Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Electricity-Driven Three-Component Reductive Coupling Reaction for the Synthesis of Diarylmethylamine

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A: General Remarks

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV-400/600 spectrometer (400/600 MHz and 100/150 MHz). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvent peak. Chemical shifts (δ) for carbon are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, quint = quintet, m = multiplet), coupling constants (*J*) in Hertz (Hz), integration; "app" is used to denote the apparent splitting of a signal.

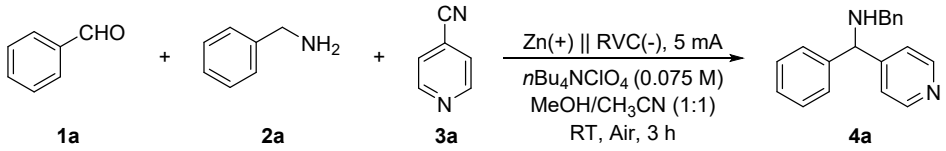
High resolution mass spectrometry (HRMS) was carried out using MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer.

The CV experiments were carried out in a three-electrode cell configuration with a glassy carbon (GC) working electrode (3 mm diameter) and a platinum wire counter electrode. The potentials were measured versus an Ag/AgCl reference electrode.

All solvents and substrates were from commercial sources (Adamas-beta, TCI, or Energy Chemical) and used without purification unless otherwise noted.

B: Optimization Tables

Table S1. Optimization of three-component reductive coupling reaction[a]

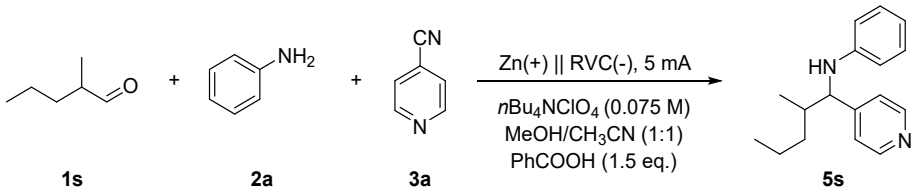


1a **2a** **3a** **4a**

Entry	Condition	Yield [%][b]
1	MeCN as a solvent	24
2	MeOH as solvent	33
3	DCM as solvent	13
4	DMSO as solvent	trace
5[c]	None	44
6[d]	DCM/MeCN (1:1) as solvents	43
7	MeOH/MeCN (1:2) as solvents	25
8	MeOH/MeCN (2:1) as solvents	35
9	1.5 equiv. C_6H_5COOH added	81
10	1.5 equiv. C_2H_5COOH added	43
11	1.5 equiv. CF_3COOH added	25
12	1.5 equiv. *p*-TsOH added	55
13	1.5 equiv. $ZnCl_2$ added	40
14	1.5 equiv. $Zn(OTf)_2$ added	42
15	1.5 equiv. 2-OMe-C_6H_4COOH added	66
16	1.5 equiv. 2-F-C_6H_4COOH added	80
17	1.5 equiv. 2-F-4-NO_2-C_6H_4COOH added	n.d.
18	0.5 equiv. C_6H_5COOH added	58
19	2.0 equiv. C_6H_5COOH added	79
20[e]	C(+)-RVC(-) as electrodes	38
21[e]	CF(+)-RVC(-) as electrodes	20
22[e]	RVC(+)-Pt(-) as electrodes	trace
23[e]	RVC(+)-Ni(-) as electrodes	trace
24[e]	RVC(+)-Zn(-) as electrodes	trace
25[e]	The ratio of **1a**, **2a** and **3a** (1:1:2, 1:1:3, 1:2:3)	trace
26[e]	*n*Bu_4NBF_4 as electrolyte	60
27[e]	nBu_4NBr as electrolyte	32
28[e]	$LiClO_4$ as electrolyte	46
29[e]	3 mA (5 h)	44
30[e]	8 mA (2 h)	75
31[e]	0 °C	44
32[e]	50 °C	70
33[e]	Inert gas protection	75
34[e]	No electric current	n.d.
35[e]	Electrolysis overnight	65

[a] Reactions were performed with **1a** (0.9 mmol), **2a** (0.9 mmol), **3a** (0.3 mmol), *n*Bu_4NClO_4 (0.3 mmol), MeOH/MeCN (2/2 mL), Zn(+)–RVC(-) as electrodes, undivided cell, 5 mA constant current for 3 h. [b] Isolated yield. [c] 2.2 V cell voltage after 3 h of electrolysis. [d] 5.7 V cell voltage after 3 h of electrolysis. [e] 1.5 equiv. PhCOOH added.

Table S2. Optimization of reductive coupling reaction involving 2-methylpentanal[a]



1s **2a** **3a** **5s**

Entry	Condition	Yield [%][b]
1	None	6
2	Inert gas protection	trace
3	DMA, CH_3CN, DCM, MeOH as solvents	n.d.
4	CH_3CN/DCM (1:1) as solvents	22
5[c]	4Å MS (100 mg)	n.d.
6[c]	3.0 equiv. Et_3N added	n.d.
7[c]	3.0 equiv. Ph_3SiH added	15
8[c]	3.0 equiv. iPr_3SiH added	20
9[c]	C_2H_5COOH as additive acid	27
10[c]	*p*-TsOH as additive acid	trace

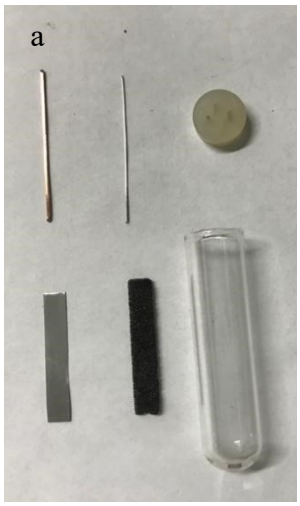
[a] Reactions were performed with **1s** (0.9 mmol), **2a** (0.9 mmol), **3a** (0.3 mmol), nBu_4NClO_4 (0.3 mmol), PhCOOH (0.45 mmol), additive (0.9 mmol), MeOH/MeCN (2/2 mL), Zn(+)–RVC(-) as electrodes, undivided cell, 5 mA constant current for 3 h. [b] Isolated yield. [c] CH_3CN/DCM (1:1) as solvents.

C: General Procedure for the Electrolysis

C1: General procedure for the making of electrolytic cell

The anode and cathode were home-made using the commercially available material (Zinc flakes, RVC, silica gel plug, copper wire and stainless steel wire and glass test tube, Figure S1a). A Zinc flake electrode (33 × 6 × 0.2 mm^3) with a copper wire and a RVC electrode (33 × 6 × 2.5 mm^3) with a stainless wire were cross the silica gel plug. And the distance between two electrodes was almost 5 mm (Figure S1b).

a

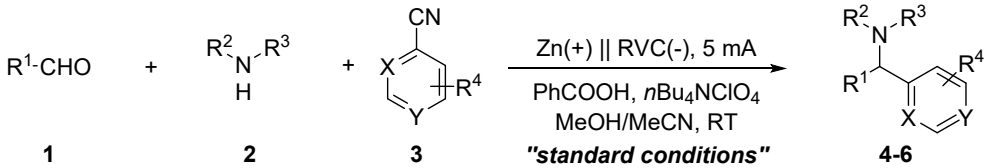


b

c

Figure S1. General procedure for the electrolysis. a) The materials used to make the electrolytic cell; b) The assemble of electrolytic cell; c) The electrolysis.

C2: General procedure for electrolysis



1 **2** **3** ***"standard conditions"*** **4-6**

The test cube was charged with a stir bar, 0.9 mmol aldehydes, 0.9 mmol secondary or tertiary arylamines, 0.3 mmol cyanopyridine, 0.3 mmol nBu$_4$NClO$_4$, 0.45 mmol benzoic acid, 2 mL CH_3CN and 2 mL MeOH, and the suspension was stirred until the solids resolve. Then the assembled electrodes were placed into the solution and the silica gel plug was sealed with film. Then the mixture was electrolyzed at a constant current of 5 mA (Figure S1c) until the cyanopyridine was completely consumed. The RVC electrodes were ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with saturated sodium bicarbonate (30 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford the final product.

C3: Large scale general procedure for electrolysis

a

b

c

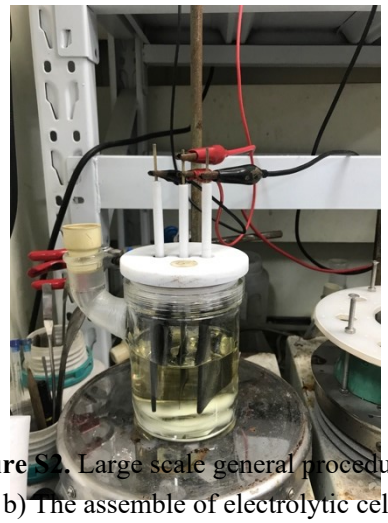


Figure S2. Large scale general procedure for the electrolysis. a) The materials used to make the electrolytic cell; b) The assemble of electrolytic cell; c) The electrolysis.

The Zinc flake anode (50 × 55 × 0.2 mm^3) and two RVC cathodes (50 × 50 × 0.25 mm^3) were assembled into sealed cap (Figure S2a and S2b). A beaker was charged with a stir bar, benzaldehyde **1a** (3.66 mL, 36 mmol), allylamine hydrochloride (3.37 g, 36 mmol) or *N*-methylbenzylamine (4.65 mL, 36 mmol), 4-cyanopyridine **3a** (1.25 g, 12 mmol), nBu_4NClO_4 (4.10 g, 12 mmol), benzoic acid (2.20 g, 20 mmol), 80 mL CH_3CN and 80 mL MeOH, and the suspension was stirred until the solids resolve. Then the assembled electrode was placed into the solution. The mixture was electrolyzed at a constant current of 100 mA for 12 h (Figure S2c) until the substrate was completely consumed. The reaction electrodes were ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (200 mL) was added to the residue, washed with saturated sodium bicarbonate (300 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford **4p** (1.56 g, 56%) or **4aj** (1.67 g, 61%).

D: Cyclic Voltammograms Studies

D1: Cyclic voltammetry experiments for some substrates

The cyclic voltammograms were recorded in an electrolyte of nBu_4NClO_4 (0.075 M) in CH_3CN (4 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary and the Ag/AgCl reference electrode. The scan rate is 100 mV/s. Each measurement was preceded by 3 minutes of N_2 pumped through a long needle.

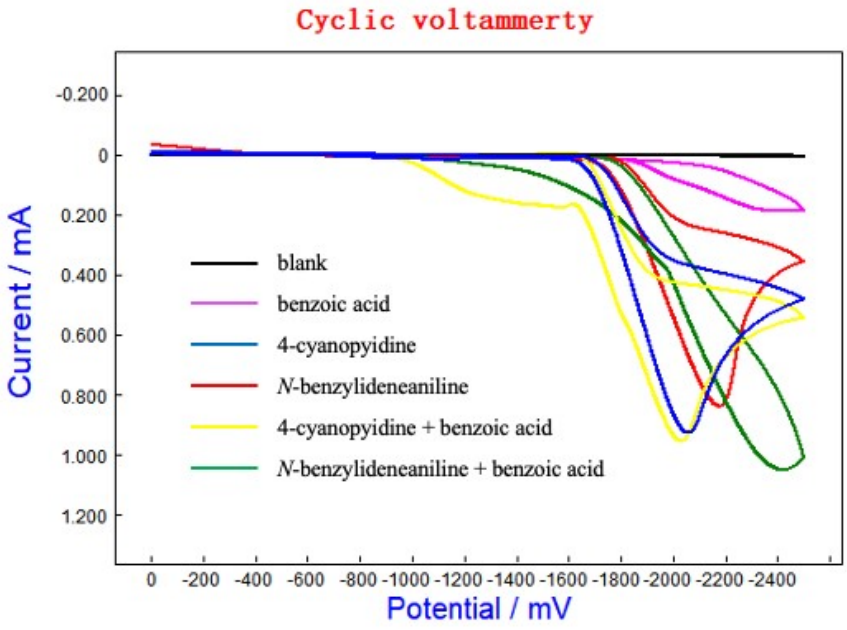


Figure S3. Black line: cyclic voltammogram of none in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Purple line: cyclic voltammogram of benzoic acid (0.025M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of 4-cyanopyridine (0.025 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN, $E_{p/2}$= -1.85 V; Red line: cyclic voltammogram of *N*-benzylideneaniline (0.025 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN, $E_{p/2}$= -1.95 V; Yellow line: cyclic voltammogram of 4-cyanopyridine and benzoic acid (0.025 M, respectively) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Green line: cyclic voltammogram of *N*-benzylideneaniline and benzoic acid (0.025 M, respectively, electrolysis after stirring for 5 min) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN.

In Figure S3, cyclic voltammetry experiments showed that the reduction potential of 4-cyanopyridine was lower than that of pre-separated imine *N*-Benzylideneaniline. With the participation of benzoic acid, imine started reducing behavior at around -1.30 V, and 4-cyanopyridine also had obvious reduction behavior from -1.10 V, while benzoic acid itself had no reduction characteristic peak. In Figure S4, cyclic voltammetry experiments showed that compared with 4-cyanopyridine, the initial reduction potential was greatly reduced after adding an equivalent amount of benzoic acid, and the more benzoic acid was added, the stronger the current signal.

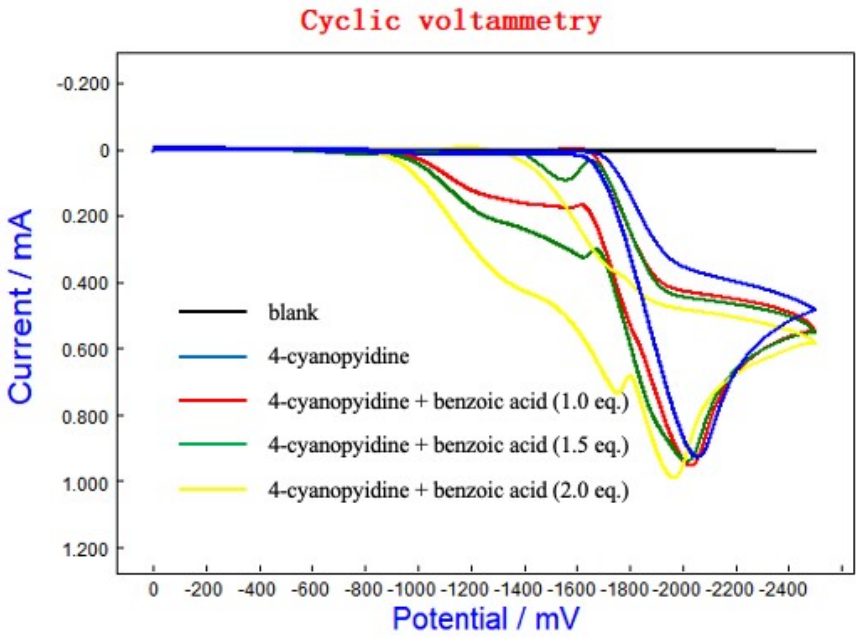
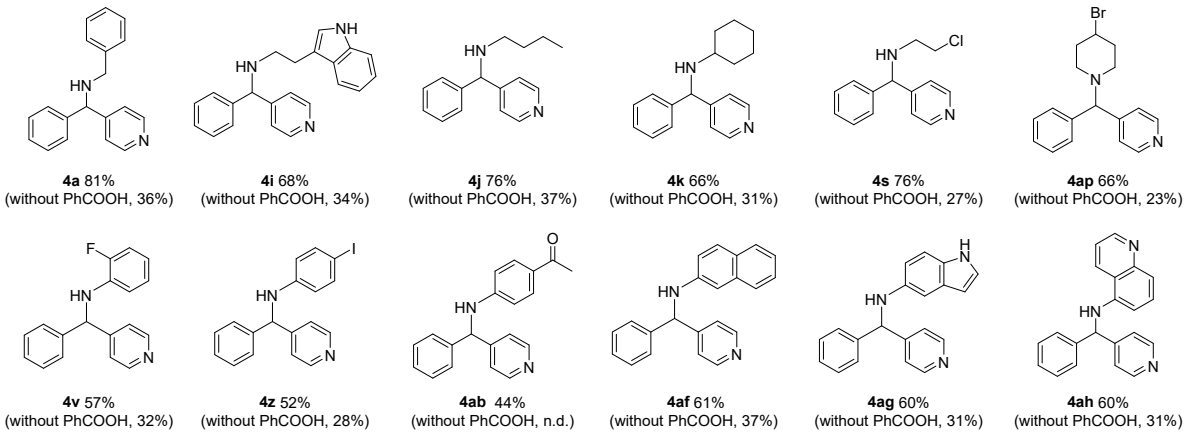


Figure S4. Black line: cyclic voltammogram of none in an electrolyte of nBu$_4$NClO$_4$ (0.075 M) in CH$_3$CN (4 mL); Blue line: cyclic voltammogram of 4-cyanopyridine (0.025 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Red line: cyclic voltammogram of 4-cyanopyridine (0.025 M) and benzoic acid (0.025 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Green line: cyclic voltammogram of 4-cyanopyridine (0.025 M) and benzoic acid (0.0375 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN; Yellow line: cyclic voltammogram of 4-cyanopyridine (0.025 M) and benzoic acid (0.05 M) in an electrolyte of nBu$_4$NClO$_4$ in CH$_3$CN.

D2: Comparison with and without benzoic acid involved in the reaction

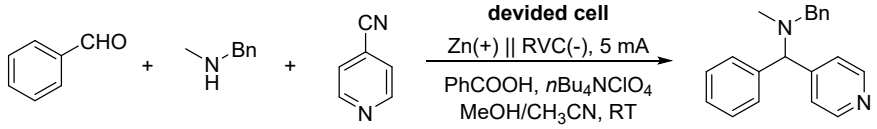
In general, benzoic acid has a promotion effect on this electrochemical reaction process. Scheme S1 exemplifies some products and compares the reaction results with or without the participation of benzoic acid.



Scheme S1. Reaction results of some products with or without benzoic acid.

E: Mechanistic Experiments

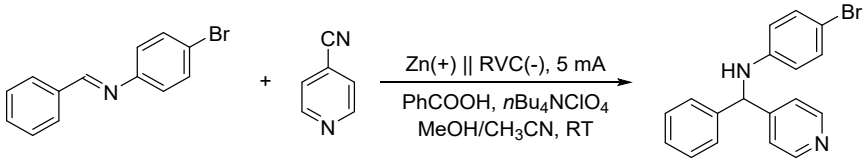
E1: Divided cell experiment



1a **2aj** **3a** **4aj**, 74%

This control experiment was carried out in an H-type divided cell. The two compartments were separated by a DuPont Nafion PFSA membrane N-117. The anodic and cathodic chambers were charged with 0.9 mmol benzaldehyde **1a**, 0.9 mmol *N*-methylbenzylamine, 0.3 mmol 4-cyanopyridine **3a**, 0.3 mmol nBu$_4$NClO$_4$, 0.45 mmol benzoic acid, 2 mL CH_3CN and 2 mL MeOH respectively, and the suspension was stirred until the solids resolve. Then the assembled electrodes were placed into the solution. The mixture was electrolyzed at a constant current of 5 mA for 3 h. The cathodic RVC electrode was ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with saturated sodium bicarbonate (30 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford **4aj** (64 mg,74% yield).

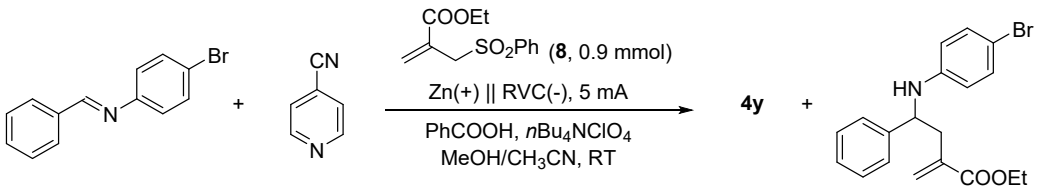
E2: The determination of the imine intermediate



7, 0.9 mmol **3a**, 0.3 mmol **4y**, 66%

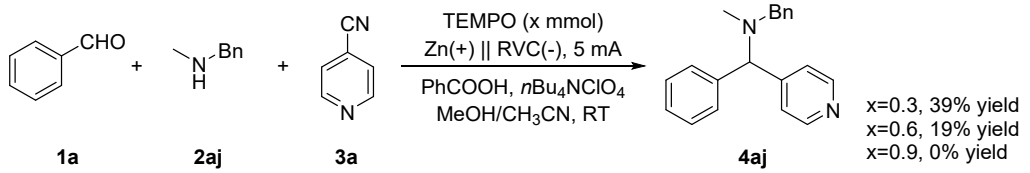
The test cube was charged with 0.9 mmol pre-separated imine **7**, 0.3 mmol 4-cyanopyridine **3a**, 0.3 mmol nBu$_4$NClO$_4$, 0.45 mmol benzoic acid, 2 mL CH_3CN and 2 mL MeOH, and the suspension was stirred until the solids resolve. Then the assembled electrodes were placed into the solution. The mixture was electrolyzed at a constant current of 5 mA for 3 h. The cathodic RVC electrode was ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with saturated sodium bicarbonate (30 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford **4y** (67 mg, 66% yield).

E3: The radical trapping experiment



The test cube was charged with 0.9 mmol pre-separated imine **7**, 0.9 mmol **8**, 0.3 mmol 4-cyanopyridine **3a**, 0.3 mmol nBu$_4$NClO$_4$, 0.45 mmol benzoic acid, 2 mL CH_3CN and 2 mL MeOH, and the suspension was stirred until the solids resolve. Then the assembled electrodes were placed into the solution. The mixture was electrolyzed at a constant current of 5 mA for 3 h. The RVC electrode was ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with saturated sodium bicarbonate (30 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford **9** (38 mg, 34% yield), and the coupled product **4y** (14 mg, 14% yield) was greatly reduced.

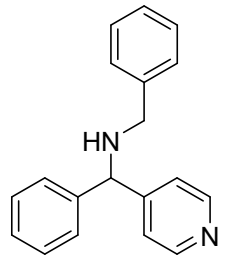
E4: The radical quenching experiment



The test cube was charged with 0.9 mmol benzaldehyde **1a**, 0.9 mmol *N*-methylbenzylamine, 0.3 mmol (or 0.6 mmol, or 0.9 mmol) 2,2,6,6-tetramethylpiperidinooxy (TEMPO) respectively, 0.3 mmol 4-cyanopyridine **3a**, 0.3 mmol nBu$_4$NClO$_4$, 0.45 mmol benzoic acid, 2 mL CH_3CN and 2 mL MeOH, and the suspension was stirred until the solids resolve. Then the assembled electrodes were placed into the solution. The mixture was electrolyzed at a constant current of 5 mA for 3 h. The RVC electrode was ultrasonic washed with ethyl acetate twice and the reaction mixture was concentrated under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with saturated sodium bicarbonate (30 mL) to remove benzoic acid, then washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford **4aj**. The yields of coupling products obtained from the reactions involving 1 equivalent TEMPO, 2 equivalents TEMPO, and 3 equivalents TEMPO were 39%, 19%, and 0%, respectively.

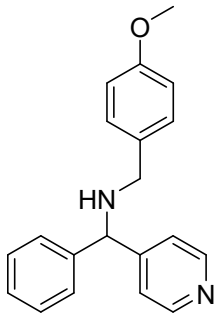
F: Characterization Data for the Electrolysis Products

4a: *N*-benzyl-1-phenyl-1-(pyridin-4-yl)methanamine



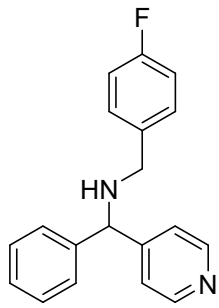
The product was obtained in 81% yield (66.4 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.01 (s, 1H), 3.71 (s, 2H), 4.80 (s, 1H), 7.21 – 7.27 (m, 2H), 7.28 – 7.33 (m, 6H), 7.34 – 7.38 (m, 4H), 8.48–8.52 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 51.8, 65.6, 122.5, 127.2, 127.4, 127.8, 128.2, 128.6, 128.9, 140.0, 142.5, 150.0, 152.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{18}N_2$) requires m/z 274.1470, found m/z 274.1471.

4b: *N*-(4-methoxybenzyl)-1-phenyl-1-(pyridin-4-yl)methanamine



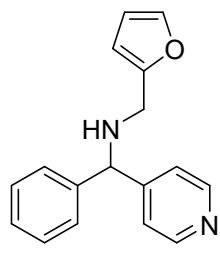
The product was obtained in 79% yield (71.7 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.87 (s, 1H), 3.67 (s, 2H), 3.81 (s, 3H), 4.80 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.28 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.41 (m, 4H), 8.46 – 8.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 51.2, 55.3, 65.4, 113.9, 122.5, 127.4, 127.7, 128.8, 129.4, 131.9, 142.4, 150.0, 152.8, 158.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2O$) requires m/z 304.1576, found m/z 304.1578.

4c: *N*-(4-fluorobenzyl)-1-phenyl-1-(pyridin-4-yl)methanamine



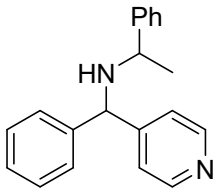
The product was obtained in 75% yield (65.8 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.88 (s, 1H), 3.61 (s, 2H), 4.71 (s, 1H), 6.93 (t, *J* = 8.6 Hz, 2H), 7.13 – 7.33 (m, 9H), 8.44 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 51.0, 65.6, 115.3 (d, *J* = 21.2 Hz), 122.4, 127.4, 127.8, 128.9, 129.7 (d, *J* = 8.0 Hz), 135.6 (d, *J* = 3.3 Hz), 142.3, 150.0, 152.6, 162.0 (d, *J* = 245.0 Hz). ^{19}F NMR (377MHz, $CDCl_3$): δ (ppm) -115.6 – -115.5 (m). HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{17}FN_2$) requires m/z 292.1376, found m/z 292.1375.

4d: *N*-(furan-2-ylmethyl)-1-phenyl-1-(pyridin-4-yl)methanamine



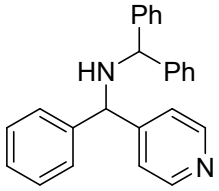
The product was obtained in 67% yield (53.2 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 1H), 3.67 – 3.74 (m, 2H), 4.78 (s, 1H), 6.11 (d, *J* = 3.1 Hz, 1H), 6.28 – 6.33 (m, 1H), 7.21 – 7.24 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.37 (m, 5H), 8.50 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 44.0, 65.0, 107.4, 110.2, 122.5, 127.5, 127.8, 128.8, 142.0, 142.1, 150.0, 152.5, 153.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{16}N_2O$) requires m/z 264.1263, found m/z 264.1262.

4e: 1-phenyl-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



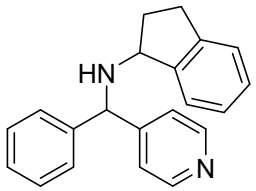
The product was obtained in 54% yield (46.5 mg) with an eluent of PE/EA = 3/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.30 (d, *J* = 6.7 Hz, 3H), 2.04 (s, 1H), 3.55 (q, *J* = 6.7 Hz, 1H), 4.51 (s, 1H), 7.10 – 7.18 (m, 8H), 7.19 – 7.23 (m, 2H), 7.24 – 7.28 (m, 2H), 8.44 (dd, *J* = 4.5, 1.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.3, 55.6, 61.2, 122.8, 126.6, 127.2, 127.4, 127.6, 128.6, 128.7, 142.9, 144.9, 149.9, 152.7. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2$) requires m/z 288.1626, found m/z 288.1629.

4f: *N*-benzhydryl-1-phenyl-1-(pyridin-4-yl)methanamine



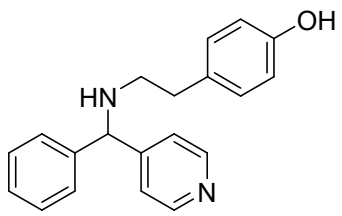
The product was obtained in 72% yield (75.6 mg) with an eluent of PE/EA = 3/1, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.23 (s, 1H), 4.68 – 4.72 (m, 2H), 7.18 – 7.24 (m, 2H), 7.25 – 7.37 (m, 15H), 8.48 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.8, 63.7, 122.7, 127.2, 127.3, 127.5, 127.5, 127.6, 127.7, 128.6, 128.7, 128.8, 142.2, 143.2, 143.4, 150.0, 152.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{25}H_{22}N_2$) requires m/z 350.1783, found m/z 350.1784.

4g: *N*-(phenyl(pyridin-4-yl)methyl)-2,3-dihydro-1*H*-inden-1-amine



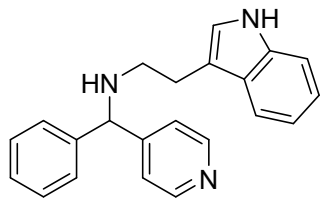
The product was obtained in 51% yield (46.3 mg) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.68 – 2.05 (m, 2H), 2.43 – 2.59 (m, 1H), 2.76 – 2.87 (m, 1H), 2.97 – 3.10 (m, 1H), 4.21 (t, *J* = 6.9 Hz, 1H), 5.14 (s, 1H), 7.26 – 7.34 (m, 4H), 7.35 – 7.43 (m, 2H), 7.46 – 7.59 (m, 5H), 8.56 – 8.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 30.3, 34.5, 61.1, 64.4, 122.6, 124.2, 124.8, 126.4, 127.4, 127.6, 127.7, 128.9, 142.4, 143.3, 145.5, 150.0, 153.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{21}H_{20}N_2$) requires m/z 300.1626, found m/z 300.1625.

4h: 4-(2-((phenyl(pyridin-4-yl)methyl)amino)ethyl)phenol



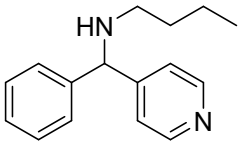
The product was obtained in 64% yield (58.4 mg) with an eluent of PE/EA = 1/2, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.70 – 2.85 (m, 4H), 4.78 (s, 1H), 4.78 (s, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.25 (m, 1H), 7.27 – 7.36 (m, 6H), 8.46 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 35.4, 49.4, 66.5, 115.6, 122.8, 127.3, 127.7, 128.8, 129.8, 130.8, 142.3, 149.1, 153.9, 155.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2O$) requires m/z 304.1576, found m/z 304.1577.

4i: 2-(1*H*-indol-3-yl)-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



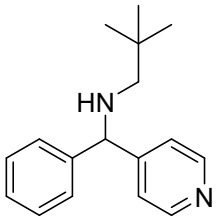
The product was obtained in 68% yield (66.8 mg) with an eluent of PE/EA = 1/2, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.14 (s, 1H), 2.85 – 2.93 (m, 2H), 2.96 – 3.02 (m, 2H), 4.76 (s, 1H), 6.95 (d, *J* = 1.7 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.22 (m, 1H), 7.24 – 7.31 (m, 7H), 7.56 (d, *J* = 7.9 Hz, 1H), 8.44 (d, *J* = 5.8 Hz, 2H), 8.52 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 25.9, 48.1, 66.6, 111.3, 113.6, 118.9, 119.2, 122.0, 122.2, 122.5, 127.3, 127.4, 127.6, 128.8, 136.5, 142.7, 149.8, 153.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{21}N_3$) requires m/z 327.1735, found m/z 327.1736.

4j: *N*-(phenyl(pyridin-4-yl)methyl)butan-1-amine



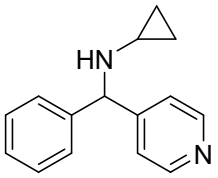
The product was obtained in 76% yield (54.8 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t, J = 7.3 Hz, 3H), 1.30 – 1.40 (m, 2H), 1.44 – 1.55 (m, 2H), 2.26 (s, 1H), 2.48 – 2.63 (m, 2H), 4.77 (s, 1H), 7.20 – 7.37 (m, 7H), 8.50 (dd, *J* = 4.6, 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 20.4, 32.3, 48.0, 66.9, 122.5, 127.3, 127.6, 128.7, 142.9, 149.8, 153.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{20}N_2$) requires m/z 240.1626, found m/z 240.1629.

4k: 2,2-dimethyl-*N*-(phenyl(pyridin-4-yl)methyl)propan-1-amine



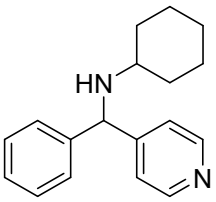
The product was obtained in 80% yield (61.2 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.93 (s, 9H), 2.25 (d, *J* = 11.2 Hz, 1H), 2.34 (d, *J* = 11.2 Hz, 1H), 4.72 (s, 1H), 7.25 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.40 (m, 4H), 8.50 (d, *J* = 3.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.8, 31.6, 60.3, 67.3, 122.5, 127.3, 127.6, 128.7, 143.2, 149.8, 153.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{22}N_2$) requires m/z 254.1783, found m/z 254.1781.

4l: *N*-(phenyl(pyridin-4-yl)methyl)cyclopropanamine



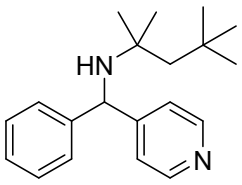
The product was obtained in 87% yield (58.7 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.35 – 0.44 (m, 4H), 2.01 – 2.11 (m, 1H), 2.36 (s, 1H), 4.87 (s, 1H), 7.21 – 7.27 (m, 1H), 7.28 – 7.34 (m, 6H), 8.50 (dd, *J* = 4.6, 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 6.6, 6.8, 29.5, 66.5, 122.7, 127.4, 127.5, 128.7, 142.7, 149.7, 153.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{15}H_{16}N_2$) requires m/z 224.1313, found m/z 224.1315.

4m: *N*-(phenyl(pyridin-4-yl)methyl)cyclohexanamine



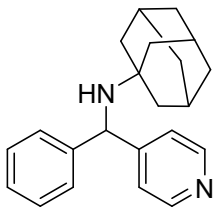
The product was obtained in 66% yield (52.9 mg) with an eluent of PE/EA = 3/1, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.02 – 1.20 (m, 5H) 1.51 – 1.60 (m, 1H), 1.65 – 1.74 (m, 2H), 1.87 – 1.98 (m, 2H), 2.31 – 2.42 (m, 1H), 4.99 (s, 1H), 7.20 – 7.26 (m, 1H), 7.26 – 7.36 (m, 6H), 8.50 (d, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.1, 26.1, 33.9, 54.2, 63.0, 122.6, 127.4, 127.5, 128.7, 143.3, 149.8, 153.7. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{22}N_2$) requires m/z 266.1783, found m/z 266.1781.

4n: 2,4,4-trimethyl-*N*-(phenyl(pyridin-4-yl)methyl)pentan-2-amine



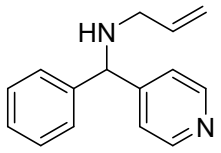
The product was obtained in 87% yield (77.5 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.01 (s, 9H), 1.04 (s, 3H), 1.09 (s, 3H), 1.47 (s, 2H), 4.98 (s, 1H), 7.16 – 7.22 (m, 1H), 7.24 – 7.33 (m, 4H), 7.41 (d, J = 5.9 Hz, 2H), 8.48 (d, J = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.4, 31.8, 32.0, 55.9, 56.1, 60.6, 122.6, 127.1, 127.3, 128.8, 145.4, 149.7, 156.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{28}N_2$) requires m/z 296.2252, found m/z 296.2253.

4o: *N*-(phenyl(pyridin-4-yl)methyl)adamantan-1-amine



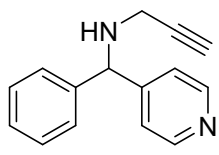
The product was obtained in 55% yield (52.3 mg) with an eluent of PE/EA = 4/1, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.51 – 1.58 (m, 6H), 1.60 – 1.68 (m, 7H), 1.98 – 2.04 (m, 3H), 5.11 (s, 1H), 7.18 – 7.24 (m, 1H), 7.27 – 7.30 (m, 4H), 7.42 (d, J = 5.7 Hz, 2H), 8.49 (d, J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.6, 36.6, 43.8, 52.1, 58.5, 122.8, 127.1, 127.5, 128.7, 145.2, 149.6, 155.9. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{26}N_2$) requires m/z 318.2096, found m/z 318.2098.

4p: *N*-(phenyl(pyridin-4-yl)methyl)prop-2-en-1-amine



The product was obtained in 66% yield (44.5 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.17 – 3.20 (m, 2H), 4.83 (s, 1H), 5.10 – 5.13 (m, 1H), 5.15 – 5.19 (m, 1H), 5.87 – 5.95 (m, 1H), 7.21 – 7.25 (m, 1H), 7.28 – 7.32 (m, 2H), 7.33 – 7.36 (m, 4H), 8.50 (d, J = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 50.3, 65.6, 116.3, 122.4, 127.4, 127.7, 128.8, 136.3, 142.5, 150.0, 152.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{15}H_{16}N_2$) requires m/z 224.1313, found m/z 224.1311.

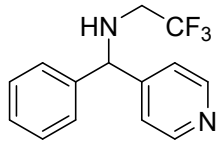
4q: *N*-(phenyl(pyridin-4-yl)methyl)prop-2-yn-1-amine



The product was obtained in 76% yield (50.7 mg) with an eluent of PE/EA = 3/2, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.22 (s, 1H), 2.28 (t, J = 2.3 Hz, 1H), 3.30 – 3.40 (m, 2H), 5.09 (s, 1H), 7.22 – 7.28 (m, 1H),

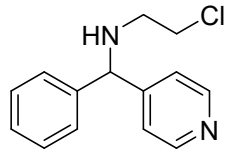
7.29 – 7.35 (m, 2H), 7.36 – 7.41 (m, 4H), 8.52 (d, J = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 36.1, 64.3, 72.1, 81.6, 122.5, 127.5, 127.9, 128.9, 141.6, 150.0, 152.0. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{15}H_{14}N_2$) requires m/z 222.1157, found m/z 222.1158.

4r: 2,2,2-trifluoro-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



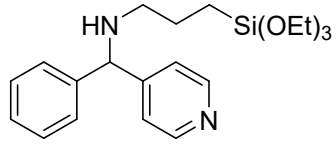
The product was obtained in 67% yield (53.5 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.89 (s, 1H), 3.01 – 3.15 (m, 2H), 4.89 (s, 1H), 7.18 – 7.23 (m, 1H), 7.24 – 7.32 (m, 6H), 8.47 (dd, *J* = 4.6, 1.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.2 (q, *J* = 31.4 Hz), 65.2, 122.2, 125.5 (q, *J* = 279.1 Hz), 127.3, 128.2, 129.0, 141.2, 150.1, 151.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -71.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{14}H_{13}F_3N_2$) requires m/z 266.1031, found m/z 266.1030.

4s: 2-chloro-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



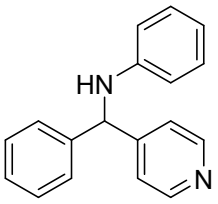
The product was obtained in 76% yield (56.0 mg) with an eluent of PE/EA = 3/2, light red oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.86 – 2.94 (m, 2H), 3.66 (t, *J* = 5.6 Hz, 2H), 4.82 (s, 1H), 7.22 – 7.26 (m, 1H), 7.29 – 7.33 (m, 2H), 7.35 – 7.39 (m, 4H), 8.51 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 44.8, 48.9, 65.8, 122.3, 127.3, 127.9, 128.9, 142.1, 150.0, 152.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{14}H_{15}ClN_2$) requires m/z 246.0924, found m/z 246.0926.

4t: *N*-(phenyl(pyridin-4-yl)methyl)-3-(triethoxysilyl)propan-1-amine



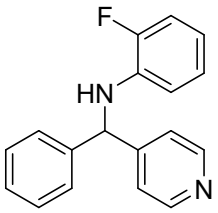
The product was obtained in 48% yield (56.1 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.62 – 0.68 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 9H), 1.60 – 1.68 (m, 2H), 1.90 (s, 1H), 2.52 – 2.62 (m, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 4.78 (s, 1H), 7.21 – 7.25 (m, 1H), 7.28 – 7.32 (m, 2H), 7.33 – 7.37 (m, 4H), 8.50 (dd, *J* = 4.6, 1.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 8.0, 18.3, 23.4, 50.8, 58.4, 66.6, 122.4, 127.3, 127.6, 128.7, 142.3, 149.9, 153.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{21}H_{32}N_2O_3Si$) requires m/z 388.2182, found m/z 388.2183.

4u: *N*-(phenyl(pyridin-4-yl)methyl)aniline



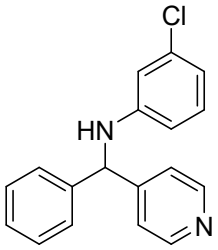
The product was obtained in 71% yield (55.6 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.29 (s, 1H), 5.44 (d, *J* = 3.2 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.25 – 7.37 (m, 7H), 8.52 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 63.4, 113.6, 118.3, 122.4, 127.7, 128.2, 129.1, 129.3, 141.6, 146.8, 150.2, 151.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{16}N_2$) requires m/z 260.1313, found m/z 260.1314.

4v: 2-fluoro-*N*-(phenyl(pyridin-4-yl)methyl)aniline



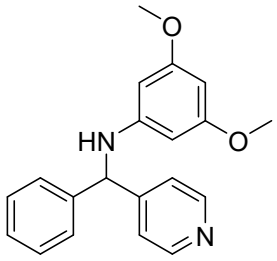
The product was obtained in 57% yield (47.7 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.50 (s, 1H), 5.47 (d, *J* = 4.2 Hz, 1H), 6.38 – 6.44 (m, 1H), 6.61 – 6.68 (m, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.96 – 7.02 (m, 1H), 7.27 – 7.39 (m, 7H), 8.55 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 62.0, 113.3 (d, *J* = 2.5 Hz), 114.6 (d, *J* = 18.1 Hz), 117.8 (d, *J* = 6.9 Hz), 122.3, 124.6 (d, *J* = 2.9 Hz), 127.6, 128.3, 129.2, 135.3 (d, *J* = 11.6 Hz), 141.1, 150.3, 151.3, 151.6 (d, *J* = 239.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -135.5 – -135.4 (m). HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}FN_2$) requires m/z 278.1219, found m/z 278.1221.

4w: 3-chloro-*N*-(phenyl(pyridin-4-yl)methyl)aniline



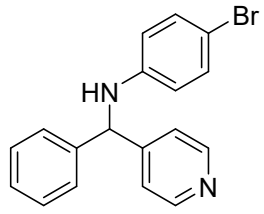
The product was obtained in 51% yield (44.8 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.39 (d, *J* = 3.9 Hz, 1H), 5.44 (d, *J* = 4.2 Hz, 1H), 6.38 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.50 (t, *J* = 1.9 Hz, 1H), 6.69 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.02 (t, *J* = 8.1 Hz, 1H), 7.23 – 7.38 (m, 7H), 8.54 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.1, 111.7, 113.4, 118.3, 122.3, 127.7, 128.3, 129.2, 130.3, 135.0, 141.0, 147.9, 150.3, 151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}ClN_2$) requires m/z 294.0924, found m/z 294.0925.

4x: 3,5-dimethoxy-*N*-(phenyl(pyridin-4-yl)methyl)aniline



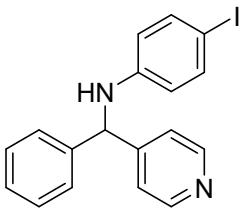
The product was obtained in 58% yield (55.9 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.68 (s, 6H), 4.25 (d, *J* = 3.6 Hz, 1H), 5.45 (d, *J* = 3.6 Hz, 1H), 5.71 (d, *J* = 2.0 Hz, 2H), 5.90 (t, *J* = 2.0 Hz, 1H), 7.27 – 7.36 (m, 7H), 8.55 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 55.1, 62.3, 90.4, 92.6, 122.3, 127.7, 128.2, 129.1, 141.4, 148.7, 150.2, 151.6, 161.6. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2O_2$) requires m/z 320.1525, found m/z 320.1526.

4y: 4-bromo-*N*-(phenyl(pyridin-4-yl)methyl)aniline



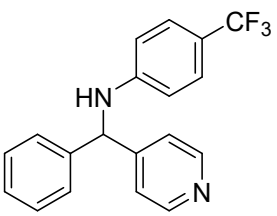
The product was obtained in 63% yield (64.0 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.36 (s, 1H), 5.40 (d, *J* = 3.4 Hz, 1H), 6.33 – 6.45 (m, 2H), 7.14 – 7.22 (m, 2H), 7.25 – 7.38 (m, 7H), 8.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.3, 110.0, 115.2, 122.3, 127.7, 128.3, 129.2, 132.0, 141.1, 145.7, 150.2, 151.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}BrN_2$) requires m/z 338.0419, found m/z 338.0418.

4z: 4-iodo-*N*-(phenyl(pyridin-4-yl)methyl)aniline



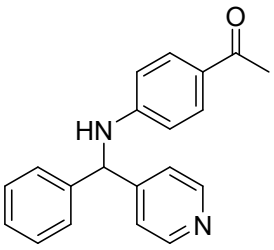
The product was obtained in 52% yield (60.1 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.35 (d, *J* = 3.7 Hz, 1H), 5.40 (d, *J* = 4.0 Hz, 1H), 6.30 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.39 (m, 9H), 8.53 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.1, 79.3, 115.8, 122.3, 127.7, 128.3, 129.2, 137.9, 141.0, 146.3, 150.3, 151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}IN_2$) requires m/z 386.0280, found m/z 386.0282.

4aa: *N*-(phenyl(pyridin-4-yl)methyl)-4-(trifluoromethyl)aniline



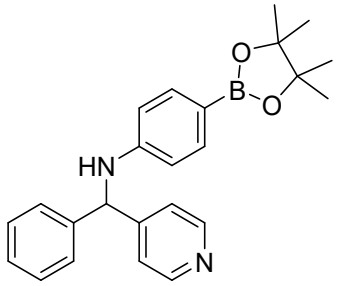
The product was obtained in 45% yield (44.1 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.64 (d, *J* = 4.2 Hz, 1H), 5.41 (d, *J* = 4.2 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 2H), 7.16 – 7.21 (m, 4H), 7.22 – 7.30 (m, 5H), 8.44 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.9, 112.8, 119.9 (q, *J* = 32.7 Hz), 122.3, 124.8 (q, *J* = 270.6 Hz), 126.6 (q, *J* = 3.7 Hz), 127.7, 128.4, 129.3, 140.7, 149.2, 150.3, 150.8. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -61.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{15}F_3N_2$) requires m/z 328.1187, found m/z 328.1185.

4ab: 1-(4-((phenyl(pyridin-4-yl)methyl)amino)phenyl)ethan-1-one



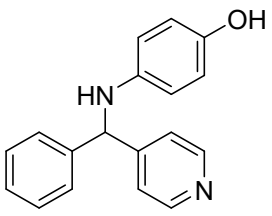
The product was obtained in 44% yield (40.1 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.46 (s, 3H), 4.94 (d, *J* = 4.6 Hz, 1H), 5.57 (d, *J* = 4.7 Hz, 1H), 6.52 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.30 (m, 4H), 7.31 – 7.38 (m, 3H), 7.77 (d, *J* = 8.7 Hz, 2H), 8.54 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 25.1, 60.6, 111.4, 121.2, 126.6, 126.7, 127.4, 128.2, 129.6, 139.4, 149.2, 149.5, 149.6, 195.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{18}N_2O$) requires m/z 302.1419, found m/z 302.1420.

4ac:
_N_-(phenyl(pyridin-4-yl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



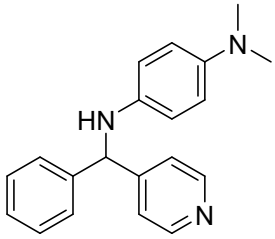
The product was obtained in 48% yield (55.9 mg) with an eluent of PE/EA = 5/2, colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.29 (s, 12H), 4.46 (d, *J* = 4.3 Hz, 1H), 5.52 (d, *J* = 4.3 Hz, 1H), 6.50 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.31 (m, 5H), 7.33 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 8.53 (dd, *J* = 4.5, 1.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 61.7, 83.3, 112.7, 122.4, 127.7, 128.2, 129.1, 136.3, 141.2, 149.2, 150.2, 151.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{24}H_{27}BN_2O_2$) requires m/z 386.2166, found m/z 386.2167.

4ad: 4-((phenyl(pyridin-4-yl)methyl)amino)phenol



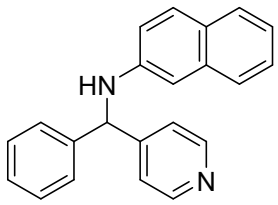
The product was obtained in 52% yield (42.7 mg) with an eluent of PE/EA = 2/1, colorless solid. ^{1}H NMR (400 MHz, d6-DMSO): δ (ppm) 5.55 (d, *J* = 7.4 Hz, 1H), 5.93 (d, *J* = 7.4 Hz, 1H), 6.46 – 6.55 (m, 4H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.39 – 7.45 (m, 4H), 8.44 – 8.52 (m, 3H). ^{13}C NMR (100 MHz, d6-DMSO): δ (ppm) 61.3, 115.3, 115.9, 122.9, 127.6, 127.9, 129.0, 140.7, 143.1, 149.3, 150.1, 153.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{16}N_2O$) requires m/z 276.1263, found m/z 276.1265.

4ae: *N*^{1},*N*^{1}-dimethyl-*N*^{4}-(phenyl(pyridin-4-yl)methyl)benzene-1,4-diamine



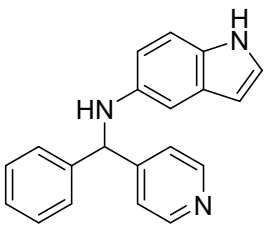
The product was obtained in 47% yield (43.0 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.79 (s, 6H), 3.91 (s, 1H), 5.36 (s, 1H), 6.49 (d, *J* = 8.9 Hz, 2H), 6.64 – 6.68 (m, 2H), 7.27 – 7.35 (m, 7H), 8.53 (dd, *J* = 4.5, 1.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 42.0, 63.3, 115.0, 115.5, 122.4, 127.7, 128.0, 129.0, 139.2, 142.1, 144.5, 150.1, 150.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{21}N_3$) requires m/z 303.1735, found m/z 303.1738.

4af: *N*-(phenyl(pyridin-4-yl)methyl)naphthalen-2-amine



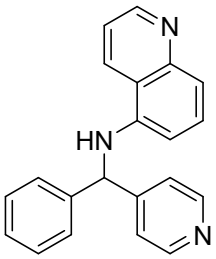
The product was obtained in 61% yield (57.0 mg) with an eluent of PE/EA = 2/1, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.43 (s, 1H), 5.60 (d, *J* = 2.7 Hz, 1H), 6.60 (d, *J* = 1.9 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.41 (m, 8H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 9.1 Hz, 2H), 8.57 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.4, 106.1, 117.9, 122.5, 122.6, 126.2, 126.5, 127.6, 127.7, 127.8, 128.3, 129.1, 129.2, 134.8, 141.4, 144.3, 150.0, 151.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{18}N_2$) requires m/z 310.1470, found m/z 310.1472.

4ag: *N*-(phenyl(pyridin-4-yl)methyl)-1*H*-indol-5-amine



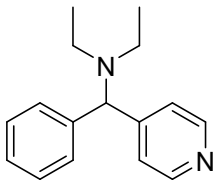
The product was obtained in 60% yield (53.7 mg) with an eluent of PE/EA = 2/1, yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.05 (s, 1H), 5.47 (s, 1H), 6.28 – 6.32 (m, 1H), 6.59 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.63 (d, *J* = 2.0 Hz, 1H), 7.09 (t, *J* = 2.8 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.31 (m, 1H), 7.32 – 7.36 (m, 4H), 7.39 (d, *J* = 5.9 Hz, 2H), 8.11 (s, 1H), 8.54 (dd, *J* = 4.6, 1.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 63.5, 101.9, 103.1, 111.7, 112.2, 122.5, 124.7, 127.8, 128.0, 128.6, 129.0, 130.3, 141.0, 142.3, 150.0, 152.6. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{17}N_3$) requires m/z 299.1422, found m/z 299.1424.

4ah: *N*-(phenyl(pyridin-4-yl)methyl)quinolin-5-amine



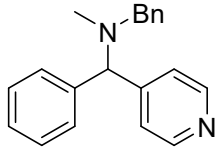
The product was obtained in 60% yield (55.9 mg) with an eluent of PE/EA = 1/1, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.91 (d, *J* = 2.7 Hz, 1H), 5.65 (d, *J* = 3.1 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.41 (m, 8H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 5.6 Hz, 2H), 8.89 (dd, *J* = 4.2, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.6, 107.2, 118.8, 119.5, 119.8, 122.4, 127.9, 128.6, 129.3, 129.4, 130.5, 141.1, 141.9, 148.7, 149.9, 150.4, 151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{21}H_{17}N_3$) requires m/z 311.1422, found m/z 311.1423.

4ai: *N*-ethyl-*N*-(phenyl(pyridin-4-yl)methyl)ethanamine



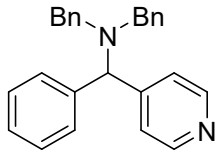
The product was obtained in 70% yield (50.2 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.98 (t, *J* = 7.1 Hz, 6H), 2.47 – 2.60 (m, 4H), 4.71 (s, 1H), 7.18 – 7.23 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.38 (m, 4H), 8.47 (dd, *J* = 4.7, 1.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.2, 42.9, 70.4, 123.2, 127.4, 128.4, 128.5, 141.2, 149.7, 152.9. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{20}N_2$) requires m/z 240.1626, found m/z 240.1627.

4aj: *N*-benzyl-*N*-methyl-1-phenyl-1-(pyridin-4-yl)methanamine



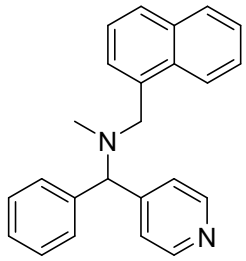
The product was obtained in 81% yield (69.8 mg) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 3.44 (d, *J* = 13.5 Hz, 1H), 3.53 (d, *J* = 13.5 Hz, 1H), 4.48 (s, 1H), 7.20 – 7.27 (m, 2H), 7.28 – 7.35 (m, 4H), 7.36 – 7.43 (m, 4H), 7.45 (d, *J* = 6.0 Hz, 2H), 8.52 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 40.1, 59.6, 74.1, 123.2, 127.1, 127.7, 128.3, 128.4, 128.6, 128.8, 139.2, 140.7, 149.8, 152.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2$) requires m/z 288.1626, found m/z 288.1623.

4ak: *N*,*N*-dibenzyl-1-phenyl-1-(pyridin-4-yl)methanamine



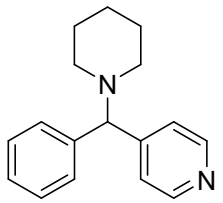
The product was obtained in 59% yield (64.4 mg) with an eluent of PE/EA = 2/1, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.39 (d, *J* = 14.1 Hz, 2H), 3.61 (d, *J* = 14.1 Hz, 2H), 4.91 (s, 1H), 7.16 – 7.23 (m, 2H), 7.24 – 7.32 (m, 8H), 7.33 – 7.39 (m, 7H), 8.50 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 53.9, 66.4, 124.2, 127.3, 127.7, 128.4, 128.5, 128.6, 129.6, 137.6, 138.9, 149.7, 150.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{26}H_{24}N_2$) requires m/z 364.1939, found m/z 364.1941.

4al: *N*-methyl-*N*-(naphthalen-1-ylmethyl)-1-phenyl-1-(pyridin-4-yl)methanamine



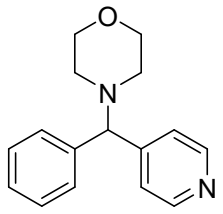
The product was obtained in 84% yield (85.0 mg) with an eluent of PE/EA = 4/1, white oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.10 (s, 3H), 3.85 (d, *J* = 13.6 Hz, 1H), 3.96 (d, *J* = 13.6 Hz, 1H), 4.65 (s, 1H), 7.22 – 7.28 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.55 (m, 7H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.88 (m, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 40.0, 58.0, 74.2, 123.3, 124.2, 125.4, 125.7, 125.8, 126.8, 127.8, 127.9, 128.6, 128.7, 128.7, 132.3, 133.9, 134.7, 140.1, 149.9, 151.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{24}H_{22}N_2$) requires m/z 338.1783, found m/z 338.1784.

4am: 4-(phenyl(piperidin-1-yl)methyl)pyridine



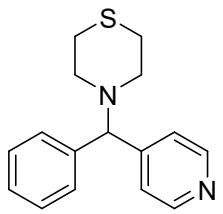
The product was obtained in 65% yield (49.2 mg) with an eluent of PE/EA = 2/1, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38 – 1.48 (m, 2H), 1.53 – 1.62 (m, 4H), 2.21 – 2.38 (m, 4H), 4.23 (s, 1H), 7.18 – 7.24 (m, 1H), 7.25 – 7.31 (m, 2H), 7.31 – 7.38 (m, 4H), 8.48 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.5, 26.2, 53.0, 75.7, 123.1, 127.4, 128.2, 128.6, 141.1, 149.8, 152.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{20}N_2$) requires m/z 252.1626, found m/z 252.1628.

4an: 4-(phenyl(pyridin-4-yl)methyl)morpholine



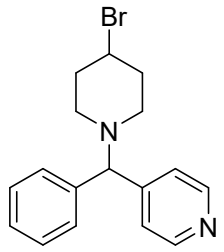
The product was obtained in 68% yield (52.1 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.33 – 2.42 (m, 4H), 3.65 – 3.78 (m, 4H), 4.20 (s, 1H), 7.19 – 7.25 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.42 (m, 4H), 8.50 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 52.5, 67.1, 75.7, 123.0, 127.8, 128.1, 128.8, 140.3, 150.0, 151.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{18}N_2O$) requires m/z 254.1419, found m/z 254.1420.

4ao: 4-(phenyl(pyridin-4-yl)methyl)thiomorpholine



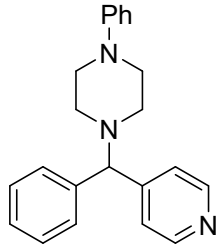
The product was obtained in 77% yield (62.1 mg) with an eluent of PE/EA = 2/1, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.62 – 2.72 (m, 8H), 4.39 (s, 1H), 7.20 – 7.26 (m, 1H), 7.28 – 7.35 (m, 6H), 8.50 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 28.1, 53.3, 75.0, 123.0, 127.7, 128.3, 128.8, 140.0, 150.0, 151.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{18}N_2S$) requires m/z 270.1191, found m/z 270.1190.

4ap: 4-((4-bromopiperidin-1-yl)(phenyl)methyl)pyridine



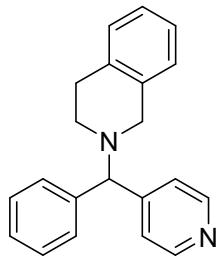
The product was obtained in 56% yield (55.2 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.00 – 2.30 (m, 6H), 2.62 – 2.74 (m, 2H), 4.11 – 4.24 (m, 1H), 4.29 (s, 1H), 7.19 – 7.39 (m, 7H), 8.49 (d, J = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 36.5, 50.0, 50.6, 75.0, 122.9, 127.7, 128.0, 128.8, 140.6, 150.0, 151.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{19}BrN_2$) requires m/z 330.0732, found m/z 330.0735.

4aq: 1-phenyl-4-(phenyl(pyridin-4-yl)methyl)piperazine



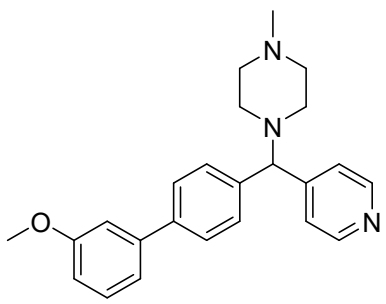
The product was obtained in 65% yield (63.9 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.41 – 2.53 (m, 4H), 3.07 – 3.18 (m, 4H), 4.20 (s, 1H), 6.77 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 2H), 7.13 – 7.20 (m, 3H), 7.23 (t, J = 7.5 Hz, 2H), 7.29 – 7.36 (m, 4H), 8.44 (d, J = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.1, 50.8, 74.2, 114.9, 118.7, 121.9, 126.7, 127.0, 127.8, 128.1, 139.6, 149.0, 150.1, 150.7. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{23}N_3$) requires m/z 329.1892, found m/z 329.1894.

4ar: 2-(phenyl(pyridin-4-yl)methyl)-1,2,3,4-tetrahydroisoquinoline



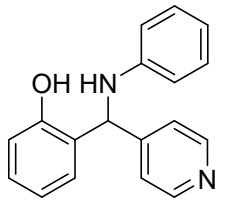
The product was obtained in 73% yield (65.7 mg) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.66 – 2.74 (m, 2H), 2.86 – 2.92 (m, 2H), 3.56 (s, 2H), 4.41 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.05 – 7.09 (m, 1H), 7.10 – 7.14 (m, 2H), 7.21 – 7.25 (m, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.40 – 7.44 (m, 4H), 8.50 (dd, J = 4.6, 1.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 29.2, 49.2, 55.0, 75.0, 122.9, 125.7, 126.3, 126.8, 127.8, 128.1, 128.7, 128.9, 134.5, 134.8, 141.0, 150.1, 152.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{21}H_{20}N_2$) requires m/z 300.1626, found m/z 300.1625.

4as: 1-((3'-methoxy-[1,1'-biphenyl]-4-yl)(pyridin-4-yl)methyl)-4-methylpiperazine



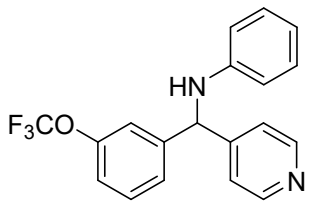
The product was obtained in 42% yield (47.4 mg) with an eluent of DCM/MeOH = 30/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 3H), 2.28 – 2.60 (m, 8H), 3.76 (s, 3H), 4.19 (s, 1H), 6.80 (dd, J = 8.2, 2.1 Hz, 1H), 6.97 – 7.00 (m, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.30 – 7.37 (m, 4H), 7.43 (d, J = 8.1 Hz, 2H), 8.44 (d, J = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 45.8, 51.6, 55.2, 55.3, 74.9, 112.7, 112.8, 119.6, 123.0, 127.5, 128.4, 129.8, 139.9, 140.5, 142.1, 150.1, 151.7, 159.9. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{24}H_{27}N_3O$) requires m/z 373.2154, found m/z 373.2151.

5a: 2-((phenylamino)(pyridin-4-yl)methyl)phenol



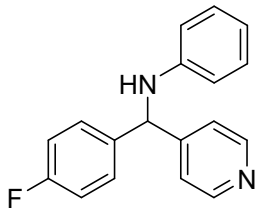
The product was obtained in 82% yield (67.8 mg) with an eluent of PE/EA = 2/1, yellow solid. ^{1}H NMR (400 MHz, d6-DMSO): δ (ppm) 5.90 (d, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 7.5 Hz, 1H), 6.53 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.73 – 6.80 (m, 1H), 6.83 – 6.89 (m, 1H), 6.99 – 7.12 (m, 3H), 7.25 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.36 (d, *J* = 5.9 Hz, 2H), 8.48 (d, *J* = 5.9 Hz, 2H), 9.79 (s, 1H). ^{13}C NMR (100 MHz, d6-DMSO): δ (ppm) 53.4, 113.5, 115.8, 116.8, 119.7, 122.9, 128.3, 128.5, 128.7, 129.2, 148.2, 150.0, 152.6, 155.0. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{16}N_2O$) requires m/z 276.1263, found m/z 276.1264.

5b: *N*-(pyridin-4-yl(3-(trifluoromethoxy)phenyl)methyl)aniline



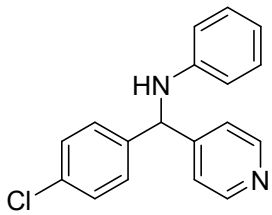
The product was obtained in 74% yield (76.5 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.33 (d, *J* = 2.5 Hz, 1H), 5.48 (d, *J* = 2.5 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 7.11 – 7.16 (m, 3H), 7.17 – 7.20 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.9, 113.7, 118.7, 119.1, 120.3 (d, *J* = 17.8 Hz), 120.4 (q, *J* = 257.5 Hz), 122.4, 125.9, 129.3, 130.5, 143.7, 146.4, 149.8, 150.3, 151.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -57.7. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{15}F_3N_2O$) requires m/z 344.1136, found m/z 344.1138.

5c: *N*-((4-fluorophenyl)(pyridin-4-yl)methyl)aniline



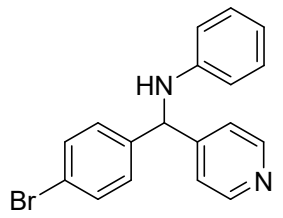
The product was obtained in 66% yield (54.9 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.17 (s, 1H), 5.45 (s, 1H), 6.52 (d, *J* = 6.7 Hz, 2H), 6.72 – 6.78 (m, 1H), 7.00 – 7.08 (m, 2H), 7.11 – 7.17 (m, 2H), 7.24 – 7.32 (m, 4H), 8.56 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 61.6, 113.6, 116.0 (d, *J* = 22.0 Hz), 118.5, 122.3, 129.3, 129.4 (d, *J* = 8.4 Hz), 137.3 (d, *J* = 2.9 Hz), 146.6, 150.3, 151.5, 162.4 (d, *J* = 248.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -113.8 – -113.7 (m). HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}FN_2$) requires m/z 278.1219, found m/z 278.1221.

5d: *N*-((4-chlorophenyl)(pyridin-4-yl)methyl)aniline



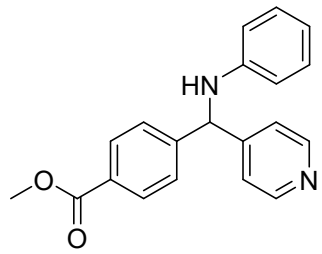
The product was obtained in 71% yield (62.8 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.15 (d, *J* = 3.5 Hz, 1H), 5.44 (d, *J* = 3.5 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.36 (m, 6H), 8.57 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 61.8, 113.7, 118.7, 122.4, 129.0, 129.3, 129.4, 134.1, 140.0, 146.6, 150.4, 151.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}ClN_2$) requires m/z 294.0924, found m/z 294.0925.

5e: *N*-((4-bromophenyl)(pyridin-4-yl)methyl)aniline



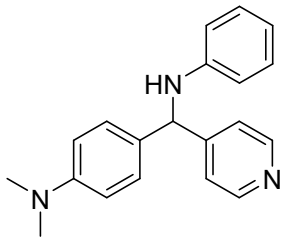
The product was obtained in 69% yield (69.7 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.22 (d, *J* = 3.5 Hz, 1H), 5.42 (d, *J* = 3.5 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 5.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 8.55 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 61.8, 113.6, 118.6, 122.1, 122.4, 129.2, 129.3, 132.2, 140.5, 146.5, 150.3, 151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}BrN_2$) requires m/z 338.0419, found m/z 338.0420.

5f: methyl 4-((phenylamino)(pyridin-4-yl)methyl)benzoate



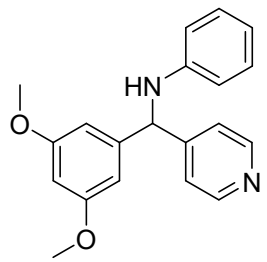
The product was obtained in 34% yield (32.8 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.91 (s, 3H), 4.24 (s, 1H), 5.52 (s, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.16 (m, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 8.57 (dd, *J* = 4.6, 1.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 52.3, 62.1, 113.7, 118.7, 122.4, 127.6, 129.3, 130.0, 130.4, 146.3, 146.5, 150.3, 151.0, 166.6. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{18}N_2O_2$) requires m/z 318.1368, found m/z 318.1369.

5g: *N*,*N*-dimethyl-4-((phenylamino)(pyridin-4-yl)methyl)aniline



The product was obtained in 78% yield (71.1 mg) with an eluent of PE/EA = 2/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.92 (s, 6H), 4.20 (s, 1H), 5.35 (s, 1H), 6.48 (d, *J* = 7.9 Hz, 2H), 6.64 – 6.73 (m, 3H), 7.09 – 7.15 (m, 4H), 7.33 (d, *J* = 4.9 Hz, 2H), 8.52 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 40.5, 61.8, 112.6, 113.5, 118.0, 122.3, 128.6, 129.2, 129.3, 147.1, 150.0, 150.3, 152.6. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{21}N_3$) requires m/z 303.1735, found m/z 303.1735.

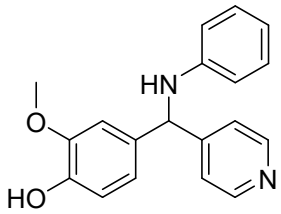
5h: *N*-((3,5-dimethoxyphenyl)(pyridin-4-yl)methyl)aniline



The product was obtained in 38% yield (36.8 mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.77 (s, 3H), 3.79 (s, 3H), 4.28 (s, 1H), 5.77 (s, 1H), 6.44 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 5.2 Hz, 2H), 8.51 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 54.4, 54.5, 54.6, 97.9, 103.5, 112.4, 116.9, 121.2, 121.3, 128.1, 128.2, 146.2, 148.8, 151.5, 156.6, 159.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{20}N_2O_2$) requires

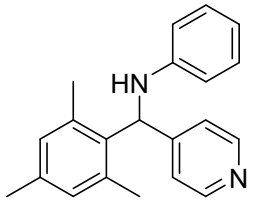
m/z 320.1525, found m/z 320.1524.

5i: 2-methoxy-4-((phenylamino)(pyridin-4-yl)methyl)phenol



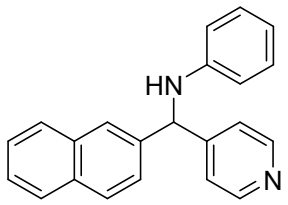
The product was obtained in 46% yield (42.3mg) with an eluent of PE/EA = 2/1, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 3H), 4.19 (s, 1H), 5.39 (s, 1H), 6.51 (d, *J* = 8.2 Hz, 2H), 6.71 – 6.79 (m, 3H), 6.88 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 5.5 Hz, 2H), 8.57 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 54.9, 61.1, 109.1, 112.5, 113.8, 117.2, 119.7, 121.3, 128.2, 132.24, 144.7, 145.8, 146.1, 148.8, 151.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{18}N_2O_2$) requires m/z 306.1368, found m/z 306.1370.

5j: *N*-(mesityl(pyridin-4-yl)methyl)aniline



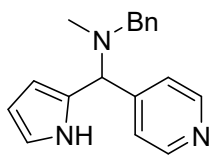
The product was obtained in 81% yield (73.2 mg) with an eluent of PE/EA = 3/1 white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.19 (s, 6H), 2.28 (s, 3H), 4.13 (d, *J* = 3.5 Hz, 1H), 5.86 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.88 (s, 2H), 7.14 – 7.21(m, 4H), 8.49 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 20.8, 21.2, 57.1, 112.9, 118.1, 122.2, 129.4, 130.4, 136.6, 137.8, 147.8, 149.6, 149.7, 152.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{21}H_{22}N_2$) requires m/z 302.1783, found m/z 302.1784.

5k: *N*-(naphthalen-2-yl(pyridin-4-yl)methyl)aniline



The product was obtained in 67% yield (62.0 mg) with an eluent of PE/EA = 2/1, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.34 (d, *J* = 3.1 Hz, 1H), 5.64 (d, *J* = 3.3 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 7.12 – 7.20 (m, 2H), 7.36 – 7.45 (m, 3H), 7.47 – 7.54 (m, 2H), 7.75 – 7.90 (m, 4H), 8.58 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 62.5, 113.6, 118.4, 122.6, 125.4, 126.5, 126.6, 126.7, 127.8, 128.1, 129.1, 129.3, 133.0, 133.4, 138.8, 146.8, 150.2, 151.7. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{18}N_2$) requires m/z 310.1470, found m/z 310.1471.

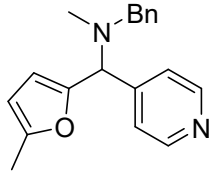
5l: *N*-benzyl-*N*-methyl-1-(pyridin-4-yl)-1-(1*H*-pyrrol-2-yl)methanamine



The product was obtained in 65% yield (53.8 mg) with an eluent of PE/EA = 3/1, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.11 (s, 3H), 3.44 (d, *J* = 13.4 Hz, 1H), 3.52 (d, *J* = 13.4 Hz, 1H), 4.75 (s, 1H), 6.00 – 6.03 (m, 1H), 6.15 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.77 – 6.81 (m, 1H), 7.24 – 7.29 (m, 1H), 7.31 – 7.37 (m, 4H), 7.39 (dd, *J* = 4.6, 1.4 Hz, 2H), 8.57 (dd, *J* = 4.5, 1.4 Hz, 2H), 8.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 39.2, 59.0, 66.0, 108.3, 108.5, 118.0, 123.8, 127.3, 128.6, 128.7, 129.8, 139.0, 148.7, 149.9. HRMS (EI): exact mass calculated for $[M]^+$

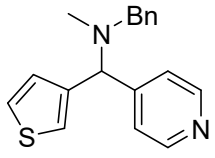
($C_{18}H_{19}N_3$) requires m/z 277.1579, found m/z 277.1580.

5m: *N*-benzyl-*N*-methyl-1-(5-methylfuran-2-yl)-1-(pyridin-4-yl)methanamine



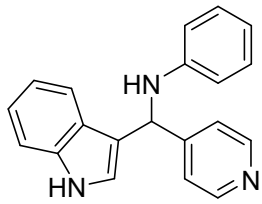
The product was obtained in 58% yield (51.1 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.14 (s, 3H), 2.29 (s, 3H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.56 (d, *J* = 13.4 Hz, 1H), 4.69 (s, 1H), 5.95 (d, *J* = 2.1 Hz, 1H), 6.14 (d, *J* = 3.0 Hz, 1H), 7.23 – 7.27 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 5.6 Hz, 2H), 8.55 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 13.8, 39.3, 59.0, 64.9, 106.1, 110.7, 123.4, 127.1, 128.3, 128.7, 139.2, 149.7, 149.7, 150.1, 152.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{20}N_2O$) requires m/z 292.1576, found m/z 292.1576.

5n: *N*-benzyl-*N*-methyl-1-(pyridin-4-yl)-1-(thiophen-3-yl)methanamine



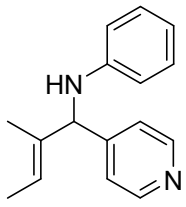
The product was obtained in 65% yield (57.6 mg) with an eluent of PE/EA = 3/1, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 3.43 (d, *J* = 13.5 Hz, 1H), 3.51 (d, *J* = 13.5 Hz, 1H), 4.70 (s, 1H), 7.05 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.15 – 7.17 (m, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.26 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.41 (m, 4H), 8.53 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 39.5, 59.2, 68.2, 123.3, 126.1, 127.1, 127.5, 128.4, 128.6, 139.2, 140.8, 149.9, 151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{18}N_2S$) requires m/z 294.1191, found m/z 294.1192.

5o: *N*-((1*H*-indol-3-yl)(pyridin-4-yl)methyl)aniline



The product was obtained in 38% yield (34.0 mg) with an eluent of PE/EA = 1/1, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.40 (s, 1H), 5.81 (s, 1H), 6.53 – 6.58 (m, 2H), 6.73 – 6.79 (m, 2H), 7.11 – 7.20 (m, 3H), 7.22 – 7.28 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 5.9 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 8.58 (dd, *J* = 4.5, 1.5 Hz, 2H), 8.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.1, 111.6, 113.3, 117.4, 118.0, 119.1, 120.1, 122.5, 122.8, 123.4, 125.7, 129.3, 136.7, 147.2, 149.8, 152.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{17}N_3$) requires m/z 299.1422, found m/z 299.1425.

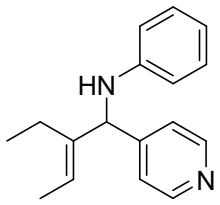
5p: *N*-(2-methyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



The product was obtained in 31% yield (22.3 mg, *E*:*Z* = 4.5:1) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.56 (dt, J = 22.3 Hz, 6.9 Hz, 3H), 1.65 (d, *J* = 6.7 Hz, 2.45H), 1.82 (dd, *J* = 6.9, 1.1 Hz, 0.55H), 4.00 (s, 1H), 4.79 (s, 0.82H), 5.39 (s, 0.18H), 5.54 – 5.65 (m, 1H), 6.52 (dd, *J* = 24.7, 8.0 Hz, 2H), 6.73 (dt, *J* = 14.7, 7.3 Hz, 1H), 7.14 (dt, *J* = 15.6, 7.8 Hz, 2H), 7.31 (dd, *J* = 10.5, 5.8 Hz, 2H), 8.55 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 13.2, 13.4, 65.1, 113.5, 118.1, 122.2, 124.2, 129.3, 134.6, 147.1, 149.9,

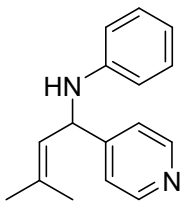
151.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{18}N_2$) requires m/z 238.1470, found m/z 238.1473.

5q: *N*-(2-ethyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



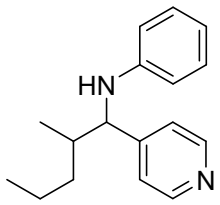
The product was obtained in 43% yield (32.7 mg, *E*:*Z* = 3:1) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.95 (dt, *J* = 24.3, 7.4 Hz, 3H), 1.64 (d, *J* = 6.8 Hz, 2.25H), 1.80 (d, *J* = 6.9 Hz, 0.75H), 1.91 – 2.02 (m, 0.5H), 2.07 – 2.17 (m, 1.5H), 3.98 (s, 1H), 4.82 (s, 0.75H), 5.36 – 5.42 (m, 1H), 5.57 (q, *J* = 6.9 Hz, 0.25H), 6.51 (dd, *J* = 24.9, 7.8 Hz, 2H), 6.72 (dt, *J* = 20.4, 7.3 Hz, 1H), 7.09 – 7.18 (m, 2H), 7.30 (dd, *J* = 11.6, 5.5 Hz, 2H), 8.54 (d, *J* = 3.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 12.9, 13.6, 23.4, 59.8, 113.3, 118.0, 122.1, 123.8, 129.2, 140.9, 147.2, 149.9, 151.4. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{20}N_2$) requires m/z 252.1626, found m/z 252.1628.

5r: *N*-(3-methyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



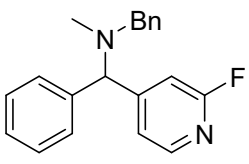
The product was obtained in 40% yield (28.8 mg) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.76 (d, *J* = 1.0 Hz, 3H), 1.83 (d, *J* = 1.0 Hz, 3H), 3.99 (s, 1H), 5.05 (d, *J* = 8.7 Hz, 1H), 5.20 – 5.26 (m, 1H), 6.49 (d, *J* = 7.7 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 7.09 – 7.14 (m, 2H), 7.30 (d, *J* = 5.9 Hz, 2H), 8.52 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 18.8, 25.7, 56.0, 113.4, 117.9, 121.7, 125.7, 129.2, 136.3, 146.9, 150.0, 153.2. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{16}H_{18}N_2$) requires m/z 238.1470, found m/z 238.1472.

5s: *N*-(2-methyl-1-(pyridin-4-yl)pentyl)aniline



The product was obtained in 27% yield (20.7 mg) with an eluent of PE/EA = 4/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84 – 0.95 (m, 6H), 1.09 – 1.26 (m, 2H), 1.37 – 1.51 (m, 2H), 1.85 – 2.00 (m, 1H), 4.05 (s, 1H), 4.20 – 4.32 (m, 1H), 6.44 (d, *J* = 8.1 Hz, 2H), 6.66 (td, *J* = 7.3, 2.8 Hz, 1H), 7.08 (td, *J* = 8.1, 3.1 Hz, 2H), 7.24 (d, *J* = 5.6 Hz, 2H), 8.52 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.3, 15.6, 20.6, 35.5, 39.3, 61.6, 113.3, 117.8, 122.7, 129.4, 147.2, 149.8, 152.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{22}N_2$) requires m/z 254.1783, found m/z 254.1786.

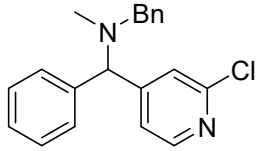
6a: *N*-benzyl-1-(2-fluoropyridin-4-yl)-*N*-methyl-1-phenylmethanamine



The product was obtained in 18% yield (16.3 mg) with an eluent of PE/EA = 30/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.09 (s, 3H), 3.44 (d, *J* = 13.5 Hz, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 4.53 (s, 1H), 7.12 (s, 1H), 7.27 – 7.43 (m, 11H), 8.13 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 40.1, 59.7, 73.8 (d, *J* = 2.4 Hz), 108.6 (d, *J* = 37.6 Hz),

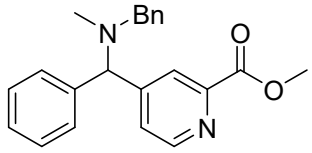
120.9 (d, J = 3.8 Hz), 127.3, 128.0, 128.5, 128.6, 128.7, 129.0, 139.1, 139.9, 147.8 (d, J = 14.8 Hz), 158.5 (d, J = 7.3 Hz), 164.4 (d, J = 238.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -68.1. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{19}FN_2$) requires m/z 306.1532, found m/z 306.1533.

6b: *N*-benzyl-1-(2-chloropyridin-4-yl)-*N*-methyl-1-phenylmethanamine



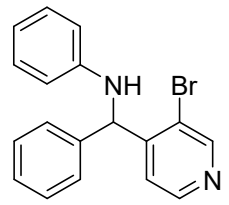
The product was obtained in 29% yield (28.3 mg) with an eluent of PE/EA = 30/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 3.41 (d, J = 13.5 Hz, 1H), 3.54 (d, J = 13.5 Hz, 1H), 4.48 (s, 1H), 7.23 – 7.29 (m, 2H), 7.30 – 7.41 (m, 9H), 7.48 (s, 1H), 8.29 (d, J = 5.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 40.0, 59.6, 73.7, 121.8, 123.4, 127.2, 128.0, 128.3, 128.4, 128.6, 128.9, 138.9, 139.8, 149.8, 151.9, 155.8. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{20}H_{19}ClN_2$) requires m/z 322.1237, found m/z 322.1239.

6c: methyl 4-((benzyl(methyl)amino)(phenyl)methyl)picolinate



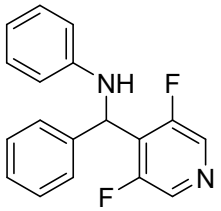
The product was obtained in 40% yield (41.7 mg) with an eluent of PE/EA = 3/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.08 (s, 3H), 3.42 (d, J = 13.4 Hz, 1H), 3.54 (d, J = 13.4 Hz, 1H), 4.01 (s, 3H), 4.53 (s, 1H), 7.22 – 7.28 (m, 1H), 7.30 – 7.40 (m, 7H), 7.41 – 7.46 (m, 2H), 7.56 (d, J = 5.0 Hz, 1H), 7.97 (s, 1H), 8.56 (d, J = 5.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 40.1, 53.9, 59.6, 74.3, 120.5, 124.6, 127.1, 127.8, 128.3, 1284, 128.6, 128.8, 139.0, 140.5, 147.9, 149.4, 153.9, 166.9. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{22}H_{22}N_2O_2$) requires m/z 346.1681, found m/z 346.1684.

6d: *N*-((3-bromopyridin-4-yl)(phenyl)methyl)aniline



The product was obtained in 32% yield (32.7 mg) with an eluent of PE/EA = 12/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.24 (s, 1H), 5.75 (d, J = 2.4 Hz, 1H), 6.46 (d, J = 8.0 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 7.6 Hz, 2H), 7.28 – 7.40 (m, 5H), 7.59 (d, J = 4.9 Hz, 1H), 8.49 (d, J = 4.9 Hz, 1H), 8.69 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 61.6, 113.4, 118.5, 122.1, 123.4, 128.3, 128.4, 129.0, 129.4, 139.4, 146.3, 148.8, 150.0, 152.5. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{15}BrN_2$) requires m/z 338.0419, found m/z 338.0421.

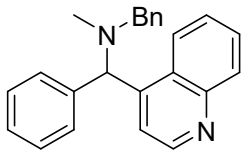
6e: *N*-((3,5-difluoropyridin-4-yl)(phenyl)methyl)aniline



The product was obtained in 34% yield (30.5 mg) with an eluent of PE/EA = 30/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.60 (s, 1H), 6.18 (s, 1H), 6.69 (d, J = 8.3 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.7 Hz, 2H), 7.27 – 7.43 (m, 5H), 8.32 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 52.1, 113.4, 118.9, 126.6, 127.7 (t, J = 14.4 Hz), 128.2,

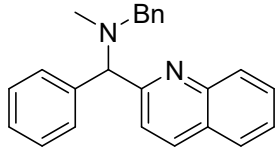
129.0, 129.5, 134.8 (dd, J = 24.4, 4.4 Hz), 139.0, 146.1, 157.3 (dd, J = 259.6, 2.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -129.3. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{18}H_{14}F_2N_2$) requires m/z 296.1125, found m/z 296.1124.

6f: *N*-benzyl-*N*-methyl-1-phenyl-1-(pyridin-4-yl)methanamine



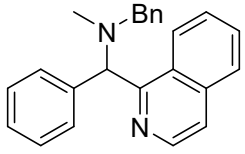
The product was obtained in 50% yield (50.5 mg) with an eluent of PE/EA = 30/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.08 (s, 3H), 3.33 (d, J = 13.5 Hz, 1H), 3.68 (d, J = 13.5 Hz, 1H), 4.79 (s, 1H), 7.14 – 7.23 (m, 3H), 7.24 – 7.33 (m, 6H), 7.60 (dd, J = 16.8, 7.7 Hz, 3H), 7.74 (t, J = 7.7 Hz, 1H), 8.06 (dd, J = 16.8, 8.2 Hz, 2H), 8.15 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 39.6, 58.7, 76.8, 114.9, 118.4, 123.4, 123.7, 123.8, 126.1, 126.9, 127.1, 127.4, 127.6, 128.0, 129.0, 130.0, 137.8, 139.4, 146.3, 162.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}N_2$) requires m/z 339.1861, found m/z 339.1862.

6g: *N*-benzyl-*N*-methyl-1-phenyl-1-(quinolin-2-yl)methanamine



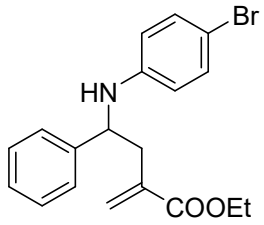
The product was obtained in 30% yield (30.8 mg) with an eluent of PE/EA = 30/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.14 (s, 3H), 3.47 (d, J = 13.6 Hz, 1H), 3.68 (d, J = 13.6 Hz, 1H), 4.84 (s, 1H), 7.16 – 7.26 (m, 2H), 7.27 – 7.35 (m, 4H), 7.41 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.63 – 7.76 (m, 4H), 7.89 (d, J = 8.6 Hz, 1H), 8.08 (dd, J = 8.6, 4.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 40.6, 59.8, 78.5, 119.9, 126.2, 126.9, 127.4, 127.5, 128.2, 128.2, 128.3, 128.7, 128.7, 129.2, 129.4, 136.8, 139.5, 141.6, 147.5, 163.2. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}N_2$) requires m/z 339.1861, found m/z 339.1862.

6h: *N*-benzyl-1-(isoquinolin-1-yl)-*N*-methyl-1-phenylmethanamine



The product was obtained in 71% yield (72.3 mg) with an eluent of PE/EA = 10/1, colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 3H), 3.55 (d, J = 13.4 Hz, 1H), 3.84 (d, J = 13.4 Hz, 1H), 5.47 (s, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.21 – 7.32 (m, 5H), 7.35 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 5.6 Hz, 1H), 7.54 – 7.62 (m, 2H), 7.68 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 5.6 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 40.6, 60.0, 74.8, 120.2, 125.7, 126.9, 127.0, 127.2, 127.5, 128.2, 128.3, 129.0, 129.1, 129.8, 136.8, 139.1, 140.8, 142.0, 160.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}N_2$) requires m/z 339.1861, found m/z 339.1864.

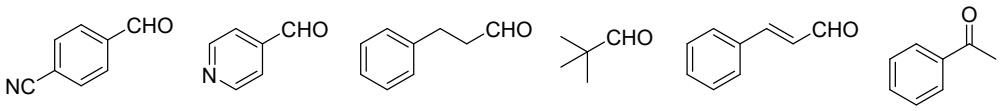
9: ethyl 4-((4-bromophenyl)amino)-2-methylene-4-phenylbutanoate



The product was obtained in 71% yield (38.5 mg) with an eluent of PE/EA = 25/1, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.24 (t, *J* = 7.2 Hz, 3H), 2.60 – 2.75 (m, 2H), 4.15 (q, *J* = 6.8 Hz, 2H), 4.34 – 4.42 (m, 1H), 4.57 (s, 1H), 5.47 (s, 1H), 6.15 (s, 1H), 6.28 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.12 – 7.20 (m, 1H), 7.22 – 7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 41.2, 58.3, 61.2, 108.8, 114.9, 126.3, 127.3, 128.1, 128.7, 131.7, 137.3, 142.8, 146.2, 167.6. HRMS (EI): exact mass calculated for $[M]^+$ ($C_{19}H_{20}BrNO_2$) requires m/z 373.0677, found m/z 373.0678.

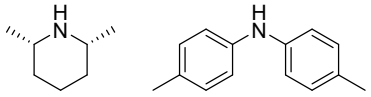
G: Unsuccessful Substrates

unsuccessful aldehyde or ketone



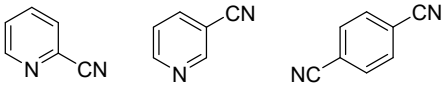
S1 **S2** **S3** **S4** **S5** **S6**

unsuccessful amine



S7 **S8**

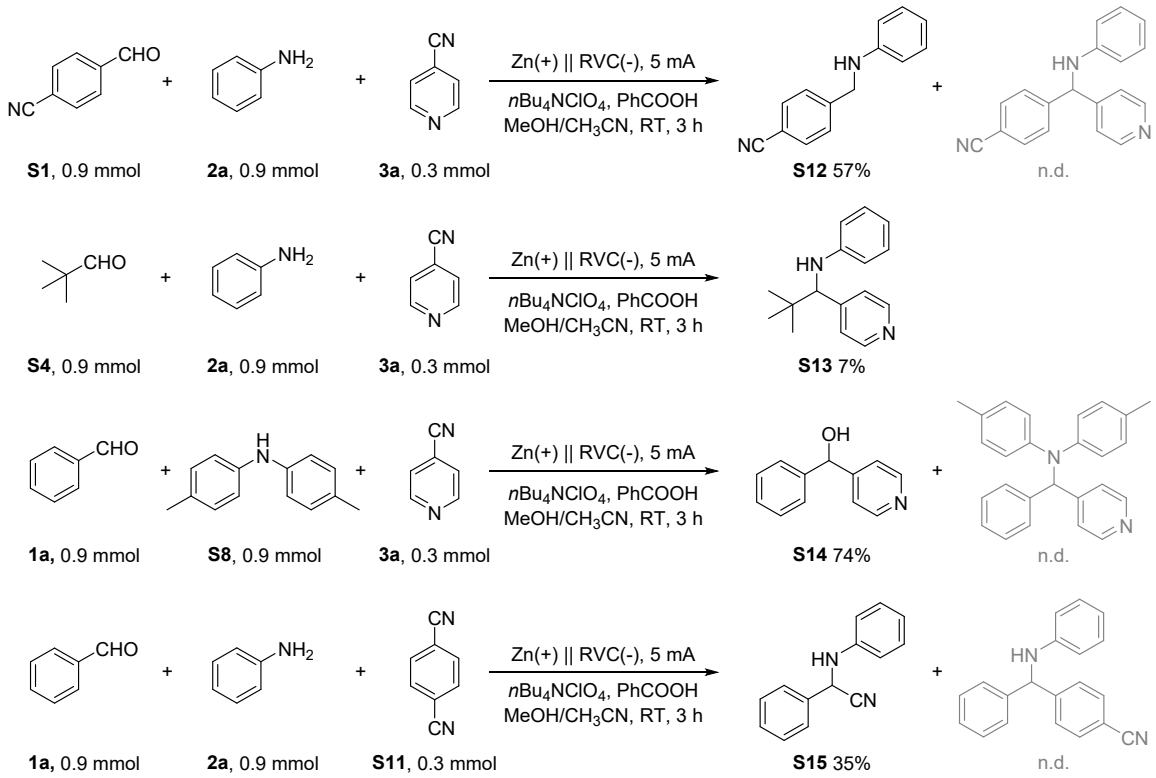
unsuccessful aromatic nitrile



S9 **S10** **S11**

The unsuccessful substrates were listed above, a series of screening were conducted to explore the viable reaction conditions and provided some side products (Scheme S2). But some meaningful insights were extracted from the side reactions.

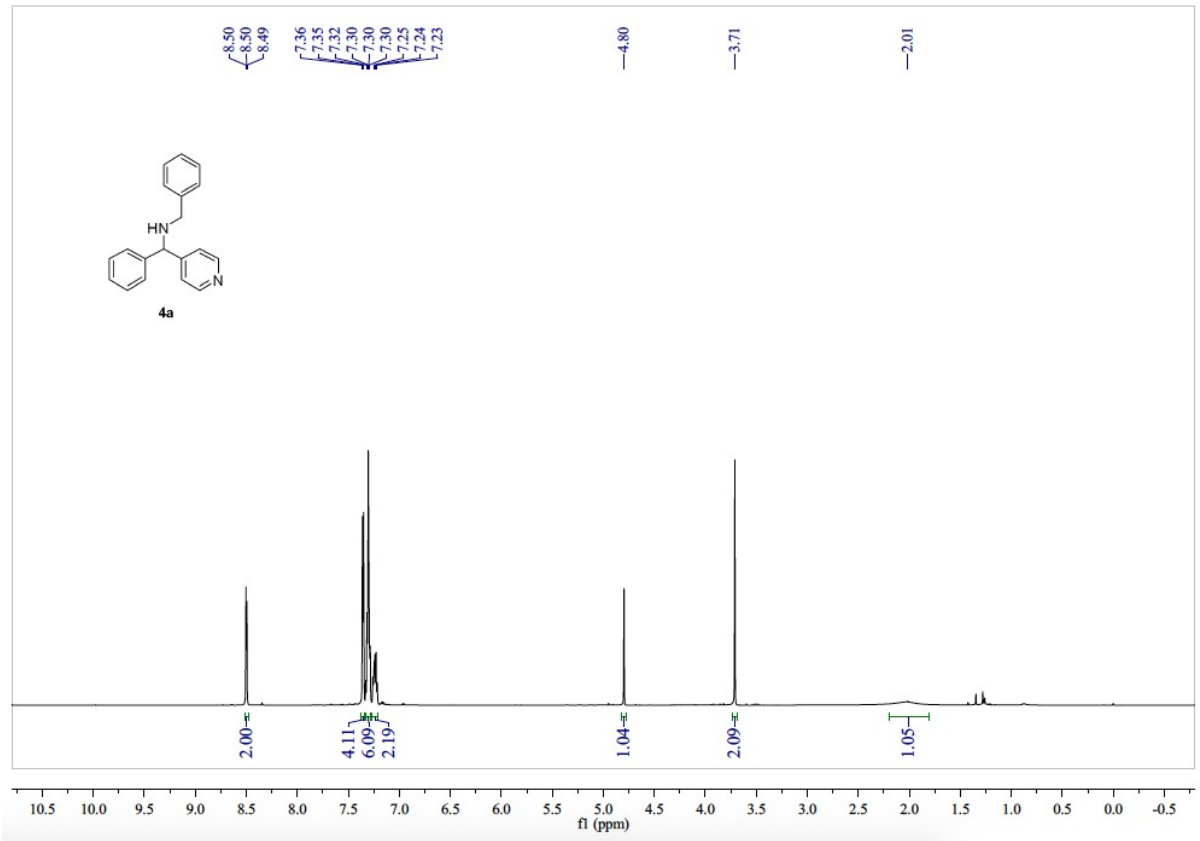
Aromatic aldehydes with electron-withdrawing groups proved to be unsuitable substrates, because the *in-situ* formed imine intermediate was reduced prior to coupling with **3a**. For example, the electrochemical reaction involving the substrate **S1** afforded the reductive amination product **S12** in a yield of 57%. The result of the 4-pyridinecarboxaldehyde **S2** was similar, and the reductive amination product was obtained (47% yield). The effect of fatty aldehyde was generally poor, like the substrate **1r**, when 3-phenylpropanaldehyde **S3** and pivalaldehyde **S4** as substrates, the desired product could only be obtained in single-digit yield. In addition, cinnamaldehyde **S5** and acetophenone **S6** could not achieve electrochemical reductive coupling. Large sterically hindered secondary amines might not be suitable coupling components. For example, the reaction involving substrates **S7** and **S8** only yielded the product **S14**, which coupled from benzaldehyde with **3a**. Finally, some aromatic nitriles such as 2-cyanopyridine **S9**, 3-cyanopyridine **S10** and 1,4-Dicyanobenzene **S11** could not afford the coupling products, but they had reduction behavior at the cathode, and the imine intermediate was attacked by the cyano anion to give the side product **S15**.

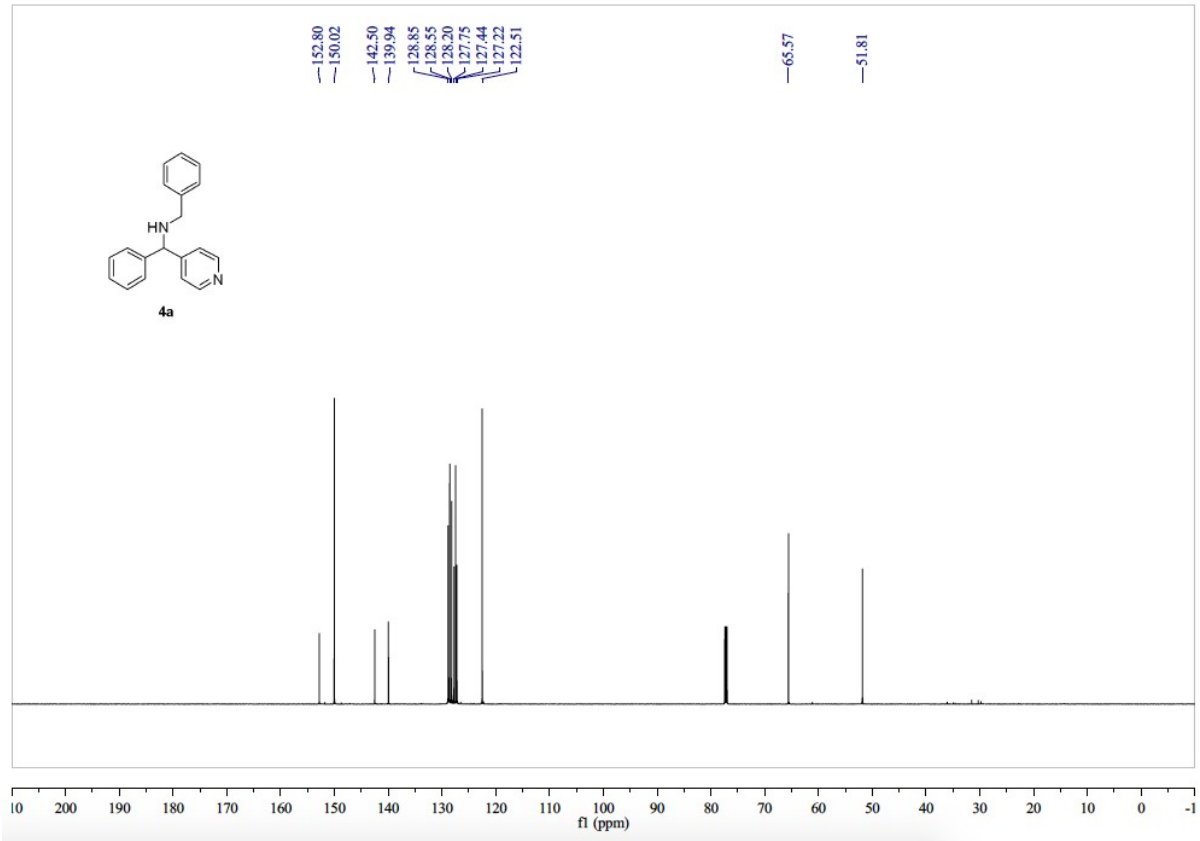


Scheme S2. Some unsuccessful reactions and their side products.

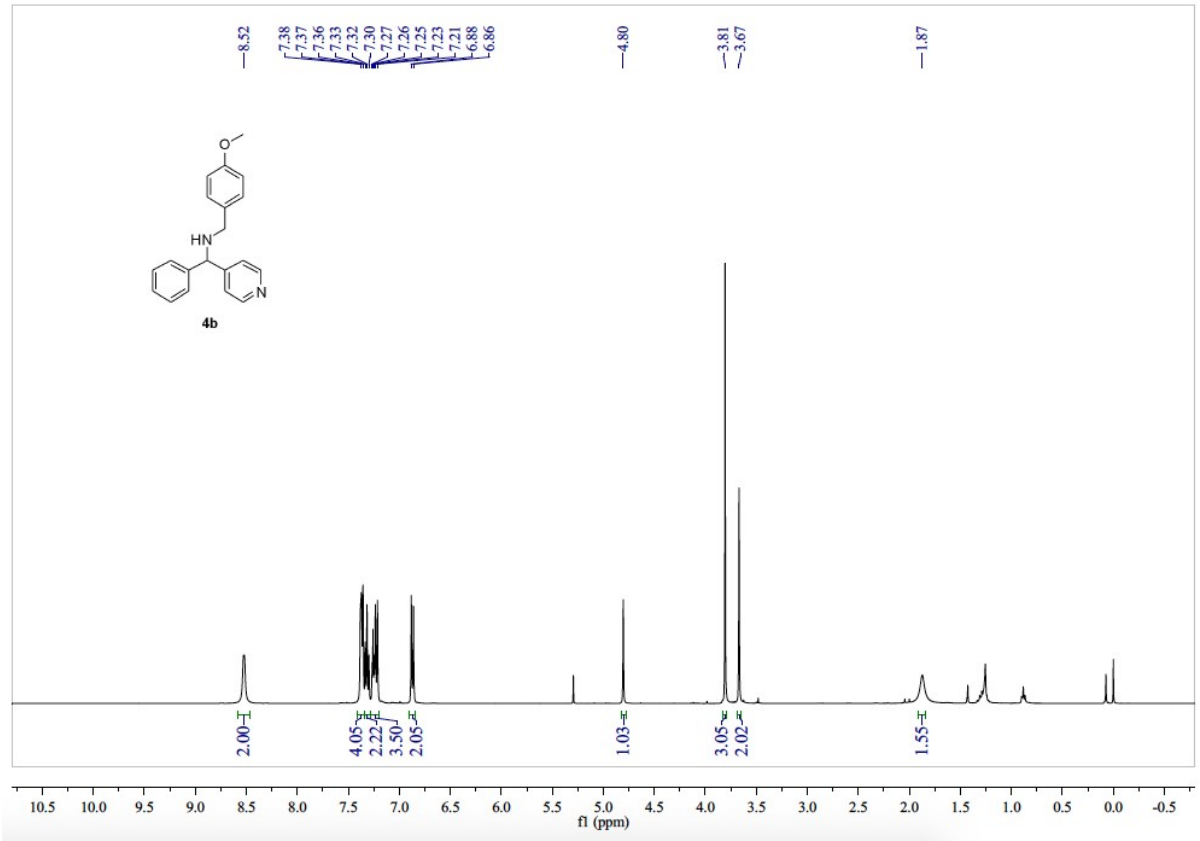
H: NMR Spectra of Products.

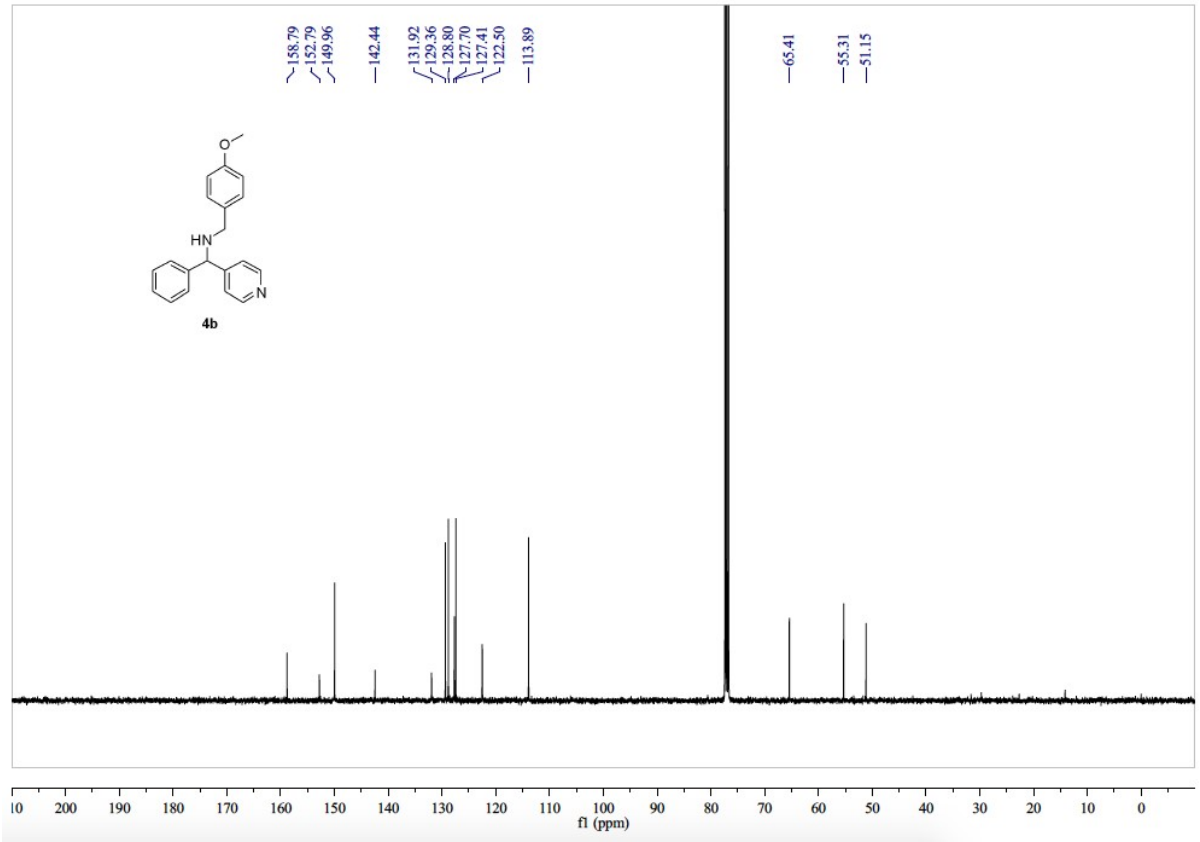
4a: *N*-benzyl-1-phenyl-1-(pyridin-4-yl)methanamine



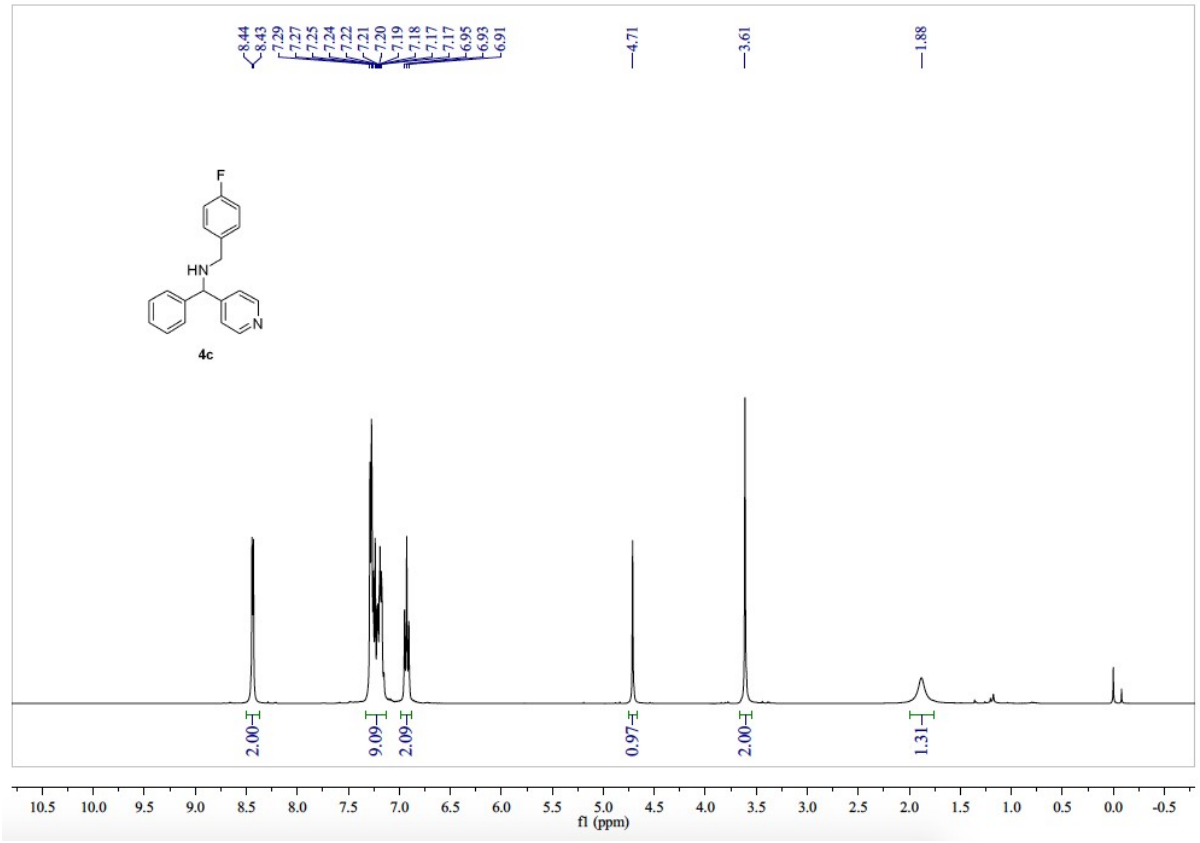


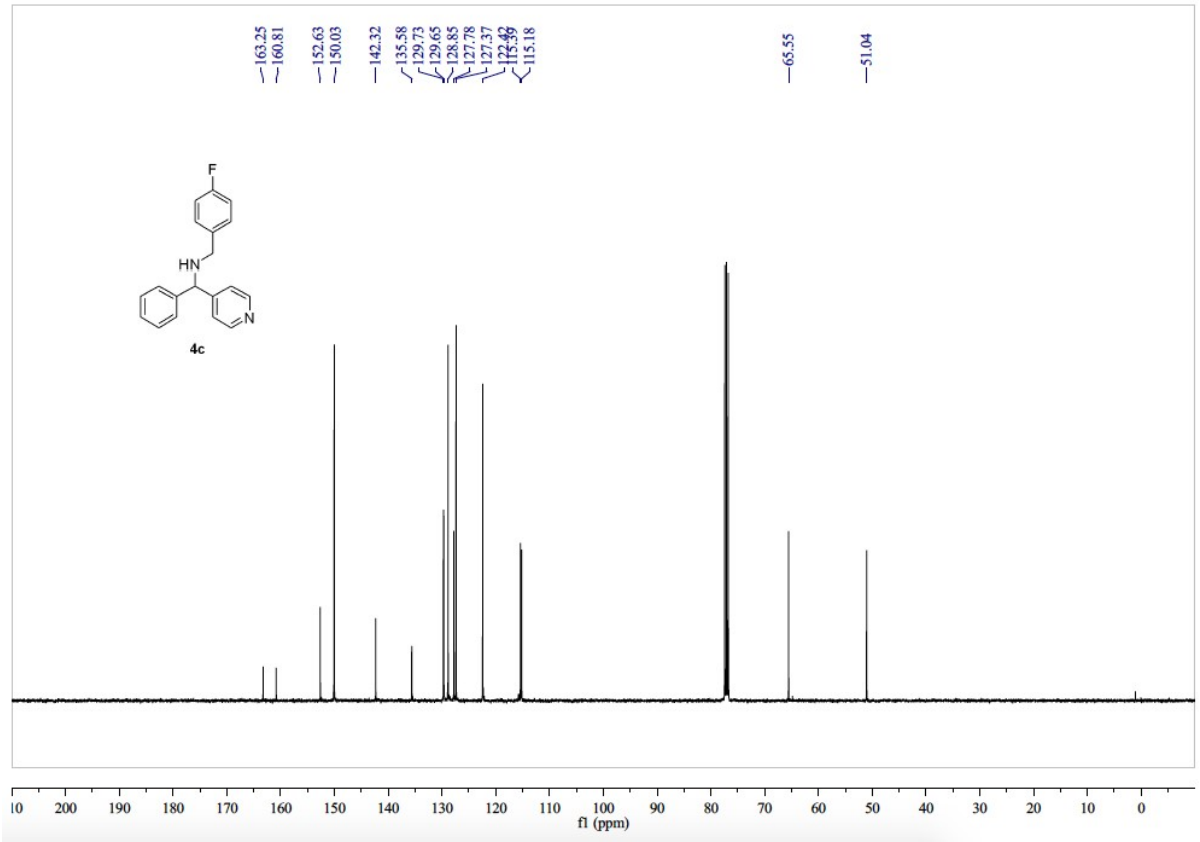
4b: *N*-(4-methoxybenzyl)-1-phenyl-1-(pyridin-4-yl)methanamine

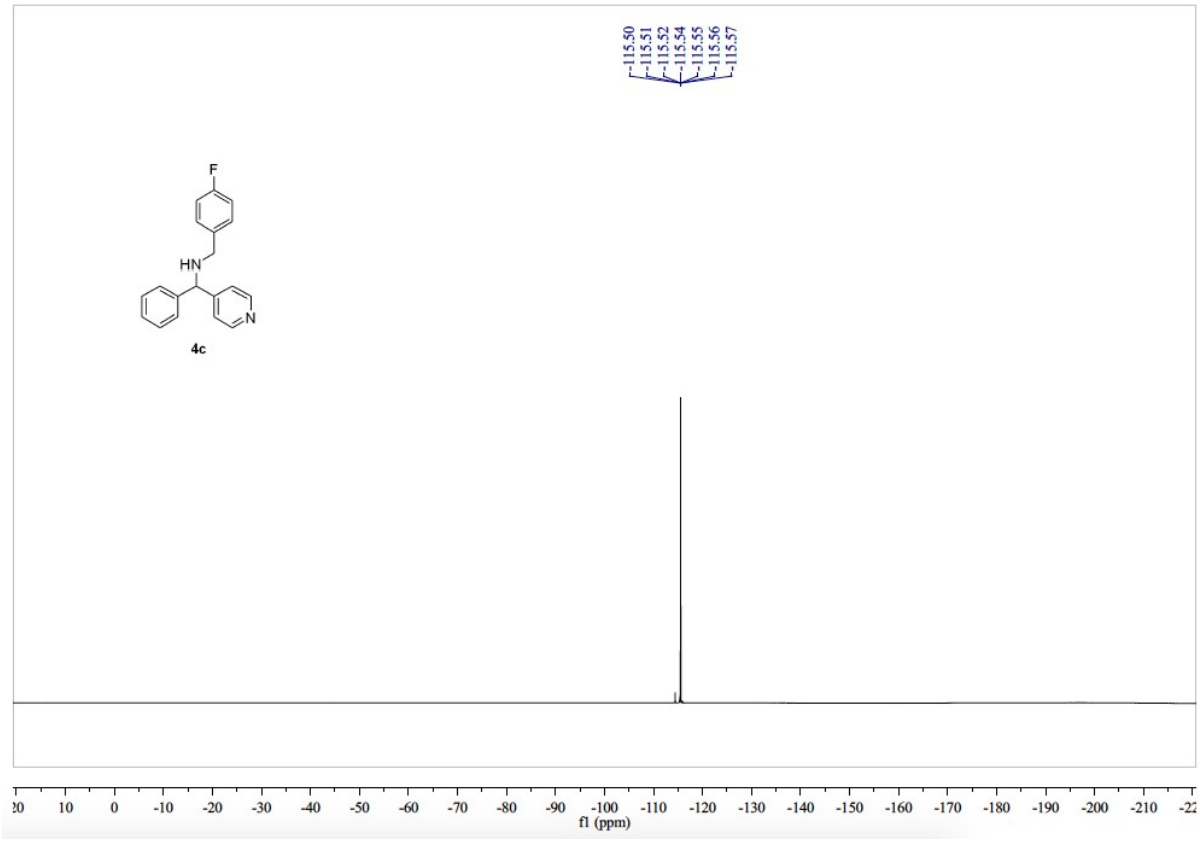




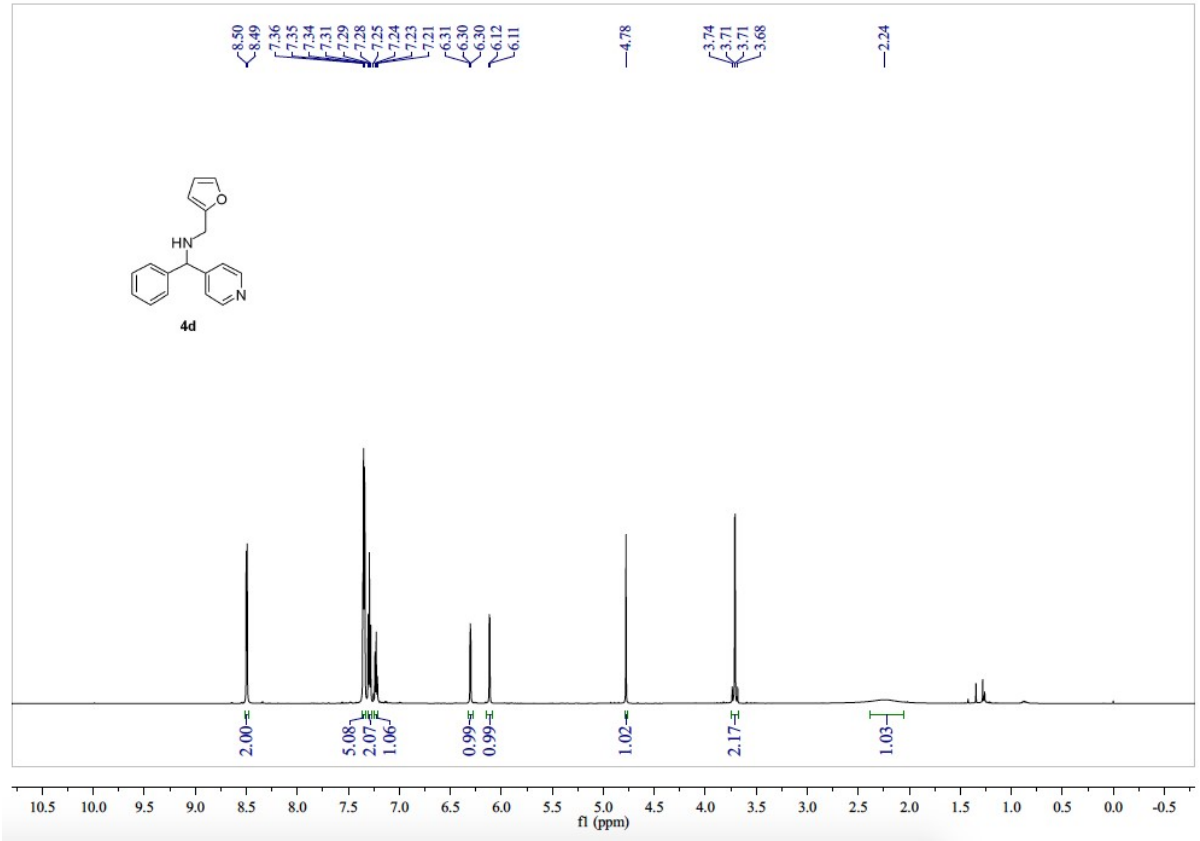
4c: *N*-(4-fluorobenzyl)-1-phenyl-1-(pyridin-4-yl)methanamine

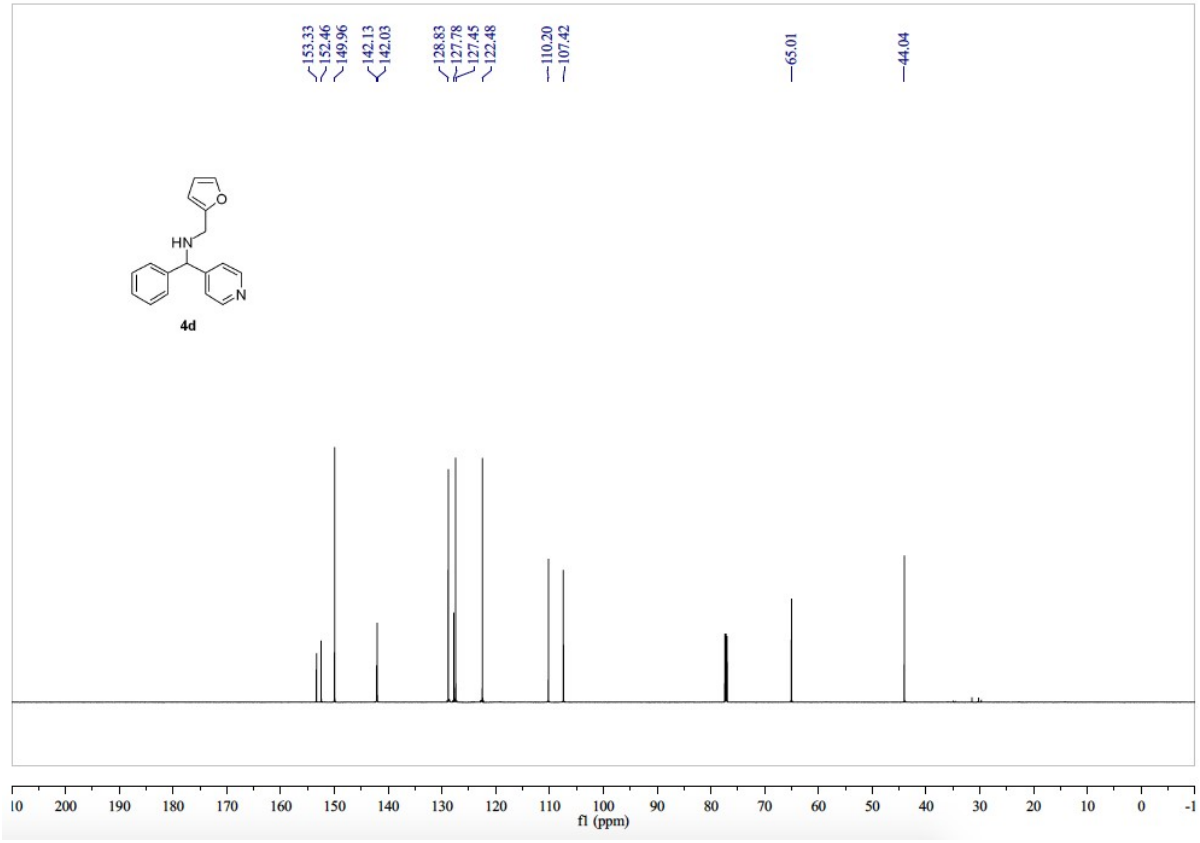




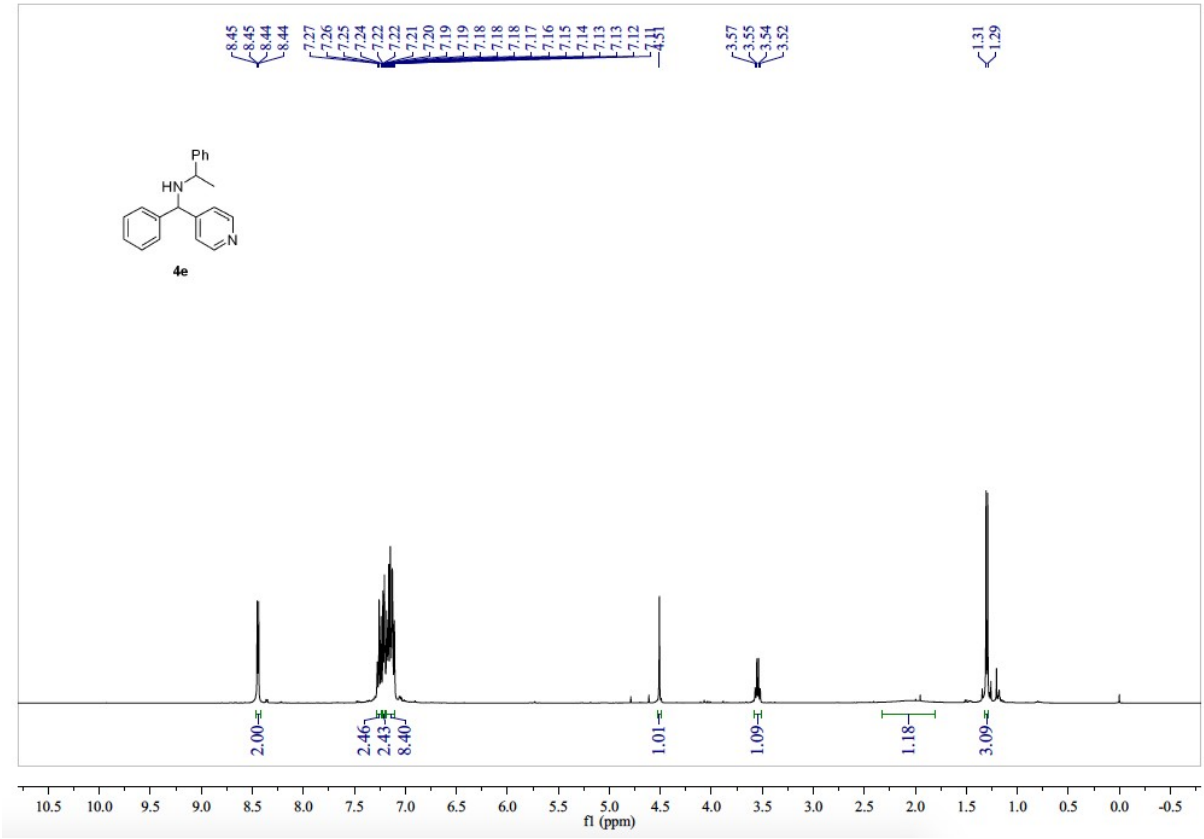


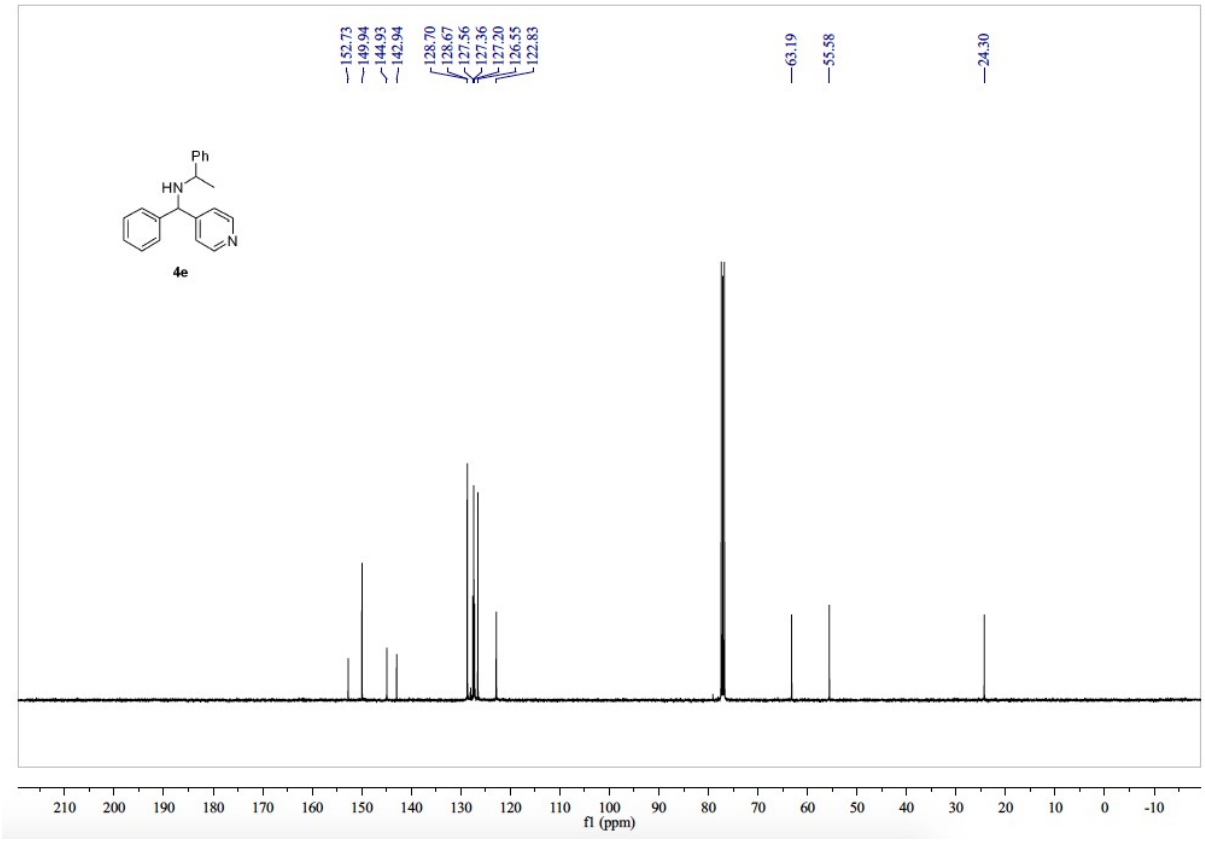
4d: *N*-(furan-2-ylmethyl)-1-phenyl-1-(pyridin-4-yl)methanamine



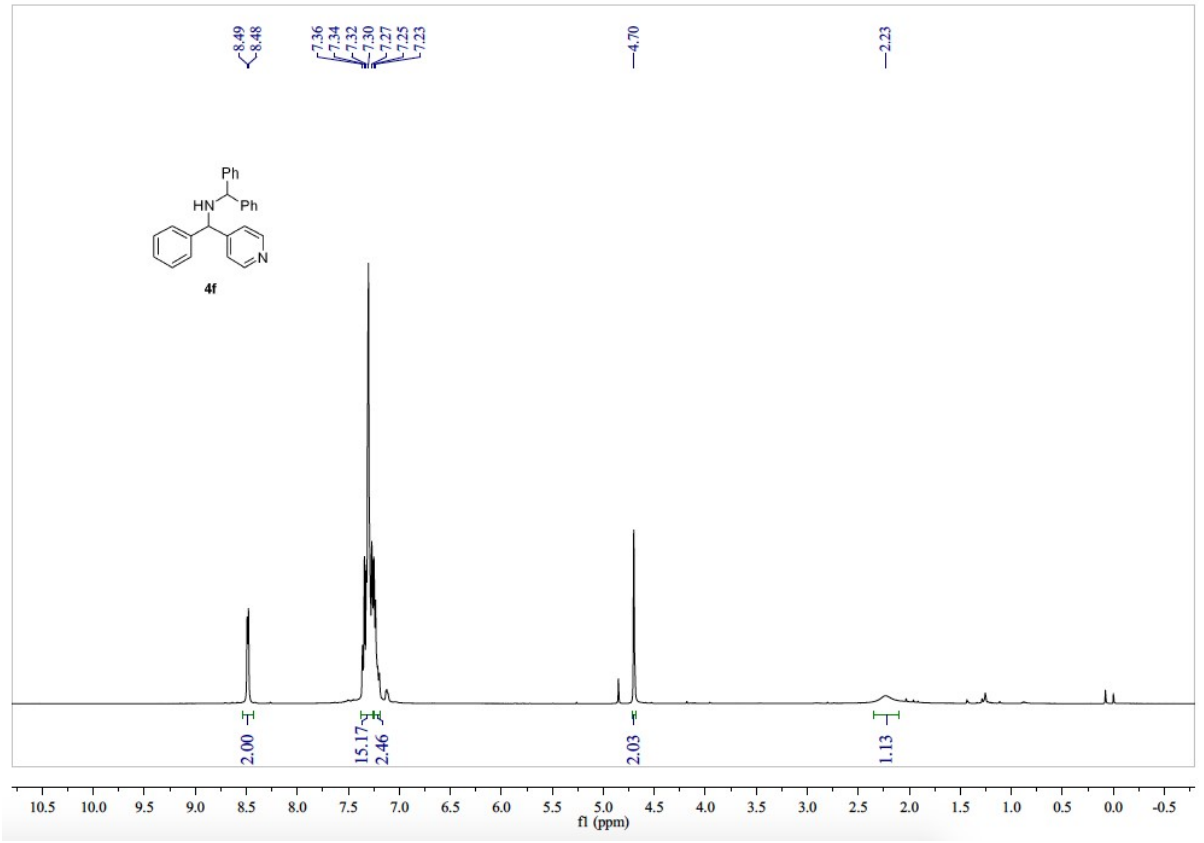


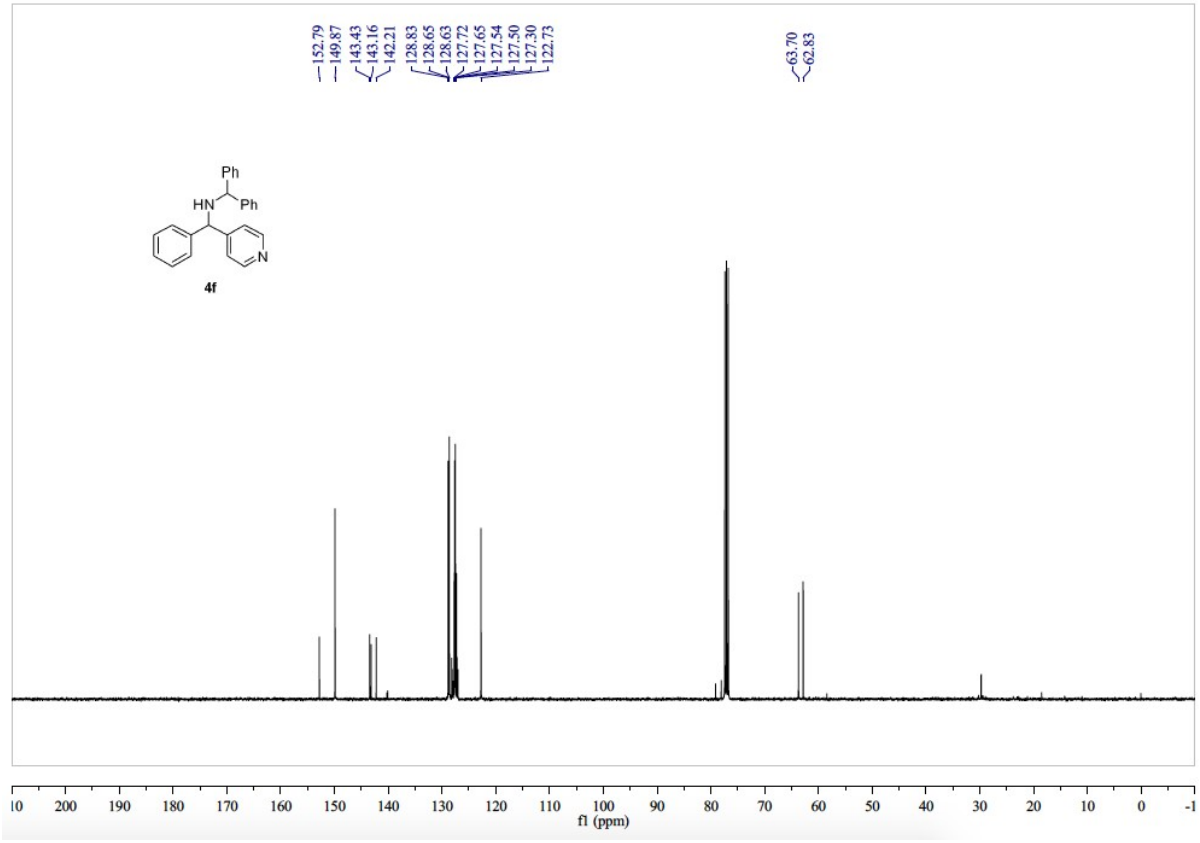
4e: 1-phenyl-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



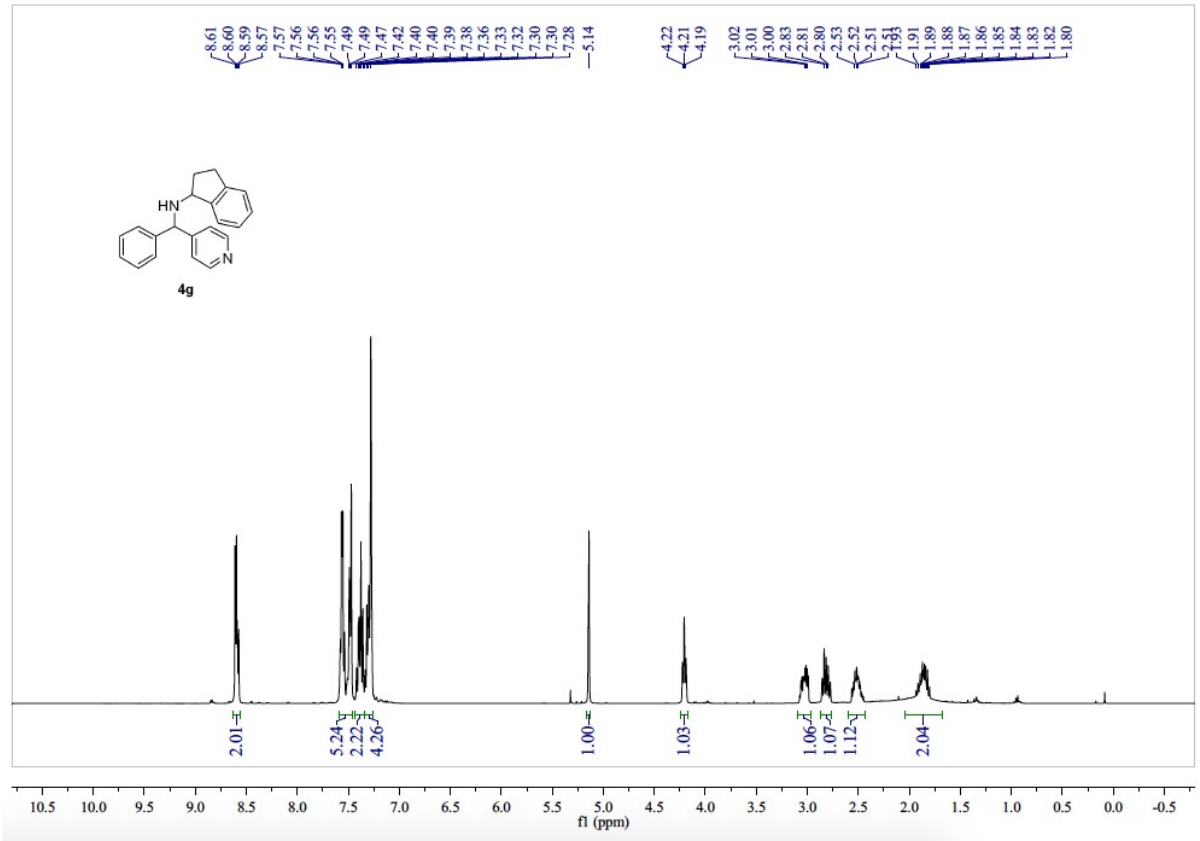


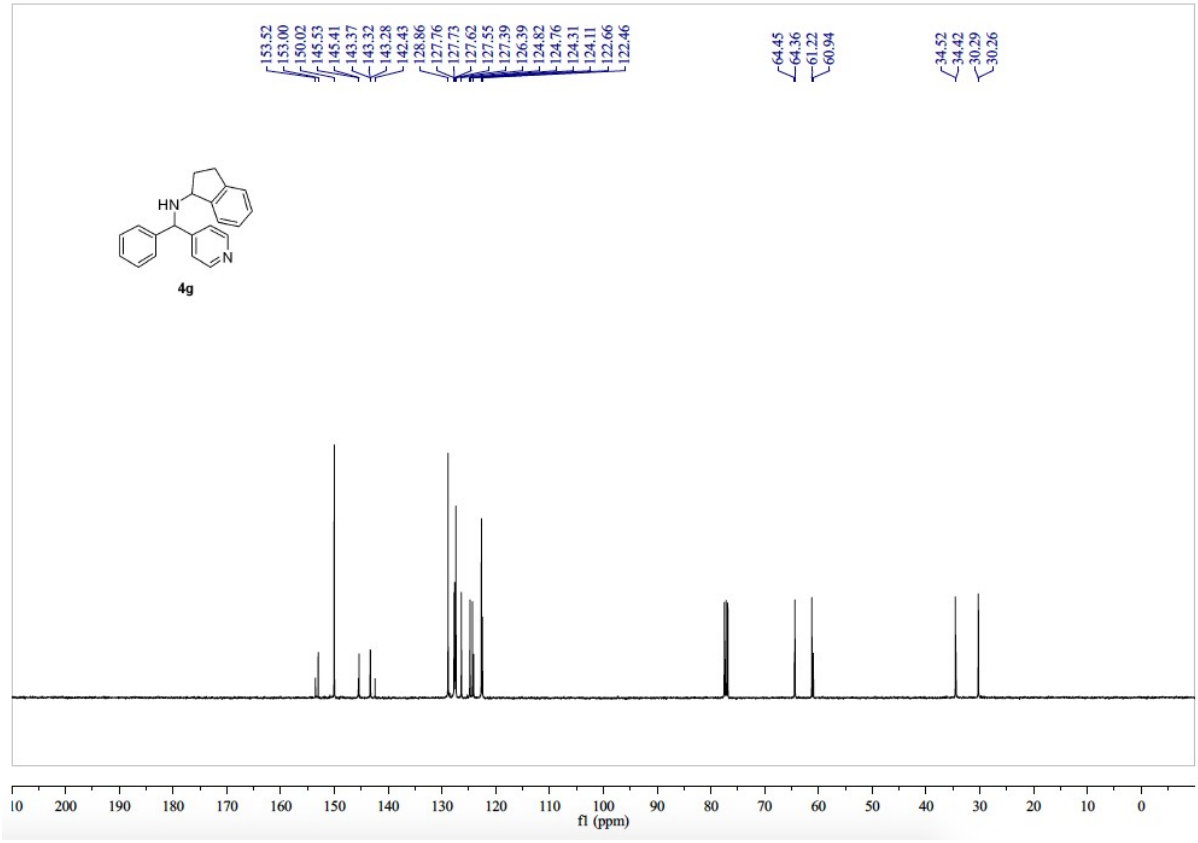
4f: *N*-benzhydryl-1-phenyl-1-(pyridin-4-yl)methanamine



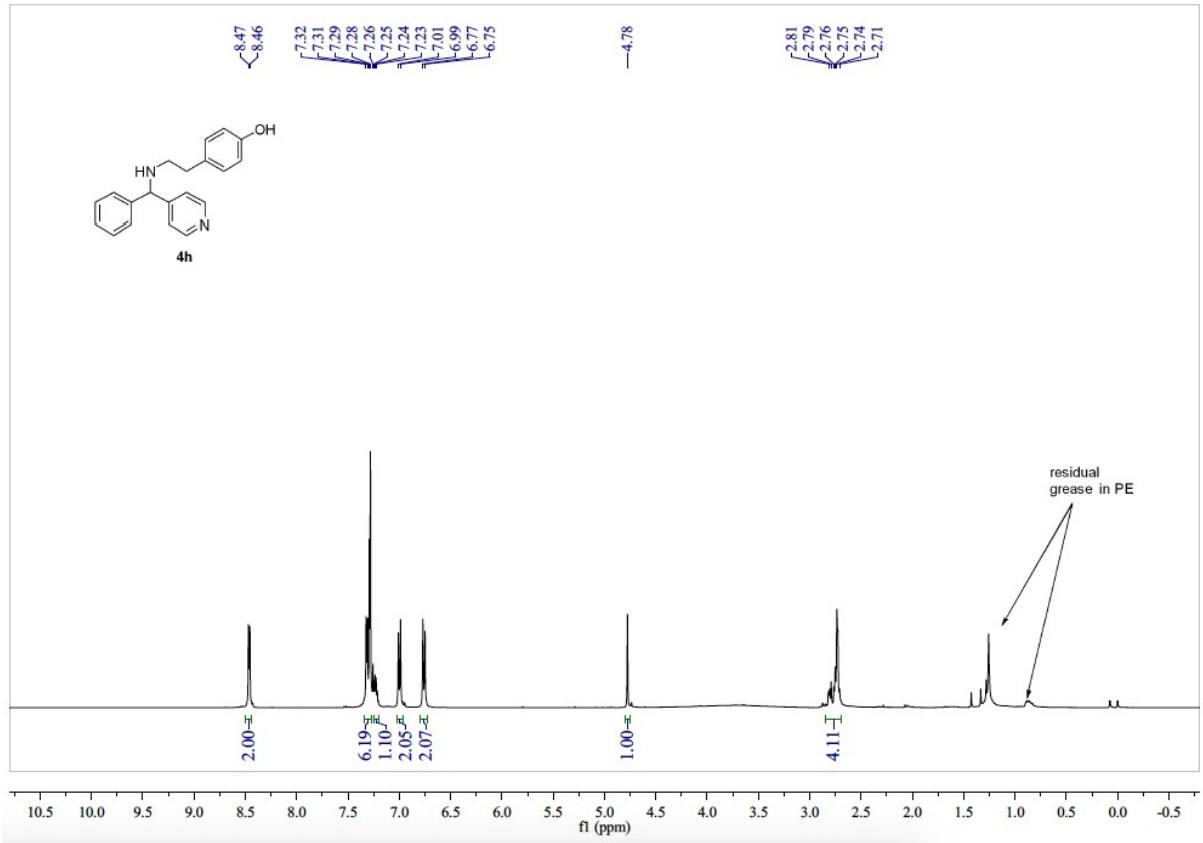


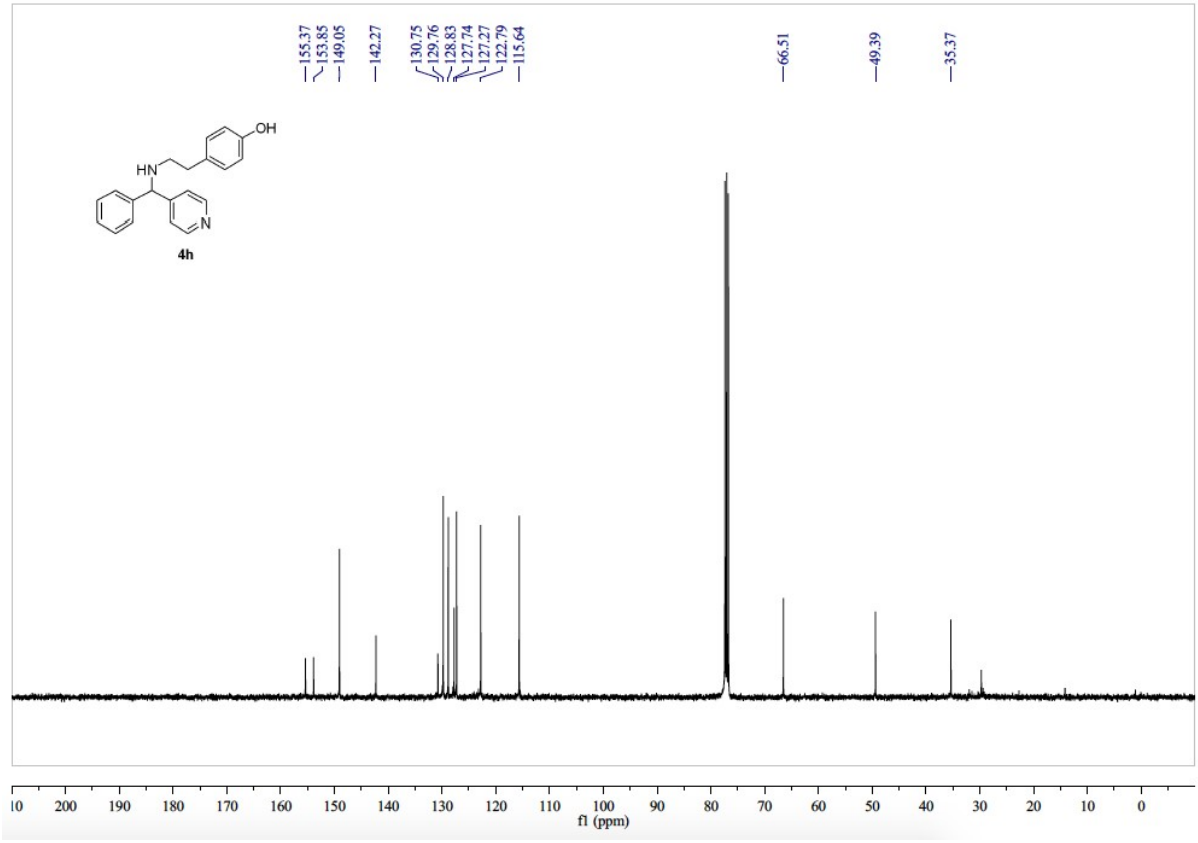
4g: *N*-(phenyl(pyridin-4-yl)methyl)-2,3-dihydro-1*H*-inden-1-amine



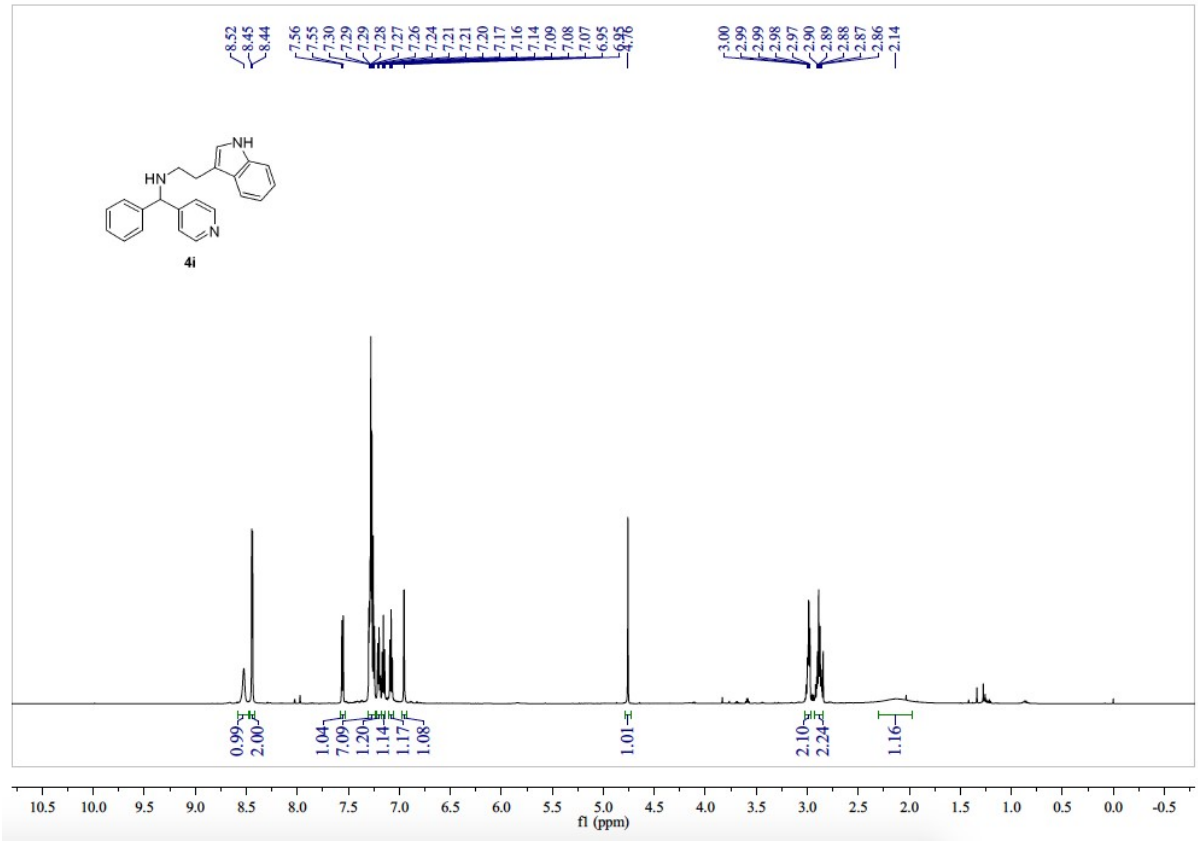


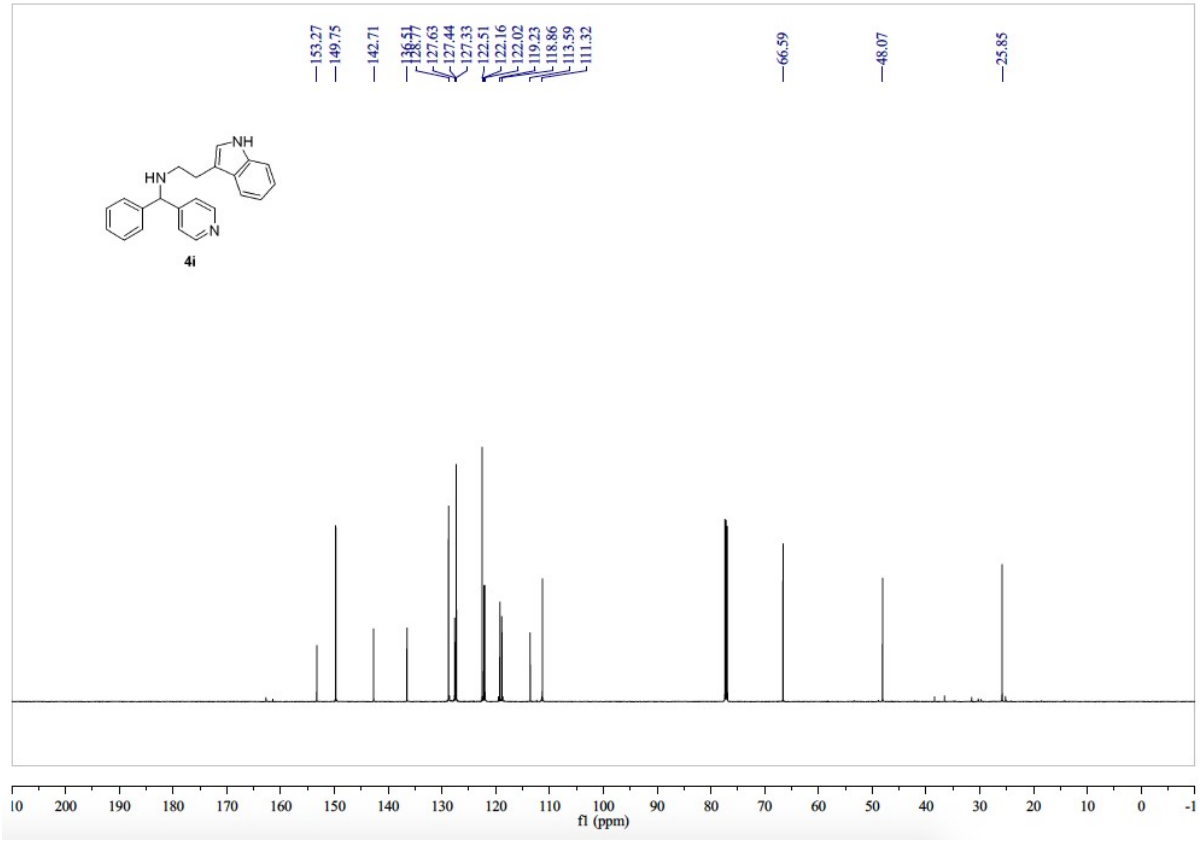
4h: 4-(2-((phenyl(pyridin-4-yl)methyl)amino)ethyl)phenol



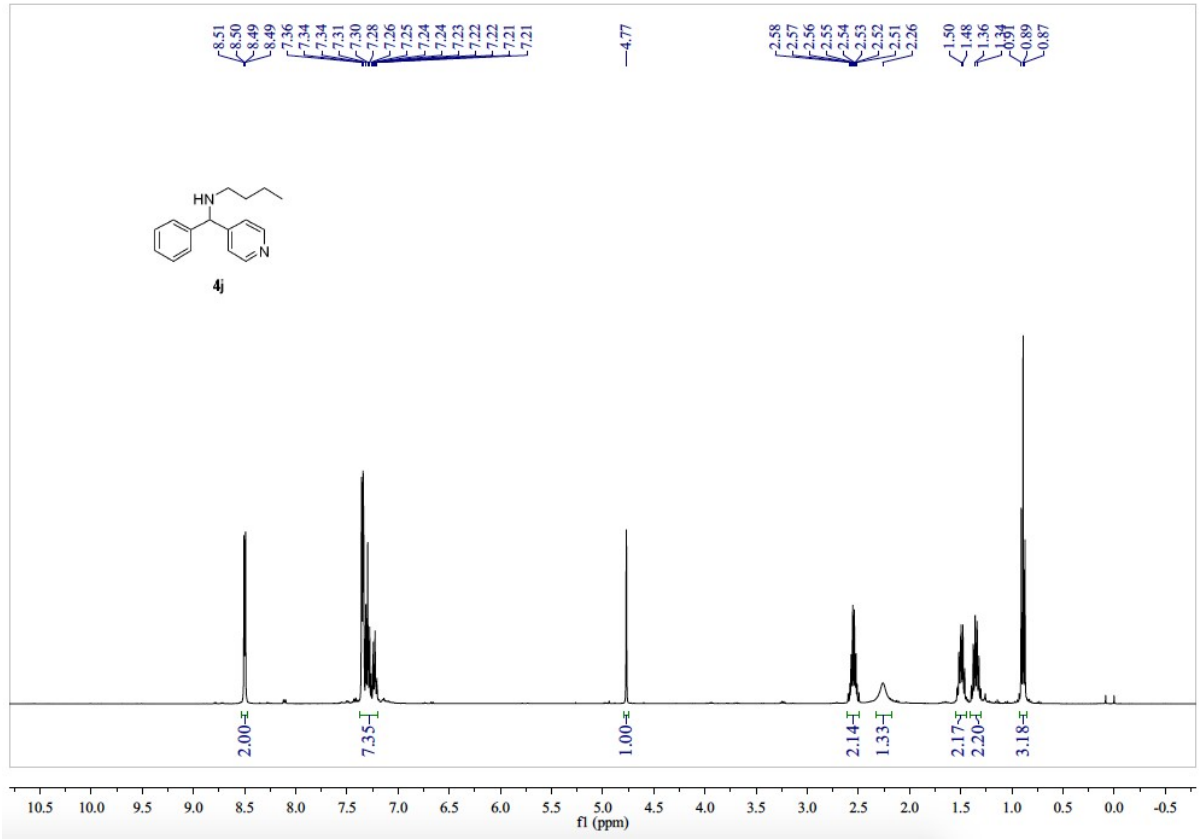


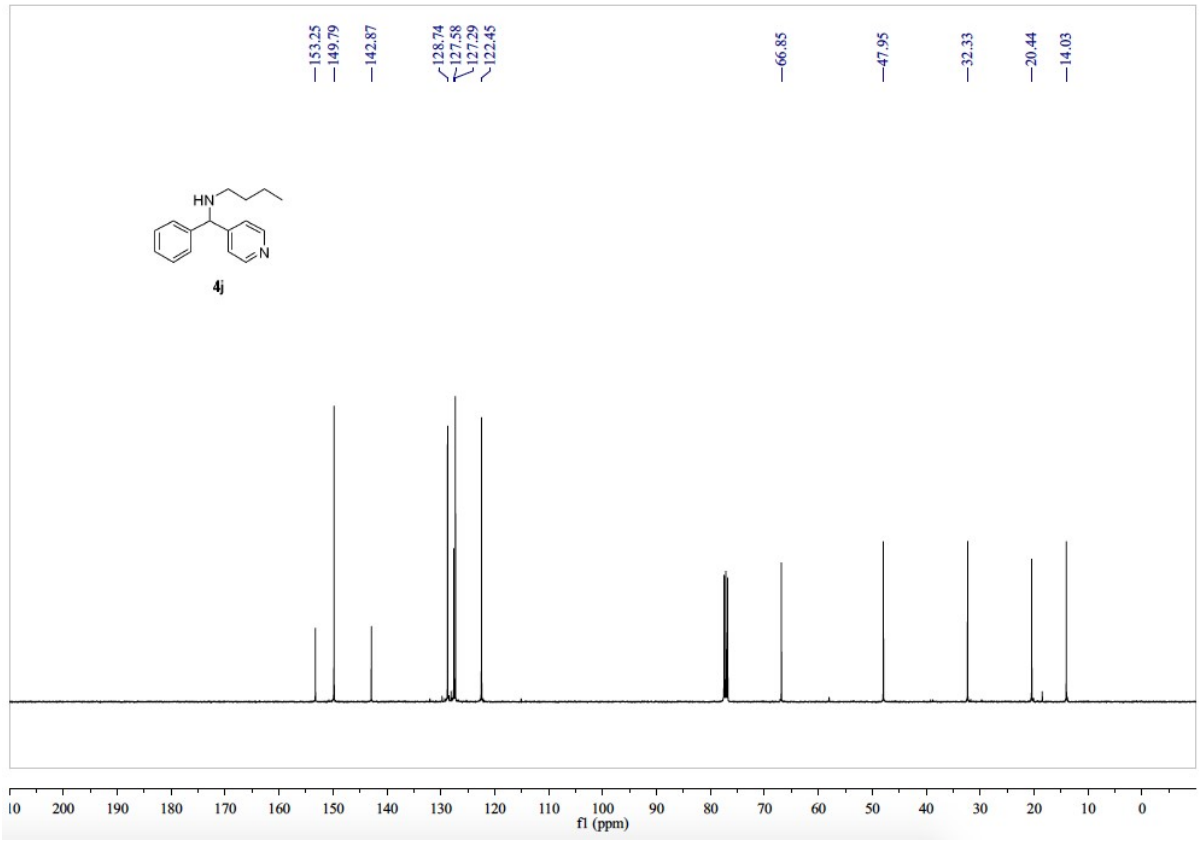
4i: 2-(1*H*-indol-3-yl)-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



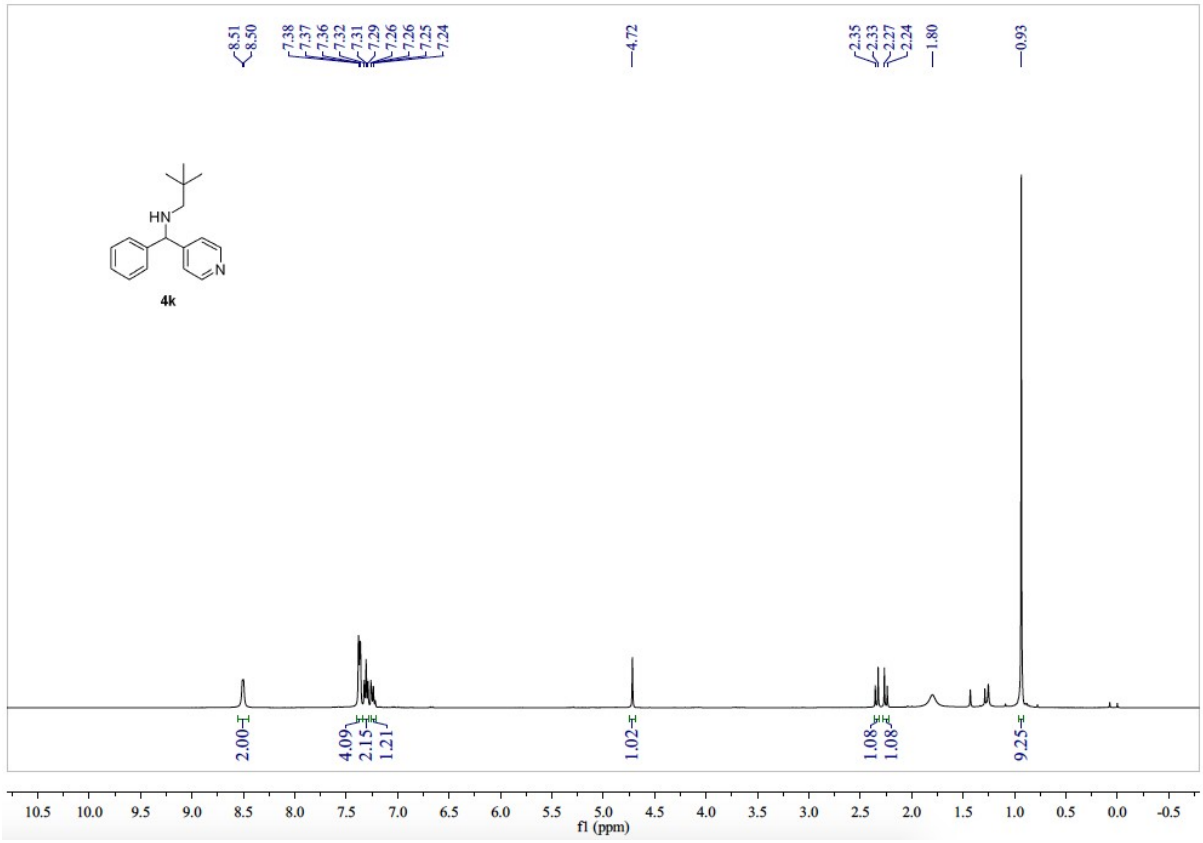


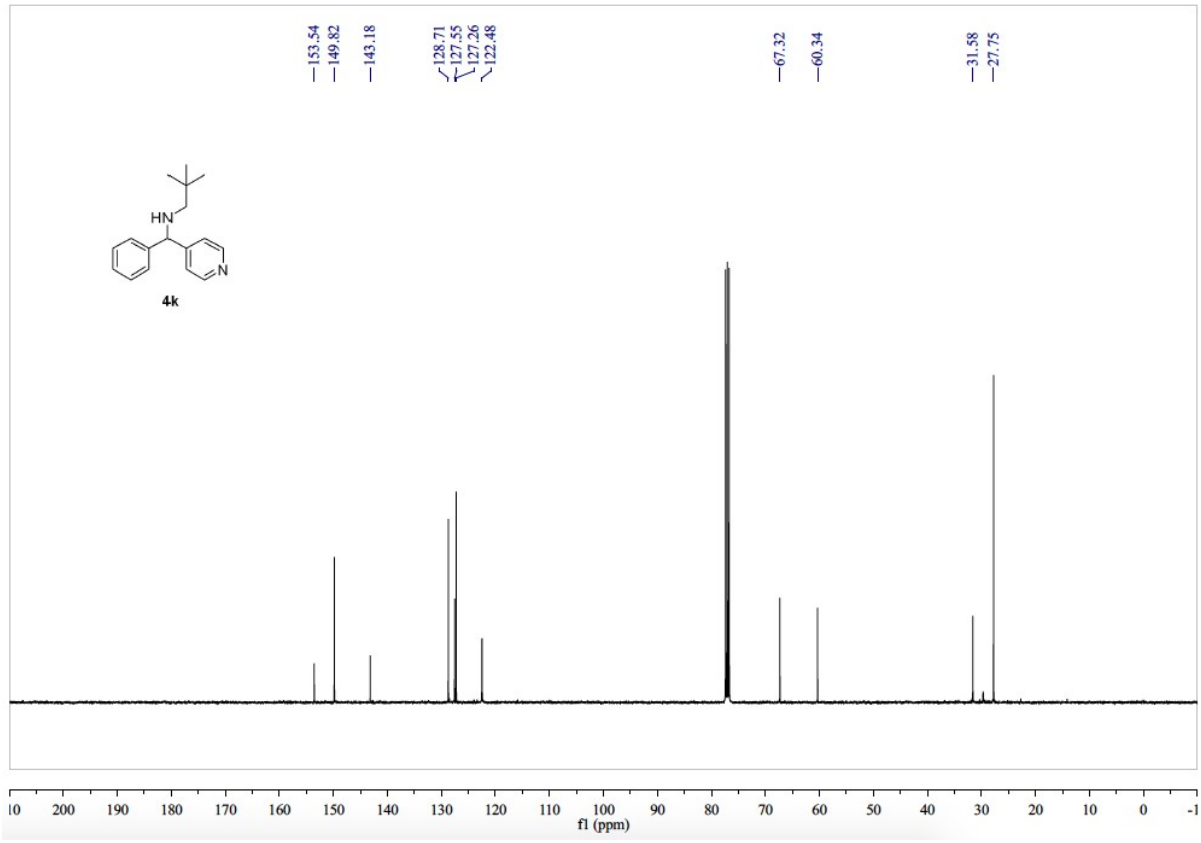
4j: *N*-(phenyl(pyridin-4-yl)methyl)butan-1-amine



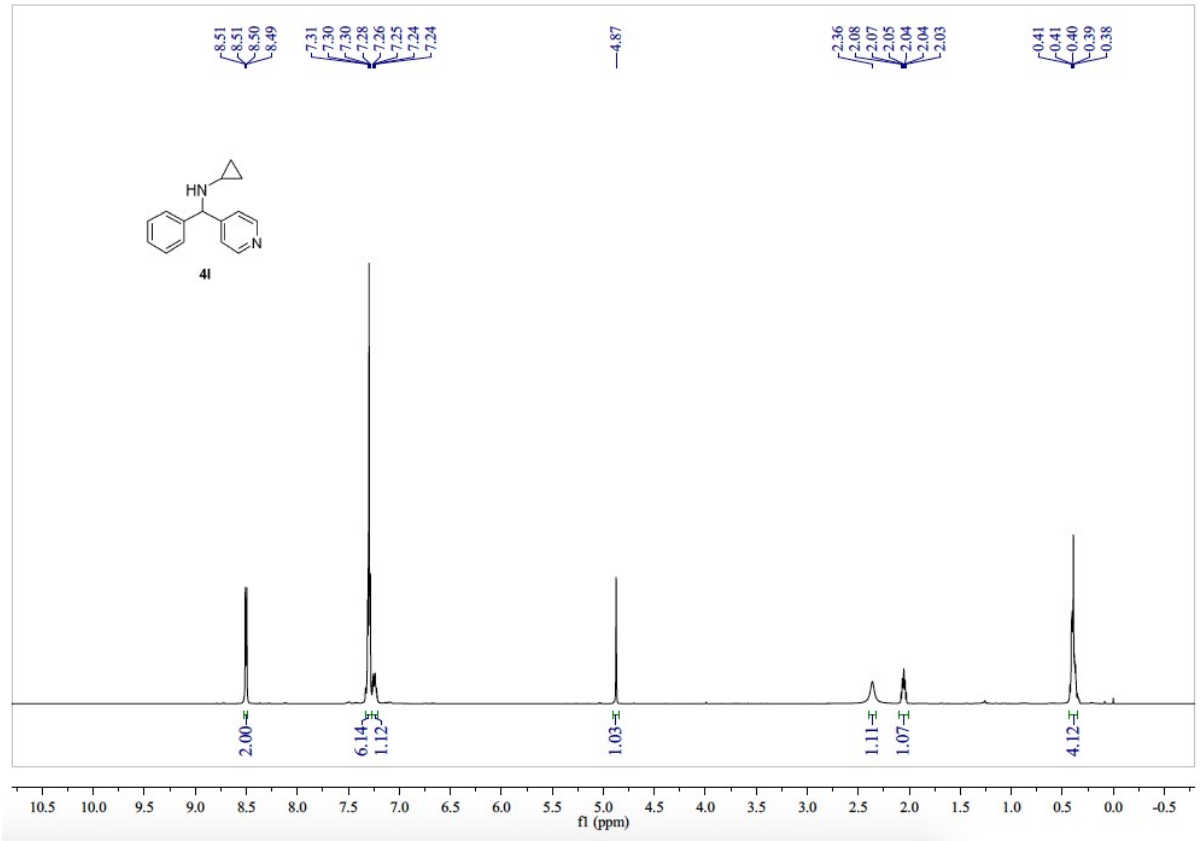


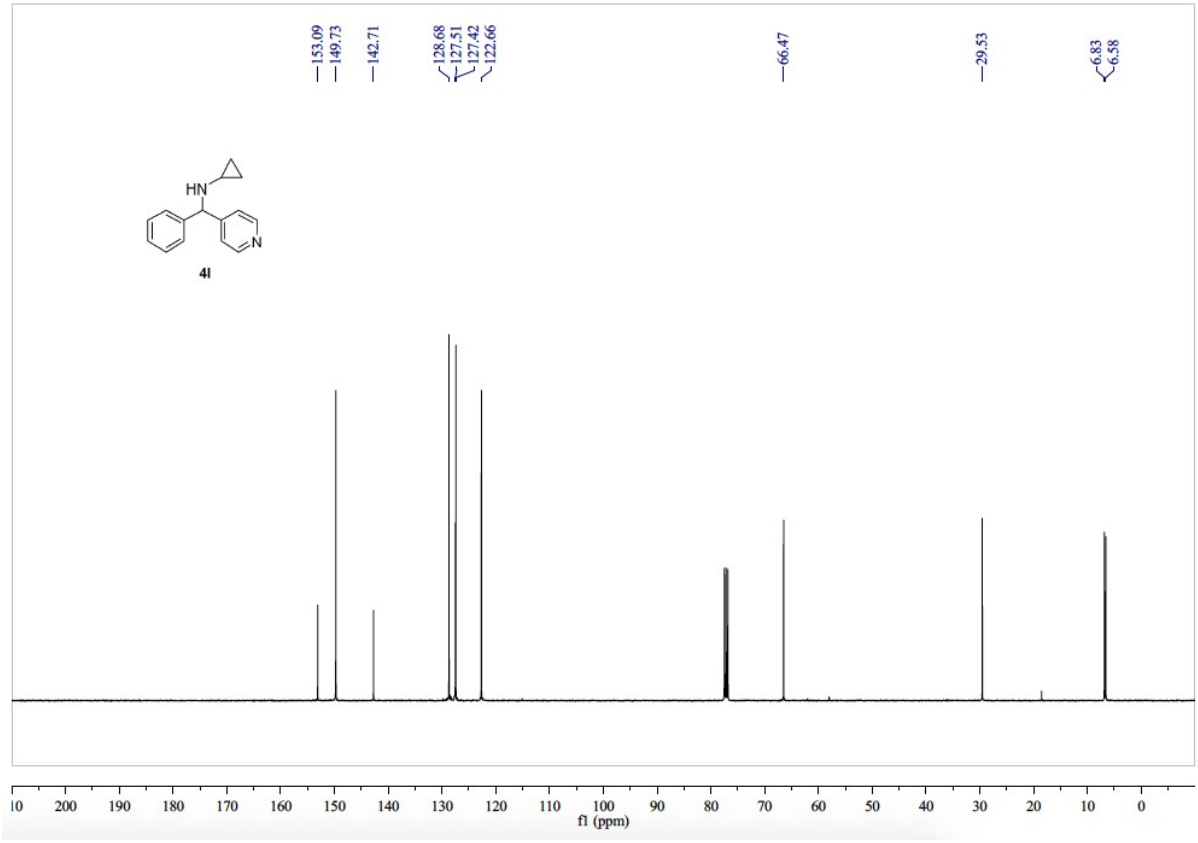
4k: 2,2-dimethyl-*N*-(phenyl(pyridin-4-yl)methyl)propan-1-amine



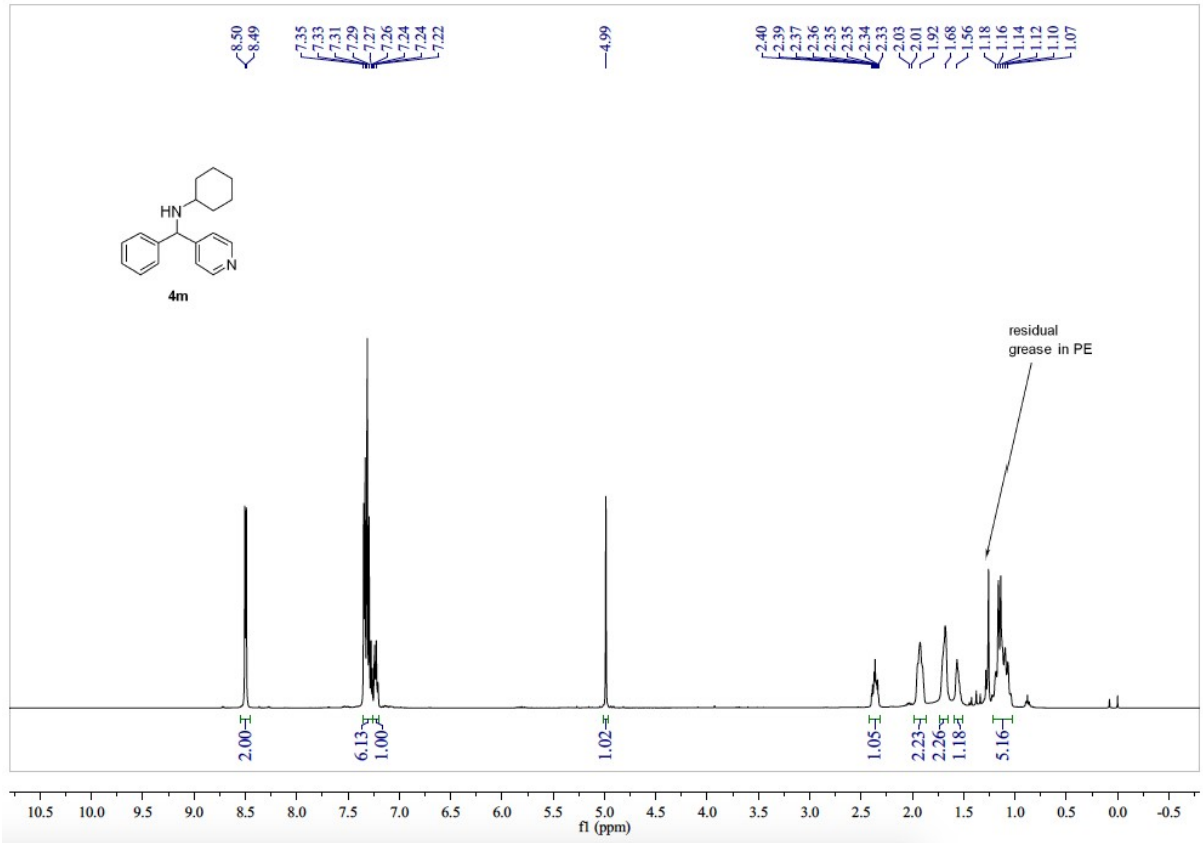


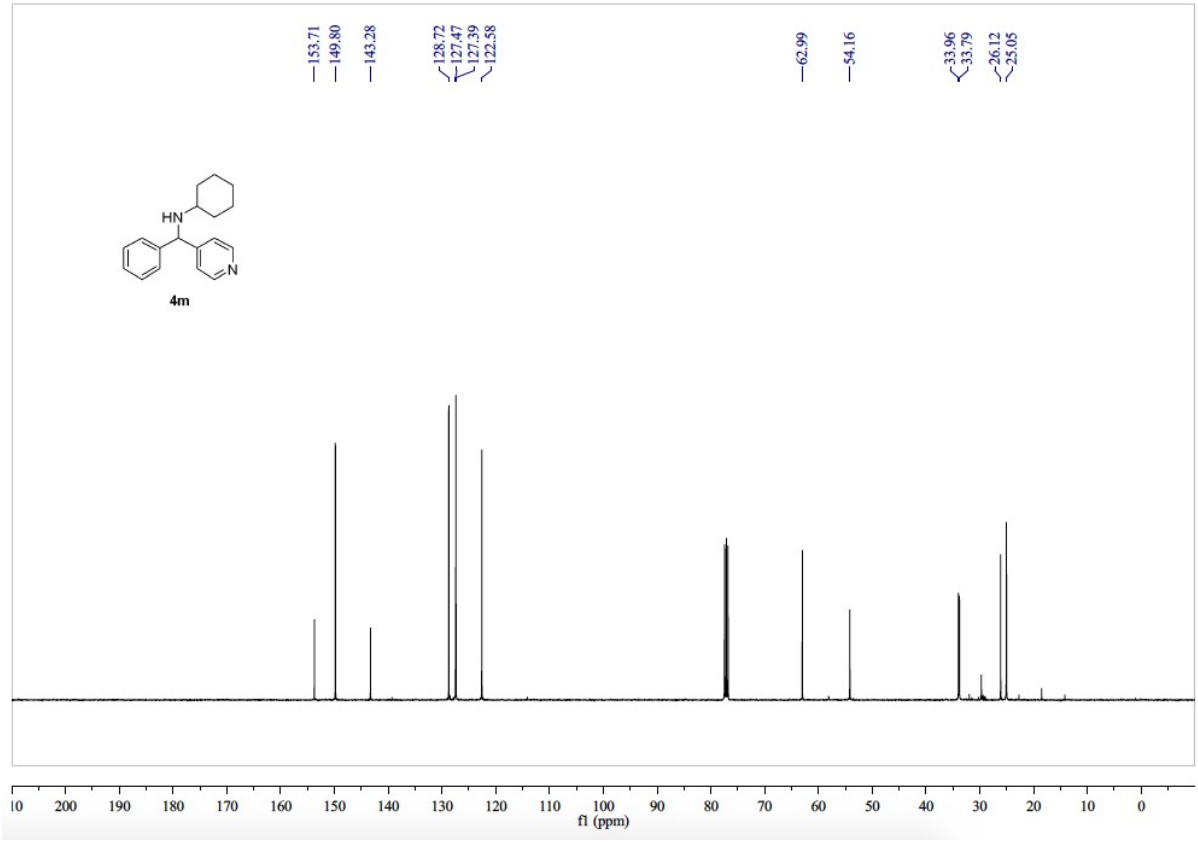
4l: *N*-(phenyl(pyridin-4-yl)methyl)cyclopropanamine



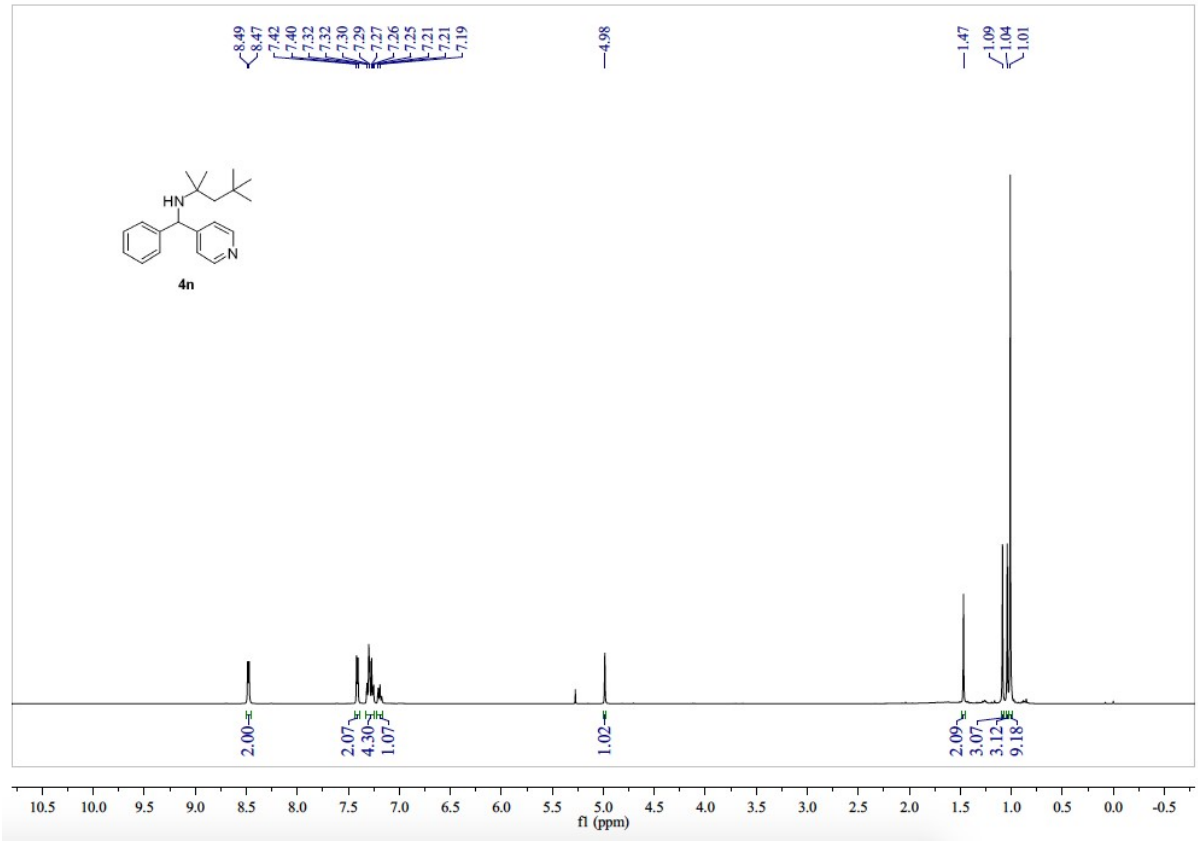


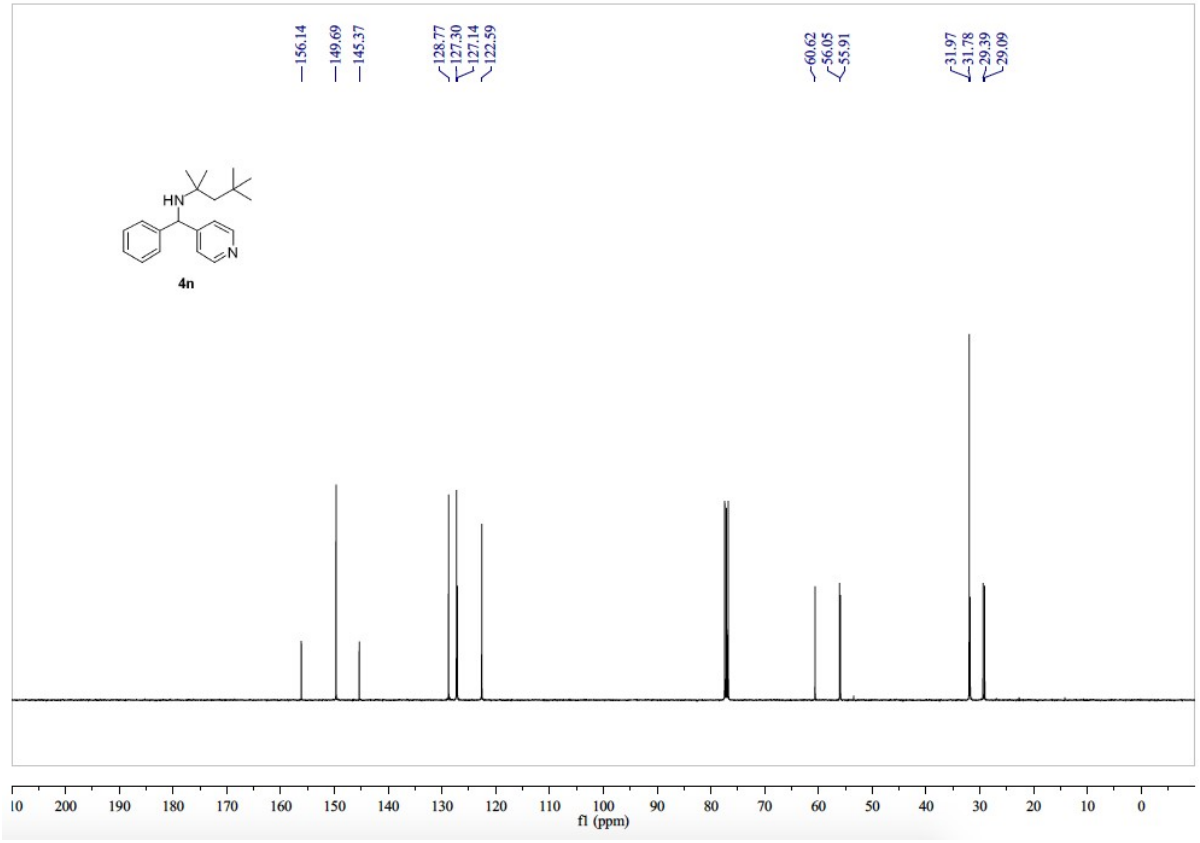
4m: *N*-(phenyl(pyridin-4-yl)methyl)cyclohexanamine



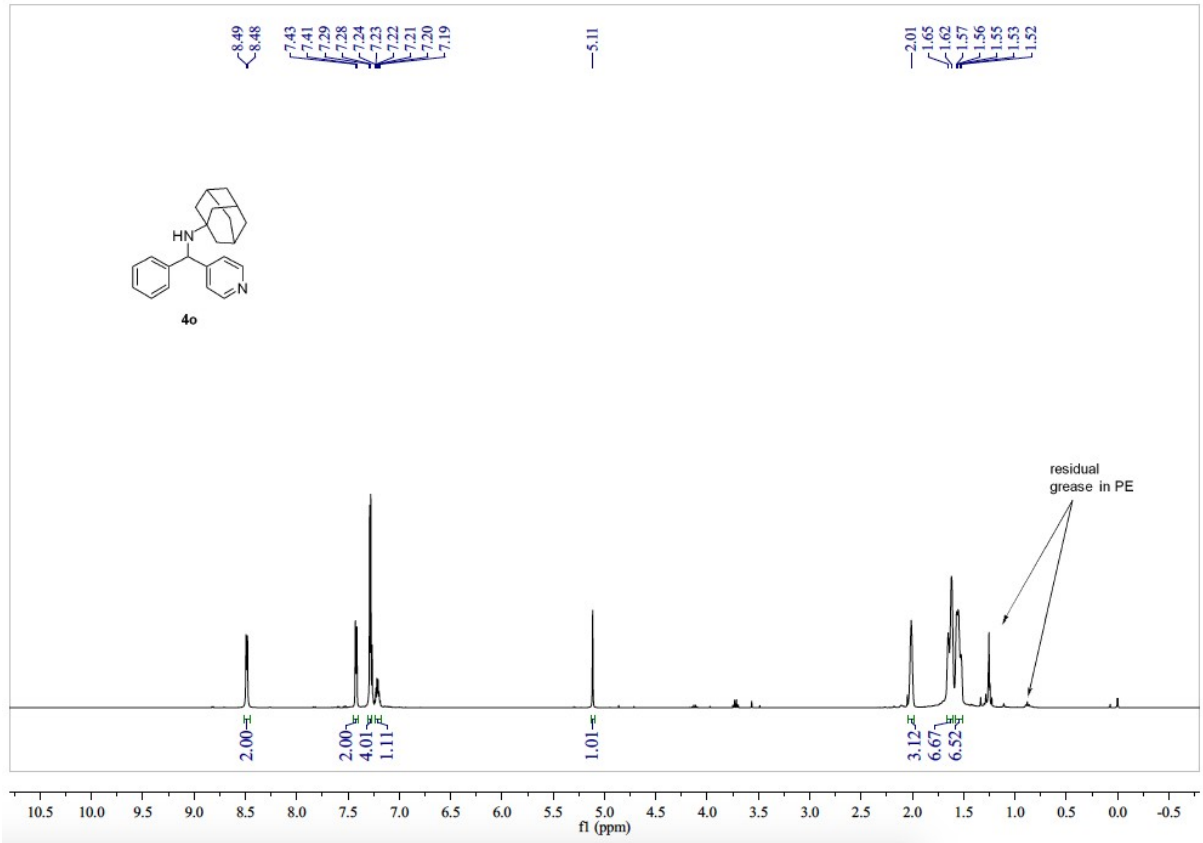


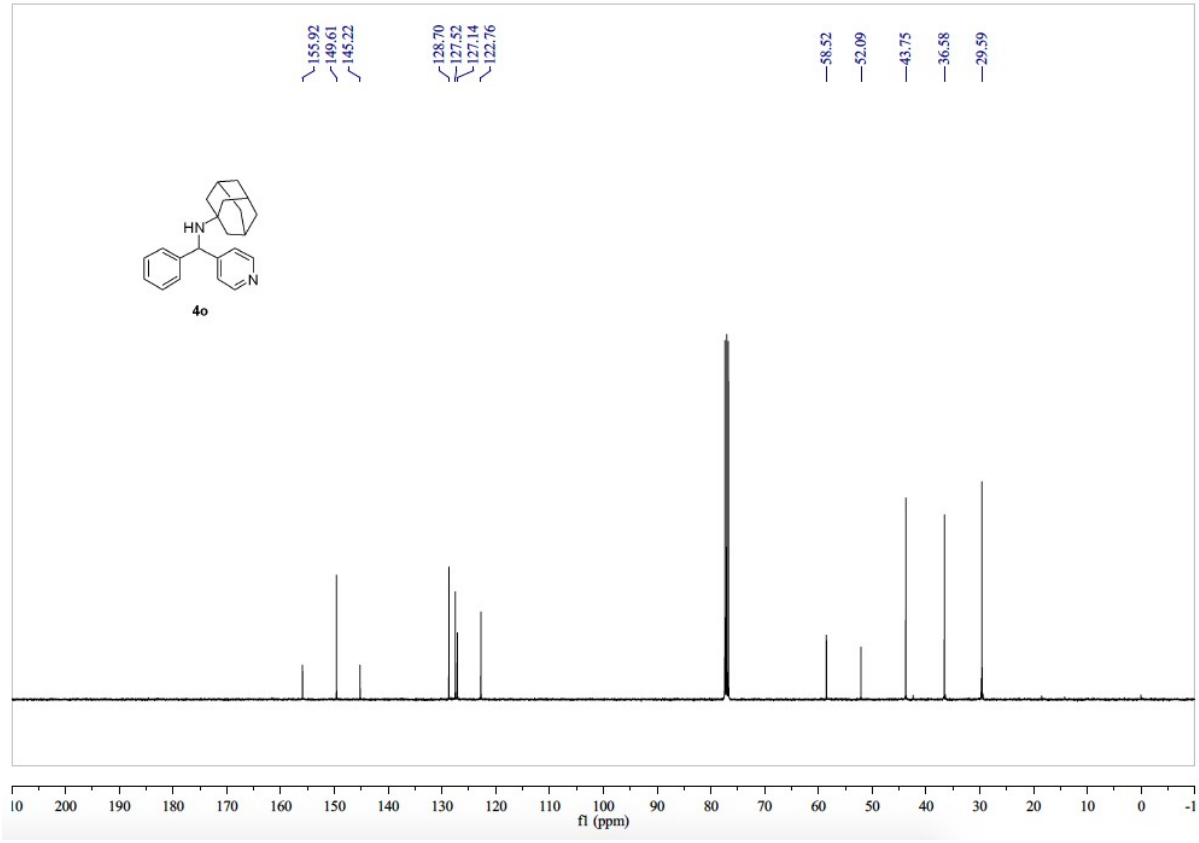
4n: 2,4,4-trimethyl-*N*-(phenyl(pyridin-4-yl)methyl)pentan-2-amine



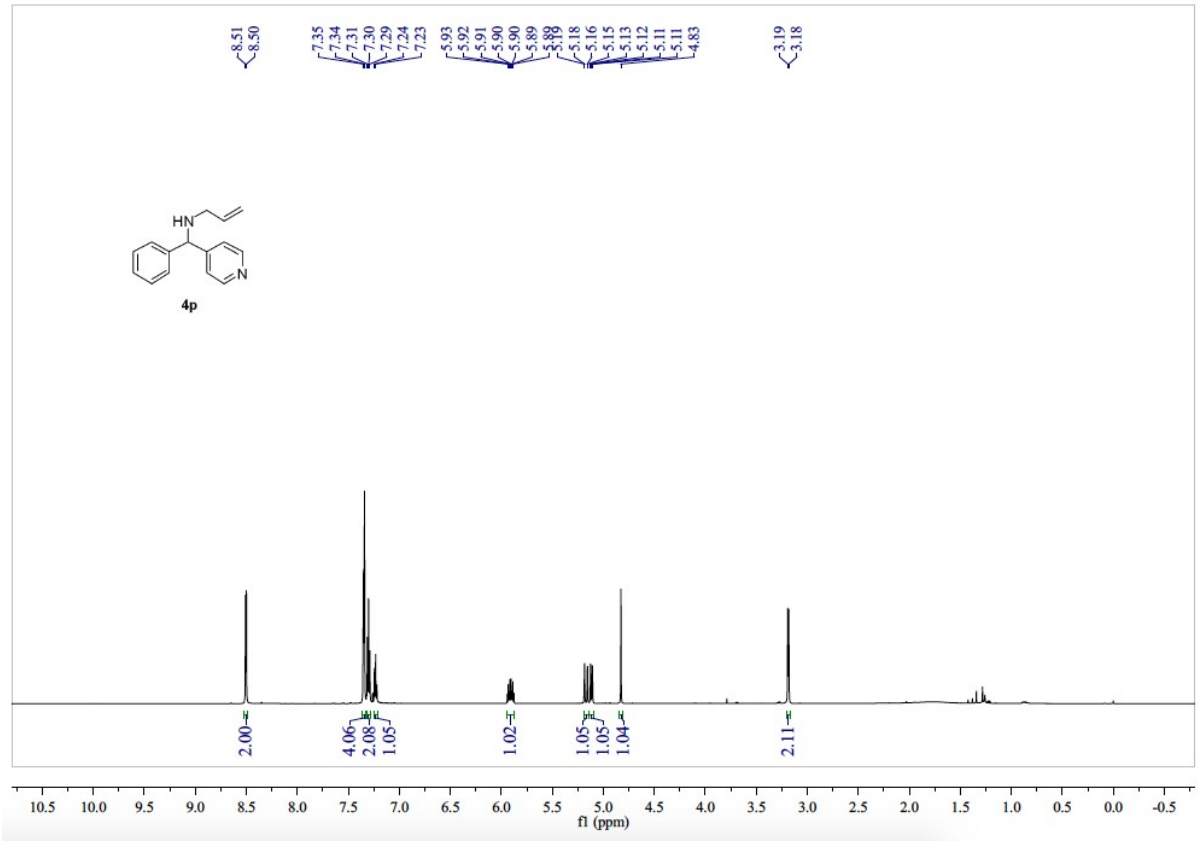


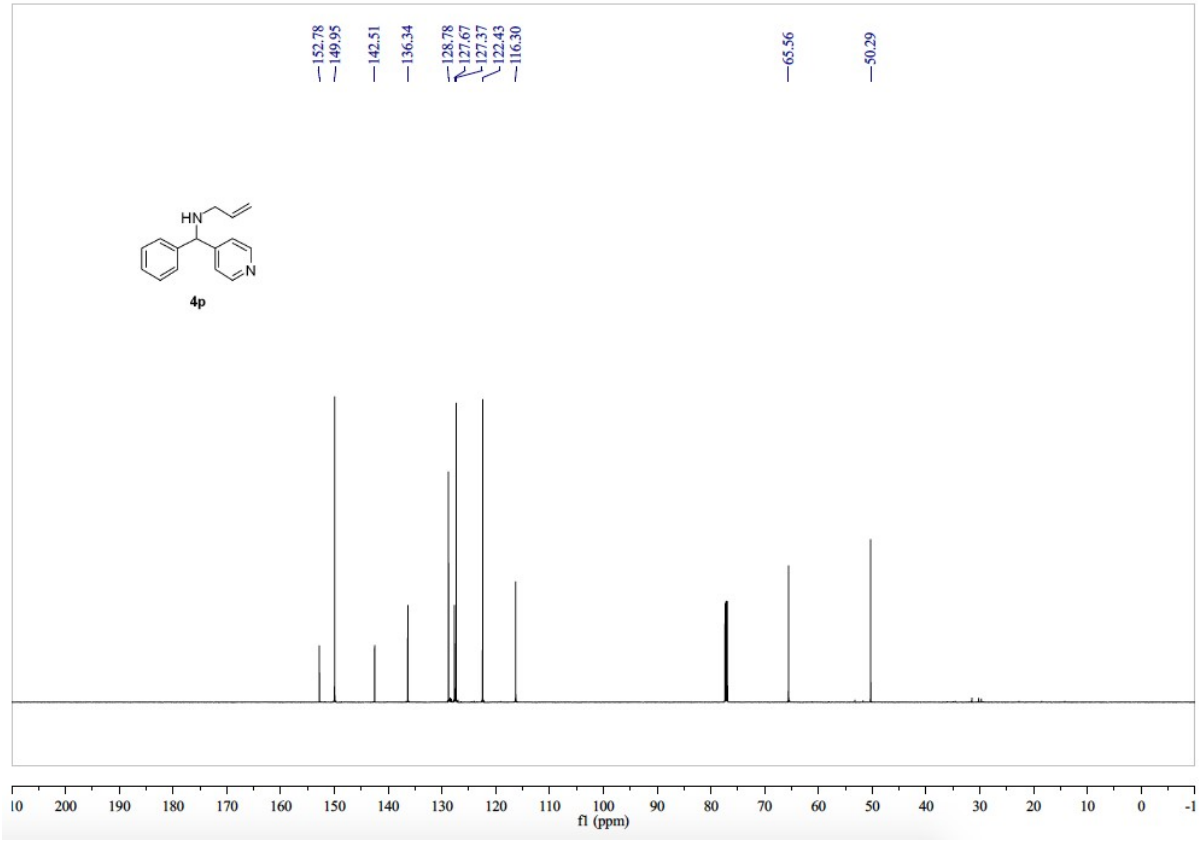
4o: *N*-(phenyl(pyridin-4-yl)methyl)adamantan-1-amine



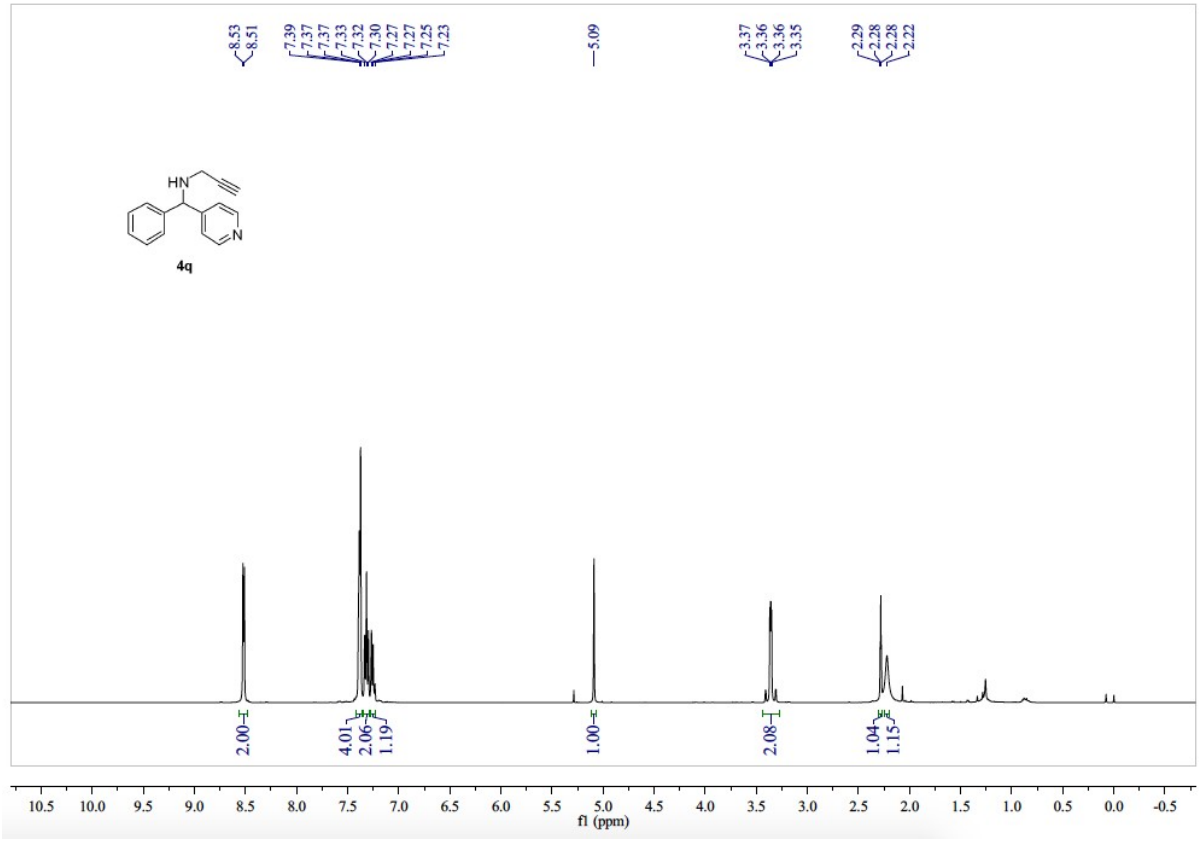


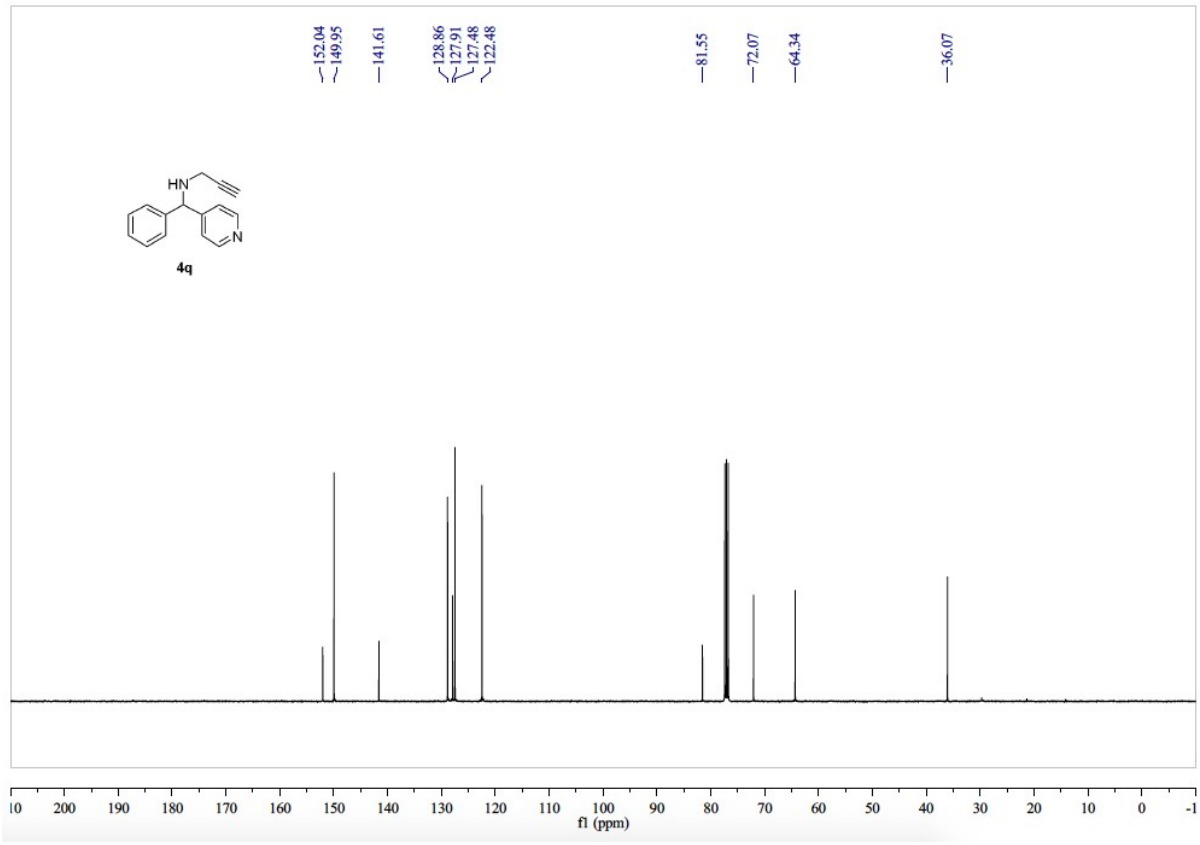
4p: *N*-(phenyl(pyridin-4-yl)methyl)prop-2-en-1-amine



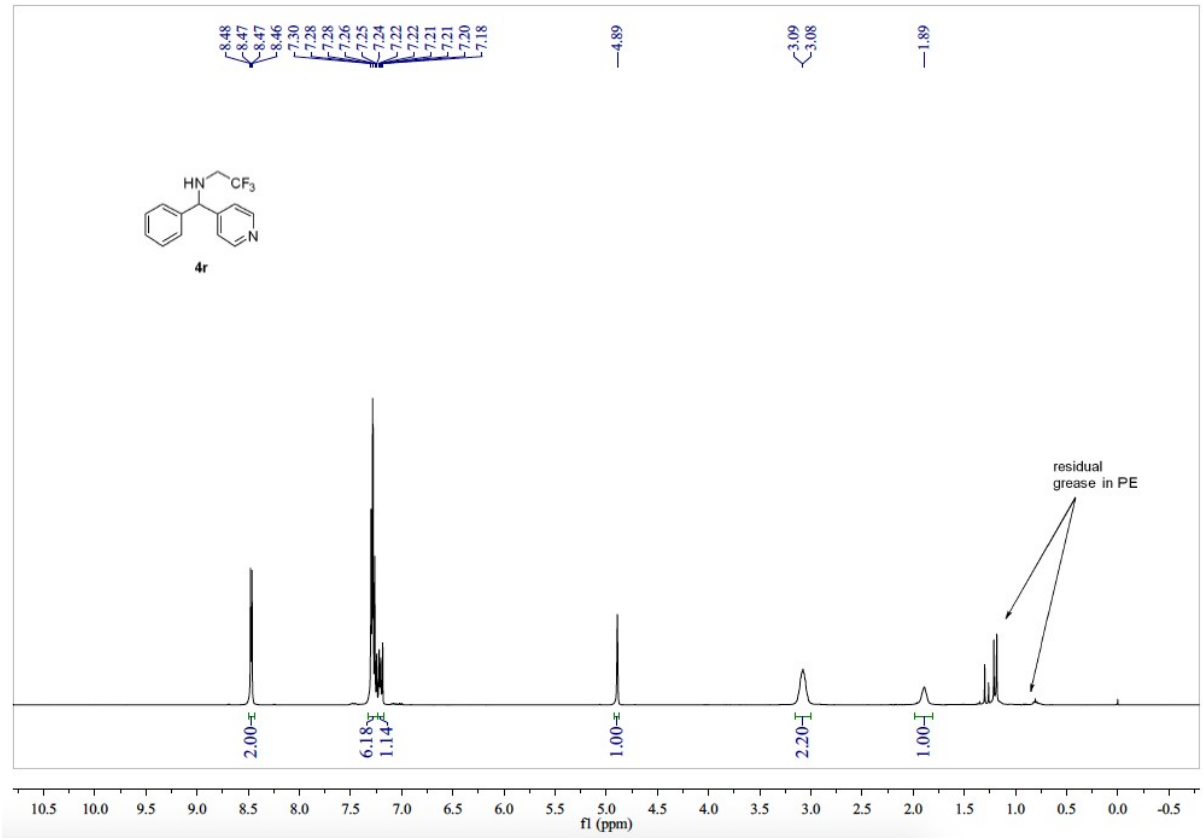


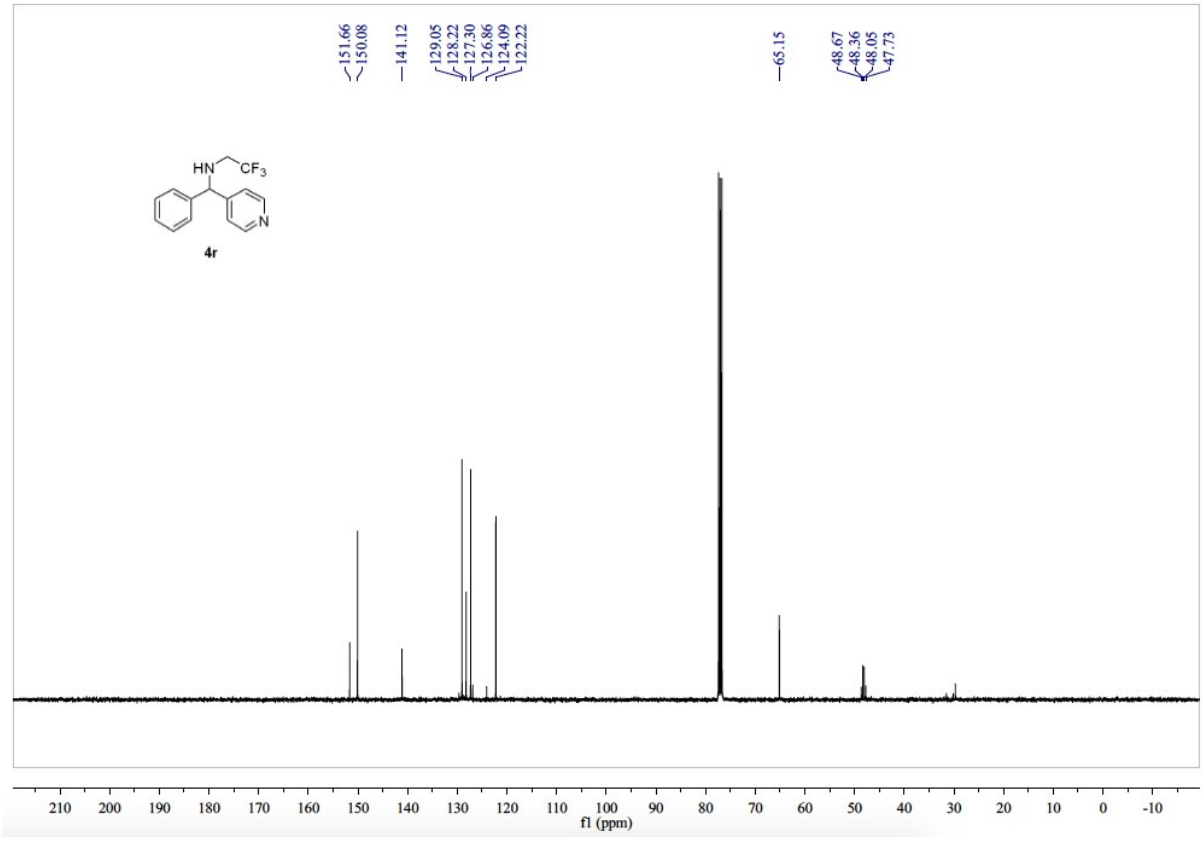
4q: *N*-(phenyl(pyridin-4-yl)methyl)prop-2-yn-1-amine

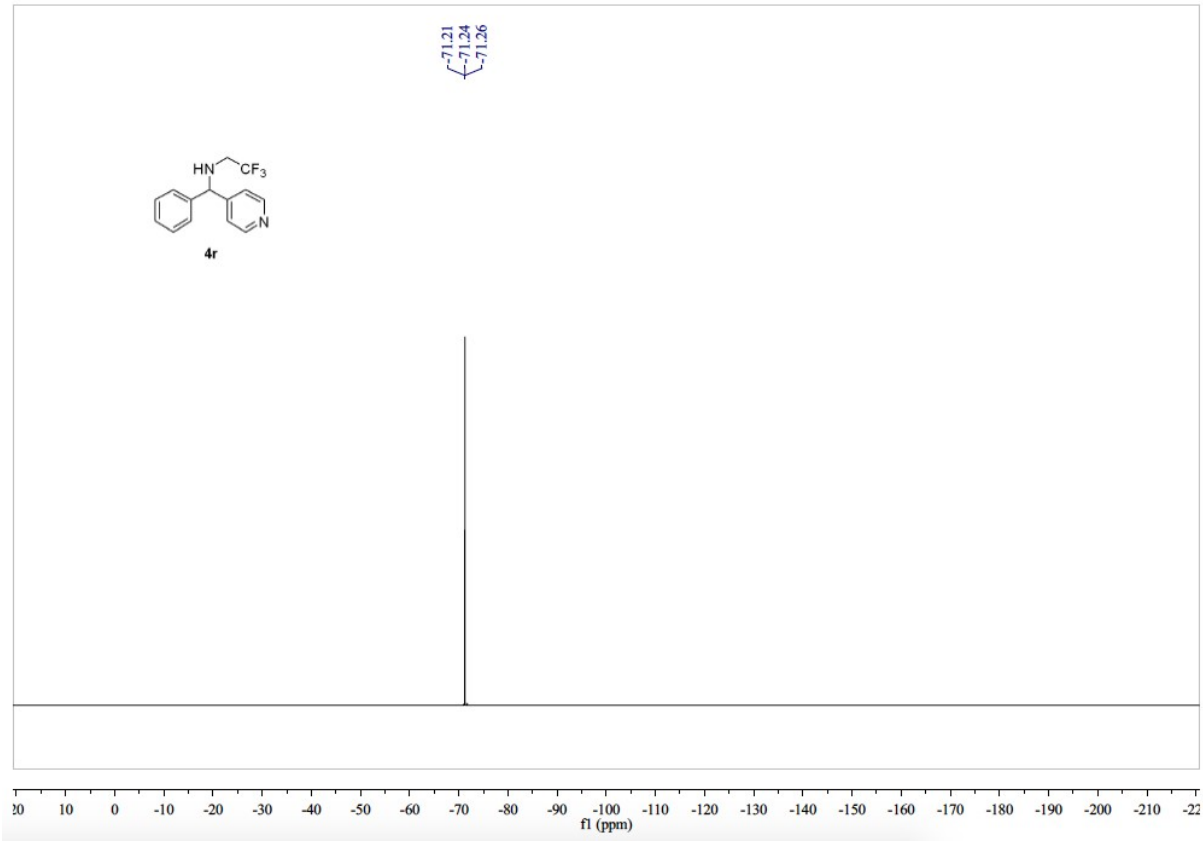




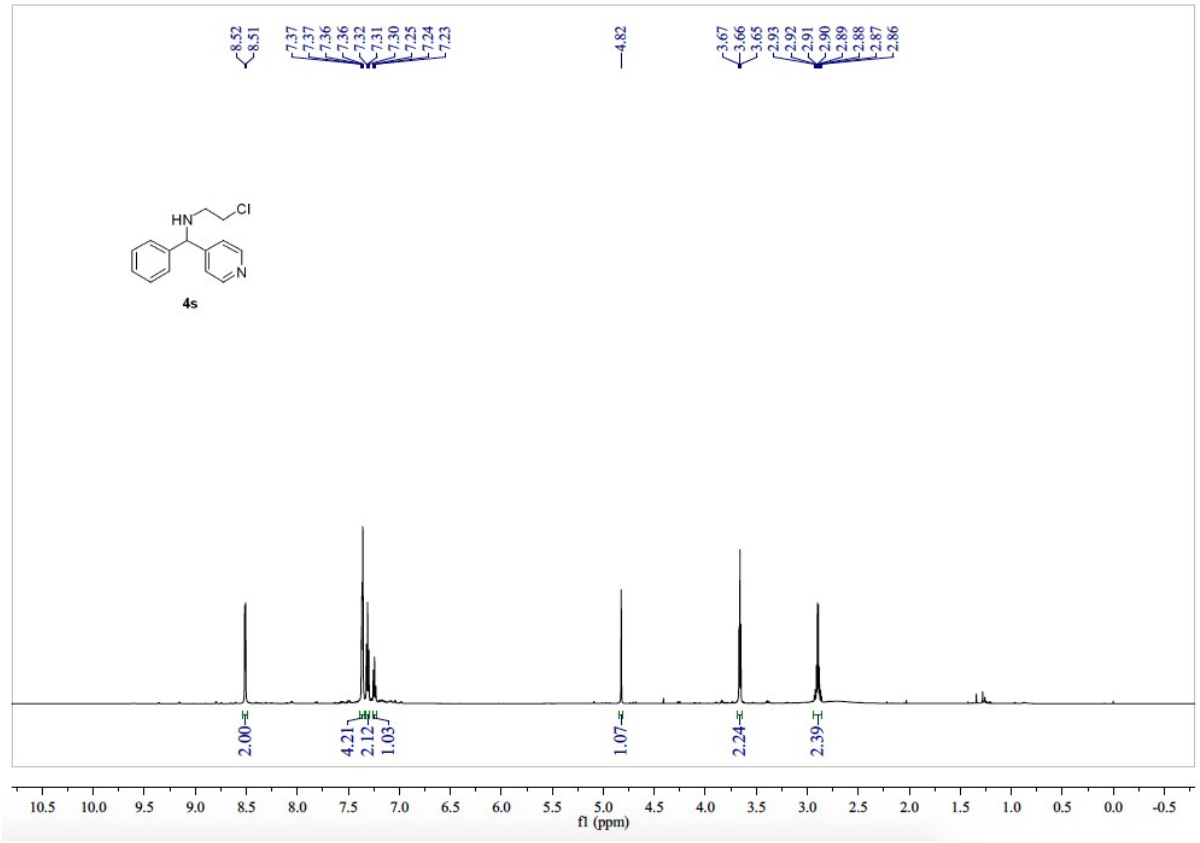
4r: 2,2,2-trifluoro-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine

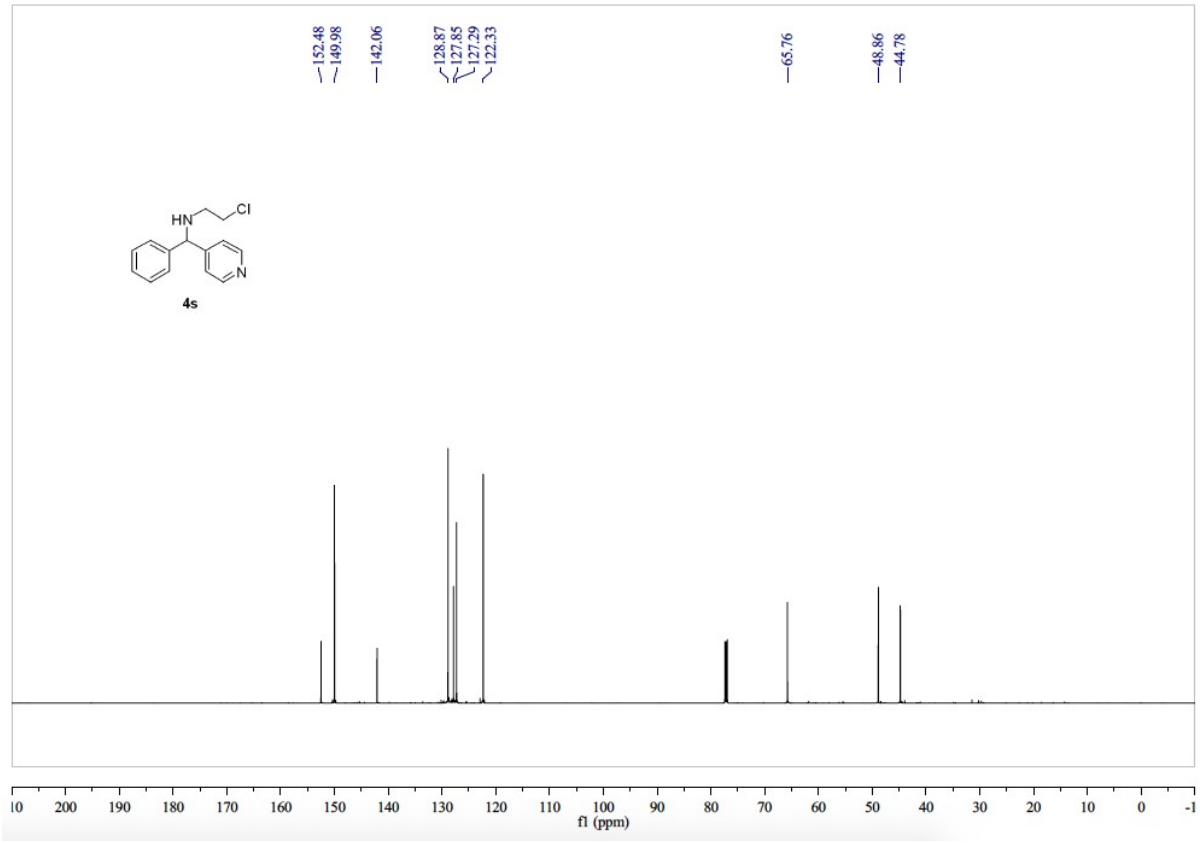



151.66
150.08
141.12
129.05
128.22
127.30
126.86
124.09
122.22
65.15
48.67
48.36
48.05
47.73
HN
CF3
N
4r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

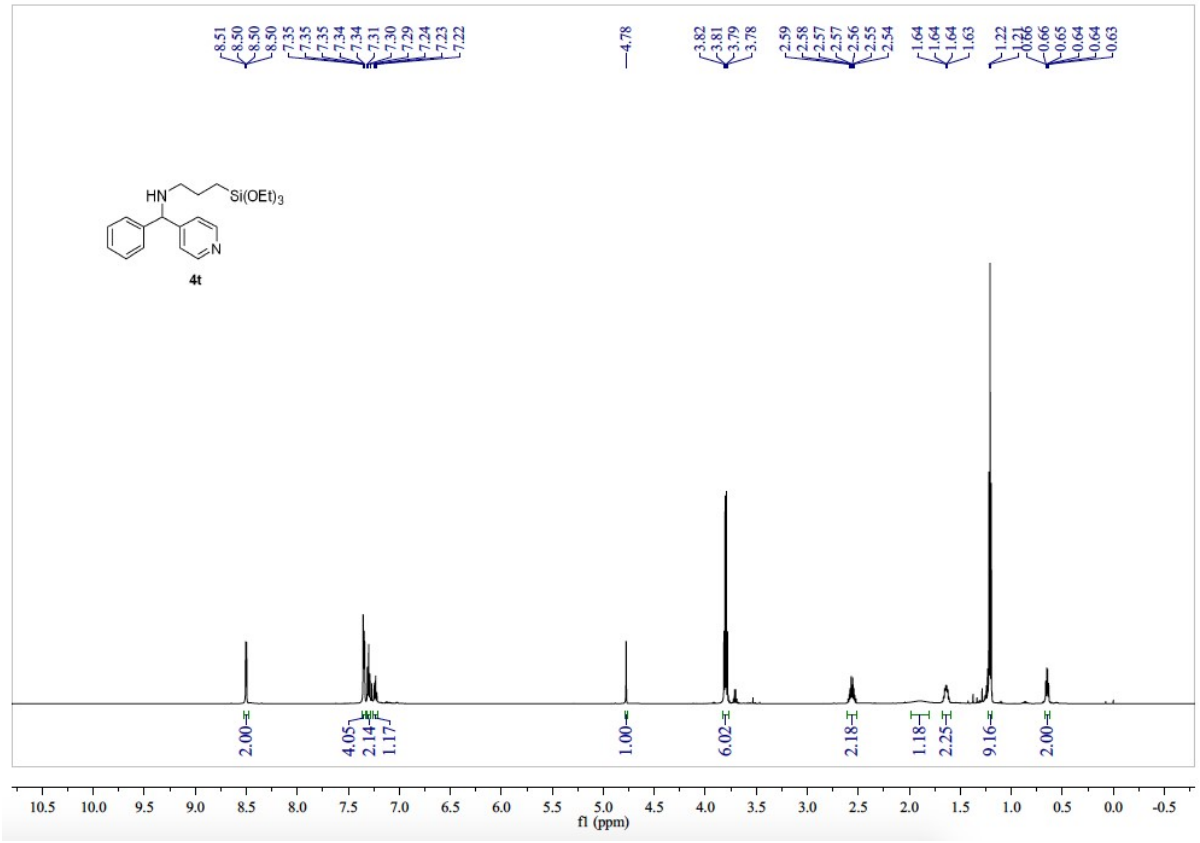

-71.21
-71.24
-71.26
HN
CF3
N
4r
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

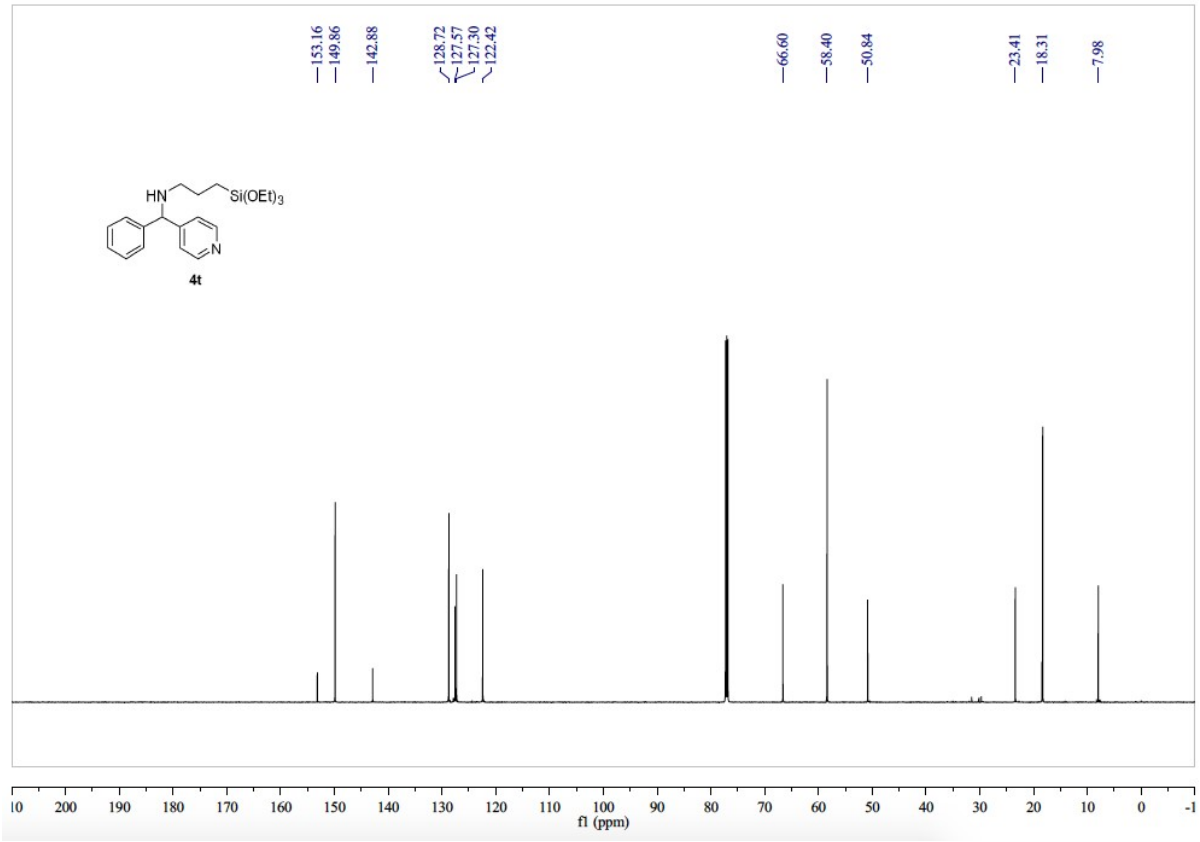
4s: 2-chloro-*N*-(phenyl(pyridin-4-yl)methyl)ethan-1-amine



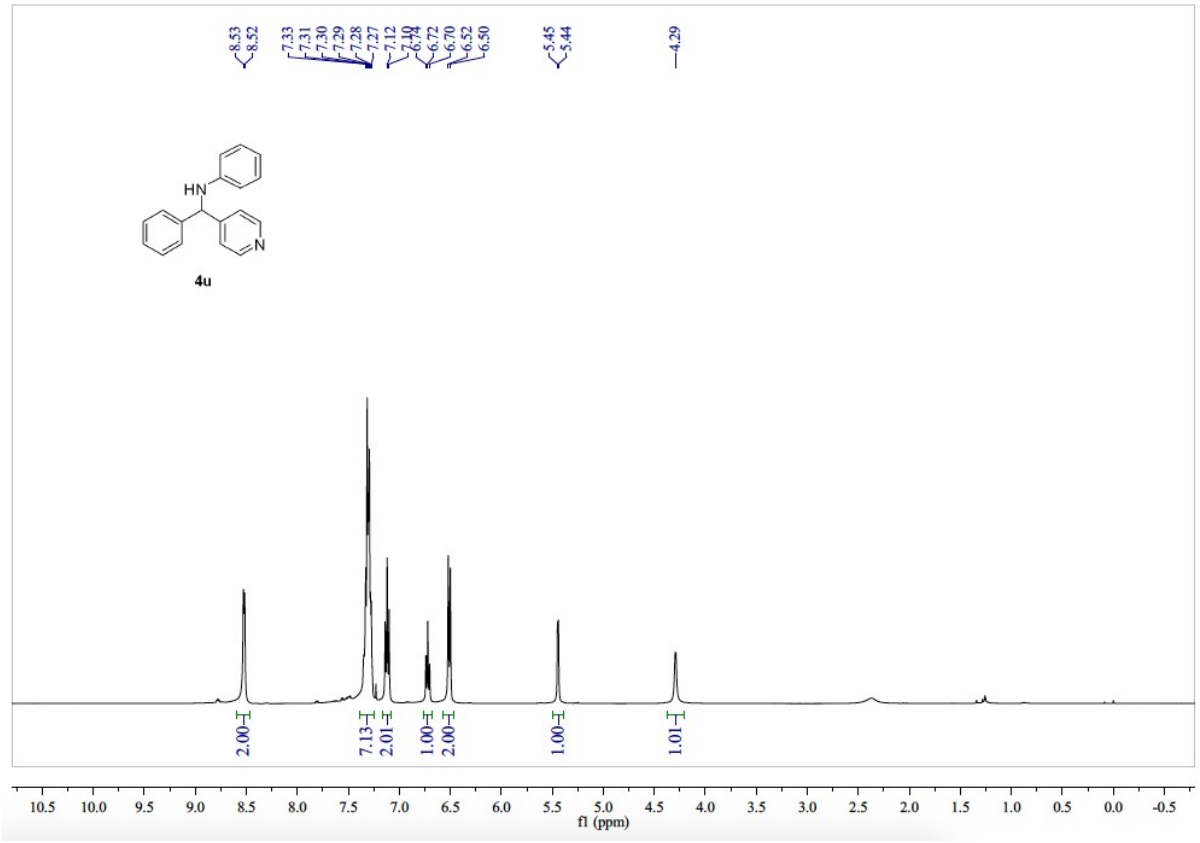


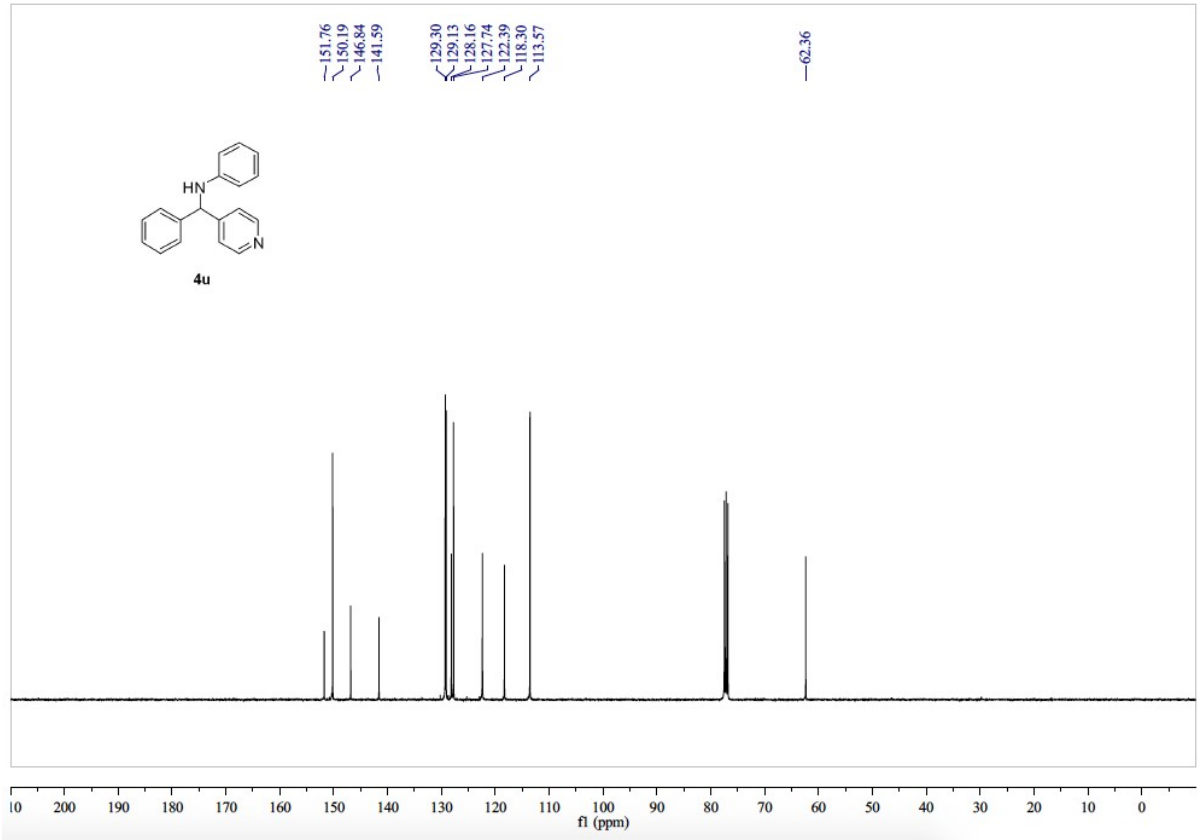
4t: *N*-(phenyl(pyridin-4-yl)methyl)-3-(triethoxysilyl)propan-1-amine



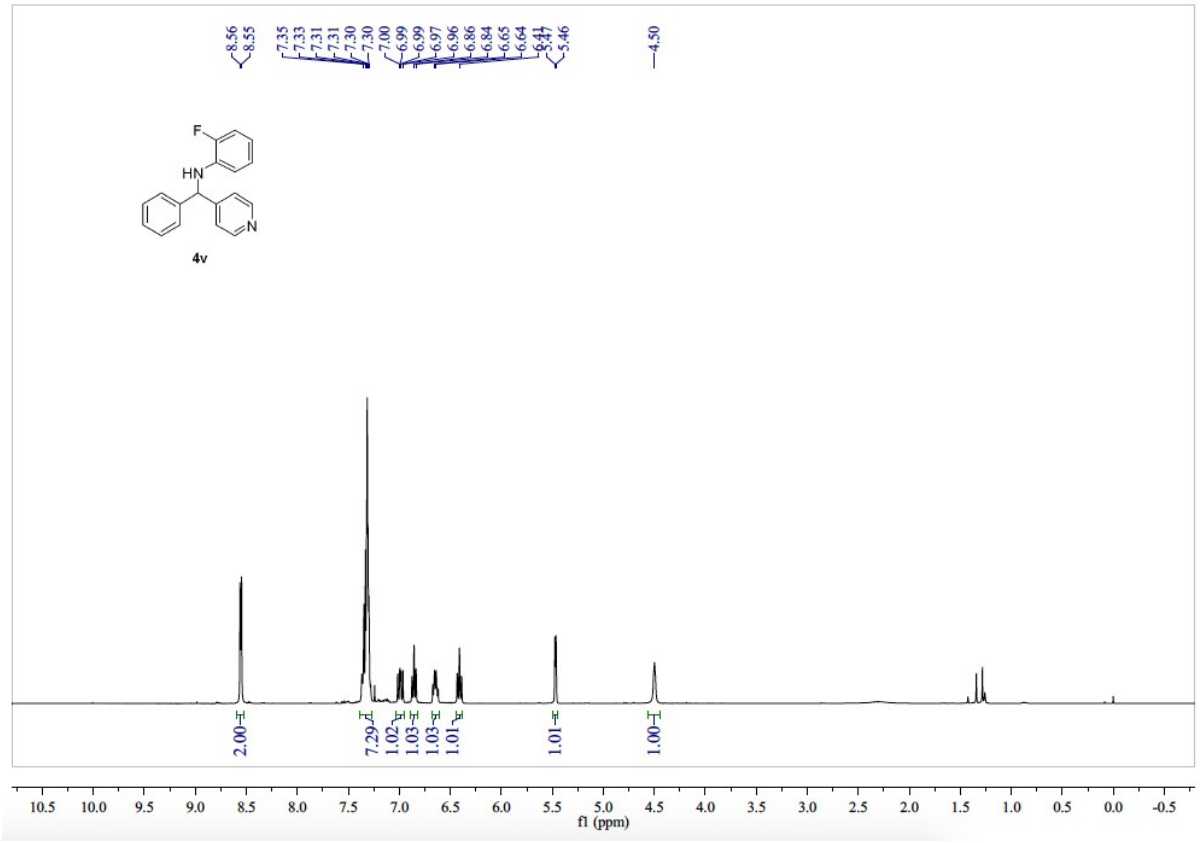


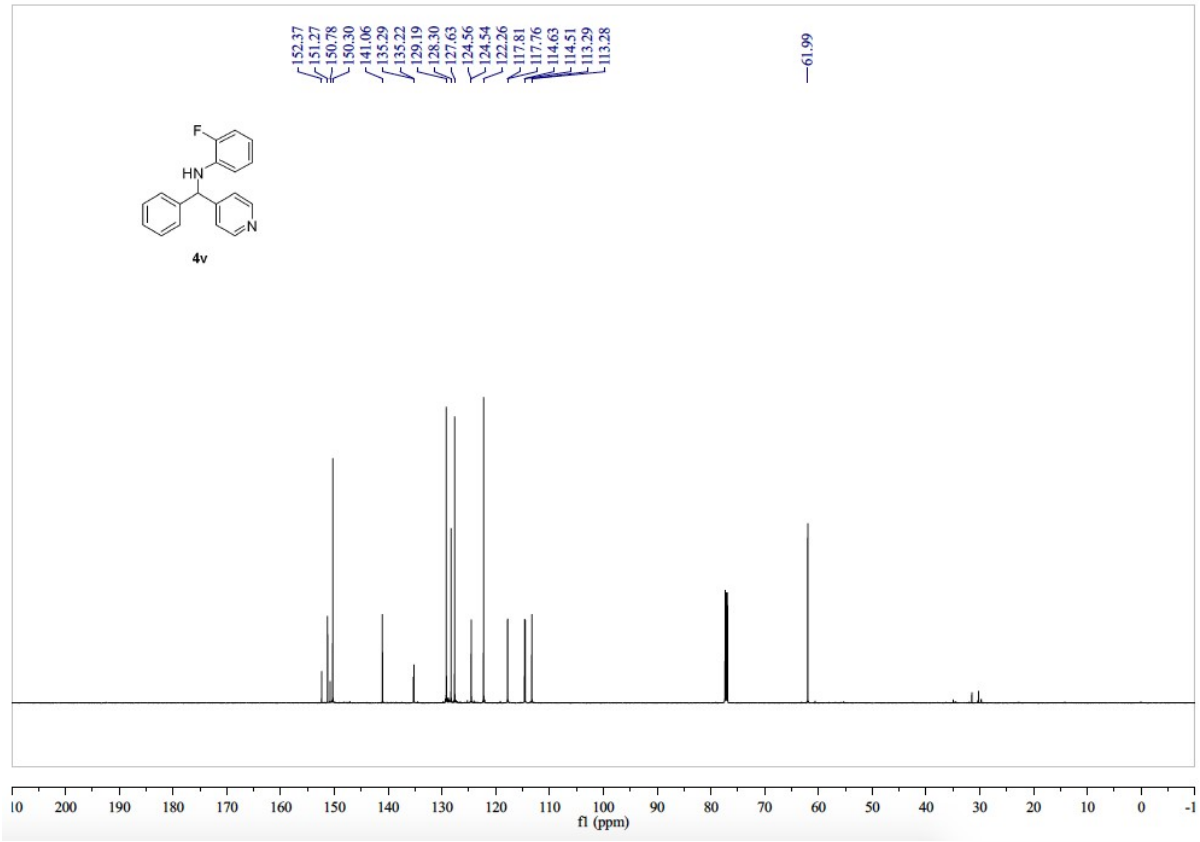
4u: *N*-(phenyl(pyridin-4-yl)methyl)aniline

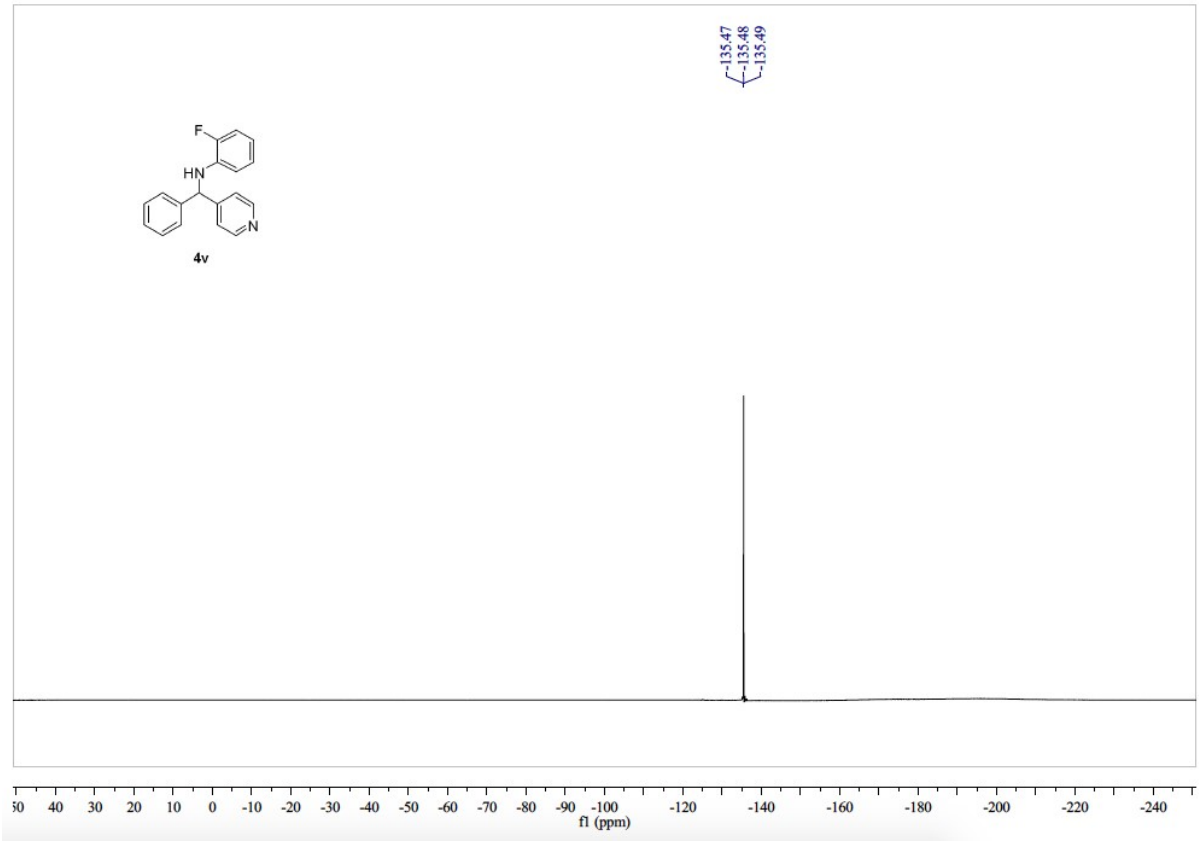




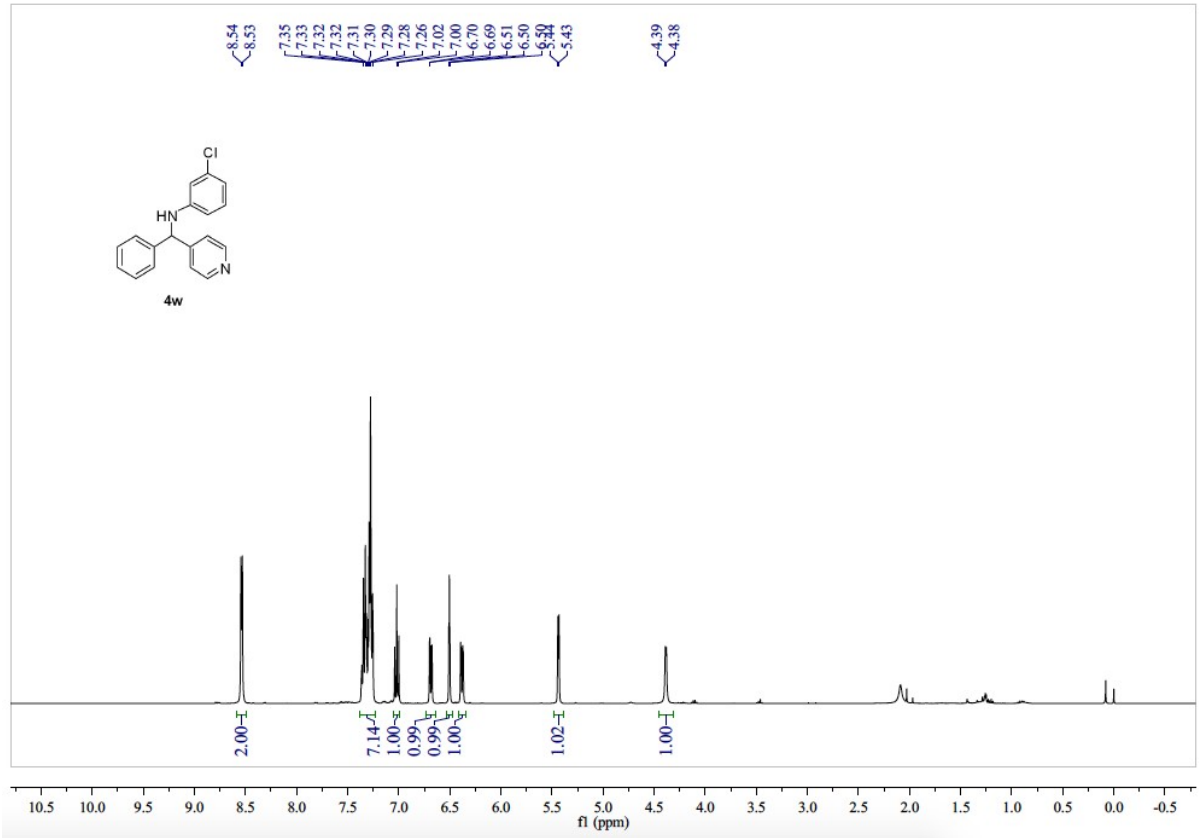
4v: 2-fluoro-*N*-(phenyl(pyridin-4-yl)methyl)aniline

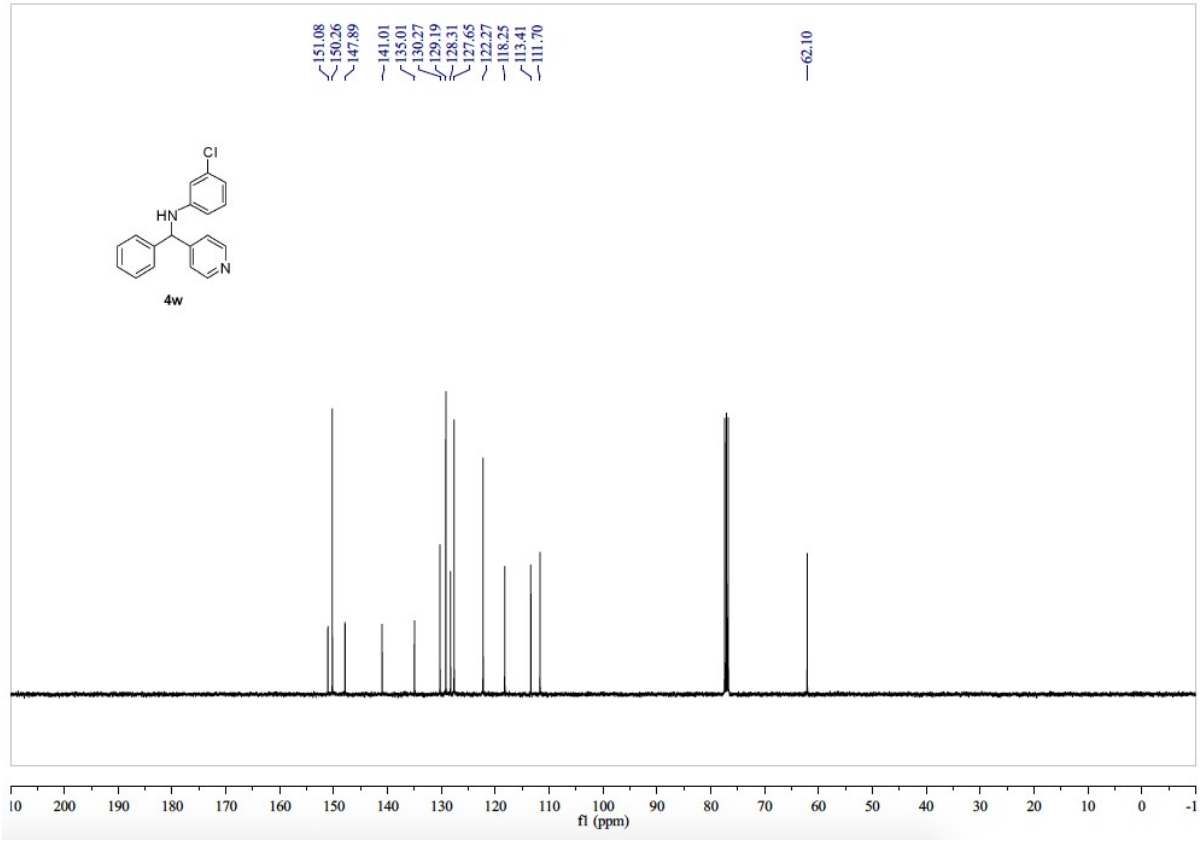




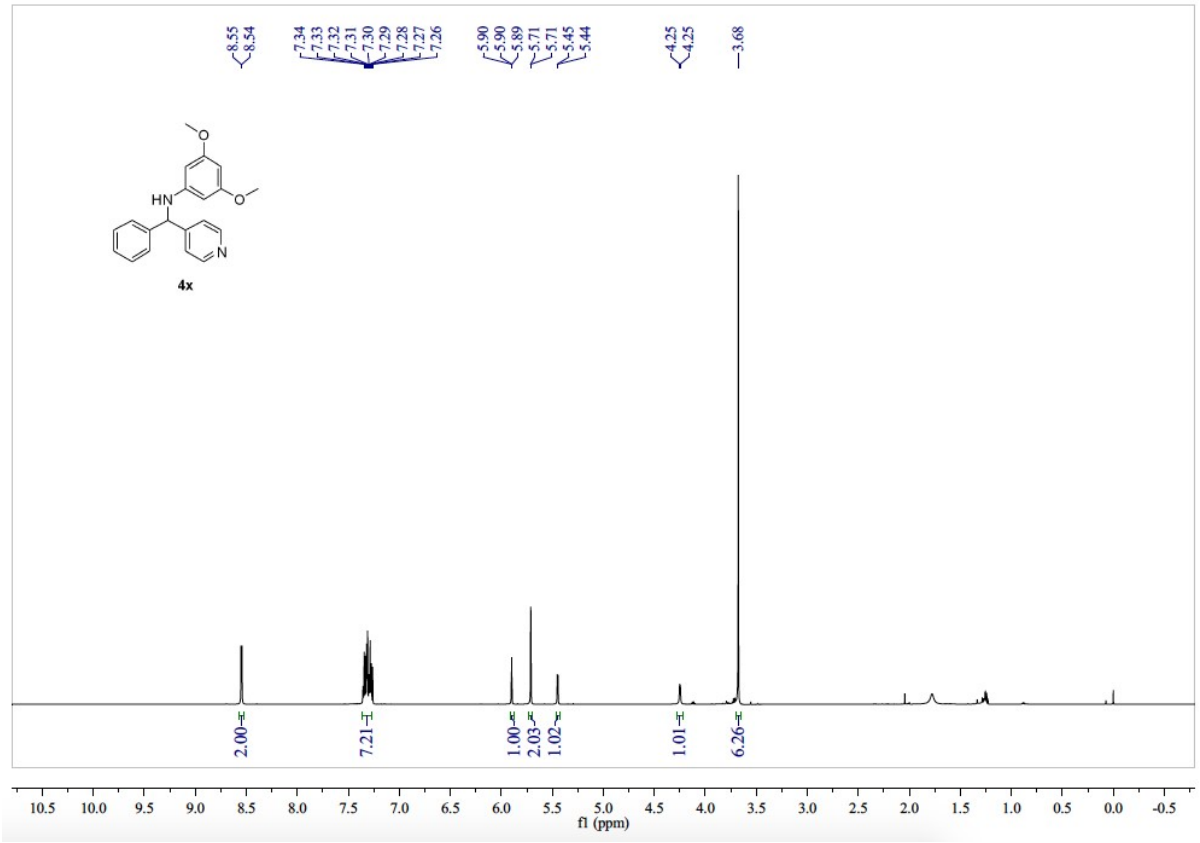


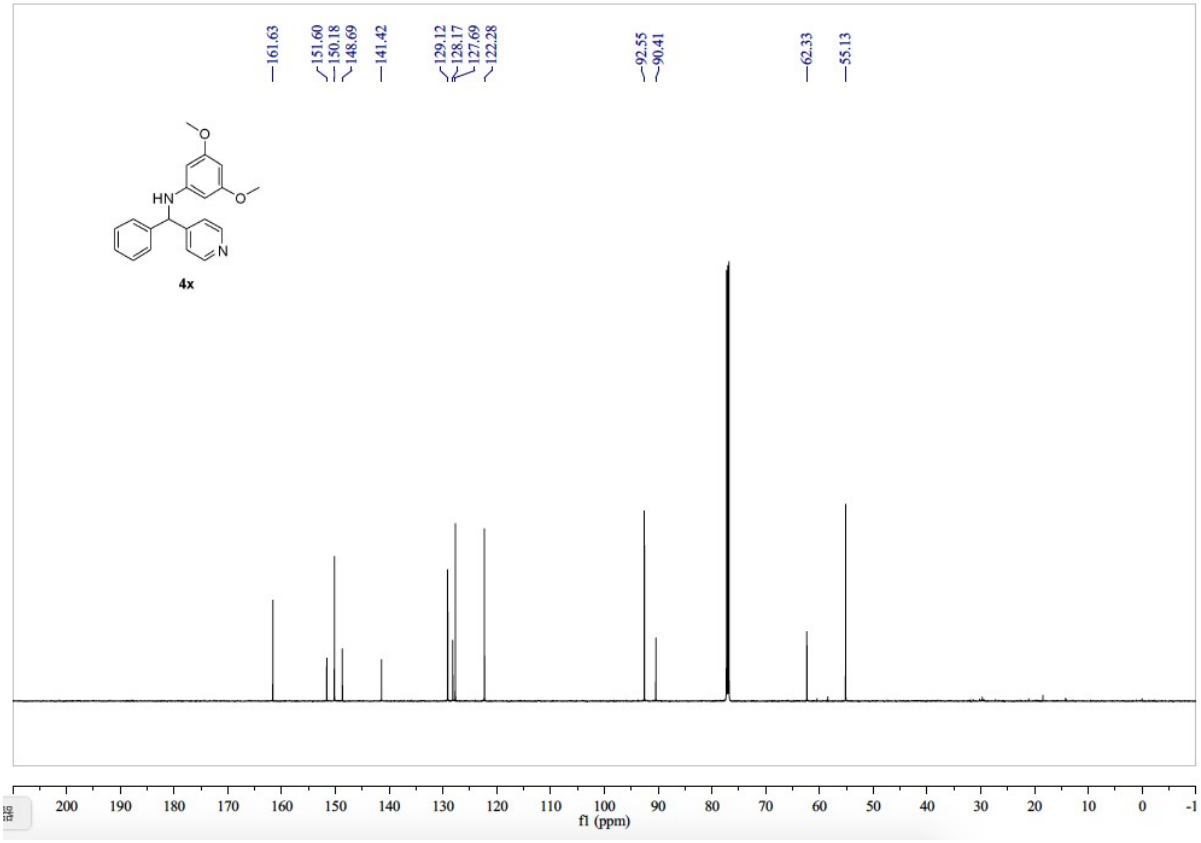
4w: 3-chloro-*N*-(phenyl(pyridin-4-yl)methyl)aniline



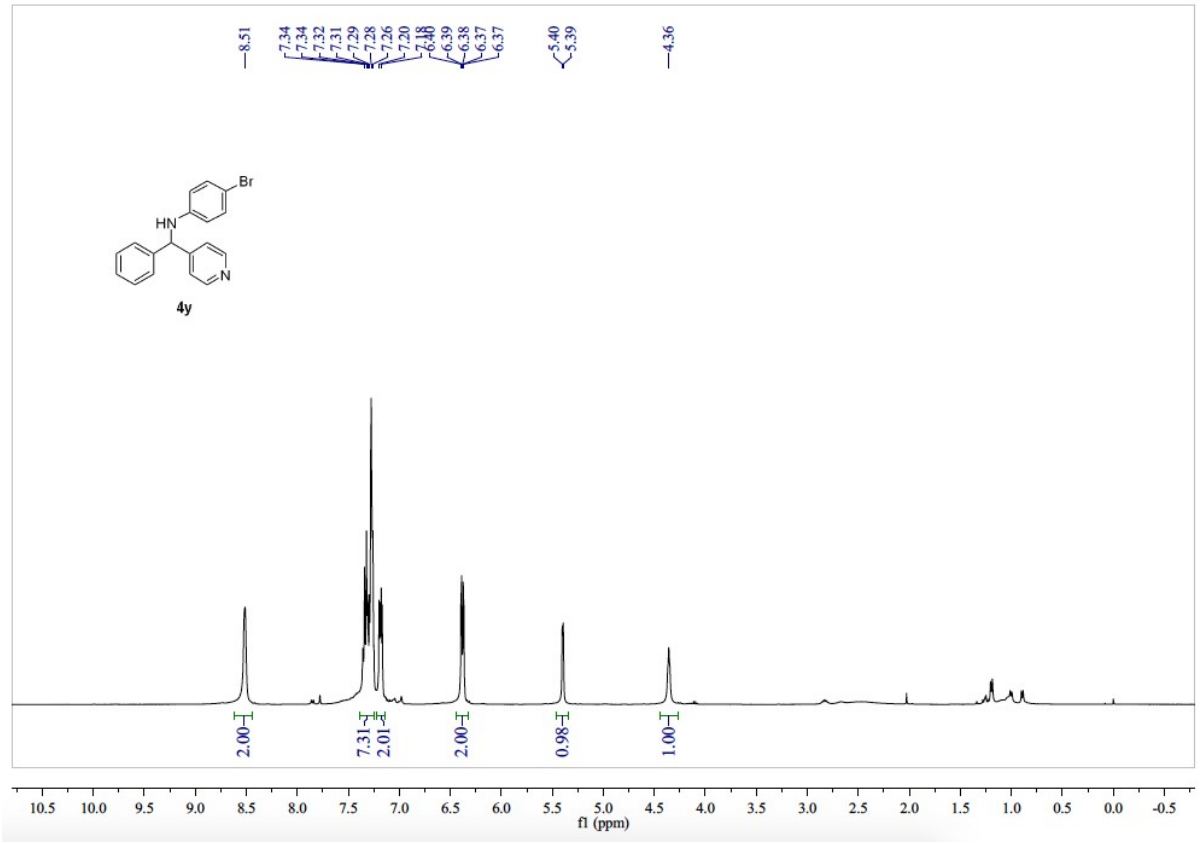


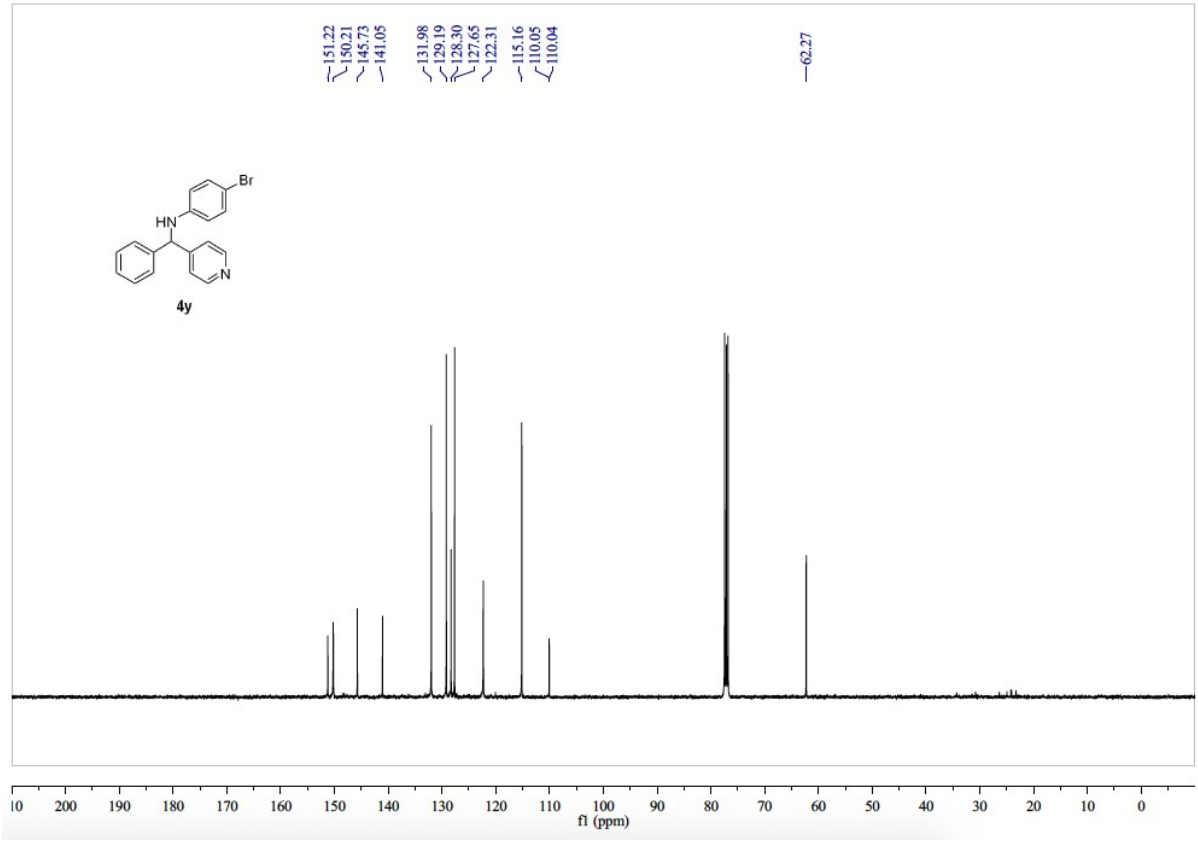
4x: 3,5-dimethoxy-*N*-(phenyl(pyridin-4-yl)methyl)aniline



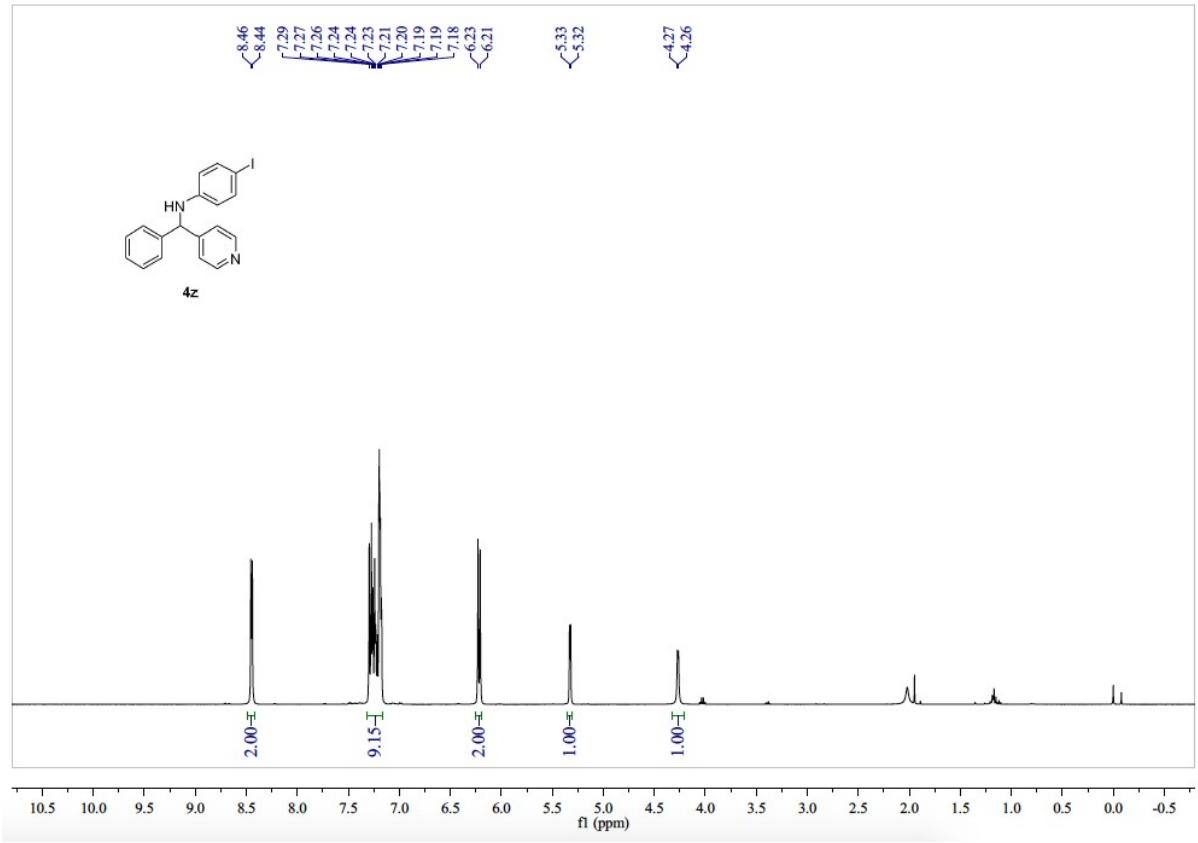


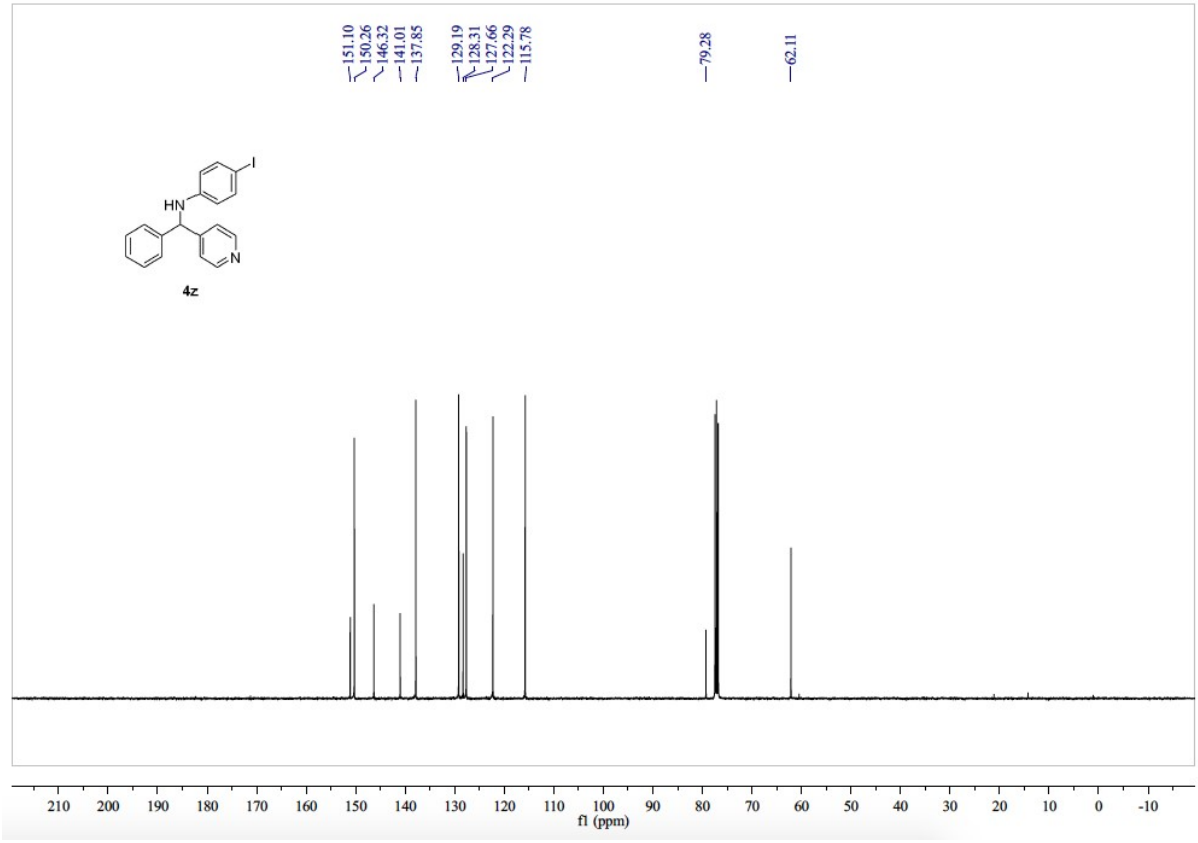
4y: 4-bromo-*N*-(phenyl(pyridin-4-yl)methyl)aniline



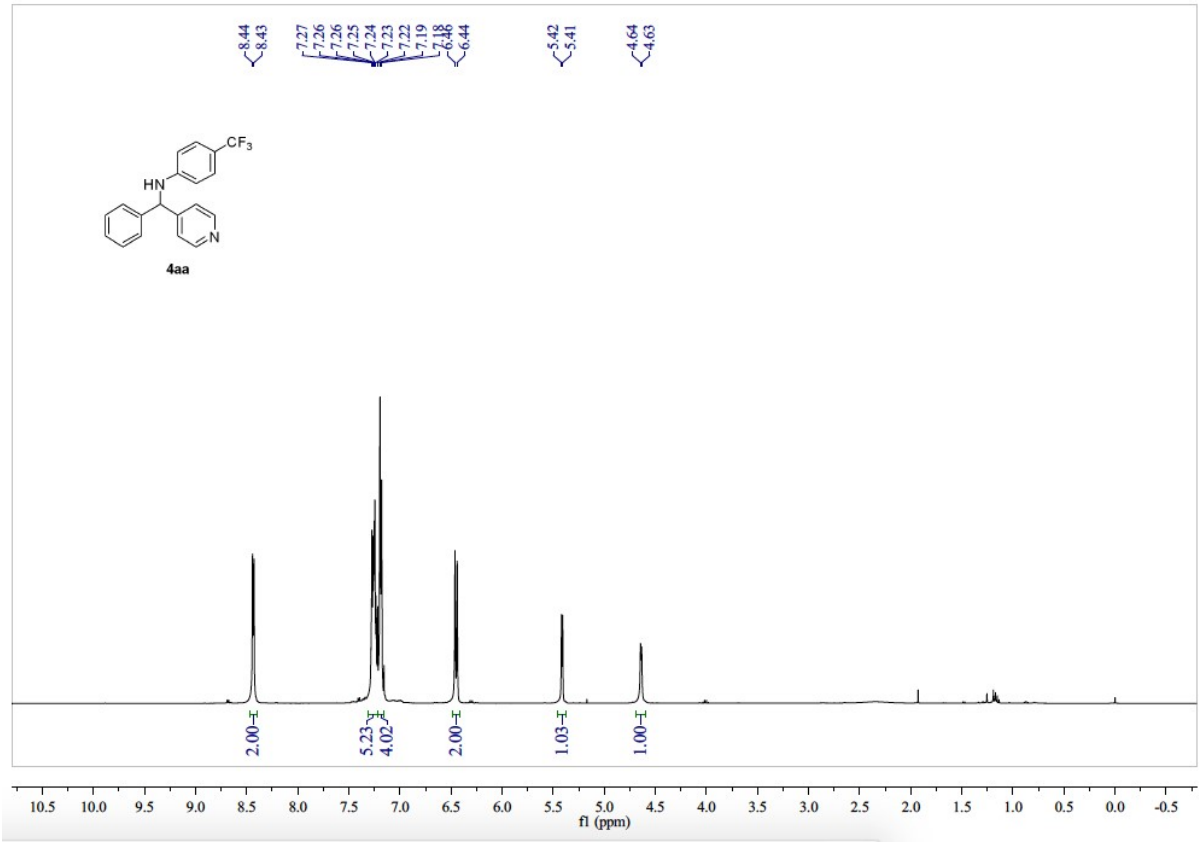


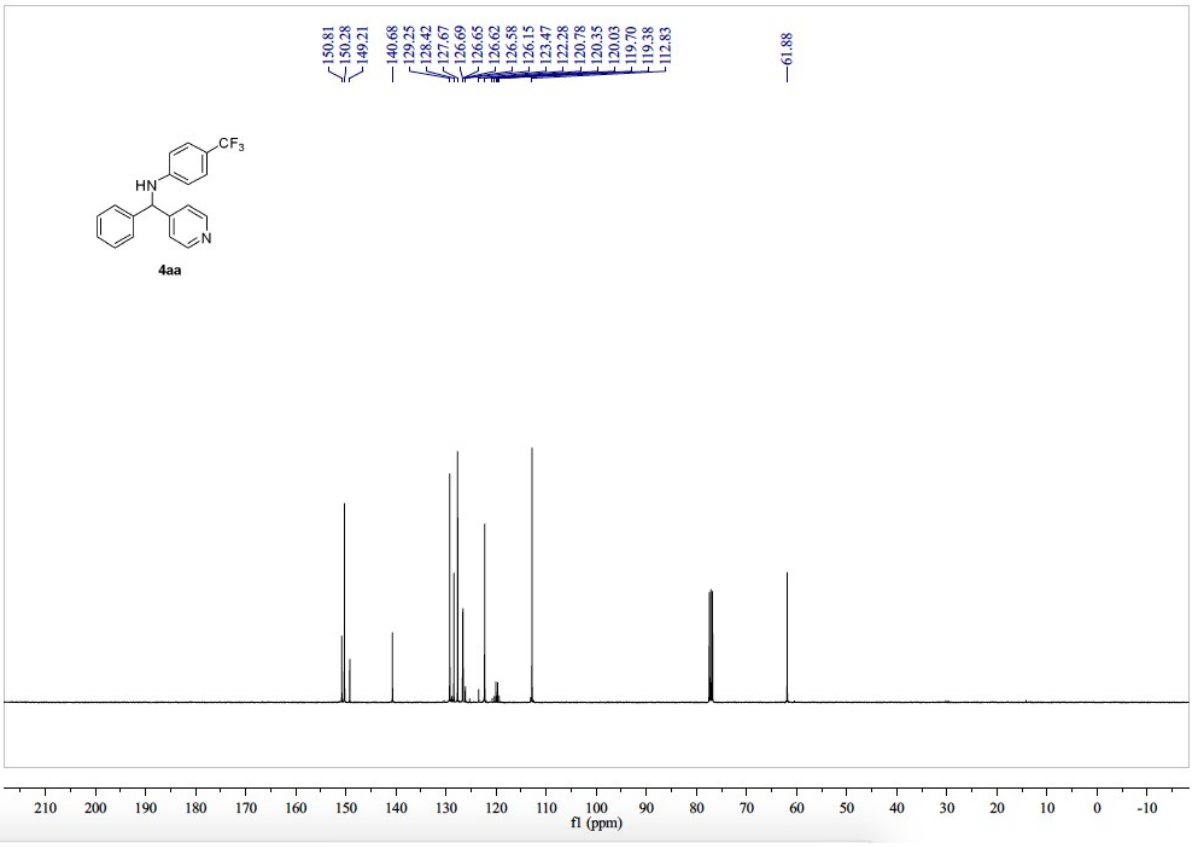
4z: 4-iodo-*N*-(phenyl(pyridin-4-yl)methyl)aniline





4aa: *N*-(phenyl(pyridin-4-yl)methyl)-4-(trifluoromethyl)aniline

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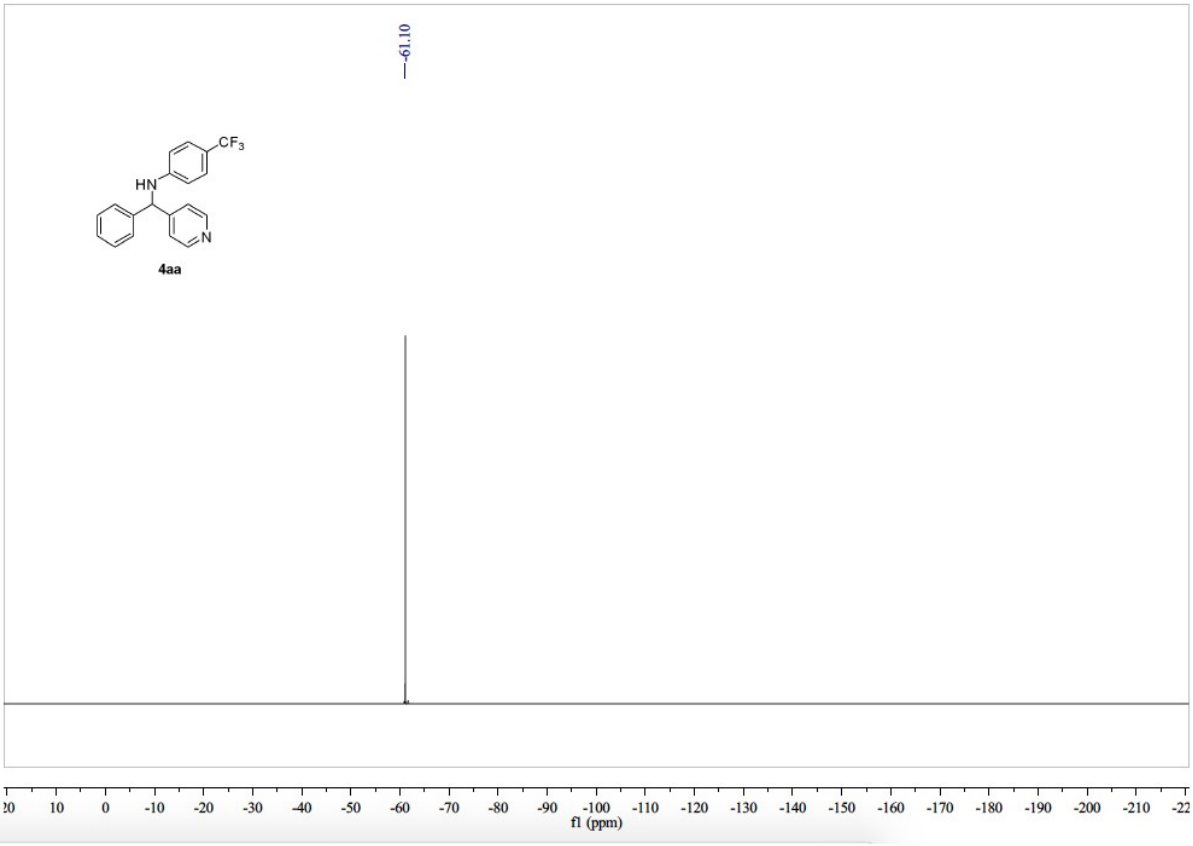
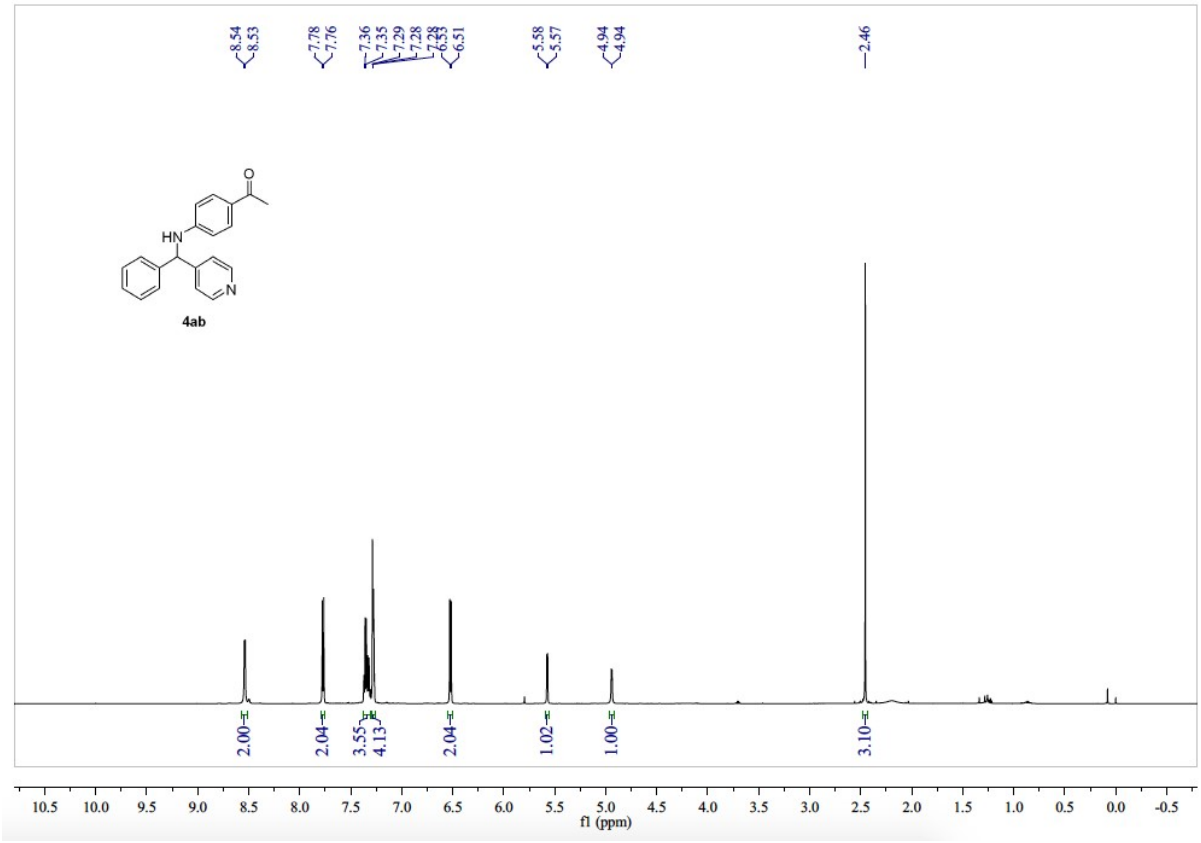
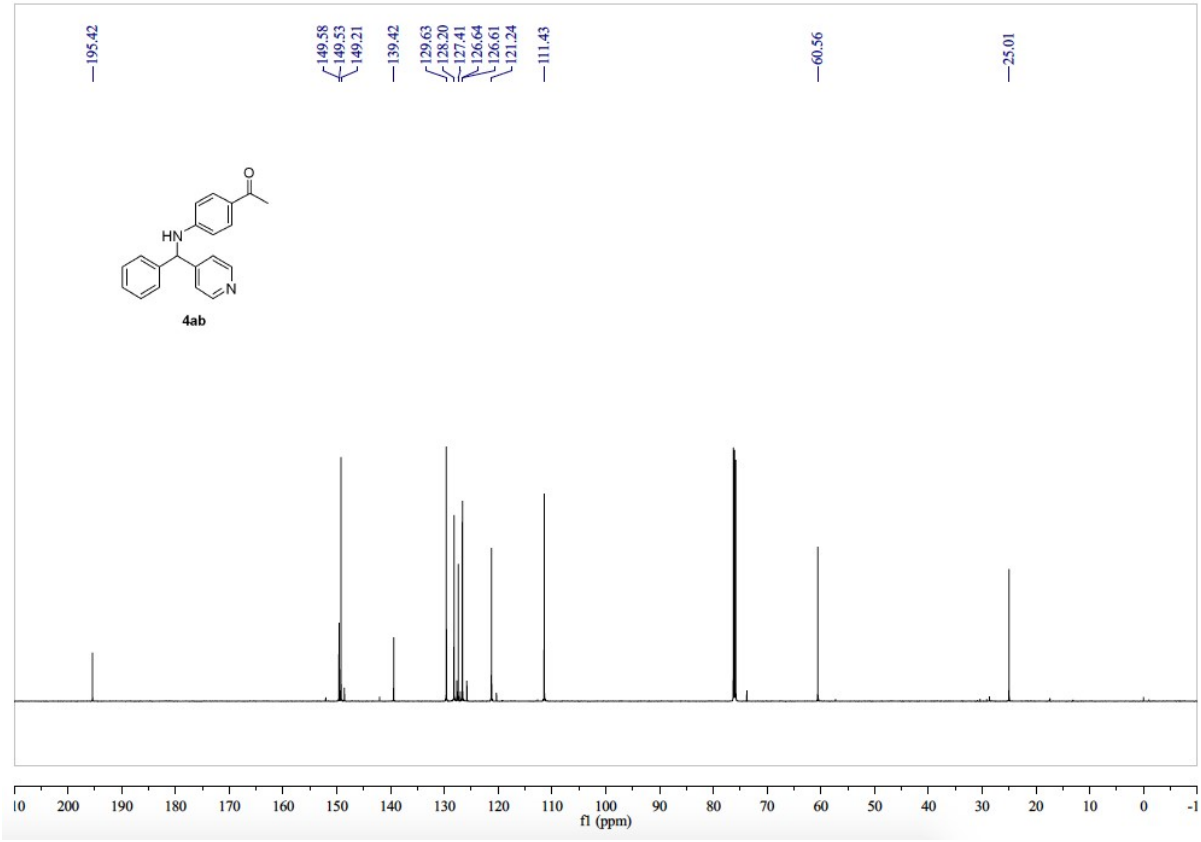
150.28
149.21
140.68
129.25
128.42
127.67
126.69
126.65
126.62
126.58
126.15
123.47
122.28
120.78
120.35
120.03
119.70
119.38
112.83
61.88
CF3
HN
N
4aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


61.10
CF3
HN
N
4aa
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

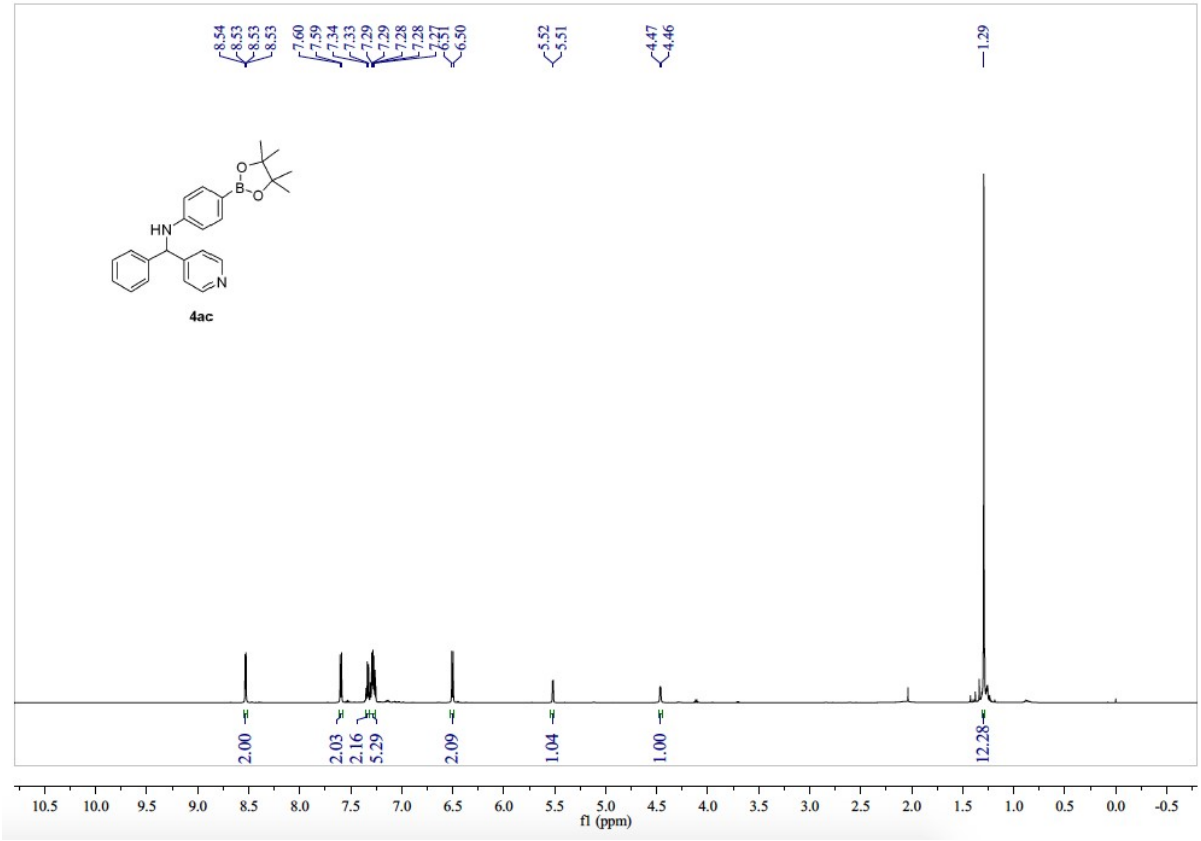
4ab: 1-(4-((phenyl(pyridin-4-yl)methyl)amino)phenyl)ethan-1-one

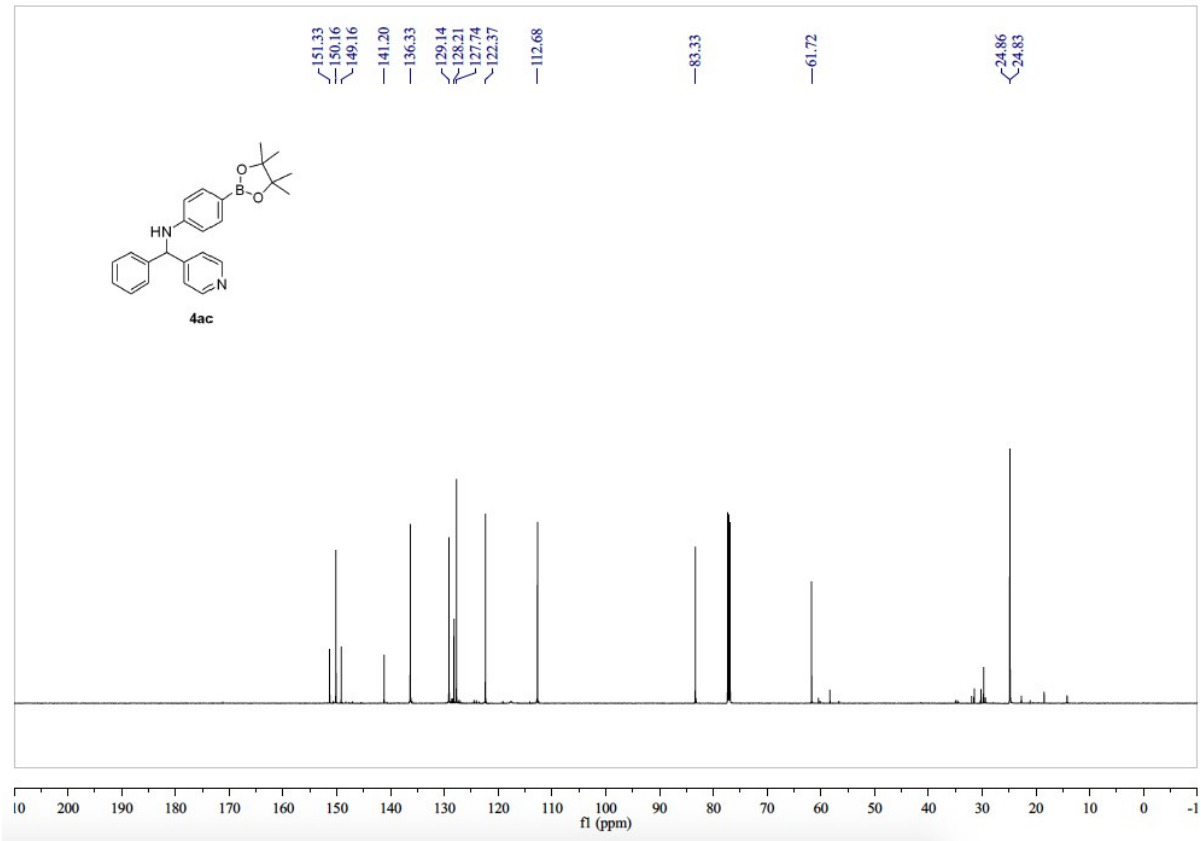




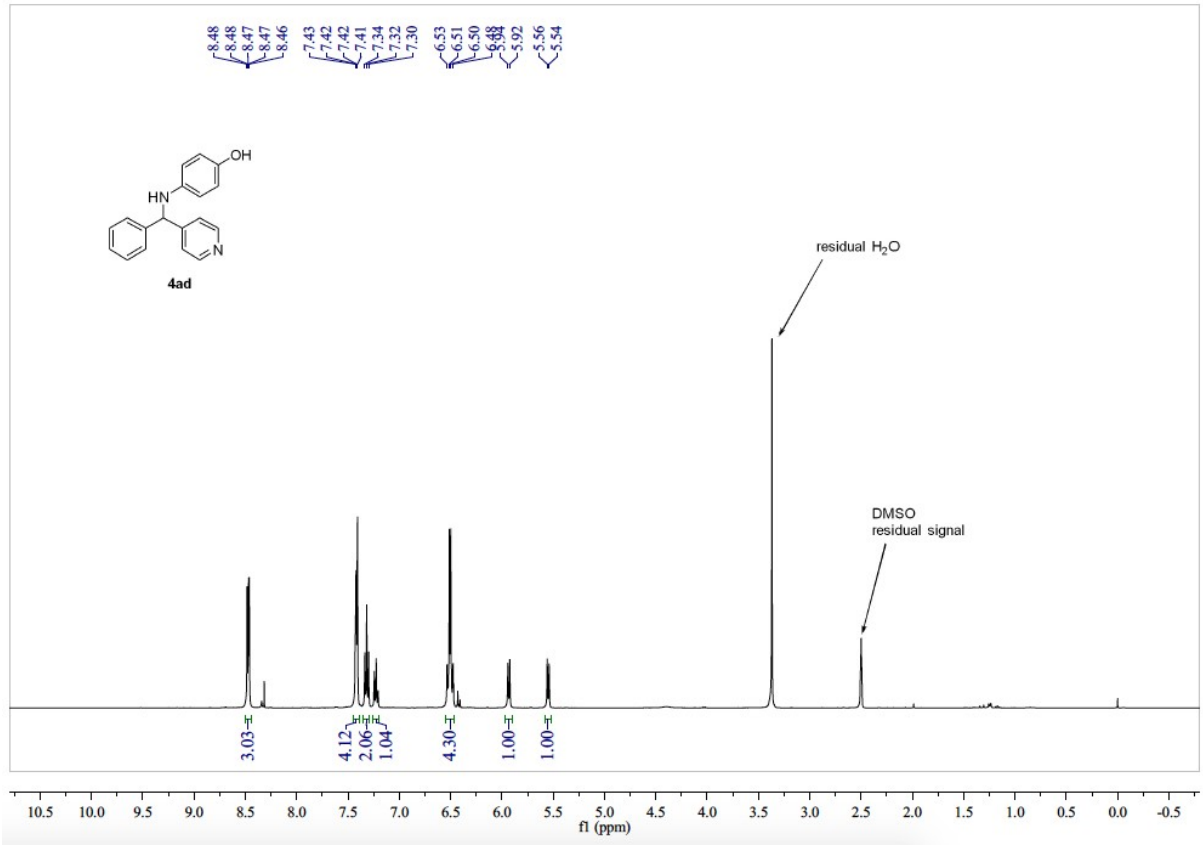
4ac:

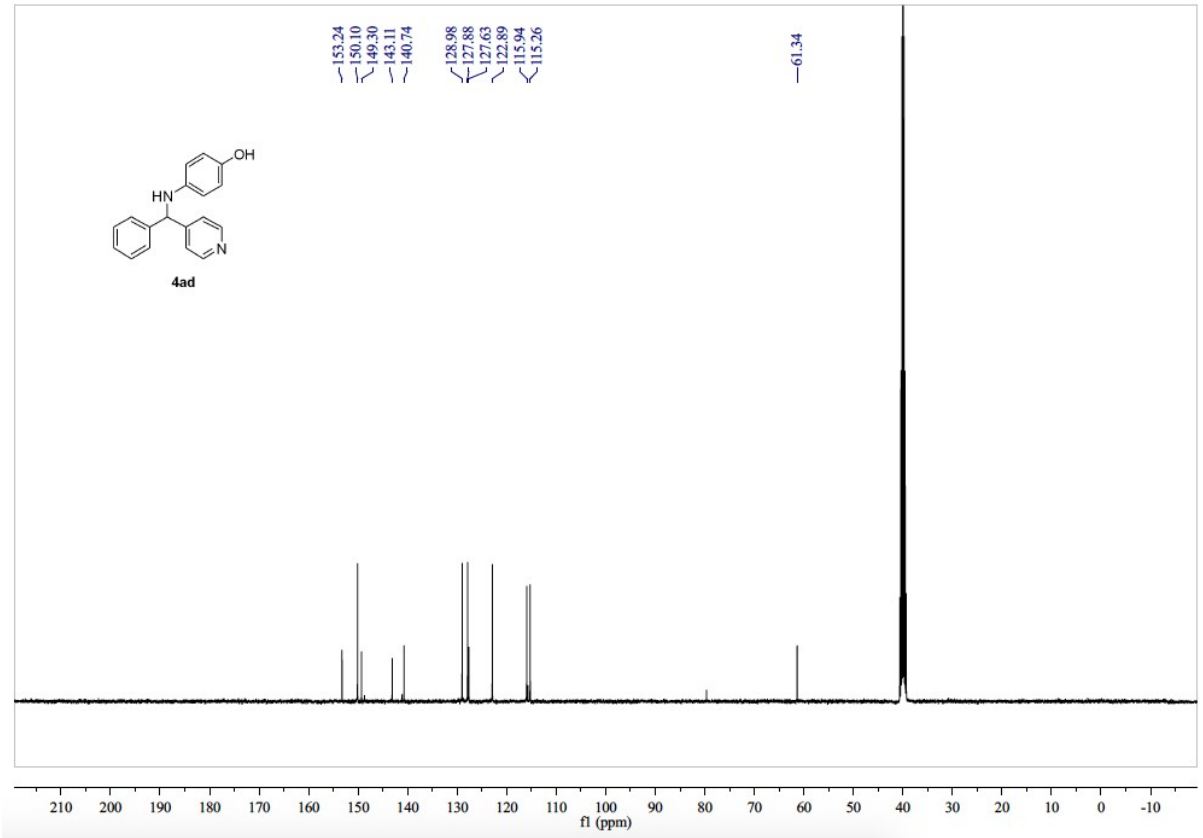
***N*-(phenyl(pyridin-4-yl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline**



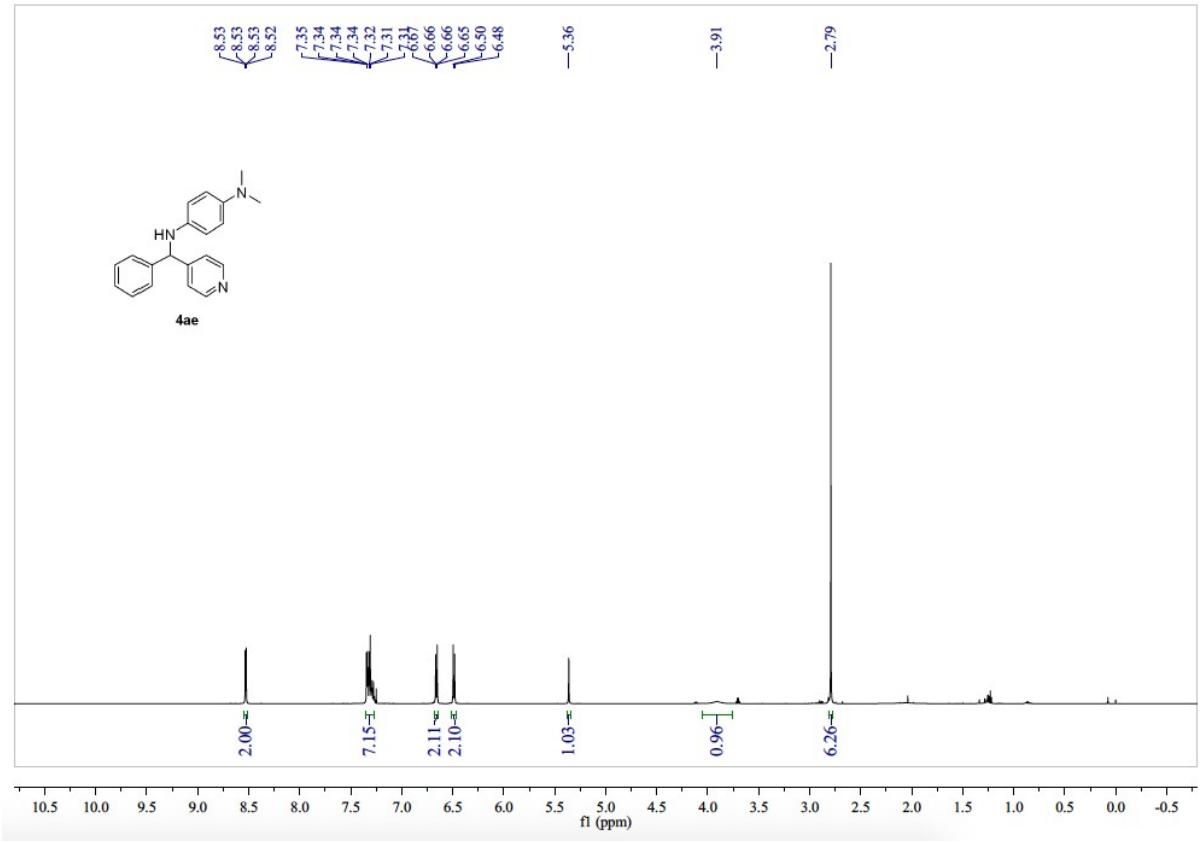


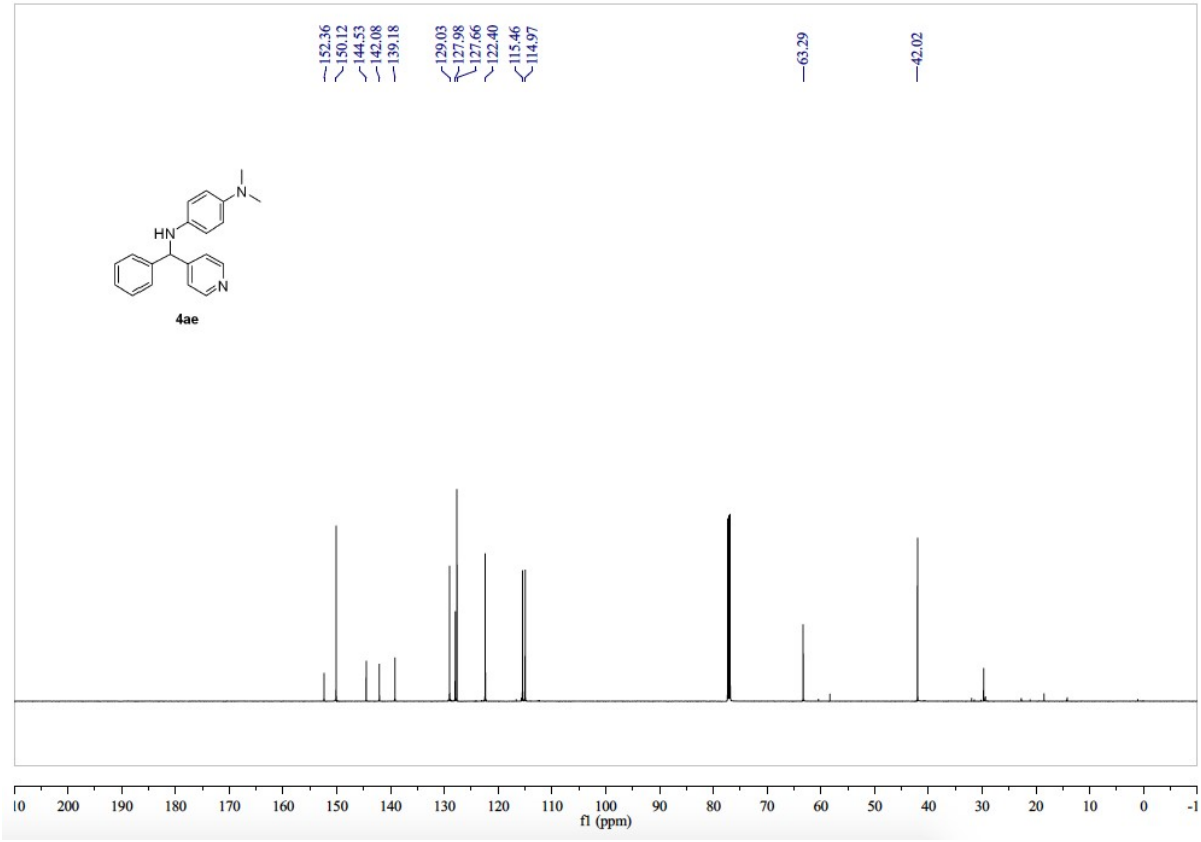
4ad: 4-((phenyl(pyridin-4-yl)methyl)amino)phenol



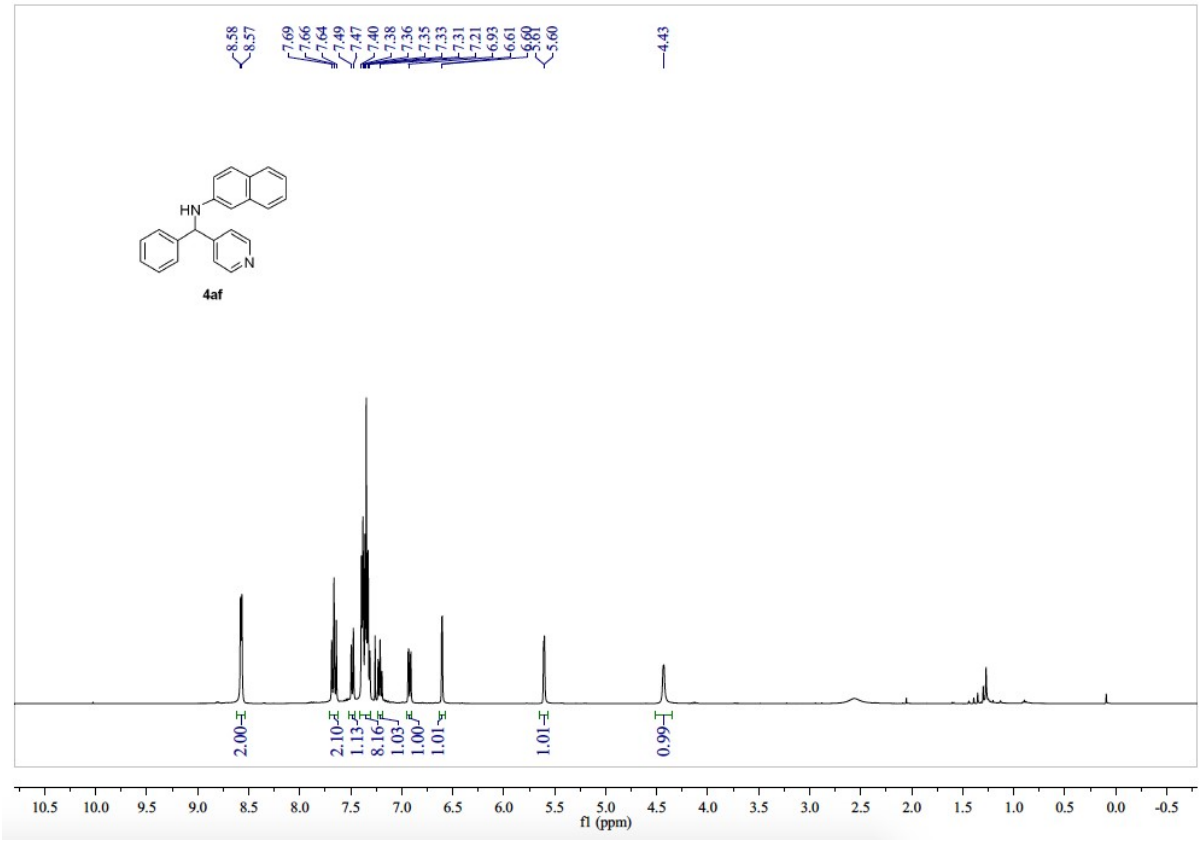


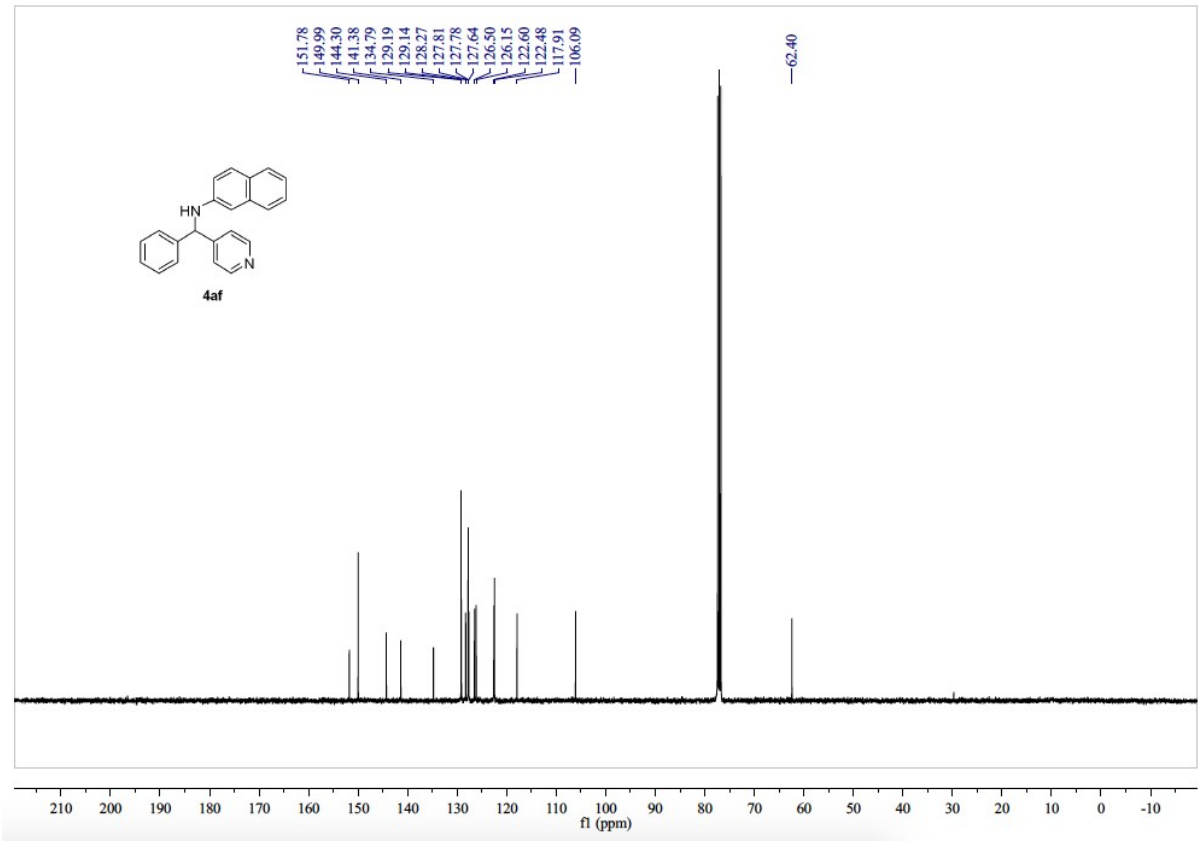
4ae: N^1,N^1-dimethyl-N^4-(phenyl(pyridin-4-yl)methyl)benzene-1,4-diamine



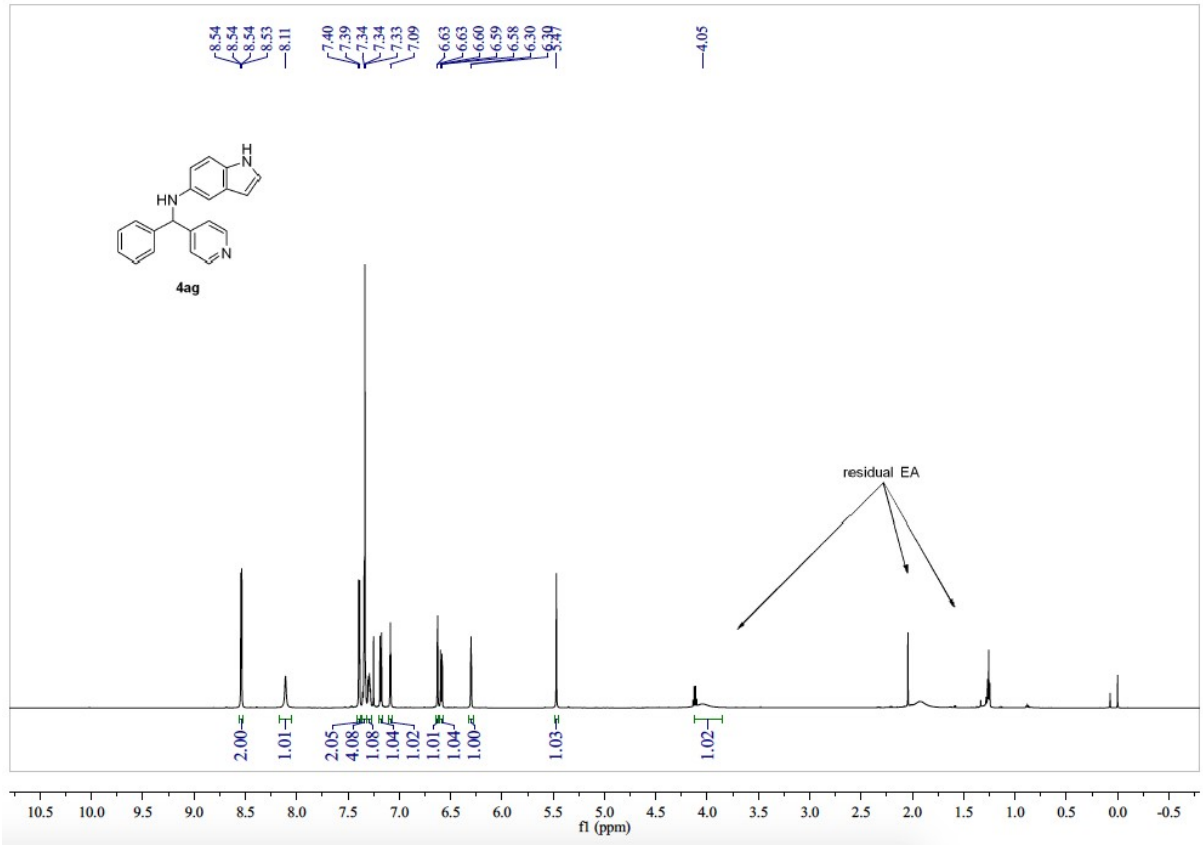


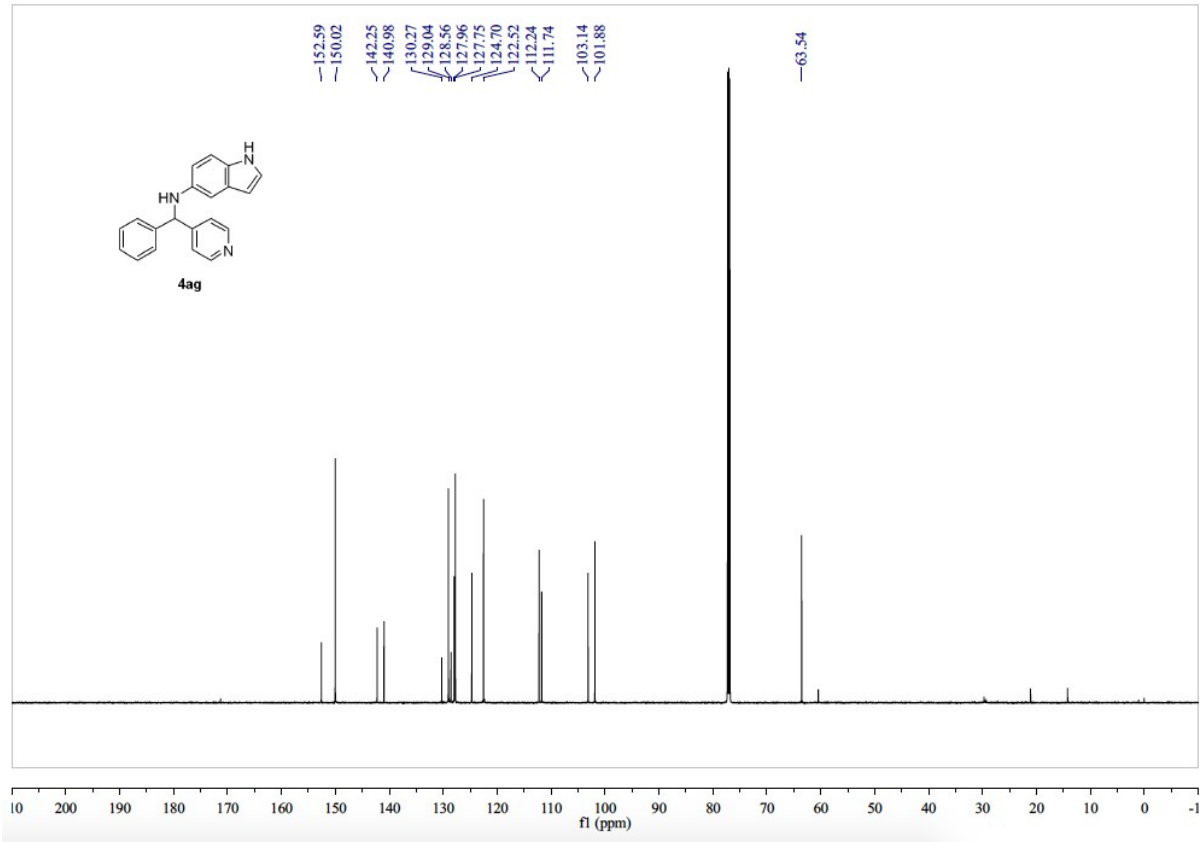
4af: *N*-(phenyl(pyridin-4-yl)methyl)naphthalen-2-amine



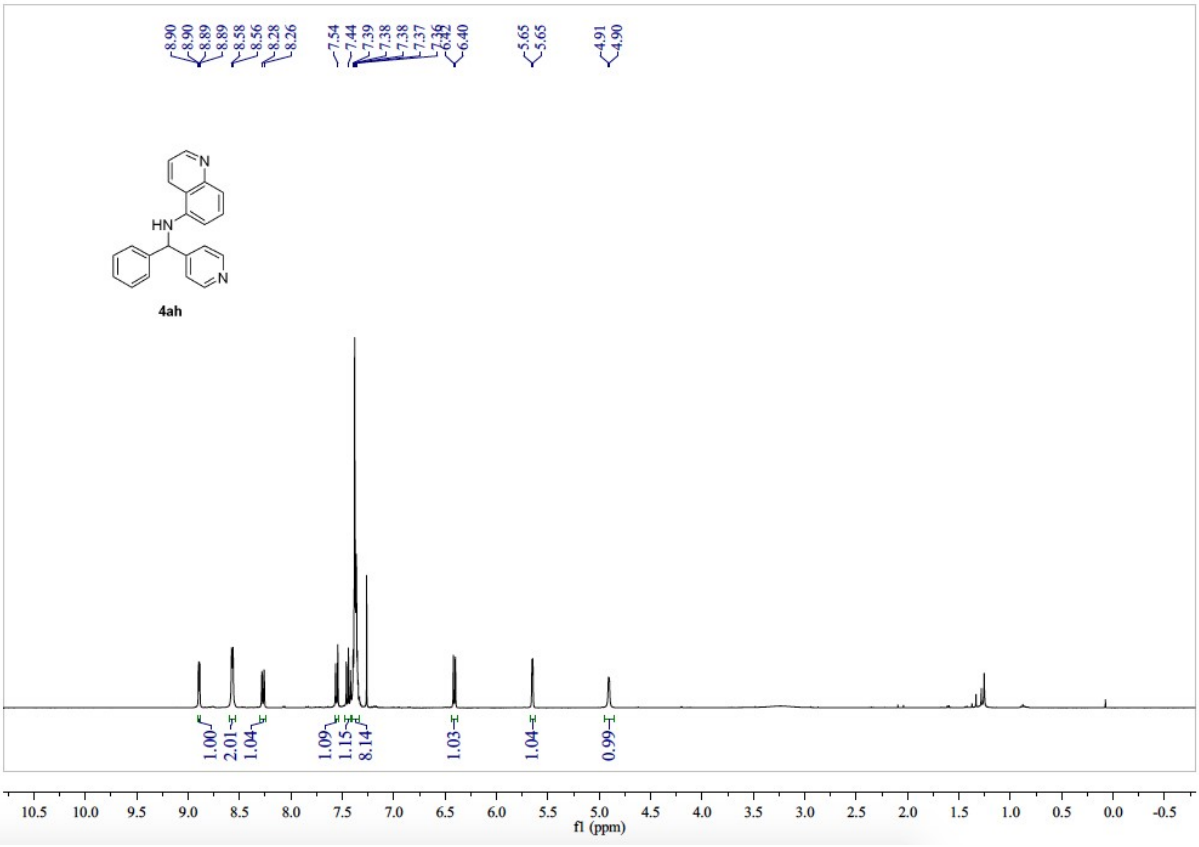


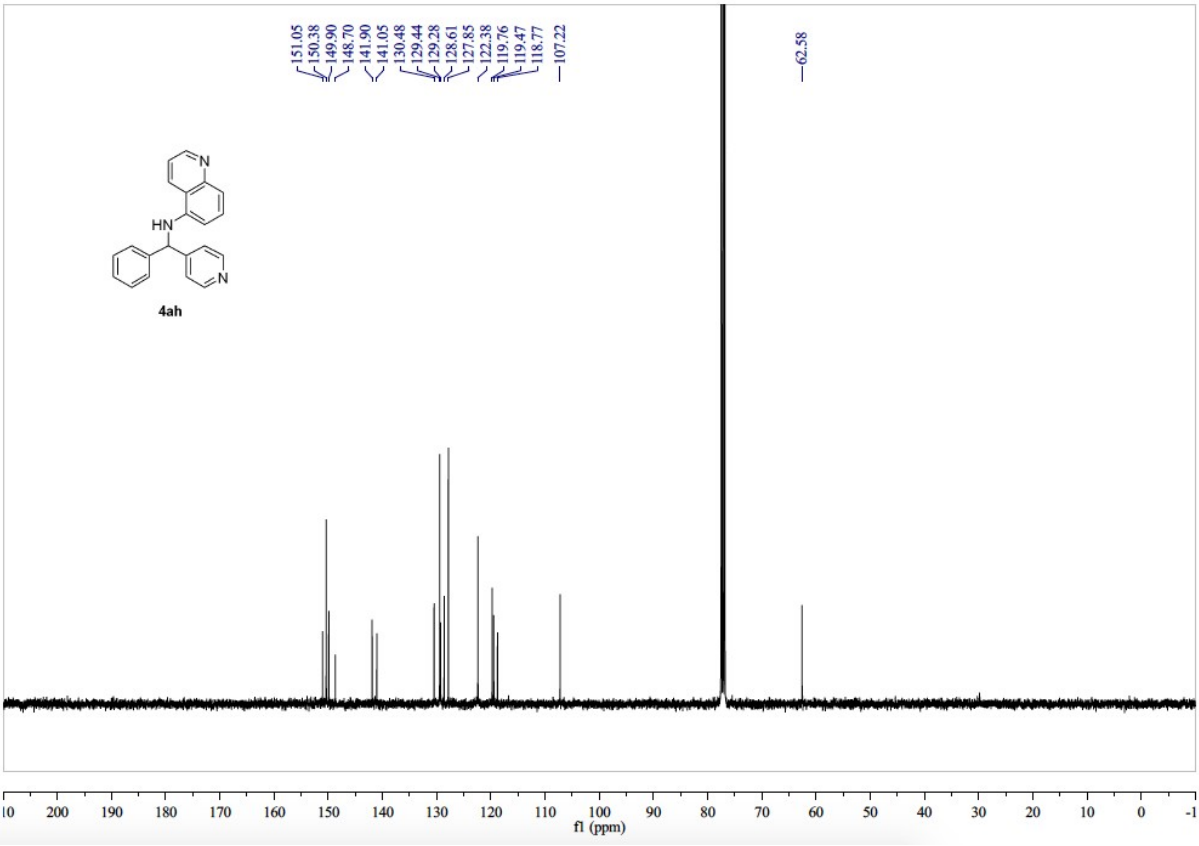
4ag: *N*-(phenyl(pyridin-4-yl)methyl)-1*H*-indol-5-amine



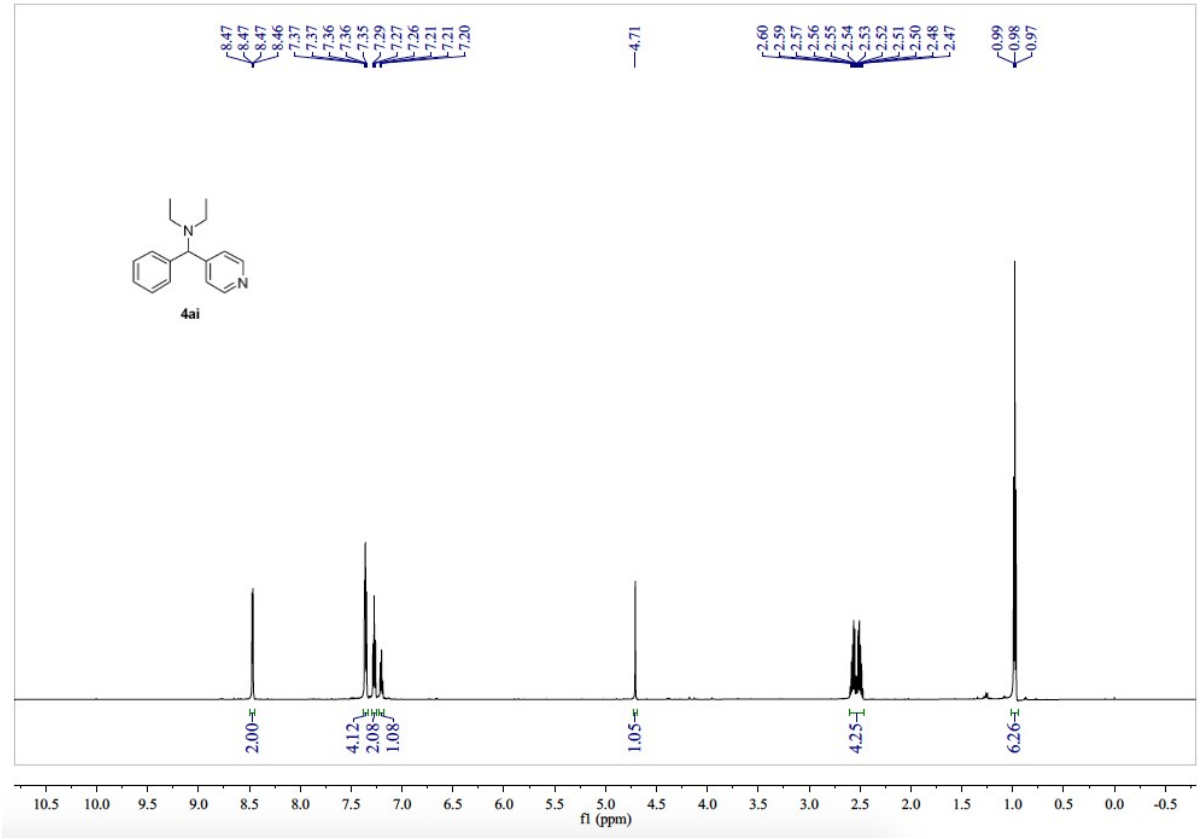


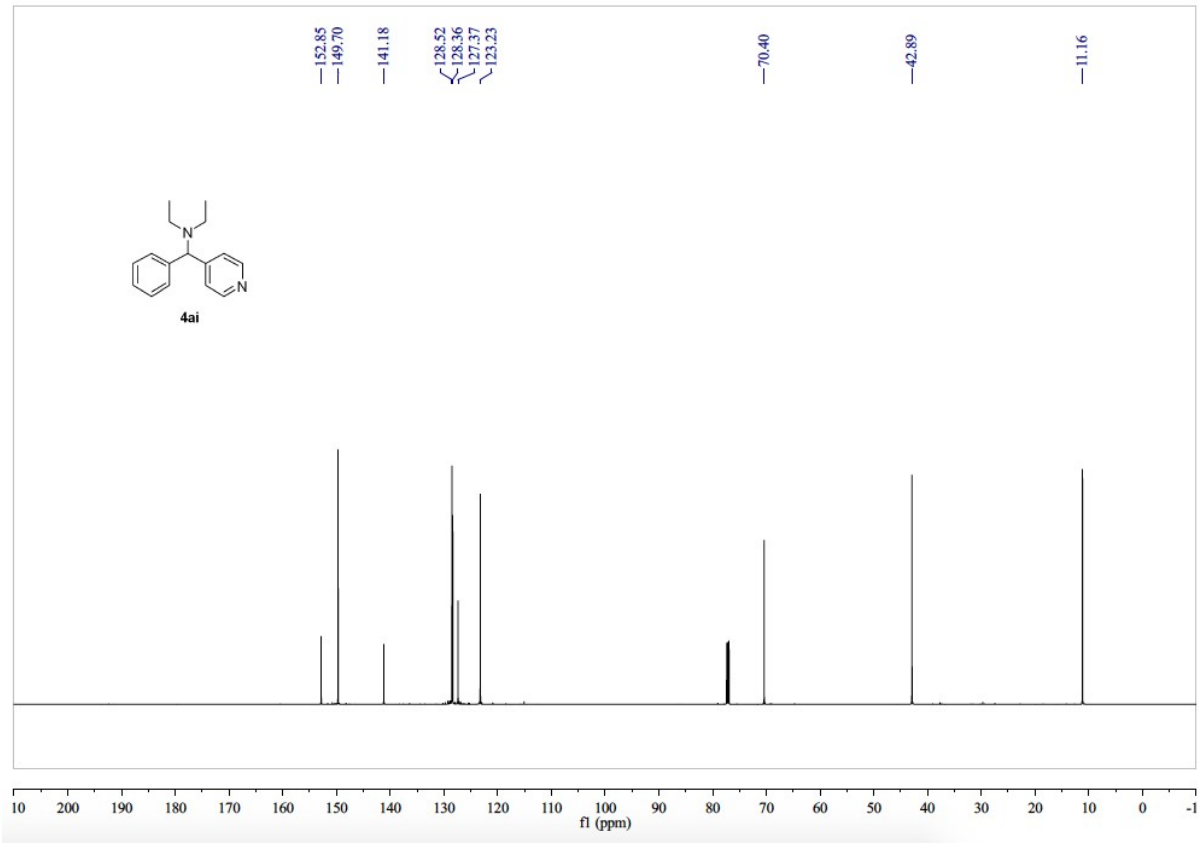
4ah: *N*-(phenyl(pyridin-4-yl)methyl)quinolin-5-amine



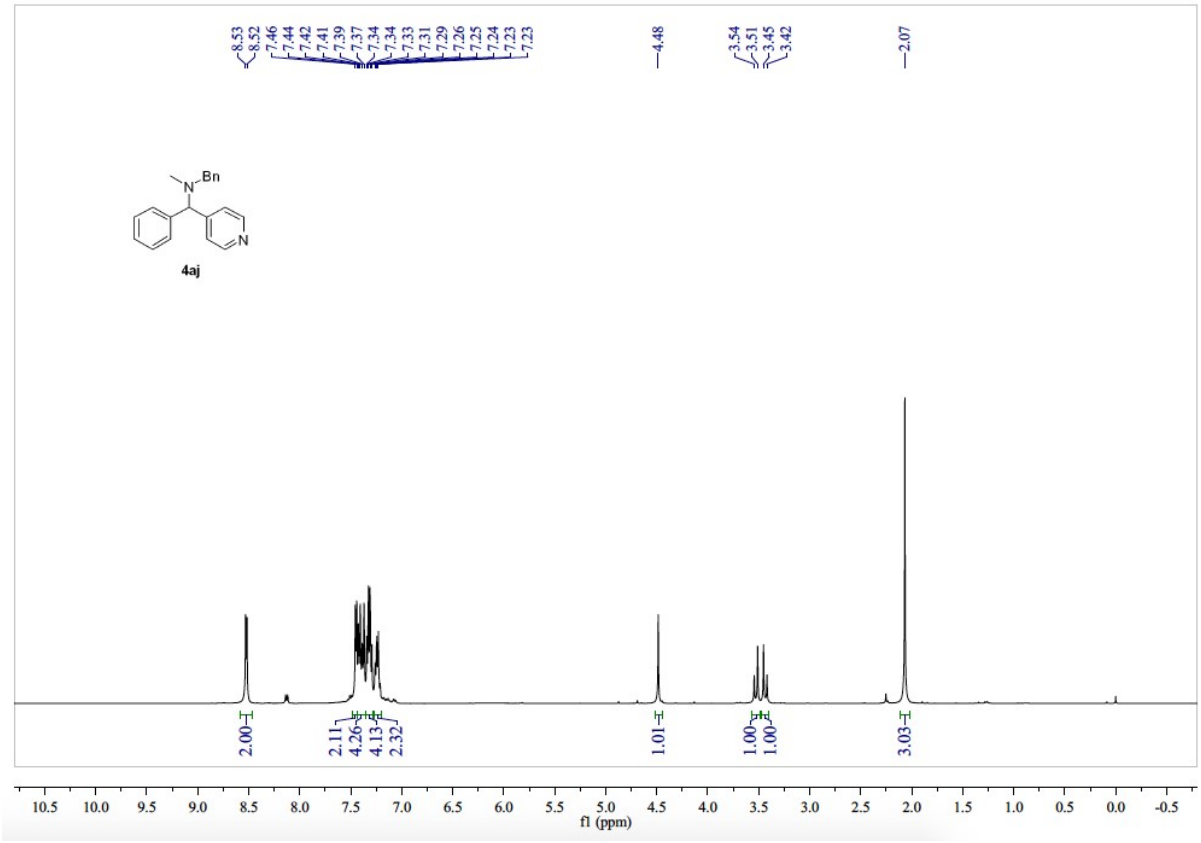


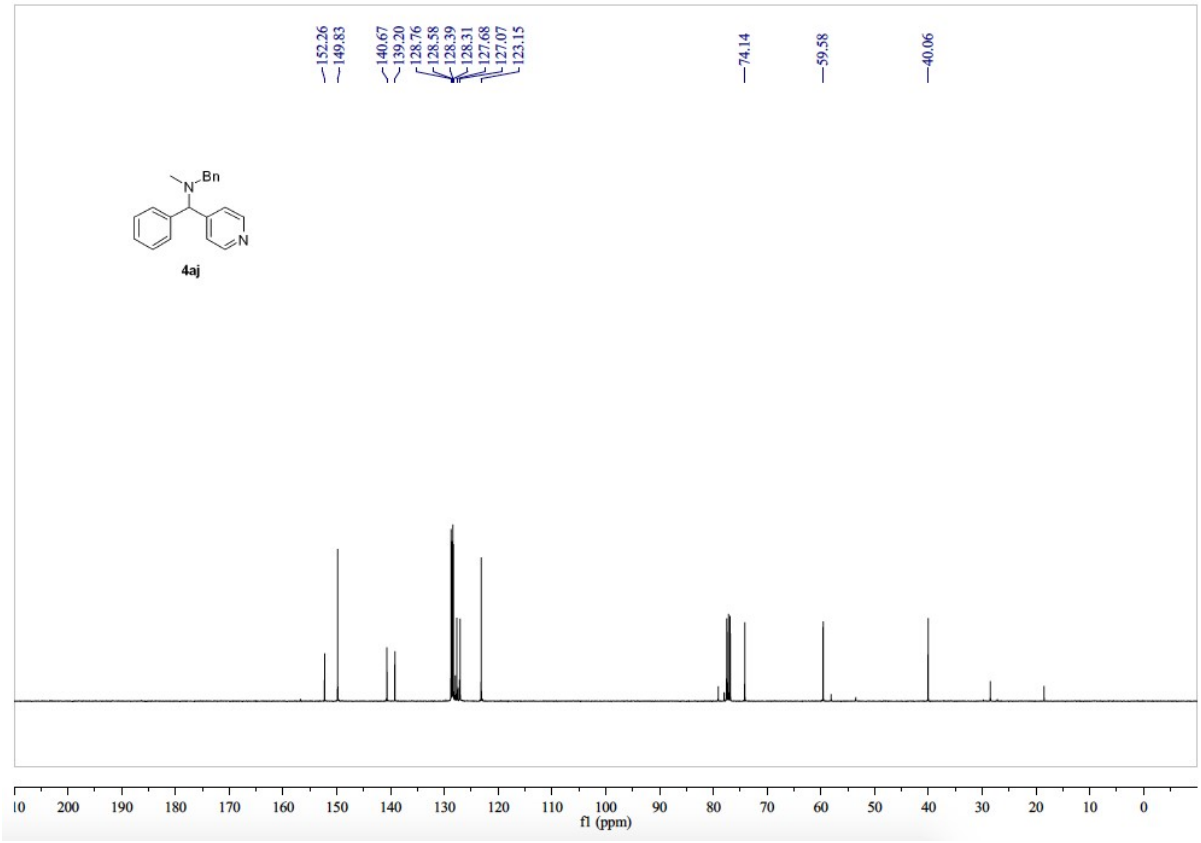
4ai: *N*-ethyl-*N*-(phenyl(pyridin-4-yl)methyl)ethanamine



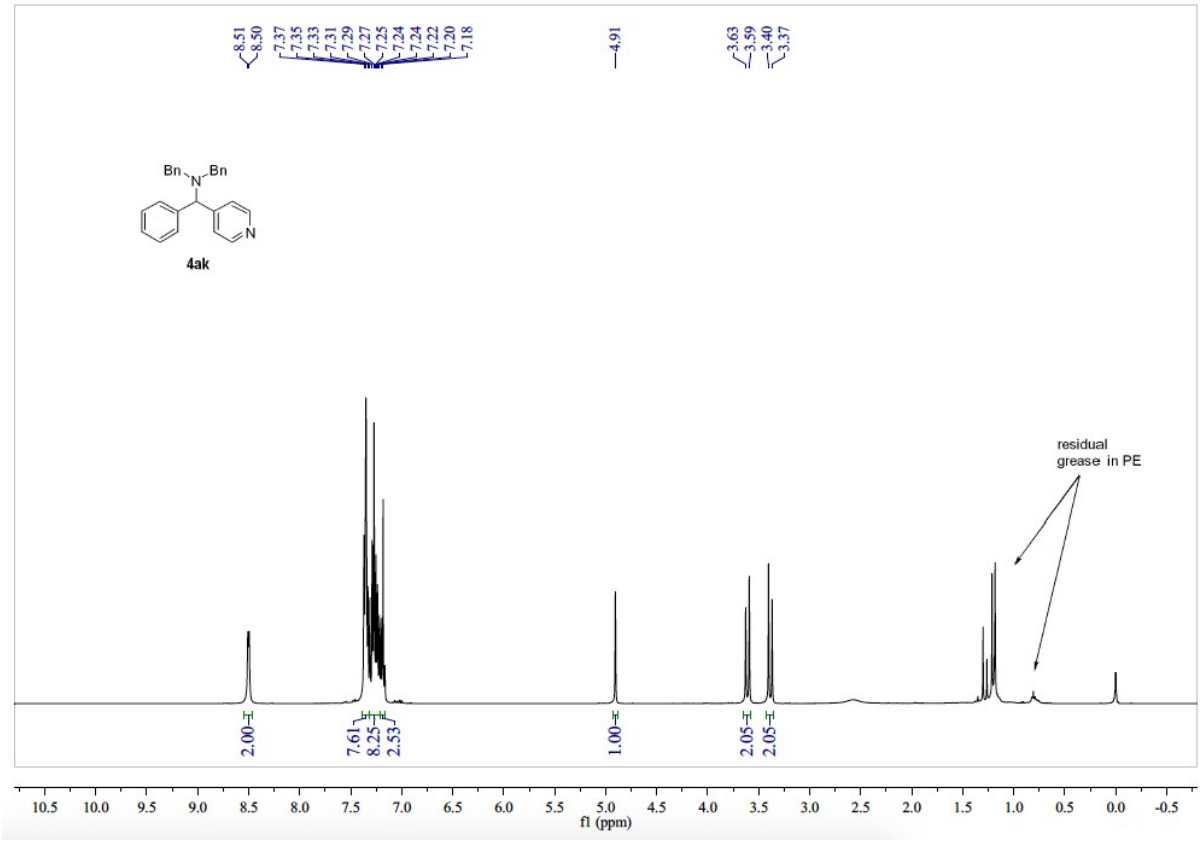


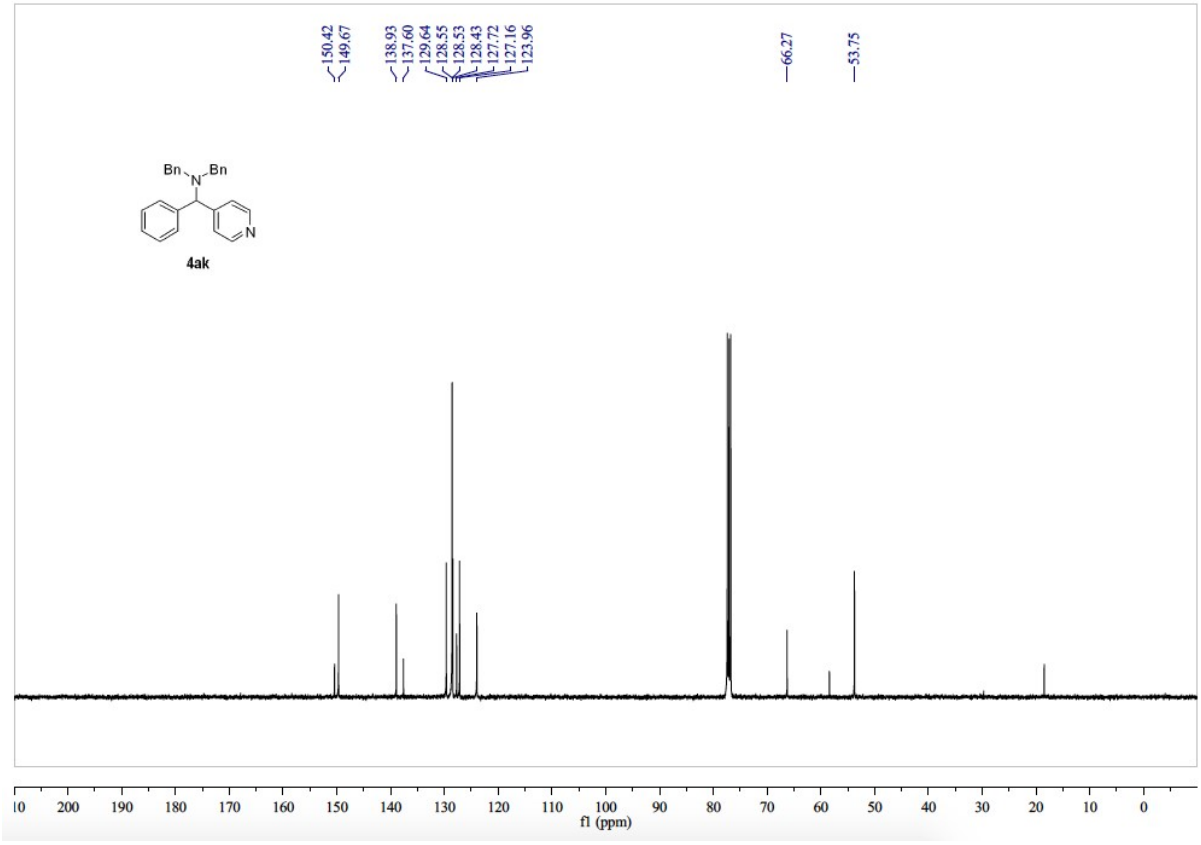
4aj: *N*-benzyl-*N*-methyl-1-phenyl-1-(pyridin-4-yl)methanamine



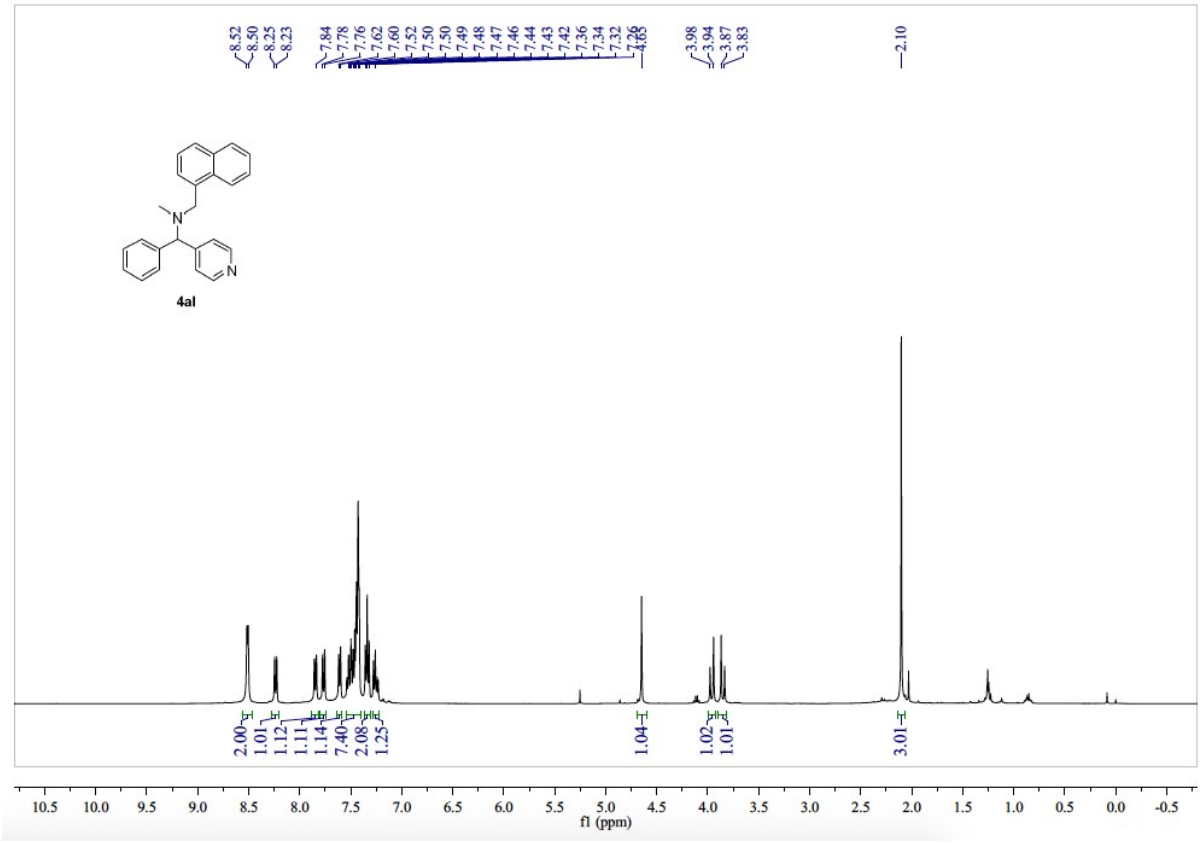


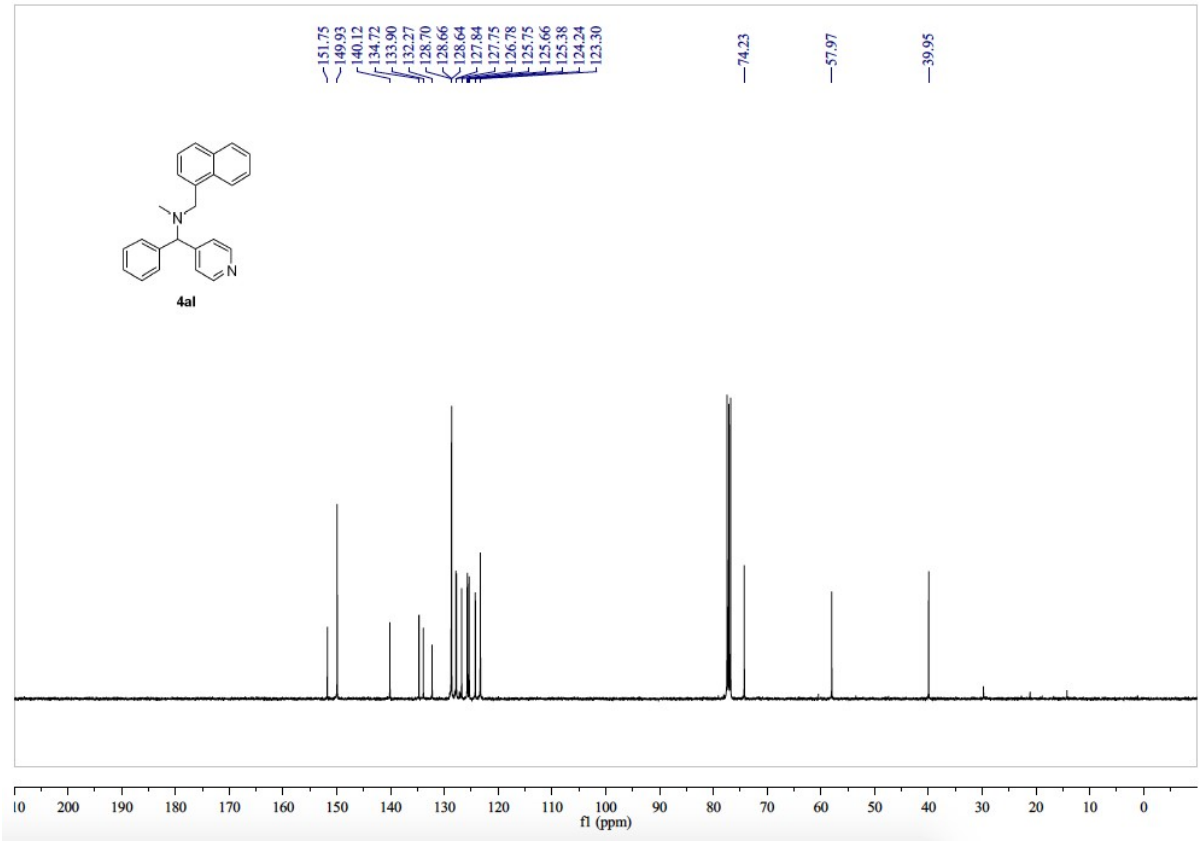
4ak: *N*,*N*-dibenzyl-1-phenyl-1-(pyridin-4-yl)methanamine



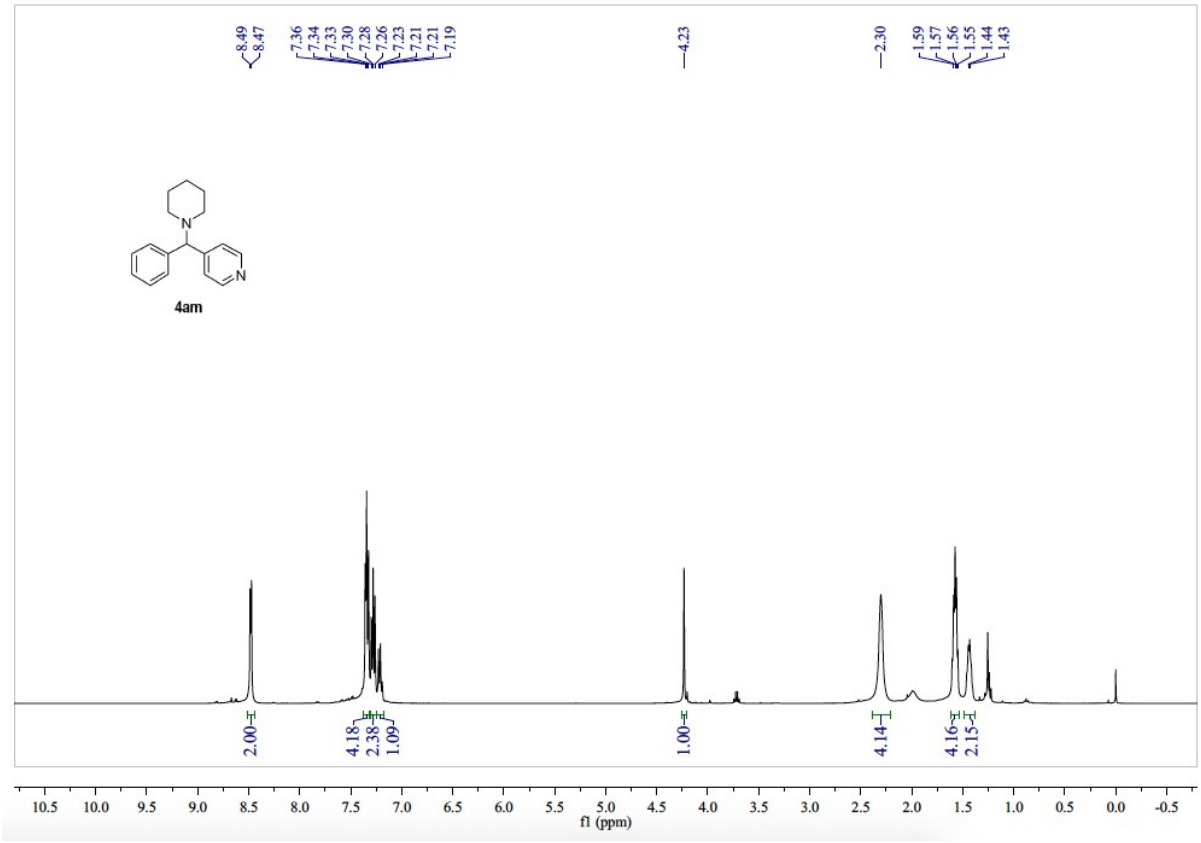


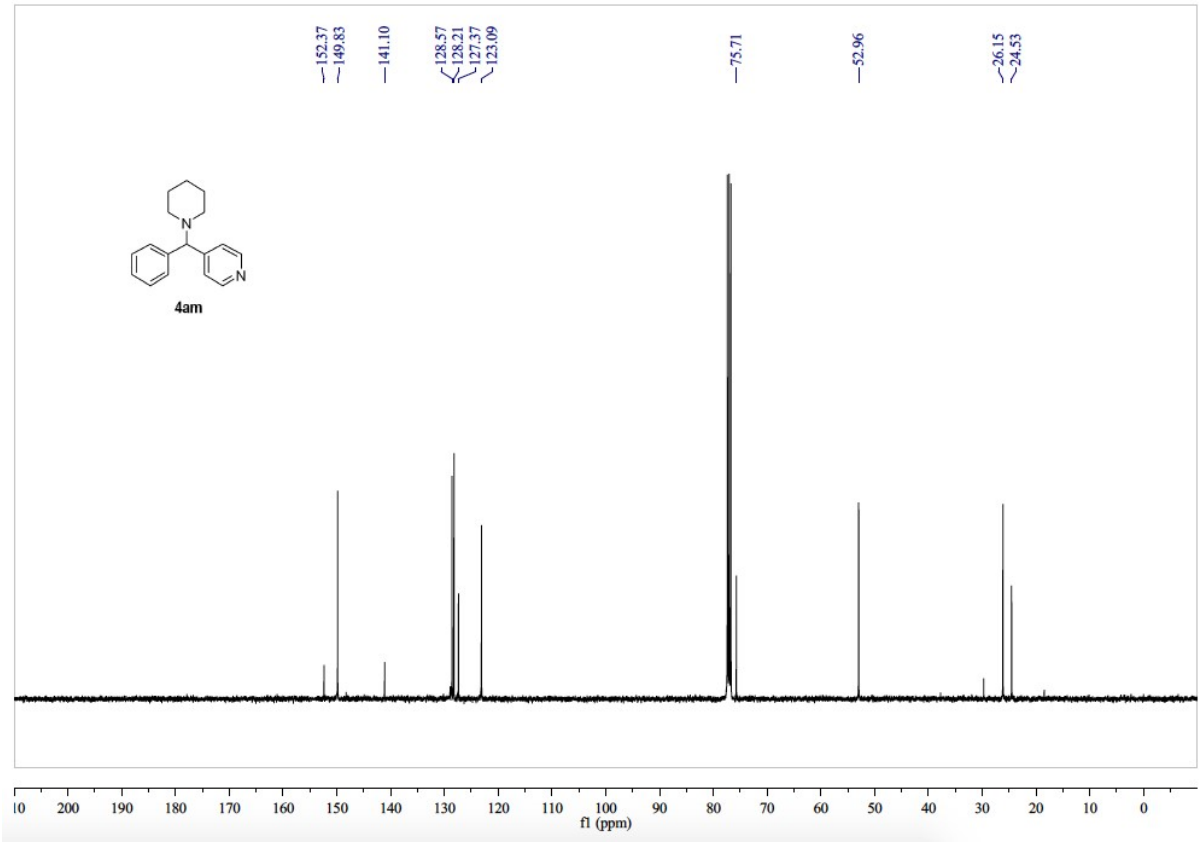
4al: *N*-methyl-*N*-(naphthalen-1-ylmethyl)-1-phenyl-1-(pyridin-4-yl)methanamine



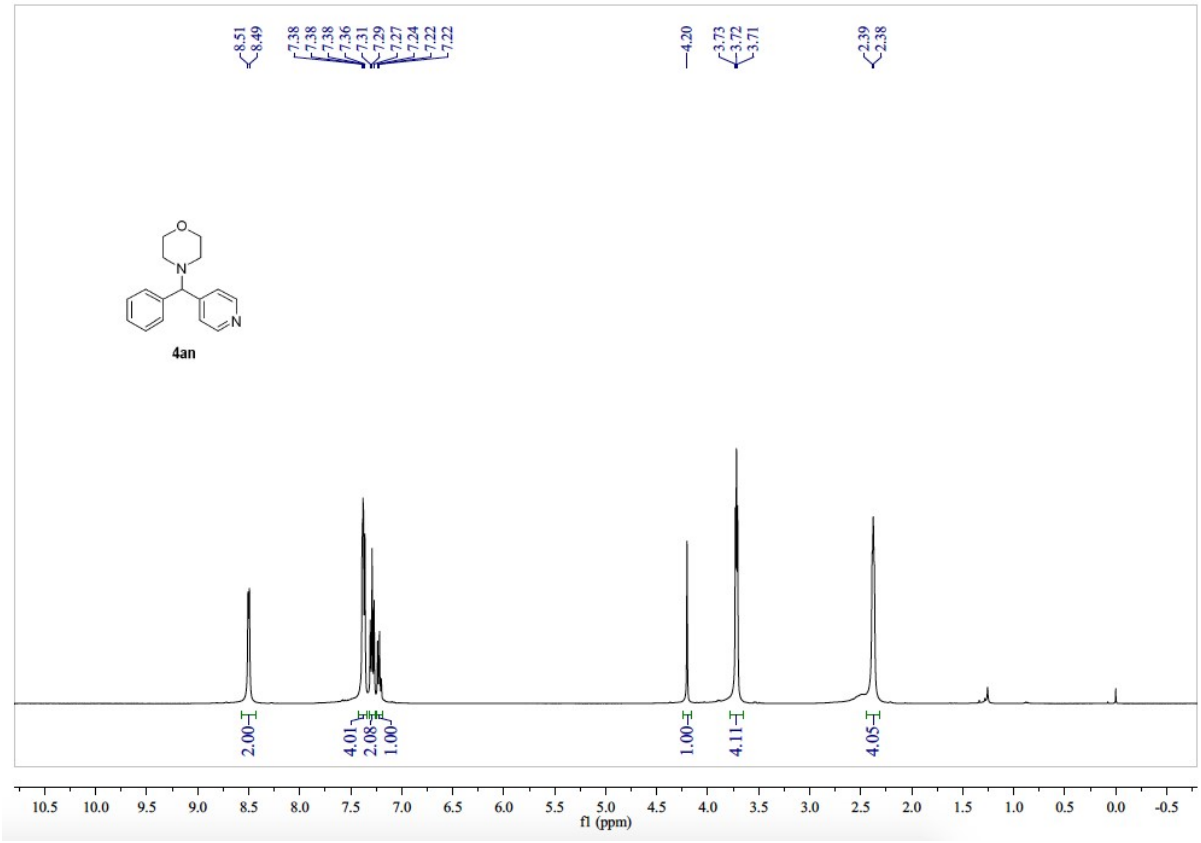


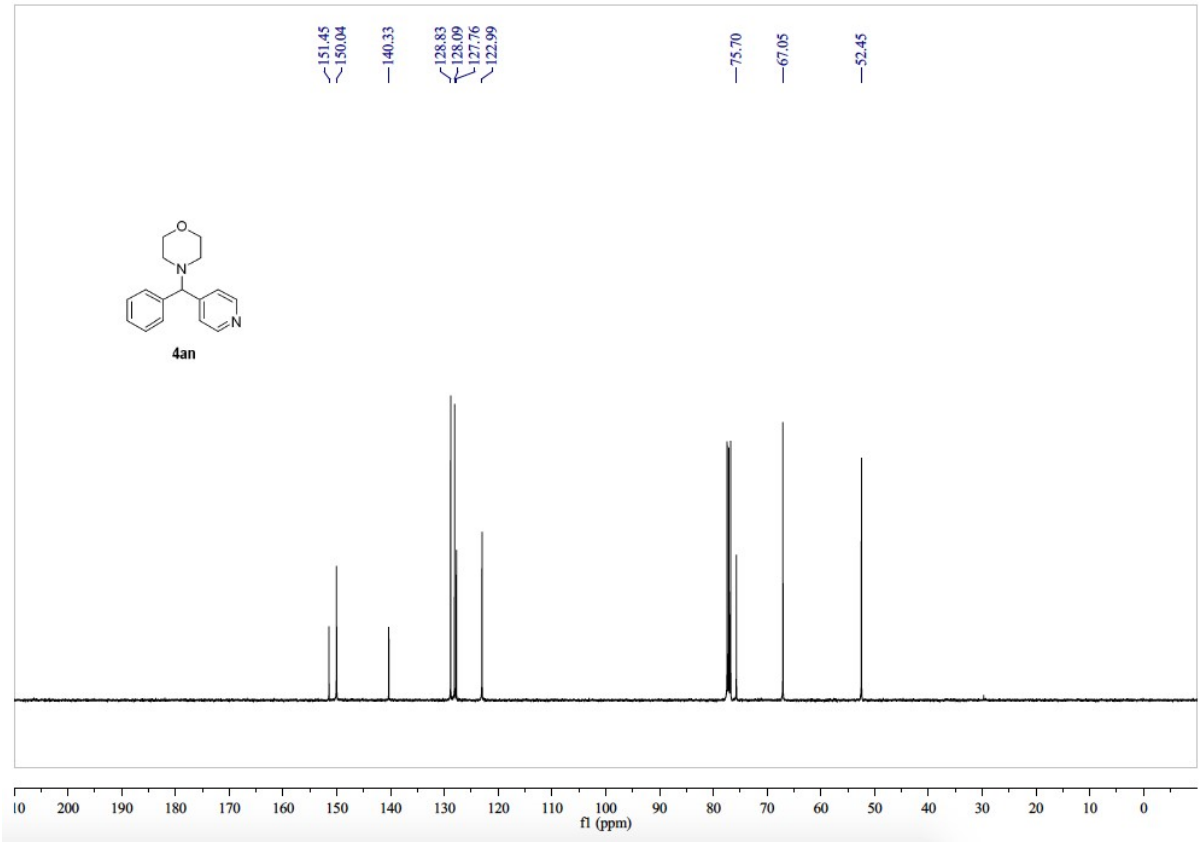
4am: 4-(phenyl(piperidin-1-yl)methyl)pyridine



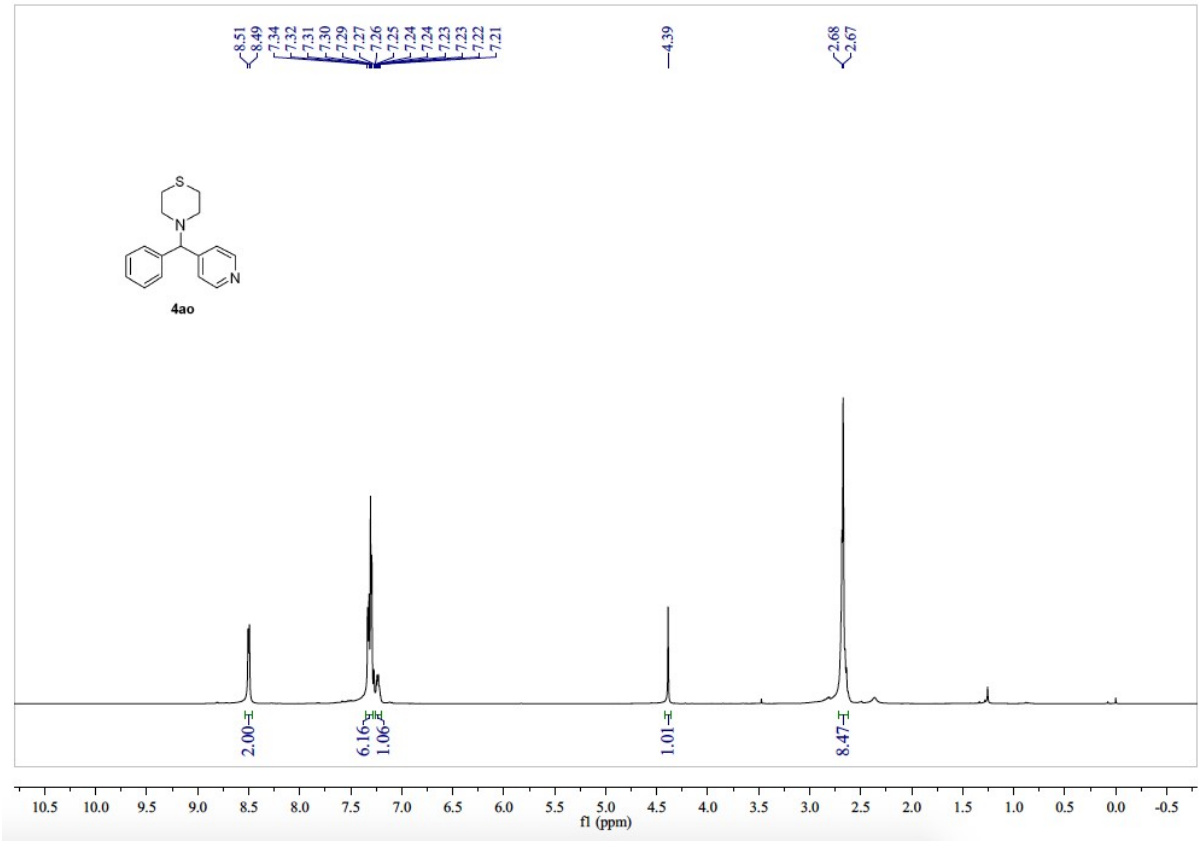


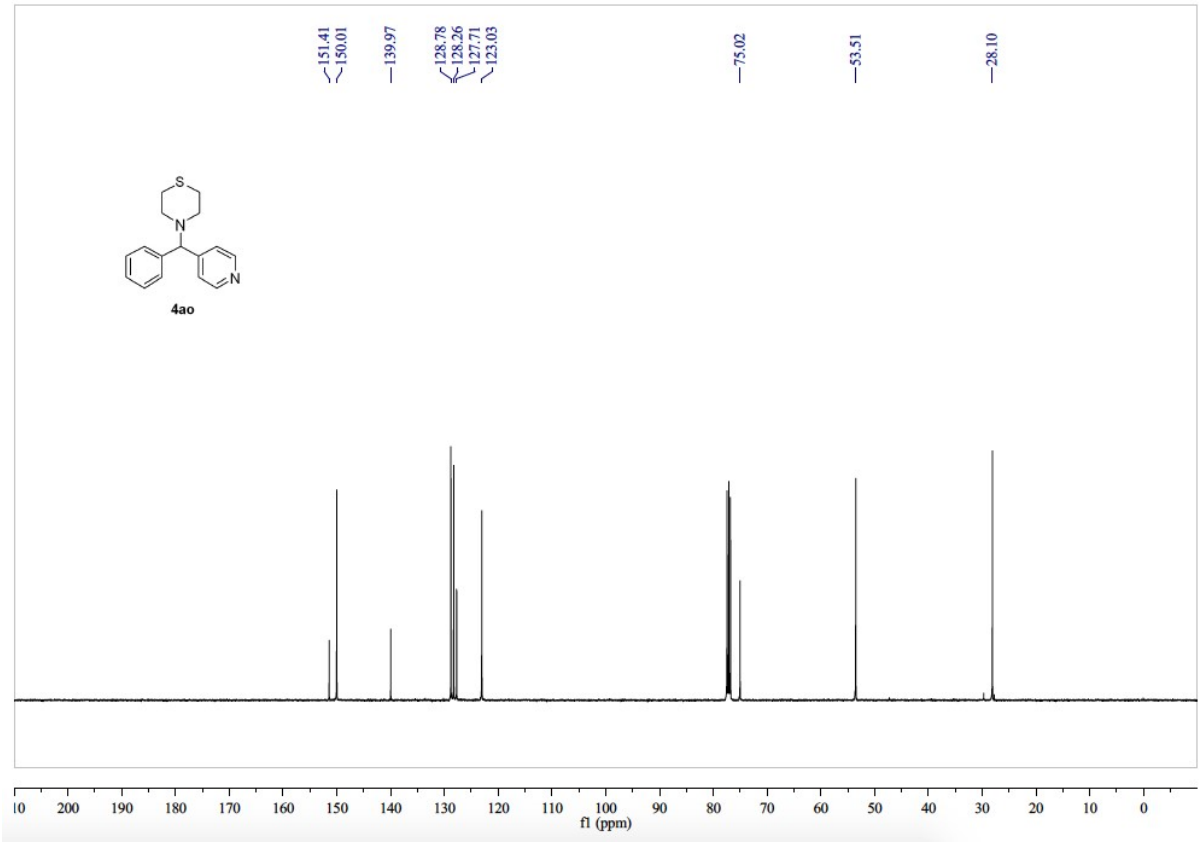
4an: 4-(phenyl(pyridin-4-yl)methyl)morpholine



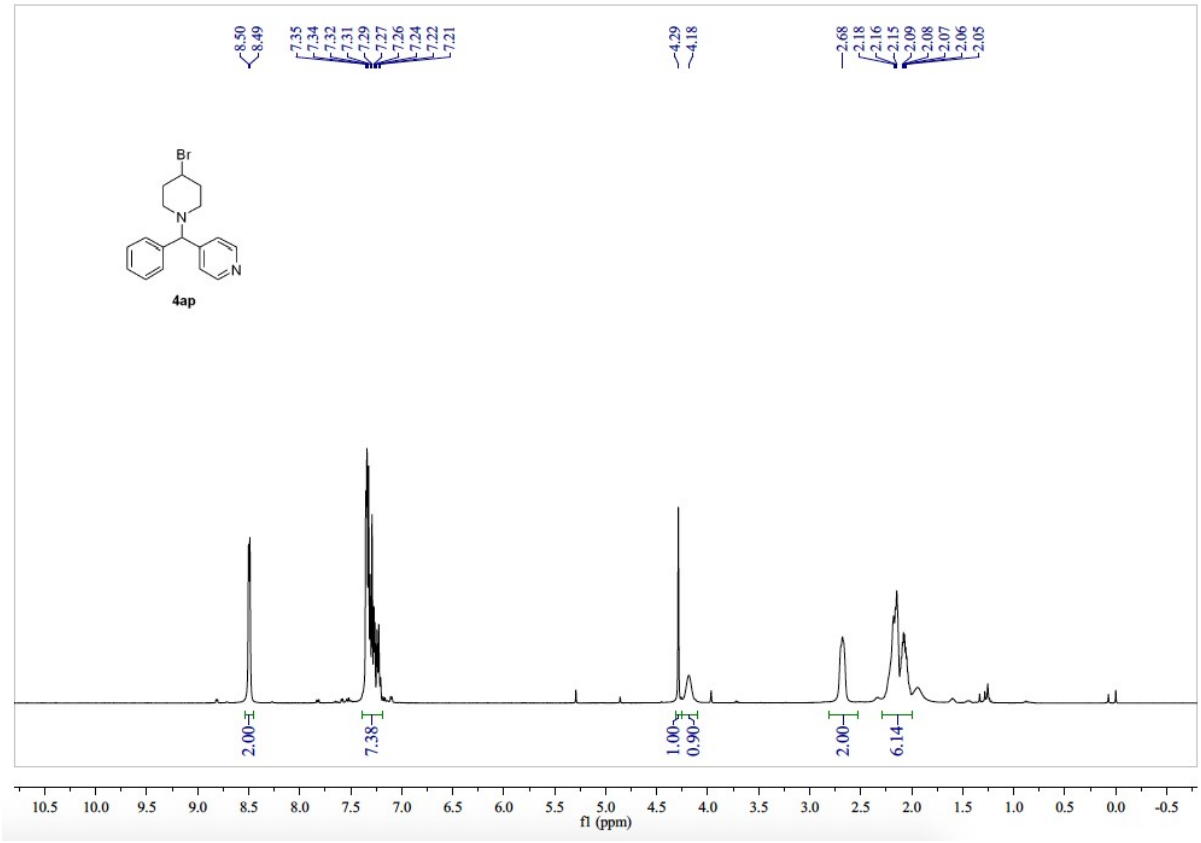


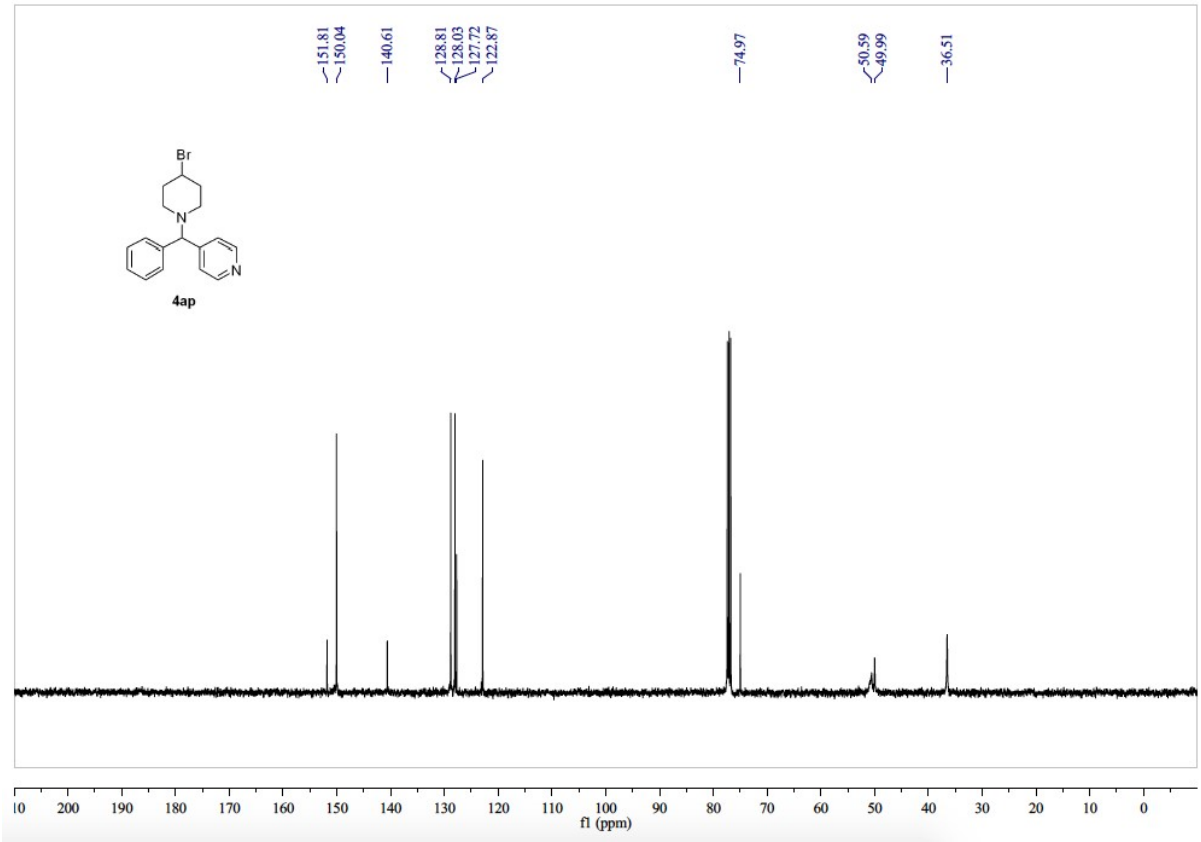
4ao: 4-(phenyl(pyridin-4-yl)methyl)thiomorpholine



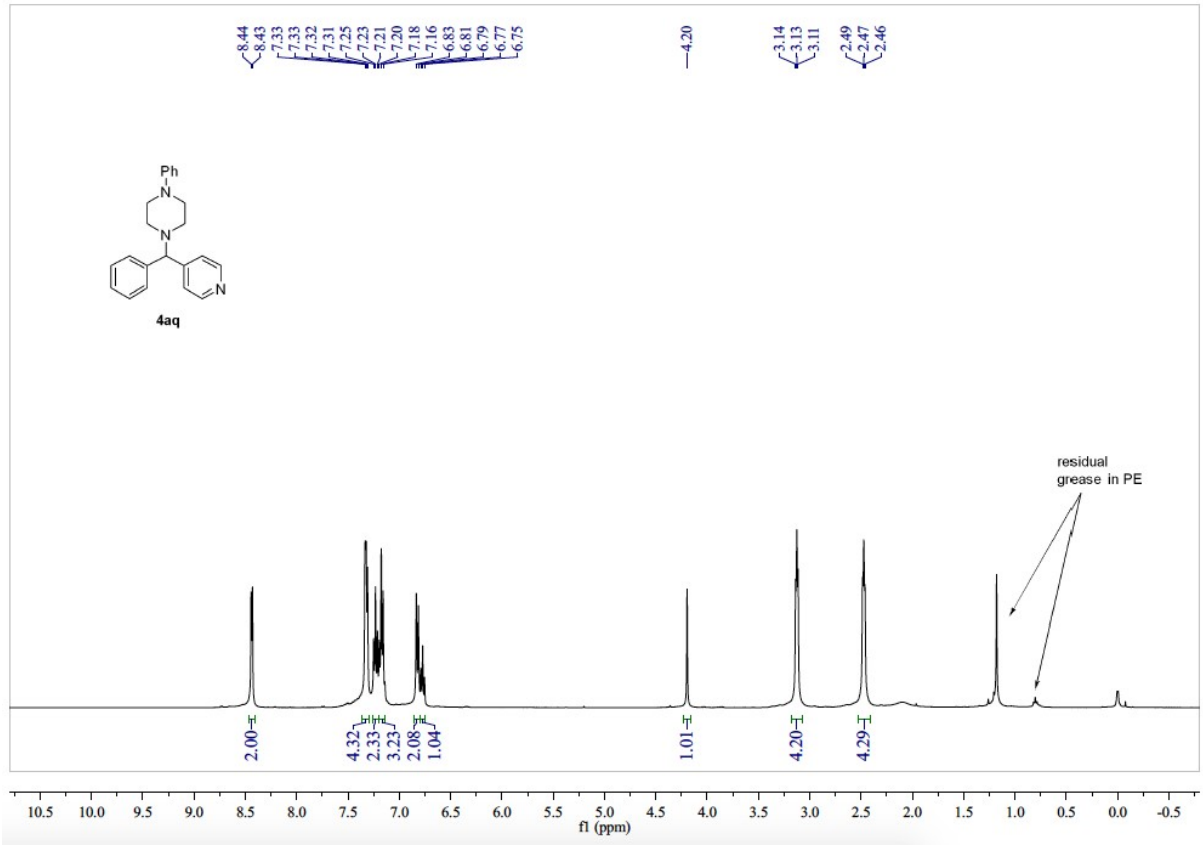


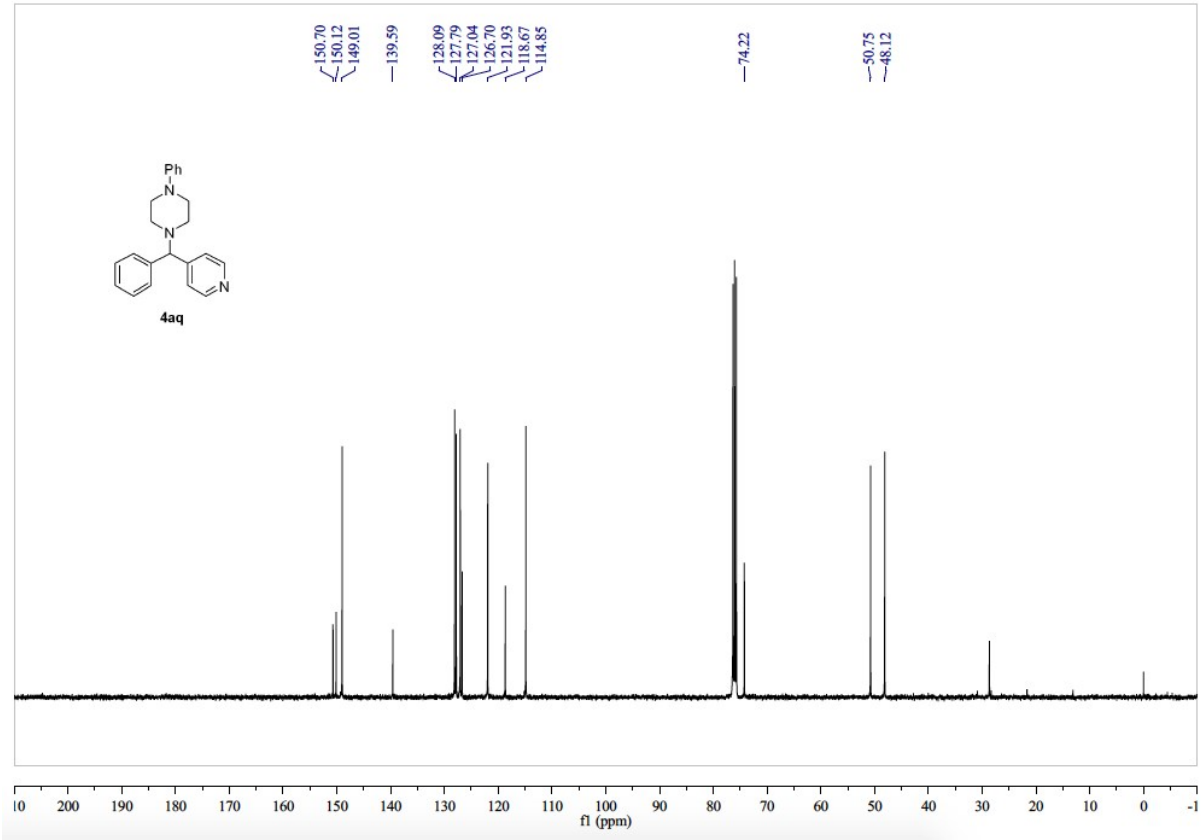
4ap: 4-((4-bromopiperidin-1-yl)(phenyl)methyl)pyridine



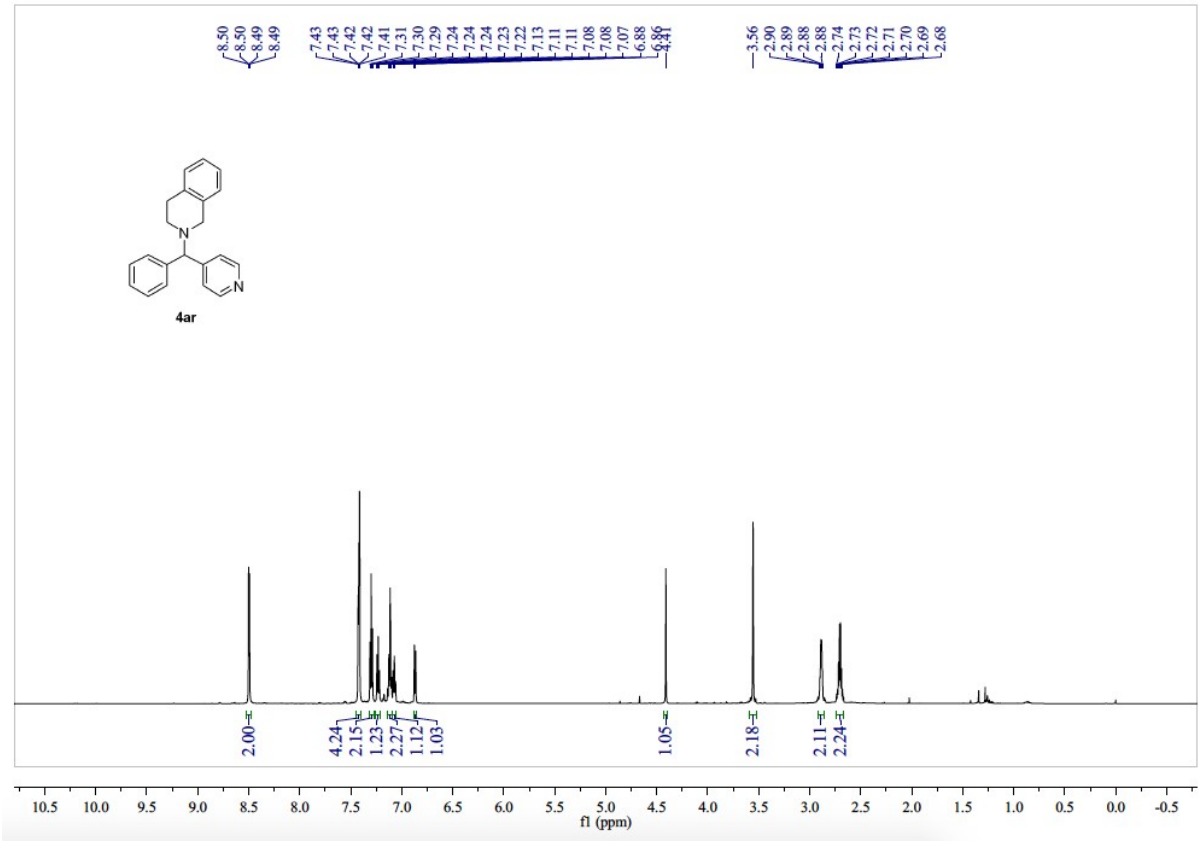


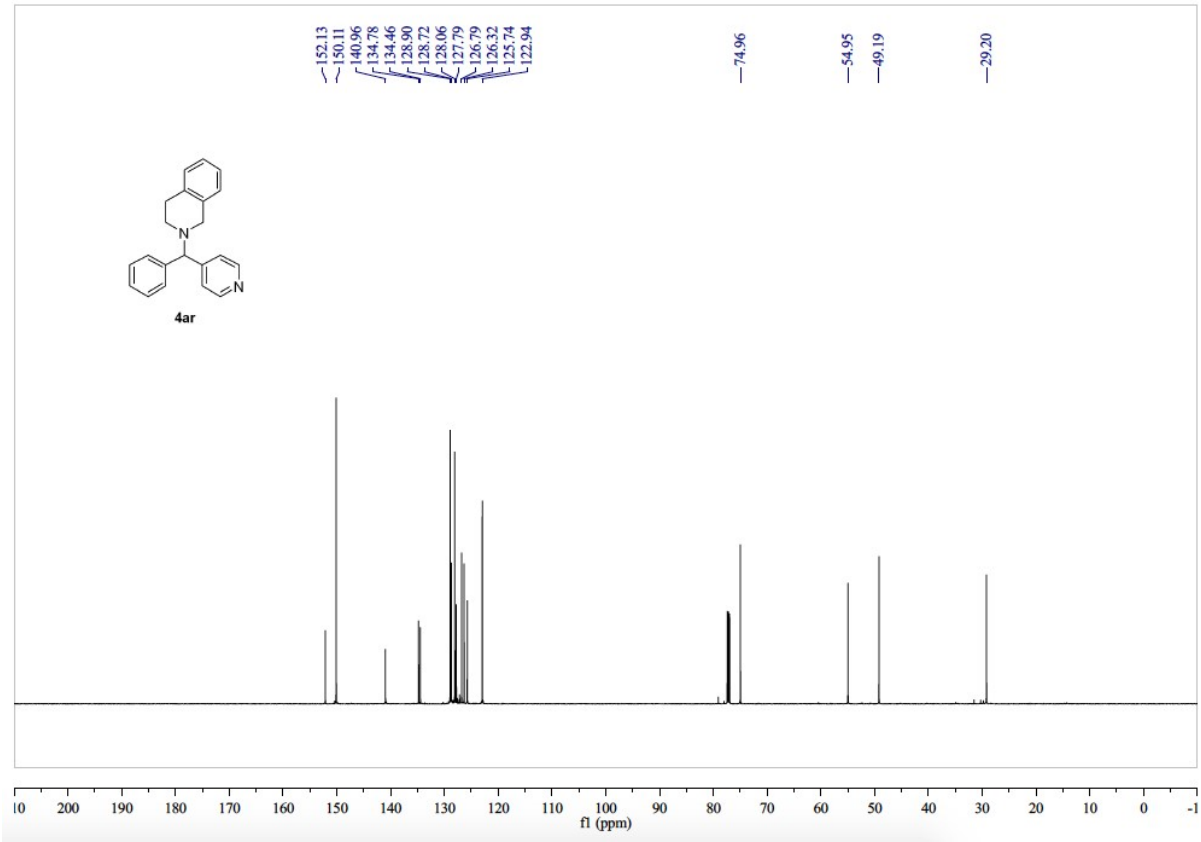
4aq: 1-phenyl-4-(phenyl(pyridin-4-yl)methyl)piperazine



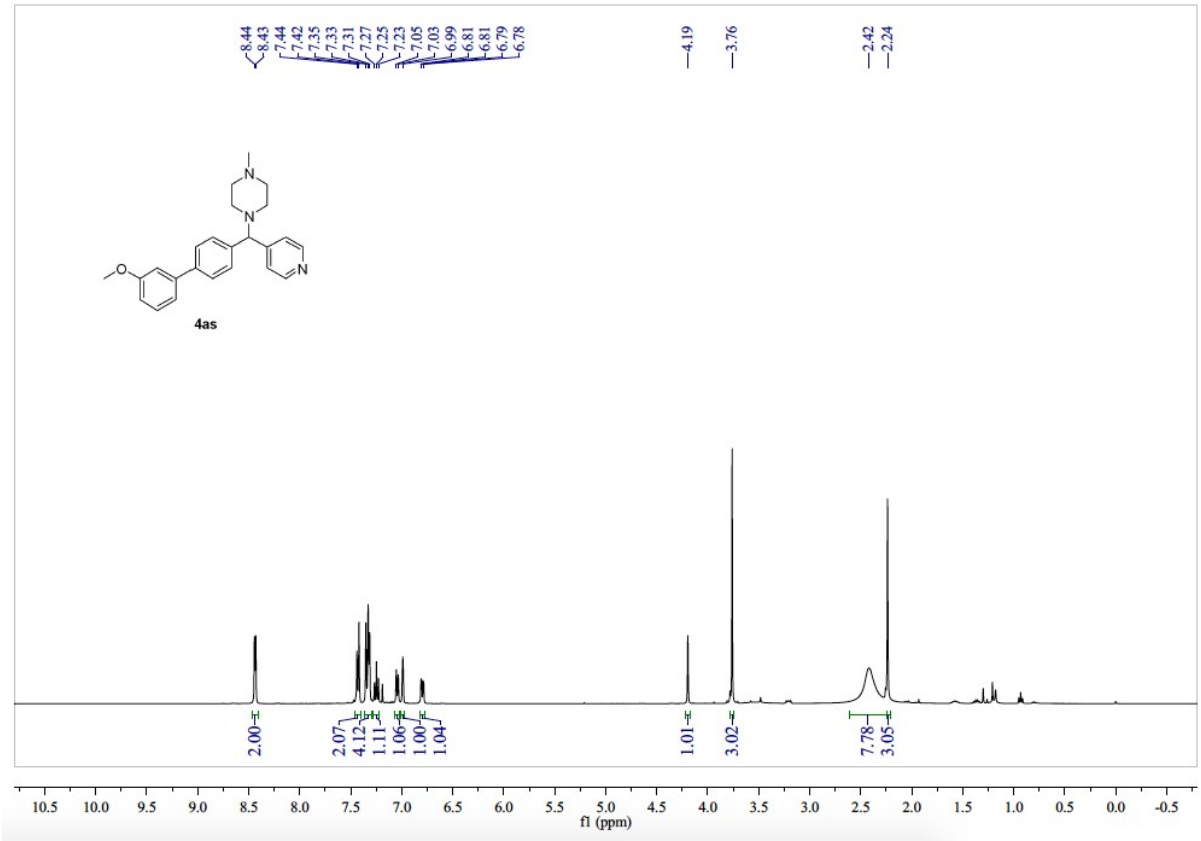


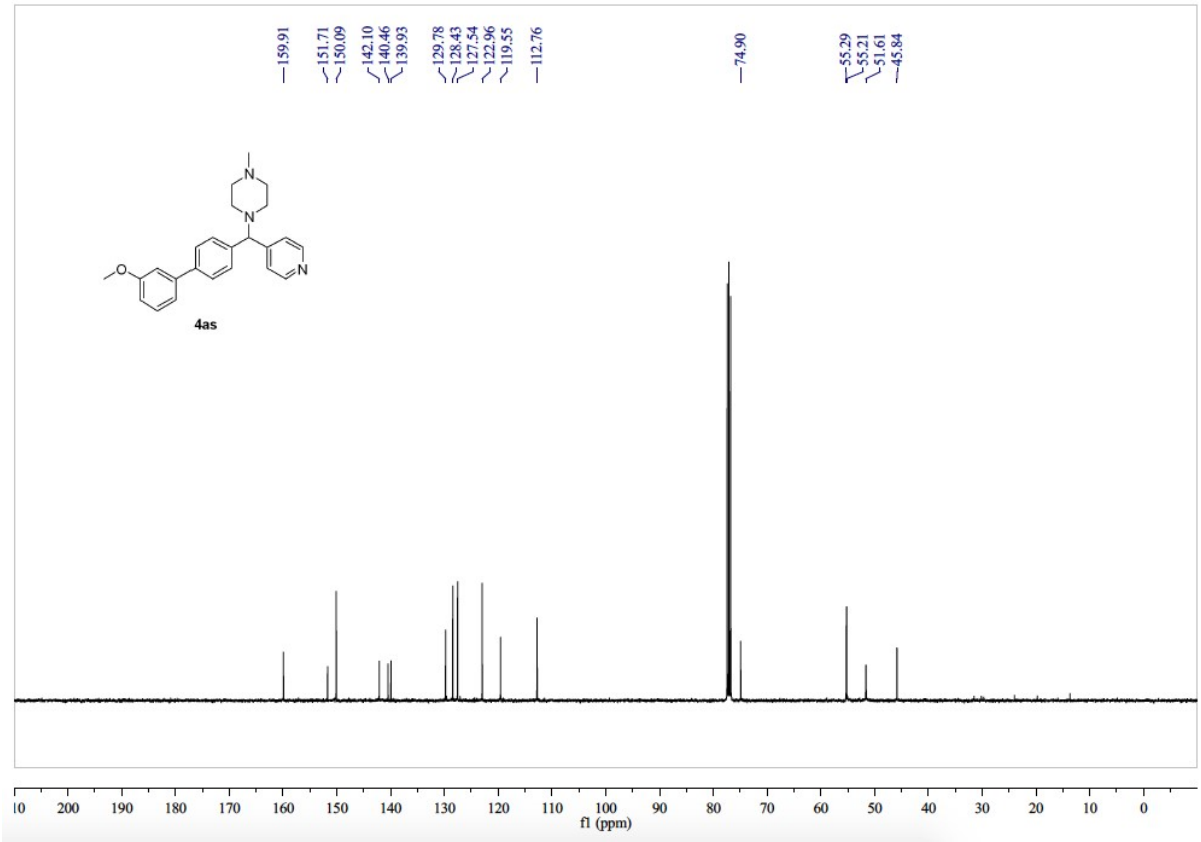
4ar: 2-(phenyl(pyridin-4-yl)methyl)-1,2,3,4-tetrahydroisoquinoline



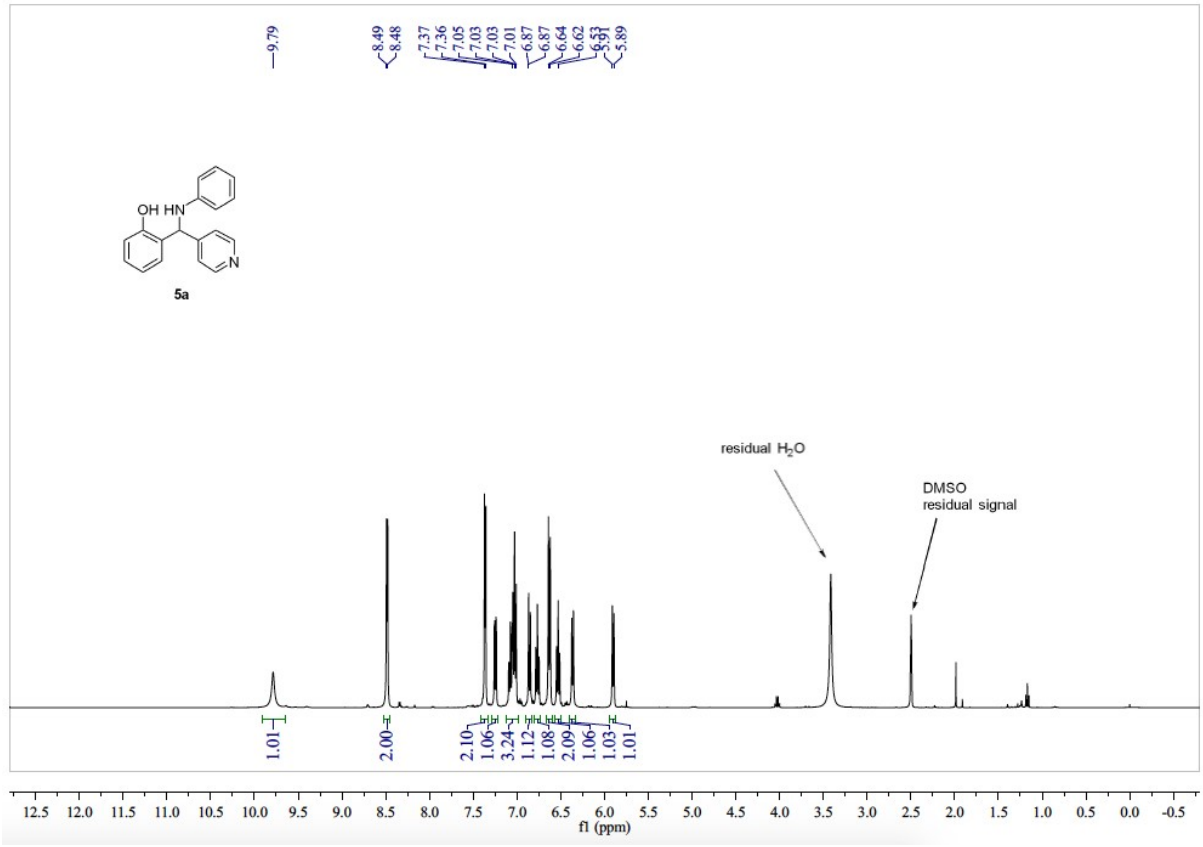


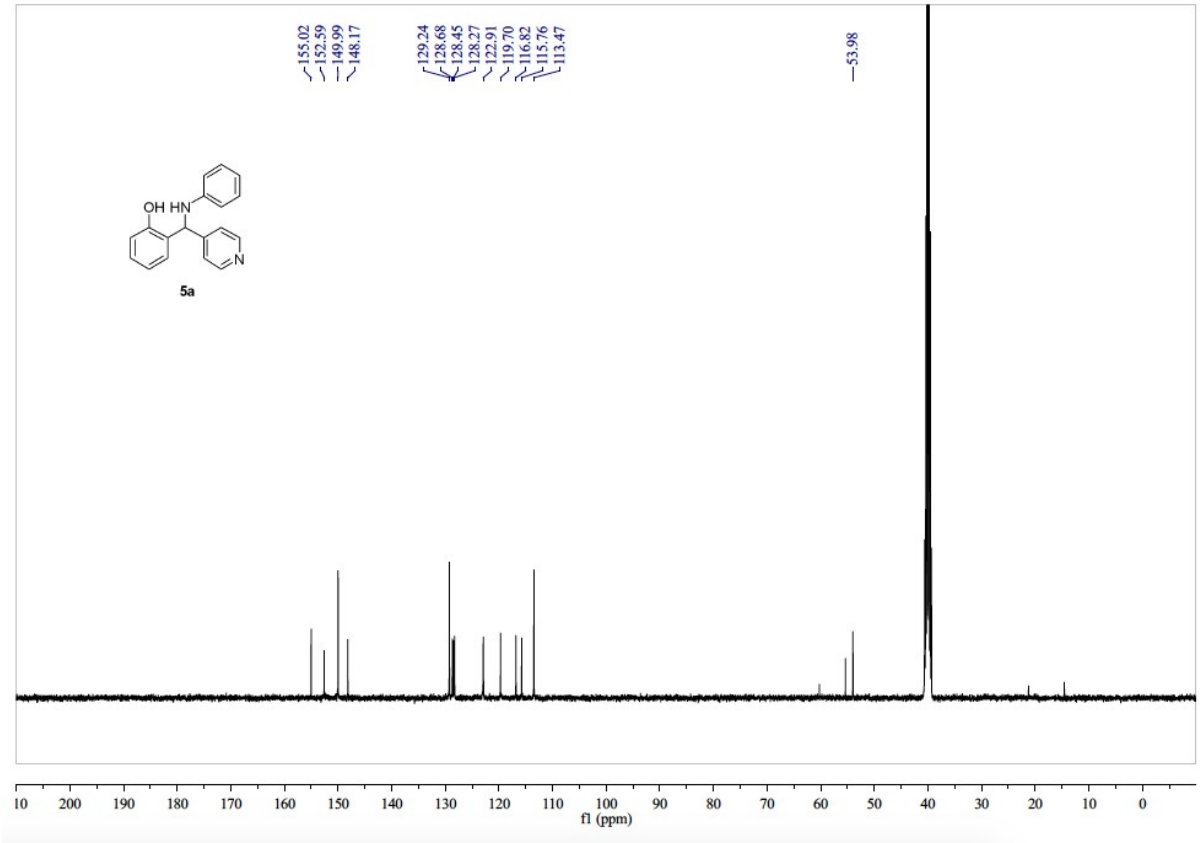
4as: 1-((3'-methoxy-[1,1'-biphenyl]-4-yl)(pyridin-4-yl)methyl)-4-methylpiperazine



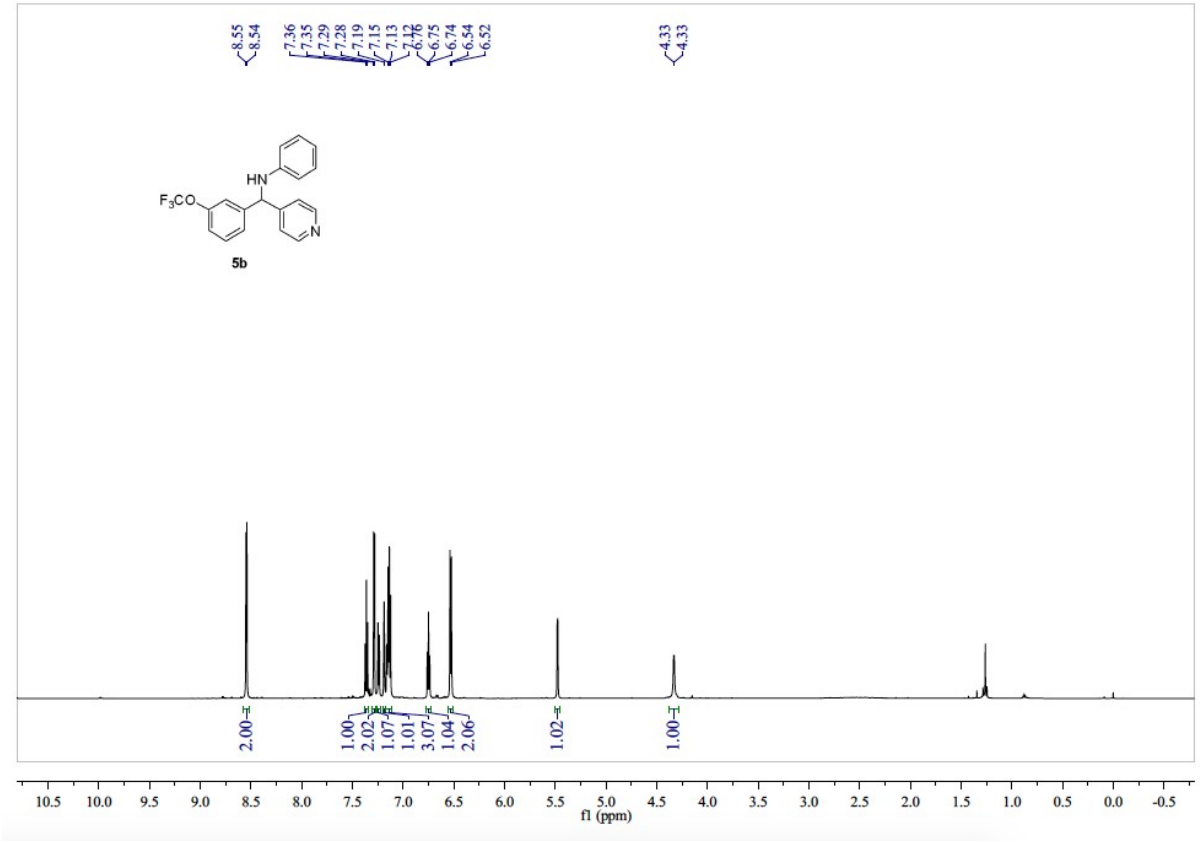


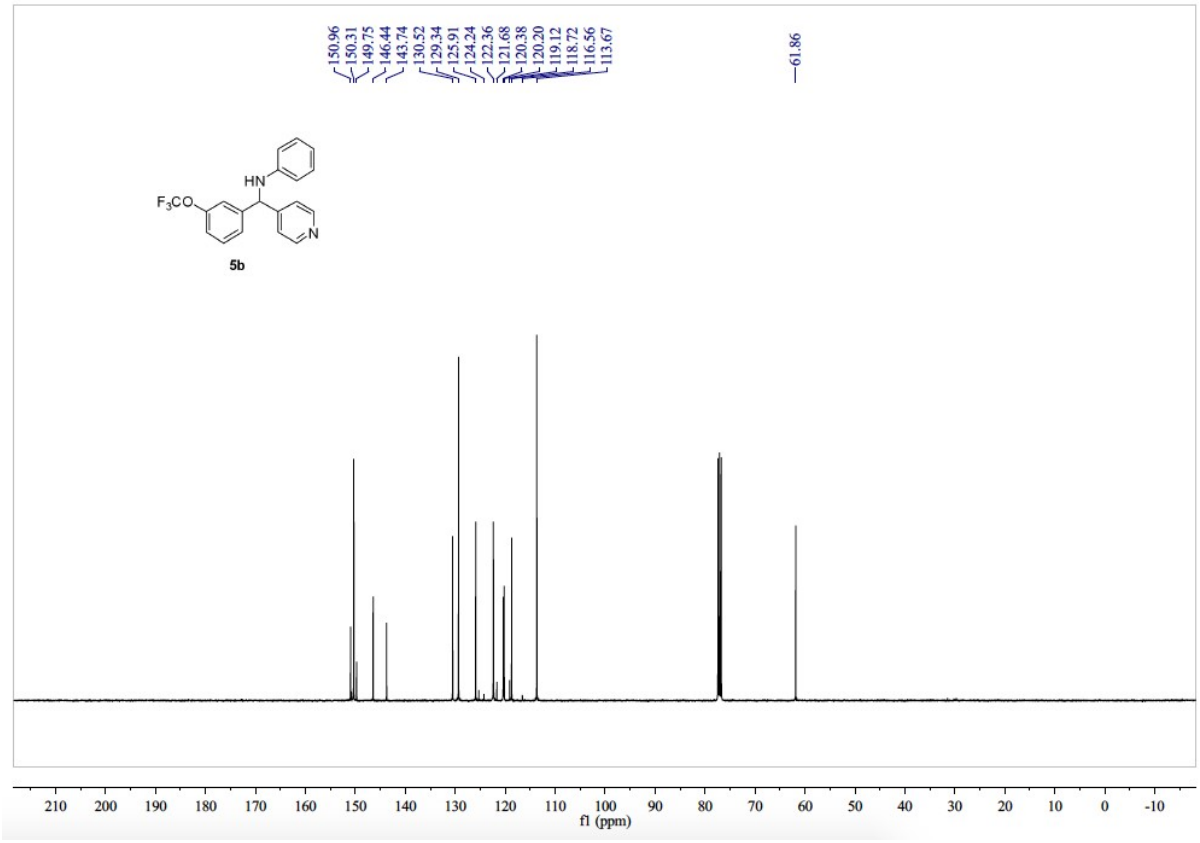
5a: 2-((phenylamino)(pyridin-4-yl)methyl)phenol

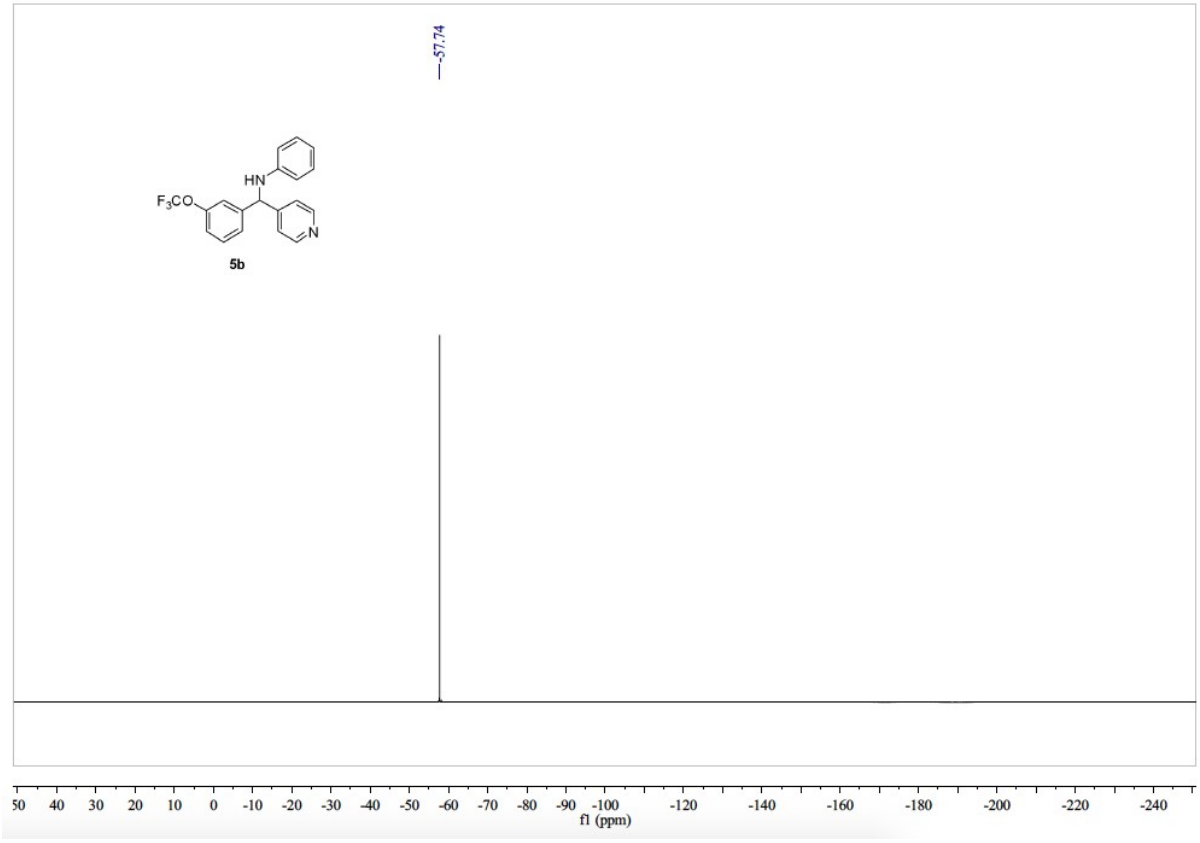




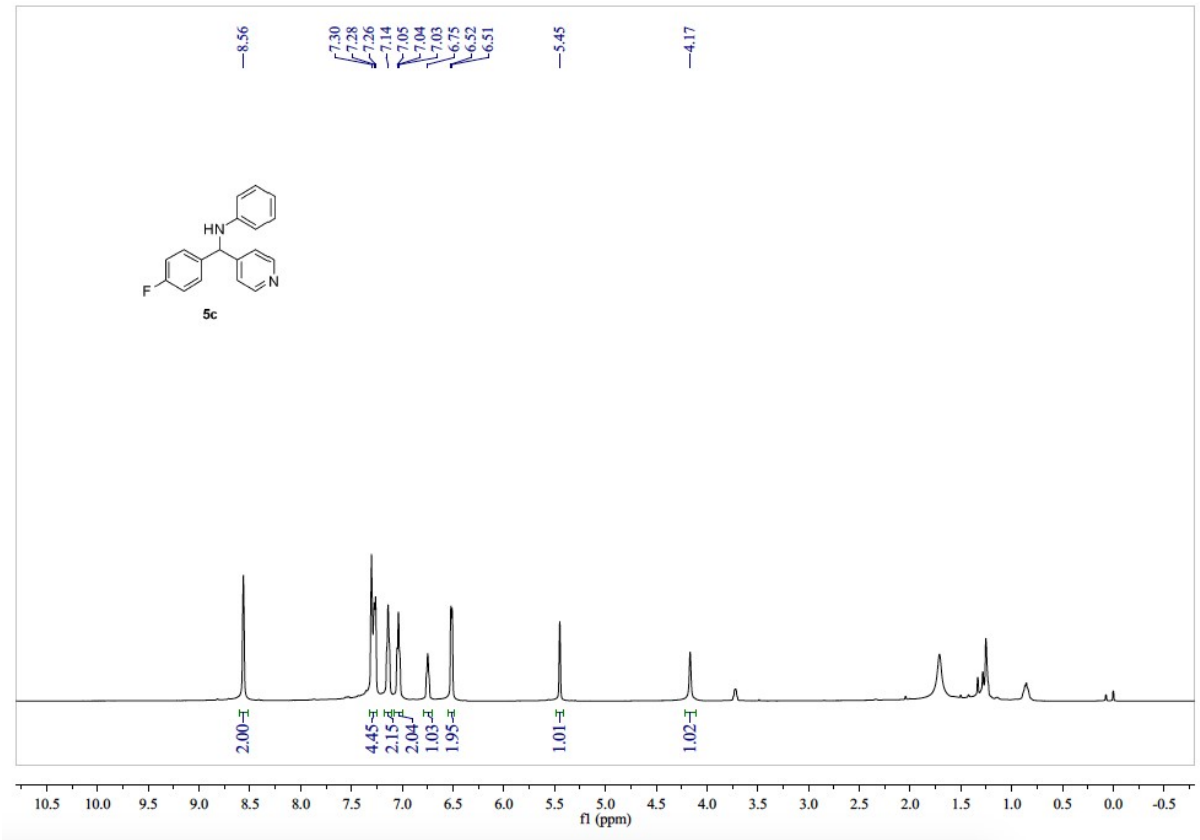
5b: *N*-(pyridin-4-yl(3-(trifluoromethoxy)phenyl)methyl)aniline

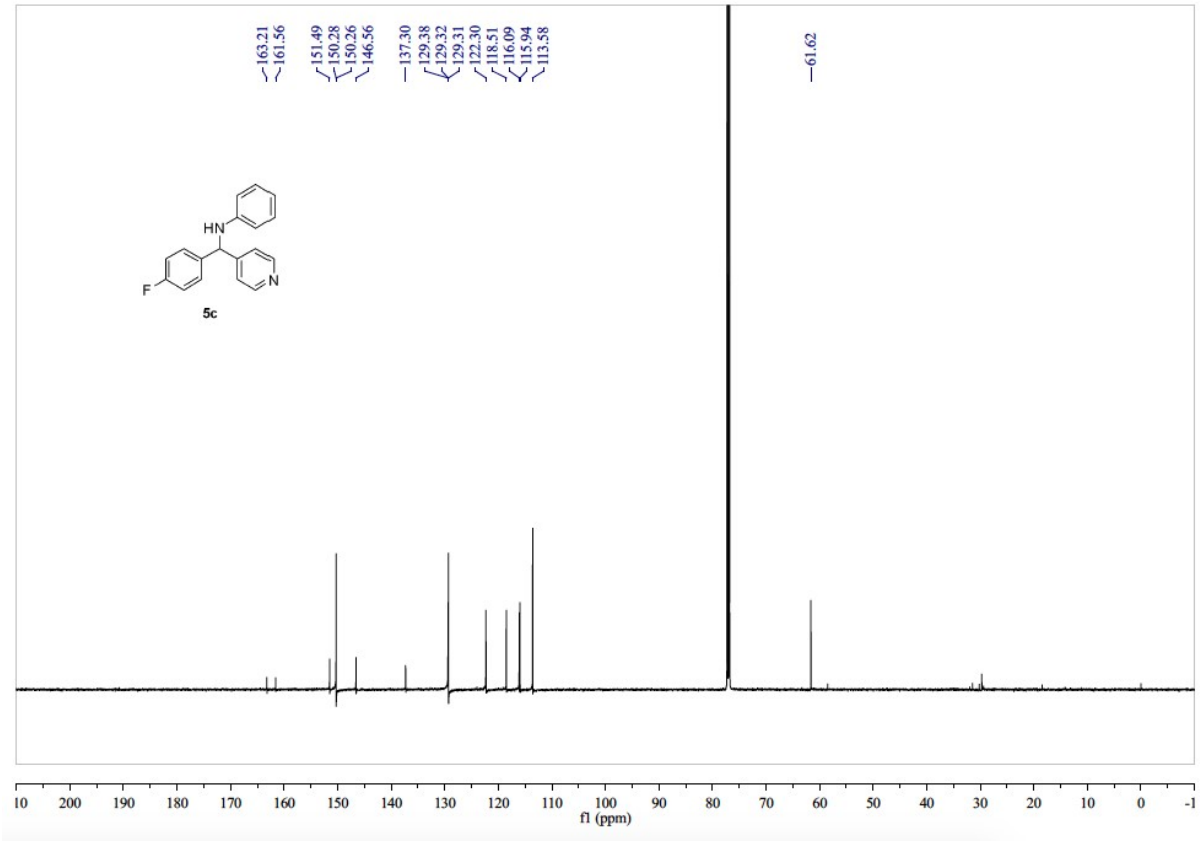






5c: *N*-((4-fluorophenyl)(pyridin-4-yl)methyl)aniline

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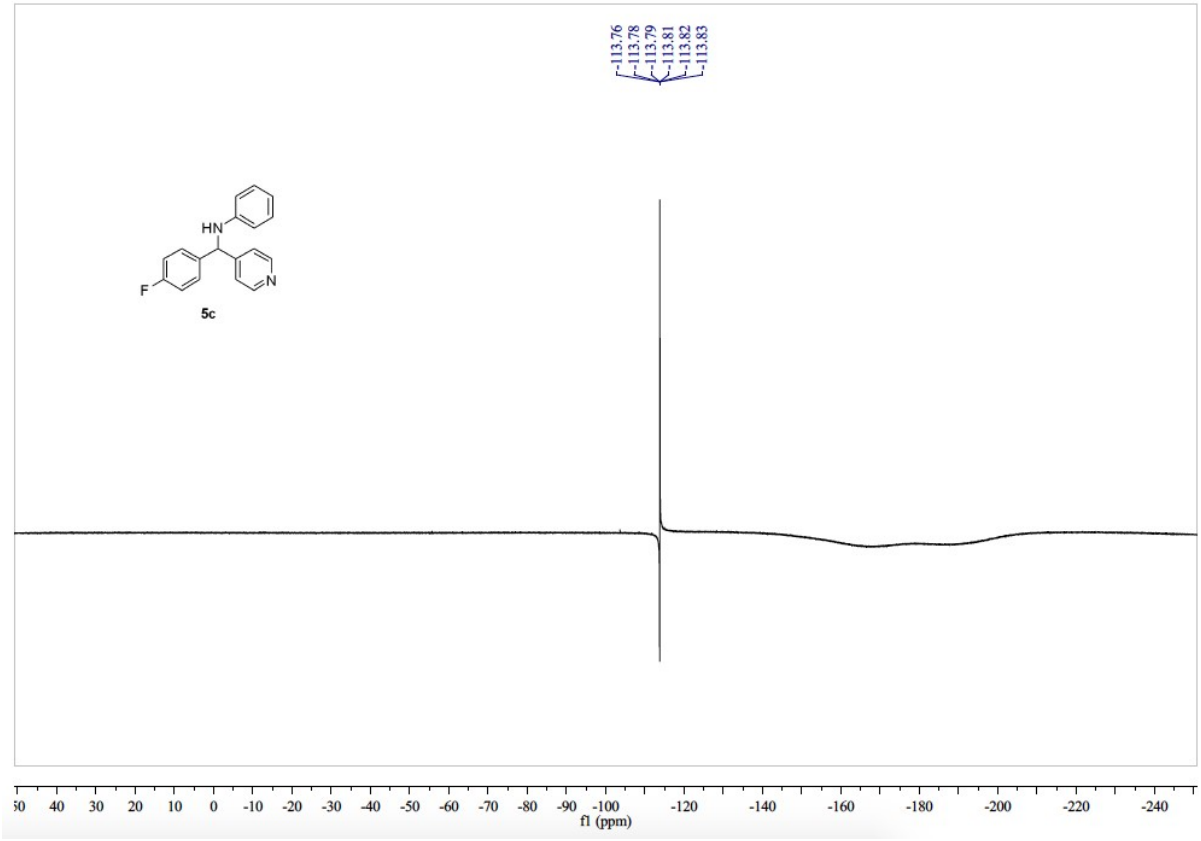
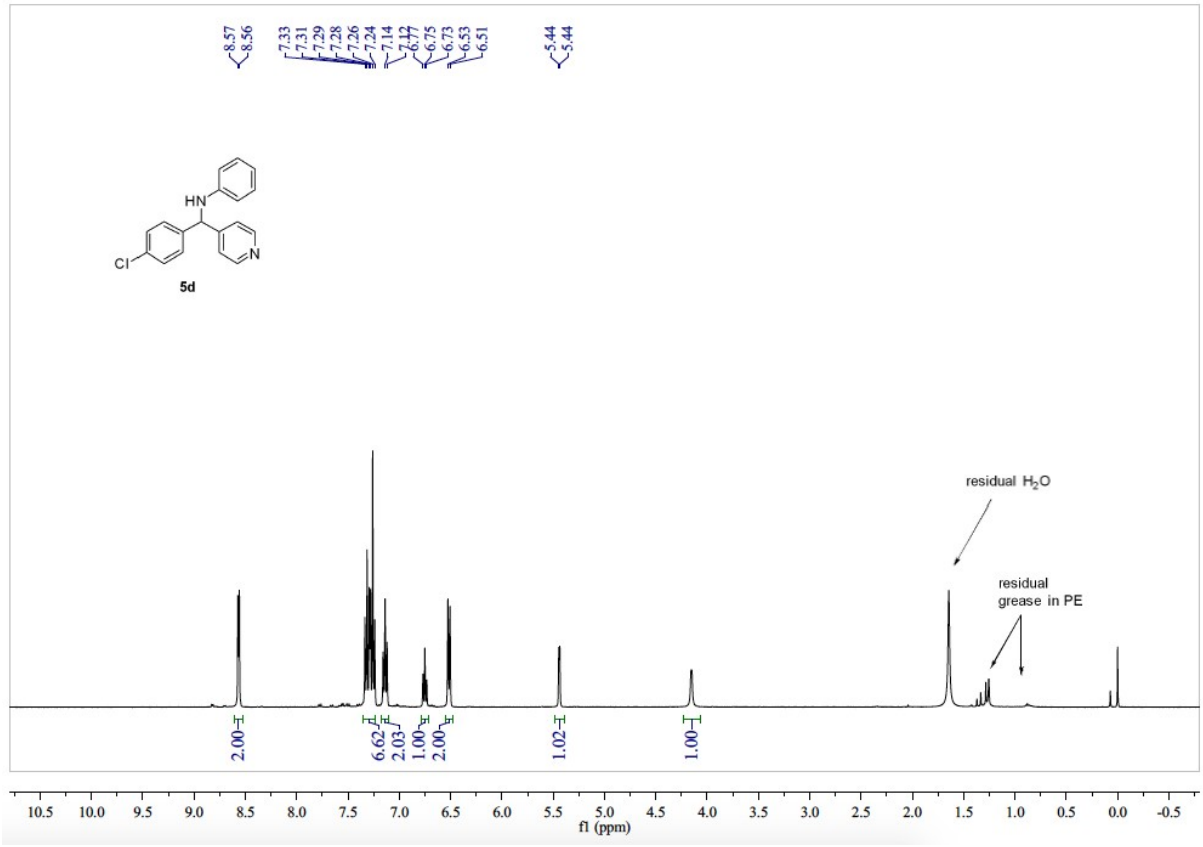
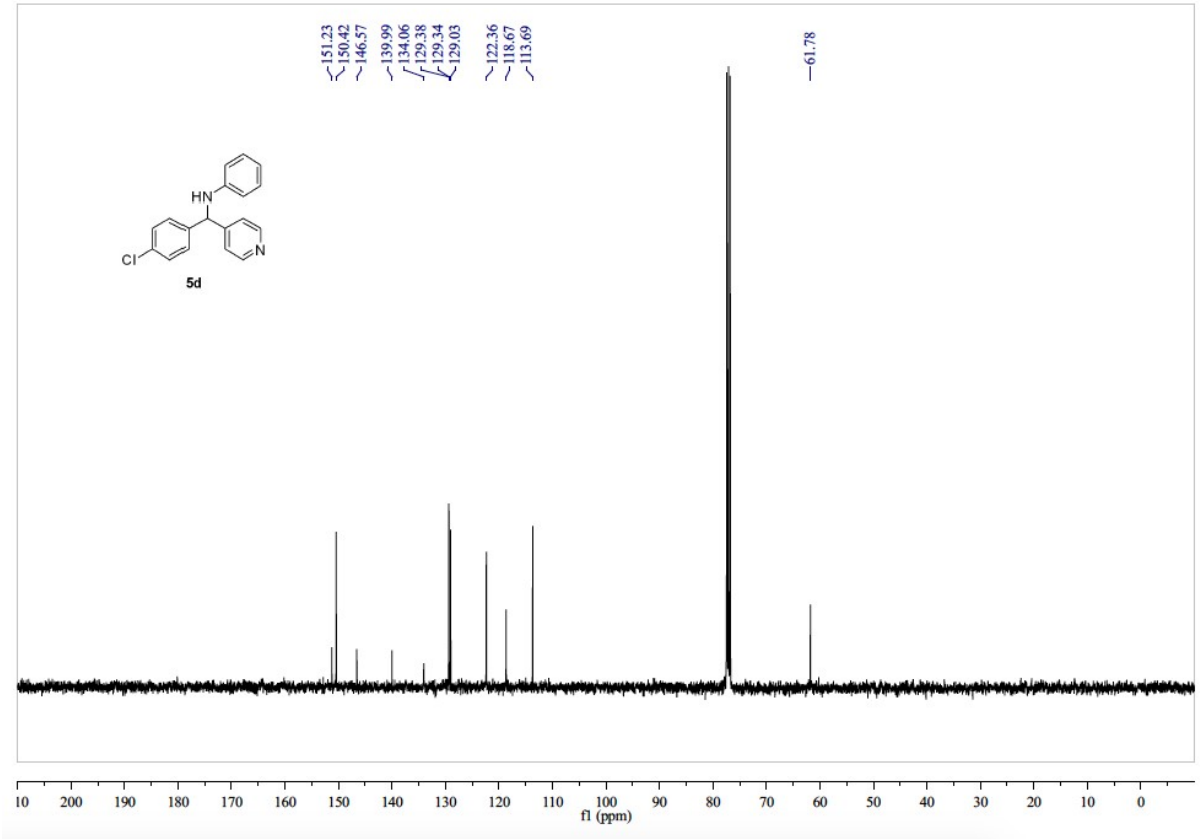
146.56
137.30
129.38
129.32
129.31
122.30
118.51
116.09
115.94
113.58
61.62
HN
F
N
5c
f1 (ppm)

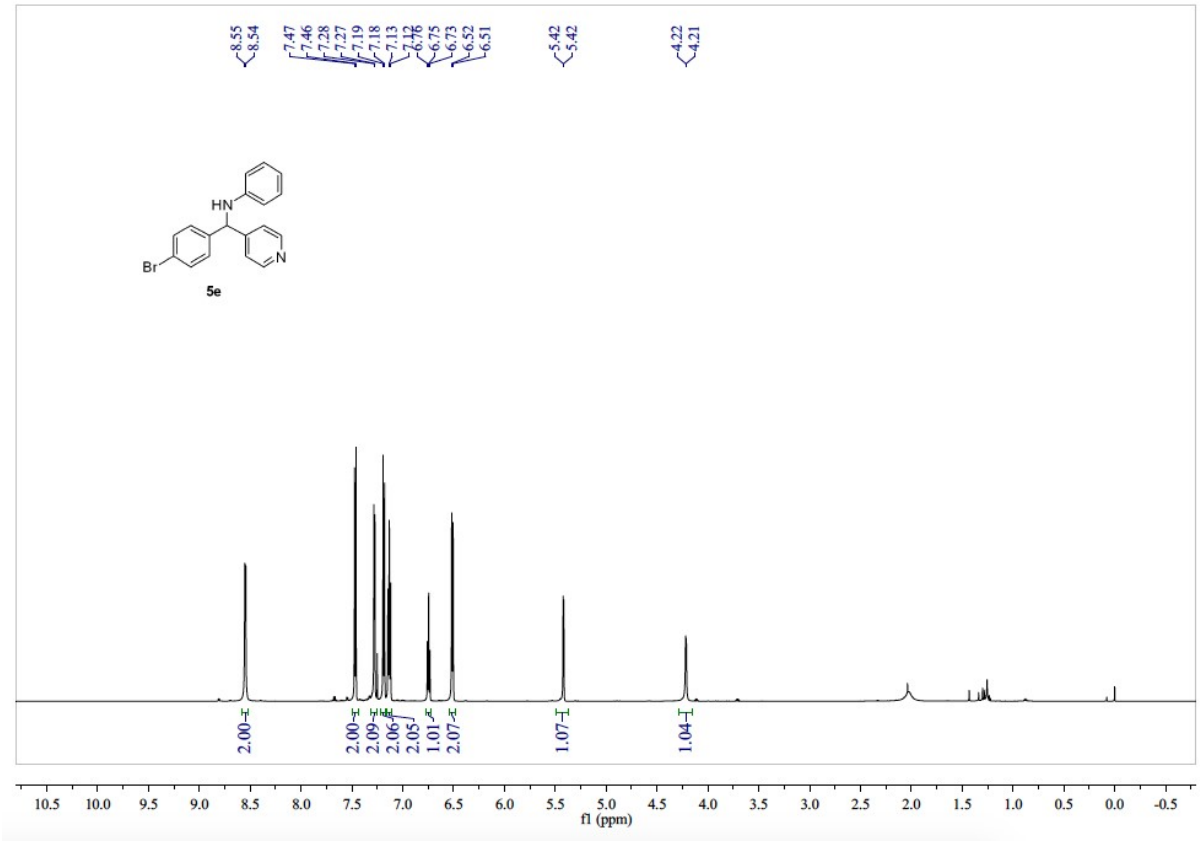

113.76
113.78
113.79
113.81
113.82
113.83
HN
F
N
5c
f1 (ppm)

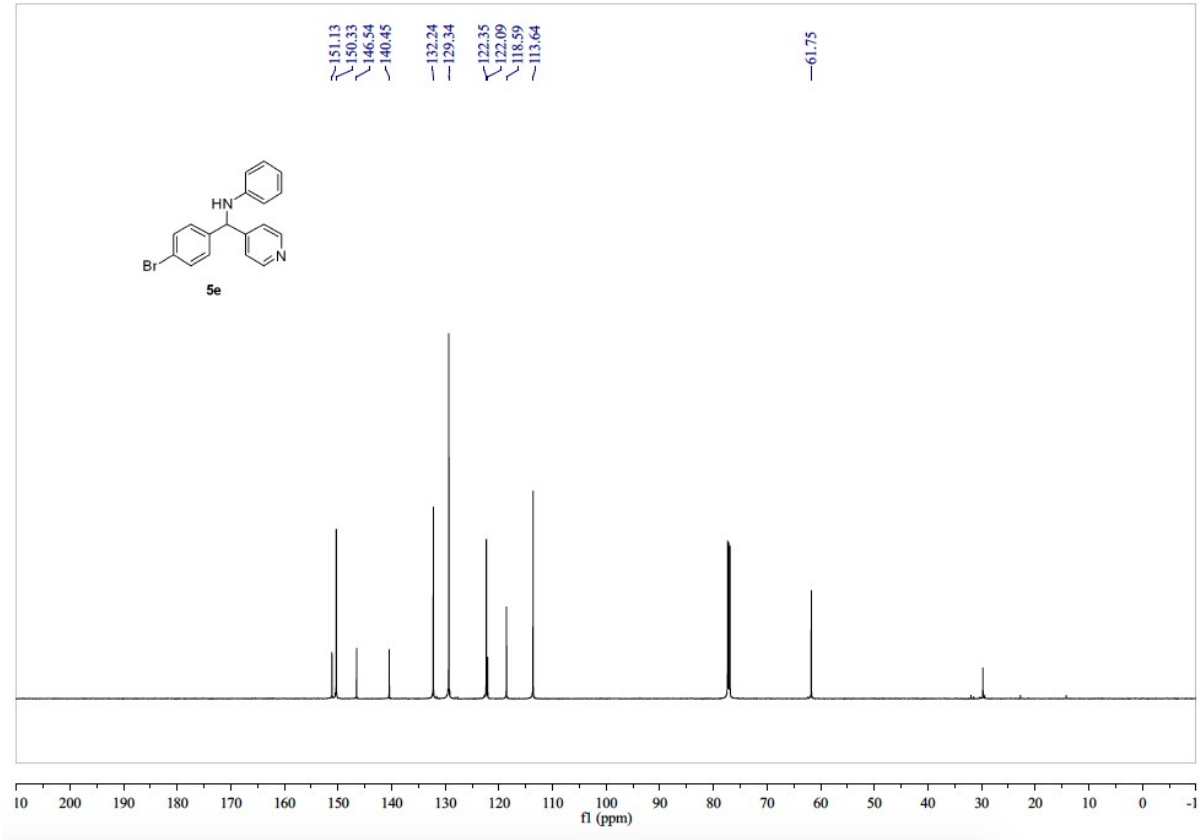
5d: *N*-((4-chlorophenyl)(pyridin-4-yl)methyl)aniline



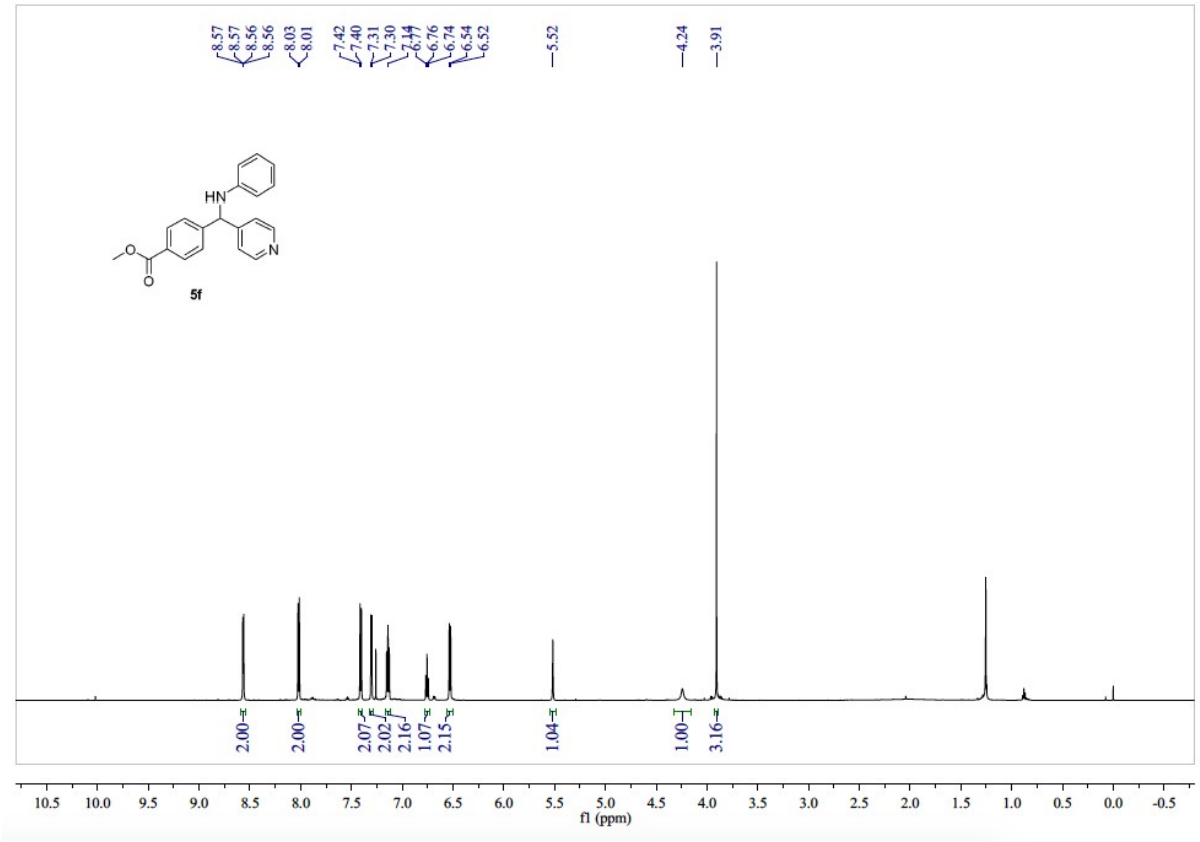


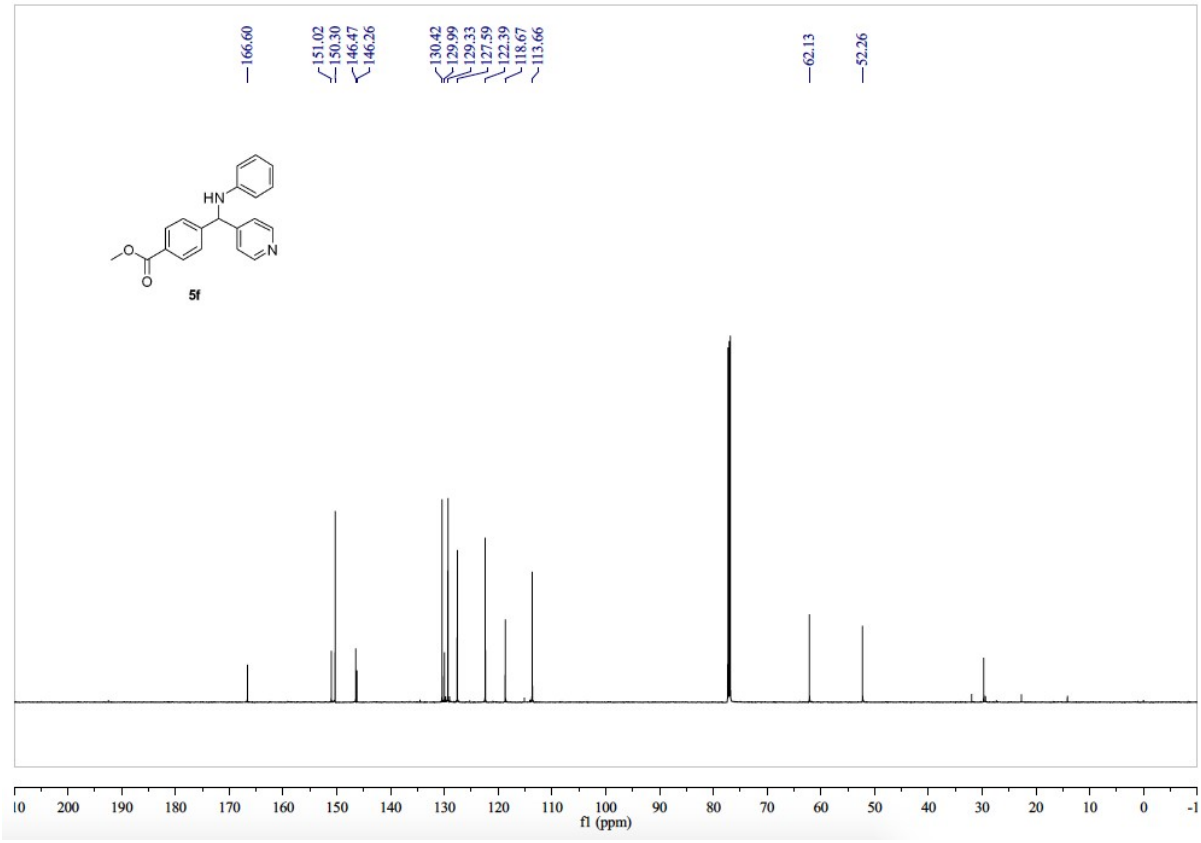
5e: *N*-((4-bromophenyl)(pyridin-4-yl)methyl)aniline



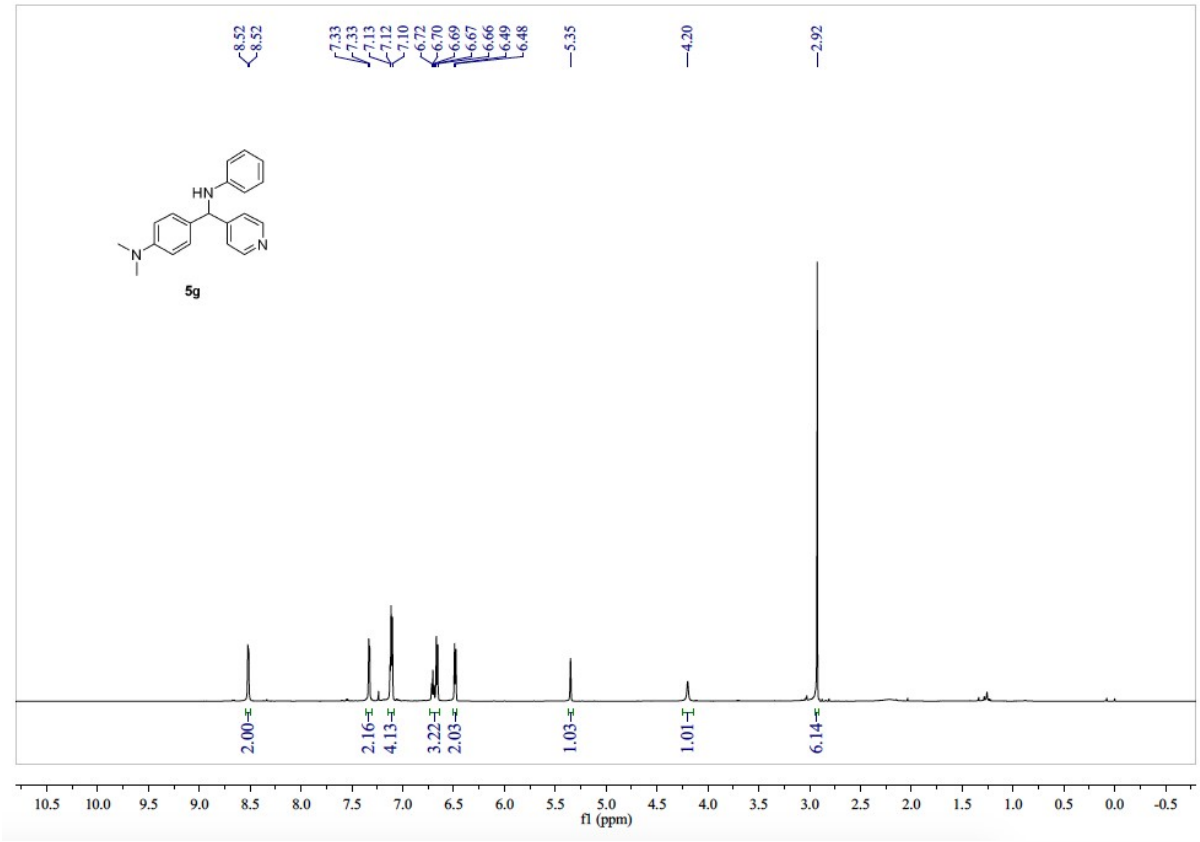


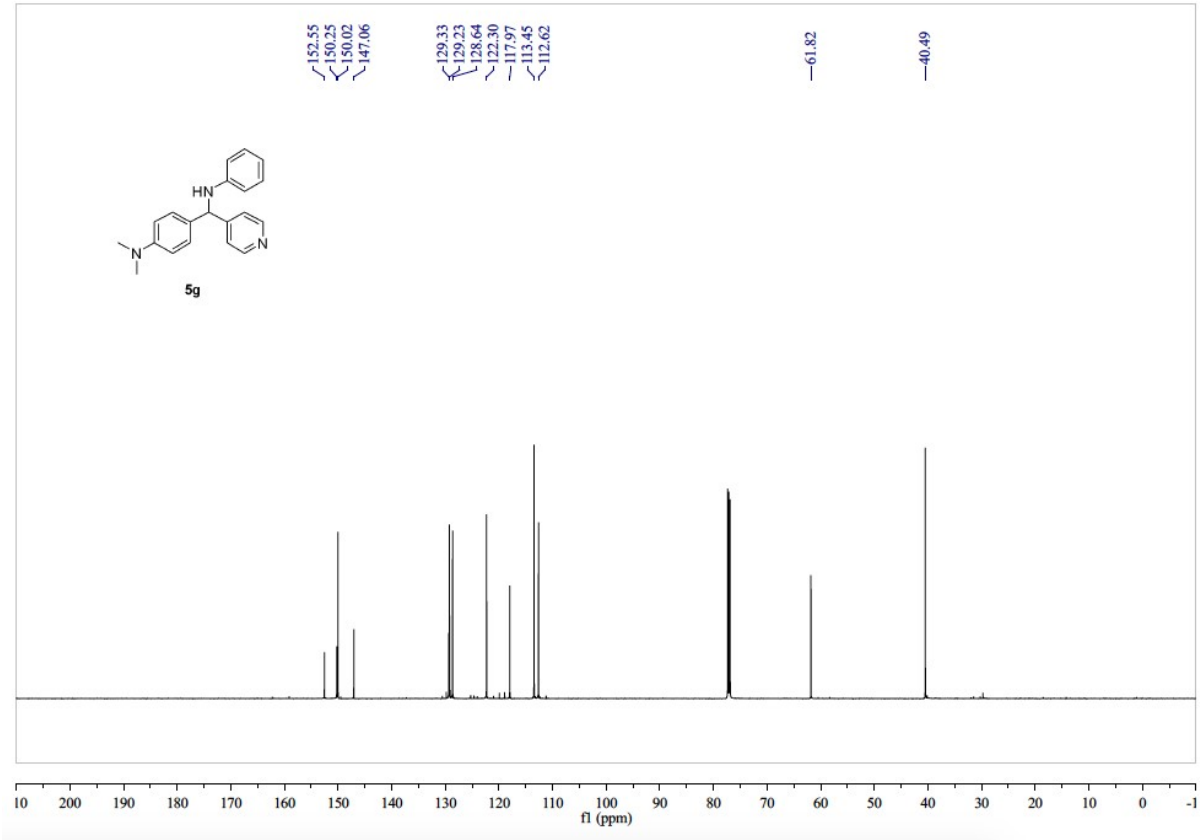
5f: methyl 4-((phenylamino)(pyridin-4-yl)methyl)benzoate



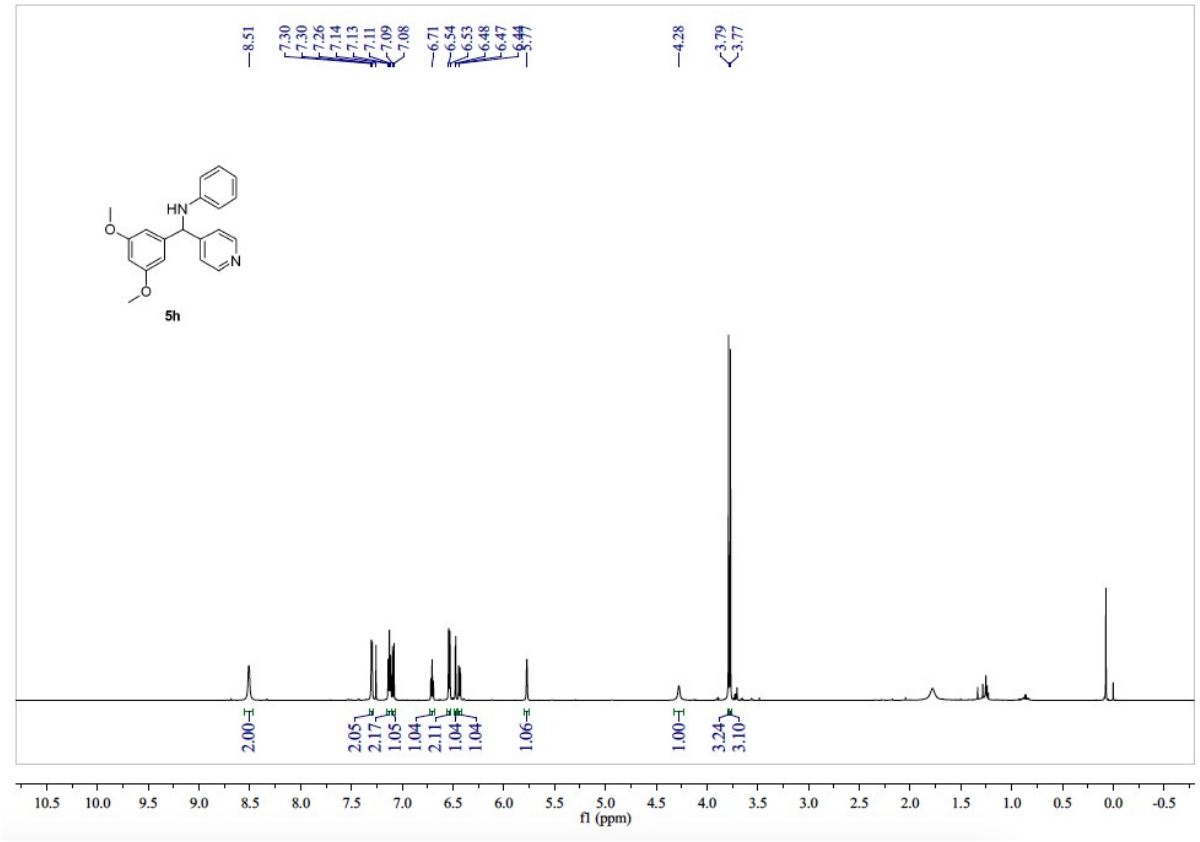


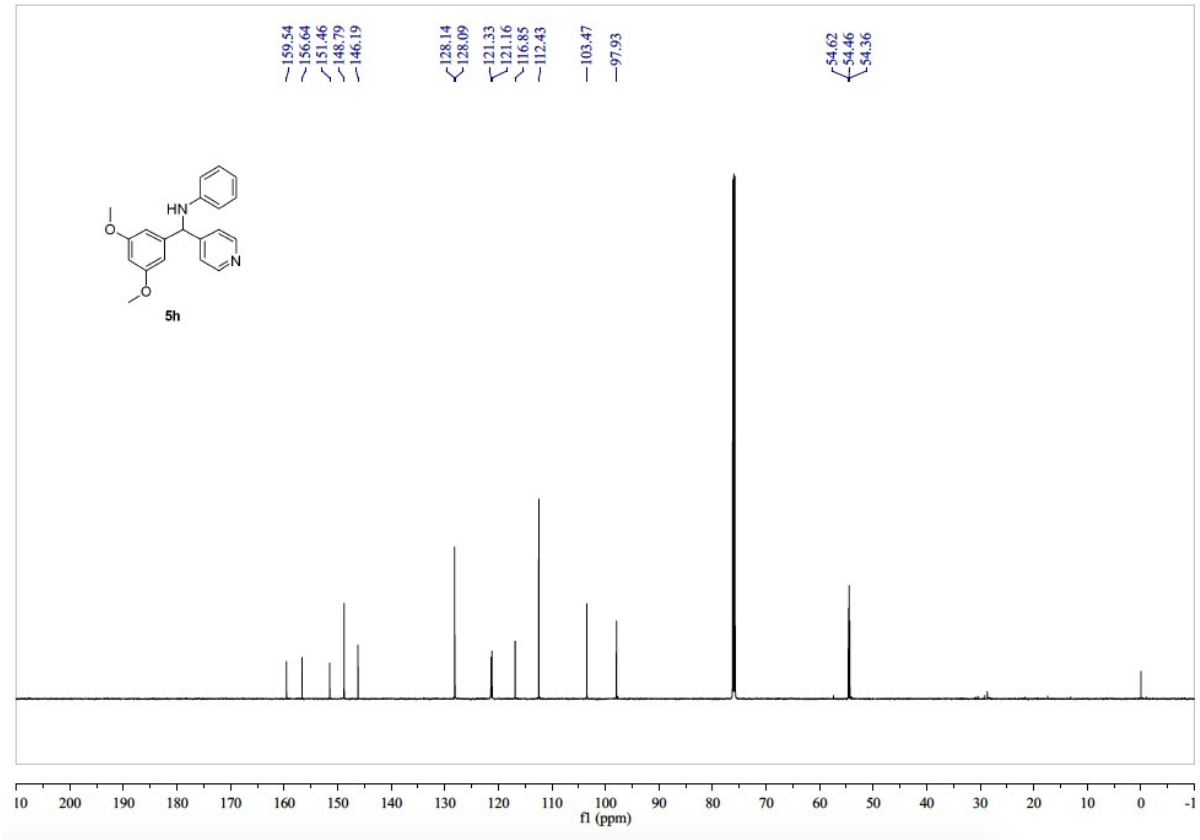
5g: *N,N*-dimethyl-4-((phenylamino)(pyridin-4-yl)methyl)aniline



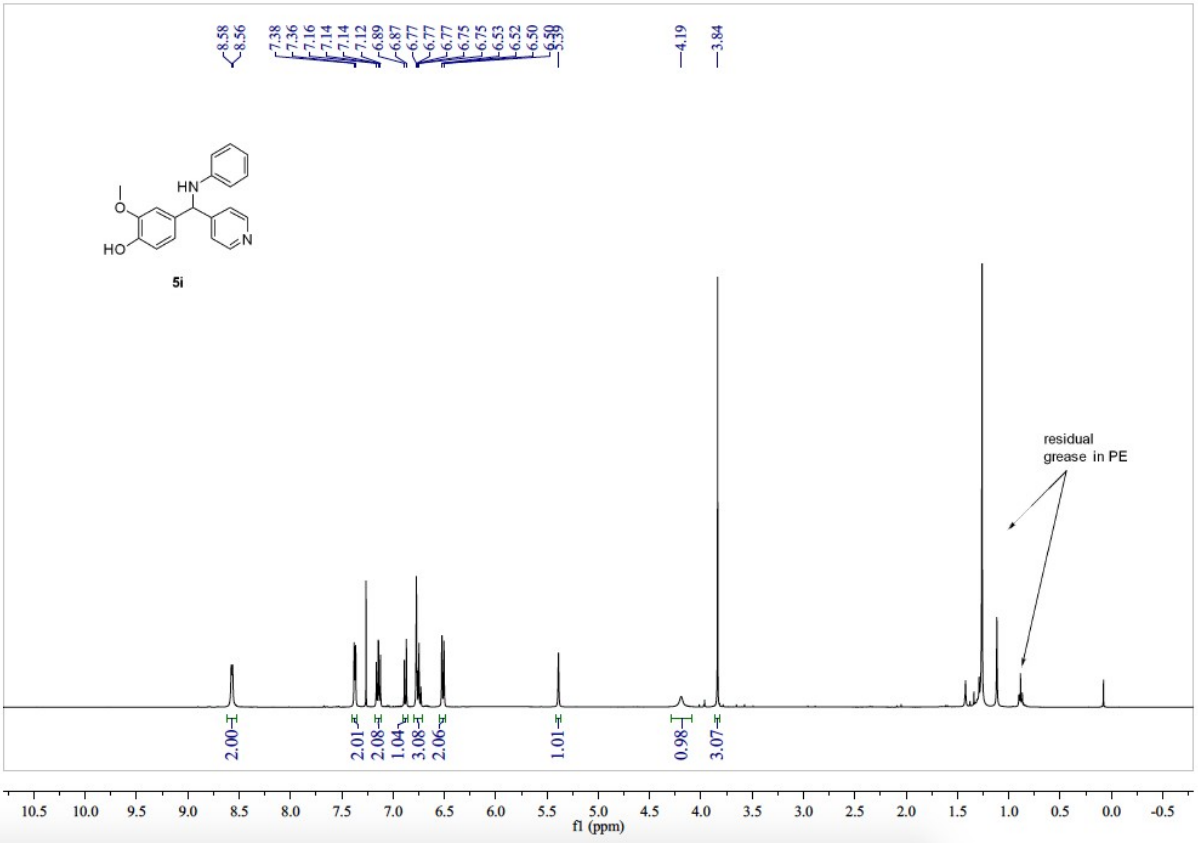


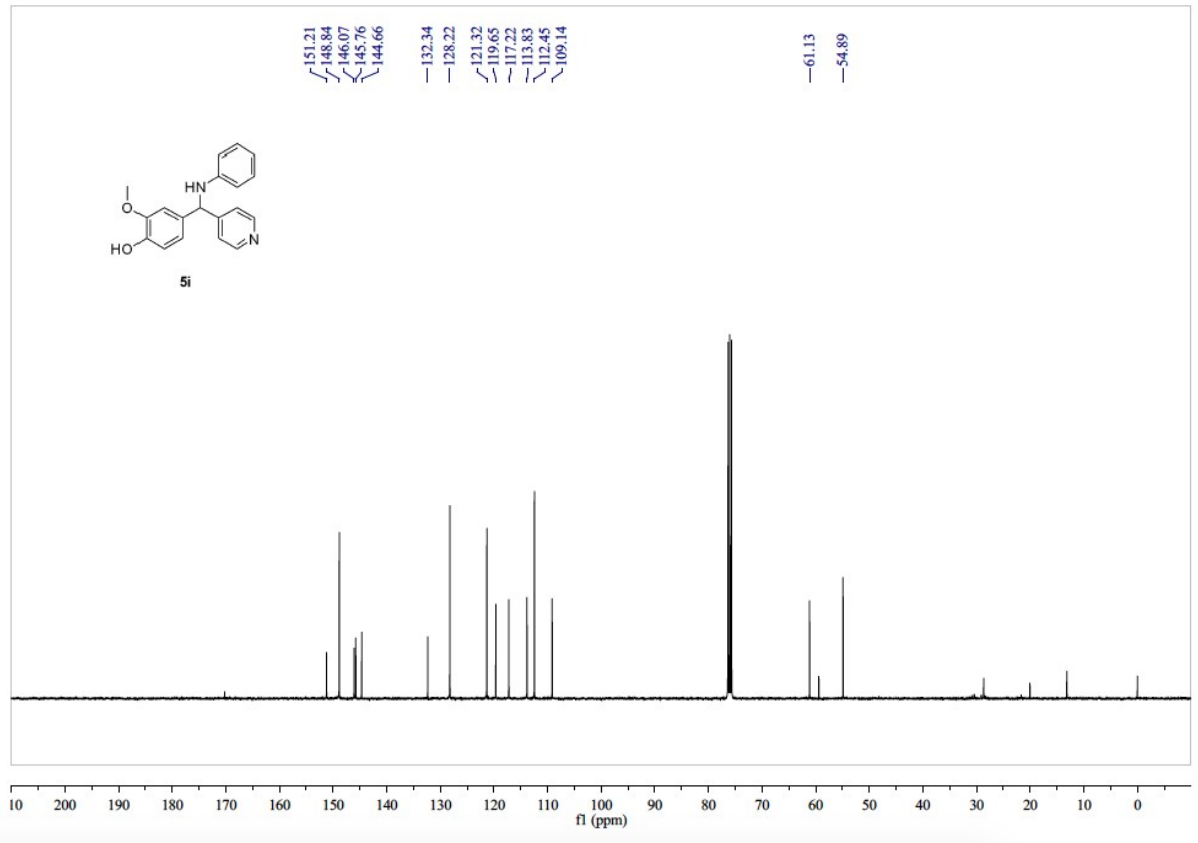
5h: *N*-((3,5-dimethoxyphenyl)(pyridin-4-yl)methyl)aniline



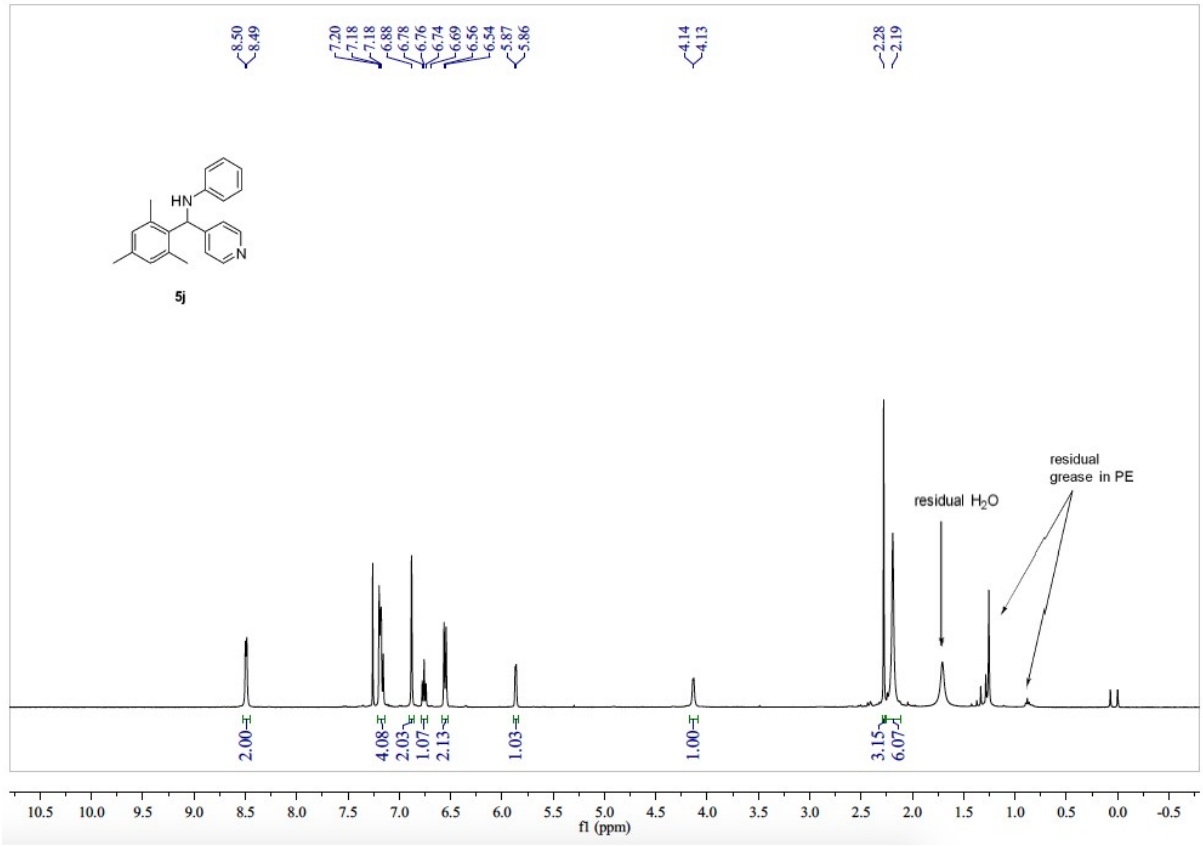


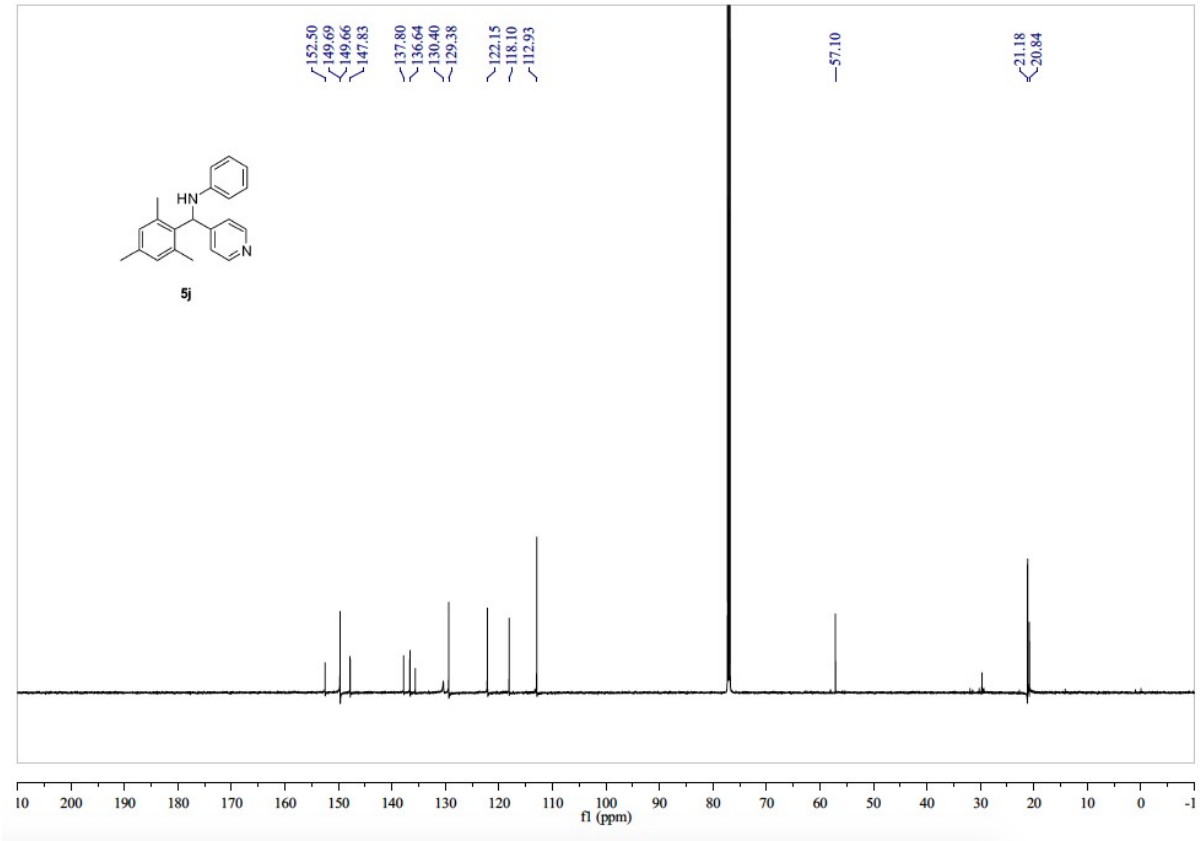
5i: 2-methoxy-4-((phenylamino)(pyridin-4-yl)methyl)phenol



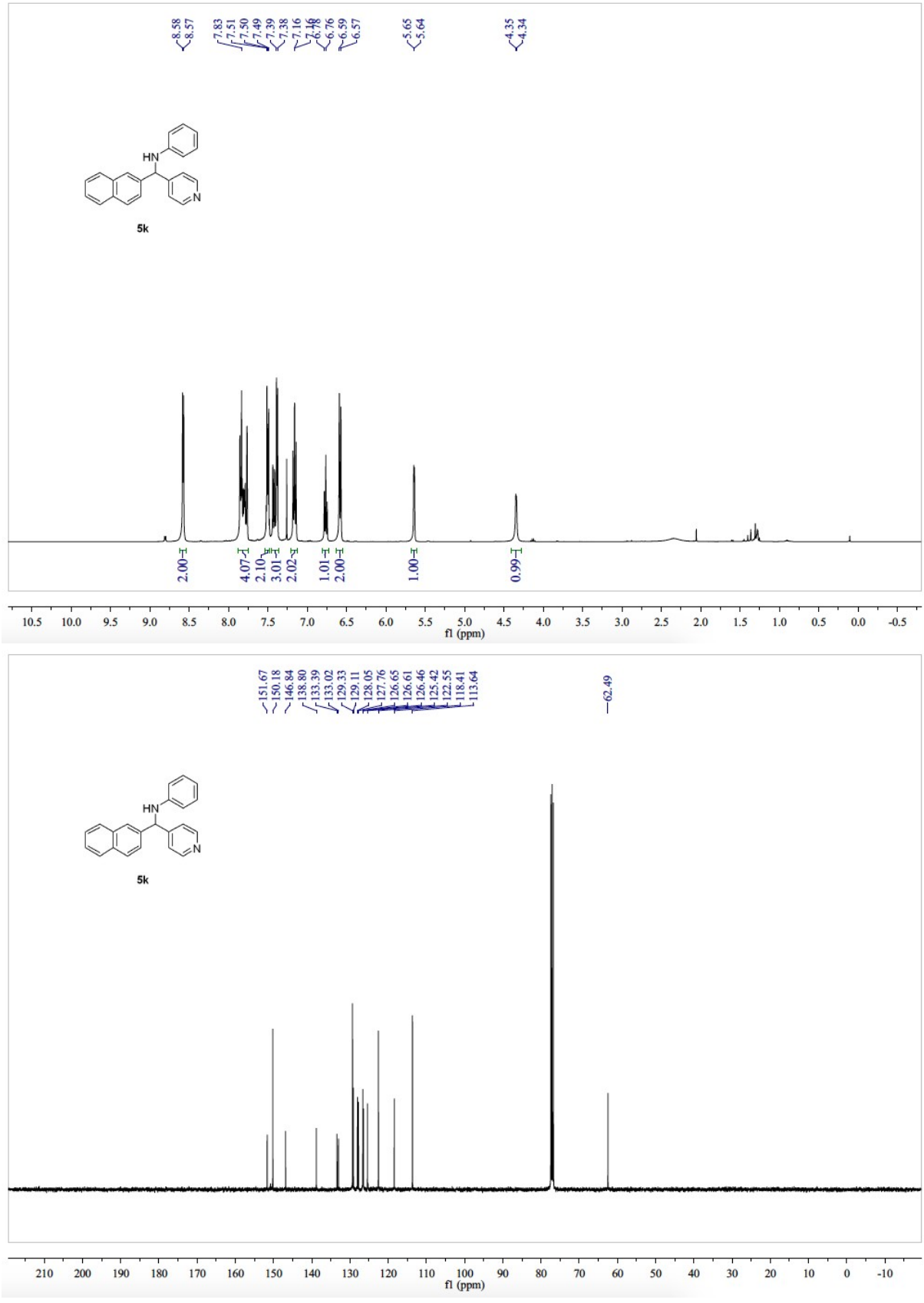


5j: *N*-(mesityl(pyridin-4-yl)methyl)aniline

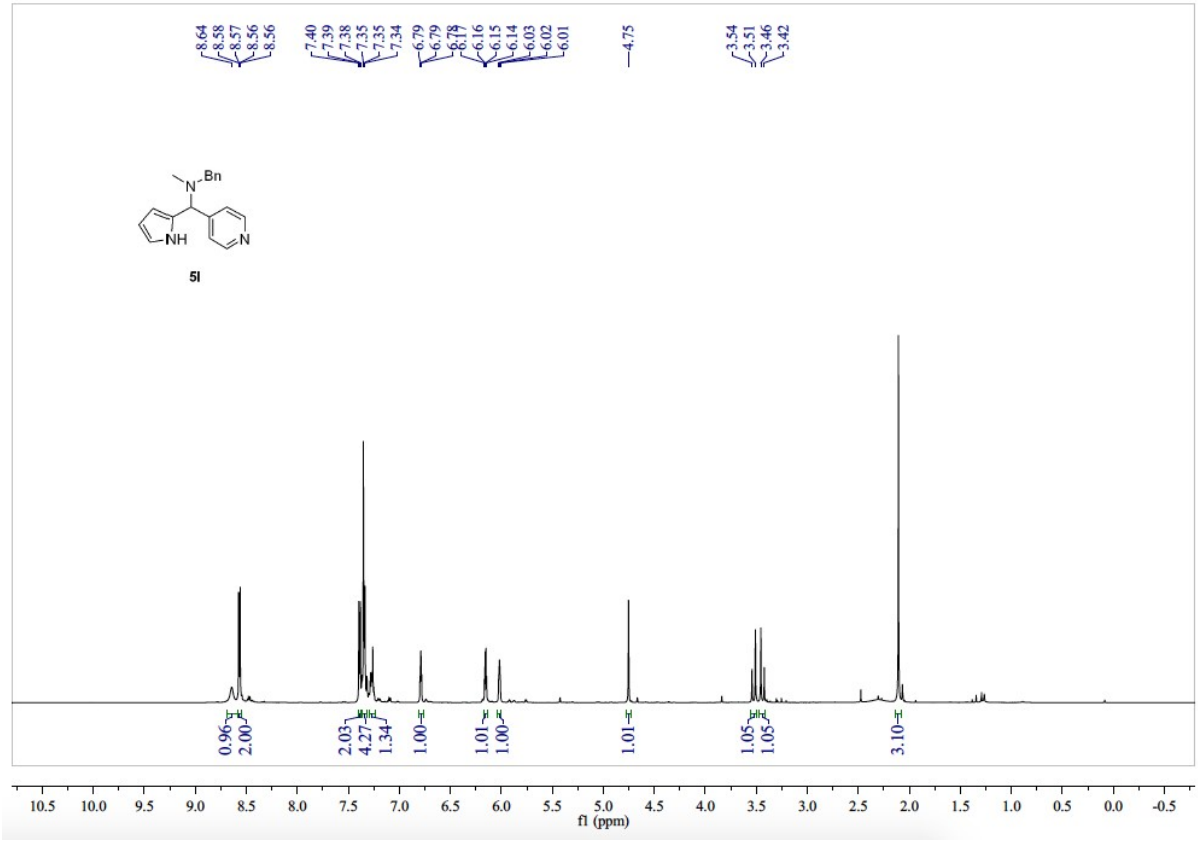


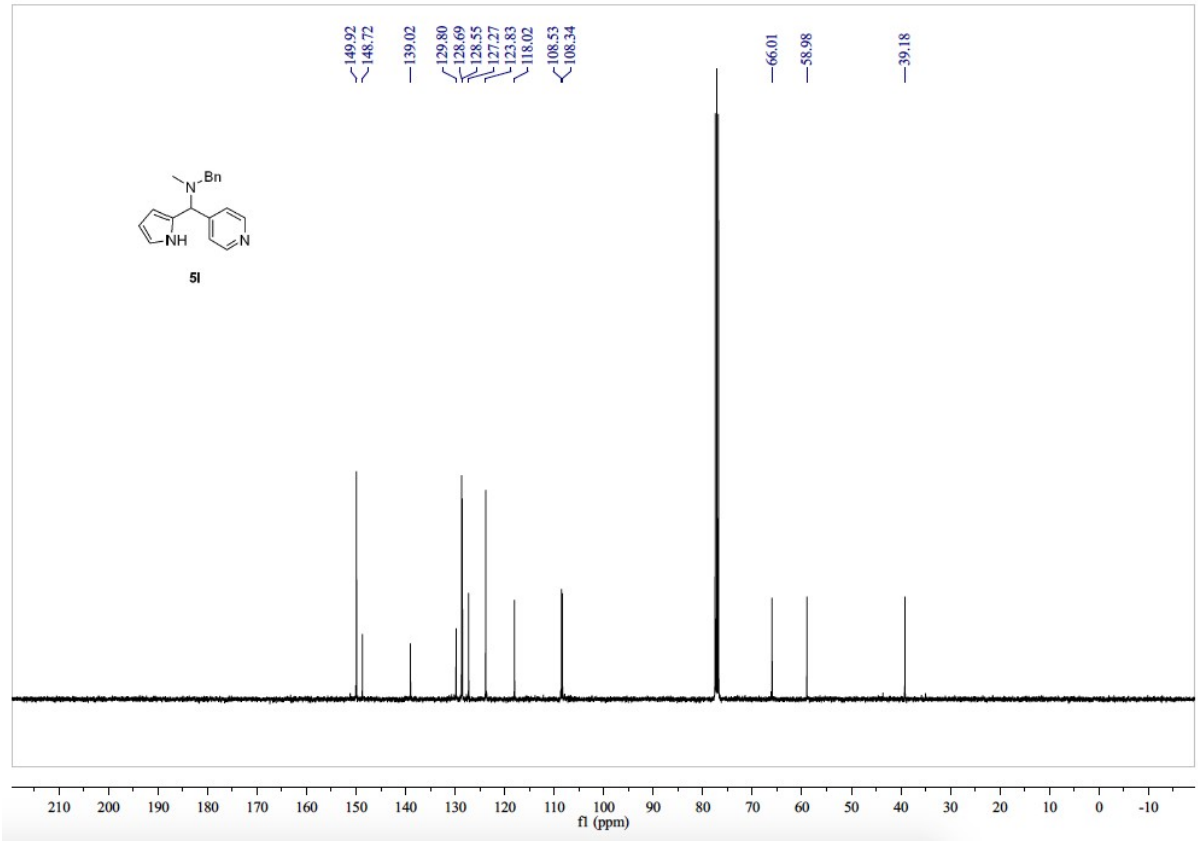


5k: *N*-(naphthalen-2-yl(pyridin-4-yl)methyl)aniline

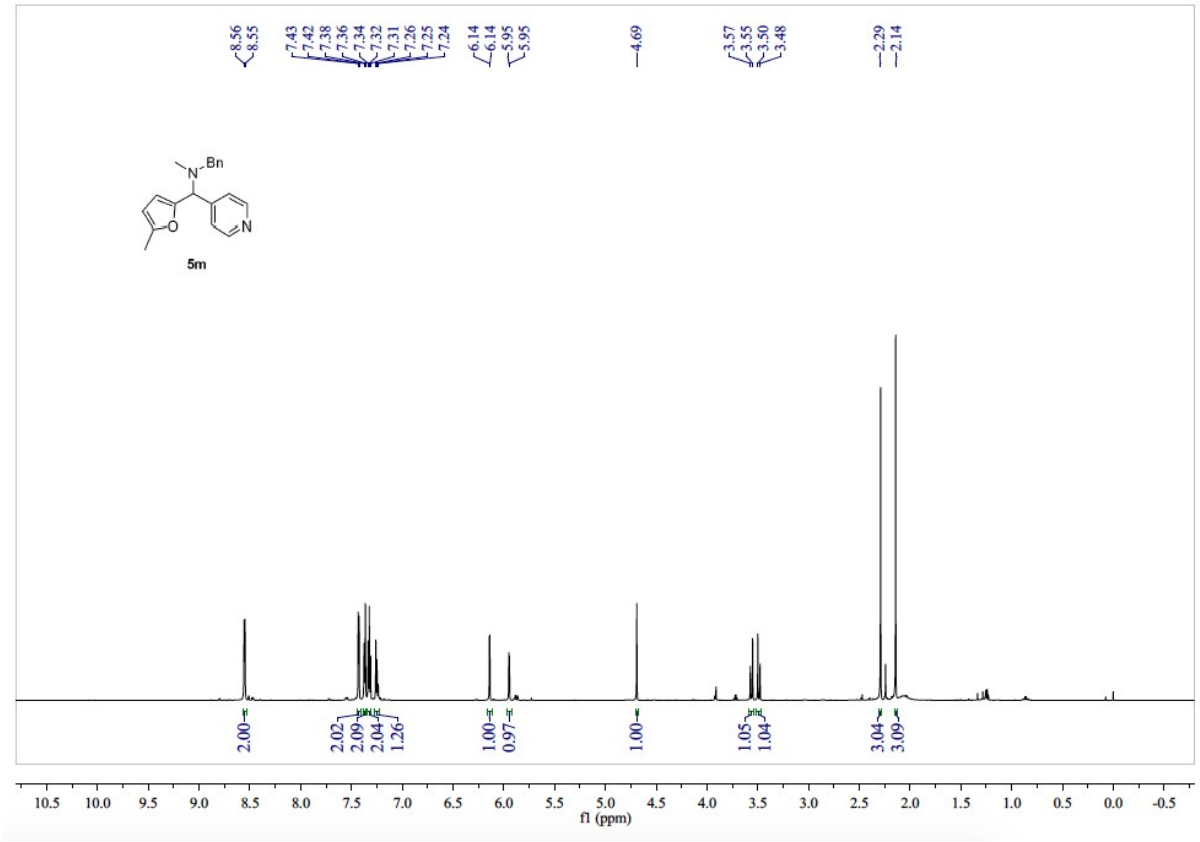


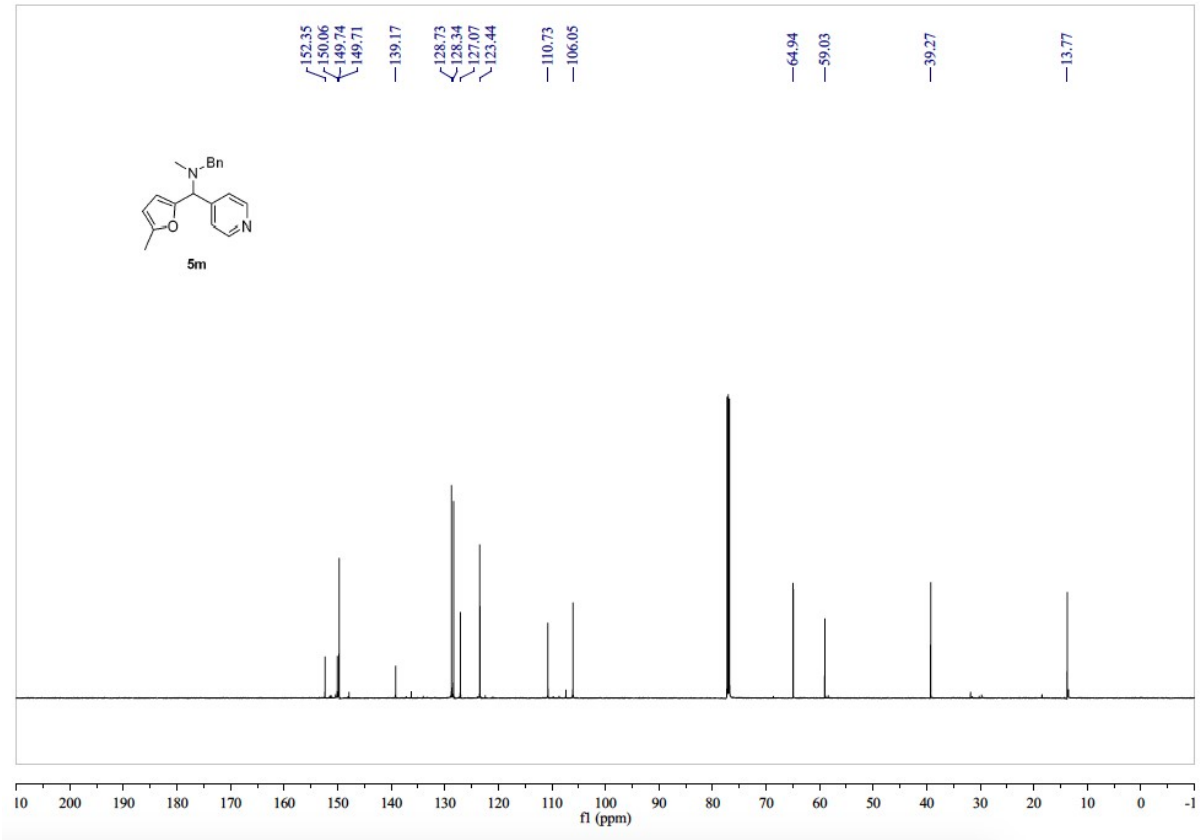
5l: *N*-benzyl-*N*-methyl-1-(pyridin-4-yl)-1-(1*H*-pyrrol-2-yl)methanamine]



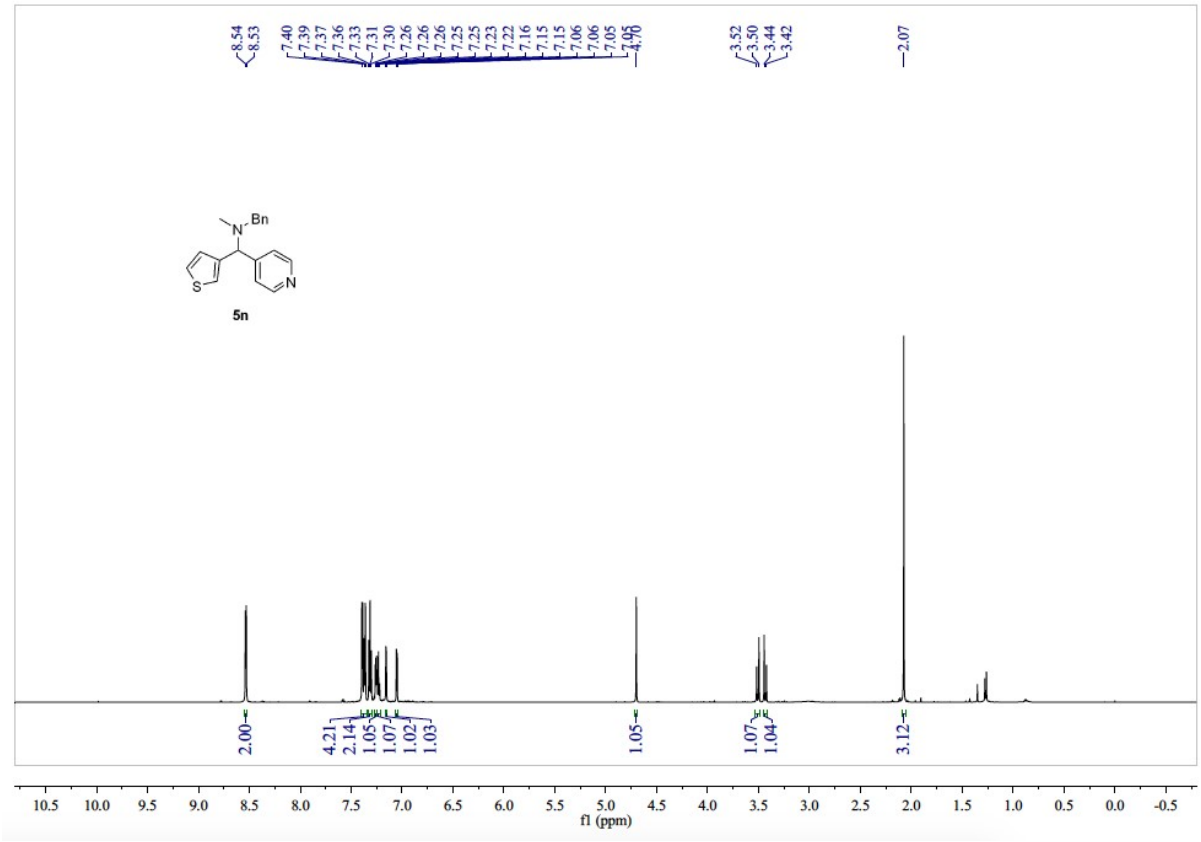


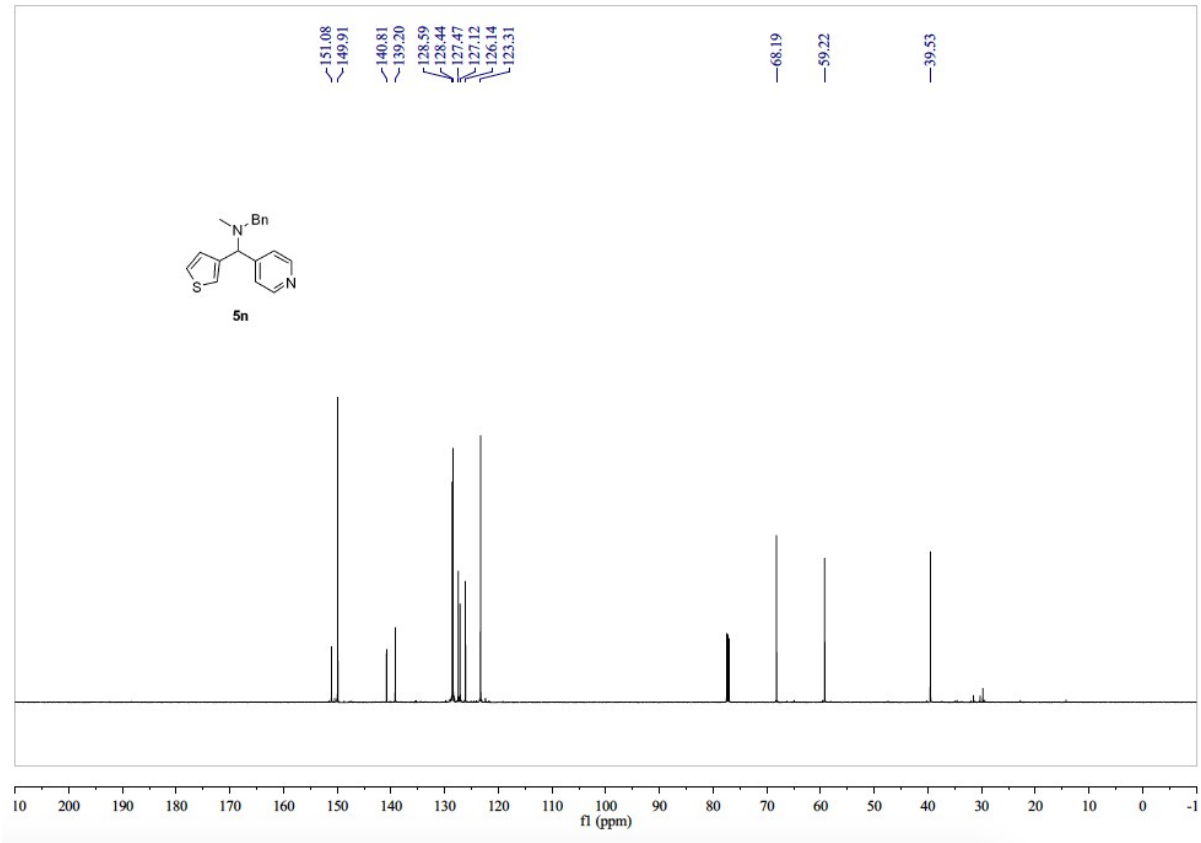
5m: *N*-benzyl-*N*-methyl-1-(5-methylfuran-2-yl)-1-(pyridin-4-yl)methanamine



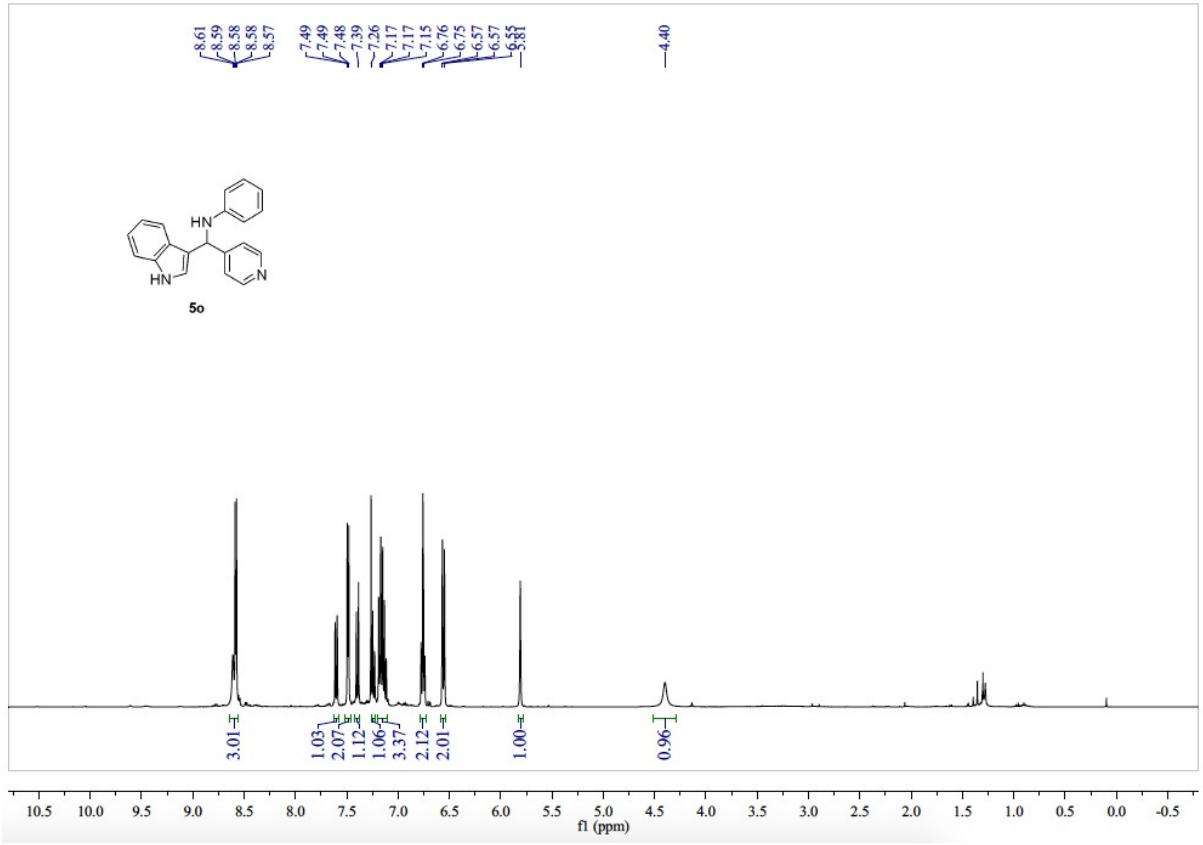


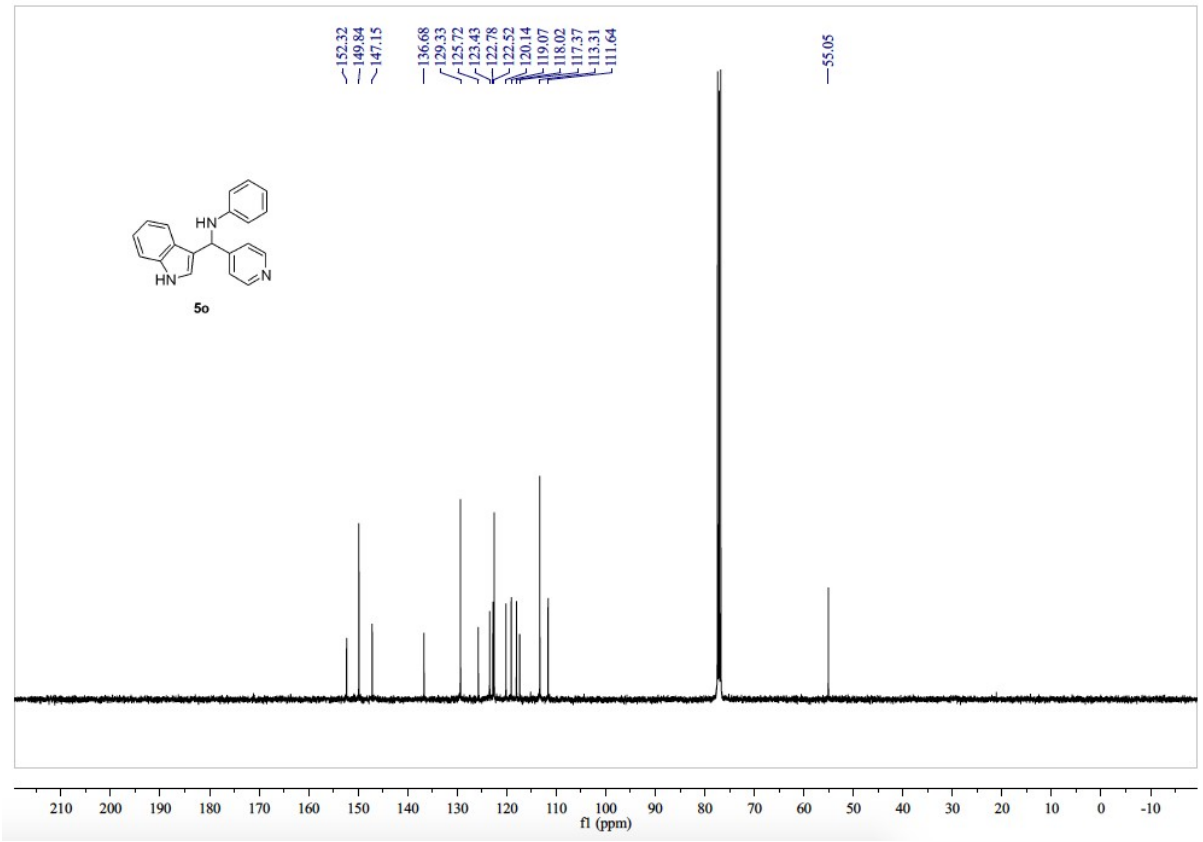
5n: *N*-benzyl-*N*-methyl-1-(pyridin-4-yl)-1-(thiophen-3-yl)methanamine



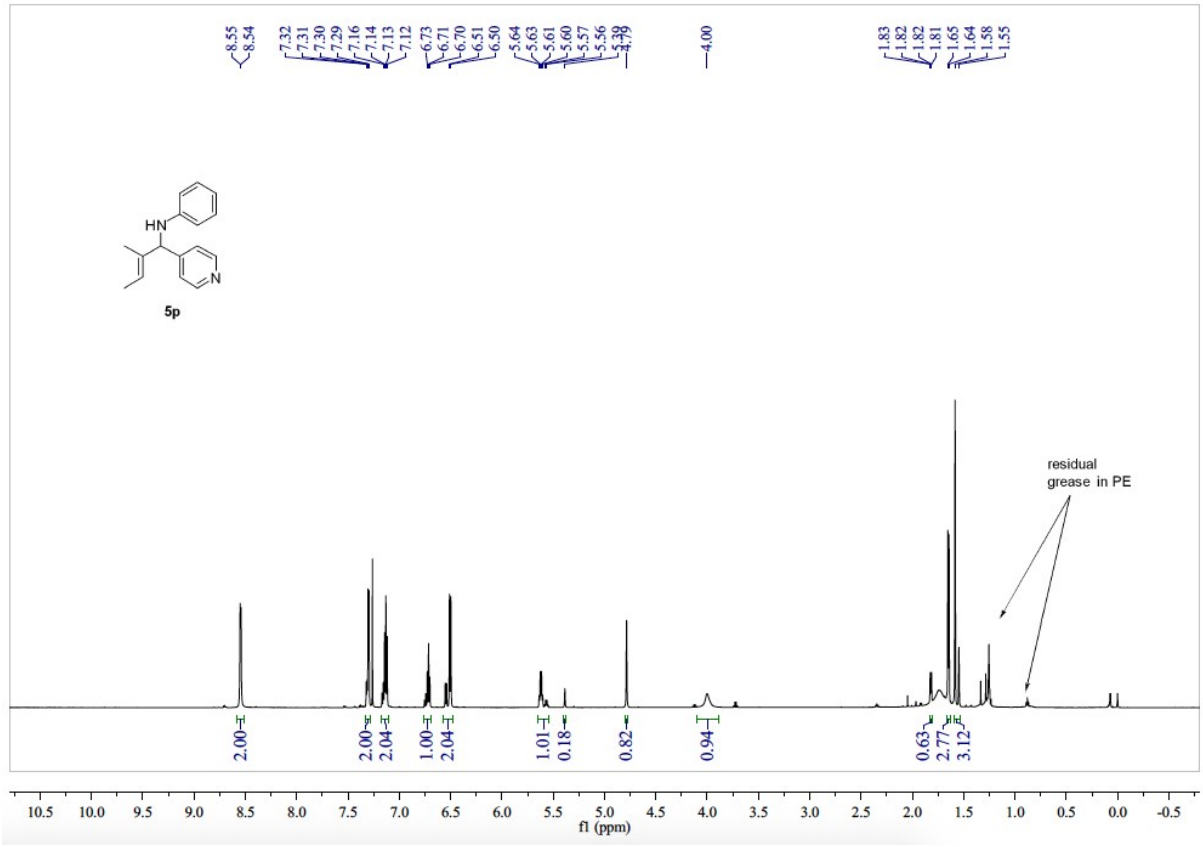


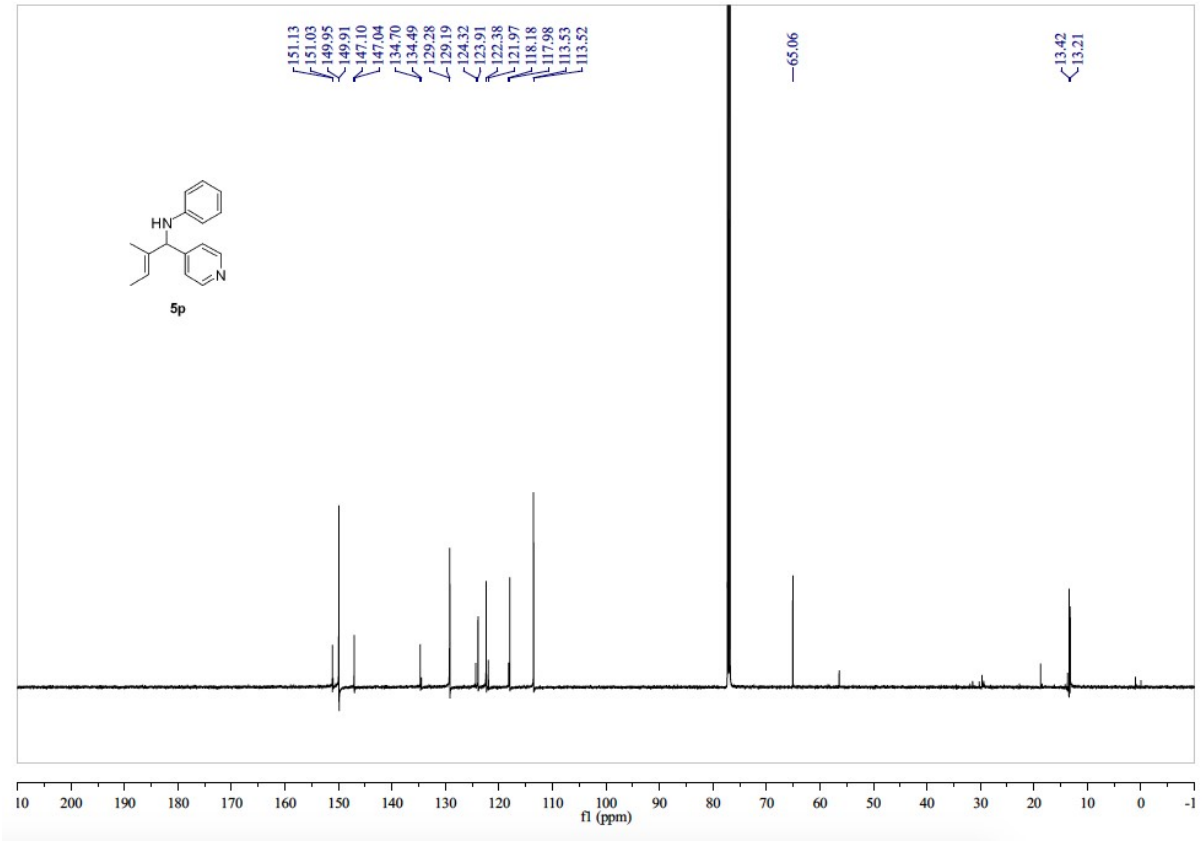
5o: *N*-((1*H*-indol-3-yl)(pyridin-4-yl)methyl)aniline



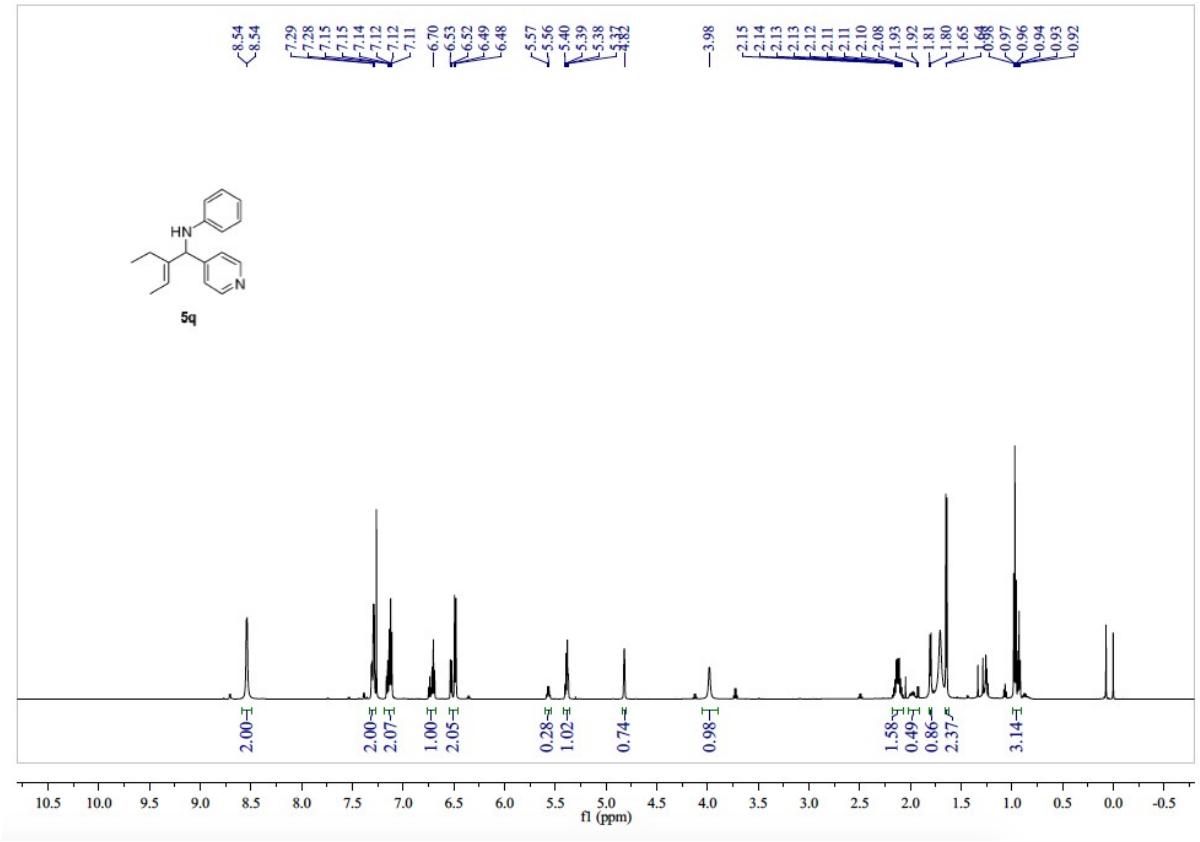


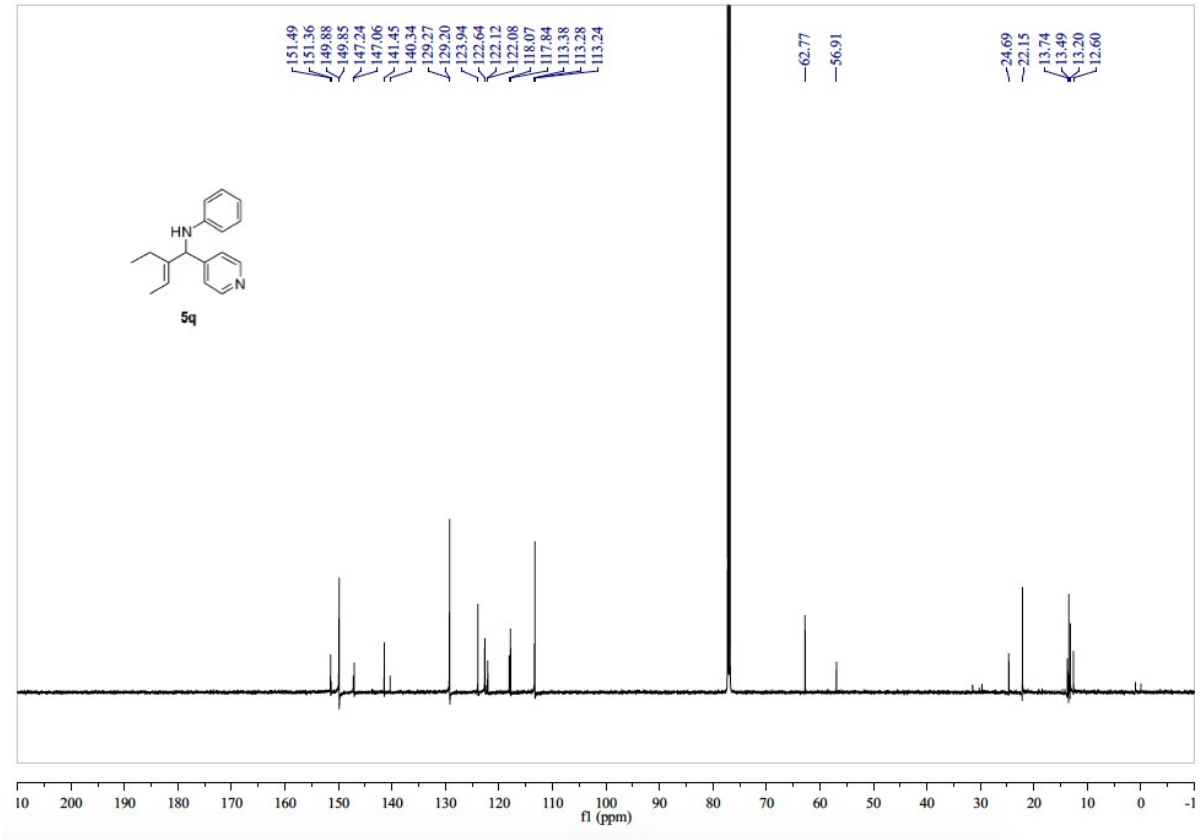
5p: *N*-(2-methyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



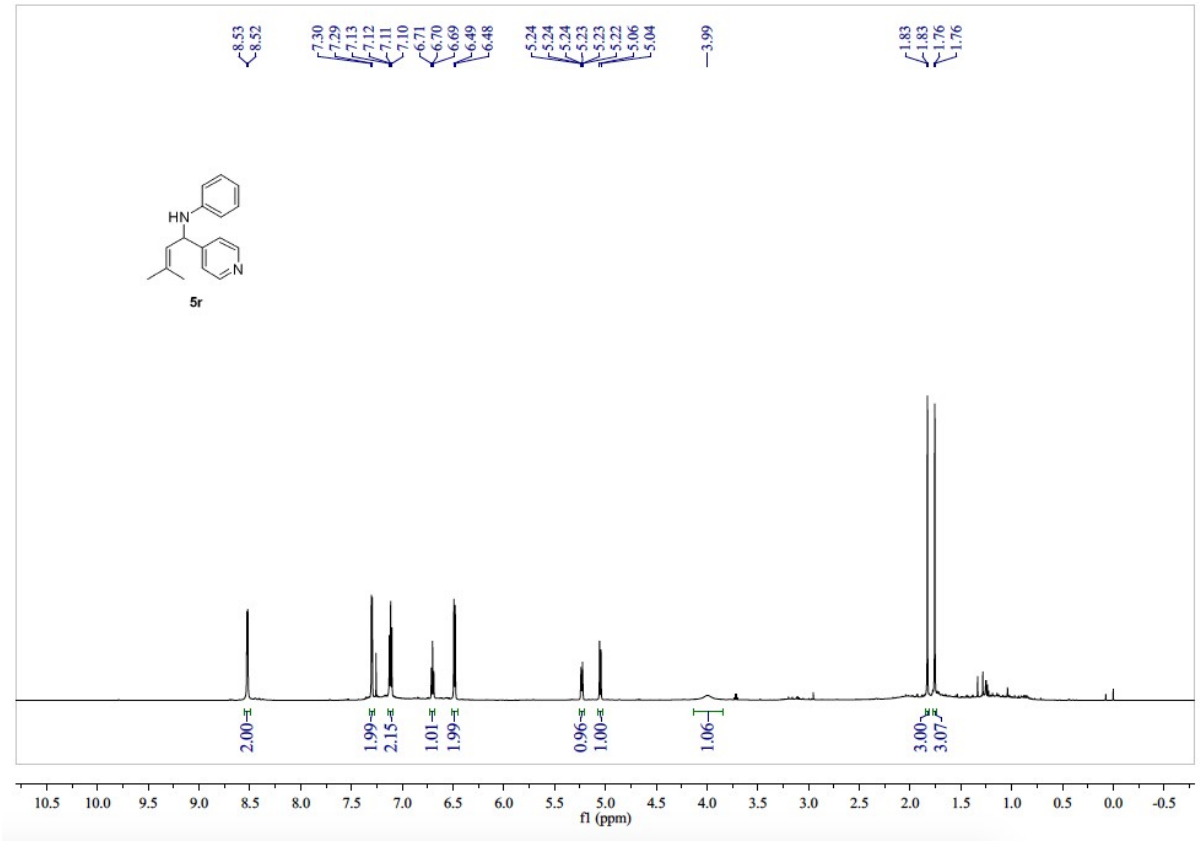


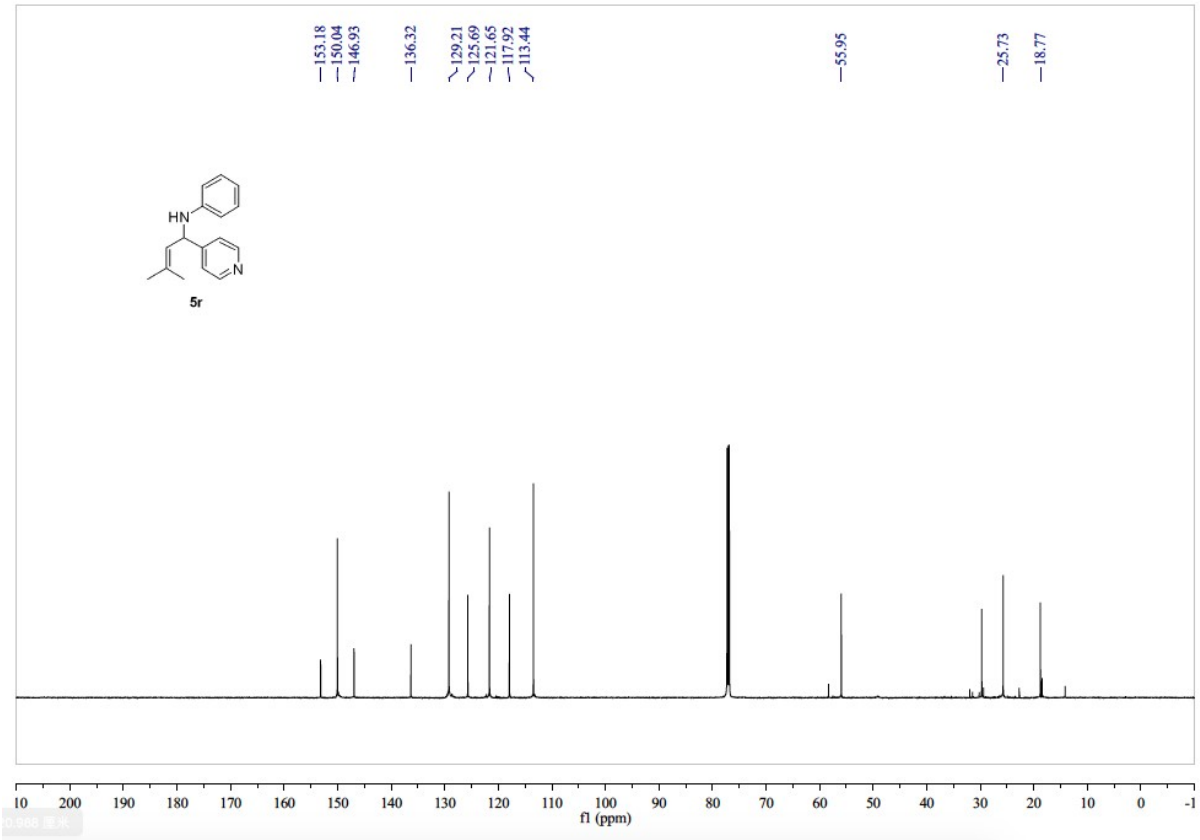
5q: *N*-(2-ethyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



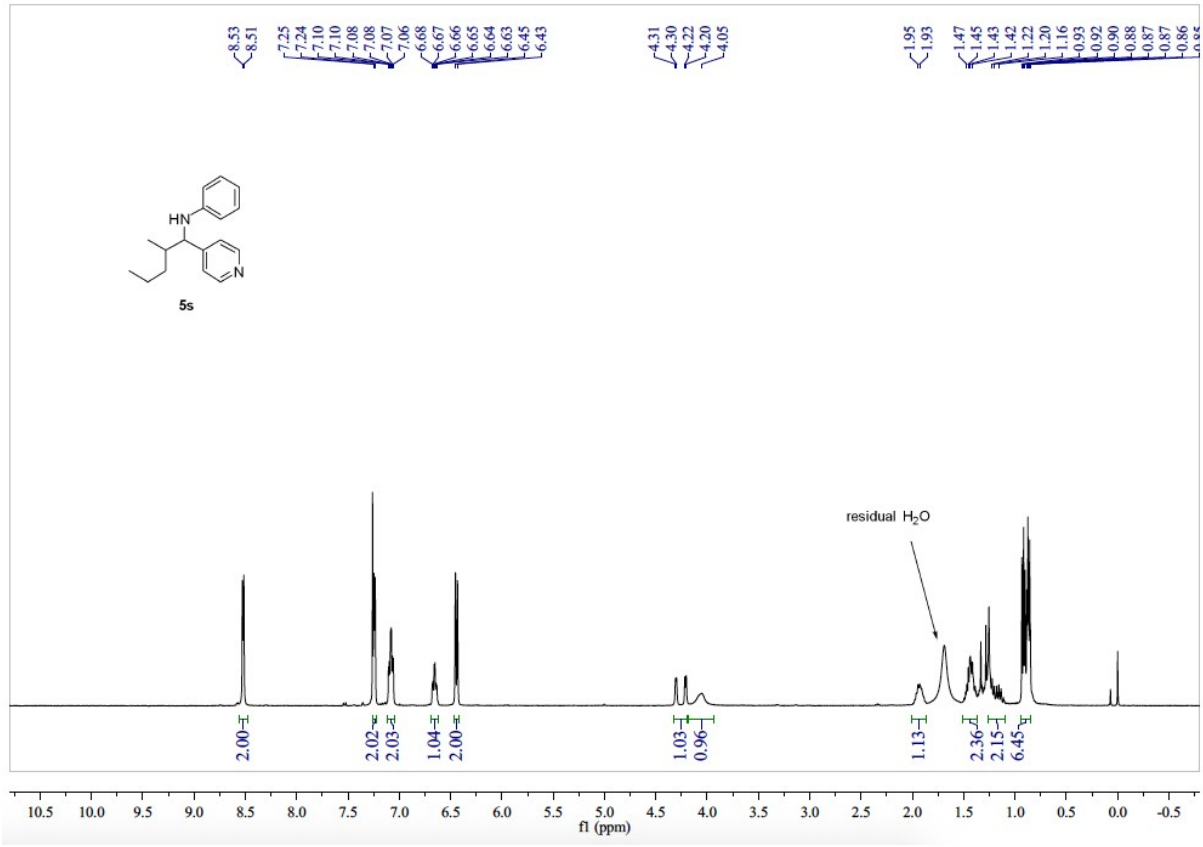


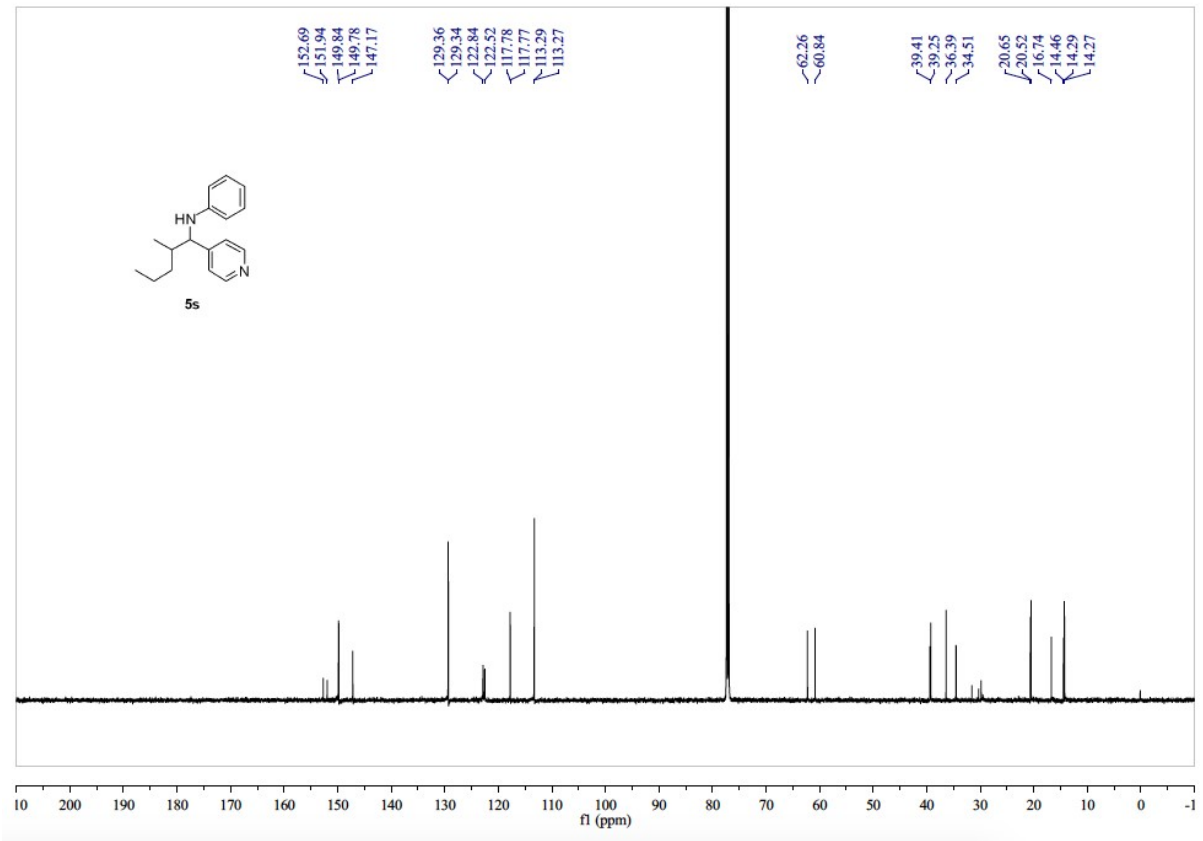
5r: *N*-(3-methyl-1-(pyridin-4-yl)but-2-en-1-yl)aniline



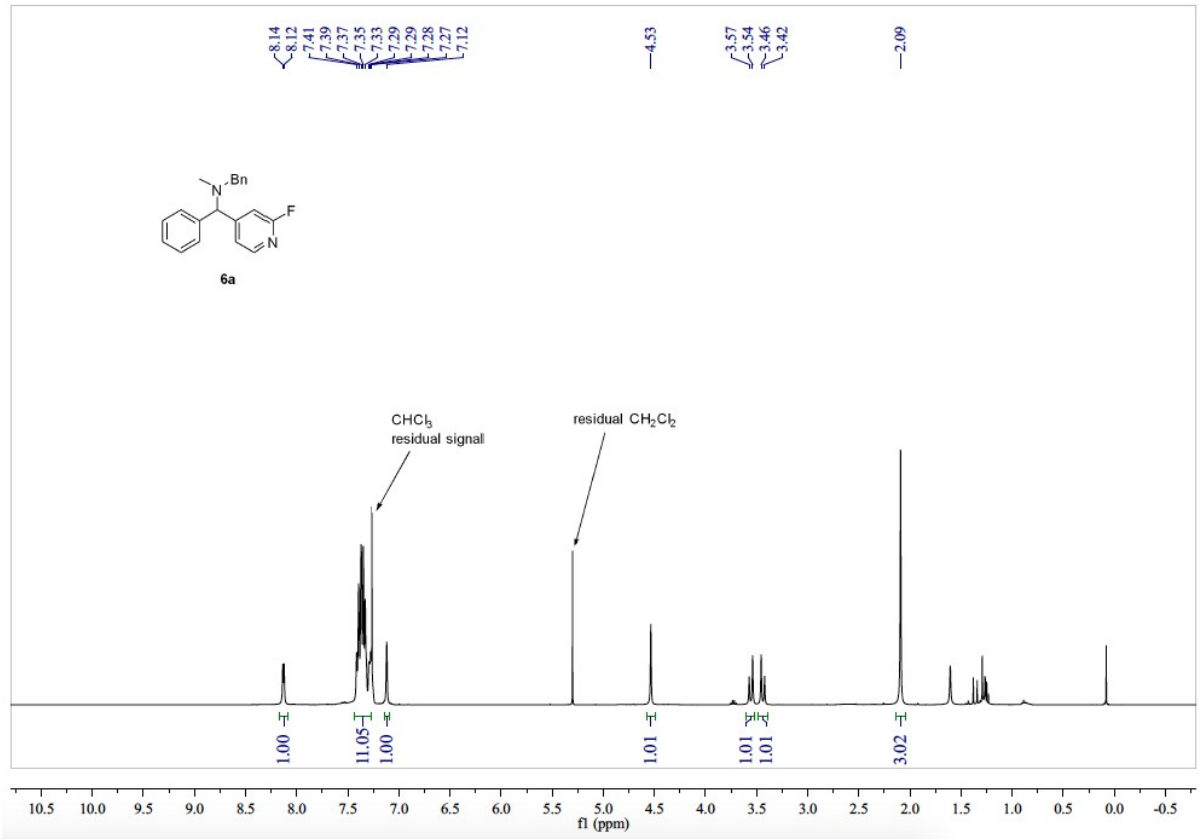


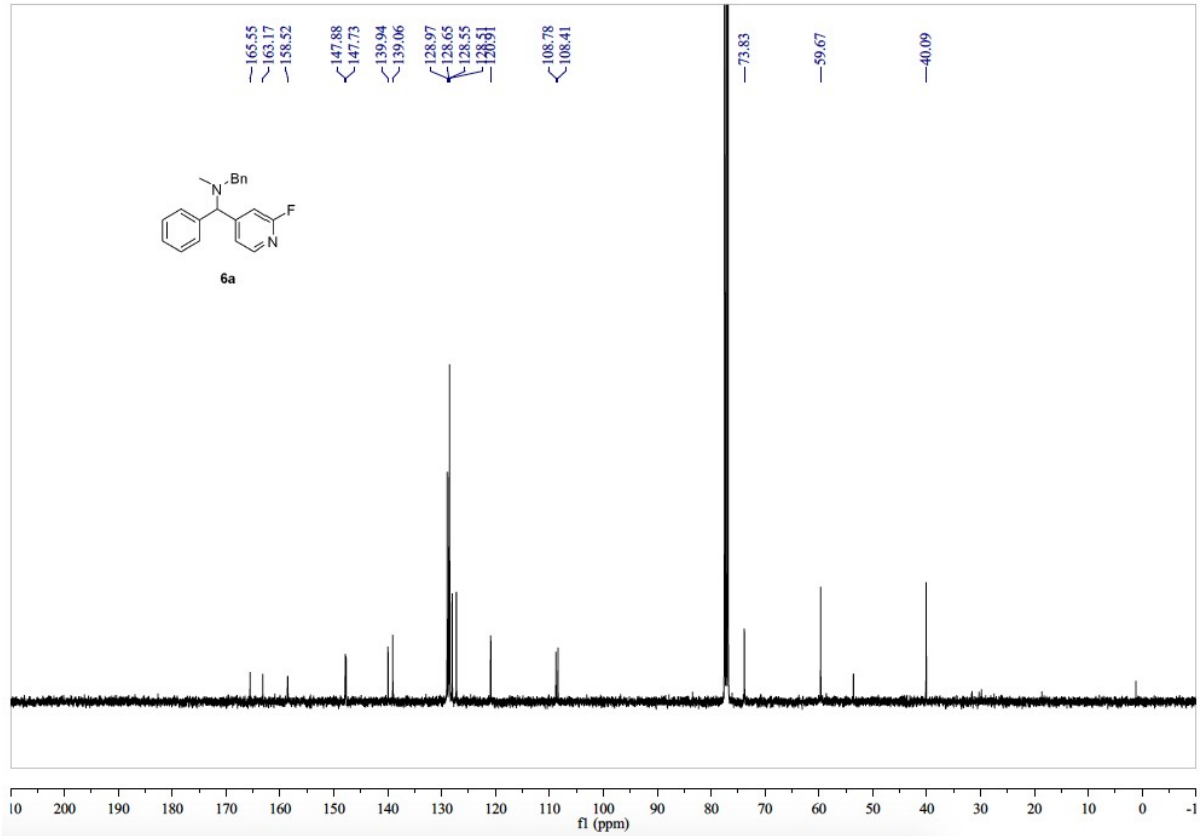
5s: *N*-(2-methyl-1-(pyridin-4-yl)pentyl)aniline

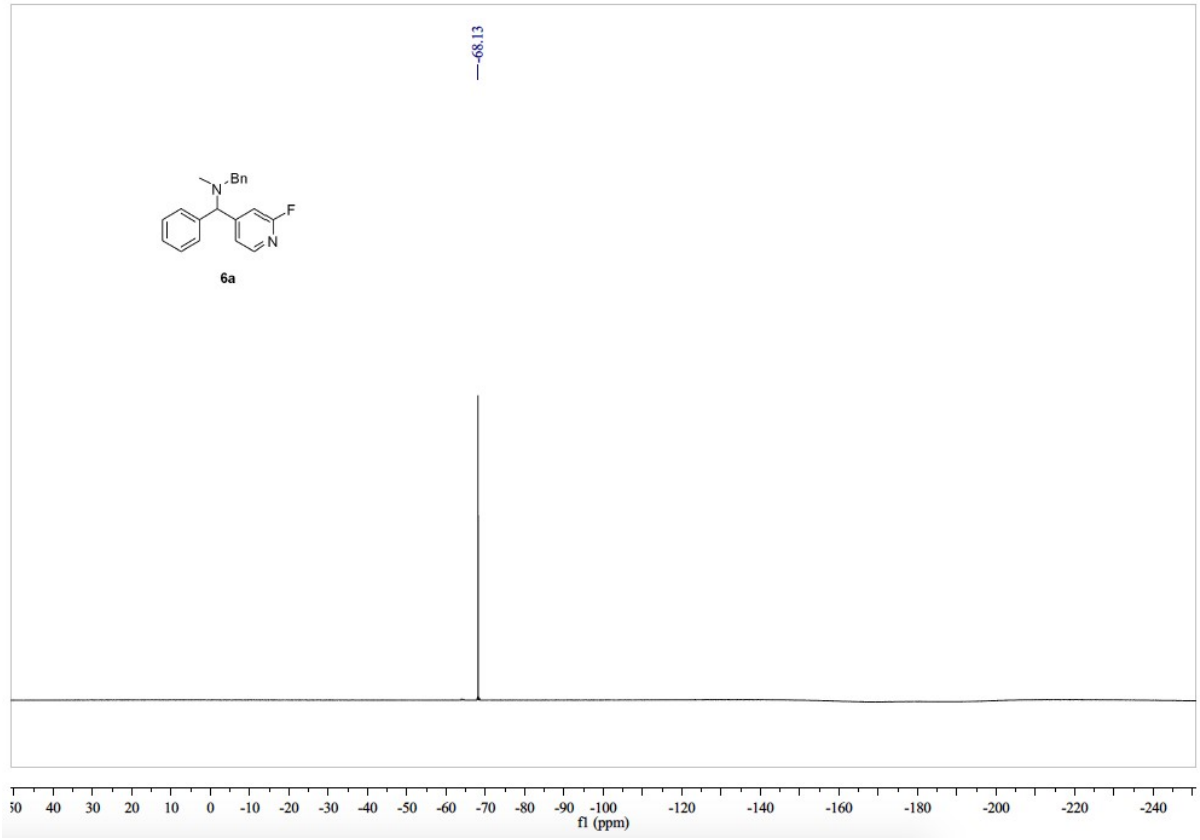




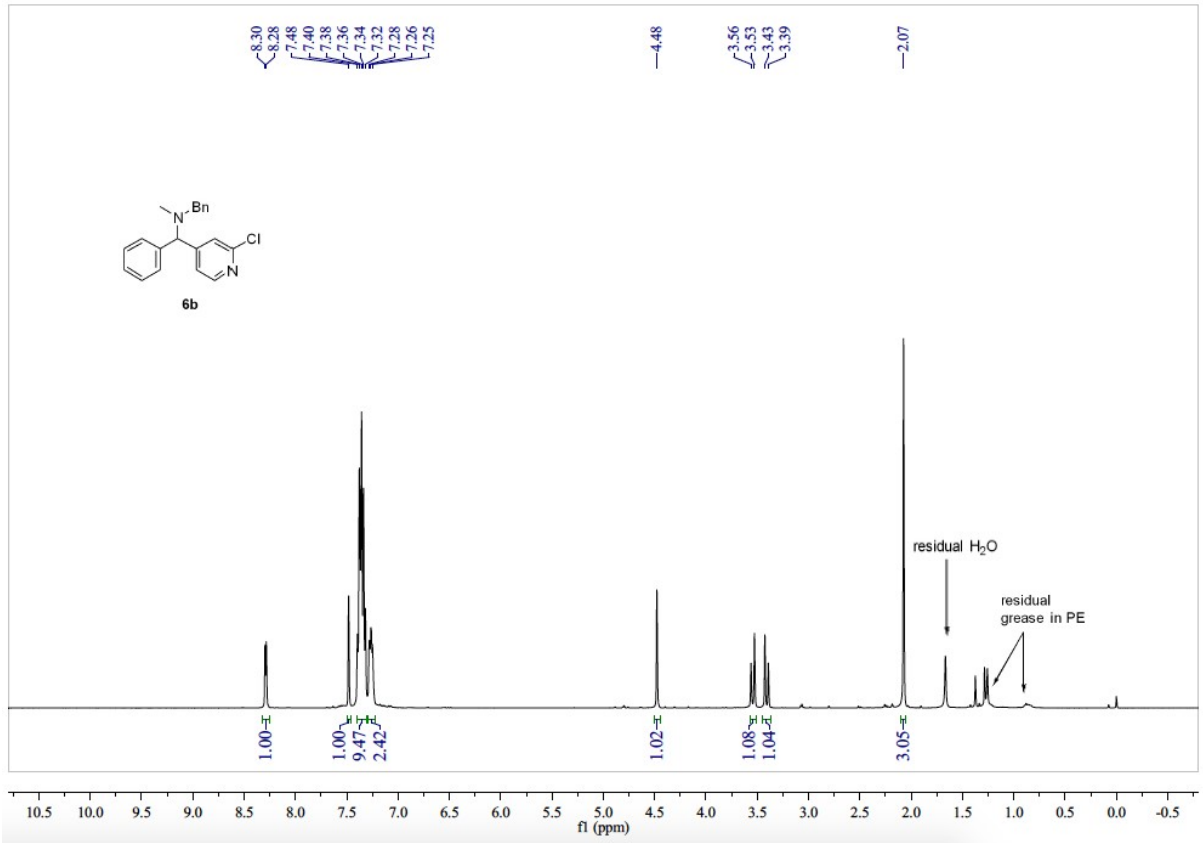
6a: *N*-benzyl-1-(2-fluoropyridin-4-yl)-*N*-methyl-1-phenylmethanamine

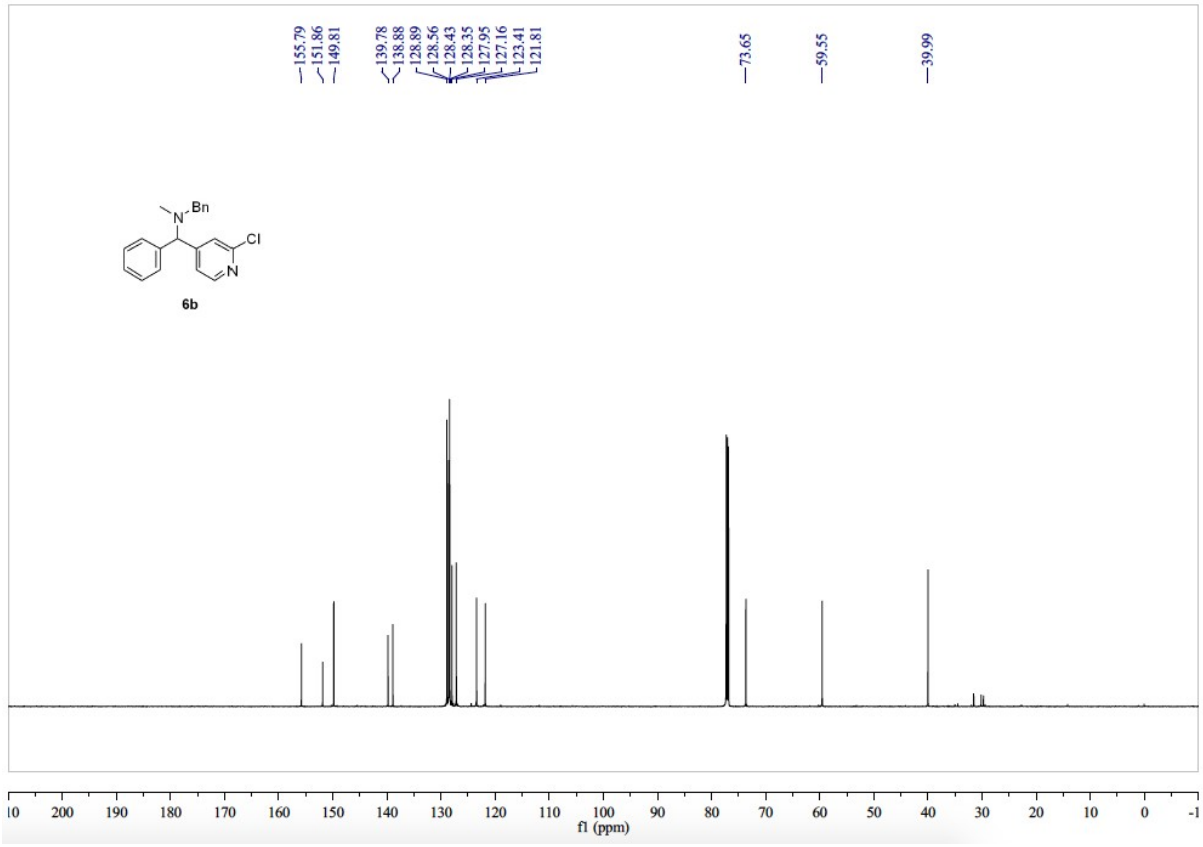




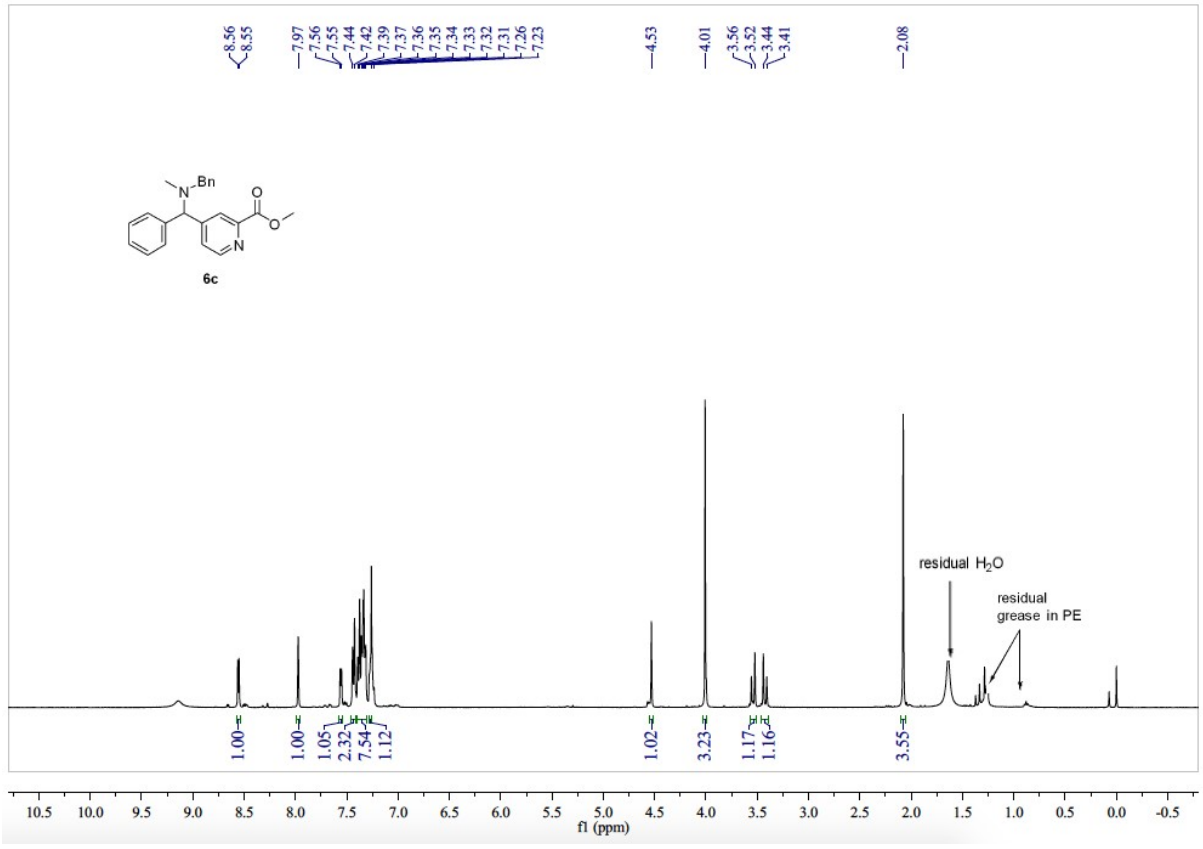


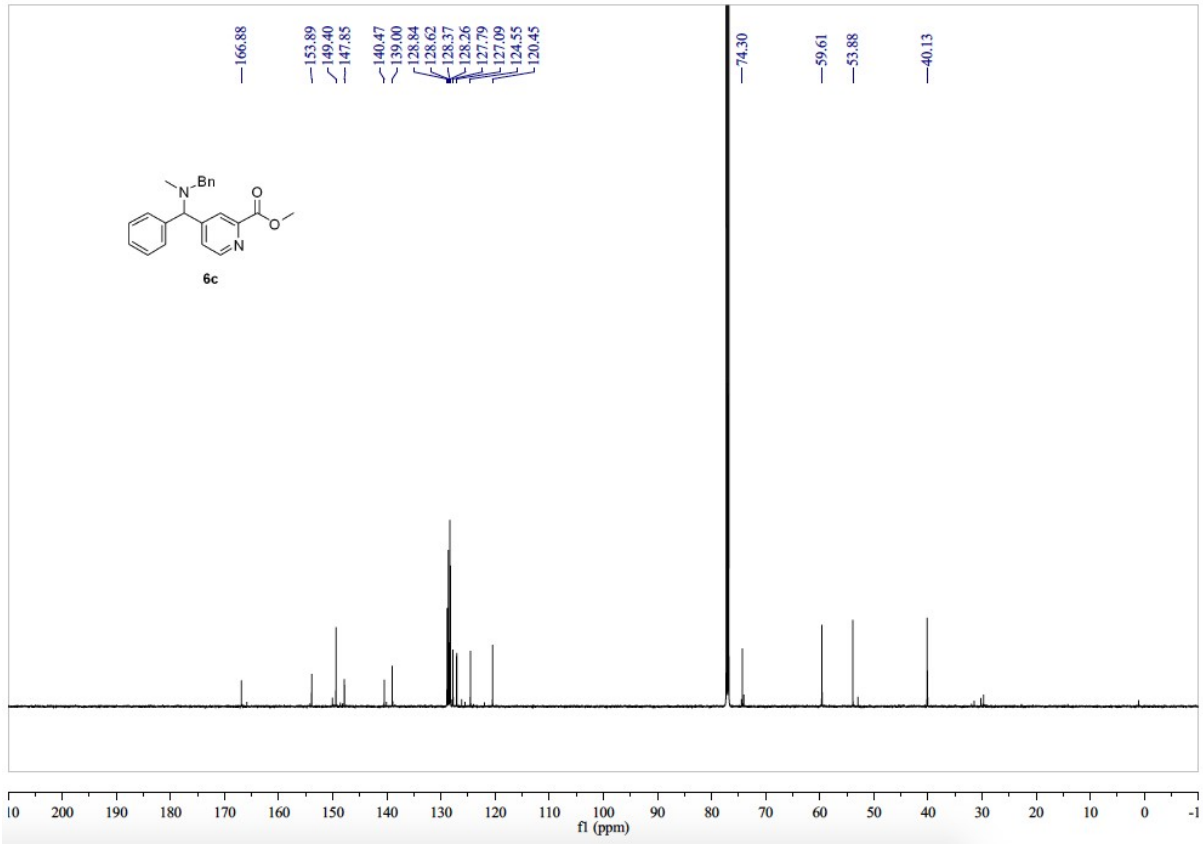
6b: *N*-benzyl-1-(2-chloropyridin-4-yl)-*N*-methyl-1-phenylmethanamine



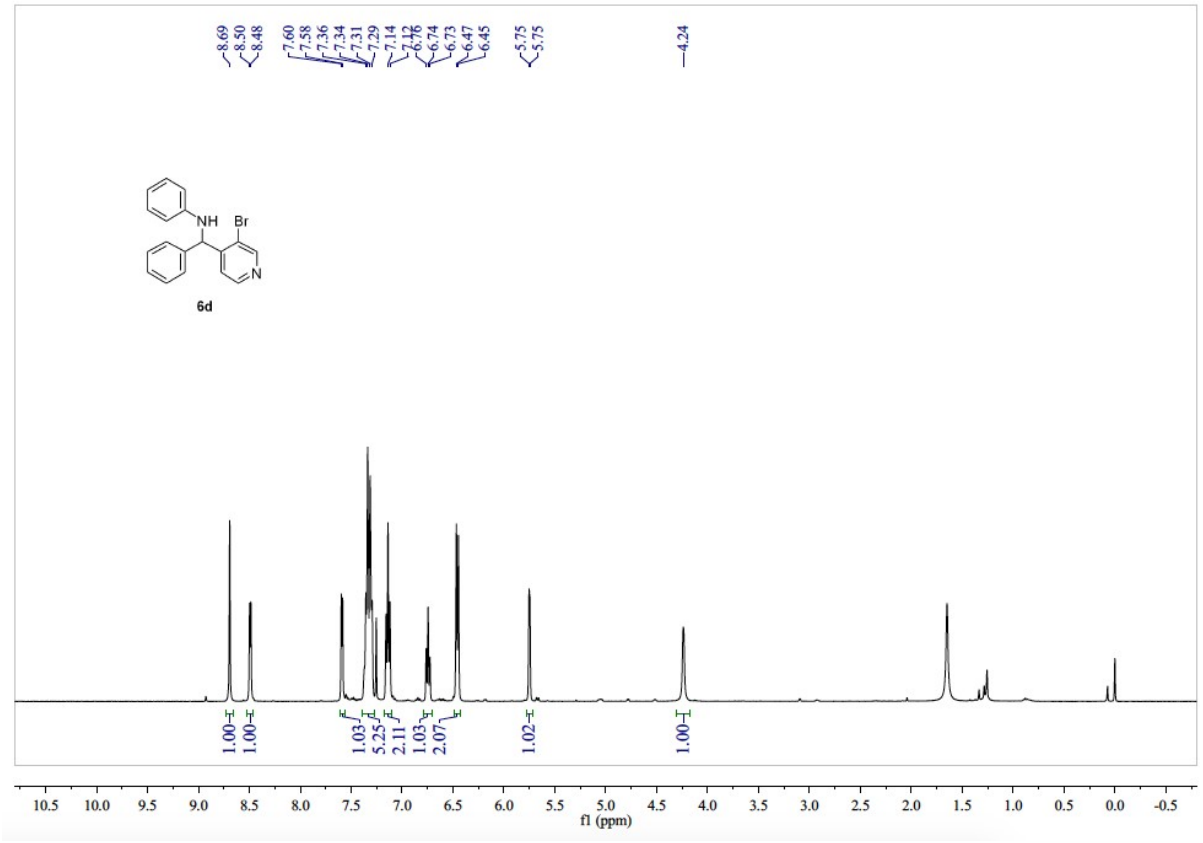


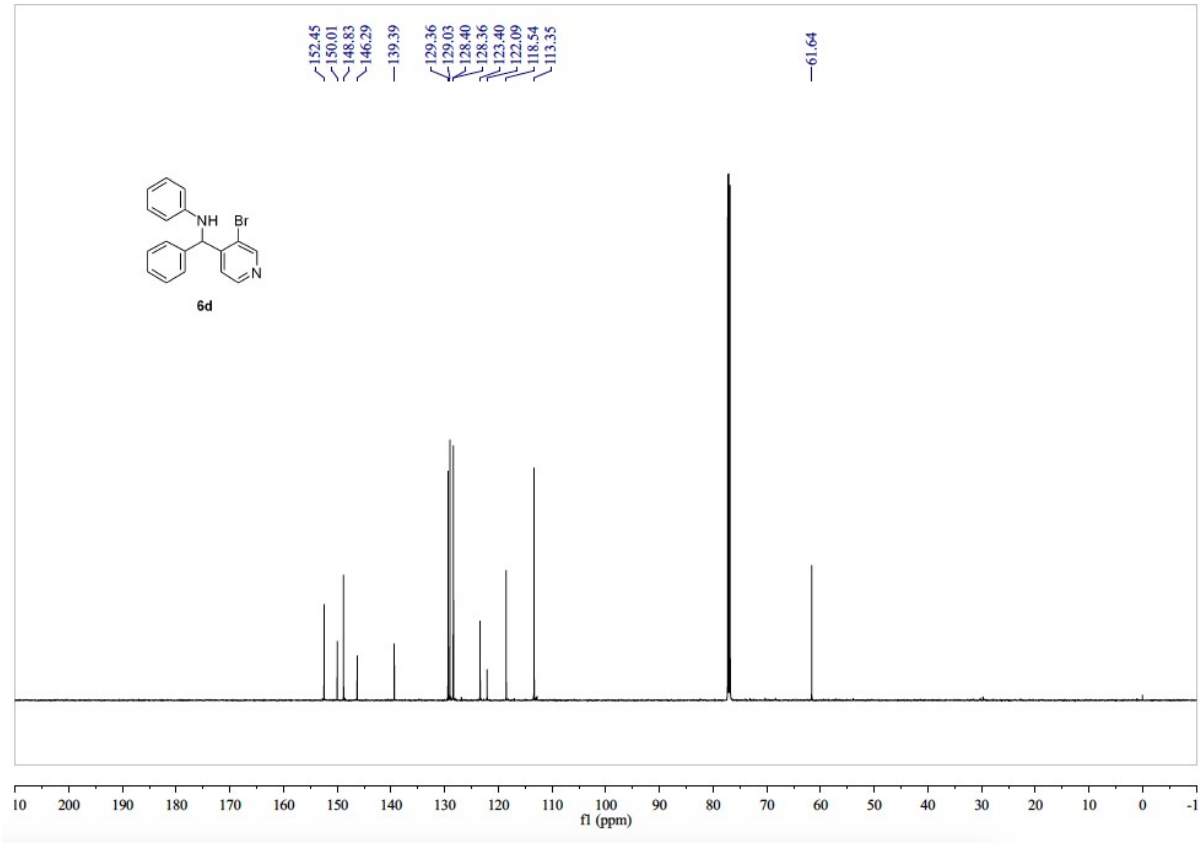
6c: methyl 4-((benzyl(methyl)amino)(phenyl)methyl)picolinate



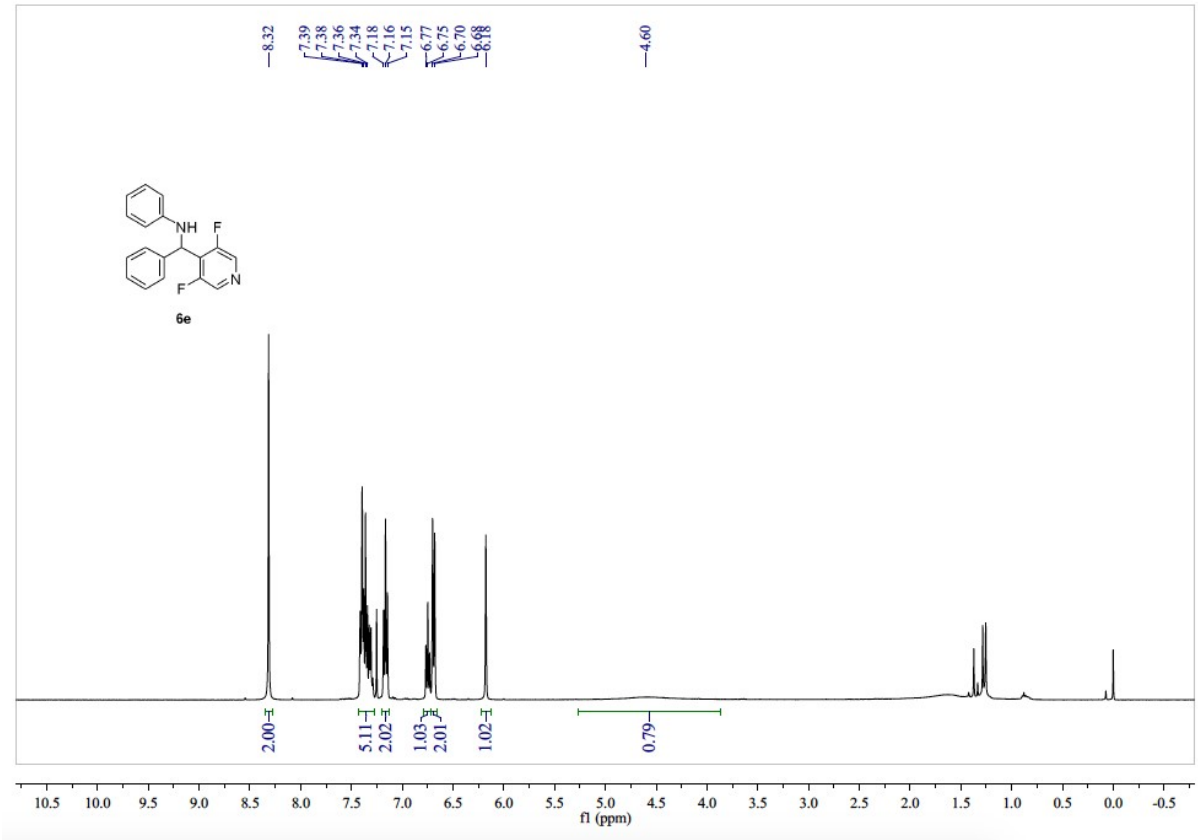


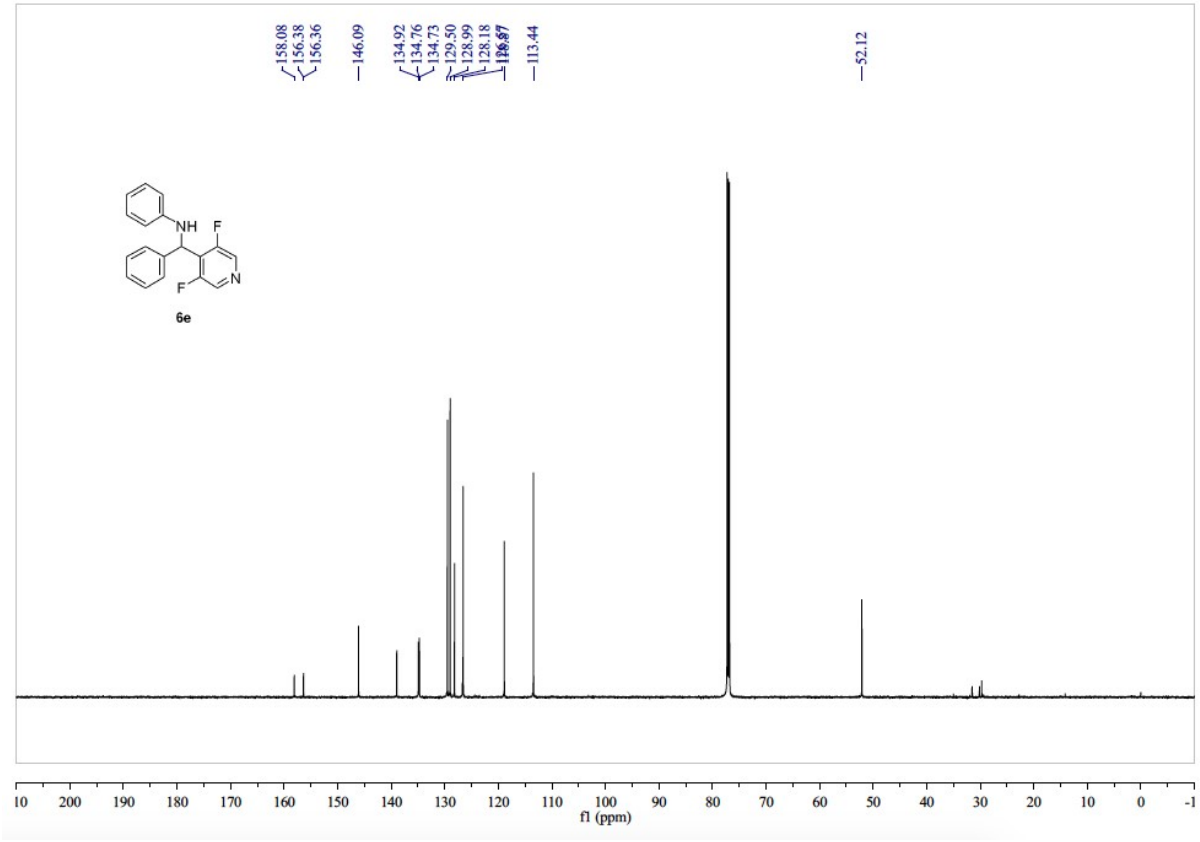
6d: *N*-((3-bromopyridin-4-yl)(phenyl)methyl)aniline





6e: *N*-((3,5-difluoropyridin-4-yl)(phenyl)methyl)aniline

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128.18
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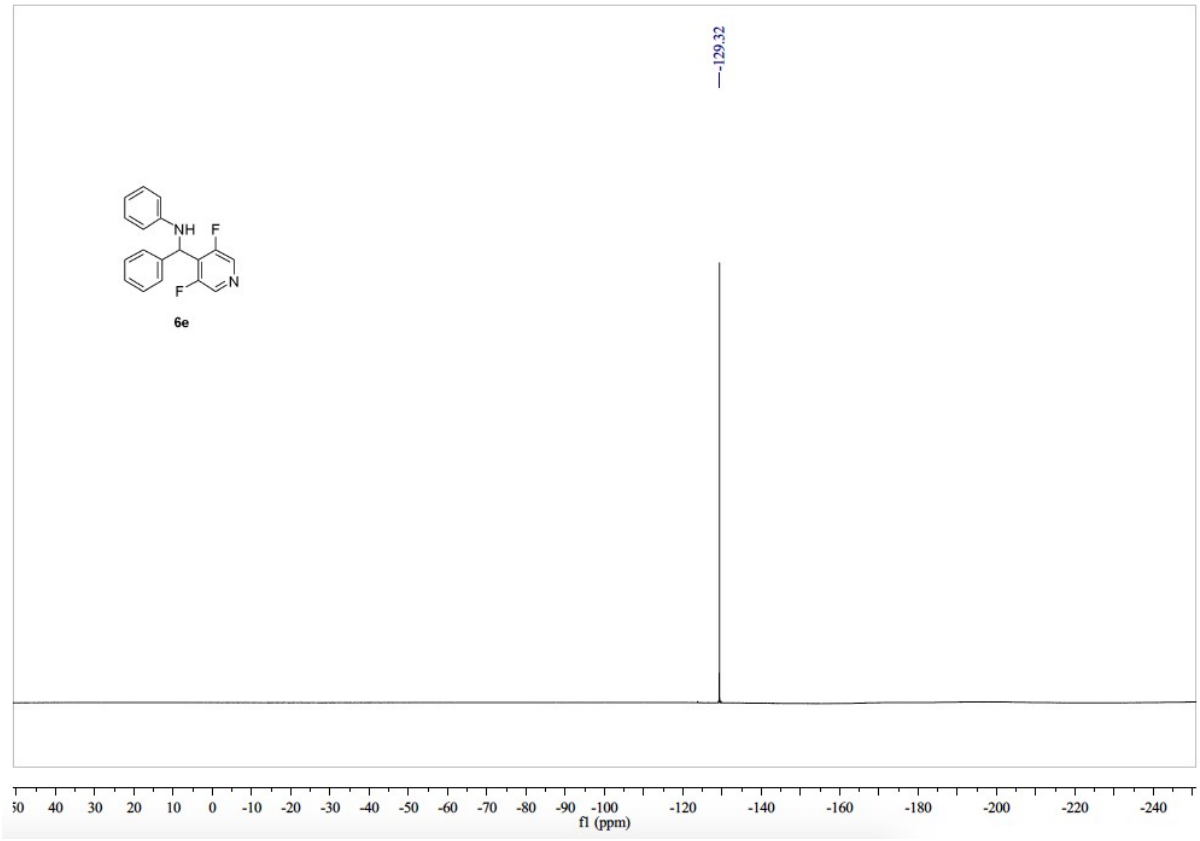
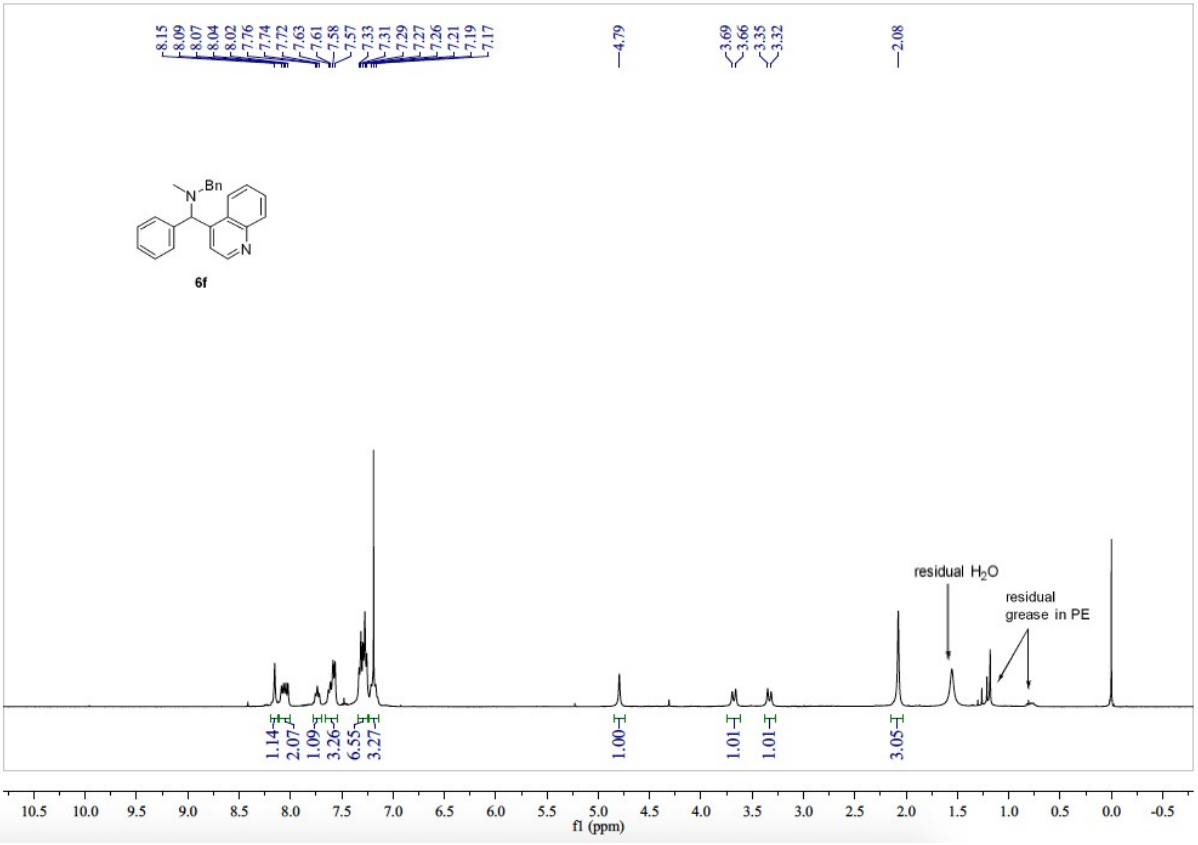
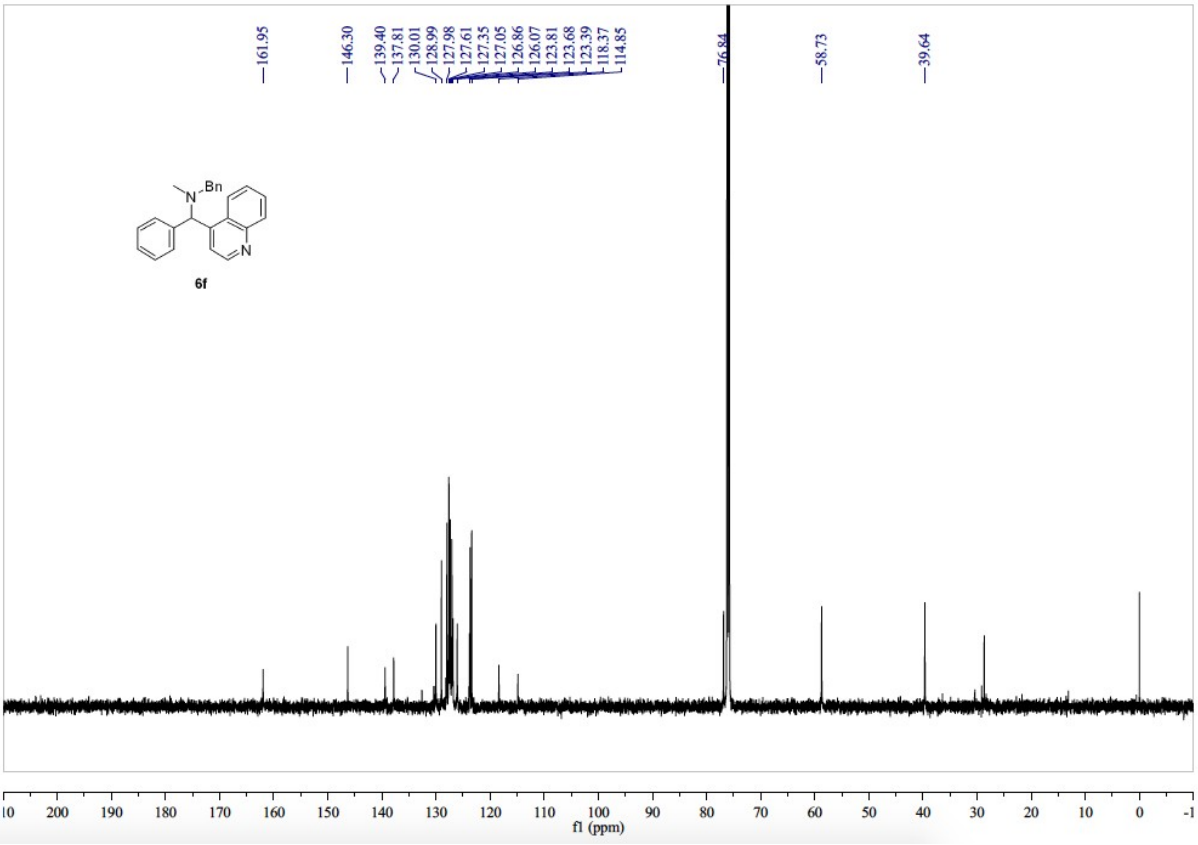
52.12
NH
F
F
N
6e
f1 (ppm)

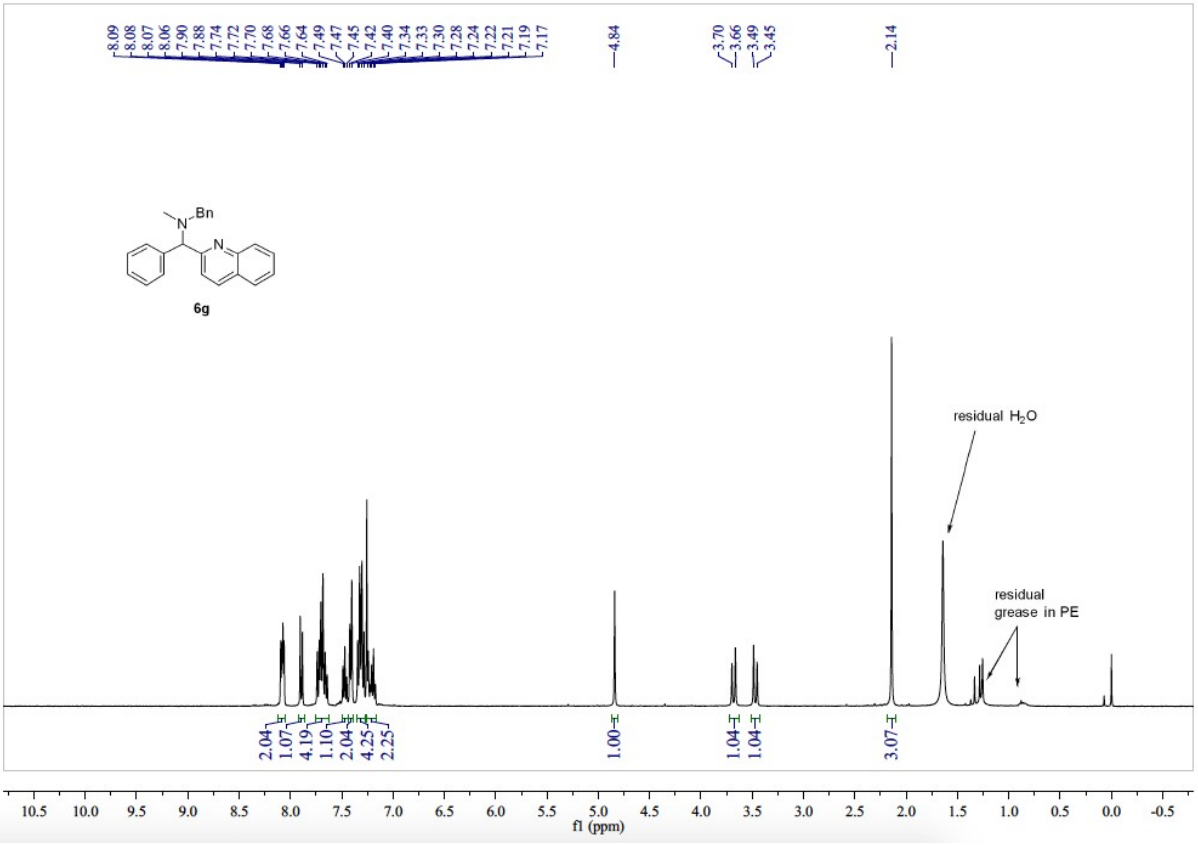

129.32
NH
F
F
N
6e
f1 (ppm)

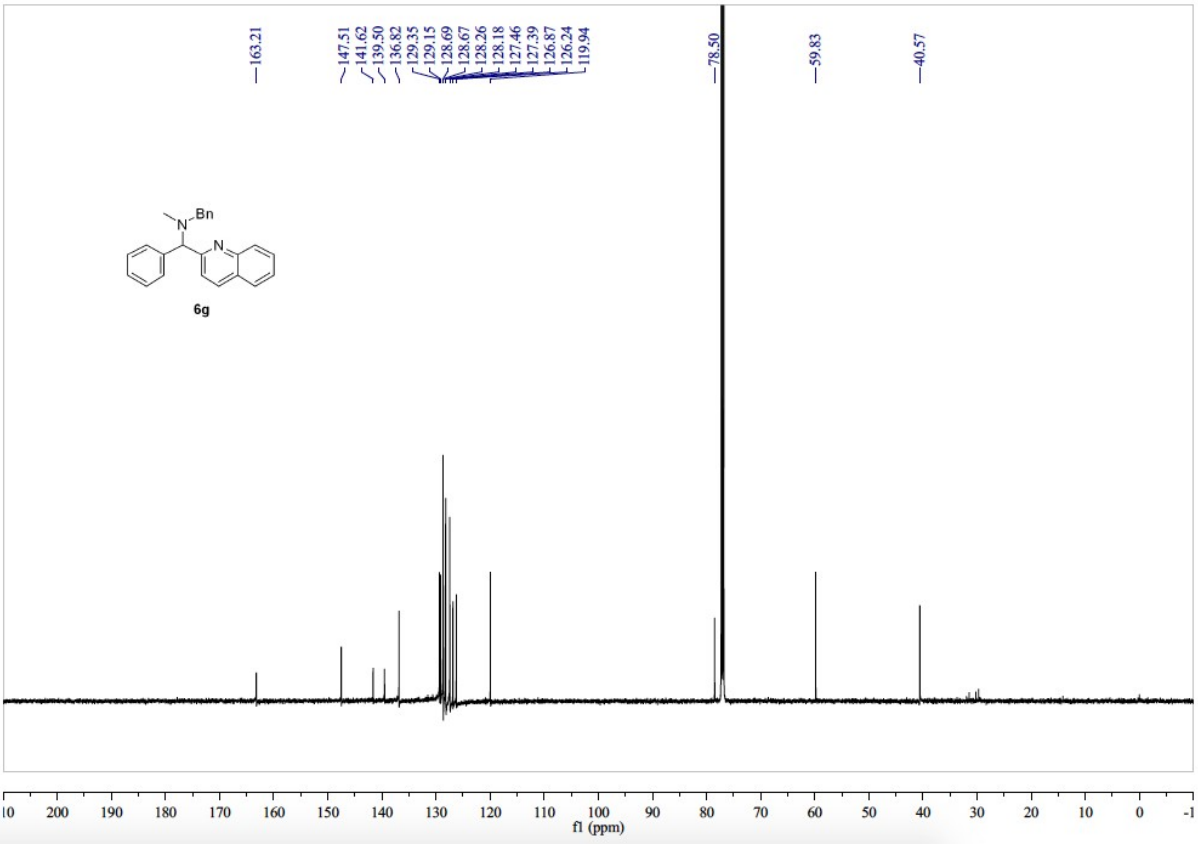
6f: *N*-benzyl-*N*-methyl-1-phenyl-1-(pyridin-4-yl)methanamine



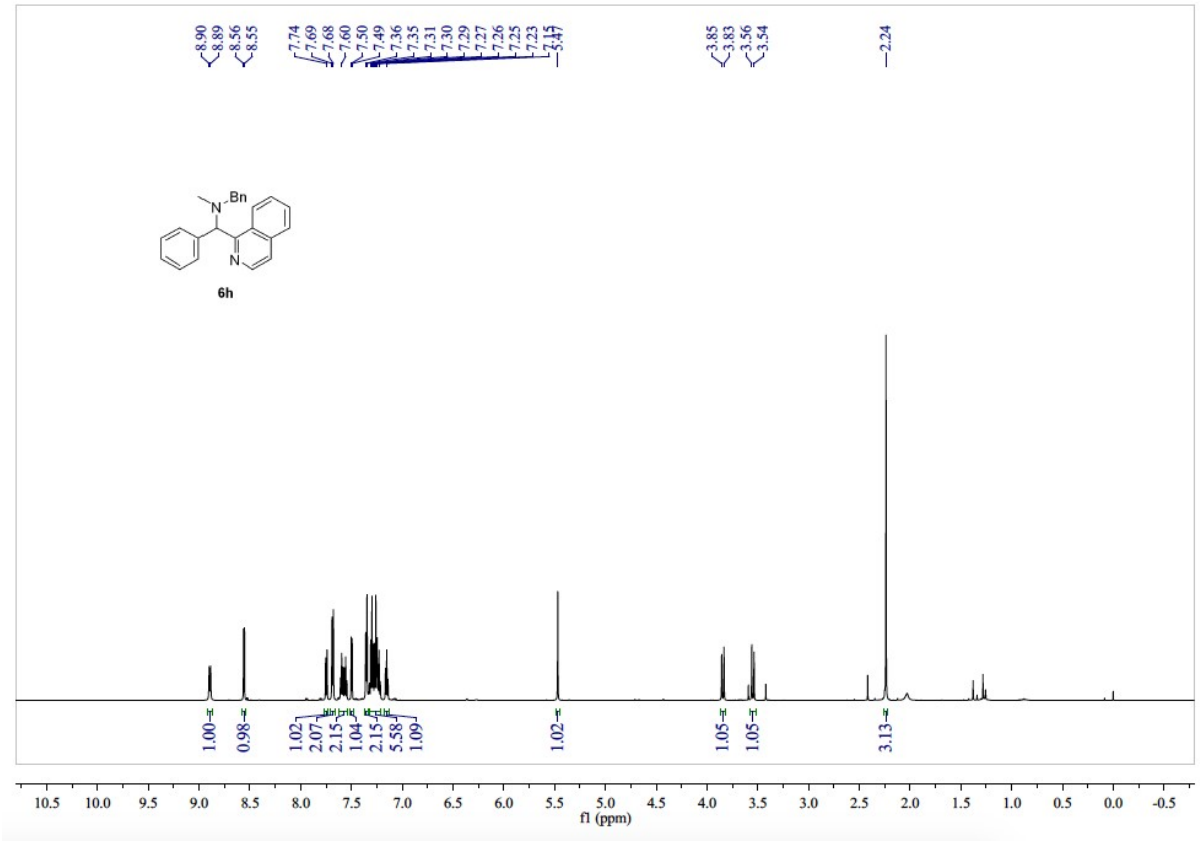


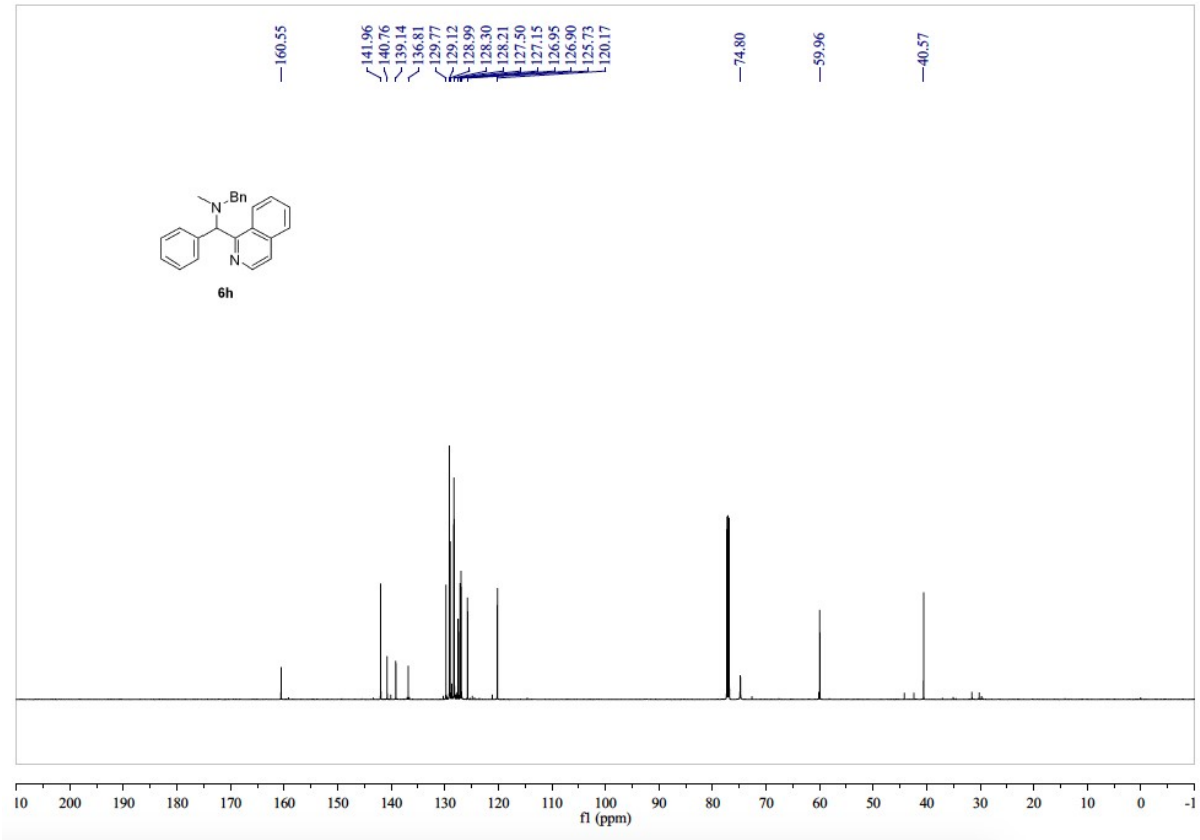
6g: *N*-benzyl-*N*-methyl-1-phenyl-1-(quinolin-2-yl)methanamine





6h: *N*-benzyl-1-(isoquinolin-1-yl)-*N*-methyl-1-phenylmethanamine





9: ethyl 4-((4-bromophenyl)amino)-2-methylene-4-phenylbutanoate