SUPPLEMENTARY INFORMATION

Site-Selective Electrochemical C–H Silylations of Pyridines Enabled by Temporary Reductive Dearomatization

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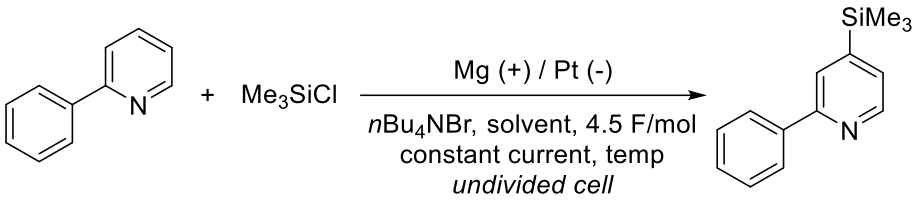
Table of the contents

General information

All reactions were performed under an argon atmosphere using oven-dried glassware unless otherwise noted. The platinum plate was cleaned with acetone and dried before use, the magnesium plate was polished with 400-mesh sandpaper prior to use. Starting materials that was commercially available were used as received, others were synthesized according to a reported procedure. Calcium granules were purchased from Alfa Aesar (41653, 9 mesh, 98.8% metals basis), and used as supplied. Chlorotrimethylsilane was purchased from Aladdin Chemicals and Energy Chemicals, and was distilled before use. Other chlorosilanes and reagents were purchased from Energy Chemicals, Aladdin Chemicals, Meryer Chemical Technology, and J&K Scientific, and were used as received.

All electrochemical reactions were carried out using an hspy-36-03 DC power supply. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were measured on an Agilent 400-MR (400 MHz), a Bruker Avance Neo 400 (400 MHz), or a Bruker Ascend 600 (600 MHz) spectrometer. Proton chemical shifts were expressed in parts per million δ (ppm) downfield from the residual signal of chloroform (7.26 ppm). Carbon chemical shifts were referenced to the carbon signal of the solvent ($CDCl_3$) at 77.0 ppm. Fluorine chemical shifts were referenced to the external fluorine signal of trifluoroacetic acid (CF_3CO_2H) at -76.50 ppm. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum Two FT-IR Spectrometer. Mass spectra were recorded on a SHIMADZU GCMS-QP2020 in electron ionization (EI) mode. High-resolution mass spectra were recorded on a Thermo Scientific QE plus or an Agilent 6546 LC/Q-TOF in electrospray ionization (ESI) mode. Melting points were taken on a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. Cyclic Voltammograms were measured with IKA ElectraSyn 2.0 pro package.

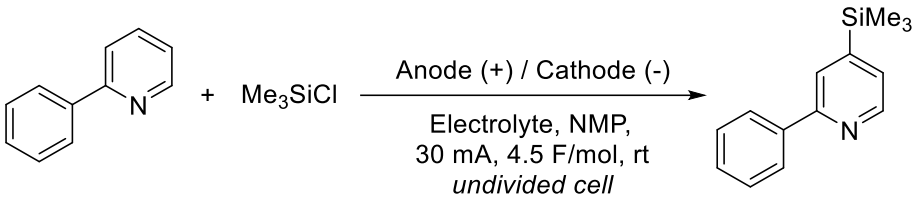
Table S1 Optimizing the conditions for electrochemical silylation of 2-phenylpyridine (1)



Entry	Current (mA)	Me_3SiCl (equiv.)	Solvents	Solvent volume (mL)/ Concentration (M)	Temperature (°C)	Isolated yield (%)
1	10	3	NMP	5/0.10	rt	41
2	20	3	NMP	5/0.10	rt	44
3	30	3	NMP	5/0.10	rt	57
4	40	3	NMP	5/0.10	rt	46
5	30	2	NMP	5/0.10	rt	26
6	30	4	NMP	5/0.10	rt	60
7	30	5	NMP	5/0.10	rt	**73**
8	30	6	NMP	5/0.10	rt	72
9	30	4	DMF	5/0.10	rt	trace
10	30	4	DMA	5/0.10	rt	62
11	30	4	DMI	5/0.10	rt	44
12	30	4	THF	5/0.10	rt	28
13	30	4	CH_3CN	5/0.10	rt	0
14	30	4	DMSO	5/0.10	rt	0
15	30	4	NMP	10/0.05	rt	47
16	30	4	NMP	3.3/0.15	rt	67
17	30	4	NMP	2.5/0.20	rt	53
18	30	4	NMP	5/0.10	50	67
19	30	4	NMP	5/0.10	0	58
20	30	4	NMP	5/0.10	−10	50

Reactions conditions: 2-phenylpyridine (0.5 mmol, 1 equiv.), chlorotrimethylsilane (2–6 equiv.), Mg (+) / Pt (−), *n*Bu_4NBr (0.03 M, 0.3 equiv.), 10–40 mA, 4.5 F/mol in solvent (2.5–10 mL), Ar, −10 °C to 50 °C. NMP = *N*-methylpyrrolidone; DMF = *N*,*N*-dimethylformamide; DMA = *N*,*N*-dimethylacetamide; DMI = 1,3-dimethyl-2-imidazolidinone.

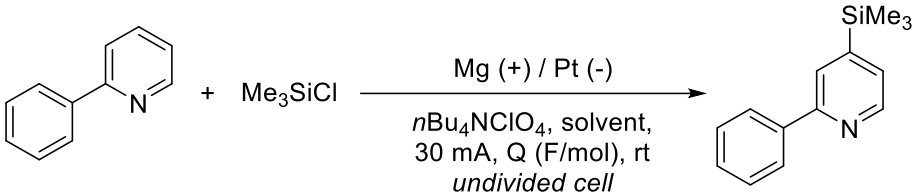
Table S2 Optimizing the conditions for electrochemical silylation of 2-phenylpyridine (2)



Entry	Electrolyte	Anode (+)	Cathode (−)	Isolated yield (%)
1	*n*Bu$_4$NBr	Mg	Pt	73
2	*n*Bu$_4$NI	Mg	Pt	67
3	*n*Bu$_4$NClO$_4$	Mg	Pt	**77**
4	*n*Bu$_4$NBF$_4$	Mg	Pt	55
5	*n*Bu$_4$NPF$_6$	Mg	Pt	59
6	*n*Bu$_4$NOTs	Mg	Pt	21
7	LiBr	Mg	Pt	49
8	*n*Bu$_4$NClO$_4$	Zn	Pt	42
9	*n*Bu$_4$NClO$_4$	Fe	Pt	10
10	*n*Bu$_4$NClO$_4$	Al	Pt	26
11	*n*Bu$_4$NClO$_4$	Mg	Graphite felt	38
12	*n*Bu$_4$NClO$_4$	Mg	Stainless steel	66
13	*n*Bu$_4$NClO$_4$	Mg	Ni	64
14	*n*Bu$_4$NClO$_4$	Mg	Ni foam	65
15	*n*Bu$_4$NClO$_4$	Mg	RVC	37
16	*n*Bu$_4$NClO$_4$	Mg	Graphite	42
17	*n*Bu$_4$NClO$_4$	Mg	Glassy carbon	33
18	*n*Bu$_4$NClO$_4$	Mg	Cu	42
19	*n*Bu$_4$NClO$_4$	Mg	Mo	trace
20	*n*Bu$_4$NClO$_4$	Pt	Pt	nr
21	*n*Bu$_4$NClO$_4$	Graphite felt	Graphite felt	nr

Reactions conditions: 2-phenylpyridine (0.5 mmol, 1 equiv.), chlorotrimethylsilane (5 equiv.), Anode (+) / Cathode (−), electrolyte (0.03 M, 0.3 equiv.), 30 mA, 4.5 F/mol, in NMP (5 mL, 0.1 M) at rt, Ar. nr = no reaction.

Table S3 Optimizing the conditions for electrochemical silylation of 2-phenylpyridine (3)



Entry	Solvent	Concentration of Electrolyte (M)	Q (mol/F)	Isolated yield (%)
1	NMP	0.03	4.5	77
2	THF	0.03	4.5	28
3	THF	0.30	4.5	77
4	NMP/THF = 9:1 (*v*/*v*)	0.03	4.5	77
5	NMP/THF = 4:1 (*v*/*v*)	0.03	4.5	82
6	NMP/THF = 2:1 (*v*/*v*)	0.03	4.5	**87**
7	NMP/THF = 1:1 (*v*/*v*)	0.03	4.5	81
8	NMP/THF = 1:1 (*v*/*v*)	0.03	4.5	74
9	NMP	0	4.5	70
10	THF	0	4.5	nr
11	NMP/THF = 2:1 (*v*/*v*)	0	4.5	81
12	NMP/THF = 2:1 (*v*/*v*)	0.03	0	nr
12	NMP/THF = 2:1 (*v*/*v*)	0.03	4.0	77
13	NMP/THF = 2:1 (*v*/*v*)	0.03	5.0	87
14	NMP/THF = 2:1 (*v*/*v*)	0.03	6.0	66

Reactions conditions: 2-phenylpyridine (0.5 mmol, 1 equiv.), chlorotrimethylsilane (5 equiv.), Mg (+) / Pt (−), *n*Bu_4NClO_4 (0–0.30 M), 30 mA, 0–6.0 F/mol, solvent (5 mL, 0.1 M) at rt, Ar. nr = no reaction.

Note:

In entry 9 and entry 11 of Table S3, the results indicated that when using NMP as solvent, the reaction could proceed without supporting electrolyte. This may be attributed to the formation of a soluble magnesium salt in the solvent, effectively acting as the electrolyte and facilitating a smooth reaction. In contrast, magnesium salt has very low solubility in THF solvent, resulting in no transformation of the starting materials (entry 10). For the cell potential during the reactions in entries 9–11 and the standard conditions (entry 6), refer to the following graph.

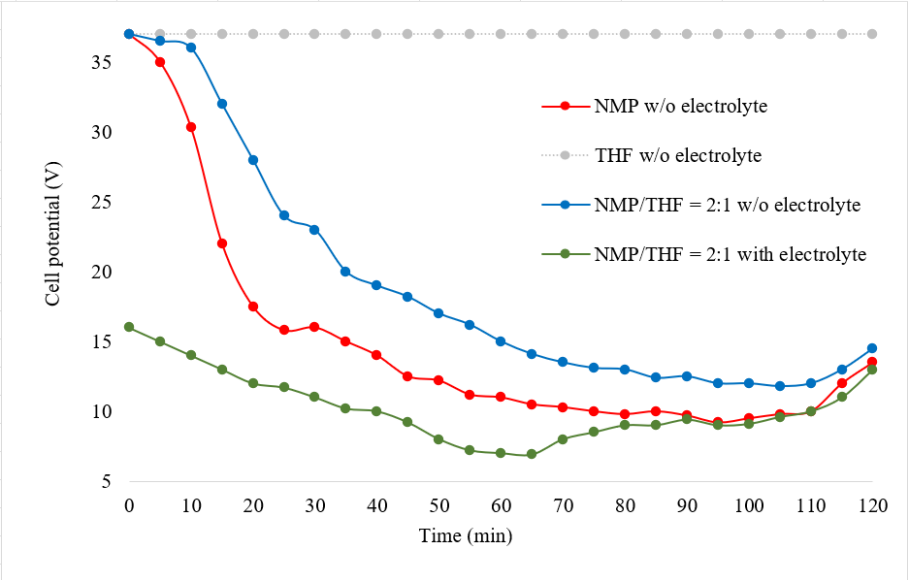
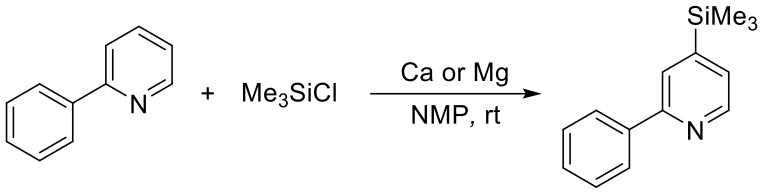


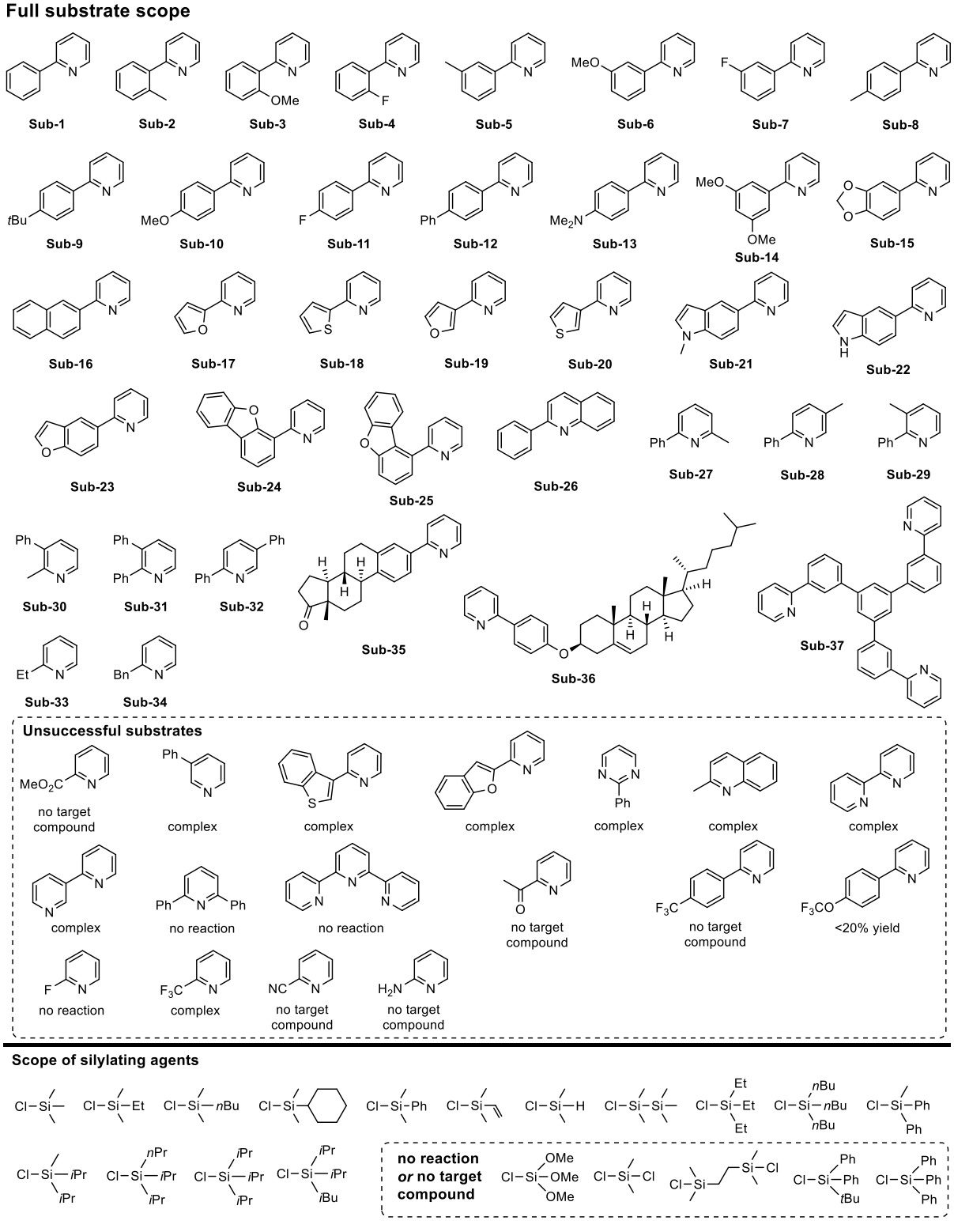
Figure S1 Cell potentials of entry 9, entry 10, entry 11 and entry 6

Table S4 Optimizing the conditions for Ca- or Mg-promoted silylation

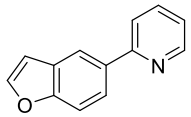


Entry	Reductant	Reductant (equiv.)	Me_3SiCl (equiv.)	Solvent	Isolated yield (%)
1	Ca	2	5	NMP	35
2	Ca	3	5	NMP	77
3	Ca	4	5	NMP	49
4	Ca	3	4	NMP	66
5	Ca	3	6	NMP	**80**
6	Ca	3	7	NMP	65
7	Ca	3	6	NMP/THF (2:1)	78
8	Mg	3	6	NMP	41

Reactions conditions: 2-phenylpyridine (0.5 mmol, 1 equiv.), reductant (2–4 equiv.) and chlorotrimethyl-silane (4–7 equiv.) in solvent (5 mL, 0.1 M) at rt, 18 h, Ar.

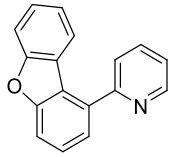


Scheme S1 Full scope of substrates scope and unsuccessful substrates. All substrates, except **Sub-23**, **Sub-25** and **Sub-36**, are known compounds and were synthesized according to the reported procedures[1-4] or directly purchased from chemical companies. All chlorosilanes are known compounds and were directly purchased from chemical companies or synthesized according to the reported procedures[5].



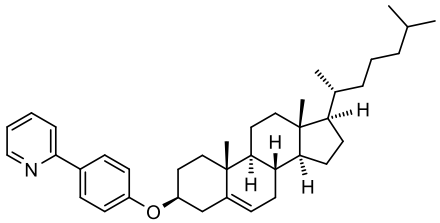
2-(Benzofuran-5-yl)pyridine (Sub-23)

90% yield (527 mg) in 3 mmol scale, synthesized from the Suzuki coupling of 2-bromopyridine with corresponding boronic acid pinacol ester,[1] colorless oil. Rf = 0.30 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.69 (d, *J* = 4.8 Hz, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.71-7.66 (m, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.18-7.15 (m, 1H), 6.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):157.5, 155.4, 149.4, 145.5, 136.6, 134.4, 127.8, 123.5, 121.6, 120.4, 119.8, 111.4, 106.9. IR (neat): (cm^{-1}) 3152, 3114, 3050, 2998, 2926, 2854, 1586, 1426, 1130. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{10}NO$ 196.0757, found 196.0756.



2-(Dibenzo[b,d]furan-1-yl)pyridine (Sub-25)

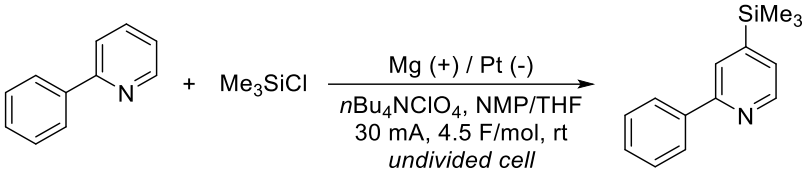
54% yield (400 mg) in 3 mmol scale, synthesized from the Suzuki coupling of 2-bromopyridine with corresponding boronic acid pinacol ester,[1] white viscous liquid. Rf = 0.30 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.87 (d, *J* = 4.9 Hz, 1H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.49-7.38 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.0, 156.6, 156.5, 149.4, 136.8, 136.2, 127.3, 127.0, 124.0, 123.8, 123.4, 123.3, 122.7, 122.3, 121.8, 111.7, 111.4. IR (neat): (cm^{-1}) 3052, 3008, 2927, 2849, 1580, 1449, 1410, 1239, 1195. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{12}NO$ 246.0913, found 246.0915.



2-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)phenyl)pyridine (Sub-36)

46% yield (749 mg) in 3 mmol scale, synthesized according to the reported procedure.[3] White solid, melting point 44-45 °C. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.71-7.65 (m, 2H), 7.16-7.15 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.41 (s, 1H), 4.22-4.17 (m, 1H), 2.54-2.51 (m, 1H), 2.42 (t, *J* = 11.4 Hz, 1H), 2.07-1.99 (m, 3H), 1.94-1.92 (m, 1H), 1.87-1.81 (m, 1H), 1.75-1.68 (m, 1H), 1.59-1.45 (m, 6H), 1.40-1.26 (m, 4H), 1.21-1.10 (m, 7H), 1.07 (s, 3H), 1.04-0.96 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 2.4 Hz, 3H), 0.87 (d, *J* = 2.4 Hz, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.6, 157.1, 149.5, 140.2, 136.6, 131.8, 128.1, 122.4, 121.3, 119.7, 115.9, 77.0, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 38.6, 37.1, 36.8, 36.2, 35.8, 31.9, 31.8, 28.21, 28.15, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.8. IR (KBr): (cm^{-1}) 3036, 2931, 2901, 2864, 1606, 1585, 1512, 1437, 1269, 1177. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{54}NO$ 540.4200, found 540.4198.

Electrochemical silylation of 2-phenylpyridine using undivided cell



In an oven-dried 10 mL Schlenk tube equipped with a magnesium plate (10×15×0.5 mm) as the anode and a platinum plate (10×15×0.2 mm) as the cathode under an argon atmosphere, nBu$_4$NClO$_4$ (0.03 M, 0.15 mmol, 0.3 equiv.), 2-phenylpyridine (0.5 mmol, 1 equiv.), and dry NMP/THF (5 mL in total, v/v = 2:1) were added. Then, chlorotrimethylsilane (2.5 mmol, 5 equiv.) was added to the mixture, and the reaction mixture was electrolyzed at a constant current of 30 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was quenched with 50 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, v/v = 5:1).

*For all other pyridine derivatives unless otherwise noted, the electrochemical silylation reactions were conducted under the above reaction conditions.

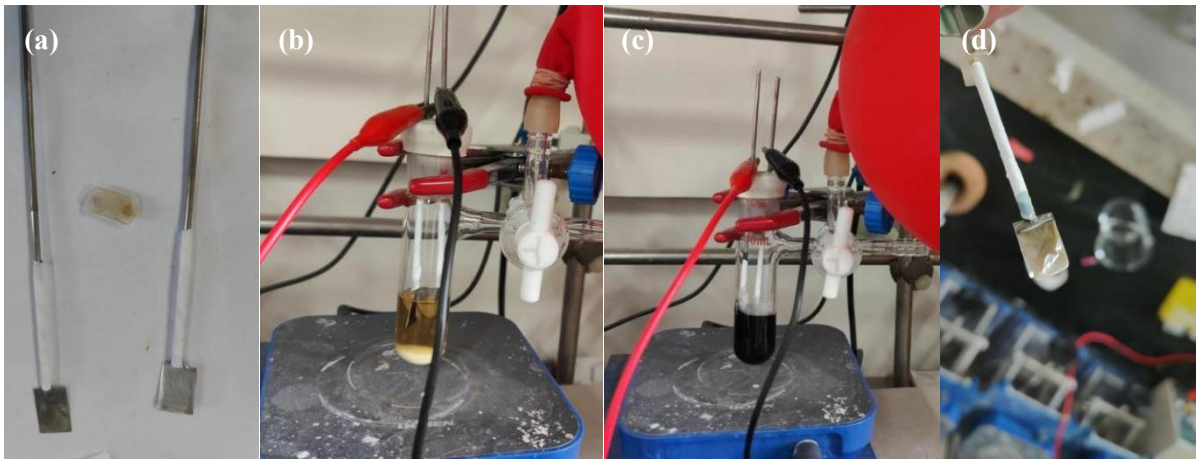
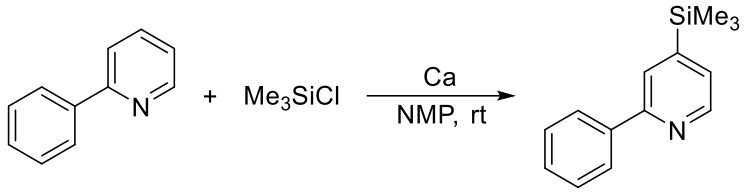


Figure S2 Reaction set-up for reaction using undivided cell. (a) Electrodes used in the reaction; (b) Before electrolysis; (c) After electrolysis; (d) Electrode after reaction.

Ca-promoted reductive silylation of 2-phenylpyridine



Under argon atmosphere, to a 50 mL three-necked flask, 9 mesh calcium granules (1.5 mmol, 3 equiv.), NMP (2.5 mL), chlorotrimethylsilane (3 mmol, 6 equiv.) were added in order. The mixture was stirred at room temperature for 0.5 h, and then to the resulting mixture was added dropwise 2-phenylpyridine (0.5 mmol) in NMP (2.5 mL) within 5 min. After the addition, the reaction mixture was stirred at room temperature until the consumption of starting materials (usually 18 h). The reaction mixture was quenched with 50 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 5:1).

*For all other pyridine derivatives unless otherwise noted, the calcium-promoted silylation reactions were conducted under the above reaction conditions.

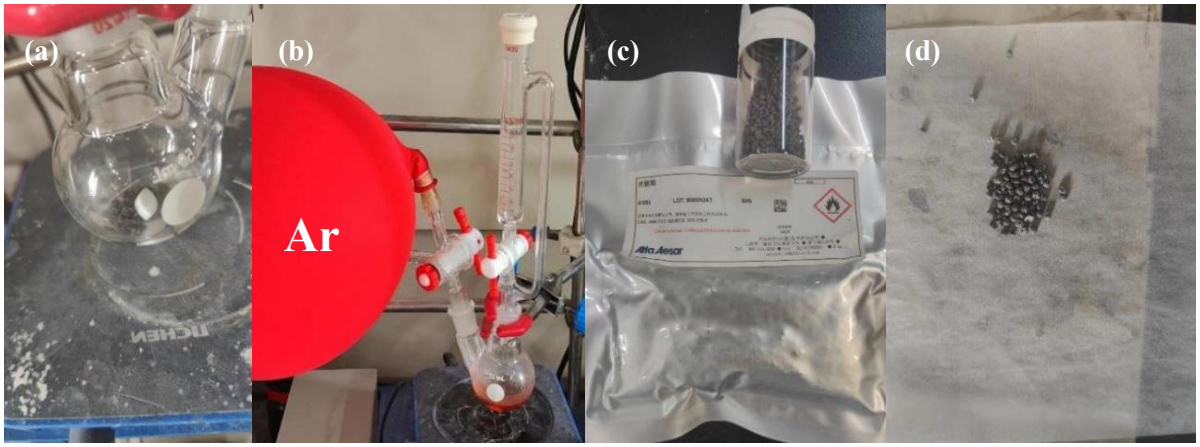
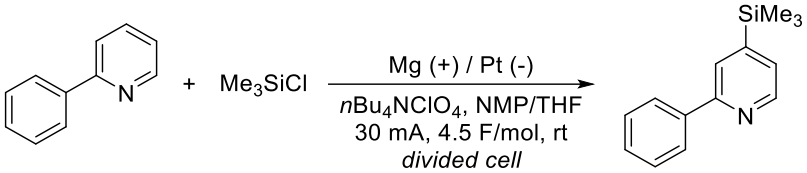


Figure S3 Reaction set-up for Ca-promoted reductive silylation. (a) Before calcium activation; (b) General reaction setup; (c) Commercially available calcium granules; (d) Calcium granules size ~ 2 mm.

Electrochemical silylation of 2-phenylpyridine using divided cell



In an oven-dried 15 mL divided electrochemical cell equipped with a magnesium plate (10×15×0.5 mm) as the anode and a platinum plate (10×15×0.2 mm) as the cathode under an argon atmosphere. nBu$_4$NClO$_4$ (0.3 M, 1.5 mmol, 1.5 equiv.), dry NMP/THF (5 mL in total, v/v = 2:1), and chlorotrimethylsilane (1 mmol, 1 equiv.) were added to the anode chamber in sequence; nBu$_4$NClO$_4$ (0.3 M, 1.5 mmol, 1.5 equiv.), 2-phenylpyridine (1 mmol, 1 equiv.), dry NMP/THF (5 mL in total, v/v = 2:1) and chlorotrimethylsilane (5 mmol, 5 equiv.) were added to the cathode chamber in sequence. The reaction mixture was electrolyzed at a constant current of 30 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was quenched with 50 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, v/v = 5:1).

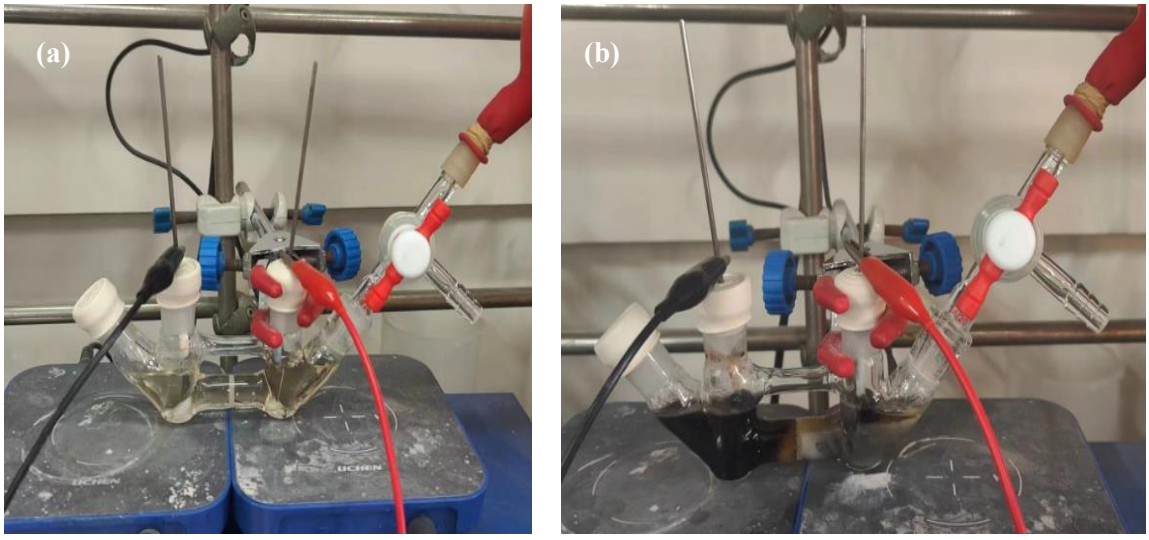
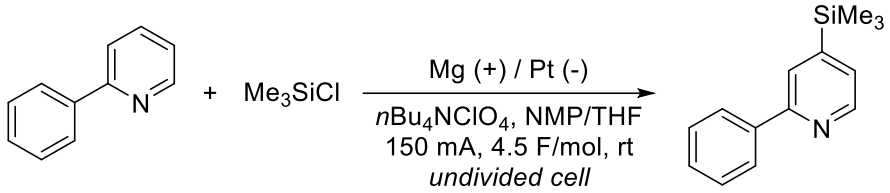


Figure S4 Reaction set-up for reaction using divided cell. (a) Before electrolysis; (b) After electrolysis.

Gram-scale reaction for electrochemical silylation of 2-phenylpyridine



10 mmol, 1.55 g

1.80 g

In an oven-dried 100 mL Schlenk flask, equipped with a magnesium plate (20×45×0.5 mm) as the anode and a platinum plate (20×45×0.1 mm) as the cathode under an argon atmosphere, nBu$_4$NClO$_4$ (0.03 M, 3 mmol, 0.3 equiv.), 2-phenylpyridine (10 mmol, 1 equiv.), and dry NMP/THF (100 mL in total, v/v = 2:1) were added. Then, chlorotrimethylsilane (50 mmol, 5 equiv.) was added to the mixture, and the reaction mixture was electrolyzed at a constant current of 150 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was quenched with 100 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (50 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE: AcOEt, v/v = 5:1) to give 1.80 g (79%) of product**.**

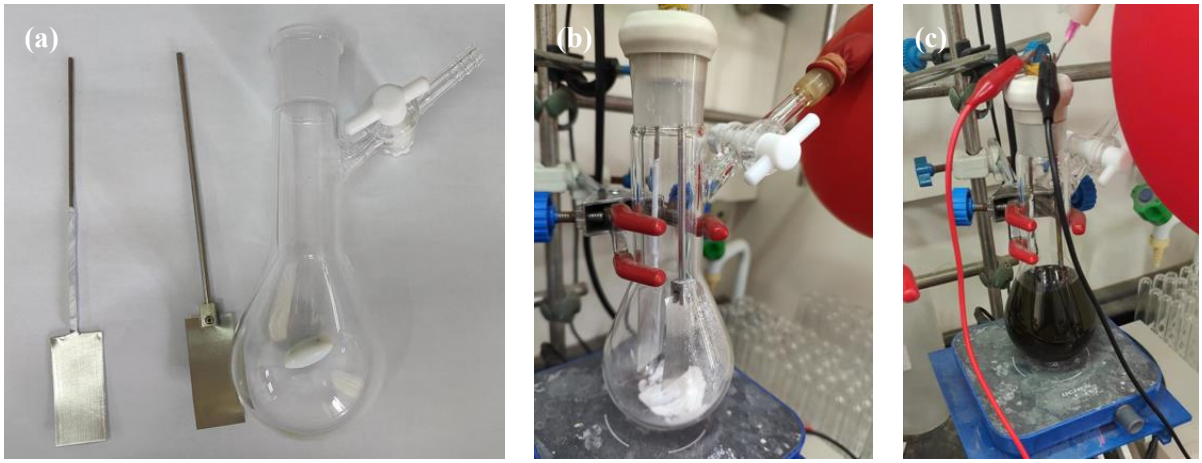
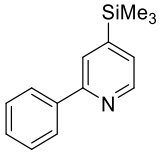
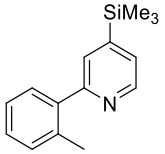


Figure S5 Reaction set-up for gram-scale reaction. (a) Electrodes (20×45 mm) and flask (100 mL); (b) Before electrolysis; (c) After electrolysis.



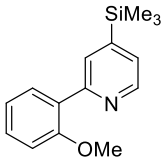
2-Phenyl-4-trimethylsilylpyridine (3)

Known compound.[6] 87% yield (99 mg) using electroreductive silylation; 80% yield (91 mg) using calcium-promoted silylation, colorless oil. Rf = 0.55 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.68 (d, *J* = 4.7 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.85 (s, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 4.7 Hz, 1H), 0.35 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.1, 150.8, 148.4, 139.7, 128.6, 128.5, 126.9, 126.4, 124.9, -1.8.



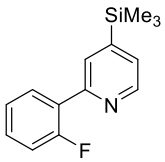
2-(2-Methylphenyl)-4-trimethylsilylpyridine (4)

62% yield (75 mg), colorless oil. Rf = 0.55 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.8 Hz, 1H), 7.52 (s, 1H), 7.43-7.41 (m, 1H), 7.36 (d, *J* = 4.8 Hz, 1H), 7.31-7.28 (m, 3H), 2.38 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.7, 150.4, 148.0, 140.7, 135.7, 130.6, 129.6, 128.4, 128.1, 125.9, 125.8, 20.2, -1.8. IR (neat): (cm^{-1}) 3064, 3024, 2955, 2923, 2899, 2853, 1583, 1524, 1363, 1249. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1362.



2-(2-Methoxyphenyl)-4-trimethylsilylpyridine (5)

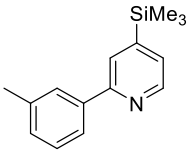
54% yield (70 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.8 Hz, 1H), 7.89 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 4.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.8, 154.9, 149.6, 148.2, 131.1, 129.7, 129.51, 129.48, 126.0, 121.0, 111.3, 55.6, -1.7. IR (neat): (cm^{-1}) 3053, 3030, 3000, 2955, 2902, 2836, 1600, 1524, 1493, 1367, 1244. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NOSi$ 258.1309, found 258.1311.



2-(2-Fluorophenyl)-4-trimethylsilylpyridine (6)

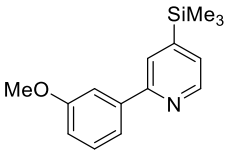
46% yield (56 mg) using electroreductive silylation; 40% yield (49 mg) using calcium-promoted silylation, colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.69 (d, *J* = 4.7 Hz, 1H), 7.92 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.86 (s, 1H), 7.39-7.34 (m, 2H), 7.26 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.16 (dd, *J* = 11.3 Hz, 7.8 Hz, 1H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3 (d, $^{1}J_{CF}$ = 249.4 Hz), 152.2, 150.8, 148.5, 131.1, 130.2 (d, $^{3}J_{CF}$ = 8.4 Hz), 128.9 (d, $^{3}J_{CF}$ = 8.4 Hz), 127.8

(d, $^{2}J_{CF}$ = 12.1 Hz), 126.8, 124.4, 116.1 (d, $^{2}J_{CF}$ = 22.9 Hz), -1.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -117.42. IR (neat): (cm^{-1}) 3091, 3040, 2956, 2902, 2850, 1587, 1450, 1370, 1250. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}FNSi$ 246.1109, found 246.1109.



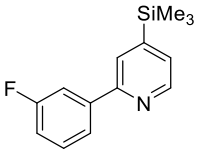
2-(3-Methylphenyl)-4-trimethylsilylpyridine (7)

80% yield (97 mg), colorless oil. Rf = 0.65 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 4.7 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 2.45 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.4, 151.0, 148.4, 139.7, 138.3, 129.5, 128.5, 127.7, 126.4, 125.1, 124.1, 21.5, -1.7. IR (neat): (cm^{-1}) 3053, 3034, 2954, 2922, 2898, 2856, 1580, 1524, 1462, 1357, 1250. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1360.



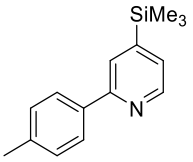
2-(3-Methoxyphenyl)-4-trimethylsilylpyridine (8)

75% yield (96 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.7 Hz, 1H), 7.81 (s, 1H), 7.58 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 4.7 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 3.89 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.0, 156.0, 151.0, 148.4, 141.3, 129.6, 126.7, 125.1, 119.4, 114.6, 112.2, 55.3, -1.8. IR (neat): (cm^{-1}) 3077, 2998, 2952, 2898, 2835, 1578, 1462, 1358, 1286, 1131. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NOSi$ 258.1309, found 258.1310.



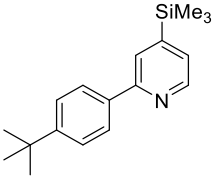
2-(3-Fluorophenyl)-4-trimethylsilylpyridine (9)

51% yield (62 mg) using electroreductive silylation; 46% yield (56 mg) using calcium-promoted silylation, colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.7 Hz, 1H), 7.79 (s, 1H), 7.78-7.70 (m, 2H), 7.44 (td, *J* = 8.0 Hz, 5.9 Hz, 1H), 7.37 (d, *J* = 4.7 Hz, 1H), 7.12-7.08 (m, 1H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.3 (d, $^{1}J_{CF}$ = 245.3 Hz), 154.9, 151.4, 148.5, 142.1 (d, $^{3}J_{CF}$= 7.4 Hz), 130.1 (d, $^{3}J_{CF}$ = 8.2 Hz), 127.1, 125.0, 122.5 (d, $^{4}J_{CF}$ = 2.8 Hz), 115.6 (d, $^{2}J_{CF}$ = 21.3 Hz), 114.0 (d, $^{2}J_{CF}$= 22.8 Hz), -1.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -113.01. IR (neat): (cm^{-1}) 3091, 3040, 2956, 2902, 2850, 1587, 1450, 1370, 1250, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}FNSi$ 246.1109, found 246.1110.



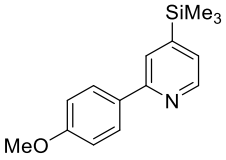
2-(4-Methylphenyl)-4-trimethylsilylpyridine (10)

84% yield (101 mg) using electroreductive silylation; 61% yield (74 mg) using calcium-promoted silylation, colorless oil. Rf = 0.55 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.64 (d, *J* = 4.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.79 (s, 1H), 7.32-7.28 (m, 3H), 2.41 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.3, 150.9, 149.1, 138.3, 136.4, 129.9, 126.9, 126.2, 124.8, 23.6, -1.7. IR (neat): (cm^{-1}) 3056, 3029, 2954, 2922, 2899, 2856, 1587, 1465, 1367. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1360.



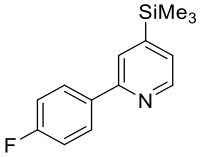
2-(4-(tert-Butyl)phenyl)-4-trimethylsilylpyridine (11)

92% yield (130 mg) using electroreductive silylation; 76% yield (108 mg) using calcium-promoted silylation, colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.82 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 4.7 Hz, 1H), 1.38 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.2, 151.8, 150.8, 148.4, 136.9, 126.7, 126.2, 125.6, 124.9, 34.6, 31.2, -1.7. IR (neat): (cm^{-1}) 3034, 2956, 2926, 2904, 2869, 1589, 1523, 1370, 1250, 1133. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NSi$ 284.1829, found 284.1833.



2-(4-Methoxyphenyl)-4-trimethylsilylpyridine (12)

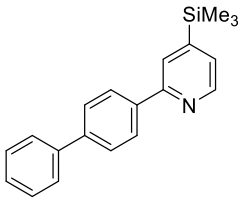
79% yield (102 mg) using electroreductive silylation; 62% yield (80 mg) using calcium-promoted silylation, colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 (d, *J* = 4.7 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 7.28 (d, *J* = 4.7 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 155.9, 150.8, 148.3, 132.4, 128.2, 125.8, 124.3, 114.0, 55.3, -1.7. IR (neat): (cm^{-1}) 3069, 3031, 3001, 2954, 2929, 2899, 2836, 1607,1587, 1512, 1247. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NOSi$ 258.1309, found 258.1311.



2-(4-Fluorophenyl)-4-trimethylsilylpyridine (13)

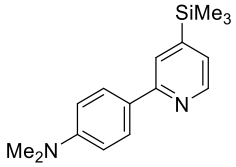
49% yield (60 mg) using electroreductive silylation; 64% yield (78 mg) using calcium-promoted silylation, colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (d, *J* = 4.7 Hz), 7.97 (dd, *J* = 8.4 Hz, 5.5 Hz, 2H), 7.76 (s, 1H), 7.33 (d, *J* = 4.7 Hz, 1H), 7.16 (dd, $J_1 = J_2$ = 8.4

Hz, 2H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.4 (d, $^1J_{CF}$ = 248.0 Hz), 155.3, 151.2, 148.5, 135.9 (d, $^4J_{CF}$ = 3.1 Hz), 128.8 (d, $^3J_{CF}$ = 8.4 Hz), 126.5, 124.7, 115.6 (d, $^2J_{CF}$ = 21.7 Hz), -1.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm): -113.43. IR (neat): (cm^{-1}) 3074, 3054, 3032, 2956, 2898,1602, 1510, 1366. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}FNSi$ 246.1109, found 246.1109.



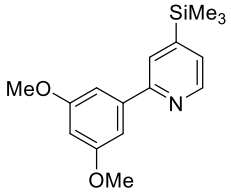
2-([1,1'-Biphenyl]-4-yl)-4-trimethylsilylpyridine (14)

52% yield (79 mg), pale yellow oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.71 (d, *J* = 4.7 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.41-7.37 (m, 2H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.8, 151.0, 148.5, 141.5, 140.6, 138.6, 128.8, 127.42, 127.37 (×2), 127.0, 126.6, 124.9, -1.7. IR (neat): (cm^{-1}) 3061, 3031, 2953, 2896, 1589, 1524, 1470, 1249, 1131. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NSi$ 304.1516, found 304.1518.



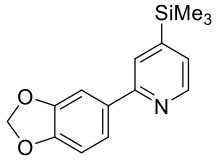
N,N-Dimethyl-4-(4-(trimethylsilyl)pyridin-2-yl)aniline (15)

70% yield (95 mg), yellow oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.76 (s, 1H), 7.22 (d, *J* = 4.7 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.01 (s, 6H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.2, 150.9, 150.5, 148.1, 127.7, 127.4, 125.0, 123.7, 112.2, 40.3, -1.7. IR (neat): (cm^{-1}) 3026, 2956, 2896, 2848, 2799, 1609, 1519, 1465, 1249, 1194. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2Si$ 271.1625, found 271.1627.



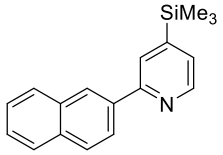
2-(3,5-Dimethoxyphenyl)-4-trimethylsilylpyridine (16)

61% yield (87 mg), colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (d, *J* = 4.7 Hz, 1H), 7.77 (s, 1H), 7.34 (d, *J* = 4.7 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 2H), 6.53 (t, *J* = 2.3 Hz, 1H), 3.87 (s, 6H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.0, 155.9, 151.1, 148.3, 142.0, 126.8, 125.3, 105.1, 100.9, 55.5, -1.7. IR (neat): (cm^{-1}) 3037, 3004, 2953, 2899, 2837, 1595, 1524, 1454, 1366, 1250, 1153. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}NO_2Si$ 288.1414, found 288.1417.



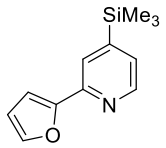
2-(Benzo[d][1,3]dioxol-5-yl)-4-trimethylsilylpyridine (17)

81% yield (110 mg), colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.59 (d, *J* = 4.7 Hz, 1H), 7.72 (s, 1H), 7.52-7.48 (m, 2H), 7.29 (d, *J* = 4.7 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.00 (s, 2H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.7, 151.1, 148.3, 148.24, 148.18, 134.1, 126.1, 124.5, 121.0, 108.4, 107.4, 101.2, -1.7. IR (neat): (cm^{-1}) 3085, 3029, 2956, 2888, 2780, 1583, 1491, 1469, 1248, 1037. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_2Si$ 272.1101, found 272.1102.



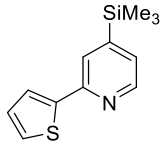
2-(2-Naphthalenyl)-4-trimethylsilylpyridine (18)

45% yield (62 mg), pale yellow oil. Rf = 0.55 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.74 (d, *J* = 4.7 Hz, 1H), 8.50 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.00-7.96 (m, 3H), 7.90-7.88 (m, 1H), 7.53-7.51 (m, 2H), 7.39 (d, *J* = 4.7 Hz, 1H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.1, 151.2, 148.6, 137.0, 133.49, 133.47, 128.6, 128.4, 127.6, 126.6, 126.4, 126.3, 126.2, 125.3, 124.7, -1.7. IR (neat): (cm^{-1}) 3061, 2956, 2926, 2850, 1584, 1524, 1378, 1249, 1134. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NSi$ 278.1360, found 278.1362.



2-(2-Furyl)-4-trimethylsilylpyridine (19)

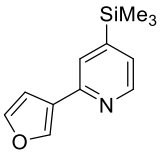
63% yield (68 mg), colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.53 (d, *J* = 4.7 Hz, 1H), 7.79 (s, 1H), 7.53 (s, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 4.7 Hz, 1H), 7.06 (d, *J* = 3.4 Hz, 1H), 6.52 (dd, *J* = 3.4, 1.8 Hz, 1H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 151.1, 148.3, 148.0, 143.1, 126.3, 122.8, 112.0, 108.5, -1.8. IR (neat): (cm^{-1}) 3129, 3107, 3064, 2956, 2896, 2853, 1599, 1492, 1354, 1247, 1162. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}NOSi$ 218.0996, found 218.0996.



2-(2-Thiophenyl)-4-trimethylsilylpyridine (20)

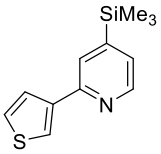
70% yield (82 mg) using electroreductive silylation; 59% yield (69 mg) using calcium-promoted silylation, colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.52 (d, *J* = 4.8 Hz, 1H), 7.74 (s, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.39 (d, *J* = 5.0 Hz, 1H), 7.24 (d, *J* = 4.8 Hz, 1H), 7.12 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.3, 151.0,

148.3, 145.1, 127.9, 127.4, 126.4, 124.3, 123.1, -1.8. IR (neat): (cm^{-1}) 3057, 3033, 2955, 2900, 2851, 1493, 1383, 1250. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}NSSi$ 234.0767, found 234.0767.



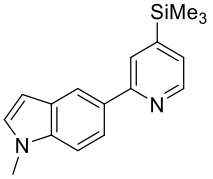
2-(3-Furyl)-4-trimethylsilylpyridine (21)

48% yield (52 mg). yellow oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (d, *J* = 4.7 Hz, 1H), 8.03 (s, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 4.7 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.0, 150.4, 148.3, 143.7, 141.1, 127.1, 126.2, 124.5, 108.6, -1.8. IR (neat): (cm^{-1}) 3029, 2959, 2921, 2902, 2853, 1602, 1493, 1340, 1250, 1162. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}NOSi$ 218.0996, found 218.0997.



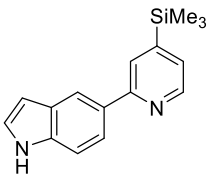
2-(3-Thiophenyl)-4-trimethylsilylpyridine (22)

58% yield (68 mg), pale yellow oil. Rf = 0.55 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.58 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 3.0 Hz, 1H), 7.71 (s, 1H), 7.68 (d, *J* = 5.1 Hz, 1H), 7.40 (dd, *J* = 5.1 Hz, 3.0 Hz, 1H), 7.27 (d, *J* = 4.8 Hz, 1H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.3, 151.0, 148.4, 142.4, 126.27, 126.26, 126.18, 124.7, 123.3, -1.7. IR (neat): (cm^{-1}) 3110, 3064, 3030, 2954, 2926, 2896, 2853, 1585, 1522, 1249. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}NSSi$ 234.0767, found 234.0766.



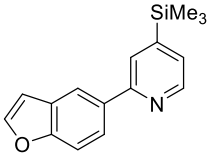
1-Methyl-5-(4-(trimethylsilyl)pyridin-2-yl)-1H-indole (23)

49% yield (69 mg), pale yellow oil. Rf = 0.40 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 8.25 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.89 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.30 (d, *J* = 4.7 Hz, 1H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.59 (d, *J* = 3.1 Hz, 1H), 3.82 (s, 3H), 0.35 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.4, 150.9, 148.1, 137.2, 131.2, 129.6, 128.8, 125.5, 125.0, 121.1, 119.8, 109.4, 101.8, 32.9, -1.7. IR (neat): (cm^{-1}) 3106, 3031, 2957, 2930, 2898, 2854, 1630, 1522, 1384, 1247, 1128. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}NSi$ 281.1469, found 281.1471.



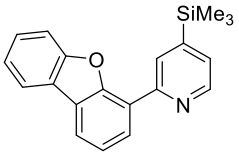
5-(4-(Trimethylsilyl)pyridin-2-yl)-1H-indole (24)

51% yield (68 mg), pale yellow solid, melting point 103-104 °C. Rf = 0.50 (PE/AcOEt = 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.95 (s, 1H), 8.69 (d, *J* = 4.7 Hz, 1H), 8.28 (s, 1H), 7.91 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 4.7 Hz, 1H), 7.19 (t, *J* = 2.7 Hz, 1H), 6.63 (t, *J* = 2.7 Hz, 1H), 0.36 (s, 9H).^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.7, 150.9, 148.2, 136.4, 131.7, 128.3, 125.6, 125.2 (×2), 121.4, 119.6, 111.4, 103.0, -1.7. IR (KBr): (cm^{-1}) 3179, 3032, 2953, 2854, 1588, 1451, 1376, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NSi$ 267.1312, found 267.1314.



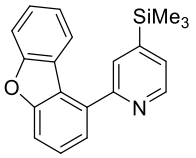
2-(Benzofuran-5-yl)-4-trimethylsilylpyridine (25)

58% yield (77 mg) using electroreductive silylation; 47% yield (63 mg) using calcium-promoted silylation, pale yellow oil. Rf = 0.40 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 8.23 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.86 (s, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 4.7 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.5, 155.4, 151.0, 148.4, 145.6, 135.0, 127.9, 126.1, 125.1, 123.7, 120.0, 111.4, 107.0, -1.7. IR (neat): (cm^{-1}) 3034, 2953, 2926, 2848, 1583, 1527, 1465, 1438, 1376, 1250, 1109. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NOSi$ 268.1152, found 268.1155.



2-(Dibenzo[b,d]furan-4-yl)-4-(trimethylsilyl)pyridine (26)

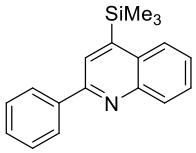
70% yield (111 mg) using electroreductive silylation; 69% yield (110 mg) using calcium-promoted silylation, white solid, melting point 102-103 °C. Rf = 0.30 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.78 (d, *J* = 4.7 Hz, 1H), 8.50 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.02-7.99 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.43 (d, *J* = 4.7 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 0.41 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.0, 153.6, 152.6, 150.9, 148.6, 128.7, 127.3, 127.1, 126.8, 125.0, 124.5, 123.9, 123.2, 122.8, 121.0, 120.6, 111.7, -1.7. IR (KBr): (cm^{-1}) 3018, 2956, 2926, 2850, 1578, 1483, 1451, 1366, 1248, 1190. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NOSi$ 318.1309, found 318.1311.



2-(Dibenzo[b,d]furan-1-yl)-4-(trimethylsilyl)pyridine (27)

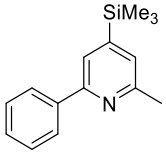
69% yield (110 mg), colorless oil. Rf = 0.40 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.81 (d, *J* = 4.8 Hz, 1H), 7.87 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.60-7.50 (m, 4H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 0.36 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.63, 156.59, 156.5, 151.2, 148.4, 136.7, 128.4, 127.3, 127.1, 127.0, 124.1, 123.5, 123.2, 122.2, 121.8, 111.6, 111.5, -1.7. IR (neat): (cm^{-1}) 3034, 2950, 2926, 2896, 2856, 1583, 1524, 1450, 1367, 1249, 1195.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NOSi$ 318.1309, found 318.1311.



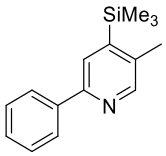
2-Phenyl-4-trimethylsilylquinoline (28)

Known compound.[7] 95% yield (132 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.57-7.53 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 1H), 0.54 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.0, 149.5, 147.5, 140.0, 130.8, 130.6, 129.2, 129.0, 128.8, 127.7, 127.6, 125.9, 125.5, -0.2.



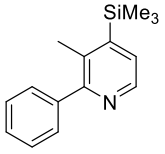
2-Methyl-6-phenyl-4-trimethylsilylpyridine (29)

Known compound.[8] 33% yield (40 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, *J* = 7.6 Hz, 2H), 7.61 (s, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.22 (s, 1H), 2.64 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.0, 155.9, 151.0, 140.1, 128.6, 128.5, 127.1, 126.1, 122.2, 24.6, -1.7.



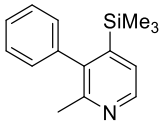
5-Methyl-2-phenyl-4-trimethylsilylpyridine (30)

71% yield (86 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.46 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.77 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.8, 149.7, 148.6, 139.7, 136.4, 128.6, 128.4, 126.7, 125.3, 19.4, -0.9. IR (neat): (cm^{-1}) 3063, 3028, 2957, 2925, 2898, 2854, 1588, 1469, 1339, 1250, 1083. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1361.



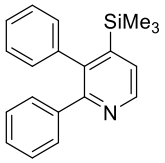
3-Methyl-2-phenyl-4-trimethylsilylpyridine (31)

61% yield (74 mg), colorless oil. Rf = 0.40 (PE/AcOEt = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.48 (d, *J* = 4.7 Hz, 1H), 7.49-7.42 (m, 4H), 7.40-7.36 (m, 1H), 7.32 (d, *J* = 4.7 Hz, 1H), 2.39 (s, 1H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.4, 149.6, 145.7, 141.3, 135.5, 129.0, 128.1, 127.6, 127.5, 20.5, -0.5. IR (neat): (cm^{-1}) 3063, 2953, 2930, 2897, 2859, 1521, 1432, 1247. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 241.1361.



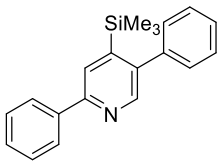
2-Methyl-3-phenyl-4-trimethylsilylpyridine (32)

39% yield (47 mg), yellow oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.46 (d, *J* = 4.9 Hz, 1H), 7.42-7.36 (m, 3H), 7.31 (d, *J* = 4.9 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 2.25 (s, 3H), -0.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.3, 148.7, 146.7, 142.5, 140.8, 129.6, 128.1, 127.5, 126.3, 23.6, -0.3. IR (neat): (cm^{-1}) 3061, 3031, 2953, 2926, 2899, 2853, 1567, 1387, 1248, 1180. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1361.



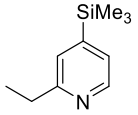
2,3-Diphenyl-4-trimethylsilylpyridine (33)

23% yield (35 mg), yellow oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.9 Hz, 1H), 7.50 (d, *J* = 4.9 Hz, 1H), 7.25-7.20 (m, 5H), 7.16-7.14 (m, 3H), 7.10-7.08 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.8, 150.2, 147.1, 141.8, 140.6, 140.5, 130.8, 129.7, 127.7, 127.6, 127.4, 127.3, 127.1, 0.0. IR (neat): (cm^{-1}) 3061, 3031, 2954, 2923, 2896, 2850, 1620, 1383, 1251, 1038. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NSi$ 304.1516, found 304.1518.



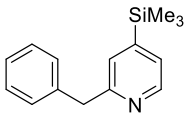
2,5-Diphenyl-4-trimethylsilylpyridine (34)

54% yield (82 mg) using electroreductive silylation; 39% yield (59 mg) using calcium-promoted silylation, yellow oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.93 (s, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.46-7.43 (m, 4H), 7.36-7.34 (m, 2H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.9, 149.0, 148.9, 142.4, 140.6, 139.5, 129.6, 128.8, 128.7, 128.0, 127.8, 127.0, 125.7, -0.1. IR (neat): (cm^{-1}) 3056, 3023, 2956, 2926, 2853, 1573, 1466, 1382, 1337, 1249, 1103. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NSi$ 304.1516, found 304.1517.



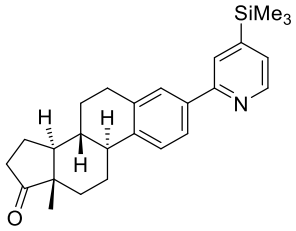
2-Ehyl-4-(trimethylsilyl)pyridine (35)

40% yield (36 mg), colorless oil. Rf = 0.50 (PE : AcOEt = 1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.47 (d, *J* = 4.8 Hz, 1H), 7.24 (s, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.27 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 162.1, 150.6, 148.0, 126.5, 125.3, 31.3, 14.0, -1.7. IR (neat): (cm^{-1}) 3050, 2941, 2892, 2865, 1578, 1463, 1253, 1081, 1052, 882, 734. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{18}NSi$ 180.1203, found 180.1214.



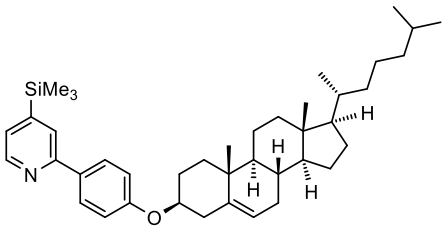
2-Benzyl-4-(trimethylsilyl)pyridine (36)

47% yield (57 mg), colorless oil. Rf = 0.40 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.48 (d, *J* = 4.8 Hz, 1H), 7.28-7.25 (m, 4H), 7.23 (s, 1H), 7.19-7.17 (m, 2H), 4.12 (s, 2H), 0.22 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 159.4, 150.9, 148.2, 139.7, 129.0, 128.5, 127.5, 126.2, 125.6, 44.6, -1.8. IR (neat): (cm^{-1}) 3067, 3046, 3032, 2955, 2920, 2857, 1586, 1428, 1111, 838. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1377.



(8R,9S,13S,14S)-13-Methyl-3-(4-(trimethylsilyl)pyridin-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (37)

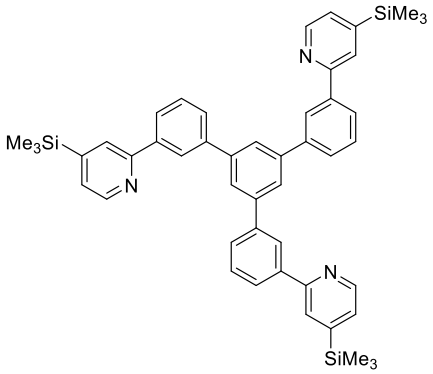
64% yield (129 mg), white solid, melting point 142-143 °C. Rf = 0.60 (PE/AcOEt = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (d, *J* = 4.7 Hz, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 4.7 Hz, 1H), 3.02-2.97 (m, 2H), 2.54-2.45 (m, 2H), 2.39-2.33 (m, 1H), 2.19-1.97 (m, 4H), 1.69-1.48 (m, 6H), 0.92 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 220.8, 156.1, 150.9, 148.4, 140.5, 137.3, 136.9, 127.5, 126.3, 125.7, 124.8, 124.3, 50.5, 47.9, 44.4, 38.0, 35.8, 31.5, 29.4, 26.5, 25.7, 21.5, 13.8, -1.7. IR (KBr): (cm^{-1}) 3031, 2953, 2926, 2867, 1739, 1586, 1411, 1373, 1249, 1229. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{34}NOSi$ 404.2404, found 404.2408.



2-(4-(((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)phenyl)-4-(trimethylsilyl)pyridine (38)

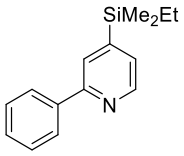
75% yield (228 mg), white solid, melting point 44-45 °C. Rf = 0.50 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 7.26 (d, *J* = 4.7 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.41-5.40 (m, 1H), 4.23-4.15 (m, 1H), 2.56-2.51 (m, 1H), 2.45-2.38 (m, 1H), 2.08-1.98 (m, 3H), 1.94-1.91 (m, 1H), 1.87-1.80 (m, 1H), 1.75-1.67 (m, 1H), 1.60-1.46 (m, 6H), 1.43 (s, 1H), 1.38-1.31 (m, 3H), 1.22-1.09 (m, 7H), 1.07 (s, 3H), 1.04-0.98 (m, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.88 (dd, *J* = 1.8 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.69 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.4, 155.9, 150.6, 148.3, 140.1, 132.2, 128.2, 125.7, 124.2, 122.3, 115.9, 76.9, 56.7, 56.1, 50.1, 42.2, 39.7, 39.5, 38.6, 37.1, 36.8, 36.1, 35.7, 31.9, 31.8, 28.2, 28.1, 28.0, 24.2,

23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8, -1.7. IR (KBr): (cm^{-1}) 3054, 2936, 2909, 2864, 2849, 1608, 1510, 1465, 1367, 1245, 1133. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{62}NOSi$ 612.4595, found 612.4602.



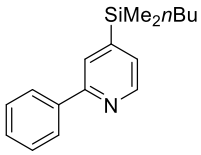
2,2'-(5'-(3-(4-(Trimethylsilyl)pyridin-2-yl)phenyl)-[1,1':3',1''-terphenyl]-3,3''-diyl)bis(4-trimethyl silylpyridine) (39)

56% yield (210 mg), colorless solid, melting point 78-79 °C. Rf = 0.70 (PE/AcOEt = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.69 (d, *J* = 4.7 Hz, 3H), 8.33 (s, 3H), 8.00-7.98 (m, 6H), 7.88 (s, 3H), 7.79 (d, *J* = 7.7 Hz, 3H), 7.62 (t, *J* = 7.7 Hz, 3H), 7.38 (d, *J* = 4.7 Hz, 3H), 0.34 (s, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.1, 151.4, 148.4, 142.4, 141.7, 140.4, 129.2, 128.0, 126.8, 126.33, 126.32, 125.7, 125.4, -1.7. IR (neat): (cm^{-1}) 3064, 3034, 2953, 2896, 2867, 1578, 1352, 1248, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{48}H_{52}N_3Si_3$ 754.3464, found 754.3391.



4-Ethyldimethylsilyl-2-phenylpyridine (40)

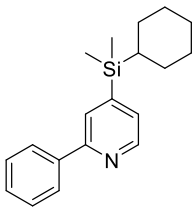
77% yield (93 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.83 (s, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 4.8 Hz, 1H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.80 (q, *J* = 7.6 Hz, 2H), 0.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.2, 150.1, 148.4, 139.7, 128.7, 128.6, 127.0, 126.8, 125.3, 7.2, 6.8, -4.1. IR (neat): (cm^{-1}) 3064, 3029, 2956, 2915, 2872, 1588, 1524, 1444, 1369, 1249, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NSi$ 242.1360, found 242.1362.



4-Butyldimethylsilyl-2-phenylpyridine (41)

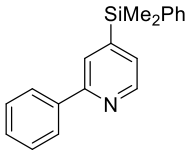
57% yield (77 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.81 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 4.7 Hz, 1H), 1.36-1.31 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 2H), 0.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.2, 150.5, 148.4, 139.8, 128.73, 128.67, 127.0, 126.8, 125.3, 26.4, 25.9, 14.7, 13.7, -3.6. IR (neat): (cm^{-1}) 3037, 2955, 2920, 2869, 2850, 1589, 1578,

1524, 1369, 1249, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NSi$ 270.1673, found 270.1675.



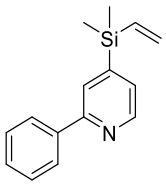
4-Cyclohexyldimethylsilyl-2-phenylpyridine (42)

60% yield (88 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.1 Hz, 2H), 7.78 (s, 1H), 7.49 (t, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 4.7 Hz, 1H), 1.74-1.67 (m, 5H), 1.26-1.05 (m, 6H), 0.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.0, 149.7, 148.2, 139.7, 128.8, 128.7, 127.3, 127.1, 125.8, 27.9, 27.2, 26.7, 25.2, -5.7. IR (neat): (cm^{-1}) 3058, 3952, 3918, 2843, 1605, 1445, 1368, 1248, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}NSi$ 296.1829, found 296.1830.



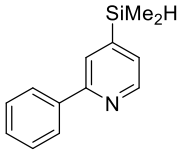
4-Dimethylphenylsilyl-2-phenylpyridine (43)

68% yield (98 mg), colorless oil. Rf = 0.45 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.71 (d, *J* = 4.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.88 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.46-7.42 (m, 4H), 7.38 (d, *J* = 4.7 Hz, 1H), 0.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.3, 149.1, 148.5, 139.6, 136.2, 134.0, 129.6, 128.8, 128.6, 128.0, 127.2, 127.0, 125.7, -3.0. IR (neat): (cm^{-1}) 3063, 3029, 2915, 2872, 1589, 1524, 1446, 1369, 1249, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NSi$ 290.1360, found 290.1361.



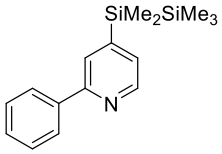
4-Dimethylvinylsilyl-2-phenylpyridine (44)

43% yield (51 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.8 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 4.8, 1H), 6.29 (dd, *J* = 20.1, 14.6 Hz, 1H), 6.14 (dd, *J* = 14.6, 3.7 Hz, 1H), 5.83 (dd, *J* = 20.1, 3.7 Hz, 1H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.3, 149.2, 148.5, 139.7, 136.1, 134.2, 128.8, 128.7, 127.02, 126.96, 125.5, -3.5. IR (neat): (cm^{-1}) 3048, 3031, 2956, 2926, 2848, 1589, 1524, 1446, 1340, 1250, 1132. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NSi$ 240.1203, found 240.1206.



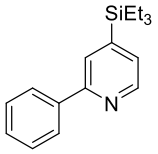
4-Dimethylsilyl-2-phenylpyridine (45)

55% yield (59 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.86 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 4.7 Hz, 1H), 4.47 (hept, *J* = 3.8 Hz, 1H), 0.42 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.3, 148.4, 148.2, 139.5, 128.9, 128.7, 127.1, 127.0, 125.8, -4.5. IR (neat): (cm^{-1}) 3061, 3056, 3002, 3029, 2961, 2129, 1589, 1429, 1369, 1109. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NSi$ 214.1047, found 214.1047.



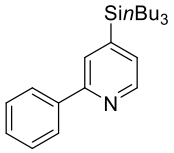
4-(1,1,2,2,2-Pentamethyldisilaneyl)-2-phenylpyridine (46)

79% yield (113 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.64 (d, *J* = 4.8 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.77 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 4.8 Hz, 1H), 0.41 (s, 6H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.0, 151.0, 148.3, 139.8, 128.7, 128.6, 127.0 (×2), 125.4, -2.5, -4.8. IR (neat): (cm^{-1}) 3069, 3034, 2953, 2853, 1605, 1585, 1368. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}NSi_2$ 286.1442, found 286.1444.



2-Phenyl-4-triethylsilylpyridine (47)

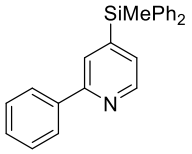
Known compound.[4] 70% yield (94 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.81 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 4.7 Hz, 1H), 1.01 (t, *J* = 7.7 Hz, 9H), 0.86 (q, *J* = 7.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.1, 148.4, 148.3, 139.8, 128.7, 128.6, 127.4, 127.0, 125.9, 7.2, 2.8.



2-Phenyl-4-(tributylsilyl)pyridine (48)

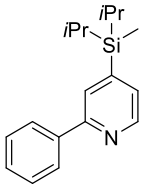
63% yield (111 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J* = 4.6 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.80 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 4.6 Hz, 1H), 1.39-1.30 (m, 12H), 0.90 (t, *J* = 7.2 Hz, 9H), 0.87-0.84 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.1, 149.2, 148.4, 139.9, 128.71, 128.68, 127.4, 127.0, 125.8, 26.6, 25.9, 13.7, 11.6. IR (neat): (cm^{-1}) 3069, 2954, 2941, 2893, 2864, 1577, 1428, 1252, 1111, 1053, 882,

775, 728, 697. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{36}NSi$ 354.2612, found 354.2593.



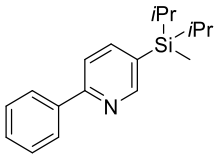
4-(Methyldiphenylsilyl)-2-phenylpyridine (49)

55% yield (97 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.70 (d, *J* = 4.5 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.86 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 4H), 7.47-7.41 (m, 9H), 7.35 (d, *J* = 4.5 Hz, 1H), 0.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.4, 148.7, 147.2, 139.6, 135.2, 134.3, 129.9, 128.8, 128.7, 128.2, 128.1, 127.0, 126.6, -3.9. IR (neat): (cm^{-1}) 3068, 3048, 2956, 2923, 2853, 1586, 1428, 1111, 791, 775, 728. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}NSi$ 352.1516, found 352.1539.



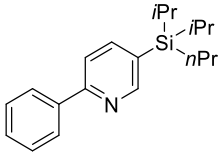
4-(Diisopropylmethylsilyl)-2-phenylpyridine (50-C4)

25% yield (36 mg), colorless oil. Rf = 0.60 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.7 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.77 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 4.7 Hz, 1H), 1.27-1.20 (m, 2H), 1.03 (d, *J* = 7.2 Hz, 6H), 0.97 (d, *J* = 7.2 Hz, 6H), 0.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 156.1, 148.3, 147.5, 139.9, 128.8, 128.7, 127.9, 127.1, 126.4, 17.8, 17.5, 11.1, -10.8. IR (neat): (cm^{-1}) 3068, 3051, 2941, 2896, 2864, 1587, 1524, 1428, 1251, 1111, 775, 729, 697. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NSi$ 284.1829, found 284.1847.



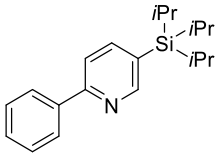
5-(Diisopropylmethylsilyl)-2-phenylpyridine (50-C5)

19% yield (27 mg), colorless oil. Rf = 0.65 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.74 (s, 1H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.83 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 1.26-1.19 (m, 2H), 1.03 (d, *J* = 7.3 Hz, 6H), 0.97 (d, *J* = 7.3 Hz, 6H), 0.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.3, 154.9, 143.2, 139.3, 129.4, 129.0, 128.7, 126.8, 119.7, 17.8, 17.5, 11.2, -10.5. IR (neat): (cm^{-1}) 3068, 2958, 2941, 2895, 2863, 1577, 1428, 1252, 1111, 1054, 774, 728, 697. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NSi$ 284.1829, found 284.1848.



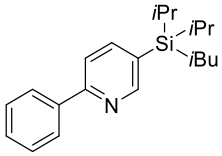
5-(Diisopropylpropylsilyl)-2-phenylpyridine (51)

40% yield (63 mg), colorless oil. Rf = 0.70 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.76 (s, 1H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.84 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 1.51-1.45 (m, 2H), 1.32-1.27 (m, 2H), 1.07 (d, *J* = 7.5 Hz, 6H), 1.034 (t, *J* = 7.5 Hz, 3H), 1.028 (d, *J* = 7.5 Hz, 6H), 0.95-0.93 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.1, 155.1, 143.4, 139.3, 129.0 (×2), 128.7, 126.8, 119.7, 19.0, 18.1, 18.0, 17.8, 12.0, 10.9. IR (neat): (cm^{-1}) 3068, 3053, 3027, 2955, 2935, 2863, 1586, 1428, 1251, 1111, 729, 697. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}NSi$ 312.2142, found 312.2168.



2-Phenyl-5-triisopropylsilylpyridine (52)

Known compound.[9] 45% yield (70 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.77 (dd, *J* = 1.9, 1.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.86 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.74 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 1.45 (hept, *J* = 7.5 Hz, 3H), 1.11 (d, *J* = 7.5 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.0, 155.3, 143.8, 139.2, 129.0, 128.7, 128.1, 126.8, 119.7, 18.4, 10.6.



5-(Isobutyldiisopropylsilyl)-2-phenylpyridine (53)

23% yield (37 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 1.98-1.92 (m, 1H), 1.37-1.30 (m, 2H), 1.09 (d, *J* = 7.7 Hz, 6H), 1.05 (d, *J* = 7.7 Hz, 6H), 0.98 (d, *J* = 7.7 Hz, 6H), 0.96 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 157.2, 155.2, 143.4, 139.5, 129.5, 129.0, 128.7, 126.9, 119.5, 26.8, 24.7, 20.4, 18.2, 18.1, 11.5. IR (neat): (cm^{-1}) 3053, 2954, 2930, 2898, 2864, 1582, 1444, 1249, 1039, 843, 813. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{32}NSi$ 326.2299, found 326.2322.

Cyclic voltammetry studies

The cyclic voltammogram were recorded on an IKA ElectraSyn 2.0 pro. The measurement cell equipped with a 3 mm glassy carbon disk as the working electrode, a platinum coated plate as the counter electrode, and an Ag/AgCl reference electrode was used. The results were recorded using NMP (5 mL) as solvent, nBu$_4$NClO$_4$ (0.10 M) as the supporting electrolyte. The results were recorded under ambient air conditions at room temperature, sweeping reductively from the initial potential of 0 V to the final potential of -3.00 V in the scan rate of 200 mVs^{-1}. Prior to use, the solvent NMP was deoxygenated by nitrogen bubbling for 0.5 h. And the glassy carbon working electrode was polished with alumina powder before use. The reduction potentials of some representative substrates (10 mM concentration) are shown below.

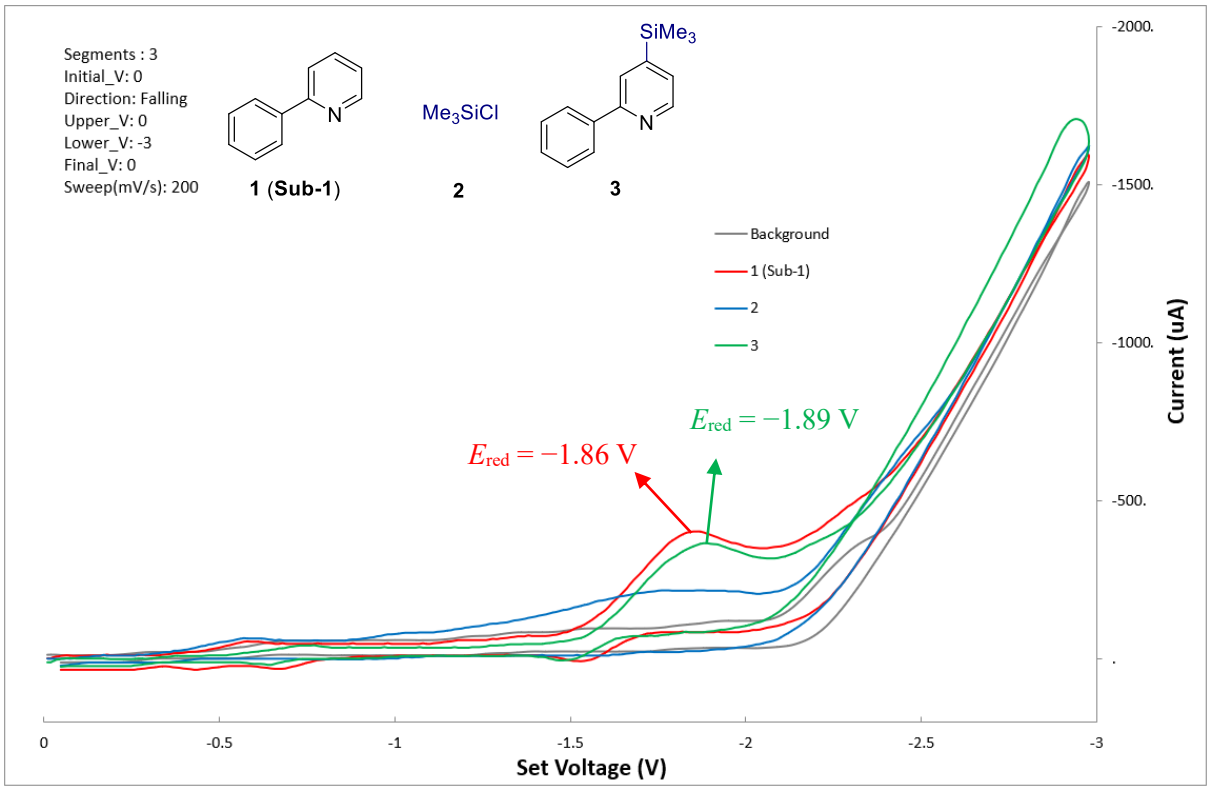


Figure S6 Cyclic voltammogram of the **1** (**sub-1**), **2** and **3**. The reduction peak (E_{red}) of **1** was observed at −1.86 V; No significant reduction peak (E_{red}) of **2** was observed ranging from 0 to −3.00 V; The reduction peak (E_{red}) of **3** was observed at −1.89 V.

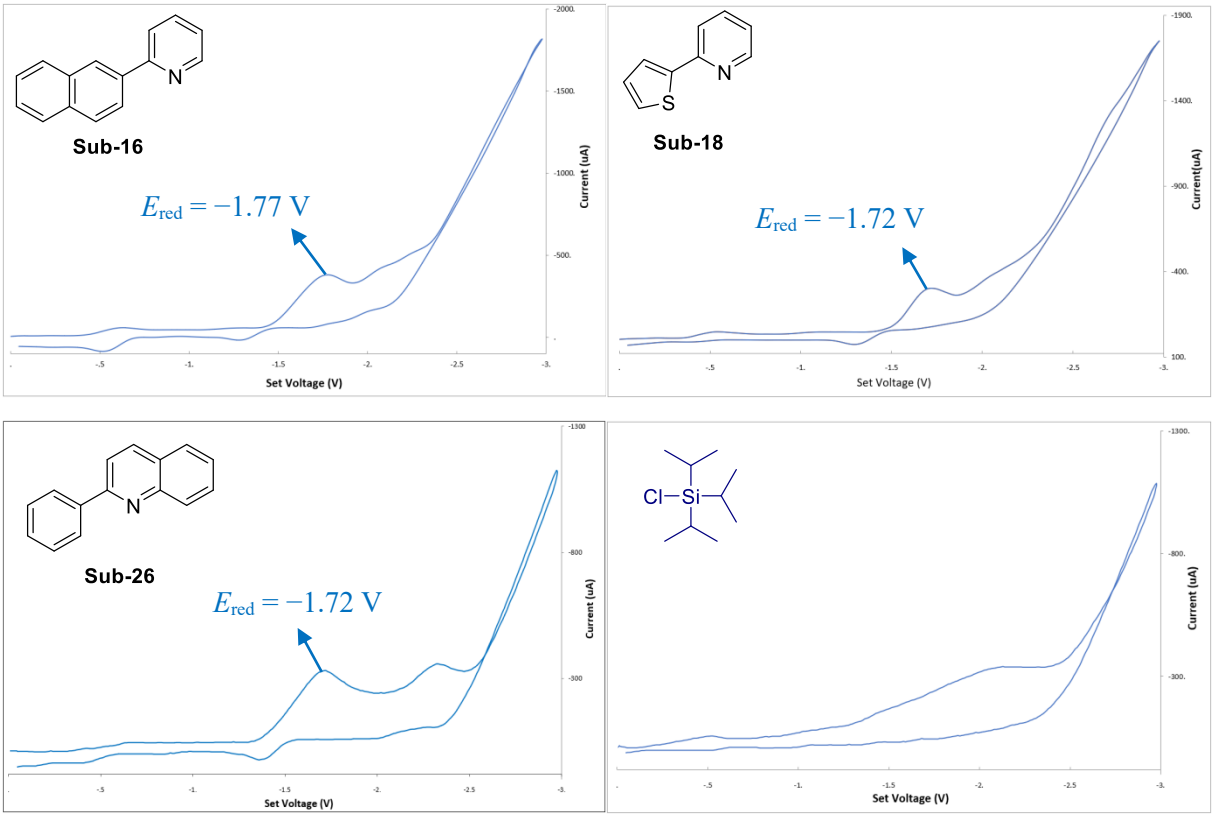
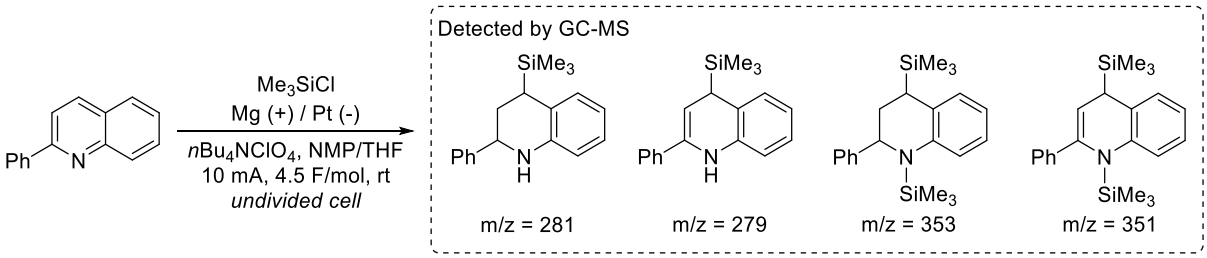
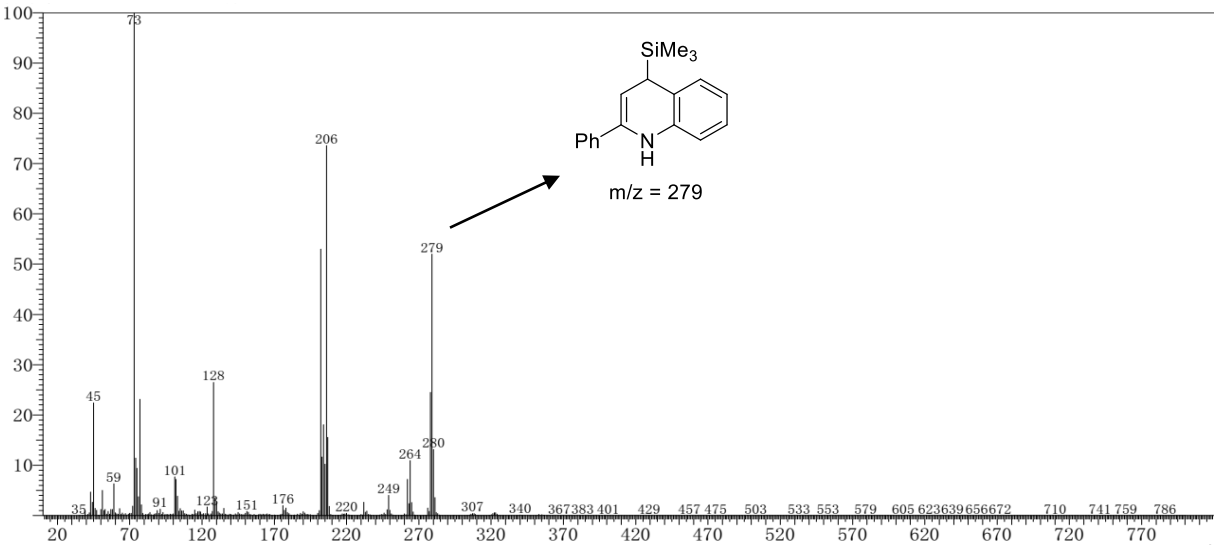


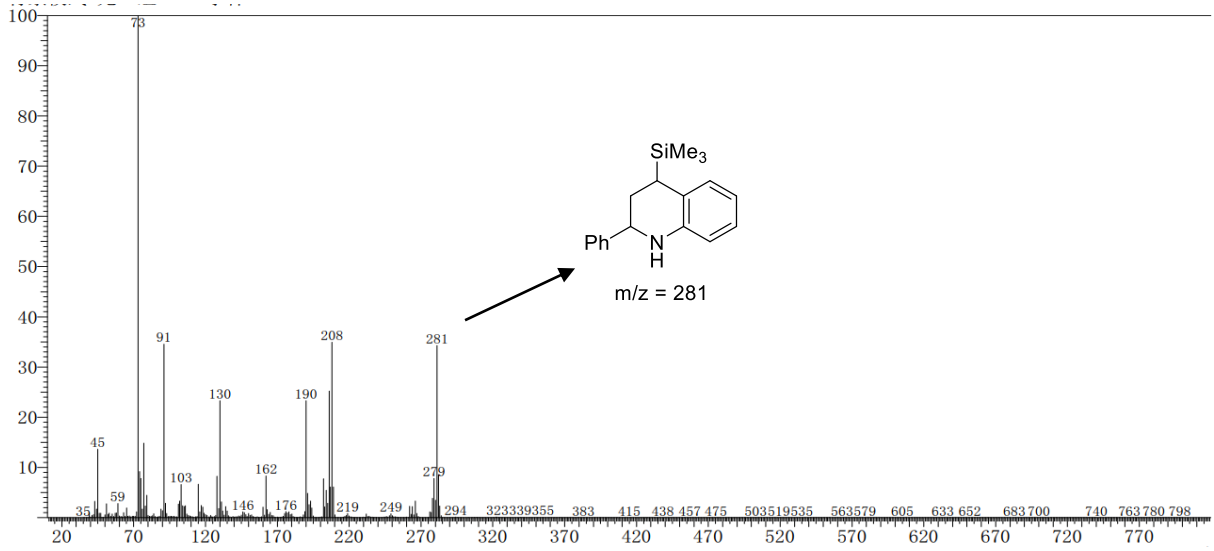
Figure S7 Cyclic voltammogram of the **Sub-16**, **Sub-18**, **Sub-26**, and chlorotriisopropylsilane. The reduction peak (E_{red}) of **Sub-16**, **Sub-18**, and **Sub-26** were observed at −1.77 V, −1.72 V, and −1.72 V, respectively.

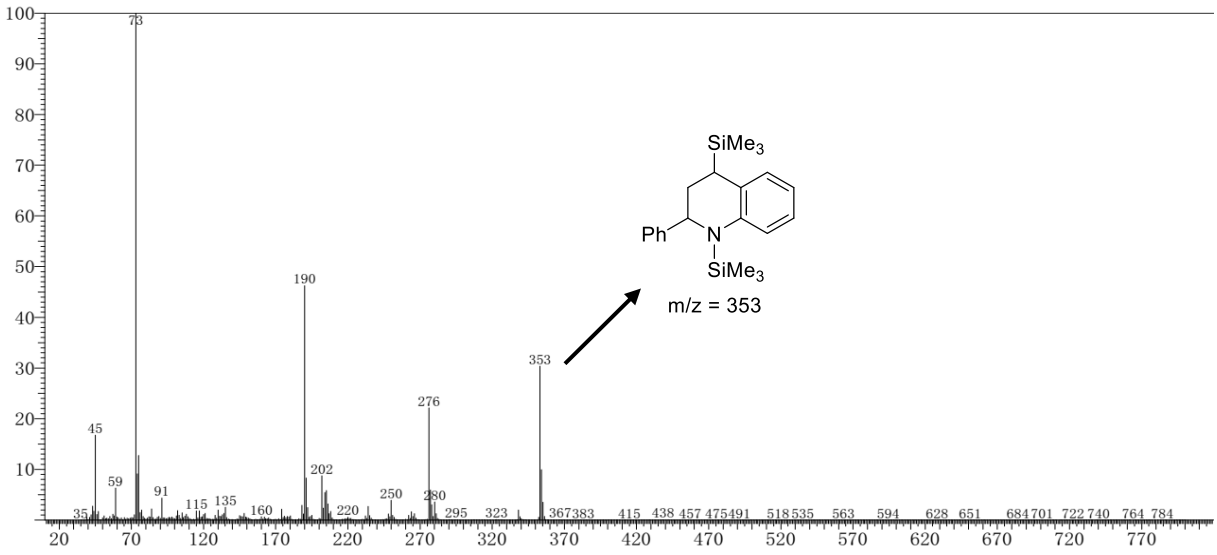
Detection of intermediates by GC-MS

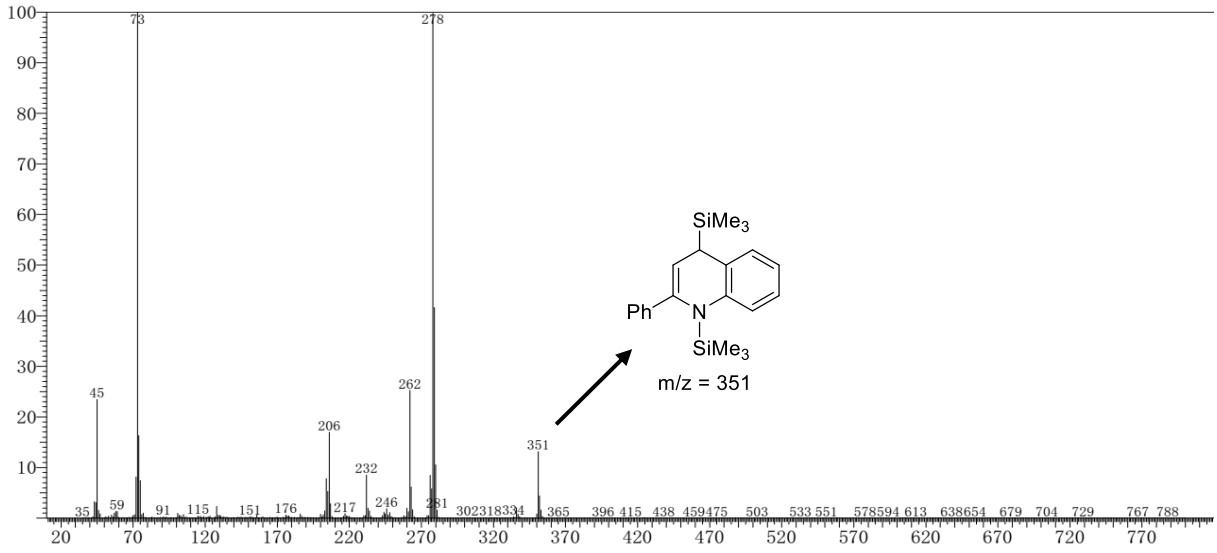


In an oven-dried 10 mL Schlenk tube equipped with a magnesium plate (10×15×0.5 mm) as the anode and a platinum plate (10×15×0.2 mm) as the cathode under an argon atmosphere, nBu$_4$NClO$_4$ (0.03 M, 0.15 mmol, 0.3 equiv.), 2-phenylquinoline (0.5 mmol, 1 equiv.), and dry NMP/THF (5 mL in total, v/v = 2:1) were added. Then, chlorotrimethylsilane (2.5 mmol, 5 equiv.) was added to the mixture, and the reaction mixture was electrolyzed at a constant current of 10 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was poured into a beaker containing a mixture of saturated sodium bicarbonate (50 mL) and ethyl acetate (20 mL), the organic phase was directly submitted to GC-MS analysis.

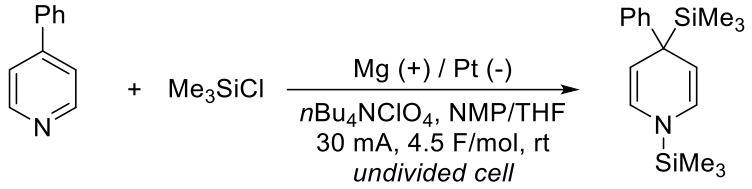




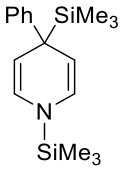

SiMe3
Ph
N
SiMe3
m/z = 353


SiMe3
Ph
N
SiMe3
m/z = 351

General procedure for silylation of 4-phenylpyridine



In an oven-dried 10 mL Schlenk tube equipped with a magnesium plate (10×15×0.5 mm) as the anode and a platinum plate (10×15×0.2 mm) as the cathode under an argon atmosphere, nBu$_4$NClO$_4$ (0.03 M, 0.15 mmol, 0.3 equiv.), 4-phenylpyridine (0.5 mmol, 1 equiv.), and dry NMP/THF (5 mL in total, *v*/*v* = 2:1) were added. Then, chlorotrimethylsilane (2.5 mmol, 5 equiv.) was added to the mixture, and the reaction mixture was electrolyzed at a constant current of 30 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was quenched with 50 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 10:1).

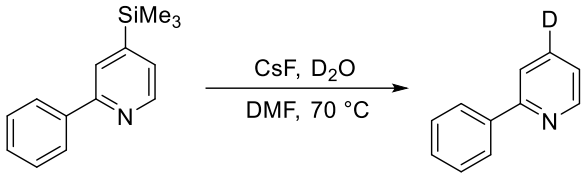


4-Phenyl-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (55)

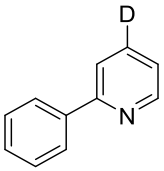
70% yield (105 mg), colorless oil. Rf = 0.80 (PE/AcOEt = 10:1). The targeted compound decomposed quickly and transformed into 4-phenylpyridine after 2 h of exposure to air. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.33 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 5.96 (d, *J* = 8.4 Hz, 2H), 4.76 (d, *J* = 8.4 Hz, 2H), 0.20 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (151 MHz, CDCl$_3$) δ (ppm): 149.1, 128.1, 126.8, 125.4, 124.2, 103.3, 35.3, -1.2, -4.6.

Derivatization reactions of products

A. Deuteration of 2-phenyl-4-trimethylsilylpyridine



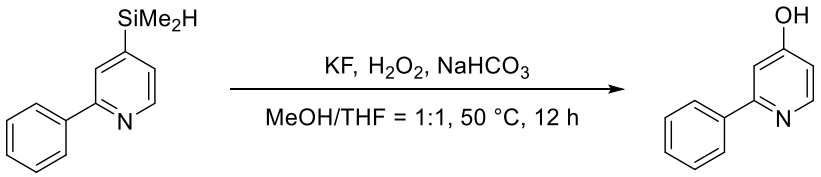
In an oven-dried 50 mL two neck flask under an argon atmosphere, 2-phenyl-4-trimethylsilylpyridine (0.5 mmol, 1 equiv.), deuterium oxide (5 mmol, 10 equiv.), cesium fluoride (5 mmol, 10 equiv.) and dry DMF (5 mL) were added. The reaction mixture was stirred at 70 ℃ for 12 h. Afterwards, the reaction mixture was quenched with 20 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 5:1).



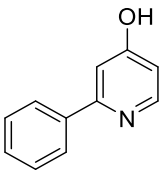
2-Phenylpyridine-4-d (56)

Known compound.[11] 95% yield (74 mg), colorless oil. Rf = 0.50 (PE/AcOEt = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.71 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.71 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.3, 149.6, 139.3, 136.3 (t, *J* = 24.2 Hz), 128.8, 128.6, 126.8, 121.9, 120.3.

B. Tamao-Fleming oxidation of 4-dimethylsilyl-2-phenylpyridine



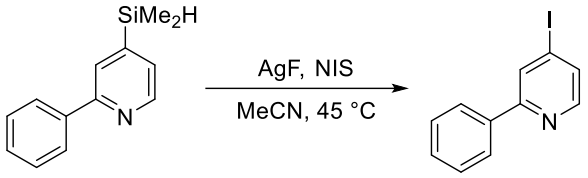
In a 50 mL two-neck flask under an argon atmosphere, potassium fluoride (2 mmol, 4 equiv.), sodium bicarbonate (2 mmol, 4 equiv.) and 6 mL of solvent THF/MeOH = 1:1 (*v*/*v*) were added. The reaction was cooled to 0 ℃, following the addition of 4-dimethylsilyl-2-phenylpyridine (0.5 mmol, 1 equiv.) and hydrogen peroxide (1.5 mL). The reaction was then stirred at 50 ℃ for 12 h. Afterwards, the reaction mixture was quenched with 20 mL of saturated ammonium chloride solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 1:1).



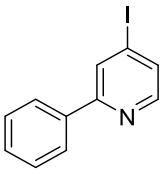
2-Phenylpyridin-4-ol (57)

Known compound.[12] 61% yield (52 mg), colorless oil. Rf = 0.50 (DCM/MeOH = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.1 Hz, 1H), 7.60-7.57 (m, 2H), 7.37-7.34 (m, 3H), 6.55 (s, 1H), 6.32 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.9, 151.0, 139.7, 133.8, 130.2, 129.0, 127.0, 115.5, 114.6.

C. Iodination of 4-dimethylsilyl-2-phenylpyridine



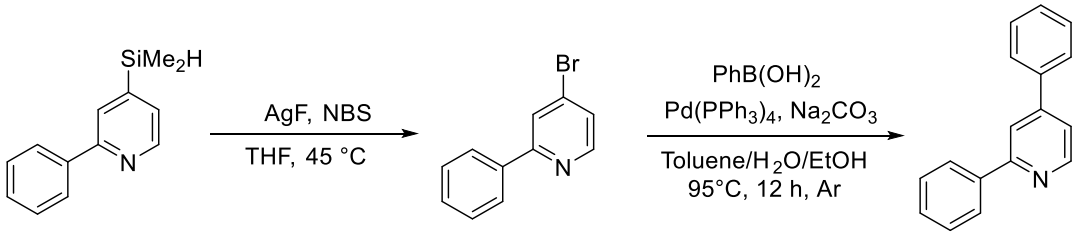
To an oven-dried 50 mL two neck flask under an argon atmosphere, 4-(dimethylsilyl)-2-phenylpyridine (0.5 mmol, 1 equiv.), *N*-iodosuccinimide (NIS) (2 mmol, 4 equiv.), silver(I) fluoride (0.8 mmol, 4 equiv.) and acetonitrile (5mL) were added. The reaction mixture was stirred at 45 ℃ for 24 h. The solvent was then removed in vacuo and the crude product was purified using flash column chromatography (PE/AcOEt, *v*/*v* = 10:1).



4-Iodo-2-phenylpyridine (58)

Known compound.[13] 72% yield (101 mg), yellow oil. Rf = 0.50 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (d, *J* = 5.2 Hz, 1H), 8.12 (s, 1H), 7.95 (d, *J* = 6.6 Hz, 2H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.50-7.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.2, 149.8, 137.7, 131.1, 129.9, 129.6, 128.8, 127.0, 106.3.

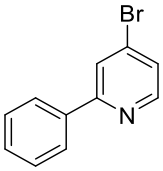
D. Functionalization of 4-dimethylsilyl-2-phenylpyridine



To an oven-dried 50 mL two neck flask under an argon atmosphere, 4-(dimethylsilyl)-2-phenylpyridine (0.5 mmol, 1 equiv.), *N*-bromosuccinimide (NBS) (2 mmol, 4 equiv.), silver(I) fluoride (0.8 mmol, 4 equiv.) and acetonitrile (5mL) were added. The reaction mixture was stirred at 45 ℃ for

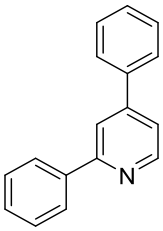
24 h. The solvent was then removed in vacuo and the crude product was purified using flash column chromatography (PE/AcOEt, *v*/*v* = 10:1).

In an oven-dried 20 mL two-neck flask under an argon atmosphere, 4-bromo-2-phenylpyridine (0.3 mmol, 1 equiv.) obtained from the previous step, $Pd(PPh_3)_4$ (3 mol%), sodium carbonate (2.25 mmol, 7.5 equiv.), phenylboronic acid (0.39 mmol, 1.3 equiv.), and a toluene/H_2O/EtOH mixed solvent (4.2 mL, *v*/*v*/*v* = 3:3:1) were added. The reaction mixture was stirred at 95 ℃ for 12 h. Afterward, the reaction mixture was diluted with 10 mL of ethyl acetate and 10 mL of water, and extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. Following filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 10:1).



4-Bromo-2-phenylpyridine (59)

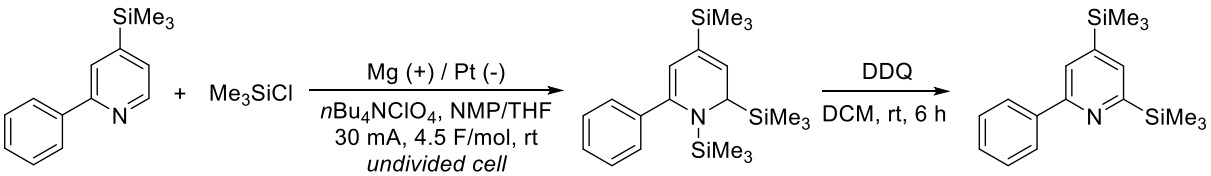
Known compound.[13] 86% yield (101 mg), yellow oil. Rf = 0.50 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.51 (d, *J* = 5.3 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.91 (s, 1H), 7.50-7.44 (m, 3H), 7.41 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.8, 150.3, 137.9, 133.4, 129.5, 128.8, 126.9, 125.2, 123.8.



2,4-Diphenylpyridine (60)

Known compound.[14] 94% yield (65 mg), yellow oil. Rf = 0.50 (PE/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.75 (d, *J* = 5.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.94 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.54-7.43 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.1, 150.1, 149.2, 139.5, 138.5, 129.1, 129.01, 129.00, 128.8, 127.1, 127.0, 120.2, 118.8.

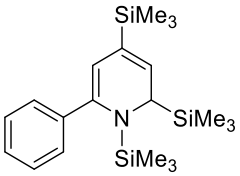
E. Electroreductive silylation of 2-phenyl-4-trimethylsilylpyridine



In an oven-dried 10 mL Schlenk tube equipped with a magnesium plate (10×15×0.5 mm) as the anode and a platinum plate (10×15×0.2 mm) as the cathode under an argon atmosphere, nBu$_4$NClO$_4$ (0.03 M, 0.15 mmol, 0.3 equiv.), 2-phenyl-4-trimethylsilylpyridine (0.5 mmol, 1 equiv.), and dry NMP/THF (5 mL in total, *v*/*v* = 2:1) were added. Then, chlorotrimethylsilane (2.5 mmol, 5 equiv.) was added to the

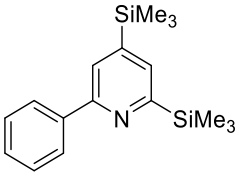
mixture, and the reaction mixture was electrolyzed at a constant current of 30 mA at room temperature until 4.5 F/mol of charge had passed. After electrolysis, the reaction mixture was quenched with 50 mL of saturated sodium bicarbonate solution and extracted with ethyl acetate (30 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 10:1).

For the DDQ-assisted oxidation, the crude product obtained from the previous step was placed in a 20 mL flask. Dichloromethane (1 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1 equiv., 0.5 mmol) were added, and the mixture was stirred at room temperature for 6 h. Subsequently, the resulting mixture was quenched with 10 mL of sodium hydroxide solution (1 M) and extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with brine and dried over anhydrous magnesium sulfate. After filtration and concentration, the crude products were purified by column chromatography (PE/AcOEt, *v*/*v* = 10:1).



2-Phenyl-1,4,6-tris(trimethylsilyl)-1,4-dihydropyridine (61)

66% yield (123 mg), colorless oil. Rf = 0.80 (PE/AcOEt = 10:1). The targeted compound rapidly decomposes upon contact with air. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.49 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 5.67 (s, 1H), 5.60 (d, *J* = 6.4 Hz, 1H), 3.46 (d, *J* = 6.4 Hz, 1H), 0.13 (s, 9H), 0.06 (s, 9H), -0.09 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 145.2, 141.6, 135.2, 127.9, 127.8, 127.6, 126.9, 113.8, 49.4, 1.2, -1.7, -2.7. IR (neat): (cm^{-1}) 3045, 2923, 2910, 2857, 1565, 1500, 1341, 1240, 1061. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{36}NSi_3$ 374.2150, found 374.2148.



2-Phenyl-4,6-bistrimethylsilylpyridine (62)

62% yield (93 mg) total yield, colorless oil. Rf = 0.65 (PE/AcOEt = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.08 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 1.1 Hz, 1H), 7.52 (d, *J* = 1.1 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 0.37 (s, 9H), 0.33 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 166.5, 155.4, 147.7, 140.4, 131.1, 128.6, 128.5, 127.0, 123.8, -1.61, -1.64. IR (neat): (cm^{-1}) 3052, 955, 2926, 2852, 1569, 1494, 1370, 1247, 1078. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{26}NSi_2$ 300.1598, found 300.1599.

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[13] The spectral data was consistent with the literature: J. N. Levy, J. V. Alegre-Requena, R. Liu, R. S. Paton, A. McNally, *J. Am. Chem. Soc.* **2020**, *142*, 11295–11305.

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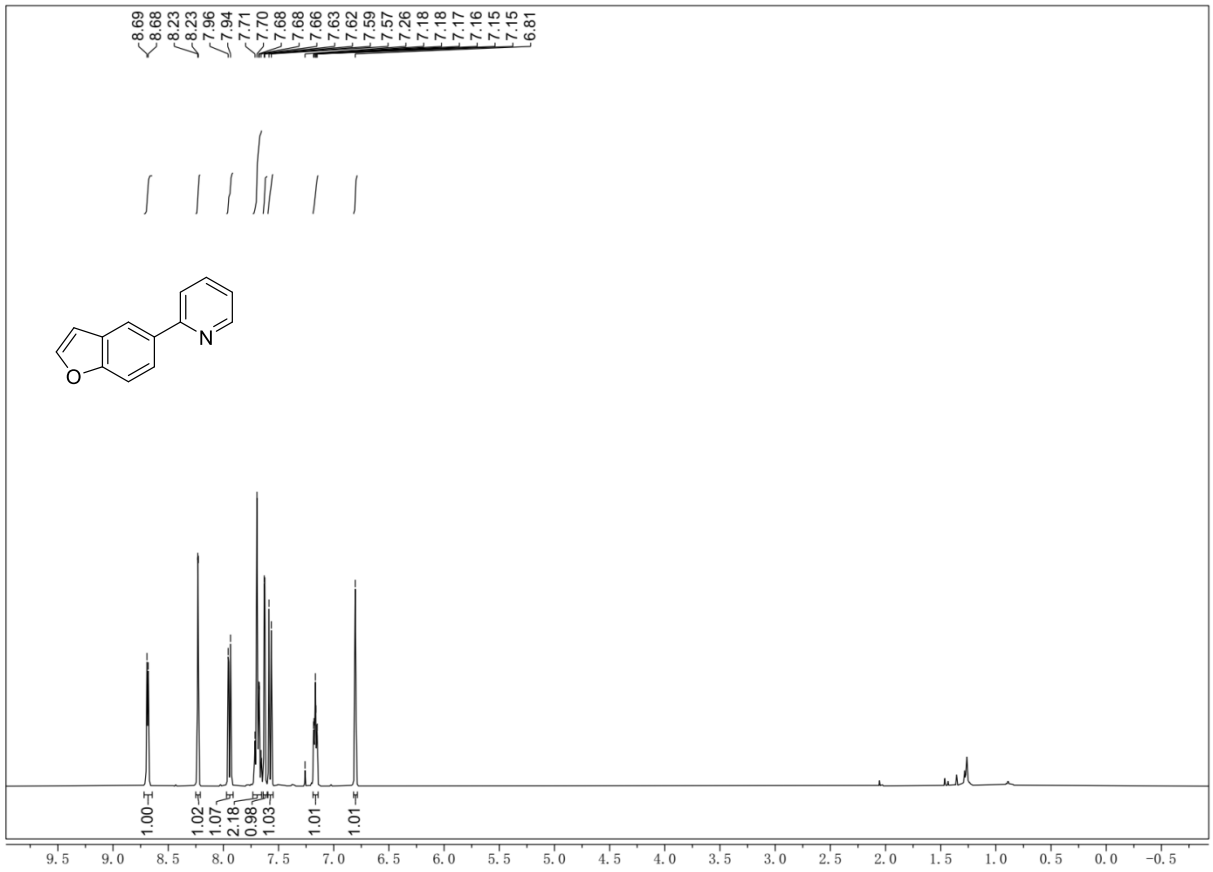
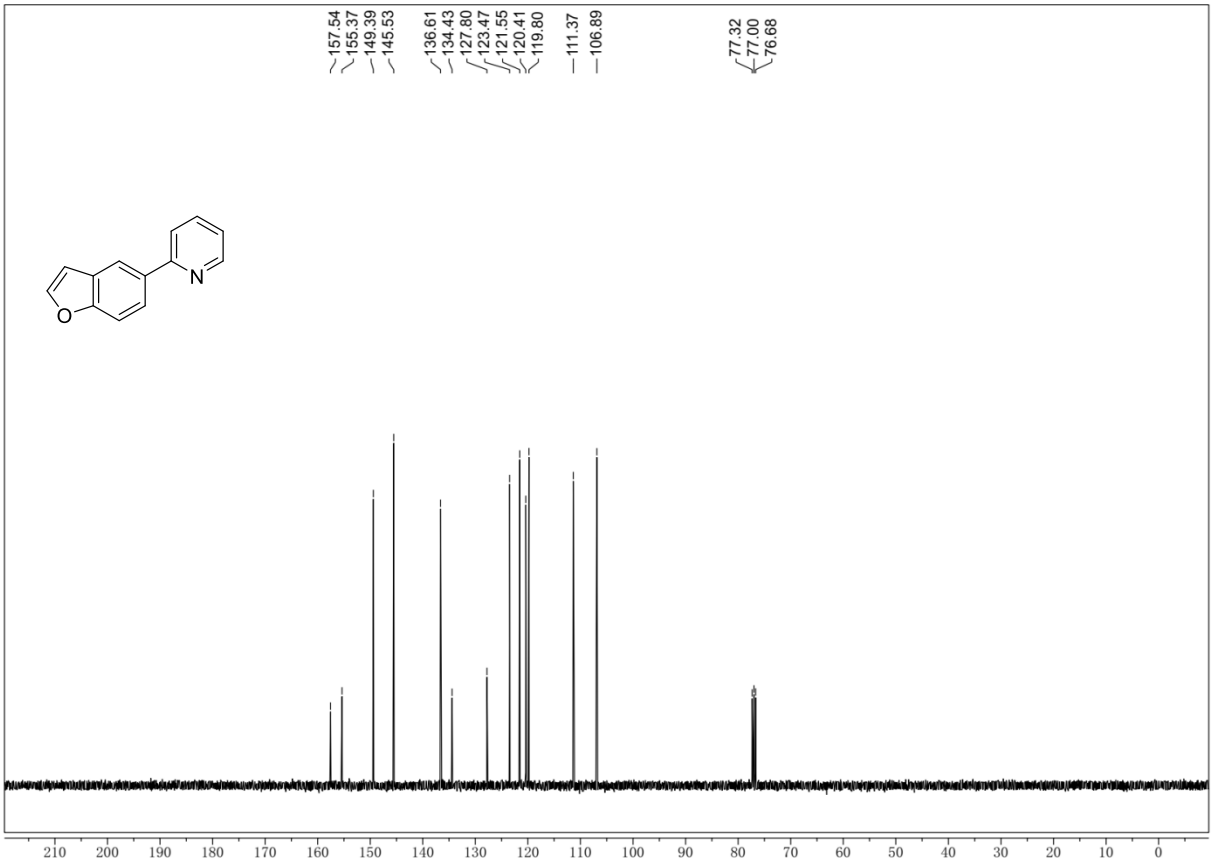
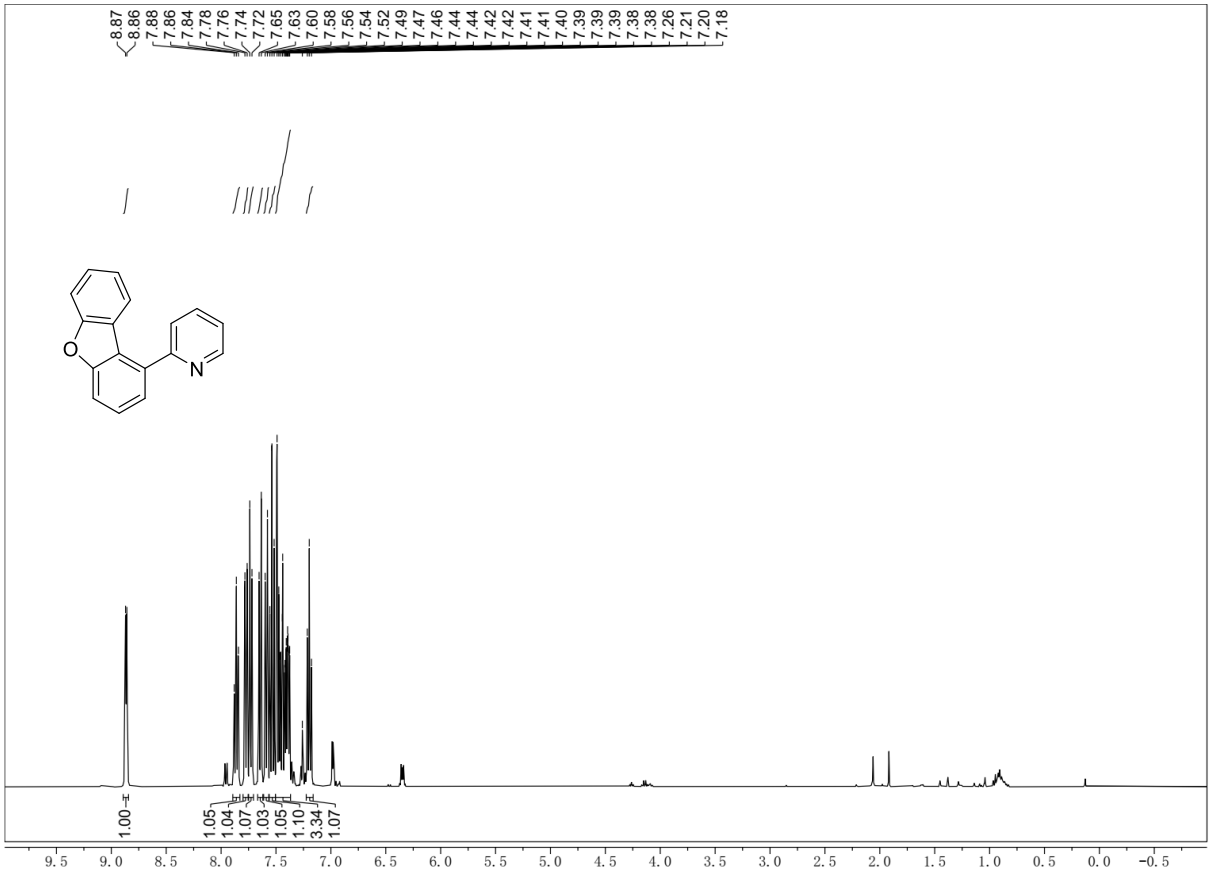
Sub-23 ^{1}H $CDCl_3$, 400 MHz



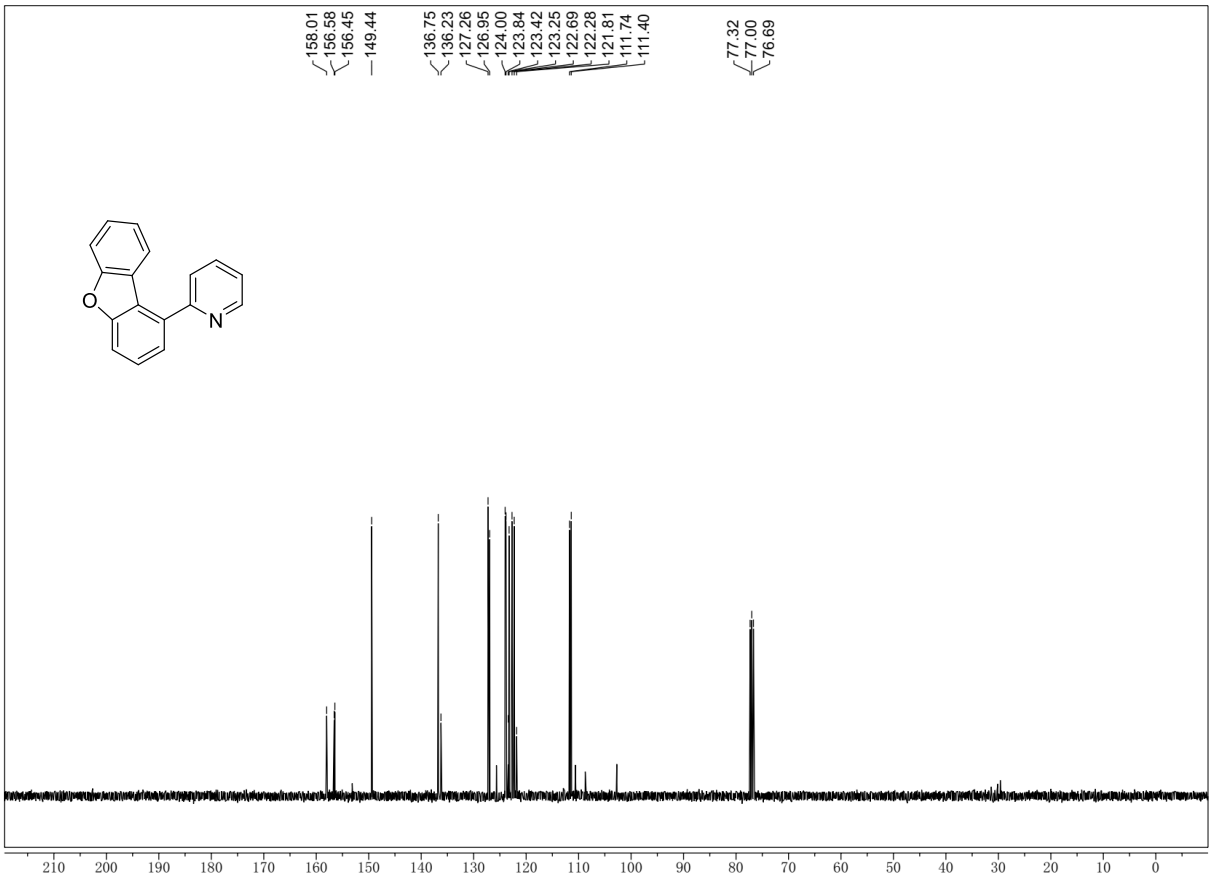
Sub-23 ^{13}C $CDCl_3$, 100 MHz



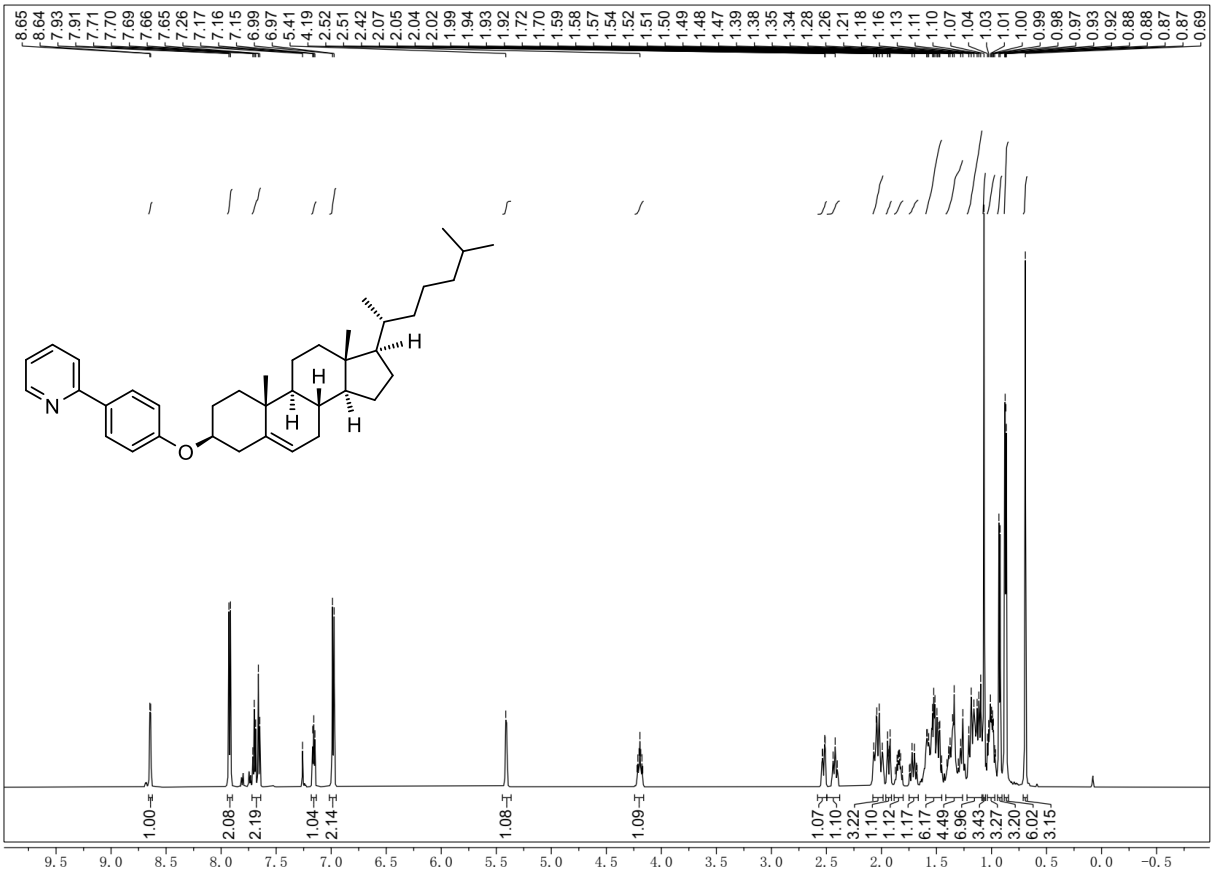
Sub-25 ^{1}H $CDCl_3$, 400 MHz



Sub-25 ^{13}C $CDCl_3$, 100 MHz



Sub-36 ^{1}H $CDCl_3$, 400 MHz



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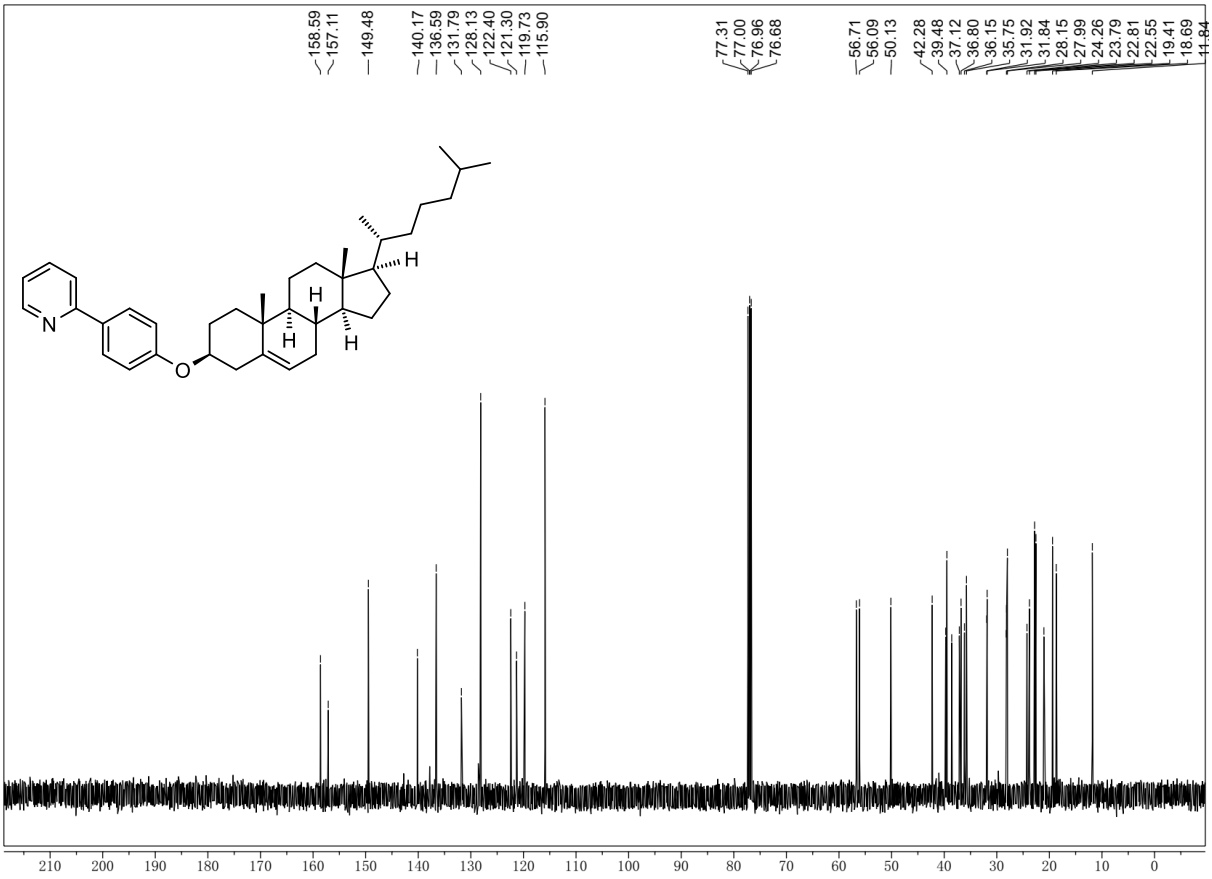
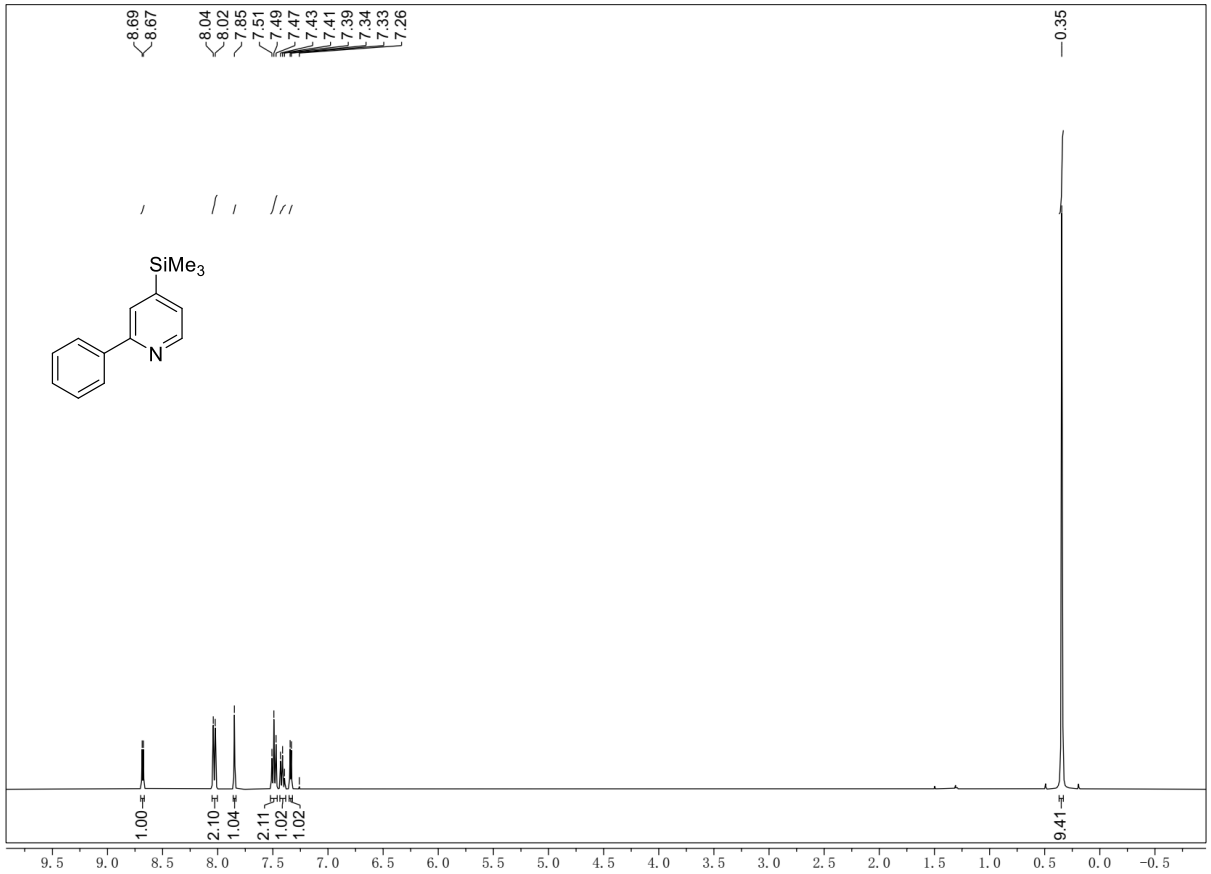
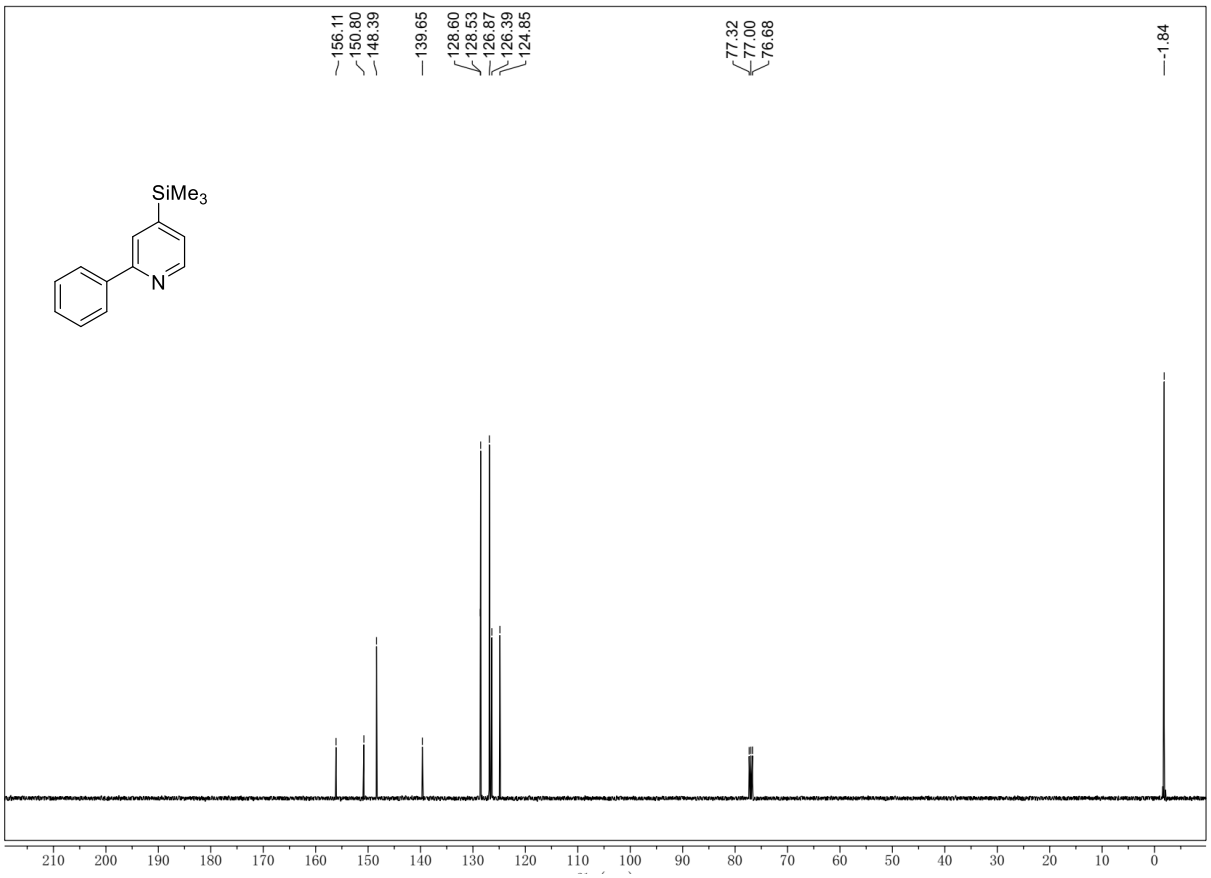


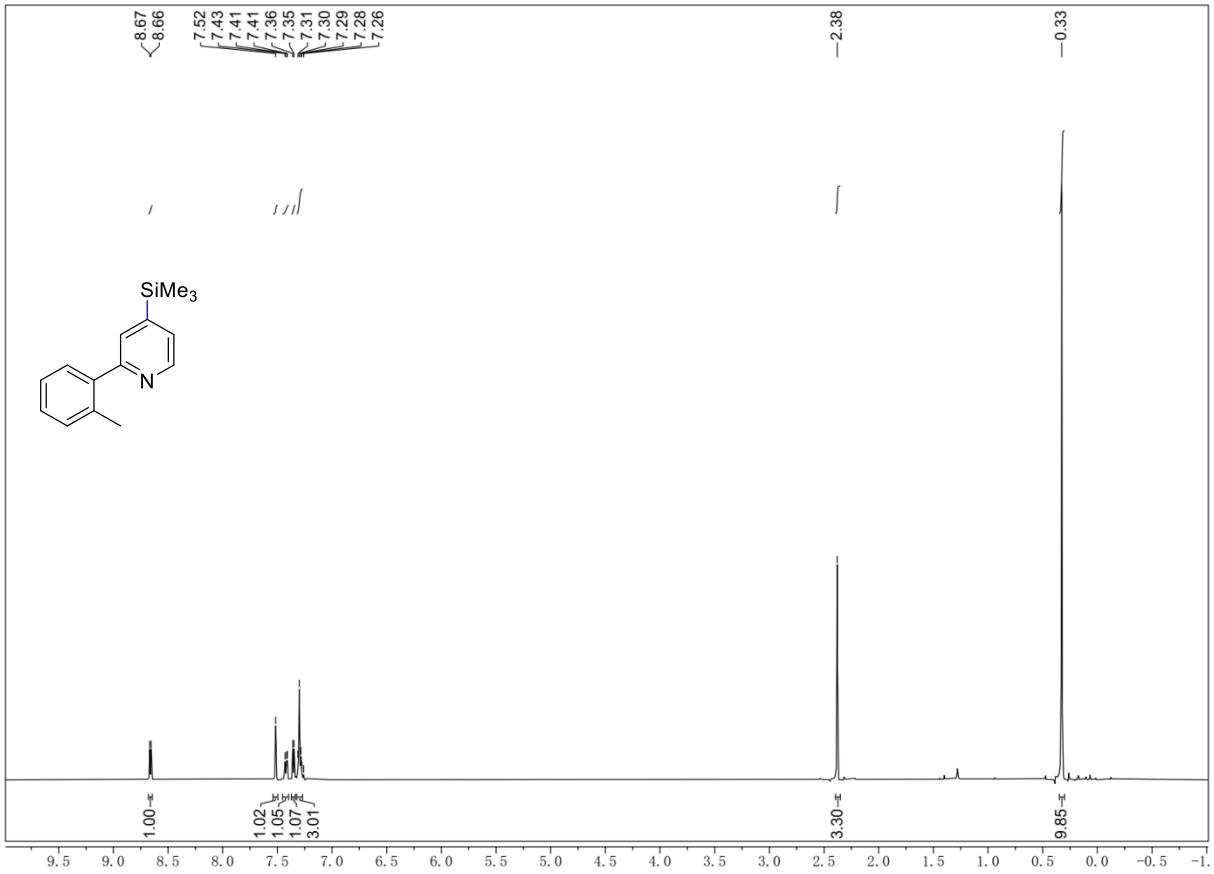
3 ^{1}H $CDCl_3$, 400 MHz



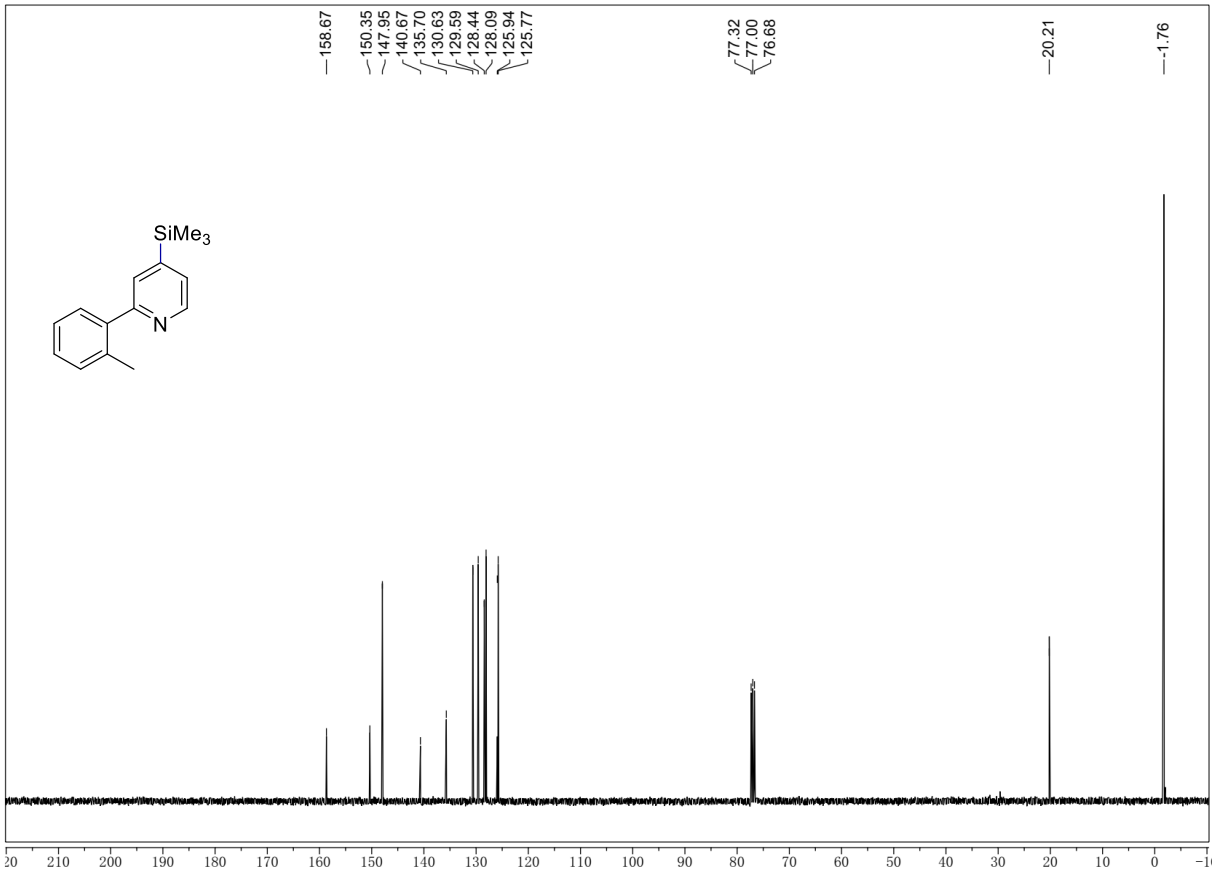
3 ^{13}C $CDCl_3$, 151 MHz



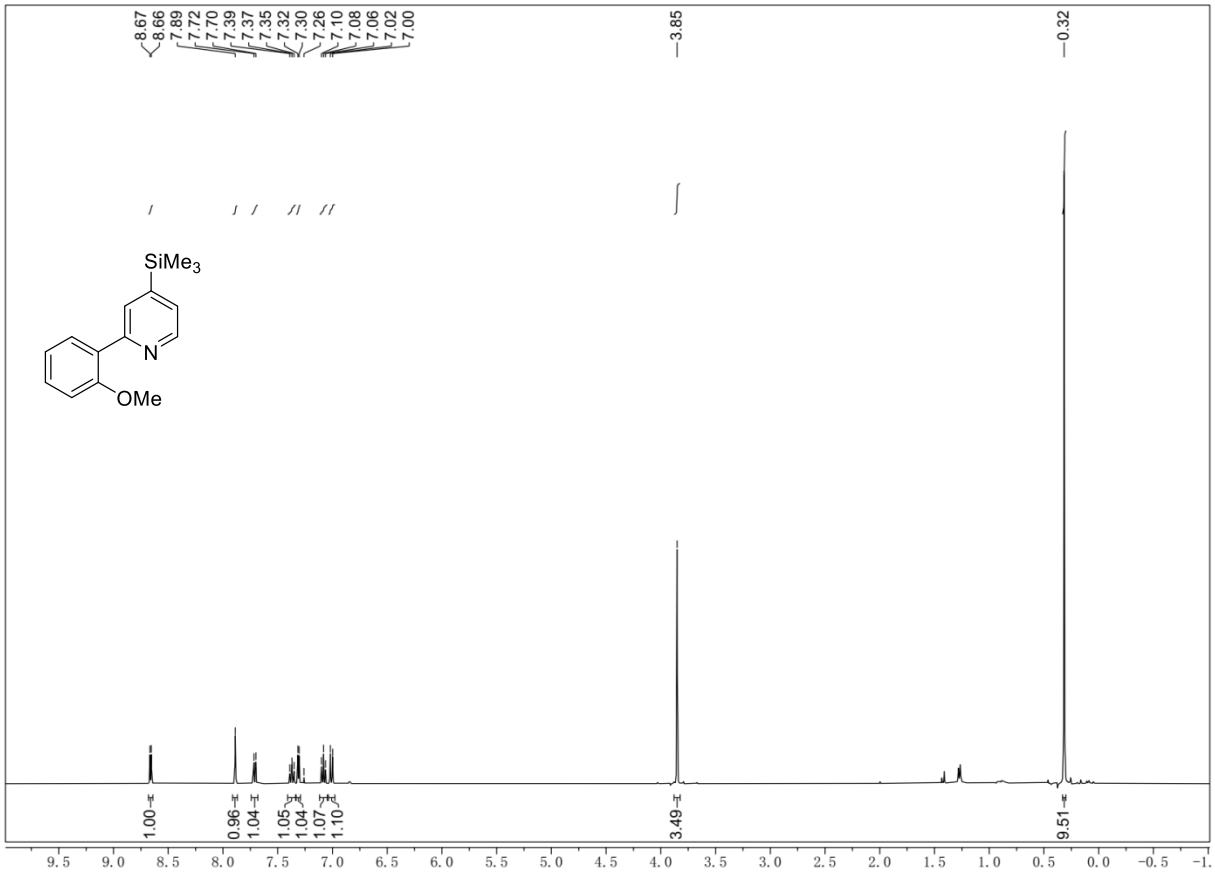
4 ^{1}H $CDCl_3$, 400 MHz



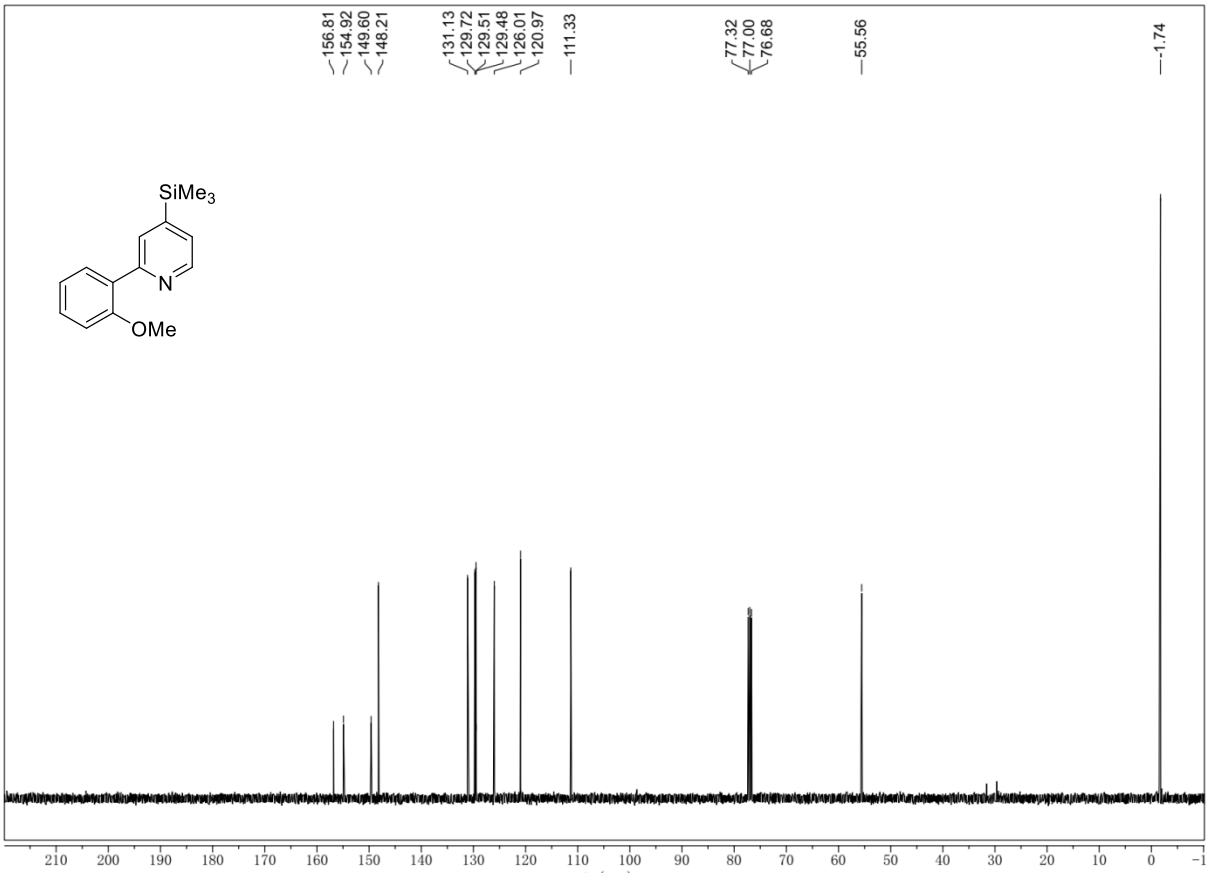
4 ^{13}C $CDCl_3$, 100 MHz



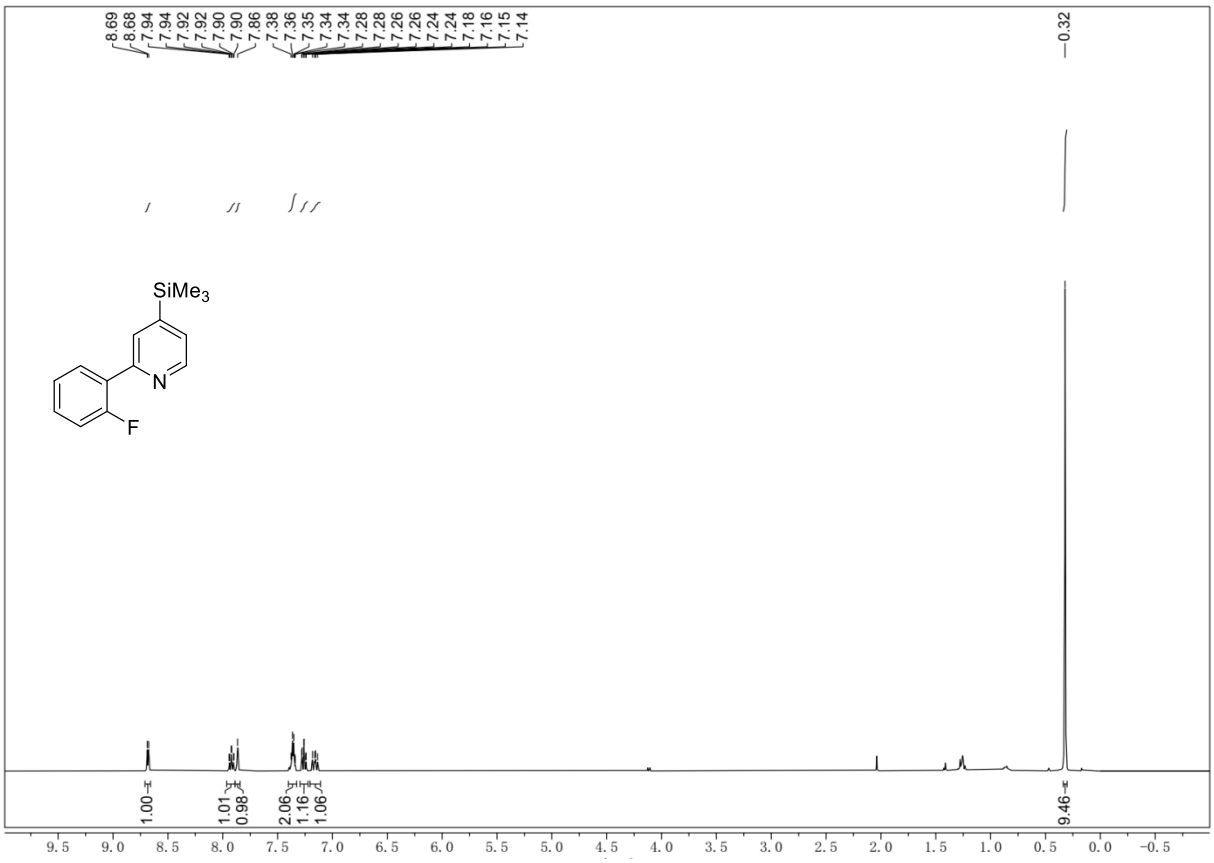
5 ^{1}H $CDCl_3$, 400 MHz



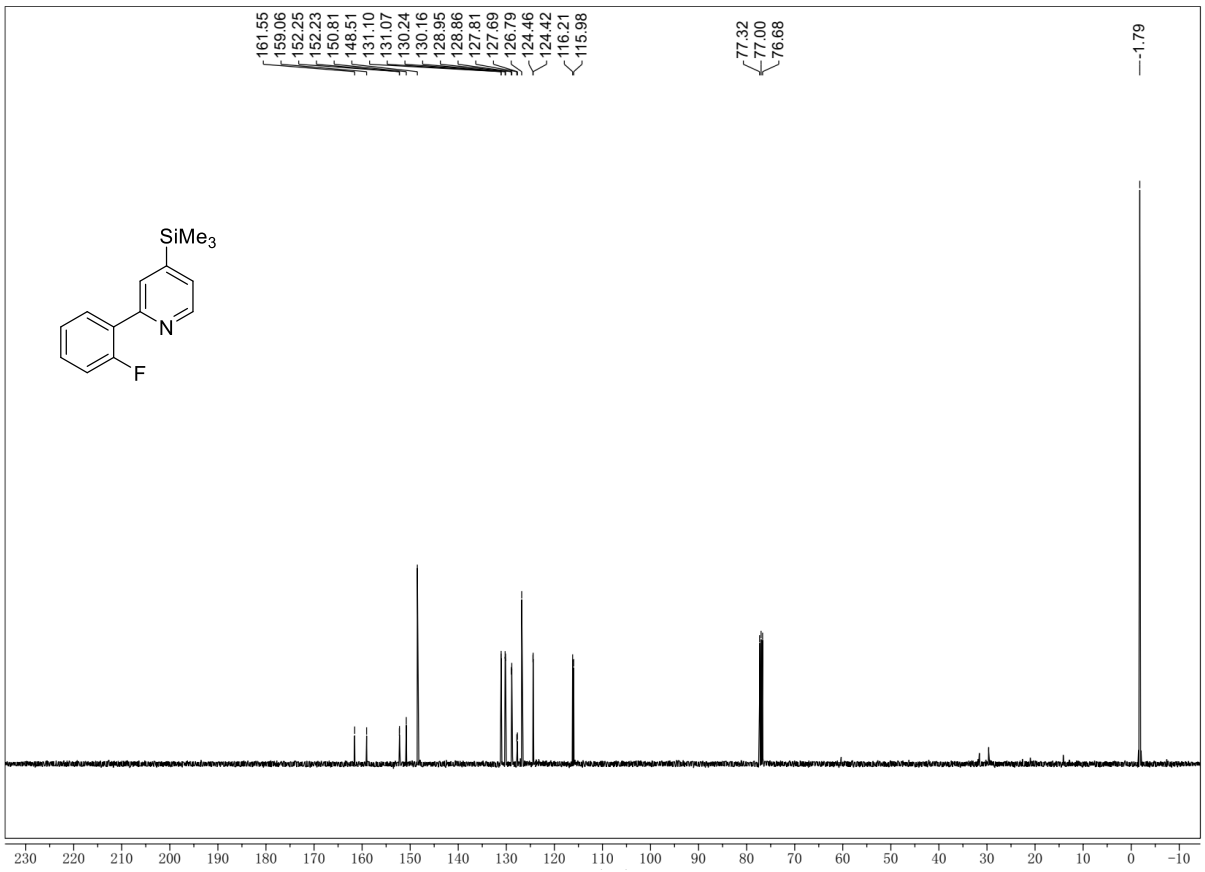
5 ^{13}C $CDCl_3$, 100 MHz



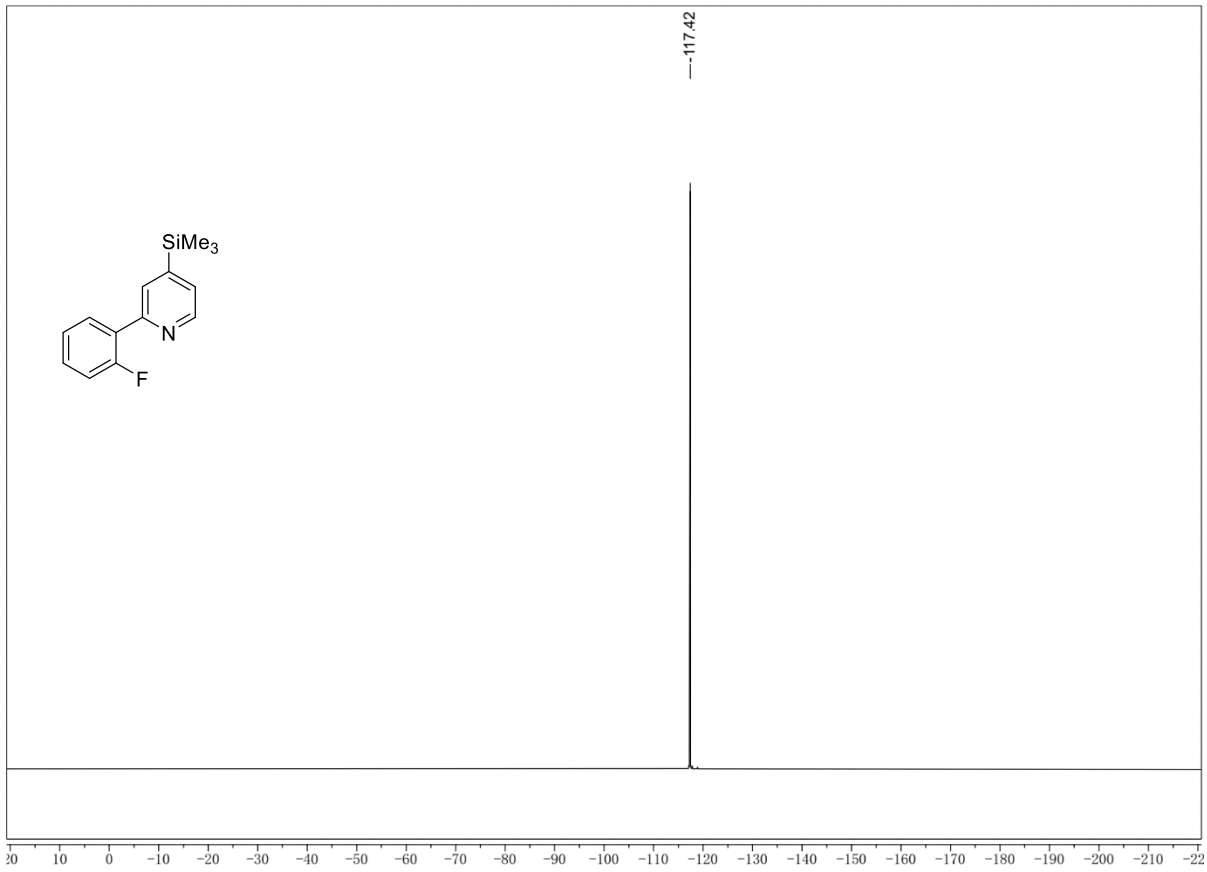
6 ^{1}H $CDCl_3$, 400 MHz



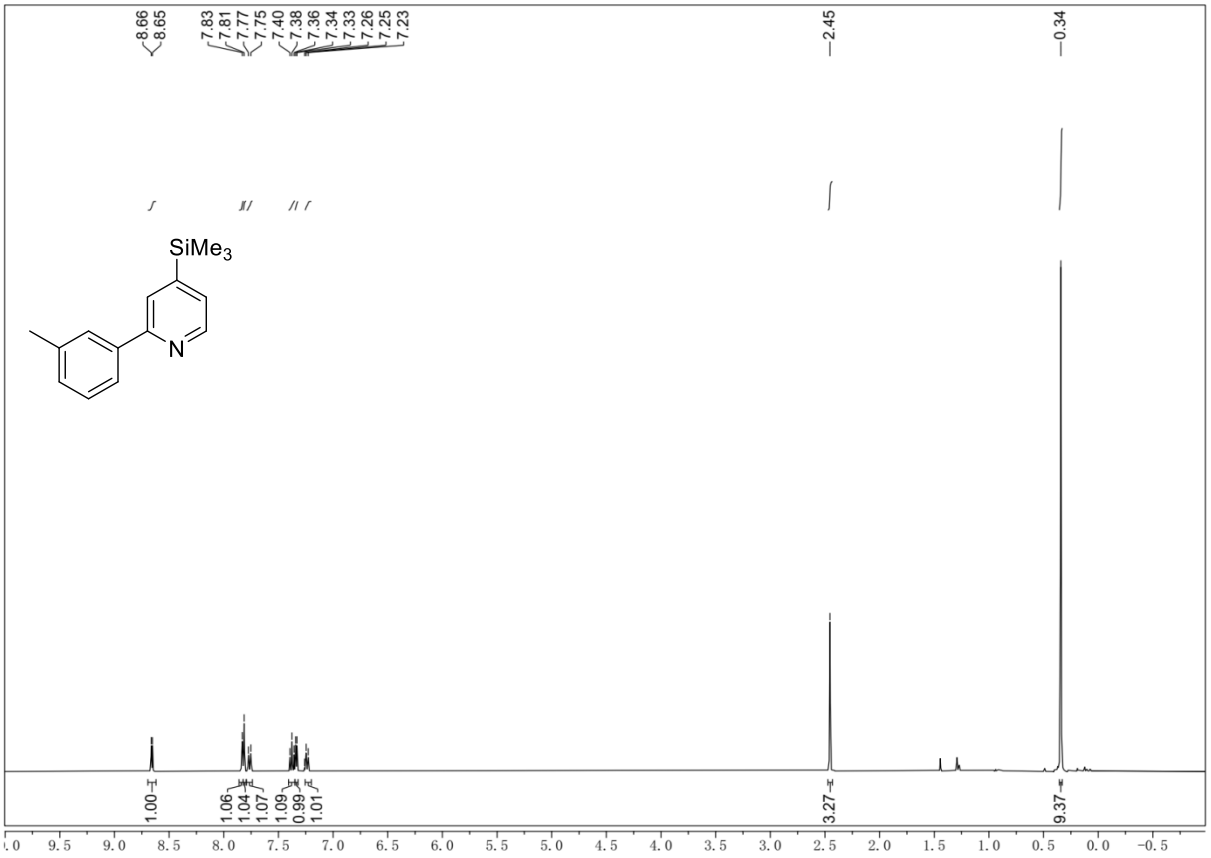
6 ^{13}C $CDCl_3$, 100 MHz



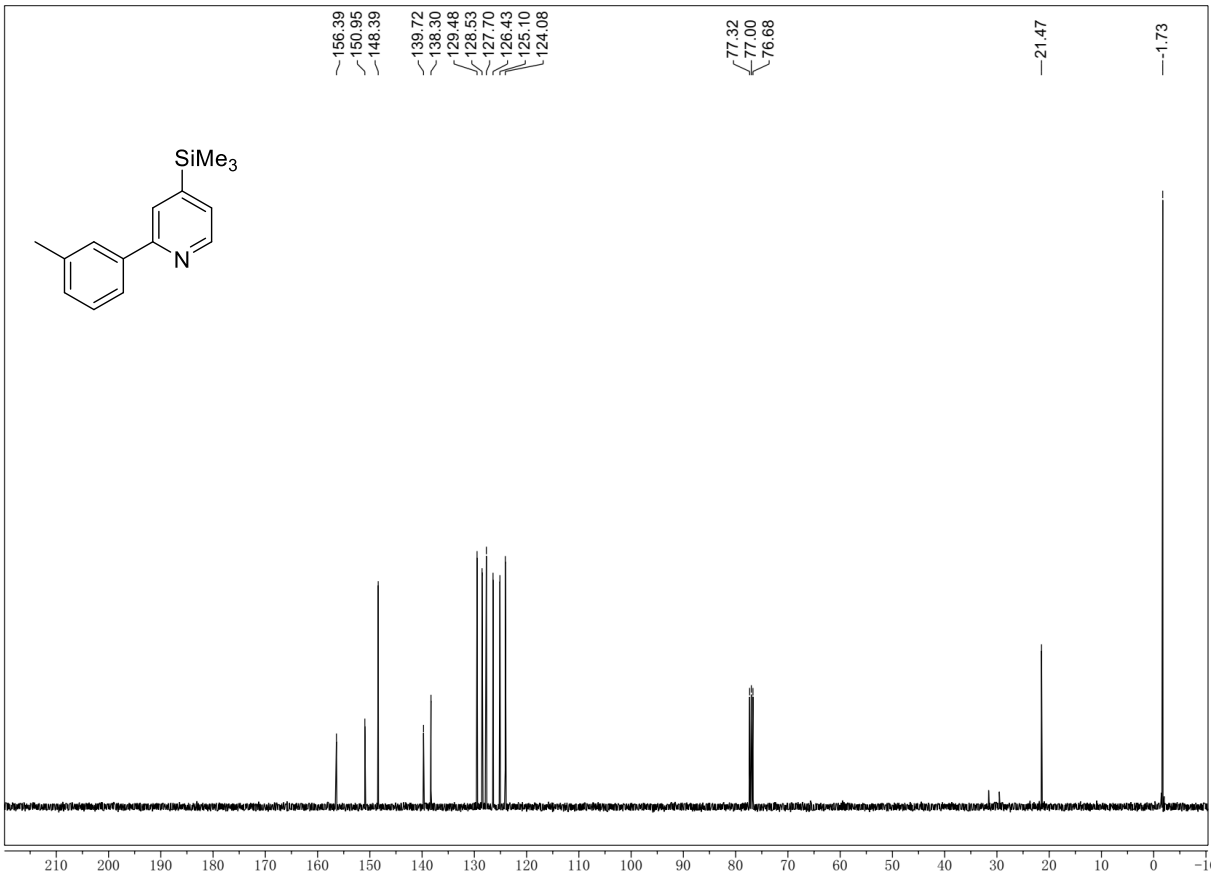
6 ^{19}F $CDCl_3$, 376 MHz



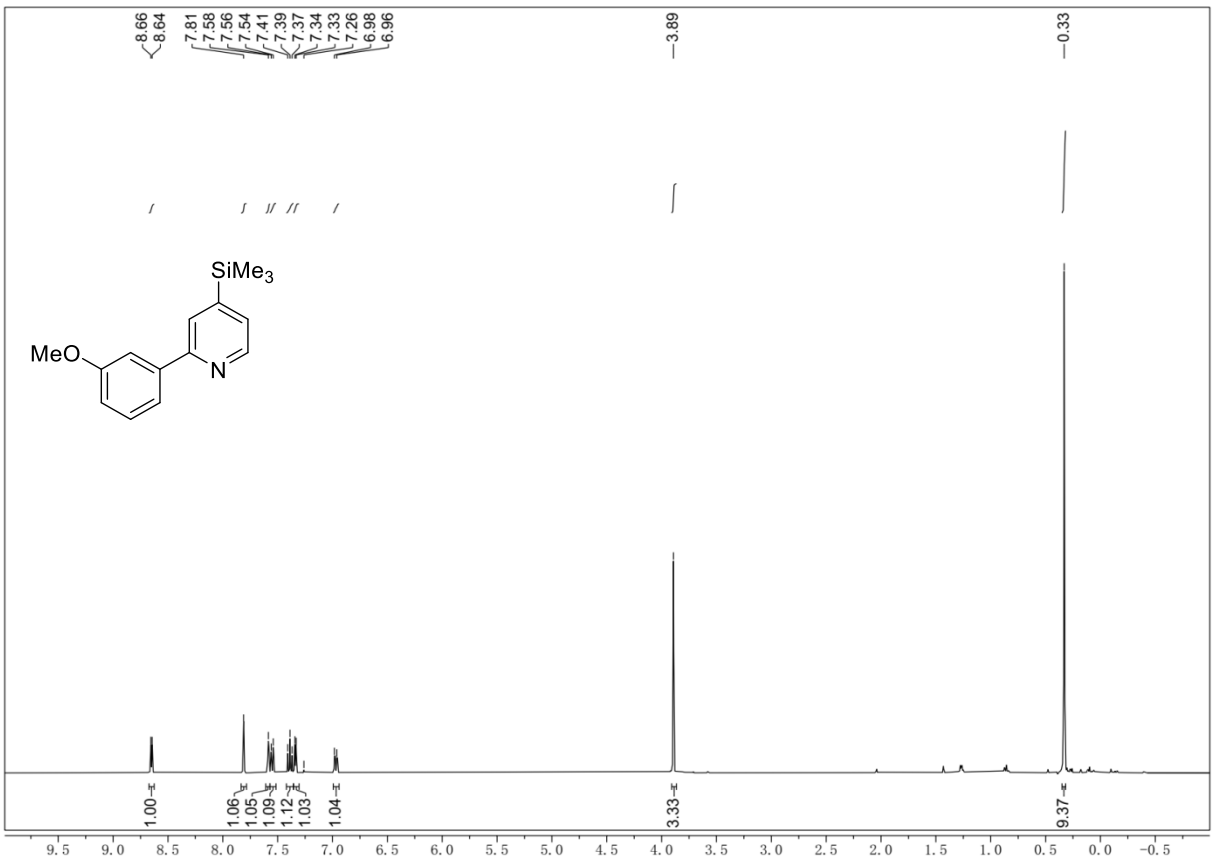
7 ^{1}H $CDCl_3$, 400 MHz



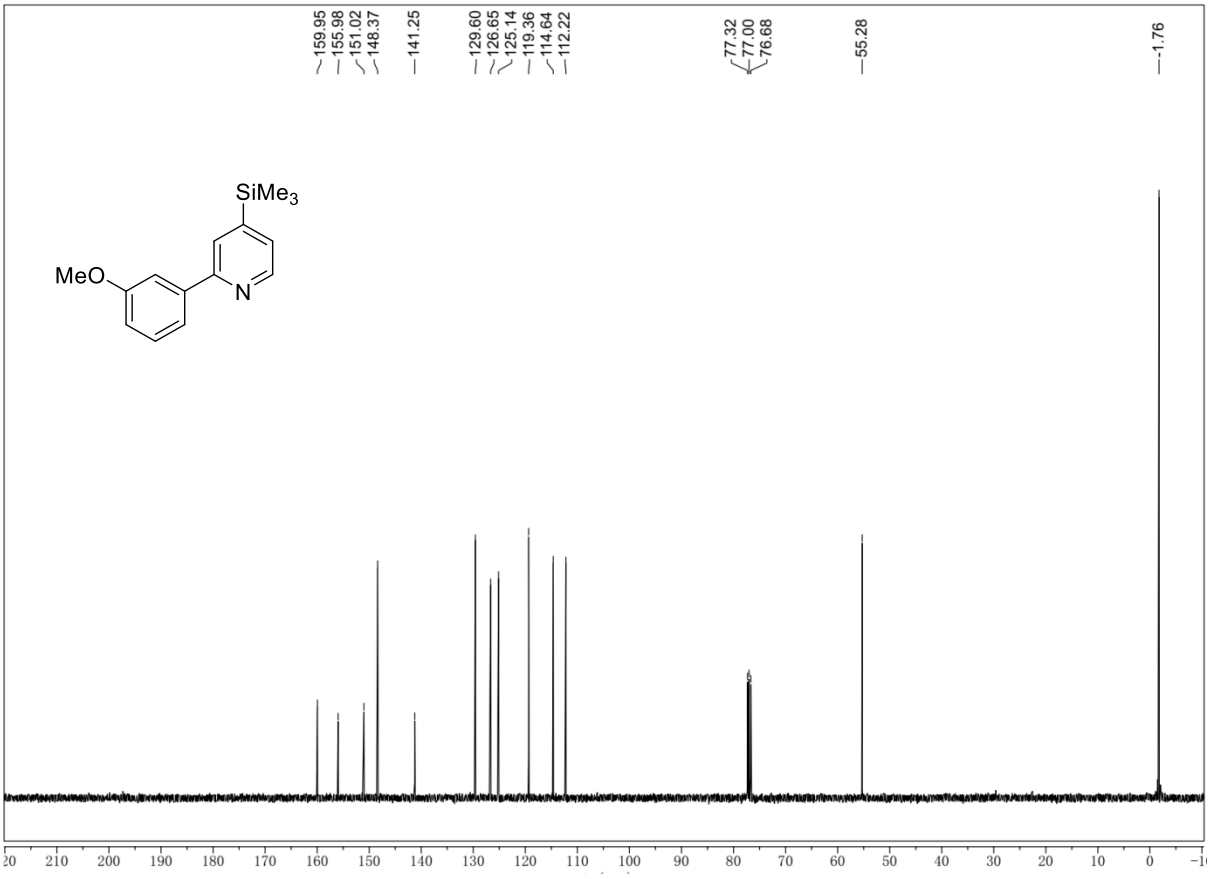
7 ^{13}C $CDCl_3$, 100 MHz



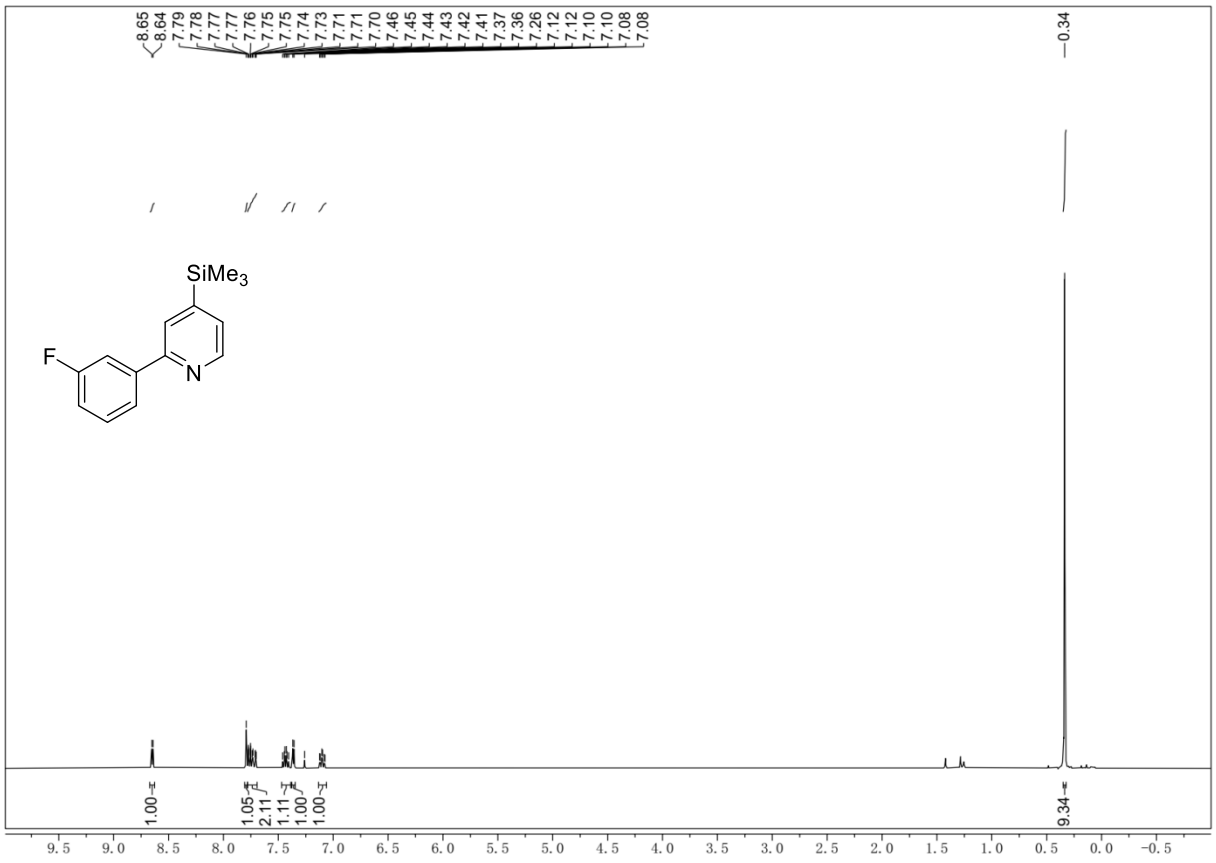
8 ^{1}H $CDCl_3$, 400 MHz



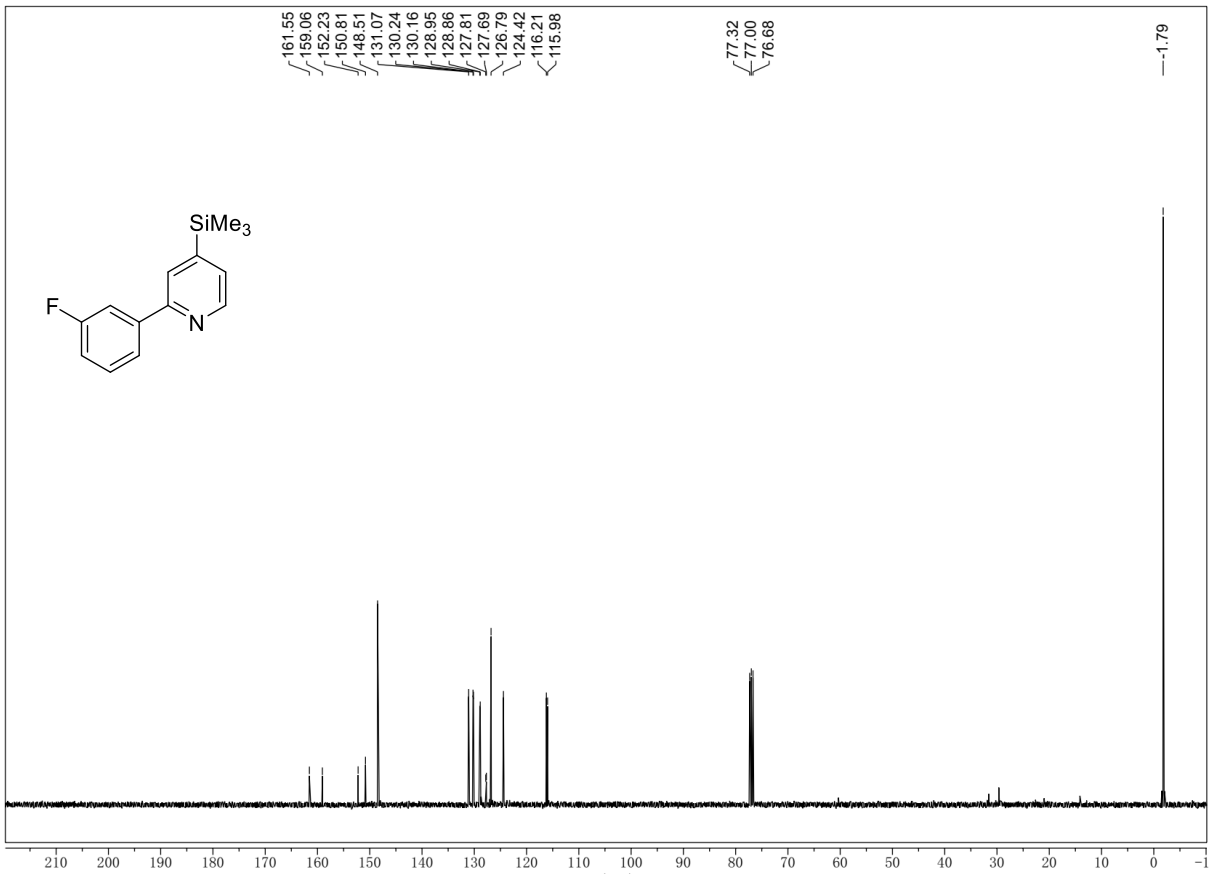
8 ^{13}C $CDCl_3$, 100 MHz



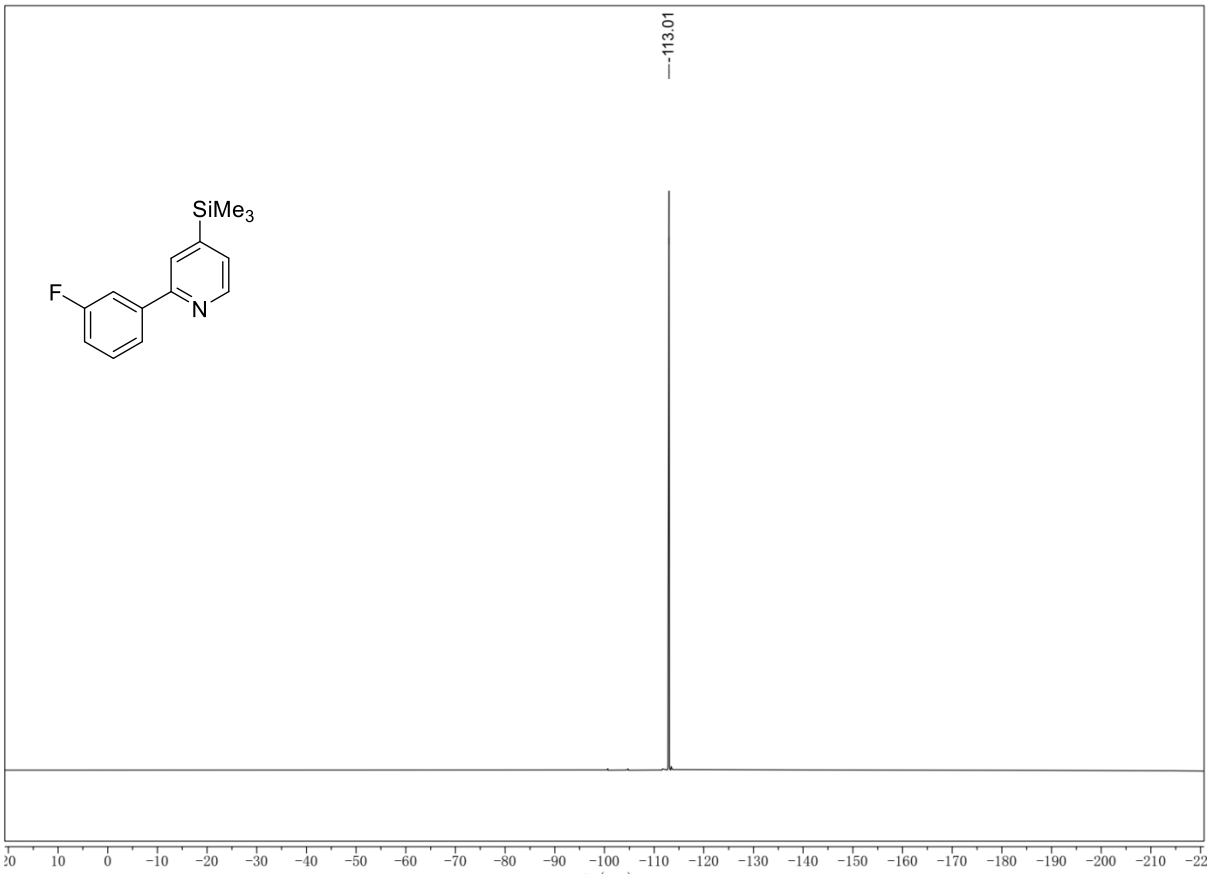
9 ^{1}H $CDCl_3$, 400 MHz



9 ^{13}C $CDCl_3$, 100 MHz



9 ^{19}F $CDCl_3$, 376 MHz



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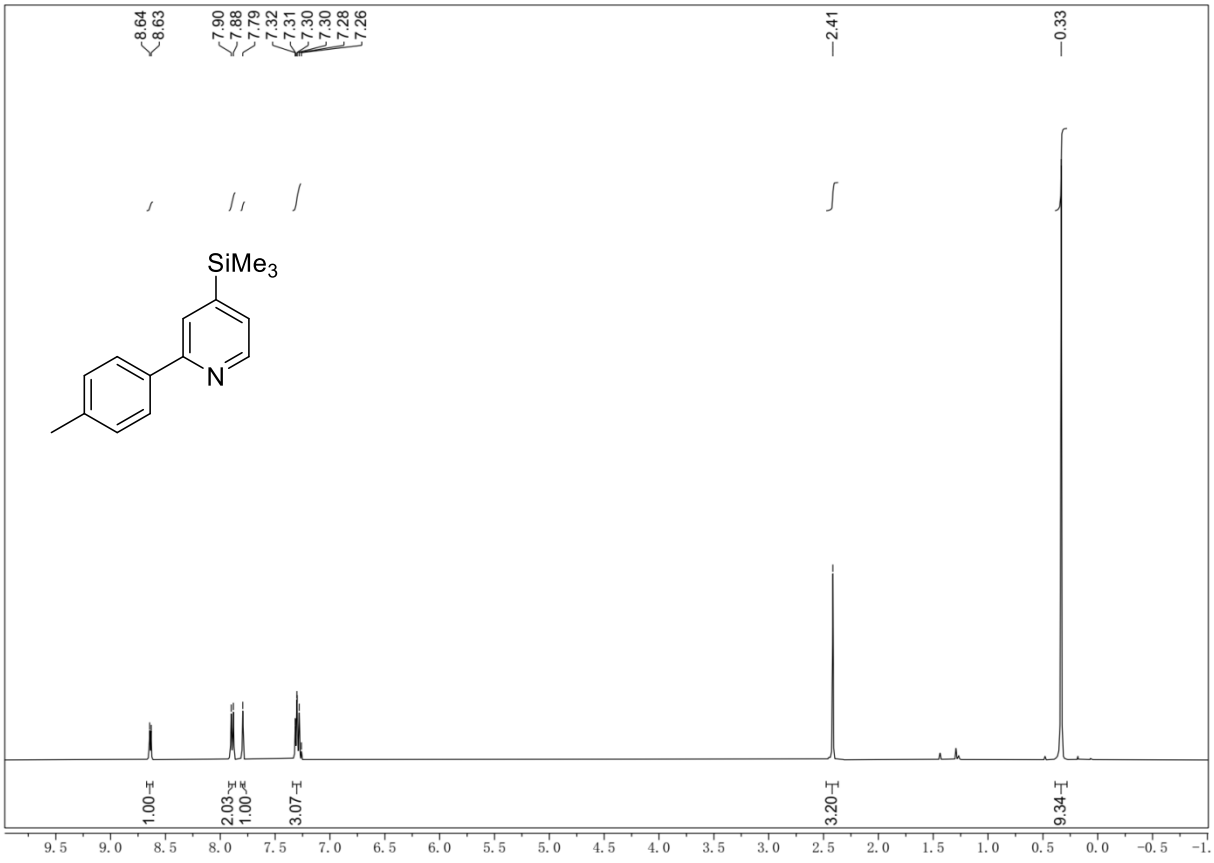
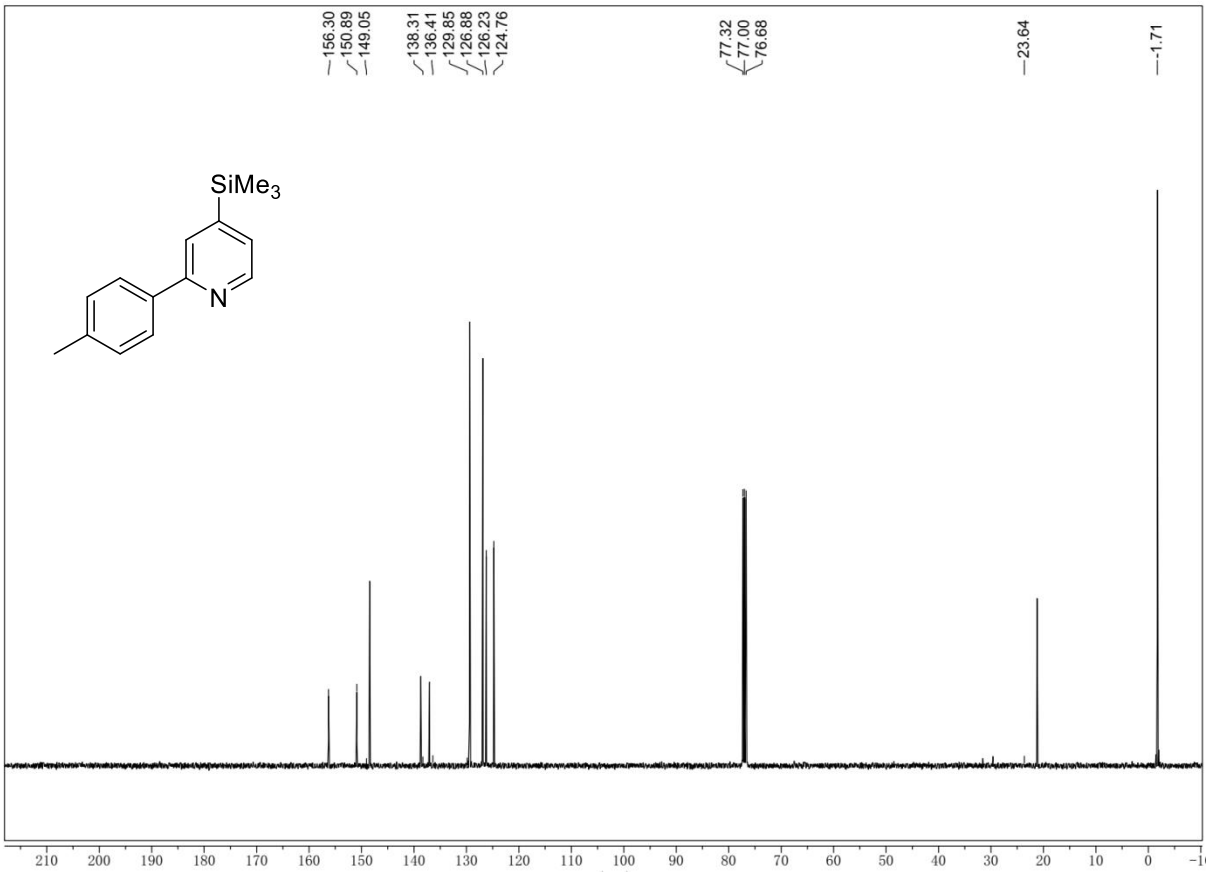
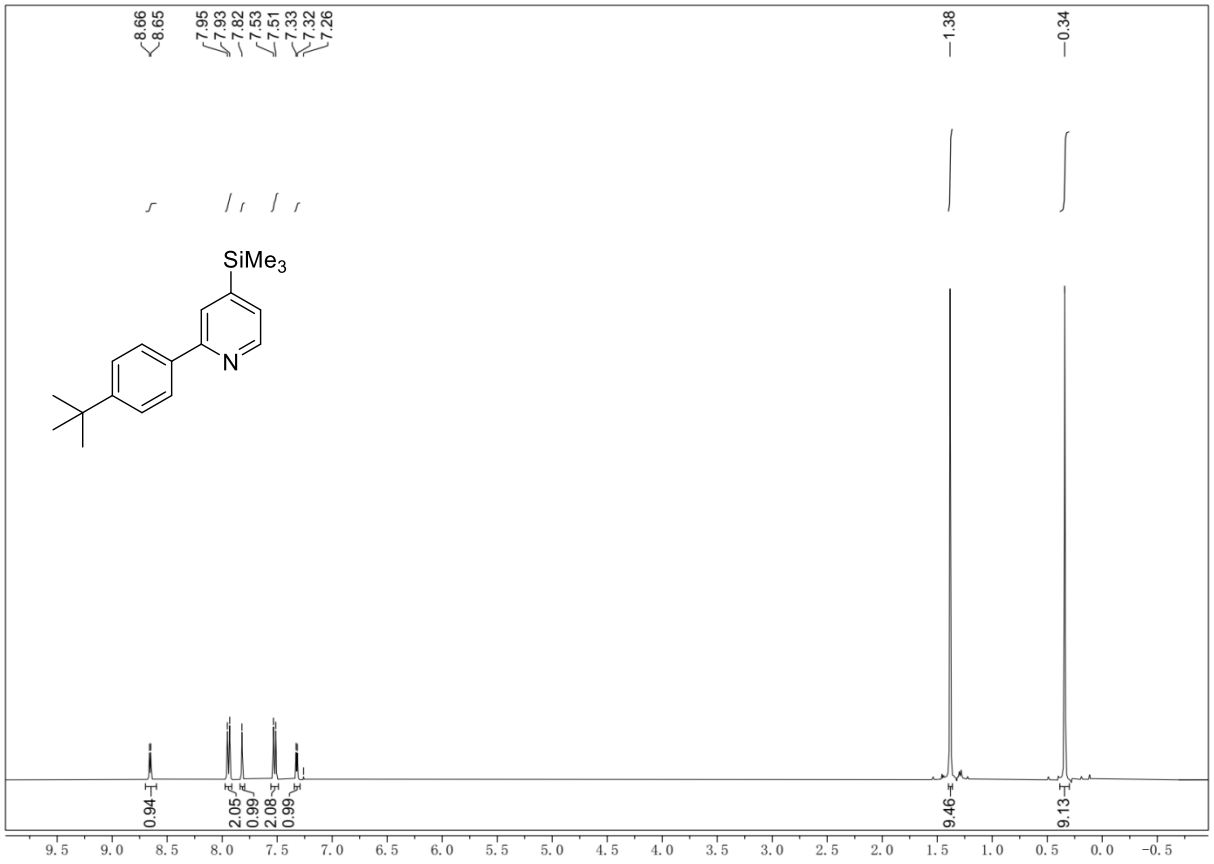


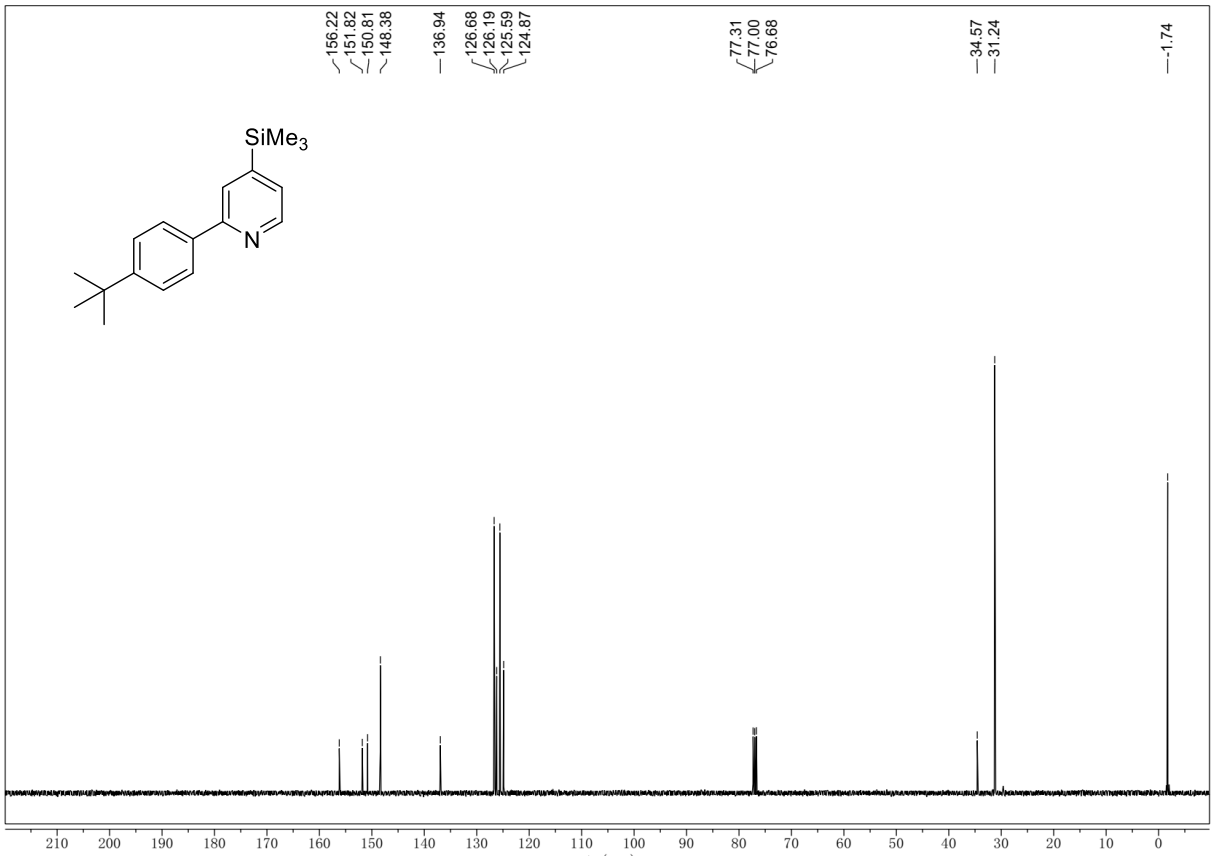
10 ^{13}C $CDCl_3$, 100 MHz



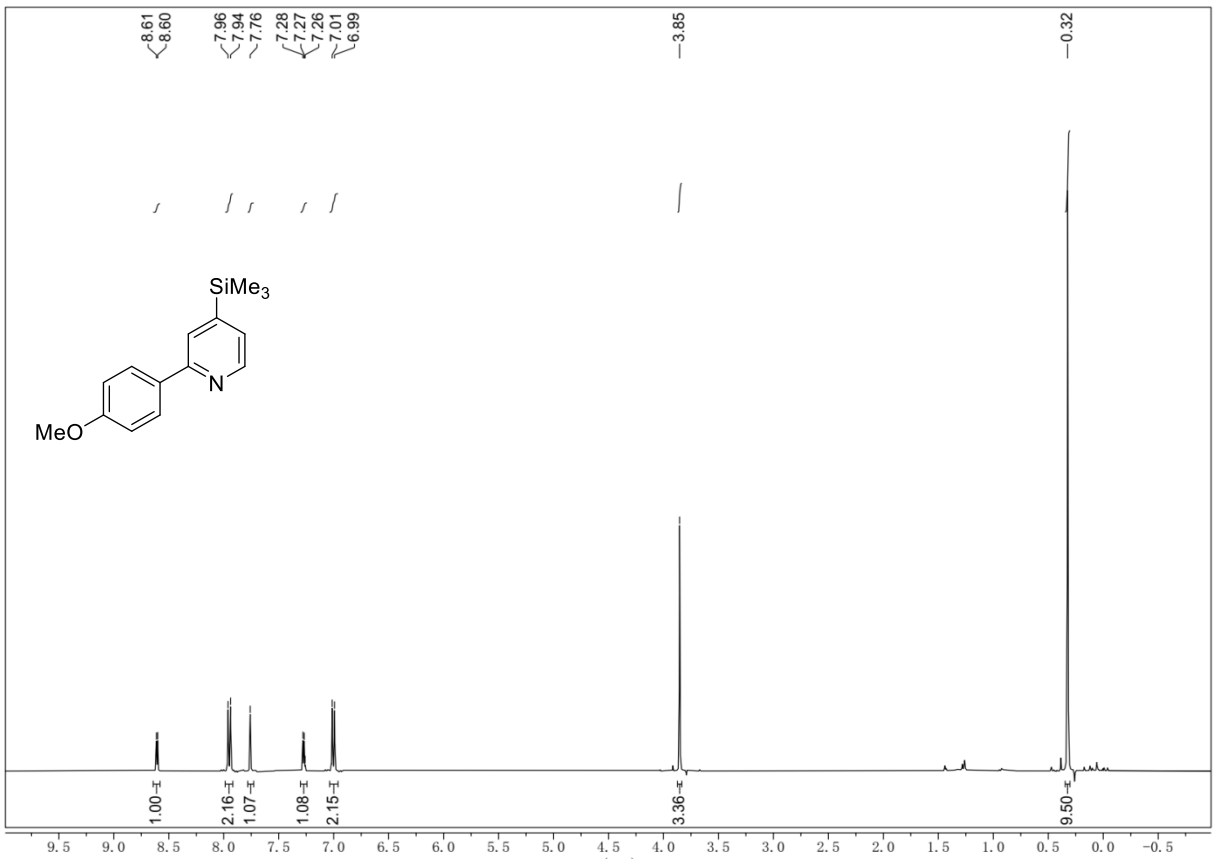
11 ^{1}H $CDCl_3$, 400 MHz



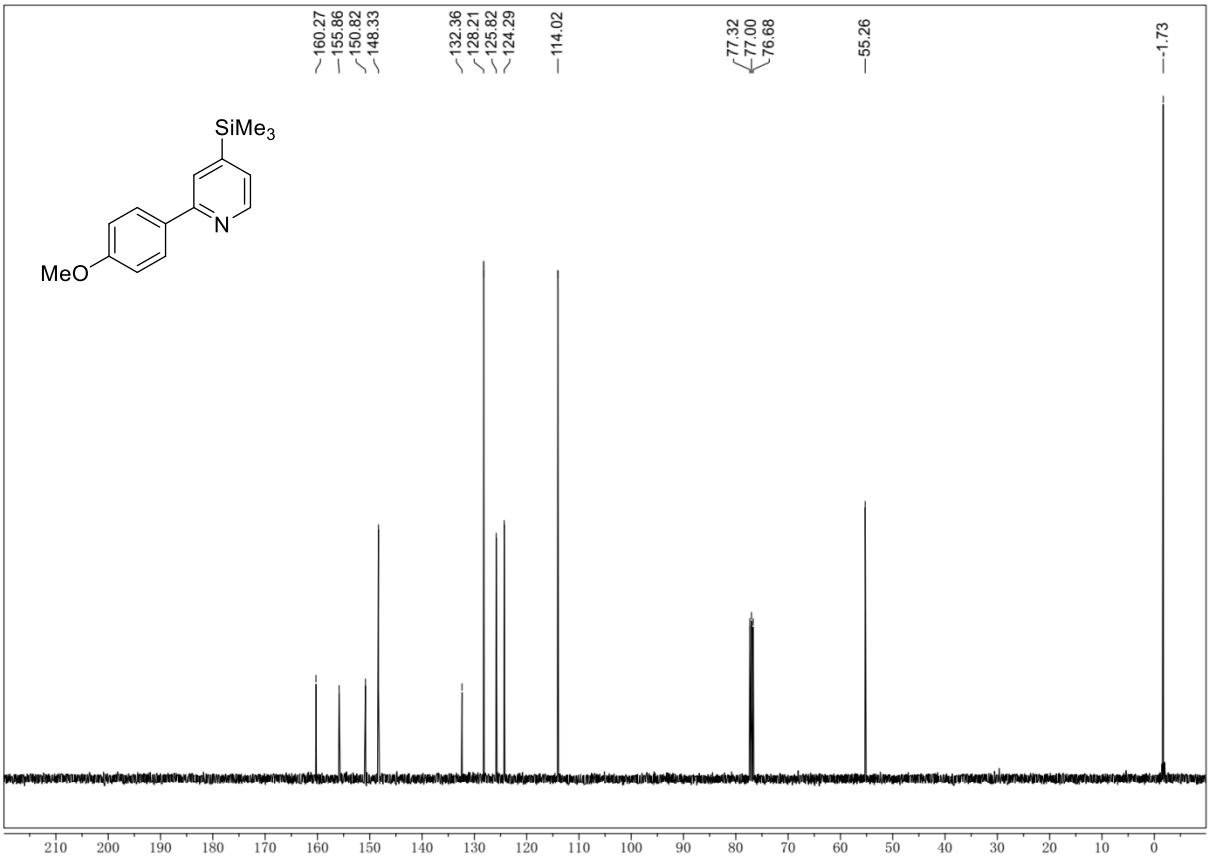
11 ^{13}C $CDCl_3$, 100 MHz



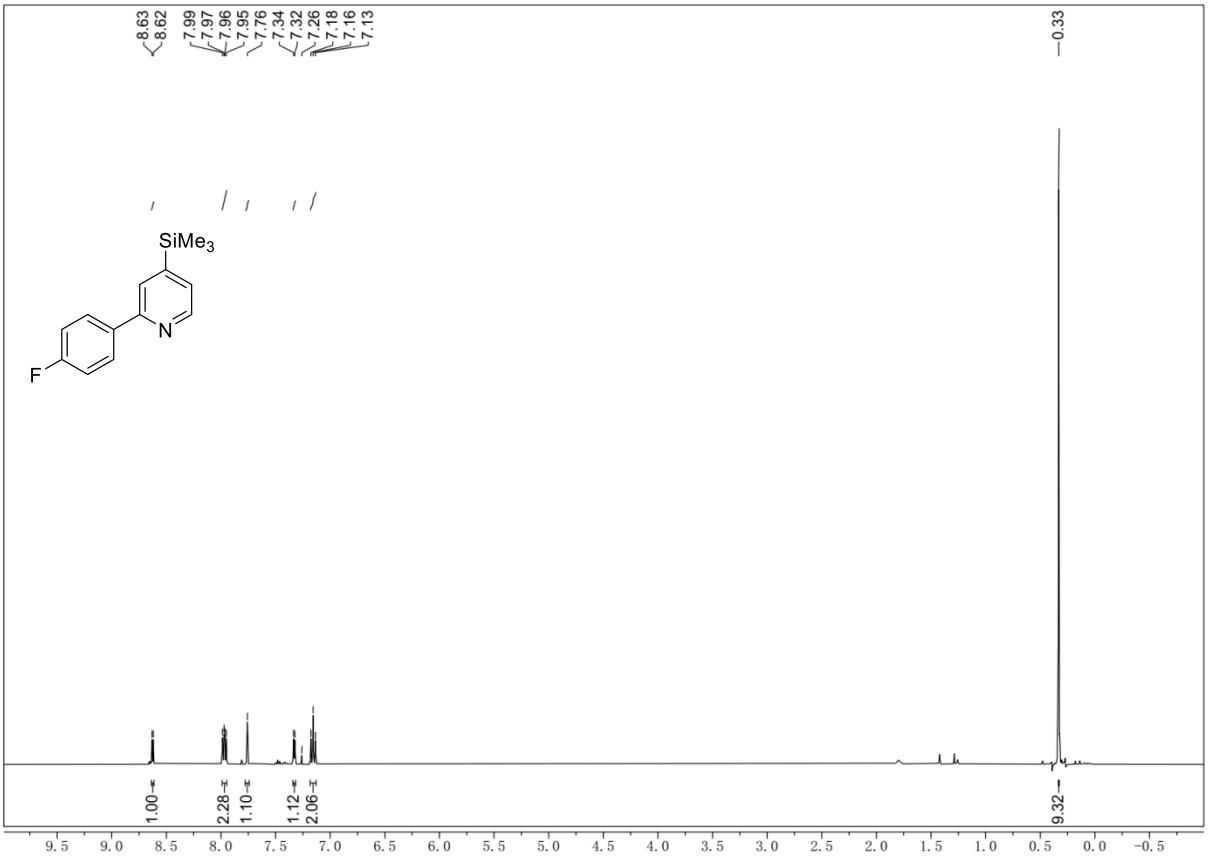
12 ^{1}H $CDCl_3$, 400 MHz



12 ^{13}C $CDCl_3$, 100 MHz



13 ^{1}H $CDCl_3$, 400 MHz



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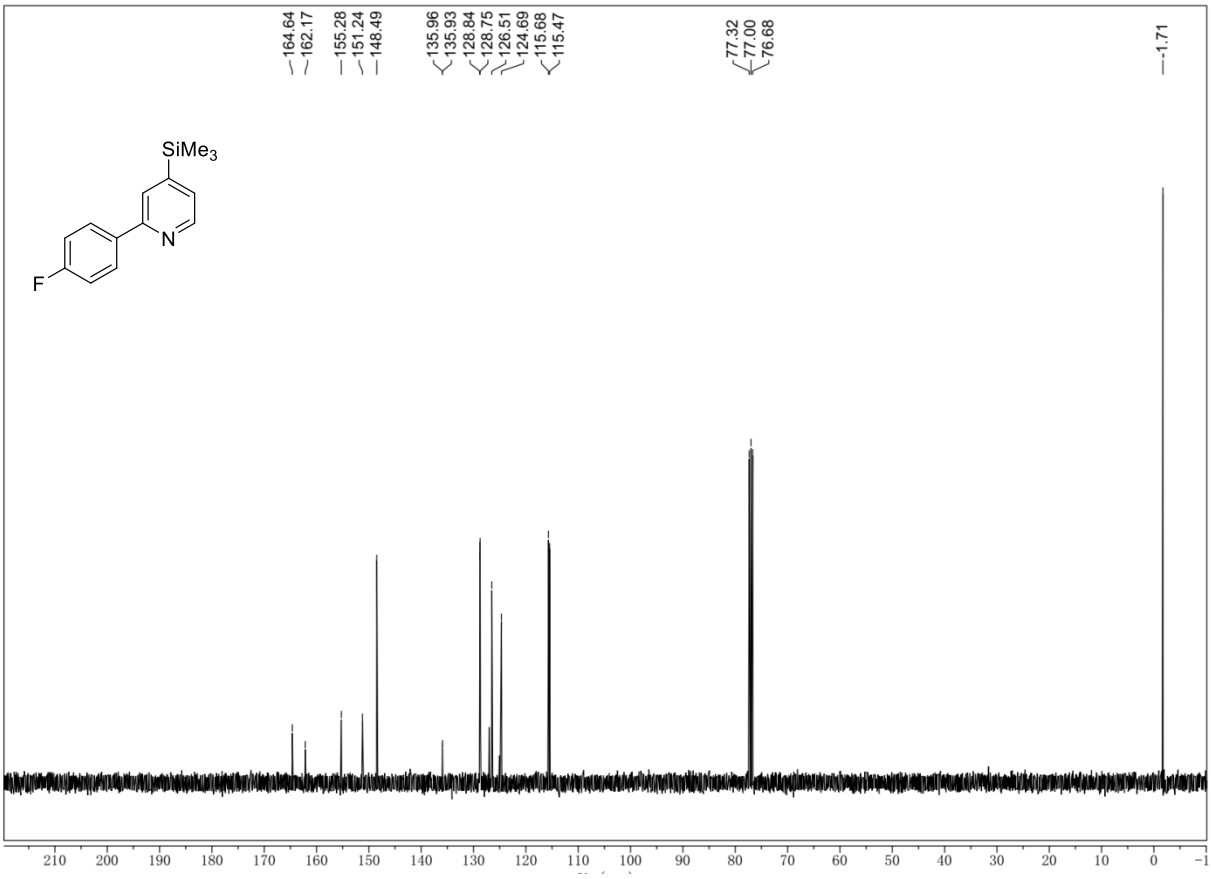
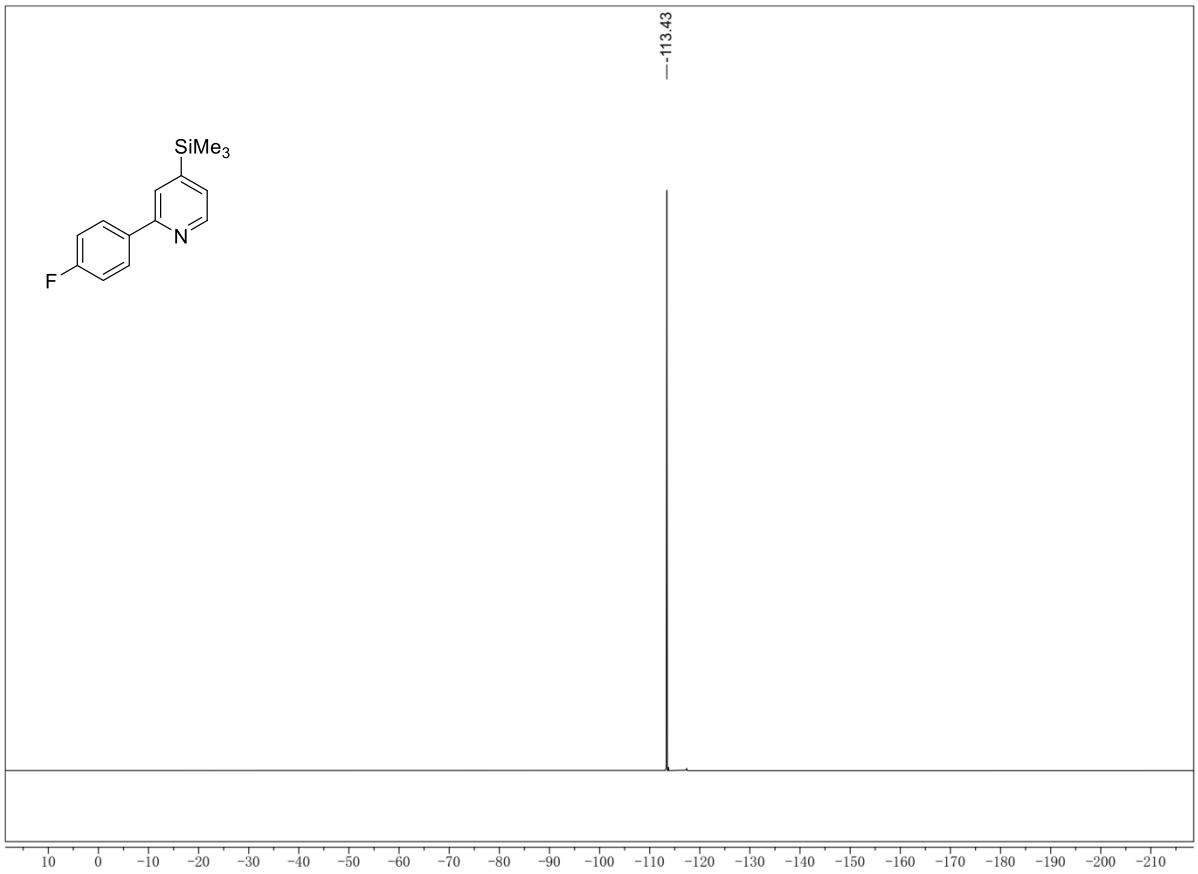
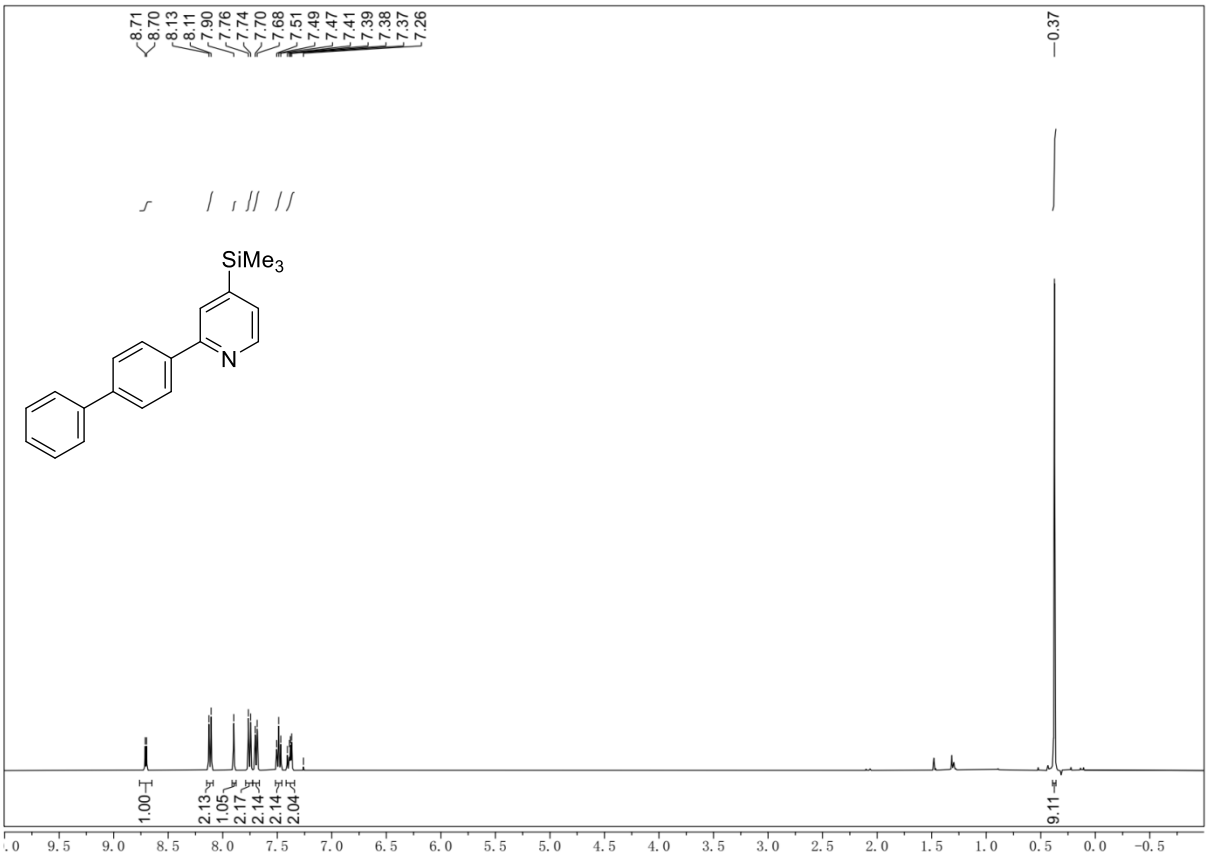


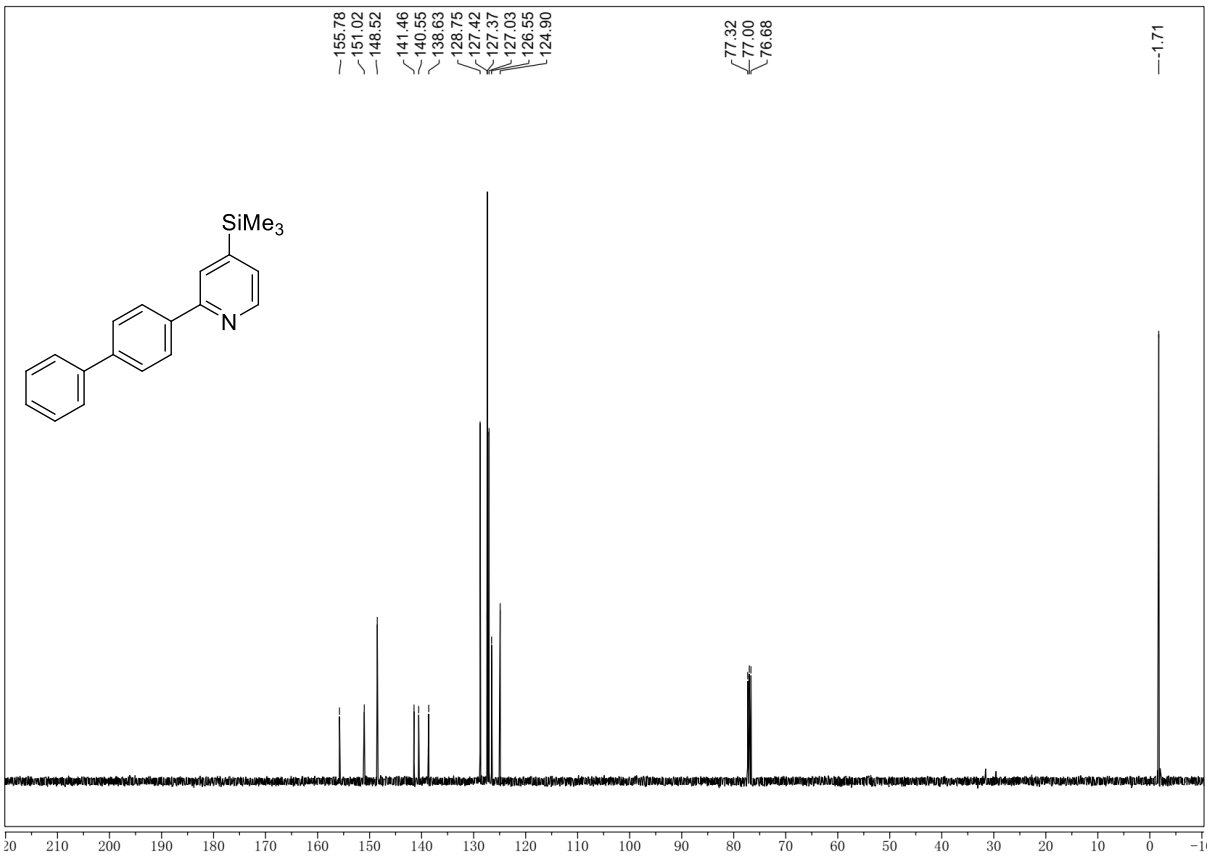
13 ^{19}F $CDCl_3$, 565 MHz



14 ^{1}H $CDCl_3$, 400 MHz



14 ^{13}C $CDCl_3$, 100 MHz



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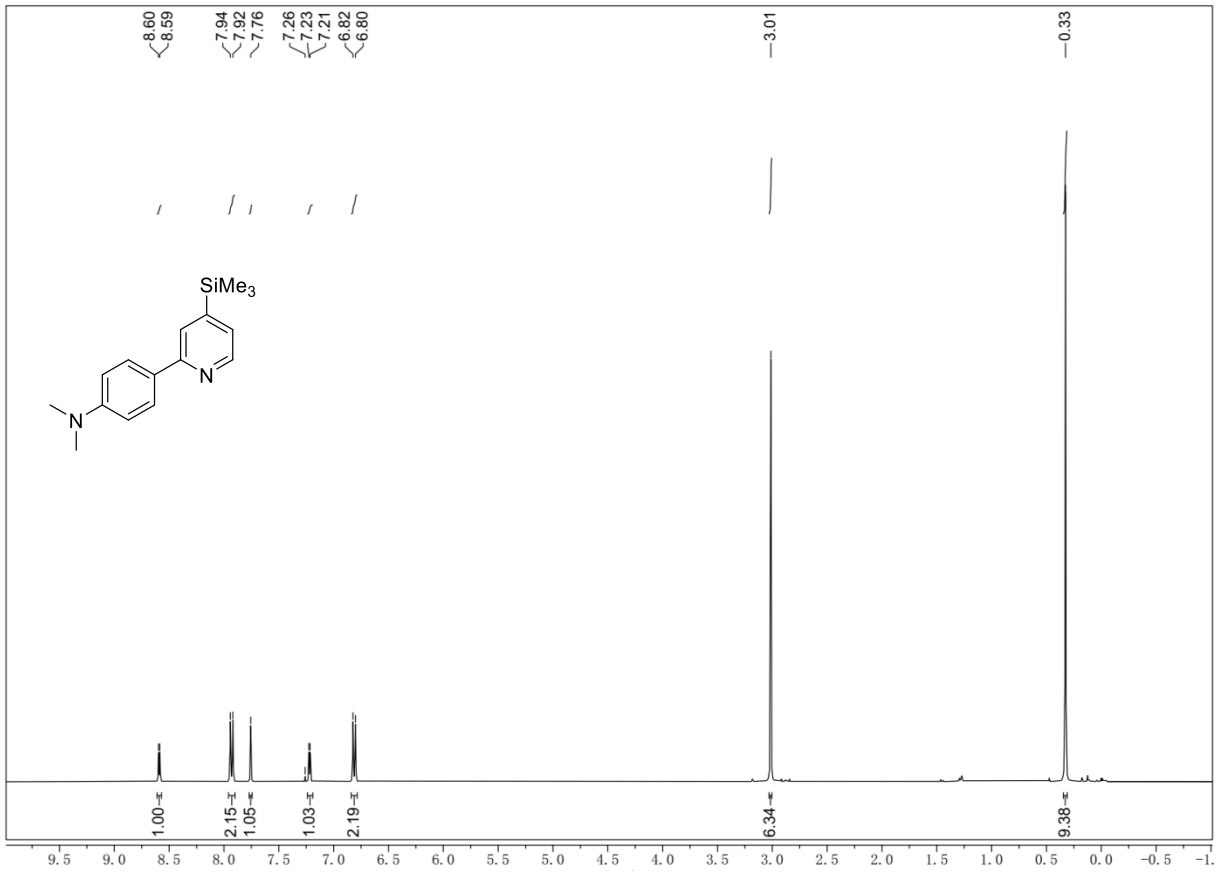
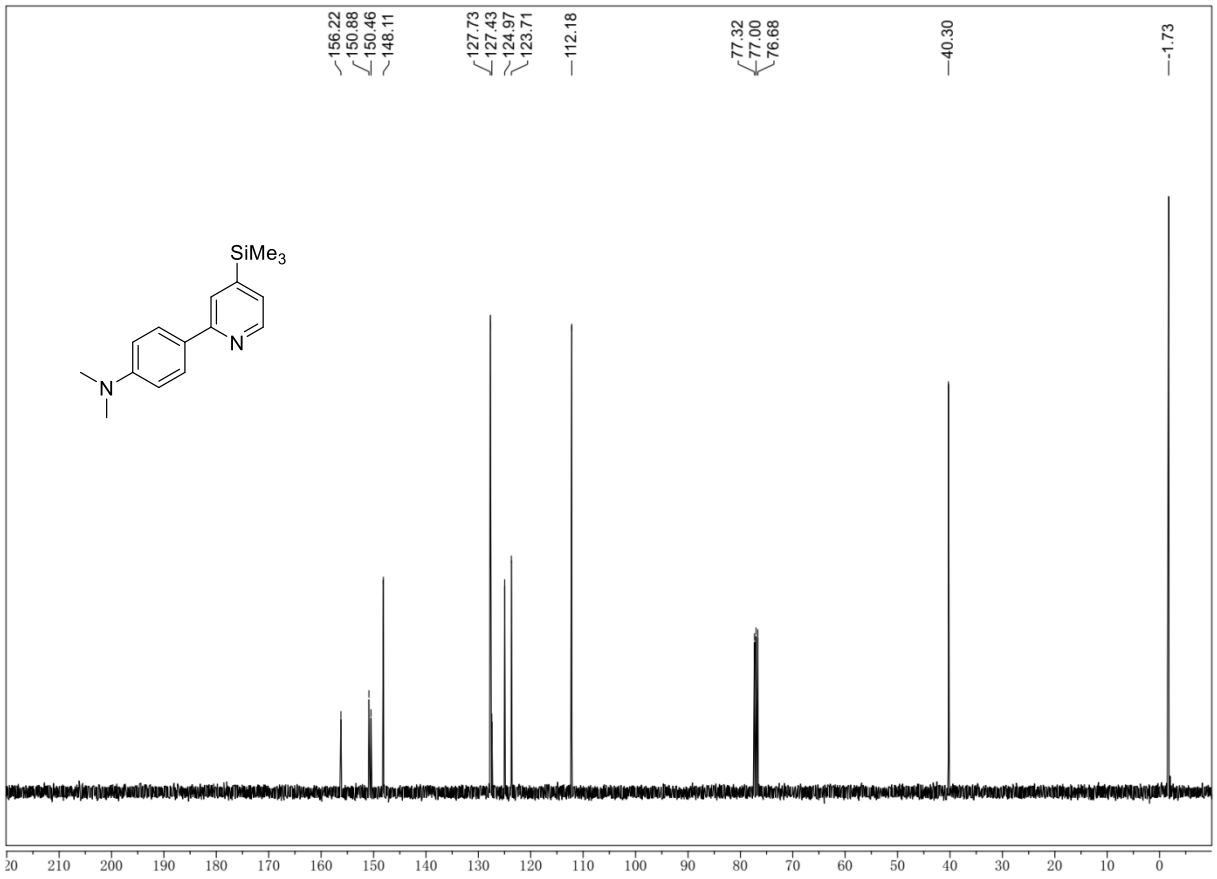
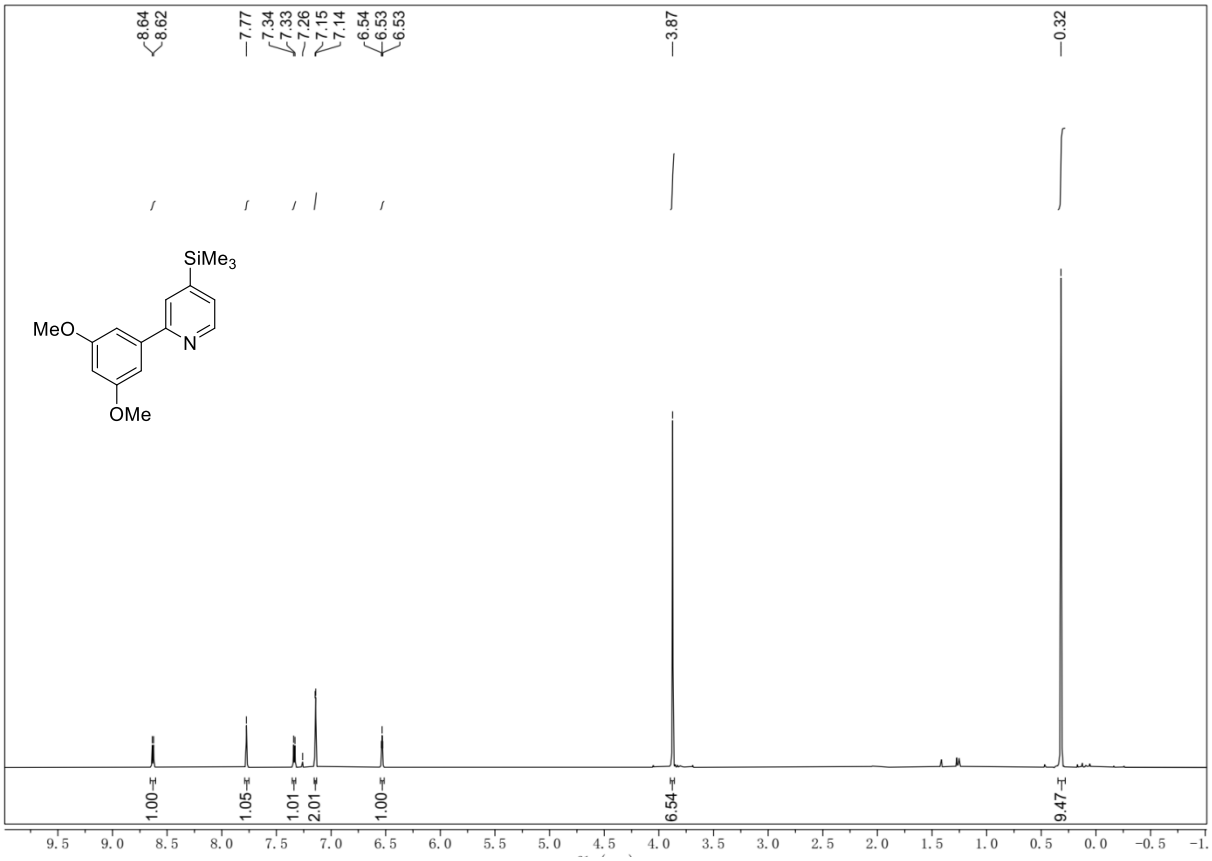


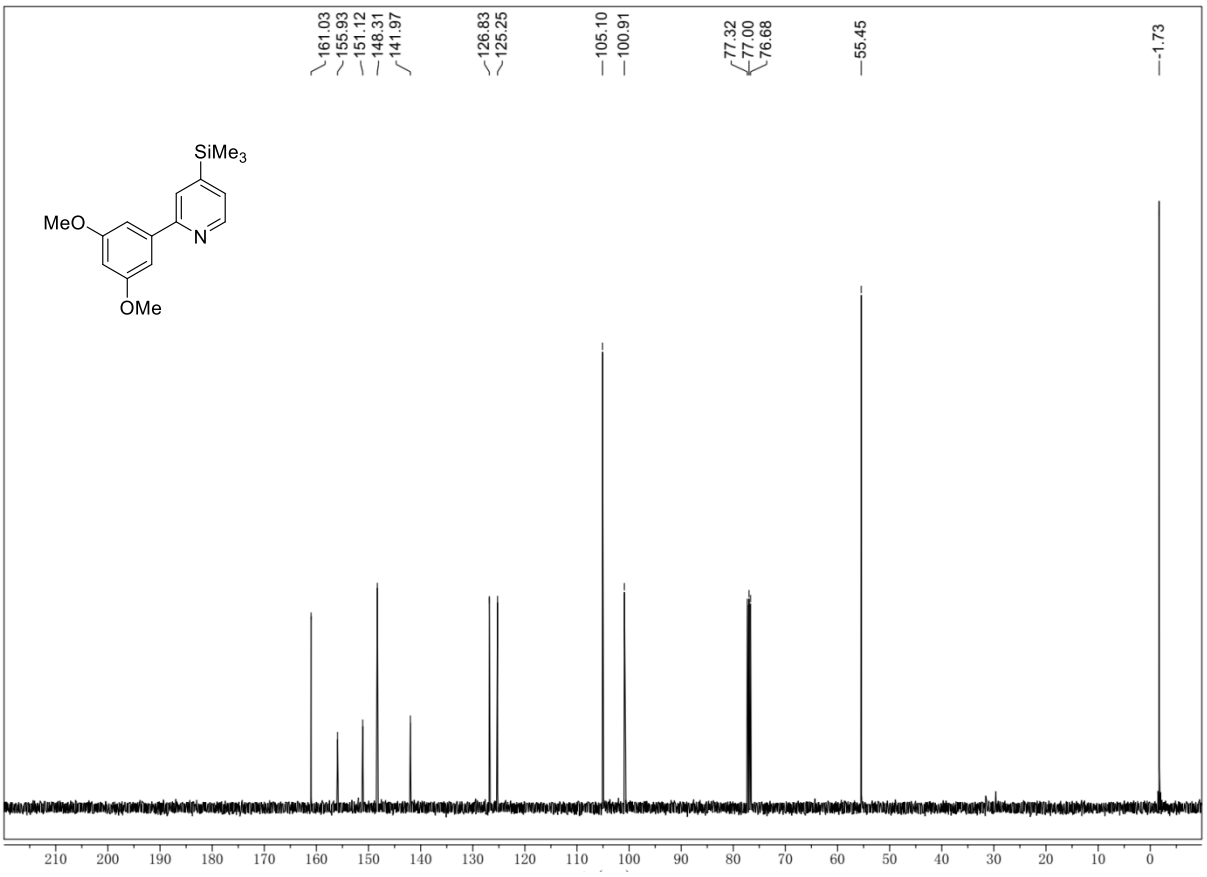
15 ^{13}C $CDCl_3$, 100 MHz



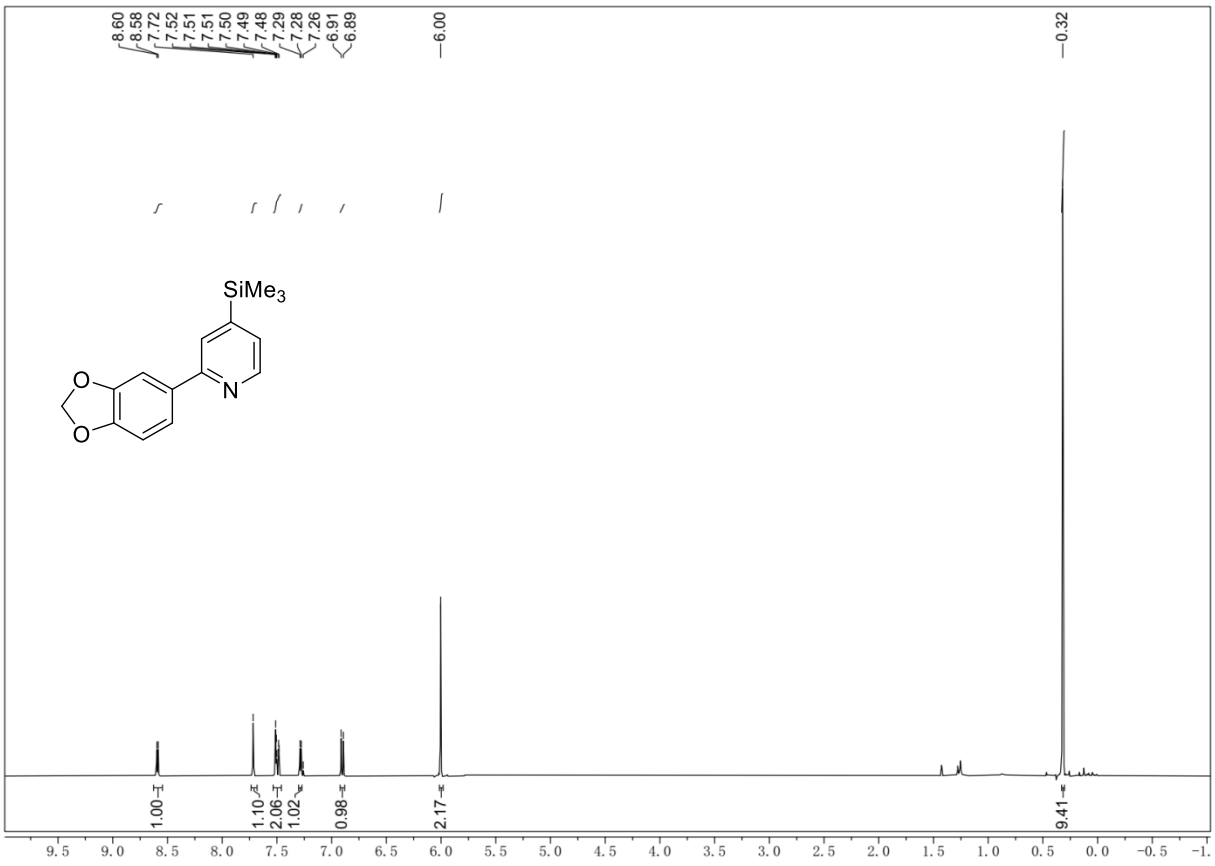
16 ^{1}H $CDCl_3$, 400 MHz



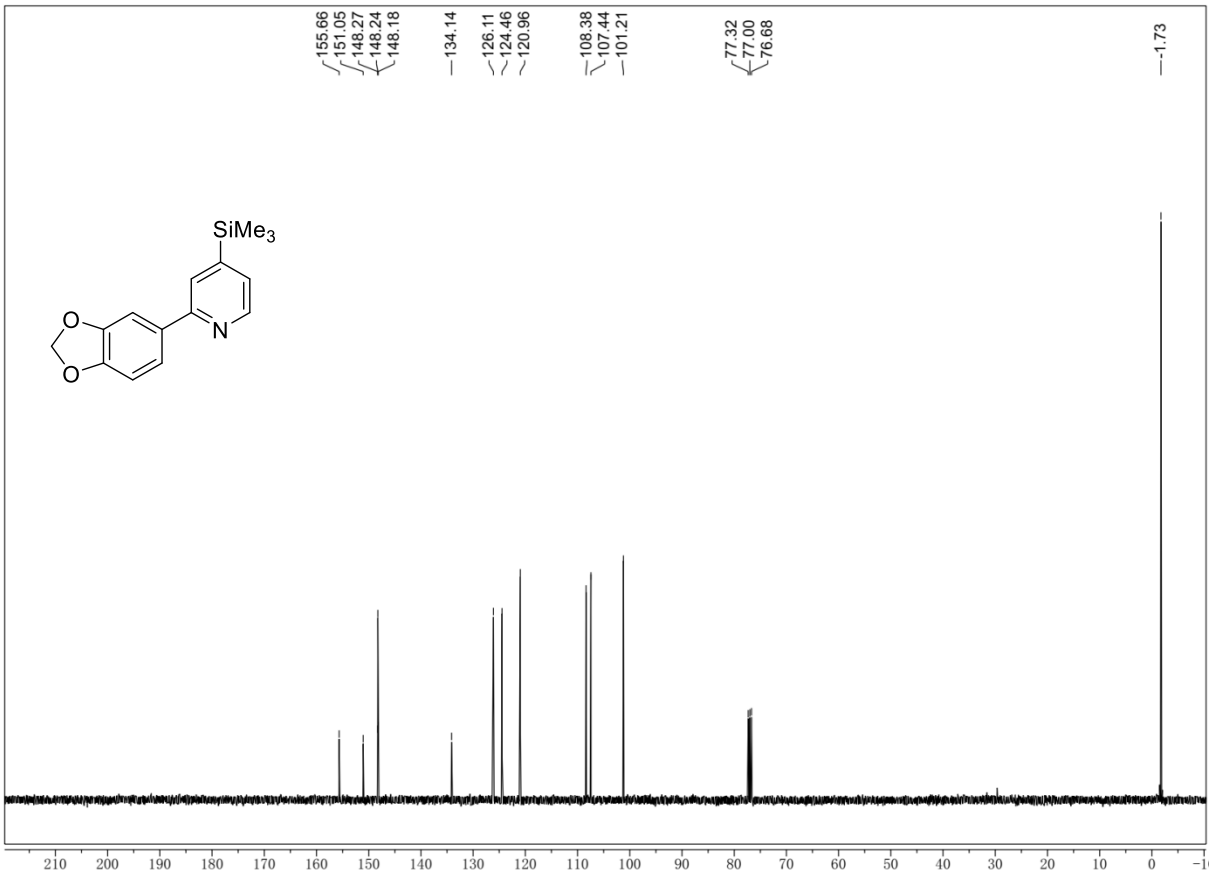
16 ^{13}C $CDCl_3$, 100 MHz



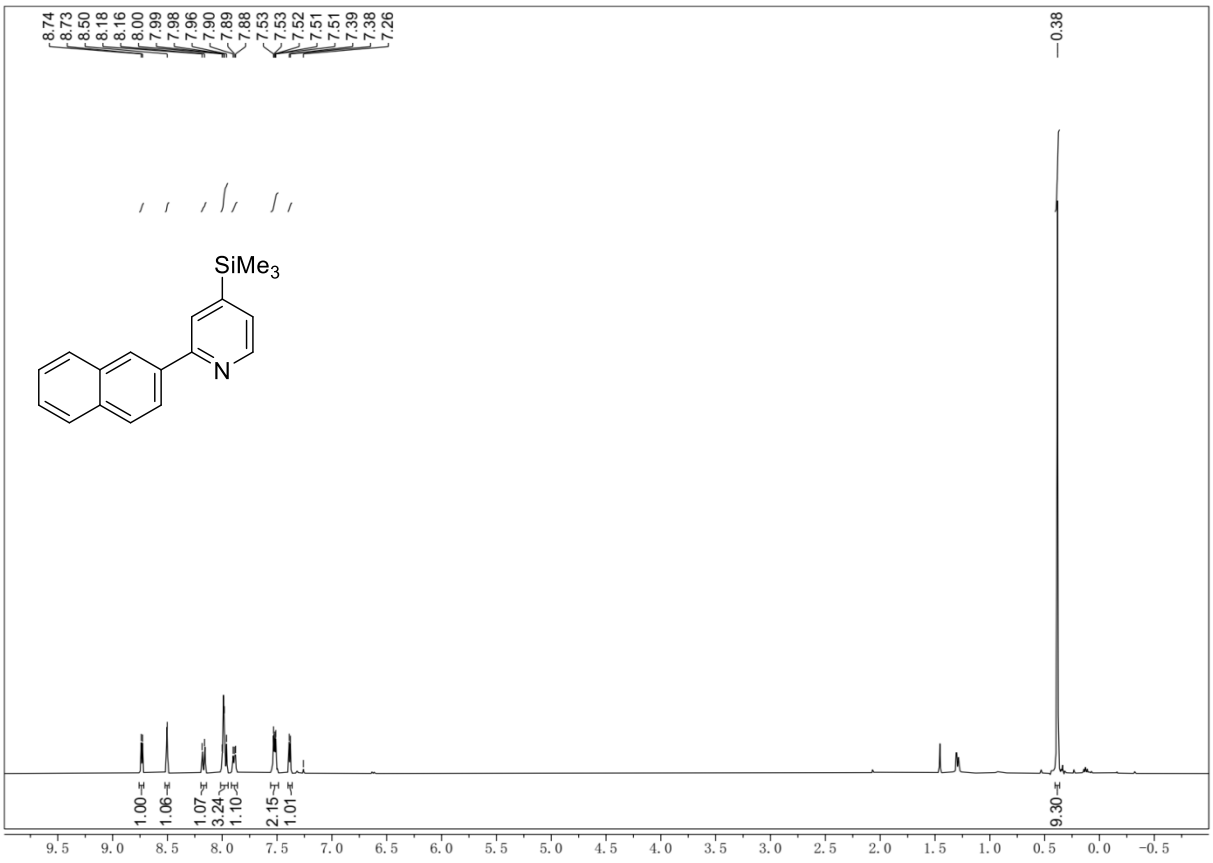
17 ^{1}H $CDCl_3$, 400 MHz



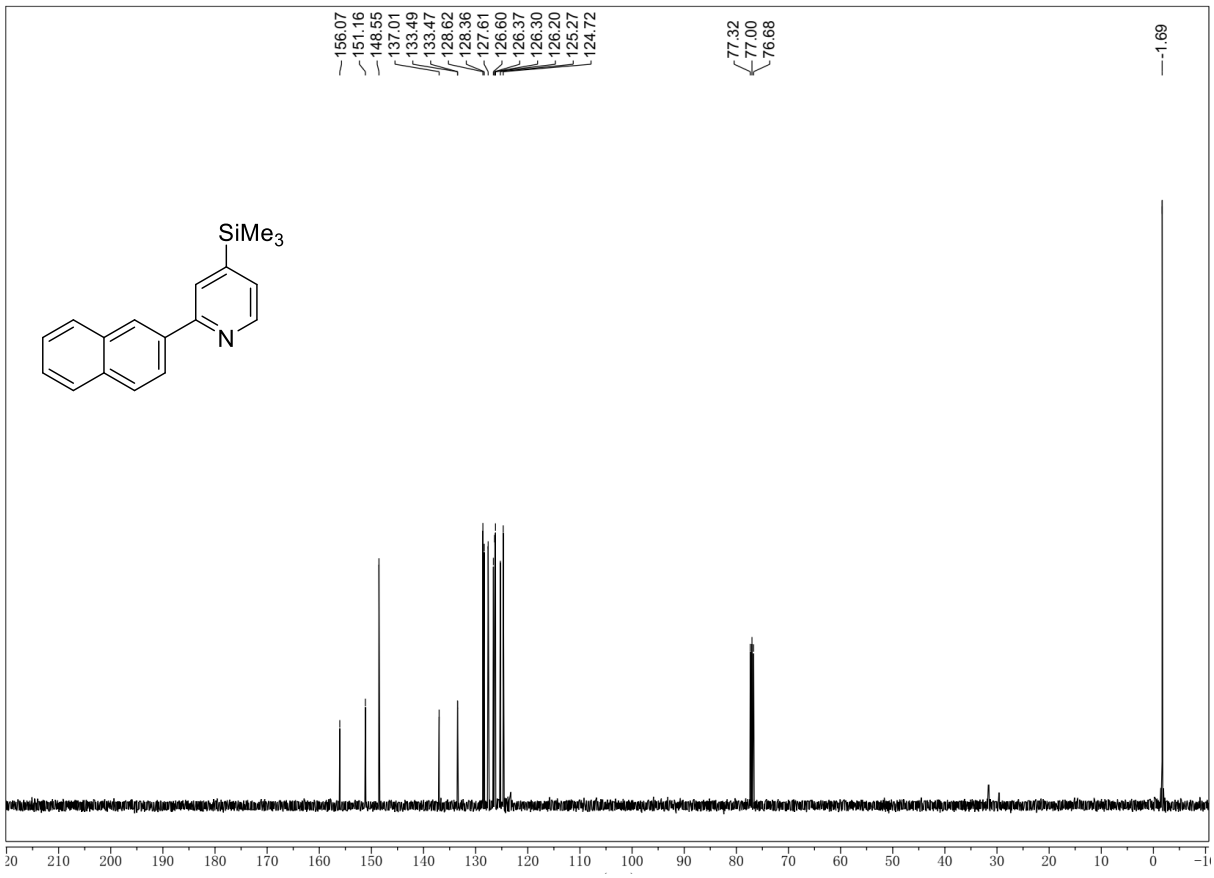
17 ^{13}C $CDCl_3$, 100 MHz



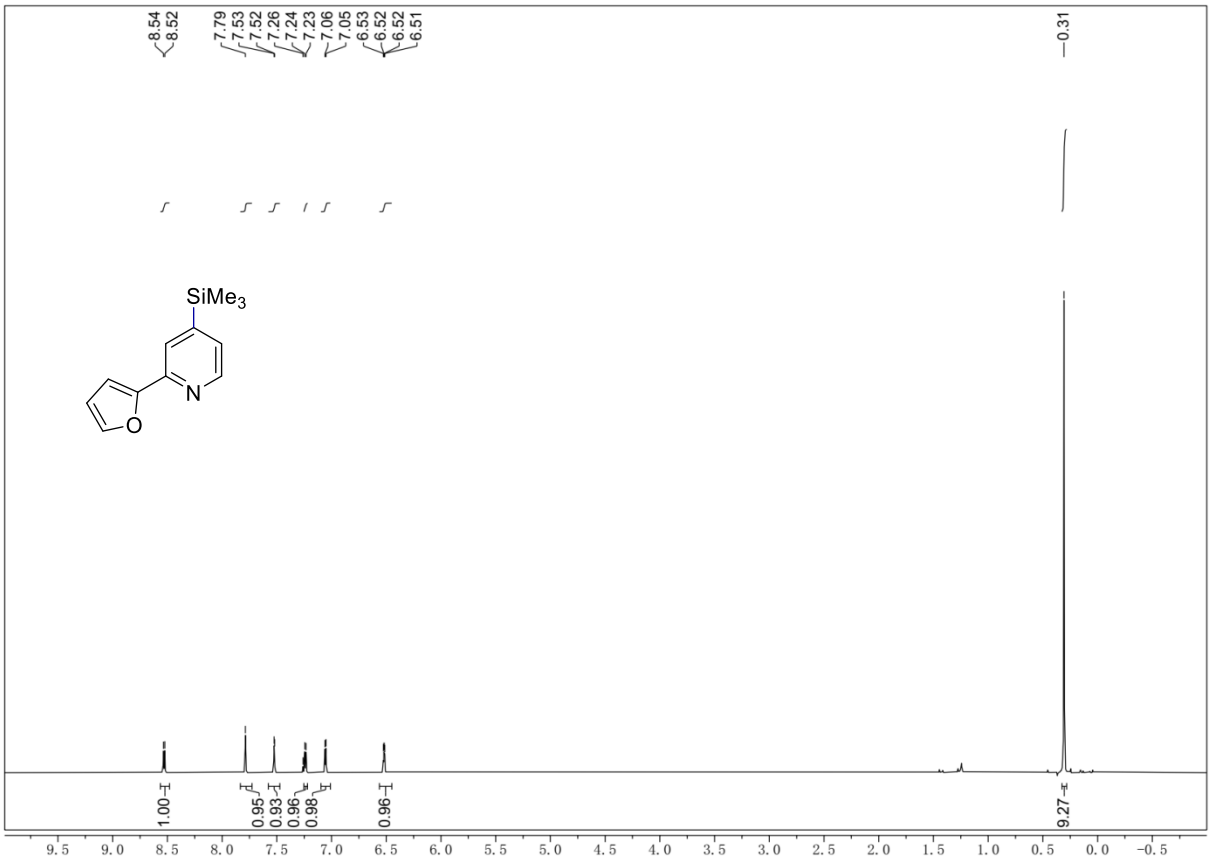
18 ^{1}H $CDCl_3$, 400 MHz



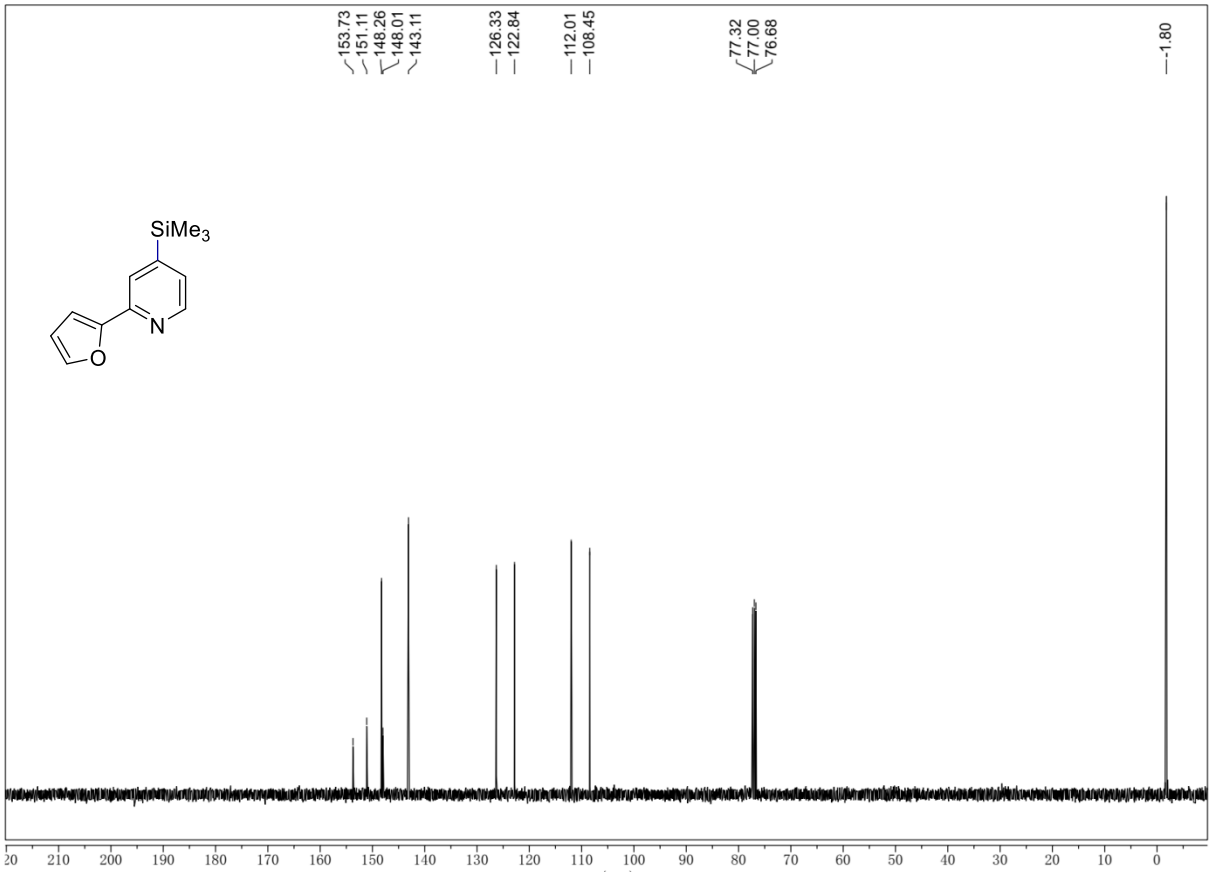
18 ^{13}C $CDCl_3$, 100 MHz



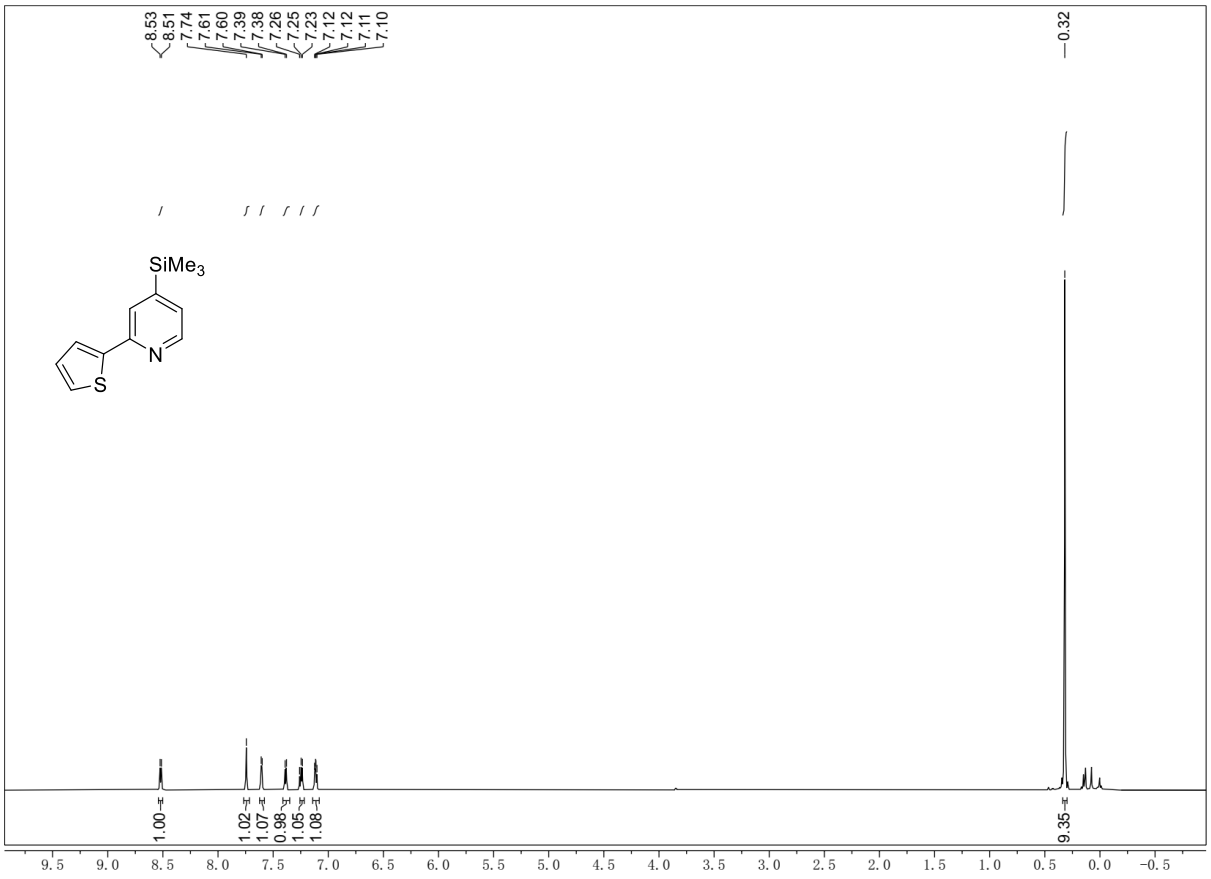
19 ^{1}H $CDCl_3$, 400 MHz



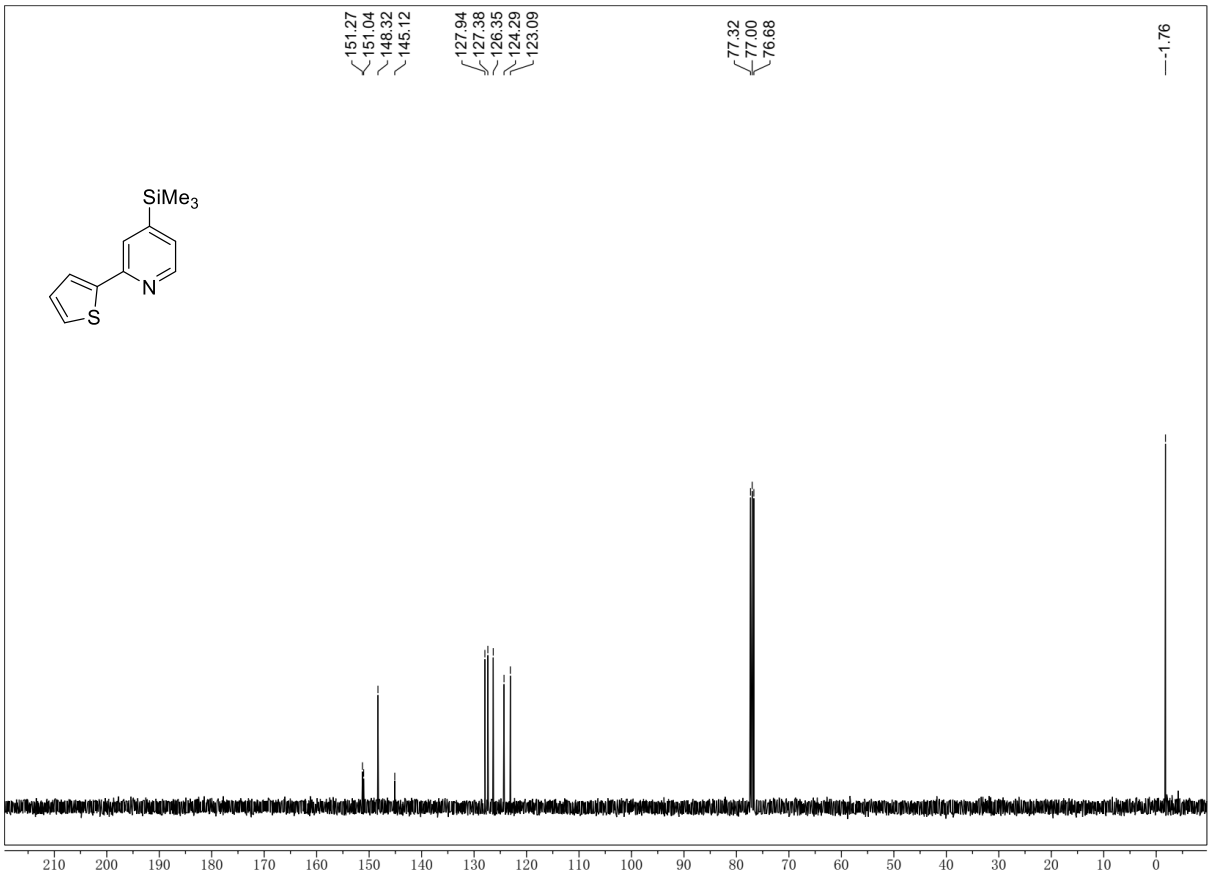
19 ^{13}C $CDCl_3$, 100 MHz



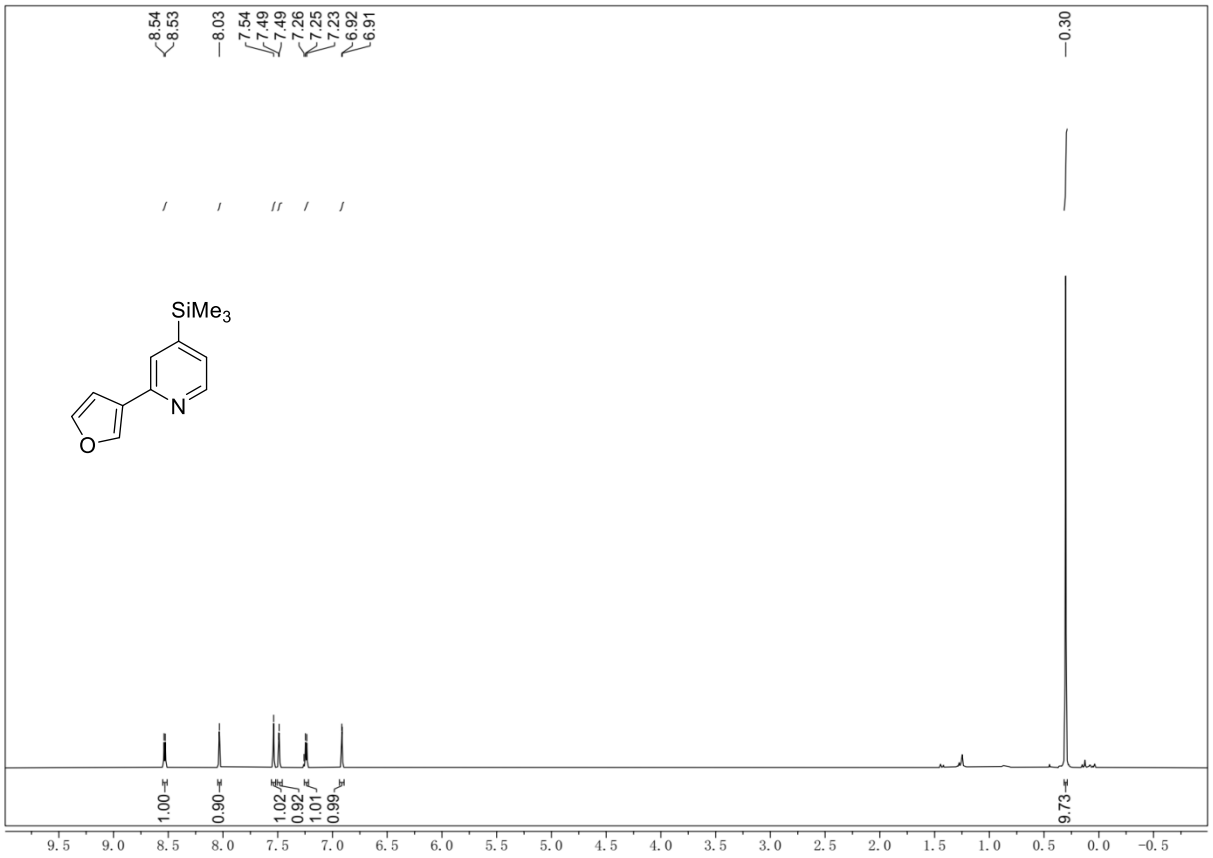
20 ^{1}H $CDCl_3$, 400 MHz



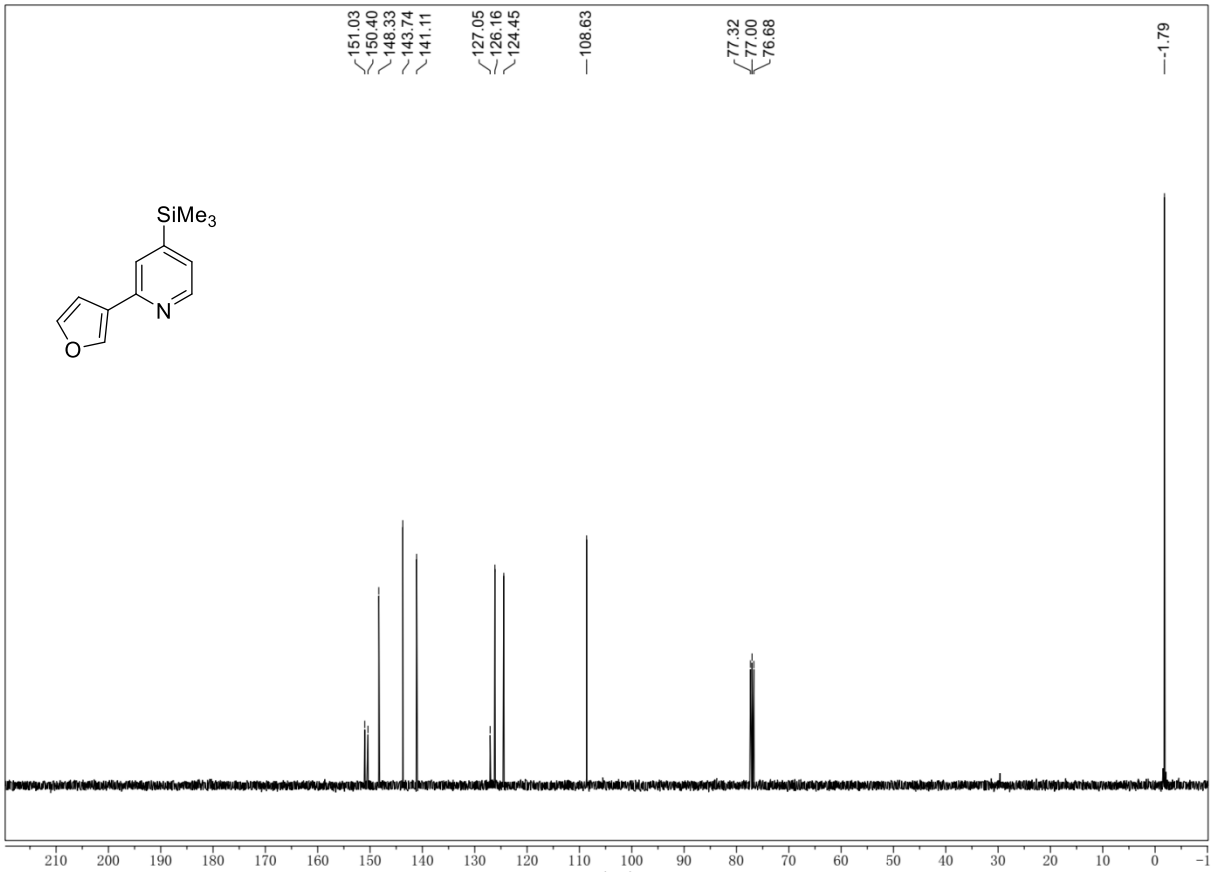
20 ^{13}C $CDCl_3$, 100 MHz



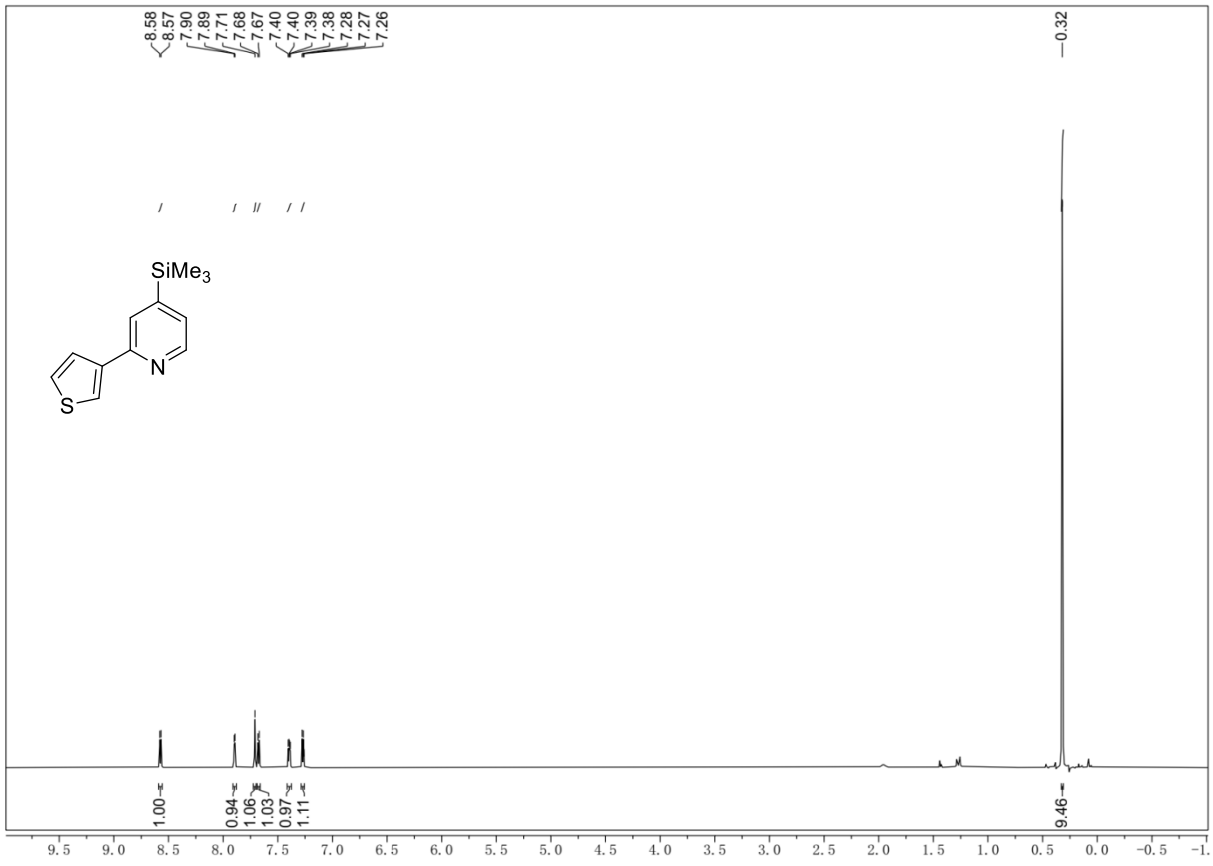
21 ^{1}H $CDCl_3$, 400 MHz



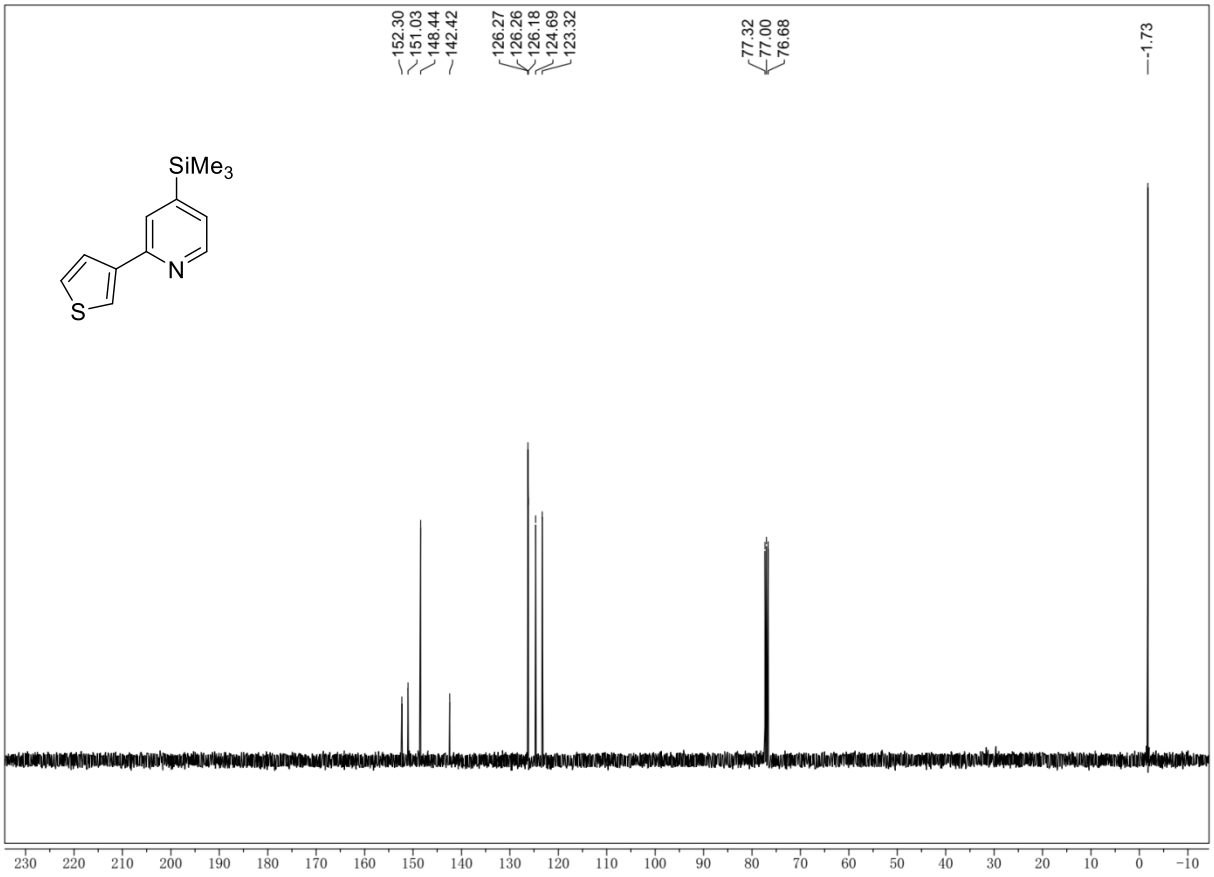
21 ^{13}C $CDCl_3$, 100 MHz



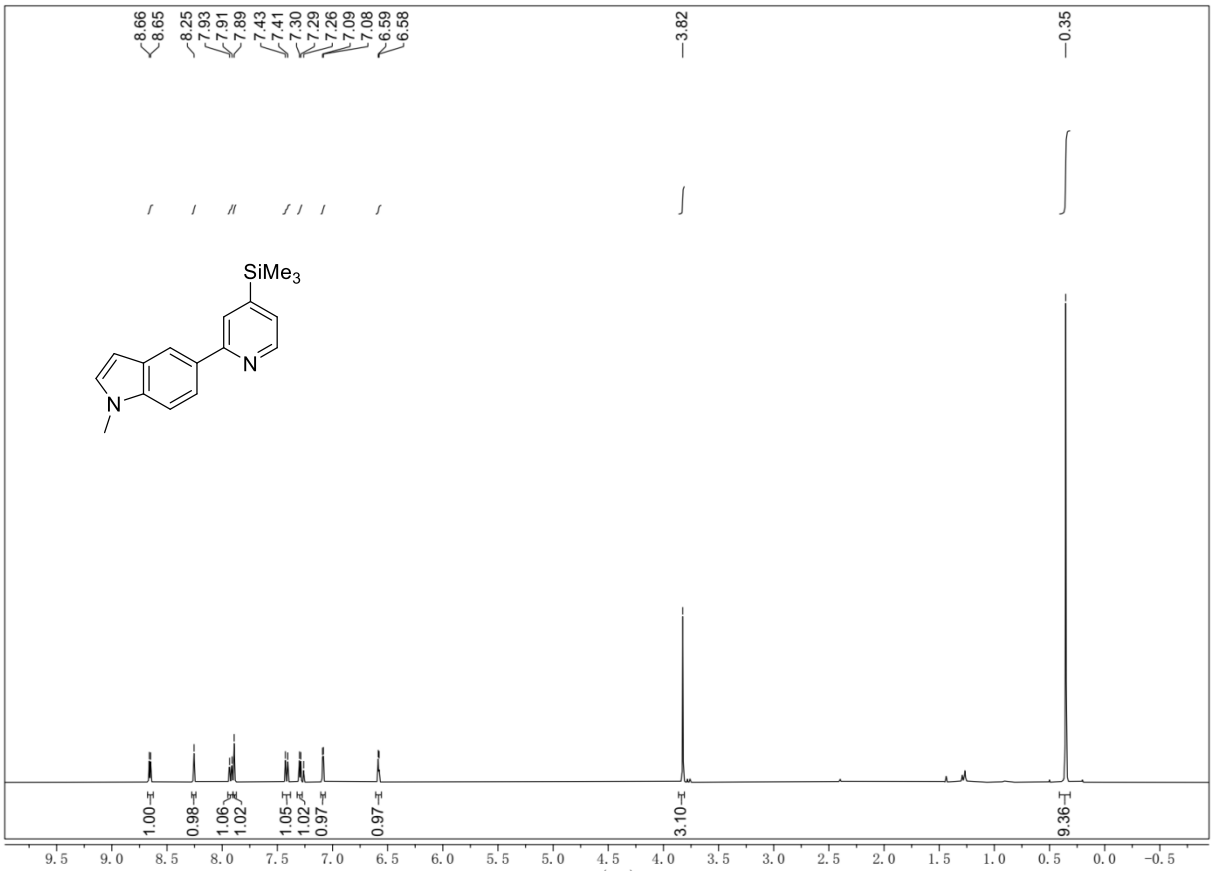
22 ^{1}H $CDCl_3$, 400 MHz



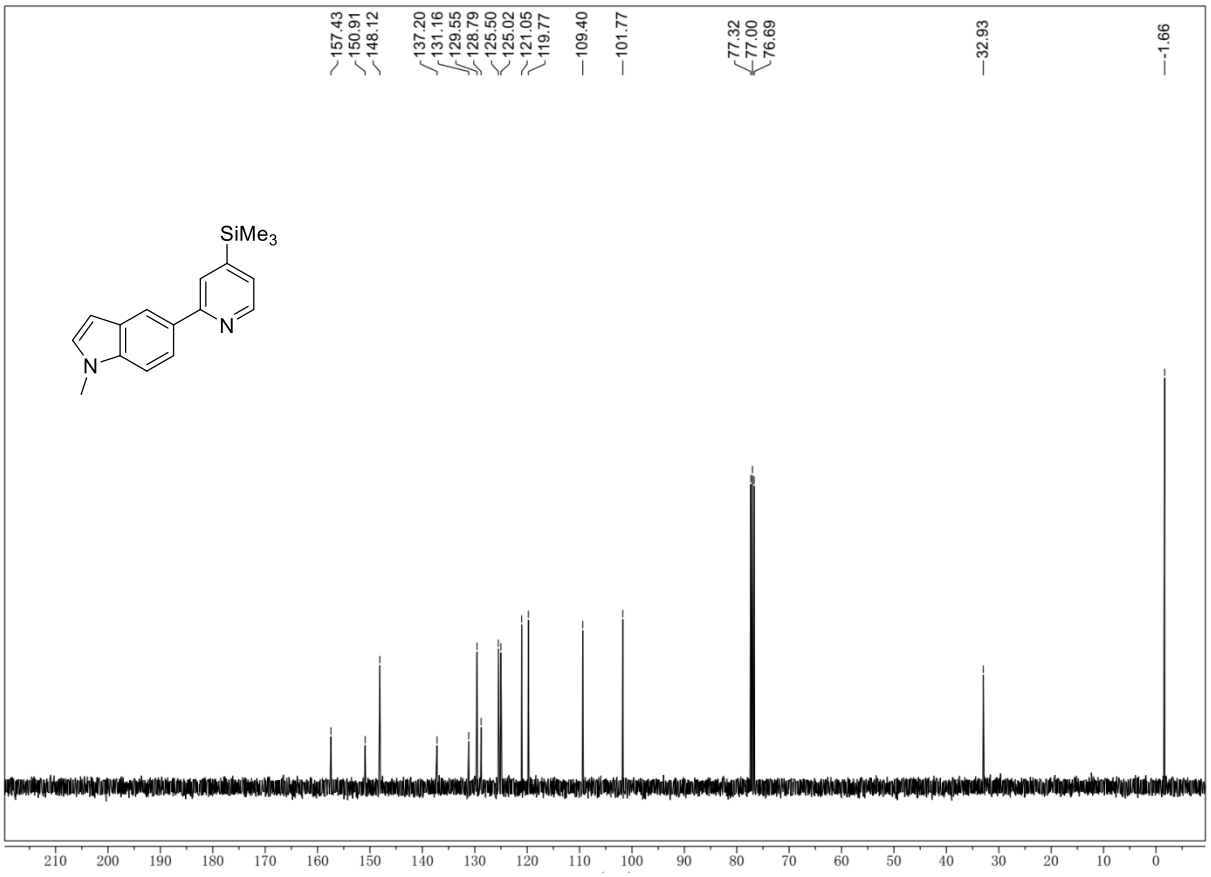
22 ^{13}C $CDCl_3$, 100 MHz



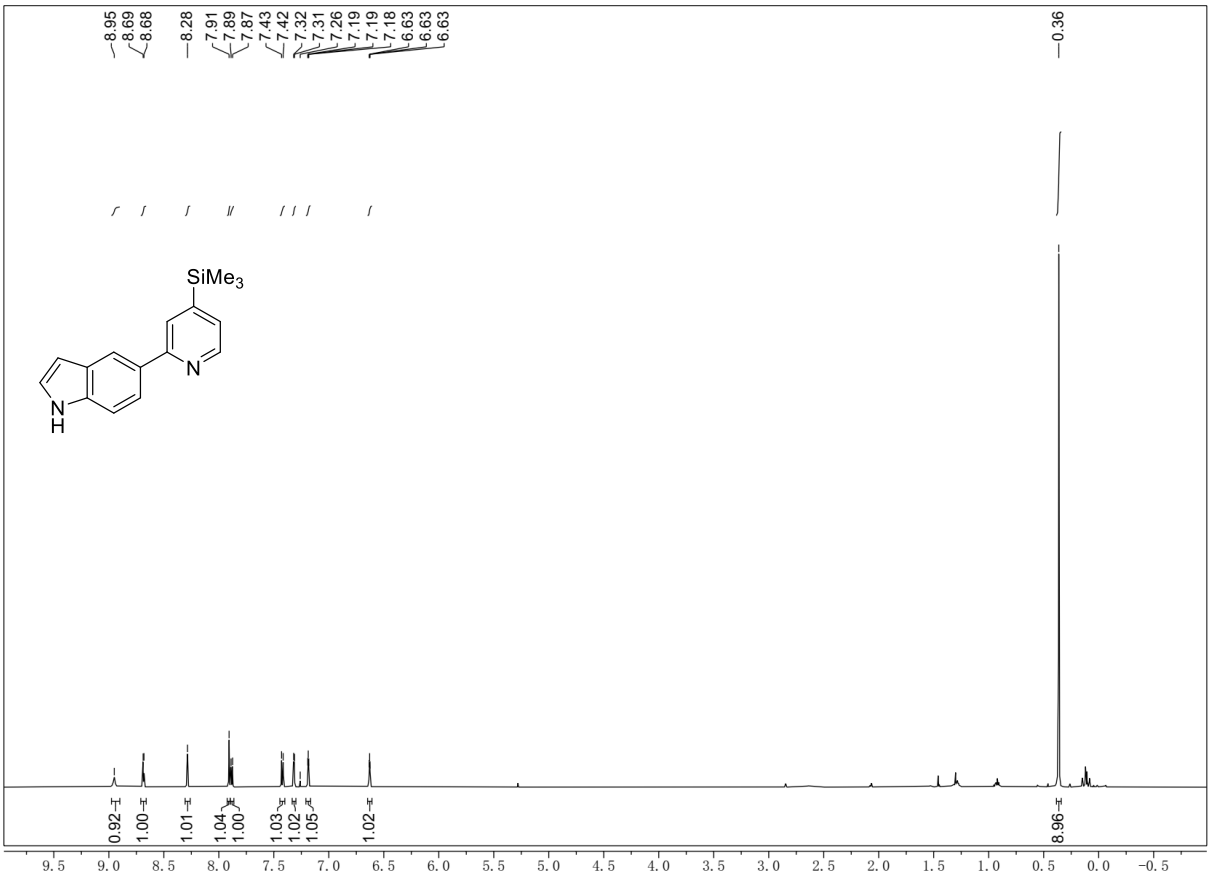
23 ^{1}H $CDCl_3$, 400 MHz



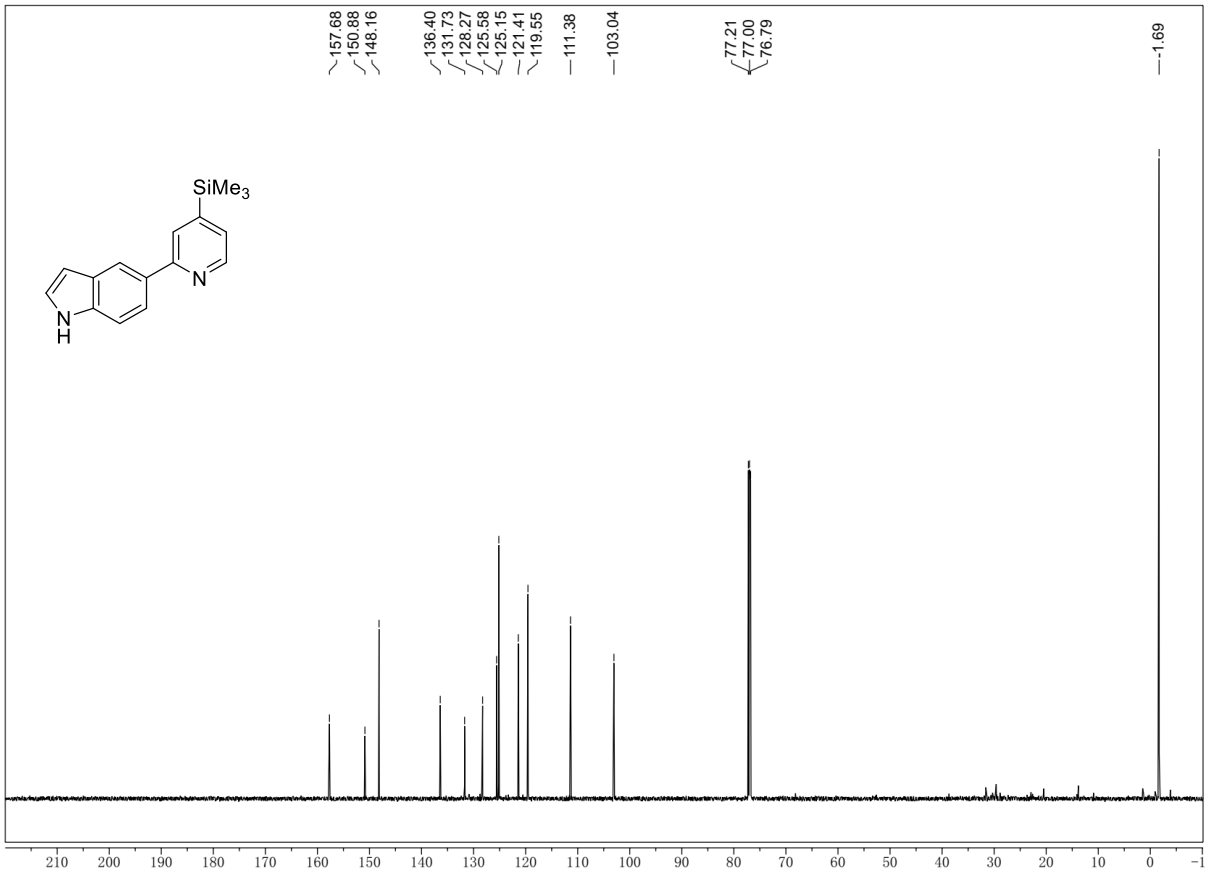
23 ^{13}C $CDCl_3$, 100 MHz



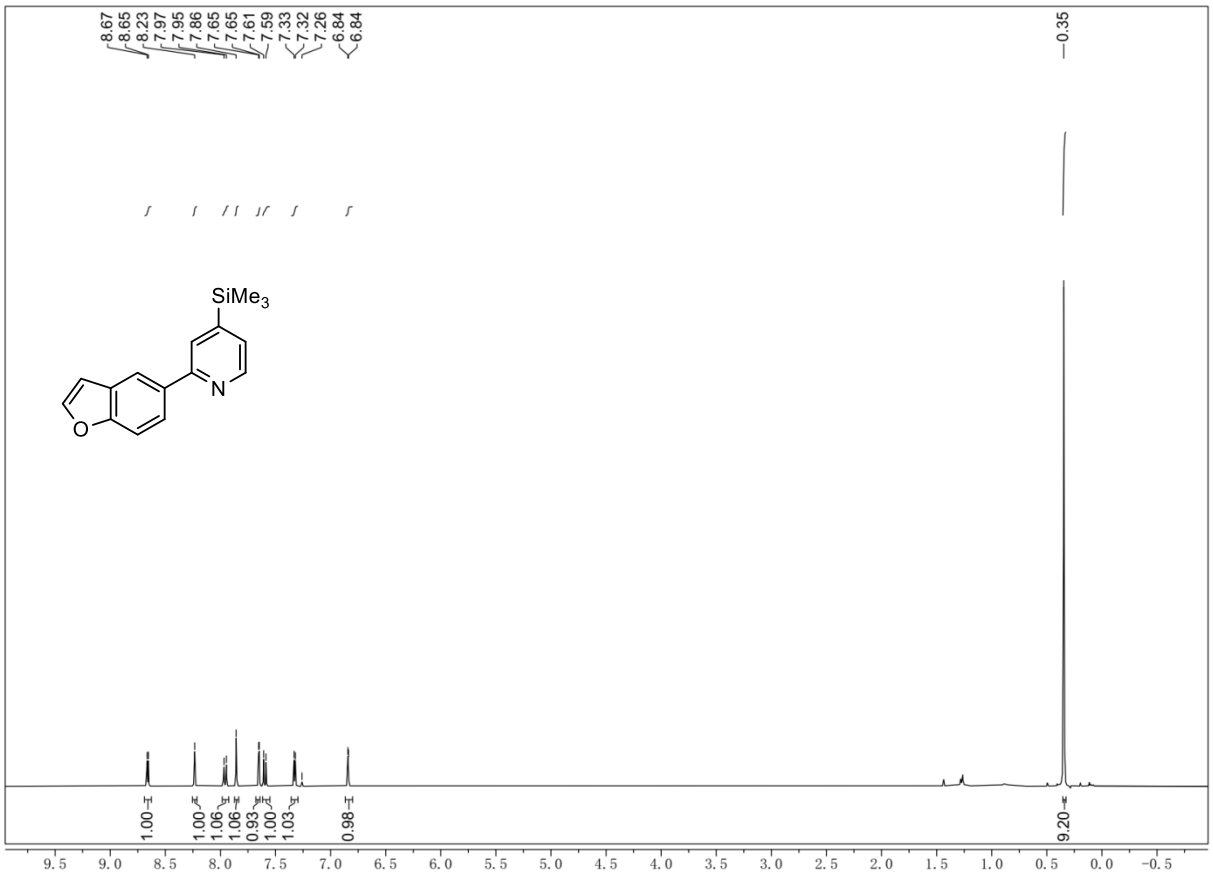
24 ^{1}H $CDCl_3$, 600 MHz



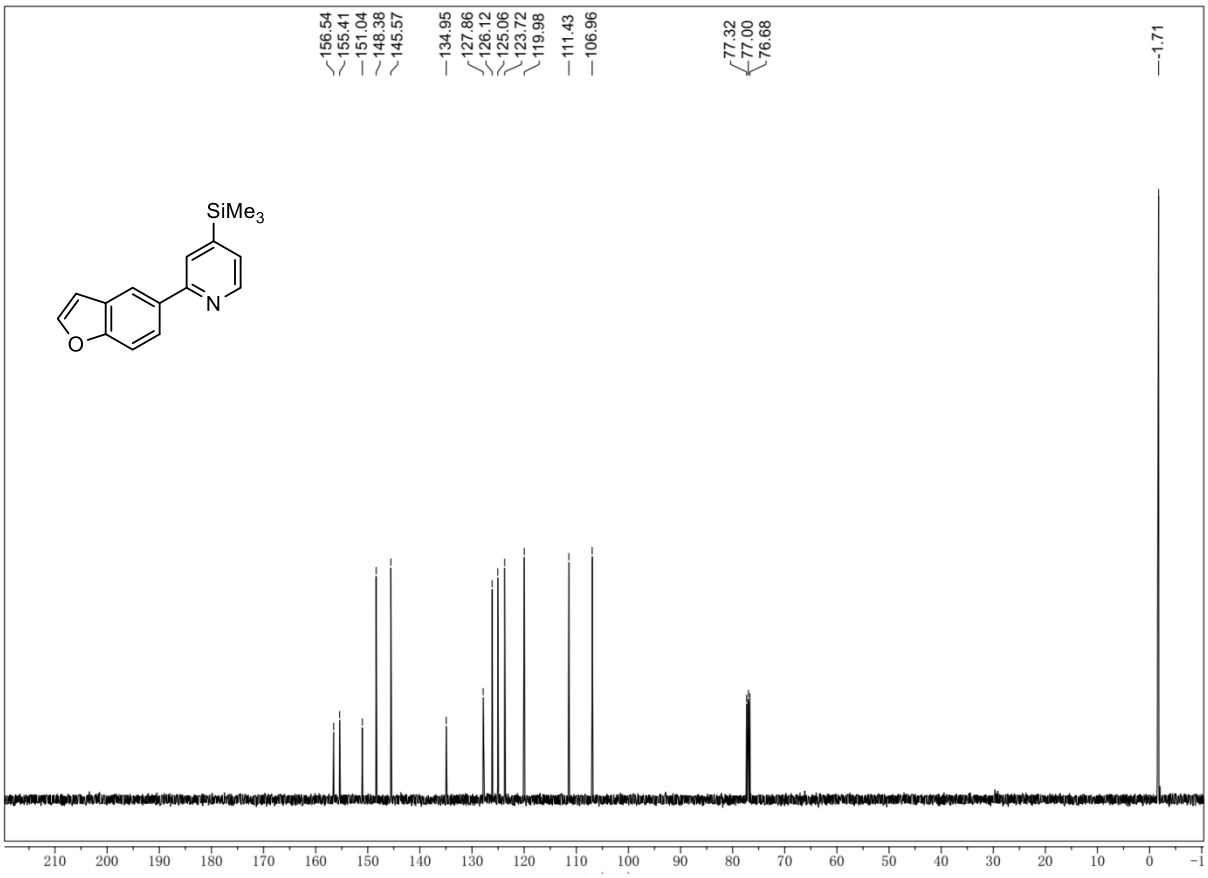
24 ^{13}C $CDCl_3$, 151 MHz



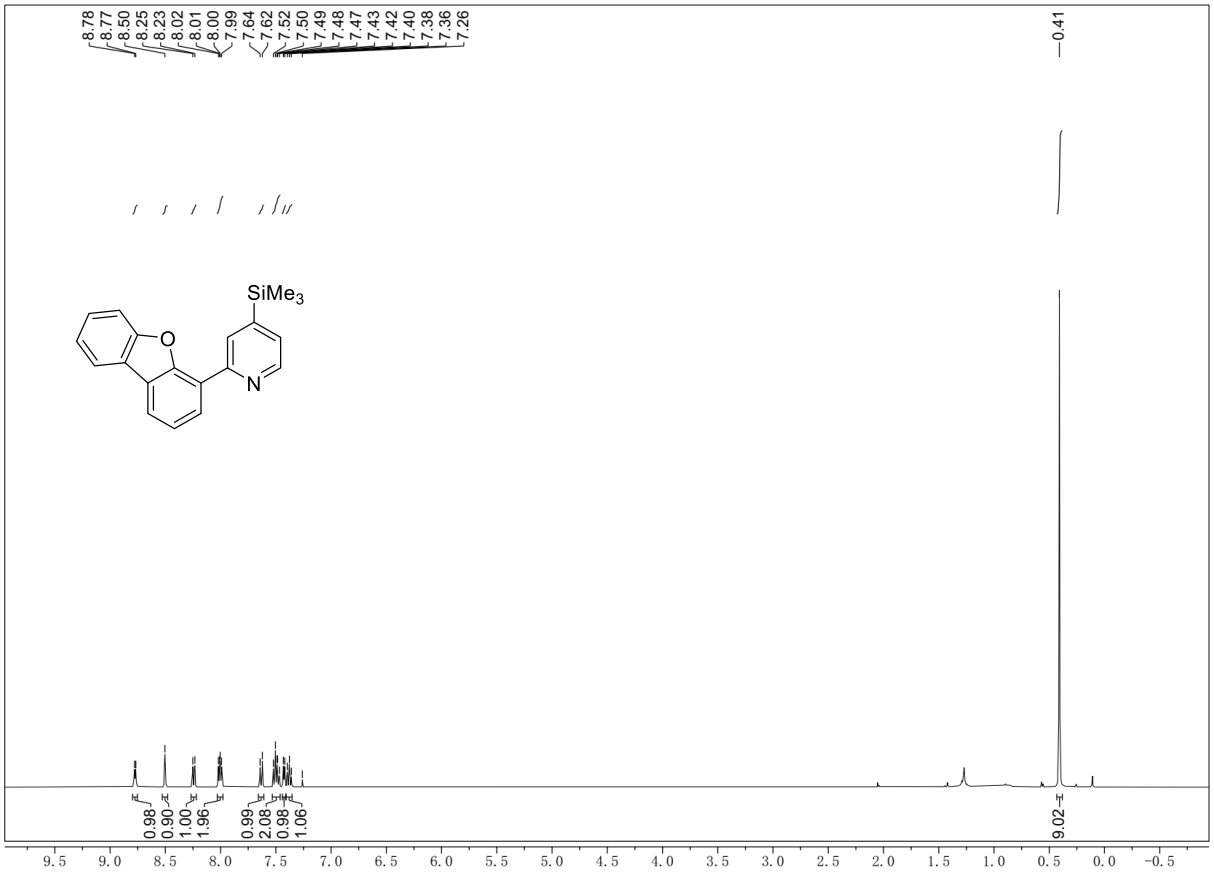
25 ^{1}H $CDCl_3$, 400 MHz



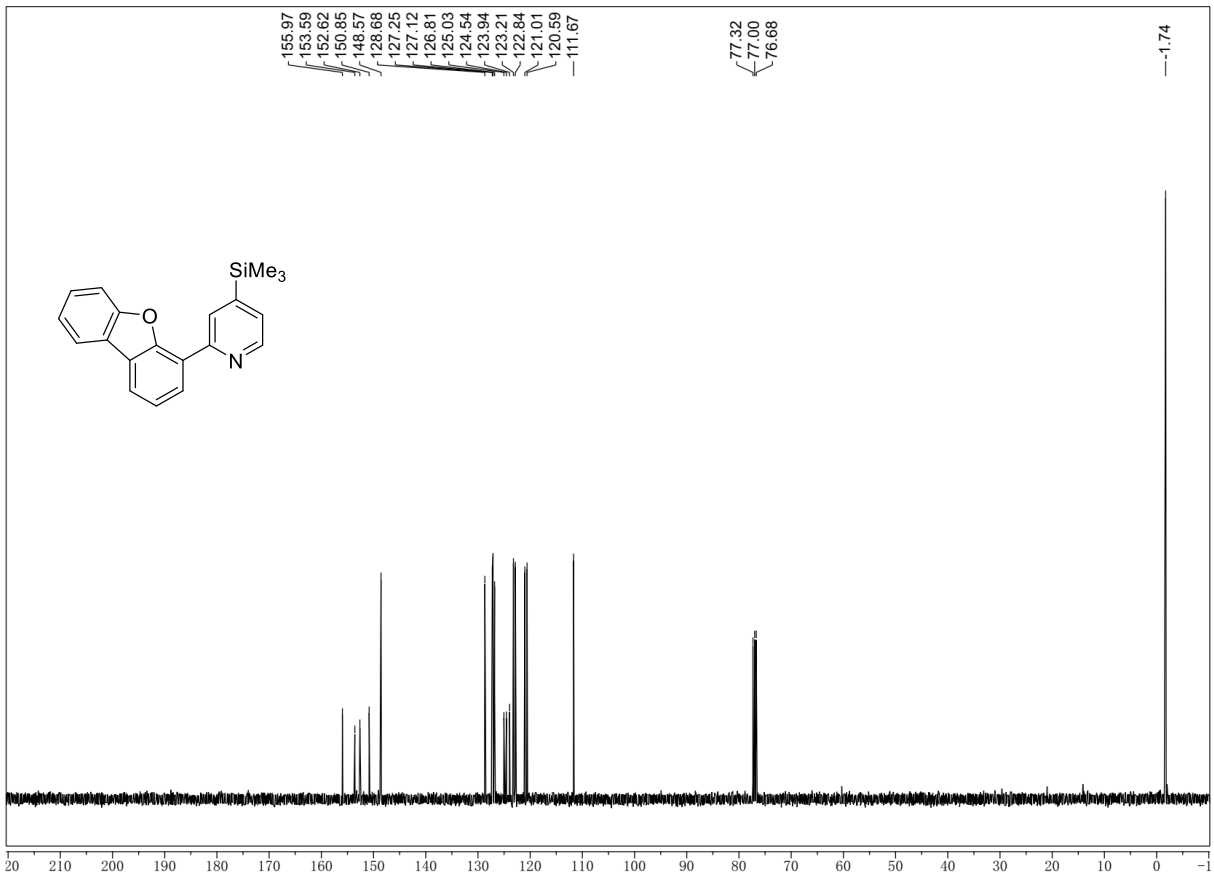
25 ^{13}C $CDCl_3$, 100 MHz



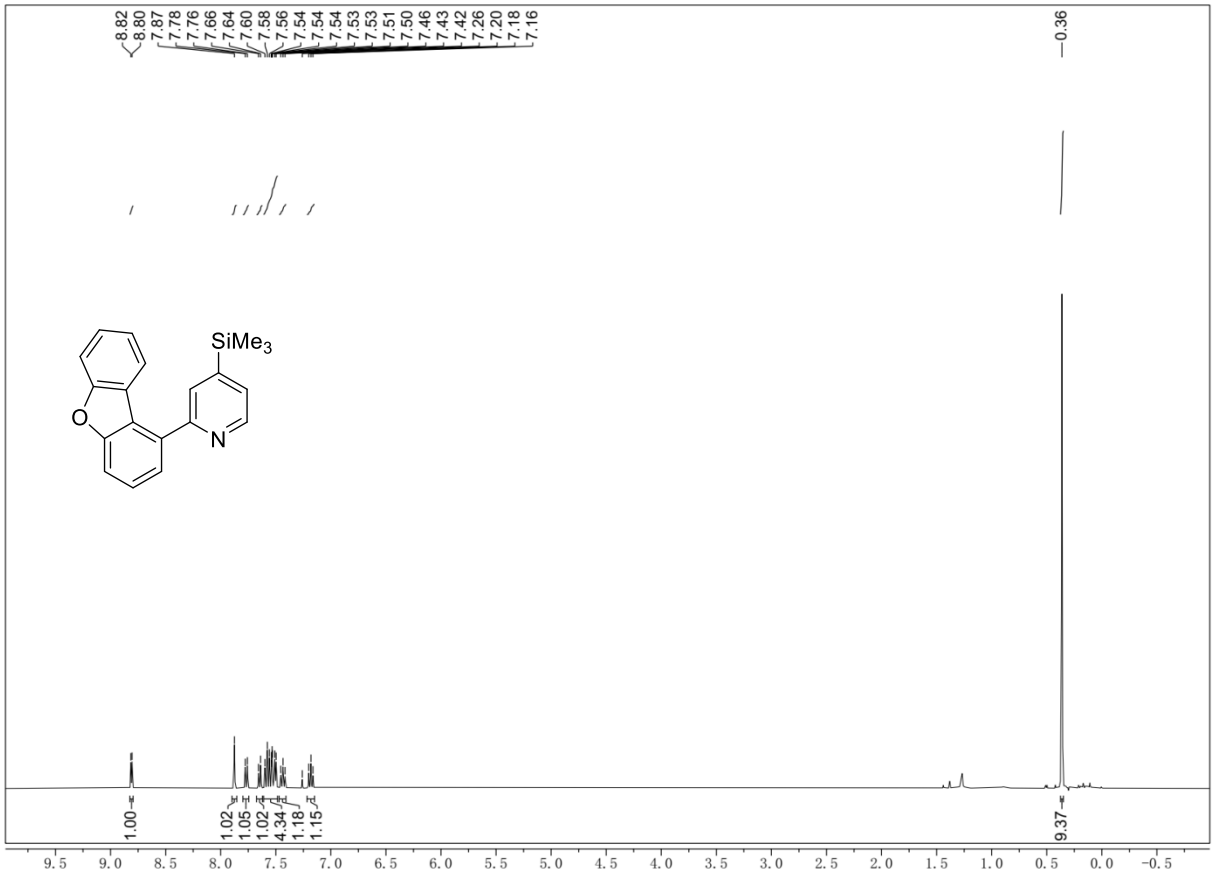
26 ^{1}H $CDCl_3$, 400 MHz



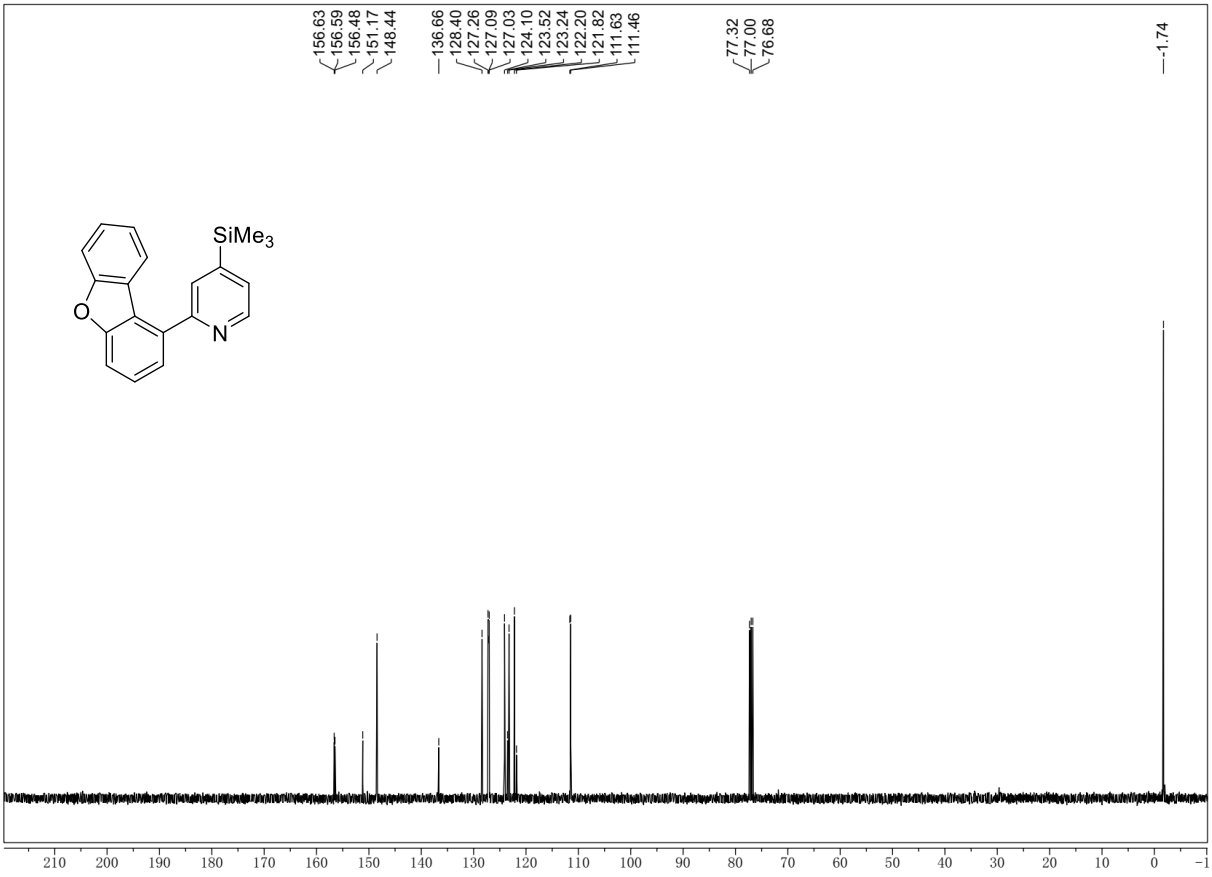
26 ^{13}C $CDCl_3$, 100 MHz



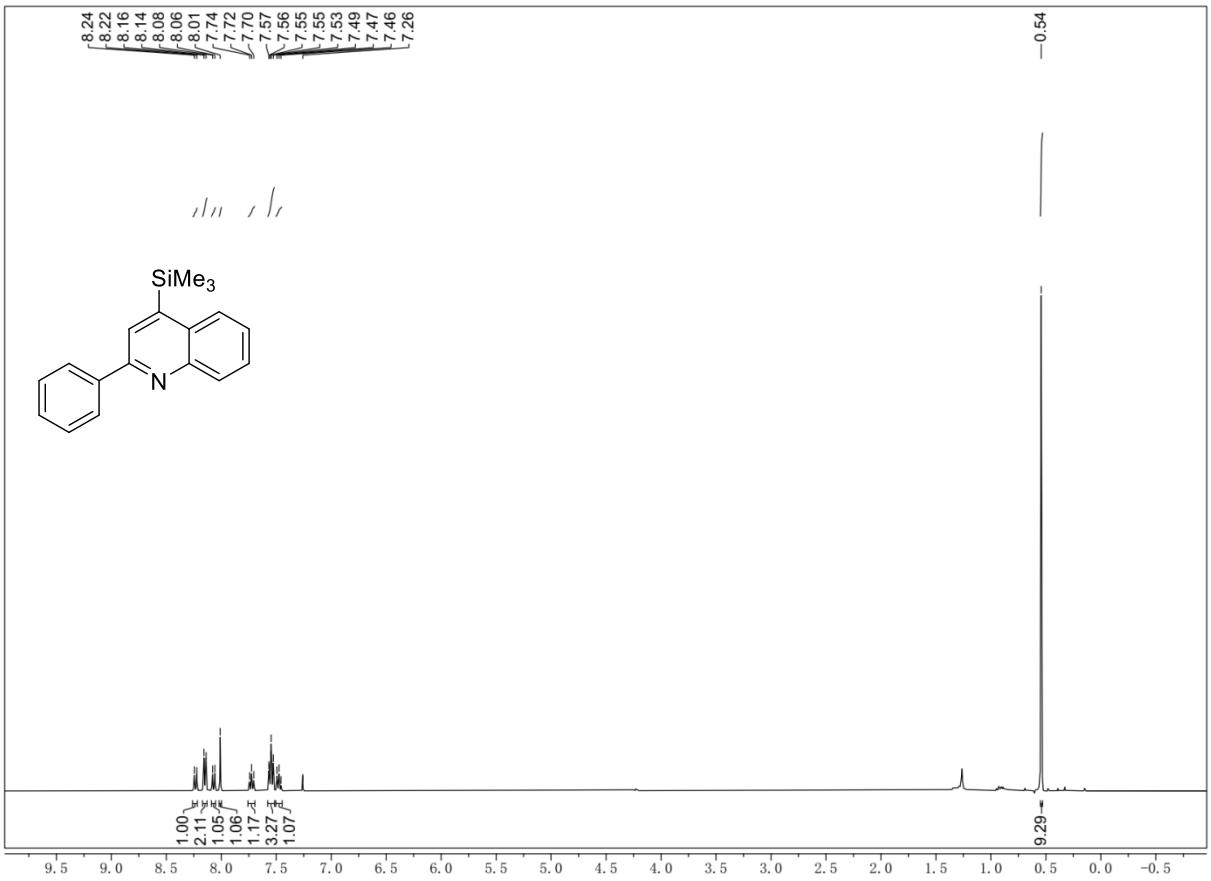
27 ^{1}H $CDCl_3$, 400 MHz



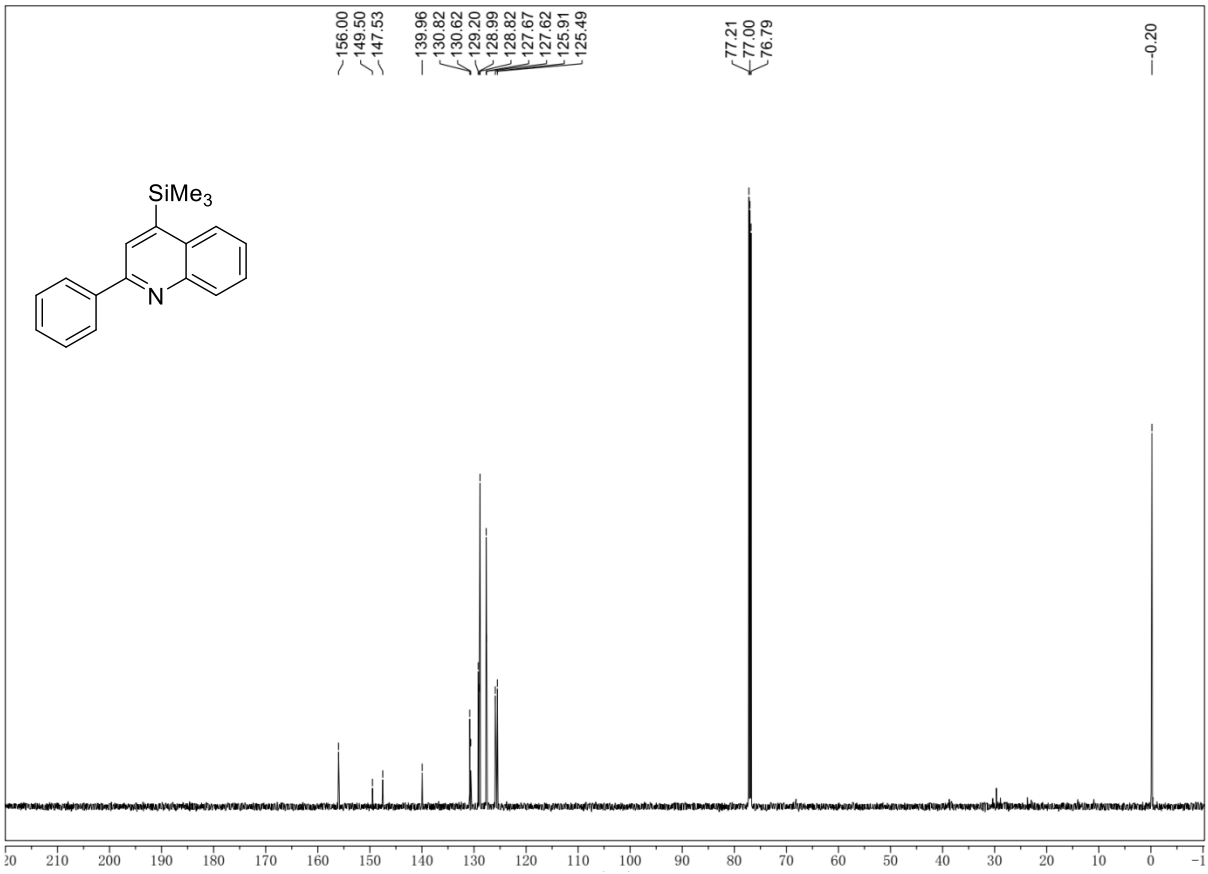
27 ^{13}C $CDCl_3$, 100 MHz



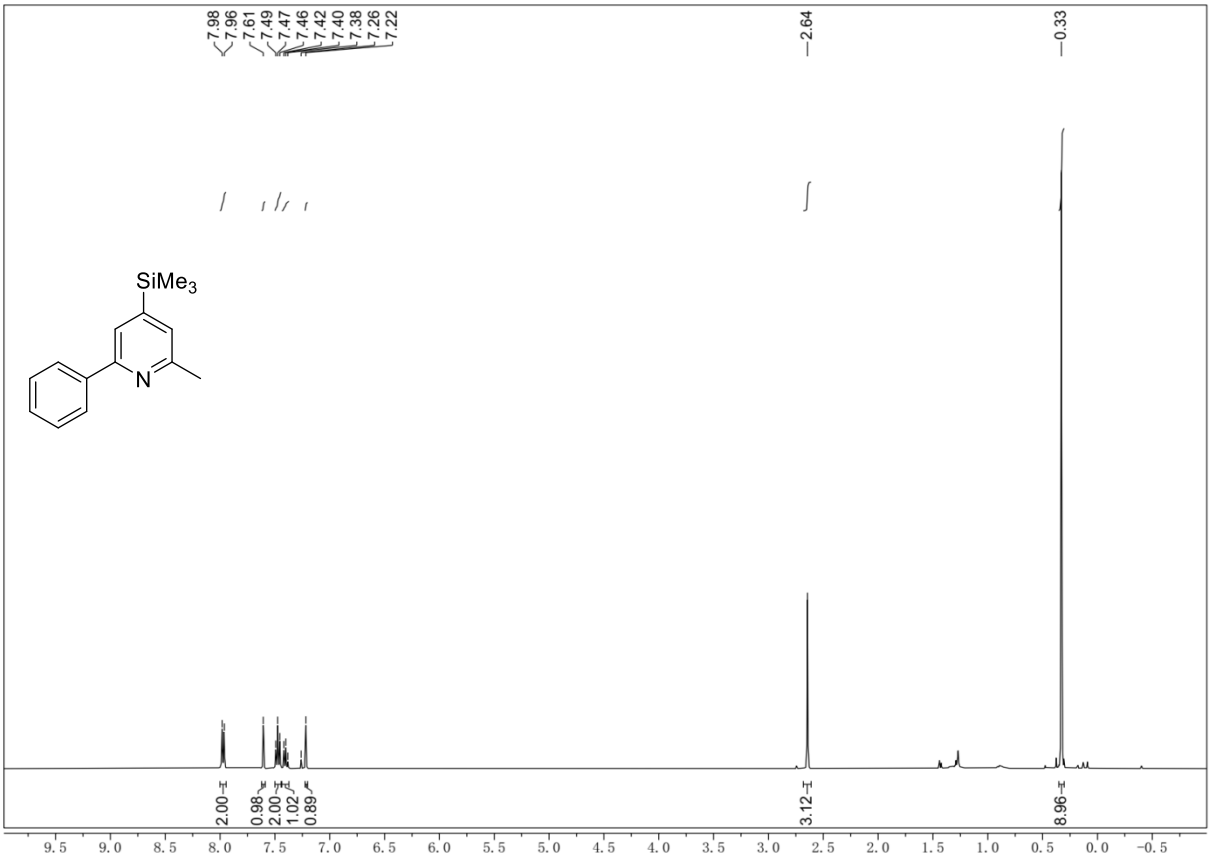
28 ^{1}H $CDCl_3$, 400 MHz



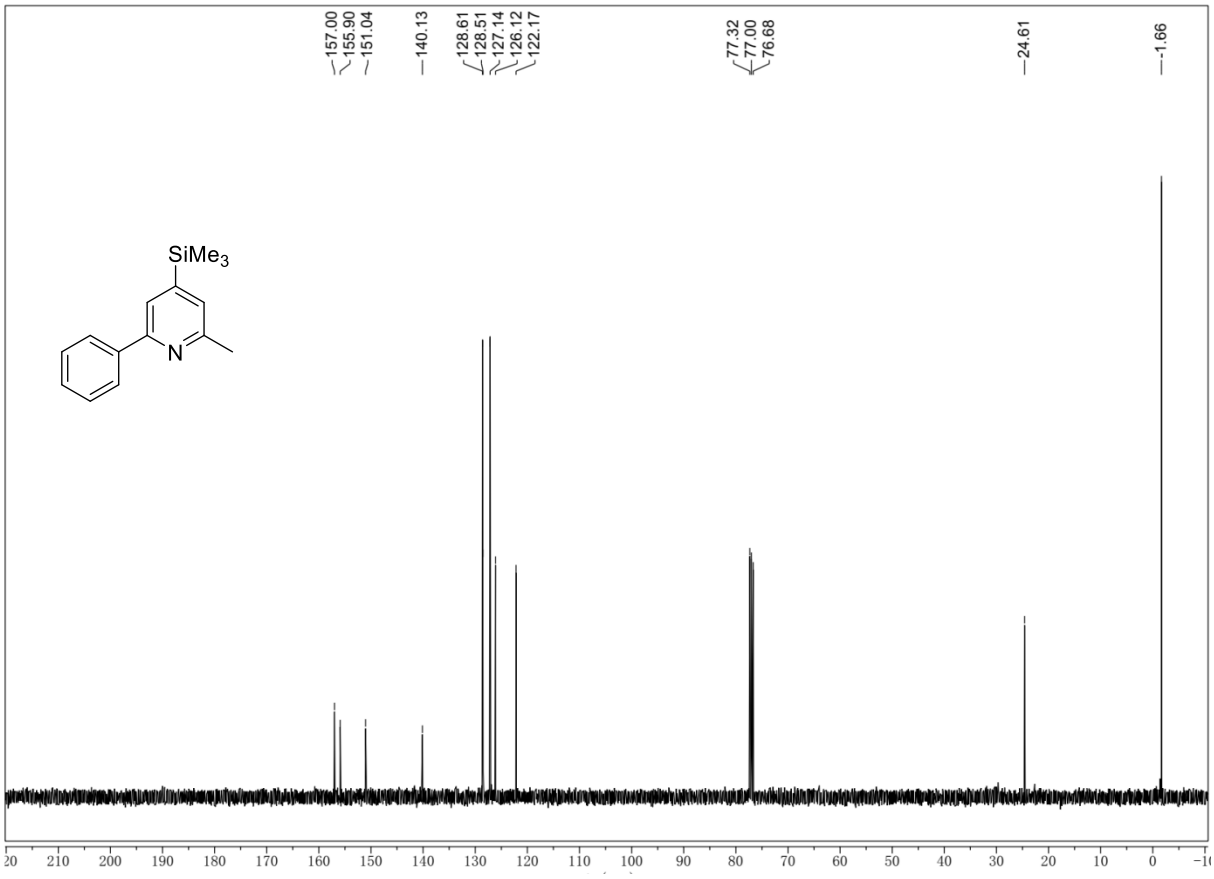
28 ^{13}C $CDCl_3$, 151 MHz



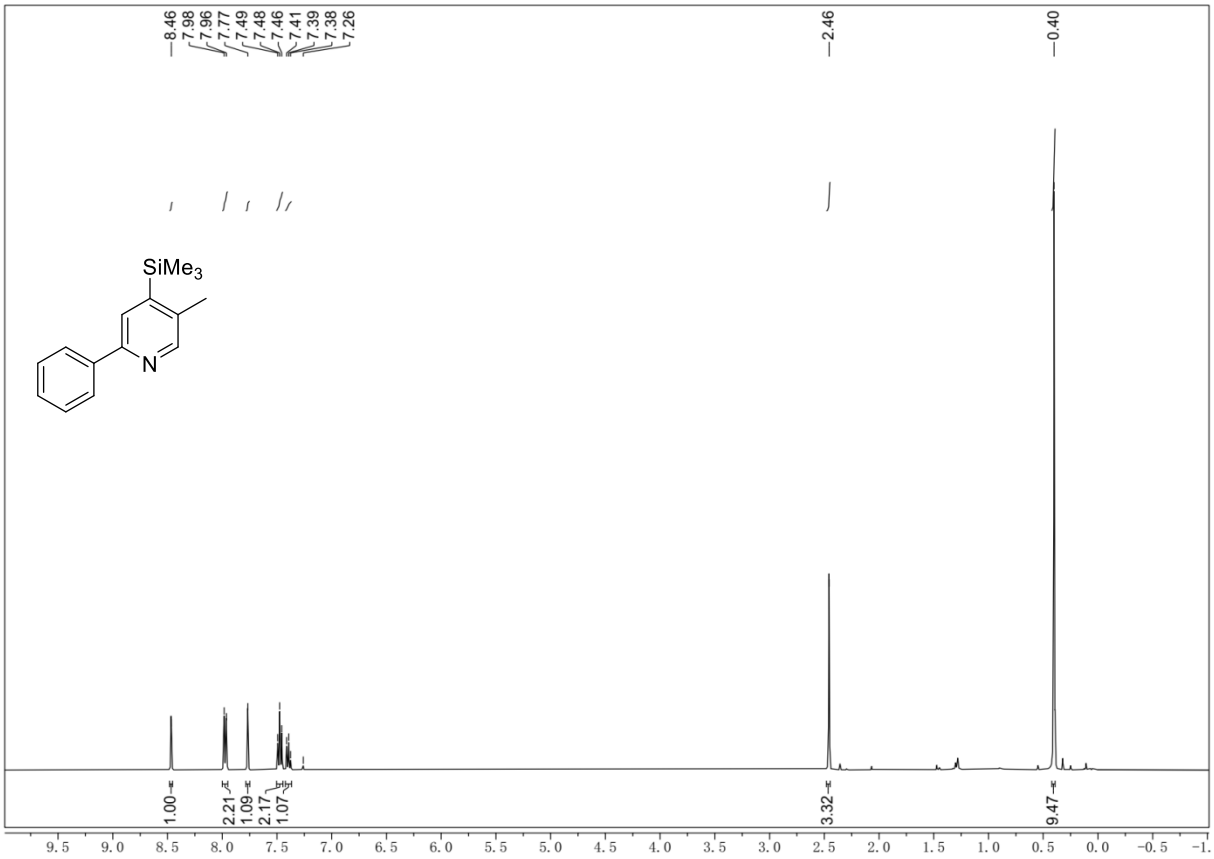
29 ^{1}H $CDCl_3$, 400 MHz



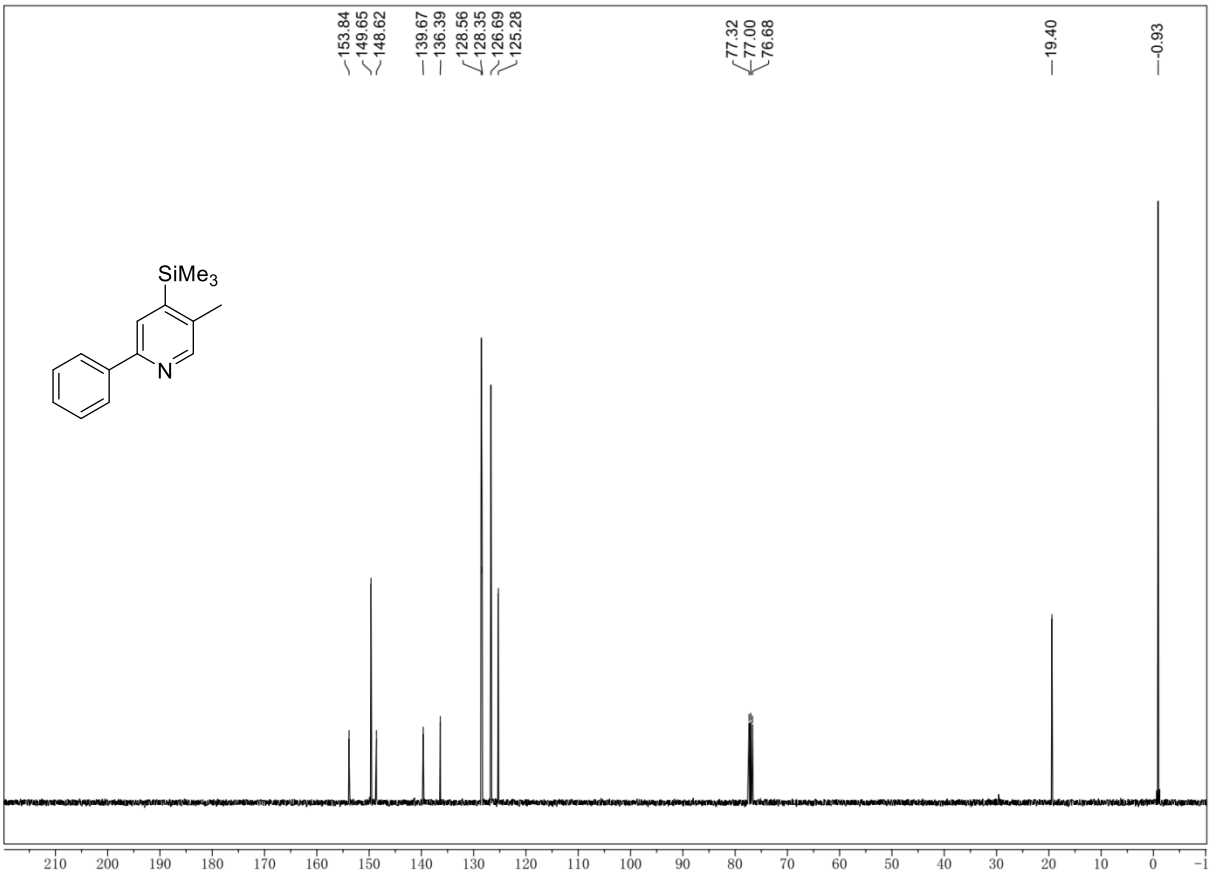
29 ^{13}C $CDCl_3$, 100 MHz



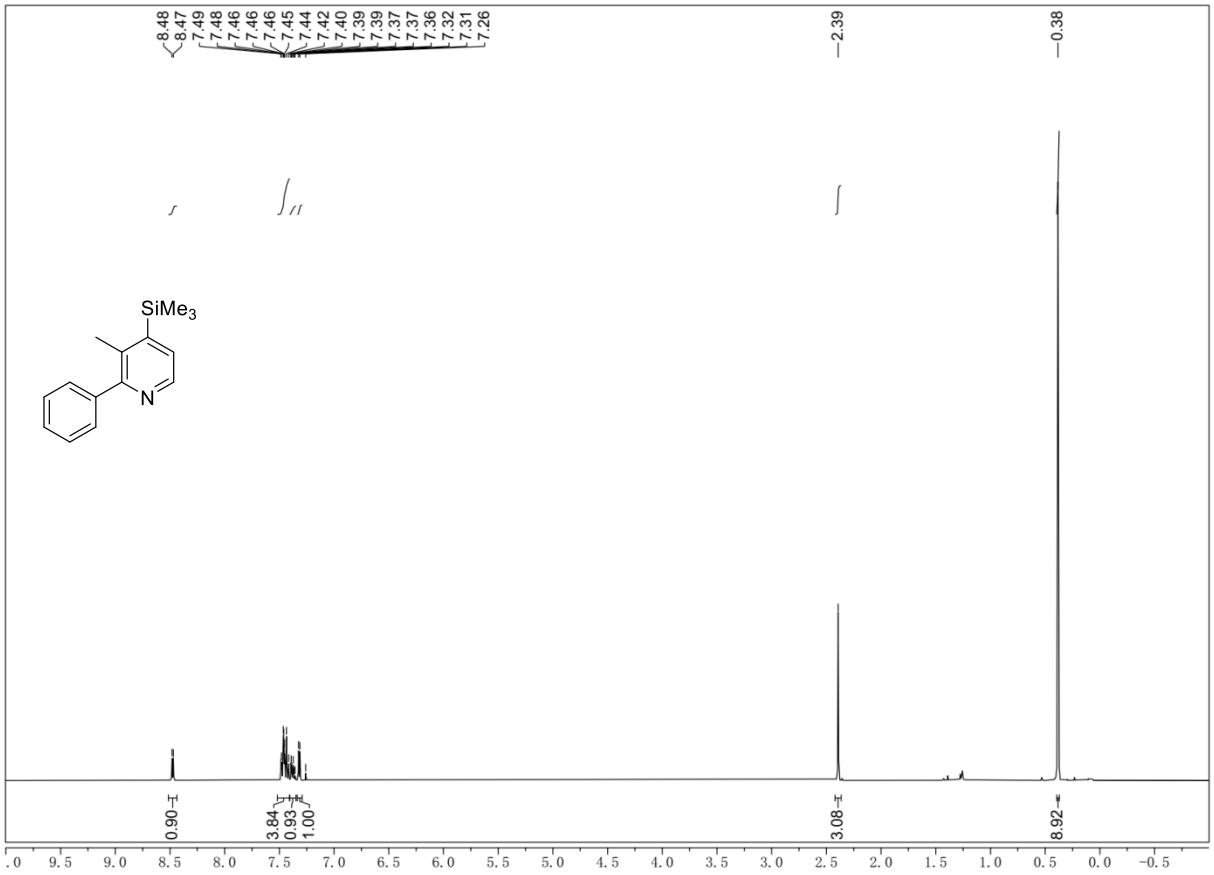
30 ^{1}H $CDCl_3$, 400 MHz



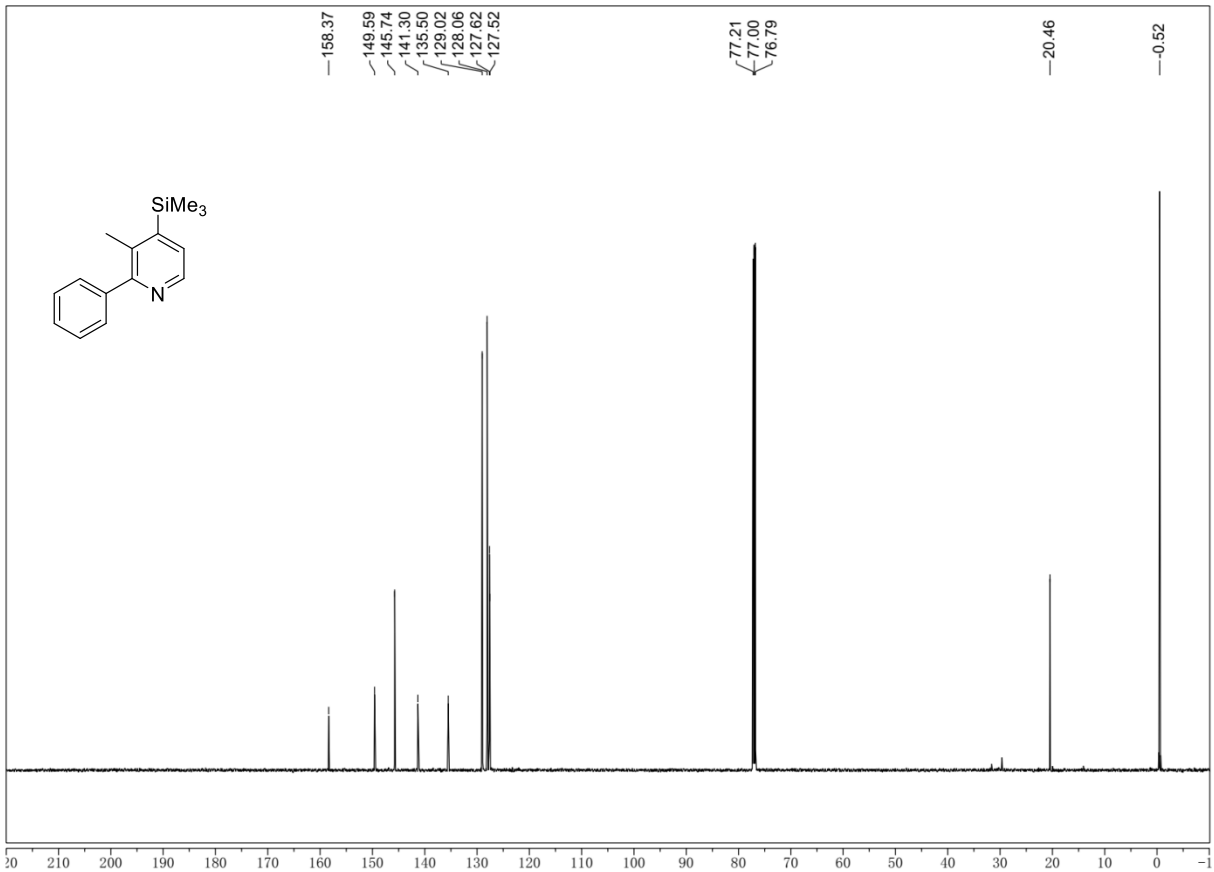
30 ^{13}C $CDCl_3$, 100 MHz



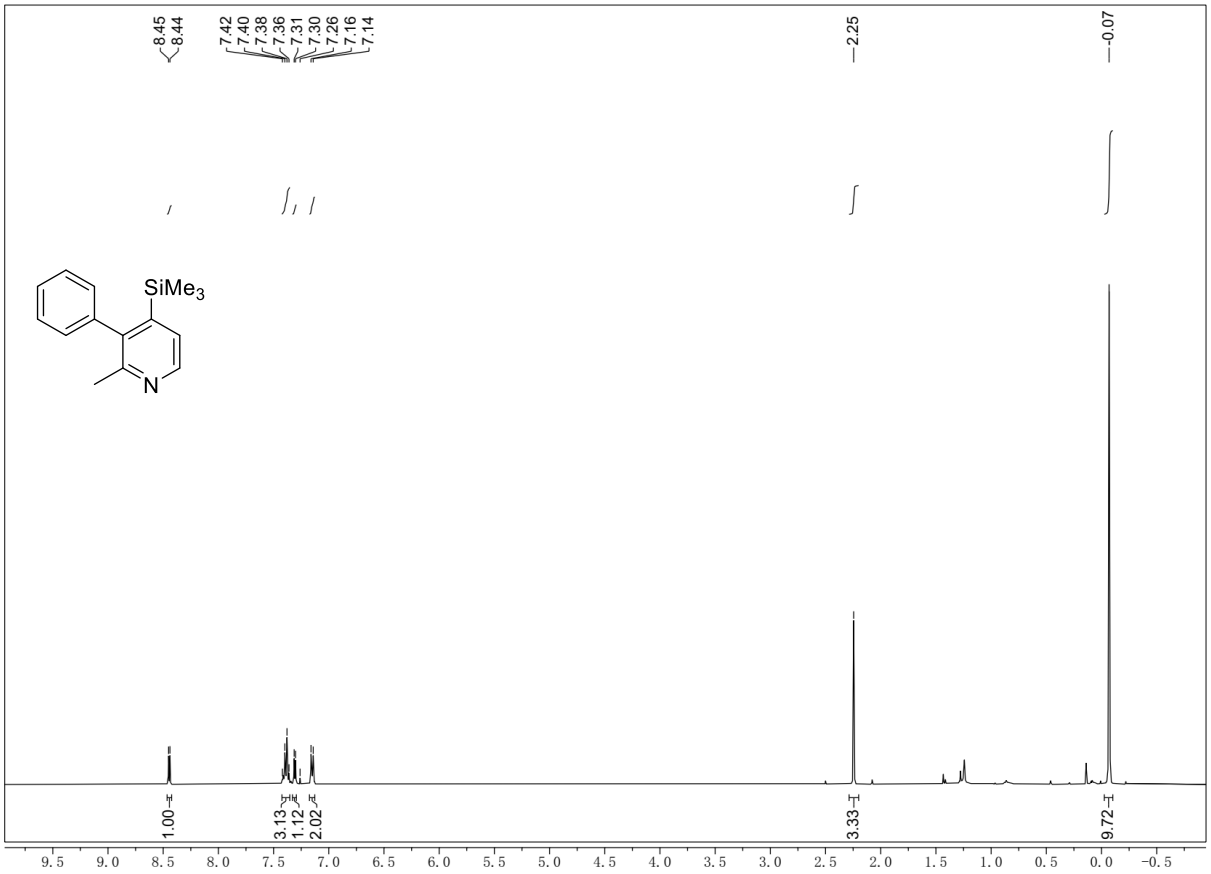
31 ^{1}H $CDCl_3$, 400 MHz



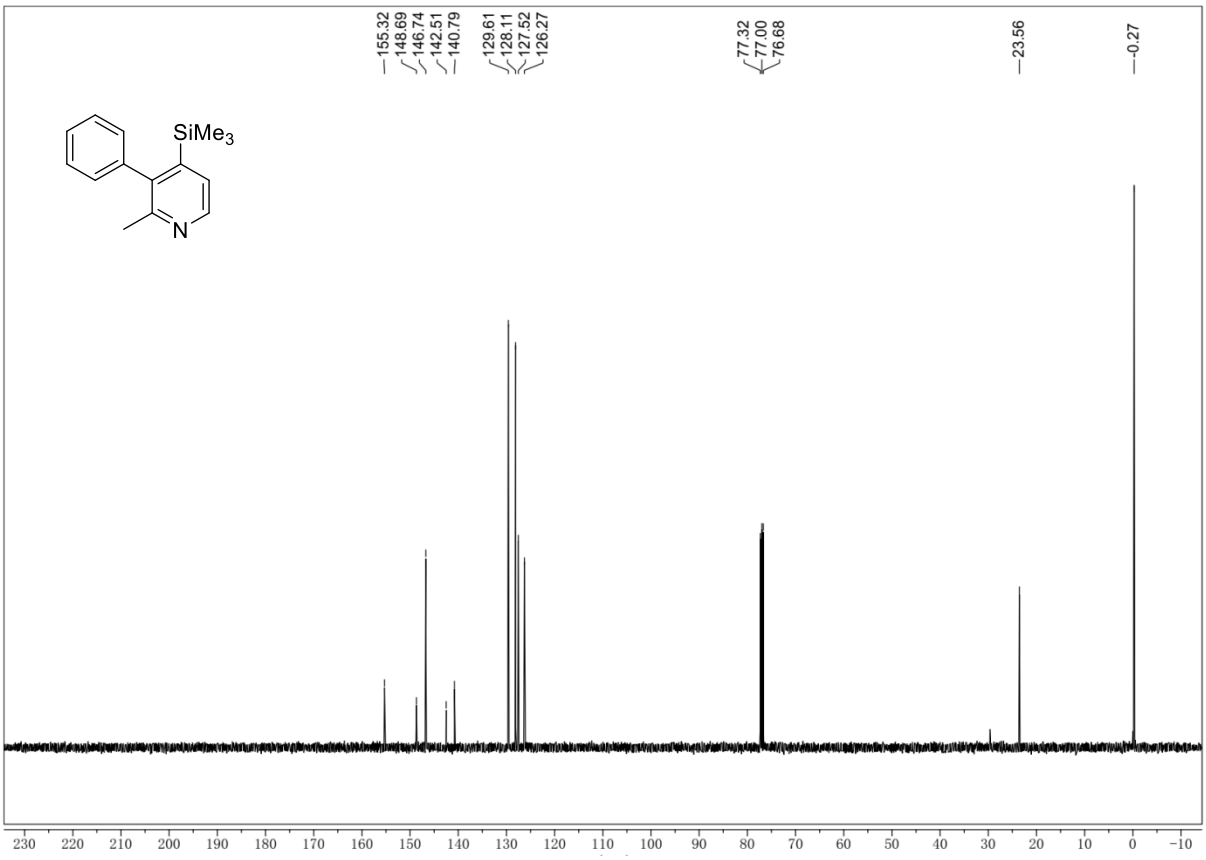
31 ^{13}C $CDCl_3$, 100 MHz



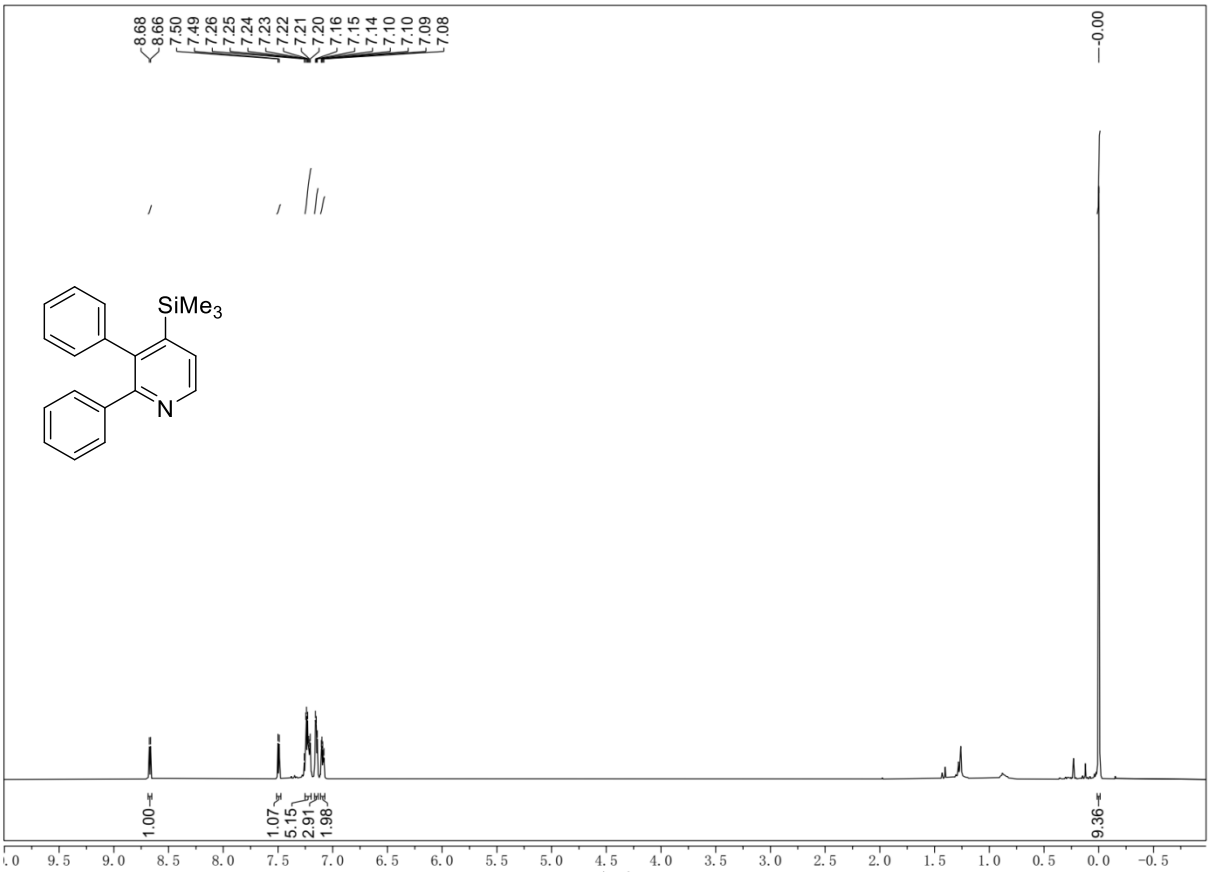
32 ^{1}H $CDCl_3$, 400 MHz



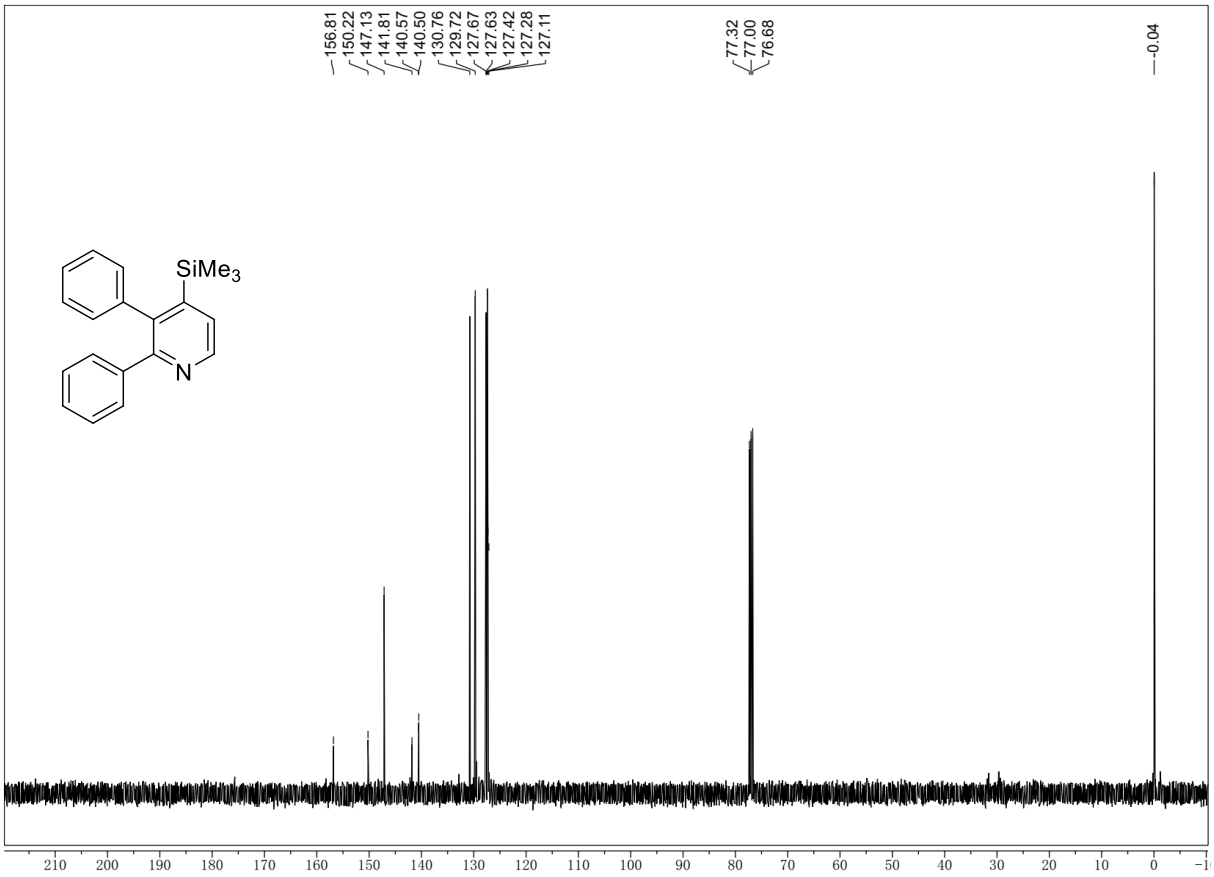
32 ^{13}C $CDCl_3$, 100 MHz



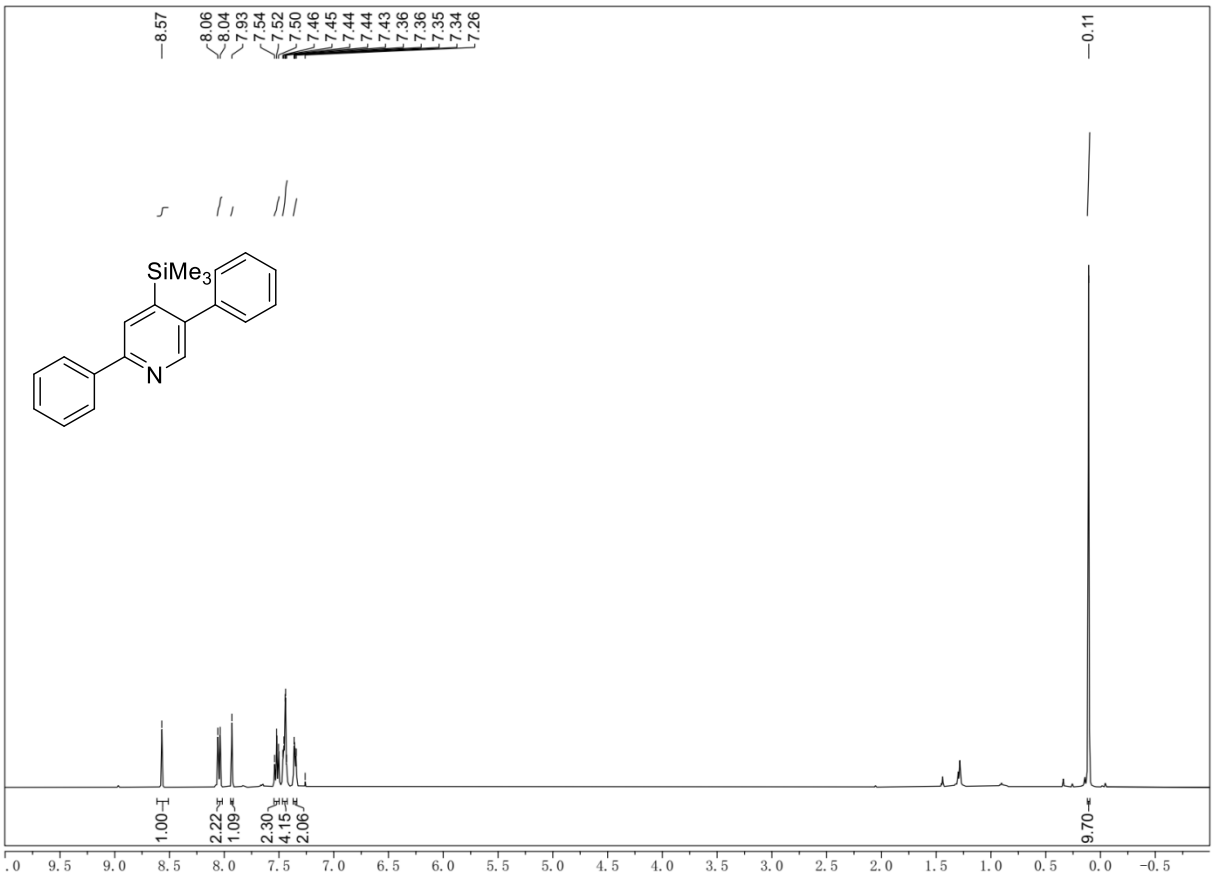
33 ^{1}H $CDCl_3$, 400 MHz



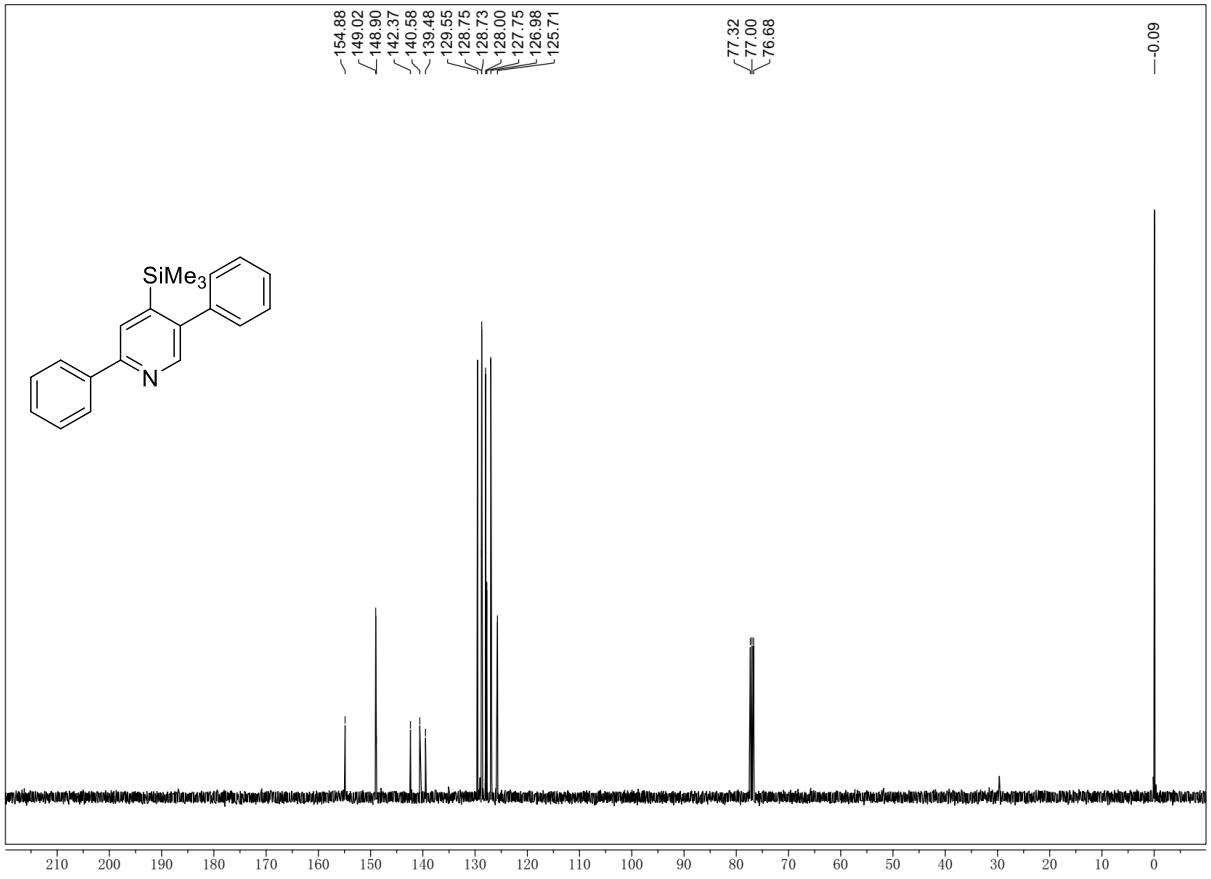
33 ^{13}C $CDCl_3$, 100 MHz



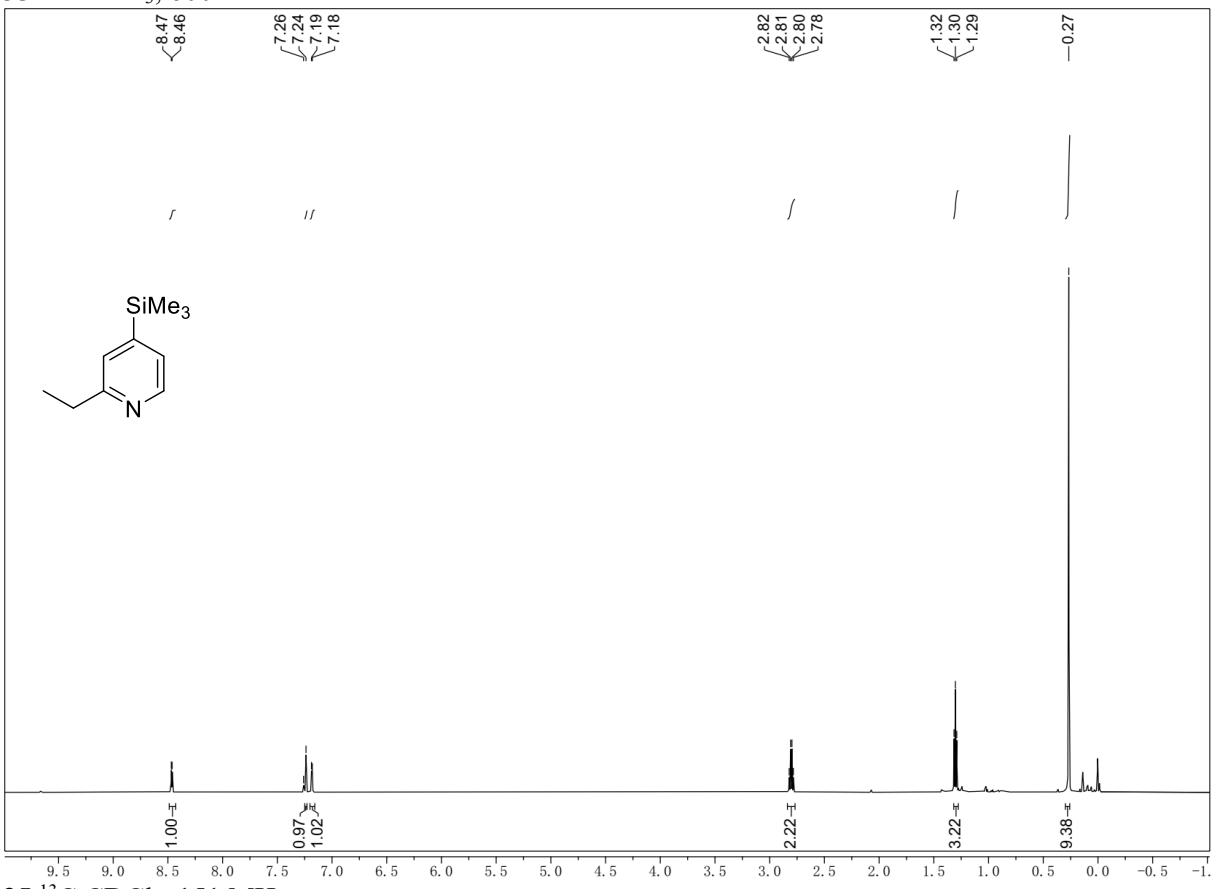
34 ^{1}H $CDCl_3$, 400 MHz



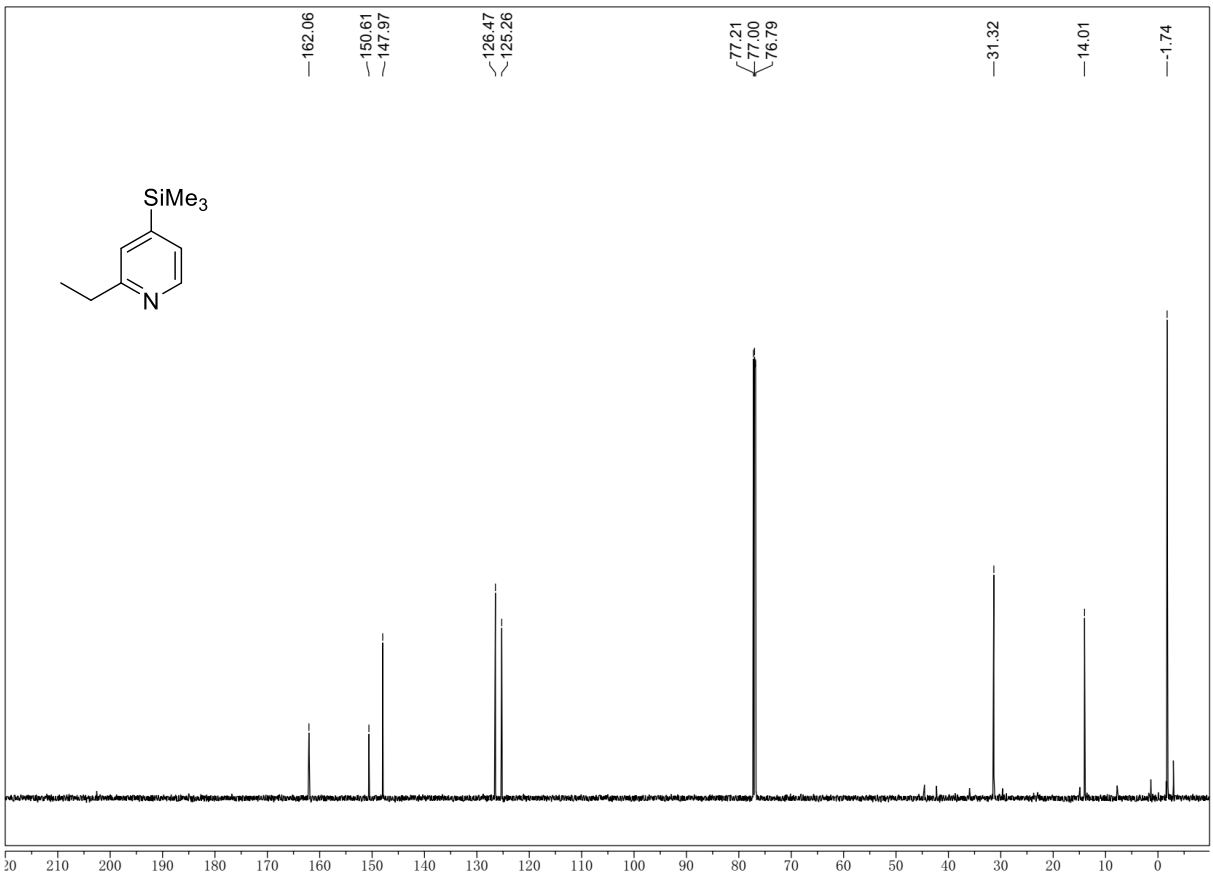
34 ^{13}C $CDCl_3$, 100 MHz



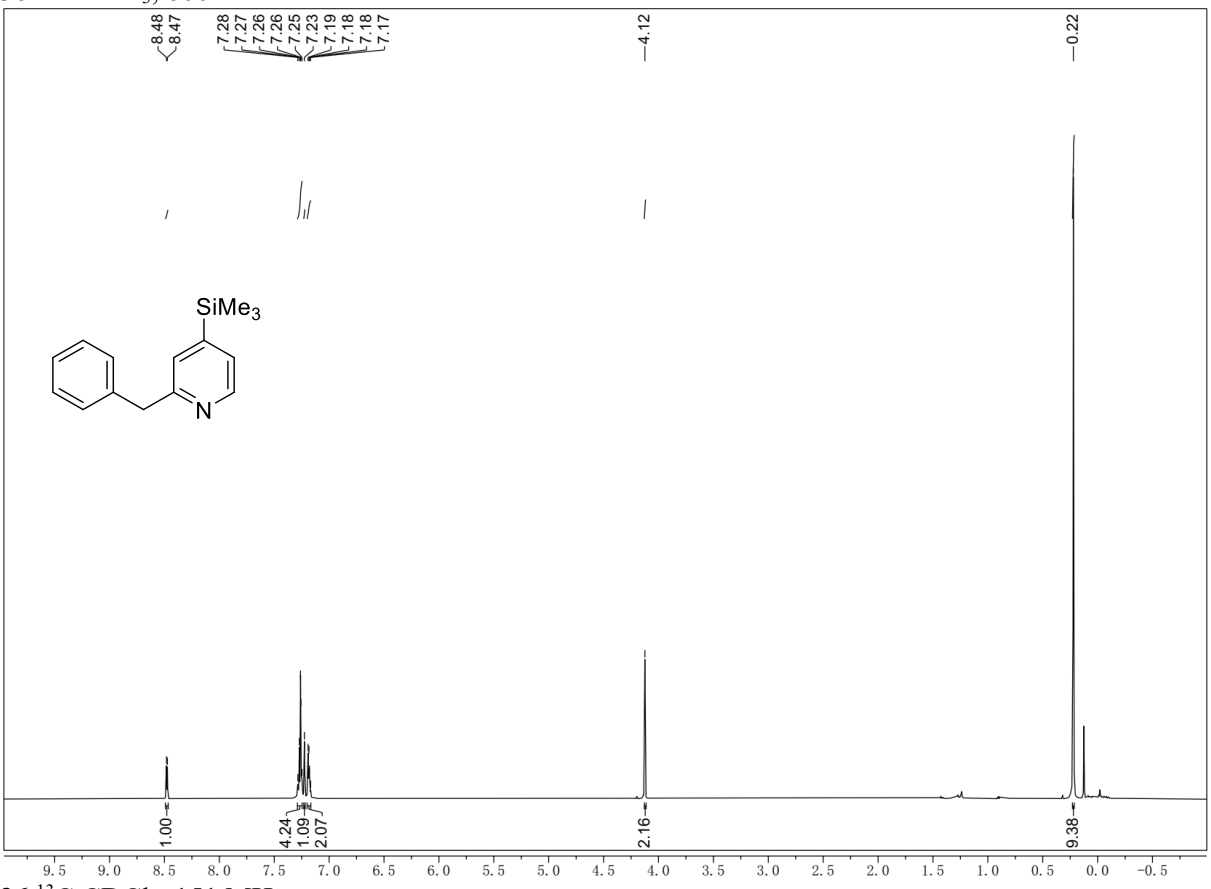
35 ^{1}H $CDCl_3$, 600 MHz



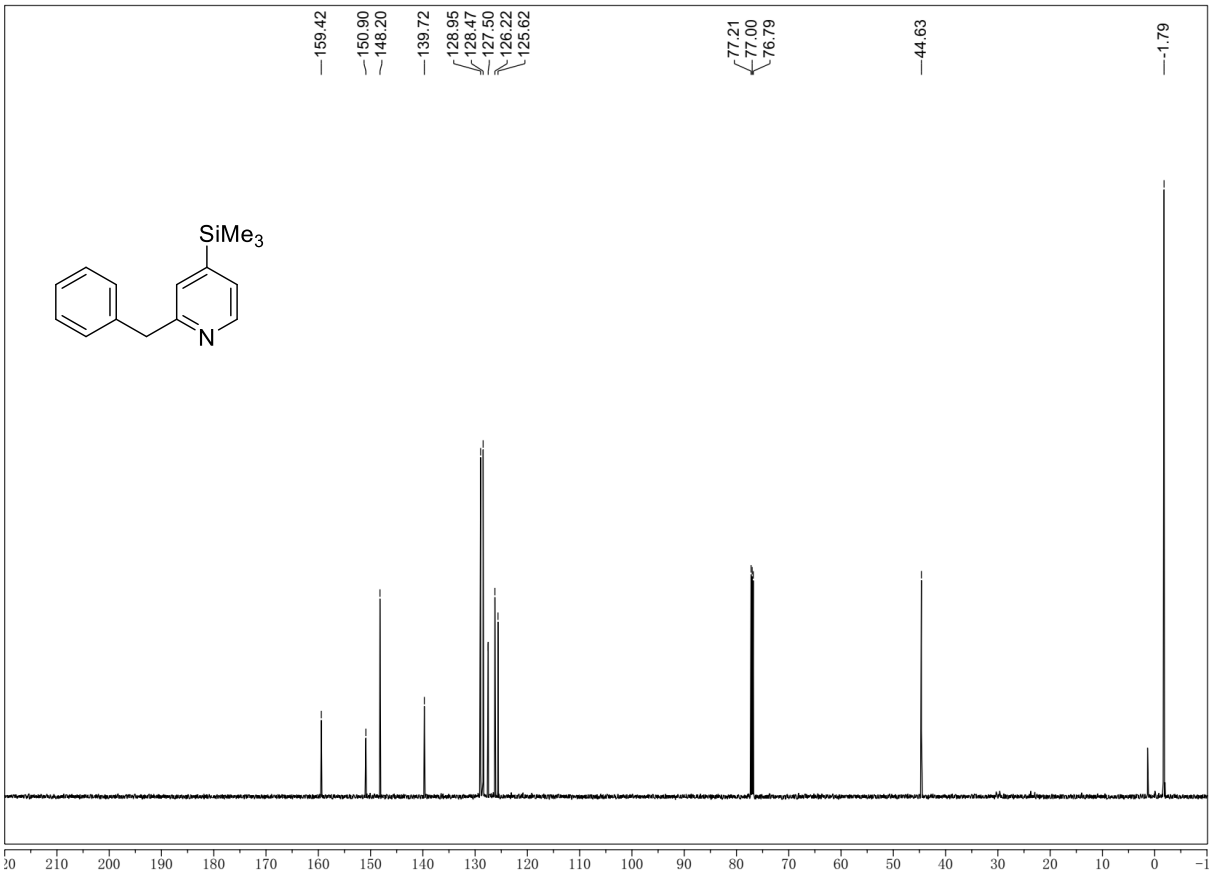
35 ^{13}C $CDCl_3$, 151 MHz



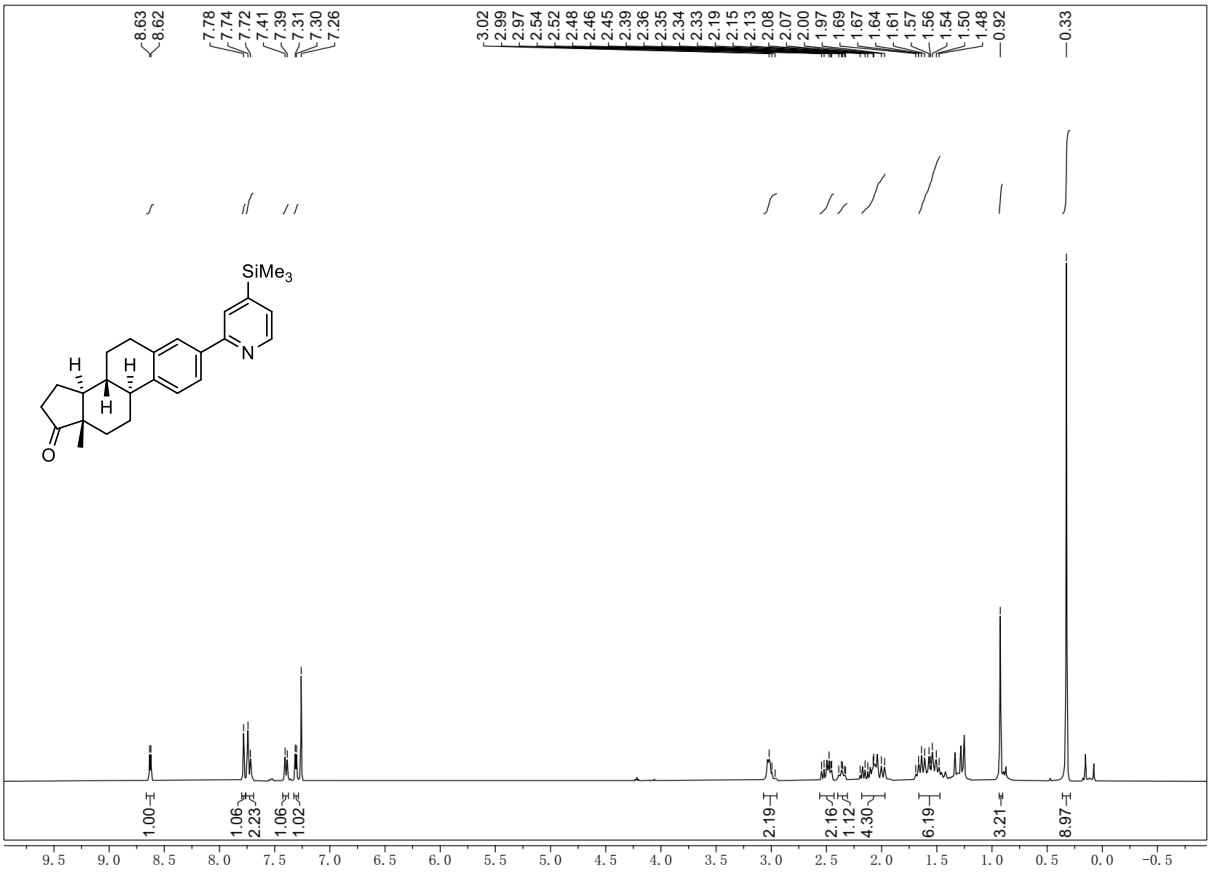
36 ^{1}H $CDCl_3$, 600 MHz



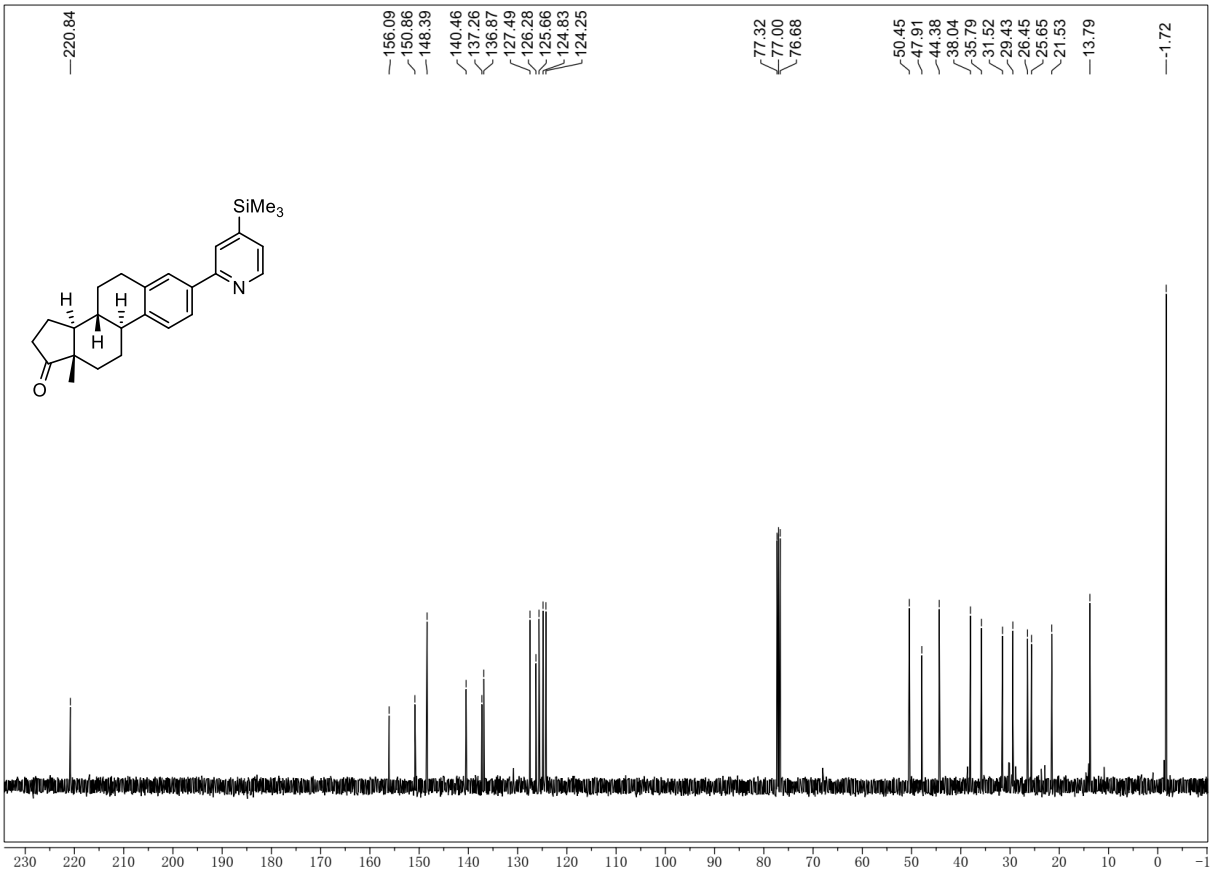
36 ^{13}C $CDCl_3$, 151 MHz



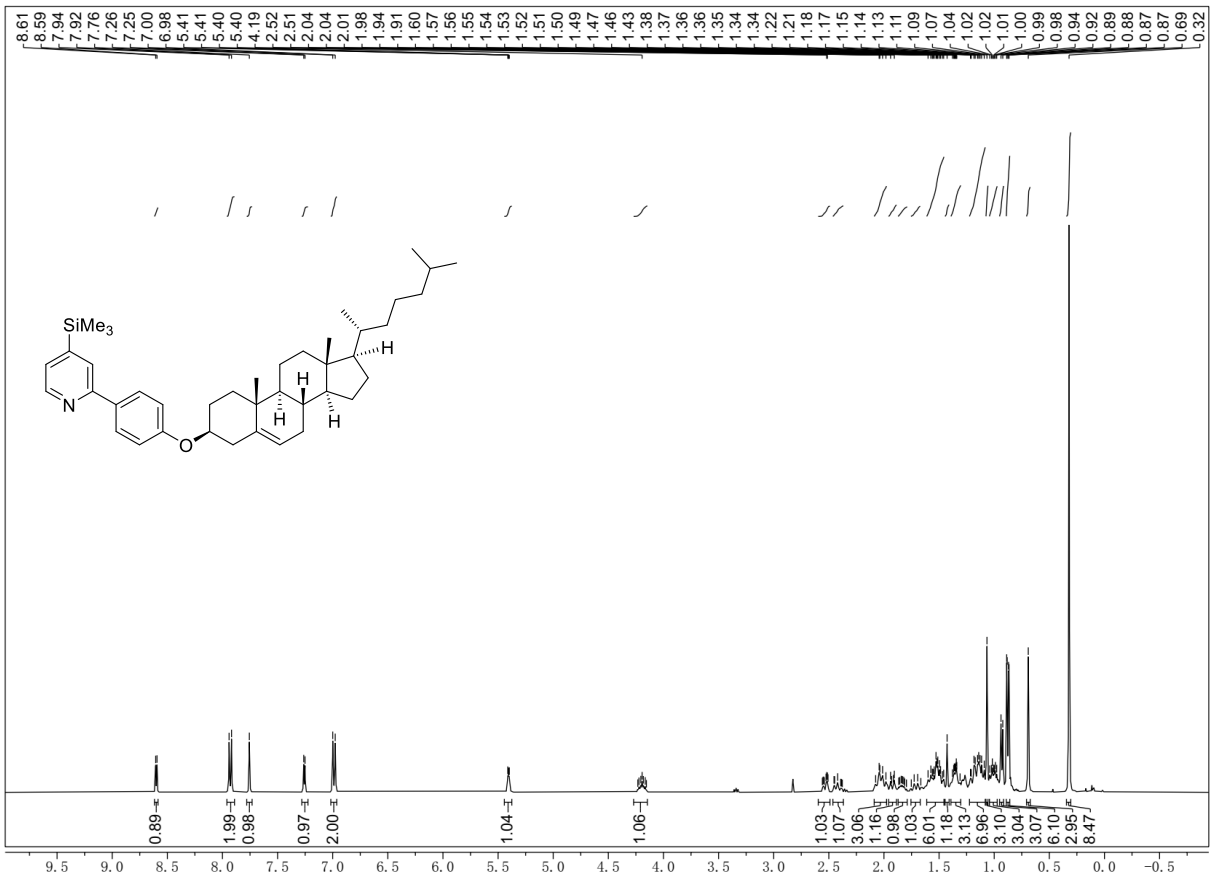
37 ^{1}H $CDCl_3$, 400 MHz



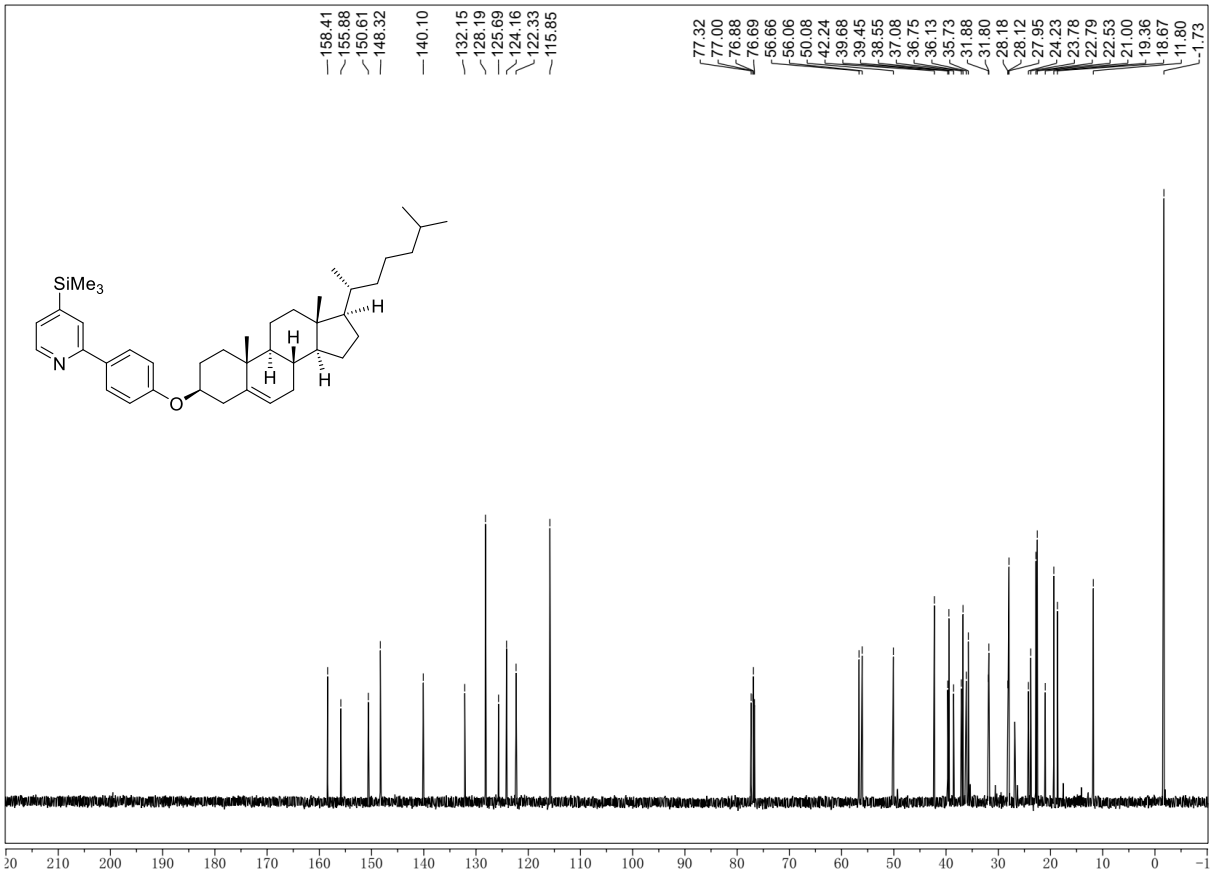
37 ^{13}C $CDCl_3$, 100 MHz



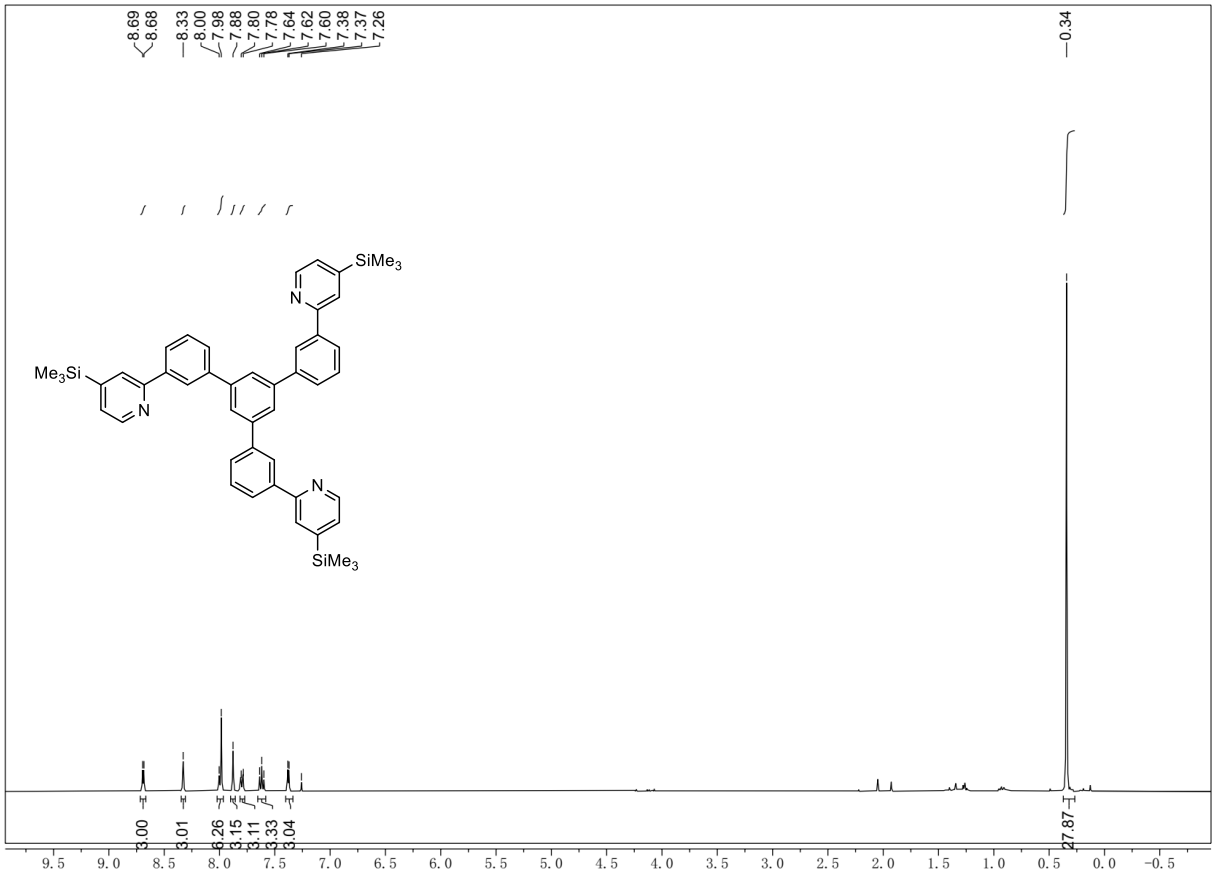
38 ^{1}H $CDCl_3$, 400 MHz



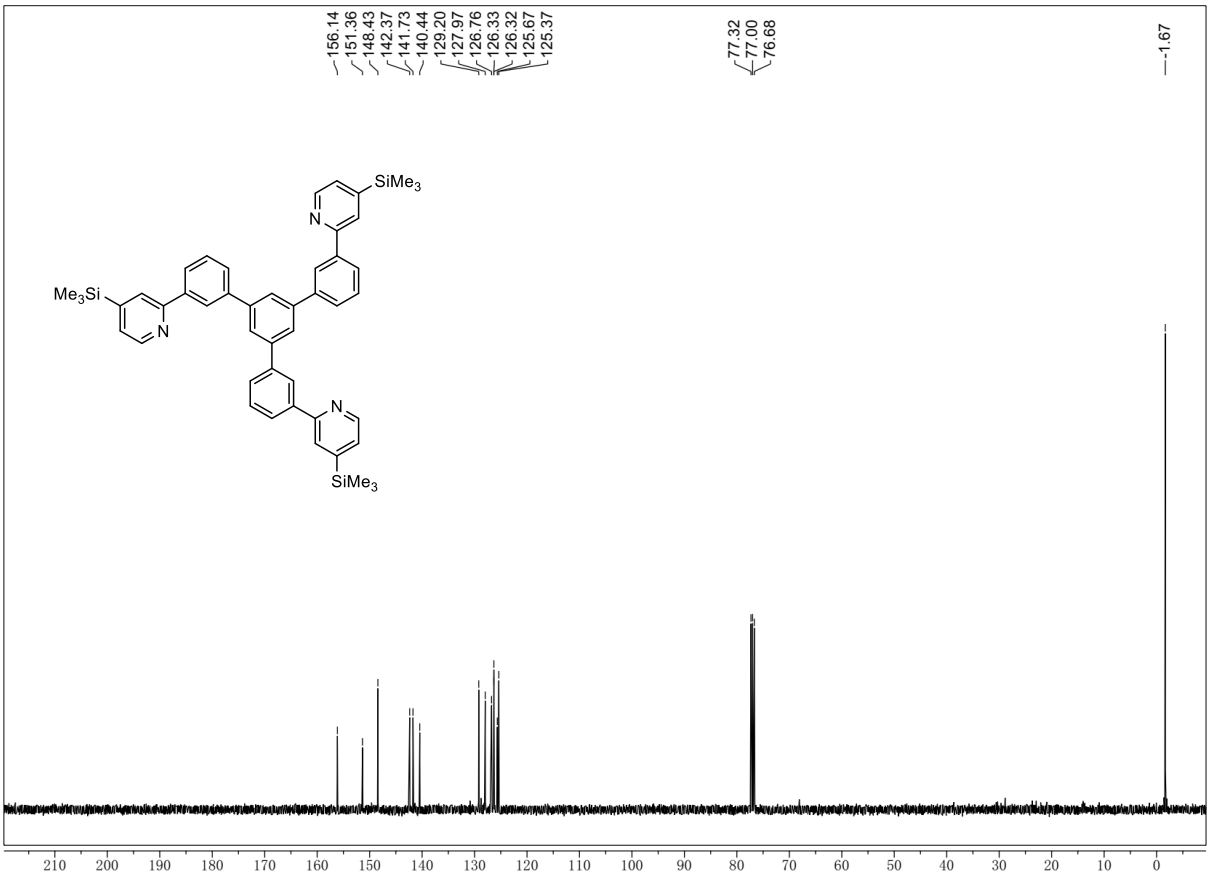
38 ^{13}C $CDCl_3$, 100 MHz



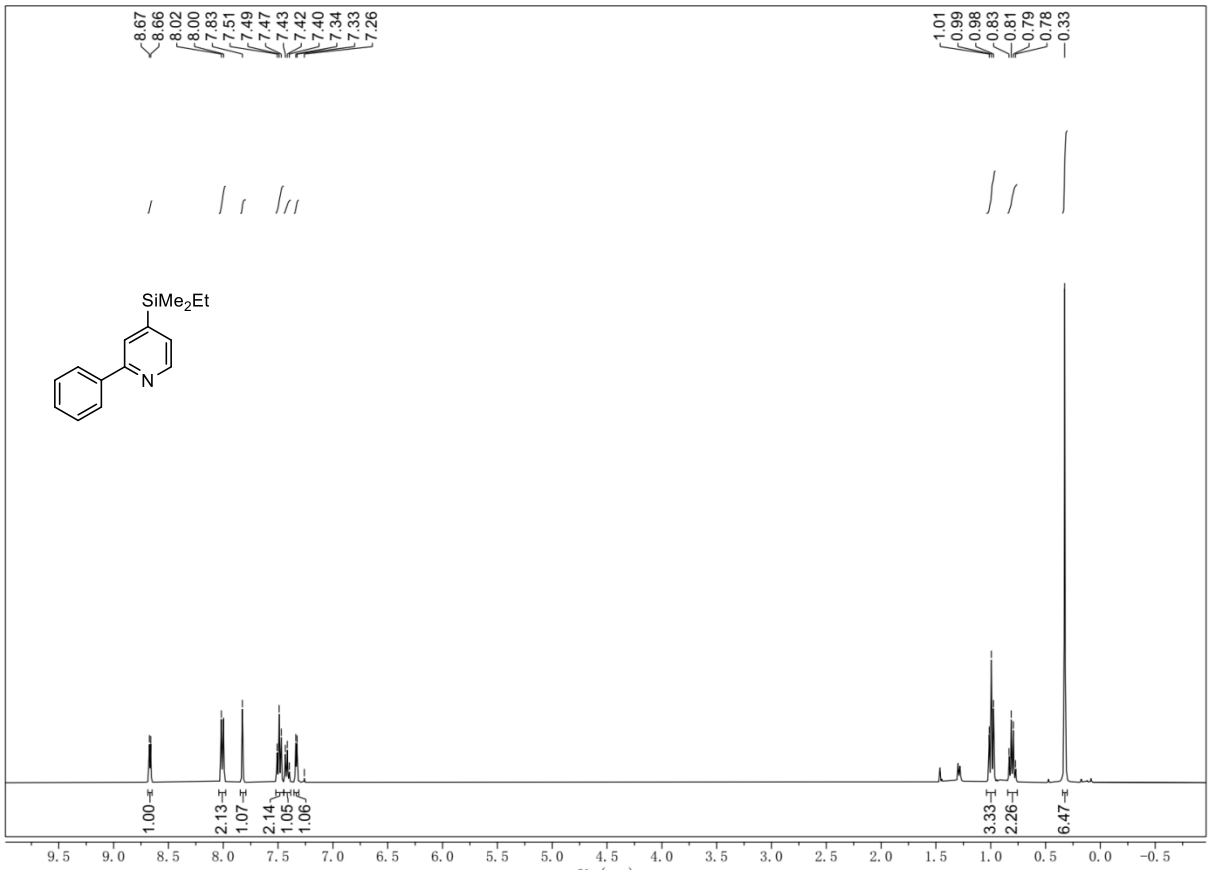
39 ^{1}H $CDCl_3$, 400 MHz



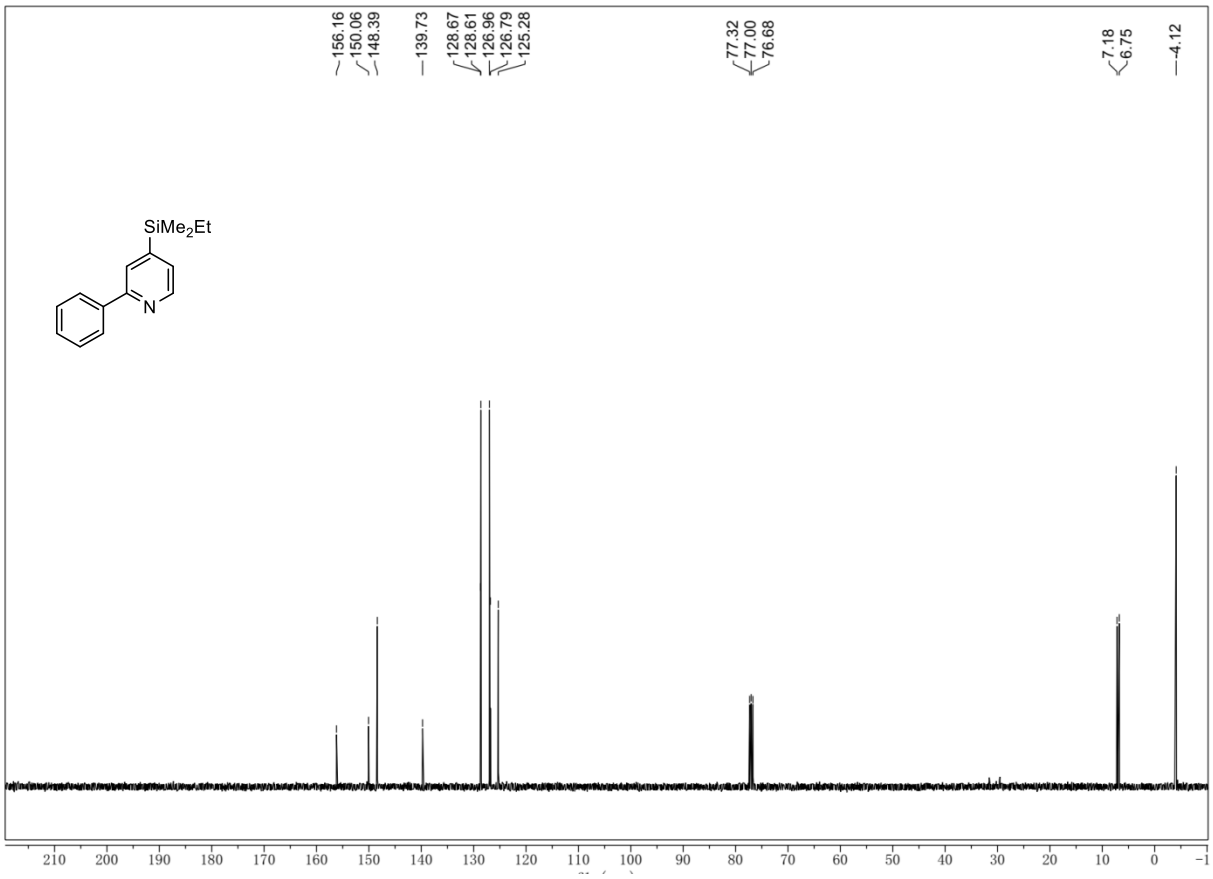
39 ^{13}C $CDCl_3$, 100 MHz



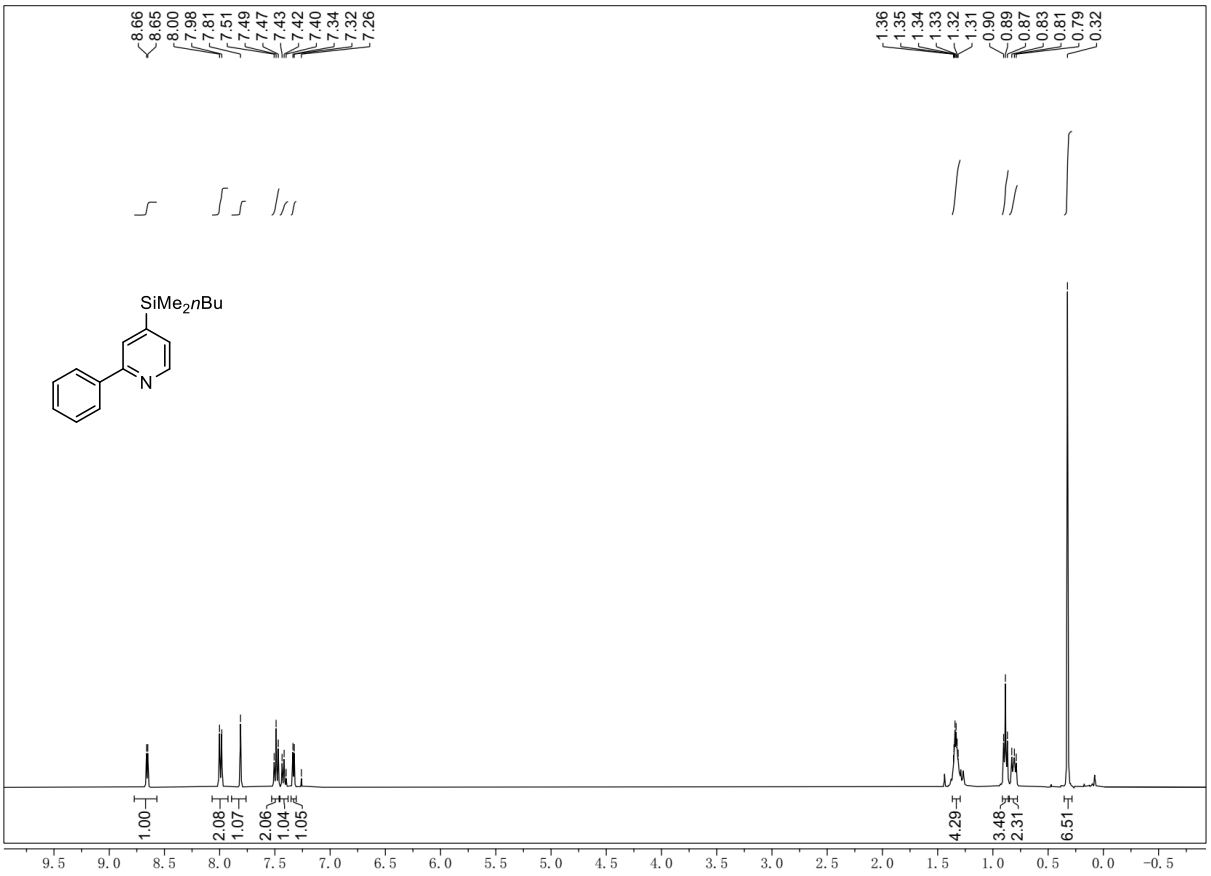
40 ^{1}H $CDCl_3$, 400 MHz



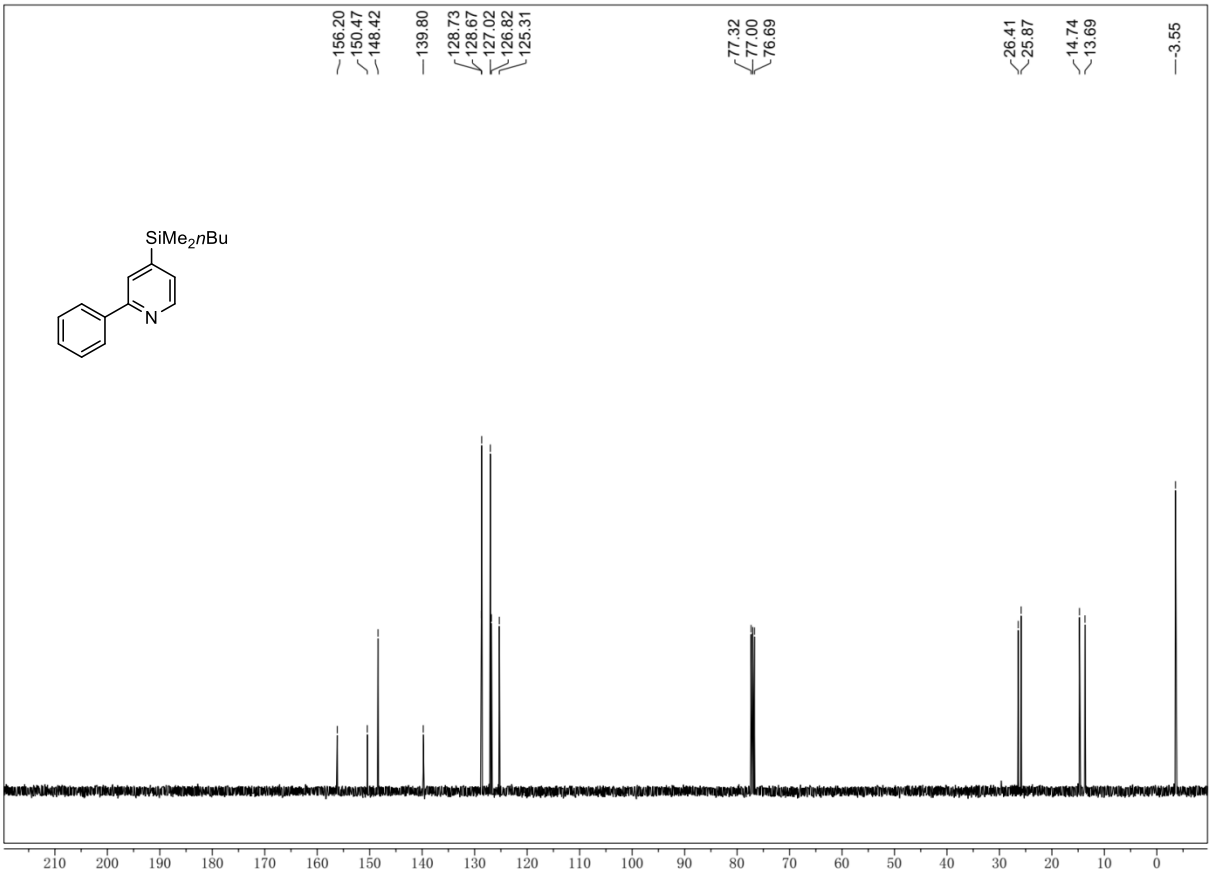
40 ^{13}C $CDCl_3$, 100 MHz



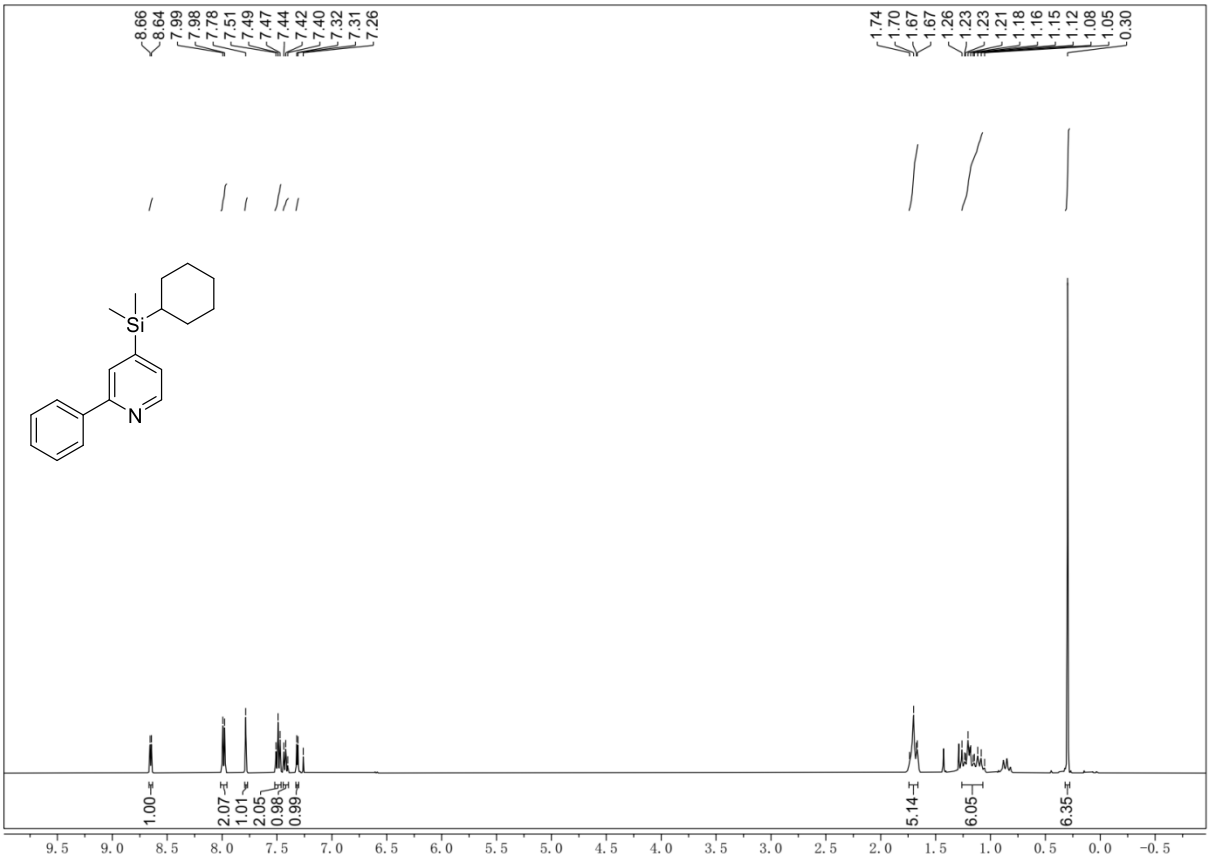
41 ^{1}H $CDCl_3$, 400 MHz



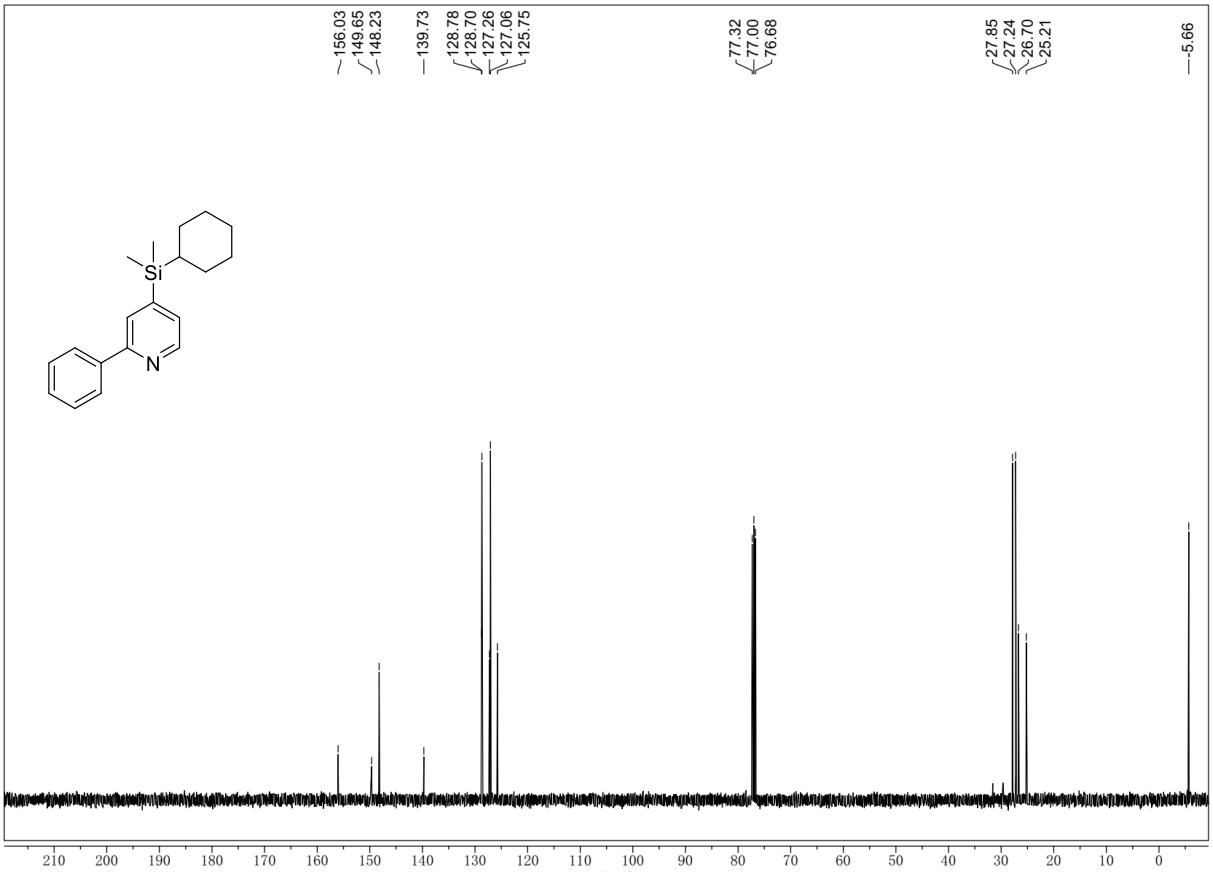
41 ^{13}C $CDCl_3$, 100 MHz



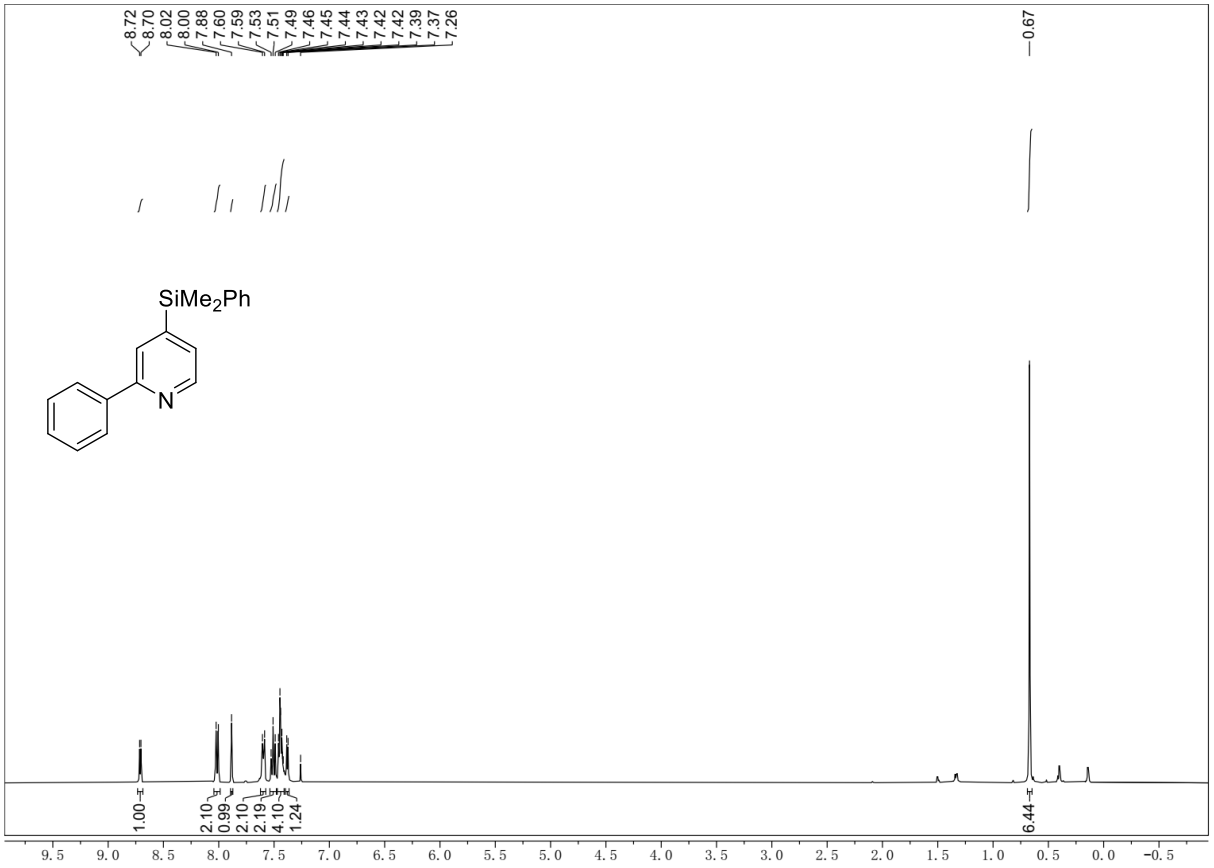
42 ^{1}H $CDCl_3$, 400 MHz



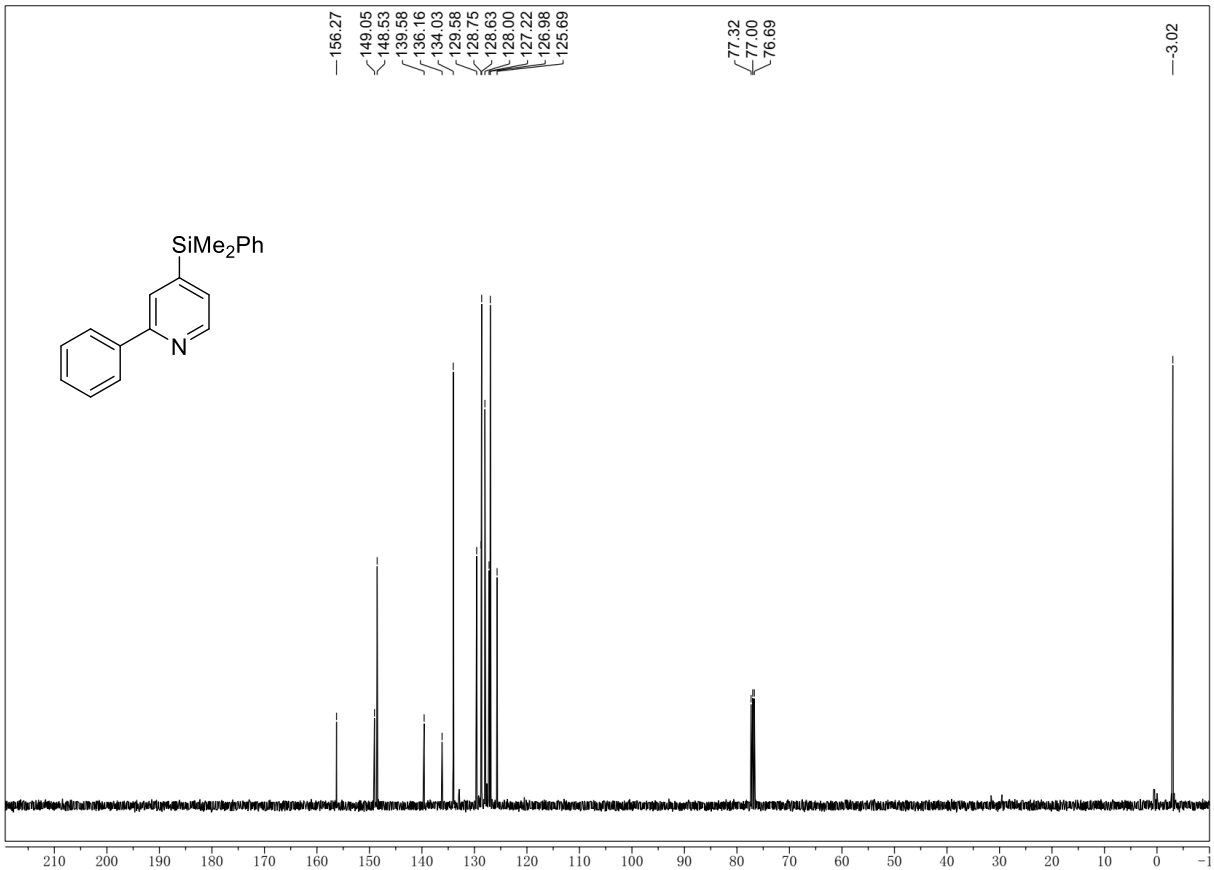
42 ^{13}C $CDCl_3$, 100 MHz



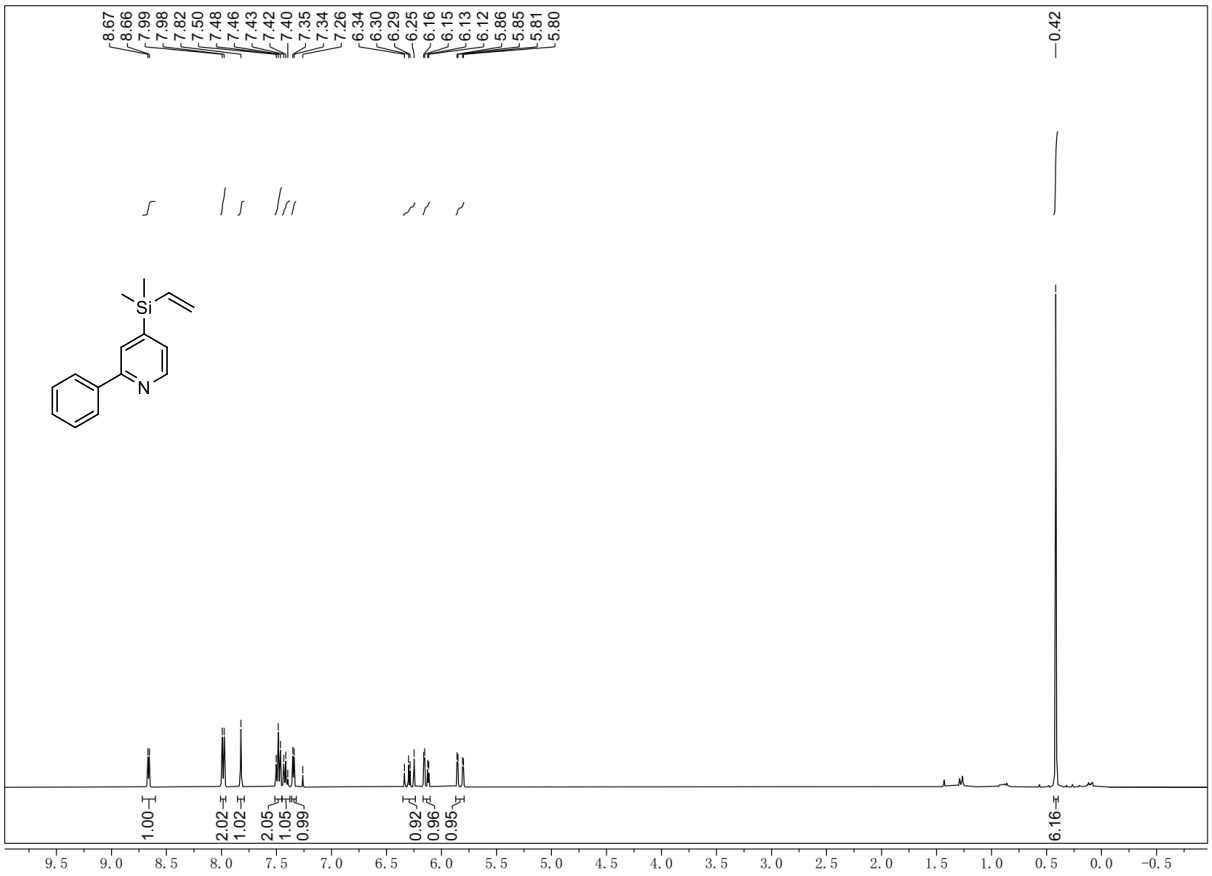
43 ^{1}H $CDCl_3$, 400 MHz



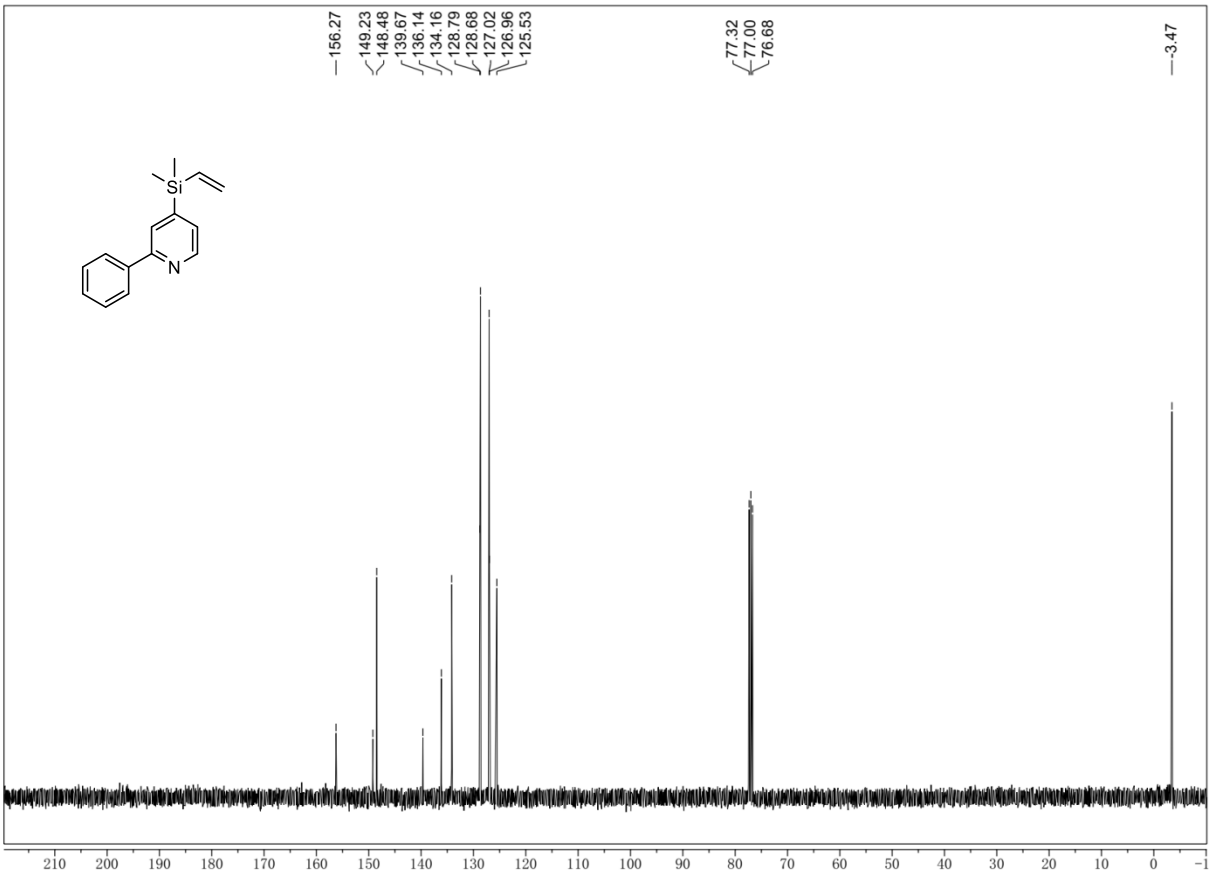
43 ^{13}C $CDCl_3$, 100 MHz



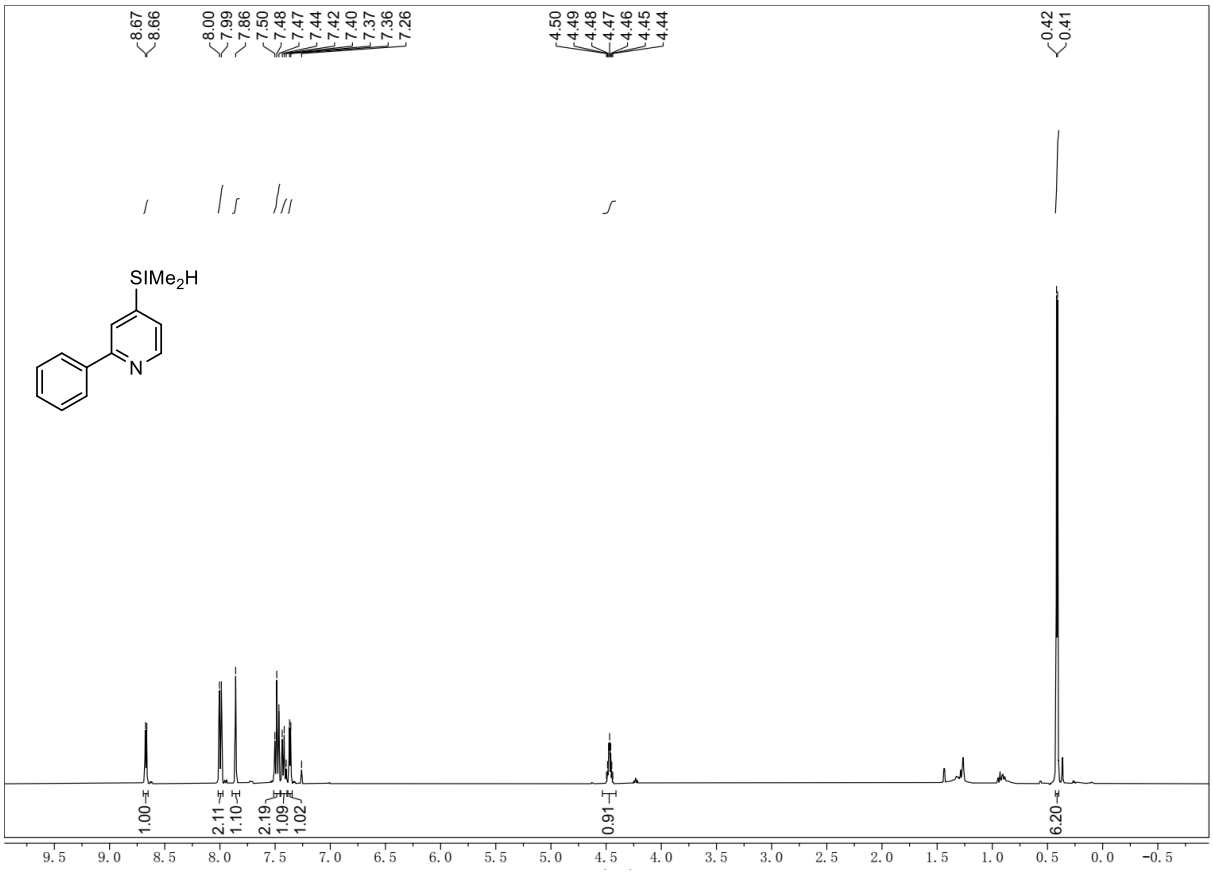
44 ^{1}H $CDCl_3$, 400 MHz



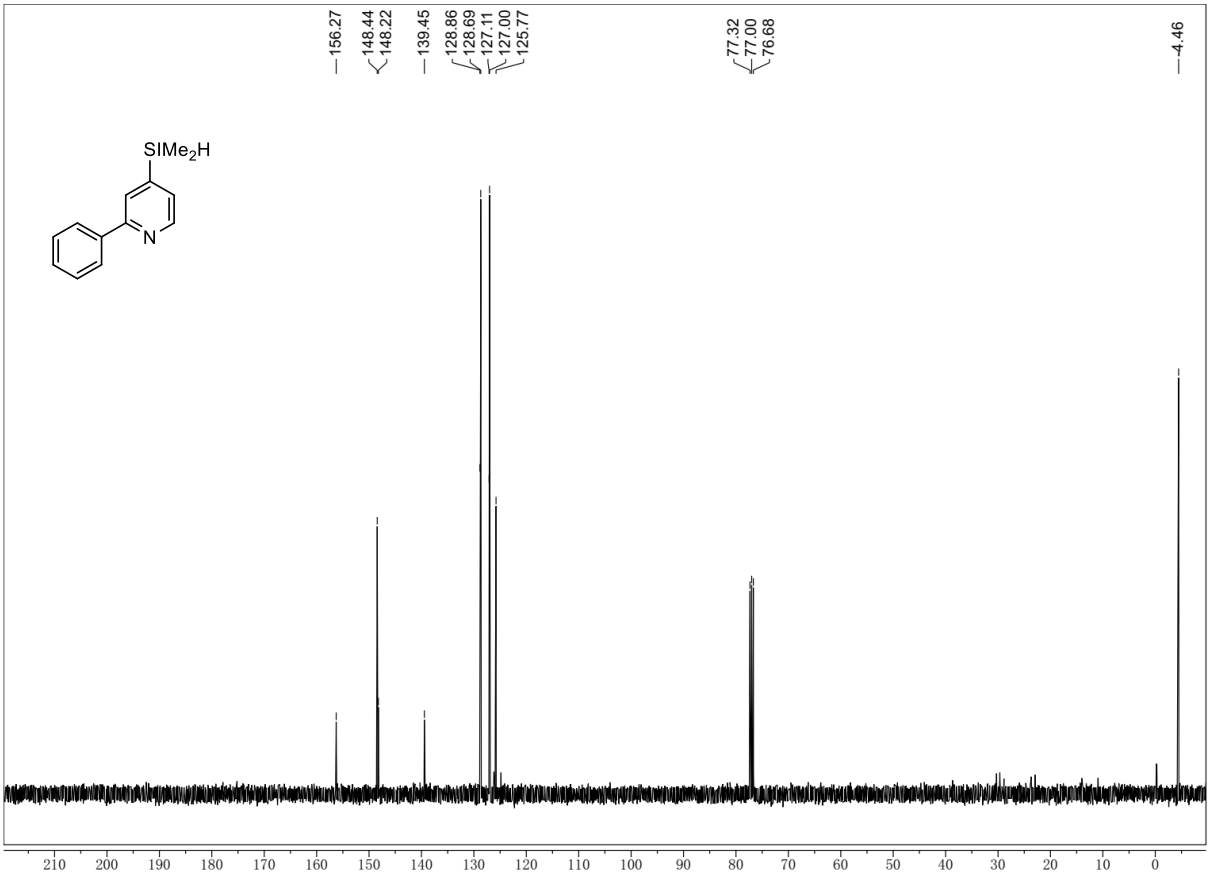
44 ^{13}C $CDCl_3$, 100 MHz



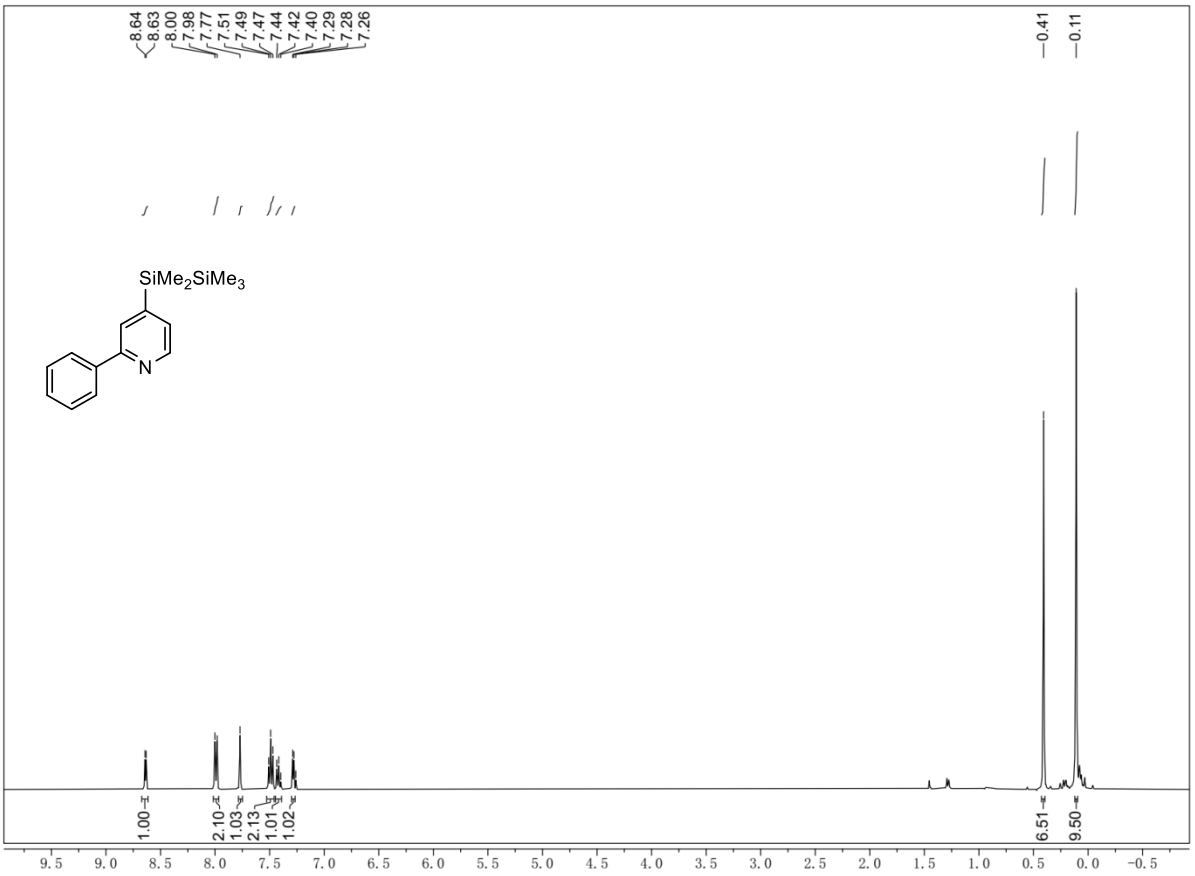
45 ^{1}H $CDCl_3$, 400 MHz



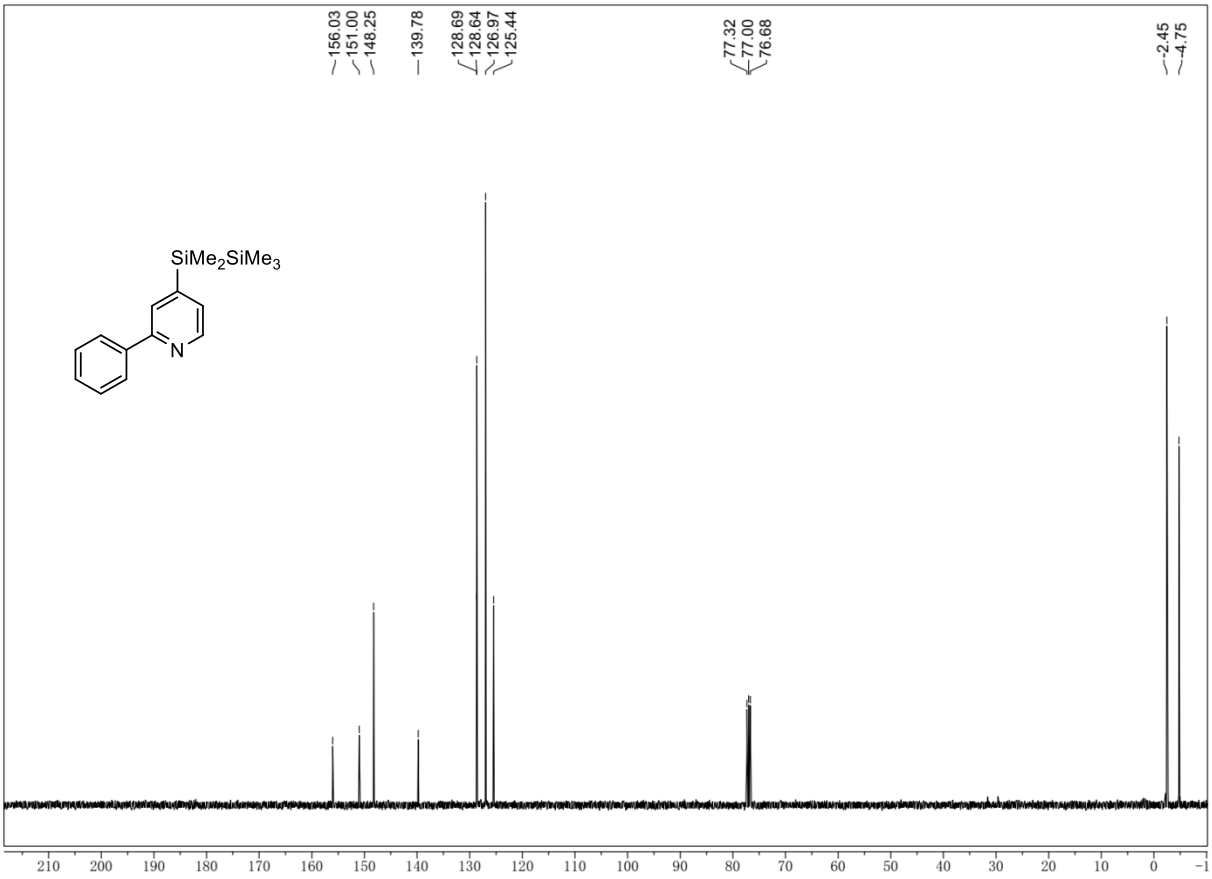
45 ^{13}C $CDCl_3$, 100 MHz



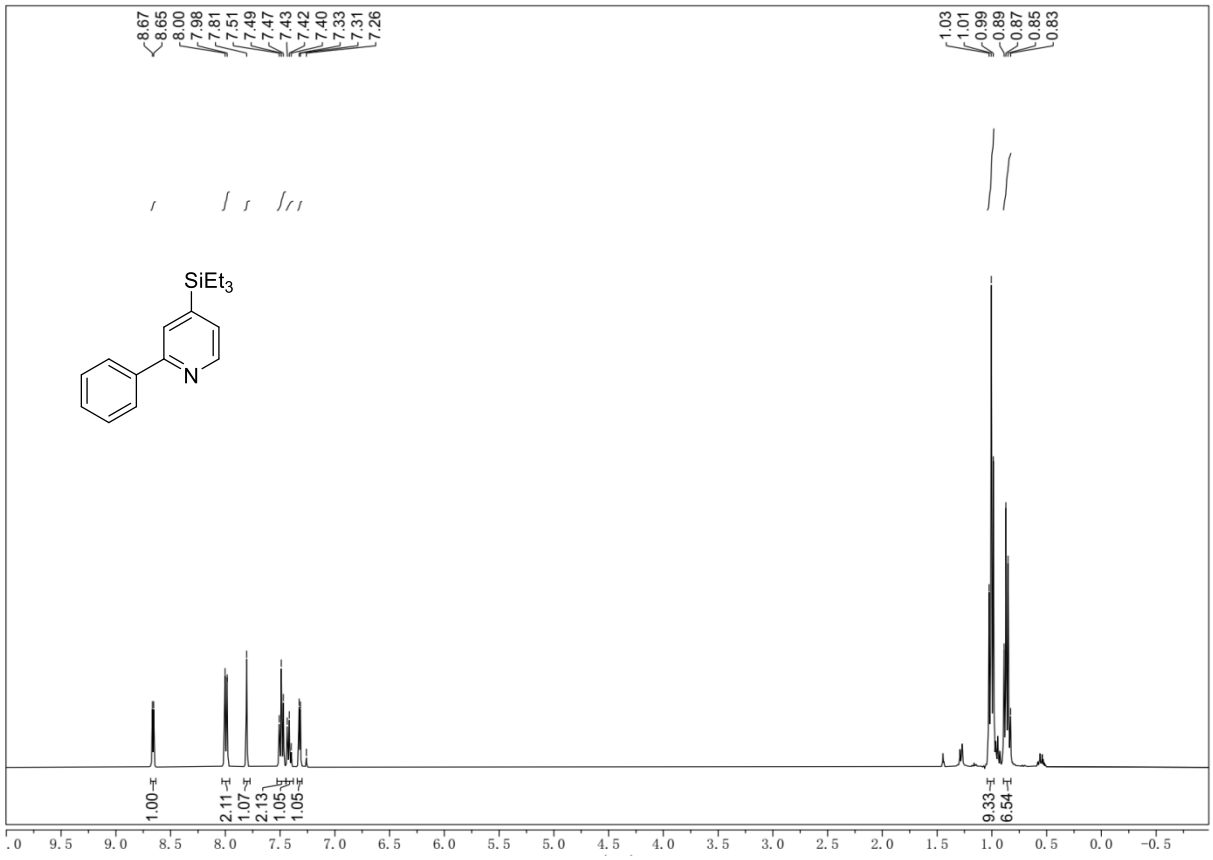
46 ^{1}H $CDCl_3$, 400 MHz



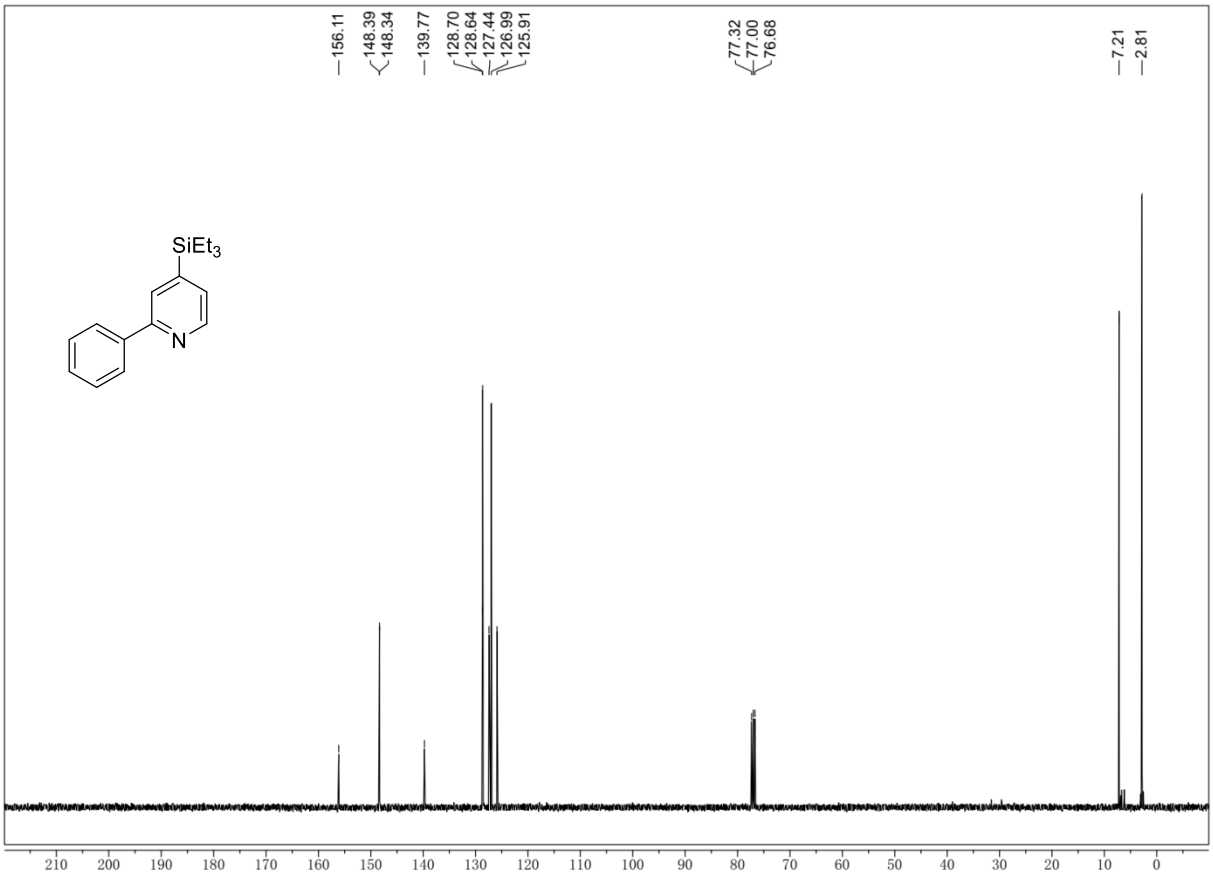
46 ^{13}C $CDCl_3$, 100 MHz



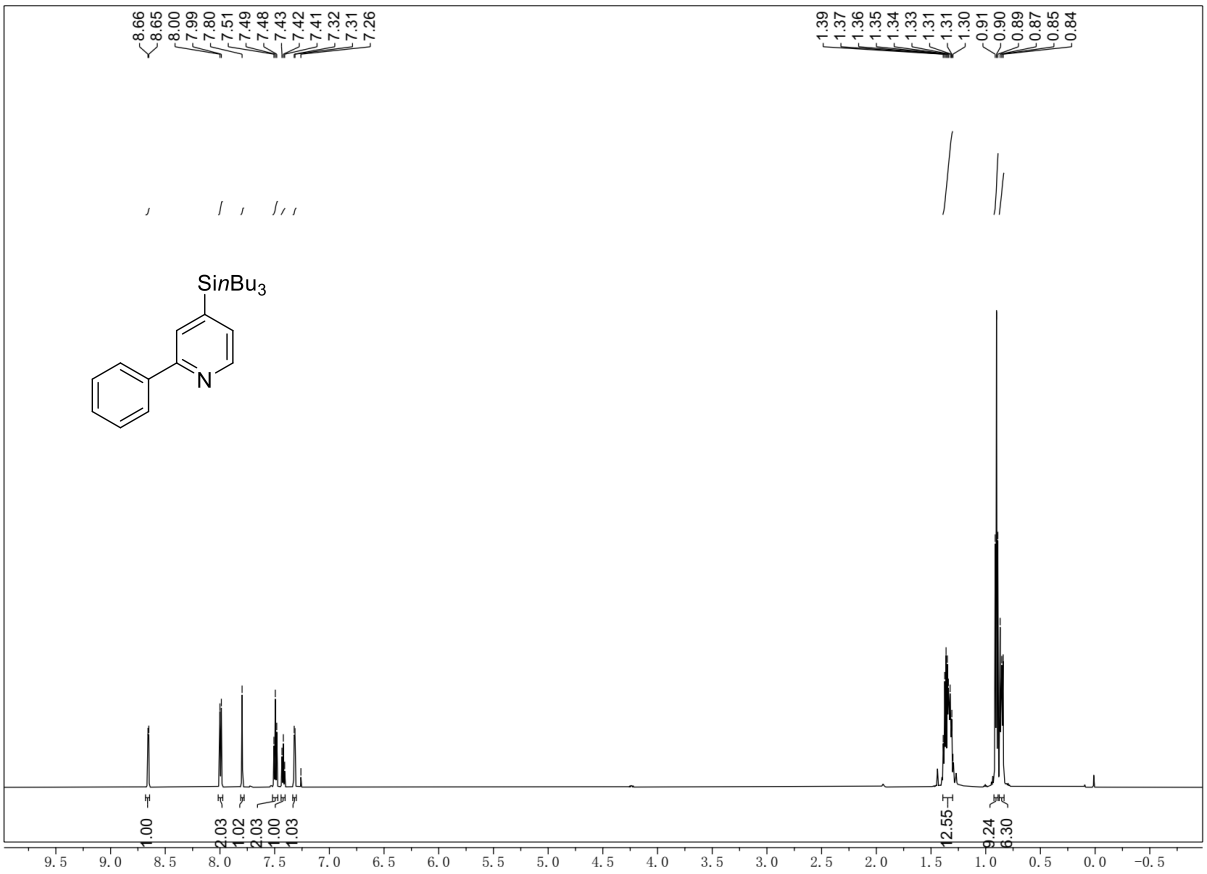
47 ^{1}H $CDCl_3$, 400 MHz



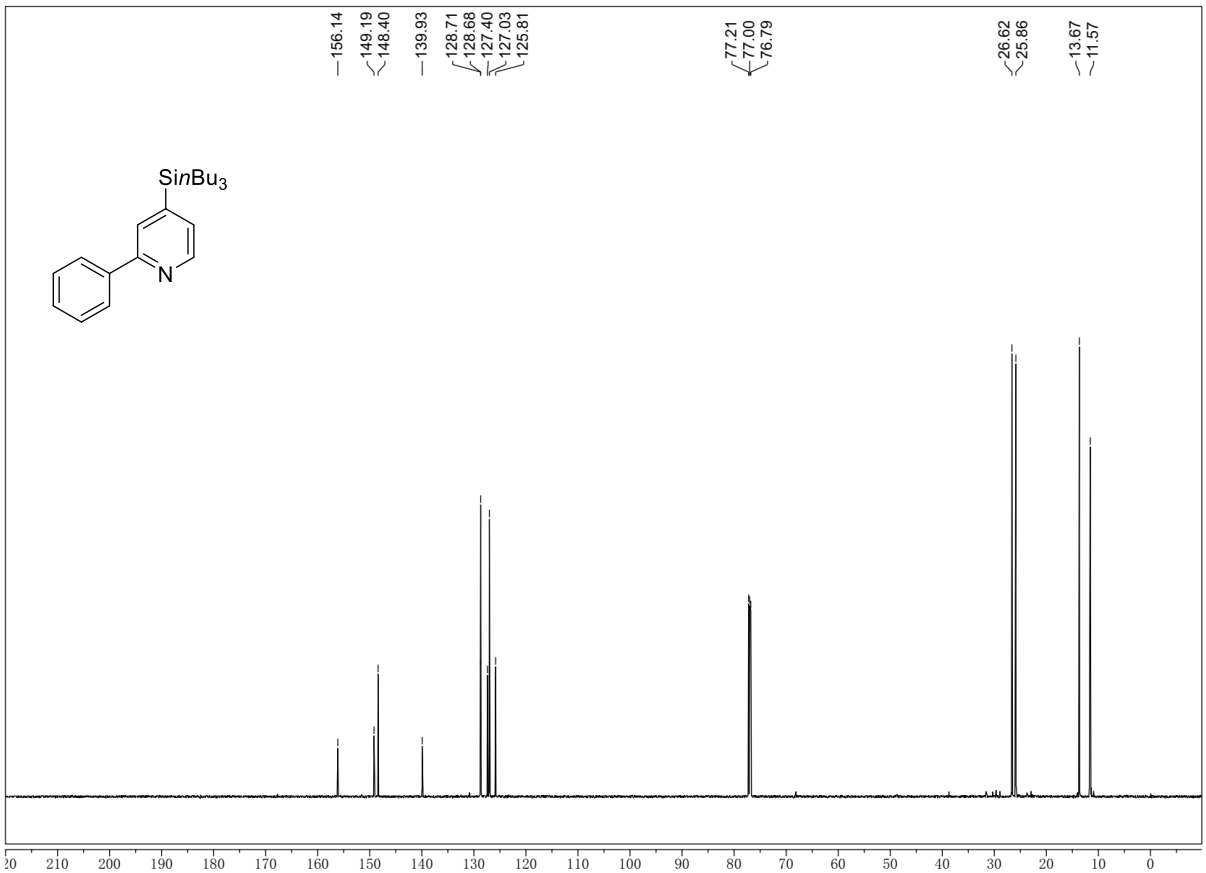
47 ^{13}C $CDCl_3$, 100 MHz



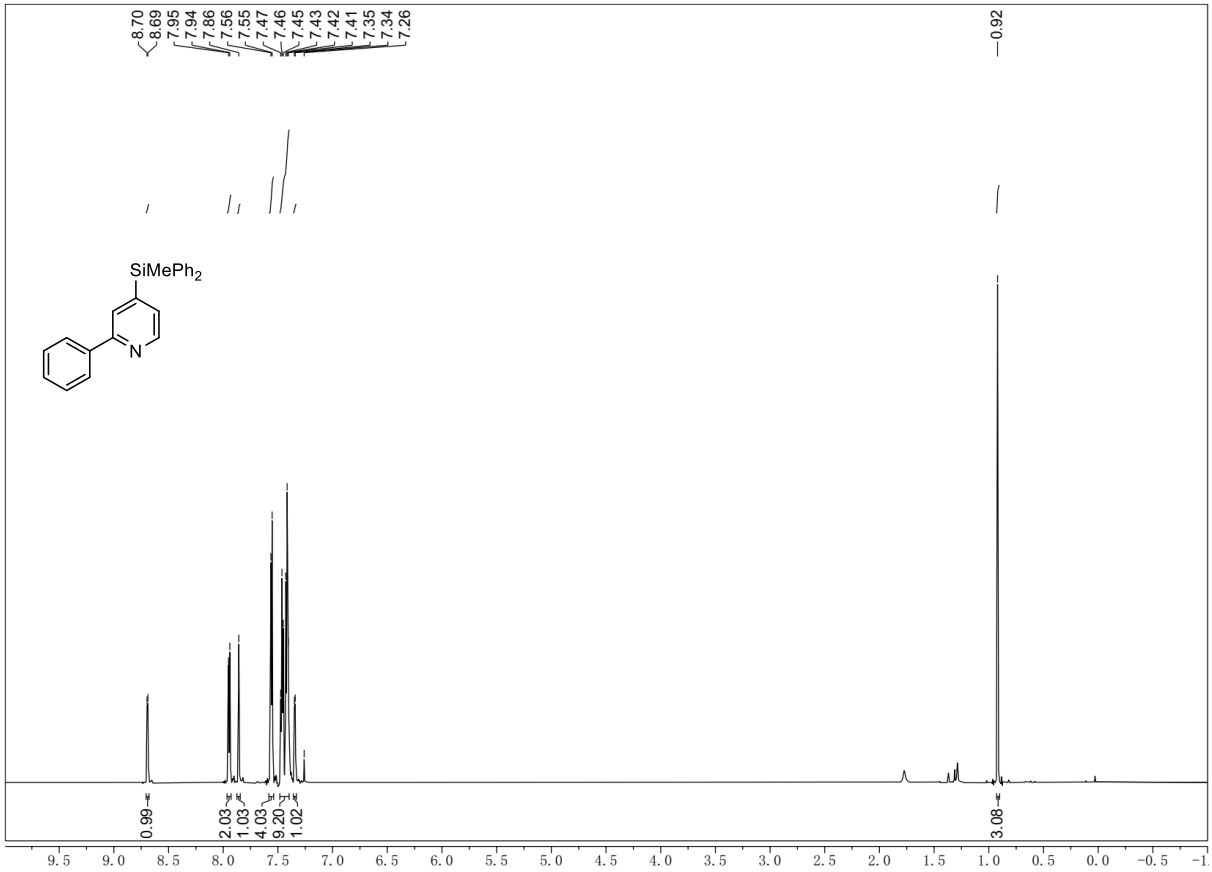
48 ^{1}H $CDCl_3$, 600 MHz



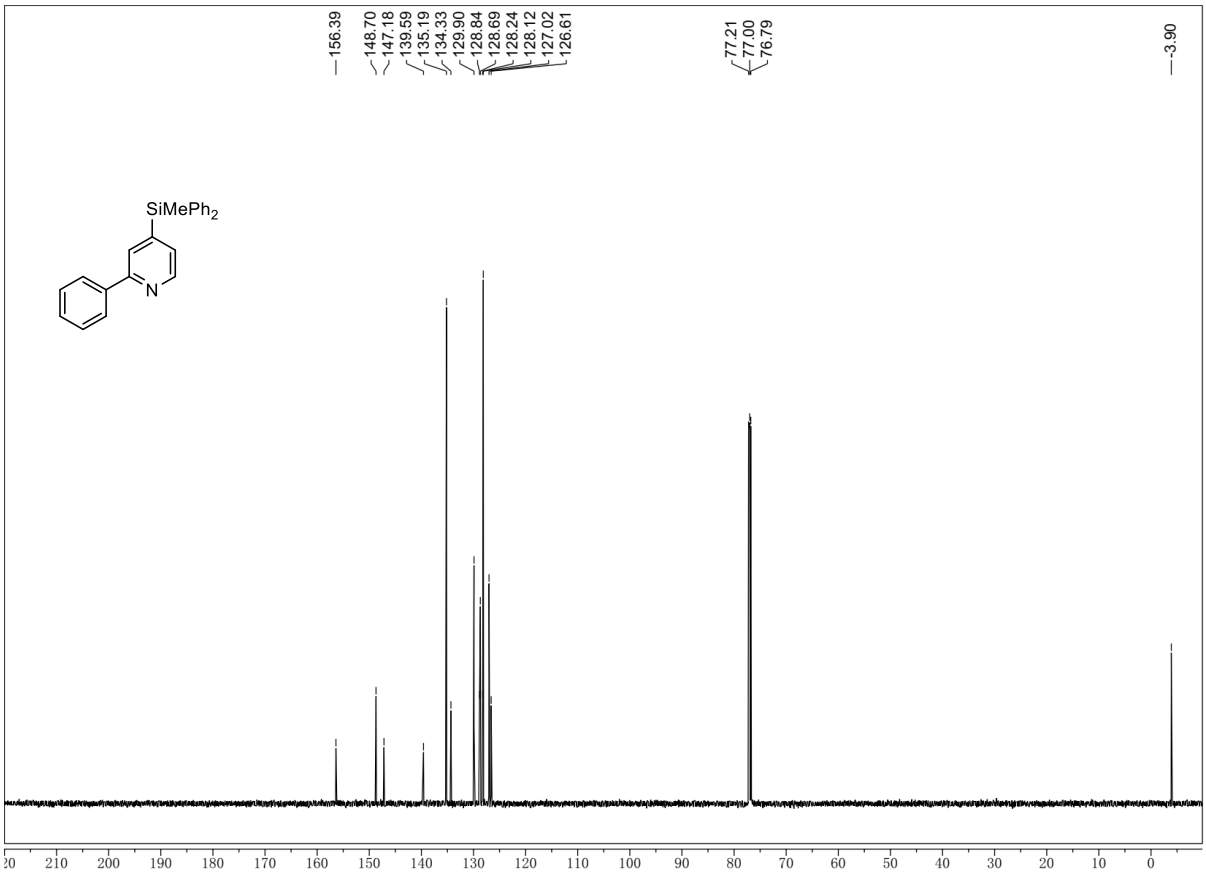
48 ^{13}C $CDCl_3$, 151 MHz



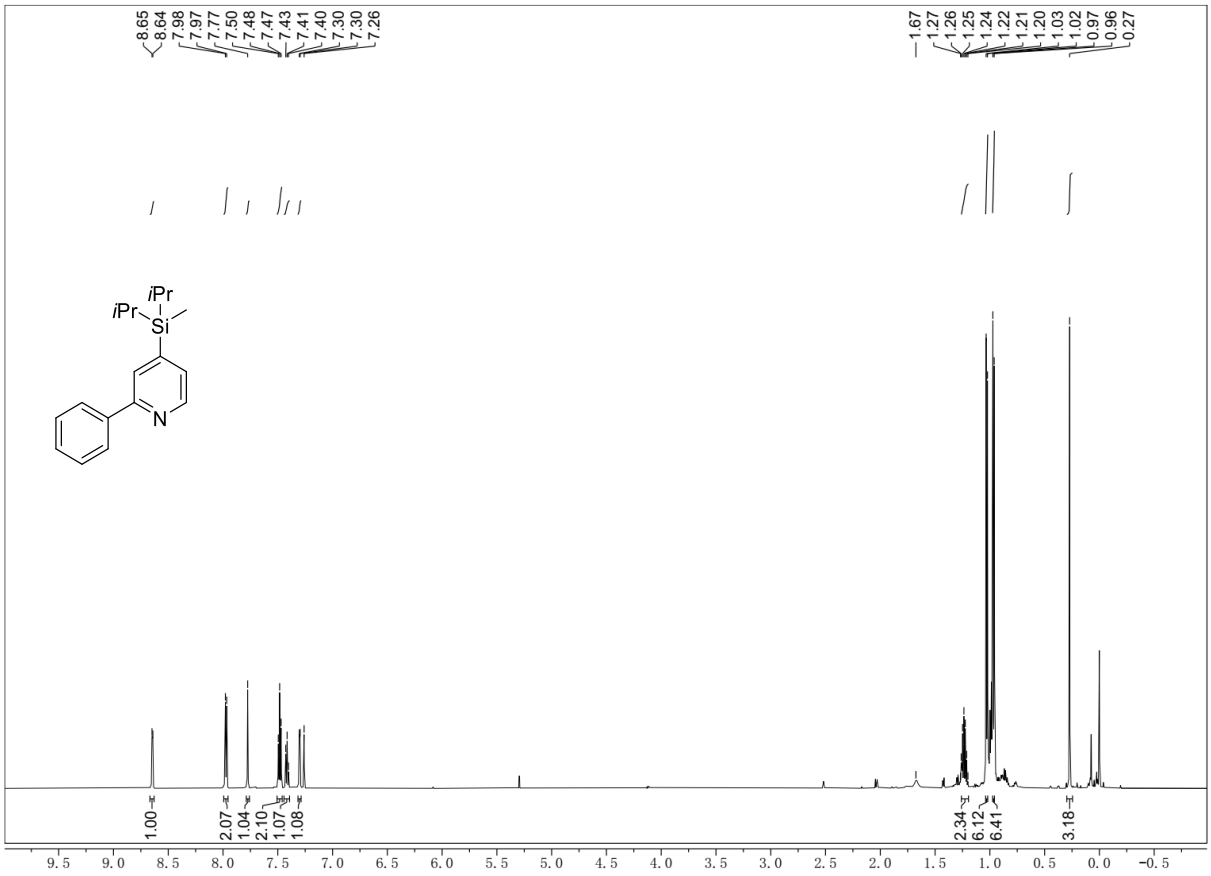
49 ^{1}H $CDCl_3$, 600 MHz



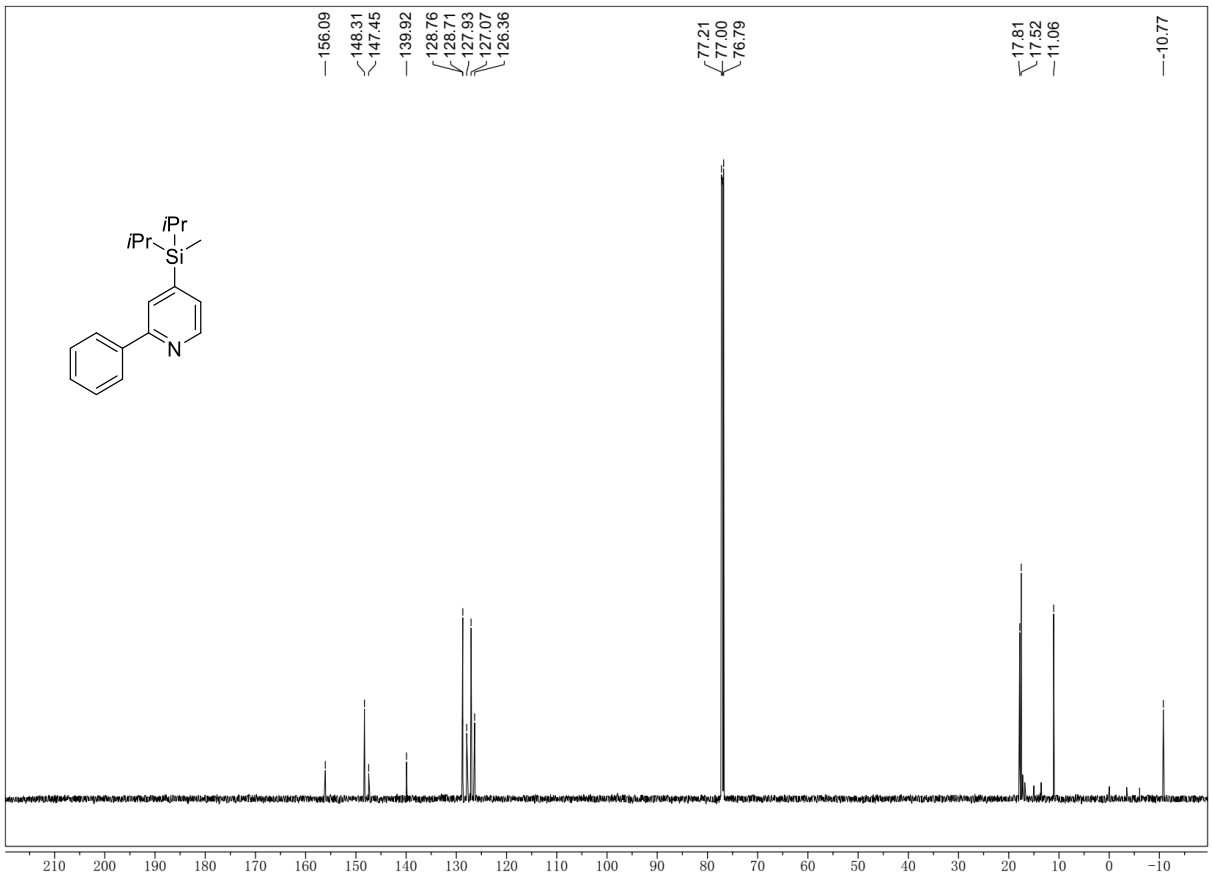
49 ^{13}C $CDCl_3$, 151 MHz



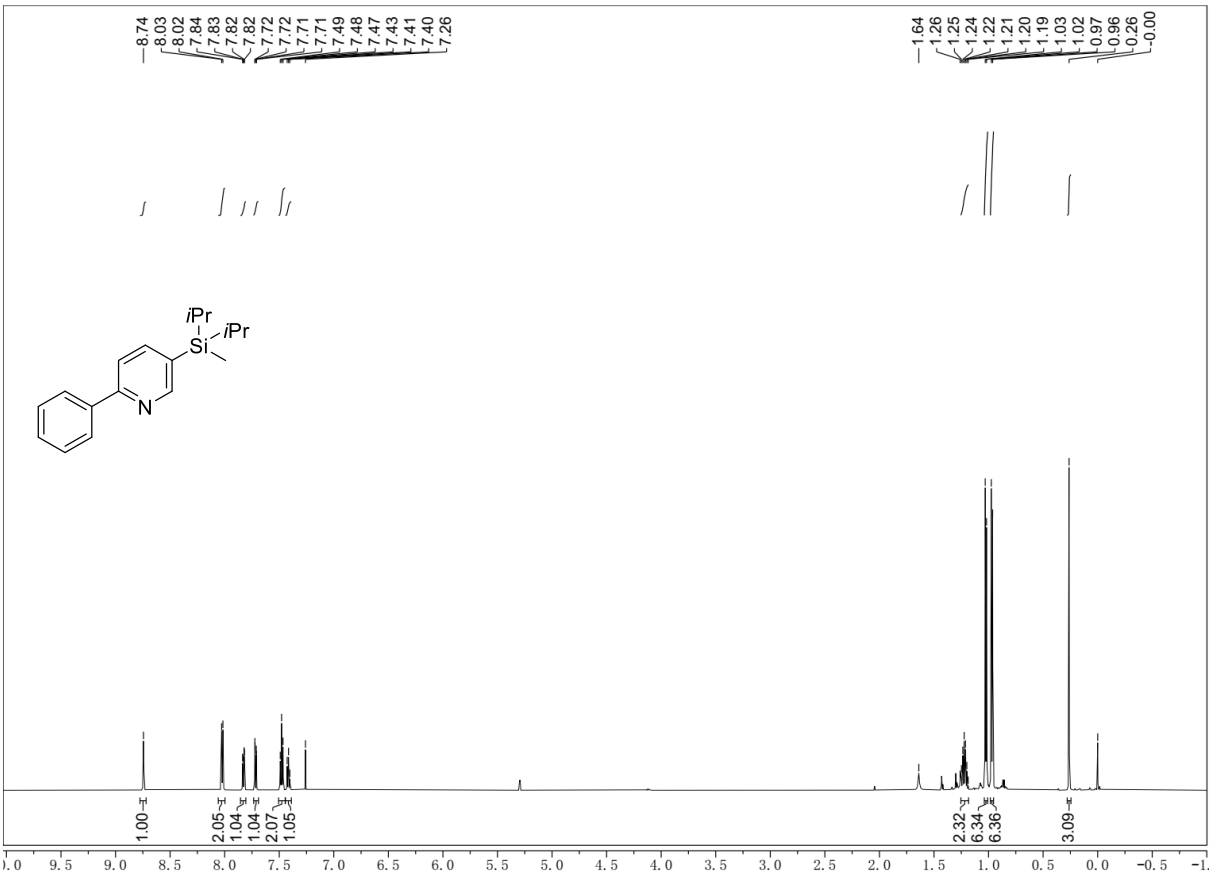
50-C4 ^{1}H $CDCl_3$, 600 MHz



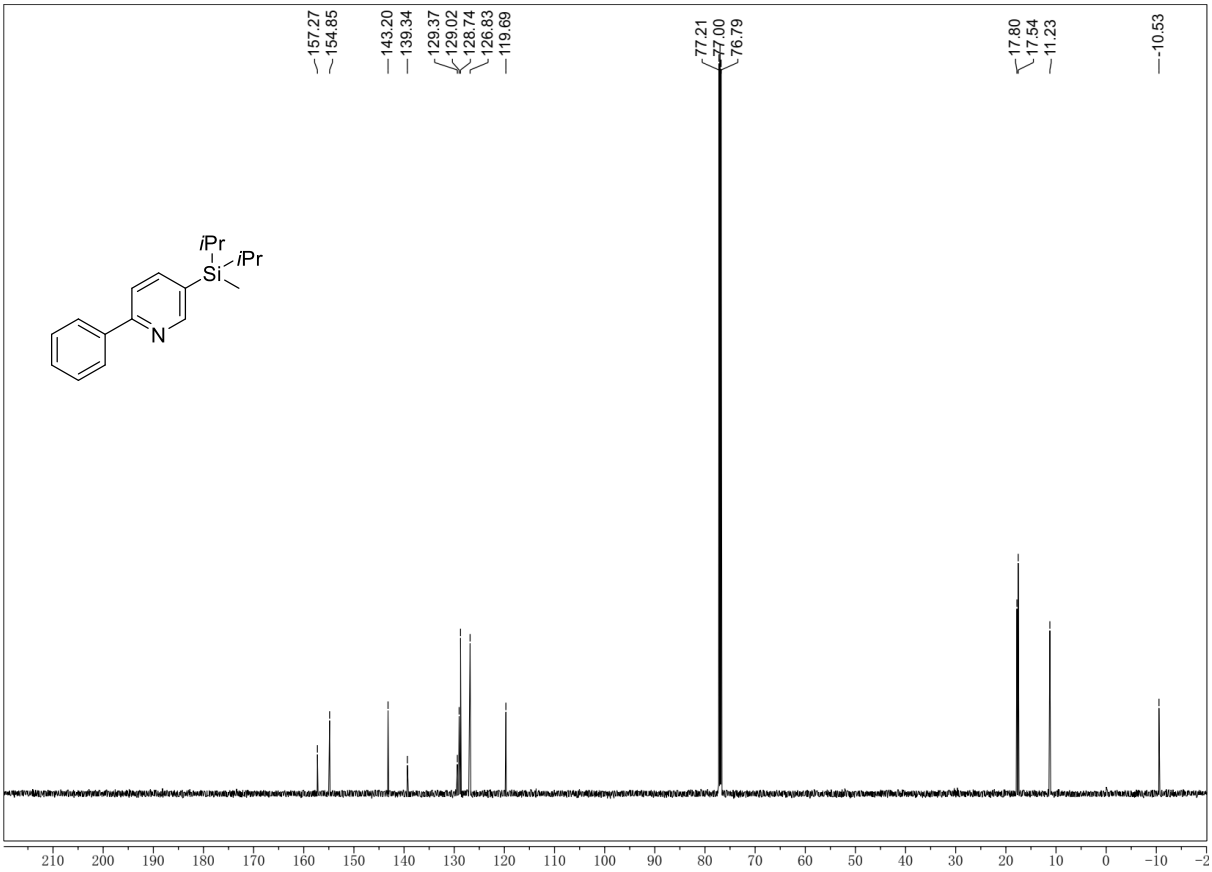
50-C4 ^{13}C $CDCl_3$, 151 MHz



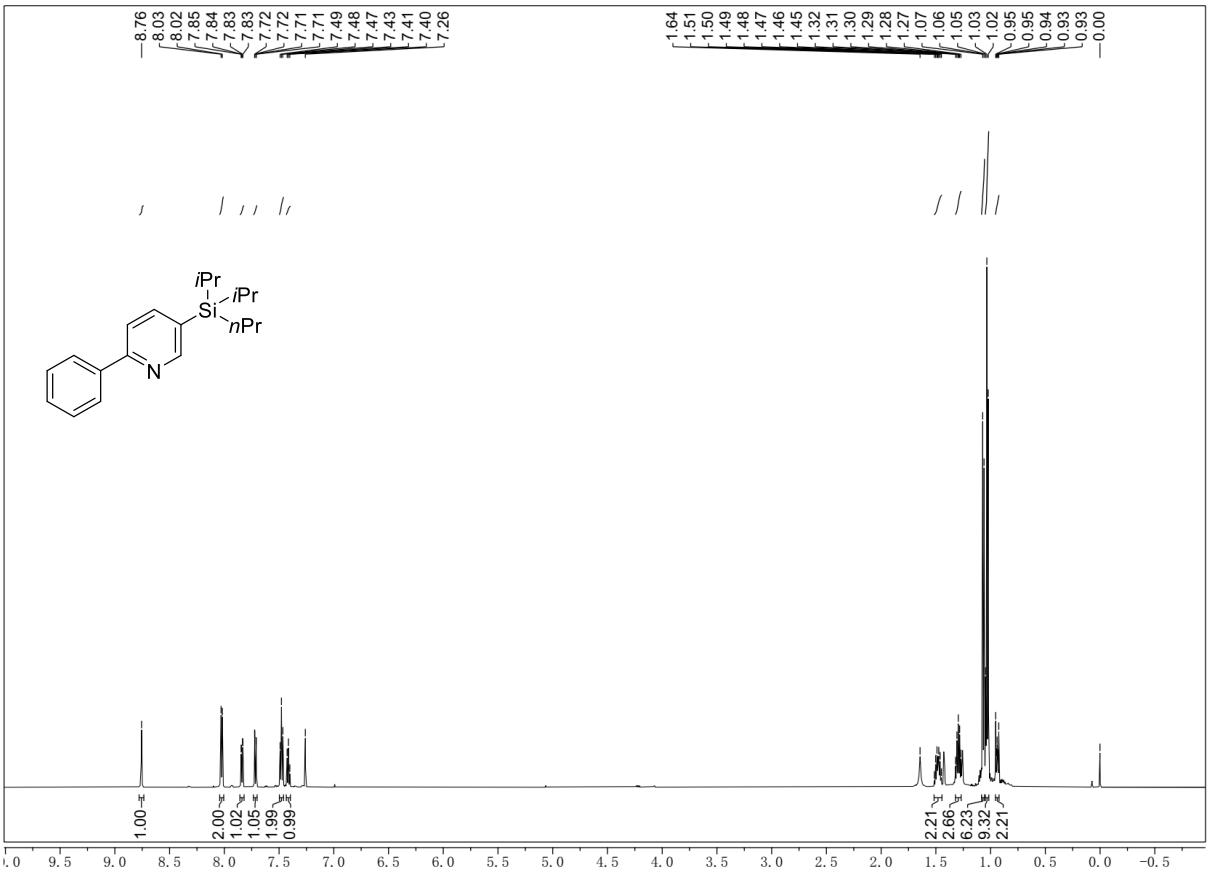
50-C5 ^{1}H $CDCl_3$, 600 MHz



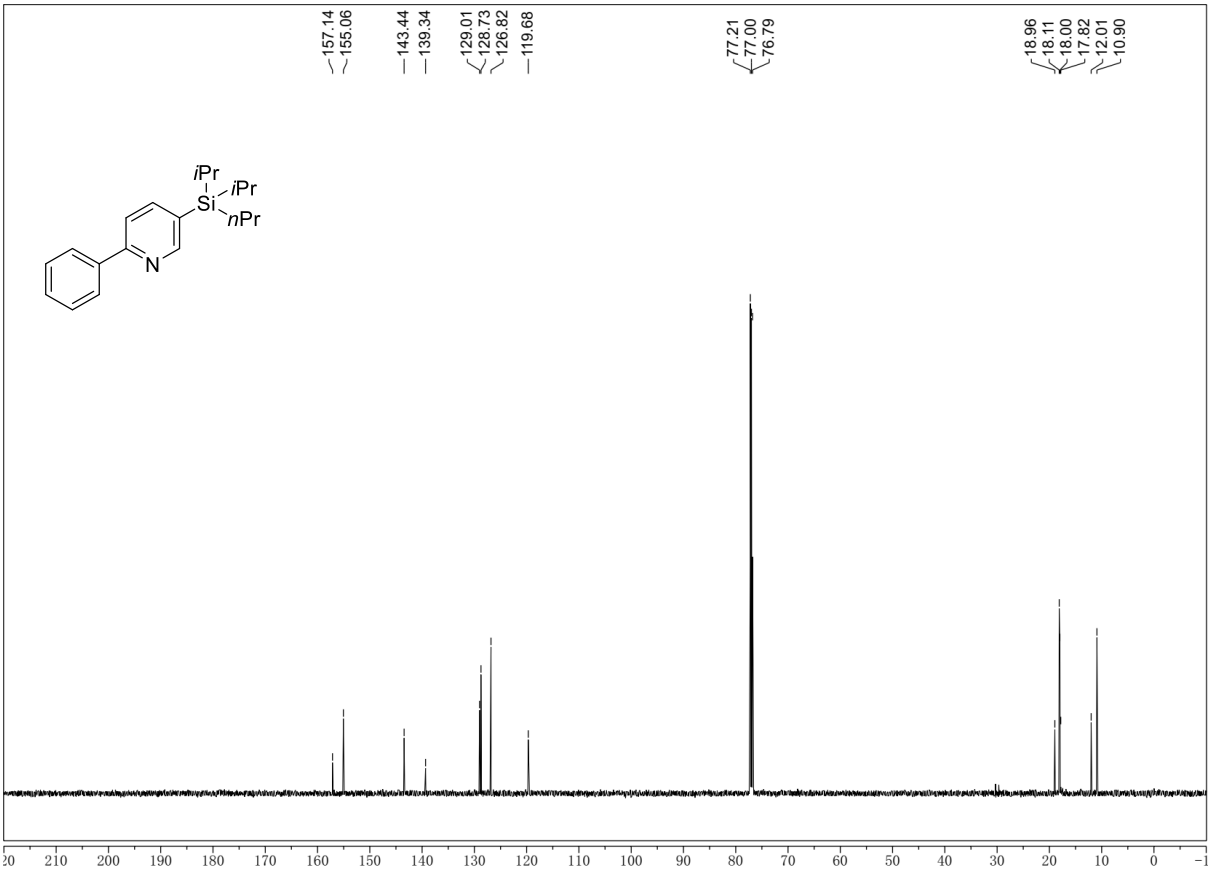
50-C5 ^{13}C $CDCl_3$, 151 MHz



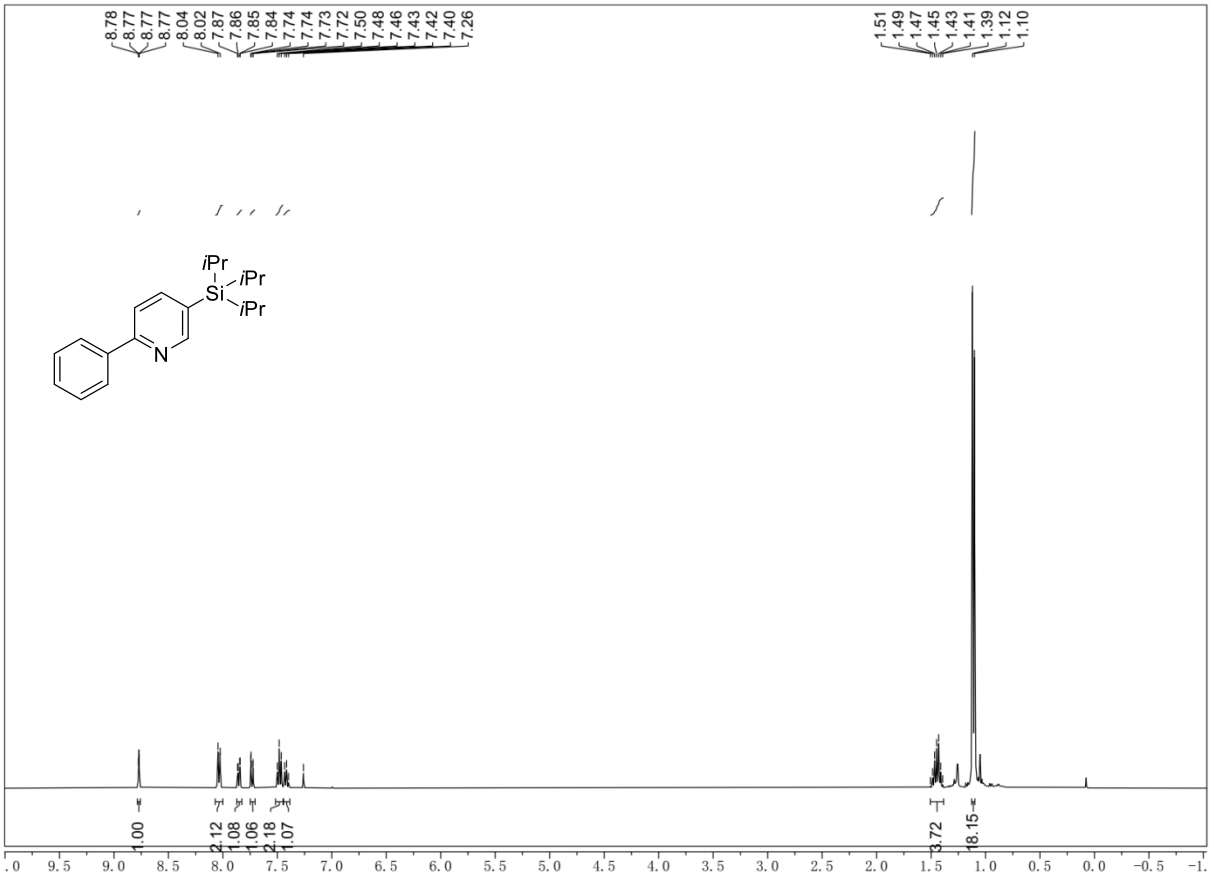
51 ^{1}H $CDCl_3$, 600 MHz



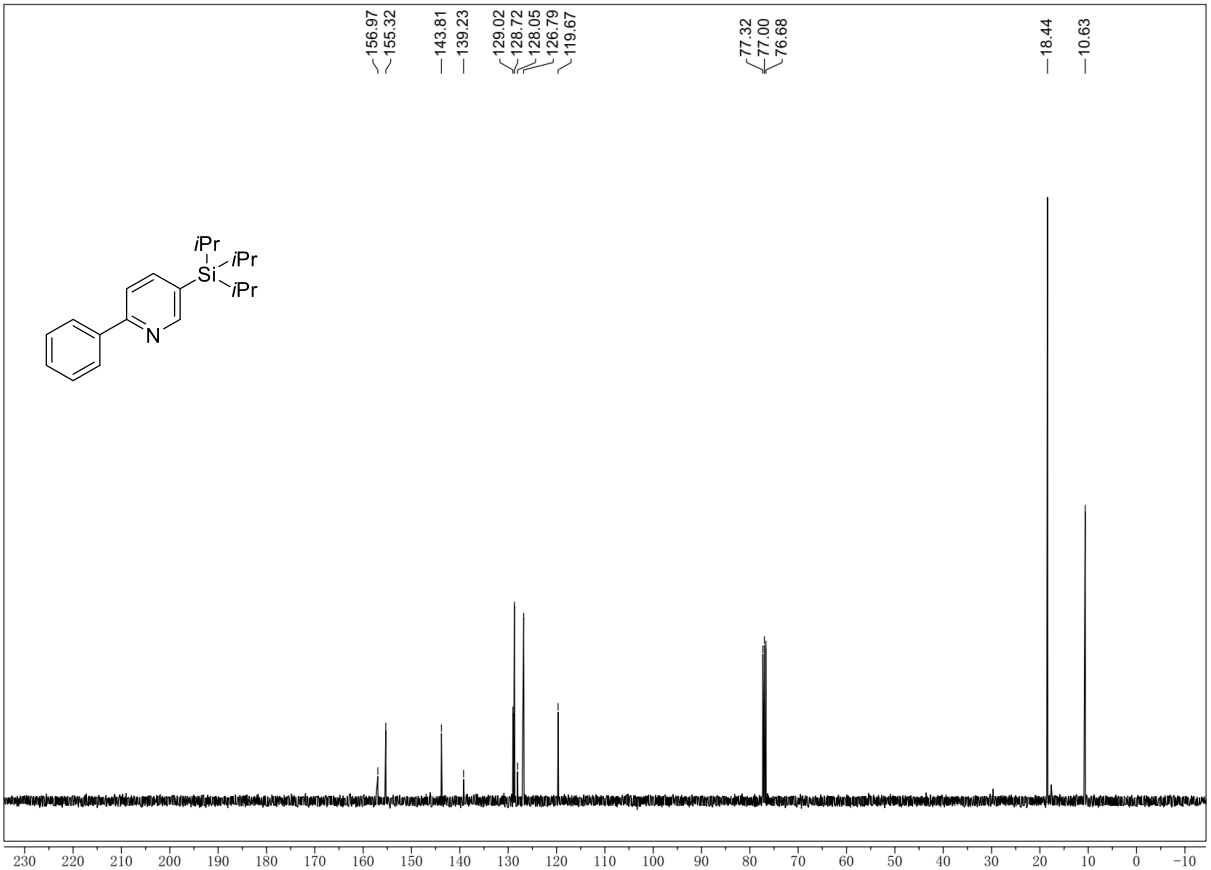
51 ^{13}C $CDCl_3$, 151 MHz



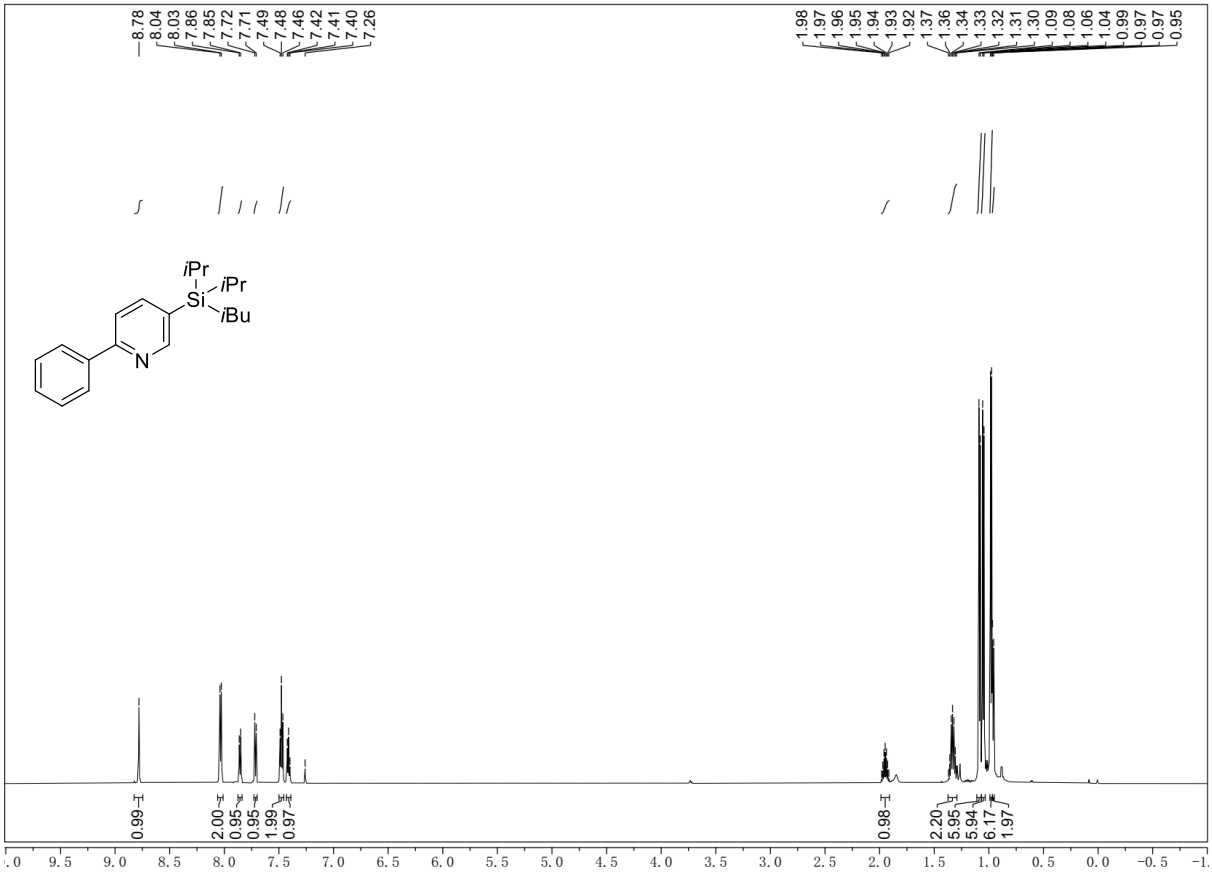
52 ^{1}H $CDCl_3$, 400 MHz



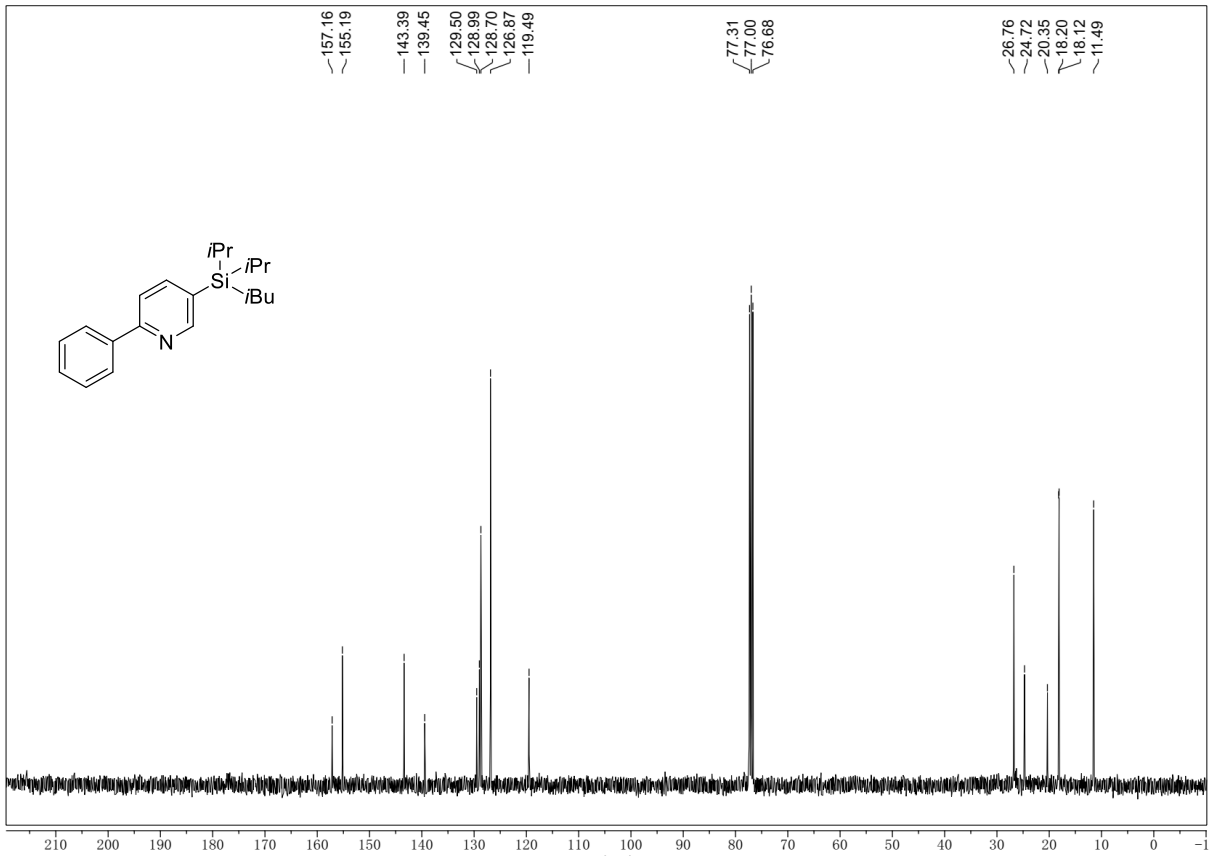
52 ^{13}C $CDCl_3$, 100 MHz



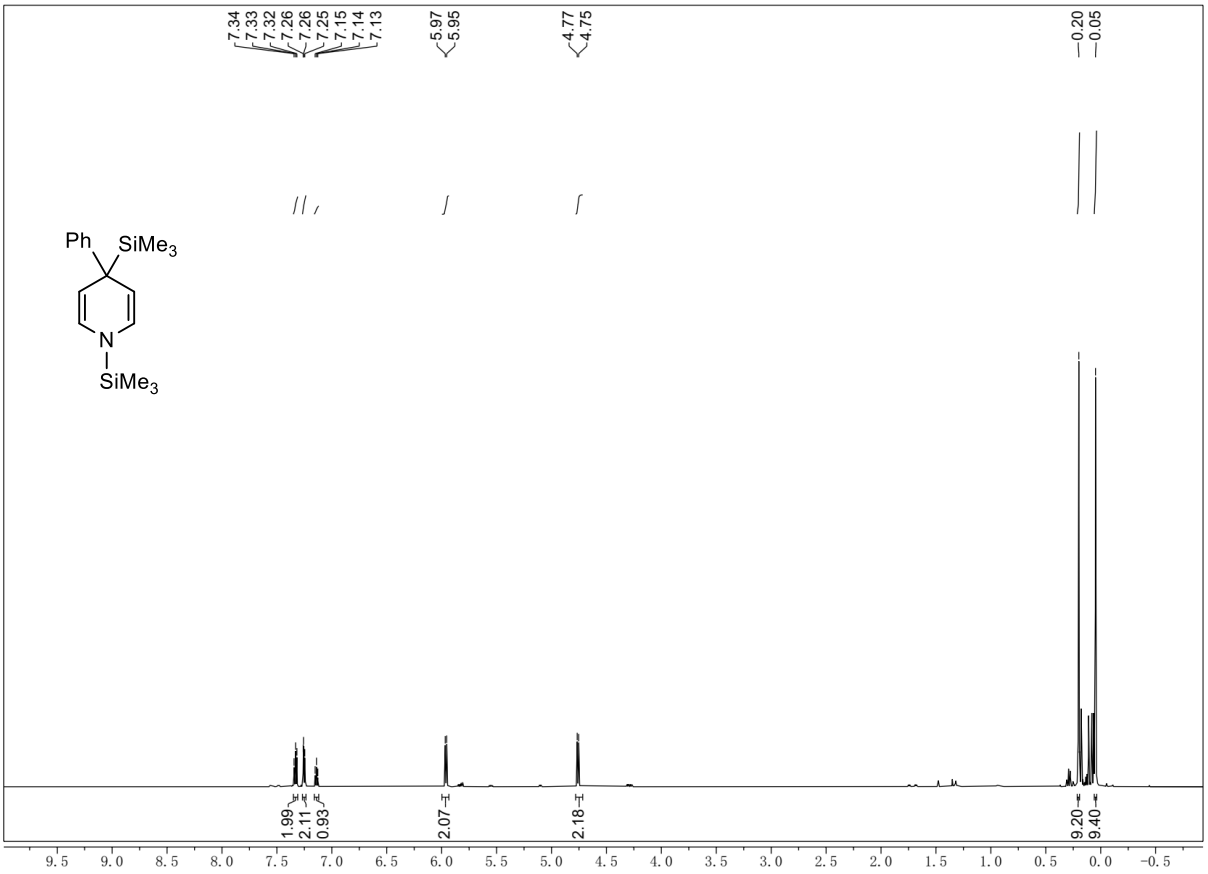
53 ^{1}H $CDCl_3$, 600 MHz



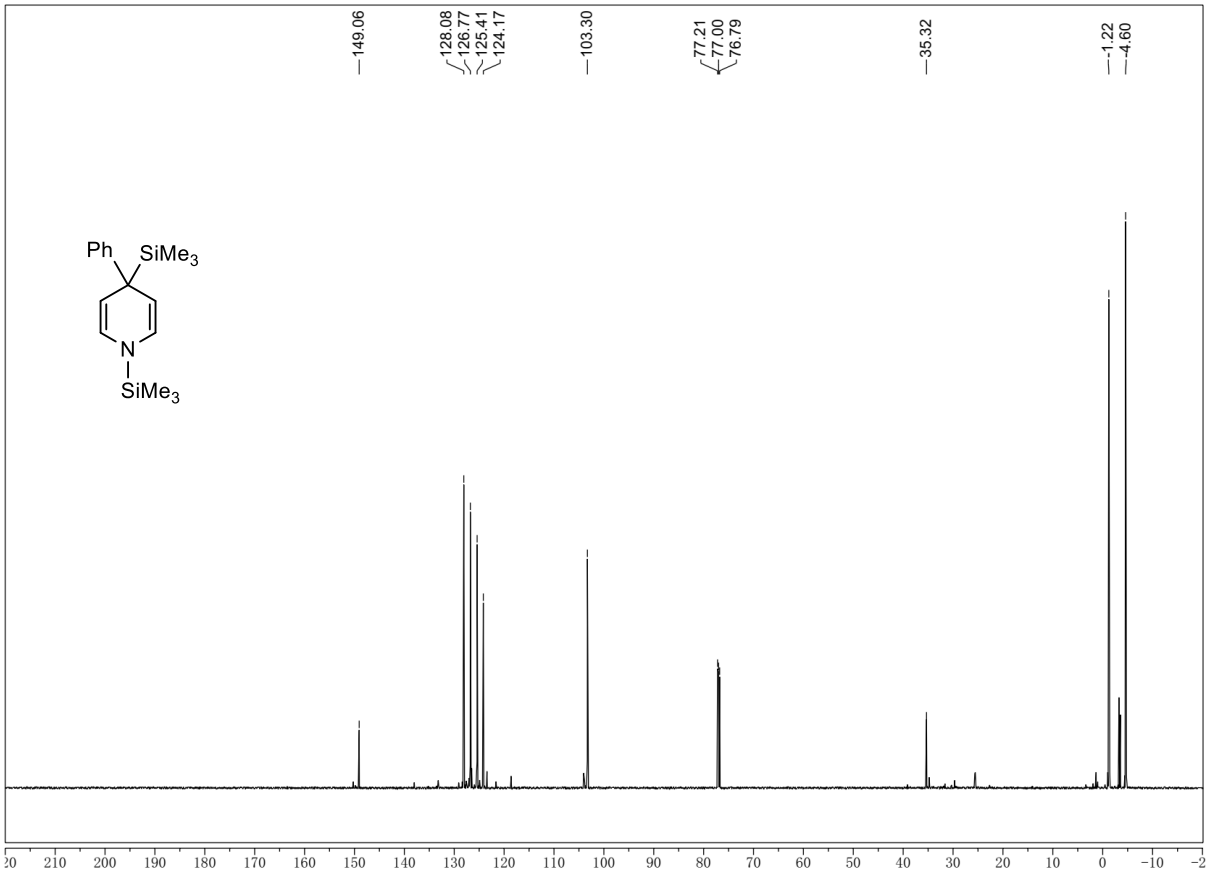
53 ^{13}C $CDCl_3$, 100 MHz



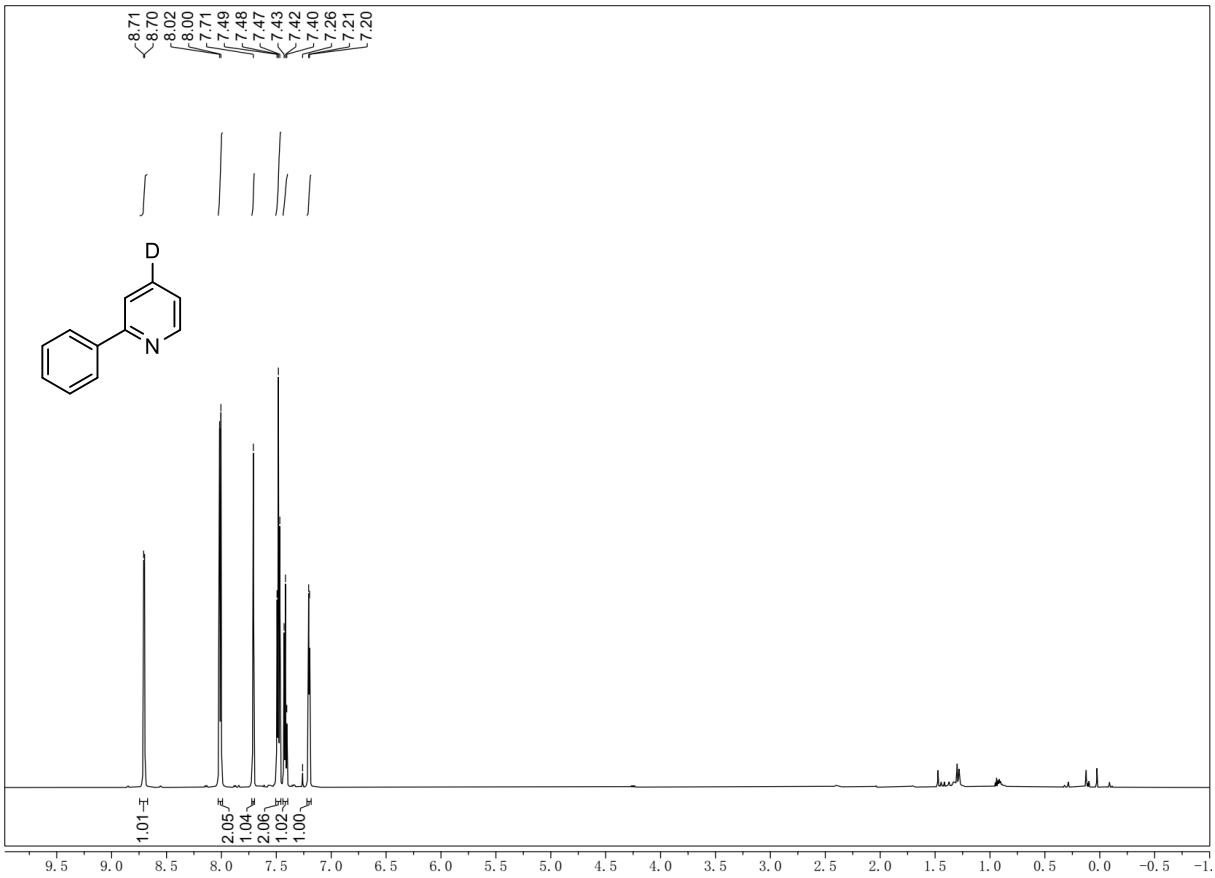
55 ^{1}H $CDCl_3$, 600 MHz



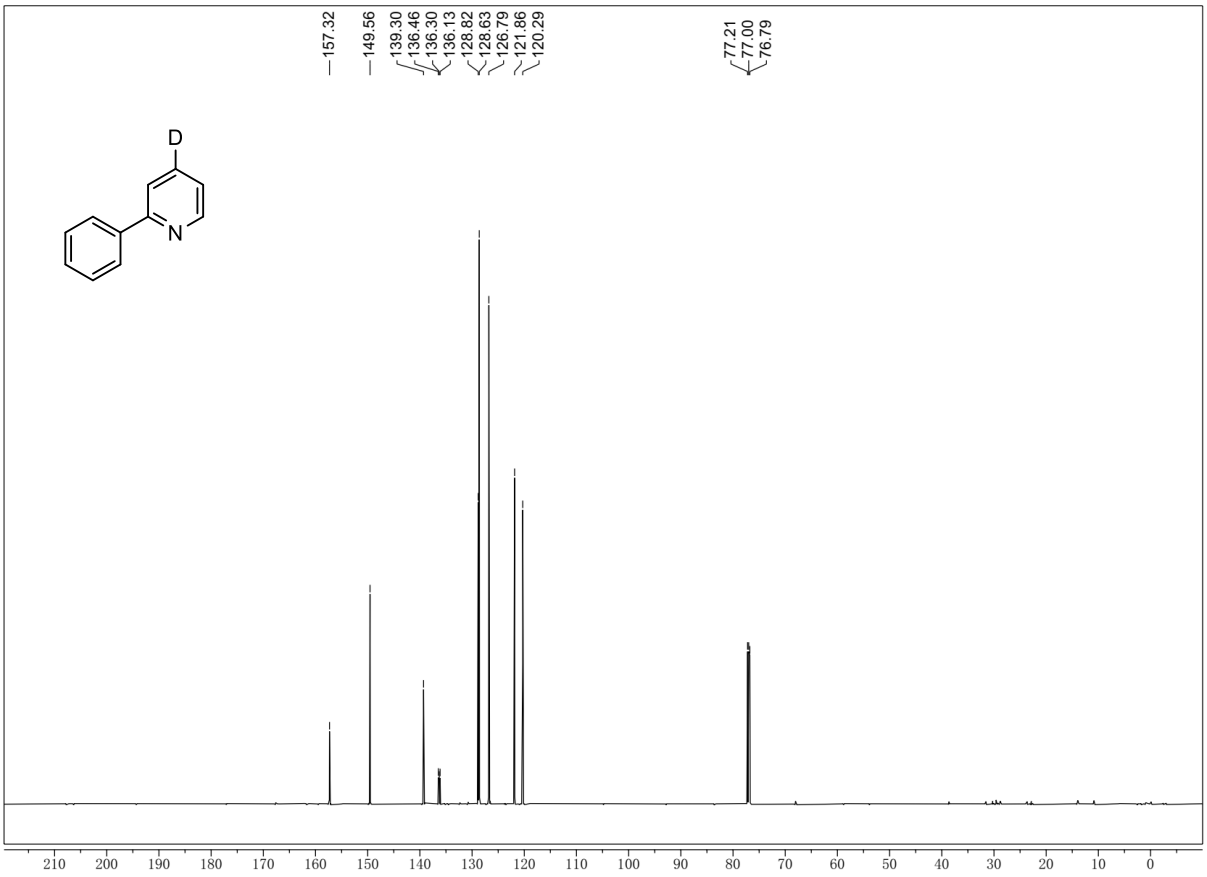
55 ^{13}C $CDCl_3$, 151 MHz



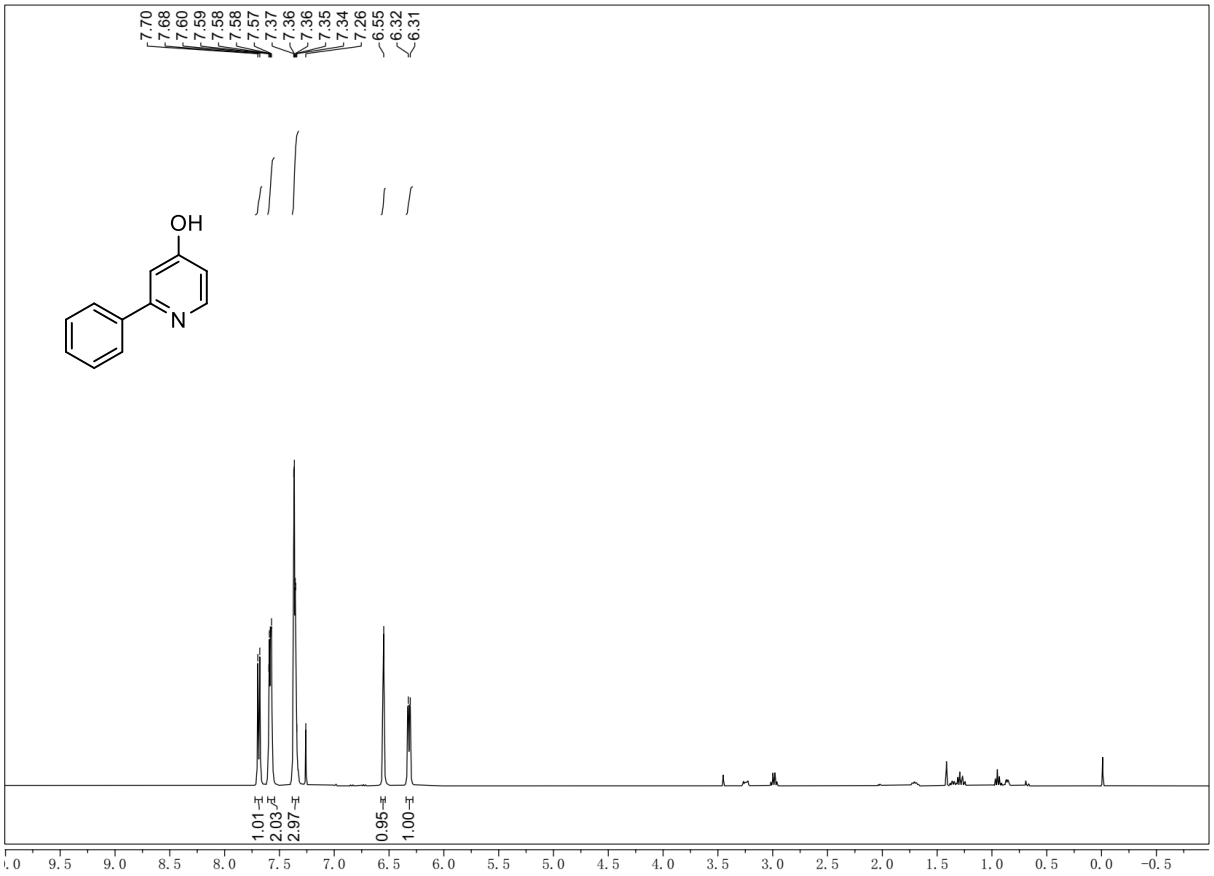
56 ^{1}H $CDCl_3$, 600 MHz



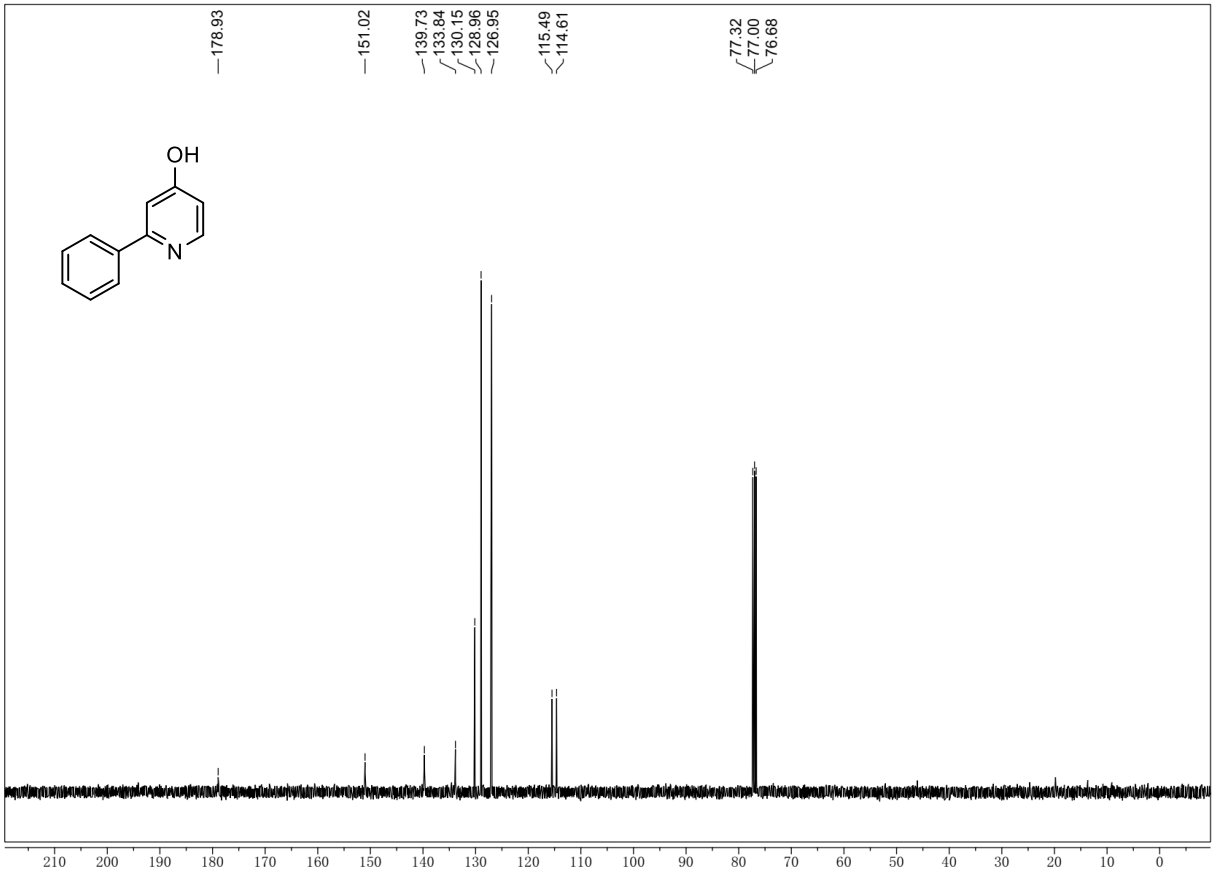
56 ^{13}C $CDCl_3$, 151 MHz



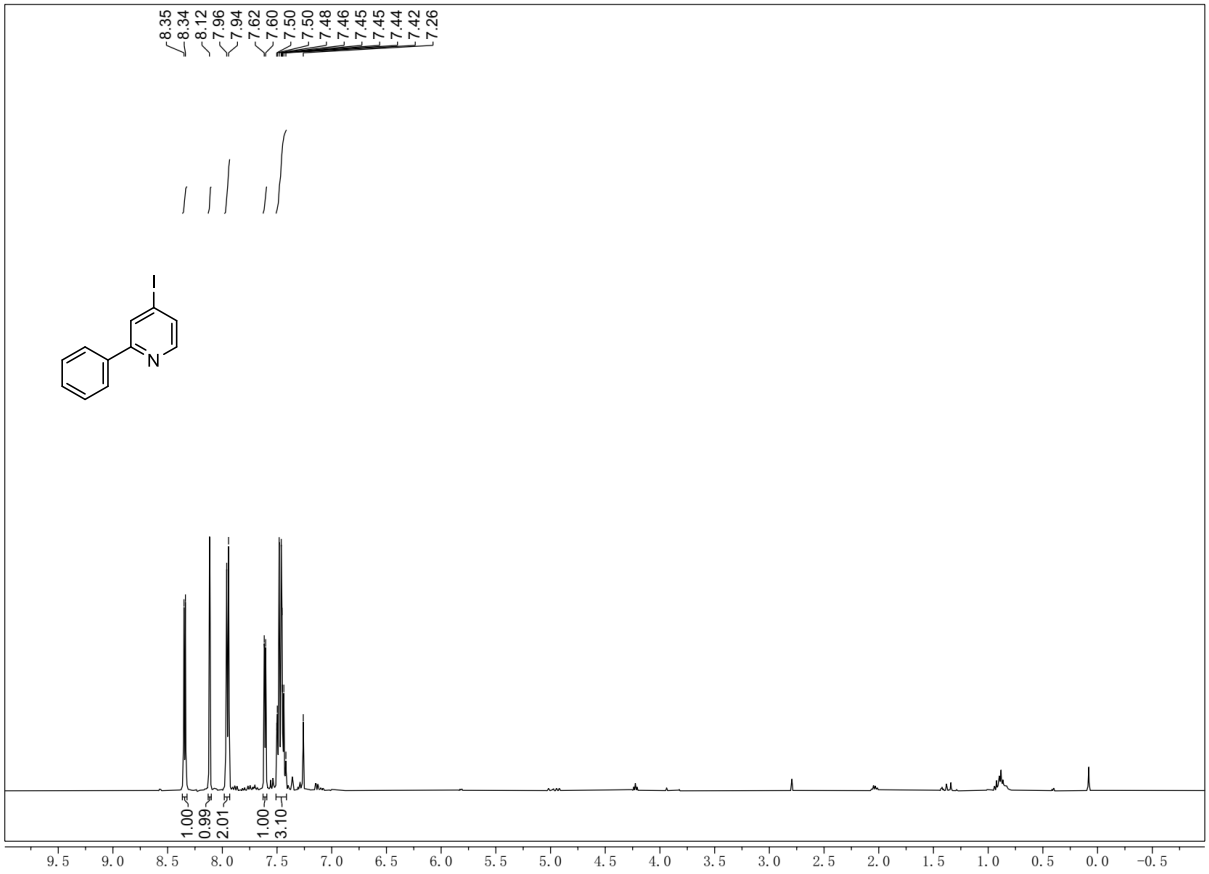
57 ^{1}H $CDCl_3$, 400 MHz



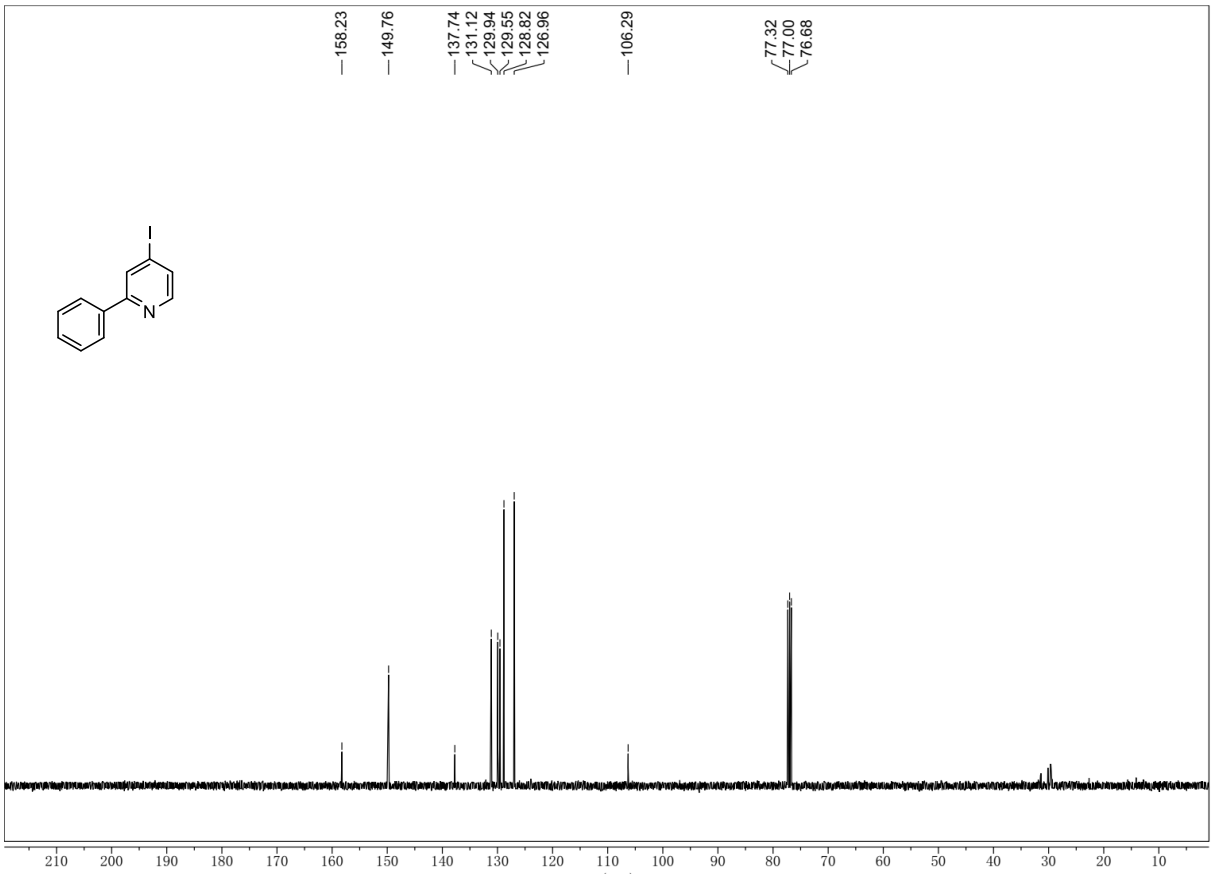
57 ^{13}C $CDCl_3$, 100 MHz



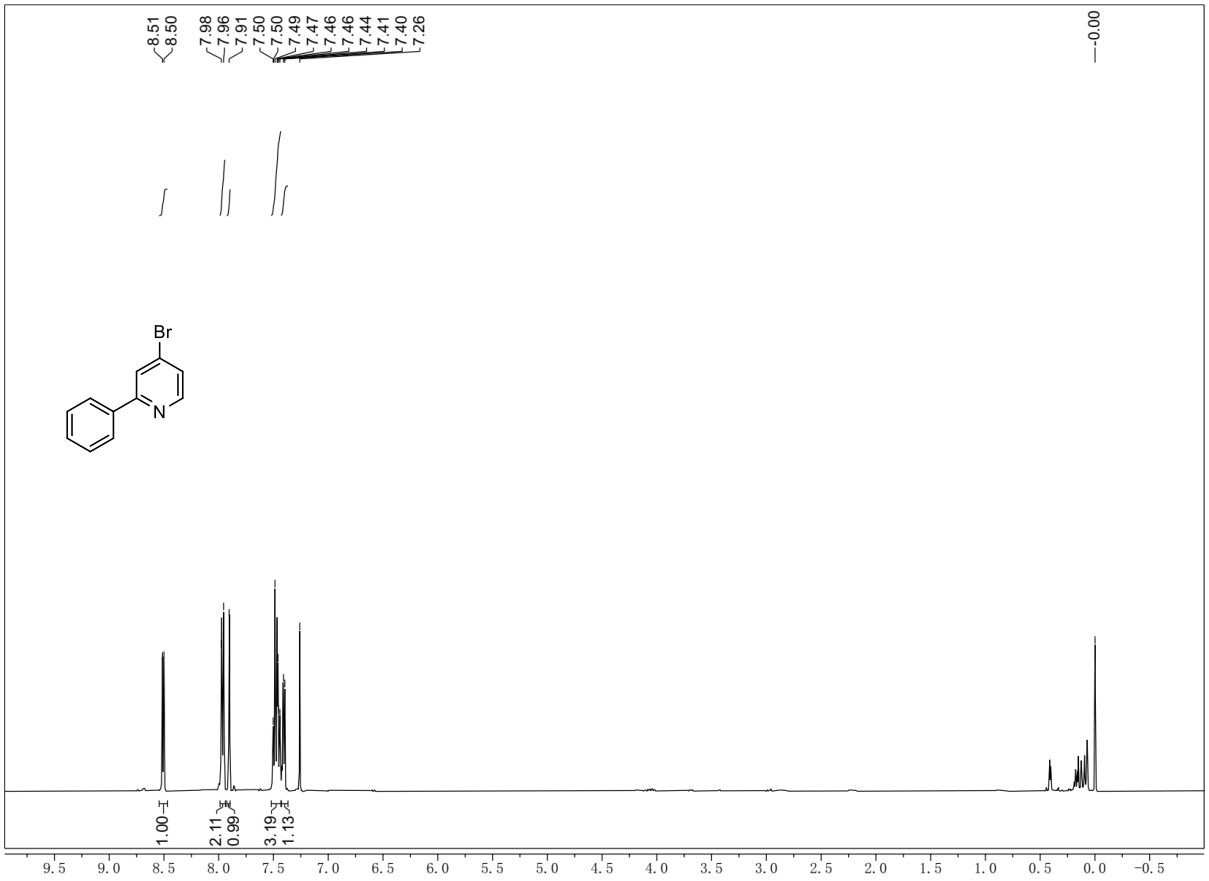
58 ^{1}H $CDCl_3$, 400 MHz



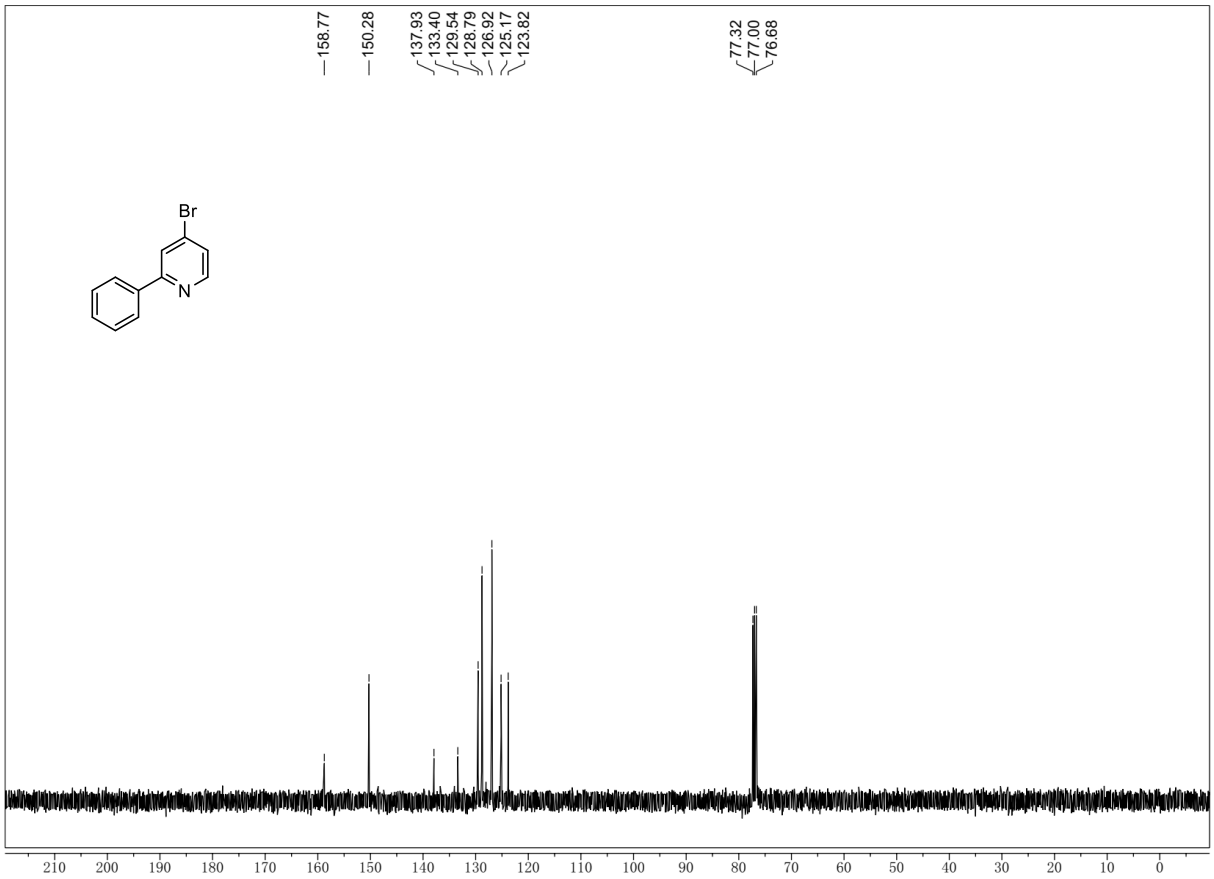
58 ^{13}C $CDCl_3$, 100 MHz



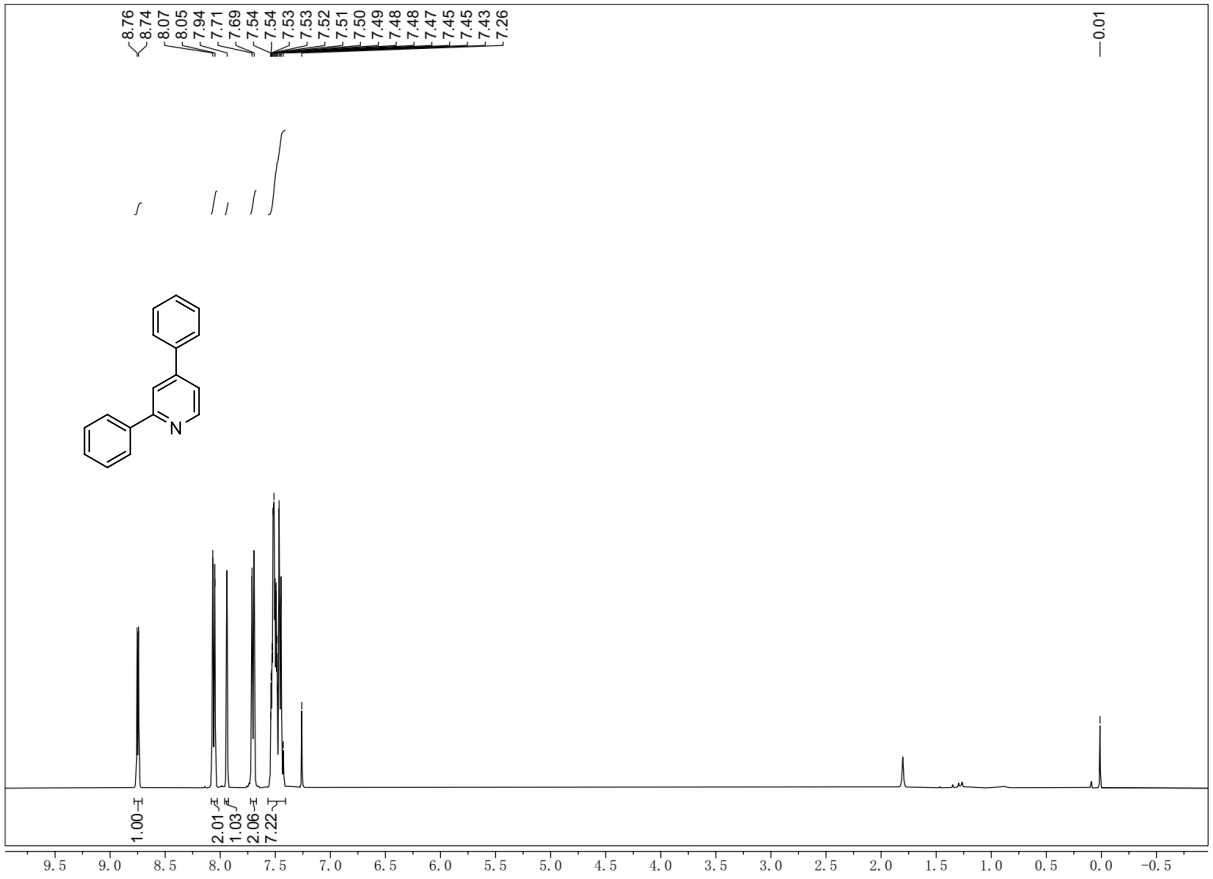
59 ^{1}H $CDCl_3$, 400 MHz



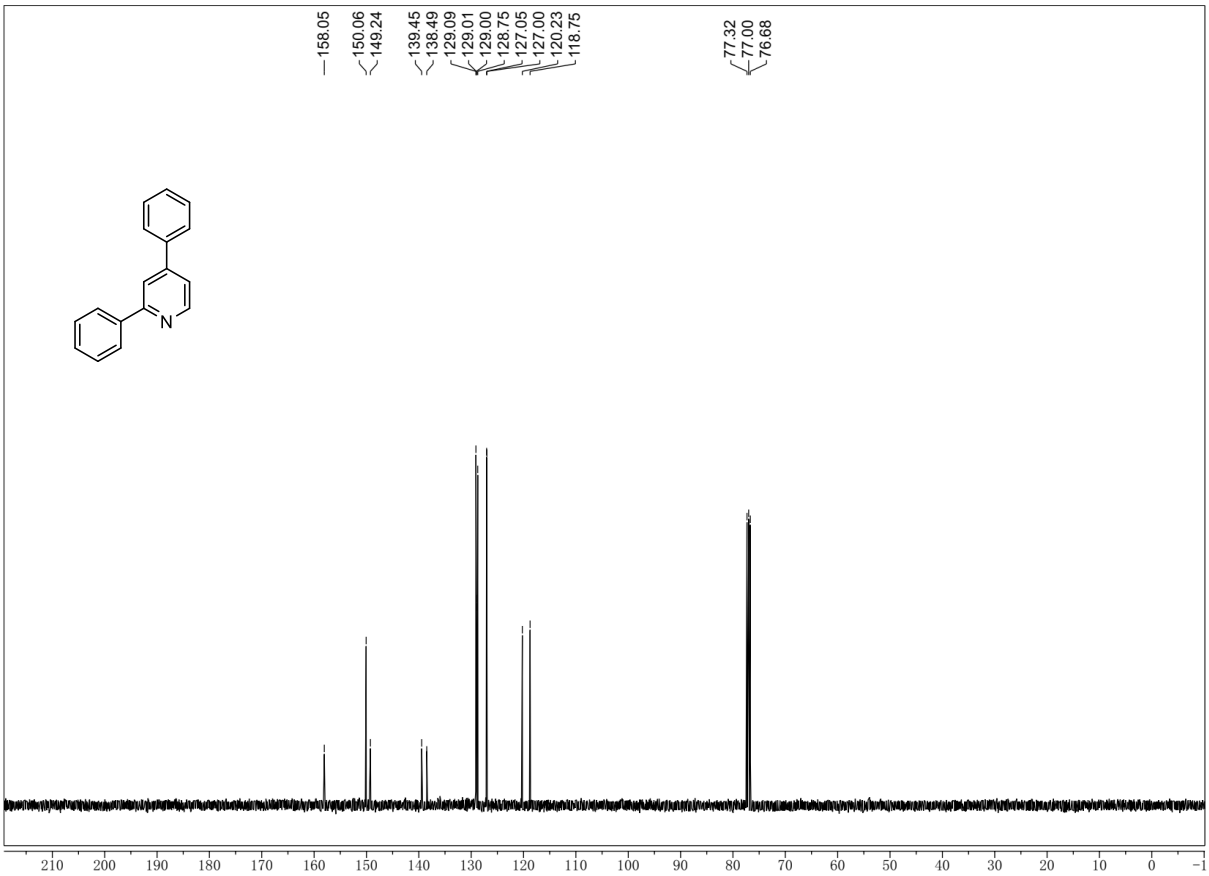
59 ^{13}C $CDCl_3$, 100 MHz



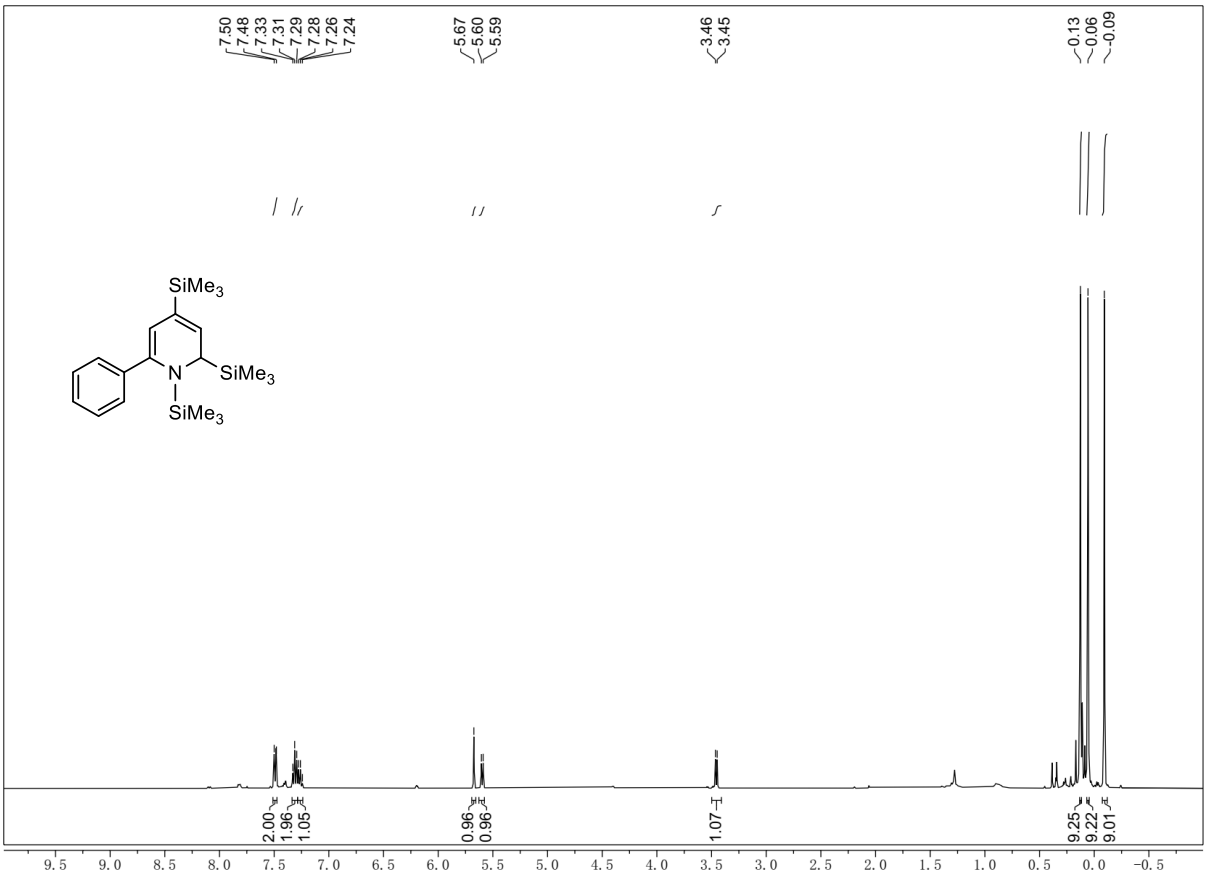
60 ^{1}H $CDCl_3$, 400 MHz



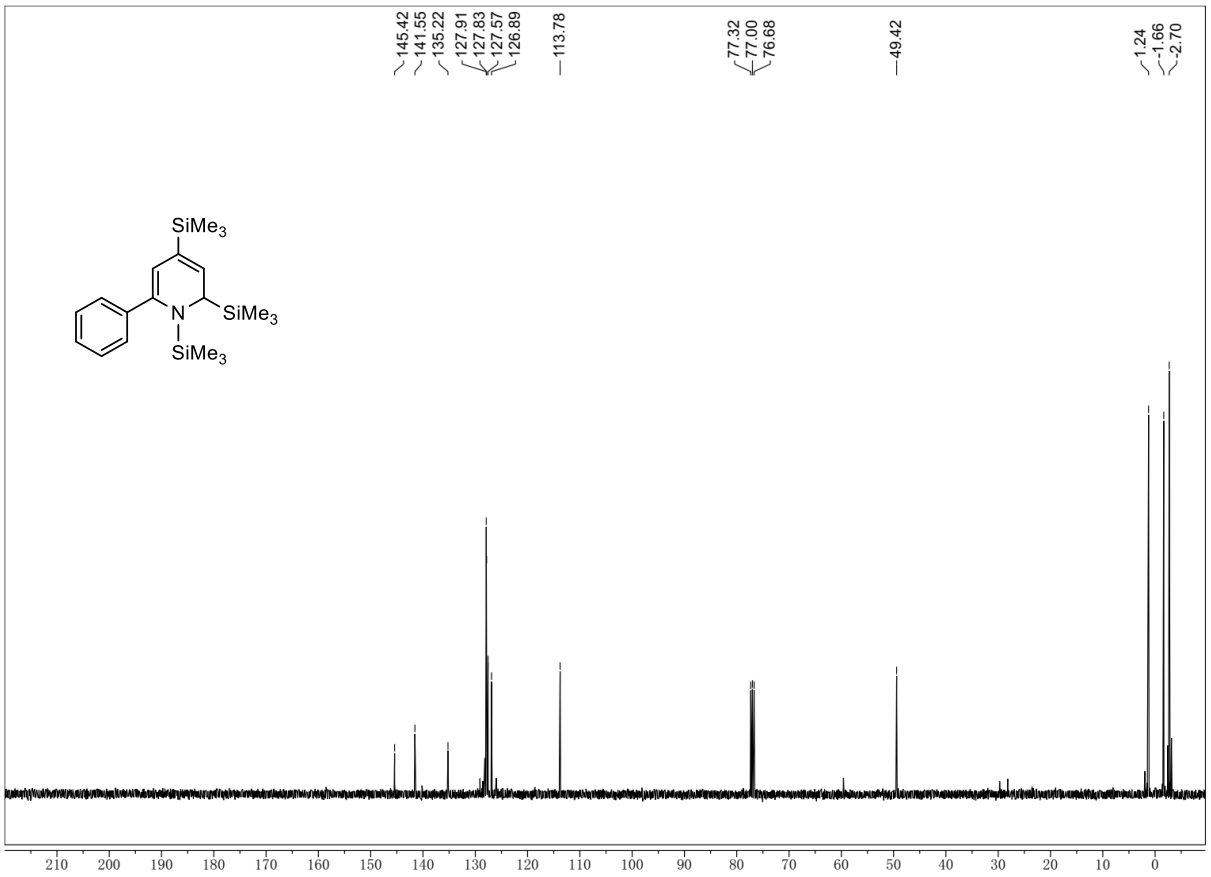
60 ^{13}C $CDCl_3$, 100 MHz



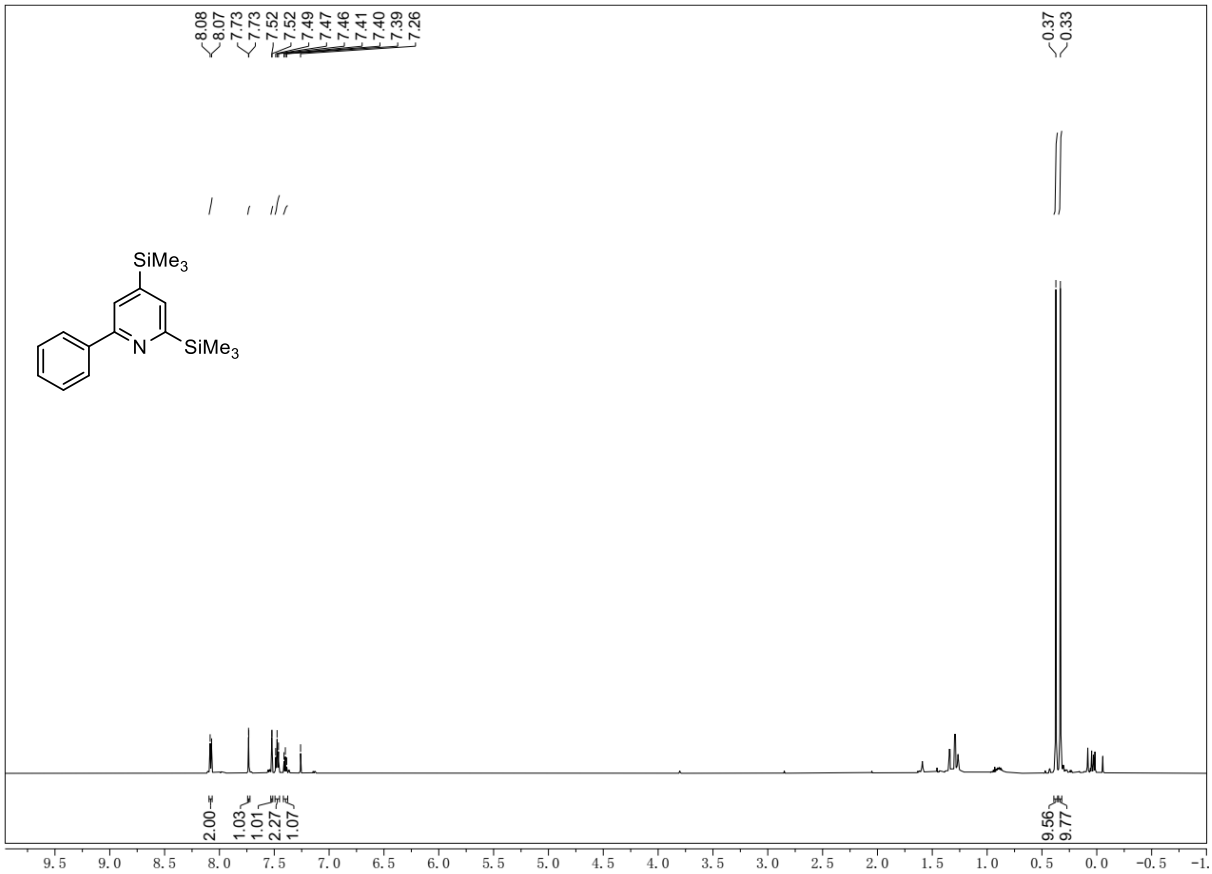
61 ^{1}H $CDCl_3$, 600 MHz



61 ^{13}C $CDCl_3$, 151 MHz



62 ^{1}H $CDCl_3$, 600 MHz



62 ^{13}C $CDCl_3$, 151 MHz