ESI for

Palladium-Catalyzed Ligand-Free and Aqueous Suzuki Reaction for the Construction of (Hetero)aryl-Substituted Triphenylamine Derivatives

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Contents

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-(diphenylamino)phenylboronic acid (**DPBA**) was 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), unless otherwise noted. Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

General Procedure for the Suzuki Cross-Coupling of DPBA with Heteroaryl Halides: A mixture of heteroaryl halide (0.25 mmol), **DPBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (1.5 mol-%), ethanol (3 mL) and distilled water (1 mL) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times 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 DPBA with Aryl Bromides: A mixture of aryl bromide (0.25 mmol), **DPBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.5 mol-%), ethanol (3 mL) and distilled water (1 mL) was stirred at room temperature in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times 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

N,N-diphenyl-4-(pyridin-2-yl)aniline[1]

^{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.

4-(4-methylpyridin-2-yl)-N,N-diphenylaniline

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.50 (d, J = 2.4 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.28-7.25 (m, 4H), 7.14-7.12 (m, 6H), 7.06-7.02 (m, 3H), 2.40 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ = 157.16, 149.50, 148.72, 147.76, 147.70, 133.51, 129.46, 127.91, 124.83, 123.49, 123.31, 122.73, 121.04, 21.47 ppm. MS (EI): m/z = 336.1632 $[M]^+$.

4-(5-methylpyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.47 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.58-7.51 (m, 2H), 7.28-7.24 (m, 4H), 7.15-7.12 (m, 6H), 7.04 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H) ppm.

4-(5-methoxypyridin-2-yl)-N,N-diphenylaniline

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.35 (d, J = 4.4 Hz, 1H), 7.81-7.79 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.28-7.23 (m, 5H), 7.14-7.11 (m, 6H), 7.05-7.01 (m, 2H), 3.89 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ = 154.47, 149.89, 148.01, 147.61, 136.83, 133.11, 129.29, 127.25, 124.55, 123.63, 123.05, 121.54, 120.22, 55.71 ppm. MS (EI): m/z =352.1585 $[M]^+$.

4-(5-fluoropyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.50 (d, J = 2.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.67-7.64 (m, 1H), 7.46-7.41 (m, 1H), 7.29-7.26 (t, 4H), 7.15-7.12 (m, 6H), 7.05 (t, J = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(5-(trifluoromethyl)pyridin-2-yl)aniline[3]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.88 (s, 1H), 7.91-7.89 (m, 3H), 7.76 (d, J = 7.6 Hz, 1H), 7.31-7.27 (m, 4H), 7.16-7.13 (m, 6H), 7.10-7.07 (m, 2H) ppm.

4-(5-nitropyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.39 (d, J = 2.4 Hz, 1H), 8.42-8.39 (m, 1H), 7.94 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 1H), 7.29 (t, J = 8.0 Hz, 4H), 7.16-7.08 (m, 8H) ppm.

6-(4-(diphenylamino)phenyl)nicotinonitrile

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.87 (s, 1H), 7.92-7.90 (m, 3H), 7.74 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 8.0 Hz, 4.4 Hz, 4H), 7.16-7.11 (m, 8H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ = 159.97, 152.46, 150.30, 146.94, 139.57, 130.01, 129.51, 128.31, 125.42, 124.05,121.88, 118.90, 117.32, 106.63 ppm. MS (EI): m/z = 347.1426 $[M]^+$.

4-(6-methylpyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.84 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 4H), 7.15-7.11 (m, 6H), 7.03-7.02 (m, 3H), 2.60 (s, 3H) ppm.

4-(6-methoxypyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.92 (d, *J* = 8.8 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 5H), 7.15-7.11 (m, 6H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 3H) ppm.

4-(6-fluoropyridin-2-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.86 (d, *J* = 8.4 Hz, 2H), 7.81-7.75 (m, 1H), 7.55-7.52 (dd, *J* = 2.4 Hz, 7.6 Hz, 1H), 7.30-7.25 (m, 4H), 7.13 (t, 6H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.79-6.77 (m, 1H) ppm.

6-(4-(diphenylamino)phenyl)picolinaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 10.14 (s, 1H), 7.97-7.94 (m, 2H), 7.89-7.83 (m, 3H), 7.31-7.27 (m, 4H), 7.19-7.14 (m, 6H), 7.10-7.06 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ = 194.08, 157.60, 152.70, 149.40, 147.31, 137.65, 131.49, 129.43, 127.87, 125.01, 123.75, 123.59, 122.85, 119.06 ppm. MS (EI): *m*/*z* = 350.1421 $[M]^+$.

6-(4-(diphenylamino)phenyl)picolinonitrile[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.89-7.79 (m, 4H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.15-7.09 (m, 8H) ppm.

1-(6-(4-(diphenylamino)phenyl)pyridin-2-yl)ethanone[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.92-7.83 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.17-7.15 (t, 6H), 7.06 (t, *J* = 7.2 Hz, 2H), 2.79 (s, 3H) ppm.

N,N-diphenyl-4-(pyridin-3-yl)aniline[4]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.83 (d, *J* = 1.6 Hz, 1H), 8.55 (dd, *J* = 1.2 Hz, 4.8 Hz, 1H), 7.85-7.83 (m, 1H), 7.46-7.44 (m, 2H), 7.35-7.26 (m, 5H), 7.17-7.13 (m, 6H), 7.06 (t, *J* = 7.2 Hz, 2H) ppm.

4-(6-methoxypyridin-3-yl)-N,N-diphenylaniline[5]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.37 (s, 1H), 7.76 (dd, *J* = 12.0, 4.0 Hz, 1H), 7.40-7.37 (d, *J* = 7.6 Hz, 2H), 7.27-7.25 (m, 4H), 7.14-7.12 (m, 6H), 7.05-7.02 (t, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 1H) ppm.

N,N-diphenyl-4-(quinolin-2-yl)aniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.18 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.81 (t, *J* = 8.8 Hz, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 4H), 7.20-7.15 (m, 6H), 7.06 (t, *J* = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(quinolin-3-yl)aniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.18 (d, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.60-7.55 (m, 3H), 7.30-7.26 (m, 4H),

7.21-7.15 (m, 6H), 7.07 (t, *J* = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(quinolin-8-yl)aniline

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.97-8.96 (m, 1H), 8.21-8.18 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H), 7.80-7.74 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H,), 7.59 (d, *J* = 7.6 Hz, 1H), 7.43-7.40 (m, 1H), 7.30-7.26 (m, 4H), 7.21-7.17 (m, 6H), 7.03 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ = 150.08, 147.81, 147.05, 146.04, 140.34, 136.36, 133.35, 131.47, 130.14, 129.25, 128.85, 127.15, 126.37, 124.73, 122.92, 122.84, 120.93 ppm. MS (EI): *m*/*z* = 372.1631 $[M]^+$.

4-(1H-indol-5-yl)-N,N-diphenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.16 (s, 1H), 7.83 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 2H), 7.28-7.23 (m, 5H), 7.16-7.13 (m, 6H), 7.01 (t, *J* = 7.2 Hz, 2H), 6.59 (t, *J* = 2.4 Hz, 1H) ppm.

N,N-diphenyl-4-(pyrimidin-5-yl)aniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 9.15 (s, 1H), 8.92 (s, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.16 (t, *J* = 8.8 Hz, 6H), 7.09 (t, *J* = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(pyrimidin-2-yl)aniline[5]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.74 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.30-7.26 (m, 4H), 7.16-7.13 (m, 5H), 7.11-7.05 (m, 4H) ppm.

N,N-diphenyl-4-(pyrazin-2-yl)aniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.96 (s, 1H), 8.56 (s, 1H), 8.42 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 6H), 7.08 (t, *J* = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(thiophen-2-yl)aniline[6]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.48-7.46 (m, 2H), 7.28-7.21 (m, 6H), 7.12 (d, *J* = 7.6 Hz, 4H), 7.08-7.01 (m, 5H) ppm.

N,N-diphenyl-4-(thiophen-3-yl)aniline[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.47 (d, *J* = 8.4 Hz, 2H), 7.37-7.35 (m, 3H), 7.28-7.24 (t, 4H), 7.10 (t, *J* = 8.0 Hz, 6H), 7.02 (t, *J* = 7.2 Hz, 2H) ppm.

N,N-diphenyl-4-(thiazol-2-yl)aniline[7]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.82-7.80 (m, 3H), 7.31-7.27 (t, *J* = 8.4 Hz, 3H), 7.25-7.24 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 4H), 7.10-7.07 (m, 4H) ppm.

4,4'-(pyridine-2,6-diyl)bis(N,N-diphenylaniline) [2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.00 (d, *J* = 8.4 Hz, 4H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 8H), 7.16-7.13 (m, 12H), 7.04 (t, *J* = 7.2 Hz, 4H) ppm.

4'-(diphenylamino)-[1,1'-biphenyl]-4-carbonitrile[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.70-7.64 (m, 4H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.15-7.12 (m, 6H), 7.07 (t, *J* = 7.2 Hz, 2H) ppm.

4'-(diphenylamino)-[1,1'-biphenyl]-2-carbonitrile[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.74-7.71 (m, 1H), 7.60-7.57 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43-7.41 (m, 2H), 7.39-7.35 (m, 1H), 7.30-7.26 (m, 4H), 7.17-7.12 (m, 6H),7.06 (t, *J* = 7.2 Hz, 2H) ppm.

4'-nitro-N,N-diphenyl-[1,1'-biphenyl]-4-amine[4]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.28-8.26 (m, 2H), 7.71-7.69 (m, 2H), 7.51-7.49 (m, 2H), 7.30-7.28 (m, 4H), 7.16-7.14 (m, 6H), 7.08 (t, *J* = 7.2 Hz, 2H) ppm.

4'-methoxy-N,N-diphenyl-[1,1'-biphenyl]-4-amine[8]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.50 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 7.6 Hz, 6H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H) ppm.

N^4,N^4,$N^{4'}$,$N^{4'}$-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine[9]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 7.44 (s, 4H), 7.30-7.24 (t, 10H), 7.13-7.08 (m, 10H), 7.01 (s, 4H) ppm.

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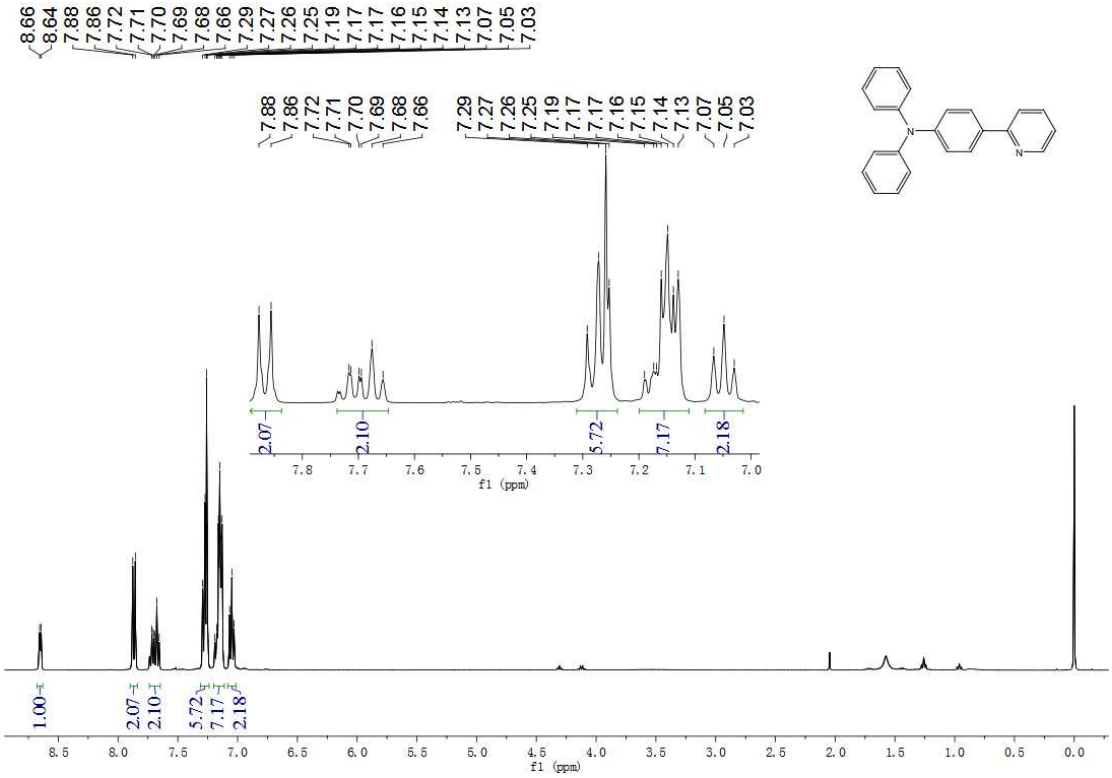
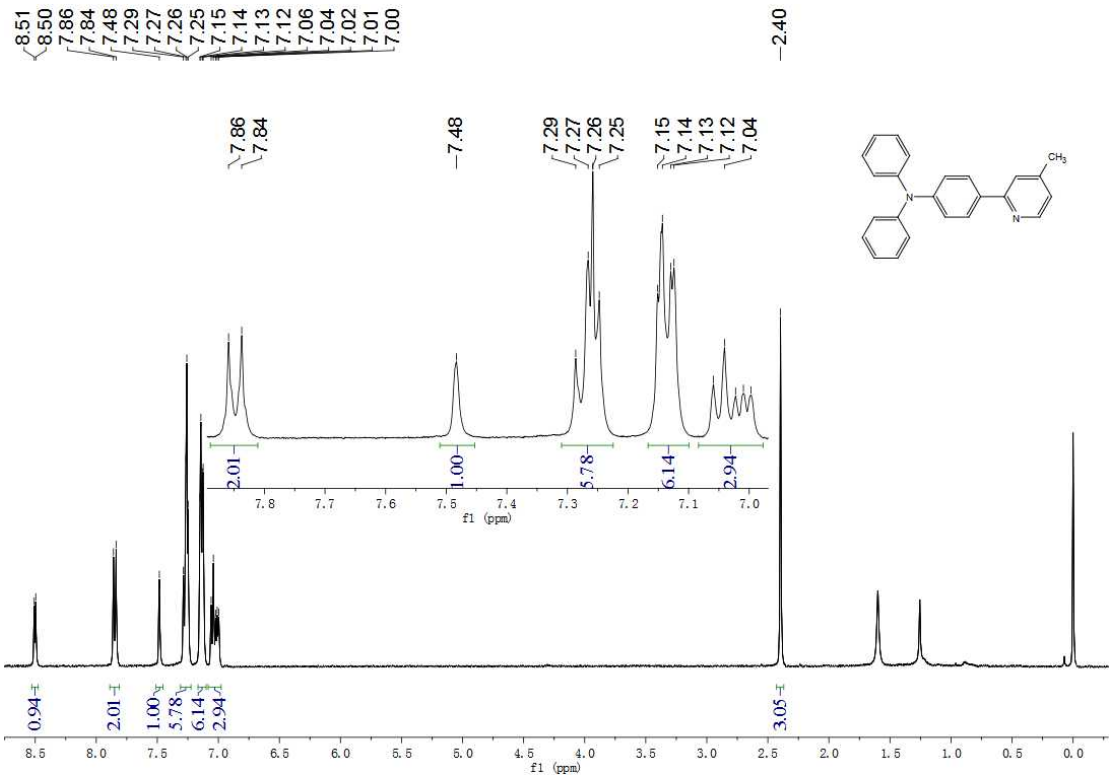
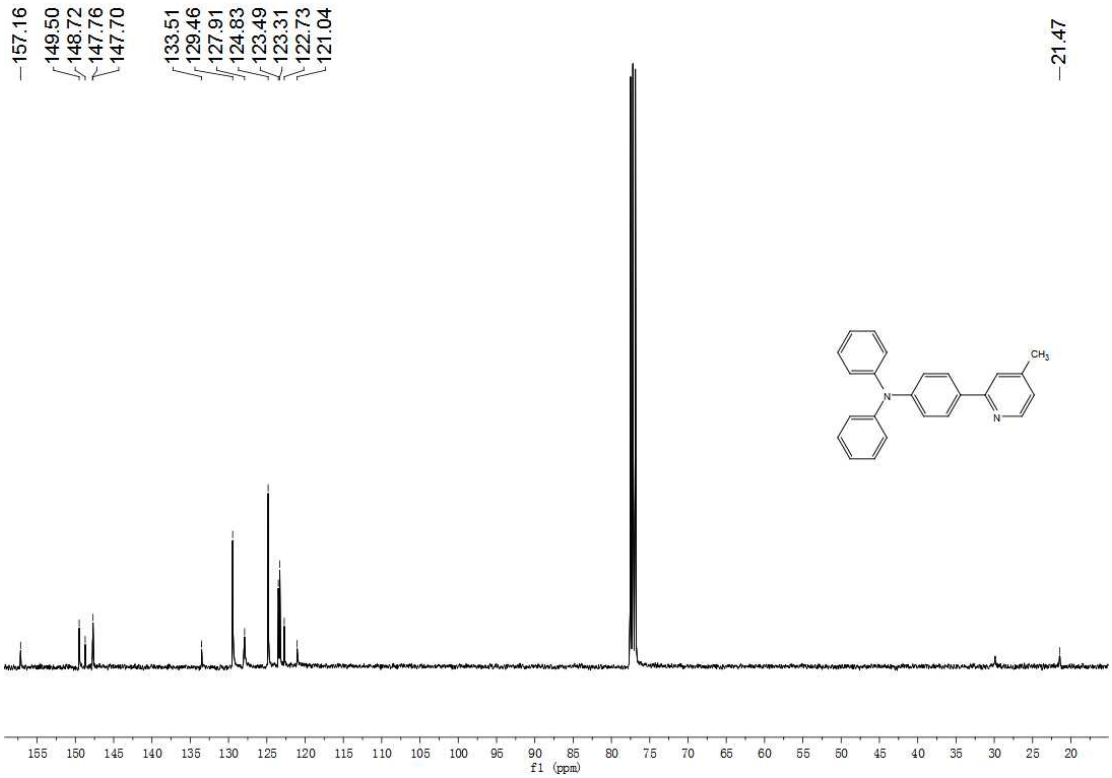
NMR Spectra for Products



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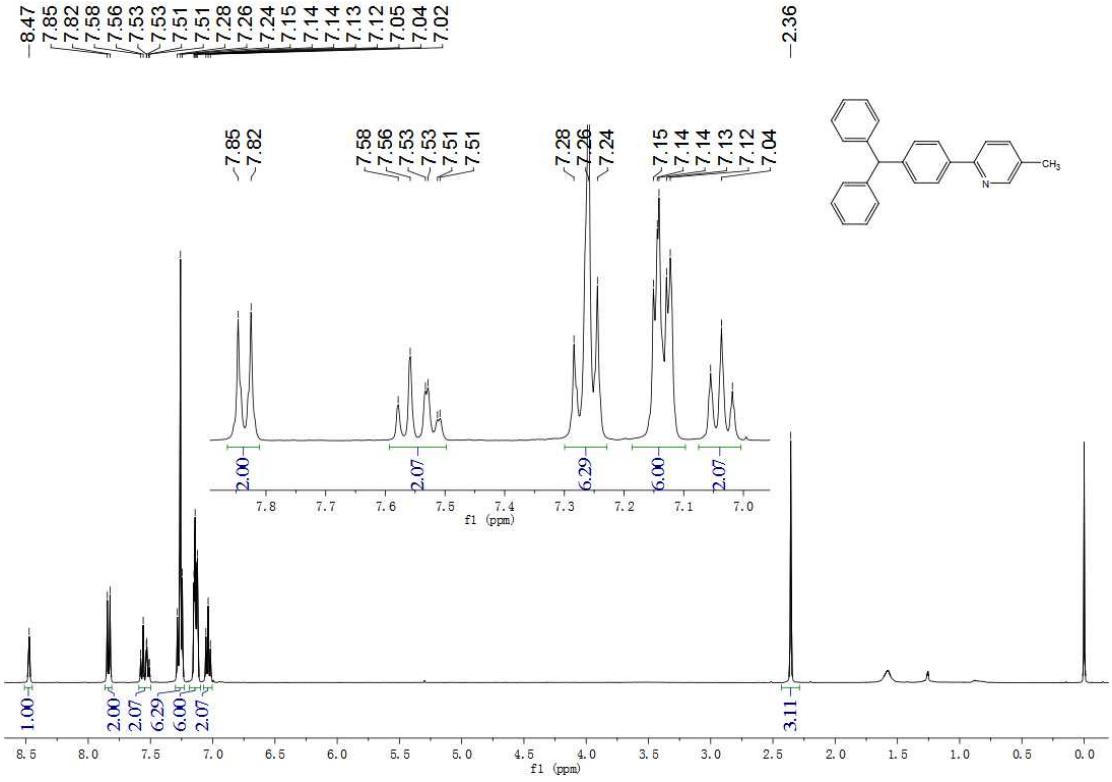
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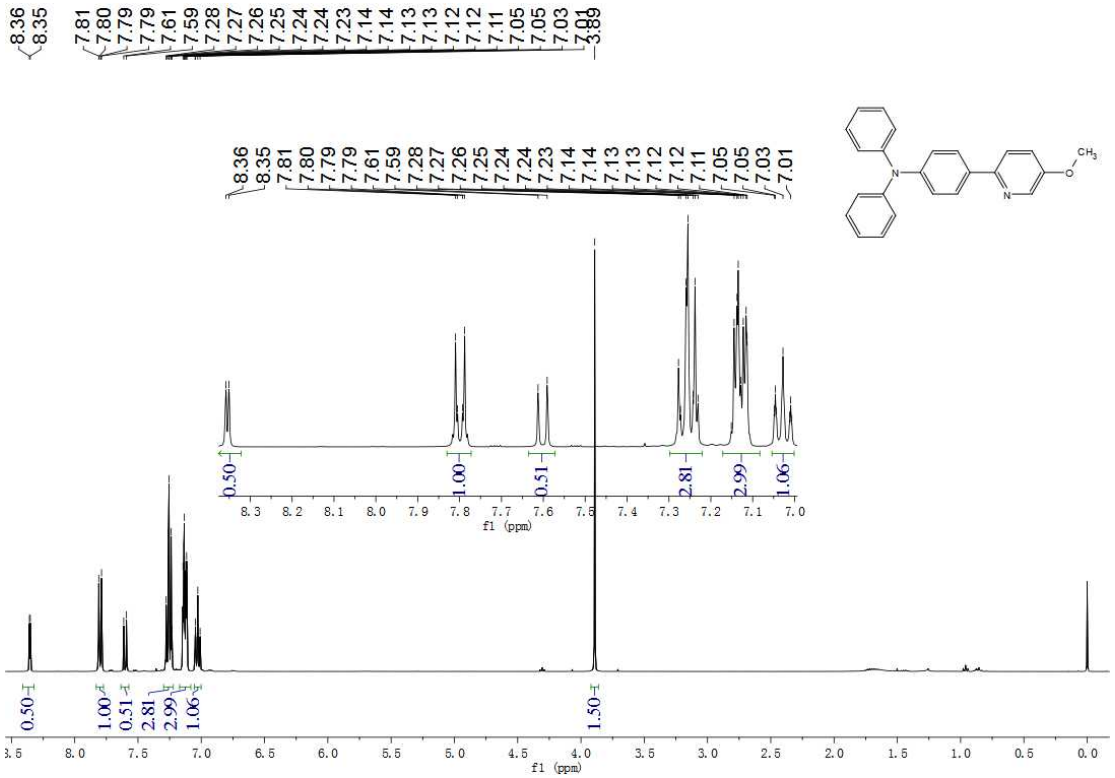
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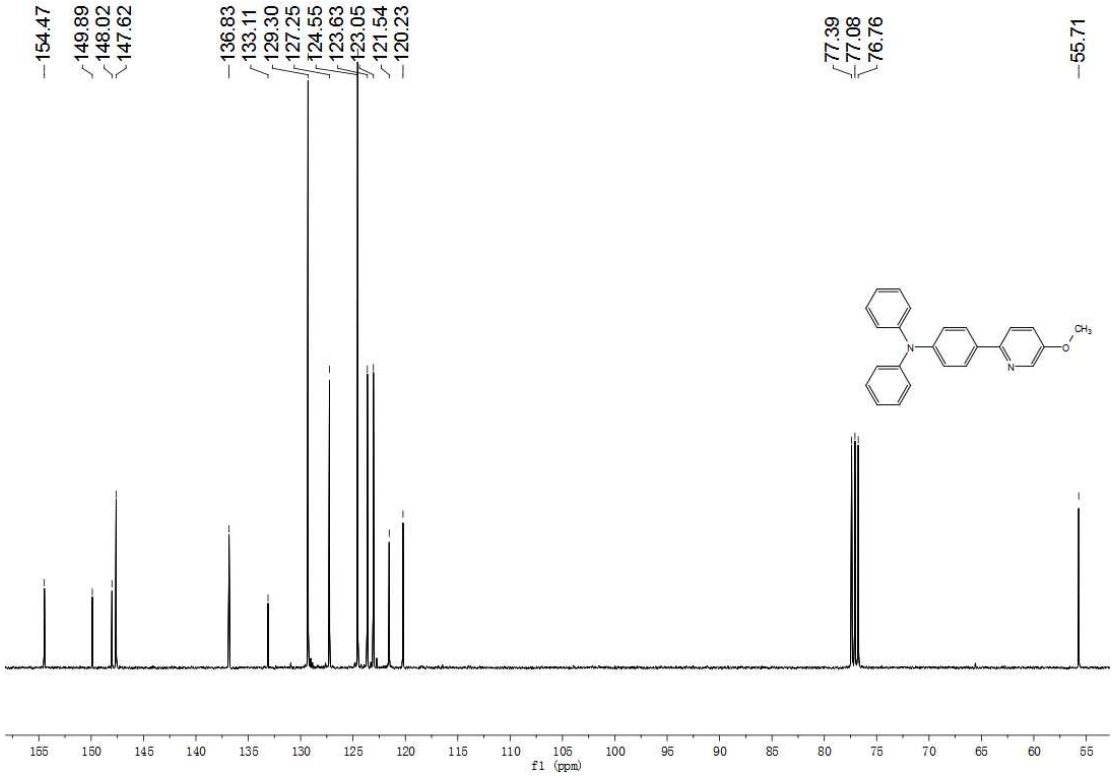
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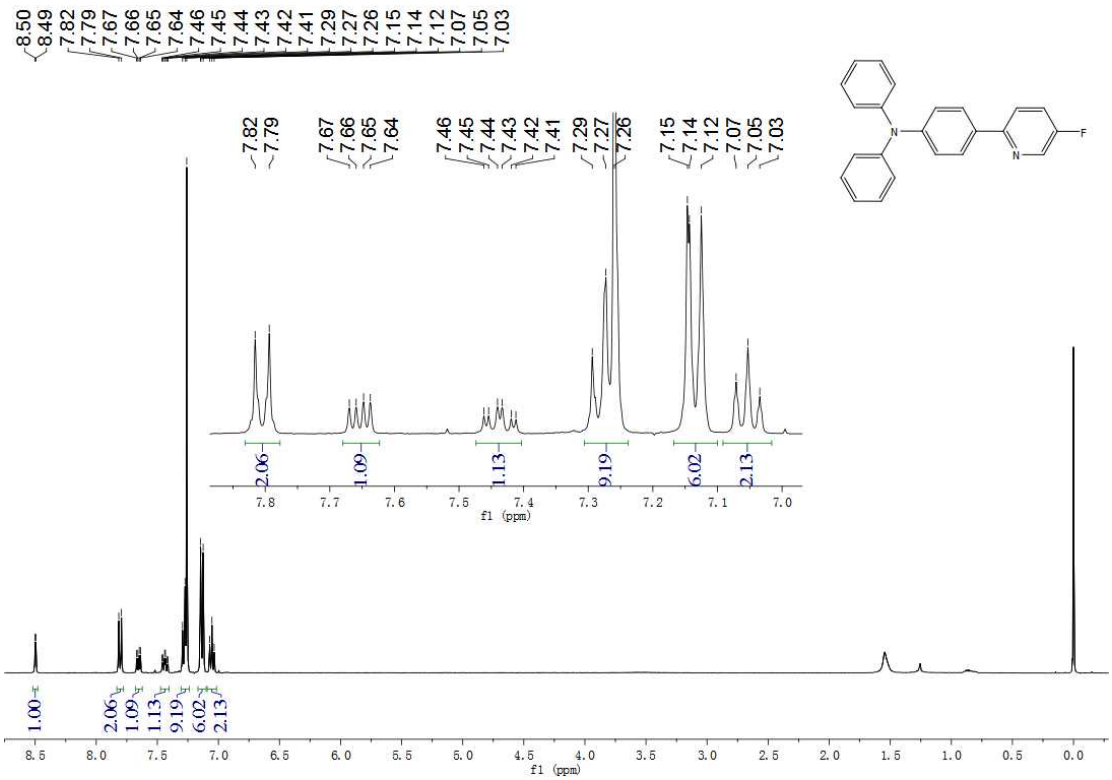
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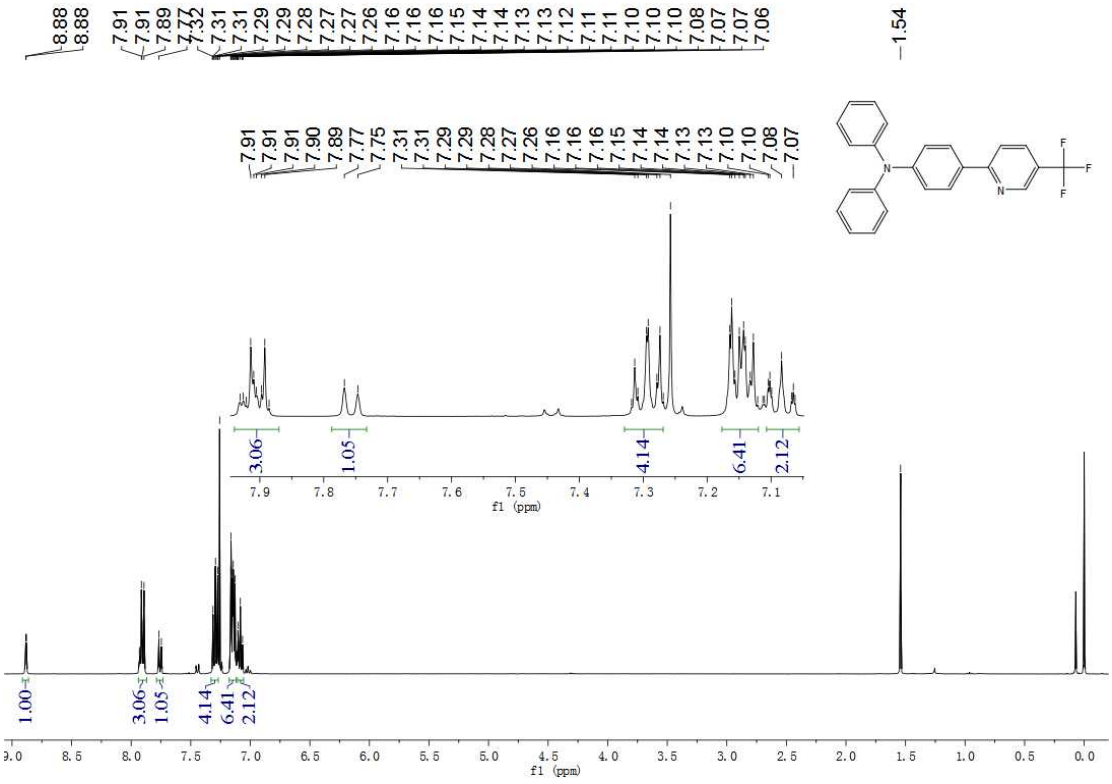
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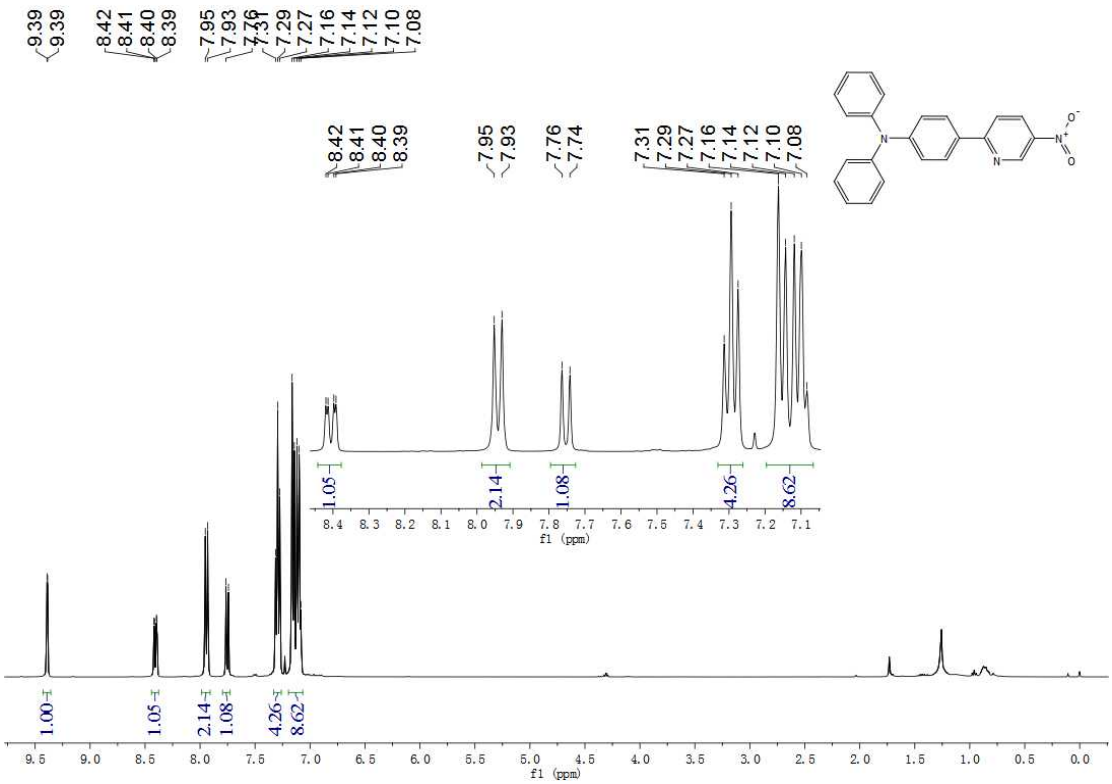
2.12
f1 (ppm)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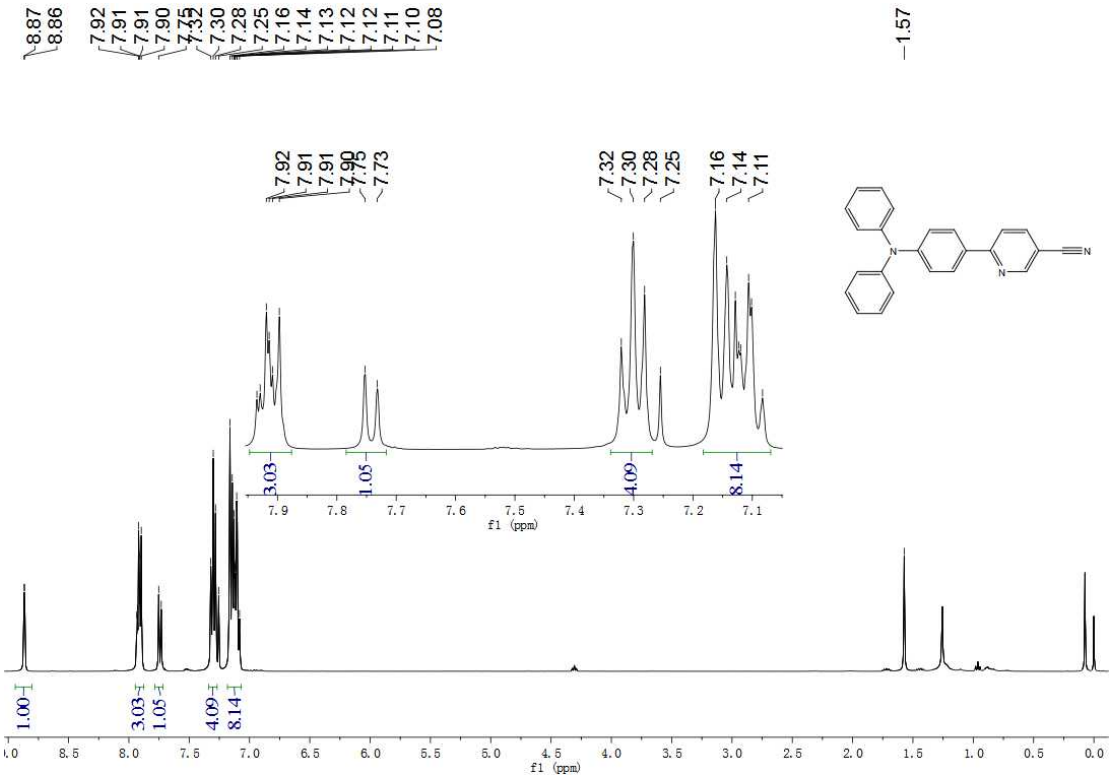
f1 (ppm)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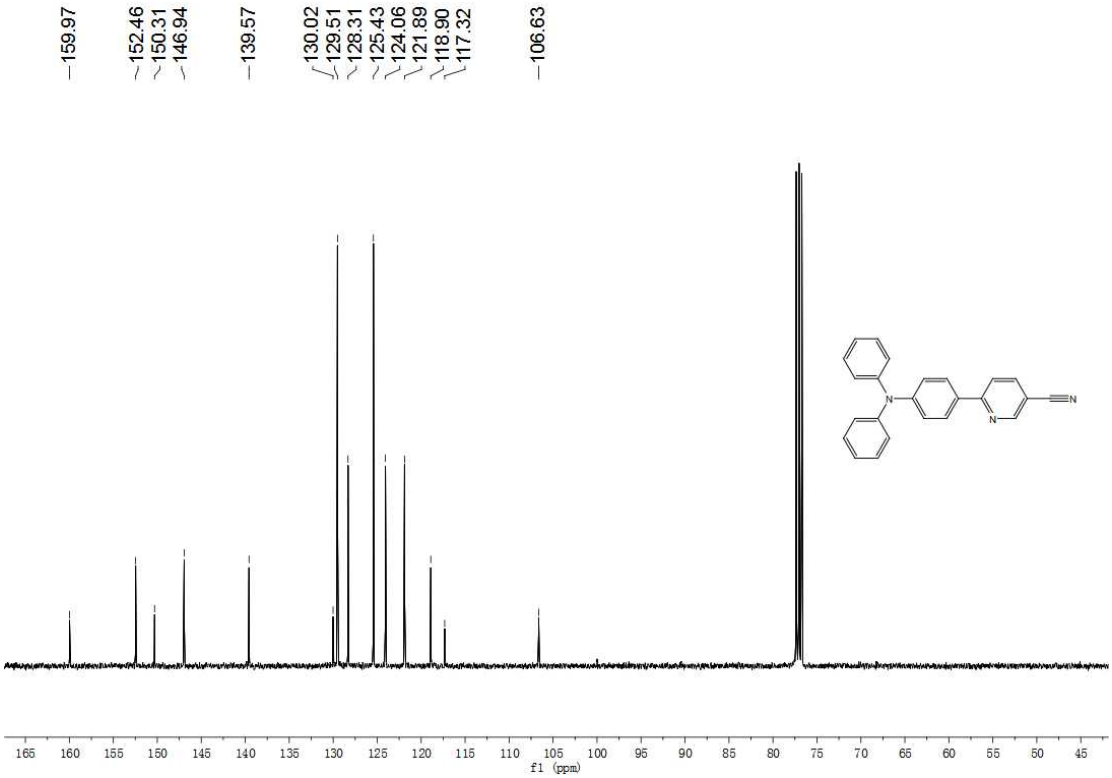
f1 (ppm)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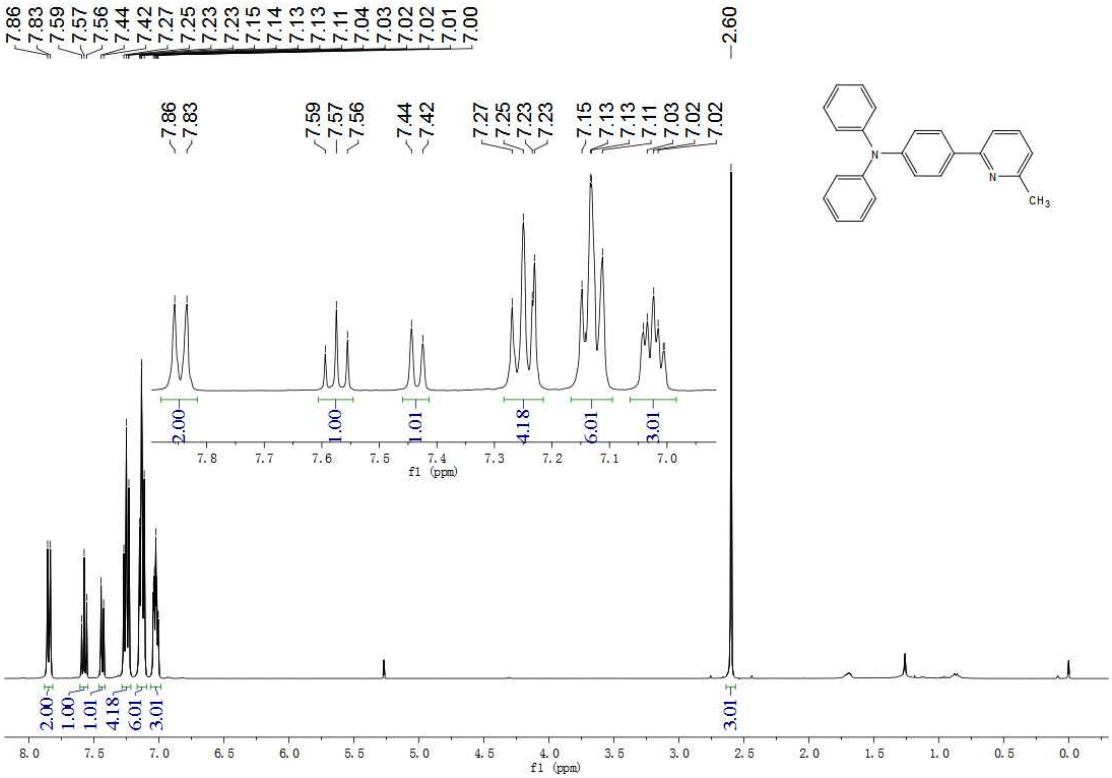
f1 (ppm)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7.03
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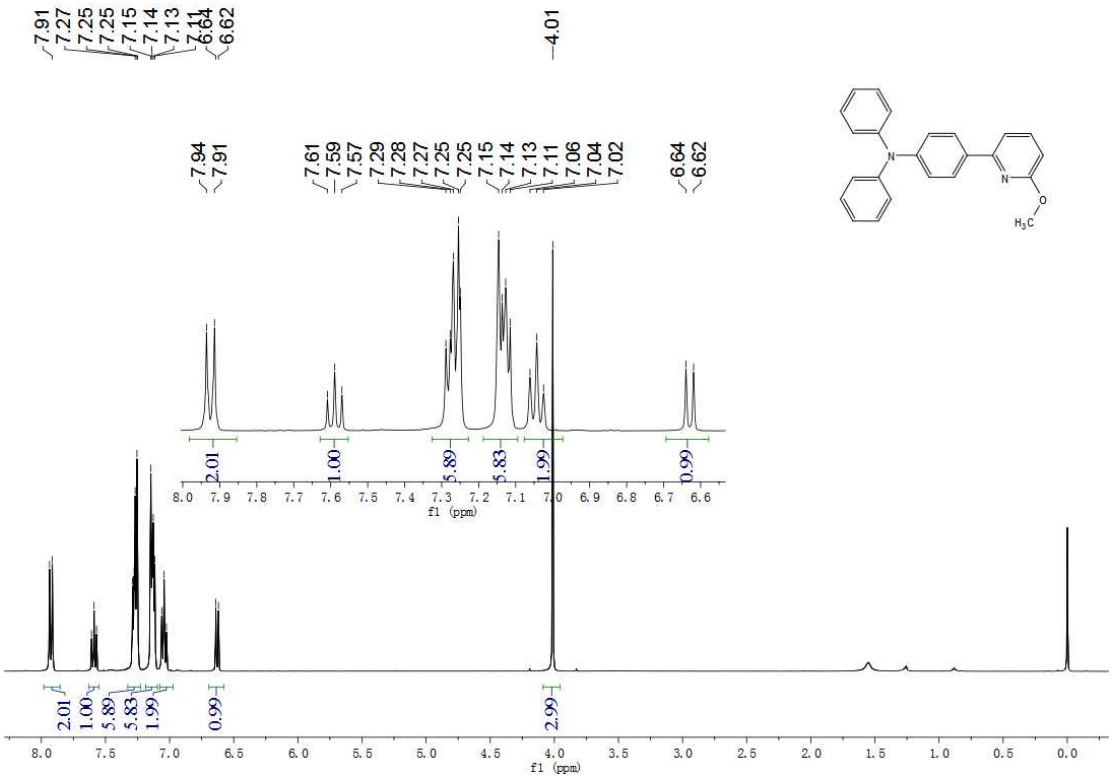
3.01
f1 (ppm)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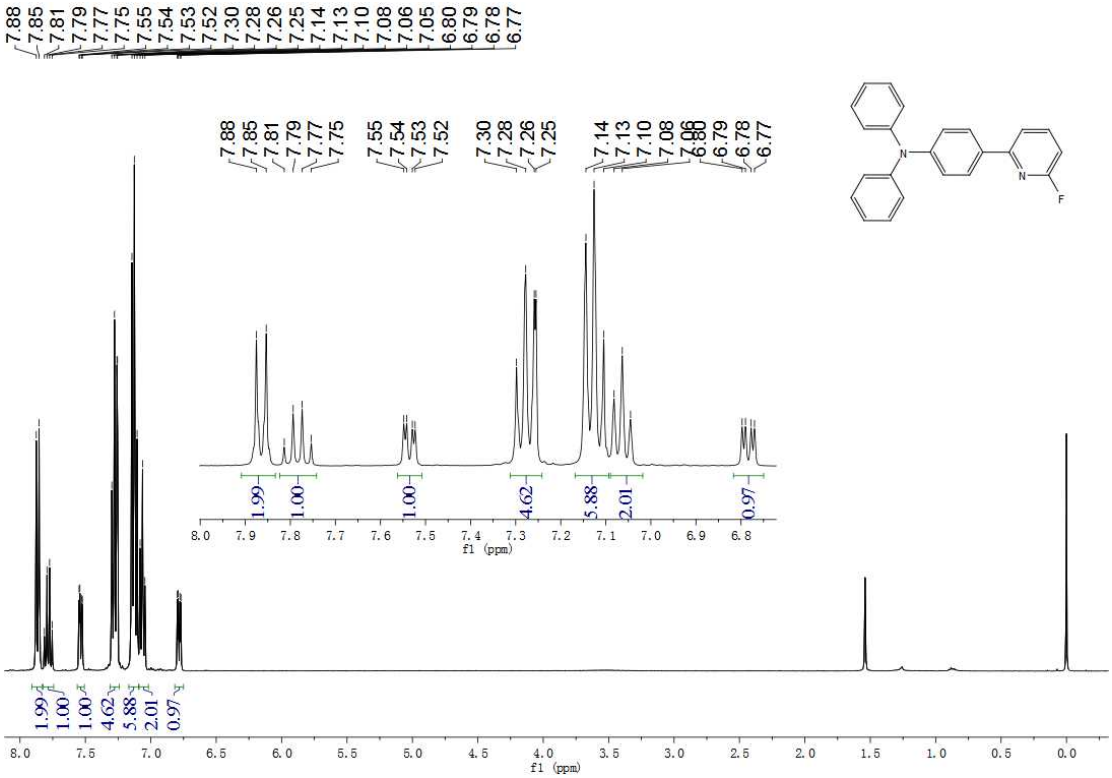
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7.13
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7.08
7.06
7.05
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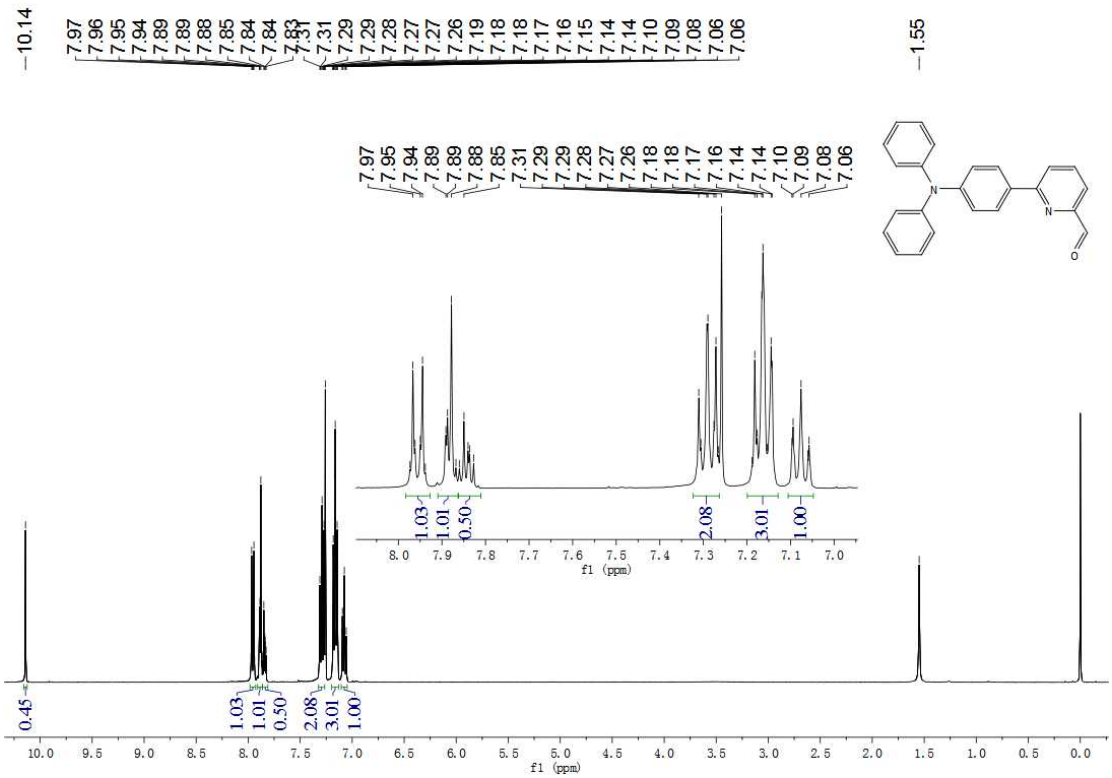
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7.15
7.14
7.14
7.10
7.09
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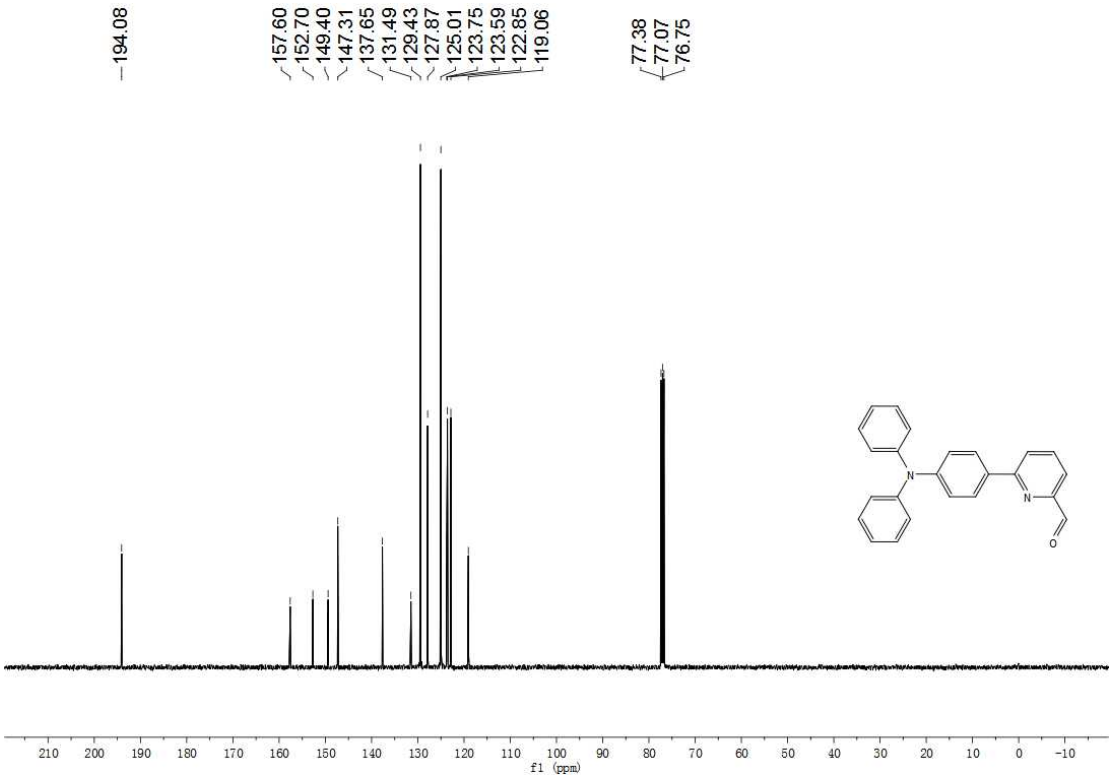
1.00
f1 (ppm)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123.59
122.85
119.06
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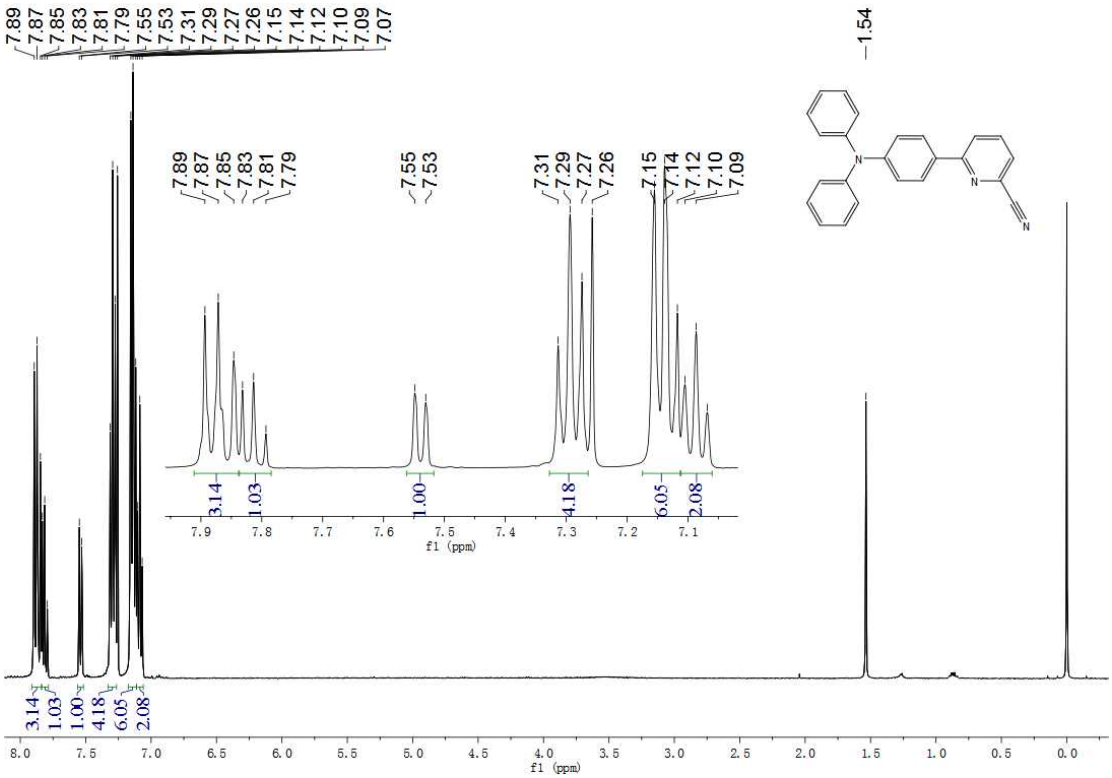
77.07
76.75
f1 (ppm)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7.14
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7.07
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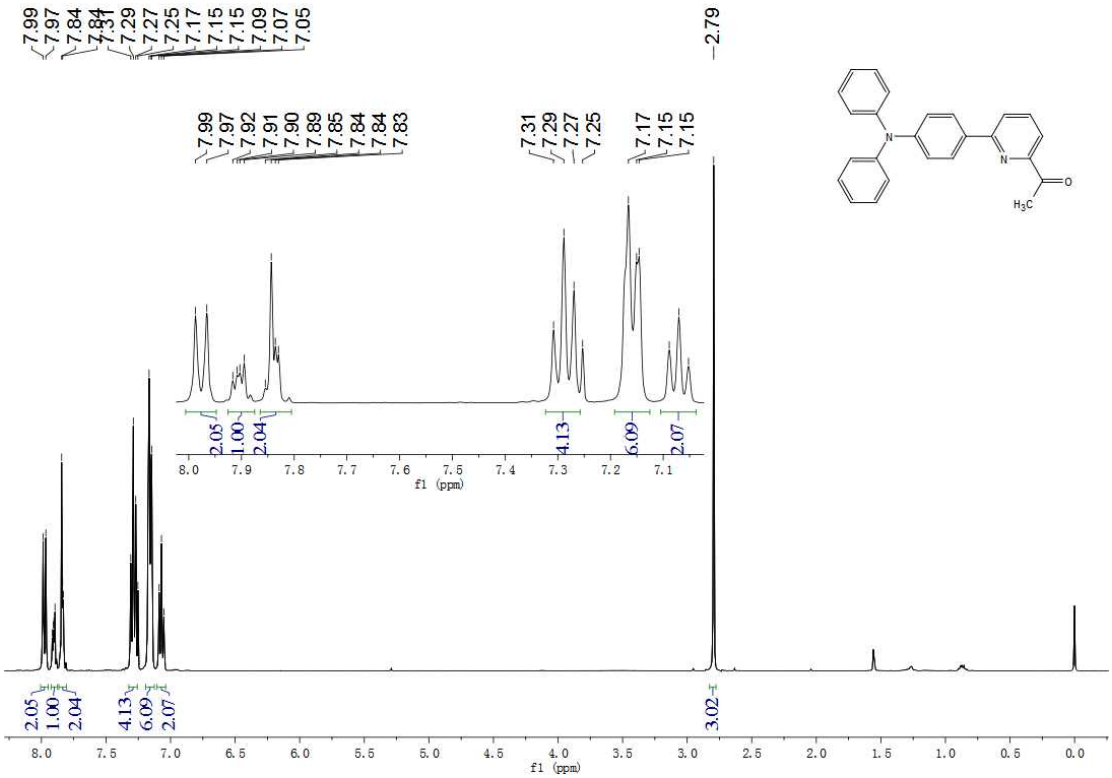
3.14
1.03
1.00
4.18
6.05
2.08
f1 (ppm)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7.17
7.15
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7.07
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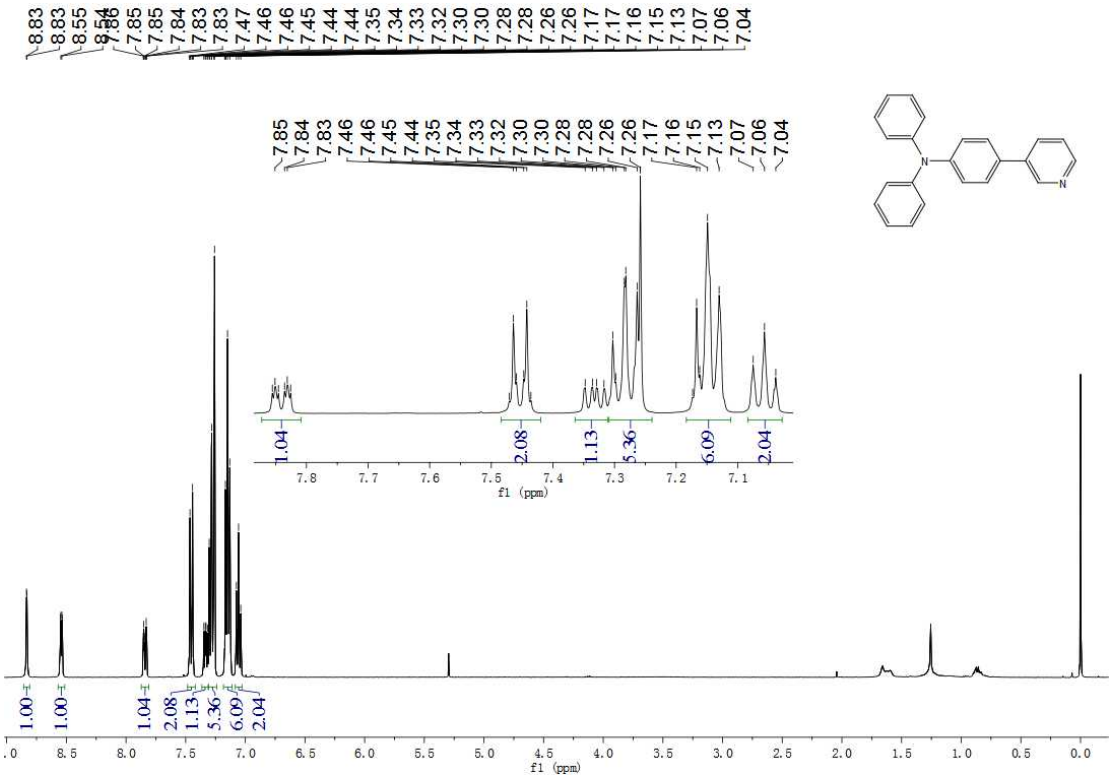
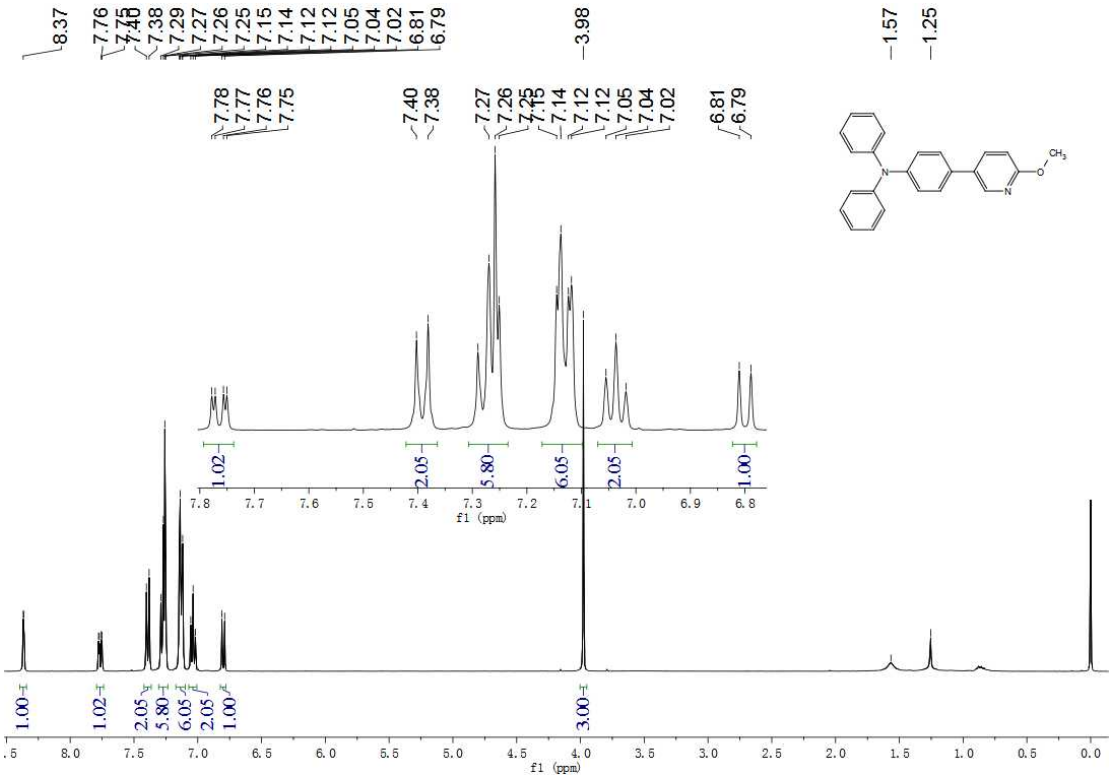
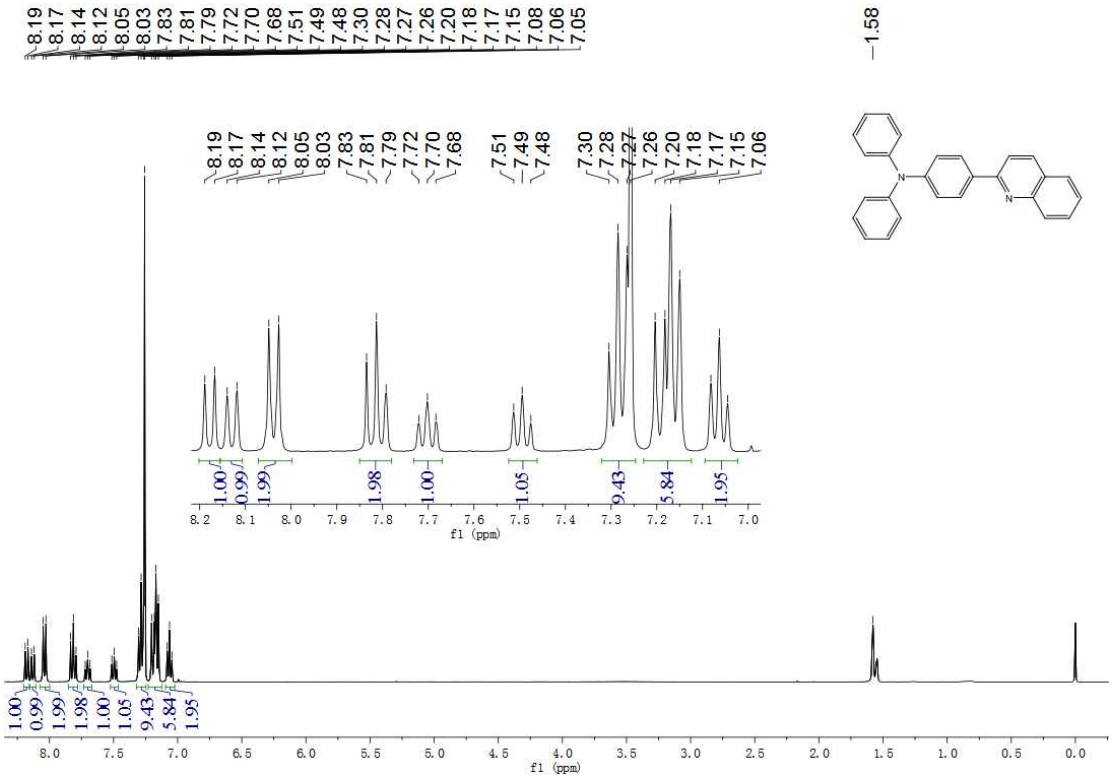
2.05
1.00
2.04
4.13
6.09
2.07
3.02
f1 (ppm)



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7.28
7.27
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7.20
7.18
7.17
7.15
7.08
7.06
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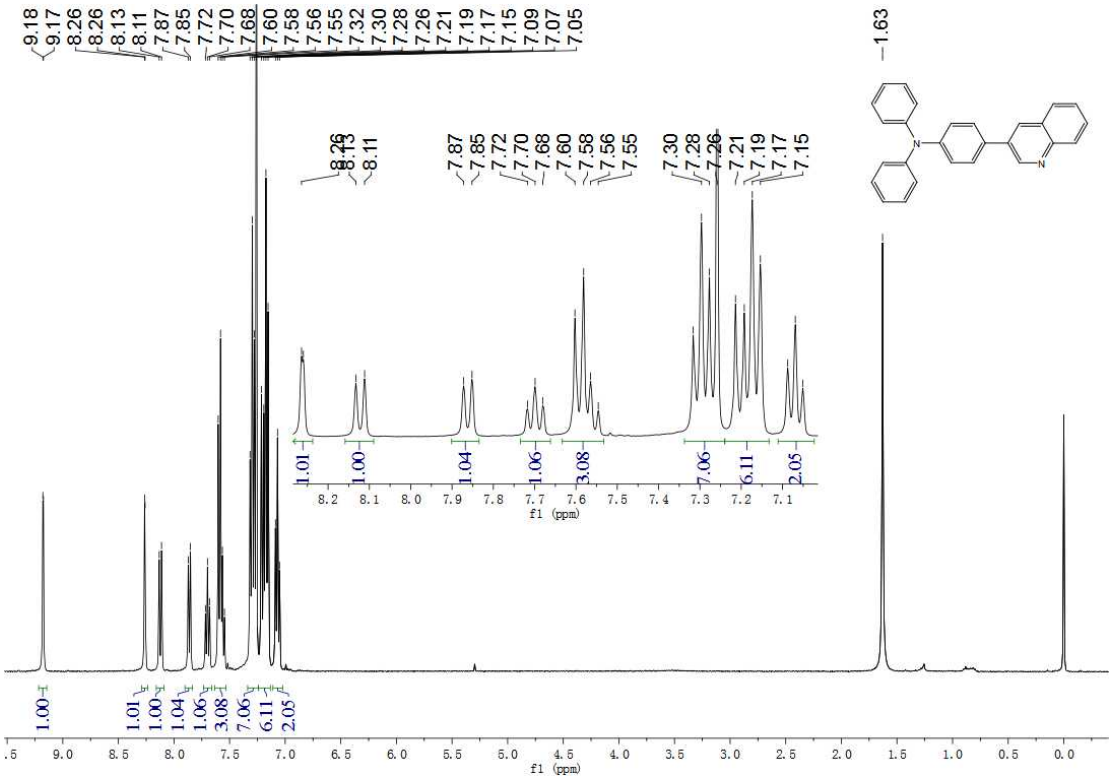
1.95
f1 (ppm)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7.07
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3.08
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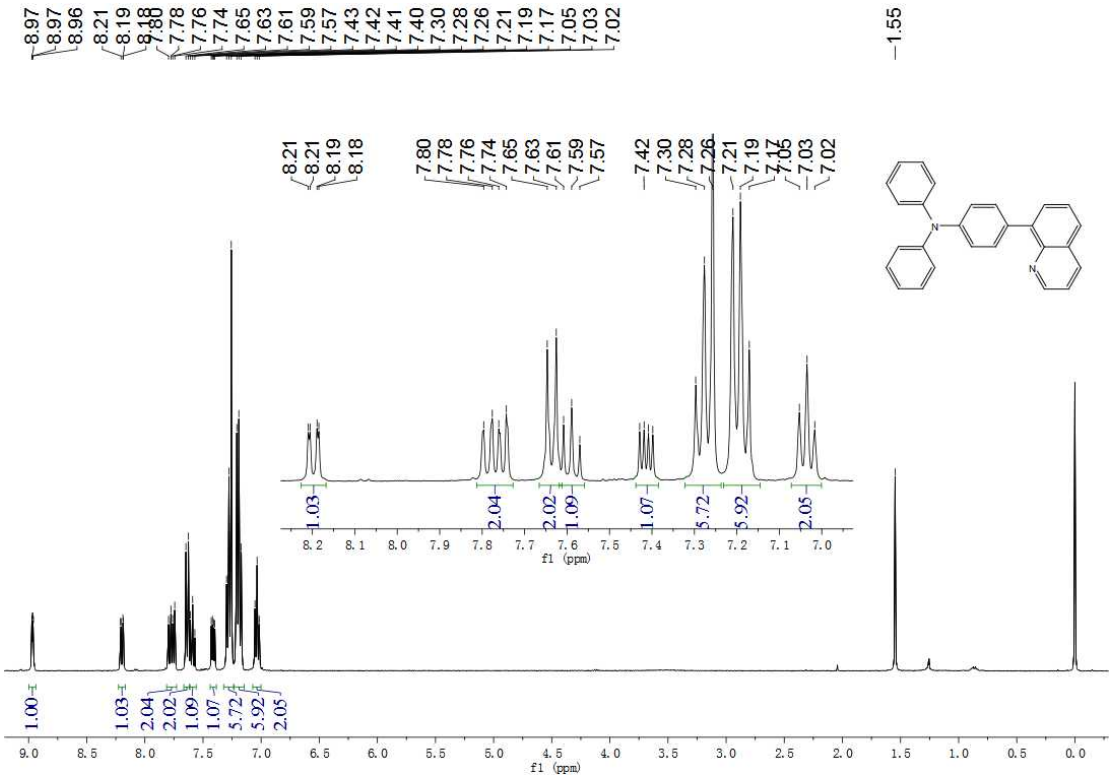
f1 (ppm)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1.07
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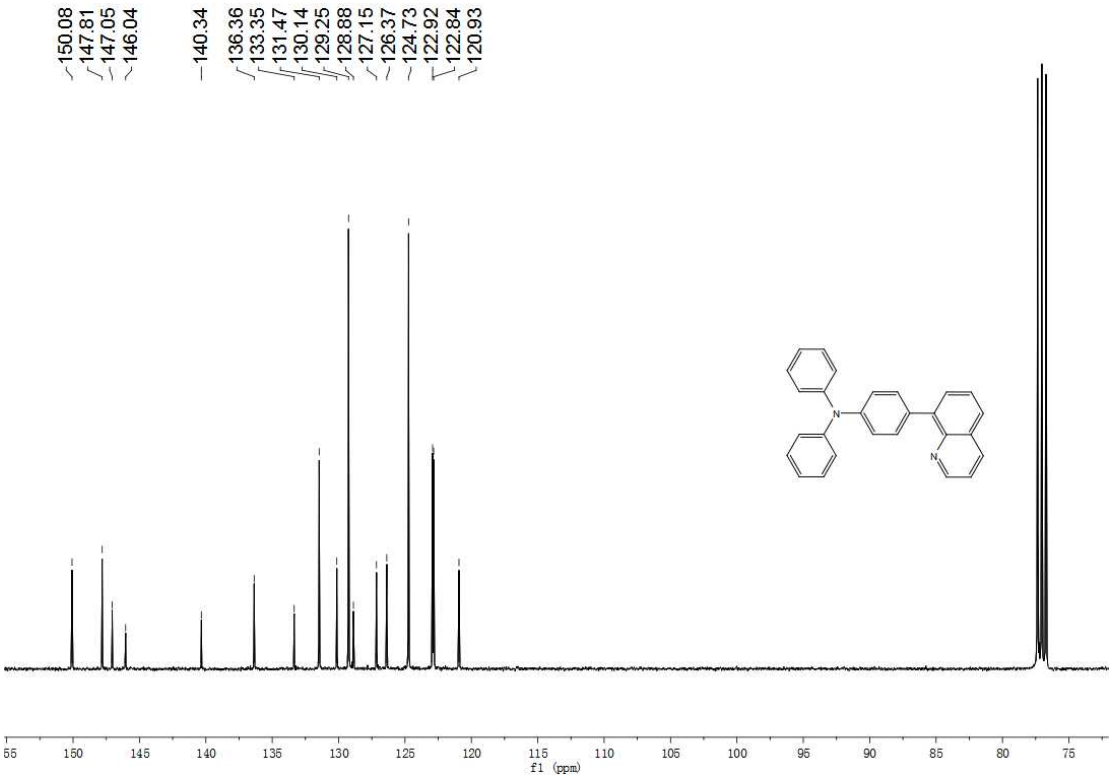
2.05
f1 (ppm)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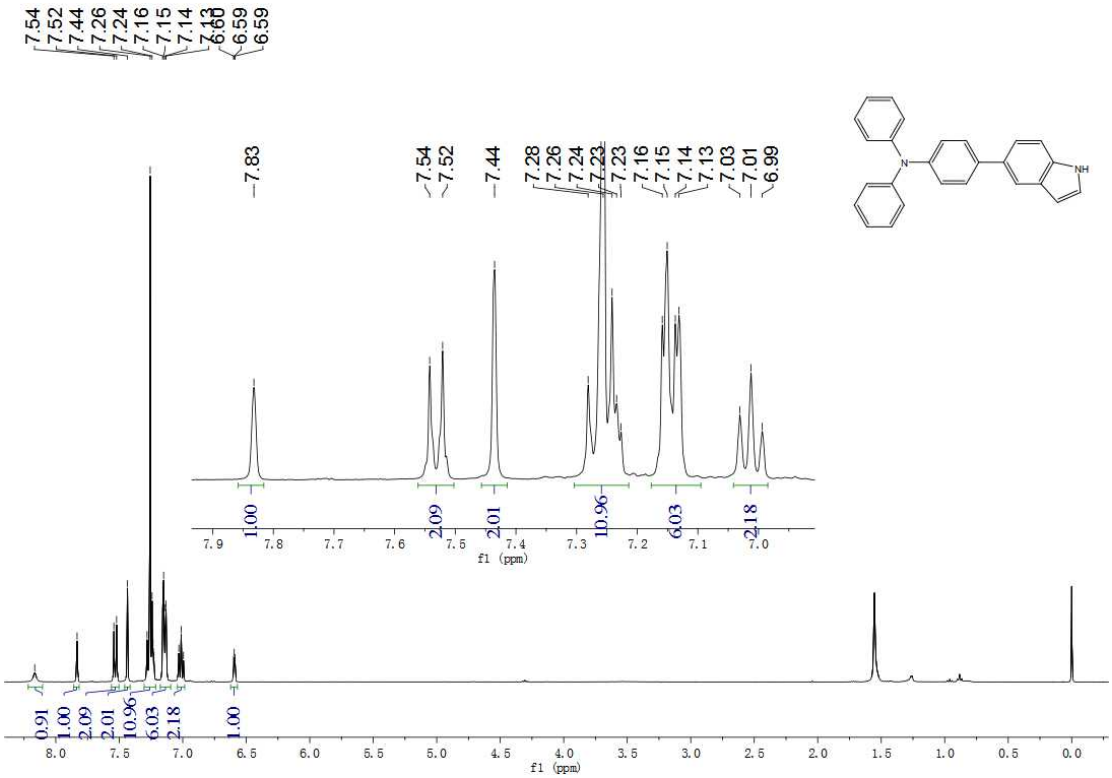
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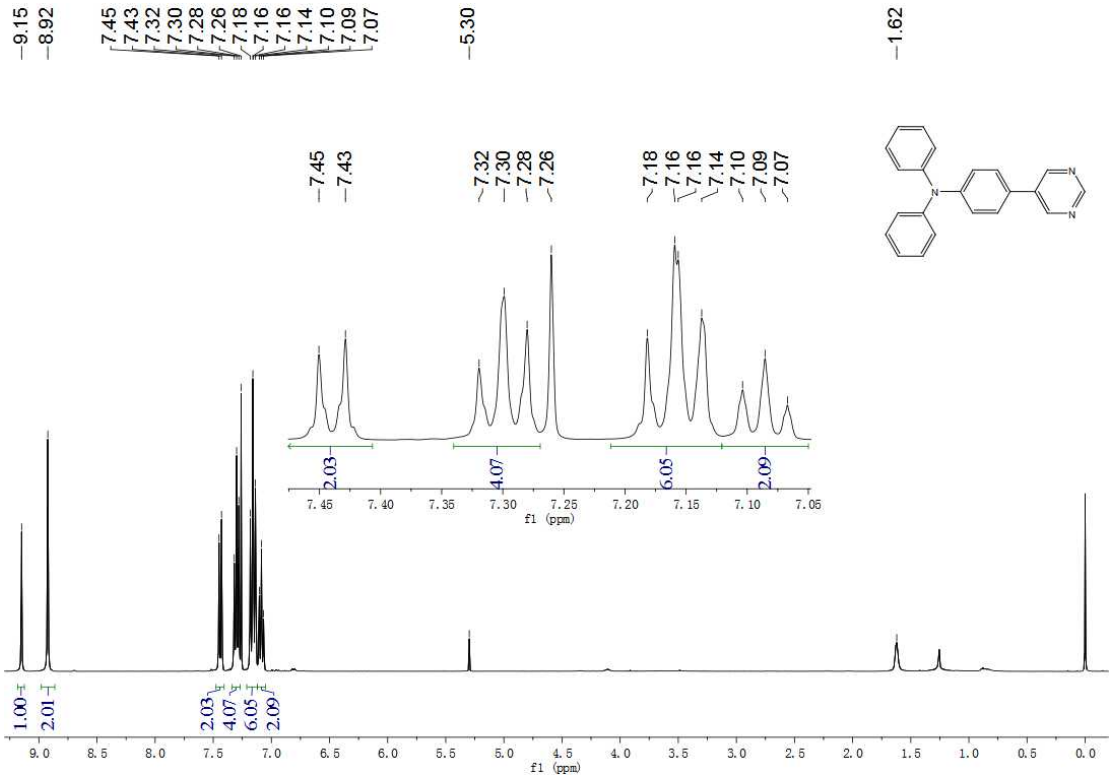
f1 (ppm)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N
N
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f1 (ppm)
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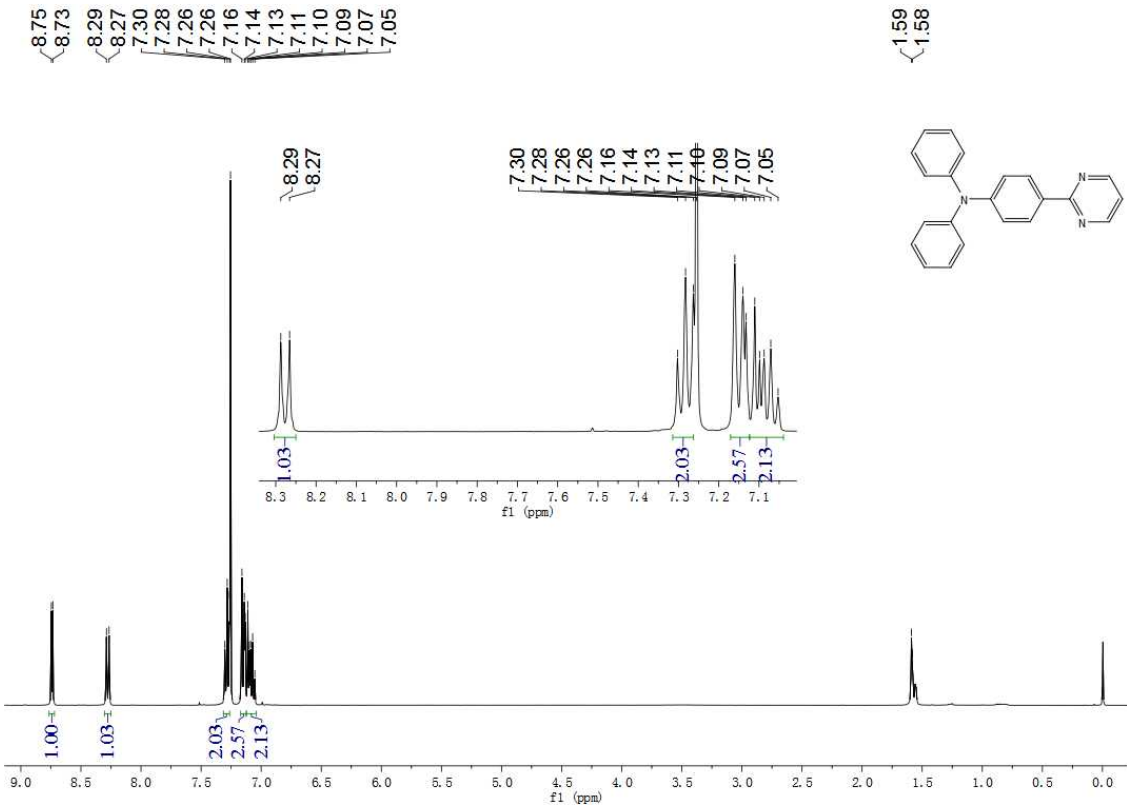
6.05
2.09
f1 (ppm)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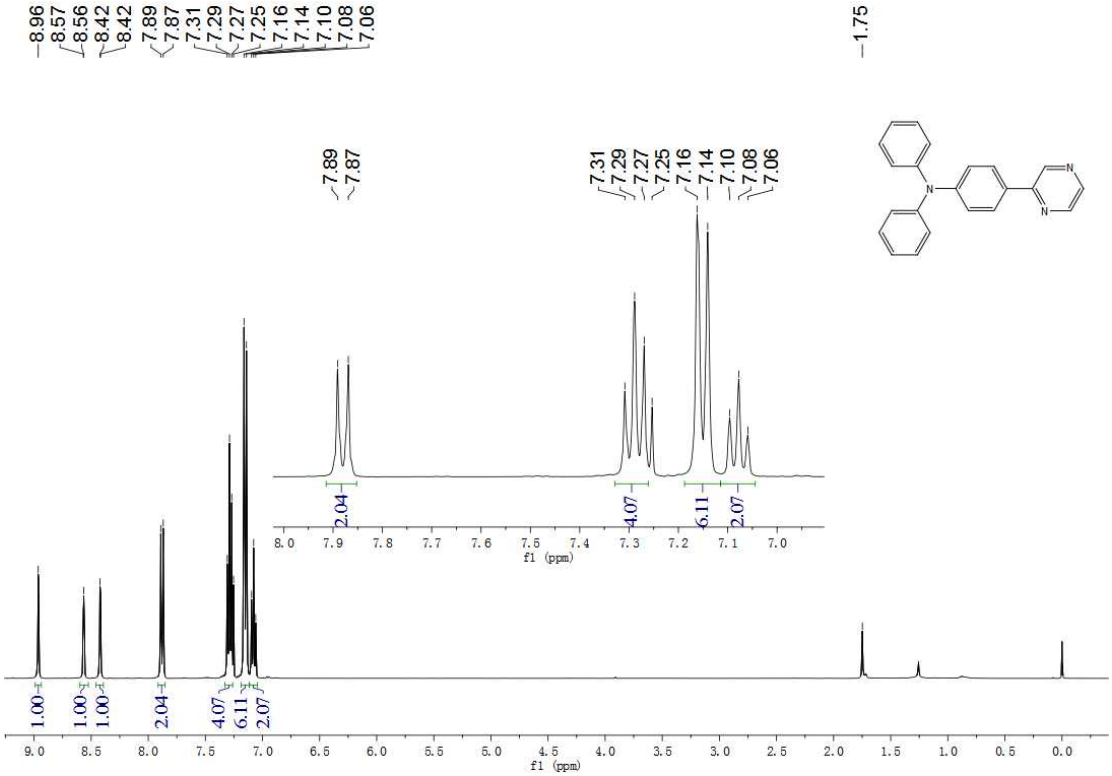
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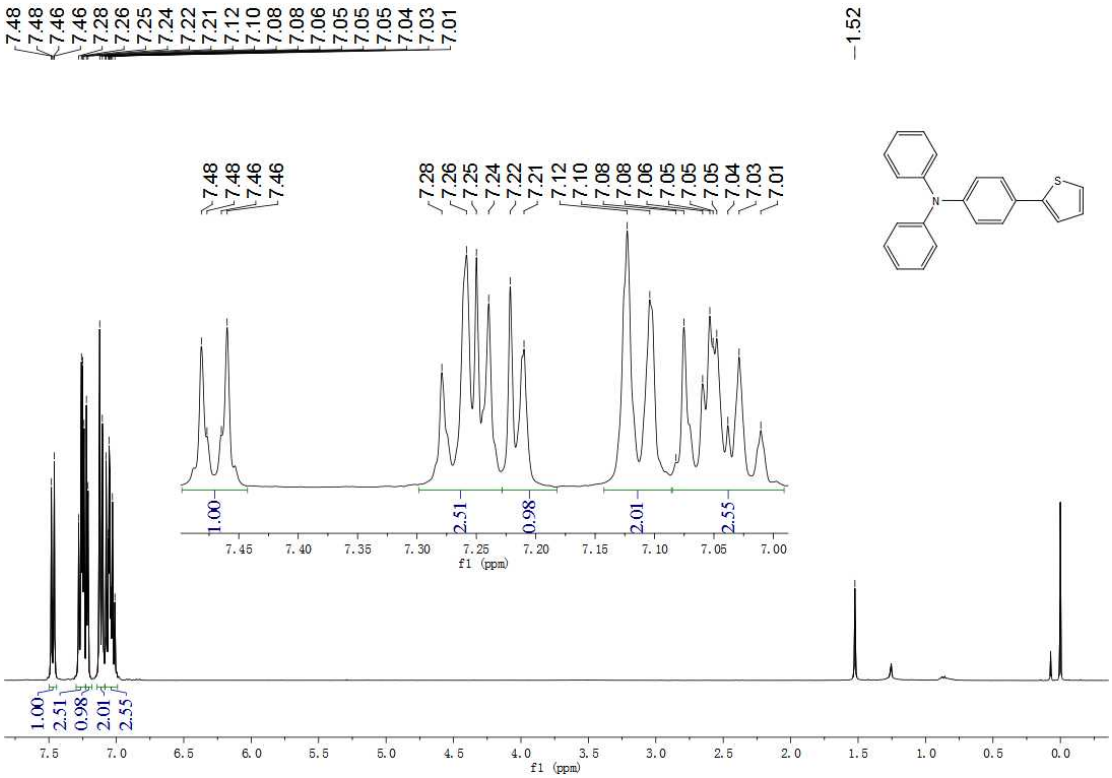
f1 (ppm)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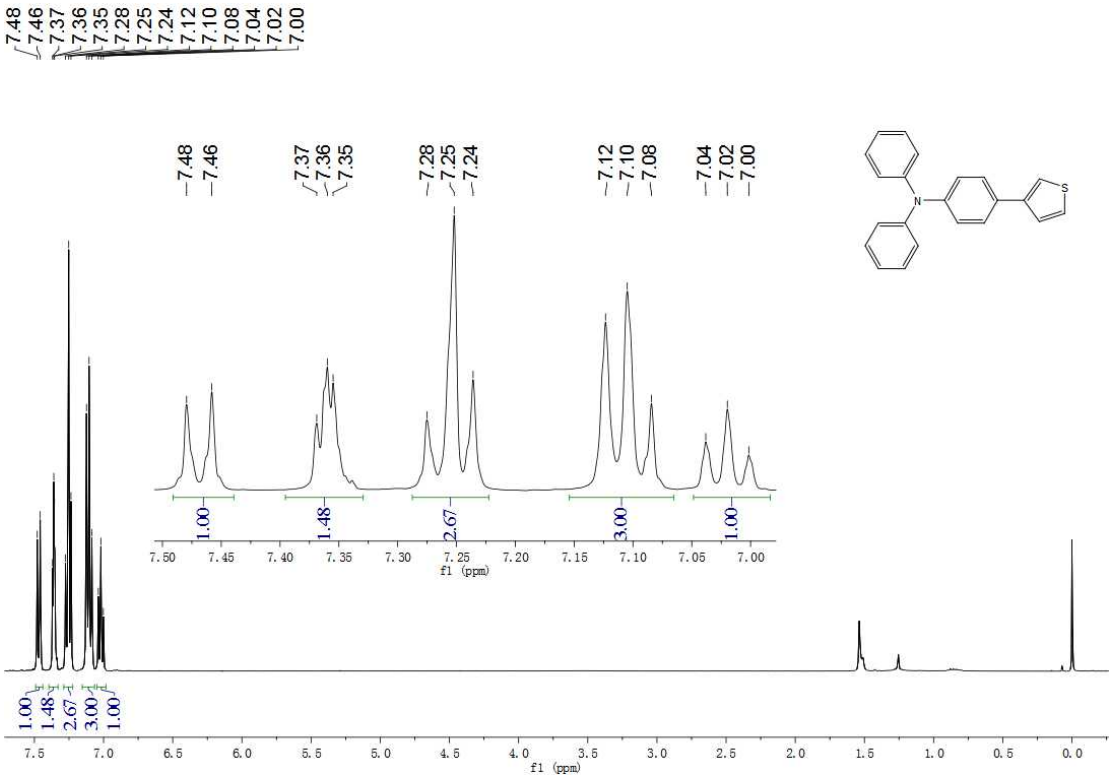
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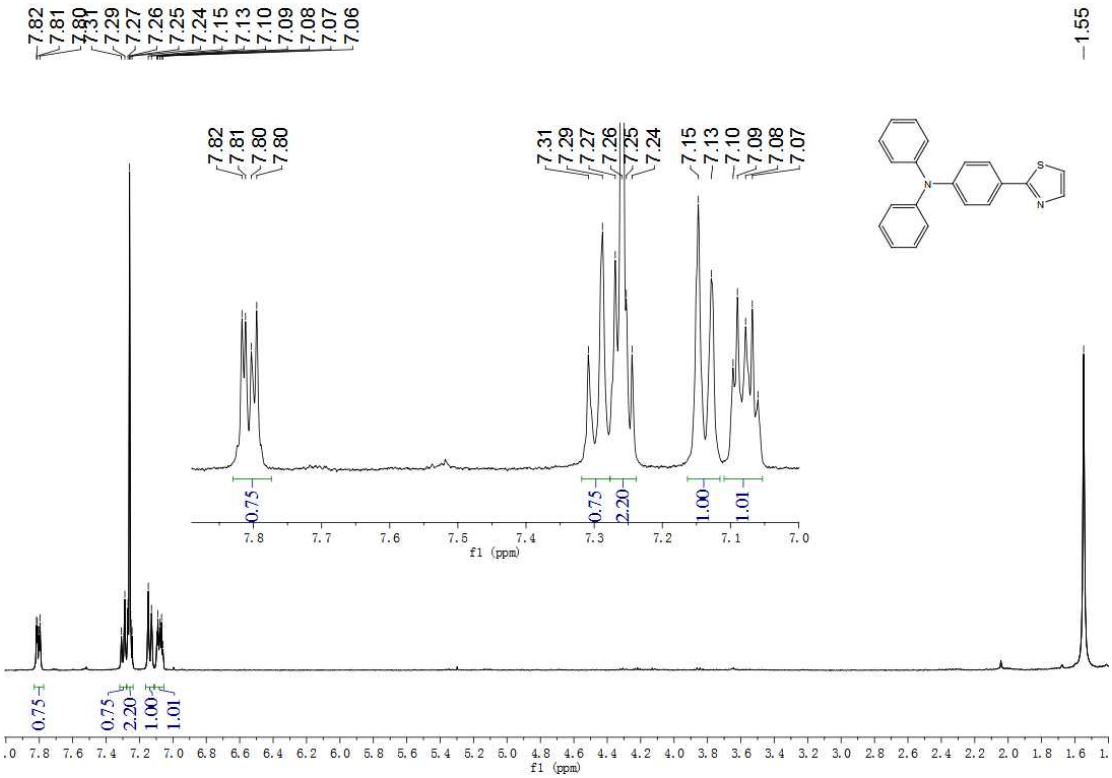
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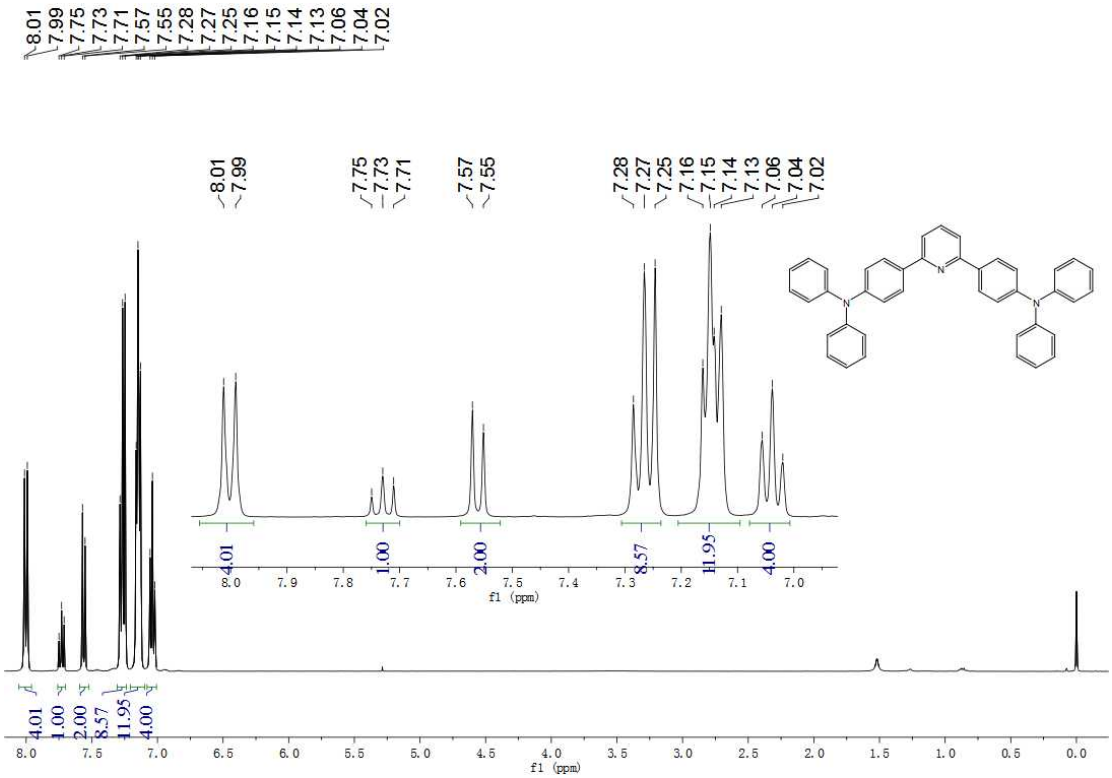
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4.00
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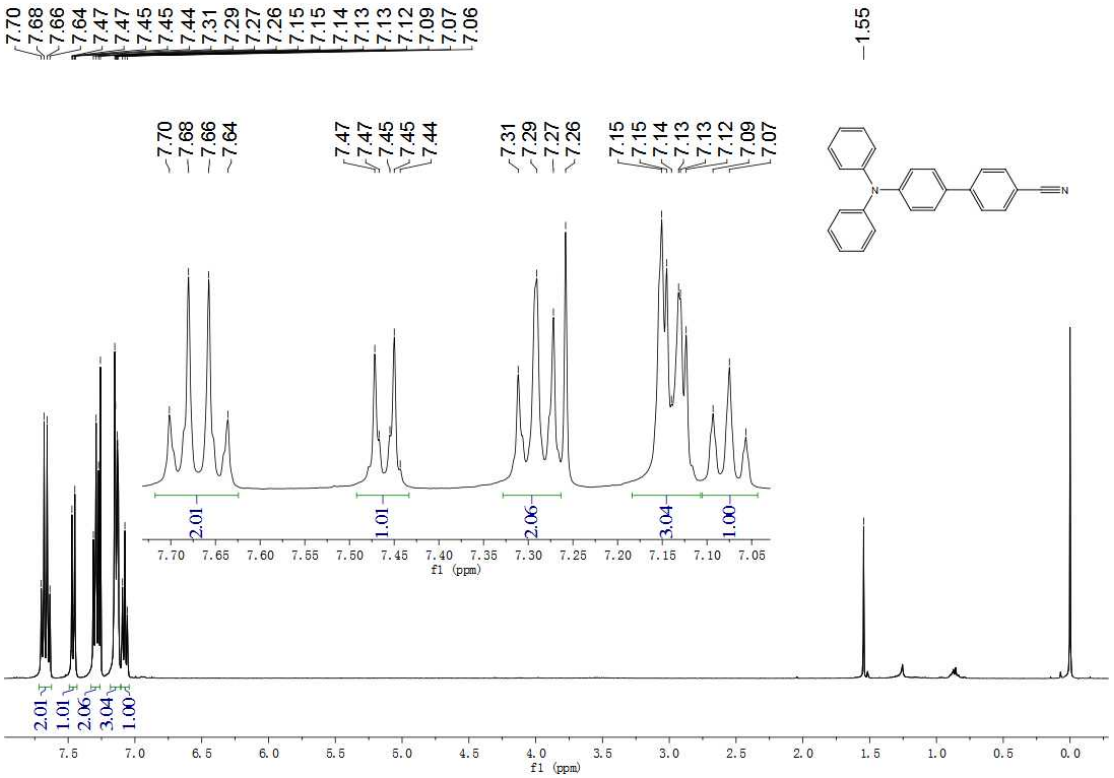
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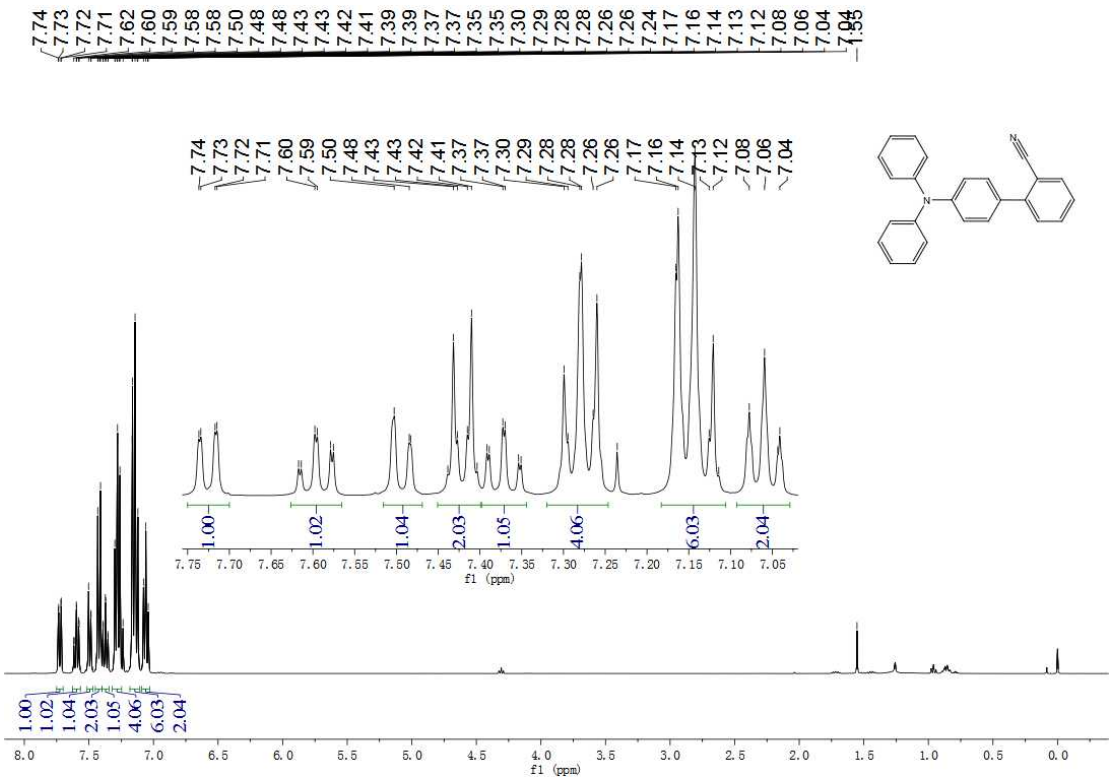
f1 (ppm)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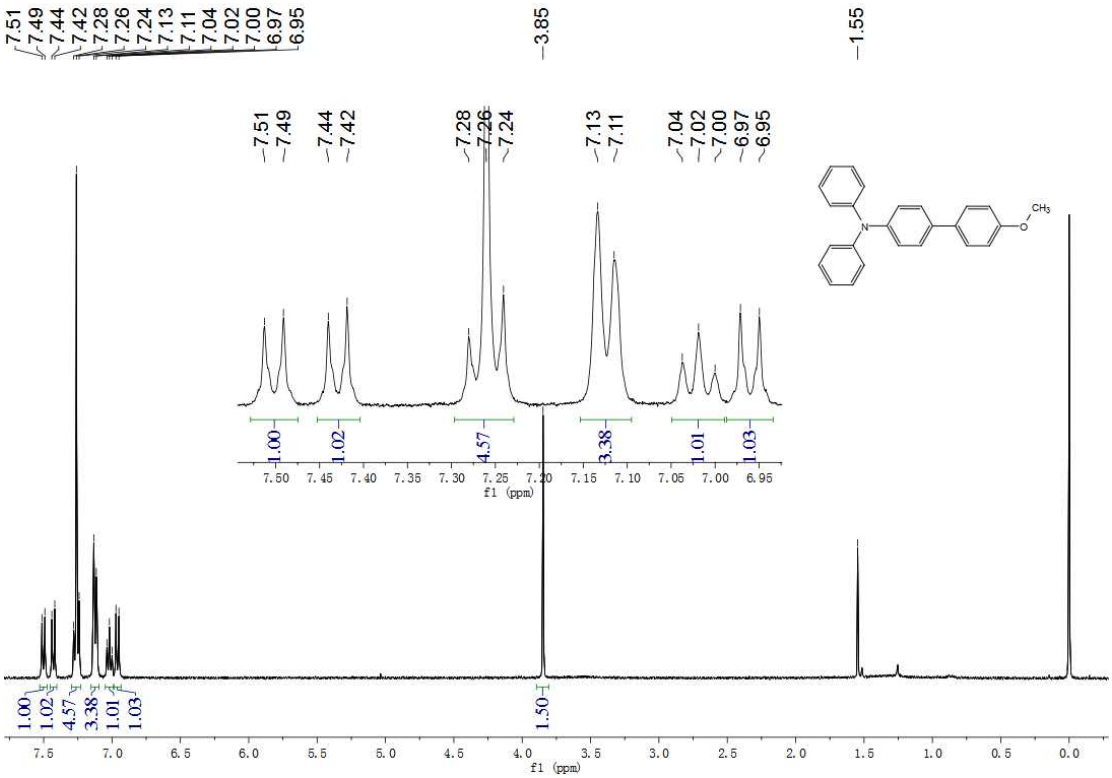
2.04
f1 (ppm)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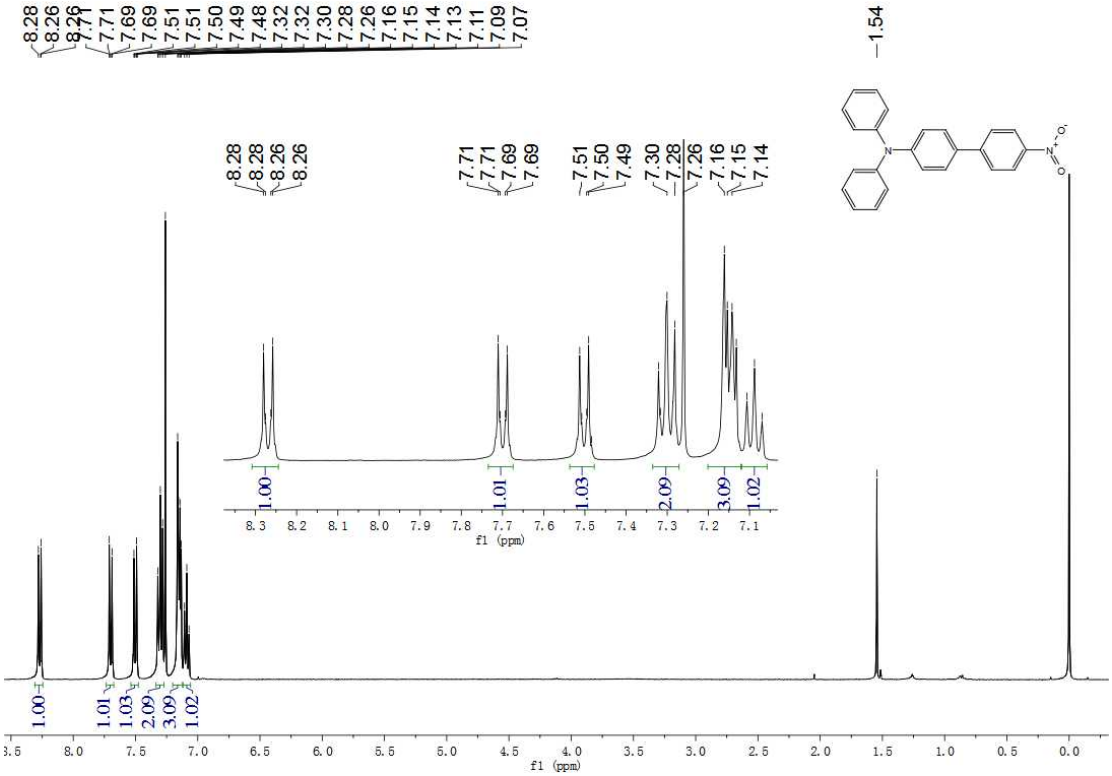
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1.02
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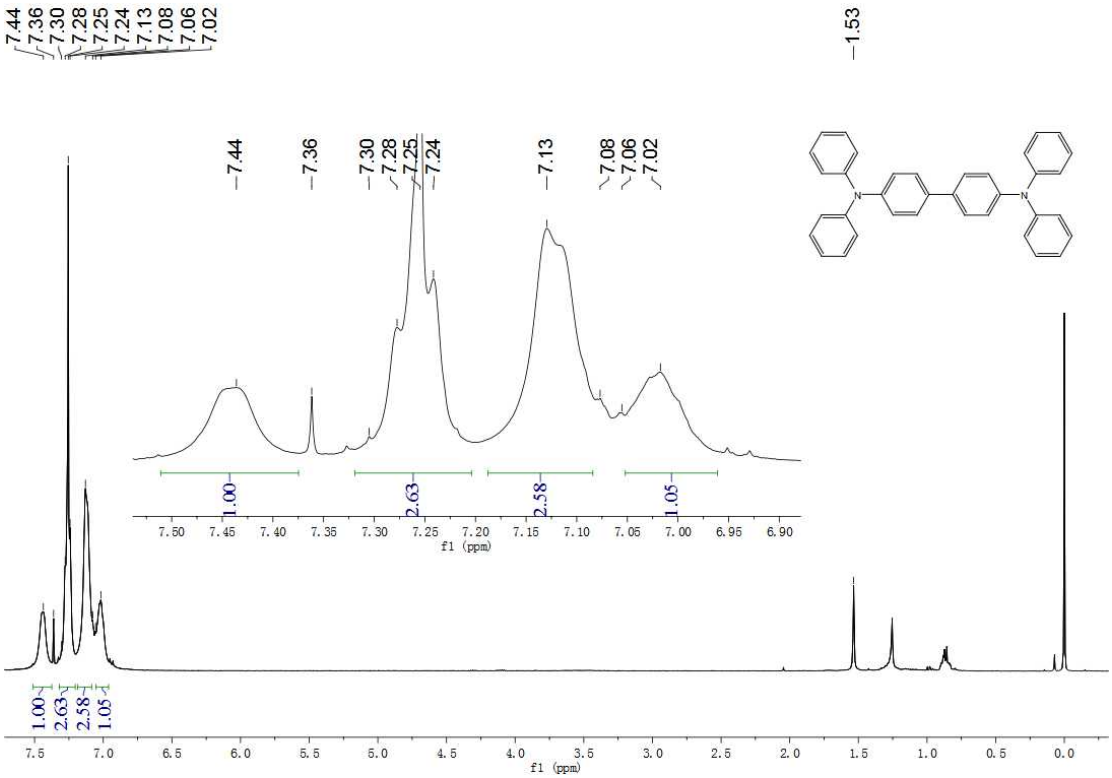
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f1 (ppm)