Supporting Information

Direct hydroxyethylation of amines from carbohydrates *via* ruthenium catalysis

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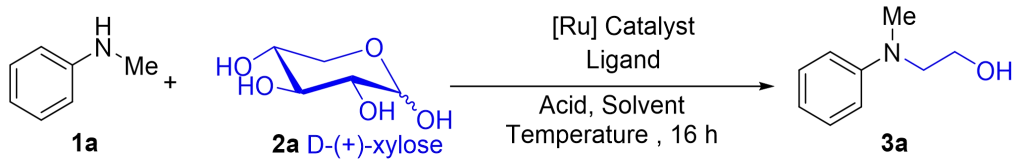
1. General experiment details and materials

Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. All reactions were carried out in glovebox. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Bruker 400 MHz spectrometer. The NMR chemical shift values refer to $CDCl_3$ (δ (1H), 7.26 ppm; δ (13C), 77.00 ppm). GC-MS data were obtained a Shaimadzu GCMS-QP2010 SE, GC data were obtained Shaimadzu GC-2010 Plus, HRMS data were obtained on Agilent 6530 spectrometer at Suzhou Research Institute of LICP.

2. Optimization of the reaction conditions

Take the reaction of N-methylaniline and D-(+)-xylose as an example: $Ru(cod)(2\text{-methylallyl})_2$ (3.3 mg, 0.01 mmol), Xantphos (5.8 mg, 0.01mmol) and the anhydrous 1,4-dioxane (0.5 mL) was mixed in 15 mL pressure-resistant tube containing magneons. Then the mixture was allowed to stir under a nitrogen atmosphere in the pressure-resistant tube at room temperature for 10 minutes, the catalyst solution is prepared. To pressure-resistant tube containing prefabricated catalyst solution was added the representative N-Methylaniline (53.6 mg, 0.5 mmol), the representative D-(+)-xylose (225.0 mg, 1.5 mmol) and CH_3COOH (9.0 mg, 0.15 mmol) followed by the anhydrous 1,4-dioxane (1.5 mL). The reaction mixture was allowed to stir under a nitrogen atmosphere in the closed pressure-resistant tube heated to 150 ℃ for 16 h. After the reaction finished, the reaction tube was cooled to room temperature and the pressure was carefully released. The yield were measured by GC using n-dodecane as the internal standard, respectively. The crude reaction mixture was concentrated in vacuo and purified by column chromatography [petroleum ether /ethyl acetate = 5:1] to give the corresponding β-amino alcohols in good yields.

Table S1. Optimization of the reaction conditions[a]



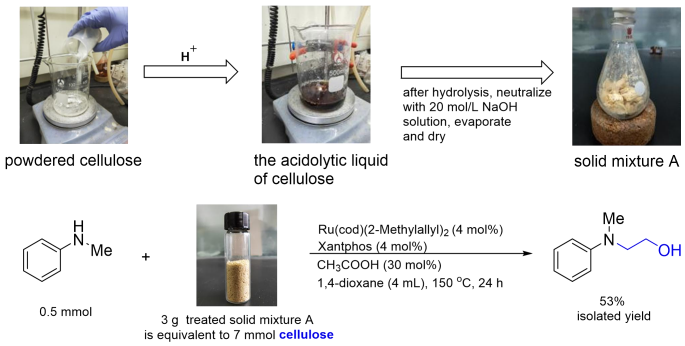
1a 2a D-(+)-xylose 3a

Entry	Catalyst (mmol)	Ligand (mmol)	Acid (mmol)	Solvent (mL)	Temperature (°C)	Time (h)	Yield[b] (%)
1	-	-	CH_3COOH	1,4-dioxane	150	16	n.d.
2	-	Xantphos	CH_3COOH	1,4-dioxane	150	16	n.d.
3	$Ru(cod)(2\text{-methylallyl})_2$	-	CH_3COOH	1,4-dioxane	150	16	24
4	$Ru(cod)(2\text{-methylallyl})_2$	Xantphos	-	1,4-dioxane	150	16	29
5	$(CH_3COO)_2Cu$	-	CH_3COOH	1,4-dioxane	150	16	n.d.
6	$NiCl_2(dppp)$	-	CH_3COOH	1,4-dioxane	150	16	n.d.
7	$CoCl_2$	dppm	CH_3COOH	1,4-dioxane	150	16	n.d.
8	$Fe(acac)_3$	-	CH_3COOH	1,4-dioxane	150	16	n.d.
9	$Ru(cod)(2\text{-methylallyl})_2$	Xantphos	CH_3COOH	1,4-dioxane	150	16	**87**

10	$Ru_3(CO)_{12}$	Xantphos	CH_3COOH	1,4-dioxane	150	16	60
11	$RuCl_2(PPh_3)_3$	Xantphos	CH_3COOH	1,4-dioxane	150	16	37
12	$Ru(acca)_3$	Xantphos	CH_3COOH	1,4-dioxane	150	16	56
13	$[Ru(p\text{-}cymene)Cl]_2$	Xantphos	CH_3COOH	1,4-dioxane	150	16	n.d.
14	Ru(cod)(2-methylallyl)$_2$	DPPF	CH_3COOH	1,4-dioxane	150	16	9
15	Ru(cod)(2-methylallyl)$_2$	DPPM	CH_3COOH	1,4-dioxane	150	16	16
16	Ru(cod)(2-methylallyl)$_2$	DPPE	CH_3COOH	1,4-dioxane	150	16	23
17	Ru(cod)(2-methylallyl)$_2$	DPPP	CH_3COOH	1,4-dioxane	150	16	18
18	Ru(cod)(2-methylallyl)$_2$	DPPPen	CH_3COOH	1,4-dioxane	150	16	23
19	Ru(cod)(2-methylallyl)$_2$	DPEPhos	CH_3COOH	1,4-dioxane	150	16	9
20	Ru(cod)(2-methylallyl)$_2$	Trianisylphosphine	CH_3COOH	1,4-dioxane	150	16	23
21	Ru(cod)(2-methylallyl)$_2$	DCype	CH_3COOH	1,4-dioxane	150	16	16
22	Ru(cod)(2-methylallyl)$_2$	Xantphos	CF_3COOH	1,4-dioxane	150	16	n.d.
23	Ru(cod)(2-methylallyl)$_2$	Xantphos	HCOOH	1,4-dioxane	150	16	24
24	Ru(cod)(2-methylallyl)$_2$	Xantphos	H_3PO_4	1,4-dioxane	150	16	n.d.
25	Ru(cod)(2-methylallyl)$_2$	Xantphos	H_2SO_4	1,4-dioxane	150	16	n.d.
26	Ru(cod)(2-methylallyl)$_2$	Xantphos	$(CH_3)_3CCOOH$	1,4-dioxane	150	16	15
27	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	Toluene	150	16	trace
28	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	DMF	150	16	trace
29	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	CH_3CN	150	16	trace
30	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	Mesitylene	150	16	trace
31	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	130	16	61
32	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	170	16	78
33	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	150	8	60
34	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	150	24	81
35[c]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	150	16	74
36[d]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	150	16	83
37[e]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	1,4-dioxane	150	16	63

[a] General conditions: **1a** (0.5 mmol), D-(+)-xylose (1.5 mmol), catalyst (0.01 mmol), ligand (0.01 mmol), acid (0.15 mmol), solvent (2.0 mL), at 150 °C in the nitrogen atmosphere for 16h. [b] Yields were determined by GC analysis using n-docecane as the internal standard. [c] 1.0 mol% Ru(cod)(2-methylallyl)$_2$, 1.0 mol% Xantphos; [d] 3.0 mol% Ru(cod)(2-methylallyl)$_2$, 6.0 mol% Xantphos; [e] 1 mL 1,4-dioxane.

3. Cellulose pre-treatment experiment

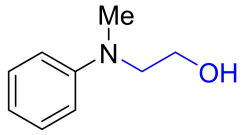


10 g of α-cellulose (particle size about 25 μm) was stirred with 60 g of a 7:3 mixture of

phosphoric acid (originally 85%) and sulfuric acid (95-98%) at room temperature. The mixture was allowed to stir for 15 hours to effect de-polymerization and partial degradation of cellulose. This is followed by hydrolysis with 100 g water at 80 ºC for 2 hours. Upon cooling to room temperature, the solution was neutralized with 20 M NaOH solution to pH = 7. Due to the difference of solubility of inorganic salts (Na_2SO_4 and Na_3PO_4) and degradation products of cellulose, recrystallization was attempted to remove large amounts of inorganic salts (Na_2SO_4 and Na_3PO_4). Cooling the neutralized solution in an ice water bath resulted in precipitation of large amount of white crystalline solid of Na_2SO_4 and Na_3PO_4, and removed by filtration. Recrystalization is continued to remove the inorganics by adding small amount of water to the filtrate, cooling in an ice bath and filtering to remove precipitates. Finally, the filtrate was evaporated to dryness to obtain 24 g of solid mixture A. This mixture was used as obtained to convert N-methylaniline to N-(2-Hydroxyethyl)-N-methylaniline in 53% isolated yield (reaction loading was based on the calculated cellulose content in the solid mixture A of 42%).

4. Experimental characterization data for products

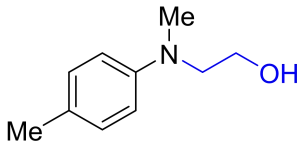
2-(methyl(phenyl)amino)ethan-1-ol (3a)



Yield: 78% (59 mg), light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.24 (t, *J* = 7.2 Hz, 2H), 6.81-6.73 (m, 3H), 3.80 (t, *J* = 4.8 Hz, 2H), 3.46 (t, *J* = 4.8 Hz, 2H), 2.95 (s, 3H), 1.87 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 150.1, 129.2 (2C), 117.2, 113.0 (2C), 60.0, 55.4, 38.7.

Spectroscopic data are consistent with those previously reported: *Org. Lett.* **2017**, *19*, 1490-1493.

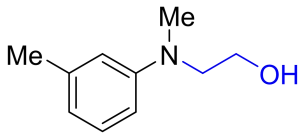
2-(methyl(p-tolyl)amino)ethan-1-ol (3b)



Yield: 75% (62 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.07 (d, *J* = 7.5Hz, 2H), 6.76 (d, *J* = 7.5Hz, 2H), 3.79 (t, *J* = 5.6 Hz, 2H), 3.42 (t, *J* = 5.6 Hz, 2H), 2.92 (s, 3H), 2.27 (s, 3H), 2.05 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.2, 129.7 (2C), 126.8, 113.7 (2C), 59.9, 56.0, 38.8, 20.2.

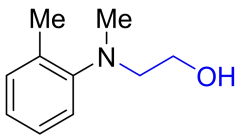
Spectroscopic data are consistent with those previously reported: *Arch Pharm Res*, **2007**, *30*, 1055-1061.

2-(methyl(m-tolyl)amino)ethan-1-ol (3c)



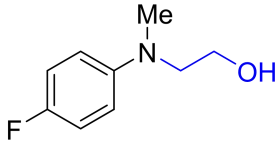
Yield: 71% (58 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.15 (t, *J* = 7.3 Hz 1H), 6.65-6.59 (m, 3H), 3.81 (t, *J* = 5.5 Hz, 2H), 3.46 (t, *J* = 5.5 Hz, 2H), 2.95 (s, 3H), 2.33 (s, 3H), 1.88 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 150.2, 138.9, 129.0, 118.2, 113.9, 110.3, 60.0, 55.5, 38.7, 21.9. **HRMS**(ESI) calcd for $C_{10}H_{15}NOH^+$: 166.1226. Found: 166.1225 (MH^+).

2-(methyl(o-tolyl)amino)ethan-1-ol (3d)



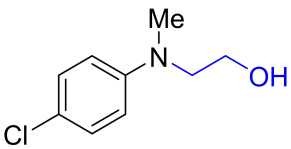
Yield: 58% (48 mg), dark green oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.19 (t, *J* = 7.3 Hz, 2H), 7.11(d, *J* = 8.2 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 3.69 (t, *J* = 4.5 Hz, 2H), 3.10 (t, *J* = 5.0 Hz, 2H), 2.66 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 151.6, 133.5, 131.2, 126.7, 124.0, 120.8, 58.8, 57.5, 42.1, 18.2. **HRMS**(ESI) calcd for $C_{10}H_{15}NOH^+$: 166.1226. Found: 166.1224 (MH^+).

2-((4-fluorophenyl)(methyl)amino)ethan-1-ol (3e)



Yield: 69% (58 mg), brown yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.94 (t, *J* = 8.4 Hz, 2H), 6.77-6.74 (m, 2H), 3.78 (t, *J* = 5.6 Hz, 2H), 3.38 (t, *J* = 5.6 Hz, 2H), 2.89 (s, 3H), 2.12 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 157.0, 154.7, 147.0, 115.6, 115.4, 114.8, 114.7, 59.8, 56.4, 39.1. **HRMS**(ESI) calcd for $C_9H_{12}FNOH^+$: 170.0976. Found: 170.0975 (MH^+).

2-((4-chlorophenyl)(methyl)amino)ethan-1-ol (3f)

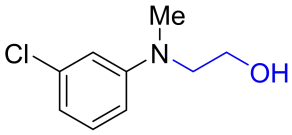


Yield: 75% (69 mg), a White solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.17-7.14 (m, 2H), 6.70-6.67 (m, 2H), 3.78 (t, *J* = 5.6 Hz, 2H),

3.43 (t, J = 5.6 Hz, 2H), 2.93 (s, 3H), 1.92 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.6, 128.9 (2C), 121.9, 114.0 (2C), 60.0, 55.4, 38.8.

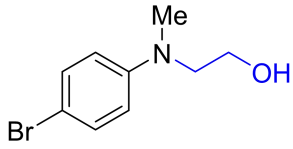
Spectroscopic data are consistent with those previously reported: *Chem. Eur. J.,* **2014**, *20*, 14063-14073.

2-((3-chlorophenyl)(methyl)amino)ethan-1-ol (3g)



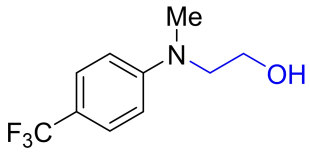
Yield: 66% (61 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.12 (t, J = 8.1 Hz, 1H), 6.72-6.62 (m, 3H), 3.78 (t, J = 4.8 Hz, 2H), 3.45 (t, J = 5.3 Hz, 2H), 2.95 (s, 3H), 2.00 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 150.8, 135.0, 130.0, 116.6, 112.4, 110.7, 60.0, 54.9, 38.7. **HRMS**(ESI) calcd for $C_9H_{12}ClNOH^+$: 186.0680. Found: 186.0680 (MH^+).

2-((4-bromophenyl)(methyl)amino)ethan-1-ol (3h)



Yield: 57% (65 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.29 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 3.79 (t, J = 5.6 Hz, 2H), 3.44 (t, J = 5.6 Hz, 2H), 2.93 (s, 3H), 1.87 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.9, 131.8 (2C), 114.4 (2C), 108.9, 60.0, 55.3, 38.8. **HRMS**(ESI) calcd for $C_9H_{12}BrNOH^+$: 230.0175. Found: 230.0174 (MH^+).

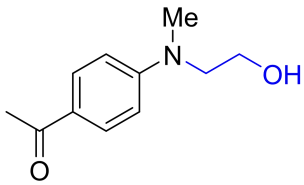
2-(methyl(4-(trifluoromethyl)phenyl)amino)ethan-1-ol (3i)



Yield: 43% (47 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.45 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.83 (t, J = 5.6 Hz, 2H), 3.54 (t, J = 5.6 Hz, 2H), 3.04 (s, 3H), 1.78 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 151.7, 126.5, 126.4, 118.2, 117.8, 111.4, 60.1, 54.6, 38.9.

Spectroscopic data are consistent with those previously reported: *J. Am. Chem. Soc.,* **1998**, *120*, 10676-10686.

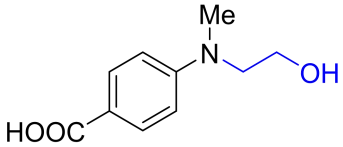
1-(4-((2-hydroxyethyl)(methyl)amino)phenyl)ethan-1-one (3j)



Yield:58% (56 mg), yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 9.1 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 3.83 (t, J = 5.8 Hz, 2H), 3.58 (t, J = 5.8 Hz, 2H), 3.07 (s, 3H), 2,47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 196.6, 152.9, 130.6 (2C), 125.4, 110.7 (2C), 60.0, 54.3, 39.0, 26.0.

Spectroscopic data are consistent with those previously reported: *Bull. Korean Chem. Soc.* **2002**, 23, 964-970.

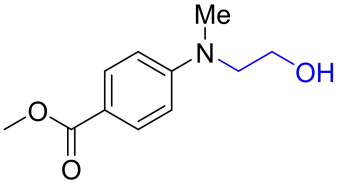
4-((2-hydroxyethyl)(methyl)amino)benzoic acid (3k)



Yield: 53% (52 mg), yellow solid. **^{1}H NMR** (400 MHz, d_6-DMSO): δ (ppm) 12.11 (br, 1H), 7.75 (d, J = 8.1 Hz, 2H), 6.72 (d, J = 8.2 Hz, 2H), 4.77 (br, 1H), 3.62-3.54 (m, 2H), 3.54-3.45 (m, 2H), 3.02 (s, 3H). **^{13}C NMR** (100 MHz, d_6-DMSO): δ (ppm)

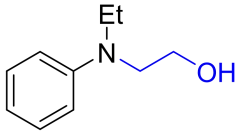
168.0, 152.7, 131.4, 116.9, 110.9, 58.5, 54.3, 39.2. **HRMS**(ESI) calcd for $C_{10}H_{13}NO_3H^+$: 196.0968. Found: 196.0967 (MH^+).

methyl 4-((2-hydroxyethyl)(methyl)amino)benzoate (3l)



Yield: 67% (70 mg), pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.78 (t, 5.6 Hz, 2H), 3.52 (t, *J* = 5.4 Hz, 2H), 3.02 (s, 3H), 2.79 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.6, 152.6, 131.2, 116.7, 110.6, 59.7, 54.2, 51.5, 38.9. **HRMS**(ESI) calcd for $C_{11}H_{15}NO_3H^+$: 210.1125. Found: 210.1126 (MH^+).

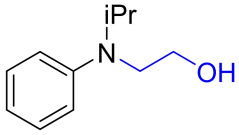
2-(ethyl(phenyl)amino)ethan-1-ol (3n)



Yield: 74% (61 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.28 (td, *J* = 8.0, 0.6 Hz, 2H), 6.84-6.75 (m, 3H), 3.83 (t, *J* = 5.8 Hz, 2H), 3.52-3.43 (m, 4H), 1.94 (br, 1H), 1.20 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.3, 129.3 (2C), 116.8, 113.0 (2C), 60.1, 52.6, 45.7, 11.8.

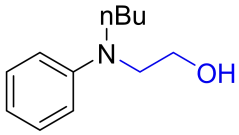
Spectroscopic data are consistent with those previously reported: *J. Am. Chem. Soc.* **2015**, *137*, 13580-13587.

2-(isopropyl(phenyl)amino)ethan-1-ol (3o)



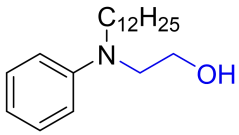
Yield: 65% (58 mg), a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.25-7.21 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 4.01-3.91 (m, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 3.30 (t, *J* = 6.2 Hz, 2H), 2.00 (br, 1H), 1.16 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.8, 129.1 (2C), 118.4, 116.2 (2C), 60.1, 50.6, 45.8, 19.9 (2C). **HRMS**(ESI) calcd for $C_{11}H_{17}NOH^+$: 180.1383. Found: 180.1382 (MH^+).

2-(butyl(phenyl)amino)ethan-1-ol (3p)



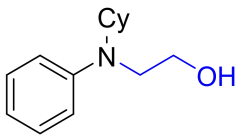
Yield: 67% (65 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.22 (t, *J* = 7.7 Hz, 2H), 6.76-6.69 (m, 3H), 3.76 (t, *J* = 5.8 Hz, 2H), 3.46 (t, *J* = 5.8 Hz, 2H), 3.31 (t, *J* = 7.6 Hz, 2H), 1.96 (br, 1H), 1.60-1.52 (m, 2H), 1.39-1.30 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.3, 129.2 (2C), 116.5, 112.7 (2C), 60.0, 53.1, 51.5, 28.8, 20.2, 14.0. **HRMS**(ESI) calcd for $C_{12}H_{19}NOH^+$: 194.1539. Found: 194.1539 (MH^+).

2-(dodecyl(phenyl)amino)ethan-1-ol (3q)



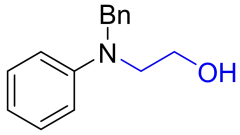
Yield: 61% (93 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.23 (t, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 3.83-3.76 (m, 2H), 3.48 (t, *J* = 5.8 Hz, 2H), 3.32-3.29 (m, 2H), 1.78 (br 1H),1.60-1.56 (m, 2H), 1.35-1.2 (m, 18H), 0.89 (t *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.4, 129.3 (2C), 116.6, 112.8 (2C), 60.0, 53.2, 51.8, 31.9, 29.7 (4C), 29.5, 29.4, 27.1, 26.7, 22.7, 14.1. **HRMS**(ESI) calcd for $C_{20}H_{35}NOH^+$: 306.2791. Found: 306.2794 (MH^+)

2-(cyclohexyl(phenyl)amino)ethan-1-ol (3r)



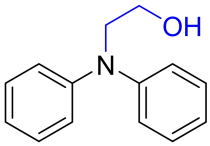
Yield: 56% (61 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.24 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.78 (t, *J* = 6.9 Hz, 1H), 3.67 (t, *J* = 5.9 Hz, 2H), 3.49-3.44 (m, 1H), 3.37 (t, *J* = 6.0 Hz, 2H), 1.83(d, *J* = 9.7 Hz, 5H), 1.67 (d, *J* = 12.5 Hz, 1H), 1.43-1.31(m, 4H), 1.16-1.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.8, 129.1 (2C), 118.2, 115.9 (2C), 60.3, 59.4, 46.9, 30.7, 26.1, 25.8. **HRMS**(ESI) calcd for $C_{14}H_{21}NOH^+$: 220.1696. Found: 220.1697 (MH^+).

2-(benzyl(phenyl)amino)ethan-1-ol (3s)



Yield: 70% (79 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.33-7.18 (m, 7H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 4.62 (s, 2H), 3.83 (t, *J* =5.7 Hz, 2H), 3.61 (t, *J* =5.7 Hz, 2H), 1.79 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.7, 138.5, 129.3, 128.6, 126.9, 126.5, 117.0, 112.7, 60.2, 55.0, 53.3.

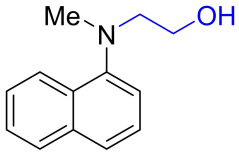
2-(diphenylamino)ethan-1-ol (3t)



Yield: 42% (45 mg), brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.27 (t, *J* = 7.4 Hz, 4H), 7.05 (d, *J* = 8.2 Hz, 4H), 6.97 (t, *J* = 7.4 Hz, 2H), 3.93 (t, *J* = 5.6 Hz, 2H), 3.83 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 148.0 (2C), 129.4 (4C), 121.7 (2C), 121.2 (4C), 59.9, 54.2.

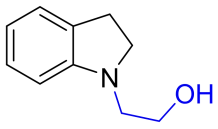
Spectroscopic data are consistent with those previously reported: *Medicinal Chemistry Research,* **2005**, *14*, 241-259.

2-(methyl(naphthalen-1-yl)amino)ethan-1-ol (3u)



Yield: 56% (56 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.30 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.54-7.47 (m, 2H), 7.42(t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.81 (t, *J* = 5.2 Hz, 2H), 3.32 (t, *J* = 5.4 Hz,2H), 2.88 (s, 3H), 2.54 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 149.5, 134.7, 129.4, 128.4, 125.9, 125.7, 125.6, 124.1, 123.2, 116.3, 59.1, 57.8, 43.2. **HRMS**(ESI) calcd for $C_{13}H_{15}NOH^+$; calculated: 202.1226. Found: 202.1227 (MH^+).

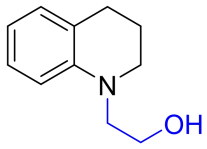
2-(indolin-1-yl)ethan-1-ol (3v)



Yield: 65% (53 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.13-7.08 (m, 2H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 3.81 (t, *J* = 5.2 Hz, 2H), 3.39 (t, *J* = 8.3 Hz, 2H), 3.24 (t, *J* = 5.1 Hz, 2H), 3.00 (t, *J* = 8.2 Hz, 2H), 2.25 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 152.7, 130.0, 127.3, 124.5, 118.3, 107.4, 60.1, 53.9, 52.5, 28.6.

Spectroscopic data are consistent with those previously reported: *Tetrahedron*, **2017**,*73*, 5552-5561

2-(3,4-dihydroquinolin-1(2H)-yl)ethan-1-ol (3w)

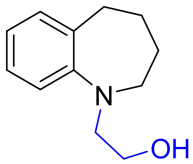


Yield: 67% (59 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.06 (t,

J = 7.7 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 3.82 (t, *J* = 5.6 Hz, 2H), 3.45 (t, *J* = 5.6 Hz, 2H), 3.33 (t, *J* = 5.6 Hz, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.00-1.94 (m, 2H), 1.87 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 145.8, 129.3, 127.1, 122.8, 116.4, 111.3, 59.8, 54.1, 50.3, 28.0, 22.2.

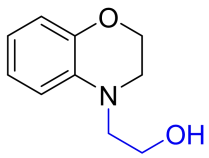
Spectroscopic data are consistent with those previously reported: *Tetrahedron*, **2017**,*73*, 5552-5561

2-(2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)ethan-1-ol (3x)



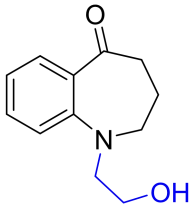
Yield: 66% (63 mg), pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.25-7.19 (m, 2H), 7.05-6.98 (m, 2H), 3.75 (t, *J* = 3.8 Hz, 2H), 3.39 (t, *J* = 3.7 Hz, 2H), 3.00-2.98 (m, 2H), 2.88-2.86 (m, 2H), 2.66 (br, 1H), 1.87-1.76(m, 2H), 1.73-1.63 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 151.7, 137.2, 130.0, 126.7, 122.3, 118.3, 59.2, 55.6, 54.2, 35.0, 30.7, 25.8. **HRMS**(ESI) calcd for $C_{12}H_{17}NOH^+$: 192.1383. Found: 192.1382(MH^+).

2-(3,4-dihydroquinolin-1(2H)-yl)ethan-1-ol (3y)



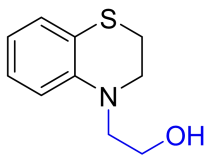
Yield: 63% (56 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.83(dd, *J* = 15.6, 7.7 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 4.23 (s, 2H), 3.80 (t, *J* = 5.3 Hz, 2H), 3.42-3.39 (m, 4H), 2.47 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 144.1, 135.3, 121.5, 117.9, 116.4, 112.6, 64.2, 59.5, 53.7, 47.9. **HRMS**(ESI) calcd for $C_{10}H_{13}NO_2H^+$: 180.1019. Found: 180.1027 (MH^+).

1-(2-hydroxyethyl)-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3z)



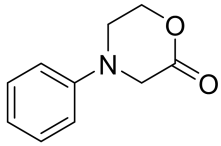
Yield: 56% (57 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 4.49 (br, 1H), 3.91 (t, *J* = 5.8 Hz, 2H), 3.69 (t, *J* = 5.8 Hz, 2H), 3.34 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.33-2.26 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 203.7, 153.3, 132.4, 129.8, 127.2, 118.1, 114.6, 60.1, 55.1, 53.5, 40.92, 31.9. **HRMS**(ESI) calcd for $C_{12}H_{15}NO_2H^+$: 206.1176. Found: 206.1175 (MH^+).

2-(2,3-dihydro-4H-benzo[b][1,4]thiazin-4-yl)ethan-1-ol (3aa)



Yield: 55% (54 mg), yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.05 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.02-6.95 (m, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 3.79 (t, *J* = 5.7 Hz, 2H), 3.66-3.60 (m, 2H), 3.45 (t, *J* = 5.7 Hz, 2H), 3.05-2.98 (m, 2H), 2.30 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 143.5, 128.0, 126.0, 118.3, 117.9, 113.7, 59.5, 55.0, 50.7, 25.5. **HRMS**(ESI) calcd for $C_{10}H_{14}NOSH^+$: 196.0791. Found: 196.0801 (MH^+).

4-phenylmorpholin-2-one (3ae)



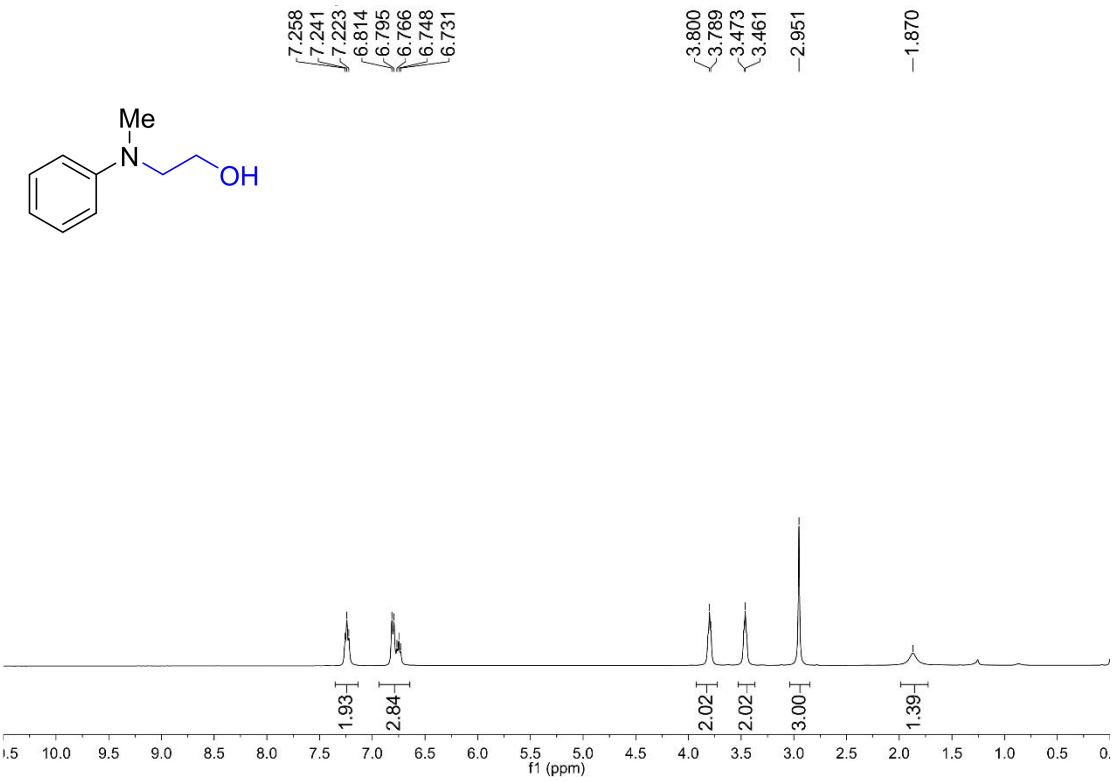
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (t, *J* = 7.5 Hz, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 2H), 4.55 (t, *J* = 5.0 Hz, 2H), 4.11 (s, 2H), 3.48 (t, *J* = 5.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.5,

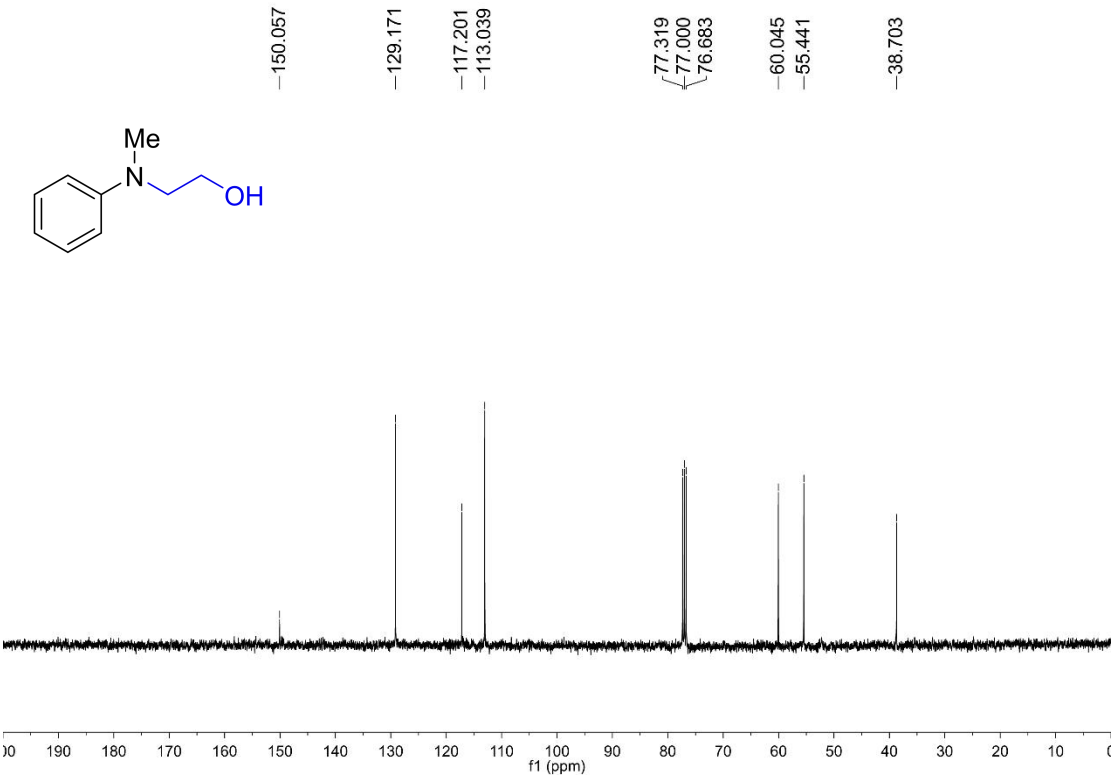
147.7, 129.4, 119.7, 113.6, 67.4, 49.9, 43.9.

Spectroscopic data are consistent with those previously reported: *J. Am. Chem. Soc*. **2014**, *136*, 9252-9255.

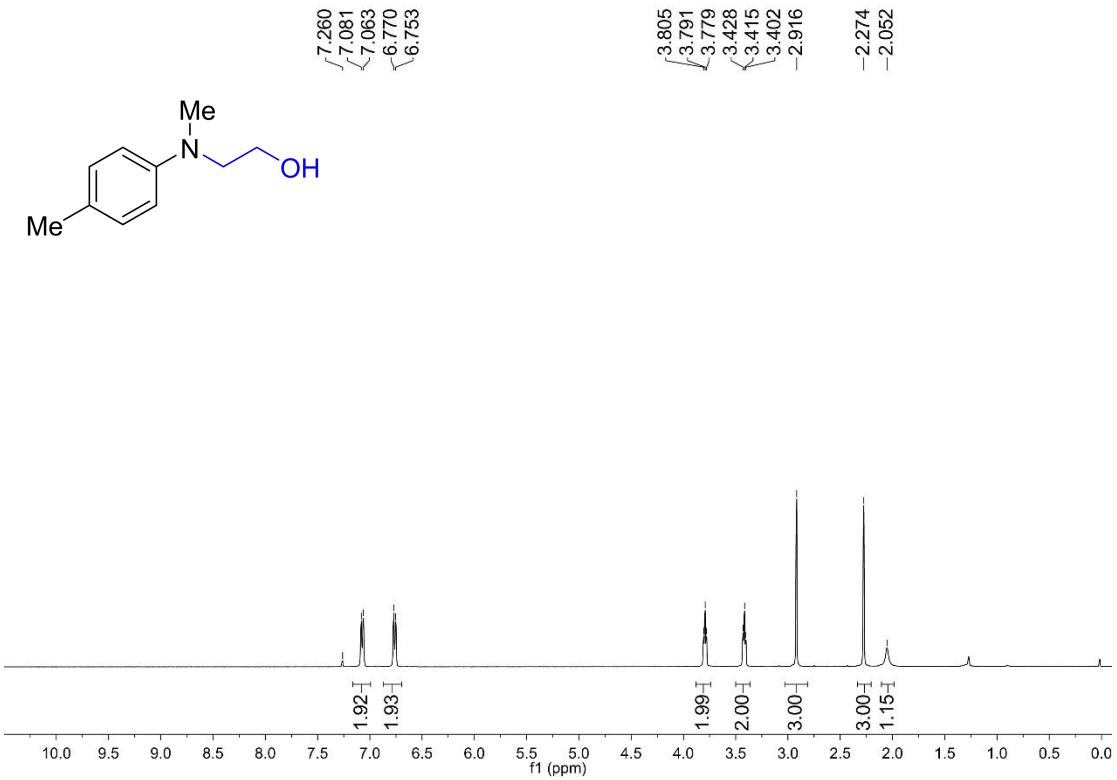
5. Spectral data

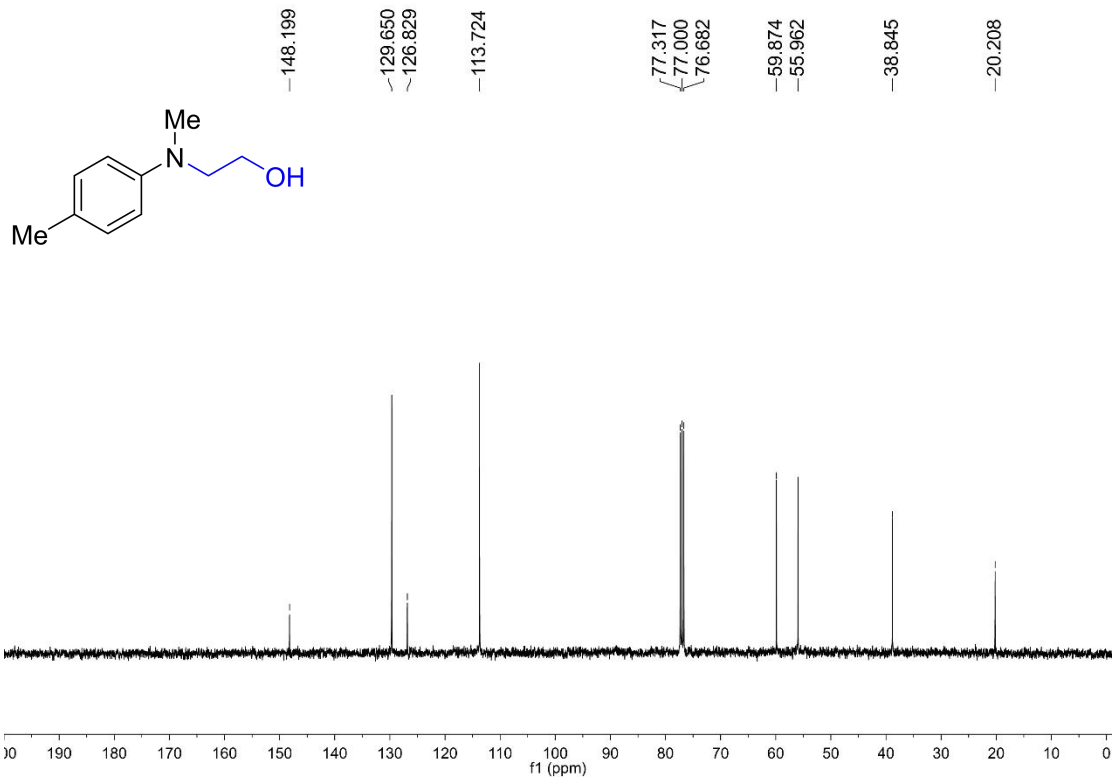
2-(methyl(phenyl)amino)ethan-1-ol (3a)



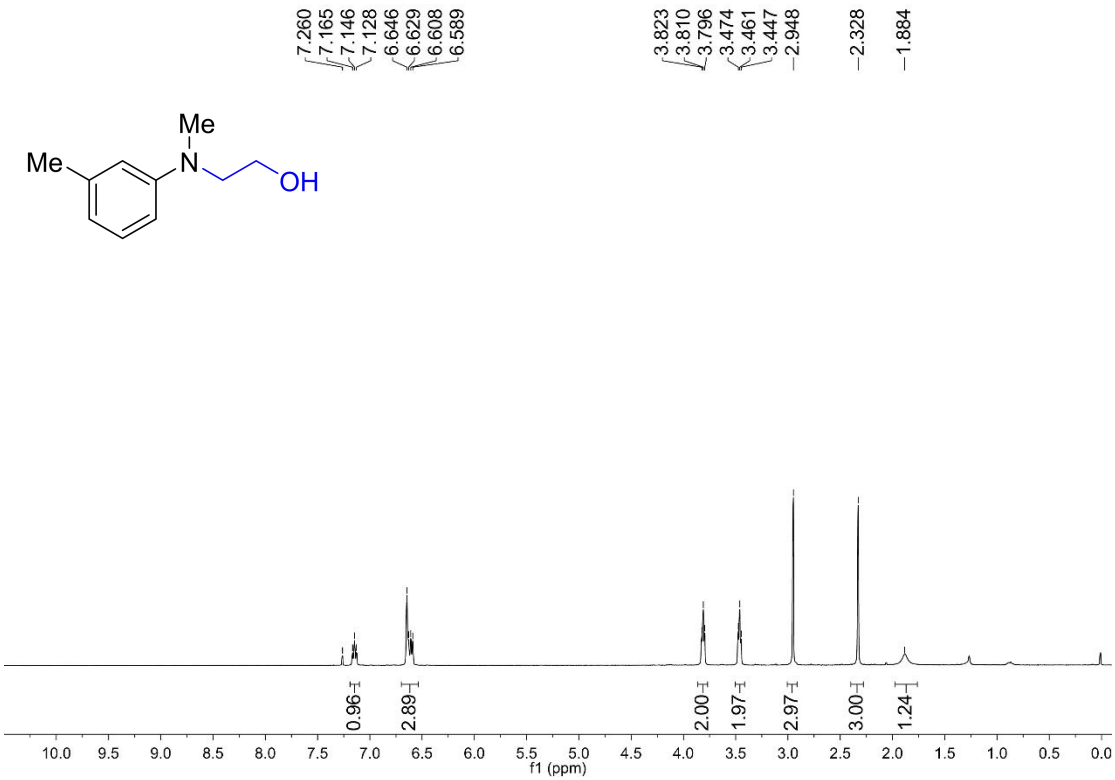


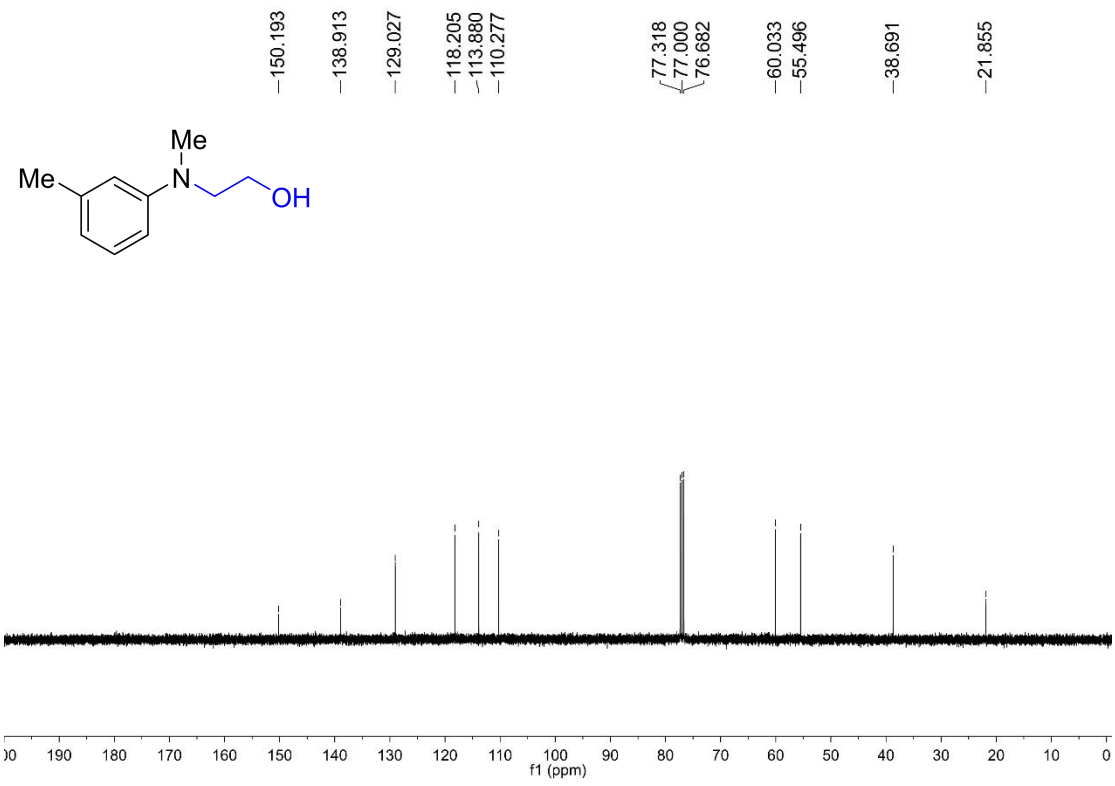
2-(methyl(p-tolyl)amino)ethan-1-ol (3b)



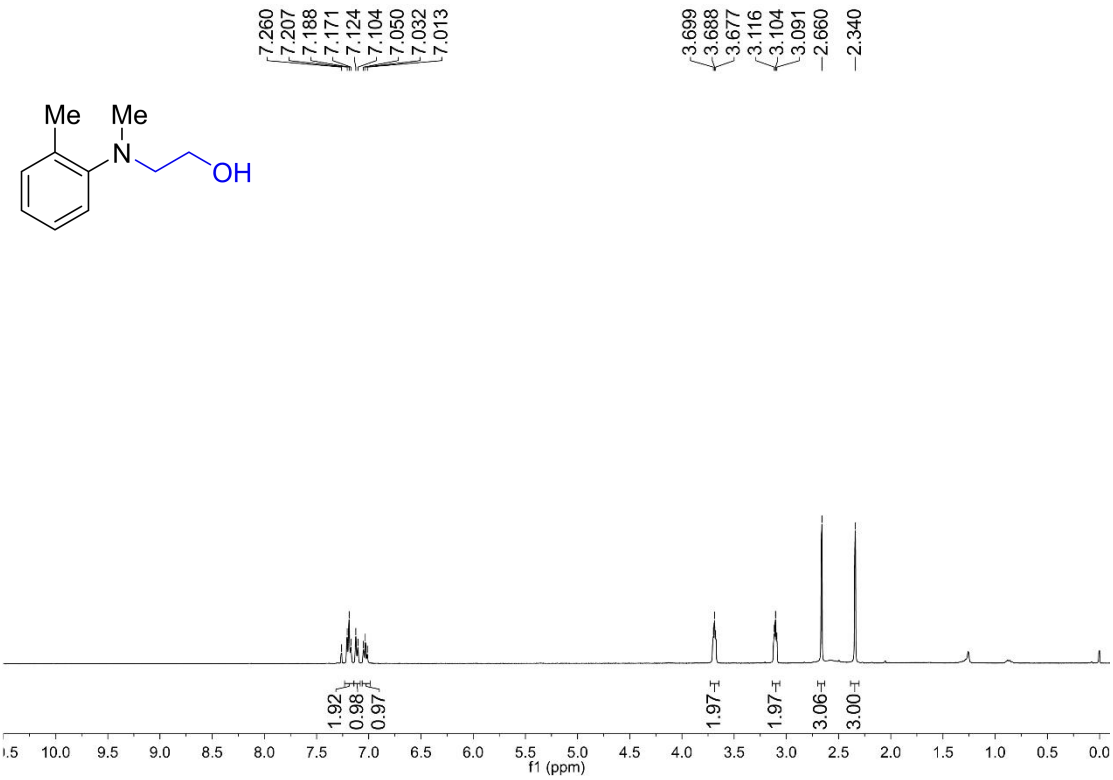


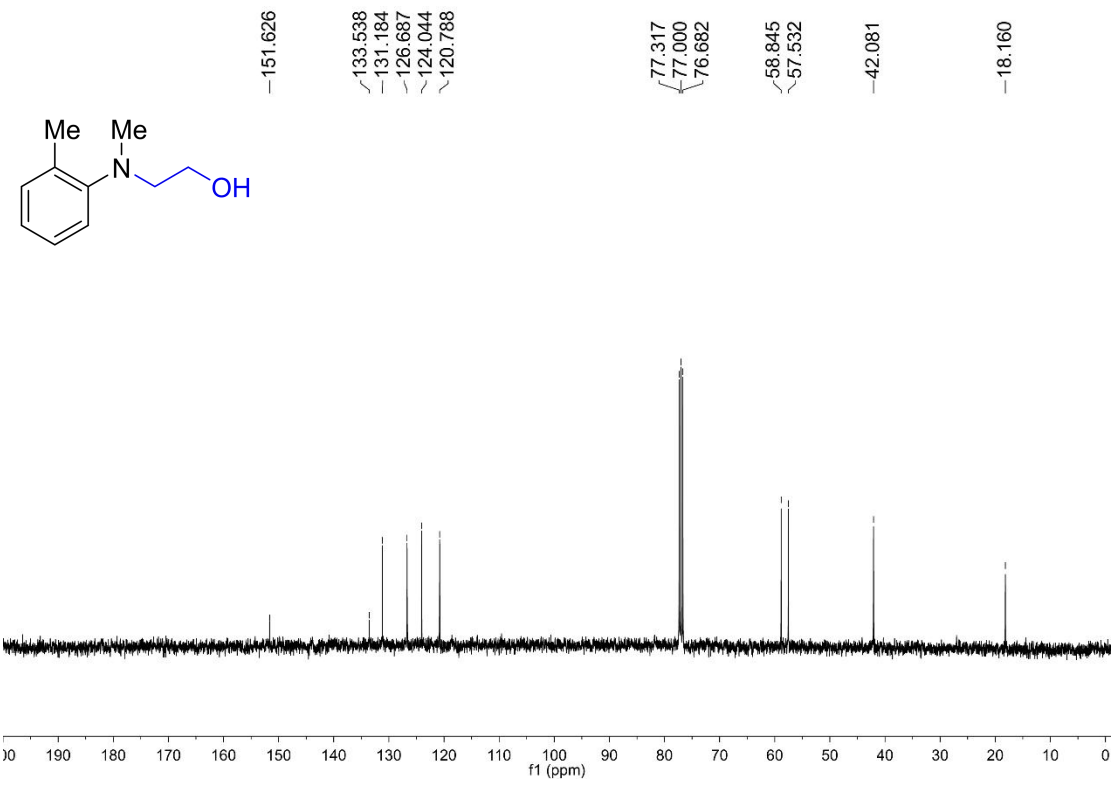
3-(methyl(m-tolyl)amino)ethan-1-ol (3c)



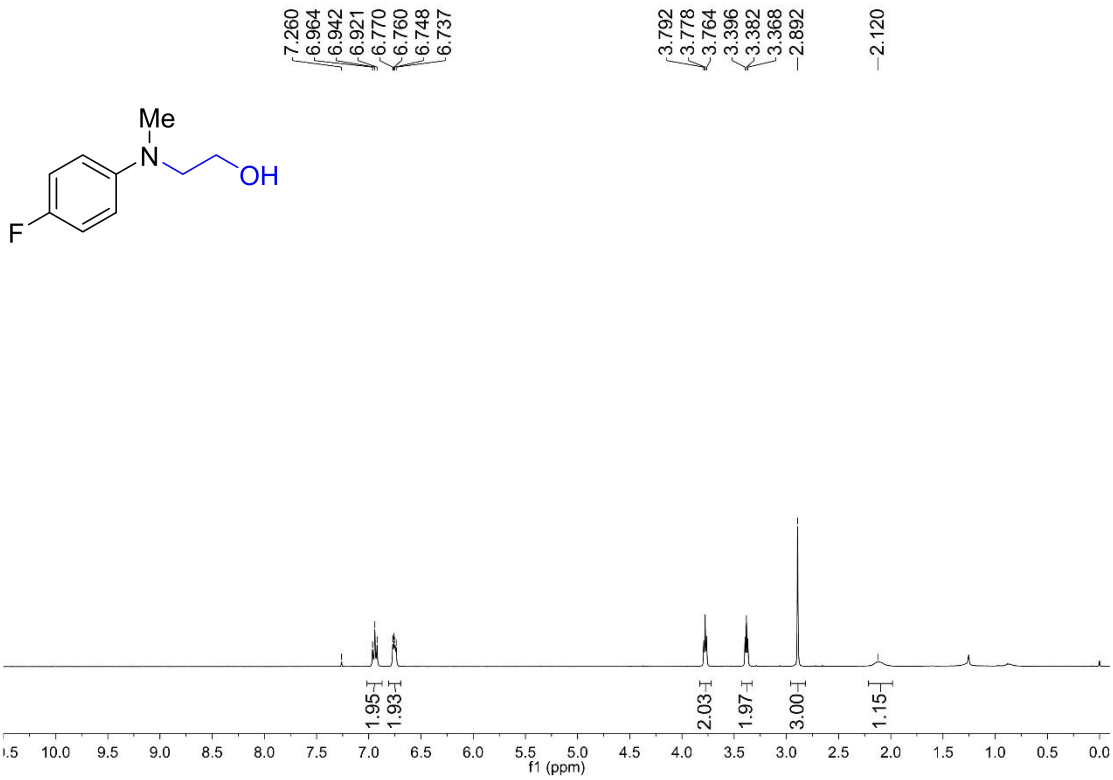


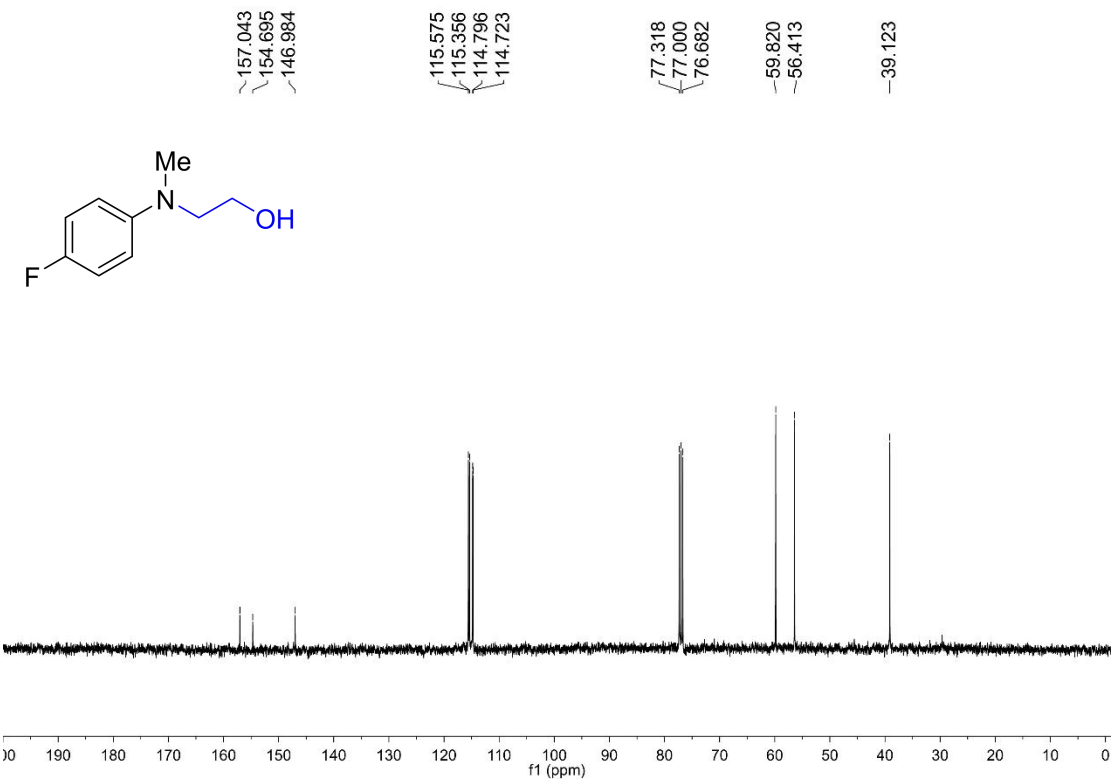
4-(methyl(o-tolyl)amino)ethan-1-ol (3d)



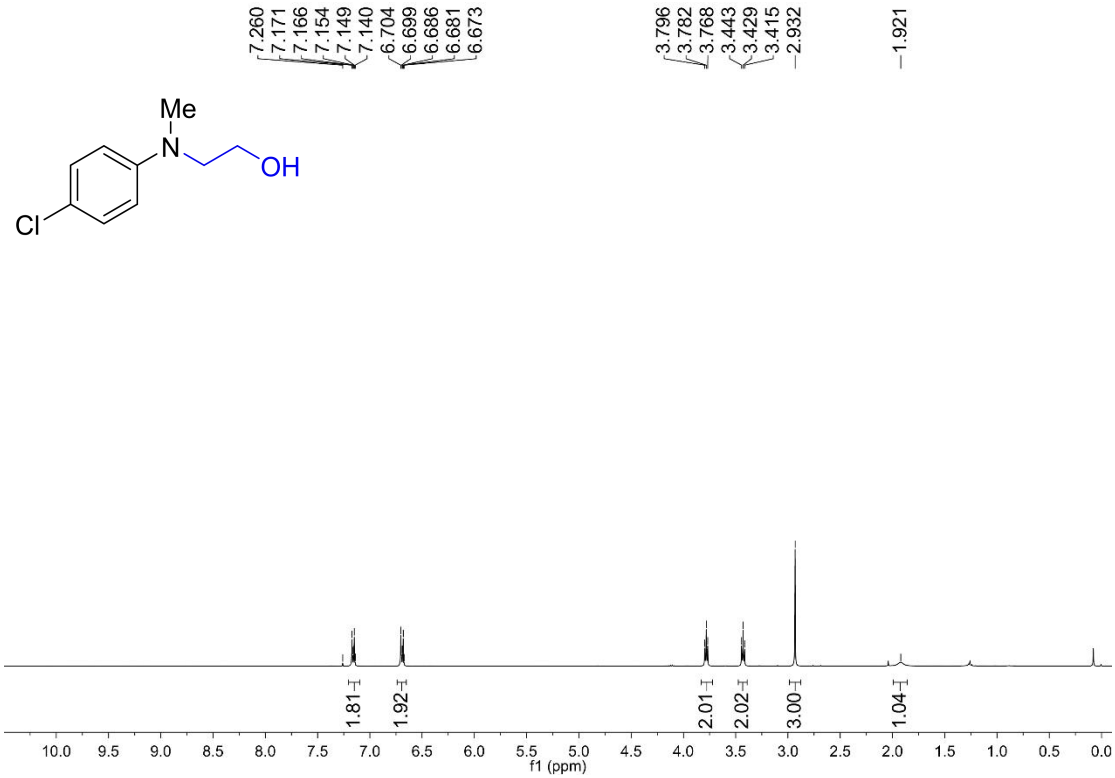


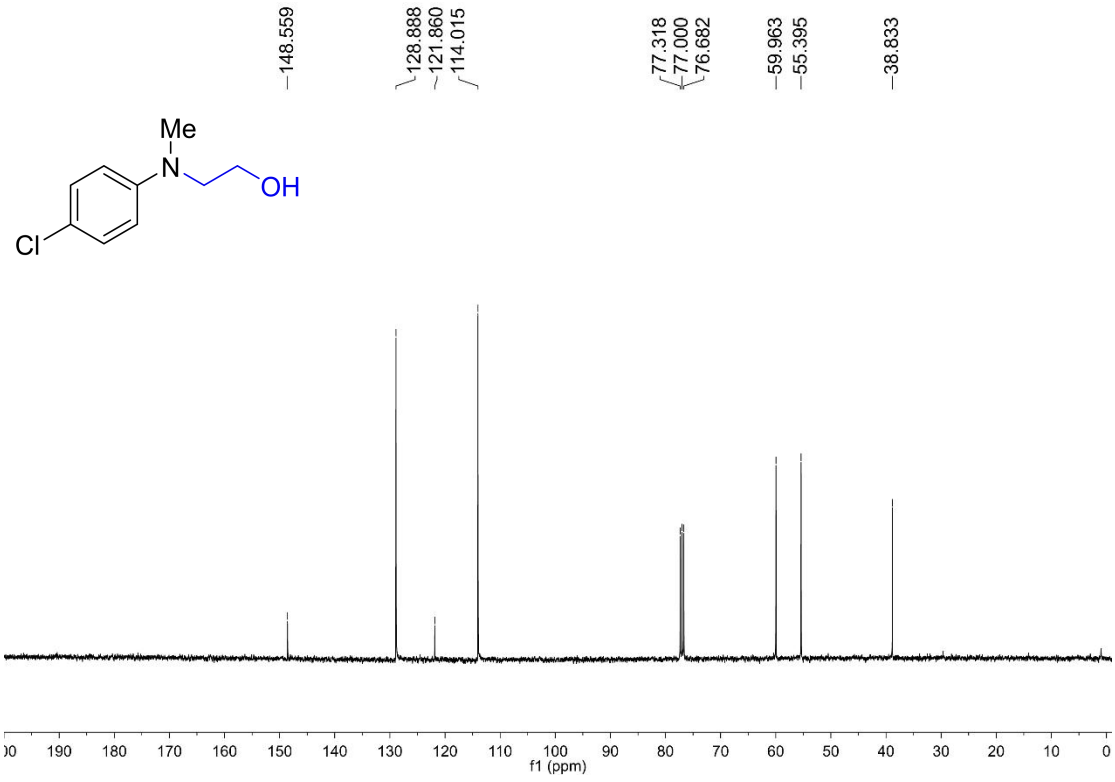
2-((4-fluorophenyl)(methyl)amino)ethan-1-ol (3e)



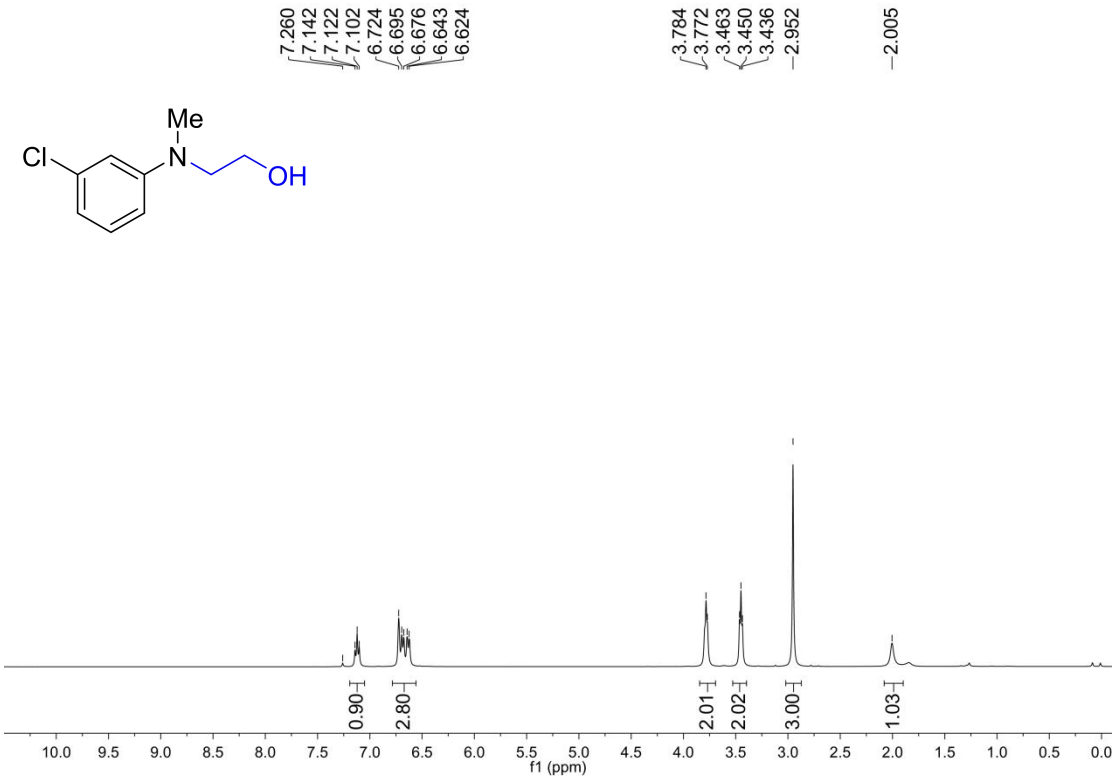


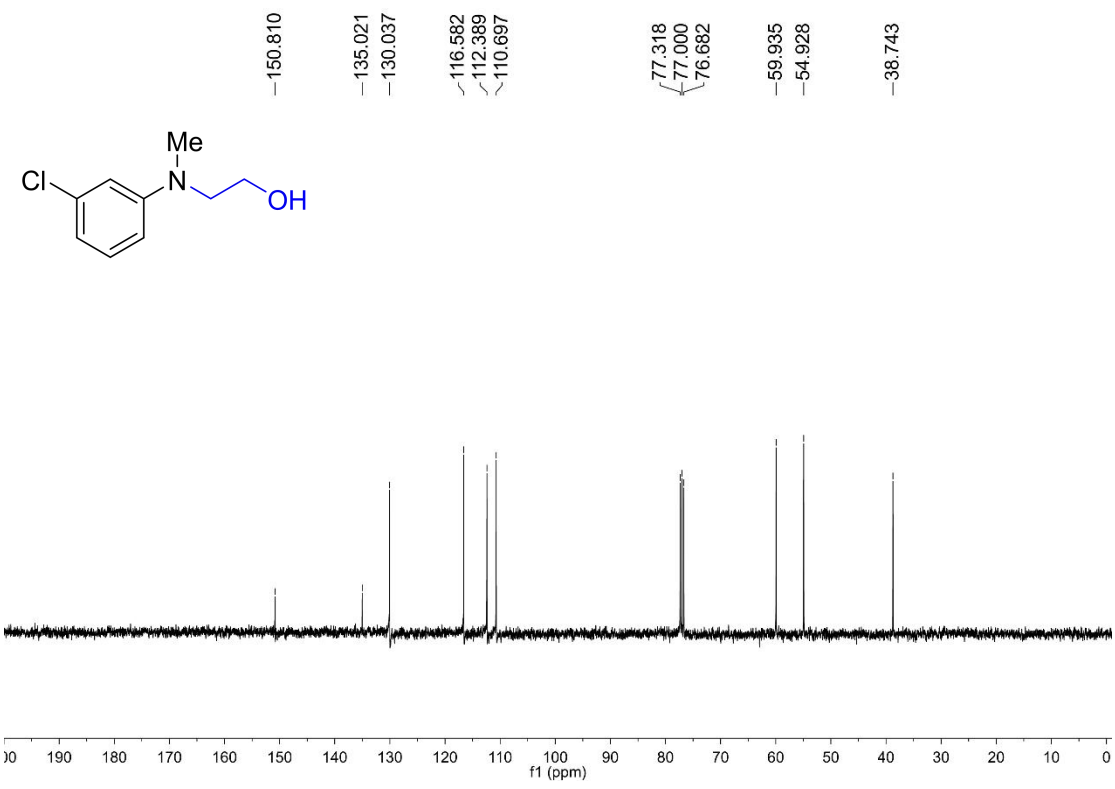
2-((4-chlorophenyl)(methyl)amino)ethan-1-ol (3f)



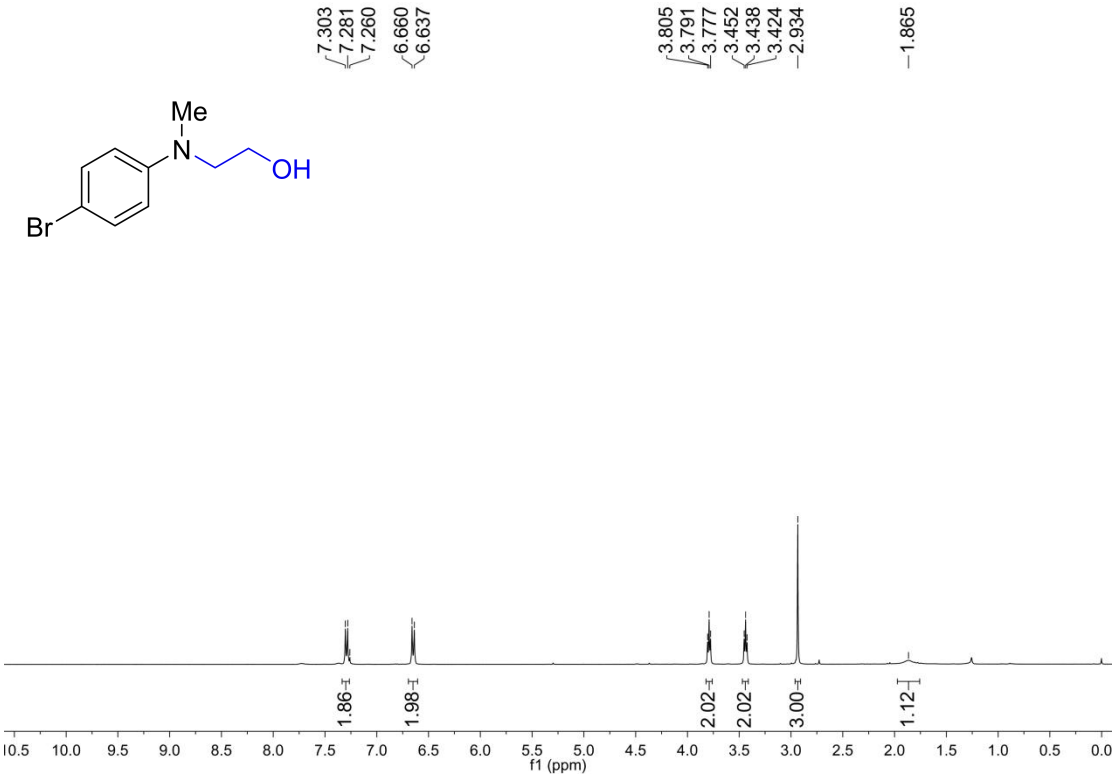


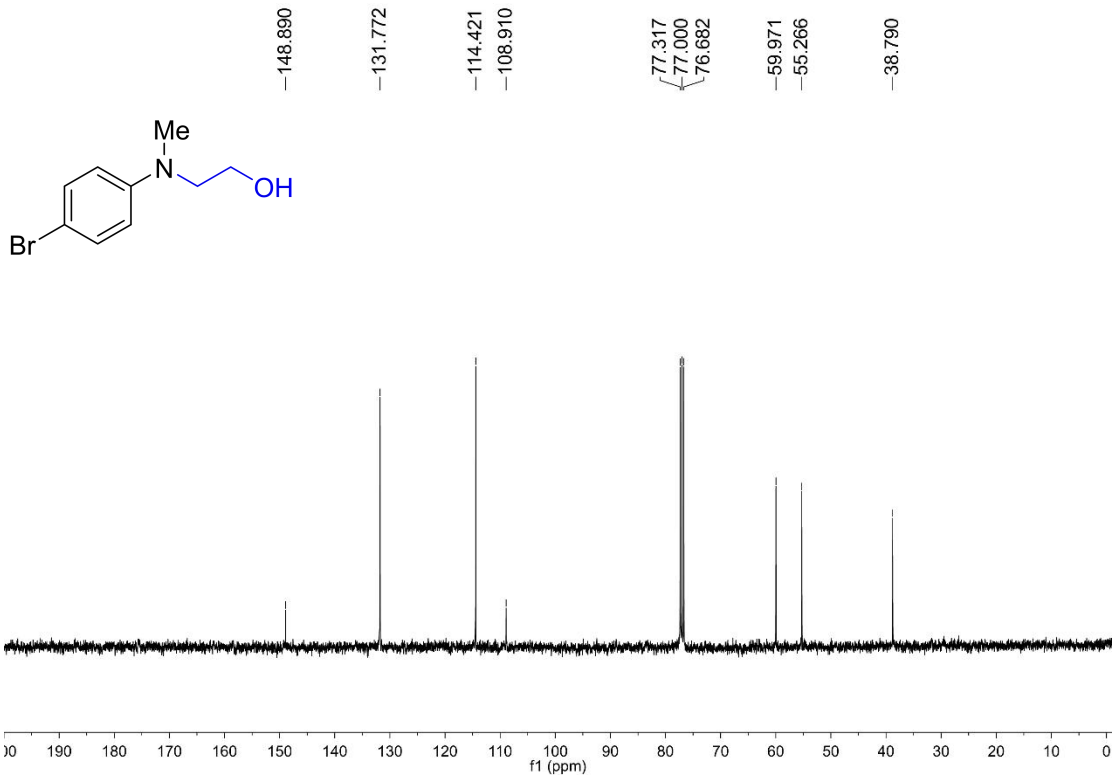
2-((3-chlorophenyl)(methyl)amino)ethan-1-ol (3g)



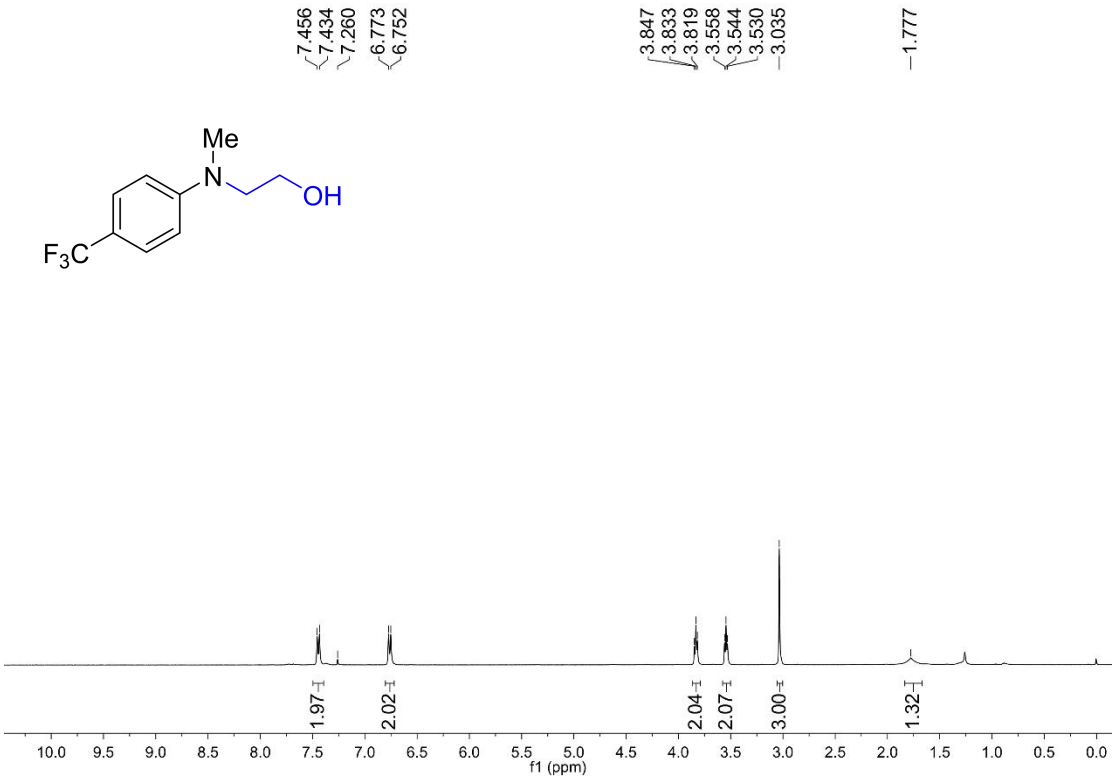


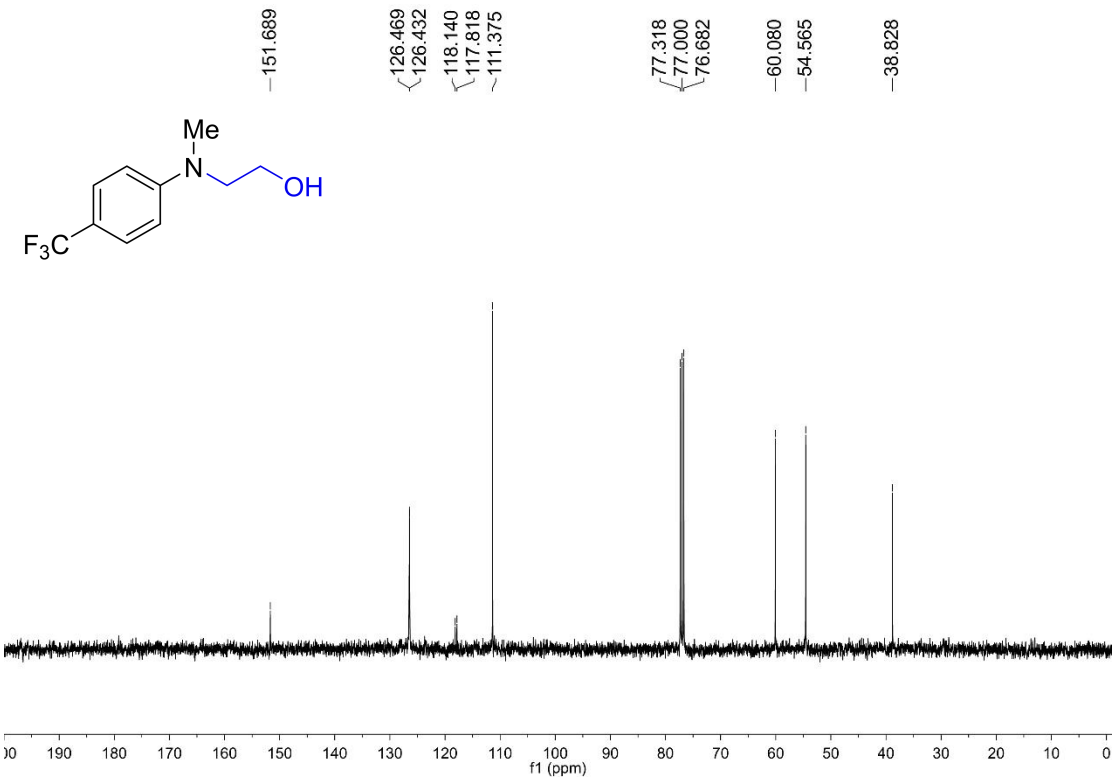
2-((4-bromophenyl)(methyl)amino)ethan-1-ol (3h)



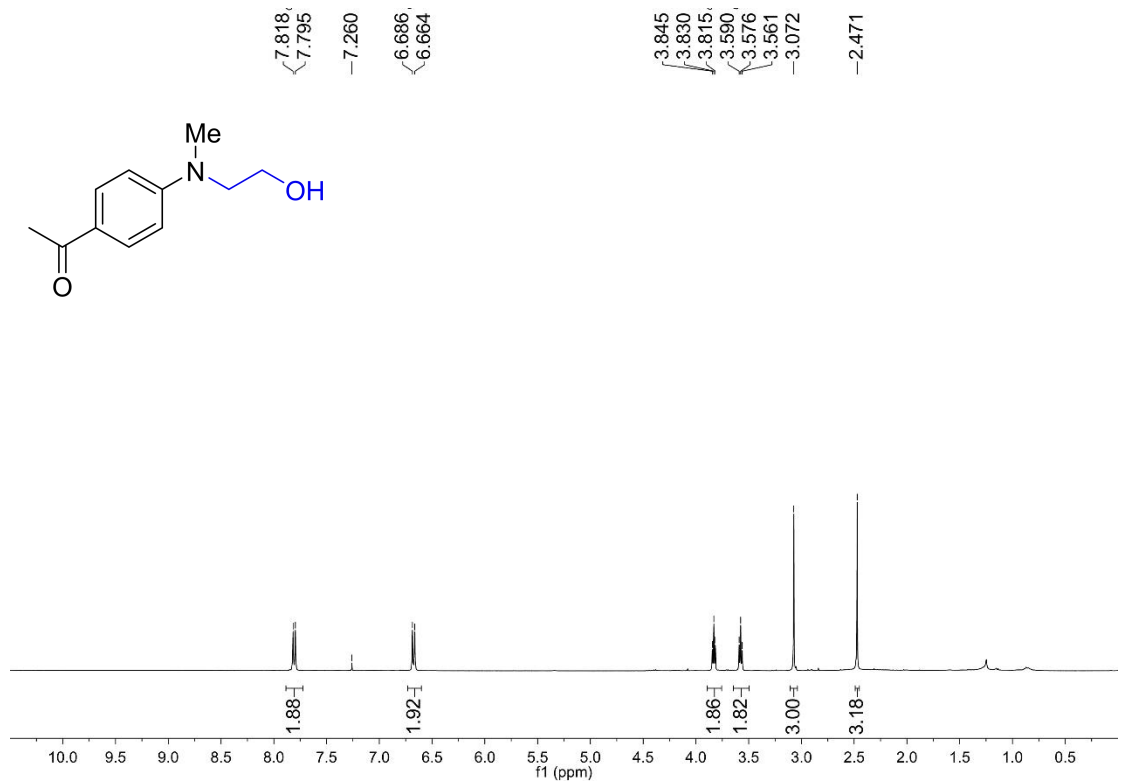


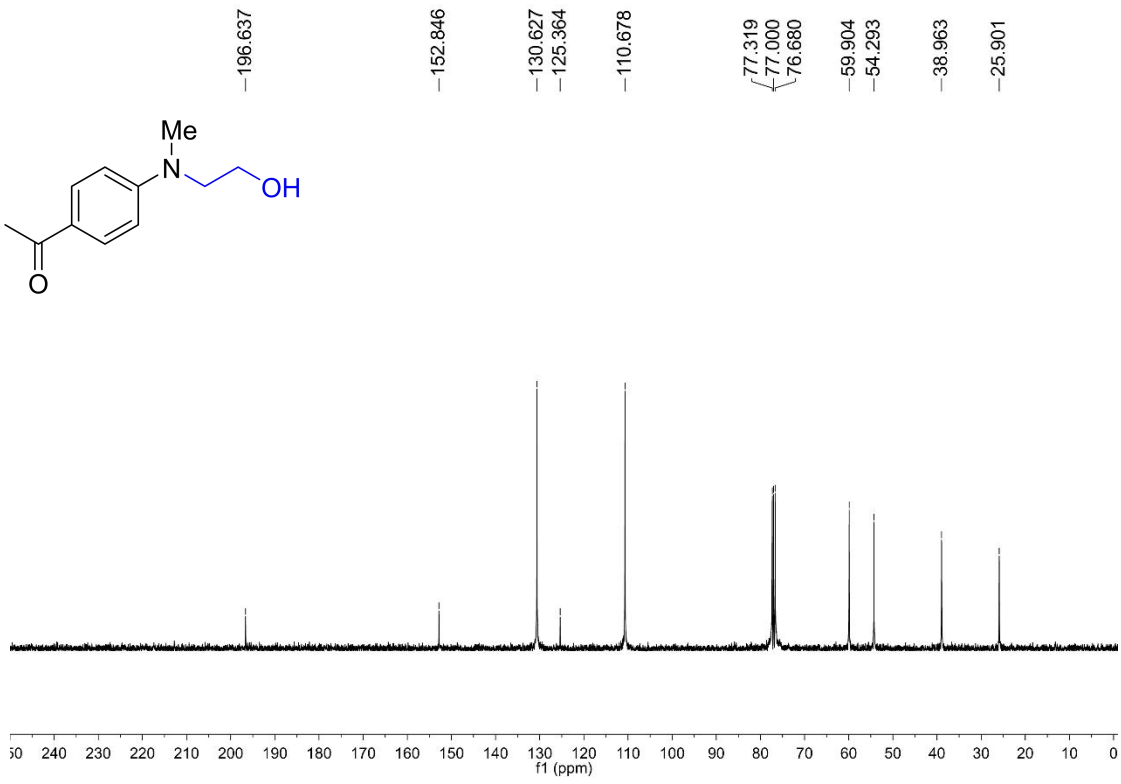
2-(methyl(4-(trifluoromethyl)phenyl)amino)ethan-1-ol (3i)



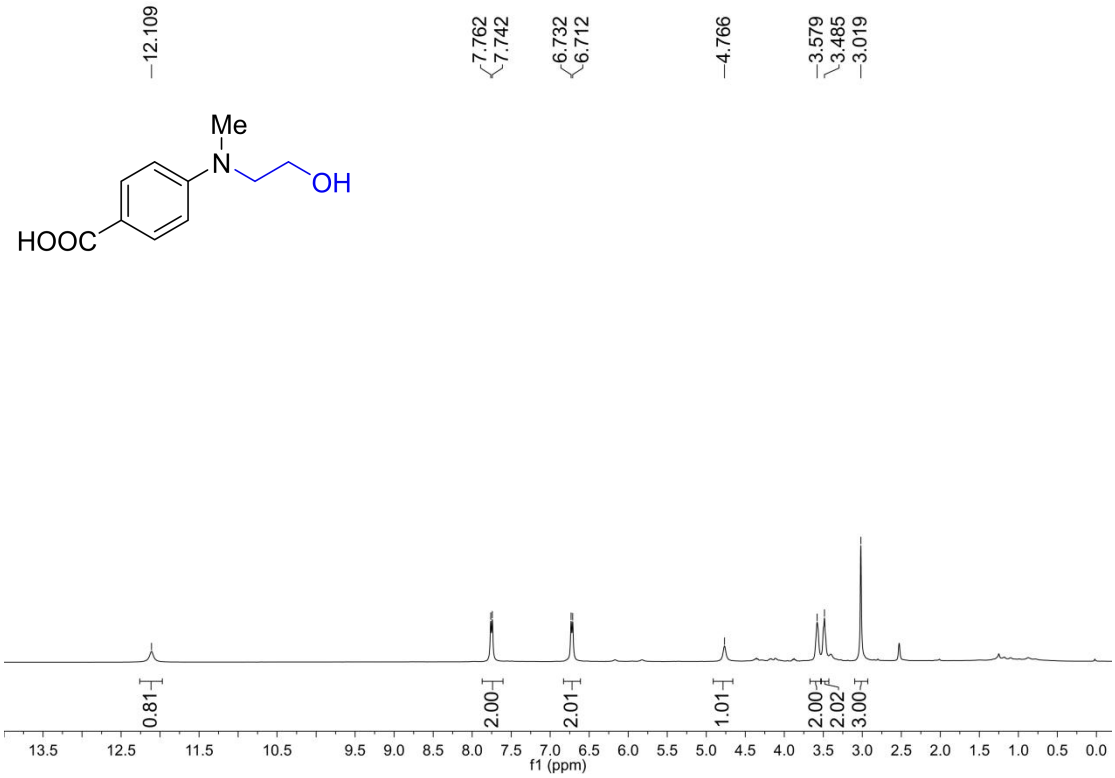


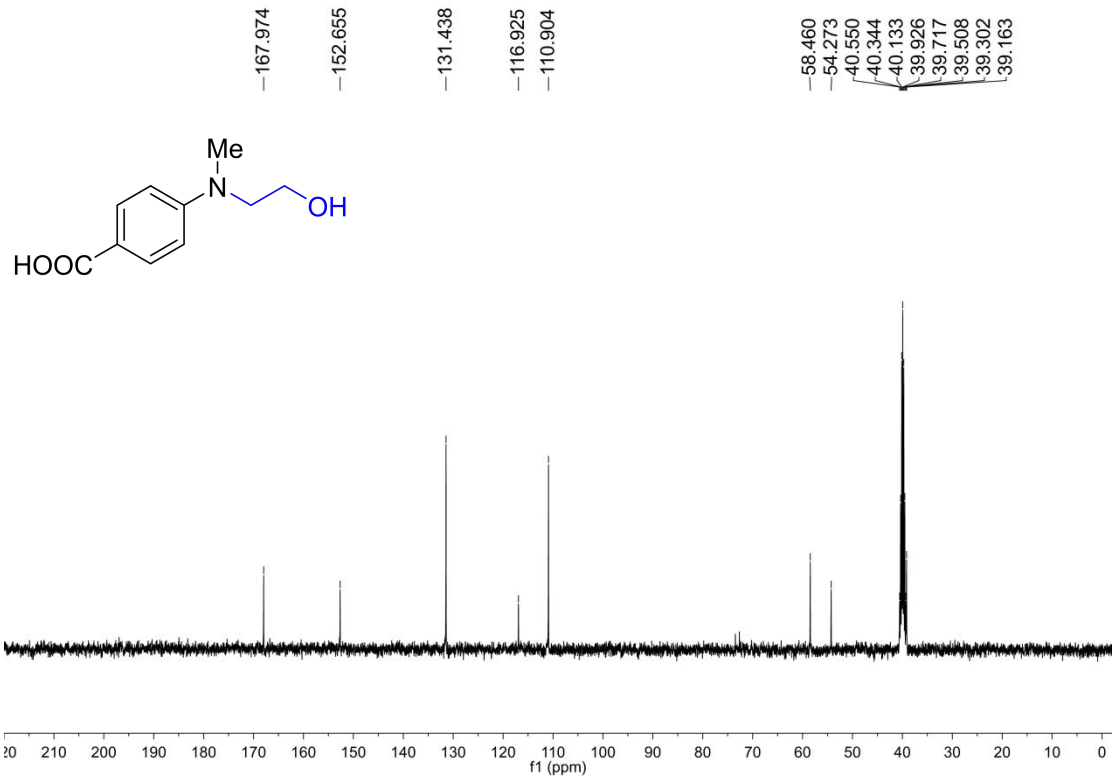
1-(4-((2-hydroxyethyl)(methyl)amino)phenyl)ethan-1-one (3j)



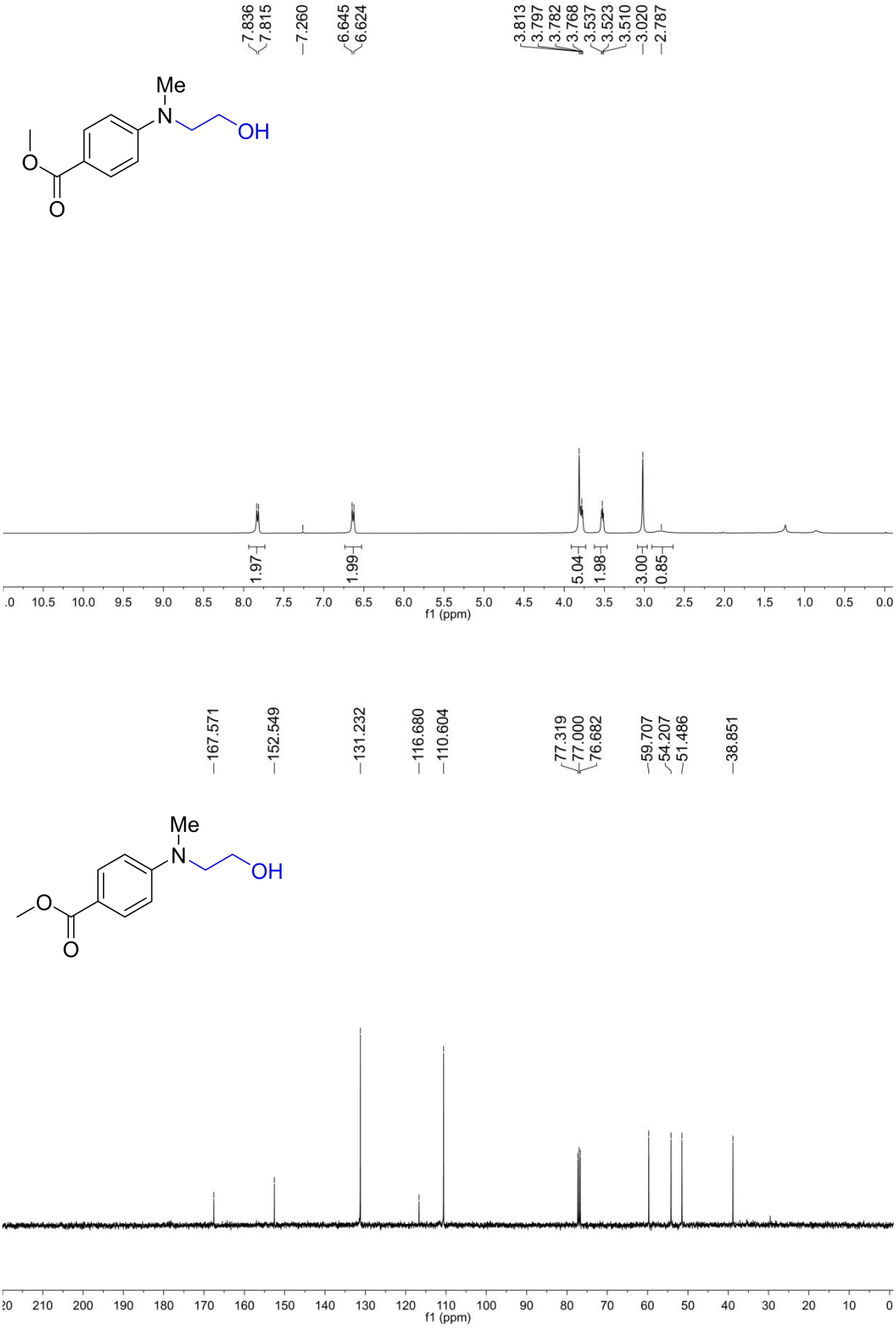


5-((2-hydroxyethyl)(methyl)amino)benzoic acid (3k)

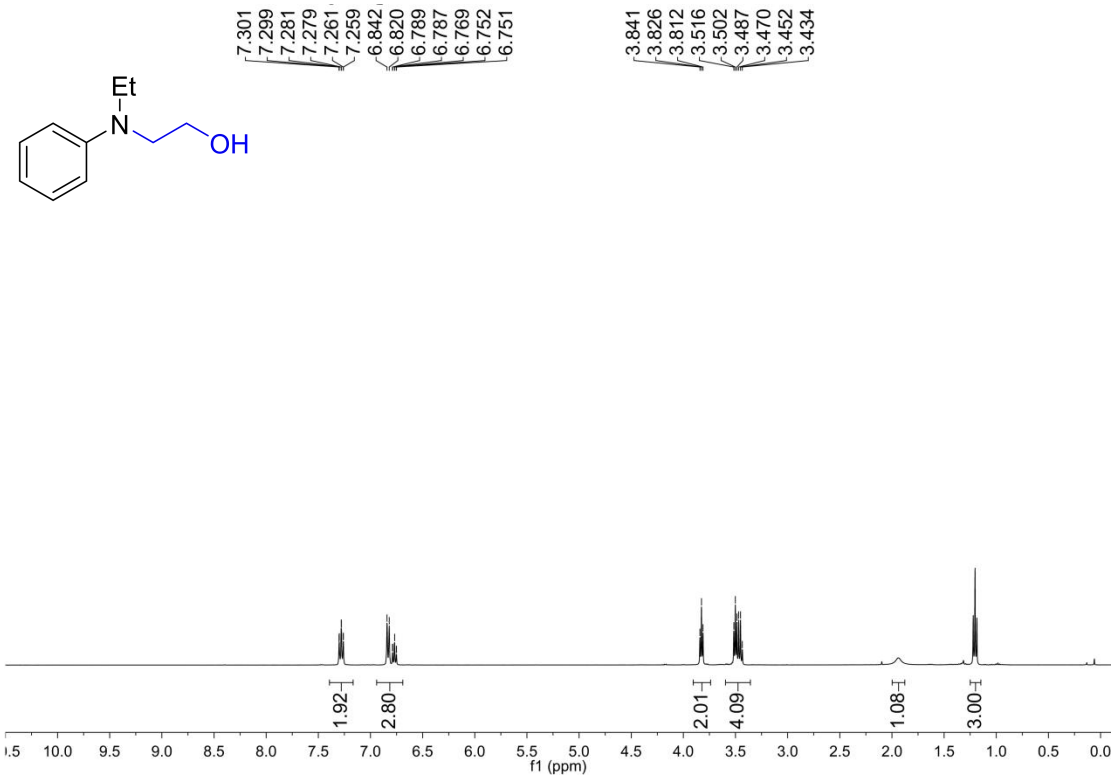


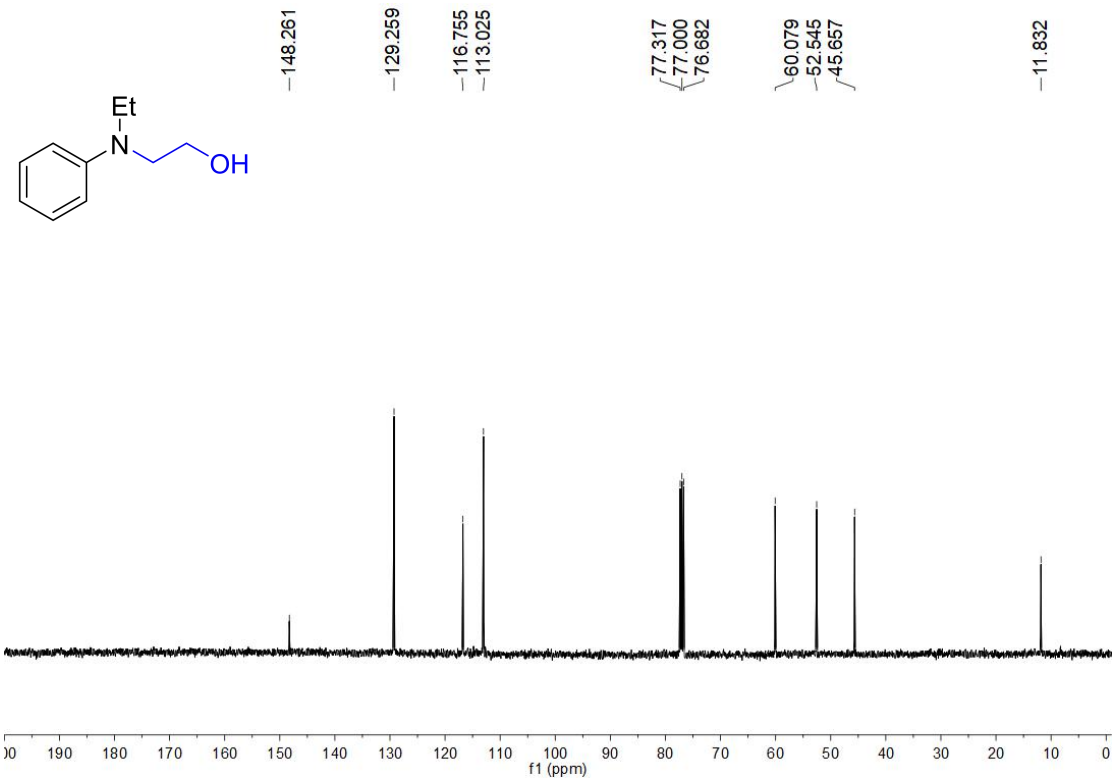


methyl 4-((2-hydroxyethyl)(methyl)amino)benzoate (3l)

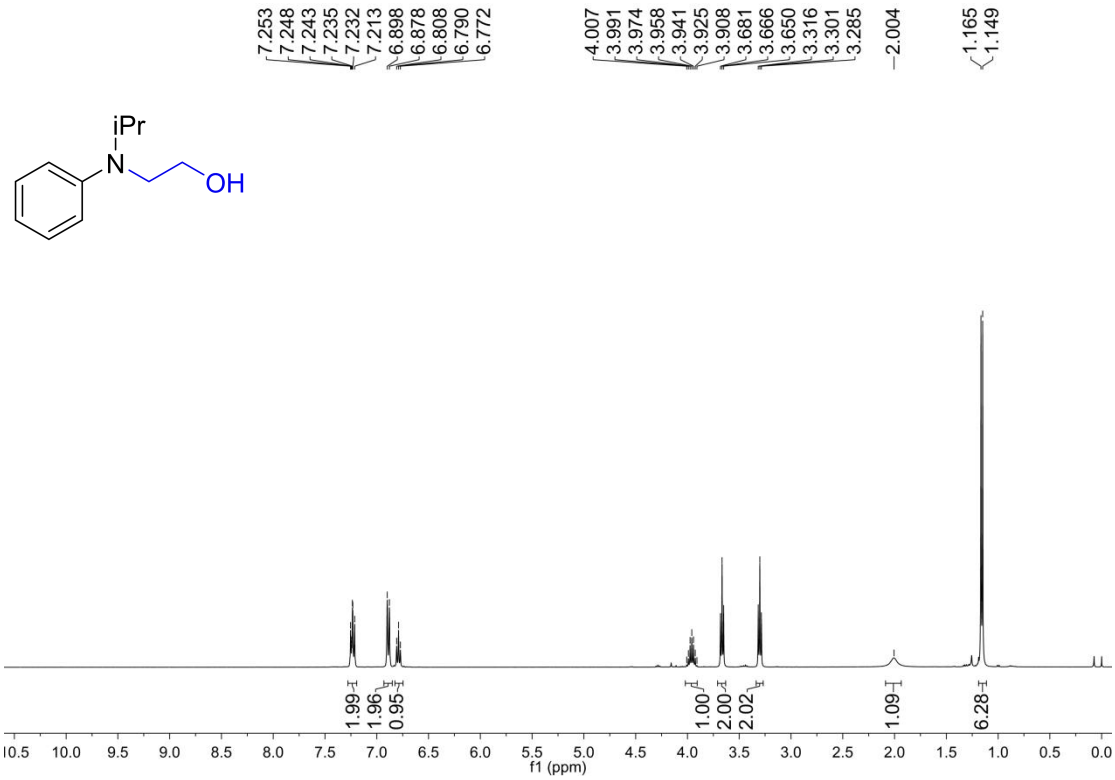


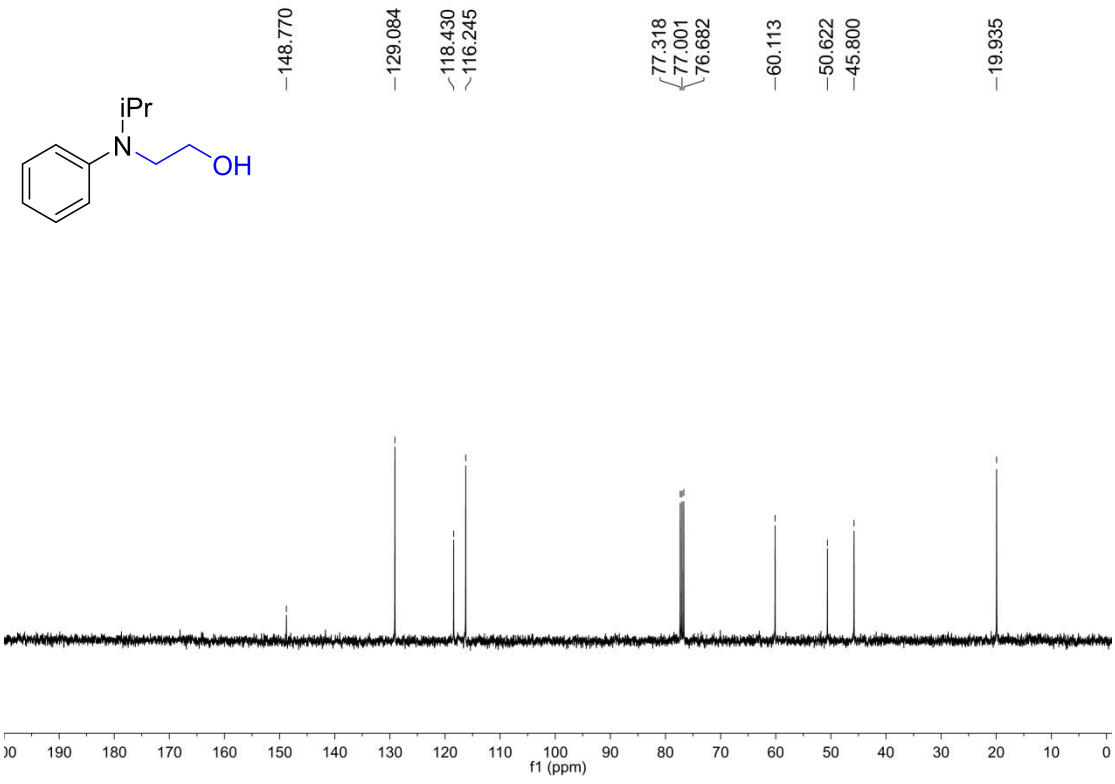
2-(ethyl(phenyl)amino)ethan-1-ol (3n)



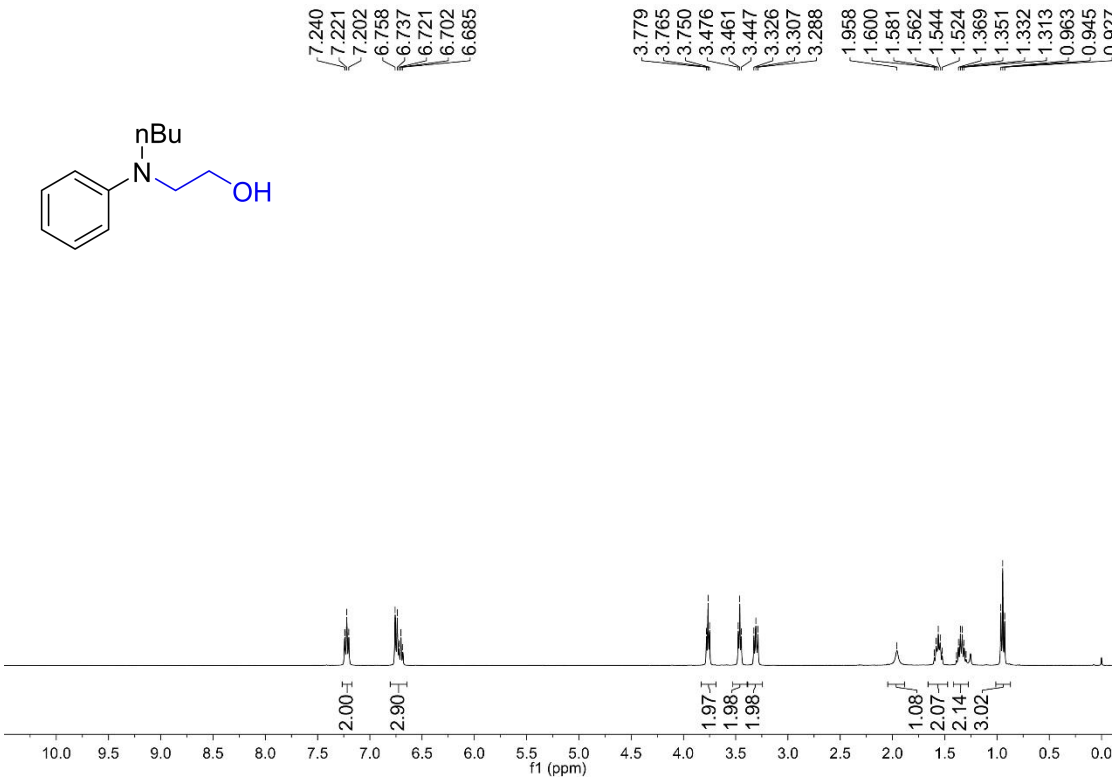


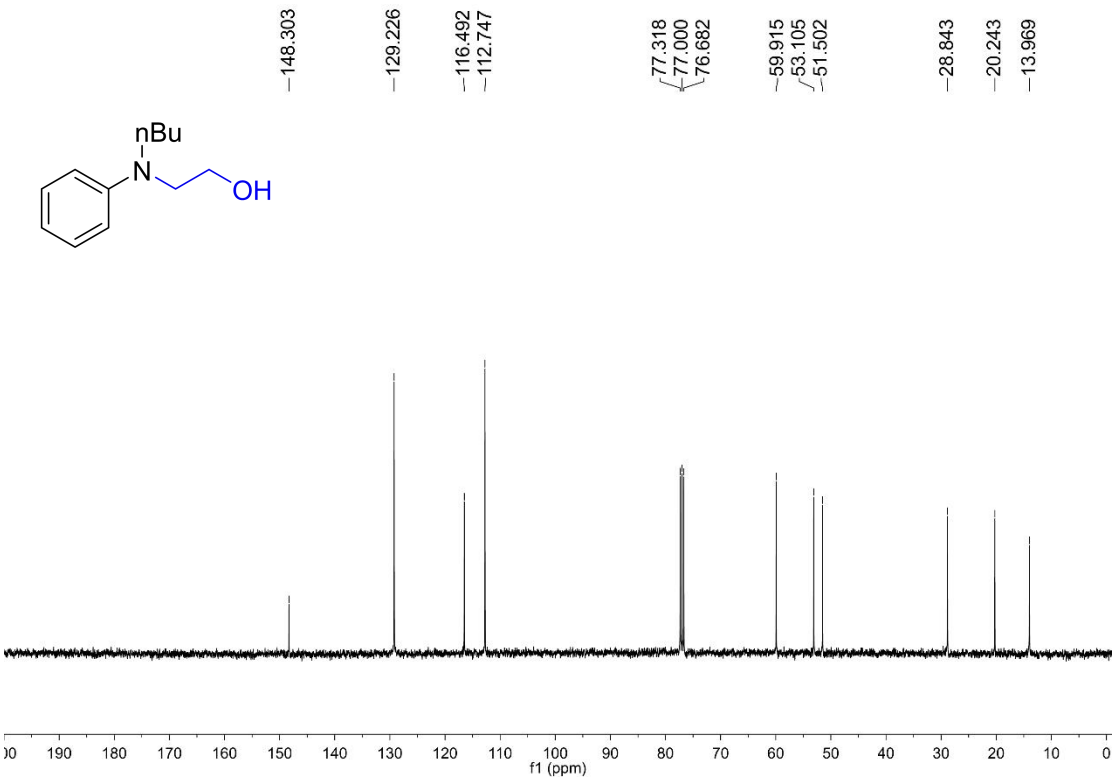
2-(isopropyl(phenyl)amino)ethan-1-ol (3o)



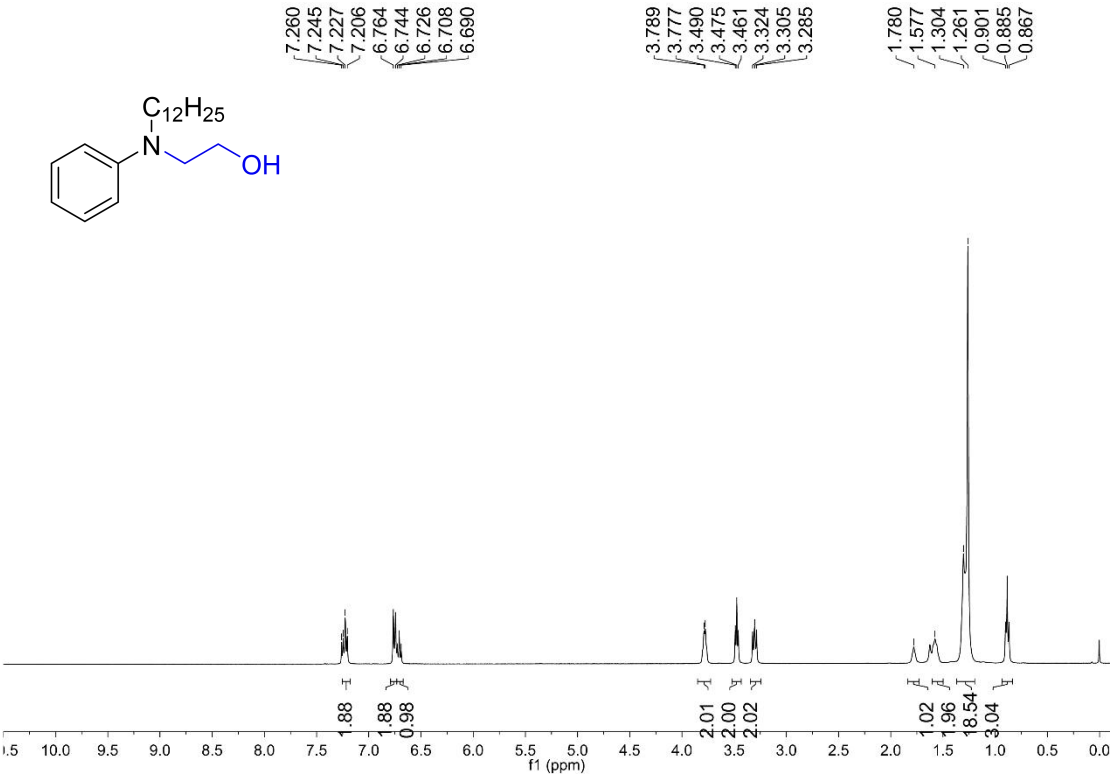


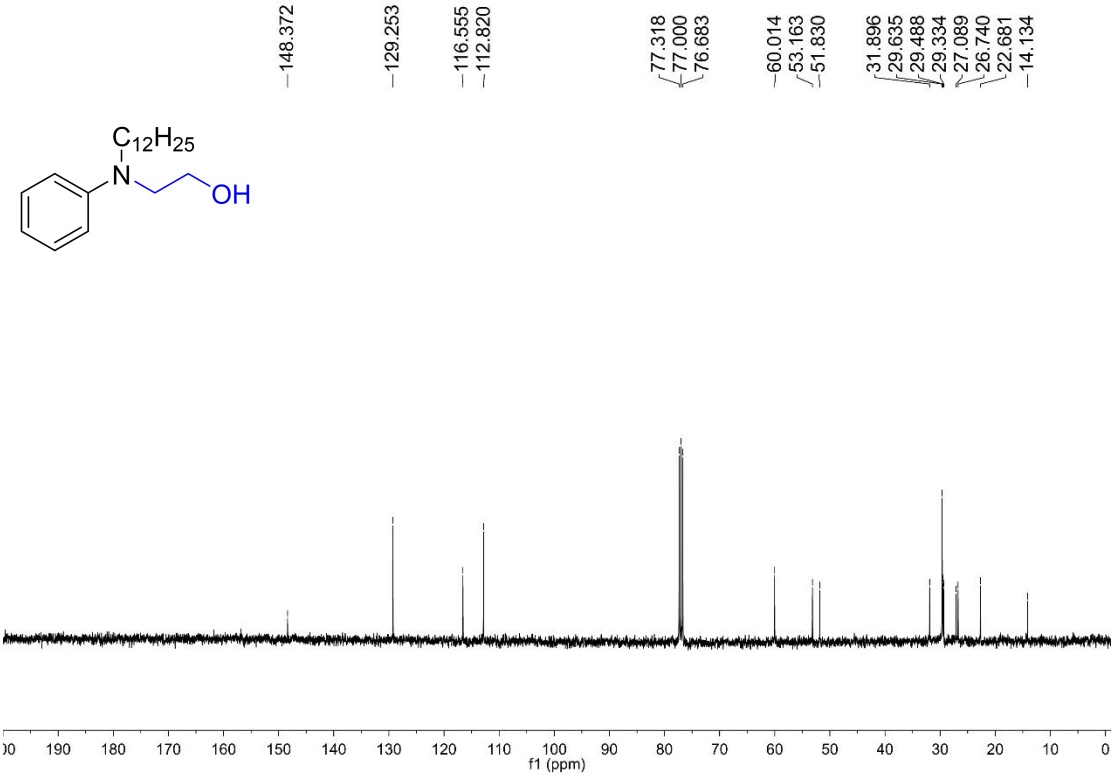
2-(butyl(phenyl)amino)ethan-1-ol (3p)



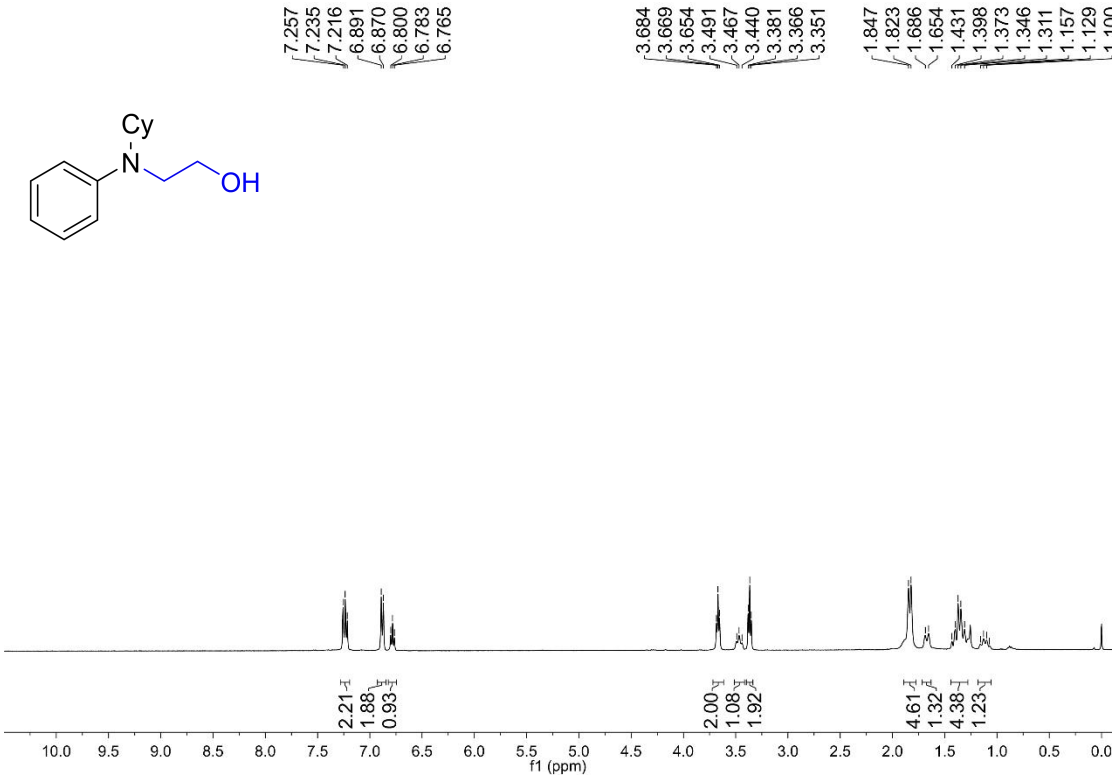


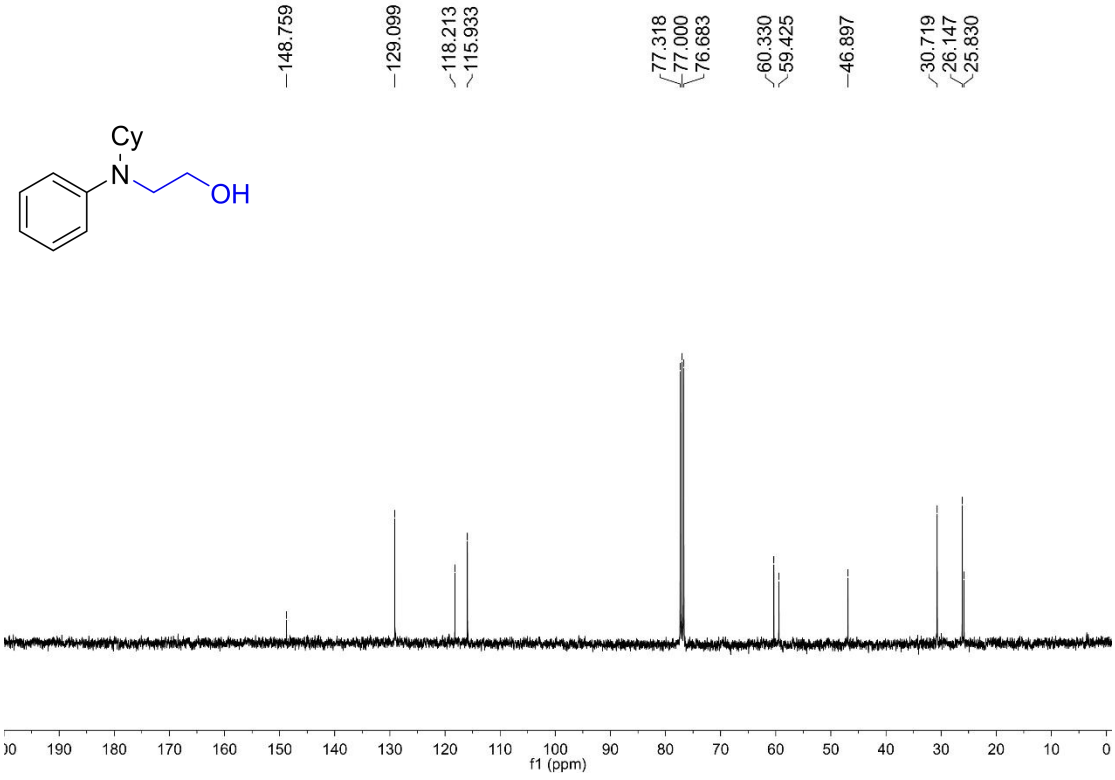
2-(dodecyl(phenyl)amino)ethan-1-ol (3q)





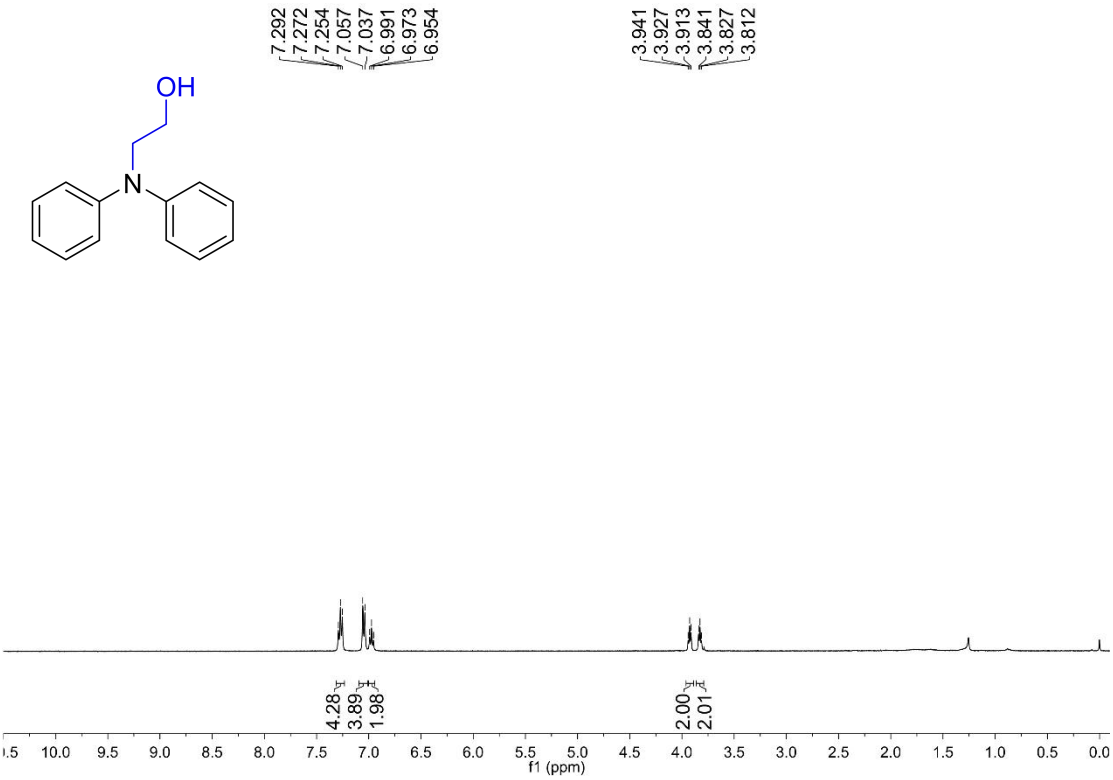
2-(cyclohexyl(phenyl)amino)ethan-1-ol (3r)

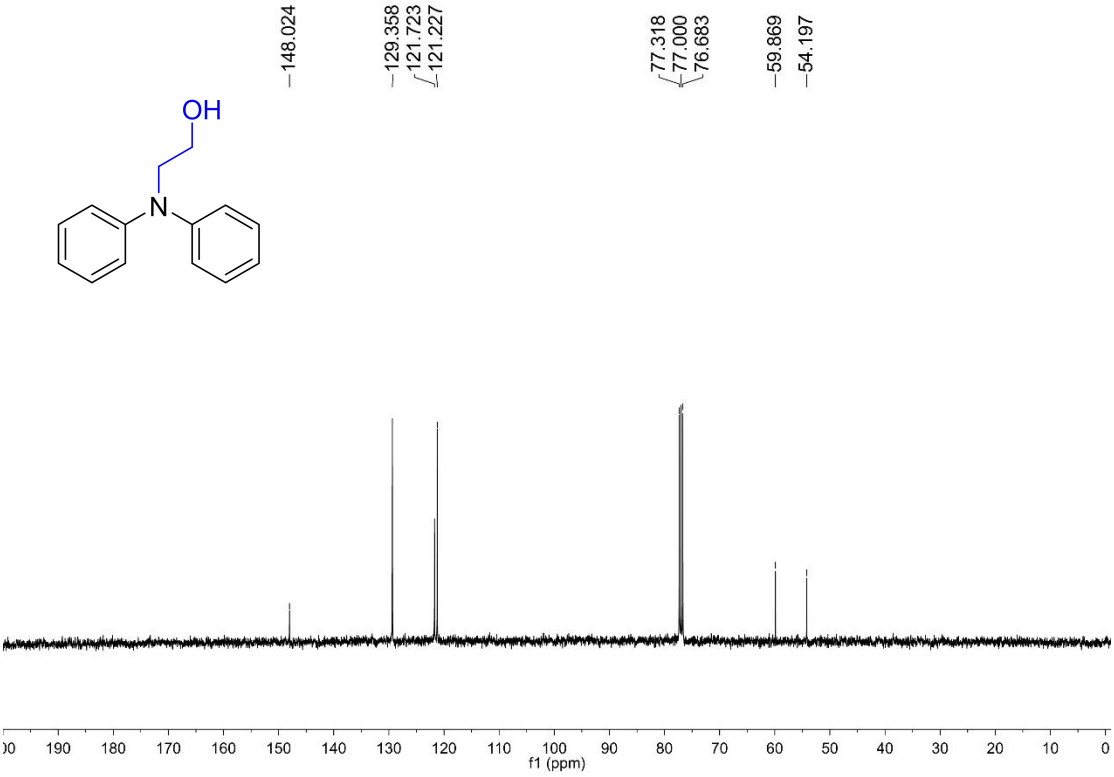




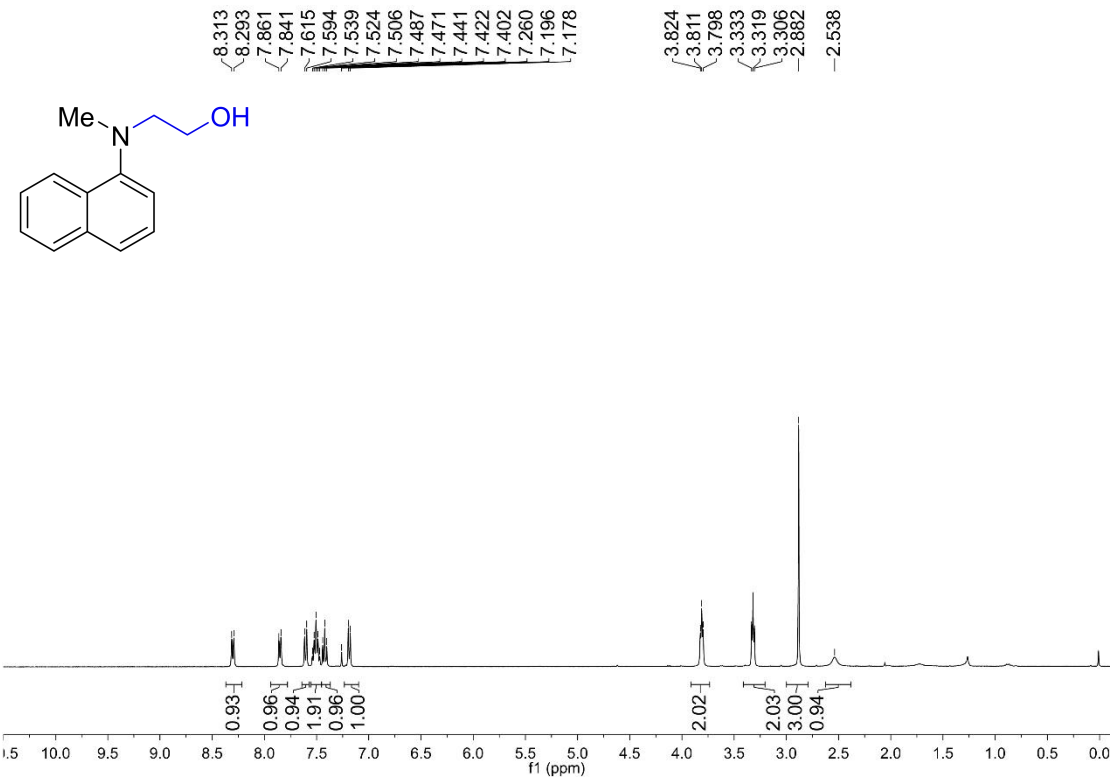
2-(benzyl(phenyl)amino)ethan-1-ol (3s)

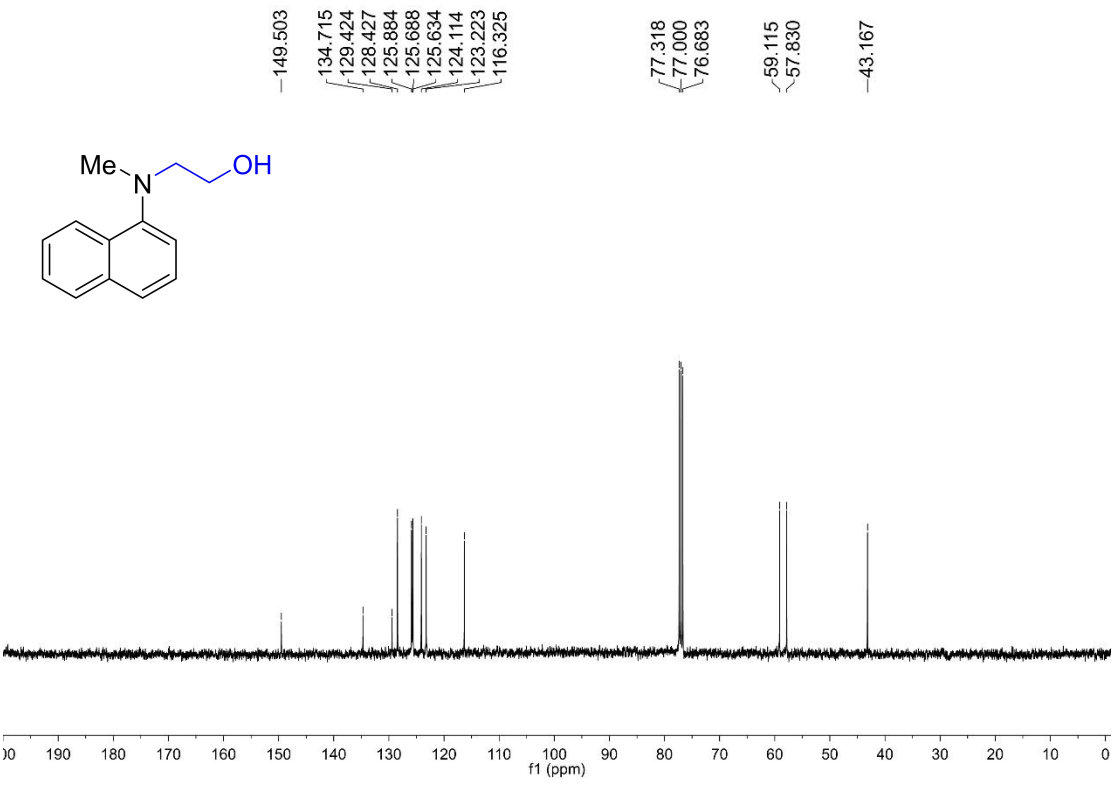
2-(diphenylamino)ethan-1-ol (3t)



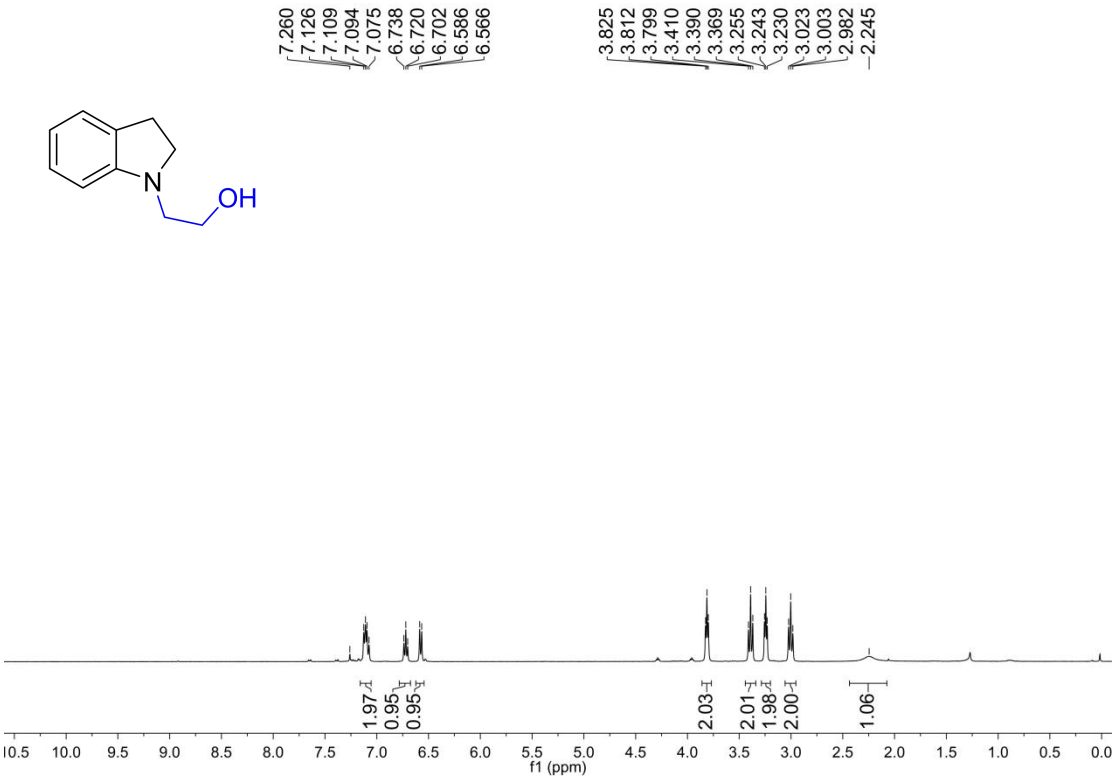


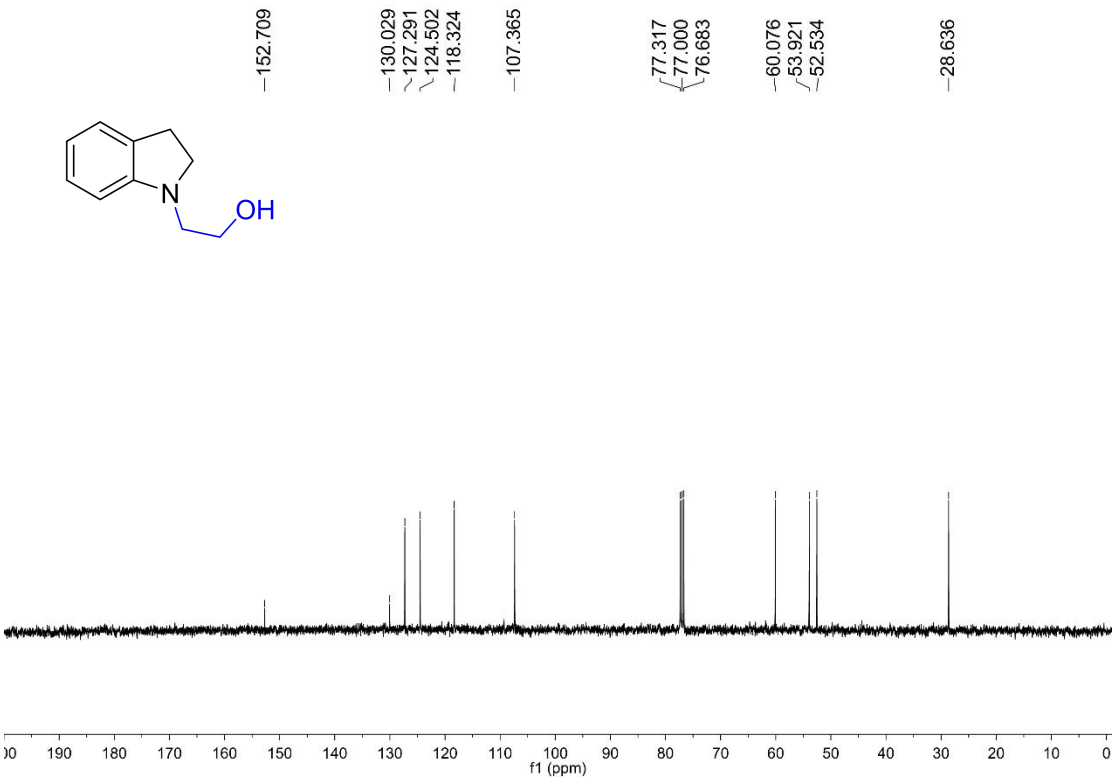
2-(methyl(naphthalen-1-yl)amino)ethan-1-ol (3u)



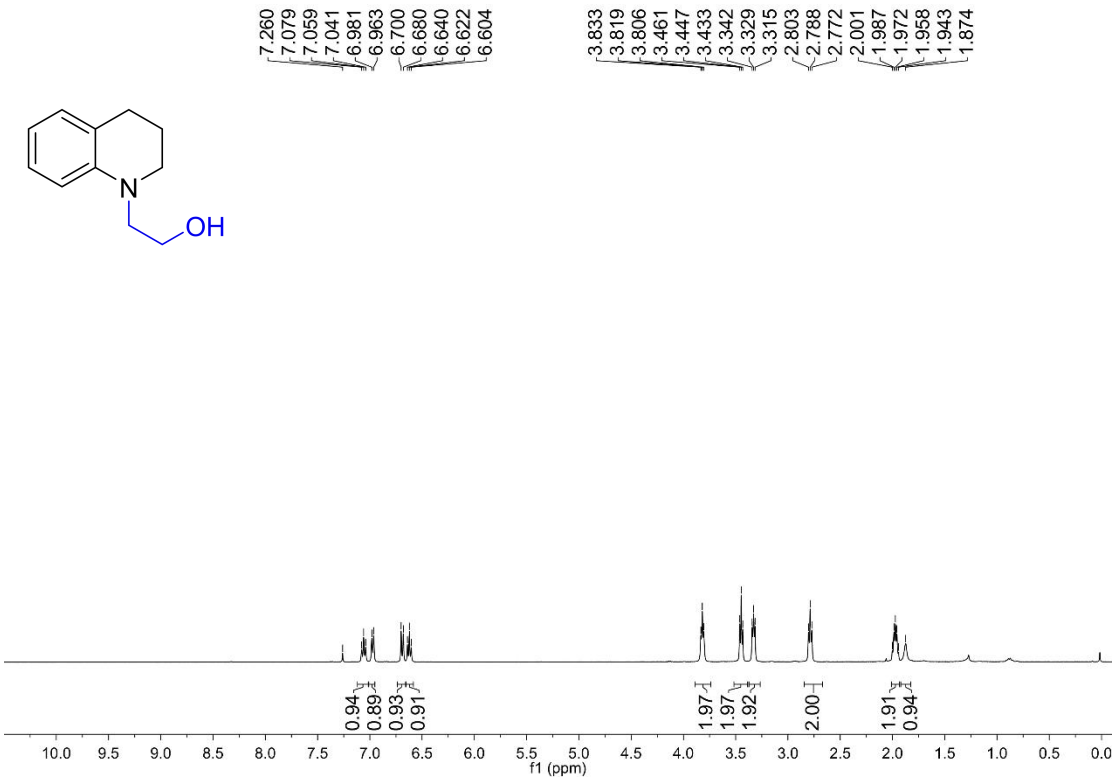


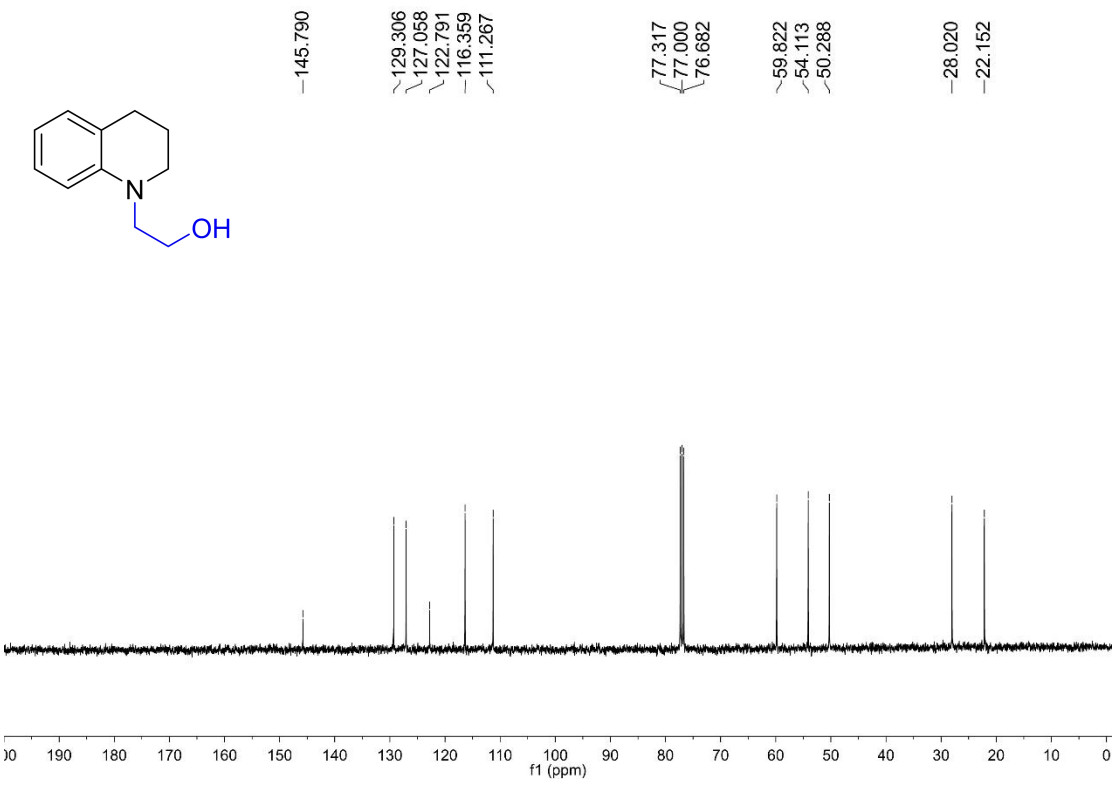
2-(indolin-1-yl)ethan-1-ol (3v)



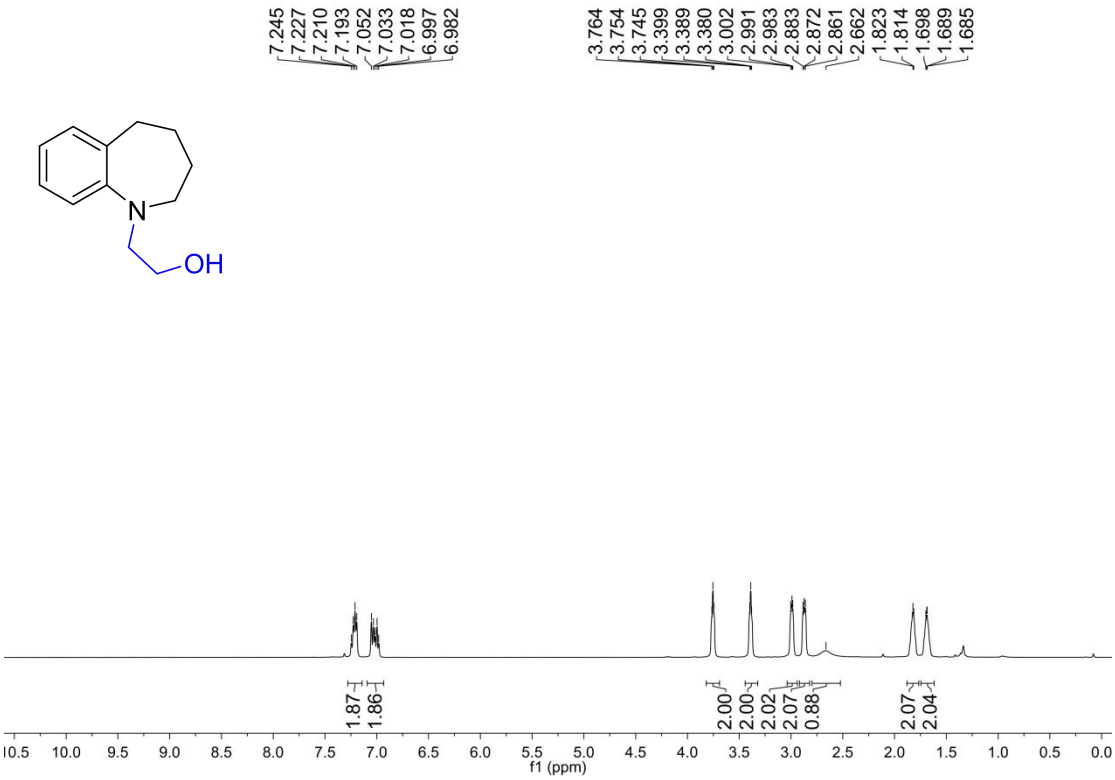


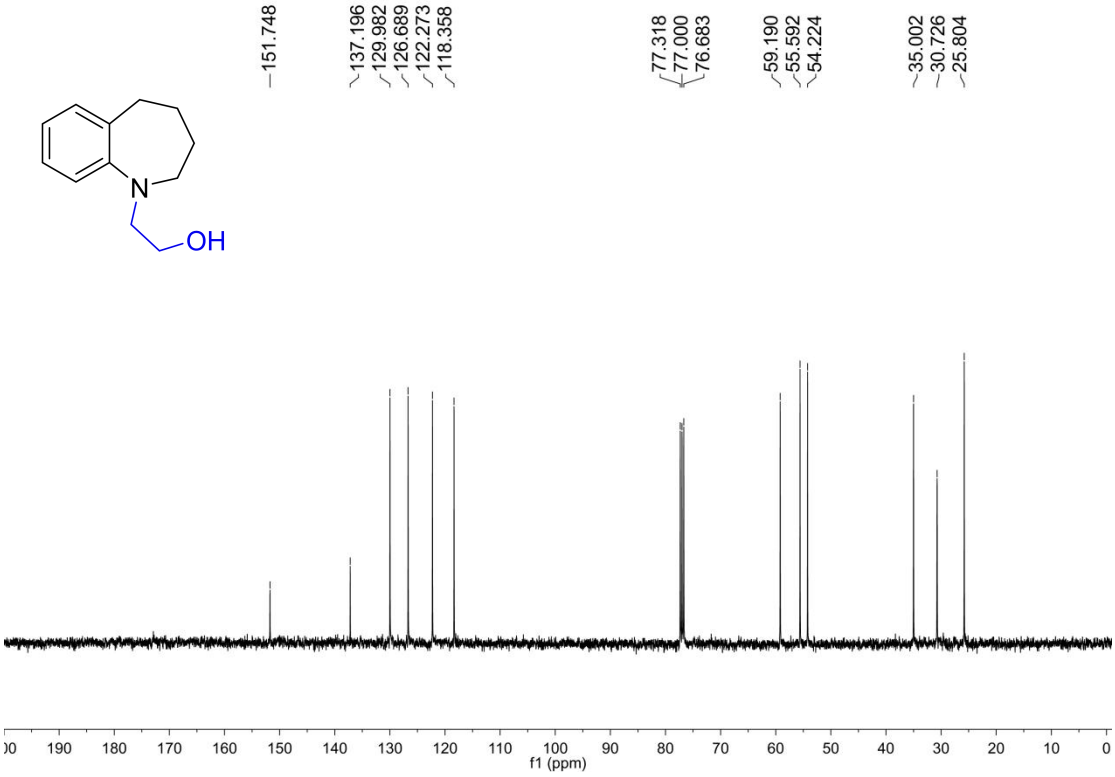
2-(3,4-dihydroquinolin-1(2H)-yl)ethan-1-ol (3w)



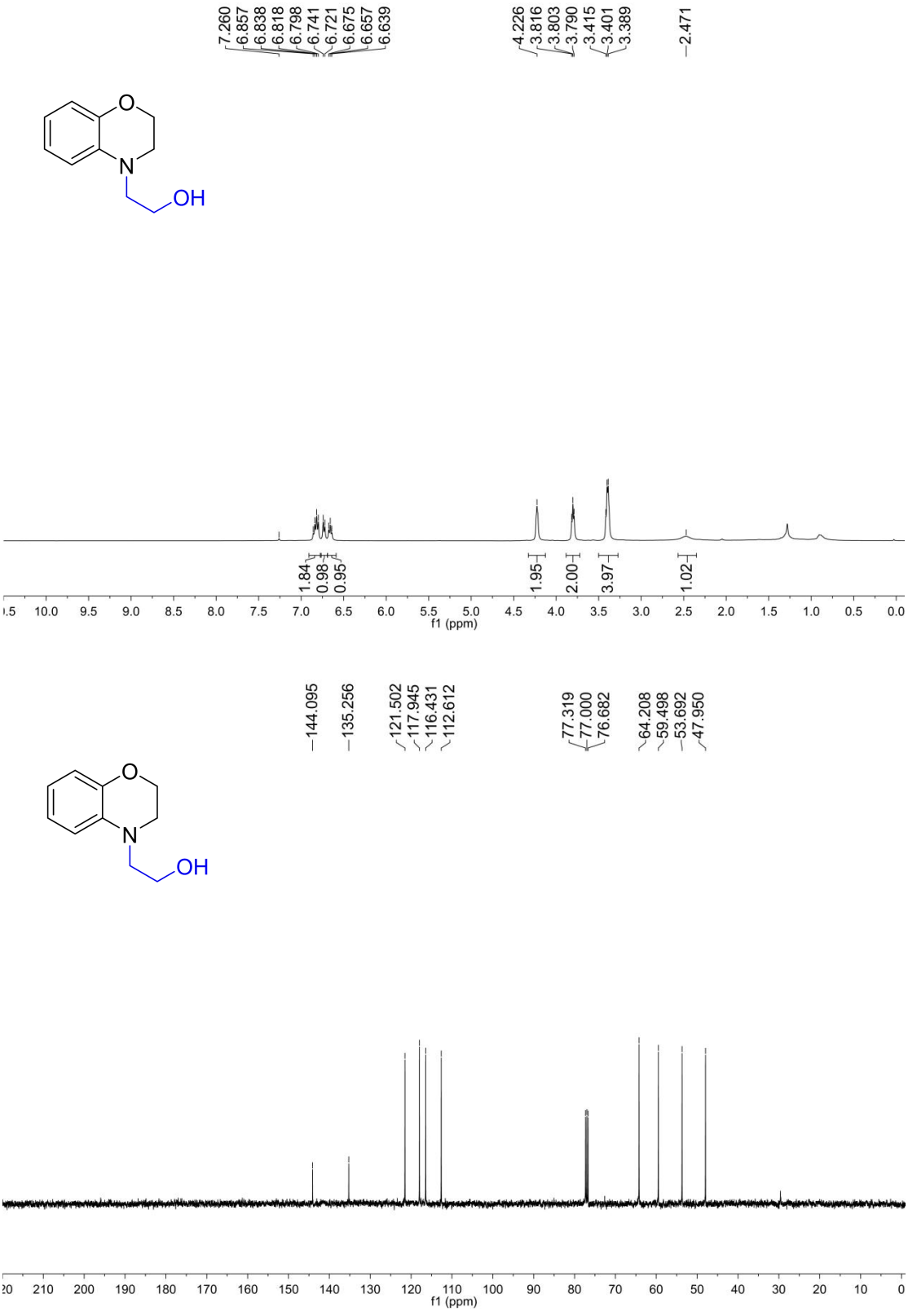


2-(2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)ethan-1-ol (3x)

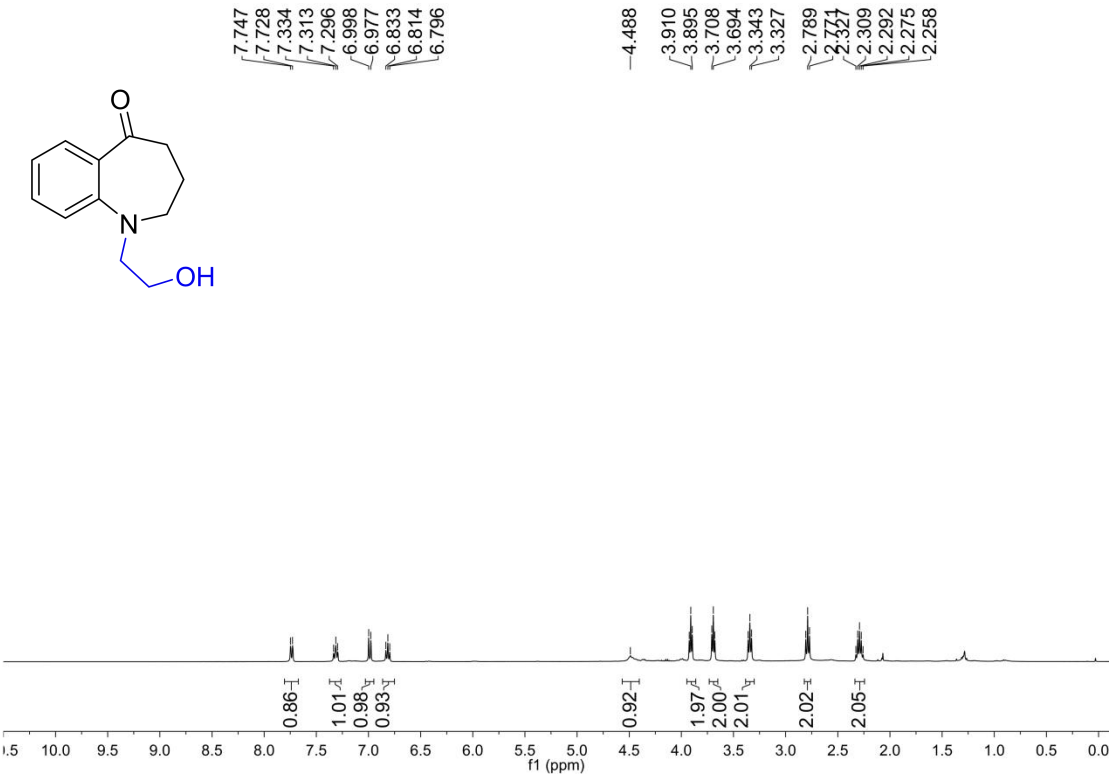


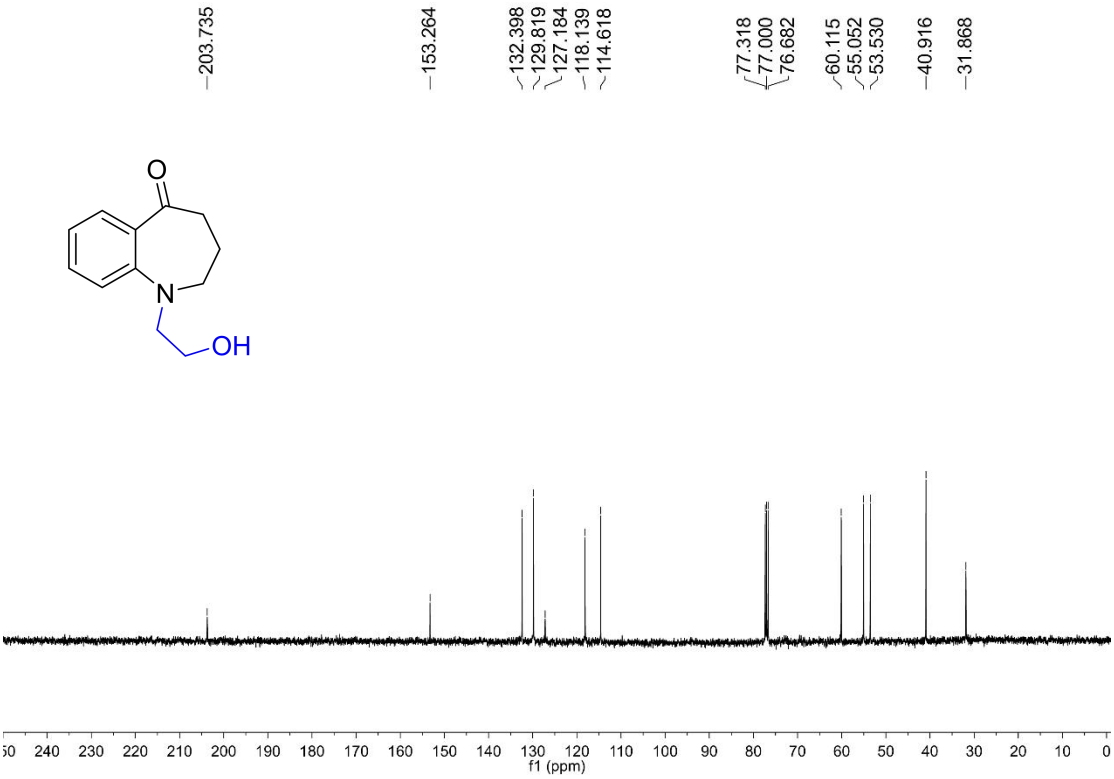


2-(3,4-dihydroquinolin-1(2H)-yl)ethan-1-ol (3y)

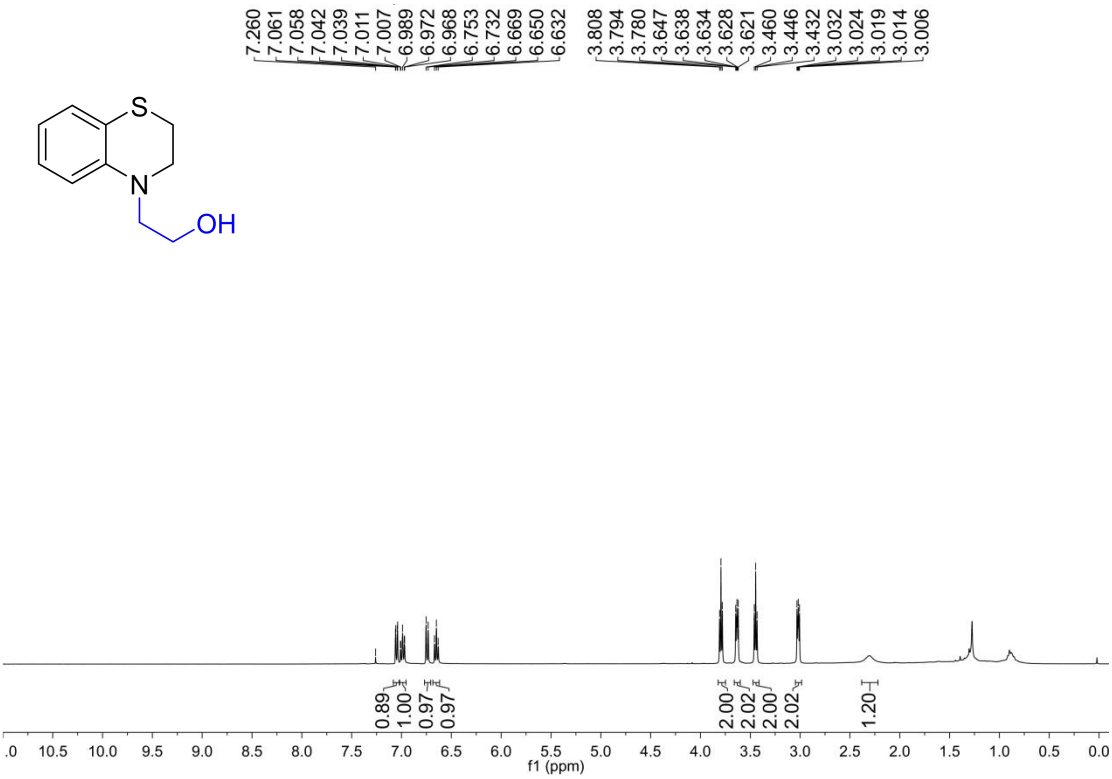


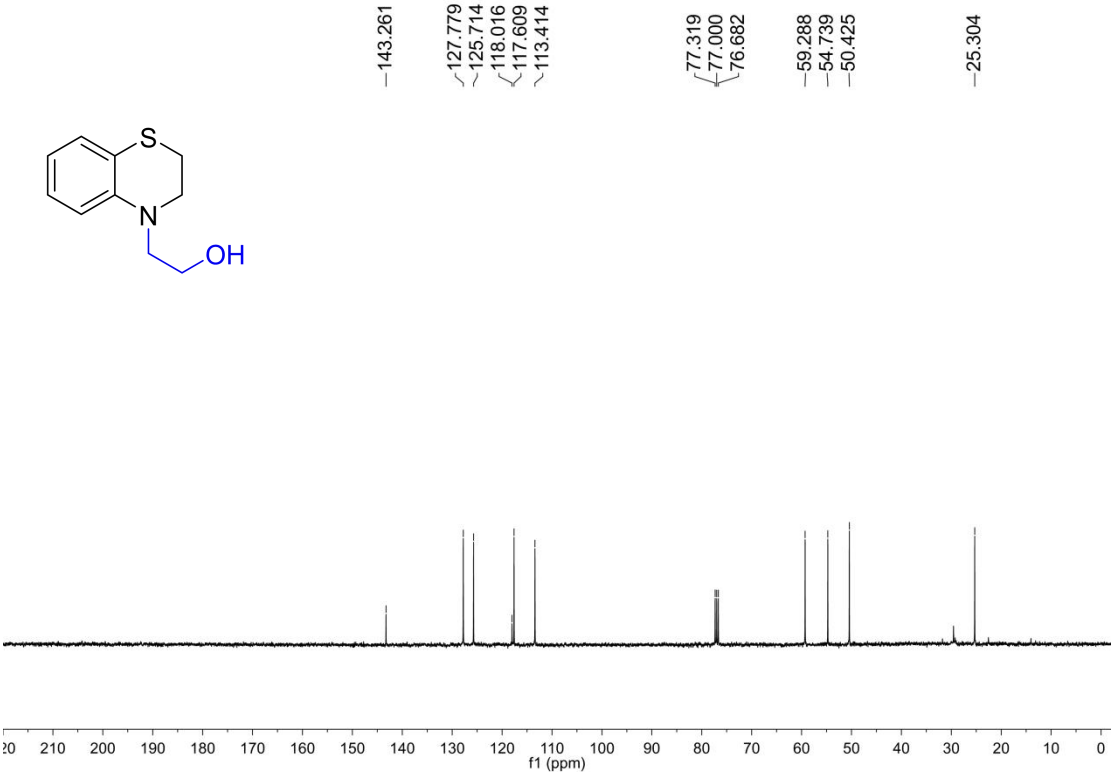
1-(2-hydroxyethyl)-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (3z)





2-(2,3-dihydro-4H-benzo[b][1,4]thiazin-4-yl)ethan-1-ol (3aa)





4-phenylmorpholin-2-one (3ae)