

Supporting Information

Direct Arylation of *N*-heterocycles Enabled by Photoredox Catalysis

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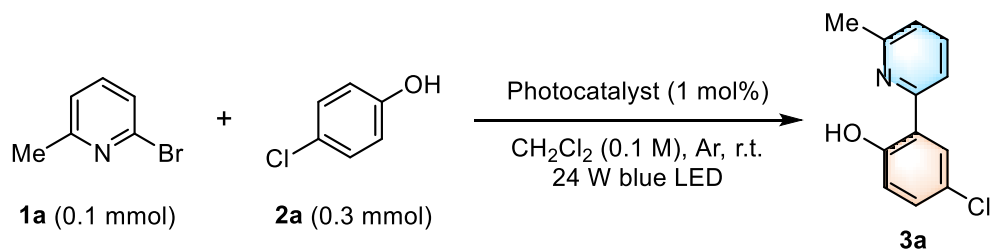
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General Information

Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed on Jiangyou TLC silica gel plates HSGF254 and visualized through UV light (254 nm). Preparative thin layer chromatography (PTLC) was performed using Huanghai (0.4-0.5 mm, 20*20 cm, Yantai Jiangyou). Flash column chromatography was performed using Tsingtao Haiyang silica gel (200-300 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III HD 400 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) referenced to TMS (0.0 ppm), CDCl_3 (7.26 ppm or 77.16 ppm), Acetone- d_6 (2.05 ppm or 29.84 ppm) and DMSO- d_6 (2.50 ppm or 39.52 ppm), respectively. The NMR data are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; m = multiplet; br = broad), coupling constant (Hz), integration. For reaction optimization, triphenylmethane was added as an internal standard (s, 5.55 ppm, 1H) and CDCl_3 was used as locking solvent. Photochemical reactions were carried out with 24 W blue LED which was purchased from Guangzhou Hongye Lighting (<https://shop111029161.taobao.com/?spm=a230r.7195193.1997079397.2.438a6ac2NnYsKB>). High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc. mass instrument (HESI).

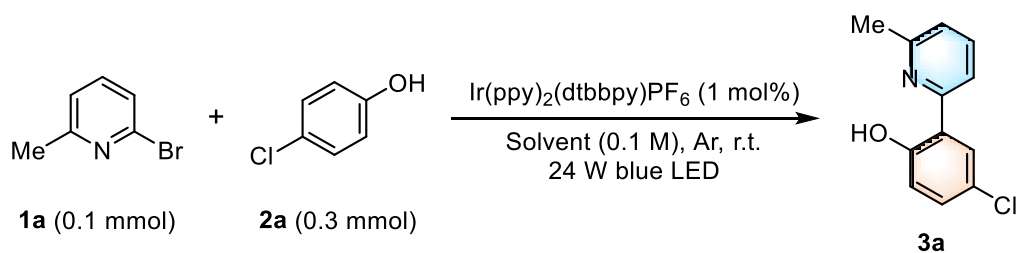
Reaction Condition Optimization

Table S1. Screening of photocatalysts




Entry	Photocatalyst	Yield (%) ^[a]
1	Ir(ppy) ₂ (dtbbpy)PF ₆	81
2	Ir[dF(Me)ppy] ₂ (dtbbpy)PF ₆	58
3	Ir[dF(CF ₃)ppy] ₂ (bpy)PF ₆	70 ^[b]
4	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	79
5	4-CzIPN	70
6	3DPAFIPN	61
7	10-Phenyl-10 <i>H</i> -phenothiazine	68
8	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	N.R.
9	Ru(phen) ₃ (PF ₆) ₂	N.R.
10	Eosin B	N.R.
11	Rhodamine B	N.R.
12	Rhodamine 6G	N.R.

[a] **1a** (0.1 mmol, 1 equiv), **2a** (3 equiv), photocatalyst (0.01 equiv), CH₂Cl₂ (1 mL) for 12 h. Yields were determined through crude ¹H NMR spectrum using triphenylmethane as internal standard. [b] The reaction was carried out for 24 h. 3DPAFIPN = 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile. N.R. = no reaction.

Table S2. Screening of solvents

Entry	Solvent	Yield (%) ^[a]
1	CH_2Cl_2	81
2	DCE	83
3	CHCl_3	69
4	Hexafluoroisopropanol	52
5	$\text{CF}_3\text{CH}_2\text{OH}$	58
6	Acetone	trace
7	1,4-dioxane	N.R.
8	THF	N.R.
9	MeCN	7
10	Toluene	17
11	PhF	trace
12	Ethyl acetate	N.R.
13	MeOH	N.R.

[a] **1a** (0.1 mmol, 1 equiv), **2a** (3 equiv), $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (0.01 equiv), solvent (1 mL) for 12 h. Yields were determined through crude ^1H NMR spectrum using triphenylmethane as internal standard.

Table S3. Control Experiments

Reaction scheme showing the synthesis of **3a** from **1a** and **2a**. **1a** (0.1 mmol) reacts with **2a** (0.3 mmol) in the presence of $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (1 mol%), DCE (0.1 M), Ar, r.t., and 24 W blue LED to yield **3a**.

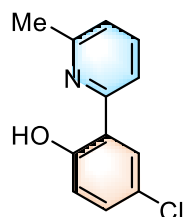
Entry	Variations from the above conditions	Yield (%) ^[a]
1	—	83 (83) ^[b]
2	No $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$	N.R.
3	No light	N.R.
4	2a (0.2 mmol)	71 ^[c]

[a] **1a** (0.1 mmol, 1 equiv), **2a** (3 equiv), $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (0.01 equiv), DCE (1 mL) for 12 h. Yields were determined through crude ^1H NMR spectrum using triphenylmethane as internal standard. [b] Yield in the parentheses was isolated yield. [c] Isolated by PTLC.

General Procedure for Photocatalytic Synthesis of *N*-Heterobiaryls

To an oven-dried Schlenk tube equipped with magnetic bar was added phenol or arene (if it's solid, 0.6 mmol, 3 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.01 equiv), bromoazaarenes (if it's solid, 0.2 mmol, 1 equiv). The mixture was then placed under vacuum and backfilled with argon three times, followed by the addition of DCE (2 mL) and arene or bromoazaarene (if it's liquid). Then the tube was placed approximate 4~5 cm away from 24 W blue LED and stir vigorously for corresponding time with a cooling fan to maintain the reaction at r.t. (about 25 °C). Upon completion of the reaction monitored by TLC, the mixture was concentrated and purified by silica chromatography or PTLC to afford the pure product.

Characterization of Products



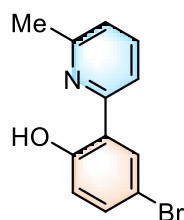
4-Chloro-2-(6-methylpyridin-2-yl)phenol (**3a**)

Following the general procedure, **3a** was obtained in 83% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 14.55 (s, 1H), 8.10 – 8.05 (m, 2H), 7.94 – 7.90 (m, 1H), 7.35 – 7.30 (m, 2H), 6.93 (d, J = 8.8 Hz, 1H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 158.05, 155.04, 154.94, 139.04, 130.80, 126.29, 122.47, 120.16, 119.70, 117.37, 23.34.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{11}\text{ClNO}]^+$: 220.0524, found: 220.0522.



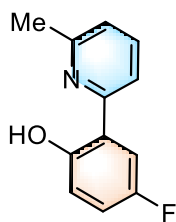
4-Bromo-2-(6-methylpyridin-2-yl)phenol (**3b**)

Following the general procedure, **3b** was obtained in 83% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 14.57 (s, 1H), 8.15 (d, J = 2.5 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.42 (dd, J = 8.8, 2.5 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 158.46, 155.00, 154.81, 138.99, 133.61, 129.09, 122.44, 120.77, 120.14, 117.36, 109.97, 23.33.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{11}\text{BrNO}]^+$: 264.0019, found: 264.0017.



4-Fluoro-2-(6-methylpyridin-2-yl)phenol (**3c**)

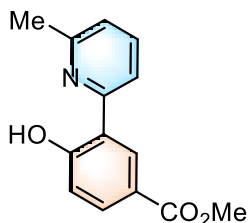
Following the general procedure, **3c** was obtained in 72% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.25 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.94 – 7.85 (m, 2H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.17 – 7.12 (m, 1H), 6.93 – 6.89 (m, 1H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 155.52, 155.27 (d, $J = 2.8$ Hz), 155.13 (d, $J = 233.0$ Hz), 155.05, 139.02, 122.38, 119.14 (d, $J = 7.4$ Hz), 119.01 (d, $J = 8.0$ Hz), 118.04 (d, $J = 23.2$ Hz), 117.36, 112.68 (d, $J = 24.3$ Hz).

^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -125.79.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{11}\text{FNO}]^+$: 204.0819, found: 204.0818.



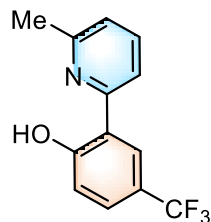
Methyl 4-hydroxy-3-(6-methylpyridin-2-yl)benzoate (**3d**)

Following the general procedure, **3d** was obtained in 75% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 15.32 (s, 1H), 8.53 (d, $J = 2.2$ Hz, 1H), 8.06 (d, $J = 8.2$ Hz, 1H), 8.00 – 7.91 (m, 1H), 7.88 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.36 (d, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 8.6$ Hz, 1H), 3.84 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 165.88, 163.61, 155.07, 154.99, 139.30, 132.15, 128.56, 122.55, 120.15, 118.53, 118.35, 117.14, 51.90, 23.29.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{14}\text{H}_{14}\text{NO}_3]^+$: 244.0968, found: 244.0966.



2-(6-Methylpyridin-2-yl)-4-(trifluoromethyl)phenol (**3e**)

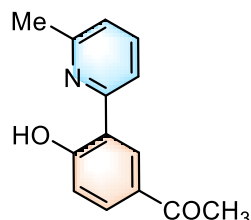
Following the general procedure, **3e** was obtained in 76% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.21 (s, 1H), 8.30 (d, $J = 2.2$ Hz, 1H), 8.19 – 8.16 (m, 1H), 7.95 – 7.91 (m, 1H), 7.60 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.6$ Hz, 1H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 162.34, 154.98, 154.79, 139.15, 127.76 (q, $J = 3.7$ Hz), 124.62 (q, $J = 271.0$ Hz), 124.37 (q, $J = 3.9$ Hz), 119.44 (q, $J = 32.2$ Hz), 118.94, 118.75, 117.50, 23.26.

^{19}F NMR (376 MHz, DMSO- d_6) δ -59.58.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{11}\text{F}_3\text{NO}]^+$: 254.0787, found: 254.0785.



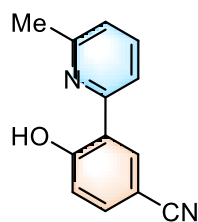
1-(4-Hydroxy-3-(6-methylpyridin-2-yl)phenyl)ethan-1-one (**3f**)

Following the general procedure, **3f** was obtained in 63% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.47 (s, 1H), 8.55 (d, $J = 2.2$ Hz, 1H), 8.17 (d, $J = 8.2$ Hz, 1H), 7.98 – 7.94 (m, 1H), 7.90 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 6.99 (d, $J = 8.6$ Hz, 1H), 2.59 (s, 3H), 2.57 (s, 3H)

^{13}C NMR (100 MHz, DMSO- d_6) δ 196.20, 163.79, 155.39, 154.83, 139.24, 131.37, 128.28, 128.01, 122.48, 118.19, 118.05, 117.18, 26.46, 23.26.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{14}\text{H}_{14}\text{NO}_2]^+$: 228.1019, found: 228.1016.



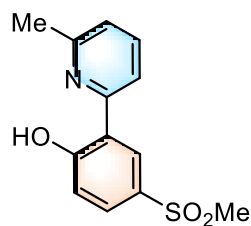
4-Hydroxy-3-(6-methylpyridin-2-yl)benzonitrile (**3g**)

Following the general procedure, **3g** was obtained in 70% yield as yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.71 (s, 1H), 8.56 (s, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 8.6 Hz, 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 163.42, 154.90, 154.43, 139.37, 134.65, 131.94, 122.98, 119.48, 119.33, 117.51, 101.04, 23.20.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}]^+$: 211.0866, found: 211.0864.



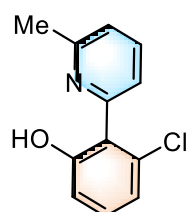
2-(6-Methylpyridin-2-yl)-4-(methylsulfonyl)phenol (**3h**)

Following the general procedure, **3h** was obtained in 69% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.44 (s, 1H), 8.49 (d, J = 2.3 Hz, 1H), 8.18 – 8.16 (m, 1H), 8.02 – 7.98 (m, 1H), 7.81 (dd, J = 8.7, 2.3 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.12 (d, J = 8.6 Hz, 1H), 3.24 (s, 3H), 2.59 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 163.40, 155.13, 154.55, 139.34, 130.94, 129.79, 126.77, 122.97, 118.99, 118.67, 117.62, 43.90, 23.29.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{14}\text{NO}_3\text{S}]^+$: 264.0689, found: 264.0687.



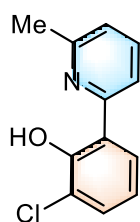
3-Chloro-2-(6-methylpyridin-2-yl)phenol (**3i**)

Following the general procedure, **3i** was obtained in 57% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.01 (s, 1H), 8.04 – 8.00 (m, 2H), 7.94 – 7.90 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 6.97 – 6.82 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 160.36, 155.37, 154.87, 139.12, 135.11, 128.47, 122.24, 118.78, 117.67, 117.46, 117.00, 23.29.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{11}\text{ClNO}]^+$: 220.0524, found: 220.0521.



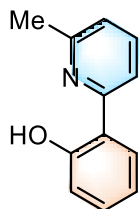
2-Chloro-6-(6-methylpyridin-2-yl)phenol (**3j**)

Following the general procedure, **3j** was obtained in 61% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 15.89 (s, 1H), 8.07 (d, J = 8.2 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.47 – 7.45 (m, 1H), 7.36 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.9 Hz, 1H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 155.46, 155.44, 154.67, 139.41, 131.26, 125.54, 122.55, 121.47, 119.59, 118.83, 117.07, 23.13.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{11}\text{ClNO}]^+$: 220.0524, found: 220.0522.



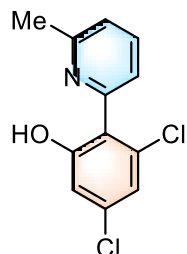
2-(6-Methylpyridin-2-yl)phenol (**3k**)

Following the general procedure, **3k** was obtained in 76% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 14.80 (s, 1H), 7.78 – 7.76 (m, 1H), 7.69 – 7.58 (m, 2H), 7.31 – 7.26 (m, 1H), 7.07 – 7.00 (m, 2H), 6.90 – 6.86 (m, 1H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.23, 157.32, 155.07, 138.12, 131.38, 126.26, 121.23, 118.92, 118.74, 118.63, 116.08, 23.90.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{12}\text{NO}]^+$: 186.0913, found: 186.0912.



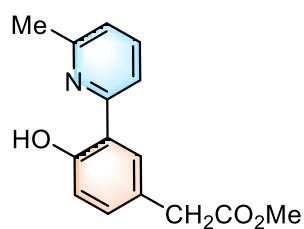
3,5-Dichloro-2-(6-methylpyridin-2-yl)phenol (**3l**)

Following the general procedure, **3l** was obtained in 73% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 13.43 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.80 – 7.76 (m, 1H), 7.19 (d, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 2.2$ Hz, 1H), 6.98 (d, $J = 2.2$ Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 160.04, 155.70, 153.64, 137.67, 135.28, 132.81, 123.07, 122.26, 121.79, 118.50, 116.92, 23.86.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{NO}]^+$: 254.0134, found: 254.0132.



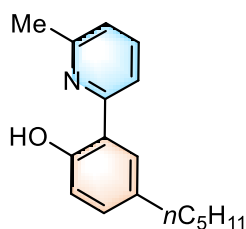
Methyl 2-(4-hydroxy-3-(6-methylpyridin-2-yl)phenyl)acetate (**3m**)

Following the general procedure, **3m** was obtained in 78% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 14.39 (s, 1H), 7.98 – 7.89 (m, 3H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.19 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 3.66 (s, 2H), 3.62 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 172.04, 158.21, 156.21, 154.94, 138.89, 132.32, 127.79, 124.52, 121.81, 118.34, 117.89, 116.69, 51.68, 39.31, 23.42.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{15}\text{H}_{16}\text{NO}_3]^+$: 258.1125, found: 258.1122



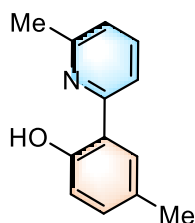
2-(6-Methylpyridin-2-yl)-4-pentylphenol (3n)

Following the general procedure, **3n** was obtained in 77% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 14.21 (s, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.90 – 7.86 (m, 1H), 7.77 (d, $J = 2.2$ Hz, 1H), 7.26 (d, $J = 7.6$ Hz, 1H), 7.09 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.81 (d, $J = 8.3$ Hz, 1H), 2.55 – 2.50 (m, 5H), 1.60 – 1.52 (m, 2H), 1.31 – 1.14 (m, 4H), 0.85 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 157.29, 156.55, 154.78, 138.73, 132.38, 131.22, 126.25, 121.53, 118.22, 117.67, 116.69, 34.44, 30.96, 30.91, 23.41, 21.99, 13.93.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1692.



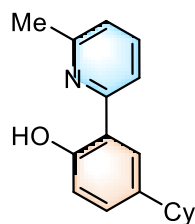
4-Methyl-2-(6-methylpyridin-2-yl)phenol (3o)

Following the general procedure, **3o** was obtained in 77% yield as a yellow solid.

^1H NMR (400 MHz, DMSO- d_6) δ 14.21 (s, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.91 – 7.87 (m, 1H), 7.79 (d, $J = 2.2$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.10 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 1H), 2.54 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 157.11, 156.51, 154.87, 138.82, 132.01, 127.23, 126.91, 121.63, 118.26, 117.74, 116.69, 23.45, 20.28.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{14}\text{NO}]^+$: 200.1070, found: 200.1068.



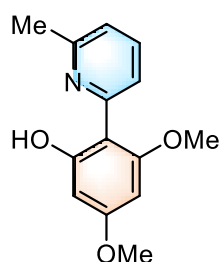
4-Cyclohexyl-2-(6-methylpyridin-2-yl)phenol (**3p**)

Following the general procedure, **3p** was obtained in 68% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.22 (s, 1H), 8.04 (d, $J = 8.2$ Hz, 1H), 7.90 – 7.86 (m, 1H), 7.78 (d, $J = 2.2$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.13 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.81 (d, $J = 8.4$ Hz, 1H), 2.54 (s, 3H), 2.48 – 2.44 (m, 1H), 1.80 – 1.76 (m, 4H), 1.47 – 1.20 (m, 6H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 157.39, 156.63, 154.79, 138.76, 137.88, 129.56, 124.75, 121.57, 118.24, 117.68, 116.78, 43.13, 34.18, 26.49, 25.61, 23.45.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{18}\text{H}_{22}\text{NO}]^+$: 268.1696, found: 268.1693.



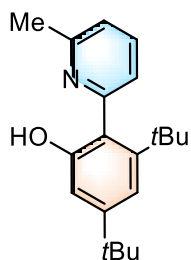
3,5-Dimethoxy-2-(6-methylpyridin-2-yl)phenol (**3q**)

Following the general procedure, **3q** was obtained in 57% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 16.12 (s, 1H), 8.21 – 8.18 (m, 1H), 7.65 – 7.61 (m, 1H), 6.97 (d, $J = 7.5$ Hz, 1H), 6.20 (s, 1H), 6.05 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 163.51, 161.65, 160.31, 155.77, 153.26, 137.65, 121.17, 119.70, 102.72, 94.70, 90.60, 55.46, 55.22, 23.51.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{14}\text{H}_{16}\text{NO}_3]^+$: 246.1125, found: 246.1122.



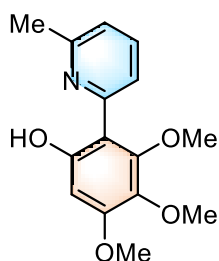
3,5-Di-*tert*-butyl-2-(6-methylpyridin-2-yl)phenol (**3r**)

Following the general procedure, **3r** was obtained in 72% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.65 (m, 1H), 7.25 – 7.17 (m, 3H), 6.88 (d, J = 1.8 Hz, 1H), 5.71 (s, 1H), 2.61 (s, 3H), 1.34 (s, 9H), 1.18 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.48, 157.89, 153.52, 152.05, 148.50, 136.78, 124.40, 124.34, 121.95, 116.91, 111.26, 37.03, 34.92, 32.89, 31.39, 24.54.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{20}\text{H}_{28}\text{NO}]^+$: 298.2165, found: 298.2161.



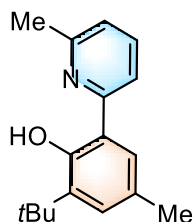
3,4,5-Trimethoxy-2-(6-methylpyridin-2-yl)phenol (**3s**)

Following the general procedure, **3s** was obtained in 60% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.49 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.35 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 156.38, 154.80, 154.65, 154.30, 152.92, 138.65, 134.77, 120.95, 120.64, 106.35, 97.19, 60.66, 55.68, 23.40.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{15}\text{H}_{18}\text{NO}_4]^+$: 276.1230, found: 276.1228.



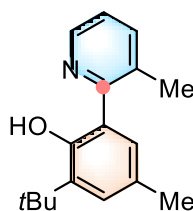
2-(*tert*-Butyl)-4-methyl-6-(6-methylpyridin-2-yl)phenol (**3t**)

Following the general procedure, **3t** was obtained in 83% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 15.13 (s, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.87 – 7.83 (m, 1H), 7.63 (d, $J = 2.0$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 2.0$ Hz, 1H), 2.54 (s, 3H), 2.27 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 157.17, 156.47, 154.24, 138.81, 137.01, 129.18, 125.90, 124.81, 121.31, 117.86, 116.96, 34.54, 29.39, 23.30, 20.68.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1693.



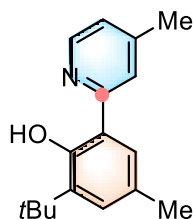
2-(*tert*-Butyl)-4-methyl-6-(3-methylpyridin-2-yl)phenol (**4a**)

Following the general procedure, **4a** was obtained in 58% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 8.35 – 8.33 (m, 1H), 7.63 – 7.61 (m, 1H), 7.11 (dd, $J = 7.7, 4.8$ Hz, 1H), 7.05 (s, 2H), 2.44 (s, 3H), 2.24 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.33, 153.70, 144.32, 141.27, 138.00, 132.33, 128.64, 128.12, 126.53, 121.80, 35.11, 29.83, 21.59, 21.20.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1693.



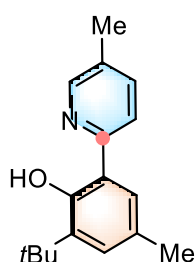
2-(*tert*-Butyl)-4-methyl-6-(4-methylpyridin-2-yl)phenol (**4b**)

Following the general procedure, **4b** was obtained in 79% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 14.80 (s, 1H), 8.30 (d, $J = 5.7$ Hz, 1H), 7.69 (s, 1H), 7.46 (d, $J = 2.1$ Hz, 1H), 7.14 (d, $J = 2.1$ Hz, 1H), 7.03 – 6.97 (m, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.42, 157.24, 148.97, 145.07, 138.22, 129.63, 126.37, 124.55, 122.34, 120.27, 118.48, 35.10, 29.71, 21.75, 21.24.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1693.



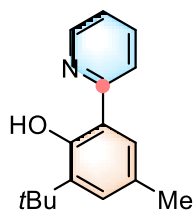
2-(*tert*-Butyl)-4-methyl-6-(5-methylpyridin-2-yl)phenol (**4c**)

Following the general procedure, **4c** was obtained in 66% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 14.50 (s, 1H), 8.28 (s, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.58 (dd, $J = 8.4, 2.3$ Hz, 1H), 7.44 (d, $J = 2.1$ Hz, 1H), 7.12 (d, $J = 2.2$ Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 156.80, 156.03, 145.40, 138.55, 138.14, 130.85, 129.33, 126.41, 124.45, 119.31, 118.57, 35.09, 29.71, 21.24, 18.27.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1694.



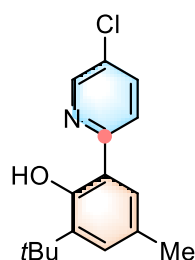
2-(*tert*-Butyl)-4-methyl-6-(pyridin-2-yl)phenol (**4d**)

Following the general procedure, **4d** was obtained in 69% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 14.54 (s, 1H), 8.47 – 8.45 (m, 1H), 7.90 – 7.88 (m, 1H), 7.80 – 7.75 (m, 1H), 7.47 (d, $J = 2.2$ Hz, 1H), 7.20 – 7.15 (m, 2H), 2.33 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.75, 157.11, 145.45, 138.31, 137.76, 129.84, 126.53, 124.65, 121.17, 119.77, 118.46, 35.11, 29.70, 21.24.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{16}\text{H}_{20}\text{NO}]^+$: 242.1539, found: 242.1537.



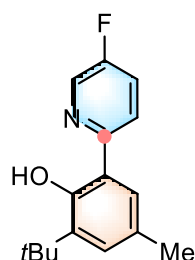
2-(*tert*-Butyl)-6-(5-chloropyridin-2-yl)-4-methylphenol (4e)

Following the general procedure, **4e** was obtained in 43% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 13.79 (s, 1H), 8.44 (d, $J = 2.5$ Hz, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.75 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.40 (s, 1H), 7.16 (d, $J = 2.1$ Hz, 1H), 2.32 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 156.97, 156.64, 144.51, 138.48, 137.62, 130.27, 129.27, 126.94, 124.74, 120.94, 117.91, 35.15, 29.67, 21.21.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{16}\text{H}_{19}\text{ClNO}]^+$: 276.1150, found: 276.1146.



2-(*tert*-Butyl)-6-(5-fluoropyridin-2-yl)-4-methylphenol (4f)

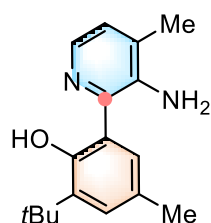
Following the general procedure, **4f** was obtained in 49% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 13.78 (s, 1H), 8.35 (d, $J = 3.0$ Hz, 1H), 7.92 – 7.89 (m, 1H), 7.60 – 7.49 (m, 1H), 7.40 (d, $J = 2.1$ Hz, 1H), 7.15 (s, 1H), 2.33 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.80 (d, $J = 254.9$ Hz), 156.13, 155.31 (d, $J = 3.9$ Hz), 138.42, 133.63 (d, $J = 25.3$ Hz), 129.83, 126.91, 125.26 (d, $J = 18.8$ Hz), 124.76, 121.45 (d, $J = 4.4$ Hz), 118.23, 35.15, 29.68, 21.22.

^{19}F NMR (376 MHz, CDCl_3) δ -129.17.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{16}\text{H}_{19}\text{FNO}]^+$: 260.1445, found: 260.1441.



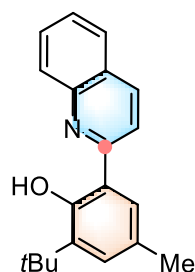
2-(3-Amino-4-methylpyridin-2-yl)-6-(*tert*-butyl)-4-methylphenol (**4g**)

Following the general procedure, **4g** was obtained in 72% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 10.95 (s, 1H), 7.93 (d, $J = 4.8$ Hz, 1H), 7.42 (s, 1H), 7.10 (d, $J = 2.2$ Hz, 1H), 6.96 (d, $J = 4.8$ Hz, 1H), 4.00 (s, 2H), 2.30 (s, 3H), 2.23 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 153.55, 142.78, 139.54, 138.45, 137.21, 132.96, 128.35, 127.12, 125.67, 124.28, 120.95, 35.11, 29.77, 21.18, 17.89.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}]^+$: 271.1805, found: 271.1800.



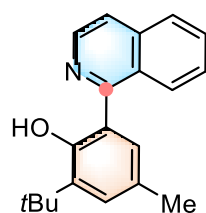
2-(*tert*-Butyl)-6-(quinolin-3-yl)-4-methylphenol (**4h**)

Following the general procedure, **4h** was obtained in 48% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 15.63 (s, 1H), 8.55 (d, $J = 8.9$ Hz, 1H), 8.36 (d, $J = 9.1$ Hz, 1H), 8.08 – 8.02 (m, 2H), 7.88 – 7.80 (m, 2H), 7.66 – 7.62 (m, 1H), 7.16 (d, $J = 2.0$ Hz, 1H), 2.32 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 158.38, 157.41, 143.65, 138.32, 137.16, 130.91, 130.18, 127.93, 126.88, 126.79, 126.18, 125.79, 118.38, 117.92, 34.64, 29.43, 20.71.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{20}\text{H}_{22}\text{NO}]^+$: 292.1696, found: 292.1690.



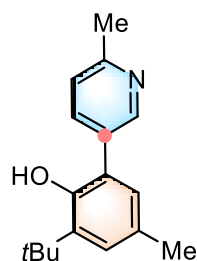
2-(*tert*-Butyl)-6-(isoquinolin-1-yl)-4-methylphenol (**4i**)

Following the general procedure, **4i** was obtained in 44% yield as a yellow solid.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.96 (s, 1H), 8.54 (d, $J = 5.7$ Hz, 1H), 8.14 – 8.12 (m, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.87 – 7.79 (m, 2H), 7.69 – 7.65 (m, 1H), 7.19 – 7.16 (m, 2H), 2.29 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 158.49, 152.53, 140.12, 137.15, 137.09, 130.66, 129.47, 128.42, 127.86, 127.38, 127.23, 126.65, 126.07, 122.70, 120.26, 34.64, 29.53, 20.62.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{20}\text{H}_{22}\text{NO}]^+$: 292.1696, found: 292.1690.



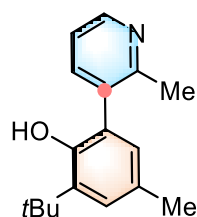
2-(*tert*-Butyl)-4-methyl-6-(6-methylpyridin-3-yl)phenol (**4j**)

Following the general procedure, **4j** was obtained in 56% yield as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.16 (d, $J = 2.2$ Hz, 1H), 6.87 (d, $J = 2.2$ Hz, 1H), 5.67 (s, 1H), 2.64 (s, 3H), 2.33 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.32, 149.50, 149.38, 139.60, 137.30, 132.39, 129.66, 128.66, 128.39, 125.12, 124.81, 34.90, 29.95, 23.91, 20.91.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1691.



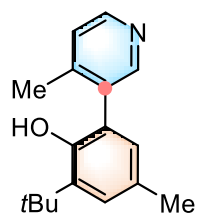
2-(*tert*-Butyl)-4-methyl-6-(2-methylpyridin-3-yl)phenol (**4k**)

Following the general procedure, **4k** was obtained in 53% yield as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.45 (s, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.18 – 7.14 (m, 1H), 7.06 (s, 1H), 6.66 (s, 1H), 5.10 (s, 1H), 2.31 (s, 3H), 2.23 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.08, 149.12, 148.88, 139.51, 136.80, 132.79, 129.18, 128.16, 128.00, 126.39, 121.77, 34.94, 29.77, 22.70, 20.91.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{17}\text{H}_{22}\text{NO}]^+$: 256.1696, found: 256.1691.



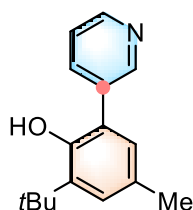
2-(*tert*-Butyl)-4-methyl-6-(4-methylpyridin-3-yl)phenol (**4l**)

Following the general procedure, **4l** was obtained in 61% yield as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 5.3$ Hz, 1H), 8.23 (s, 1H), 7.23 (d, $J = 5.3$ Hz, 1H), 7.08 (d, $J = 2.2$ Hz, 1H), 6.62 (d, $J = 2.2$ Hz, 1H), 4.99 (s, 1H), 2.22 (s, 3H), 2.16 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.38, 149.85, 149.70, 147.84, 137.37, 135.31, 129.43, 128.40, 128.32, 126.13, 124.47, 34.89, 29.83, 20.90, 19.76.

HRMS (ESI) $[M+H]^+$ calculated m/z for $[C_{17}H_{22}NO]^+$: 256.1696, found: 256.1691.



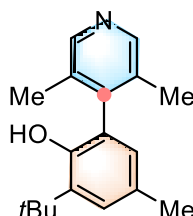
2-(*tert*-Butyl)-4-methyl-6-(pyridin-3-yl)phenol (4m)

Following the general procedure, **4m** was obtained in 43% yield as a white solid.

1H NMR (400 MHz, DMSO- d_6) δ 8.61 (s, 1H), 8.50 (d, $J = 5.0$ Hz, 1H), 8.07 (s, 1H), 7.86 – 7.83 (m, 1H), 7.45 – 7.42 (m, 1H), 7.04 (d, $J = 2.2$ Hz, 1H), 6.87 – 6.86 (m, 1H), 2.24 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 150.07, 149.79, 147.58, 138.72, 136.99, 135.12, 128.70, 127.96, 127.19, 123.48, 34.65, 29.84, 20.53.

HRMS (ESI) $[M+H]^+$ calculated m/z for $[C_{16}H_{20}NO]^+$: 242.1539, found: 242.1534.



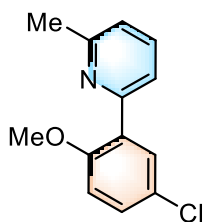
2-(*tert*-Butyl)-6-(3,5-dimethylpyridin-4-yl)-4-methylphenol (4n)

Following the general procedure, **4n** was obtained in 50% yield as a white solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, $J = 2.2$ Hz, 1H), 6.96 (s, 2H), 6.77 (d, $J = 2.2$ Hz, 1H), 5.80 (s, 1H), 2.46 (s, 6H), 2.23 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.65, 149.08, 147.25, 137.11, 129.25, 128.39, 127.83, 126.79, 121.00, 35.05, 29.84, 24.47, 20.91.

HRMS (ESI) $[M+H]^+$ calculated m/z for $[C_{18}H_{24}NO]^+$: 270.1852, found: 270.1847.



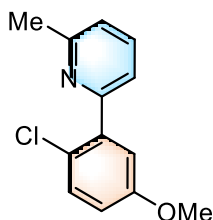
2-(5-Chloro-2-methoxyphenyl)-6-methylpyridine (6a)

Following the general procedure, **6a** was obtained in 31% yield as a white solid.

^1H NMR (400 MHz, DMSO- d_6) δ 7.75 – 7.67 (m, 3H), 7.43 (dd, J = 8.8, 2.9 Hz, 1H), 7.22 – 7.16 (m, 2H), 3.83 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 157.65, 155.71, 152.63, 136.43, 129.91, 129.83, 129.27, 124.46, 121.84, 113.93, 56.04, 24.23.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{13}\text{ClNO}]^+$: 234.0680, found: 234.0676.



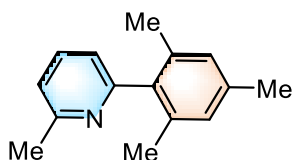
2-(2-Chloro-5-methoxyphenyl)-6-methylpyridine (6b)

Following the general procedure, **6b** was obtained in 24% yield as white solid.

^1H NMR (400 MHz, DMSO- d_6) δ 7.79 – 7.75 (m, 1H), 7.46 – 7.41 (m, 2H), 7.28 (d, J = 7.7 Hz, 1H), 7.07 – 6.00 (m, 2H), 3.79 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 158.04, 157.71, 155.38, 139.97, 136.57, 130.69, 122.35, 122.18, 121.54, 116.51, 115.70, 55.59, 24.13.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{13}\text{H}_{13}\text{ClNO}]^+$: 234.0680, found: 234.0677.



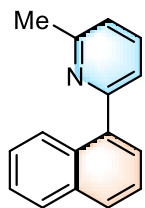
2-Mesityl-6-methylpyridine (8a)

Following the general procedure, **8** was obtained in 91% yield as white solid with HFIP as solvent (0.5 M).

^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.49 (m, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.84 (s, 2H), 2.53 (s, 3H), 2.23 (s, 3H), 1.94 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.43, 158.30, 137.96, 137.38, 136.59, 135.77, 128.39, 121.67, 121.10, 24.73, 21.19, 20.27.

HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated m/z for $[\text{C}_{15}\text{H}_{18}\text{N}]^+$: 212.1435, found: 212.1430.

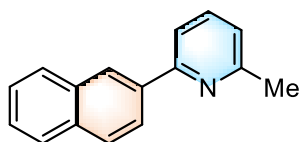


2-Methyl-6-(naphthalen-1-yl)pyridine (**8b-1**)

Following the general procedure, **8b-1** was obtained as white solid in 40% yield.

The spectra data were matched with the reported reference.¹

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.4$ Hz, 1H), 7.82 (d, $J = 7.4$ Hz, 2H), 7.65 – 7.61 (m, 1H), 7.52 – 7.36 (m, 4H), 7.29 (d, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 7.7$ Hz, 1H), 2.60 (s, 3H).



2-Methyl-6-(naphthalen-2-yl)pyridine (**8b-2**)

Following the general procedure, **8b-2** was obtained as white solid in 23% yield.

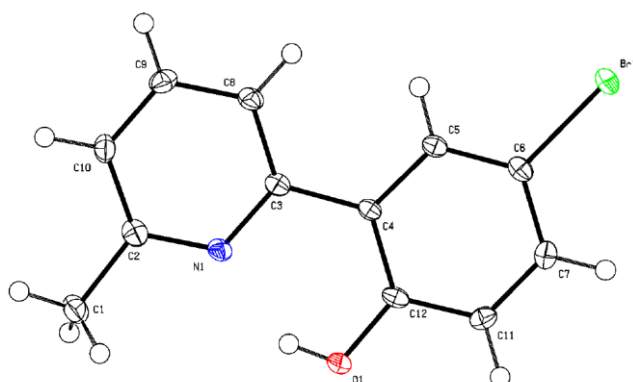
The spectra data were matched with the reported reference.²

^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 8.07 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.89 – 7.85 (m, 2H), 7.81 – 7.78 (m, 1H), 7.64 – 7.59 (m, 2H), 7.45 – 7.41 (m, 2H), 7.07 – 7.05 (m, 1H), 2.61 (s, 3H).

Reference

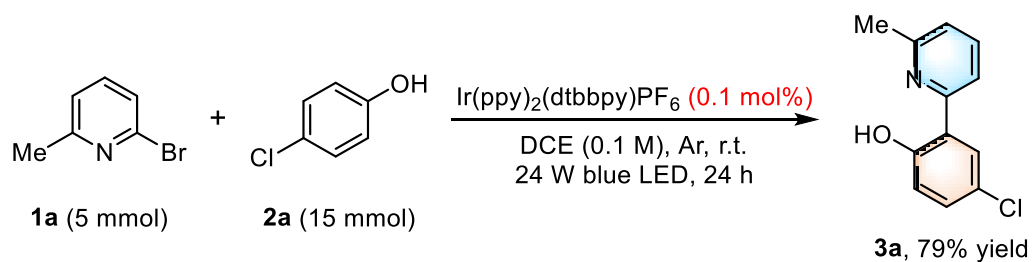
1. So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2007**, *9*, 2795.
2. Addla, D.; Kanteveri, S. *J. Heterocyclic Chem.* **2014**, *51*, E384.

Crystallographic Data



Empirical formula	C ₁₂ H ₁₀ BrNO
Formula weight	264.12
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	7.127 (2)
b/Å	7.435 (3)
c/Å	10.981 (4)
α/°	72.738 (11)
β/°	84.610 (12)
γ/°	67.998 (12)
Volume/Å ³	515.1 (3)
Z	2
ρ _{calc} /cm ³	1.703
μ/mm ⁻¹	3.959
F(000)	264.0
Crystal size/mm ³	0.38 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.162 to 56.75
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	8229
Independent reflections	2560 [R _{int} = 0.0637, R _{sigma} = 0.0590]
Data/restraints/parameters	2560/0/138
Goodness-of-fit on F ²	1.061
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0343, wR ₂ = 0.0790
Final R indexes [all data]	R ₁ = 0.0436, wR ₂ = 0.0828
Largest diff. peak/hole / e Å ⁻³	0.84/-0.73

Gram-Scale Synthesis



To an oven-dried 100 mL Schlenk bottle equipped with magnetic bar was added 4-chlorophenol **2a** (1.92 g, 15 mmol, 3 equiv), Ir(ppy)₂(dtbbpy)PF₆ (4.6 mg, 0.1 mol%). The mixture was then placed under vacuum and backfilled with argon three times, followed by the addition of DCE (50 mL) and bromopyridine **1a** (860 mg, 5 mmol, 1 equiv). Then the tube was placed approximate 4~5 cm away from 24 W blue LED and stir vigorously for 24 h with a cooling fan to maintain the reaction at r.t. (about 25 °C). Upon completion of the reaction monitored by TLC, the mixture was concentrated and purified by silica chromatography (pre-basified with Et₃N) to afford product **3a** (867 mg, yellow solid).

Mechanistic Investigations

1. Protection of hydroxyl group

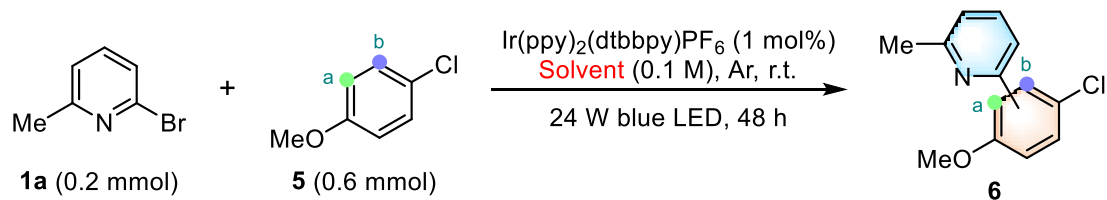
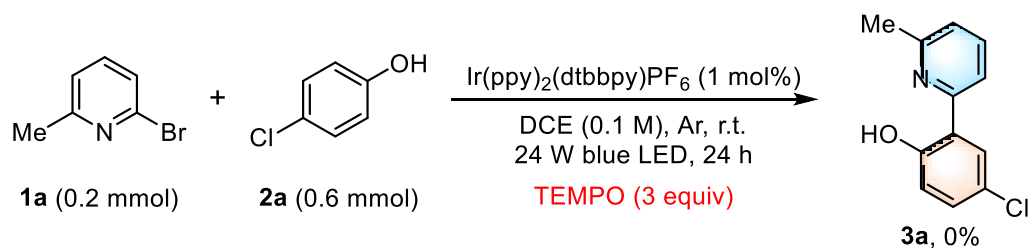


Table S4. Solvent effect

Entry	Solvent	Yield (%)
1	DCE	0
2	HFIP	55 (6a : 6b = 1.3:1)

2. Radical trapping experiment



3. ^1H NMR experiment

In order to examine the interaction between 2-bromo-6-methylpyridine (**1a**) and 4-chlorophenol (**2a**), we carried out the ^1H NMR experiment of the mixture of **1a** and **2a** in 1:3 ratio in CDCl_3 and compared the spectrum with individual ^1H NMR spectrum of **1a** and **2a** (CDCl_3 as locking solvent). As can be seen from Fig. S1, the mixing of **1a** and **2a** caused noticeable shift in the proton signals of both substrates. In particular, the hydroxyl proton of **2a** has shifted from 5.17 ppm to the region between 6.88 to 6.71 ppm, and the proton adjacent to methyl group in **1a** has shifted from 7.10 ppm to the region of 6.88-6.71 ppm. Besides, there were only three sets of proton signals observed for **2a**, indicating that the protonation process was in an equilibrium between **1a** and **2a**.

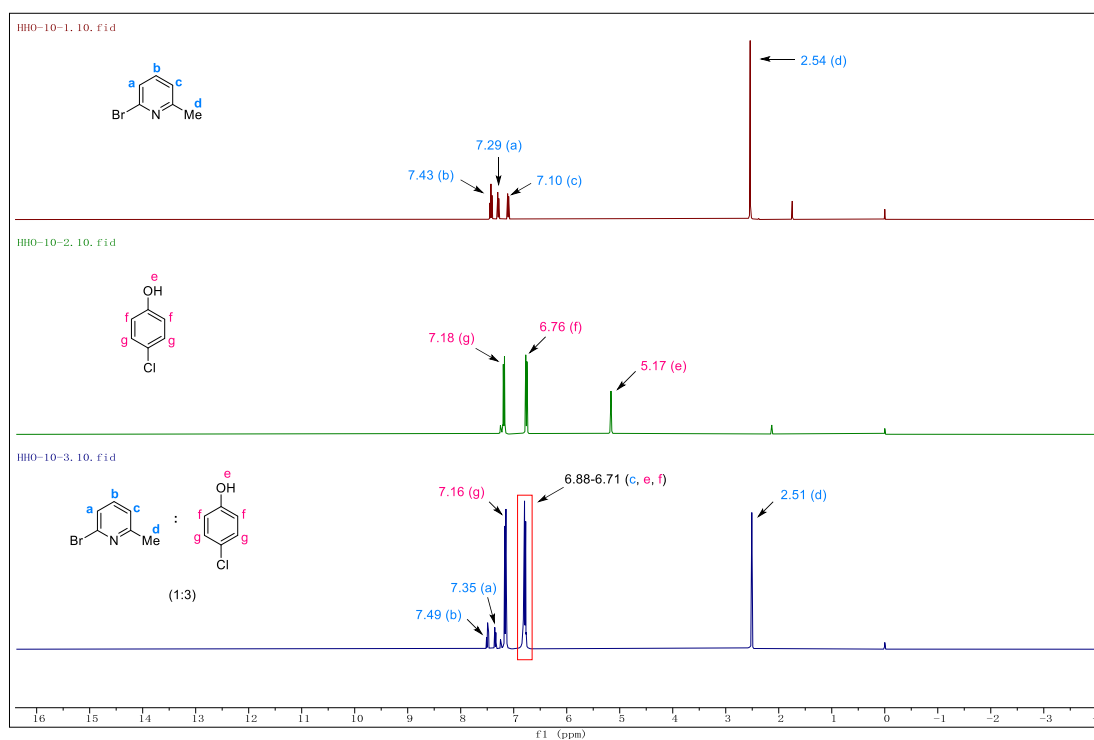


Fig.S1 ^1H NMR experiment of **1a** and **2a** in CDCl_3

4. Control experiment

In order to examine the possible mechanistic pathway of oxidation of phenolate to radical intermediate or the formation of EDA complex between 2-bromo-6-methylpyridine (**1a**) and phenolate ion, we designed and carried out the experiments using sodium phenolate as substrate using reaction conditions that include and exclude the photocatalyst. According to the results in Fig.S2, there was no product detected in both scenarios, ruling out the plausible involvement of EDA complex and phenol radical in the mechanistic pathway.

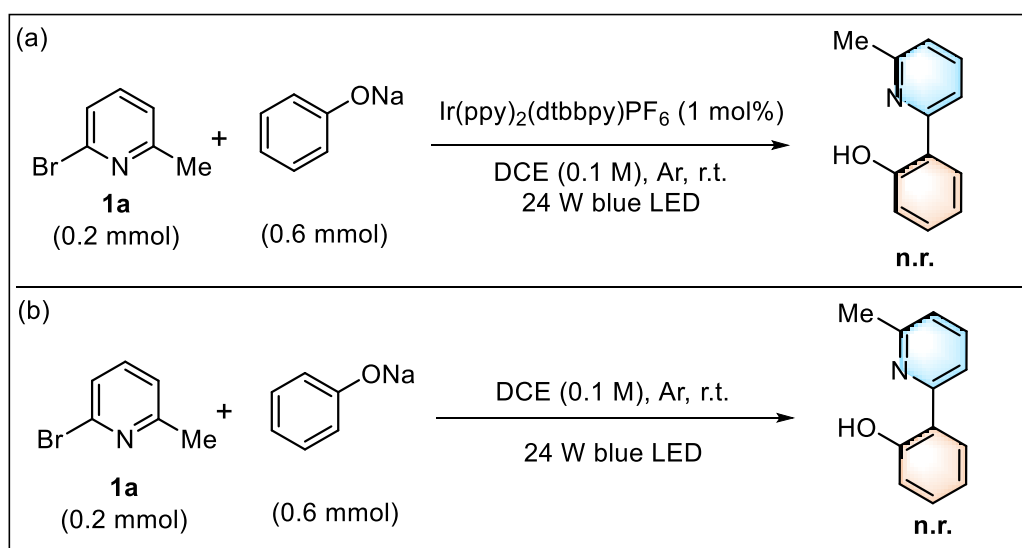
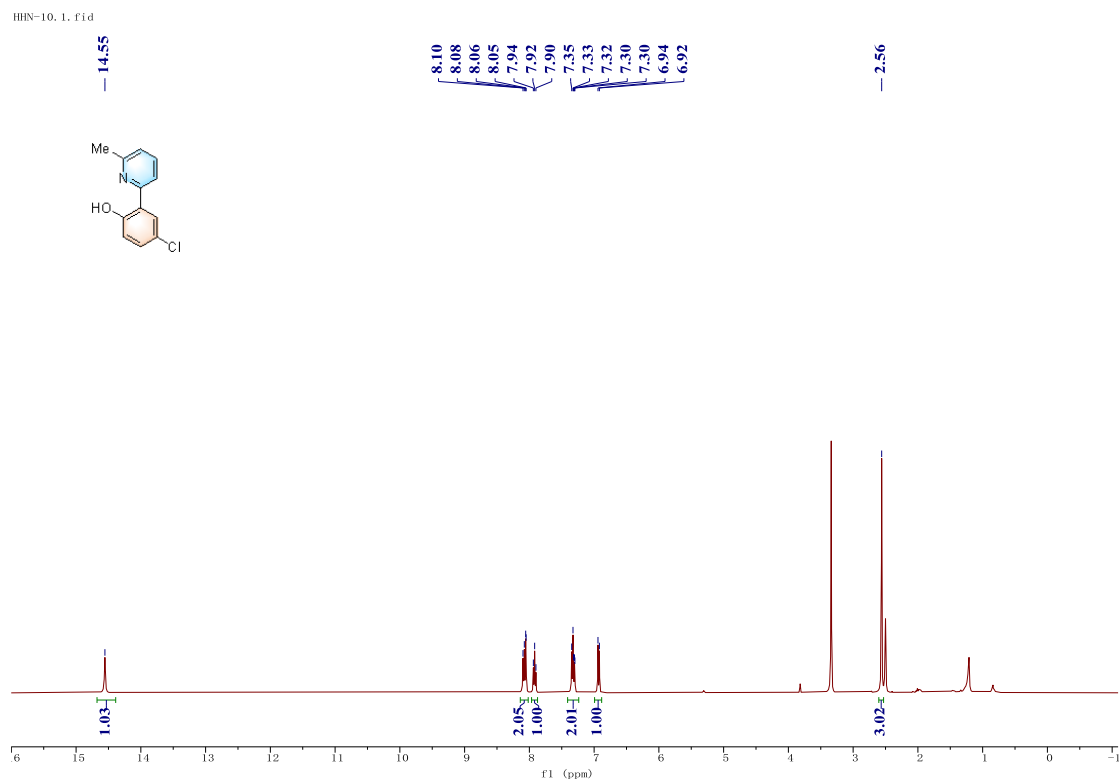
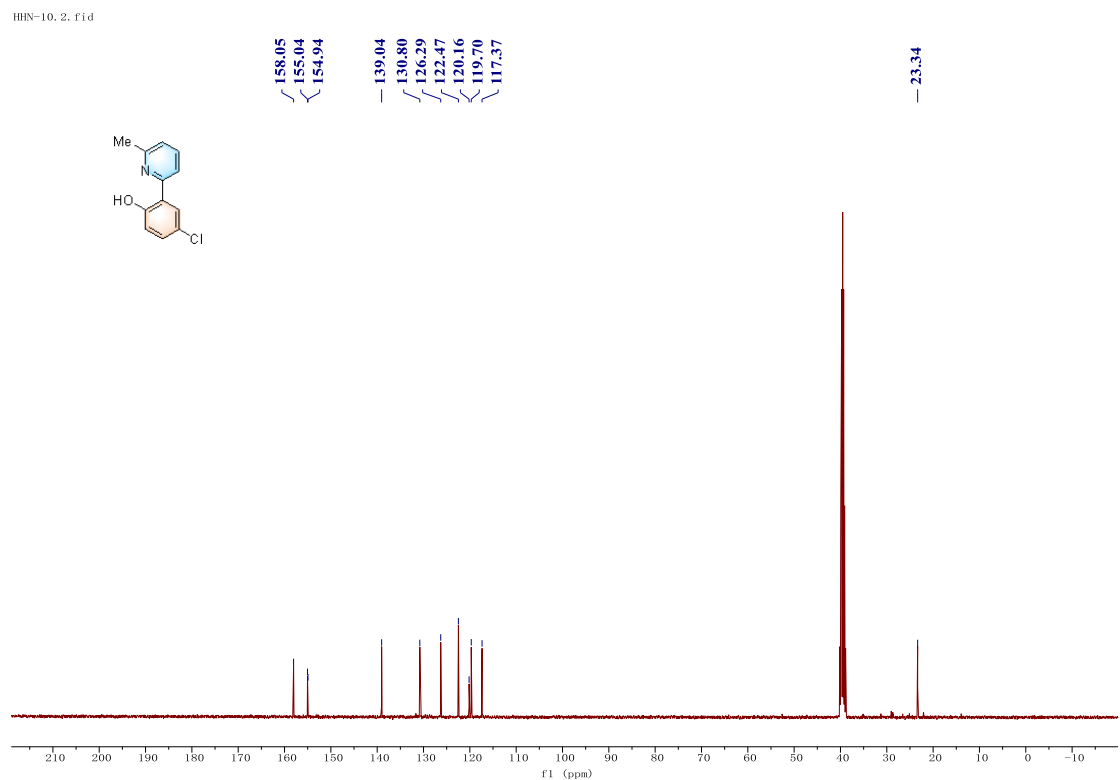


Fig.S2 Control experiment with sodium phenolate

Copies of ^1H , ^{13}C and ^{19}F NMR Spectra

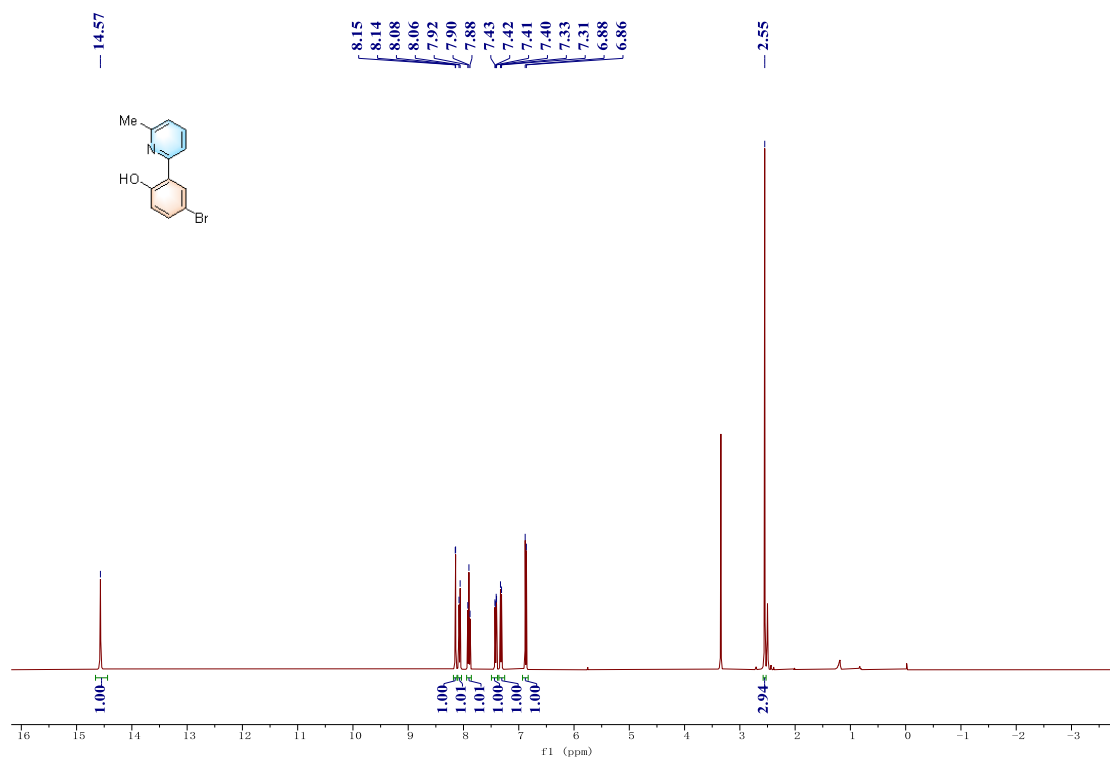


^1H NMR spectrum of 3a



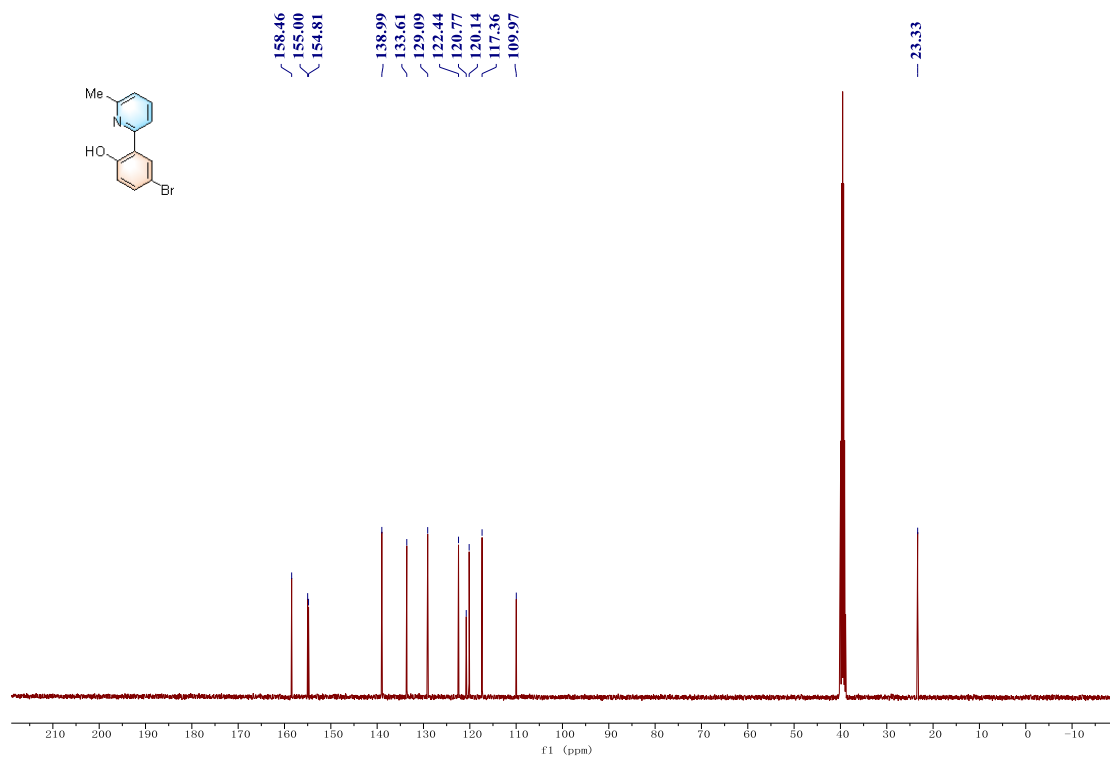
^{13}C NMR spectrum of 3a

HN-31.1.fid

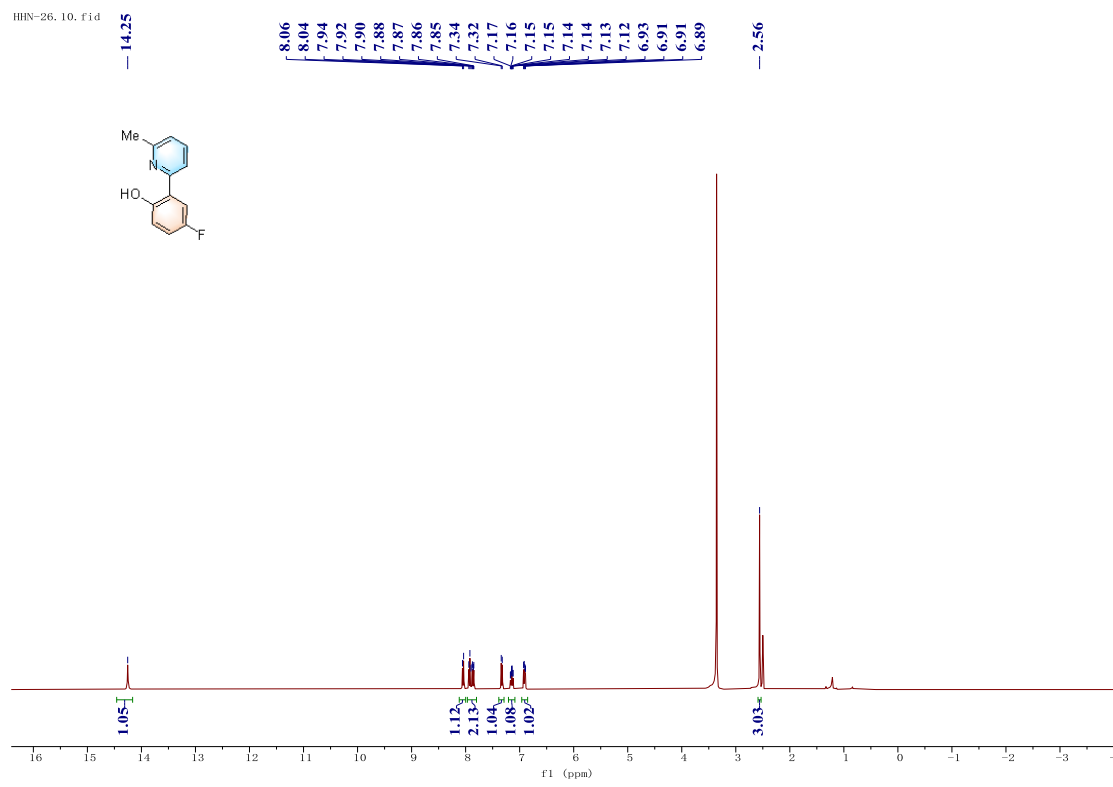


¹H NMR spectrum of 3b

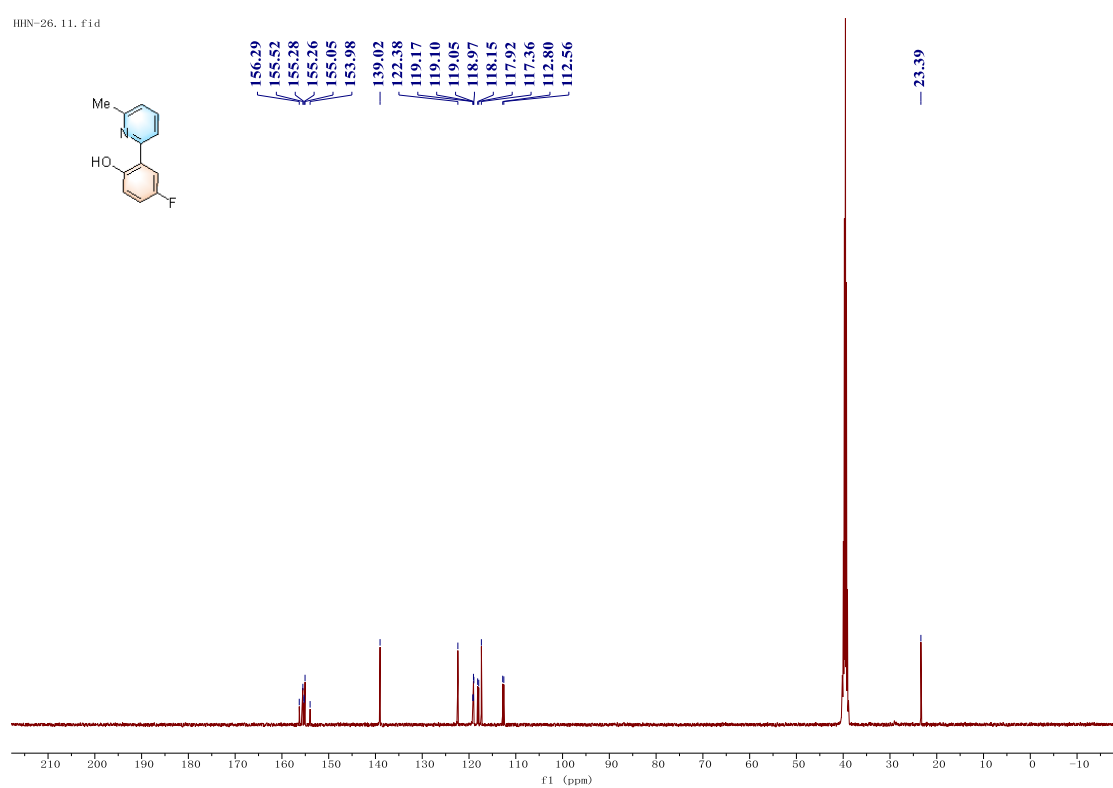
HN-31.2.fid



¹³C NMR spectrum of 3b

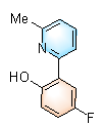


¹H NMR spectrum of 3c

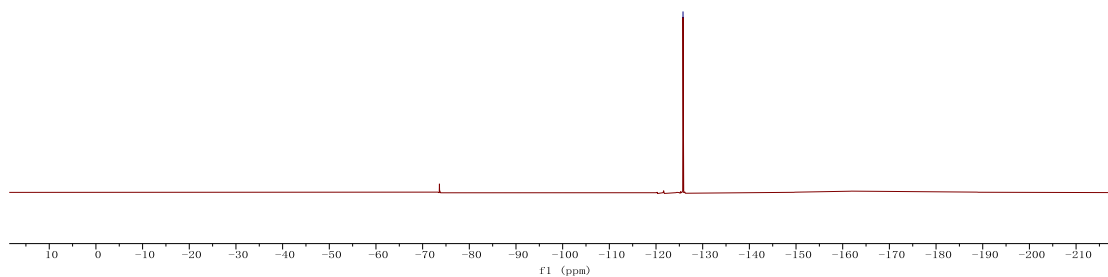


¹³C NMR spectrum of 3c

HIN-26.2.fid

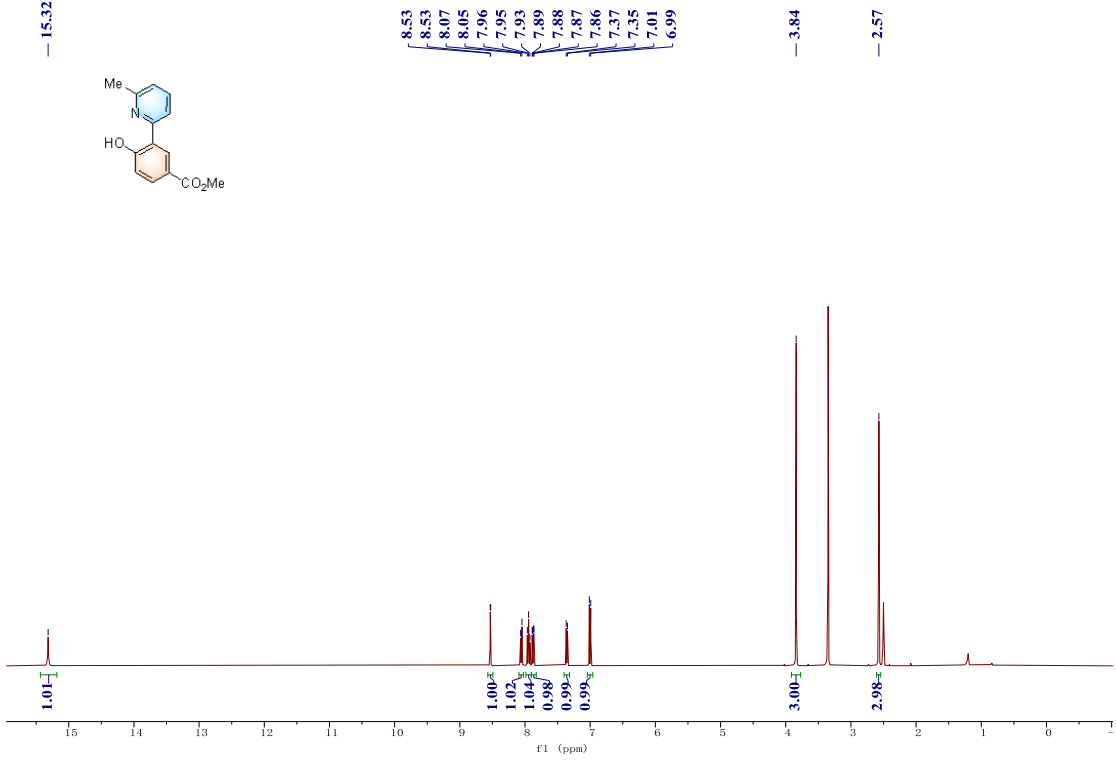


-125.79



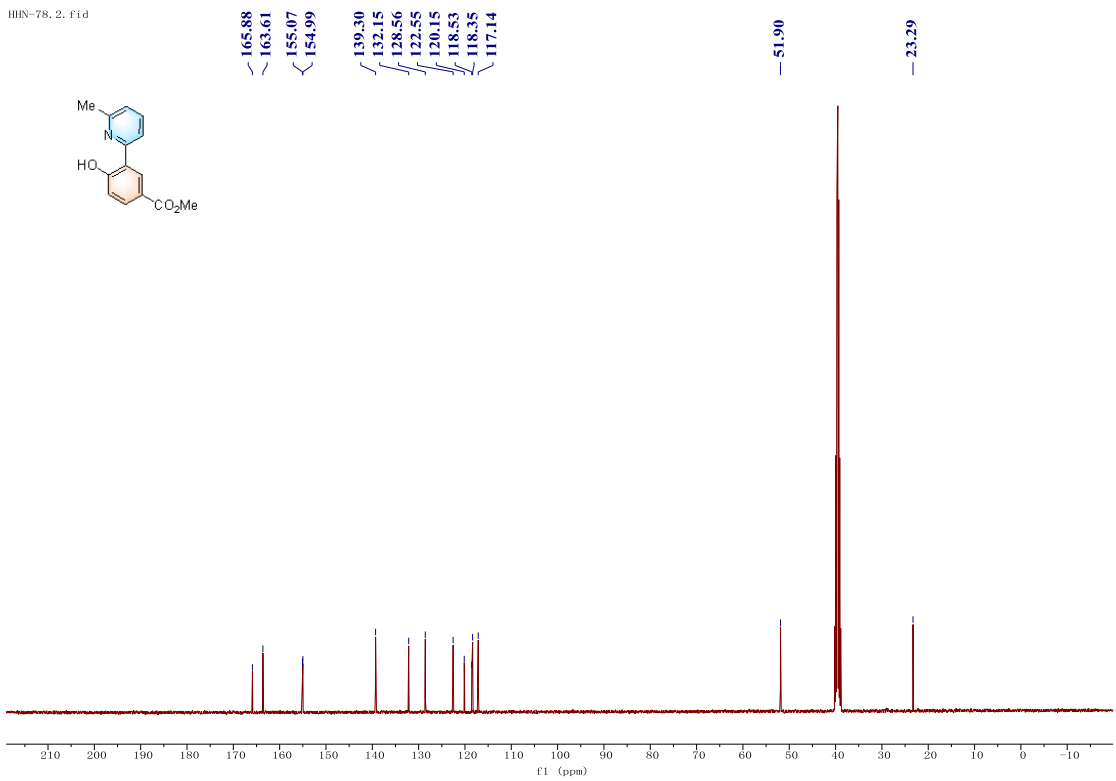
¹⁹F NMR spectrum of 3c

HN-78.1.fid



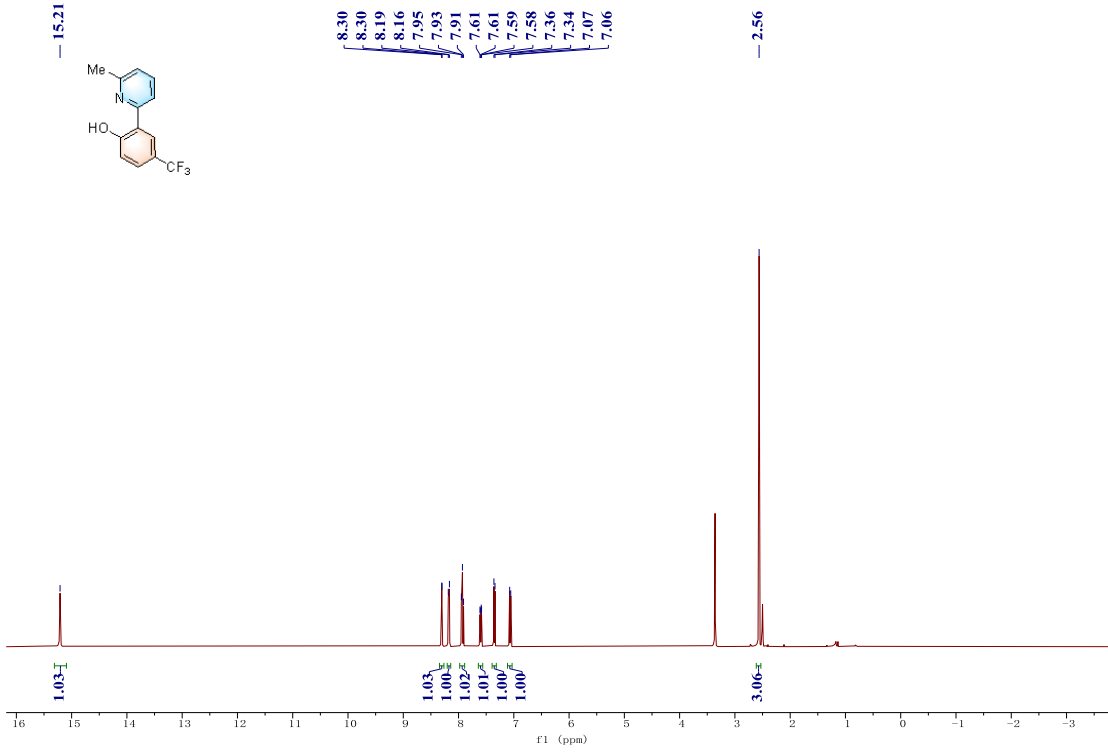
¹H NMR spectrum of 3d

HN-78.2.fid



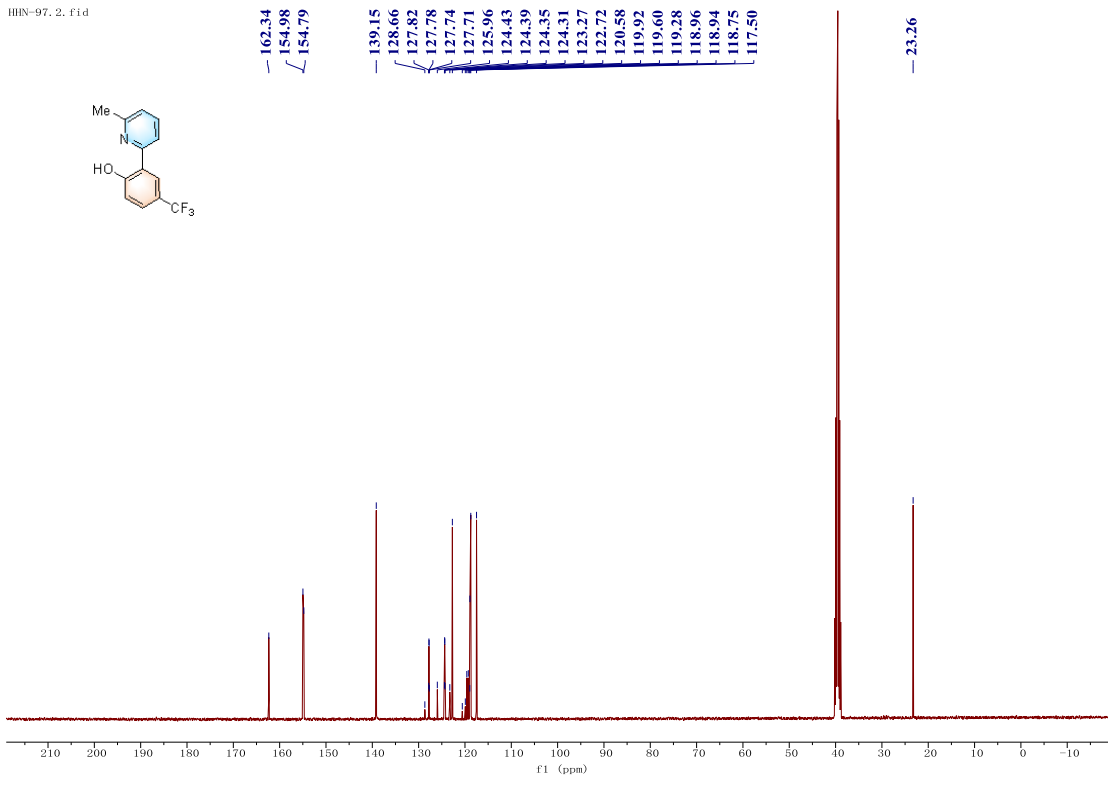
¹³C NMR spectrum of 3d

HN-97.1.fid



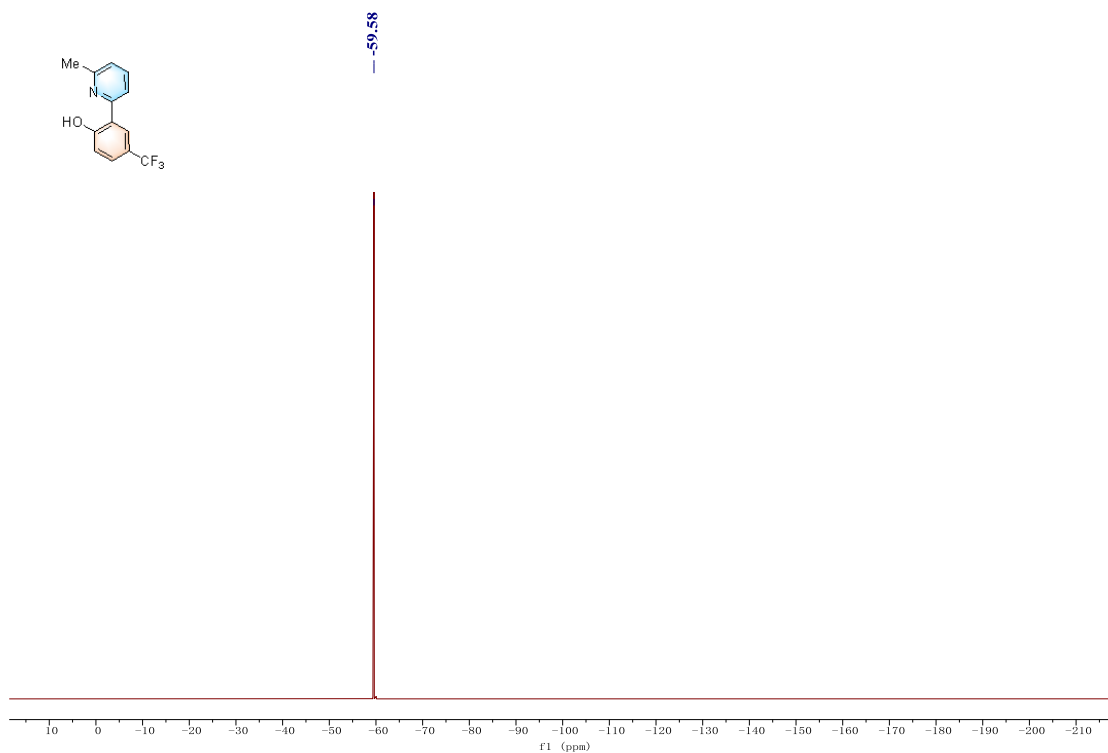
¹H NMR spectrum of 3e

HN-97.2.fid



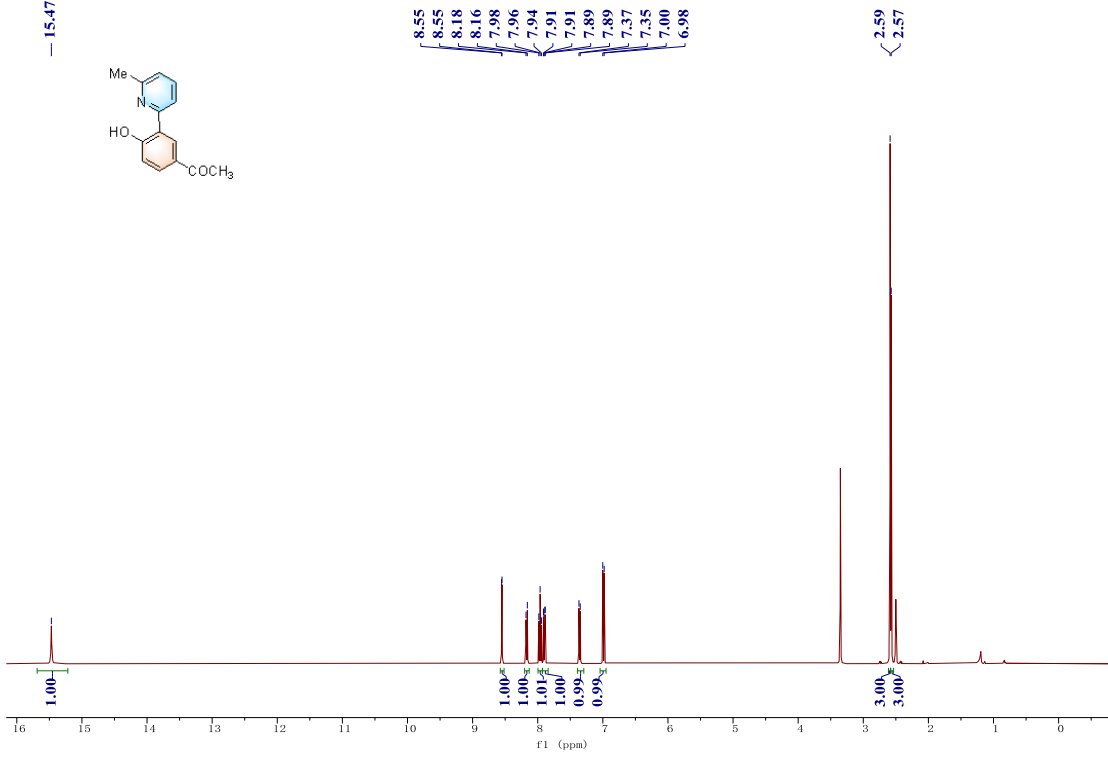
¹³C NMR spectrum of 3e

HIN-97_4.fid



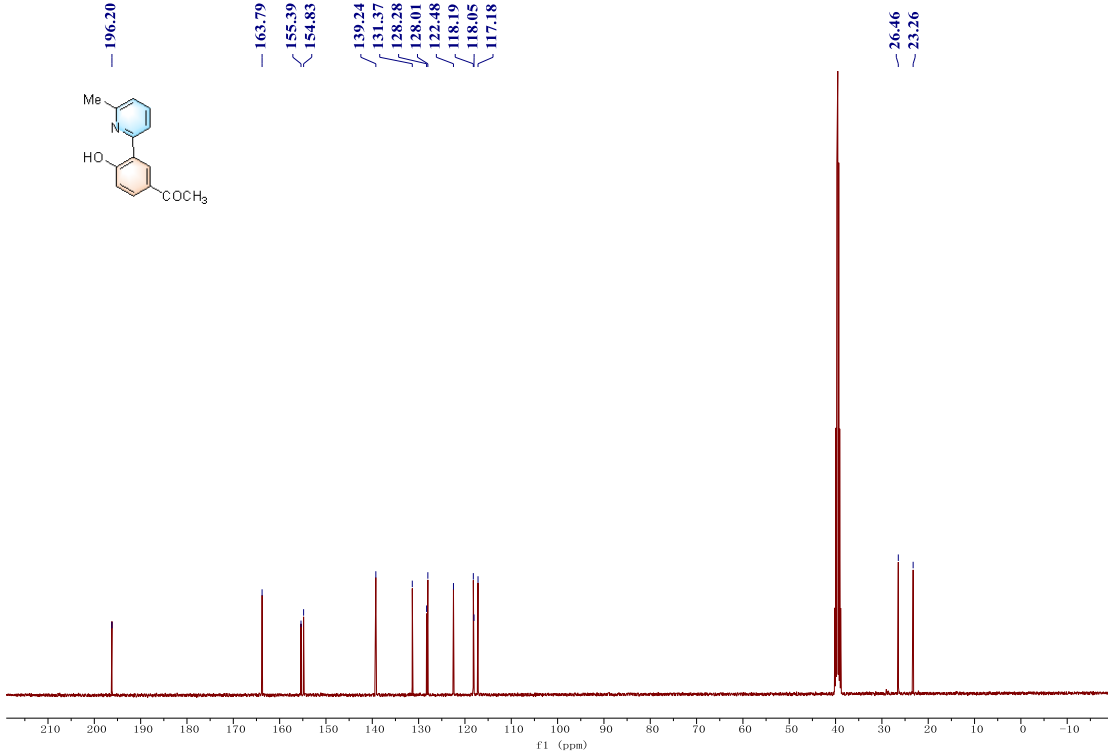
^{19}F NMR spectrum of 3e

HN-75.2.fid



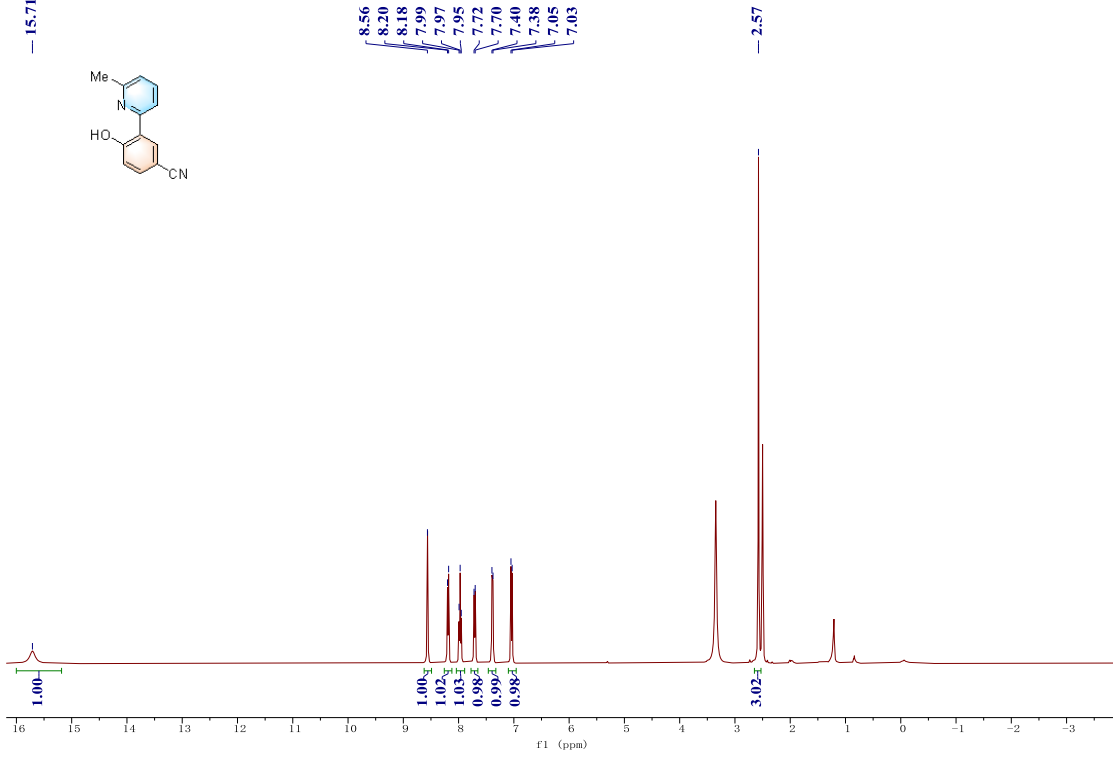
¹H NMR spectrum of 3f

HN-75.3.fid



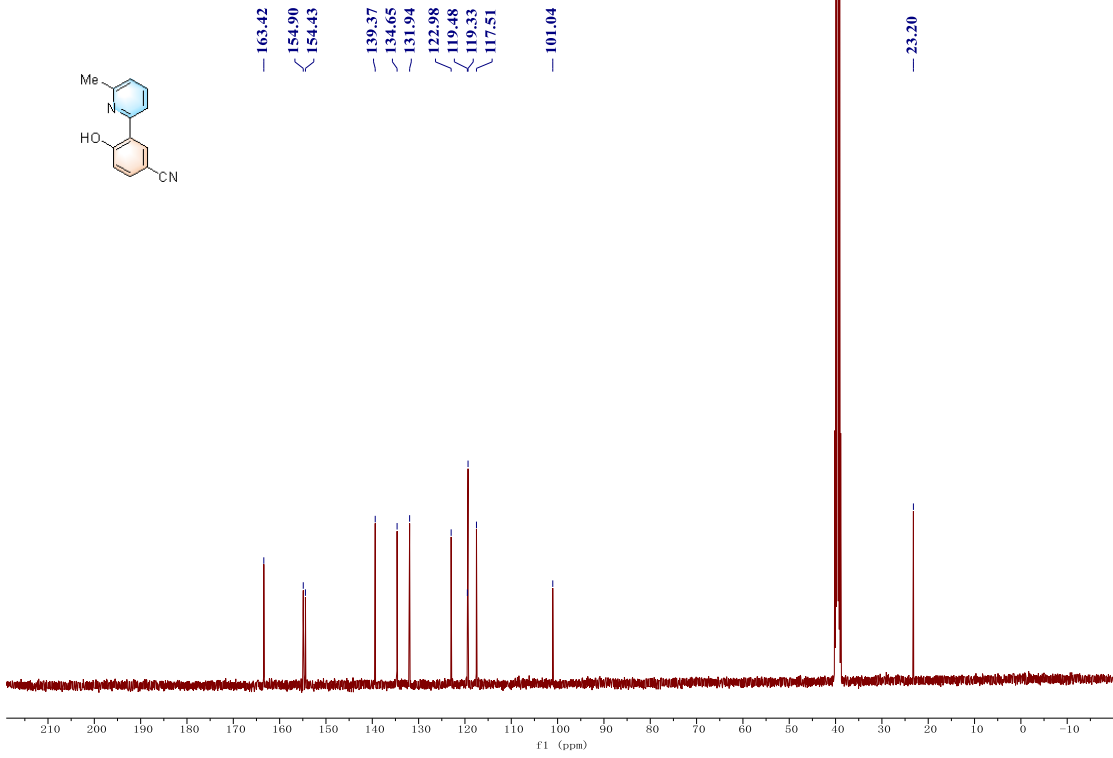
¹³C NMR spectrum of 3f

HN-74.2. F1d

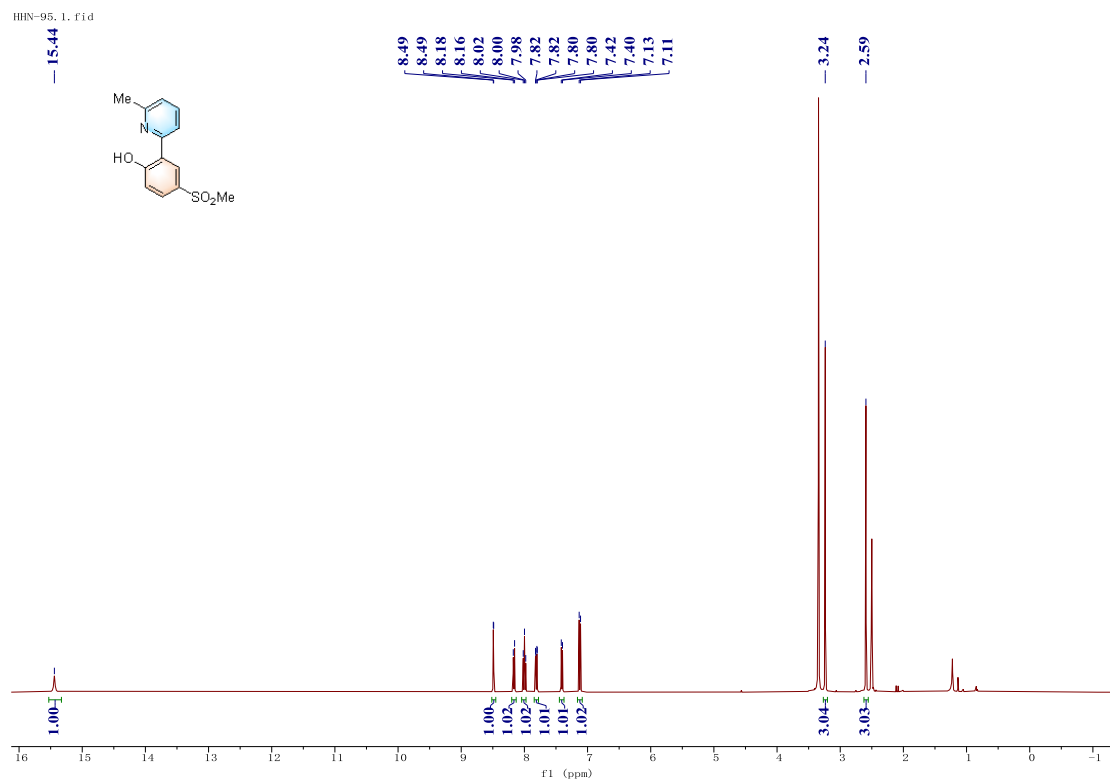


¹H NMR spectrum of 3g

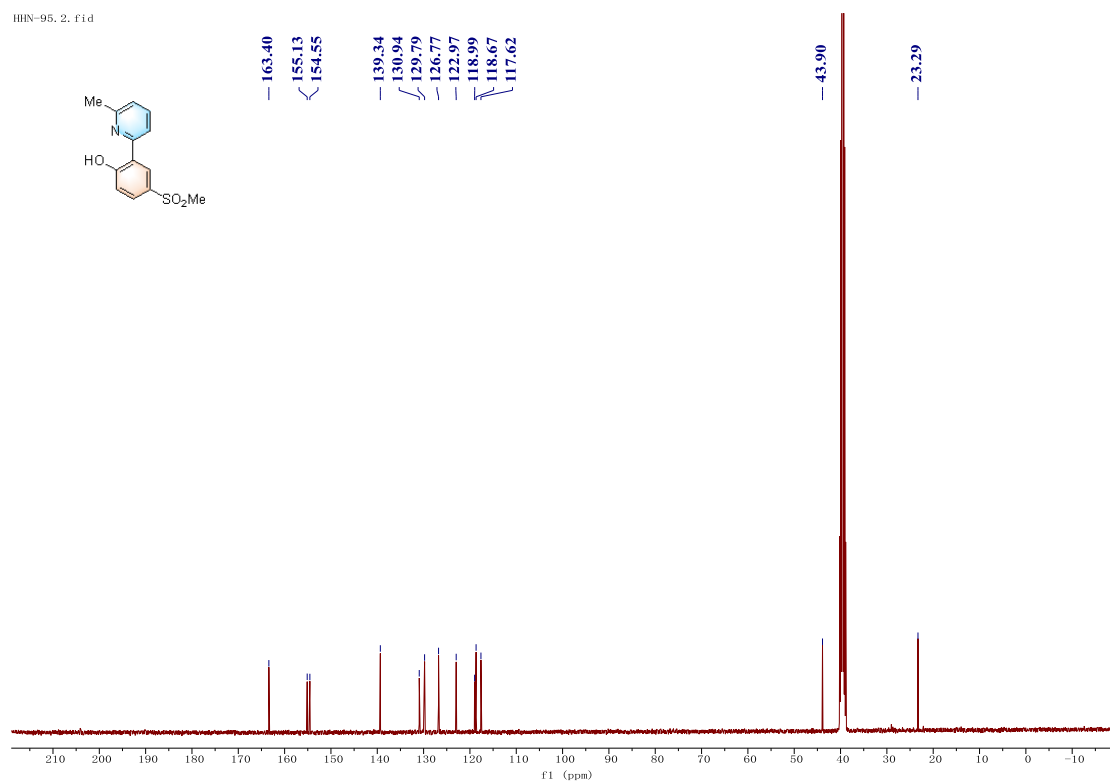
HN-74.3. F1d



¹³C NMR spectrum of 3g

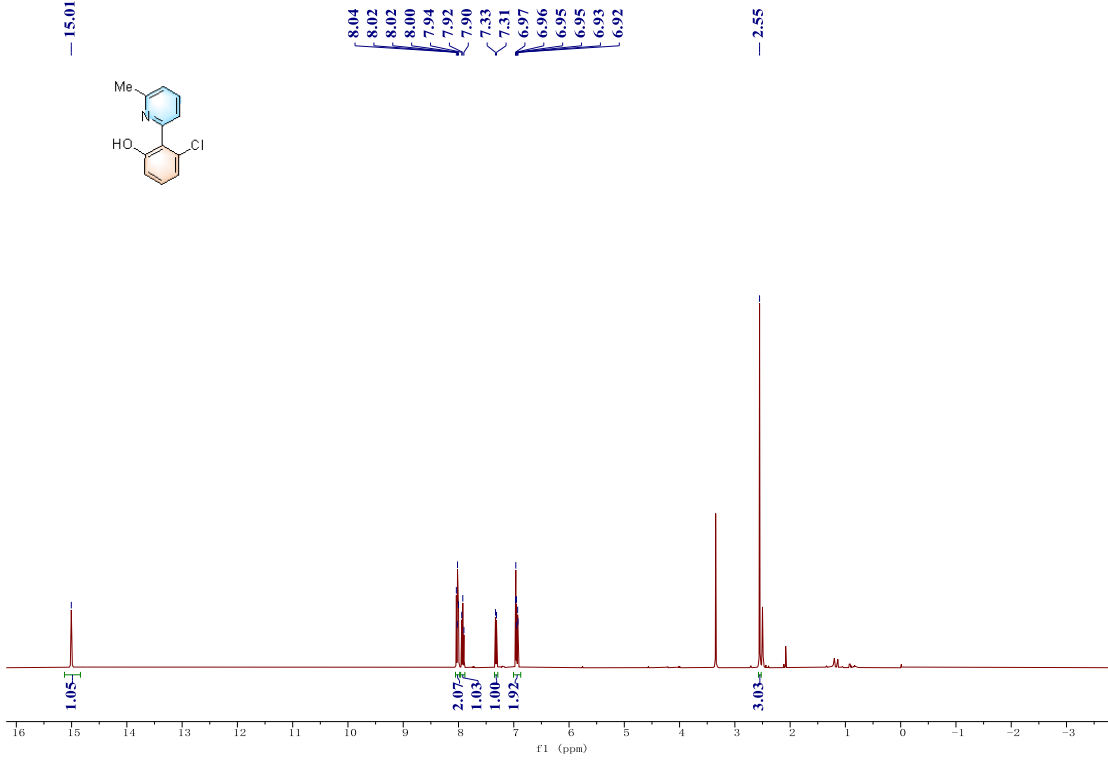


¹H NMR spectrum of 3h



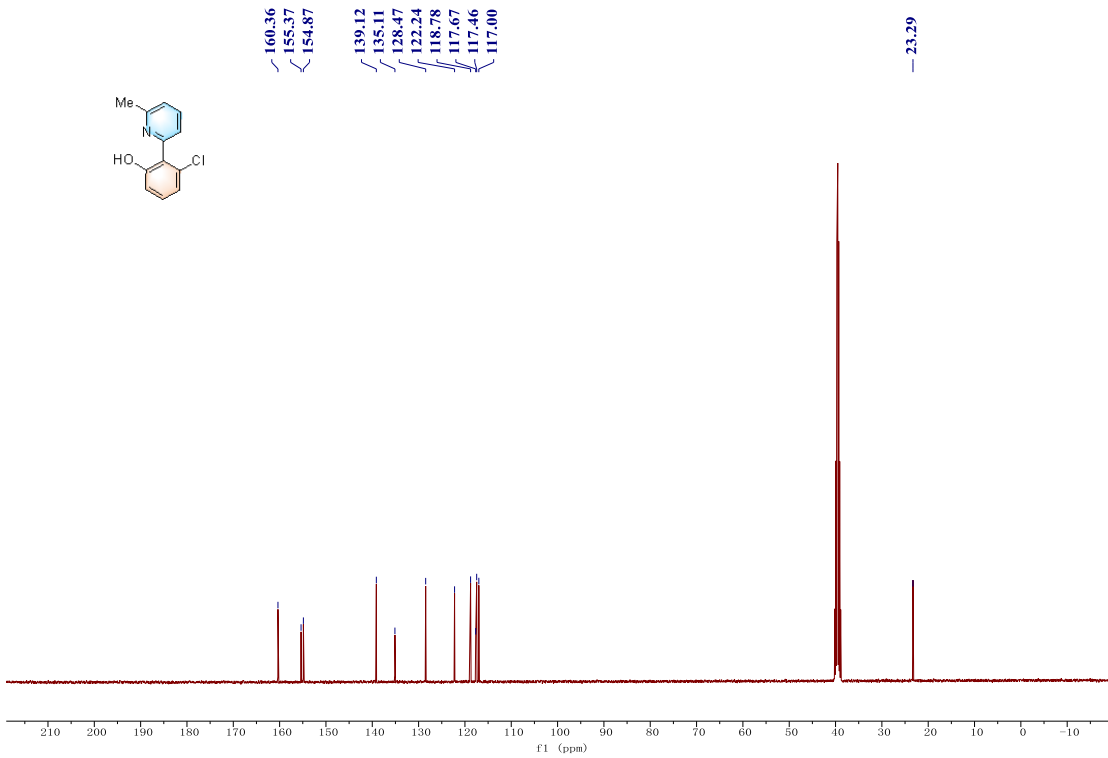
¹³C NMR spectrum of 3h

HN-70a.1.fid



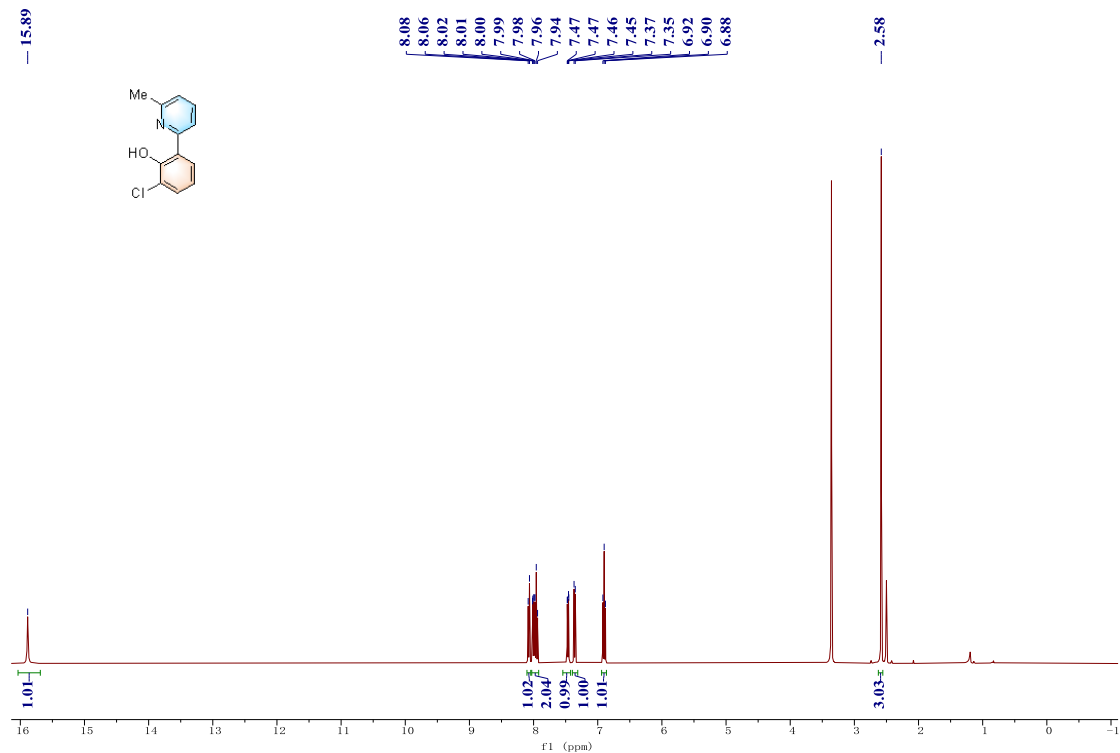
¹H NMR spectrum of 3i

HN-70a.2.fid



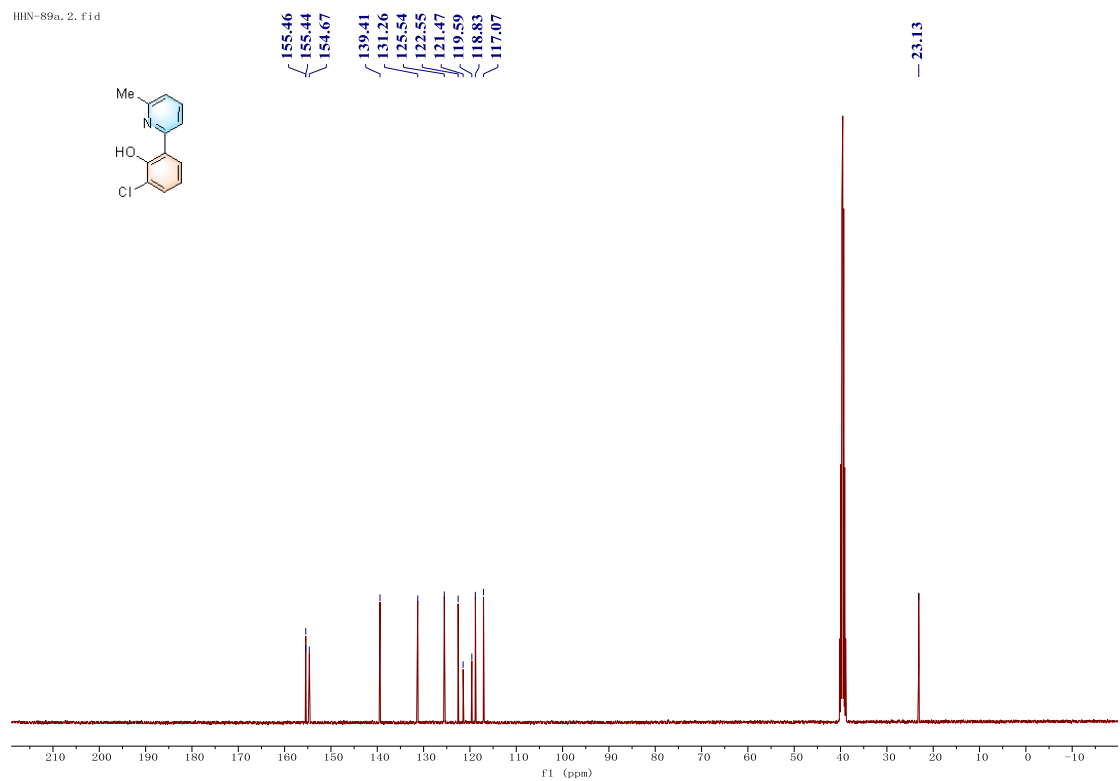
¹³C NMR spectrum of 3i

HN-89a. 1. fid



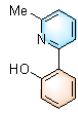
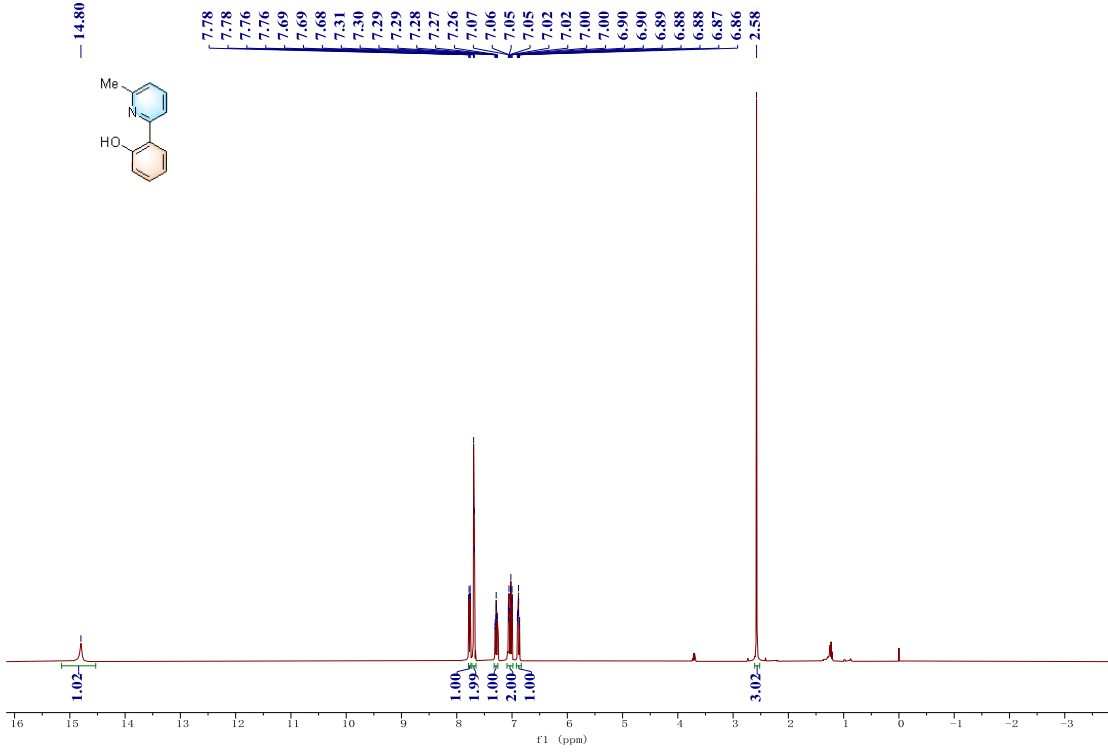
¹H NMR spectrum of 3j

HN-89a. 2. fid



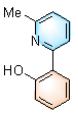
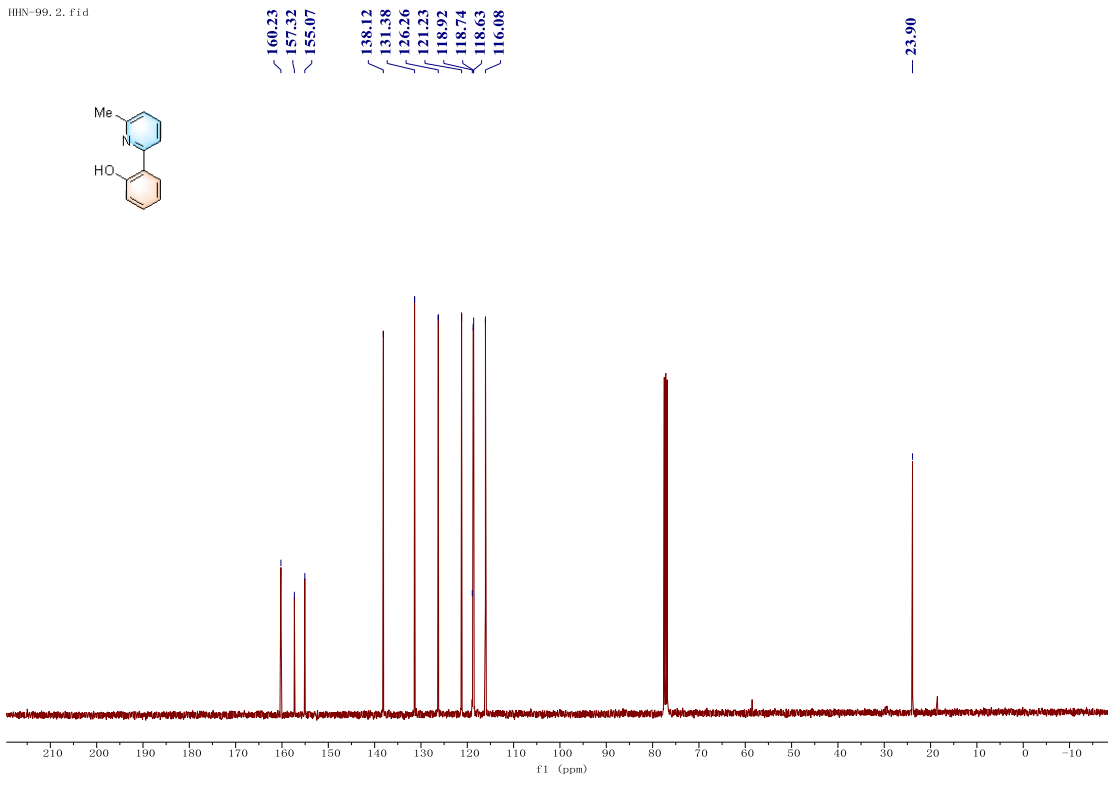
¹³C NMR spectrum of 3j

HN-99.1.fid



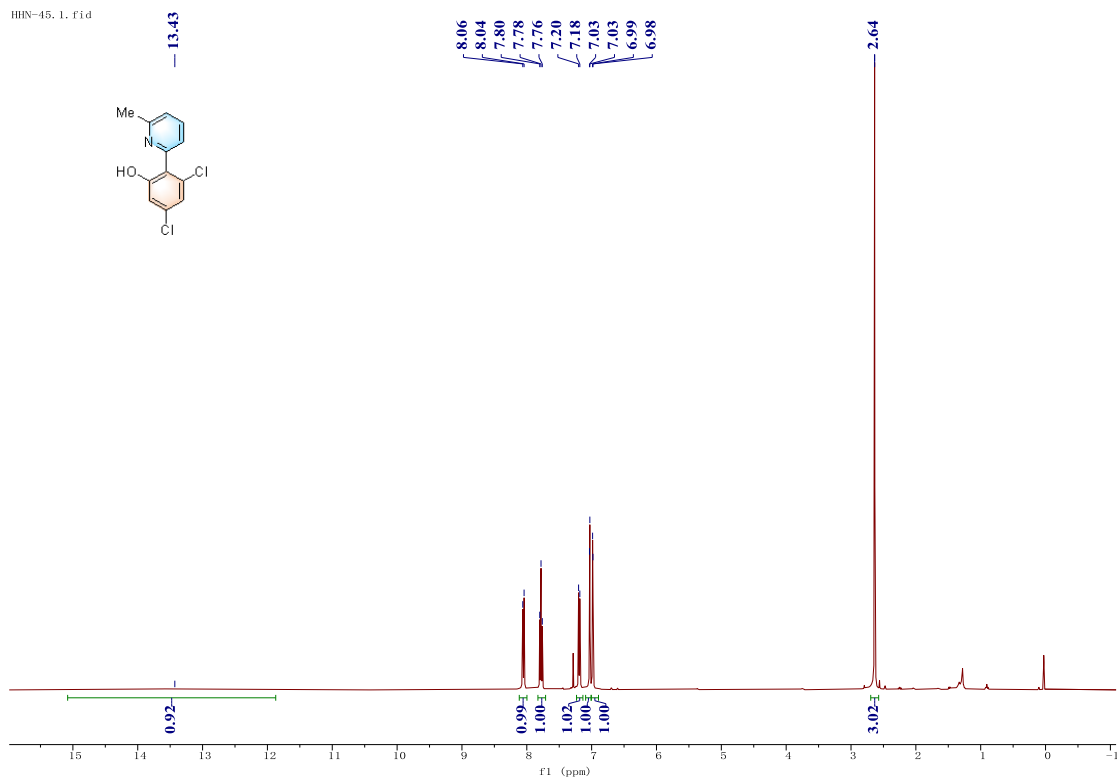
¹H NMR spectrum of 3k

HN-99.2.fid



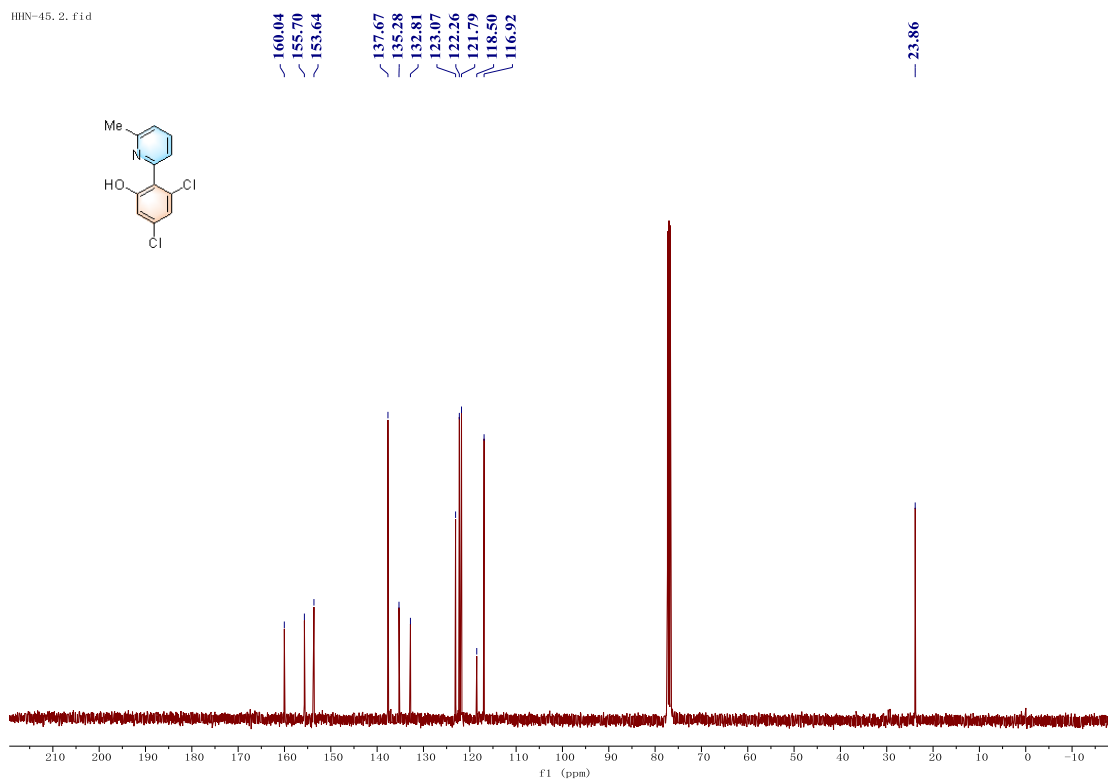
¹³C NMR spectrum of 3k

HN-45.1. F1d



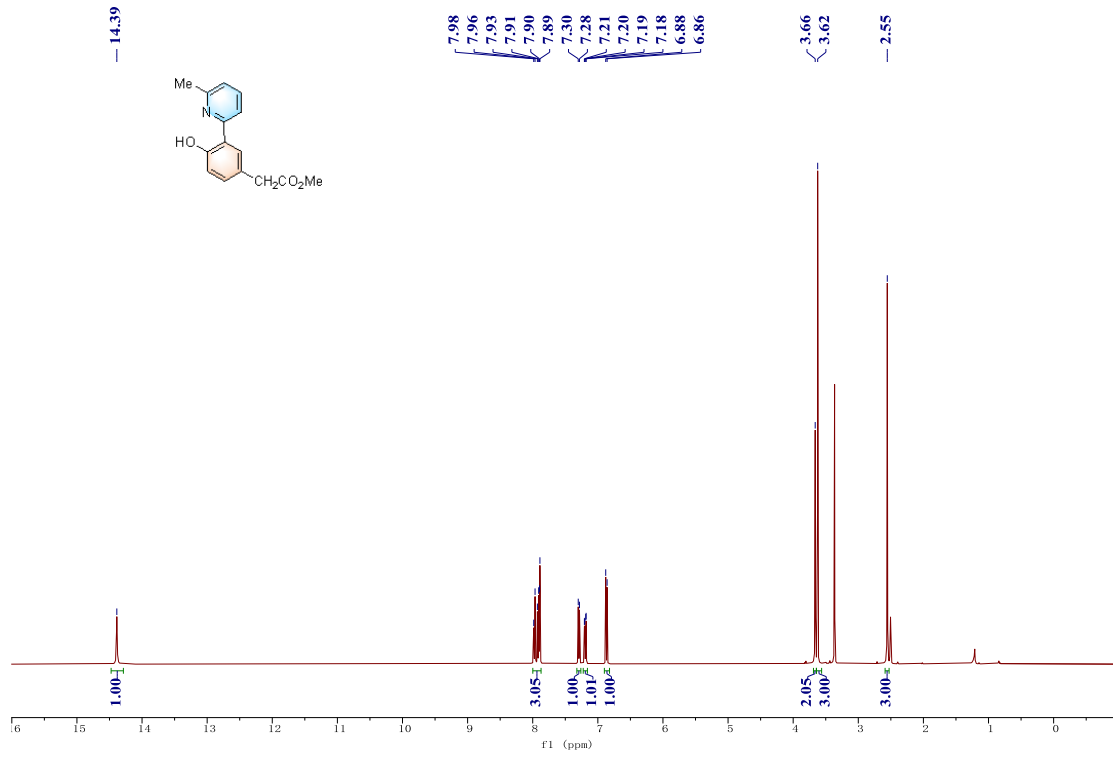
¹H NMR spectrum of 3l

HN-45.2. F1d



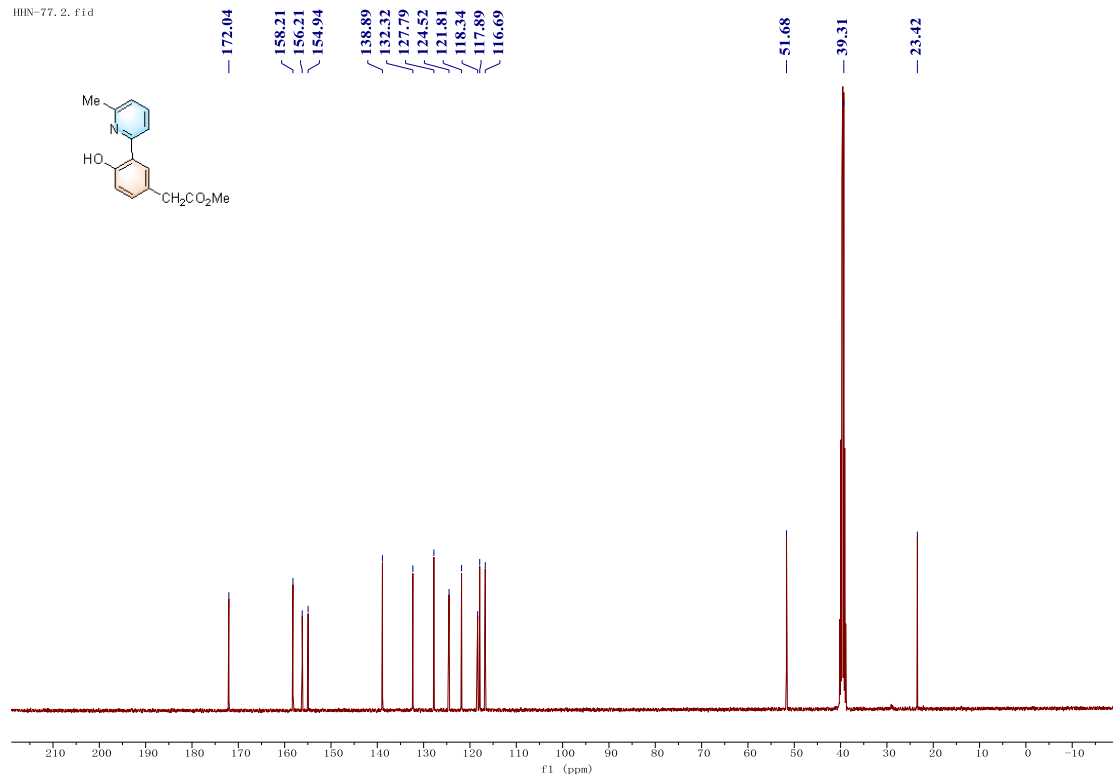
¹³C NMR spectrum of 3l

HN-77.1.Fid



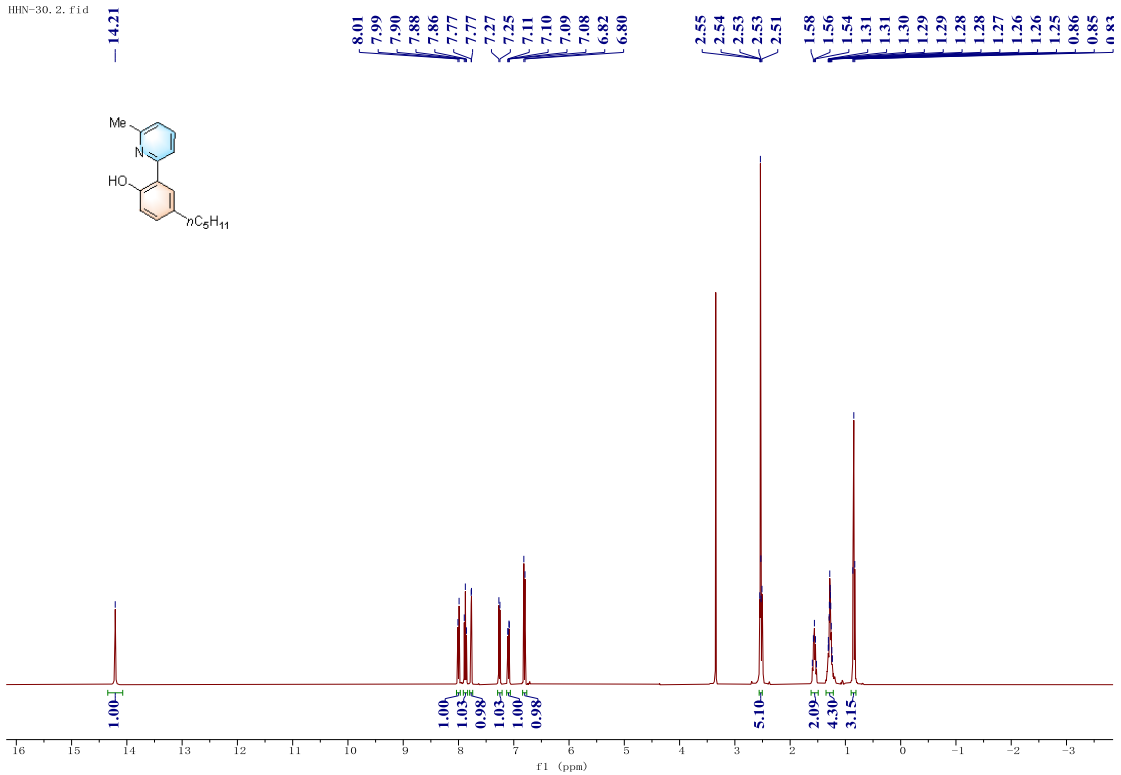
¹H NMR spectrum of 3m

HN-77.2.Fid



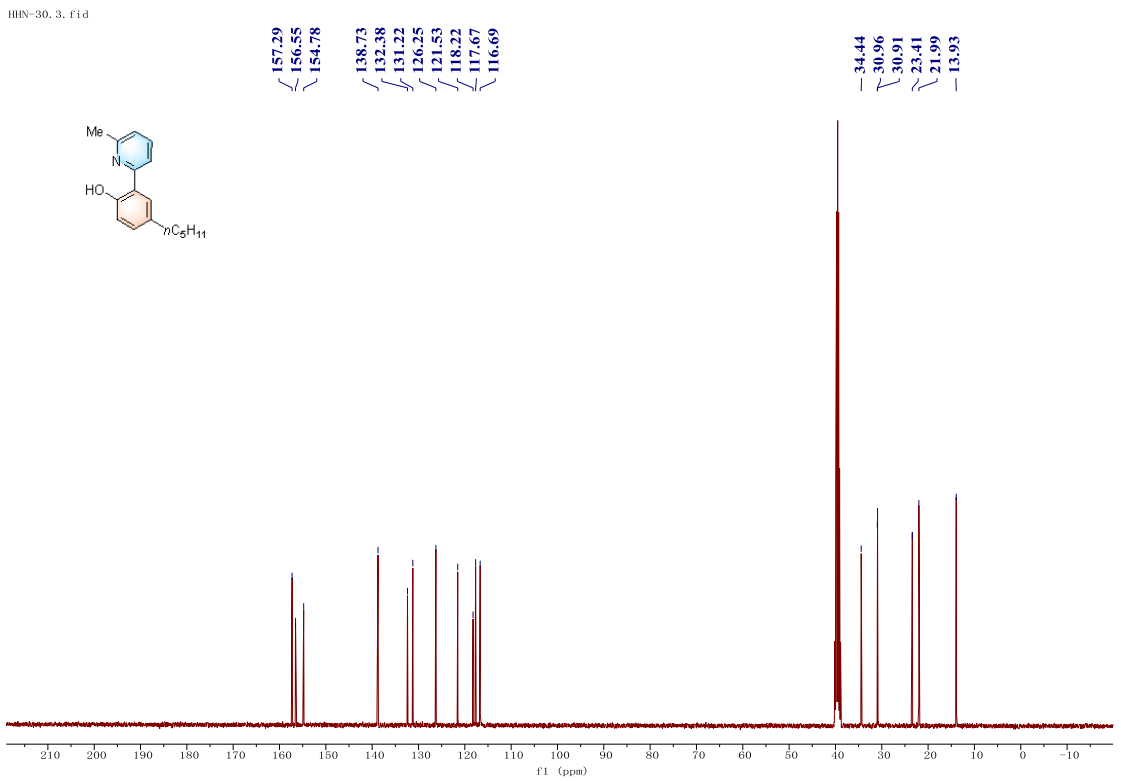
¹³C NMR spectrum of 3m

HN-30.2. F1d



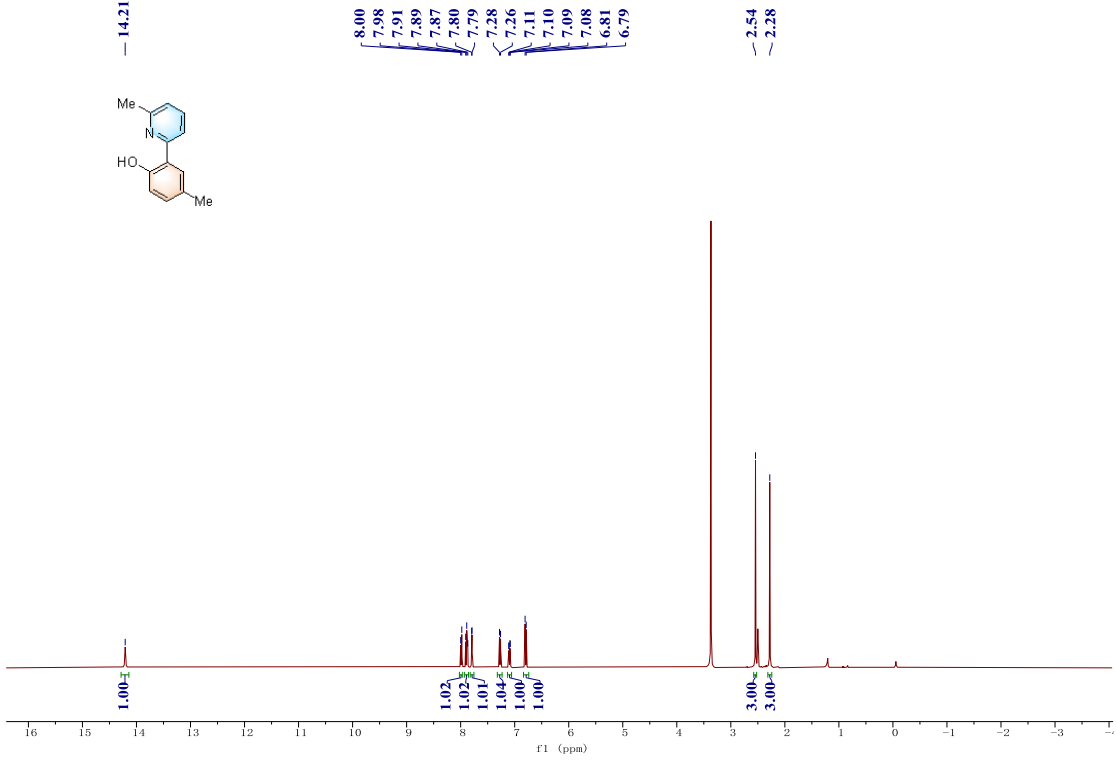
¹H NMR spectrum of 3n

HN-30.3. F1d



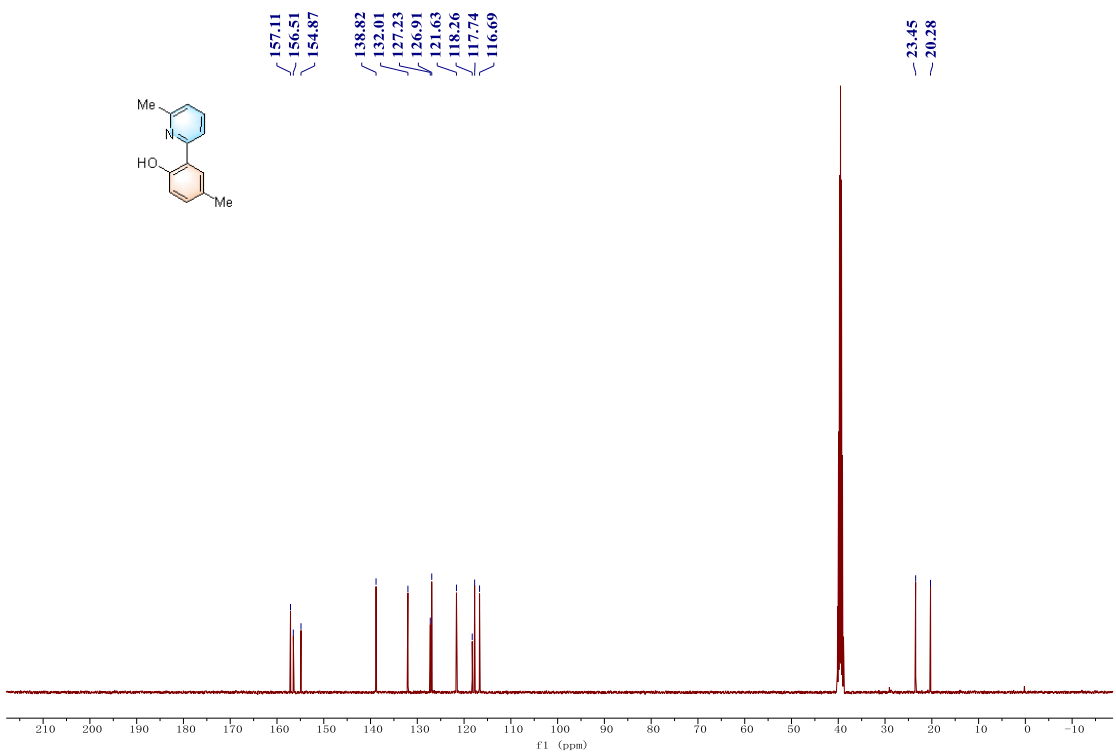
¹³C NMR spectrum of 3n

HN-85.10.fid



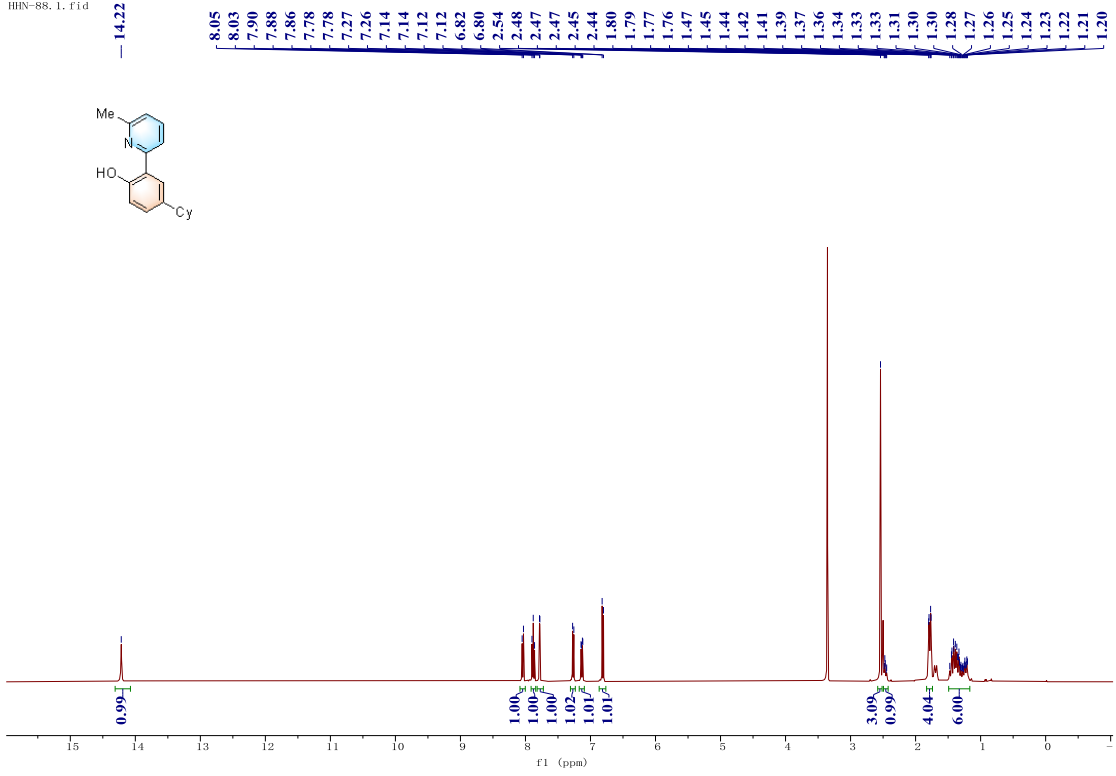
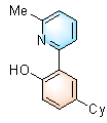
¹H NMR spectrum of 3o

HN-85.11.fid



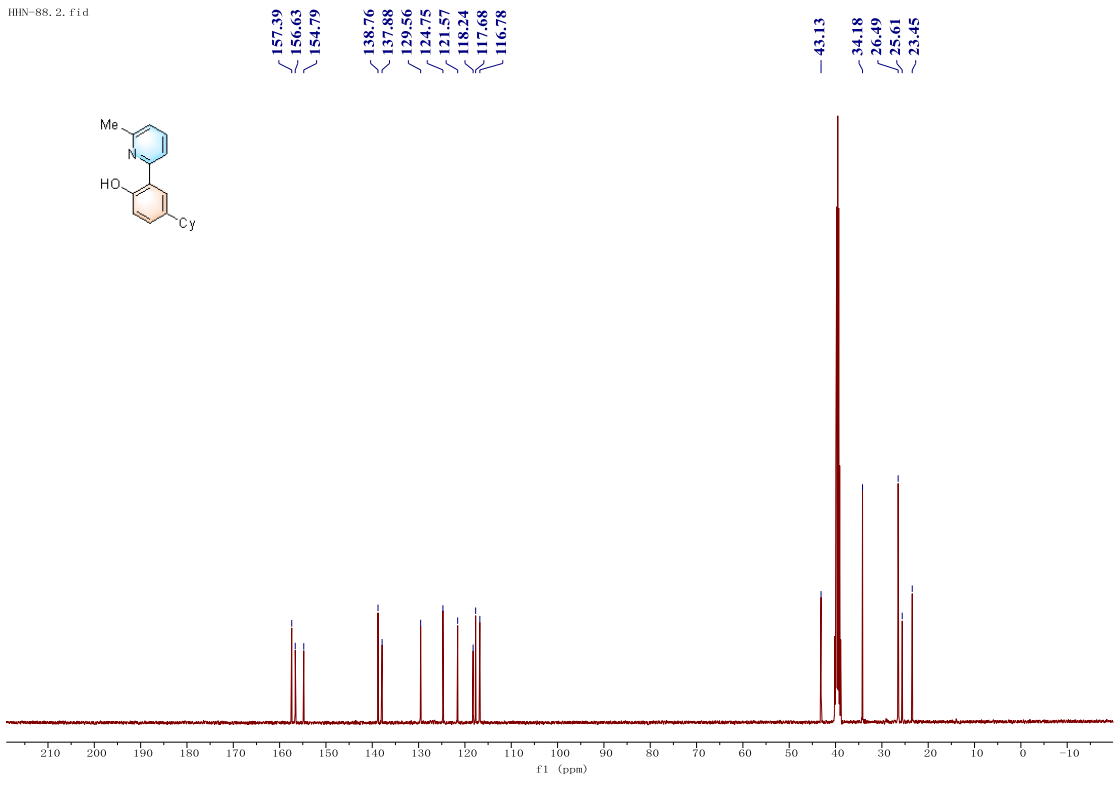
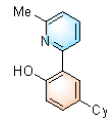
¹³C NMR spectrum of 3o

HN-88.1.fid



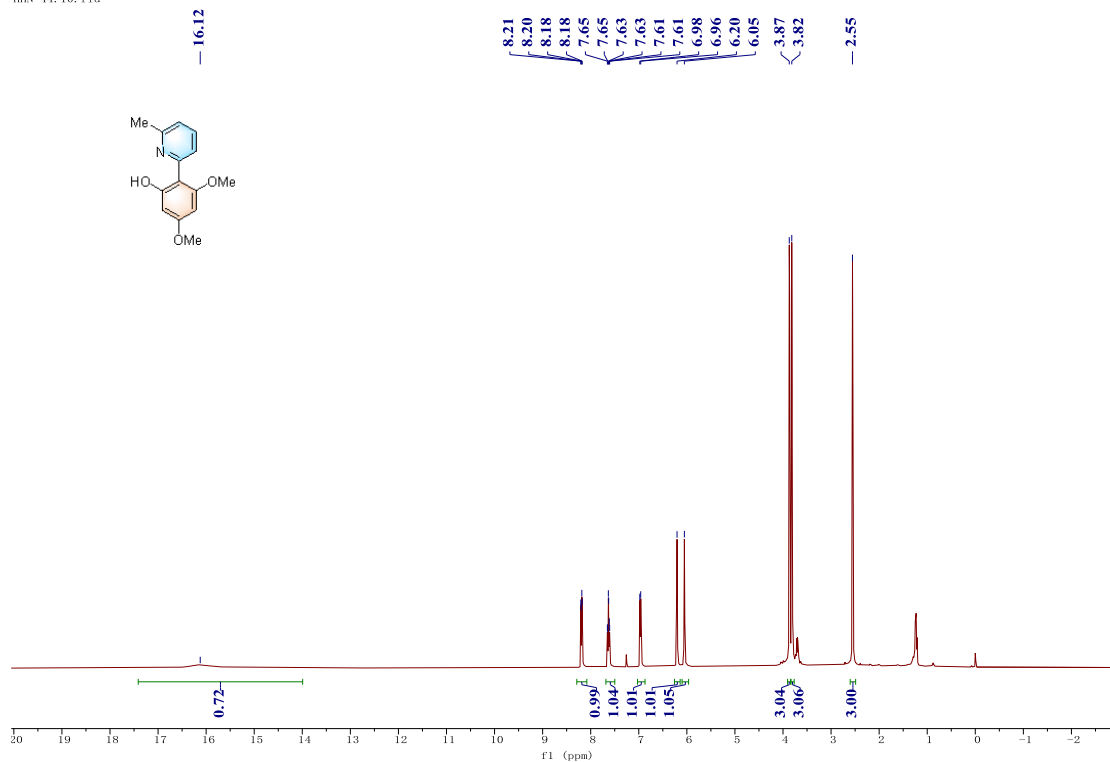
¹H NMR spectrum of 3p

HN-88.2.fid



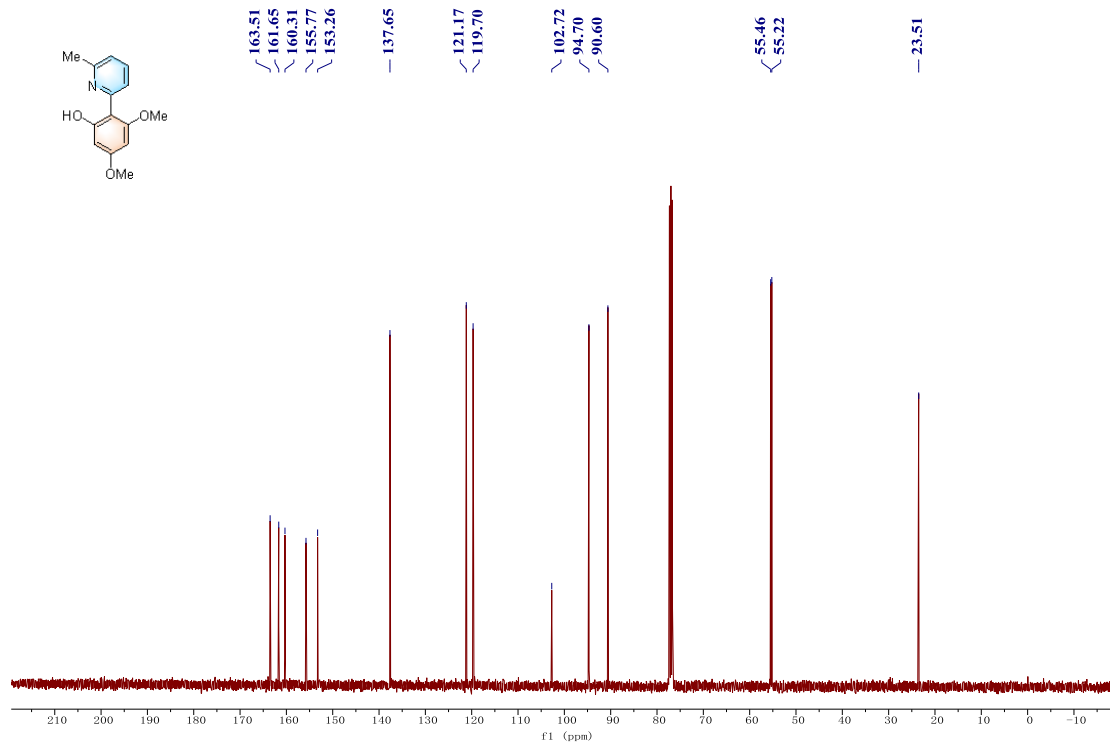
¹³C NMR spectrum of 3p

HN-44.10.fid



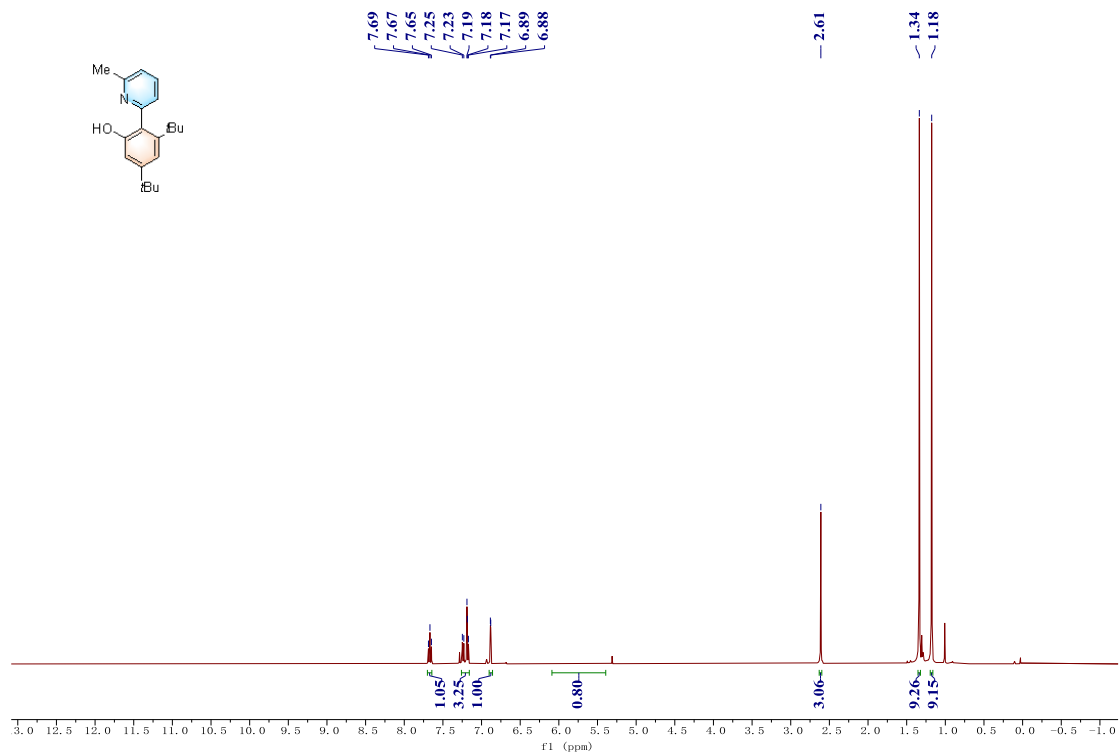
^1H NMR spectrum of 3q

HN-44.2.fid



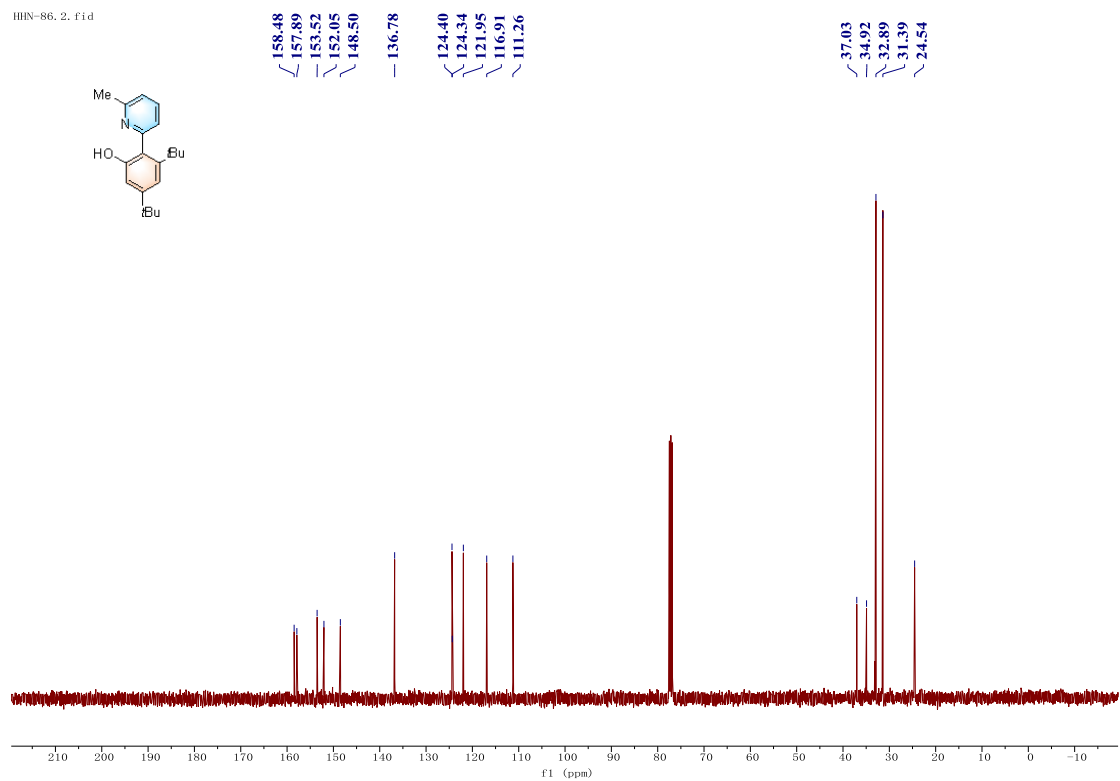
^{13}C NMR spectrum of 3q

HN-86.1.fid



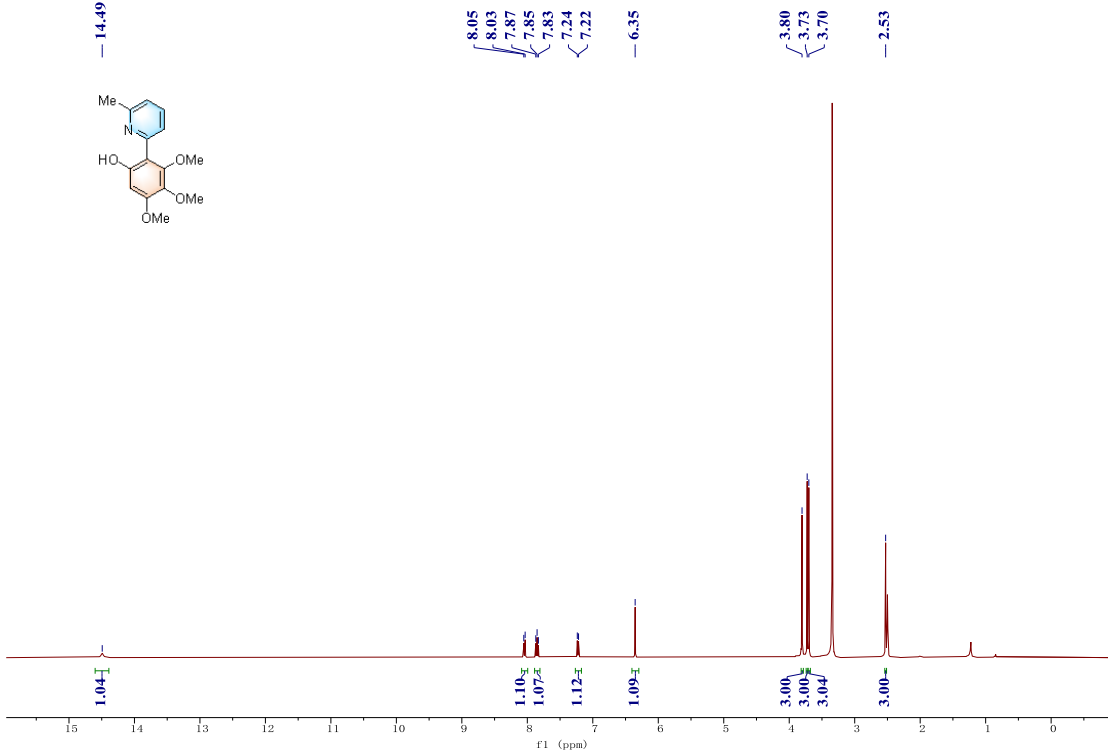
¹H NMR spectrum of 3r

HN-86.2.fid



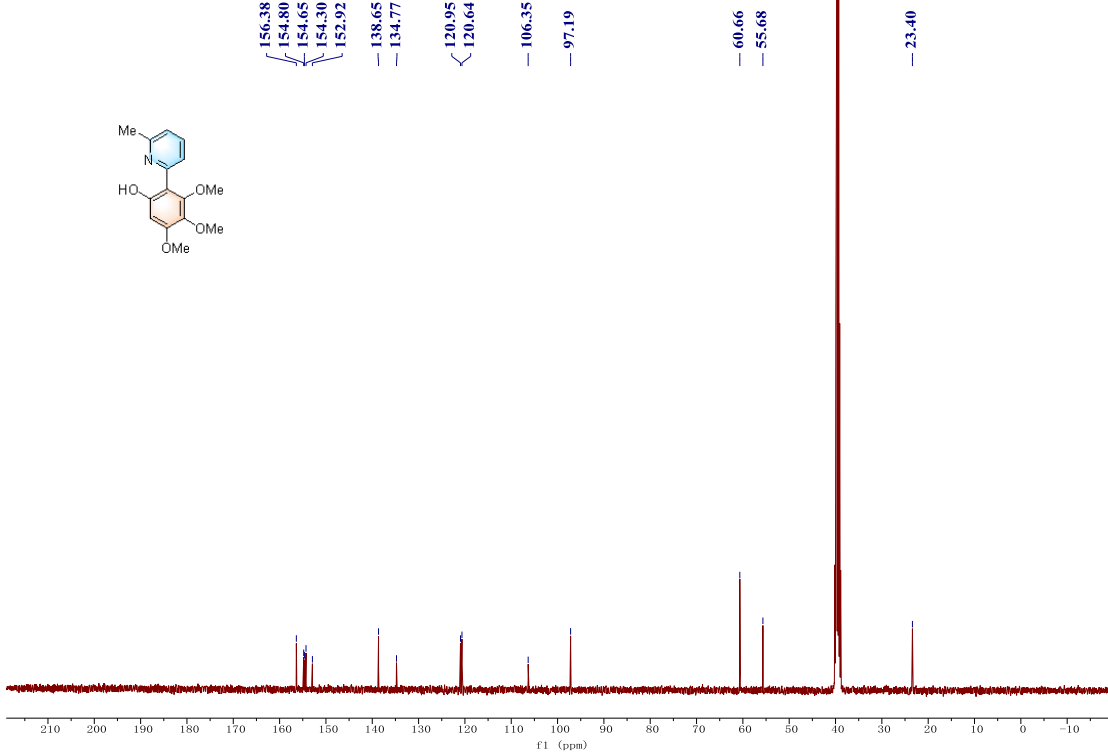
¹³C NMR spectrum of 3r

HN-20.1.Fid



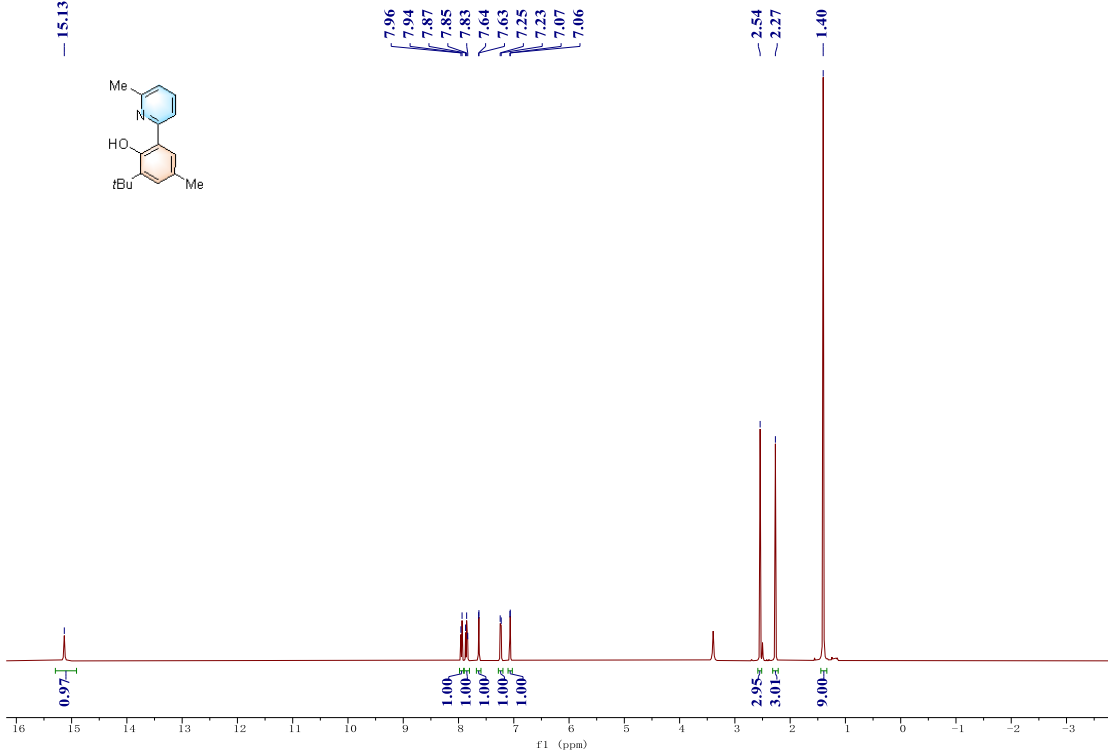
¹H NMR spectrum of 3s

HN-20.2.Fid



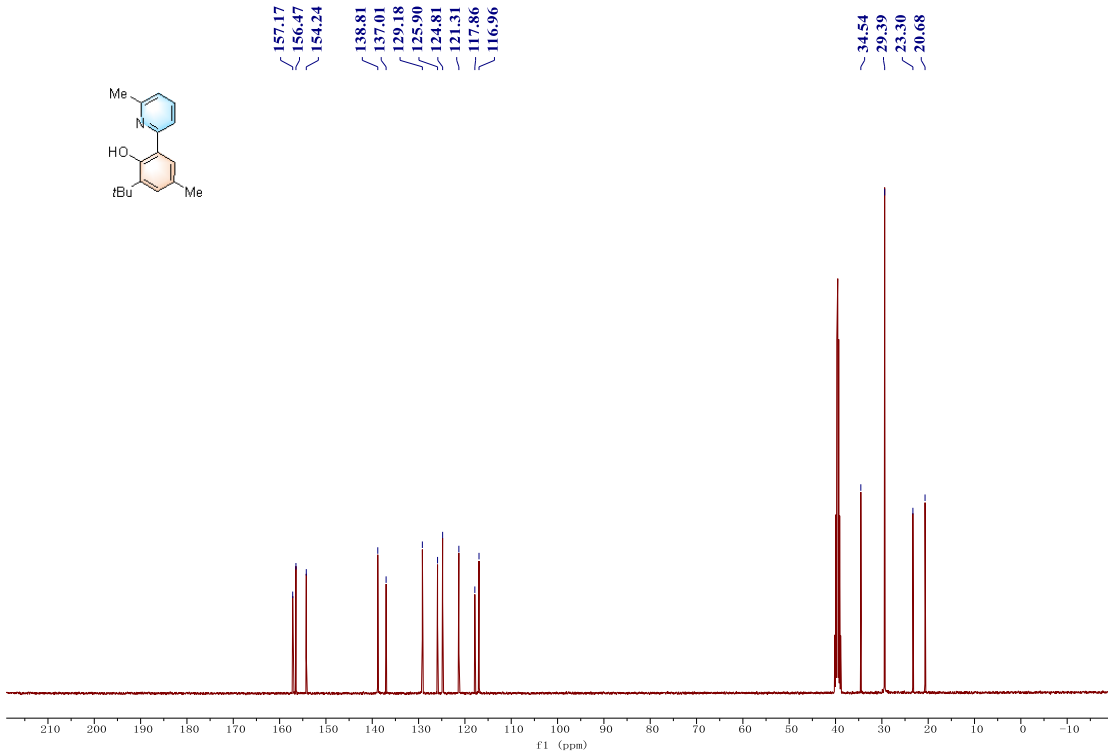
¹³C NMR spectrum of 3s

HN-90.3.fid



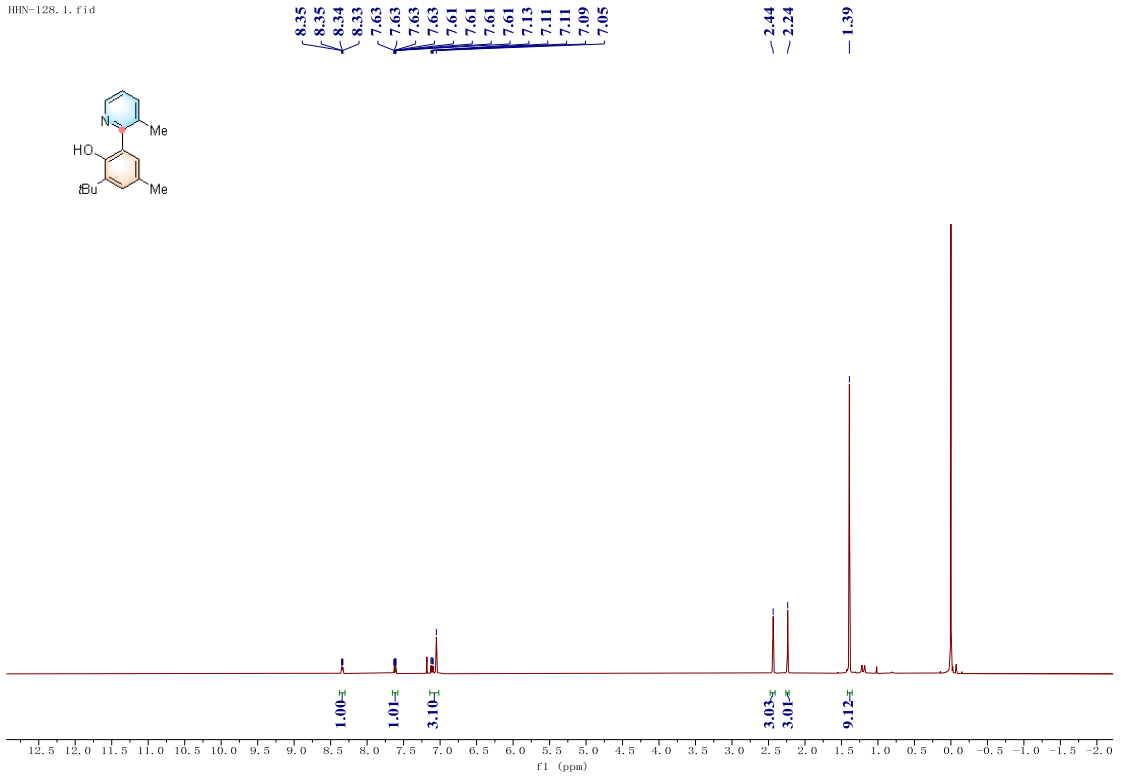
¹H NMR spectrum of 3t

HN-90.4.fid



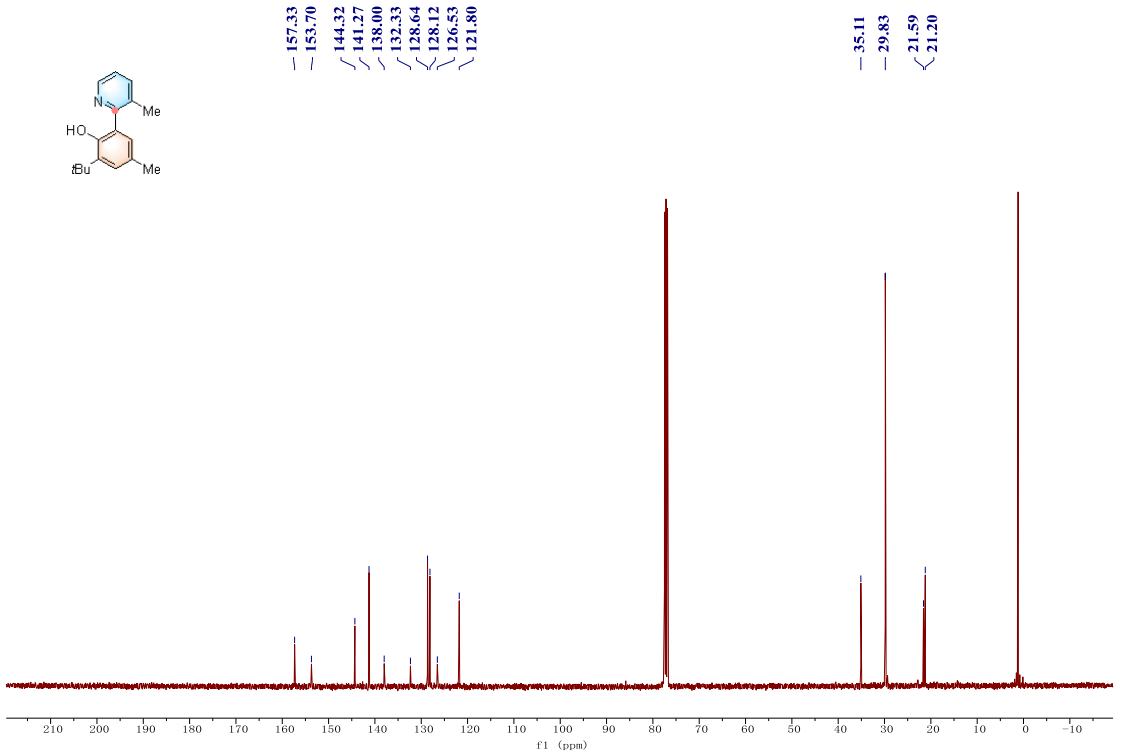
¹³C NMR spectrum of 3t

HN-128.1.fid



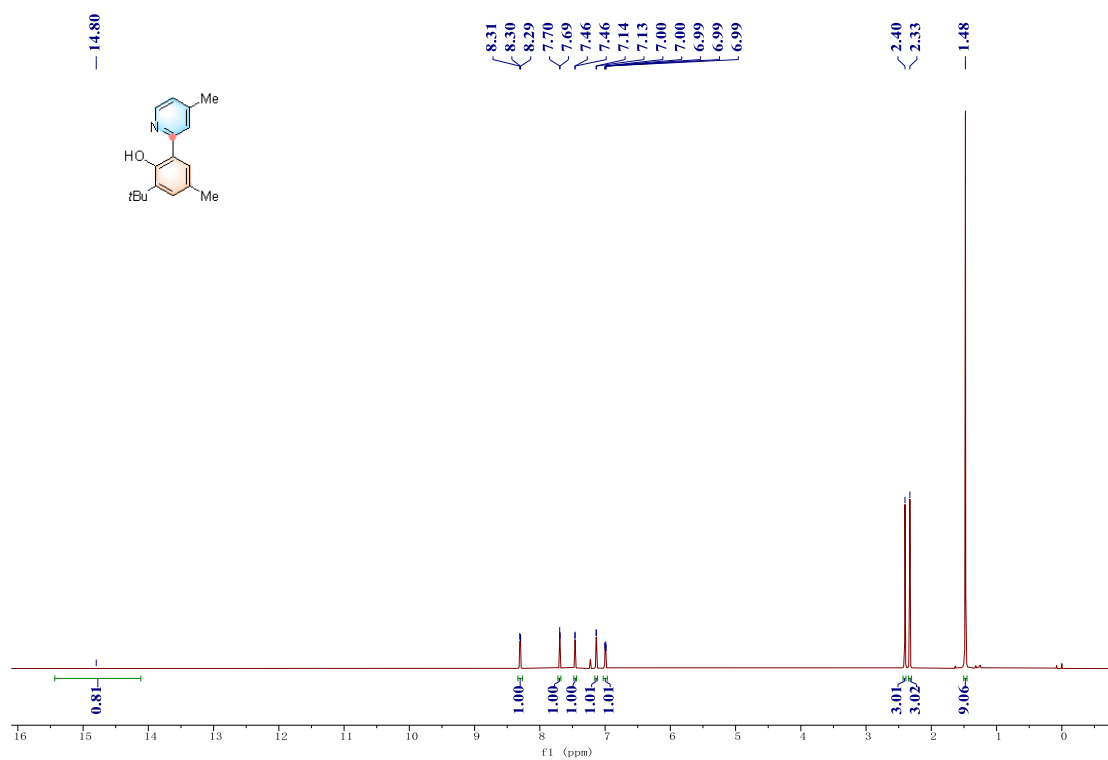
^1H NMR spectrum of 4a

HN-128.2.fid



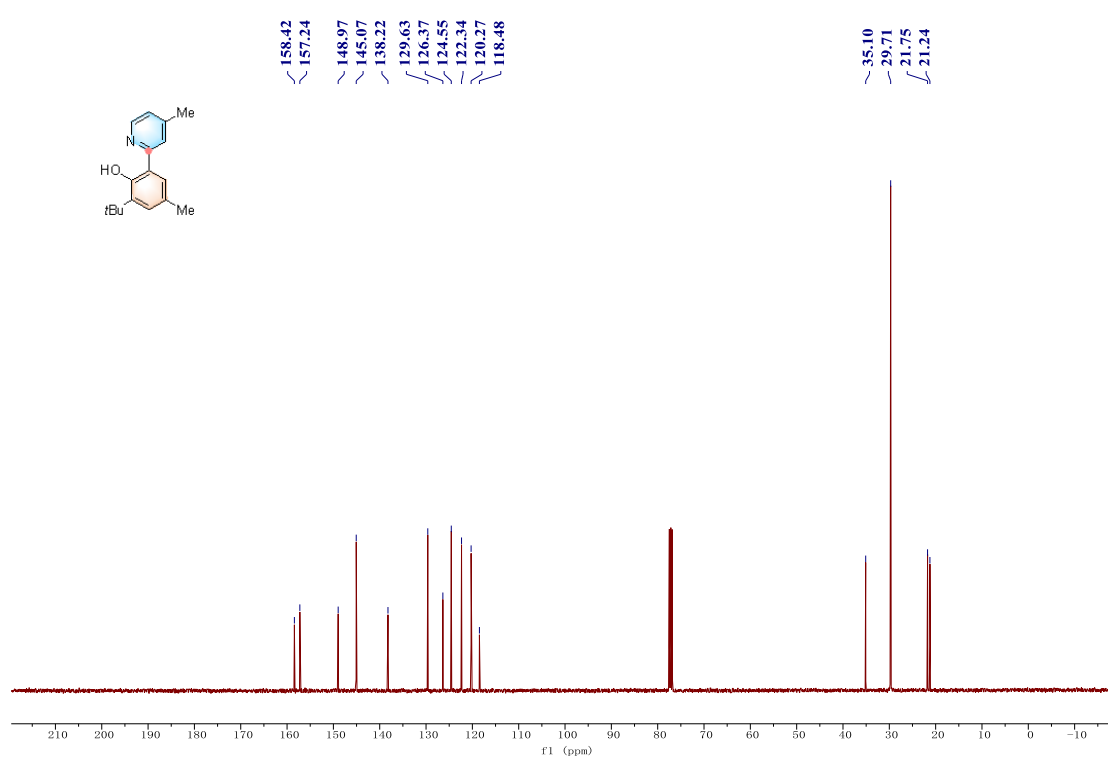
^{13}C NMR spectrum of 4a

HN-117.1.fid

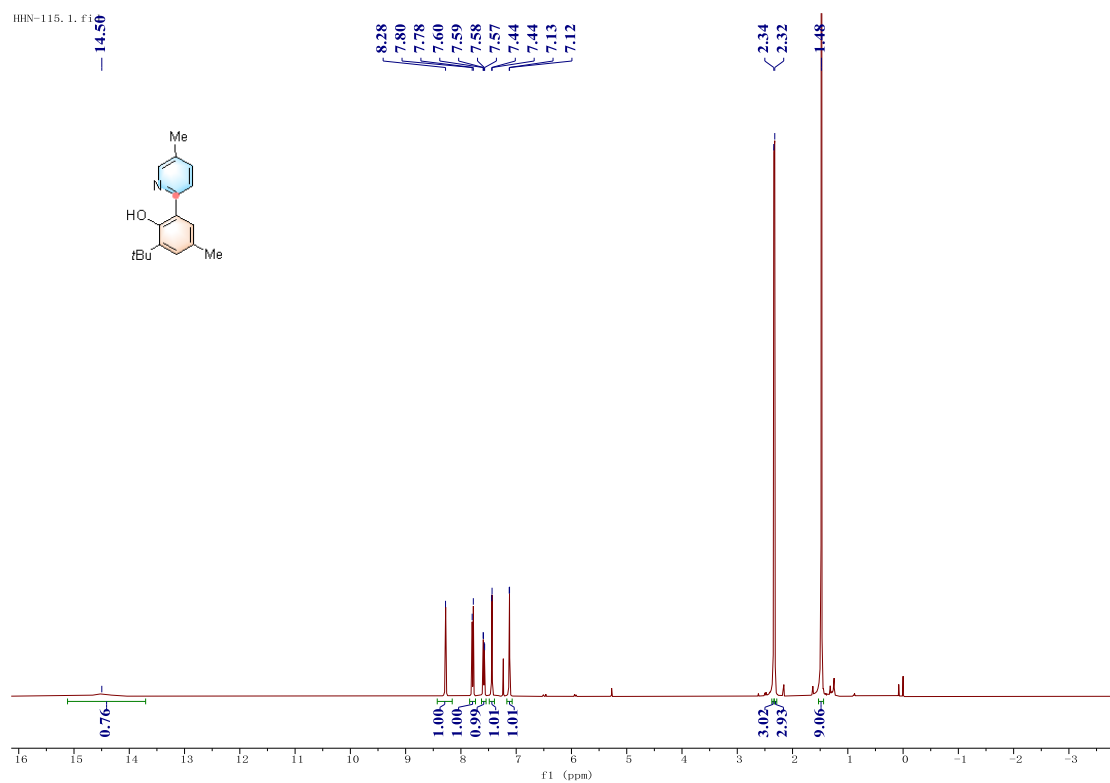


^1H NMR spectrum of 4b

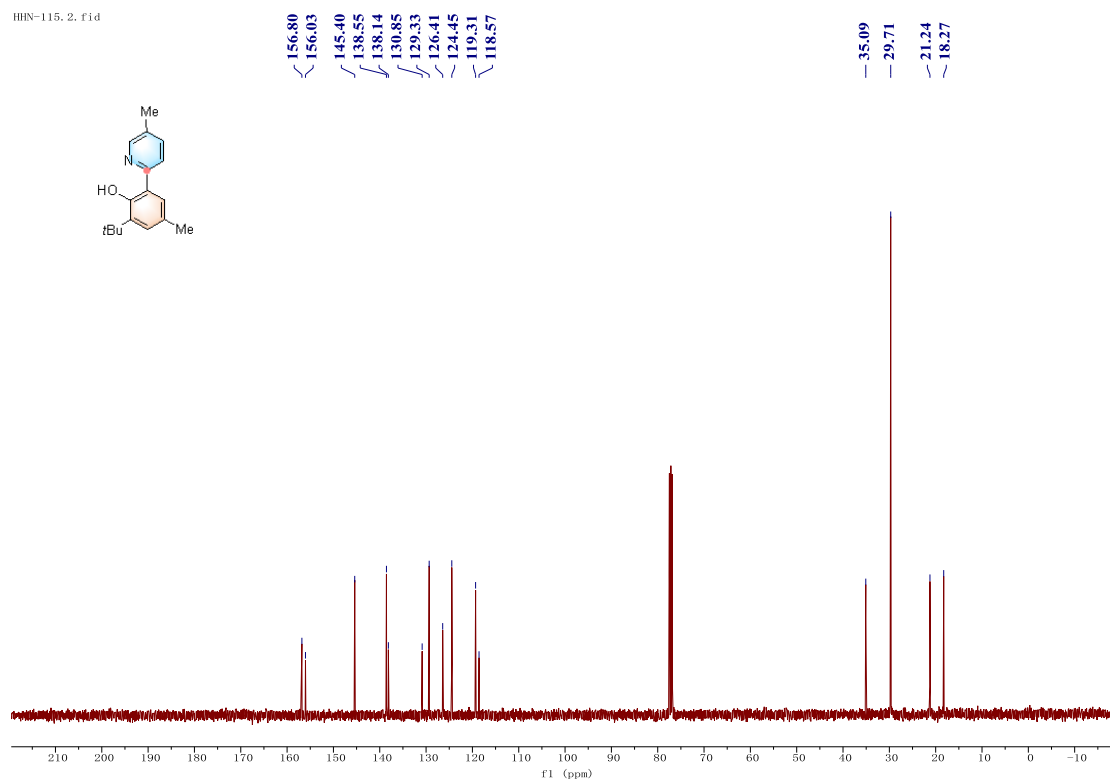
HN-117.2.fid



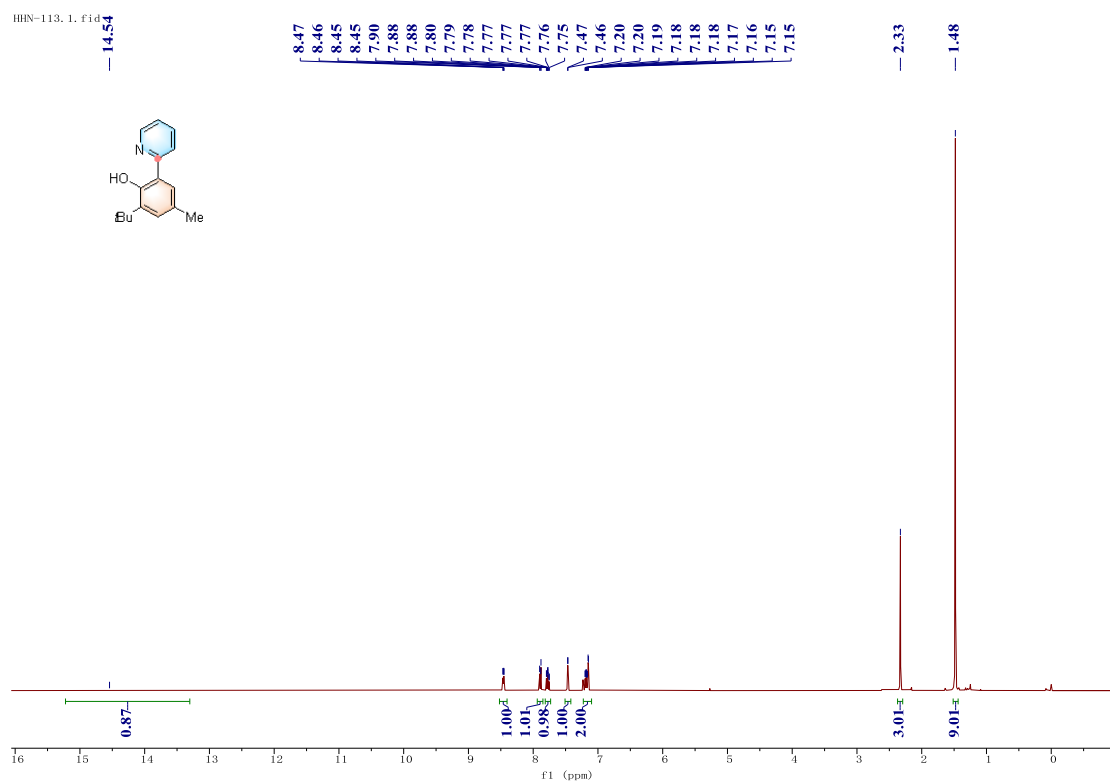
^{13}C NMR spectrum of 4b



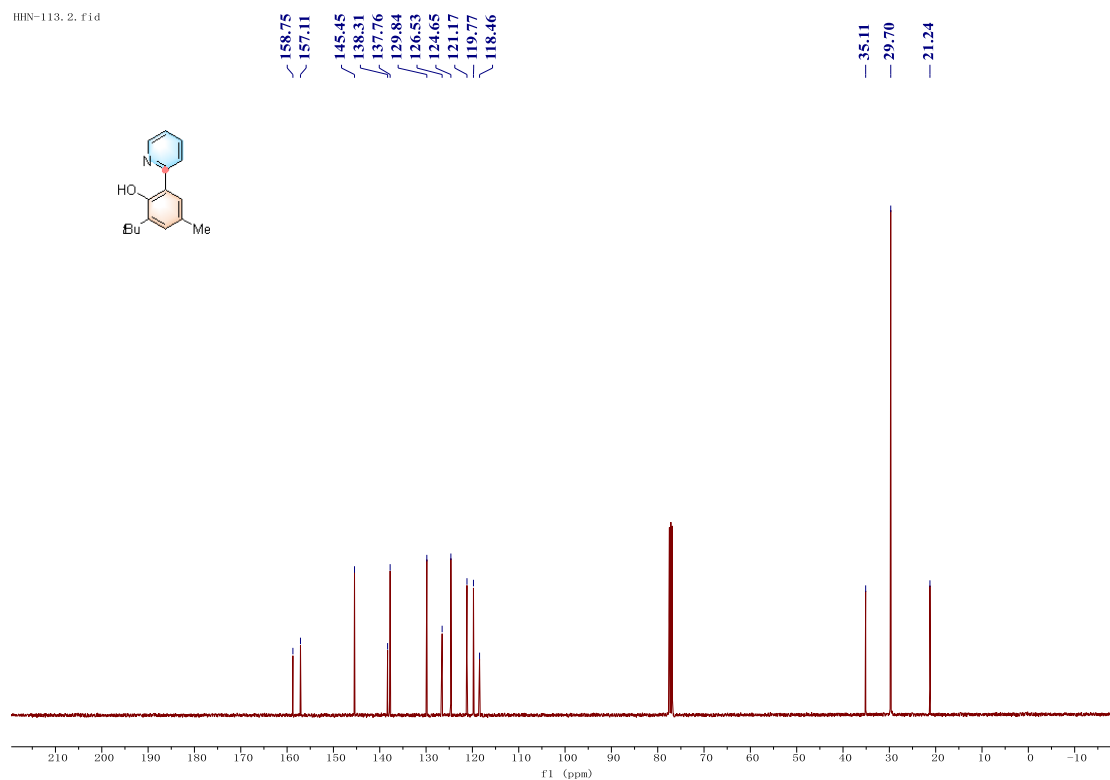
¹H NMR spectrum of 4c



¹³C NMR spectrum of 4c

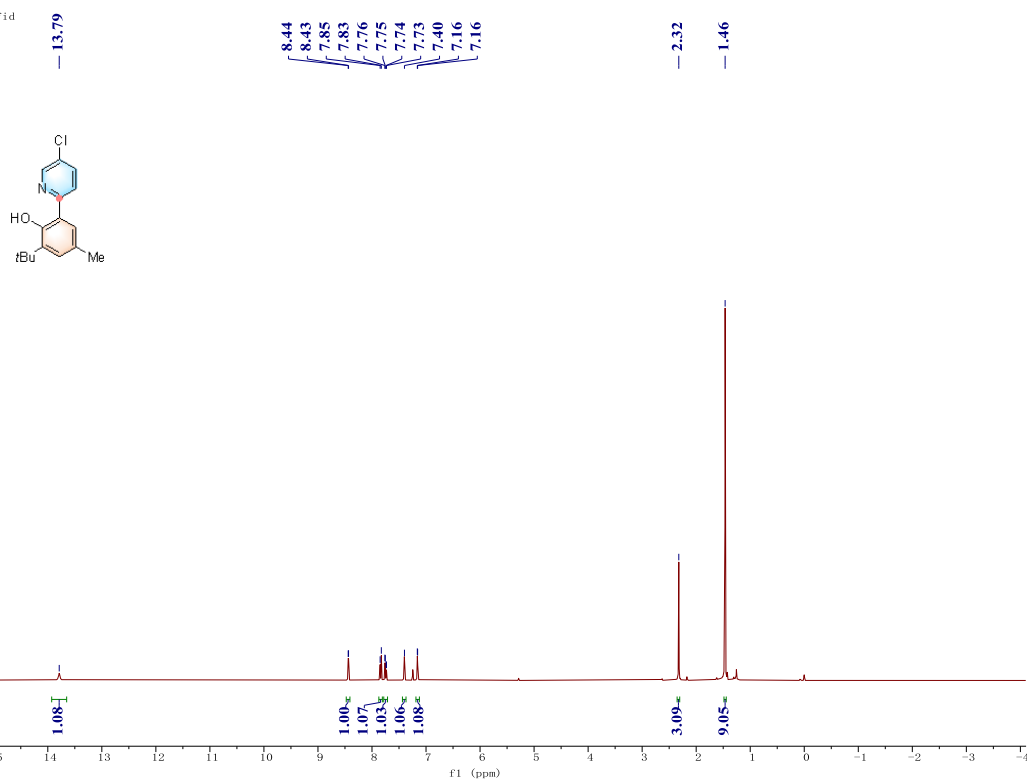


¹H NMR spectrum of 4d



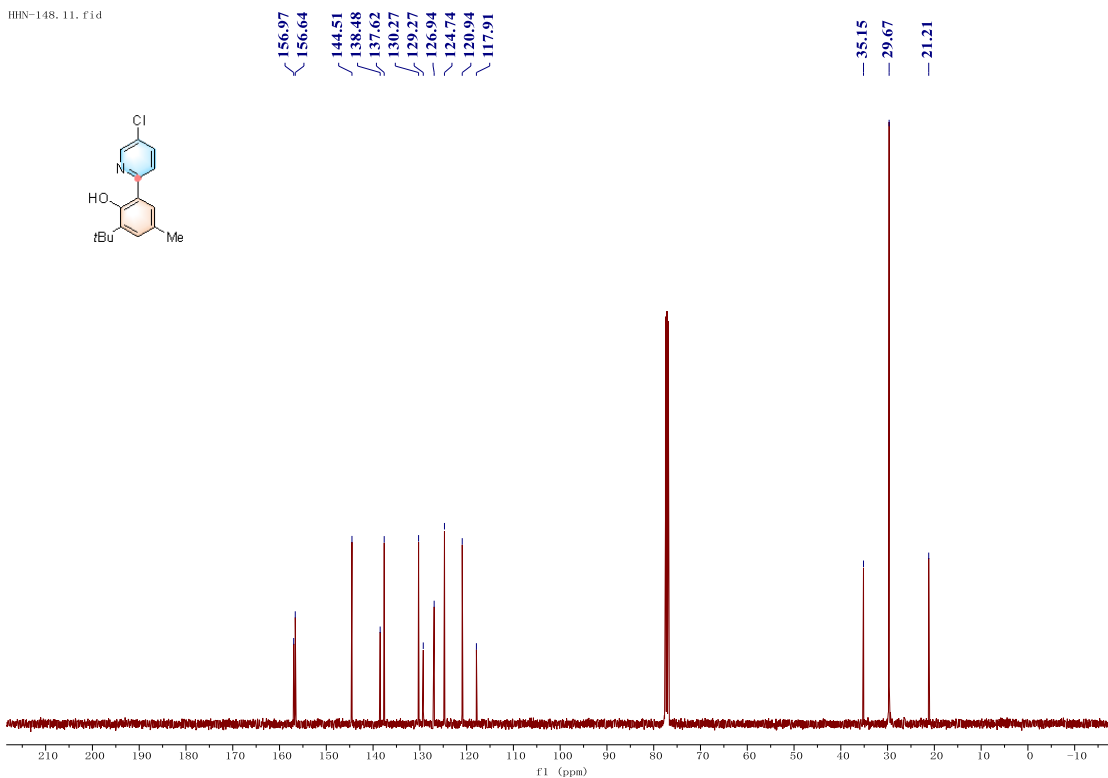
¹³C NMR spectrum of 4d

HN-148, 10, fid



¹H NMR spectrum of 4e

HN-148, 11, fid



¹³C NMR spectrum of 4e

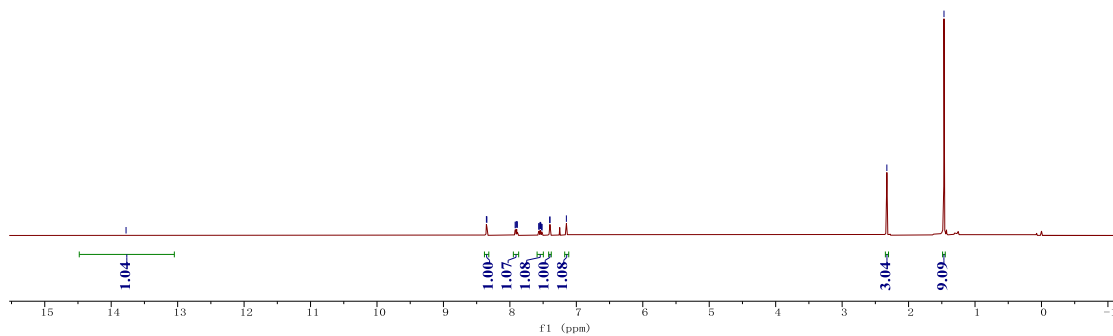
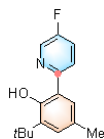
HN-137.1.fid

13.78

8.35
8.35
7.92
7.91
7.90
7.89
7.89
7.57
7.56
7.55
7.54
7.54
7.54
7.52
7.52
7.40
7.40
7.15

2.33

1.47



¹H NMR spectrum of 4f

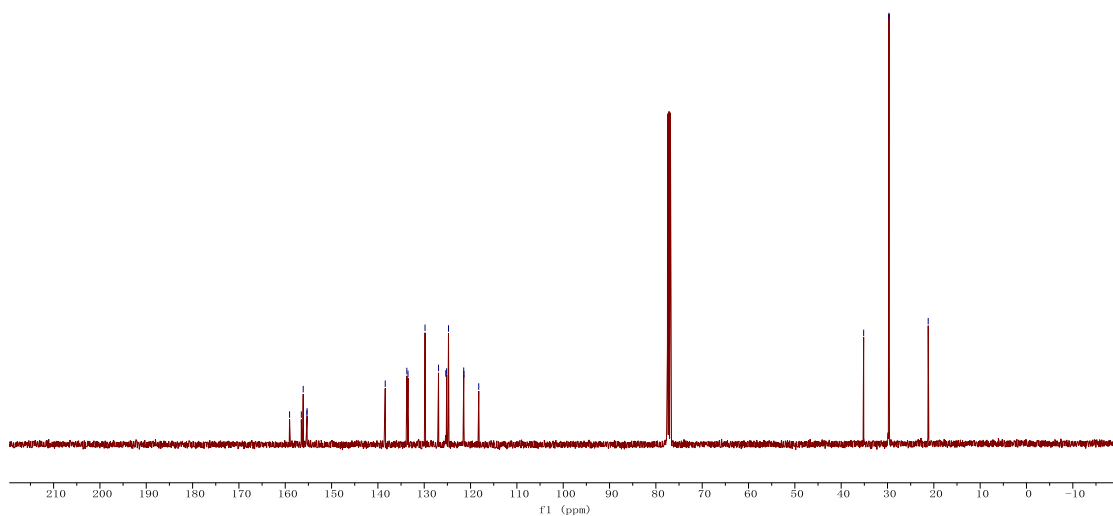
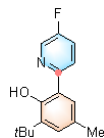
HN-137.2.fid

159.06
156.53
156.13
155.33
155.29
138.42
133.76
133.50
129.83
126.91
125.35
125.16
124.76
121.48
121.43
118.23

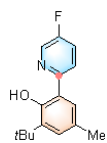
35.15

29.68

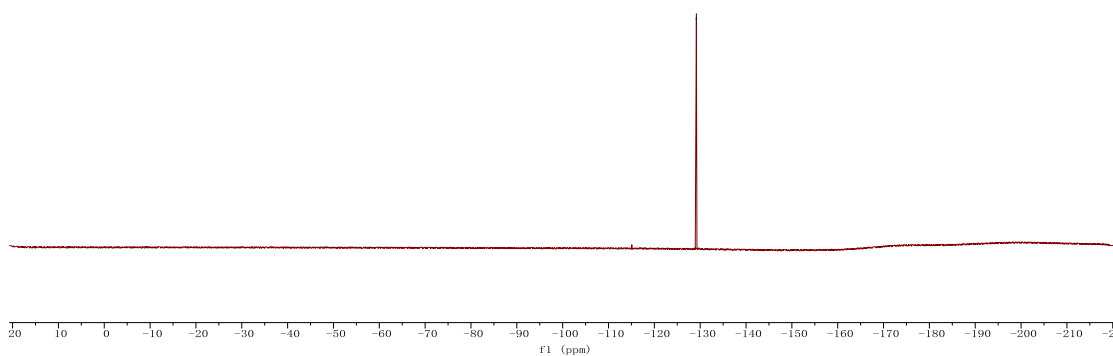
21.22



¹³C NMR spectrum of 4f

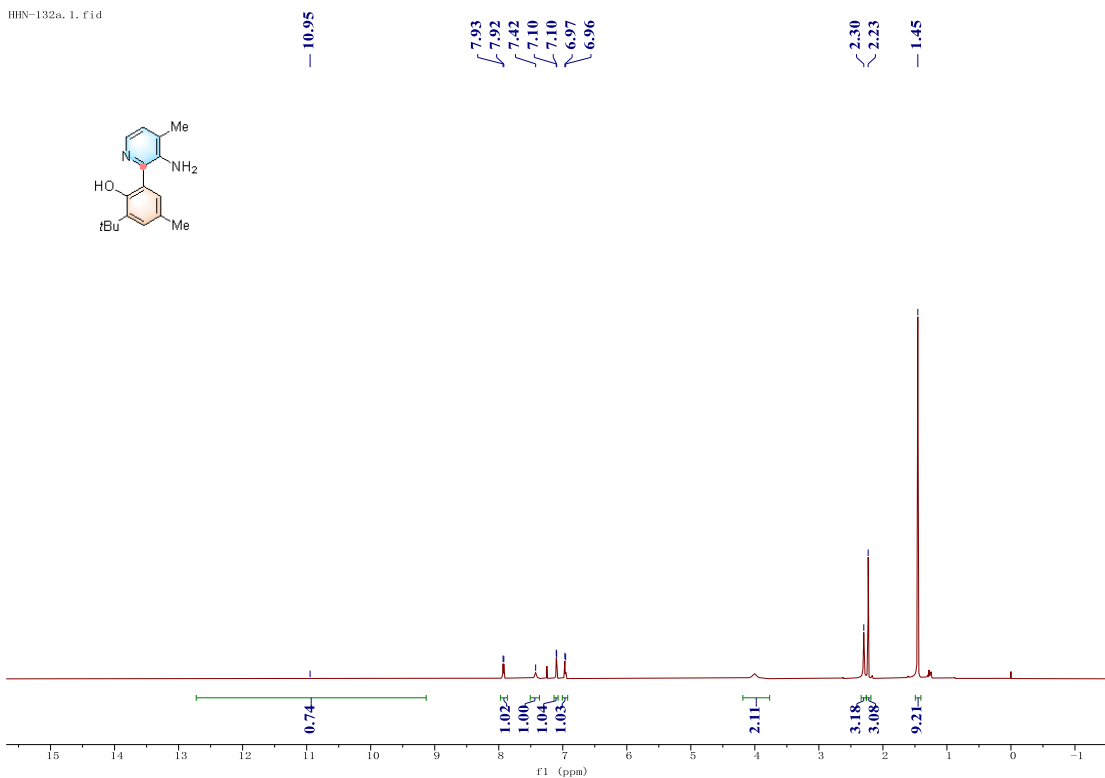


-129.17



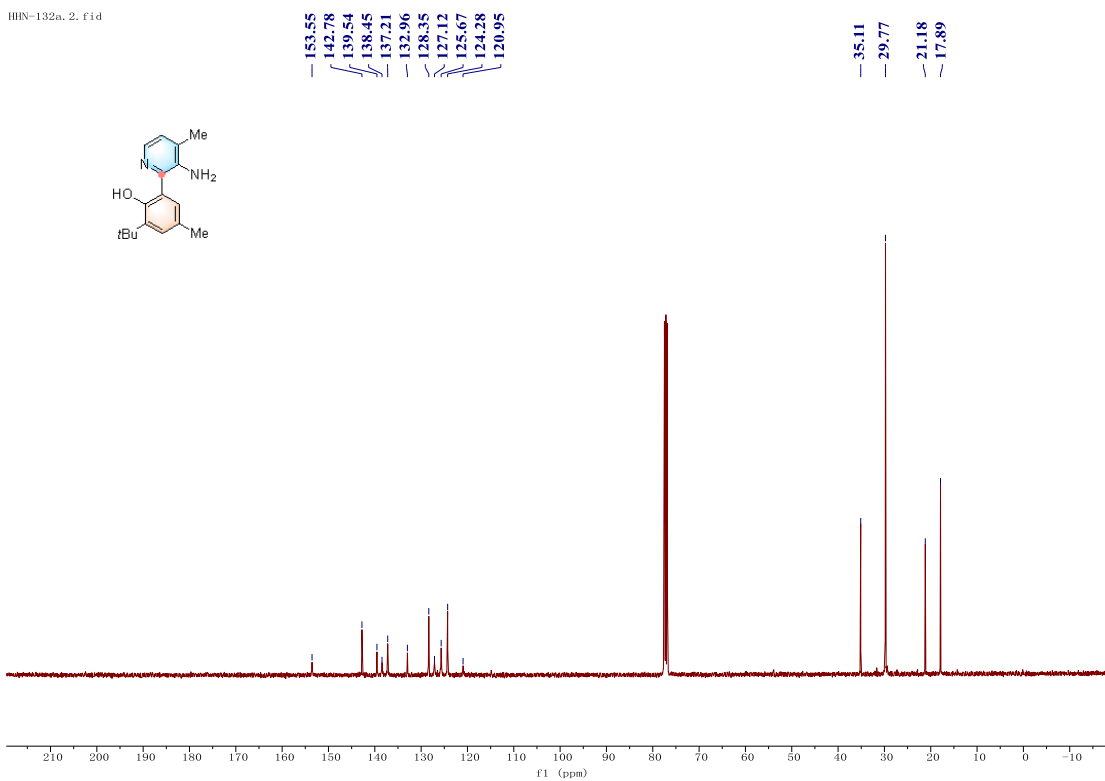
^{19}F NMR spectrum of 4f

HN-132a. 1. fid



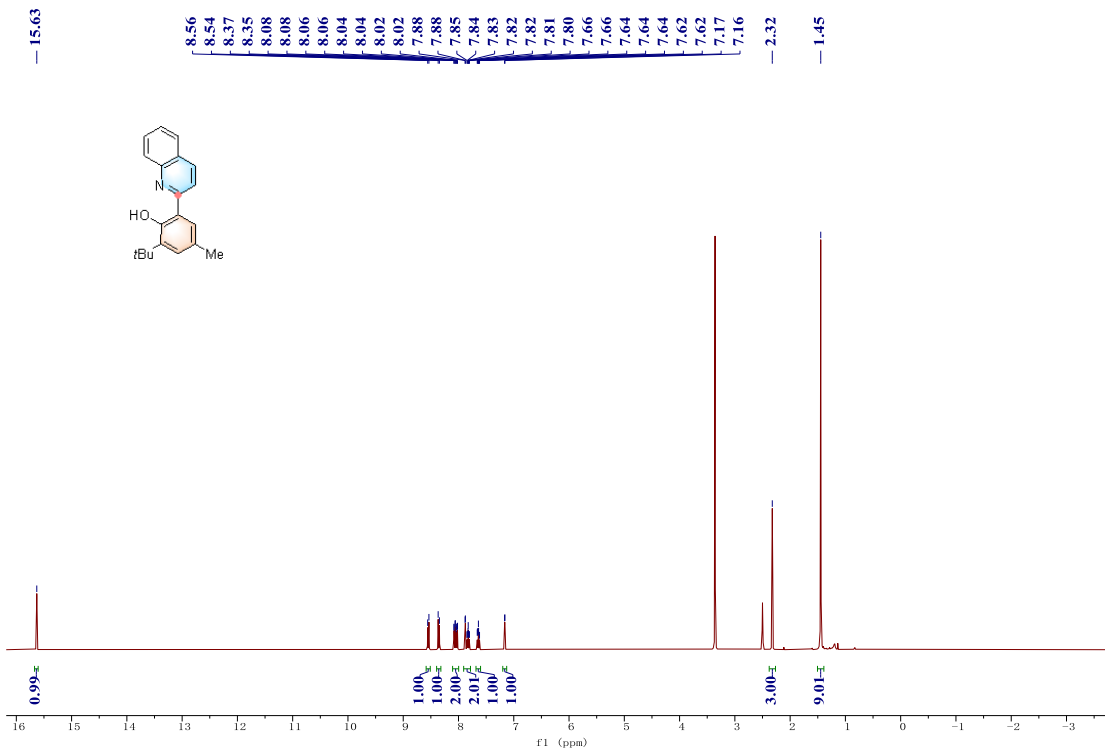
¹H NMR spectrum of 4g

HN-132a. 2. fid



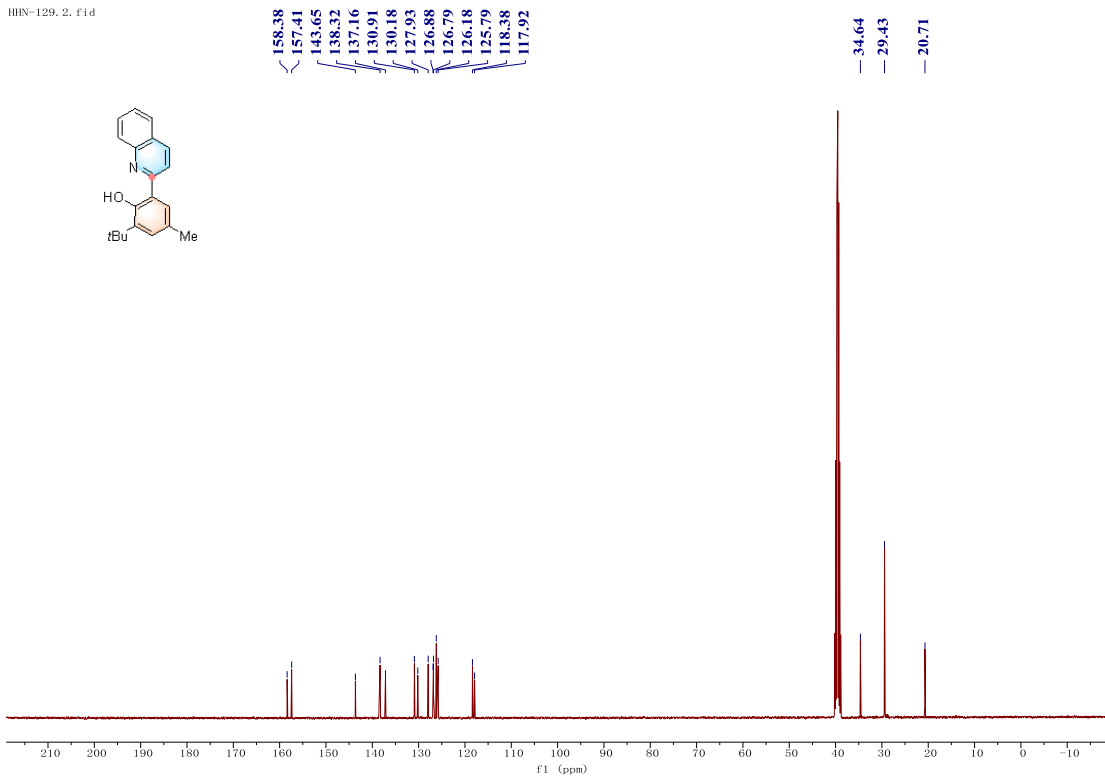
¹³C NMR spectrum of 4g

HN-129.1.fid



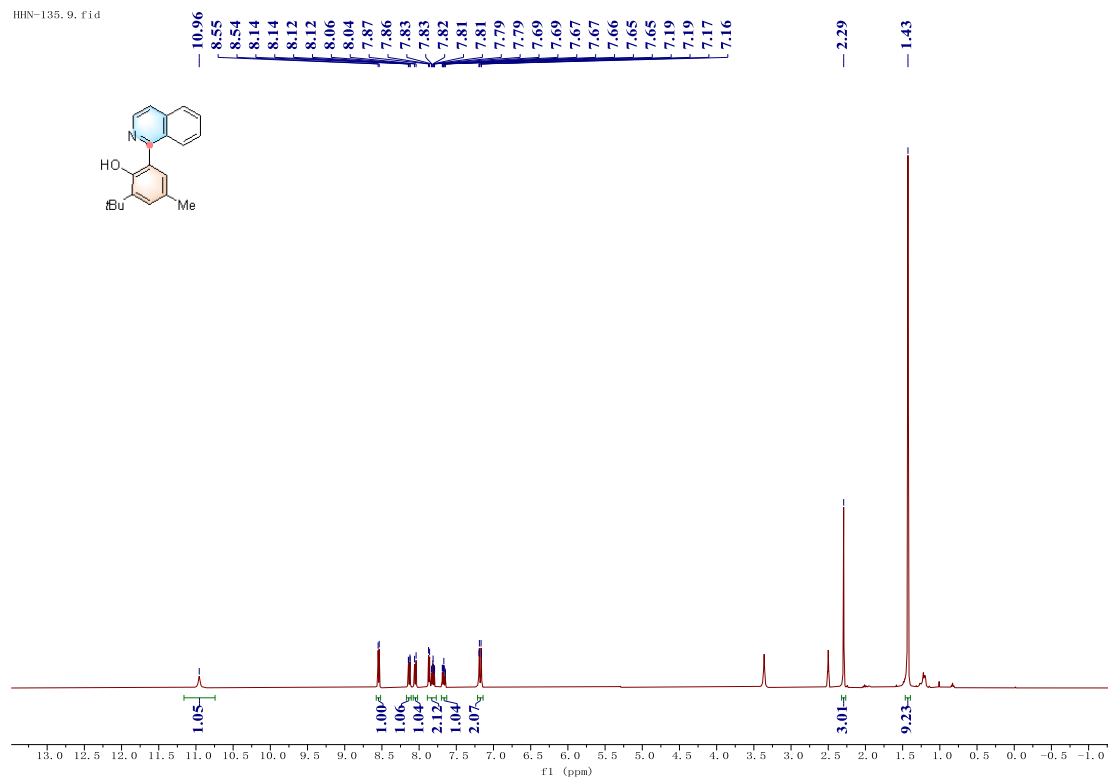
¹H NMR spectrum of 4h

HN-129.2.fid



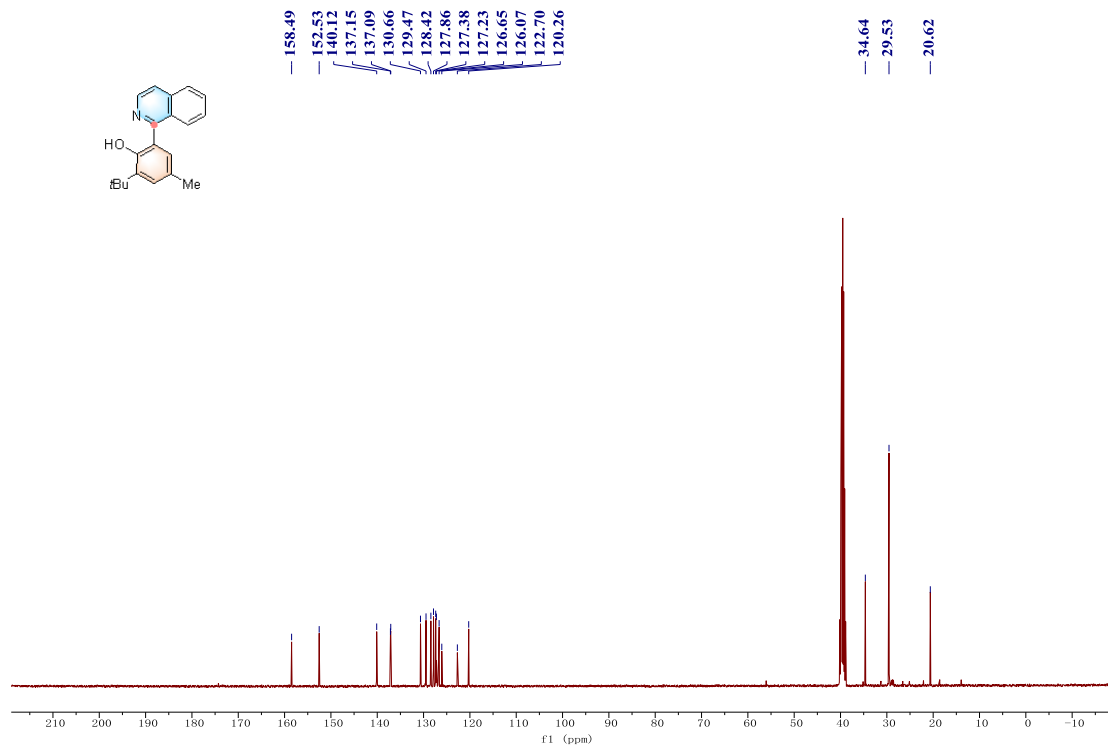
¹³C NMR spectrum of 4h

HN-135.9.fid



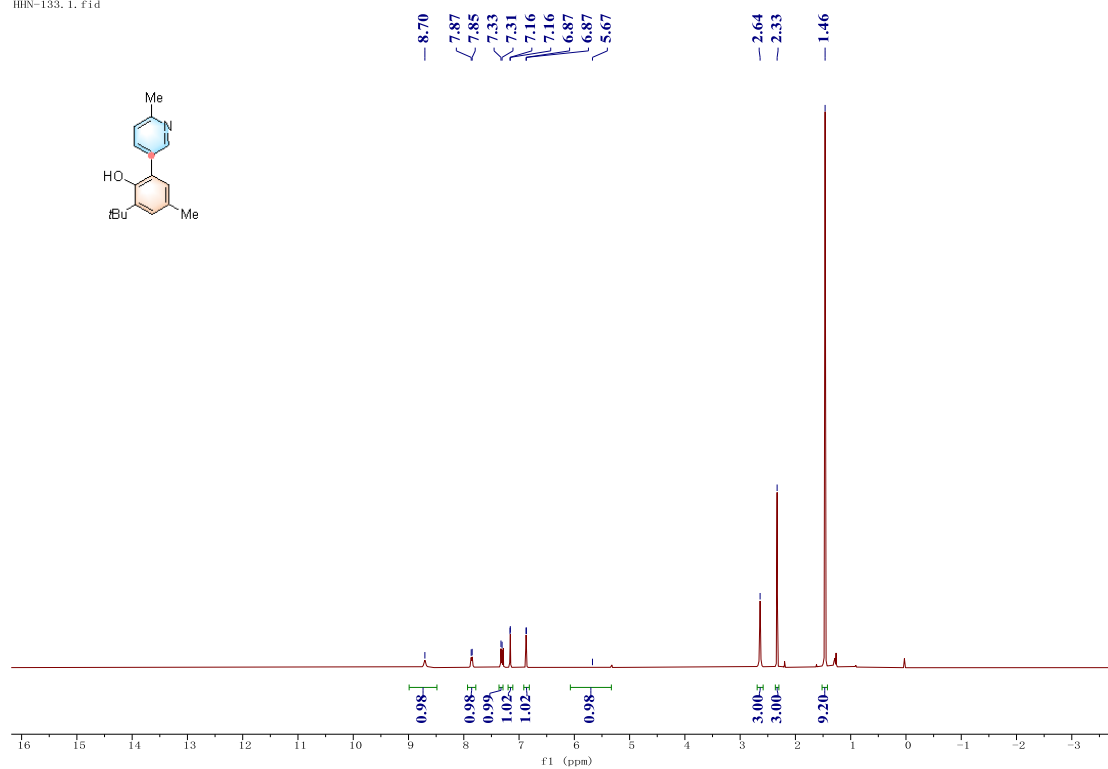
¹H NMR spectrum of 4i

1s1-20220110.10.fid



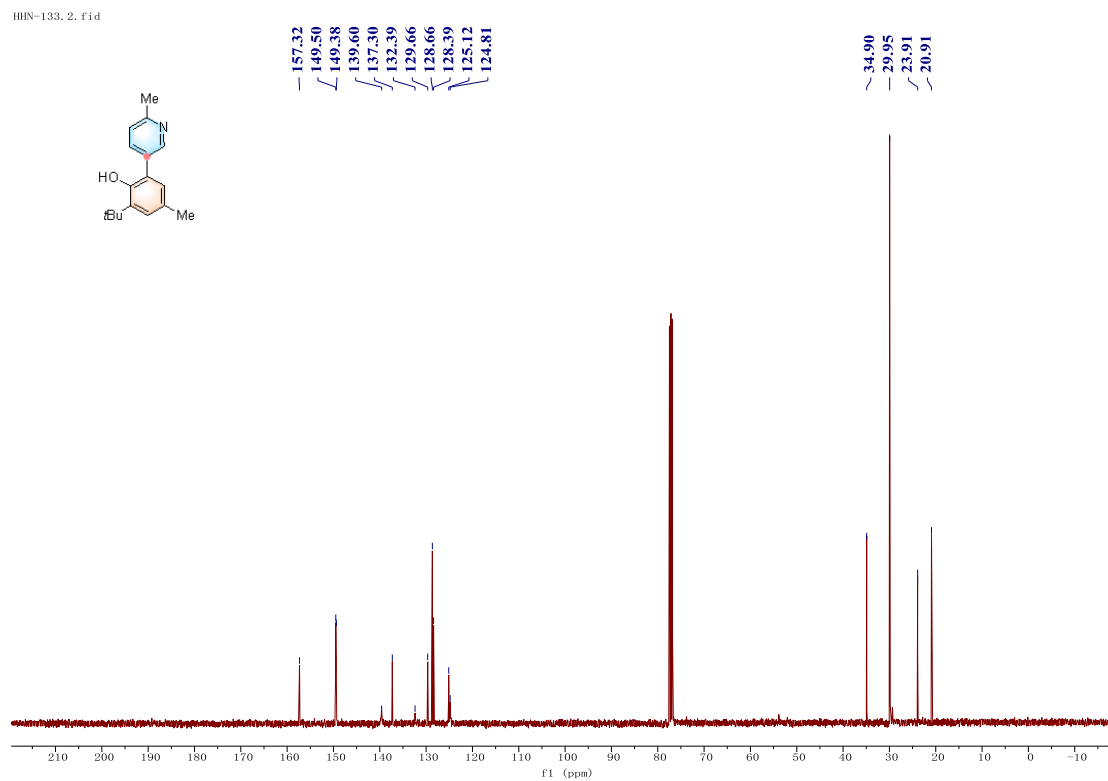
¹³C NMR spectrum of 4i

HN-133, 1. fid



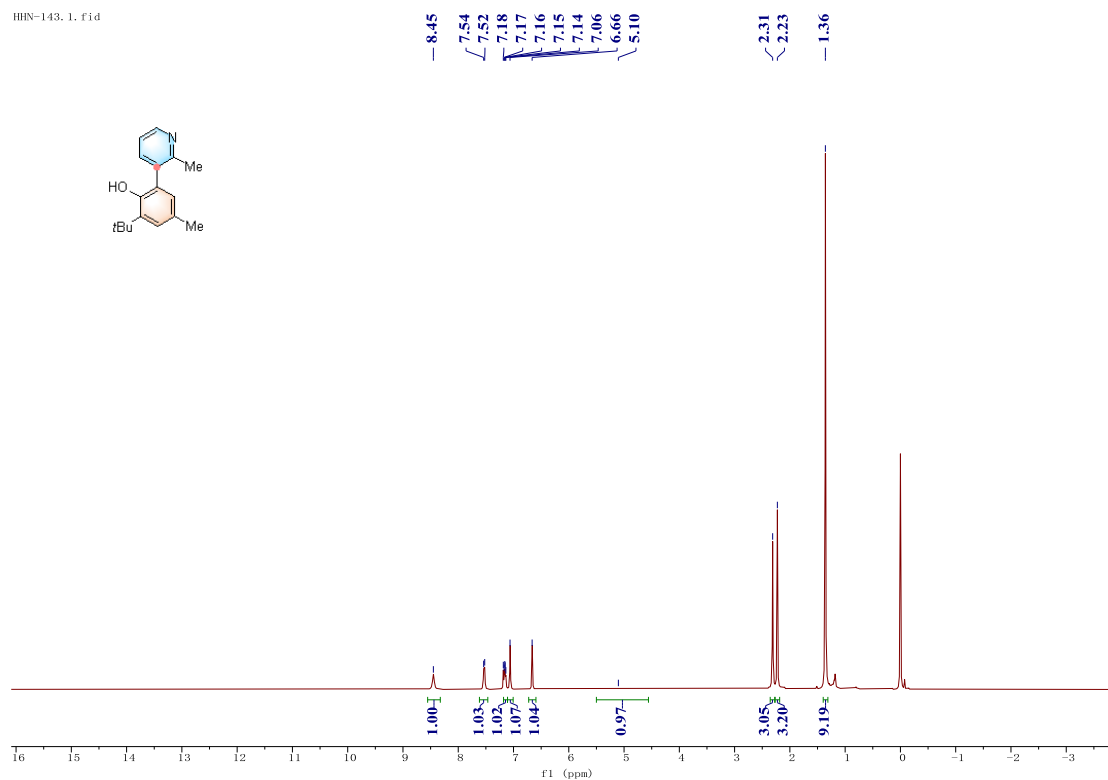
^1H NMR spectrum of 4j

HN-133, 2. fid



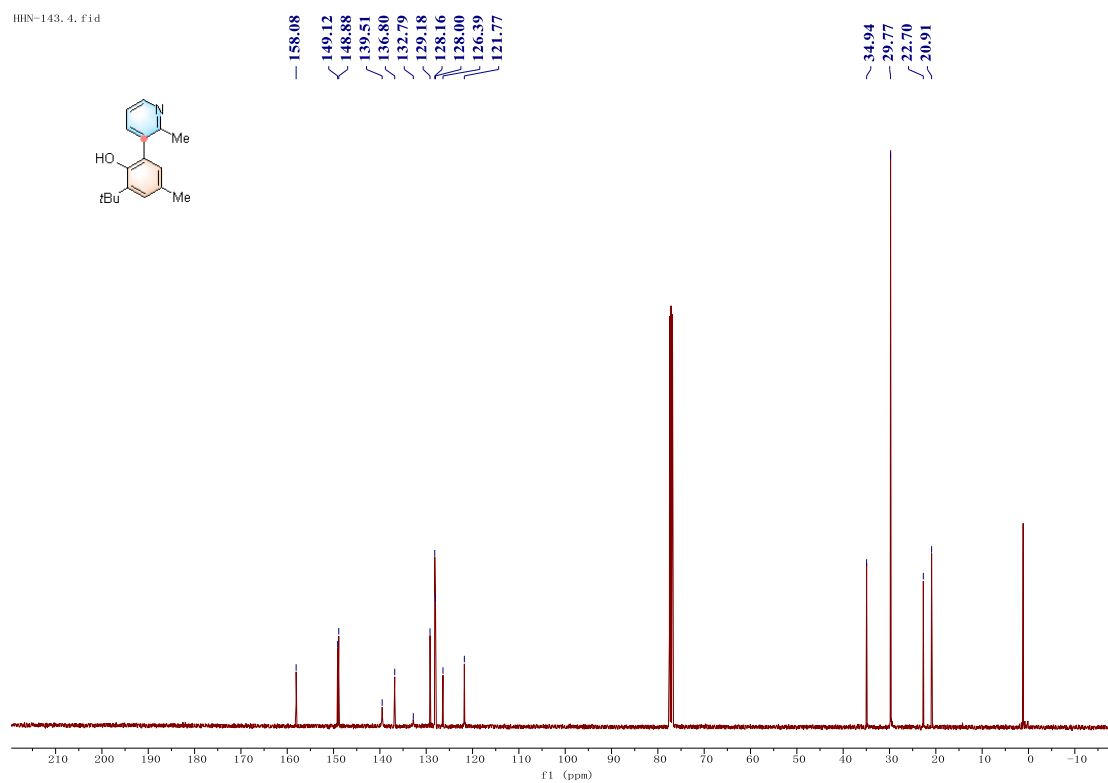
^{13}C NMR spectrum of 4j

HN-143. 1. fid



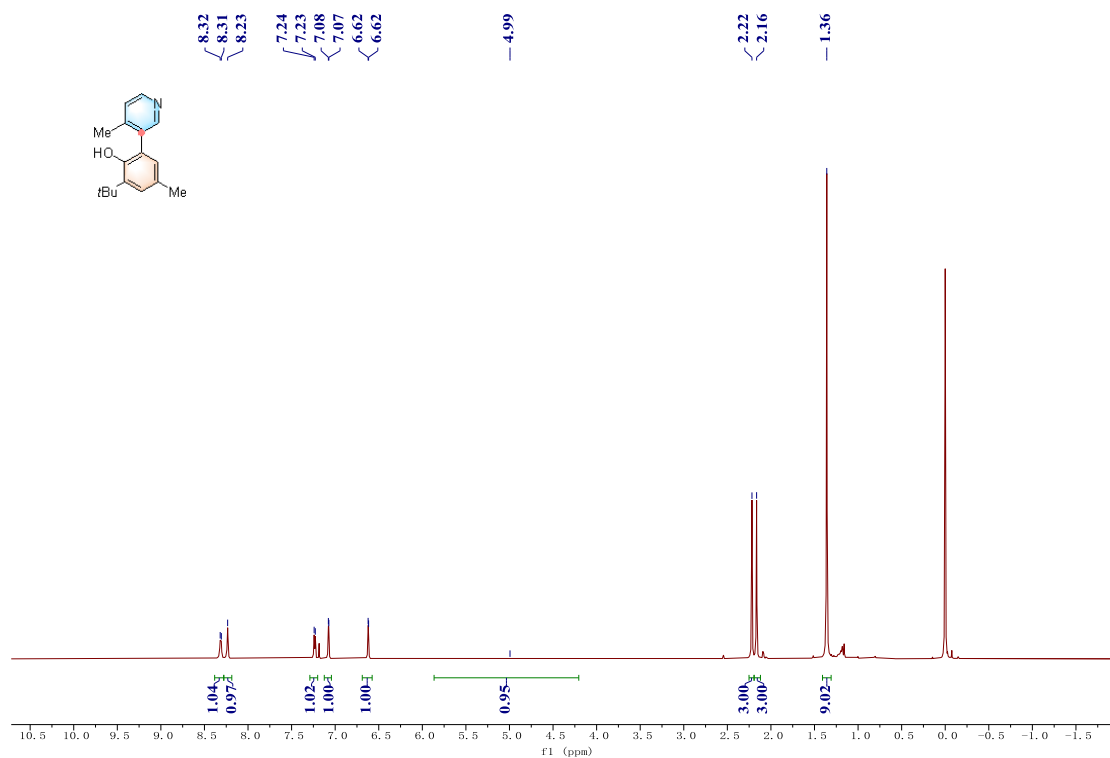
¹H NMR spectrum of 4k

HN-143. 4. fid



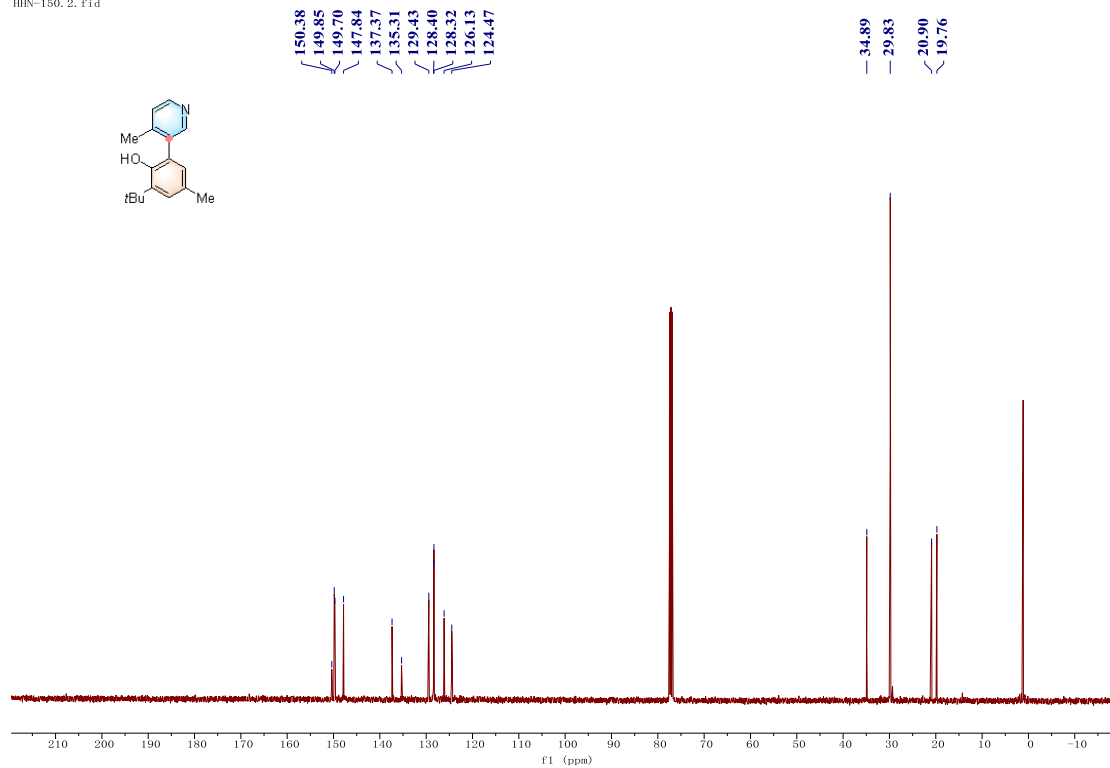
¹³C NMR spectrum of 4k

HN-150.1.fid



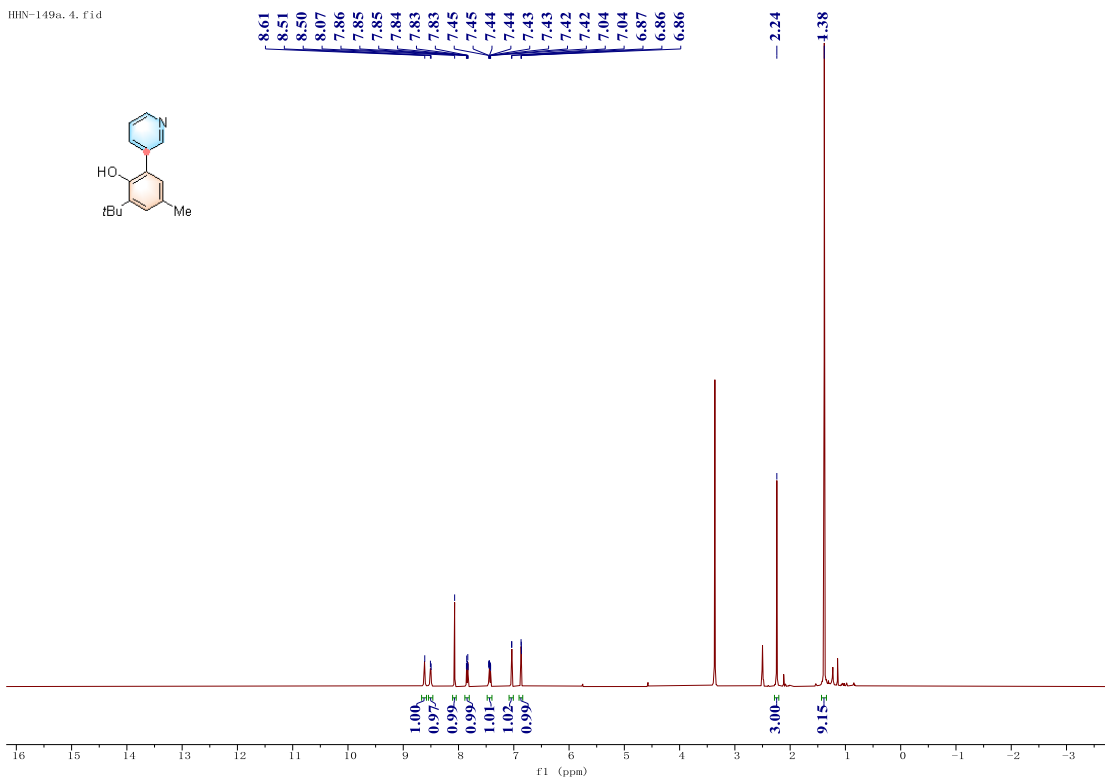
¹H NMR spectrum of 4l

HN-150.2.fid



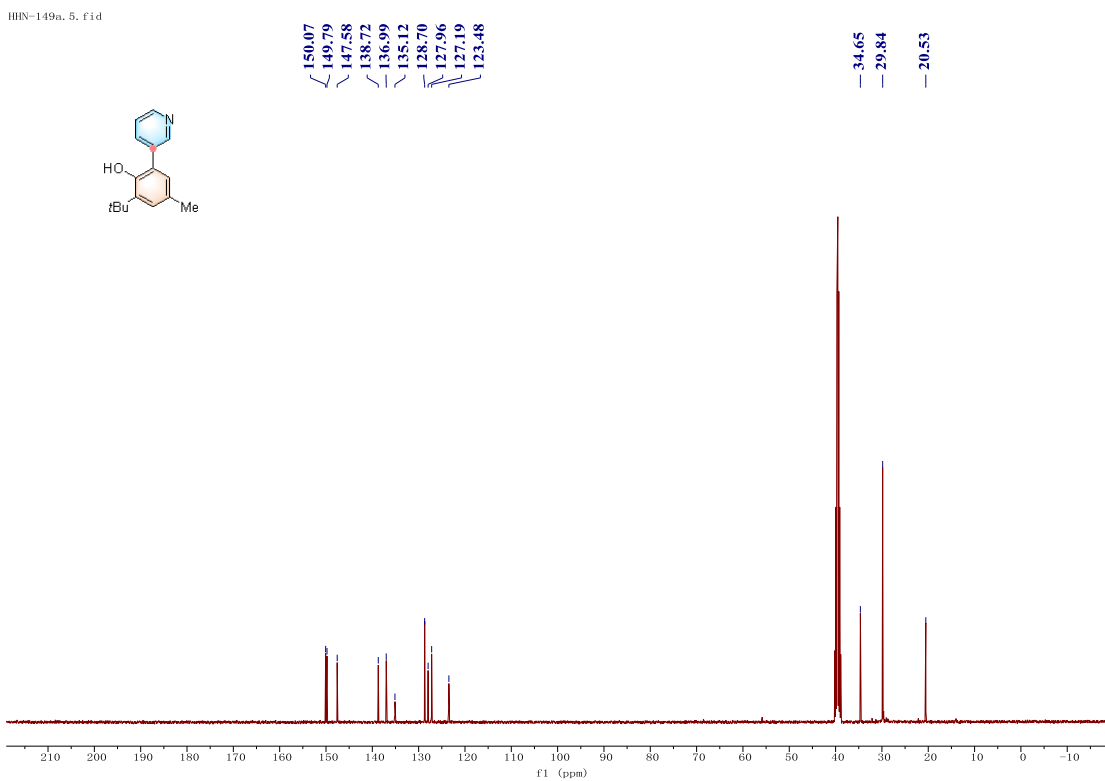
¹³C NMR spectrum of 4l

HN-149a. 4. fid



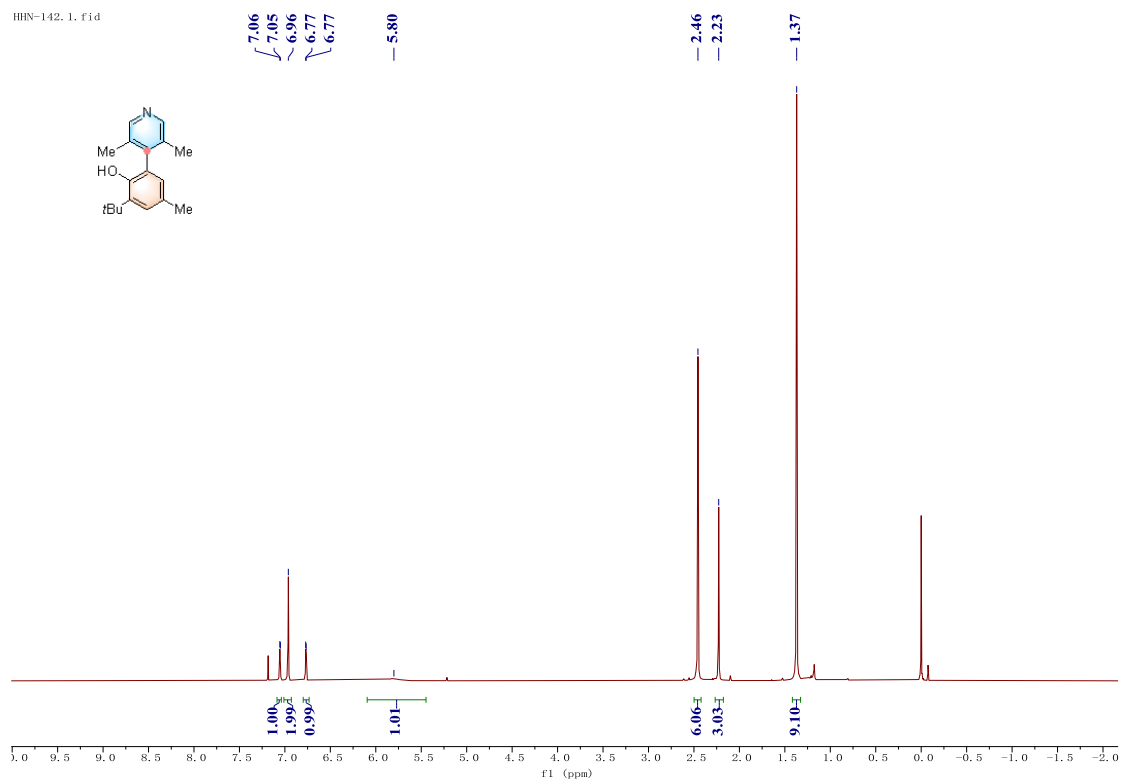
¹H NMR spectrum of 4m

HN-149a. 5. fid



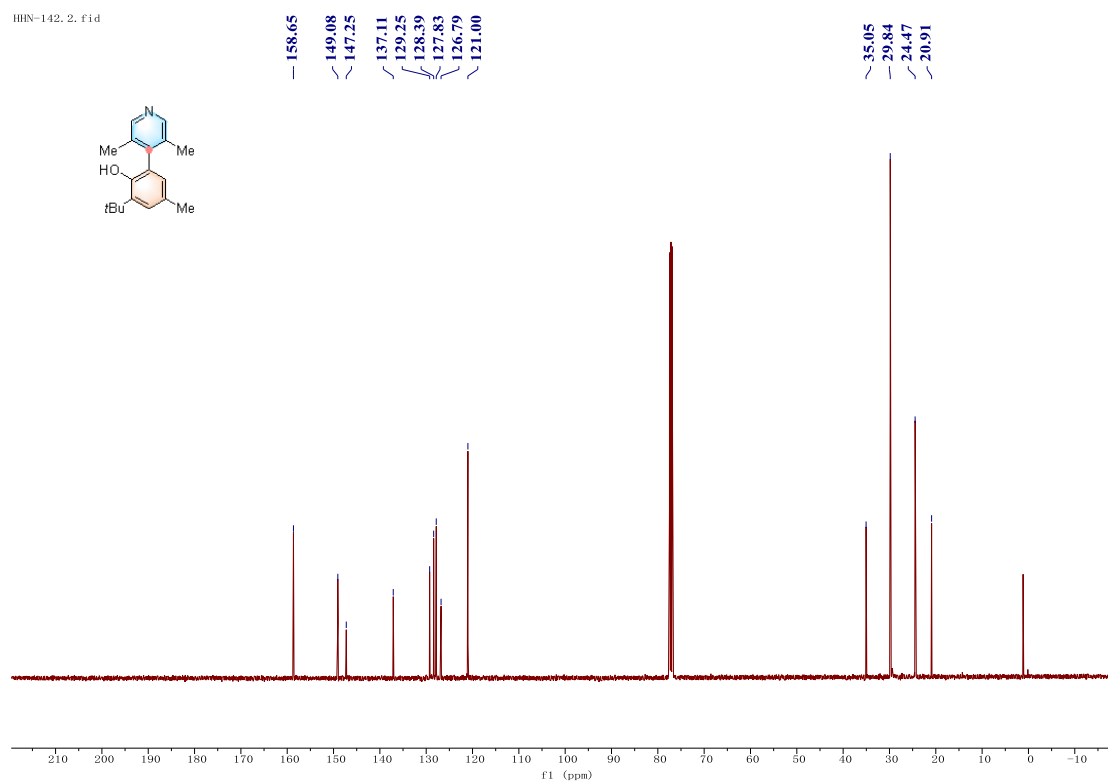
¹³C NMR spectrum of 4m

HN-142.1.fid



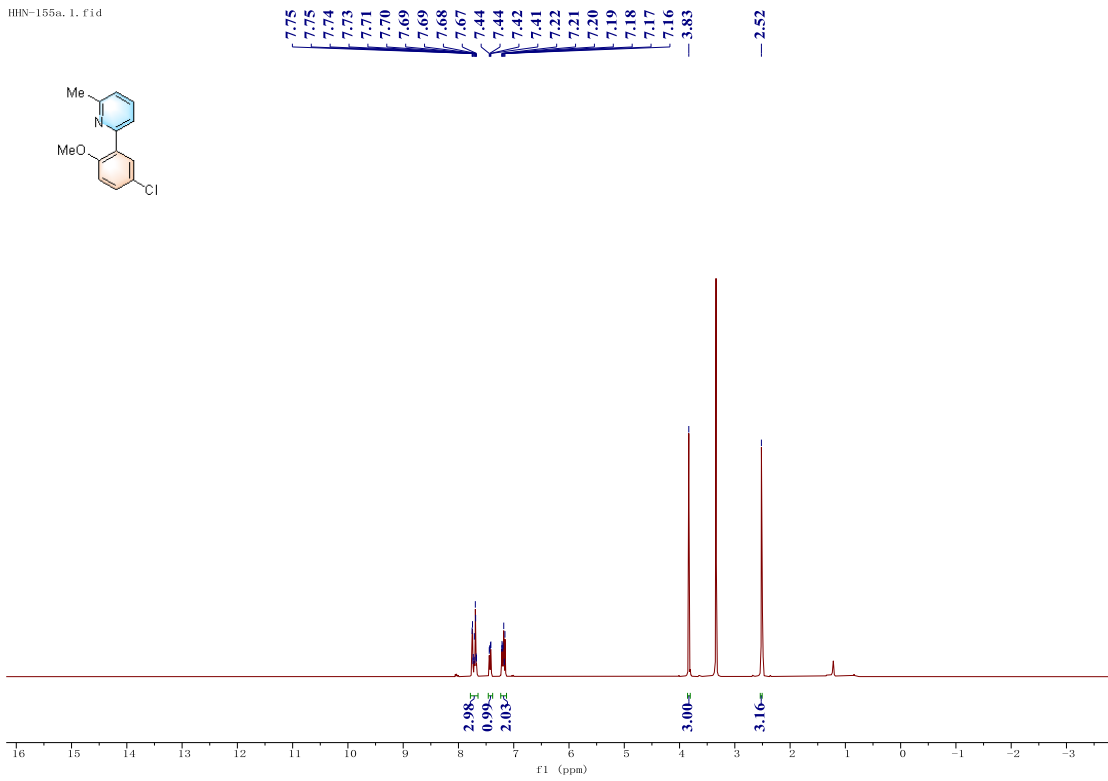
^1H NMR spectrum of 4n

HN-142.2.fid



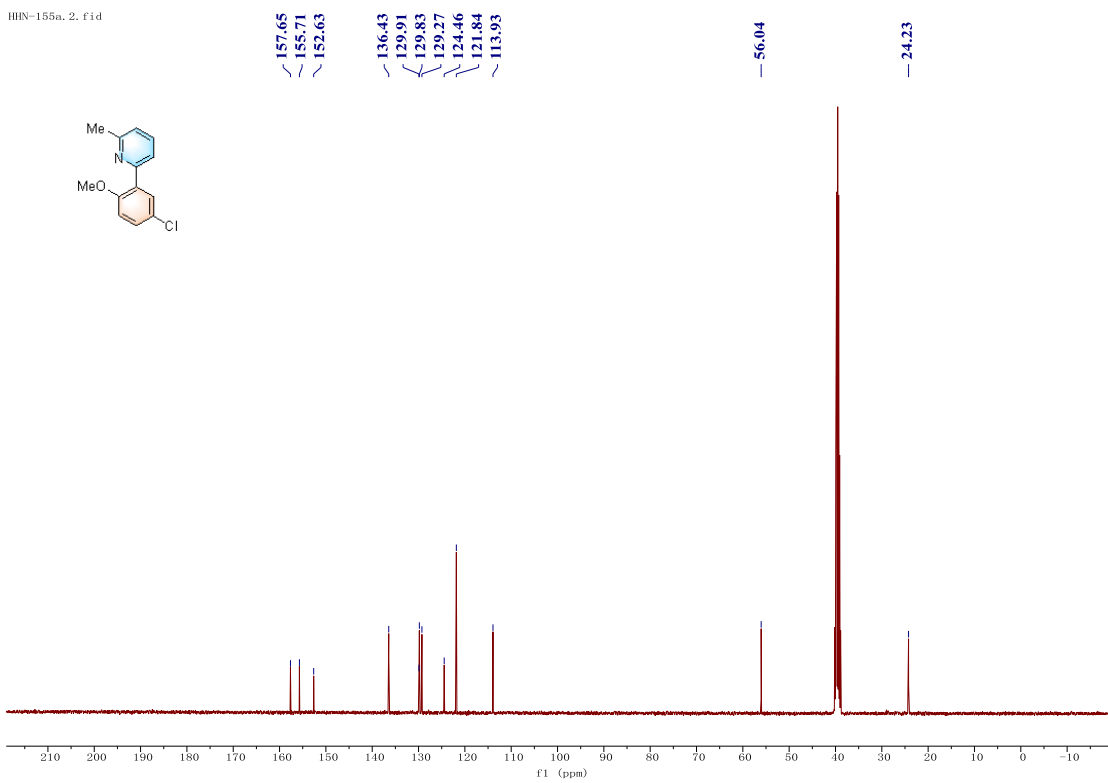
^{13}C NMR spectrum of 4n

HN-155a. 1.fid

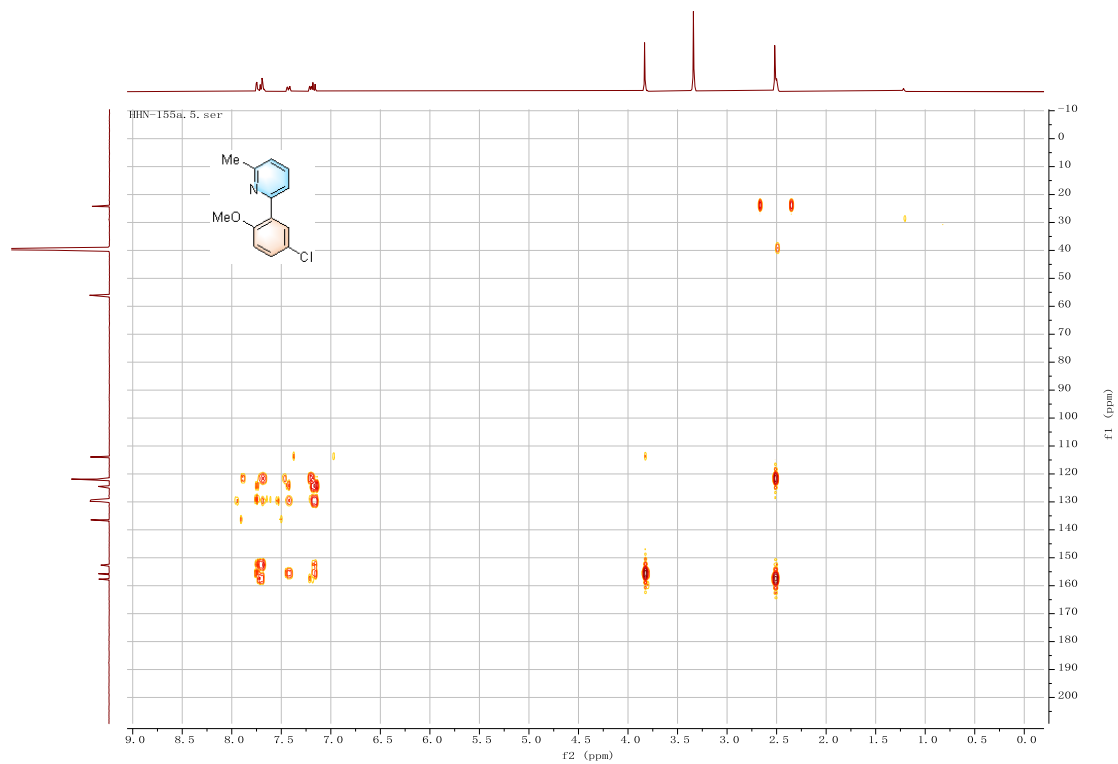


¹H NMR spectrum of 6a

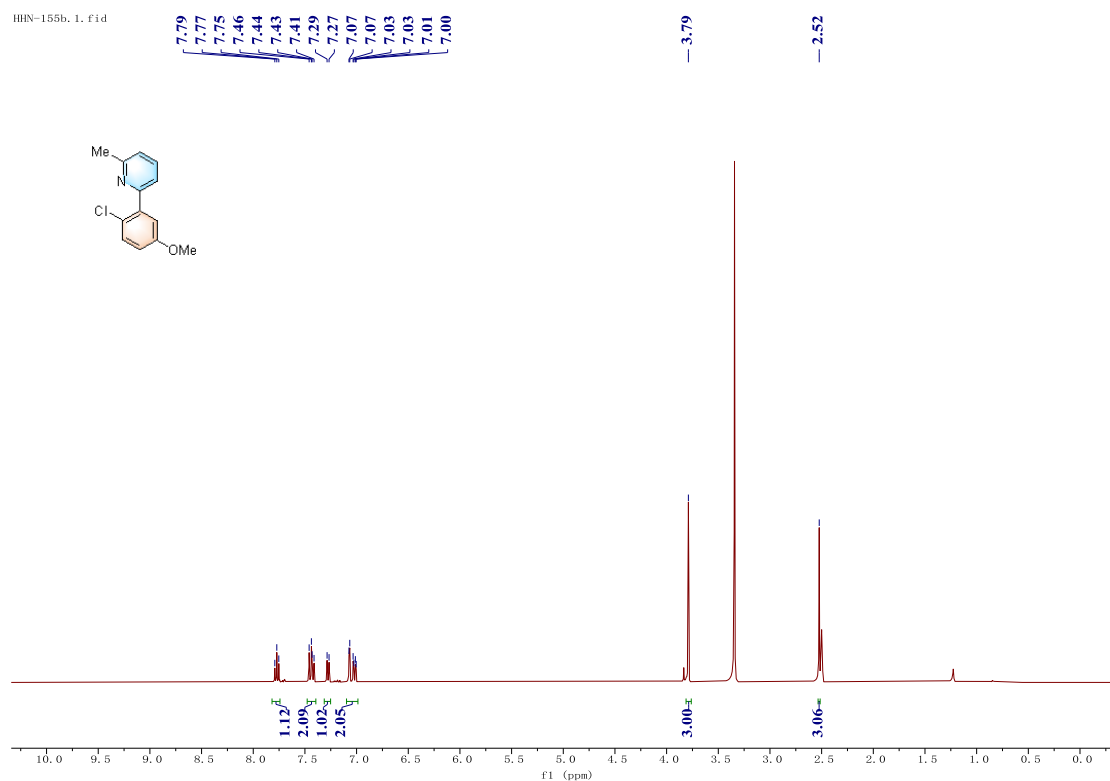
HN-155a. 2.fid



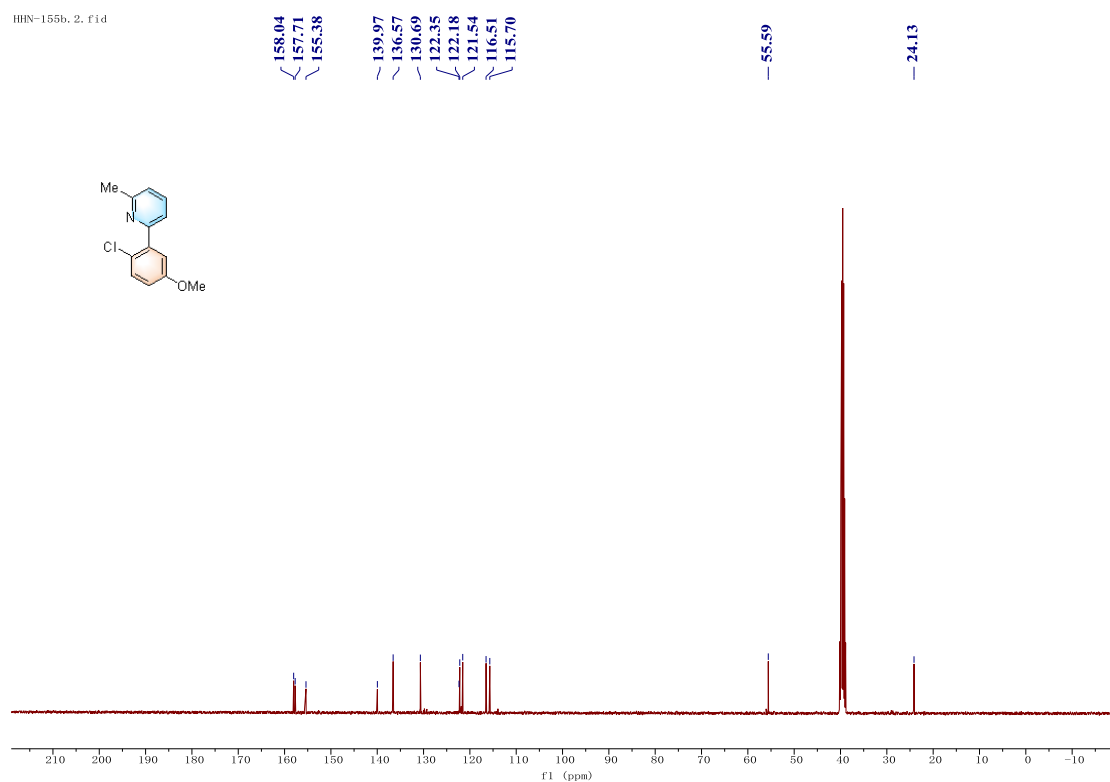
¹³C NMR spectrum of 6a



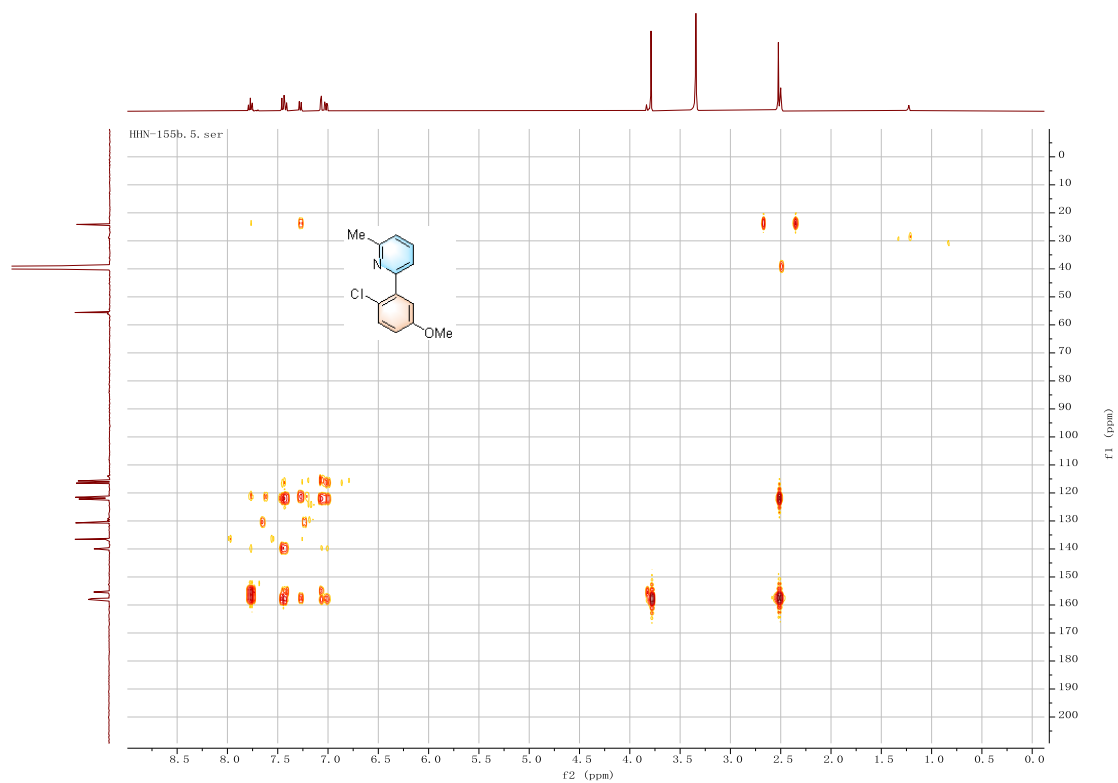
HMBC spectrum of 6a



¹H NMR spectrum of 6b

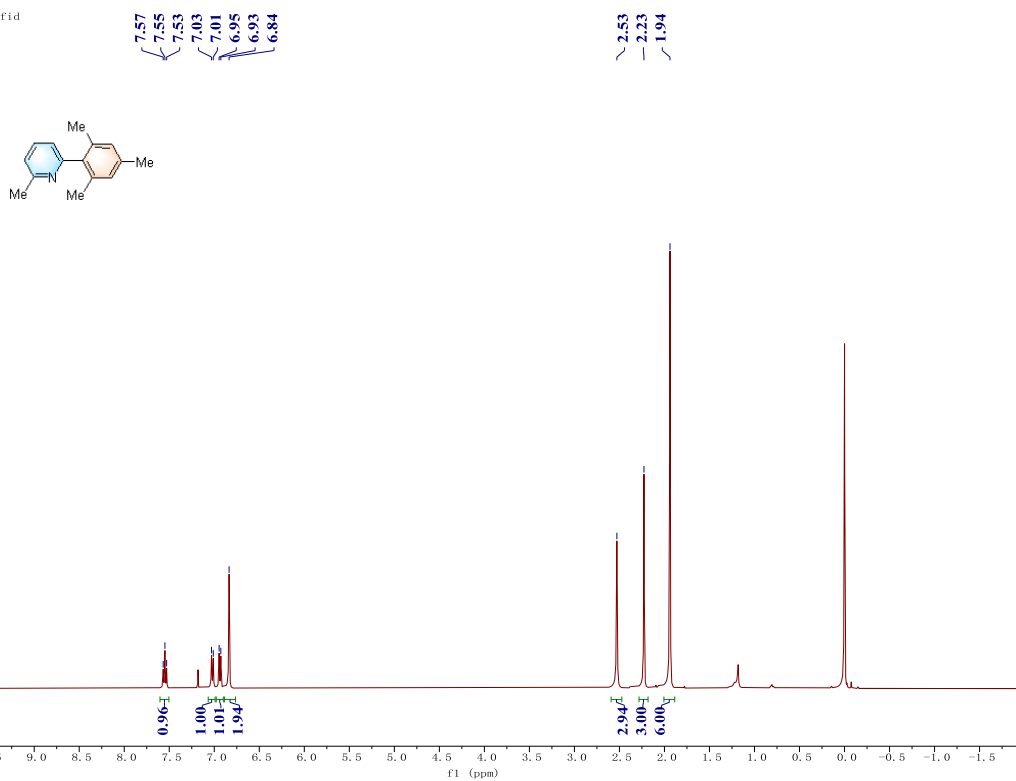


¹³C NMR spectrum of 6b



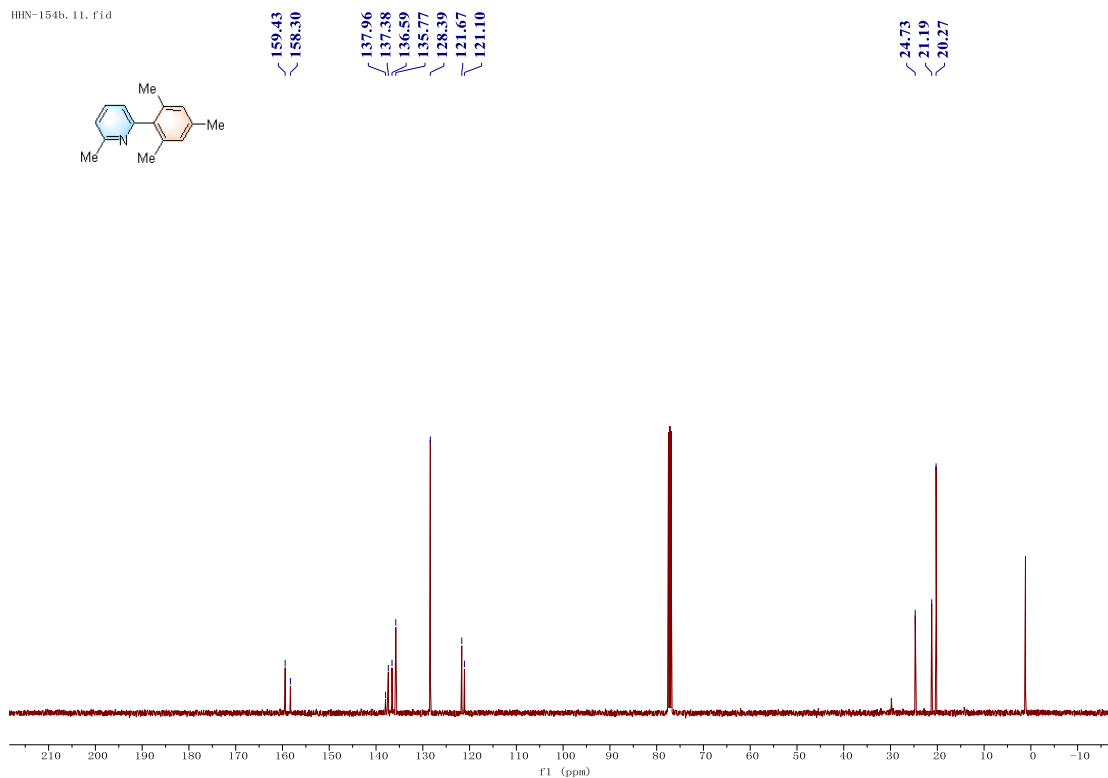
HMBC spectrum of 6b

HN-154b, 10, f1d

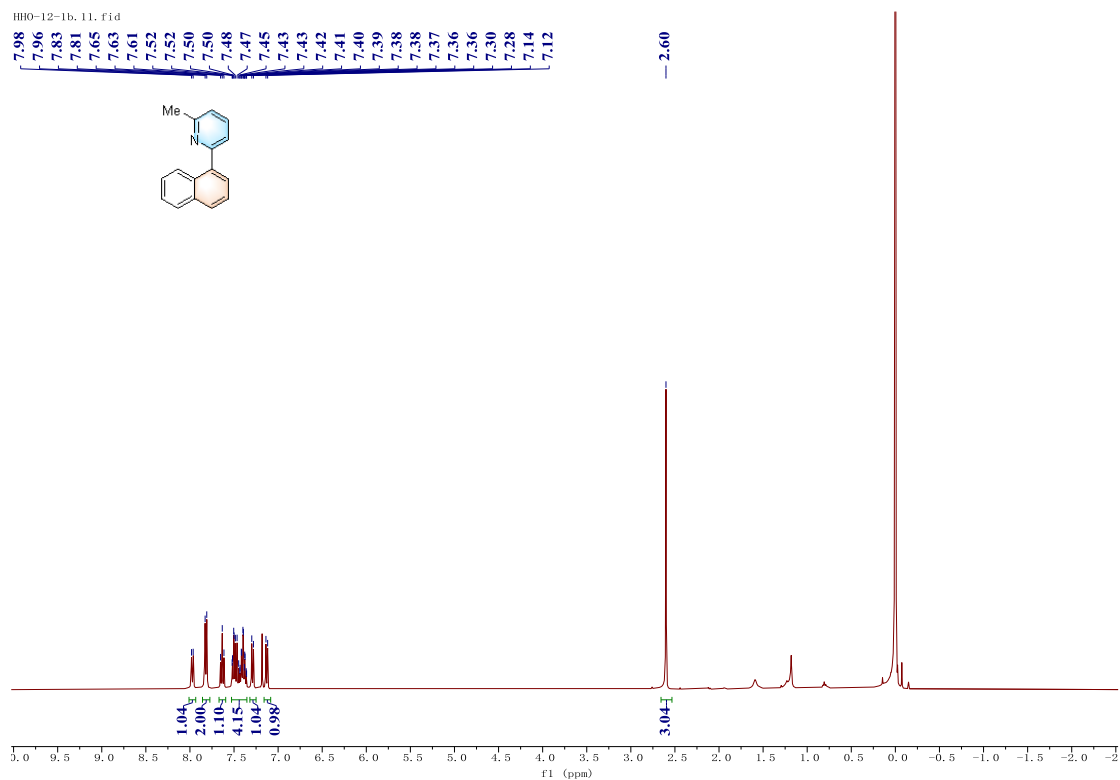


¹H NMR spectrum of 8a

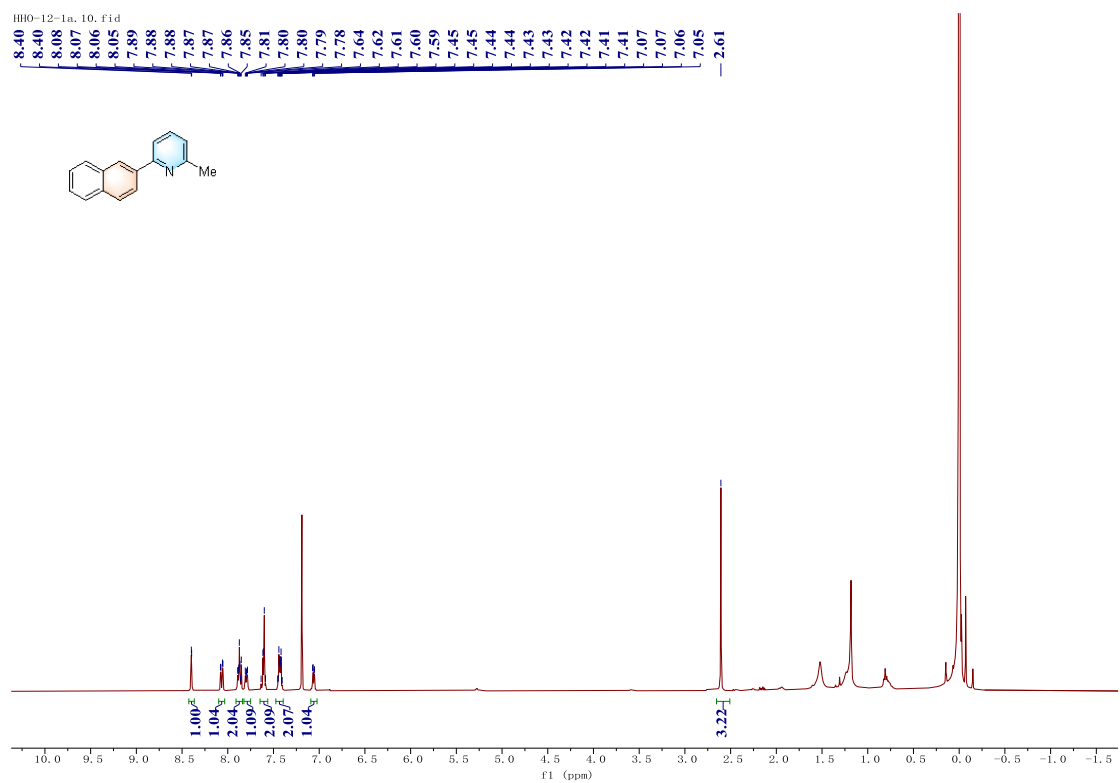
HN-154b, 11, f1d



¹³C NMR spectrum of 8a



¹H NMR spectrum of 8b-1



¹H NMR spectrum of 8b-2