Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of tetra-substituted olefins via annulation by Pd-catalyzed carbopalladation/C-H activation and solid state fluorescence properties

Kanagaraj Naveen, Avanashiappan Nandakumar and Paramasivan Thirumalai Perumal*

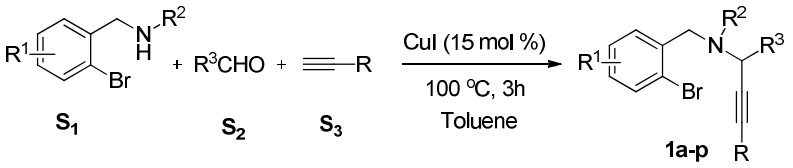
Organic & Bio-organic Chemistry Division, CSIR-Central Leather Research Institute, Adyar, Chennai-600 020,

India

E-mail id:ptperumal@gmail.com

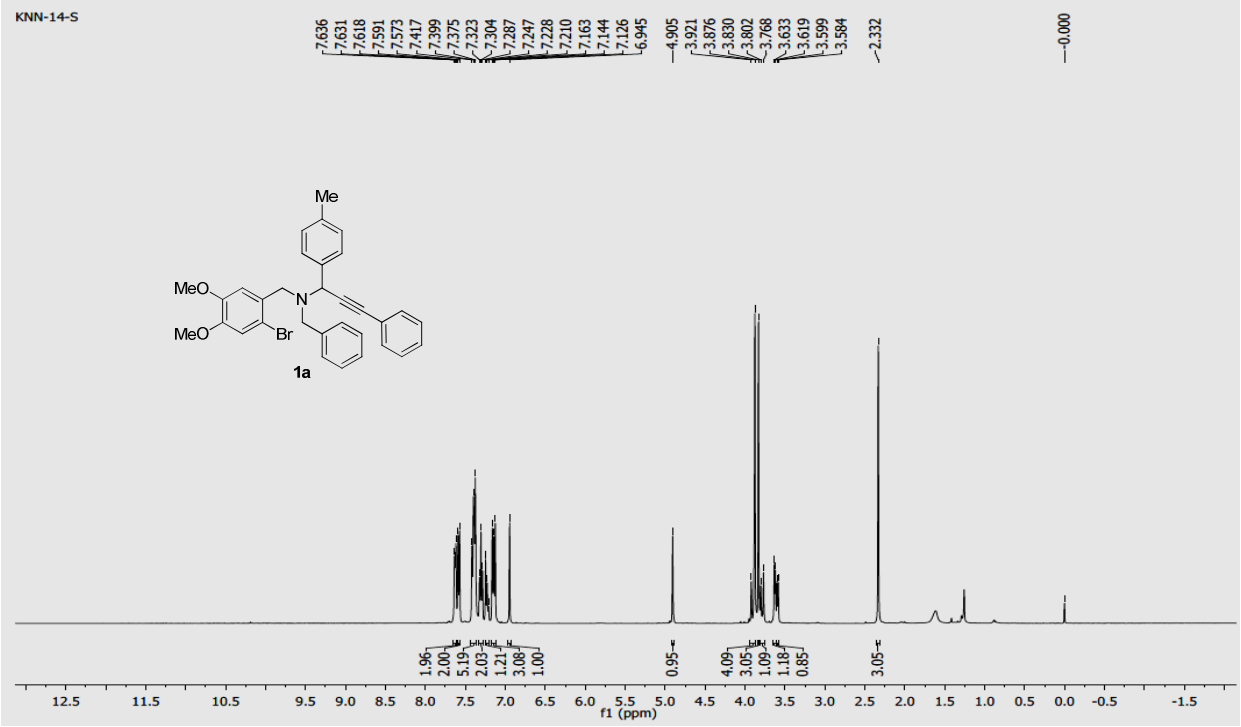
Table of contents

General procedure for the preparation of starting materials (1a-p)

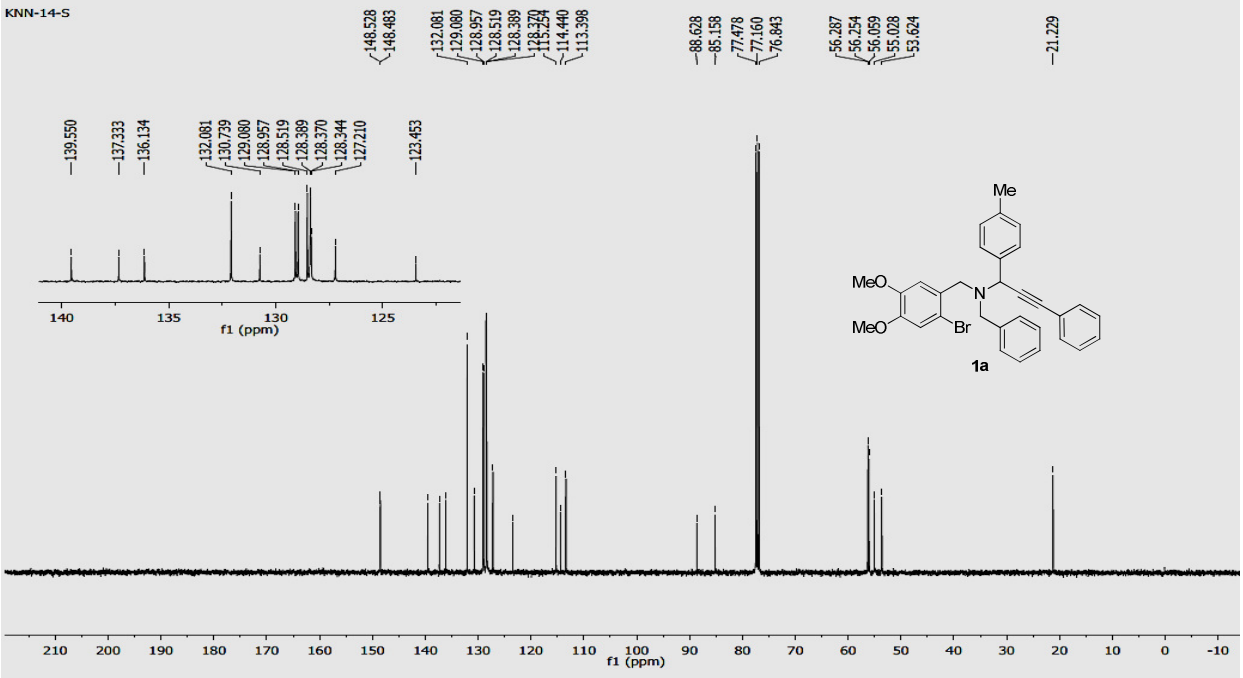


A mixture of CuI (15 mol %), amine S_1 (0.50 mmol), aldehyde S_2 (0.55 mmol) and alkyne S_3 (0.75 mmol) in toluene (3mL) was heated at 100 ^{o}C for 3 h. Then the reaction mixture was filtered through Celite and washed with ethyl acetate. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate as eluent, affording 2-bromo-N-benzylpropargylamines compounds (1a-p).

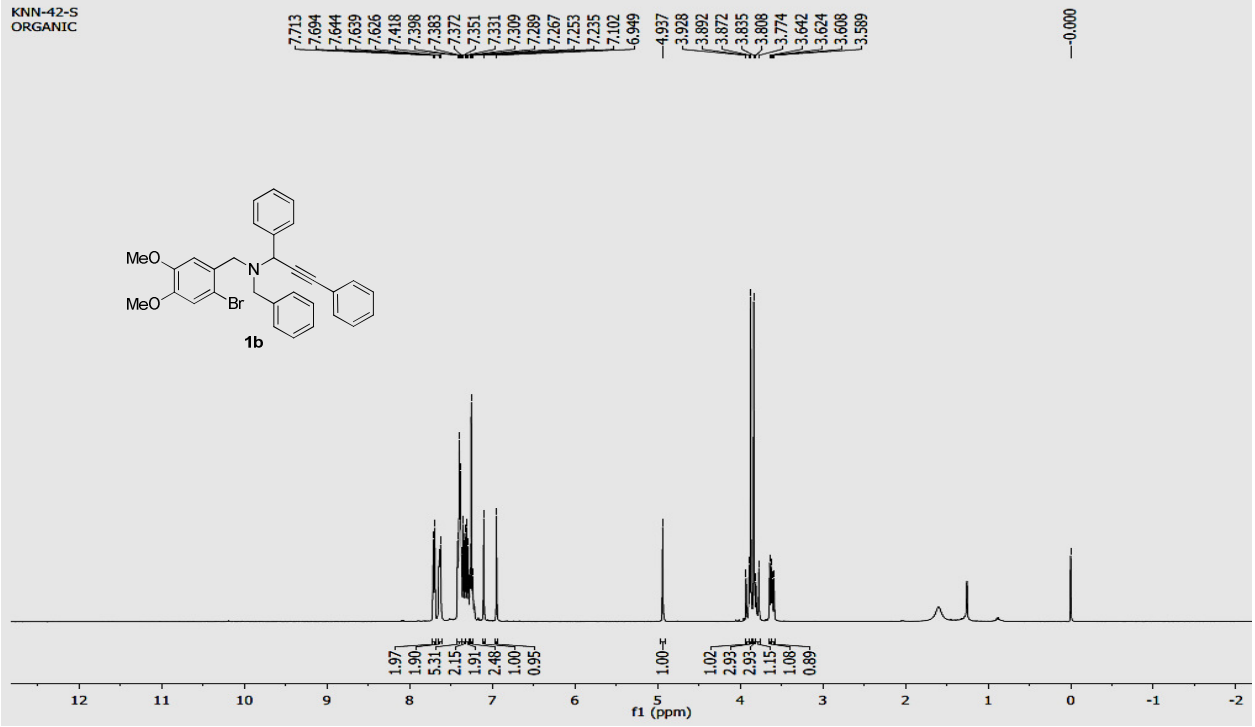
Copies of ^{1}H NMR and ^{13}C NMR of the compounds (1a-p)



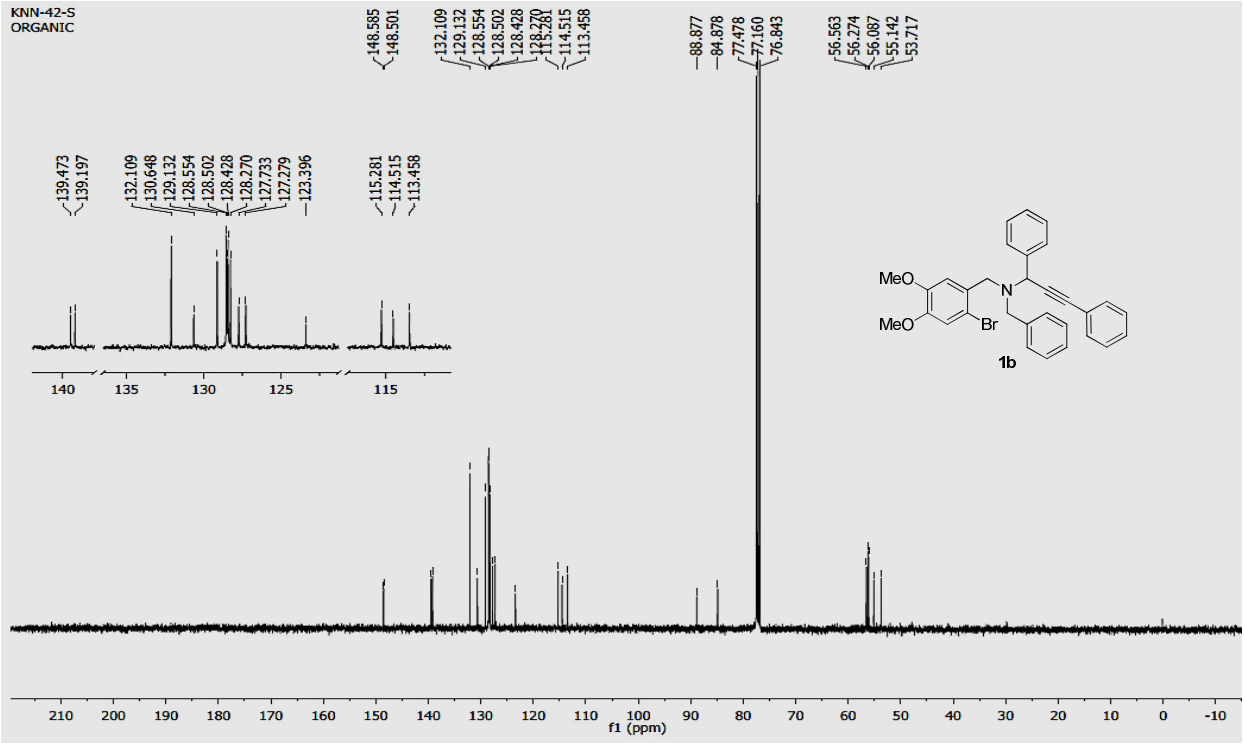
^{1}H-NMR spectrum of compound **1a**



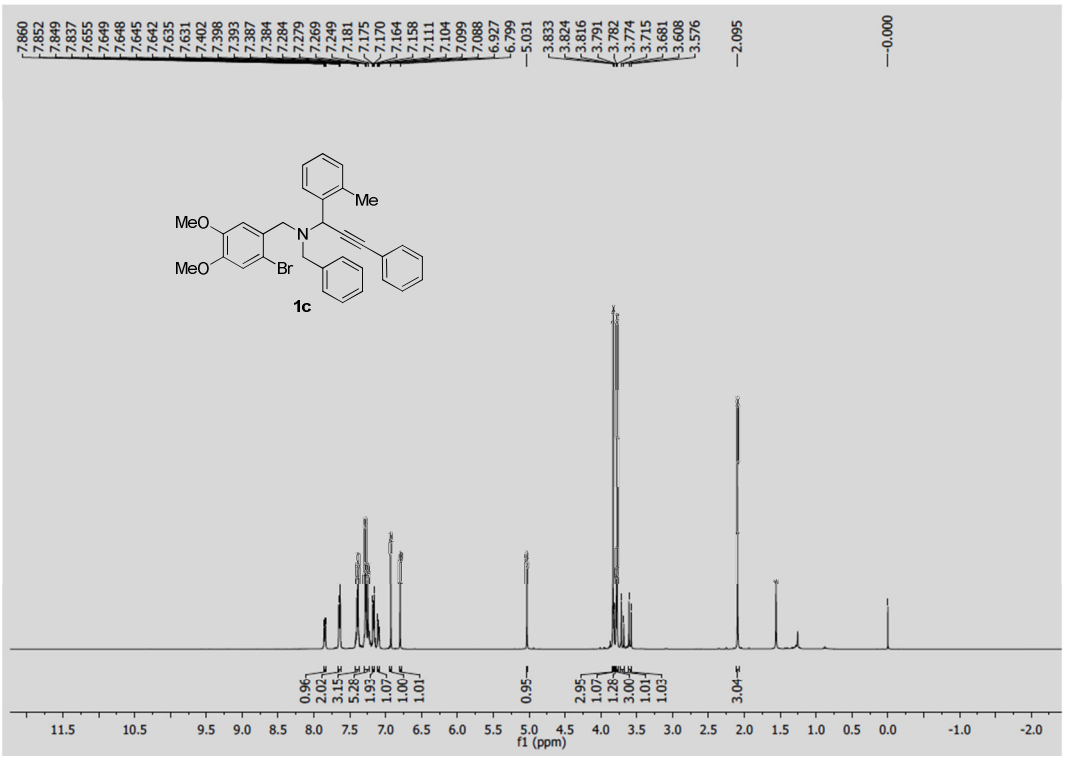
^{13}C-NMR spectrum of compound **1a**



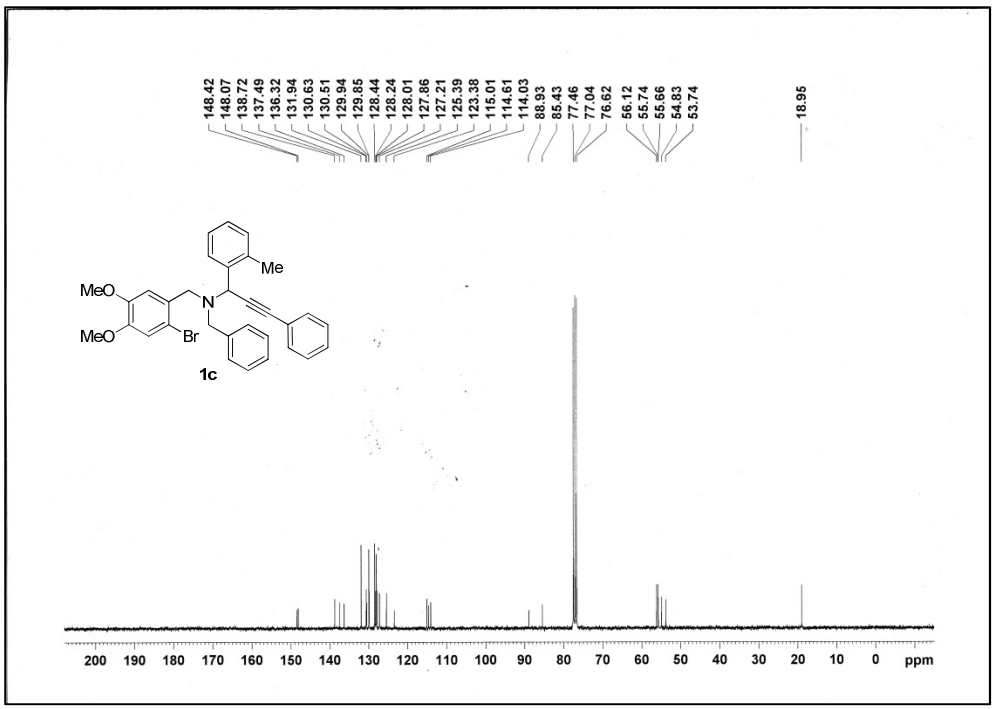
^{1}H-NMR spectrum of compound **1b**



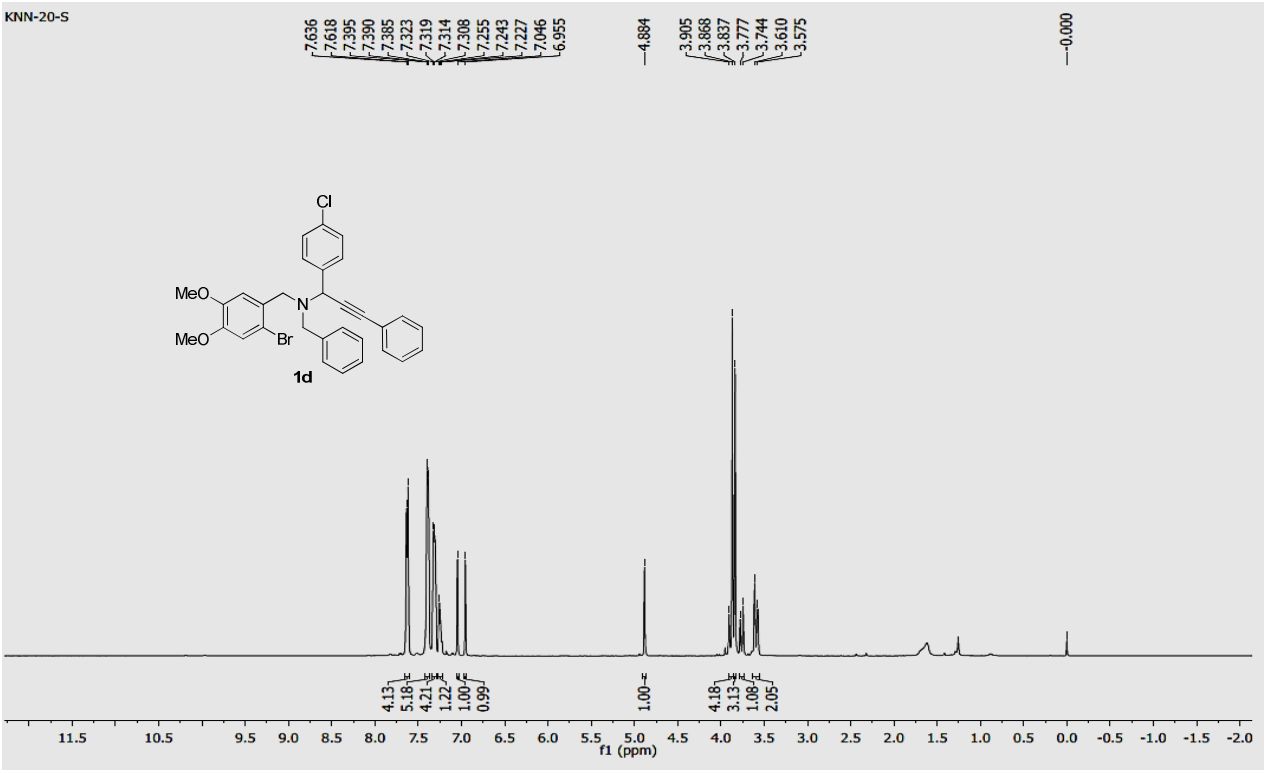
^{13}C-NMR spectrum of compound **1b**



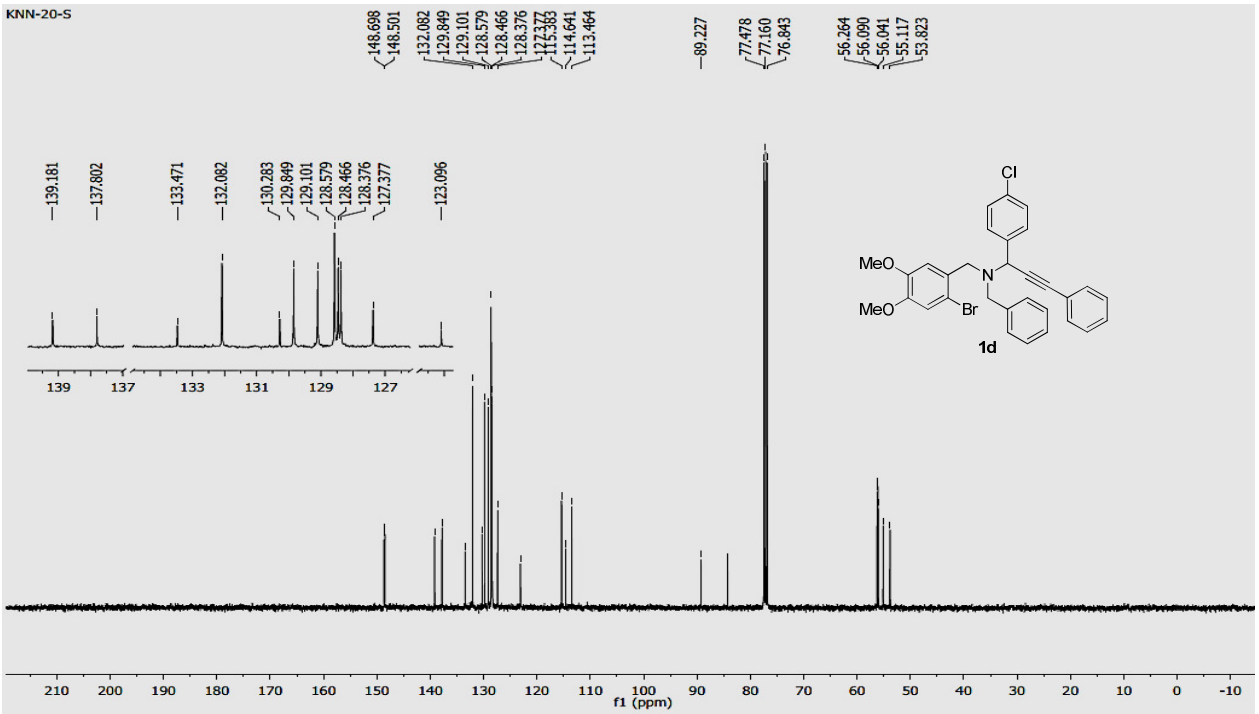
^{1}H-NMR spectrum of compound **1c**



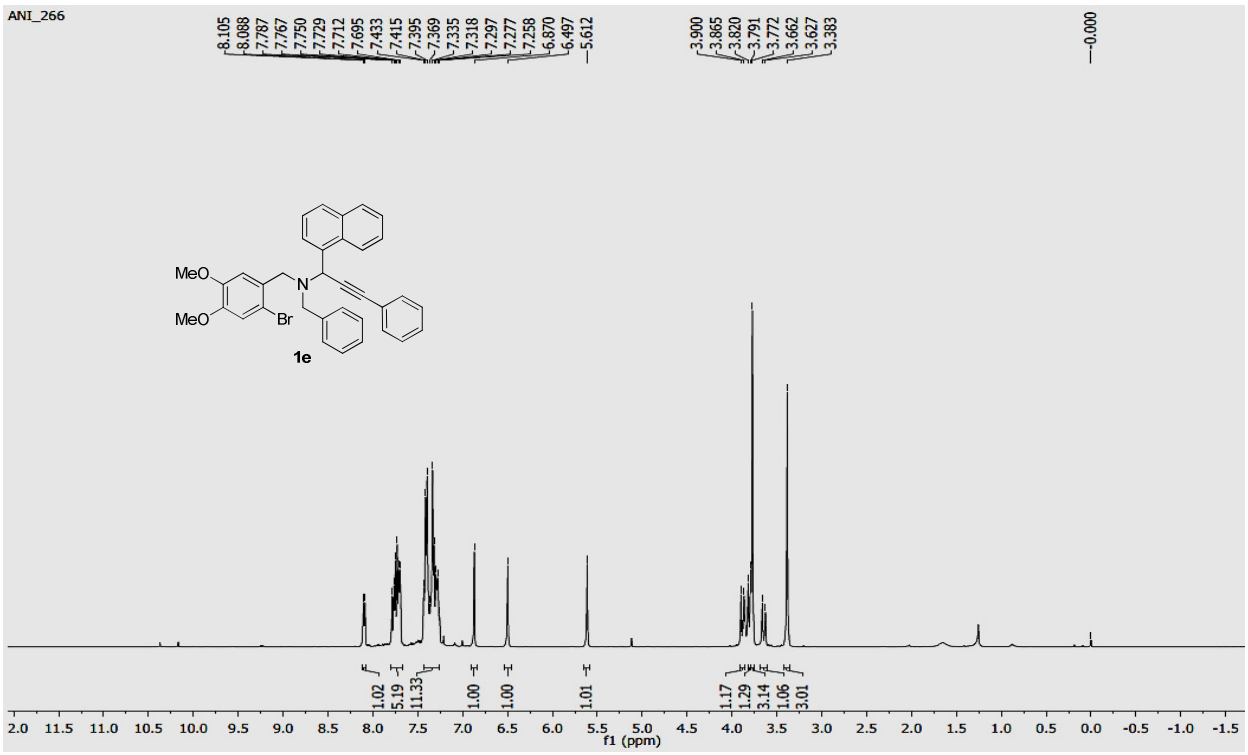
^{13}C-NMR spectrum of compound **1c**



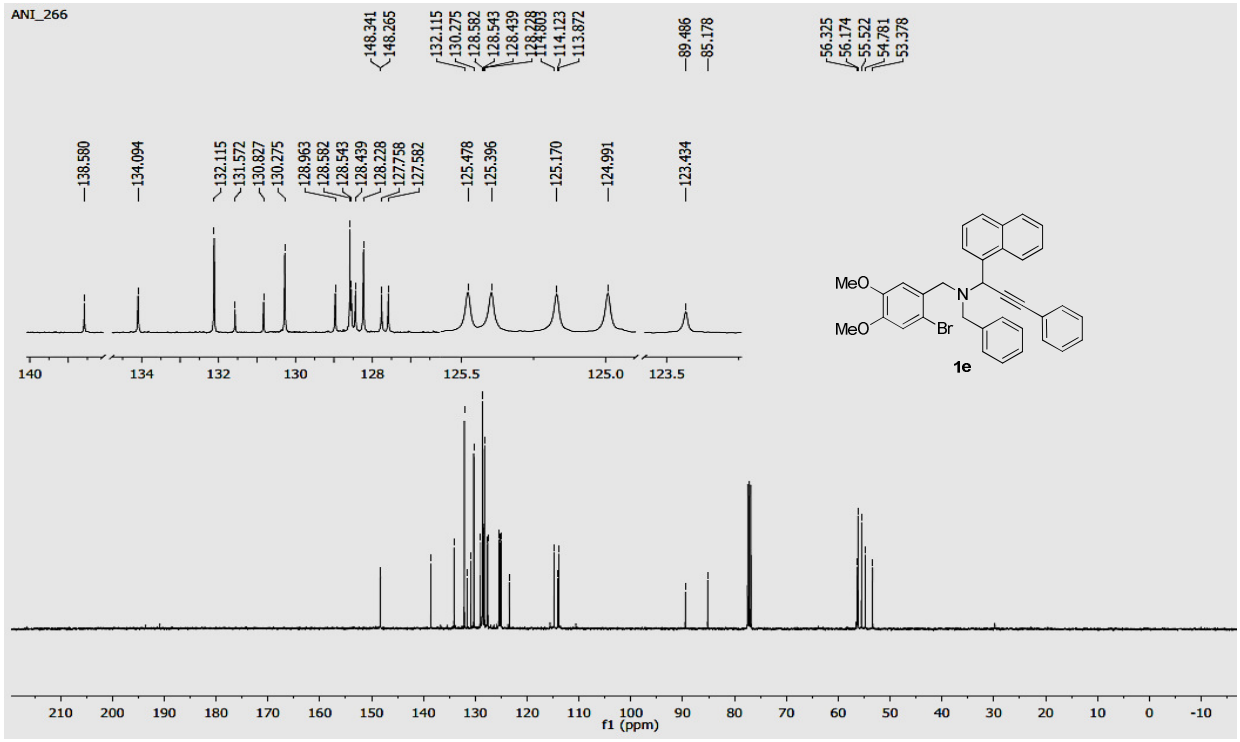
^{1}H-NMR spectrum of compound **1d**



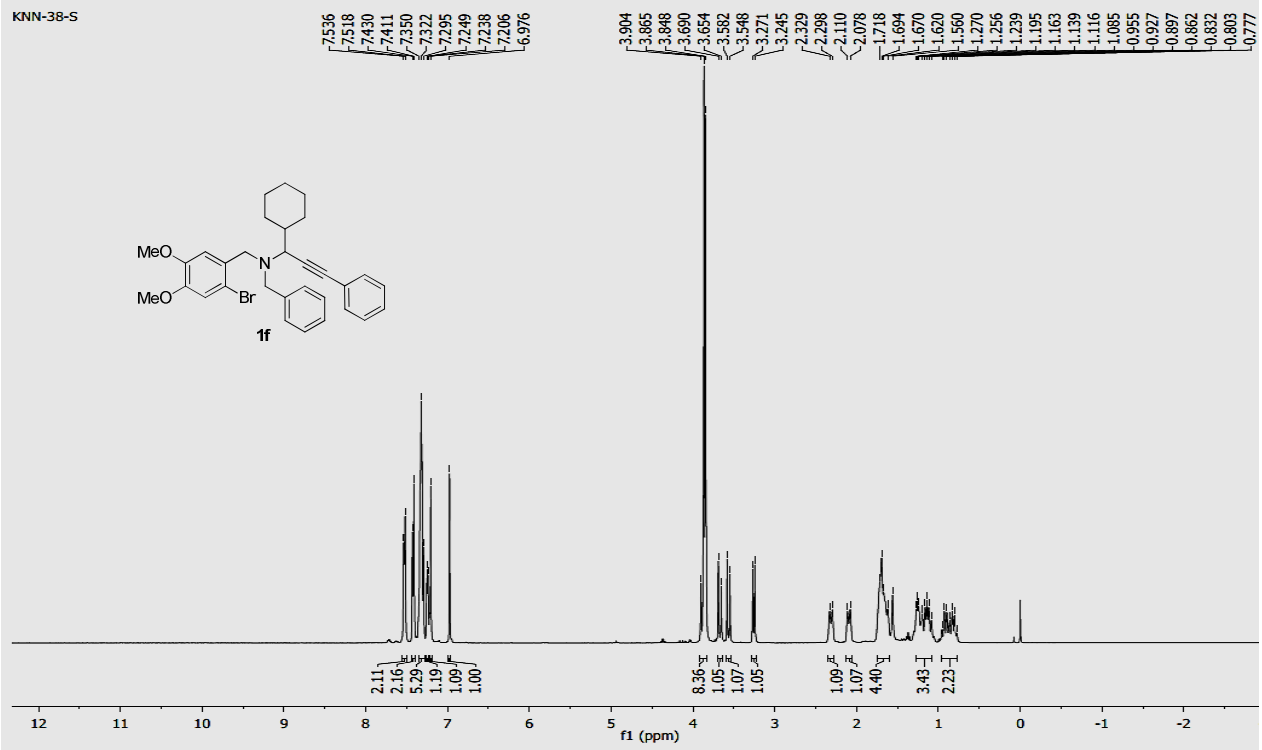
^{13}C-NMR spectrum of compound **1d**



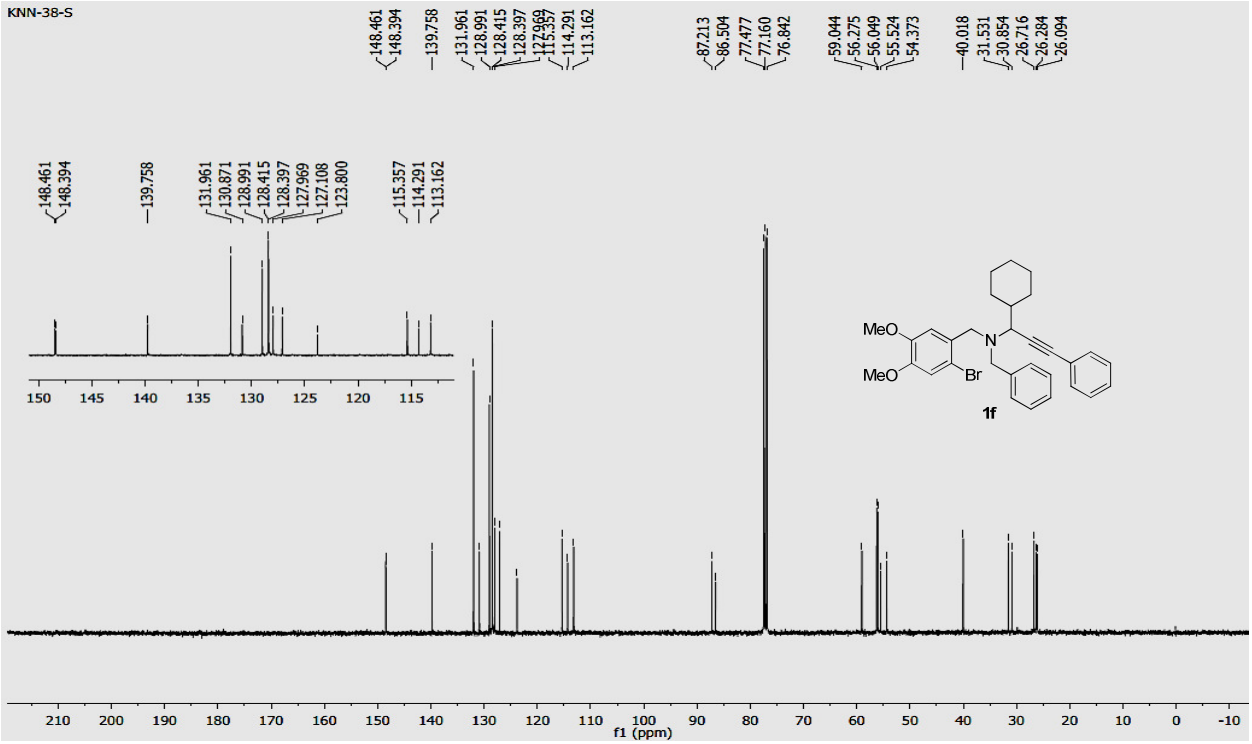
^{1}H-NMR spectrum of compound **1e**



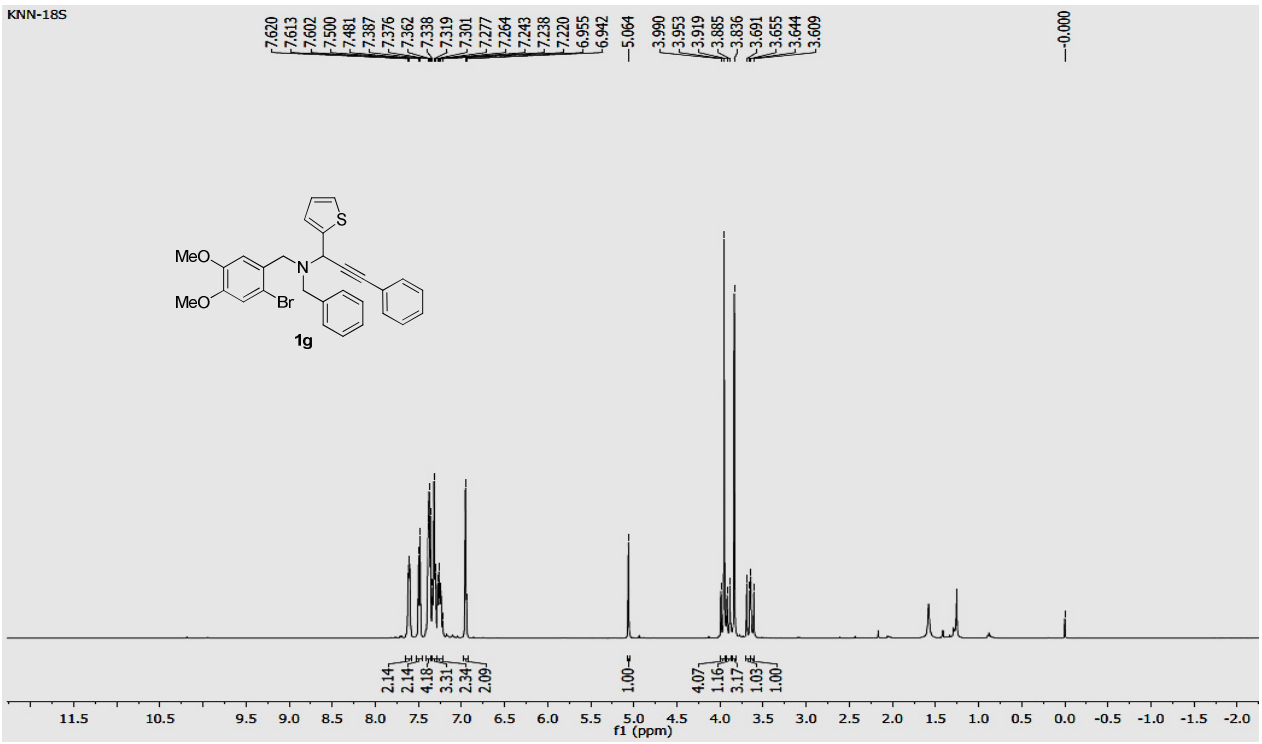
^{13}C-NMR spectrum of compound **1e**



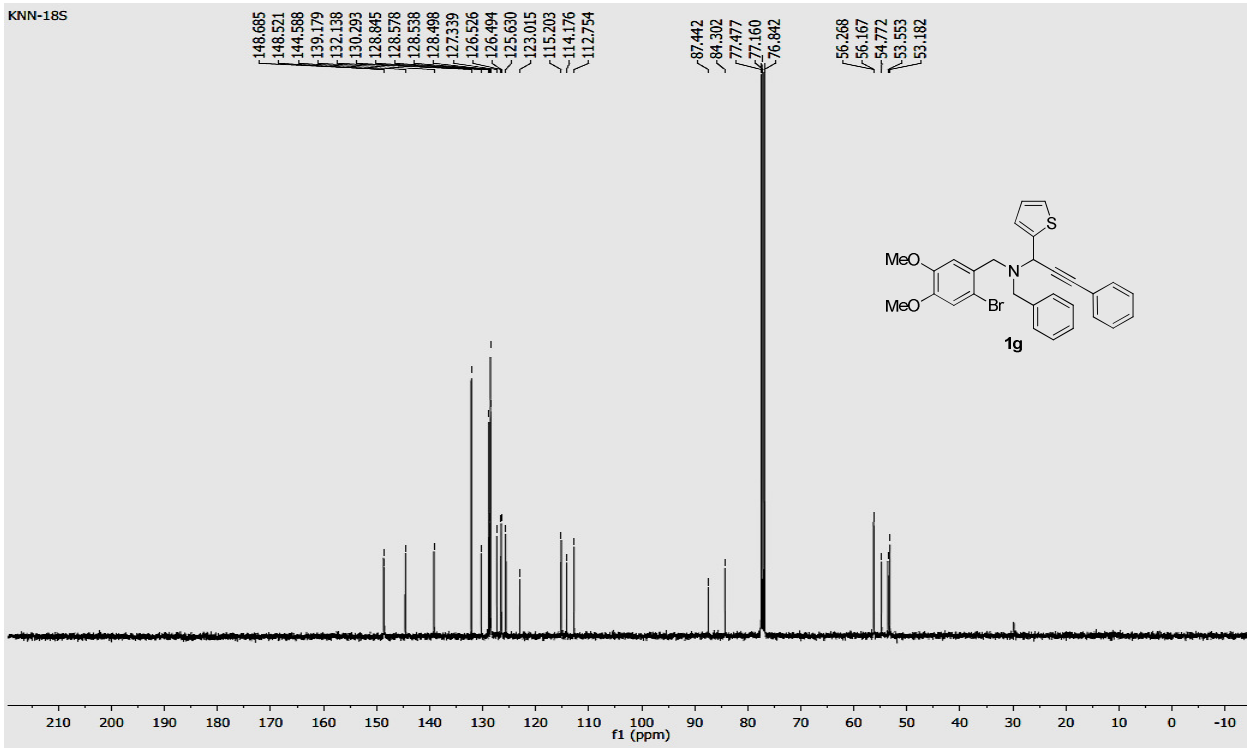
^{1}H-NMR spectrum of compound **1f**



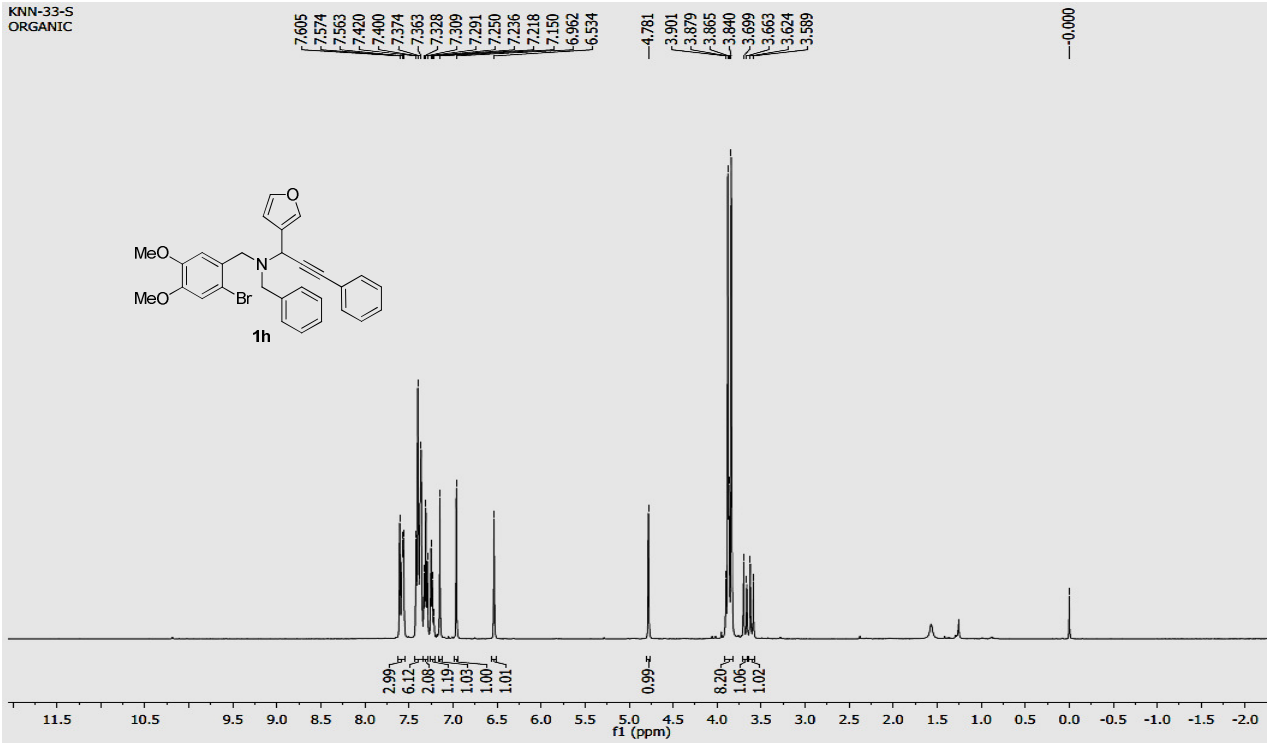
^{13}C-NMR spectrum of compound **1f**



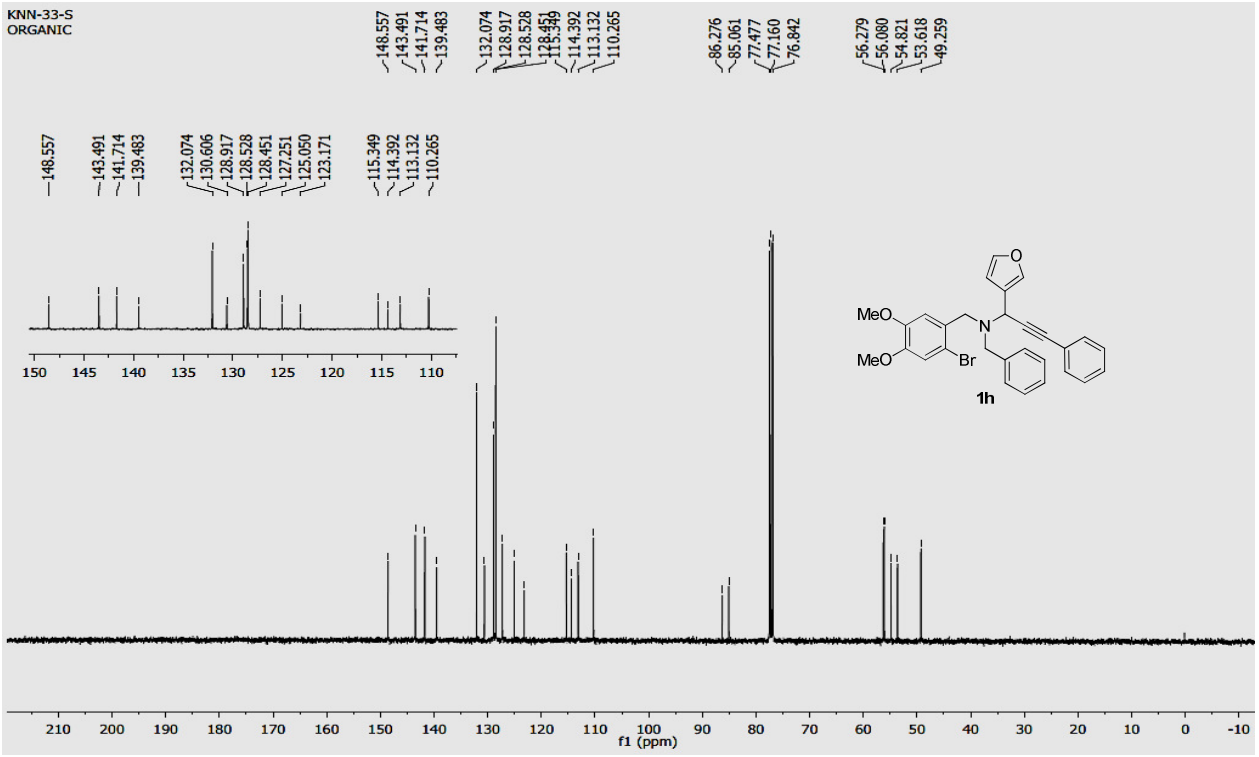
^{1}H-NMR spectrum of compound **1g**



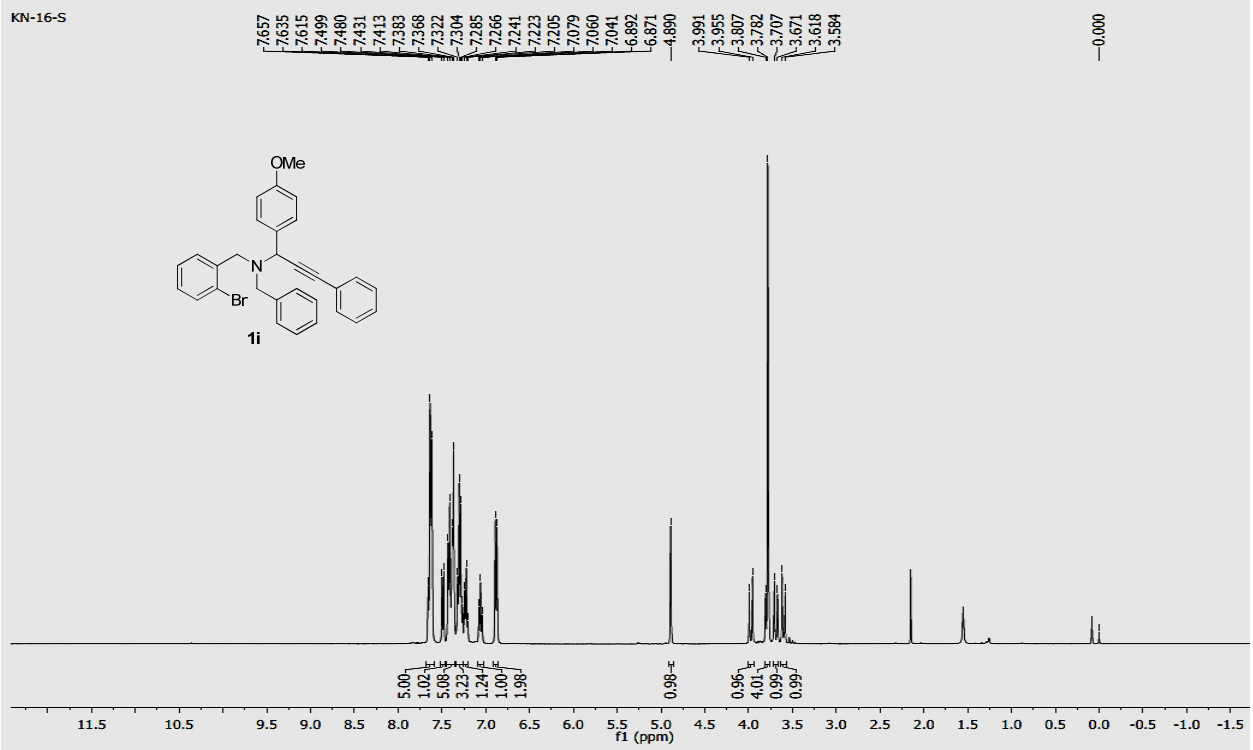
^{13}C-NMR spectrum of compound **1g**



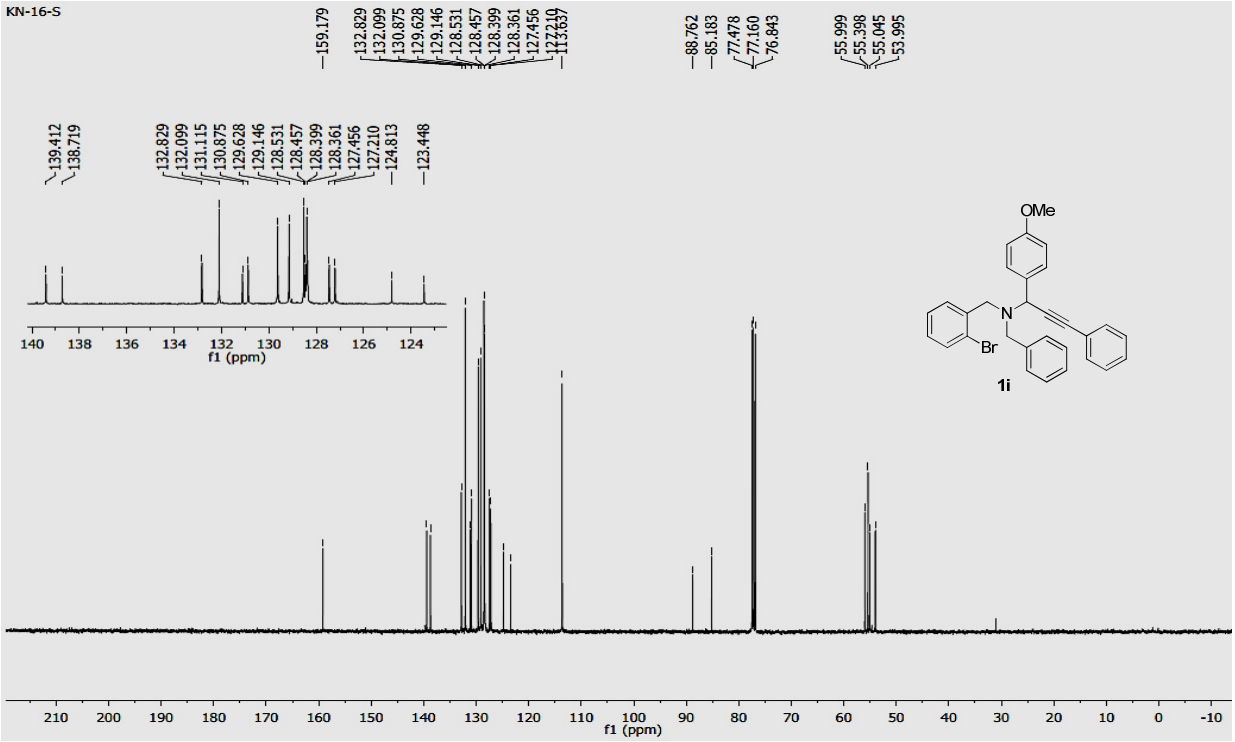
^{1}H-NMR spectrum of compound **1h**



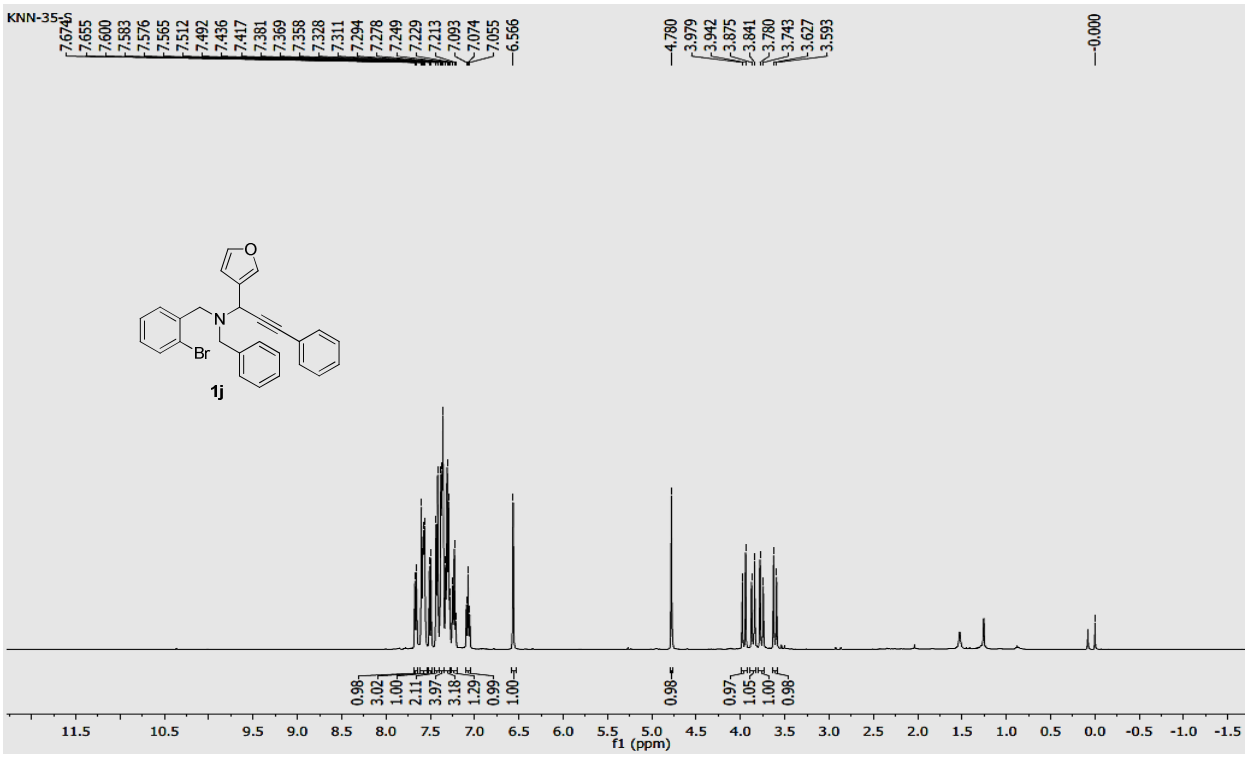
^{13}C-NMR spectrum of compound **1h**



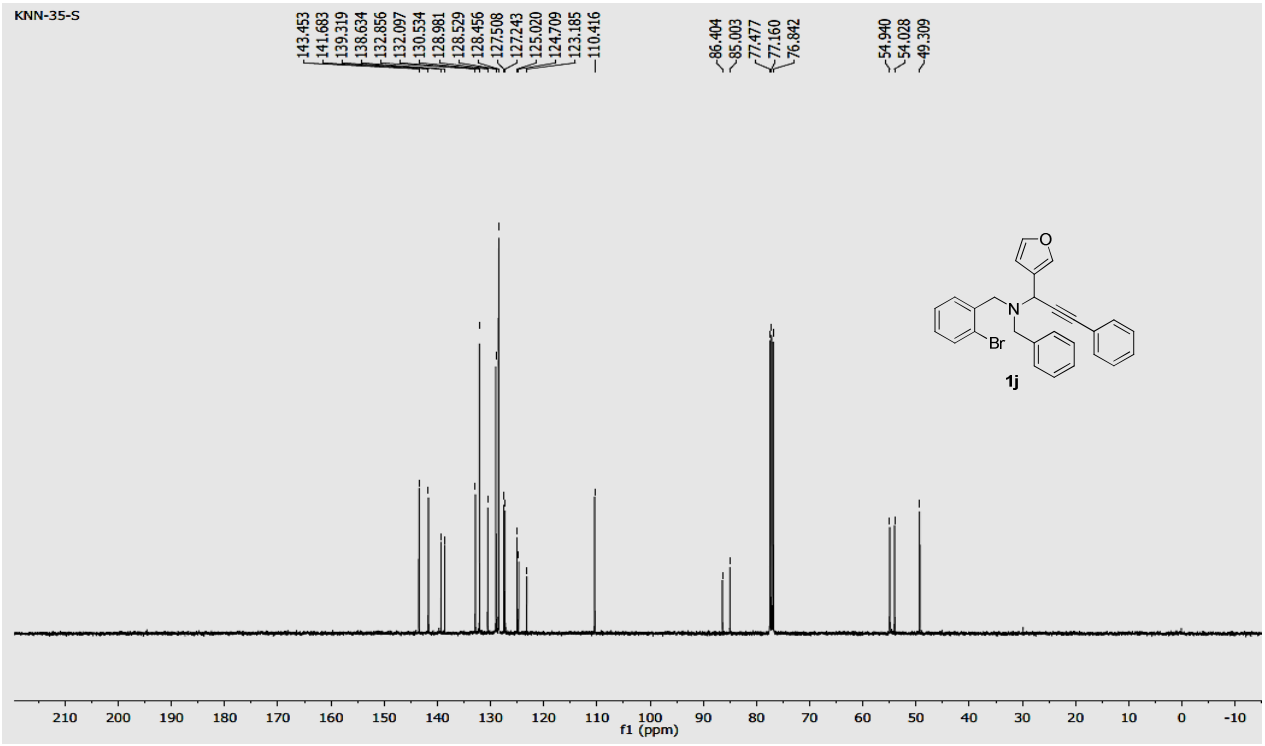
^{1}H-NMR spectrum of compound **1i**



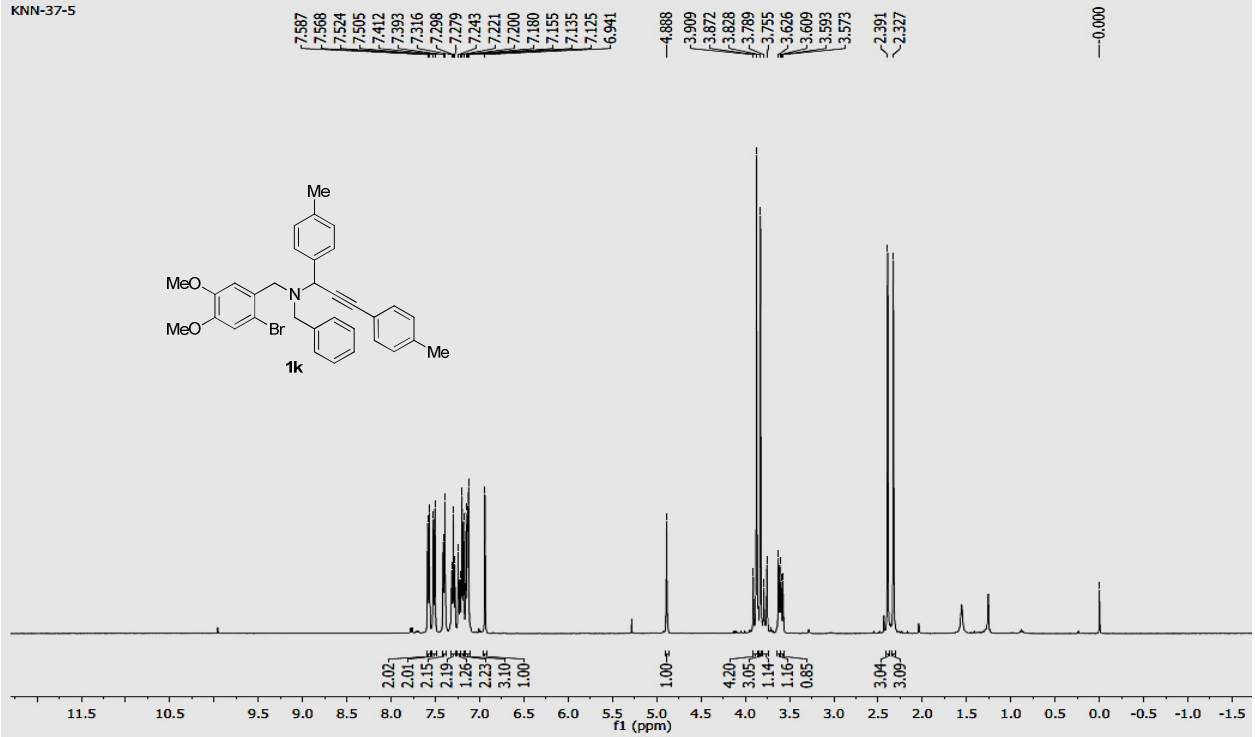
^{13}C-NMR spectrum of compound **1i**



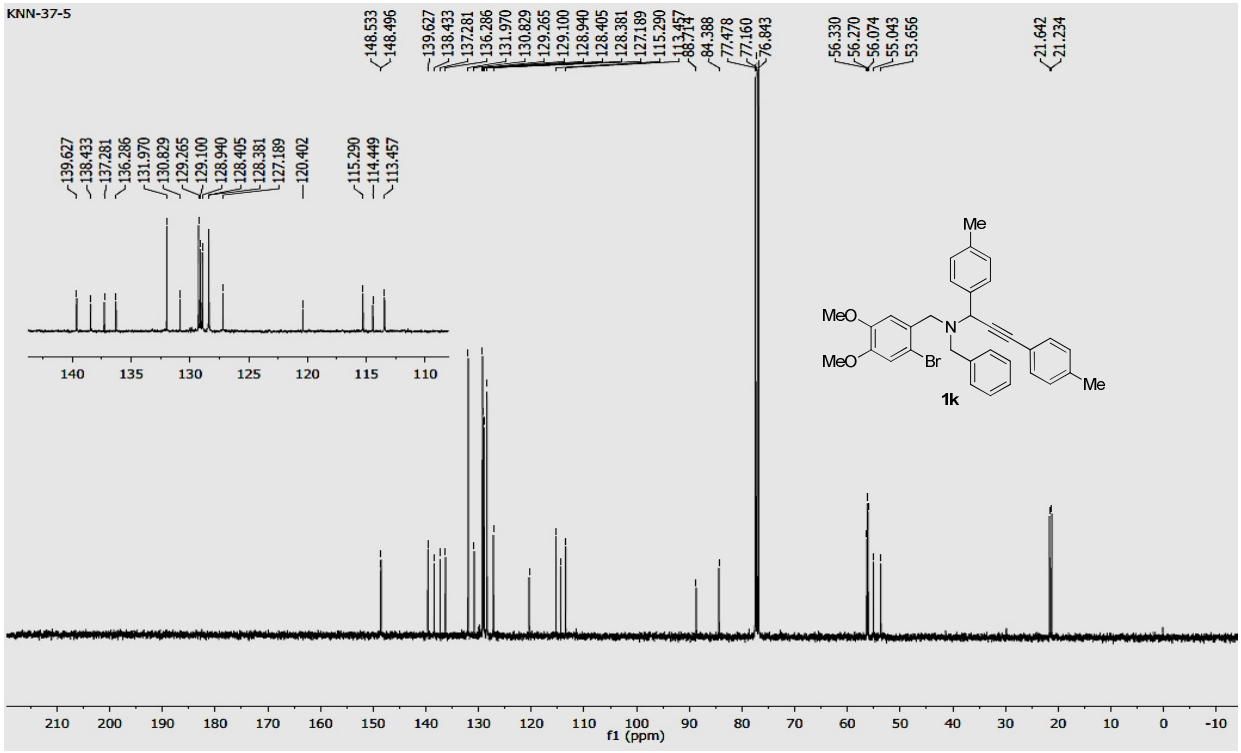
^{1}H-NMR spectrum of compound **1j**



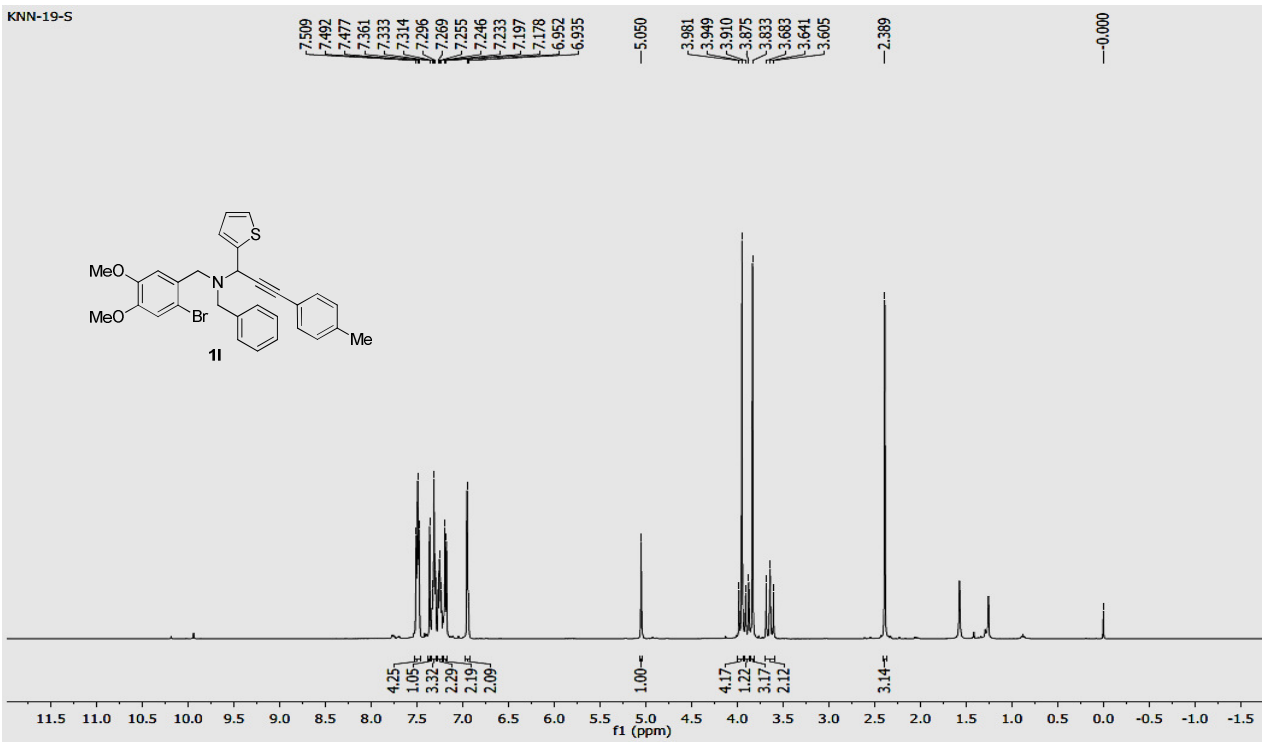
^{13}C-NMR spectrum of compound **1j**



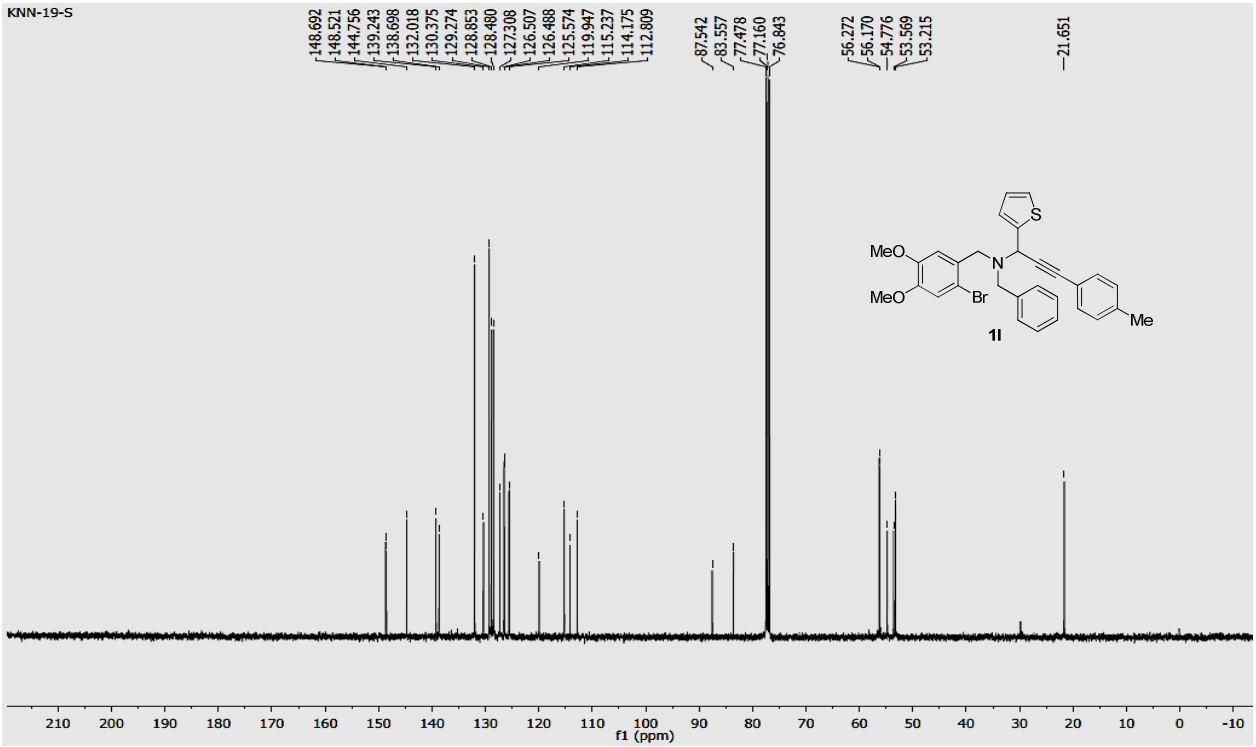
^{1}H-NMR spectrum of compound **1k**



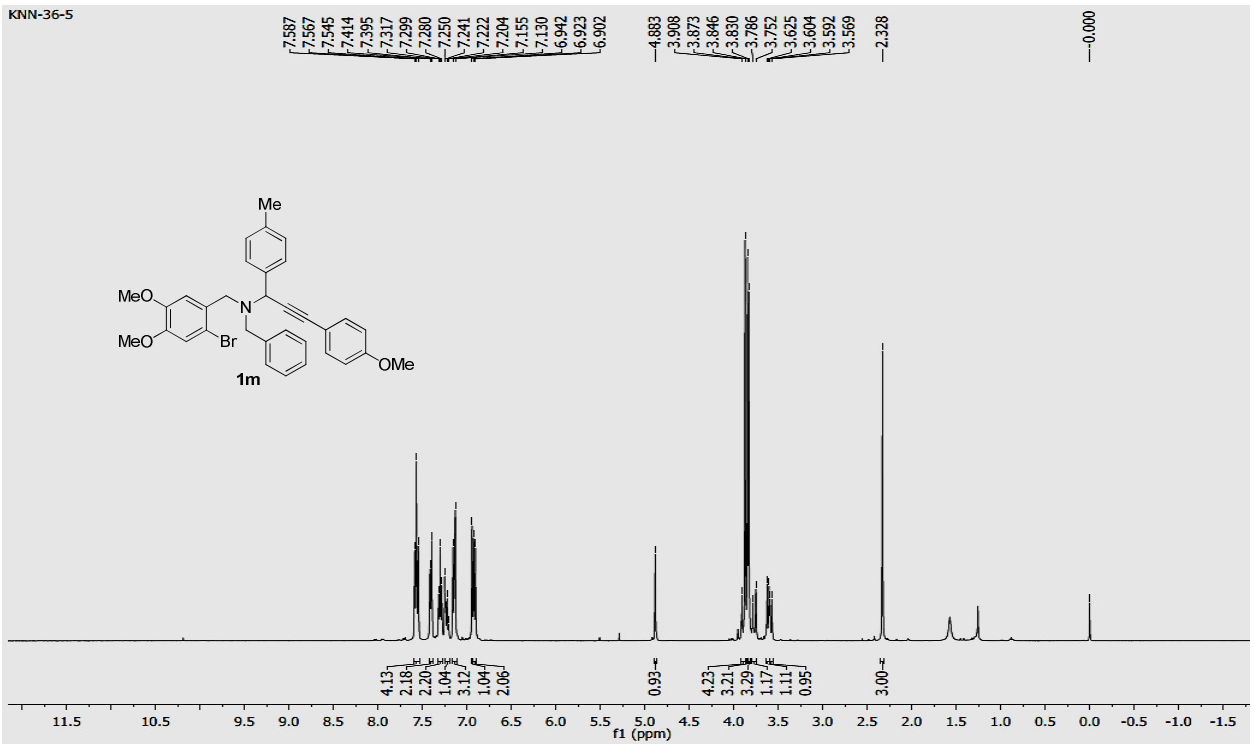
^{13}C-NMR spectrum of compound **1k**



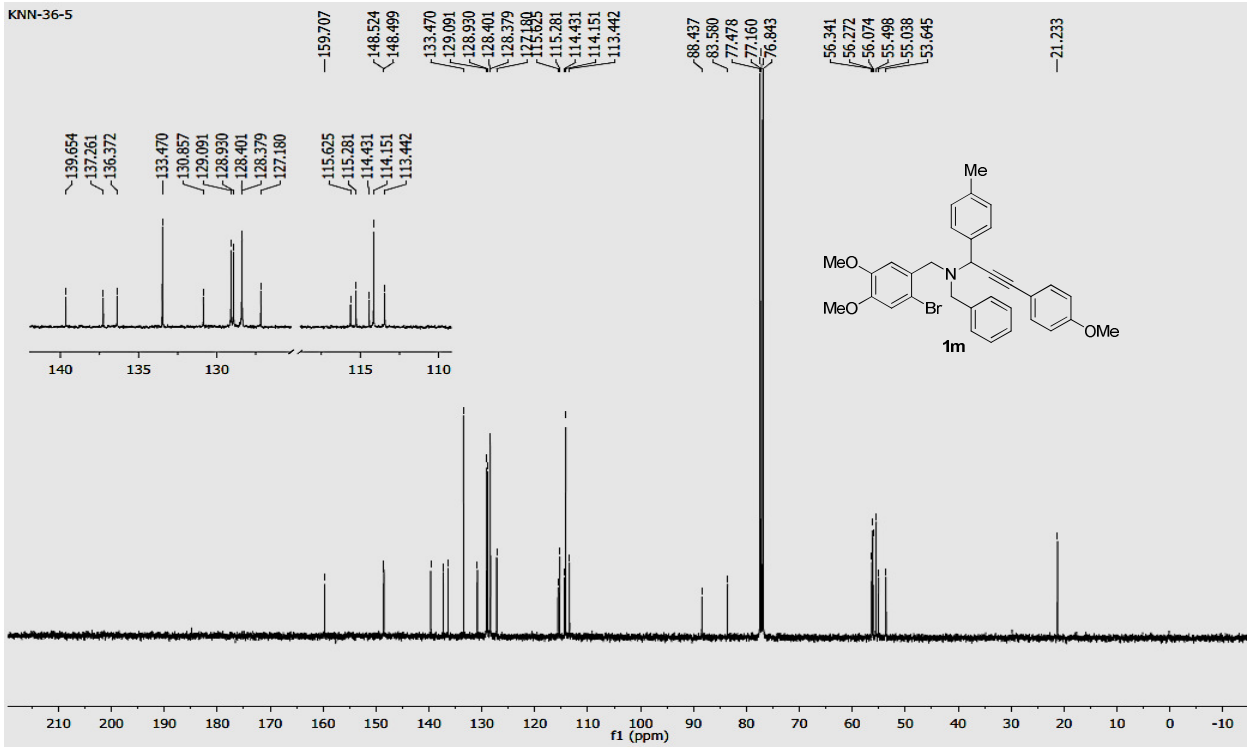
^{1}H-NMR spectrum of compound **1l**



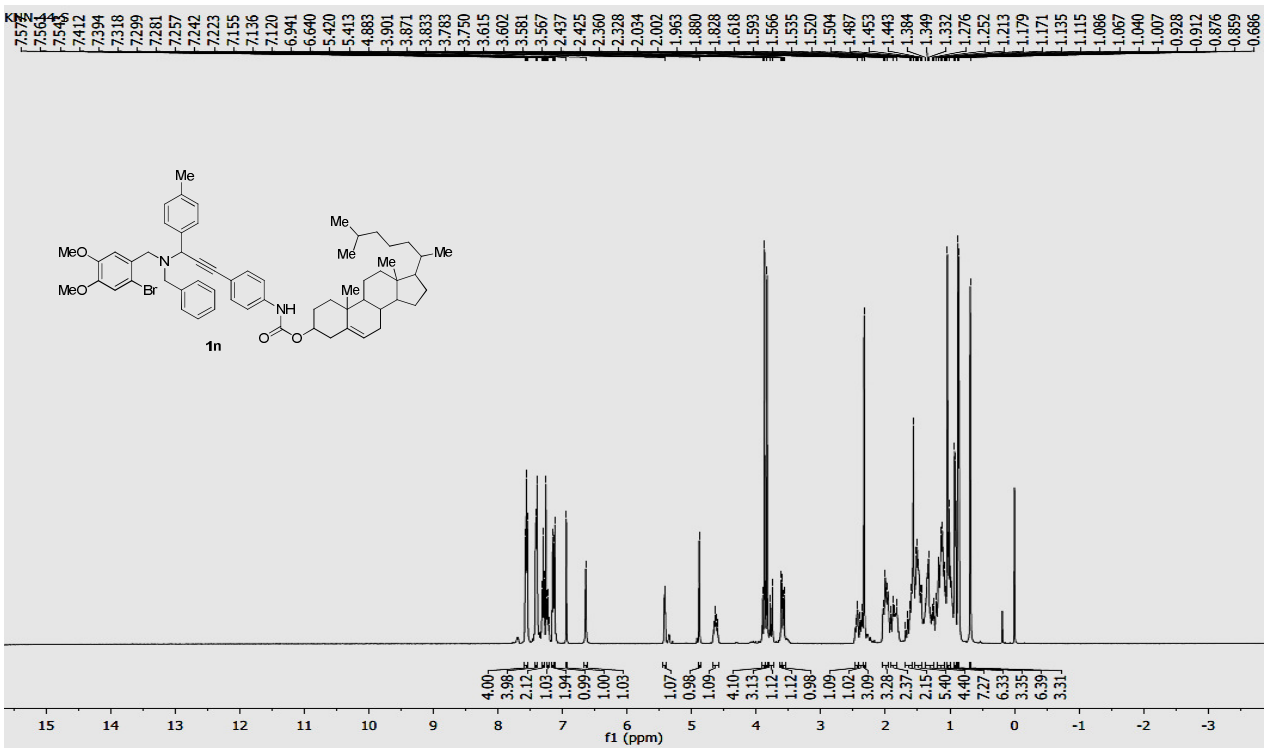
^{13}C-NMR spectrum of compound **1l**



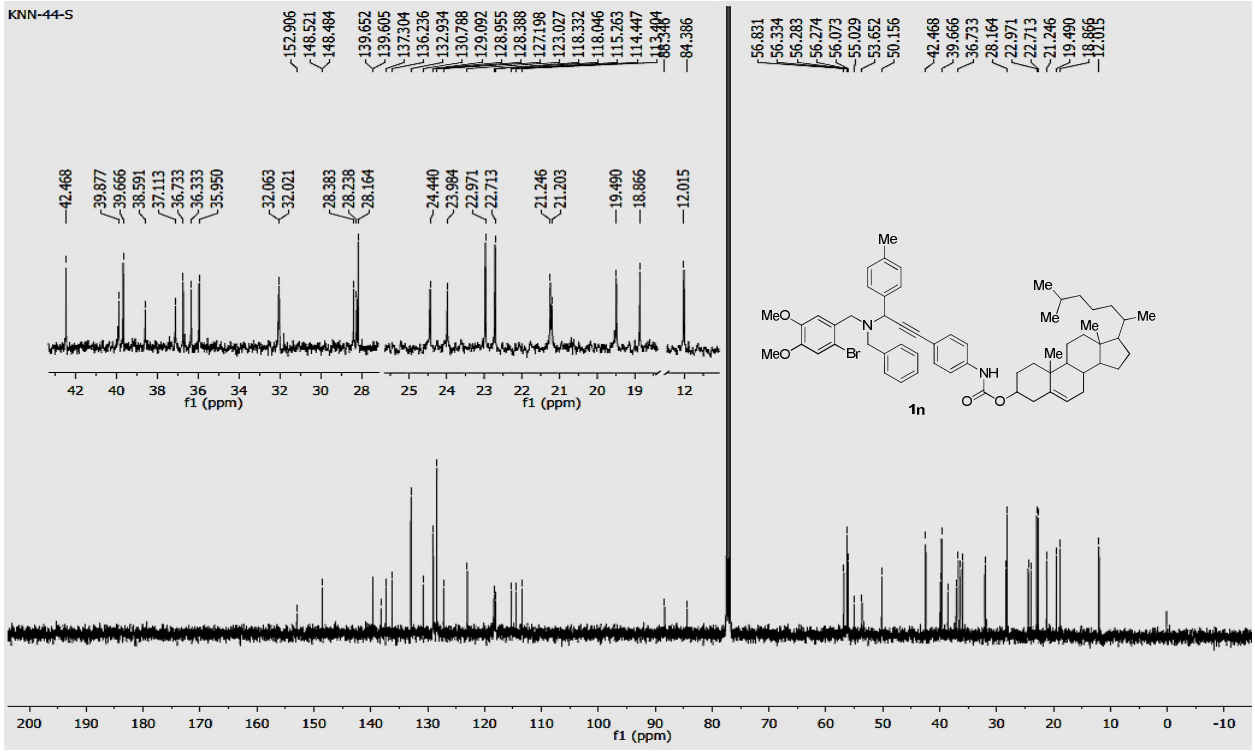
^{1}H-NMR spectrum of compound **1m**



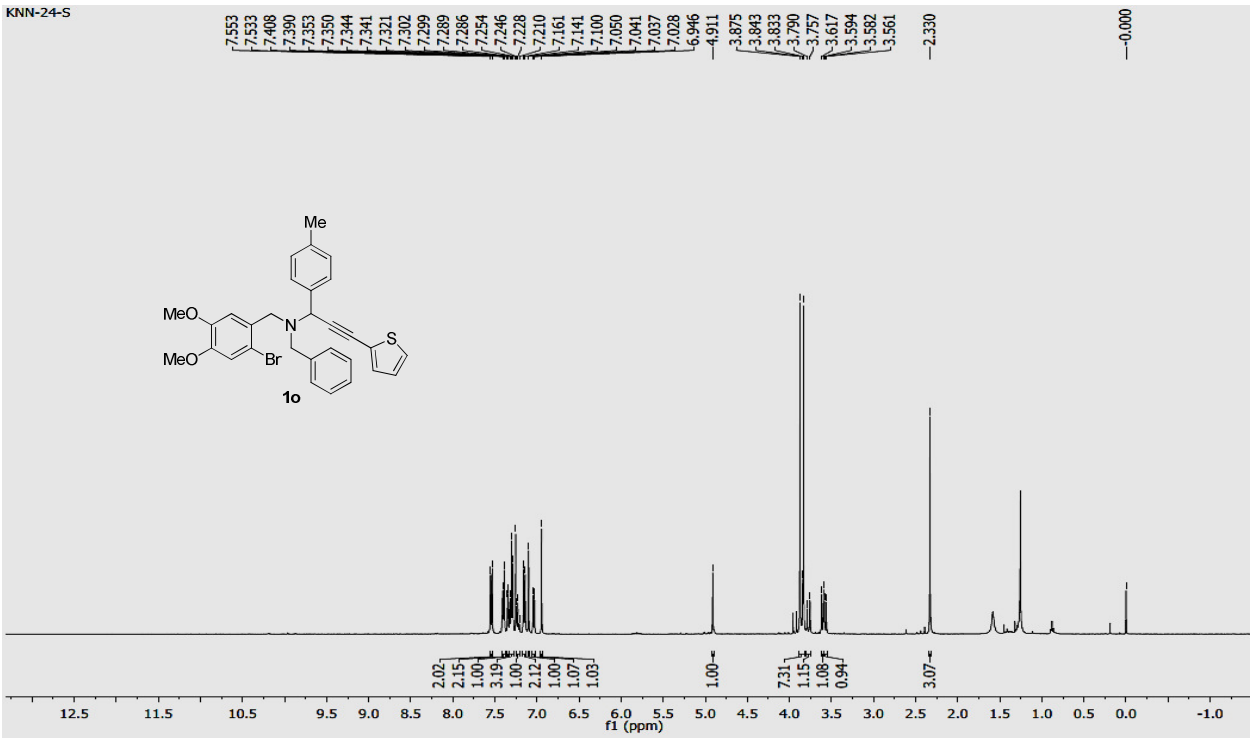
^{13}C-NMR spectrum of compound **1m**



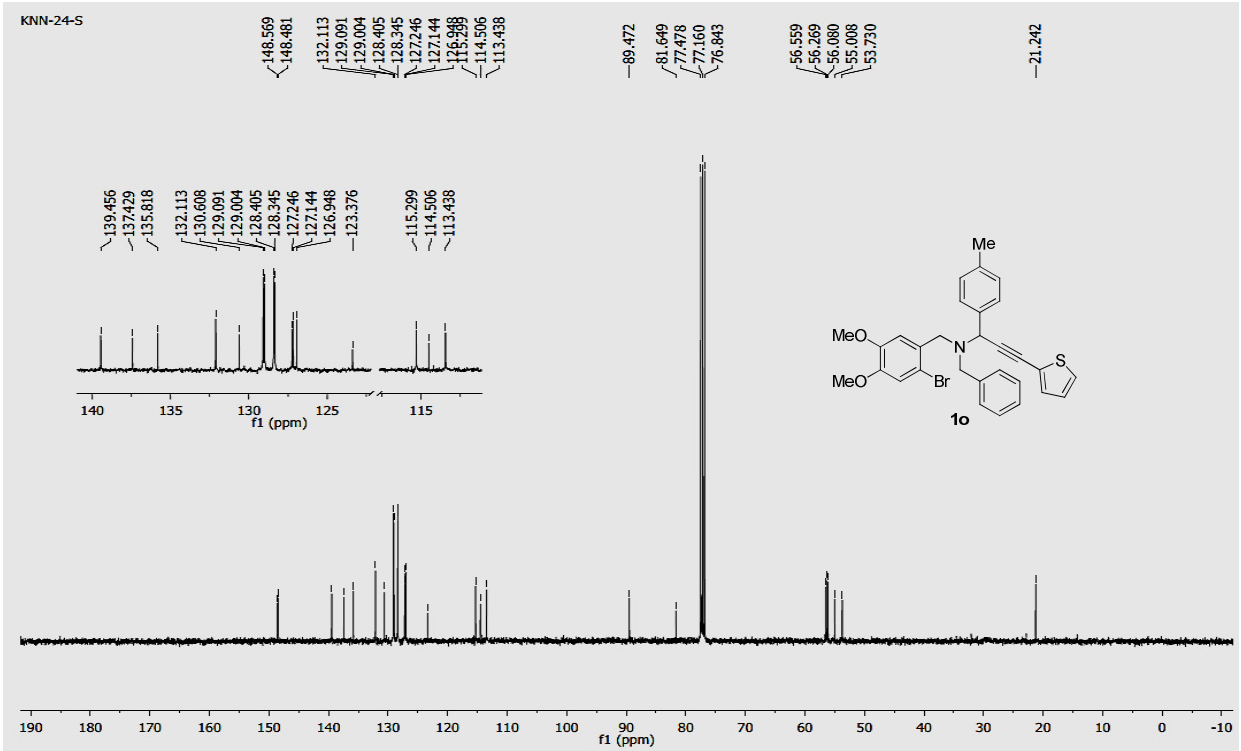
^{1}H-NMR spectrum of compound **1n**



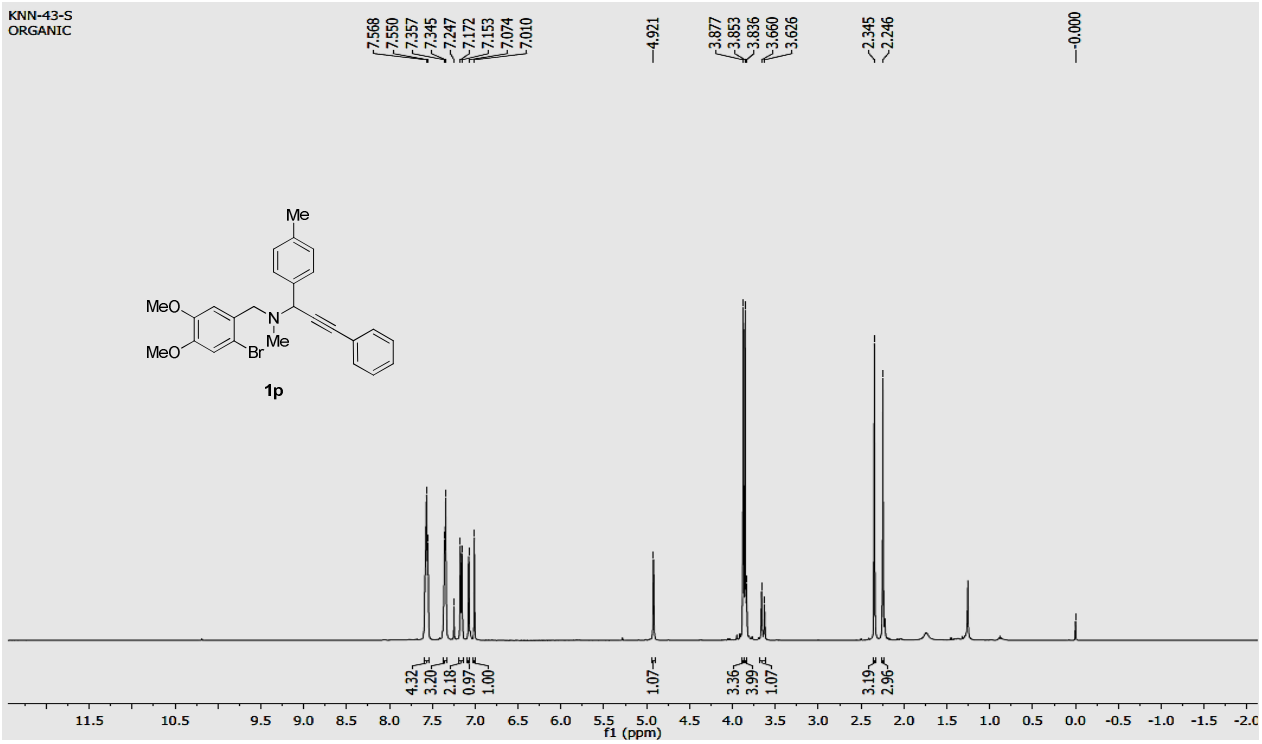
^{13}C-NMR spectrum of compound **1n**



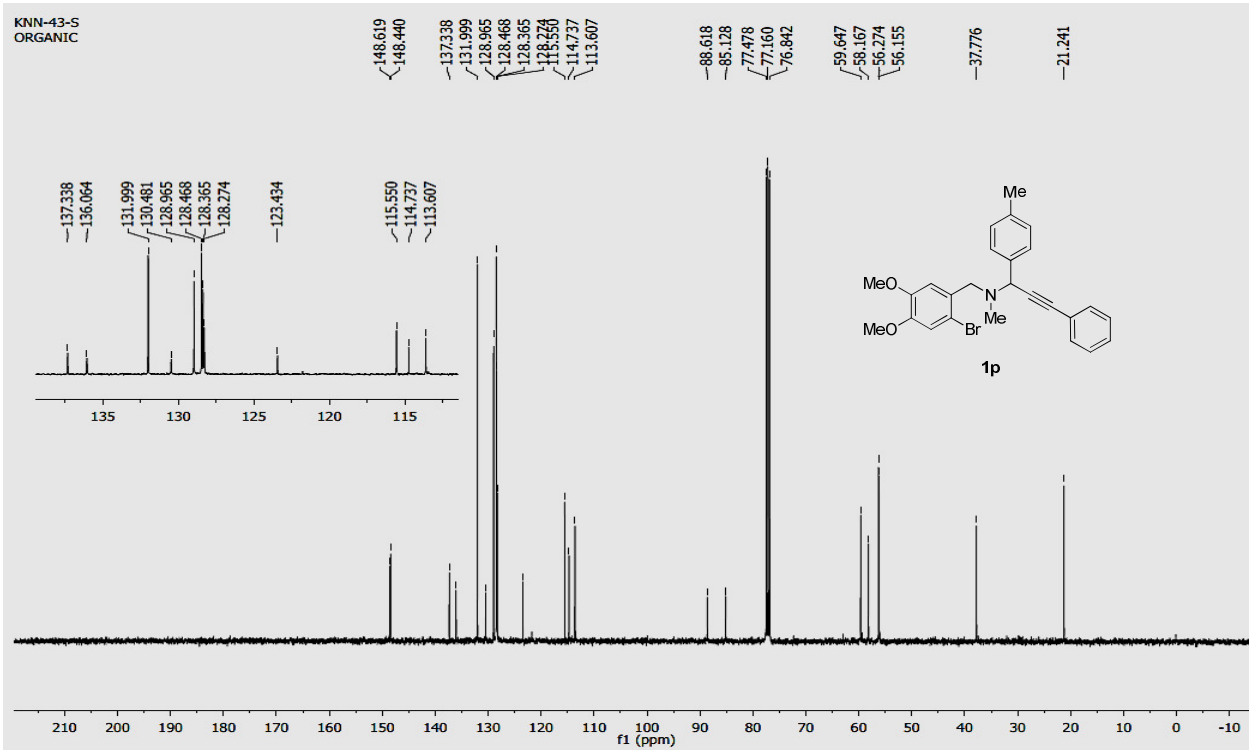
^{1}H-NMR spectrum of compound **1o**



^{13}C-NMR spectrum of compound **1o**

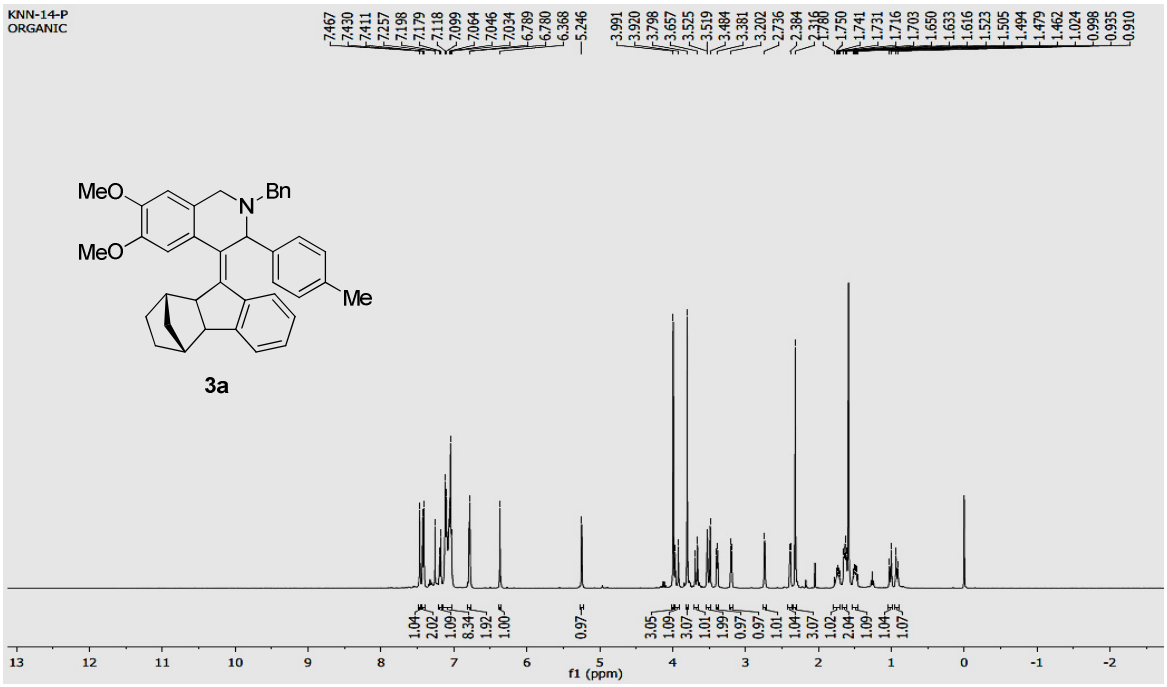


^{1}H-NMR spectrum of compound **1p**

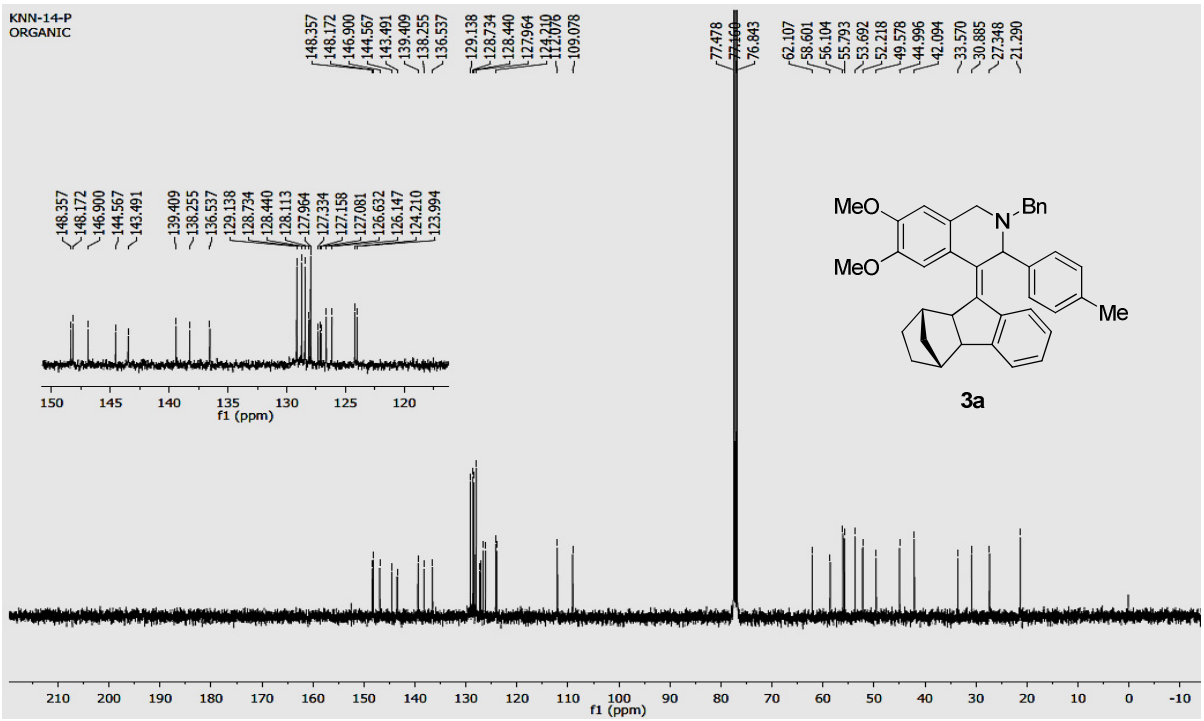


^{13}C-NMR spectrum of compound **1p**

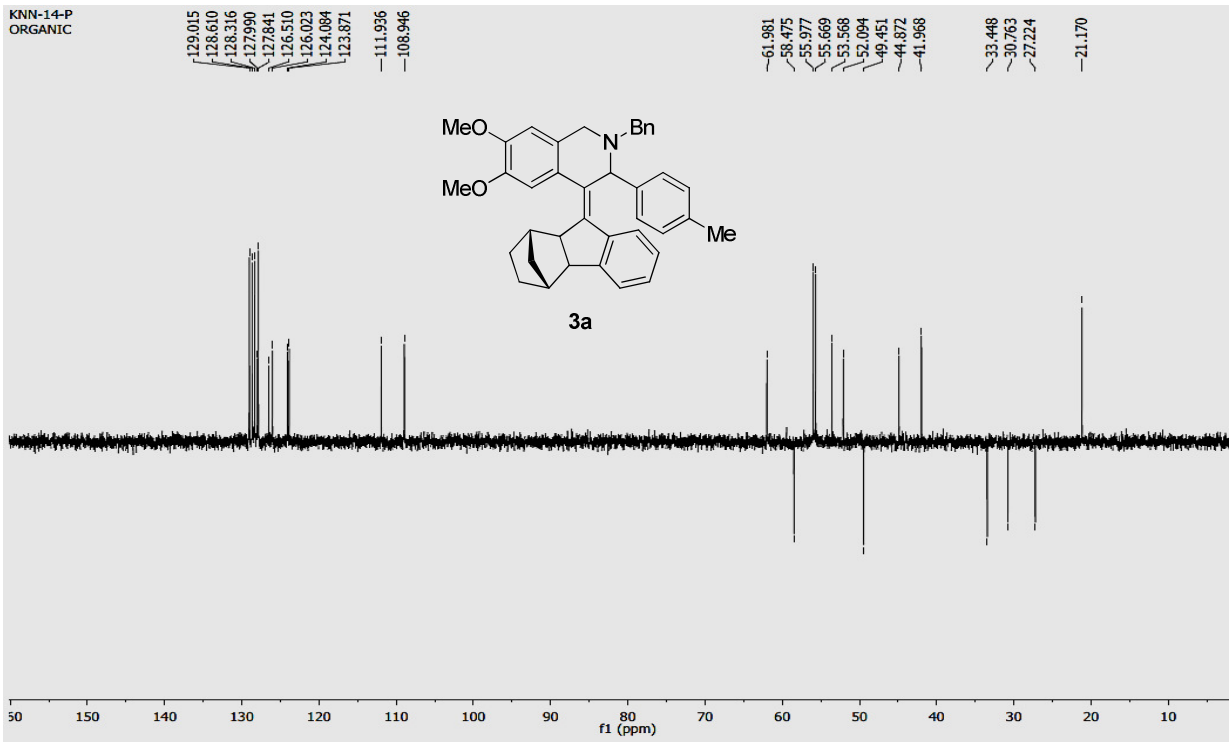
Copies of 1H and 13C NMR and HR-MS of the compounds (3a-p)



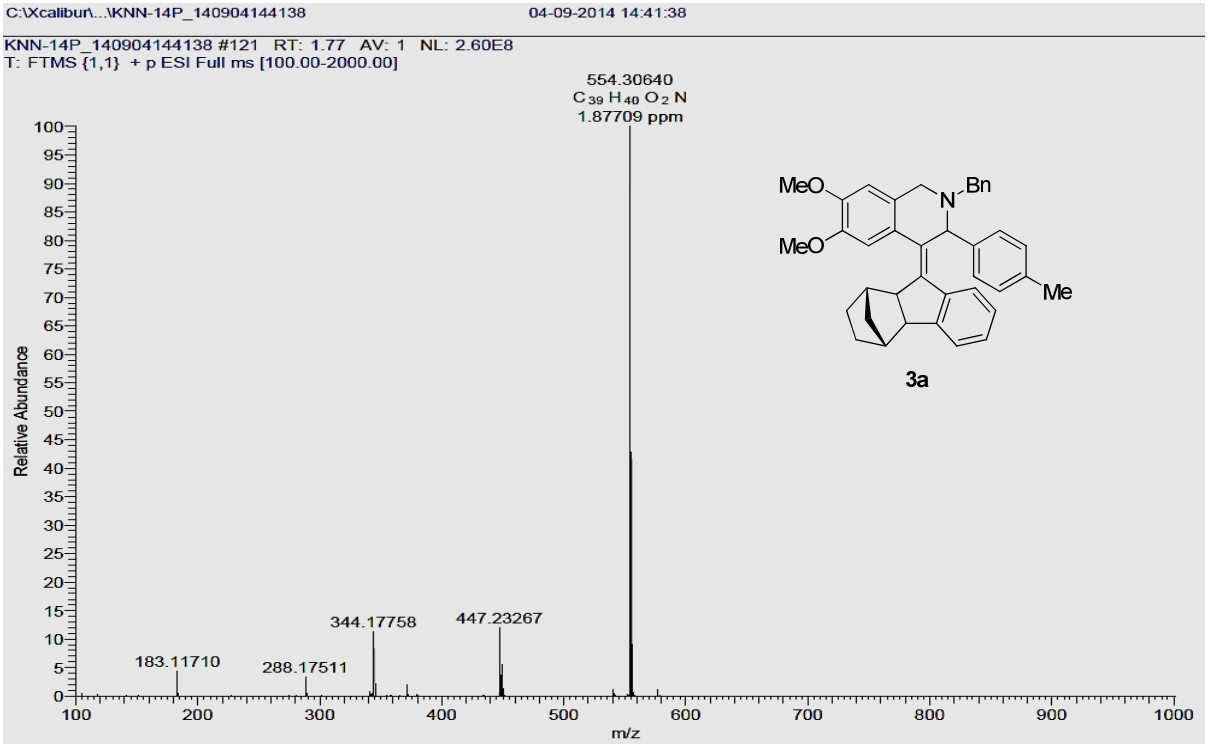
^{1}H-NMR spectrum of compound **3a**



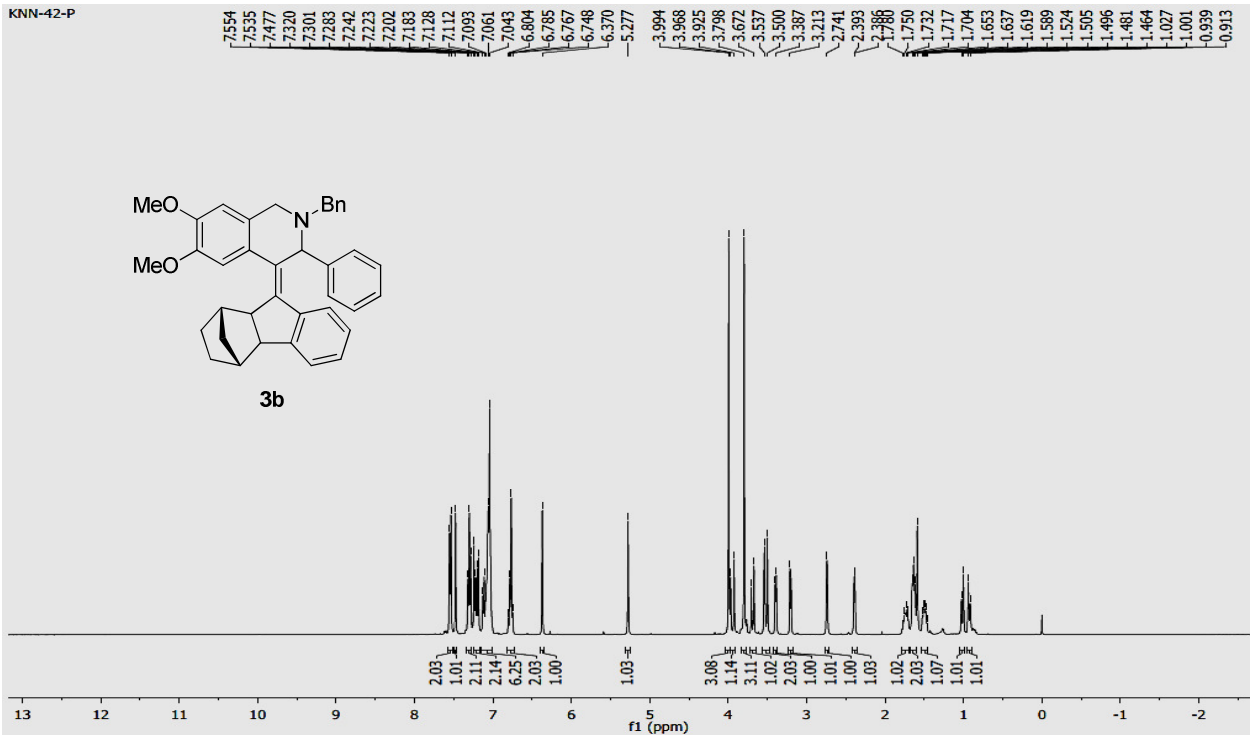
^{13}C-NMR spectrum of compound **3a**



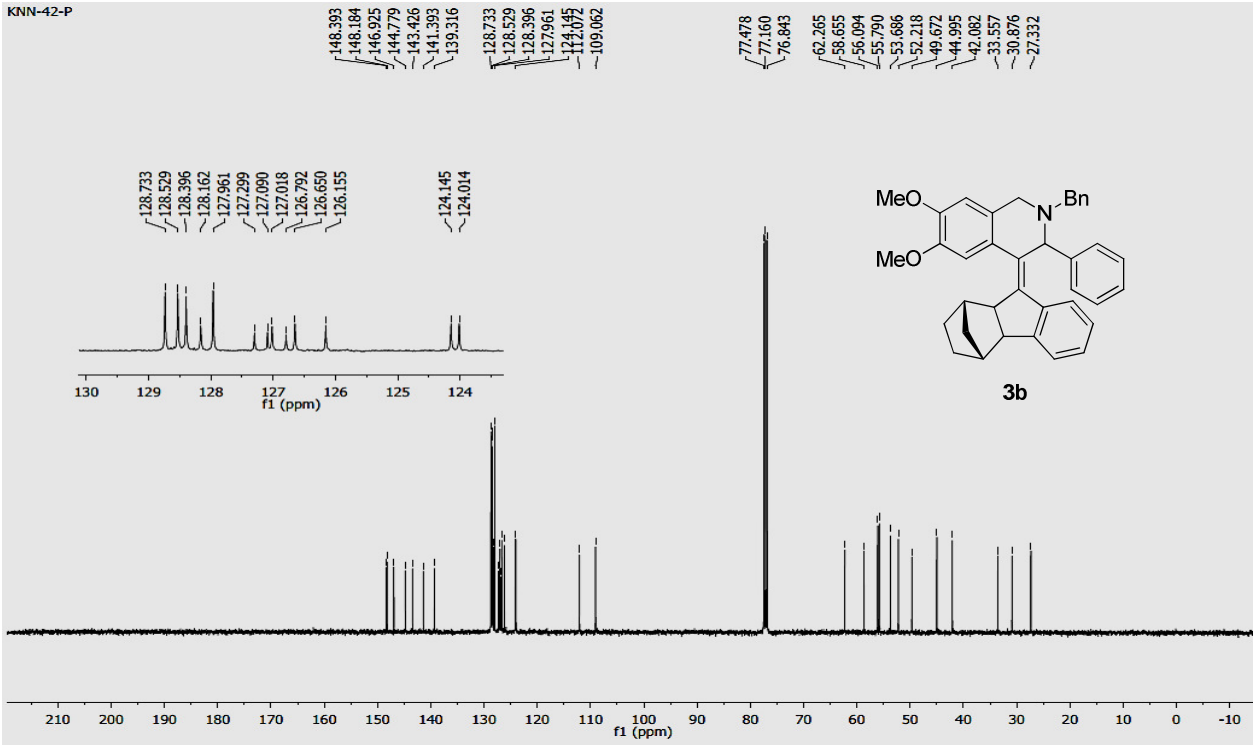
DEPT-135 NMR spectrum of compound **3a**



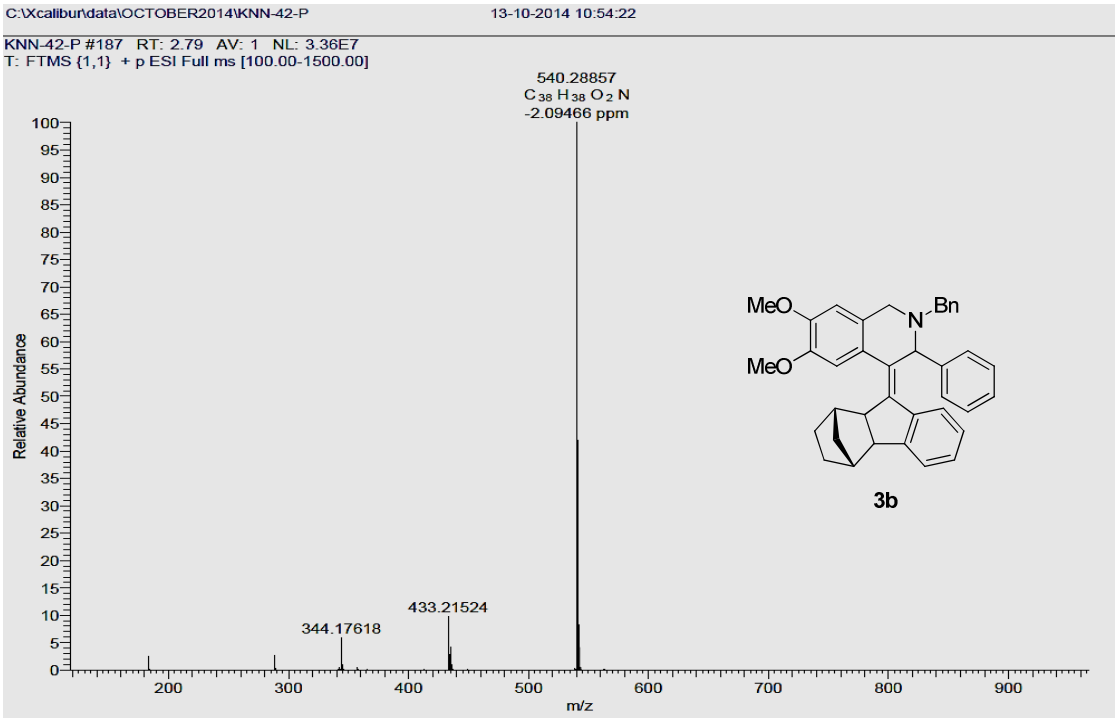
HRMS spectrum of compound **3a**



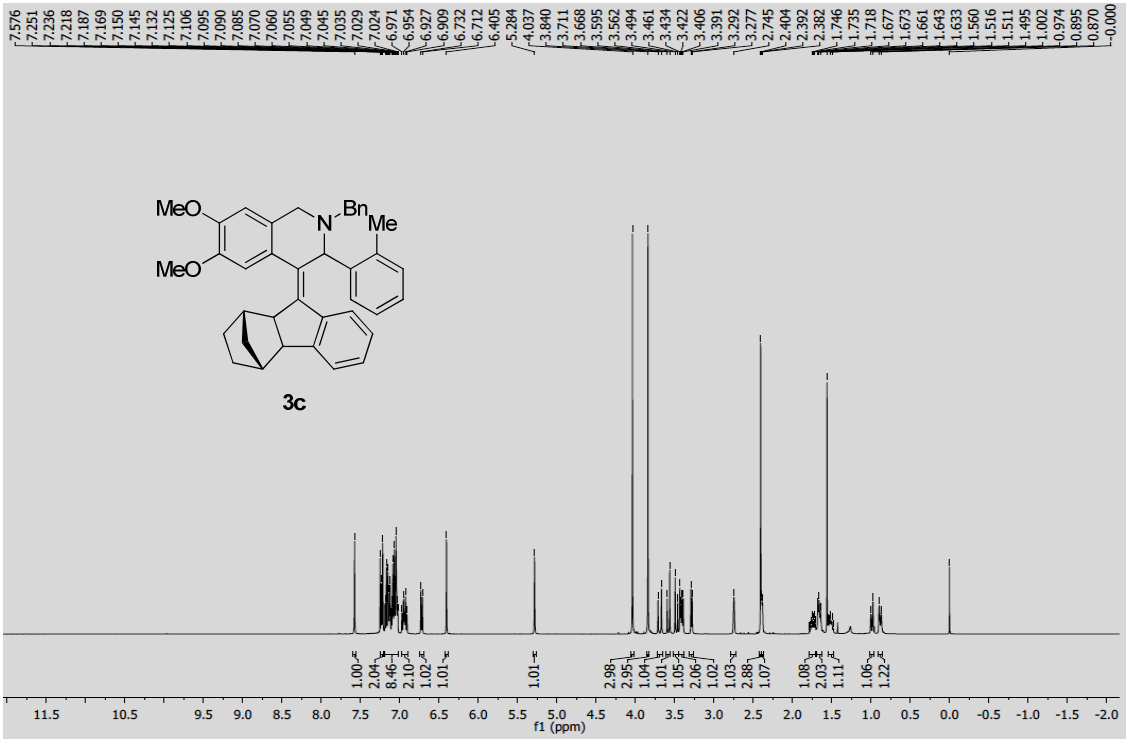
^{1}H-NMR spectrum of compound **3b**



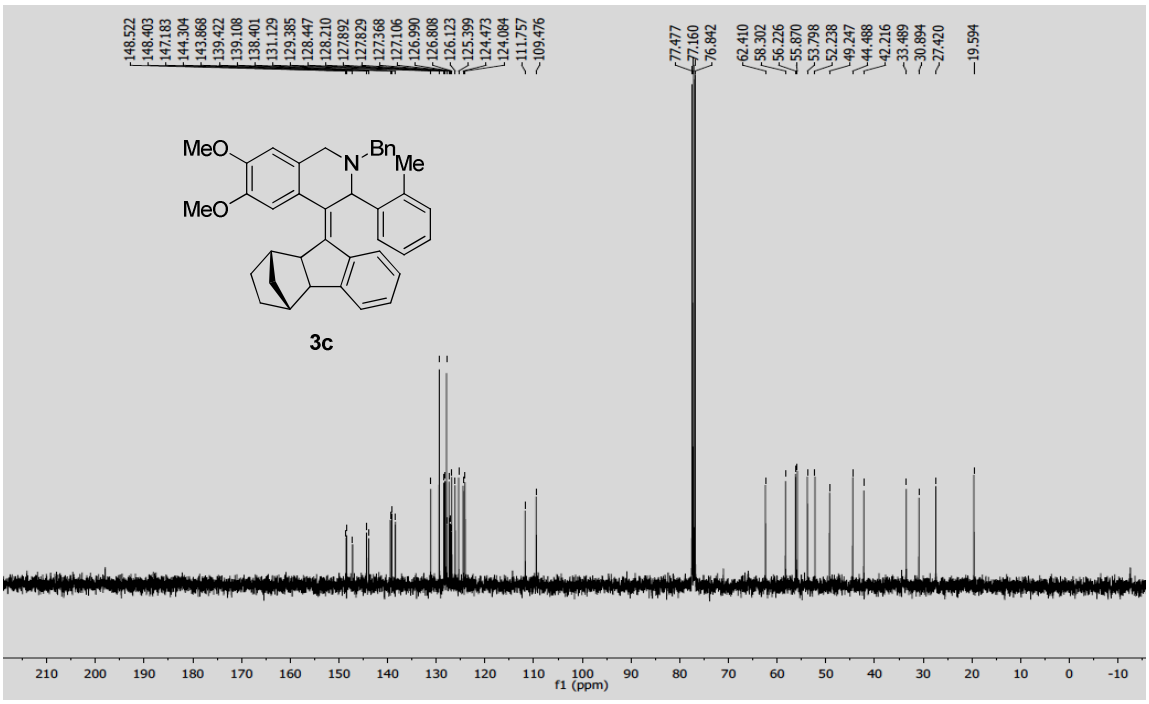
^{13}C-NMR spectrum of compound **3b**



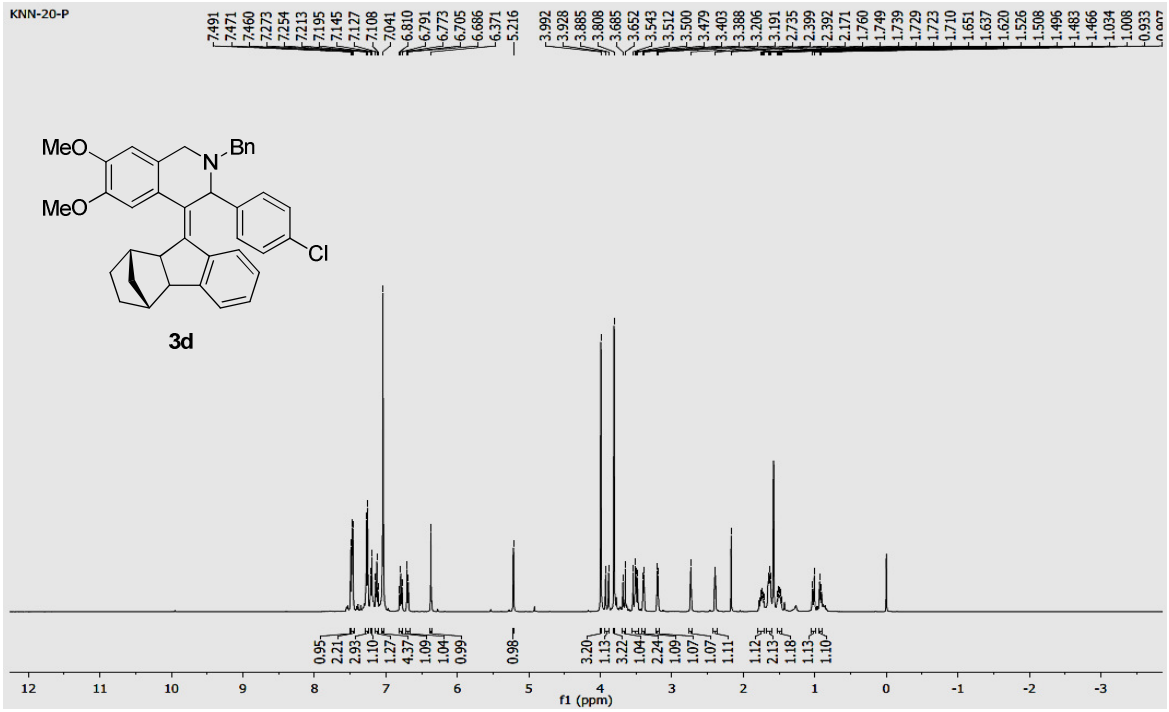
HRMS spectrum of compound **3b**



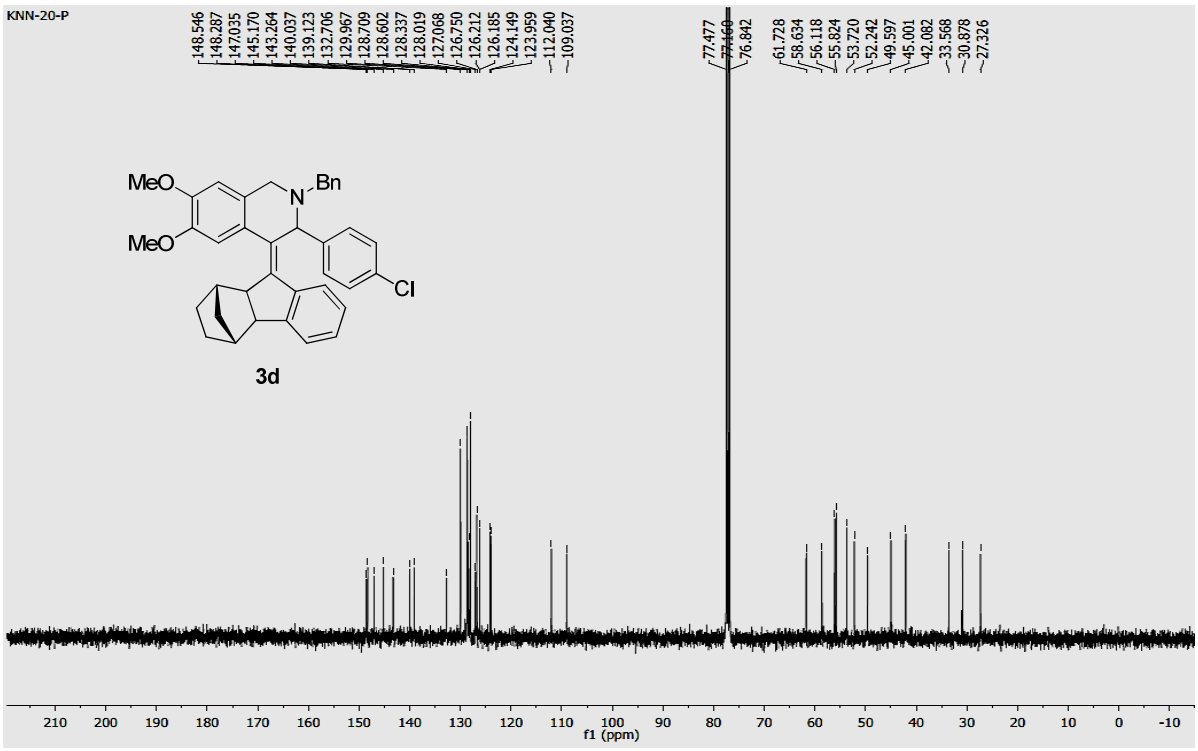
^{1}H-NMR spectrum of compound 3c



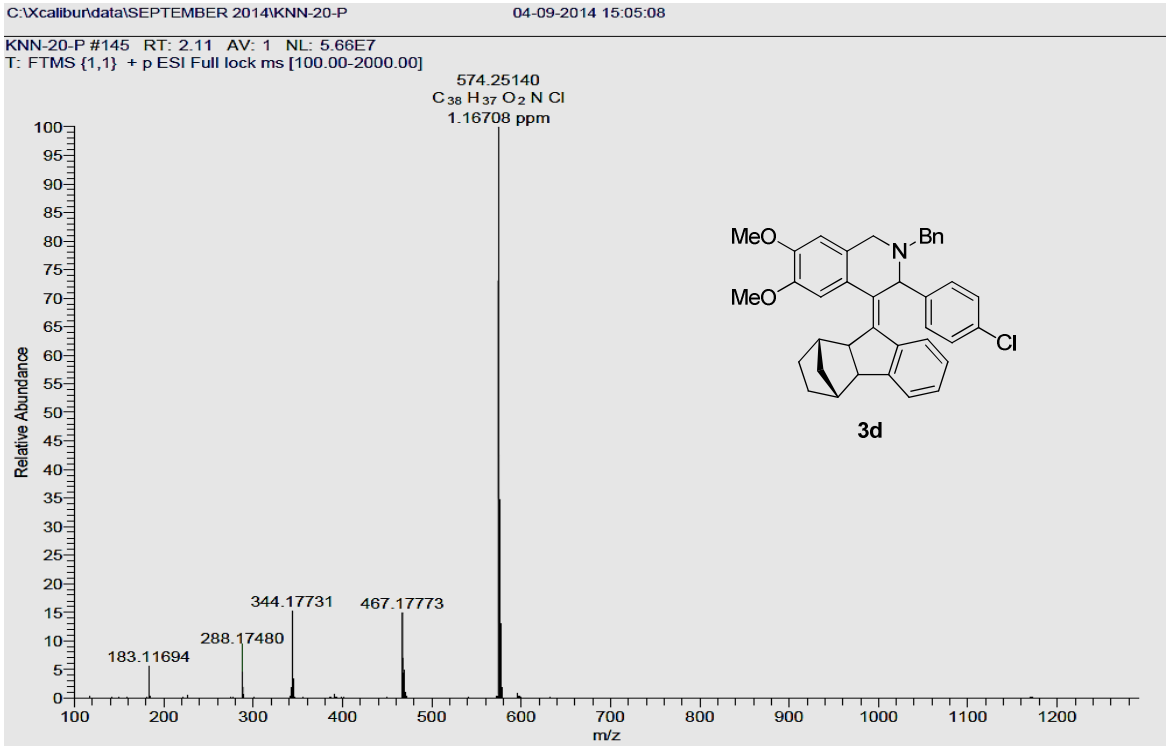
^{13}C-NMR spectrum of compound 3c



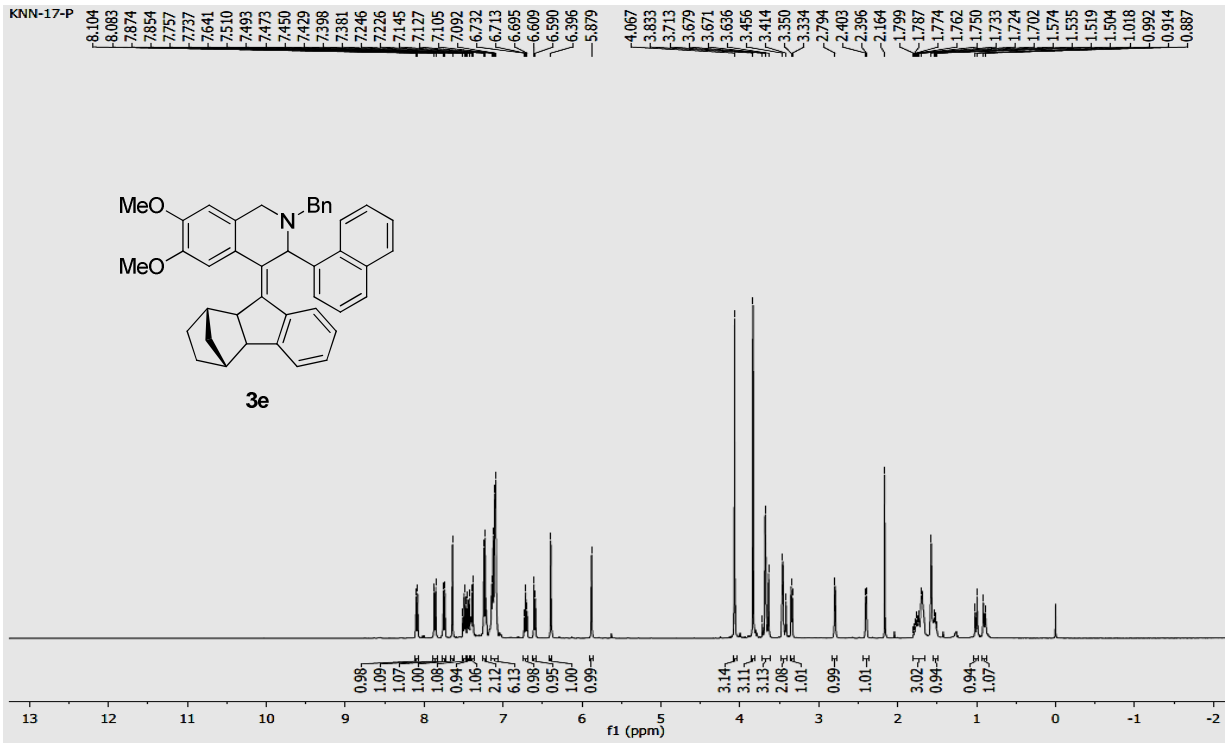
^{1}H-NMR spectrum of compound **3d**



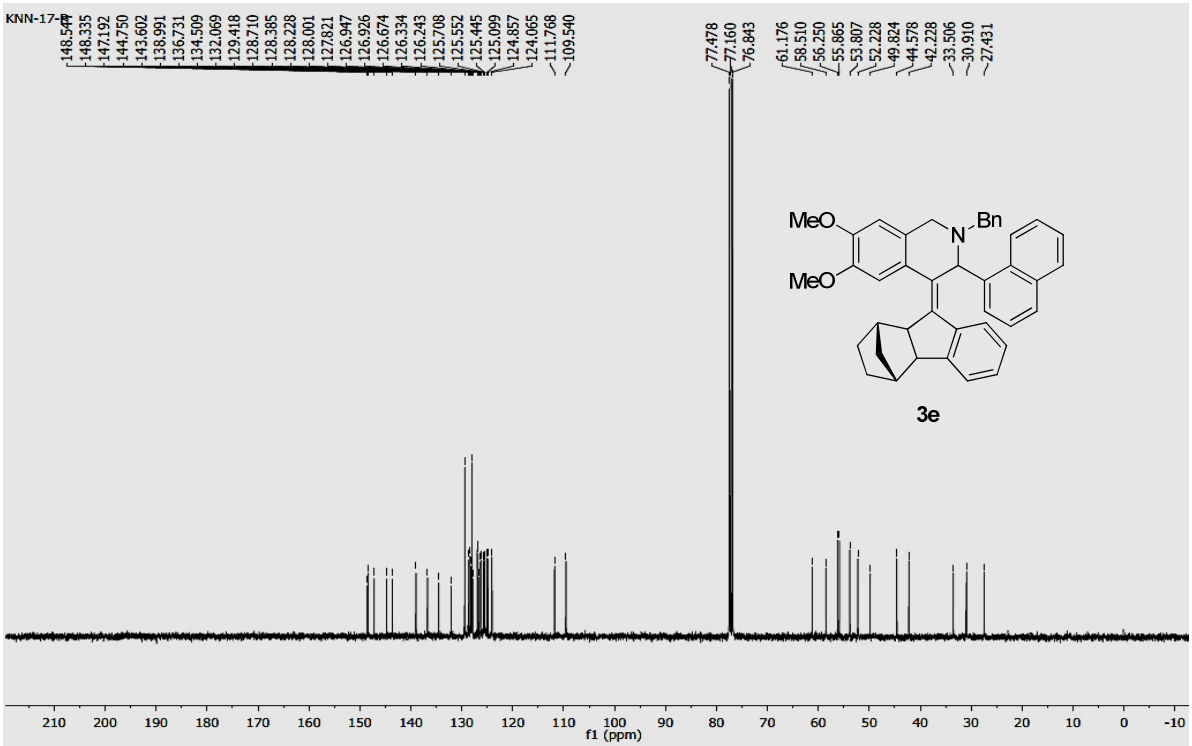
^{13}C-NMR spectrum of compound **3d**



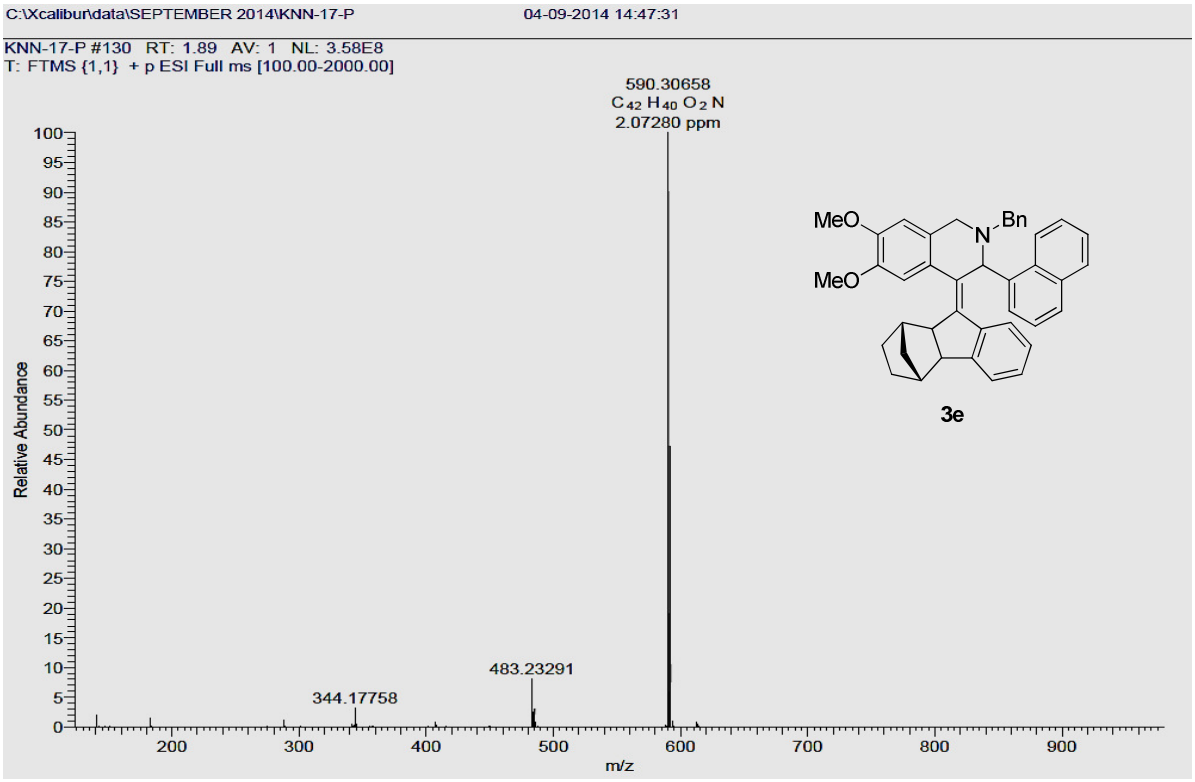
HRMS spectrum of compound **3d**



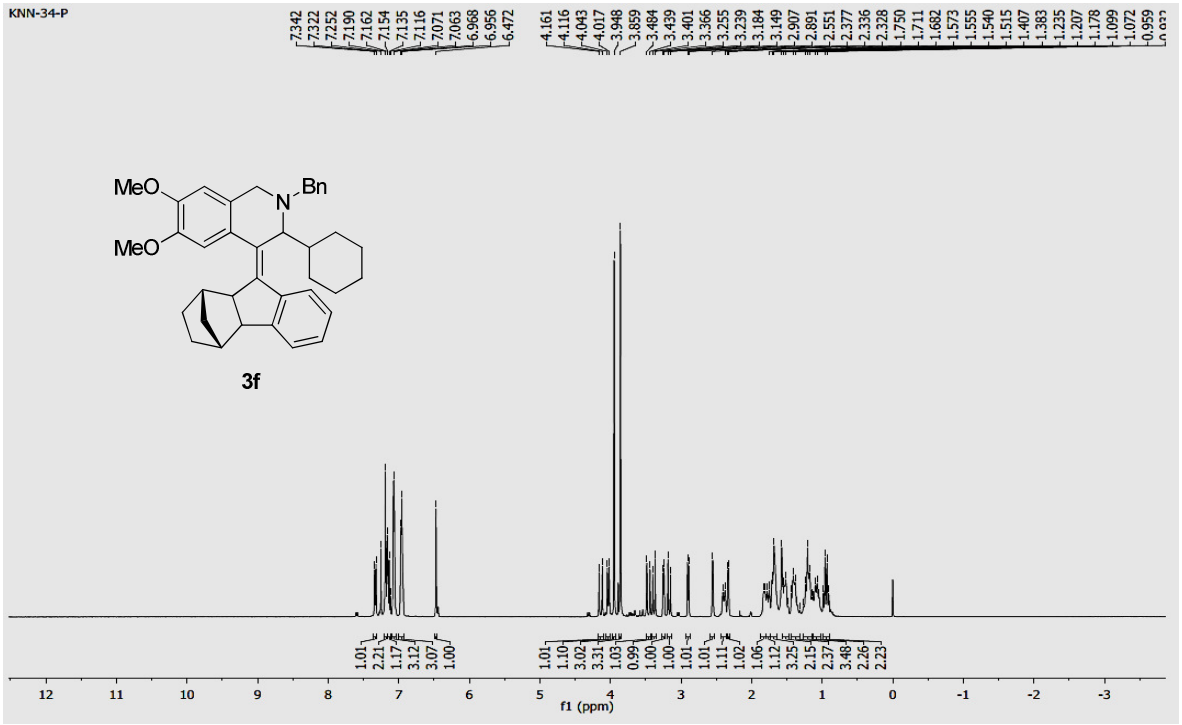
^{1}H-NMR spectrum of compound **3e**



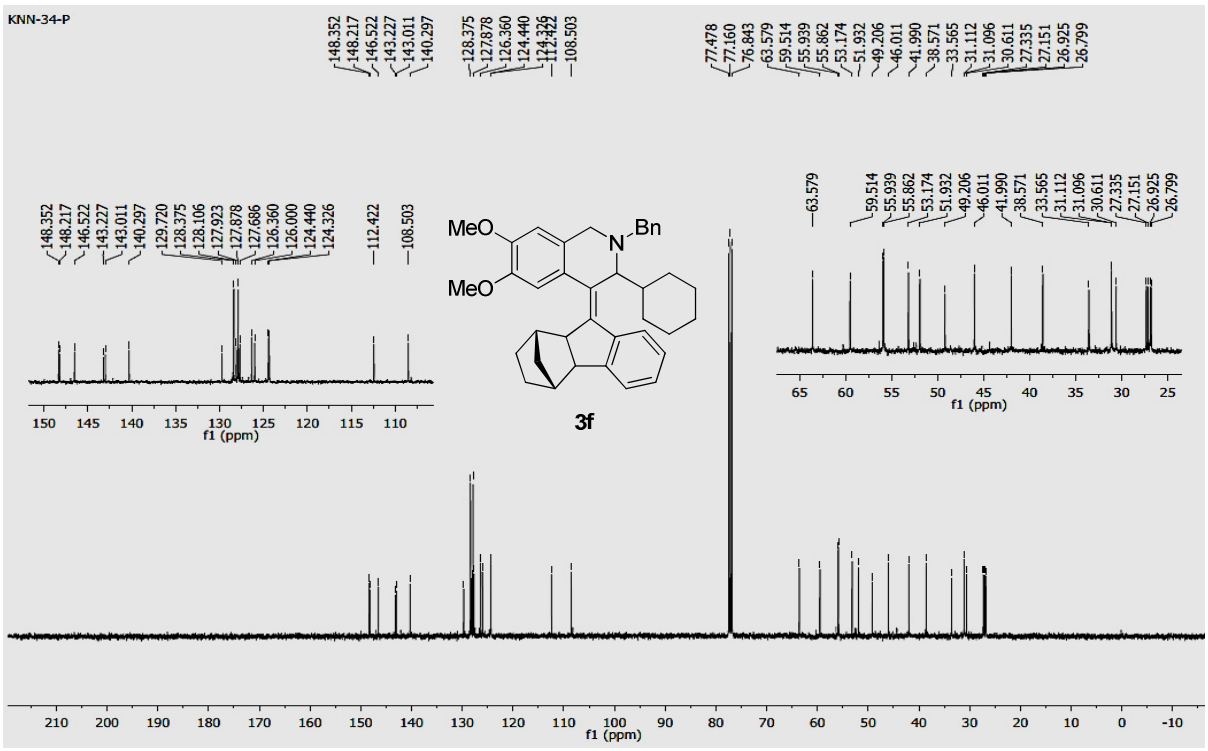
^{13}C-NMR spectrum of compound **3e**



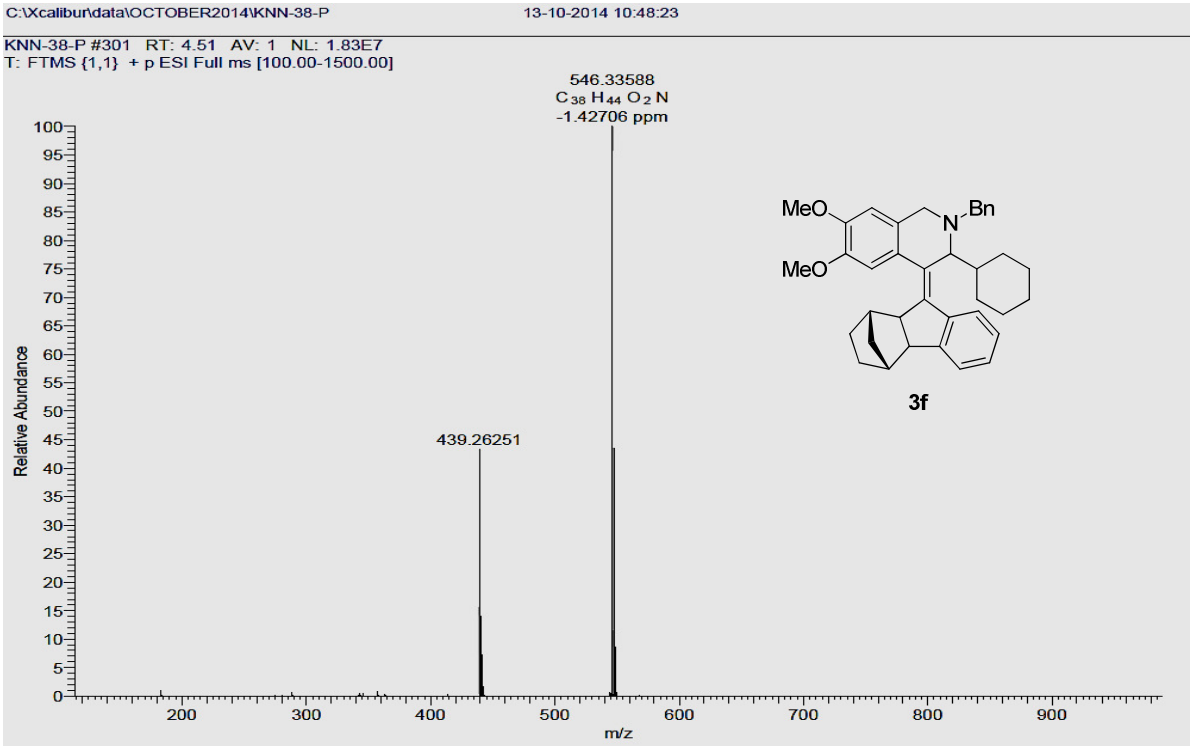
HRMS spectrum of compound **3e**



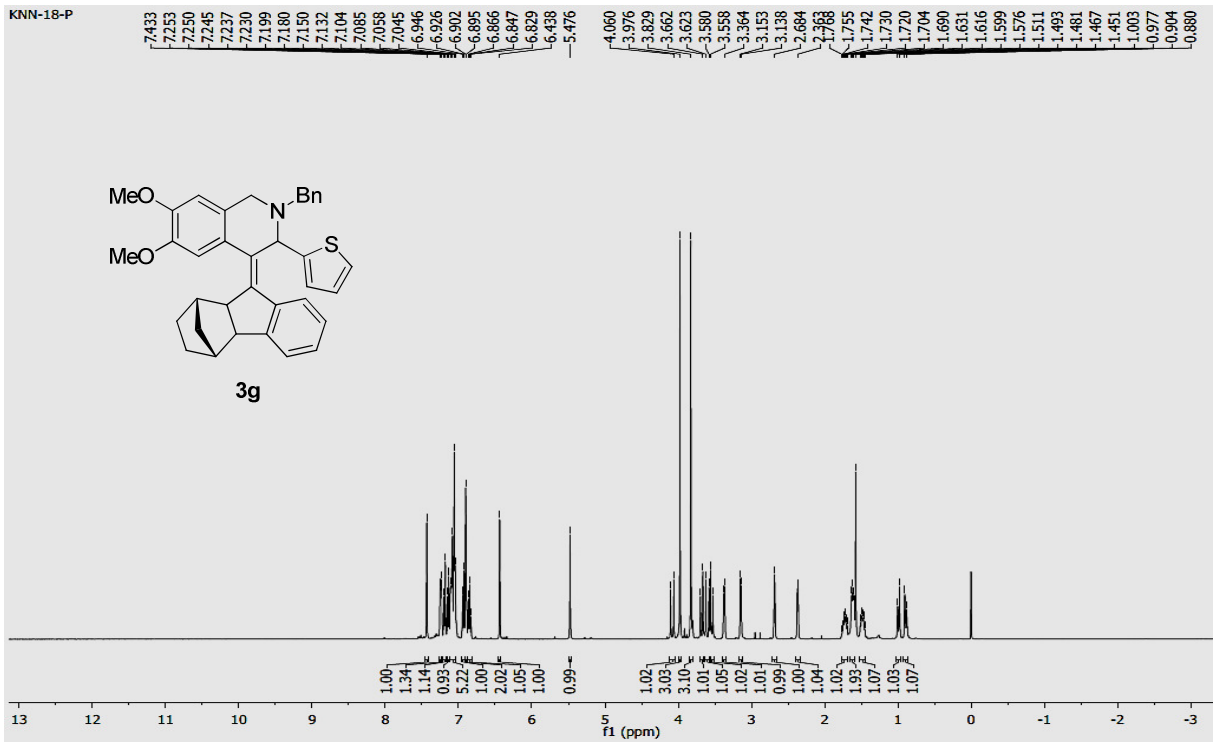
^{1}H-NMR spectrum of compound **3f**



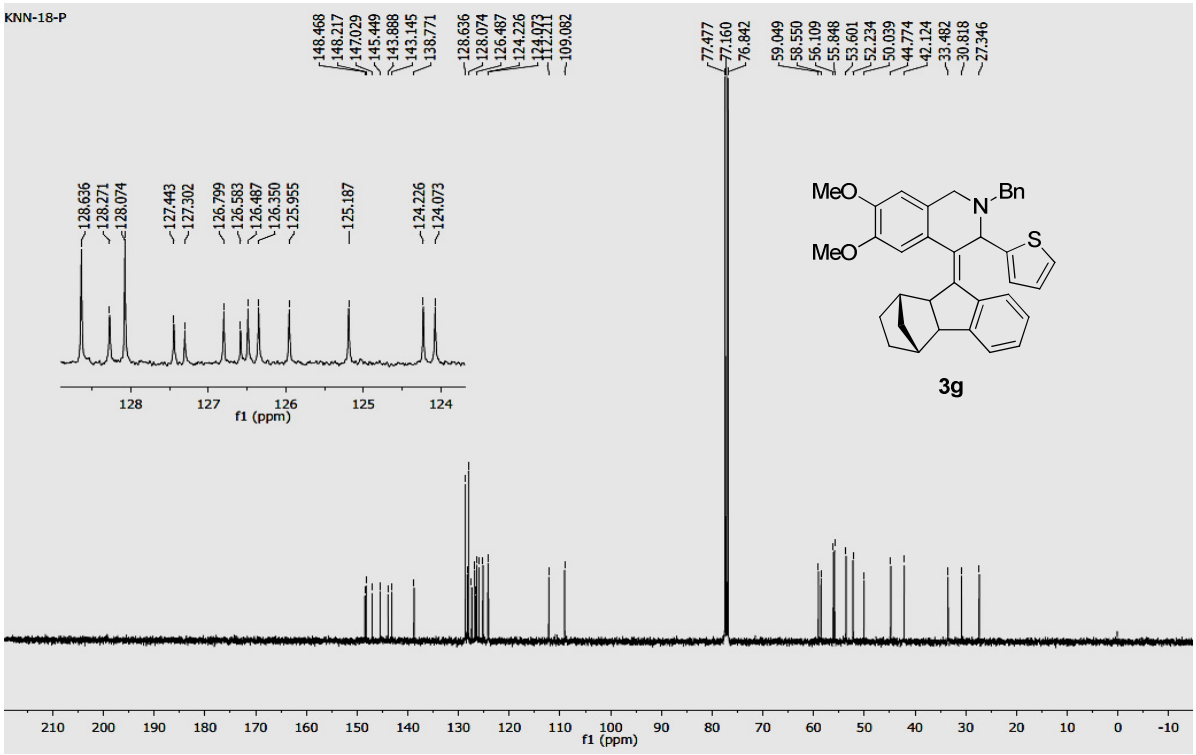
^{13}C-NMR spectrum of compound **3f**



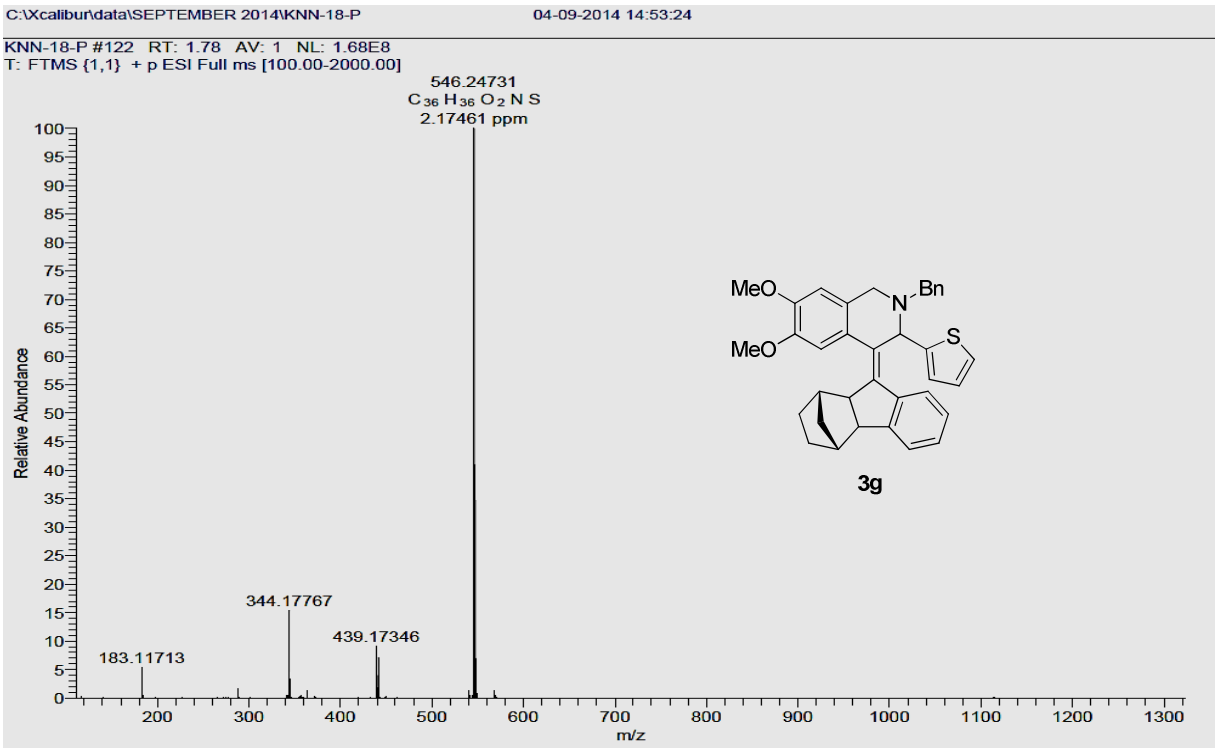
HRMS spectrum of compound **3f**



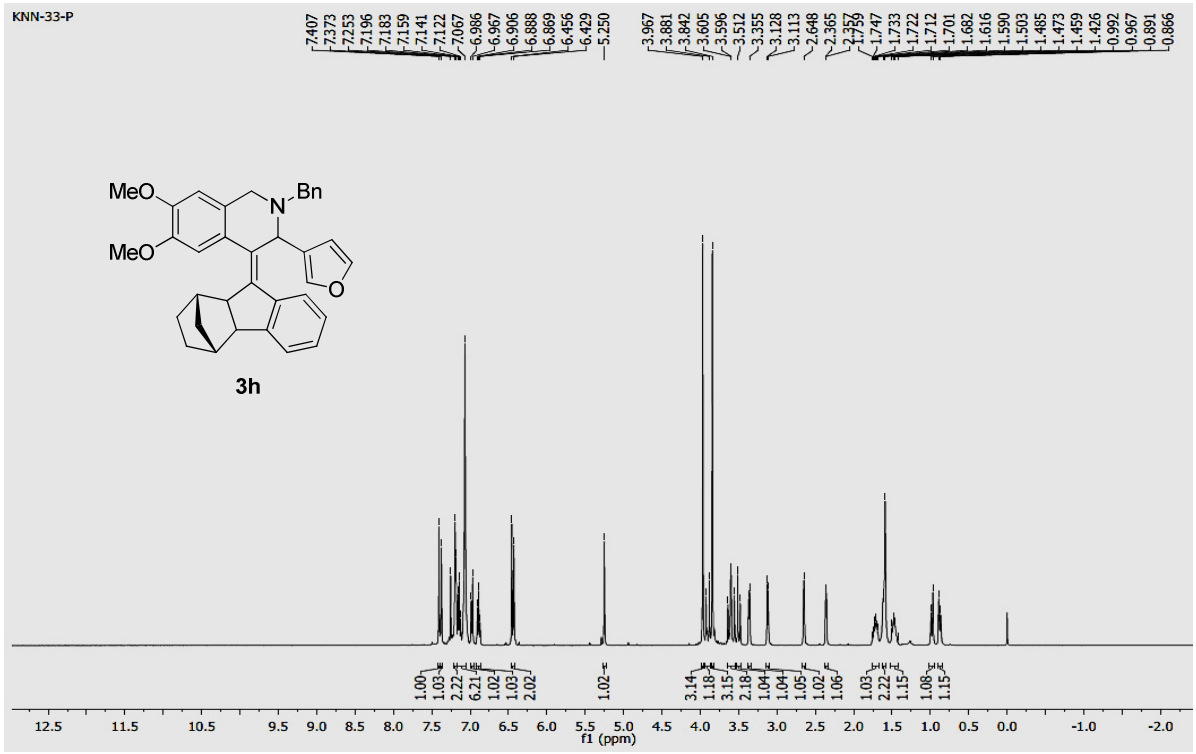
^{1}H-NMR spectrum of compound **3g**



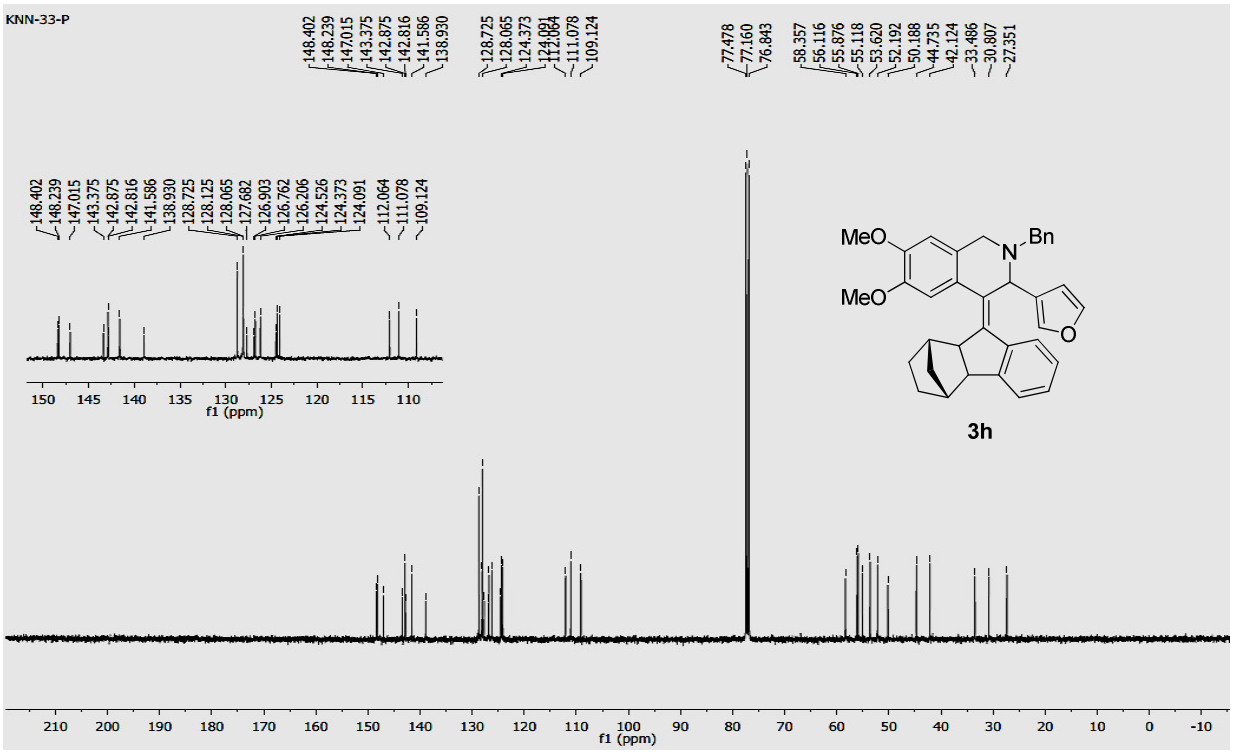
^{13}C-NMR spectrum of compound **3g**



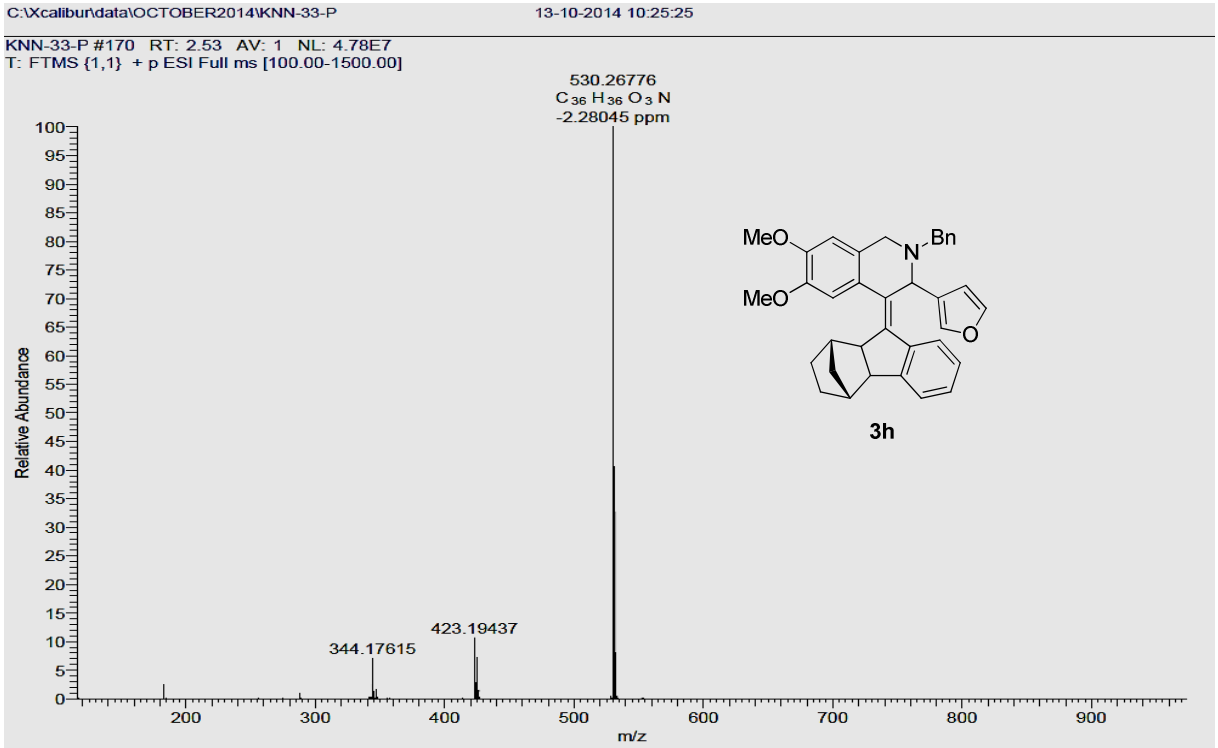
HRMS spectrum of compound **3g**



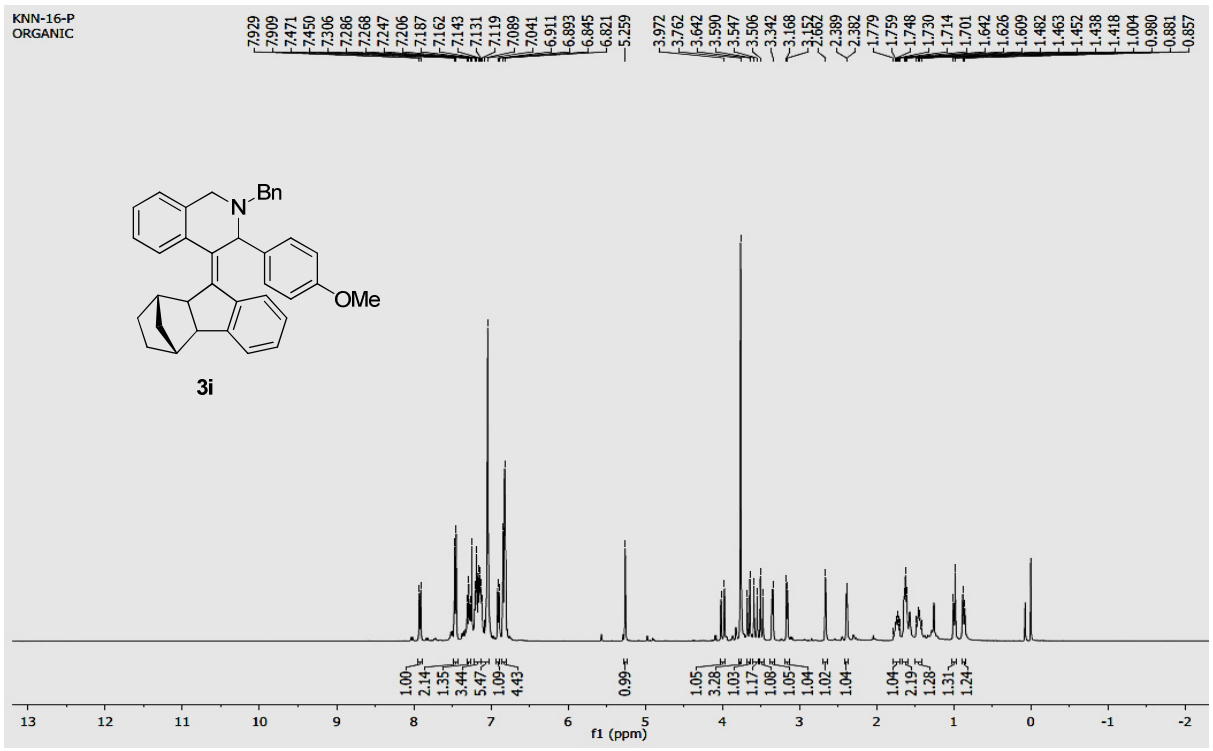
^{1}H-NMR spectrum of compound **3h**



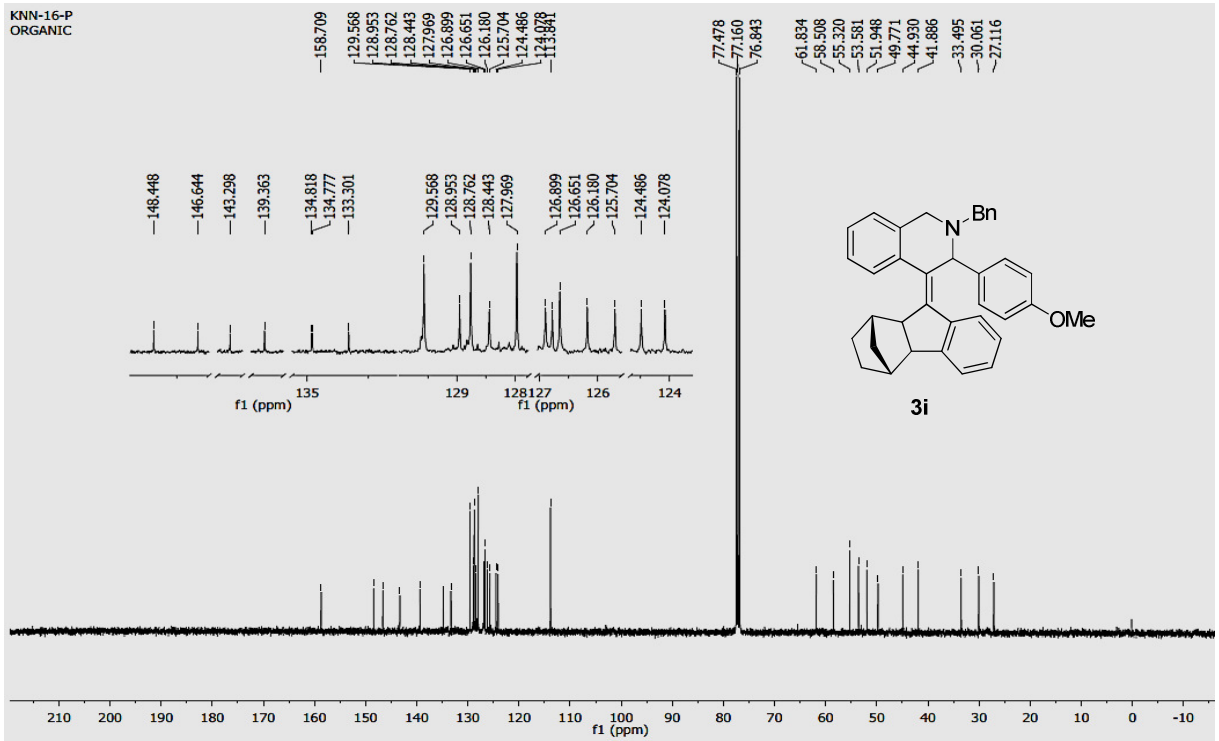
^{13}C-NMR spectrum of compound **3h**



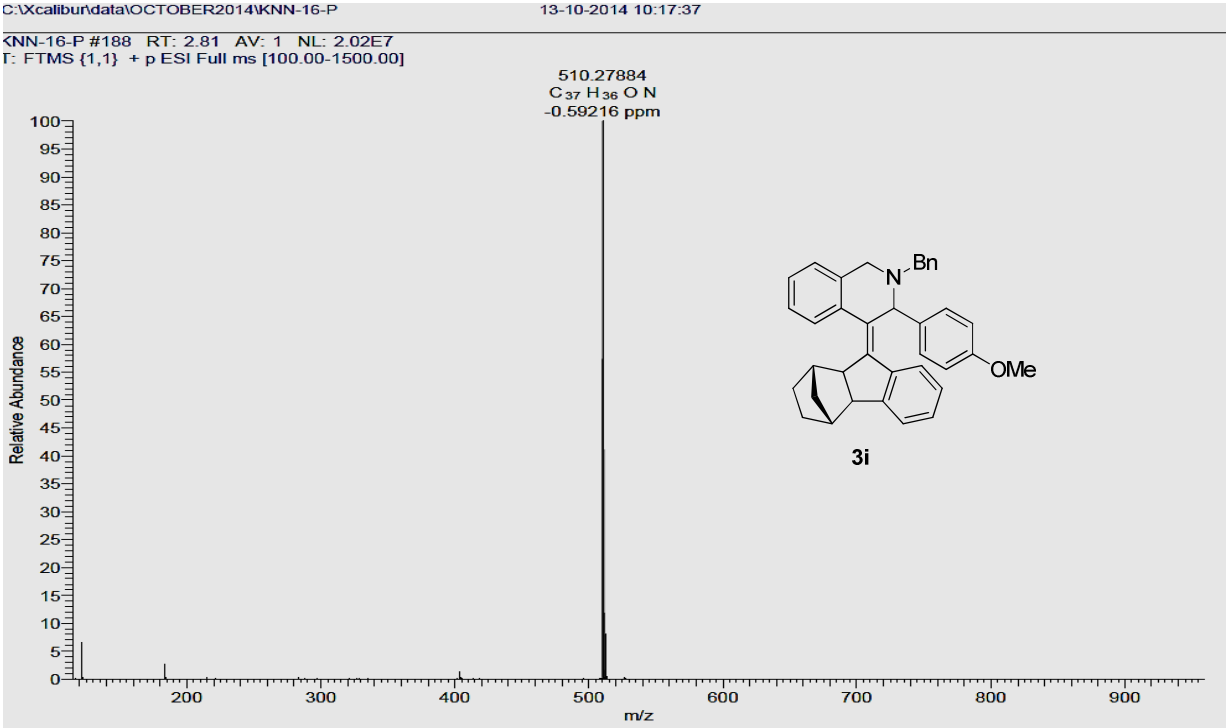
HRMS spectrum of compound **3h**



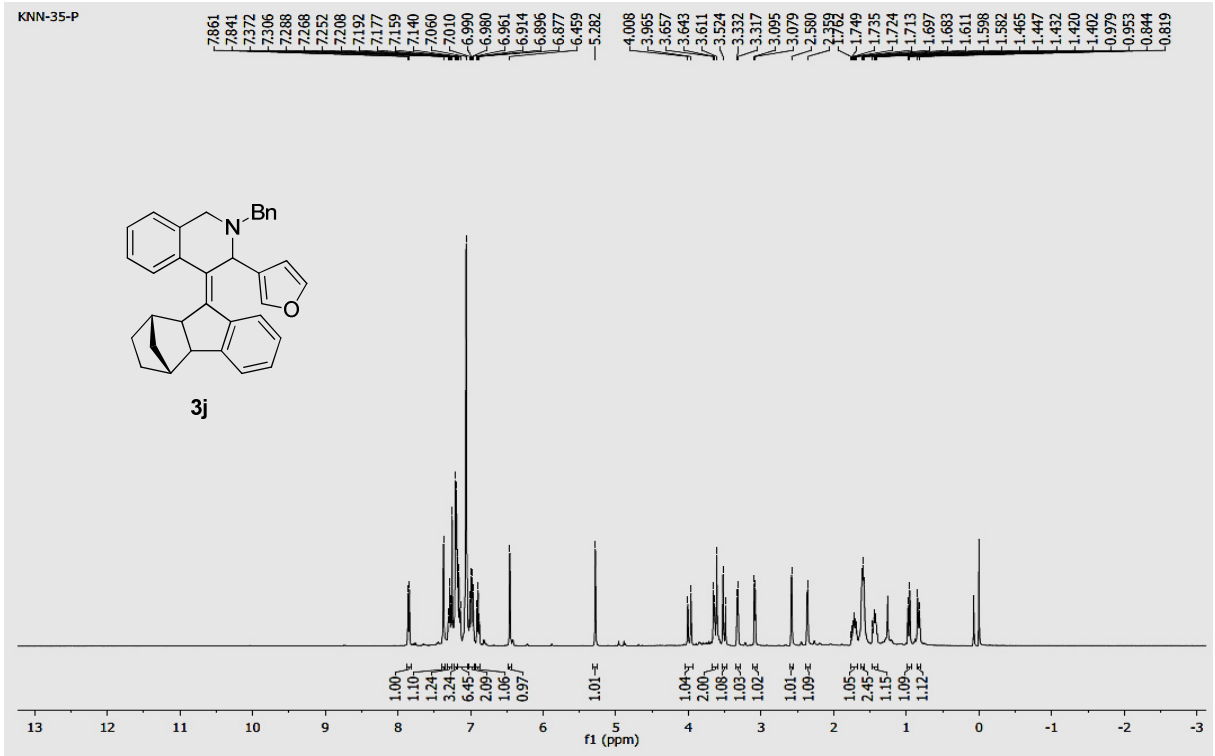
^{1}H-NMR spectrum of compound **3i**



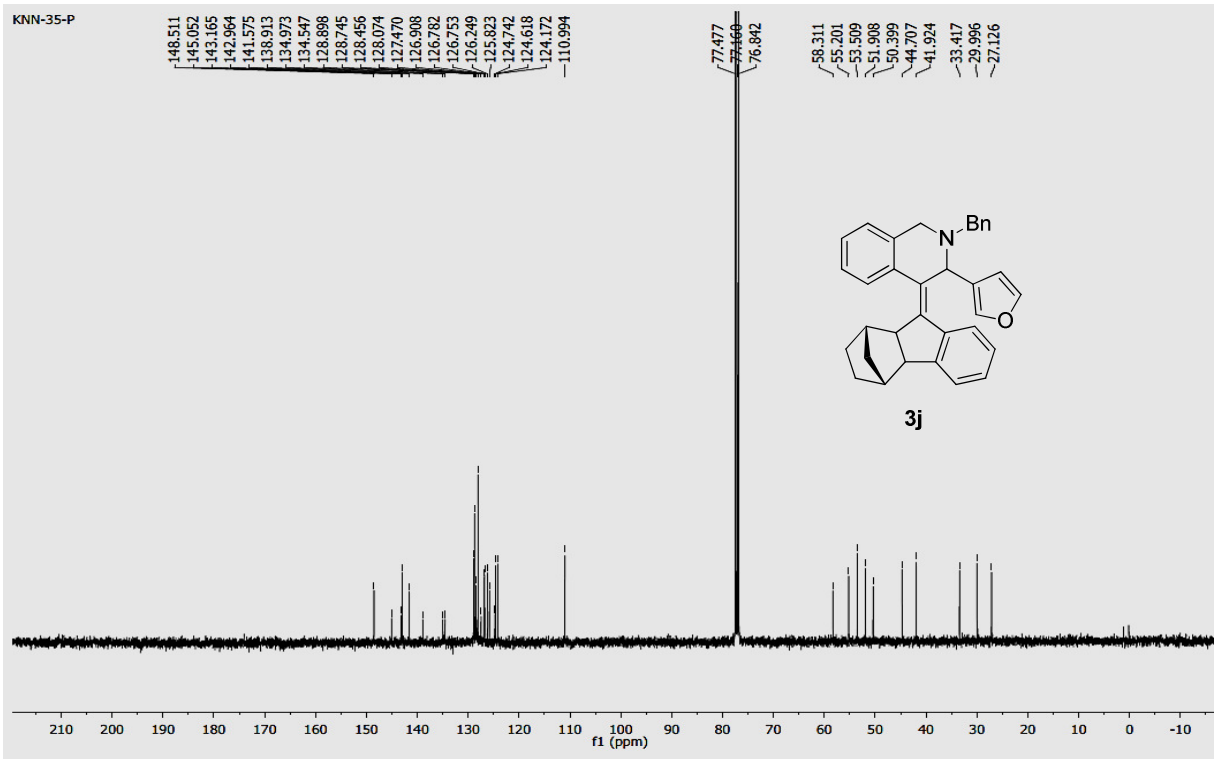
^{13}C-NMR spectrum of compound **3i**



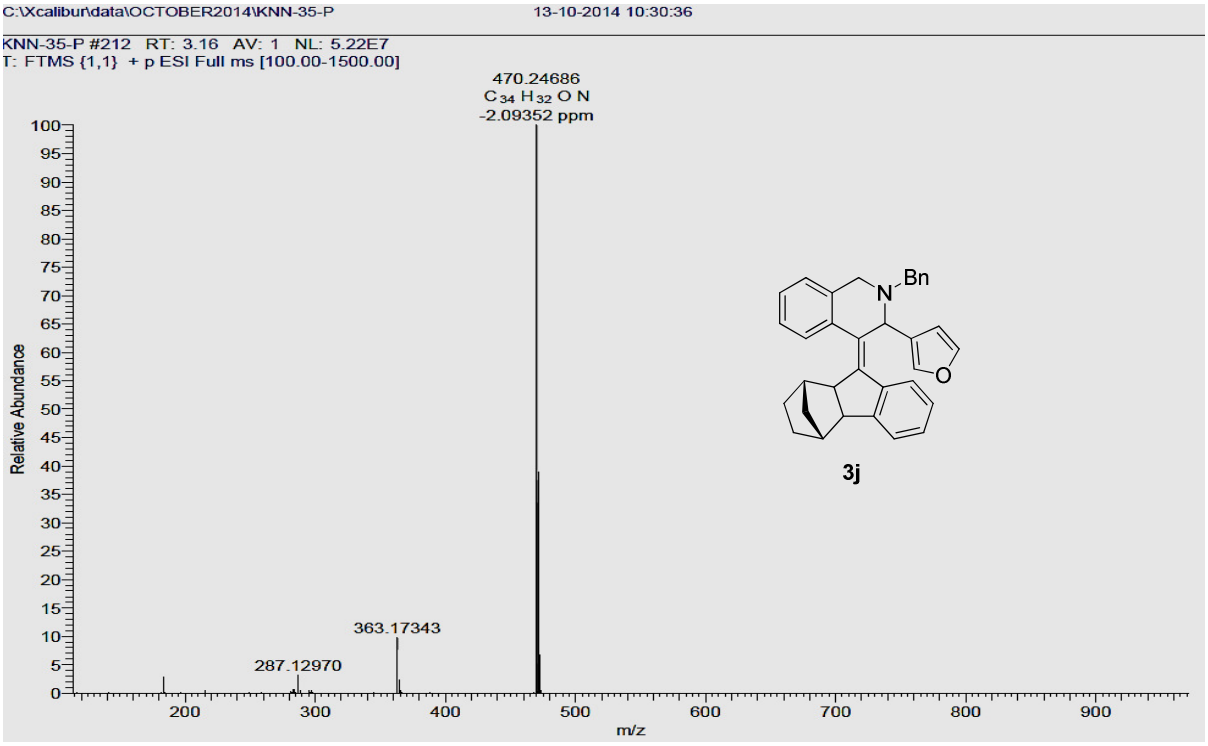
HRMS spectrum of compound **3i**



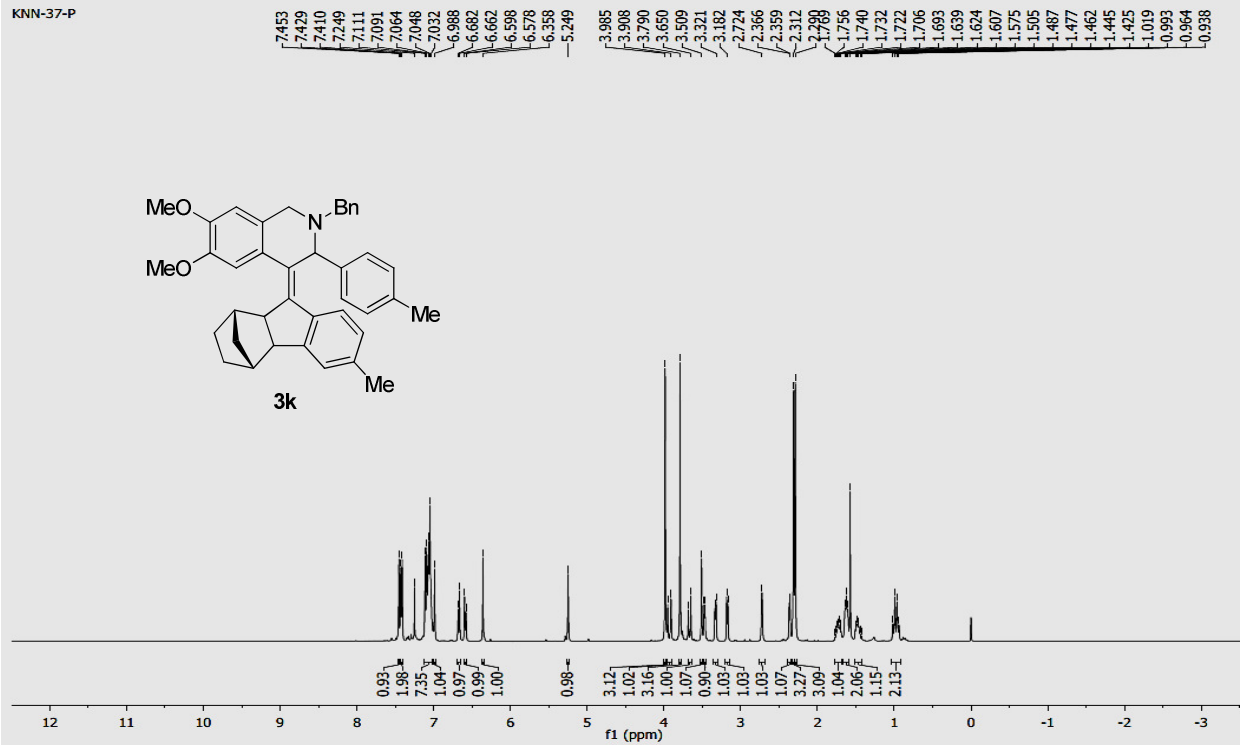
^{1}H-NMR spectrum of compound **3j**



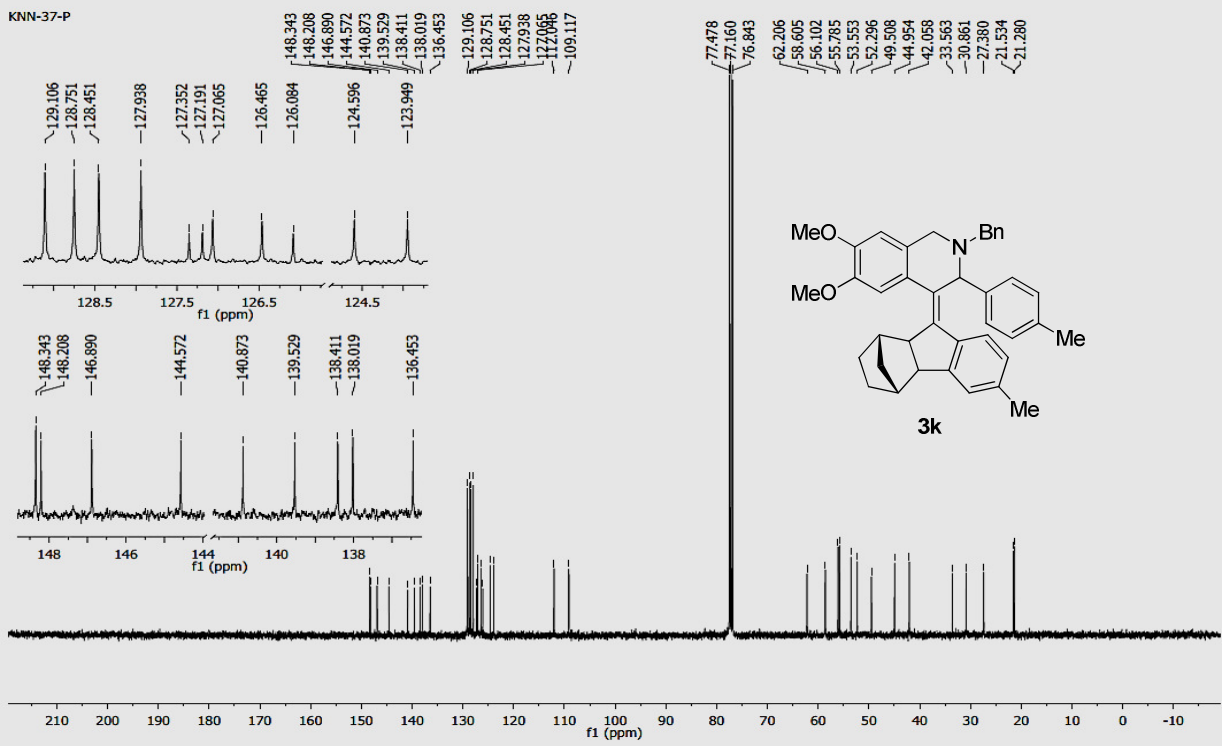
^{13}C-NMR spectrum of compound **3j**



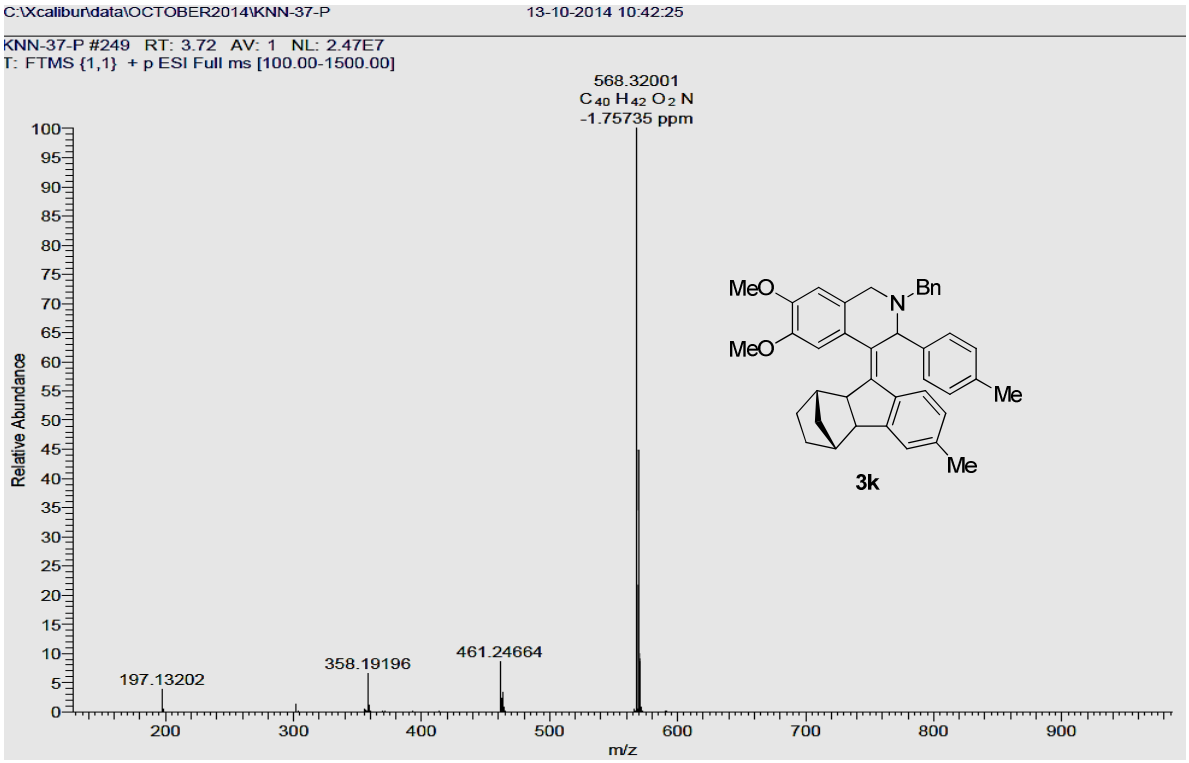
HRMS spectrum of compound **3j**



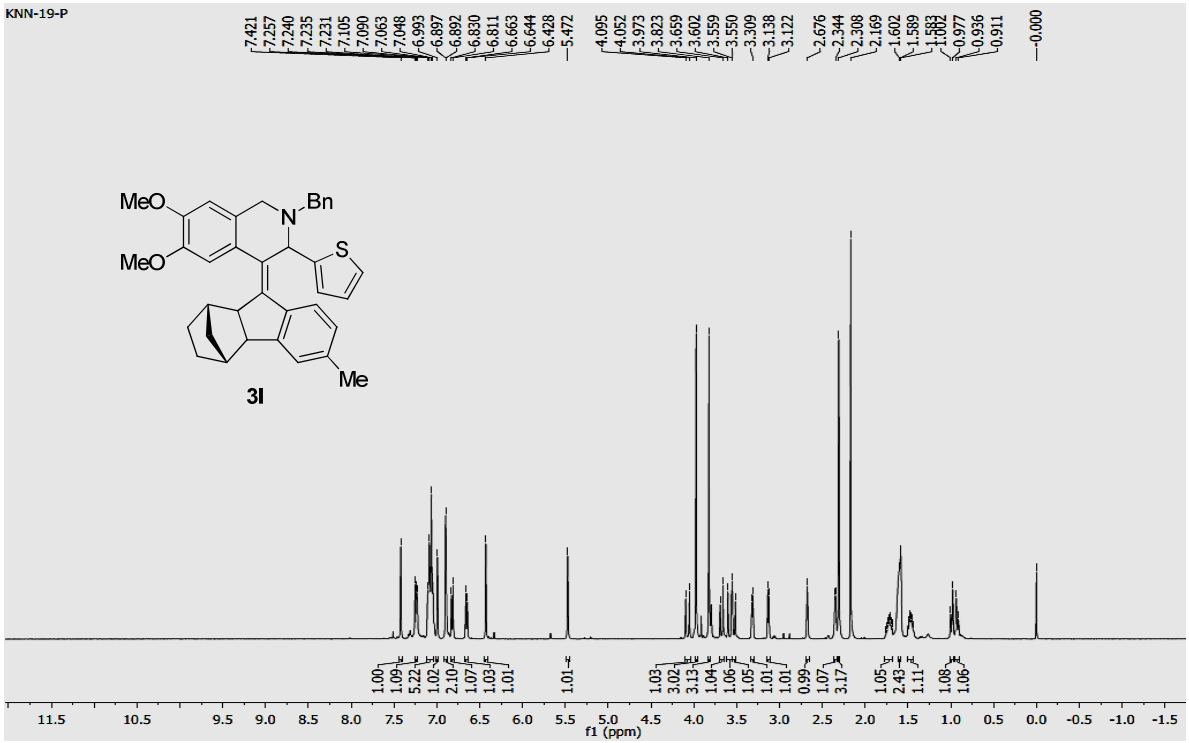
^{1}H-NMR spectrum of compound **3k**



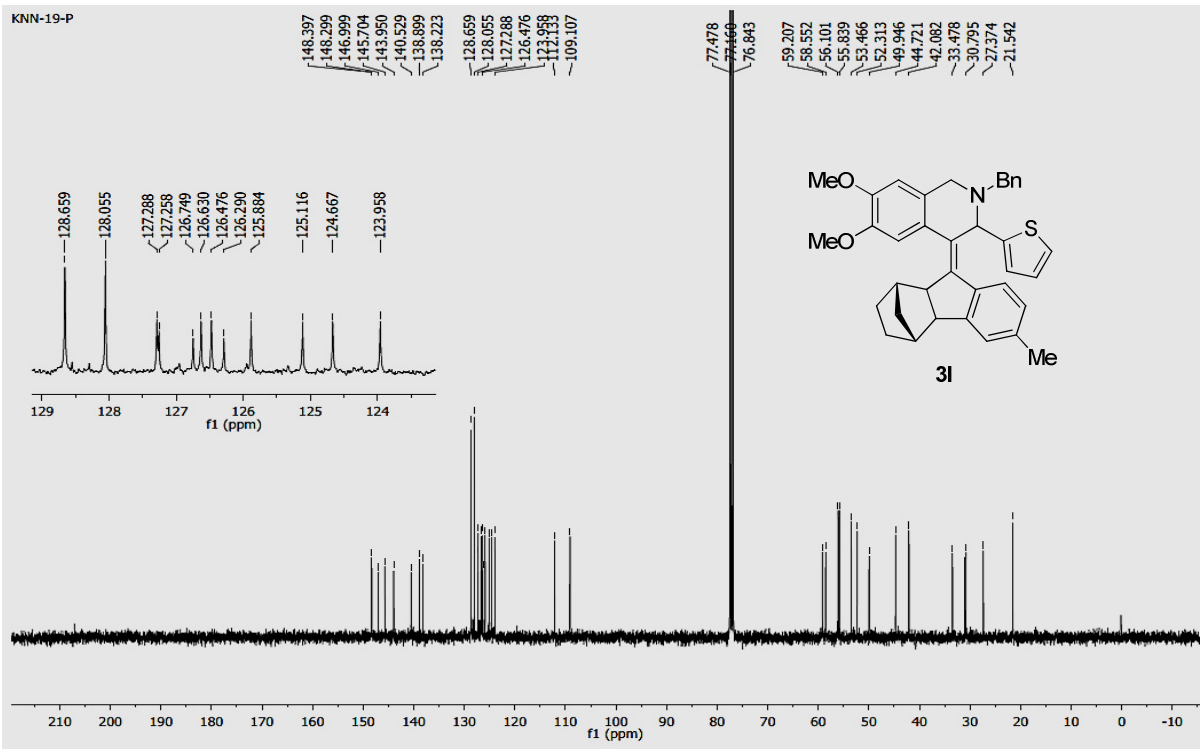
^{13}C-NMR spectrum of compound **3k**



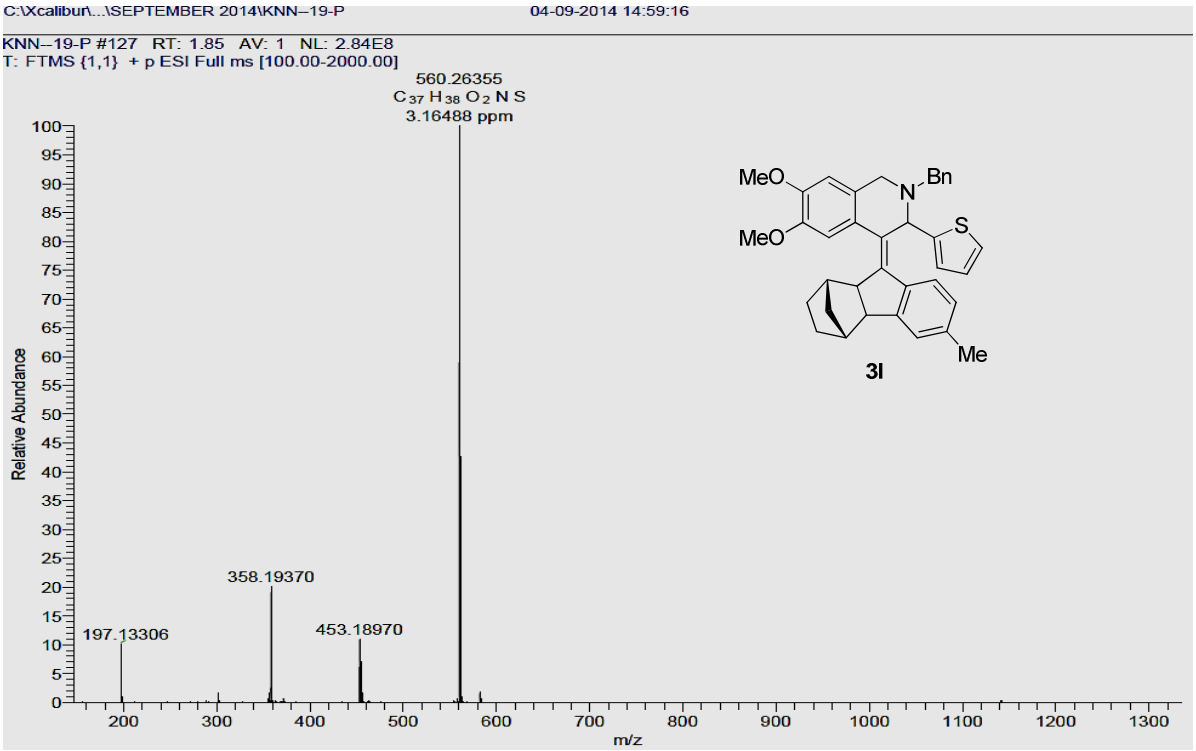
HRMS spectrum of compound **3k**



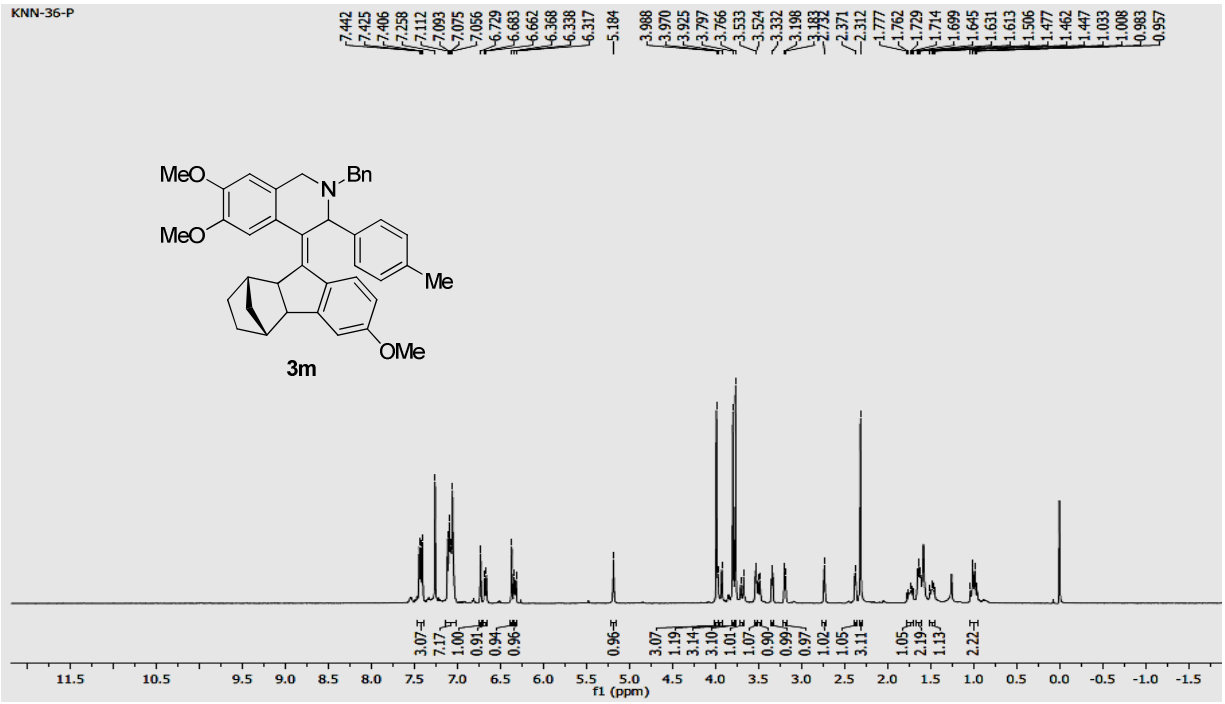
^{1}H-NMR spectrum of compound **3l**



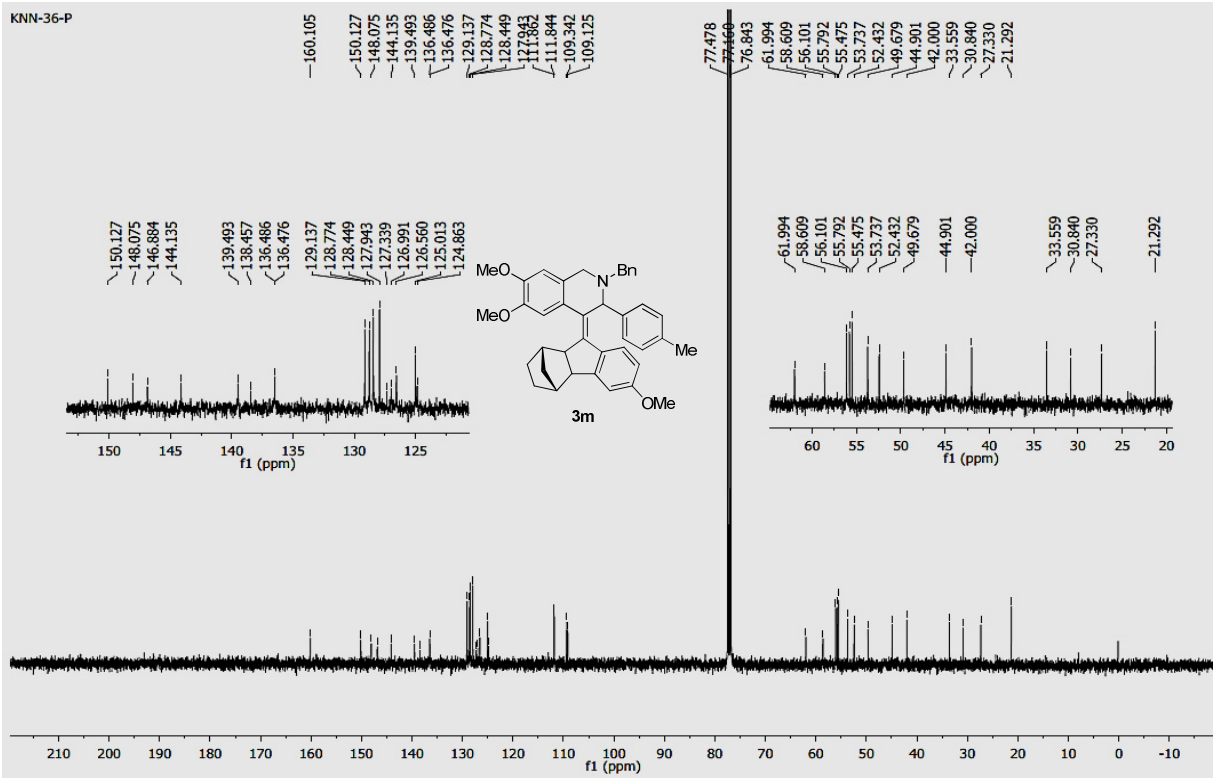
^{13}C-NMR spectrum of compound **3l**



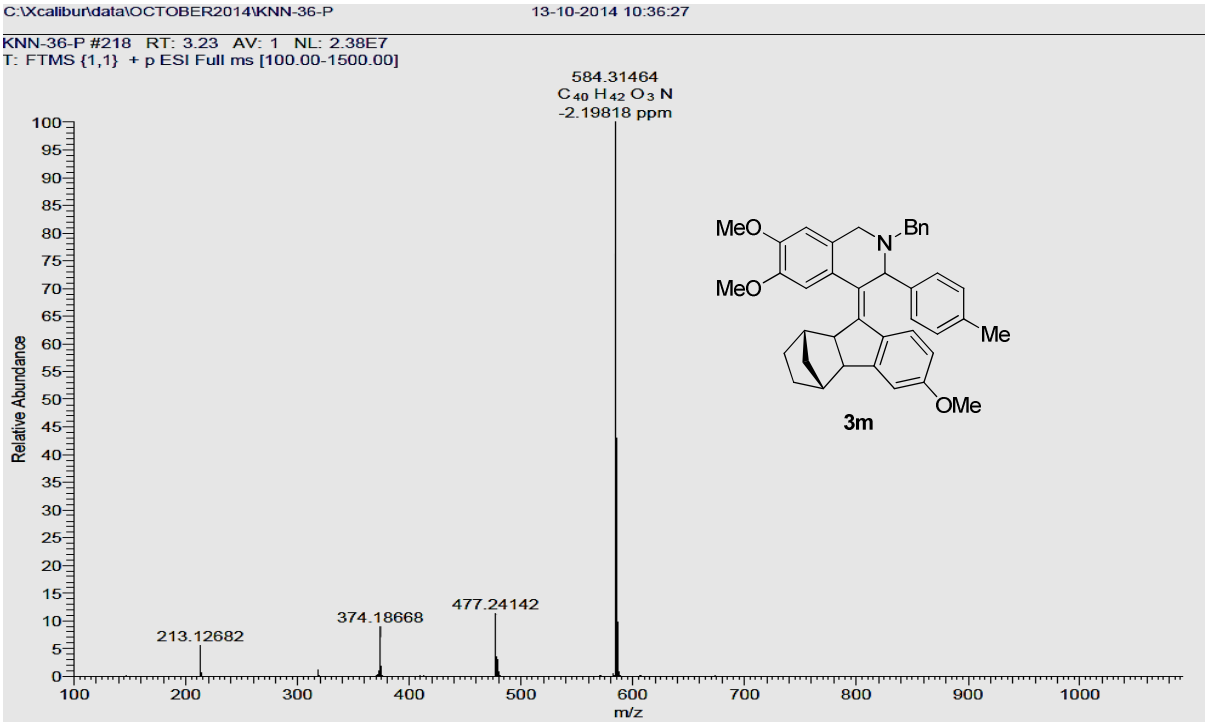
HRMS spectrum of compound **3l**



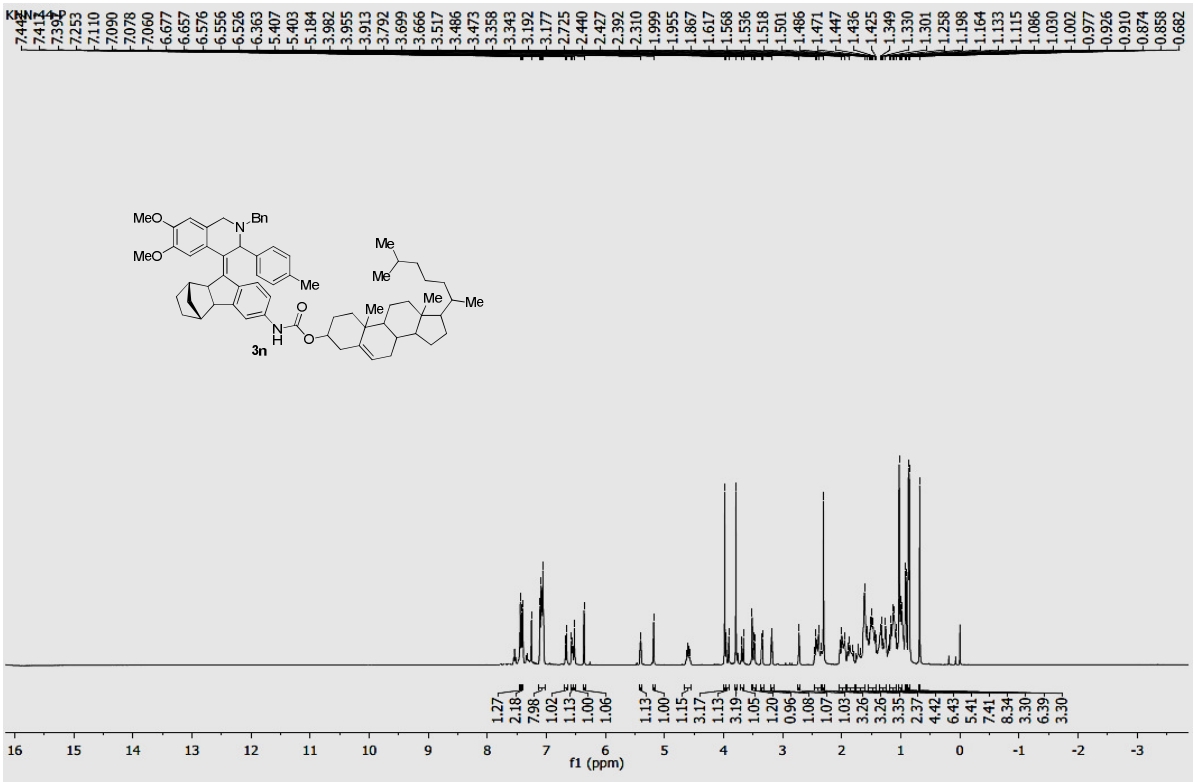
^{1}H-NMR spectrum of compound **3m**



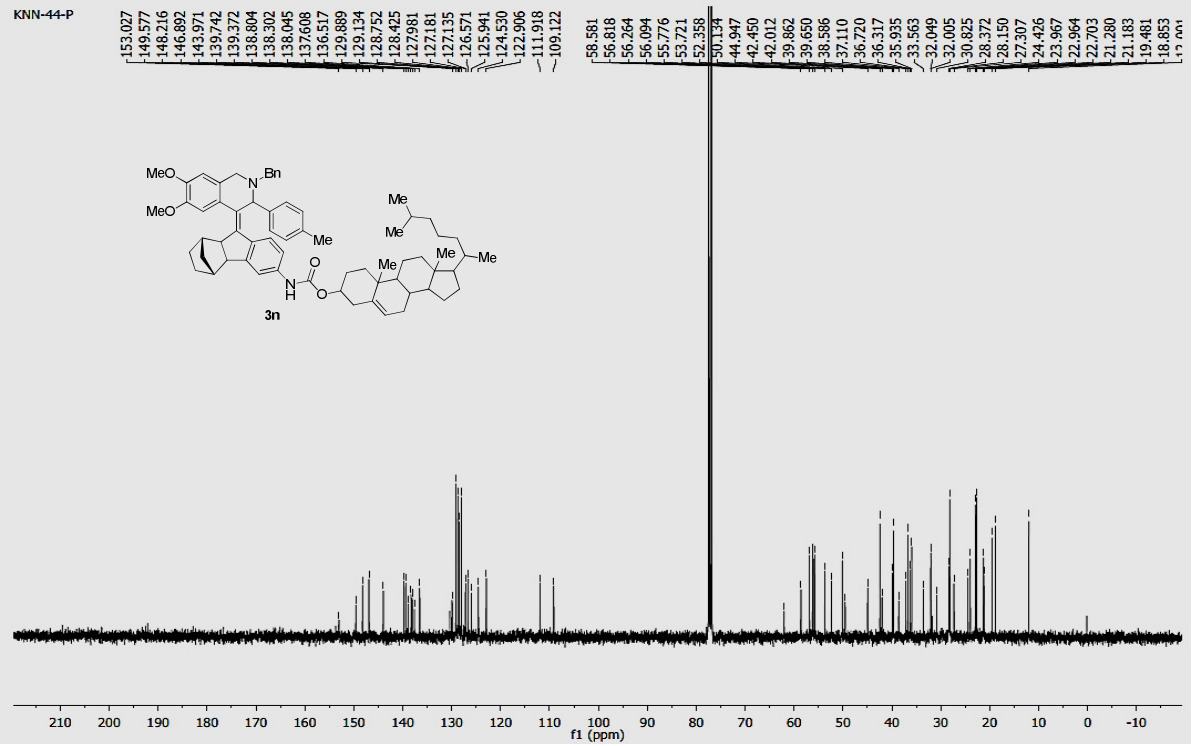
^{13}C-NMR spectrum of compound **3m**



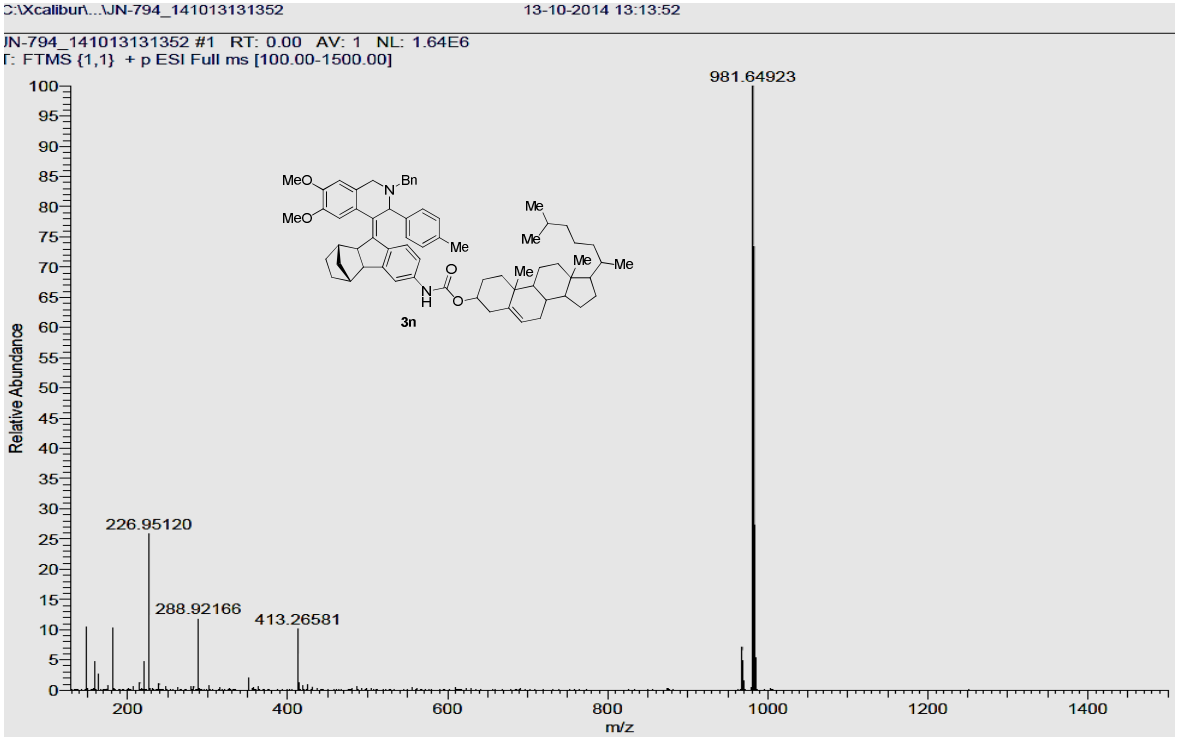
HRMS spectrum of compound **3m**



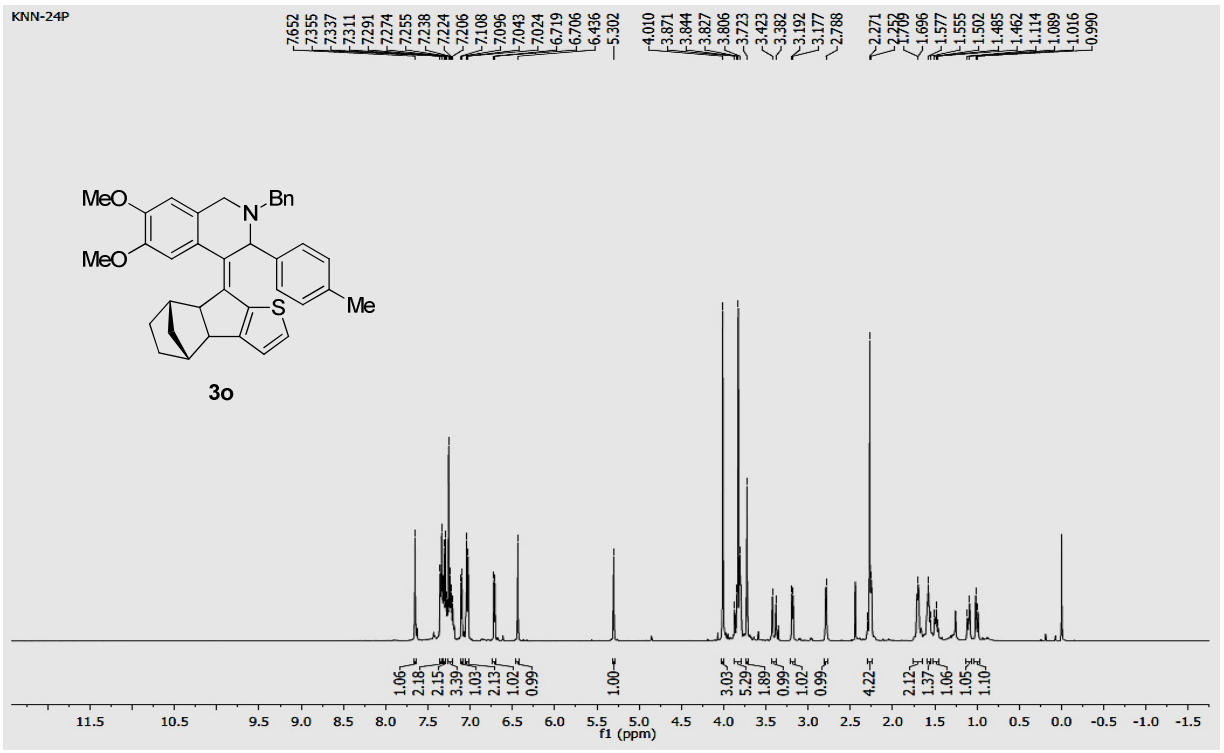
^{1}H-NMR spectrum of compound **3n**



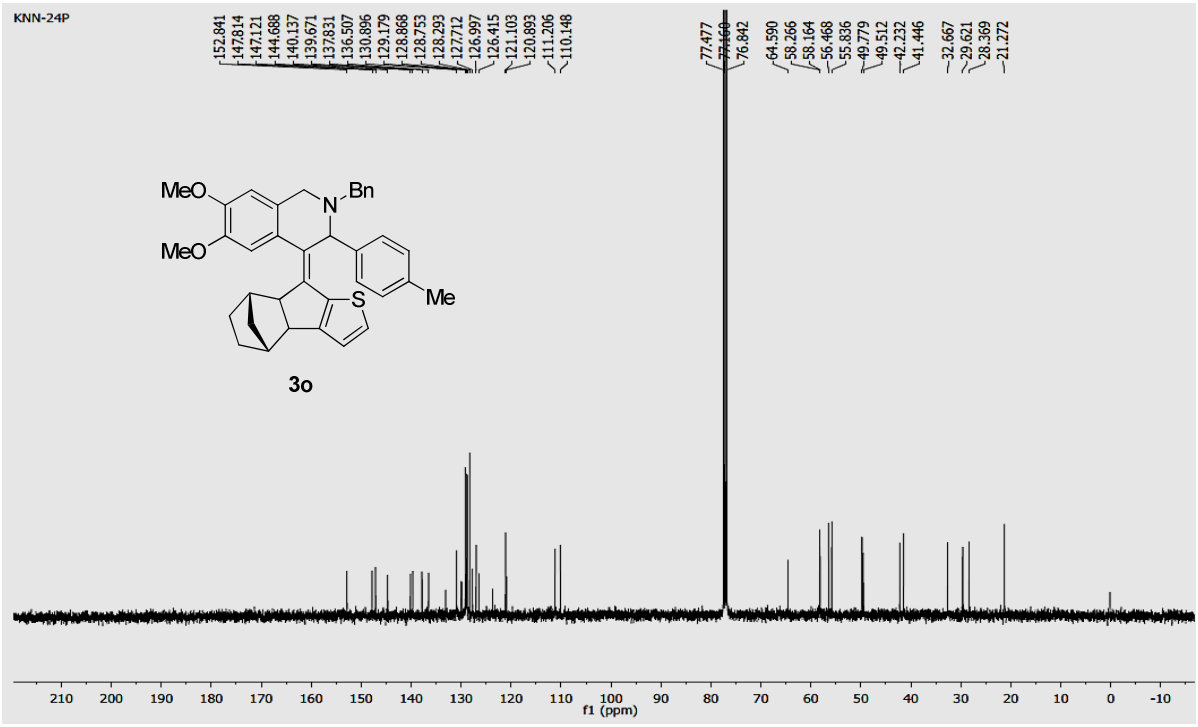
^{13}C-NMR spectrum of compound **3n**



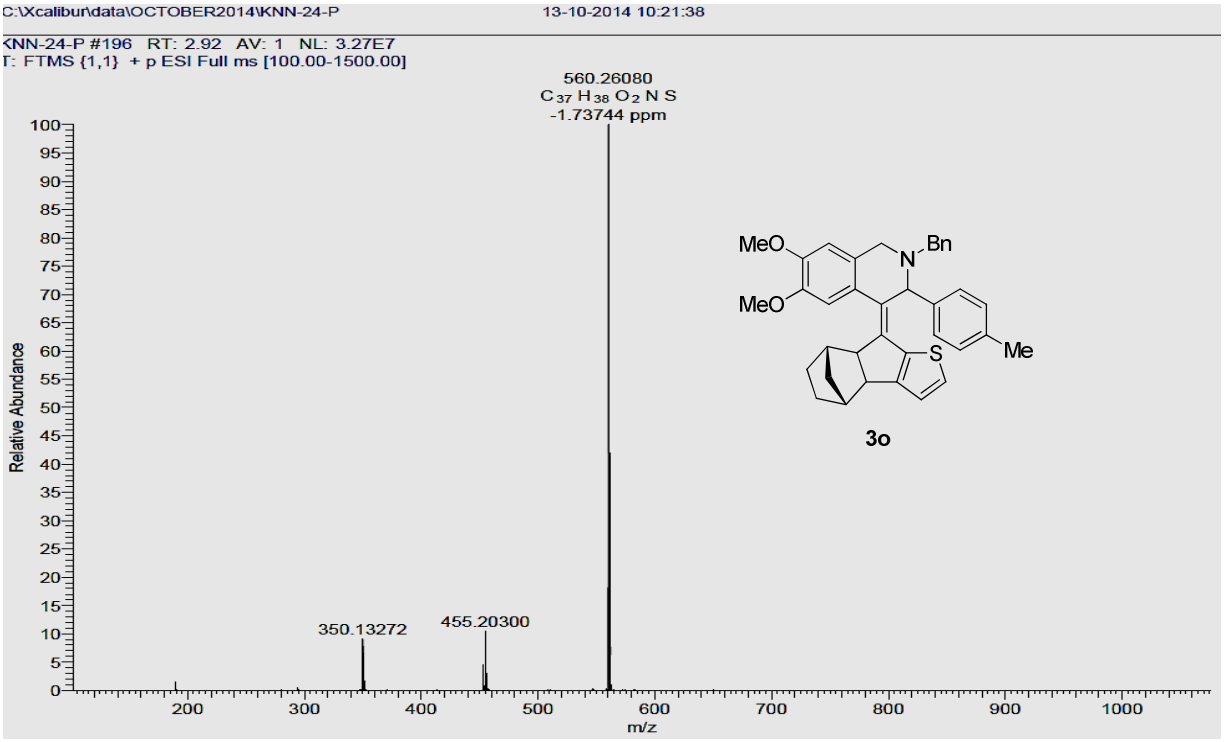
HRMS spectrum of compound **3n**



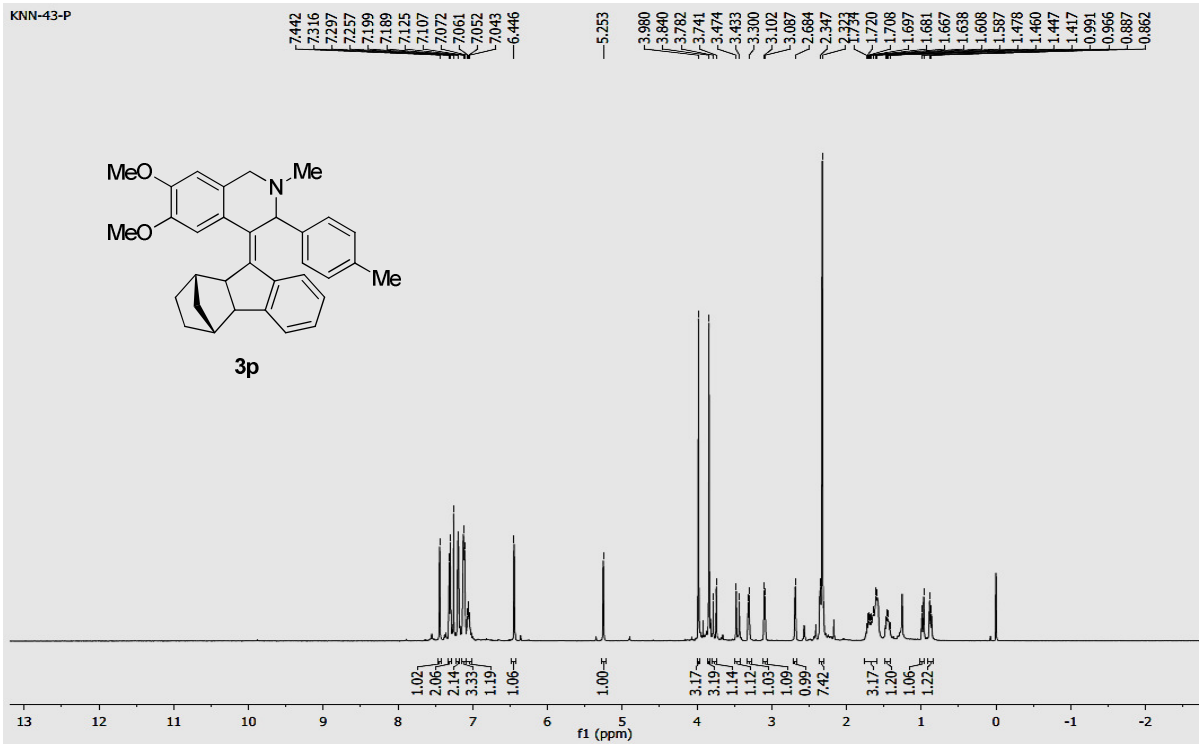
^{1}H-NMR spectrum of compound **3o**



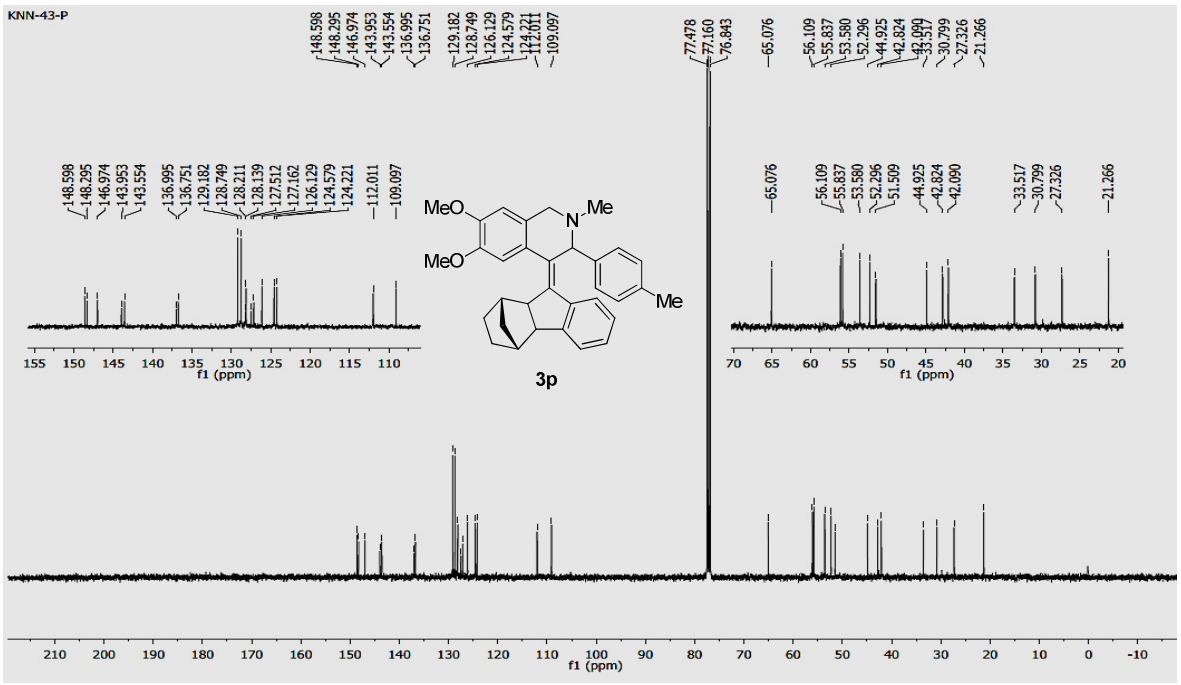
^{13}C-NMR spectrum of compound **3o**



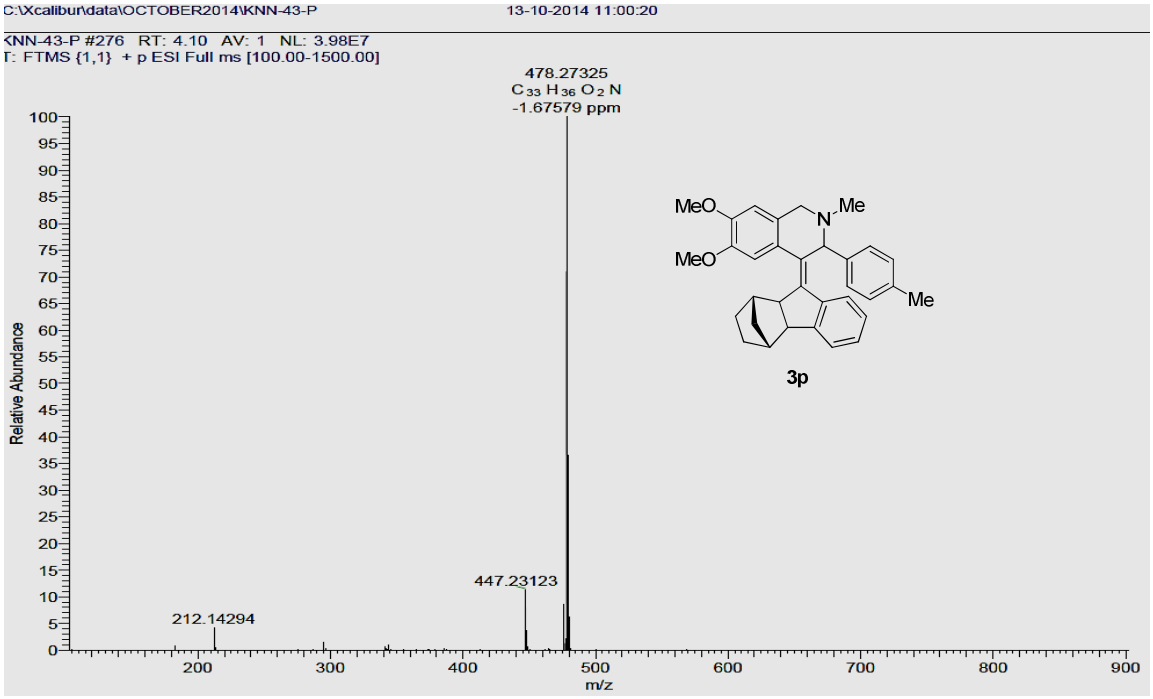
HRMS spectrum of compound **3o**



^{1}H-NMR spectrum of compound **3p**

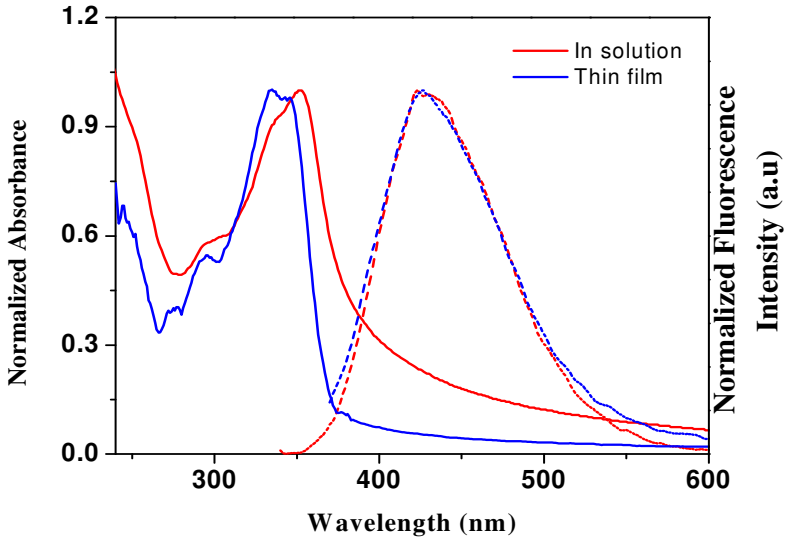


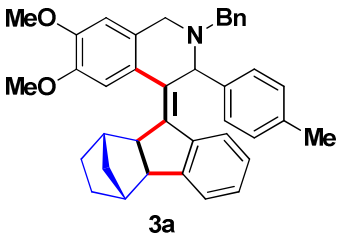
^{13}C-NMR spectrum of compound **3p**



HRMS spectrum of compound **3p**

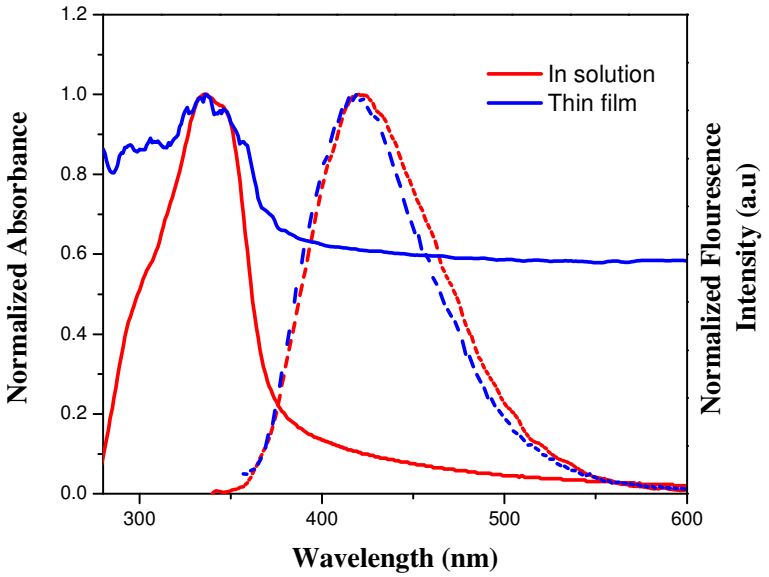
Uv visible and emission spectra of compounds (3a-p) in solution 90% of H_2O/CH_3CN and thin film states

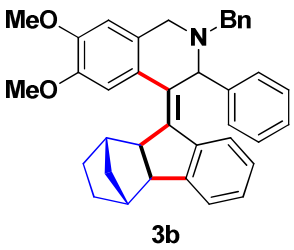




3a

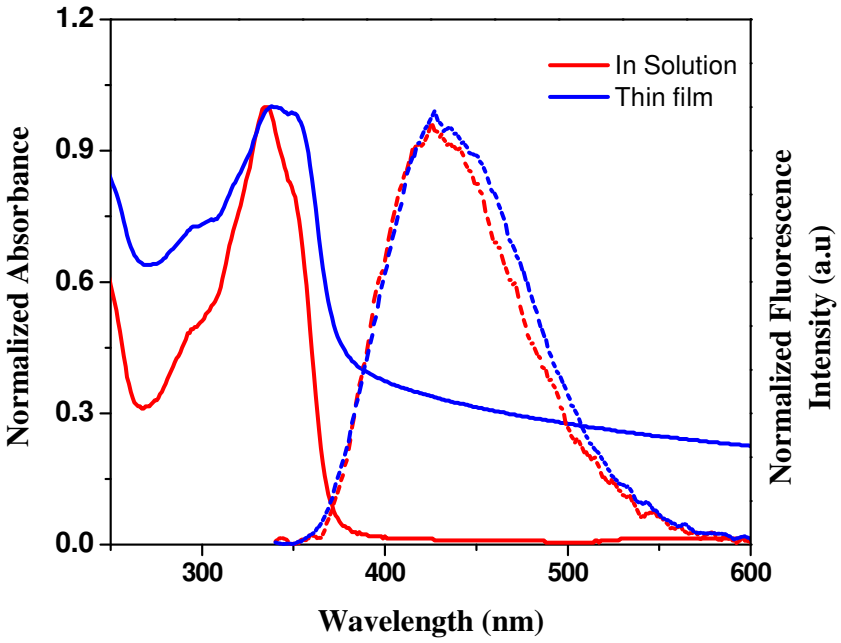
Uv visible (solid line) and emission (dashed line) spectra of compound **3a** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

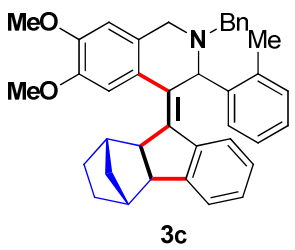




3b

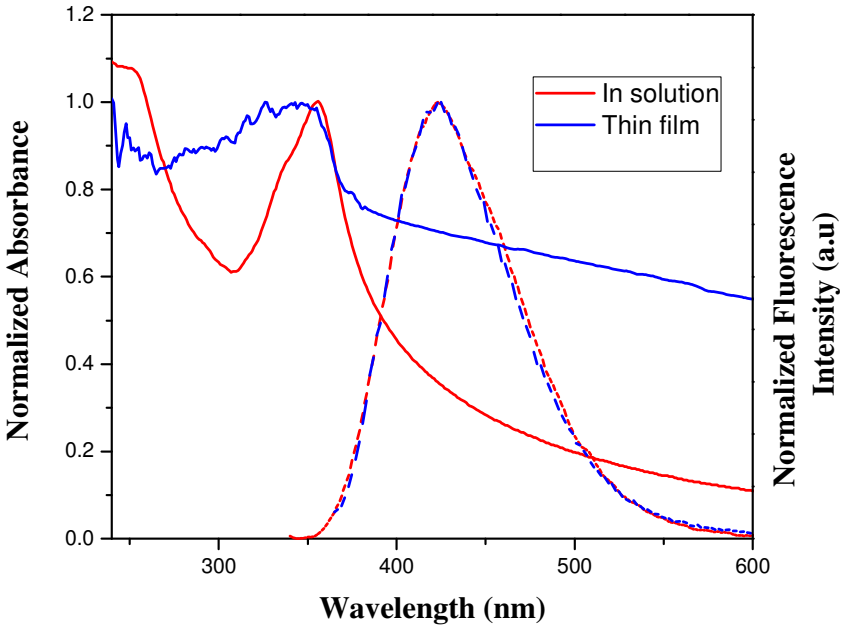
Uv visible (solid line) and emission (dashed line) spectra of compound **3b** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

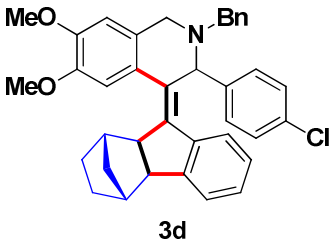




3c

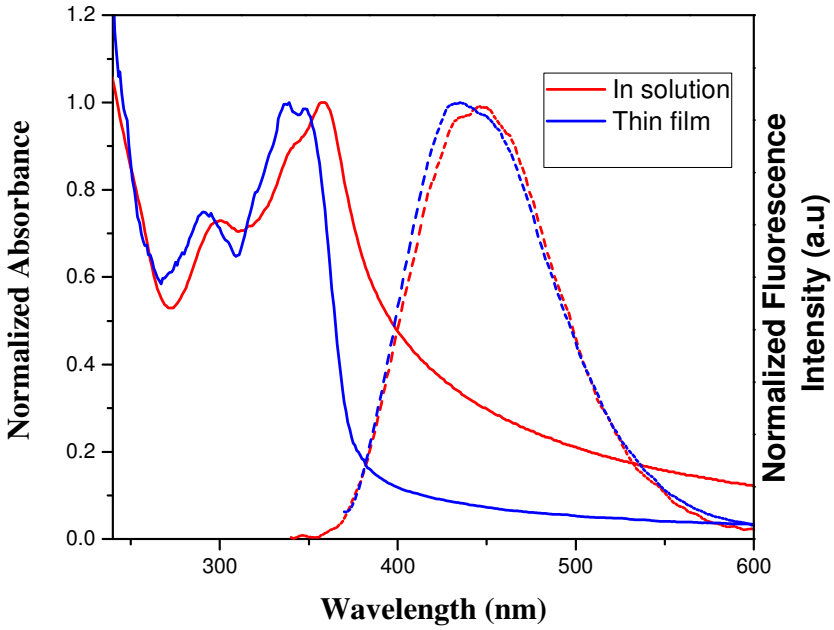
Uv visible (solid line) and emission (dashed line) spectra of compound **3c** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

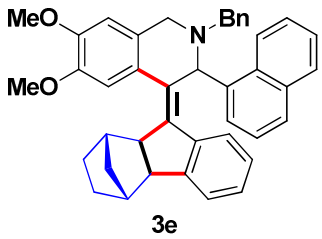




3d

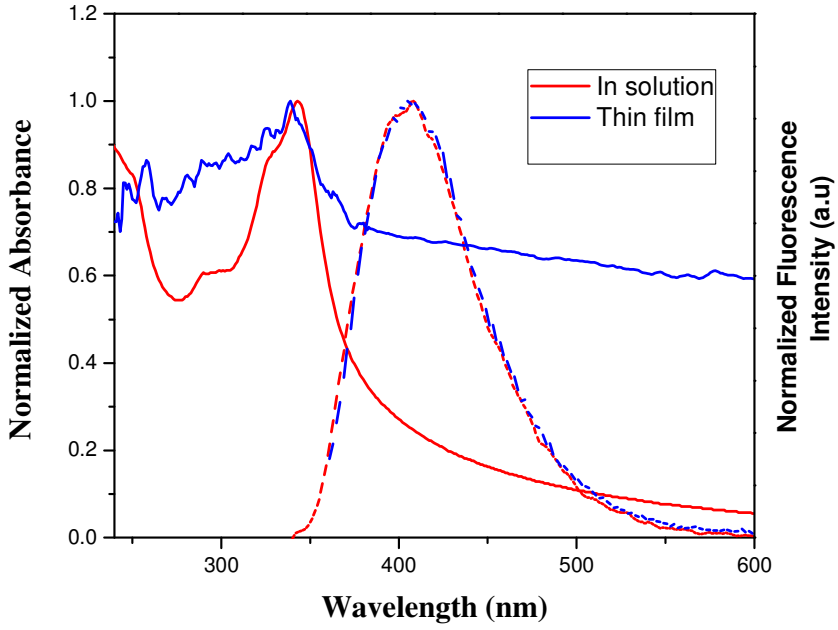
Uv visible (solid line) and emission (dashed line) spectra of compound **3d** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

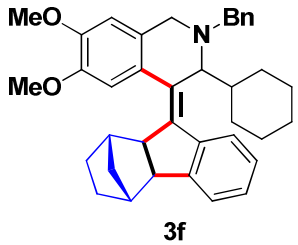




3e

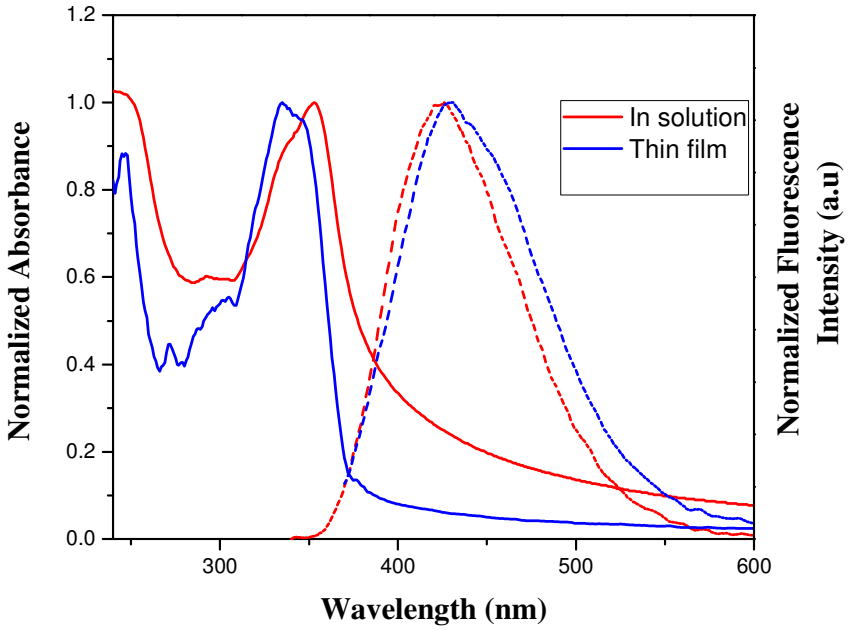
Uv visible (solid line) and emission (dashed line) spectra of compound **3e** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

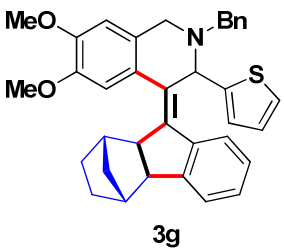




3f

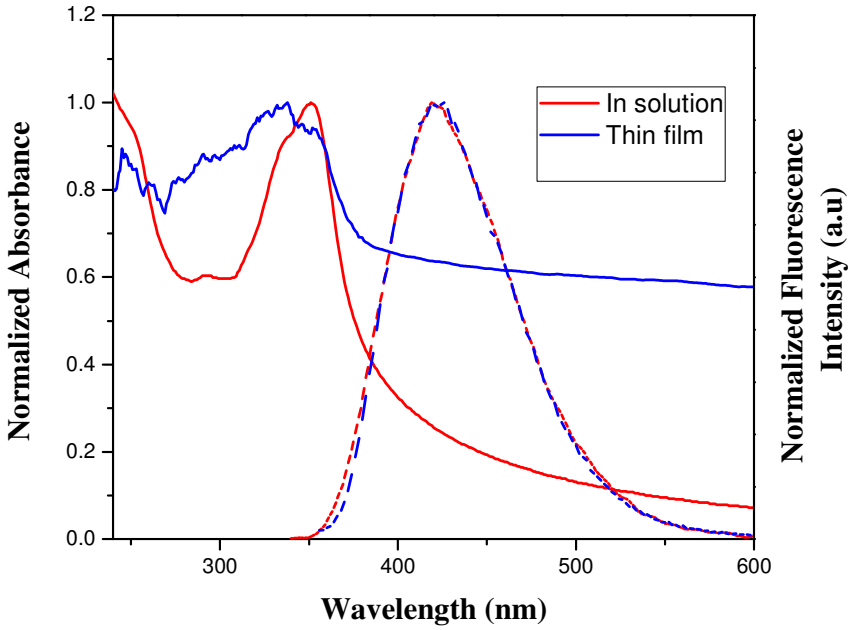
Uv visible (solid line) and emission (dashed line) spectra of compound **3f** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

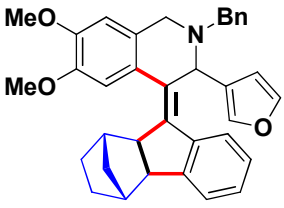




3g

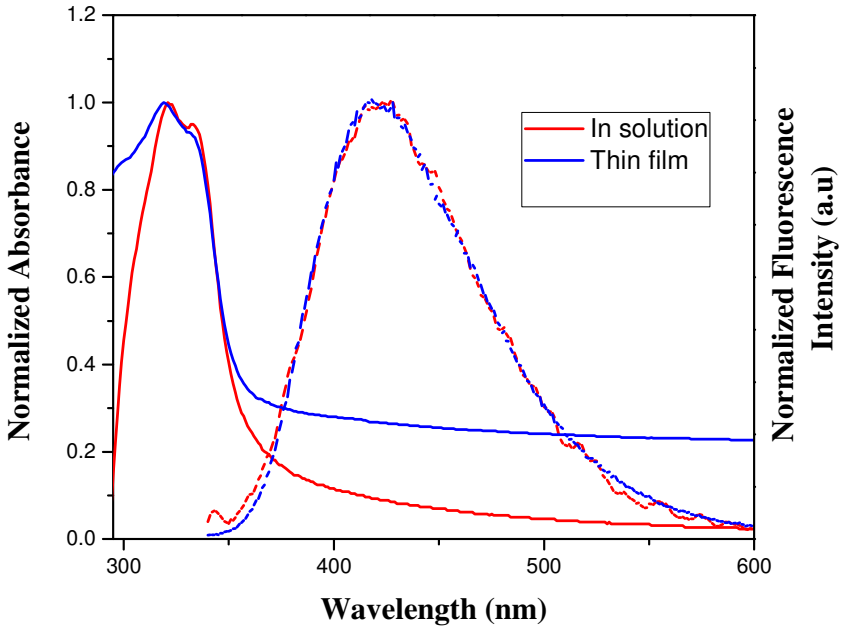
Uv visible (solid line) and emission (dashed line) spectra of compound **3g** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

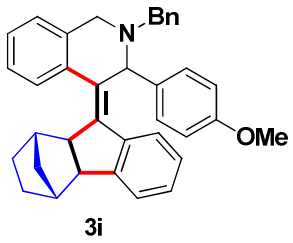




3h

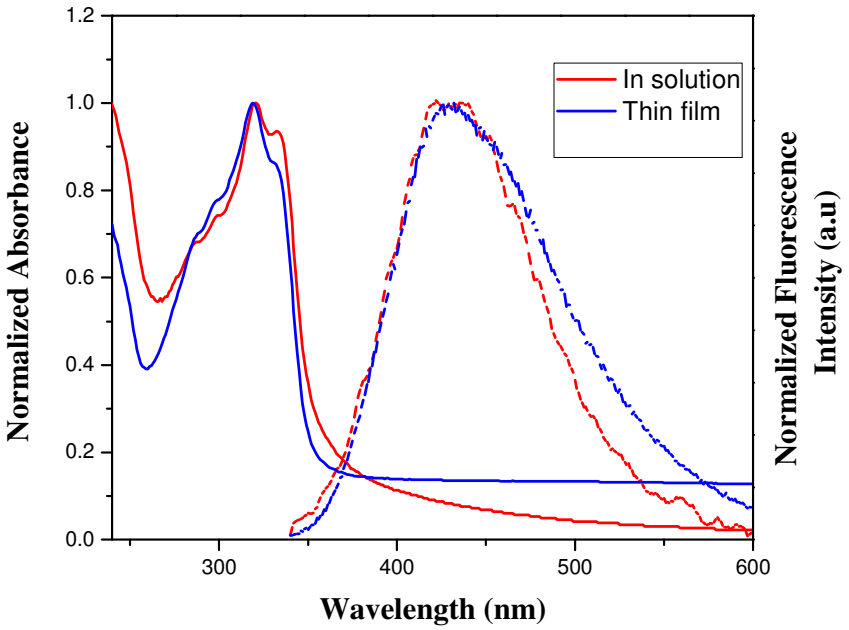
Uv visible (solid line) and emission (dashed line) spectra of compound **3h** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

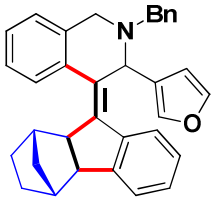




3i

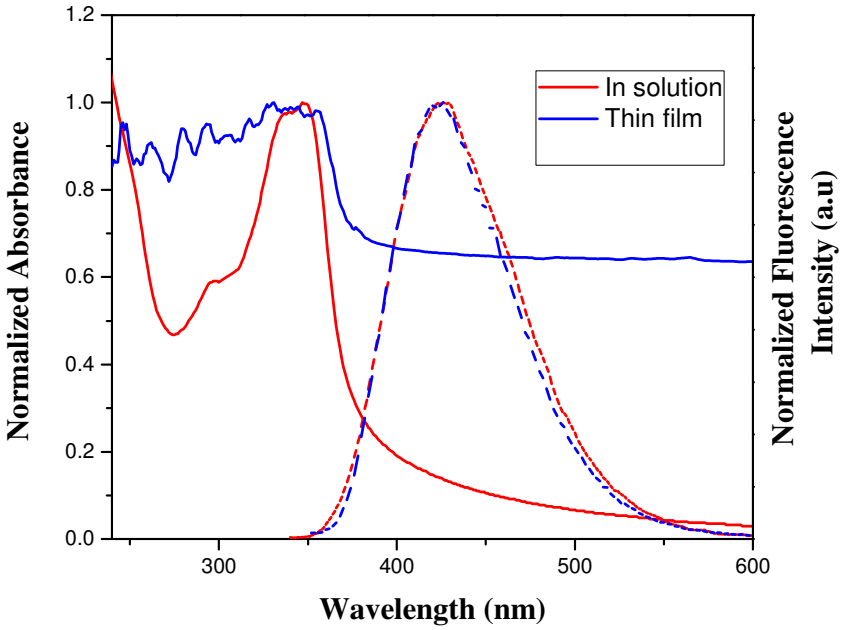
Uv visible (solid line) and emission (dashed line) spectra of compound **3i** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

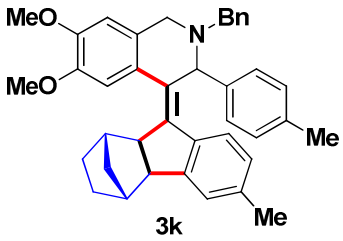




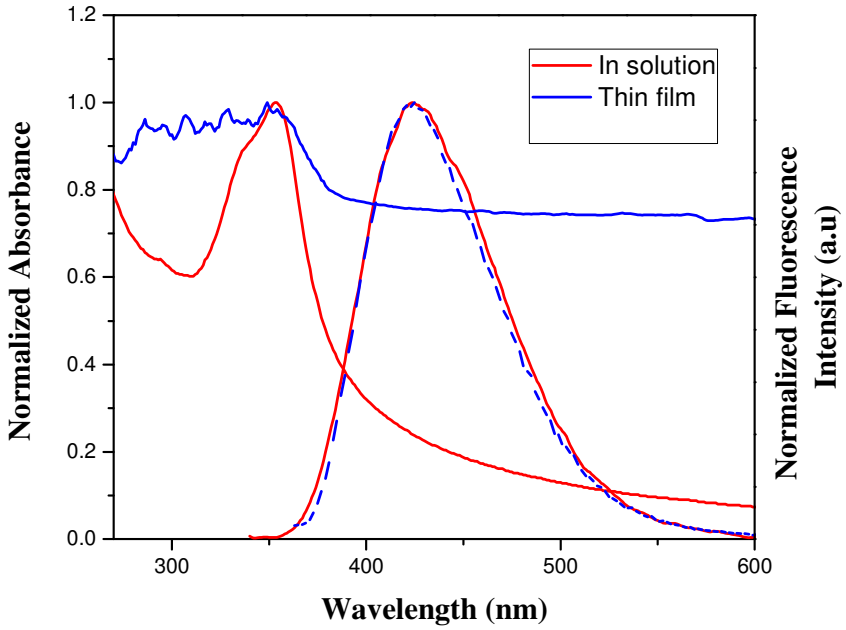
3j

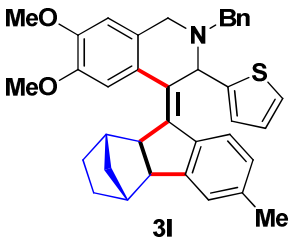
Uv visible (solid line) and emission (dashed line) spectra of compound **3j** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)



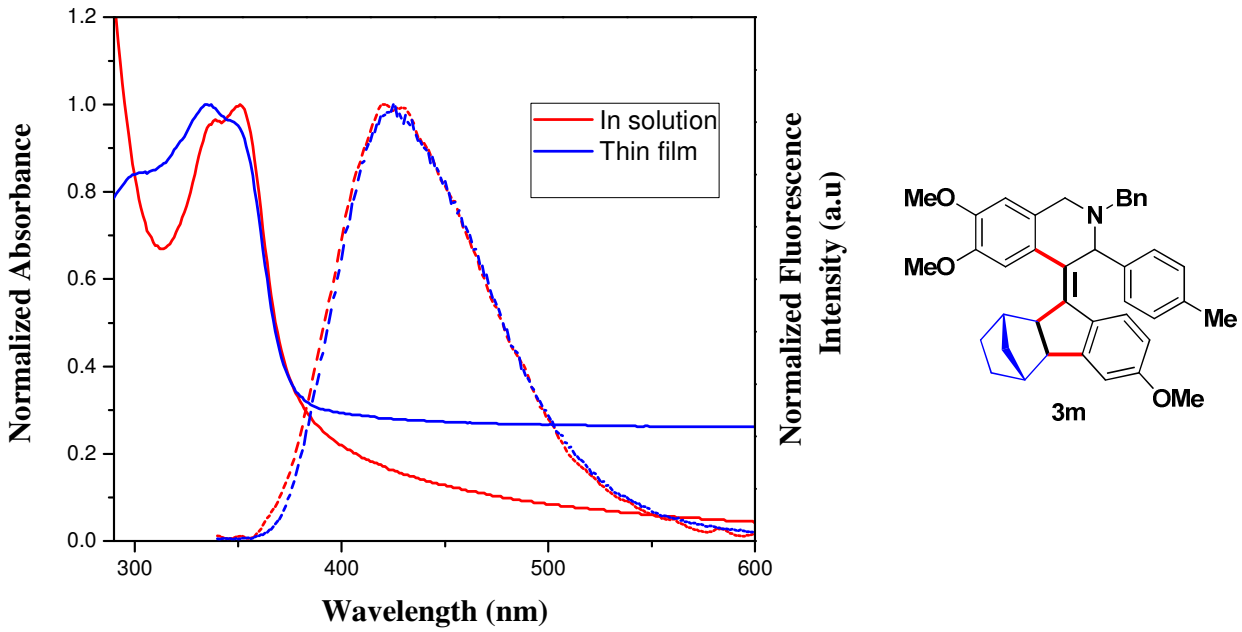


Uv visible (solid line) and emission (dashed line) spectra of compound **3k** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

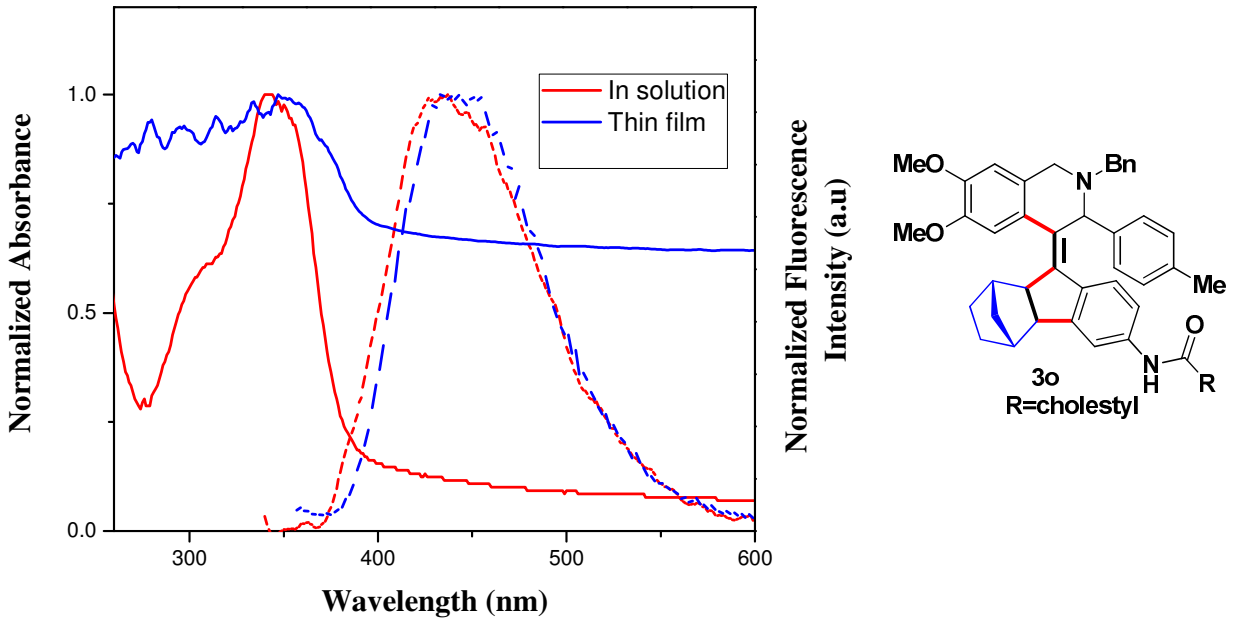




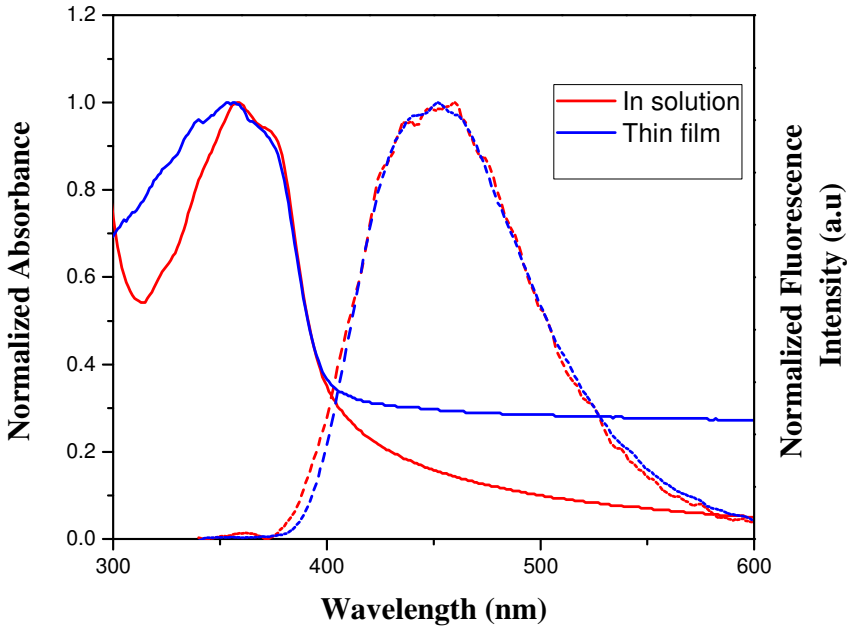
Uv visible (solid line) and emission (dashed line) spectra of compound **3l** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

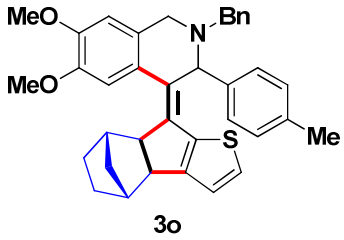


Uv visible (solid line) and emission (dashed line) spectra of compound **3m** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)



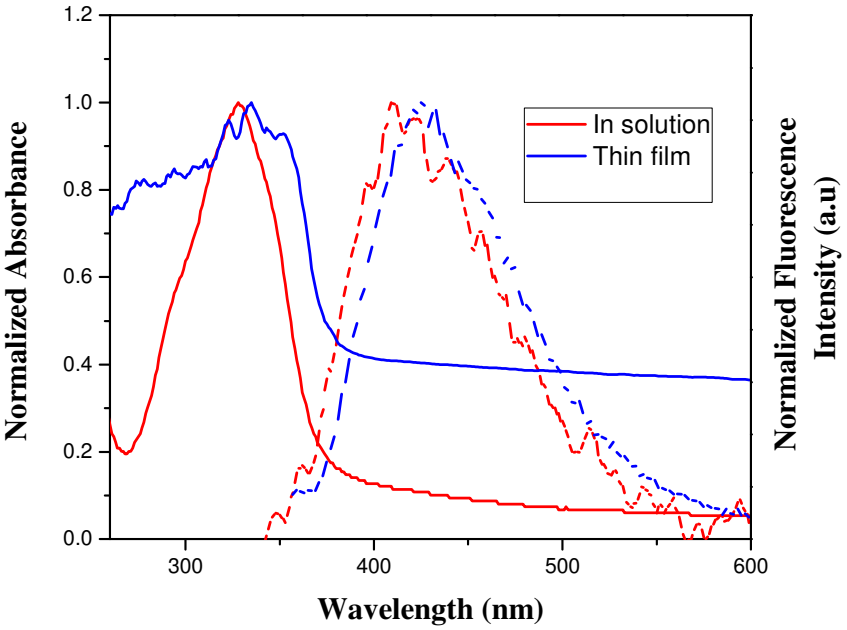
Uv visible (solid line) and emission (dashed line) spectra of compound **3o** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

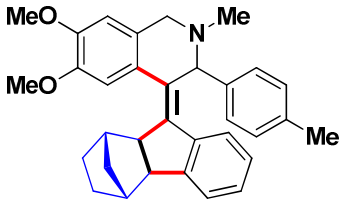




3o

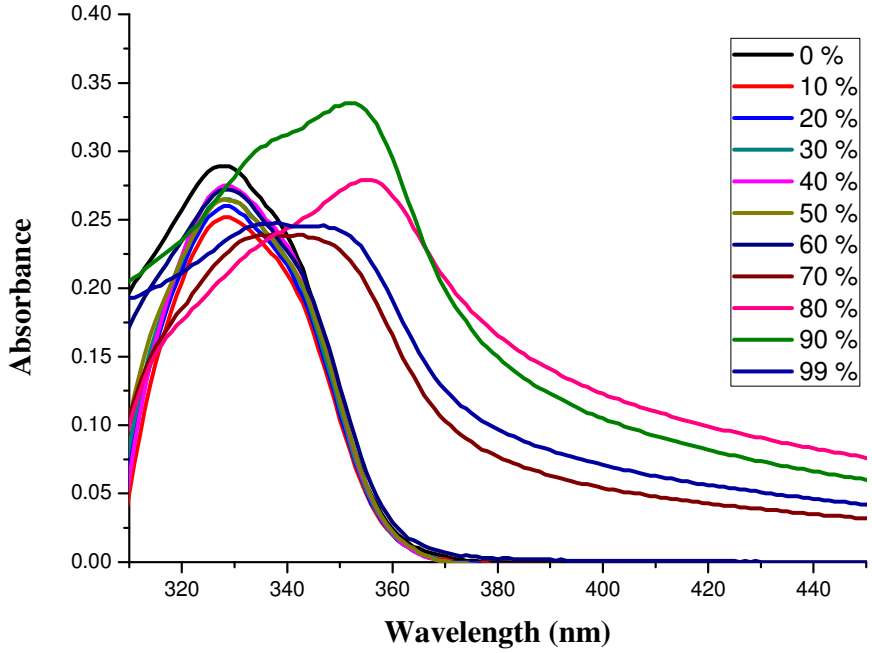
Uv visible (solid line) and emission (dashed line) spectra of compound **3o** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

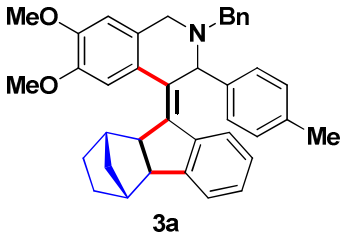




3p

Uv visible (solid line) and emission (dashed line) spectra of compound **3p** in solution 90% H_2O/CH_3CN mixture (red) and in thin film (blue)

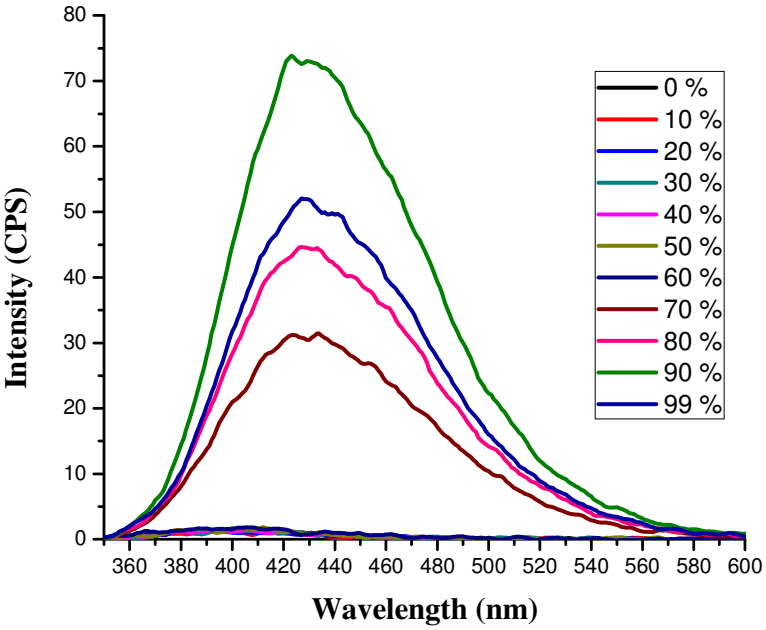


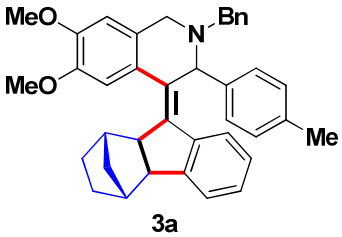


3a

Absorption spectra of **3a** in CH_3CN/H_2O mixtures with different water fraction (f_w),

Concentration (μM): 10





3a

PL spectra of **3a** in CH_3CN/H_2O mixtures with different water fraction (f_w), Concentration (μM): 10; excitation wavelength (nm): 320

Photos of **3a** in CH_3CN/H_2O mixtures (f_w = 70%, f_w = 80%, f_w = 90%, f_w = 99% from left to right) taken under UV luminescent

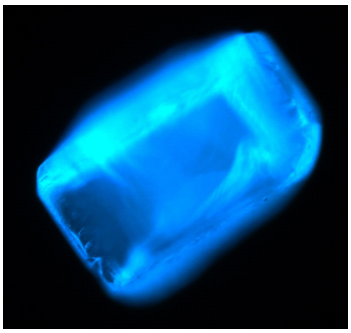


Photo of microscopic image of **3a** in crystal state

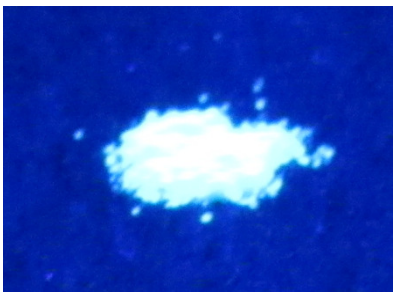
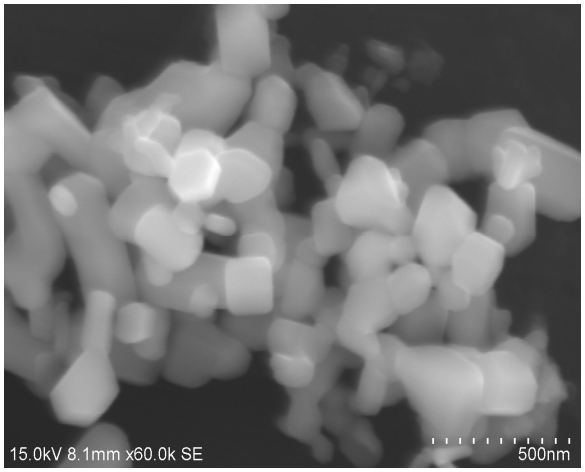
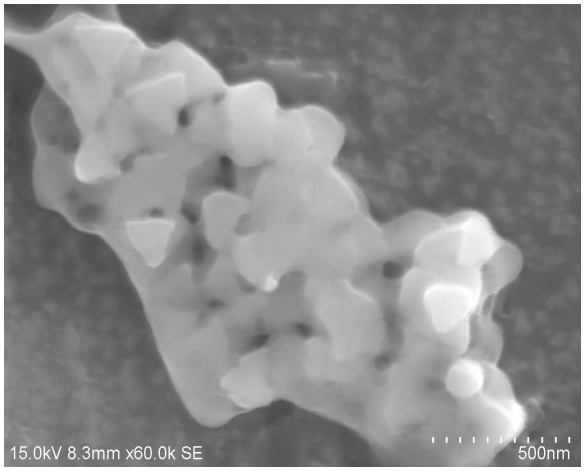


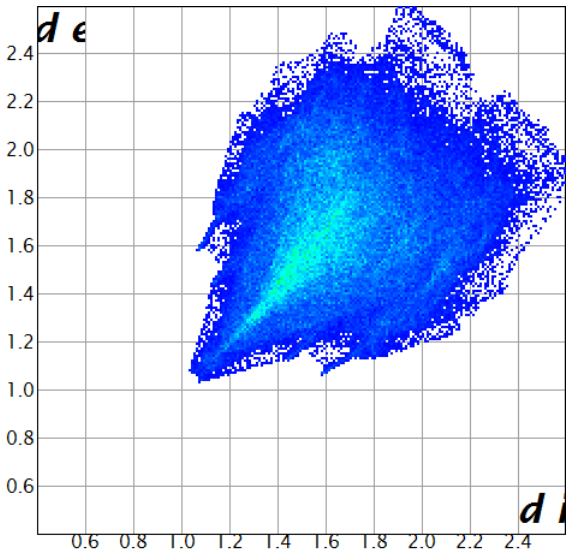
Photo of **3a** has taken under UV luminescent

FE-SEM analysis of 3a in 90 % (left) and 99 % (right) of water in acetonitrile

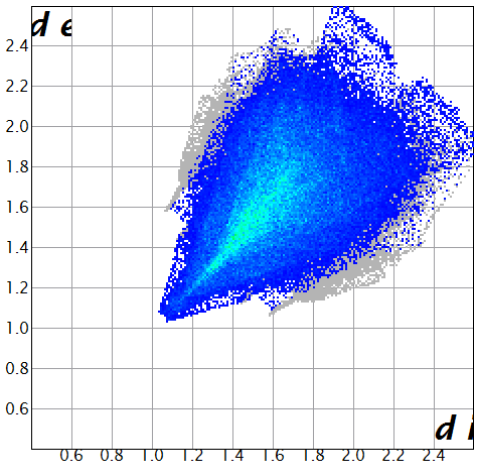




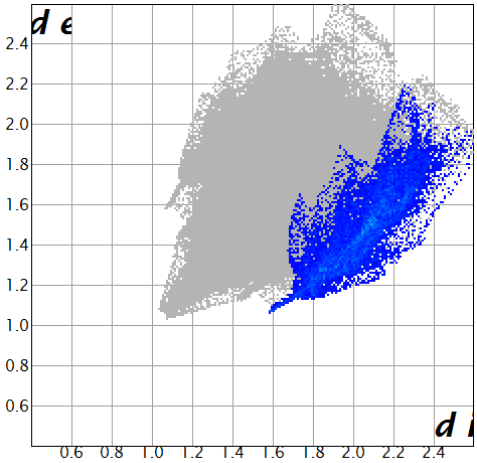
Hirshfeld Surface Analyses of 3a



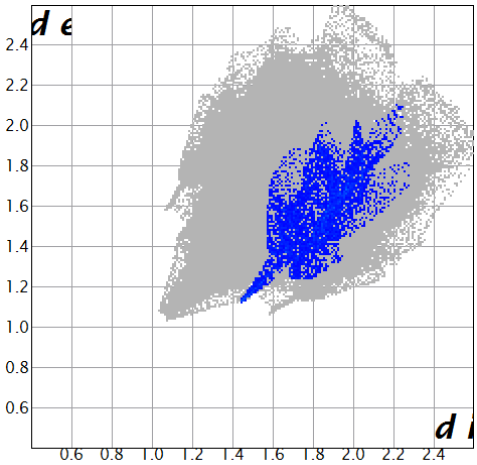
Total interactions



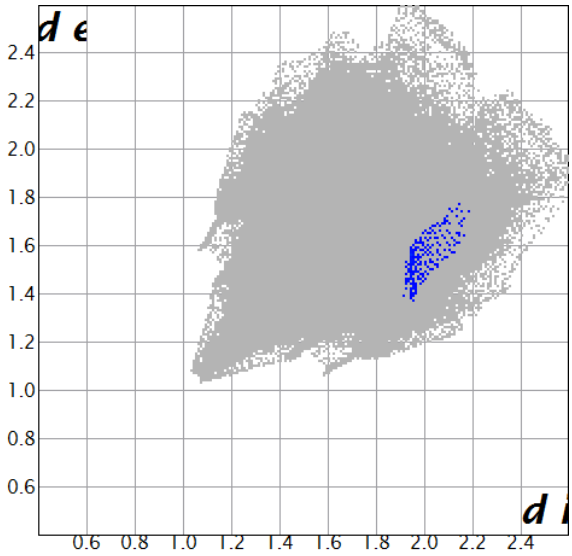
H…H interaction (75.4 %)



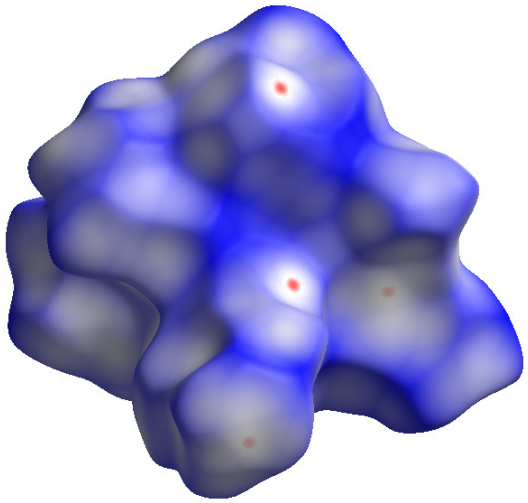
C…H interaction (9.7 %)



O…H interaction(3.8 %)



N…H interaction (0.1 %)



Hirshfield surface diagram of compound **3a**

Compounds 3b-p (from left to right) in solution (90 % of H_2O inCH_3CN) and in the condensed phase under UV irradiation