Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bromine Radical Enhanced Stoichiometric Pyridylation of Alkylarenes and Diarylmethanes at Room Temperature

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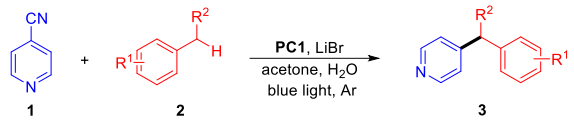
1. General information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. The reactions via general procedure was carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those in literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected.

2. Experiment section

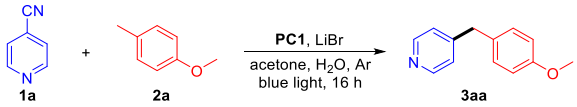
2.1 Typical experimental procedure for the pyridylation



To a Schlenk tube was added **1** (0.2 mmol), **2** (0.4 mmol, 2.0 eqiuv), **PC1** (0.004 mmol, 2 mol%), LiBr (20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in argon atmosphere (1 atm) under 35 W blue LED light for 16 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 20 : 1 to 5 : 1) to afford the desired products **3**.

2.2 Optimization of reaction conditions

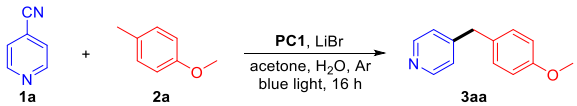
Table S1. Screening of amount **2a** [a]



Entry	Variation from standard conditions	Yield (%) [b]
1	10 equiv	84
2	2 equiv	88

[a] Reaction conditions: **1a** (0.2 mmol), **2a**, **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

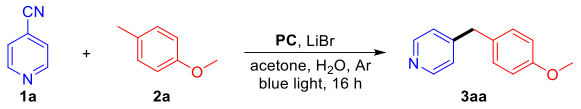
Table S2. Control experiments [a]



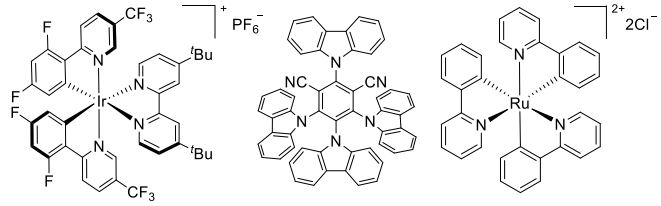
Entry	Variation from standard conditions	Yield (%) [b]
1	none	88
2	No **PC1**	0
3	No light	0
4	No LiBr	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 eqiuv), photocatalyst (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

Table S3. Screening of phototcatalyst [a]



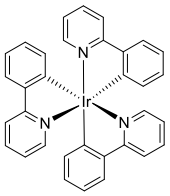
Entry	Photocatalyst	Yield (%) [b]
1	**PC1**	88
2	**PC2**	0
3	**PC3**	0
4	**PC4**	0
5	**PC5**	0
6	**PC6**	58



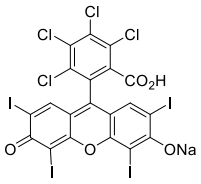
PC1: Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$

PC2: 4CzIPN

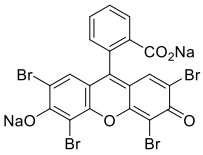
PC3: Ru(bpy)$_3$Cl$_2$



PC4: *fac*-Ir(ppy)$_3$



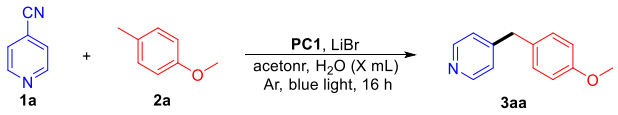
PC5: Rose Bengal



PC6: Eosin Y

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 eqiuv), **PC** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

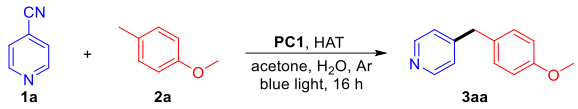
Table S4. Screening of H_2O [a]



Entry	H_2O (X mL)	Yield (%) [b]
1	1.0	66
2	1.1	78
3	1.2	88
4	1.3	71
5	1.4	63
6	1.5	56

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 eqiuv), **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (X mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

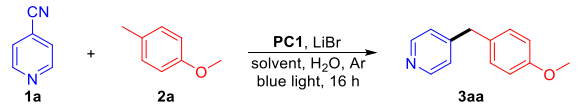
Table S5. Screening of HAT reagents [a]



Entry	HAT	Yield (%) [b]
1	LiBr	88
2	NH_4Br	62
3	NaBr	50
4	TBAB	60
5	NBS	22
6	LiCl	52
7	NH_4I	0
8	LiF	trace
9	CH_2Br_2	20
10	$NiBr_2$	23
11	LiBr (10 mol%)	65
12	LiBr (50 mol%)	72

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 eqiuv), **PC1** (0.004 mmol, 2 mol%), HAT (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

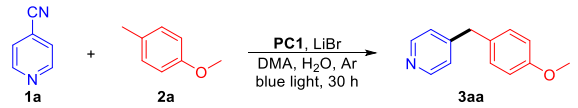
Table S6. Screening of solvent [a]



Entry	solvent	Yield (%) [b]
1	acetone	88
2	CH_3CN	22
3	THF	14
4	DCM	9
5	DMSO	47
6	EtOH	48

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 eqiuv), **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), solvent (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 16 h at room temperature. [b] Isolated yields.

2.3 Scale-up experiment

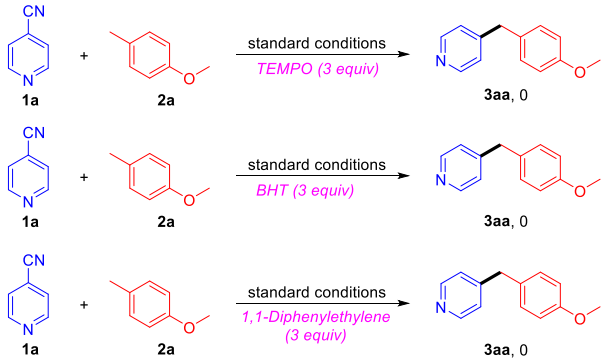


A 50 mL Schlenk tube was added **1a** (4.0 mmol), **2a** (8 mmol, 2.0 eqiuv), **PC1** (0.06 mmol, 1.5 mol%), LiBr (0.8 mmol, 20 mol%), H_2O (18 mL), acetone (30 mL). Then the mixture was stirred at room temperature in argon atmosphere (1 atm) under 35 W blue LED light for 30 h. After the reaction was

finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 5 : 1) to afford the desired products **3aa** in 66% yield.

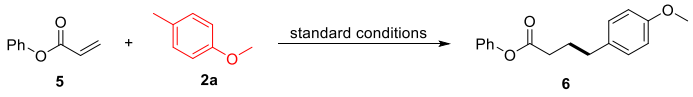
3. Mechanistic studies

3.1 Radical trapping experiments

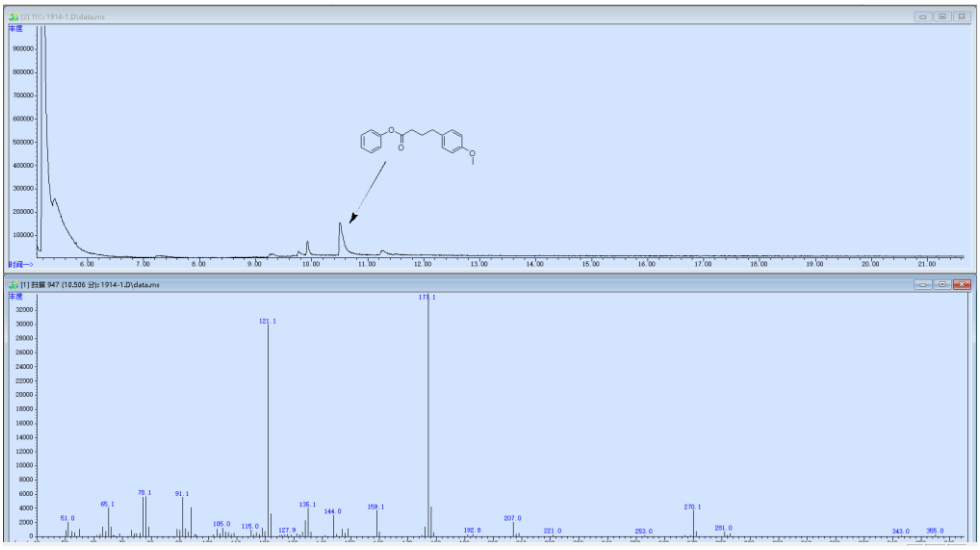


Three reactions of radical trapping experiments were performed. A solution of TEMPO (3.0 equiv, 0.6 mmol), BHT (3 equiv, 0.6 mmol) or 1,1-diphenylethene (3 equiv, 0.6 mmol), **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 eqiuv), **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in argon atmosphere (1 atm) under 35 W blue LED light for 16 h.

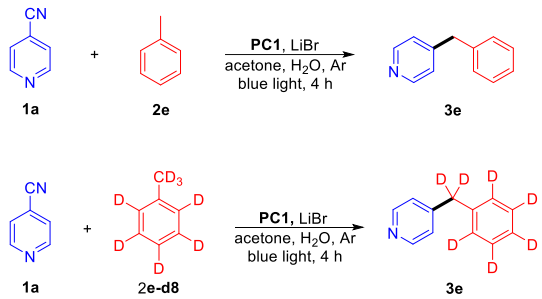
3.2 Benzyl radical trapping experiments



To a Schlenk tube was added **2a** (0.2 mmol), **5** (0.2 mmol, 1.0 eqiuv), **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in argon atmosphere (1 atm) under 35 W blue LED light for 16 h. Phenyl 4-(4-methoxyphenyl)butanoate **6** could be detected by GC-MS.



3.3 Kinetic isotope effect



Two parallel reactions of toluene (**2e)** or toluene-d_8 (**2e-d$_8$**) were performed. A solution of toluene (**2e**, 2.0 equiv), or toluene- d_8 (**2e-d$_8$**, 2.0 equiv), **1a** (0.2 mmol), **PC1** (0.004 mmol, 2 mol%), LiBr (0.04 mmol, 20 mol%), H_2O (1.2 mL), acetone (3 mL). Then the mixture was stirred at room temperature in Ar atmosphere (1 atm) under 35 W blue LED light for 4 h. The aqueous phase was re-extracted with EtOAc (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The solvent was removed on a rotary evaporator under reduced pressure. The residue was measured by GC, and the product **3g** in 17% yield and **3g-d$_7$** in 5% yield by using dodecane as the internal standard.

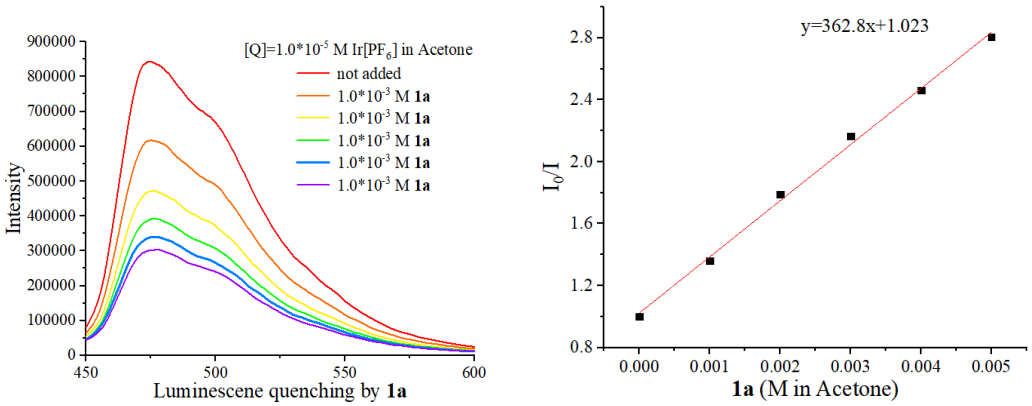
3.4 Stern–Volmer Quenching[1]

Formulation solution: Isonicotinonitrile (**1a**, 351.4 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. 1-methoxy-4-methylbenzene (**2a**, 315 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.5 M. LiBr (10.8 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.05 M. Photocatalyst

$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.8 mg) was dissolved in acetone (25.0 mL) to set the concentration to be 0.1 mM.

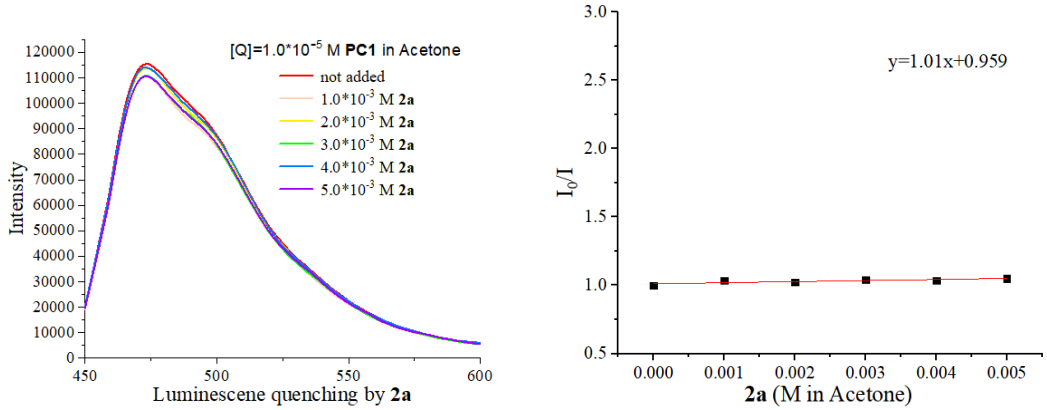
Experimental procedure: The resulting 0.1 M solution (50 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding further solvent (acetone) to prepare a 2.5 μM solution. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 425 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of isonicotinonitrile solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 375 nm. Fluorescence emission spectra of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL, 100.0 μL, fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

(a) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by **1a** in acetone.

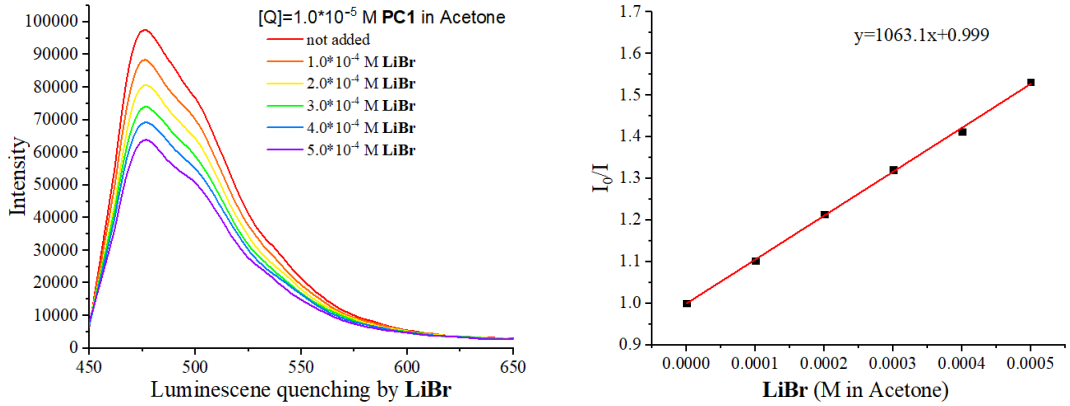


The emission intensity of the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ catalyst solution slightly affected by the gradual increase of the amount of **1a**.

(b) $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by **2a** in acetone. Linear quenching is not observed.

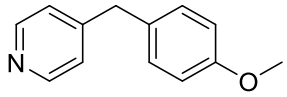


(c) Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 quenched by **LiBr** in acetone.



The emission intensity of the Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 catalyst solution slightly affected by the gradual increase of the amount of **LiBr**.

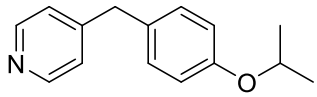
4. Analytical data



4-(4-Methoxybenzyl)pyridine (3a)

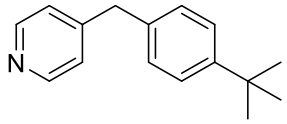
Yield: 35.0 mg, 88%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 5.1 Hz, 2H), 7.08 (d, *J* = 5.7 Hz, 4H), 6.85 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 150.5, 149.6, 130.8, 129.9, 124.0, 114.0, 55.1, 40.2.

These spectroscopic data correspond to reported data.[2]



4-(4-Isopropoxybenzyl)pyridine (3b)

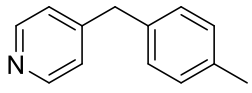
Yield: 42.2 mg, 93%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.1 Hz, 2H), 7.09 (d, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.51 (m, 1H), 3.89 (s, 2H), 1.33 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 150.5, 149.7, 130.6, 130.0, 124.1, 116.0, 69.8, 40.3, 22.0. HRMS (ESI) m/z calcd for $C_{15}H_{18}ON$ $(M+H)^+$ 228.1383, found 228.1384.



4-(4-(*tert*-Butyl)benzyl)pyridine (3c)

Yield: 41.0 mg, 91%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.1 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 7.0 Hz, 4H), 3.94 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 149.6, 149.5, 135.7, 128.6, 125.6, 124.2, 40.7, 34.4, 31.3.

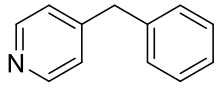
These spectroscopic data correspond to reported data.[2]



4-(4-Methylbenzyl)pyridine (3d)

Yield: 29.7 mg, 81%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 5.0 Hz, 2H), 7.16 – 7.09 (m, 4H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.93 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 149.5, 136.3, 135.7, 129.4, 128.9, 124.2, 40.8, 21.0.

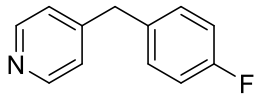
These spectroscopic data correspond to reported data.[2]



4-Benzylpyridine (3e)

Yield: 25.0 mg, 74%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.1 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 5.7 Hz, 1H), 7.17 (d, *J* = 6.9 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 2H), 3.97 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 149.7, 138.8, 129.0, 128.7, 126.7, 124.2, 41.2.

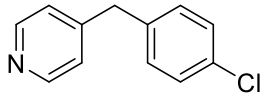
These spectroscopic data correspond to reported data.[3]



4-(4-Fluorobenzyl)pyridine (3f)

Yield: 23.2 mg, 62%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.1 Hz, 2H), 7.18 – 7.10 (m, 2H), 7.08 (d, *J* = 6.0 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7 (d, *J* = 243.6 Hz), 149.81, 134.5 (d, *J* = 3.3 Hz), 130.5, 130.4, 124.0, 115.5 (d, *J* = 21.2 Hz), 40.33.

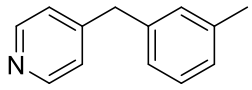
These spectroscopic data correspond to reported data.[3]



4-(4-Chlorobenzyl)pyridine (3g)

Yield: 22.7 mg, 56%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (d, *J* = 6.1 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 6.2 Hz, 2H), 3.93 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 149.4, 137.2, 132.6, 130.3, 128.8, 124.1, 40.5.

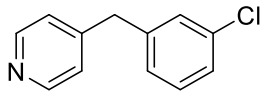
These spectroscopic data correspond to reported data.[3]



4-(3-Methylbenzyl)pyridine (3i)

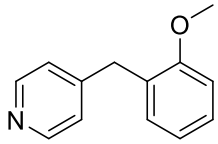
Yield: 27.5 mg, 75%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.1 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 149.7, 138.7, 138.4, 129.8, 128.6, 127.4, 126.0, 124.2, 41.2, 21.4.

These spectroscopic data correspond to reported data.[3]



4-(3-Chlorobenzyl)pyridine (3j)

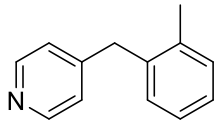
Yield: 19.1 mg, 47%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.1 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.16 (s, 1H), 7.09 (d, *J* = 6.1 Hz, 2H), 7.05 (d, *J* = 6.4 Hz, 1H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 149.1, 140.8, 134.5, 130.0, 129.1, 127.2, 126.9, 124.1, 40.8. HRMS (ESI) m/z calcd for $C_{12}H_{11}ClN$ $(M+H)^+$ 204.0575, found 204.0574.



4-(2-Methoxybenzyl)pyridine (3k)

Yield: 29.5 mg, 74%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 6.1 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.13 – 7.05 (m, 3H), 6.89 (dd, *J* = 15.1, 7.6 Hz, 2H), 3.94 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 150.2, 149.5, 130.4, 128.1, 127.3, 124.1, 120.5, 110.5, 55.2, 35.5.

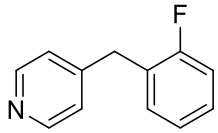
These spectroscopic data correspond to reported data.[3]



4-(2-Methylbenzyl)pyridine (3l)

Yield: 24.2 mg, 66%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.1 Hz, 2H), 7.24 – 7.15 (m, 3H), 7.13 – 7.08 (m, 1H), 7.03 (d, *J* = 5.1 Hz, 2H), 3.98 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 149.5, 136.7, 136.6, 130.5, 130.1, 127.1, 126.2, 123.9, 38.8, 19.6.

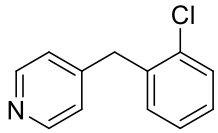
These spectroscopic data correspond to reported data.[3]



4-(2-Fluorobenzyl)pyridine (3m)

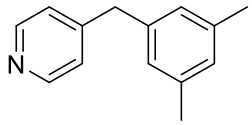
Yield: 18.0 mg, 48%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.0 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.19 – 7.03 (m, 5H), 3.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9 (d, *J* = 244.5 Hz),

149.8, 148.8, 131.0 (d, *J* = 4.4 Hz), 128.7 (d, *J* = 8.0 Hz), 125.9 (d, *J* = 15.8 Hz), 124.3 (d, *J* = 3.6 Hz), 124.0, 115.6 (d, *J* = 21.7 Hz), 34.4, 34.4. HRMS (ESI) m/z calcd for $C_{12}H_{10}FNNa$ $(M+Na)^+$ 210.0869, found 210.0872.



4-(2-Chlorobenzyl)pyridine (3n)

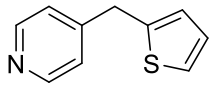
Yield: 16.2 mg, 40%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.0 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.22 (t, *J* = 4.5 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.09 (d, *J* = 5.1 Hz, 2H), 4.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 148.6, 136.5, 134.3, 131.1, 129.8, 128.4, 127.1, 124.1, 38.7. HRMS (ESI) m/z calcd for $C_{12}H_{10}ClNNa$ $(M+Na)^+$ 226.0394, found 226.0396.



4-(3,5-Dimethylbenzyl)pyridine (3o)

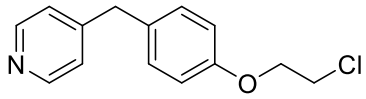
Yield: 32.3 mg, 82%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.1 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 2H), 6.88 (s, 1H), 6.79 (s, 2H), 3.88 (s, 2H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 149.7, 138.7, 138.3, 128.3, 126.8, 124.2, 41.1, 21.2.

These spectroscopic data correspond to reported data.[4]



4-(Thiophen-2-ylmethyl)pyridine (3p)

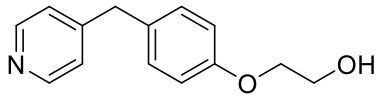
Yield: 27.7 mg, 79%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.1 Hz, 2H), 7.19 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.16 (d, *J* = 6.0 Hz, 2H), 6.96-6.94 (m, 1H), 6.83 (dd, *J* = 3.5, 1.1 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 149.2, 140.9, 127.0, 125.98 124.59, 123.7, 35.2. HRMS (ESI) m/z calcd for $C_{10}H_{10}NS$ $(M+H)^+$ 176.0528, found 176.0529.



4-(4-(2-Chloroethoxy)benzyl)pyridine (3q)

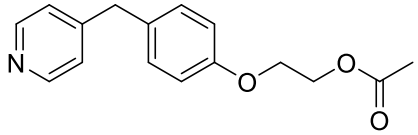
Yield: 37.1 mg, 75%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 6.1 Hz, 2H), 7.14 – 7.04 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.21 (t, *J* = 5.9 Hz, 2H), 3.91 (s, 2H), 3.81 (t, *J* = 5.9 Hz, 2H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 157.0, 150.4, 149.7, 131.7, 130.1, 124.1, 114.9, 41.9, 40.3. HRMS (ESI) m/z calcd for $C_{14}H_{15}ClNO$ $(M+H)^+$ 248.0837, found 248.0839.



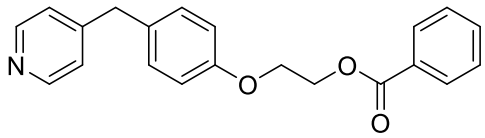
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethan-1-ol (3r)

Yield: 25.7 mg, 56%; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 6.1 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 1H), 4.07 (t, *J* = 8.1 Hz, 1H), 3.96 (t, *J* = 8.1 Hz, 1H), 3.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 150.6, 149.6, 131.3, 130.1, 124.1, 114.7, 69.2, 61.4, 40.3. HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2Na$ $(M+Na)^+$ 252.0995, found 252.0996.



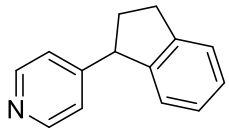
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl acetate (3s)

Yield: 43.9 mg, 81%; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.0 Hz, 2H), 7.14 – 7.03 (m, 4H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.41 (t, *J* = 4.8 Hz, 2H), 4.15 (t, *J* = 4.6 Hz, 2H), 3.90 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.0, 157.2, 150.4, 149.7, 131.4, 130.1, 124.0, 114.8, 65.9, 62.8, 40.3, 20.9. HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_3Na$ $(M+Na)^+$ 294.1101, found 294.1105.



2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl benzoate (3t)

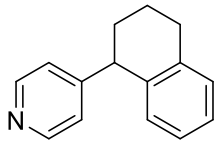
Yield: 55.3 mg, 83%; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 5.7 Hz, 2H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.14 – 7.06 (m, 4H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.66 (d, *J* = 4.4 Hz, 2H), 4.30 (d, *J* = 4.8 Hz, 2H), 3.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 157.3, 150.6, 149.6, 133.1, 131.4, 130.1, 129.8, 129.7, 128.3, 124.1, 114.9, 63.3, 40.3. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_3Na$ $(M+ Na)^+$ 356.1257, found 356.1263.



4-(2,3-Dihydro-1*H*-inden-1-yl)pyridine (4a)

Yield: 34.7 mg, 89%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.0 Hz, 2H), 7.31 (d, *J* y= 7.3 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 6.1 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 4.32 (t, *J* = 8.1 Hz, 1H), 3.12 – 2.93 (m, 2H), 2.66 – 2.55 (m, 1H), 2.09 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.4, 149.7, 144.8, 144.3, 127.0, 126.5, 124.7, 124.5, 123.4, 50.8, 35.8, 31.7.

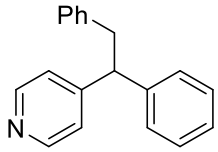
These spectroscopic data correspond to reported data.[5]



4-(1,2,3,4-Tetrahydronaphthalen-1-yl)pyridine (4b)

Yield: 36.8 mg, 88%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.1 Hz, 2H), 7.15 (d, *J* = 4.3 Hz, 2H), 7.08 – 7.03 (m, 1H), 7.02 (d, *J* = 6.2 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 1H), 2.90-2.84 (m, 2H), 2.18 – 2.15 (m, 1H), 1.86 – 1.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 149.3, 137.6, 137.1, 129.9, 129.2, 126.5, 125.9, 124.2, 44.9, 32.5, 29.5, 20.4.

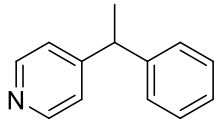
These spectroscopic data correspond to reported data.[5]



4-(1,2-Diphenylethyl)pyridine (4c)

Yield: 38.9 mg, 75%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 5.7 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.22-7.13 (m, 6H), 7.09 (d, *J* = 6.1 Hz, 2H), 6.99 (d, *J* = 6.3 Hz, 2H), 4.21 (t, *J* = 7.9 Hz, 1H), 3.42 – 3.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 149.6, 142.5, 139.1, 128.9, 128.6, 128.2, 127.9, 126.8, 126.2, 123.4, 52.5, 41.3.

These spectroscopic data correspond to reported data.[2]

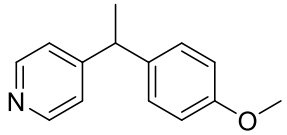


4-(1-Phenylethyl)pyridine (4d)

Yield: 33.0 mg, 90%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 6.0 Hz, 2H), 4.12 (q, *J* = 7.2 Hz,

1H), 1.64 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.5, 149.2, 144.1, 128.6, 127.5, 126.6, 123.1, 44.1, 29.4, 20.9.

These spectroscopic data correspond to reported data.[5]

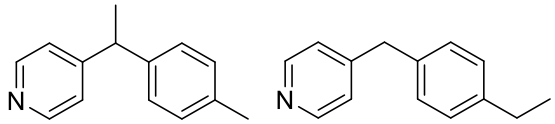


4-(1-(4-Methoxyphenyl)ethyl)pyridine (4e)

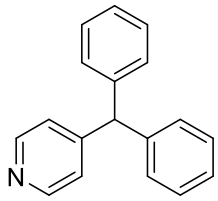
Yield: 41.3 mg, 97%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (d, *J* = 6.1 Hz, 2H), 7.15 – 7.04 (m, 4H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 155.6, 149.5, 136.4, 128.5, 122.9, 113.9, 55.2, 43.3, 21.1.

These spectroscopic data correspond to reported data.[6]

4-(1-(*p*-tolyl)ethyl)pyridine (4f) and **4-(4-ethylbenzyl)pyridine (4f')**



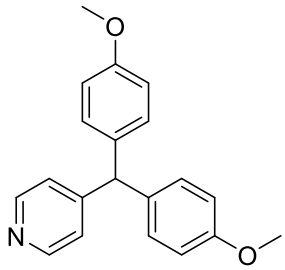
Yield: 33.5 mg, 85%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.2 Hz, 2H), 7.15 (d, *J* = 6.2 Hz, 2H), 7.10 (q, *J* = 8.1 Hz, 4H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.94 (s, 0H), 2.63 (q, *J* = 7.6 Hz, 0H), 2.32 (s, 3H), 1.61 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 0H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 149.4, 141.3, 136.2, 129.3, 128.9, 128.2, 127.4, 124.2, 123.0, 43.8, 40.8, 29.4, 28.4, 21.0, 15.5.



4-Benzhydrylpyridine (4g)

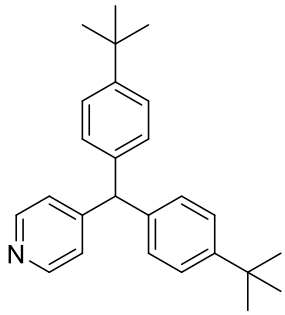
Yield: 45.6 mg, 93%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.1 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 4H), 7.28 – 7.21 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 4H), 7.05 (d, *J* = 5.9 Hz, 2H), 5.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 149.7, 142.0, 129.3, 128.6, 126.8, 124.6, 56.2.

These spectroscopic data correspond to reported data.[2]



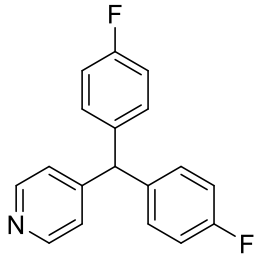
4-(bis(4-Bethoxyphenyl)methyl)pyridine (4h)

Yield: 58.6 mg, 96%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 6.2 Hz, 2H), 7.02 (d, *J* = 6.1 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 4H), 6.83 (d, *J* = 8.8 Hz, 4H), 5.39 (s, 1H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 153.4, 149.7, 134.5, 130.1, 124.4, 113.8, 55.2, 54.5. HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_2Na$ $(M+ Na)^+$ 328.1308, found 328.1318.



4-(bis(4-(*tert*-Butyl)phenyl)methyl)pyridine (4i)

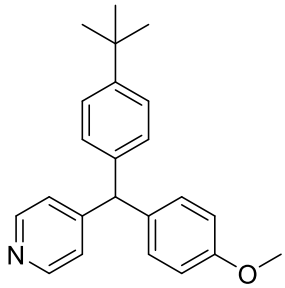
Yield: 67.2 mg, 94%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 4.7 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 4H), 7.07 (d, *J* = 5.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 4H), 5.43 (s, 1H), 1.31 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 149.6, 149.5, 139.2, 128.9, 125.4, 124.6, 55.4, 34.4, 31.3. HRMS (ESI) m/z calcd for $C_{26}H_{31}NNa$ $(M+ Na)^+$ 380.2349, found 380.2355.



4-(bis(4-Fluorophenyl)methyl)pyridine (4j)

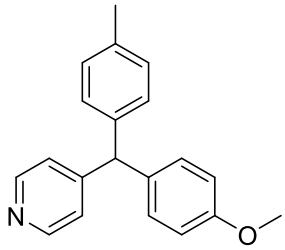
Yield: 37.7 mg, 67%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 6.1 Hz, 2H), 7.03-7.00(m, 10H), 5.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 6.1 Hz, 2H), 7.03-6.99 (m, 10H), 5.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7 (d, *J* = 244.8 Hz), 152.3, 149.9, 137.6 (d, *J* = 3.3 Hz),

130.7 (d, *J* = 8.0 Hz), 124.34, 115.5 (d, *J* = 21.2 Hz), 54.6. HRMS (ESI) m/z calcd for $C_{18}H_{13}F_2NNa$ (M+ Na)$^+$ 304.0908, found 340.0913.



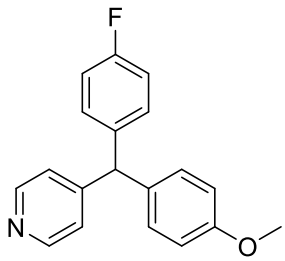
4-((4-(*tert*-Butyl)phenyl)(4-methoxyphenyl)methyl)pyridine (4k)

Yield: 62.9 mg, 95%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J* = 6.2 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 6.1 Hz, 2H), 7.02 – 6.96 (m, 4H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.40 (s, 1H), 3.78 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 153.4, 149.7, 149.5, 139.2, 134.5, 130.2, 128.8, 125.4, 124.5, 113.8, 55.20, 55.0, 34.4, 31.3. HRMS (ESI) m/z calcd for $C_{23}H_{27}NO$ (M+ H)$^+$ 332.2009, found 332.2015.



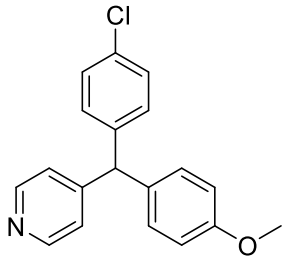
4-((4-Methoxyphenyl)(p-tolyl)methyl)pyridine (4l)

Yield: 52.0 mg, 90%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 6.1 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 6.1 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.40 (s, 1H), 3.78 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 153.4, 149.7, 139.4, 136.4, 134.4, 130.2, 129.2, 129.1, 124.5, 113.9, 55.2, 55.0, 21.0. HRMS (ESI) m/z calcd for $C_{20}H_{19}NONa$ (M+ Na)$^+$ 312.1359, found 312.1367.



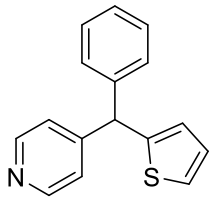
4-((4-Fluorophenyl)(4-methoxyphenyl)methyl)pyridine (4m)

Yield: 45.7 mg, 78%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 4.9 Hz, 2H), 7.10 – 6.91 (m, 8H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.42 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5 (d, *J* = 244.2 Hz), 158.4, 152.9, 149.8, 138.1 (d, *J* = 3.8 Hz), 133.9, 130.7, 130.6, 130.1, 124.4, 115.3 (d, *J* = 21.2 Hz), 113.9, 55.2, 54.5. HRMS (ESI) m/z calcd for $C_{19}H_{16}FNONa$ (M+ Na)$^+$ 316.1108, found 316.1115.



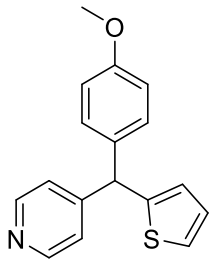
4-((4-Chlorophenyl)(4-methoxyphenyl)methyl)pyridine (4n)

Yield: 43.9 mg, 71%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 4.7 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.94 (m, 6H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.42 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 152.6, 149.9, 140.9, 133.6, 132.6, 130.5, 130.2, 128.7, 124.4, 114.0, 55.2, 54.7. HRMS (ESI) m/z calcd for $C_{19}H_{16}ClNONa$ (M+ Na)$^+$ 332.0813, found 332.0819.



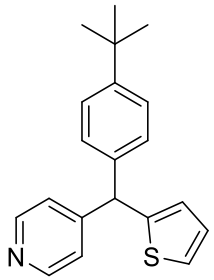
4-(Phenyl(thiophen-2-yl)methyl)pyridine (4o)

Yield: 40.2 mg, 80%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 6.1 Hz, 2H), 7.38 – 7.25 (m, 4H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 6.1 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.70 (d, *J* = 3.5 Hz, 1H), 5.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 149.9, 145.5, 142.0, 128.8, 128.7, 127.3, 126.8, 126.7, 125.1, 124.0, 51.4. HRMS (ESI) m/z calcd for $C_{16}H_{14}NS$ (M+ H)$^+$ 252.0841, found 252.0846.



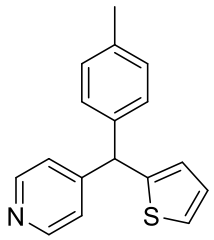
4-((4-Methoxyphenyl)(thiophen-2-yl)methyl)pyridine (4p)

Yield: 48.9 mg, 87%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.1 Hz, 2H), 7.22 (d, *J* = 5.1 Hz, 1H), 7.14 – 7.07 (m, 4H), 6.96 – 6.91 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 3.5 Hz, 1H), 5.58 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ:158.7, 152.8, 149.9, 146.1, 134.3, 129.8, 126.8, 126.6, 125.0, 123.9, 114.0, 55.3, 50.7. HRMS (ESI) m/z calcd for $C_{17}H_{15}NOSNa$ (M+ Na)$^+$ 304.0767, found 304.0775.



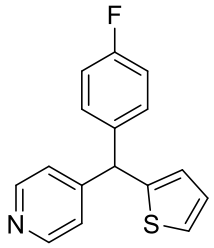
4-((4-(*tert*-Butyl)phenyl)(thiophen-2-yl)methyl)pyridine (4q)

Yield: 54.7 mg, 89%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 6.1 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 6.0 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.99 – 6.91 (m, 1H), 6.71 (d, *J* = 3.6 Hz, 1H), 5.60 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 150.1, 149.6, 145.8, 138.8, 128.3, 126.7, 126.6, 125.5, 125.0, 124.0, 51.0, 34.5, 31.3. HRMS (ESI) m/z calcd for $C_{20}H_{21}NSNa$ (M+ Na)$^+$ 330.1287, found 330.1298.



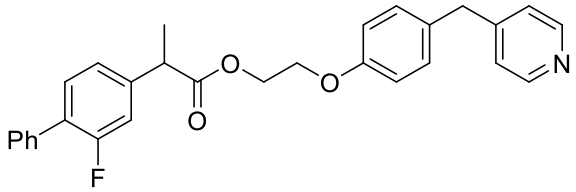
4-(Thiophen-2-yl(p-tolyl)methyl)pyridine (4r)

Yield: 44.0 mg, 83%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (d, *J* = 6.2 Hz, 2H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.14-7.12 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 5.60 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 149.5, 145.7, 139.0, 137.0, 129.3, 128.6, 126.7, 126.6, 125.0, 124.0, 51.0, 21.0. HRMS (ESI) m/z calcd for $C_{17}H_{16}NS$ (M+ H)$^+$ 266.0998, found 266.1002.



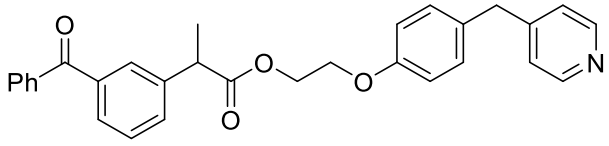
4-((4-Fluorophenyl)(thiophen-2-yl)methyl)pyridine (4s)

Yield: 37.1 mg, 69%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (d, *J* = 6.2 Hz, 2H), 7.24 (d, *J* = 3.9 Hz, 1H), 7.19 – 7.08 (m, 4H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.97 – 6.92 (m, 1H), 6.68 (d, *J* = 3.1 Hz, 1H), 5.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9 (d, *J* = 245.1 Hz), 152.4, 149.8, 145.3, 137.8 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 8.0 Hz), 126.9, 126.8, 125.3, 123.9, 115.6 (d, *J* = 21.3 Hz), 50.7. HRMS (ESI) m/z calcd for $C_{16}H_{12}FNSNa$ $(M+ Na)^+$ 292.0567, found 292.0575.



2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (5a)

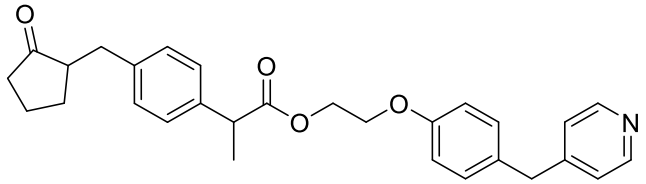
Yield: 62.8 mg, 69%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.1 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.17 – 7.10 (m, 2H), 7.10 – 7.00 (m, 4H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.51 – 4.39 (m, 2H), 4.13 (t, *J* = 4.7 Hz, 2H), 3.89 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9, 159.6 (d, *J* = 246.8 Hz), 157.2, 150.4, 149.7, 141.5 (d, *J* = 7.8 Hz), 135.41, 131.5, 130.7 (d, *J* = 4.0 Hz), 130.0, 128.9 (d, *J* = 2.8 Hz), 128.4, 127.6, 124.0, 123.5 (d, *J* = 3.3 Hz), 115.3 (d, *J* = 23.5 Hz), 114.8, 99.9, 65.8, 63.2, 44.9, 40.3, 18.3. HRMS (ESI) m/z calcd for $C_{29}H_{28}FNO_3$ $(M+ H)^+$ 456.1969, found 456.1976.



2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(3-benzoylphenyl)propanoate (5b)

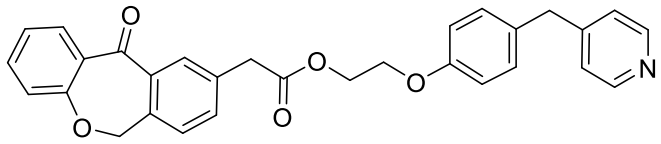
Yield: 53.0 mg, 57%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.0 Hz, 2H), 7.80 – 7.73 (m, 3H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 4H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.47 – 4.36 (m, 2H), 4.11 (t, *J* = 4.8 Hz, 2H), 3.88 (s, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 174.0,

157.1, 150.4, 149.7, 140.6, 137.8, 137.4, 132.5, 131.5, 131.4, 130.0, 129.2, 129.0, 128.5, 128.3, 124.0, 114.8, 65.8, 63.2, 45.2, 40.3, 18.4. HRMS (ESI) m/z calcd for $C_{30}H_{29}NO_4$ $(M+H)^+$ 466.2013, found 466.2018.



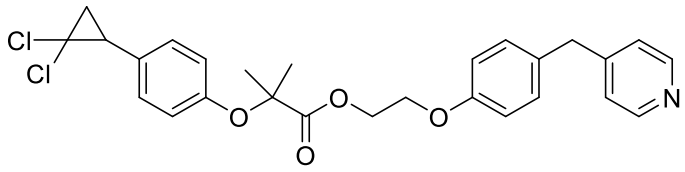
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (5c)

Yield: 55.8 mg, 61%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 5.9 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 – 7.02 (m, 6H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.45 – 4.34 (m, 2H), 4.12-4.08 (m, 2H), 3.90 (s, 2H), 3.72 (q, *J* = 7.1 Hz, 1H), 3.09 (dd, *J* = 13.9, 4.0 Hz, 1H), 2.47 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.31-2.27 (m, 2H), 2.14 – 2.02 (m, 3H), 1.96-1.89 (m, 1H), 1.73-1.68 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 220.2, 174.6, 157.3, 150.4, 149.8, 138.9, 138.1, 131.5, 130.1, 129.1, 127.5, 124.1, 114.9, 65.9, 63.0, 51.0, 45.0, 40.4, 38.2, 35.2, 29.2, 20.5, 18.5. HRMS (ESI) m/z calcd for $C_{29}H_{33}NO_4$ $(M+H)^+$ 458.2326, found 458.2328.



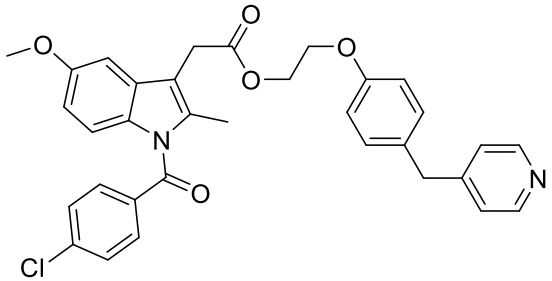
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-9-yl)acetate (5d)

Yield: 52.7 mg, 55%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 6.1 Hz, 2H), 8.11 (d, *J* = 2.4 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 7.1, 5.2 Hz, 4H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.17 (s, 2H), 4..45 (t, *J* = 4.6 Hz, 2H), 4.16 (t, *J* = 4.6 Hz, 2H), 3.90 (s, 2H), 3.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.8, 171.4, 160.5, 157.2, 150.6, 149.6, 140.4, 136.3, 135.5, 132.8, 132.5, 131.4, 130.1, 129.5, 129.3, 127.8, 127.5, 125.1, 124.1, 121.1, 114.9, 73.6, 65.9, 63.2, 40.3, 40.0. HRMS (ESI) m/z calcd for $C_{30}H_{25}NO_5Na$ $(M+Na)^+$ 502.1625, found 502.1628.



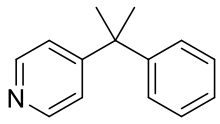
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (5e)

Yield: 48.9 mg, 49%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.1 Hz, 2H), 7.07 (m, 4H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.86 – 6.73 (m, 4H), 4.56 – 4.46 (t, *J* = 4.7 Hz, 2H), 4.10 (t, *J* = 4.7 Hz, 2H), 3.90 (s, 2H), 2.76 – 2.71 (m, 1H), 1.89 – 184 (m, 1H), 1.67 (t, *J* = 7.8 Hz, 2H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 157.1, 154.8, 150.4, 149.7, 131.5, 130.0, 129.6, 128.2, 124.1, 118.8, 114.8, 79.2, 77.3, 65.6, 63.5, 60.8, 40.3, 34.7, 25.7, 25.4, 25.4. HRMS (ESI) m/z calcd for $C_{27}H_{28}Cl_2NO_4$ $(M+H)^+$ 500.1390, found 500.1400.



2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5f)

Yield: 43.2 mg, 38%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 6.1 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.09 – 7.00 (m, 5H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.65 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.47 (d, *J* = 9.1 Hz, 1H), 4.44 (t, *J* = 4.6 Hz, 2H), 4.40 (s, 2H), 4.10 (t, *J* = 4.6 Hz, 2H), 3.80 (s, 2H), 3.79 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 168.0, 156.2, 156.1, 149.6, 147.9, 139.6, 136.3, 132.9, 131.1, 130.6, 130.0, 130.0, 129.1, 123.6, 114.9, 114.7, 114.4, 112.7, 101.5, 65.9, 63.6, 55.7, 31.3, 30.3, 20.5. HRMS (ESI) m/z calcd for $C_{33}H_{29}ClN_2O_5Na$ $(M+Na)^+$ 591.1657, found 591.1659.



4-(2-phenylpropan-2-yl)pyridine (6)

Yield: 21.3 mg, 54%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 6.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.14 (d, *J* = 6.3 Hz, 2H), 1.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 149.4, 148.6, 128.2, 126.6, 126.2, 122.1, 42.9, 29.9.

These spectroscopic data correspond to reported data.[7]

5 Reference

[1] E. D. Nacsa, D. W. C. MacMillan, *J. Am. Chem. Soc.* 2018, *140*, 3322.

[2] J. Shi, T. Yuan, M. Zheng, X. Wang, *ACS Catal.* **2021**, *11*, 3040.

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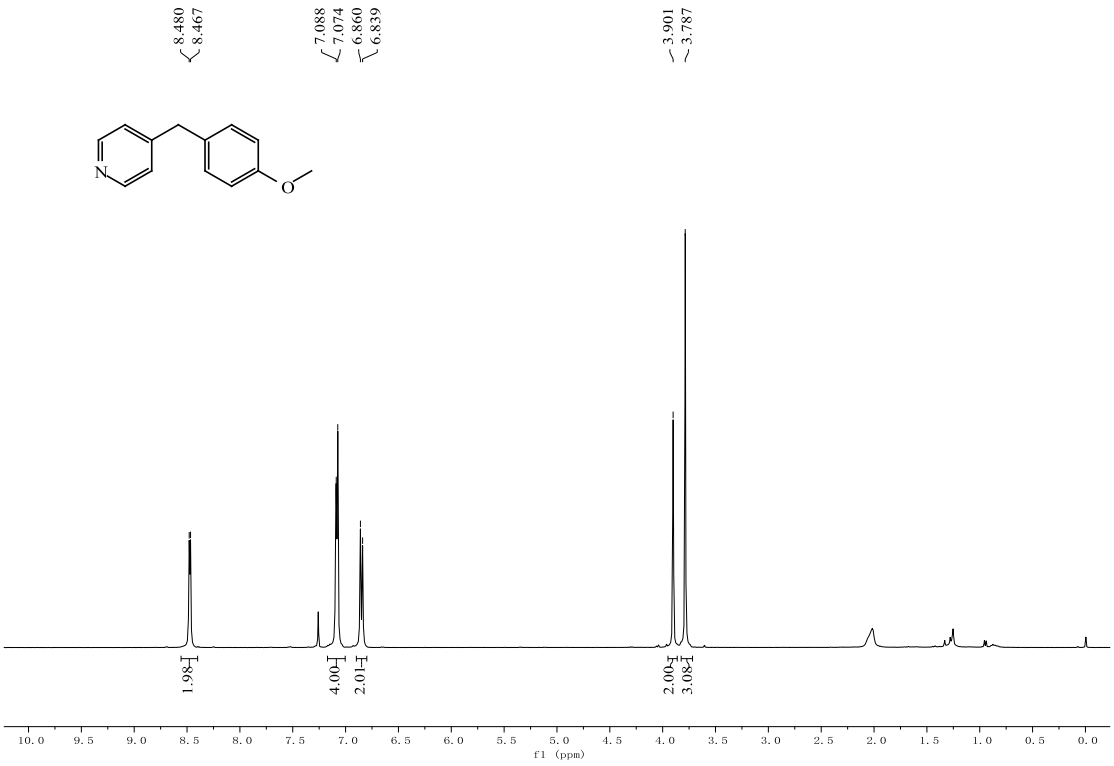
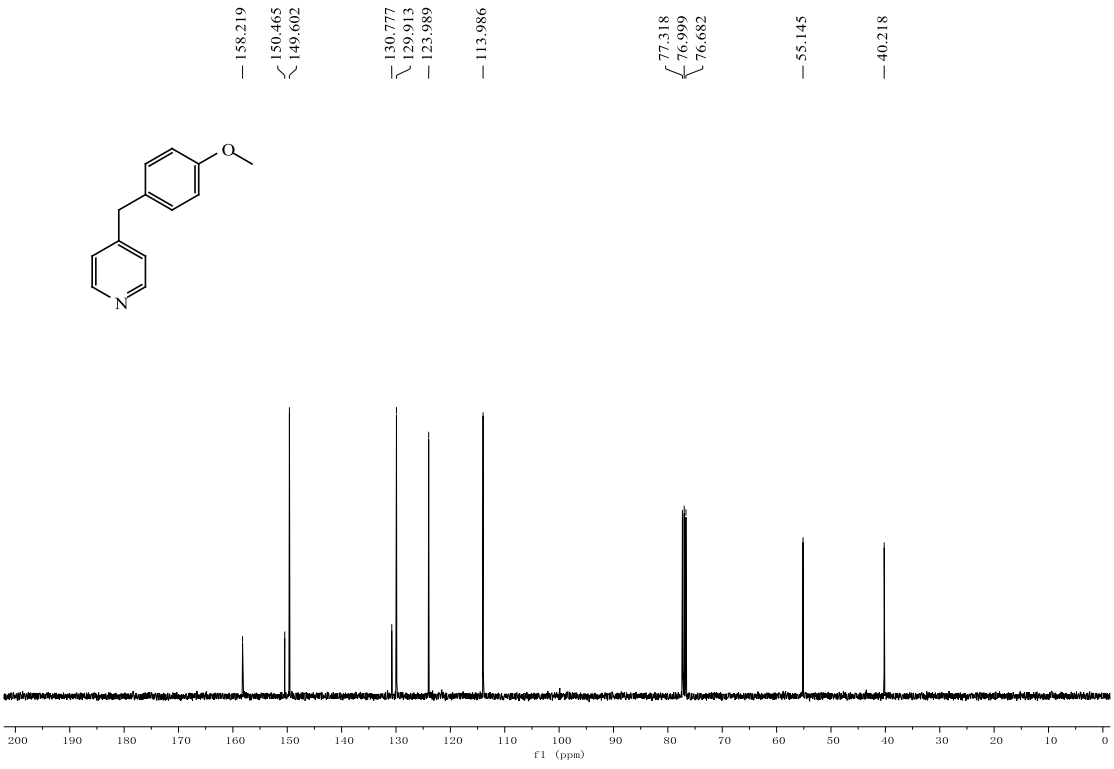
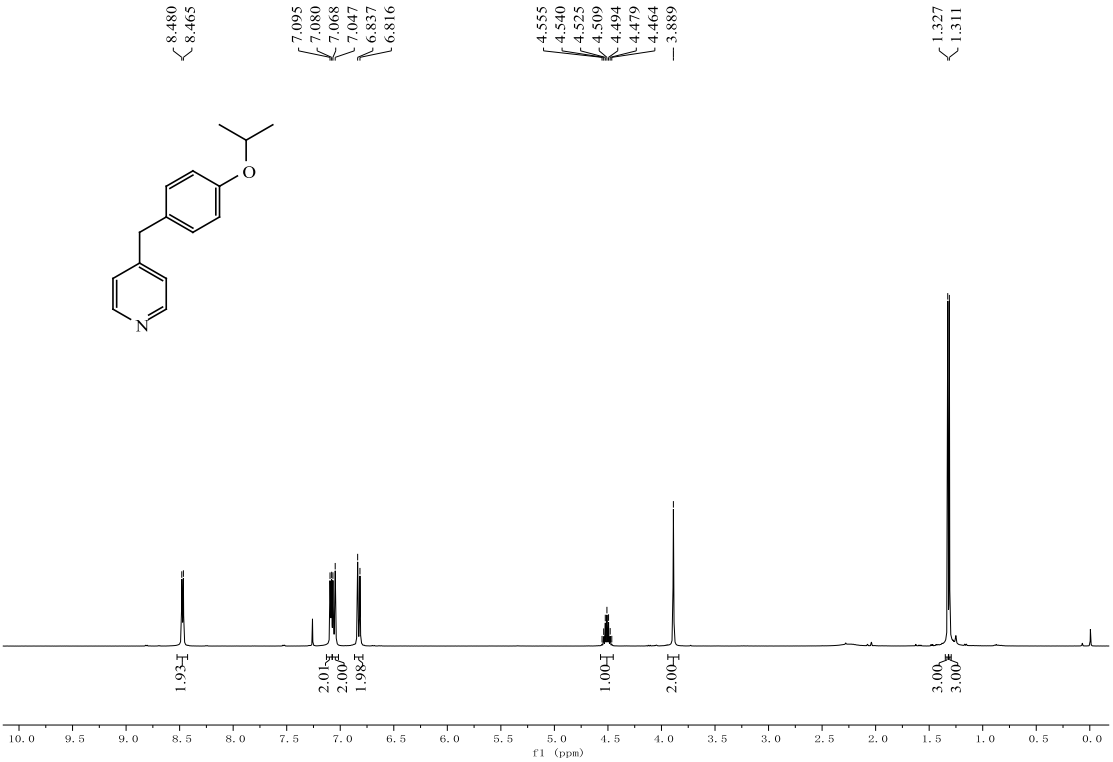
6. Spectra

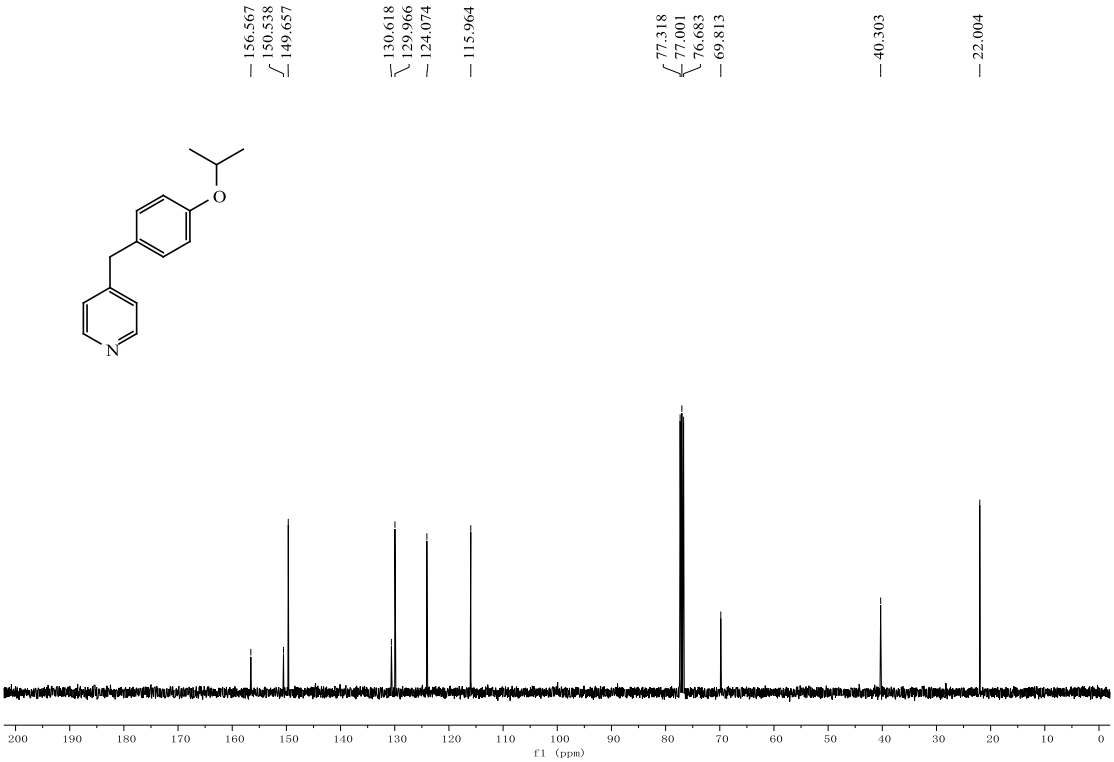
4-(4-Methoxybenzyl)pyridine (3a)



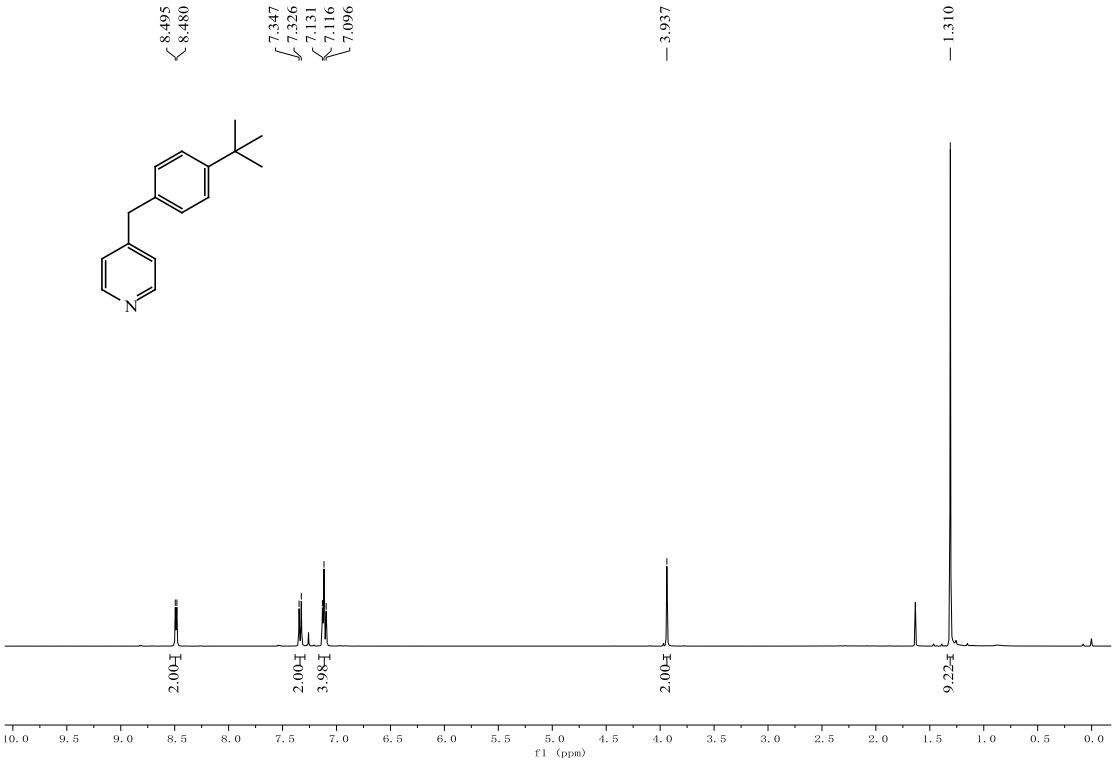


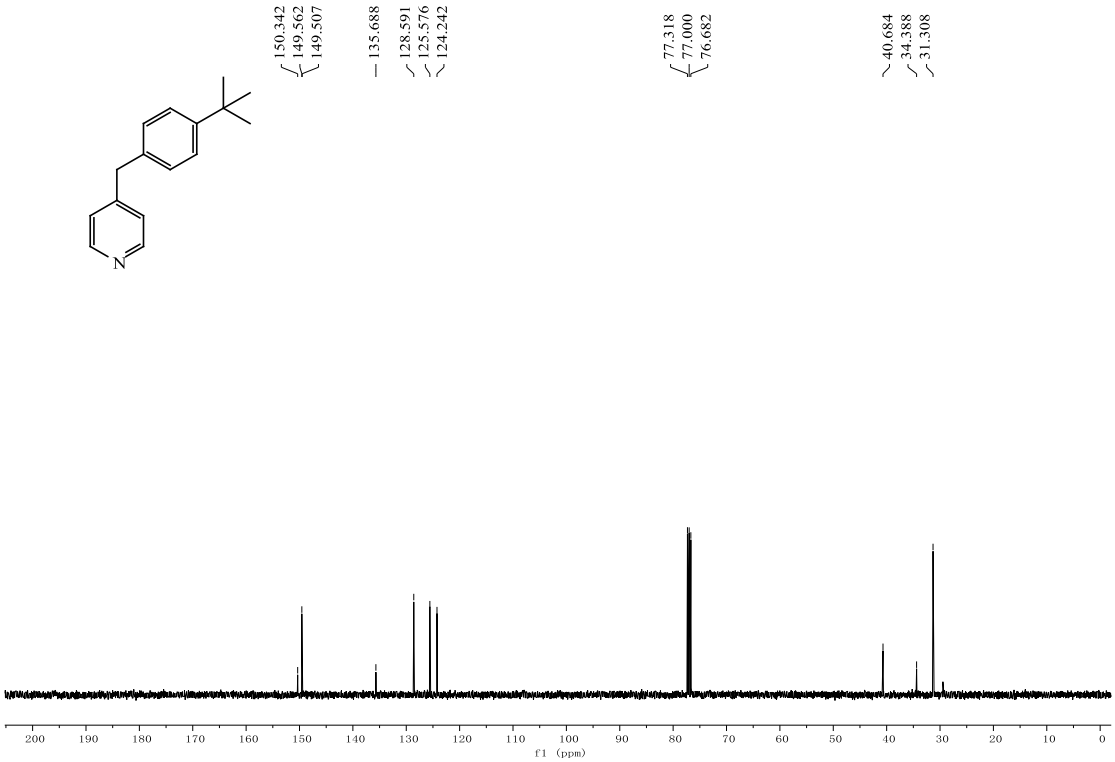
4-(4-Isopropoxybenzyl)pyridine (3b)





4-(4-(*tert*-Butyl)benzyl)pyridine (3c)





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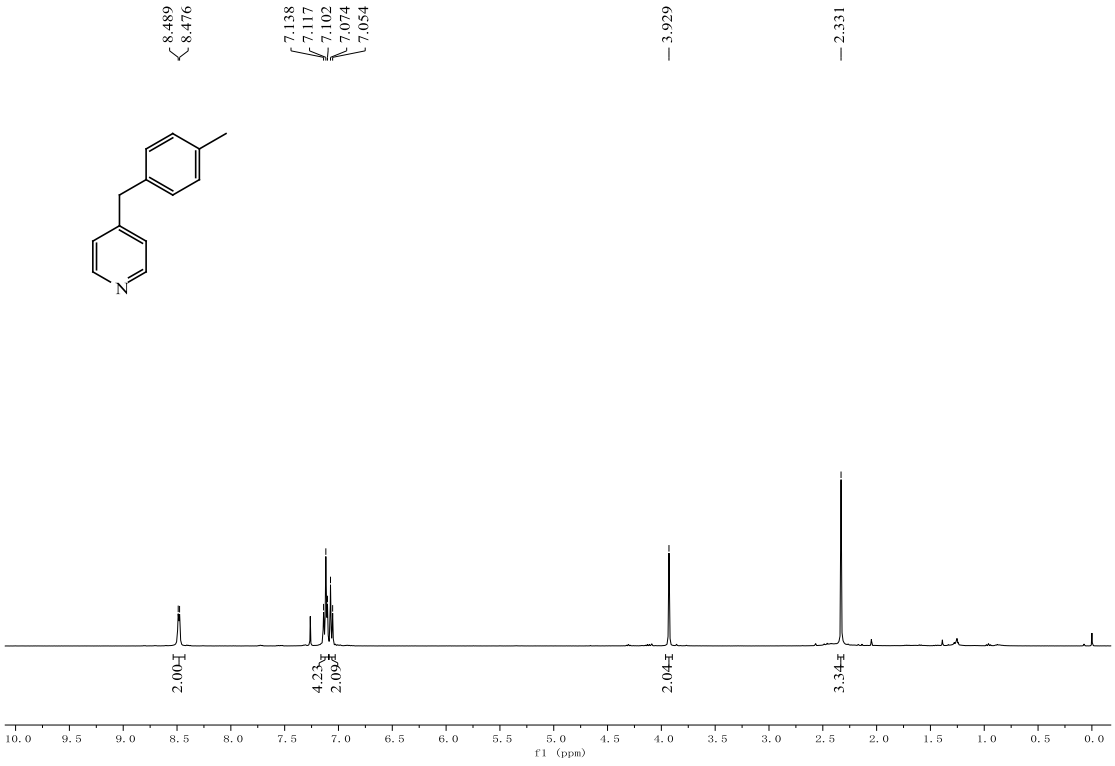

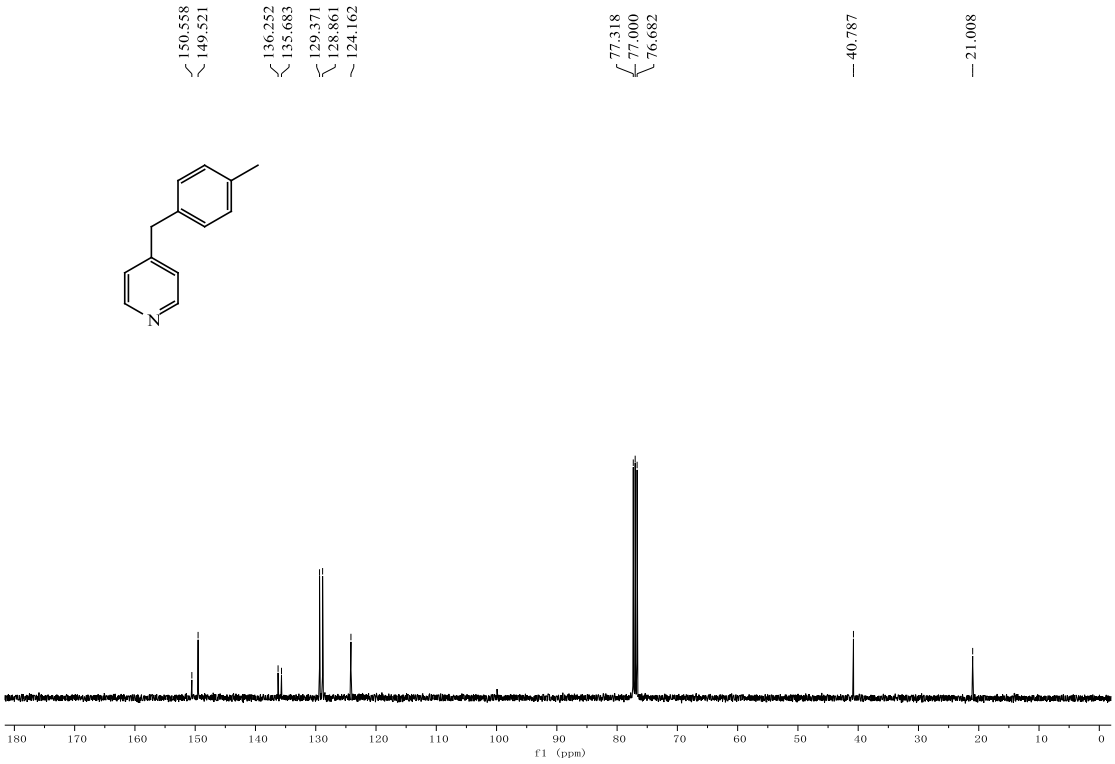

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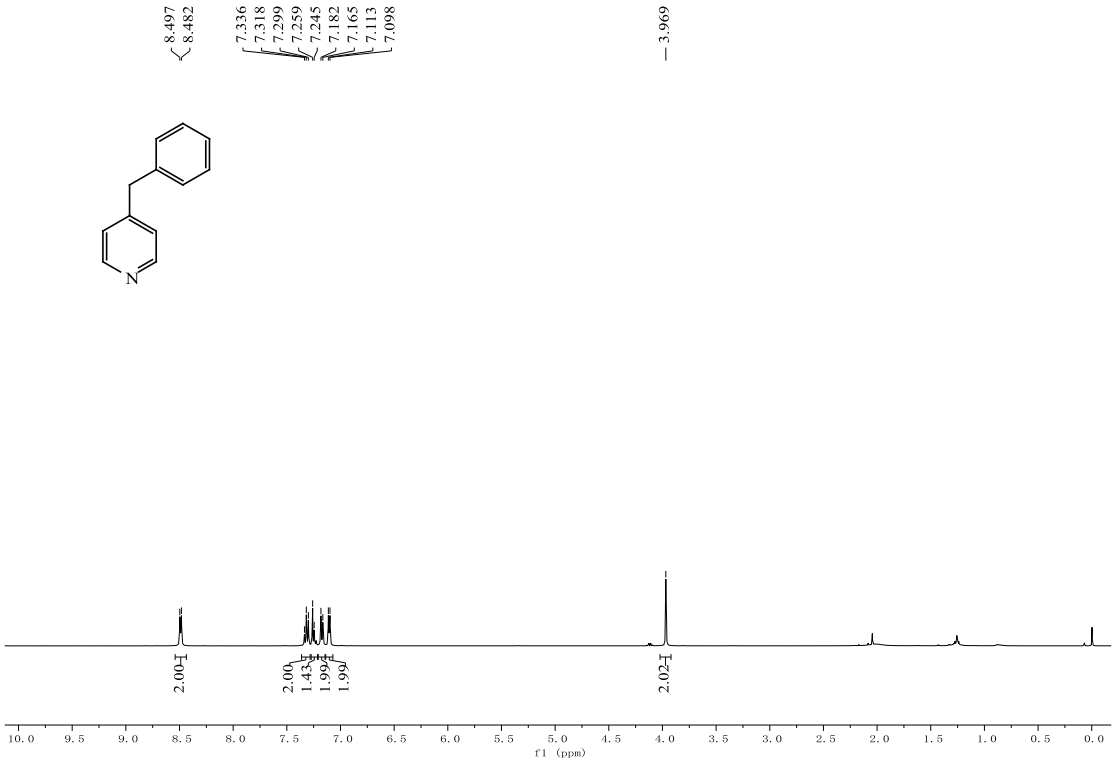

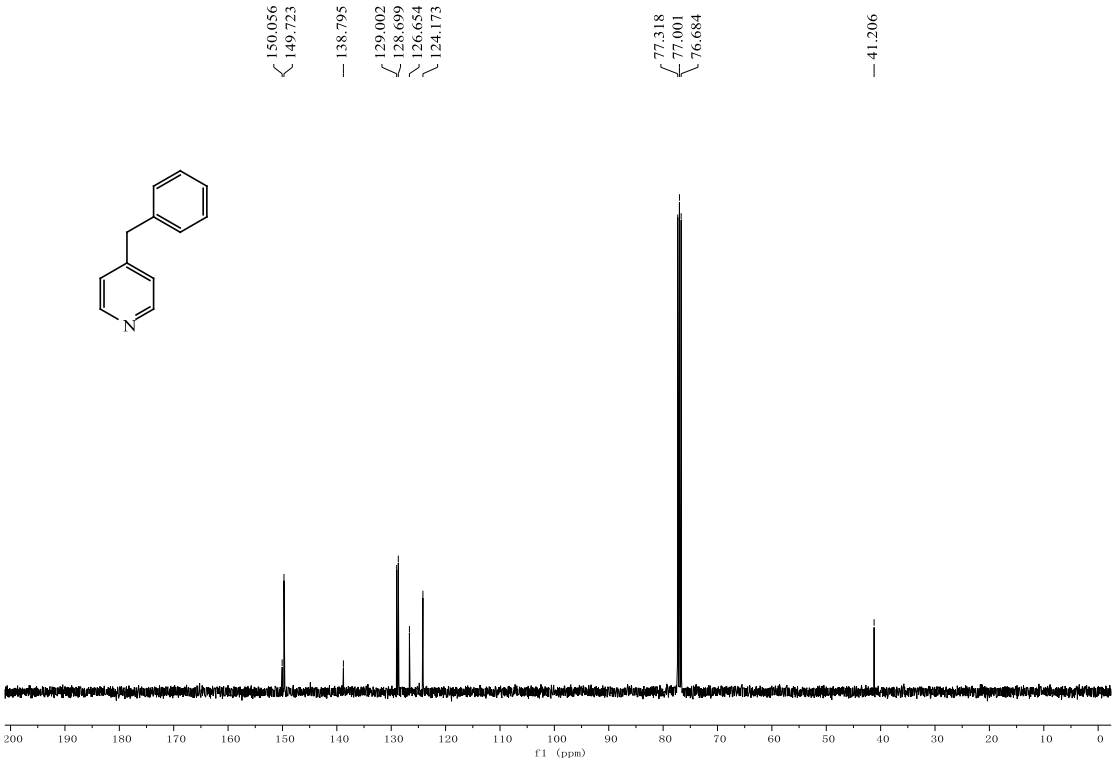

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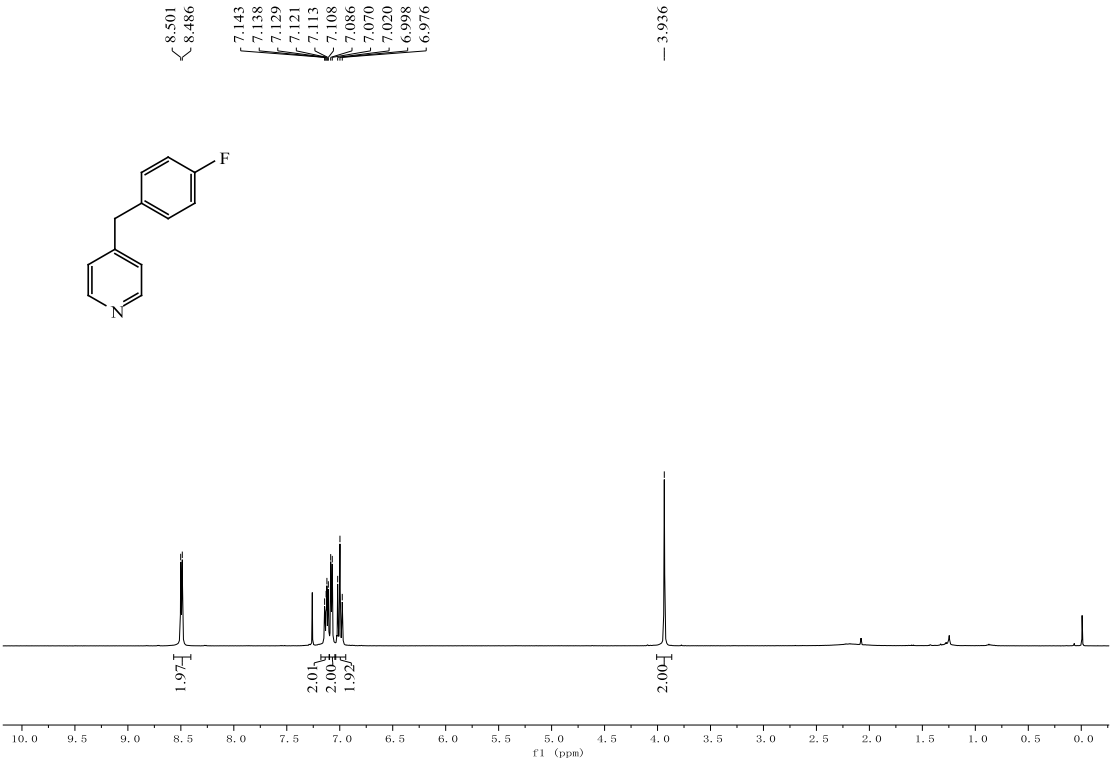
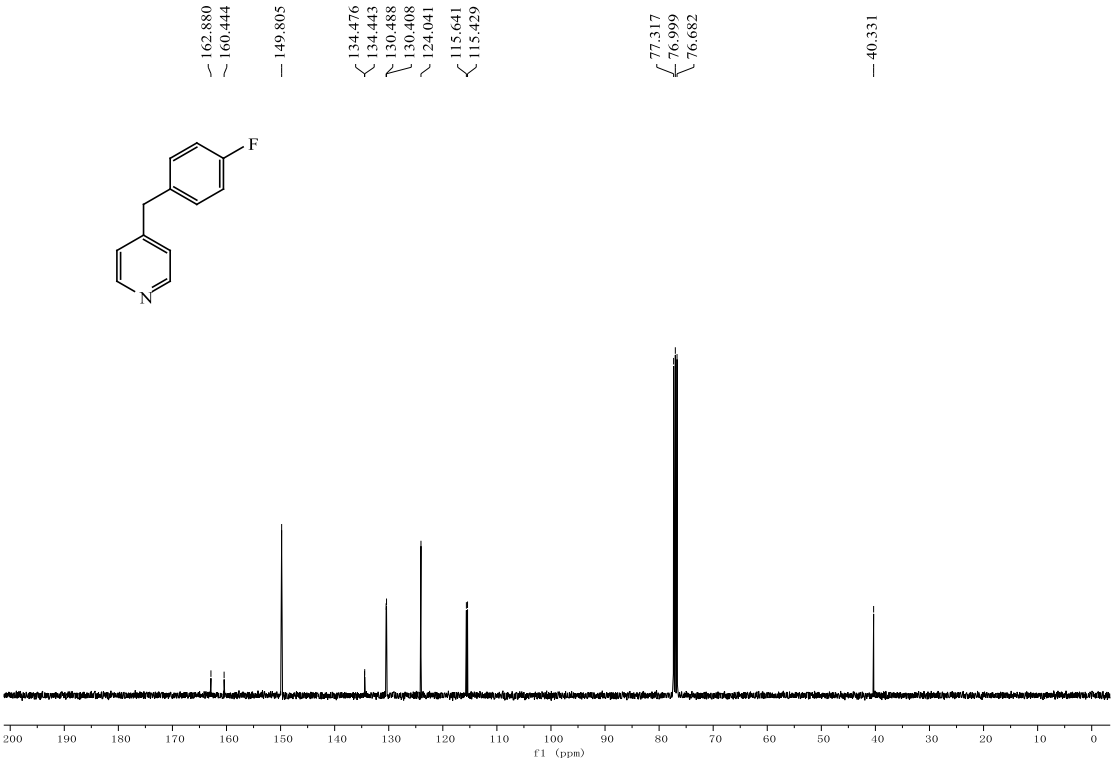
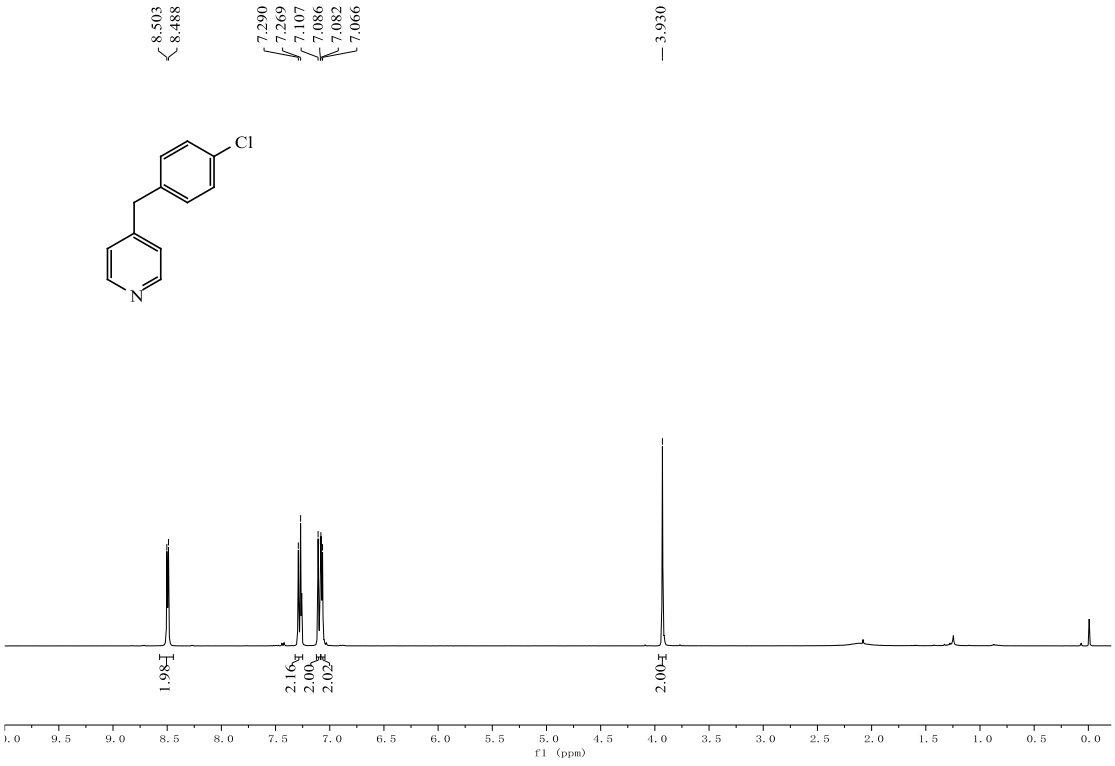
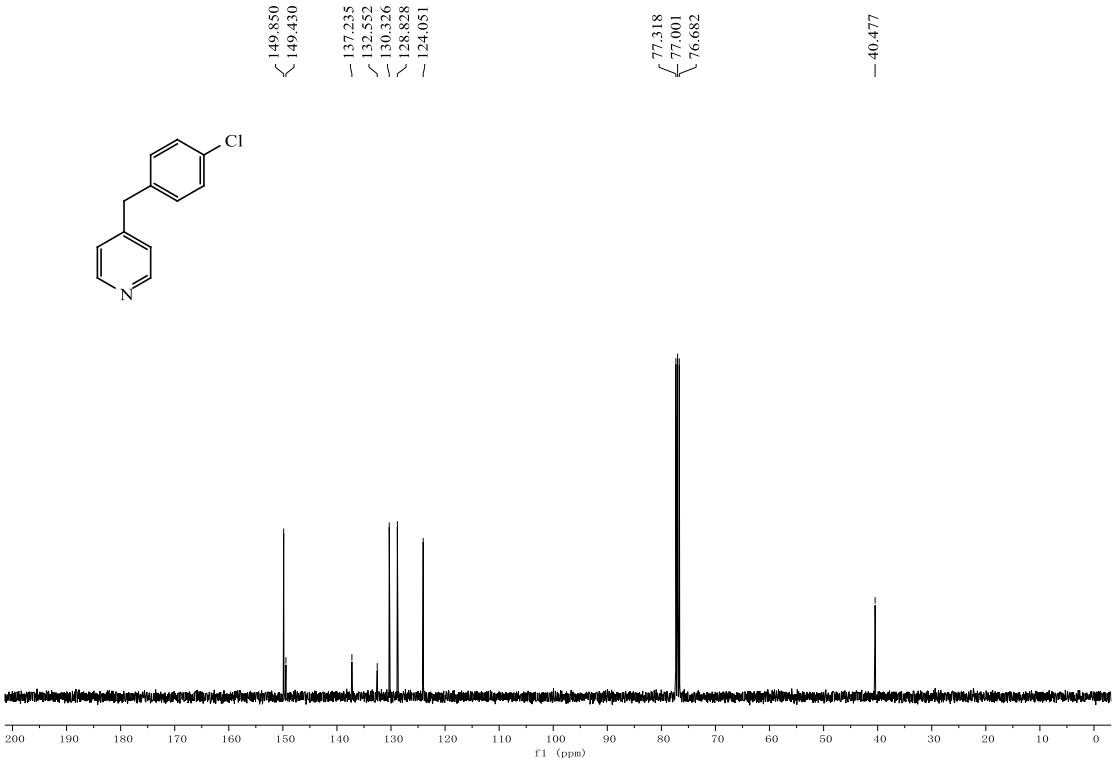




4-(4-Chlorobenzyl)pyridine (3g)





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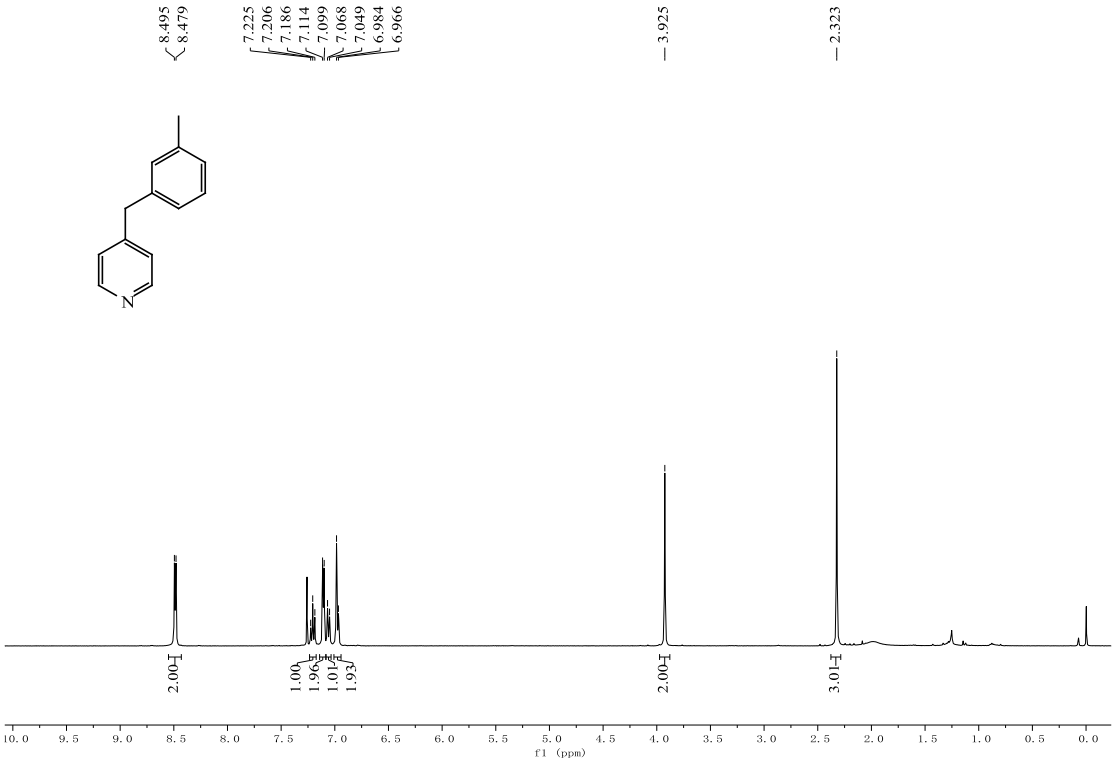

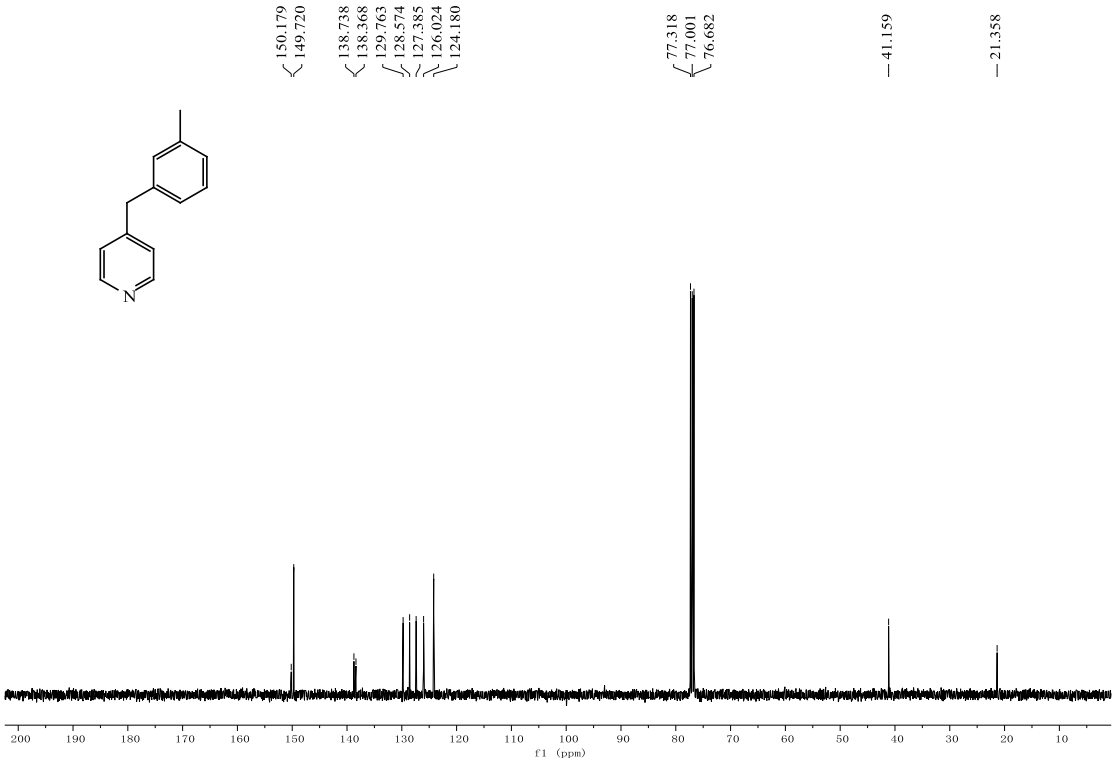

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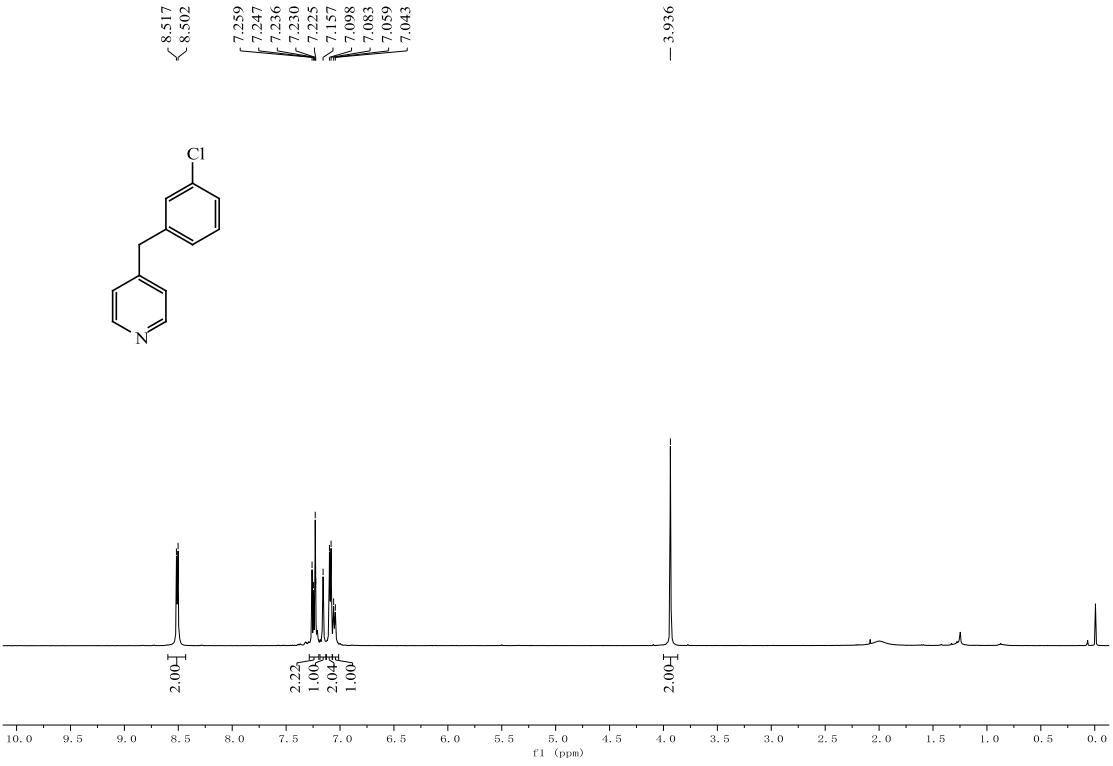

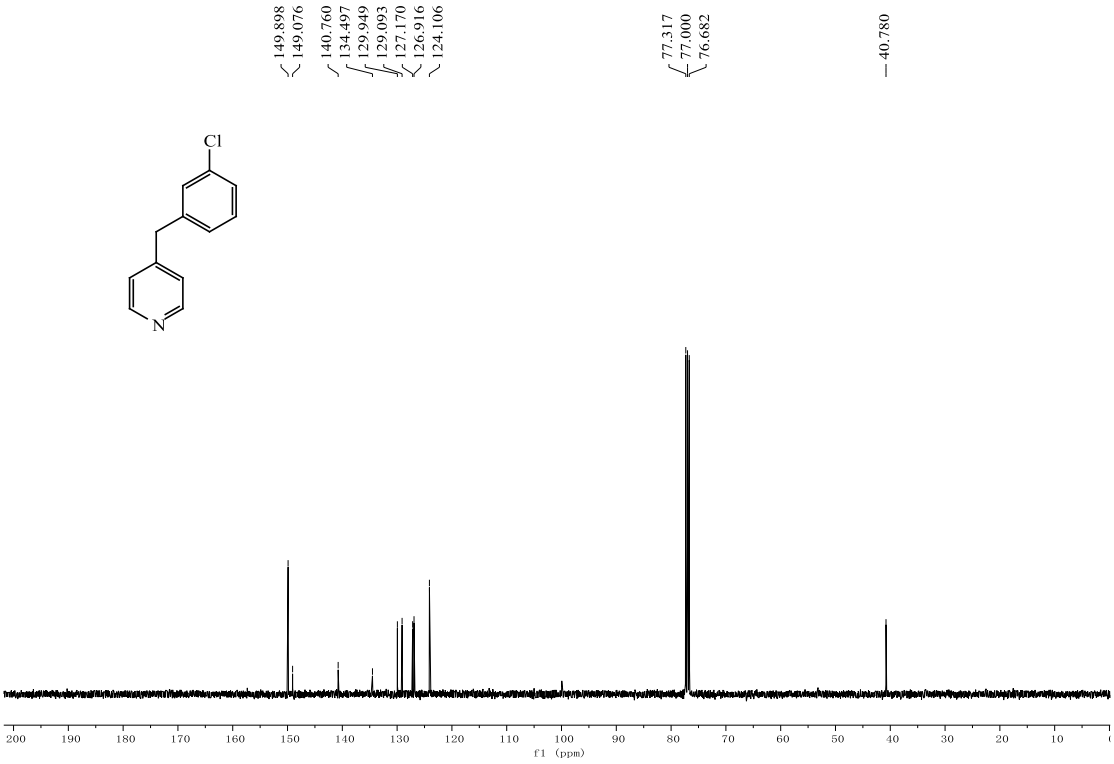

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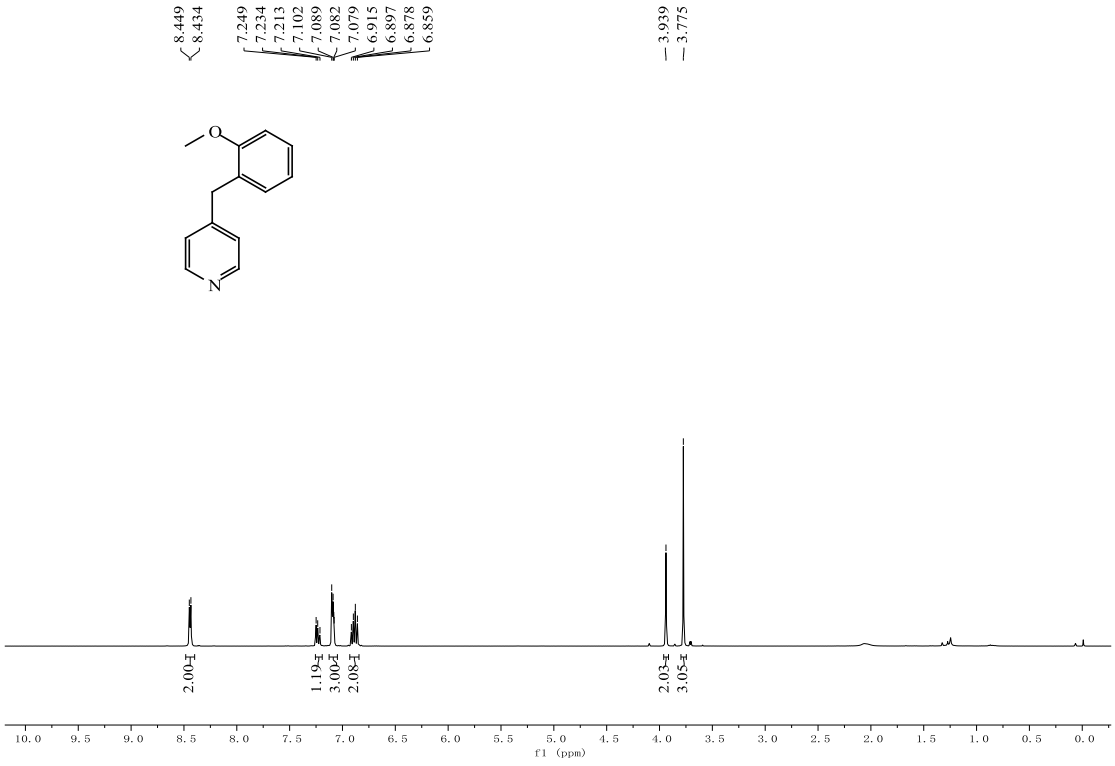
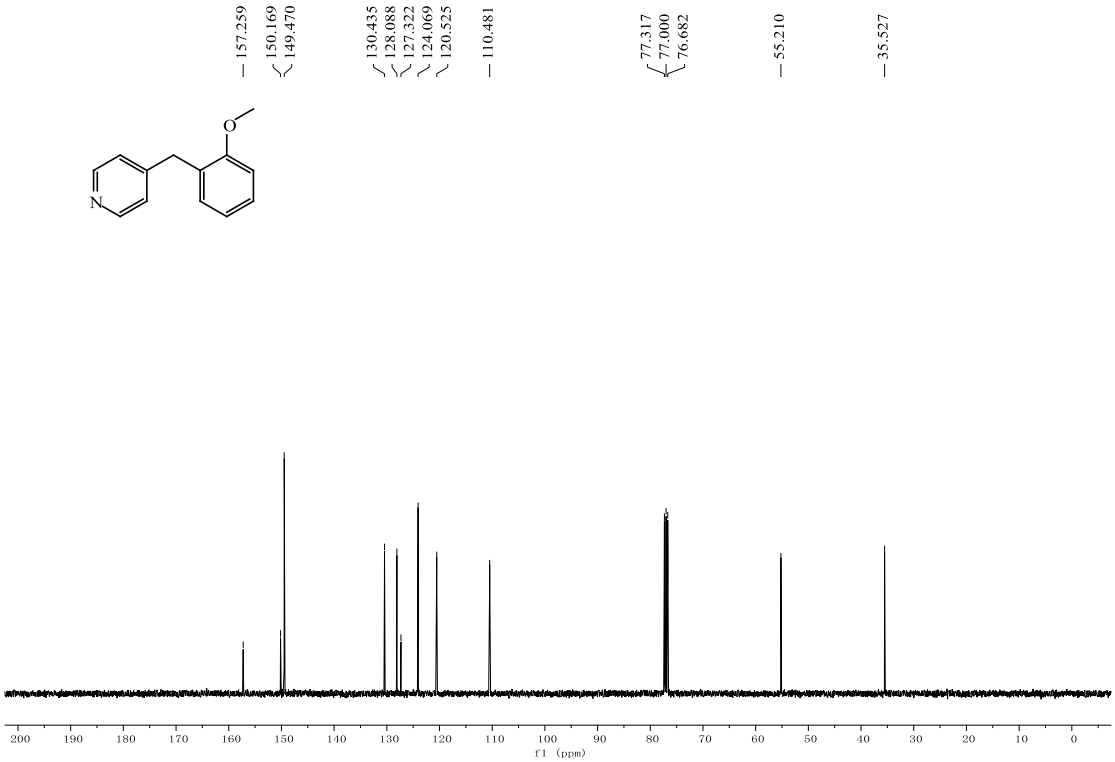
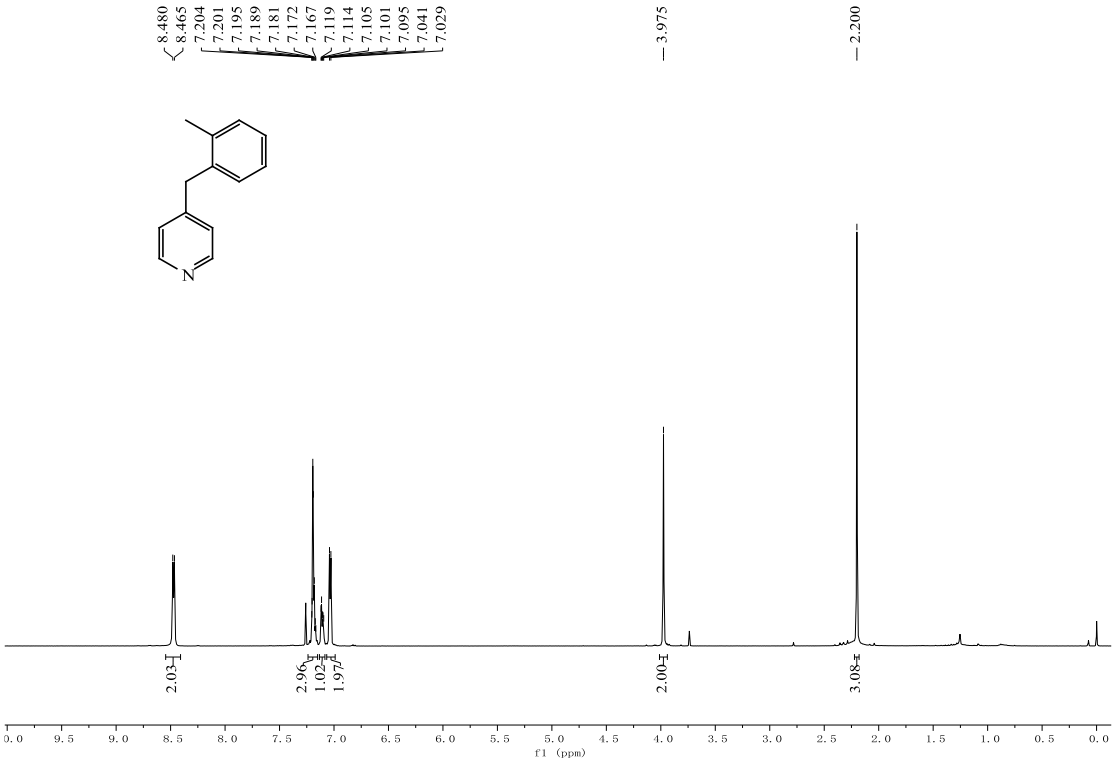
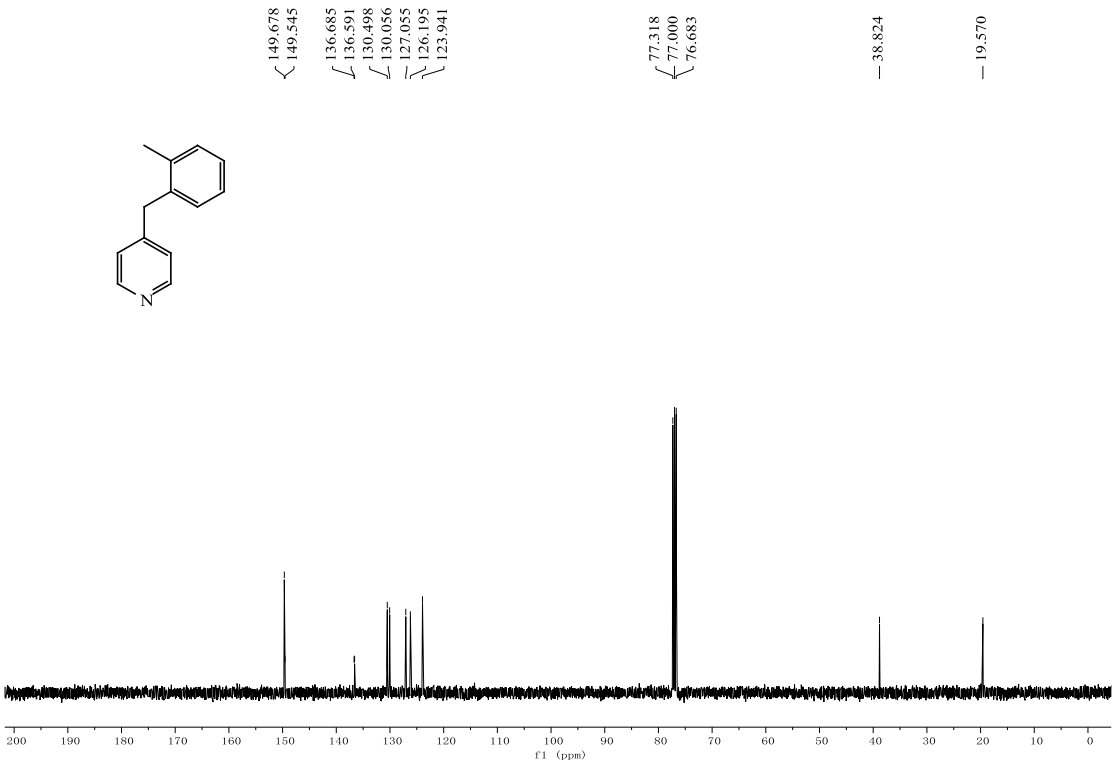


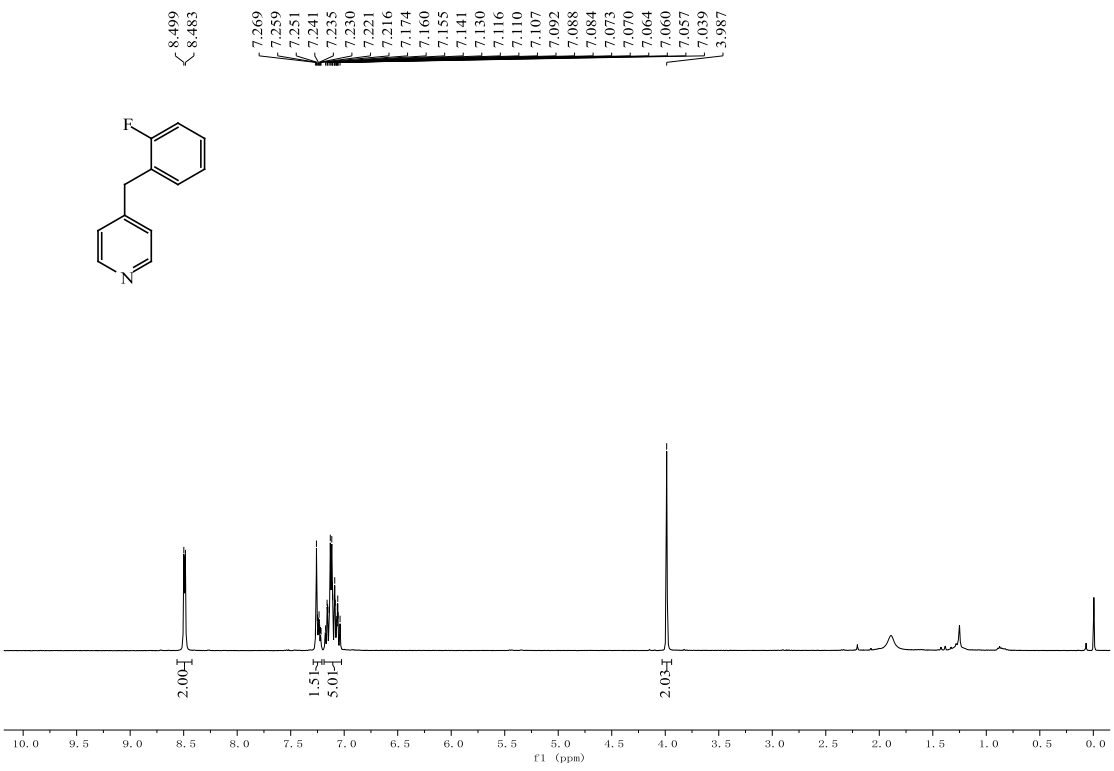


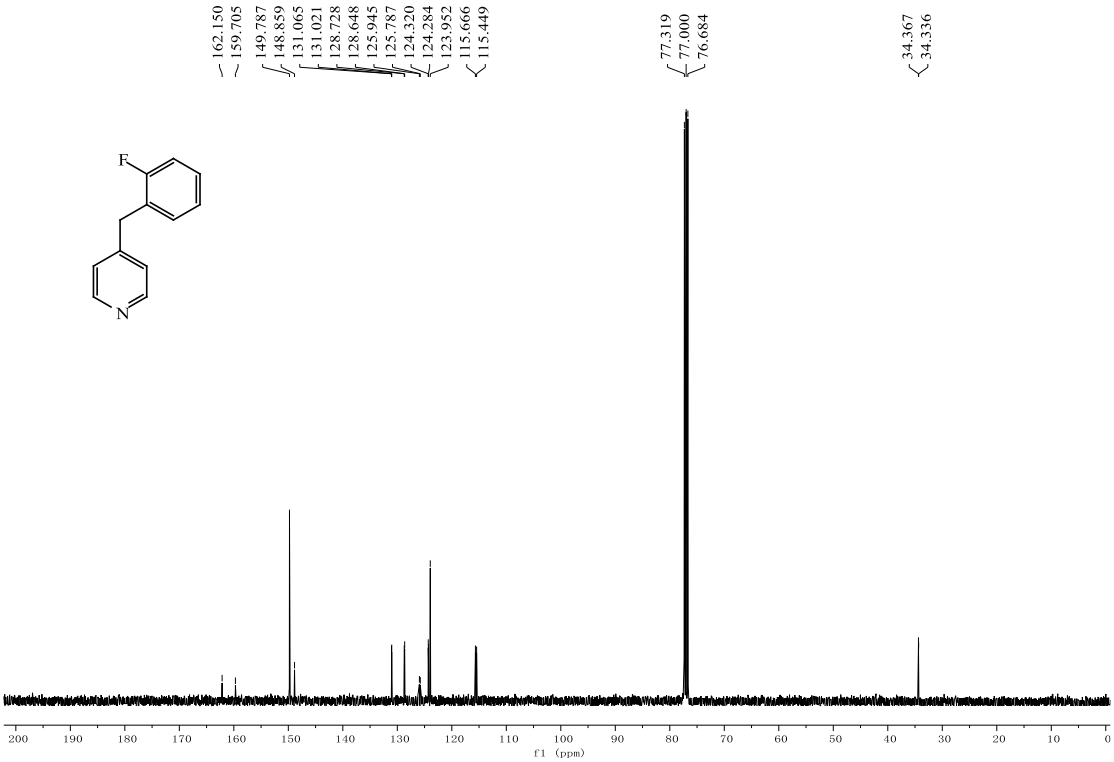
4-(2-Methylbenzyl)pyridine (3l)



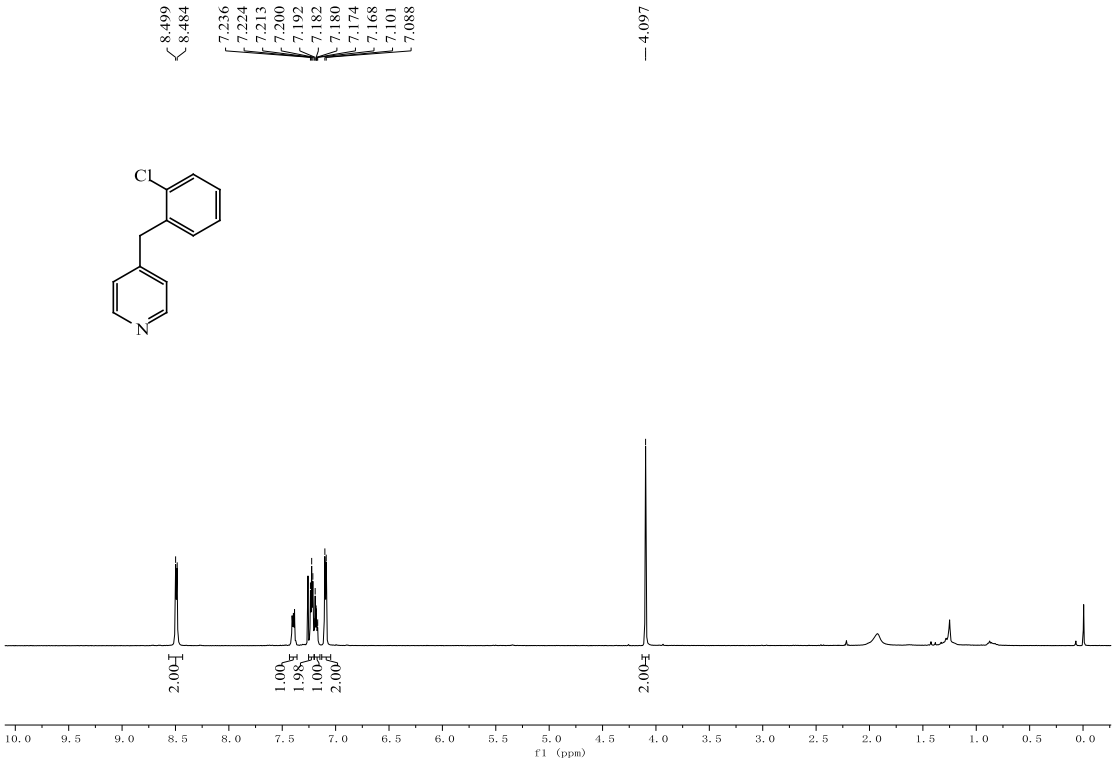


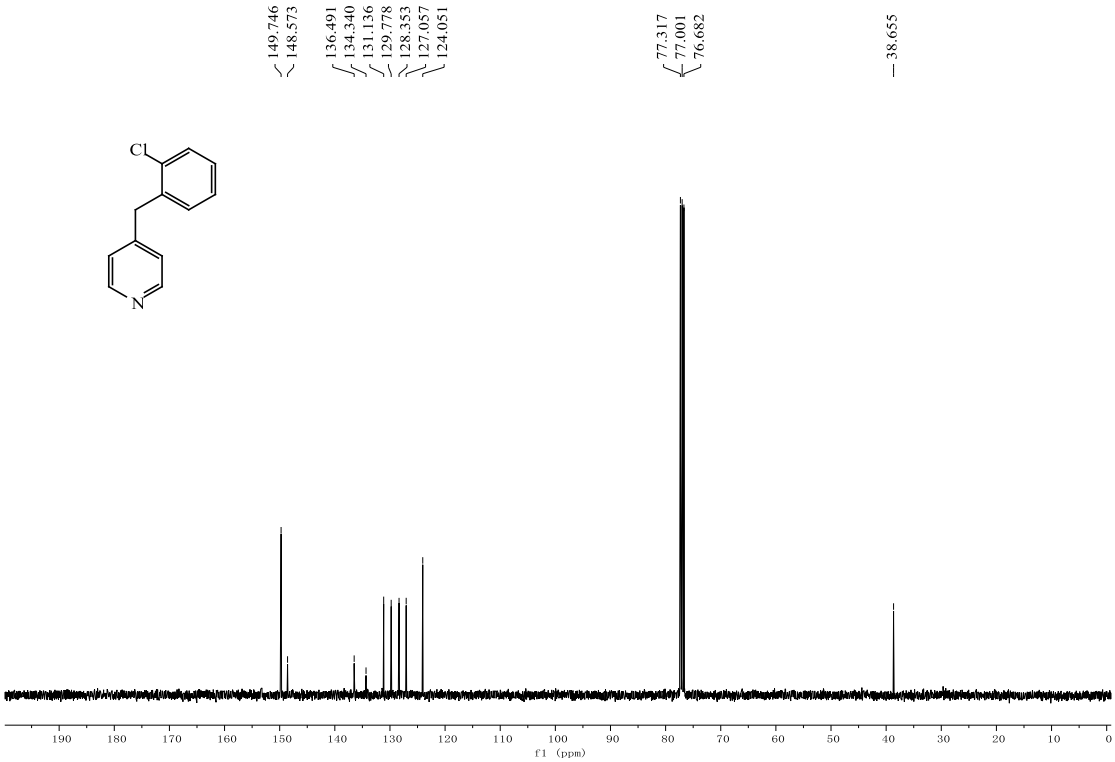
4-(2-Fluorobenzyl)pyridine (3m)





4-(2-Chlorobenzyl)pyridine (3n)





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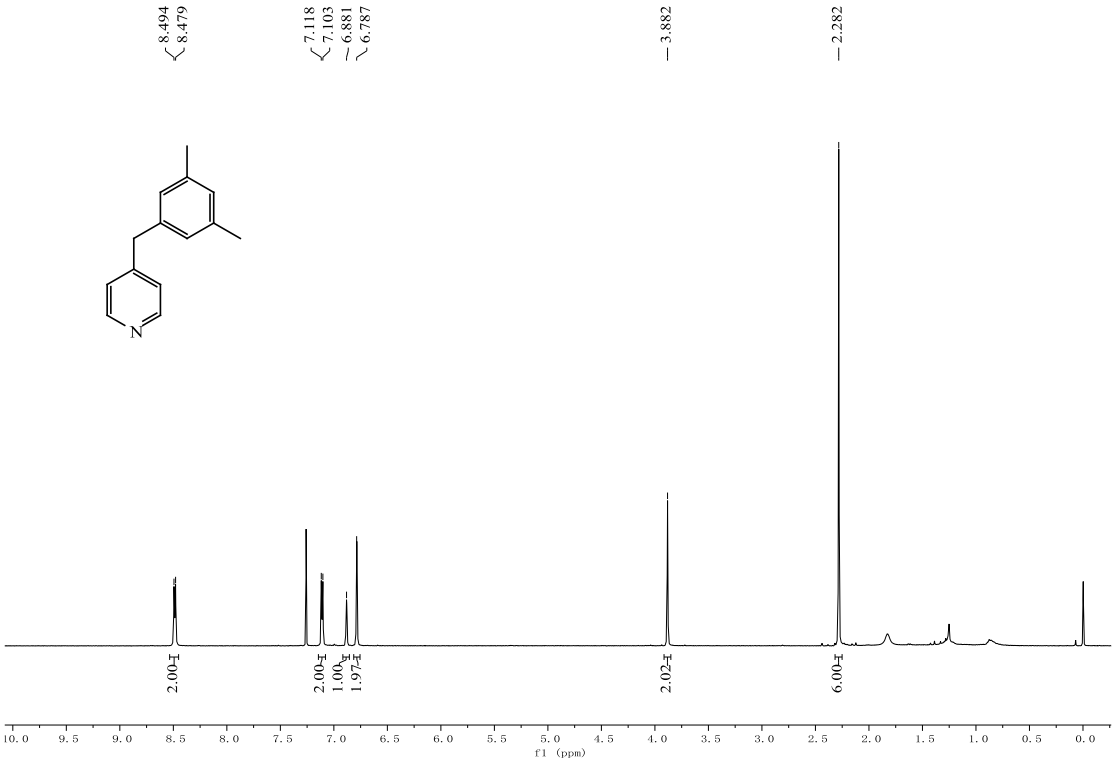
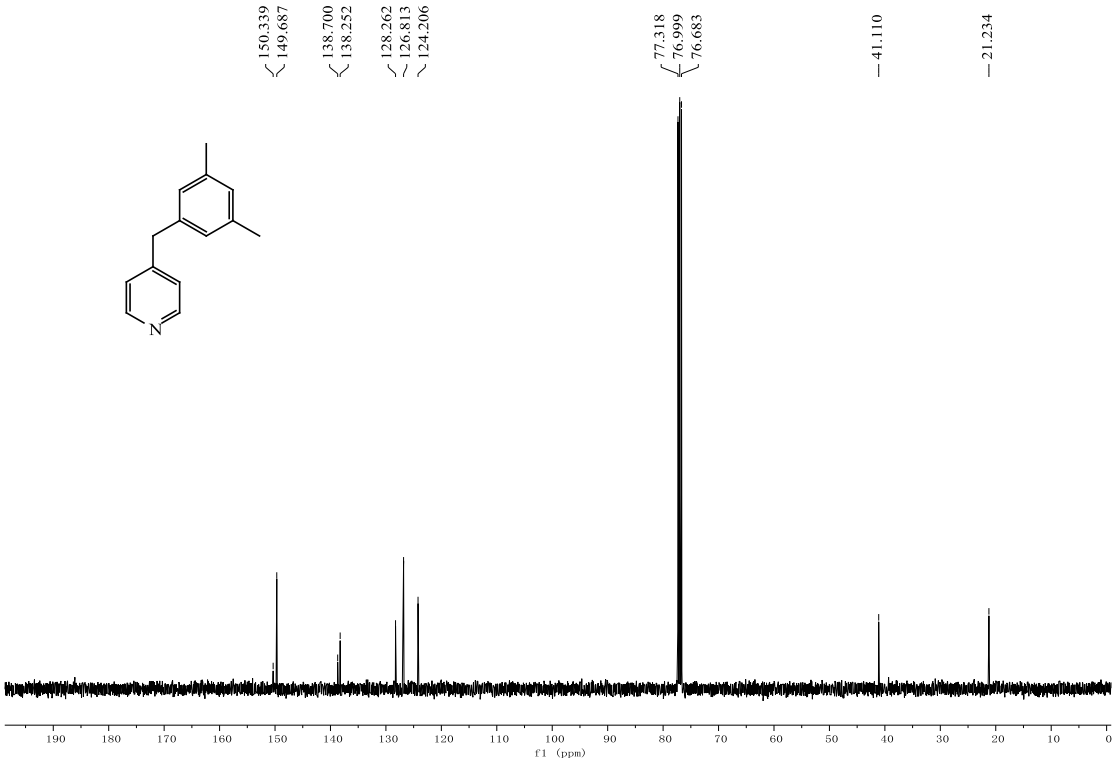
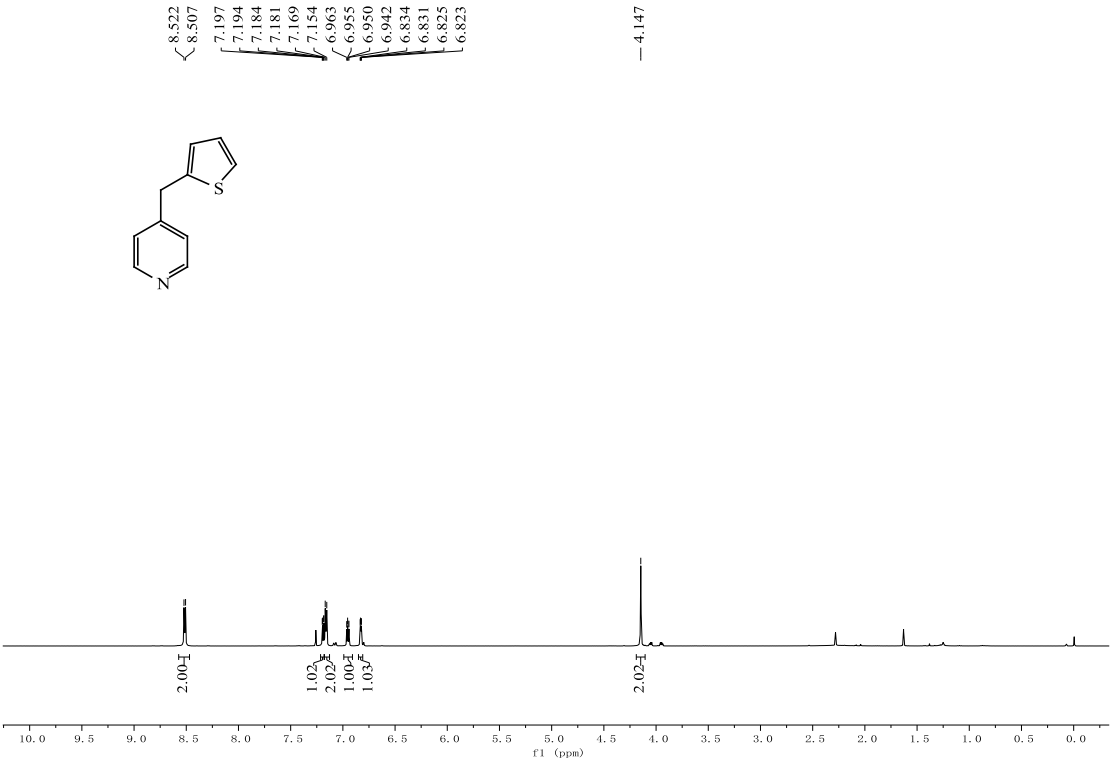
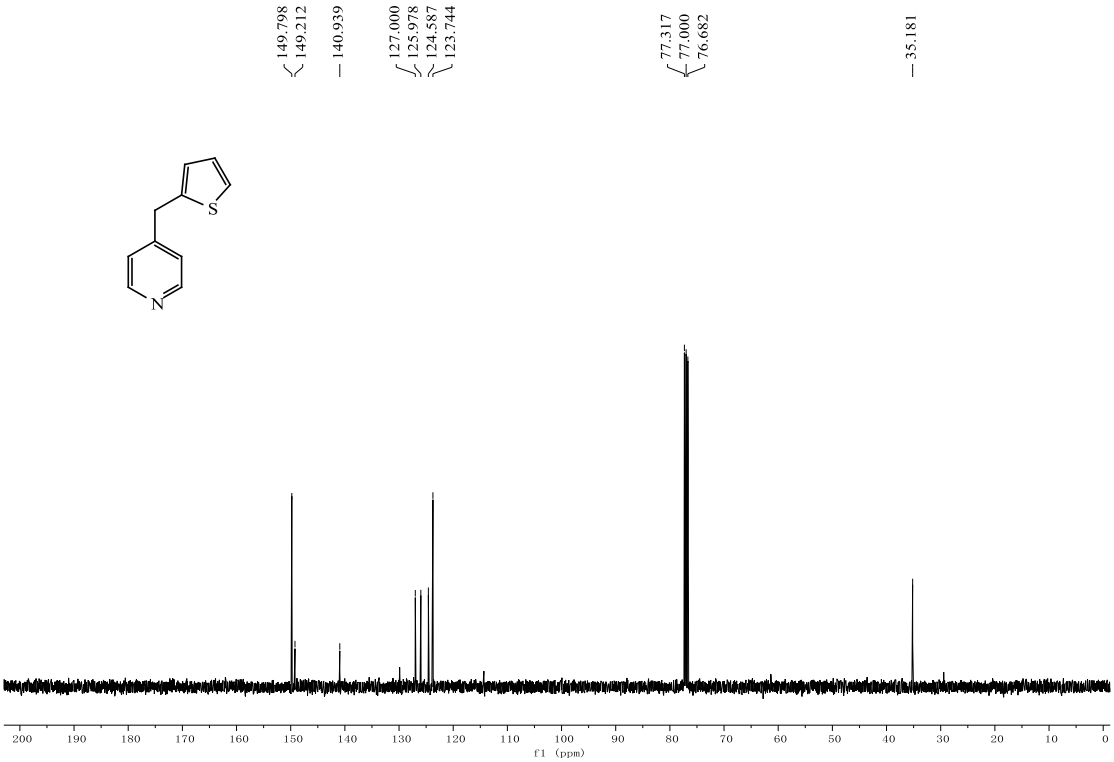


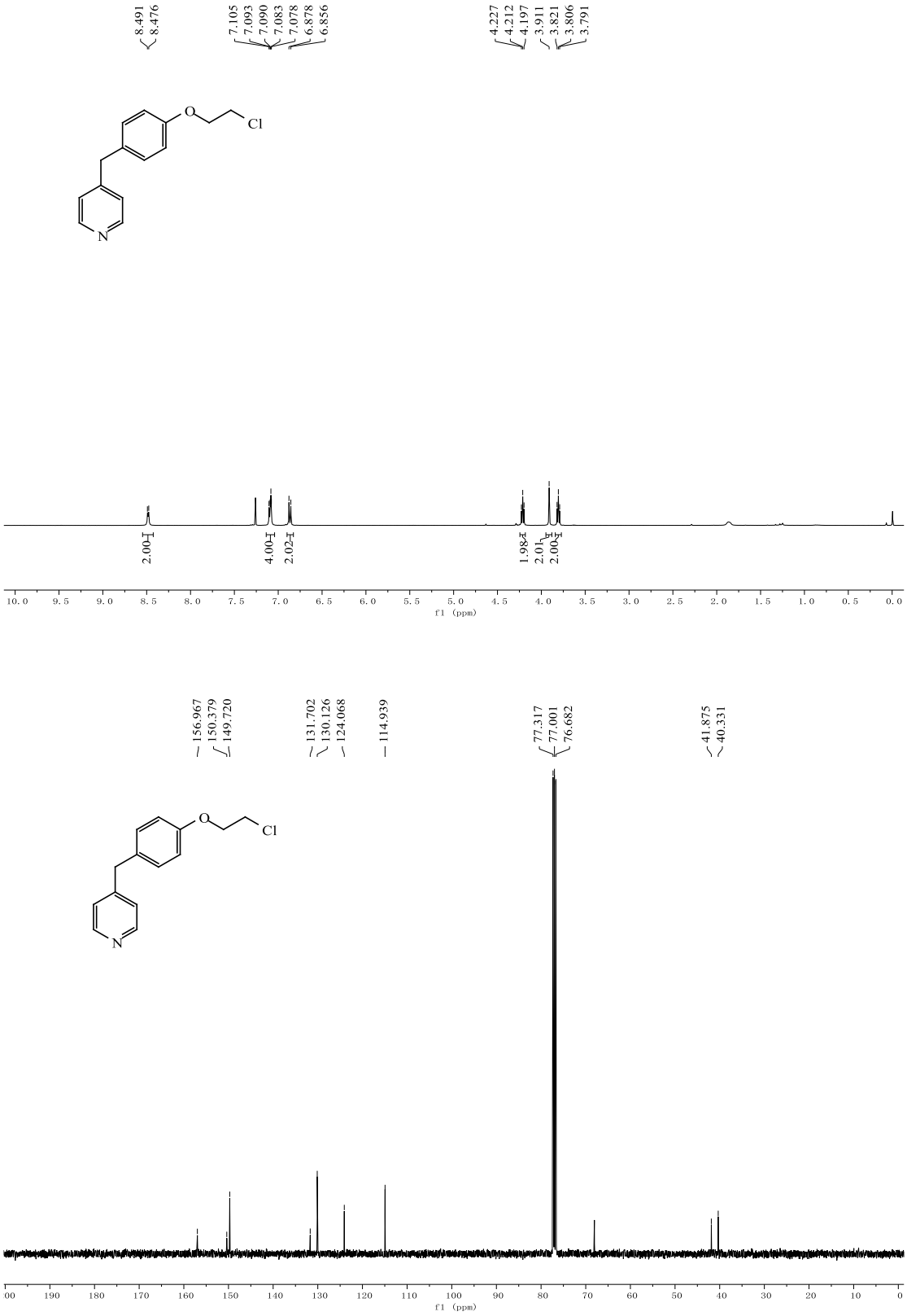


4-(Thiophen-2-ylmethyl)pyridine (3p)

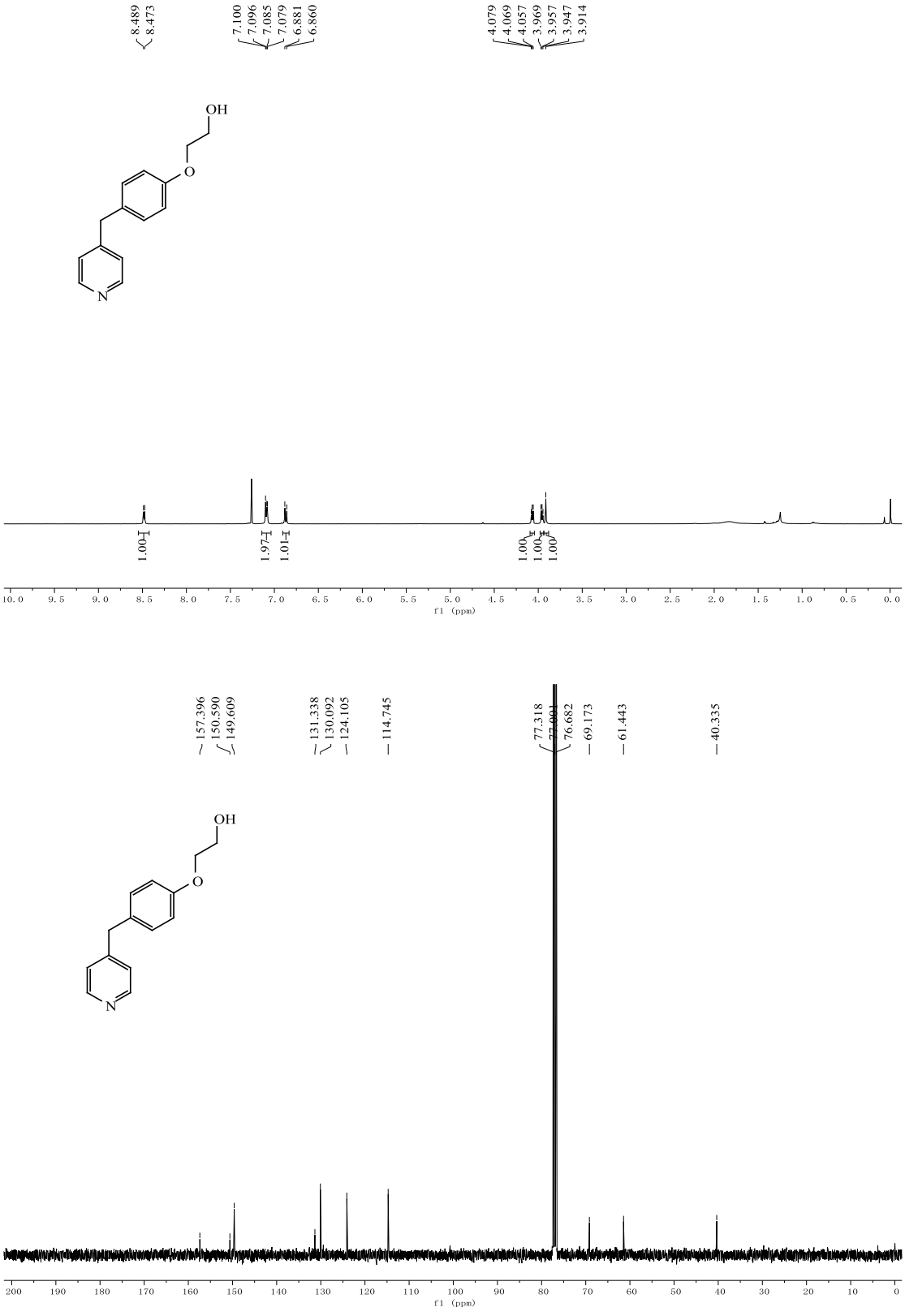




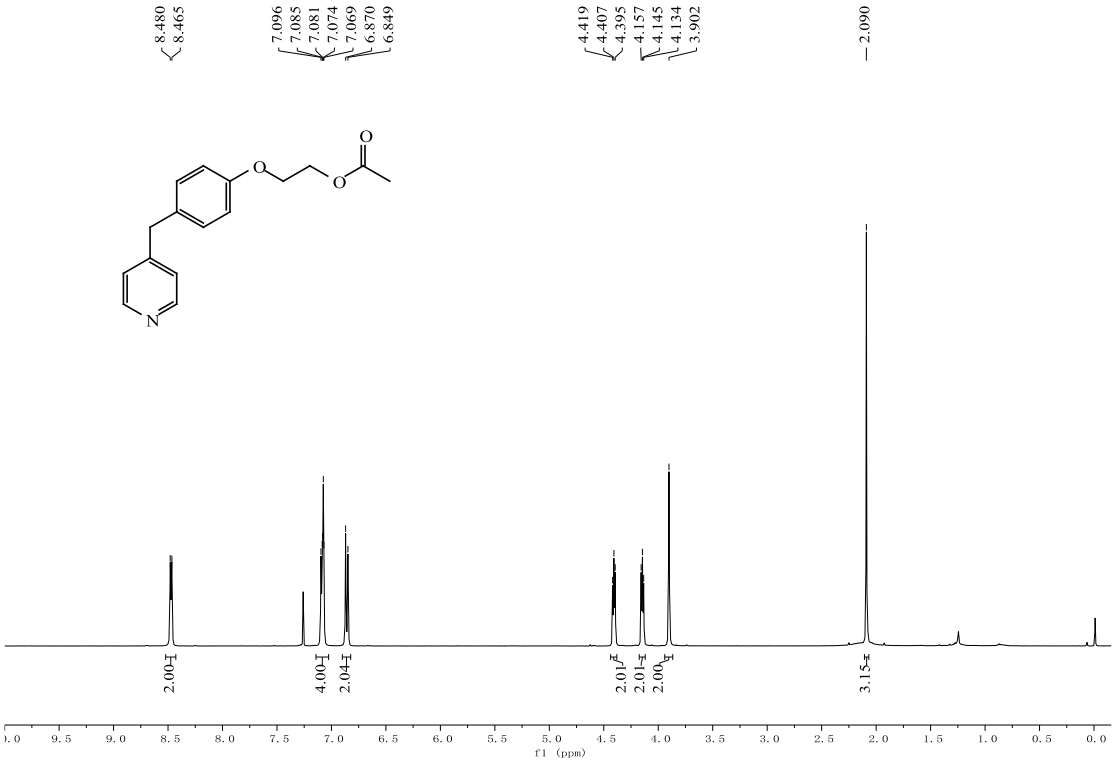
4-(4-(2-Chloroethoxy)benzyl)pyridine (3q)

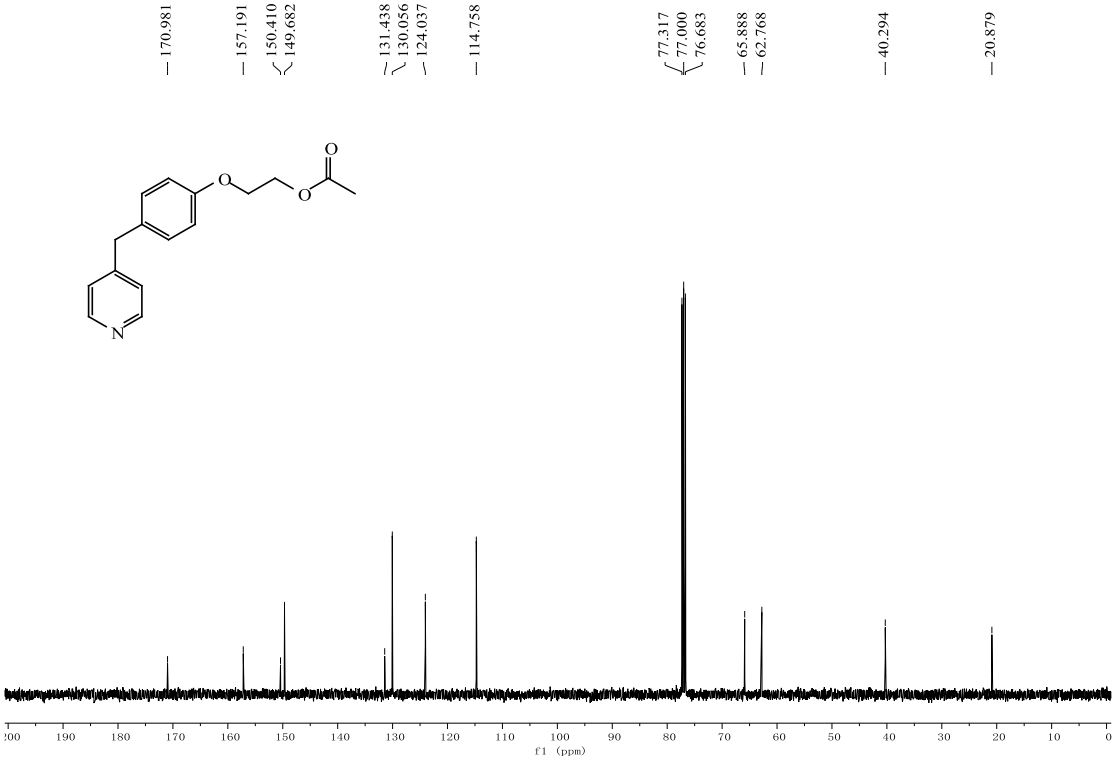


2-(4-(Pyridin-4-ylmethyl)phenoxy)ethan-1-ol (3r)

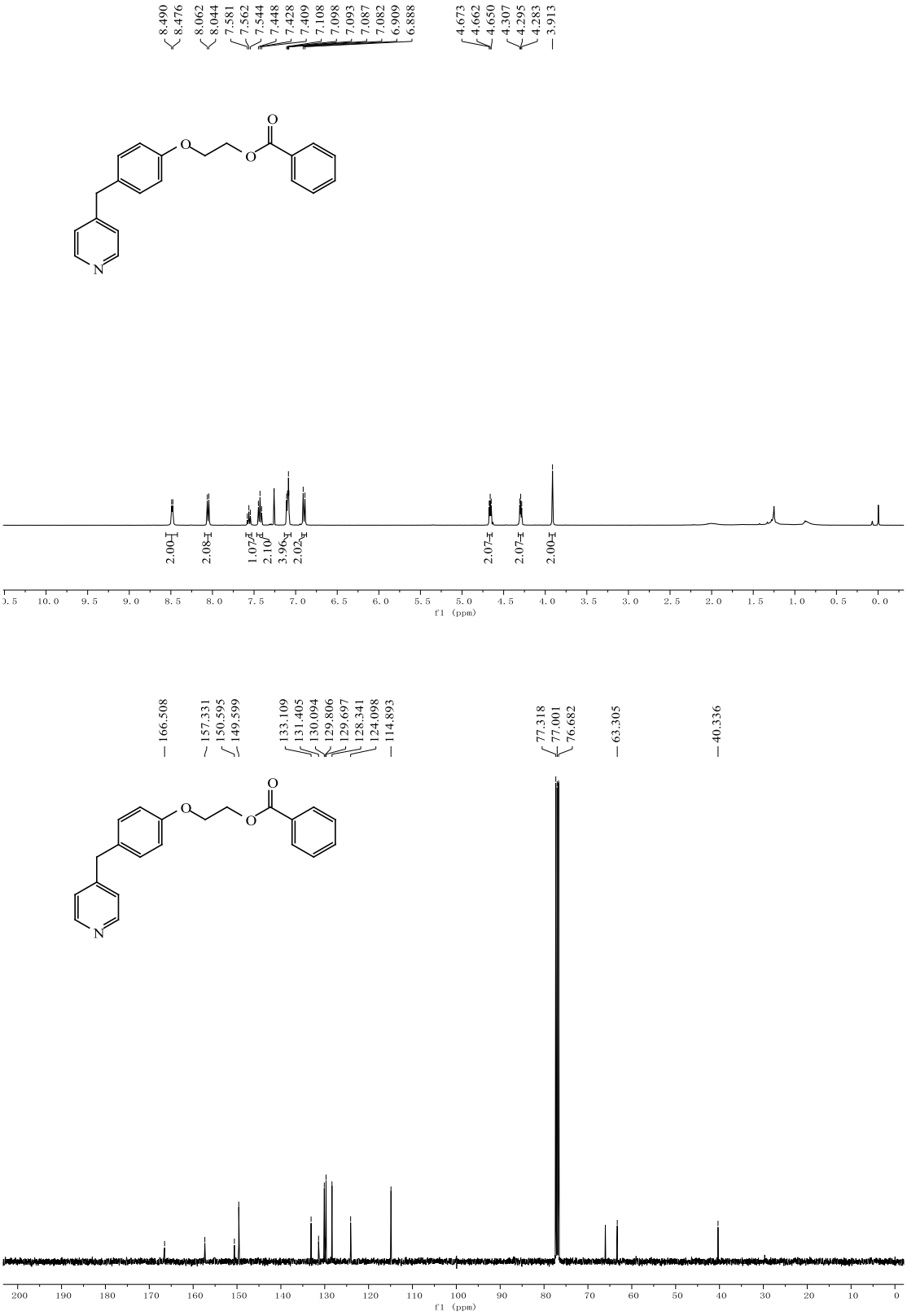


2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl acetate (3s)

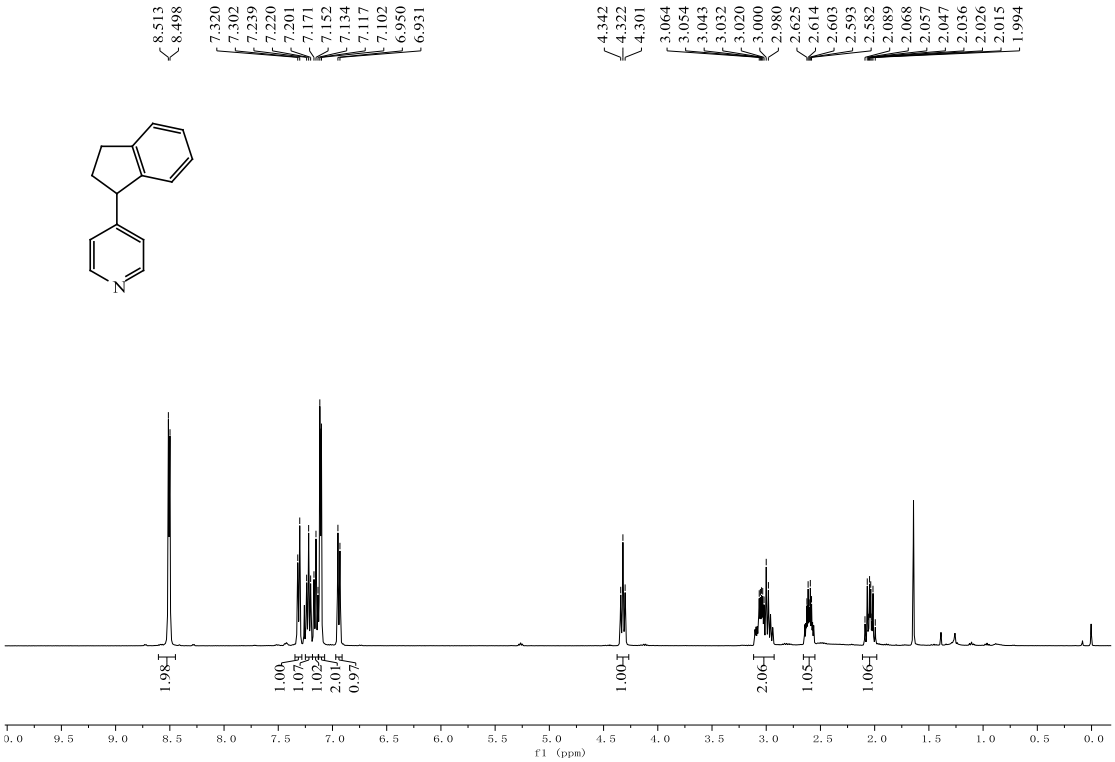


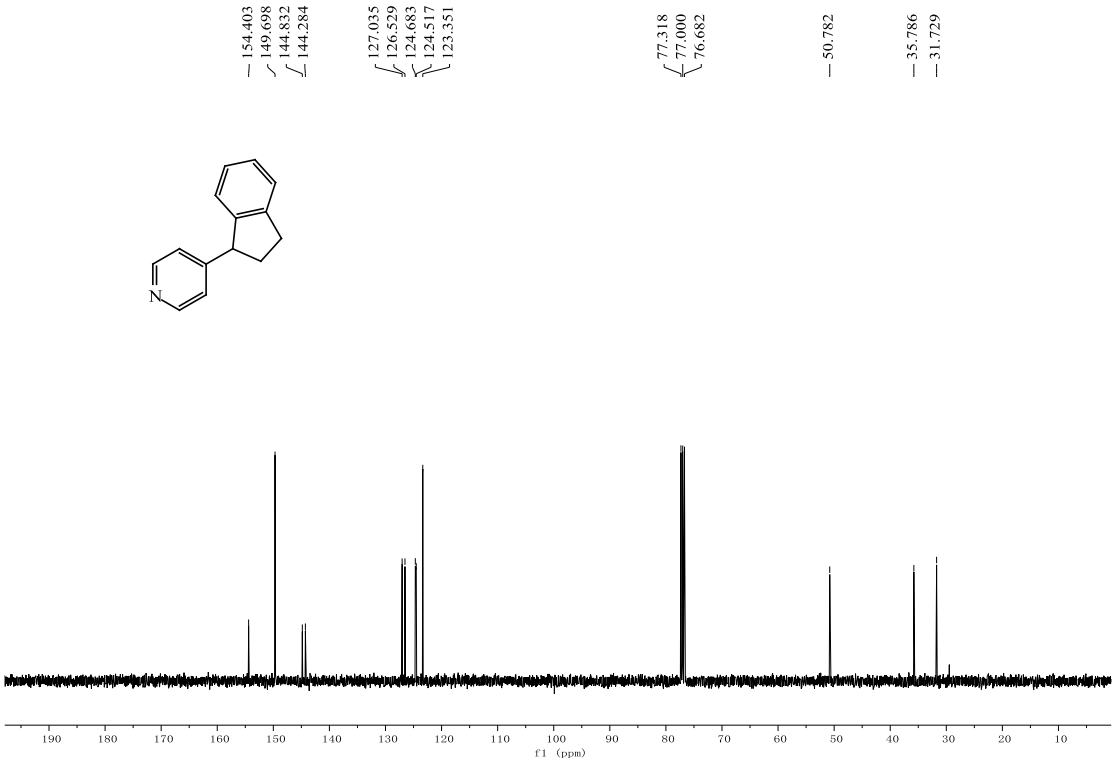


2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl benzoate (3t)

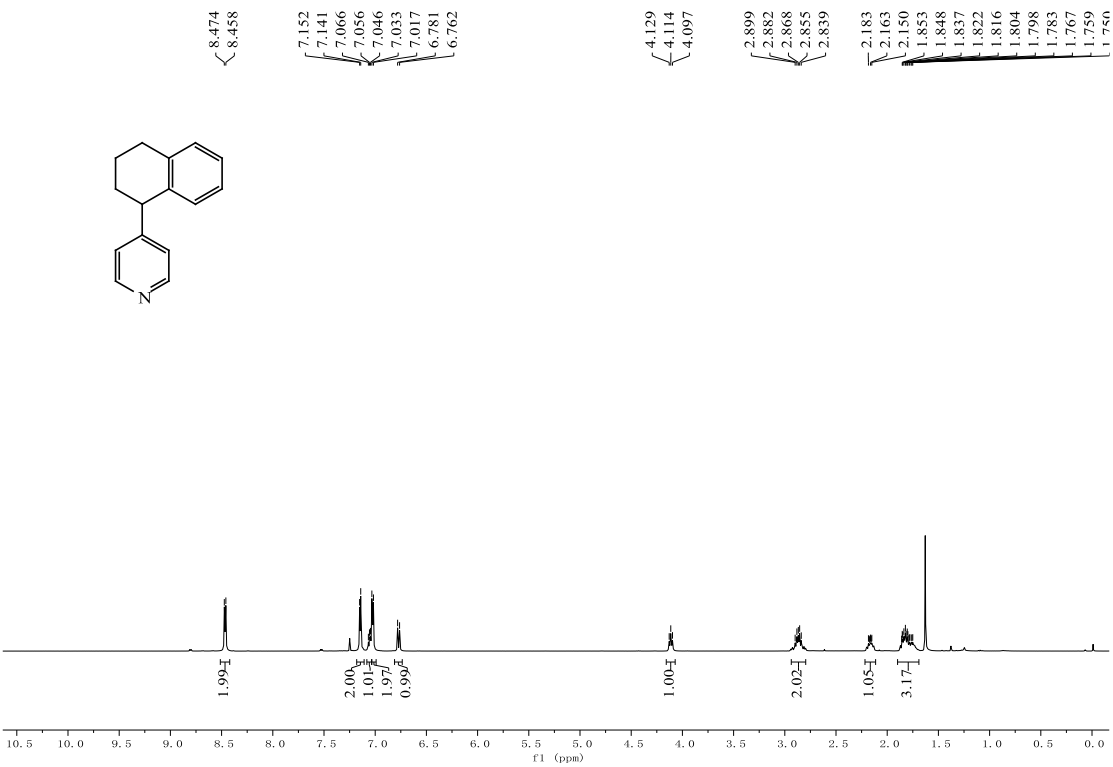


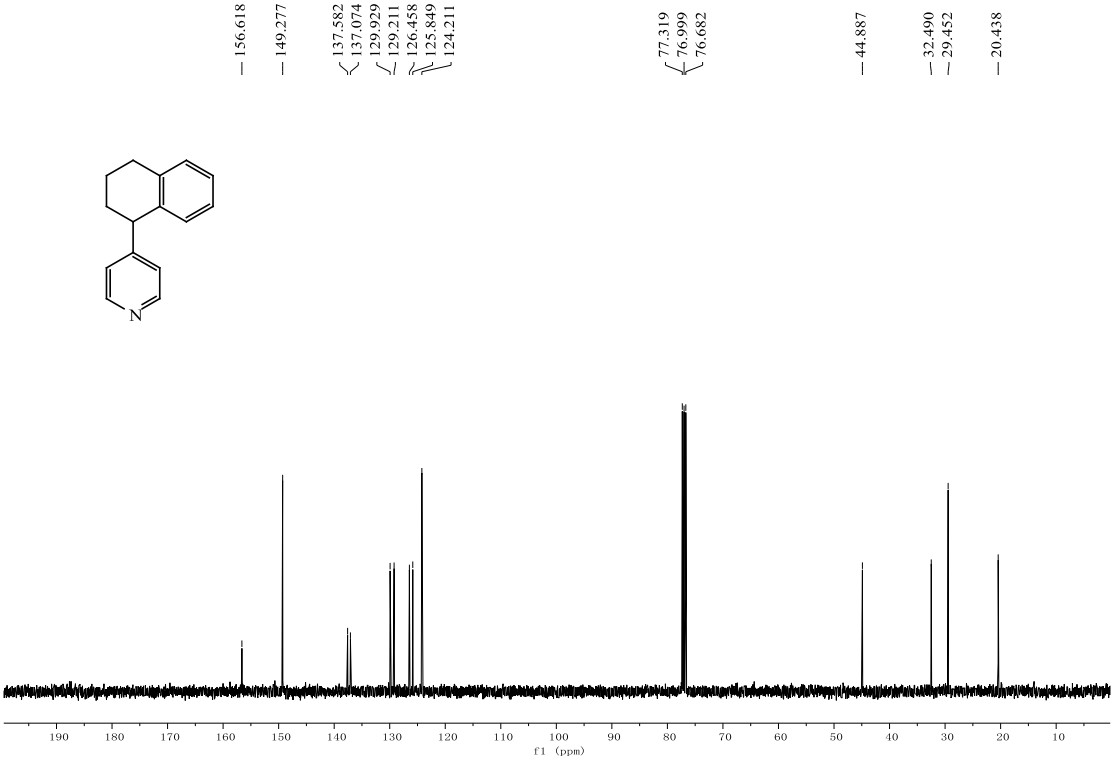
4-(2,3-Dihydro-1*H*-inden-1-yl)pyridine (4a)



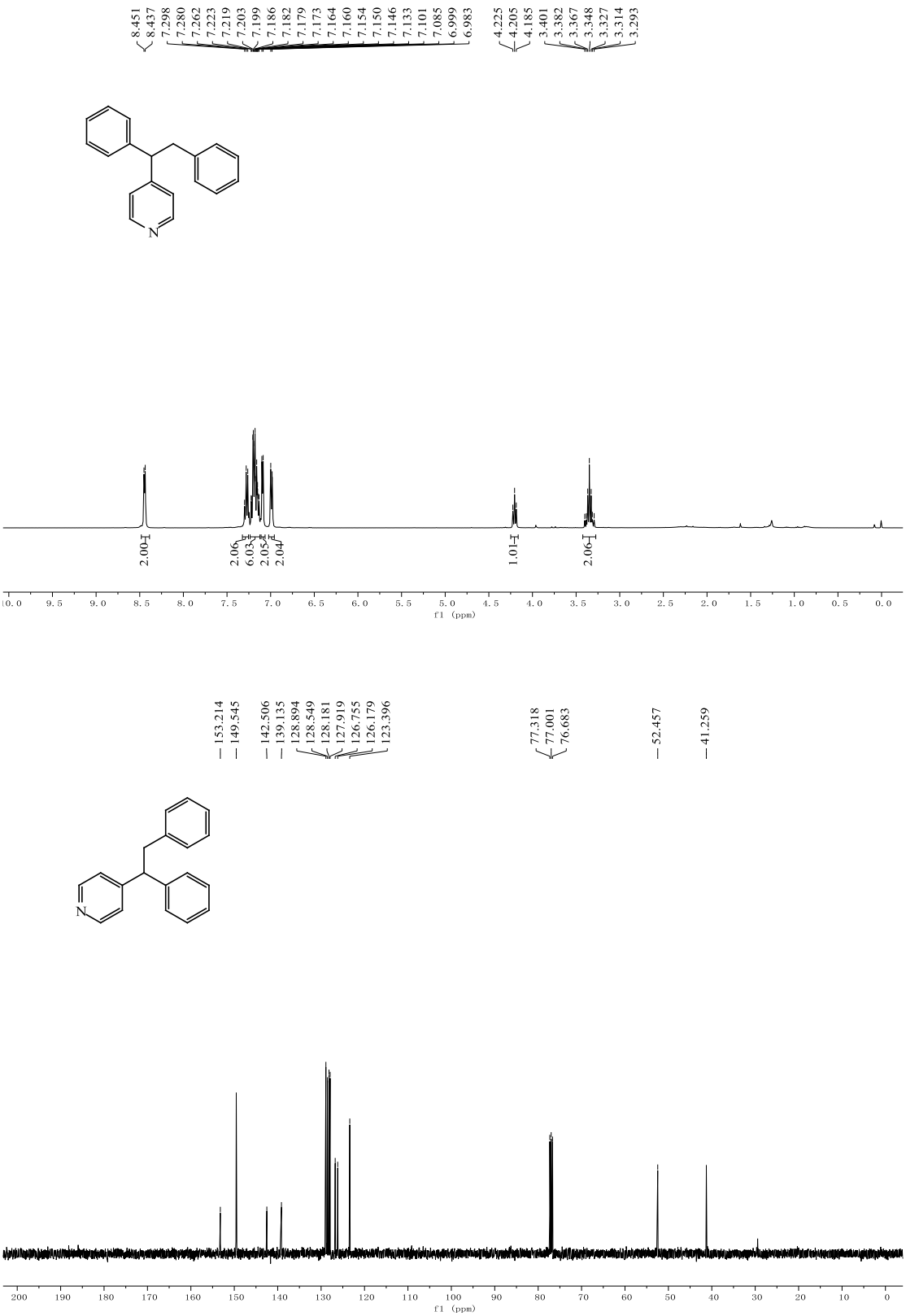


4-(1,2,3,4-Tetrahydronaphthalen-1-yl)pyridine (4b)

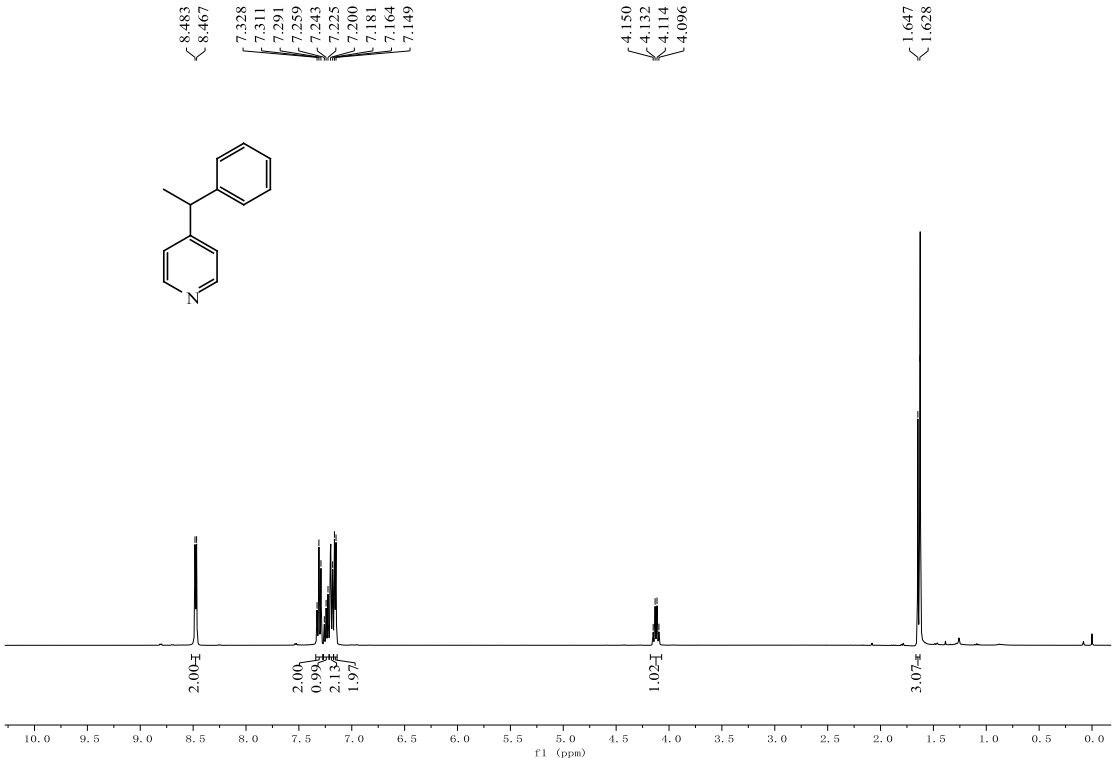


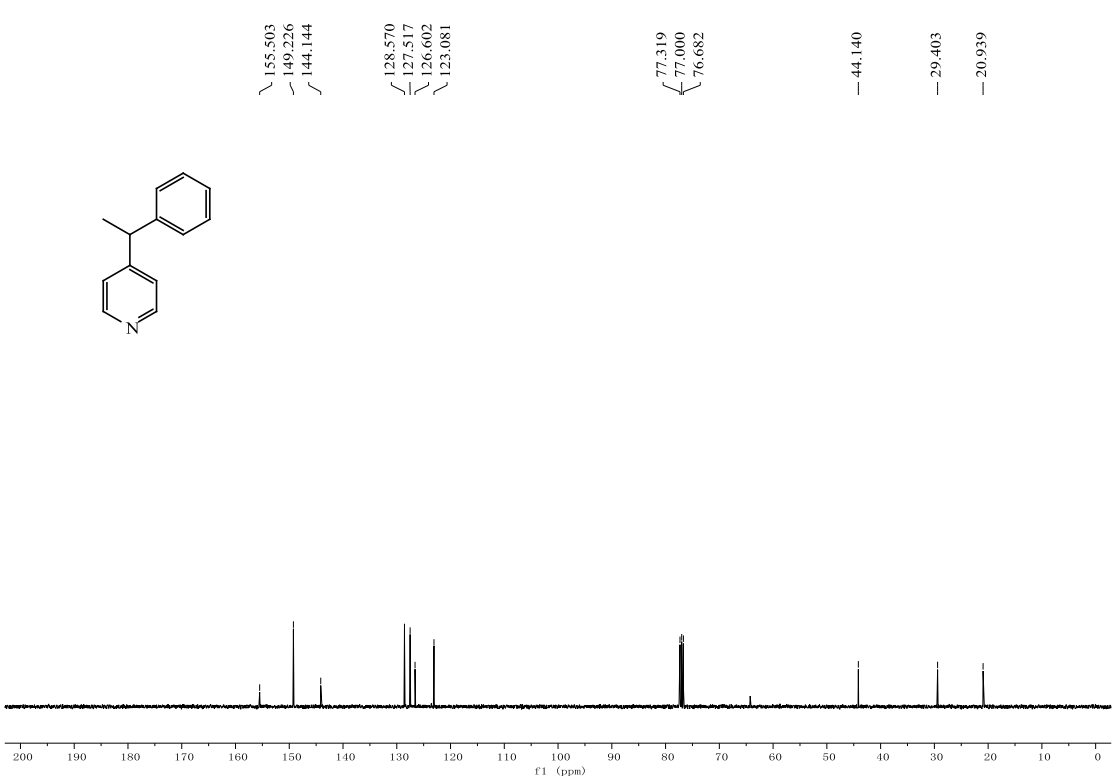


4-(1,2-Diphenylethyl)pyridine (4c)

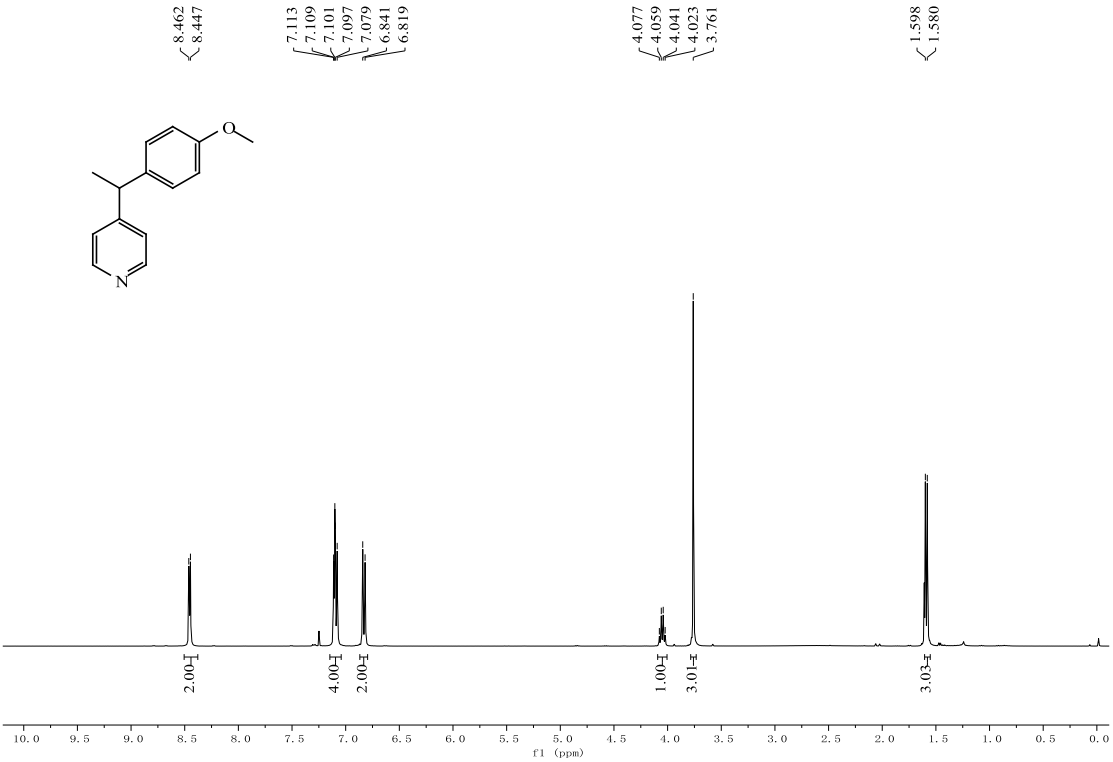


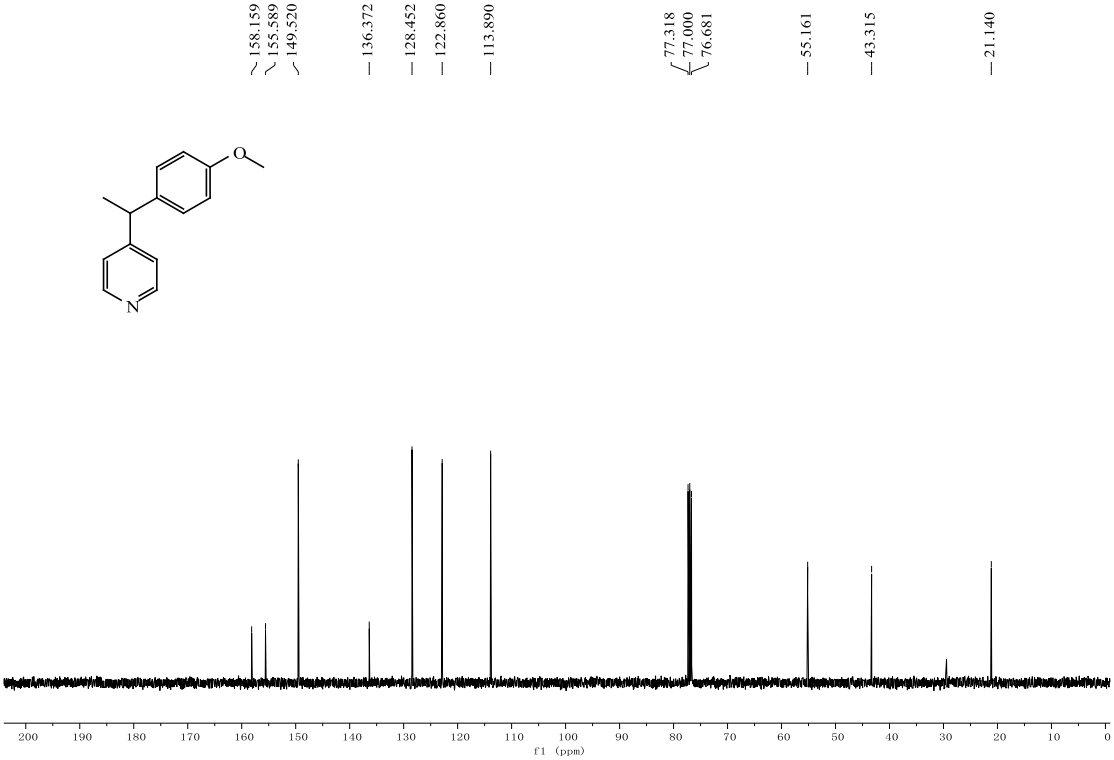
4-(1-Phenylethyl)pyridine (4d)



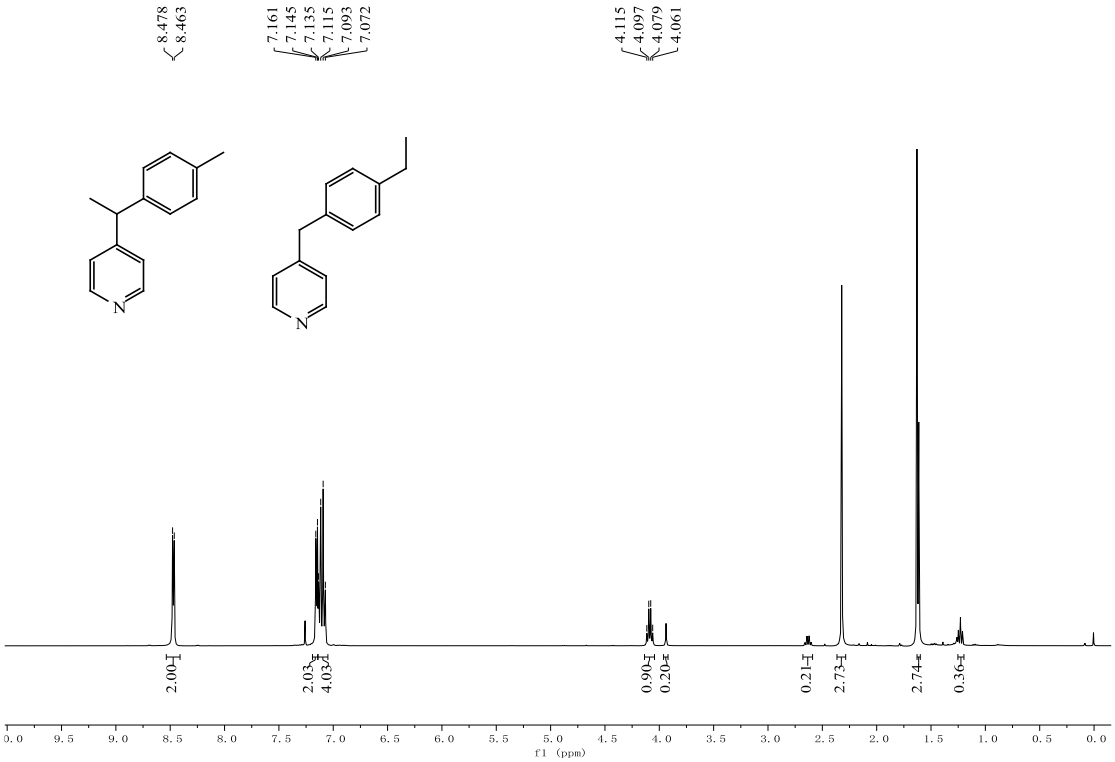


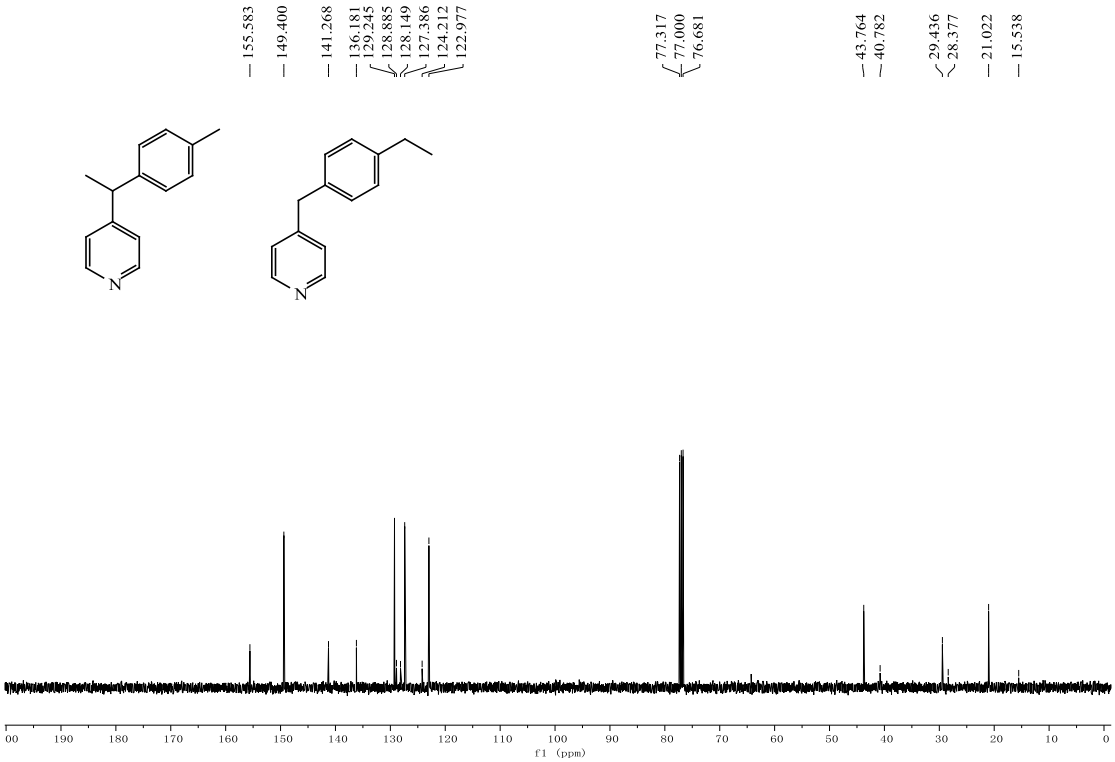
4-(1-(4-Methoxyphenyl)ethyl)pyridine (4e)



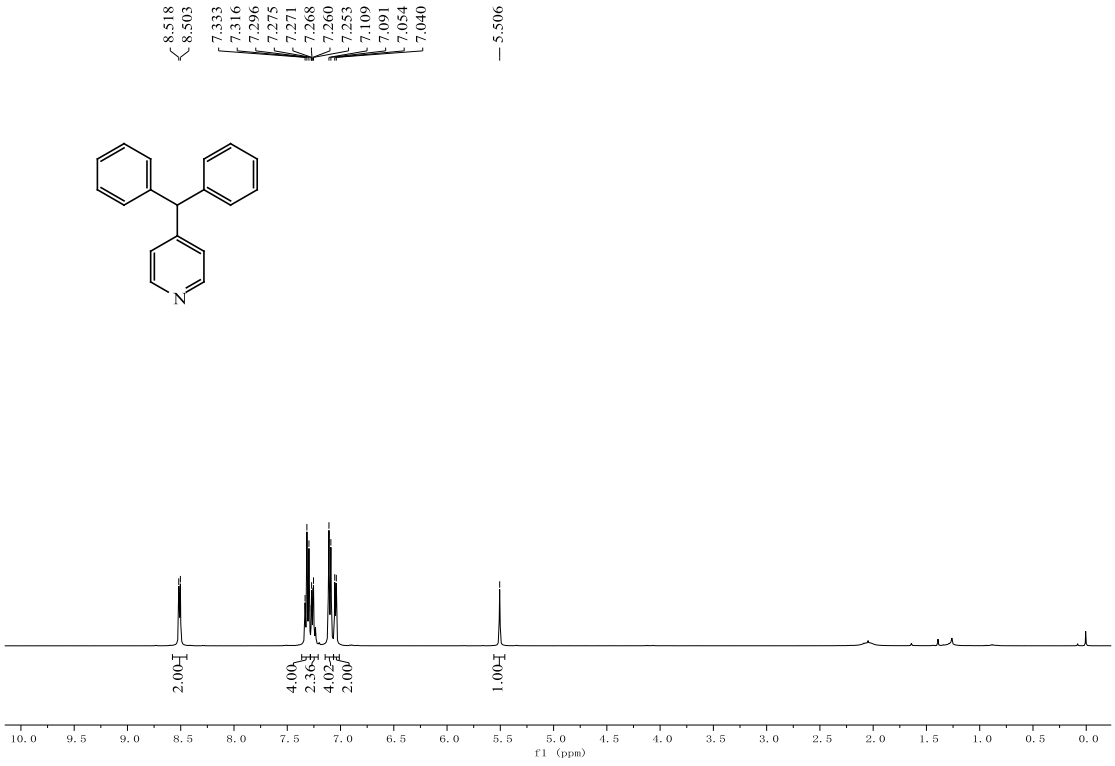


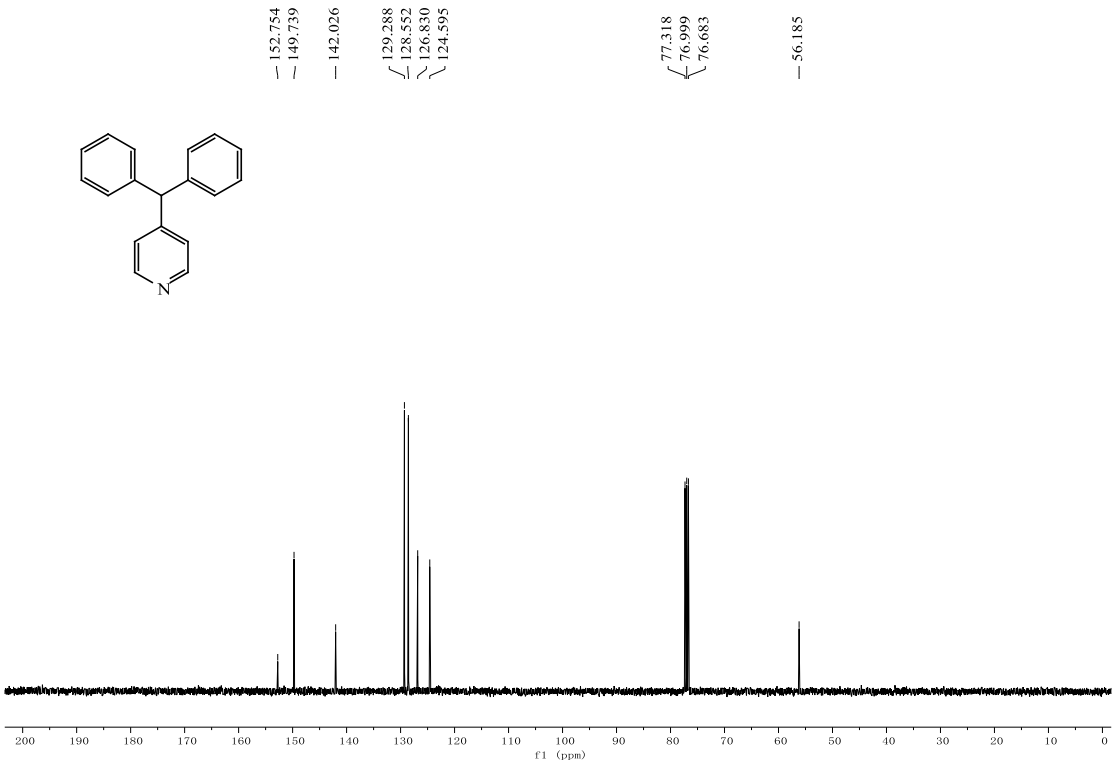
4-(1-(*p*-tolyl)ethyl)pyridine (4f) and **4-(4-ethylbenzyl)pyridine (4f')**



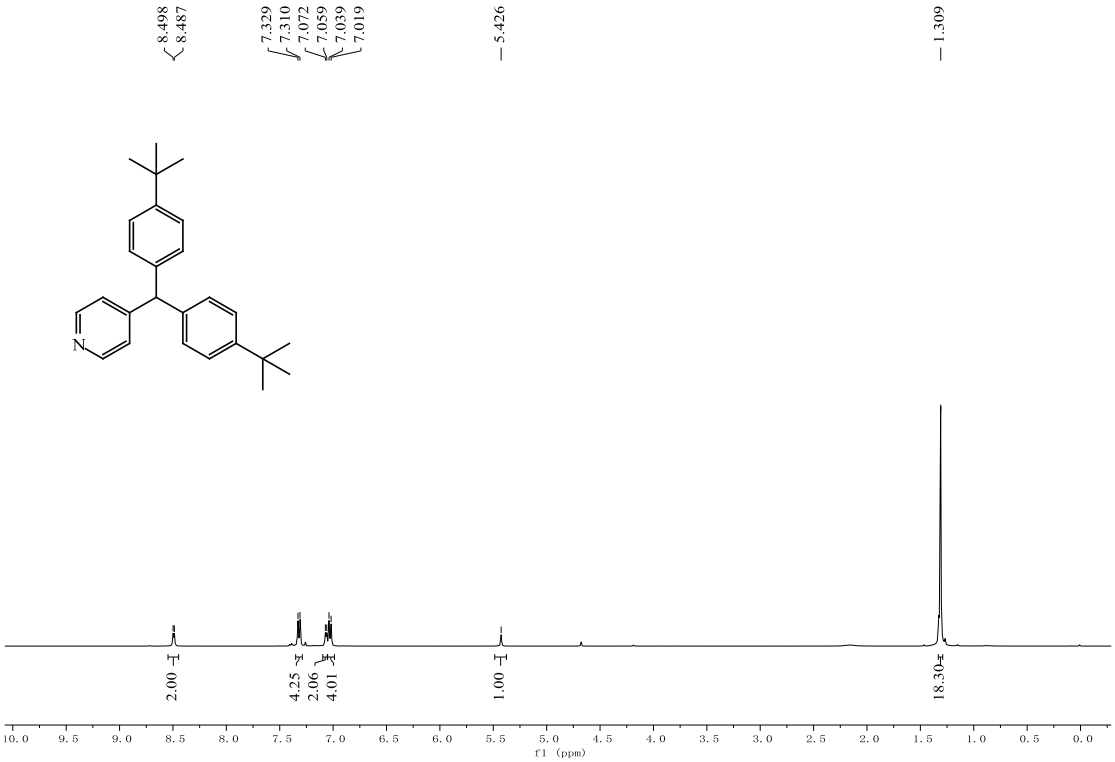


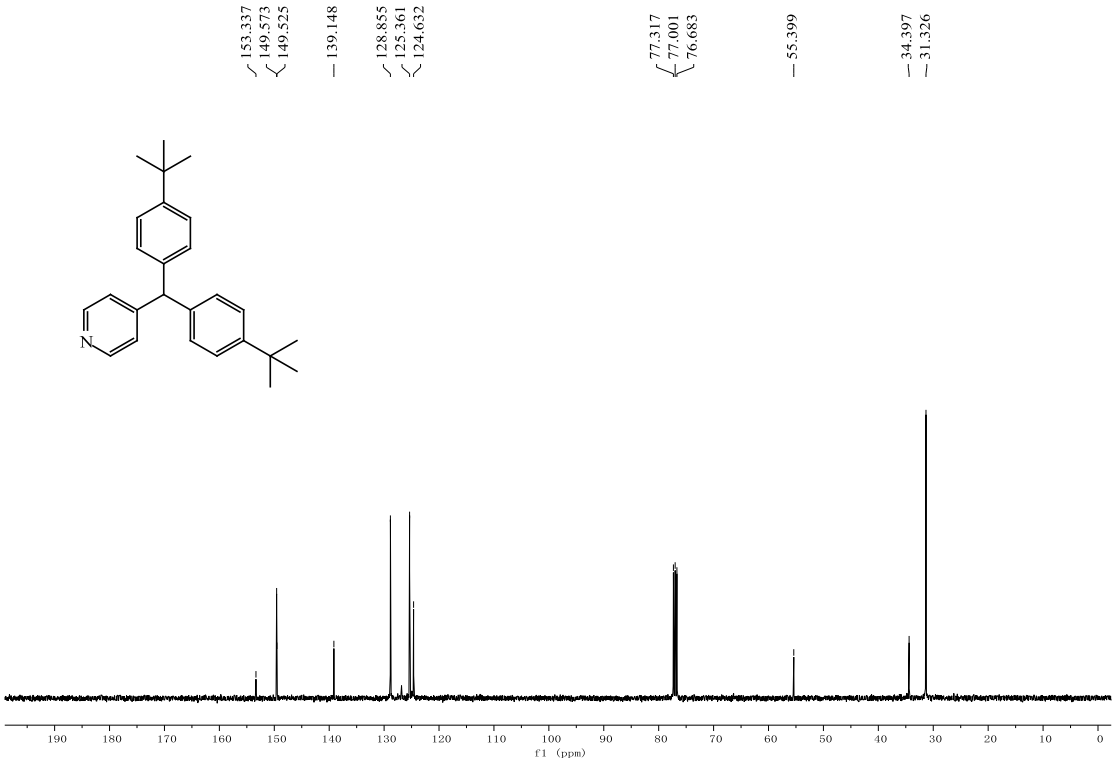
4-Benzhydrylpyridine (4g)



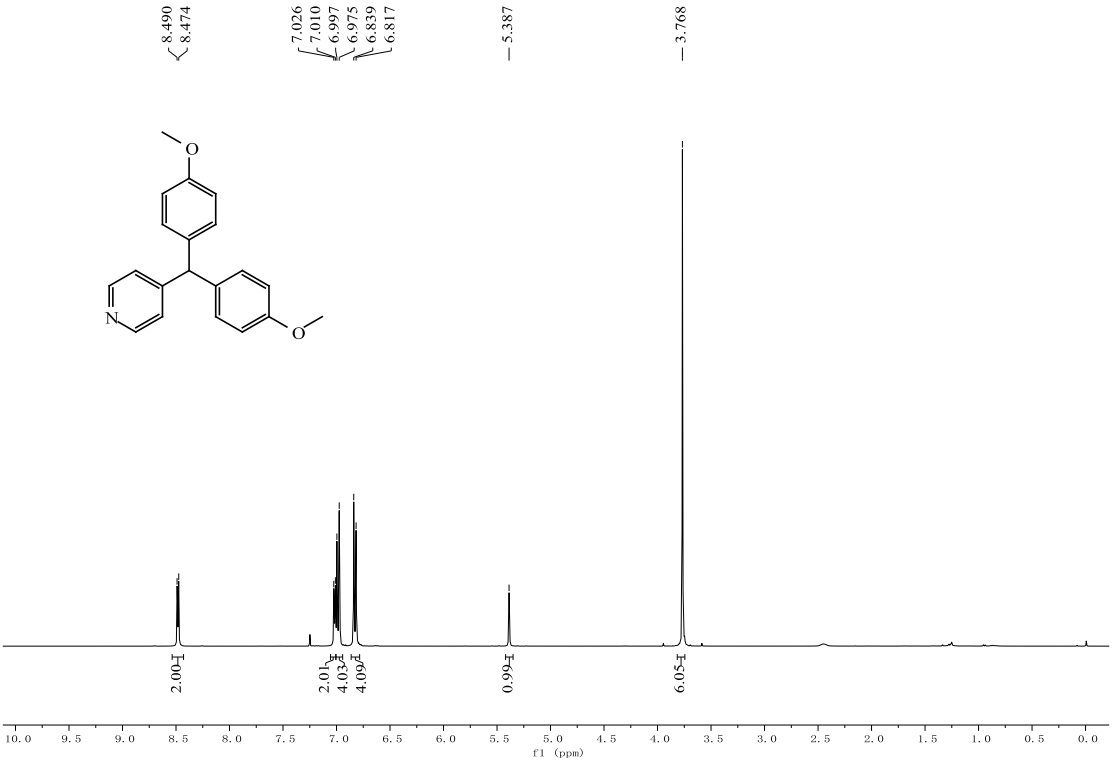


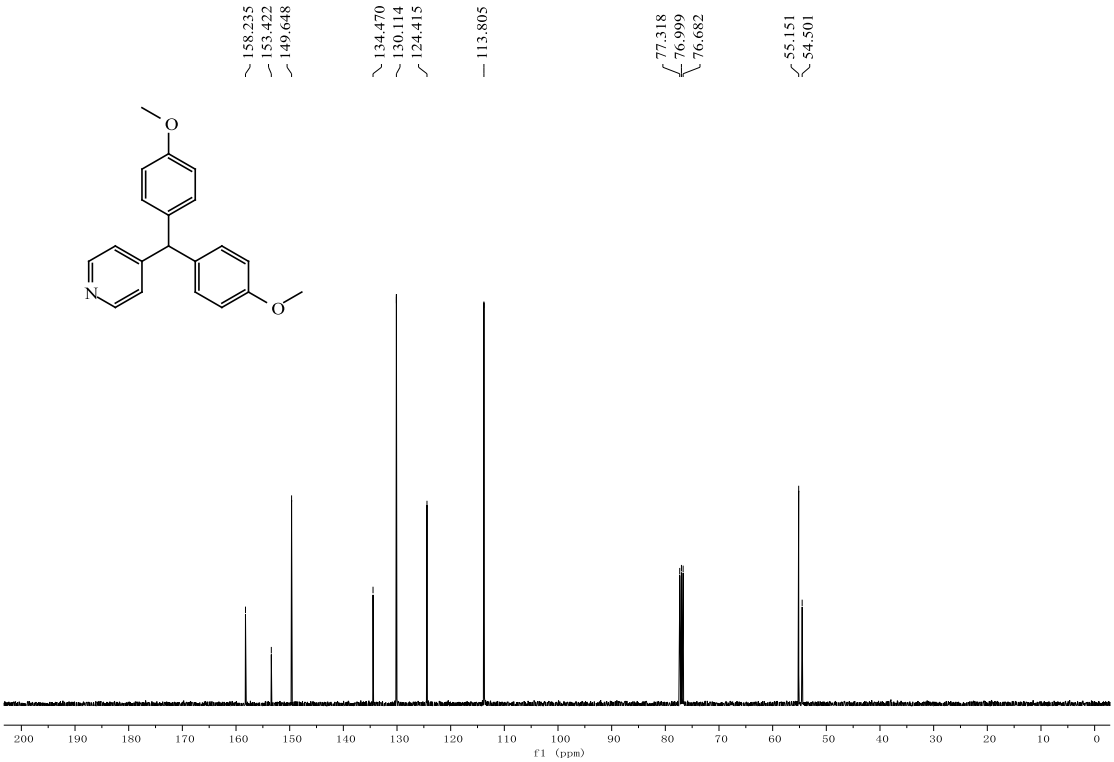
4-(bis(4-(*tert*-Butyl)phenyl)methyl)pyridine (4h)



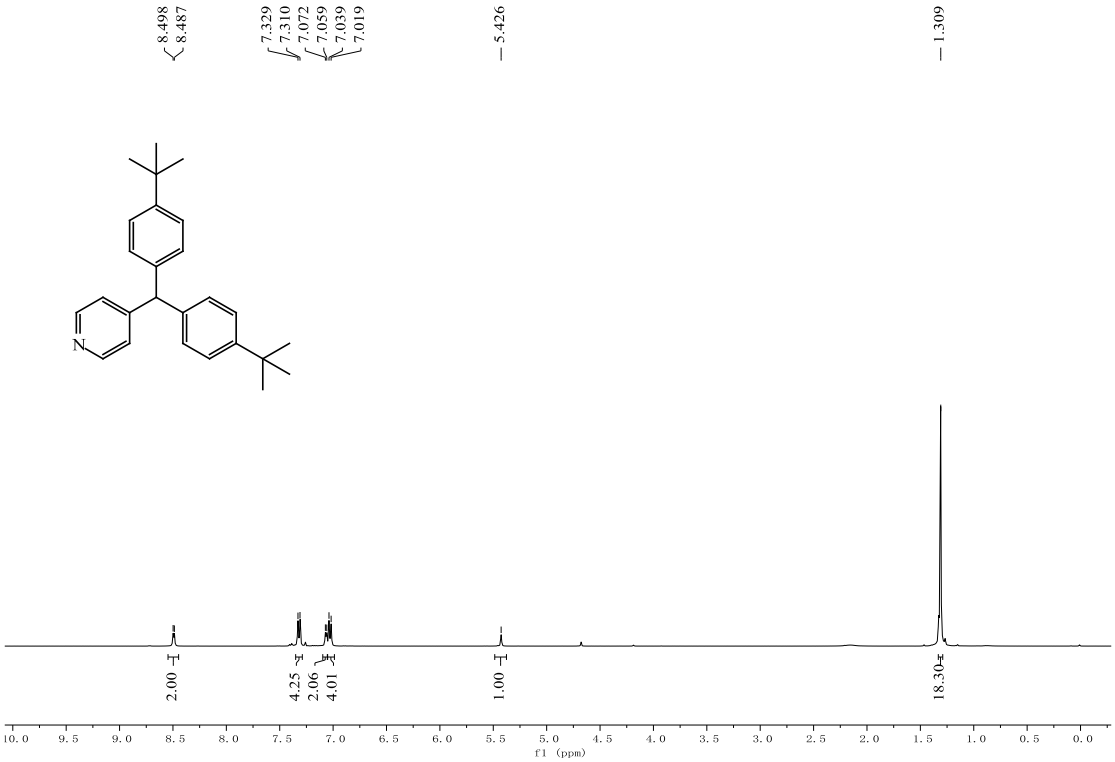


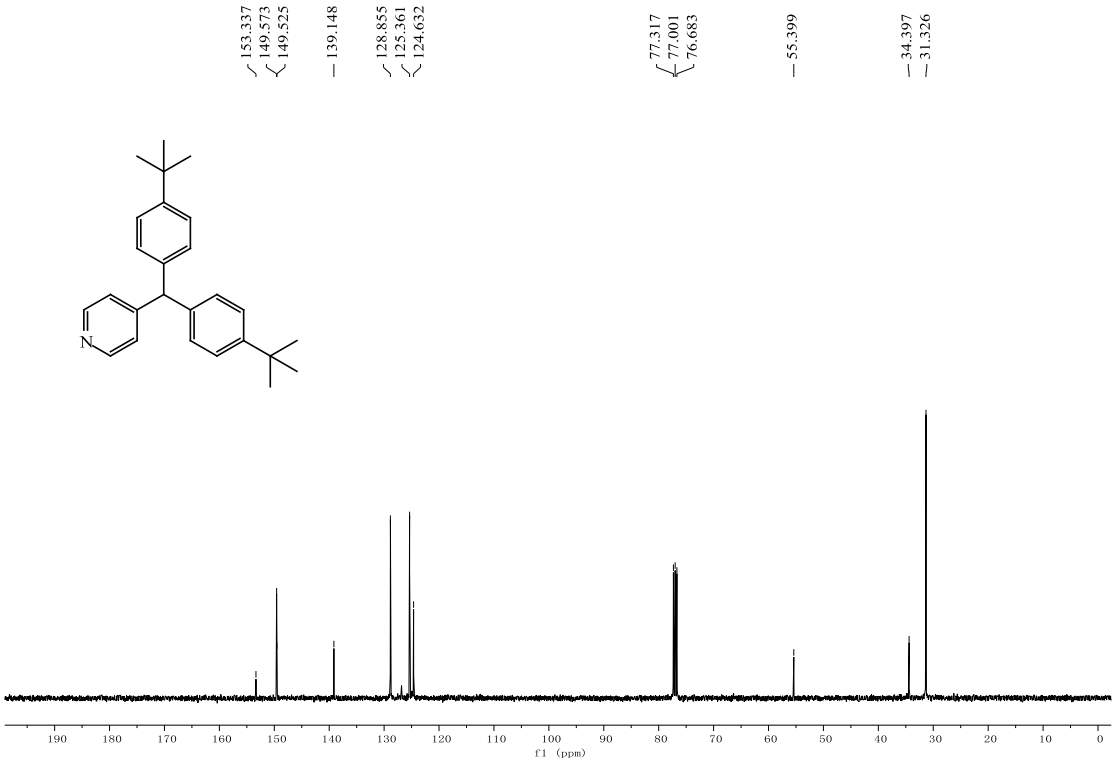
4-(bis(4-Bethoxyphenyl)methyl)pyridine (4h)



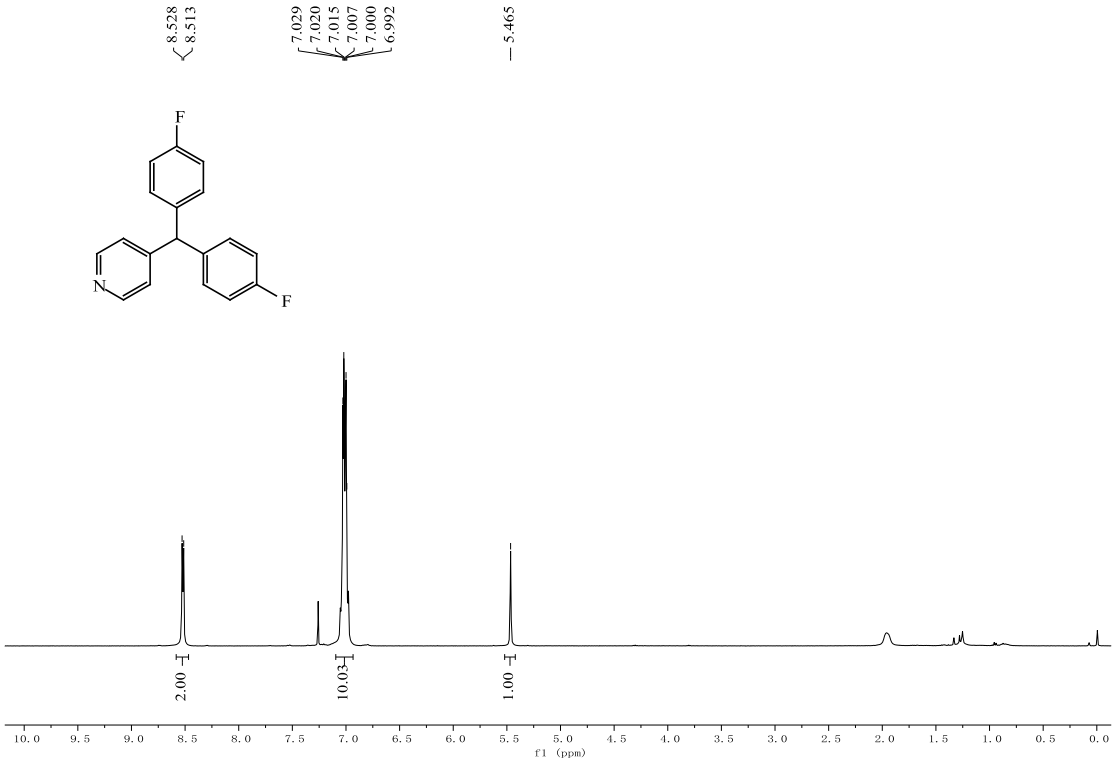


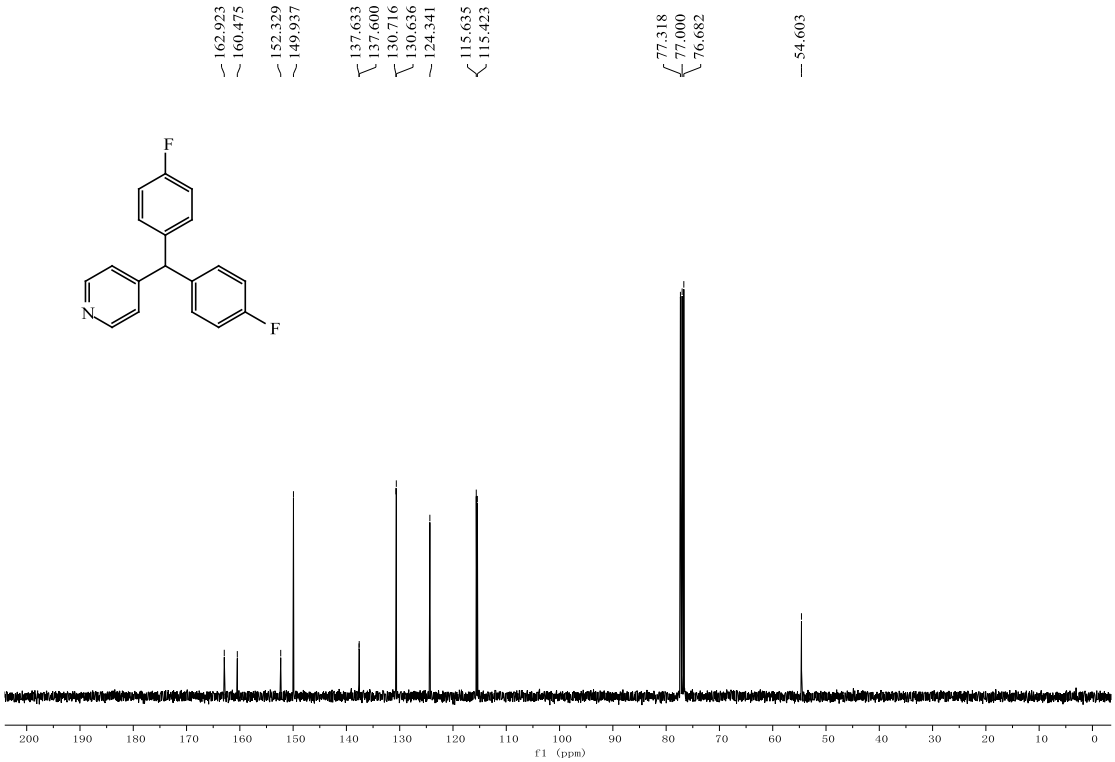
4-(bis(4-(*tert*-butyl)phenyl)methyl)pyridine (4i)



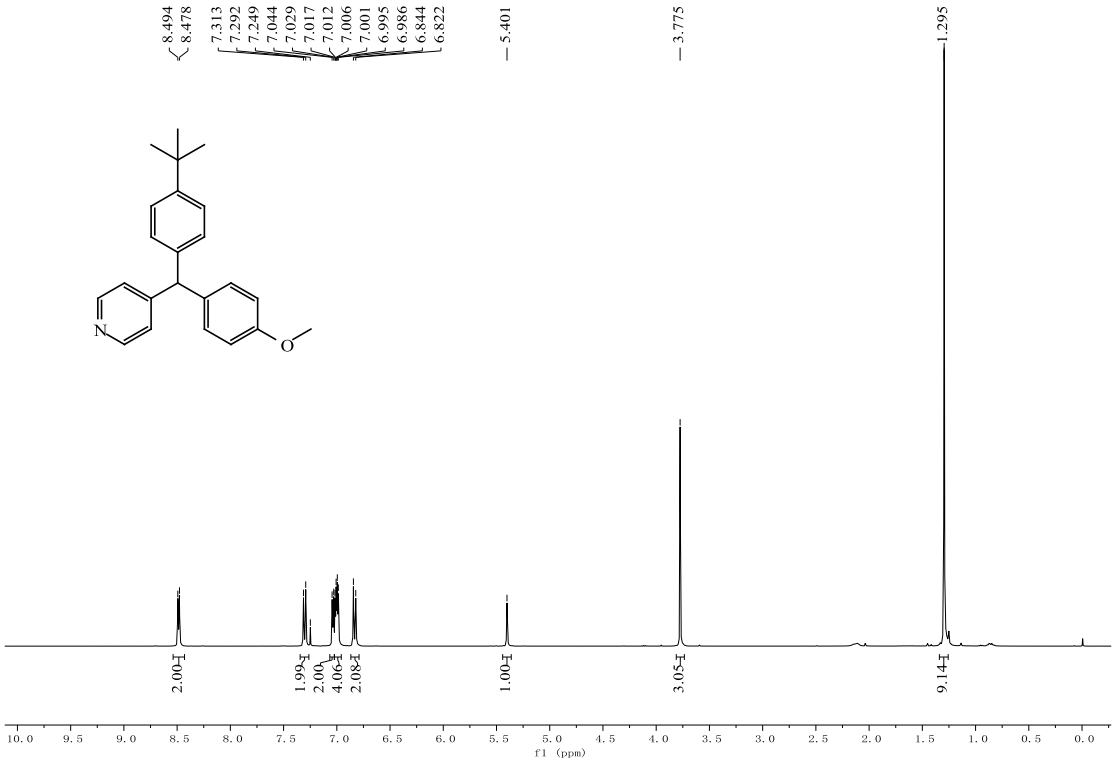


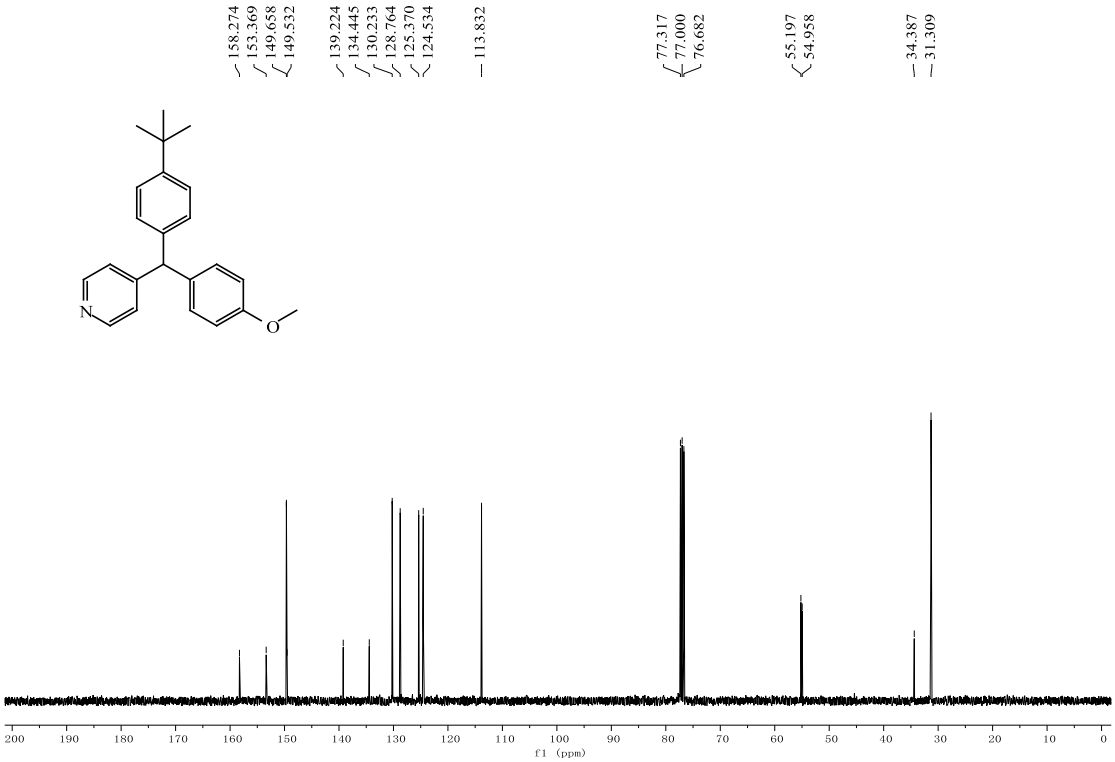
4-(bis(4-Fluorophenyl)methyl)pyridine (4j)



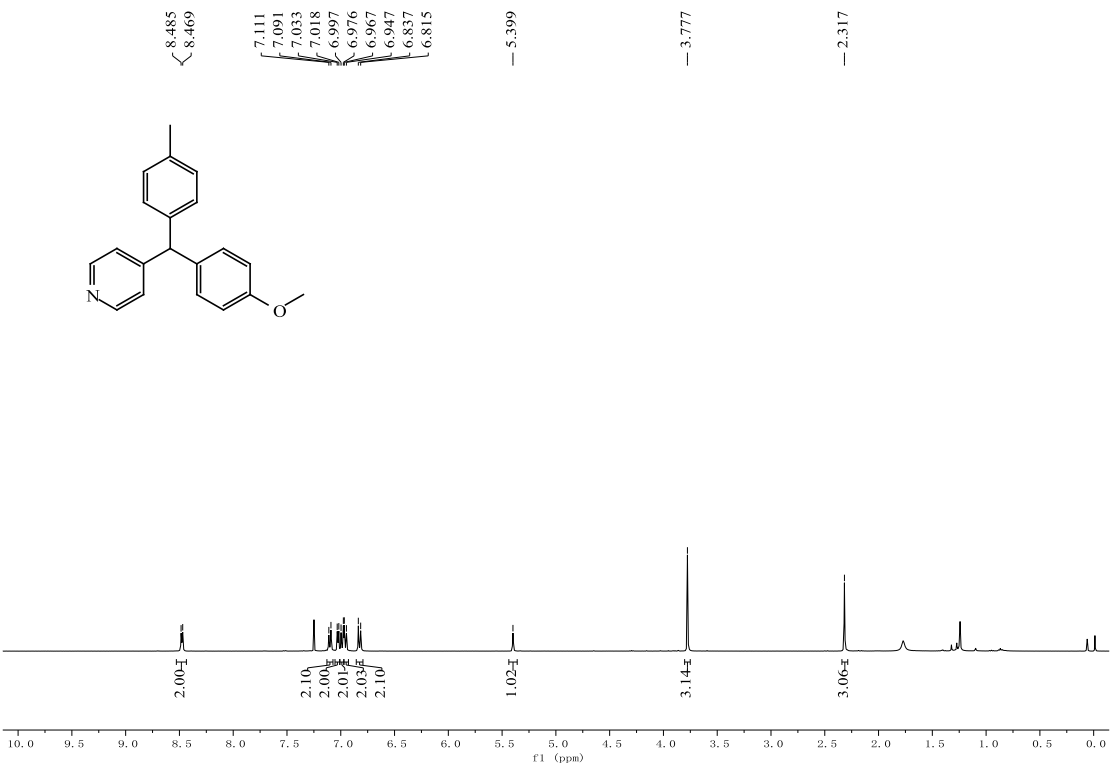


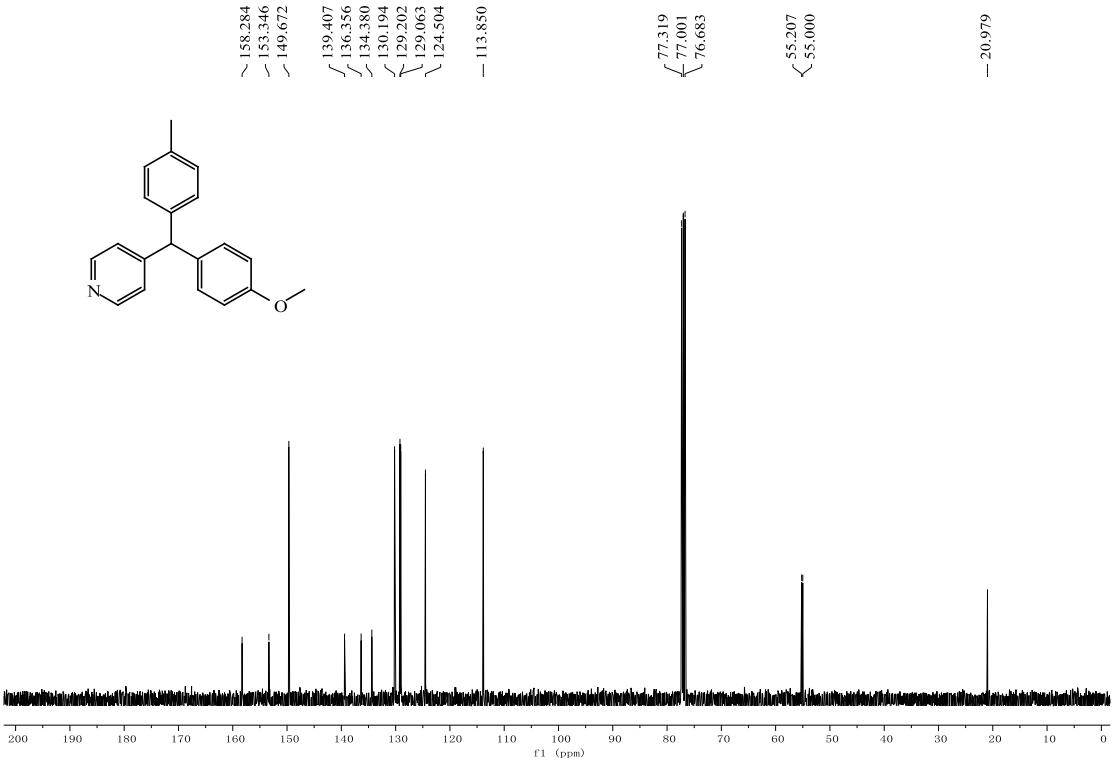
4-((4-(*tert*-Butyl)phenyl)(4-methoxyphenyl)methyl)pyridine (4k)



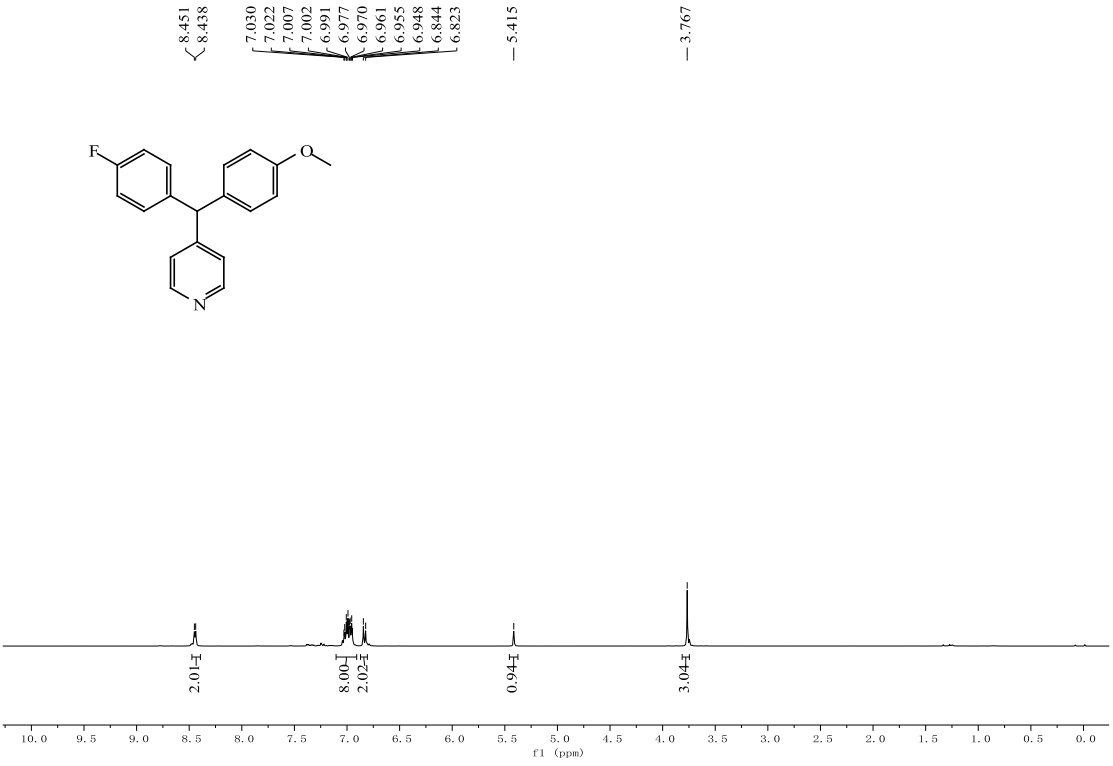


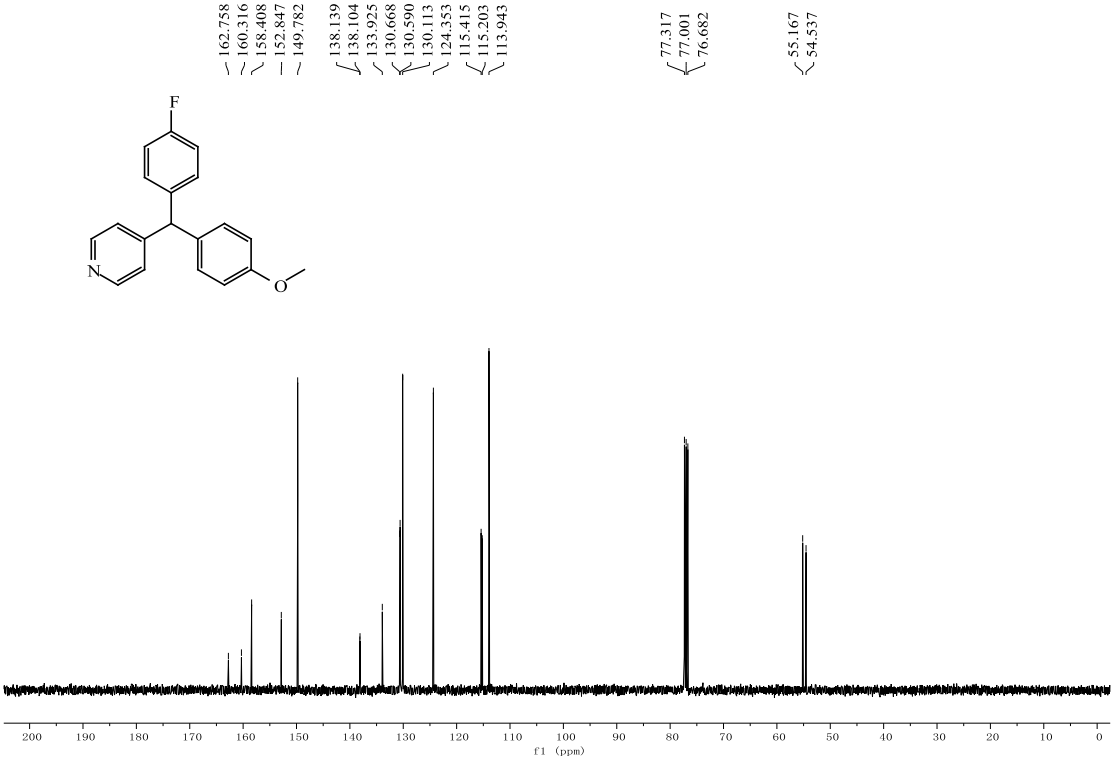
4-((4-Methoxyphenyl)(p-tolyl)methyl)pyridine (4l)



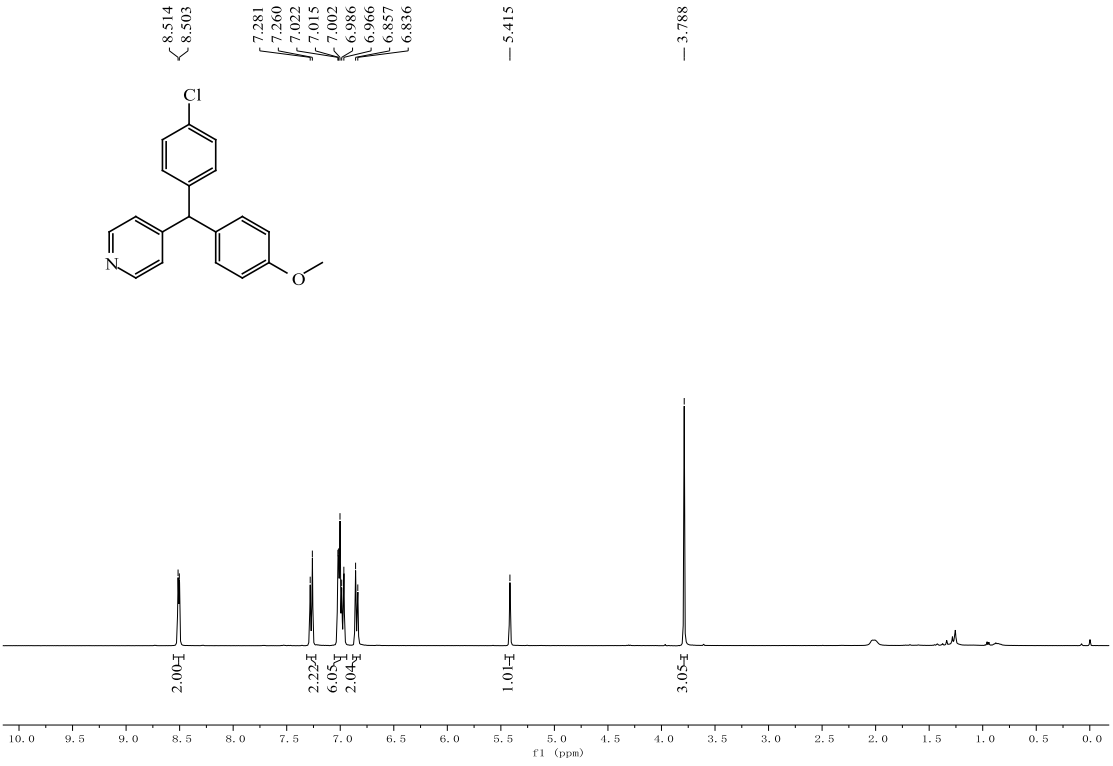


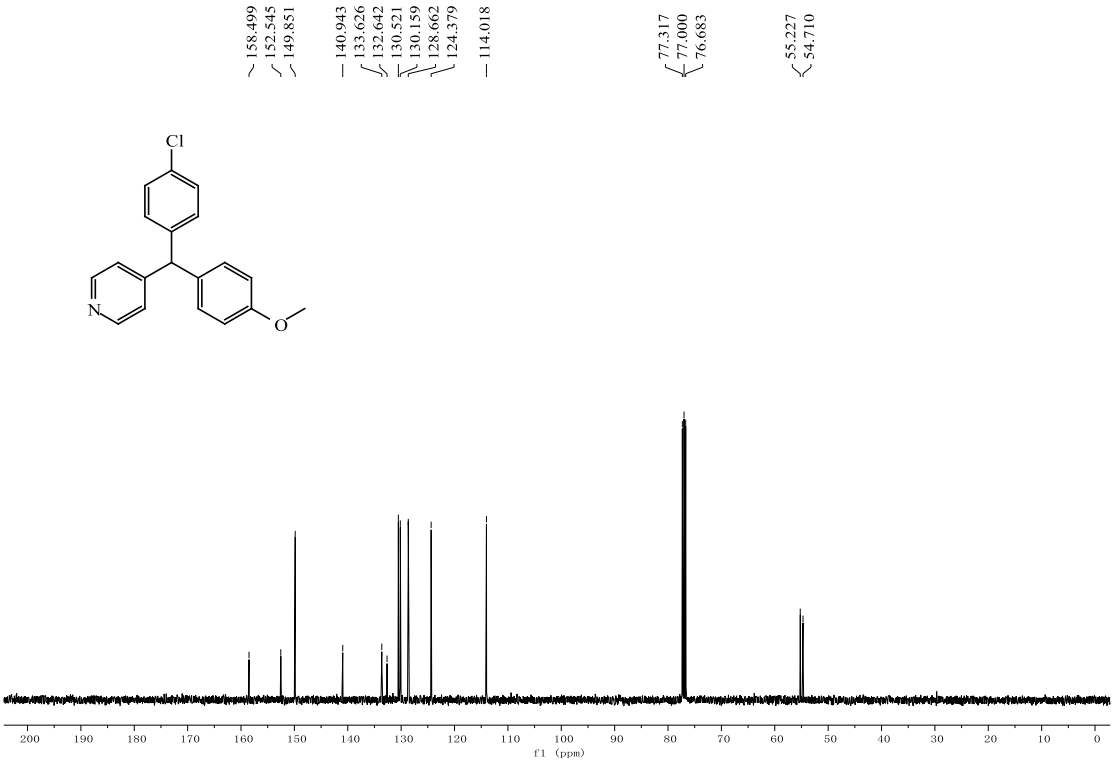
4-((4-Fluorophenyl)(4-methoxyphenyl)methyl)pyridine (4m)



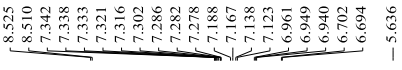


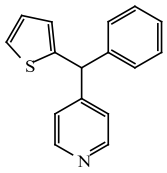
4-((4-Chlorophenyl)(4-methoxyphenyl)methyl)pyridine (4n)

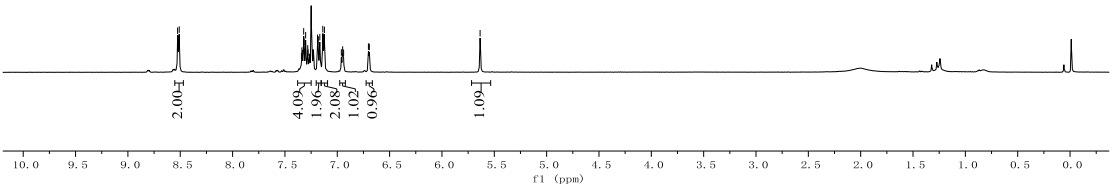


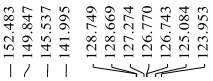


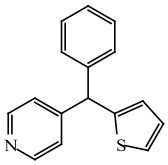
4-(Phenyl(thiophen-2-yl)methyl)pyridine (40)

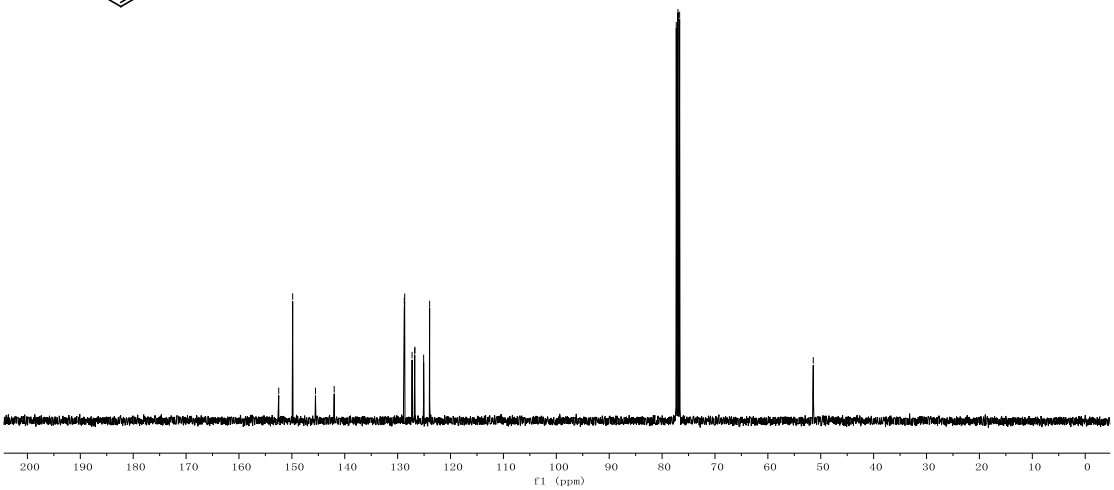




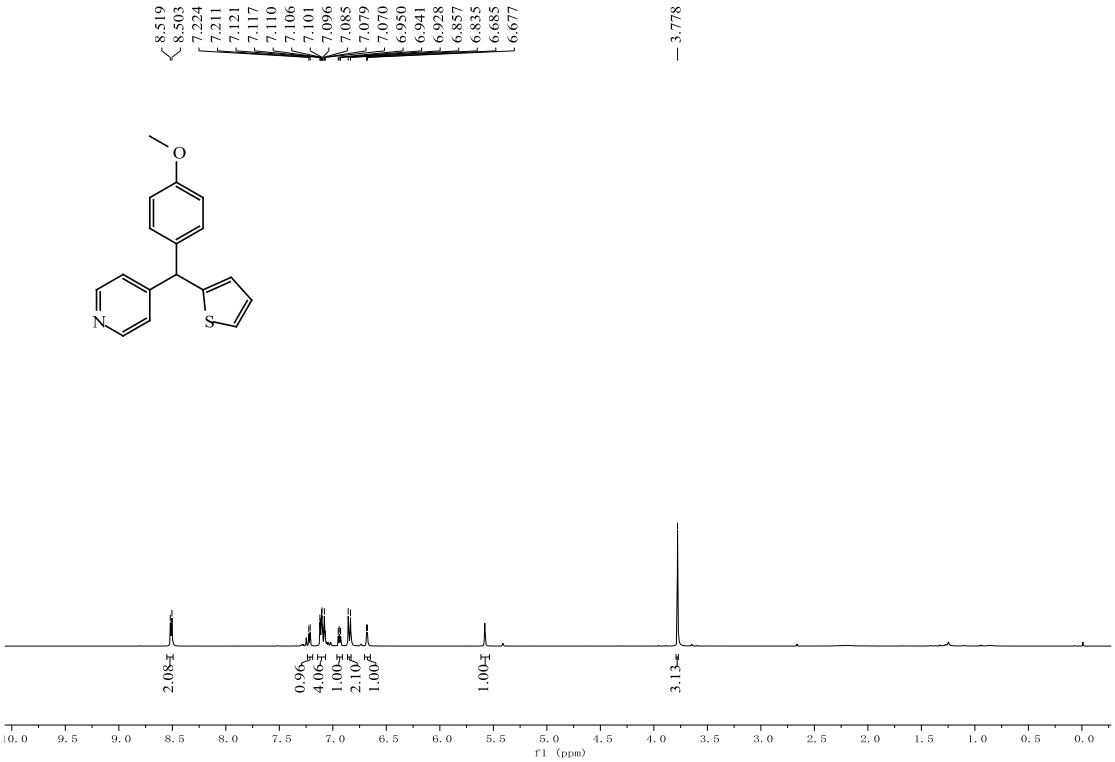


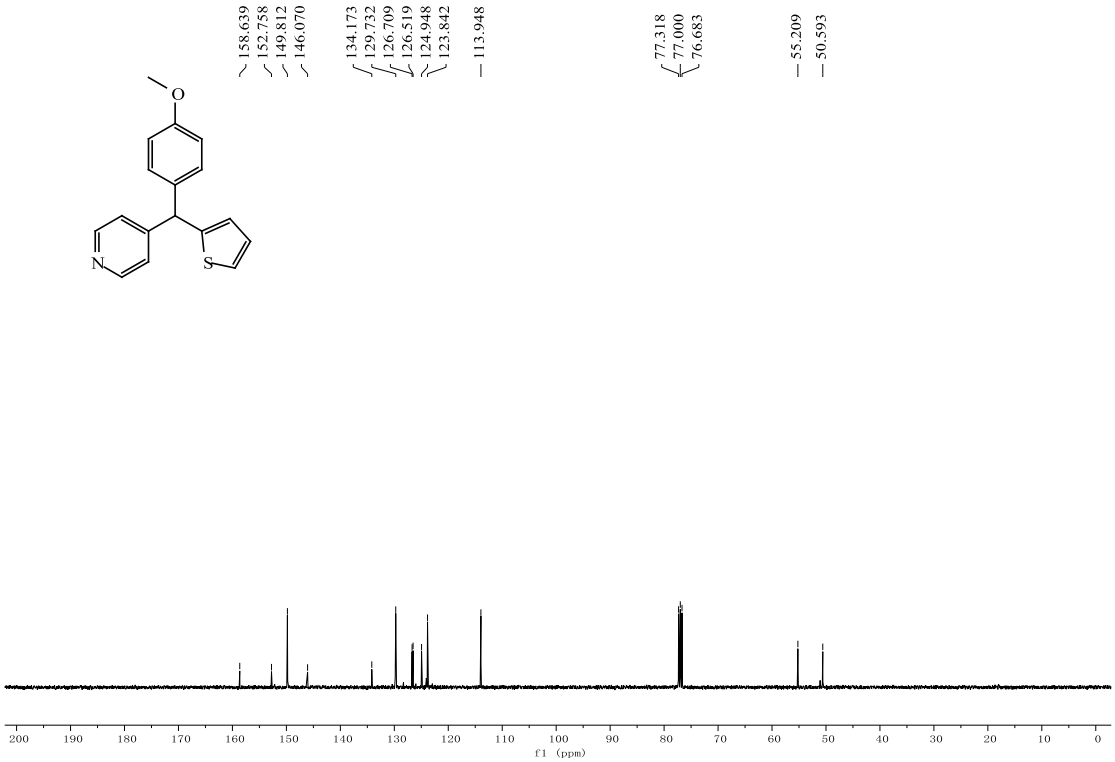




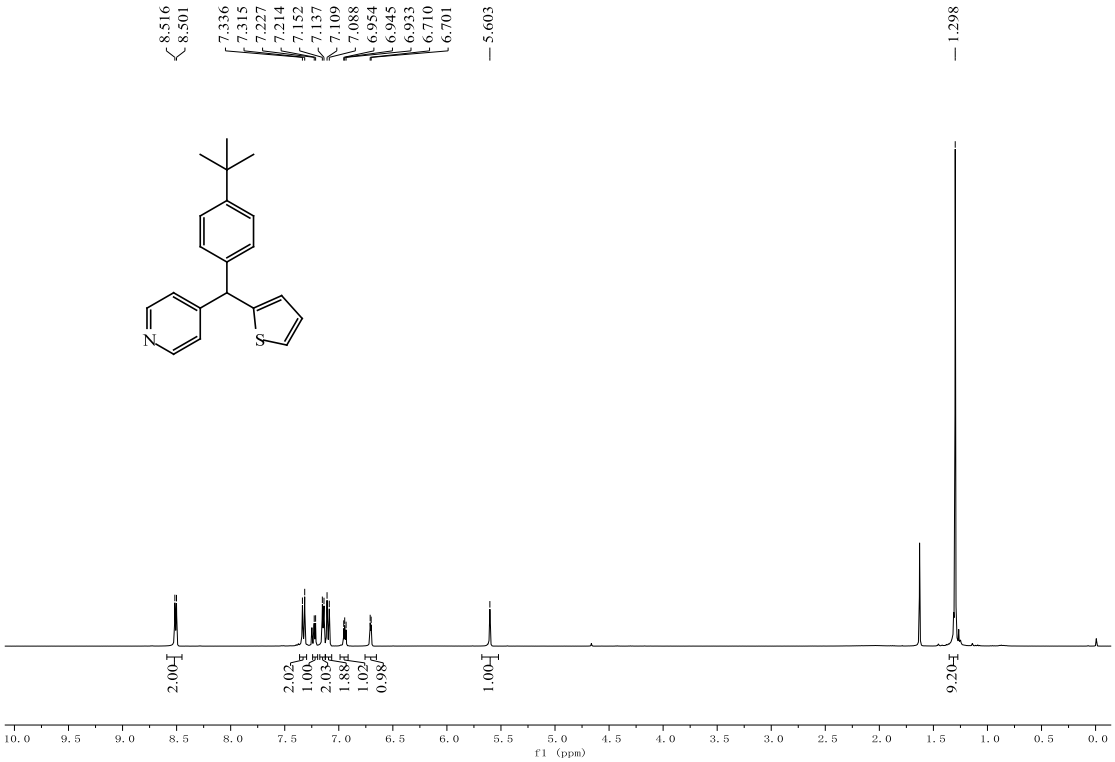


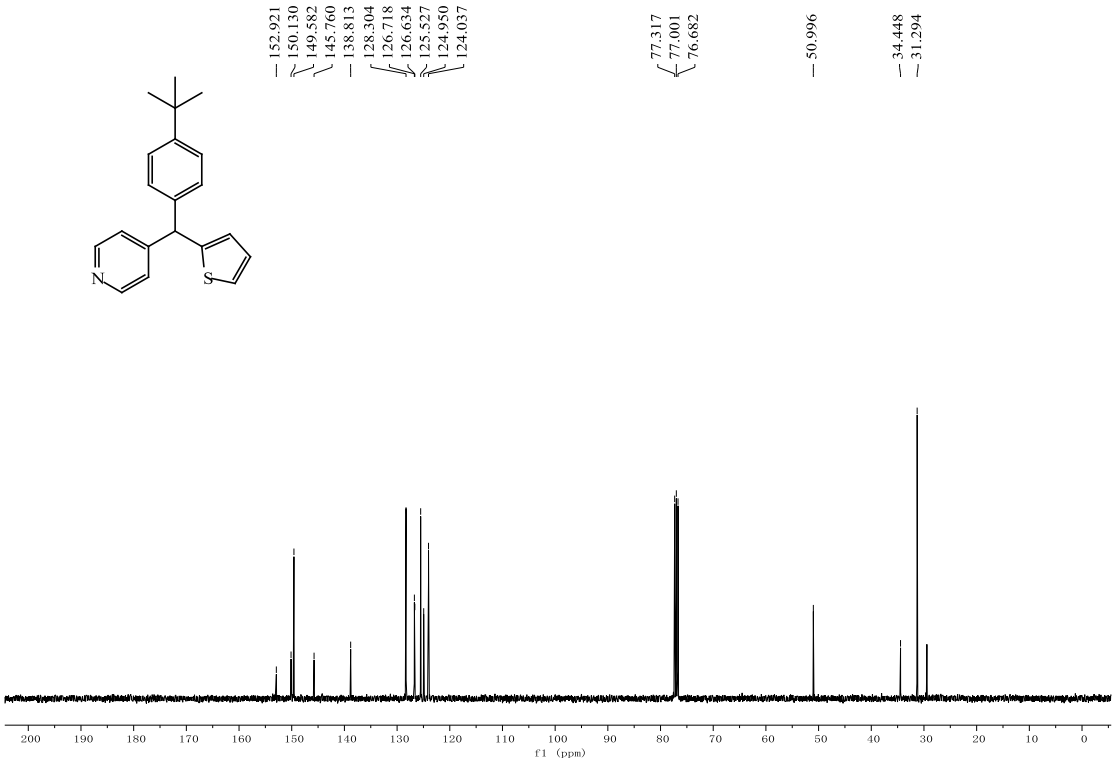
4-((4-Methoxyphenyl)(thiophen-2-yl)methyl)pyridine (4p)



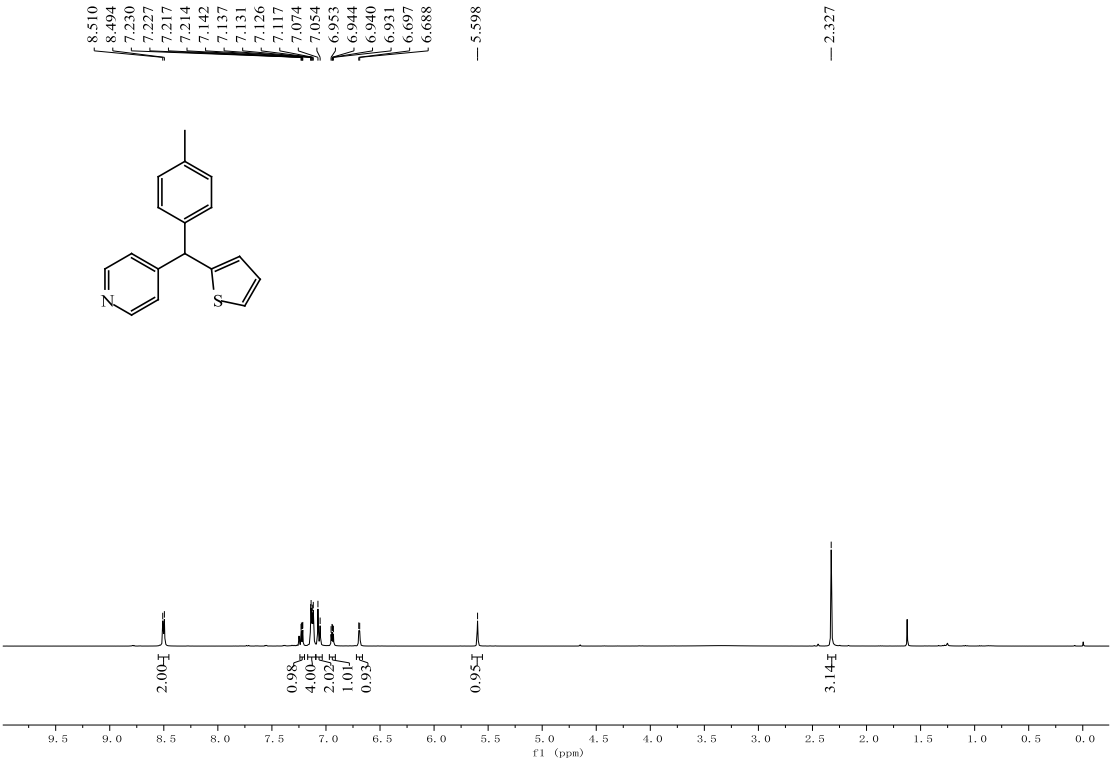


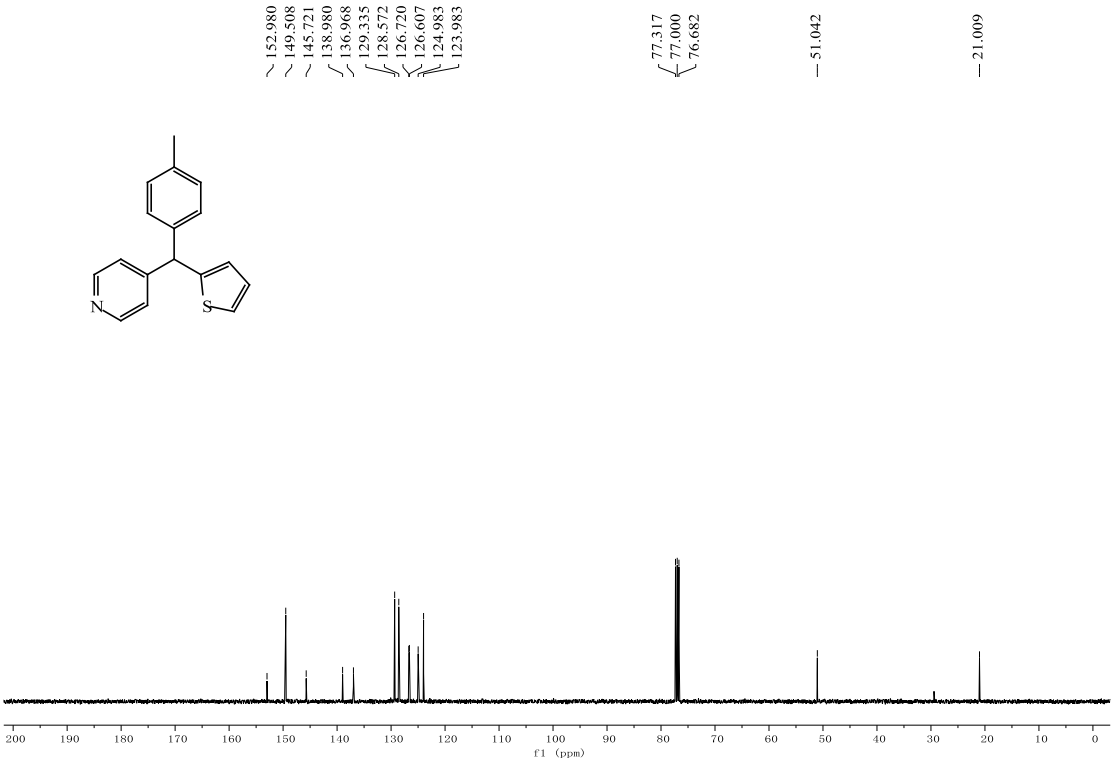
4-((4-(*tert*-Butyl)phenyl)(thiophen-2-yl)methyl)pyridine (4q)



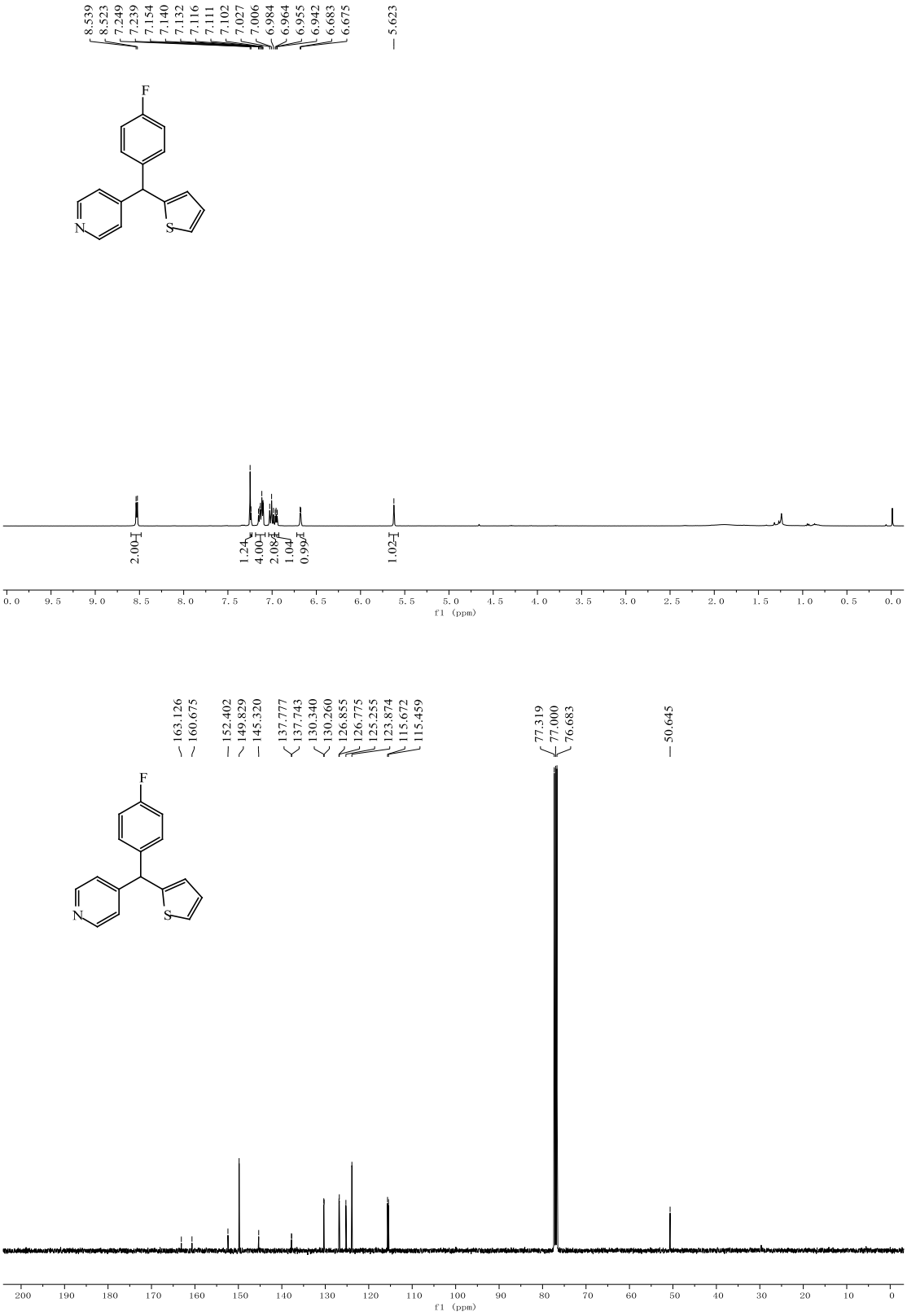


4-(Thiophen-2-yl(p-tolyl)methyl)pyridine (4r)

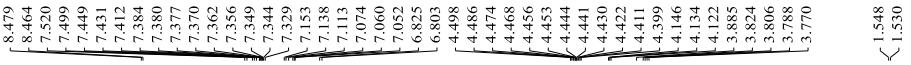


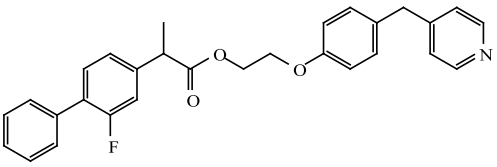


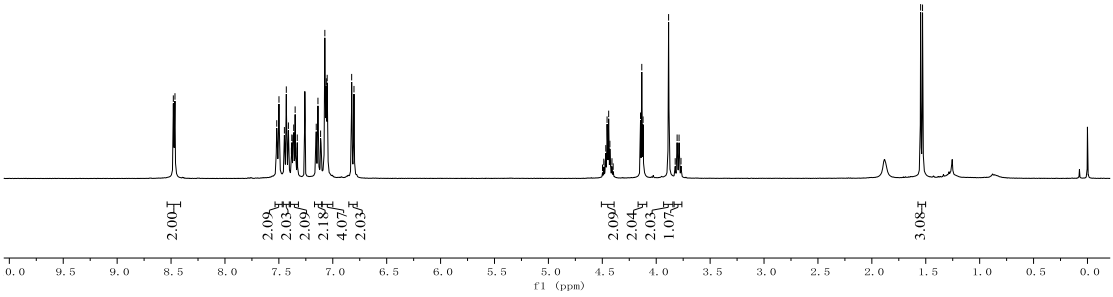
4-((4-Fluorophenyl)(thiophen-2-yl)methyl)pyridine (4s)

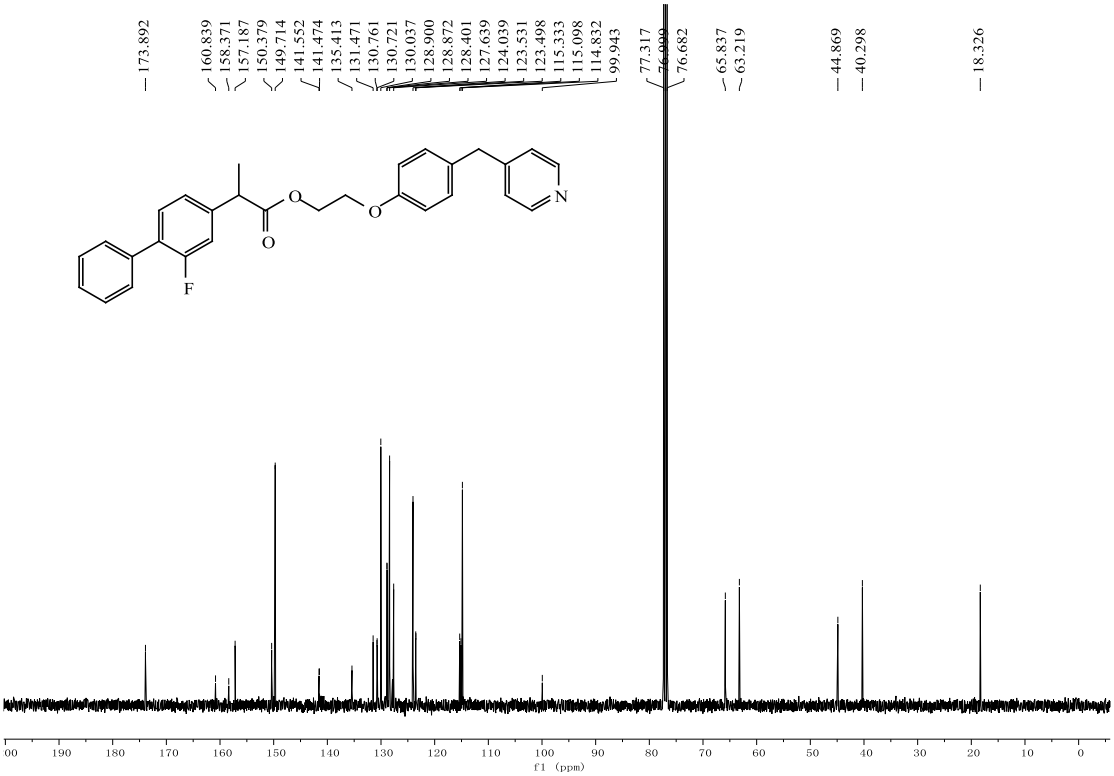


2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (5a)

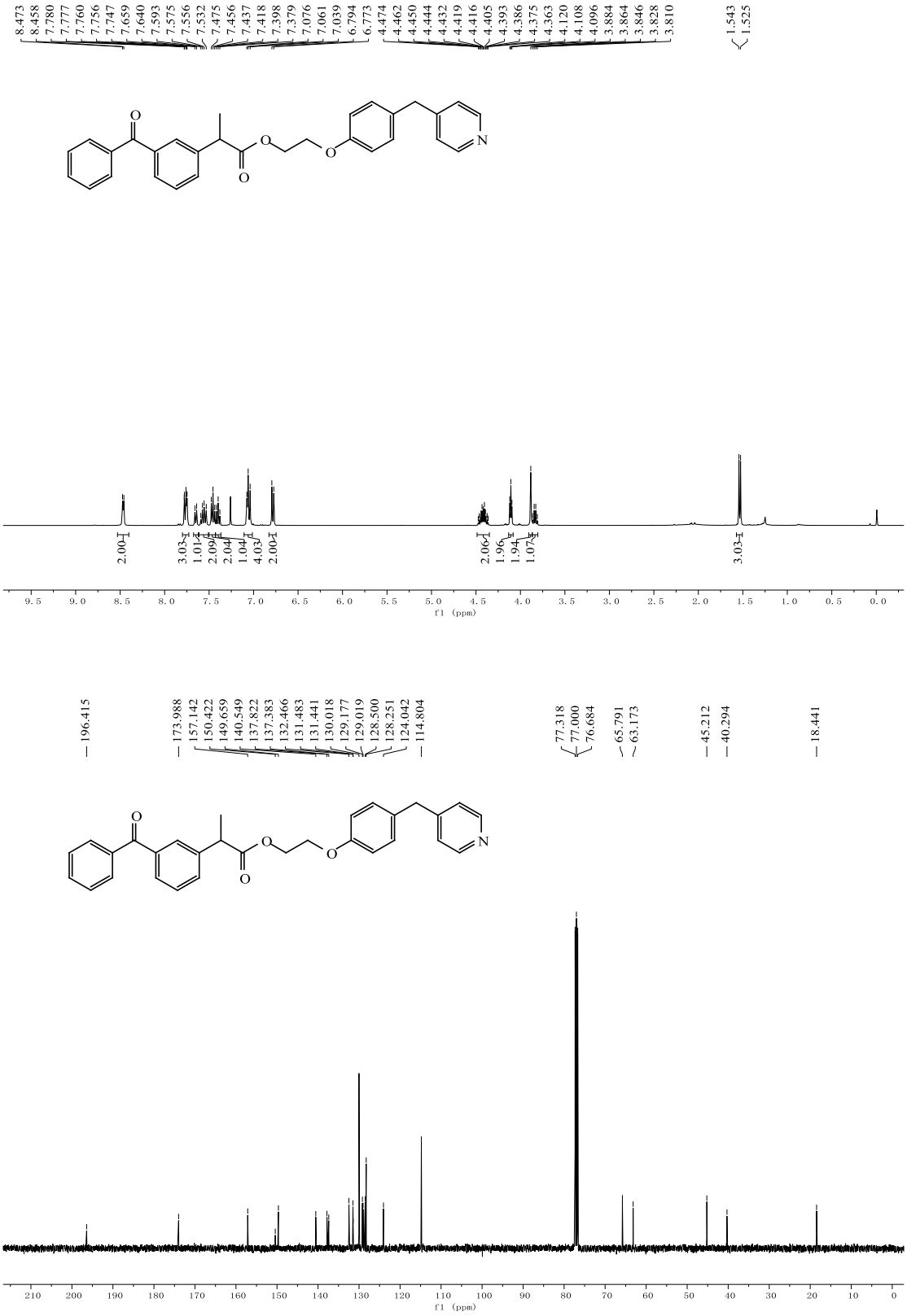




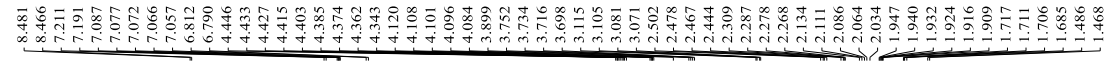


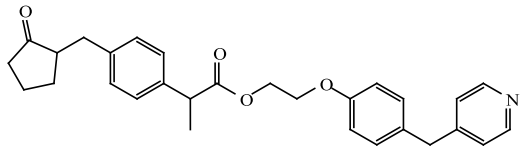


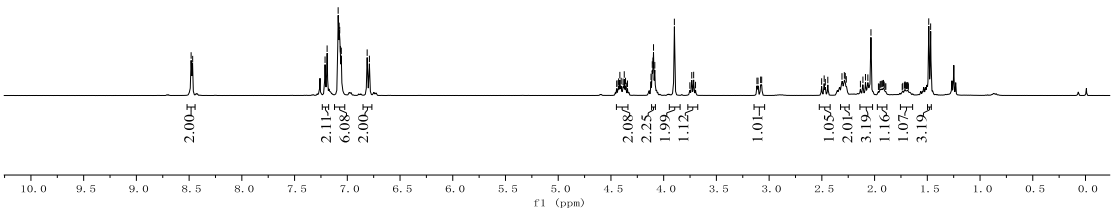
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(3-benzoylphenyl)propanoate (5b)

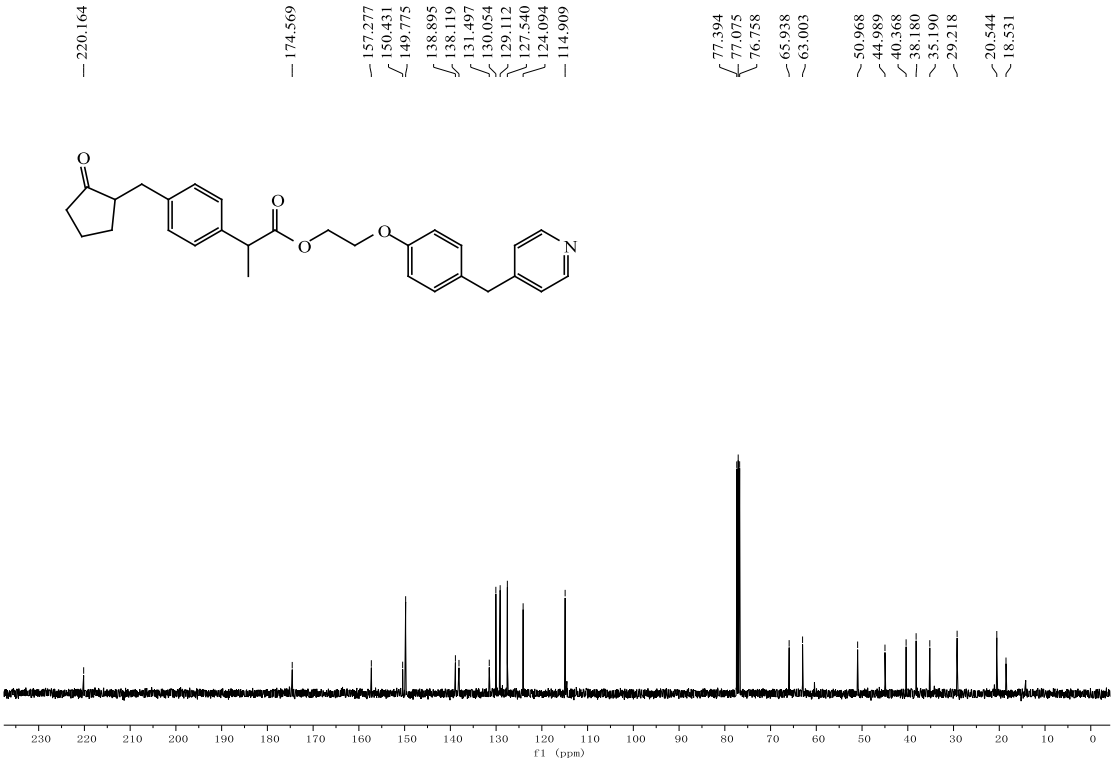


2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (5c)



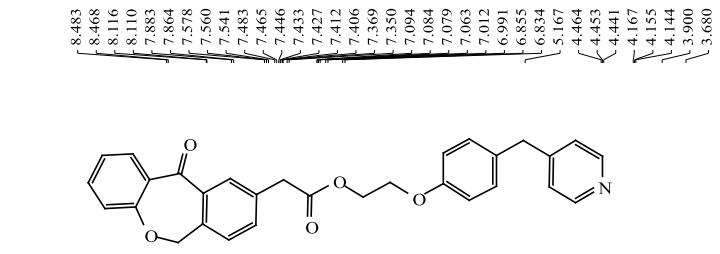


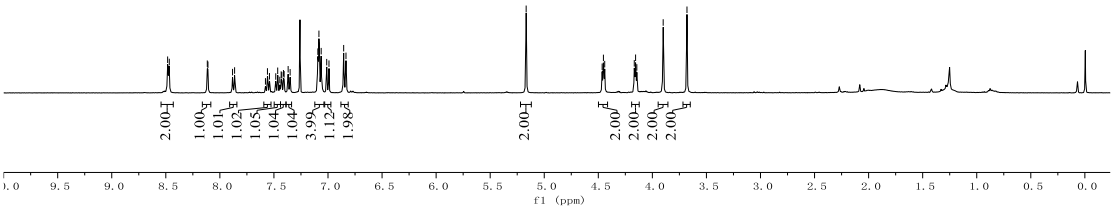




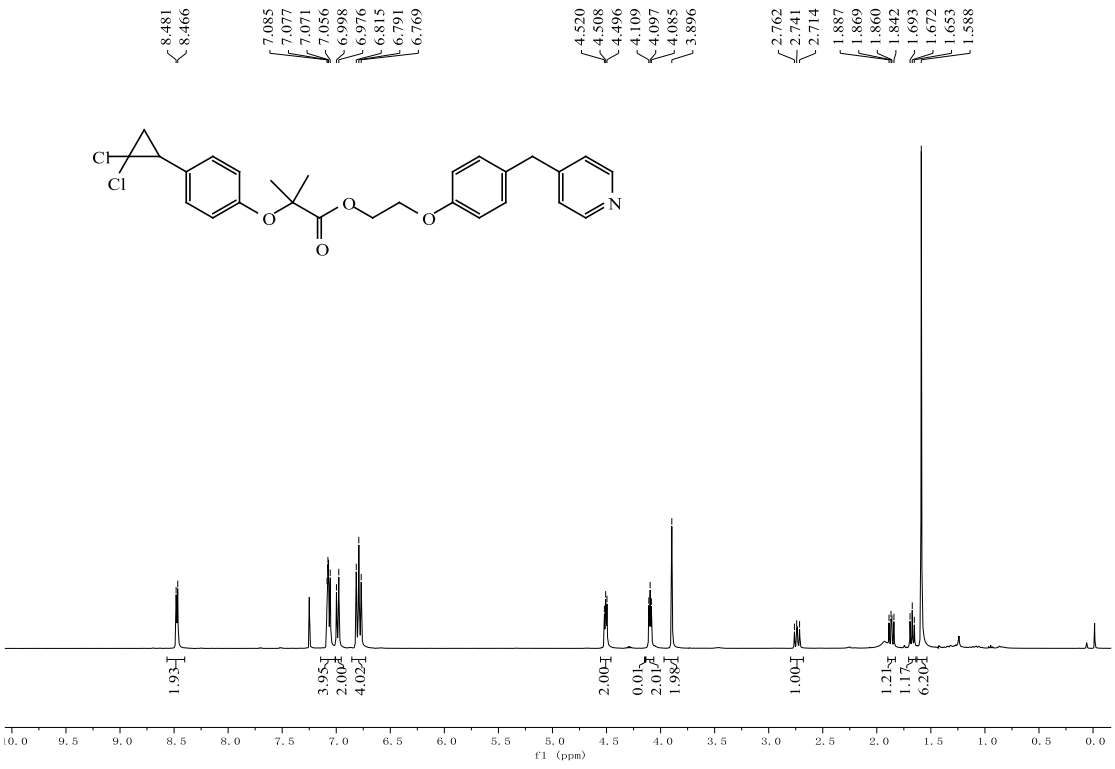
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-9-yl)acetate

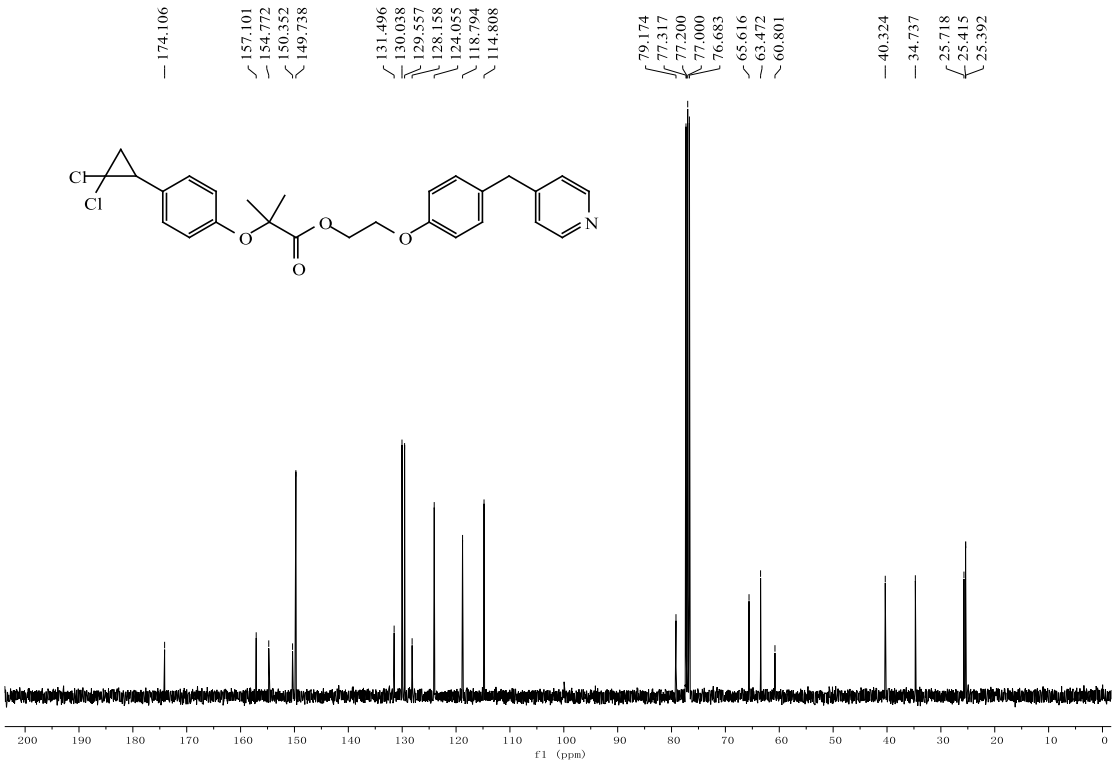
(5d)



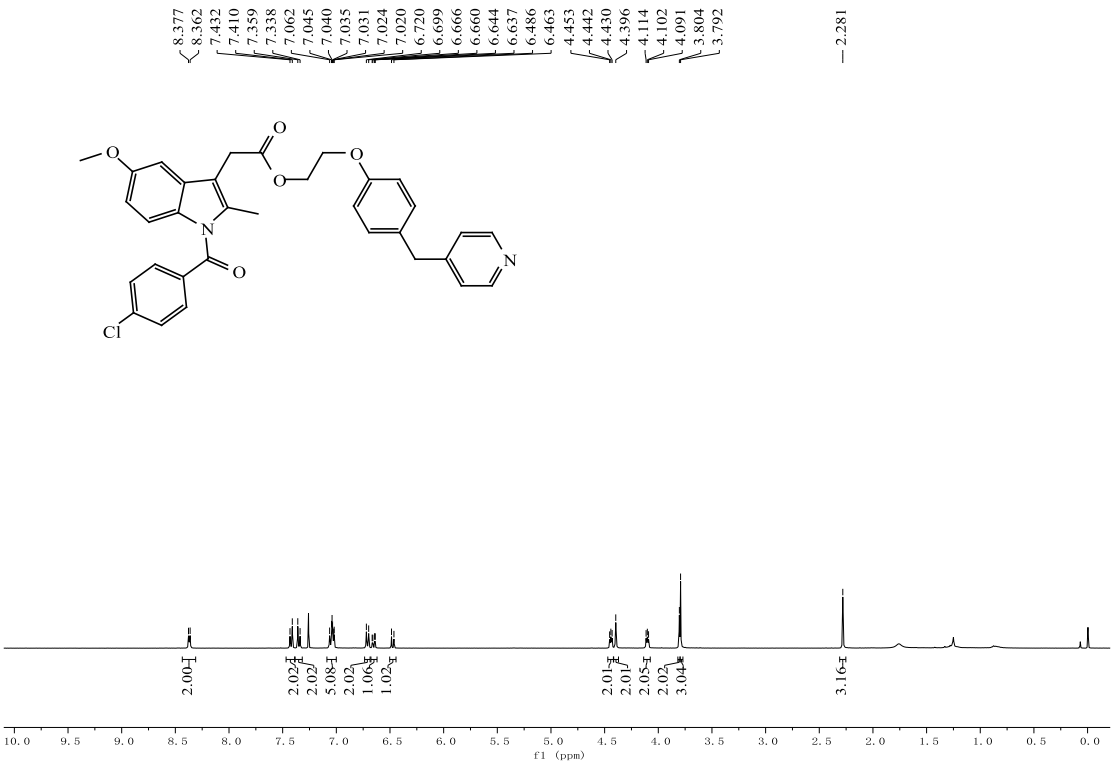


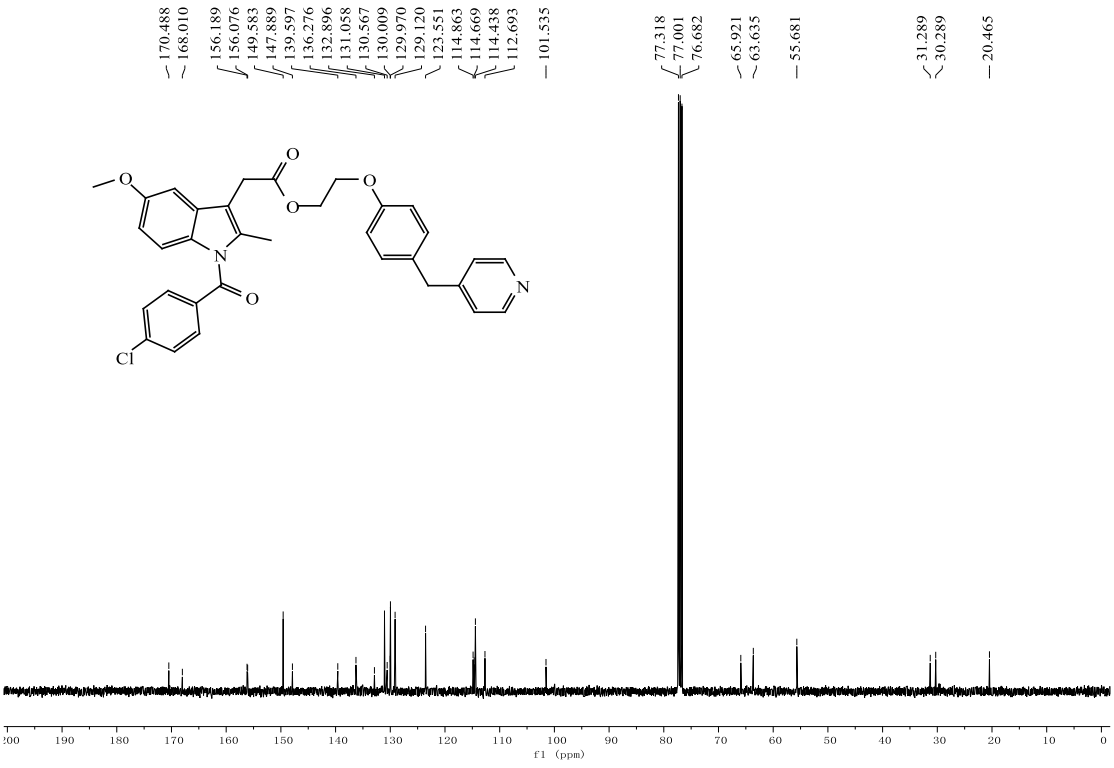
2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (5e)





2-(4-(Pyridin-4-ylmethyl)phenoxy)ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5f)





4-(2-phenylpropan-2-yl)pyridine (6)