Supporting Information

From stoichiometric to catalytic reactivity of the aryl cycloaurated species with arylboronic acids: insight into the mechanism of gold-catalyzed oxidative C(sp^2)–H arylation

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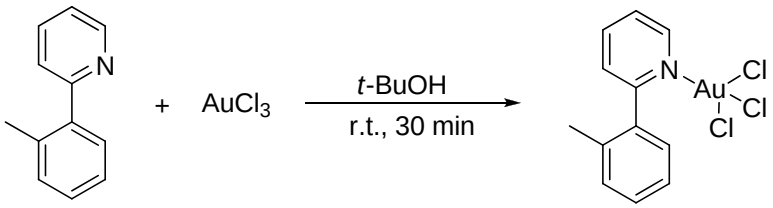
I. General remarks

NMR spectra were obtained with a Bruker AV II-400 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts and the ^{13}C NMR (100 MHz) chemical shifts were measured relative to $CDCl_3$ (H: δ = 7.26 ppm; C: δ = 77.16 ppm), DMSO-d_6 (H: δ = 2.50 ppm; C: δ = 39.52 ppm), and acetone-d_6 (H: δ = 2.05 ppm; C: δ = 29.84 ppm) as the internal references. High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). GC-Mass spectra were obtained with a Shimadzu-GCMS-QP 2010 SE (EI). X-Ray single-crystal diffraction data were collected on Oxford Xcalibur E and Xcalibur Gemini X-ray single crystal diffractometers. Elemental analysis data were obtained on EA FLASH 1112 SERIES. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $AuCl_3$, $AuBr_3$, and $Au(OAc)_3$ were purchased from Across, Alfa Aesar and Adamas, respectively. 2-(*o*-Tolyl)quinoline,[1] arylpyridine derivatives,[2] and 2-(*o*-tolyloxy)pyridine[3] were prepared according to the literature procedure. Solvents were dried by refluxing over CaH_2 (for DCE), or sodium (for 1,4-dioxane, *t*-BuOH, *t*-AmylOH, diethyl ether, benzene, hexane, and THF), and freshly distilled prior to use. All syntheses and manipulations were carried out under N_2 atmosphere.

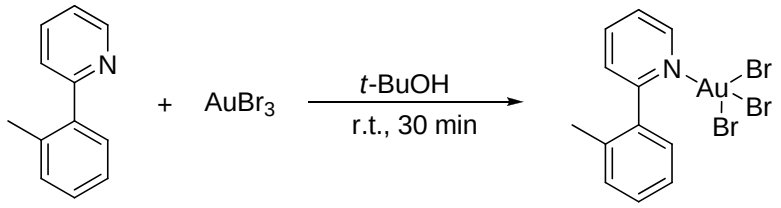
II. Synthesis of gold(III) complexes and additional experiments

(1) Synthesis of cyclometalated aryl gold(III) halides 3a and 3b[4]



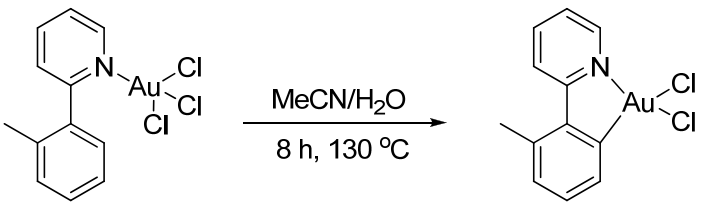
1a **2a**

To a solution of 2-(*o*-tolyl)pyridine (36.3 mg, 0.22 mmol) in *t*-BuOH (2 mL) was added $AuCl_3$ (60.3 mg, 0.2 mmol), and the yellow precipitate was formed immediately. This precipitate was filtered off, washed with petroleum ether, and dried in vacuum to afford the **2a** as a yellow solid in 93% yield (87.6 mg). M.p.: 134-136 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 2.28 (s, 3H), 7.44-7.48 (m, 2H), 7.55 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 8.02-8.06 (m, 2H), 8.46 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 9.30 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H) ppm. ^{13}C NMR (acetone-d_6, 100 MHz): δ = 20.7, 126.9, 128.1, 131.0, 131.8, 132.1, 137.8, 143.3, 151.6, 160.1 ppm. Anal. Calcd for $C_{12}H_{11}AuCl_3N$ (%): C, 30.50; H, 2.35; N, 2.96, found: C, 30.36; H, 2.24; N, 2.90.



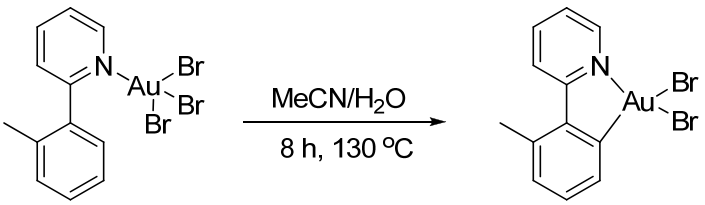
1a **2b**

To a solution of 2-(*o*-tolyl)pyridine (36.3 mg, 0.22 mmol) in *t*-BuOH (2 mL) was added $AuBr_3$ (86.7 mg, 0.2 mmol), and the red precipitate was formed immediately. This precipitate was filtered off, washed with petroleum ether, and dried in vacuum to afford the **2b** as a red solid in 88% yield (106.1 mg). M.p.: 187-189 °C. ^{1}H NMR (acetone-d_6, 400 MHz): δ = 2.31 (s, 3H), 7.42-7.44 (m, 2H), 7.51-7.55 (m, 1H), 7.80-7.82 (m, 1H), 7.98-8.01 (m, 2H), 8.43 (td, J = 8.0 Hz, J = 1.6 Hz, 1H), 9.23 (dd, J = 6.0 Hz, J = 0.8 Hz, 1H) ppm. ^{13}C NMR (acetone-d_6, 100 MHz): δ = 21.1, 126.7, 127.7, 131.0, 131.6, 131.8, 132.3, 137.6, 142.9, 152.3, 160.1 ppm. Anal. Calcd for $C_{12}H_{11}AuBr_3N$ (%): C, 23.79; H, 1.83; N, 2.31, found: C, 23.79; H, 1.50; N, 2.09.



2a **3a**

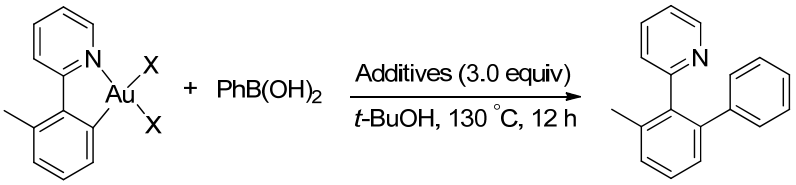
A sealed tube with a magnetic stirring bar was charged with **2a** (47.1 mg, 0.1 mmol), MeCN (2.0 mL) and H_2O (2.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 °C for 8 h. The white solid was filtered off, washed with the mixture of MeCN and H_2O (1/1, v/v), and dried in vacuum to afford the **3a** as a white solid in 53% yield (23.1 mg). M.p.: >250 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.74 (s, 3H), 7.24 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.76-7.82 (m, 2H), 8.34-8.42 (m, 2H), 9.72 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 22.9, 124.7, 125.4, 128.0, 130.2, 133.4, 138.2, 140.5, 143.9, 148.9, 152.8, 163.9 ppm. HRMS (ESI$^+$): calcd for $C_{12}H_{10}AuClN$ $[M\text{-}Cl]^+$ 400.0167, found 400.0163. Anal. Calcd for $C_{12}H_{10}AuCl_2N$ (%): C, 33.05; H, 2.31; N, 3.21, found: C, 32.78; H, 2.43; N, 3.34.



2b **3b**

A sealed tube with a magnetic stirring bar was charged with **2b** (60.3 mg, 0.1 mmol), MeCN (2.0 mL) and H_2O (2.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 °C for 8 h. The white solid was filtered off, washed with the mixture of MeCN and H_2O (1/1, v/v), and dried in vacuum to afford the **3b** as a white solid in 34% yield (17.8 mg). M.p.: 225-227 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.74 (s, 3H), 7.21 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.79 (t, J = 6.4 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.34-8.42 (m, 2H), 9.94 (d, J = 5.6 Hz, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 23.2, 124.8, 125.6, 130.2, 130.5, 133.2, 138.3, 141.2, 143.6, 150.0, 154.0, 163.9 ppm. HRMS (ESI$^+$): calcd for $C_{12}H_{10}AuBrN$ $[M\text{-}Br]^+$ 443.9662, found 443.9663. Anal. Calcd for $C_{12}H_{10}AuBr_2N$ (%): C, 27.45; H, 1.92; N, 2.67, found: C, 27.75; H, 1.58; N, 2.46.

(2) Reactivities of 3a and 3b with $PhB(OH)_2$



3a: X = Cl
3b: X = Br

4aa

A sealed tube with a magnetic stirring bar was charged with **3a** or **3b** (0.05mmol), phenylboronic acid (18.3 mg, 0.15 mmol, 3.0 equiv), additive (3.0 equiv), and *t*-BuOH (1 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 ^oC for 12 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a Celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) to provide product **4aa** as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.89 (d, J = 7.6 Hz, 1H), 7.07-7.10 (m, 3H), 7.12-7.17 (m, 3H), 7.26-7.31 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.44 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 121.4, 125.7, 126.3, 127.68, 127.69, 128.1, 129.5, 129.7, 135.8, 136.8, 139.4, 141.4, 141.8, 148.9, 159.7 ppm. M.p.: 49 °C. HRMS (ESI^+): calcd for $C_{18}H_{16}N$ $[M+H]^+$ 246.1283, found 246.1284.

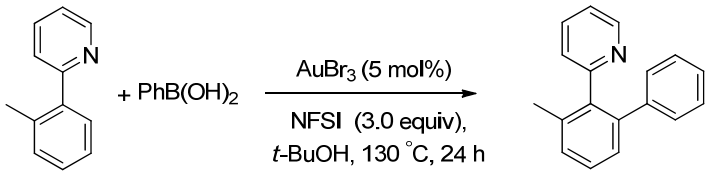
Table S1: Stoichiometric reaction of **3a** or **3b** with $PhB(OH)_2$.[a]

Entry	X	Additive	Yield (%)[b]
1	Cl	-	NR
2	Cl	*t*-BuOK	84%
3	Cl	KOH	87%
4	Cl	KF	89%
5[c]	Cl	NFSI	70%
6[d]	Cl	NFSI	NR
7	Br	-	NR

8	Br	KF	94%
9[c]	Br	NFSI	73%
10[c]	Br	Selectfluor	72%
11[c]	Br	$PhI(OAc)_2$	NR

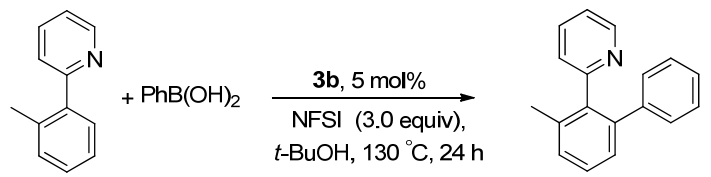
[a] Reaction conditions: **3a** or **3b** (0.05 mmol), phenylboronic acid (0.15 mmol, 3.0 equiv), additive (0.15 mmol, 3.0 equiv), and *t*-BuOH (1.0 mL) at 130 °C for 12 h under N2. [b] Yields of isolated products. [c] For 24 h. [d] At 60 °C. NR = no reaction. Selectfluor = 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate). NFSI = *N*-Fluorobenzenesulfonimide.

(3) Gold-catalyzed reactions of 2-(*o*-tolyl)pyridine (1a) with phenylboronic acid



1a **4aa**

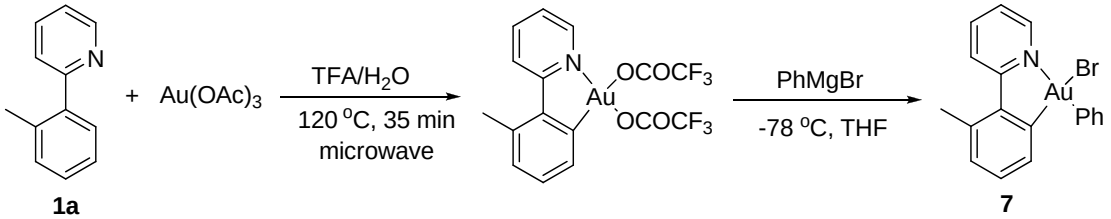
A sealed tube with a magnetic stirring bar was charged with 2-(*o*-tolyl)pyridine **1a** (33.8 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol, 3.0 equiv), gold(III) bromide (4.4 mg, 0.01 mmol, 0.05 equiv), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv), and *t*-BuOH (2 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 °C for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a Celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on neutral alumina (petroleum ether/acetone = 30:1, v/v) to provide product **4aa** as a white solid in 91% yield (44.6 mg).



1a **4aa**

A sealed tube with a magnetic stirring bar was charged with 2-(*o*-tolyl)pyridine **1a** (33.8 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol, 3.0 equiv), **3b** (5.2 mg, 0.01 mmol, 0.05 equiv), NFSI (189.2 mg, 0.6 mmol, 3.0 equiv), and *t*-BuOH (2 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 ^oC for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a Celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) to provide product **4aa** as a white solid in 94% yield (46.1 mg).

(4) Synthesis of cyclometalated biaryl gold(III) species 7[5]

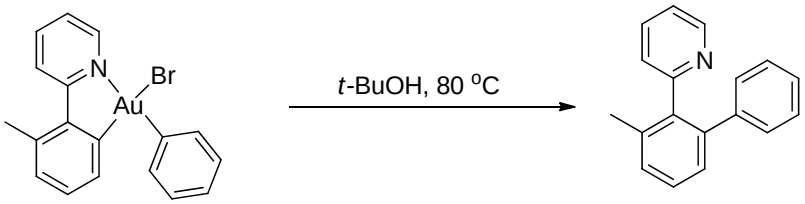


1a **7**

A sealed tube with a magnetic stirring bar was charged with gold(III) acetate (262 mg, 0.7 mmol), 2-(*o*-tolyl)pyridine (125.5 mg, 0.74 mmol, 1.06 equiv), distilled water (10 mL) and trifluoroacetic acid (10 mL). Then the reaction mixture was heated in the microwave oven at 120 °C for 35 min. After the solution was cooled to room temperature, additional trifluoroacetic acid was added until the white precipitate was dissolved. Then the yellow solution was filtered through a Celite pad, and the product was precipitated by addition of water. The precipitated solid was filtered, washed with water and dried under vacuum to give $[Au(OCOCF_3)_2(tpy)]$ in 61% yield (252.4 mg). ^1H NMR (DMSO-d_6, 400 MHz): δ = 2.74 (s, 3H), 6.87 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.76-7.80 (m, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.44-8.48 (m, 1H), 8.67 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 22.1, 125.0, 125.1, 125.8, 130.4, 134.1, 138.8, 139.5, 142.7, 145.1, 148.4, 158.7, 159.1, 163.2 ppm. HRMS (ESI^+): calcd for $C_{16}H_{10}AuF_6NNaO_4$ $[M+Na]^+$ 614.0077, found 614.0072.

A solution of $Au(OCOCF_3)_2(tpy)$ (200.9 mg, 0.34 mmol) in dried THF (20 mL) at -78 °C was added PhMgBr (1.0 M in THF, 0.76 mL, 0.76 mmol, 2.2 equiv) under a flow of N_2. The reaction mixture was stirred for 1 h at -78 °C and then at room temperature for another hour. After the solvent was removed under vacuum, the resulting solid was dissolved in dichloromethane and washed with distilled water. The organic phase was dried over $MgSO_4$ and filtered through a pad of Celite. Then the dichloromethane was removed under vacuum to give cyclometalated biaryl gold(III) species **7** as an off-white solid in 83% yield (147.0 mg). M.p.: 159-161 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.74 (s, 3H), 6.49 (d, J = 7.6 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.19-7.23 (m, 3H), 7.37 (d, J = 6.8 Hz, 2H), 7.78 (t, J = 6.0 Hz, 1H), 8.31 (td, J = 8.4 Hz, J = 1.6 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 9.64 (d, J = 5.2 Hz, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 23.8, 124.5, 124.8, 125.3, 129.0, 130.0, 130.8, 132.3, 132.7, 137.3, 141.5, 142.1, 144.4, 149.4, 150.1, 161.5 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}AuN$ $[M\text{-}Br]^+$ 442.0870, found 442.0872. Anal. Calcd for $C_{18}H_{15}AuBrN$ (%): C, 41.40; H, 2.90; N, 2.68, found: C, 41.52; H, 3.23; N, 2.55.

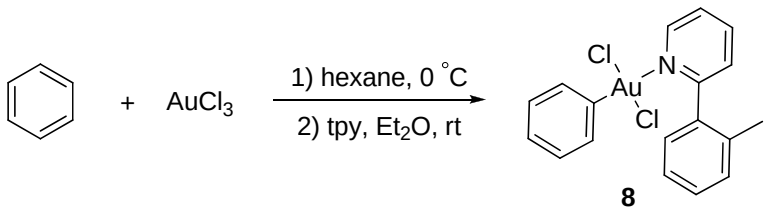
(5) Reductive elimination of 7



7 **4aa**

A sealed tube with a magnetic stirring bar was charged with **7** (26.1 mg. 0.05mmol) and *t*-BuOH (1 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a Celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on neutral alumina (petroleum ether/acetone = 30:1, v/v) to provide product **4aa** as a white solid in 98% yield or 96% yield in the presence of KF.

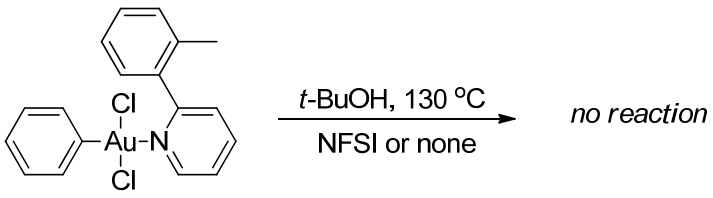
(6) Synthesis of [$AuCl_2$(Ph)(tpy)] (8)[6]



8

Under N_2, a mixture of benzene (1.06 mL, 12 mmol) and hexane (4 mL) was added dropwise to a hexane suspension of gold(III) chloride (181.1 mg, 0.6 mmol) at 0 °C. After being stirring at 0 °C for 1 h, the reaction mixture was added diethyl ether (4 mL), treated with diethyl ether solution (4 mL) of 2-(*o*-tolyl)pyridine (101.4 mg, 0.6 mmol, 1.0 equiv), and continued stirring at room temperature for 1 h. The resulting suspension was filtered through a pad of Celite, and washed with diethyl ether. The combined organic extracts were concentrated and the resulting residue was purified by silica gel chromatography (hexane/CH_2Cl_2 = 1/1, v/v) to provide [$AuCl_2$(Ph)(tpy)] (**8**) as a yellowish solid in 26% yield (80.0 mg). M.p.: 166-168 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.31 (s, 3H), 7.82-7.84 (m, 2H), 7.01-7.03 (m, 3H), 7.42 (d, J = 7.2 Hz, 1H), 7.47-7.55 (m, 2H), 7.64-7.67 (m, 2H), 7.78-7.79 (m, 1H), 8.02-8.06 (m, 1H), 8.79 (d, J = 5.2 Hz, 1H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 20.7, 125.2, 126.2, 127.0, 129.0, 129.3 130.3, 130.6, 131.1, 131.4, 132.3, 137.3, 138.0, 139.8, 149.5, 159.6 ppm. Anal. Calcd for $C_{18}H_{16}AuCl_2N$ (%): C, 42.04; H, 3.14; N, 2.72. Found: C, 42.37; H, 3.21; N, 2.67.

(7) **Stoichiometric reaction of [$AuCl_2$(Ph)(tpy)]** (**8**)

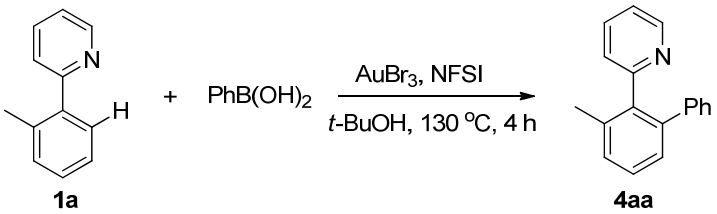


8

A sealed tube with a magnetic stirring bar was charged with [$AuCl_2$(Ph)(tpy)] **8** (22.6 mg, 0.05 mmol) and *t*-BuOH (1 mL) either in the presence or absence of NFSI (47.3 mg, 0.15 mmol) under N_2. A rubber septum was replaced with Teflon stopper, and the

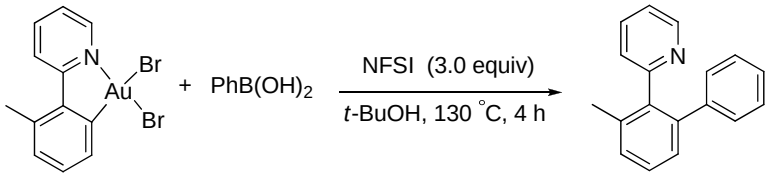
system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at 130 °C for 12 h. The reaction mixture was then cooled to ambient temperature and diluted with 10 mL of CH_2Cl_2. Then the organic phase was detected by GC-Mass, and no arylated product **4aa** was observed.

III. ESI-HRMS detection[7]



1a **4aa**

A sealed tube with a magnetic stirring bar was charged with $AuBr_3$ (2.2 mg, 0.005 mmol), 2-(*o*-tolyl)pyridine (16.9 mg, 0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), NFSI (94.6 mg, 0.3 mmol) and *t*-BuOH (1.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. After being stirred at 130 °C for 4 h, the reaction mixture was cooled to ambient temperature, diluted with methanol, and then detected by ESI-HRMS.

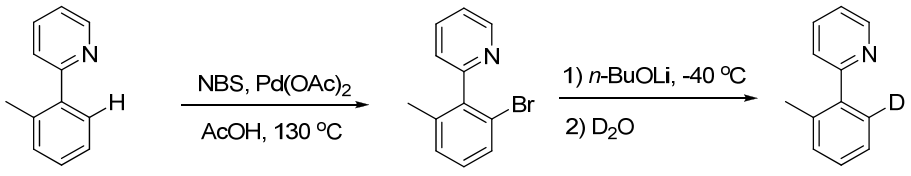


3b **4aa**

A sealed tube with a magnetic stirring bar was charged with **3b** (52.3 mg, 0.10 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), NFSI (94.6 mg, 0.3 mmol) and *t*-BuOH (1.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. After being stirred at 130 °C for 4 h, the reaction mixture was cooled to ambient temperature, diluted with methanol, and then detected by ESI-HRMS.

IV. Kinetic isotope effect experiments

(1) Synthesis of [D]-1a[8]

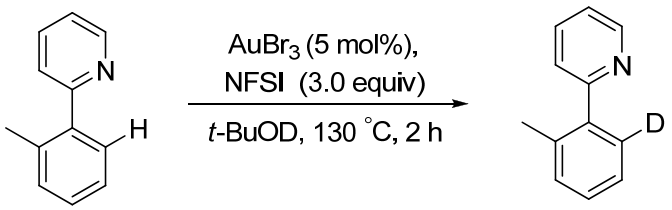


1a **[D]-1a**

To a solution of 2-(*o*-tolyl)pyridine (933.4 mg, 5.52 mmol) in AcOH (30 mL) in a sealed tube was added *N*-bromosuccinimide (1.16 g, 6.62 mmol) and $Pd(OAc)_2$ (124 mg, 0.55 mmol). The reaction mixture was heated to 120 °C for 24 h. Then the reaction mixture was cooled to room temperature and solvent was removed in vacuum. The residue was purified by silica gel chromatography (EtOAc/hexanes = 1:10, v/v) to afford 2-(2-bromo-6-methylphenyl)pyridine as pale yellow oil in 51% yield (700 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (s, 3H), 7.14 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.27-7.31 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.78 (td, J = 7.6 Hz, J = 1.2 Hz, 1H), 8.73 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.8, 122.4, 123.1, 124.8, 129.2, 129.4, 130.2, 136.4, 138.7, 141.2, 149.7, 159.2 ppm. HRMS (ESI^+): calcd for $C_{12}H_{11}BrN$ $[M+H]^+$ 248.0075, found 248.0070.

To the solution of 2-(2-bromo-6-methylphenyl)pyridine (123.5 mg, 0.5 mmol) in 8 mL of dry diethyl ether, *n*-butyl lithium (0.4 mL of 2.5 M in hexane, 1.0 mmol, 2 equiv) was added dropwise at -40 ºC under nitrogen. After stirring for 30 min, the reaction mixture was quenched with 0.8 mL of D_2O, and was continued stirring for another hour. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1, v/v) to give [D]-**1a** as colorless oil in 82% yield (69.7 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.30 (s, 3H), 7.16-7.25 (m, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.67 (td, J = 7.6 Hz, J = 2.0 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.4, 121.7, 124.2, 125.9, 128.4, 130.8, 135.9, 136.2, 140.5, 149.4, 160.2 ppm. HRMS (ESI^+): calcd for $C_{12}H_{11}DN$ $[M+H]^+$ 171.1033, found 171.1027.

(2) Hydrogen-deuterium exchange experiment



1a

[D]-**1a**: no observed
(both with and without $PhB(OH)_2$)

A sealed tube with a magnetic stirring bar was charged with $AuBr_3$ (2.2 mg, 0.005 mmol), 2-(*o*-tolyl)pyridine (16.6 mg, 0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), NFSI (94.6 mg, 0.3 mmol) and *t*-BuOD (1.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. The reaction mixture was refluxed at 130 °C in 2 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a pad of Celite, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) to recover the starting material **1a**. ^{1}H NMR (acetone-d_6, 400 MHz) analysis showed that the hydrogen at the *ortho*-position of phenyl ring of 2-(*o*-tolyl)pyridine (**1a**) was not deuterated. No [D]-**1a** was observed when the reaction was carried out in the absence of $PhB(OH)_2$ in 2 h.

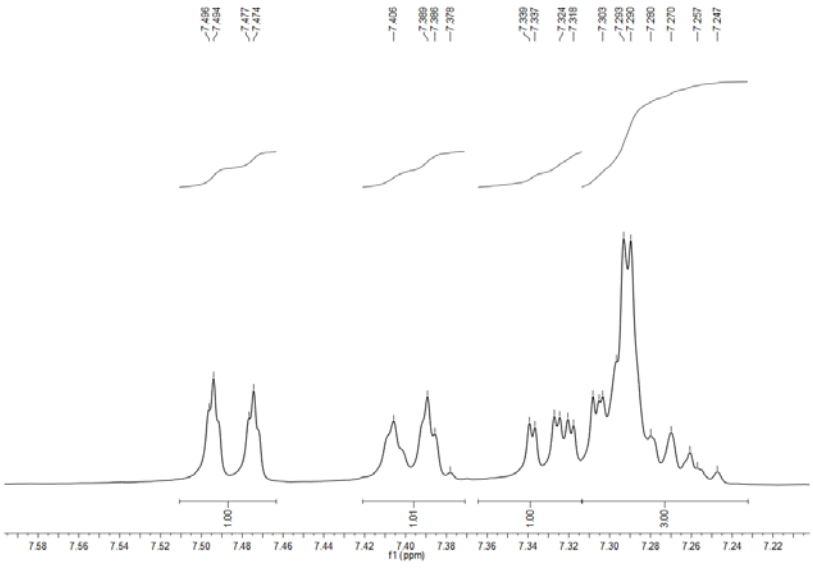
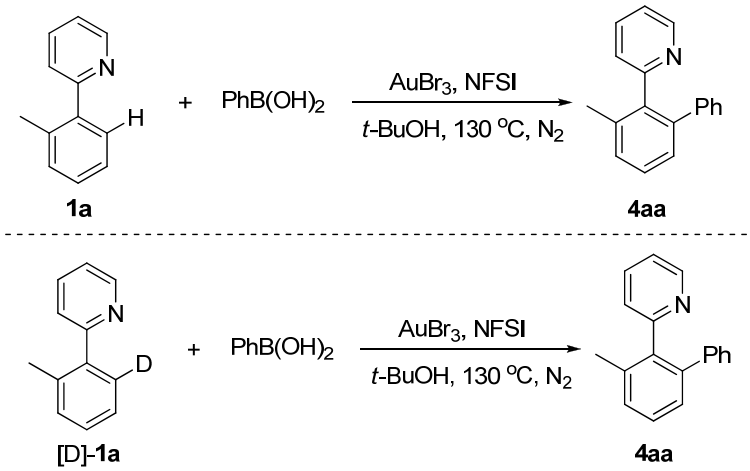


Figure S1. ^{1}H NMR spectrum of hydrogen-deuterium exchange experiment.

(3) Kinetic isotope effect[9]



A sealed tube with a magnetic stirring bar was charged with **1a** or [D]-**1a** (0.1 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), gold(III) bromide (2.2 mg, 0.005 mmol), NFSI (94.6 mg, 0.3 mmol), and *t*-BuOH (1 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. The resulting mixture was stirred at 130 °C for designated time (20 min, 40 min, 60 min, 80 min, and 120 min) and then an internal standard (1,1,2,2-tetrachloroethane, 10.5 μL, 0.1 mmol) were added. The solution was filtered through a pad of Celite and washed with 10 mL of dichloromethane. The filtrate were concentrated and subjected to ^{1}H NMR analysis to determine the concentration of product. KIE = 0.001371/0.001414 = 0.96.

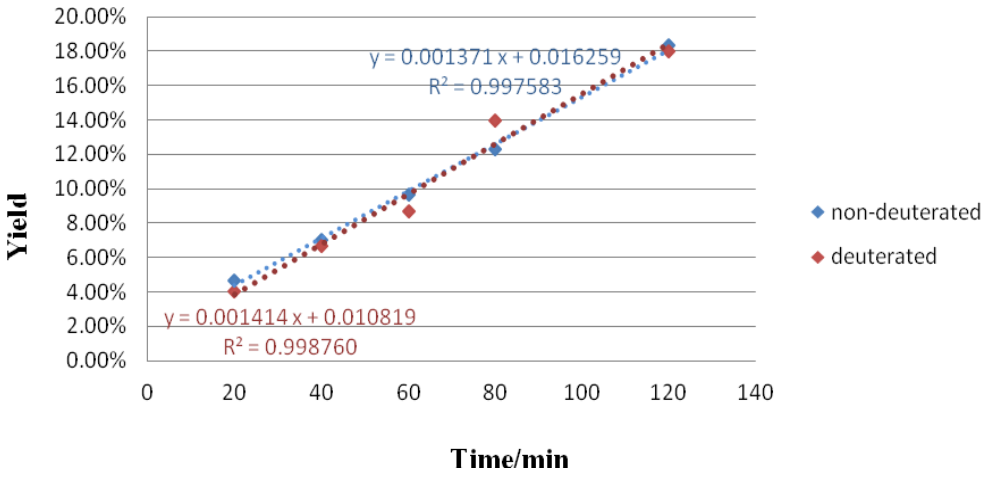


Figure S2. Plots of yield versus reaction time.

V. ORTEP diagrams of 3b, 7 and 8

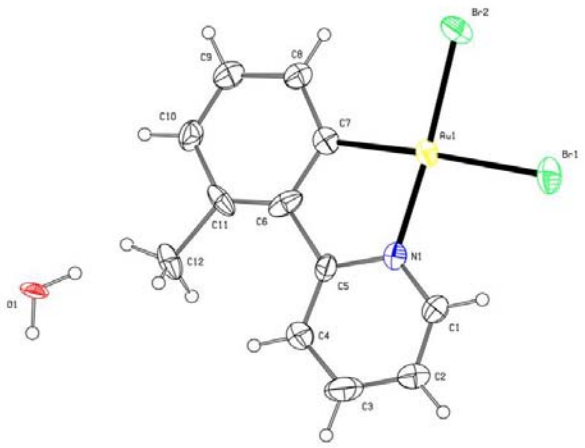


Figure S3. ORTEP drawing of **3b** with 50% probability thermal ellipsoids.

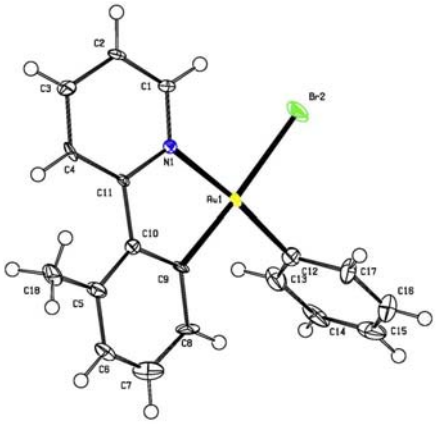


Figure S4. ORTEP drawing of **7** with 50% probability thermal ellipsoids.

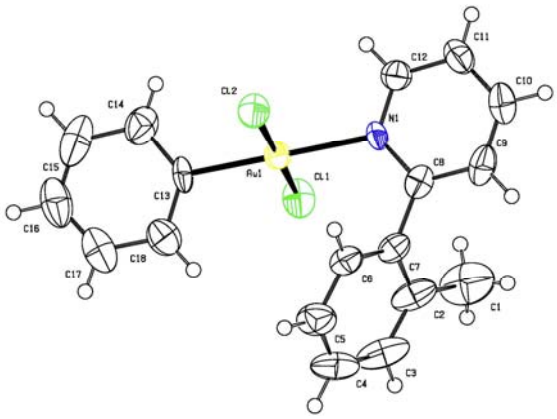
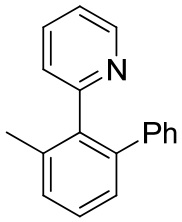


Figure S5. ORTEP drawing of **8** with 50% probability thermal ellipsoids.

VI. General procedure for gold-catalyzed directed C(sp^2)–H bond arylation with arylboronic acid

A sealed tube with a magnetic stirring bar was charged with $AuBr_3$ (4.4 mg, 0.01 mmol), *N*-heteroarene-containing arene (0.2 mmol), arylboronic acid (0.6 mmol, 3.0 equiv), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) under N_2. A rubber septum was replaced with Teflon stopper, and the system was evacuated twice and back filled with N_2. Then the reaction mixture was stirred at the indicated temperature for 24 h. The reaction mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a Celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by neutral alumina column chromatography to provide the desired product.

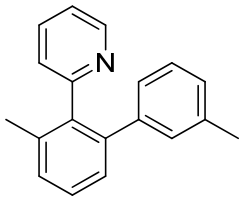
VII. Experimental data for the described substances



2-(3-Methylbiphenyl-2-yl)pyridine (4aa)

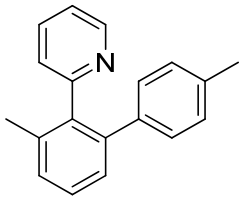
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 91% yield (44.6 mg). M.p.: 49-50 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.89 (d, J = 7.6 Hz, 1H), 7.07-7.10 (m, 3H), 7.11-7.17 (m, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.44 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 121.4, 125.7, 126.3, 127.68, 127.69, 128.1, 129.5, 129.7, 135.8, 136.8, 139.4, 141.4, 141.8, 148.9, 159.7 ppm. HRMS (ESI^+): calcd for

$C_{18}H_{16}N$ $[M+H]^+$ 246.1283, found 246.1284. *Characterization data were consistent with literature values.*[10]



2-(3'-Methyl-3-methylbiphenyl-2-yl)pyridine (4ac)

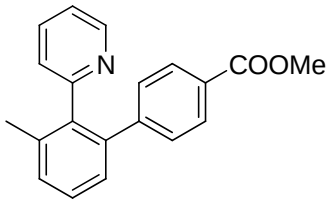
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 3-methylphenylboronic acid (81.6 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded colorless oil in 70% yield (36.3 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.19 (s, 3H), 2.20 (s, 3H), 6.86 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.92-6.94 (m, 2H), 7.01 (t, J = 8.0 Hz, 1H), 7.07-7.11 (m, 1H), 7.27-7.30 (m, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.45 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.64 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 21.4, 121.3, 125.7, 126.8, 127.0, 127.5, 127.7, 128.1, 129.4, 130.6, 135.8, 136.7, 137.2, 139.4, 141.4, 141.6, 148.9, 159.8 ppm. HRMS (ESI^+): calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1438. *Characterization data were consistent with literature values.*[10]



2-(3,4'-Dimethylbiphenyl-2-yl)pyridine (4ad)

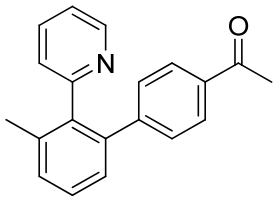
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-methylphenylboric acid (81.6 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded colorless oil 80% yield (41.5 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 2.28 (s, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.95-7.02 (m, 4H), 7.11-7.14 (m, 1H), 7.28-7.31 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H),

7.48 (td, J = 8.0 Hz, J = 2.0 Hz, 1H), 8.66 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 21.2, 121.4, 125.7, 127.8, 128.1, 128.5, 129.3, 129.6, 135.86, 135.93, 136.8, 138.8, 139.4, 141.3, 149.0, 159.9 ppm. HRMS (ESI^+): calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1440. *Characterization data were consistent with literature values.*[10]



Methyl 3'-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-carboxylate (4ae)

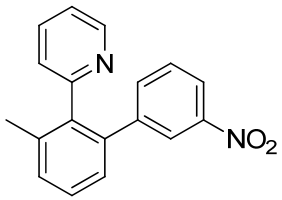
2-(*o*-Tolyl)pyridine (33.0 mg, 0.2 mmol), 4-methoxycarbonylphenylboronic acid (108.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 20:1, v/v) afforded a white solid in 61% yield (37.0 mg). M.p.: 92-93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, 3H), 3.86 (s, 3H), 6.88 (d, J = 7.6 Hz, 1H), 7.08-7.11 (m, 1H)，7.12-7.15 (m, 2H), 7.25-7.27 (m, 1H), 7.32 (d, J = 6.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.44 (td, J = 7.6 Hz, J = 2.0 Hz, 1H), 7.79-7.82 (m, 2H), 8.60-8.62 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 52.2, 121.7, 125.7, 127.5, 128.0, 128.3, 129.0, 129.7, 130.2, 136.0, 137.0, 139.4, 140.3, 146.7, 149.1, 159.2, 167.2 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.1338, found 304.1343. Anal. Calcd for $C_{20}H_{17}NO_2$ (%): C, 79.19; H, 5.65; N, 4.62, found: C, 78.81; H, 5.71; N, 4.48.



1-(3'-Methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-4-yl)ethanone (4af)

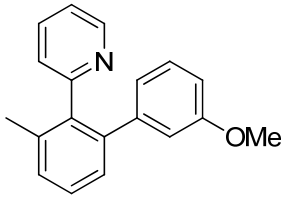
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-acetylphenylboronic acid (98.4 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL)

at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 20:1, v/v) afforded a white solid in 62% yield (35.6 mg). M.p.: 84-86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, 3H), 2.53 (s, 3H), 6.89 (d, J = 7.6 Hz, 1H), 7.09-7.12 (m, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.46 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 8.62 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 26.7, 121.7, 125.7, 127.5, 127.9, 128.3, 129.9, 130.2, 135.1, 136.0, 137.1, 139.4, 140.2, 146.9, 149.2, 159.2, 198.0 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1388, found 288.1386. *Characterization data were consistent with literature values.*[10]



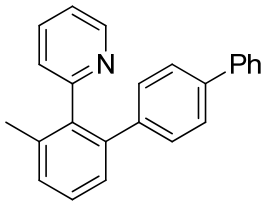
2-(3'-Nitro-3-methylbiphenyl-2-yl)pyridine (4ag)

2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 3-nitrophenylboronic acid (100.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 20:1, v/v) afforded yellow oil in 35% yield (20.3 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.95 (d, J = 7.6 Hz, 1H), 7.10-7.14 (m, 1H), 7.26-7.29 (m, 2H), 7.35-7.43 (m, 3H), 7.51 (td, J = 7.6 Hz, J = 2.0 Hz, 1H), 7.96-8.00 (m, 2H), 8.62 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 121.4, 121.9, 124.5, 125.6, 127.5, 128.5, 128.6, 130.6, 135.8, 136.2, 137.2, 138.9, 139.6, 143.4, 147.8, 149.4, 158.8 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ 291.1134, found 291.1139. *Characterization data were consistent with literature values.*[10]



2-(3'-Methoxyl-3-methylbiphenyl-2-yl)pyridine (4ah)

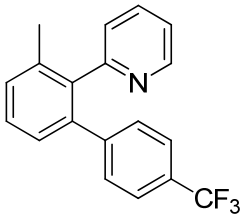
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 3-methoxylphenylboronic acid (91.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 20:1, v/v) afforded yellowish oil in 44% yield (24.2 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.19 (s, 3H), 3.59 (s, 3H), 6.58-6.59 (m, 1H), 6.66-6.69 (m, 1H), 6.70-6.73 (m, 1H), 6.89-6.91 (m, 1H), 7.07 (t, J = 8.0 Hz, 1H), 7.09-7.13 (m, 1H), 7.28-7.31 (m, 2H). 7.36 (t, J = 7.6 Hz, 1H), 7.47 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.64-8.66 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 55.2, 112.9, 114.7, 121.5, 122.2, 125.7, 127.6, 128.2, 128.8, 129.6, 136.0, 136.9, 139.3, 141.2, 143.1, 148.9, 158.8, 159.8 ppm. calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1388, found 276.1385. Anal. Calcd for $C_{19}H_{17}NO$ (%): C, 82.88; H, 6.22; N, 5.09, found: C, 82.41; H, 6.08; N, 4.77.



2-(3-Methyl-[1,1':4',1''-terphenyl]-2-yl)pyridine (4ai)

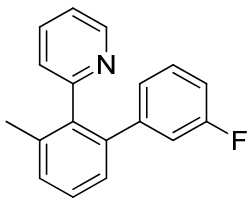
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-biphenylboric acid (118.9 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 83% yield (53.3 mg). M.p.: 109-111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 3H), 6.94 (d, J = 8.0 Hz, 1H) 7.09-7.12 (m, 1H), 7.14-7.17 (m, 2H), 7.31-7.34 (m, 3H), 7.37-7.42 (m, 5H), 7,47 (td, J = 7.6 Hz, J = 2.0 Hz, 1H), 7.54-7.56 (m, 2H), 8.65-7.67 (m, 1H) ppm. ^{13}C NMR

($CDCl_3$, 100 MHz): δ = 20.6, 121.5, 125.8, 126.4, 127.0, 127.3, 127.7, 128.2, 128.8, 129.6, 130.2, 135.9, 136.9, 139.0, 139.5, 140.76, 140.82, 140.9, 149.0, 159.7 ppm. HRMS (ESI^+): calcd for $C_{24}H_{20}N$ $[M+H]^+$ 322.1596, found 322.1595. Anal. Calcd for $C_{24}H_{19}N$ (%): C, 89.68; H, 5.96; N, 4.36, found: C, 89.58; H, 6.20; N, 4.17.



2-(4'-Trifluoromethyl-3-methylbiphenyl-2-yl)pyridine (4aj)

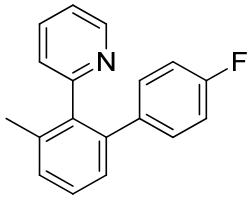
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-trifluoromethylphenylboronic acid (114.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 64% yield (40.1 mg). M.p.: 46-47 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.19 (s, 3H), 6.89 (d, J = 7.6 Hz, 1H), 7.10-7.14 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 6.8 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.37-7.40 (m, 3H), 7.48 (td, J = 8.0 Hz, J = 1.6 Hz, 1H), 8.62 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 121.8, 124.62, 124.65, 124.69, 124.73, 125.7, 127.6, 128.4, 130.0, 130.3, 136.0, 137.1, 139.5, 140.0, 145.5, 149.2, 159.2 ppm. HRMS (ESI^+): calcd for $C_{19}H_{15}F_3N$ $[M+H]^+$ 314.1157, found 314.1153. *Characterization data were consistent with literature values.*[10]



2-(3'-Fluoro-3-methylbiphenyl-2-yl)pyridine (4ak)

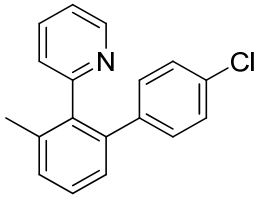
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 3-fluorophenylboronic acid (84.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography

(petroleum ether/acetone = 30:1, v/v) afforded colorless oil in 73% yield (38.4 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.81-6.86 (m , 3H), 6.93 (d, J = 8.0 Hz, 1H), 7.07-7.15 (m, 2H), 7.28 (s, 1H), 7.33 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.50 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.65 (d, J = 5.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 113.3 (d, J = 20.9 Hz), 116.6 (d, J = 21.6 Hz), 121.6, 125.57 (d, J = 2.8 Hz), 125.61, 127.6, 127.5, 128.2, 129.1 (d, J = 8.3 Hz), 130.0, 136.0, 137.0, 140.2, 144.1 (d, J = 7.8 Hz), 149.1, 159.3, 162.3 (d, J = 243.7 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}FN$ $[M+H]^+$ 264.1189, found 264.1185. Anal. Calcd for $C_{18}H_{14}FN$ (%): C, 82.11; H, 5.36; N, 5.32, found: C, 81.81; H, 5.42; N, 5.40.



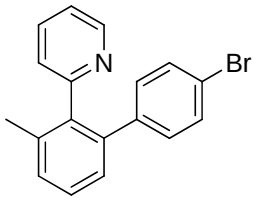
2-(4'-Fluoro-3-methylbiphenyl-2-yl)pyridine (4al)

2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-fluorophenylboronic acid (84.1 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 80% yield (42.1 mg). M.p.: 68-70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, 3H), 6.82 (t, J = 8.4 Hz, 2H), 6.88 (d, J = 7.6 Hz, 1H), 7.01-7.05 (m, 2H), 7.09-7.12 (m, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 114.6 (d, J = 21.1 Hz), 121.5, 125.7, 127.6, 128.2, 129.6, 131.2 (d, J = 7.6 Hz), 136.0, 136.9, 137.7 (d, J = 3.3 Hz), 139.5, 140.3, 149.1, 159.5, 160.6 (d, J = 244.0 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}FN$ $[M+H]^+$ 264.1189, found 264.1185. *Characterization data were consistent with literature values.*[10]



2-(4'-Chloro-3-methylbiphenyl-2-yl)pyridine (4am)

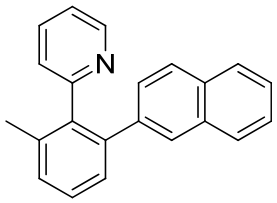
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 4-chlorophenylboronic acid (93.6 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 140 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a yellowish solid in 76% yield (42.4 mg). M.p.: 54-56 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.17 (s, 3H), 6.89 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.09-7.13 (m, 3H), 7.23 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.49 (td, J = 8.0 Hz, J = 2.0 Hz, 1H), 8.63 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 121.6, 125.6, 127.6, 127.9, 128.3, 129.8, 131.0, 132.5, 136.0, 137.0, 139.4, 140.1, 140.3, 149.1, 159.4 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}ClN$ $[M+H]^+$ 280.0893, found 280.0891. *Characterization data were consistent with literature values.*[10]



2-(4'-Bromo-3-methylbiphenyl-2-yl)pyridine (4an)

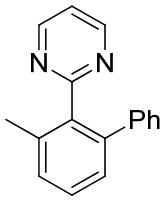
2-(*o*-Tolyl)pyridine (33.0 mg, 0.2 mmol), 4-bromophenylboronic acid (120.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 140 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 67% yield (43.3 mg). M.p.: 68-70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 7.13-7.16 (m, 1H), 7.24-7.29 (m, 3H), 7.33 (d, J = 6.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.51 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 8.65 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 120.7, 121.6, 125.6, 127.5,

128.3, 129.9, 130.9, 131.4, 136.0, 137.0, 139.4, 140.1, 140.7, 149.1, 159.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{15}BrN$ $[M+H]^+$ 324.0388, found 324.0388. *Characterization data were consistent with literature values.*[10]



2-(2-Methyl-6-(naphthalen-2-yl)phenyl)pyridine (4ao)

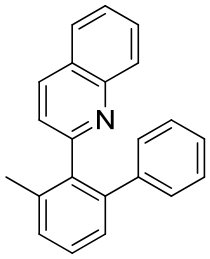
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), 2-naphthaleneboronic acid (103.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded colorless oil in 72% yield (42.5 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (s, 3H), 6.91 (d, J = 8.0 Hz, 1H), 7.04-7.07 (m, 1H), 7.15 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.33-7.42 (m, 6H), 7.56 (d, J = 8.4 Hz,1H), 7.64 (s, 1H), 7.68-7.74 (m, 2H), 8.63-8.65 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 121.4, 125.77, 125.81, 126.0, 127.0, 127.6, 128.05, 128.08, 128.1, 128.2, 128.6, 129.7, 131.9, 133.2, 135.9, 137.0, 139.4, 139.6, 141.2, 149.0, 159.6 ppm. HRMS (ESI^+): calcd for $C_{22}H_{18}N$ $[M+H]^+$ 296.1439, found 296.1440. *Characterization data were consistent with literature values.*[11]



2-(3-Methylbiphenyl-2-yl)pyrimidine (4ba)

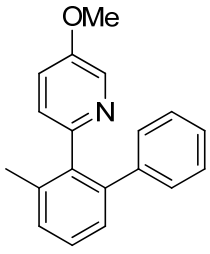
2-(*o*-Tolyl)pyrimidine (34.0 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 20:1, v/v) afforded a white solid in 41% yield (20.2 mg). M.p.: 97-98 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 3H), 7.07-7.15 (m, 6H), 7.29 (d, J

= 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 8.66 (d, *J* = 4.8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.2, 118.6, 126.4, 127.8, 127.9, 128.7, 129.2, 129.5, 136.1, 138.4, 141.2, 141.7, 156.5, 168.4 ppm. HRMS (ESI^+): calcd for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1235, found 247.1236. Anal. Calcd for $C_{17}H_{14}N_2$ (%): C, 82.90; H, 5.73; N, 11.37, found: C, 83.02; H, 5.99; N, 11.23.



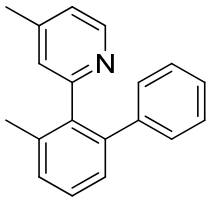
2-(3-Methyl-[1,1'-biphenyl]-2-yl)quinoline (4ca)

2-(*o*-Tolyl)quinoline (43.8 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 140 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded yellow oil in 81% yield (47.8 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.23 (s, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.06-7.08 (m, 3H), 7.12-7.14 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.70-7.76 (m, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.7, 123.9, 126.48, 126.54, 127.7, 127.8, 127.9, 128.4, 129.5, 129.9, 135.6, 137.0, 139.5, 141.3, 141.6, 147.7, 160.2 ppm. HRMS (ESI^+): calcd for $C_{22}H_{18}N$ $[M+H]^+$ 296.1439, found 260.1438. Anal. Calcd for $C_{22}H_{17}N$ (%): C, 89.46; H, 5.80; N, 4.74, found: C, 89.17; H, 6.14; N, 4.33.



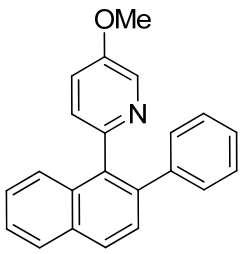
5-Methoxy-2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine (4da)

5-Methoxy-2-(*o*-tolyl)pyridine (39.8 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (hexane/acetone = 30:1, v/v) afforded colorless oil in 95% yield (52.3 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (s, 3H), 3.85 (s, 3H), 6.82 (d, J = 8.4 Hz, 1H), 7.00 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 7.10-7.12 (m, 2H), 7.15-7.18 (m, 3H), 7.30 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 8.36 (d, J = 2.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.7, 55.6, 120.5, 125.9, 126.2, 127.70, 127.72, 128.0, 129.5, 129.7, 136.2, 137.3, 139.0, 141.6, 142.0, 151.8, 153.8 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1388, found 276.1390. Anal. Calcd for $C_{19}H_{17}NO$ (%): C, 82.88; H, 6.22; N, 5.09, found: C, 82.73; H, 6.12; N, 4.81.



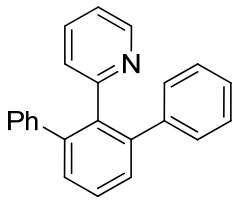
4-Methyl-2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine (4ea)

4-Methyl-2-(*o*-tolyl)pyridine (36.6 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (hexane/acetone = 30:1, v/v) afforded colorless oil in 91% yield (47.2 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.17 (s, 3H), 2.21 (s, 3H), 6.74 (s, 1H), 6.92 (dd, J = 4.8 Hz, J = 0.8 Hz, 1H), 7.10-7.17 (m, 5H), 7.28-7.31 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 8.49 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 21.0, 122.4, 126.3, 126.6, 127.62, 127.65, 128.0, 129.4, 129.7, 136.8, 139.6, 141.4, 141.9, 146.8, 148.7, 159.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{18}N$ $[M+H]^+$ 260.1439, found 260.1434.



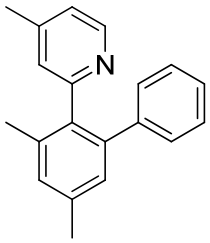
5-Methoxy-2-(2-phenylnaphthalen-1-yl)pyridine (4fa)

5-Methoxy-2-(naphthalen-1-yl)pyridine (47.0 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 140 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a yellowish solid in 45% yield (28.0 mg). M.p.: 134-136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.76 (s, 3H), 6.65 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.88-7.06 (m, 5H), 7.45 (d, J = 7.2 Hz, 1H), 7.54-7.62 (m, 3H), 7.94-8.02 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.8, 119.8, 125.3, 125.6, 126.0, 127.4, 128.7, 129.3, 129.4, 130.8, 131.0, 135.5, 135.9, 138.8, 140.1, 143.6, 152.9, 153.4 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{18}NO$ $[M+H]^+$ 312.1388, found 312.1382. Anal. Calcd for $C_{22}H_{17}NO$ (%): C, 84.86; H, 5.50; N, 4.50, found: C, 84.73; H, 5.63; N, 4.53.



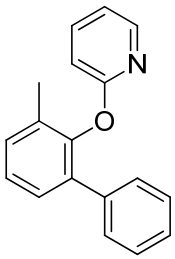
2-([1,1':3',1''-Terphenyl]-2'-yl)pyridine (4ga)

2-((1,1'-Biphenyl)-2-yl)pyridine (46.2 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 140 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded a white solid in 60% yield (36.9 mg). M.p.: 124-126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.87-6.92 (m, 2H), 7.09-7.18 (m, 10H), 7.30 (td, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.44-7.46 (m, 2H), 7.52 (td, J = 8.4 Hz, J = 6.4 Hz, 1H), 8.31 (dd, J = 4.8 Hz, J = 0.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 121.0, 126.4, 126.9, 127.8, 128.3, 129.6, 129.8, 135.0, 138.7, 141.7, 142.0, 148.6, 159.1 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{17}NNa$ $[M+Na]^+$ 330.1259, found 330.1252. *Characterization data were consistent with literature values.*[10]



2-(3,5-Dimethyl-[1,1'-biphenyl]-2-yl)-4-methylpyridine (4ha)

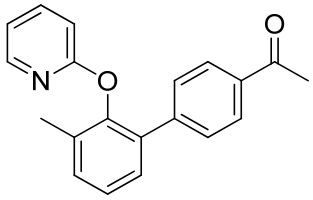
2-(2,4-Dimethylphenyl)-4-methylpyridine (39.4 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (petroleum ether/acetone = 30:1, v/v) afforded colorless oil in 52% yield (28.4 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.13 (s, 3H), 2.15 (s, 3H), 2.40 (s, 3H), 6.69 (s, 1H), 6.89 (d, J = 5.2 Hz, 1H), 7.07-7.14 (m, 7H), 8.46 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 21.0, 21.3, 122.2, 126.2, 126.8, 127.6, 128.4, 129.7, 130.2, 136.7, 136.9, 137.5, 141.3, 142.0, 146.6, 148.6, 159.5 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{20}N$ $[M+H]^+$ 274.1596, found 274.1596. Anal. Calcd for $C_{20}H_{19}N$ (%): C, 87.87; H, 7.01; N, 5.12, found: C, 87.53; H, 7.04; N, 5.05.



2-((3-Methyl-[1,1'-biphenyl]-2-yl)oxy)pyridine (4ia)

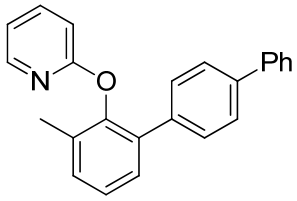
2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded a white solid in 71% yield (37.1 mg). M.p.: 57-59 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (s, 3H), 6.70 (d, J = 8.4 Hz, 1H), 6.84 (dd, J = 6.4 Hz, J = 5.2 Hz, 1H), 7.22-7.33 (m, 6H), 7.45 (d, J = 6.8 Hz, 2H), 7.51-7.56 (m, 1H), 8.09 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100

MHz): δ = 17.0, 110.3, 117.6, 125.7, 127.0, 128.0, 128.9, 129.2, 130.6, 132.1, 135.6, 138.4, 139.1, 147.7, 149.0, 163.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{15}NNaO$ $[M+Na]^+$ 284.1051, found 284.1050. Anal. Calcd for $C_{18}H_{15}NO$ (%): C, 82.73; H, 5.79; N, 5.36, found: C, 82.71; H, 5.84; N, 5.32.



1-(3'-Methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-4-yl)ethanone (4if)

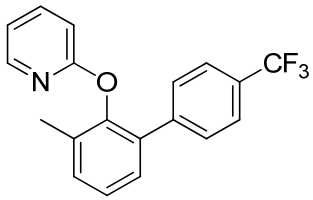
2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), 4-acetylphenylboronic acid (98.4 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded a white solid in 63% yield (38.2 mg). M.p.: 156-158 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 3H), 2.58 (s, 3H), 6.70 (d, J = 8.4 Hz, 1H), 6.84 (dd, J = 6.4 Hz, J = 5.2 Hz, 1H), 7.26-7.35 (m, 3H), 7.52-7.56 (m, 3H), 7.87 (d, J = 8.4 Hz, 2H), 8.06 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 26.7, 110.3, 117.8, 125.9, 128.2, 128.6, 129.4, 131.4, 132.4, 134.6, 135.7, 139.3, 143.5, 147.7, 149.0, 163.2, 198.0 ppm. HRMS (ESI^+): calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.1338, found 304.1335. Anal. Calcd for $C_{20}H_{17}NO_2$ (%): C, 79.19; H, 5.65; N, 4.62, found: C, 79.34; H, 5.67; N, 4.66.



2-((3-Methyl-[1,1':4',1''-terphenyl]-2-yl)oxy)pyridine (4ii)

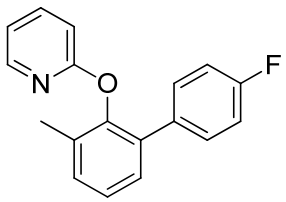
2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), [1,1'-biphenyl]-4-ylboronic acid (118.9 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded colorless oil in 70% yield (47.2 mg). ^1H NMR

($CDCl_3$, 400 MHz): δ = 2.21 (s, 3H), 6.71 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 6.81-6.84 (m, 1H), 7.25-7.36 (m, 4H), 7.40-7.44 (m, 2H), 7.50-7.54 (m, 5H), 7.57-7.59 (m, 2H), 8.08-8.09 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.1, 110.3, 117.6, 125.8, 126.7, 127.1, 127.3, 128.8, 129.6, 130.7, 132.2, 135.2, 137.4, 139.2, 139.8, 140.9, 147.8, 149.2, 163.5 ppm. HRMS (ESI^+): calcd for $C_{24}H_{20}NO$ $[M+H]^+$ 338.1545, found 338.1540. Anal. Calcd for $C_{24}H_{19}NO$ (%): C, 85.43; H, 5.68; N, 4.15, found: C, 85.05; H, 5.82; N, 4.08.



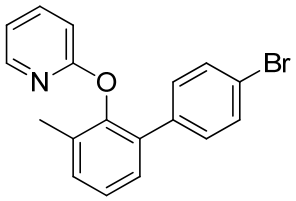
2-((3-Methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)oxy)pyridine (4ij)

2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), 4-trifluoromethylphenylboronic acid (114.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded a white solid in 89% yield (58.6 mg). M.p.: 85-87 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 3H), 6.71 (d, J = 8.4 Hz, 1H), 6.85-6.88 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.32-7.37 (m, 1H), 7.52-7.58 (m, 5H), 8.06-8.08 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 110.4, 117.9, 124.91, 124.94, 124.98, 125.0, 125.9, 128.7, 129.5, 131.4, 132.4, 134.4, 139.4, 142.2, 147.7, 149.1, 163.2 ppm. HRMS (ESI^+): calcd for $C_{19}H_{15}F_3NO$ $[M+H]^+$ 330.1106, found 330.1106. Anal. Calcd for $C_{19}H_{14}F_3NO$ (%): C, 69.30; H, 4.28; N, 4.25, found: C, 69.25; H, 3.95; N, 4.35.



2-((4'-Fluoro-3-methyl-[1,1'-biphenyl]-2-yl)oxy)pyridine (4il)

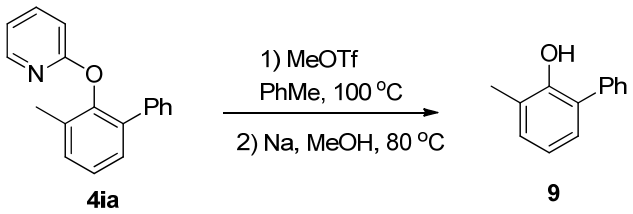
2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), 4-fluorophenylboronic acid (84.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded a white solid in 82% yield (45.8 mg). M.p.: 87-89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 3H), 6.68 (d, J = 8.4 Hz, 1H), 6.85 (dd, J = 6.8 Hz, J = 5.2 Hz, 1H), 6.93-6.99 (m, 2H), 7.23-7.32 (m, 3H), 7.37-7.42 (m, 2H), 7.52-7.56 (m, 1H), 8.07 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 110.3, 114.9 (d, J = 21.2 Hz), 117.7, 125.8, 128.7, 130.8 (d, J = 4.9 Hz), 130.9, 132.2, 134.4 (d, J = 3.2 Hz), 134.7, 139.2, 147.7, 149.1, 162.1 (d, J = 244.3 Hz), 163.4 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}FNO$ $[M+H]^+$ 280.1138, found 280.1136. Anal. Calcd for $C_{18}H_{14}FNO$ (%): C, 77.40; H, 5.05; N, 5.01, found: C, 77.17; H, 5.00; N, 5.09.



2-((4'-Bromo-3-methyl-[1,1'-biphenyl]-2-yl)oxy)pyridine (4in)

2-(*o*-Tolyloxy)pyridine (37.0 mg, 0.2 mmol), 4-bromophenylboronic acid (120.0 mg, 0.6 mmol), $AuBr_3$ (4.4 mg, 0.01 mmol), NFSI (189.2 mg, 0.6 mmol) and *t*-BuOH (2.0 mL) at 130 °C for 24 h. Purification via neutral alumina column chromatography (CH_2Cl_2/hexane = 3:1, v/v) afforded a white solid in 70% yield (47.5 mg). M.p.: 115-116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.17 (s, 3H), 6.67 (d, J = 8.4 Hz, 1H), 6.82-6.85 (m, 1H), 7.24 (d, J = 4.8 Hz, 2H), 7.28-7.30 (m, 3H), 7.37-7.39 (m, 2H), 7.51-7.56 (m, 1H), 8.04 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 110.3, 117.8, 121.4, 125.8, 128.6, 130.9, 131.0, 131.2, 132.3, 134.5, 137.4, 139.3, 147.7, 149.0, 163.3 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{15}BrNO$ $[M+H]^+$ 340.0337, found 340.0338. Anal. Calcd for $C_{18}H_{14}BrNO$ (%): C, 63.55; H, 4.15; N, 4.12, found: C, 63.75; H, 4.16; N, 4.15.

VIII. Removal of the directing group[12]



4ia **9**

A three necked flask with a magnetic stirring bar was charged with **4ia** (65.5 mg. 0.25 mmol), trifluoromethanesulfonate (100 μL, 0.88 mmol) and toluene under N_2. Then the reaction mixture was stirred at 100 °C for 2 h. The reaction mixture was then cooled to ambient temperature and the solvent was evaporated in vacuum to give a white solid. Under an N_2 atmosphere, the solid in methanol (2.5 mL) was added to a solution of sodium (150 mg, 12 mmol) in methanol (8 mL). The reaction mixture was stirred at 80 °C for 30 min. After the reaction mixture was cooled to room temperature, methanol was removed in vacuum. The resulting reaction mixture was added water (40 mL), extracted with EtOAc and dried over Na_2SO_4. The organic layer was concentrated and the resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 15/1, v/v) to provide the desired product **9** as colorless oil in 77% yield (35.3 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (s, 3H), 5 26 (s, 1H), 6.91 (d, J = 7.6 Hz, 1H), 7.09 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.39-7.44 (m, 1H), 7.46-7.53 (m, 4H) ppm. The product **9** was characterized by comparison of the ^{1}H NMR data with those reported previously.

IX. References

(1) H. V. Mierde, P. Voort and F. van der Verpoort, *Tetrahedron Lett.*, 2008, **49**, 6893.

(2) X. Rao, C. Liu, J. Qiu and Z. Jin, *Org. Biomol. Chem.*, 2012, **10**, 7875.

(3) D. Maiti and S. L. Buchwald, *J. Org. Chem.*, 2010, **75**, 1791.

(4) E. C. Constable and T. A. Leese, *J. Organomet. Chem.*, 1989, **363**, 419.

(5) E. Langseth, C. H. Görbitz, R. H. Heyn and M. Tilset, *Organometallics*, 2012, **31**, 6567.

(6) Y. Fuchita, Y. Utsunomiya and M. Yasutake, *J. Chem. Soc*., *Dalton Trans*., 2001, 2330.

(7) J. Lindh, P. J. R. Sjöberg and M. Larhed, *Angew. Chem., Int. Ed.*, 2010, **49**, 7733.

(8) D. C. Powers, M. A. L. Geibel, J. E. M. N. Klein and T. Ritter, *J. Am. Chem. Soc.*, 2009, **131**, 17050.

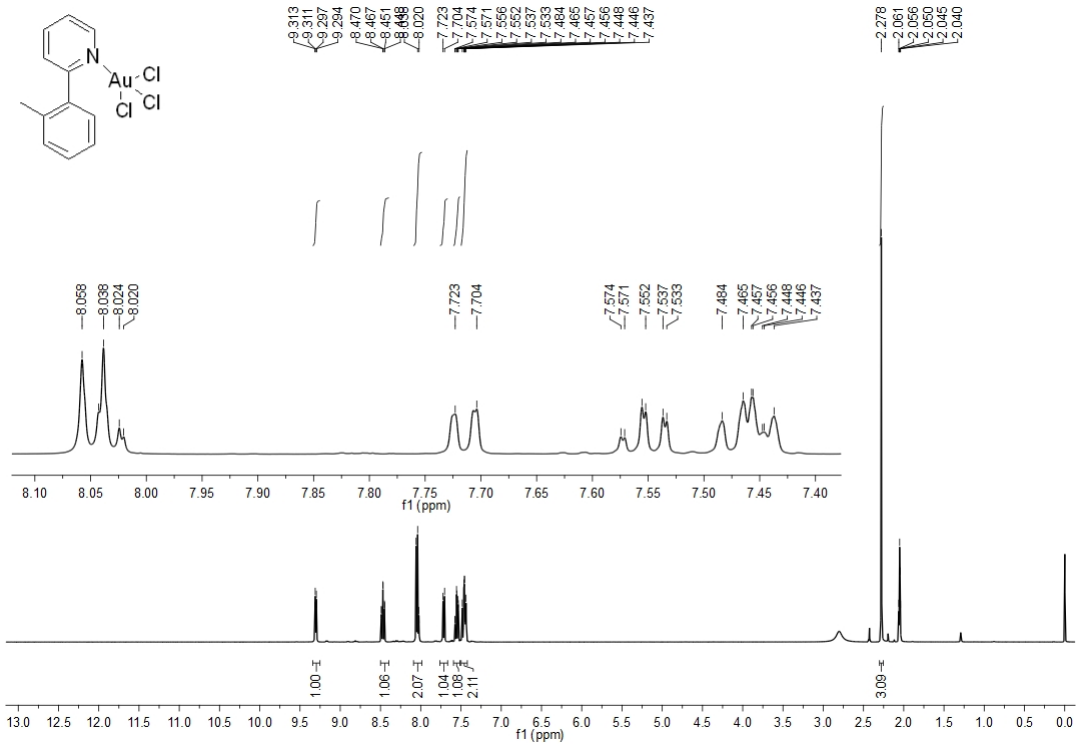
(9) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim and S. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 9110.

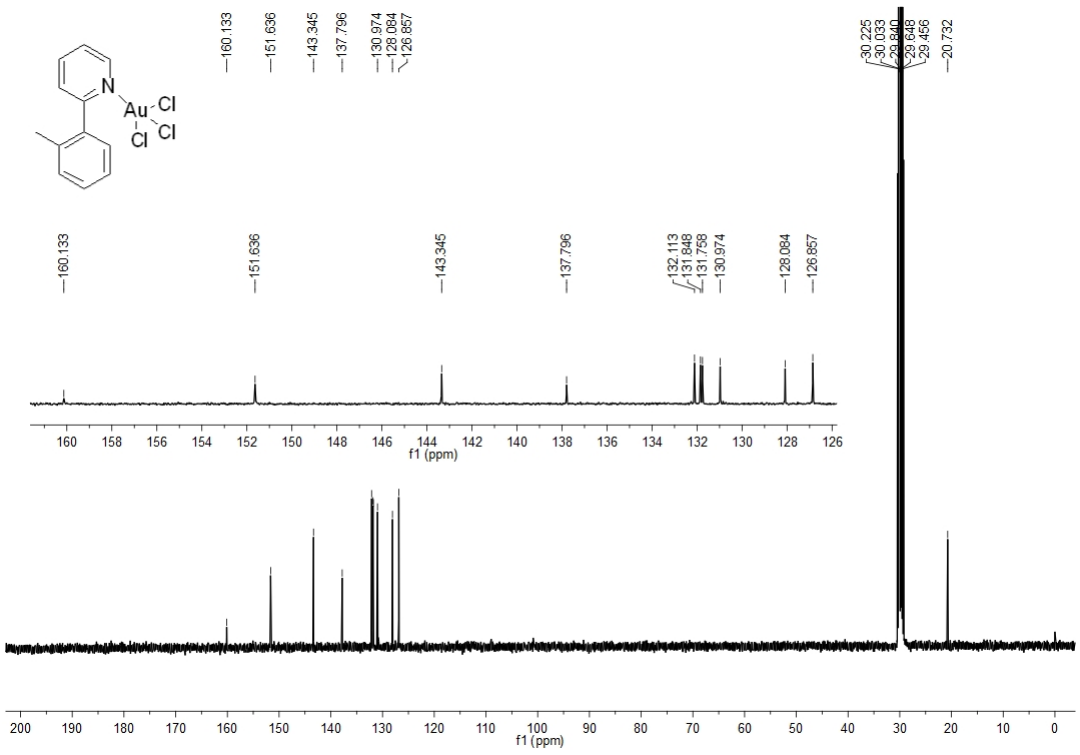
(10) H. Li, W. Wei, Y. Xu, C. Zhang and X. Wan, *Chem. Commun.*, 2011, **47**, 1497.

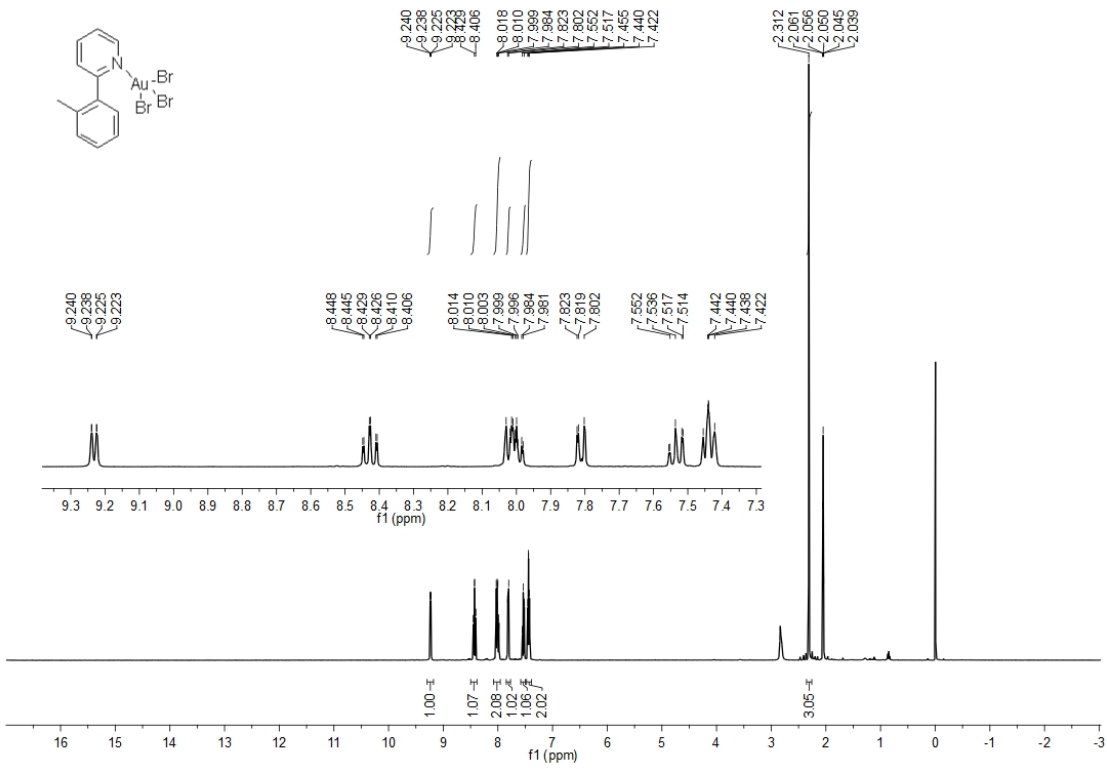
(11) Z. Qi and X. Li, *Angew. Chem., Int. Ed.*, 2013, **52**, 8995.

(12) K. Yoshida, R. Narui and T. Imamoto, *Chem*.－*Eur. J.*, 2008, **14**, 9706.

X. Copies of ^{1}H and ^{13}C NMR spectra



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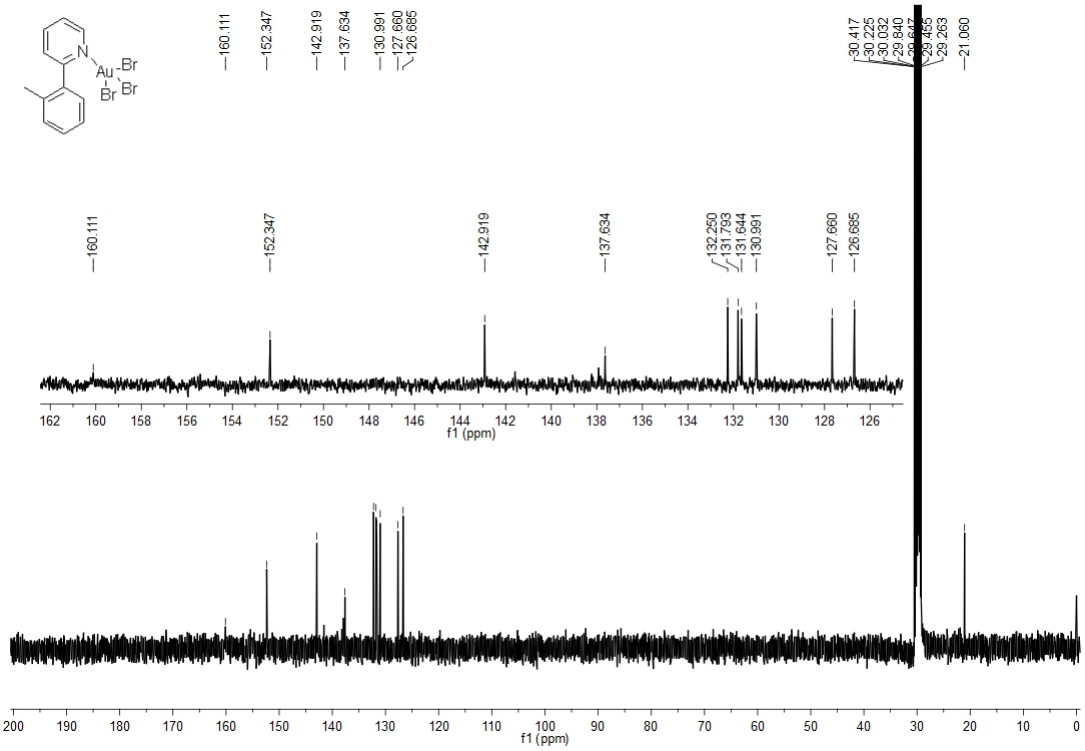
f1 (ppm)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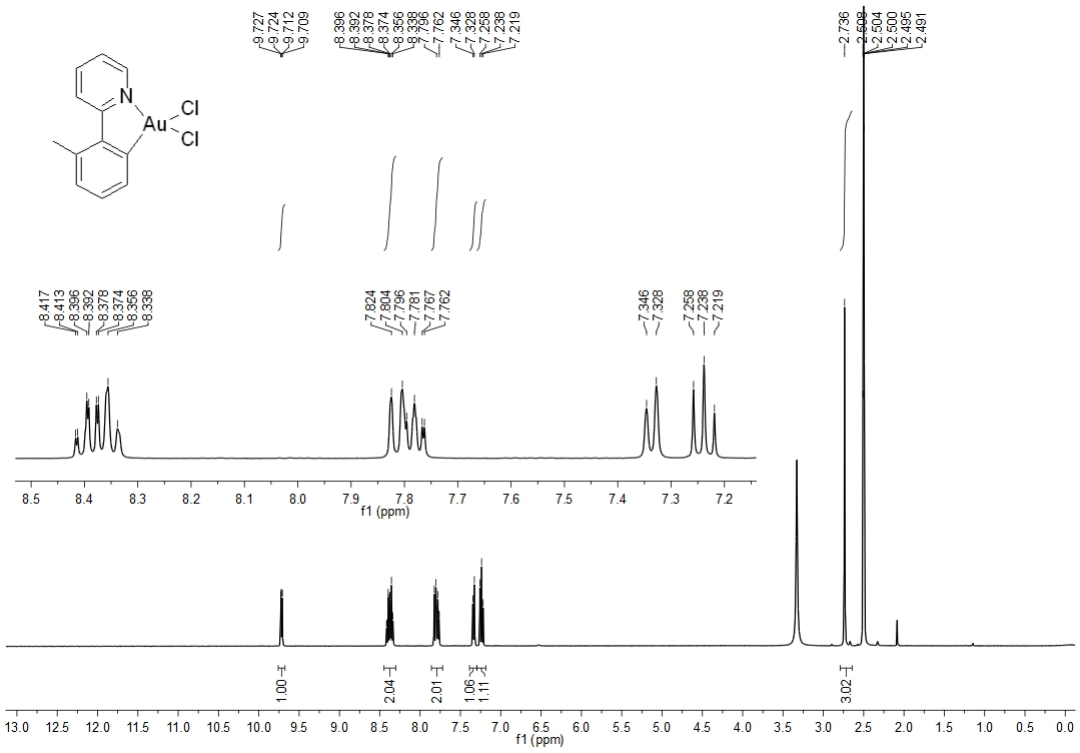
f1 (ppm)
f1 (ppm)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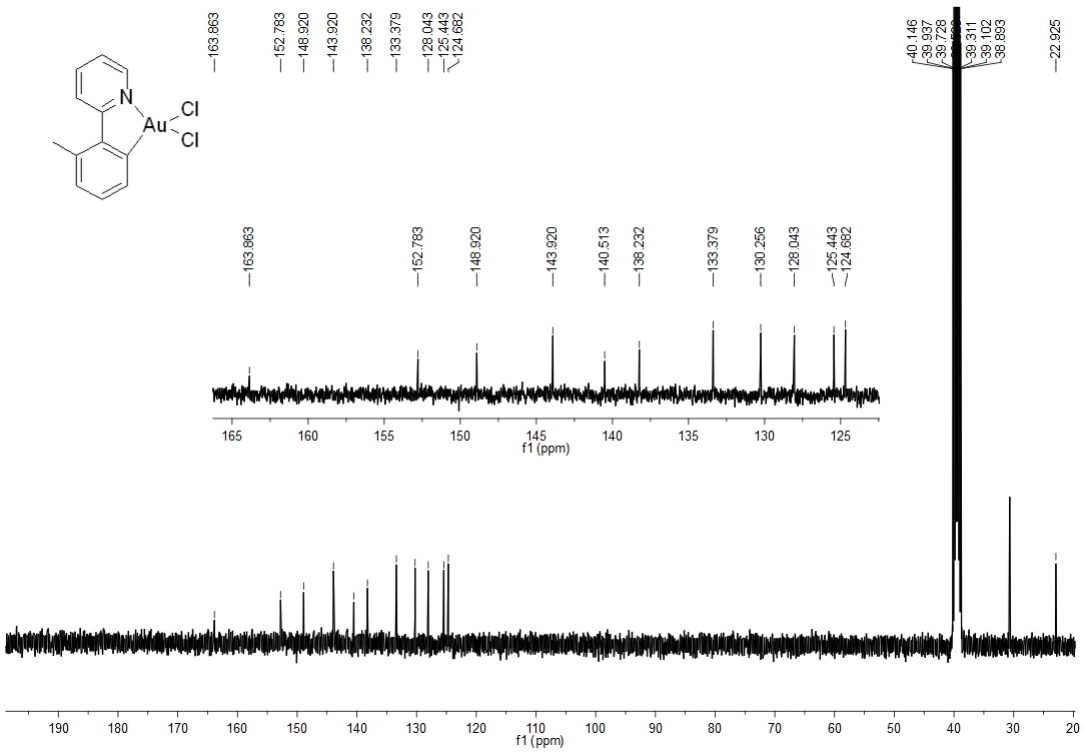
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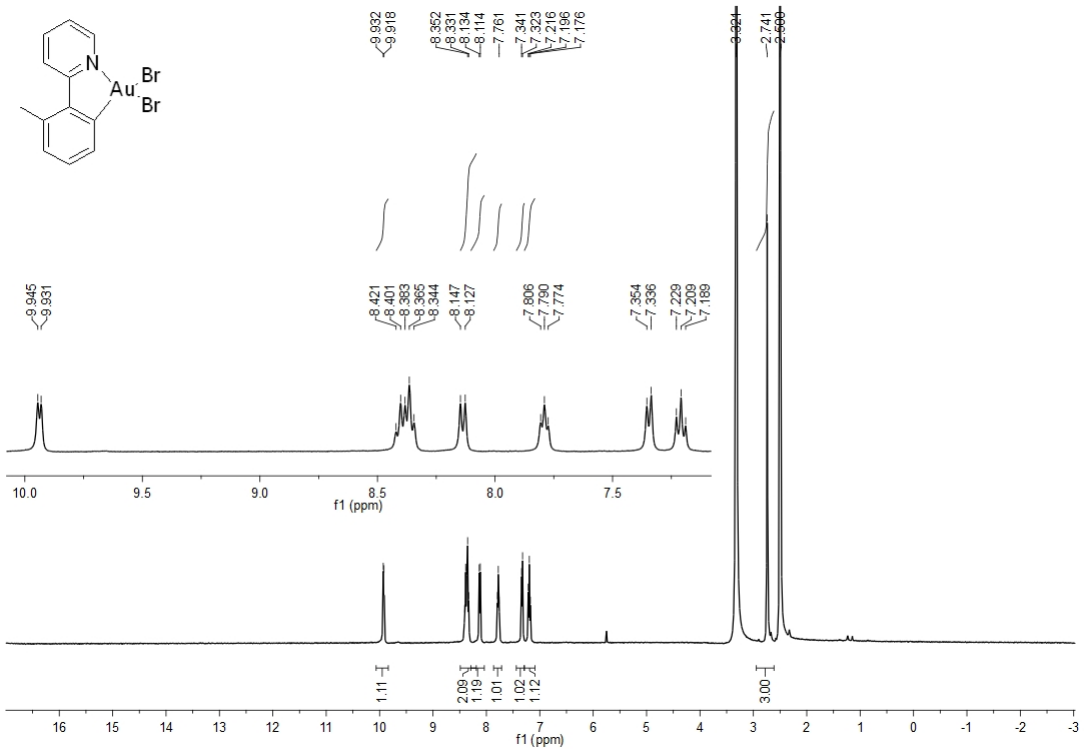
f1 (ppm)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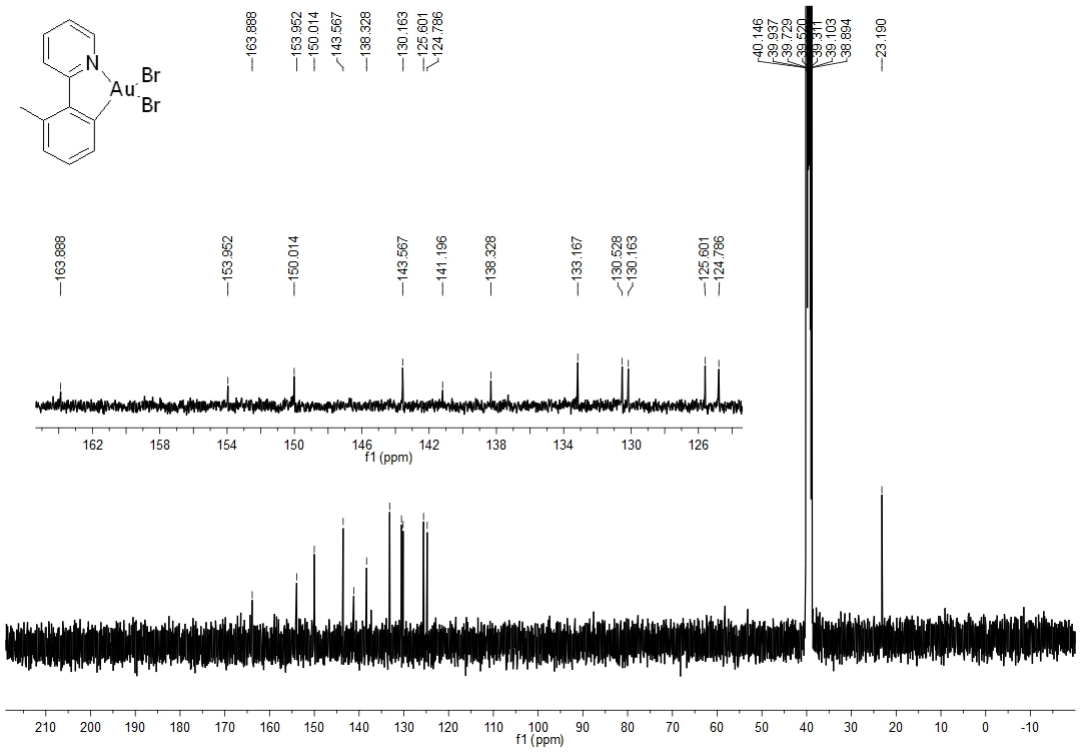
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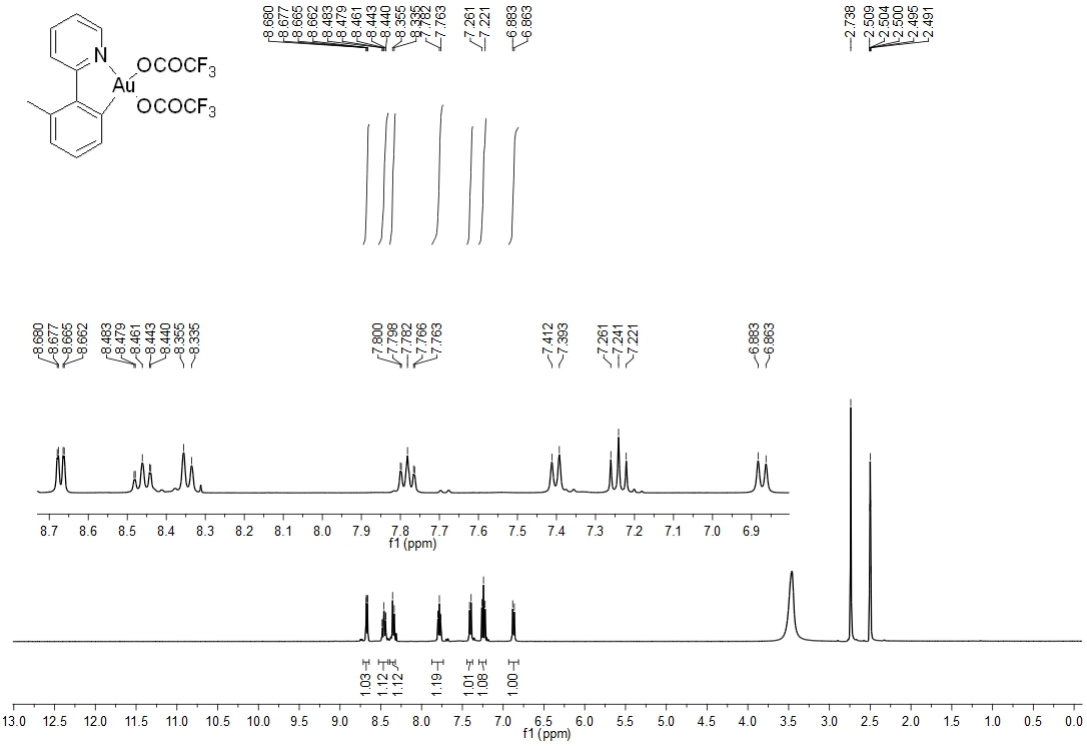
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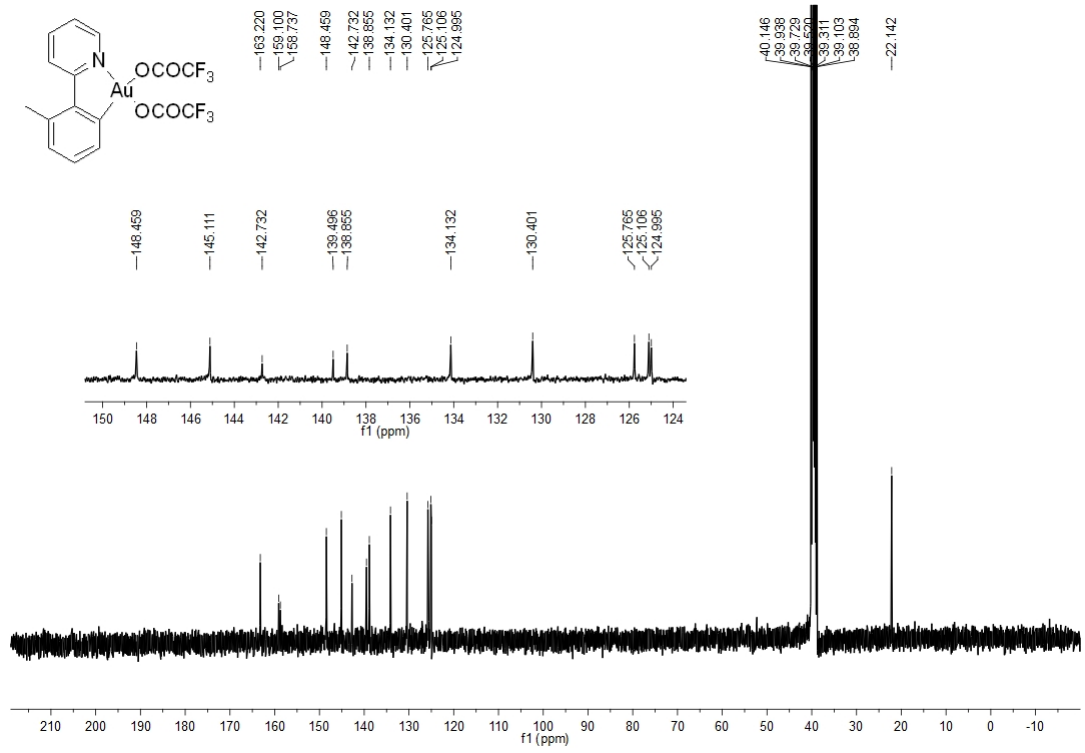
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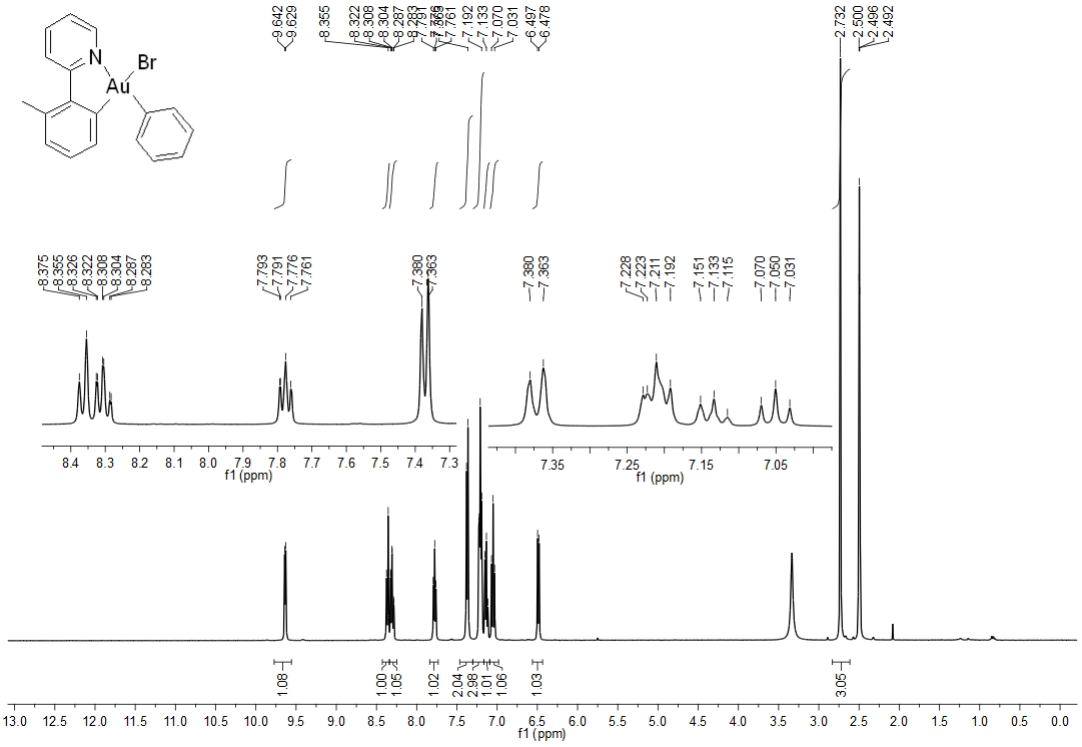
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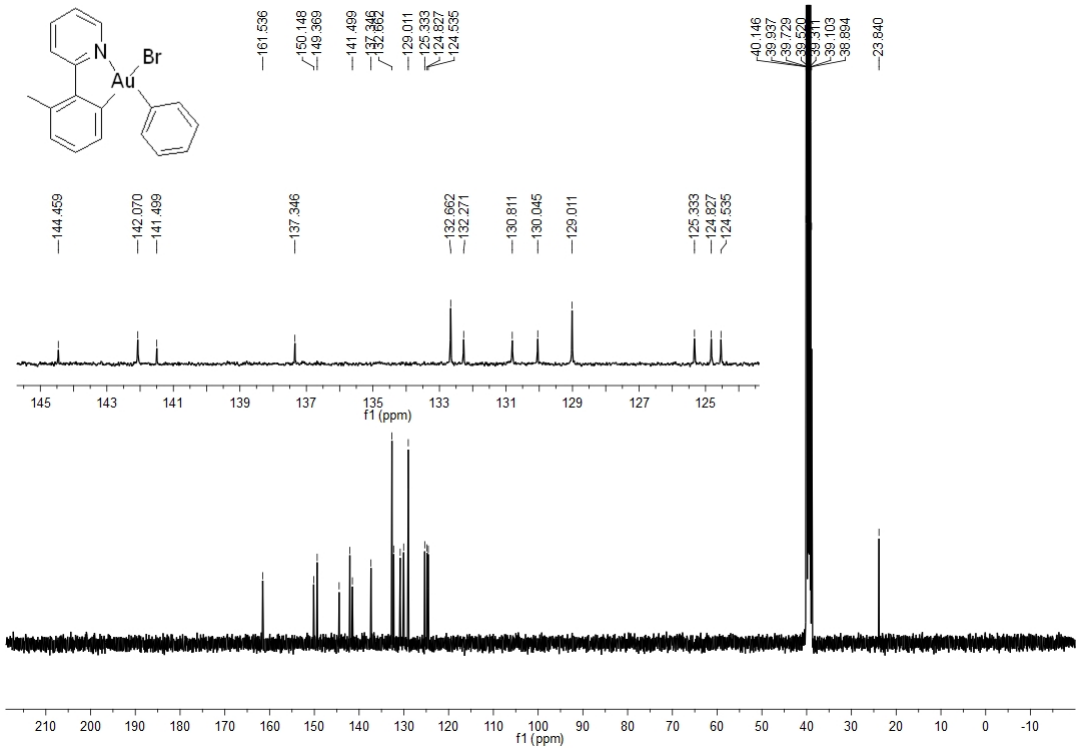
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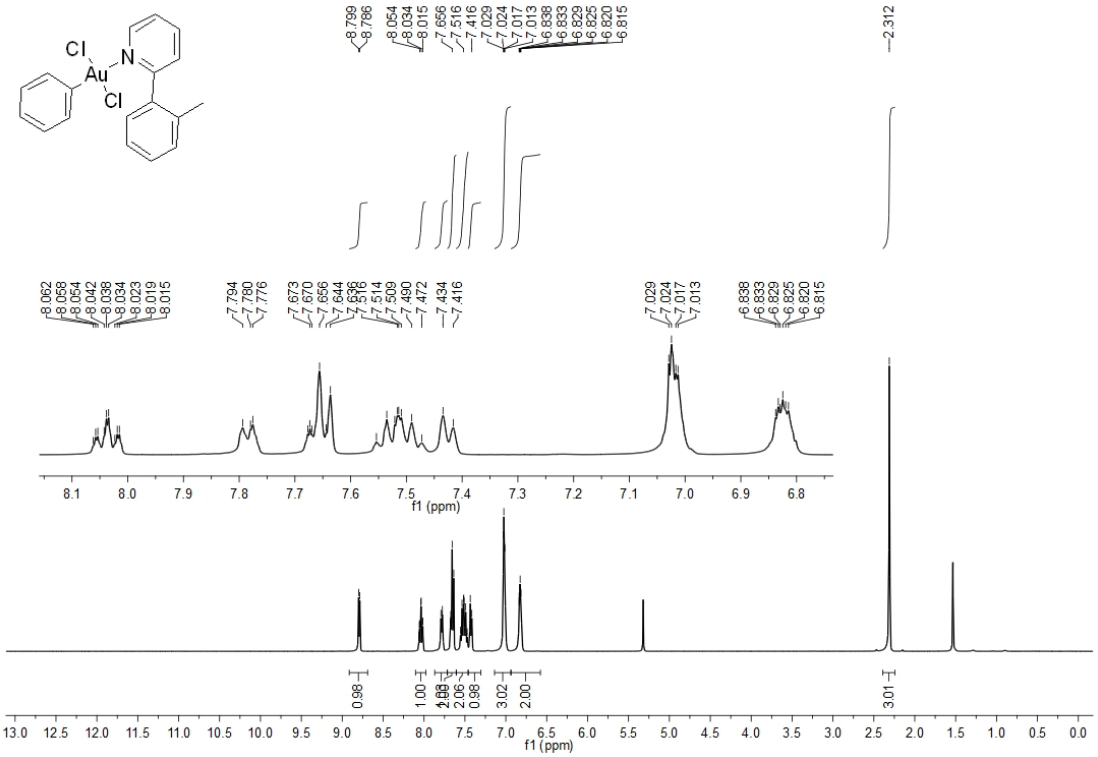
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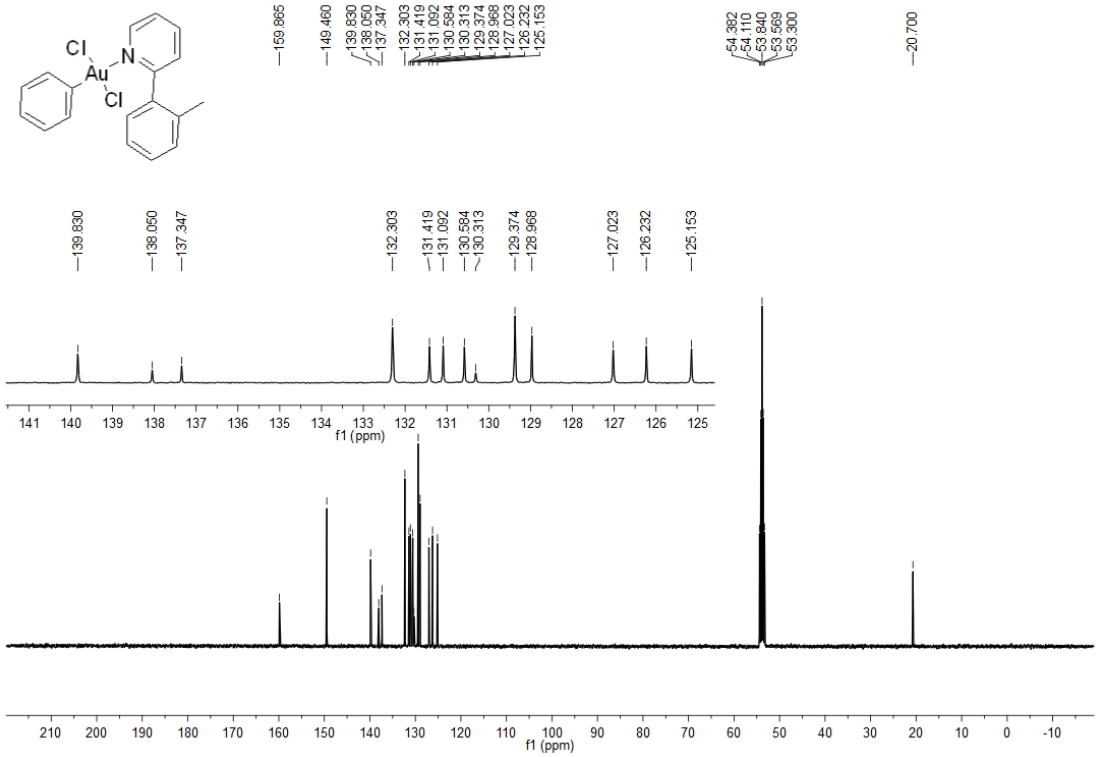
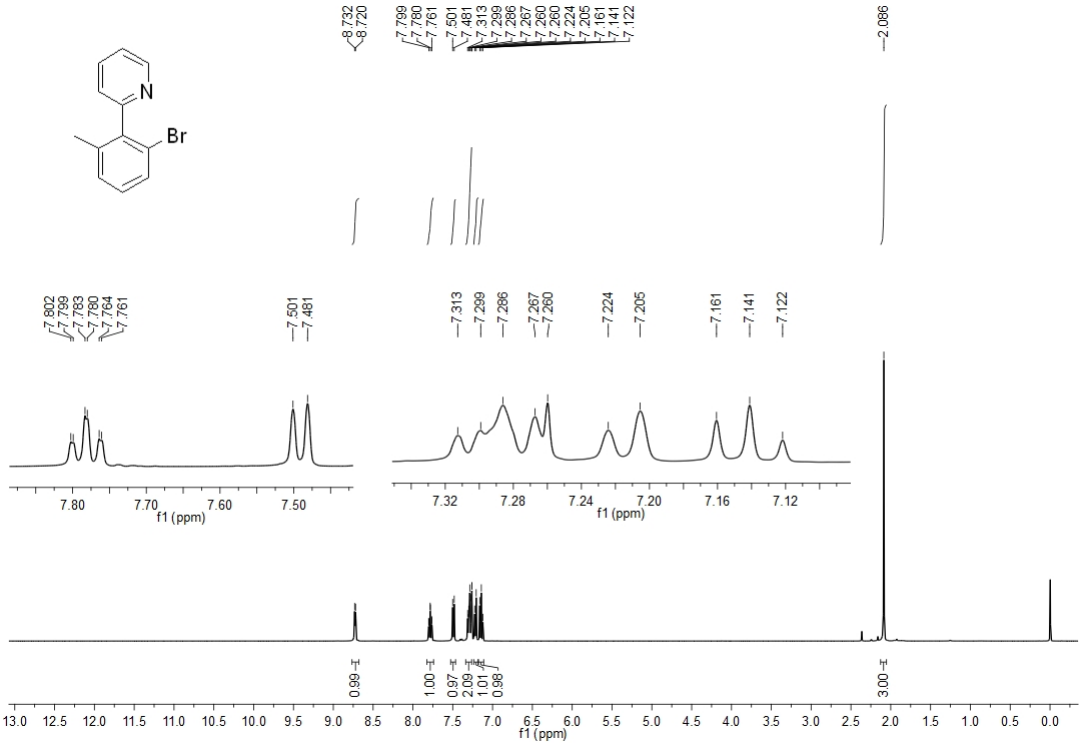
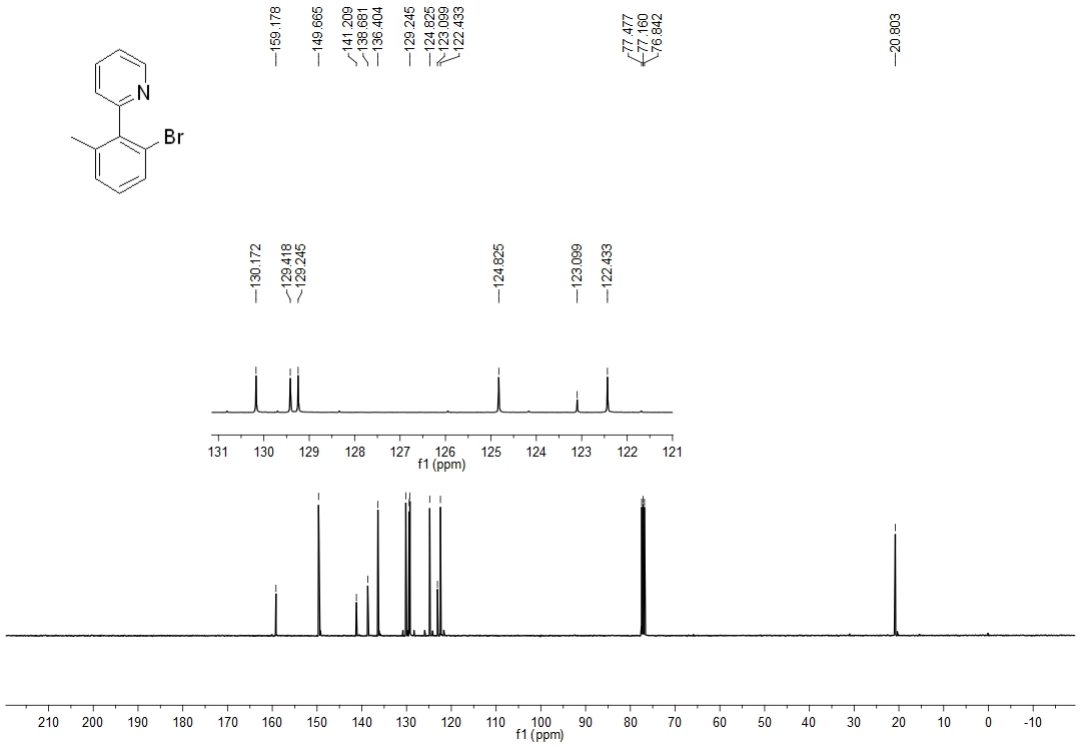
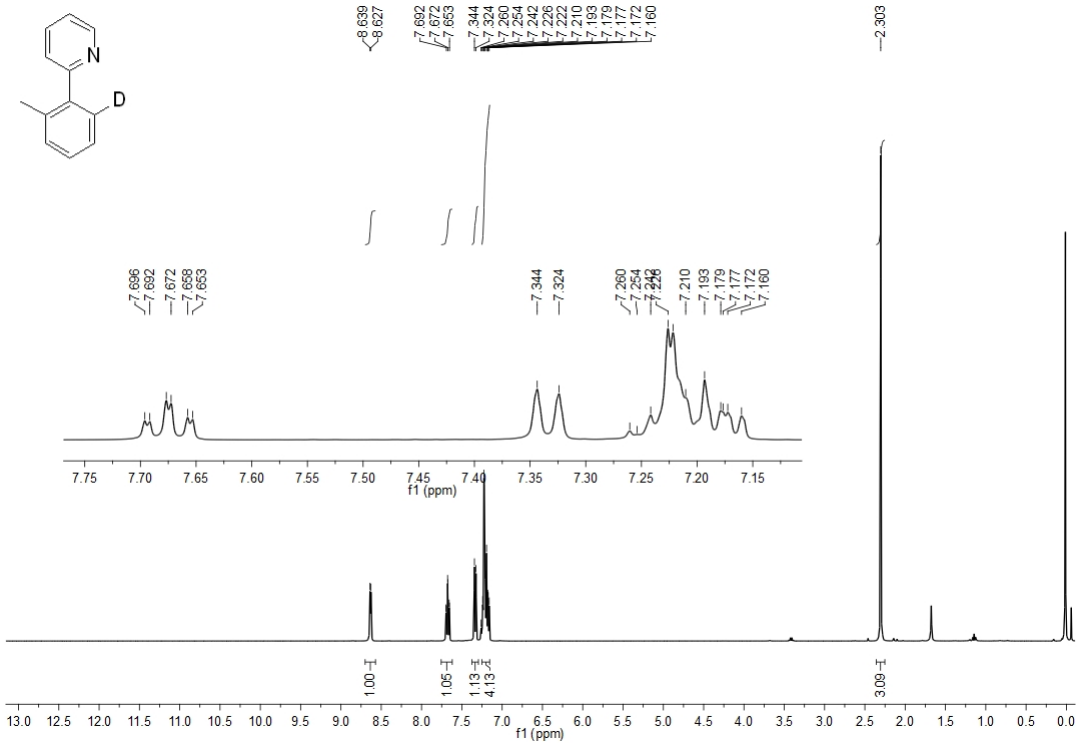
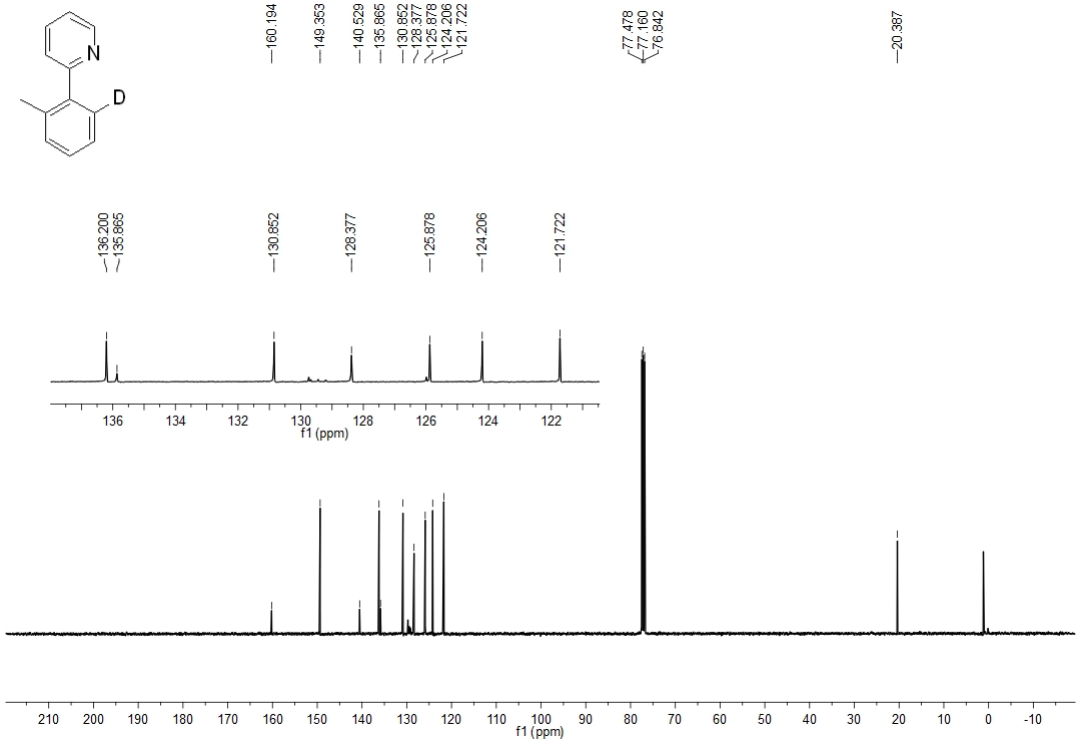
3.02
2.00
3.01

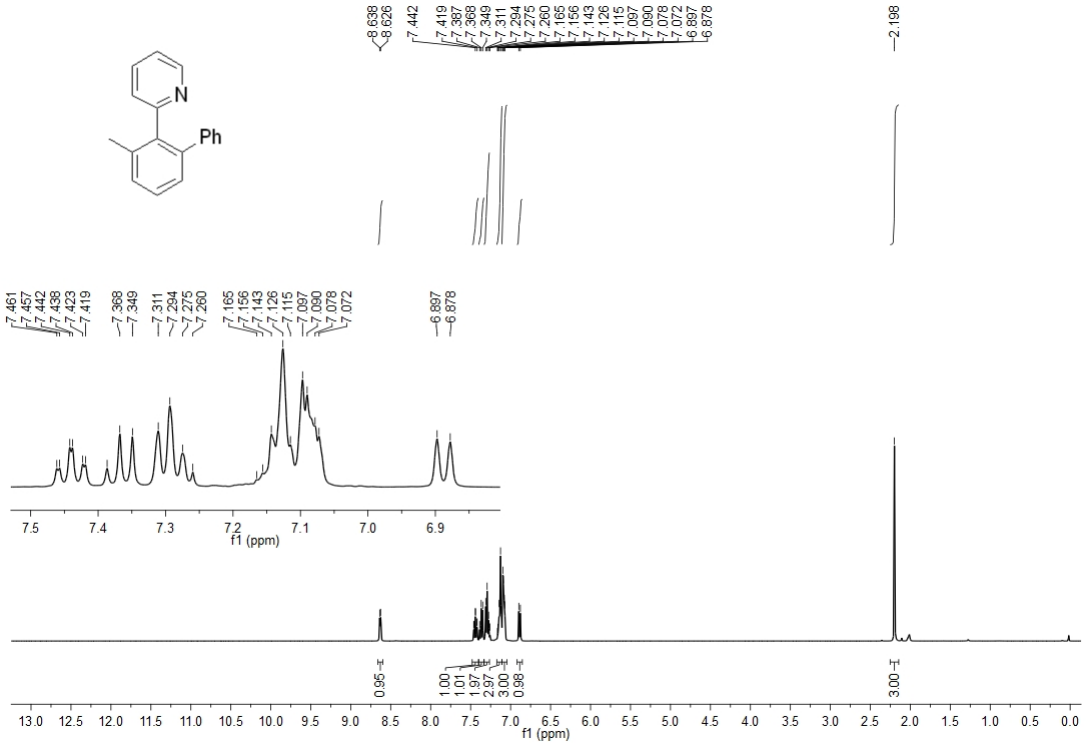

Cl
Au
N
Cl
159.865
149.460
139.830
138.050
137.347
132.303
131.419
131.092
130.584
130.313
129.374
128.968
127.023
126.232
125.153
54.382
54.110
53.840
53.569
53.300
20.700
f1 (ppm)

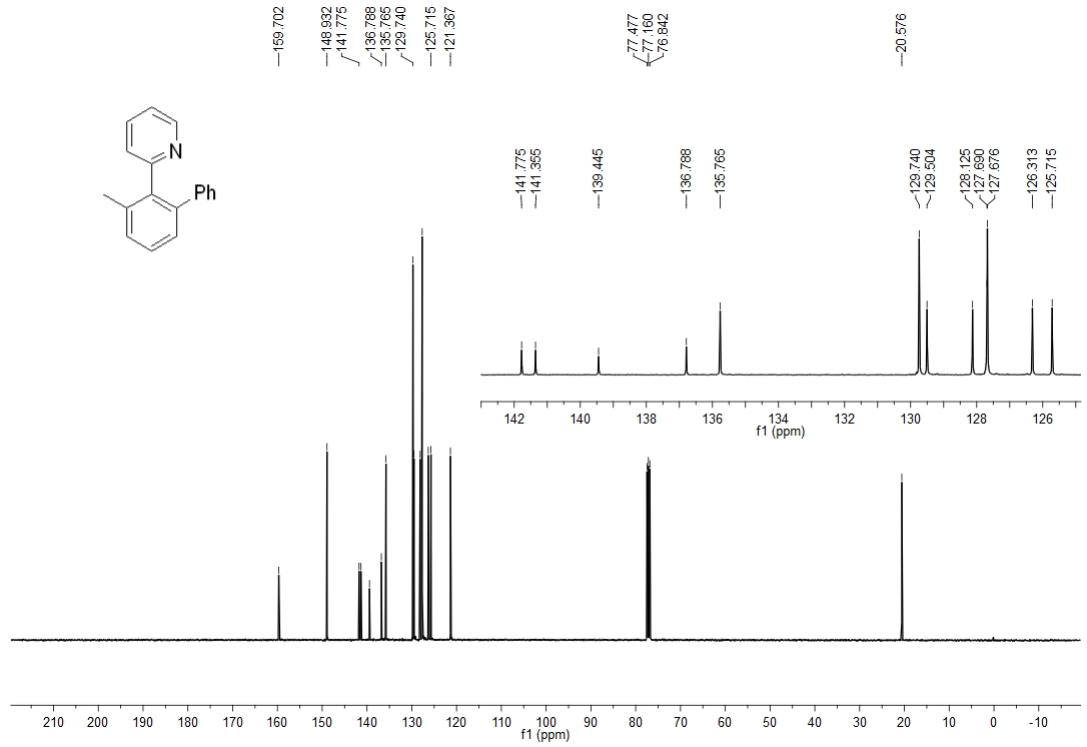

8.732
8.720
7.799
7.780
7.761
7.501
7.481
7.313
7.299
7.286
7.267
7.260
7.260
7.224
7.205
7.161
7.141
7.122
2.086
N
Br
7.802
7.799
7.783
7.780
7.764
7.761
7.501
7.481
7.313
7.299
7.286
7.267
7.260
7.224
7.205
7.161
7.141
7.122
7.80
7.70
7.60
7.50
7.32
7.28
7.24
7.20
7.16
7.12
f1 (ppm)
0.99
1.00
0.97
2.09
1.01
0.98
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

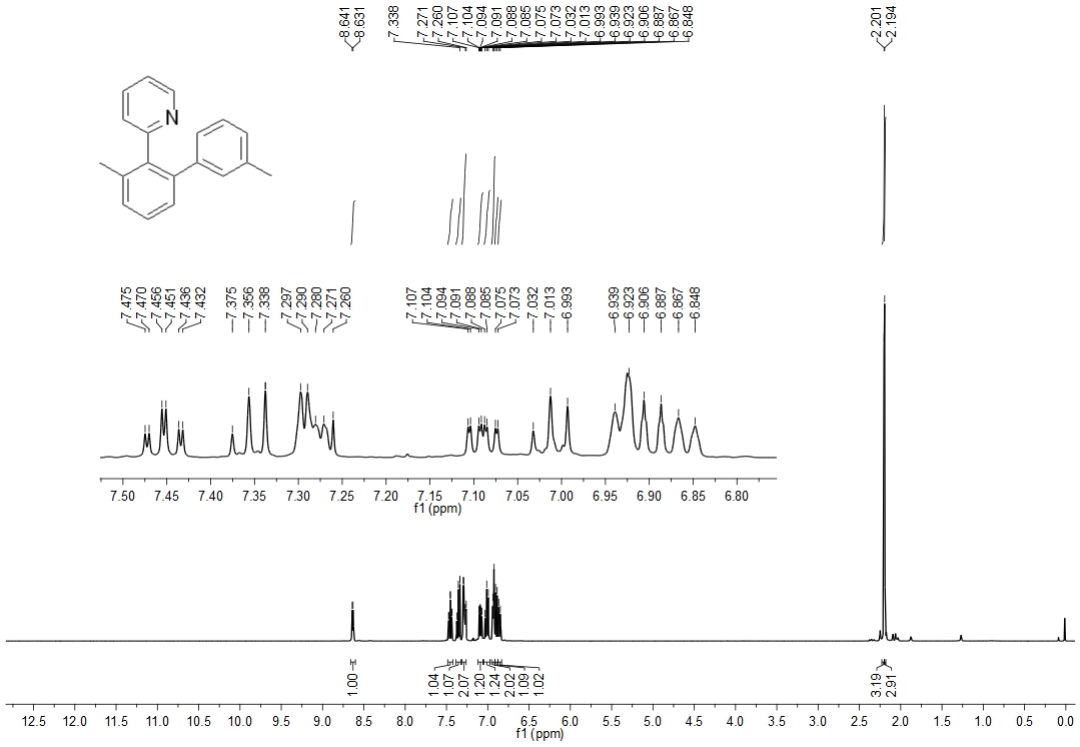

159.178
149.665
141.209
138.681
136.404
129.245
124.825
123.099
122.433
77.477
77.160
76.842
20.803
N
Br
130.172
129.418
129.245
124.825
123.099
122.433
131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

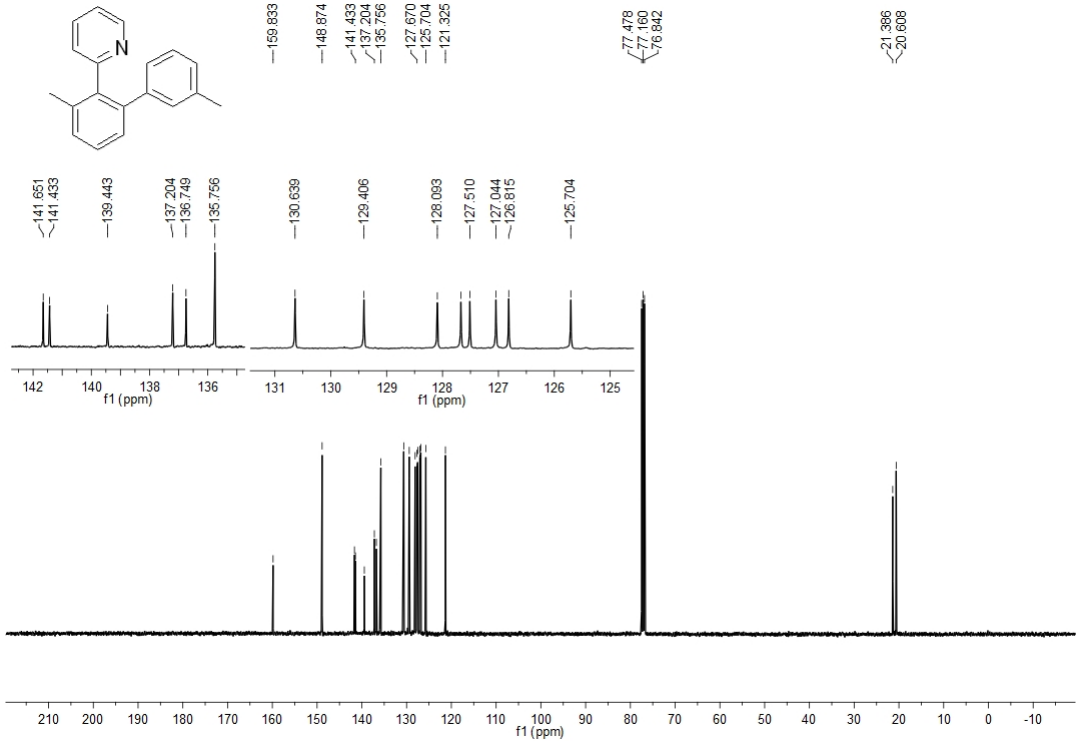

N
D
8.639
8.627
7.692
7.672
7.653
7.344
7.324
7.260
7.254
7.242
7.226
7.222
7.210
7.193
7.179
7.177
7.172
7.160
2.303
7.696
7.692
7.672
7.658
7.653
1.00
1.05
1.13
4.13
3.09
f1 (ppm)

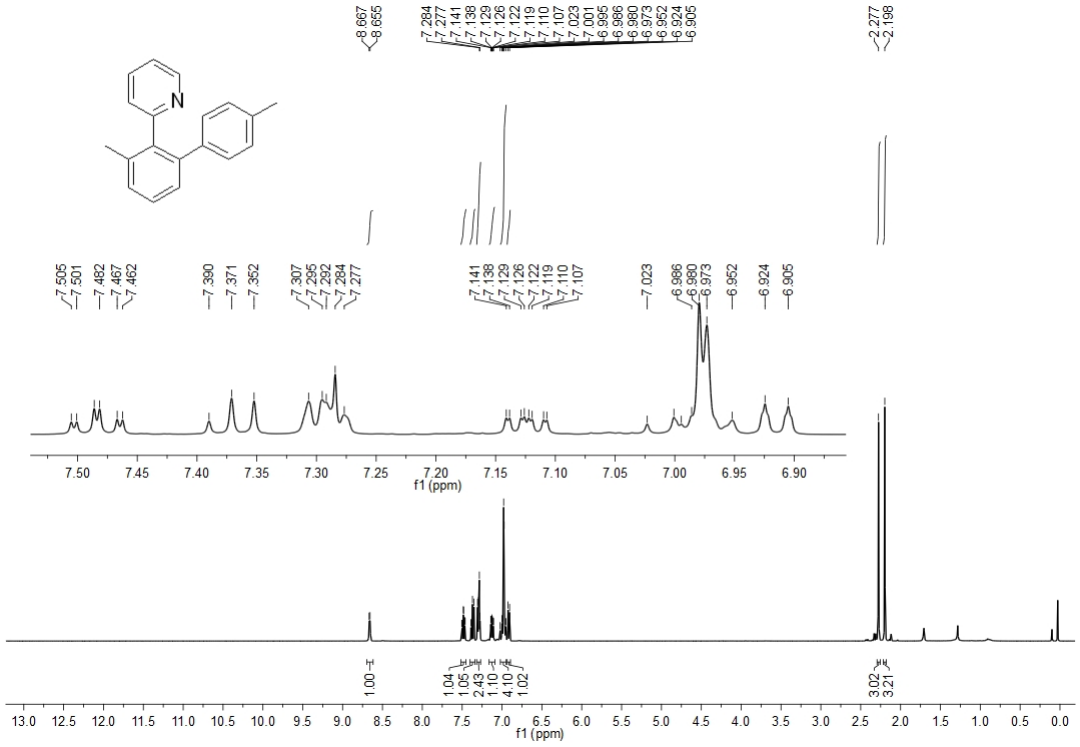

N
D
160.194
149.353
140.529
135.865
130.852
128.377
125.878
124.206
121.722
77.478
77.160
76.842
20.387
136.200
135.865
130.852
128.377
125.878
124.206
121.722
f1 (ppm)

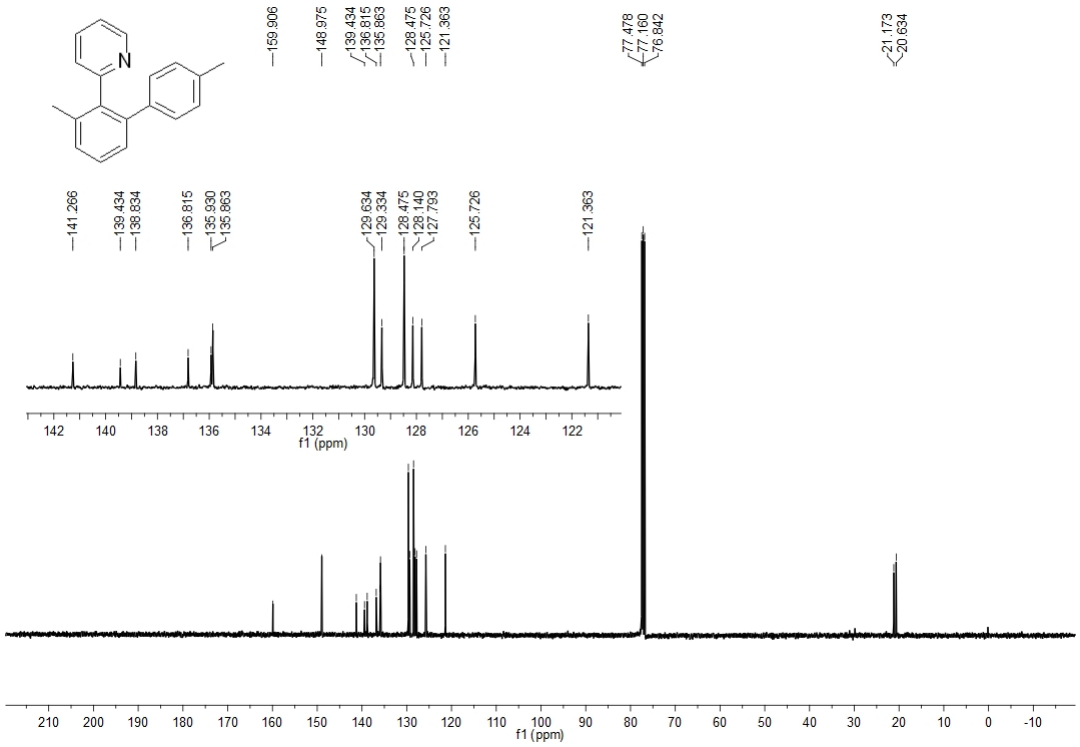

8.638
8.626
7.442
7.419
7.387
7.368
7.349
7.311
7.294
7.275
7.260
7.165
7.156
7.143
7.126
7.115
7.097
7.090
7.078
7.072
6.897
6.878
2.198
N
Ph
f1 (ppm)
0.95
1.00
1.01
1.97
2.97
3.00
0.98
3.00

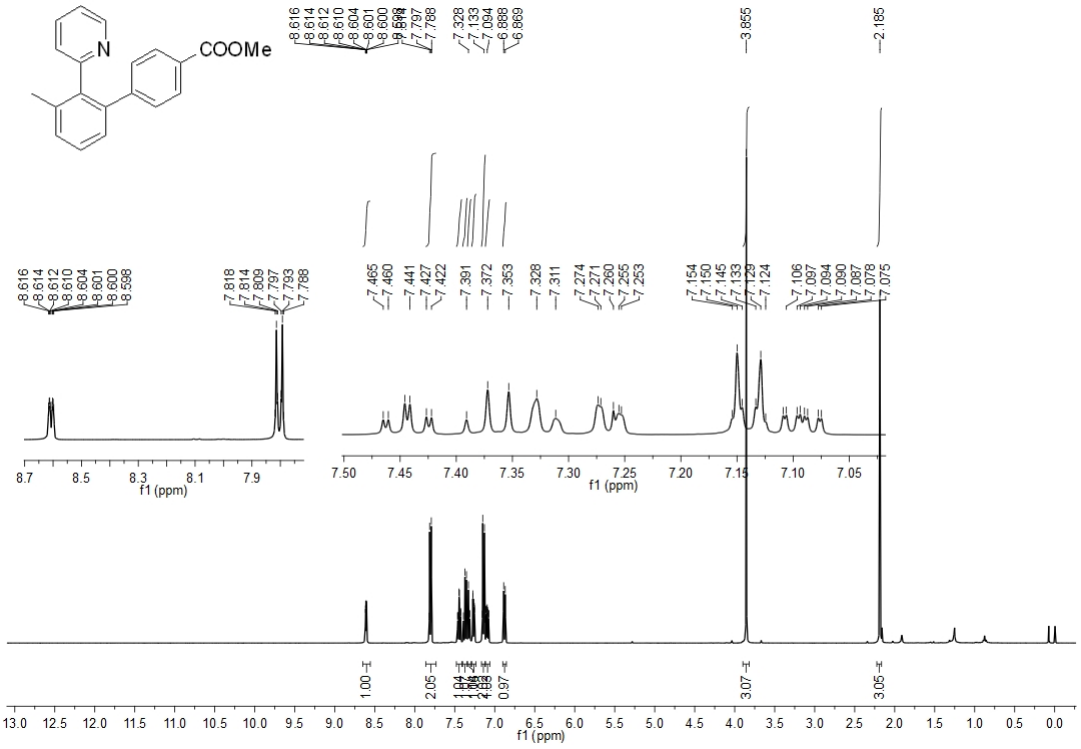

159.702
148.932
141.775
136.788
135.765
129.740
125.715
121.367
77.477
77.160
76.842
20.576
N
Ph
141.775
141.355
139.445
136.788
135.765
129.740
129.504
128.125
127.690
127.676
126.313
125.715
f1 (ppm)

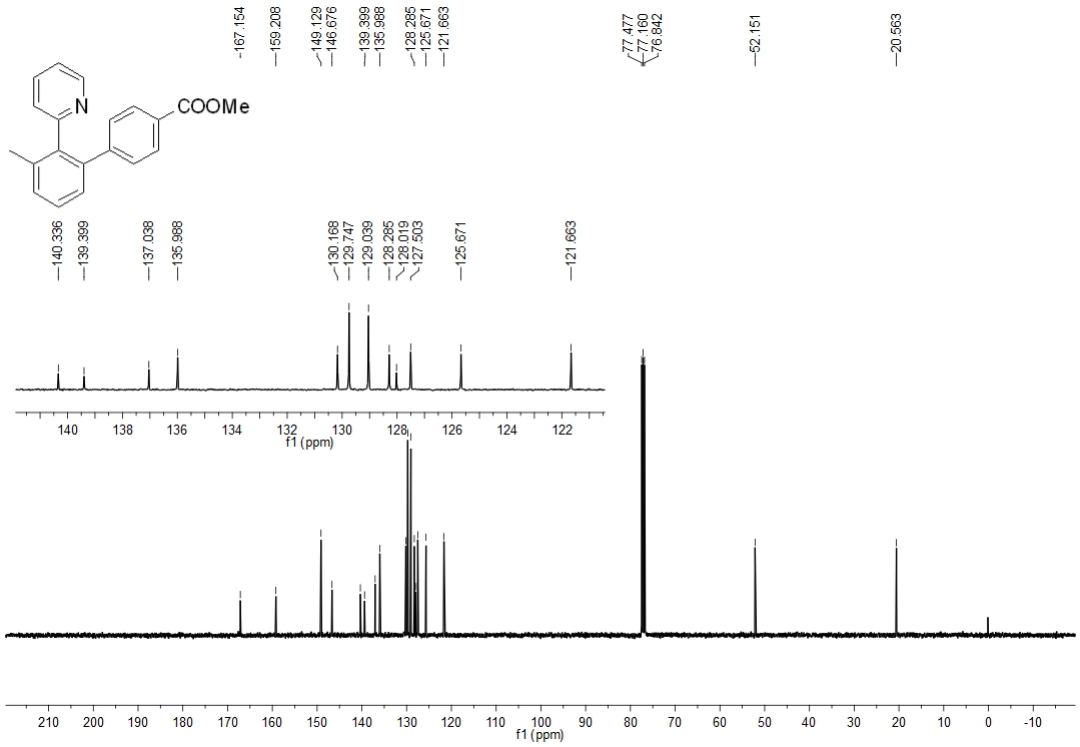

8.641
8.631
7.338
7.271
7.260
7.107
7.104
7.094
7.091
7.088
7.085
7.075
7.073
7.032
7.013
6.993
6.939
6.923
6.906
6.887
6.867
6.848
2.201
2.194
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
1.00
1.04
1.07
2.07
1.20
1.24
2.02
1.09
1.02
3.19
2.91
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

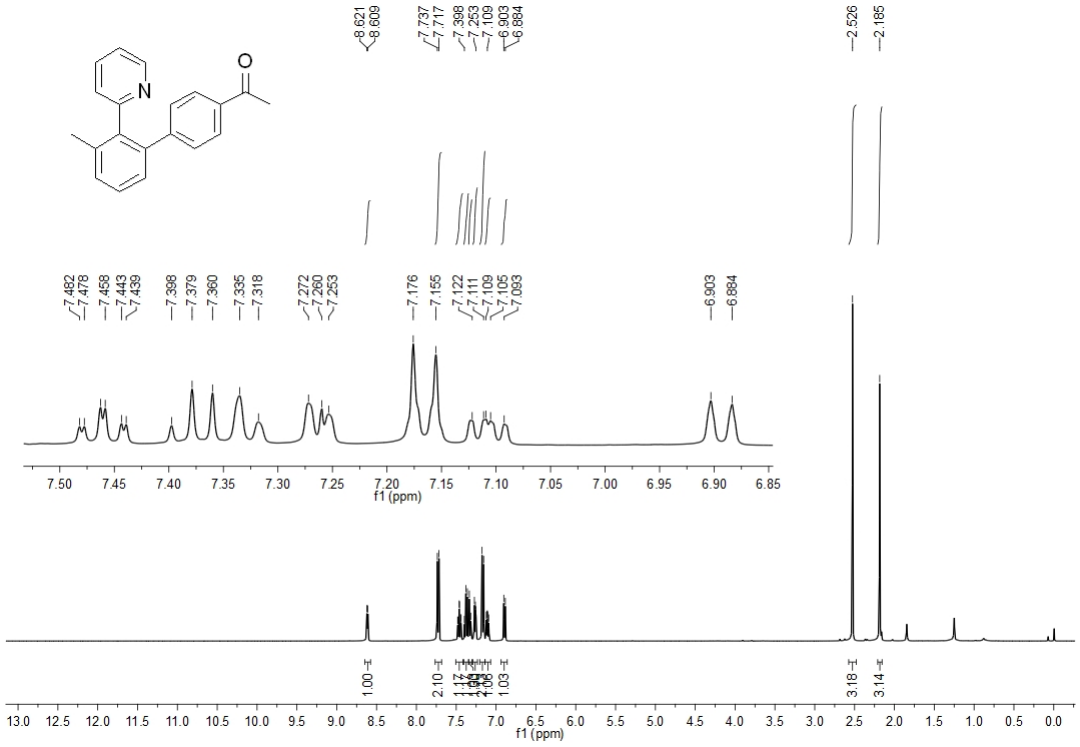

159.833
148.874
141.433
137.204
135.756
127.670
125.704
121.325
77.478
77.160
76.842
21.386
20.608
141.651
141.433
139.443
137.204
136.749
135.756
130.639
129.406
128.093
127.510
127.044
126.815
125.704
142 140 138 136
f1 (ppm)
131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

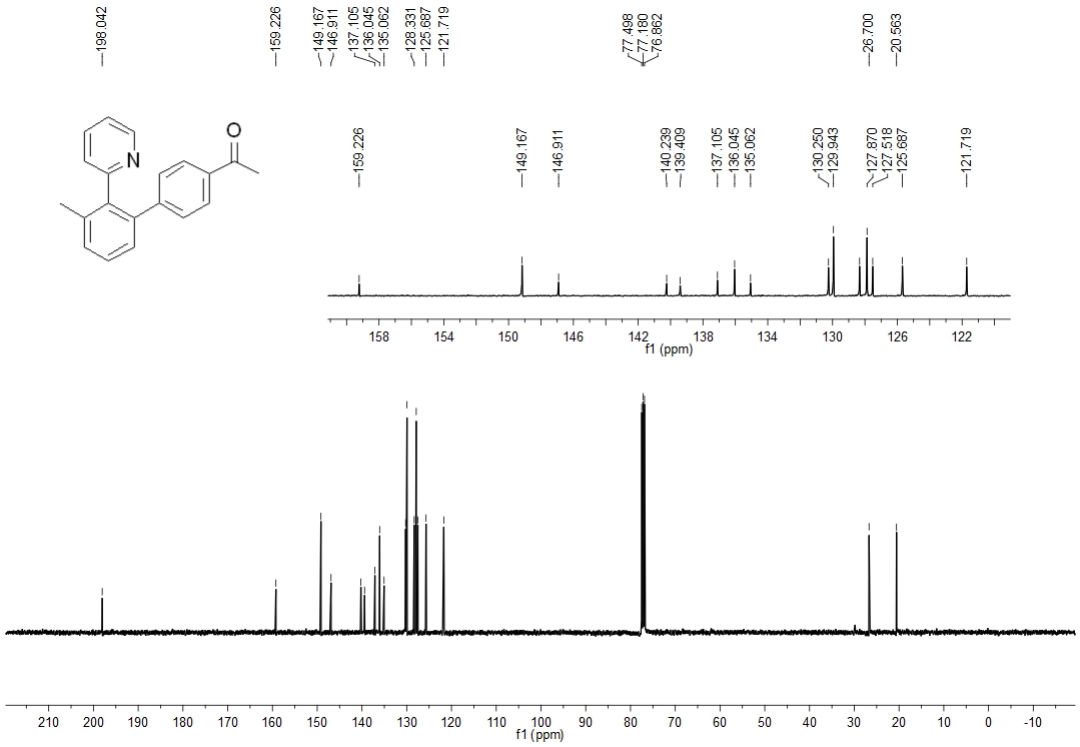

8.667
8.655
7.284
7.277
7.141
7.138
7.129
7.126
7.122
7.119
7.110
7.107
7.023
7.001
6.995
6.986
6.980
6.973
6.952
6.924
6.905
2.277
2.198
f1 (ppm)
1.00
1.04
1.05
2.43
1.10
4.10
1.02
3.02
3.21

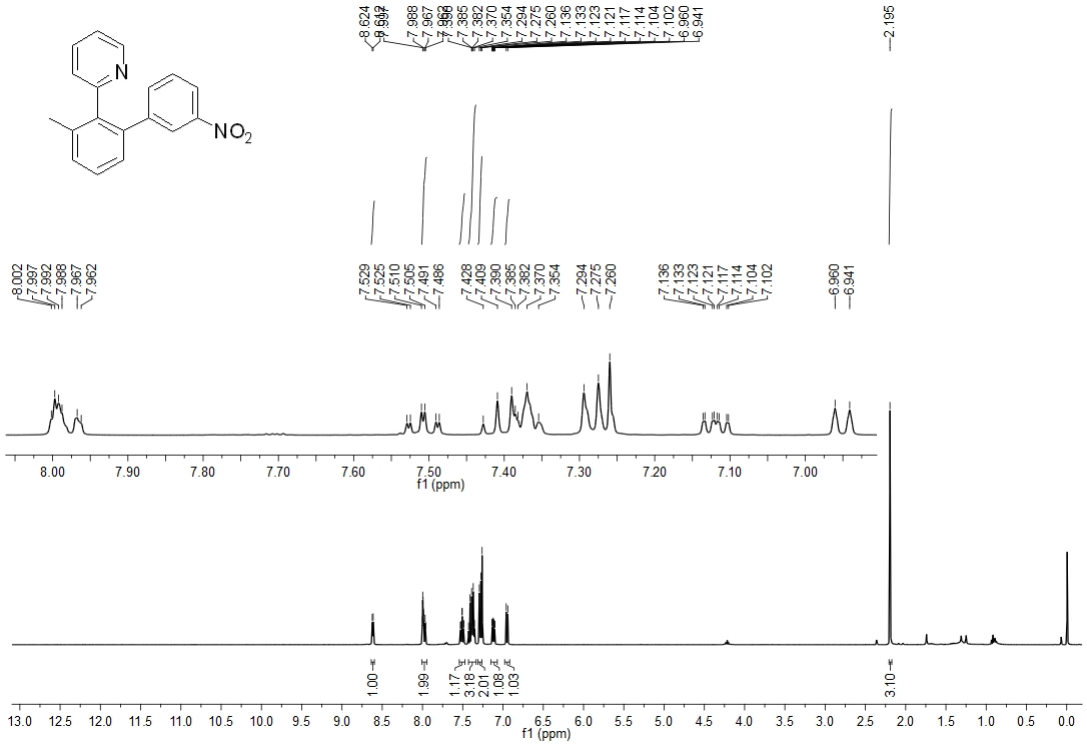

159.906
148.975
139.434
136.815
135.863
128.475
125.726
121.363
77.478
77.160
76.842
21.173
20.634
f1 (ppm)

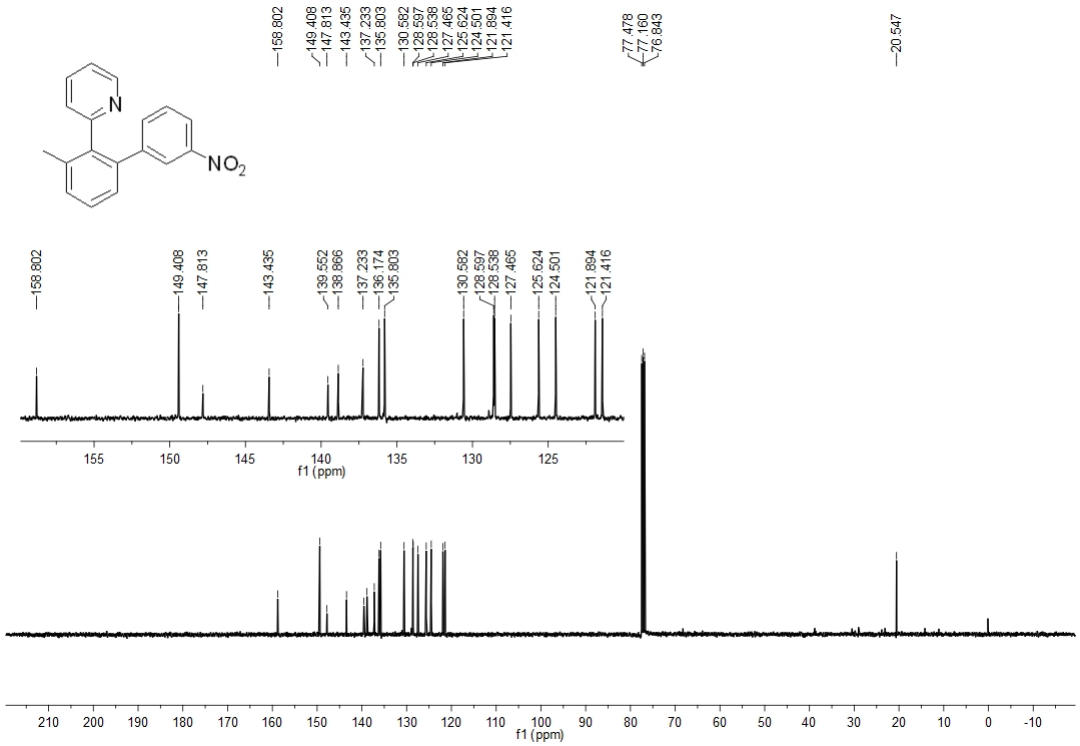

N
COOMe
8.616
8.614
8.612
8.610
8.604
8.601
8.600
8.598
7.818
7.814
7.809
7.797
7.793
7.788
7.465
7.460
7.441
7.427
7.422
7.391
7.372
7.353
7.328
7.311
7.274
7.271
7.260
7.255
7.253
7.154
7.150
7.145
7.133
7.129
7.124
7.106
7.097
7.094
7.090
7.087
7.078
7.075
7.328
7.133
7.094
6.888
6.869
3.855
2.185
f1 (ppm)
1.00
2.05
0.97
3.07
3.05

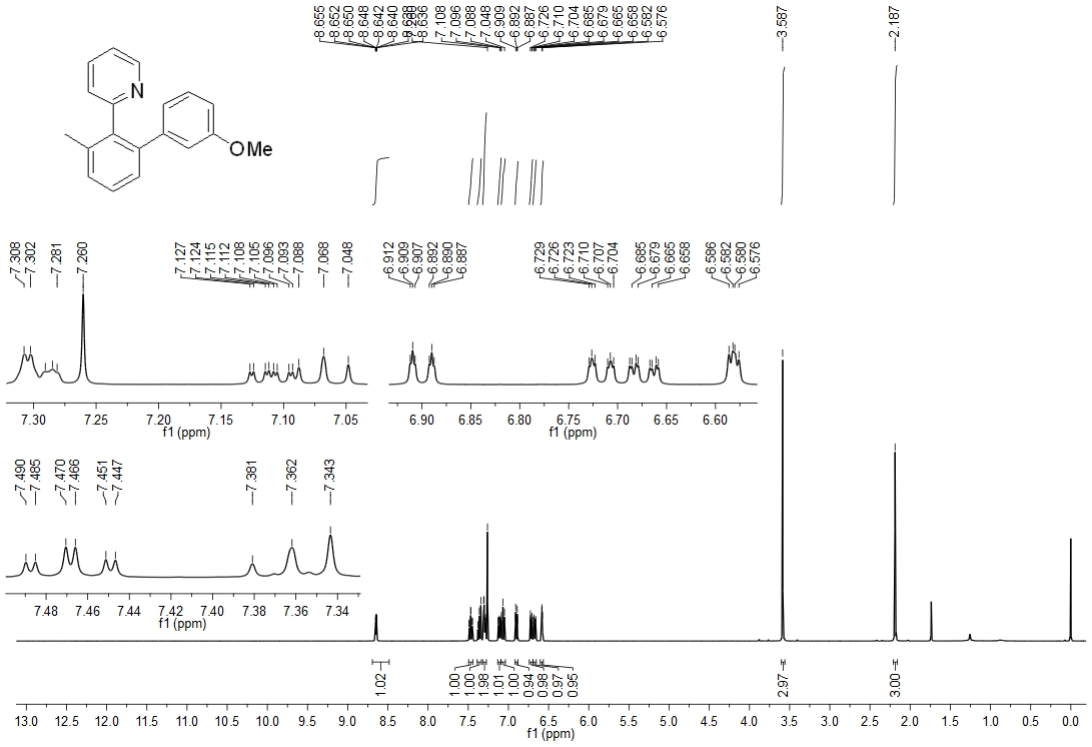

N
COOMe
167.154
159.208
149.129
146.676
139.399
135.988
128.285
125.671
121.663
77.477
77.160
76.842
52.151
20.563
140.336
139.399
137.038
135.988
130.168
129.747
129.039
128.285
128.019
127.503
125.671
121.663
f1 (ppm)

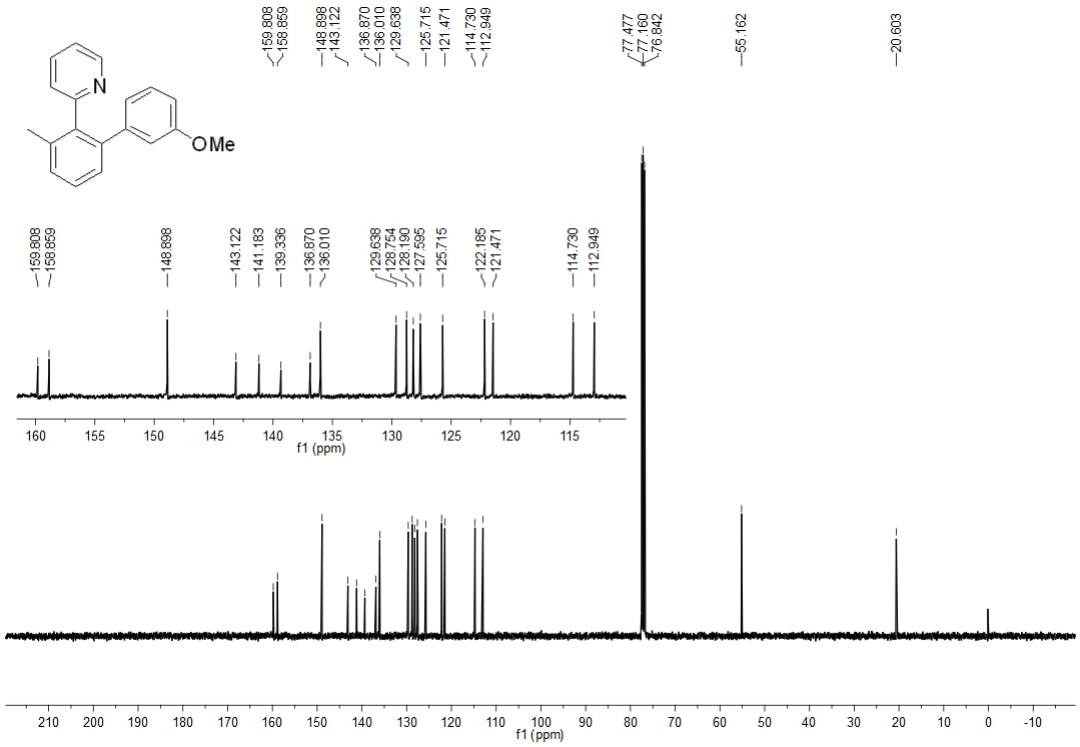

8.621
8.609
7.737
7.717
7.398
7.253
7.109
6.903
6.884
2.526
2.185
7.482
7.478
7.458
7.443
7.439
7.398
7.379
7.360
7.335
7.318
7.272
7.260
7.253
7.176
7.155
7.122
7.111
7.109
7.105
7.093
6.903
6.884
f1 (ppm)
1.00
2.10
1.03
3.18
3.14
f1 (ppm)

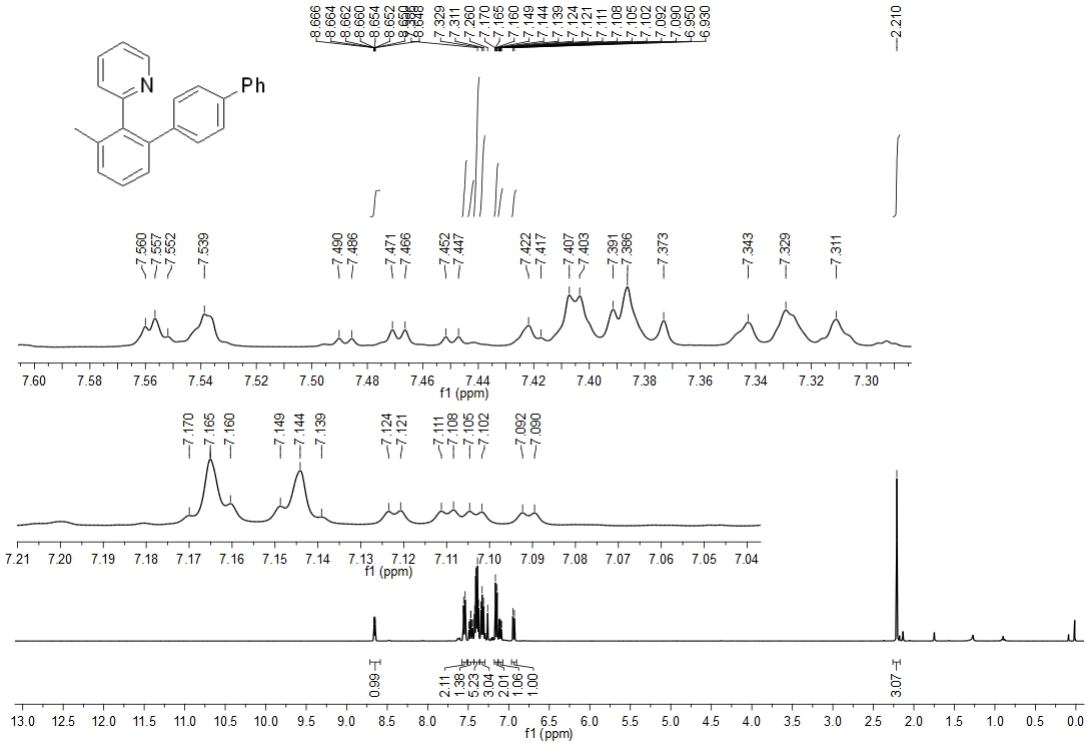

198.042
159.226
149.167
146.911
137.105
136.045
135.062
128.331
125.687
121.719
77.498
77.180
76.862
26.700
20.563
159.226
149.167
146.911
140.239
139.409
137.105
136.045
135.062
130.250
129.943
127.870
127.518
125.687
121.719
f1 (ppm)
f1 (ppm)


N
NO2
8.624
7.988
7.967
7.385
7.382
7.370
7.354
7.294
7.275
7.260
7.136
7.133
7.123
7.121
7.117
7.114
7.104
7.102
6.960
6.941
2.195
8.002
7.997
7.992
7.988
7.967
7.962
7.529
7.525
7.510
7.505
7.491
7.486
7.428
7.409
7.390
7.385
7.382
7.370
7.354
7.294
7.275
7.260
7.136
7.133
7.123
7.121
7.117
7.114
7.104
7.102
6.960
6.941
f1 (ppm)
1.00
1.99
1.17
3.18
2.01
1.08
1.03
3.10


N
NO2
158.802
149.408
147.813
143.435
139.552
138.866
137.233
136.174
135.803
130.582
128.597
128.538
127.465
125.624
124.501
121.894
121.416
77.478
77.160
76.843
20.547
f1 (ppm)


N
OMe
8.655
8.652
8.650
8.648
8.642
8.640
8.638
8.636
7.108
7.096
7.088
7.048
6.909
6.892
6.887
6.726
6.710
6.704
6.685
6.679
6.665
6.658
6.582
6.576
3.587
2.187
7.308
7.302
7.281
7.260
7.127
7.124
7.115
7.112
7.108
7.105
7.096
7.093
7.088
7.068
7.048
6.912
6.909
6.907
6.892
6.890
6.887
6.729
6.726
6.723
6.710
6.707
6.704
6.685
6.679
6.665
6.658
6.586
6.582
6.580
6.576
7.490
7.485
7.470
7.466
7.451
7.447
7.381
7.362
7.343
f1 (ppm)
1.02
1.00
1.00
1.98
1.01
1.00
0.94
0.98
0.97
0.95
2.97
3.00


N
OMe
159.808
158.859
148.898
143.122
136.870
136.010
129.638
125.715
121.471
114.730
112.949
77.477
77.160
76.842
55.162
20.603
141.183
139.336
128.754
128.190
127.595
122.185
f1 (ppm)


N
Ph
8.666
8.664
8.662
8.660
8.654
8.652
7.329
7.311
7.260
7.170
7.165
7.160
7.149
7.144
7.139
7.124
7.121
7.111
7.108
7.105
7.102
7.092
7.090
6.950
6.930
2.210
7.560
7.557
7.552
7.539
7.490
7.486
7.471
7.466
7.452
7.447
7.422
7.417
7.407
7.403
7.391
7.386
7.373
7.343
7.329
7.311
f1 (ppm)
7.170
7.165
7.160
7.149
7.144
7.139
7.124
7.121
7.111
7.108
7.105
7.102
7.092
7.090
0.99
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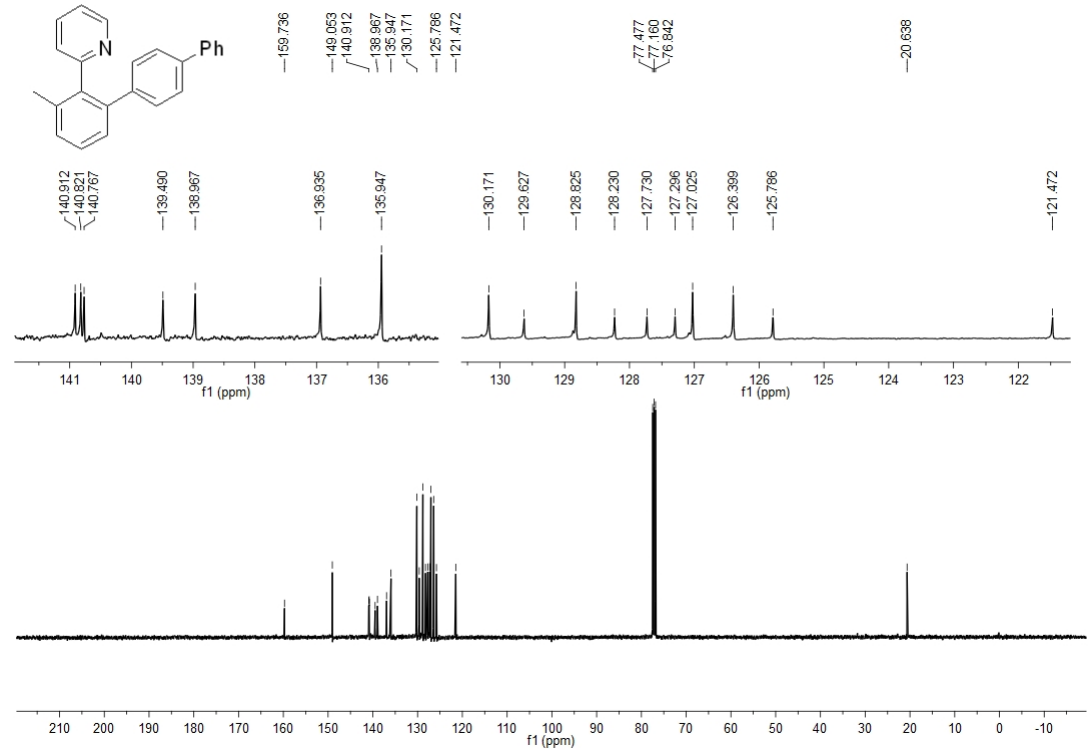
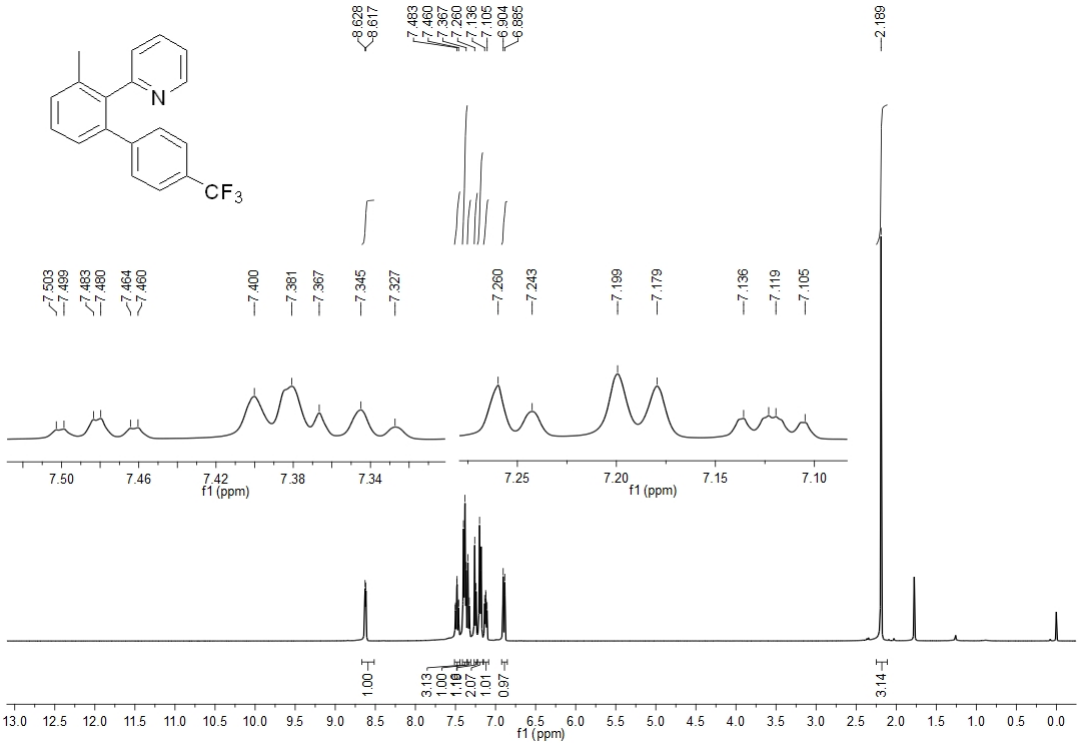
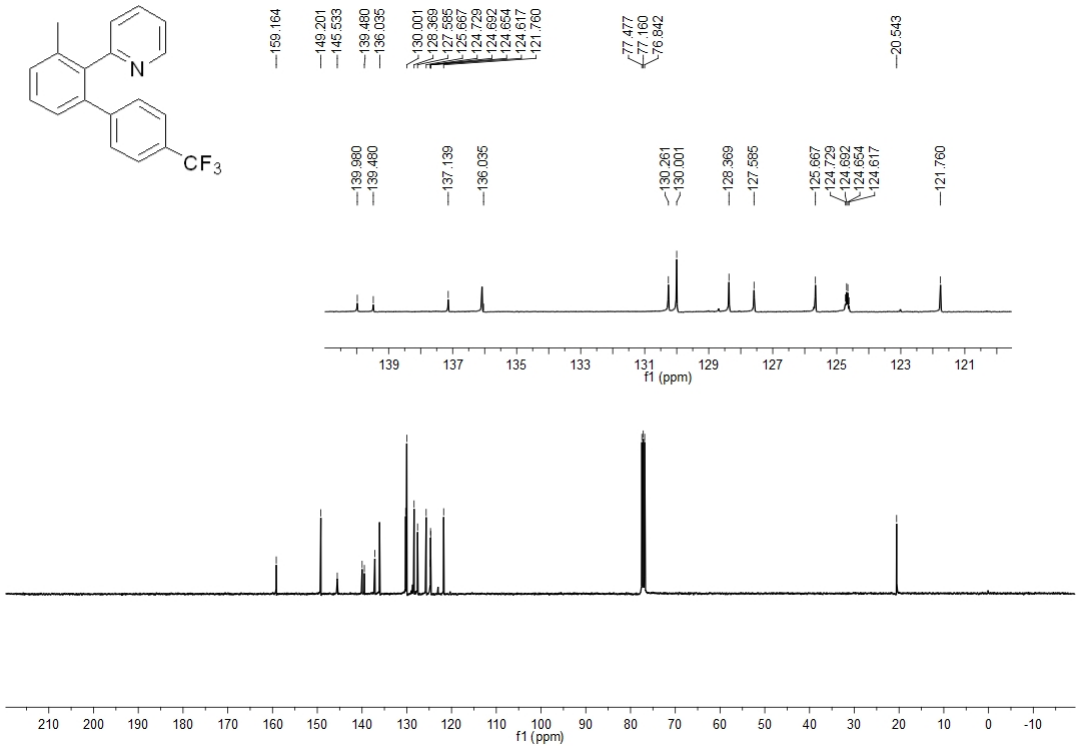
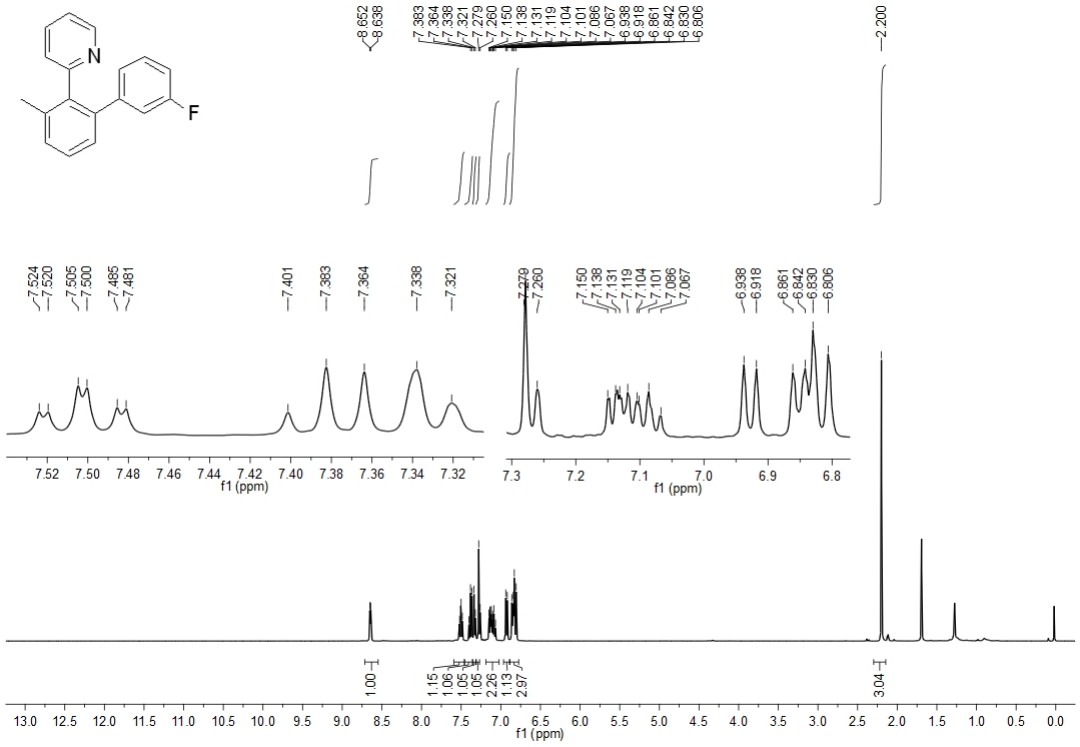
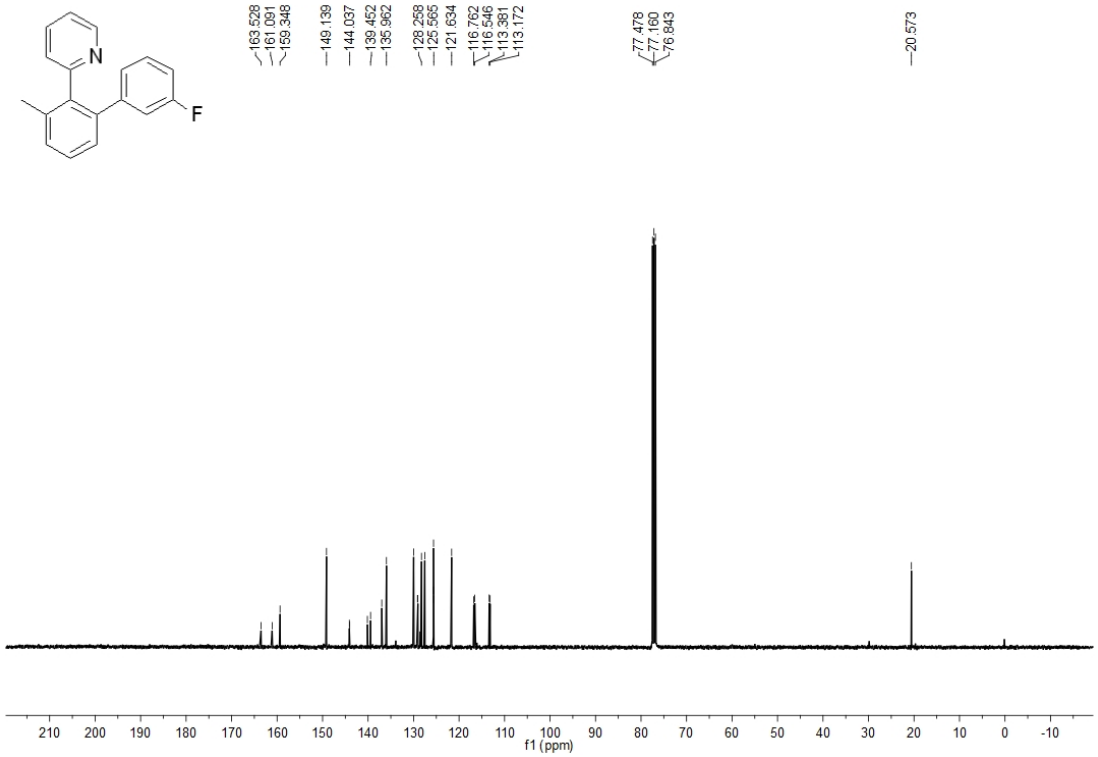
1.38
5.23
3.04
2.01
1.06
1.00
3.07

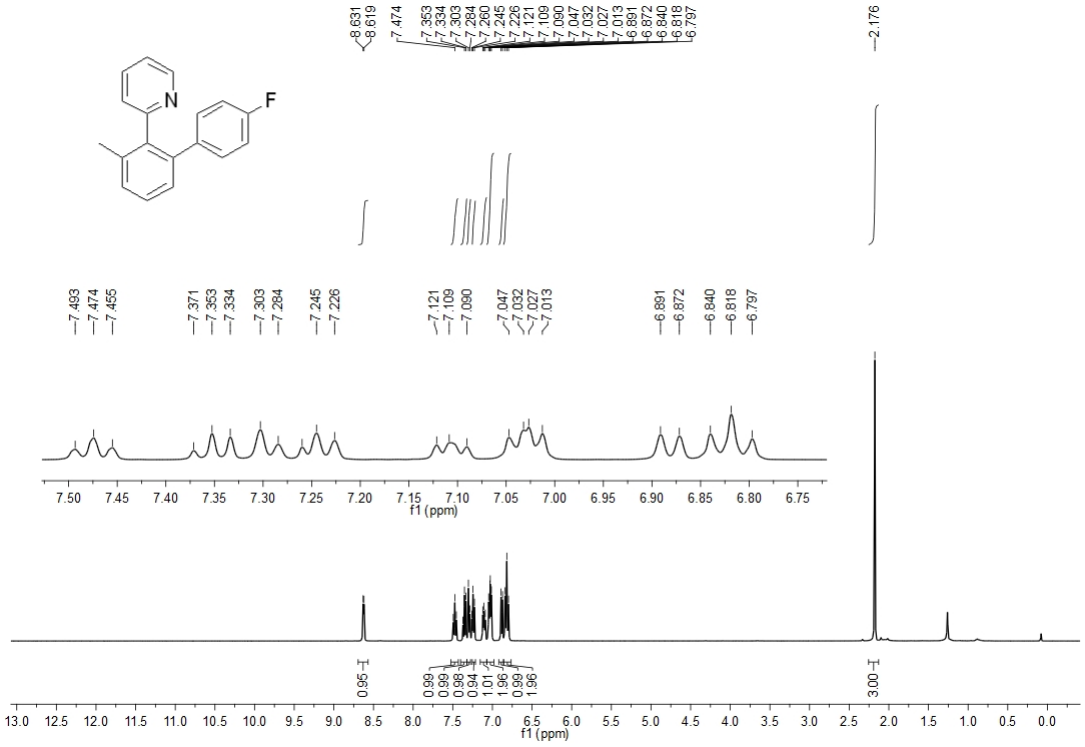

N
Ph
159.736
149.053
140.912
138.967
135.947
130.171
125.786
121.472
77.477
77.160
76.842
20.638
140.912
140.821
140.767
139.490
138.967
136.935
135.947
130.171
129.627
128.825
128.230
127.730
127.296
127.025
126.399
125.786
121.472
f1 (ppm)


8.628
8.617
7.483
7.460
7.367
7.260
7.136
7.105
6.904
6.885
2.189
7.503
7.499
7.483
7.480
7.464
7.460
7.400
7.381
7.367
7.345
7.327
7.260
7.243
7.199
7.179
7.136
7.119
7.105
f1 (ppm)
f1 (ppm)
1.00
3.13
1.00
1.19
2.07
1.01
0.97
3.14
f1 (ppm)


159.164
149.201
145.533
139.480
136.035
130.001
128.369
127.585
125.667
124.729
124.692
124.654
124.617
121.760
77.477
77.160
76.842
20.543
139.980
139.480
137.139
136.035
130.261
130.001
128.369
127.585
125.667
124.729
124.692
124.654
124.617
121.760
f1 (ppm)
f1 (ppm)


N
F
8.652
8.638
7.383
7.364
7.338
7.321
7.279
7.260
7.150
7.138
7.131
7.119
7.104
7.101
7.086
7.067
6.938
6.918
6.861
6.842
6.830
6.806
2.200
f1 (ppm)
1.00
1.15
1.06
1.05
1.05
2.26
1.13
2.97
3.04


N
F
163.528
161.091
159.348
149.139
144.037
139.452
135.962
128.258
125.565
121.634
116.762
116.546
113.381
113.172
77.478
77.160
76.843
20.573
f1 (ppm)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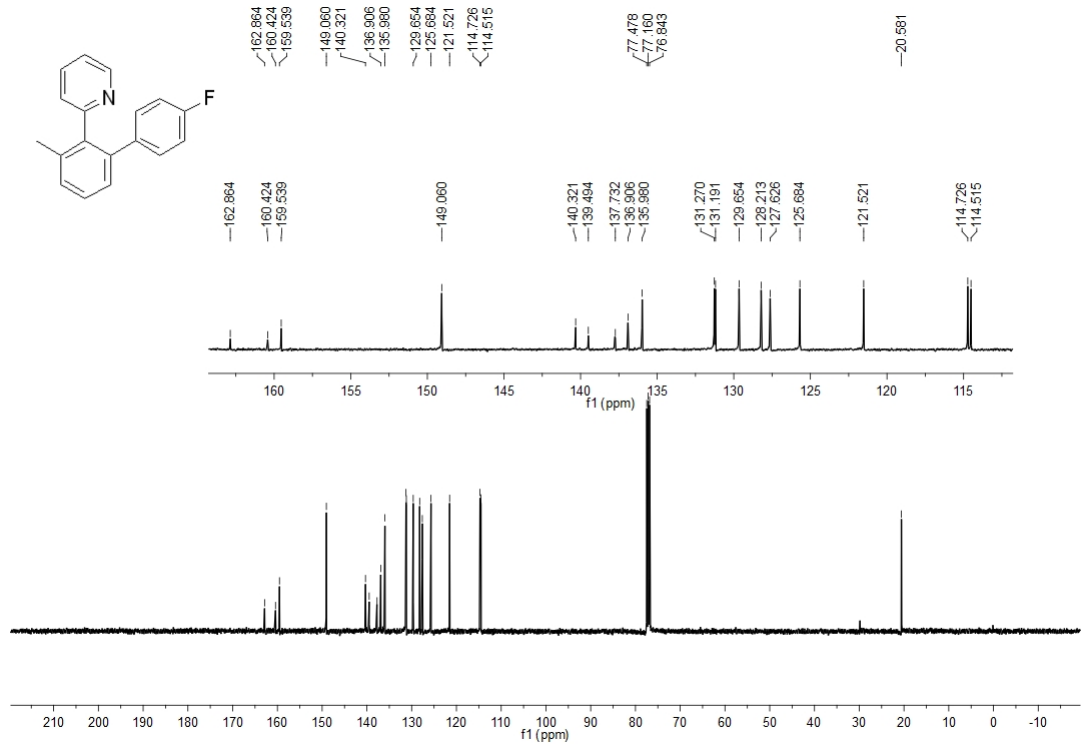
8.619
7.474
7.353
7.334
7.303
7.284
7.260
7.245
7.226
7.121
7.109
7.100
7.090
7.047
7.032
7.027
7.013
6.891
6.872
6.840
6.818
6.797
2.176
N
F
f1 (ppm)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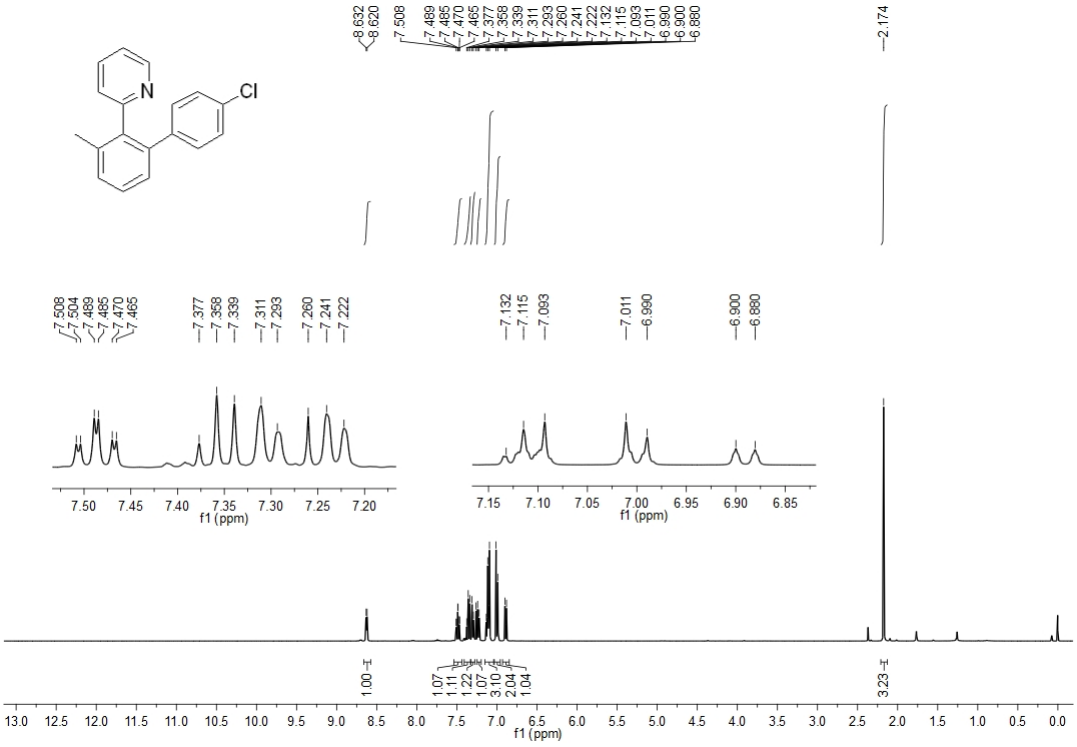
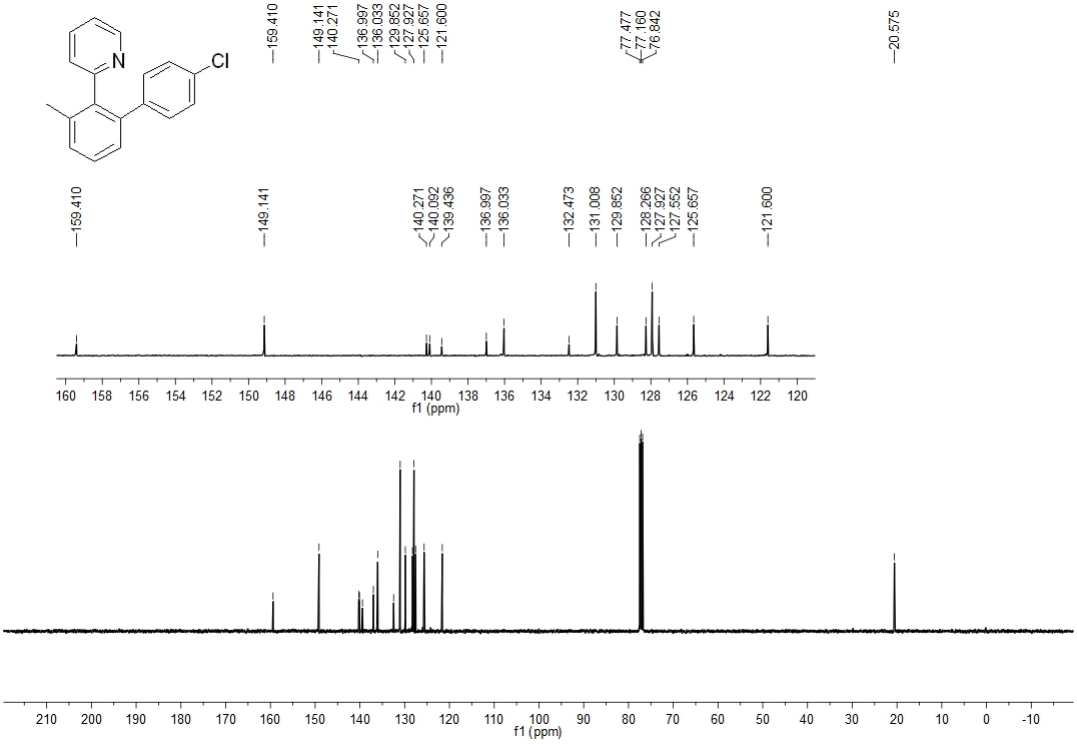
160.424
159.539
149.060
140.321
136.906
135.980
129.654
125.684
121.521
114.726
114.515
77.478
77.160
76.843
20.581
N
F
f1 (ppm)


N
Cl
8.632
8.620
7.508
7.489
7.485
7.470
7.465
7.377
7.358
7.339
7.311
7.293
7.260
7.241
7.222
7.132
7.115
7.093
7.011
6.990
6.900
6.880
2.174
f1 (ppm)
1.00
1.07
1.11
1.22
1.07
3.10
2.04
1.04
3.23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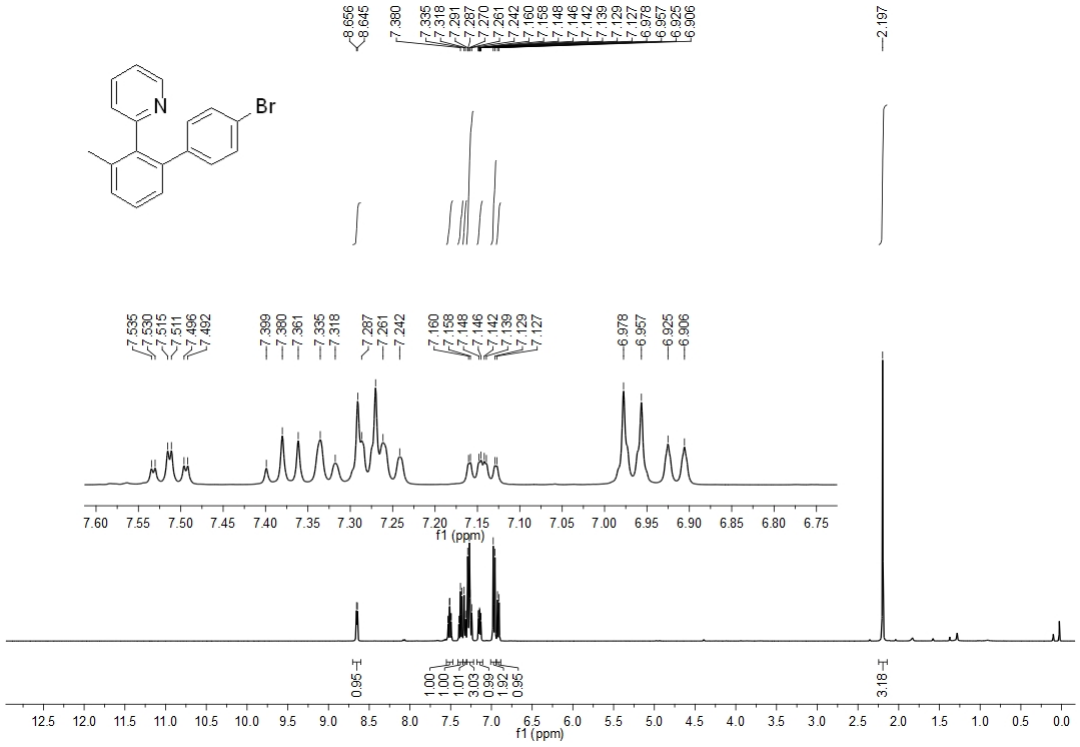
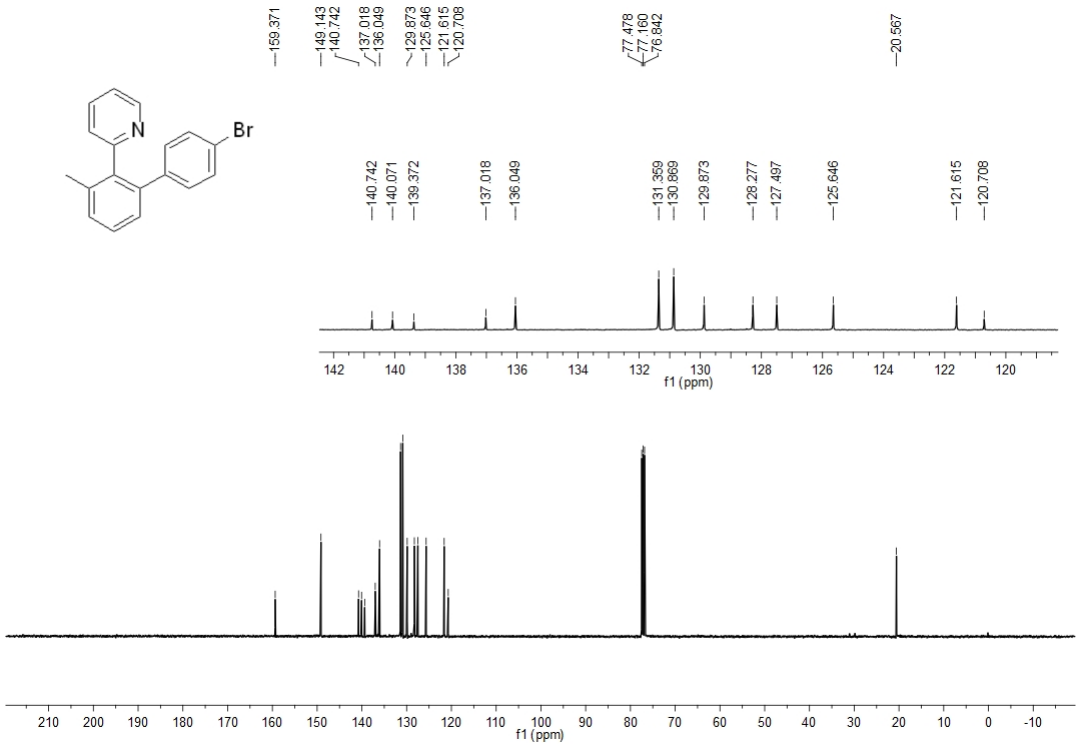
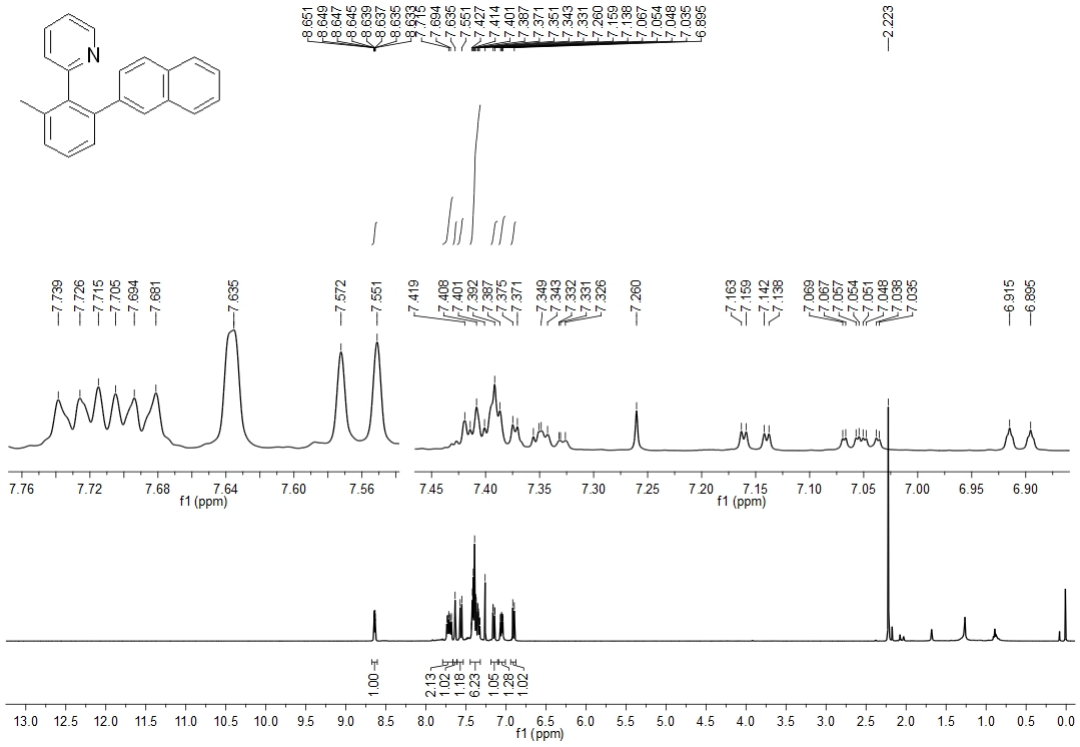
Cl
159.410
149.141
140.271
136.997
136.033
129.852
127.927
125.657
121.600
77.477
77.160
76.842
20.575
140.092
139.436
132.473
131.008
128.266
127.552
f1 (ppm)


8.656
8.645
7.380
7.335
7.318
7.291
7.287
7.270
7.261
7.242
7.160
7.158
7.148
7.146
7.142
7.139
7.129
7.127
6.978
6.957
6.925
6.906
2.197
N
Br
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)
0.95
1.00
1.00
1.01
3.03
0.99
1.92
0.95
3.18
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.371
149.143
140.742
137.018
136.049
129.873
125.646
121.615
120.708
77.478
77.160
76.842
20.567
N
Br
140.742
140.071
139.372
137.018
136.049
131.359
130.869
129.873
128.277
127.497
125.646
121.615
120.708
142 140 138 136 134 132 130 128 126 124 122 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.651
8.649
8.647
8.645
8.639
8.637
8.635
8.633
7.715
7.694
7.635
7.551
7.427
7.414
7.401
7.387
7.371
7.351
7.343
7.331
7.260
7.159
7.138
7.067
7.054
7.048
7.035
6.895
2.223
7.739
7.726
7.715
7.705
7.694
7.681
7.635
7.572
7.551
7.419
7.408
7.401
7.392
7.387
7.375
7.371
7.349
7.343
7.332
7.331
7.326
7.260
7.163
7.159
7.142
7.138
7.069
7.067
7.057
7.054
7.051
7.048
7.038
7.035
6.915
6.895
f1 (ppm)
1.00
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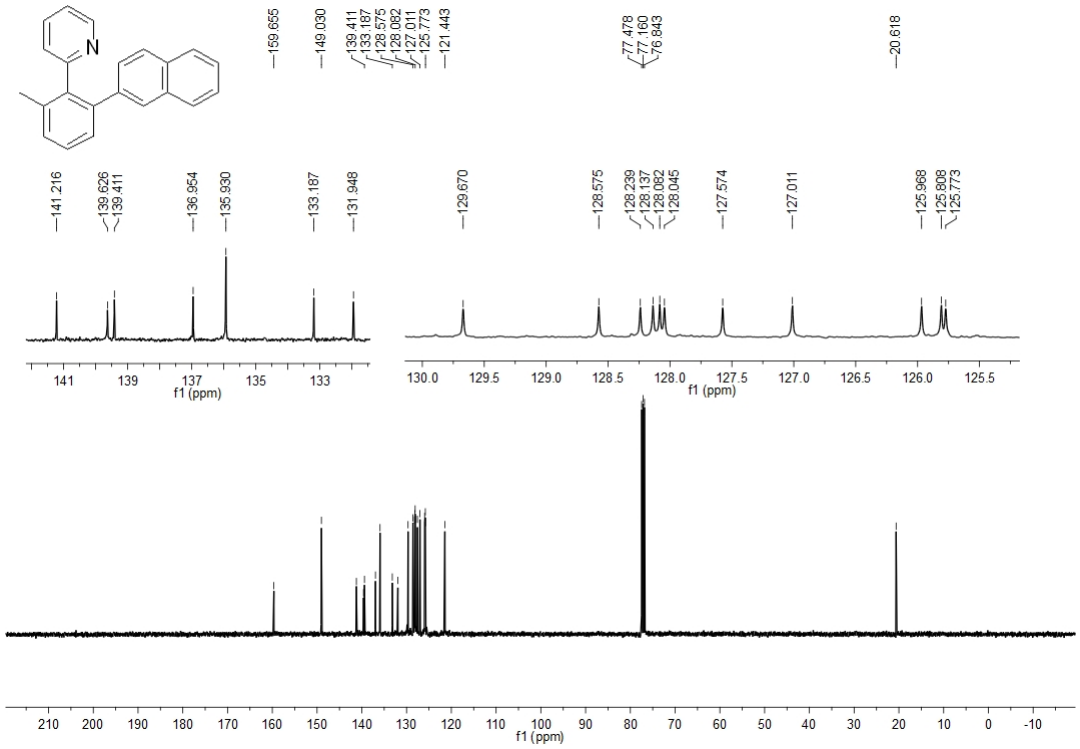
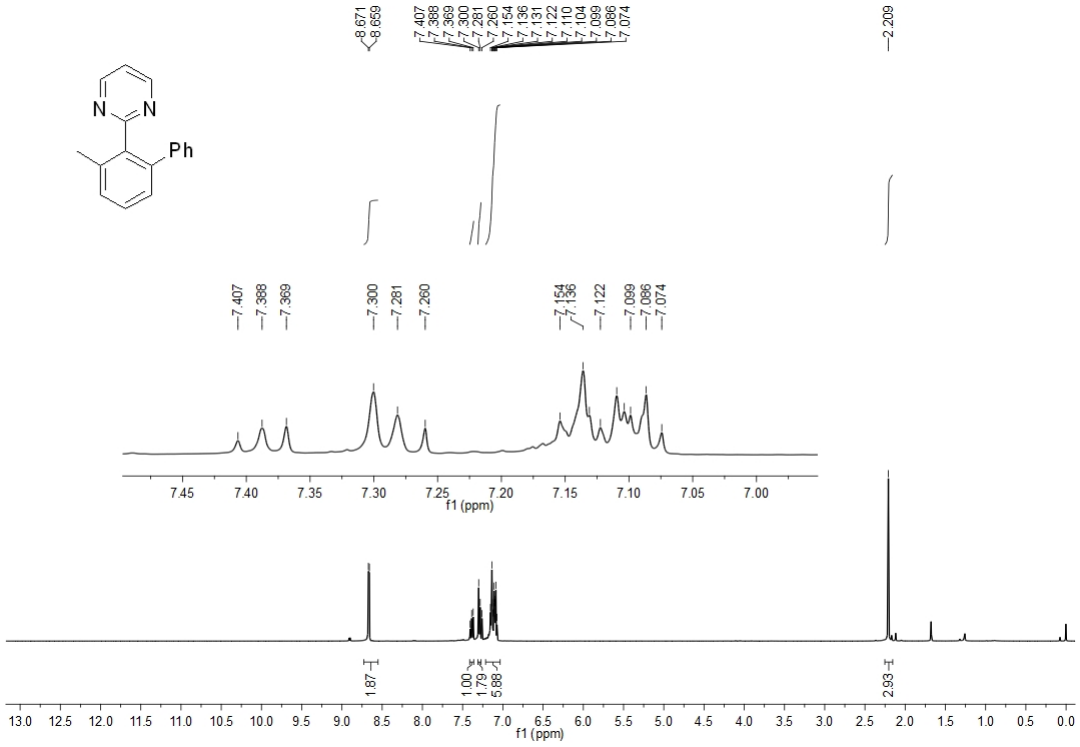
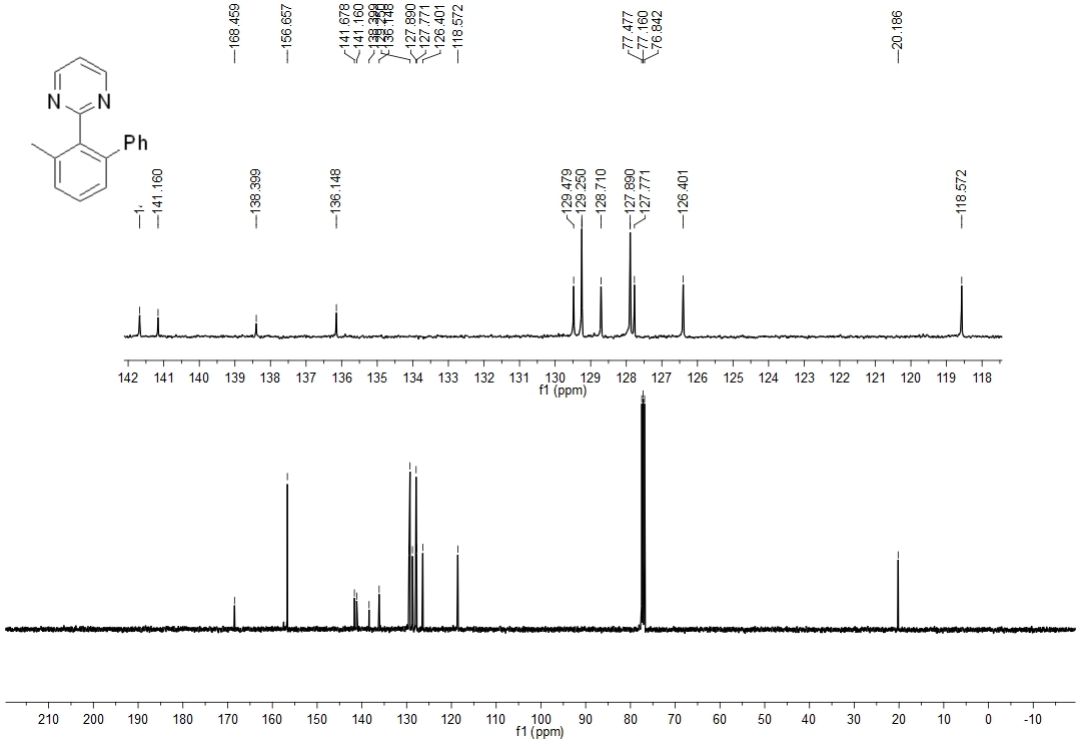
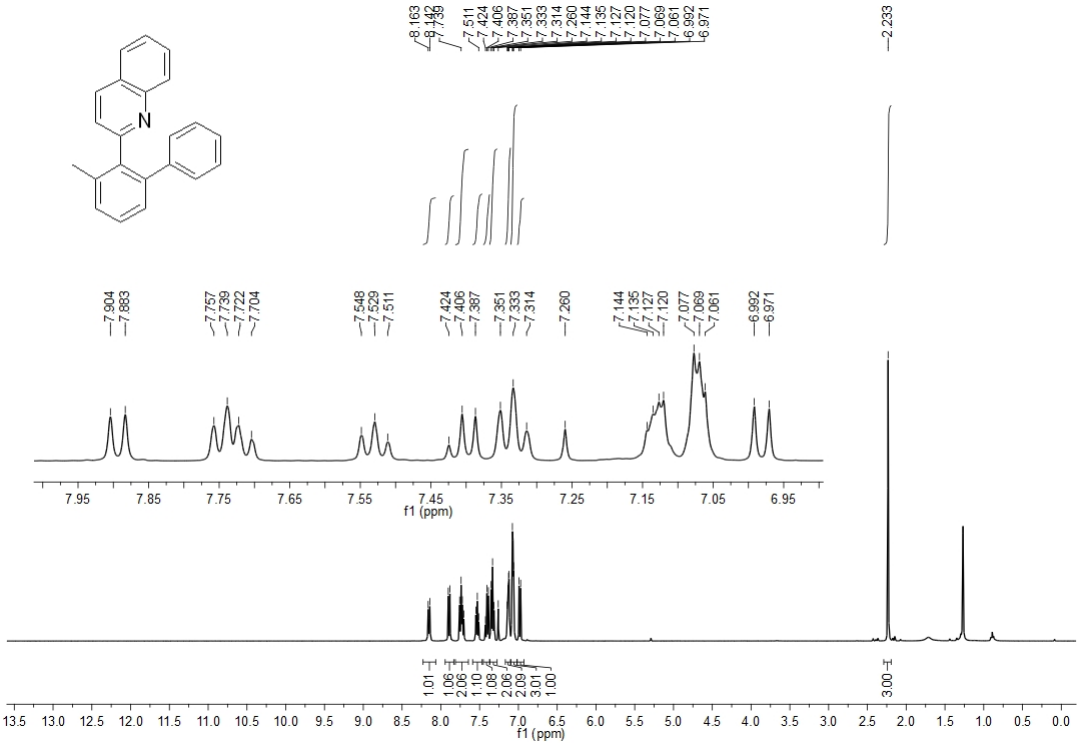
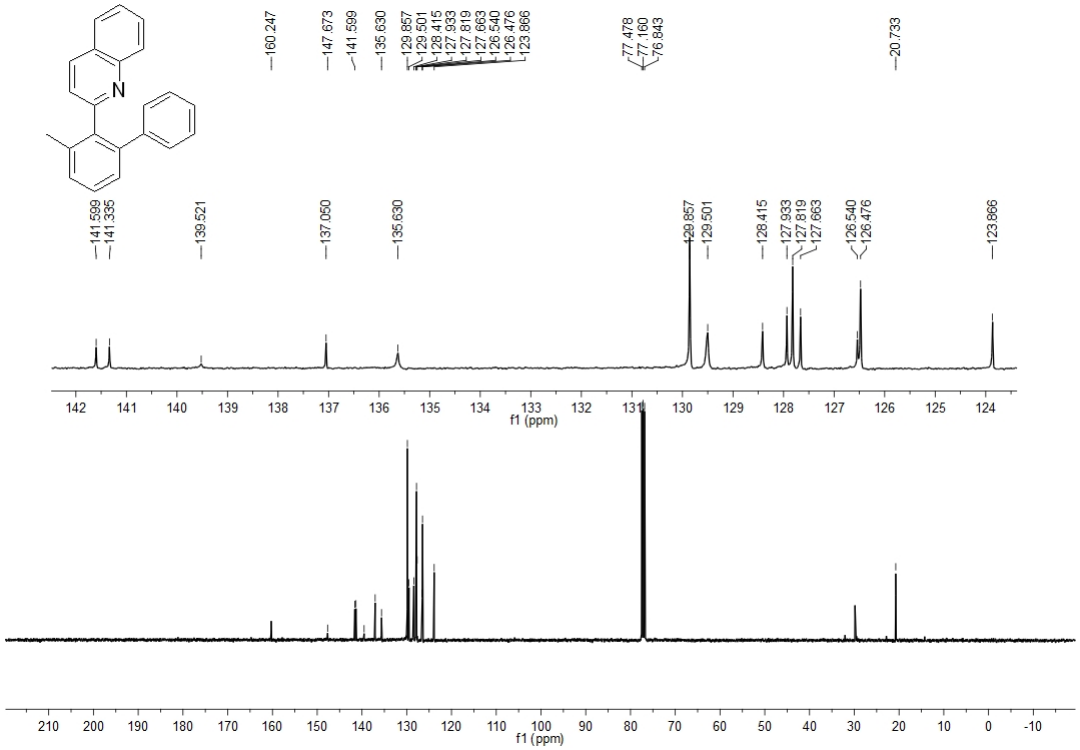
1.02
1.18
6.23
1.05
1.28
1.02

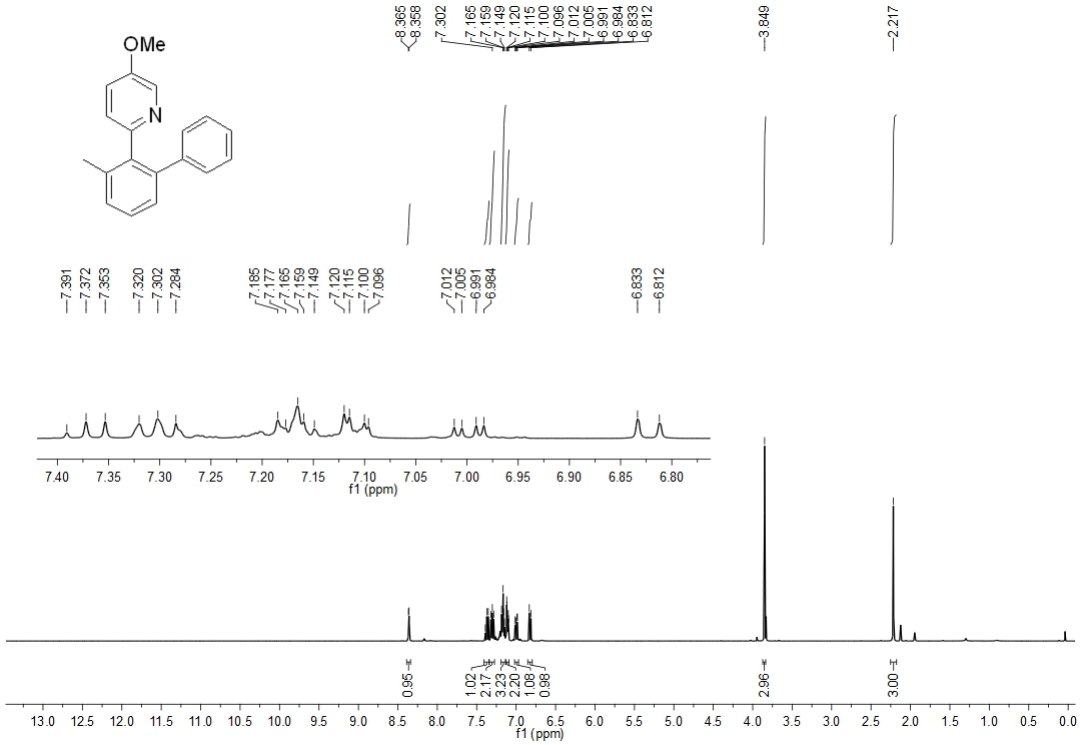

159.655
149.030
139.411
133.187
128.575
128.082
127.011
125.773
121.443
77.478
77.160
76.843
20.618
141.216
139.626
139.411
136.954
135.930
133.187
131.948
129.670
128.575
128.239
128.137
128.082
128.045
127.574
127.011
125.968
125.808
125.773
f1 (ppm)

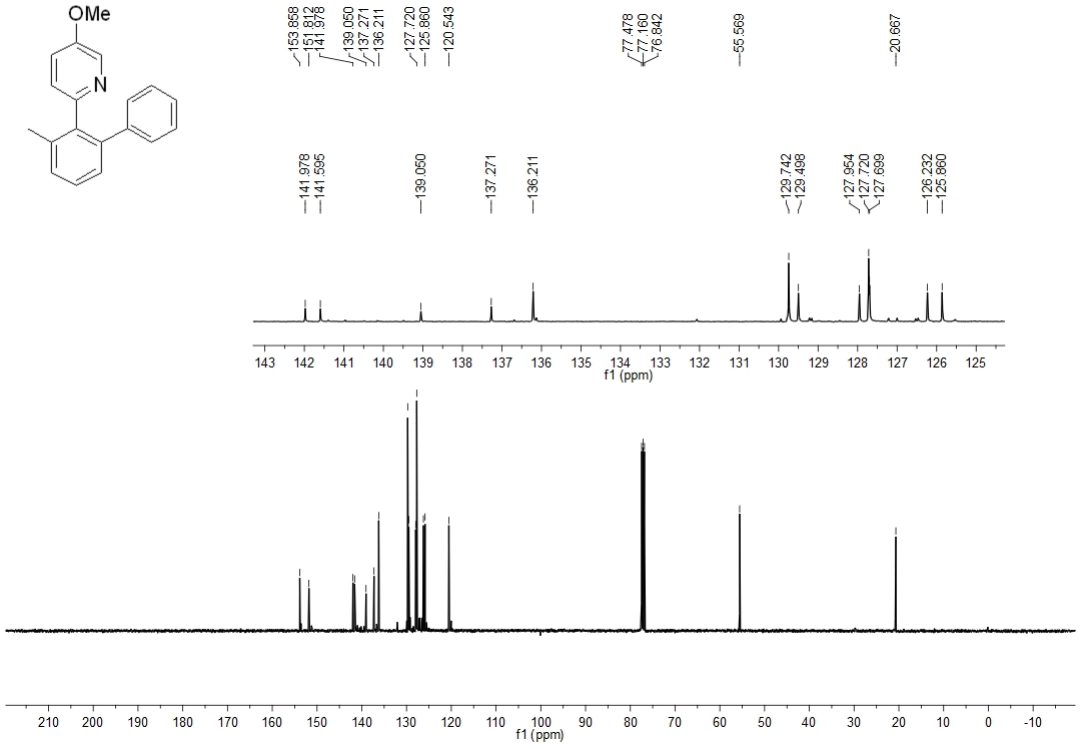

8.671
8.659
7.407
7.388
7.369
7.300
7.281
7.260
7.154
7.136
7.131
7.122
7.110
7.104
7.099
7.086
7.074
2.209
N
N
Ph
1.87
1.00
1.79
5.88
2.93
f1 (ppm)

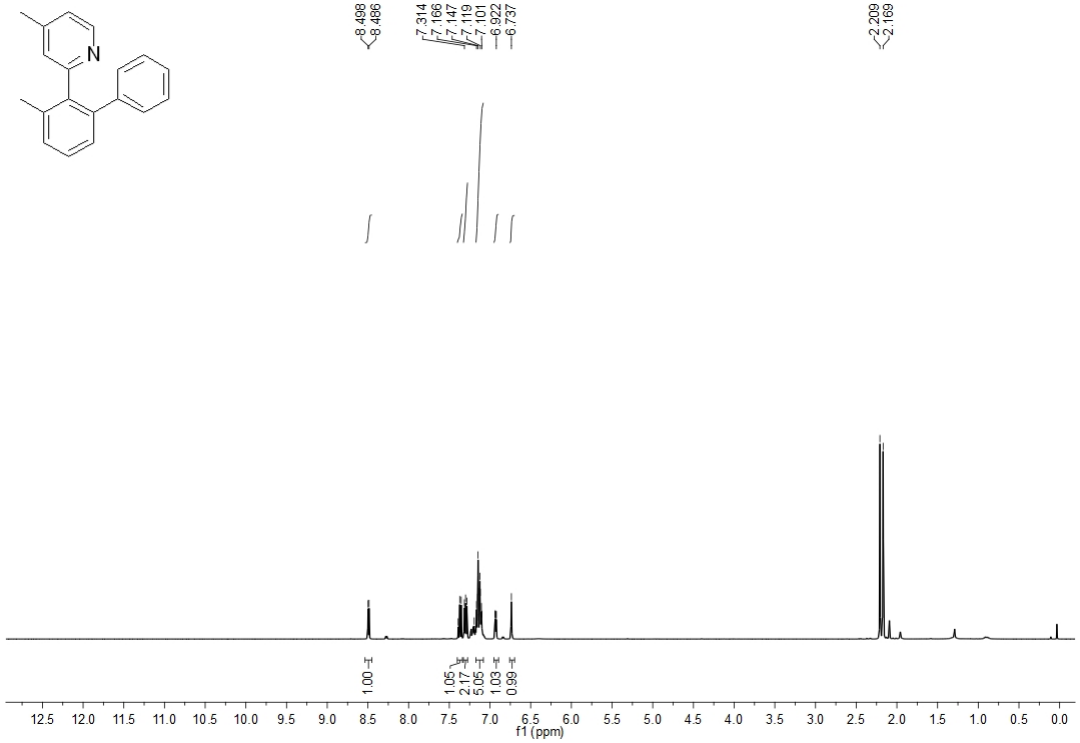

168.459
156.657
141.678
141.160
138.399
136.148
127.890
127.771
126.401
118.572
77.477
77.160
76.842
20.186
N
N
Ph
129.479
129.250
128.710
f1 (ppm)

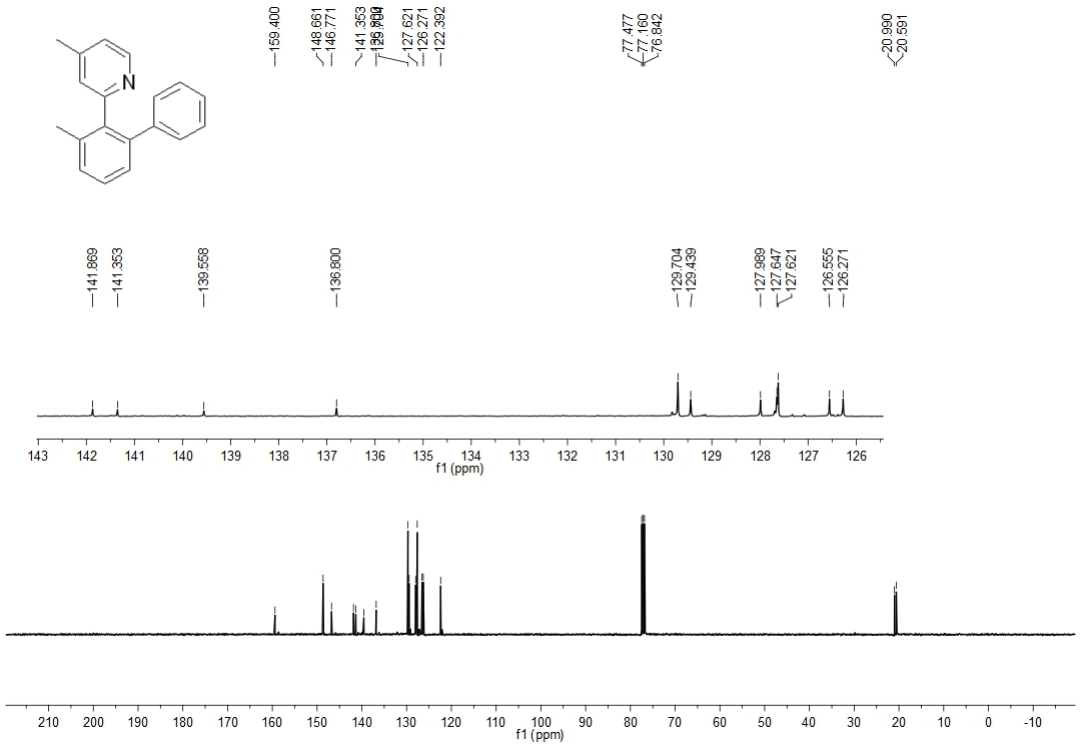

8.163
8.140
7.511
7.424
7.406
7.387
7.351
7.333
7.314
7.260
7.144
7.135
7.127
7.120
7.077
7.069
7.061
6.992
6.971
2.233
7.904
7.883
7.757
7.739
7.722
7.704
7.548
7.529
7.511
7.424
7.406
7.387
7.351
7.333
7.314
7.260
7.144
7.135
7.127
7.120
7.077
7.069
7.061
6.992
6.971
f1 (ppm)
1.01
1.06
2.06
1.10
1.08
2.06
2.09
3.01
1.00
3.00
f1 (ppm)

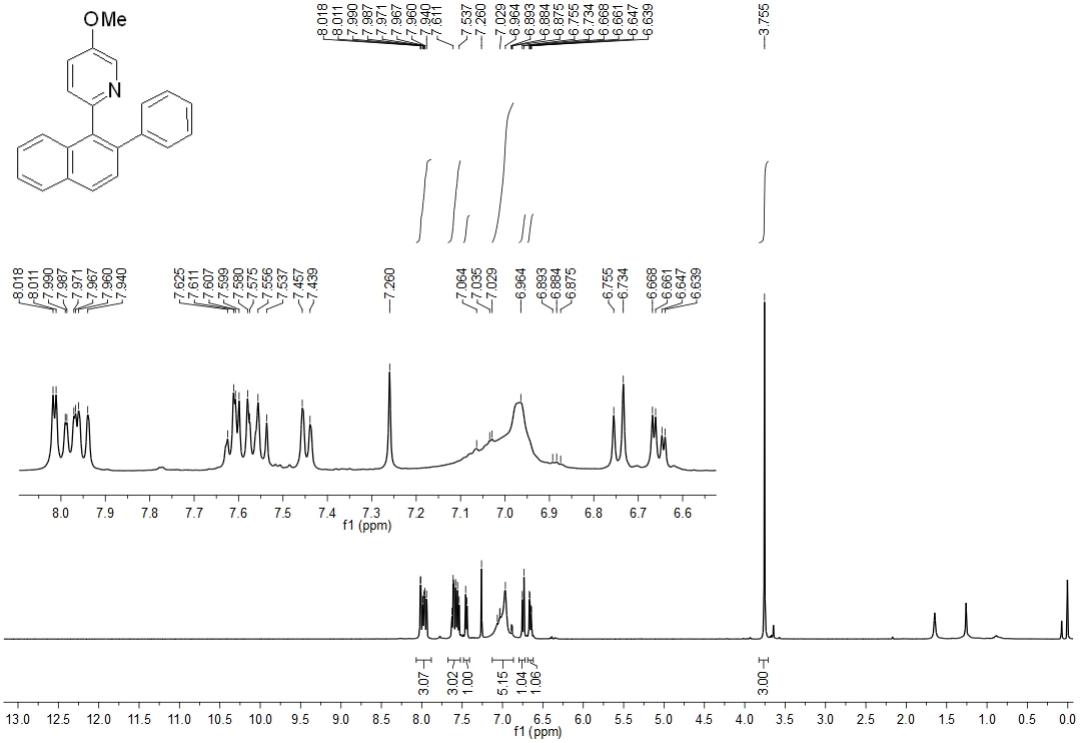

160.247
147.673
141.599
135.630
129.857
129.501
128.415
127.933
127.819
127.663
126.540
126.476
123.866
77.478
77.160
76.843
20.733
141.599
141.335
139.521
137.050
135.630
129.857
129.501
128.415
127.933
127.819
127.663
126.540
126.476
123.866
f1 (ppm)
f1 (ppm)


OMe
N
8.365
8.358
7.302
7.165
7.159
7.149
7.120
7.115
7.100
7.096
7.012
7.005
6.991
6.984
6.833
6.812
3.849
2.217
7.391
7.372
7.353
7.320
7.302
7.284
7.185
7.177
7.165
7.159
7.149
7.120
7.115
7.100
7.096
7.012
7.005
6.991
6.984
6.833
6.812
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
0.95
1.02
2.17
3.23
2.20
1.08
0.98
2.96
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OMe
N
153.858
151.812
141.978
139.050
137.271
136.211
127.720
125.860
120.543
77.478
77.160
76.842
55.569
20.667
141.978
141.595
139.050
137.271
136.211
129.742
129.498
127.954
127.720
127.699
126.232
125.860
143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.498
8.486
7.314
7.166
7.147
7.119
7.101
6.922
6.737
2.209
2.169
1.00
1.05
2.17
5.05
1.03
0.99
f1 (ppm)


159.400
148.661
146.771
141.353
127.621
126.271
122.392
77.477
77.160
76.842
20.990
20.591
141.869
141.353
139.558
136.800
129.704
129.439
127.989
127.647
127.621
126.555
126.271
f1 (ppm)


OMe
N
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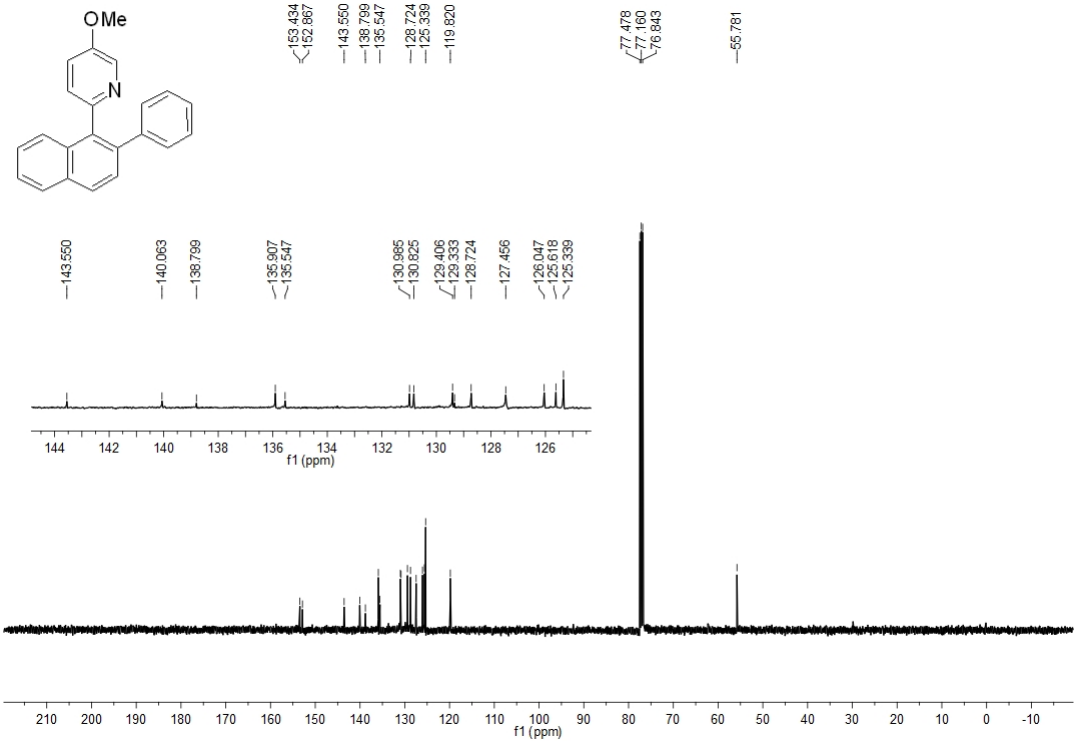
8.011
7.990
7.987
7.971
7.967
7.960
7.940
7.811
7.537
7.260
7.029
6.964
6.893
6.884
6.875
6.755
6.734
6.668
6.661
6.647
6.639
3.755
7.625
7.611
7.607
7.599
7.580
7.575
7.556
7.537
7.457
7.439
7.064
7.035
7.029
f1 (ppm)
3.07
3.02
1.00
5.15
1.04
1.06
3.00


OMe
N
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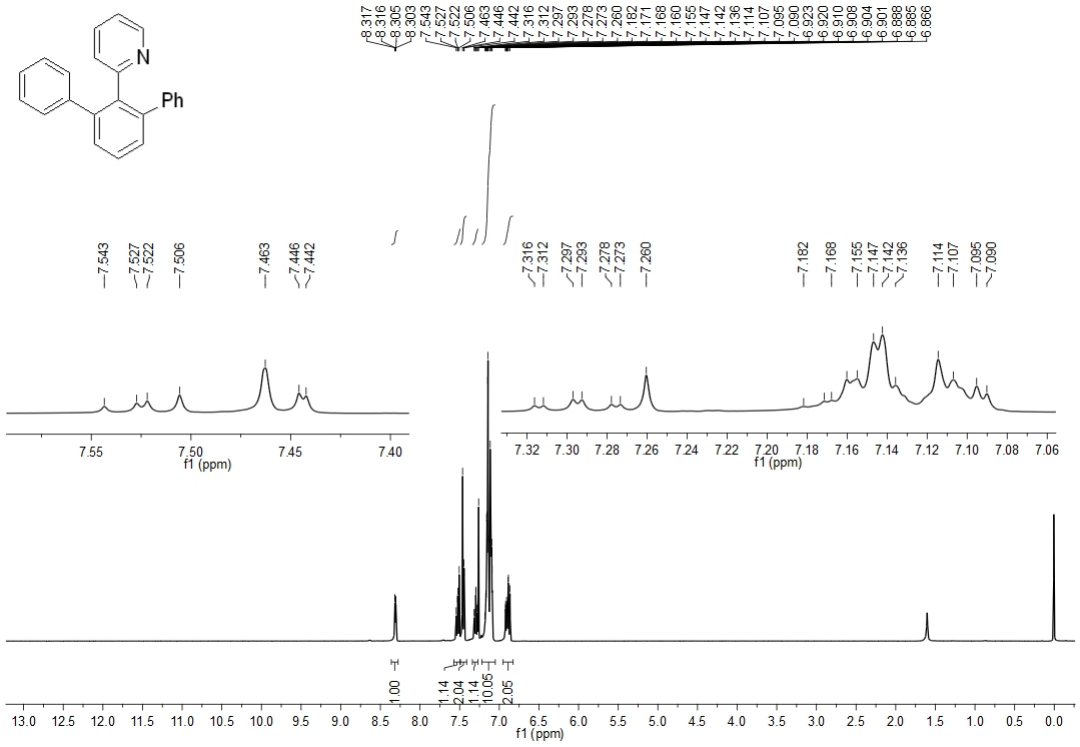
152.867
143.550
138.799
135.547
128.724
125.339
119.820
77.478
77.160
76.843
55.781
140.063
135.907
135.547
130.985
130.825
129.406
129.333
127.456
126.047
125.618
125.339
f1 (ppm)


N
Ph
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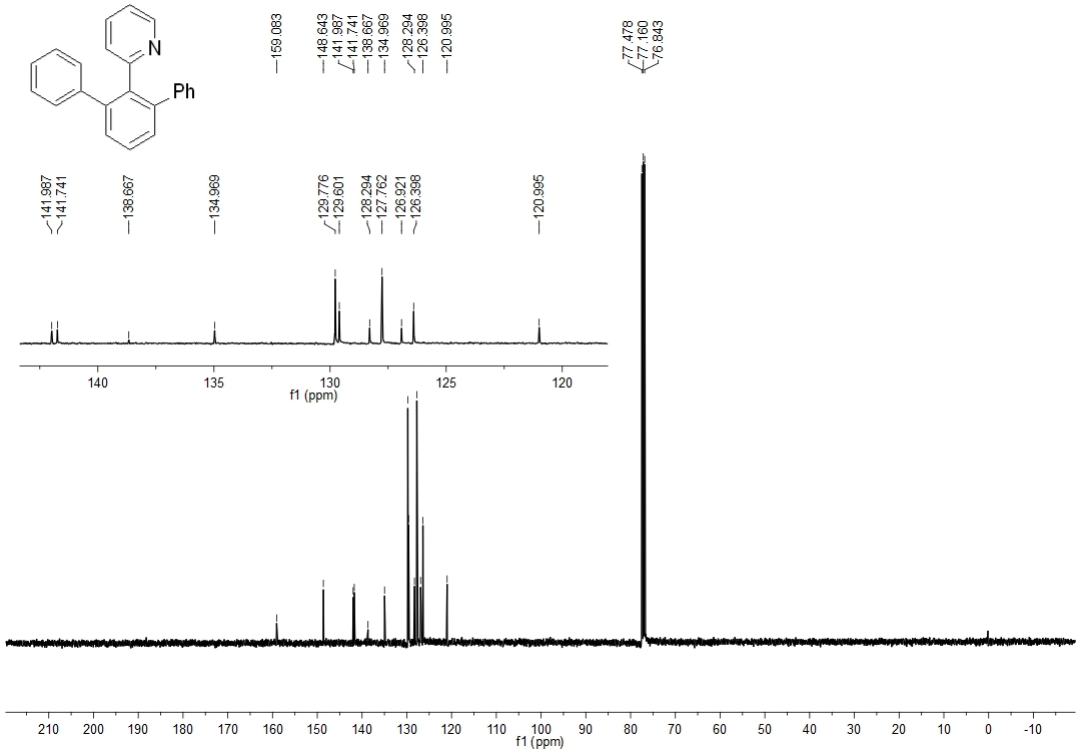
8.305
8.303
7.543
7.527
7.522
7.506
7.463
7.446
7.442
7.316
7.312
7.297
7.293
7.278
7.273
7.260
7.182
7.171
7.168
7.160
7.155
7.147
7.142
7.136
7.114
7.107
7.095
7.090
6.923
6.920
6.910
6.908
6.904
6.901
6.888
6.885
6.866
1.00
1.14
2.04
1.14
10.05
2.05
f1 (ppm)


N
Ph
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148.643
141.987
141.741
138.667
134.969
128.294
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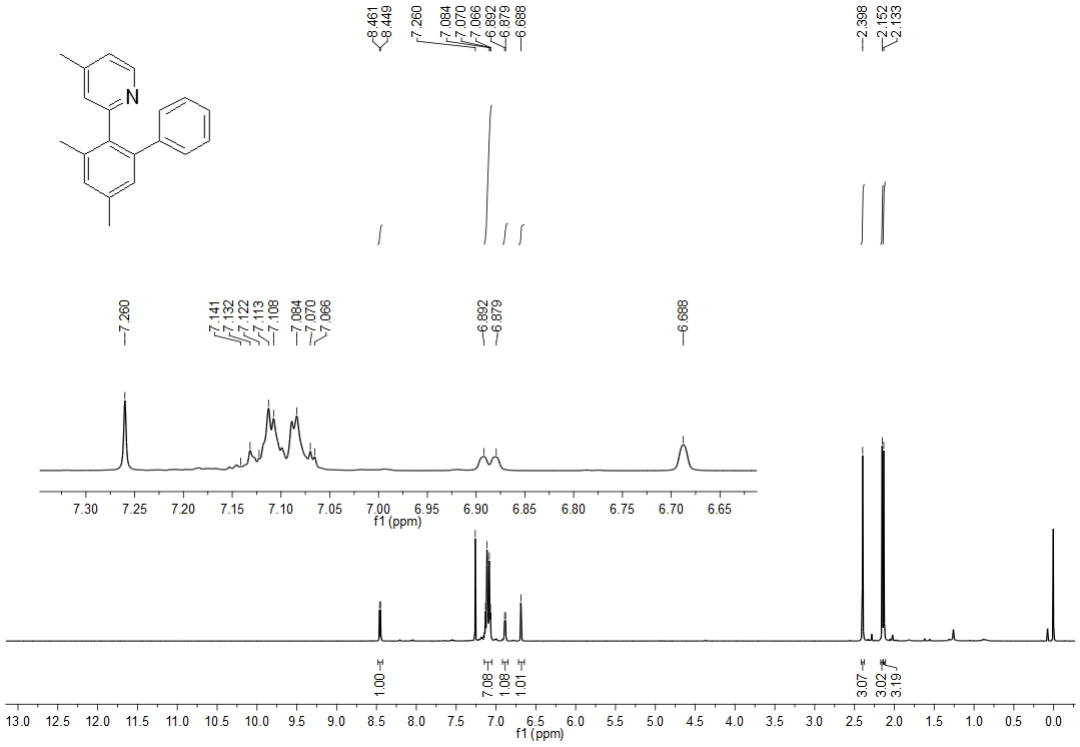
120.995
77.478
77.160
76.843
129.776
129.601
127.762
126.921
f1 (ppm)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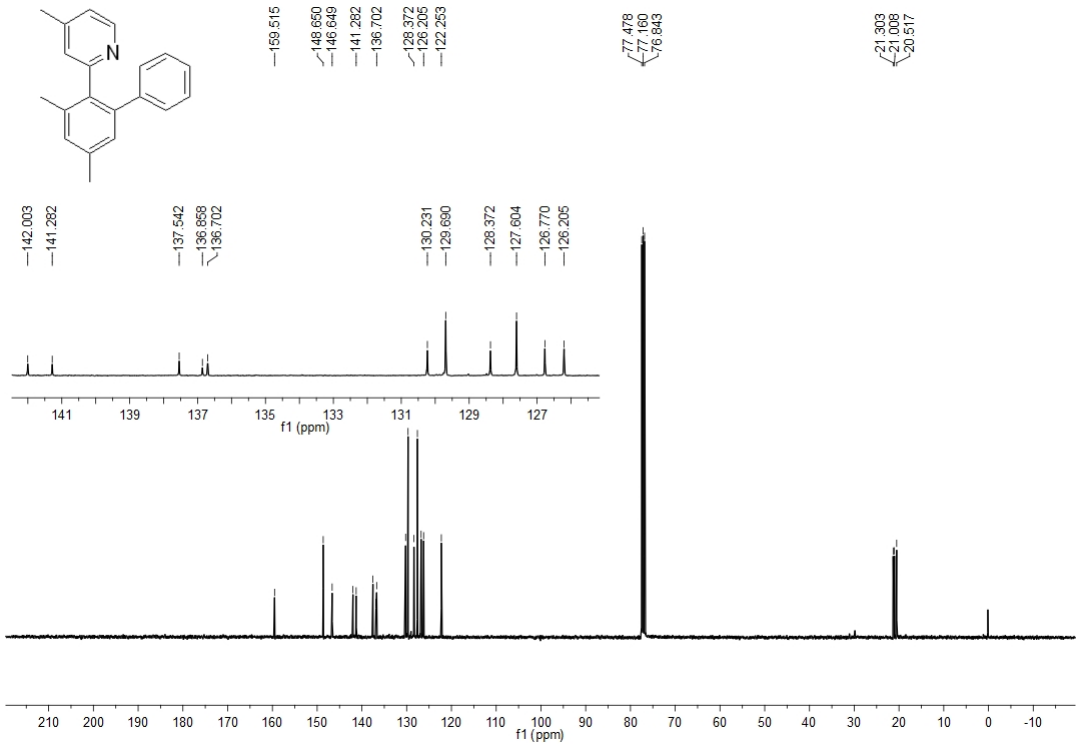
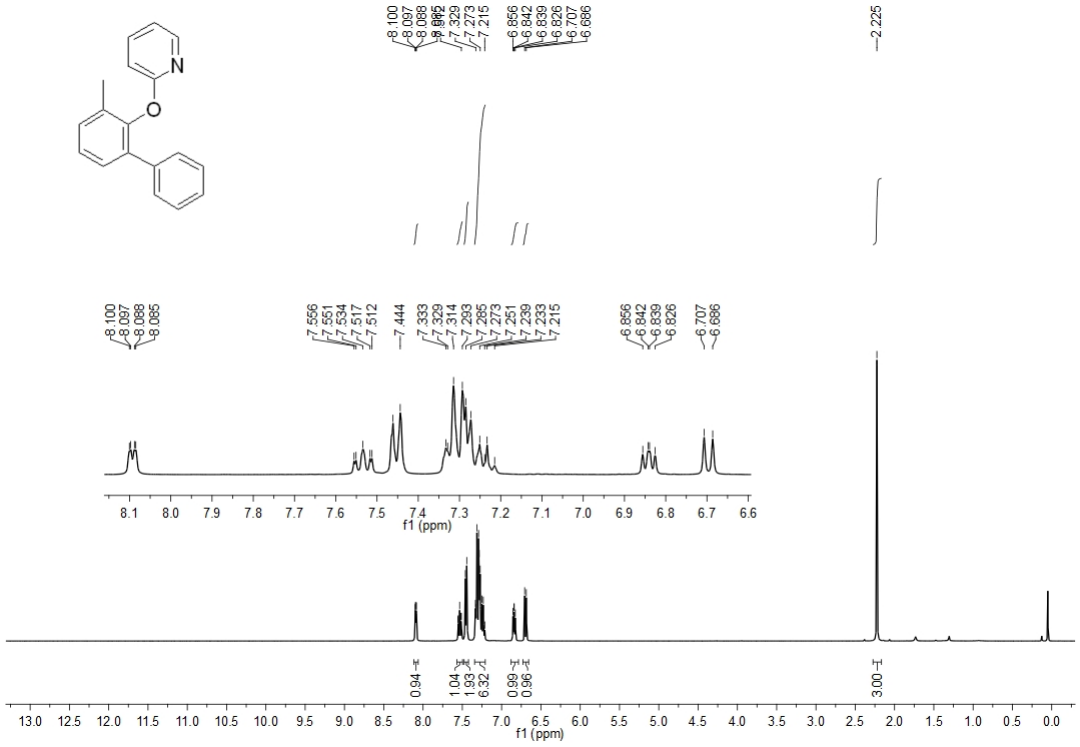
7.260
7.084
7.070
7.066
6.892
6.879
6.688
2.398
2.152
2.133
7.260
7.141
7.132
7.122
7.113
7.108
7.084
7.070
7.066
6.892
6.879
6.688
f1 (ppm)
1.00
7.08
1.08
1.01
3.07
3.02
3.19
f1 (ppm)


159.515
148.650
146.649
141.282
136.702
128.372
126.205
122.253
77.478
77.160
76.843
21.303
21.008
20.517
142.003
141.282
137.542
136.858
136.702
130.231
129.690
128.372
127.604
126.770
126.205
f1 (ppm)
f1 (ppm)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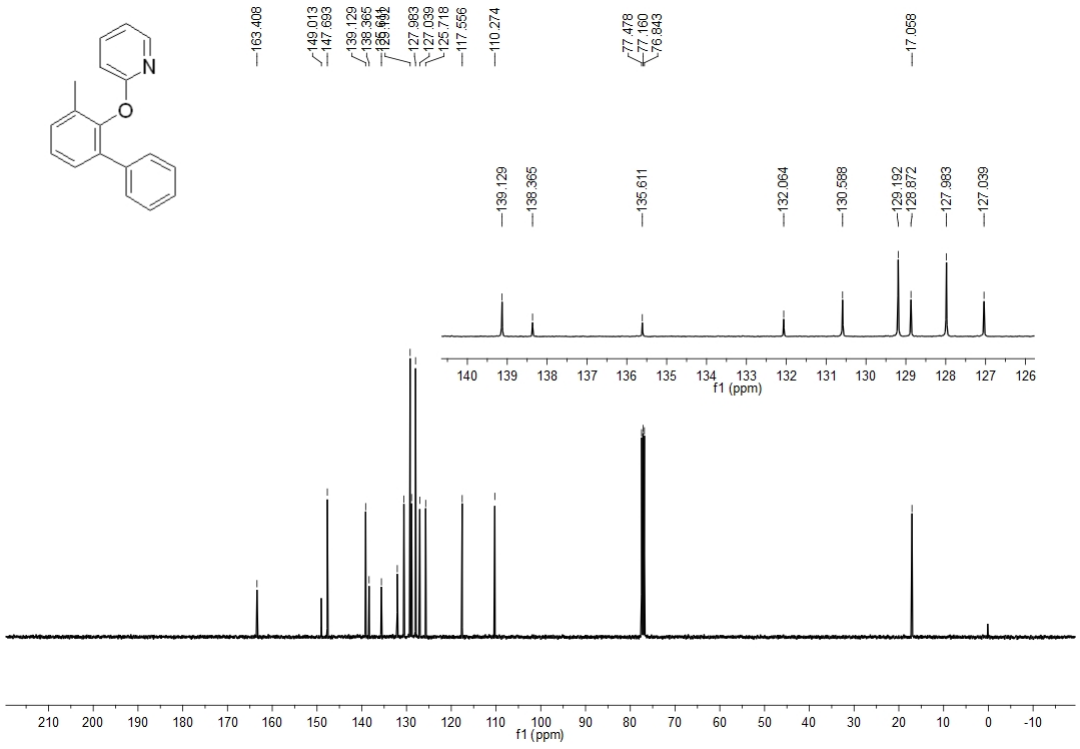
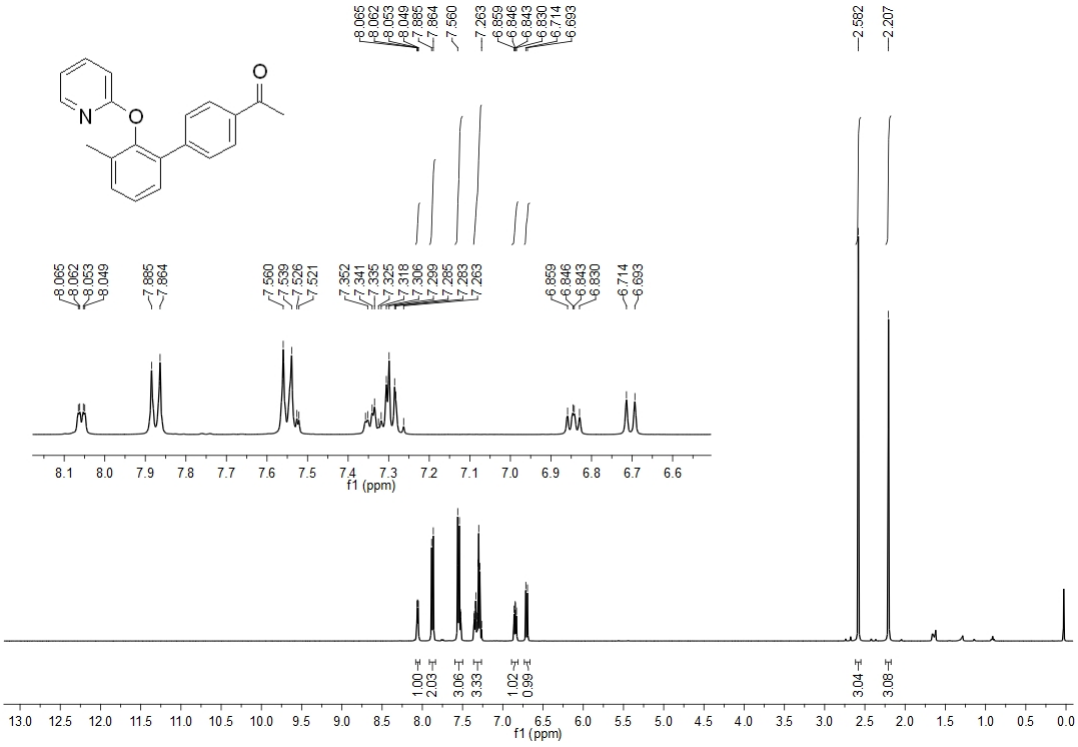
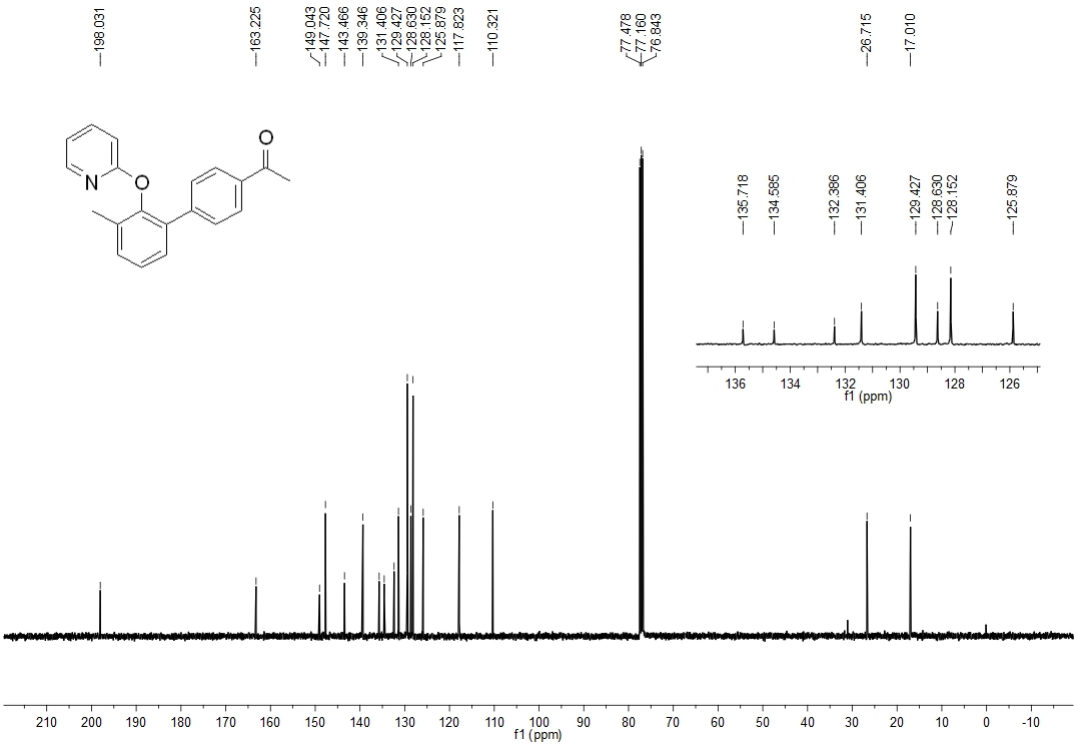
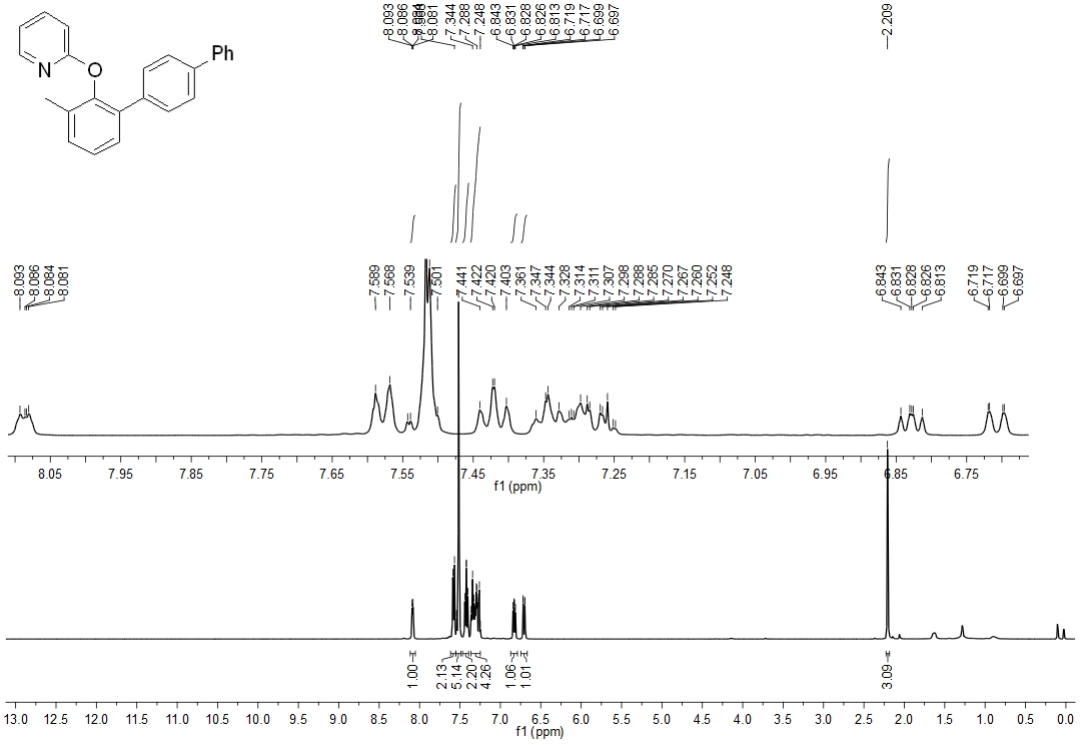
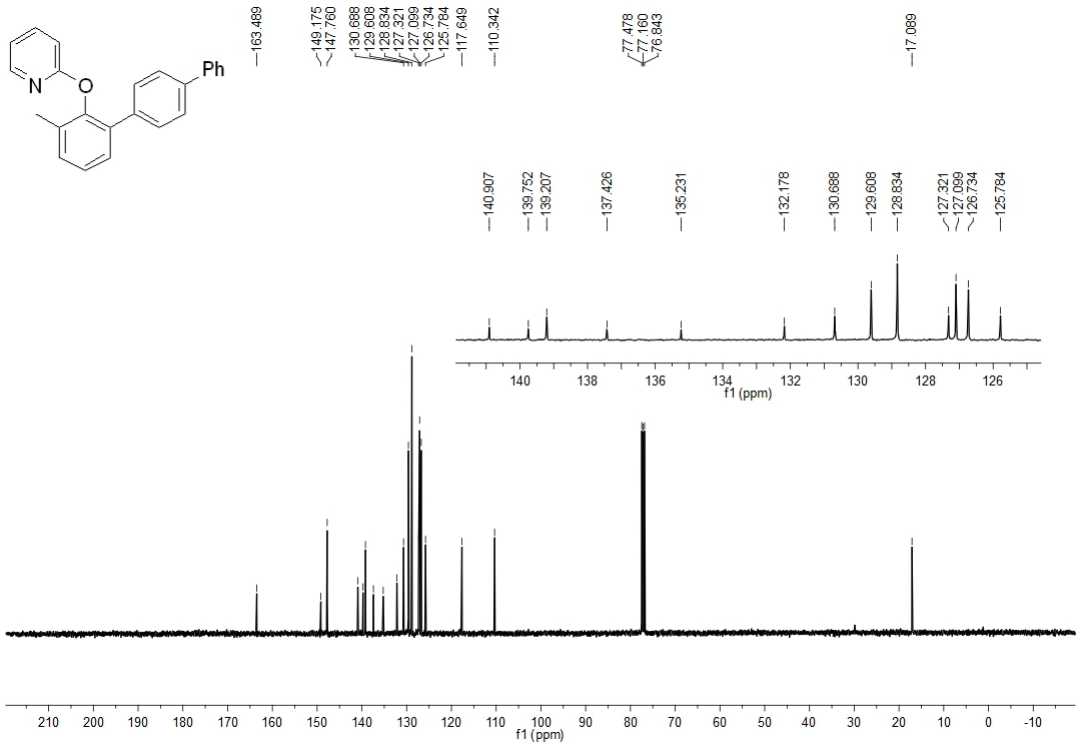
8.097
8.088
8.085
7.556
7.551
7.534
7.517
7.512
7.444
7.333
7.329
7.314
7.293
7.285
7.273
7.251
7.239
7.233
7.215
6.856
6.842
6.839
6.826
6.707
6.686
2.225
0.94
1.04
1.93
6.32
0.99
0.98
3.00
f1 (ppm)

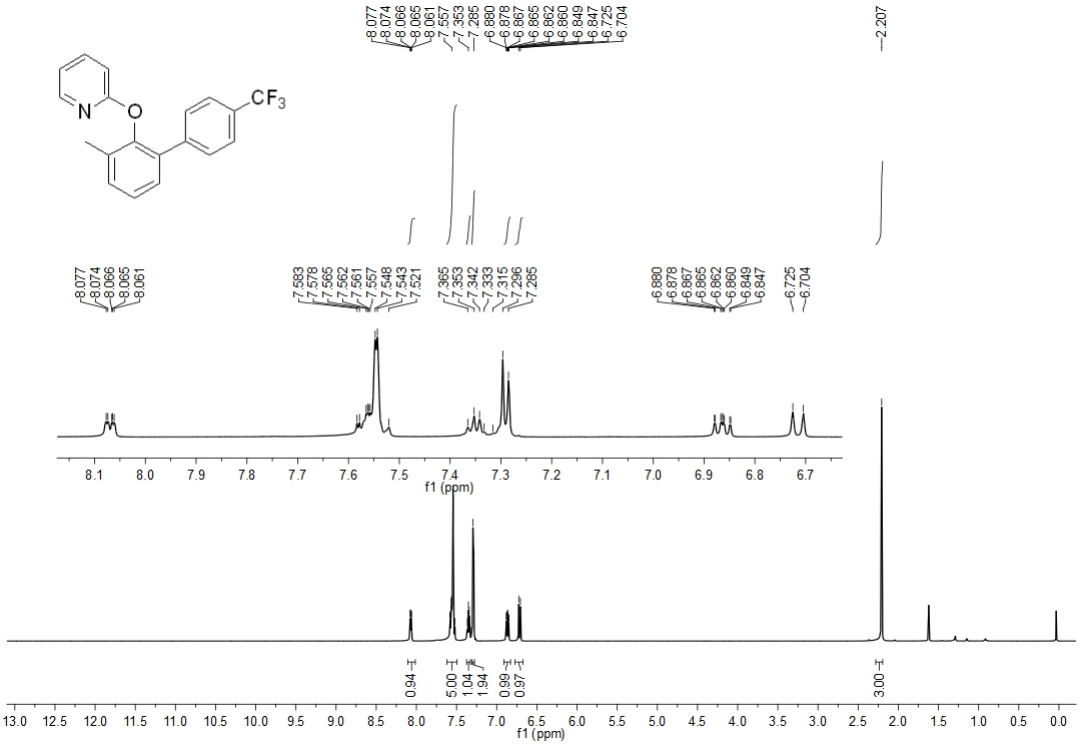

163.408
149.013
147.693
139.129
138.365
127.983
127.039
125.718
117.556
110.274
77.478
77.160
76.843
17.058
f1 (ppm)

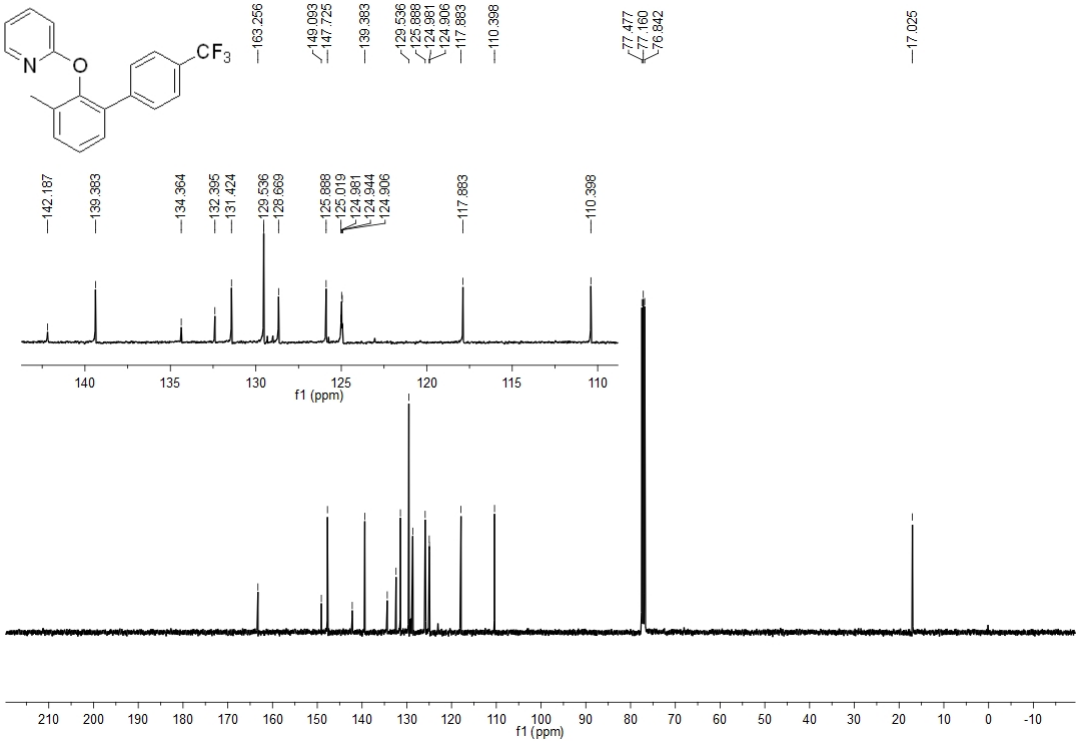

8.065
8.062
8.053
8.049
7.885
7.864
7.560
7.263
6.859
6.846
6.843
6.830
6.714
6.693
2.582
2.207
O
N
O
f1 (ppm)
1.00
2.03
3.06
3.33
1.02
0.99
3.04
3.08

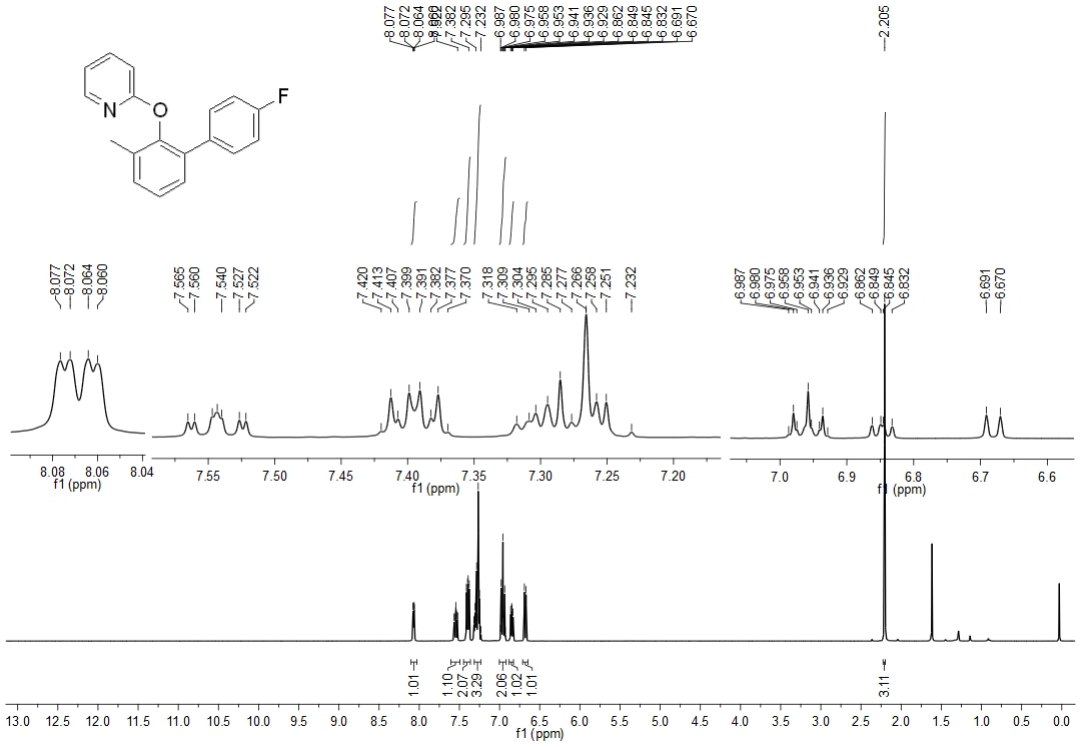

198.031
163.225
149.043
147.720
143.466
139.346
131.406
129.427
128.630
128.152
125.879
117.823
110.321
77.478
77.160
76.843
26.715
17.010
O
N
O
135.718
134.585
132.386
131.406
129.427
128.630
128.152
125.879
f1 (ppm)

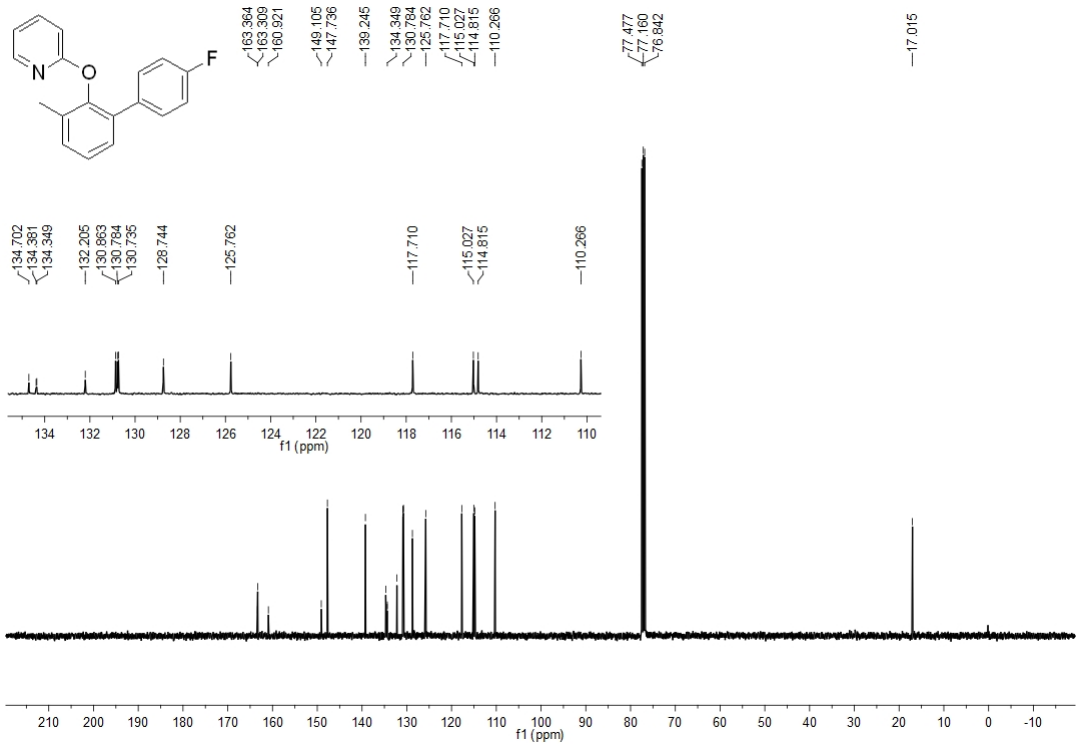

Ph
N
O
8.093
8.086
8.084
8.081
7.589
7.568
7.539
7.501
7.441
7.422
7.420
7.403
7.361
7.347
7.344
7.328
7.314
7.311
7.307
7.298
7.288
7.285
7.270
7.267
7.260
7.252
7.248
6.843
6.831
6.828
6.826
6.813
6.719
6.717
6.699
6.697
2.209
f1 (ppm)
1.00
2.13
5.14
2.20
4.26
1.06
1.01
3.09

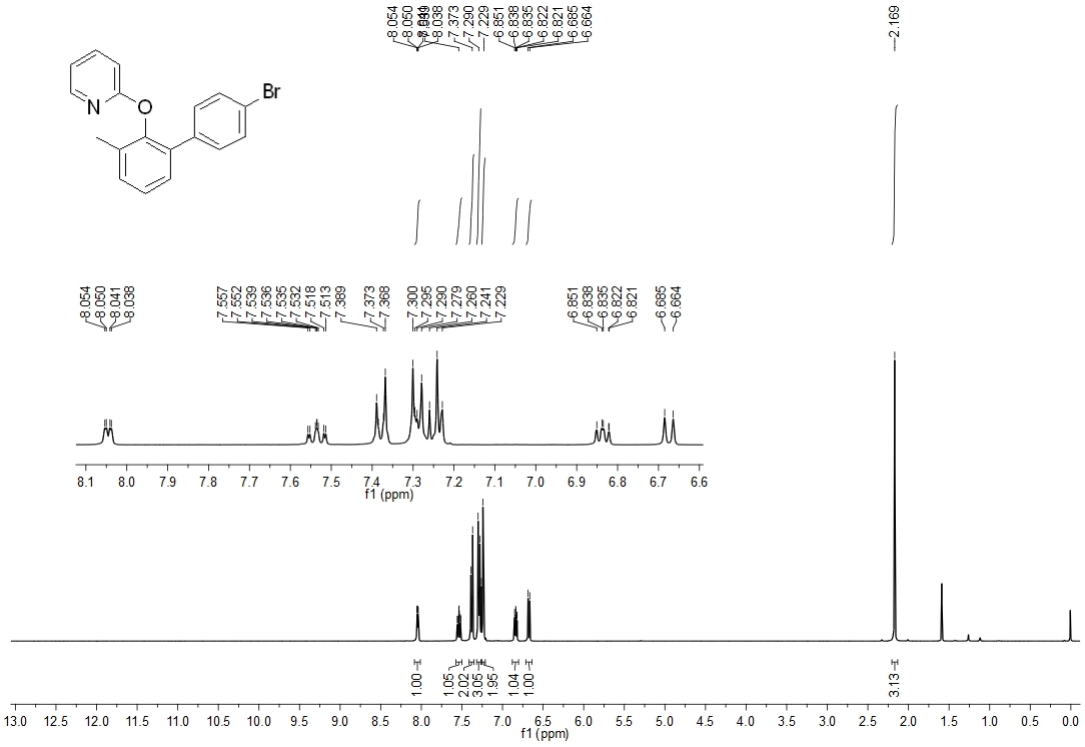

Ph
N
O
163.489
149.175
147.760
130.688
129.608
128.834
127.321
127.099
126.734
125.784
117.649
110.342
77.478
77.160
76.843
17.089
140.907
139.752
139.207
137.426
135.231
132.178
130.688
129.608
128.834
127.321
127.099
126.734
125.784
f1 (ppm)

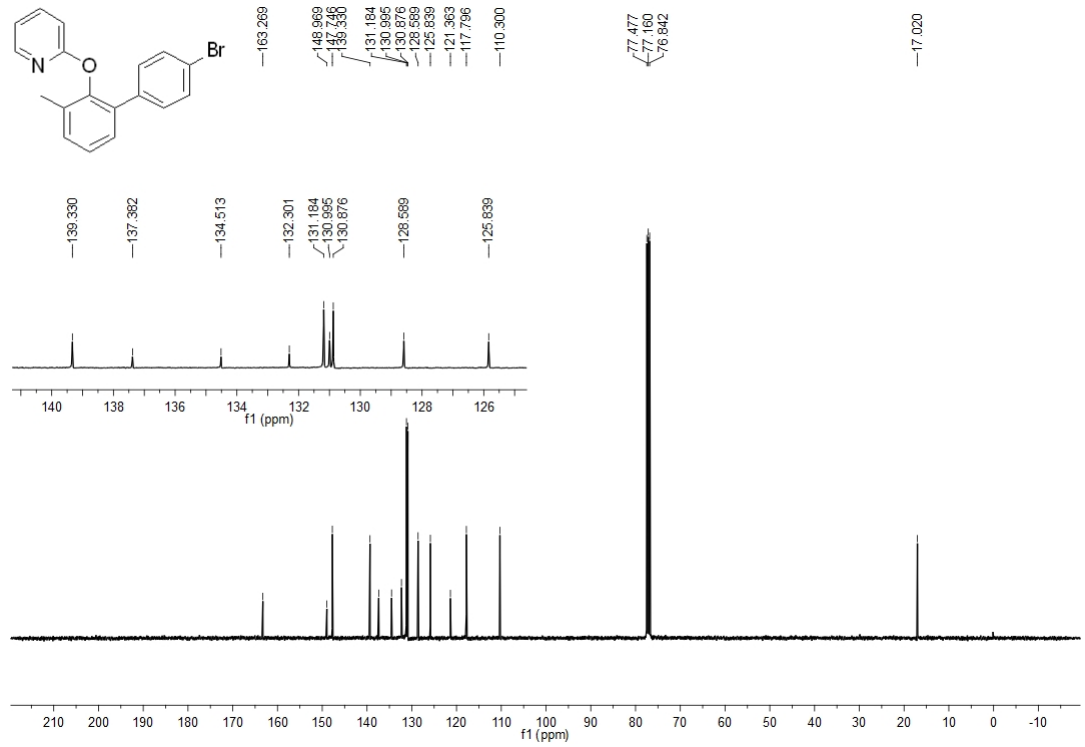

8.077
8.074
8.066
8.065
8.061
7.583
7.578
7.565
7.562
7.561
7.557
7.548
7.543
7.521
7.365
7.353
7.342
7.333
7.315
7.296
7.285
6.880
6.878
6.867
6.865
6.862
6.860
6.849
6.847
6.725
6.704
2.207
f1 (ppm)
0.94
5.00
1.04
1.94
0.99
0.97
3.00

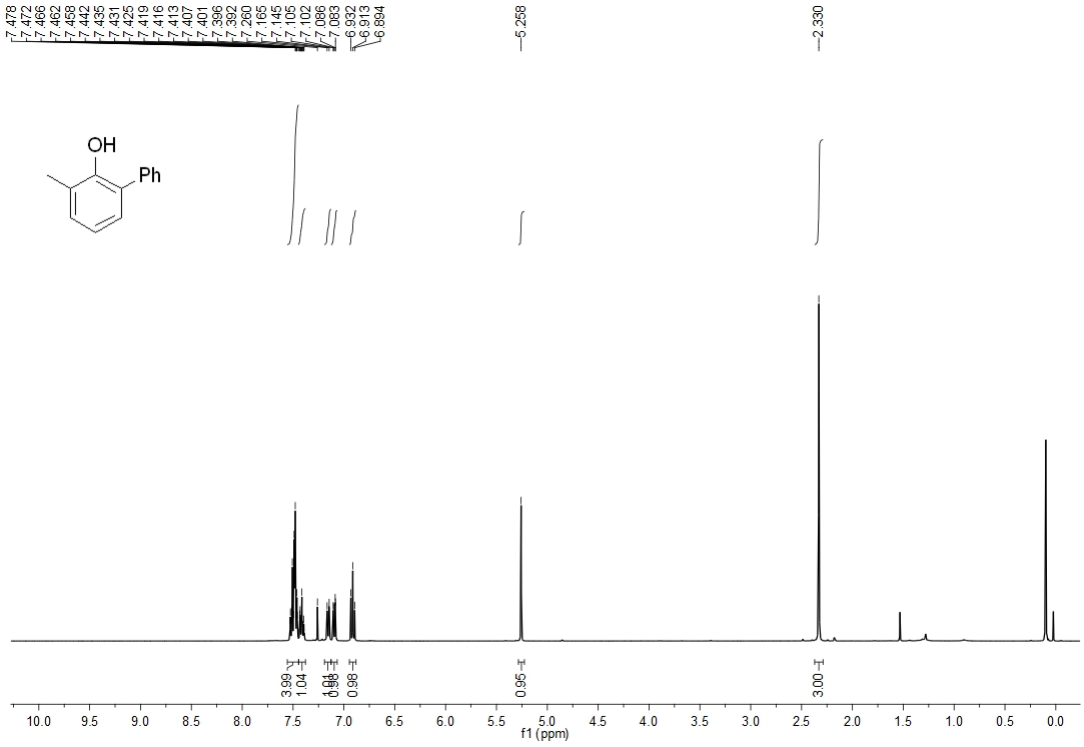

163.256
149.093
147.725
139.383
129.536
125.888
125.019
124.981
124.906
117.883
110.398
77.477
77.160
76.842
17.025
142.187
139.383
134.364
132.395
131.424
129.536
128.669
125.888
125.019
124.981
124.944
124.906
117.883
110.398
f1 (ppm)


8.077
8.072
8.064
8.060
7.565
7.560
7.540
7.527
7.522
7.420
7.413
7.407
7.399
7.391
7.382
7.377
7.370
7.318
7.309
7.304
7.295
7.285
7.277
7.266
7.258
7.251
7.232
6.987
6.980
6.975
6.968
6.953
6.941
6.936
6.929
6.862
6.849
6.845
6.832
6.691
6.670
2.205
1.01
1.10
2.07
3.29
2.06
1.02
1.01
3.11
f1 (ppm)


163.364
163.309
160.921
149.105
147.736
139.245
134.349
130.784
125.762
117.710
115.027
114.815
110.266
77.477
77.160
76.842
17.015
f1 (ppm)


Br
N
O
8.054
8.050
8.041
8.038
7.557
7.552
7.539
7.536
7.535
7.532
7.518
7.513
7.389
7.373
7.368
7.300
7.295
7.290
7.279
7.260
7.241
7.229
6.851
6.838
6.835
6.822
6.821
6.685
6.664
2.169
1.00
1.05
2.02
3.05
1.95
1.04
1.00
3.13
f1 (ppm)


Br
N
O
163.269
148.969
147.746
139.330
131.184
130.995
130.876
128.589
125.839
121.363
117.796
110.300
77.477
77.160
76.842
17.020
f1 (ppm)


7.478
7.472
7.466
7.462
7.448
7.442
7.435
7.431
7.425
7.419
7.416
7.413
7.407
7.401
7.396
7.392
7.260
7.165
7.145
7.105
7.102
7.096
7.083
6.932
6.913
6.894
5.258
2.330
OH
Ph
3.99
1.04
0.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)