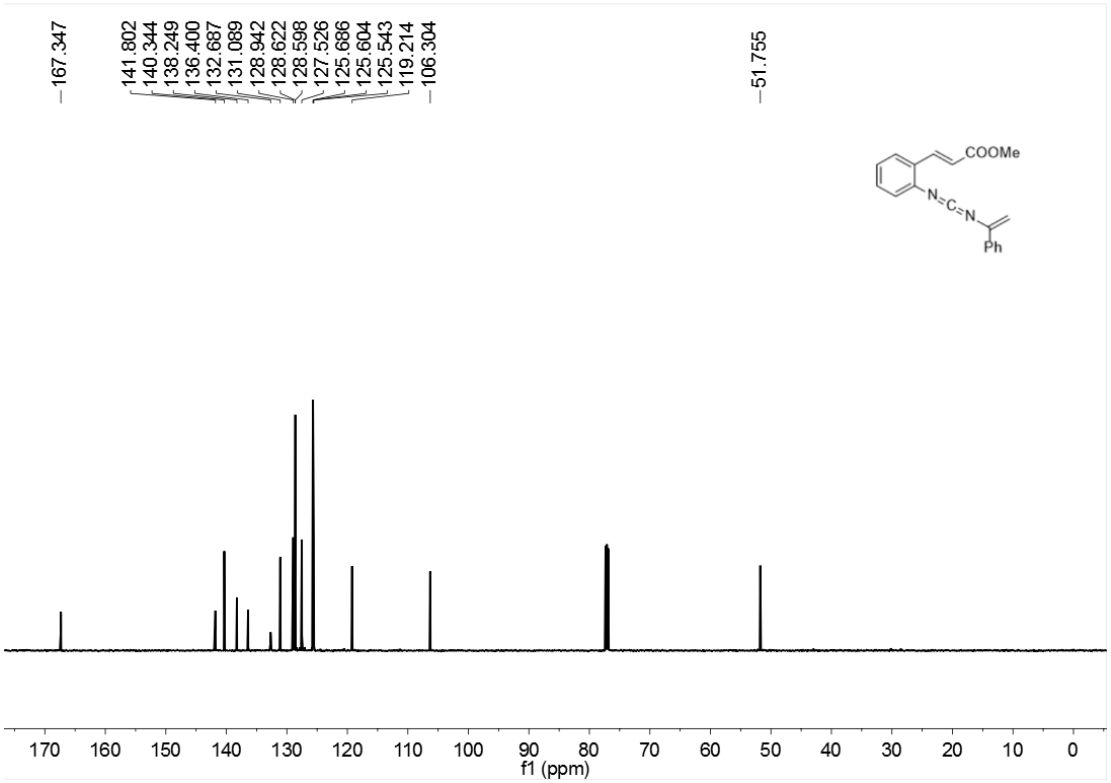


Figure 29. ^{1}H NMR, ^{13}C NMR spectra of compound **5aa**