ESI for

A Highly Efficient and Aerobic Protocol for the Synthesis of *N*-Heteroaryl Substituted Carbazole Derivatives via a Palladium-Catalyzed Ligand-Free Suzuki Reaction

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Materials and Methods and Experimental Procedure

General：Unless otherwise noted, all the reactions were carried out in air. All *N*-heteroaryl halides were purchased from Alfa Aesar or Avocado. 4-(9H-carbazol-9-yl) phenyl-boronic acid (**CPBA**) and 9-phenyl-9H-carbazol-3-ylboronic acid (**PCBA**) were purchased from Trusyn Chem-Tech Co., Ltd, China. Other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Brucker Advance II 400 spectrometer using TMS as internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data of the products were collected with a MS-EI instrument. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90 °C). Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

General Procedure for the Suzuki Cross-Coupling of *N*-Heteroaryl Halides with CPBA. A mixture of *N*-heteroaryl halide (0.25 mmol), **CPBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.00375 mmol), distilled water (1 mL) and ethanol (3 mL) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200-300 mesh).

General Procedure for the Suzuki Cross-Coupling of *N*-Heteroaryl Halides with PCBA. A mixture of *N*-heteroaryl halide (0.25 mmol), **PCBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.00375 mmol), distilled water (1 mL) and ethanol (3 mL) was stirred at 80 °C in air for indicated

time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200-300 mesh).

General Procedure for the Suzuki Cross-Coupling of *N*-Heteroaryl Halides with Arylboronic Acids. A mixture of *N*-heteroaryl halide (0.25 mmol), arylboronic acid (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.00375 mmol), distilled water (1 mL) and ethanol (3 mL) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200-300 mesh).

Characterization Data

9-(4-(pyridin-2-yl)phenyl)-9H-carbazole[1]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.76 (d, J = 4.8 Hz, 1H), 8.24 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 7.6 Hz, 2H), 7.83-7.81 (m, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.44-7.40 (m, 2H), 7.32-7.28 (m, 3H) ppm.

9-(4-(5-methylpyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.58 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.62 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.93, 150.29, 140.80, 138.48, 138.05, 137.50, 132.01, 128.18, 127.21, 126.01, 123.50, 120.33, 120.04, 109.88, 18.23 ppm. MS (EI): m/z = 334.1467 $[M]^+$.

9-(4-(5-fluoropyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.60 (d, J = 2.8 Hz, 1H), 8.19-8.15 (m, 4H), 7.83-7.81 (m, 1H), 7.70-7.68 (m, 2H), 7.56-7.51 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.45-7.40 (m, 2H), 7.32-7.28 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.28, 157.72, 152.88, 152.84, 140.75, 138.42, 138.12, 137.88, 137.38, 128.29, 127.28, 126.05, 123.82, 123.64, 123.58, 121.35, 121.31, 120.37, 120.14, 109.83 ppm. MS (EI): m/z = 338.1223 $[M]^+$.

9-(4-(5-nitropyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.55 (d, J = 2.4 Hz, 1H), 8.61-8.58 (m, 1H), 8.36-8.34 (m, 2H), 8.16 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.79-7.76 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.46-7.42 (m, 2H), 7.34-7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.44, 145.45, 143.01, 140.44, 140.33, 135.70, 132.15, 129.28, 127.29, 126.17, 123.77, 120.47, 119.99, 109.78 ppm. MS (EI): m/z = 365.1167 $[M]^+$.

9-(4-(6-methylpyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.23-8.21 (m, 2H), 8.16 (d, J = 7.6 Hz, 2H), 7.72-7.66 (m, 3H), 7.61 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.45-7.41 (m, 2H), 7.32-7.28 (m, 2H), 7.16 (d, J = 7.6 Hz, 1H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.64, 156.07, 140.85, 138.84, 138.21, 137.12, 128.55, 127.22, 126.02, 123.53, 121.95, 120.34, 120.05, 117.68,

109.88, 24.76 ppm. MS (EI): *m*/*z* = 334.1470 $[M]^+$.

9-(4-(6-fluoropyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.25-8.23 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.93-7.88 (m, 1H), 7.73-7.68 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.32-7.29 (m, 2H), 6.94-6.91 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.72, 162.34, 155.45, 155.31, 141.90, 141.82, 140.66, 139.01, 136.47, 128.48, 127.51, 127.18, 126.09, 123.62, 120.40, 120.23, 120.13, 117.35, 117.31, 109.84, 108.25, 107.87 ppm. MS (EI): *m*/*z* = 338.1222 $[M]^+$.

1-(6-(4-(9H-carbazol-9-yl)phenyl)pyridin-2-yl)ethanone

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.36-8.34 (m, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.05-8.02 (m, 2H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 2.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 200.40, 155.60, 153.59, 140.69, 138.93, 137.89, 137.33, 128.42, 127.28, 126.07, 123.61, 123.46, 120.41, 120.21, 120.09, 109.83, 25.81 ppm. MS (EI): *m*/*z* = 362.1428 $[M]^+$.

6-(4-(9H-carbazol-9-yl)phenyl)picolinaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.22 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.03-7.96 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 193.78, 157.02, 152.89, 140.65, 139.12, 138.05, 137.02, 128.58, 127.34, 126.12, 124.44, 123.63, 120.44, 120.27, 120.05, 109.83 ppm. MS (EI): *m*/*z* = 348.1268 $[M]^+$.

9-(4-(6-methoxypyridin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.71-7.65 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.94, 153.77, 140.81, 139.35, 138.24, 138.11, 128.18, 127.09, 126.03, 123.54, 120.37, 120.09, 112.89, 109.91, 109.72, 53.31 ppm. MS (EI): *m*/*z* = 350.1422 $[M]^+$.

6-(4-(9H-carbazol-9-yl)phenyl)picolinonitrile

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.95 (t, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.07, 140.56, 139.65, 137.95, 135.98, 134.07, 128.64, 127.31, 126.79, 126.12, 123.68, 123.40, 120.42, 120.33, 117.32, 109.78 ppm. MS (EI): *m*/*z* = 345.1269 $[M]^+$.

9-(4-(quinolin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.41 (d, *J* = 8.4 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.79-7.74 (m, 3H), 7.58 (t, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.44, 148.39, 140.77, 138.78, 138.72, 137.05, 129.89, 129.80, 129.10, 127.54, 127.30, 126.54, 126.05, 123.58, 120.36, 120.13, 118.85, 109.88 ppm. MS (EI): *m*/*z* = 370.1479 $[M]^+$.

9-(4-(quinolin-3-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.30 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 2.0 Hz, 1H), 8.18 (t, J = 7.6 Hz, 3H), 7.95 (t, J = 8.0 Hz, 3H), 7.79-7.74(m, 3H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.72, 147.56, 140.76, 137.79, 136.93, 133.37, 132.98, 129.68, 129.37, 128.87, 128.09, 128.03, 127.72, 127.24, 126.08, 123.57, 120.42, 120.19, 109.79 ppm. MS (EI): m/z = 370.1476 $[M]^+$.

9-(4-(pyrimidin-5-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.27 (s, 1H), 9.07 (s, 2H), 8.17 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.49-7.42 (m, 4H), 7.34-7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.78, 154.91, 140.60, 138.75, 133.60, 133.17, 128.51, 127.91, 126.14, 123.66, 120.46, 120.36, 109.67 ppm. MS (EI): m/z = 321.1257 $[M]^+$.

9-(4-(pyrazin-2-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.14 (d, J = 1.6 Hz, 1H), 8.71-8.69 (m, 1H), 8.57 (d, J = 2.4 Hz, 1H), 8.28-8.26 (m, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.77-7.73 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.45-7.42 (m, 2H), 7.33-7.29 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.06, 144.38, 143.04, 142.01, 140.59, 139.47, 135.13, 128.50, 127.43, 126.11, 123.67, 120.42, 120.31, 109.79 ppm. MS (EI): m/z = 321.1267 $[M]^+$.

9-(4-(6-methoxypyridin-3-yl)phenyl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.50 (d, J = 2.4 Hz, 1H), 8.16 (d, J = 7.6 Hz, 2H), 7.91-7.88 (m, 1H), 7.76-7.74 (m, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.33-7.29 (m, 2H), 6.89 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.88, 145.10, 140.83, 137.42, 137.02, 136.97, 129.24, 128.05, 127.58, 126.04, 123.49, 120.39, 120.09, 111.09, 109.82, 53.68 ppm. MS (EI): m/z = 350.1418 $[M]^+$.

2,6-bis(4-(9H-carbazol-9-yl)phenyl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.43 (d, J = 8.4 Hz, 4H), 8.17 (d, J = 7.6 Hz, 4H), 7.96 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.8 Hz, 4H), 7.52 (d, J = 8.0 Hz, 4H), 7.46-7.42 (m, 4H), 7.31 (t, J = 7.2 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.15, 140.75, 138.74, 138.25, 137.88, 128.70, 127.21, 126.06, 123.59, 120.37, 120.15, 119.21, 109.89 ppm. MS (EI): m/z = 561.2205 $[M]^+$.

9-phenyl-3-(pyridin-2-yl)-9H-carbazole[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.82 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 4.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.06-8.04 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.63-7.57 (m, 4H), 7.49-7.45 (m, 2H), 7.42 (d, J = 4.0 Hz, 2H), 7.33-7.29 (m, 1H), 7.21-7.18 (m, 1H) ppm.

3-(5-methylpyridin-2-yl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.78 (d, J = 1.2 Hz, 1H), 8.55 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.03-8.01 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.63-7.55 (m, 5H), 7.49-7.44 (m, 2H), 7.41 (d, J = 4.0 Hz, 2H), 7.32-7.29 (m, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ =

155.47, 149.93, 141.48, 141.31, 137.64, 137.42, 131.61, 130.75, 129.93, 127.56, 127.09, 126.15, 124.95, 123.91, 123.74, 120.61, 120.23, 119.86, 118.81, 109.95, 109.89, 18.15 ppm. MS (EI): *m*/*z* = 334.1466 $[M]^+$.

3-(5-fluoropyridin-2-yl)-9-phenyl-9H-carbazole[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.74 (d, *J* = 1.6 Hz, 1H), 8.57 (d, *J* = 2.8 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.00-7.98 (m, 1H), 7.85-7.81 (m, 1H), 7.65-7.57 (m, 4H), 7.51-7.45 (m, 3H), 7.43-7.42 (m, 2H), 7.34-7.30 (m, 1H) ppm.

3-(5-nitropyridin-2-yl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.52 (d, *J* = 2.4 Hz, 1H), 8.94 (d, *J* = 1.6 Hz, 1H), 8.54-8.51 (m, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.18-8.15 (m, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.67-7.63 (m, 2H), 7.60-7.78 (m, 2H), 7.55-7.42 (m, 4H), 7.38-7.34 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.06, 145.38, 142.52, 142.17, 141.68, 137.08, 131.86, 130.09, 128.99, 128.01, 127.09, 126.73, 125.71, 124.13, 123.38, 120.79, 120.64, 120.38, 119.37, 110.34, 110.26 ppm. MS (EI): *m*/*z* = 365.1159 $[M]^+$.

3-(6-methylpyridin-2-yl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.79 (d, *J* = 1.6 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.06-8.04 (m, 1H), 7.64-7.63 (m, 2H), 7.61-7.57 (m, 4H), 7.49-7.45 (m, 2H), 7.42-7.41 (m, 2H), 7.33-7.30 (m, 1H), 7.08-7.06 (m, 1H), 2.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.29, 157.65, 141.45, 141.37, 137.64, 136.90, 132.03, 129.93, 127.55, 127.09, 126.10, 125.28, 123.85, 123.75, 120.87, 120.66, 120.18, 119.17, 117.45, 109.93, 109.90, 24.89 ppm. MS (EI): *m*/*z* = 334.1464 $[M]^+$.

3-(6-fluoropyridin-2-yl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.84 (d, *J* = 1.6 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.07-8.05 (m, 1H), 7.88-7.82 (m, 1H), 7.75-7.72 (m, 1H), 7.65-7.61 (m, 2H), 7.59-7.57 (m, 2H), 7.51-7.47 (m, 1H), 7.46-7.40 (m, 3H), 7.35-7.31 (m, 1H), 6.84-6.82 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.70, 162.34, 157.14, 157.00, 141.78, 141.62, 141.54, 137.42, 130.00, 129.68, 127.73, 127.07, 126.39, 125.04, 123.91, 123.59, 120.67, 120.47, 119.32, 116.93, 116.89, 110.06, 109.96, 106.72, 106.34 ppm. MS (EI): *m*/*z* = 338.1217 $[M]^+$.

1-(6-(9-phenyl-9H-carbazol-3-yl)pyridin-2-yl)ethanone

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.86 (d, *J* = 1.6 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 1H), 7.89 (t, *J* = 7.6 Hz, 1H), 7.66-7.58 (m, 4H), 7.52-7.47 (m, 2H), 7.45-7.42 (m, 2H), 7.36-7.32 (m, 1H), 2.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 200.88, 157.21, 153.39, 141.73, 141.53, 137.55, 137.44, 130.64, 130.00, 127.74, 127.09, 126.39, 125.15, 123.88, 123.55, 123.21, 120.49, 120.39, 119.00, 110.11, 25.93 ppm. MS (EI): *m*/*z* = 362.1415 $[M]^+$.

3-(6-methoxypyridin-2-yl)-9-phenyl-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.82 (d, *J* = 1.2 Hz, 1H), 8.24-8.22 (m, 1H), 8.15-8.12 (m, 1H), 7.67-7.57 (m, 5H), 7.50-7.46 (m, 2H), 7.45-7.44 (m, 1H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.35-7.29

(m, 1H), 6.68-6.66 (m, 1H), 4.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.81, 155.56, 141.47, 139.24, 137.61, 131.42, 129.96, 127.61, 127.10, 126.18, 125.12, 123.75, 123.72, 120.51, 120.24, 118.81, 112.52, 110.00, 109.83, 108.11, 53.32 ppm. MS (EI): *m*/*z* = 350.1419 $[M]^+$.

6-(9-phenyl-9H-carbazol-3-yl)picolinonitrile

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.85 (d, *J* = 1.2 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.11-8.06 (m, 2H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.60-7.57 (m, 3H), 7.53-7.42 (m, 4H), 7.37-7.33 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.58, 142.04, 141.57, 137.54, 137.25, 133.70, 130.02, 129.20, 127.84, 127.07, 126.53, 125.75, 125.04, 123.96, 123.43, 123.16, 120.63, 120.56, 119.47, 117.73, 110.16, 110.12 ppm. MS (EI): *m*/*z* = 345.1261 $[M]^+$.

9-phenyl-3-(quinolin-2-yl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.99 (d, *J* = 1.6 Hz, 1H), 8.29-8.21 (m, 4H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76-7.72 (m, 1H), 7.67-7.61 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.51-7.48 (m, 1H), 7.45-7.43 (m, 2H), 7.36-7.32 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.95, 148.48, 141.75, 141.55, 137.54, 136.69, 131.80, 129.99, 129.64, 129.57, 127.67, 127.54, 127.11, 126.99, 126.29, 125.89, 125.83, 124.00, 123.75, 120.72, 120.38, 119.87, 119.15, 110.09, 110.05 ppm. MS (EI): *m*/*z* = 370.1471 $[M]^+$.

9-phenyl-3-(pyrimidin-5-yl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.20 (s, 1H), 9.08 (s, 2H), 8.35 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.66-7.57 (m, 5H), 7.54-7.50 (m, 2H), 7.49-7.43 (m, 2H), 7.37-7.33 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.79, 154.90, 141.51, 141.17, 137.24, 135.12, 130.06, 127.90, 127.10, 126.73, 126.00, 124.81, 124.33, 122.99, 120.53, 120.50, 118.89, 110.81, 110.18 ppm. MS (EI): *m*/*z* = 321.1265 $[M]^+$.

9-phenyl-3-(pyrazin-2-yl)-9H-carbazole

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.16 (d, *J* = 1.2 Hz, 1H), 8.84 (d, *J* = 1.6 Hz, 1H), 8.65 (t, *J* = 2.0 Hz, 1H), 8.48 (d, *J* = 2.8 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.10-8.07 (m, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.53-7.50 (m, 2H), 7.47-7.42 (m, 2H), 7.36-7.32 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.58, 144.07, 142.13, 142.00, 141.94, 141.57, 137.32, 130.02, 128.31, 127.83, 127.12, 126.52, 124.87, 124.10, 123.42, 120.62, 120.53, 119.28, 110.32, 110.11 ppm. MS (EI): *m*/*z* = 321.1256 $[M]^+$.

2-phenylpyridine[3]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.70 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.77-7.72 (m, 2H), 7.48-7.42 (m, 3H), 7.24-7.22 (m, 1H) ppm.

5-methyl-2-phenylpyridine[4]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.51 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 2.36 (s, 3H) ppm.

2-(*p*-tolyl)pyridine[3]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.68 (d, J = 4.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.74-7.69 (m, *2*H), 7.29 (d, J = 8.0 Hz, 2H), 7.21-7.19 (m, 1H), 2.41 (s, 3H) ppm.

2-(4-methoxyphenyl)pyridine[3]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.66 (d, J = 4.4 Hz, 1H), 7.95 (d, J = 8.8 Hz, 2H), 7.73-7.65 (m, 2H), 7.17 (t, J = 6.0 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H) ppm

2-(4-fluorophenyl)pyridine[5]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.66 (d, J = 4.8 Hz, 1H), 7.98-7.95 (m, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.22-7.20 (m, 3H), 7.14 (t, J = 8.0 Hz, 1H) ppm

2-(3-tolyl)pyridine[6]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.69 (d, J = 4.8 Hz, 1H), 7.83 (s, 1H), 7.76-7.69 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.24-7.20 (m, 2H), 2.43 (s, 3H) ppm

2-(*o*-tolyl)pyridine[7]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.68 (m, 1H), 7.72-7.68 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.29-7.26 (m, 3H), 7.24-7.19 (m, 1H), 2.36 (s, 3H) ppm.

2-(2-methoxyphenyl)pyridine[8]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.69 (d, J = 4.4 Hz, 1H), 7.78-7.75 (m, 2H), 7.65-7.63 (m, 1H), 7.35 (t, J = 1.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 3.81 (s, 3H) ppm.

Diphenyl-(4-pyridin-2-yl-phenyl)-amine[9]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.65 (d, J = 4.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.72-7.66 (m, 2H), 7.29-7.25 (m, 4H), 7.19-7.13 (m, 7H), 7.05 (t, J = 7.2 Hz, 2H) ppm.

2-phenylpyrazine[10]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.04 (s, 1H), 8.64 (s, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.02(d, J = 7.6 Hz, 2H), 7.54-7.46 (m, 3H) ppm.

2-(4-fluorophenyl)pyrazine[11]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.00 (d, J = 1.6 Hz, 1H), 8.63-8.62 (m, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.05-7.80 (m, 2H), 7.23-7.18 (m, 2H) ppm.

References

1 K. Ono, M. Joho, K. Saito, M. Tomura, Y. Matsushita, S. Naka, H. Okada and H. Onnagawa, *Eur. J. Inorg. Chem.*, 2006, 3676.

2 C.-L. Ho, W.-Y. Wong, B. Yao, Z. Xie, L. Wang and Z. Lin, *J. Organomet. Chem.*, 2009, **694**, 2735.

3 Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Commun.*, 2007, 5069.

4 T. Nokami, Y. Tomida, T. Kamei, K. Itami and J.-i. Yoshida, *Org. Lett.*, 2006, **8**, 729.

5 C. Liu and W. Yang, *Chem. Commun.*, 2009, 6267.

6 A. Núñez, A. Sánchez, C. Burgos and J. Alvarez-Builla, *Tetrahedron*, 2004, **60**, 6217.

7 C. M. So, C. C. Yeung, C. P. Lau and F. Y. Kwong, *J. Org. Chem.*, 2008, **73**, 7803.

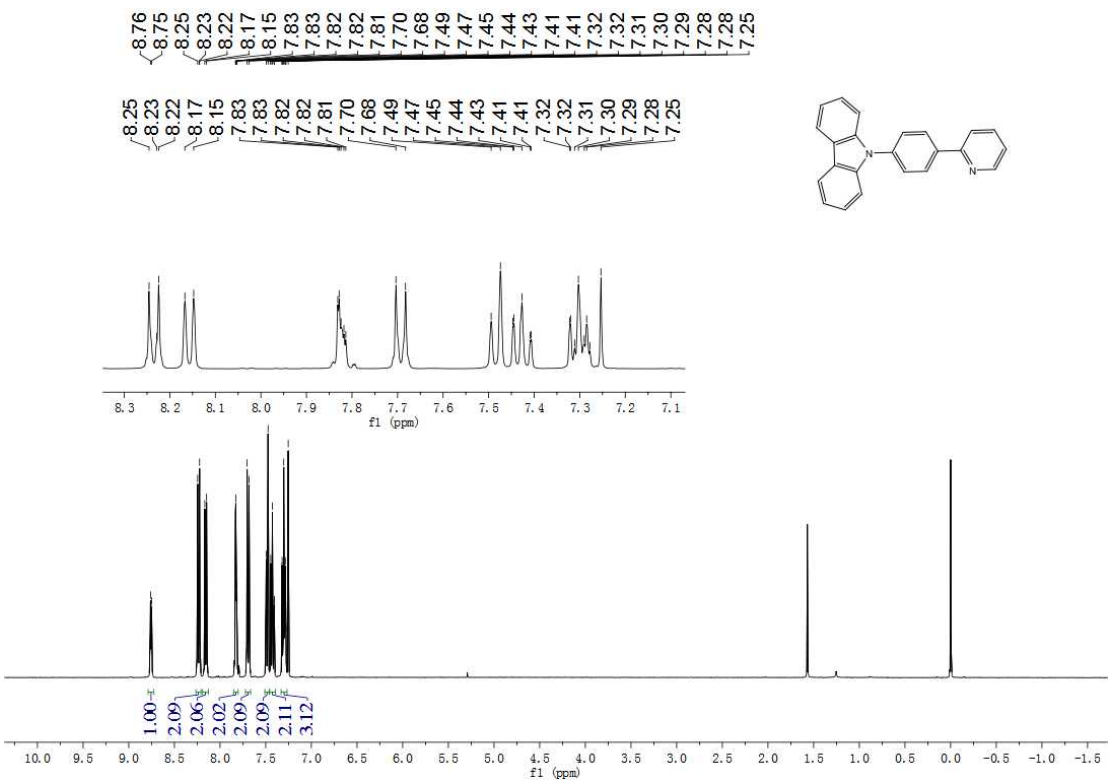
8 F. Mongin, L. Mojovic, B. Guillamet, F. Trécourt and G. Quéguiner, *J. Org. Chem.*, 2002, **67**, 8991.

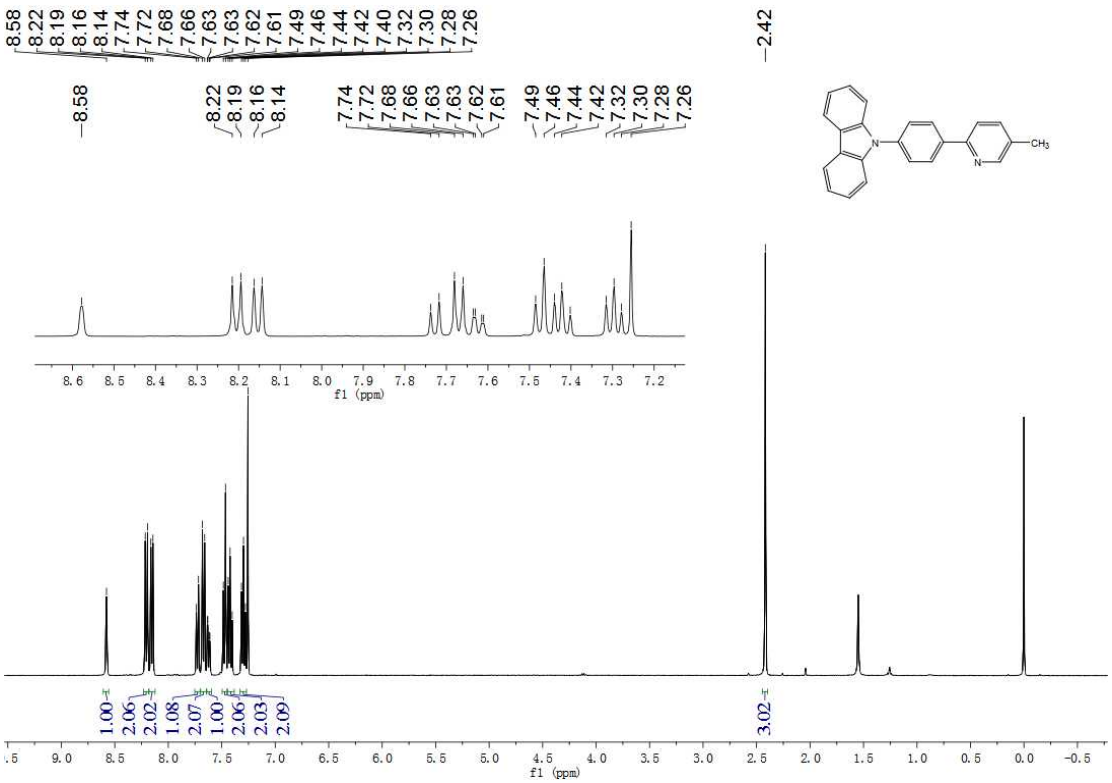
9 C. Liu, Q. Ni and J. Qiu, *Eur. J. Org. Chem.*, 2011, 3009.

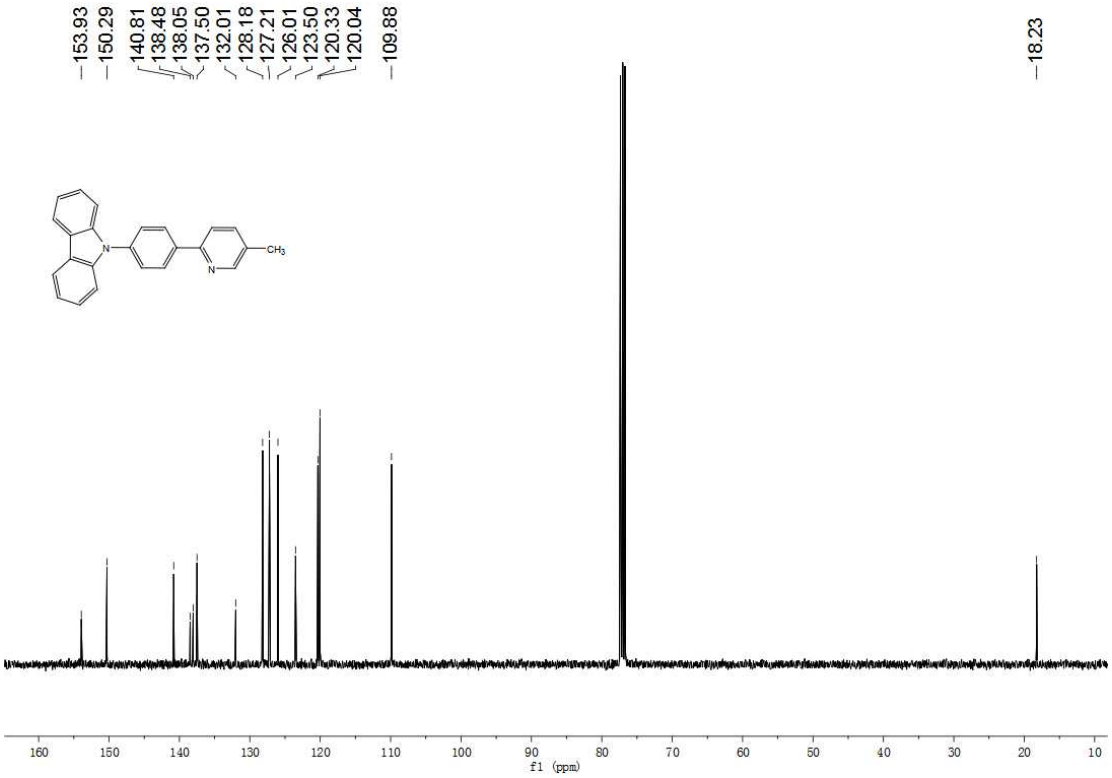
10 C.-L. Deng, S.-M. Guo, Y.-X. Xie and J.-H. Li, *Eur. J. Org. Chem.*, 2007, 1457.

11 C. Liu, N. Han, X. Song and J. Qiu, *Eur. J. Org. Chem.*, 2010, 5548.

NMR Spectra for Products



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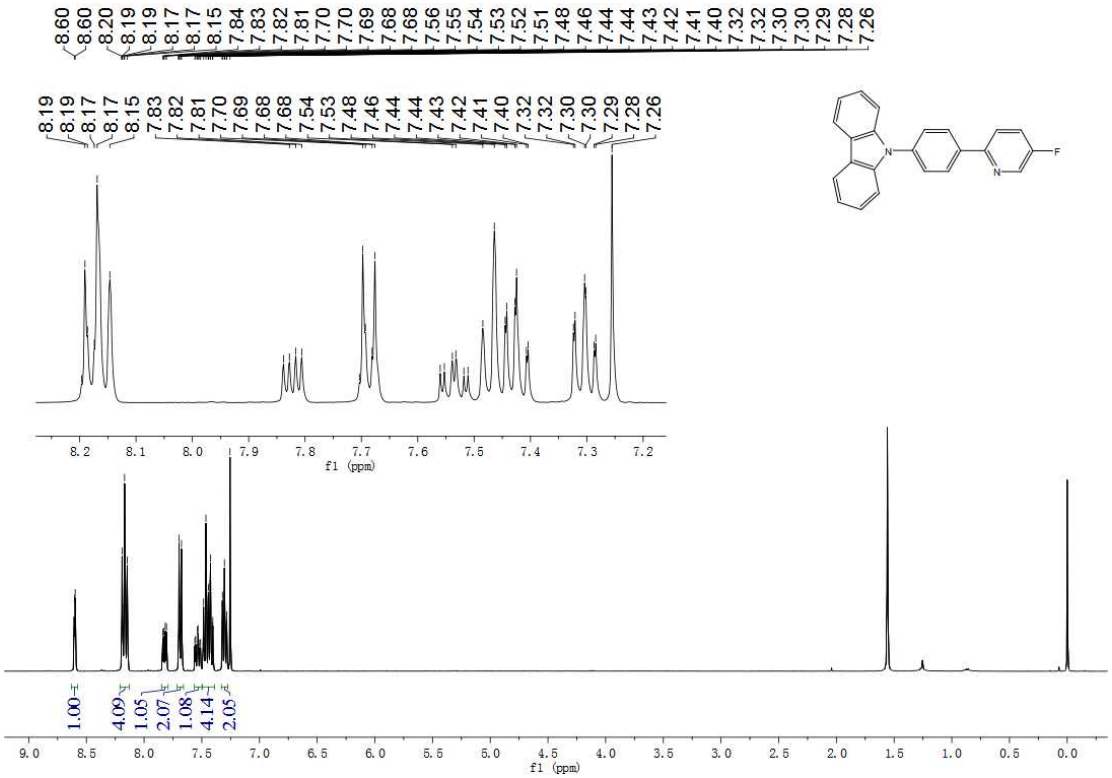
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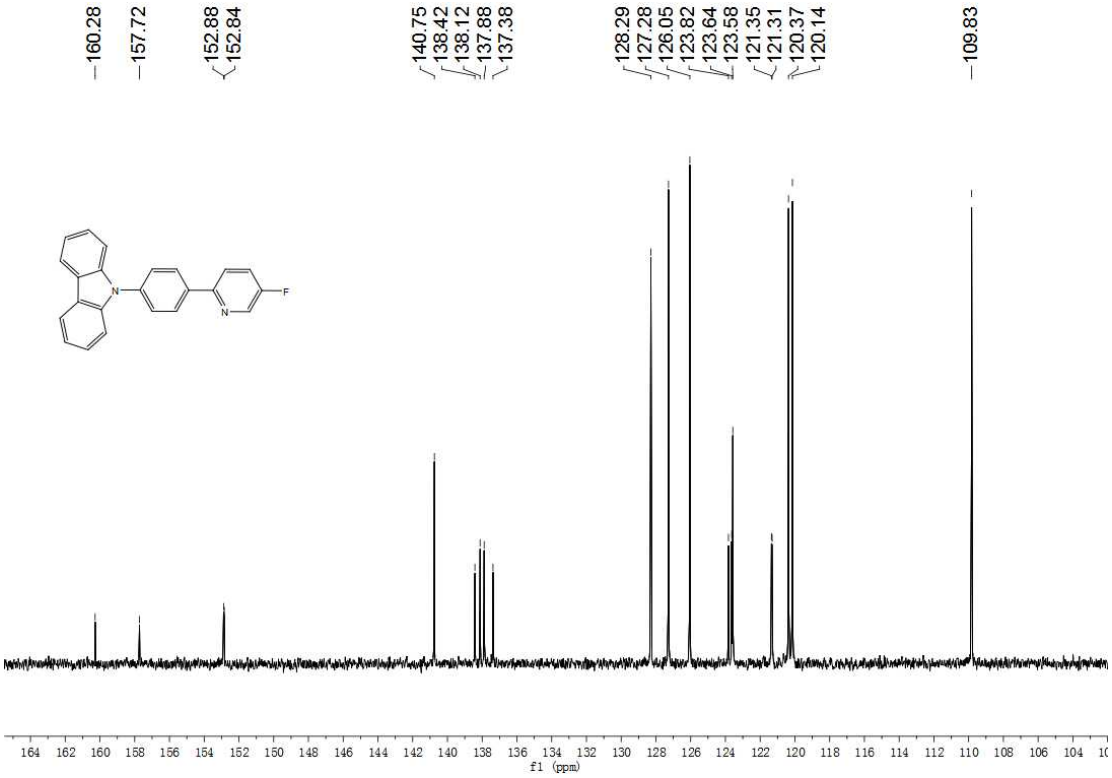
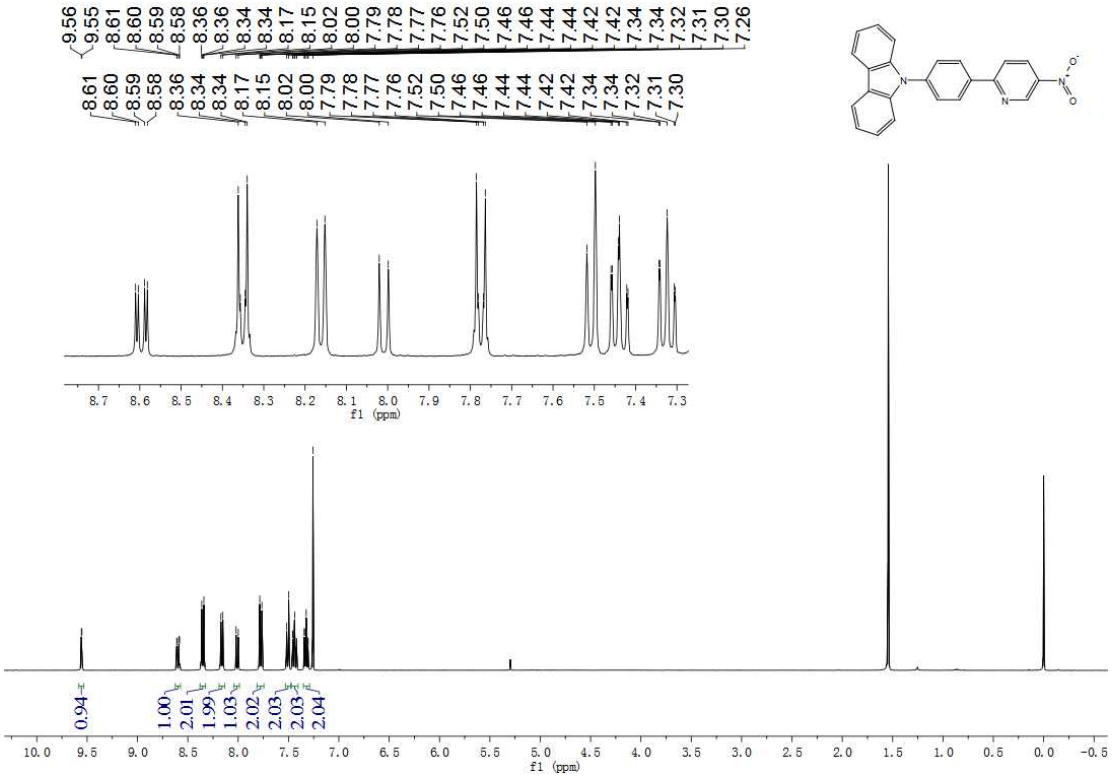
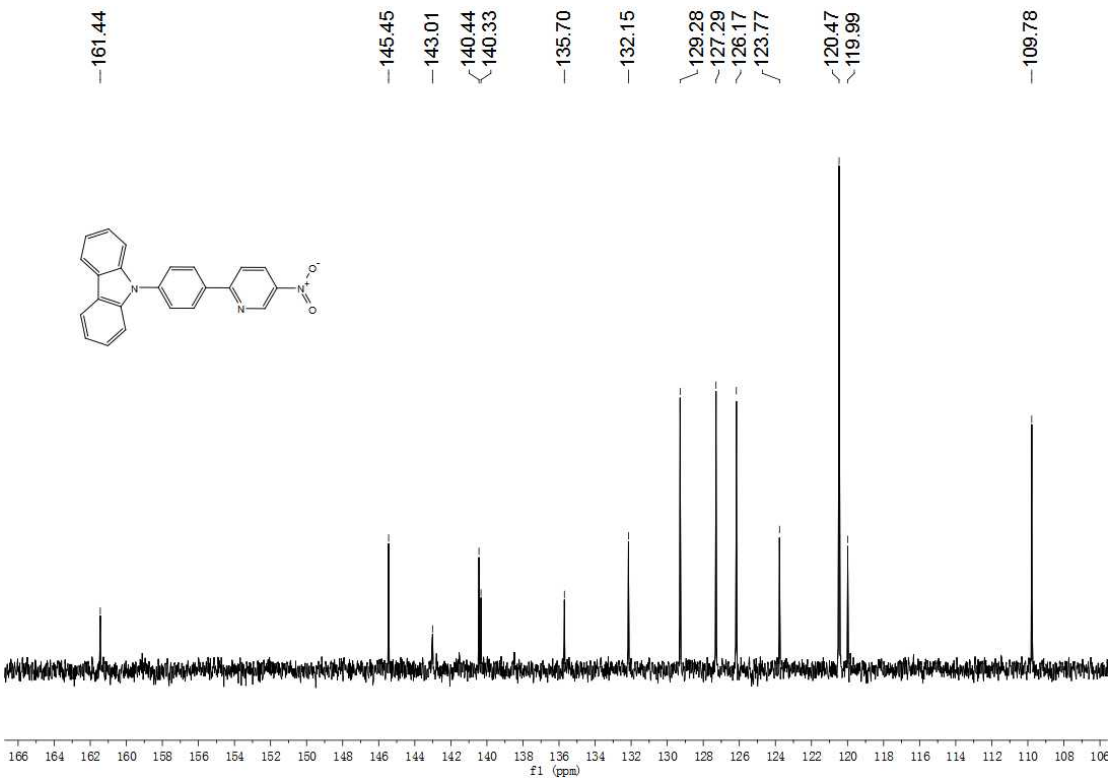
f1 (ppm)



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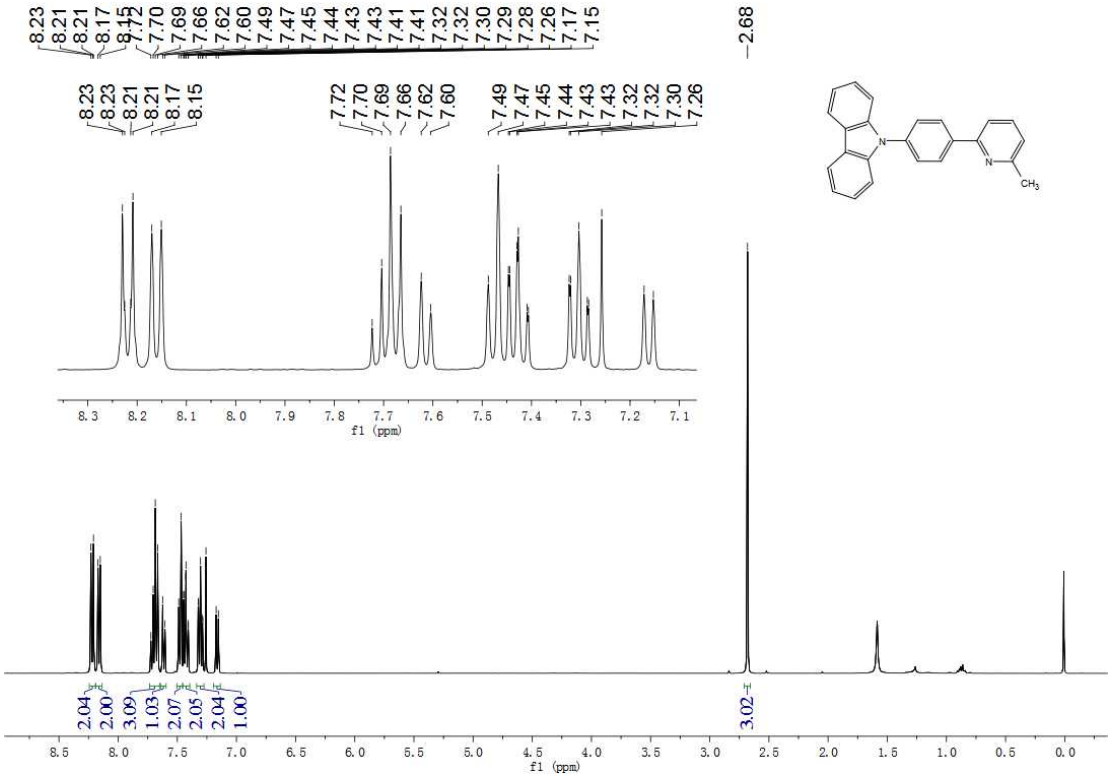
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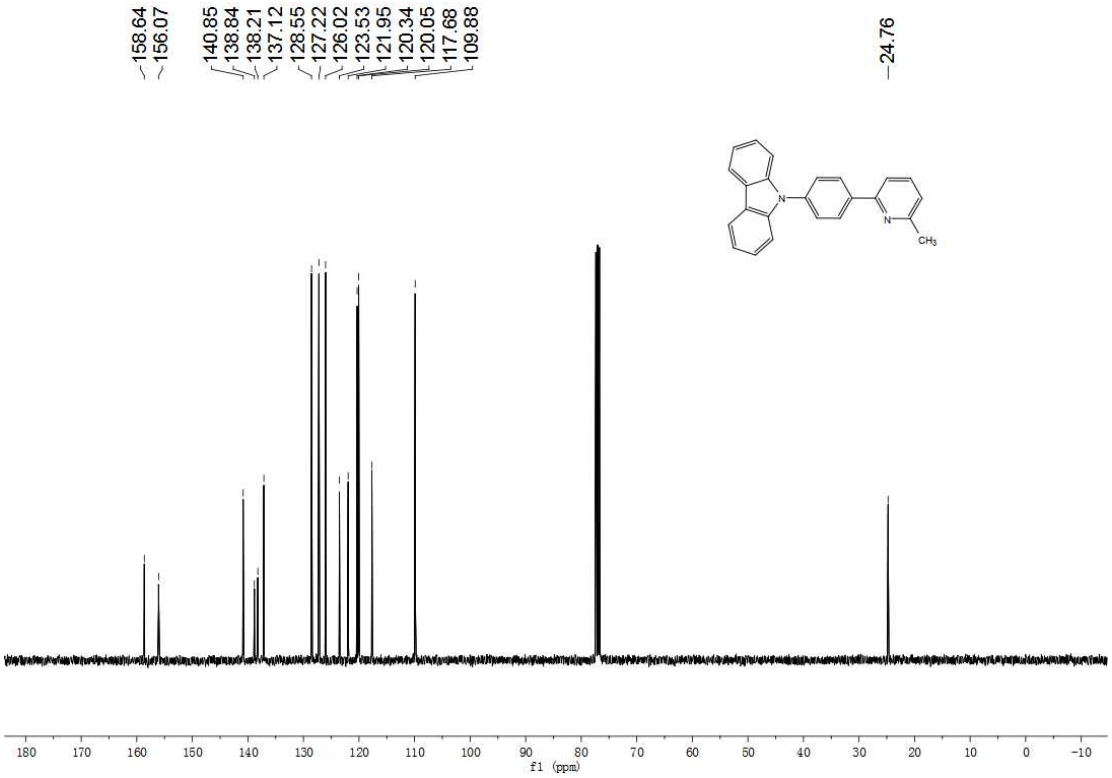
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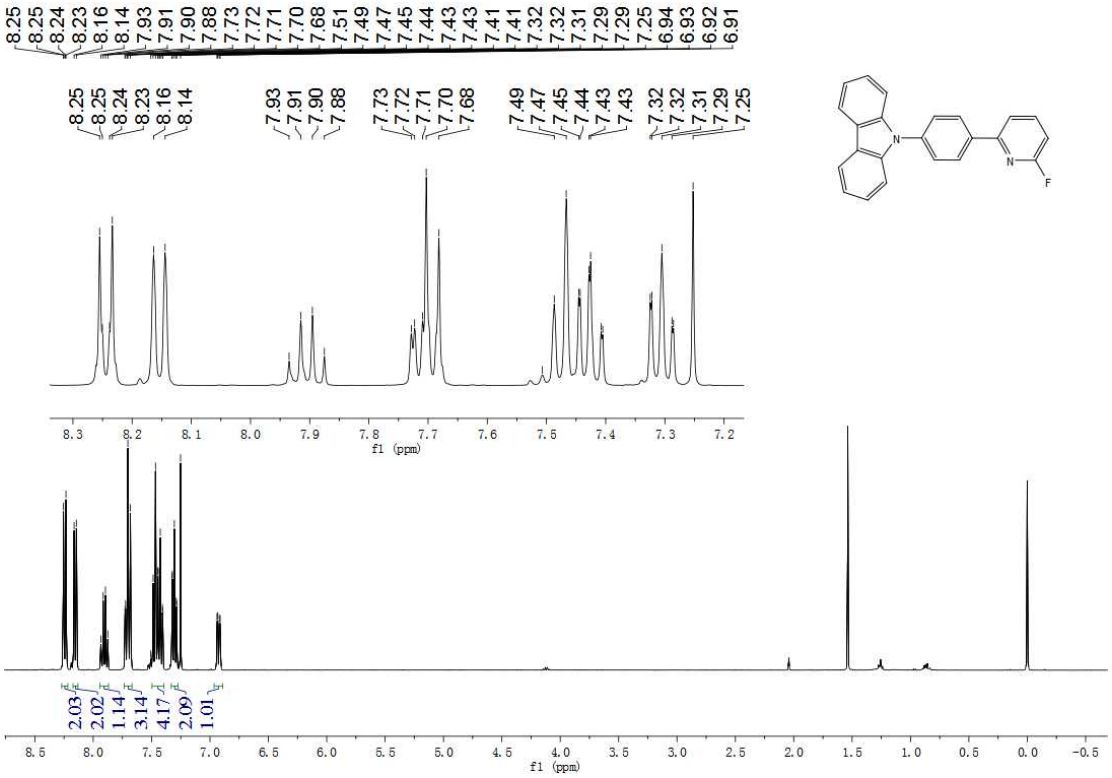
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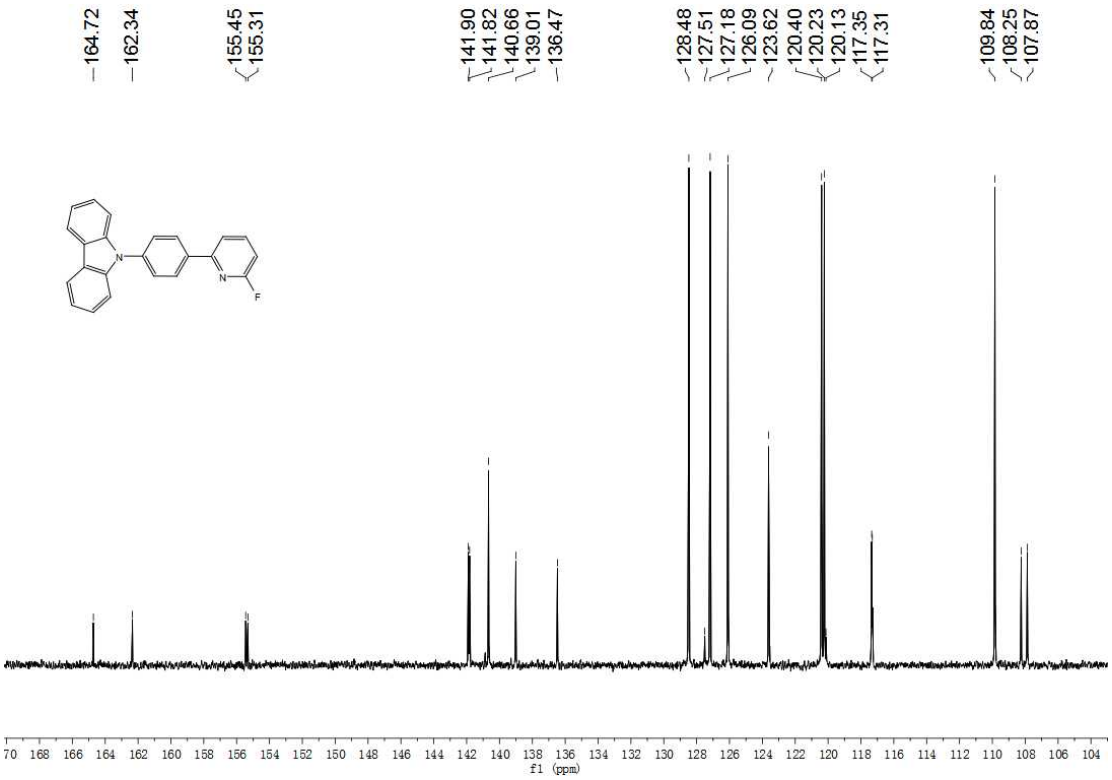
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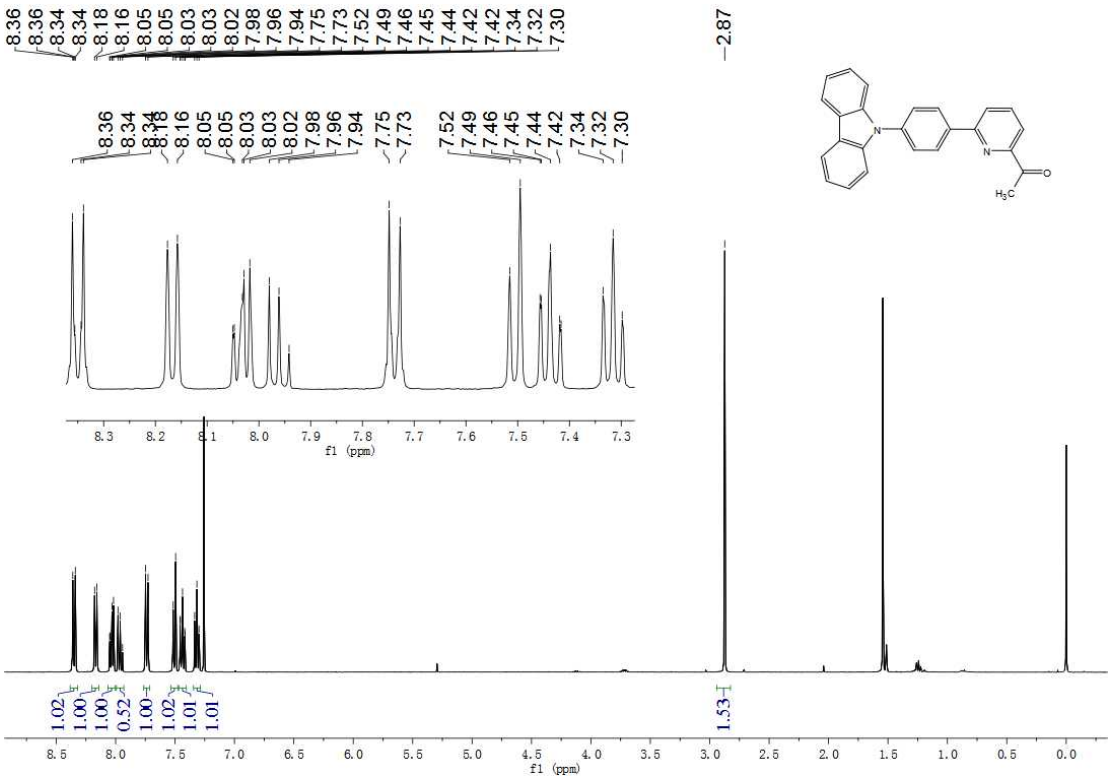
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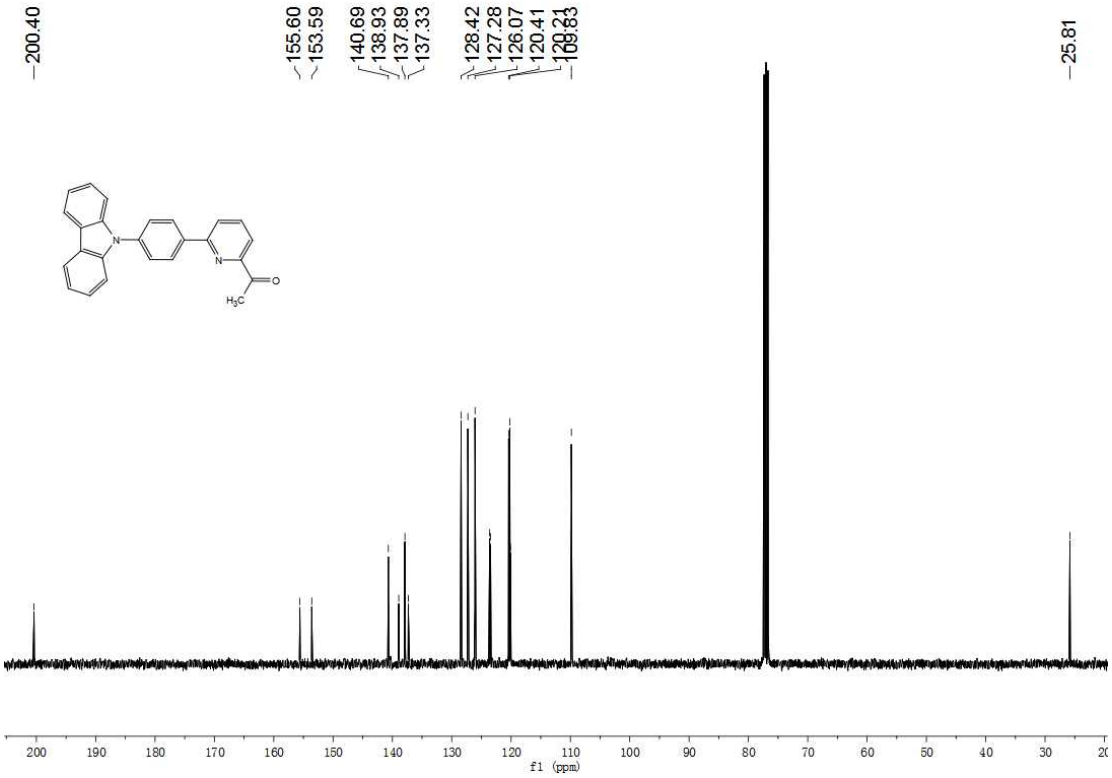
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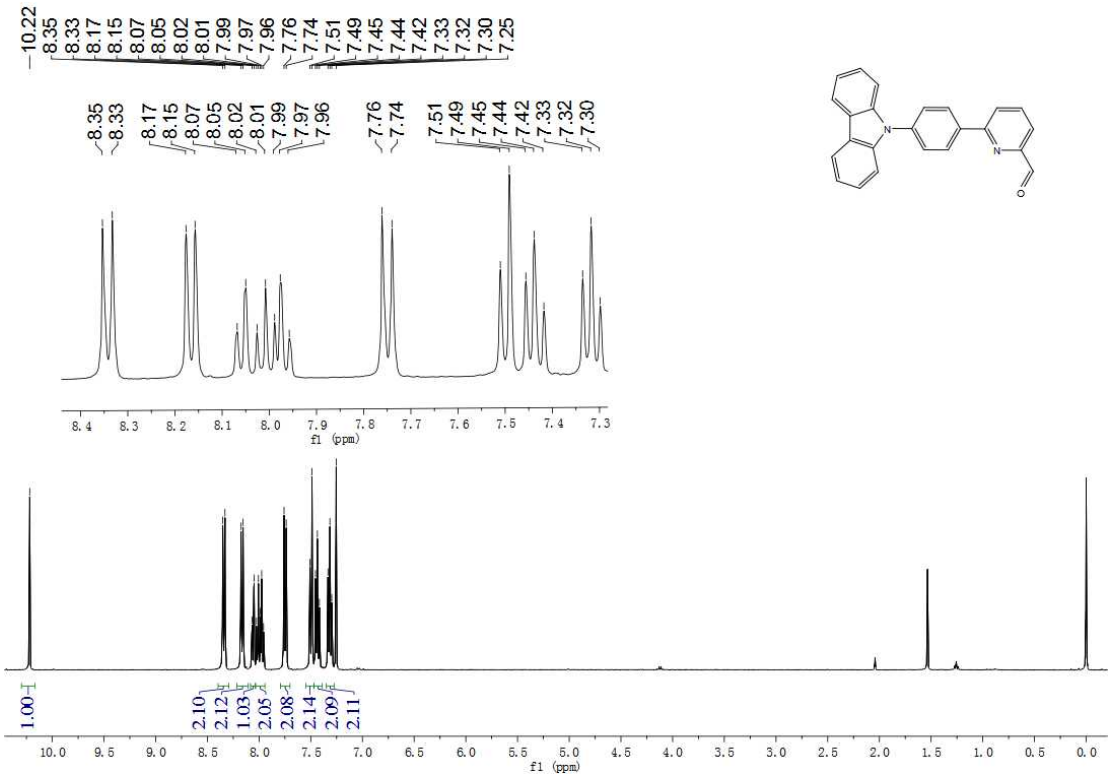
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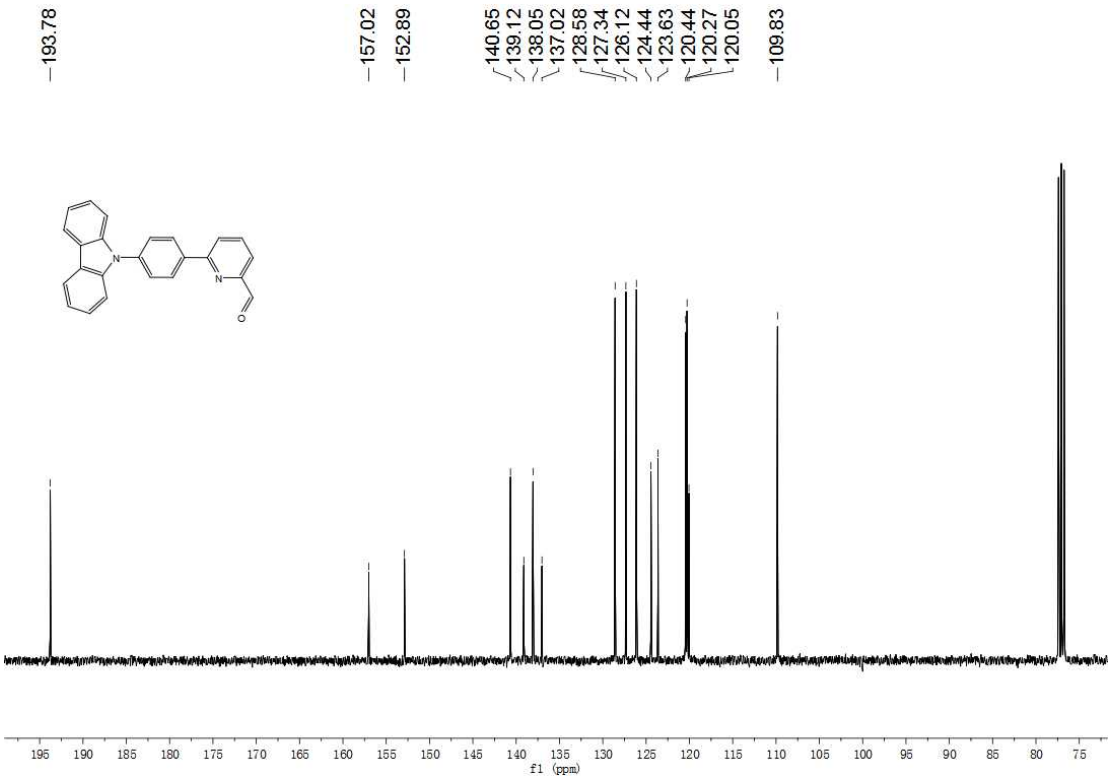

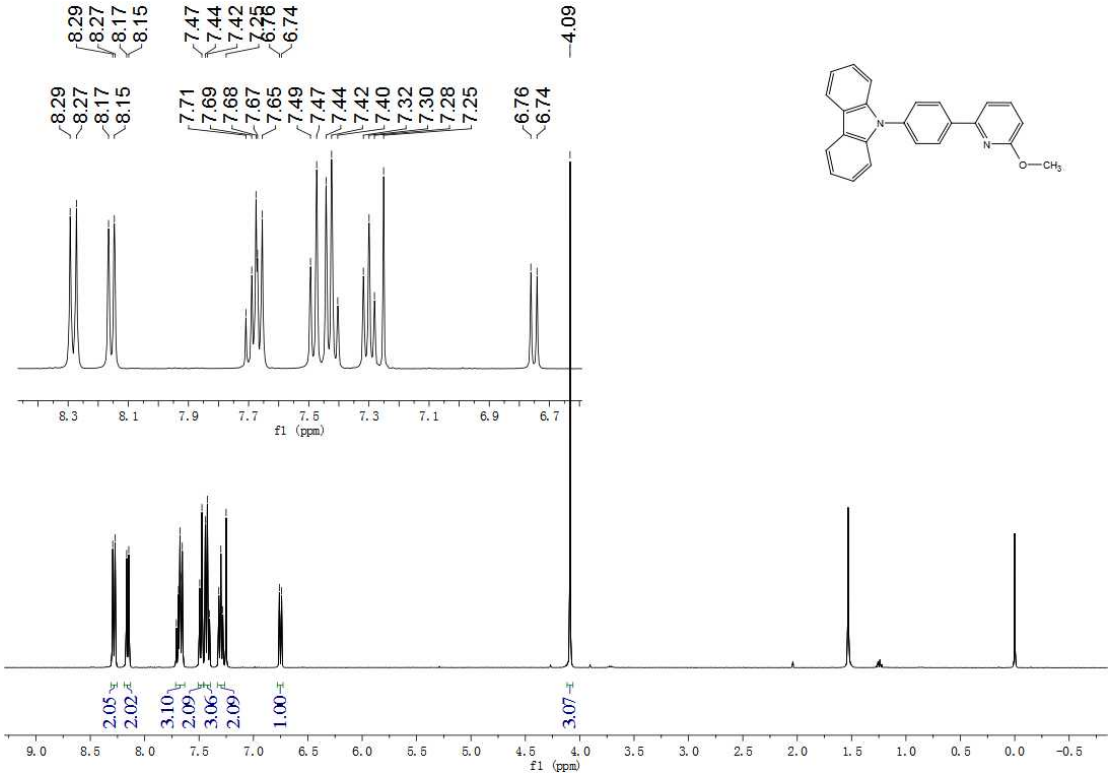

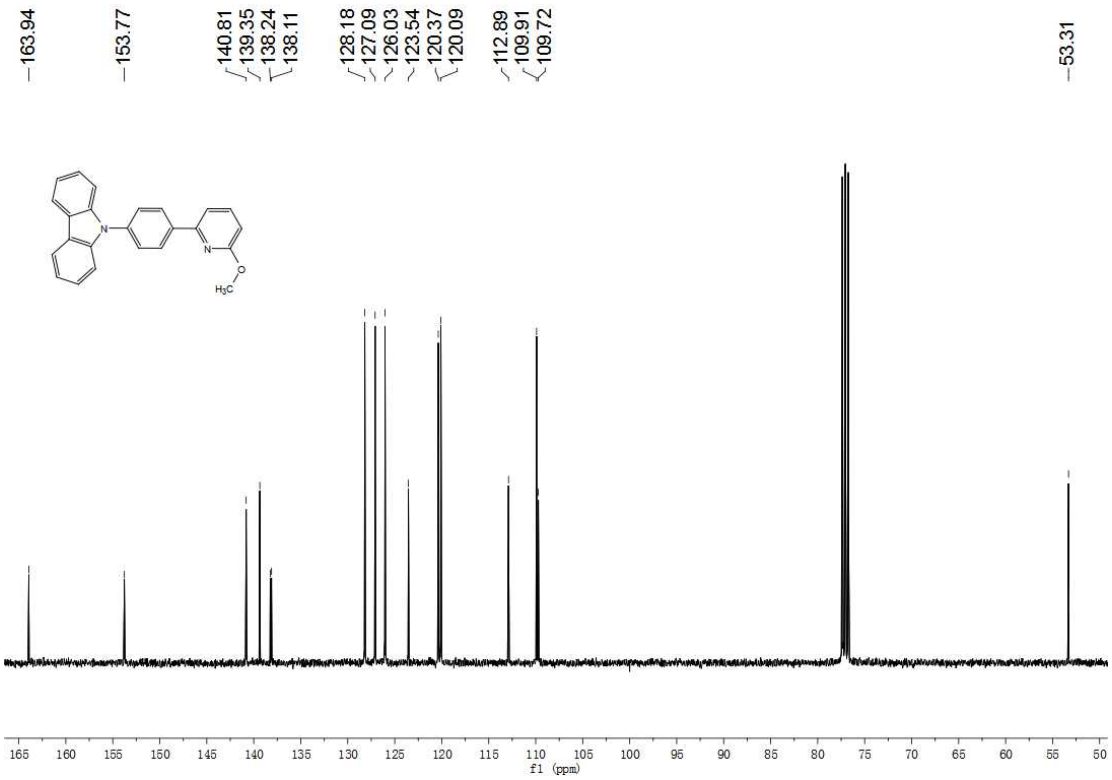
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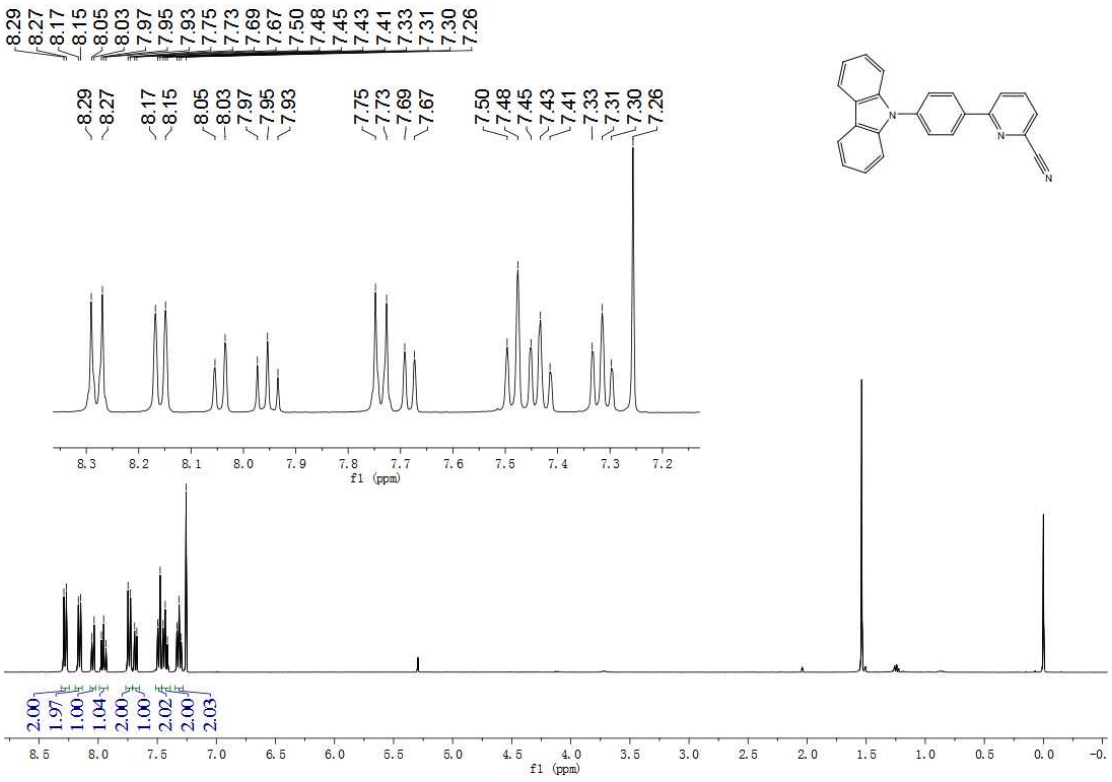
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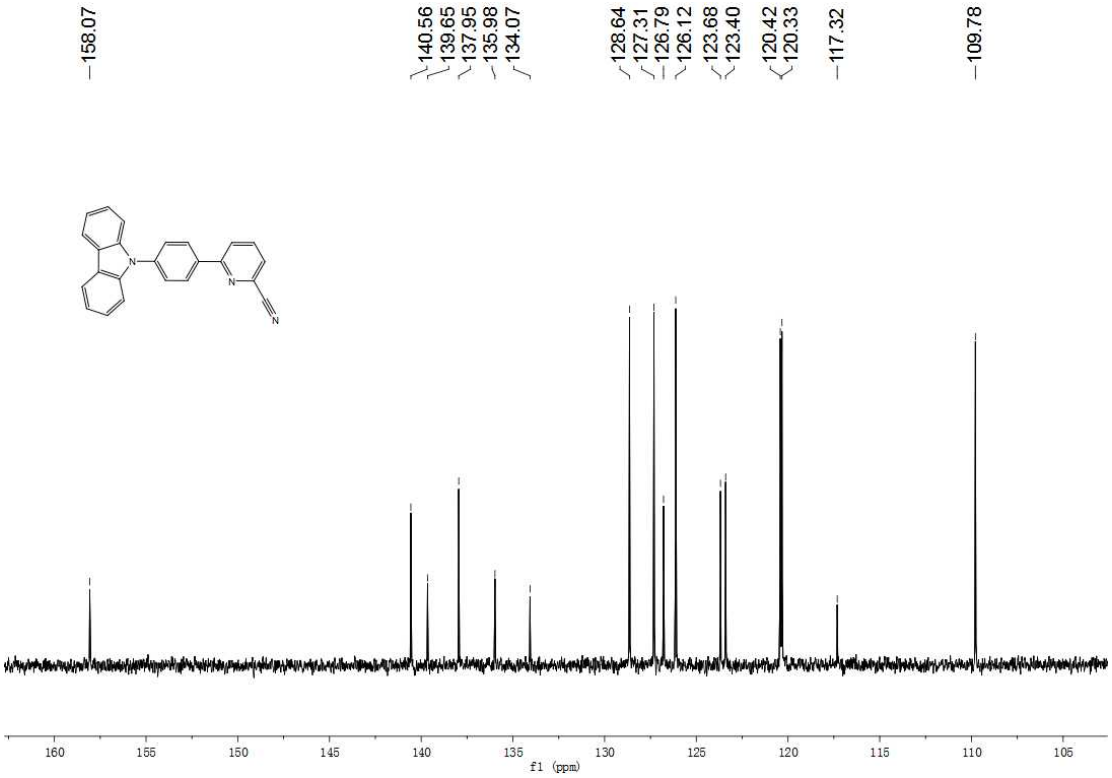
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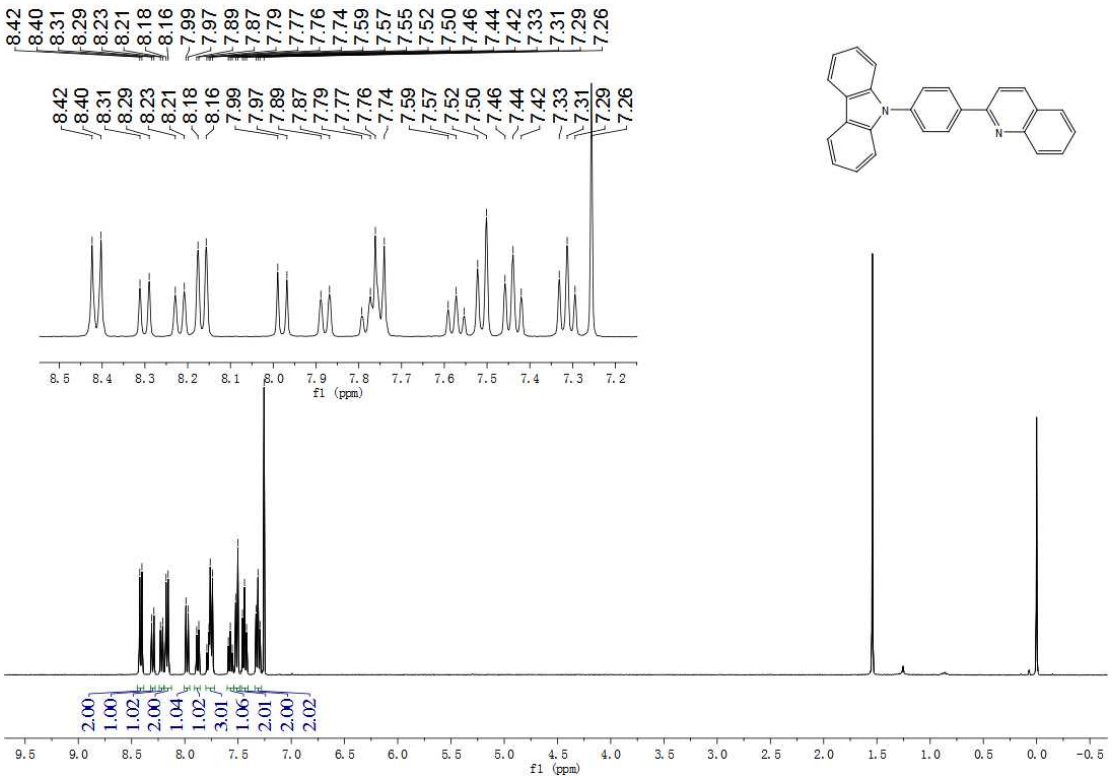
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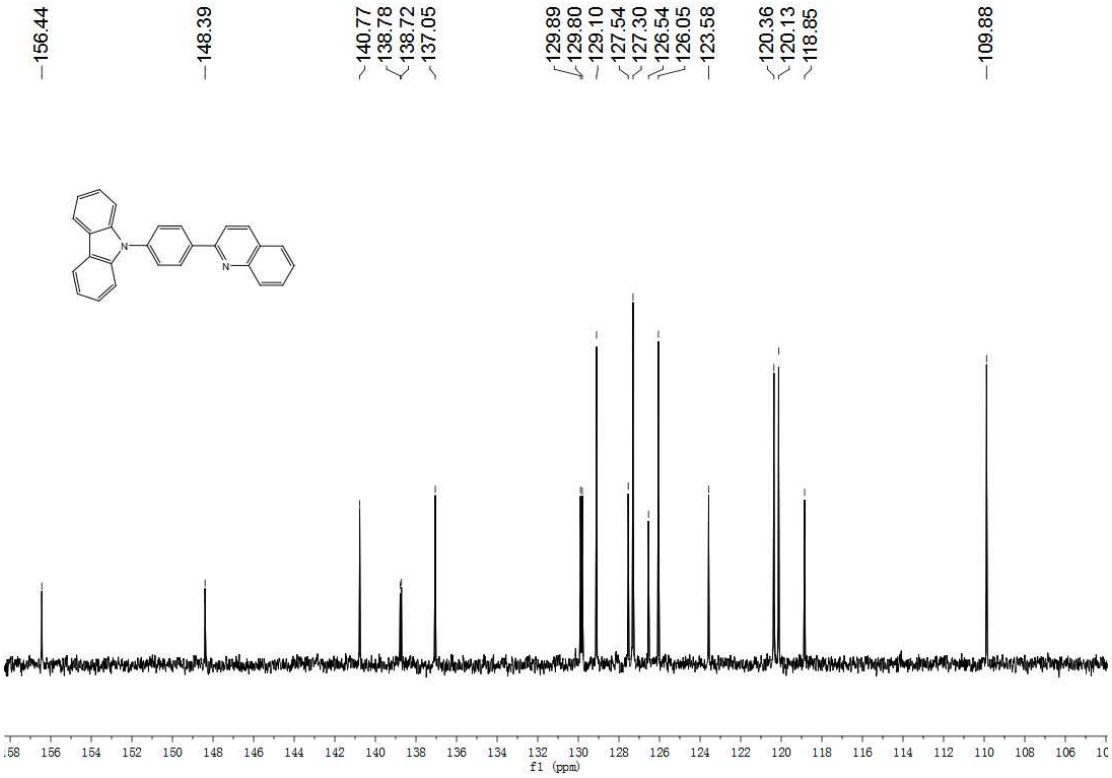

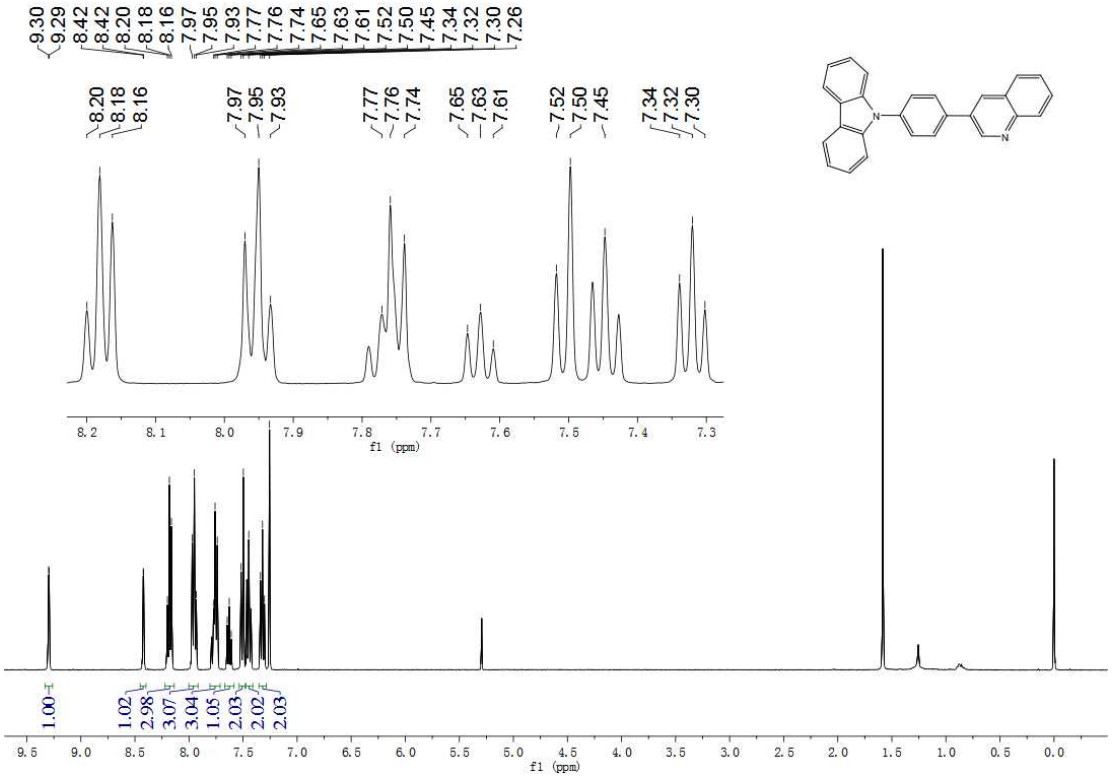

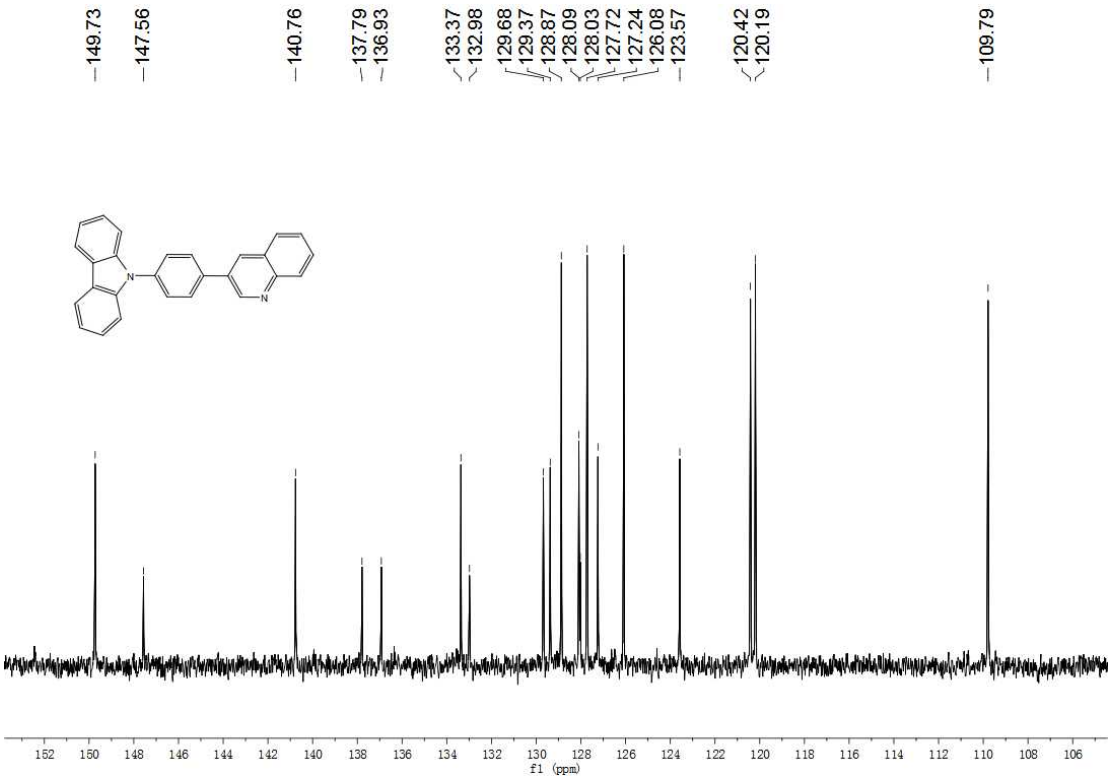

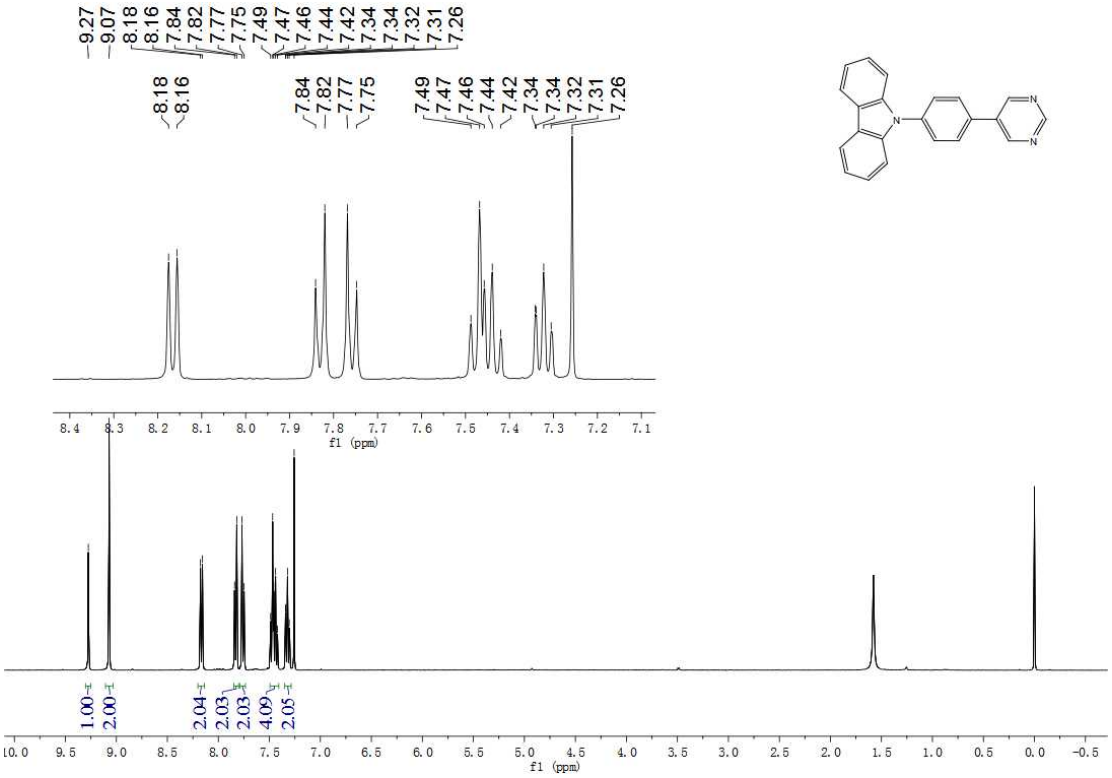

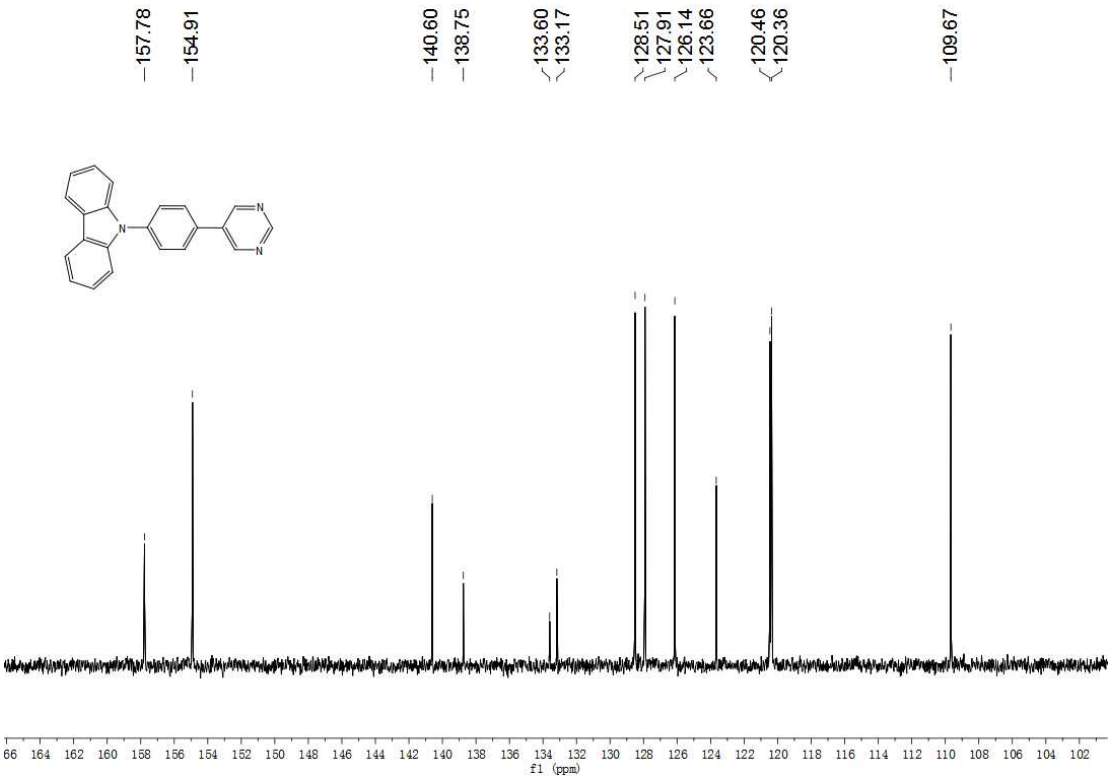
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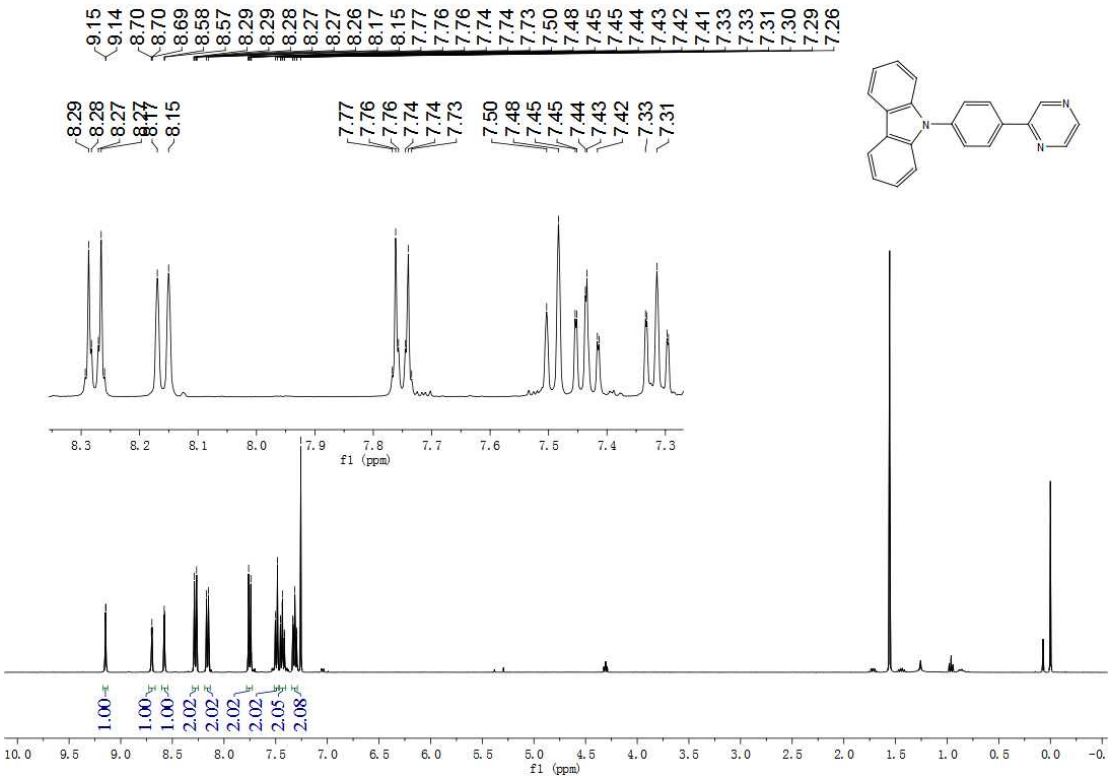
f1 (ppm)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8.15
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7.76
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7.74
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7.73
7.50
7.48
7.45
7.45
7.44
7.43
7.42
7.41
7.33
7.33
7.31
7.30
7.29
7.26
f1 (ppm)
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1.00
1.00
2.02
2.02
2.02
2.02
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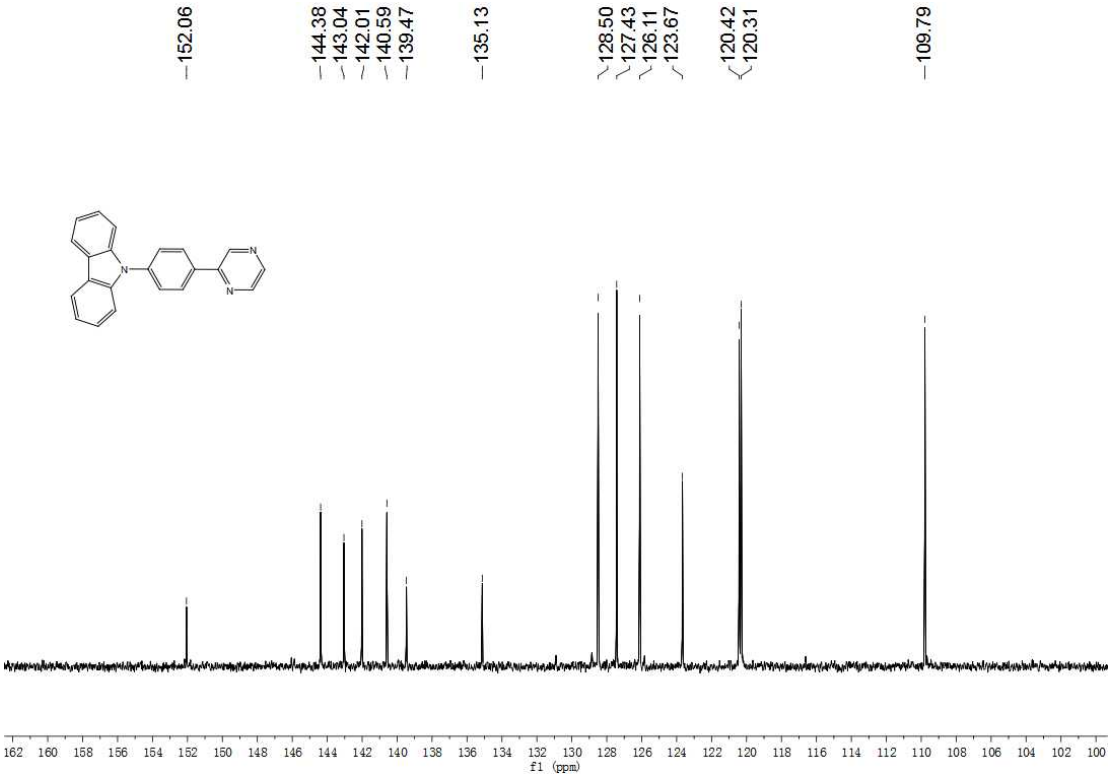
2.08
f1 (ppm)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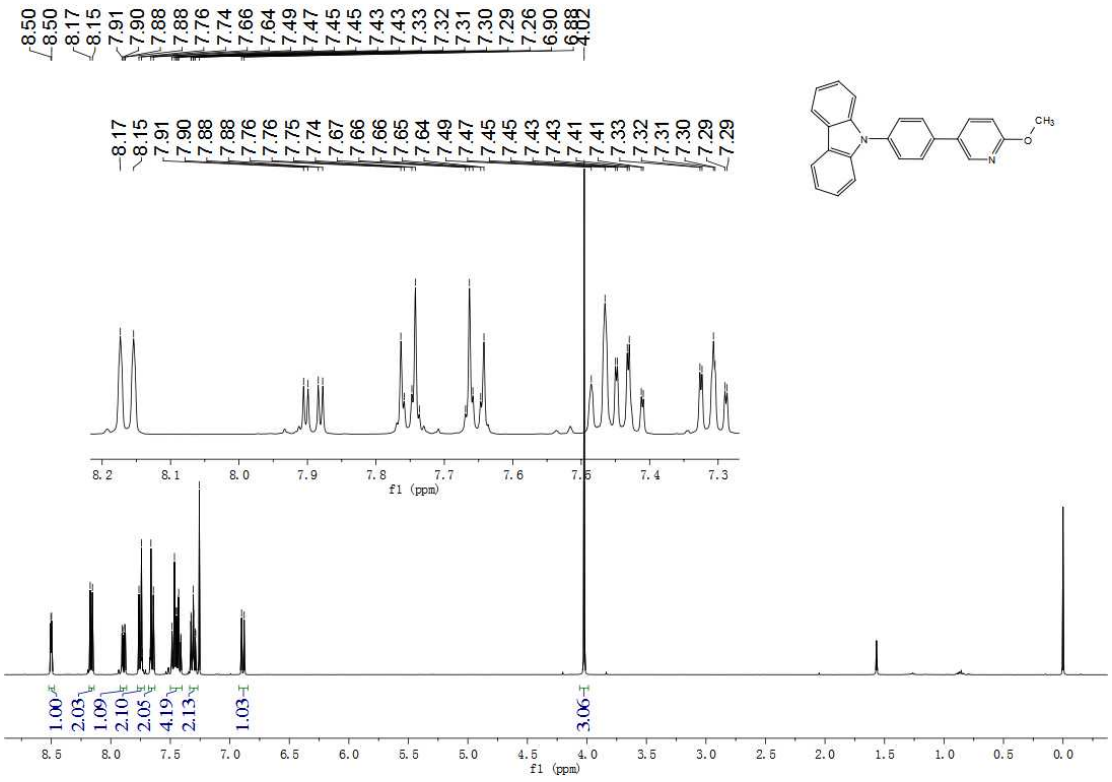
120.31
109.79
f1 (ppm)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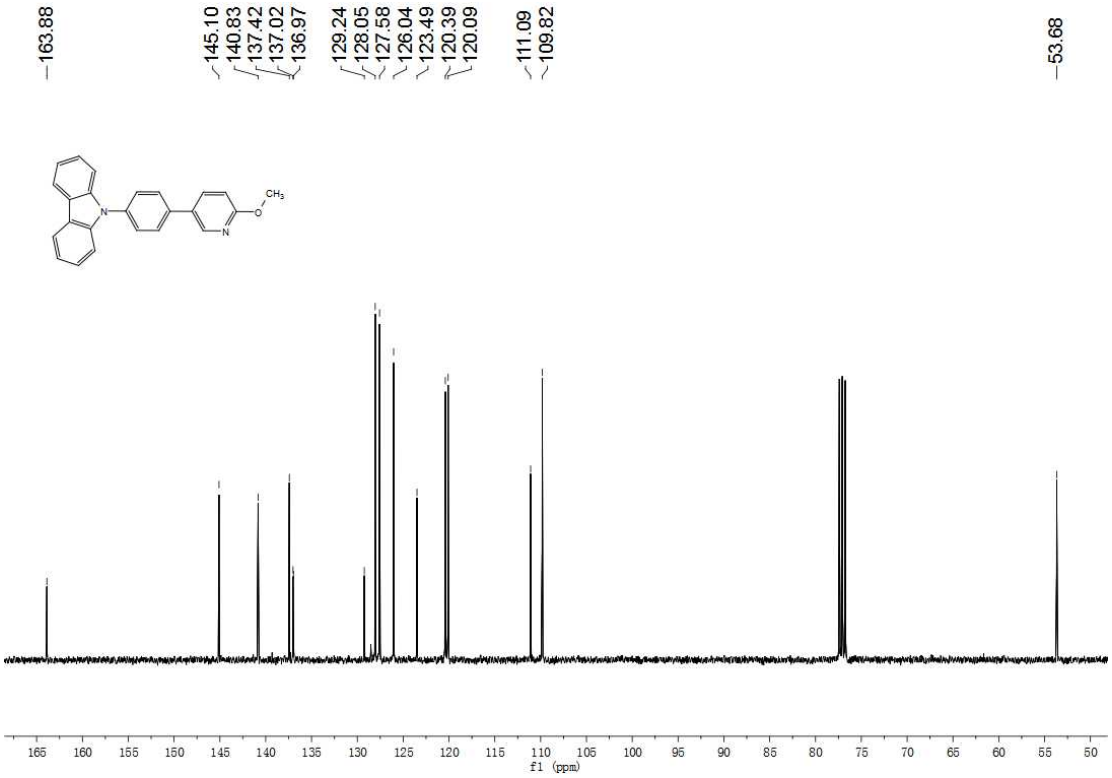
7.26
6.90
4.02
f1 (ppm)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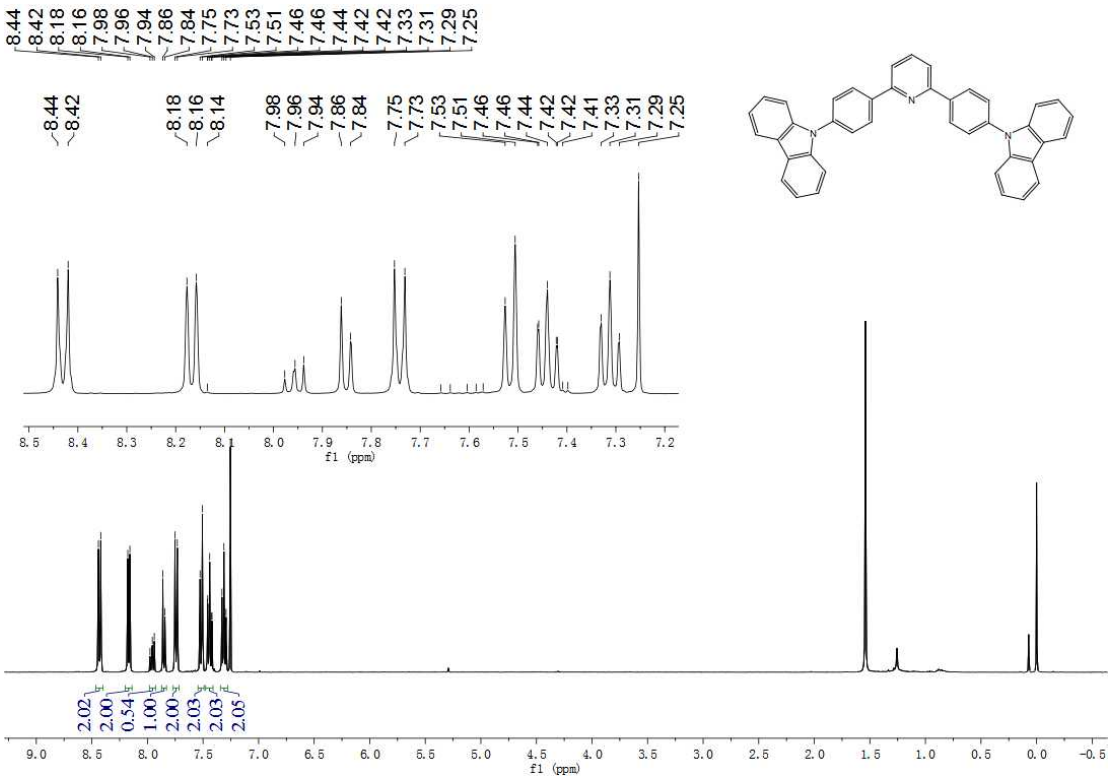
53.68
CH3
f1 (ppm)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7.53
7.51
7.46
7.46
7.44
7.42
7.42
7.33
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2.02
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0.54
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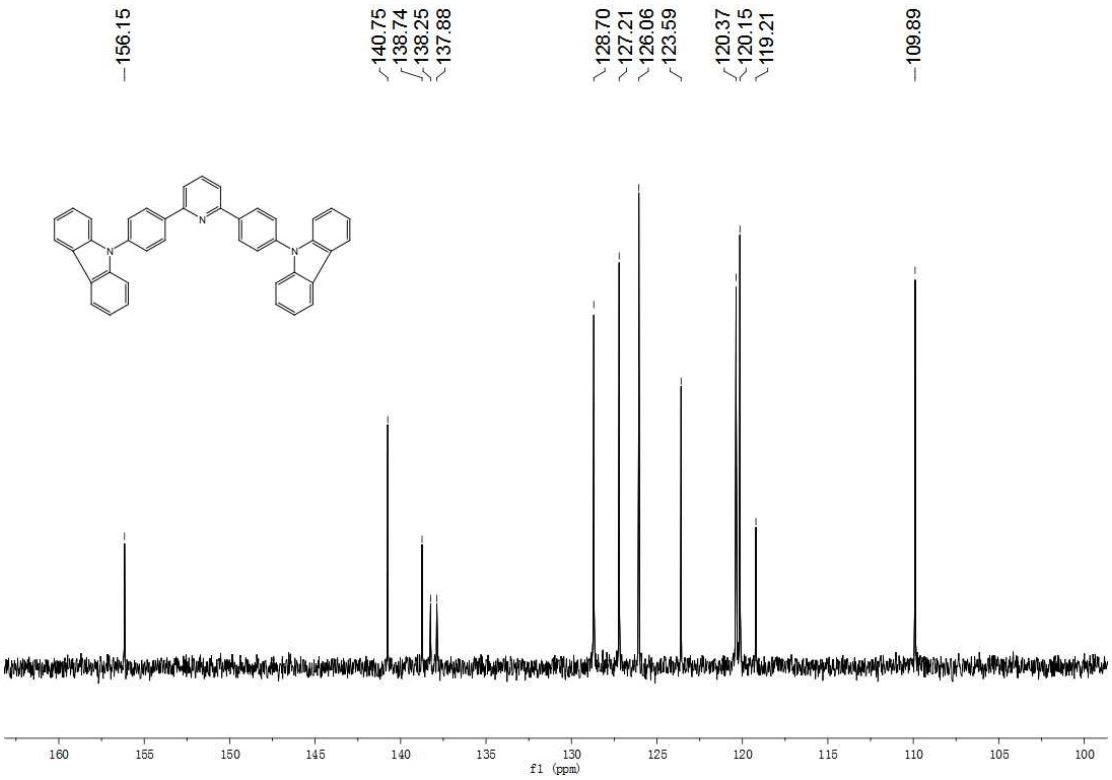
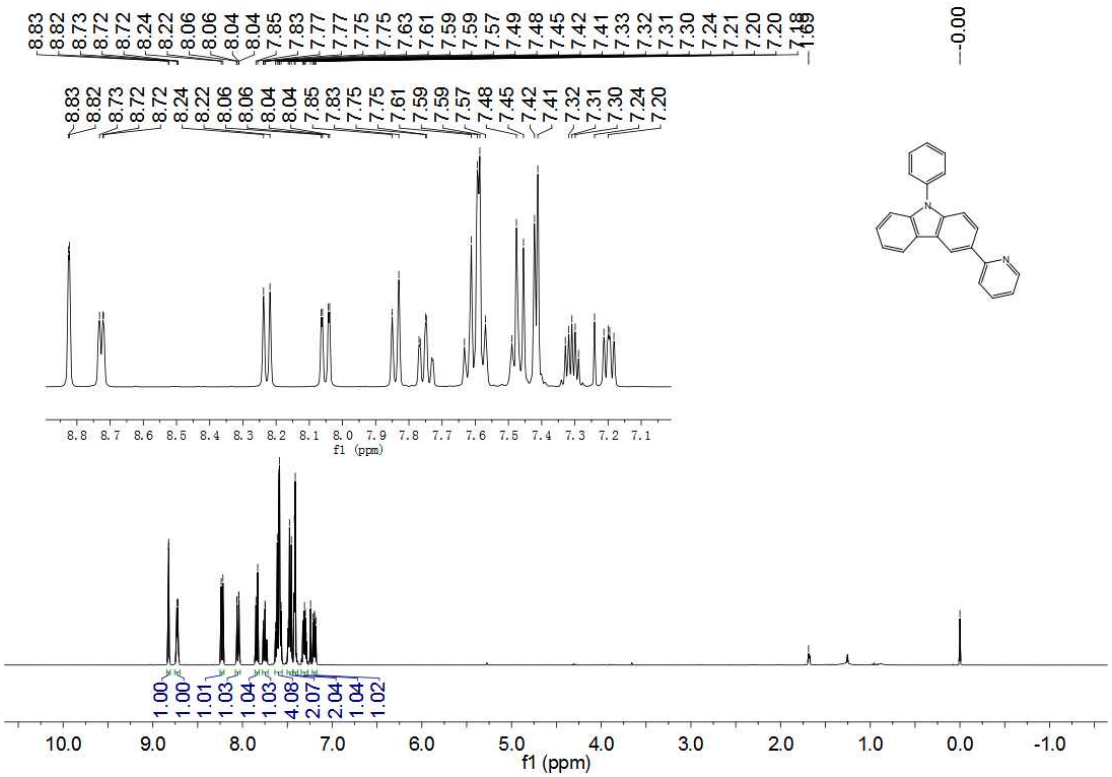
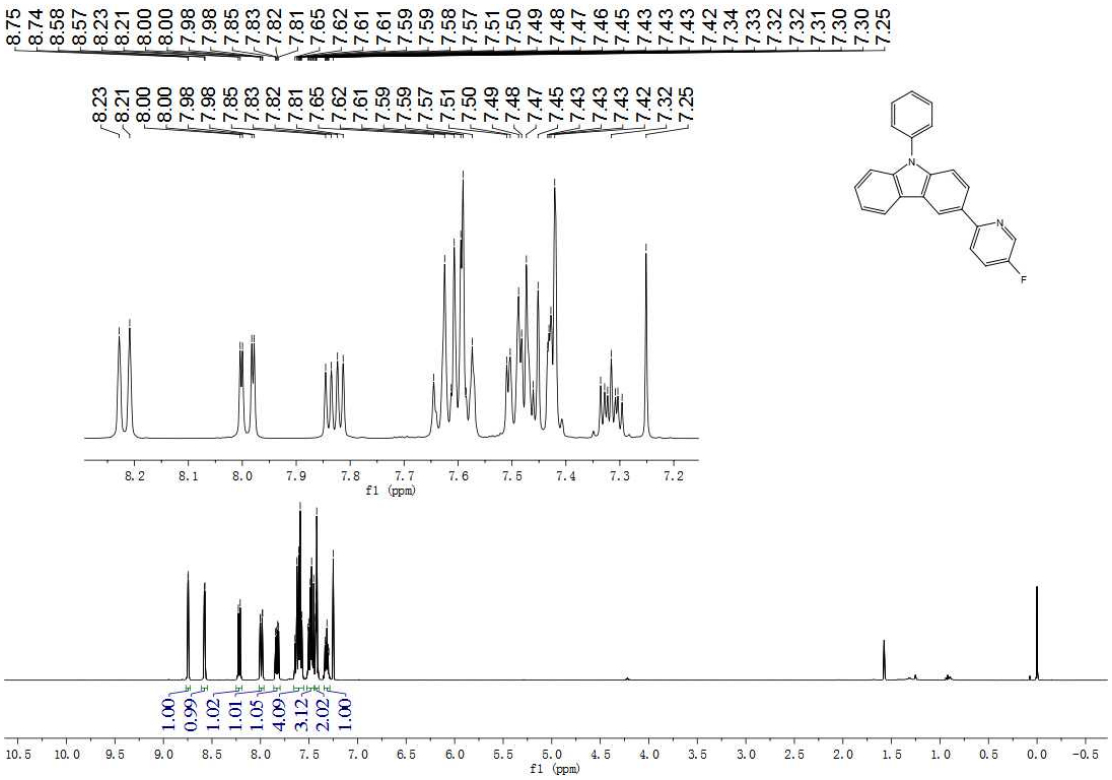
2.03
2.05
f1 (ppm)



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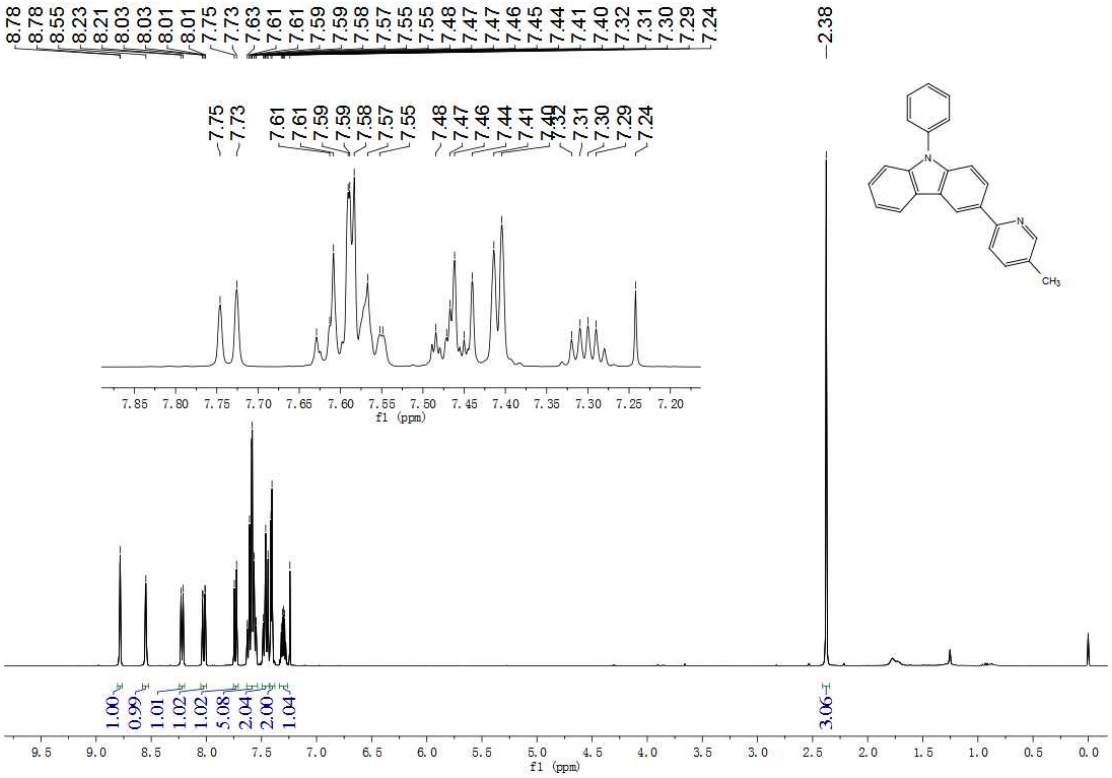
8.23 8.21 8.00 8.00 7.98 7.98 7.85 7.83 7.82 7.81 7.65 7.62 7.61 7.59 7.59 7.57 7.51 7.50 7.49 7.48 7.47 7.45 7.43 7.43 7.43 7.42 7.32 7.25
f1 (ppm)
1.00 0.99 1.02 1.01 1.05 4.09 3.12 2.02 1.00
f1 (ppm)
N
N
F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2.38
7.75 7.73 7.61 7.61 7.59 7.59 7.58 7.57 7.55 7.48 7.47 7.46 7.44 7.41 7.40 7.32 7.31 7.30 7.29 7.24
f1 (ppm)
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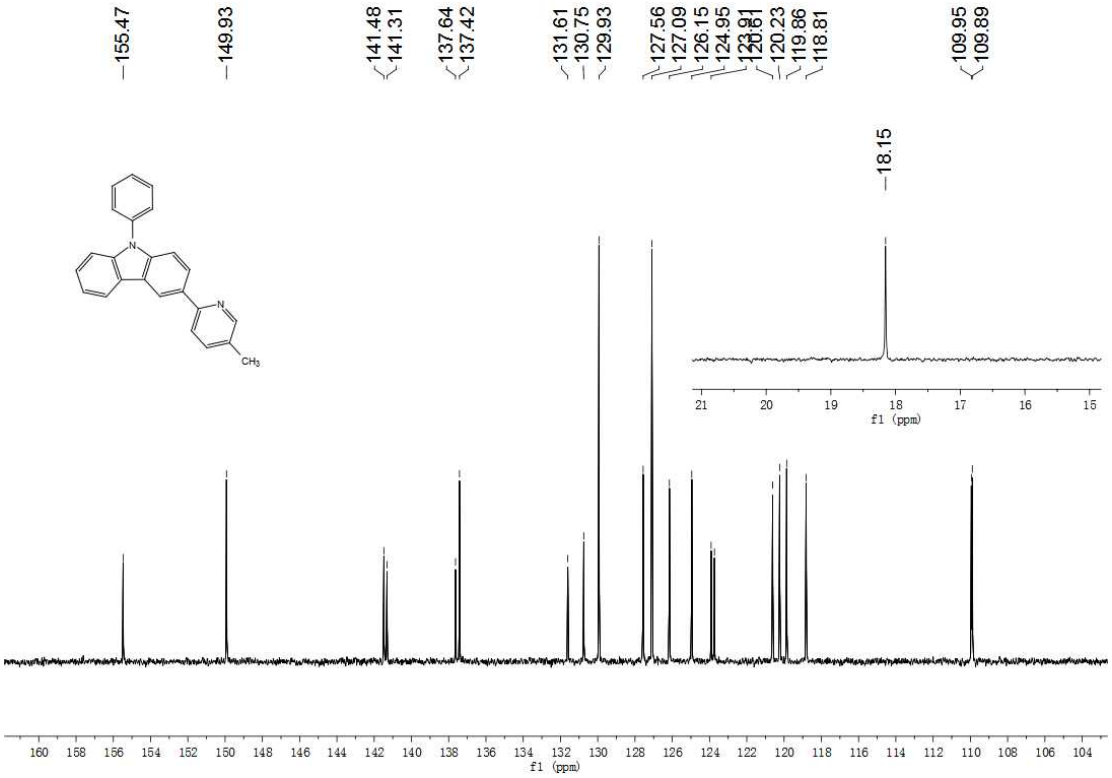
3.06
f1 (ppm)
N
N
CH3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130.75
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126.15
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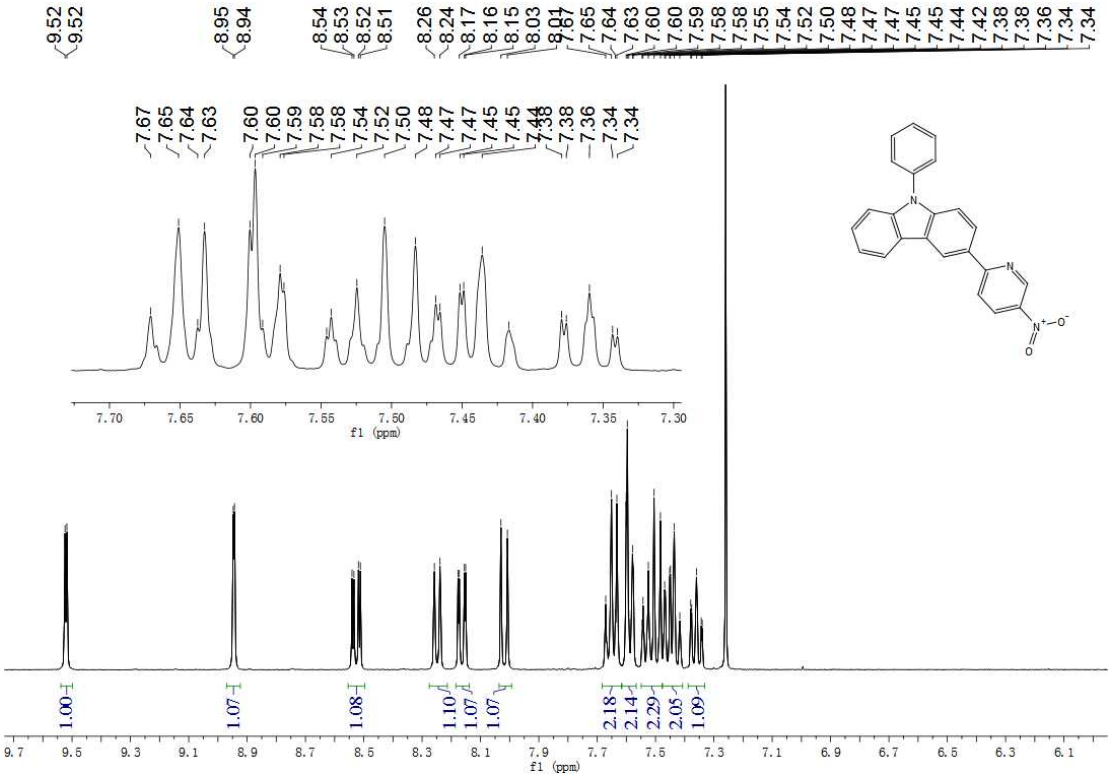
109.89
18.15
f1 (ppm)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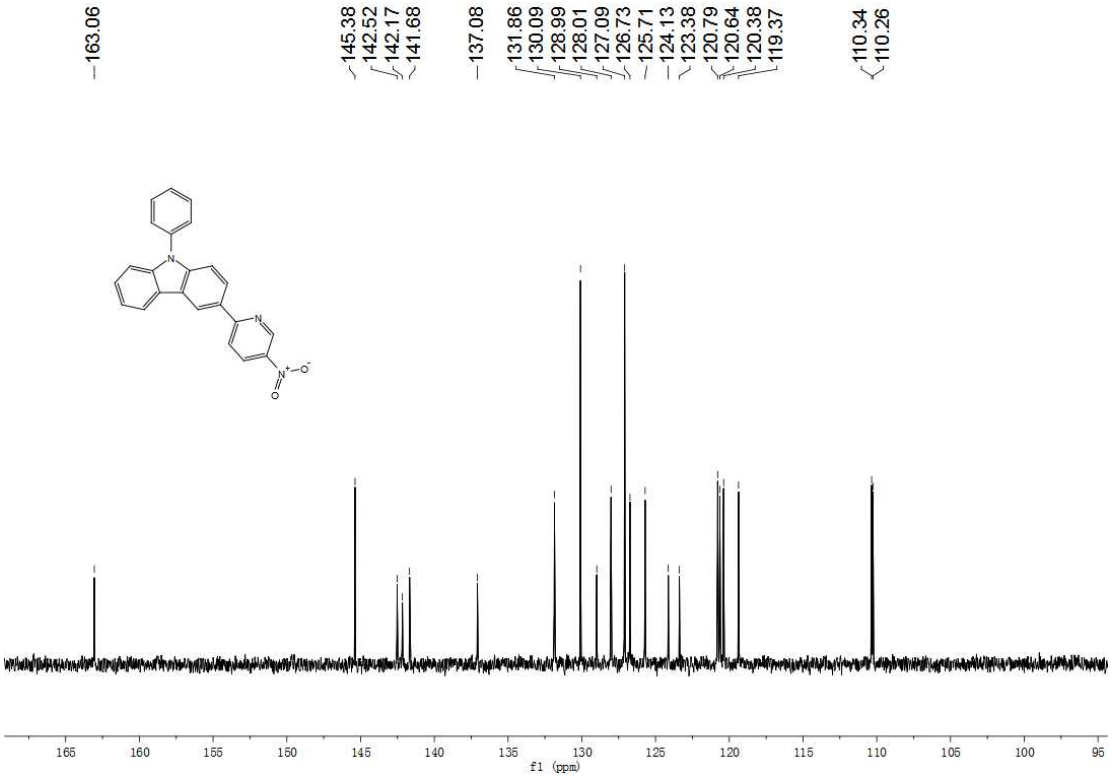
2.29
2.05
1.09
f1 (ppm)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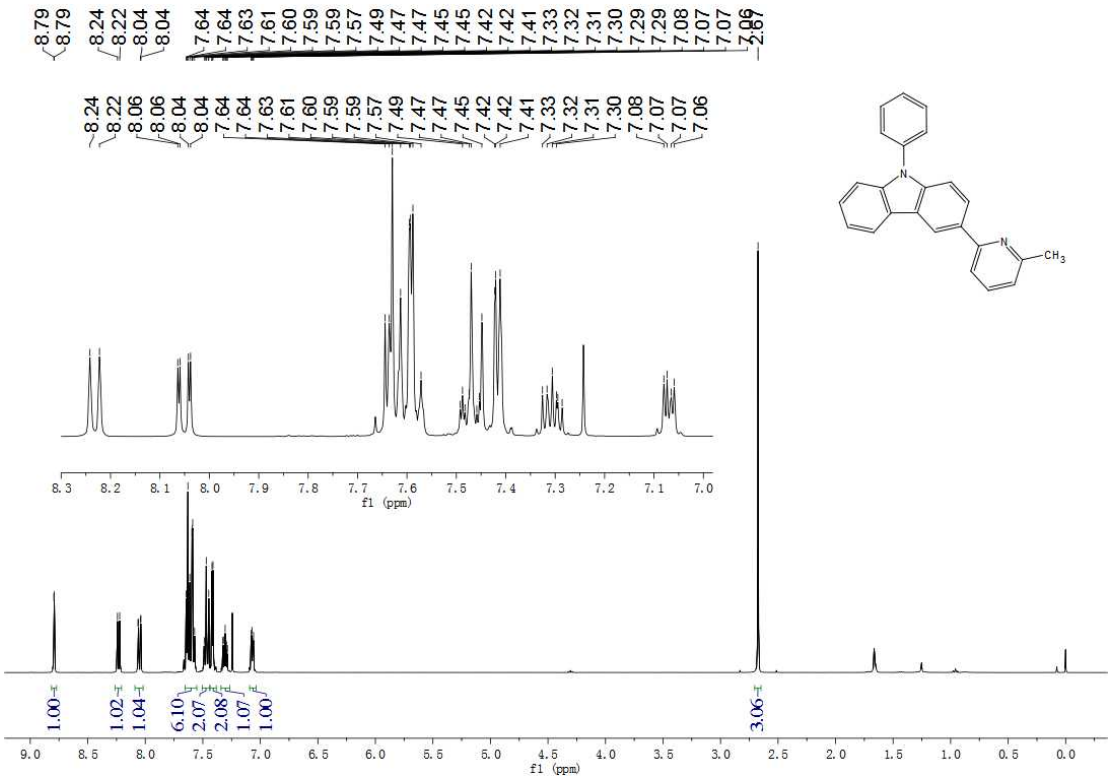
120.64
120.38
119.37
110.34
110.26
f1 (ppm)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7.33
7.32
7.31
7.30
7.29
7.08
7.07
7.06
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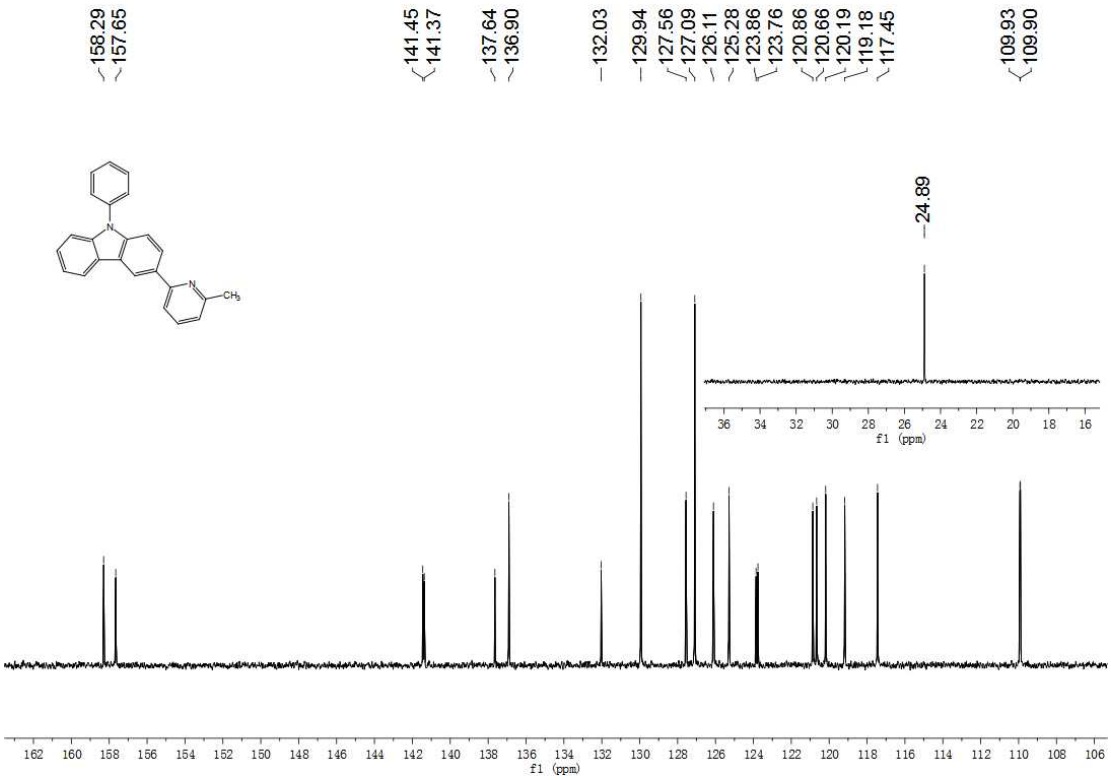
2.08
1.07
1.00
3.06
f1 (ppm)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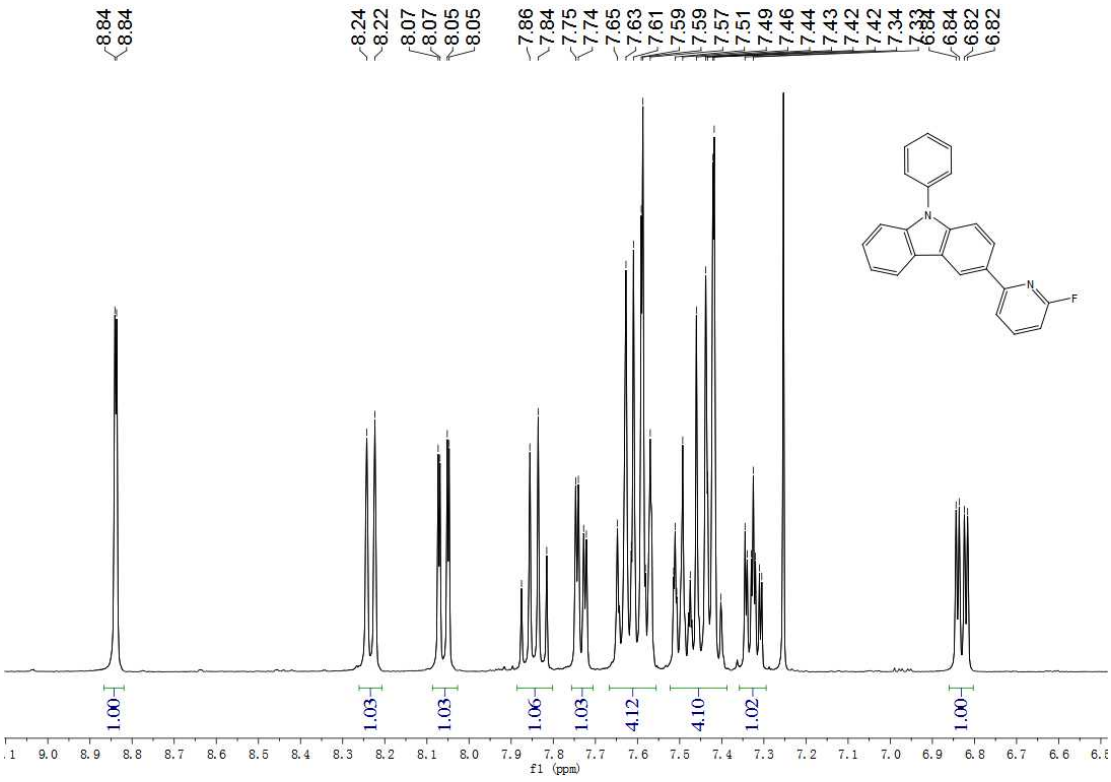
24.89
f1 (ppm)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7.34
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6.84
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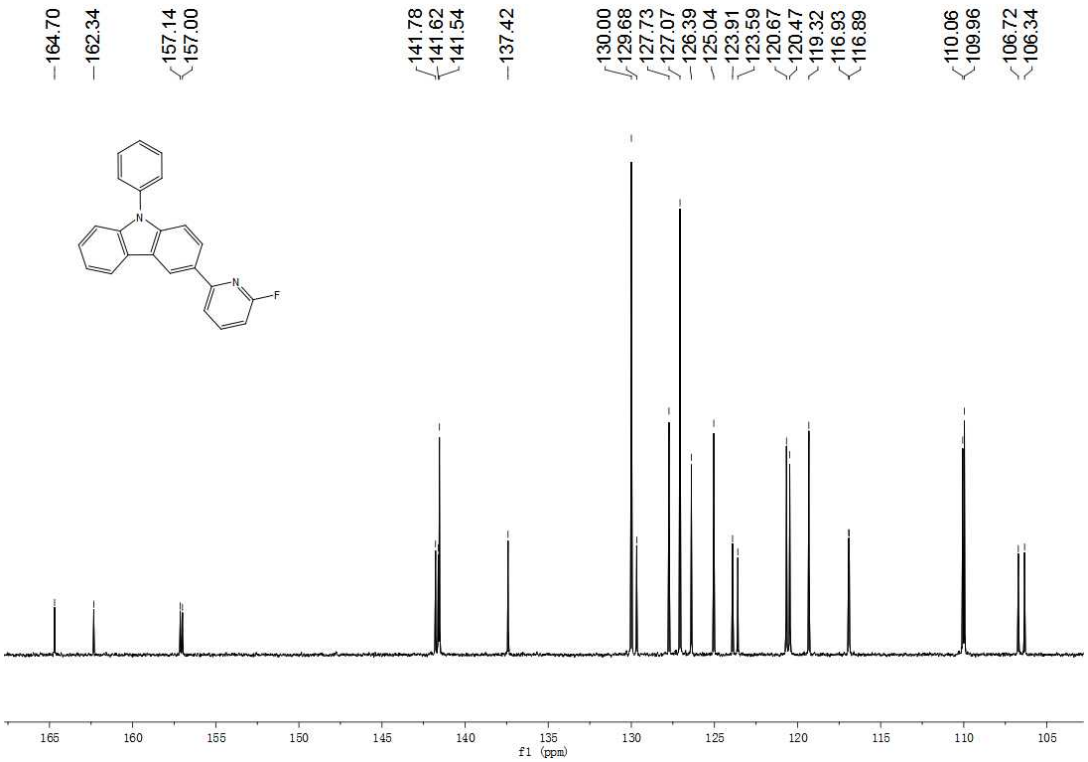
1.00
f1 (ppm)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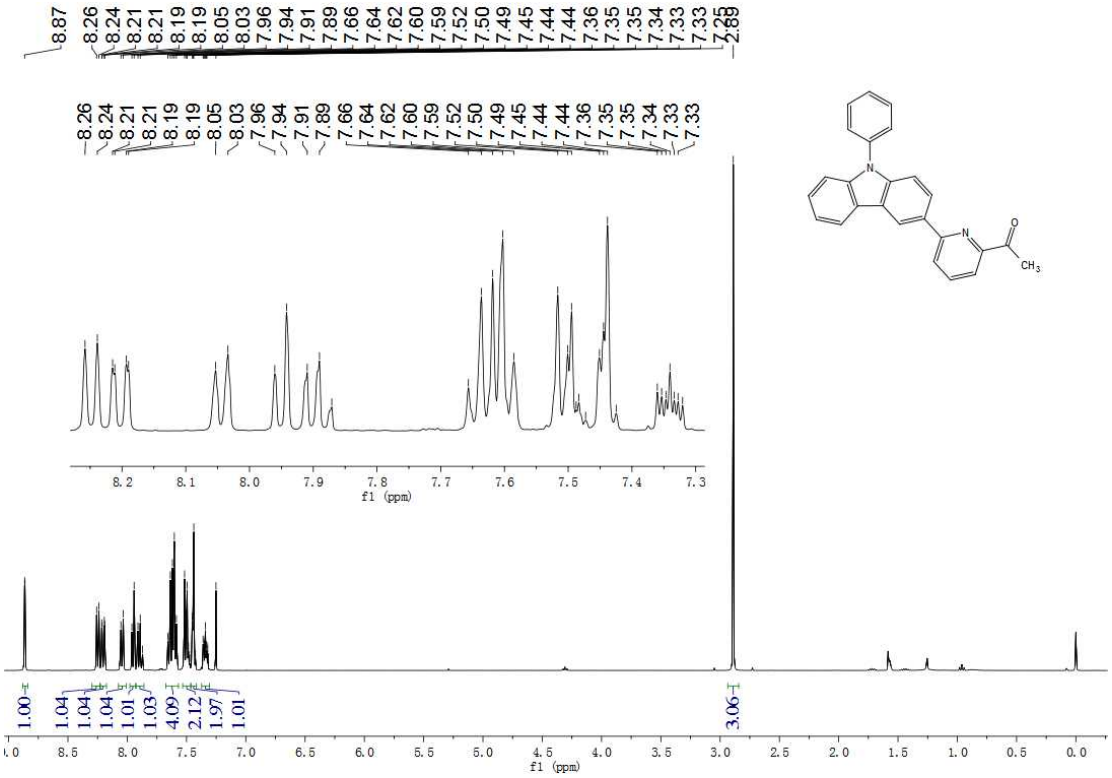
F
f1 (ppm)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7.33
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N
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CH3
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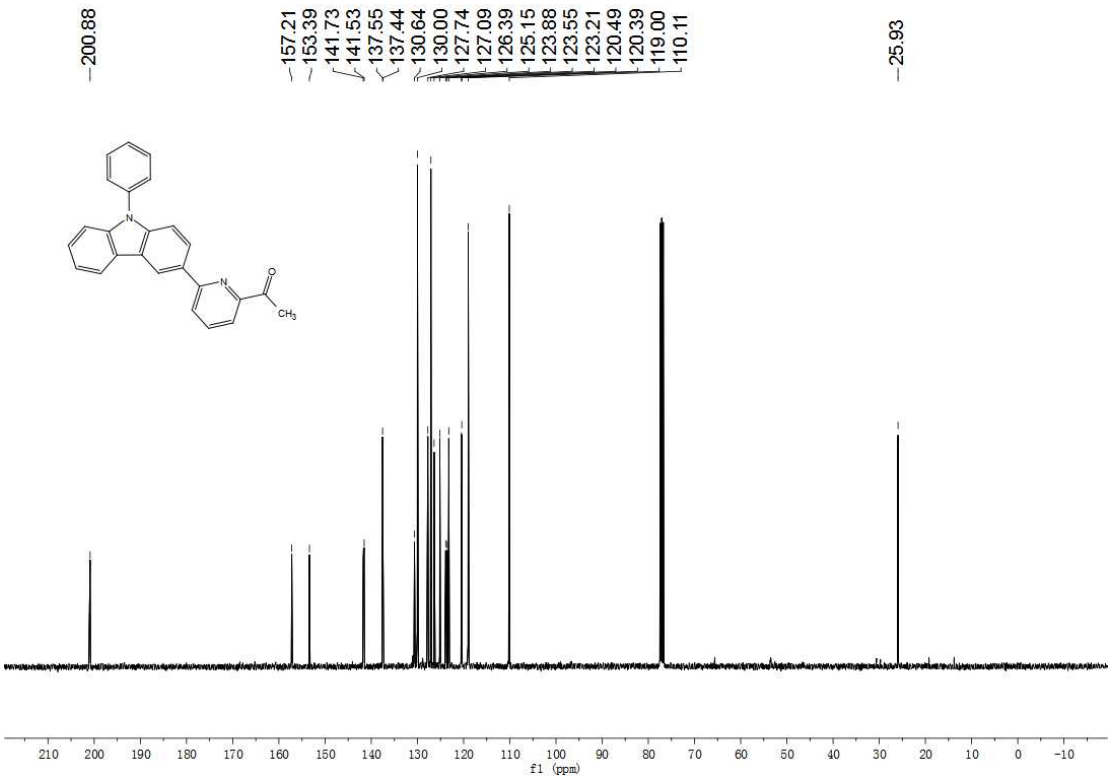
f1 (ppm)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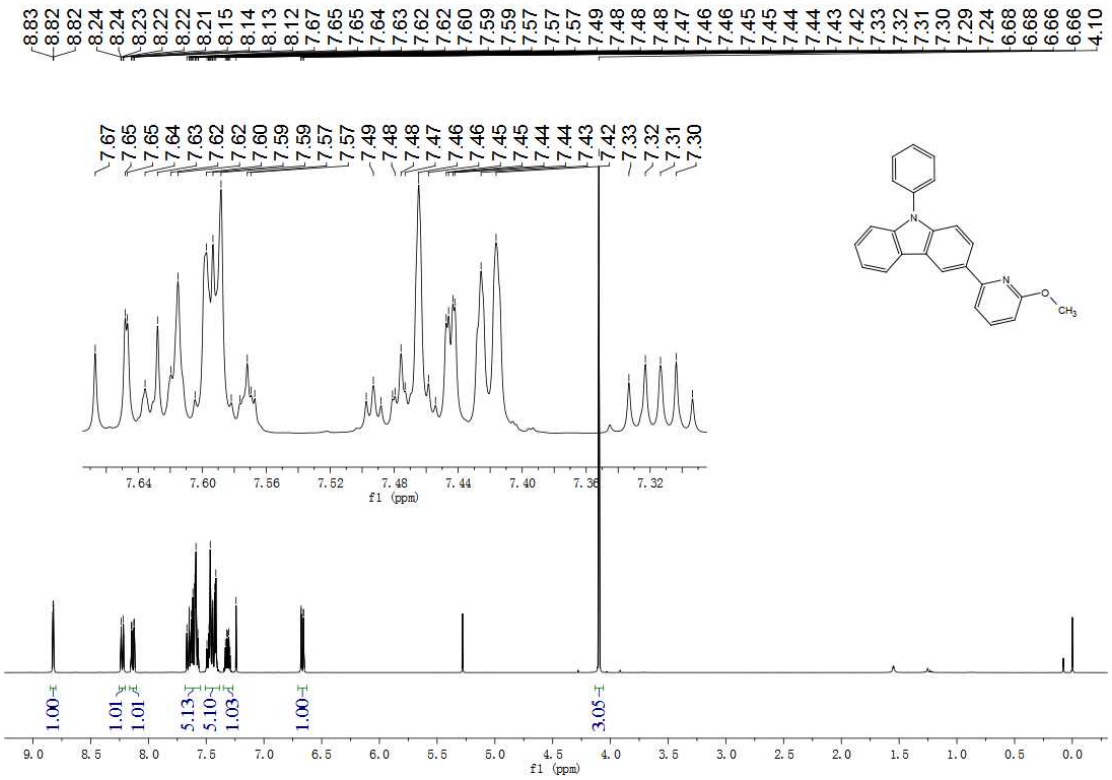
f1 (ppm)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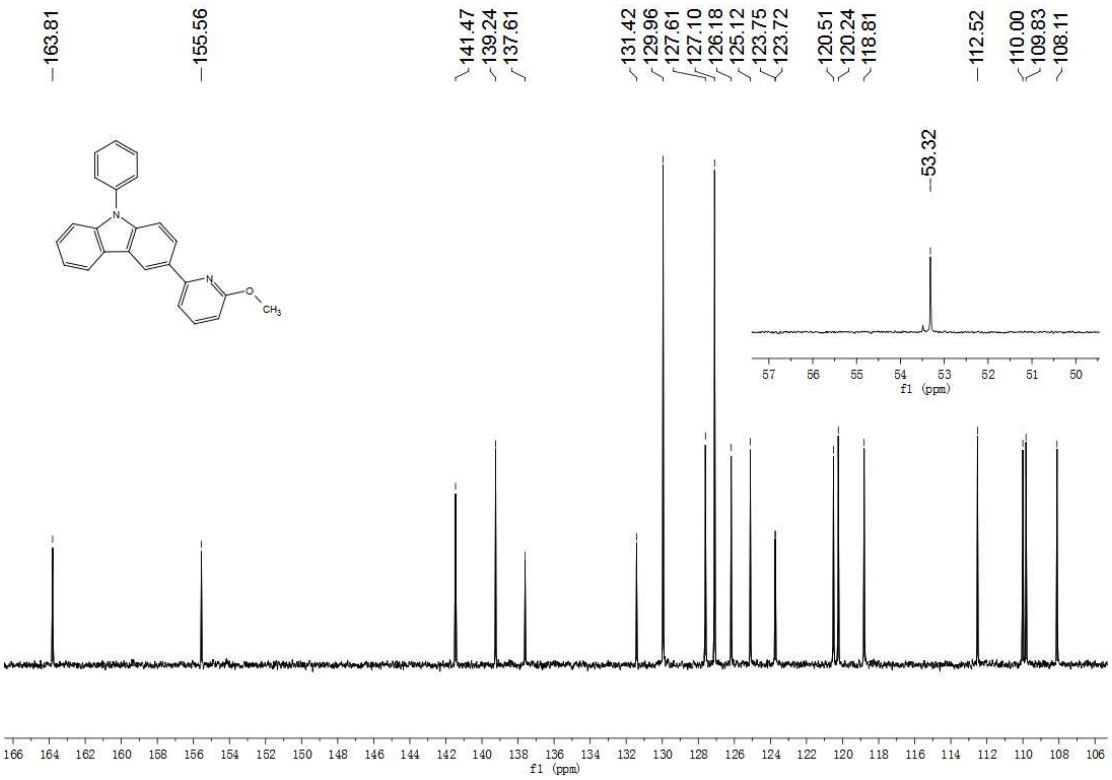
f1 (ppm)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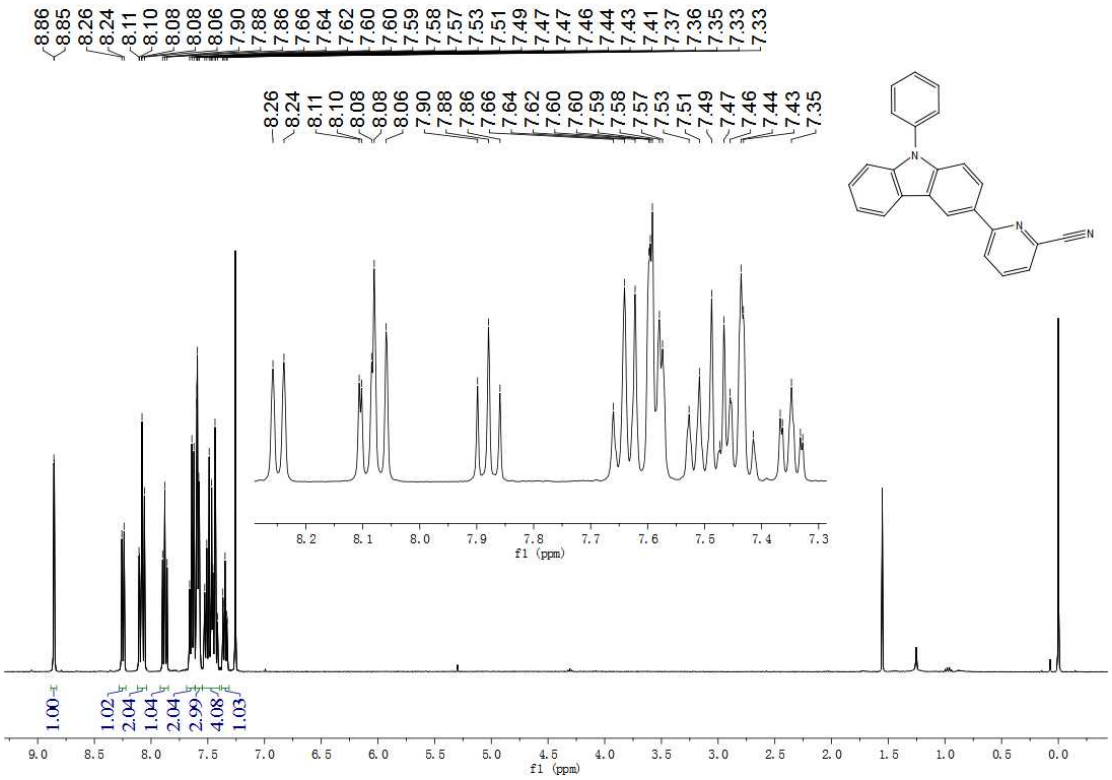
f1 (ppm)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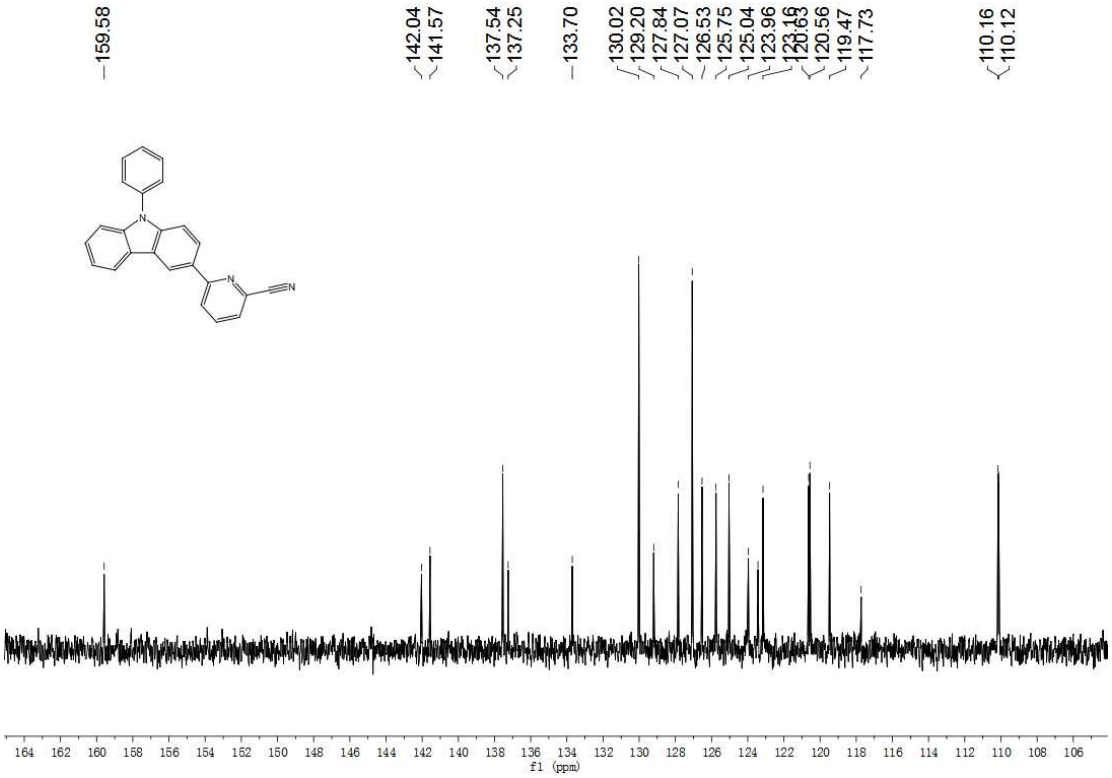
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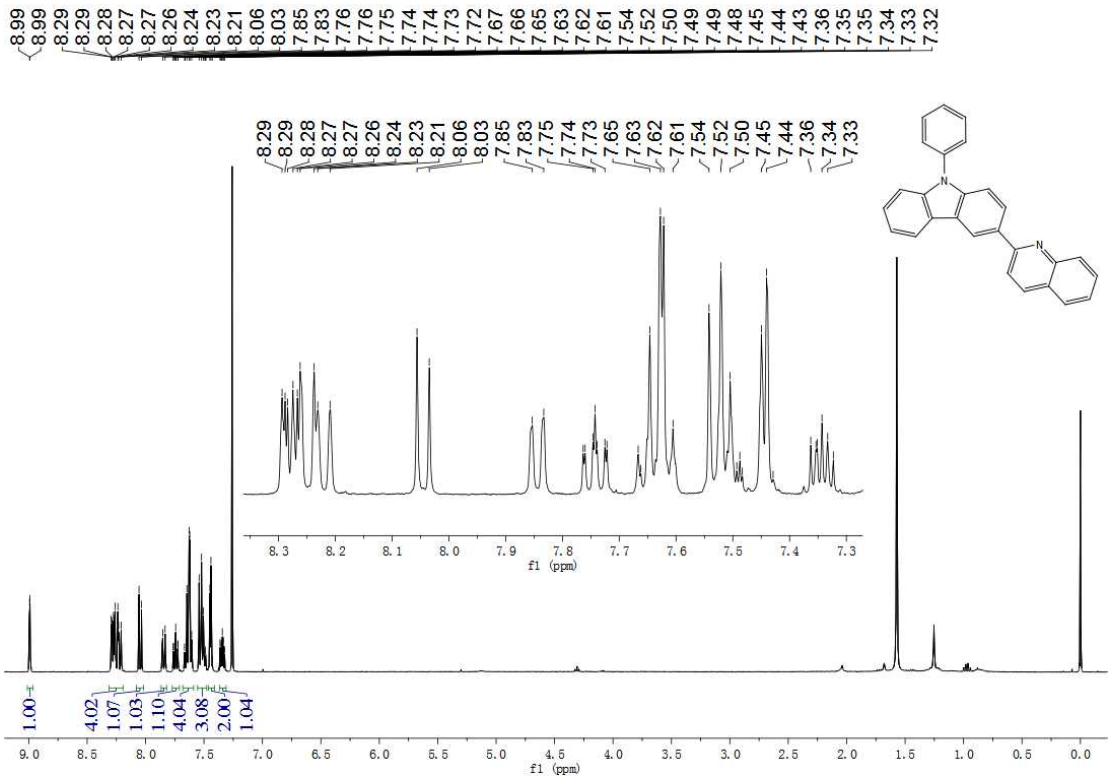
f1 (ppm)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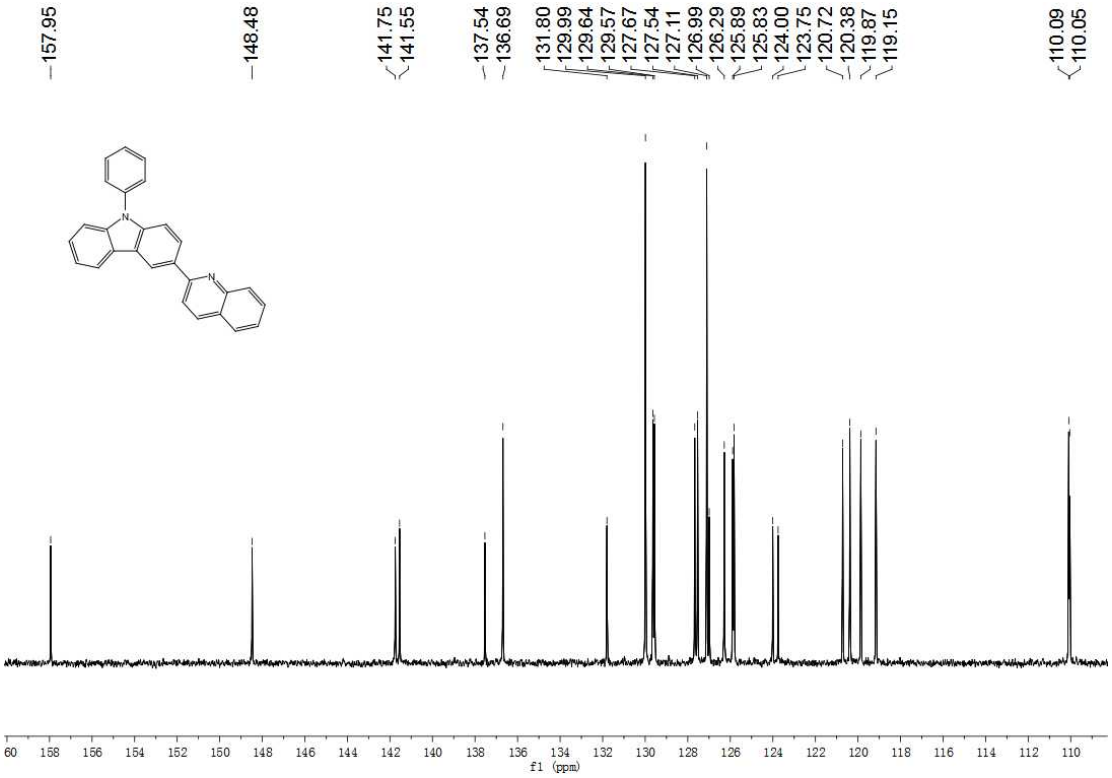
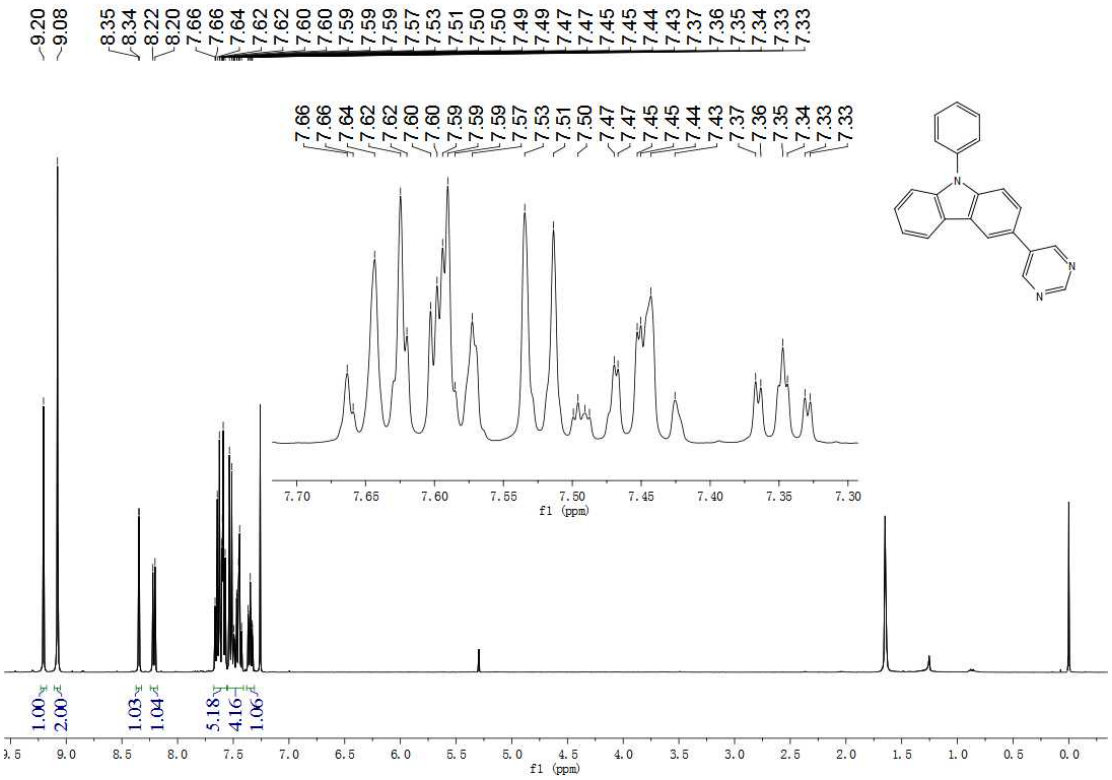
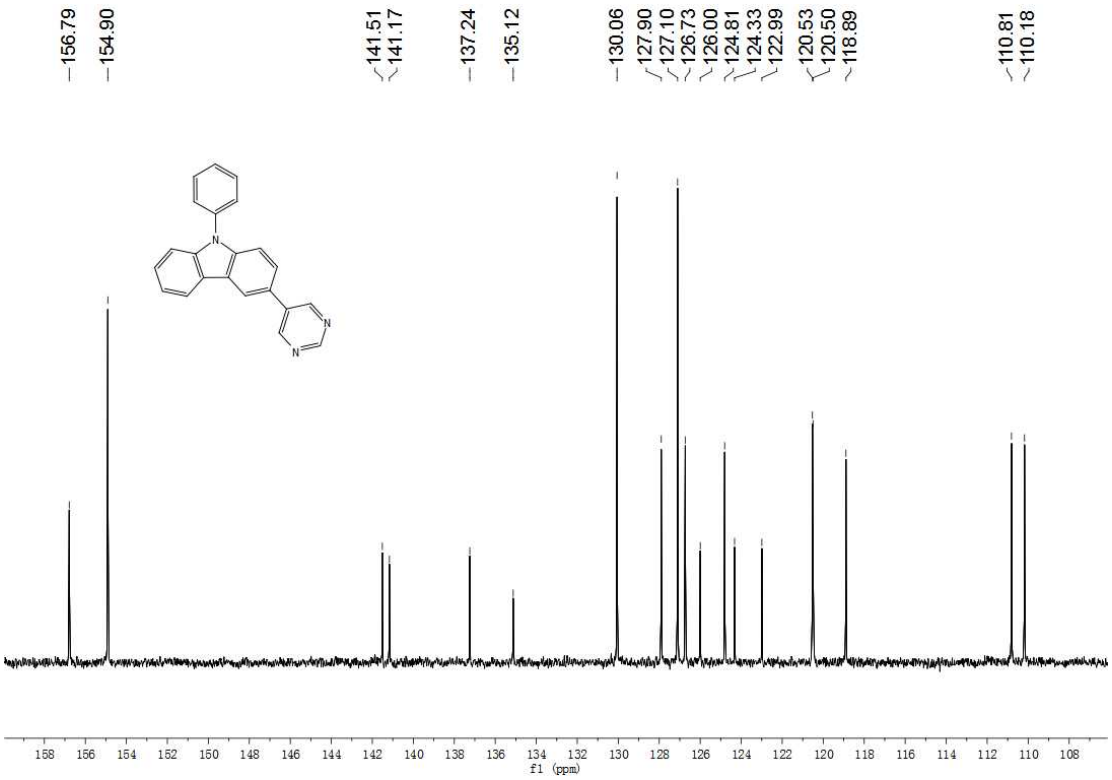
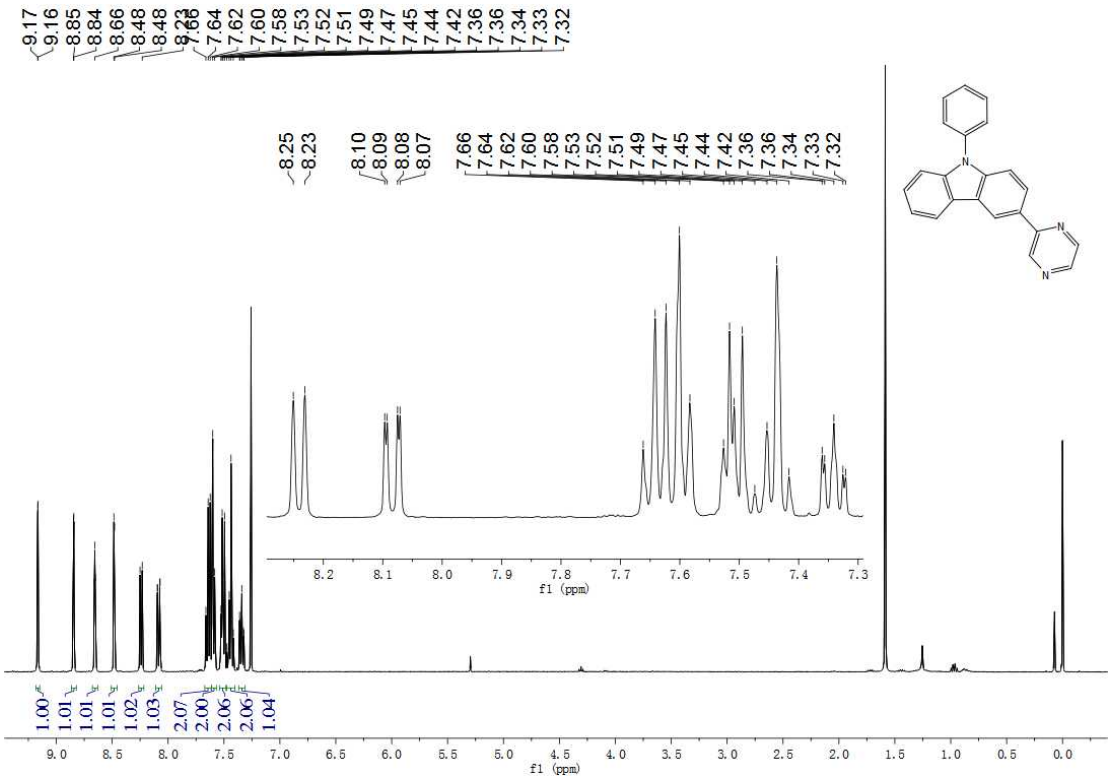
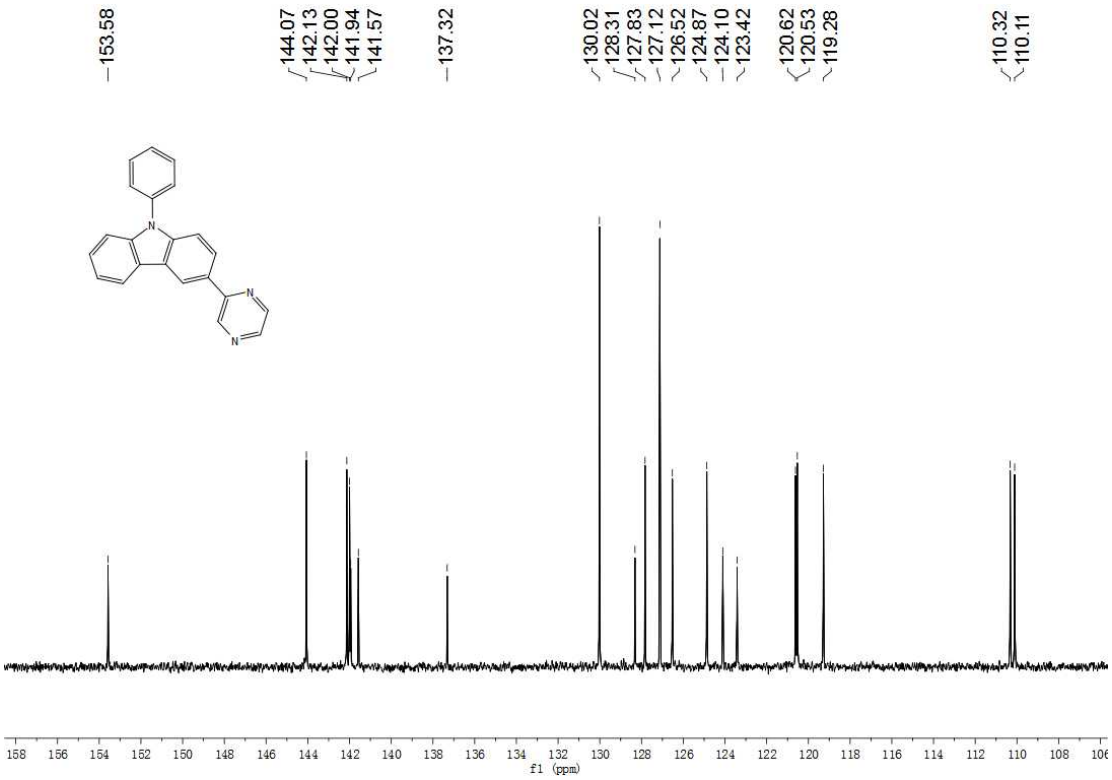
f1 (ppm)

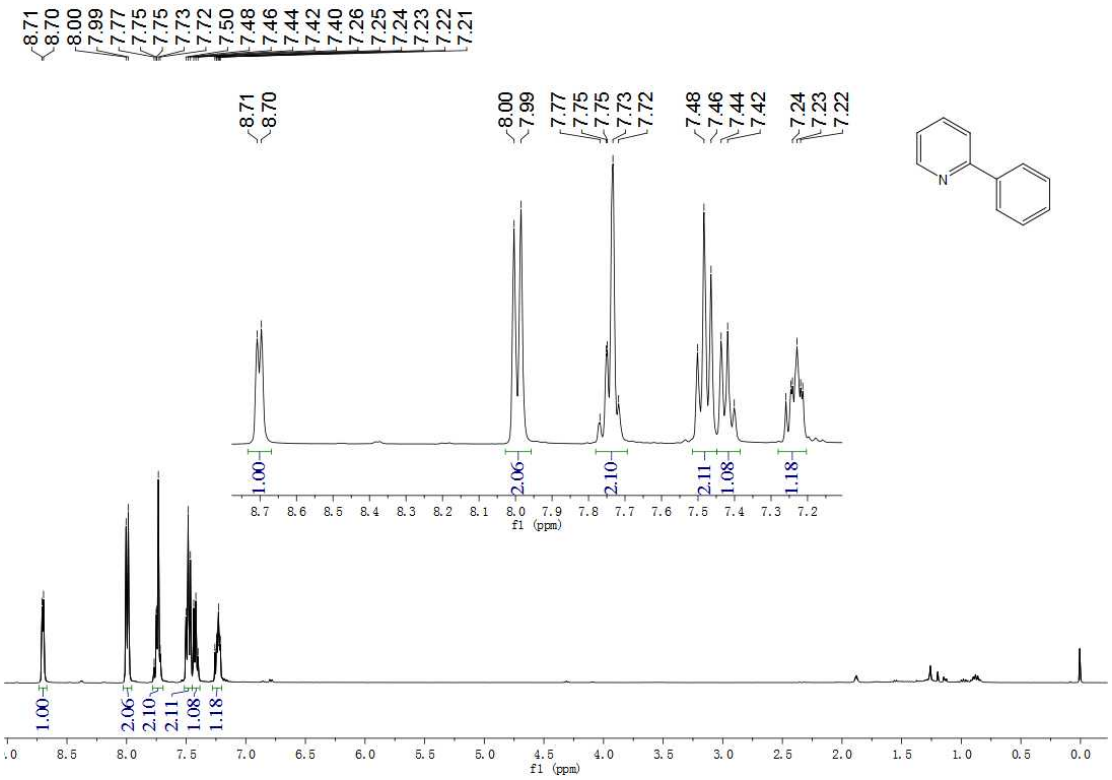


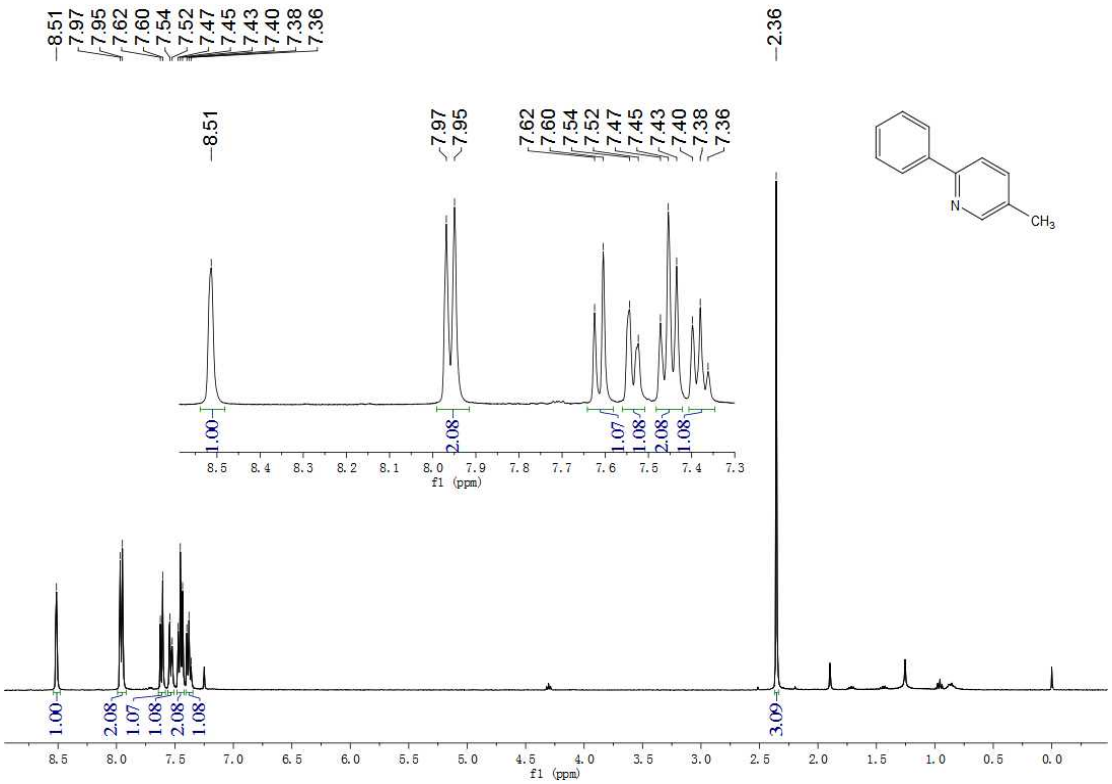


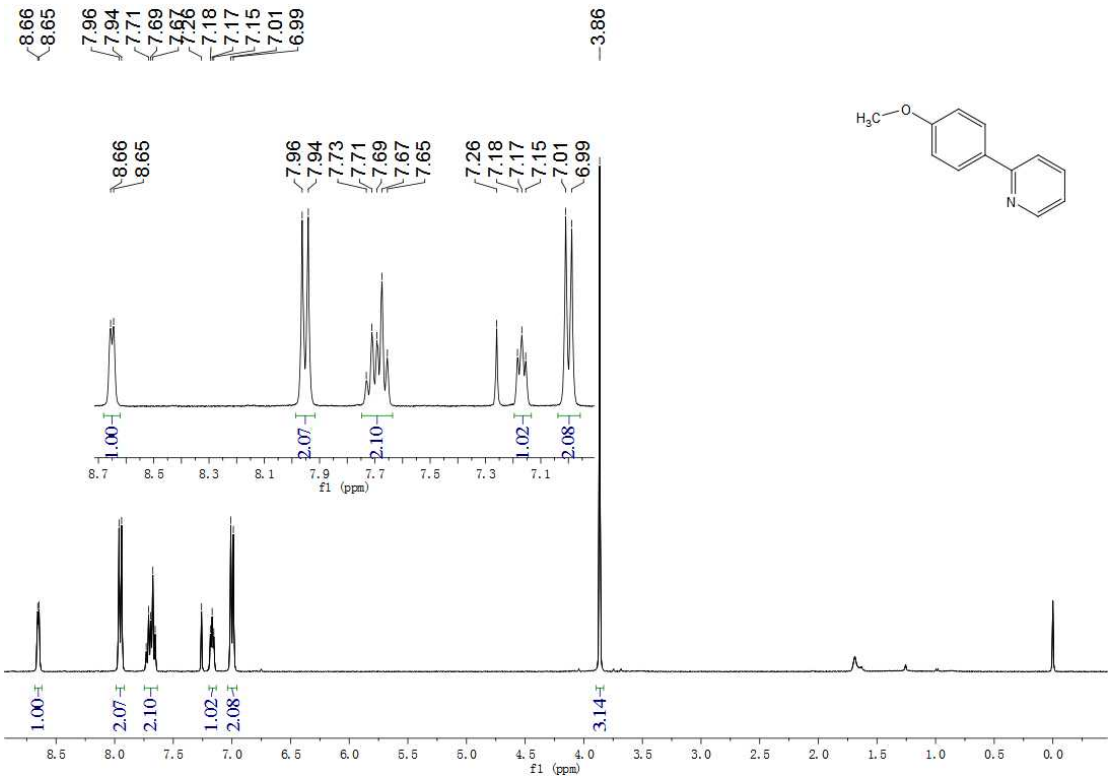


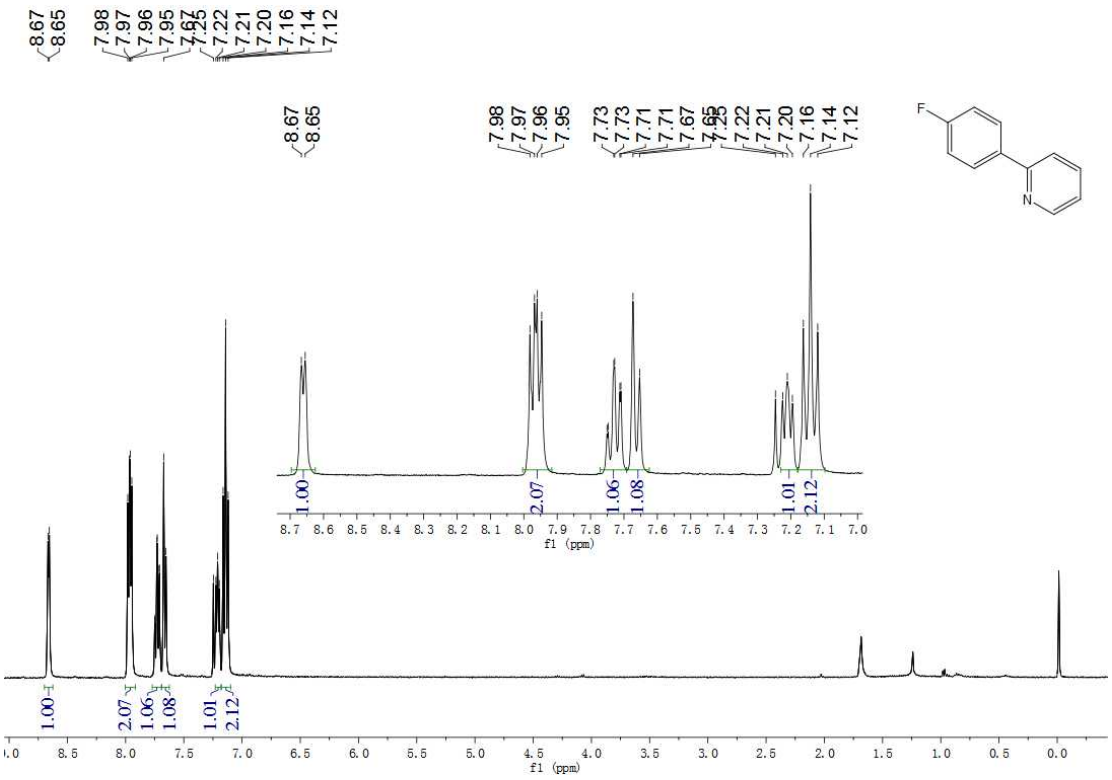









8.66
8.65
7.96
7.94
7.71
7.69
7.67
7.26
7.18
7.17
7.15
7.01
6.99
3.86
H3C
O
N
1.00
2.07
2.10
1.02
2.08
3.14
f1 (ppm)


8.67
8.65
7.98
7.97
7.96
7.95
7.73
7.71
7.67
7.22
7.21
7.20
7.16
7.14
7.12
F
N
1.00
2.07
1.06
1.08
1.01
2.12
f1 (ppm)