

Supporting Information

Bioinspired Aerobic Oxidation of Alcohols with a Bifunctional Ligand Based on Bipyridine and TEMPO

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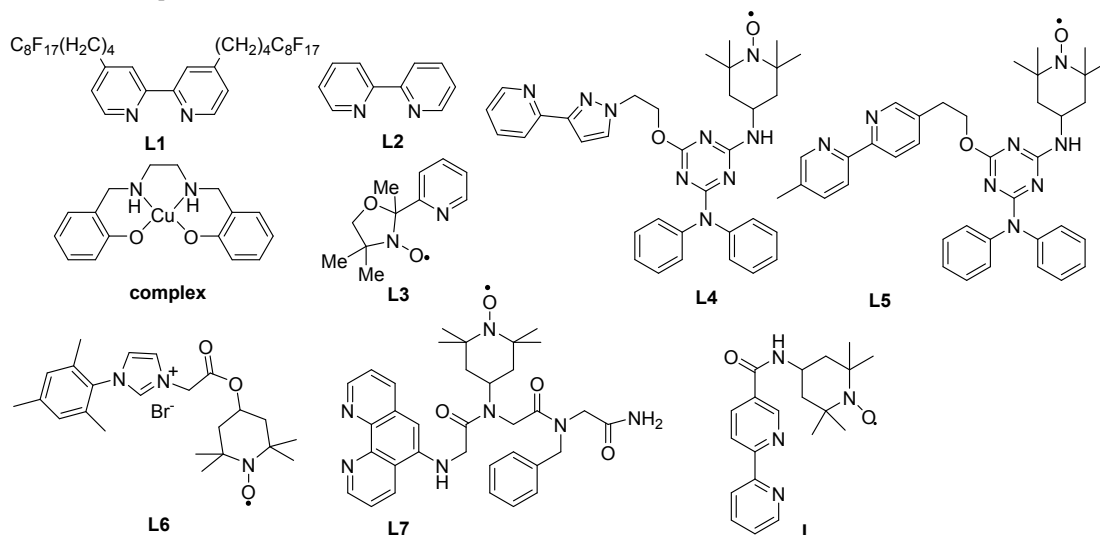
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Table of Contents	Page
Table 1S	S2-S3
The Synthetic Procedure and Characterization of bpy-TEMPO	S4
Copies of NMR Spectra	S5-S14

Table 1S Previous work on air/oxygen-based aerobic alcohol oxidations employing the copper and TEMPO catalytic system

Entry	Substrate scope	Catalyst system	Ligand	Reaction conditions	Yields (%)	Examples	Ref
1	Benzylic, allylic, 1° aliphatic	10mol%CuCl, 10mol% TEMPO		DMF, rt, 1 atm O ₂ , 1-7 h	85-96	8	1
2	Benzylic, allylic, 1° and 2° aliphatic	2mol% CuBr ₂ ·Me ₂ S, 2mol% L1, 3.5-10 mol% TEMPO	L1	C ₈ F ₁₇ Br/PhCl, 90 °C, O ₂ , 1-10 h	69-97	21	2
3	Benzylic, allylic, 1°aliphatic	5 mol% CuBr ₂ , 5 mol% L2, 5 mol% <i>t</i> -BuOK,	L2	CH ₃ CN:H ₂ O = 2:1, rt, air, 2.5-24 h	61-100	4	3
4	Benzylic, allylic, 1°aliphatic	5 mol% TEMPO, 5 mol% complex	complex	Toluene, 100 °C, O ₂ , 9-26 h	70-99	12	4
5	Benzylic, allylic, 1°aliphatic	3 mol% CuBr ₂ or Cu(OTf) ₂ , 3 mol% L2, 6 mol% NMI or DBU	L2	CH ₃ CN, rt, 1 atm O ₂ , 1-5 h,	55-94	11	5
6	Benzylic, allylic, 1°aliphatic	5 mol% CuBr ₂ , 5 mol% L3, 5 mol% <i>t</i> -BuOK,	L3	CH ₃ CN:H ₂ O = 2:1, rt, air, 84 h	64-96	17	6
7	Benzylic, allylic, propargylic, 1° aliphatic	5mol% Cu(CH ₃ CN) ₄ X, X = OTf, BF ₄ ⁻ , PF ₆ ⁻ , 5mol%L2, 5mol%TEMPO, 10 mol% NMI	L2	CH ₃ CN, rt, air or O ₂ , 1-24 h	79-98	37	7
8	Benzyl alcohol	5mol%CuBr ₂ , 5mol%L4, 5mol% <i>t</i> -BuOK	L4	CH ₃ CN:H ₂ O = 2:1, 50 °C, O ₂ , 24 h	84 (conv.)	1	8
9	Benzylic, allylic, 1°aliphatic	5mol%CuBr ₂ , 5mol%L5, 5mol% <i>t</i> -BuOK	L5	CH ₃ CN:H ₂ O = 2:1, 50 °C, O ₂ , 2-10 h	61-100 (conv.)	3	9
10	Benzylic, allylic, propargylic, 1° aliphatic	10mol%Cu, 10 mol% L6	L6	C ₆ H ₅ Cl, 80 °C, air, 15 h	trace to 99	25	10
11	Benzylic, allylic, 1°aliphatic	0.5mol%L7, 0.5mol% [Cu(MeCN) ₄]OTf, 1 mol% NMI	L7	CH ₃ CN, rt, air, 3-24 h	94-99	8	11

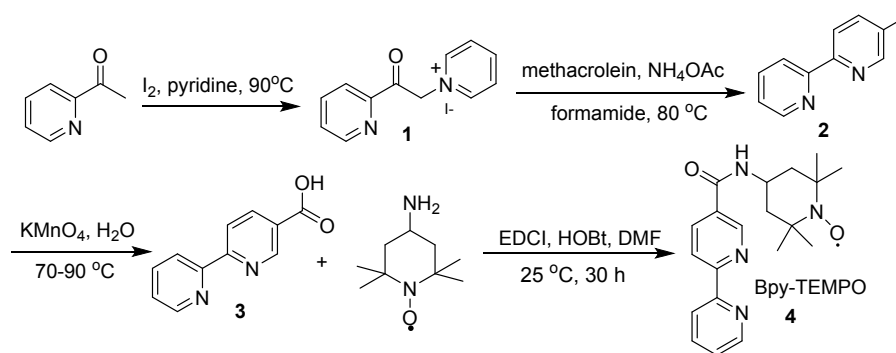
12	1° and 2° benzylic, allylic, alkynyl, 1°aliphatic	5 mol% CuI, 5 mol% L, 10 mol% NMI	L	CH ₃ CN, rt, air, 1.5-24 h	72-99	28	Present work
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References

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The Synthetic Procedure and Characterization of bpy-TEMPO



Scheme 1S Synthetic route of the bpy-TEMPO ligand

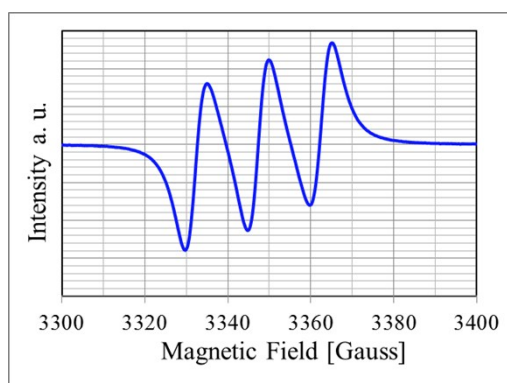
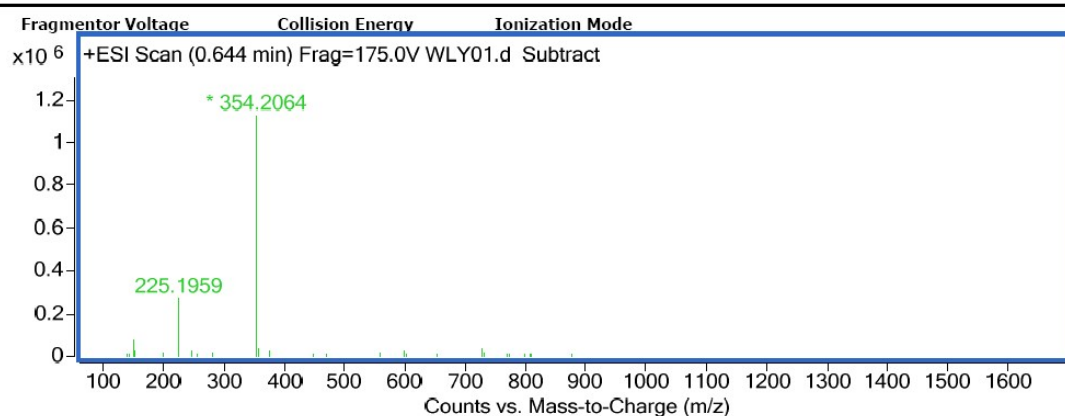


Figure 1S EPR signal of a solution of bpy-TEMPO in MeCN under ambient atmosphere at room temperature.

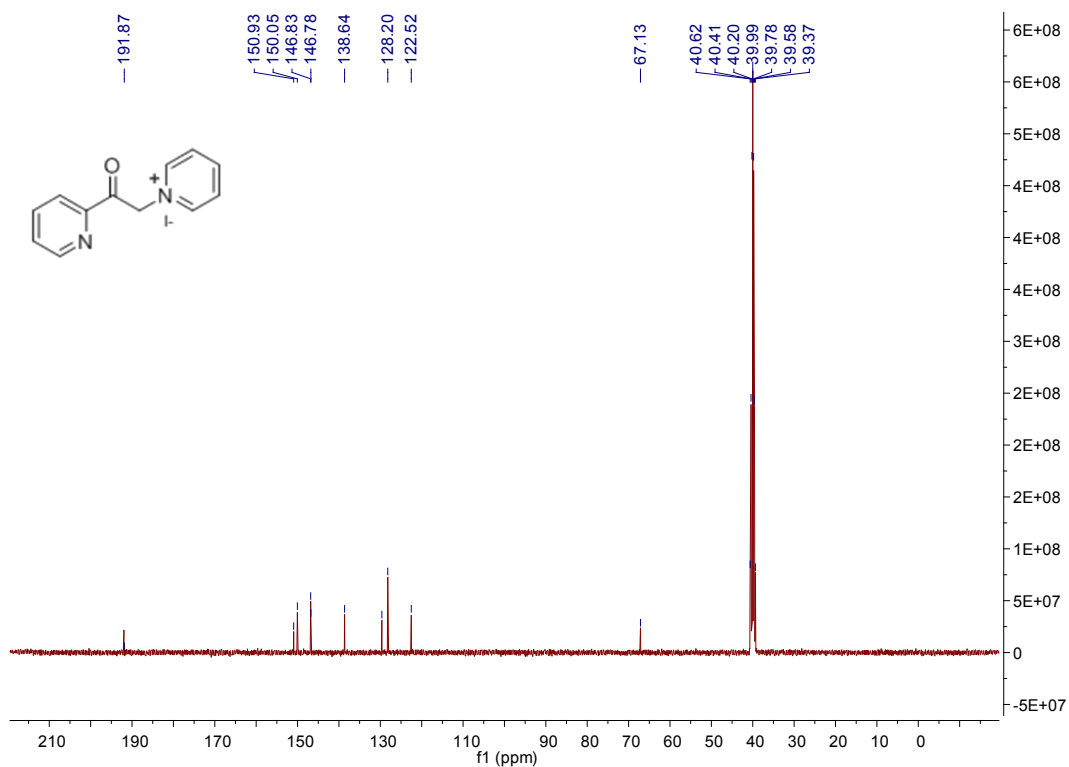
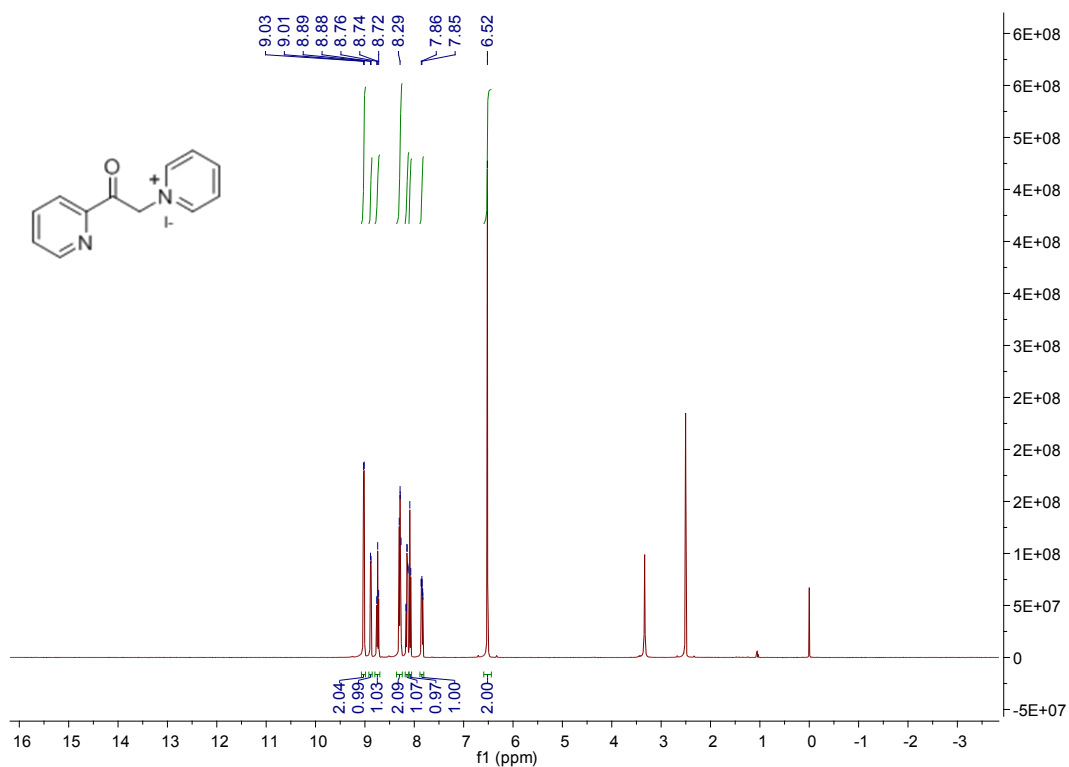
Mass data and spectra

HRMS (ESI) for $C_{20}H_{26}N_4O_2$ $[M+H]^+$, calcd: 354.2011, found: 354.2064

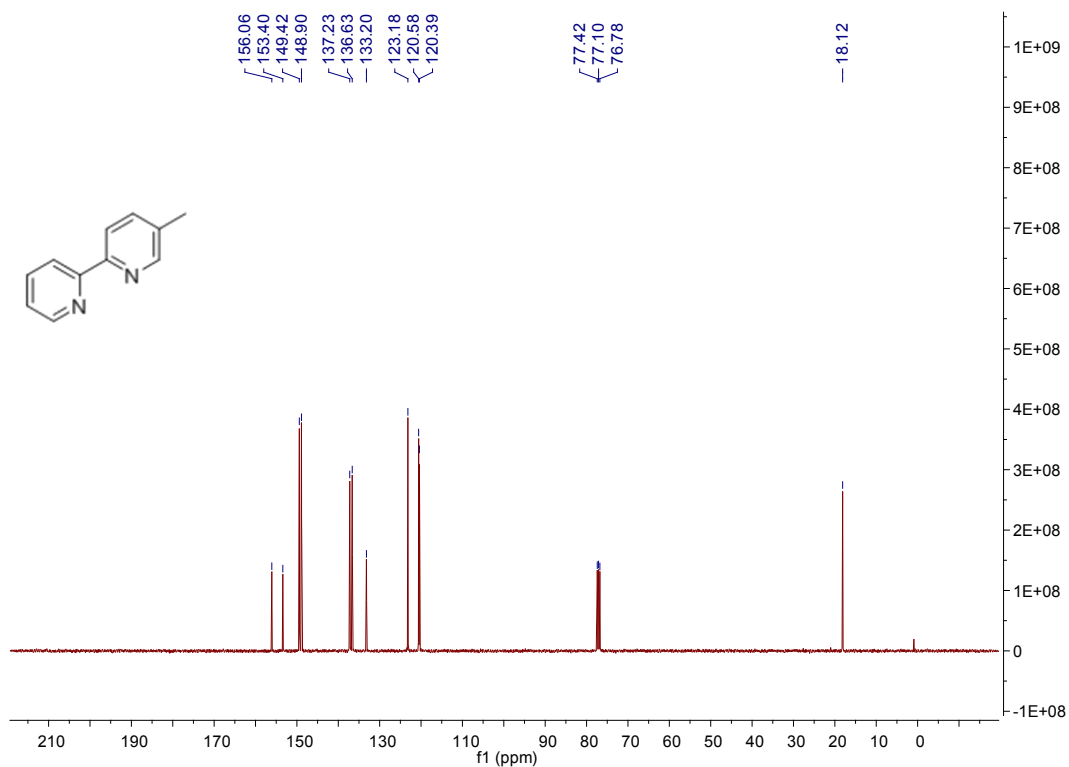
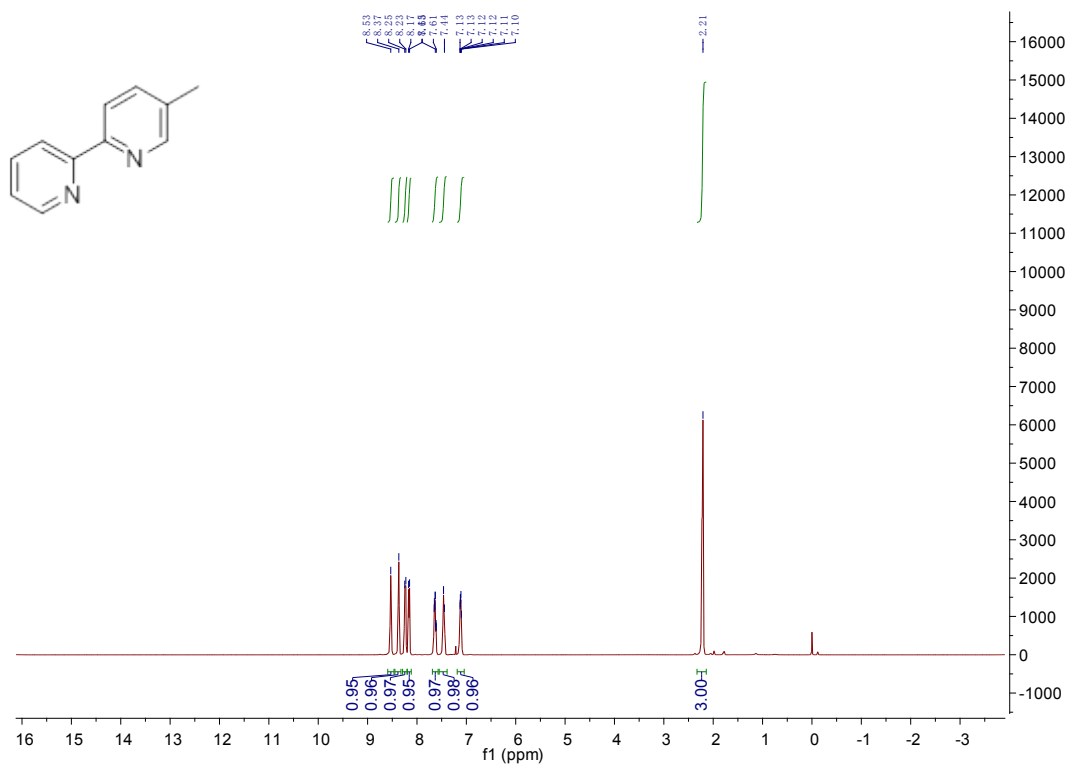
User Spectra



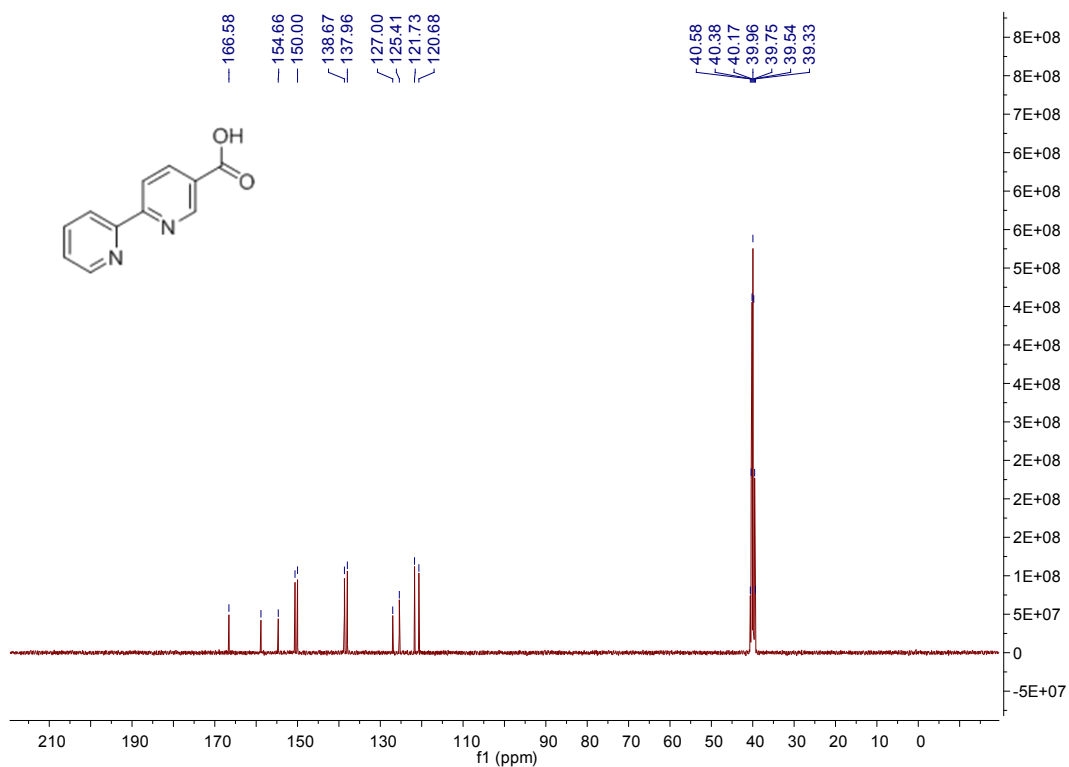
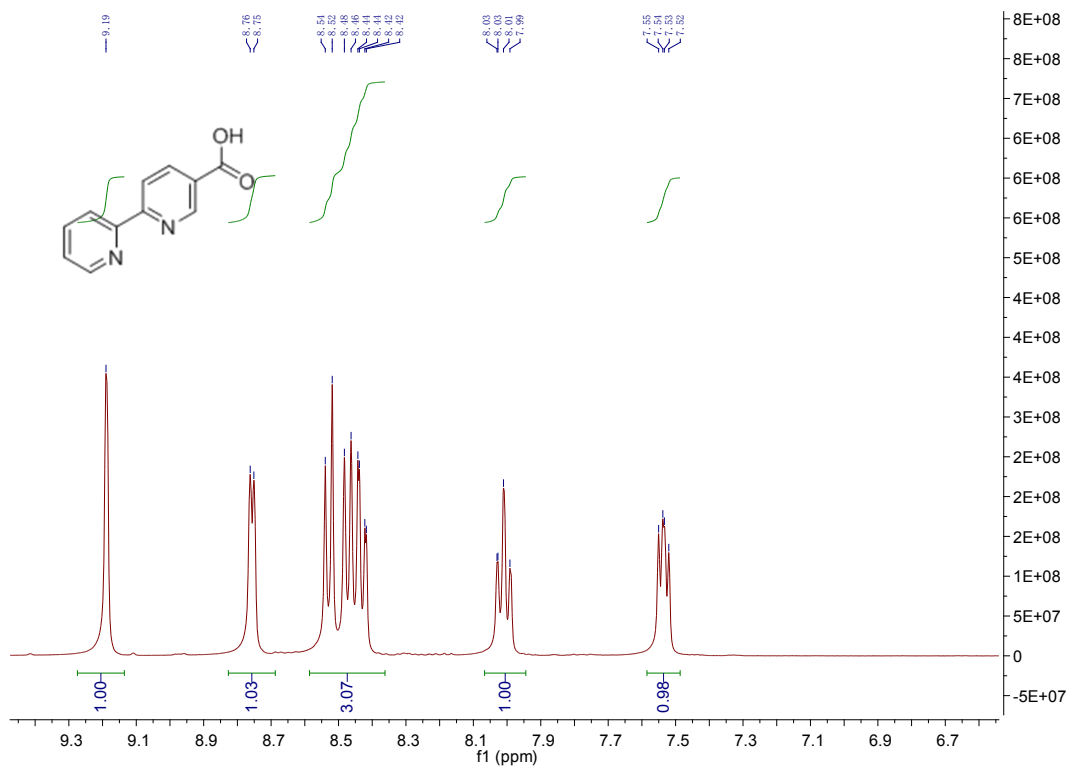
1-(2-Pyridylacetyl)pyridinium iodide



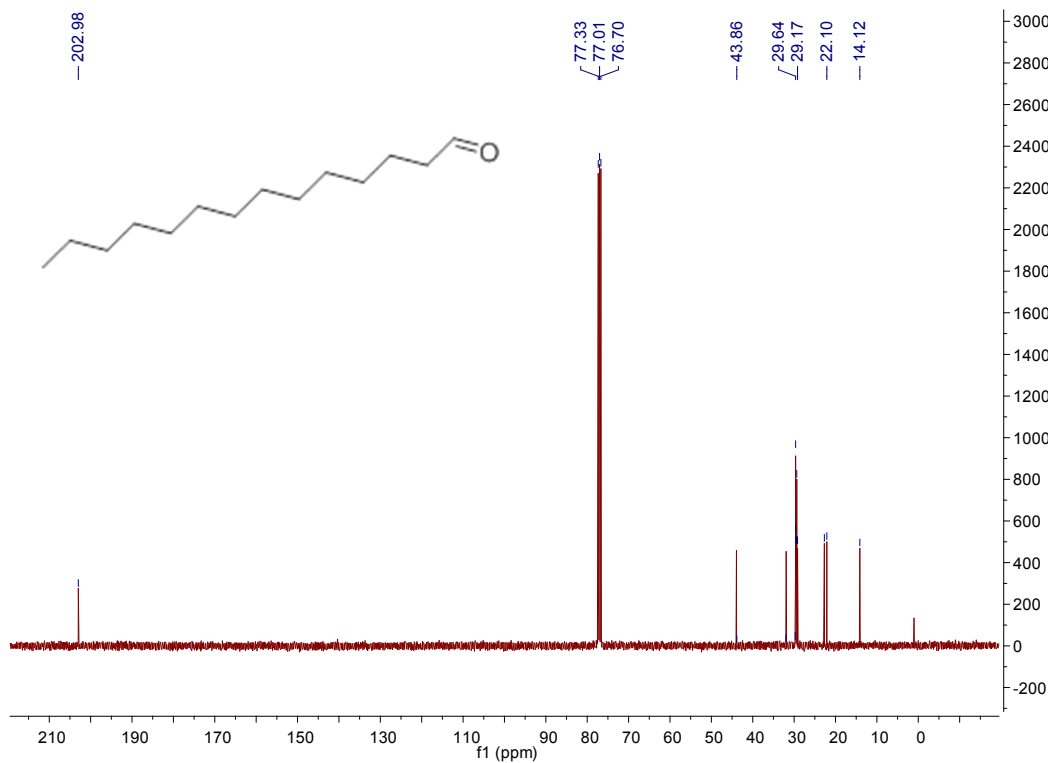
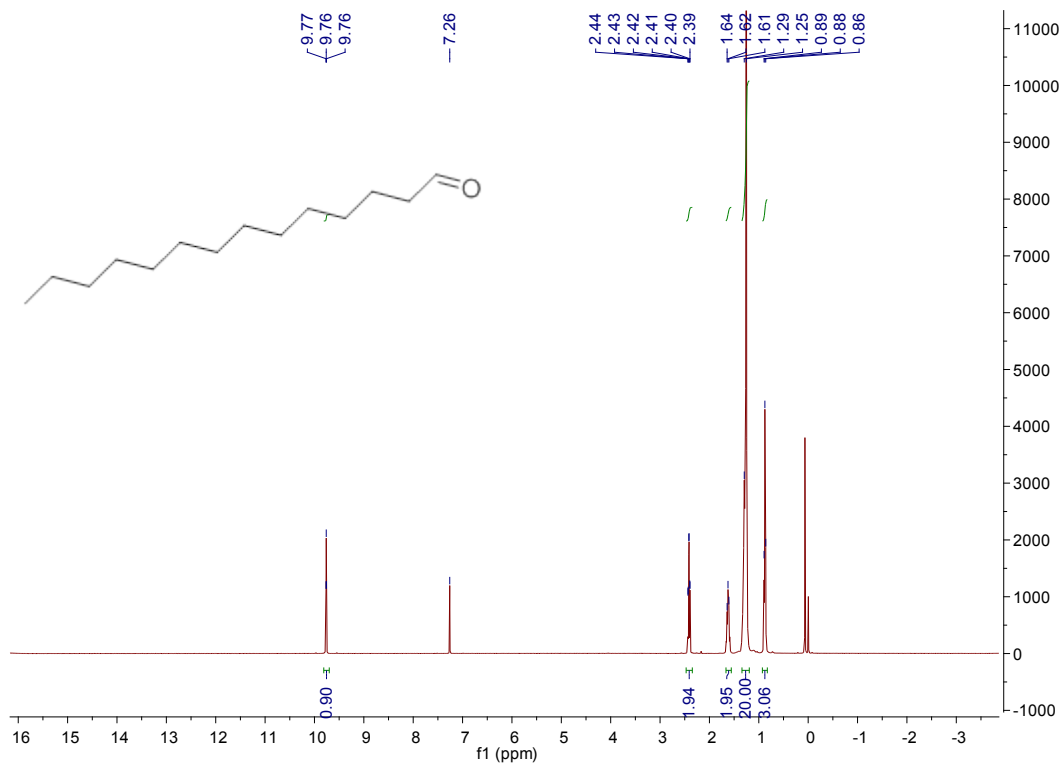
5-Methyl-2,2'-bipyridine



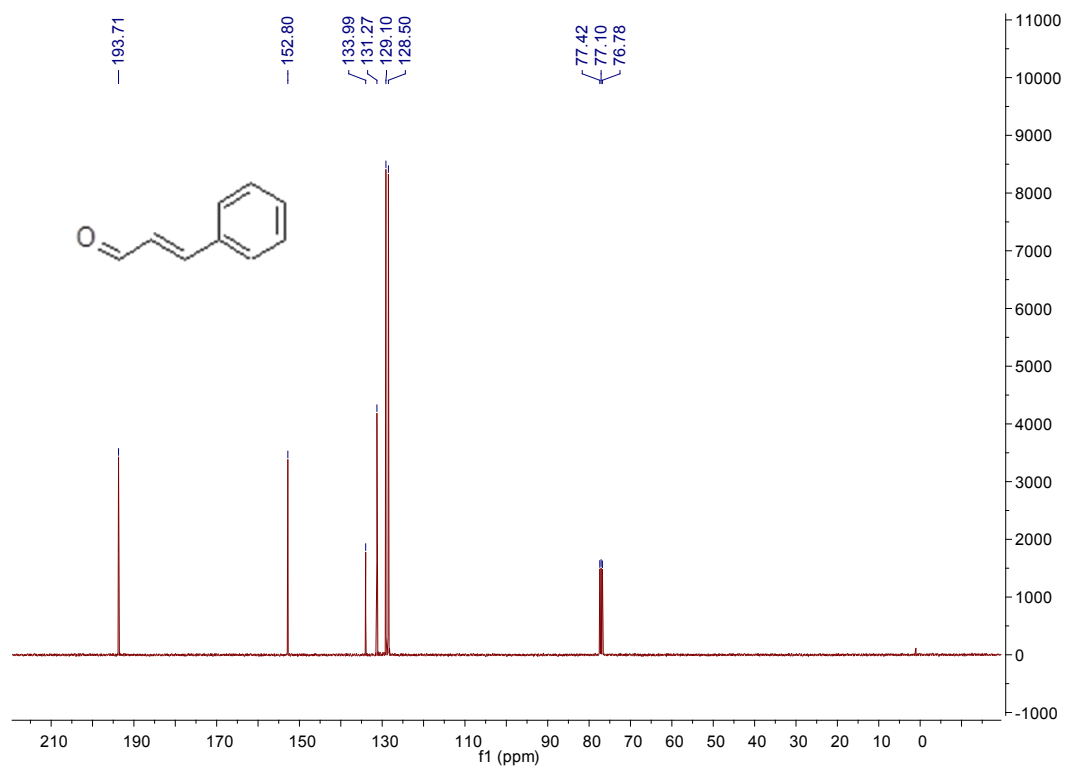
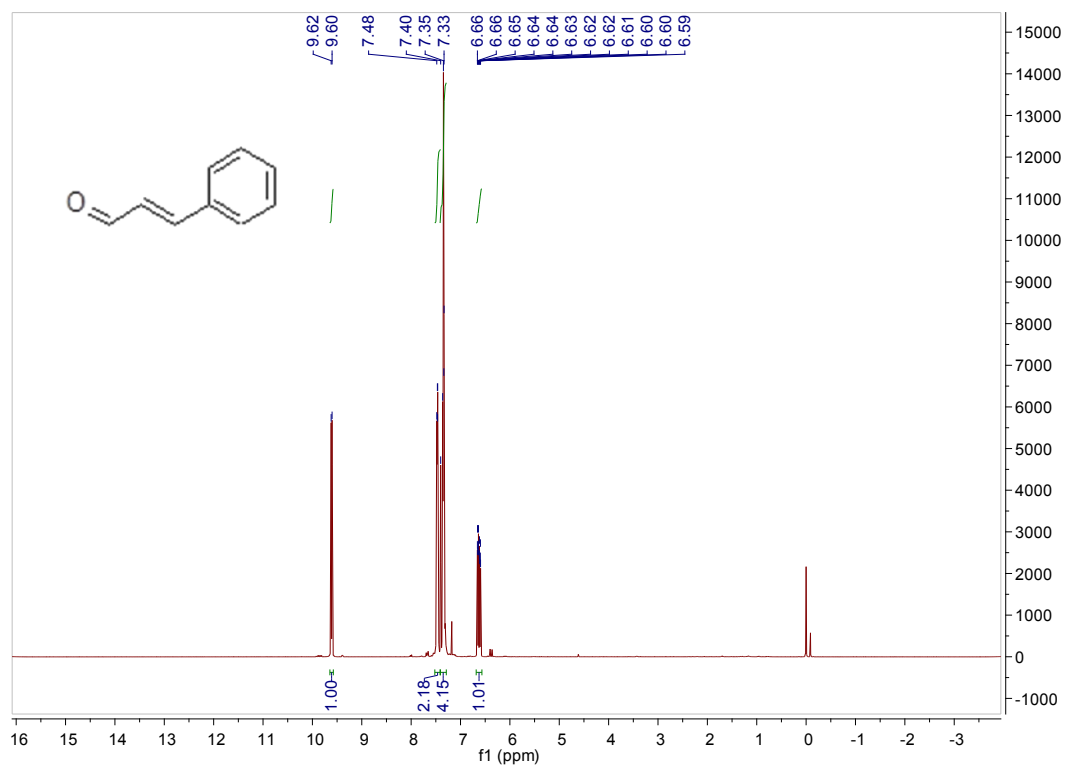
2,2-Bipyridinyl-5-carboxylic acid



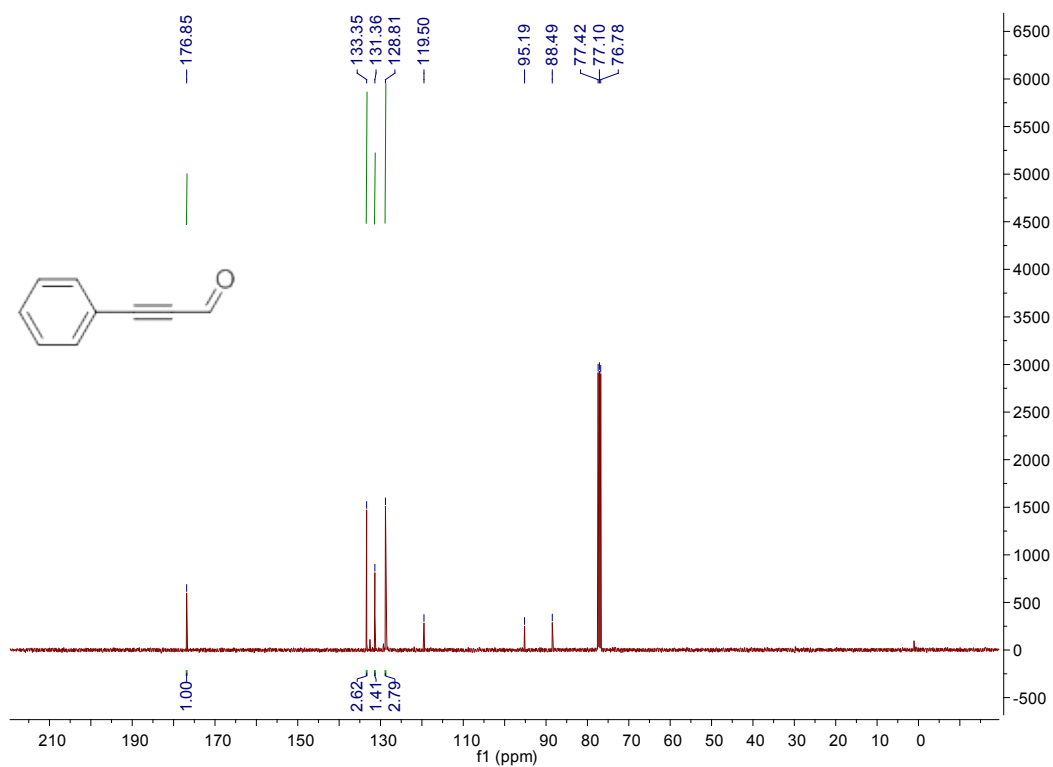
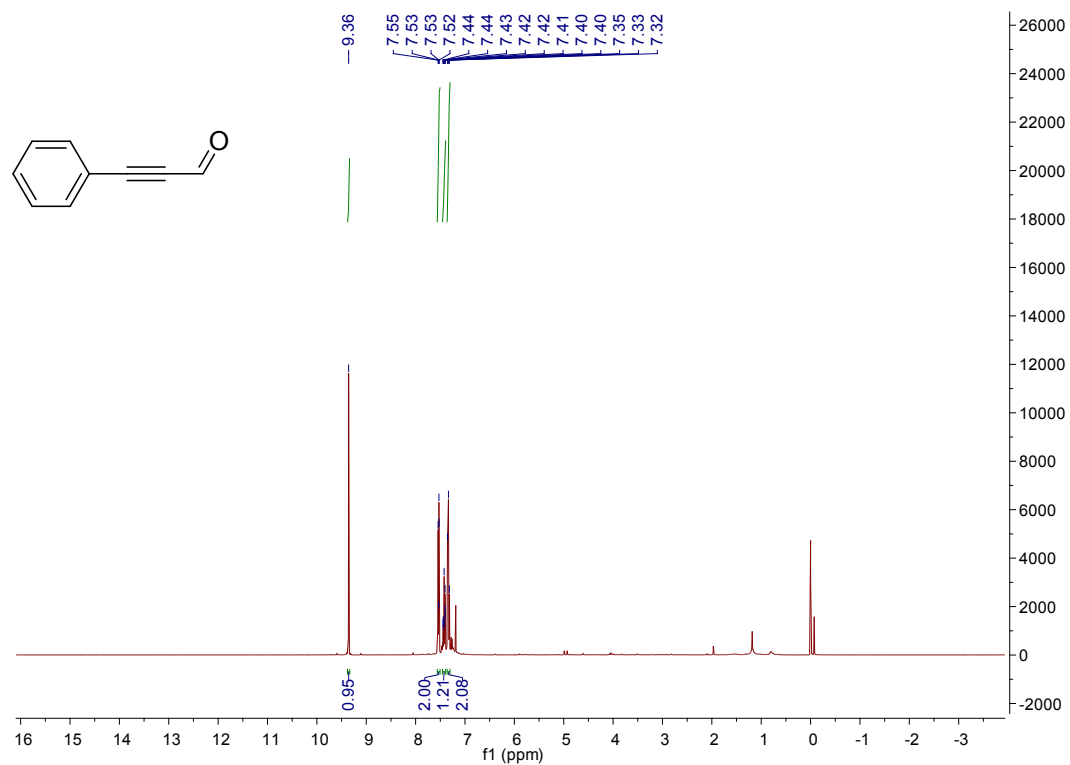
Tetradecanal (Table 2, entry 3)



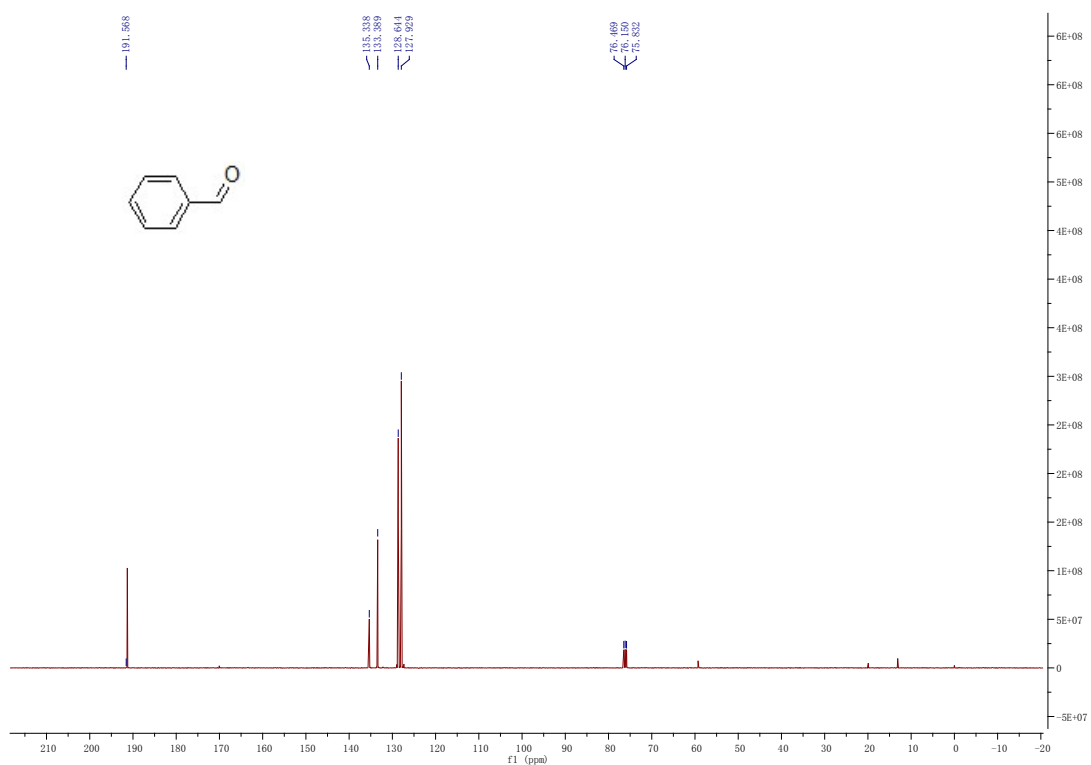
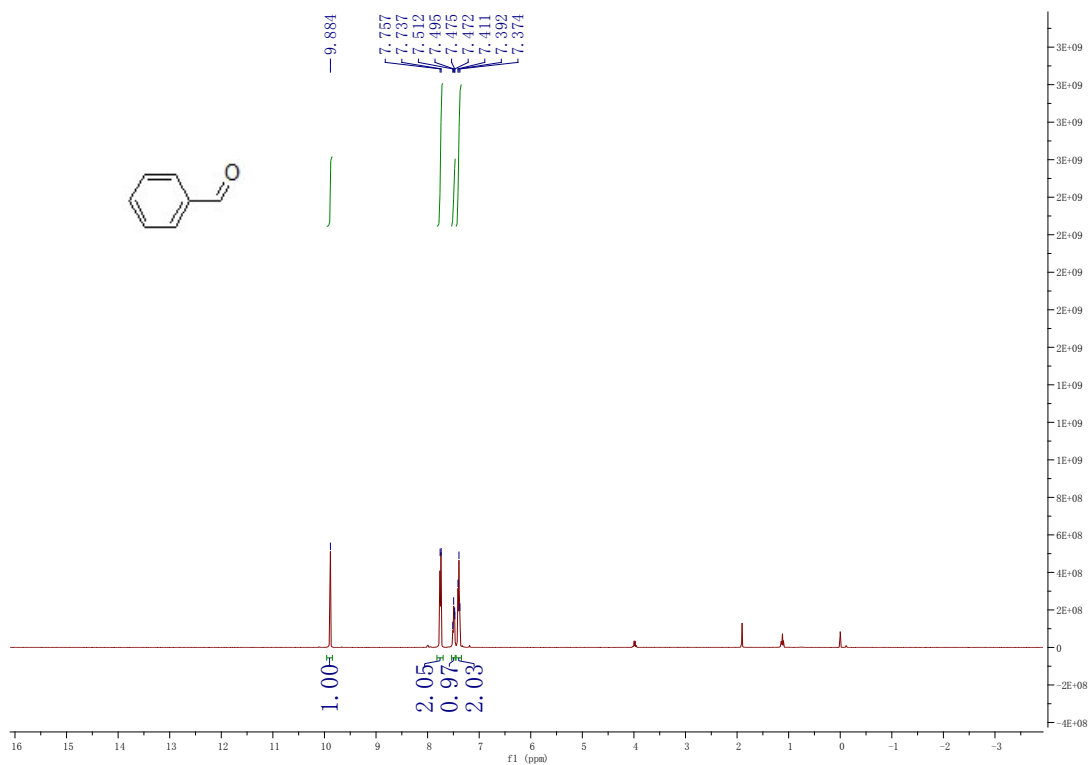
Cinnamaldehyde (Table 2, entry 9)



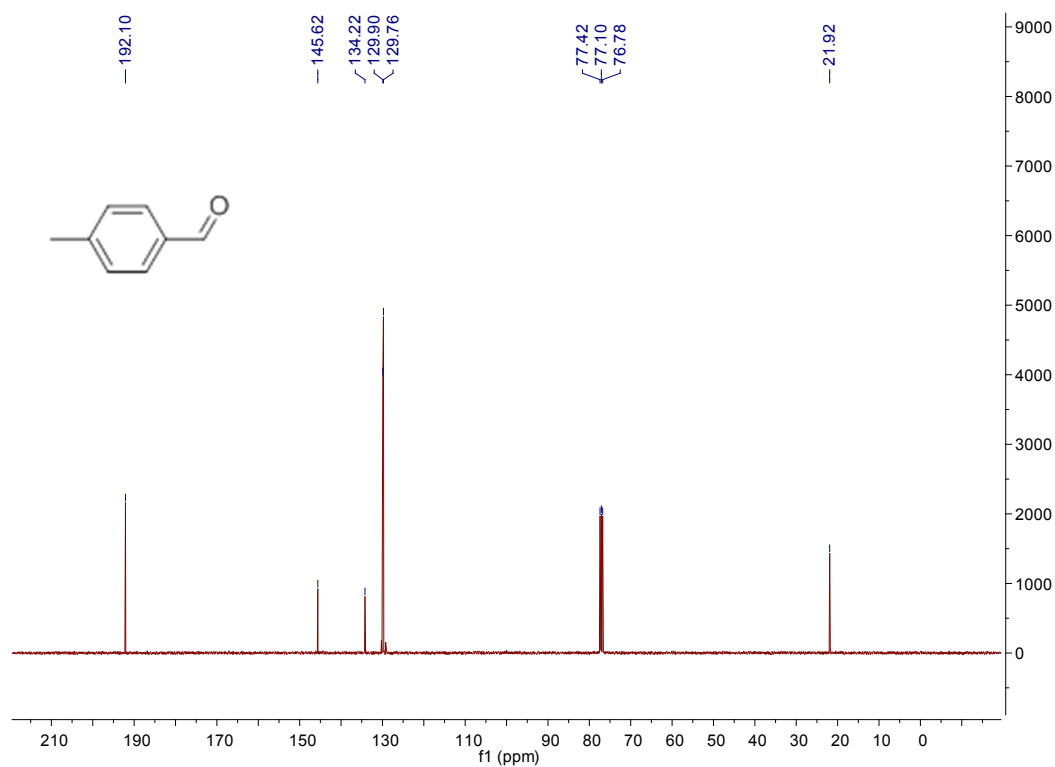
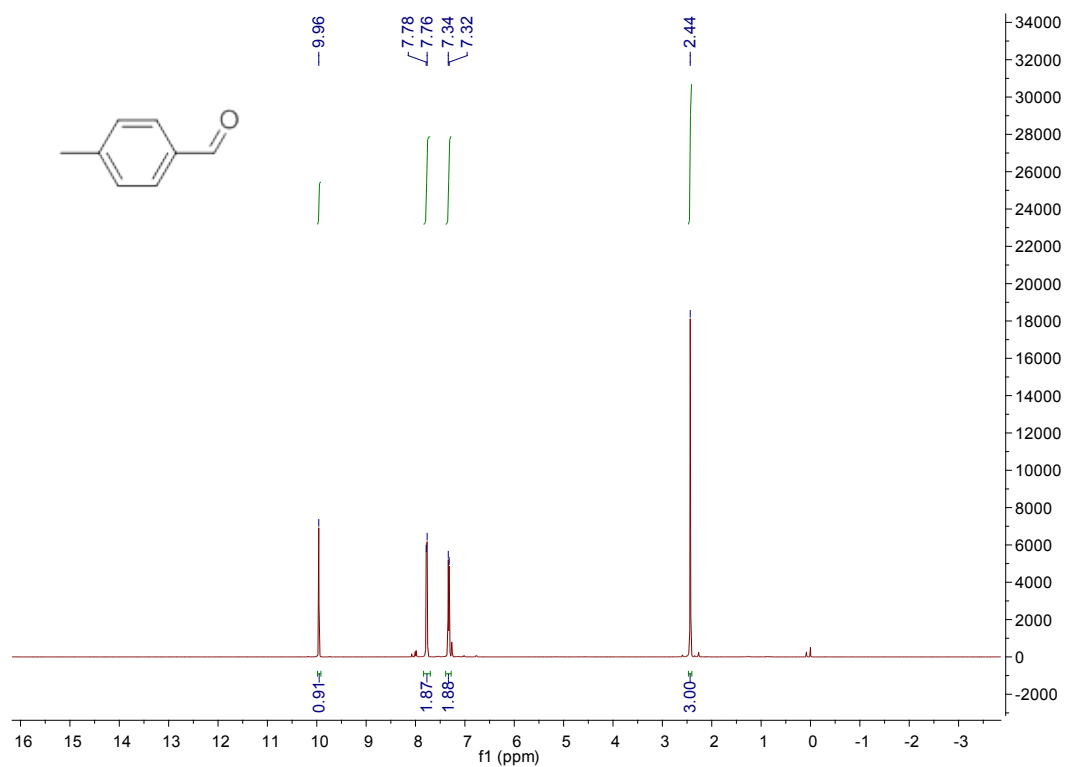
Phenylpropiolaldehyde (Table 2, entry 12)



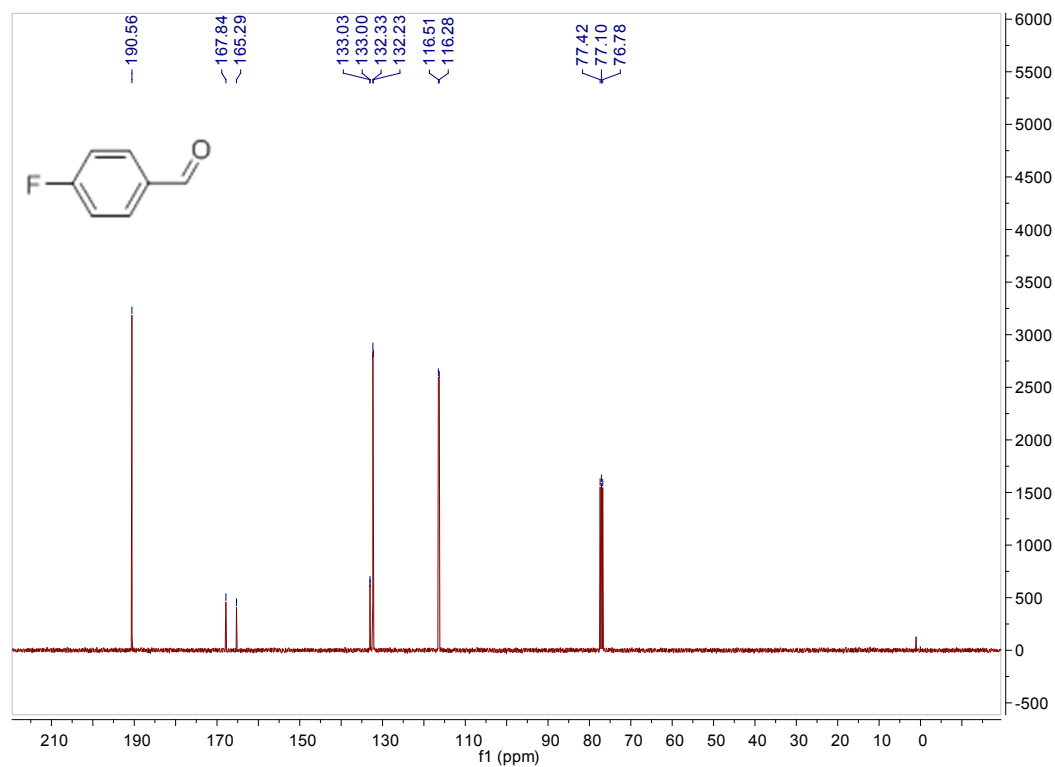
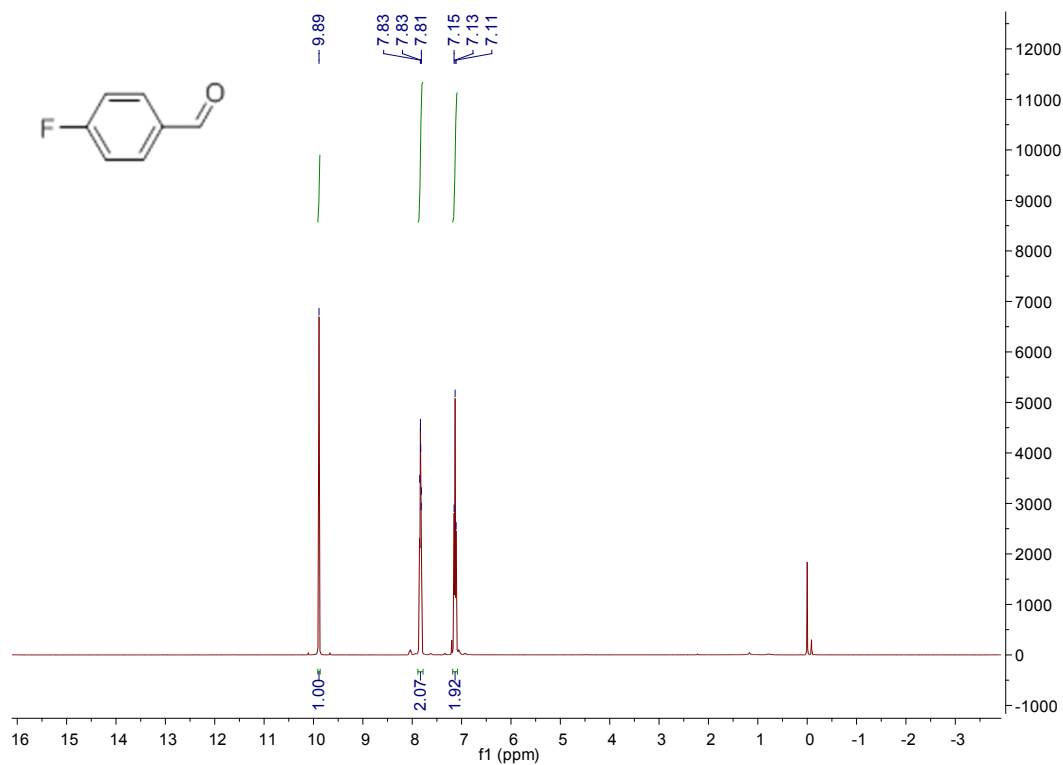
Benzaldehyde (Table 2, entry 14)



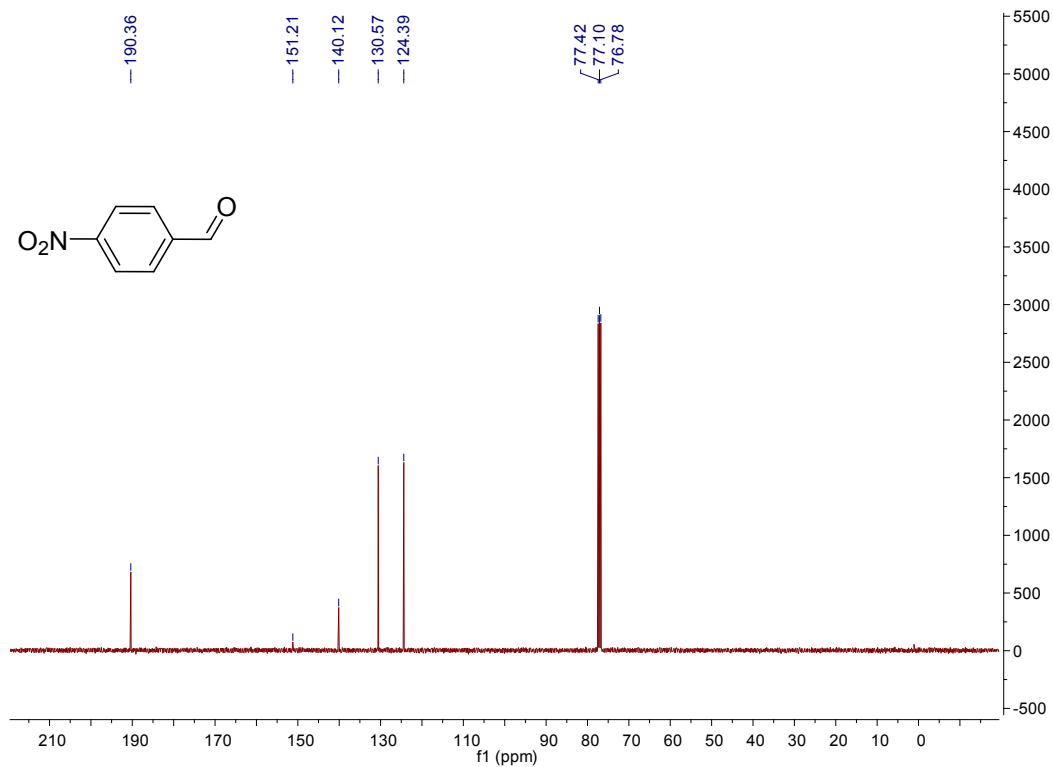
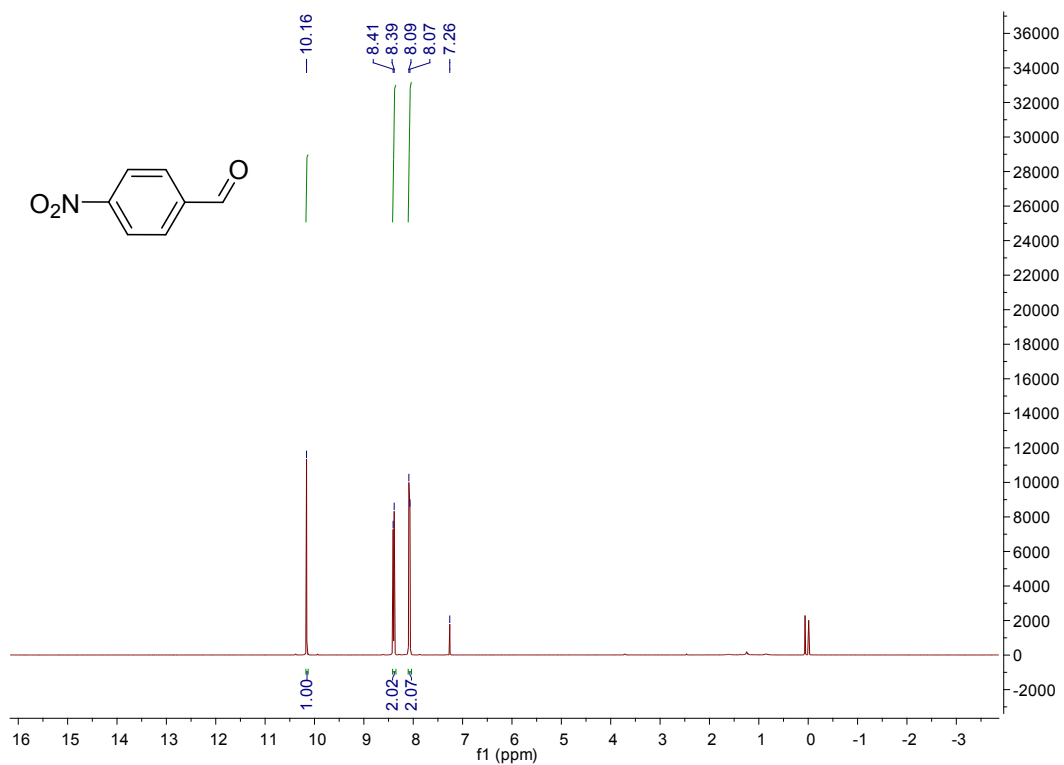
4-Methylbenzaldehyde (Table 2, entry 15)



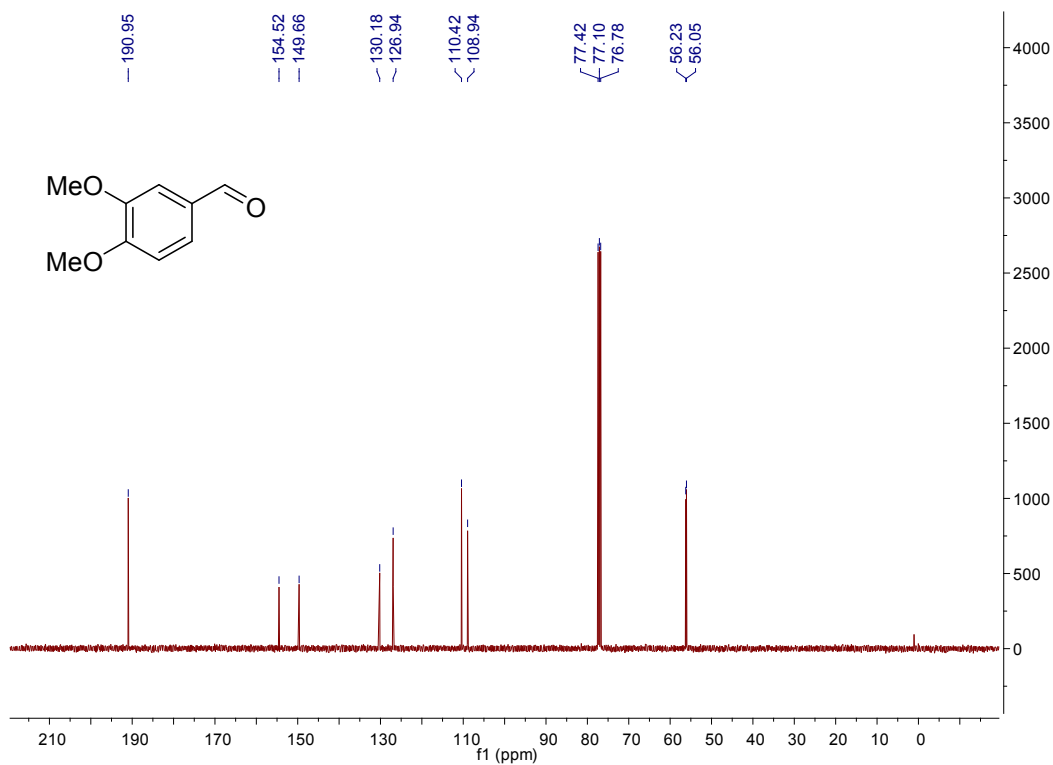
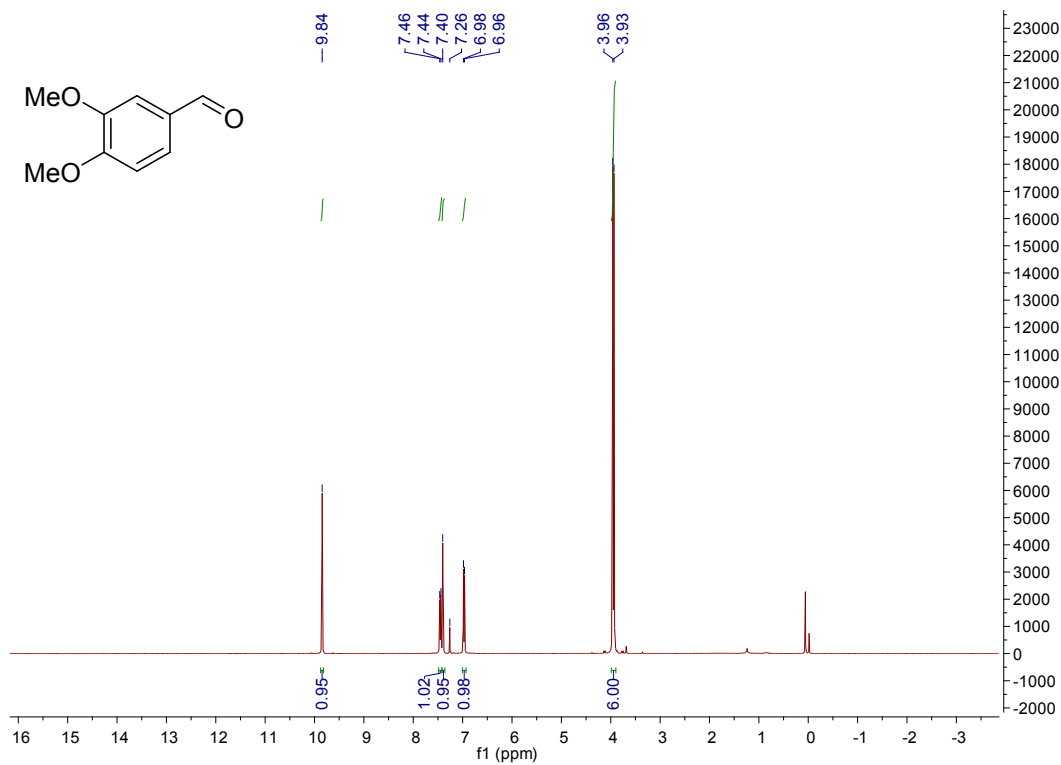
4-Fluorobenzaldehyde (Table 2, entry 18)



4-Nitrobenzaldehyde (Table 2, entry 17)



3,4-Dimethoxybenzaldehyde (Table 2, entry 21)



1-Naphthaldehyde (Table 2, entry 22)

