Advanced Synthesis & Catalysis

Supporting Information

Supporting Information

Selective oxidation of amines to aldehydes or imines using Laccase-mediated bio-oxidation

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Procedure for benzylation of amines: synthesis of **8**,[1] **9**,[2] and **10**[3]

To activated 4Å molecular sieve powder (1.140g) in DMF (8 mL) was added LiOH·H_2O (4.3 mmol) and the suspension was vigorously stirred for 20 min. The starting amine (2 mmol) was added and the mixture was additionally stirred for 45min. To the white suspension was added benzyl bromide (1.6mmol) and the mixture was allowed to stir for 12h at room temperature. After filtration through a sintered glass filter to remove insoluble inorganic salts, the residue was washed with AcOEt (3x2 mL), the combined filtrate was washed with water (3x10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified on silica gel column (cyclohexane: AcOEt 8:2). Spectroscopic data were consistent with those reported in the literature.

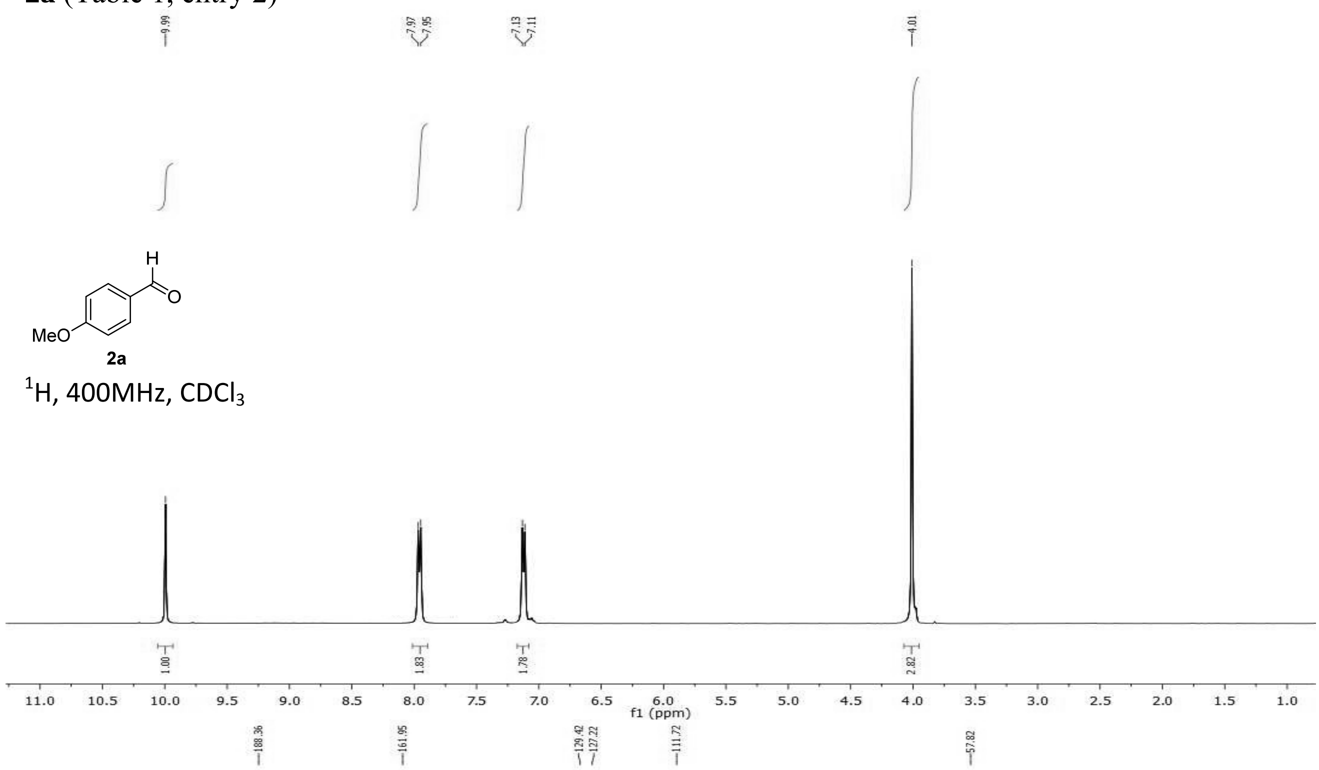
[1]. K. C. Nicolaou , C. J. N. Mathison , T. Montagnon, J. Am. Chem. Soc., **2004**, *126* , 5192–5201.

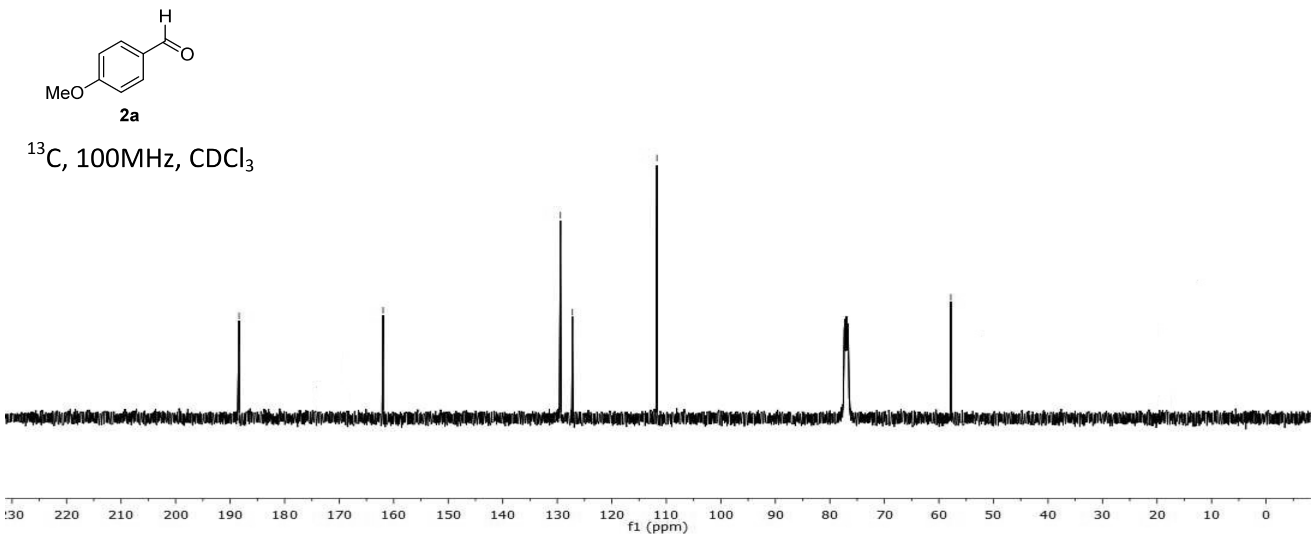
[2]. F. Paradisi, G. Porzi, S. Sandri, Tetrahedron: Asymmetry **2001**, *12*, 3319-3324.

[3]. P. Steunenberg, M. Sijm, H. Zuilhof, J. P. M. Sanders, E. L. Scott, M. C. R. Franssen, *J. Org. Chem.* **2013**, *78*, 3802−3813.

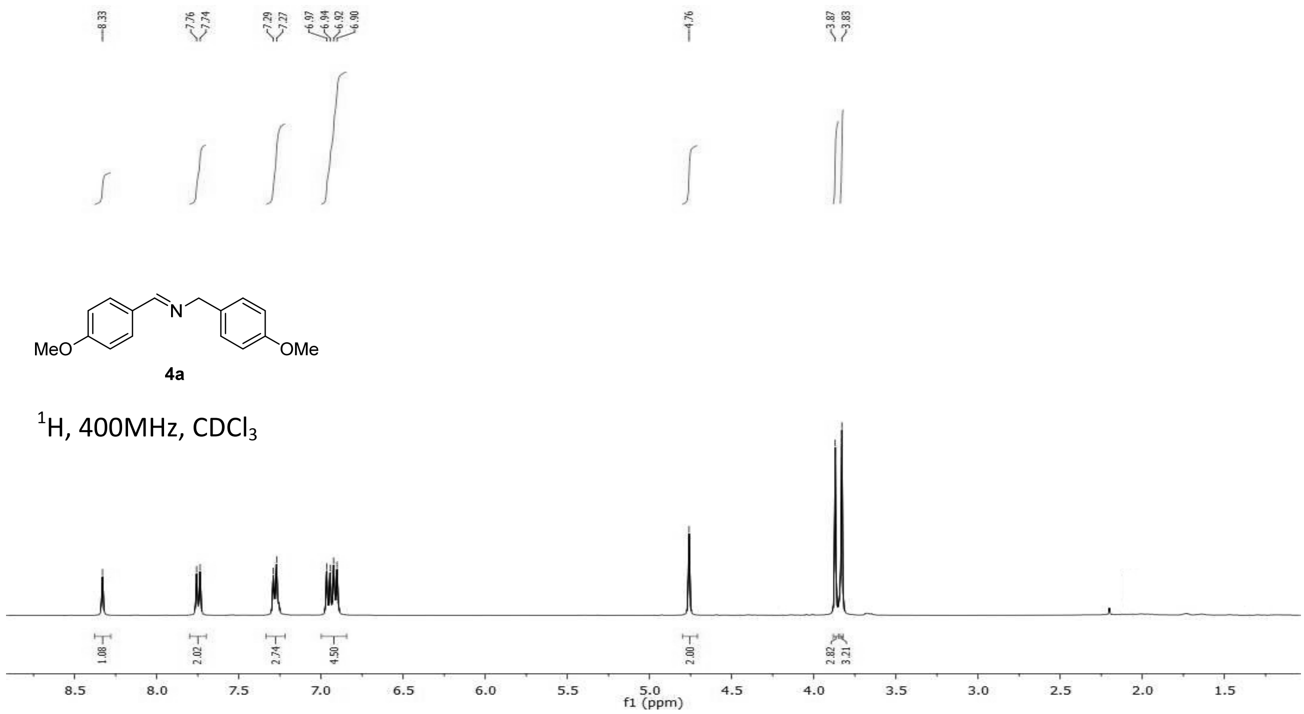
^{1}H NMR and ^{13}C NMR spectra of compounds obtained in Table 1 and 2 after work-up (reaction crudes)

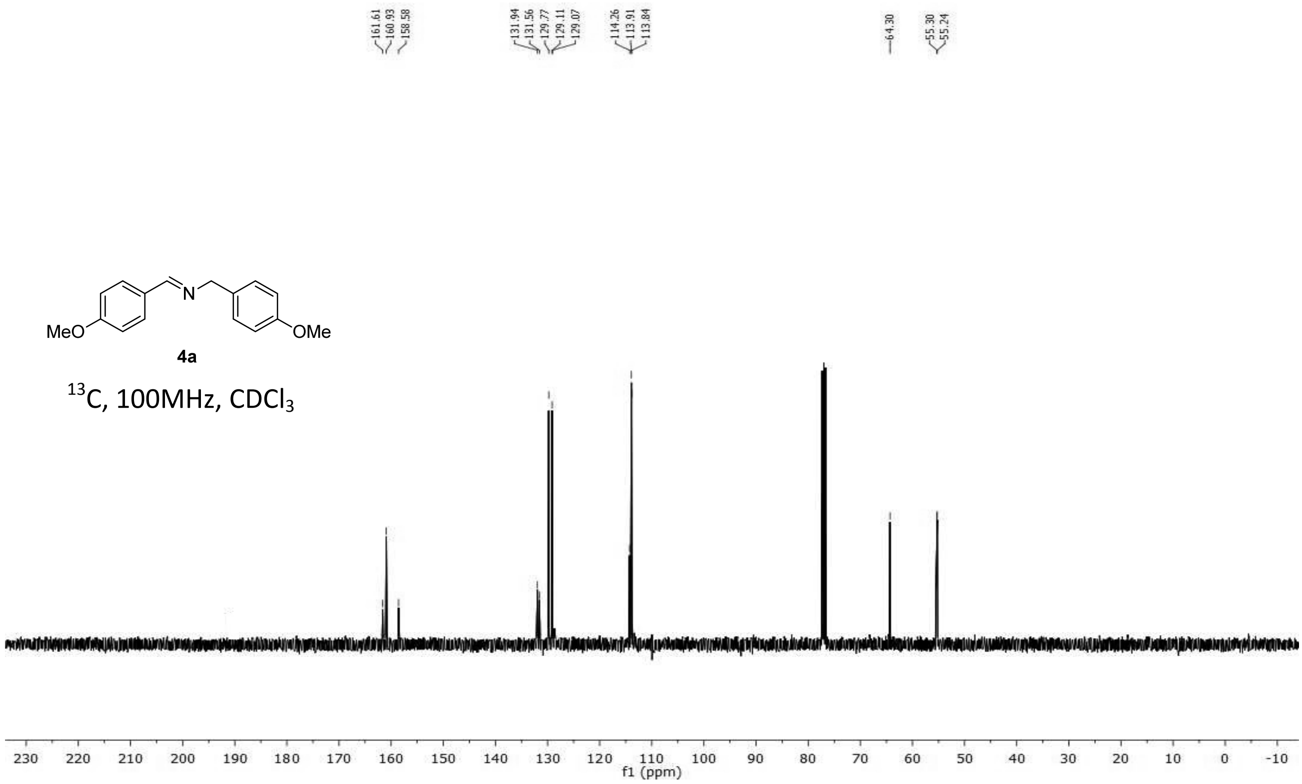
2a (Table 1, entry 2)



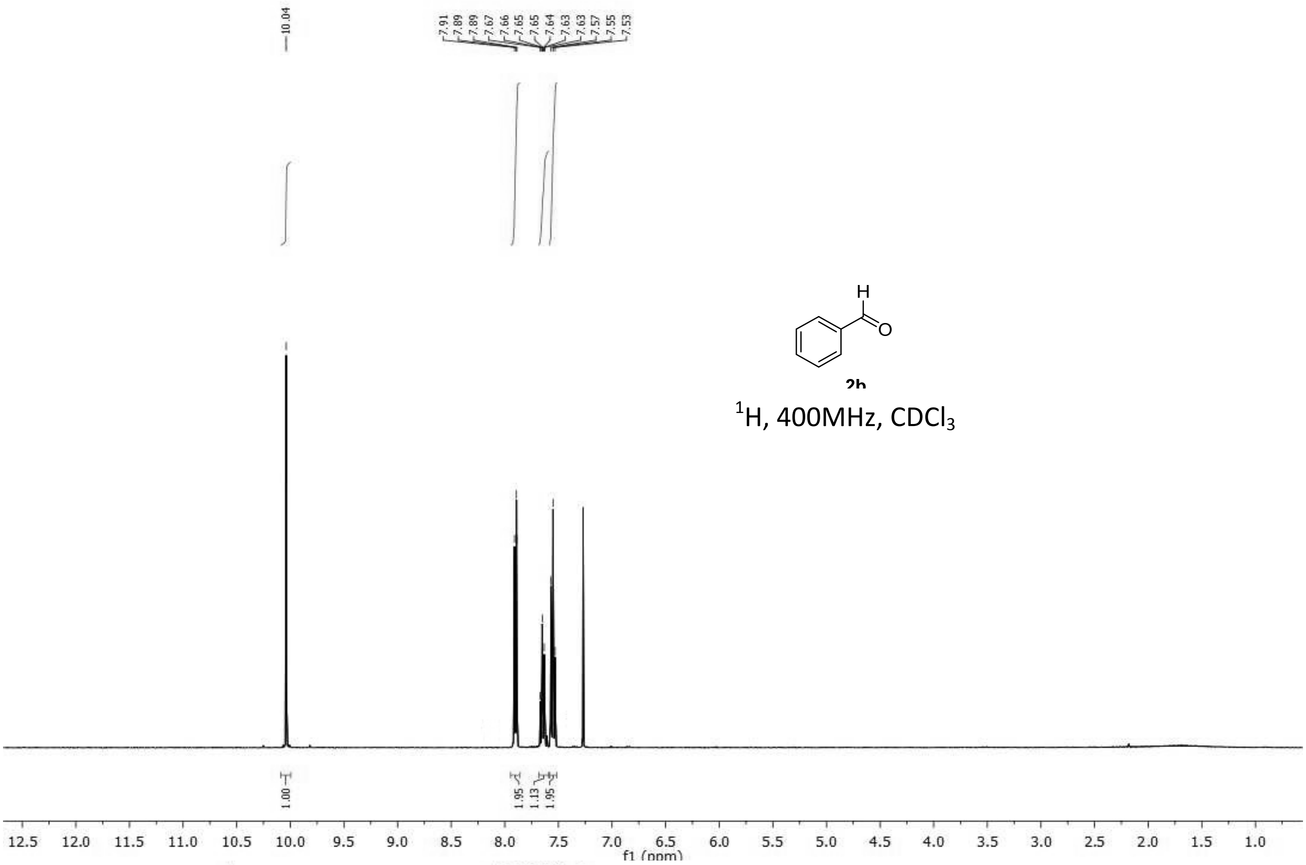


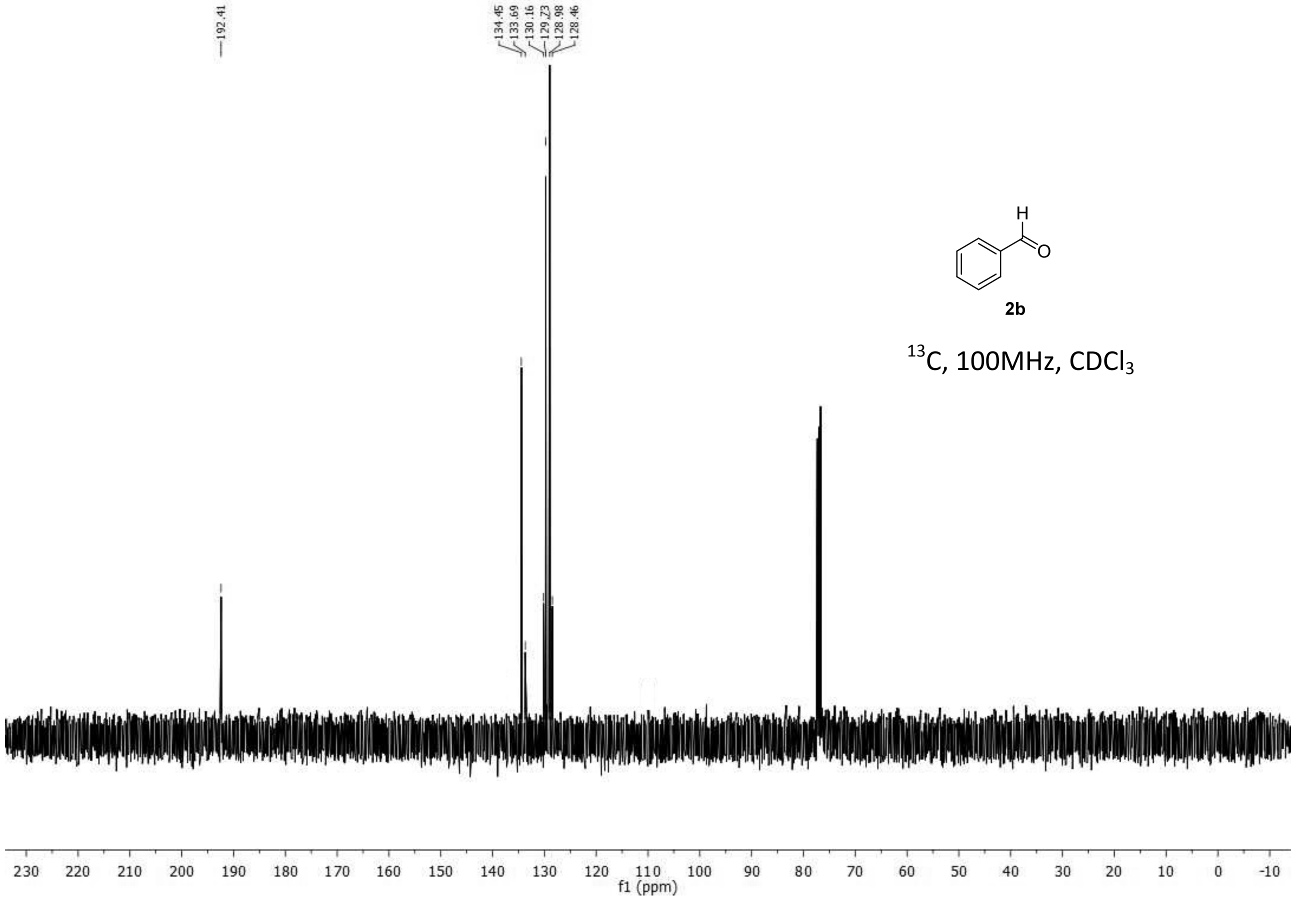
4a (Table 1, entry 18)



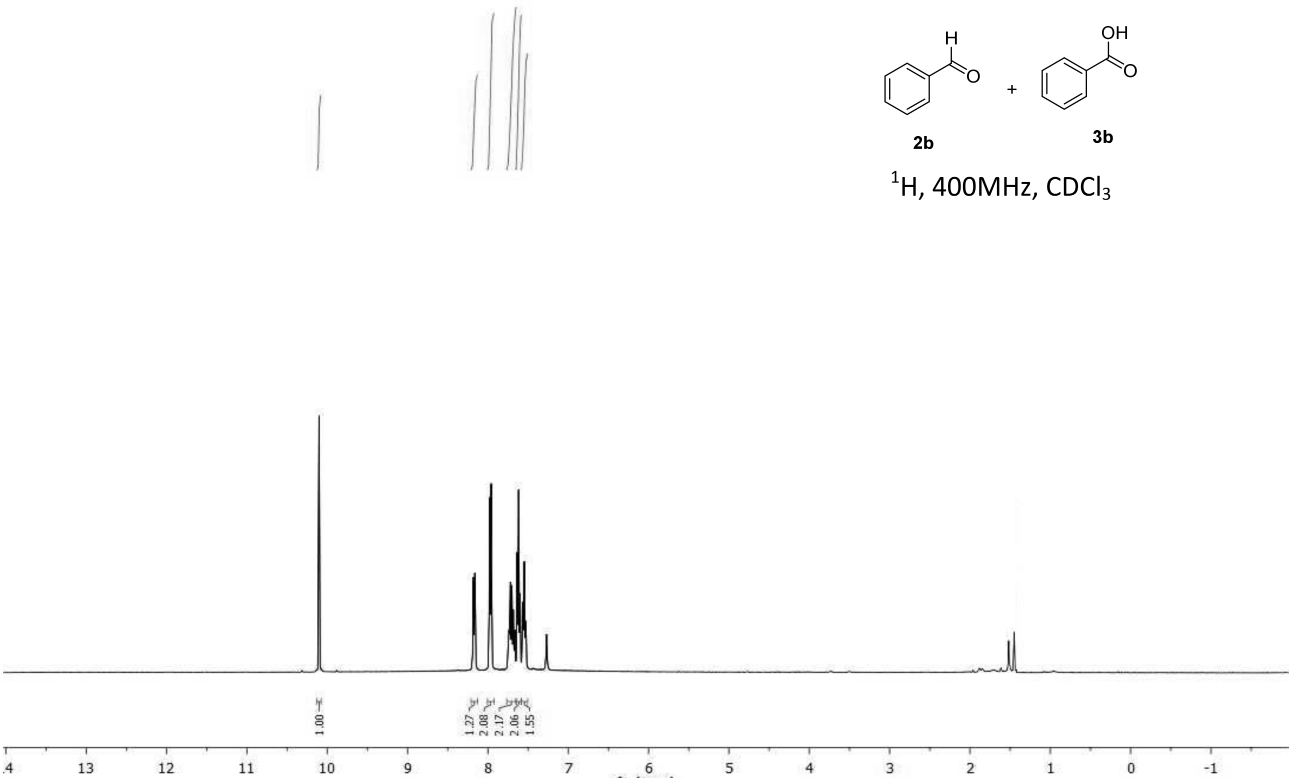


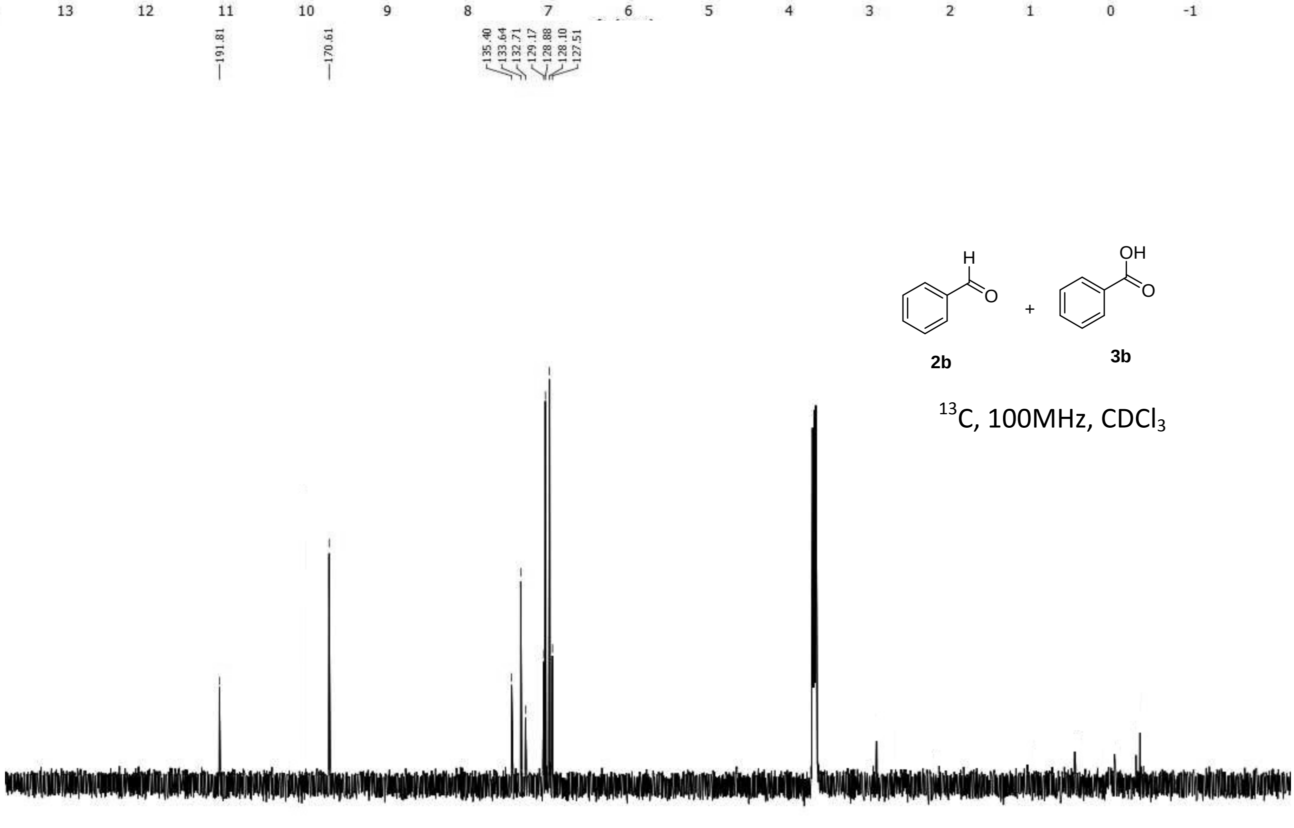
2b (Table 1, entry 19)



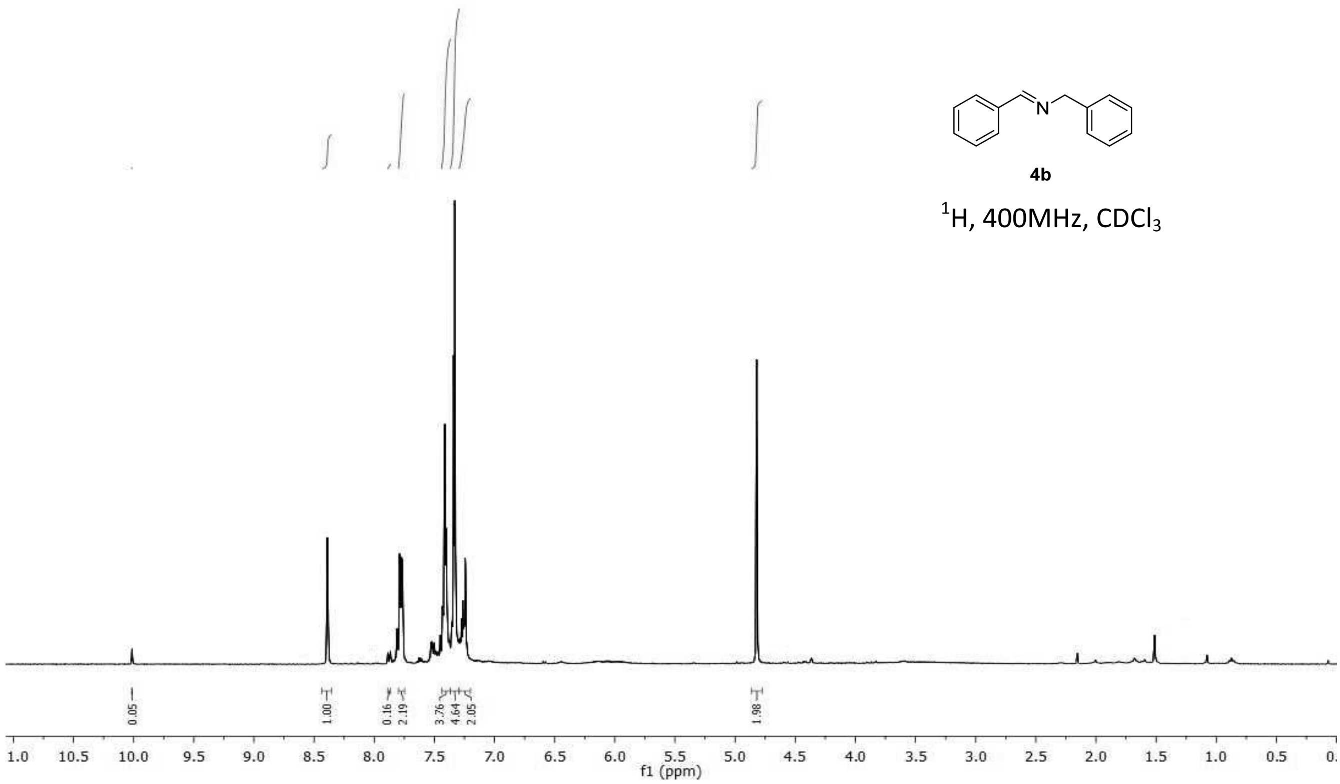


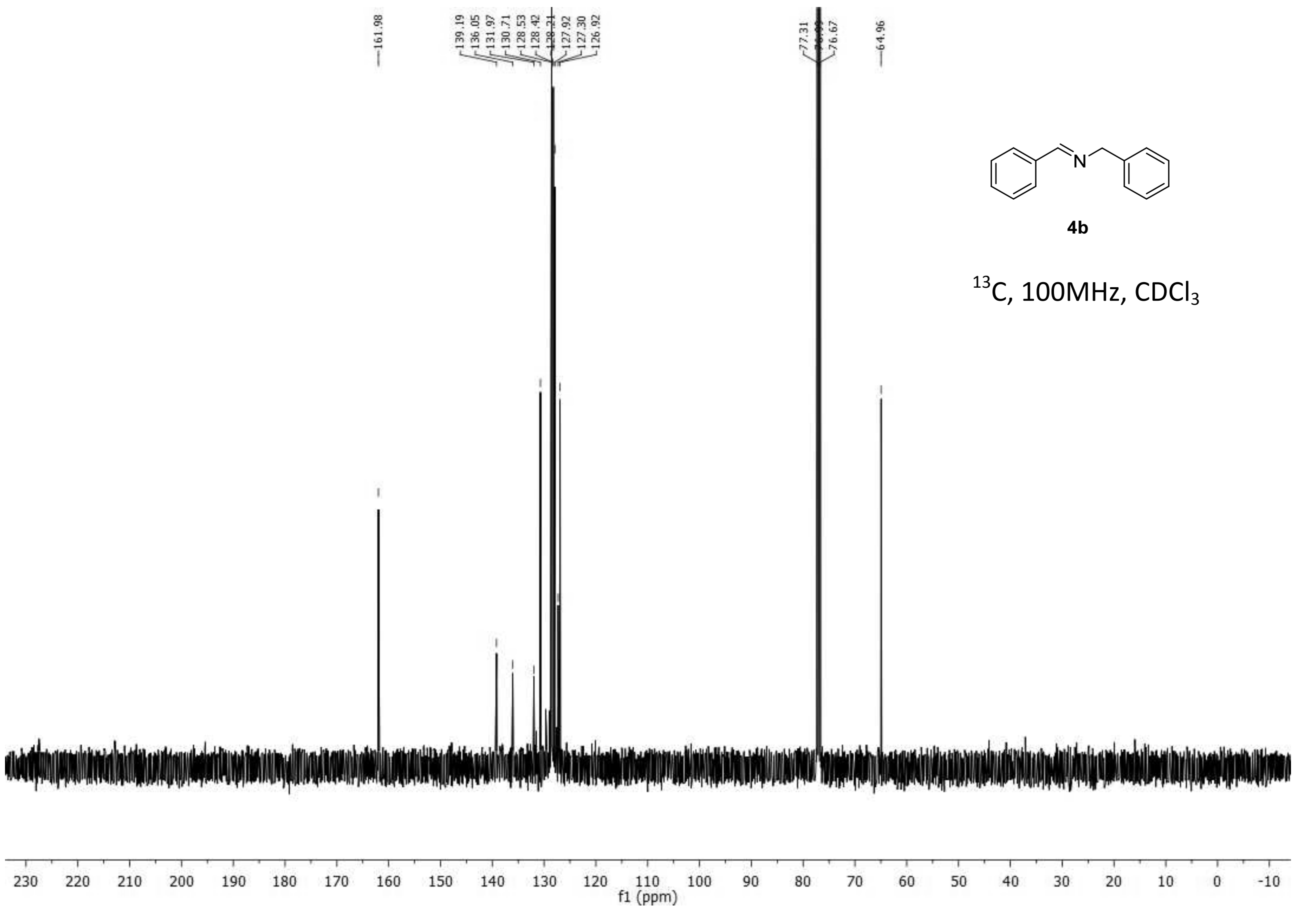
2b + 3b (Table 1, entry 20)



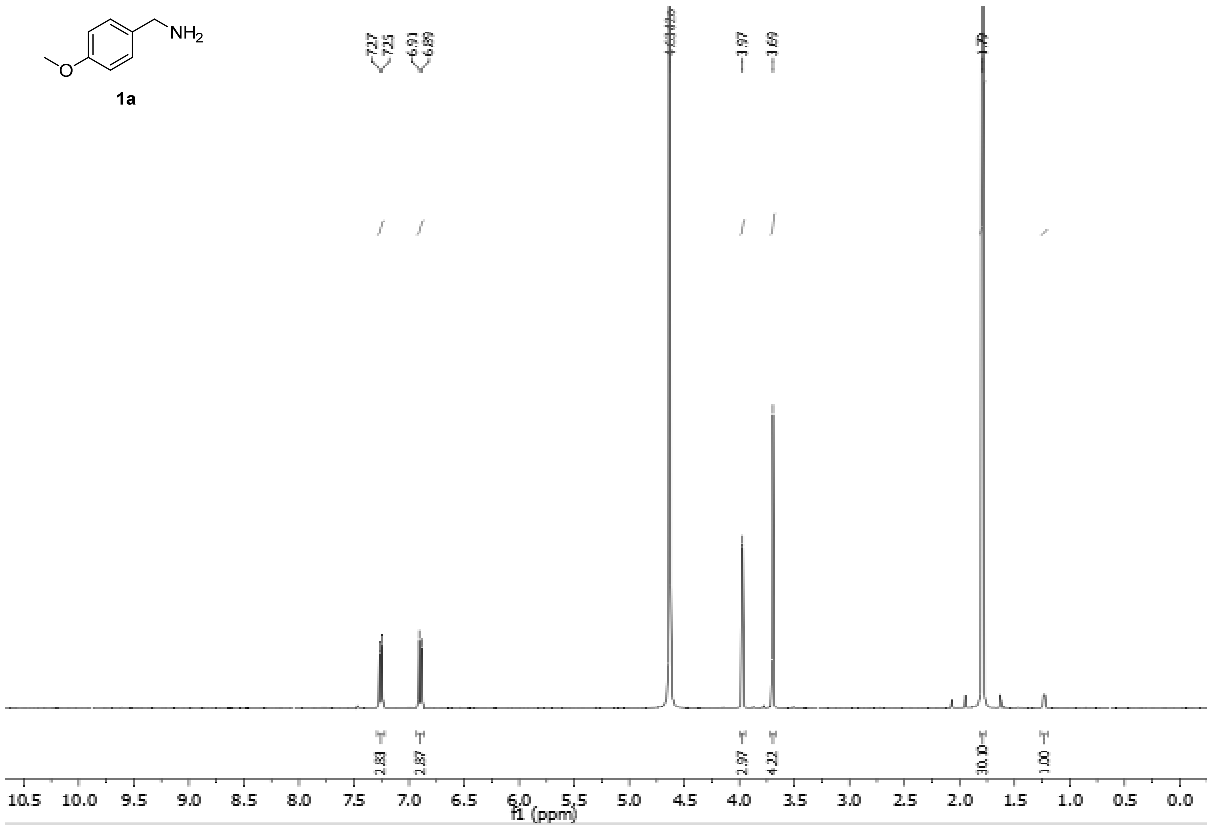


4b (Table 1, entry 25)

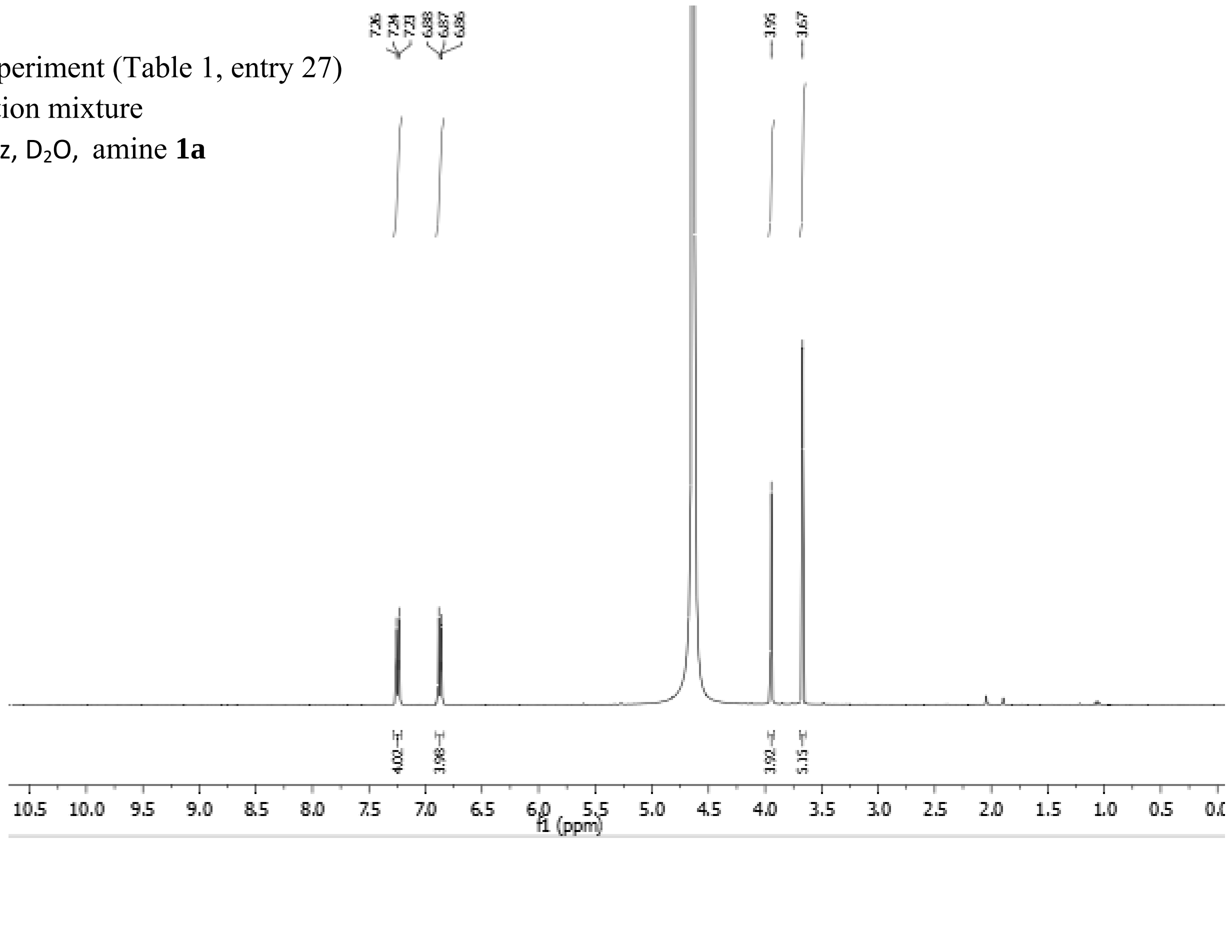




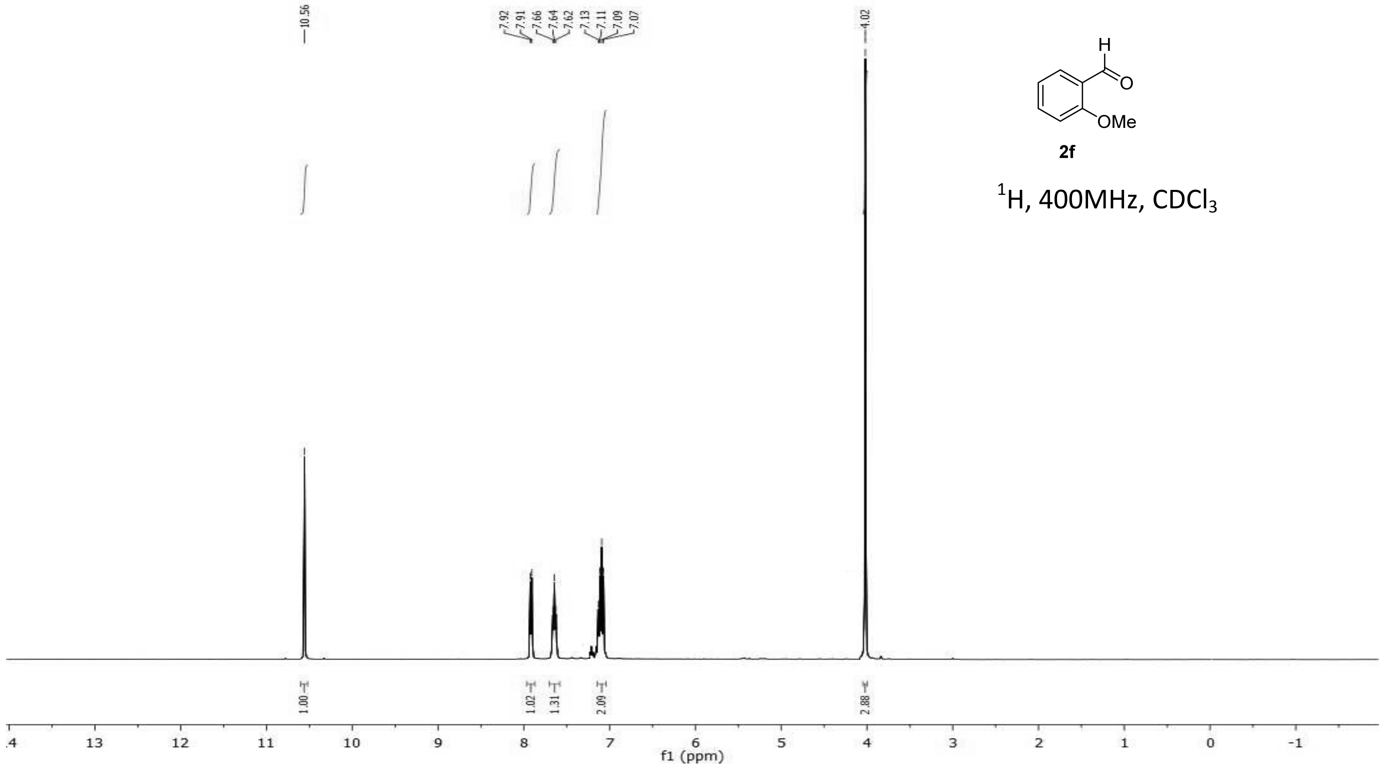
Control experiment (Table 1, entry 26) crude reaction mixture
^{1}H, 400MHz, D_2O, amine **1a**

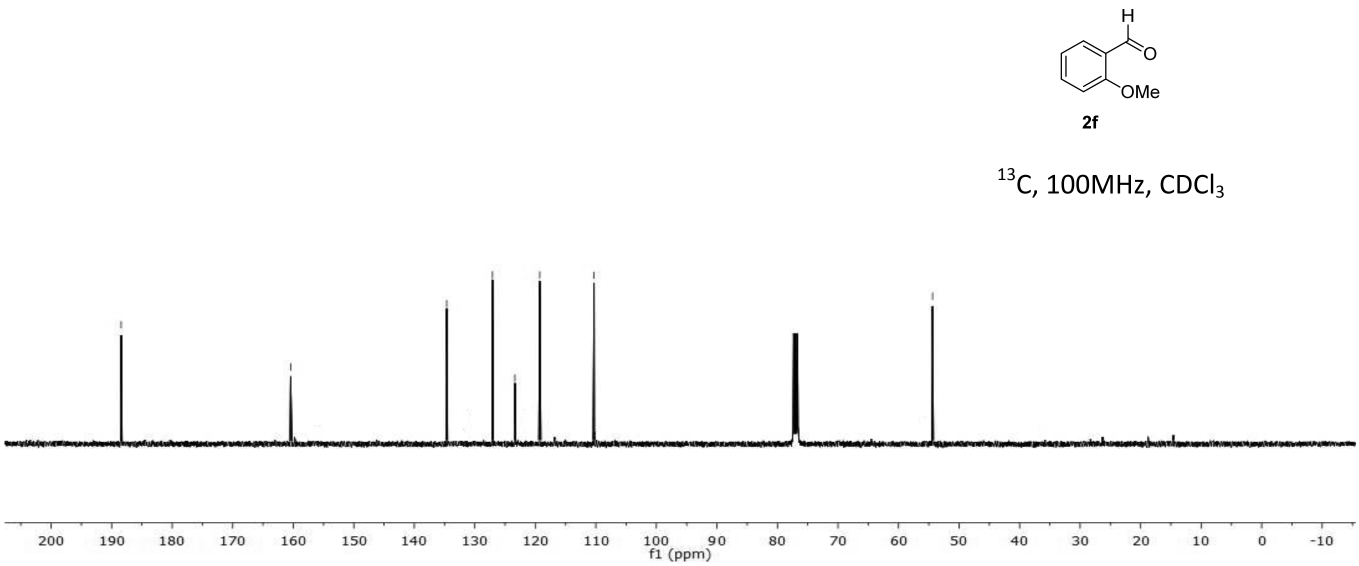


Control experiment (Table 1, entry 27)
crude reaction mixture
^{1}H, 400MHz, D_2O, amine **1a**

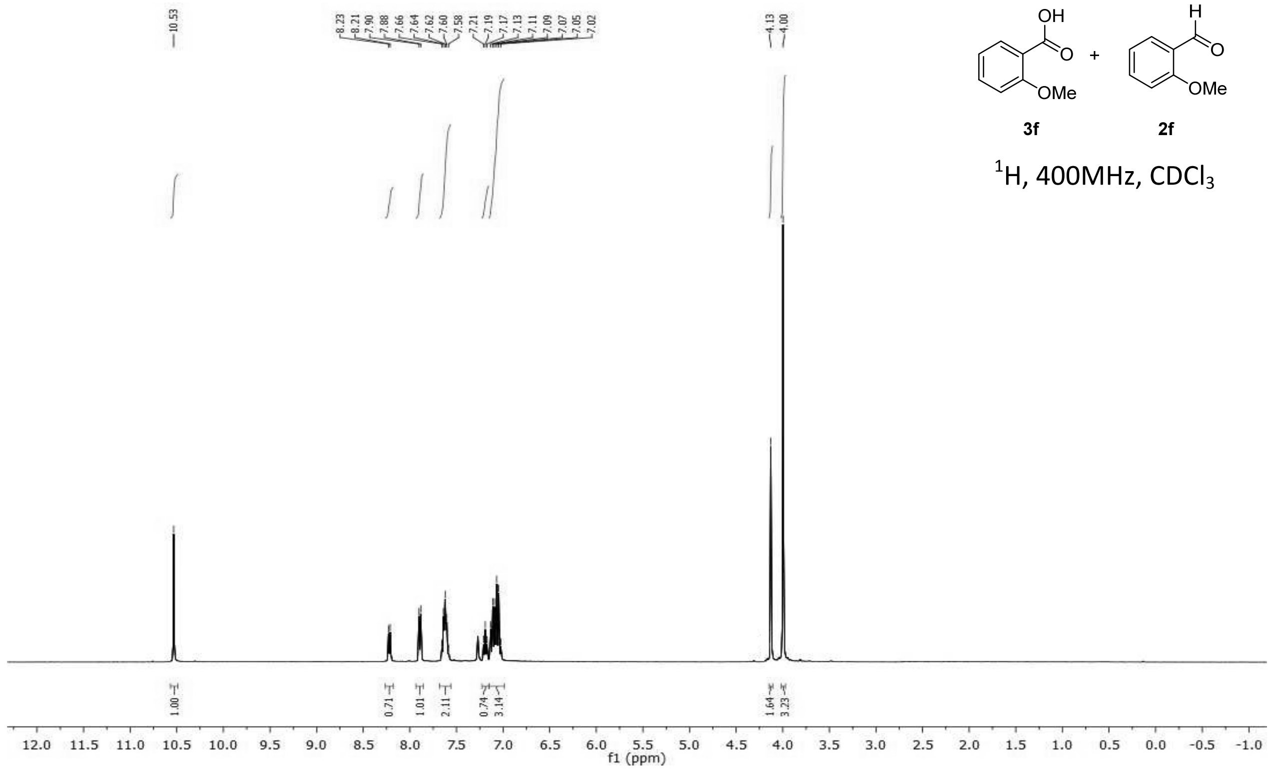


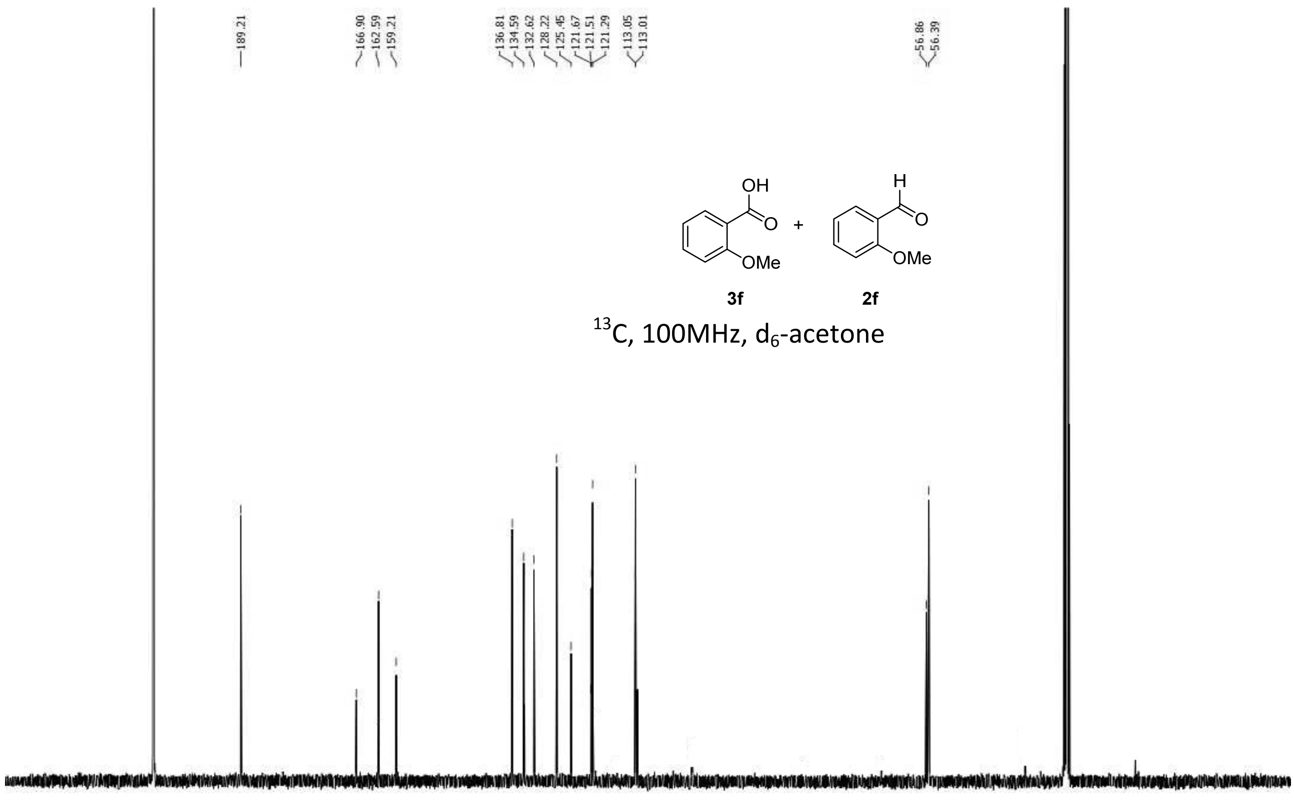
2f (Table 2, entry 4)



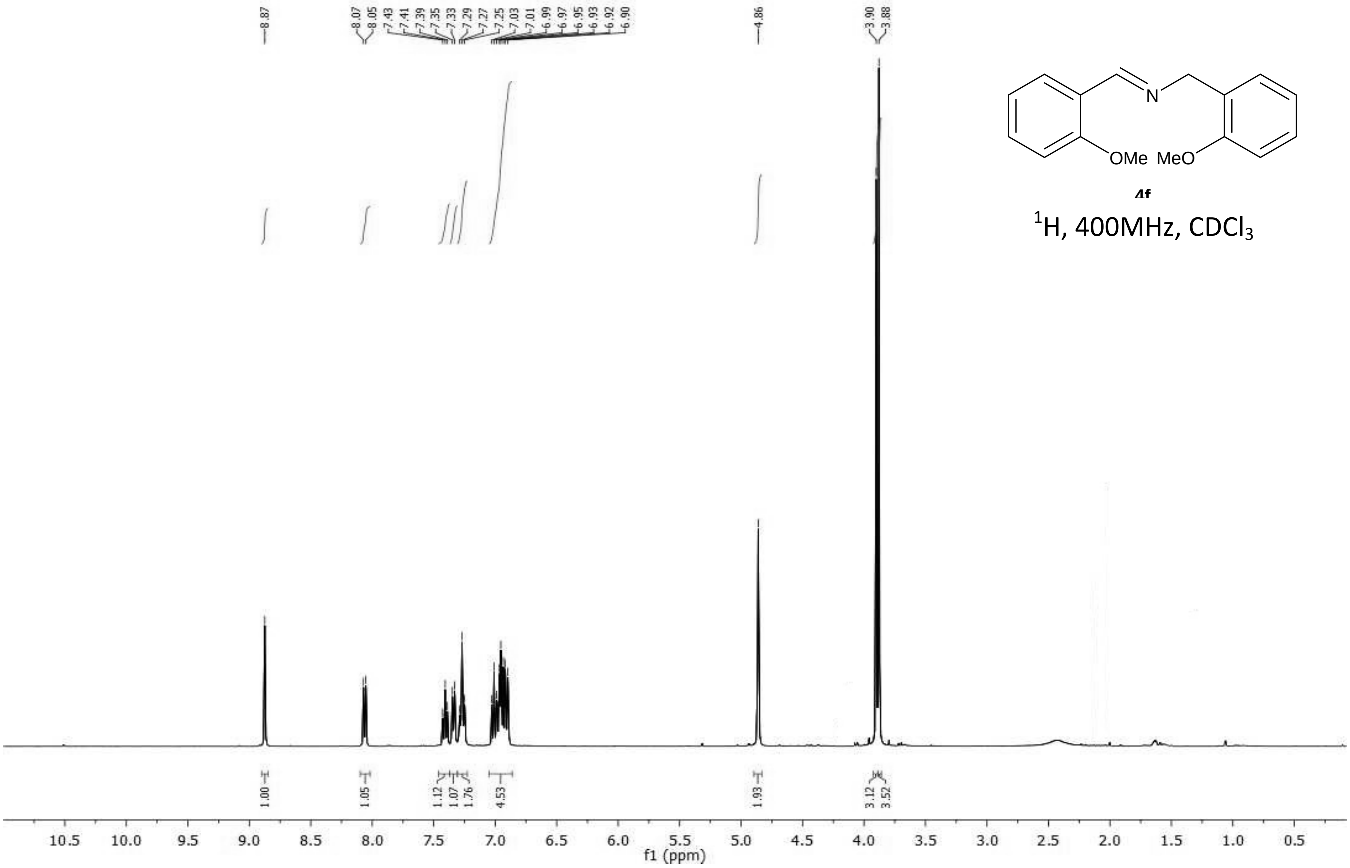


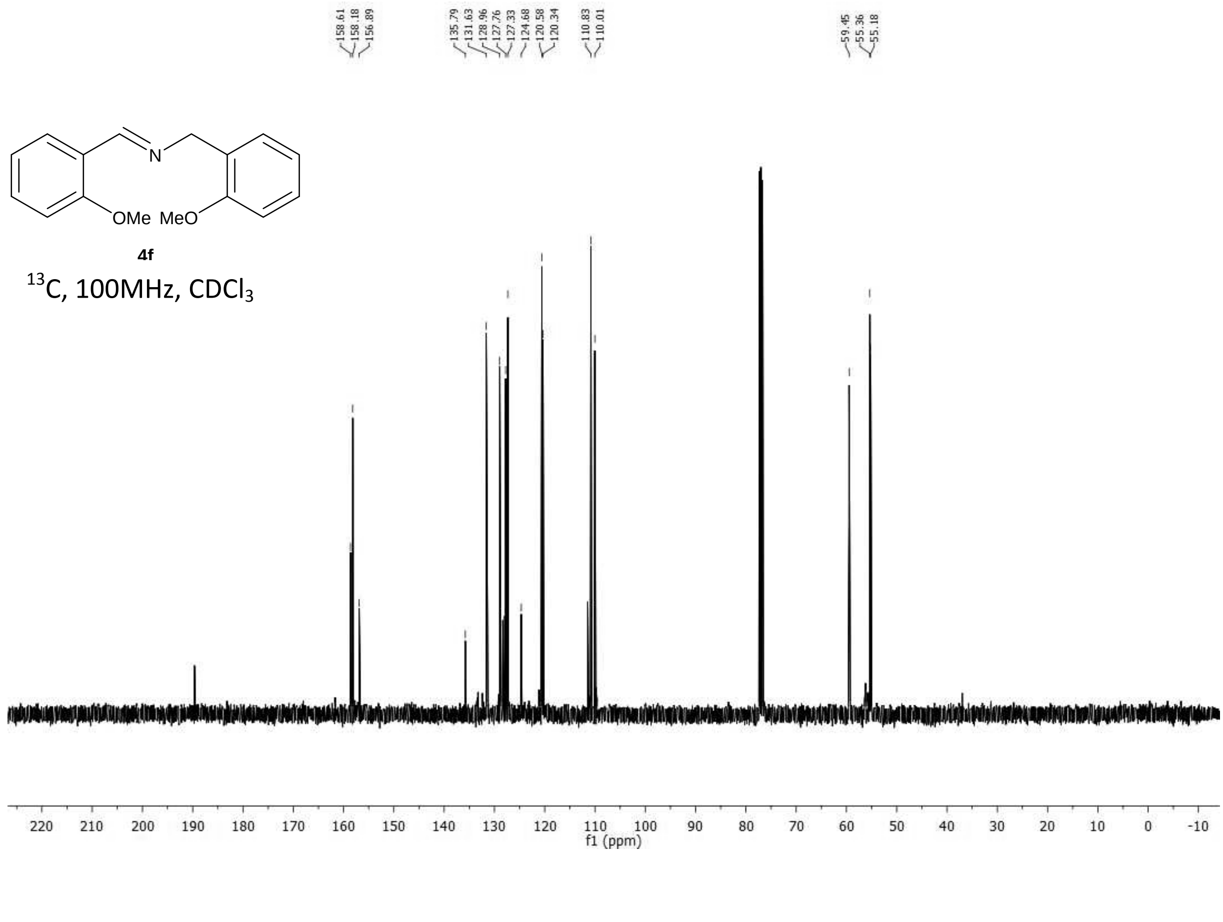
2f + 3f (Table 2, entry 6)



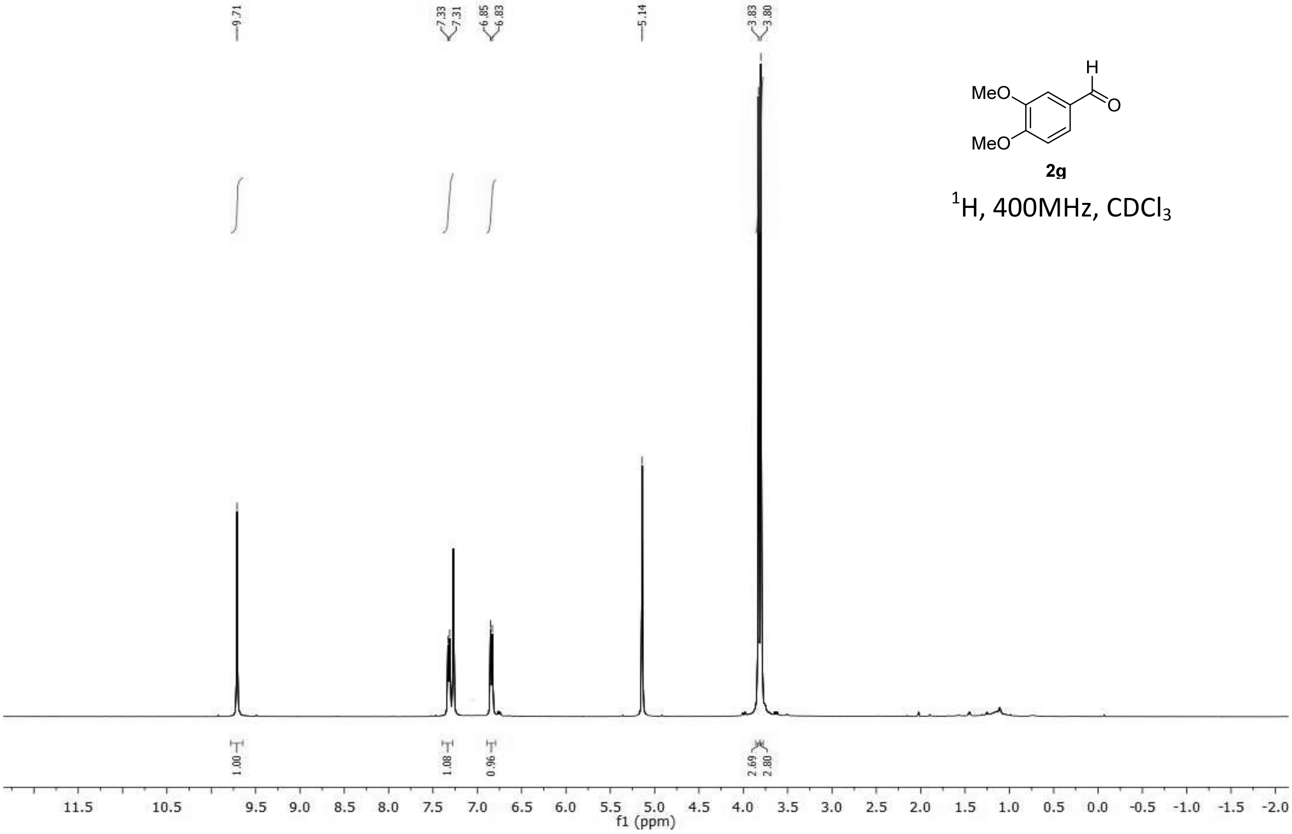


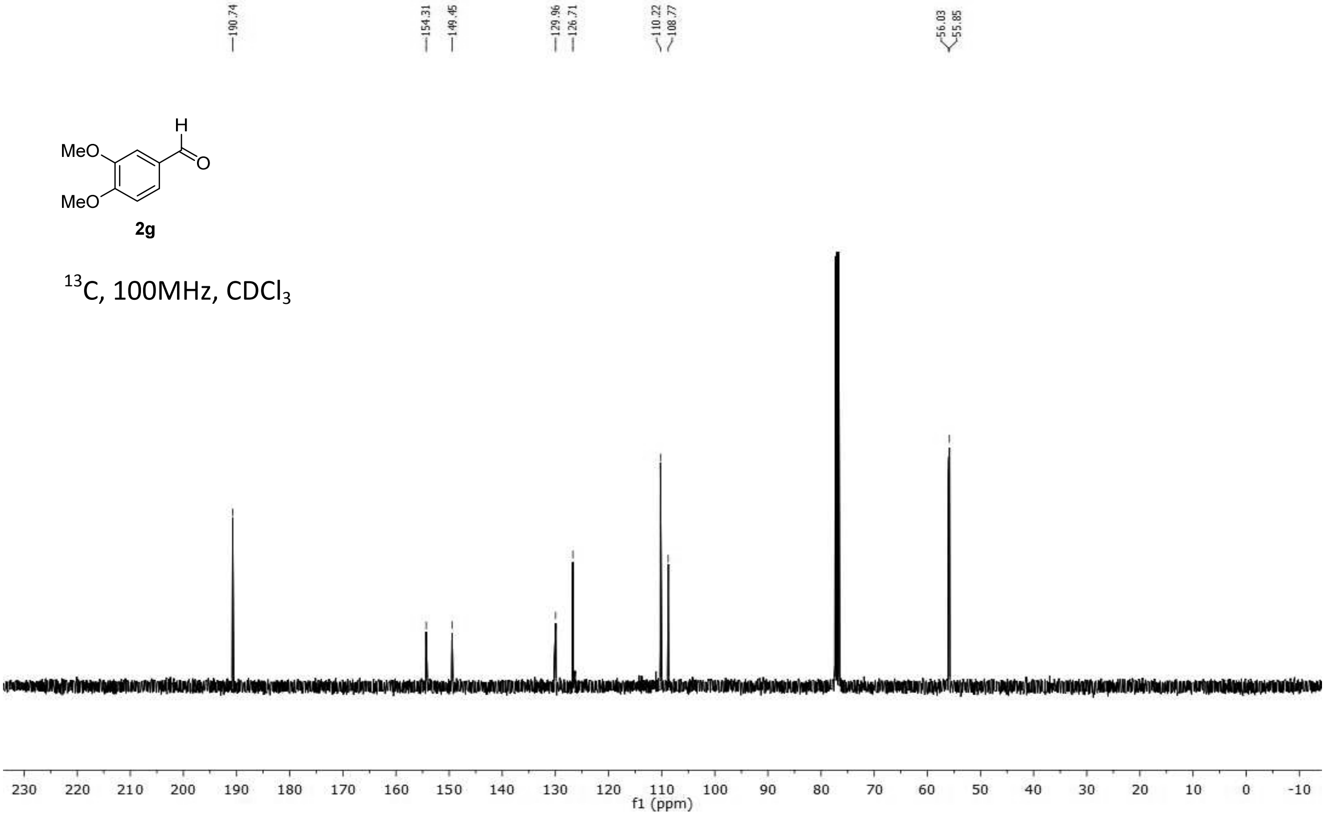
4f (Table 2, entry 7)



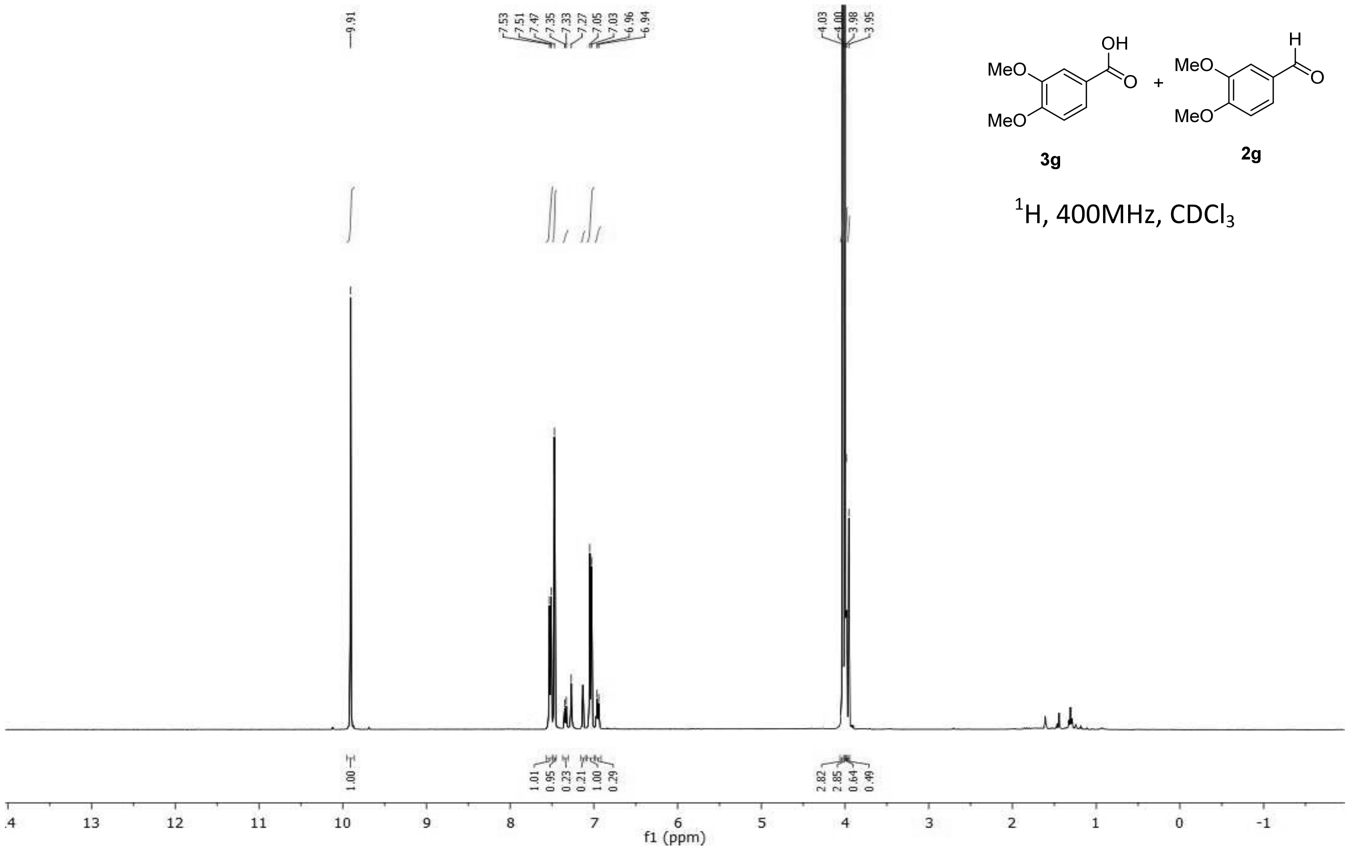


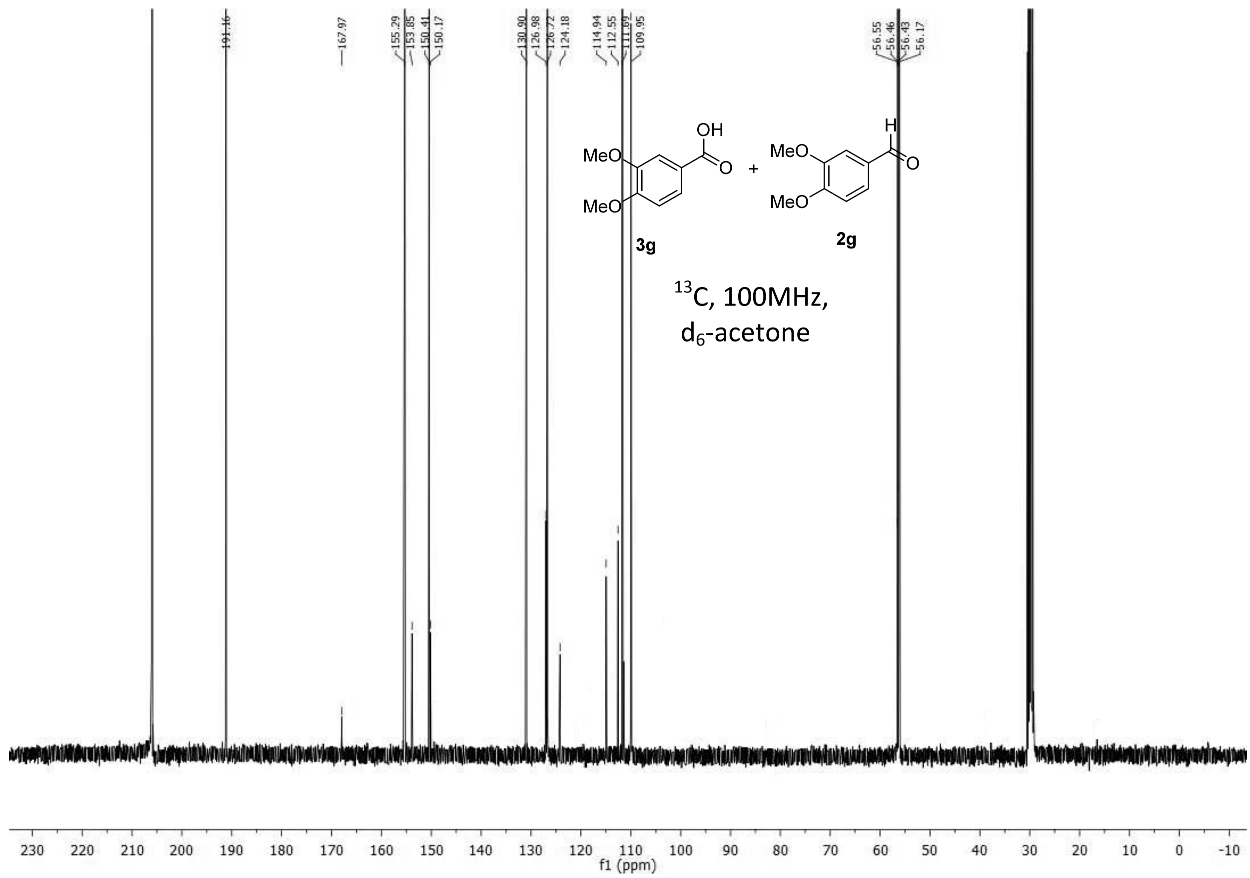
2g (Table 2, entry 8)



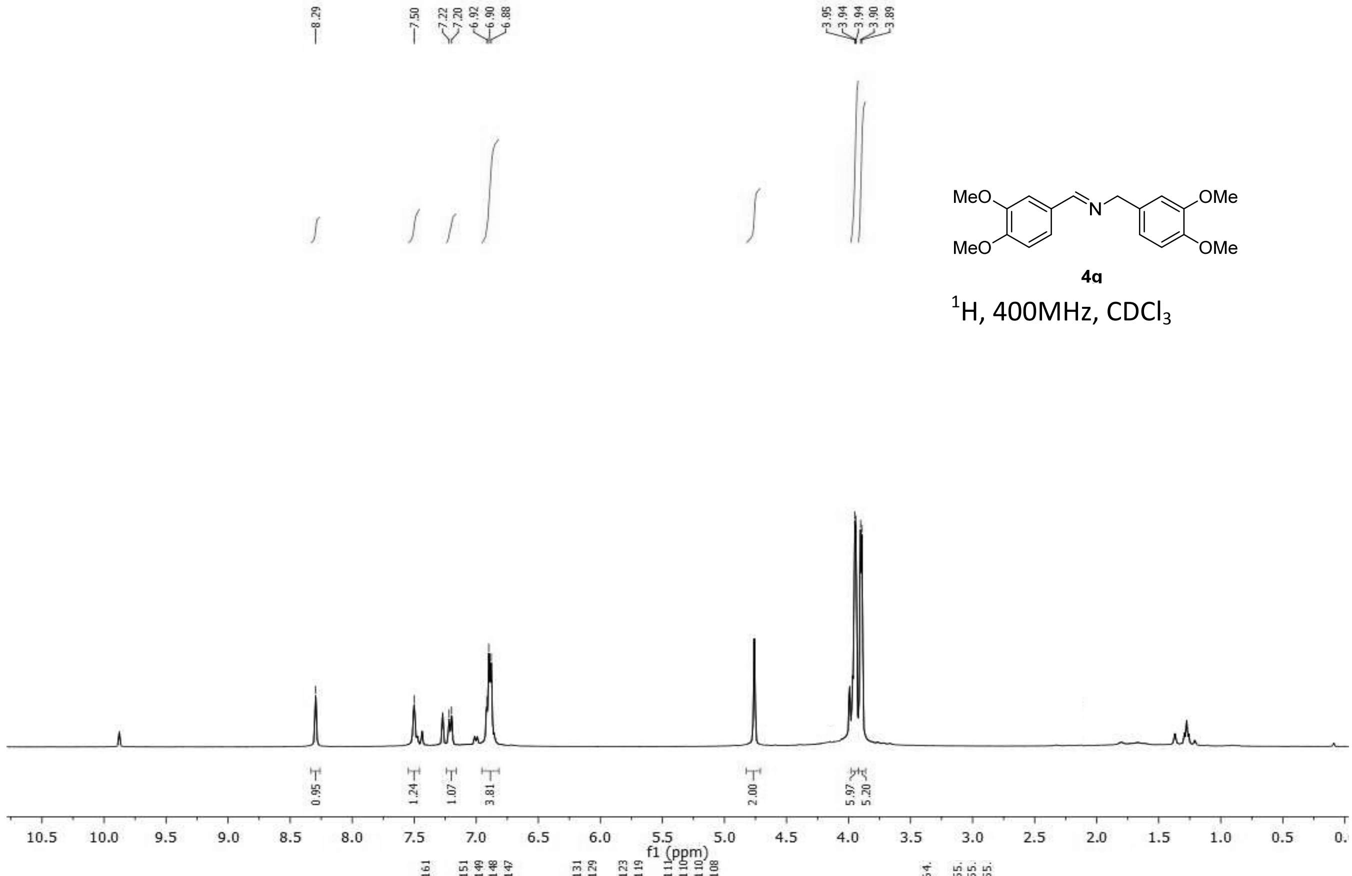


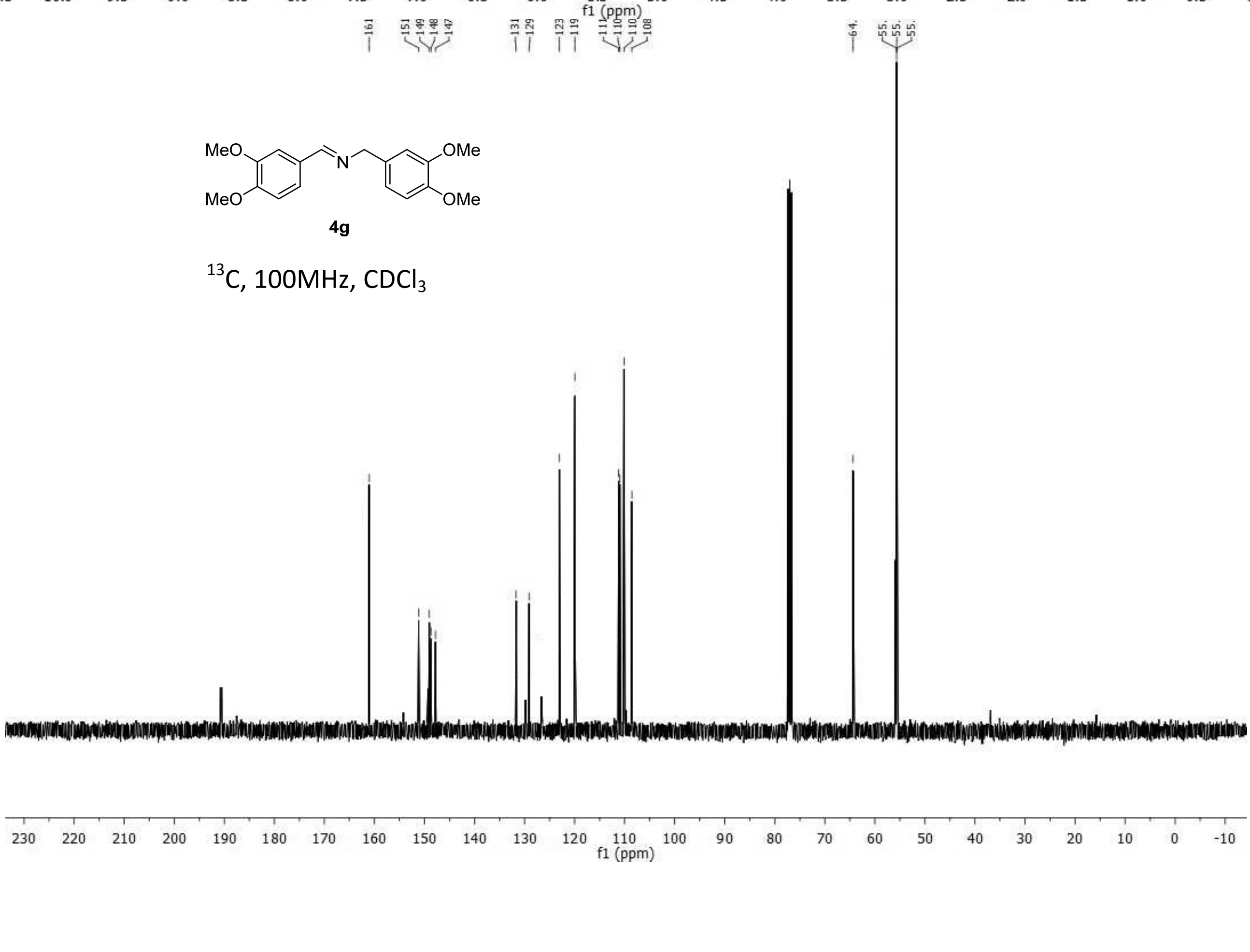
2g + 3g (Table 2, entry 10)



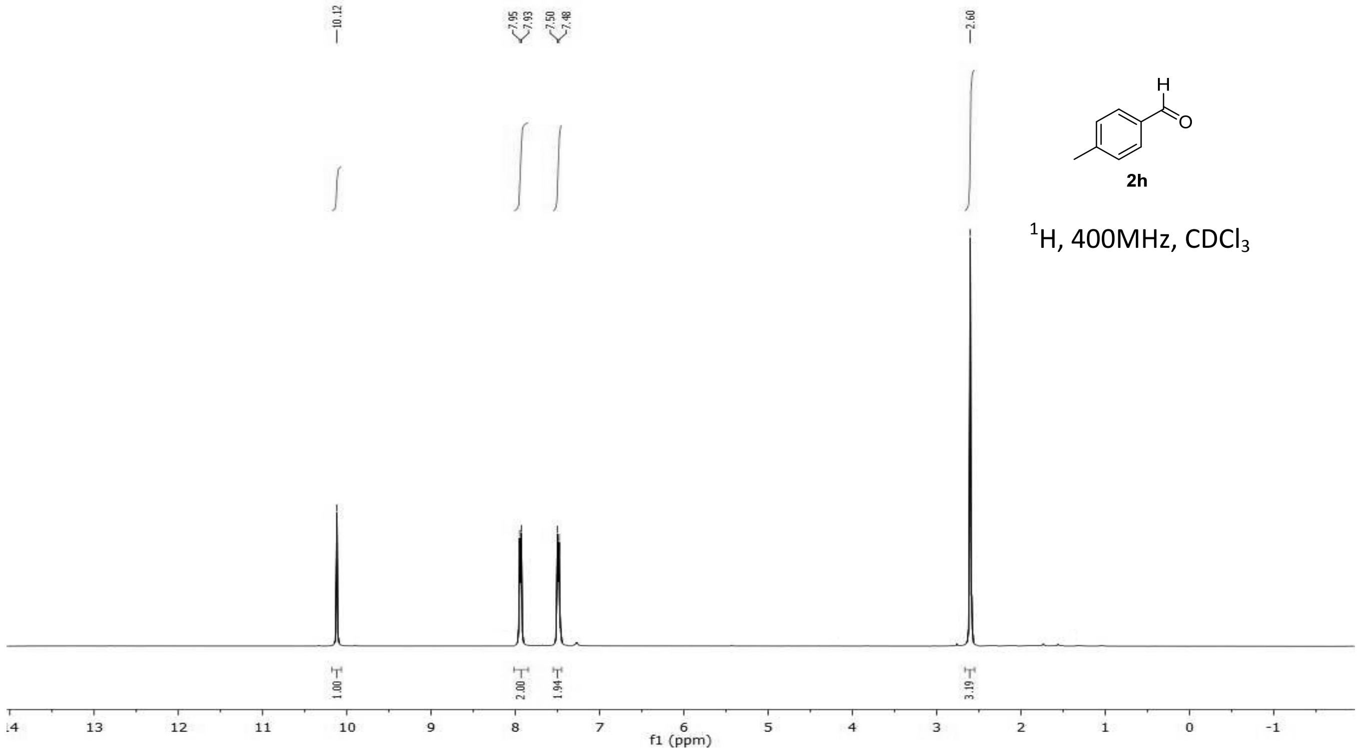


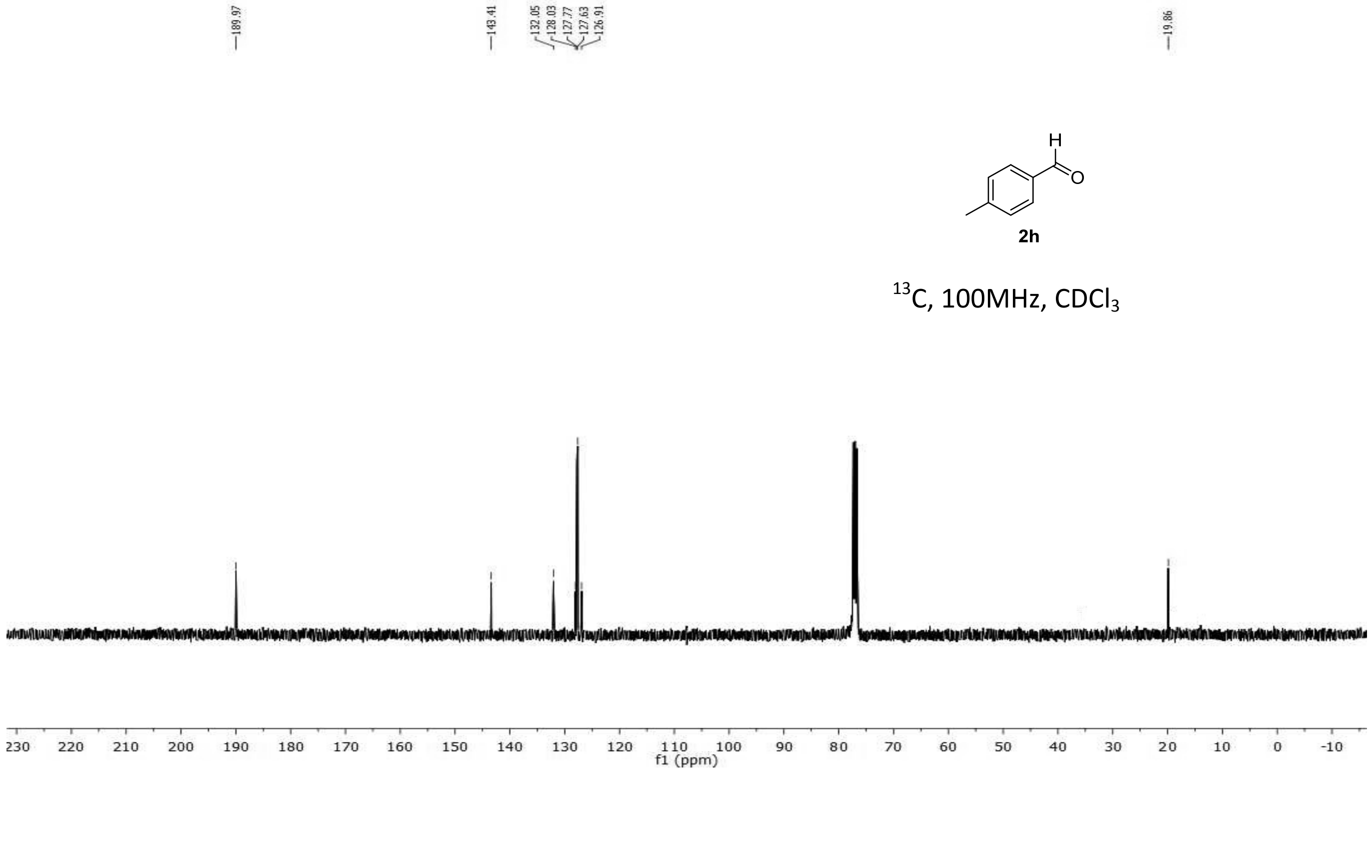
4g (Table 2, entry 11)



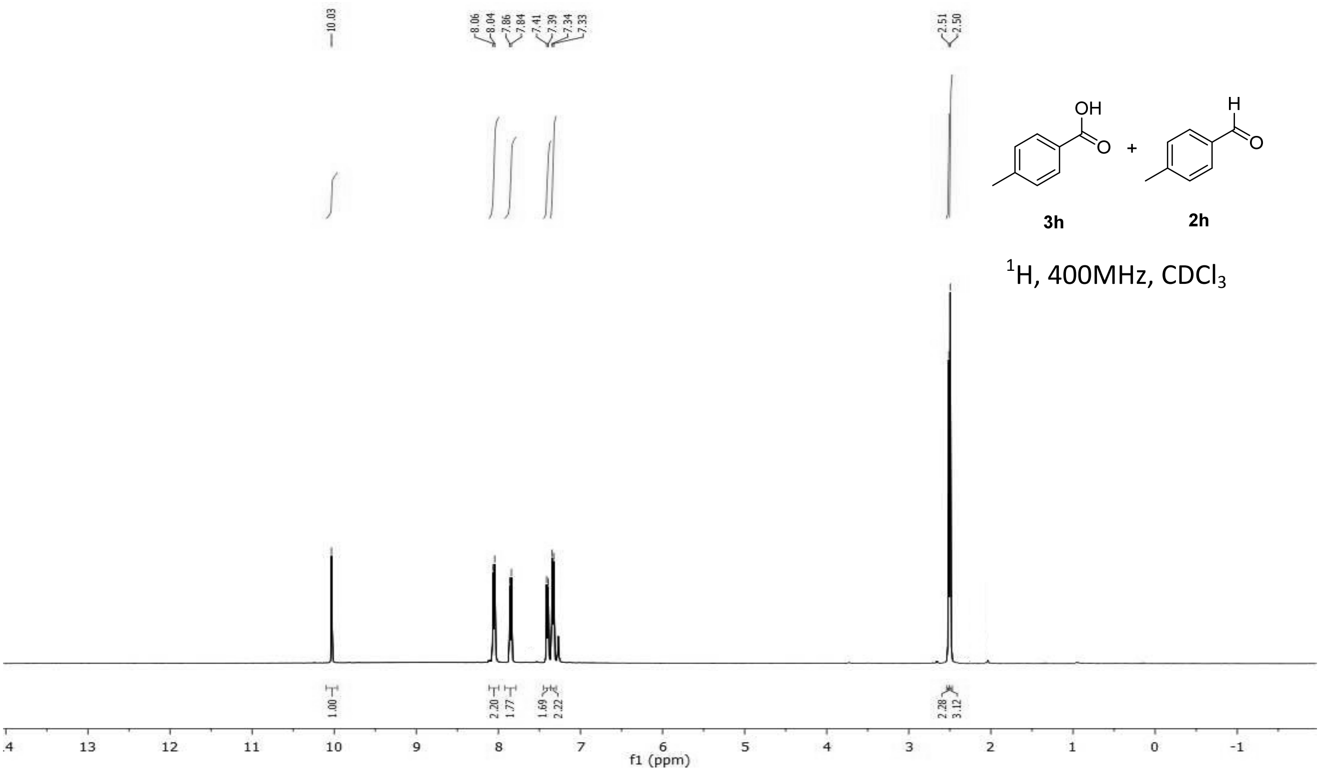


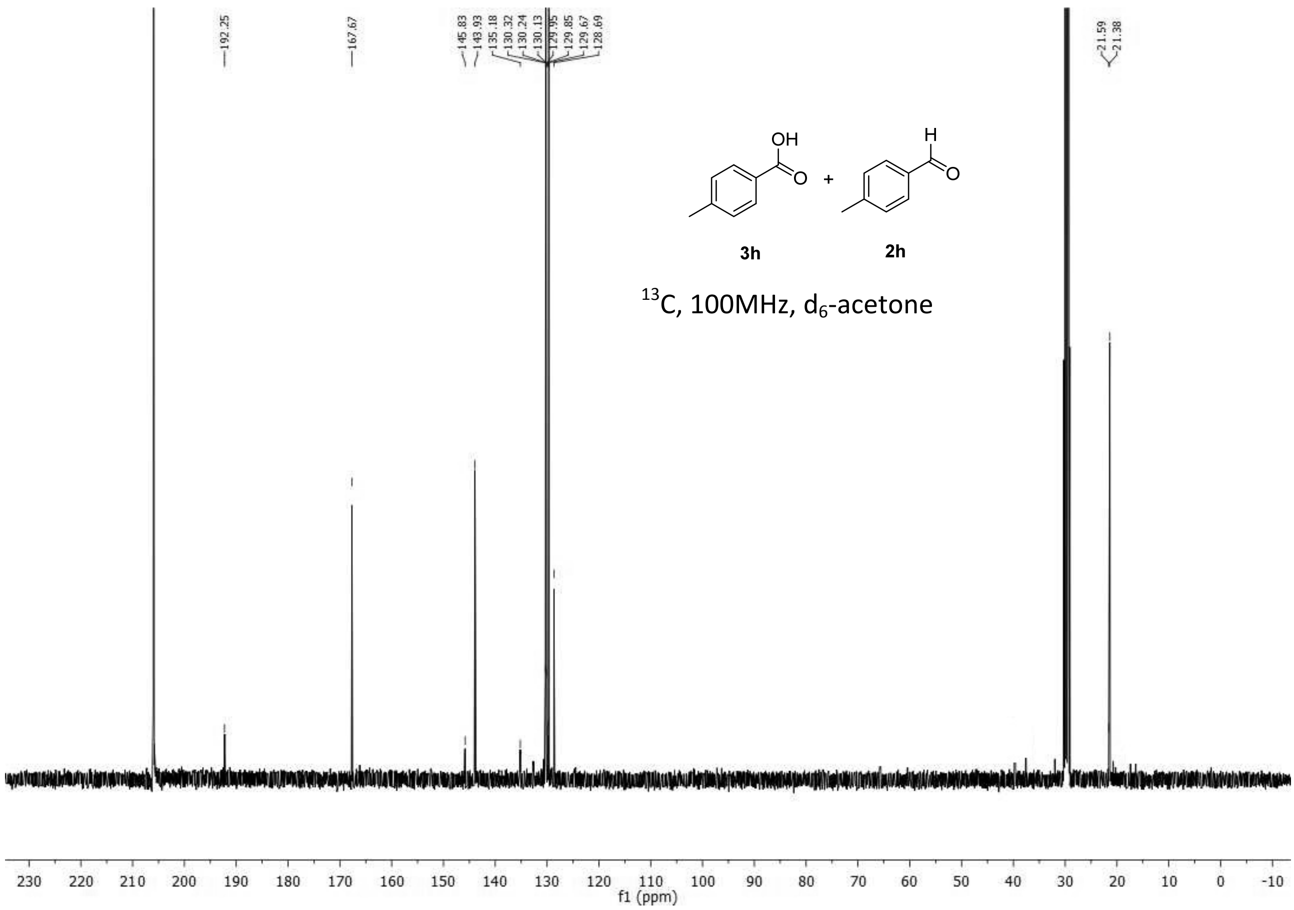
2h (Table 2, entry 12)



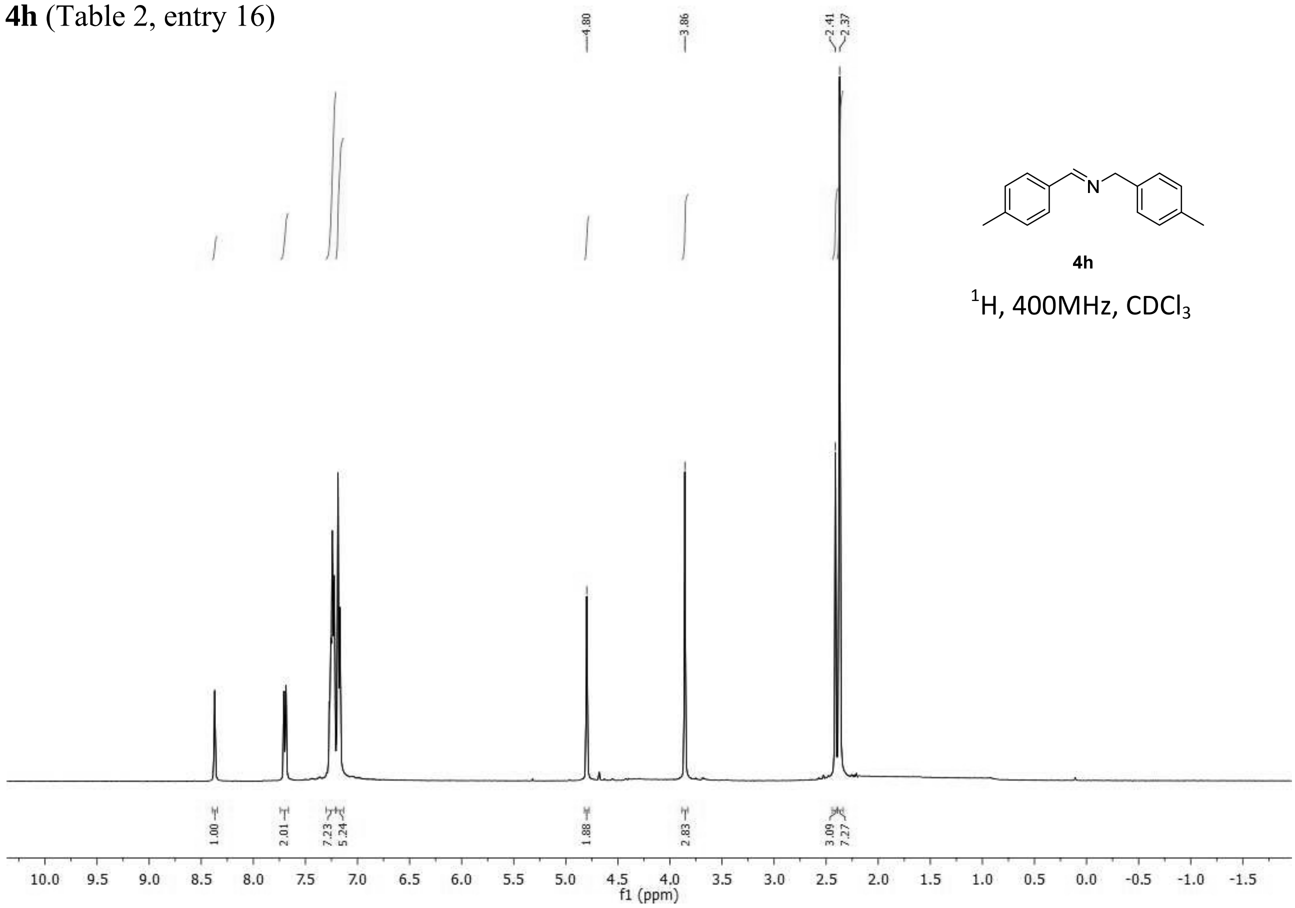


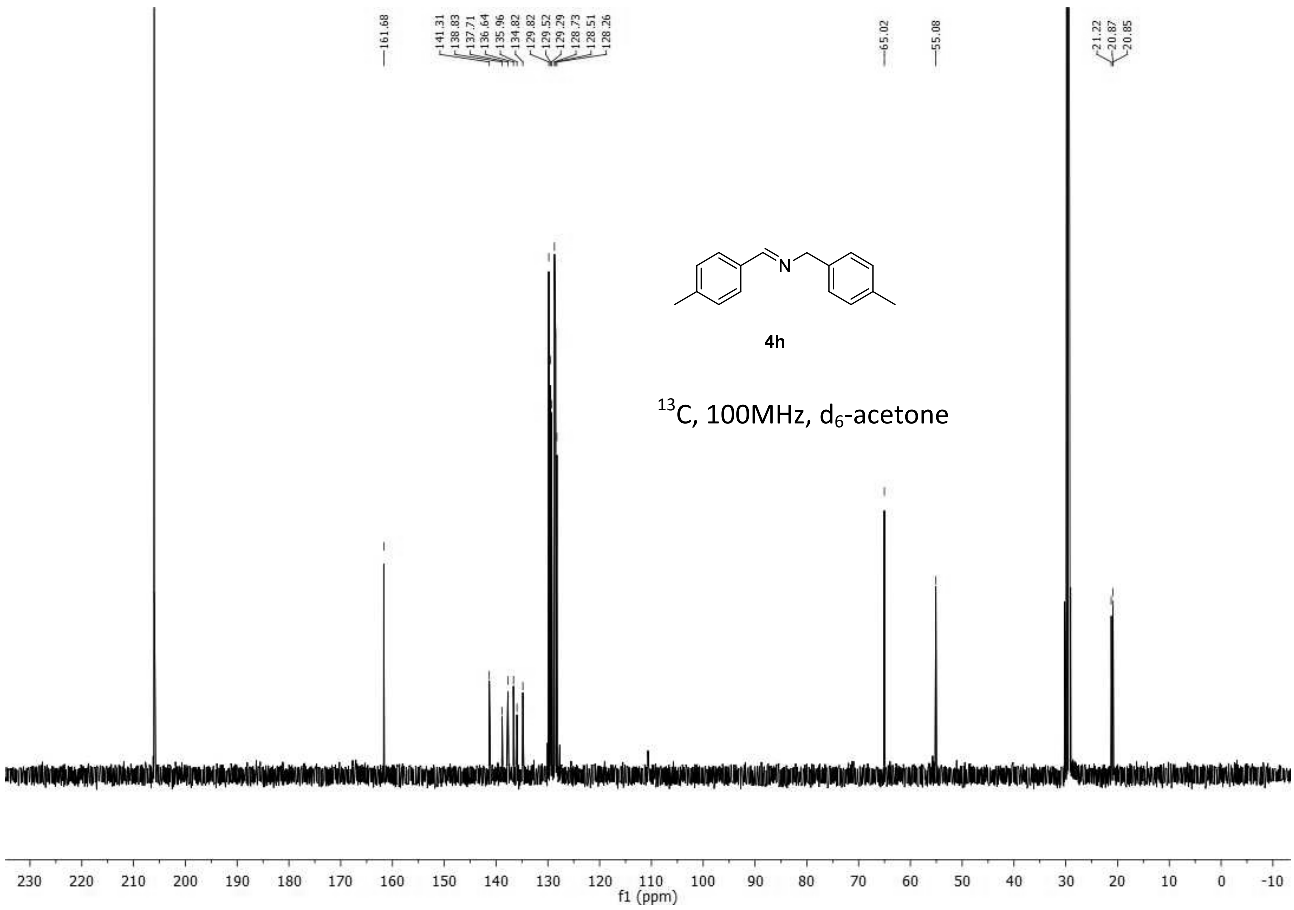
2h + 3h (Table 2, entry 14)



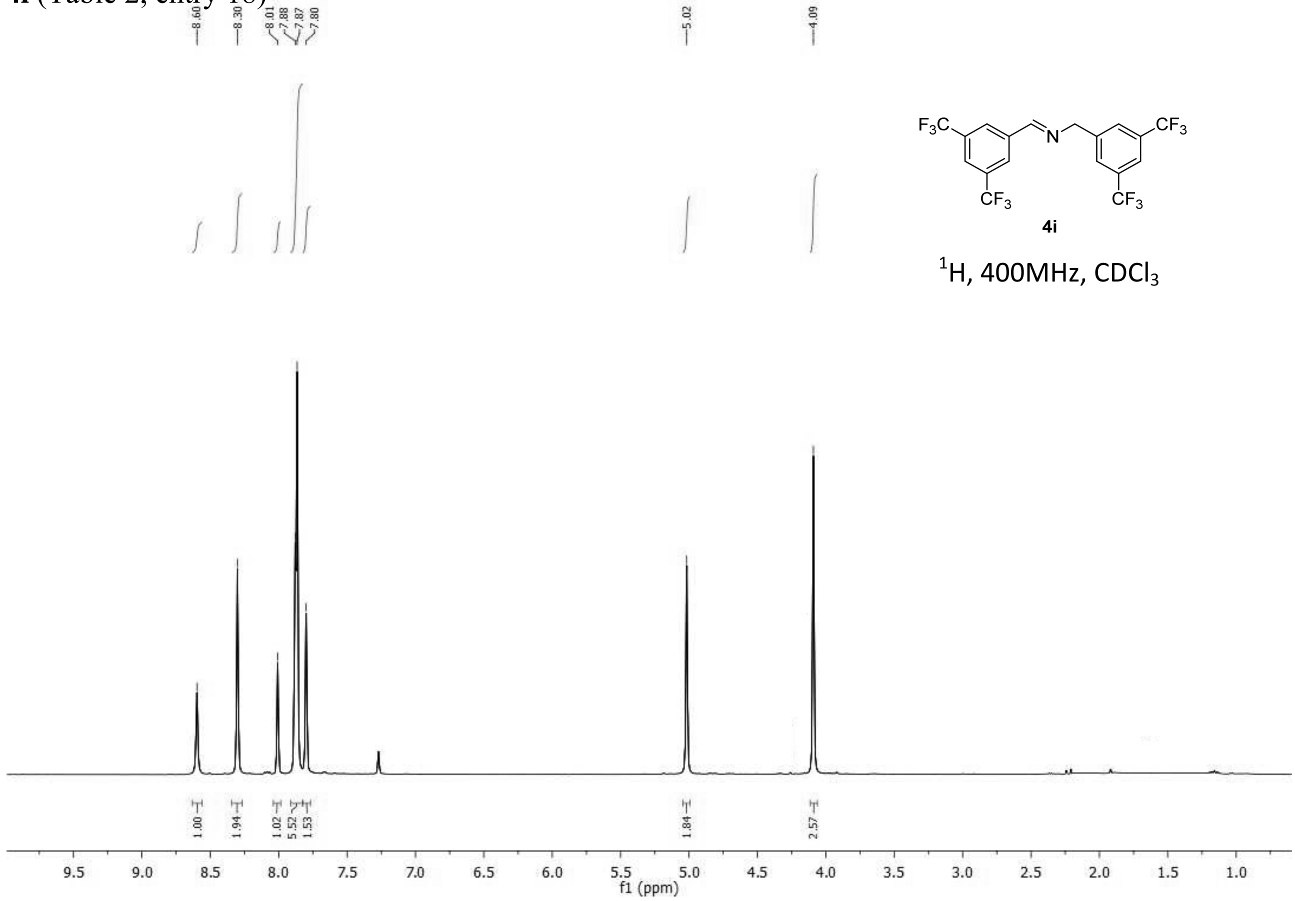


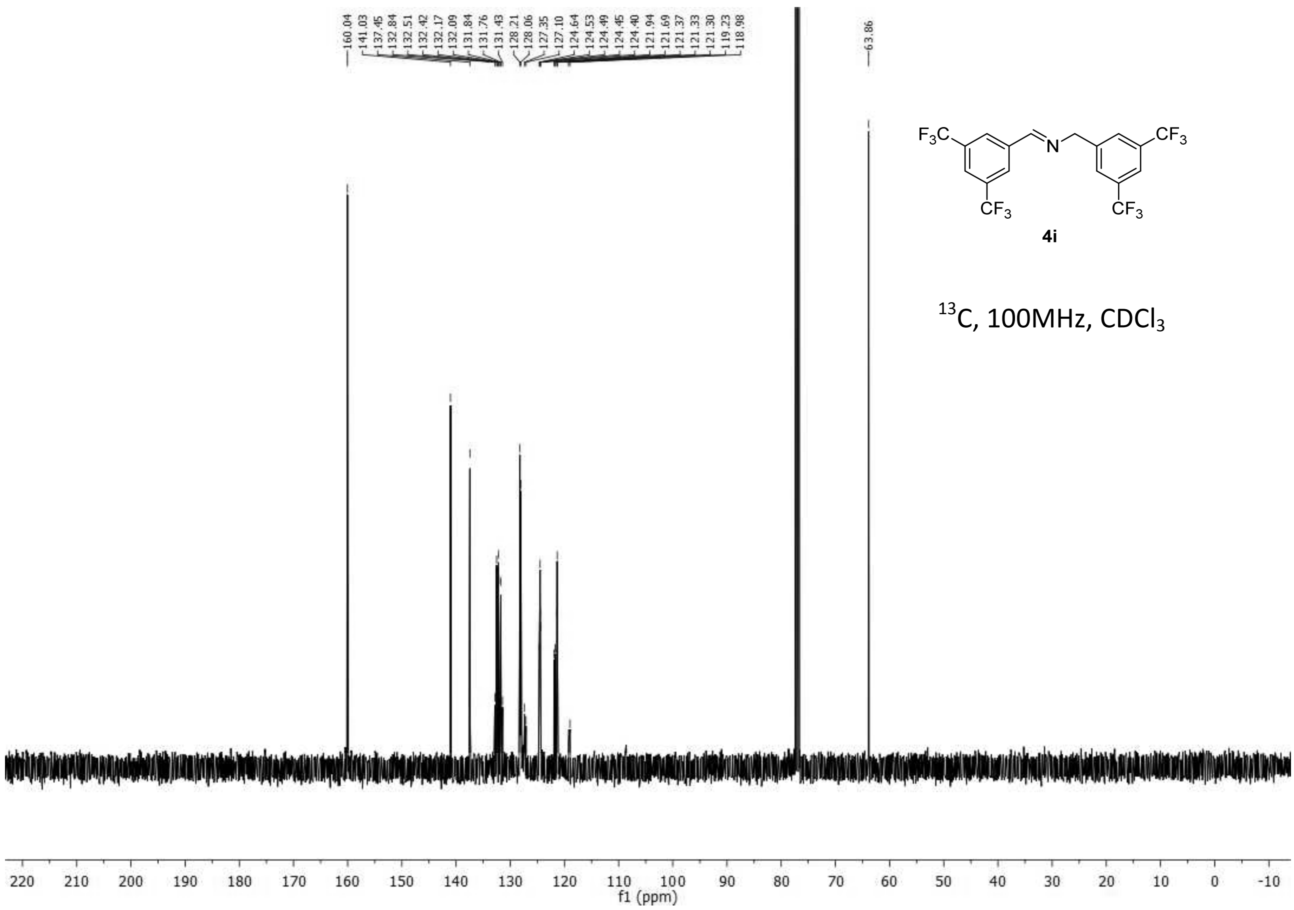
4h (Table 2, entry 16)



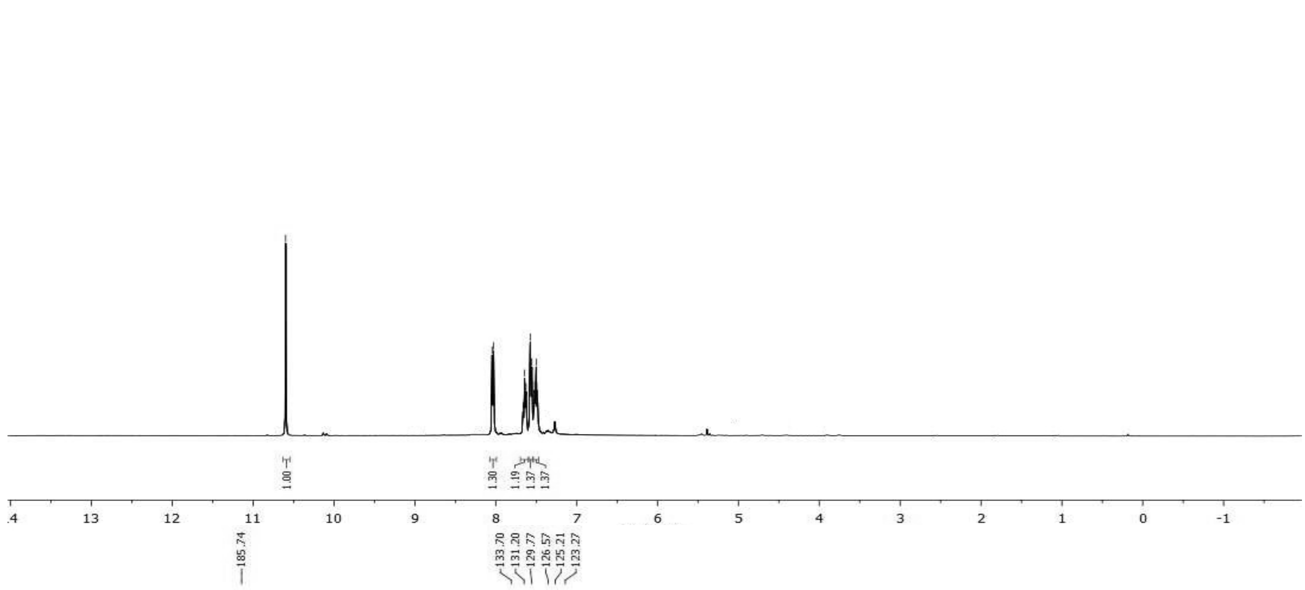


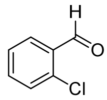
4i (Table 2, entry 18)





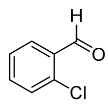
2j (Table 2, entry 19)





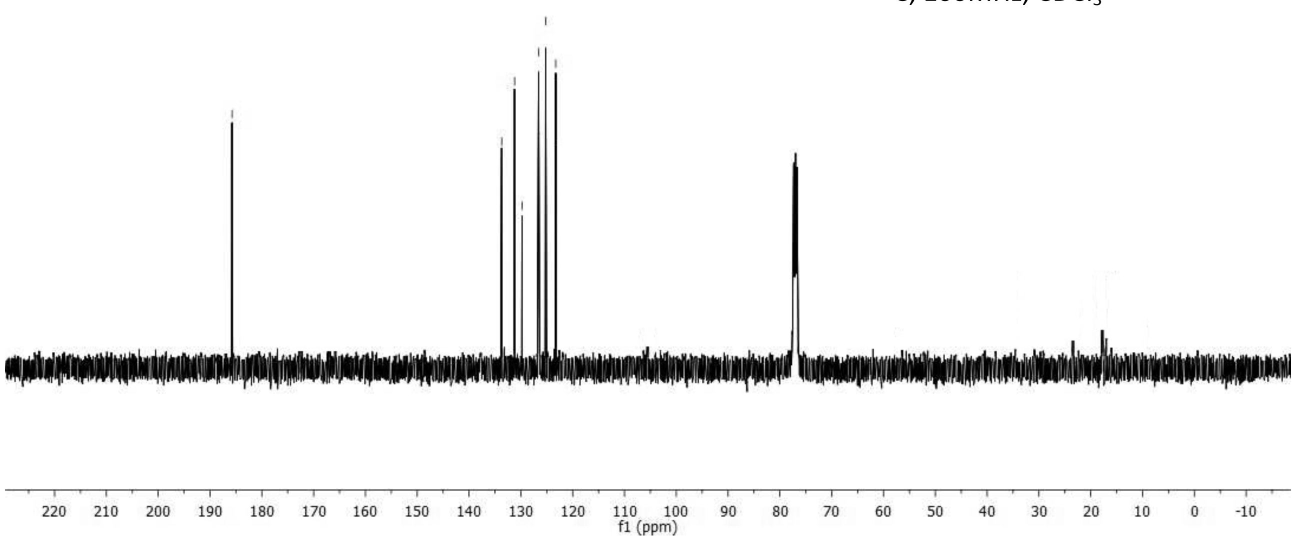
2j

^1H, 400MHz, $CDCl_3$

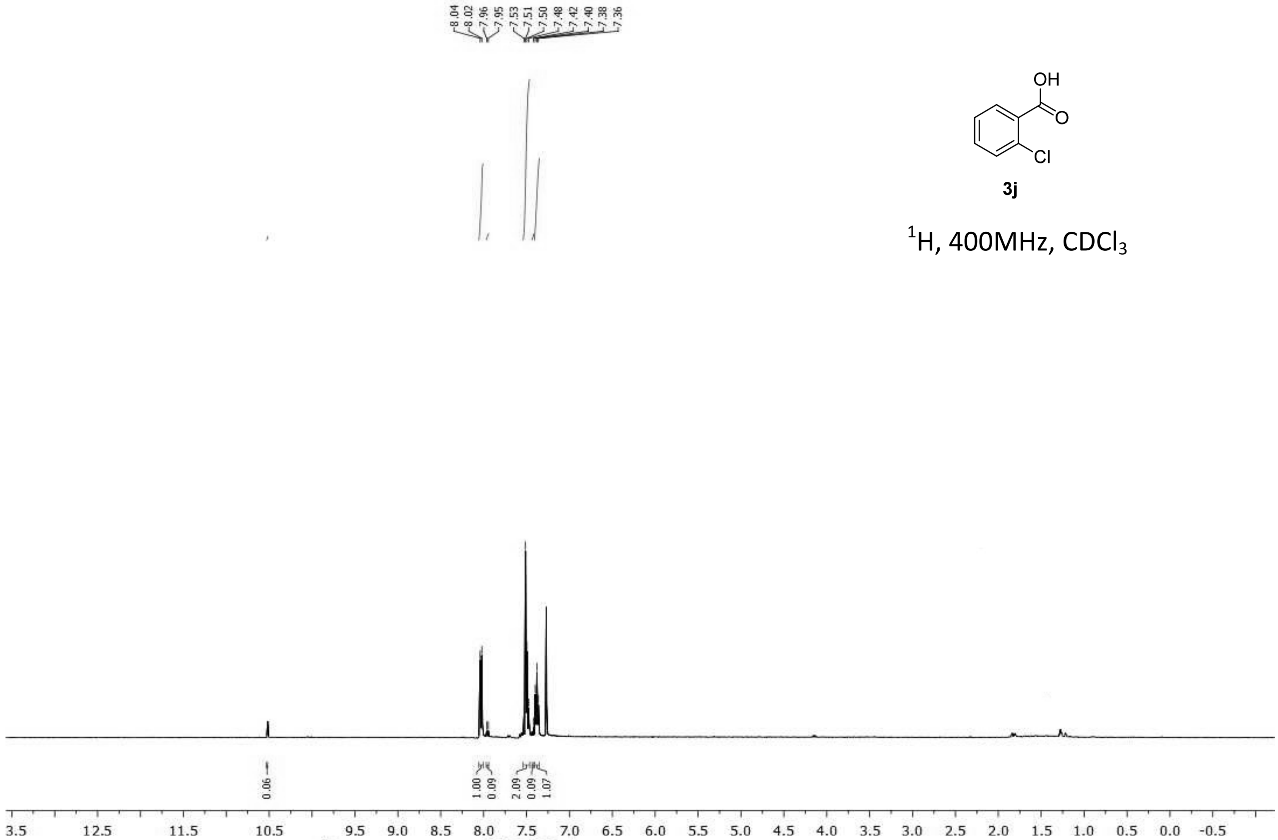


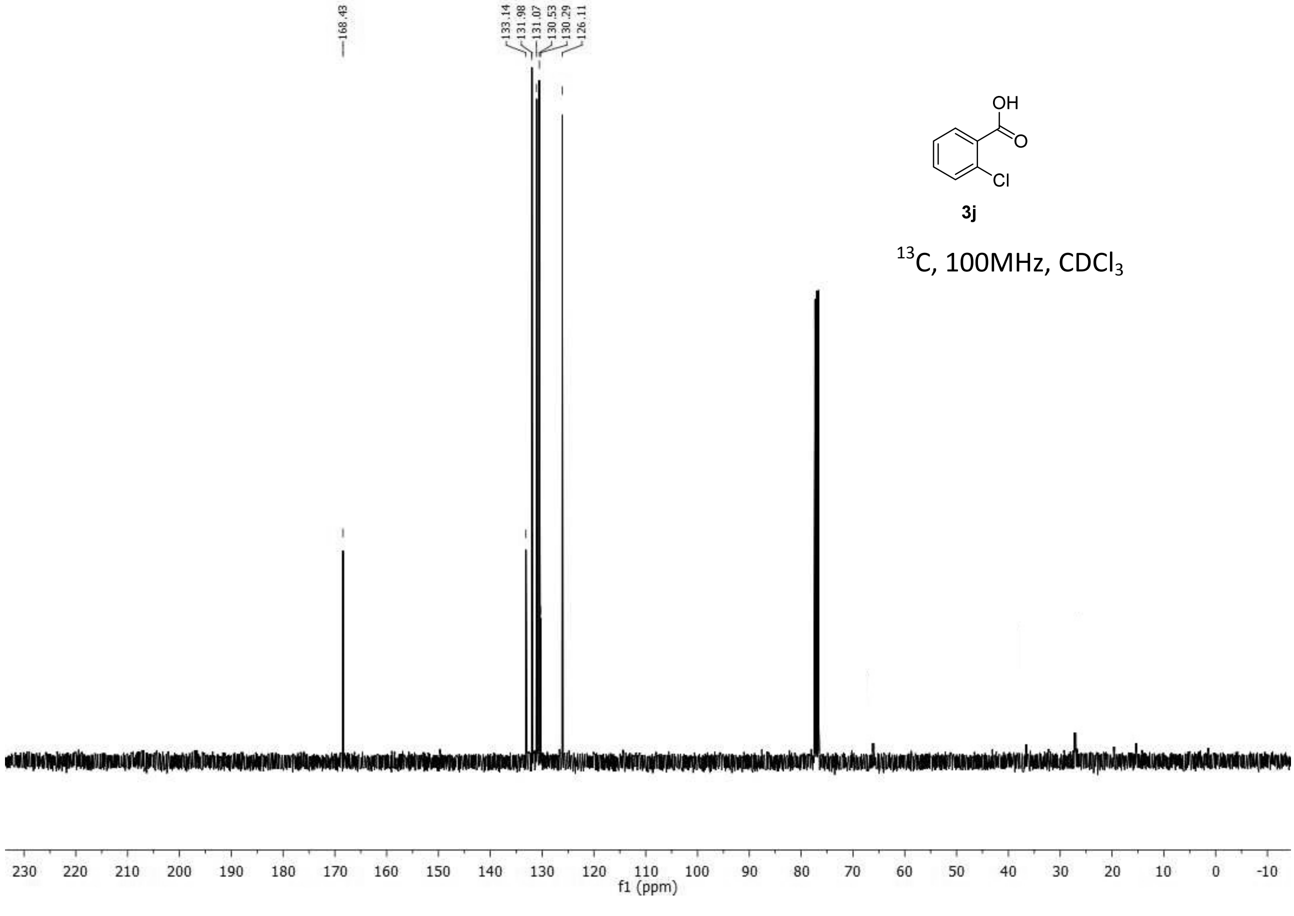
2j

^{13}C, 100MHz, $CDCl_3$

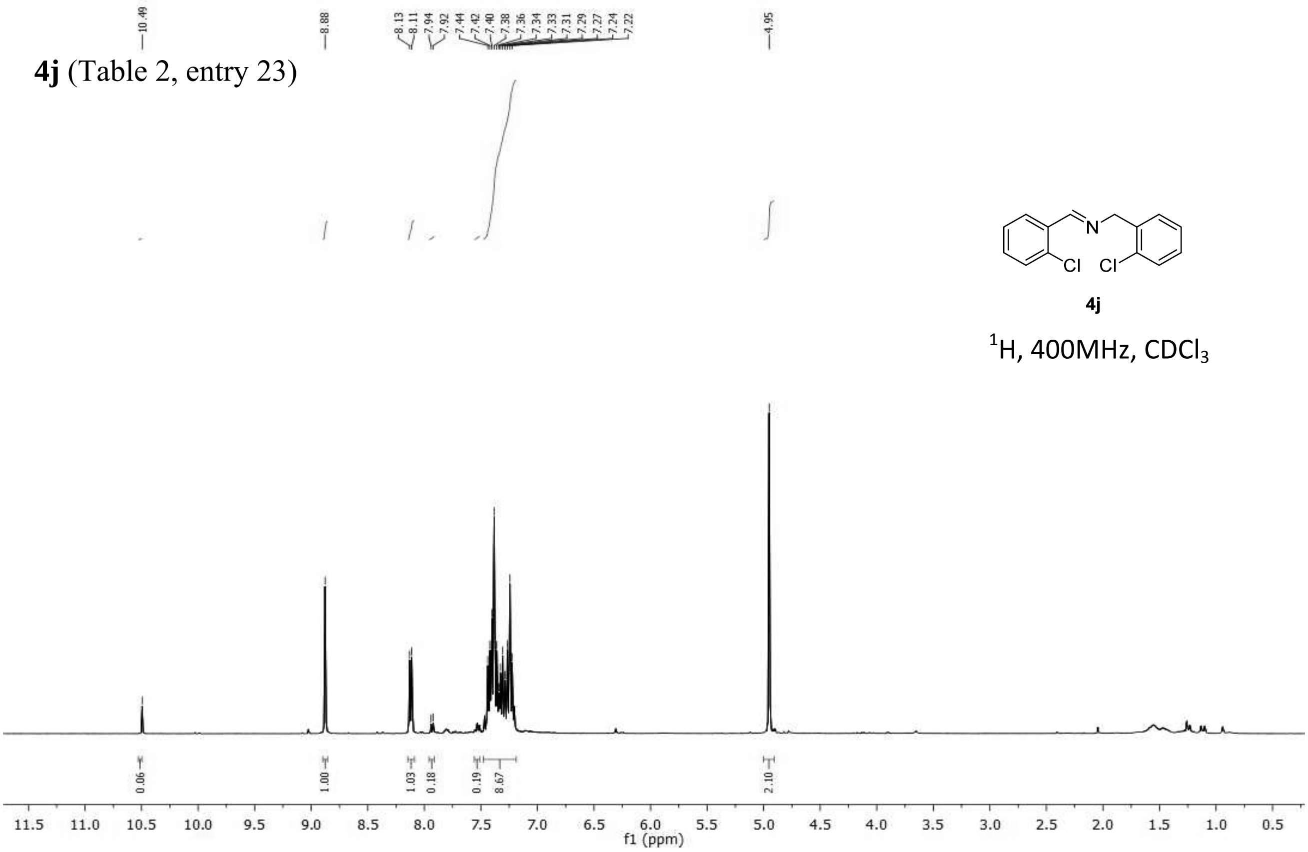


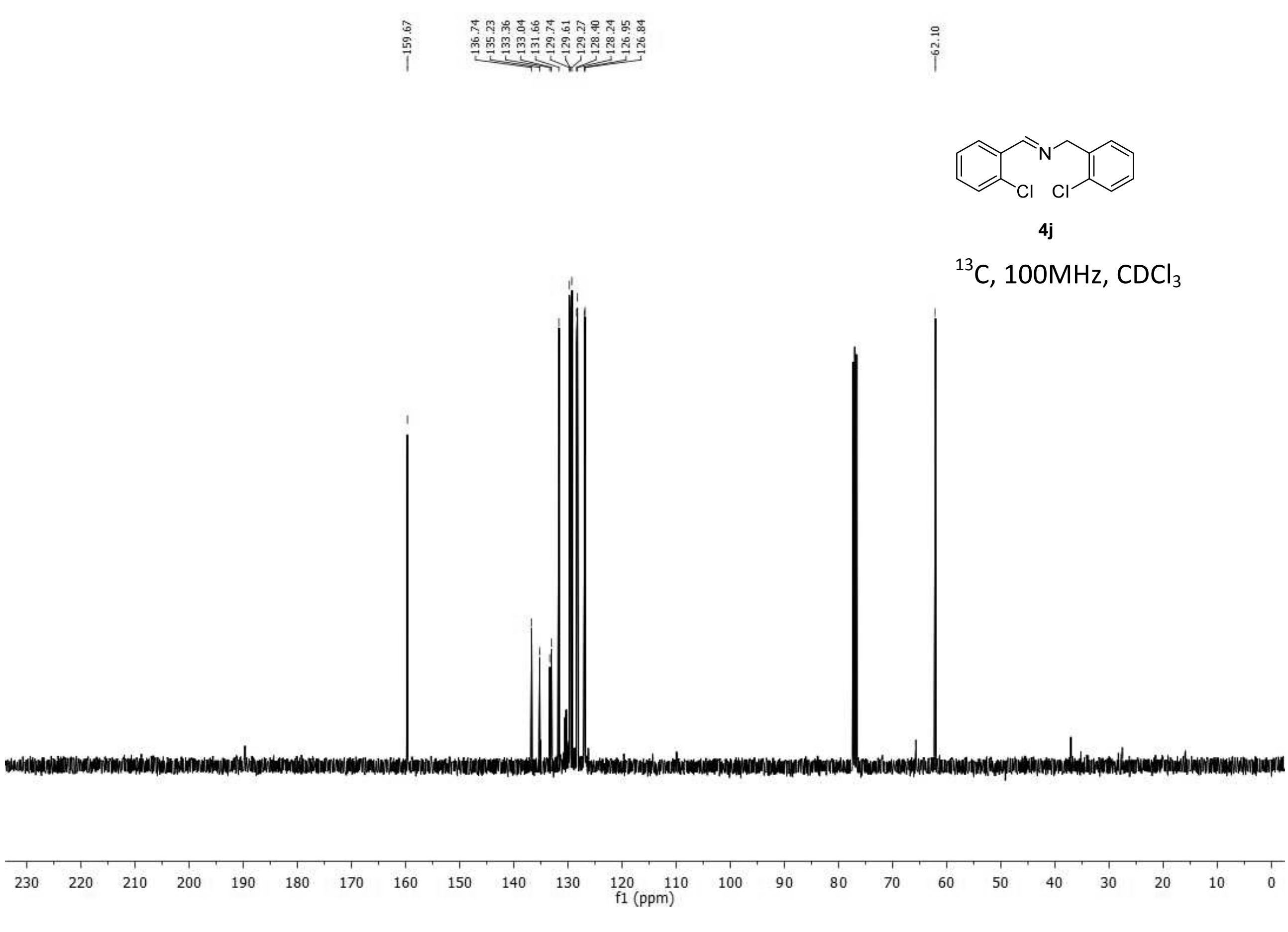
3j (Table 2, entry 21)



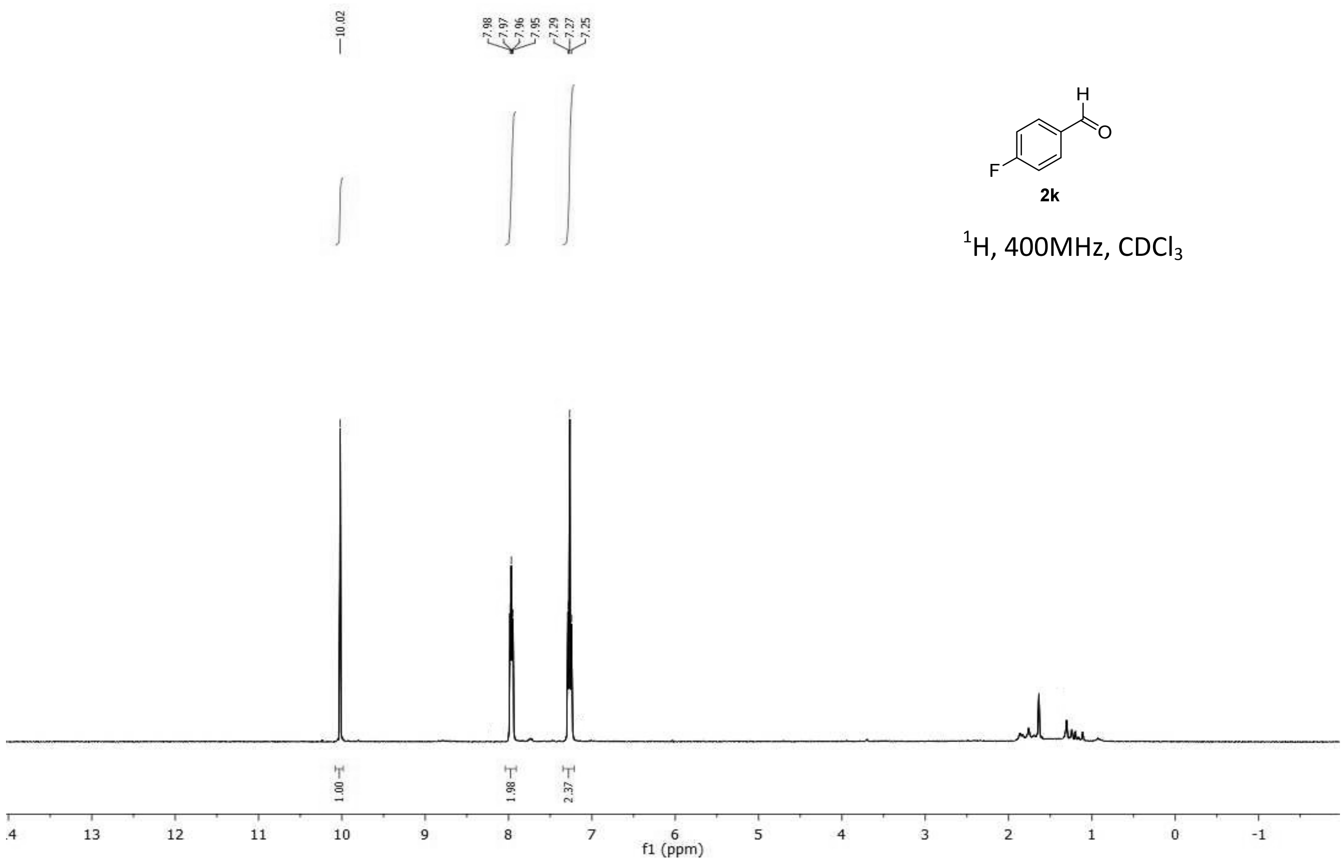


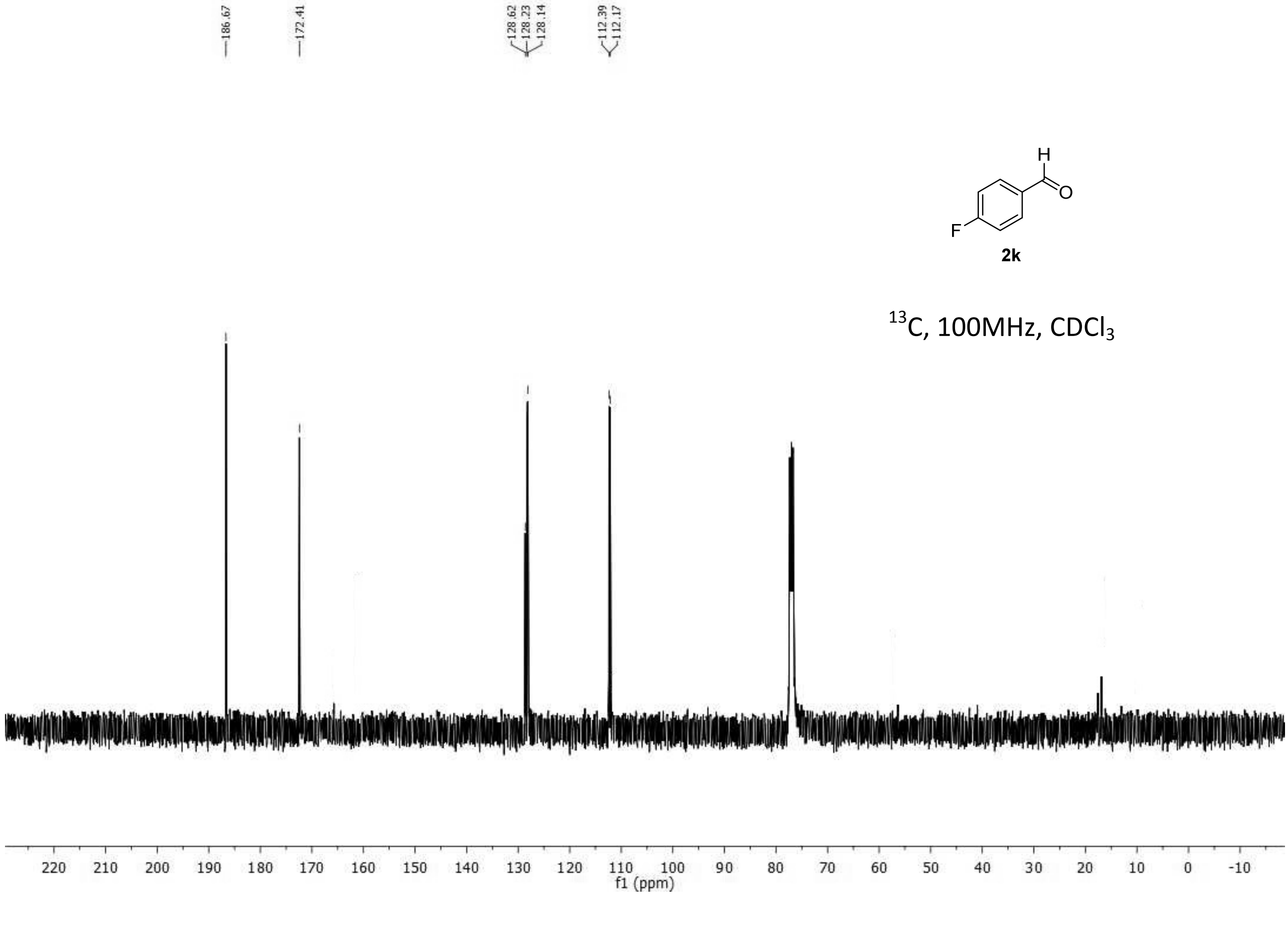
4j (Table 2, entry 23)



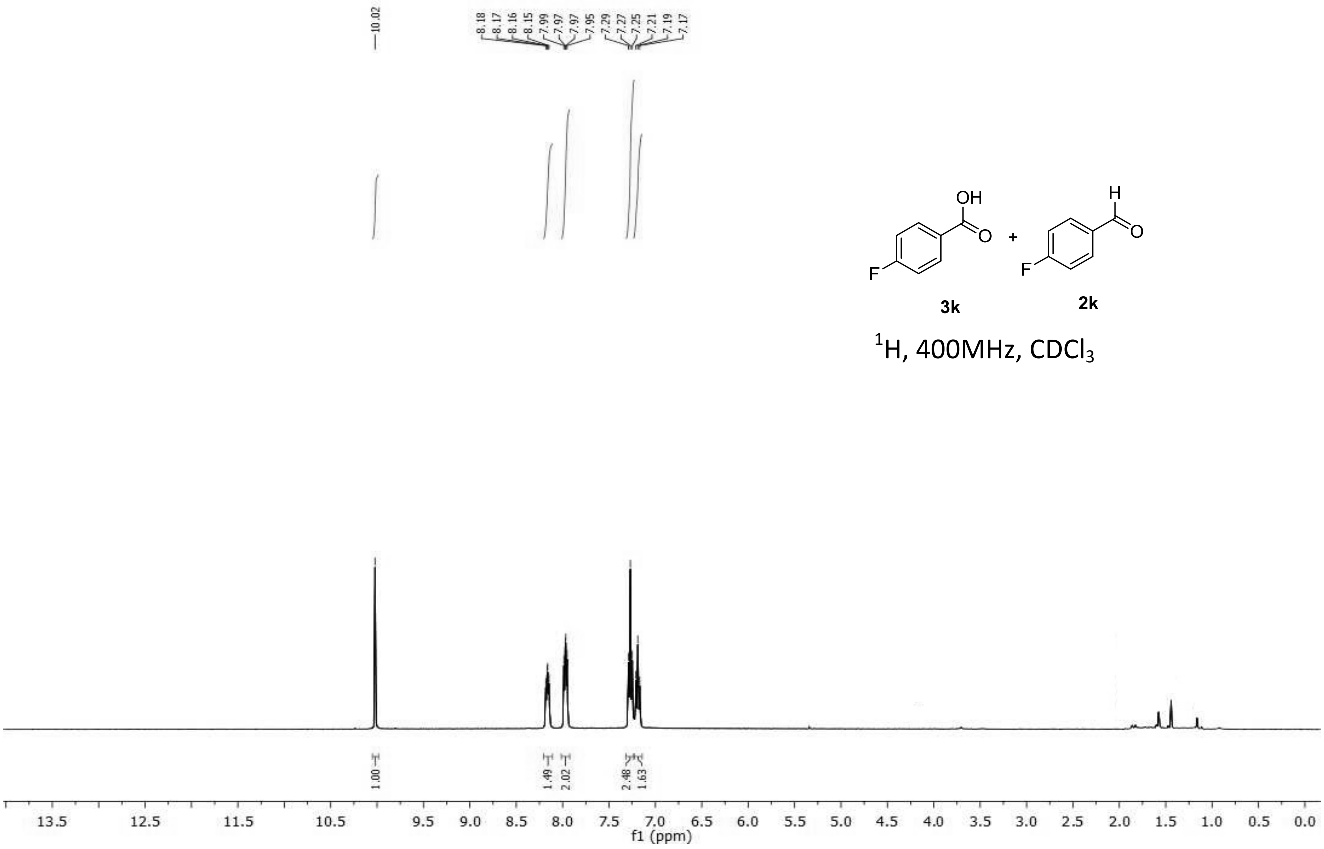


2k (Table 2, entry 24)

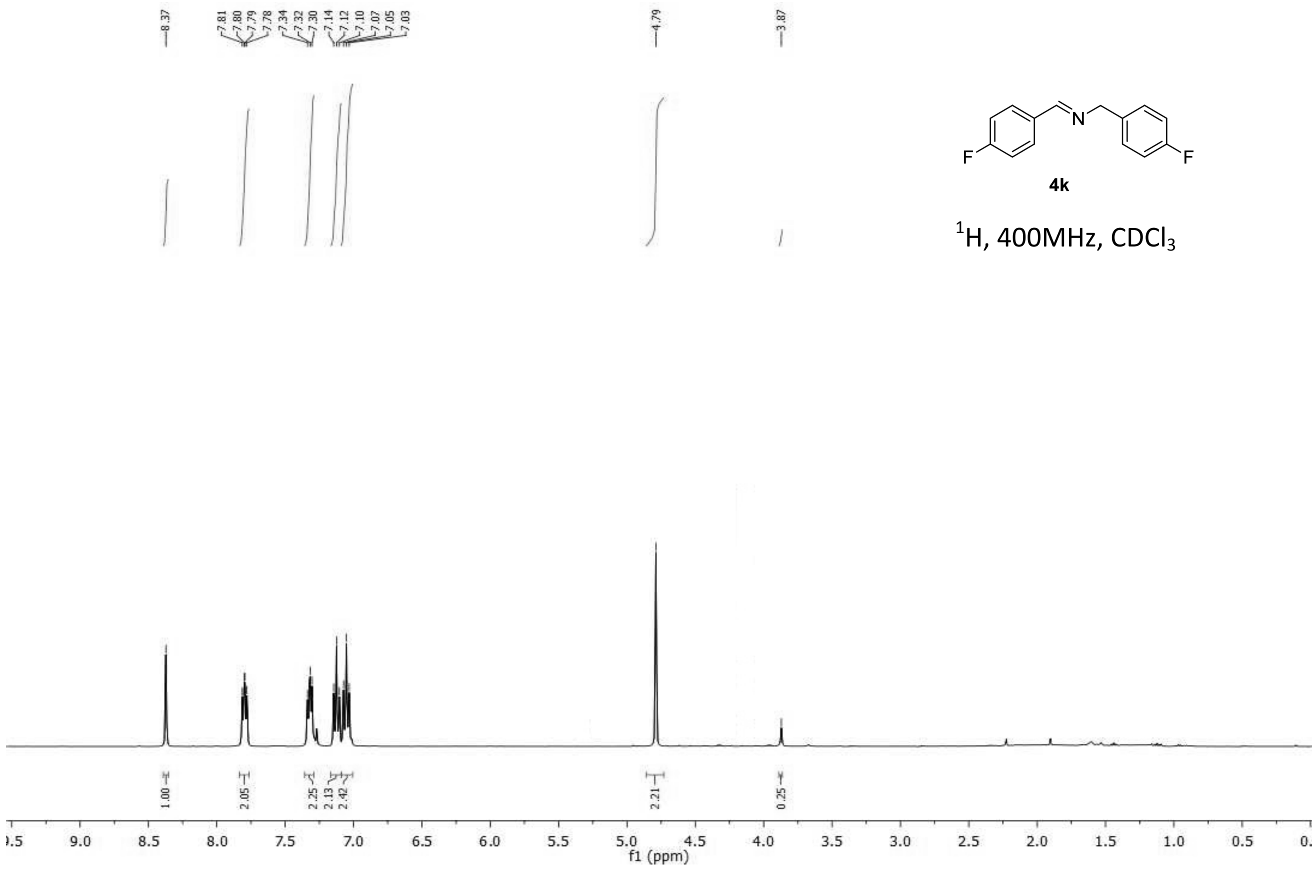


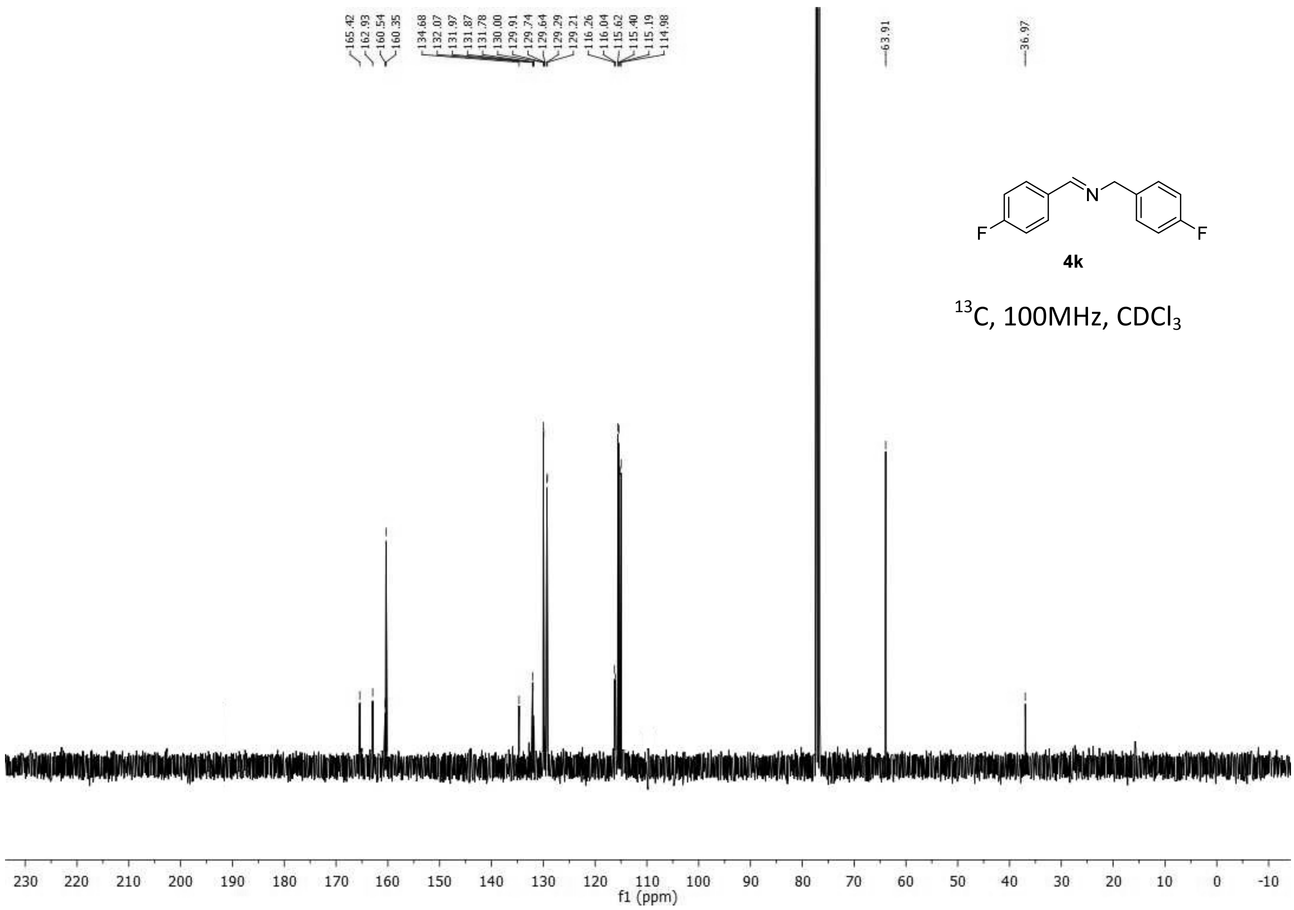


2k + **3k** (Table 2, entry 26)

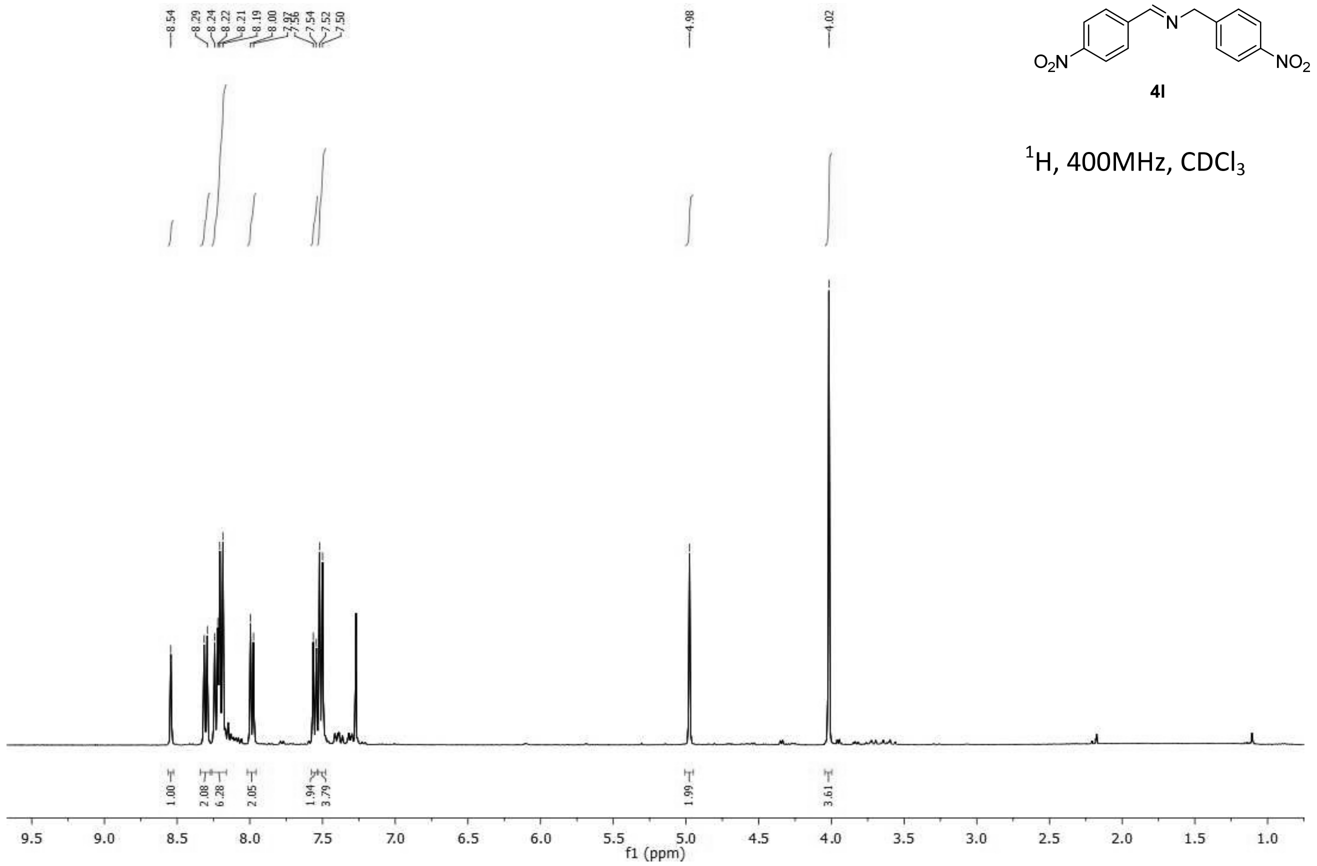


4k (Table 2, entry 27)



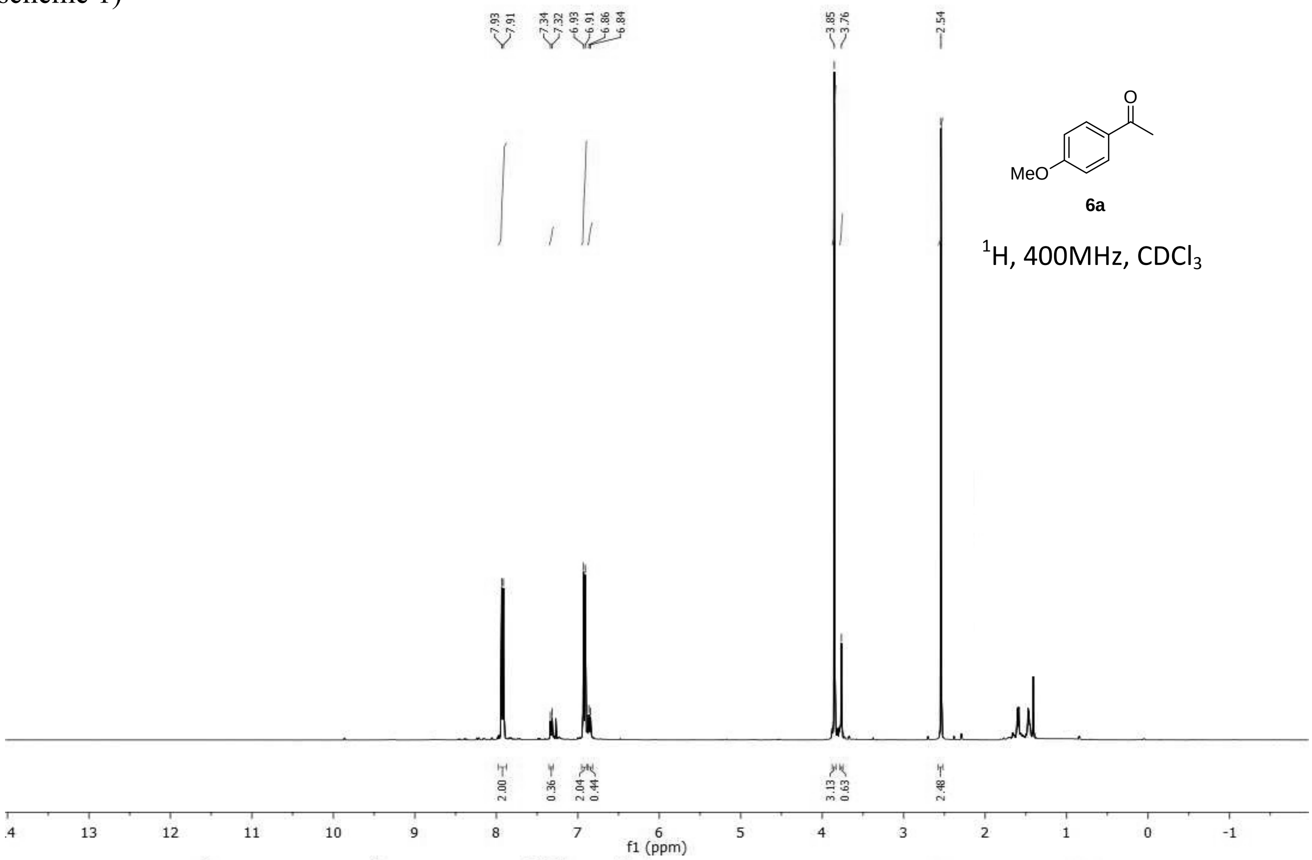


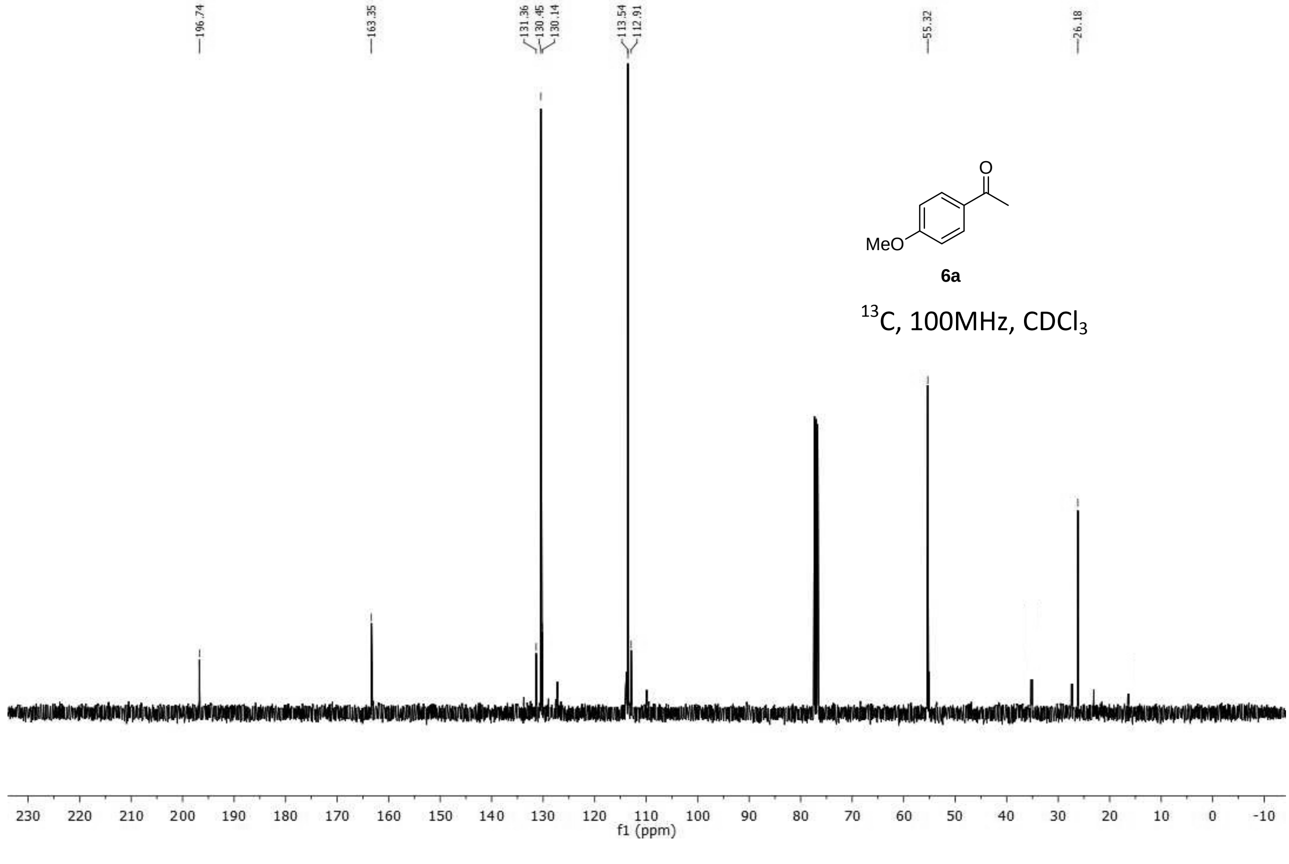
4l (Table 2, entry 29)



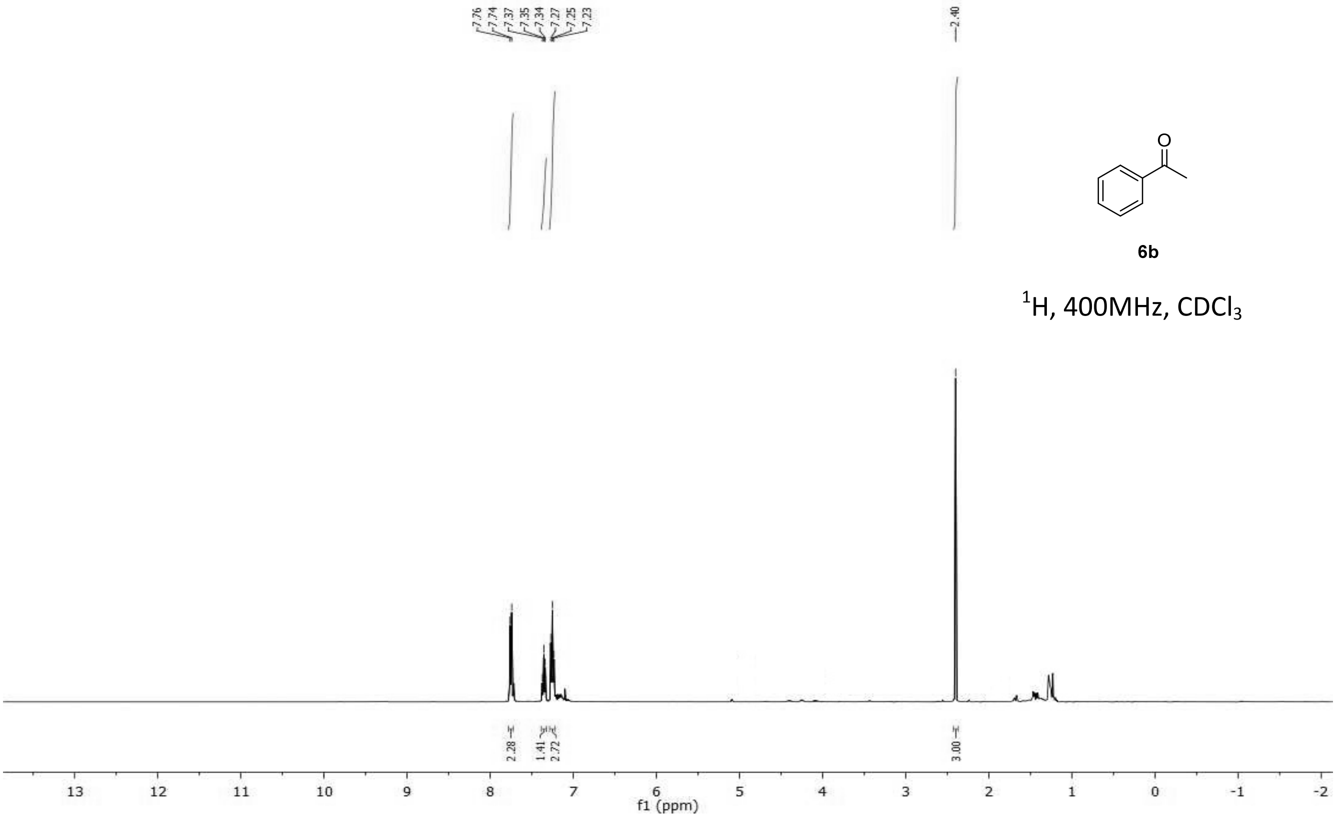
^{1}H, 400MHz, $CDCl_3$

6a (scheme 1)

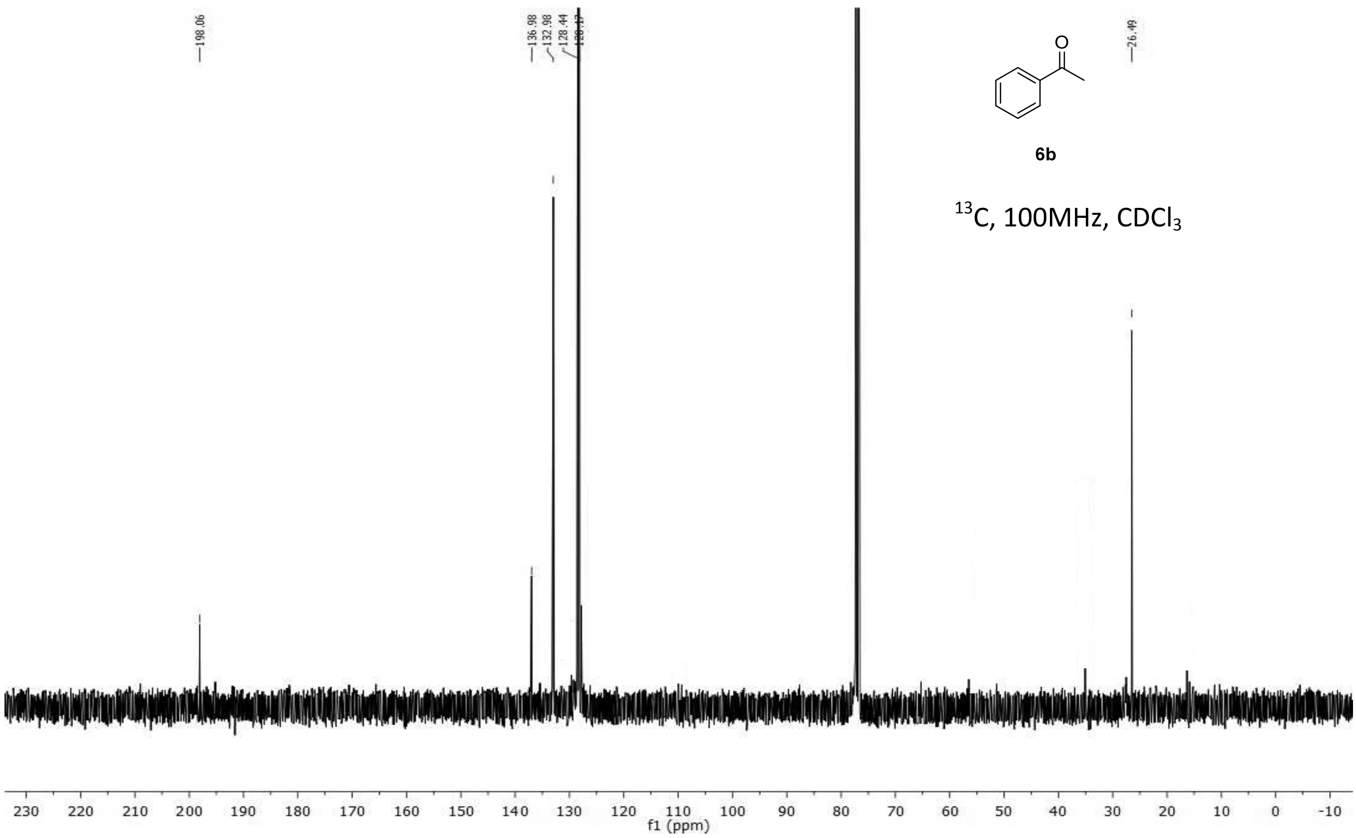

7.93
7.91
7.34
7.32
6.93
6.91
6.86
6.84
3.85
3.76
2.54
MeO
O
6a
^{1}H, 400MHz, $CDCl_3$
2.00
0.36
2.04
0.44
3.13
0.63
2.48
f1 (ppm)


196.74
163.35
131.36
130.45
130.14
113.54
112.91
55.32
26.18
MeO
O
6a
^{13}C, 100MHz, $CDCl_3$
f1 (ppm)

6b (scheme 1)

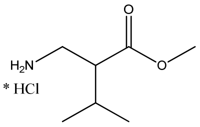


7.76
7.74
7.37
7.35
7.34
7.27
7.25
7.23
2.40
6b
^{1}H, 400MHz, CDCl$_3$
2.28
1.41
2.72
3.00
f1 (ppm)



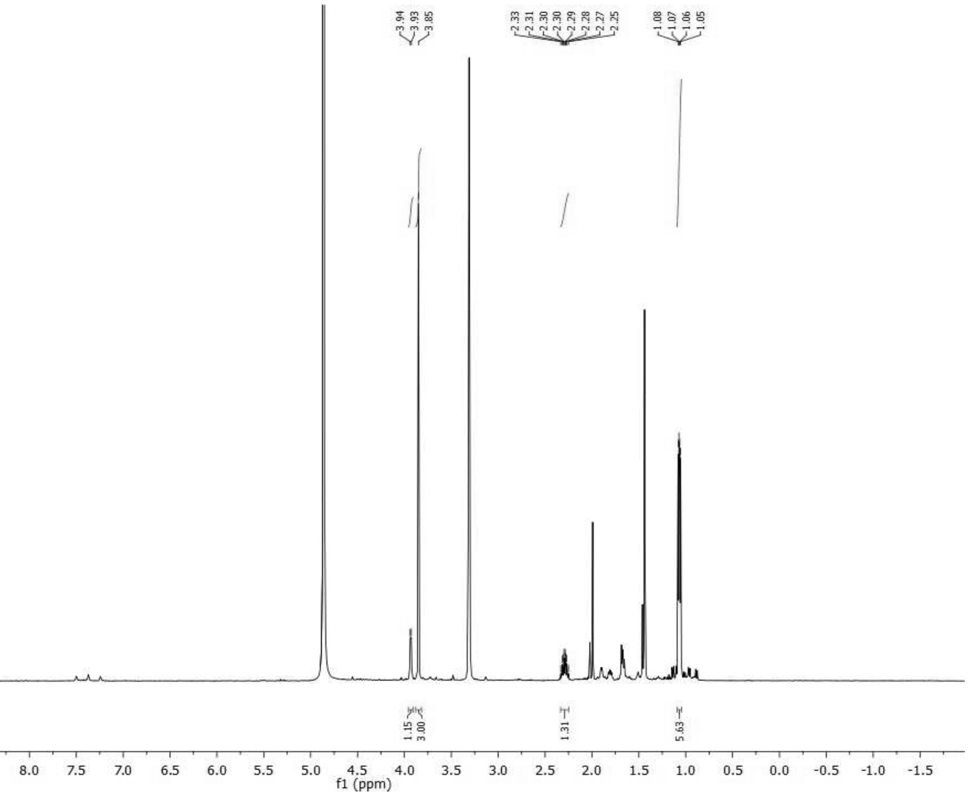
198.06
136.98
132.98
128.44
26.49
6b
^{13}C, 100MHz, CDCl$_3$
f1 (ppm)

9a (scheme 3)

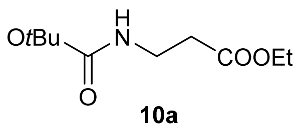


9a

[1]H, 400MHz, CD_3OD

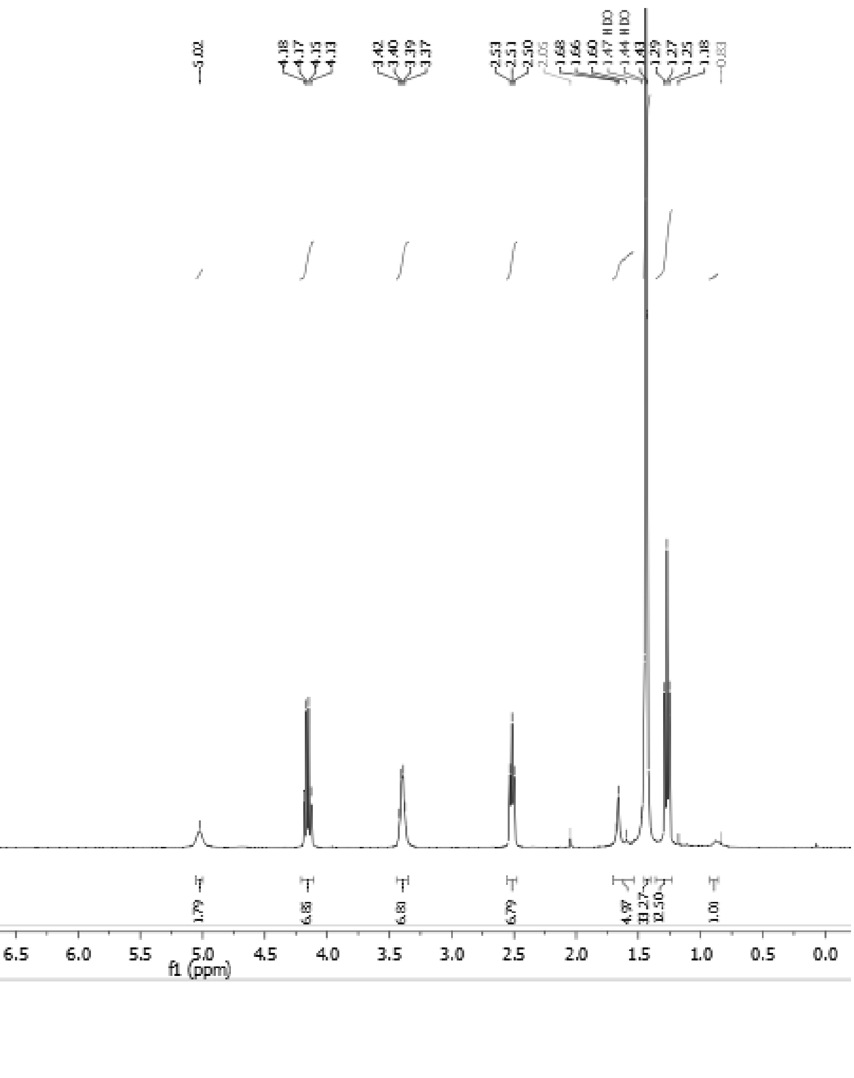


10a (scheme 3)

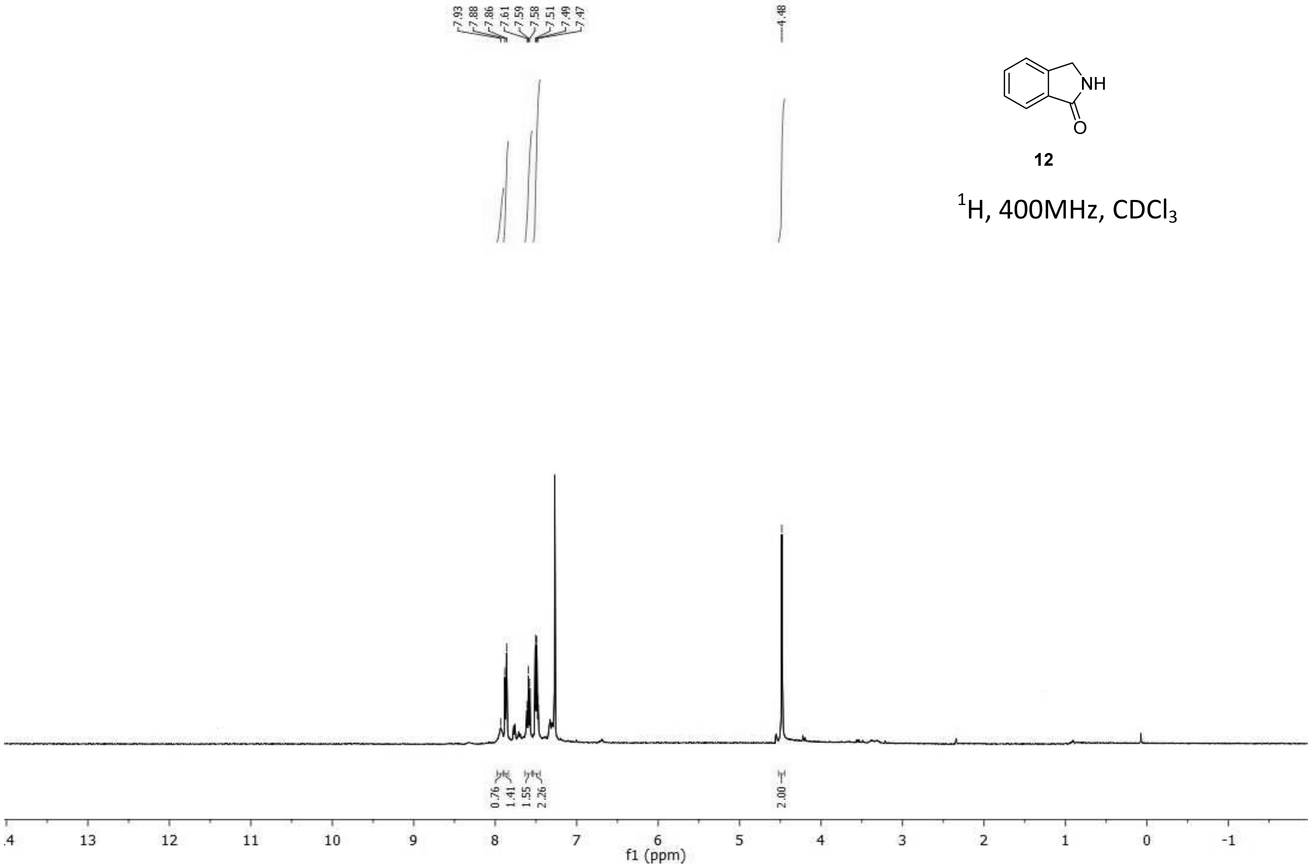


10a

[1]H, 400MHz, $CDCl_3$



12 (scheme 4)


7.93
7.88
7.86
7.61
7.59
7.58
7.51
7.49
7.47
4.48
NH
O
12
^{1}H, 400MHz, CDCl$_3$
0.76
1.41
1.55
2.26
2.00
f1 (ppm)

14, 15, 16 (scheme 4)