Nickel-catalyzed Reductive Etherification of Aldehydes at Room Temperature: C-O vs. C-C Bond Formation

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Outline

1. Preparation of Ni catalysts used in this study

Ni catalyst systems were prepared accordingly:

(a) $NiCl_2$(dppf) was prepared according to the procedure reported by Rudie et al.[1]

(b) $NiCl_2$(dppp) was synthesized according to the procedure disclosed by Van Hecke and coworkers.[2]

(c) $NiCl_2$.glyme was prepared using the procedure reported by Boudier et al.[3]

(d) For synthesize of $NiCl_2$.dmg, 5.0 mmol of $NiCl_2$.6H2O was refluxed in acetonitrile for 12h. The reaction temperature was cooled down to 40 °C. Then, 5.0 mmol of dissolved dimethylglyoxime in 5 mL acetonitrile was added drop wise and the reaction mixture was stirred for 6h at 40 °C in order to obtain catalyst as a green solid after washing and drying in oven overnight.

References

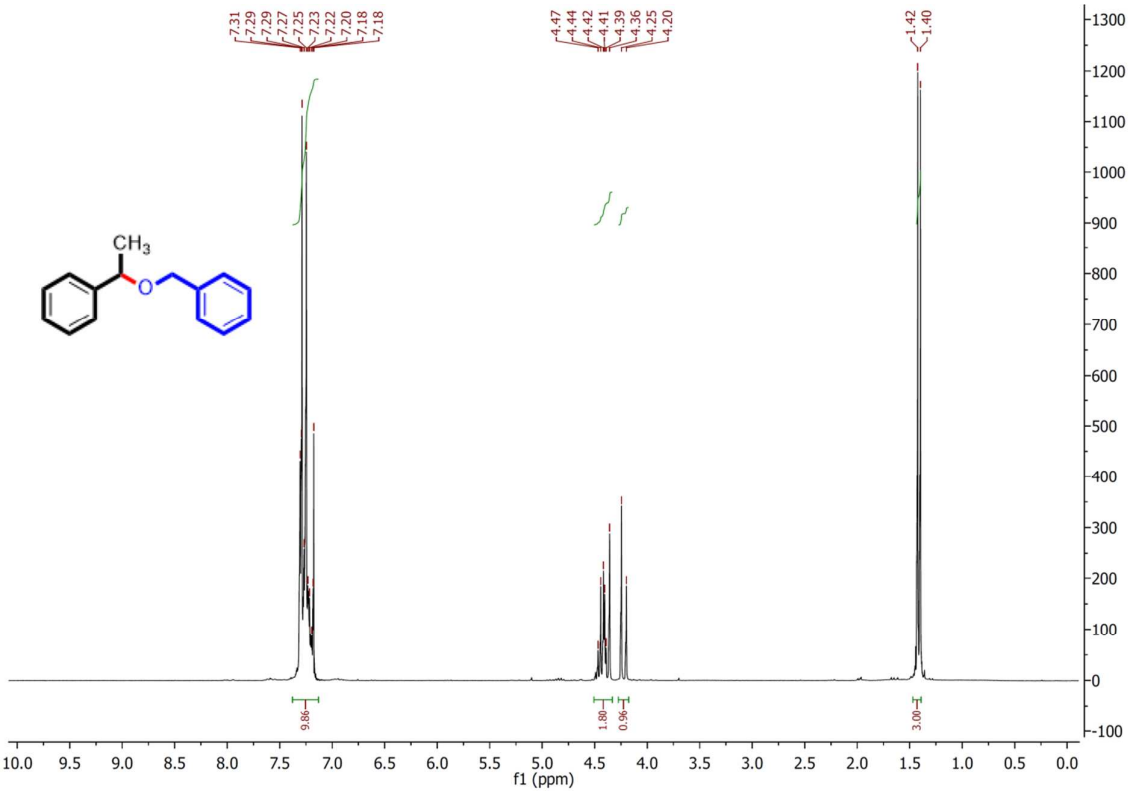
(1) Rudie, A.W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859.

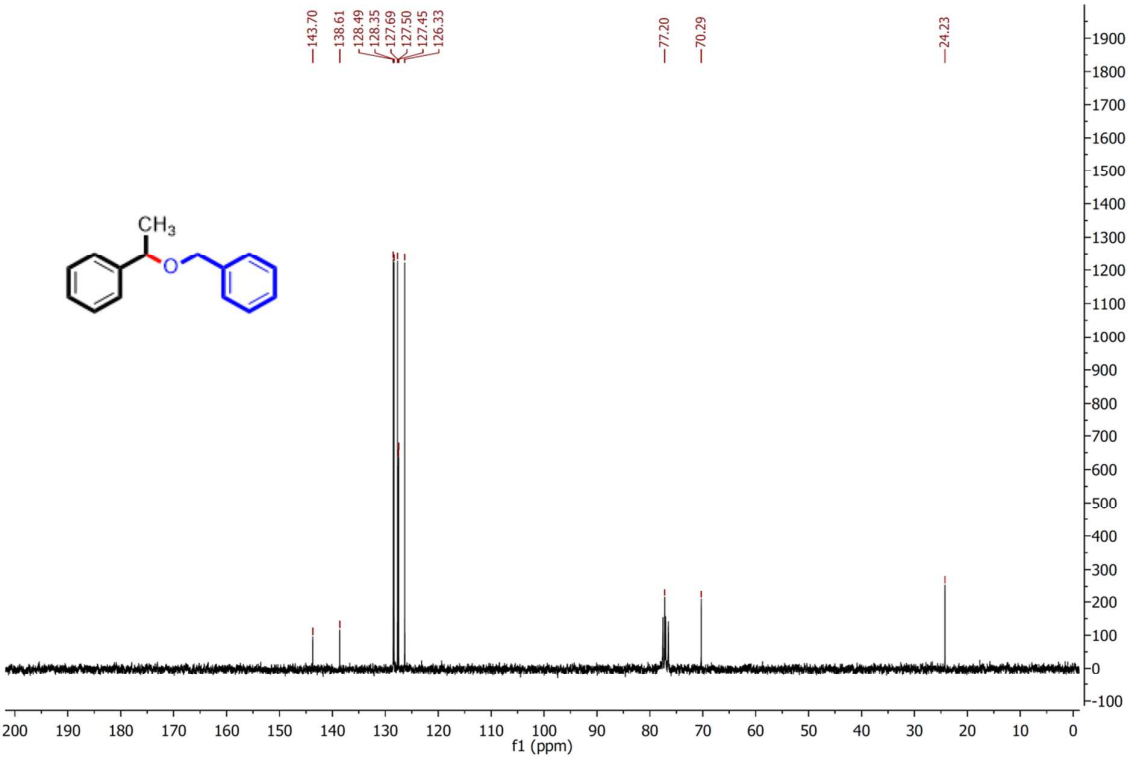
(2) Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1968.

(3) Boudier, A.; Breuil, P. R.; Magna, L.; Bourbigou, H.; Braunstein, P. *J. Organomet. Chem.* **2012**, *718*, 31.

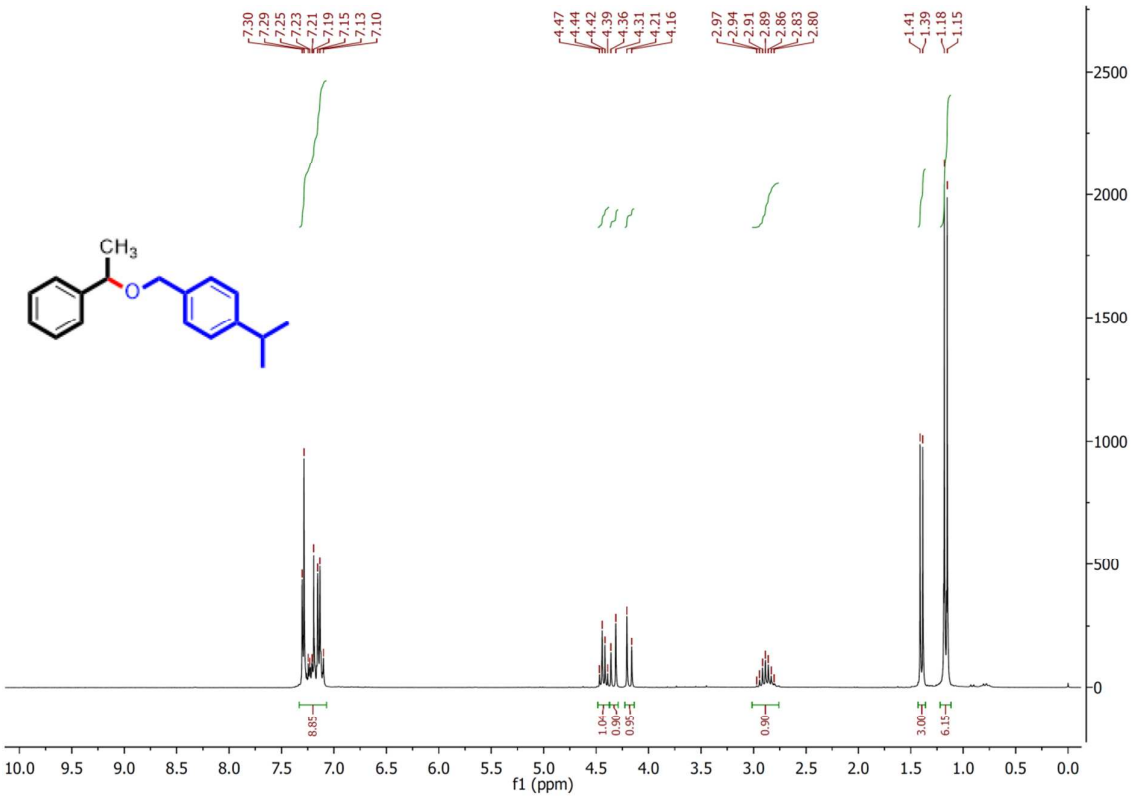
Copy of ^{1}H NMR and ^{13}C NMR of synthesized compounds

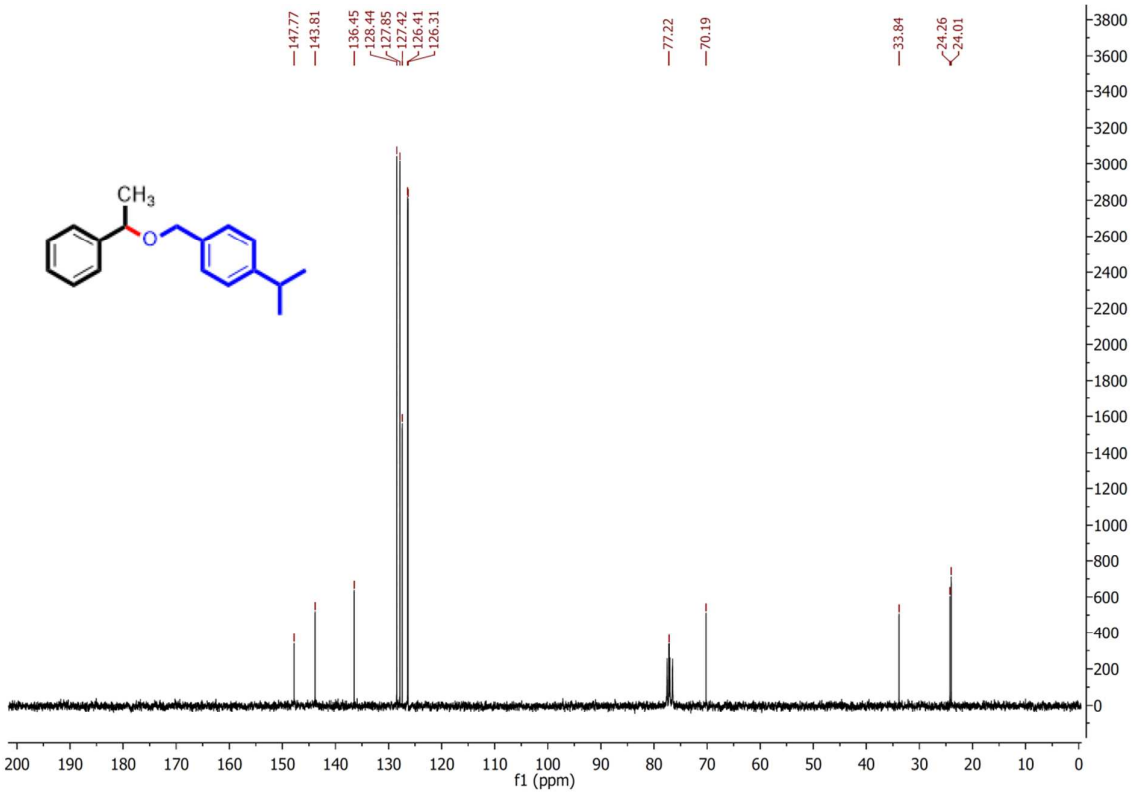
(1-(benzyloxy)ethyl)benzene (3a).





1-isopropyl-4-((1-phenylethoxy)methyl)benzene (3b).





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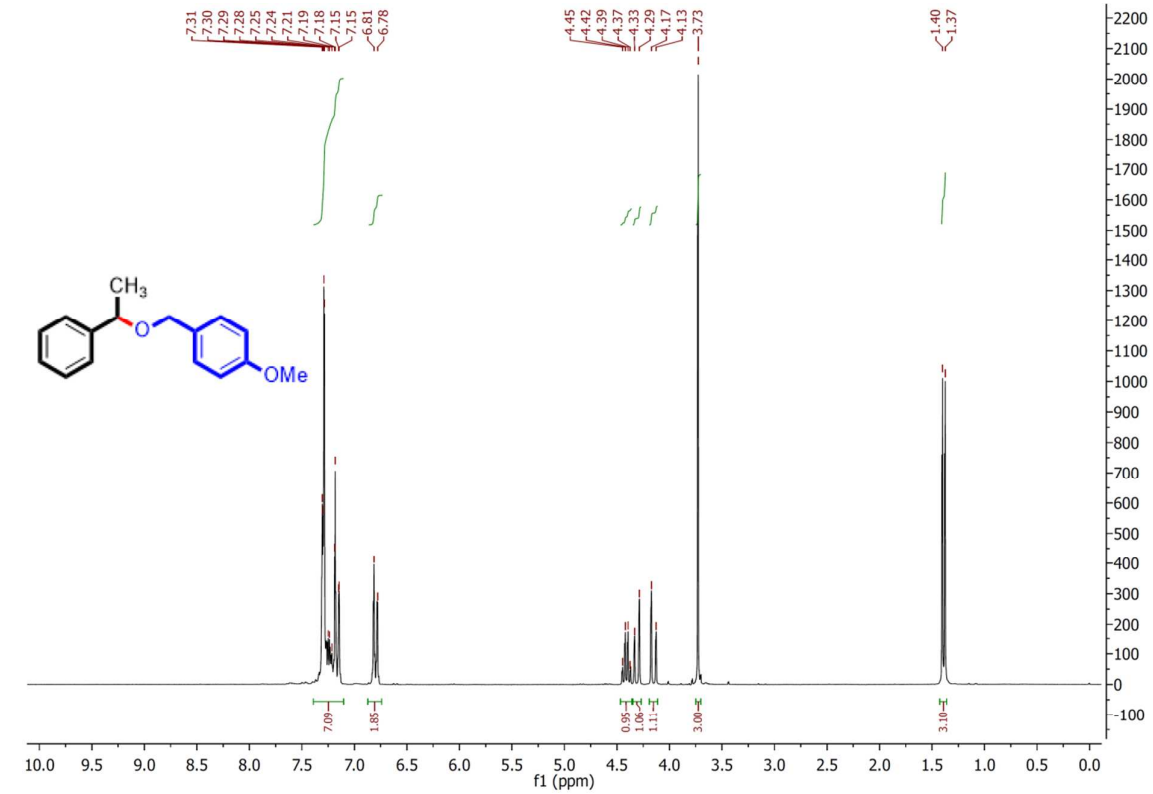

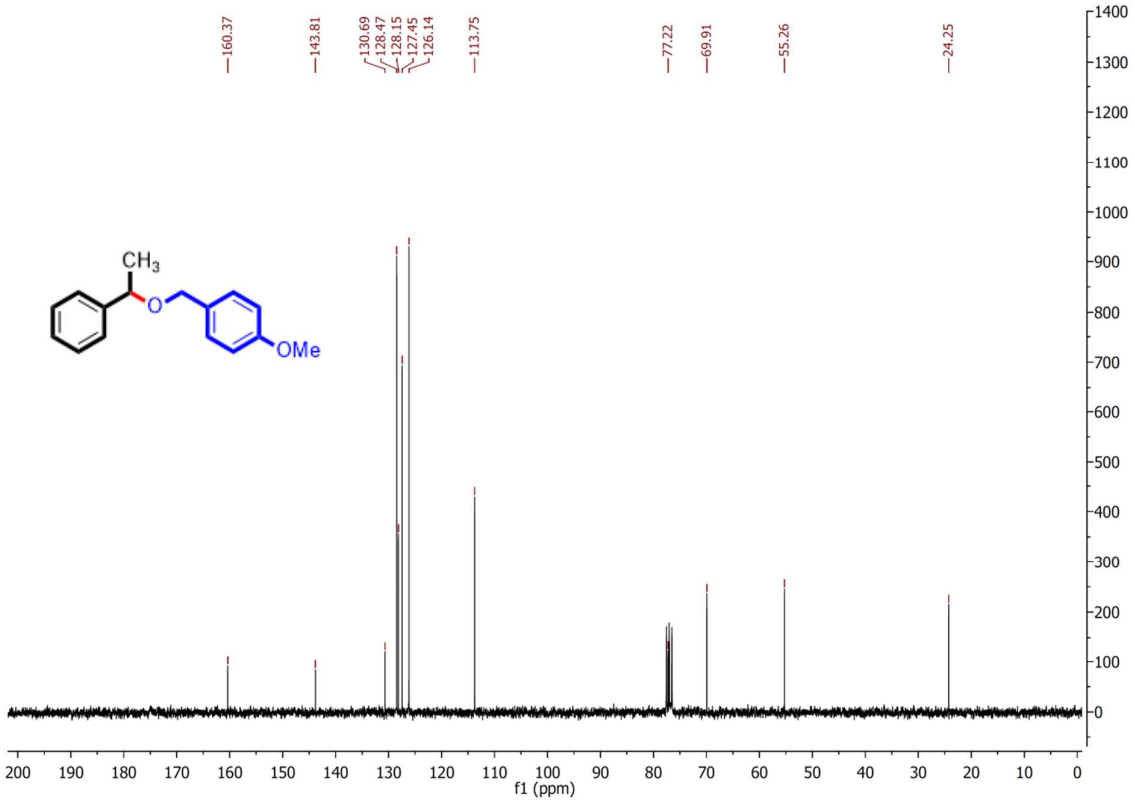

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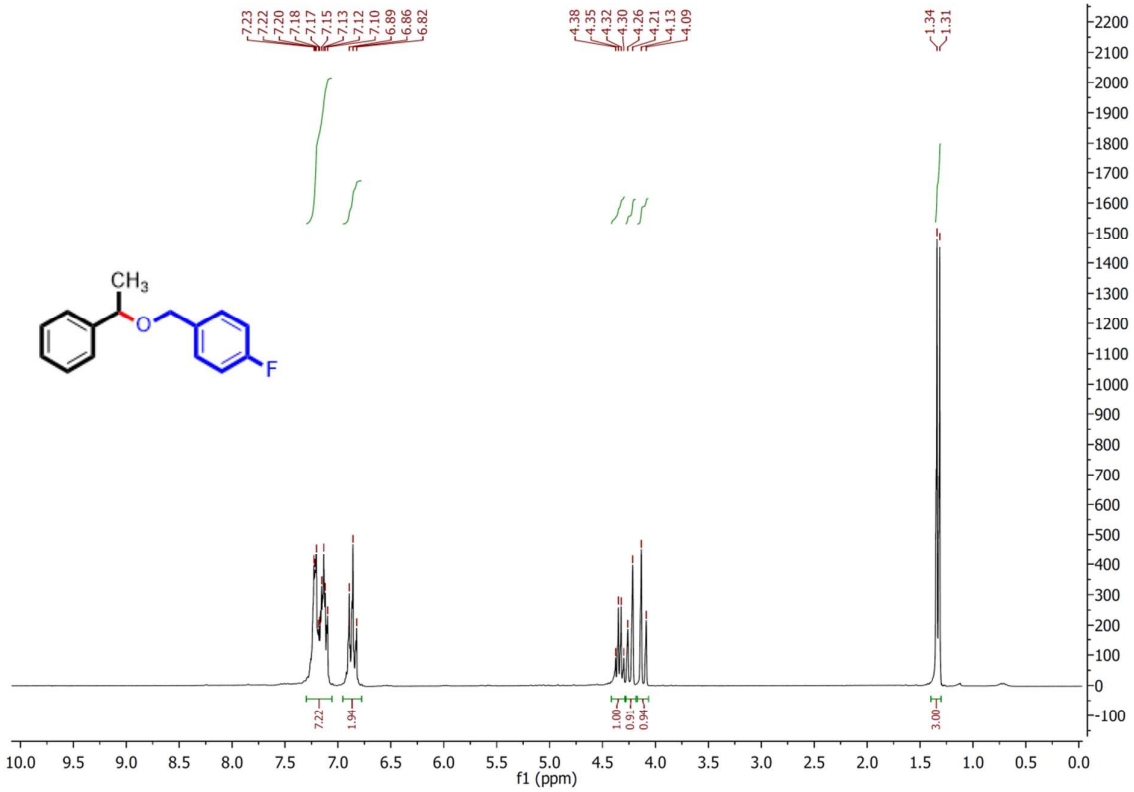

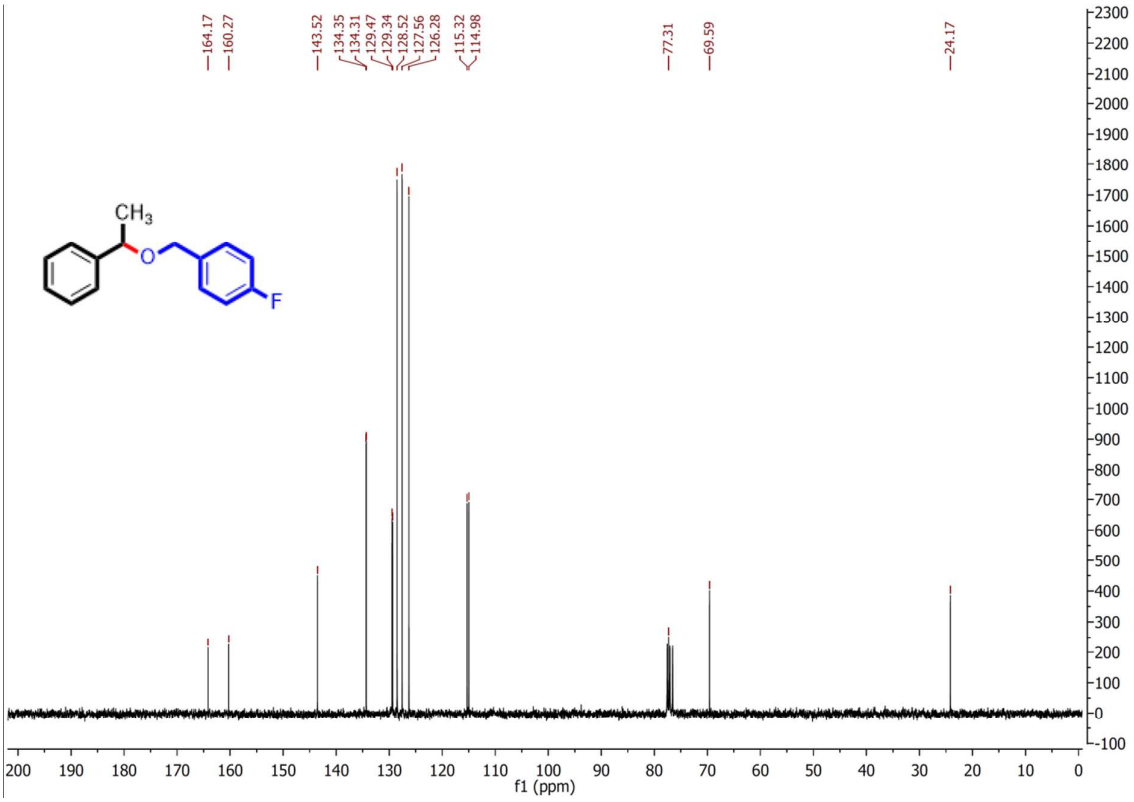

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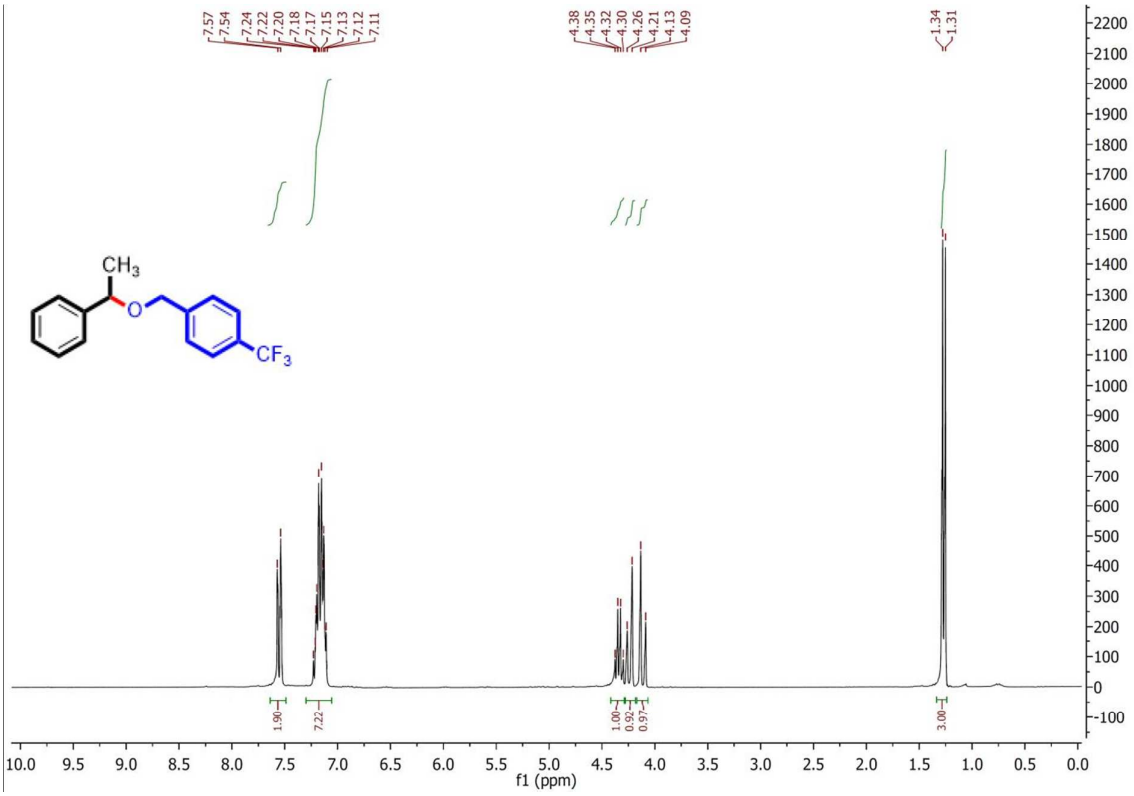
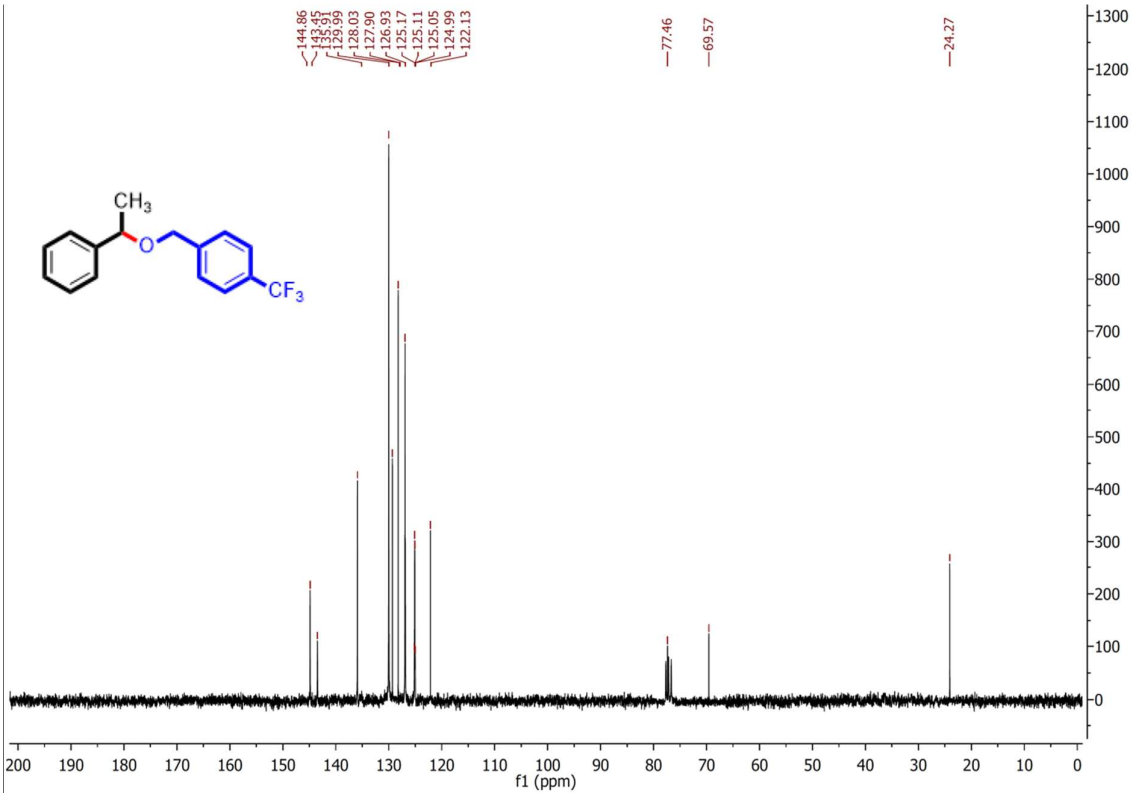
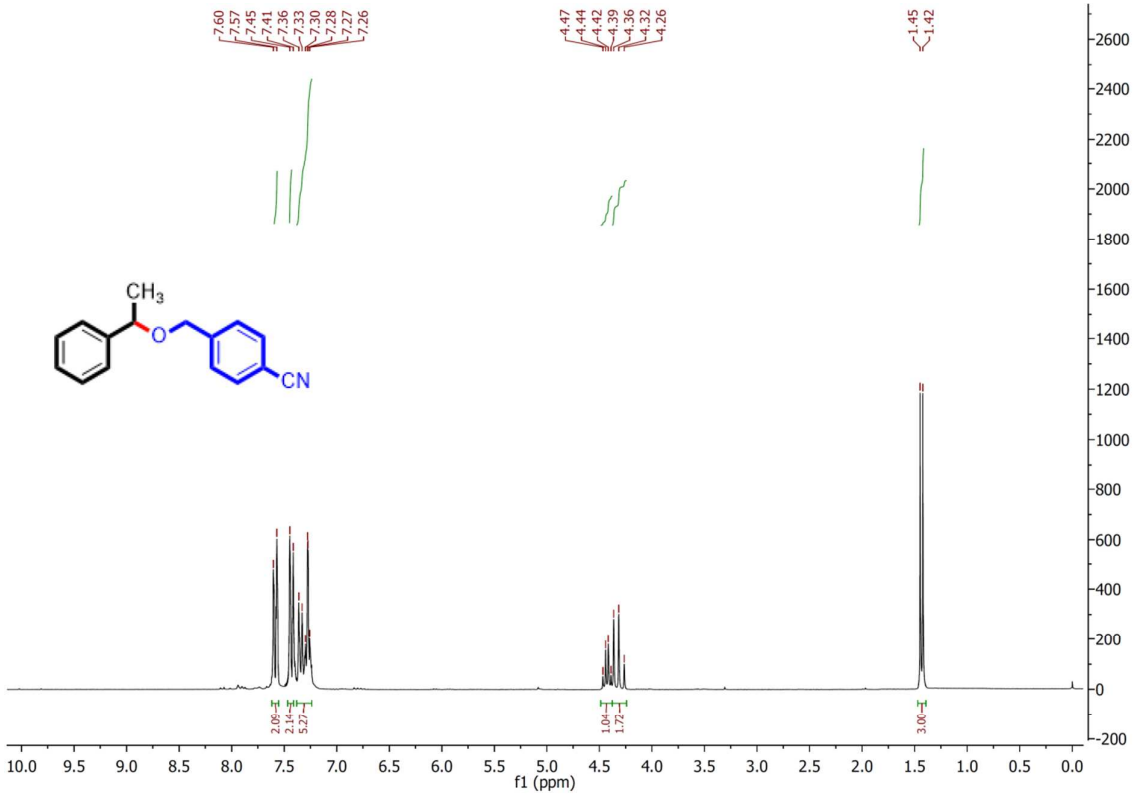
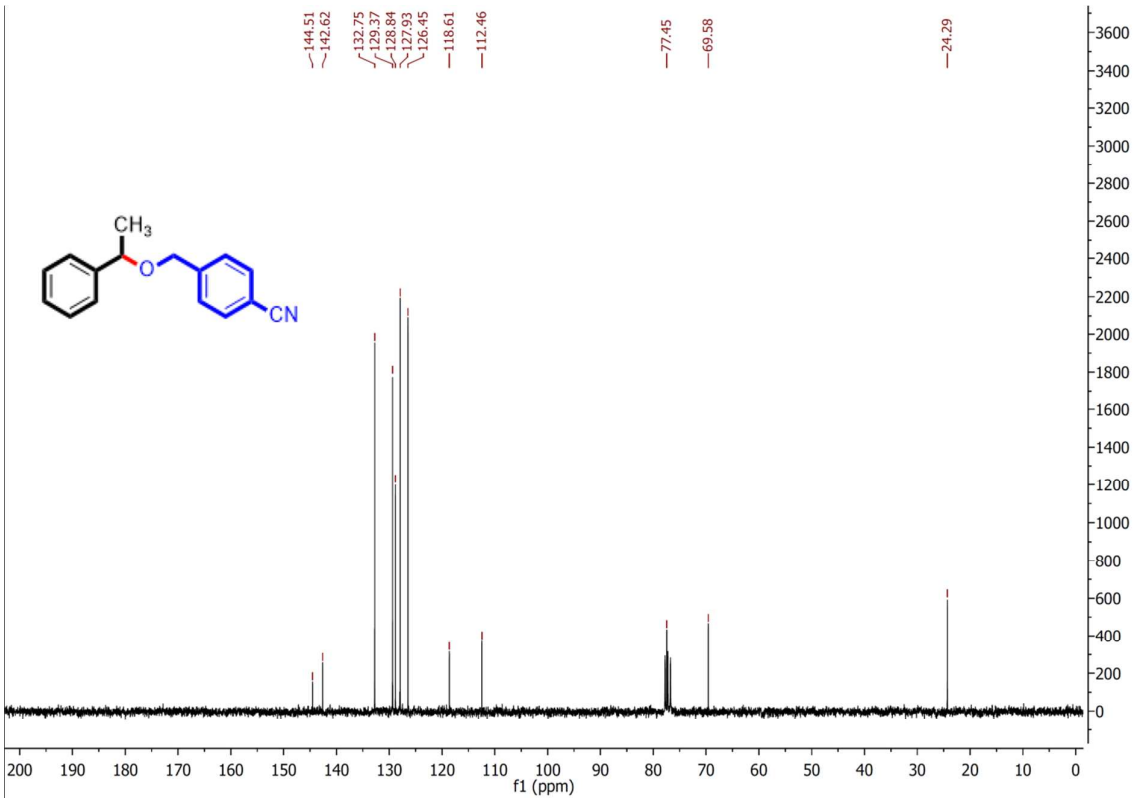


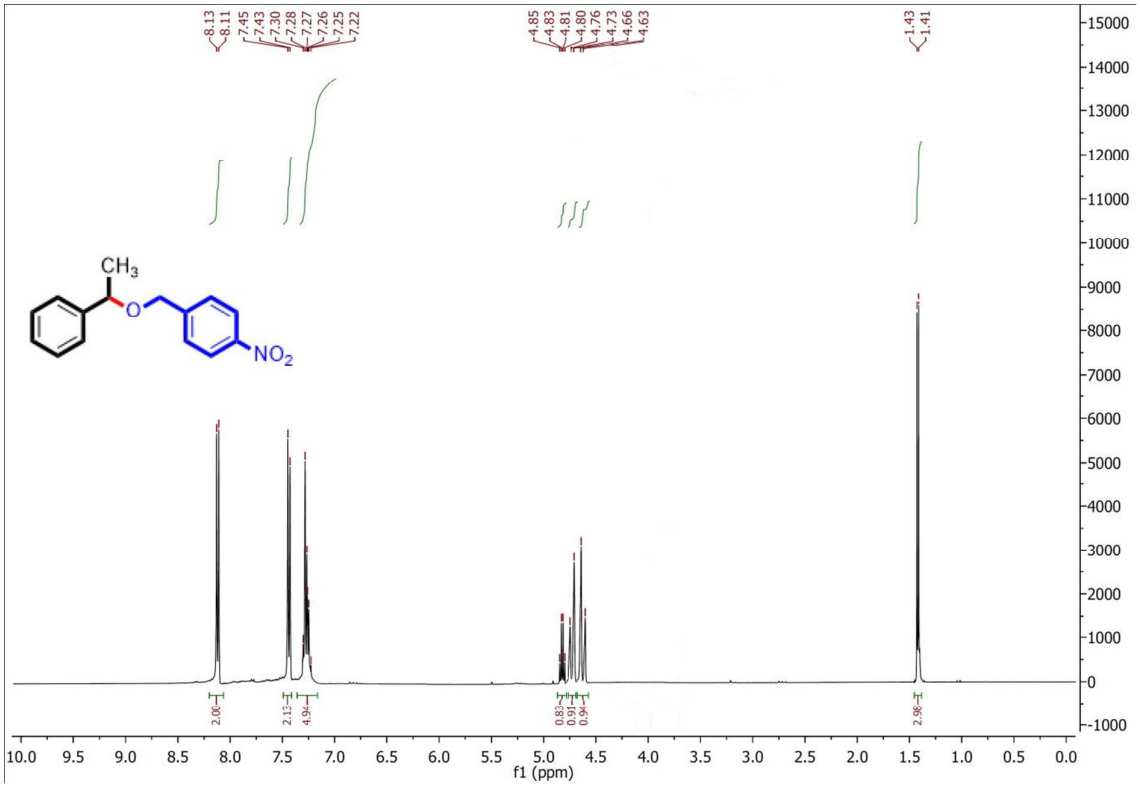


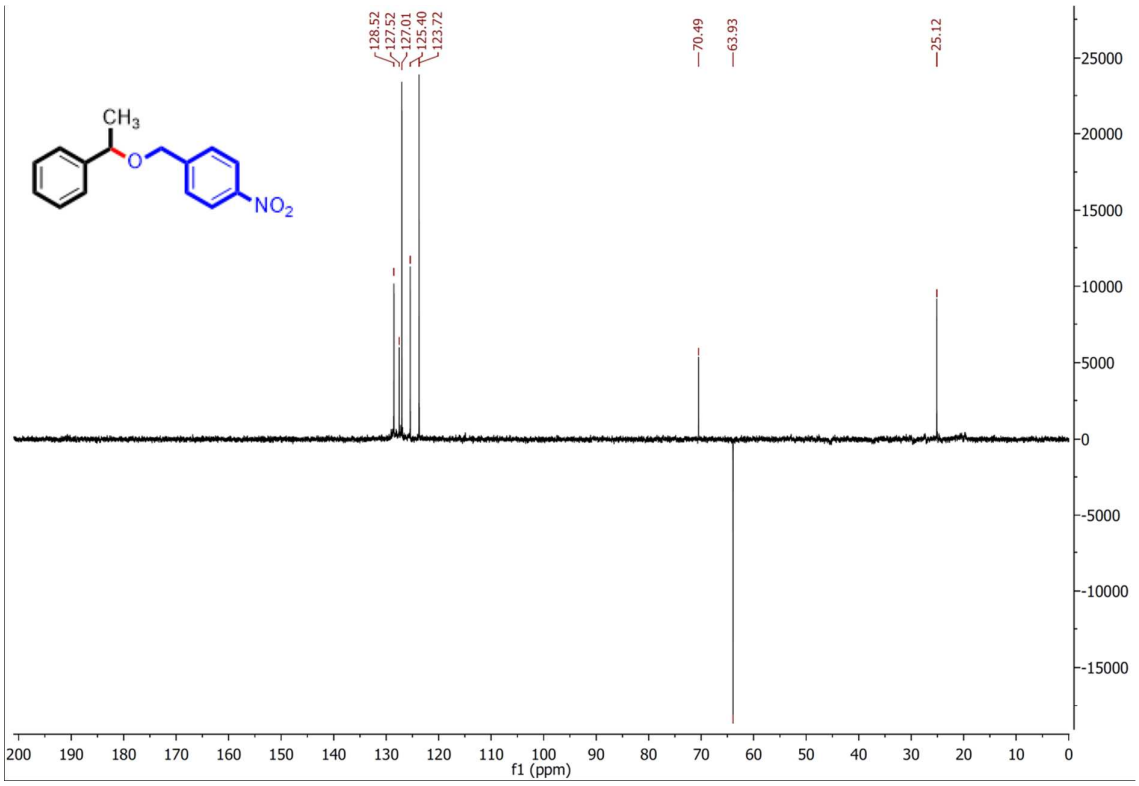
4-((1-phenylethoxy)methyl)benzonitrile (3f).



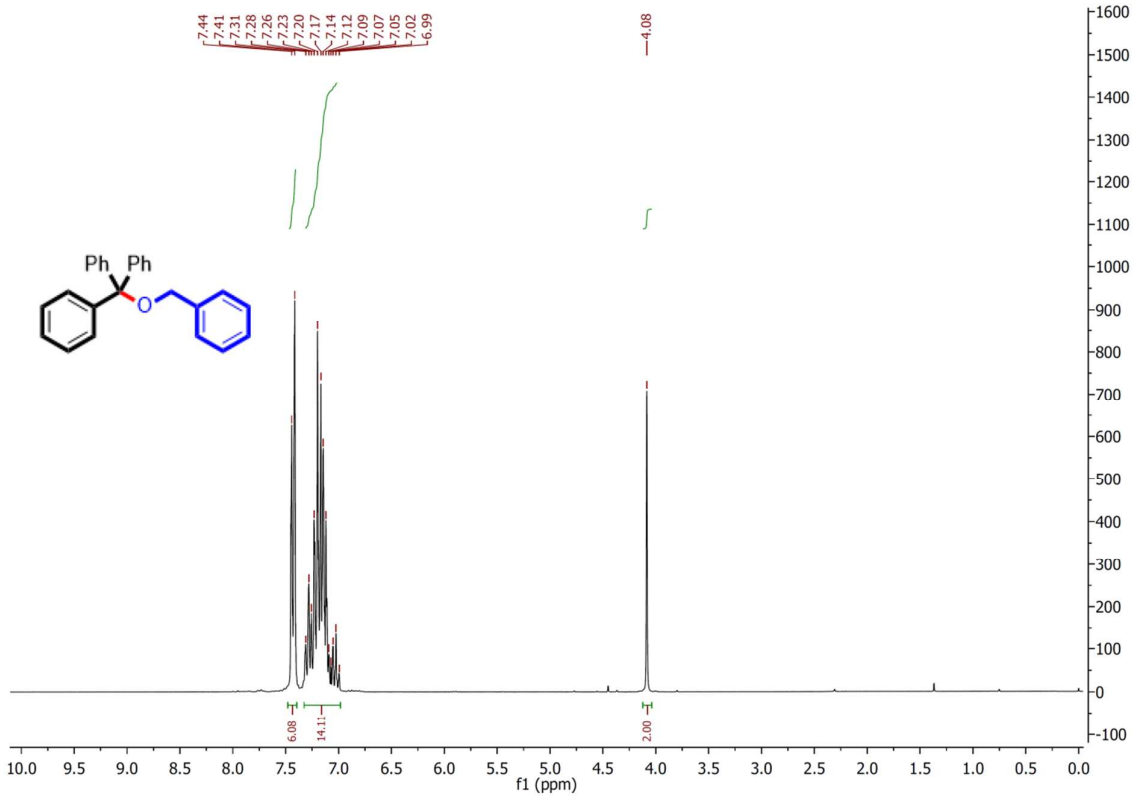


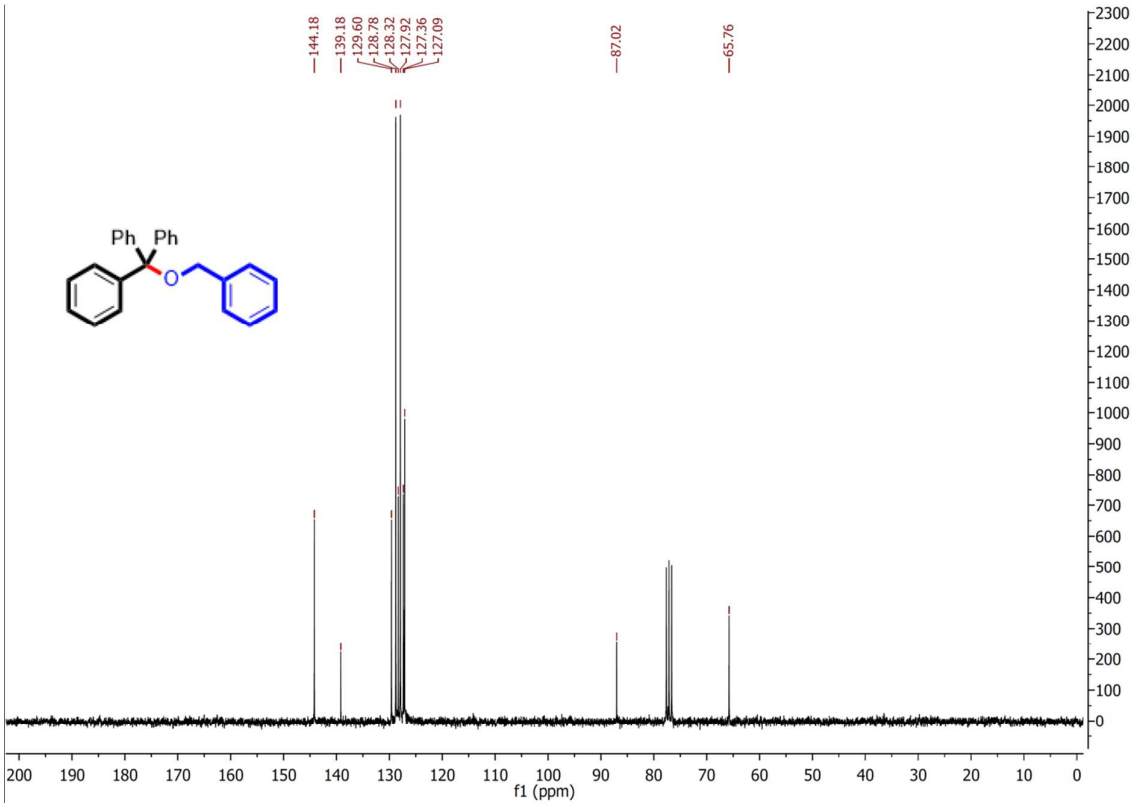
1-nitro-4-((1-phenylethoxy)methyl)benzene (3g).



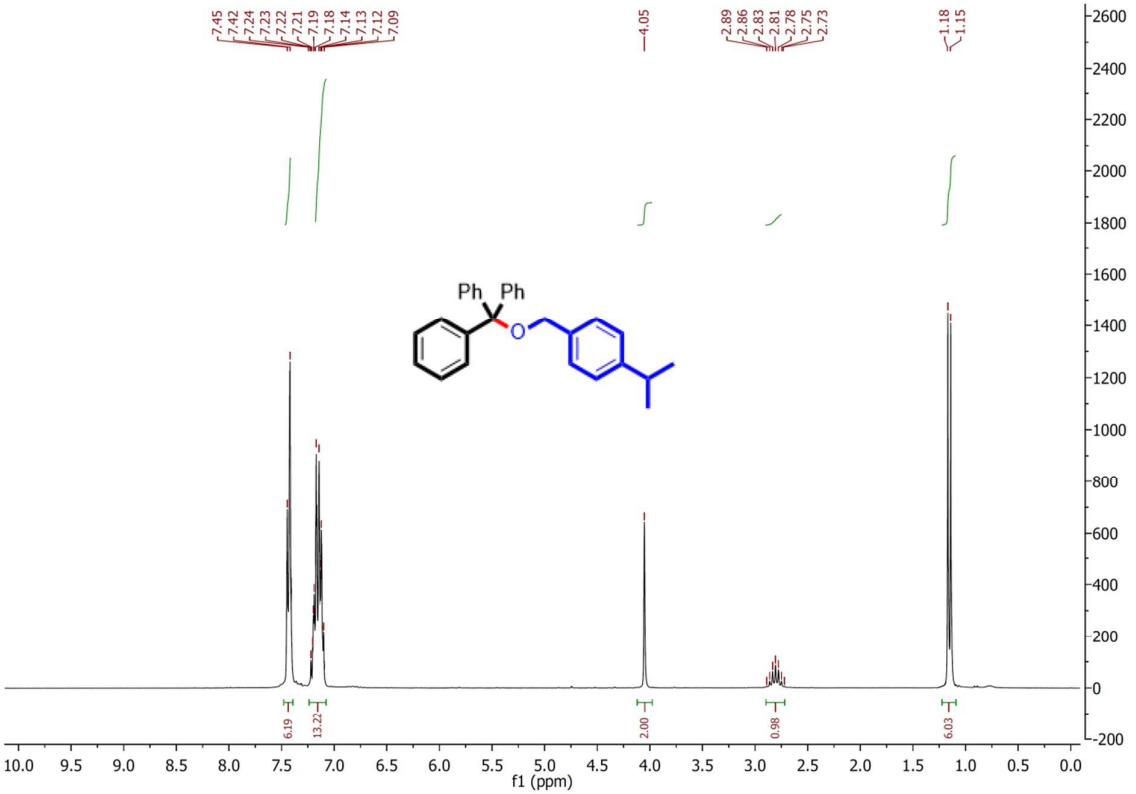


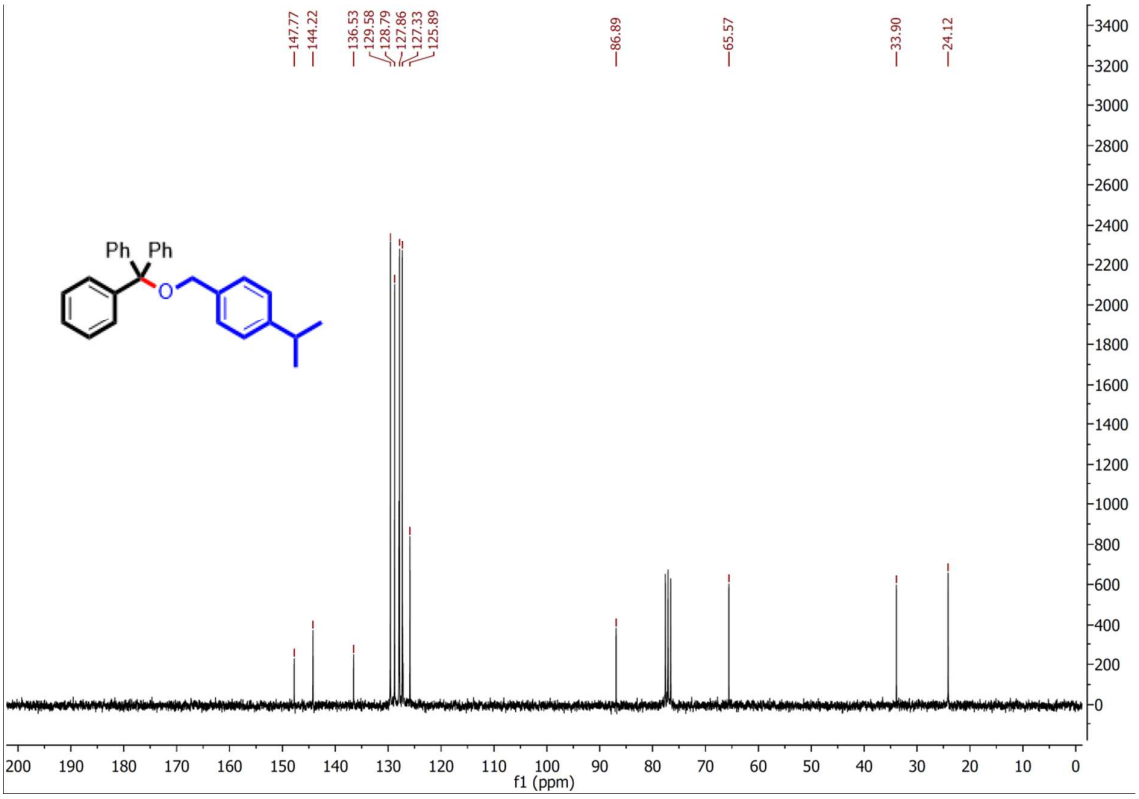
((benzyloxy)methanetriyl)tribenzene(3h).



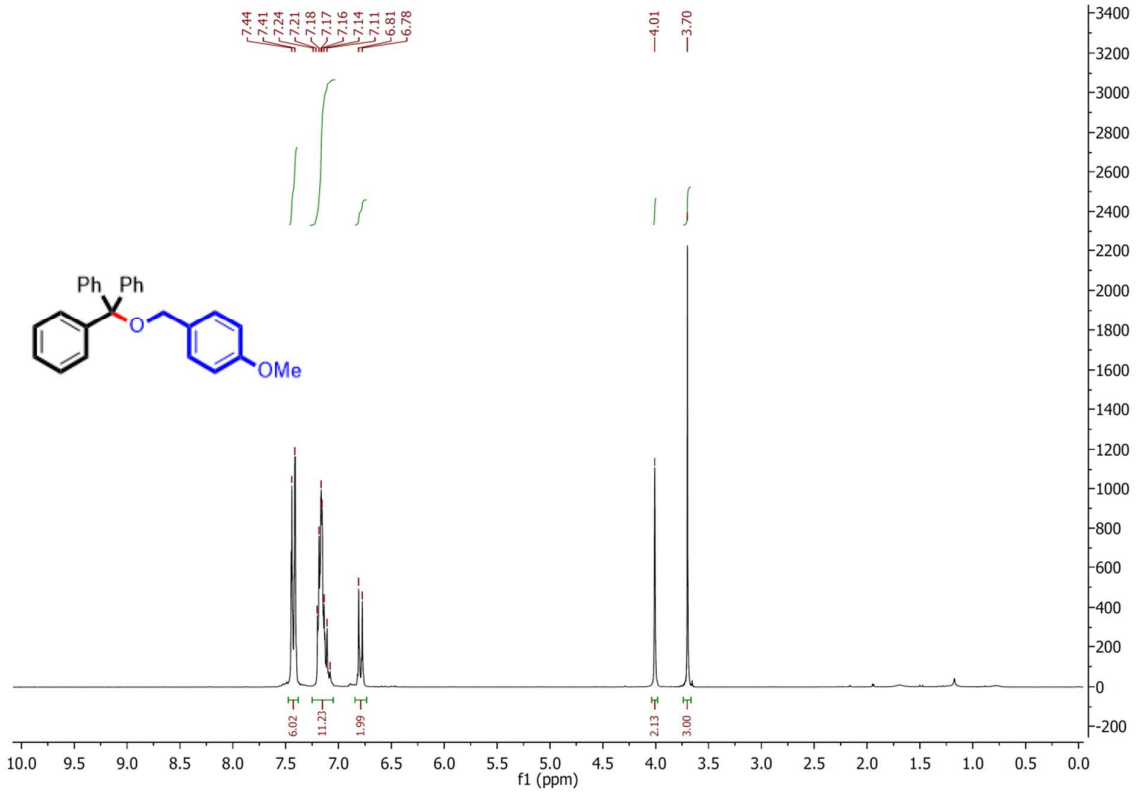


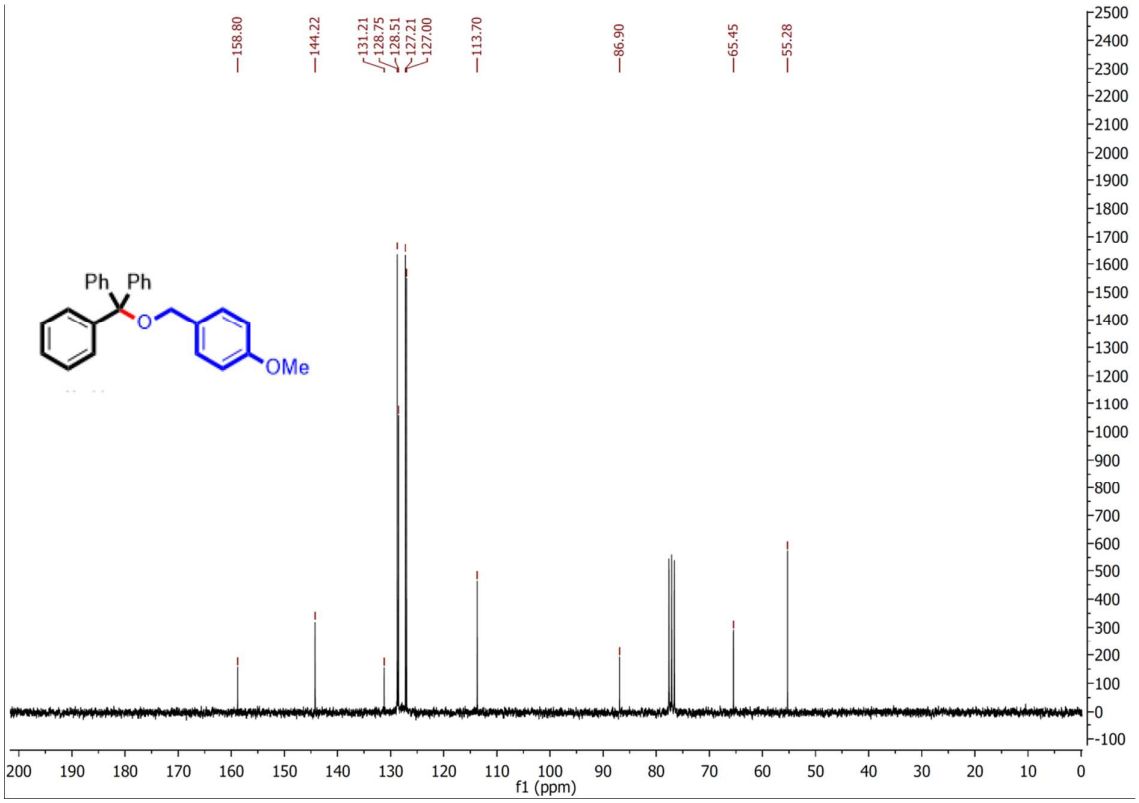
(((4-isopropylbenzyl)oxy)methanetriyl)tribenzene (3i).



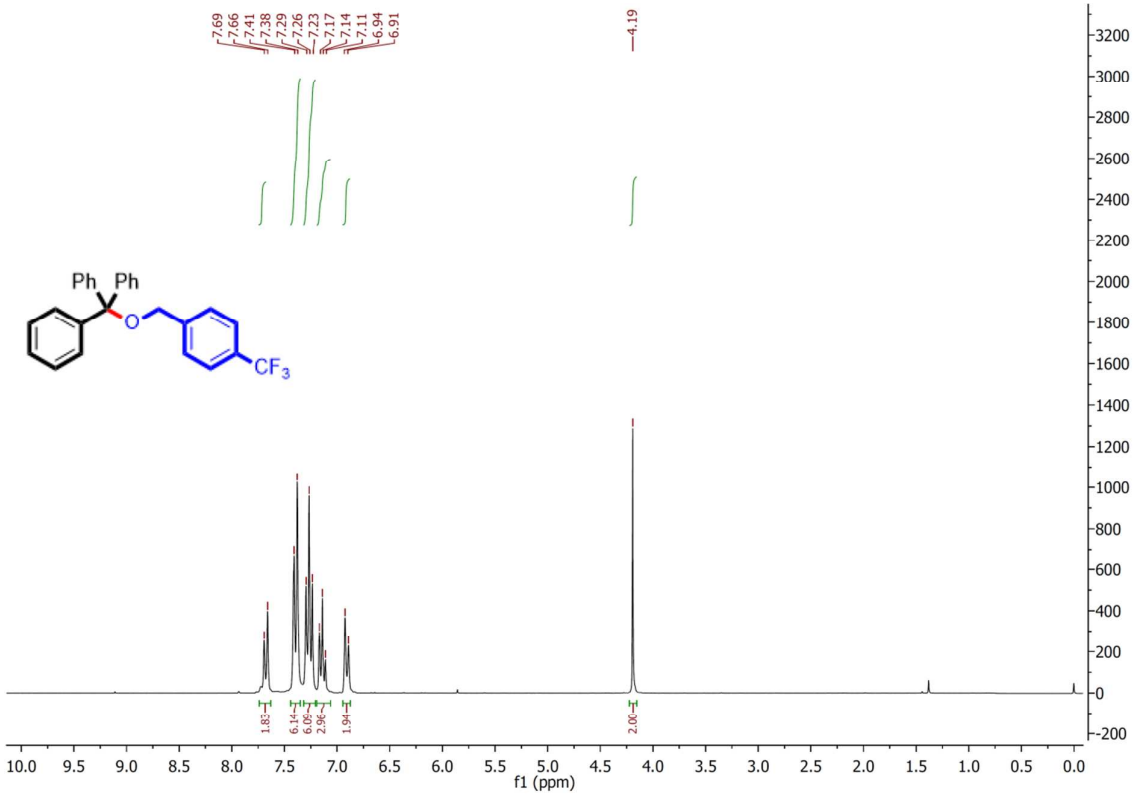


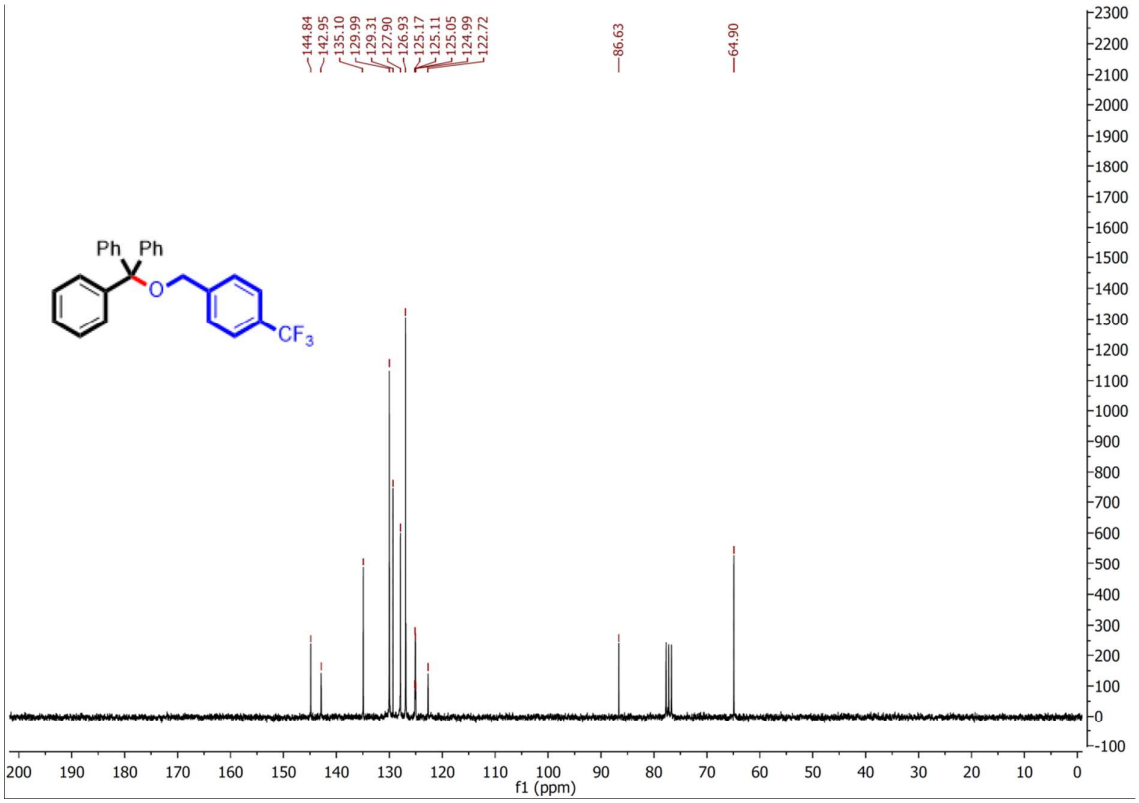
(((4-methoxybenzyl)oxy)methanetriyl)tribenzene (3j).



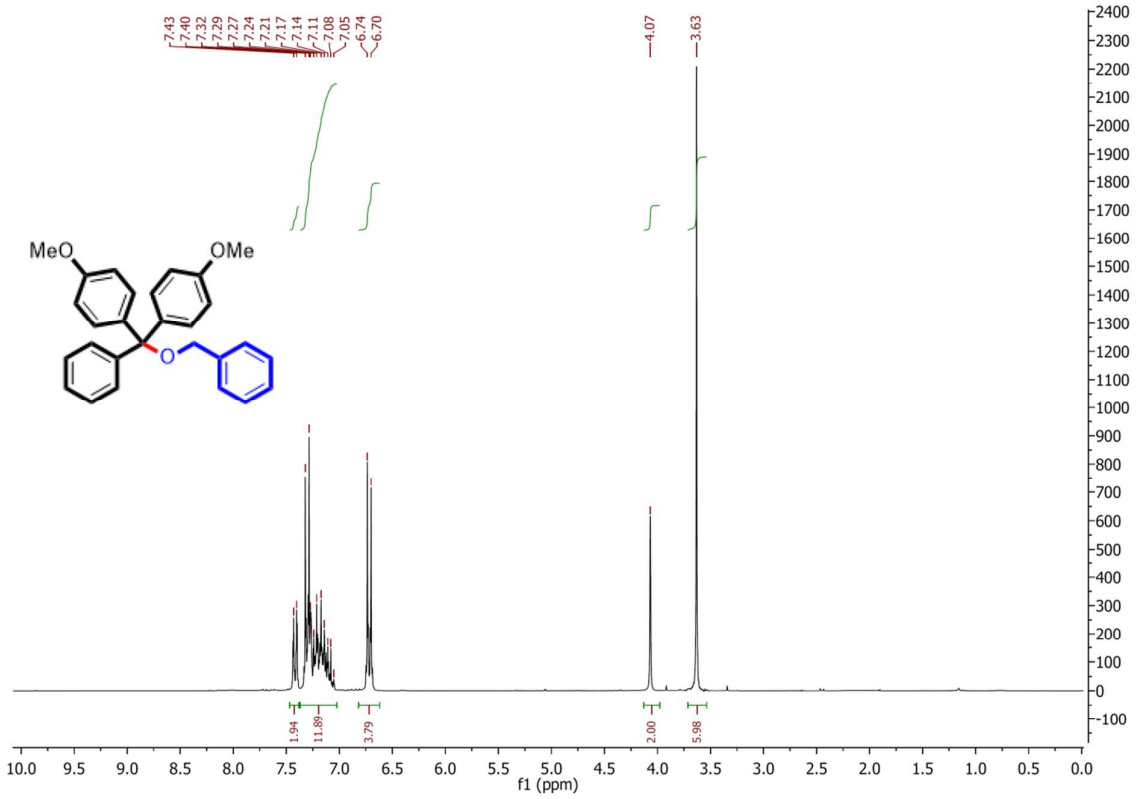


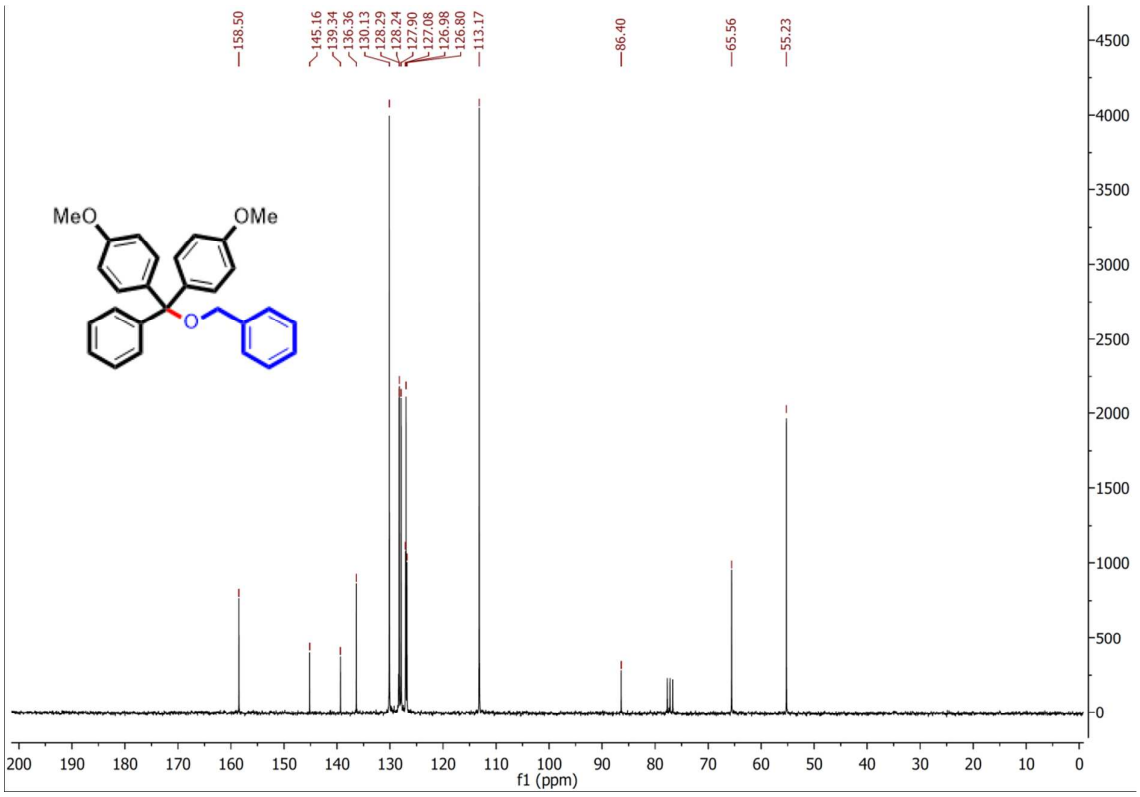
(((4-(trifluoromethyl)benzyl)oxy)methanetriyl)tribenzene (3k).



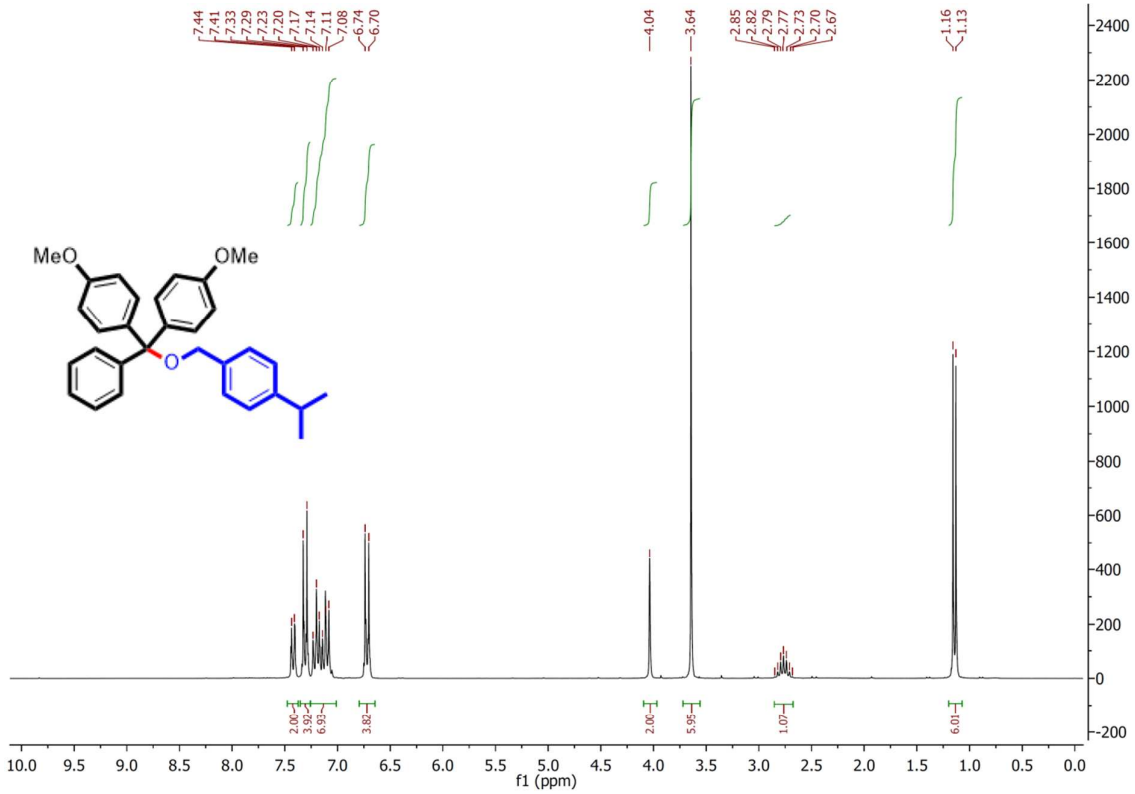


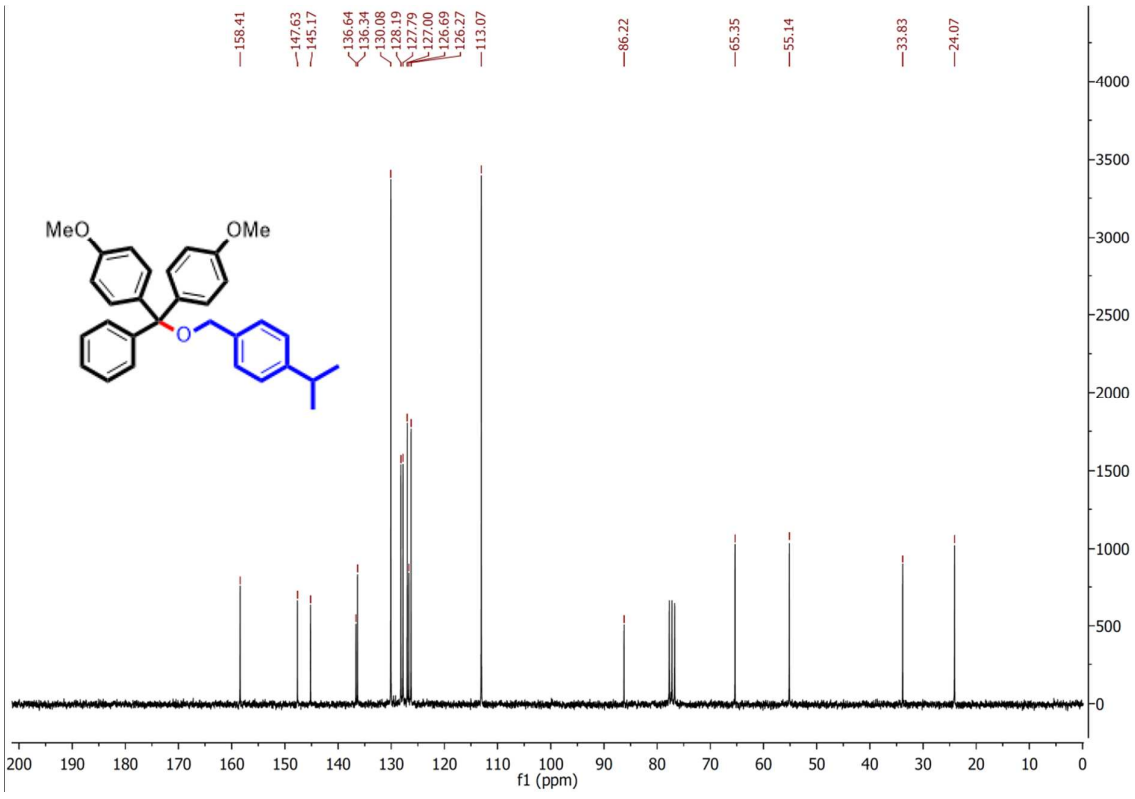
4,4'-((benzyloxy)(phenyl)methylene)bis(methoxybenzene) (3l).



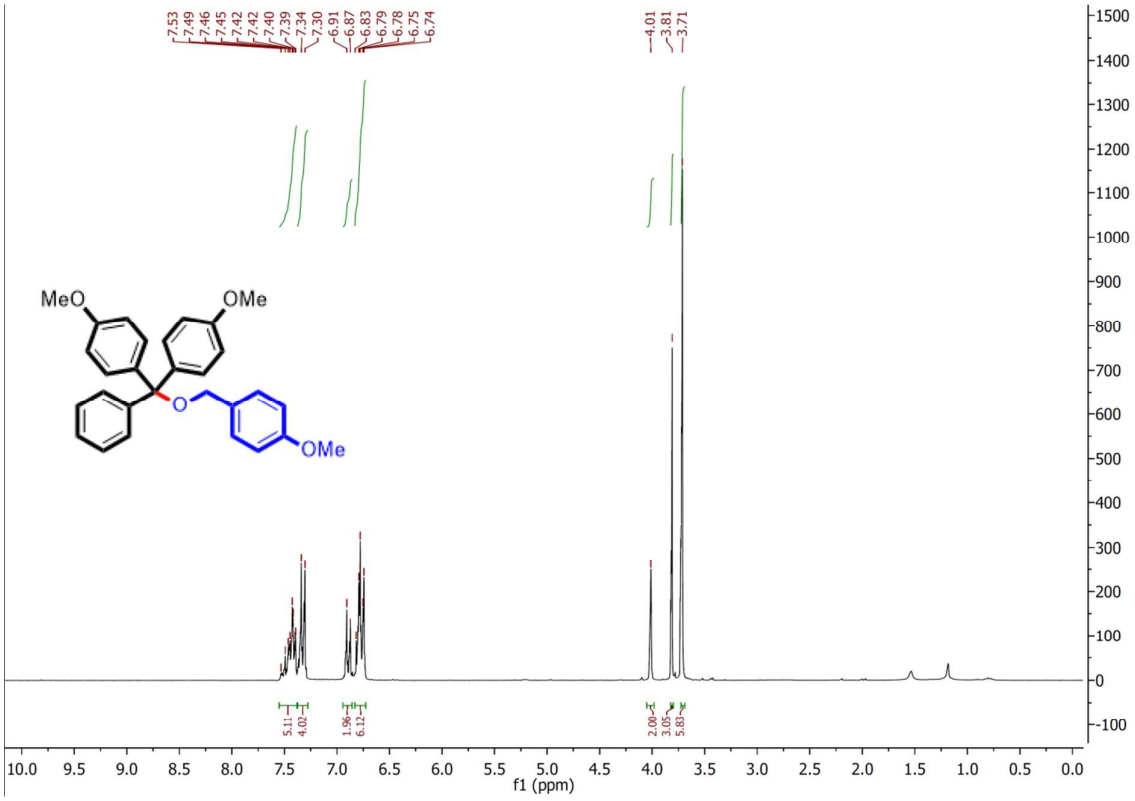


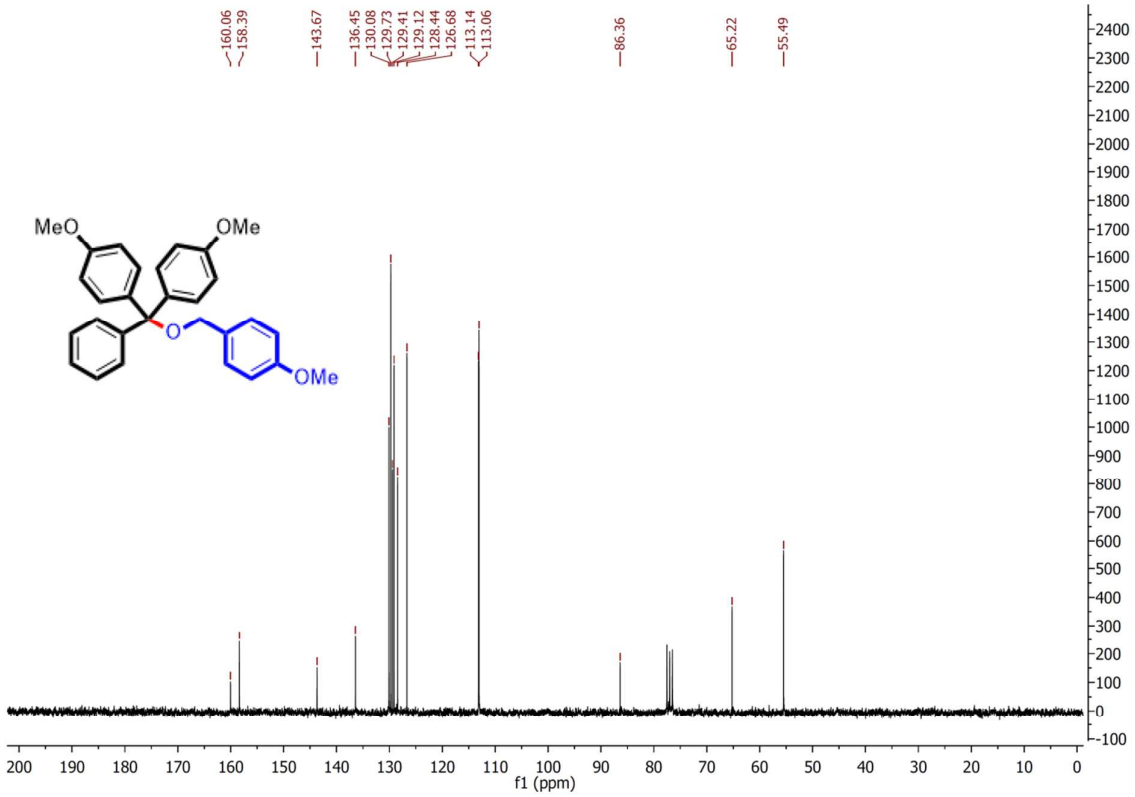
4,4'-(((4-isopropylbenzyl)oxy)(phenyl)methylene)bis(methoxybenzene) (3m).



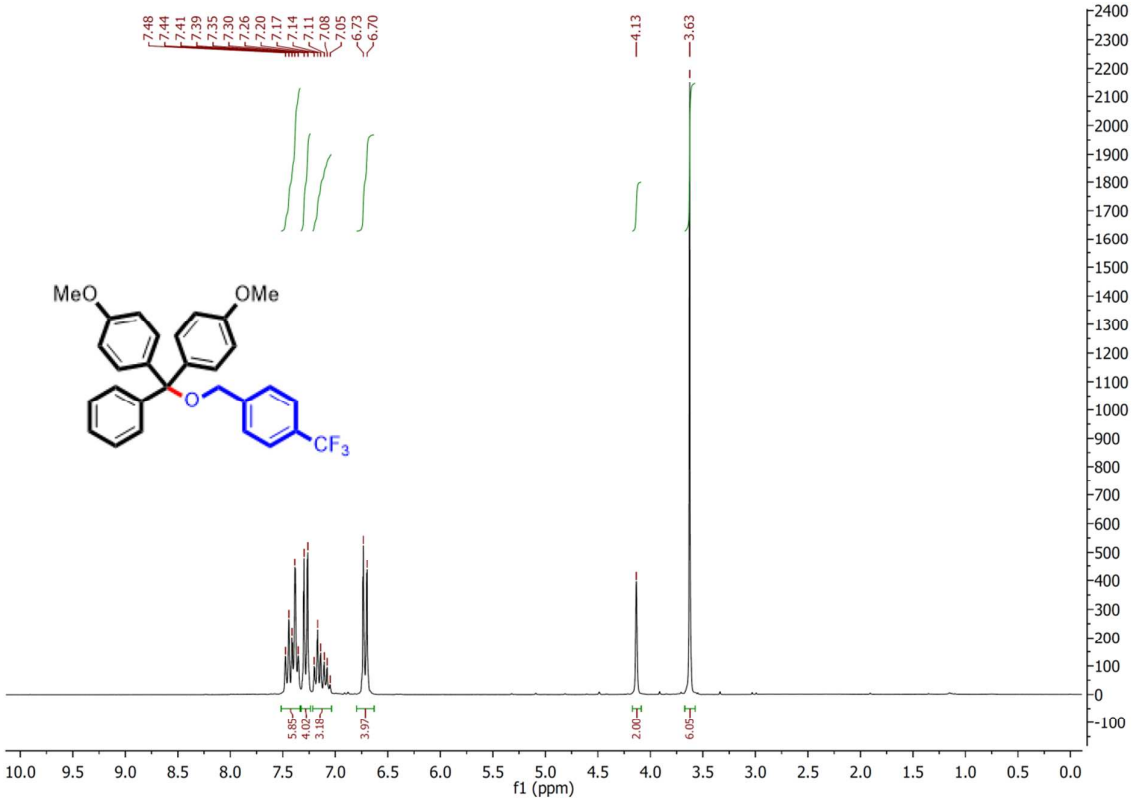


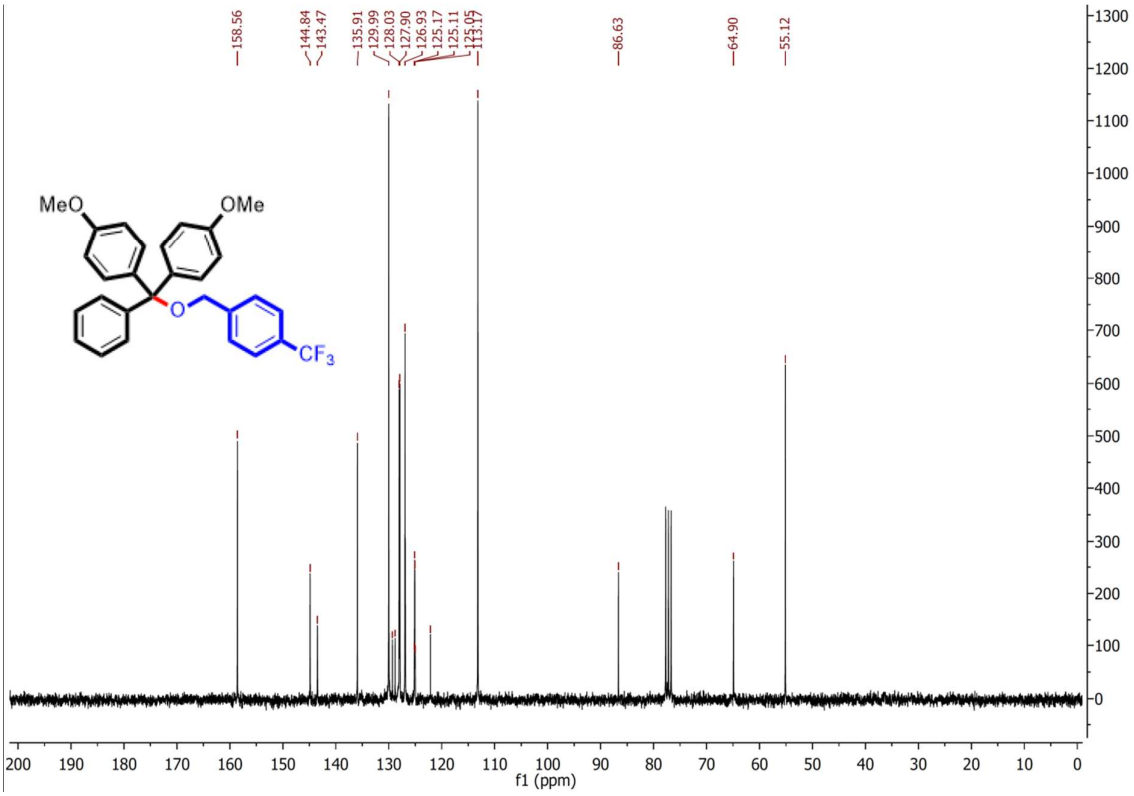
4,4'-(((4-methoxybenzyl)oxy)(phenyl)methylene)bis(methoxybenzene) (3n).



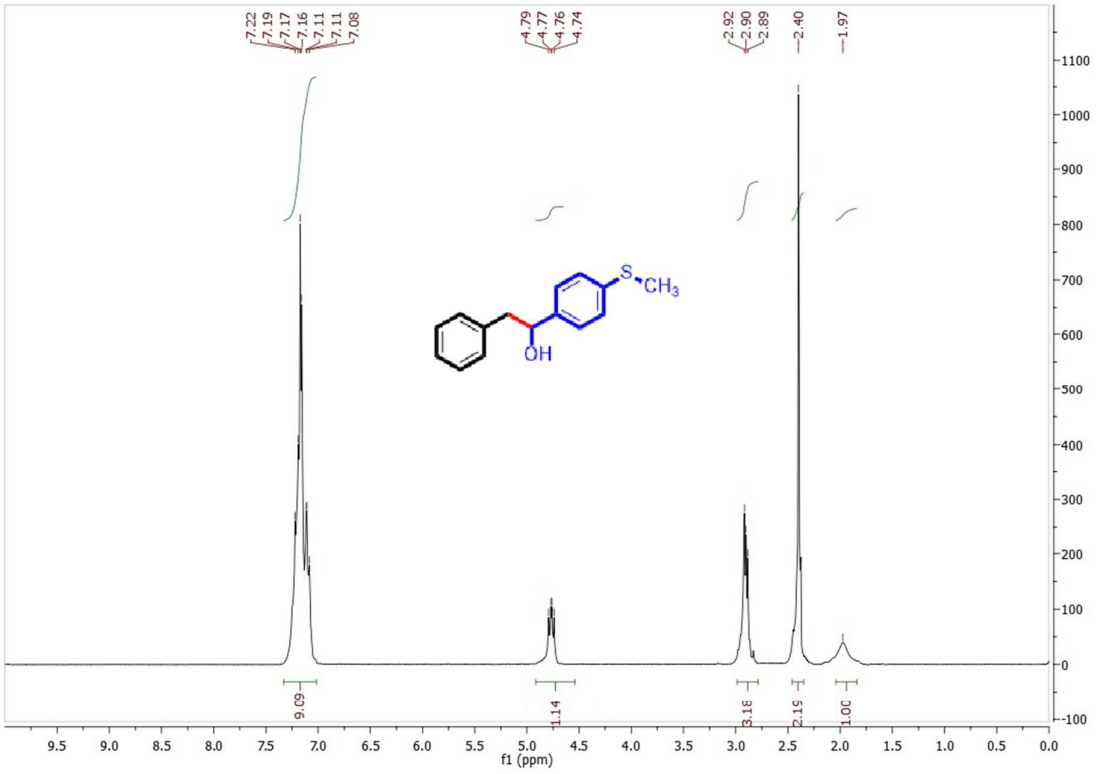


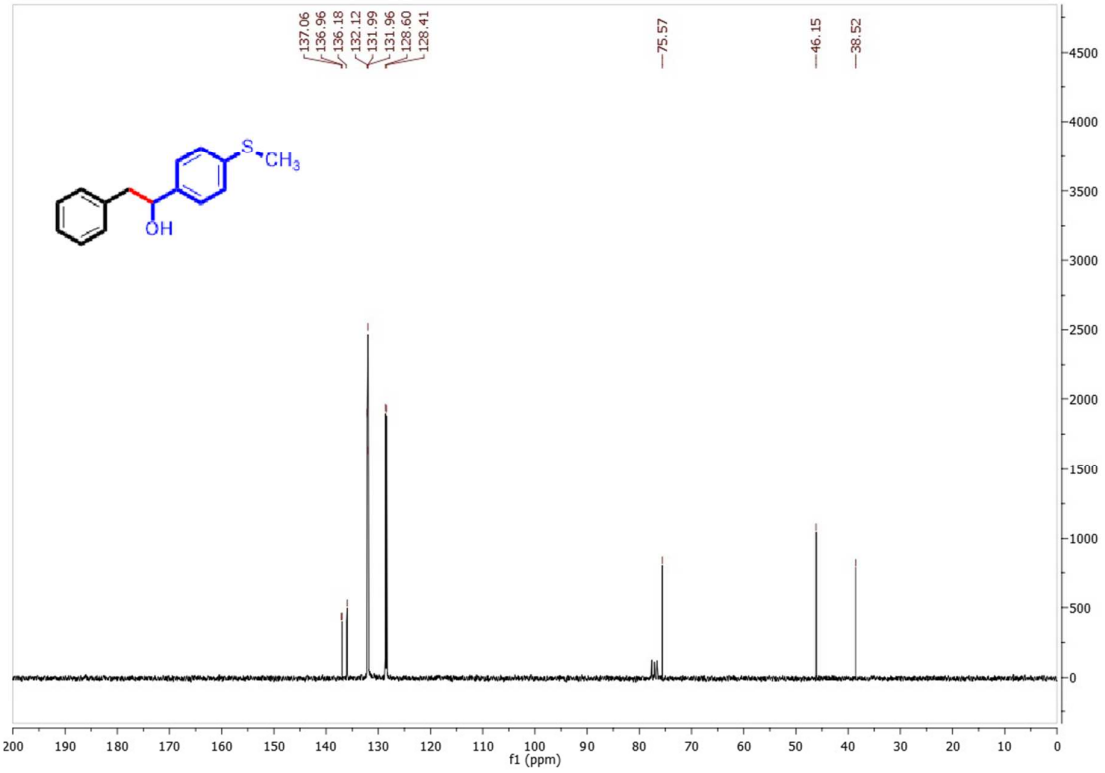
4,4'-(phenyl((4-(trifluoromethyl)benzyl)oxy)methylene)bis(methoxybenzene) (3o).



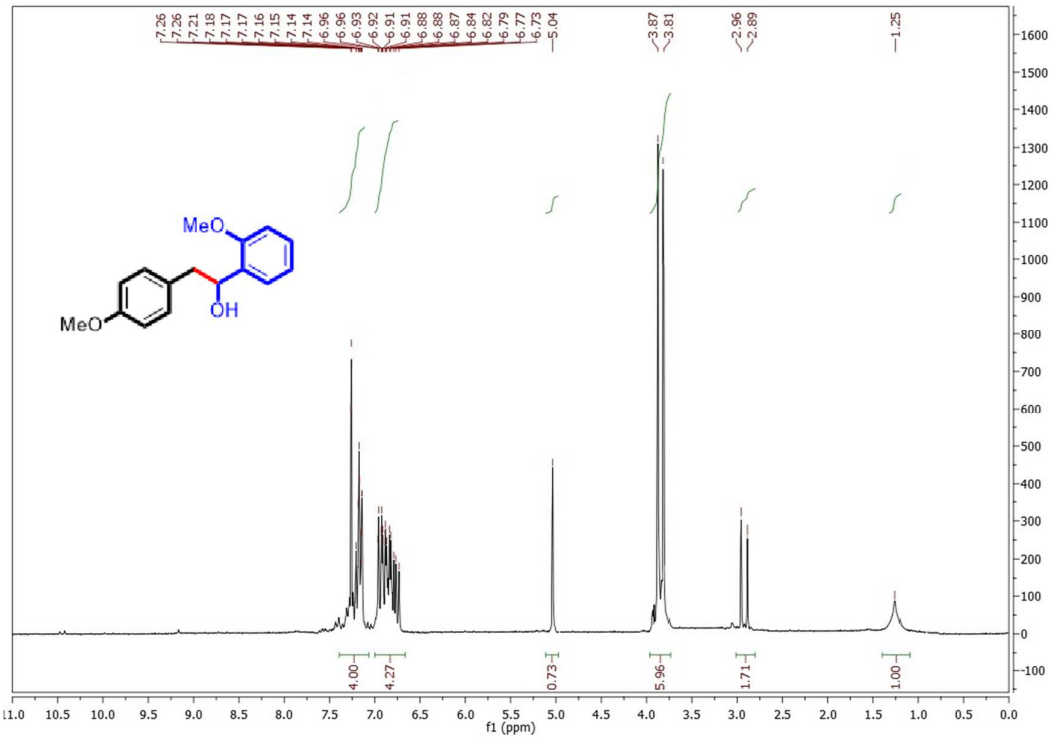


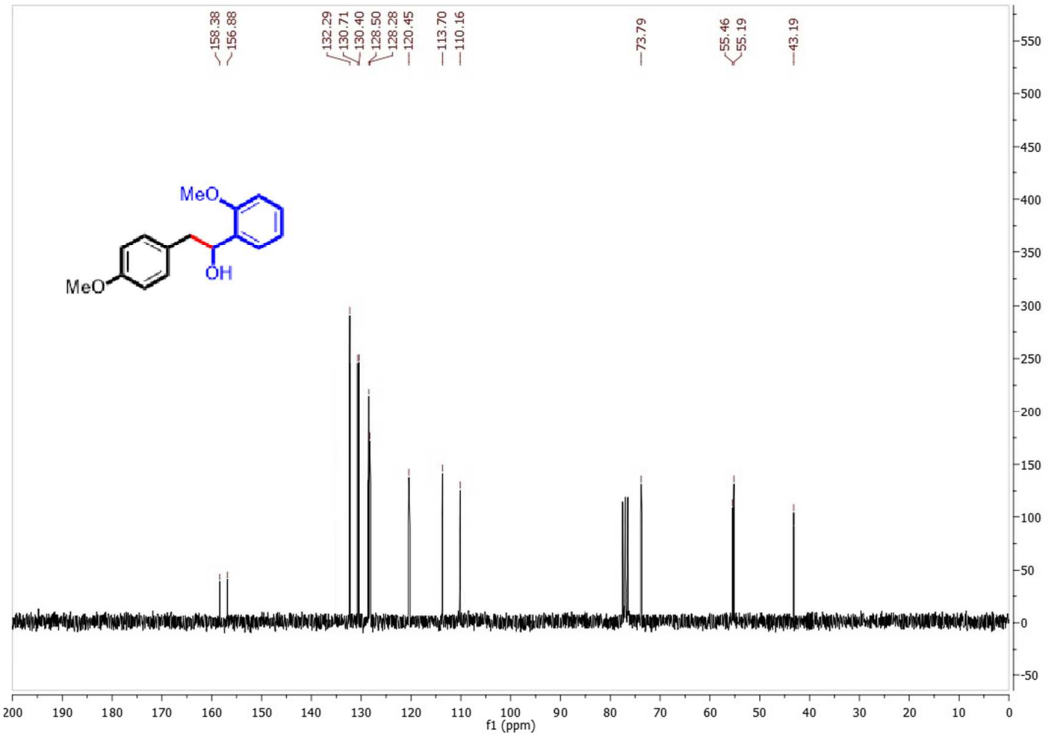
1-(4-(Methylthio)phenyl)-2-phenylethanol (4a).



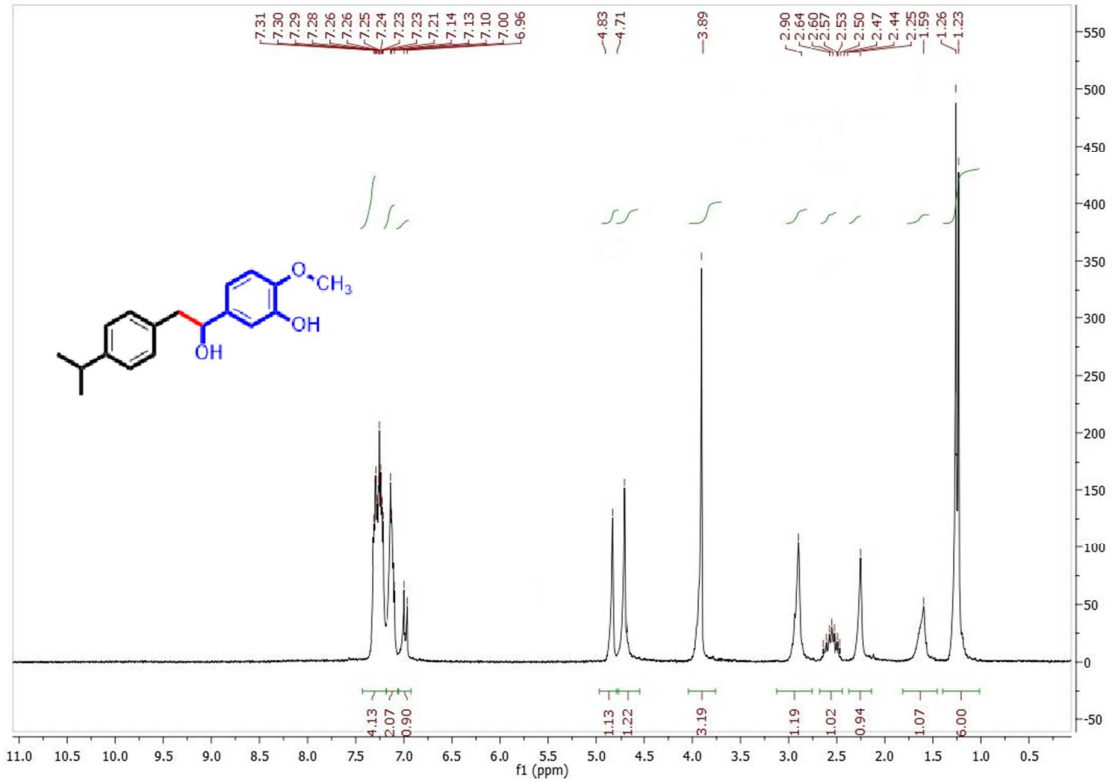


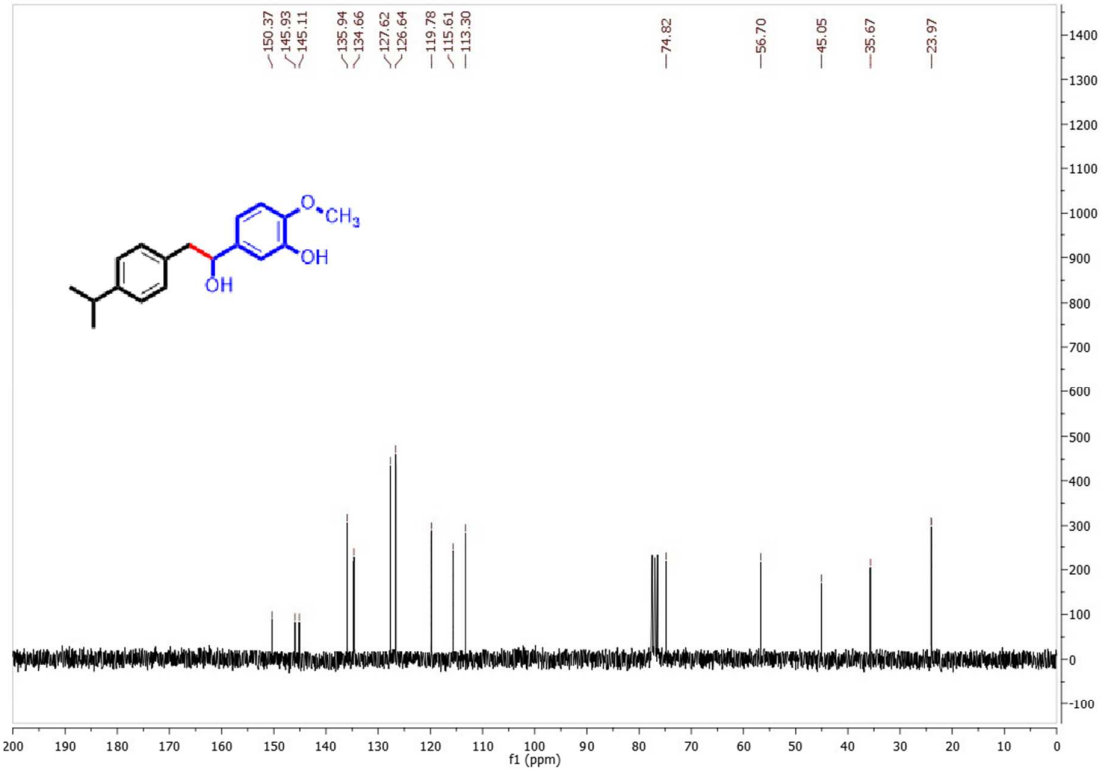
1-(2-methoxyphenyl)-2-(4-methoxyphenyl)ethanol (4b).



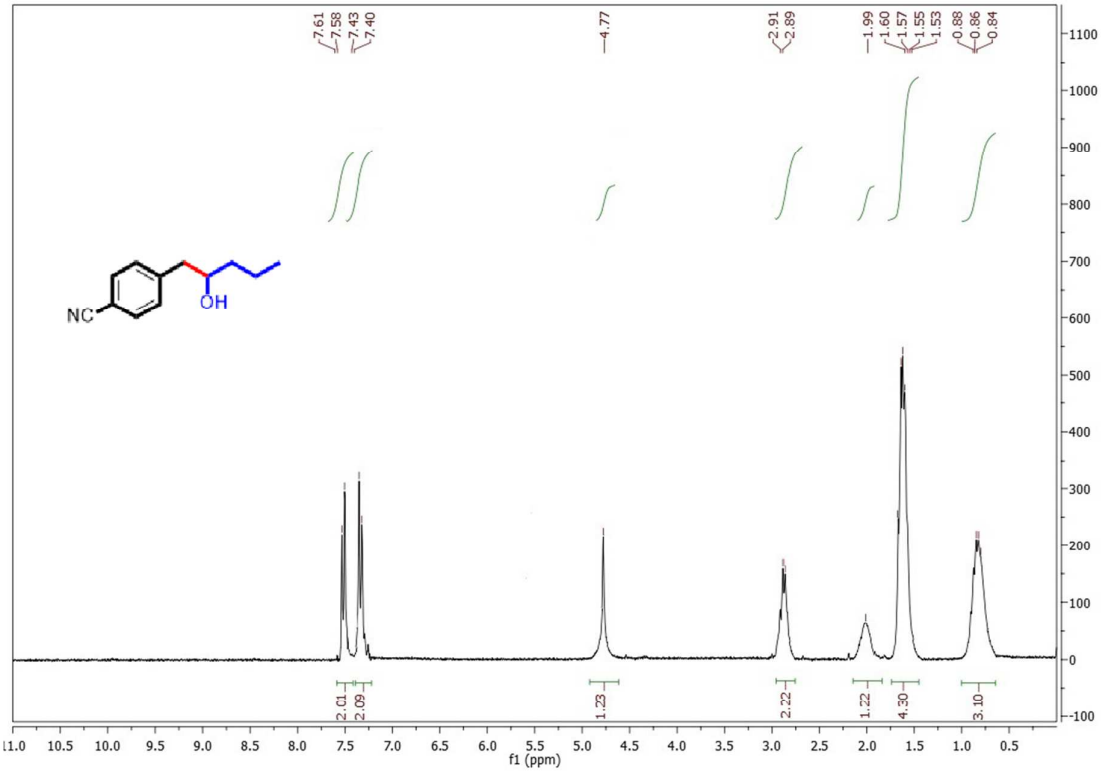


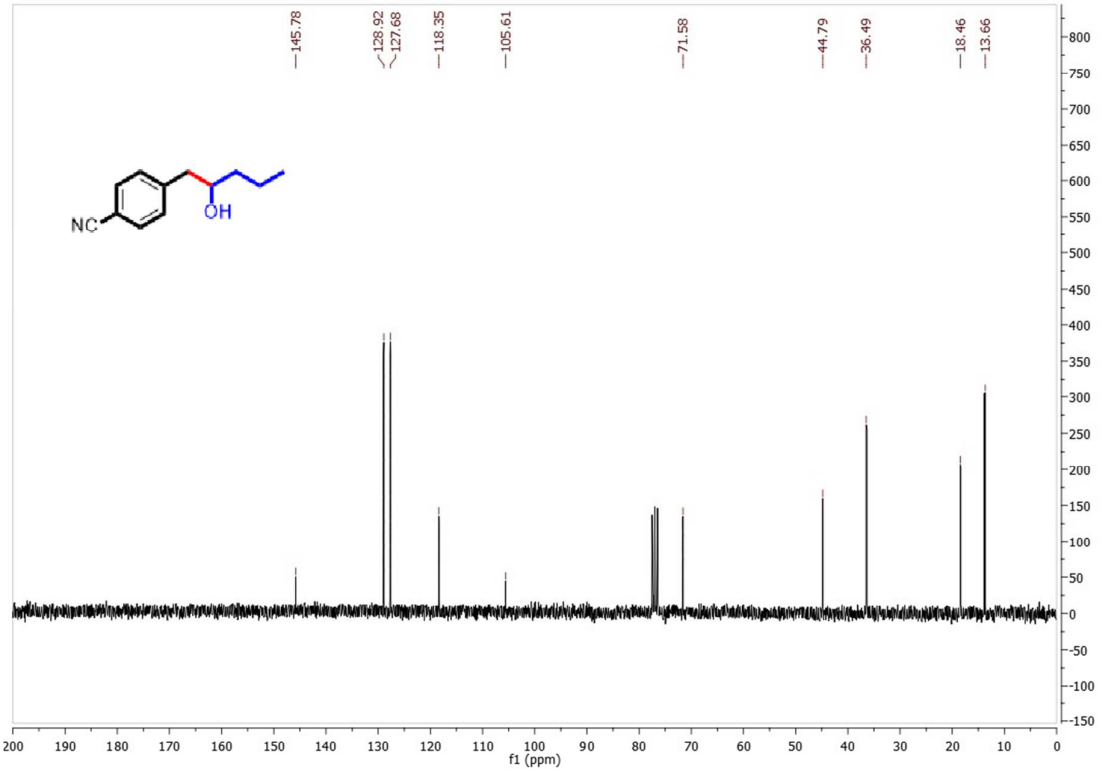
5-(1-hydroxy-2-(4-isopropylphenyl)ethyl)-2-methoxyphenol (4c).



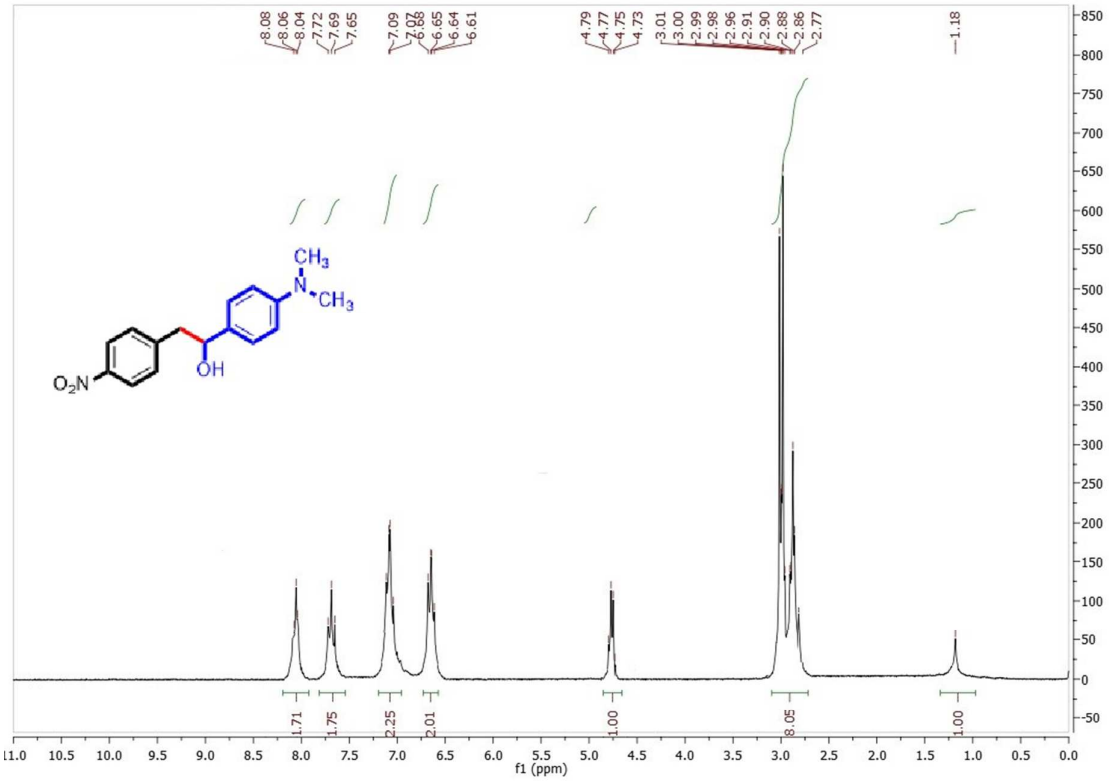


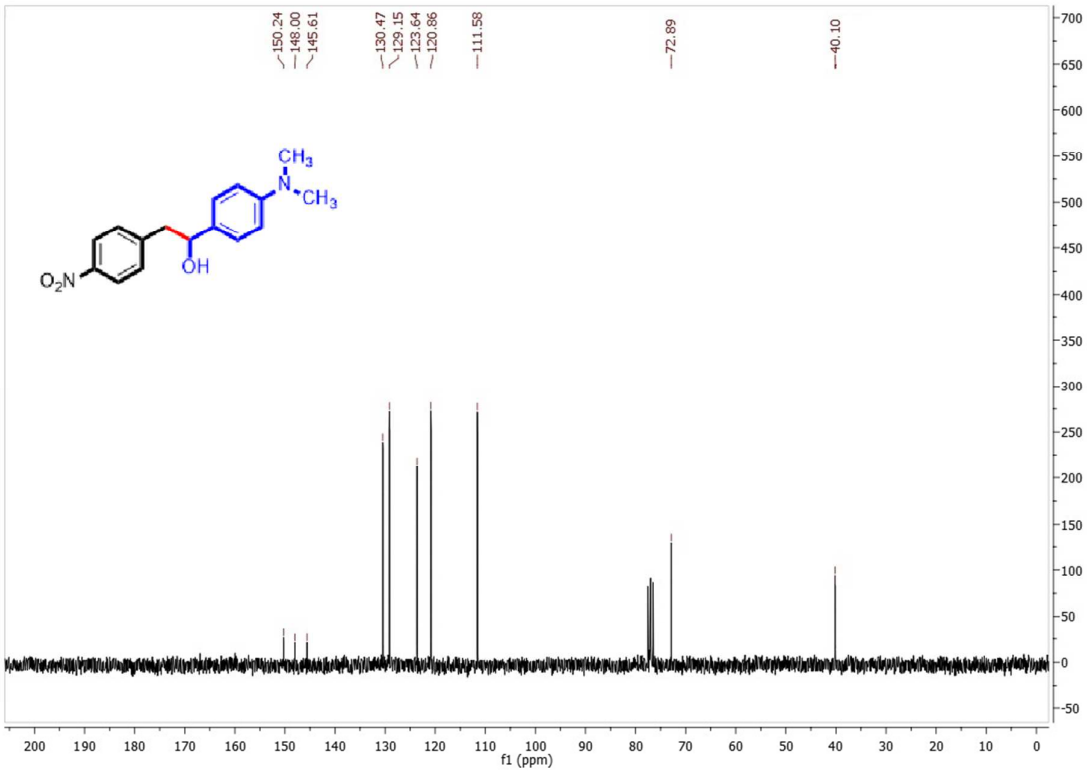
4-(2-hydroxypentyl)benzonitrile (4d).



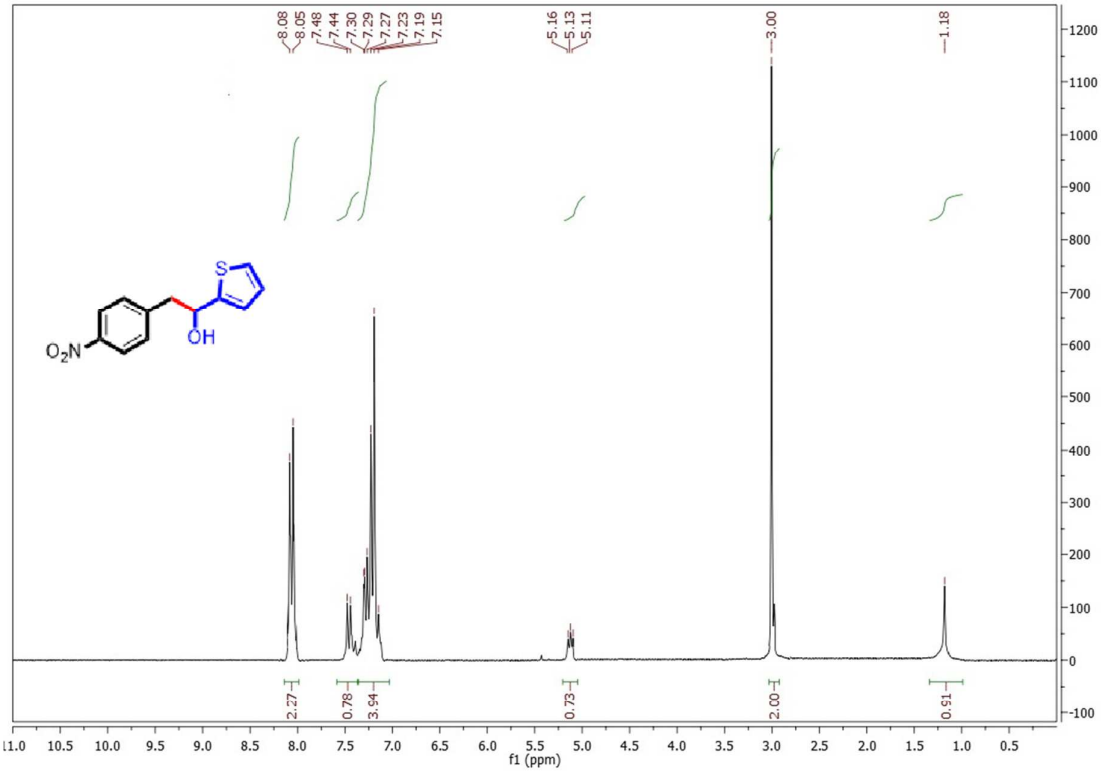


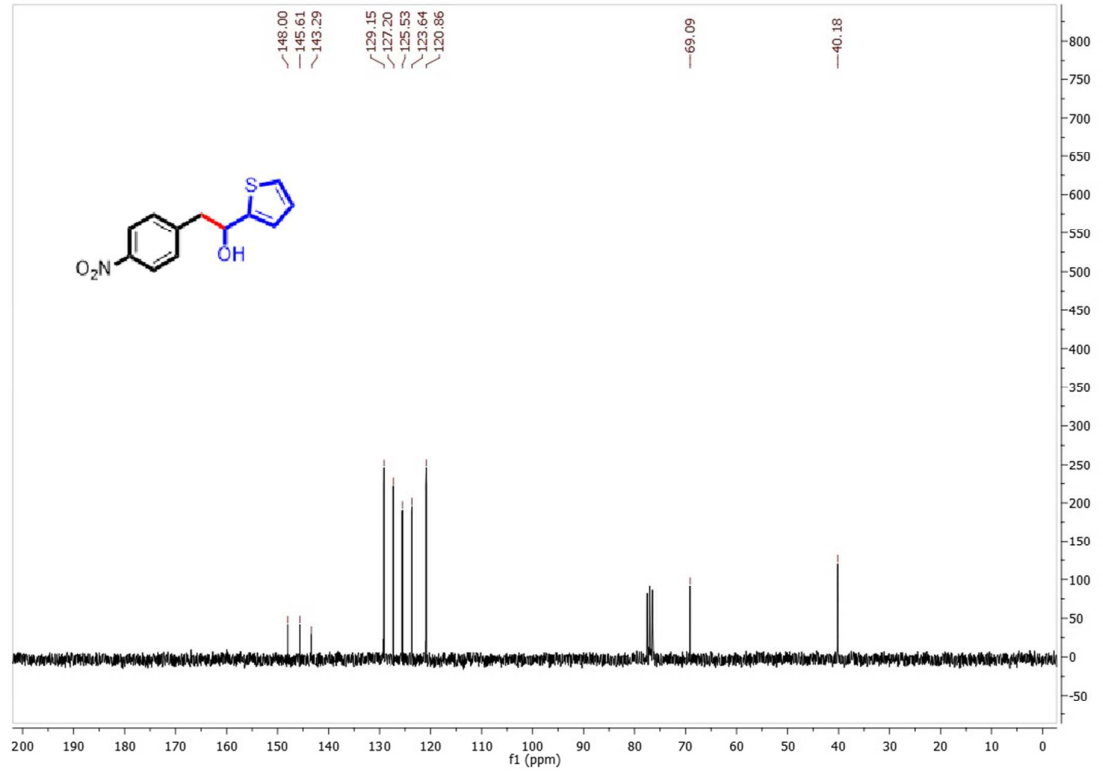
1-(4-(Dimethylamino)phenyl)-2-(4-nitrophenyl)ethanol (4e)



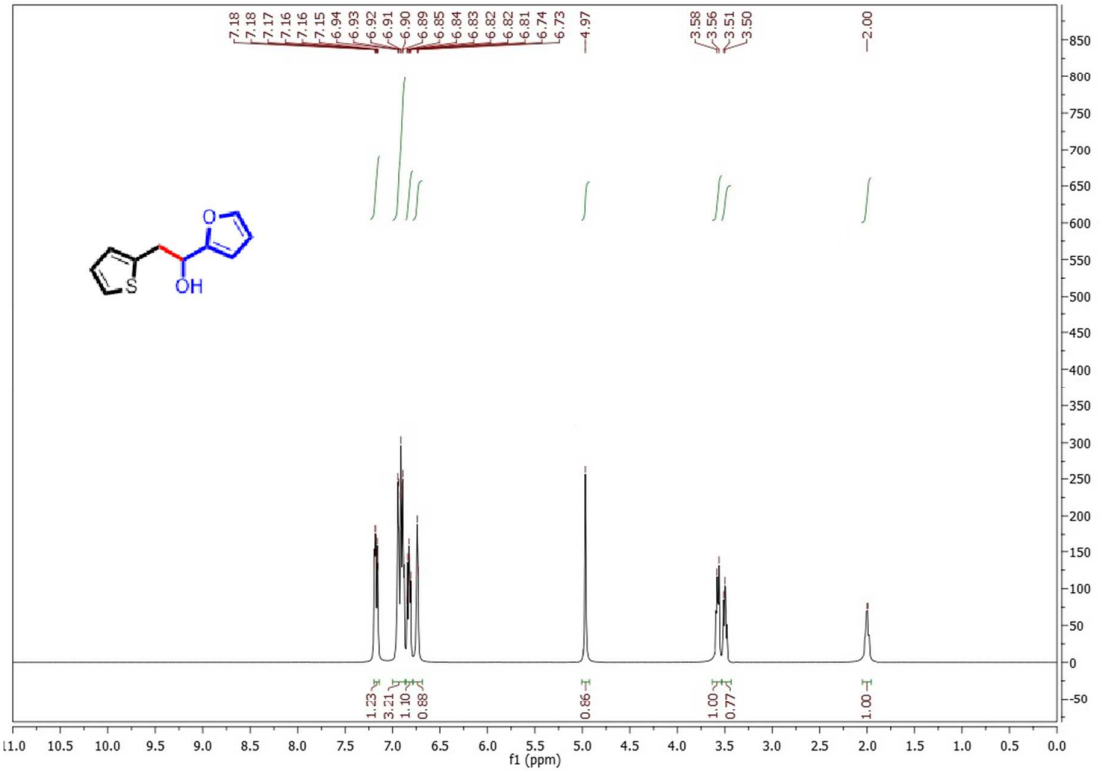


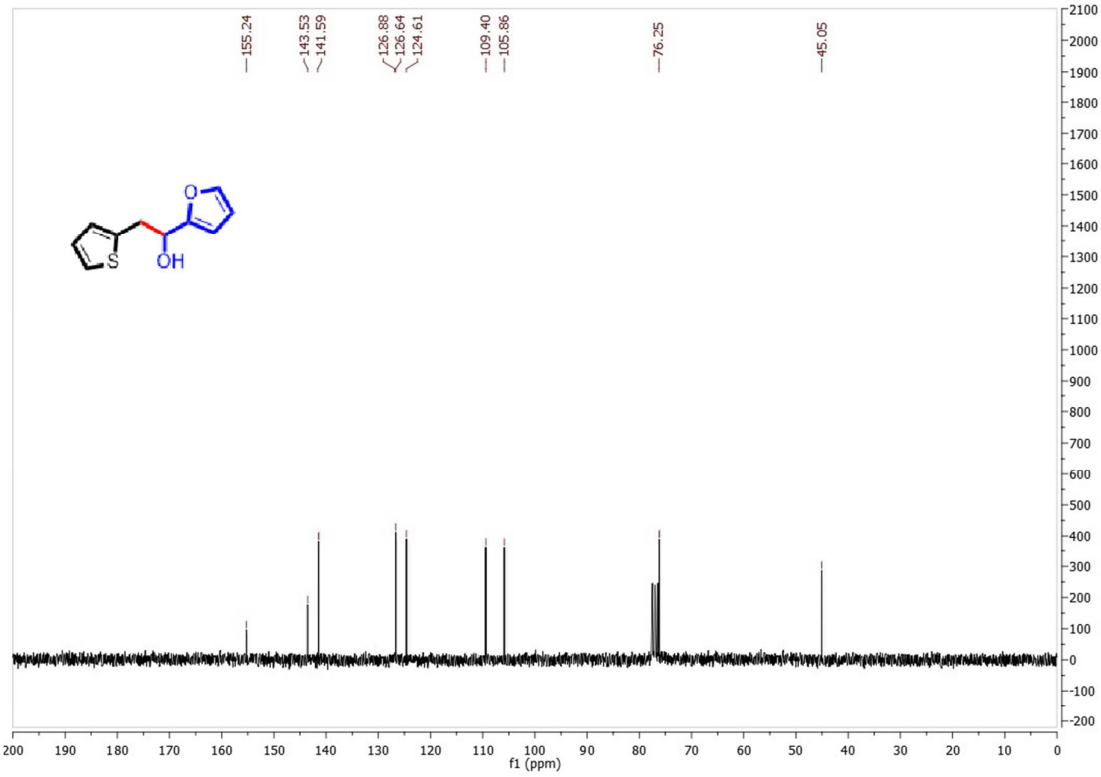
2-(4-Nitrophenyl)-1-(thiophen-2-yl)ethanol (4f).



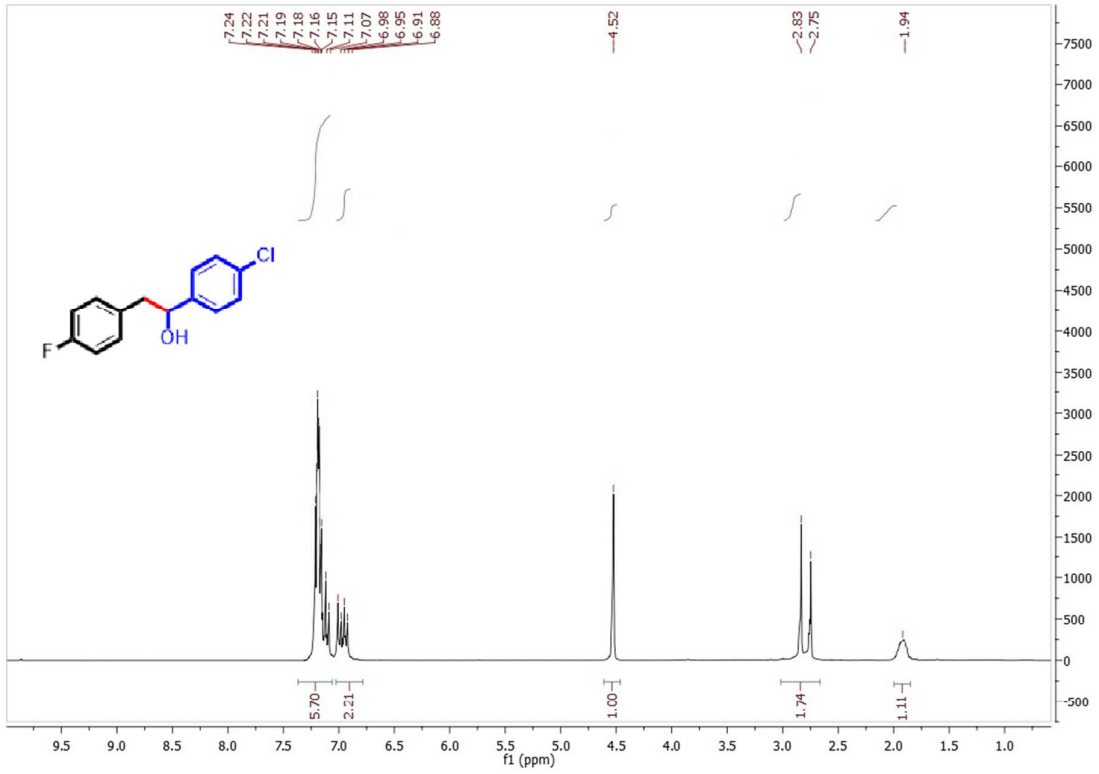


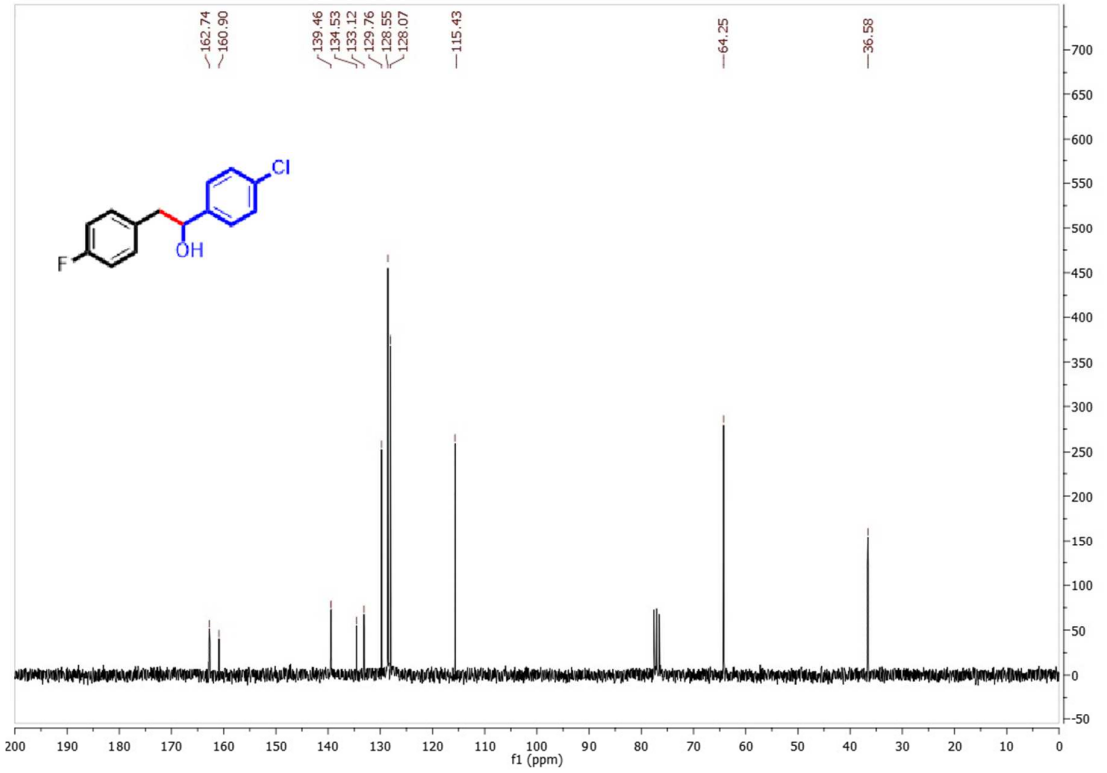
2-(furan-2-yl)-1-(thiophen-2-yl)ethanol (4g).





1-(4-Chlorophenyl)-2-(4-fluorophenyl)ethanol (4h).





4-(1-Hydroxy-2-mesitylethyl)benzonitrile (4i).