

Nickel Catalyzed Intramolecular Oxidative Coupling: Synthesis of 3-Aryl Benzofurans

Department of Chemistry, Indian Institute of Technology, Hyderabad

Kandi – 502 285, Sangareddy

Telangana, INDIA

Phone: (040) 2301 6033; Fax: (040) 2301 6003/32

E-mail: gvsatya@iith.ac.in

Supporting Information

1. General experimental procedure and characterization data S2-S3
2. ^1H and ^{13}C -NMR spectra of all benzofurans **2** S4-S27

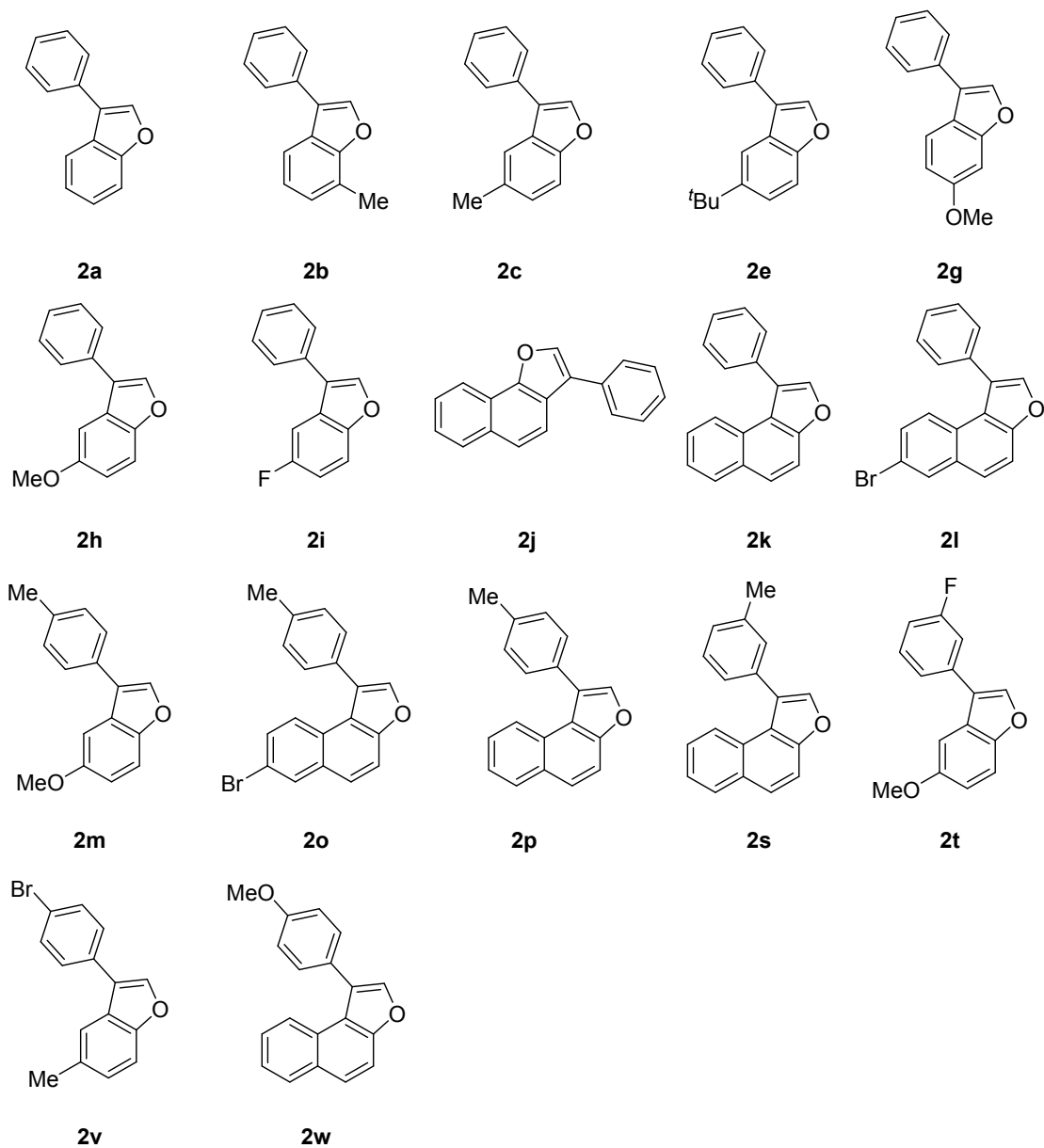
EXPERIMENTAL SECTION:

IR spectra were recorded on a Bruker Tensor 37 (FT-IR) spectrophotometer. ¹H-NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl₃; chemical shifts (δ in ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ ppm) or CHCl₃ ($\delta_{\text{H}} = 7.25$ ppm). ¹³C-NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl₃; chemical shifts (δ in ppm) are reported relative to CDCl₃ [$\delta_{\text{C}} = 77.00$ ppm (central line of triplet)]. In the ¹³C-NMR, the nature of carbons (C, CH, CH₂ and CH₃) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH₂) and q = quartet (for CH₃). In the ¹H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The assignment of signals was confirmed by ¹H, ¹³C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. Reactions were monitored by TLC on silica gel coated on alumina plate or glass plate using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were carried out under oxygen atmosphere.

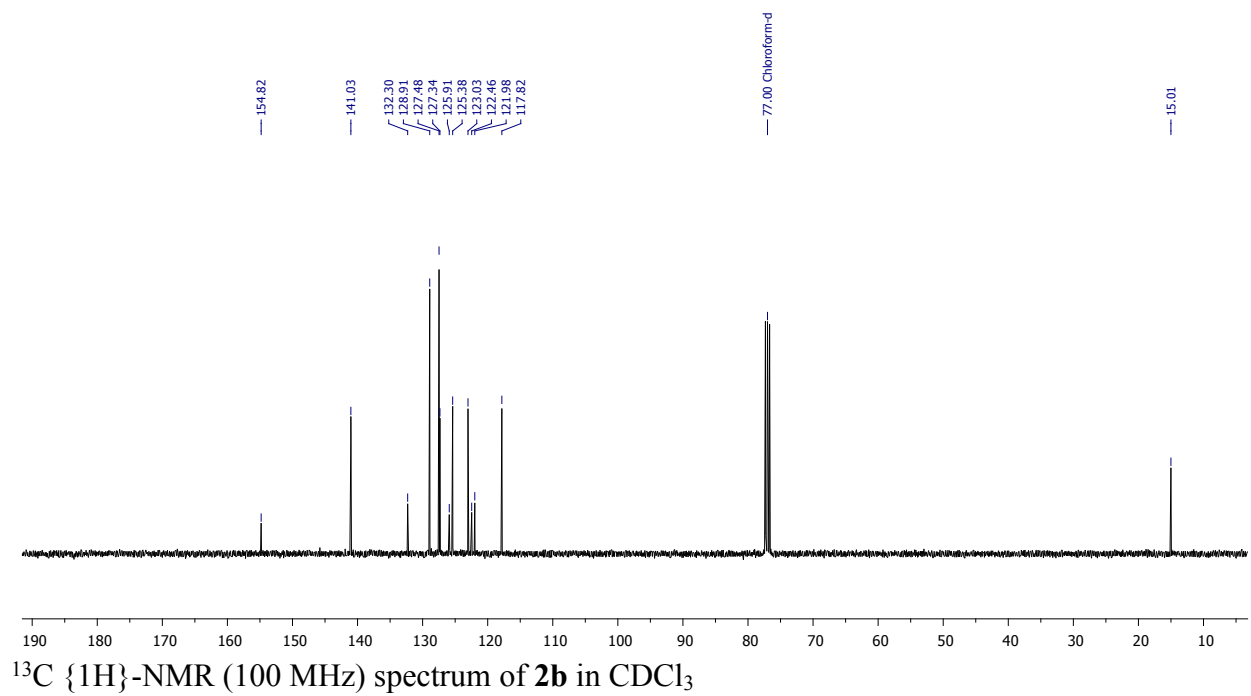
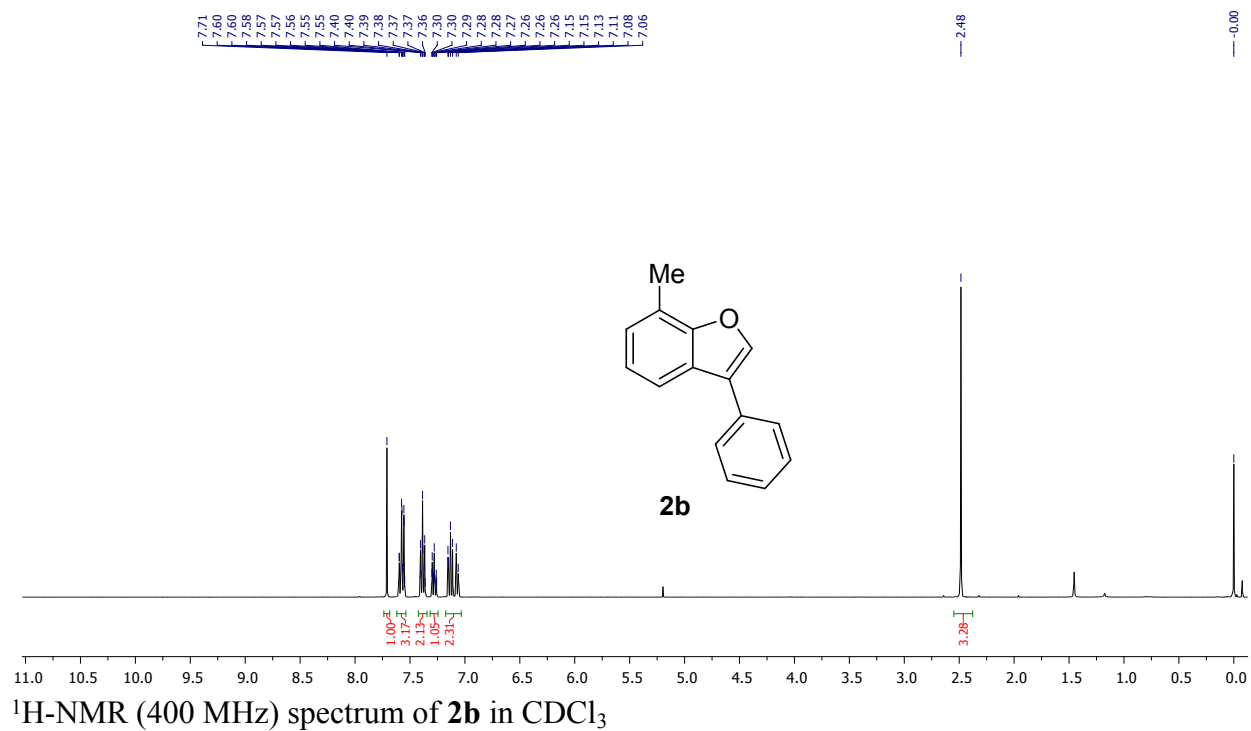
Materials: All solvents were distilled before using; petroleum ether with a boiling range of 60 to 80 °C, dichloromethane (DCM), ethyl acetate, dry DMA (boiling range 160 to 170 °C; with purity 99%) were purchased from Sigma Aldrich & locally available commercial sources were used. Acme's silica gel (100-200 mesh) was used for column chromatography.

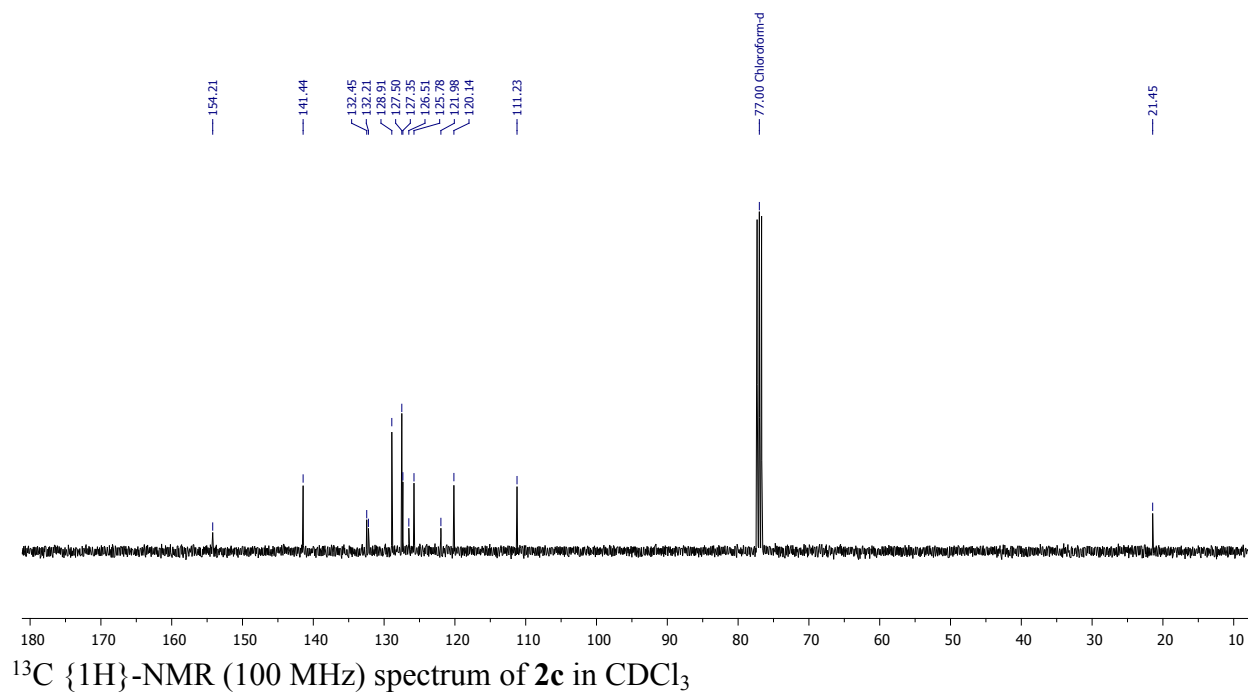
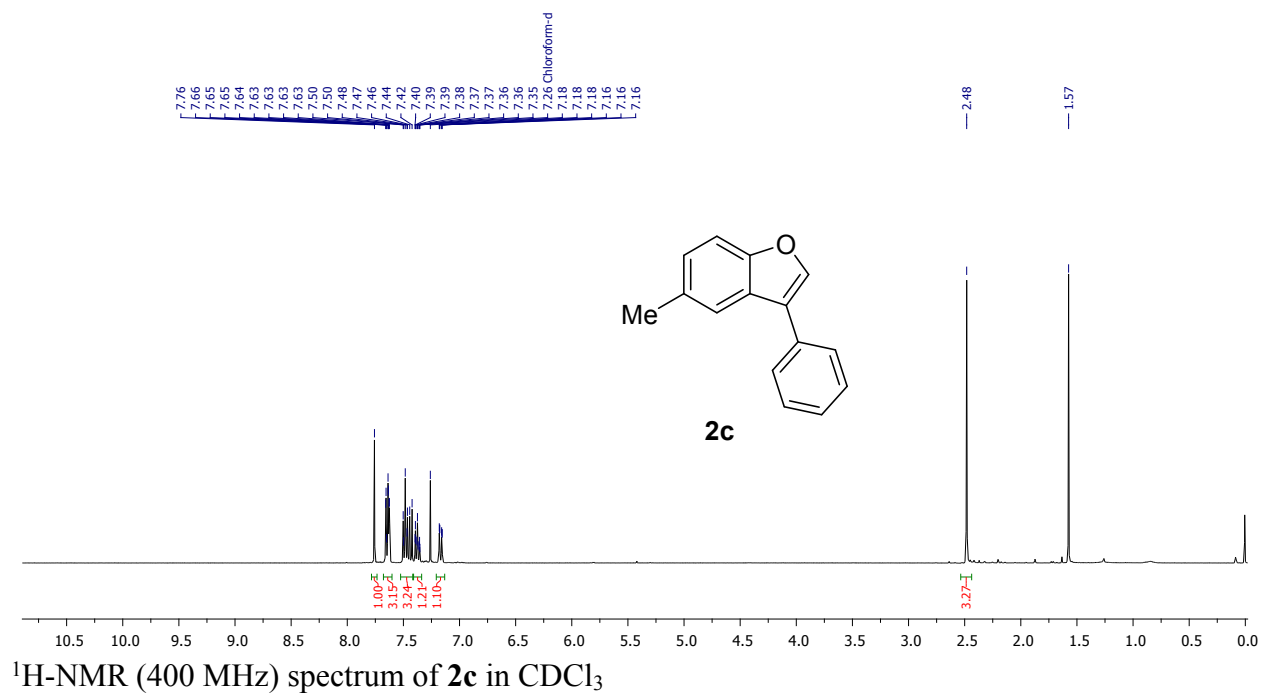
GP (General procedure for the synthesis of 3-aryl benzofurans): To an oven dry Schlenk tube was equipped with a magnetic stir bar were added Ni(acac)₂ (5.2 mg, 0.02 mmol), PPh₃ (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol), *ortho*-alkenyl phenols **1a-w** (79-110.0 mg, 0.4 mmol), and DMA (1 mL). Then a balloon filled with O₂ was attached to the schlenk tube. The reaction mixture was stirred at 140 °C for 36 h. Progress of the reaction was monitored by TLC. Reaction mixture was then cooled to room temperature and extracted by using ethyl acetate (3 × 20 mL). The organic layers were washed with saturated NH₄Cl solution, dried by Na₂SO₄ and then filtered. Evaporation of the solvent(s) under reduced pressure and refinement of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), gave the 3-aryl benzofurans (68–88%) as semi-solid or liquid.

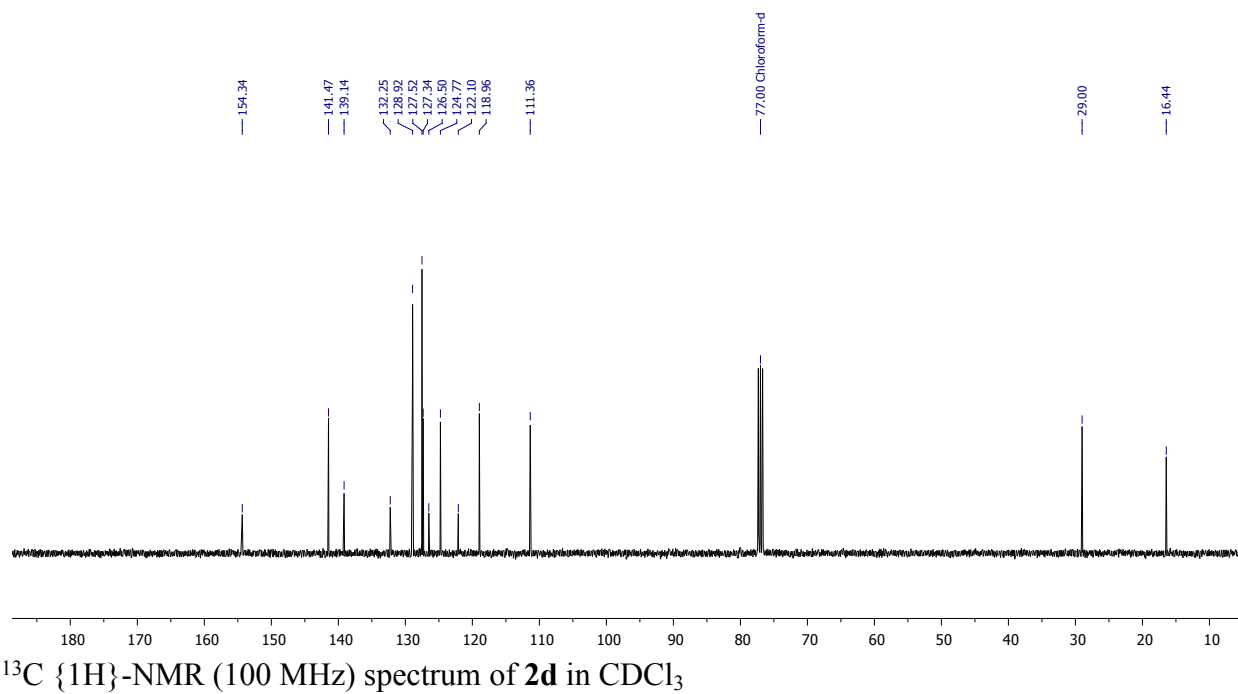
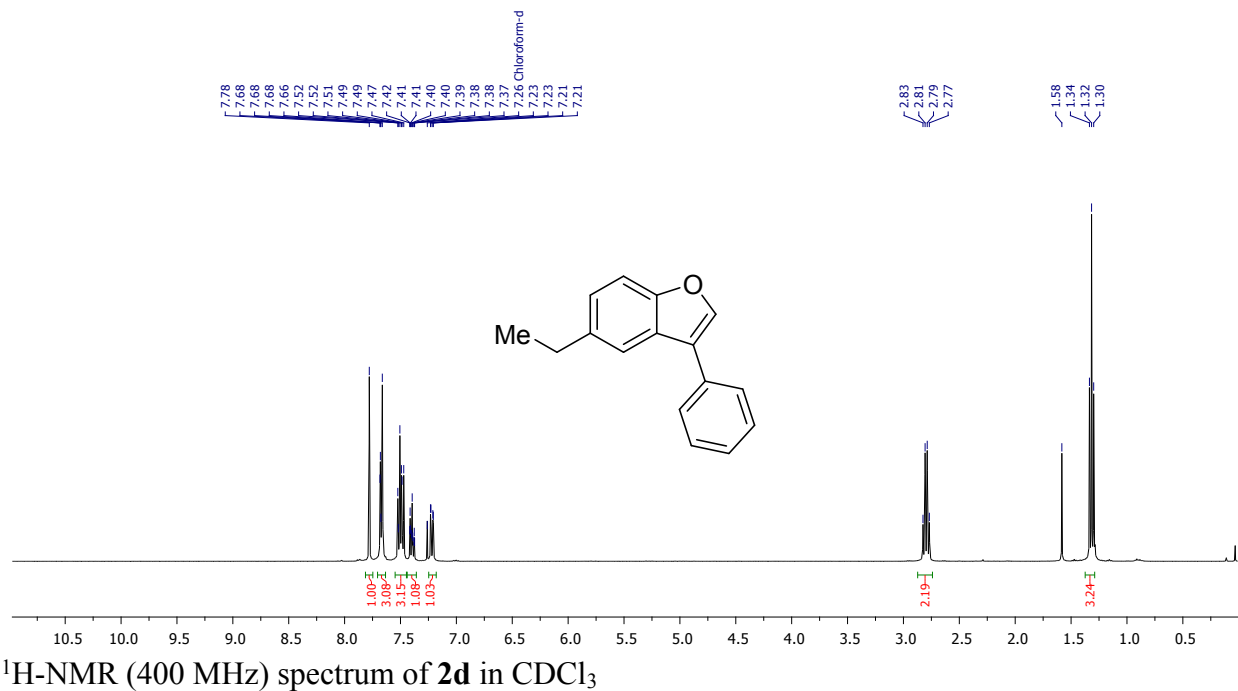
Table S1: The following compounds data are reported in the literature¹

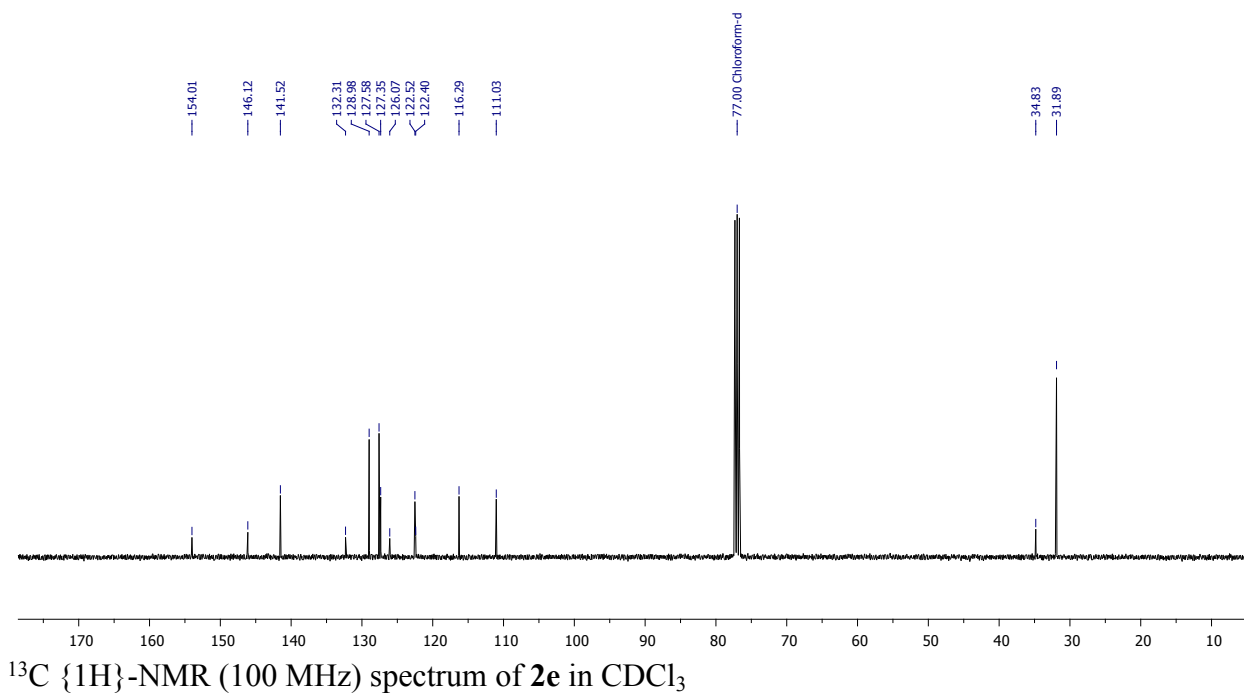
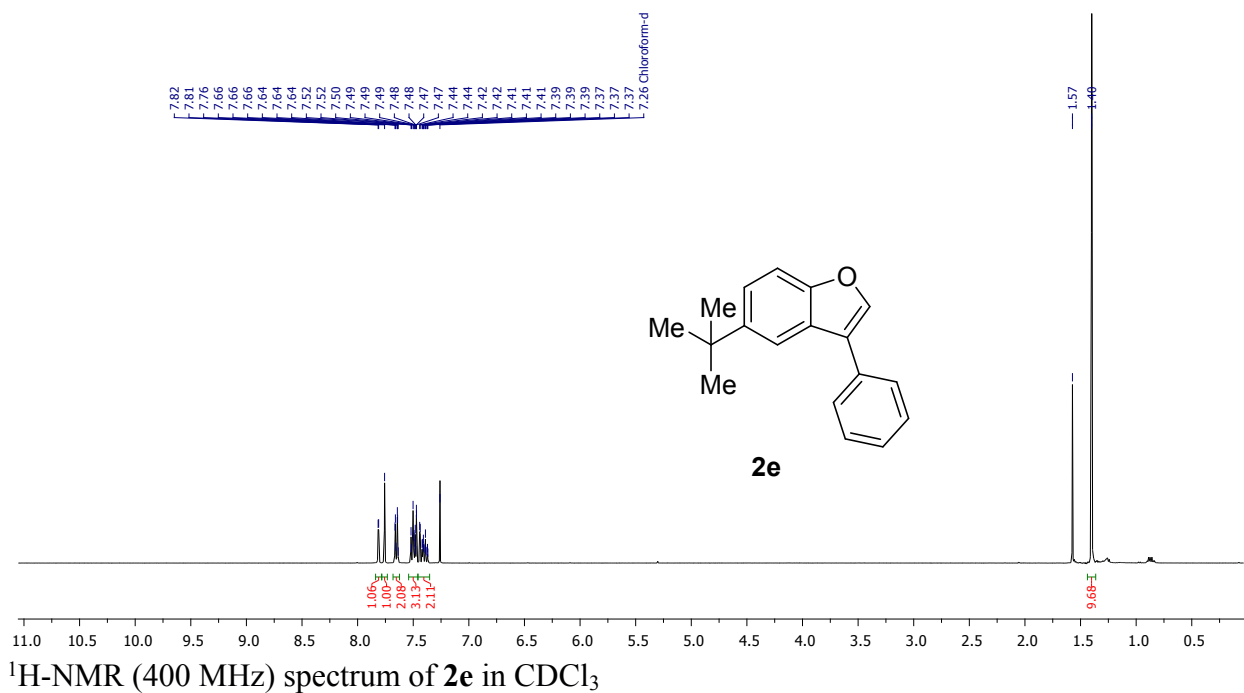


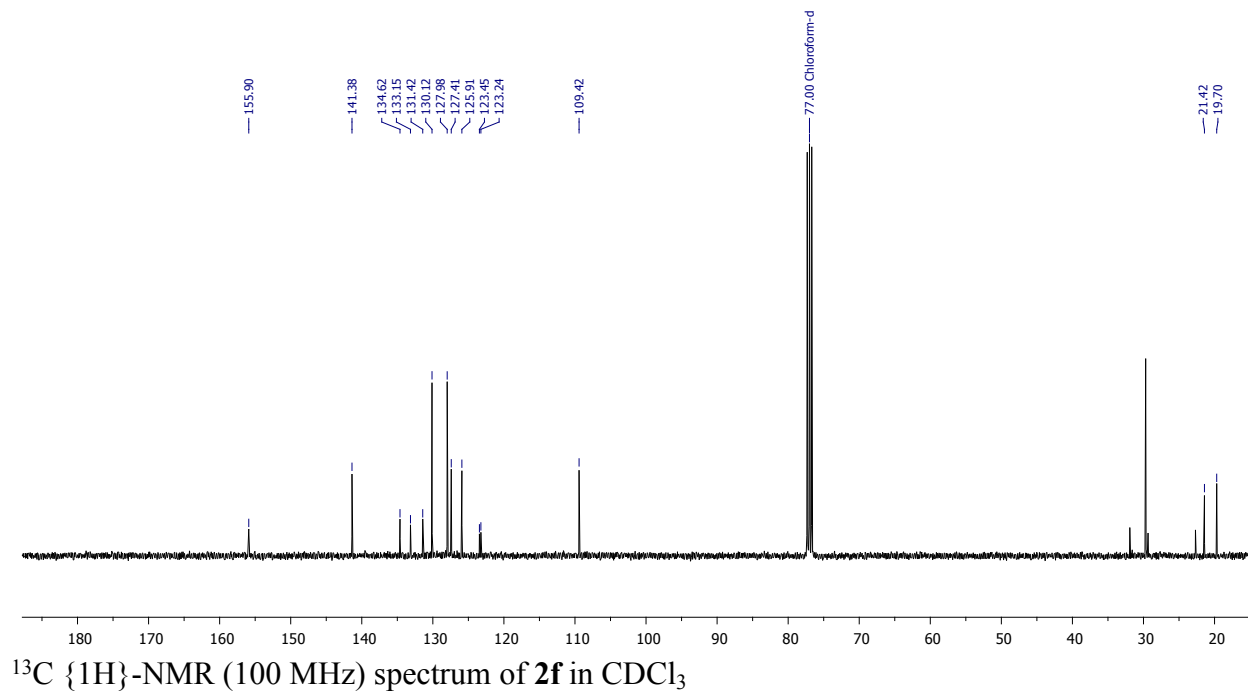
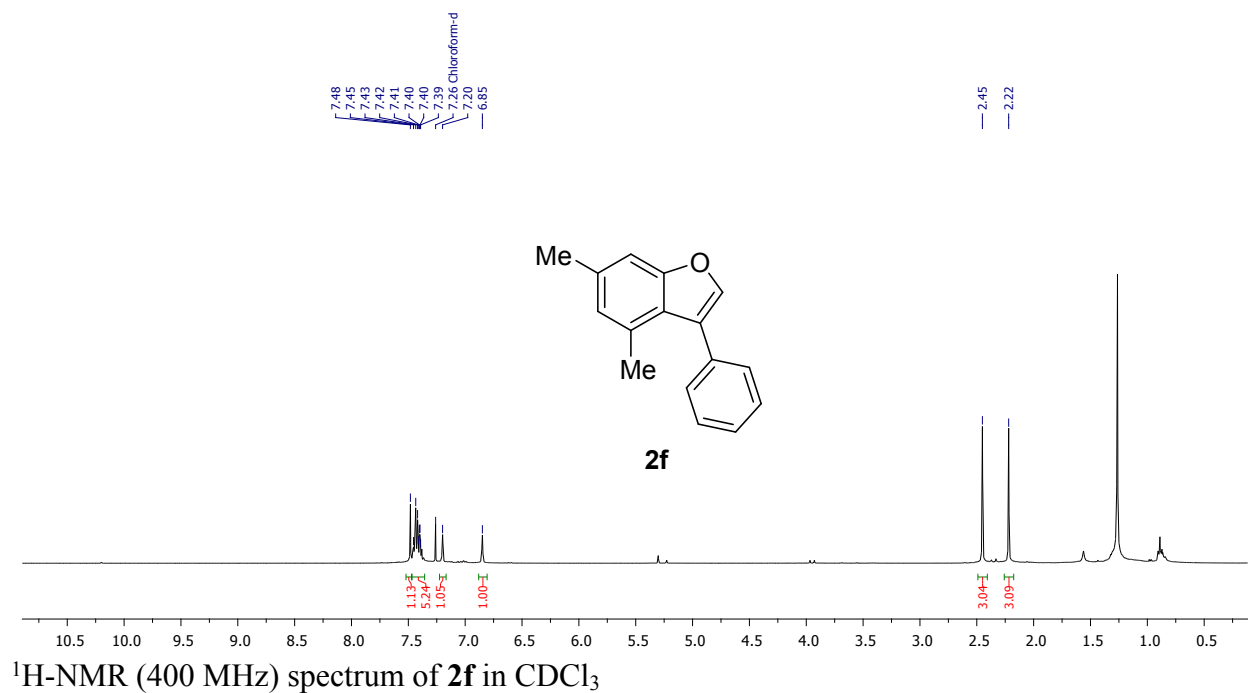
- 1) (a) D. Yang, Y. Zhu, N. Yang, Q. Jiang and R. Liua, *Adv. Synth. Catal.* 2016, **358**, 1731; (b) D. Kundu, M. D. Samim, A. Majee and A. Hajra, *Chem. Asian J.* 2011, **6**, 406; (c) J. Ghorai, A. C. S. Reddy, P. Anbarasan, *Chem. Eur. J.* 2016, **22**, 16042; (d) Z. Wang, J. Gu, H. Jing and Y. Liang, *Synth. Commun.*, 2009, **39**, 4079.

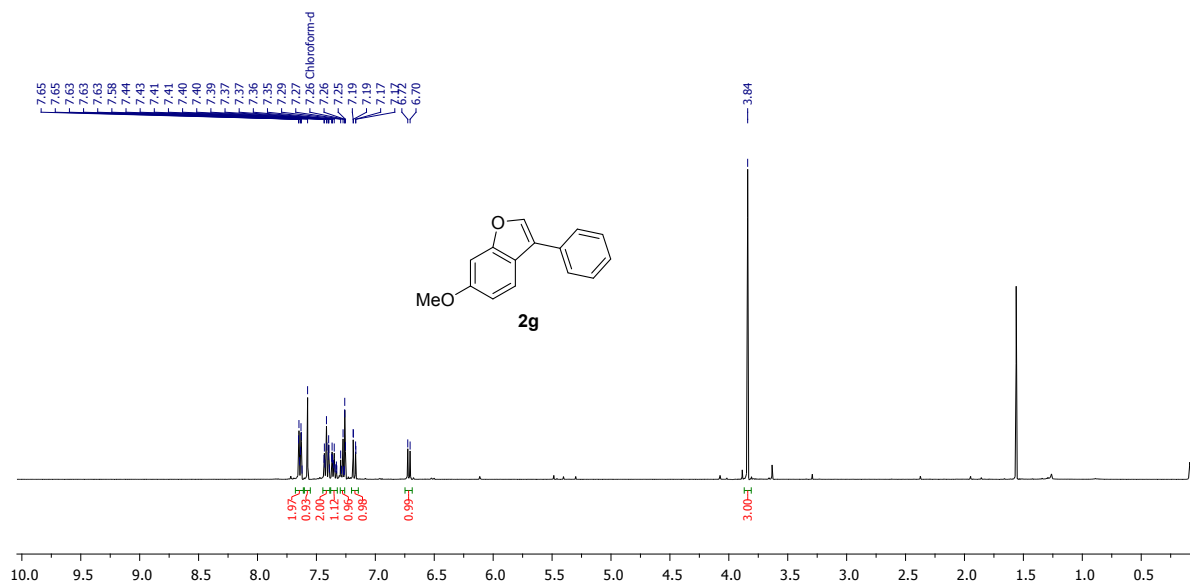




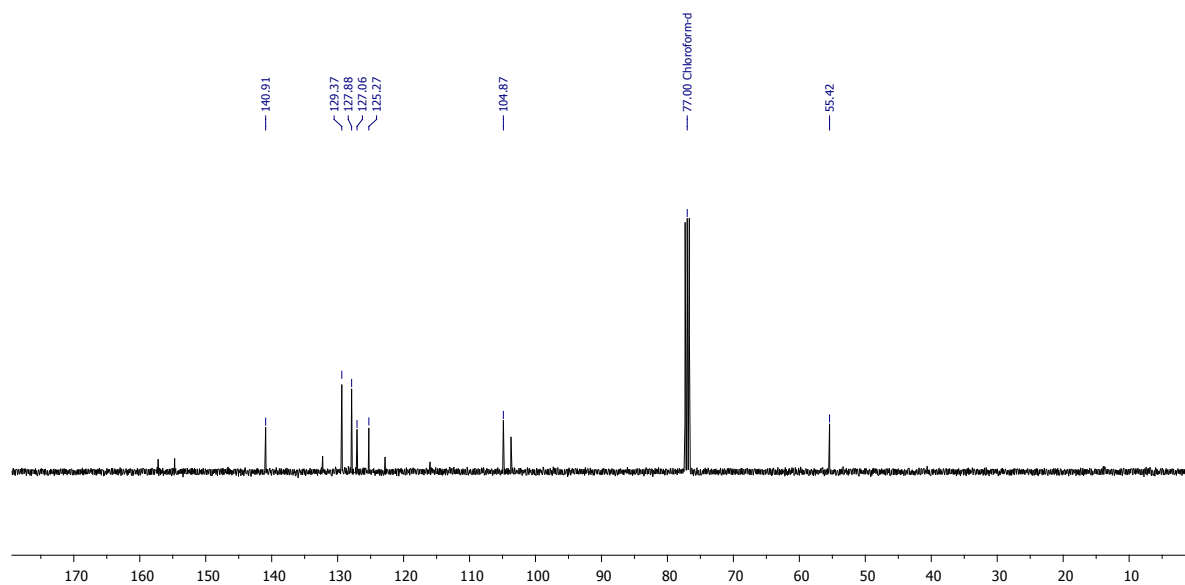




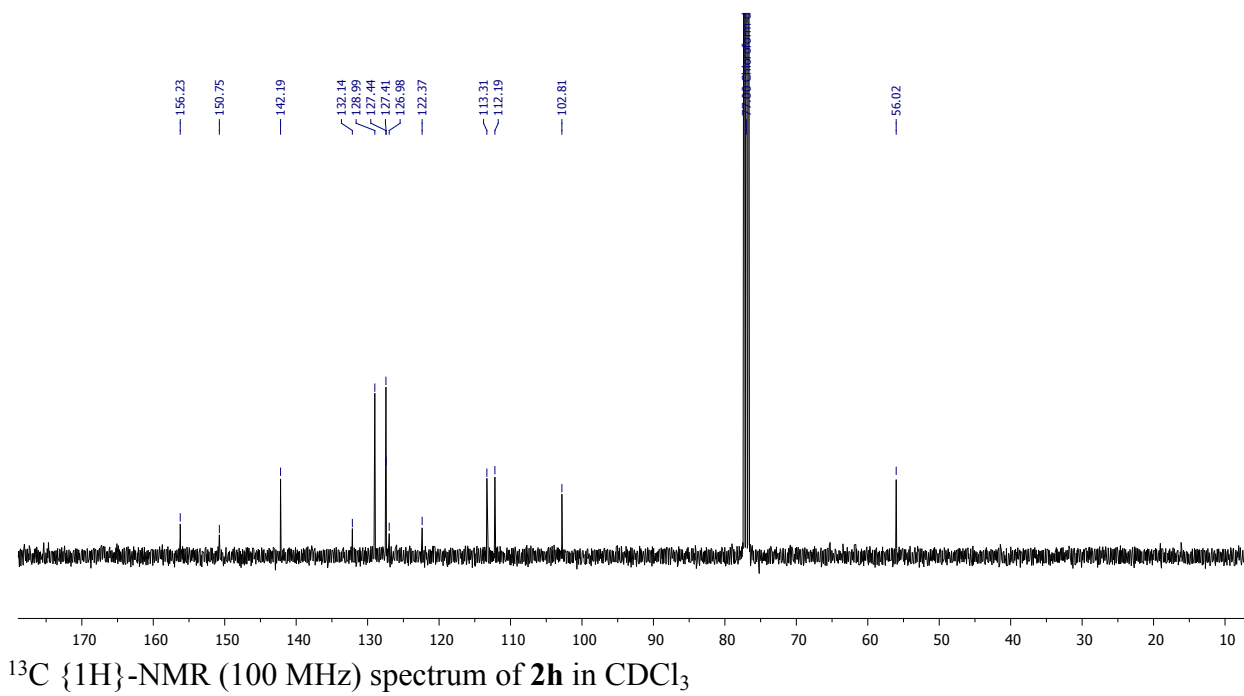
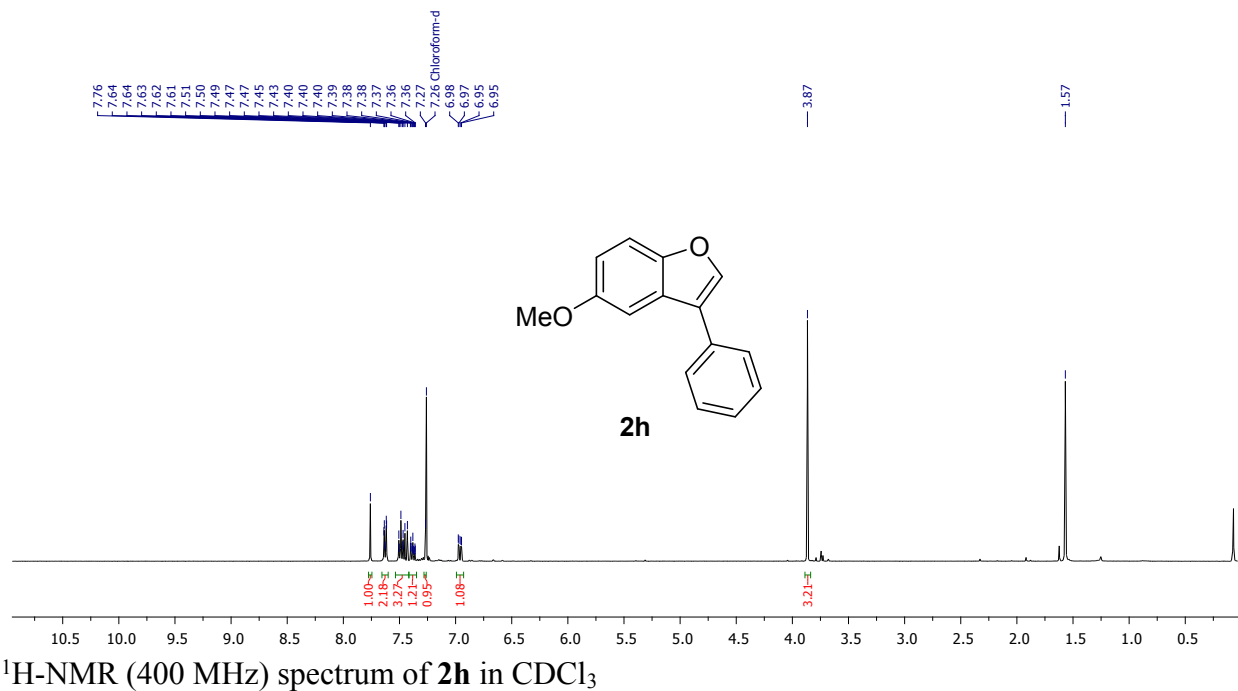


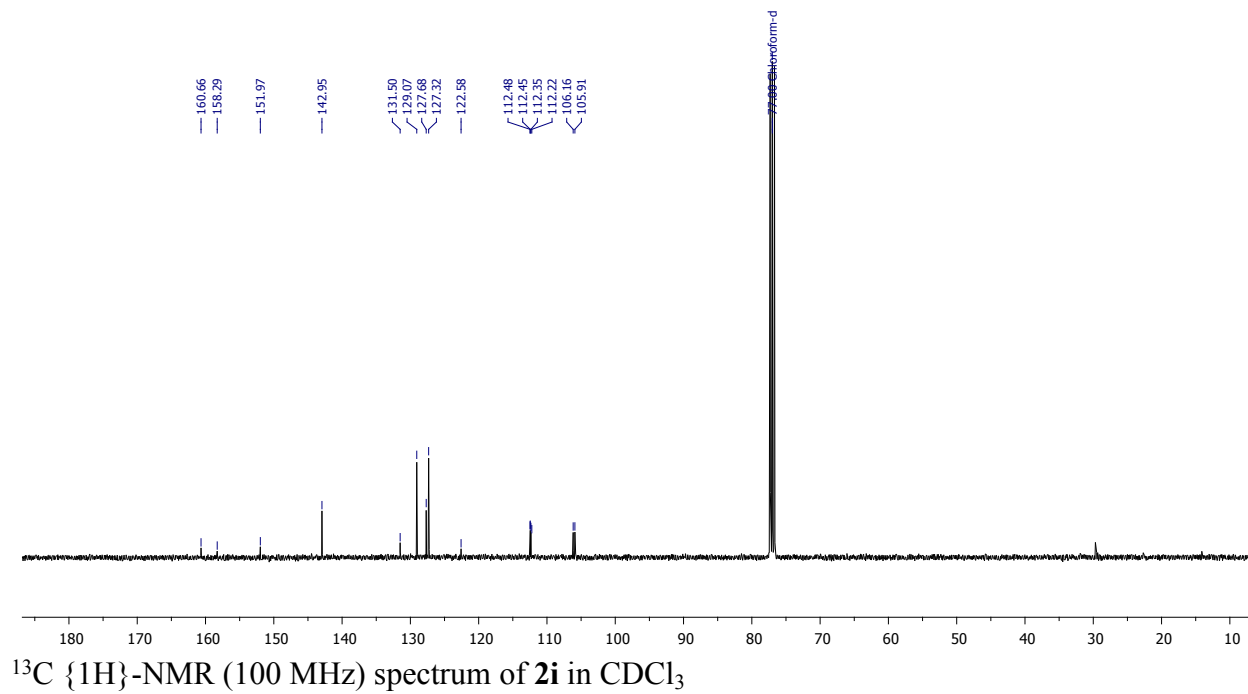
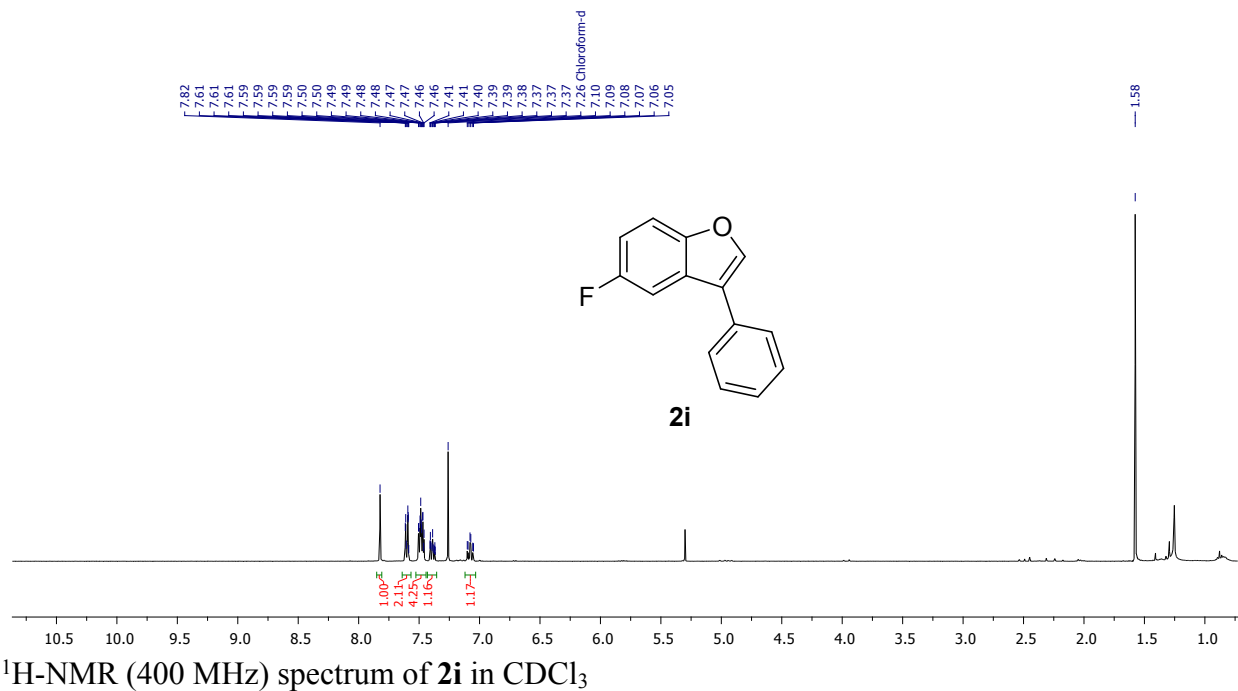


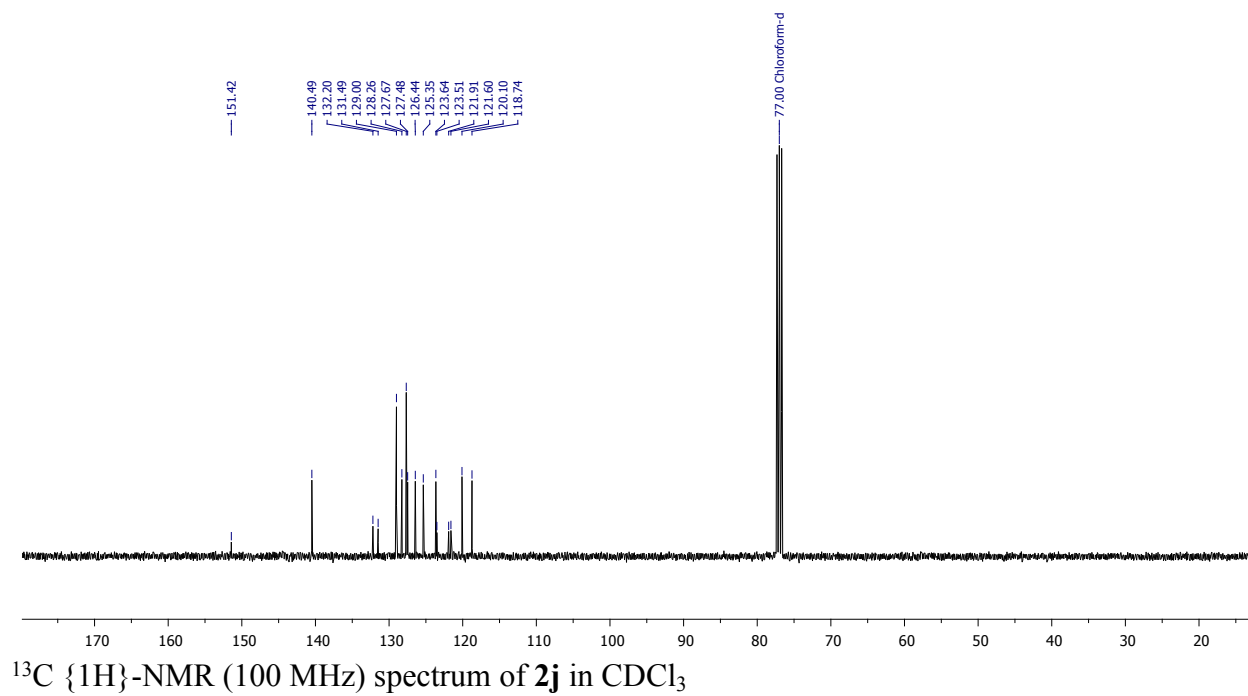
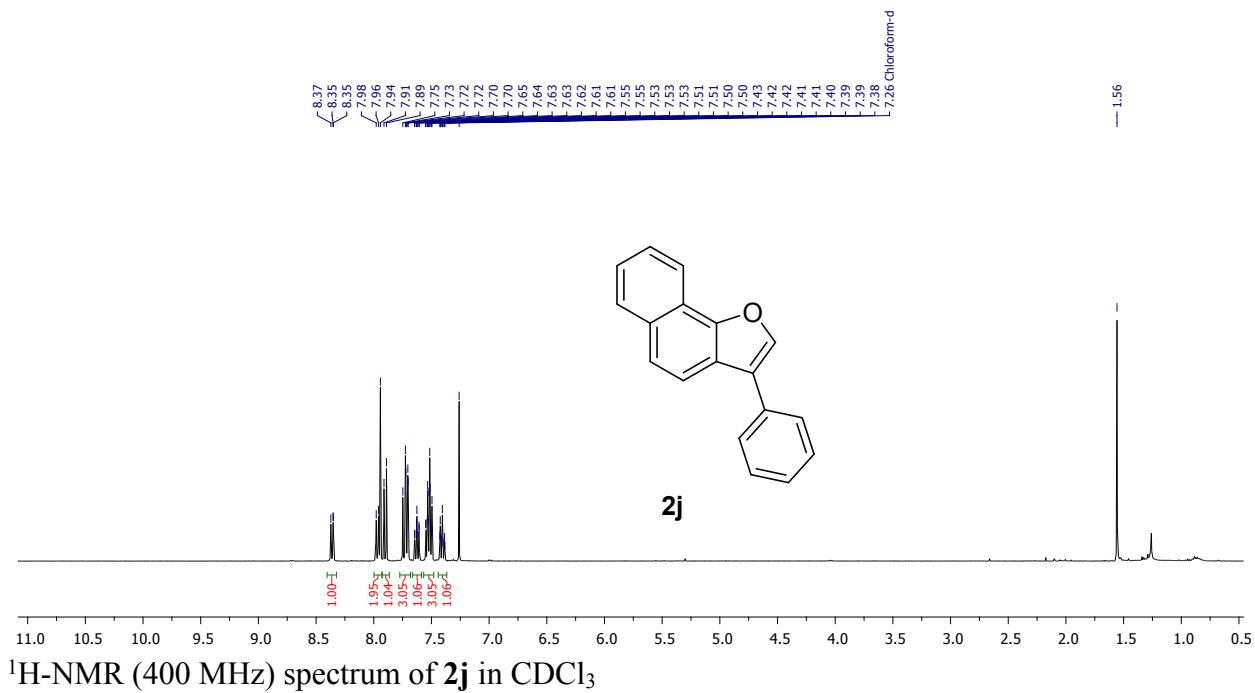
¹H-NMR (400 MHz) spectrum of **2g** in CDCl₃

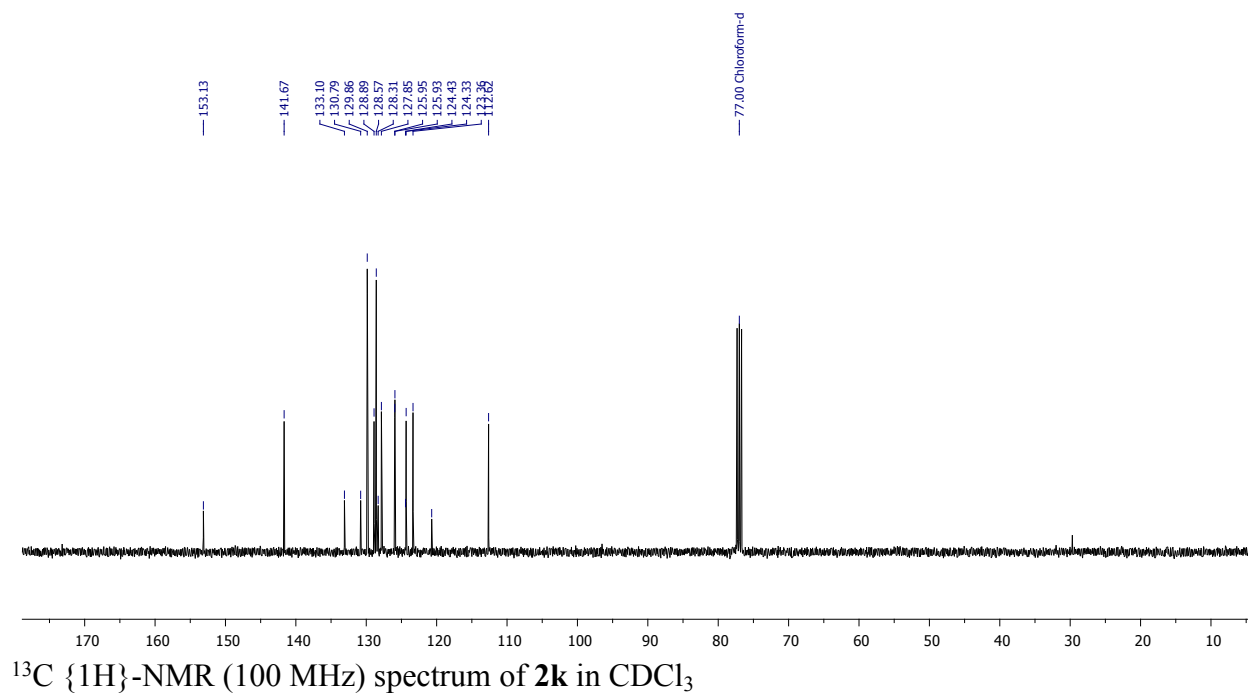
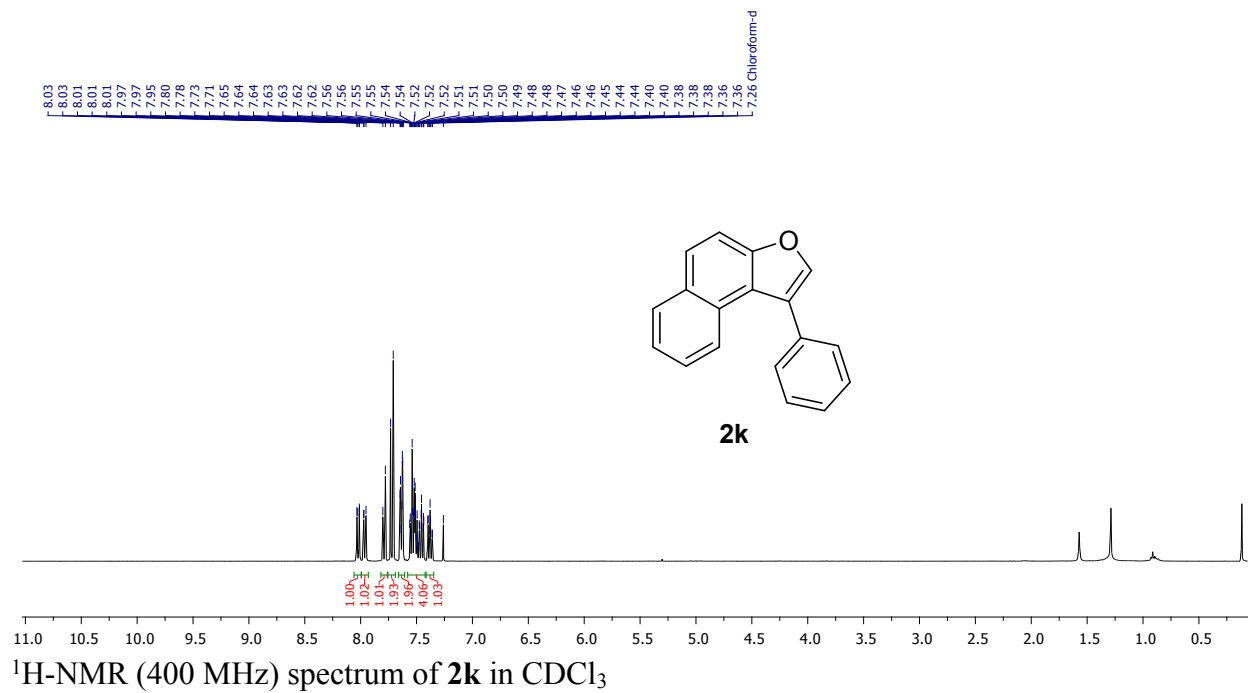


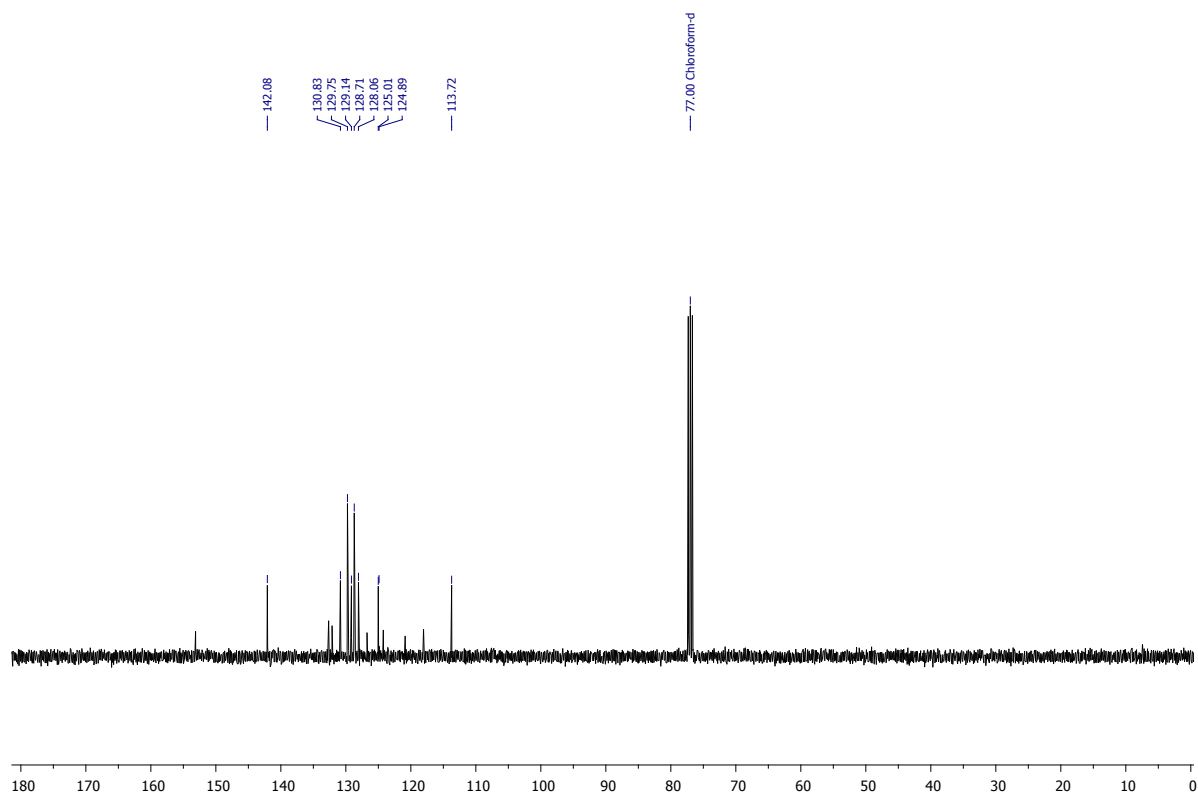
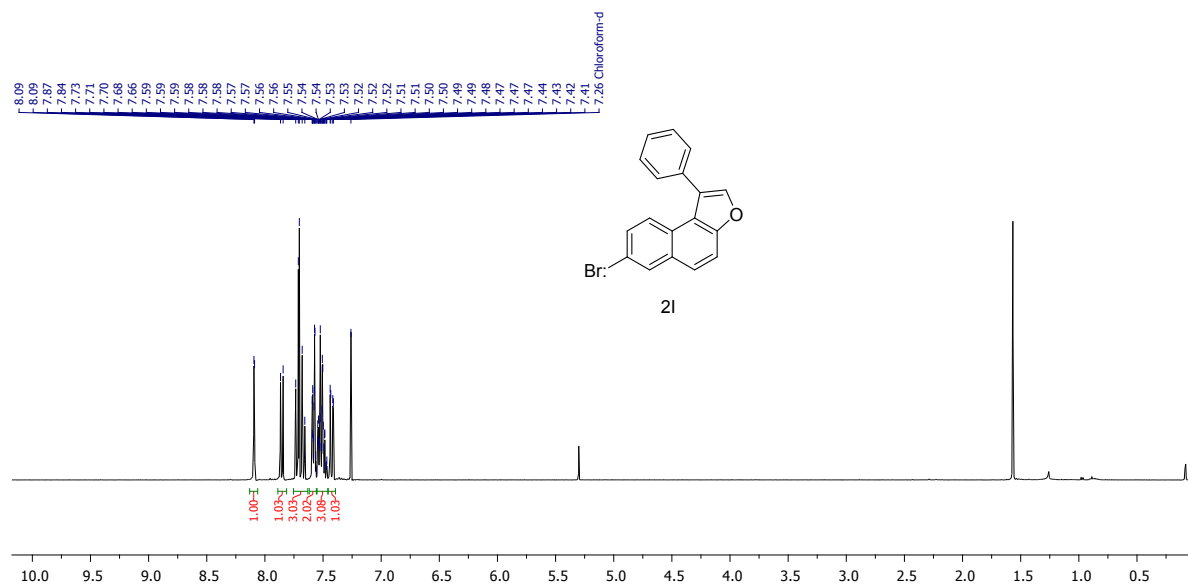
¹³C {¹H}-NMR (100 MHz) spectrum of **2g** in CDCl₃

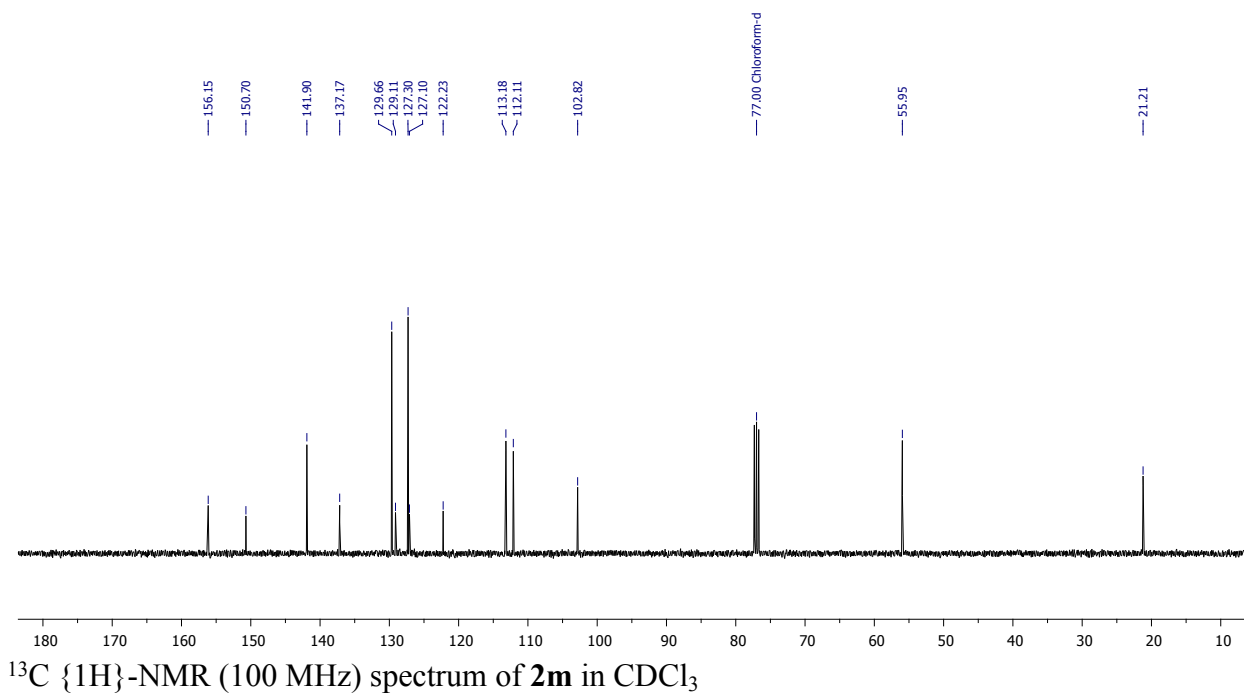
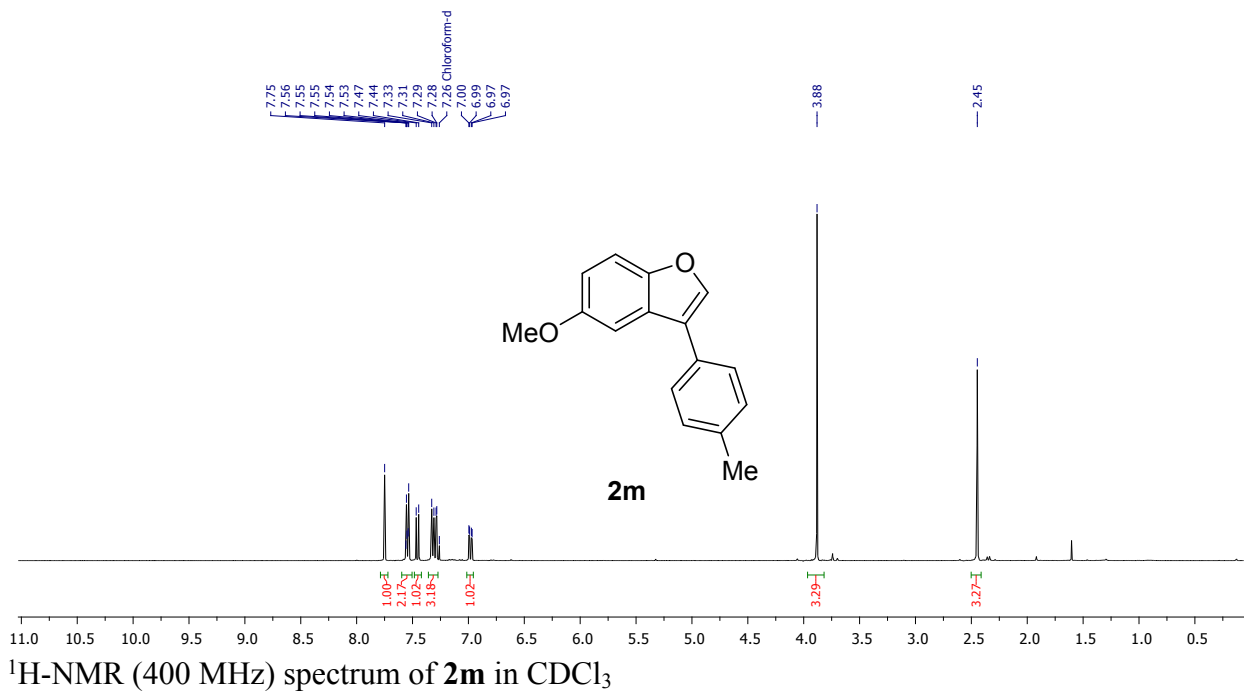


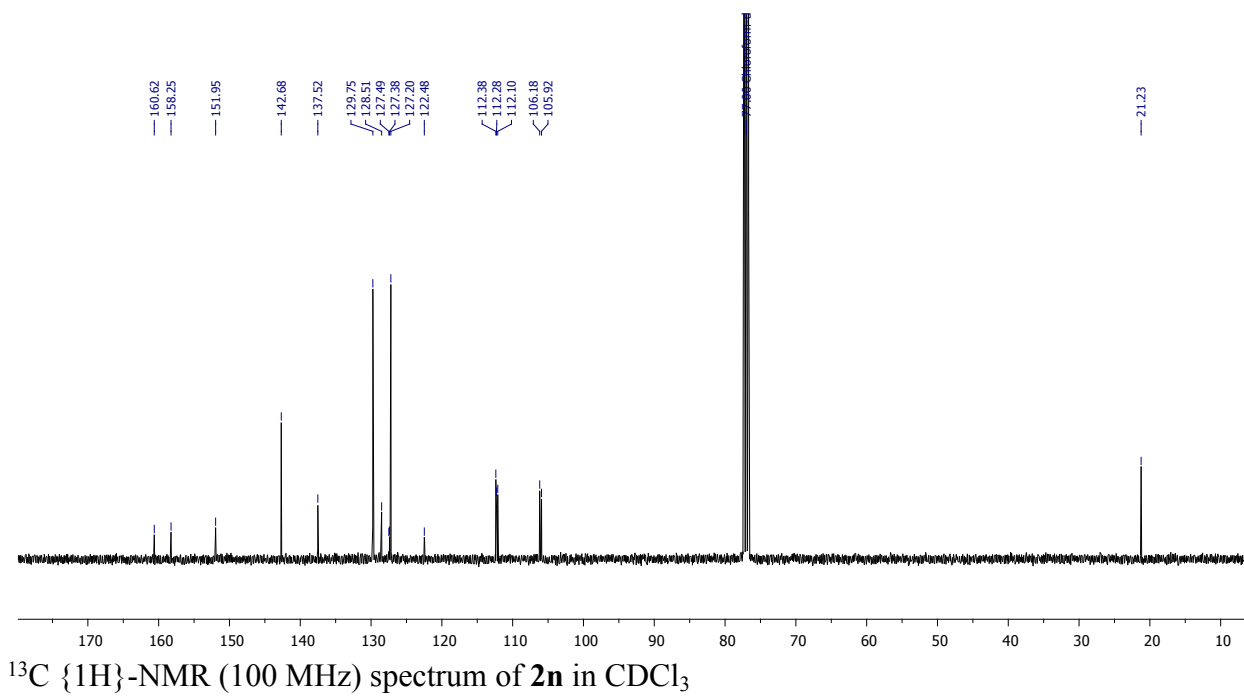
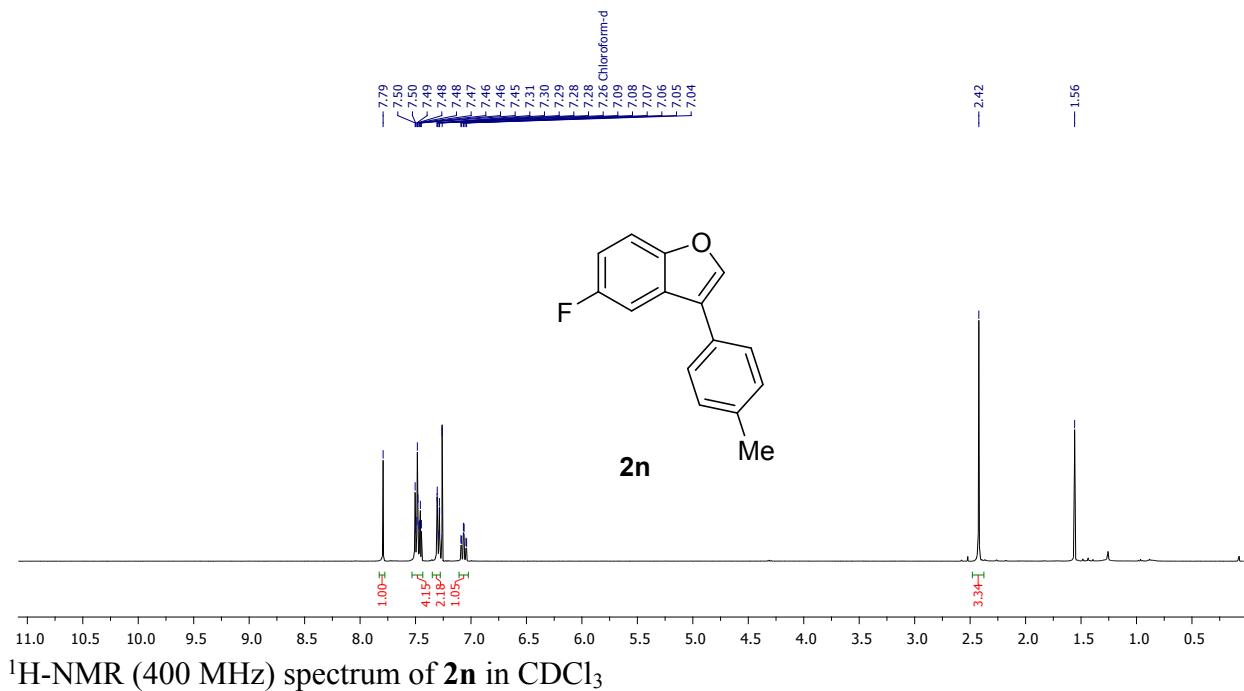


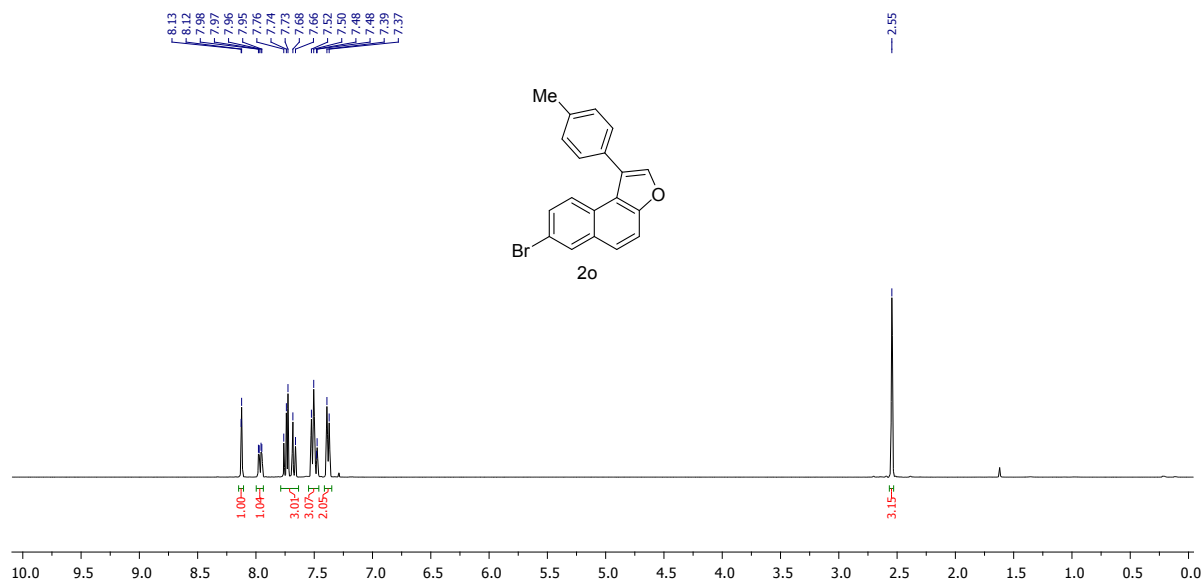




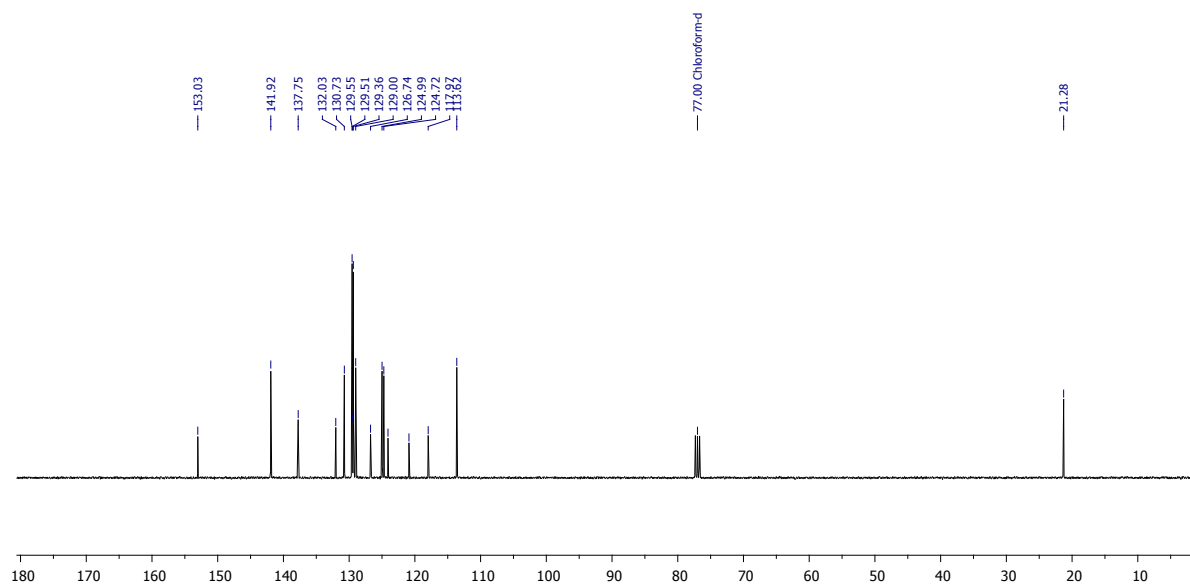




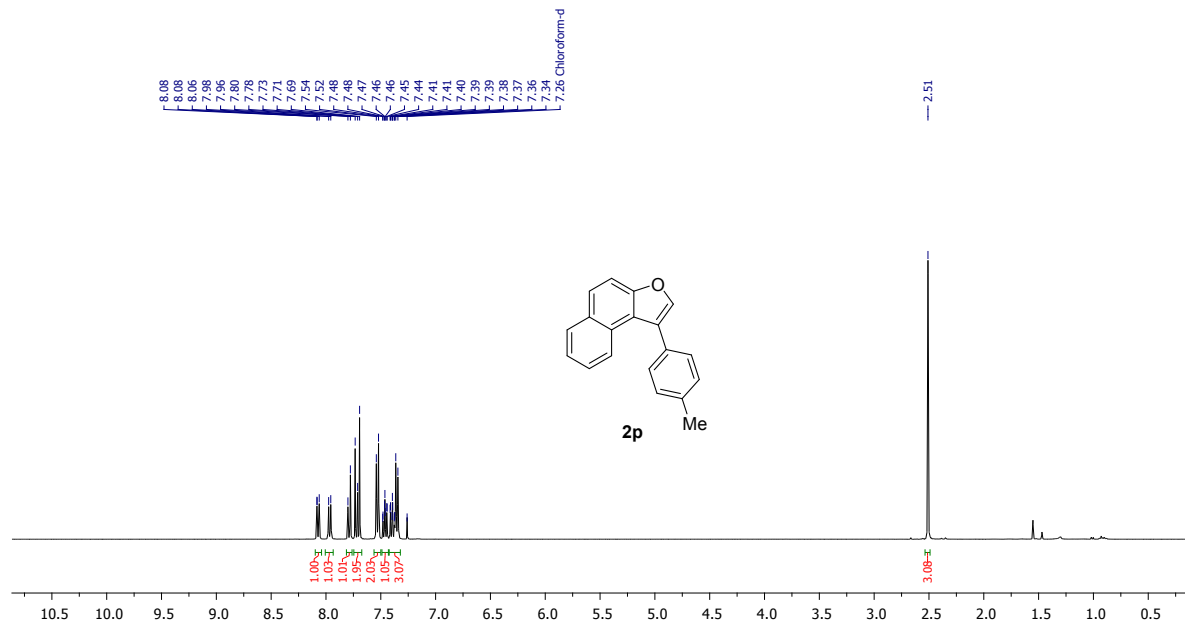




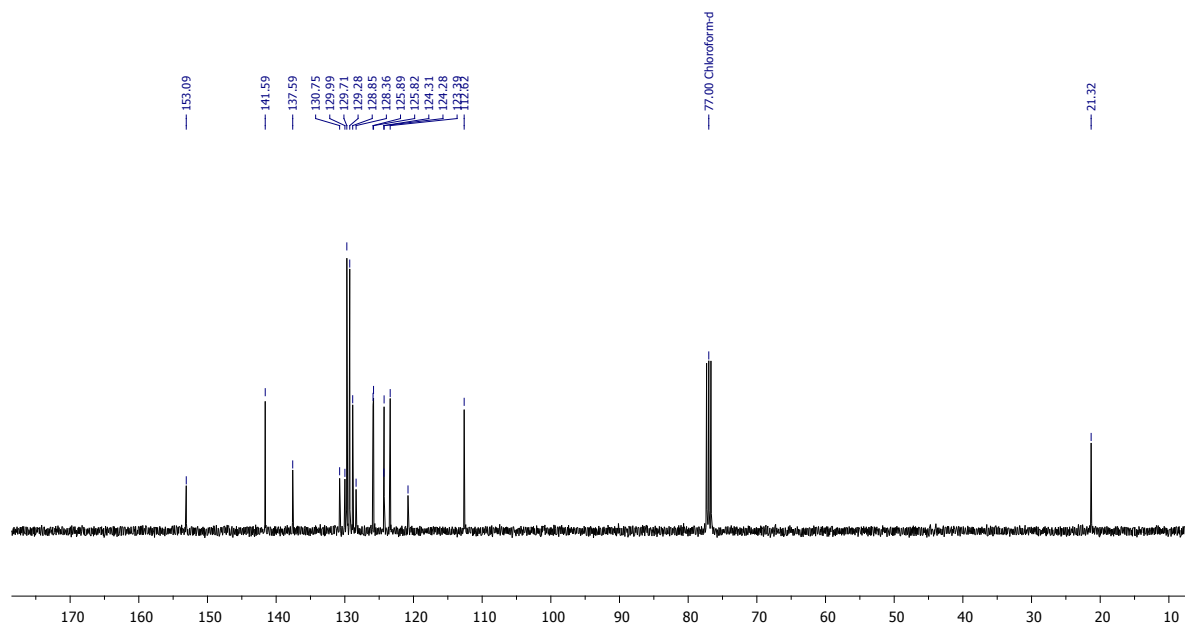
$^1\text{H-NMR}$ (400 MHz) spectrum of **2o** in CDCl_3



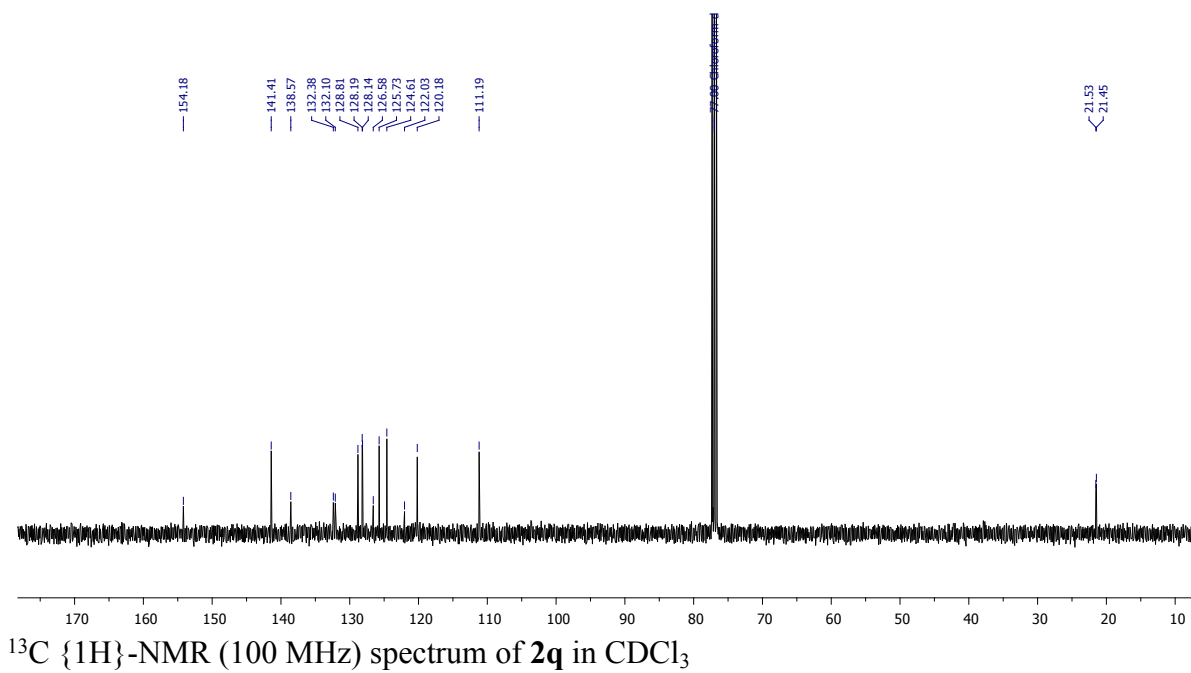
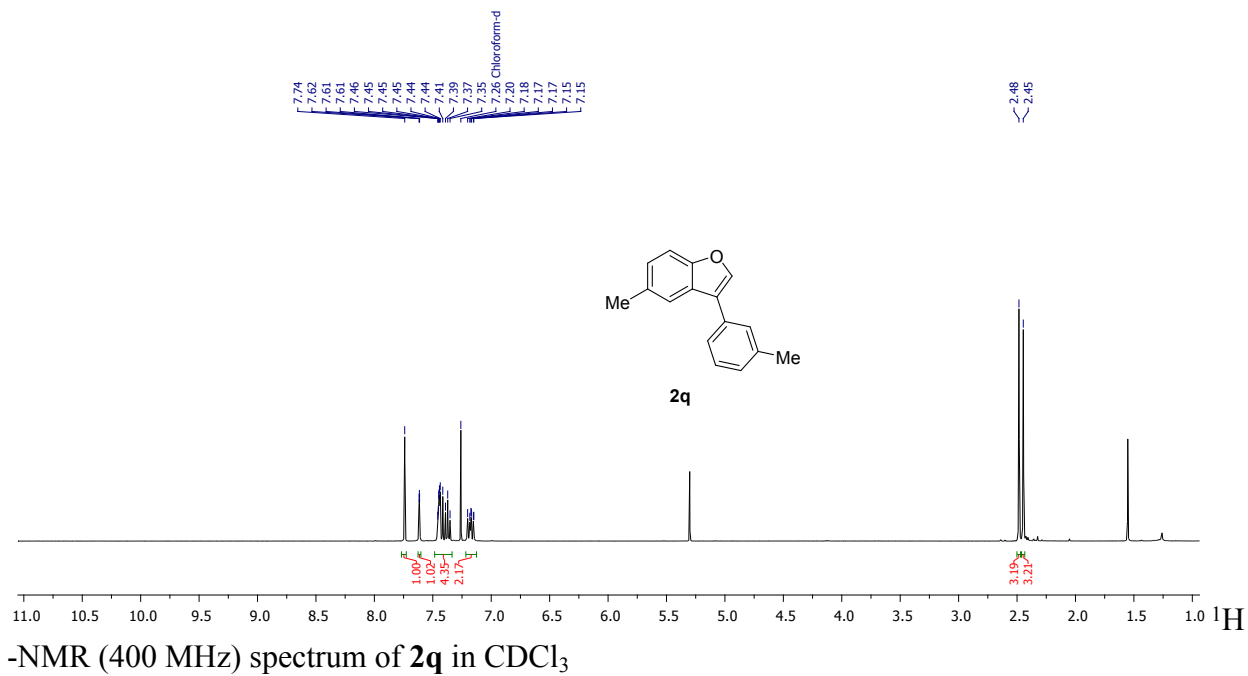
^{13}C $\{^1\text{H}\}$ -NMR (100 MHz) spectrum of **2o** in CDCl_3

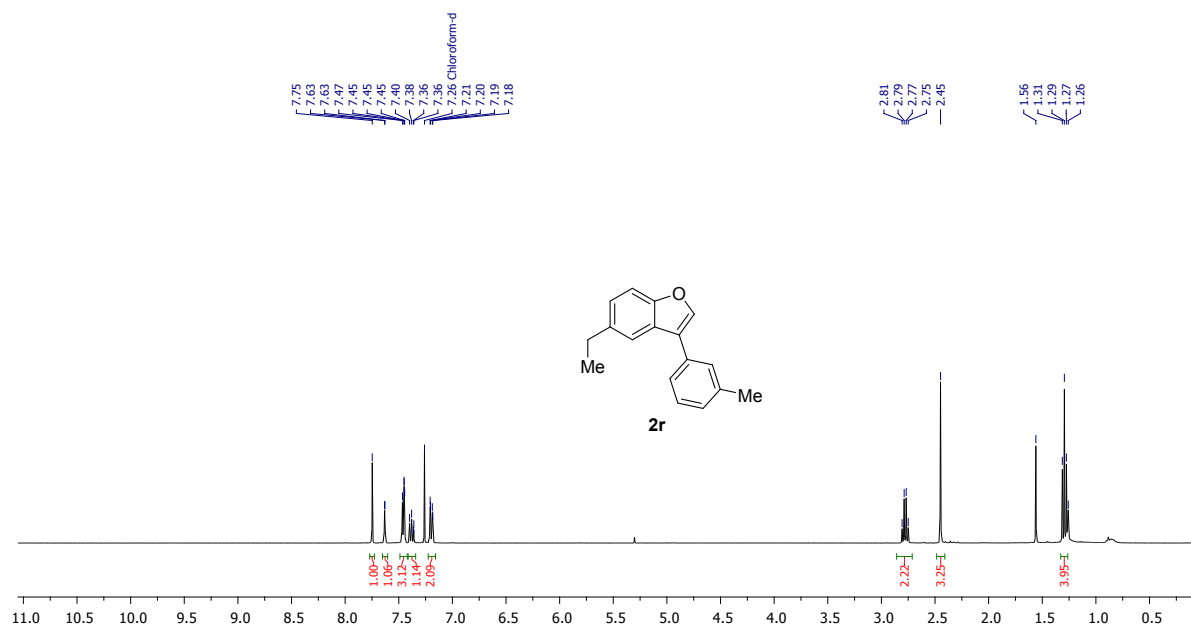


¹H-NMR (400 MHz) spectrum of **2p** in CDCl₃

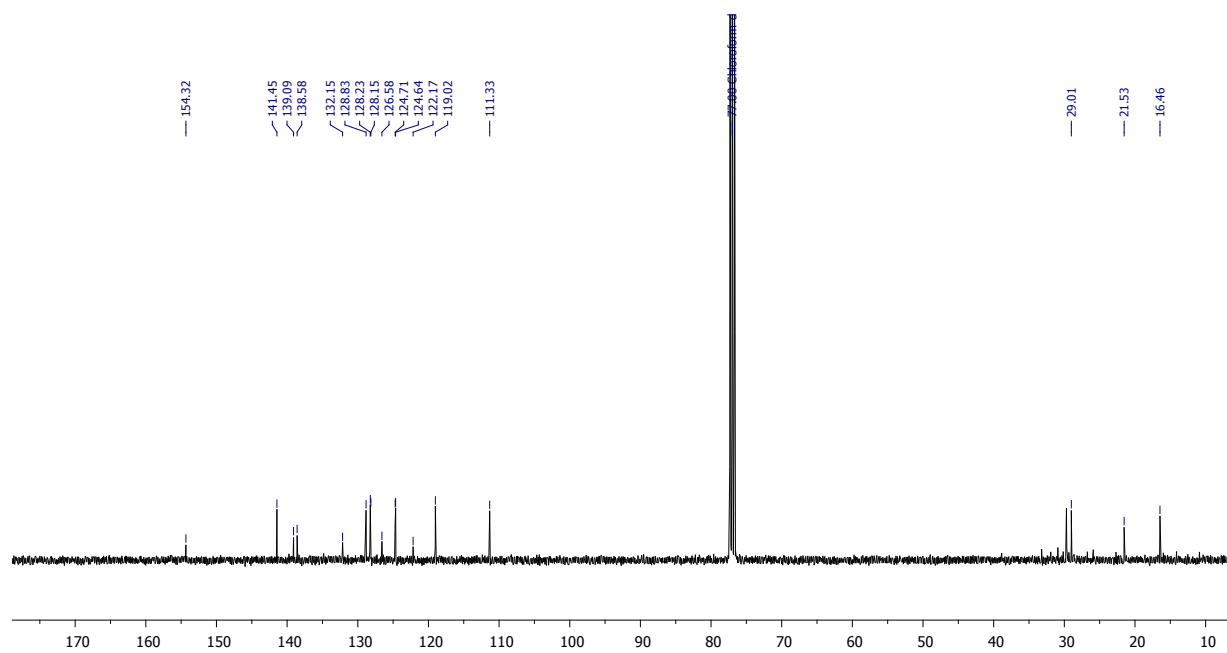


¹³C {¹H}-NMR (100 MHz) spectrum of **2p** in CDCl₃

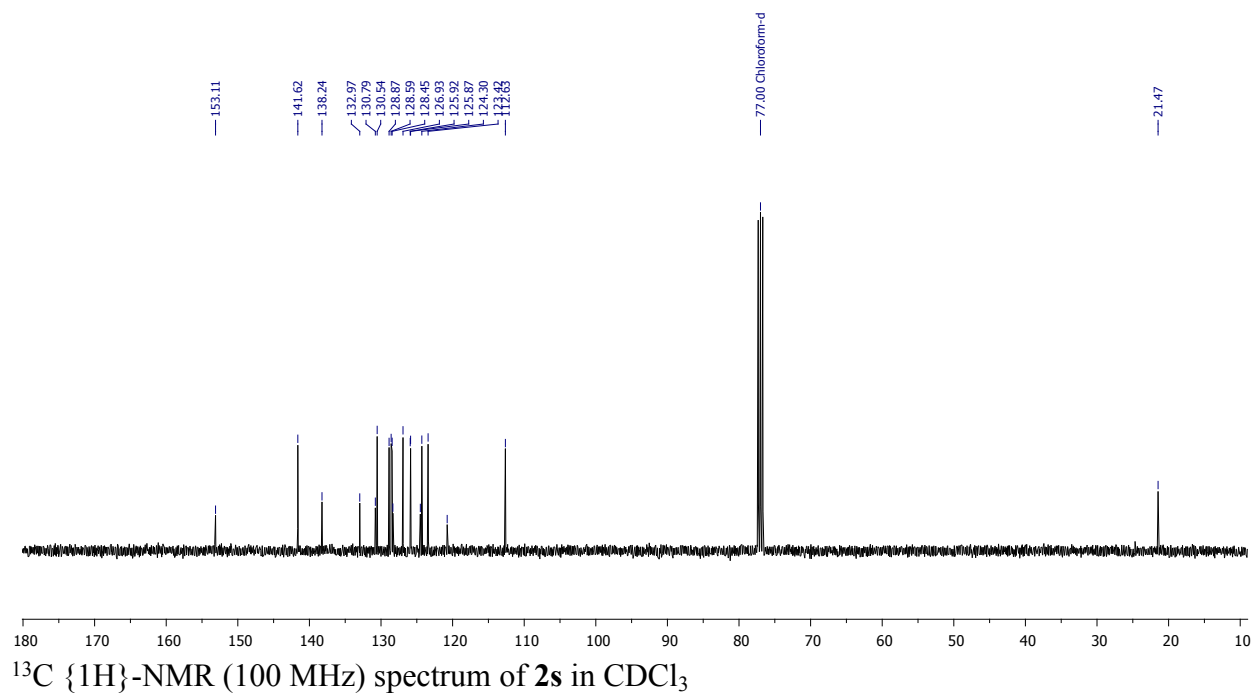
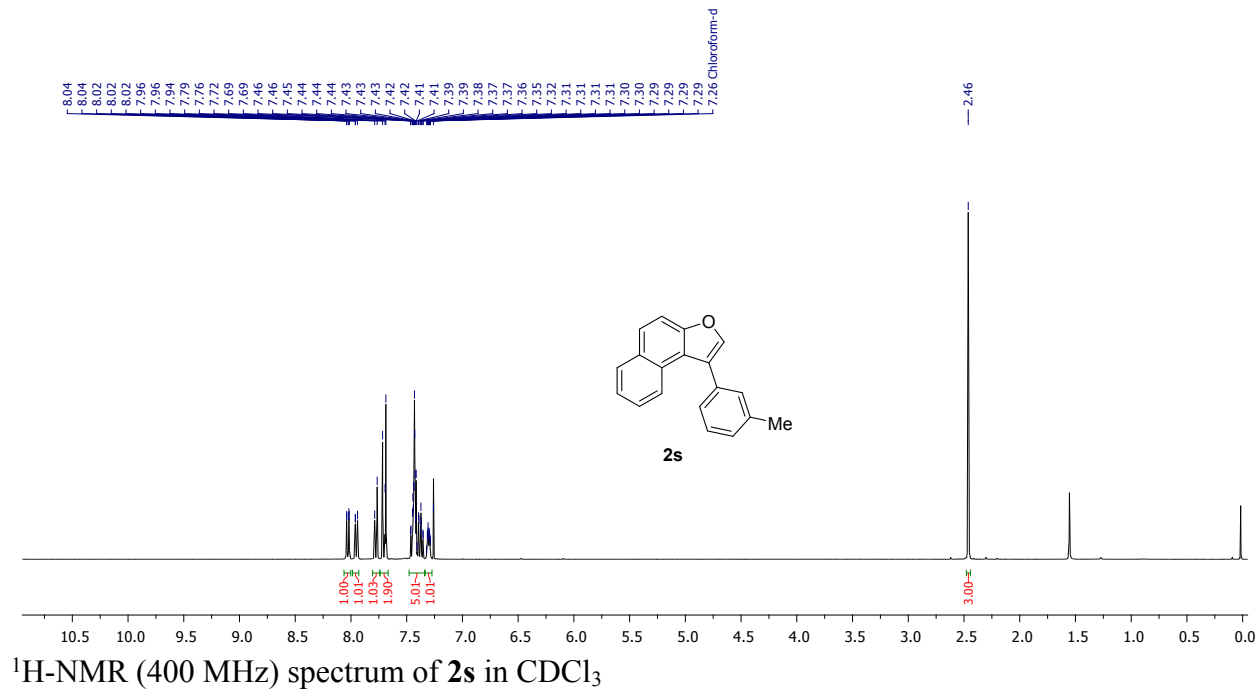


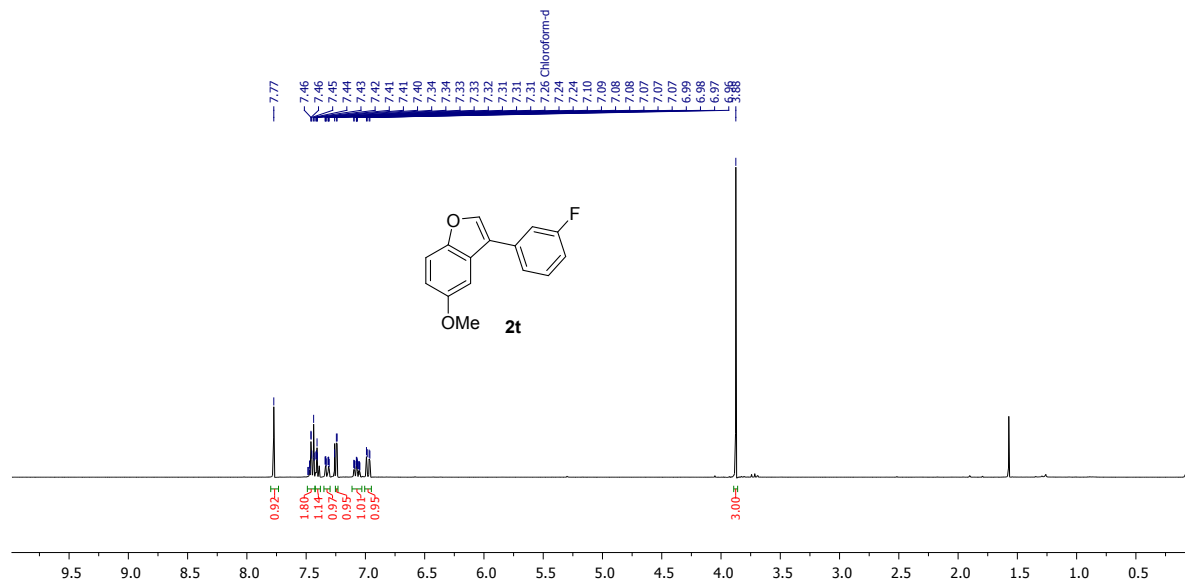


¹H-NMR (400 MHz) spectrum of **2r** in CDCl₃

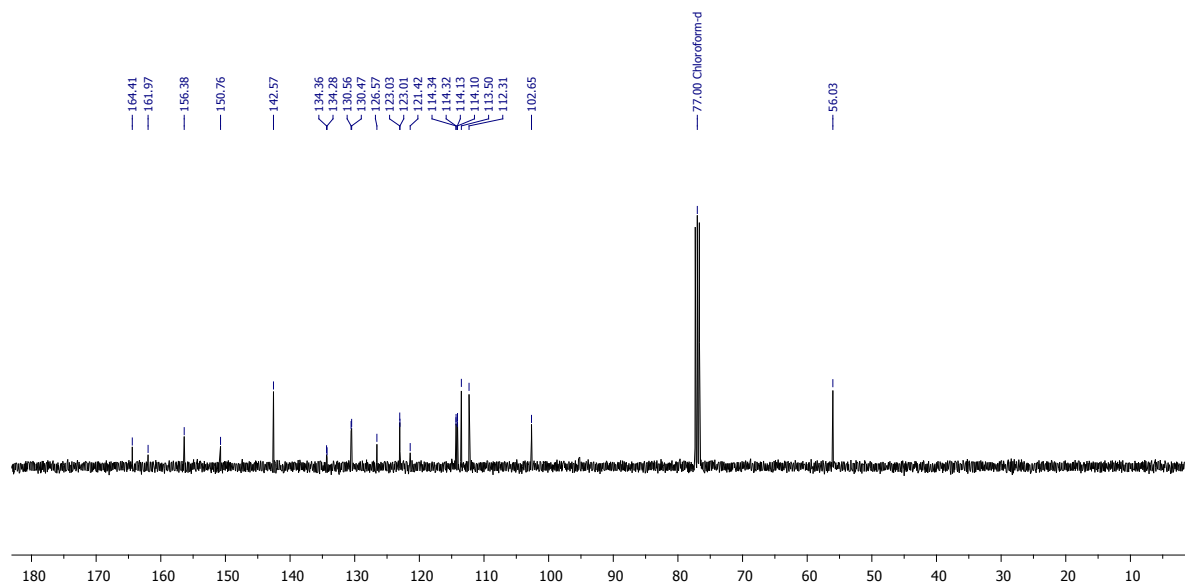


¹³C {¹H}-NMR (100 MHz) spectrum of **2r** in CDCl₃

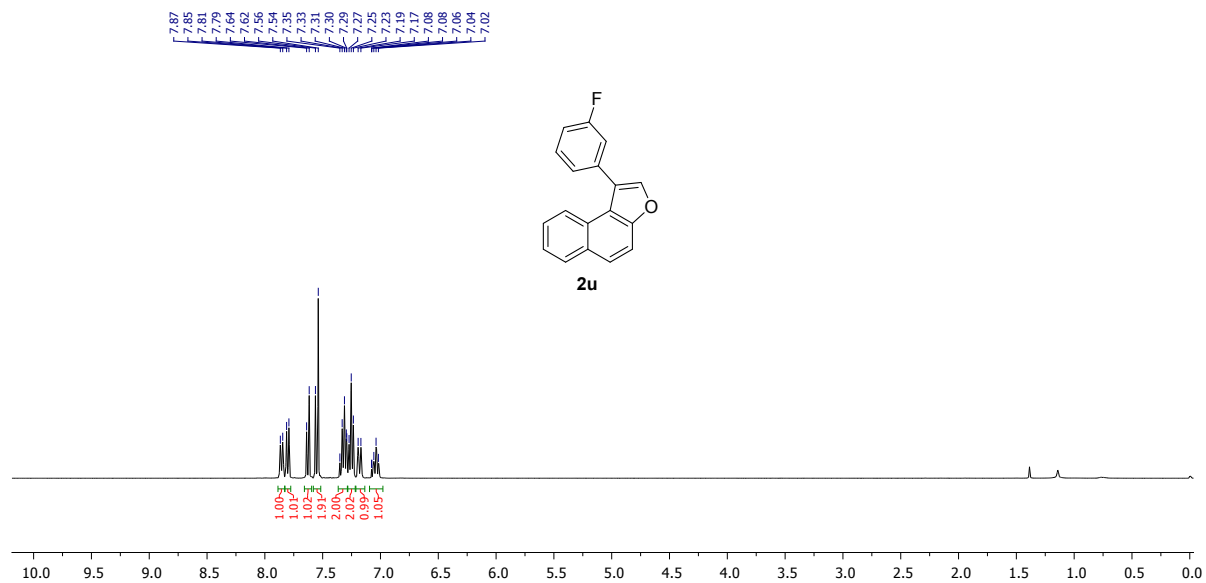




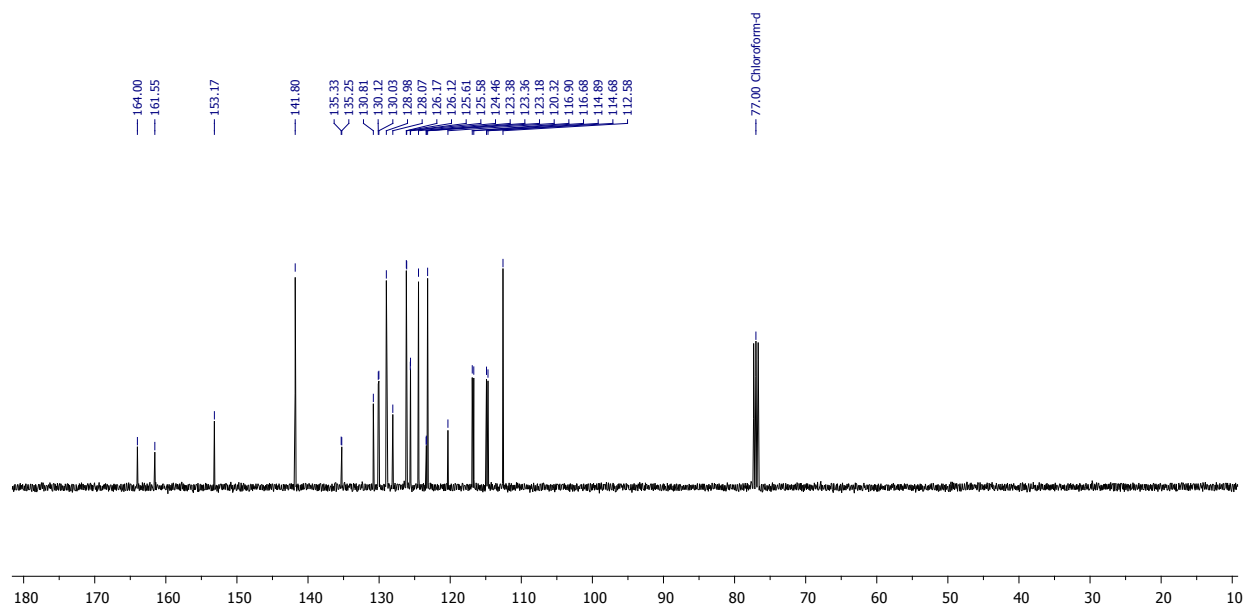
¹H-NMR (400 MHz) spectrum of **2t** in CDCl₃



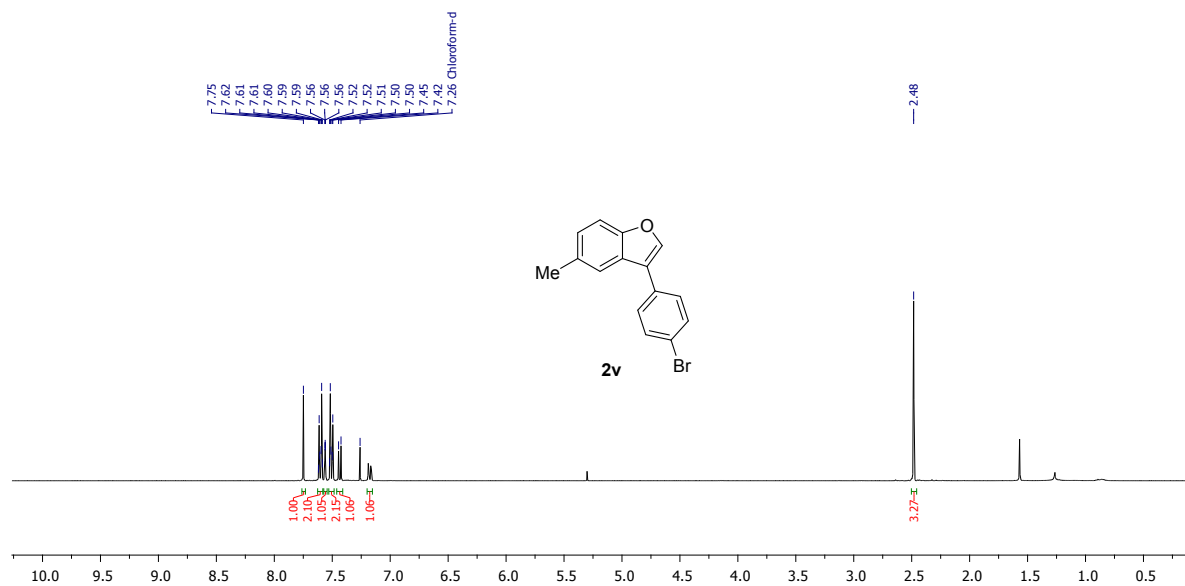
¹³C {¹H}-NMR (100 MHz) spectrum of **2t** in CDCl₃



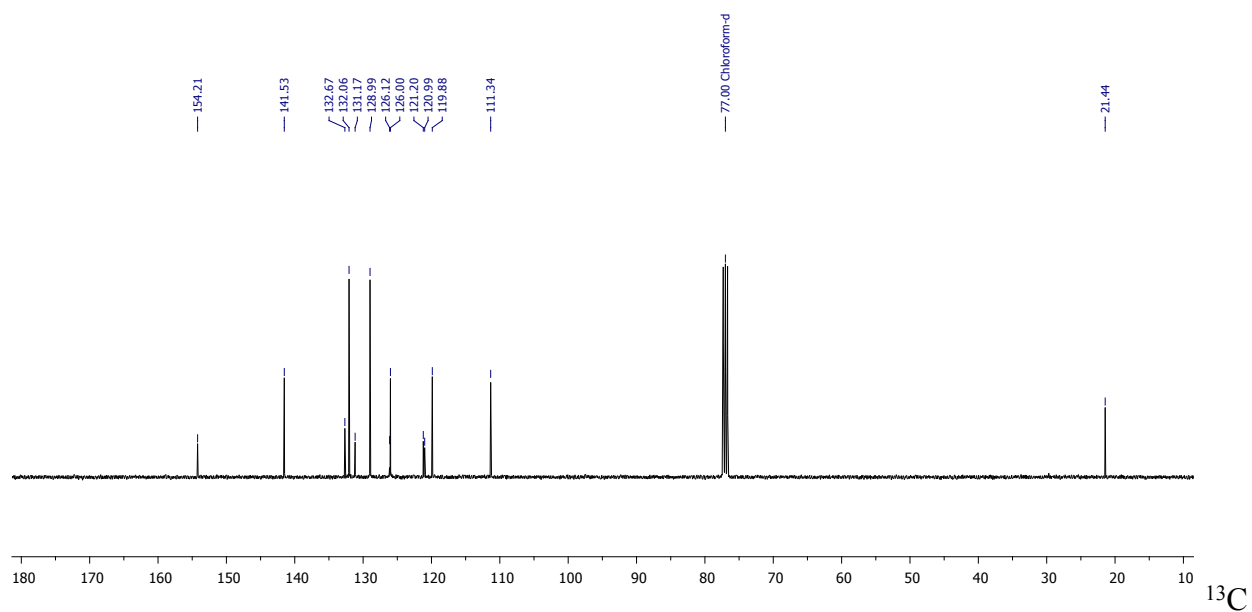
¹H-NMR (400 MHz) spectrum of **2u** in CDCl₃



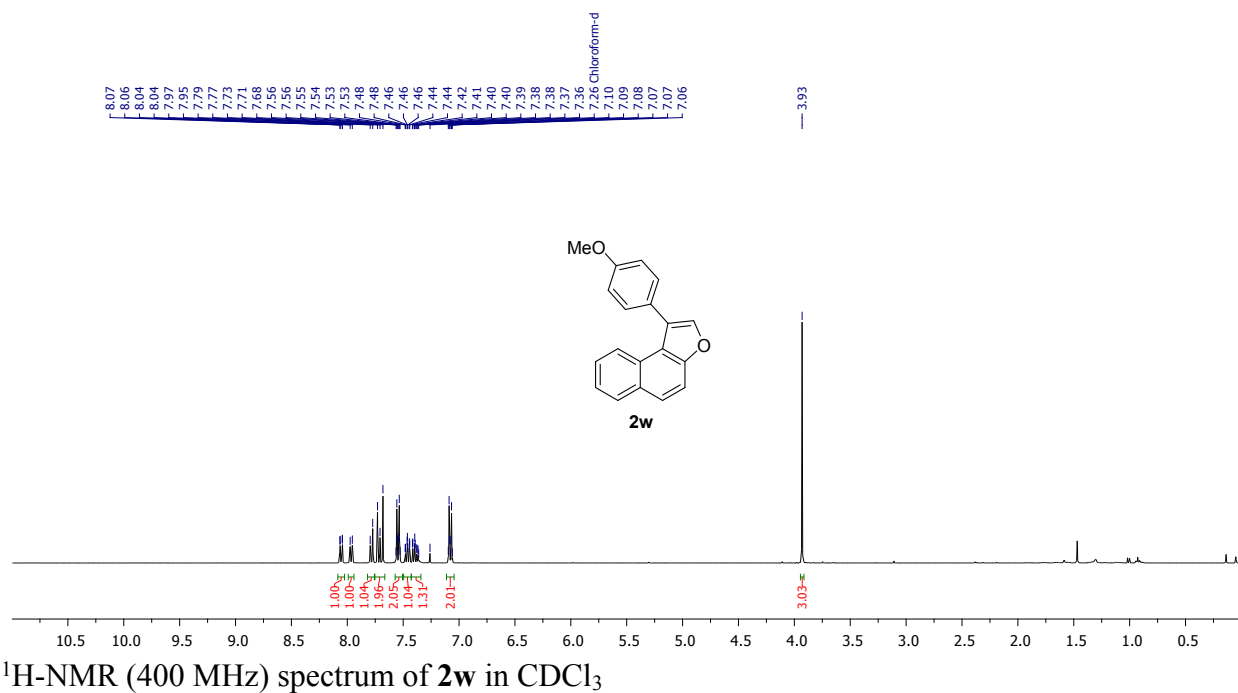
¹³C {¹H}-NMR (100 MHz) spectrum of **2u** in CDCl₃



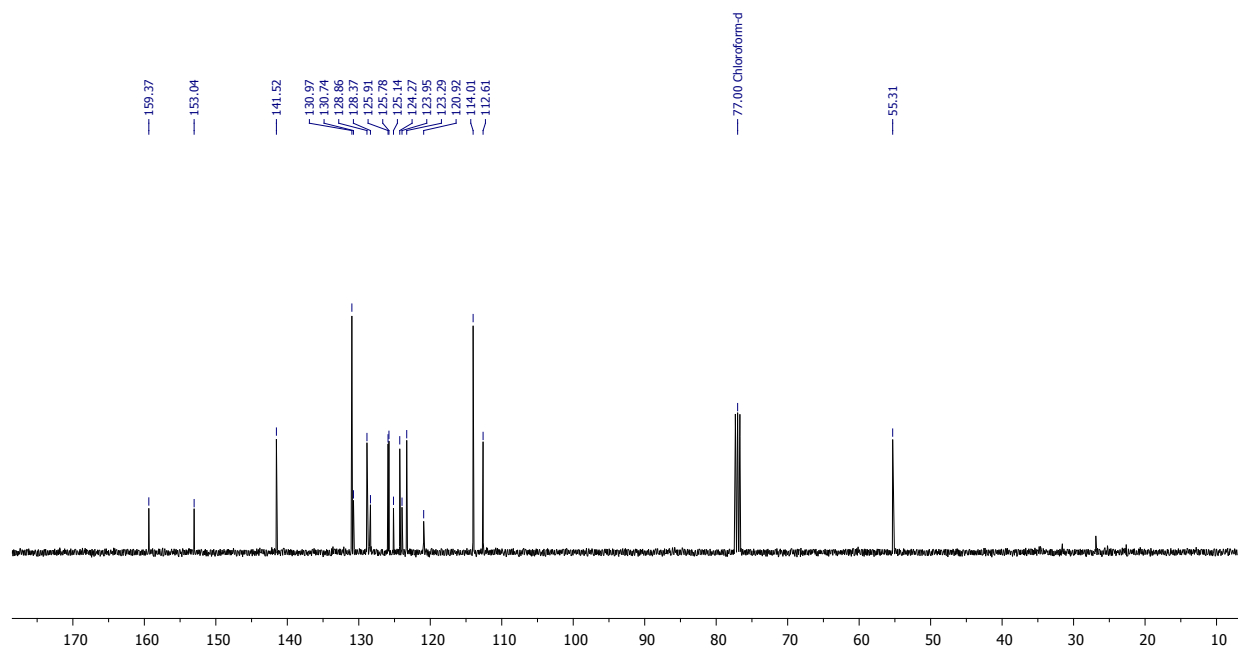
¹H-NMR (400 MHz) spectrum of **2v** in CDCl₃



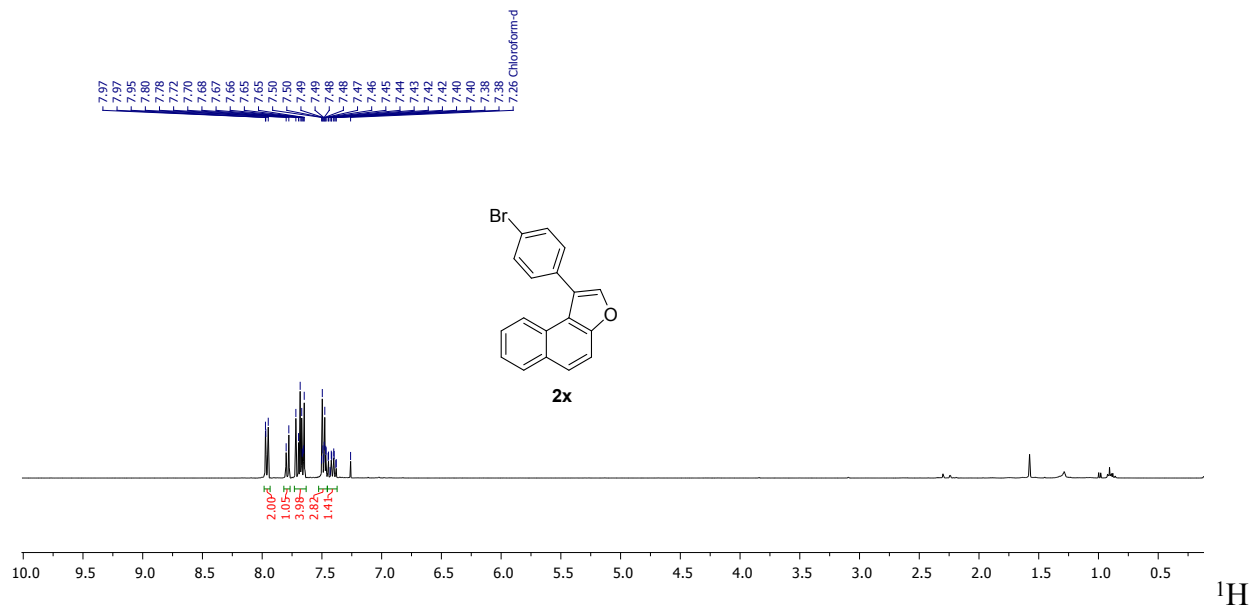
{¹H}-NMR (100 MHz) spectrum of **2v** in CDCl₃



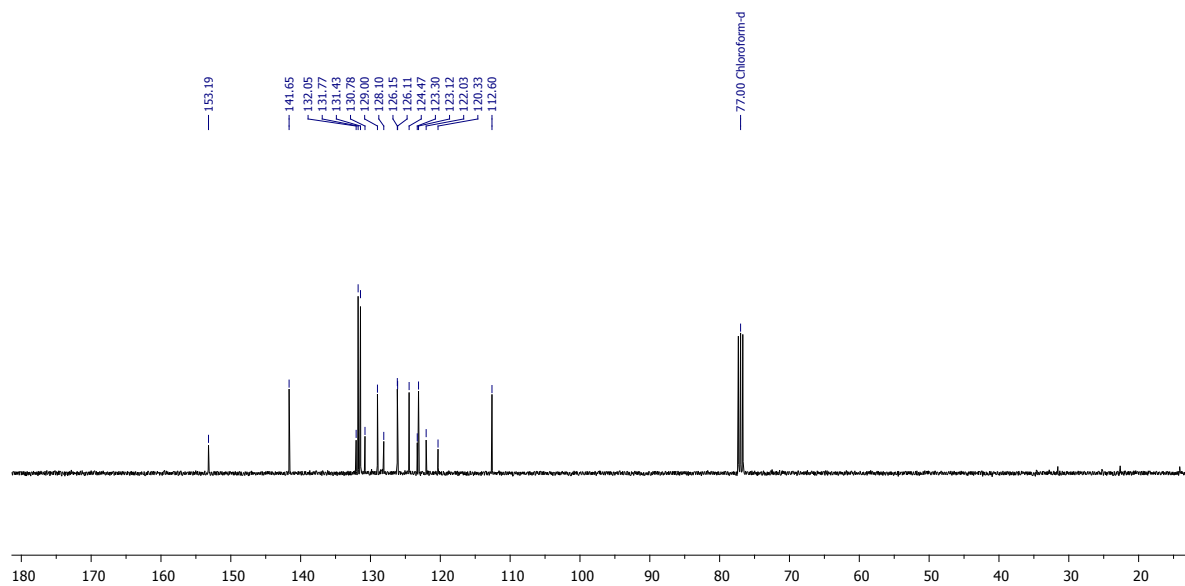
$^1\text{H-NMR}$ (400 MHz) spectrum of **2w** in CDCl_3



$^{13}\text{C} \{^1\text{H}\}$ -NMR (100 MHz) spectrum of **2w** in CDCl_3



^1H -NMR (400 MHz) spectrum of **2x** in CDCl_3



^{13}C { ^1H }-NMR (100 MHz) spectrum of **2x** in CDCl_3