

## SUPPLEMENTARY INFORMATION

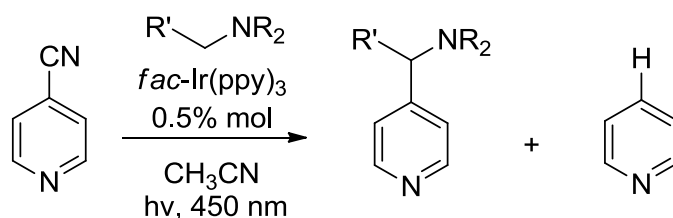
### INTERACTION OF 4-CYANOPYRIDINE WITH TERTIARY AMINES UNDER PHOTOCATALYTIC CONDITIONS

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### Experimental part.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV-300 and AV-400. Residual signals of  $\text{CDCl}_3$  were used as internal standard (7.26 ppm for  $^1\text{H}$  and 77.16 ppm for  $^{13}\text{C}$ ). HRMS were obtained on DFS Thermo Electron with EI ionization. GC-MS analysis was performed on Agilent 6890 MSD Agilent 5973. Neutral aluminium oxide was used for LC. TLC on Sorbfil  $\text{SiO}_2$  plates with UV visualization were used for monitoring of the reactions. Amines, *fac*- $\text{Ir}(\text{ppy})_3$  and 4-cyanopyridine are commercially available and were used without additional purification. Acetonitrile was distilled over  $\text{P}_2\text{O}_5$  and stored with 4Å molecular sieves.

Blue LED belt (1 m, 5 W, 450 nm) was used for irradiation. The belt was set around vial (**Pic. 1S.**) at 3 cm. Cooling was provided by air flow through the setup.



**Picture 1S.** The experimental setup for irradiation.

#### Typical experimental procedure for optimization.

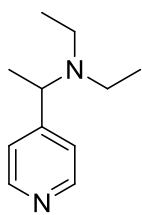
4-Cyanopyridine (20 mg, 0.19 mmol) was dissolved in 3 ml of solvent, and then triethylamine and photocatalyst were added to the solution. Mixture was irradiated until cyanopyridine consumption or for 48h if full conversion of starting material wasn't reached. Then reaction mixture was analyzed by  $^1\text{H}$ -NMR (Table 1S).

Table 1S. Reaction conditions optimization for  $\alpha$ -CH-arylation of triethylamine with 4-cyanopyridine.

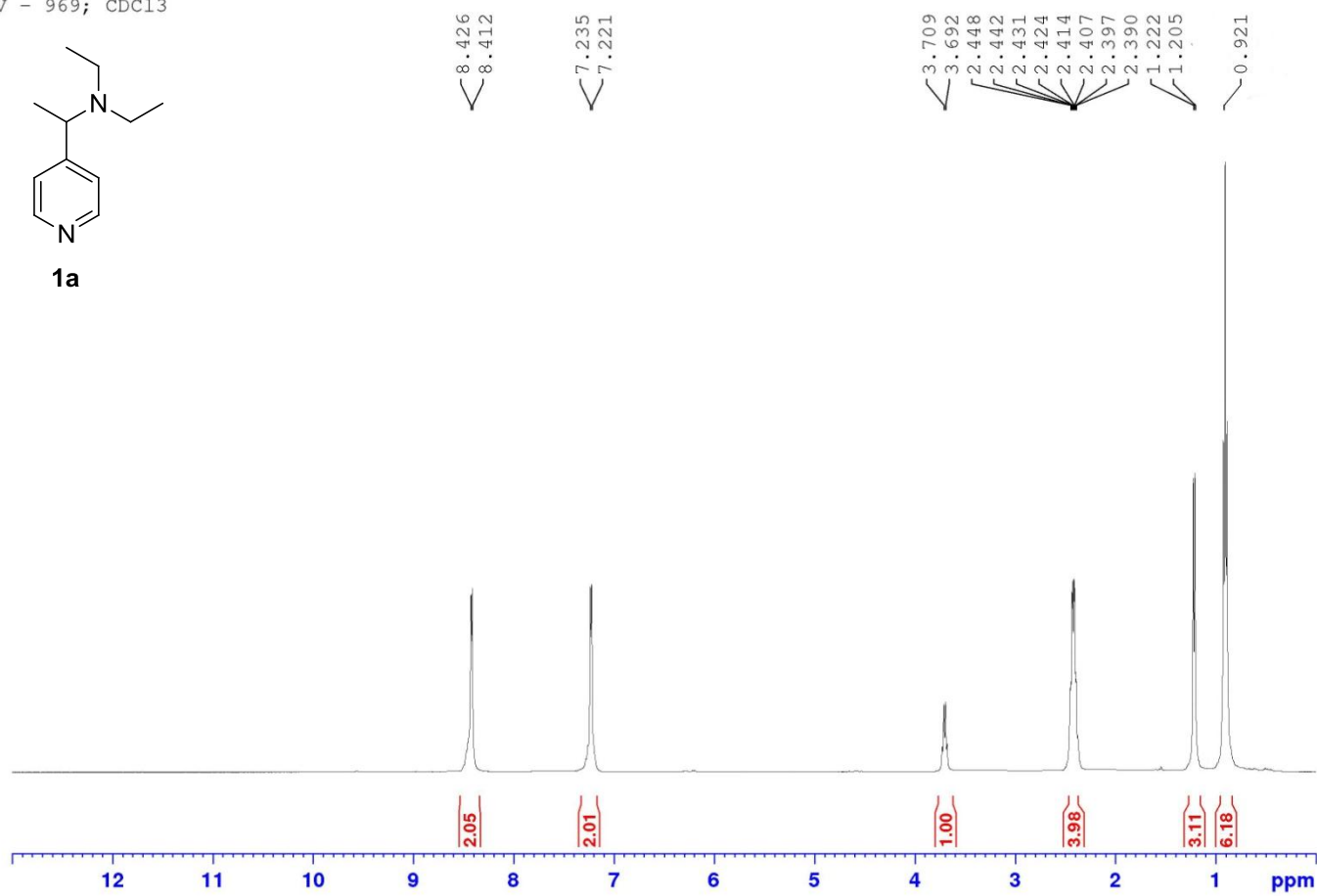
Conditions	Conversion, %	Yield of <b>1a</b> ( <b>2</b> ), %
0.5% Ir(ppy) <sub>3</sub> , 1 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN	71	18 (47)
<b>0.5% Ir(ppy)<sub>3</sub>, 2 eq NEt<sub>3</sub>, 1 ml CD<sub>3</sub>CN</b>	<b>100</b>	<b>28 (65)</b>
0.5% Ir(ppy) <sub>3</sub> , 3 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN	100	24 (70)
0.3% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN	90	21 (59)
0.75% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN	100	28 (63)
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN (no light)	0	-
2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN (blue light)	0	-
1% Ru(bpy) <sub>3</sub> [BF <sub>4</sub> ] <sub>2</sub> , 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN	~5	Not determined
1% Rose Bengal, 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN (green light ~520nm)	0	-
1% Eosin Y, 2 eq NEt <sub>3</sub> , 1 ml CD <sub>3</sub> CN (green light ~520nm)	15	Not determined
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 3 ml acetone	28	Not determined
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 3 ml THF	23	Not determined
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 3 ml benzene	~5	Not determined
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 3 ml DMF	13	Not determined
0.5% Ir(ppy) <sub>3</sub> , 2 eq NEt <sub>3</sub> , 3 ml DMSO-d <sub>6</sub>	53	traces (48)

# NMR spectra for compounds 1a-1d.

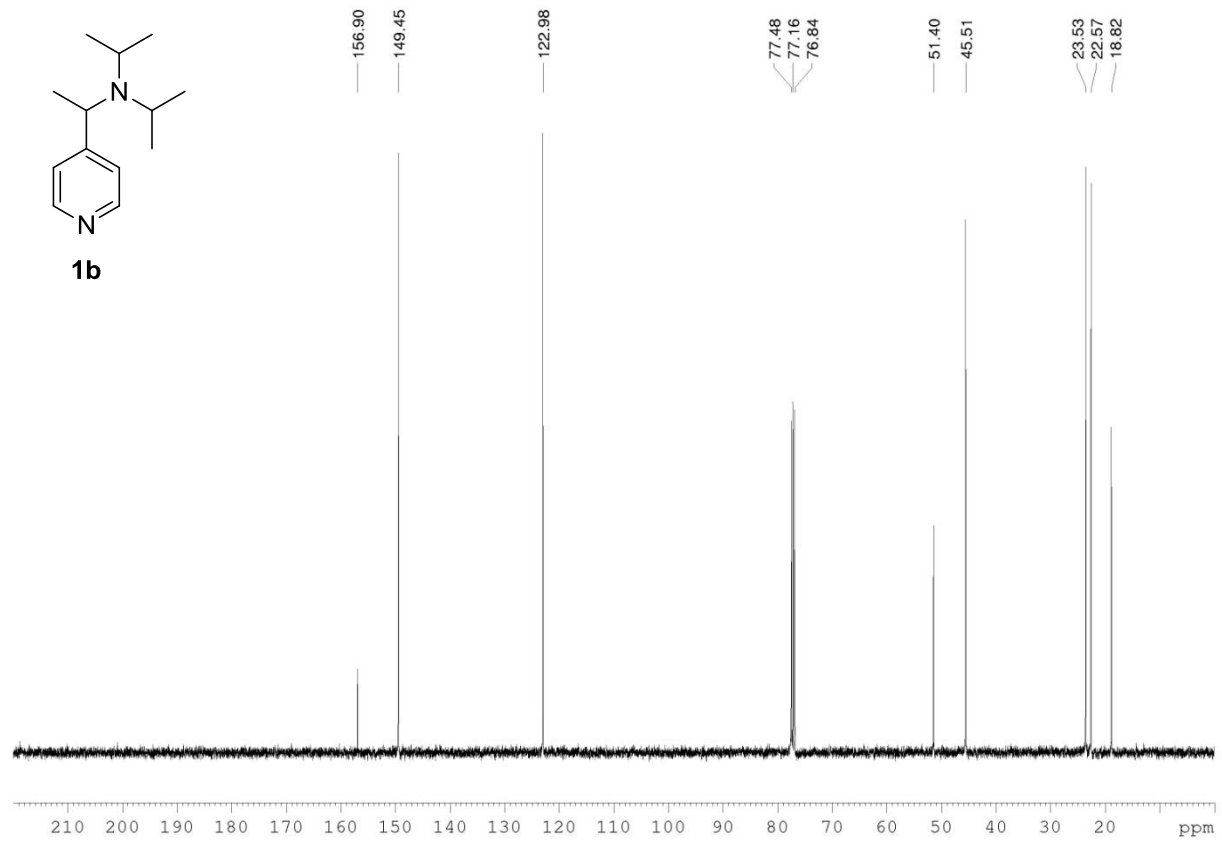
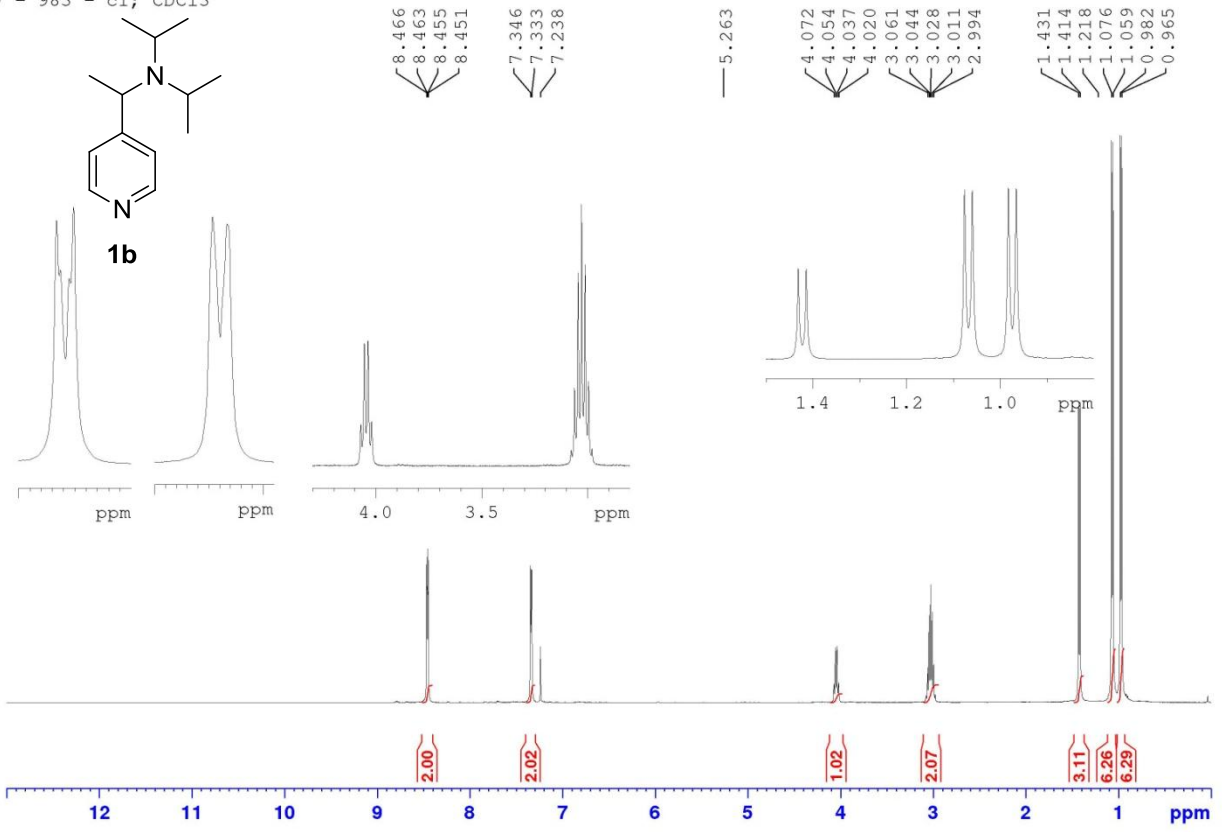
V - 969; CDCl<sub>3</sub>



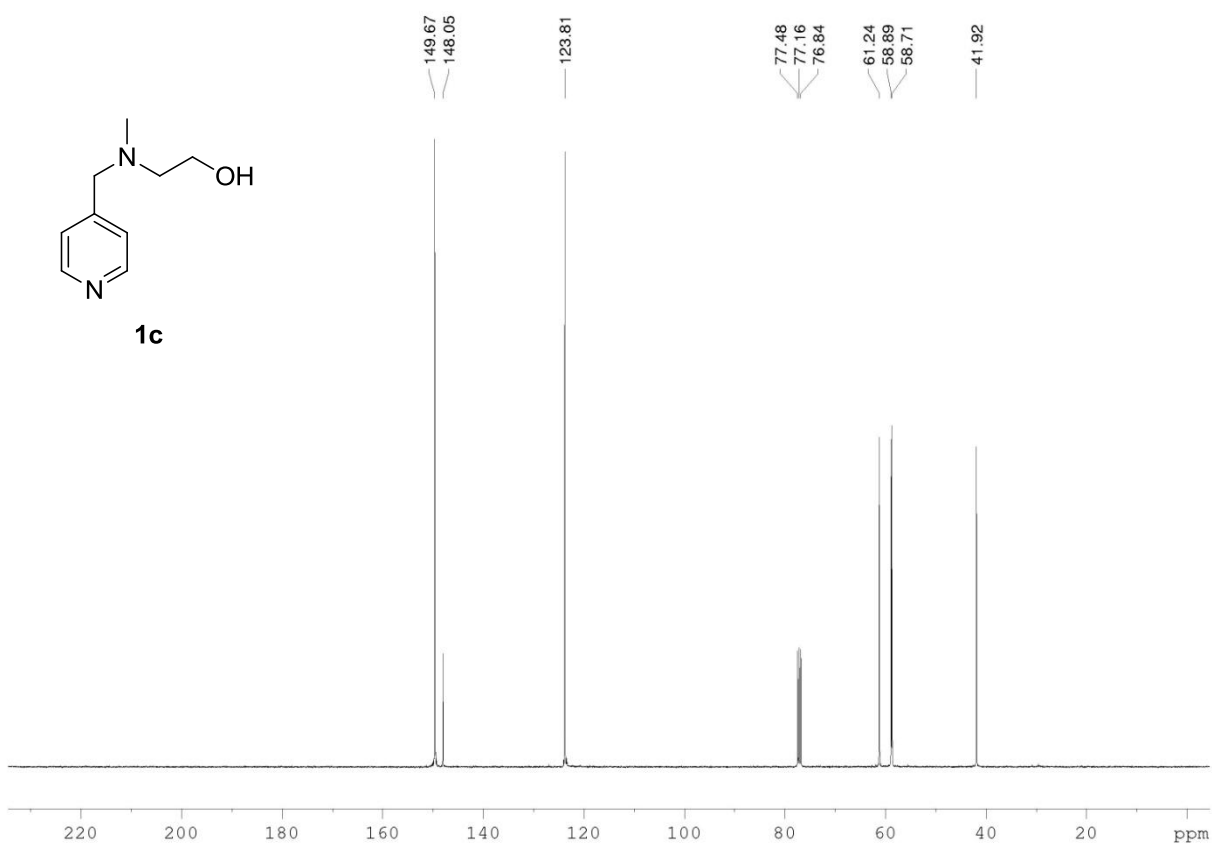
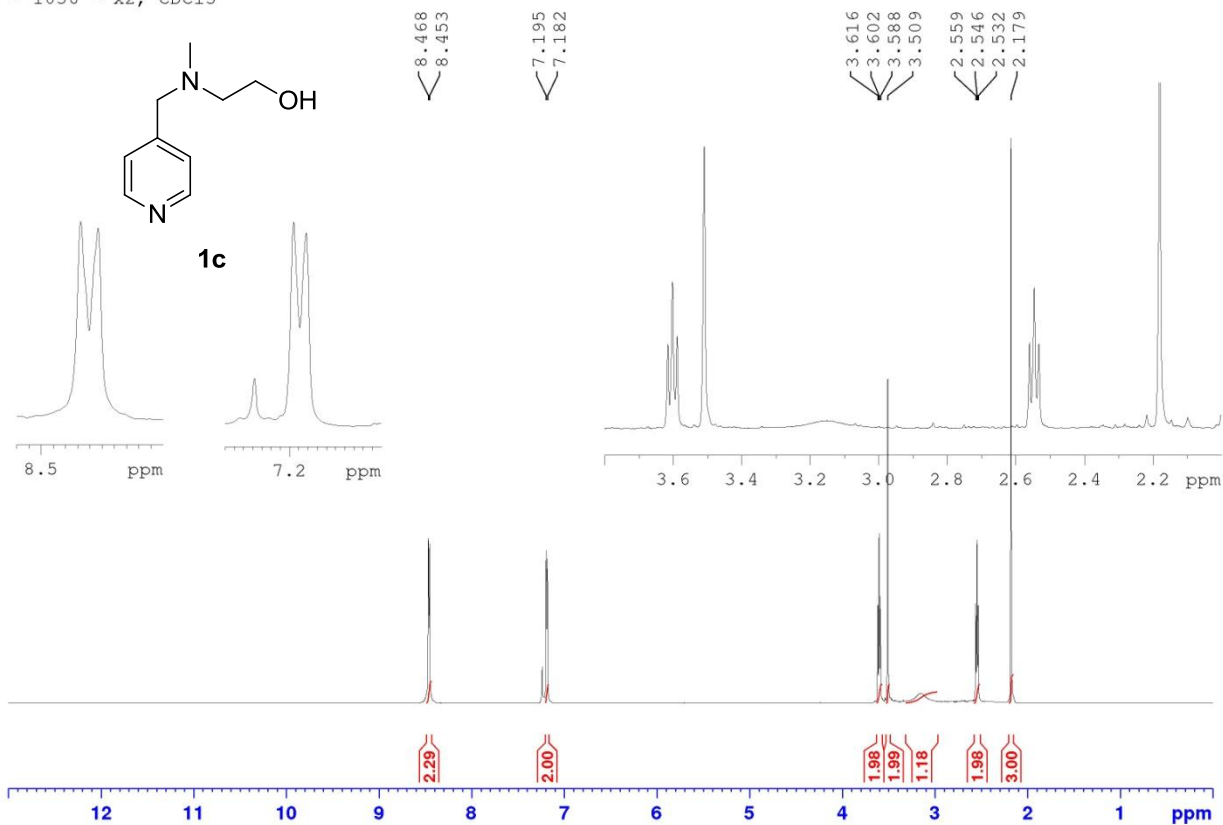
**1a**



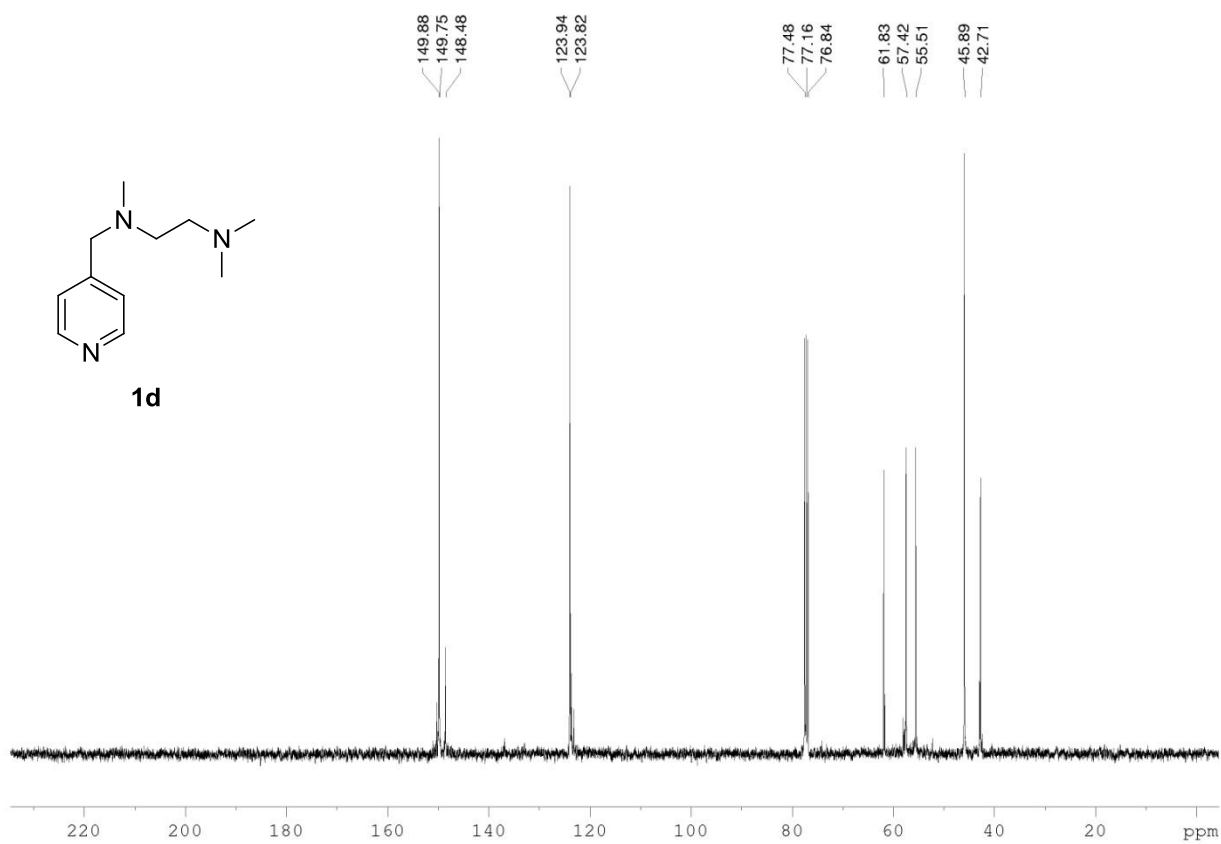
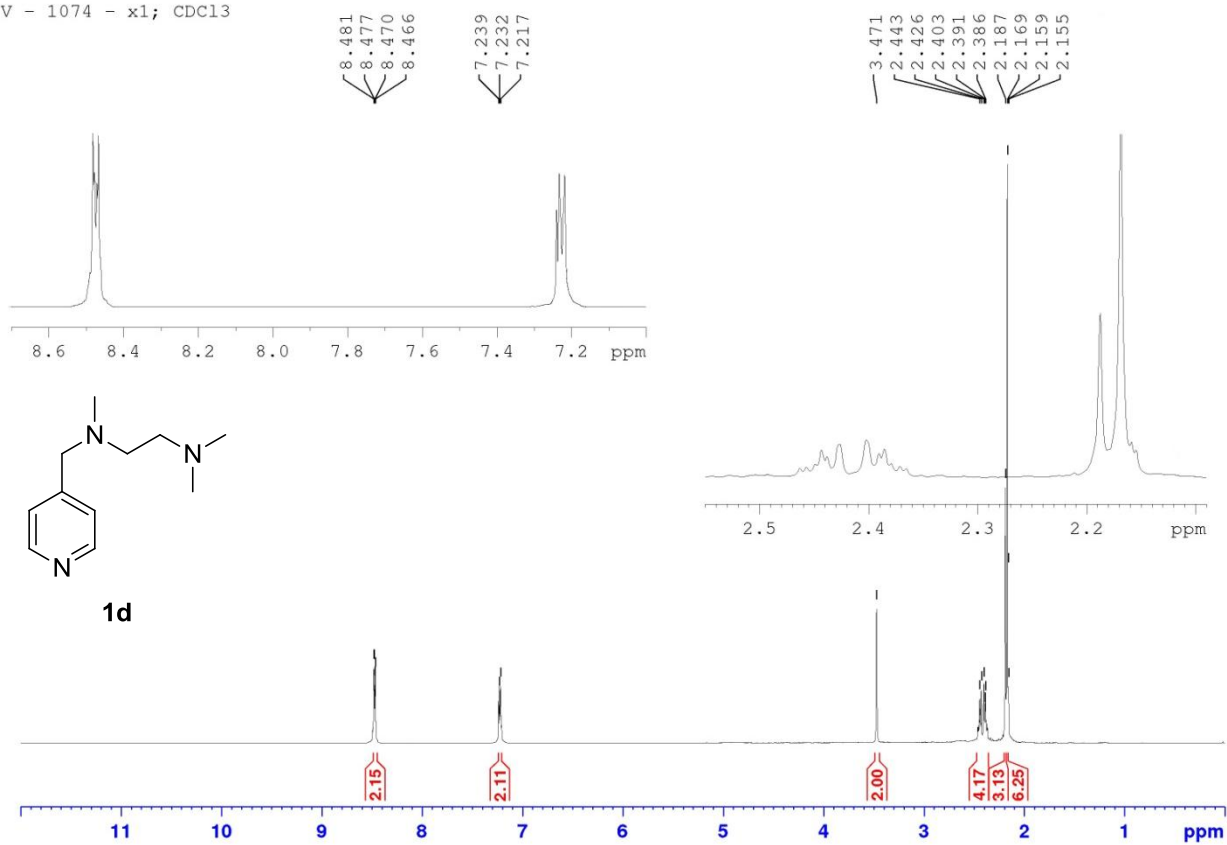
V - 983 - c1; CDCl<sub>3</sub>

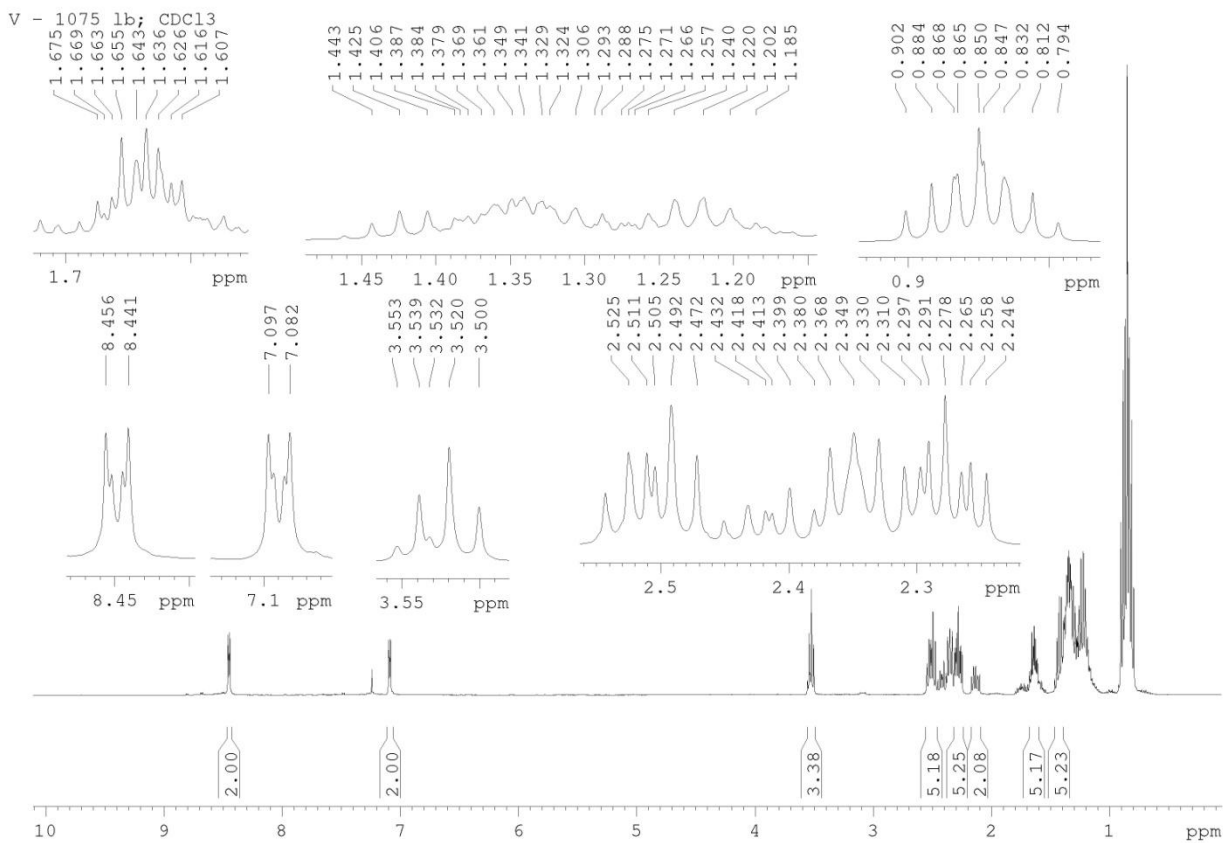
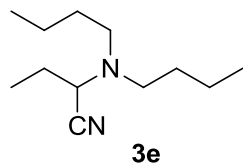
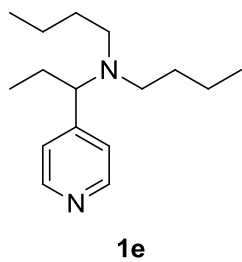


V - 1036 - x2; CDCl<sub>3</sub>



V - 1074 - x1; CDC13



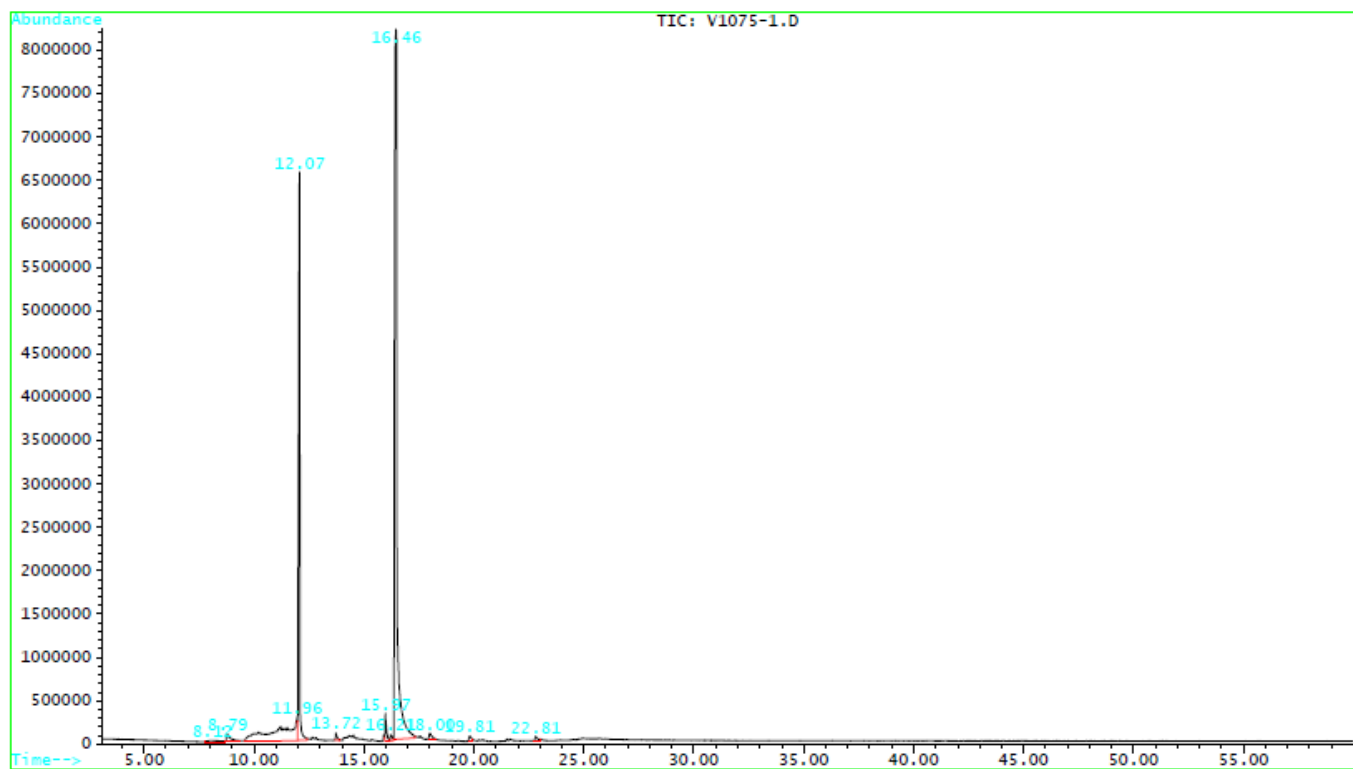




# GC-MS analysis of mixture 1d and 3d.

## Graphics Report

File : C:\HPCHEM\1\DATA\V1075-1.D  
Operator : Salnikova O.I.  
Acquired : 23 Oct 17 2:24 pm using AcqMethod AN10\_280  
Sample Name: V1075-1 Vorobev 1mk1  
Misc Info : HP-5MS inj280 2m50 10deg/min35min280  
Vial Number: 1



C:\HPCHEM\1\DATA\V1075-1.D

Mon Oct 23 16:27:28 2017

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