Rhodium-Catalyzed Synthesis of Isoquinolines and Indenes from Benzylidenehydrazines and Internal Alkynes

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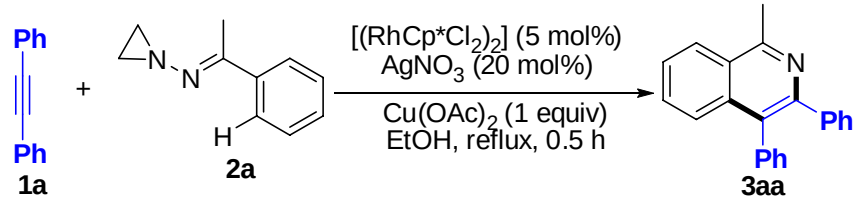
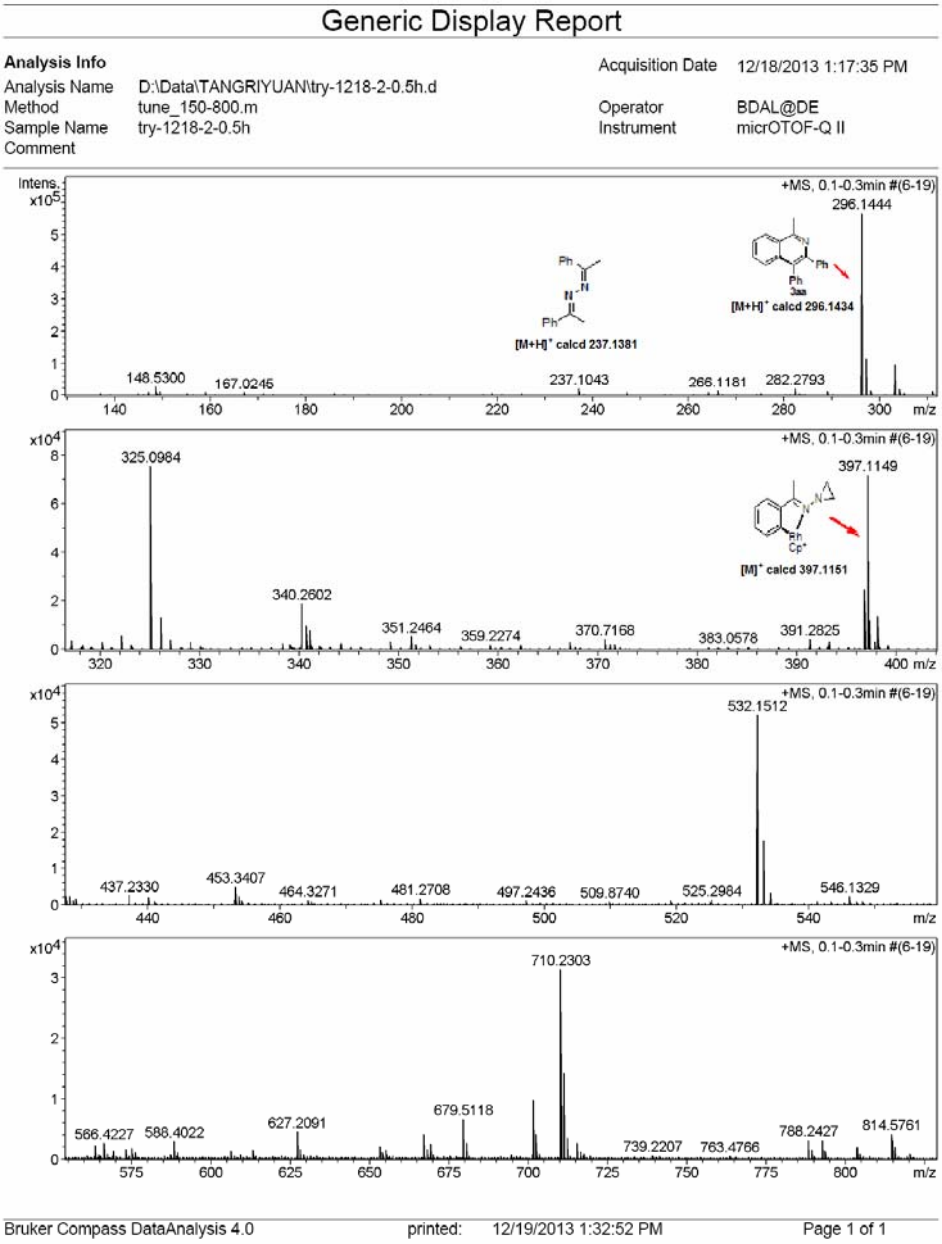
Supporting Information

List of Contents

(A) Control Experiments

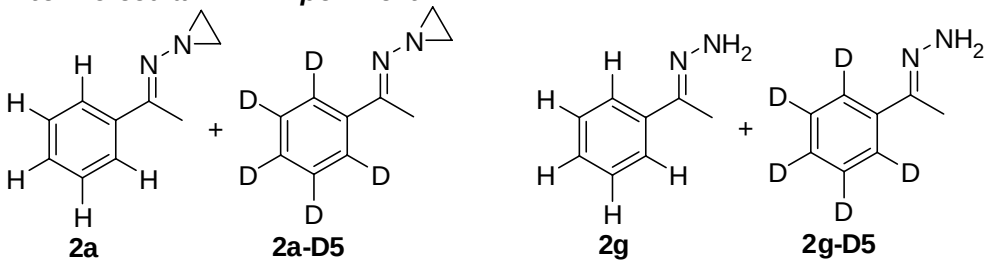
(a) Figure S1 The Reaction Determined in-situ by HRMS Analysis





(b) The Kinetic Isotope Effect Experiments

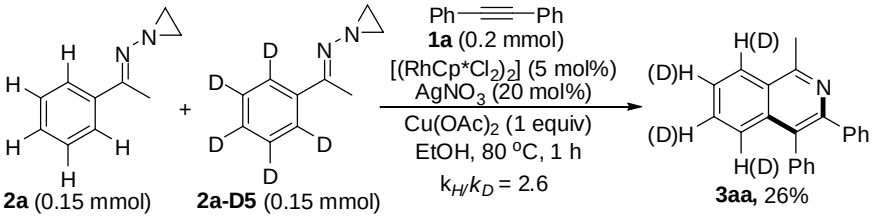
Intermolecular KIE Experiment

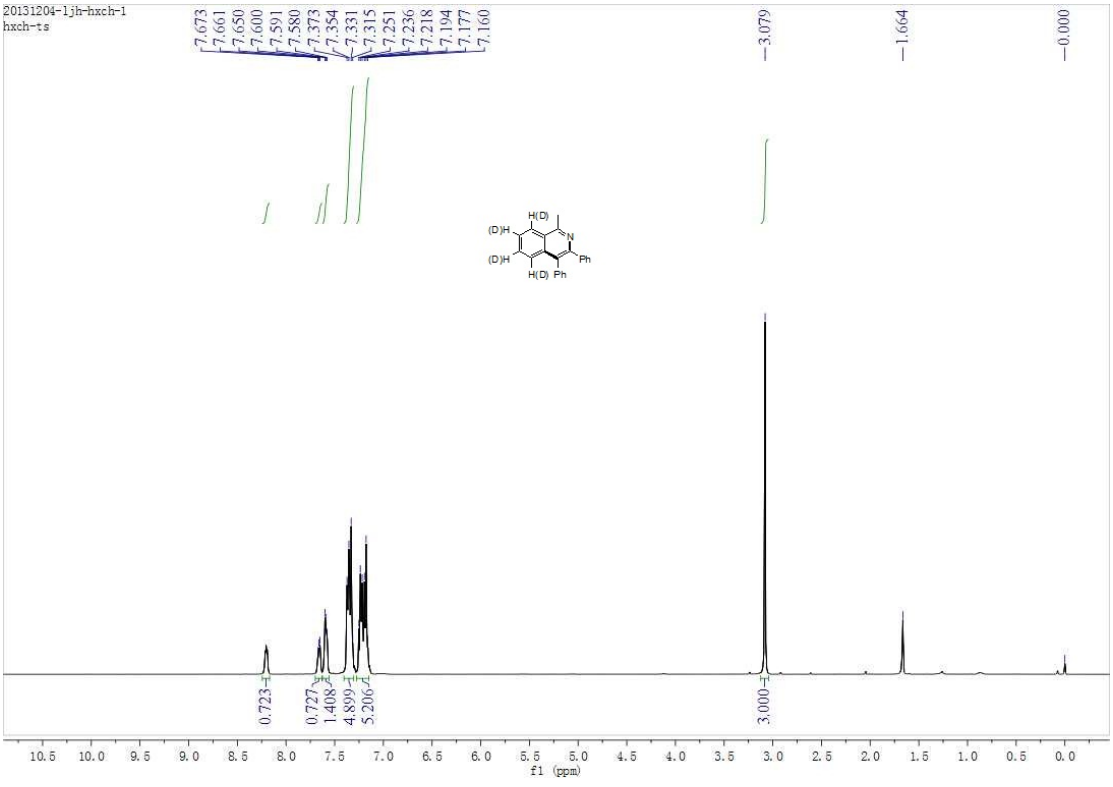


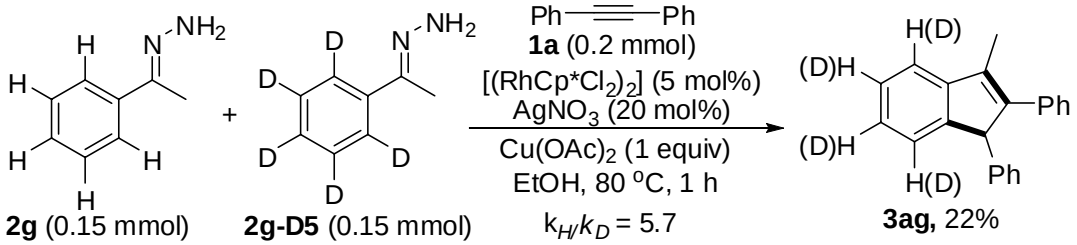
26% yield (1 h), $k_{H/}k_D$ = 2.6 　　22% yield (1 h), $k_{H/}k_D$ = 5.7

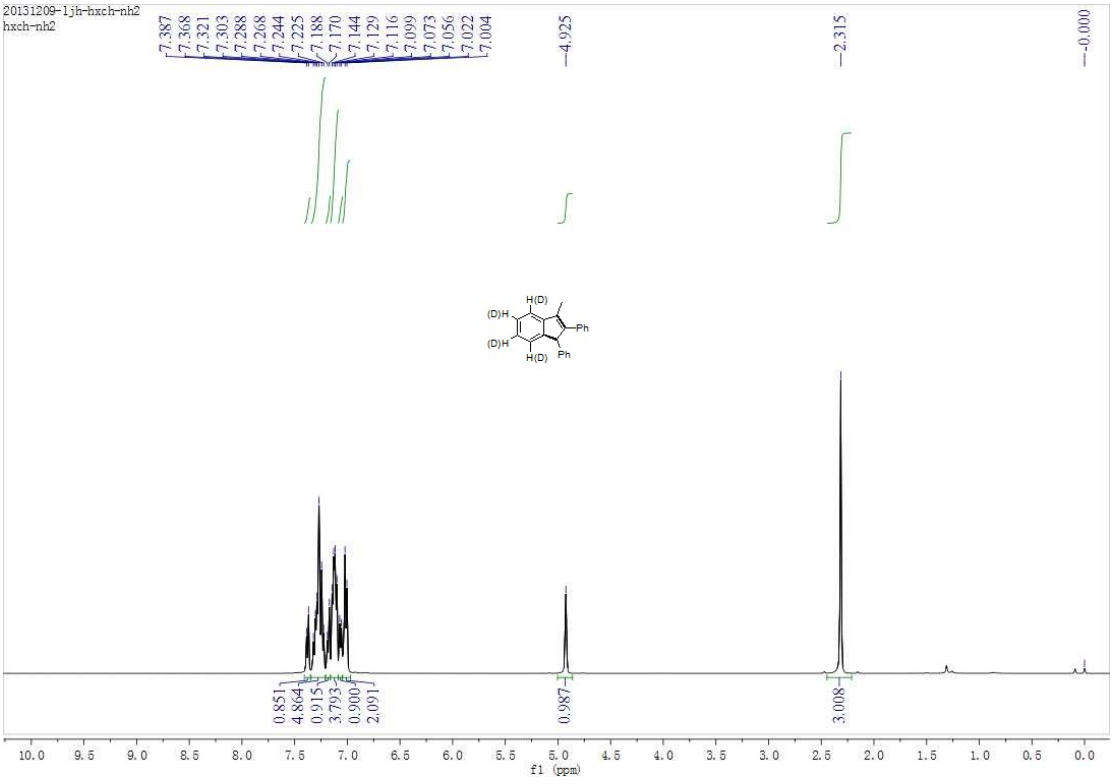
The intermolecular kinetic isotope effect experiments imply that the C(sp^2)-H cleavage is not compatible with the SEAr mechanism and the free radical mechanism.

Intermolecular KIE Experiment



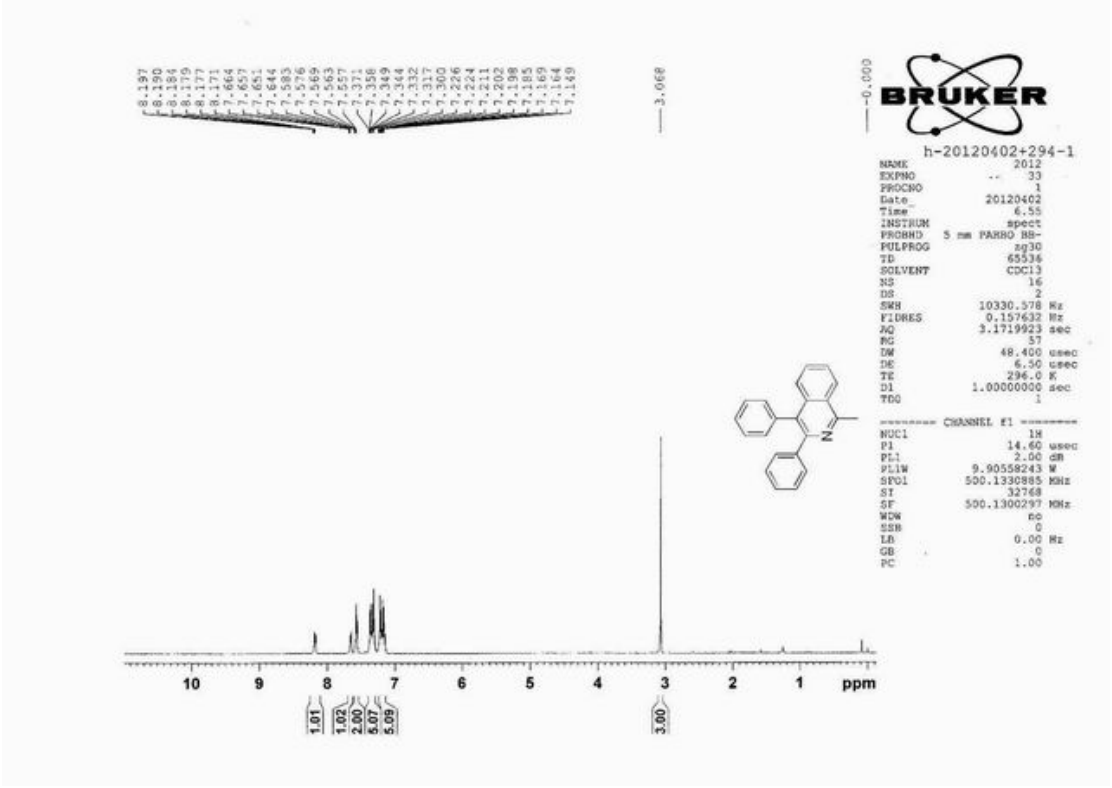


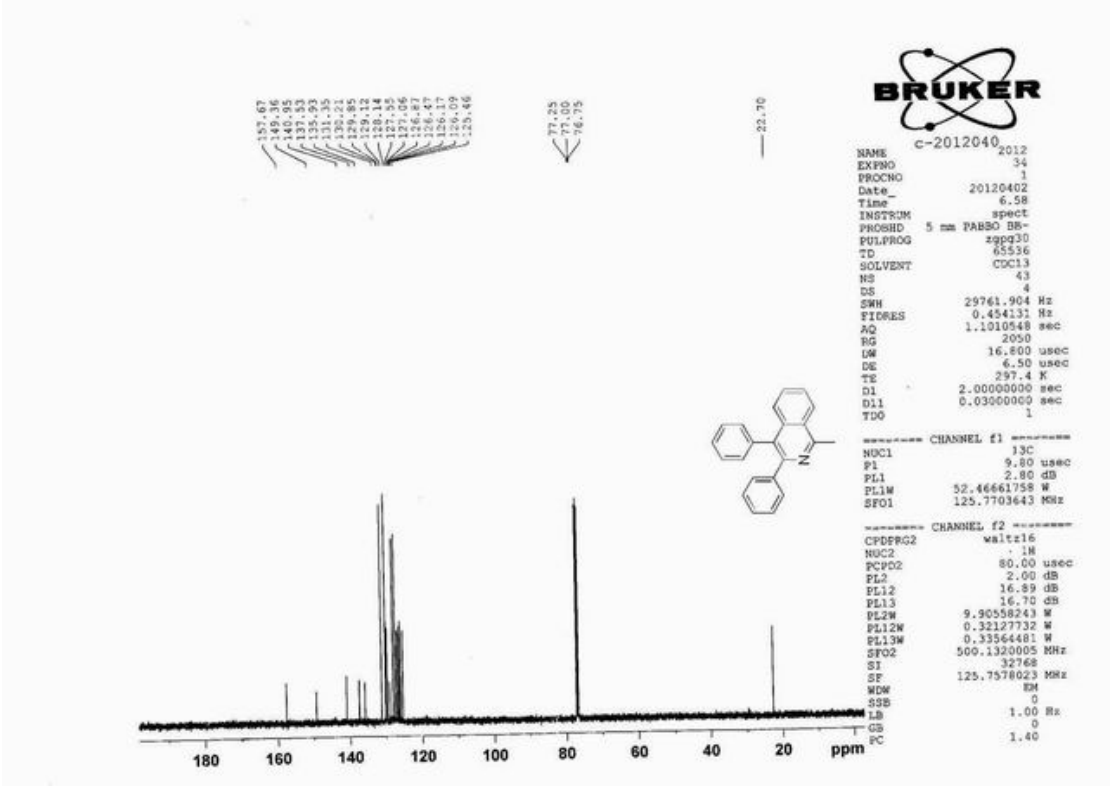

Ph—≡—Ph
1a (0.2 mmol)
[(RhCp*Cl2)2] (5 mol%)
AgNO3 (20 mol%)
Cu(OAc)2 (1 equiv)
EtOH, 80 °C, 1 h
kH/kD = 5.7
2g (0.15 mmol)
2g-D5 (0.15 mmol)
3ag, 22%


20131209-1jh-hxch-nh2
hxch-nh2
7.387
7.368
7.321
7.303
7.288
7.268
7.244
7.225
7.188
7.170
7.144
7.129
7.116
7.099
7.073
7.056
7.022
7.004
4.925
2.315
-0.000
0.851
4.864
0.915
3.793
0.900
2.091
0.987
3.008
f1 (ppm)

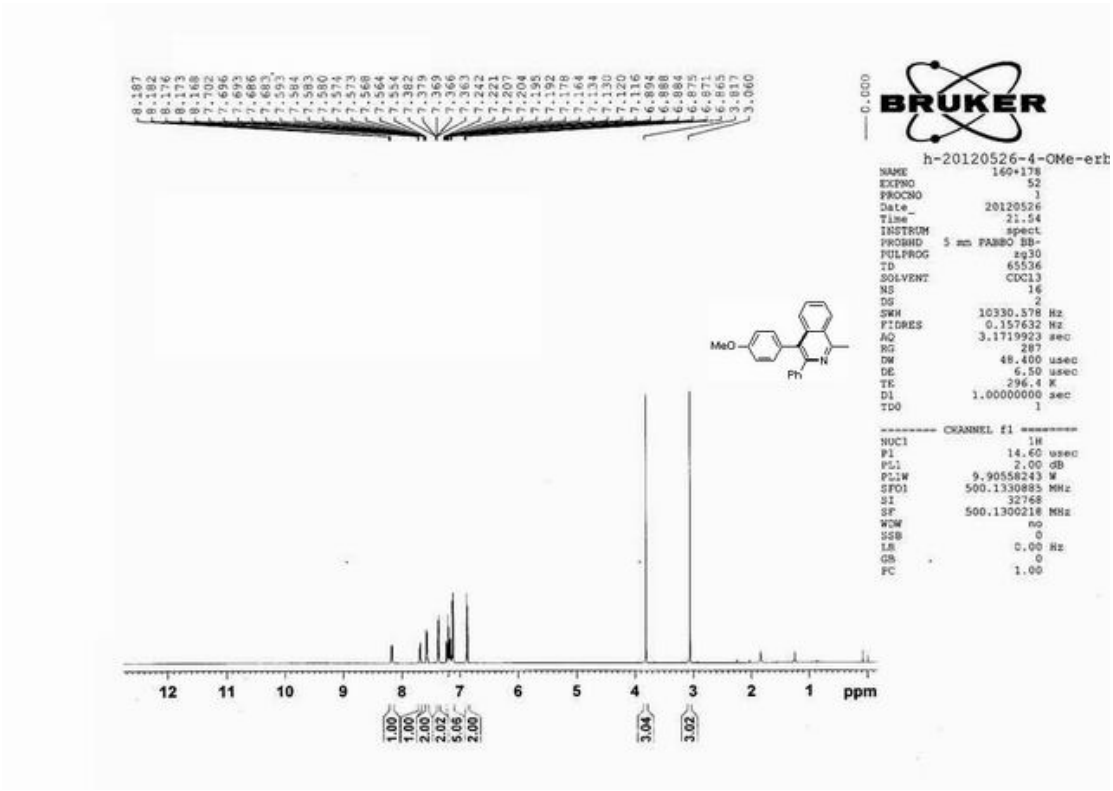
(B) Spectra

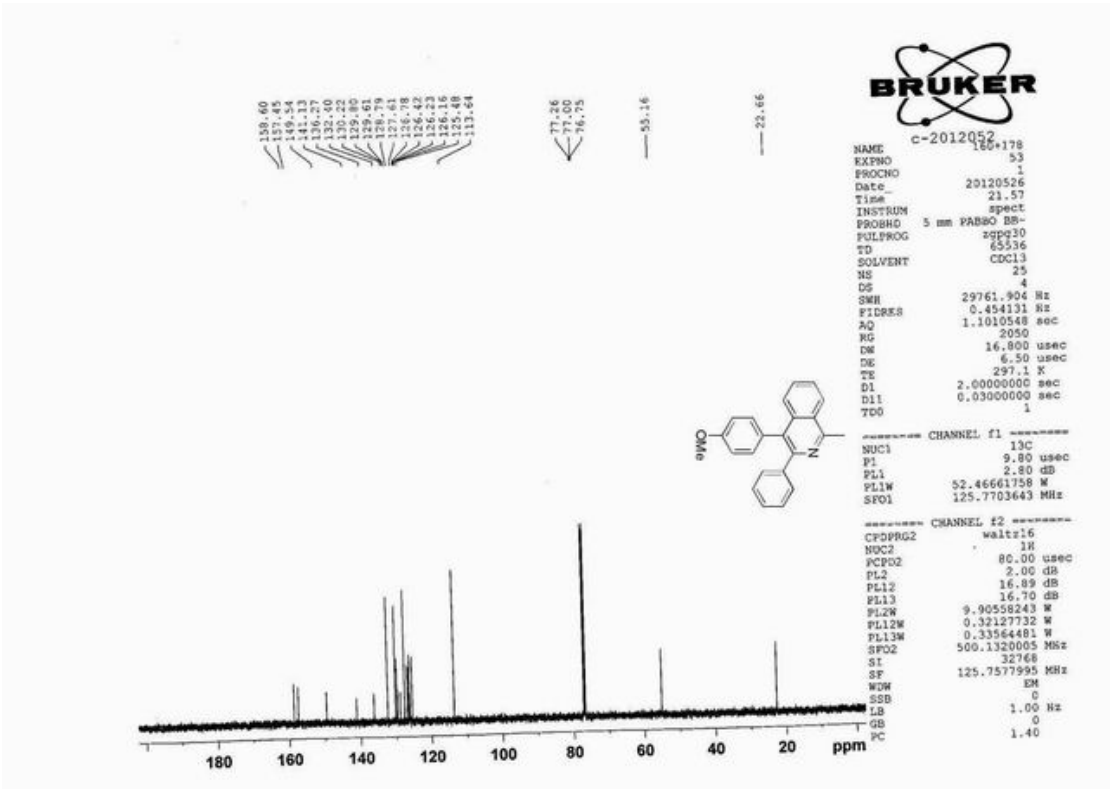
1-Methyl-3,4-diphenylisoquinoline (3aa)



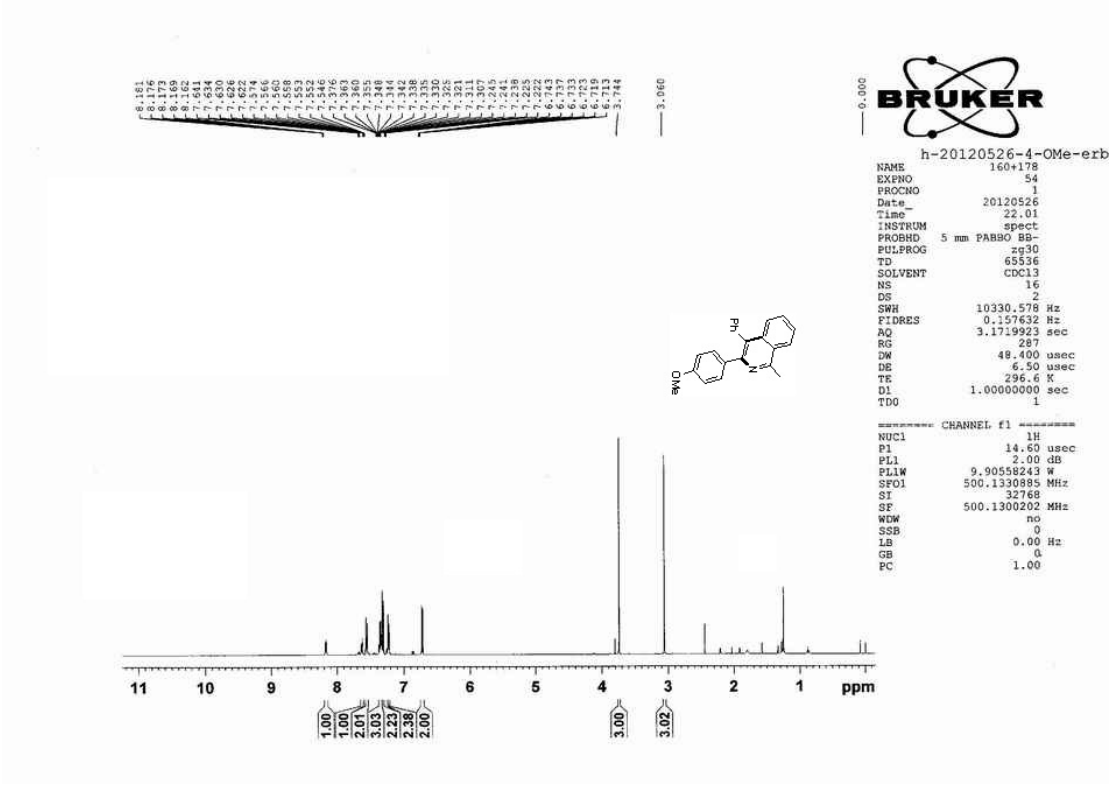


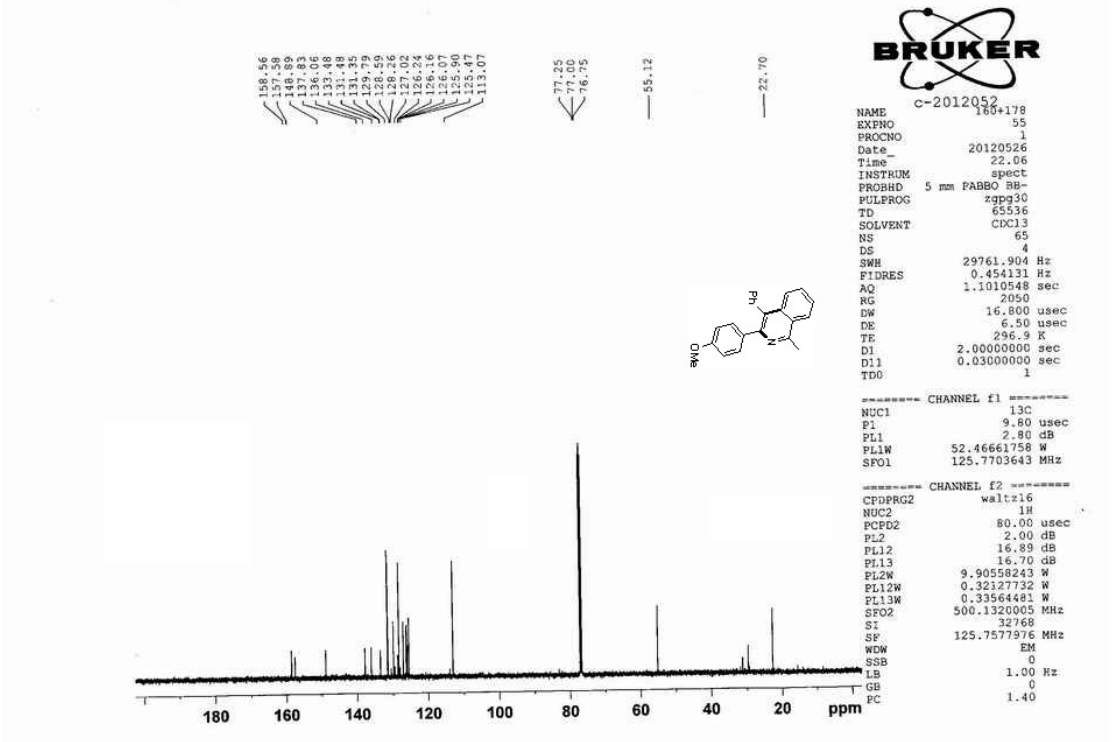
4-(4-Methoxyphenyl)-1-methyl-4-phenylisoquinoline (3ba)



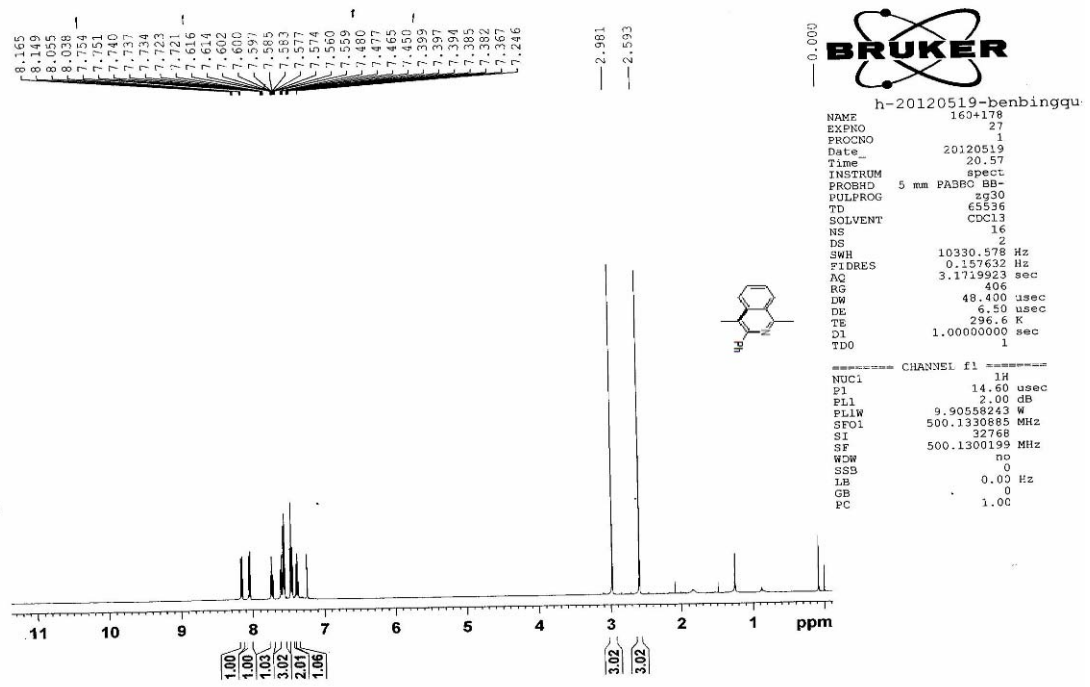


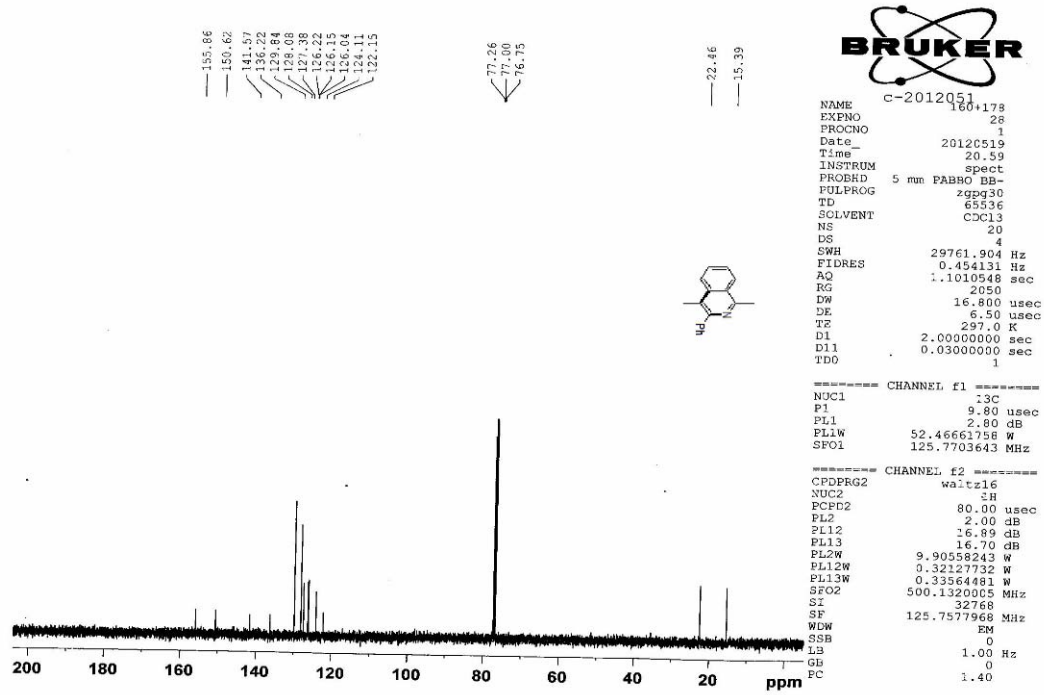
3-(4-Methoxyphenyl)-1-methyl-3-phenylisoquinoline (3ba')



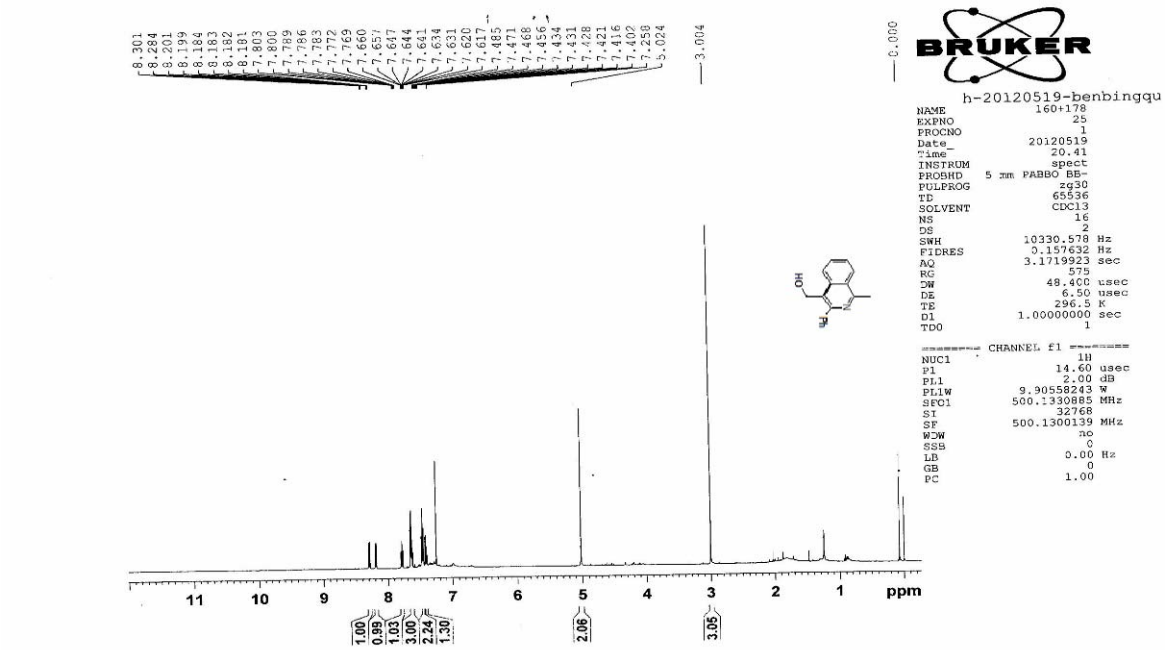


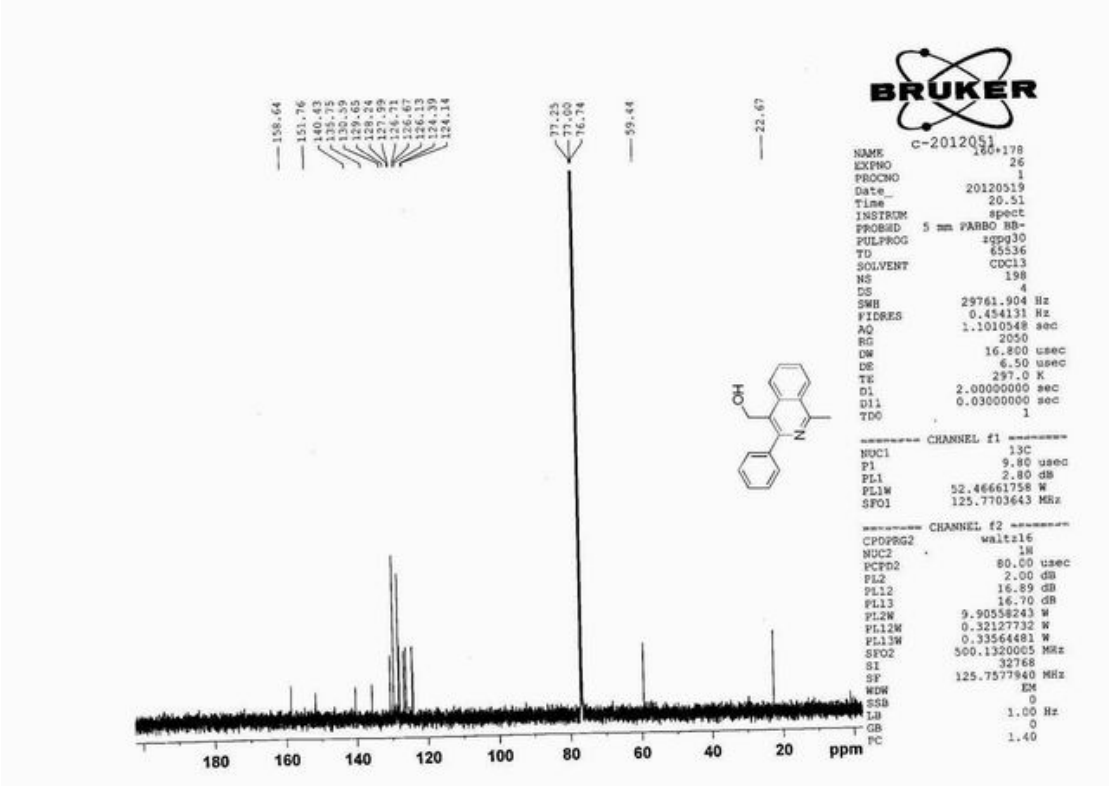
1,4-Dimethyl-3-phenylisoquinoline (3ca)



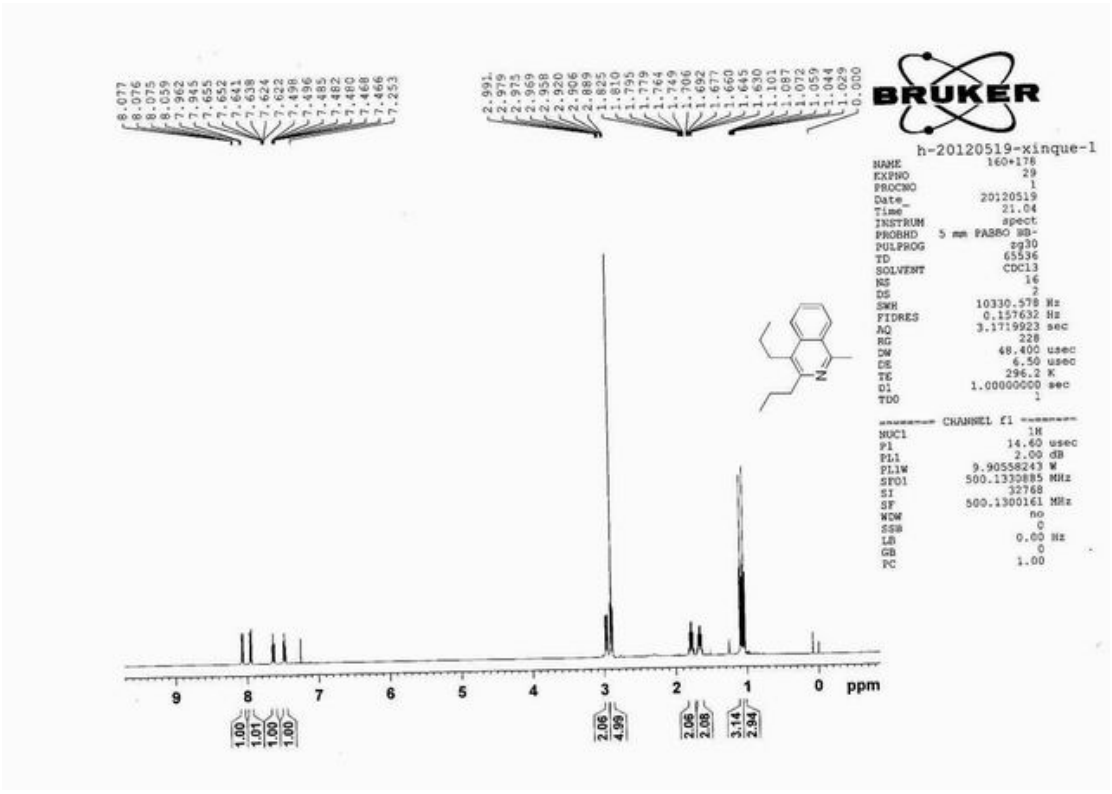


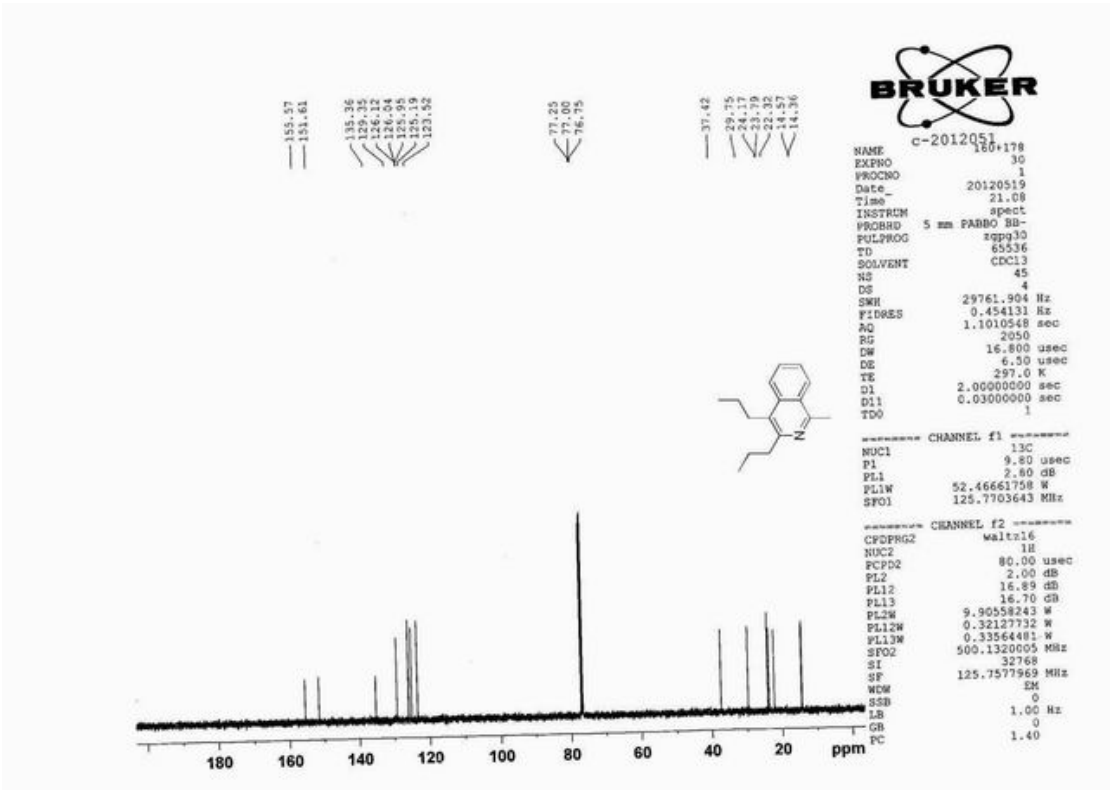
(1-Methyl-3-phenylisoquinolin-4-yl)methanol (3da)



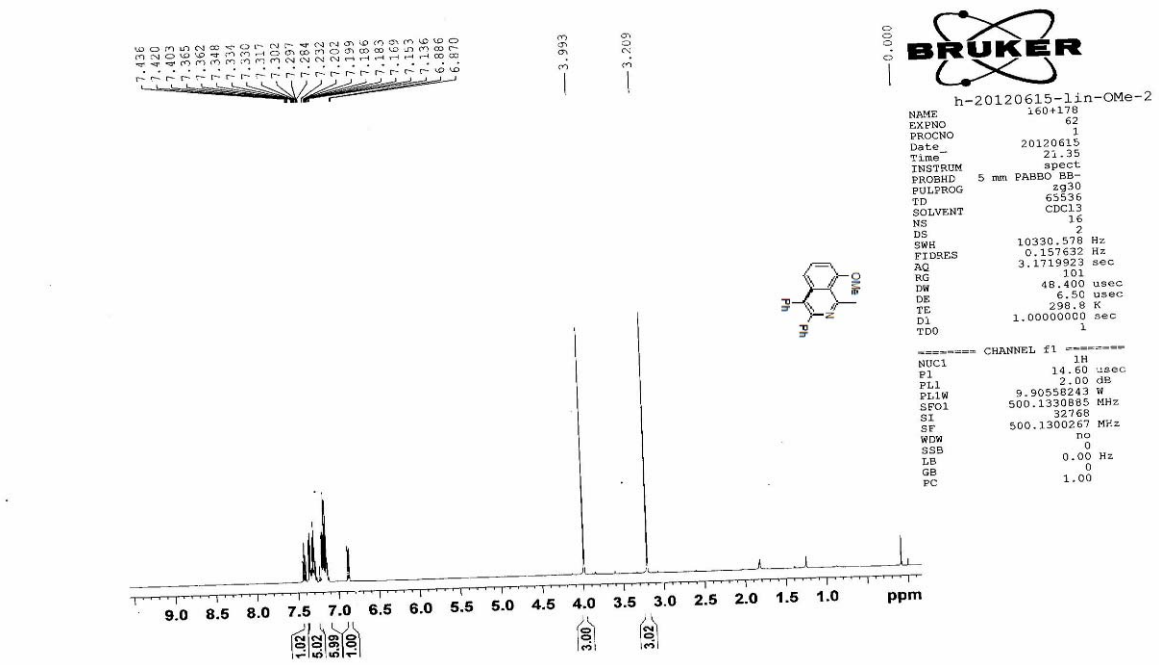


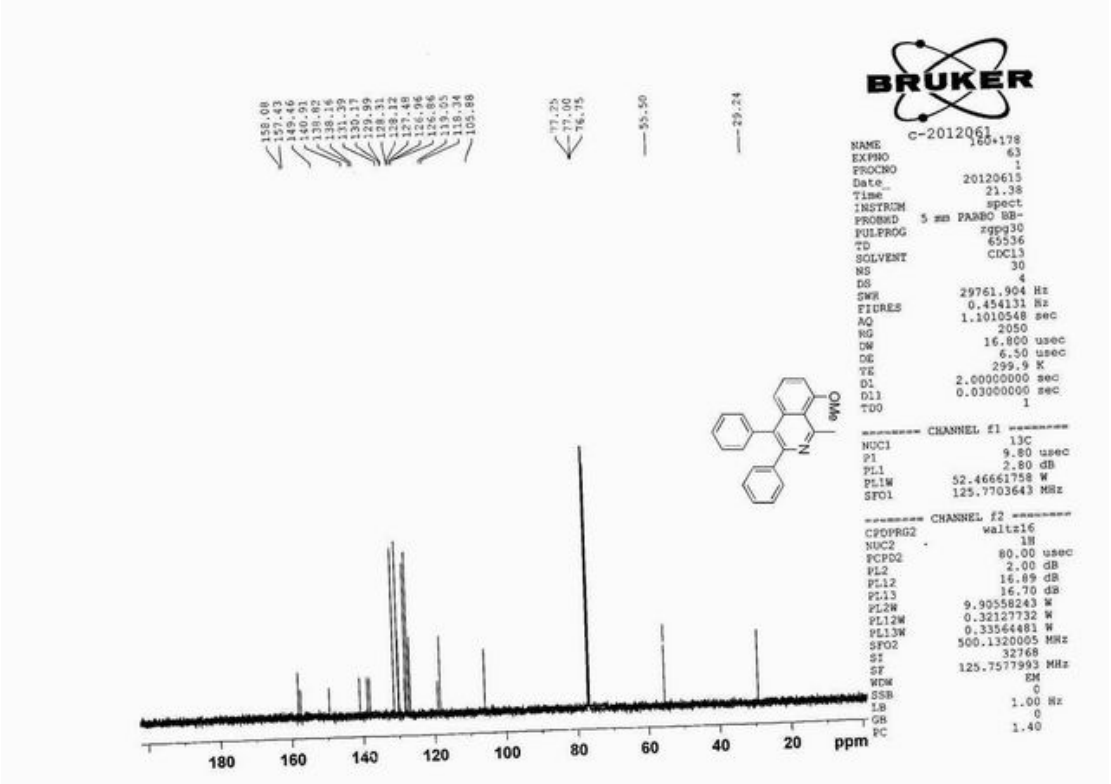
1-Methyl-3,4-dipropylisoquinoline (3ea)



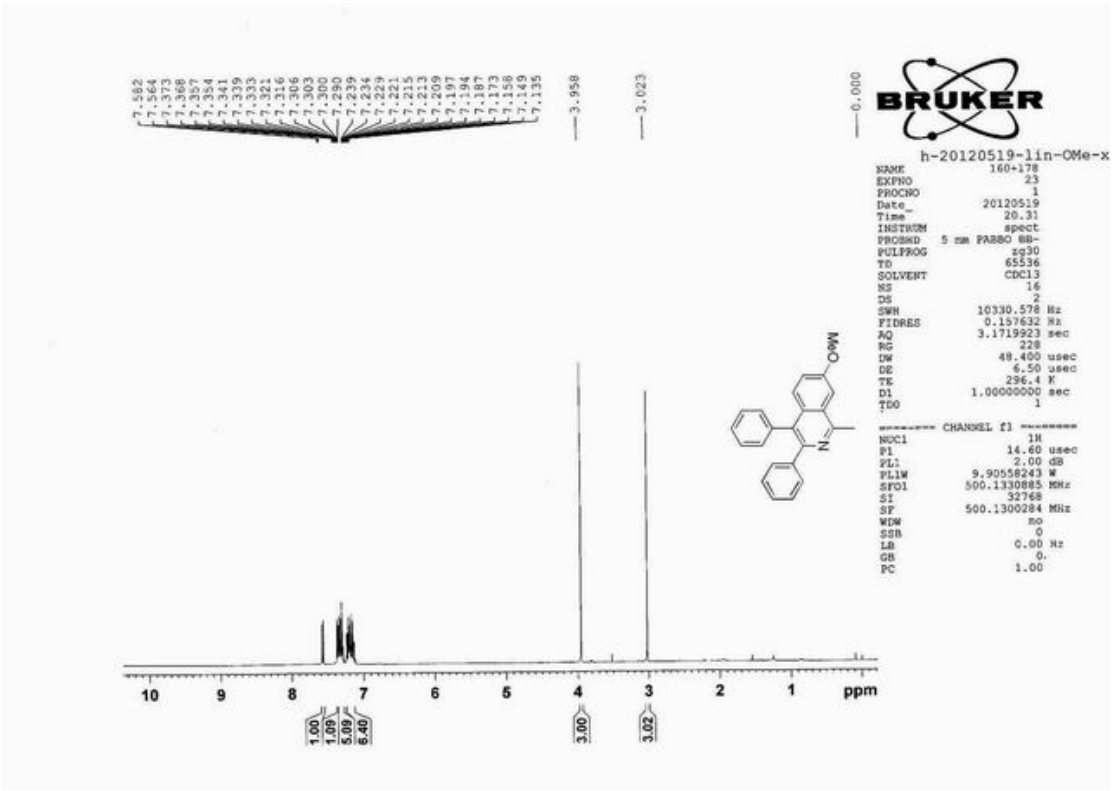


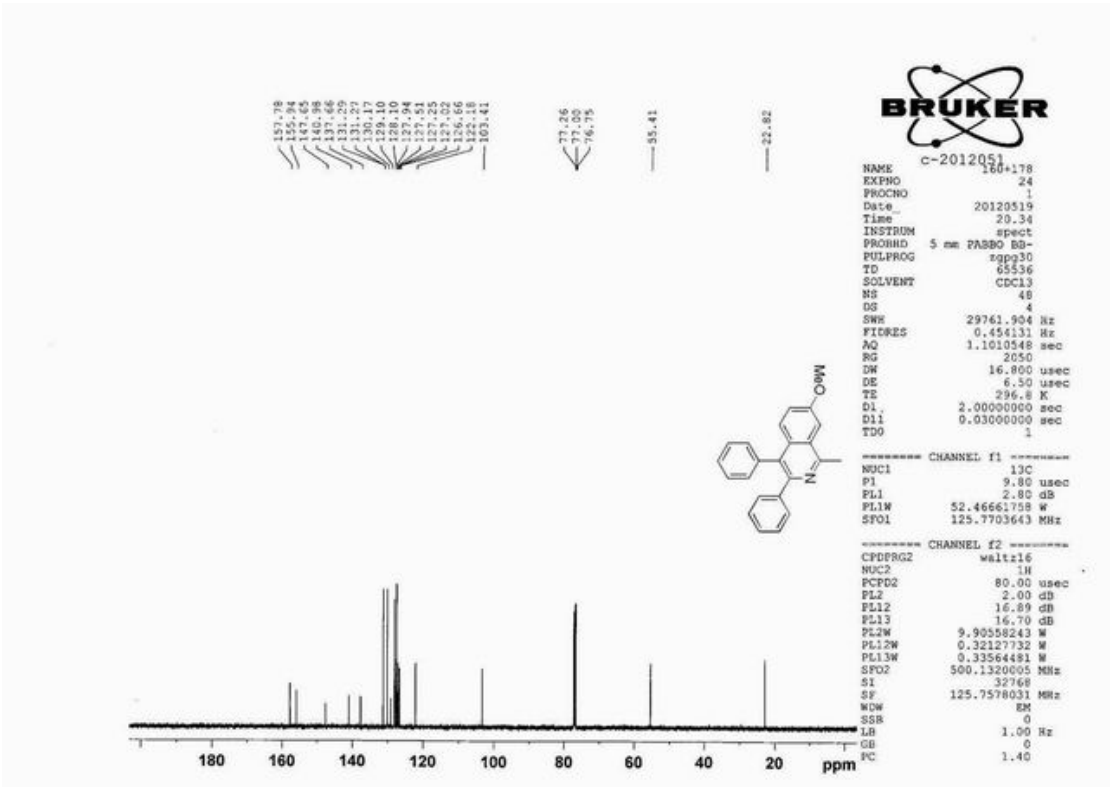
8-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ah)



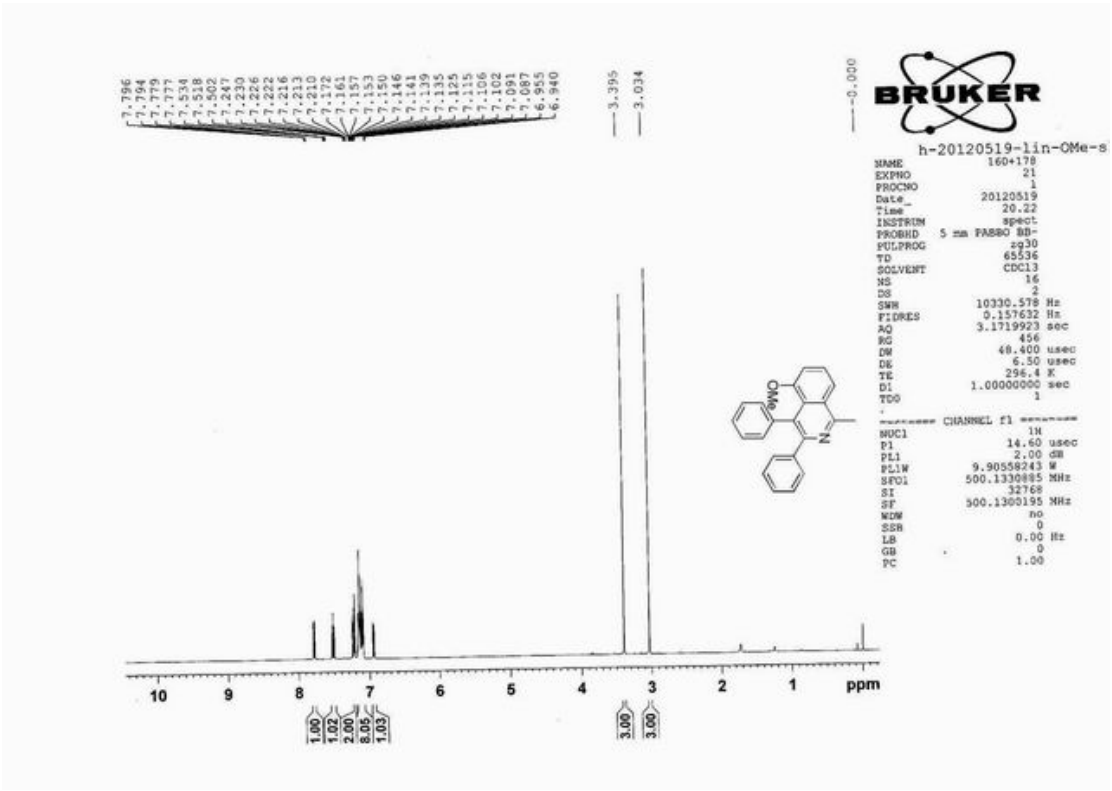


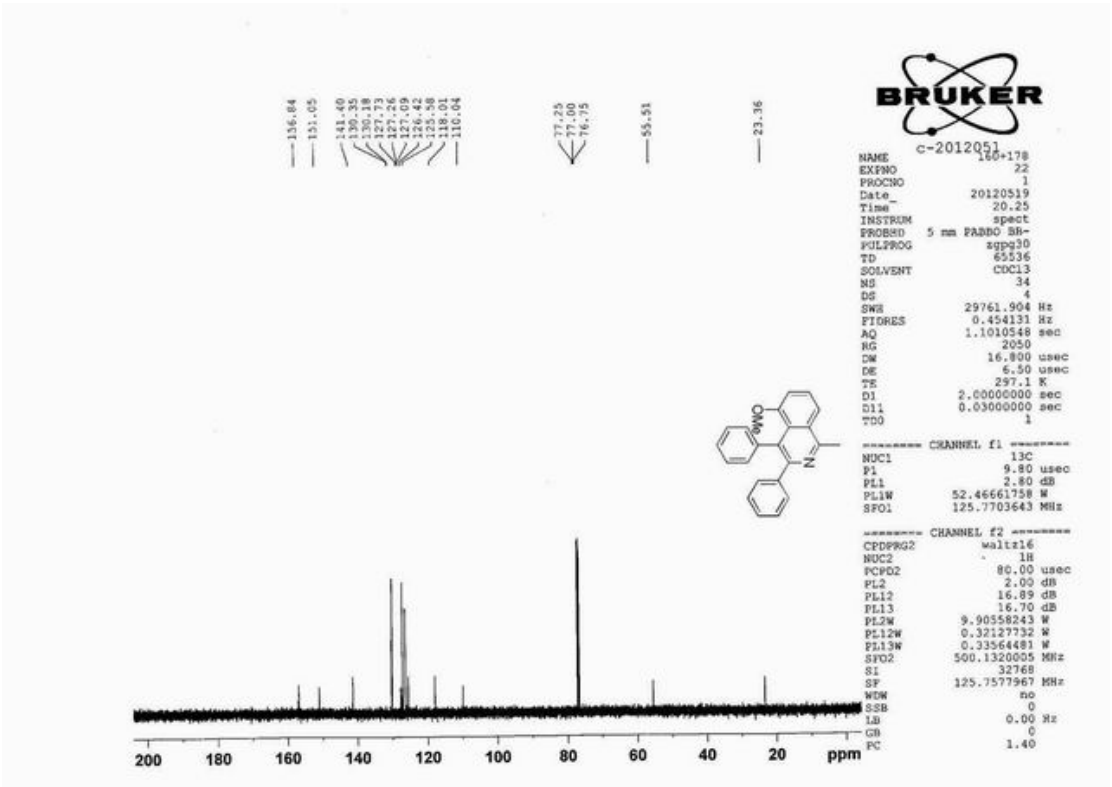
7-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ai)



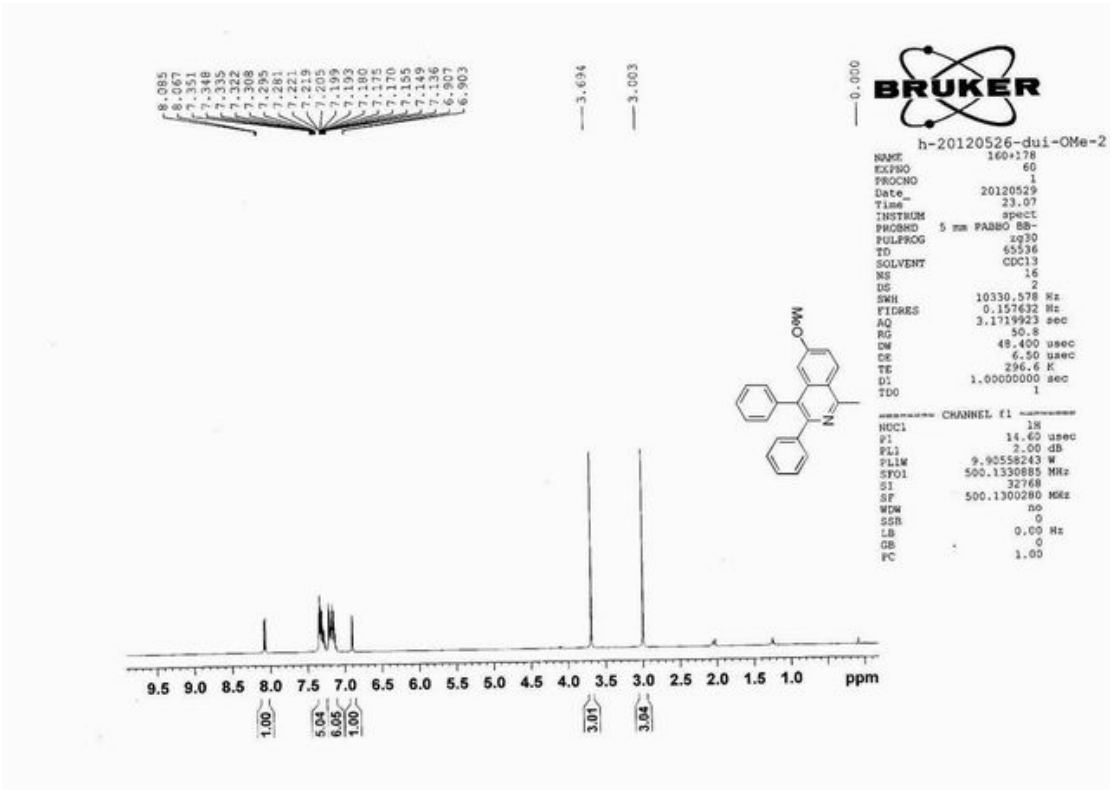


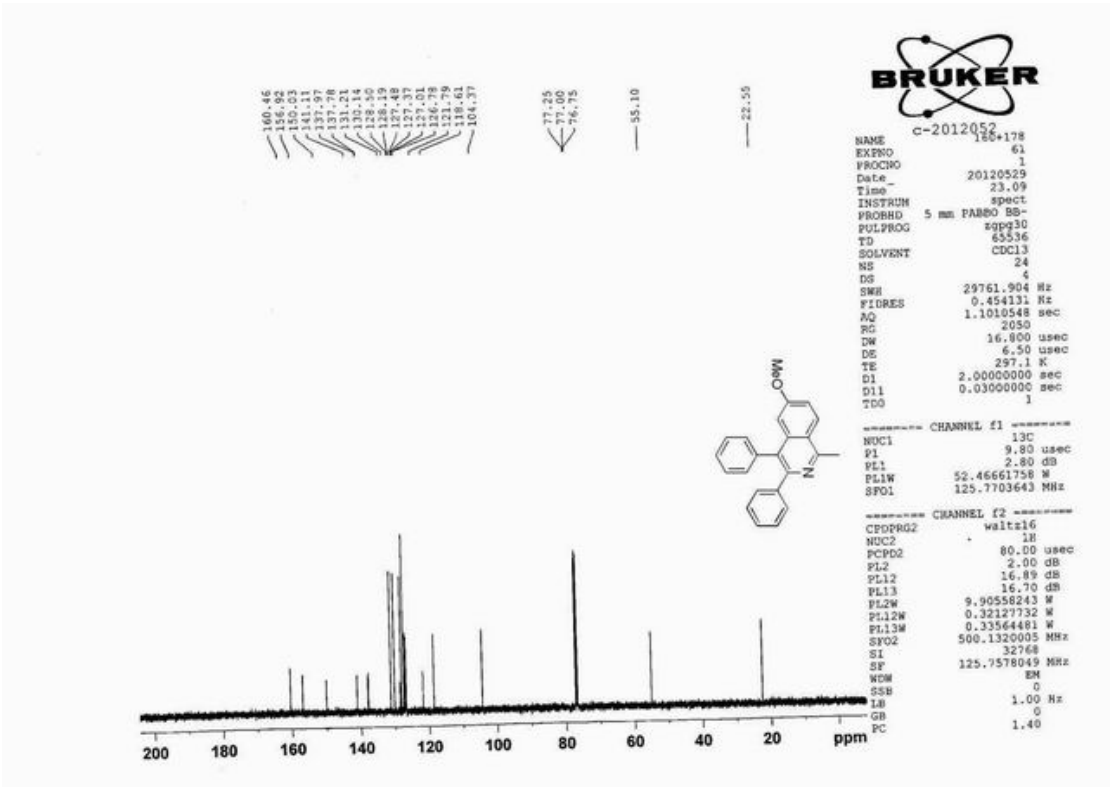
5-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ai')



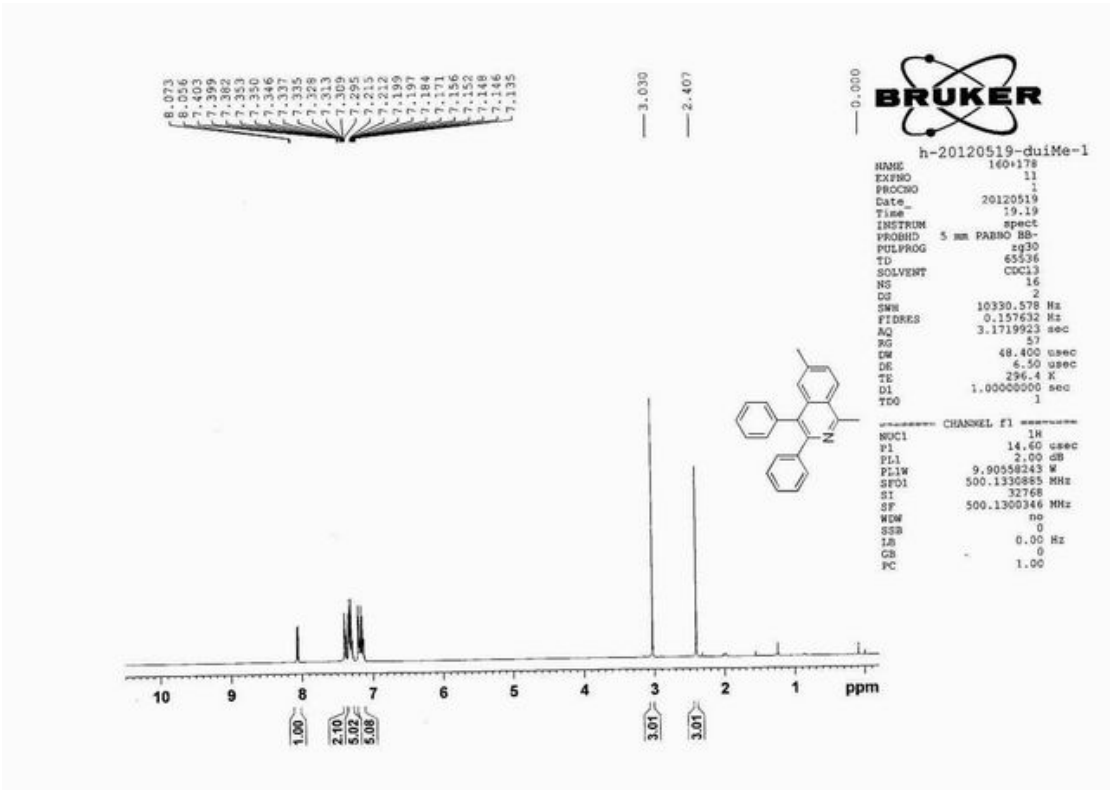


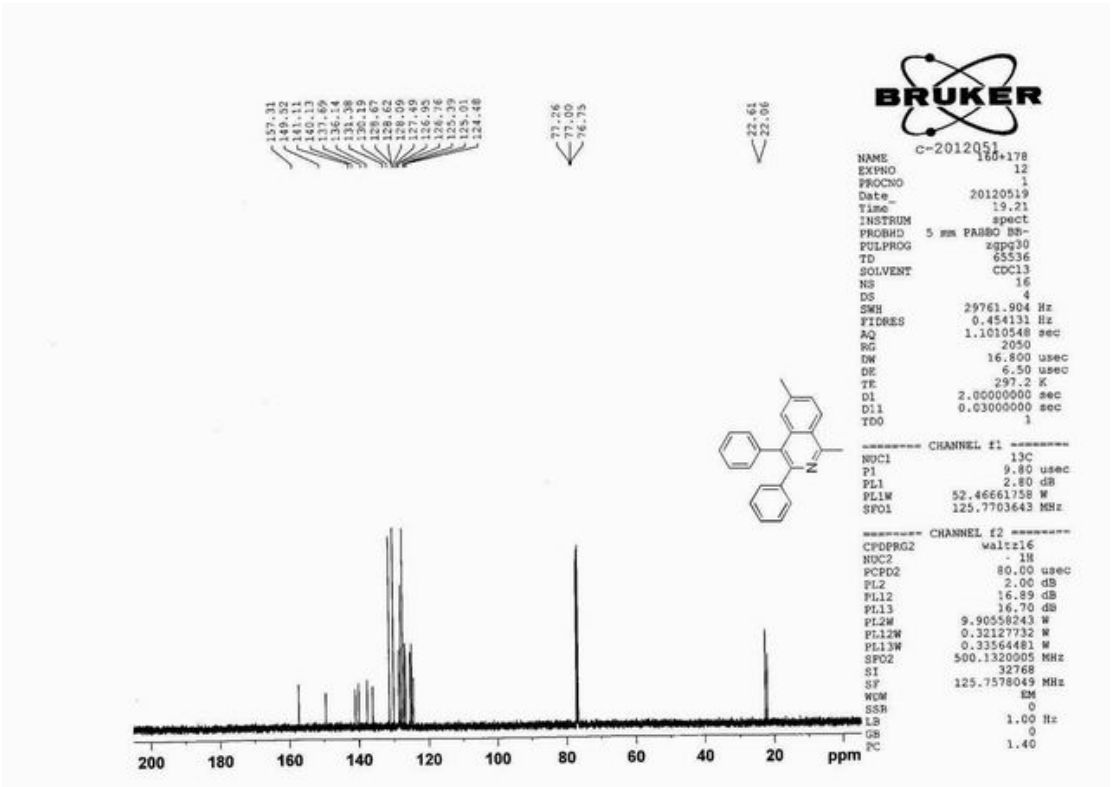
6-Methoxy-1-methyl-3,4-diphenylisoquinoline (3aj)



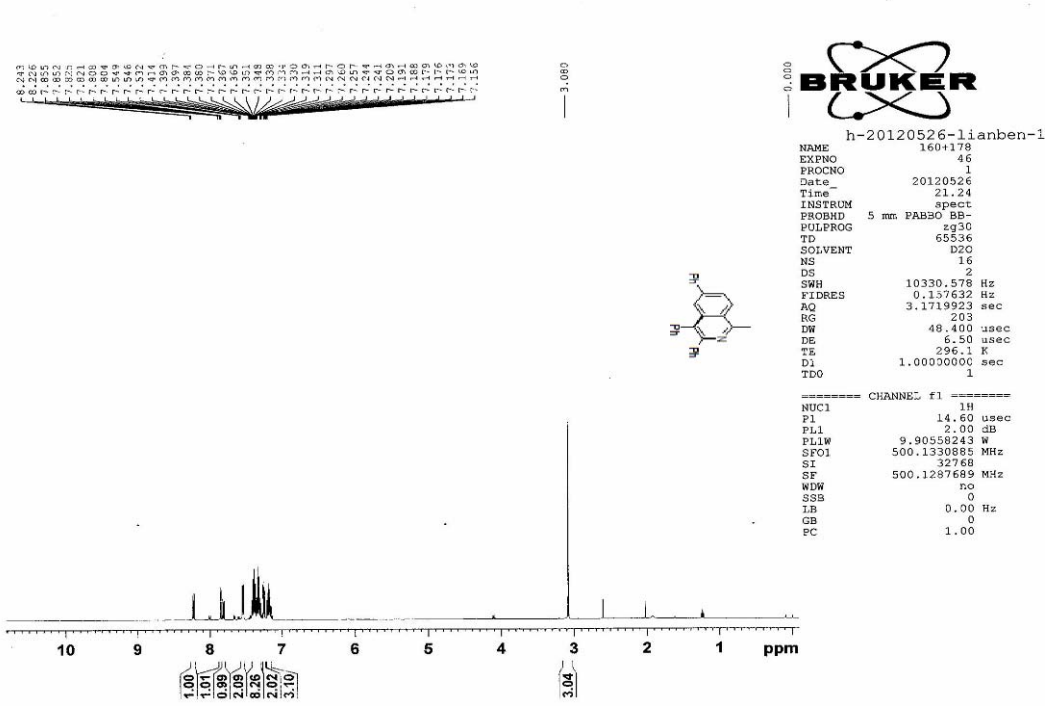


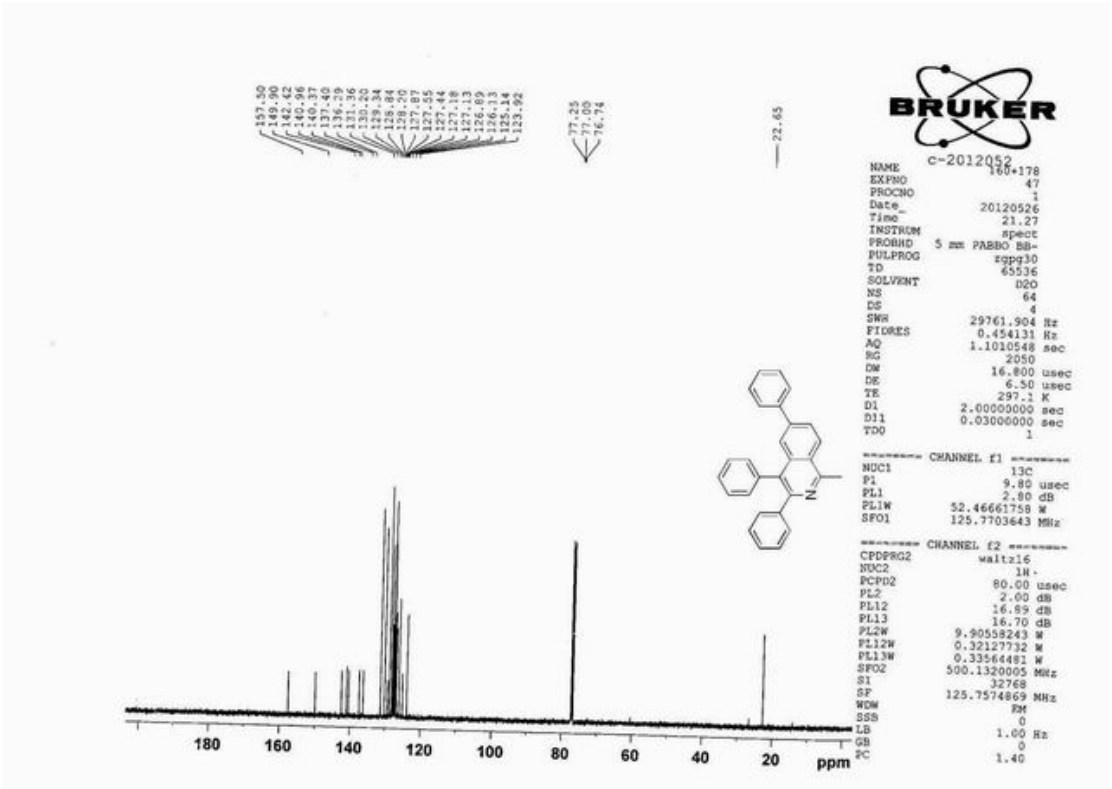
1,6-Dimethyl-3,4-diphenylisoquinoline (3ak)



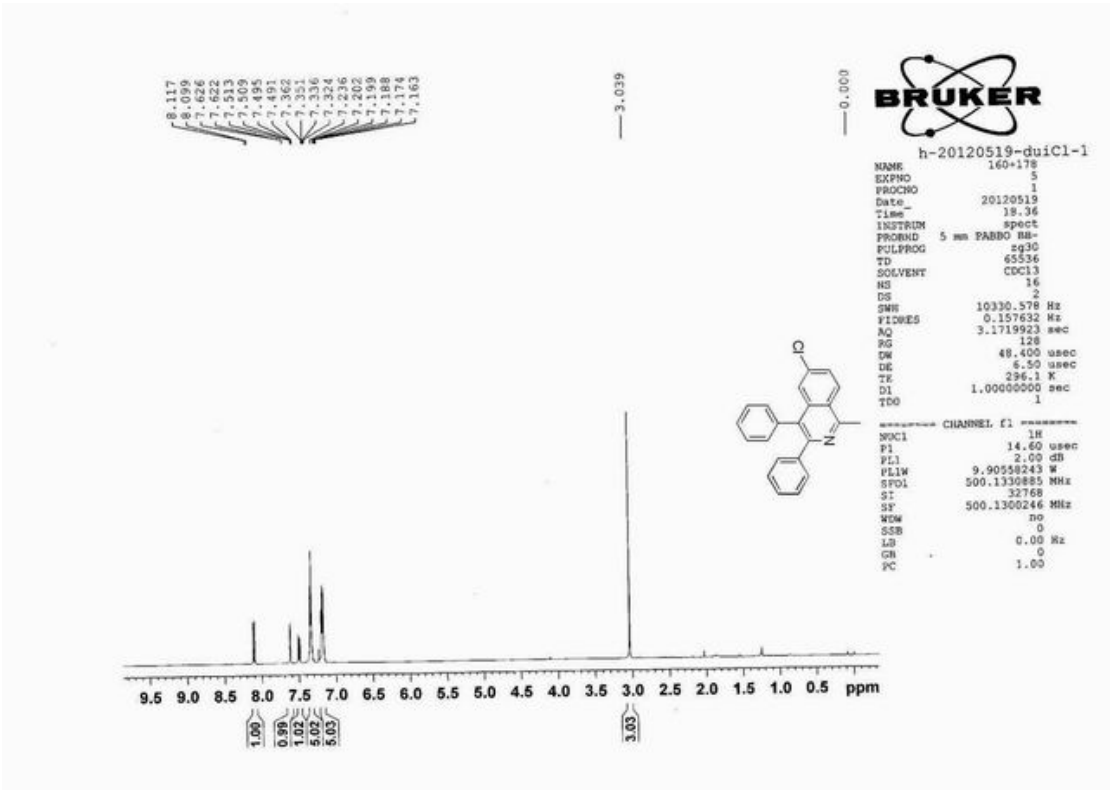


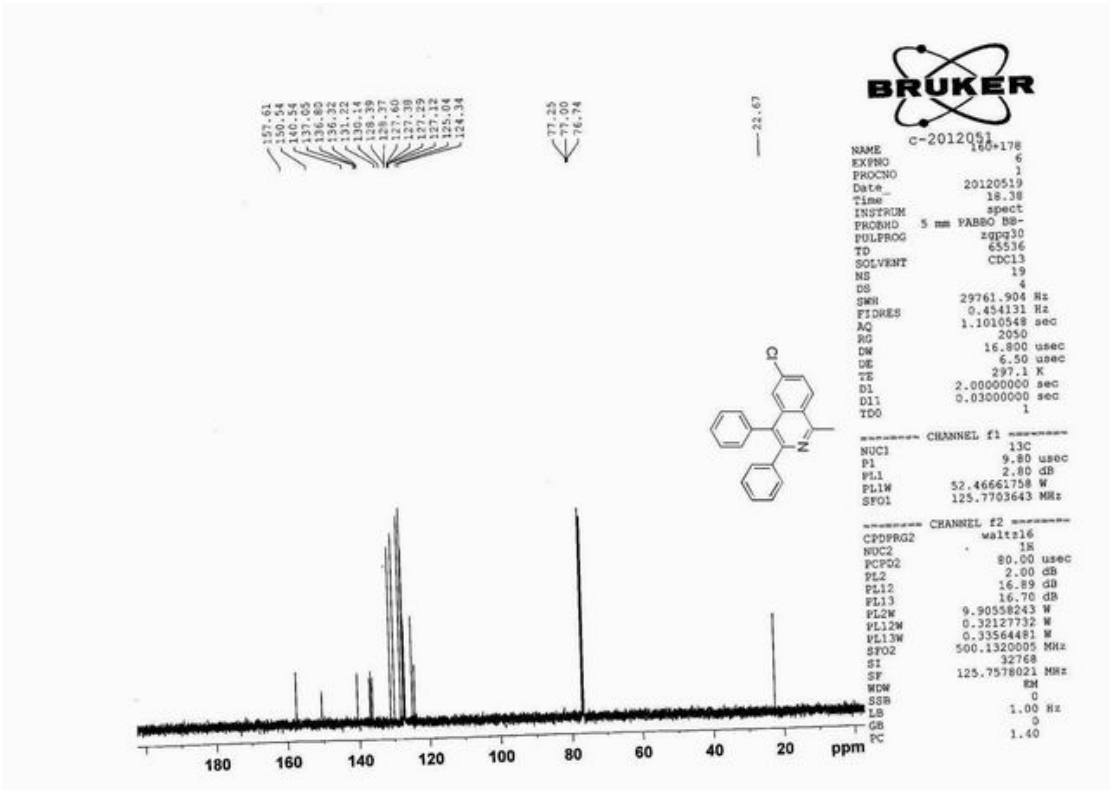
1-Methyl-3,4,6-triphenylisoquinoline (3al)



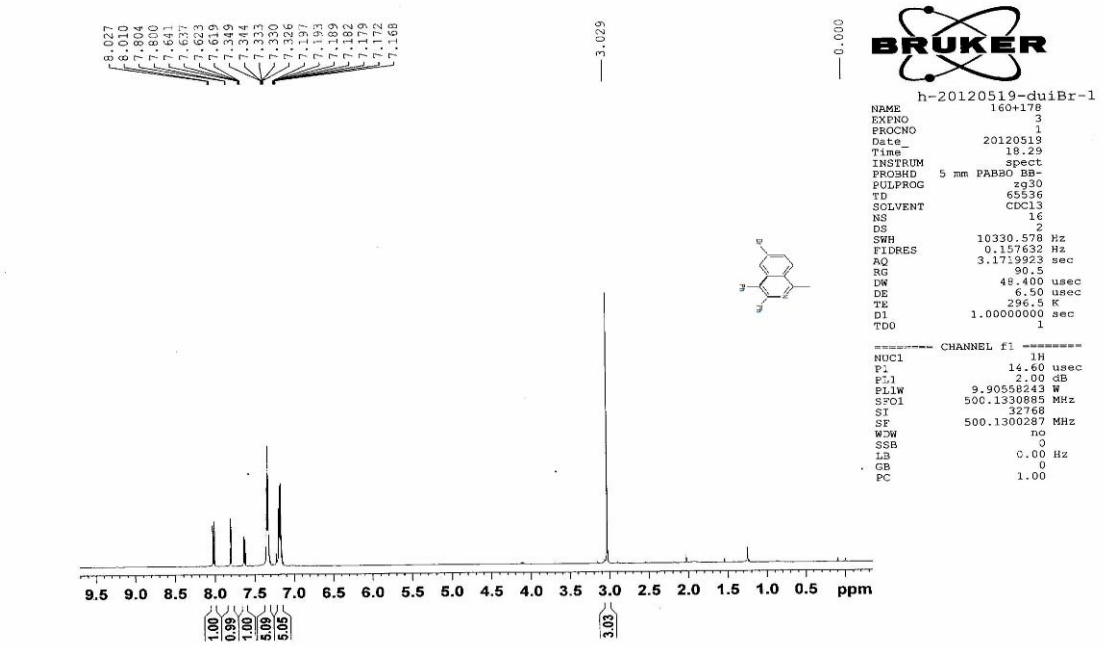


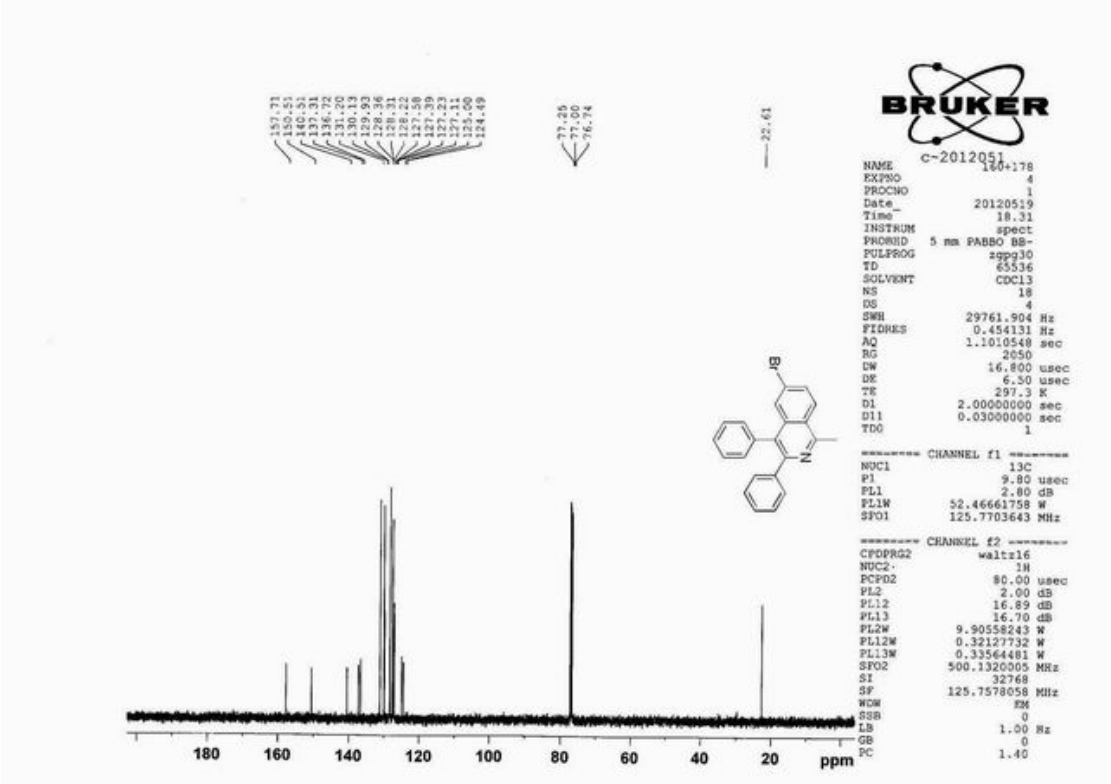
6-Chloro-1-methyl-3,4-diphenylisoquinoline (3am)



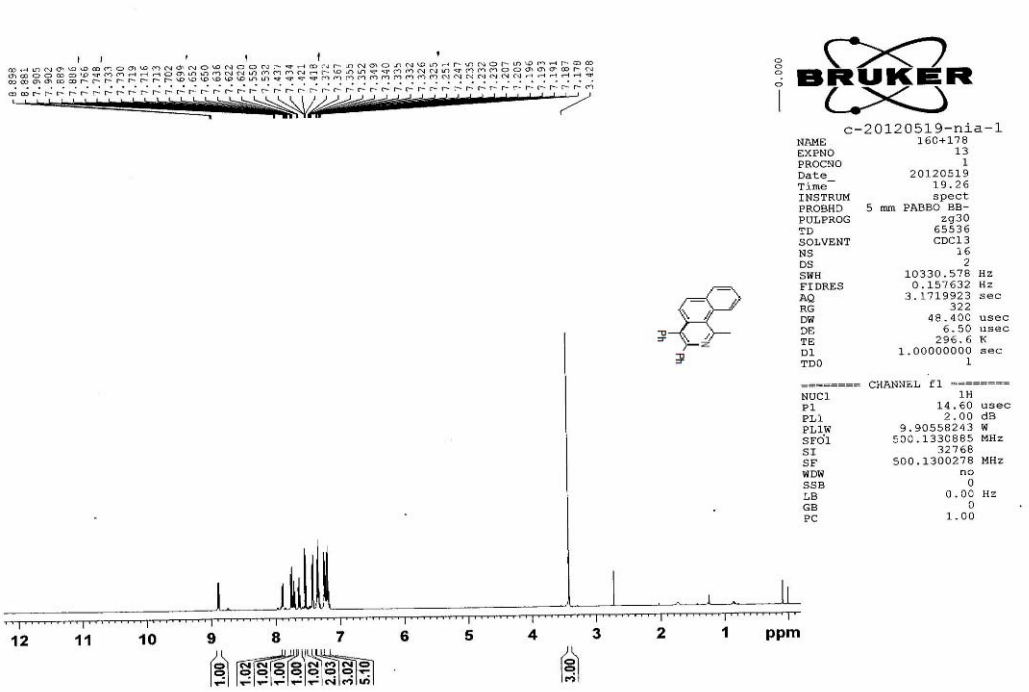


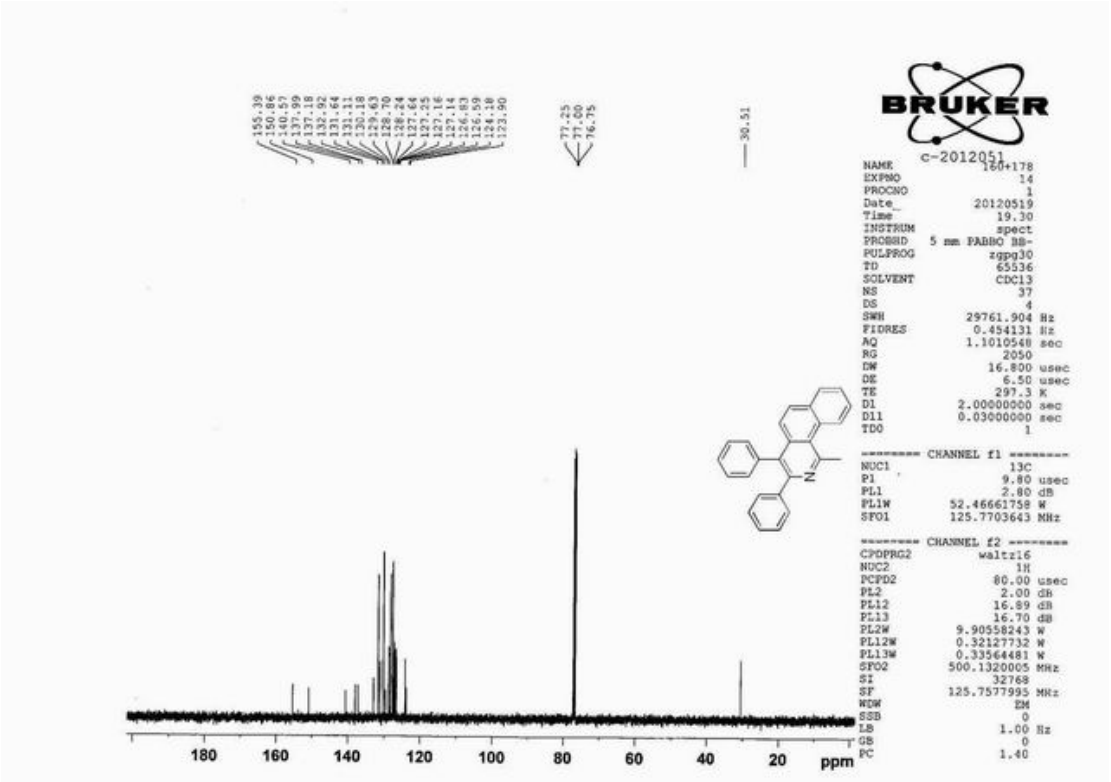
6-Bromo-1-methyl-3,4-diphenylisoquinoline (3an)



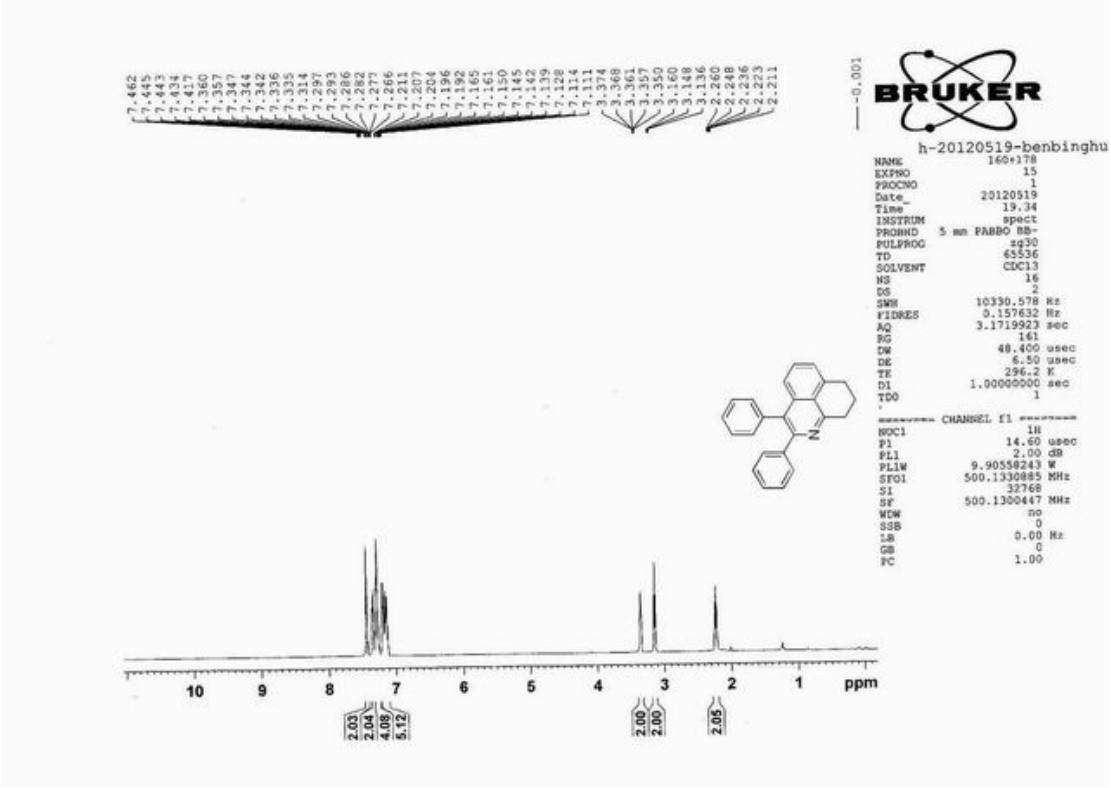


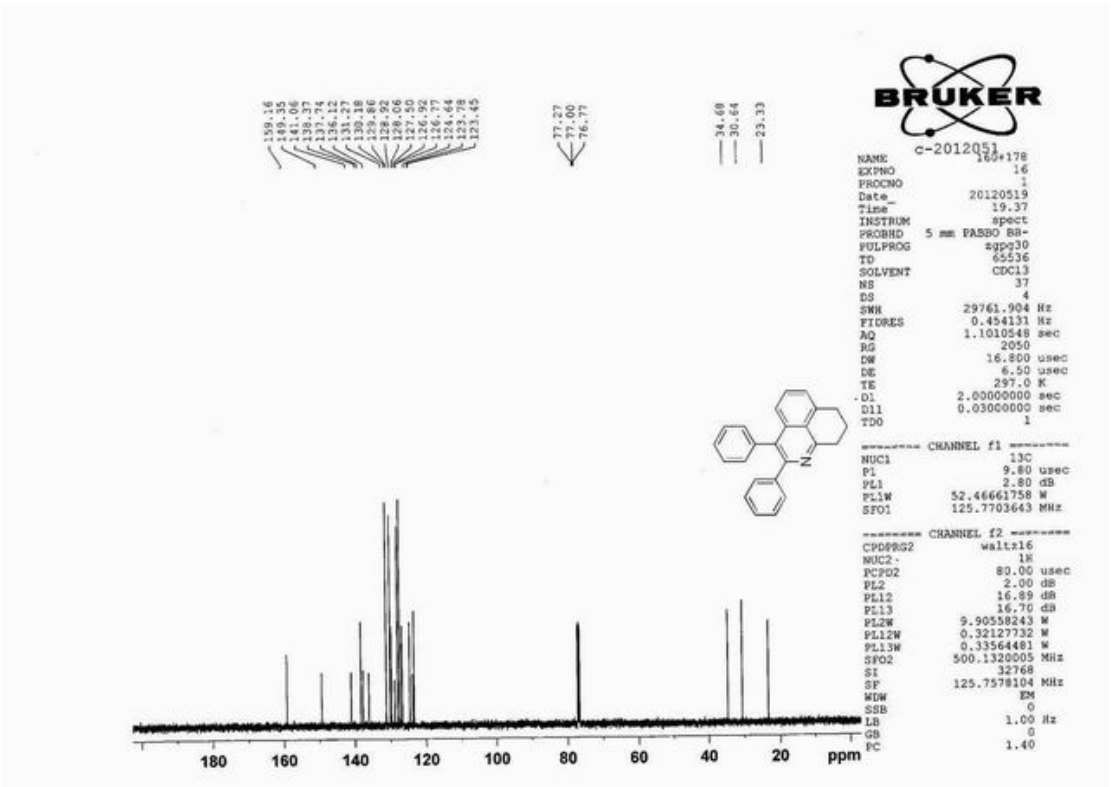
1-Methyl-3,4-diphenylbenzo[h]isoquinoline (3ao)



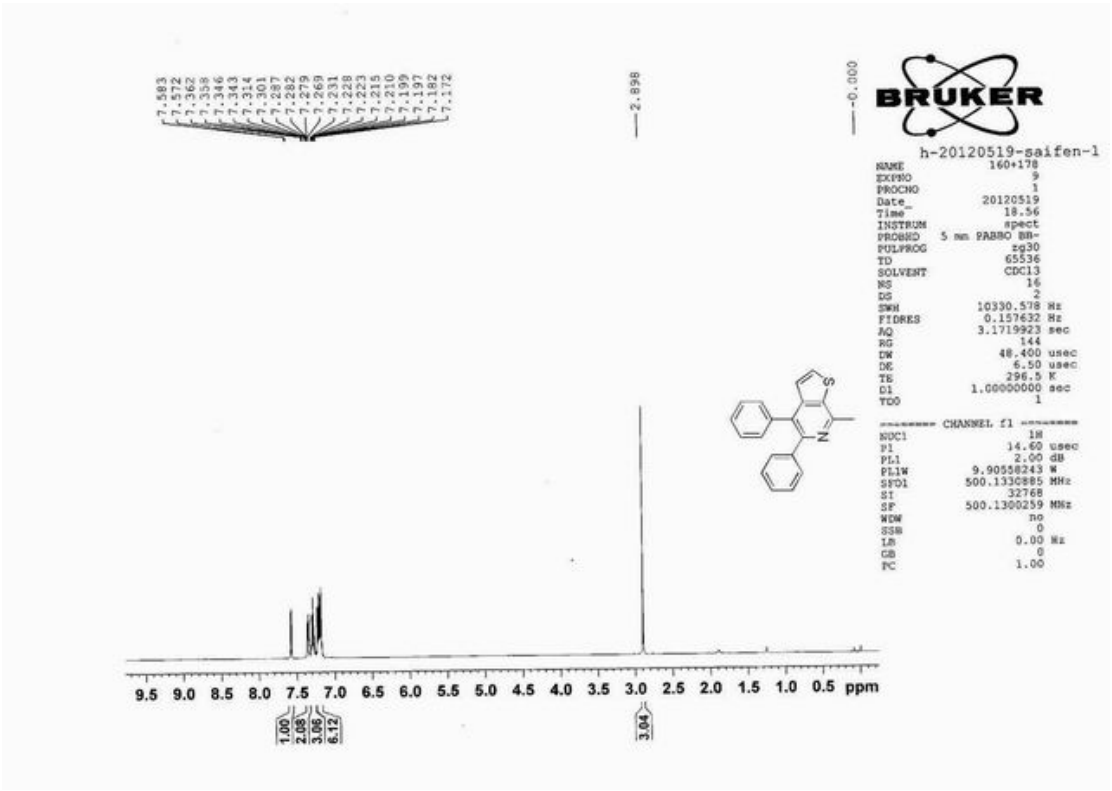


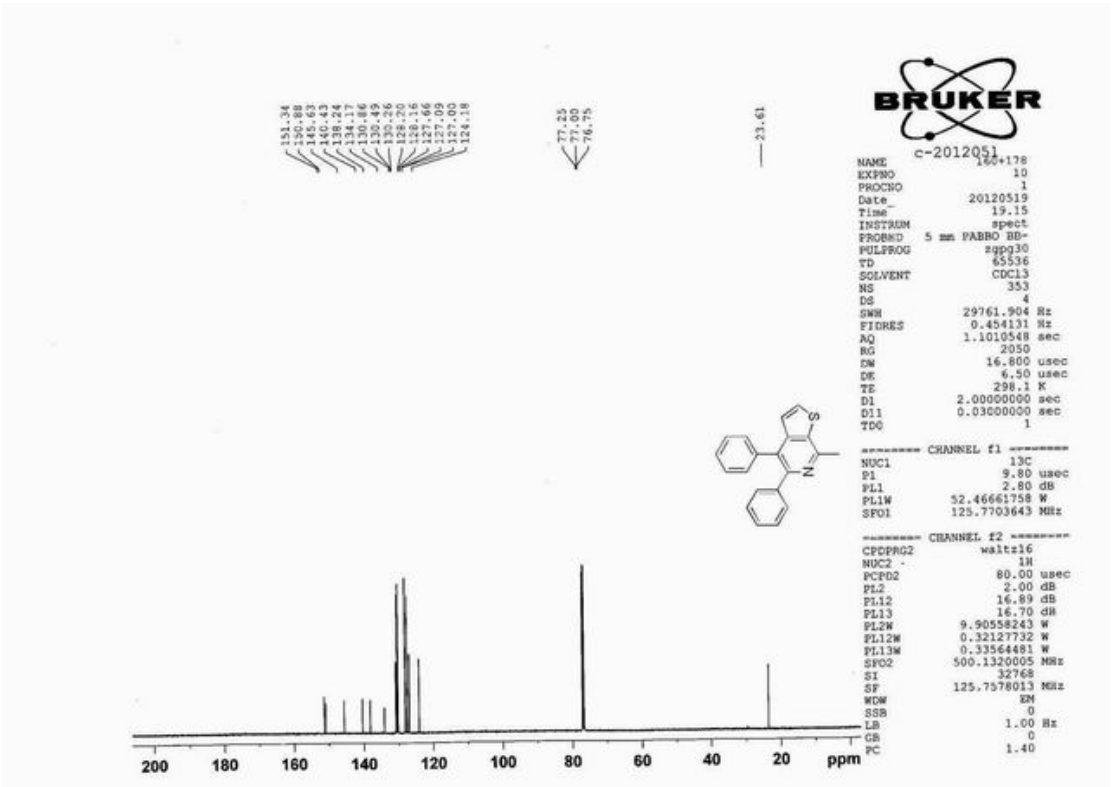
2,3-Diphenyl-8,9-dihydro-7H-benzo[de]quinoline (3ap)



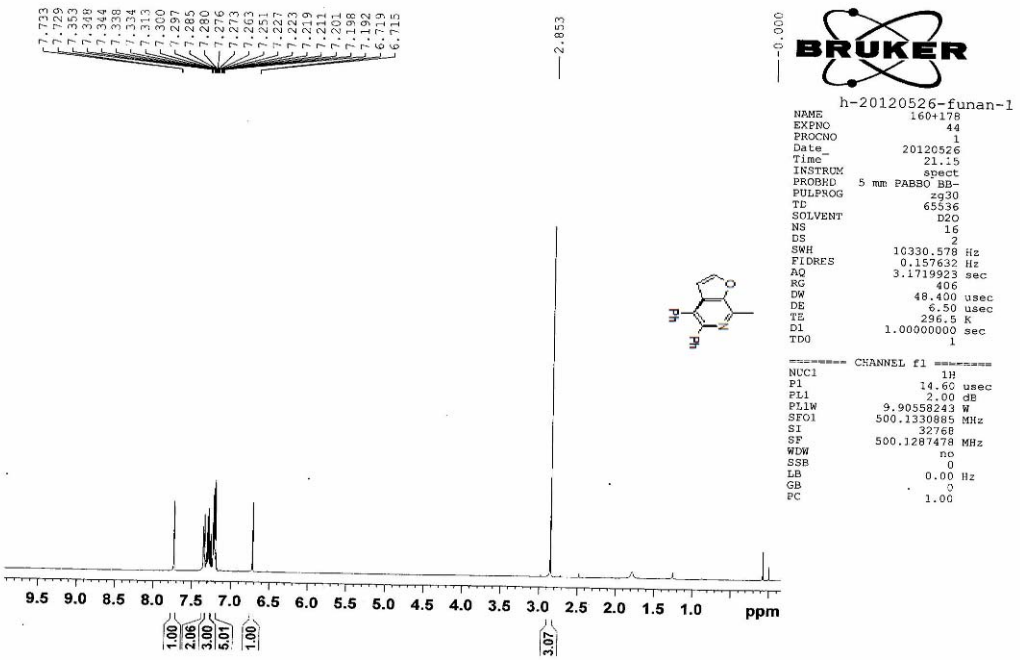


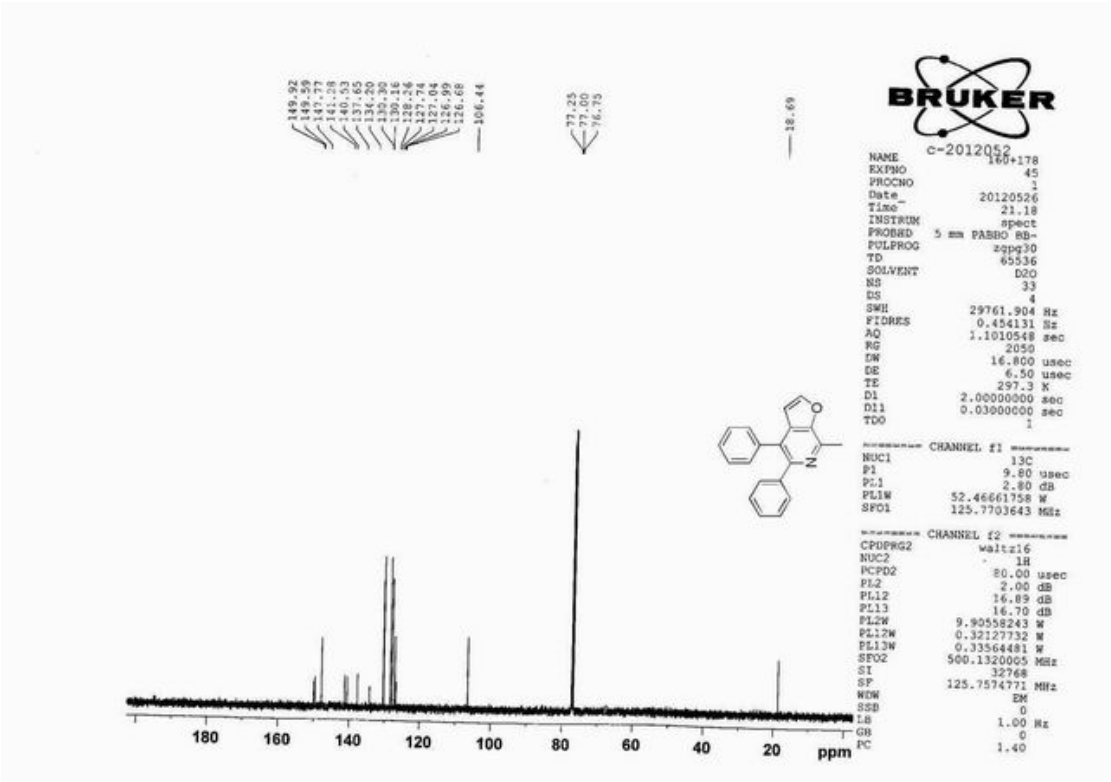
7-Methyl-4,5-diphenylthieno[2,3-c]pyridine (3aq)



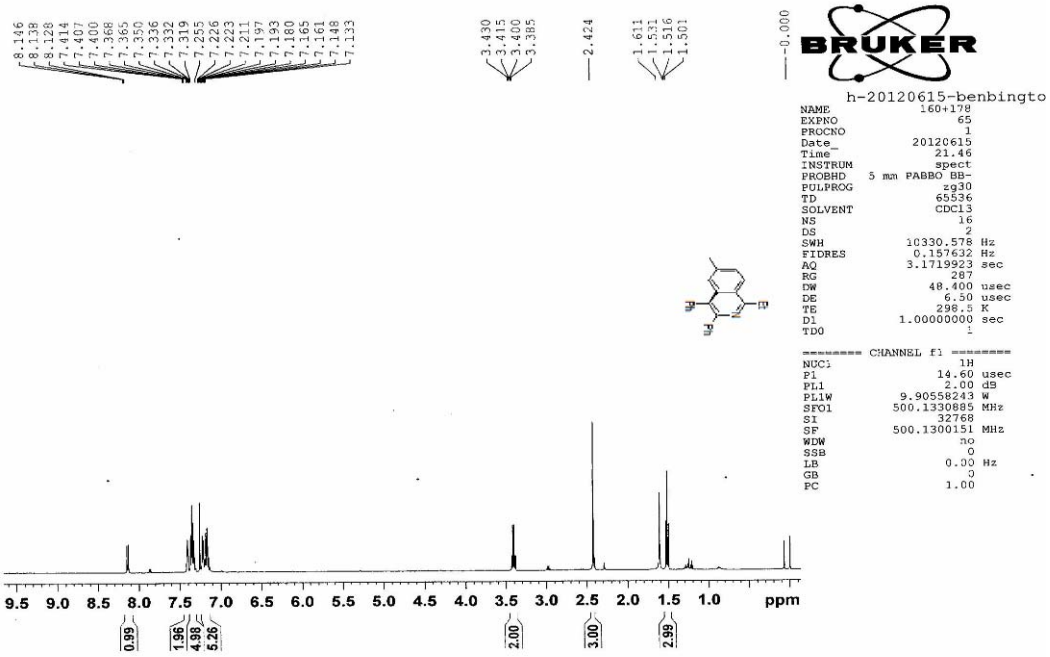


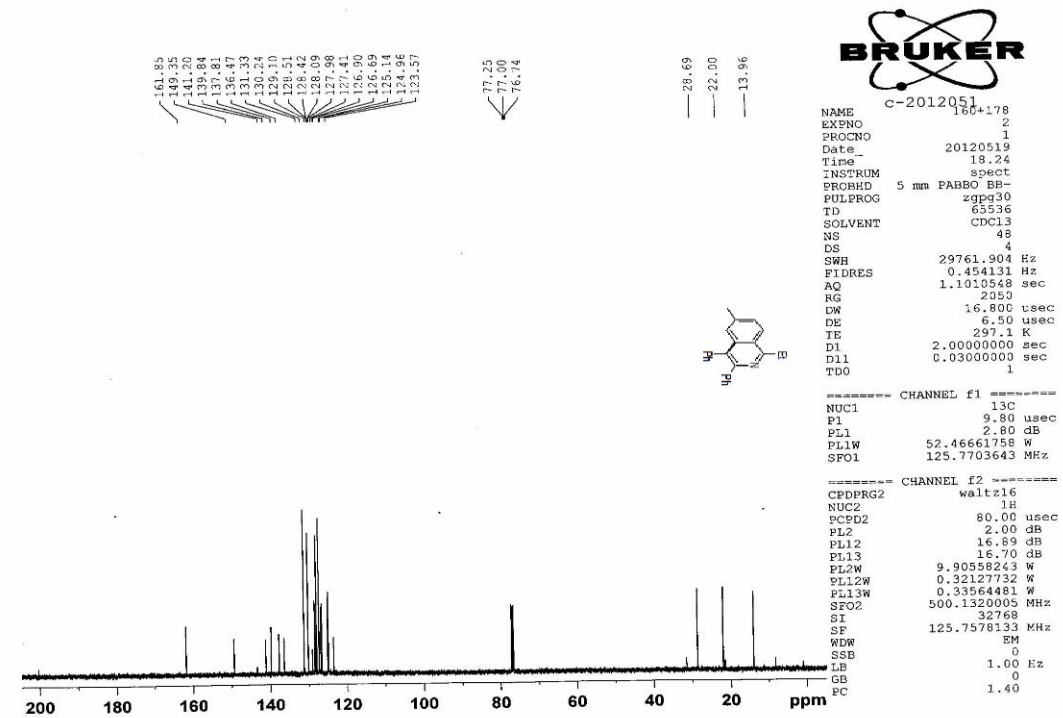
7-Methyl-4,5-diphenylfuro[2,3-c]pyridine (3ar)



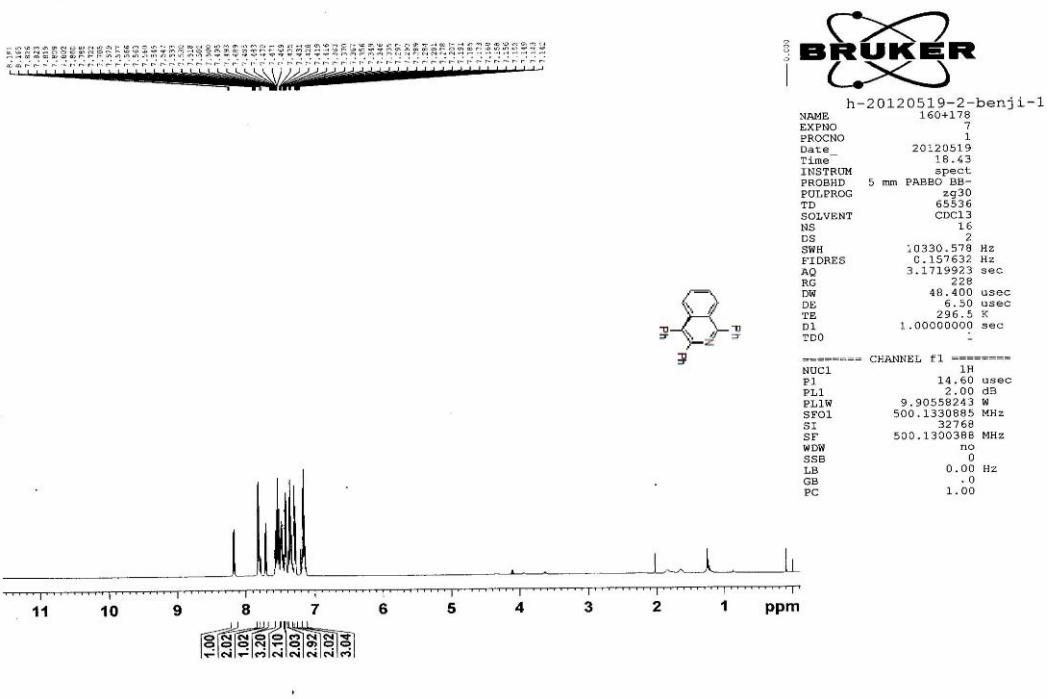


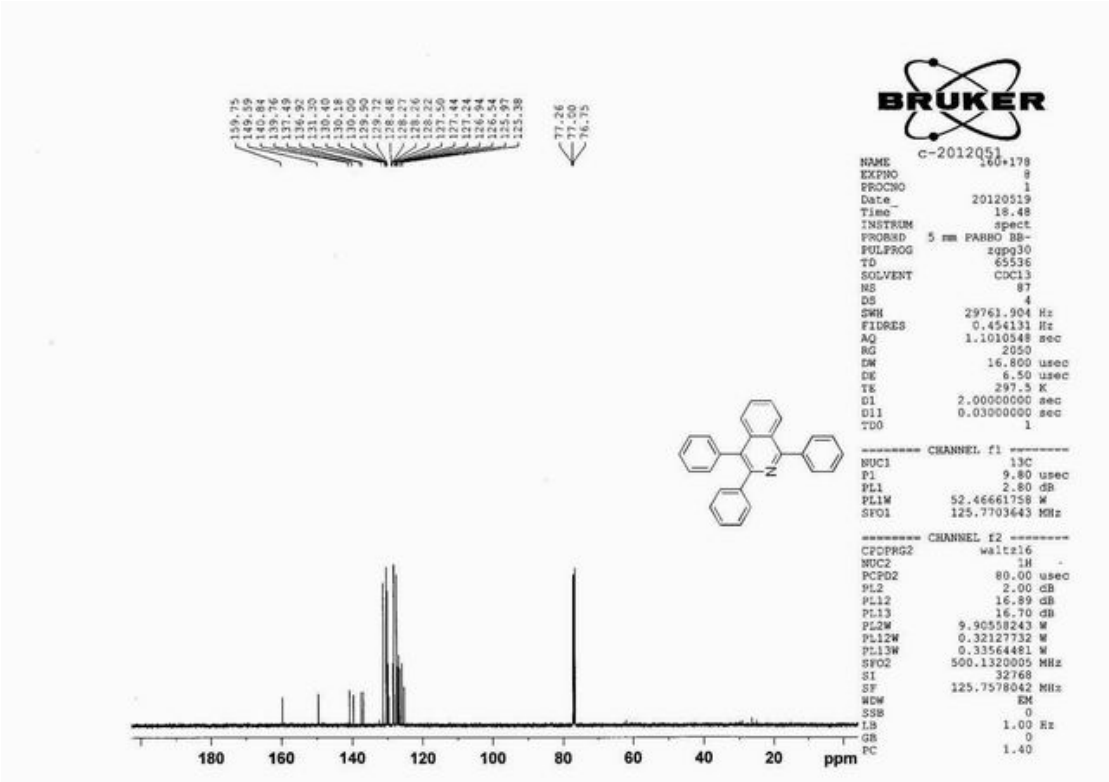
1-Ethyl-6-methyl-3,4-diphenylisoquinoline (3as)



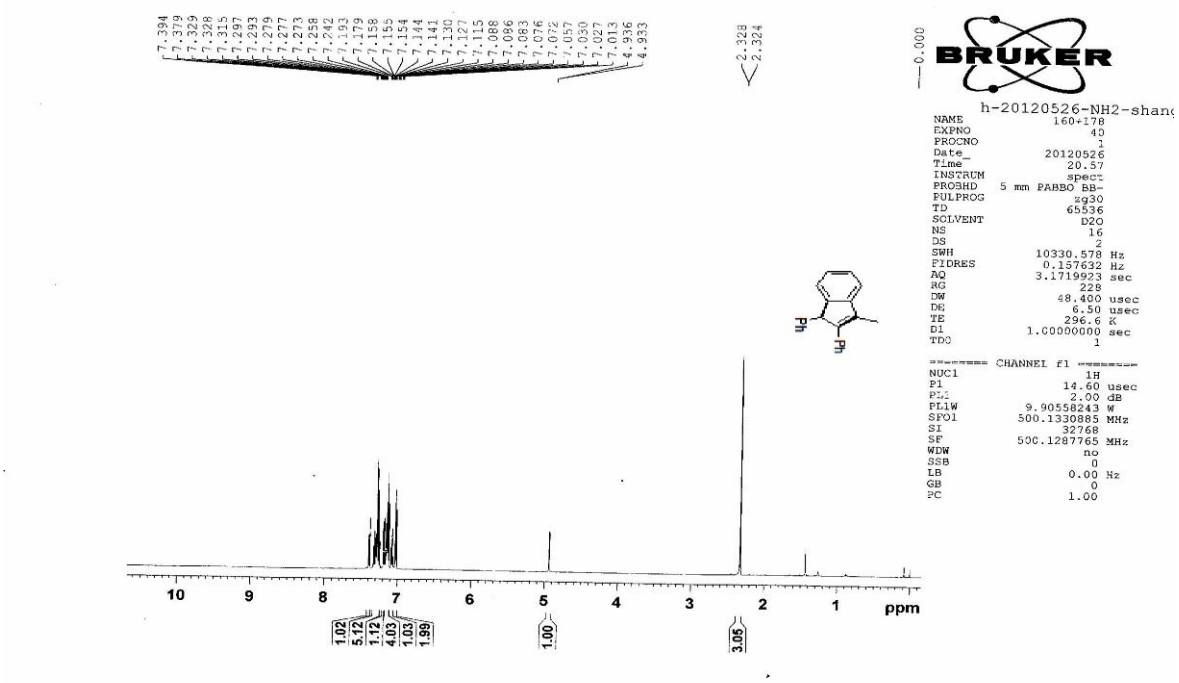


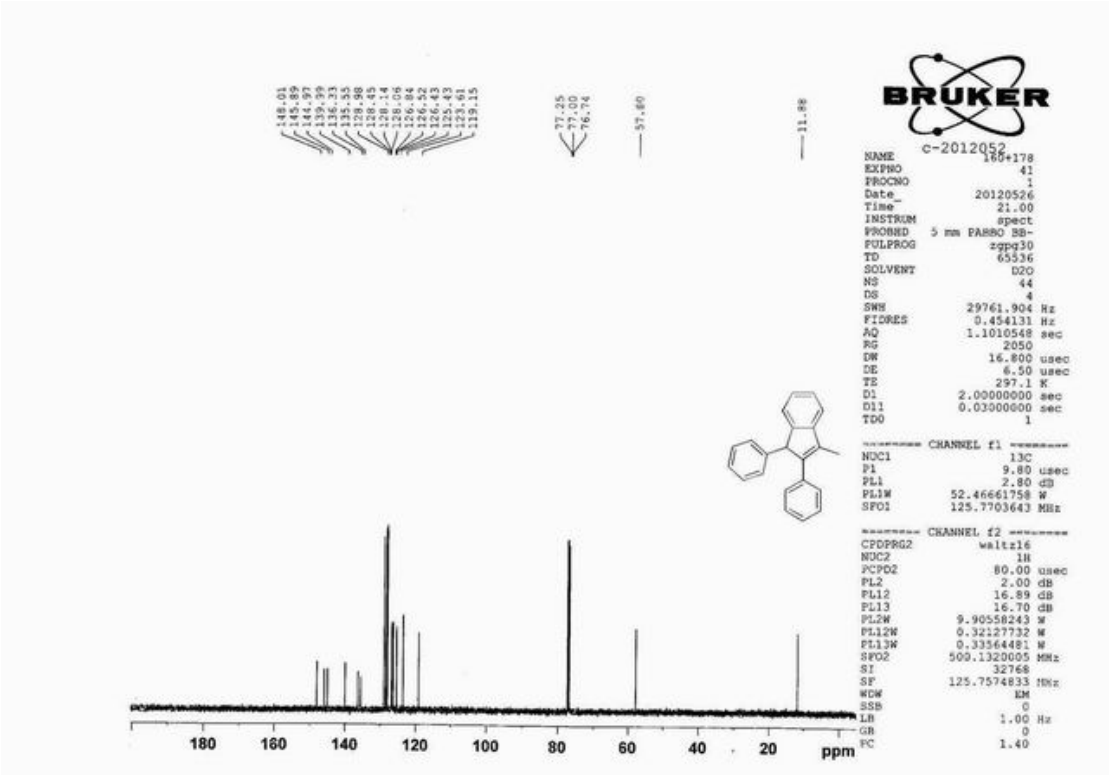
1,3,4-Triphenylisoquinoline (3at)



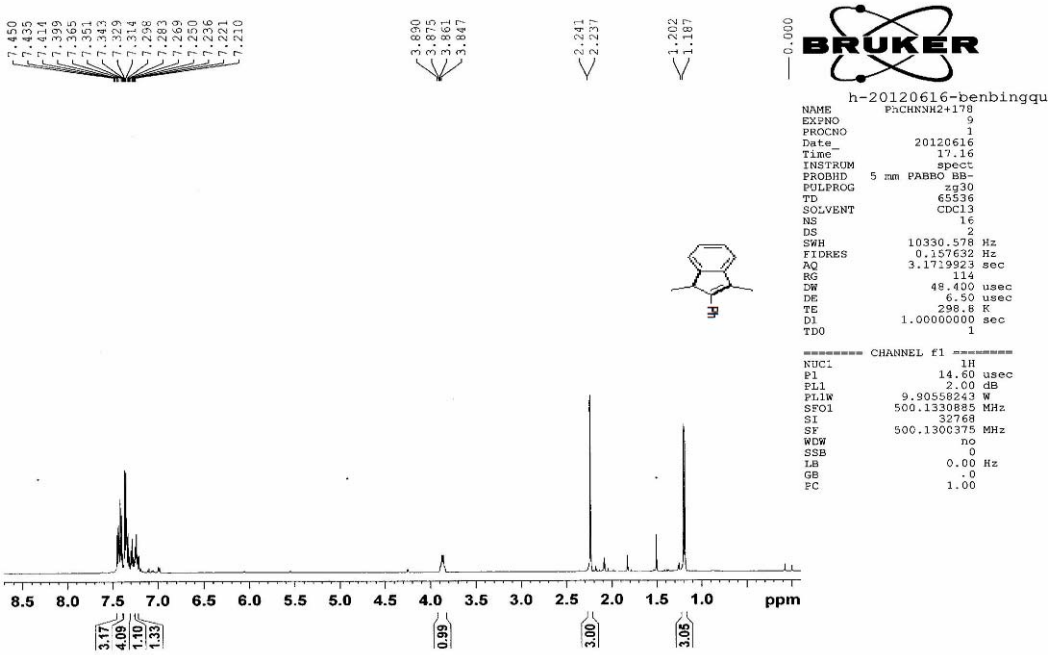


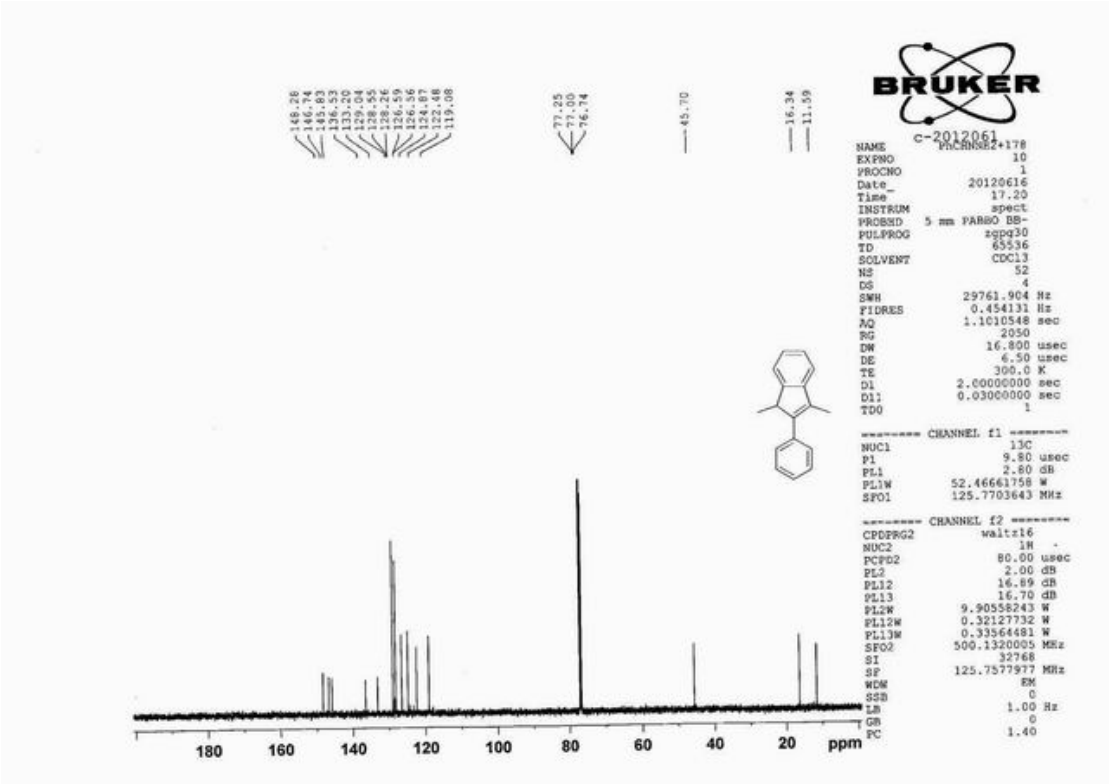
3-Methyl-1,2-diphenyl-1H-indene (4ag)



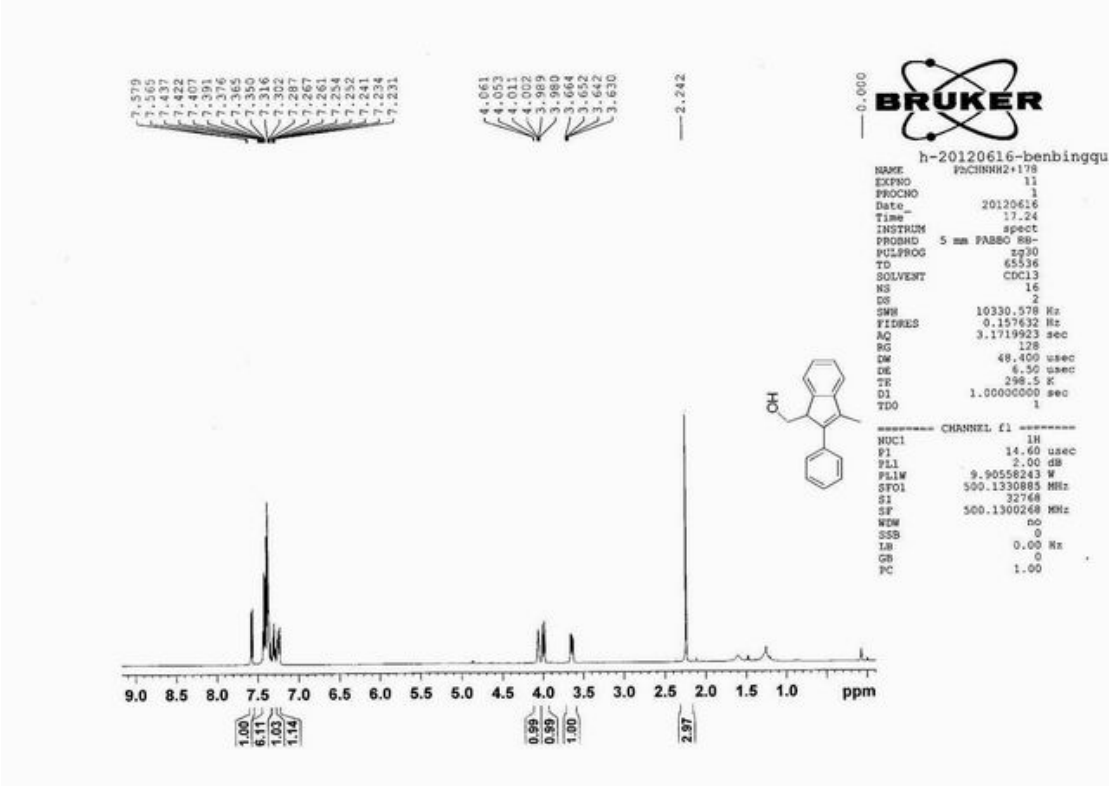


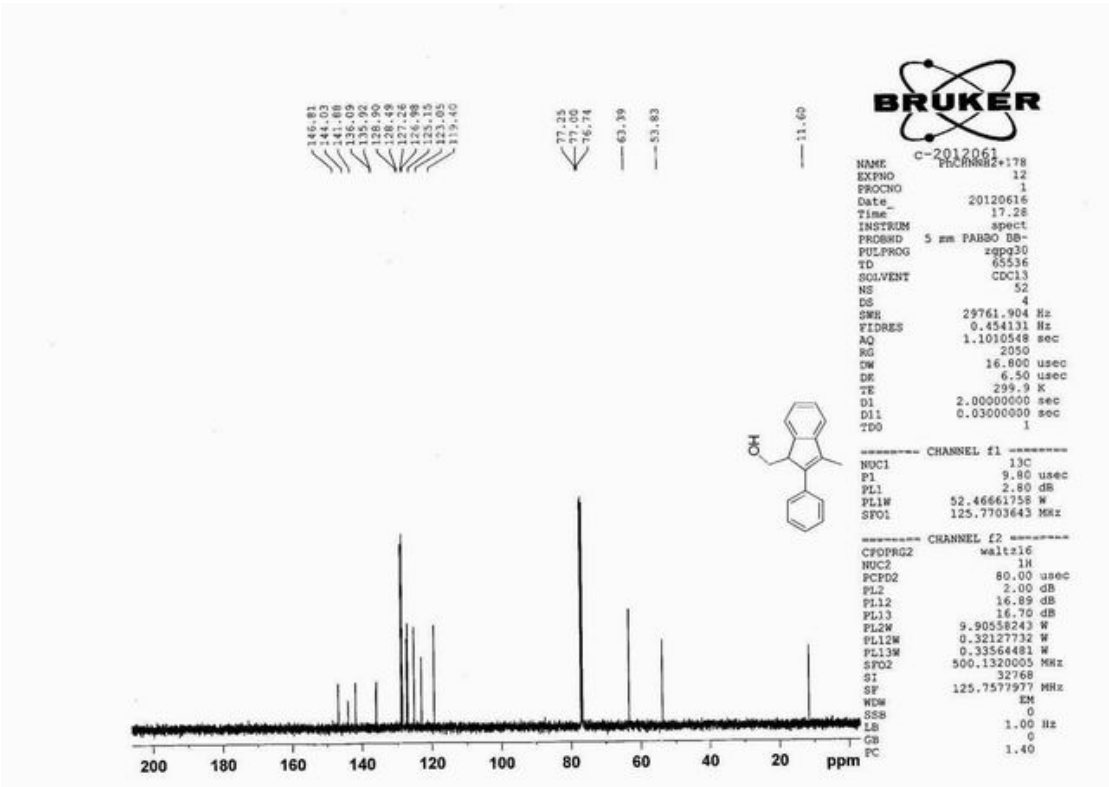
1,3-Dimethyl-2-phenyl-1H-indene (4cg)



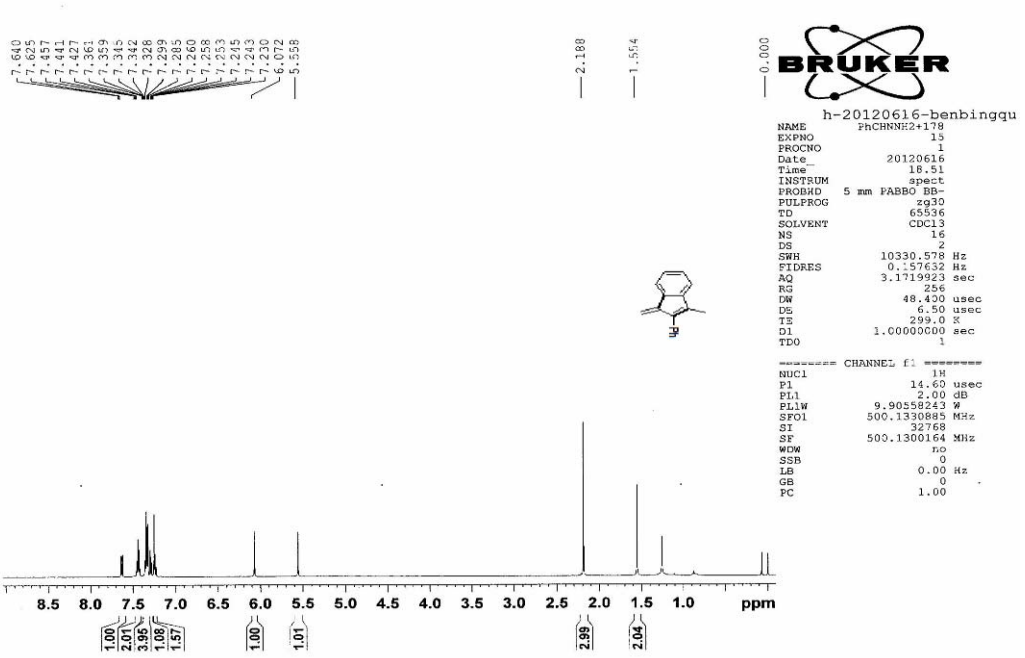


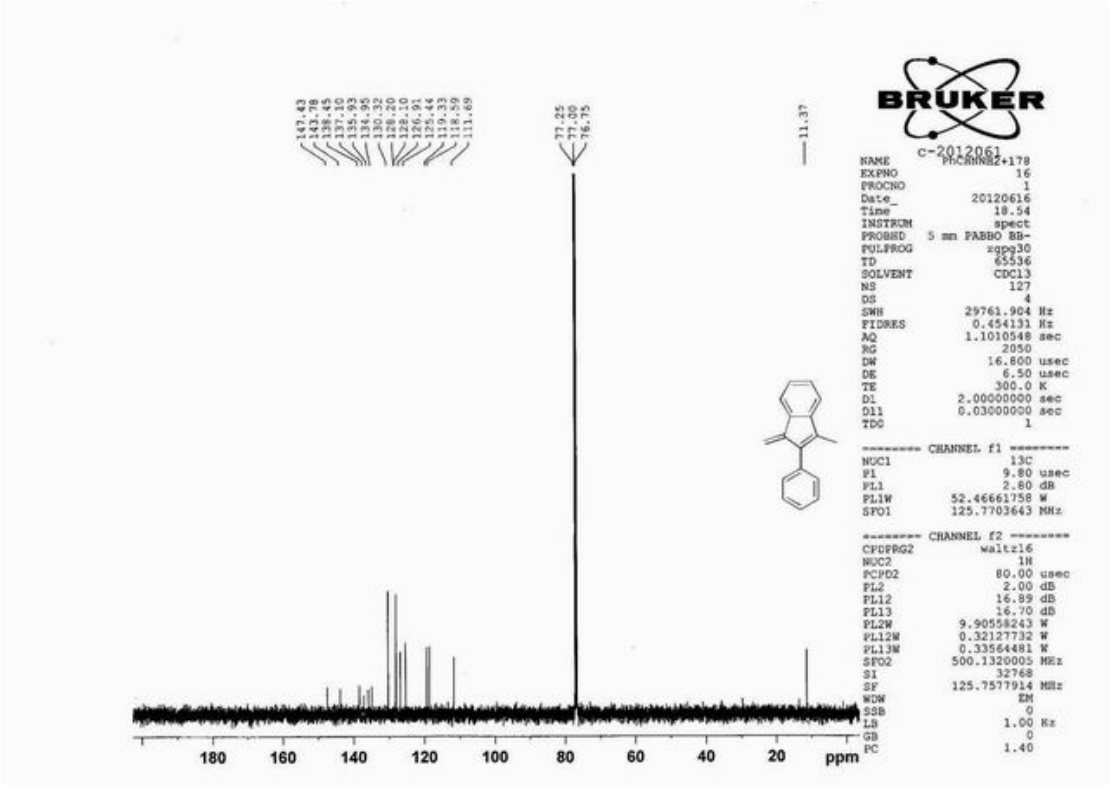
(3-methyl-2-phenyl-1H-inden-1-yl)methanol (4dg)



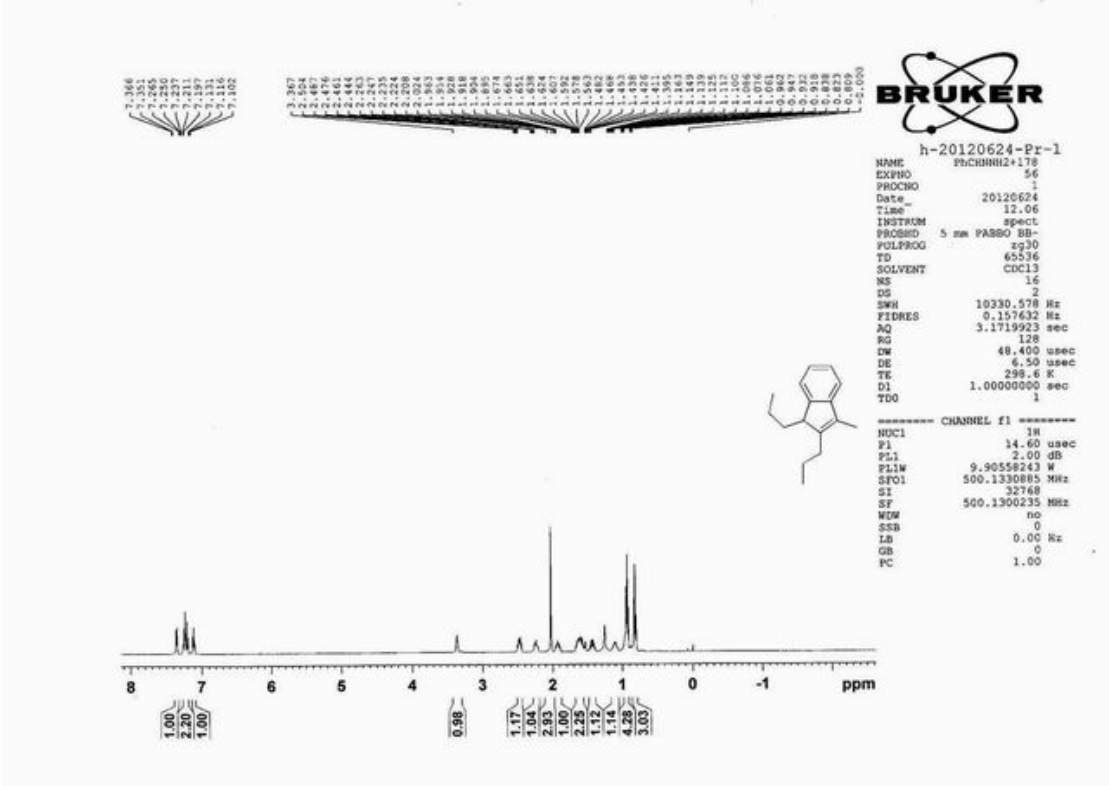


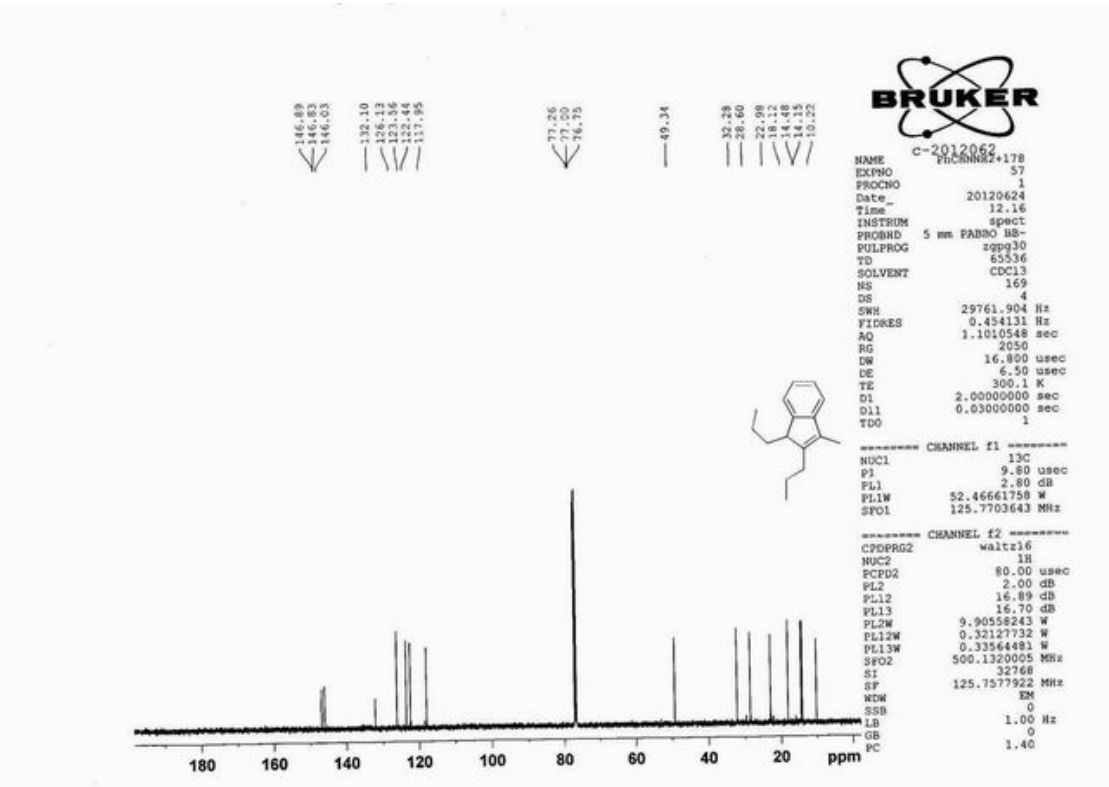
3-Methyl-1-methylene-2-phenyl-1H-indene (5dg)



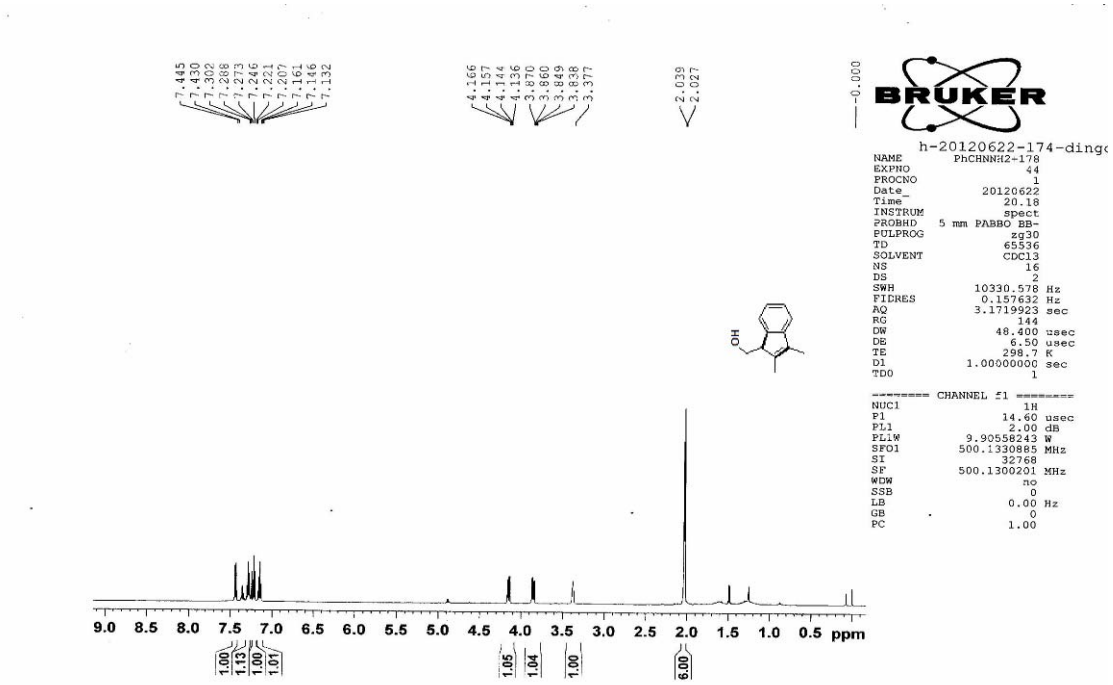


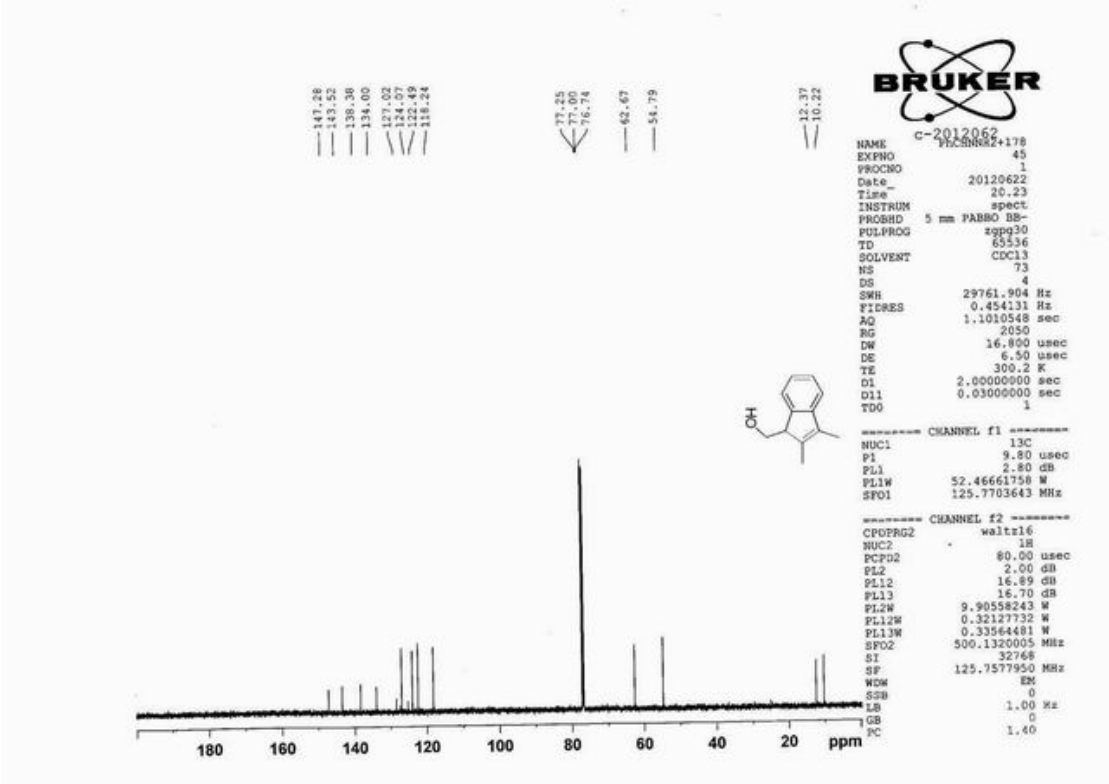
3-Methyl-1,2-dipropyl-1H-indene (4eg)



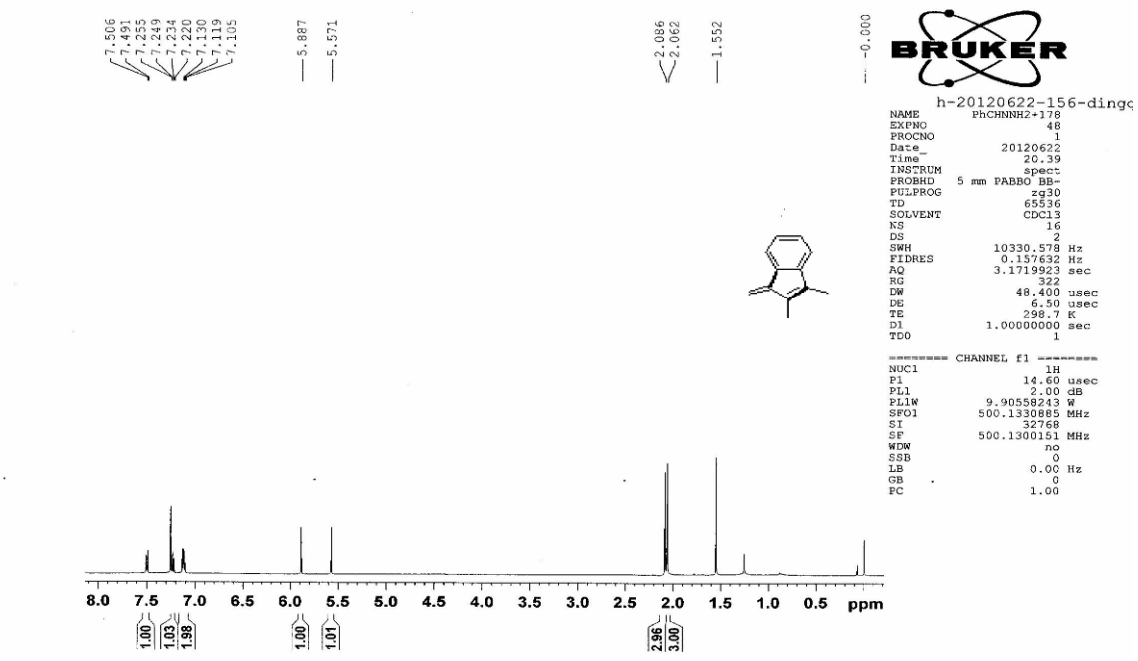


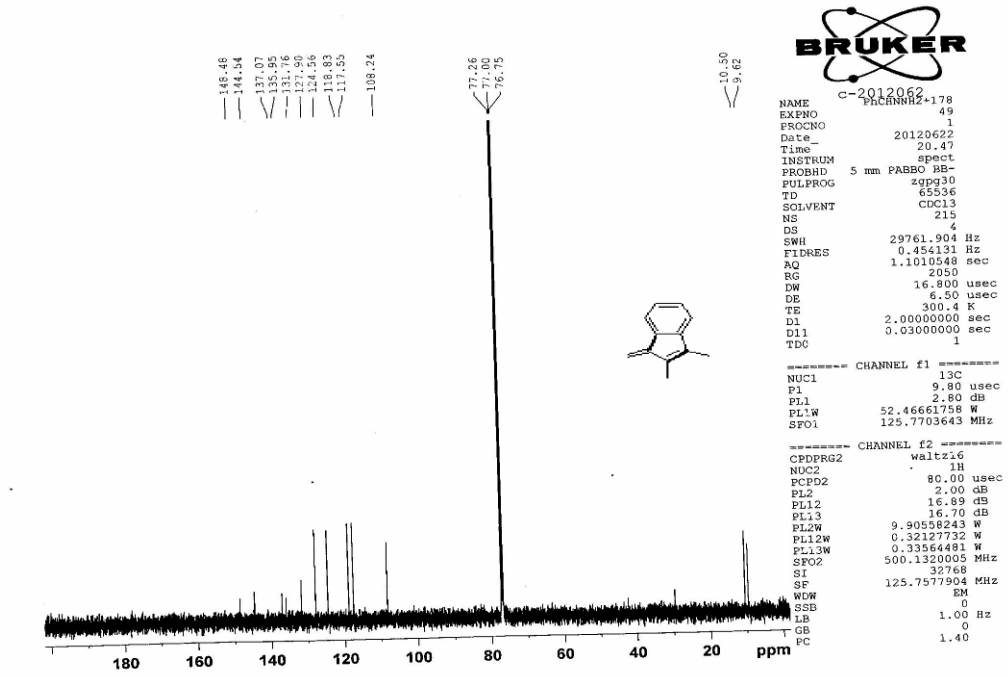
(2,3-Dimethyl-1H-inden-1-yl)methanol (4fg)



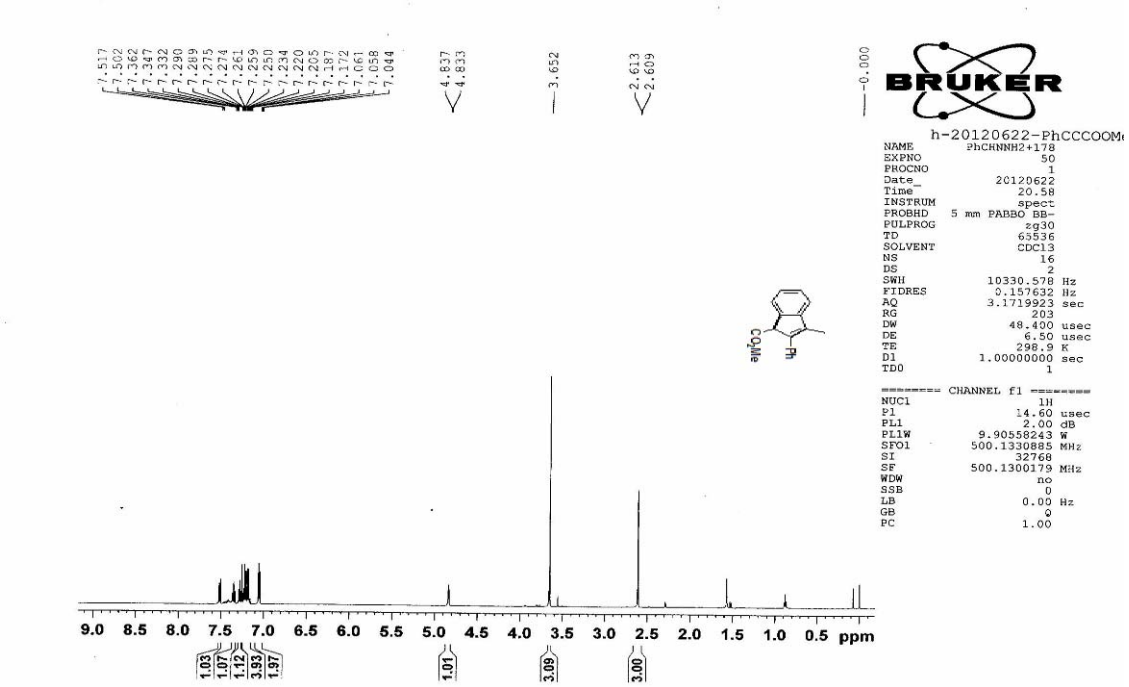


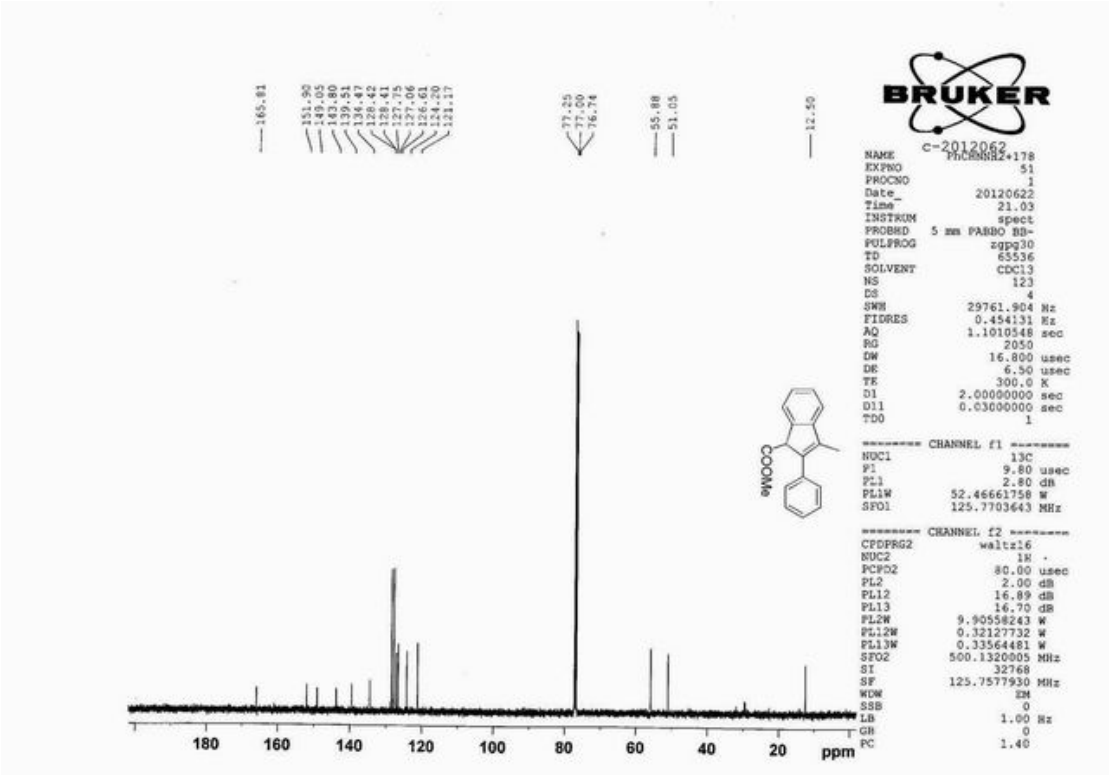
2,3-Dimethyl-1-methylene-1H-indene (5fg)



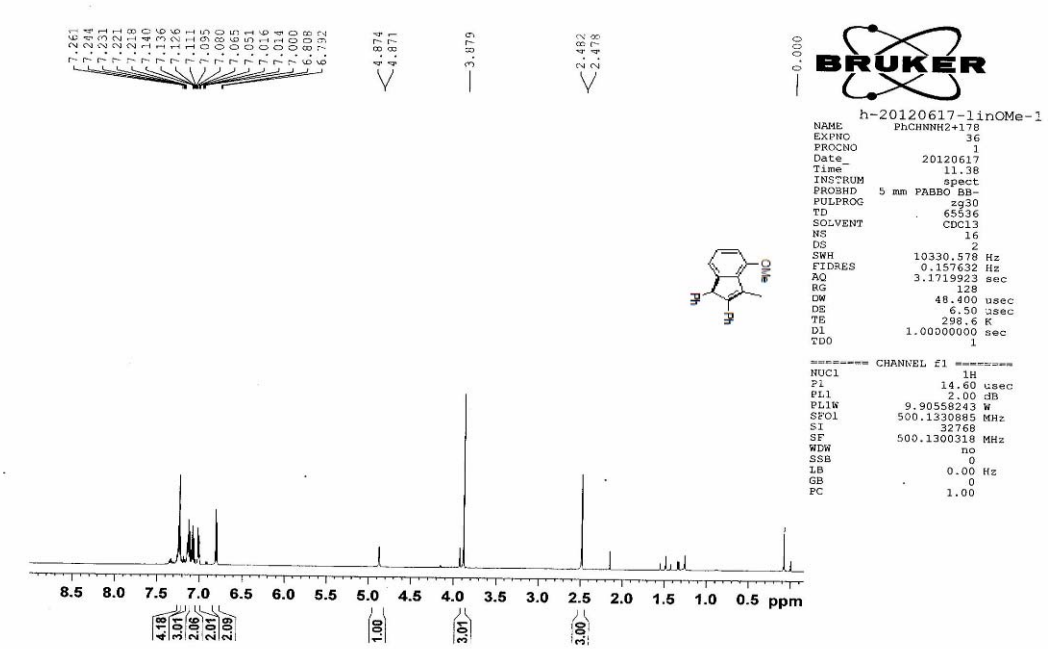


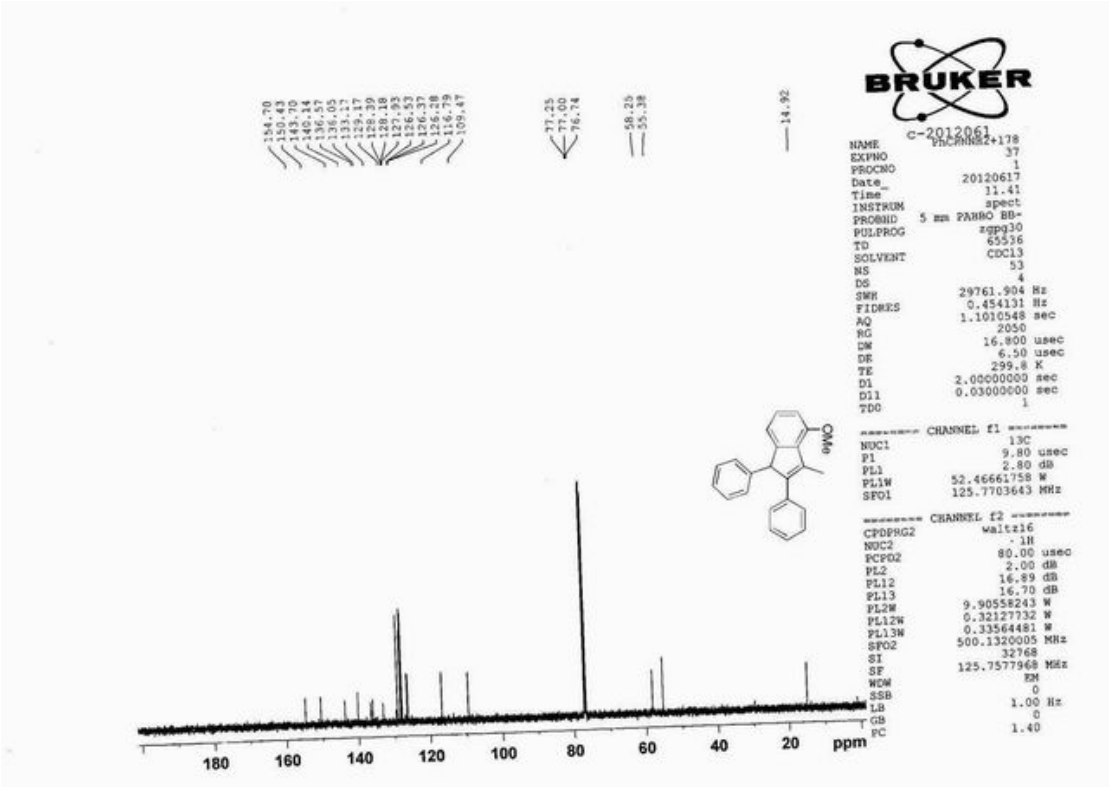
Methyl 3-methyl-2-phenyl-1H-indene-1-carboxylate (4gg)



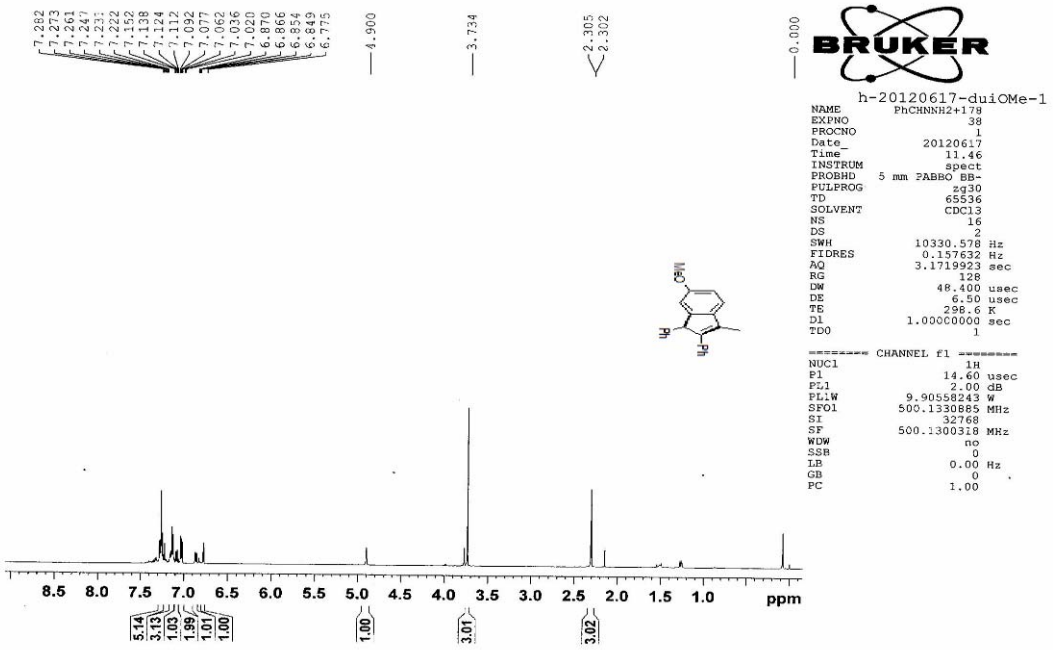


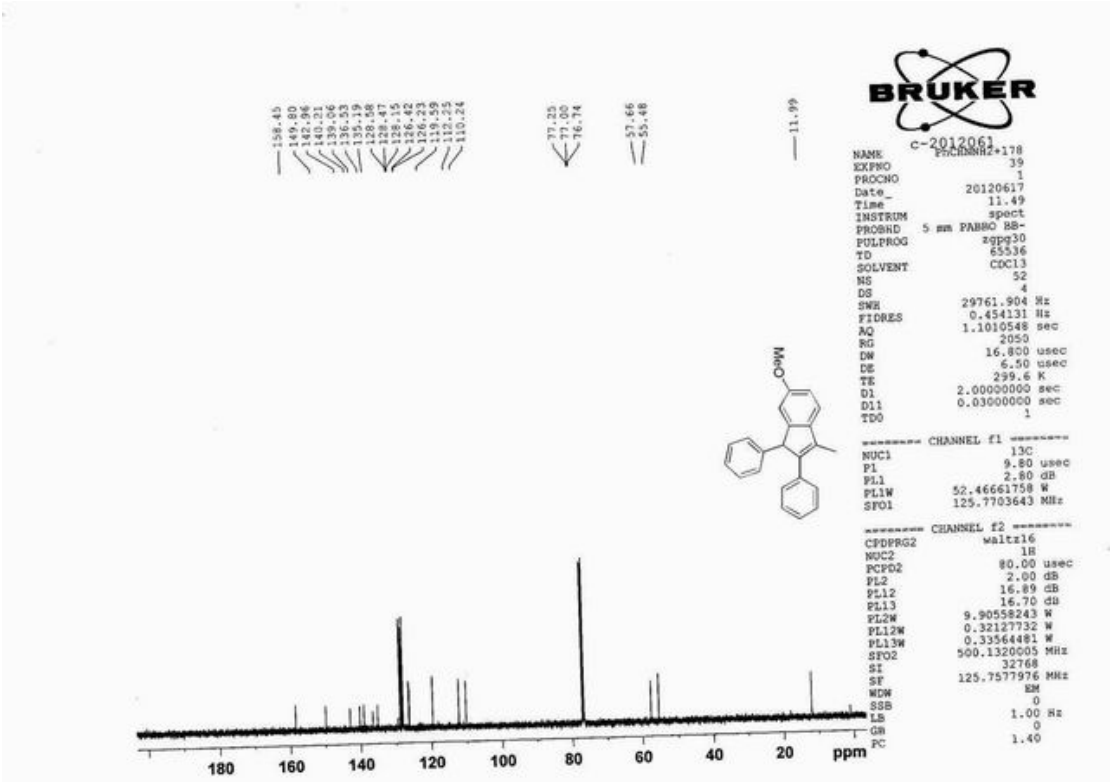
4-Methoxy-3-methyl-1,2-diphenyl-1H-indene (4au)



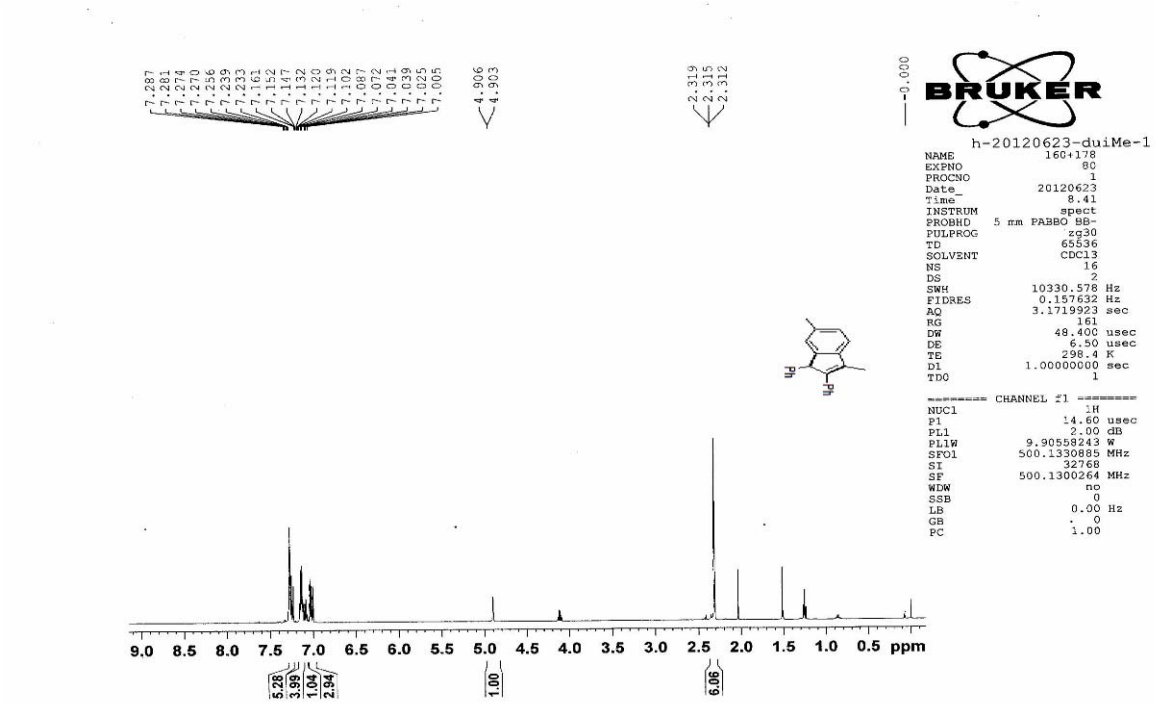


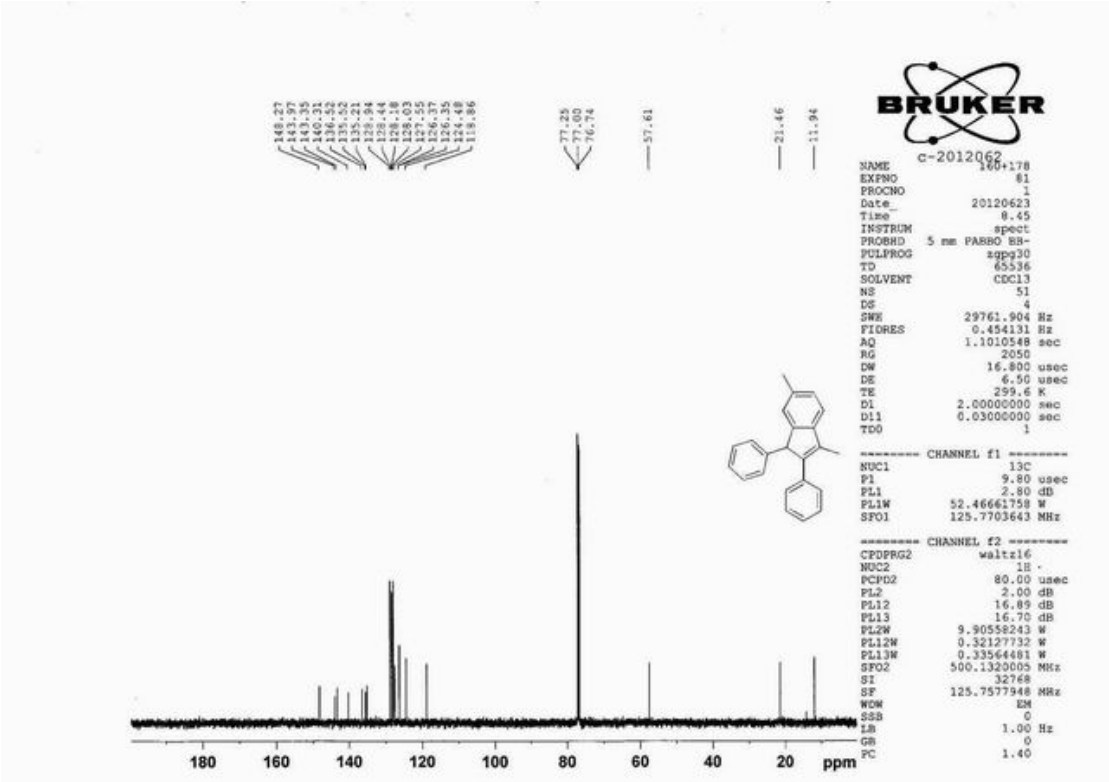
6-Methoxy-3-methyl-1,2-diphenyl-1H-indene (4av)



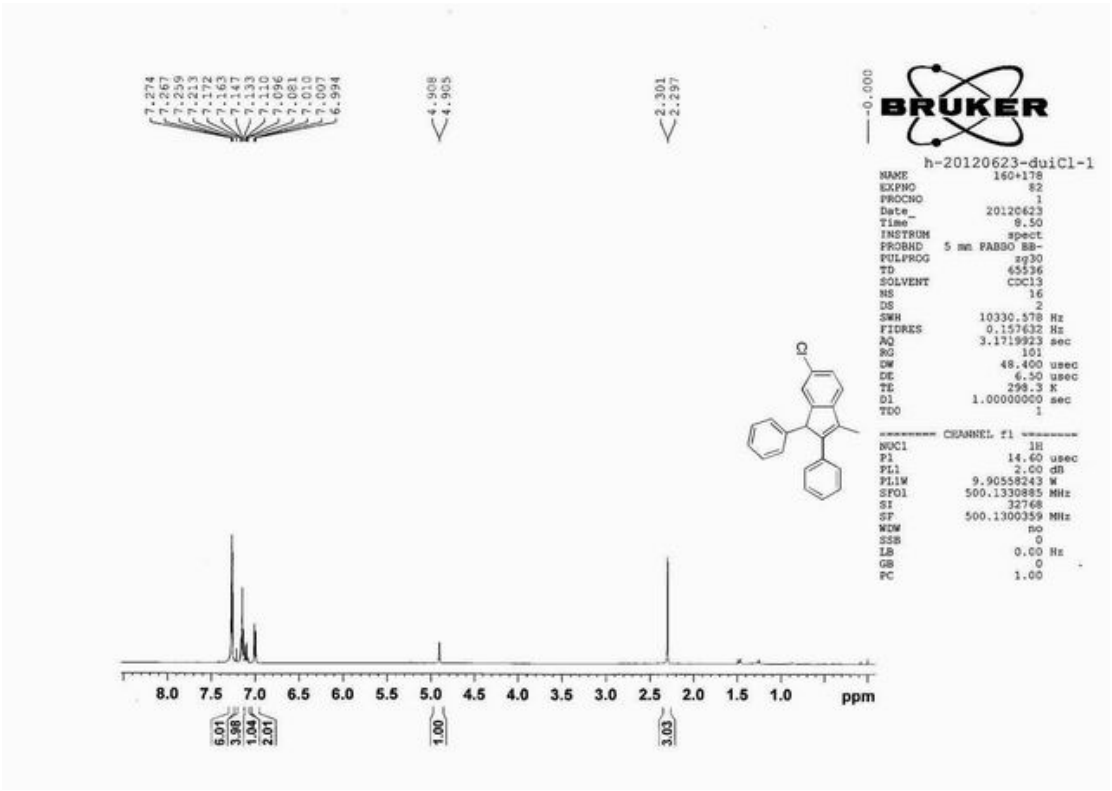


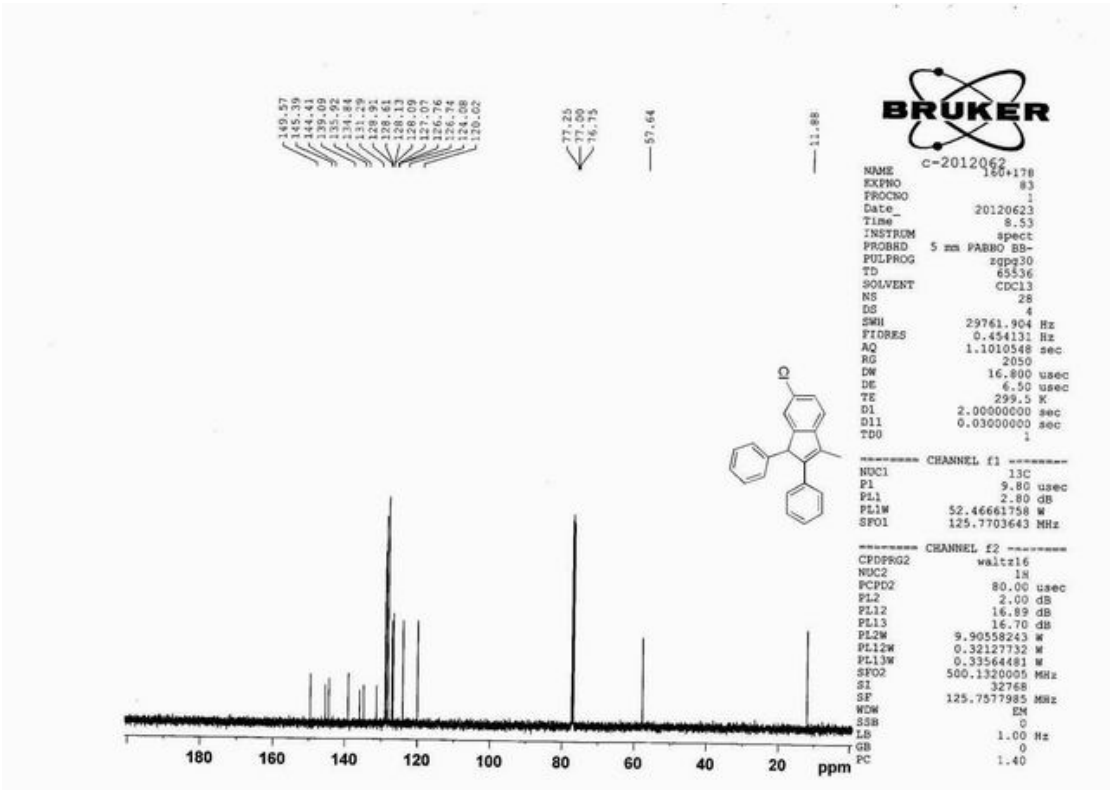
3,6-dimethyl-1,2-diphenyl-1H-indene (4aw)



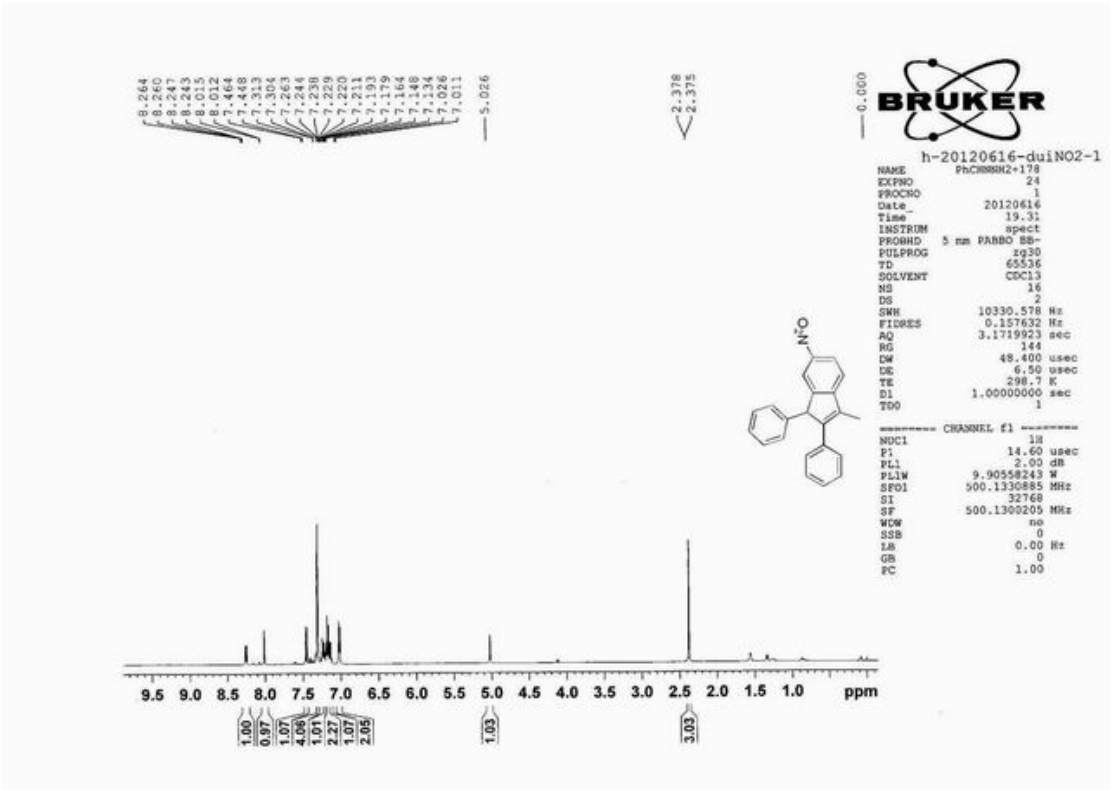


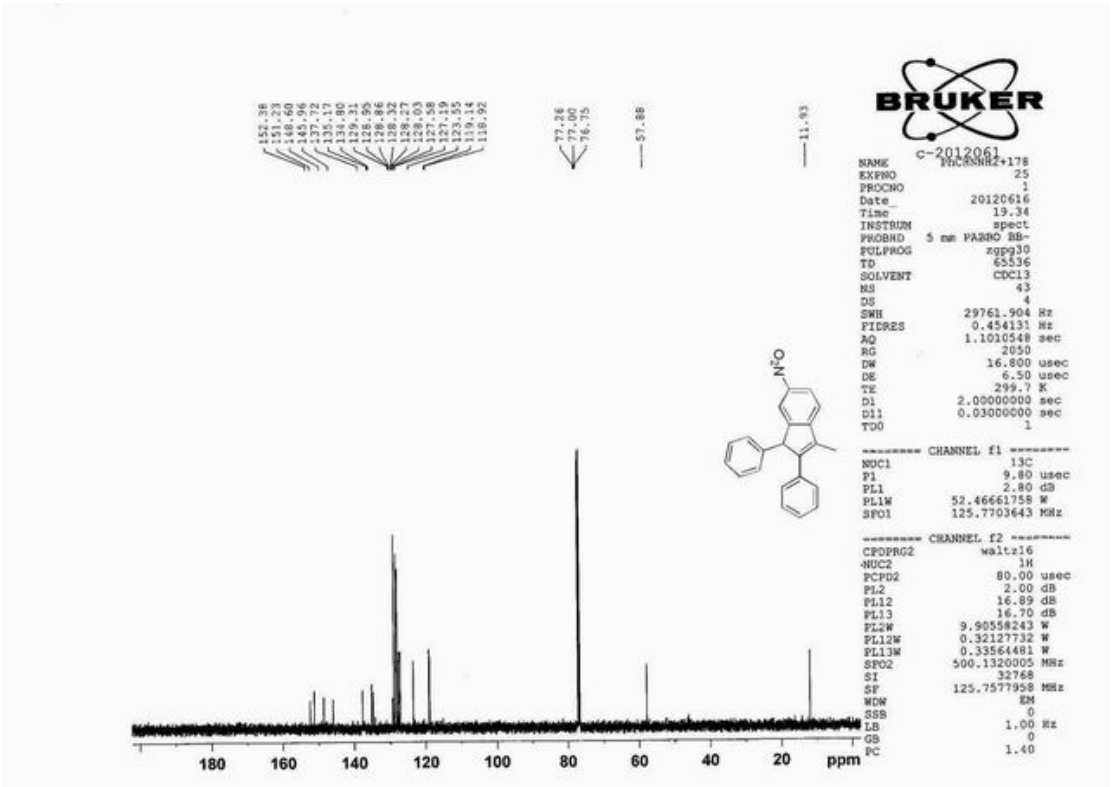
6-Chloro-3-methyl-1,2-diphenyl-1H-indene (4ax)



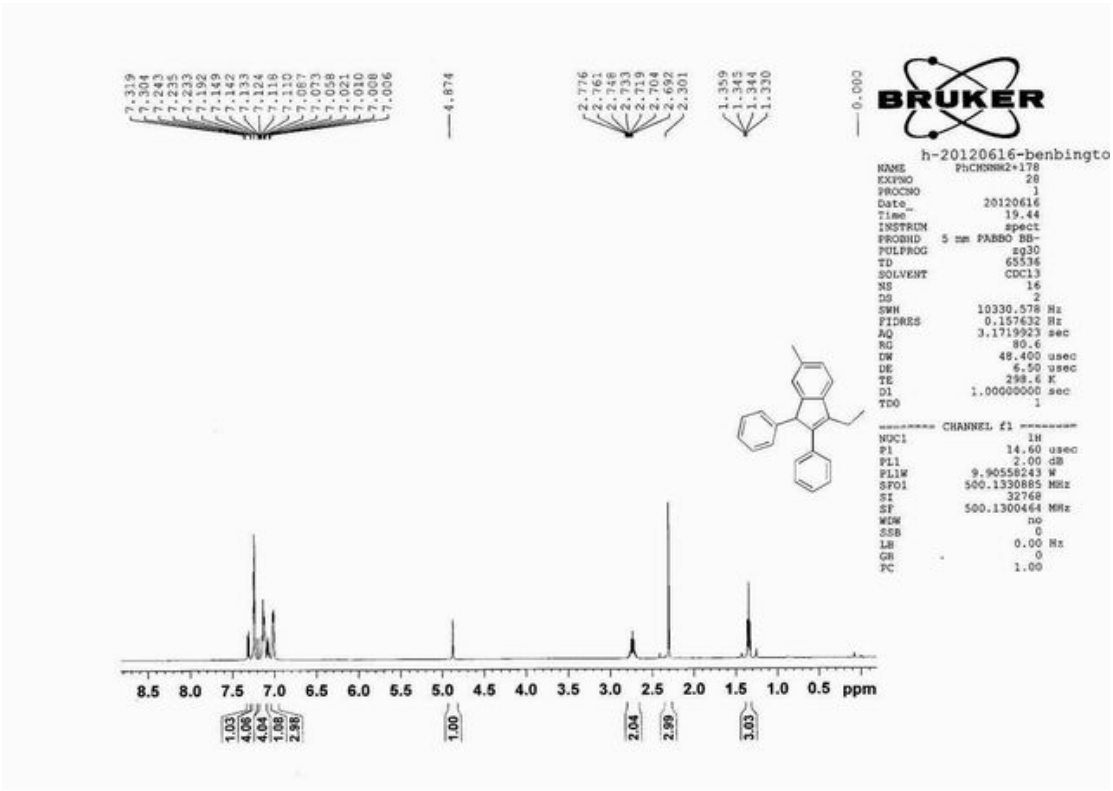


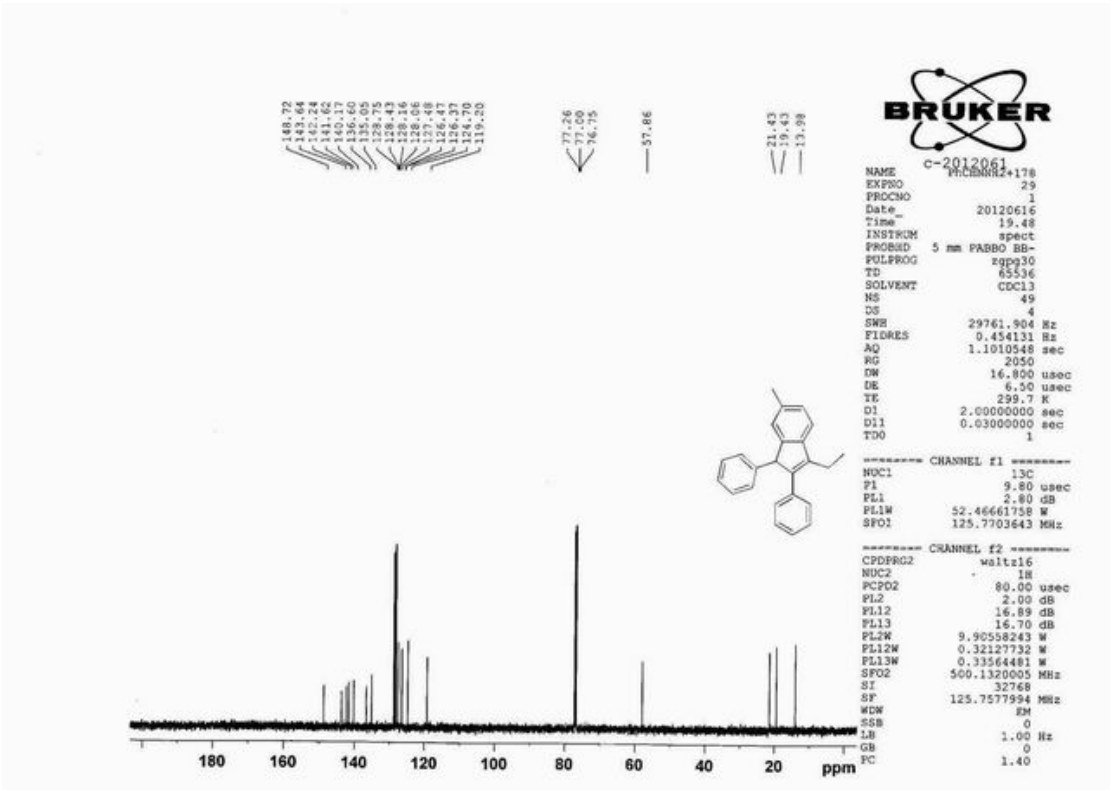
3-Methyl-6-nitro-1,2-diphenyl-1H-indene (4ay)





3-Ethyl-6-methyl-1,2-diphenyl-1H-indene (4az)





1,2-bis(1-phenylethylidene)hydrazine (6aa)