

Supporting Information

A facile one-pot synthesis of 2,3-diarylated benzo[*b*]furans via relay NHC and palladium catalysis

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1. General information

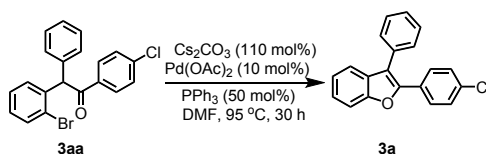
Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1} . ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 or $\text{DMF-}d_7$ (100 MHz, ^{13}C NMR) with chemical shift (δ) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q II HRMS/MS instrument (Bruker) with the technique of atmospheric pressure ionization.

2. Characterization of **3aa**

2-(2-bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone (3aa). white solid; M.P.: 106 - 107 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.97 - 7.94 (m, 2H, ArH), 7.62 - 7.60 (m, 1H, ArH), 7.40 - 7.26 (m, 7H, ArH), 7.24 - 7.22 (m, 1H, ArH), 7.16 - 7.12 (m, 1H, ArH), 7.04 - 7.02 (m, 1H, ArH), 6.40 (s, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3): δ 196.3, 139.6, 138.8, 136.7, 134.8, 133.0, 131.0, 130.3, 129.6, 129.1, 129.0, 128.9, 127.7, 127.6, 124.9, 59.1.

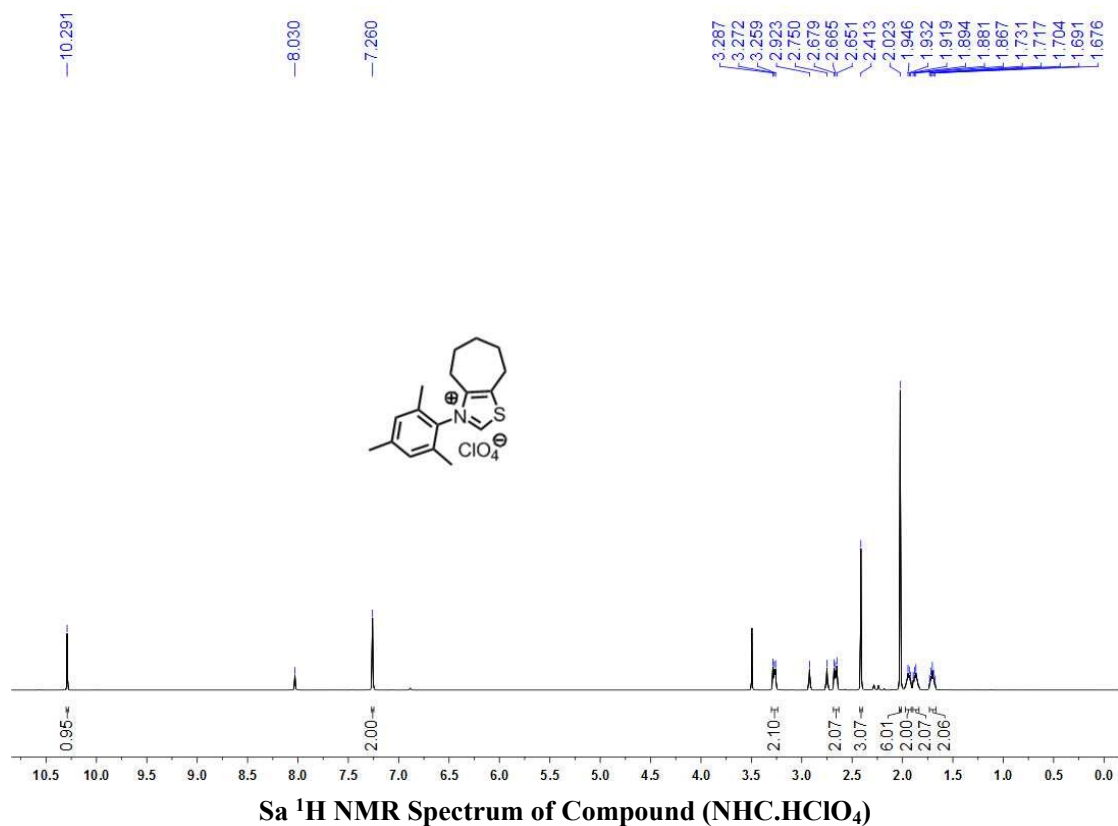
3. Synthesis of **3a** from the intermediate **3aa** and compound characterization

2-(4-chlorophenyl)-3-phenylbenzofuran (**3a**)

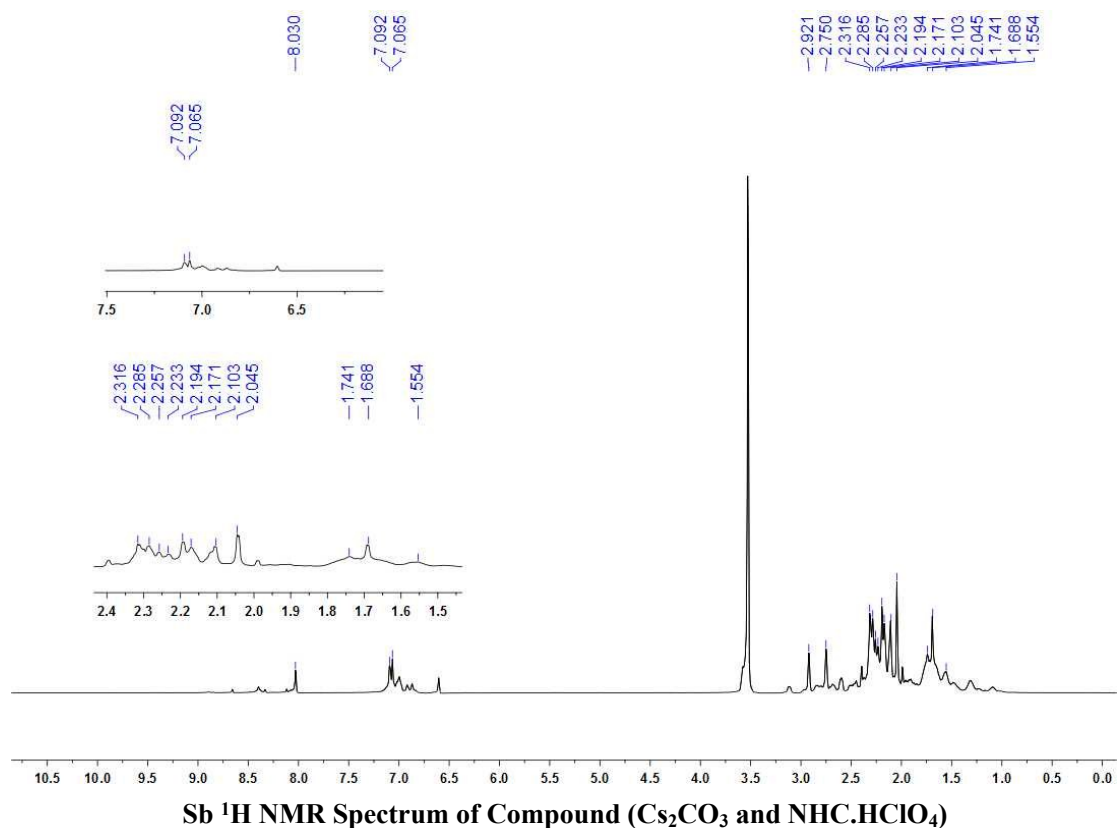


An oven-dried 25-mL flask equipped with a magnetic stir bar was charged with 2-(2-bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone (**3aa**, 191.9 mg, 0.5 mmol), Cs_2CO_3 (179.2 mg, 0.55 mmol), freshly distilled DMF (5 mL), $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol) and PPh_3 (65.6 mg, 0.25 mmol). The mixture was stirred at 95 °C until completion (monitored by TLC, 30 h). Deionized water (5 mL) was added and the mixture then extracted with EtOAc. The organic layer was dried over MgSO_4 . The desired product **3a** (129 mg, 85 %) were obtained through filtration, concentration in vacuo and purification by column chromatography (silica gel, petroleum). white solid; M.P.: 90 - 92 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.60 - 7.57 (m, 2H, ArH), 7.55 (d, J = 8.0 Hz, 1H, ArH), 7.50 - 7.40 (m, 6H, ArH), 7.36 - 7.32 (m, 1H, ArH), 7.30 - 7.22 (m, 3H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 154.0, 149.3, 134.2, 132.5, 130.1, 129.7, 129.1, 129.1, 128.7, 128.2, 127.8, 124.9, 123.1, 120.1, 118.0, 111.1; IR (potassium bromide) (ν , cm^{-1}): 1618, 1608, 1582, 1560, 1483, 1449, 1402, 1253, 1201, 1089, 1064, 1014, 962, 840, 749, 695; HRMS (APCI) m/z : Calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{20}\text{H}_{14}\text{ClO}$: 305.0733, found: 305.0723.

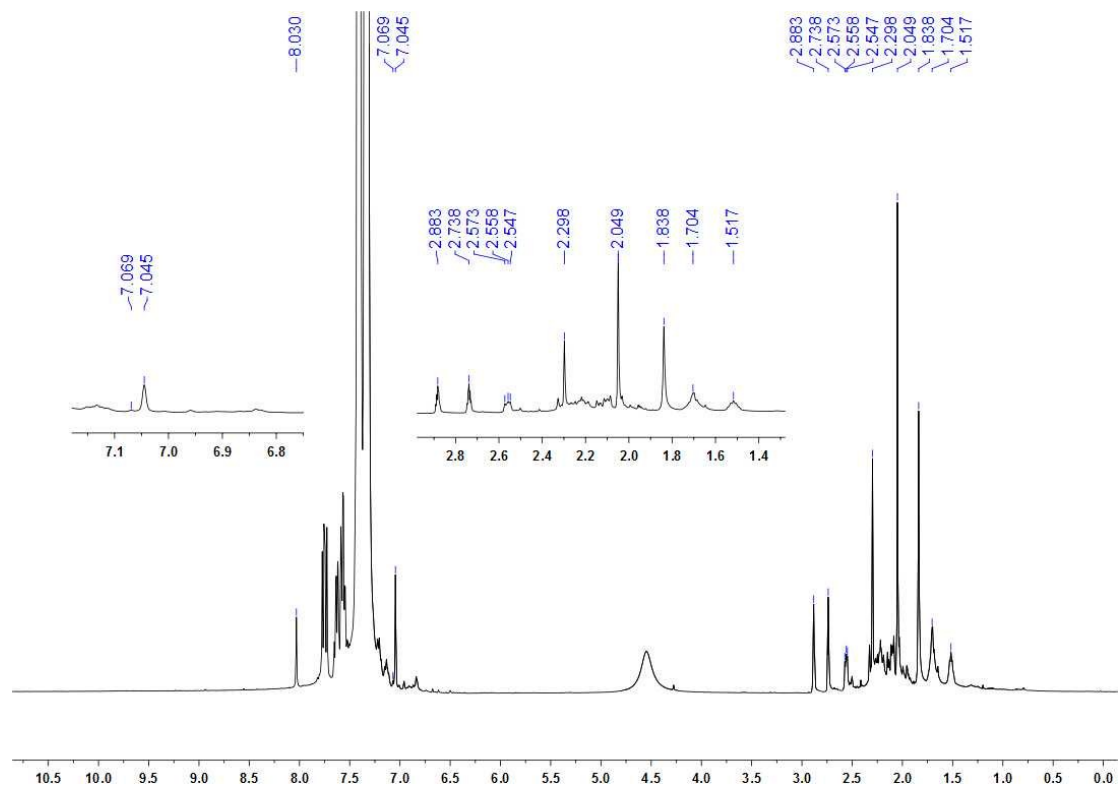
4. Evidences for compatibility of NHC and Pd catalysts



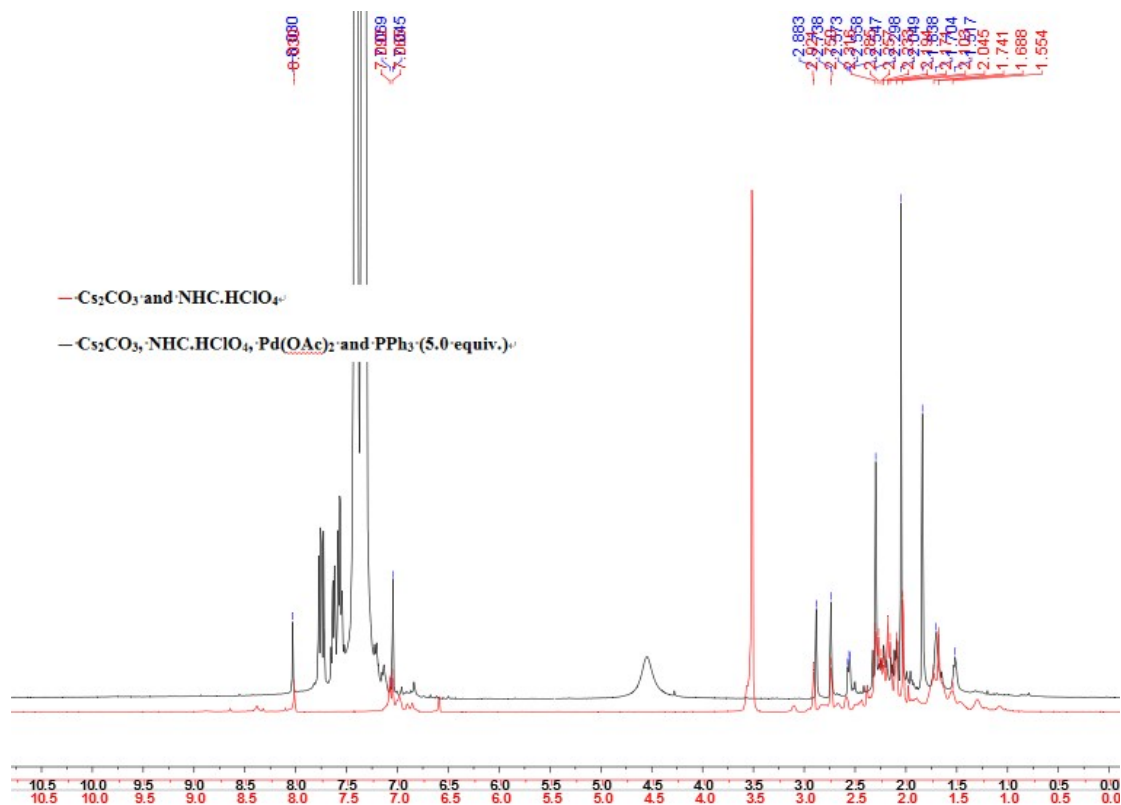
Sa ¹H NMR Spectrum of Compound (NHC.HClO₄)



Sb ¹H NMR Spectrum of Compound (C₂CO₃ and NHC.HClO₄)



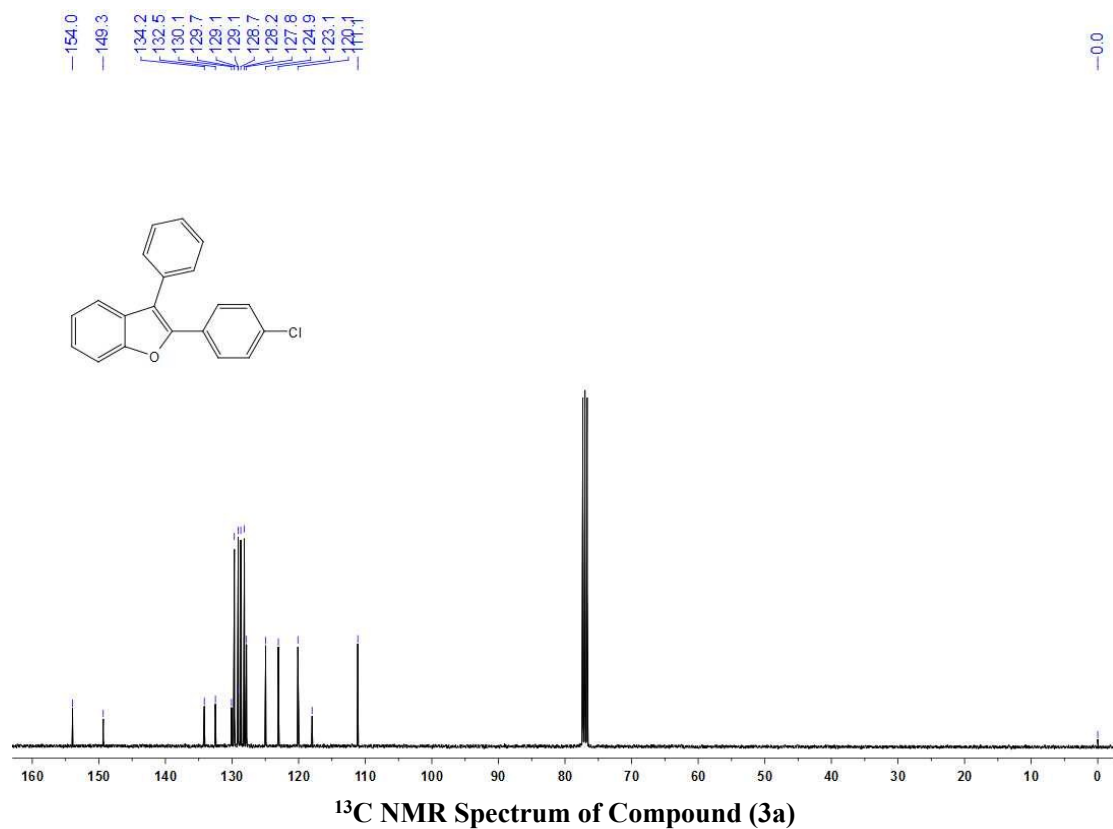
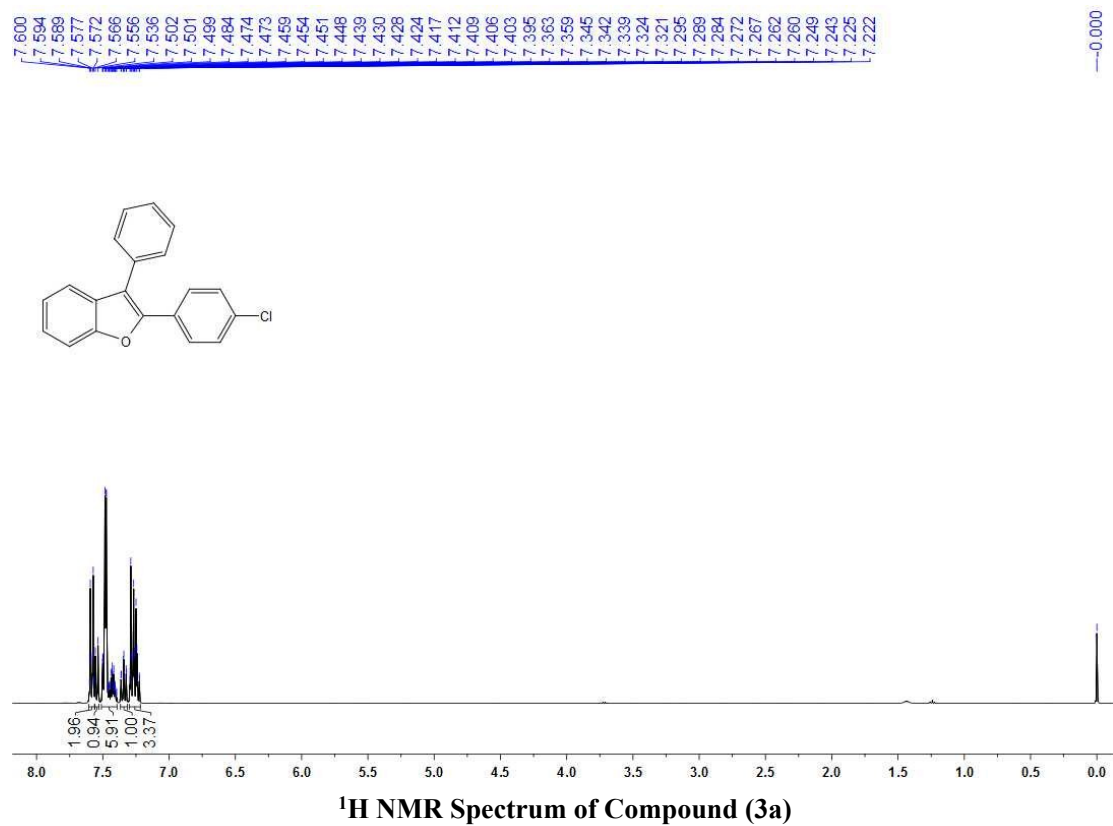
Sc ¹H NMR Spectrum of Compound (Cs₂CO₃, NHC.HClO₄, Pd(OAc)₂ and PPh₃ (5.0 equiv.))

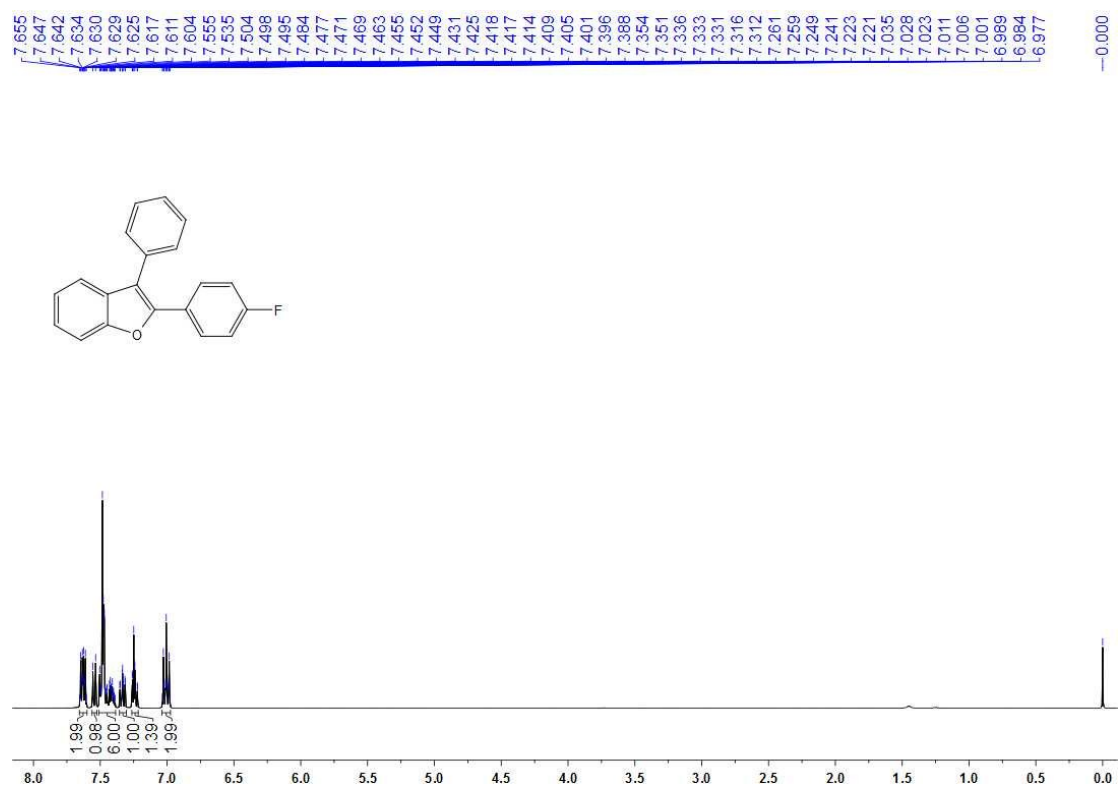


Sd A superposition of Sb and Sc

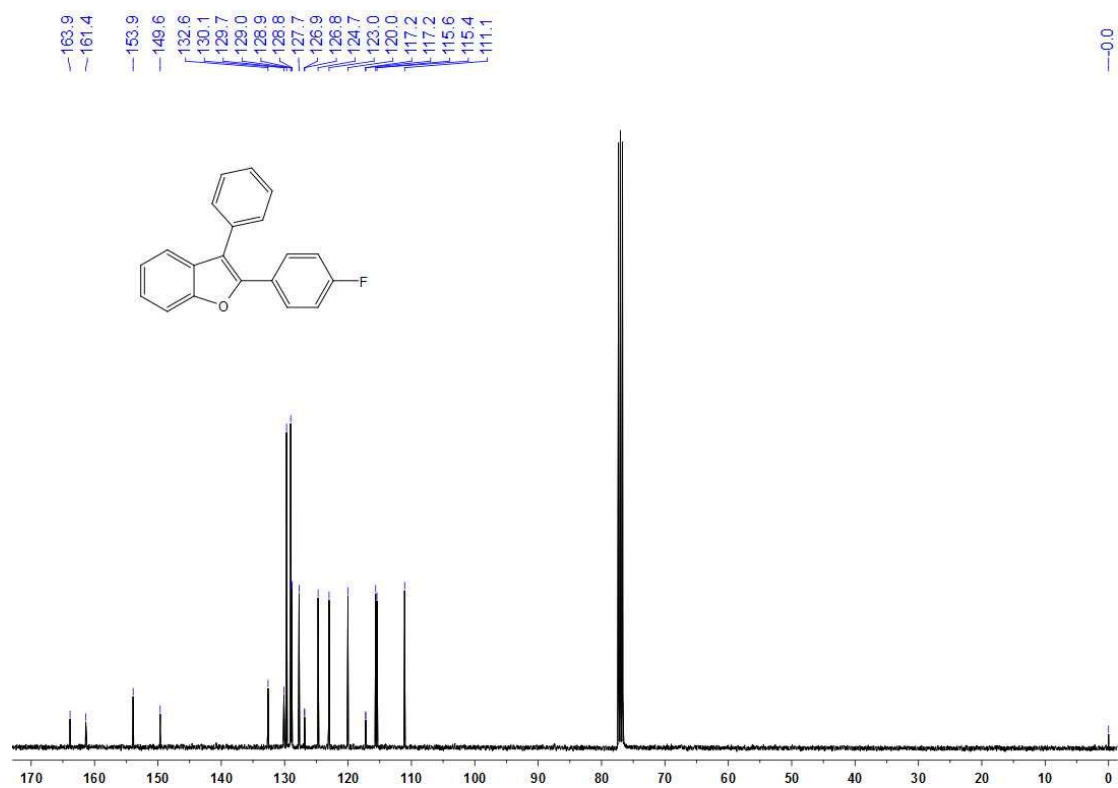
A superposition (**Sd**) of **Sb** and **Sc** showed that no striking discrepancy of chemical shift between these two NMR spectrums, apart from the signal of PPh₃. Thus, we concluded safely that the complex of NHC and Pd was not formed here.

5. NMR Spectra

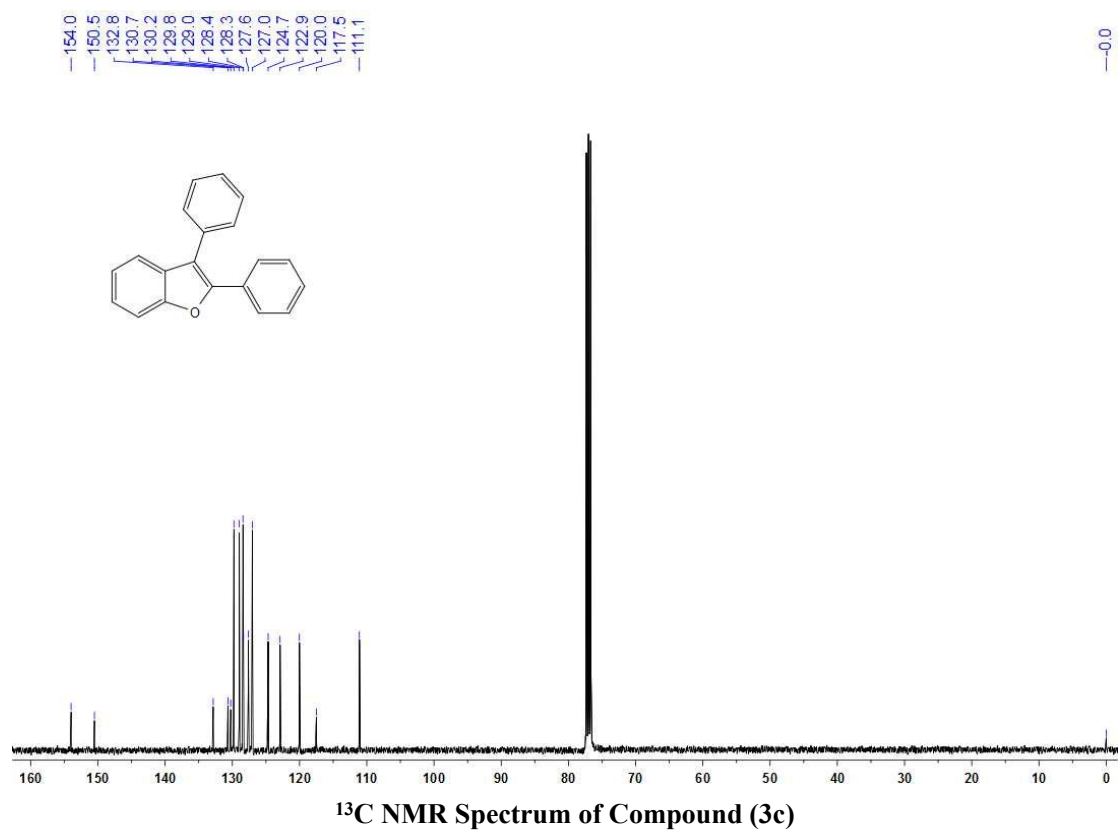
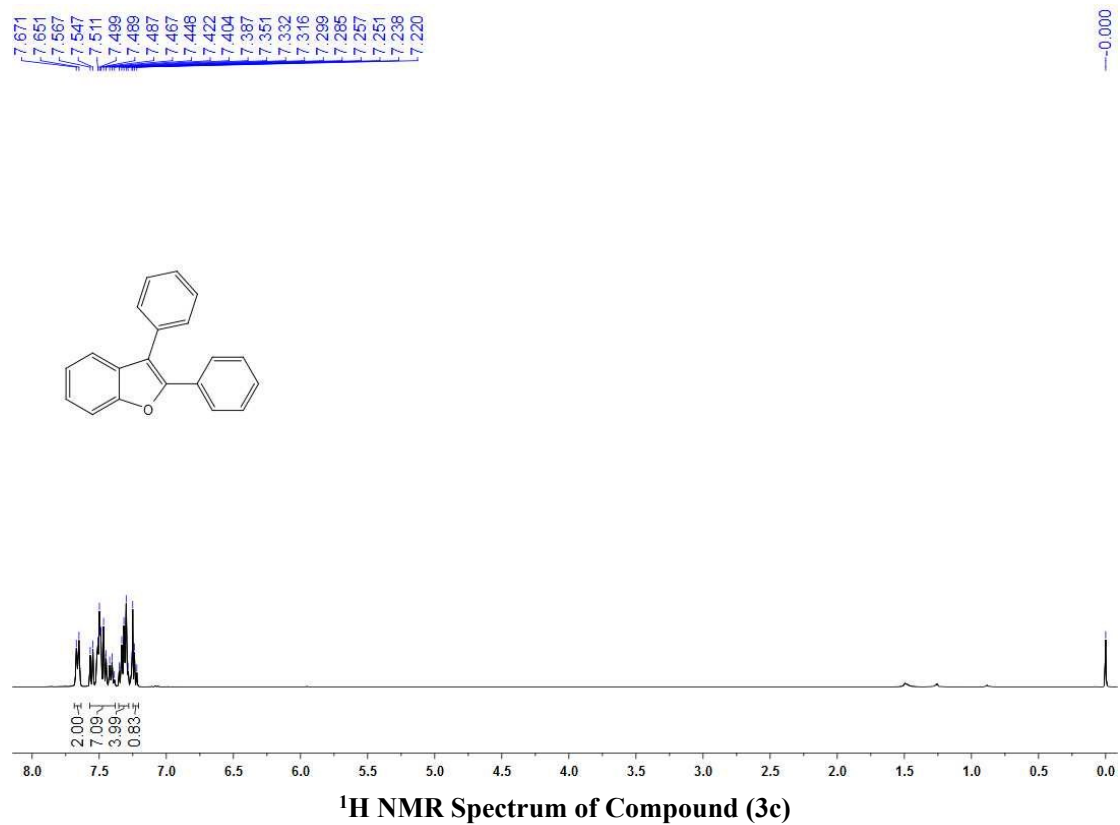


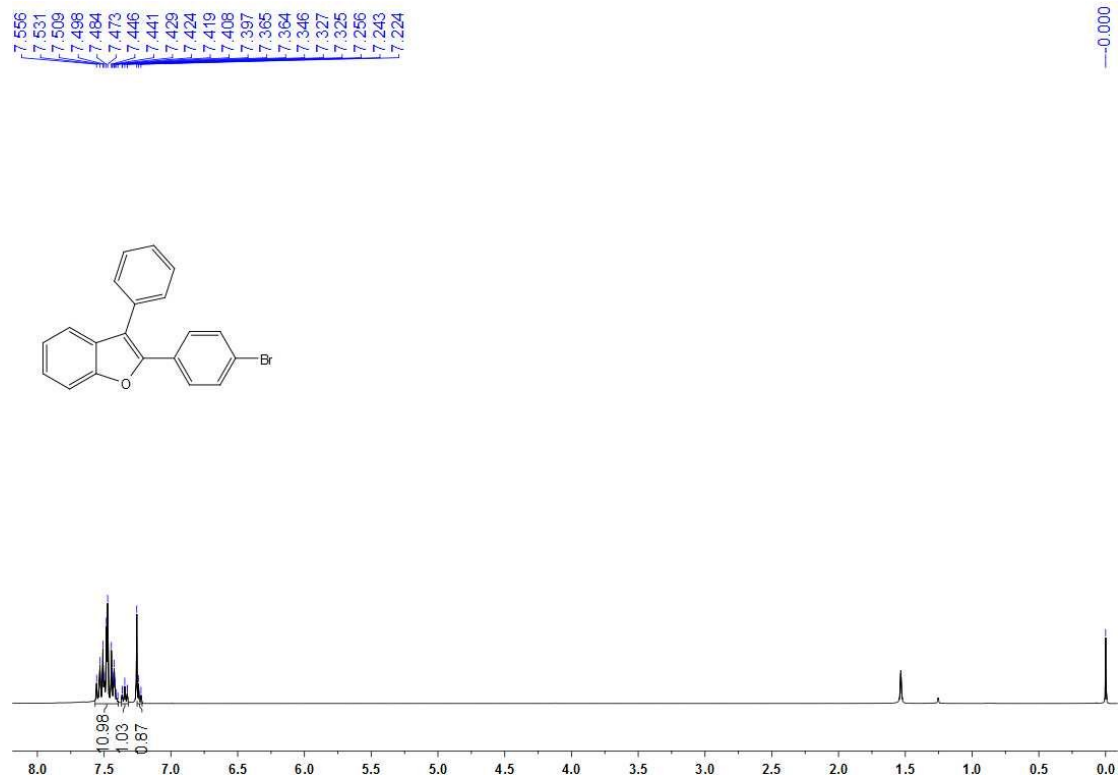


¹H NMR Spectrum of Compound (3b)

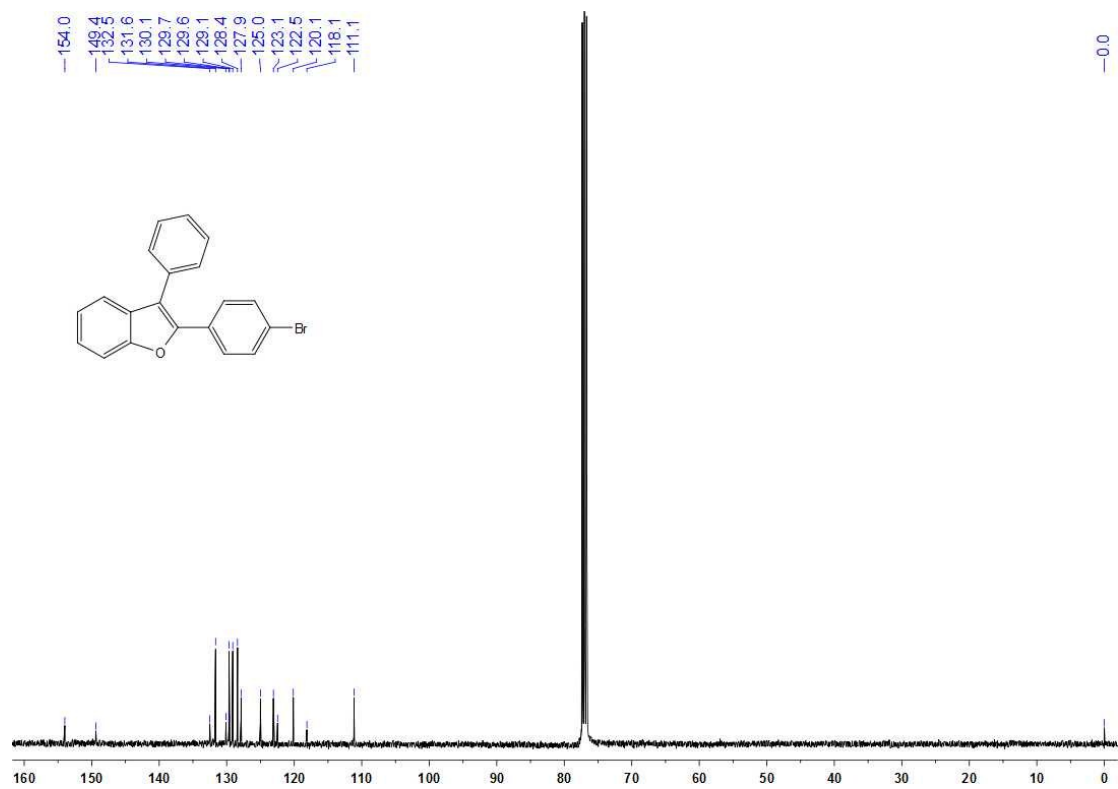


¹³C NMR Spectrum of Compound (3b)

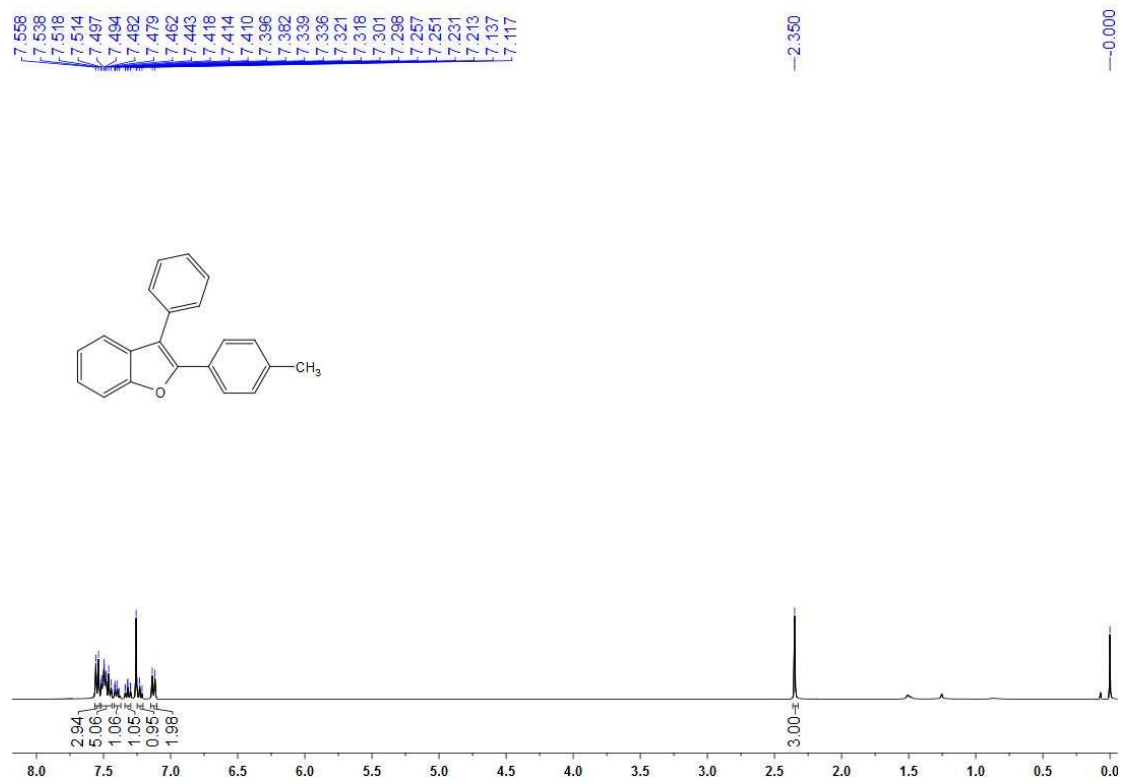




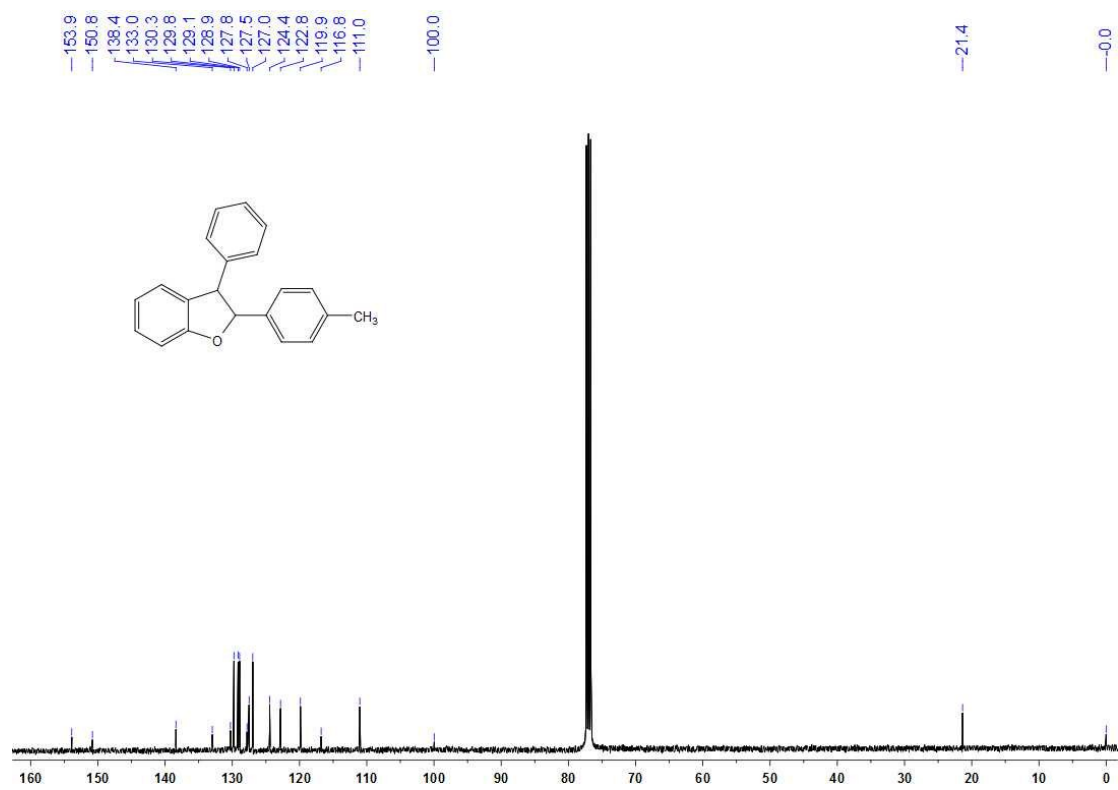
¹H NMR Spectrum of Compound (3d)



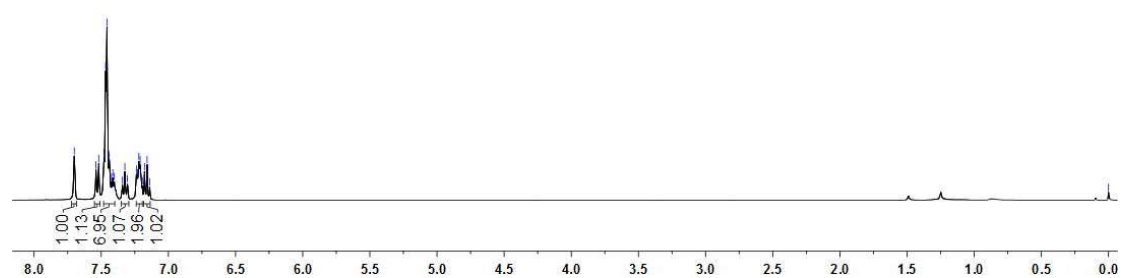
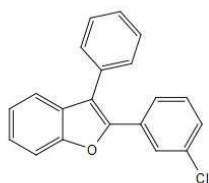
¹³C NMR Spectrum of Compound (3d)



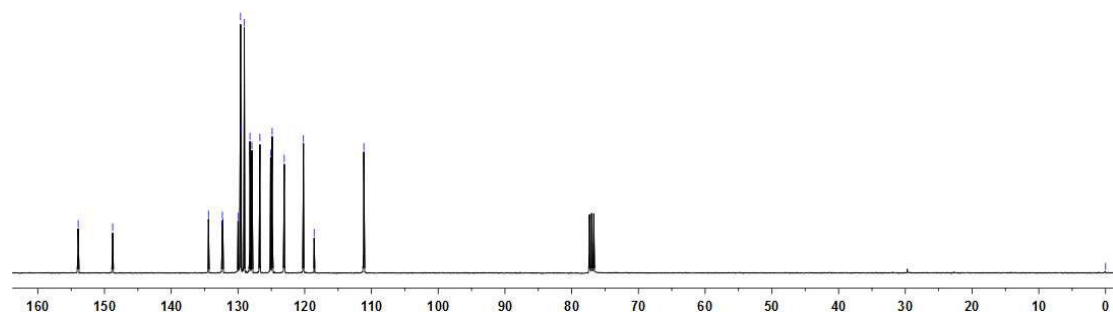
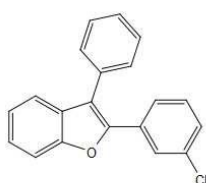
¹H NMR Spectrum of Compound (3e)



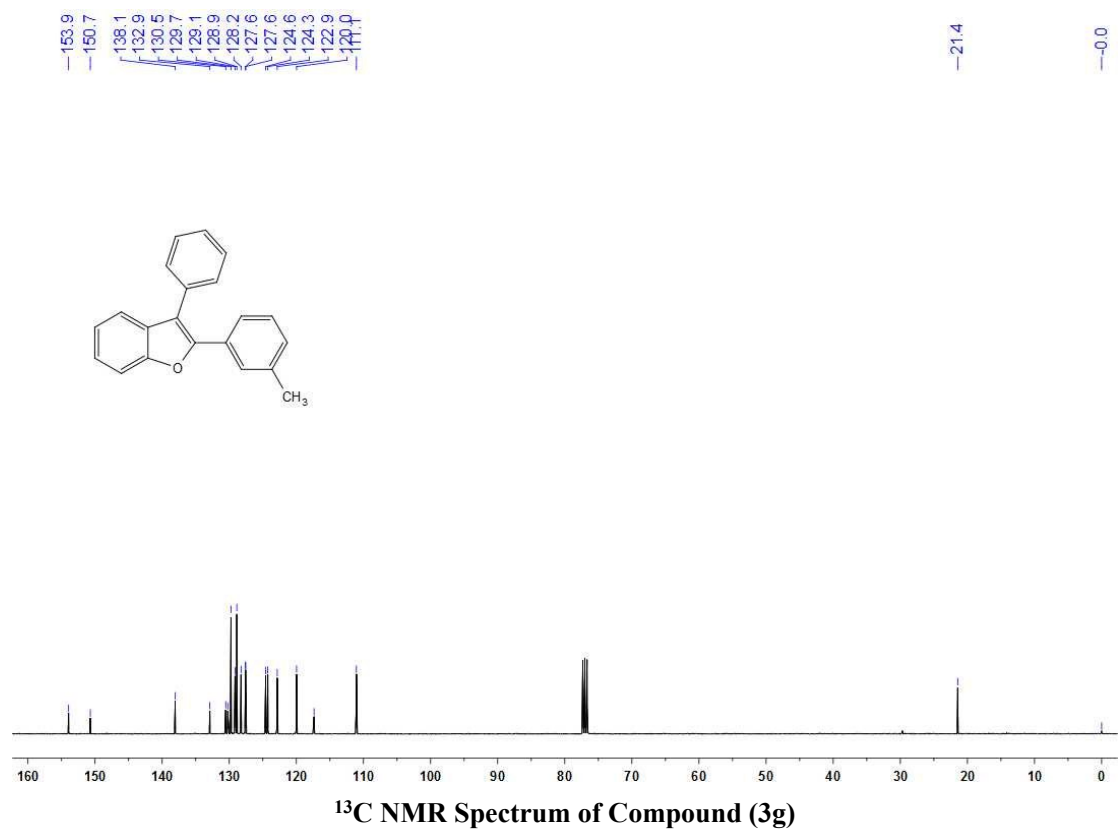
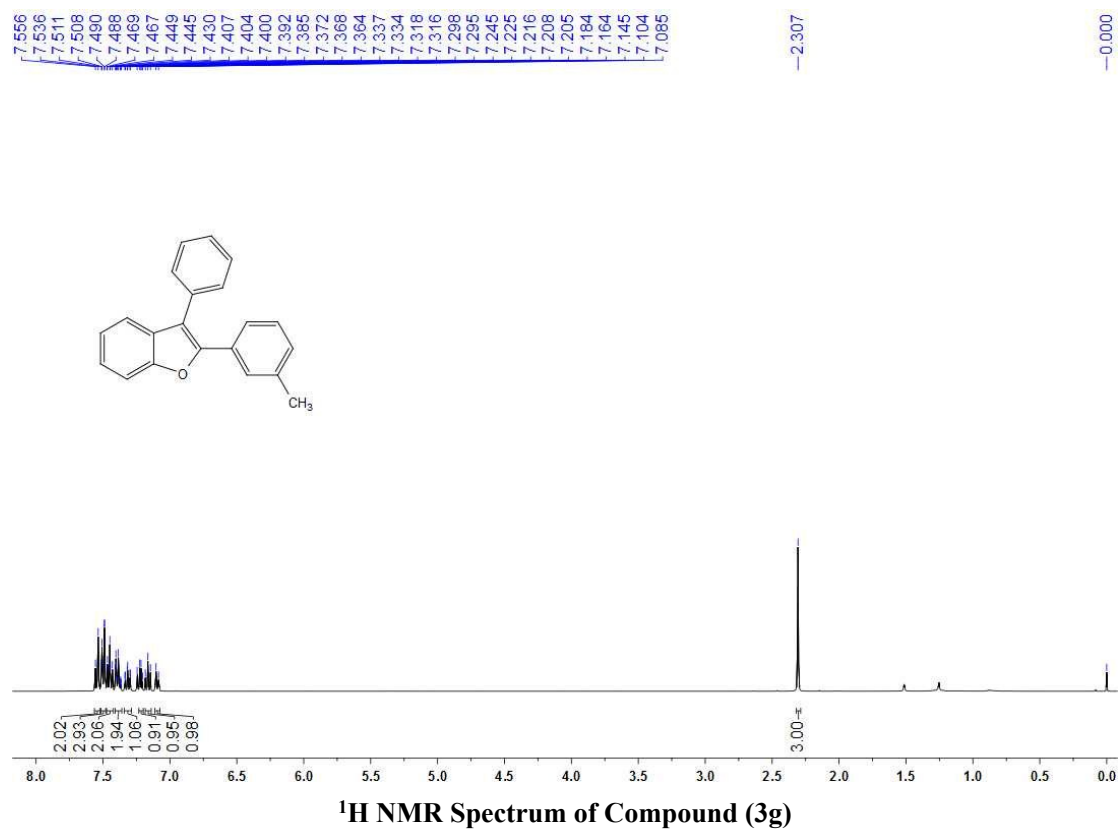
¹³C NMR Spectrum of Compound (3e)

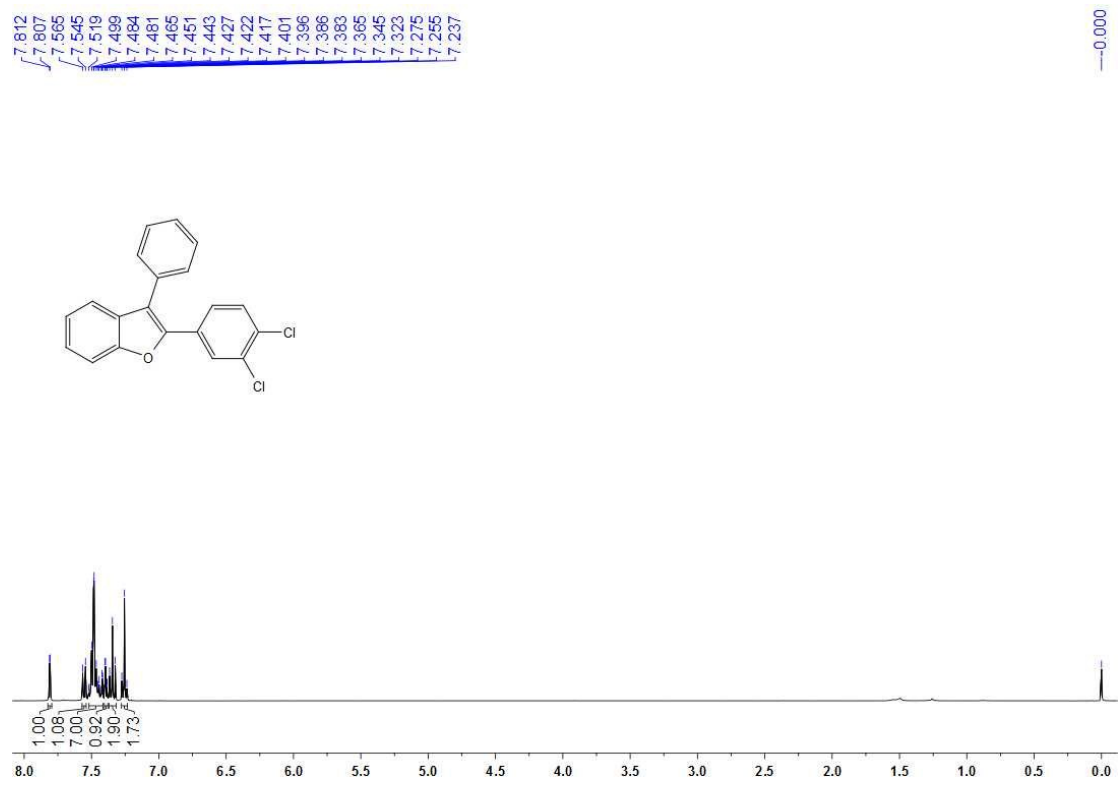


¹H NMR Spectrum of Compound (3f)

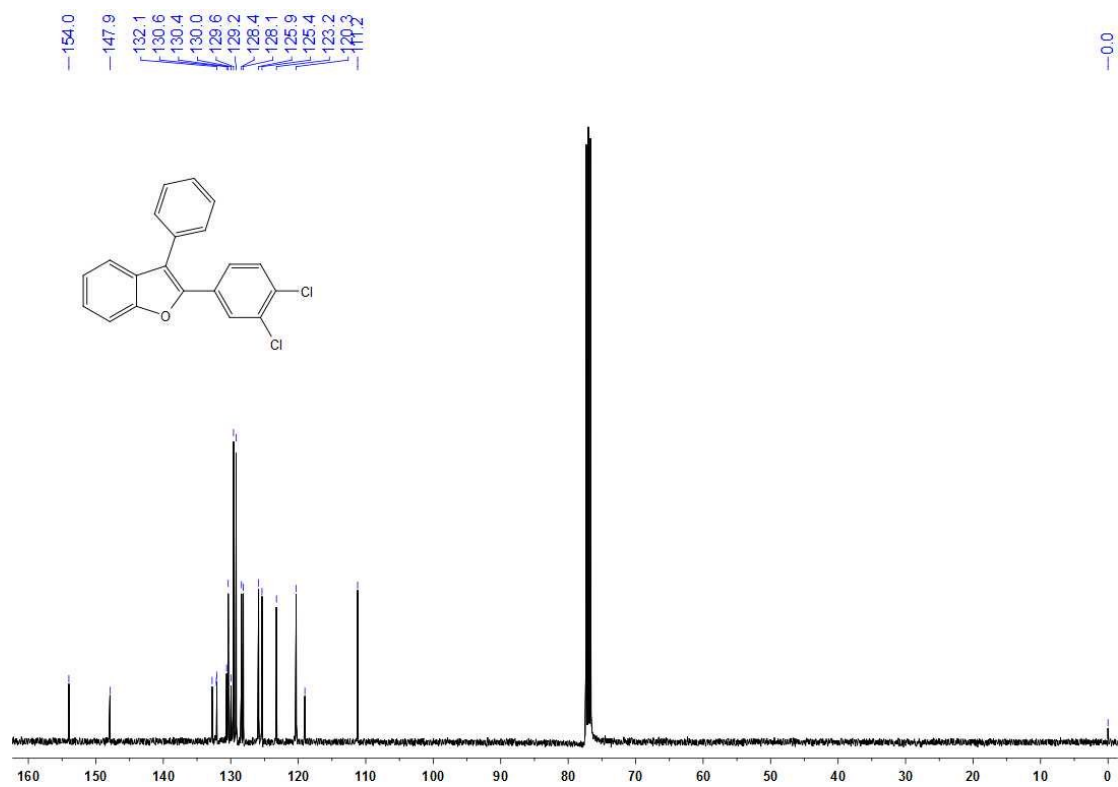


¹³C NMR Spectrum of Compound (3f)

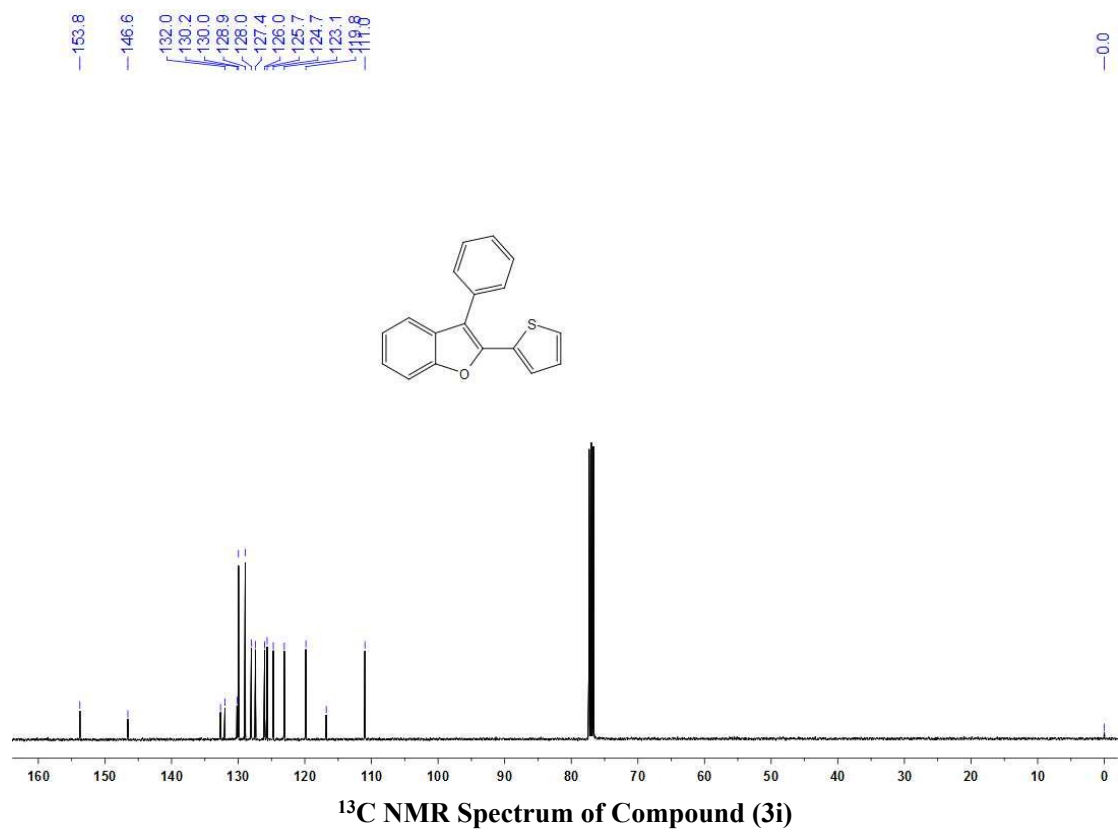
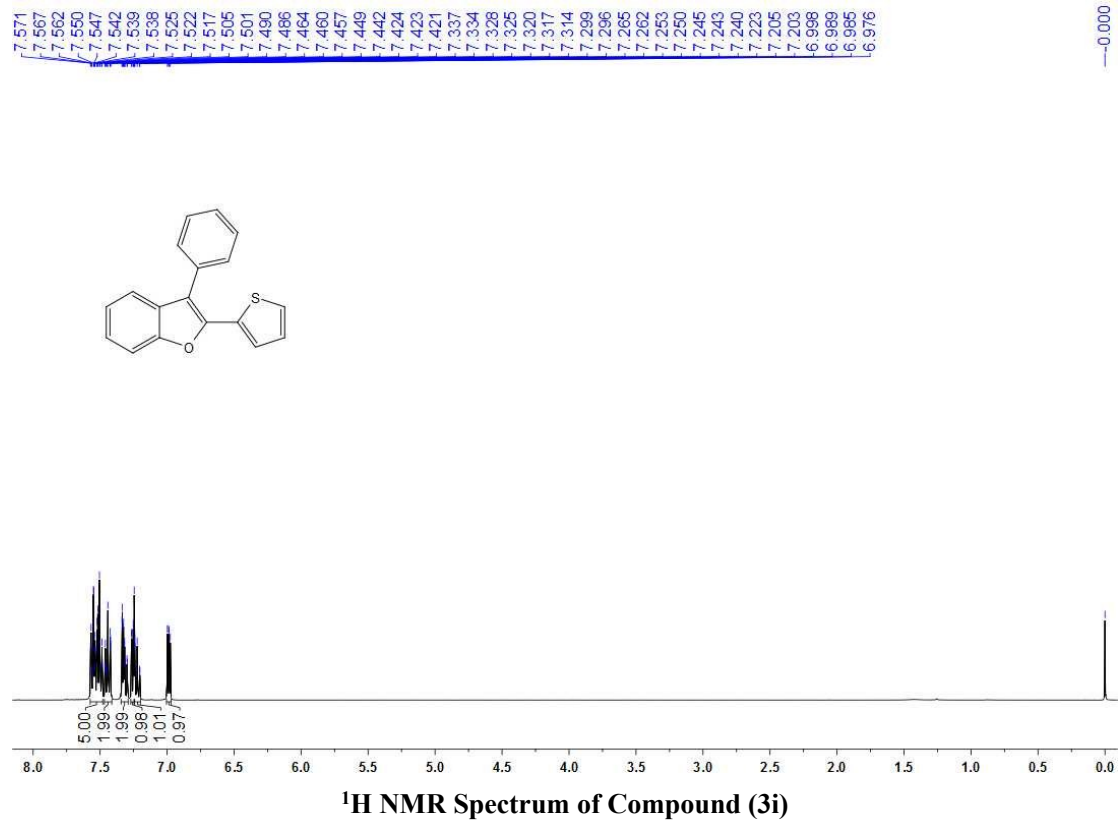


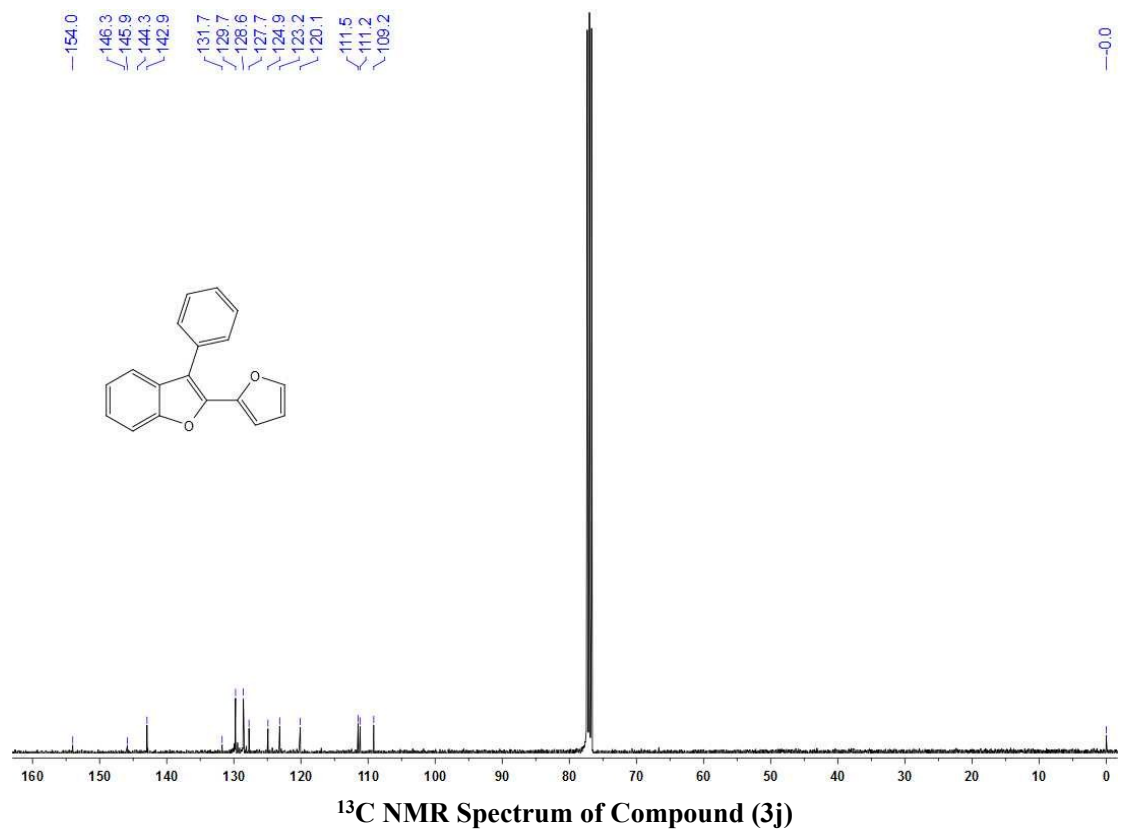
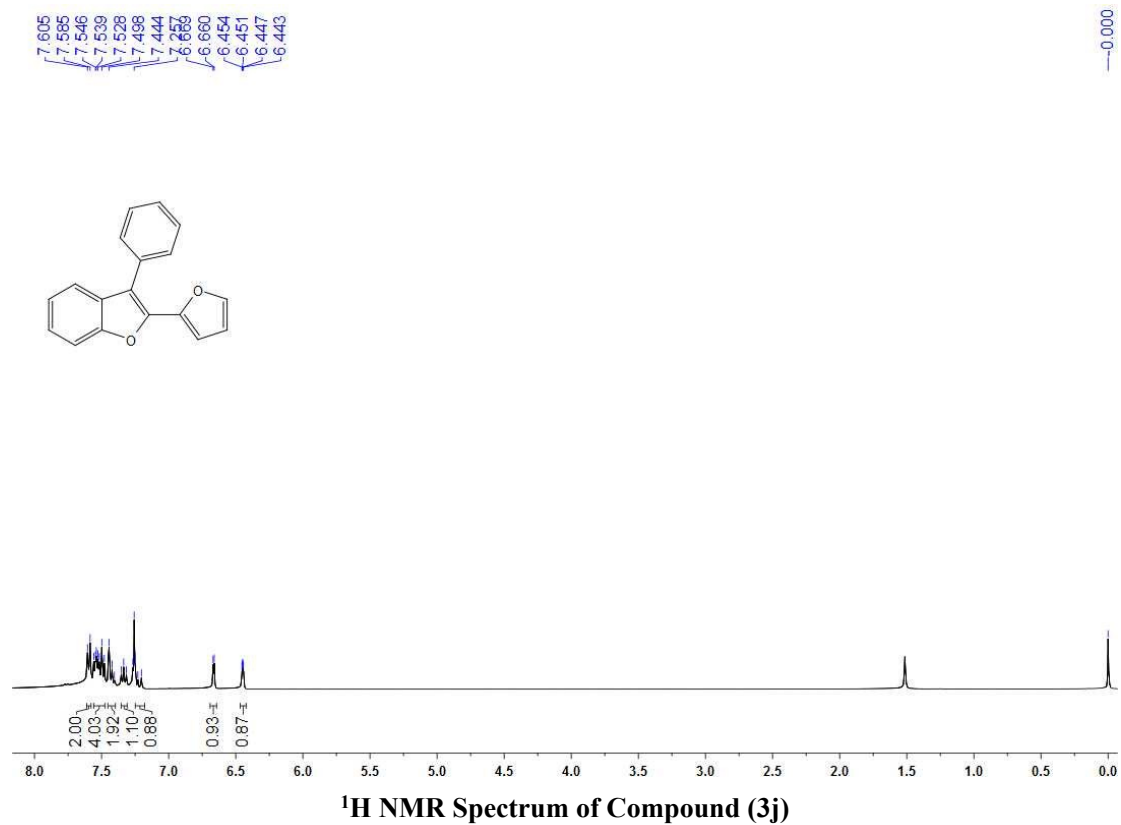


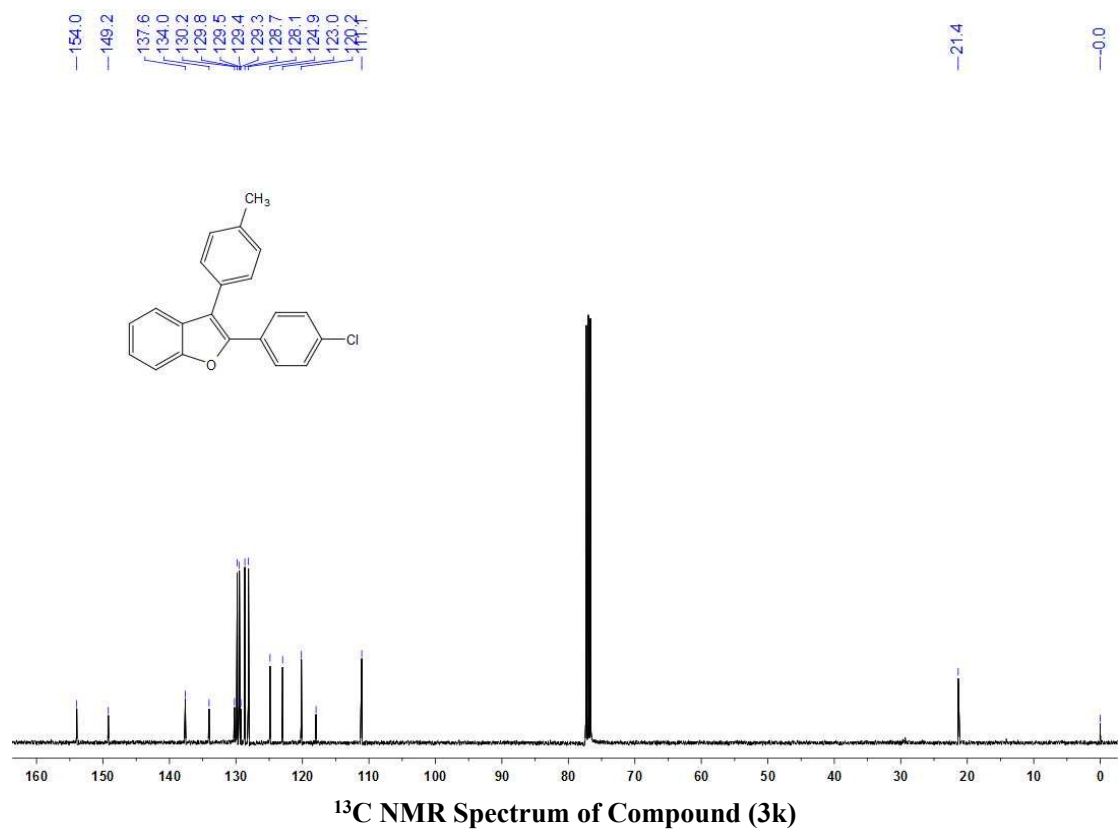
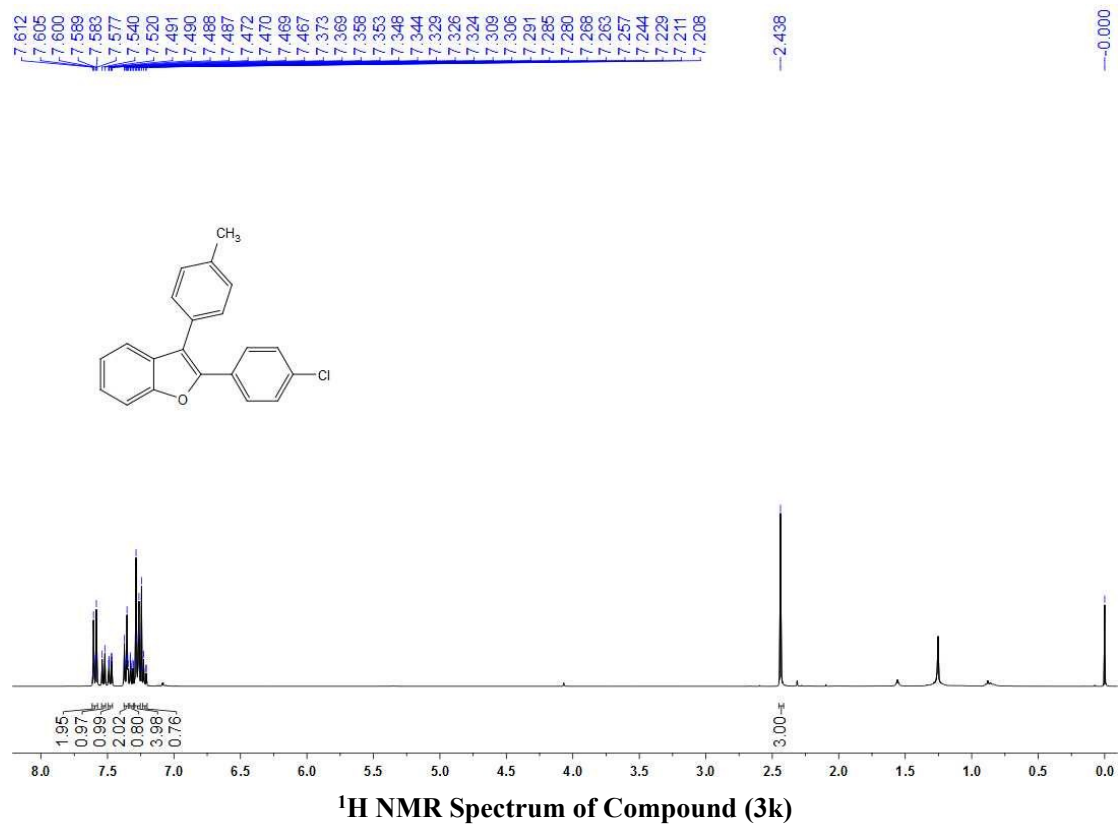
¹H NMR Spectrum of Compound (3h)

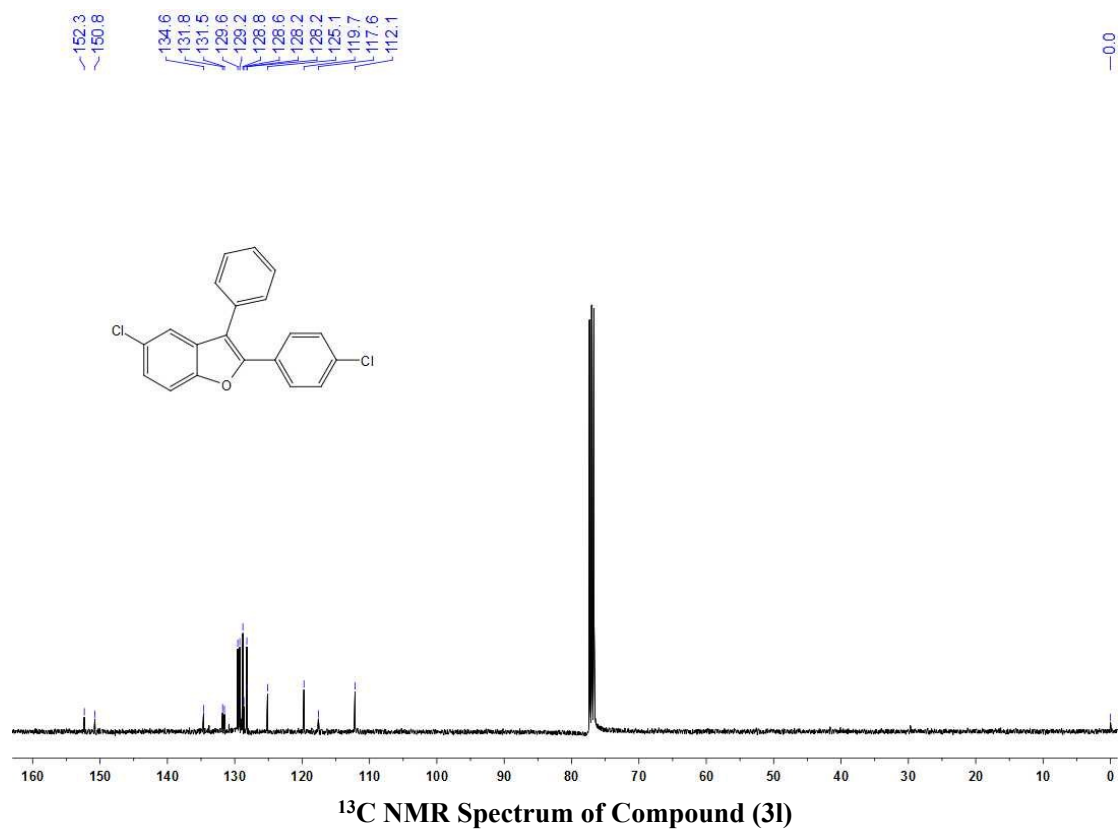
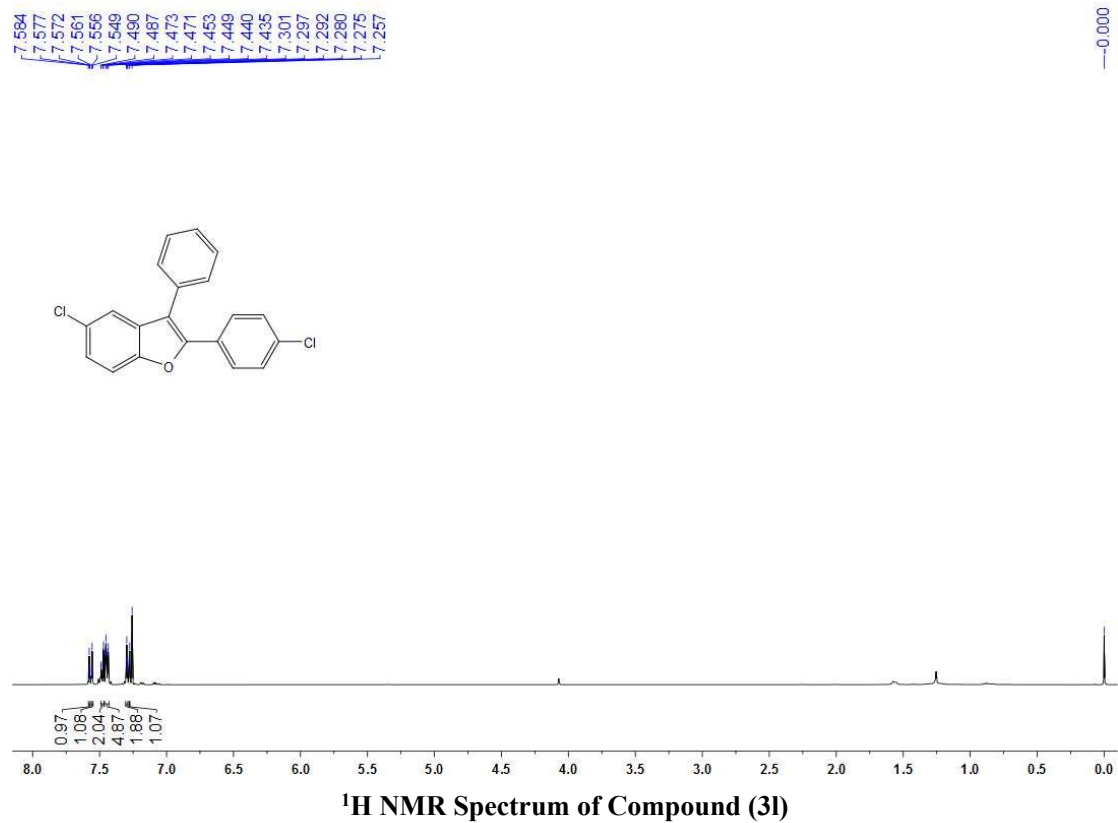


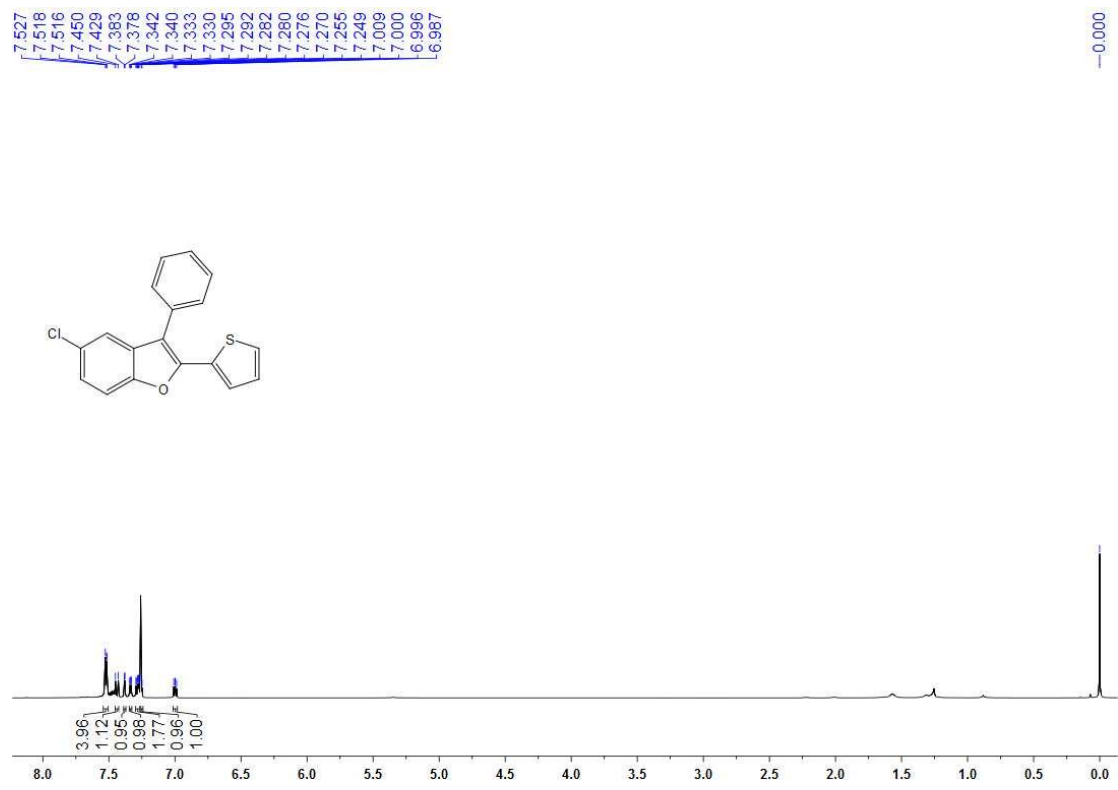
¹³C NMR Spectrum of Compound (3h)



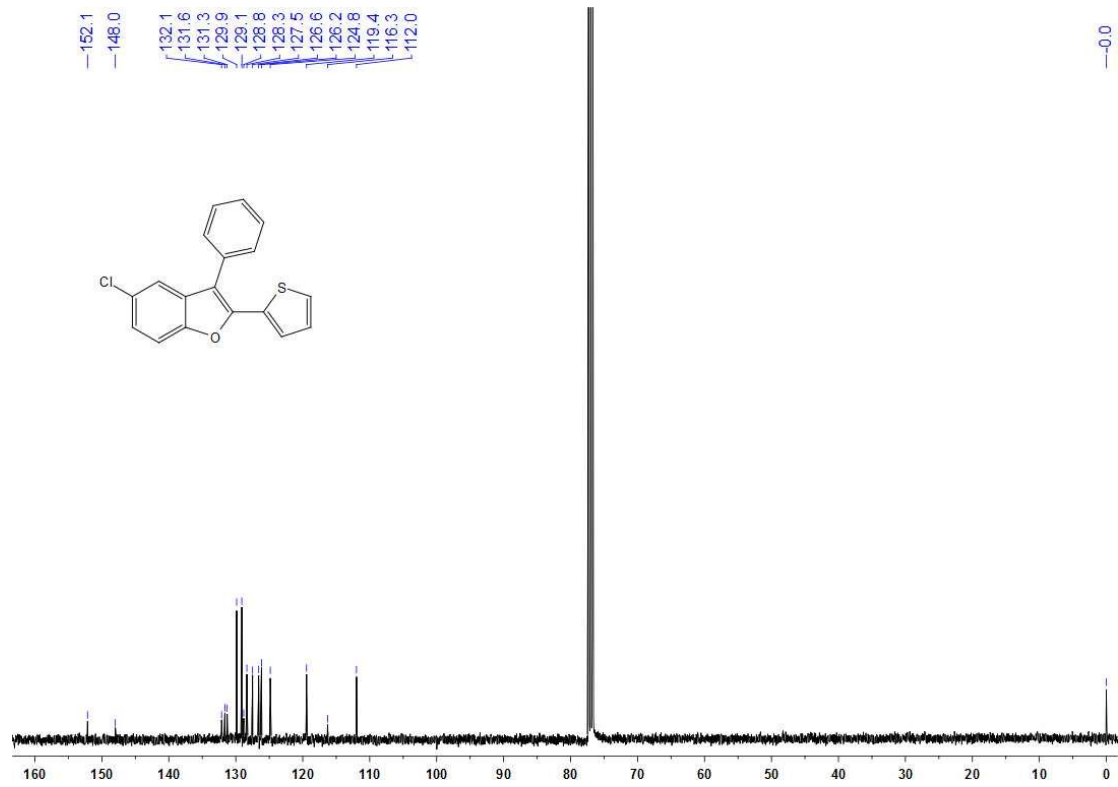




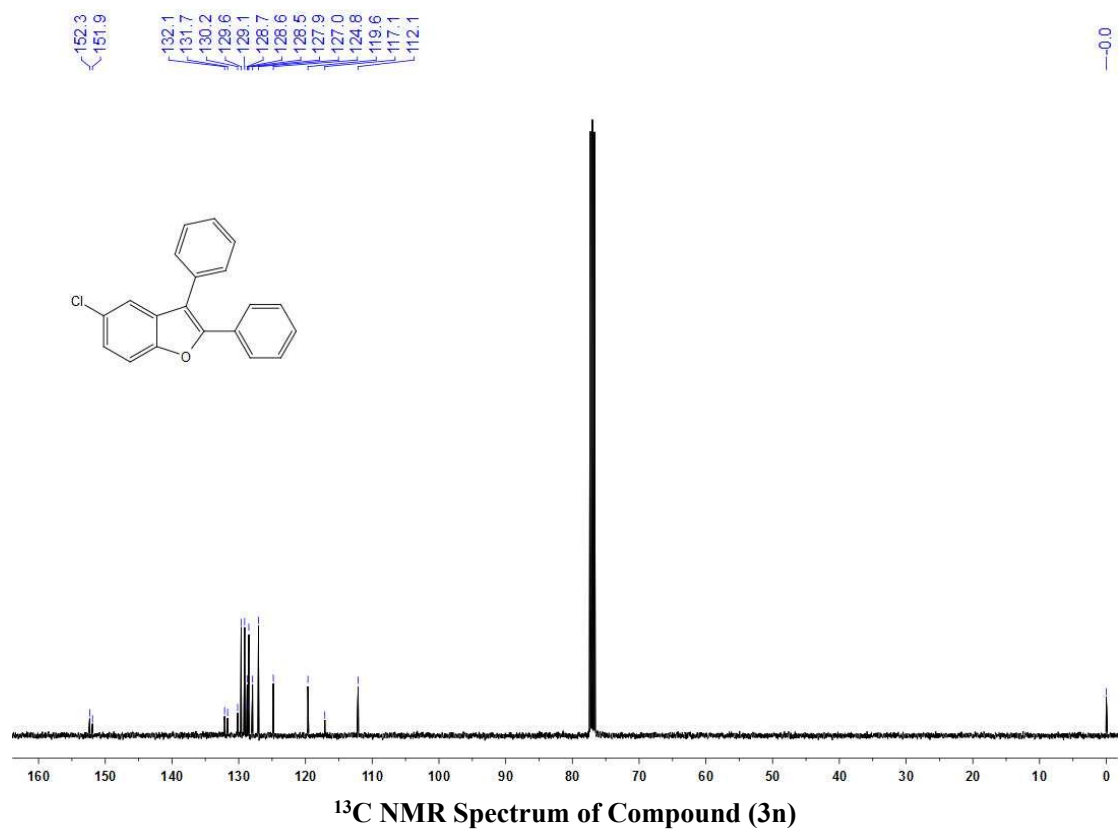
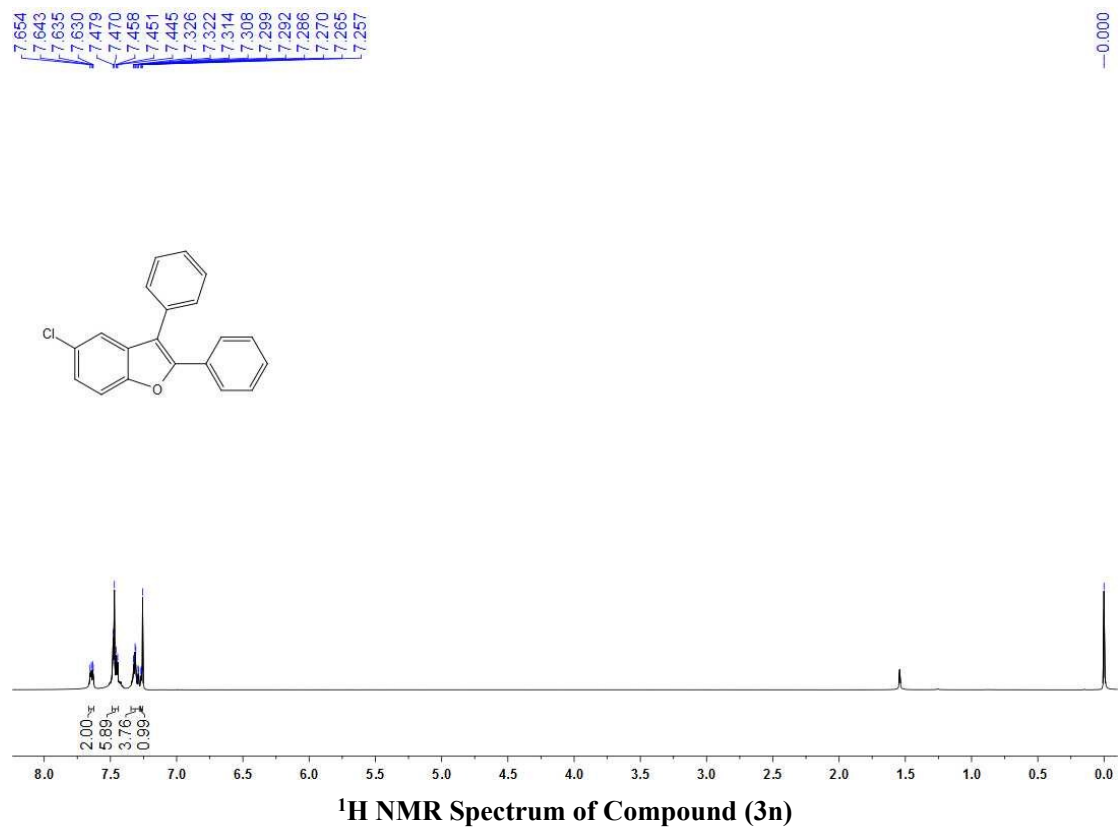




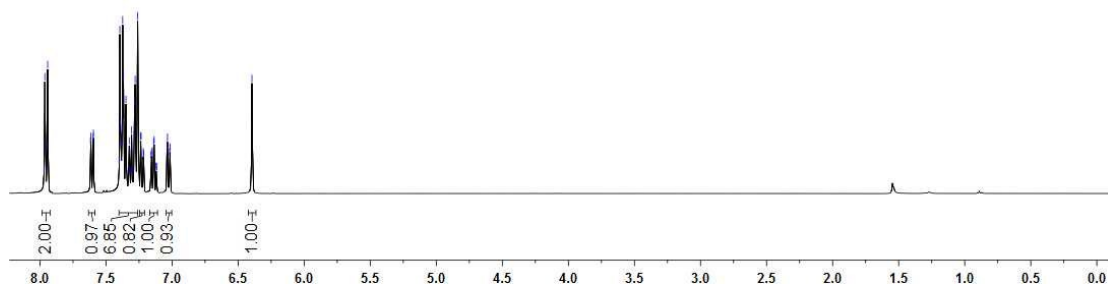
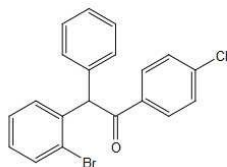
¹H NMR Spectrum of Compound (3m)



¹³C NMR Spectrum of Compound (3m)



7.963
7.946
7.942
7.395
7.390
7.379
7.374
7.368
7.349
7.283
7.280
6.395

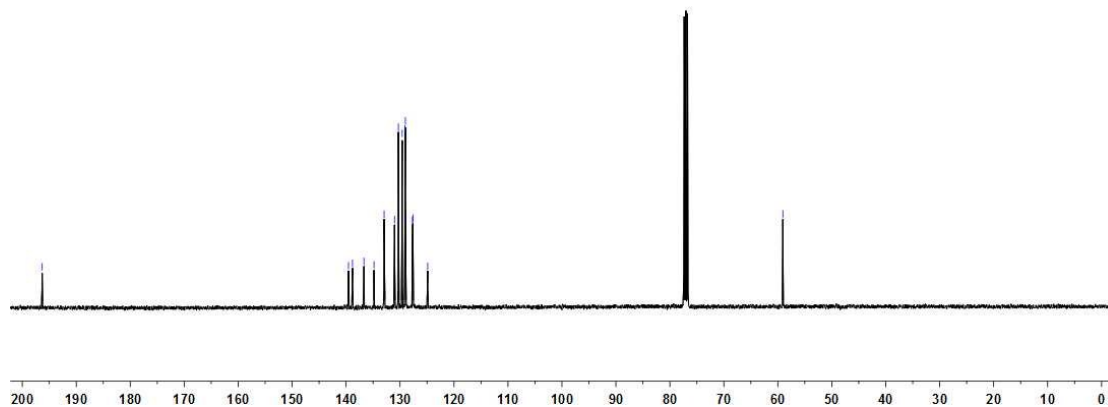
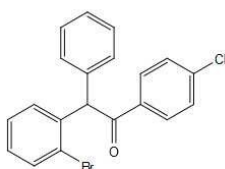


¹H NMR Spectrum of Compound (3aa)

196.3

139.6
138.8
136.7
134.8
133.0
131.0
130.3
129.6
129.1
128.9
127.7
124.9

59.1



¹³C NMR Spectrum of Compound (3aa)