Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Regioselective Brønsted Acid Catalyzed Ring Opening of Aziridines by Phenols and Thiophenols; A Gateway to Access Functionalized Indolines, Indoles, Benzothiazines, Dihydrobenzo-thiazines, Benzo-oxazines and Benzochromenes

Arnab Roy,[a] Surajit Duari,[a] Srabani Maity,[a] Subrata Biswas,[a] Abhishek Kumar Mishra,[b] Srijit Biswas[a,*]

[a]Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata – 700 009, West Bengal, India

E-mail: sbchem@caluniv.ac.in; srijit_biswas@yahoo.co.in.

[b]Department of Medicinal and Process Chemistry, CSIR-Central Drug Research Institute, Lucknow – 226031, U. P. India

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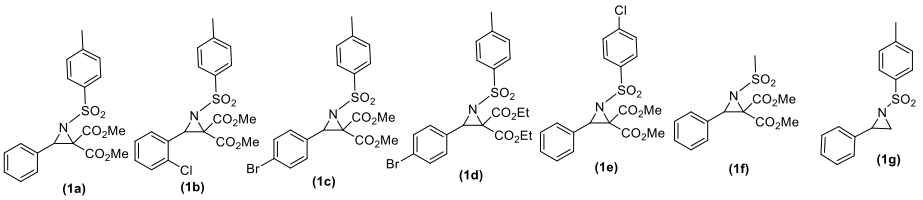
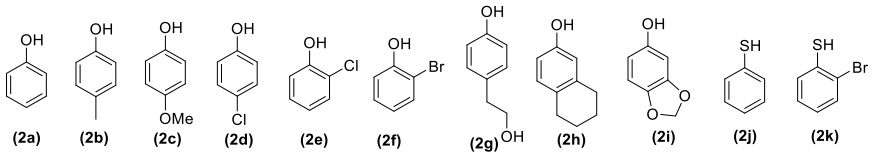
1. **Aziridines used in study:**




2. **Nucleophiles used in study:**




3. **X-ray crystallography:**

**Method for crystal growth:**

80 mg of solid compound (**3i**), was dissolved in 1 mL of ethyl acetate, and diluted with equal amount of n-hexane in a 25 mL conical flask. Then the mixture was kept at 10 $^{o}$C for one week inside a fridge. After slow evaporation of the solvent the desired crystals were formed.

Single-crystal X-ray data of compound **3i** was collected on a Bruker SMART Apex-II CCD diffractometer in the presence of graphite-monochromated Mo Kα radiation (λ = 0.71073 A°) at room temperature. The Bruker Apex-II suite program was used to perform data processing, structure solution, and refinement. Reflections available in $2\Theta_{max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.[1] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS.[2] The structures were solved using direct methods and refined by means of full-matrix least-squares techniques based on $F^2$ with with SHELX2017/1 software package.[3] Non-hydrogen atoms present in the structures were refined with anisotropic thermal parameters. C–H hydrogen atoms were introduced at geometrical positions with $U_{iso} = 1/2U_{eq}$ to those of the atoms to which they are attached.

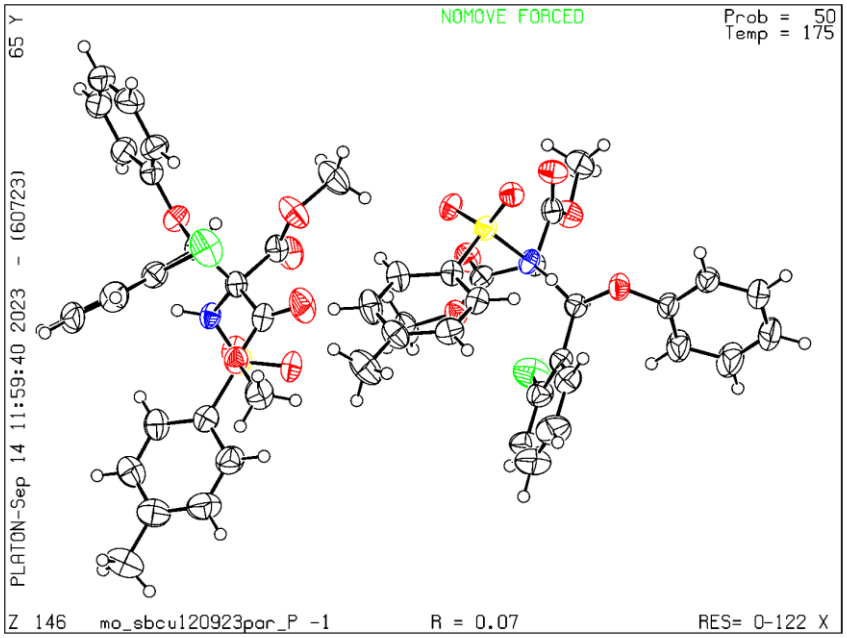



**Table 1 Crystal data and structure refinement for 3i.**

| | |
|---|---|
| Identification code | 3i |
| Empirical formula | $C_{25}H_{24}ClNO_7S$ |
| Formula weight | 517.96 |
| Temperature/K | 175.06 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.317(3) |
| b/Å | 12.681(3) |
| c/Å | 18.882(4) |
| α/° | 97.653(6) |
| β/° | 104.022(7) |
| γ/° | 92.139(7) |
| Volume/Å$^3$ | 2828.2(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.216 |
| μ/mm$^{-1}$ | 0.249 |
| F(000) | 1080.0 |
| Crystal size/mm$^3$ | 0.16 × 0.12 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.496 to 55.272 |
| Index ranges | -16 ≤ h ≤ 15, -16 ≤ k ≤ 16, -24 ≤ l ≤ 22 |
| Reflections collected | 34652 |
| Independent reflections | 12860 [$R_{int}$ = 0.1068, $R_{sigma}$ = 0.1360] |
| Data/restraints/parameters | 12860/0/638 |
| Goodness-of-fit on $F^2$ | 0.984 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0673, $wR_2$ = 0.1618 |

| | |
|---|---|
| Final R indexes [all data] | $R_1$ = 0.1467, $wR_2$ = 0.2138 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.43/-0.43 |
| CCDC Number | 2307104 |

**4. References:**

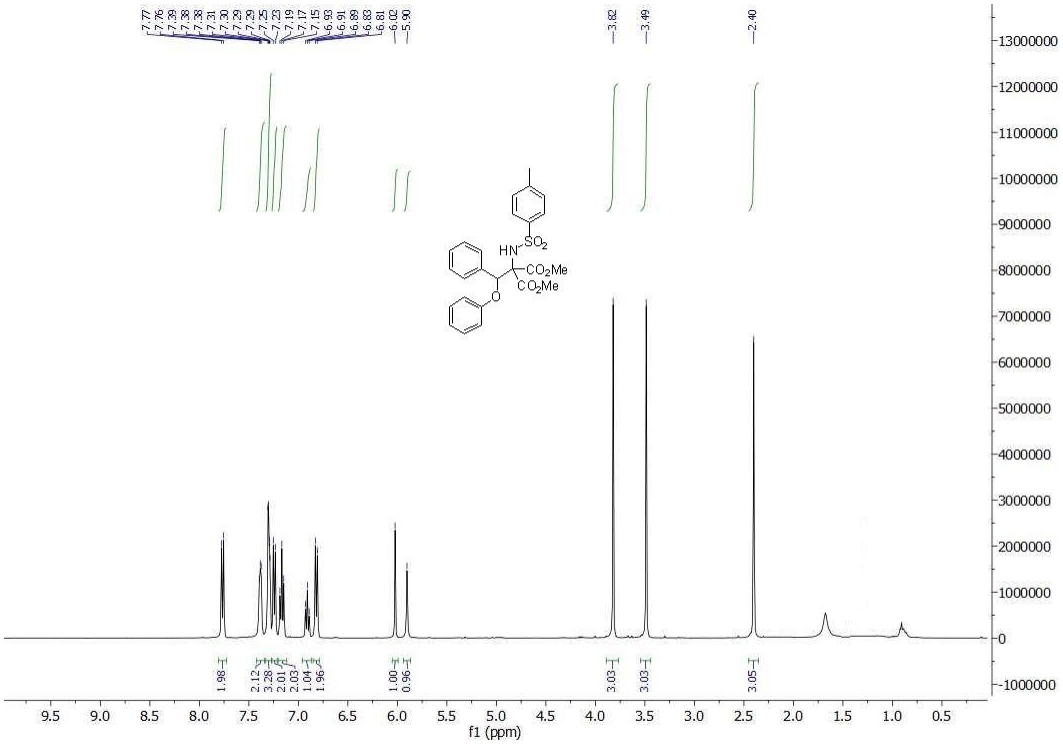

(1) G. M. Sheldrick, *SAINT, Ver. 6.02 and SADABS, Ver. 2.03,* Bruker AXS Inc.: Madison, WI, 2002.

(2) G. M. Sheldrick, *SADABS, software for empirical absorption correction,* Universitat: Göttingen, Germany, **1999**.

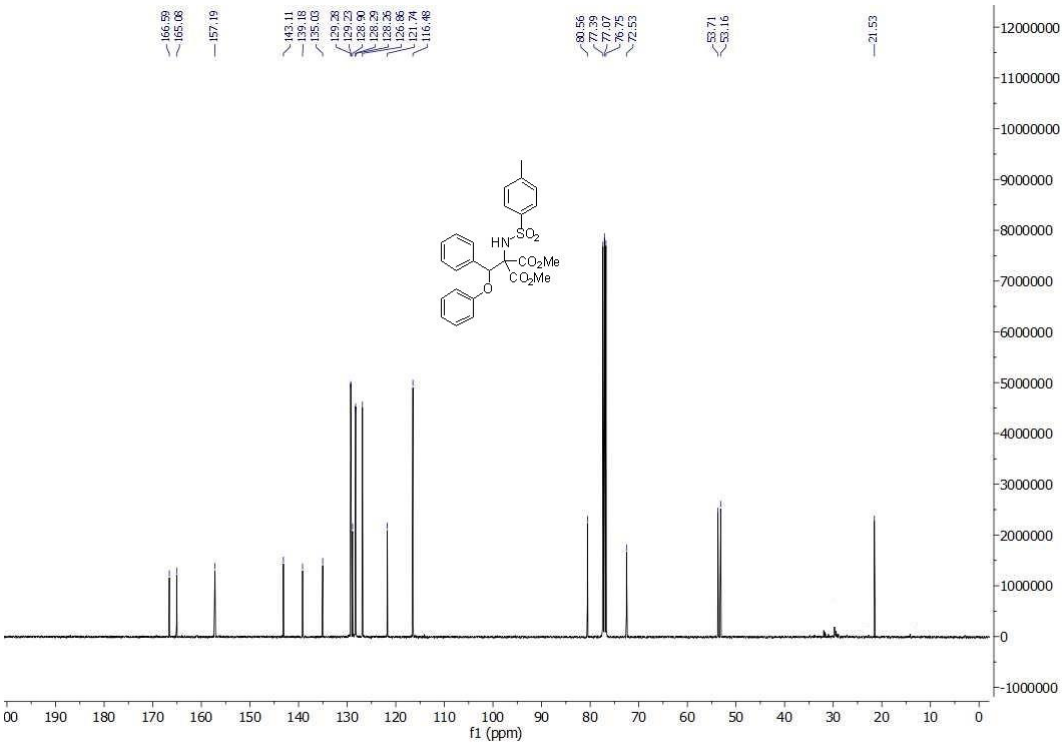
(3) *G. M. Sheldrick, SHELXS-2013 and SHELXL-2013, Program for Refinement of Crystal Structures; University of Göttigen: Göttigen, Germany*, **2013**.

## 5. Copies of $^{1}H$ and $^{13}C$ {1H} NMR spectra of all products

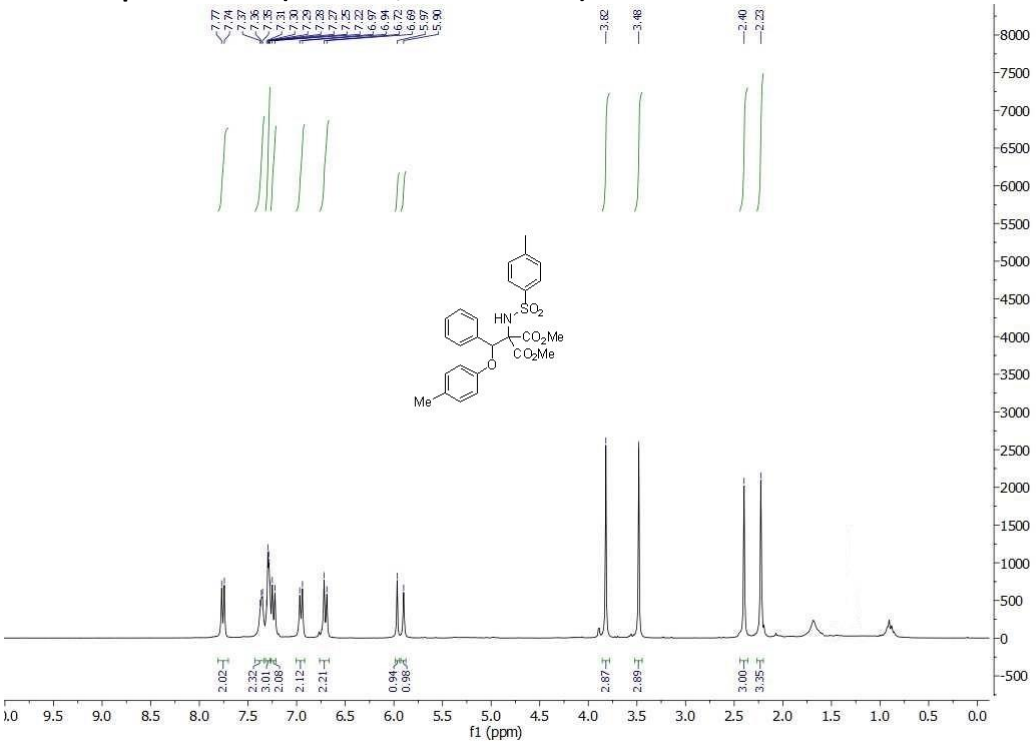
**$^{1}H$ NMR spectra of 3a (400 MHz, Chloroform-*d*):**



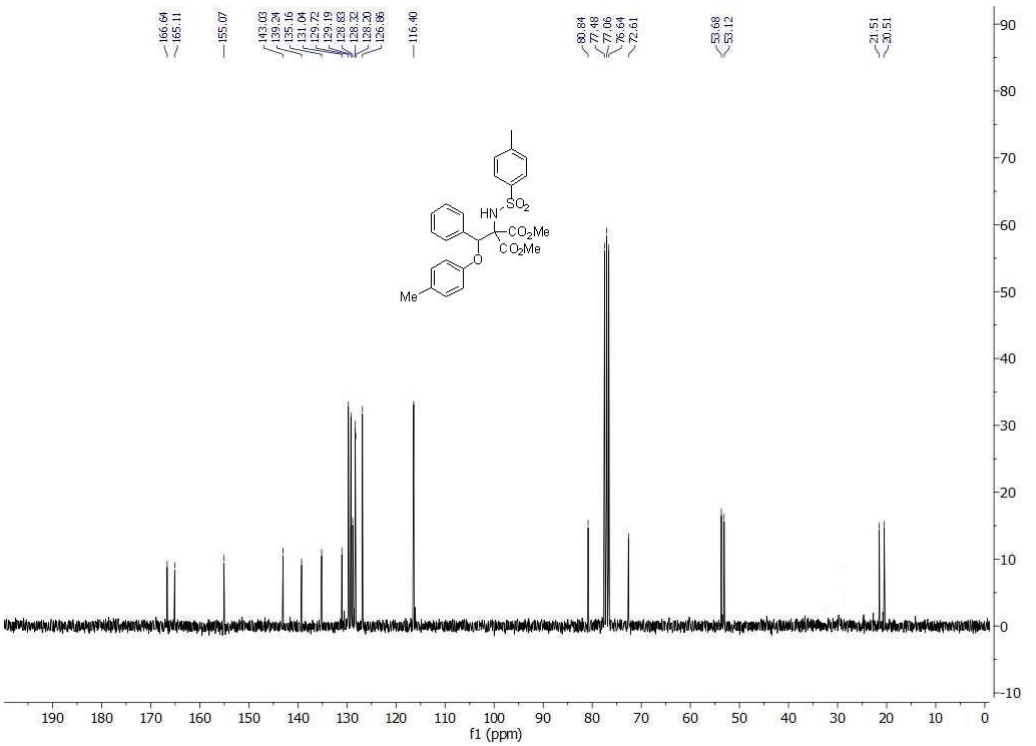

**$^{13}C$ {1H} NMR spectra of 3a (100 MHz, Chloroform-*d*):**



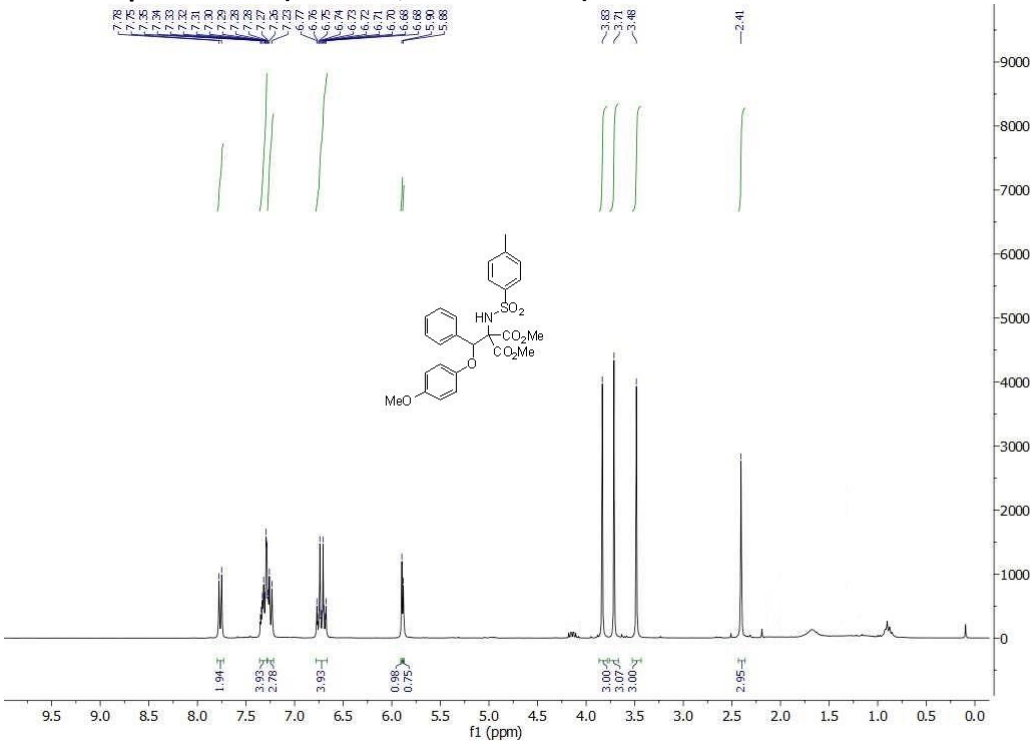
**$^{1}$H NMR spectra of 3b (300 MHz, Chloroform-*d*):**



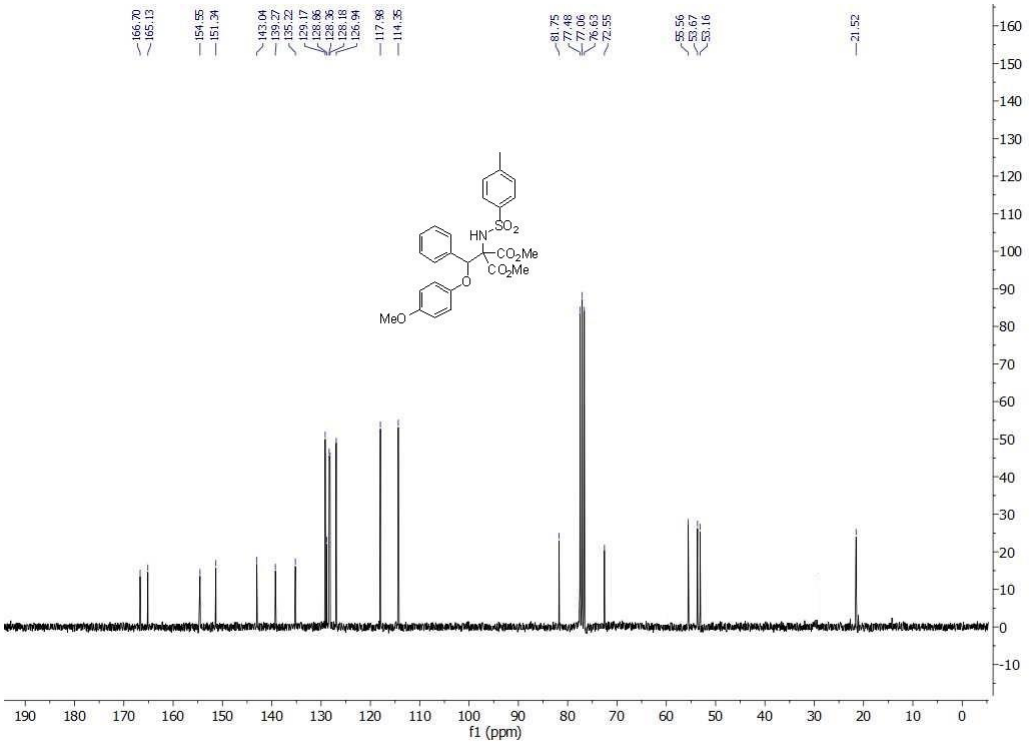

**$^{13}$C {1H} NMR spectra of 3b (75 MHz, Chloroform-*d*):**



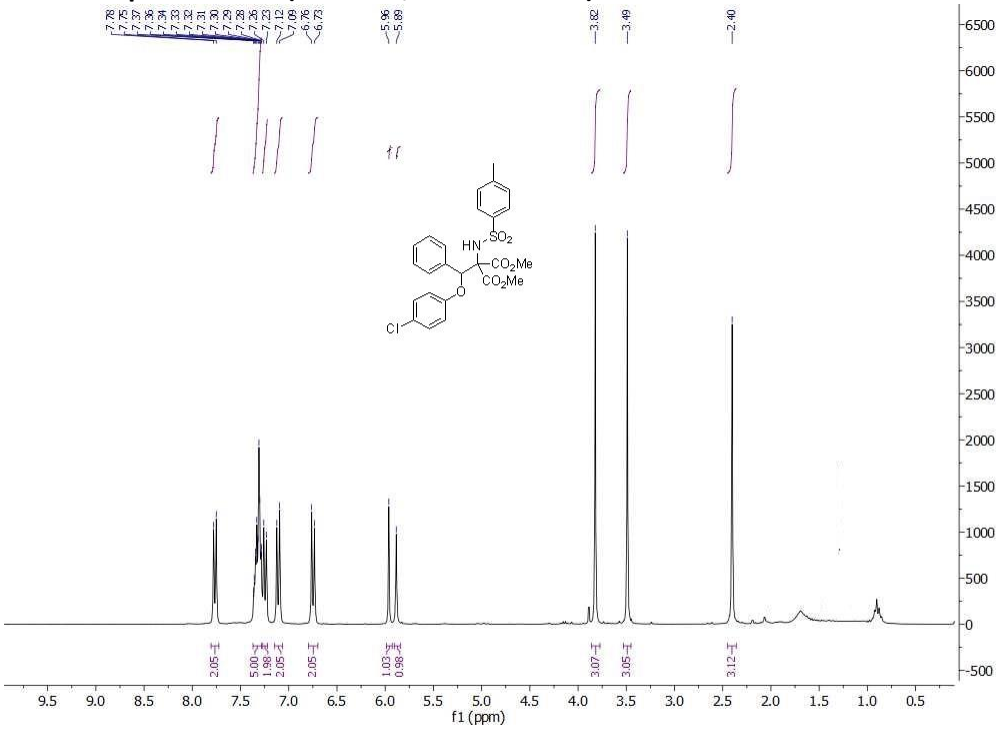
**$^{1}$H NMR spectra of 3c (300 MHz, Chloroform-*d*):**



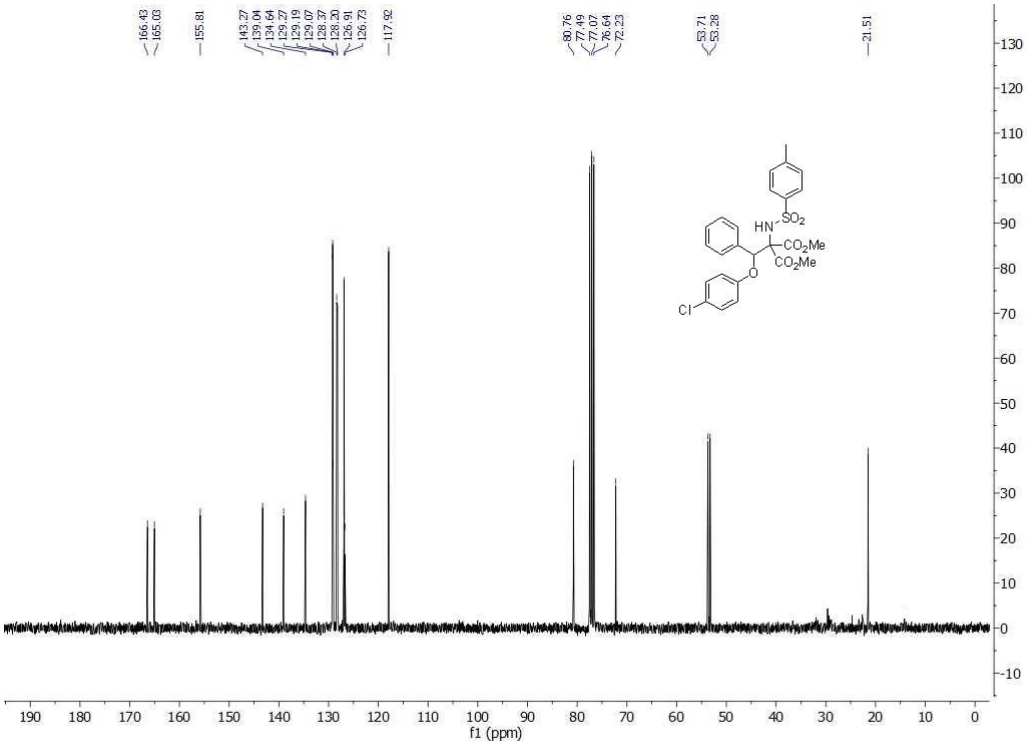

**$^{13}$C {1H} NMR spectra of 3c (75 MHz, Chloroform-*d*):**



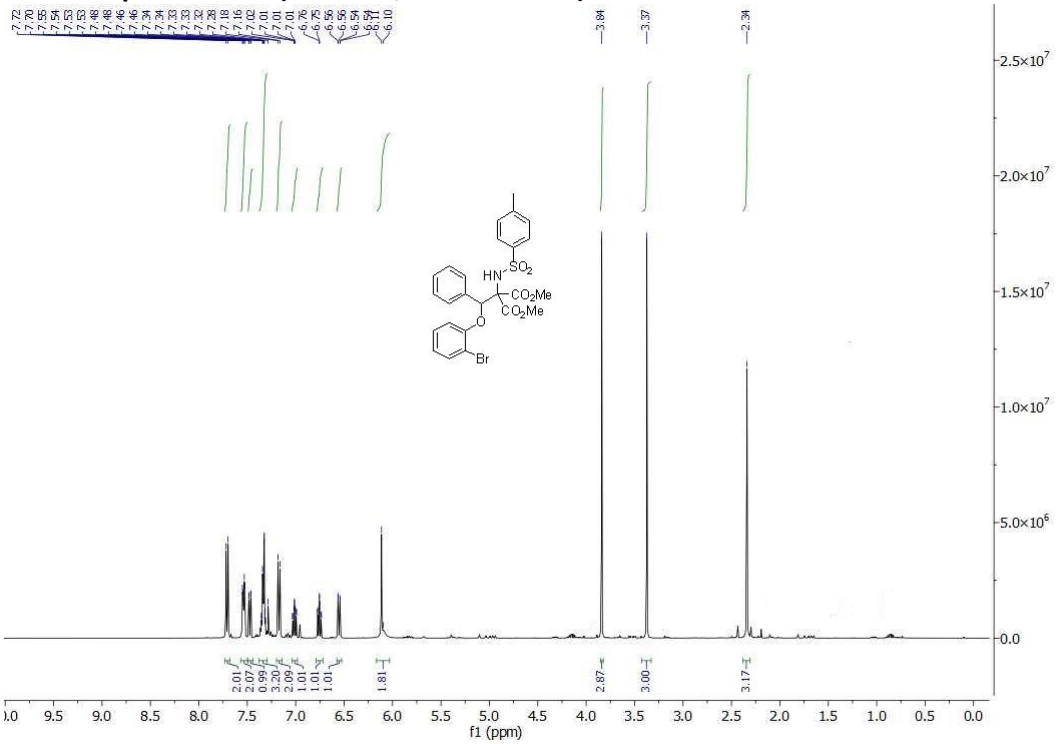
**$^{1}$H NMR spectra of 3d (300 MHz, Chloroform-*d*):**



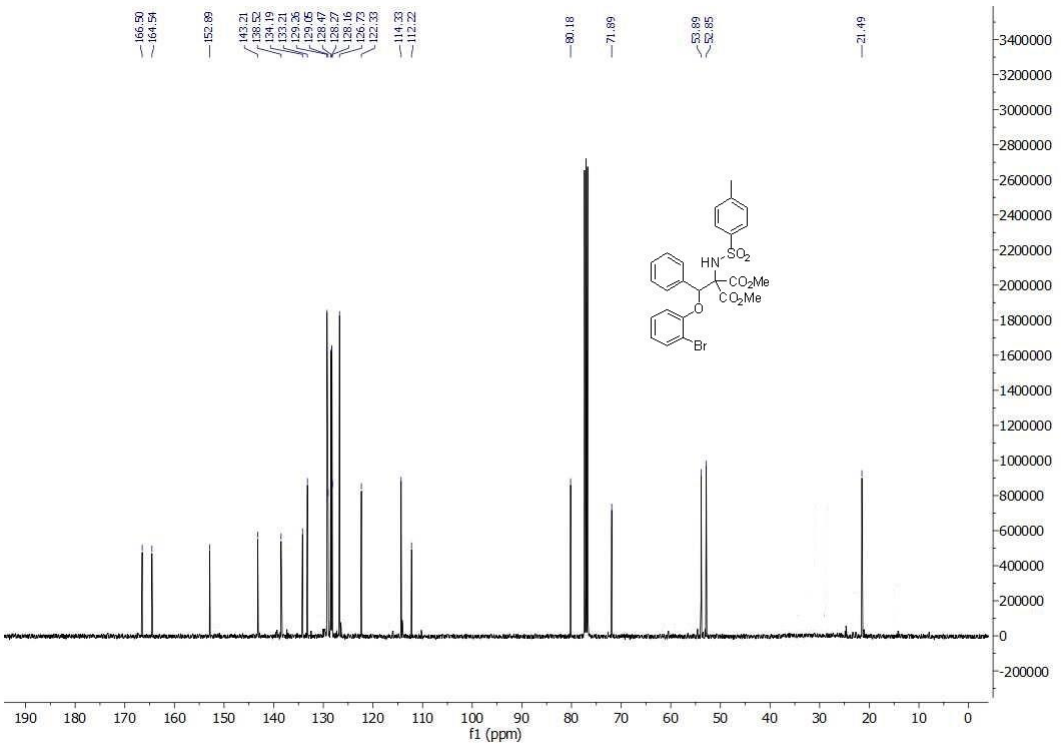

**$^{13}$C {1H} NMR spectra of 3d (75 MHz, Chloroform-*d*):**



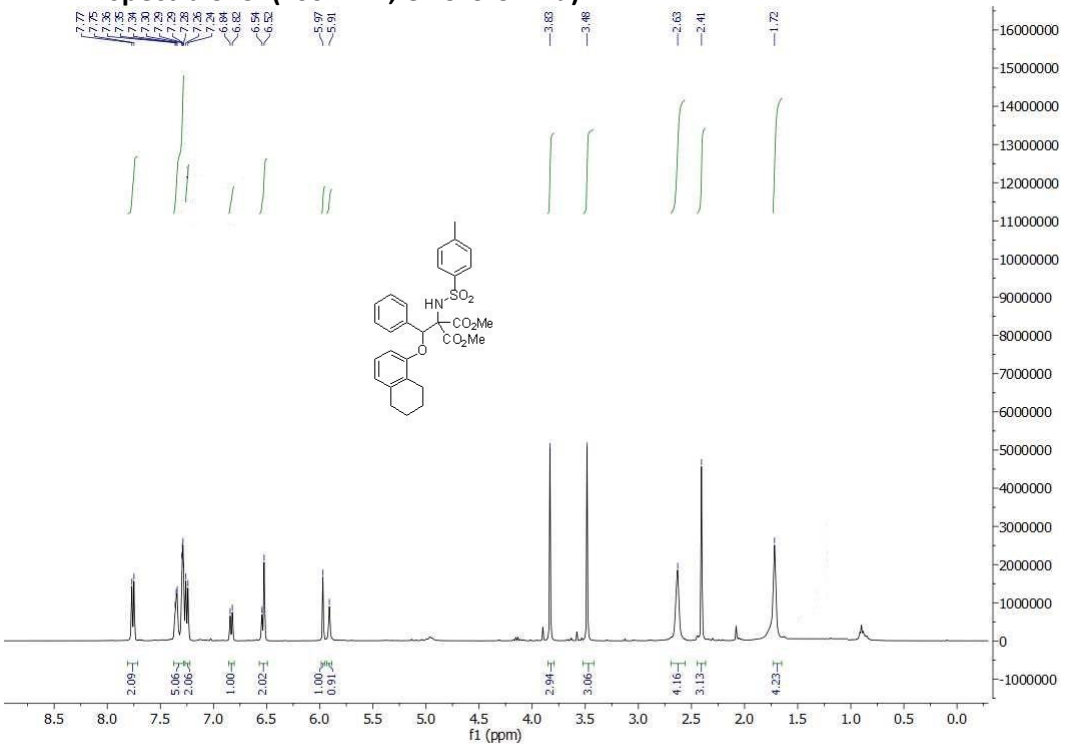
**$^{1}$H NMR spectra of 3e (400 MHz, Chloroform-*d*):**



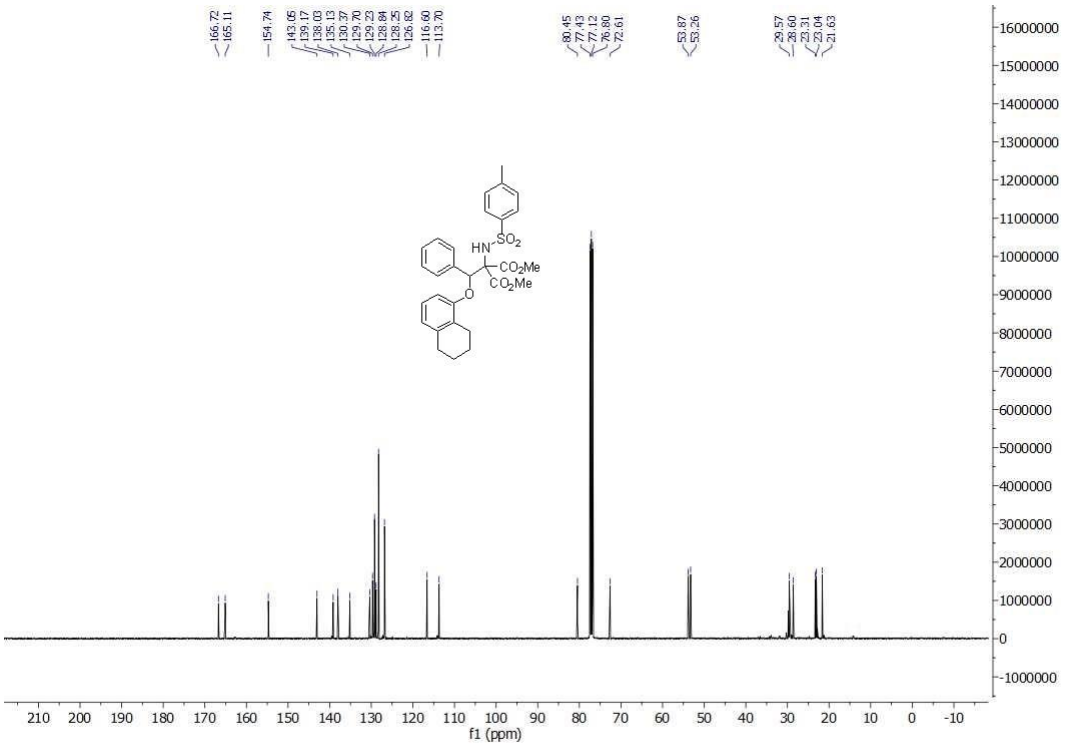

**$^{13}$C {1H} NMR spectra of 3e (100 MHz, Chloroform-*d*):**



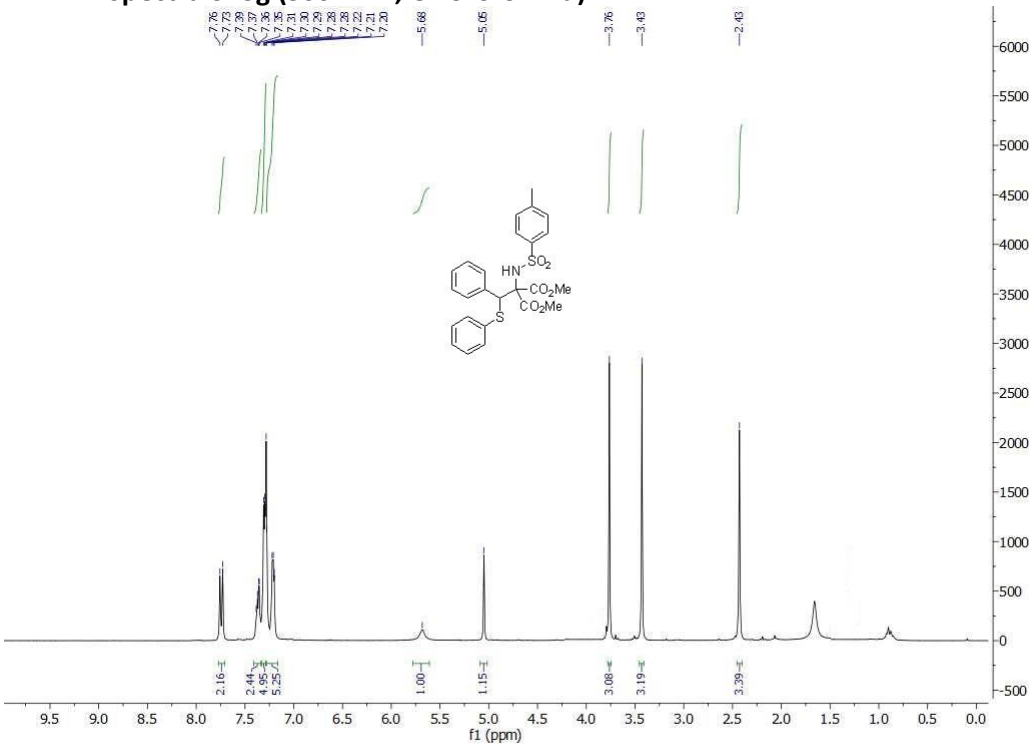
**$^{1}$H NMR spectra of 3f (400 MHz, Chloroform-*d*):**



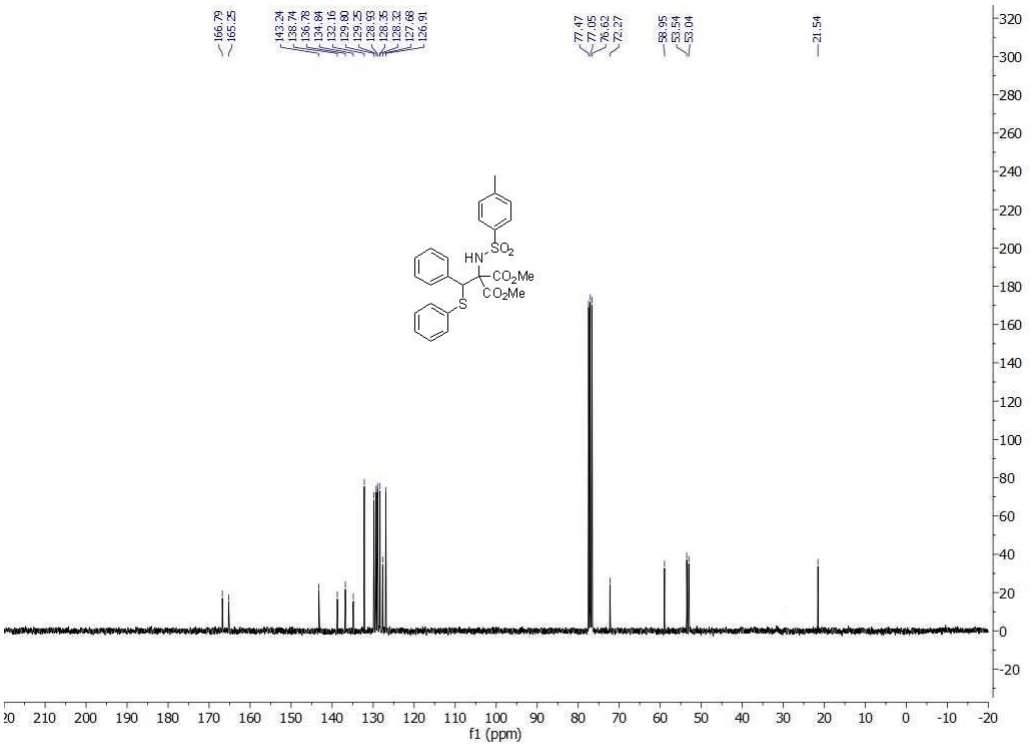

**$^{13}$C {1H} NMR spectra of 3f (100 MHz, Chloroform-*d*):**



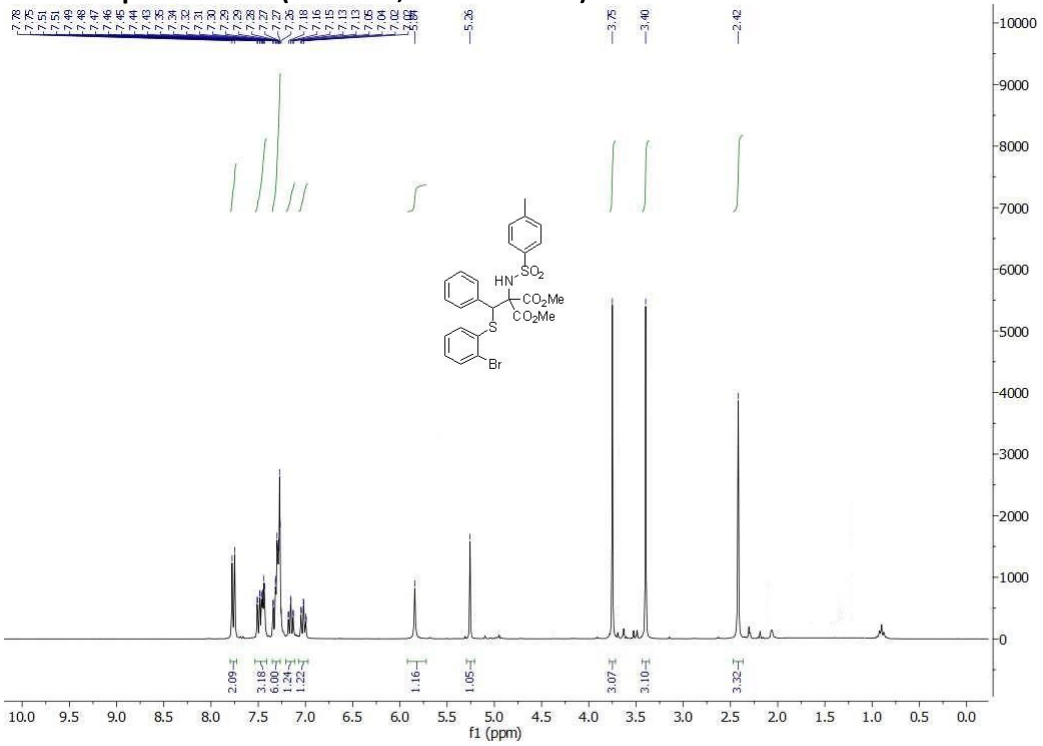
**$^{1}$H NMR spectra of 3g (300 MHz, Chloroform-*d*):**



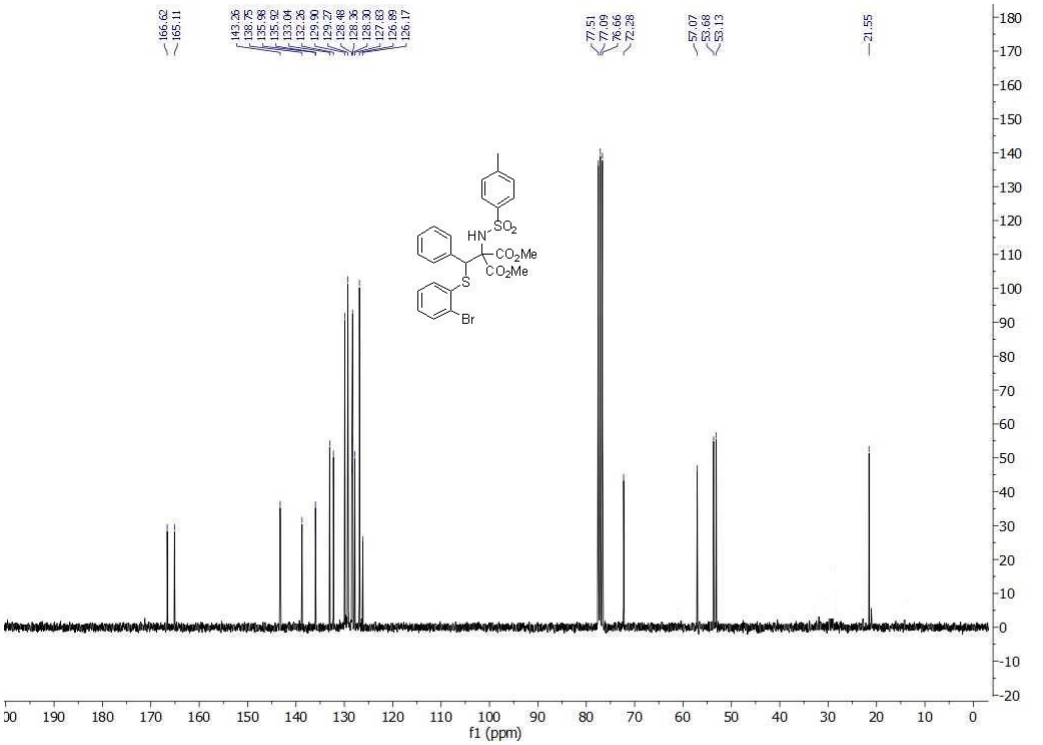

**$^{13}$C {1H} NMR spectra of 3g (75 MHz, Chloroform-*d*):**



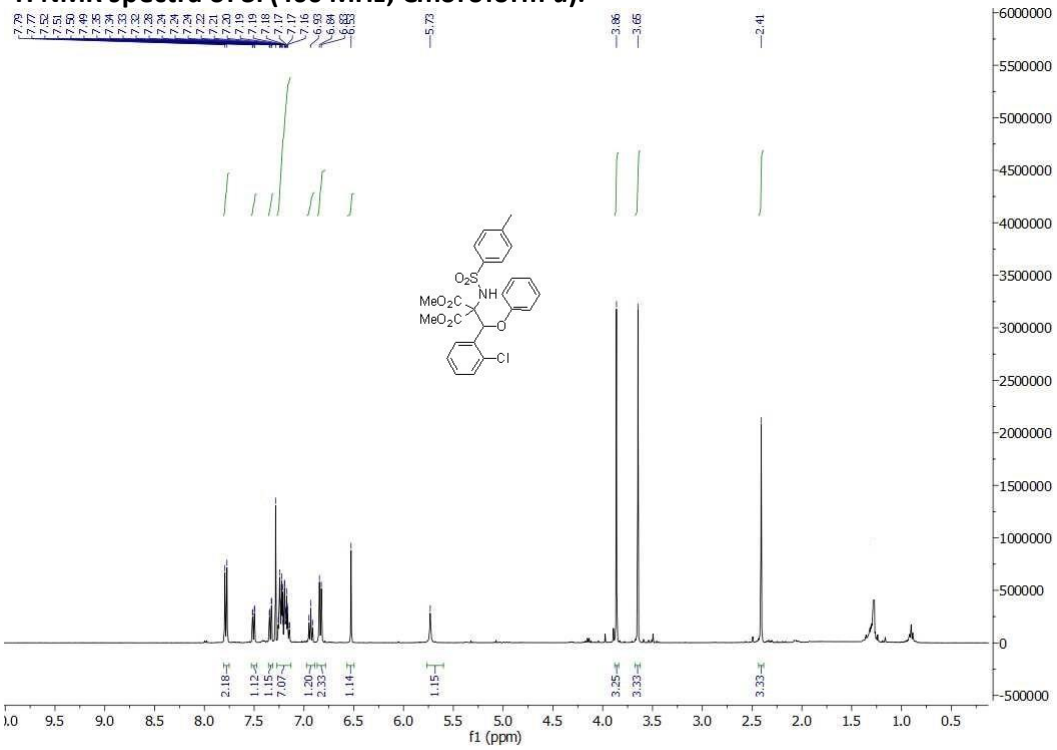
**$^{1}$H NMR spectra of 3h (300 MHz, Chloroform-*d*):**



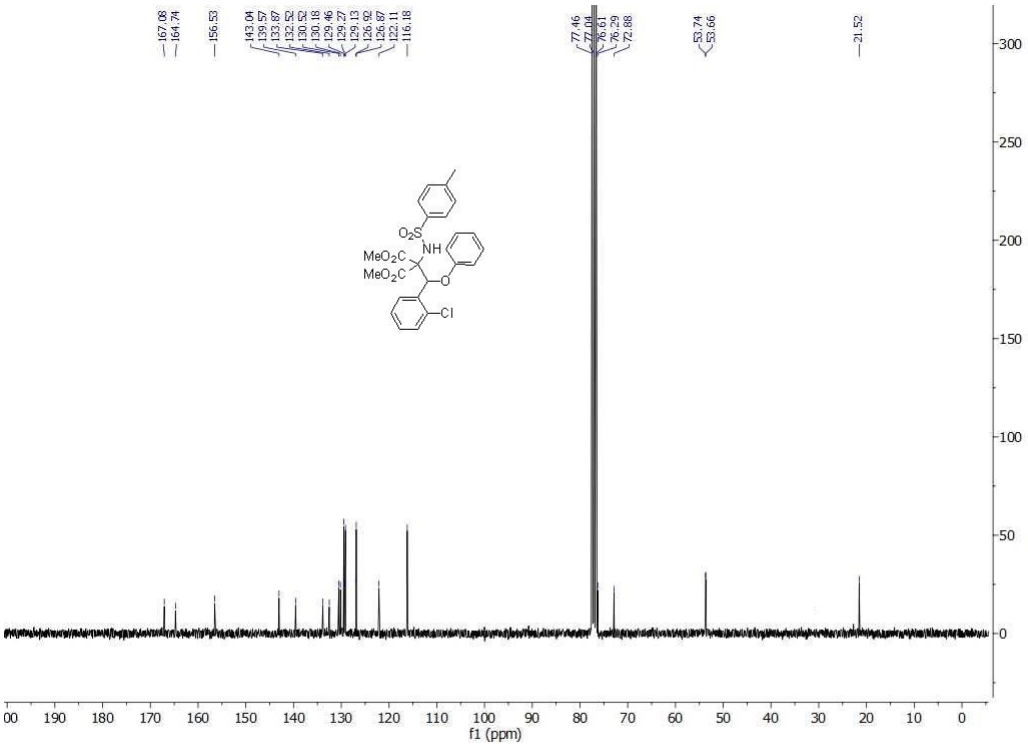

**$^{13}$C {1H} NMR spectra of 3h (75 MHz, Chloroform-*d*):**



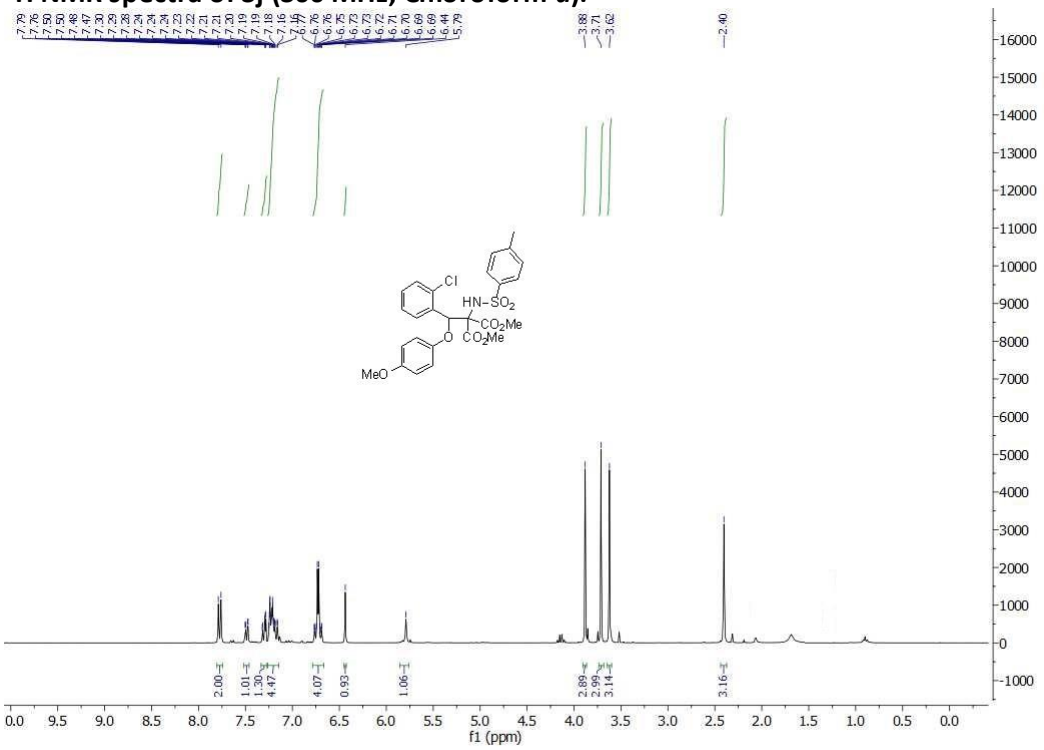
**$^{1}$H NMR spectra of 3i (400 MHz, Chloroform-*d*):**



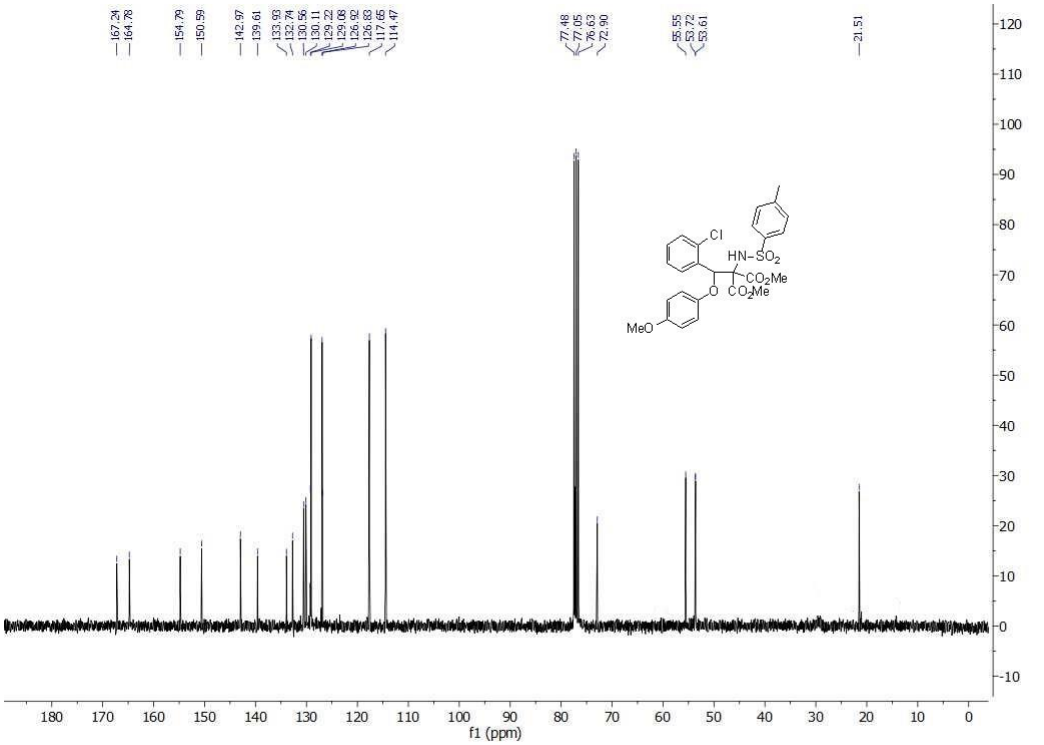

**$^{13}$C {1H} NMR spectra of 3i (75 MHz, Chloroform-*d*):**



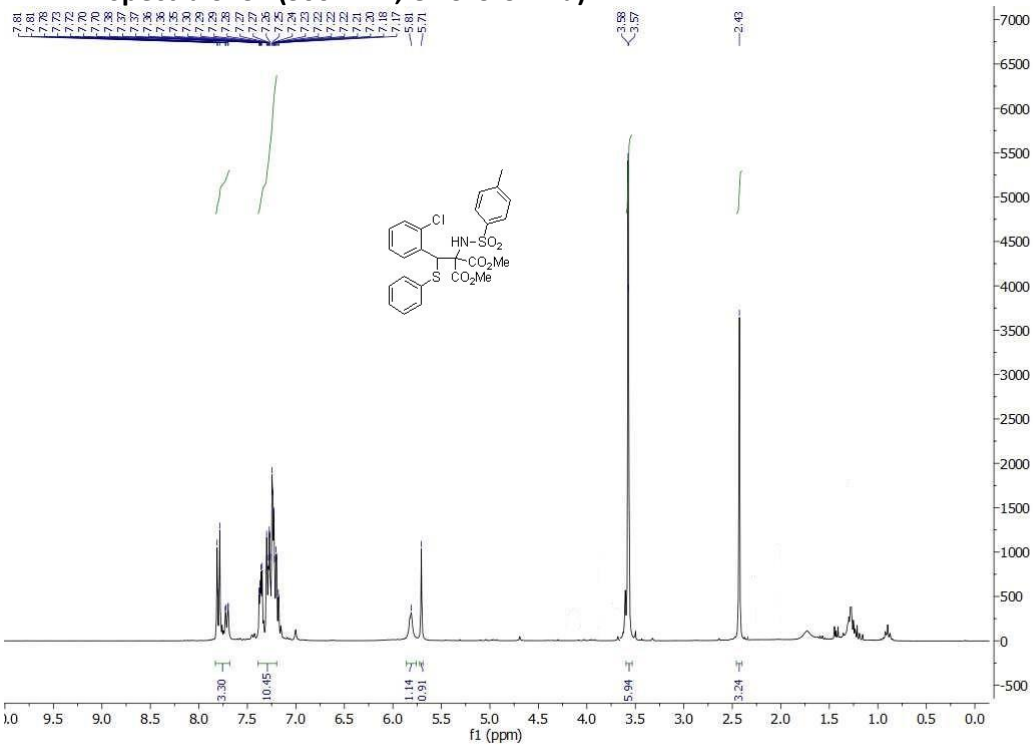
**$^{1}$H NMR spectra of 3j (300 MHz, Chloroform-*d*):**



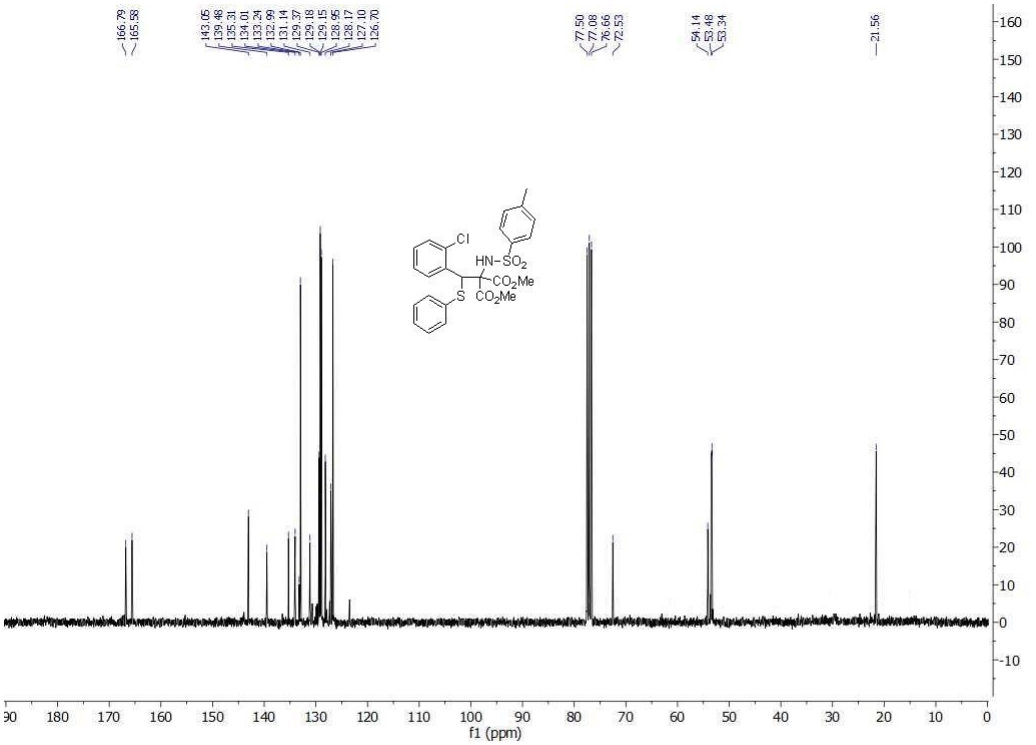

**$^{13}$C {1H} NMR spectra of 3j (75 MHz, Chloroform-*d*):**



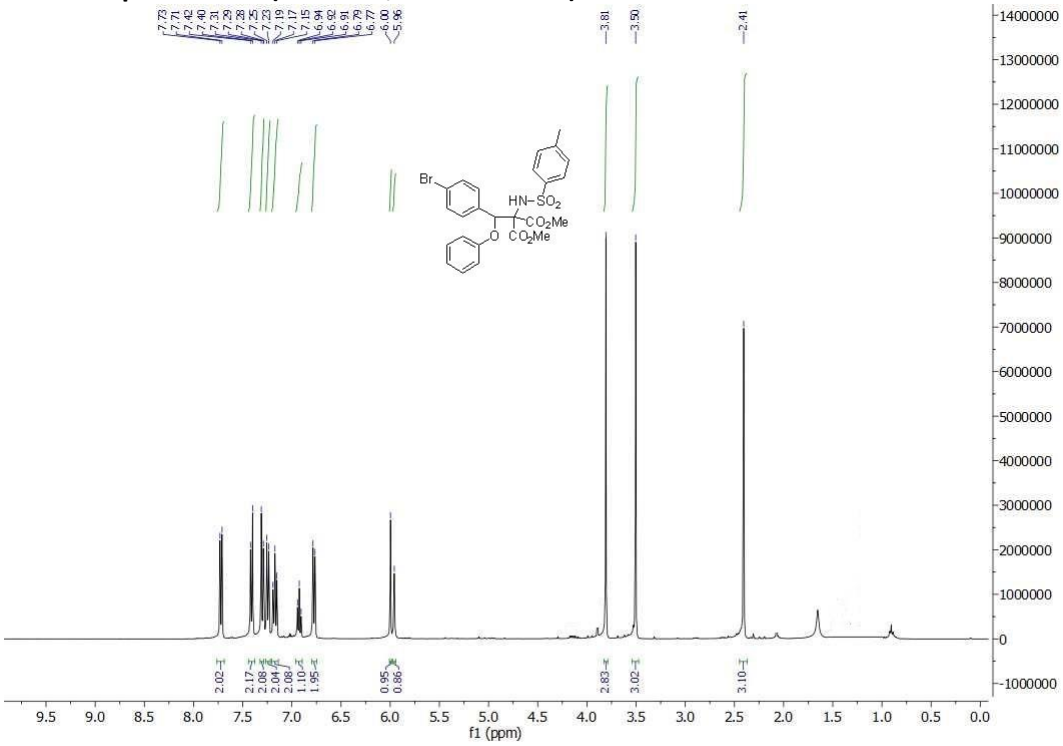
**$^{1}$H NMR spectra of 3k (300 MHz, Chloroform-*d*):**



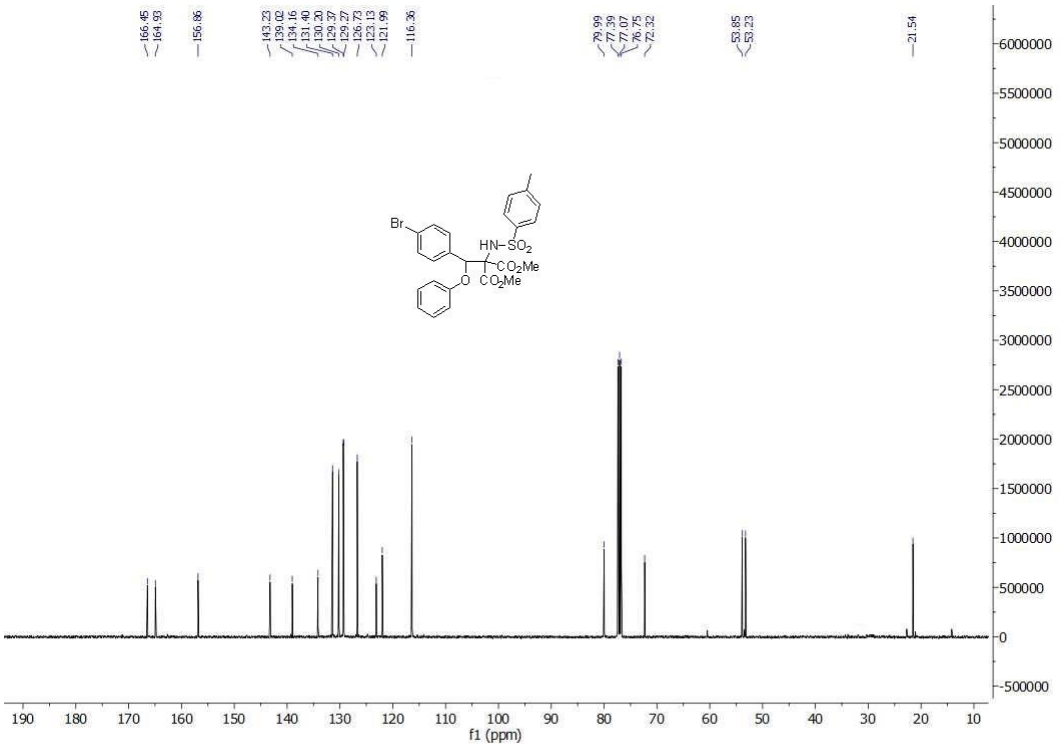

**$^{13}$C {1H} NMR spectra of 3k (75 MHz, Chloroform-*d*):**



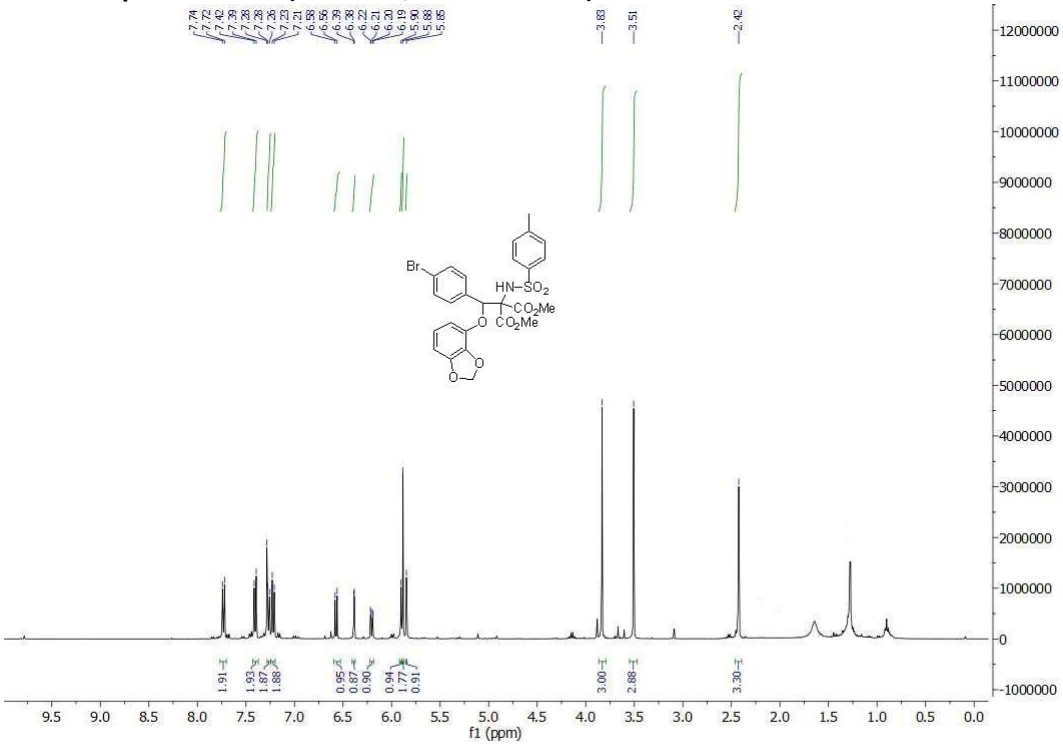
**$^{1}$H NMR spectra of 3l (400 MHz, Chloroform-*d*):**



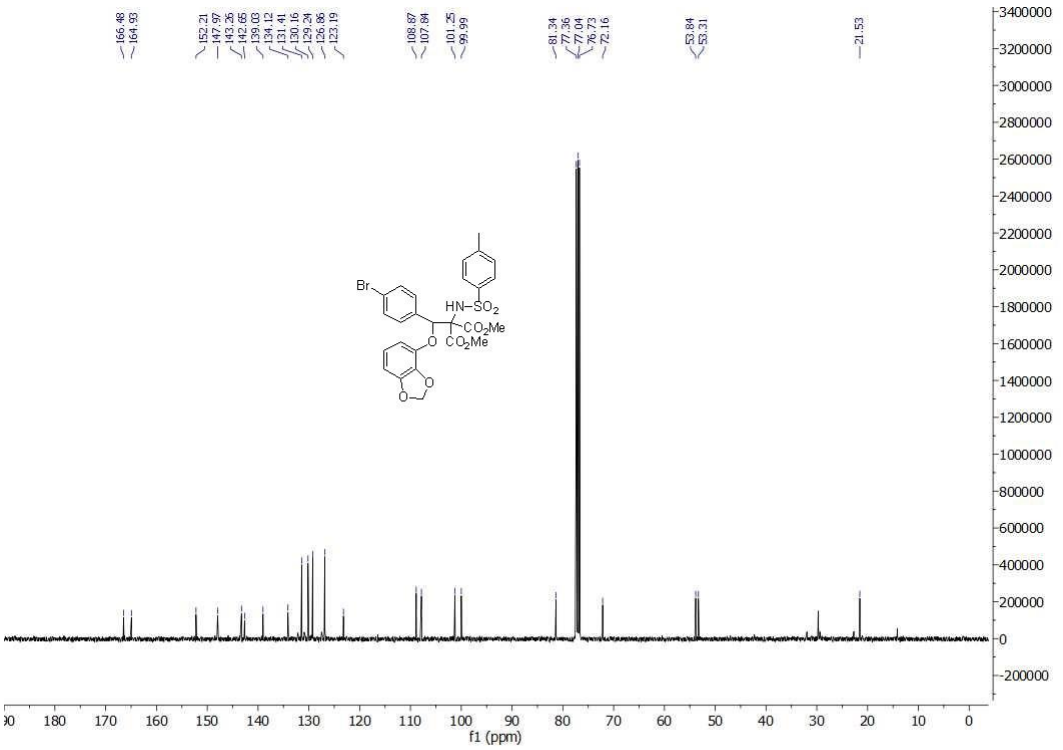

**$^{13}$C {1H} NMR spectra of 3l (100 MHz, Chloroform-*d*):**



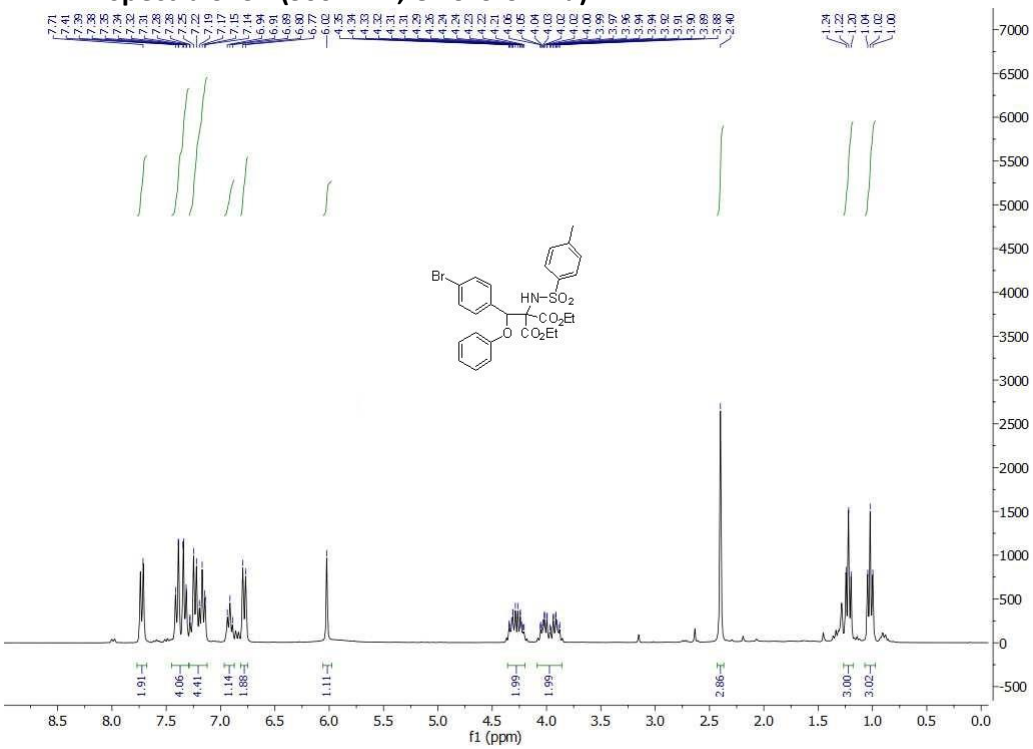
**$^{1}$H NMR spectra of 3m (400 MHz, Chloroform-*d*):**



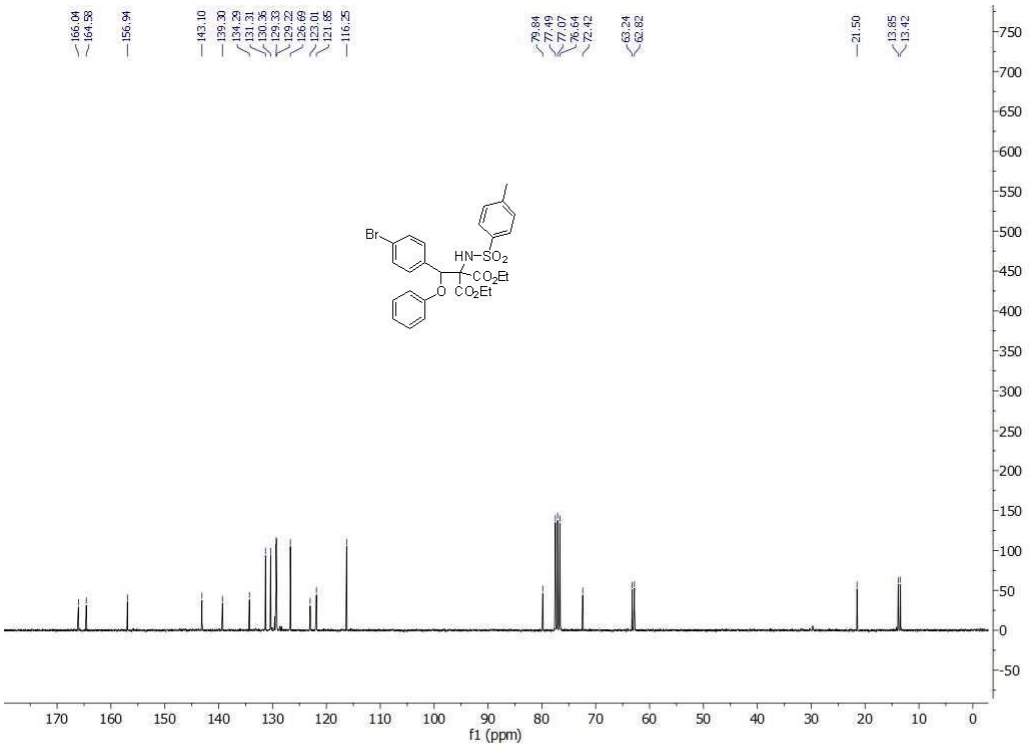

**$^{13}$C {1H} NMR spectra of 3m (100 MHz, Chloroform-*d*):**



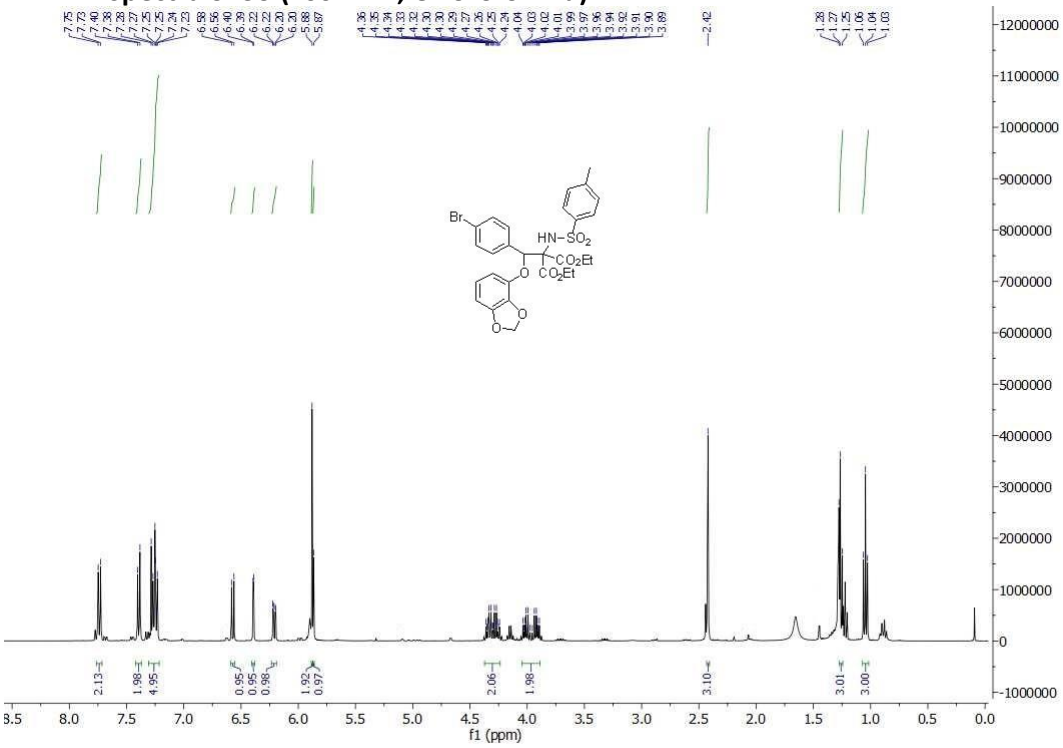
**$^{1}$H NMR spectra of 3n (300 MHz, Chloroform-*d*):**



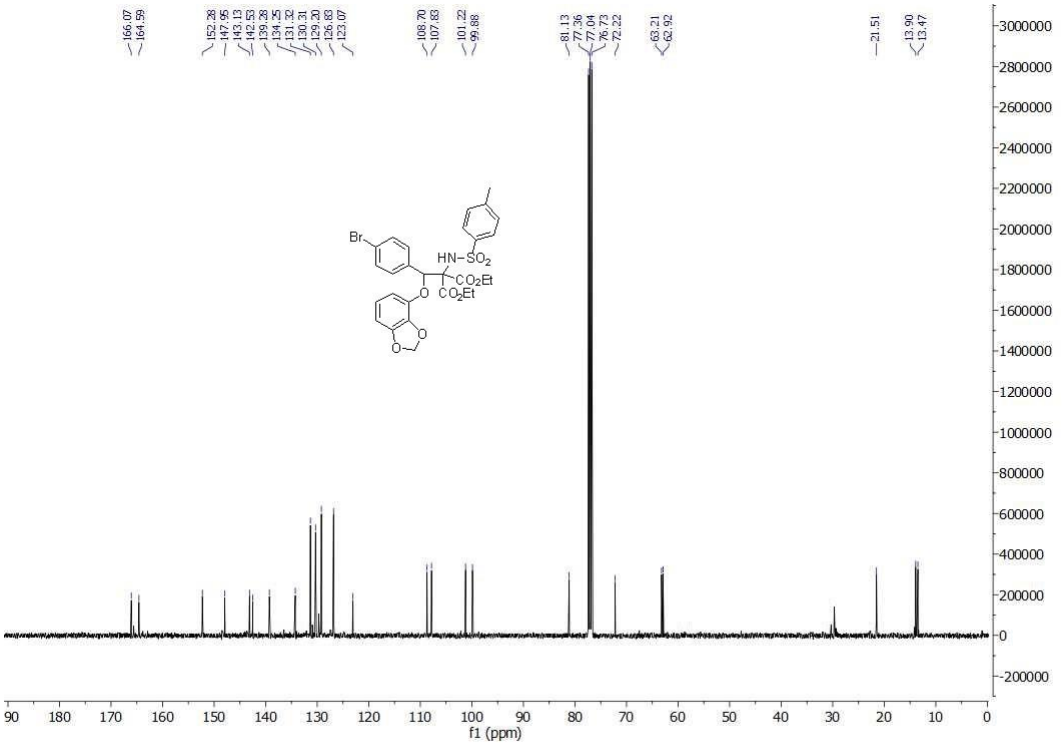

**$^{13}$C {1H} NMR spectra of 3n (75 MHz, Chloroform-*d*):**



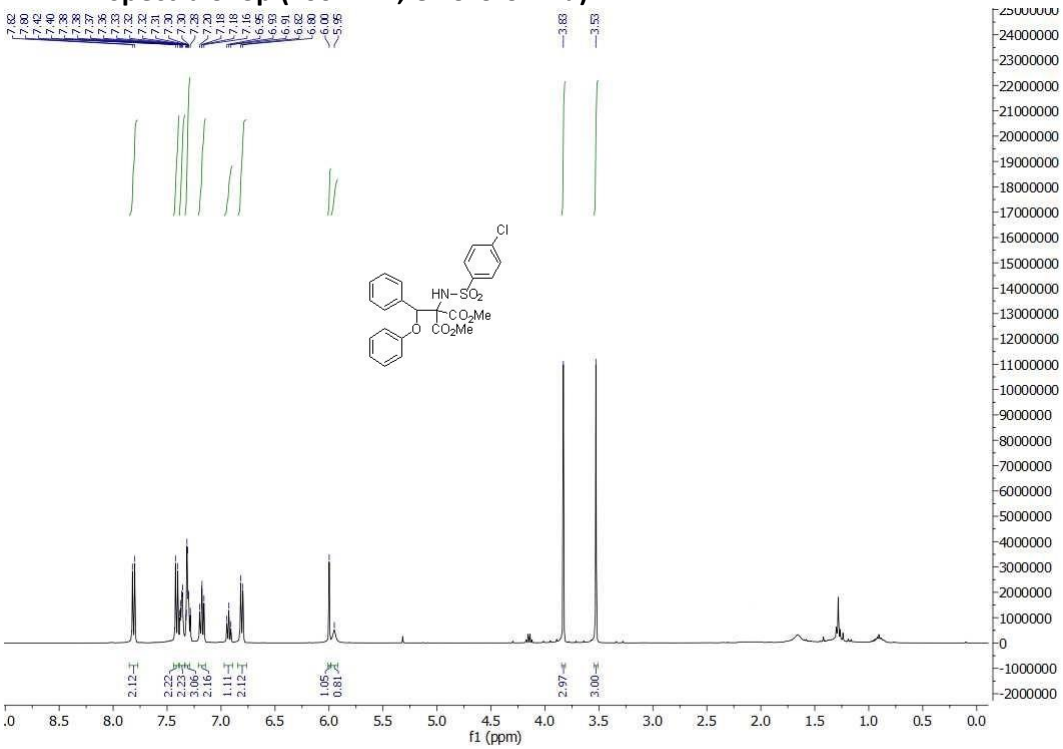
**$^{1}$H NMR spectra of 3o (400 MHz, Chloroform-*d*):**



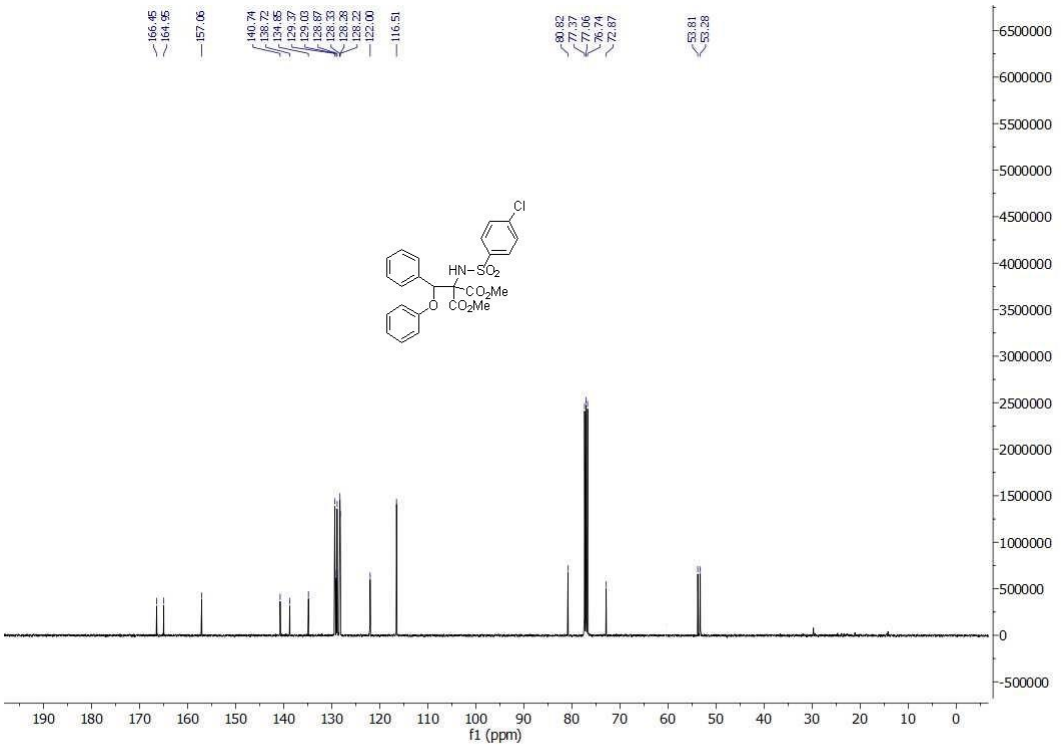

**$^{13}$C {1H} NMR spectra of 3o (100 MHz, Chloroform-*d*):**



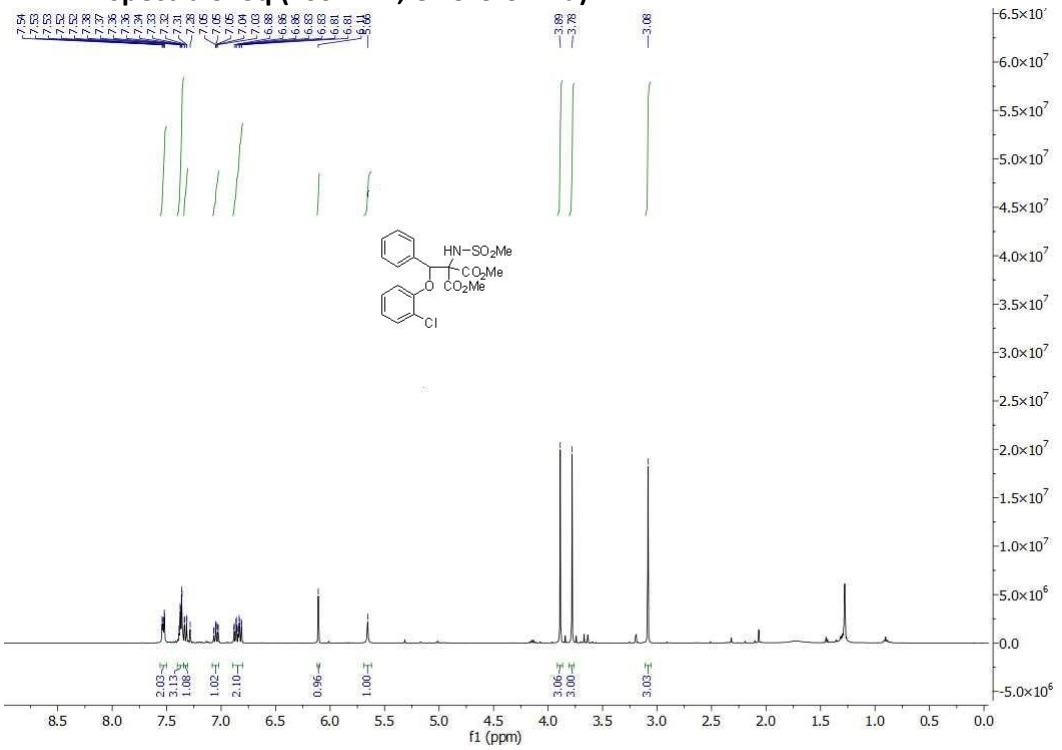
**$^{1}$H NMR spectra of 3p (400 MHz, Chloroform-*d*):**



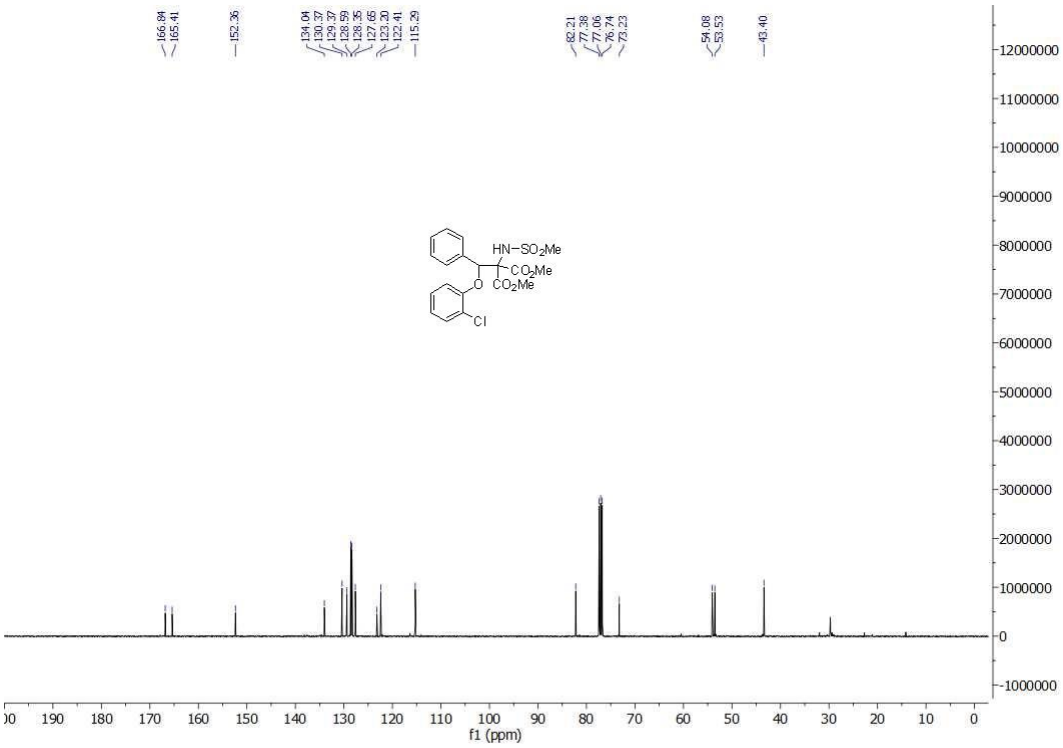

**$^{13}$C {1H} NMR spectra of 3p (100 MHz, Chloroform-*d*):**



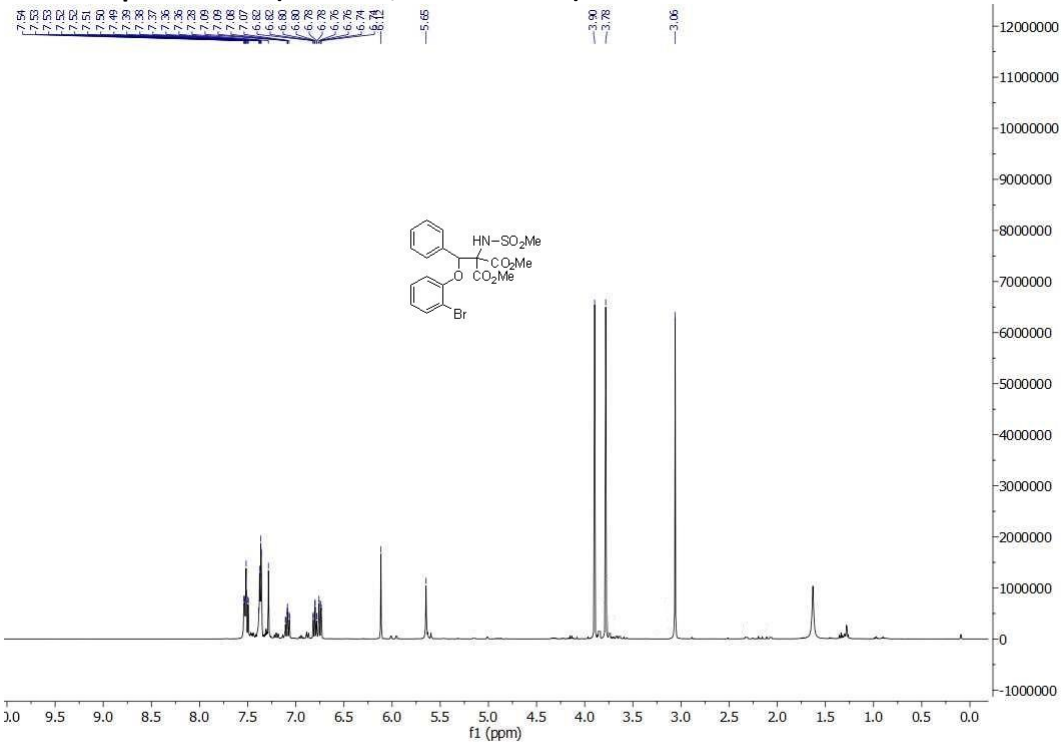
**$^{1}$H NMR spectra of 3q (400 MHz, Chloroform-*d*):**



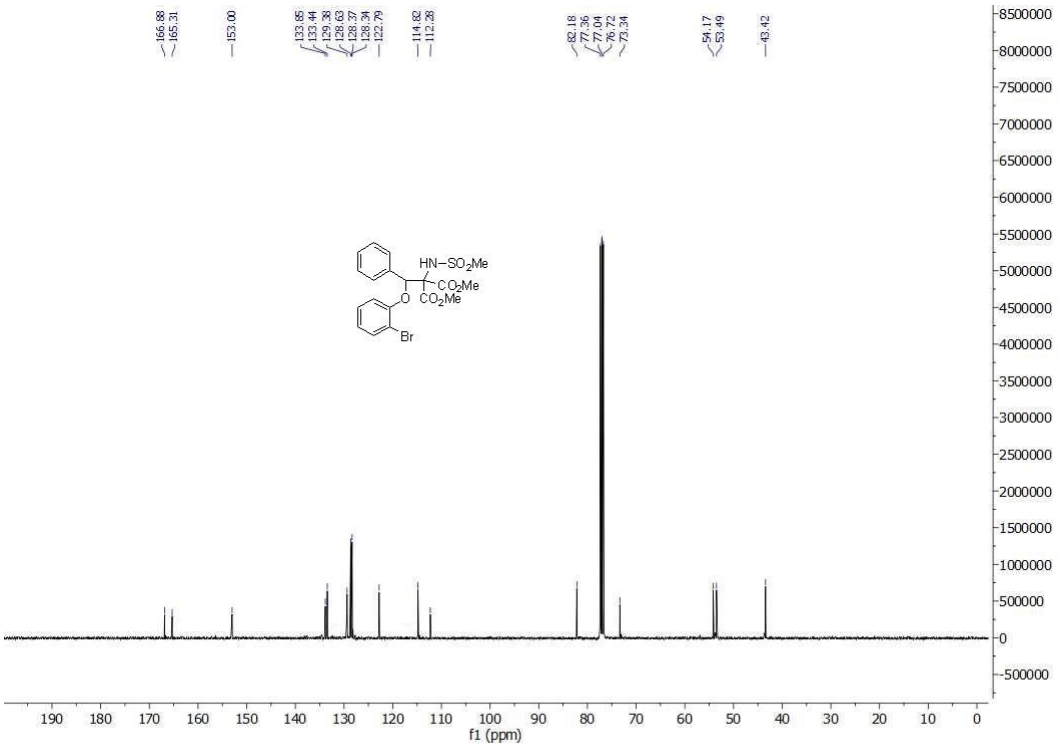

**$^{13}$C {1H} NMR spectra of 3q (100 MHz, Chloroform-*d*):**



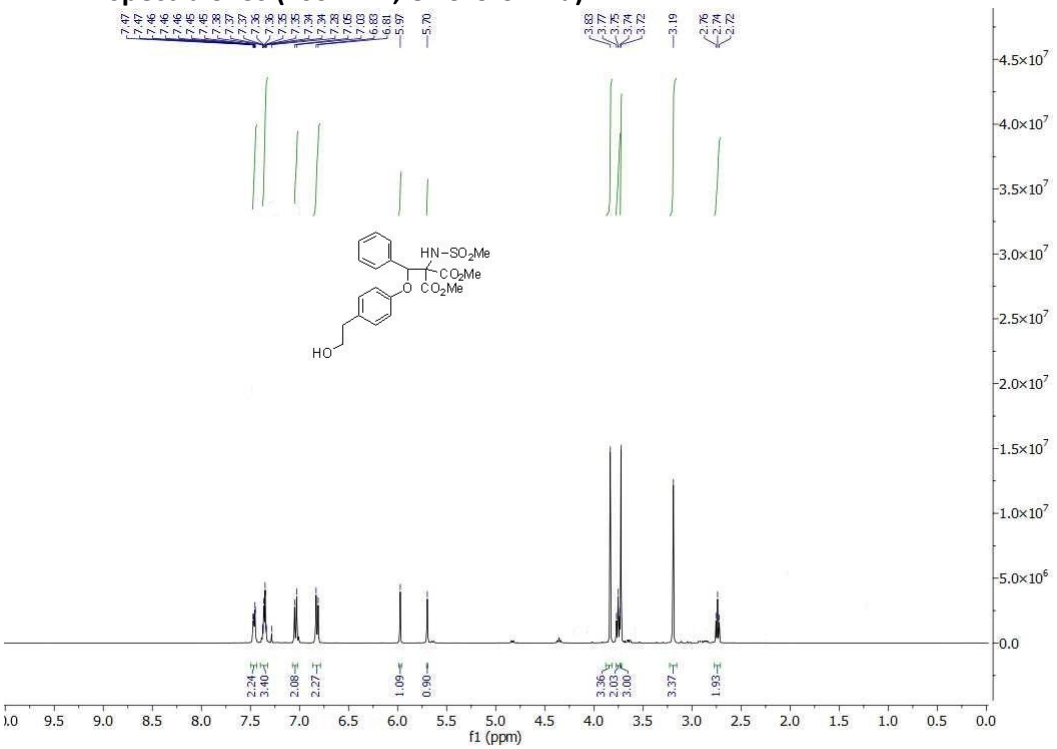
**$^{1}$H NMR spectra of 3r (400 MHz, Chloroform-*d*):**



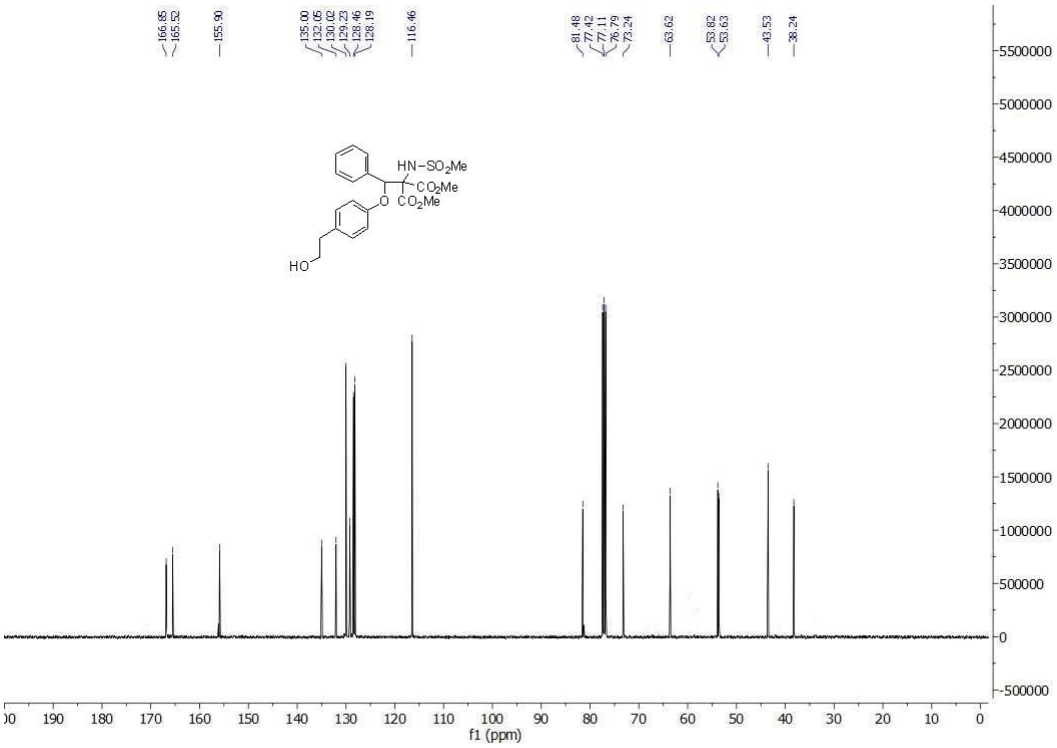

**$^{13}$C {1H} NMR spectra of 3r (100 MHz, Chloroform-*d*):**



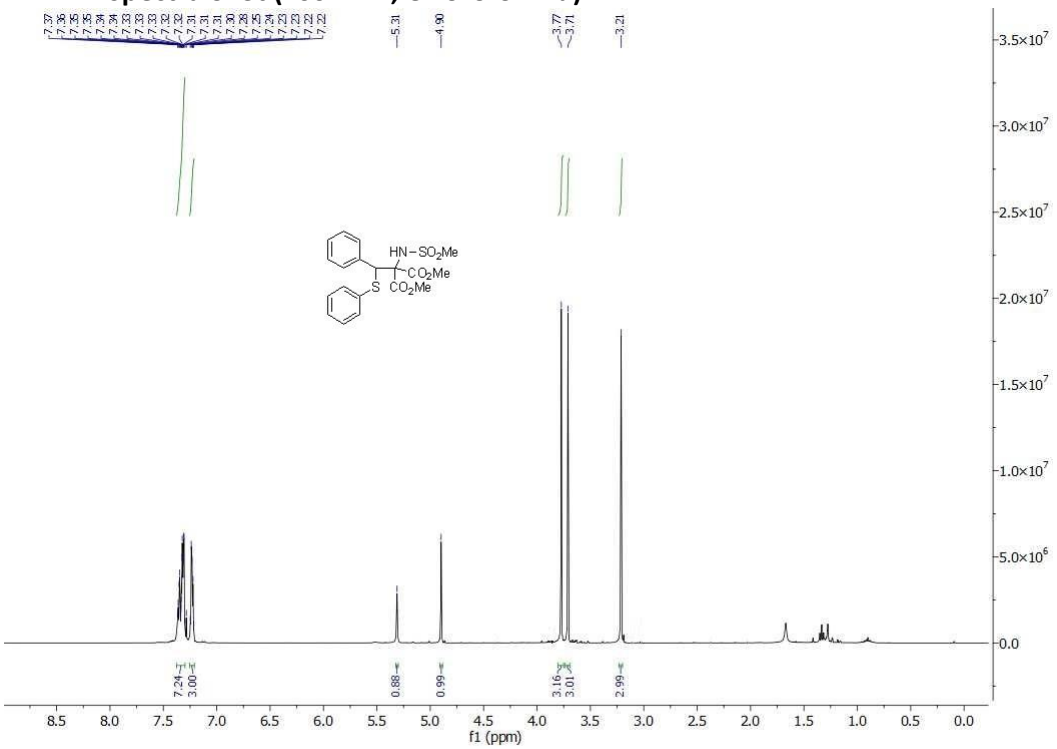
**$^{1}$H NMR spectra of 3s (400 MHz, Chloroform-*d*):**



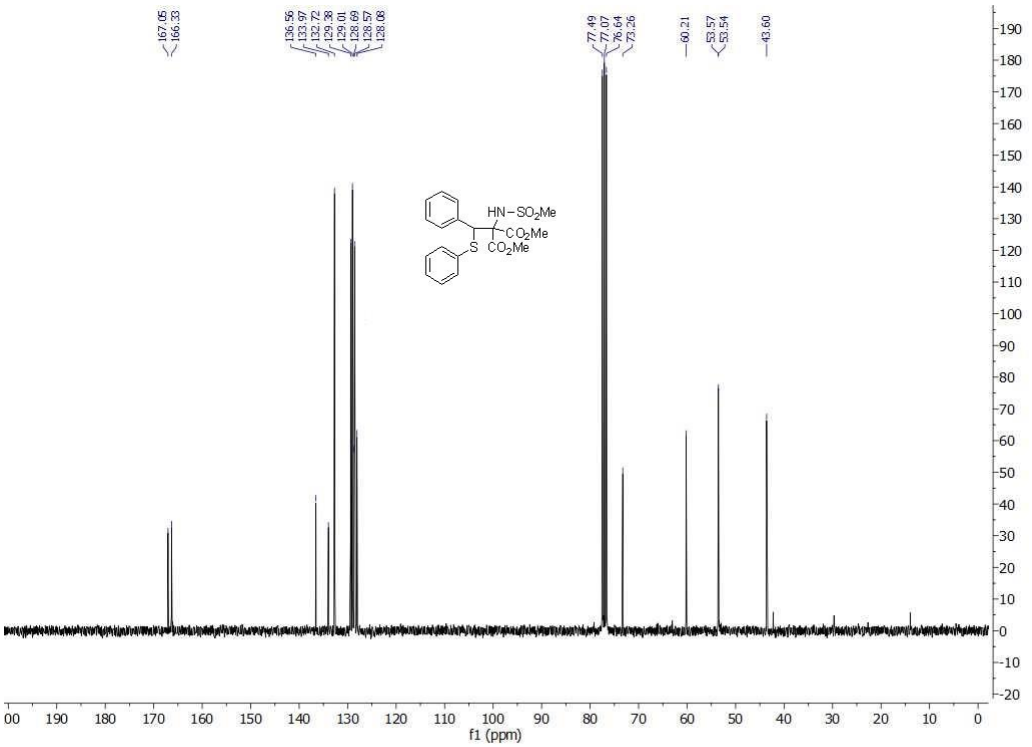

**$^{13}$C {1H} NMR spectra of 3s (100 MHz, Chloroform-*d*):**



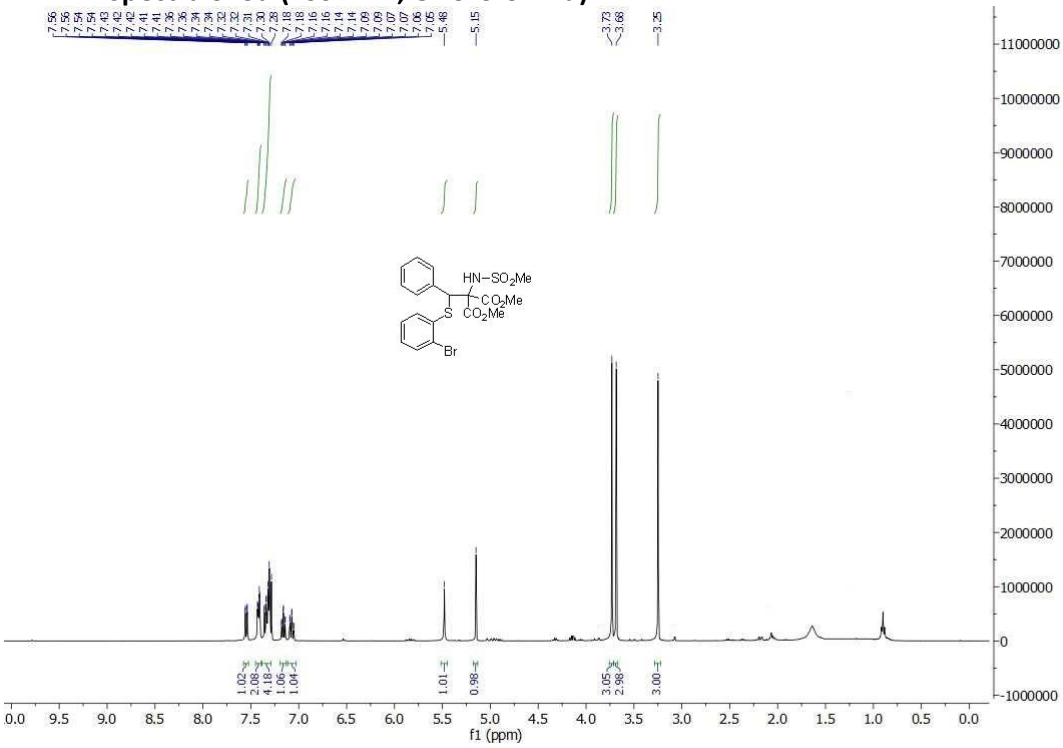
**$^{1}$H NMR spectra of 3t (400 MHz, Chloroform-*d*):**



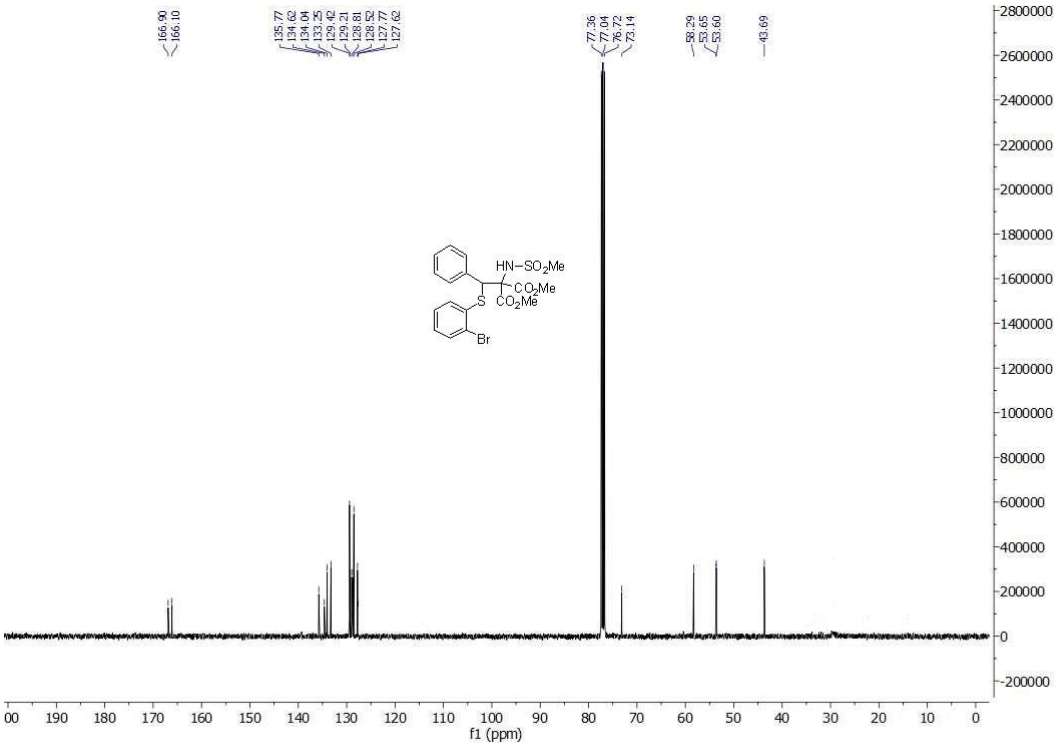

**$^{13}$C {1H} NMR spectra of 3t (75 MHz, Chloroform-*d*):**



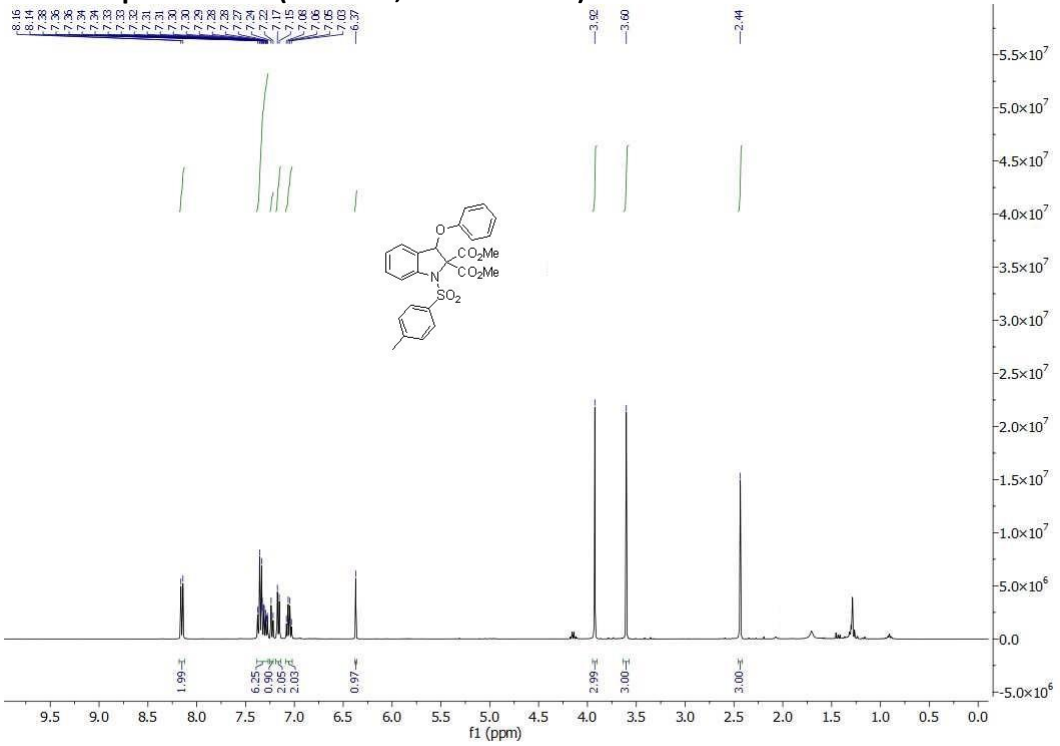
**$^{1}$H NMR spectra of 3u (400 MHz, Chloroform-*d*):**



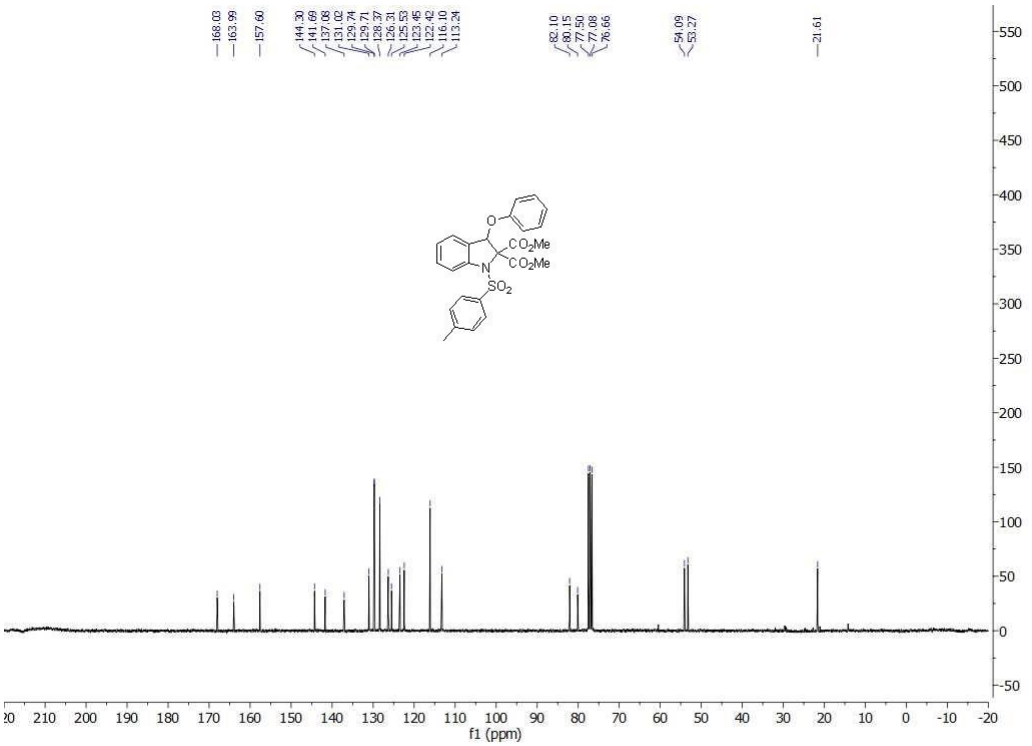

**$^{13}$C {1H} NMR spectra of 3u (100 MHz, Chloroform-*d*):**



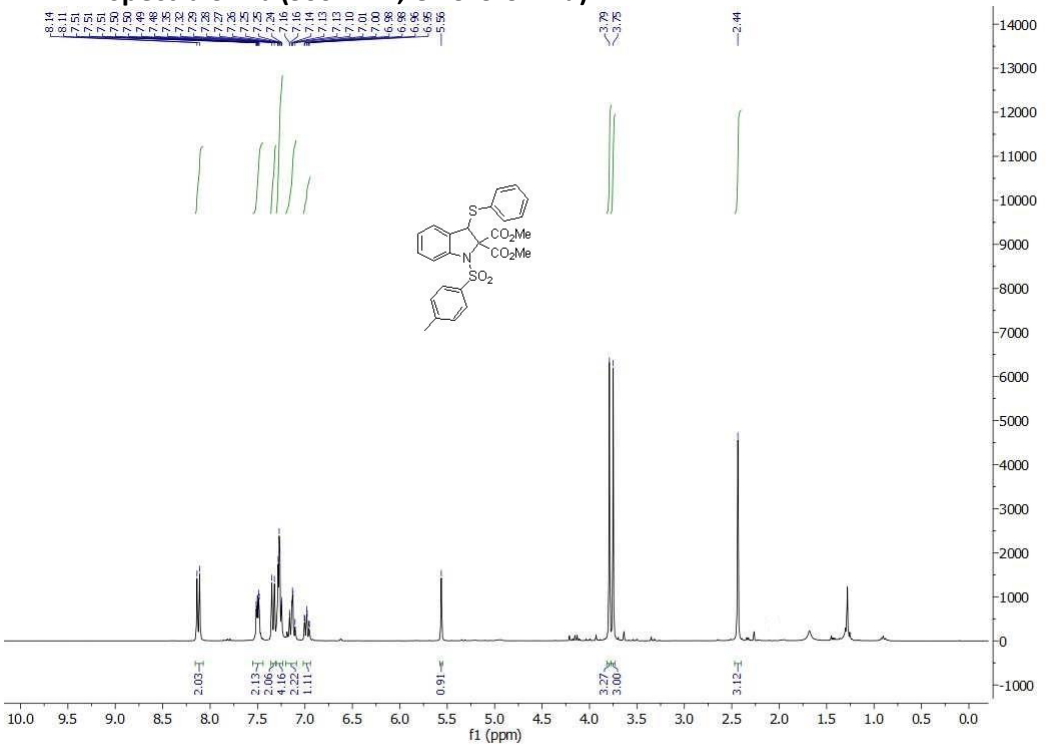
**$^{1}$H NMR spectra of 4a (400 MHz, Chloroform-*d*):**



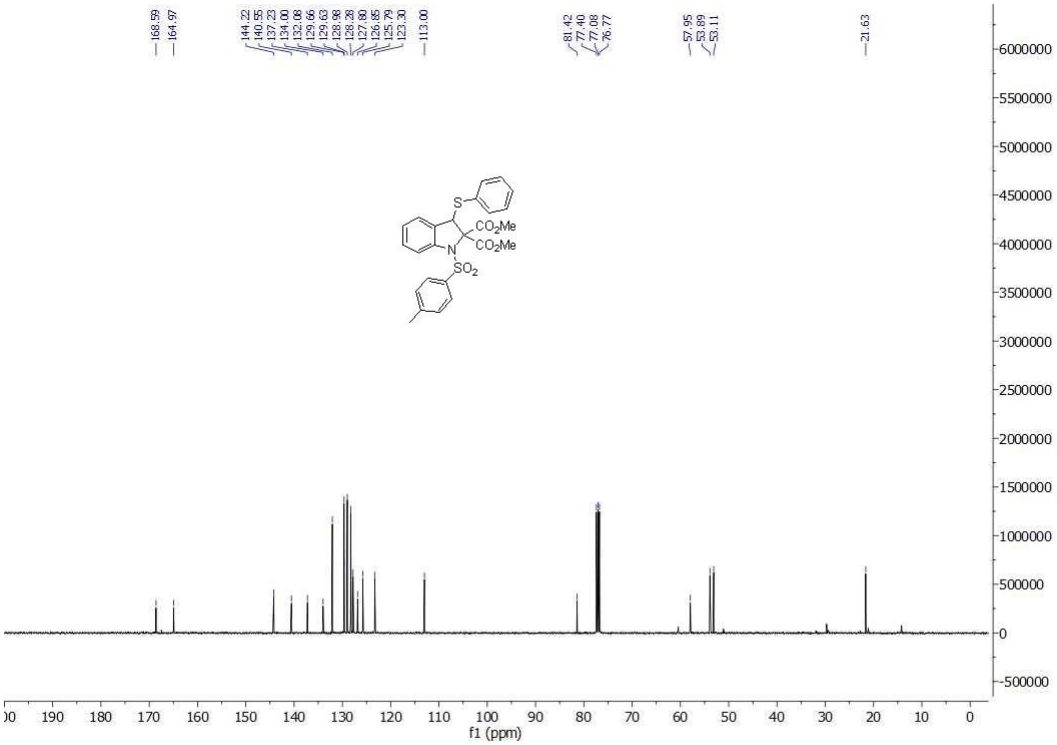

**$^{13}$C {1H} NMR spectra of 4a (75 MHz, Chloroform-*d*):**



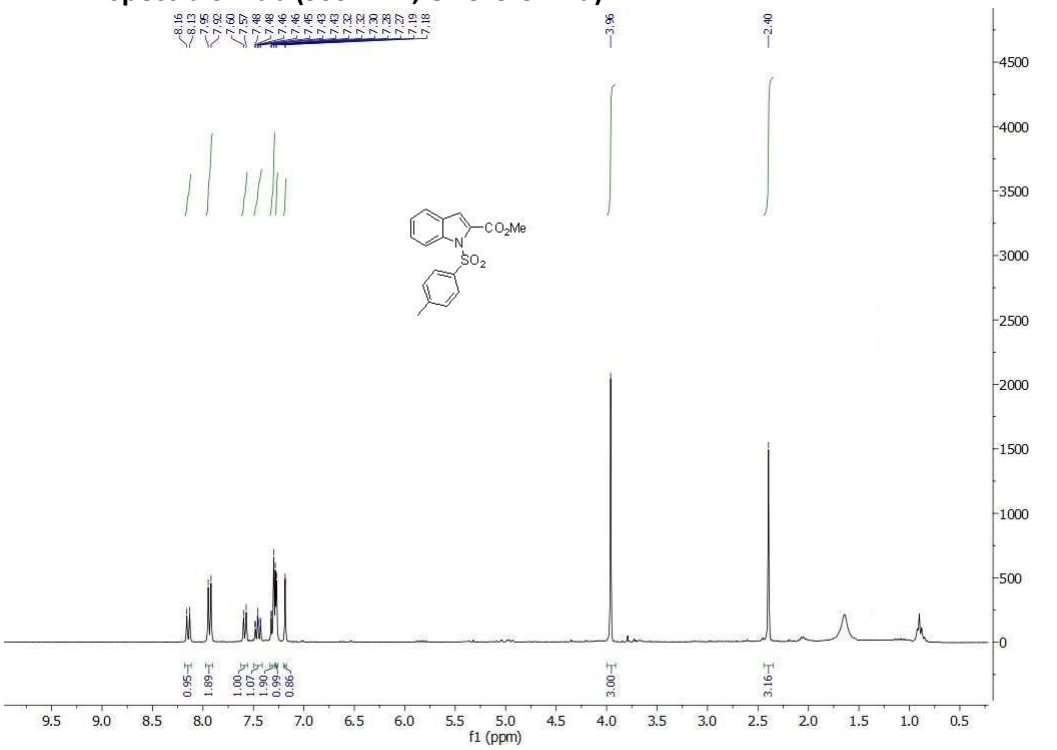
**$^{1}$H NMR spectra of 4b (300 MHz, Chloroform-*d*):**



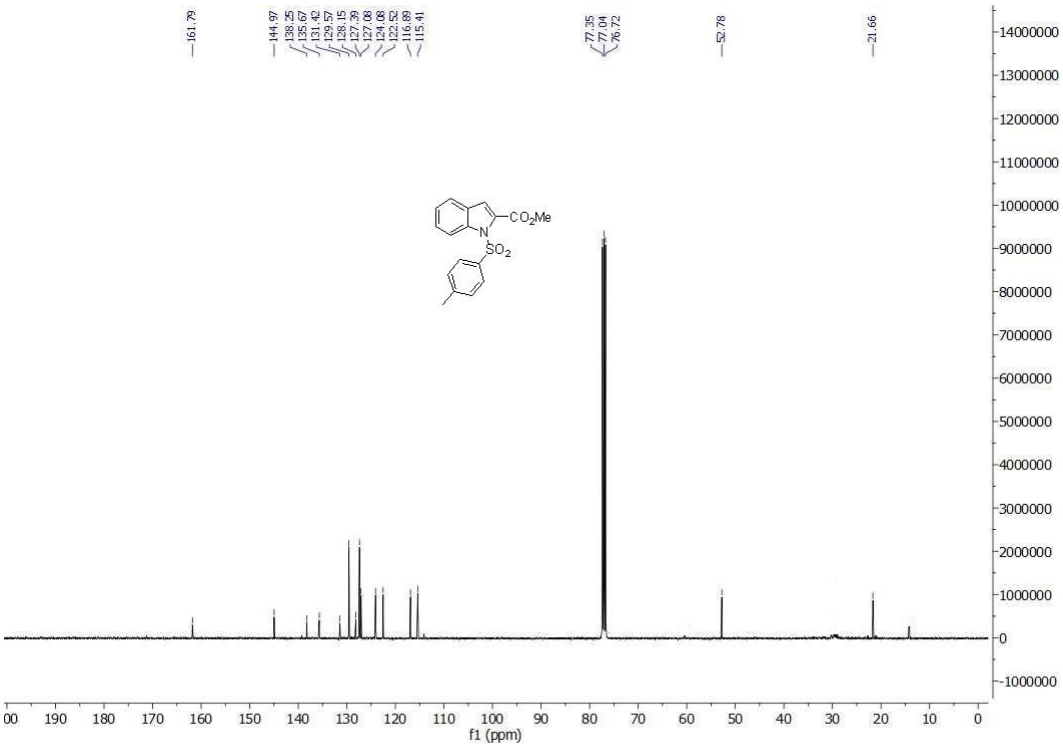

**$^{13}$C {1H} NMR spectra of 4b (100 MHz, Chloroform-*d*):**



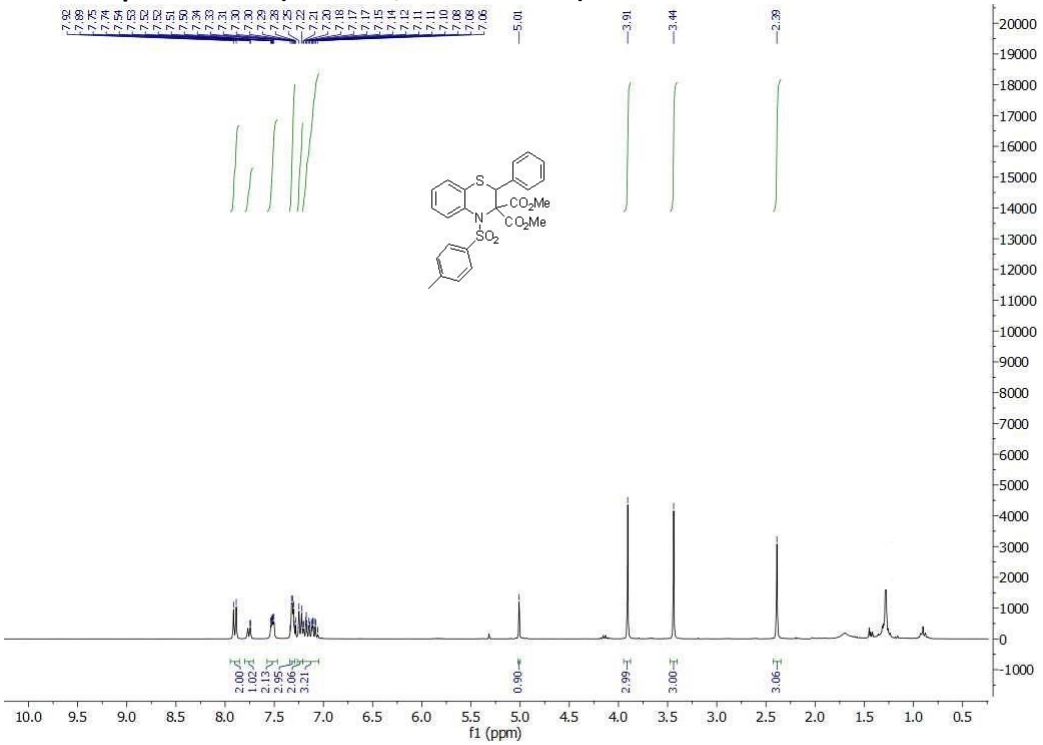
**$^{1}$H NMR spectra of 4ab (300 MHz, Chloroform-*d*):**



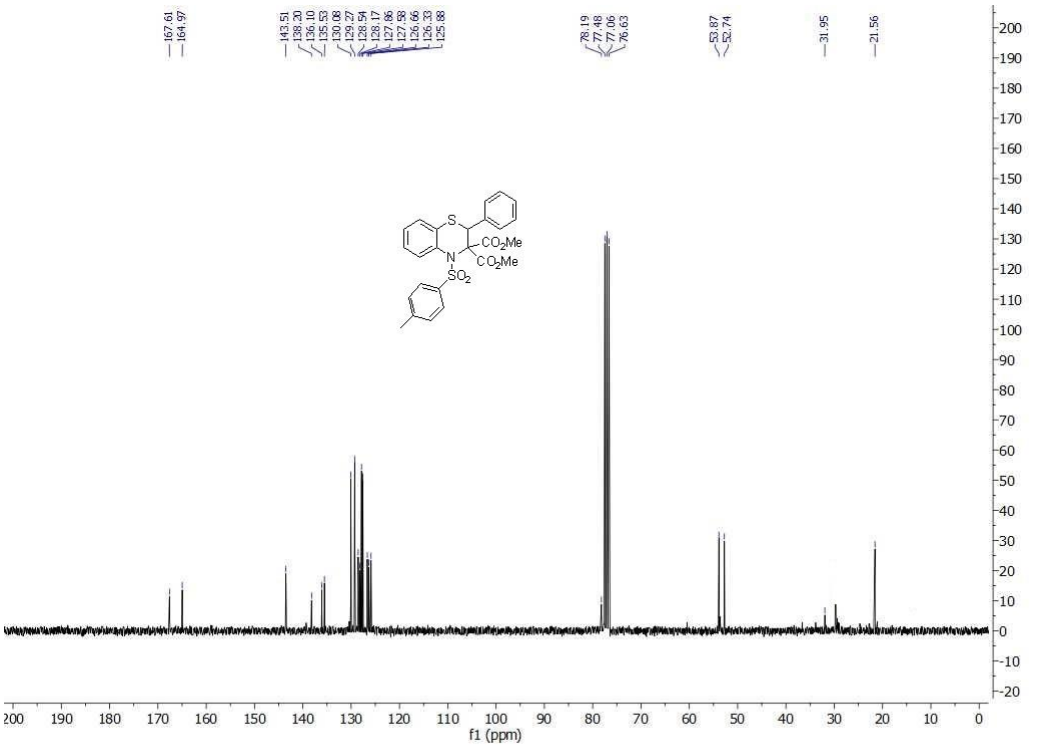

**$^{13}$C {1H} NMR spectra of 4ab (100 MHz, Chloroform-*d*):**



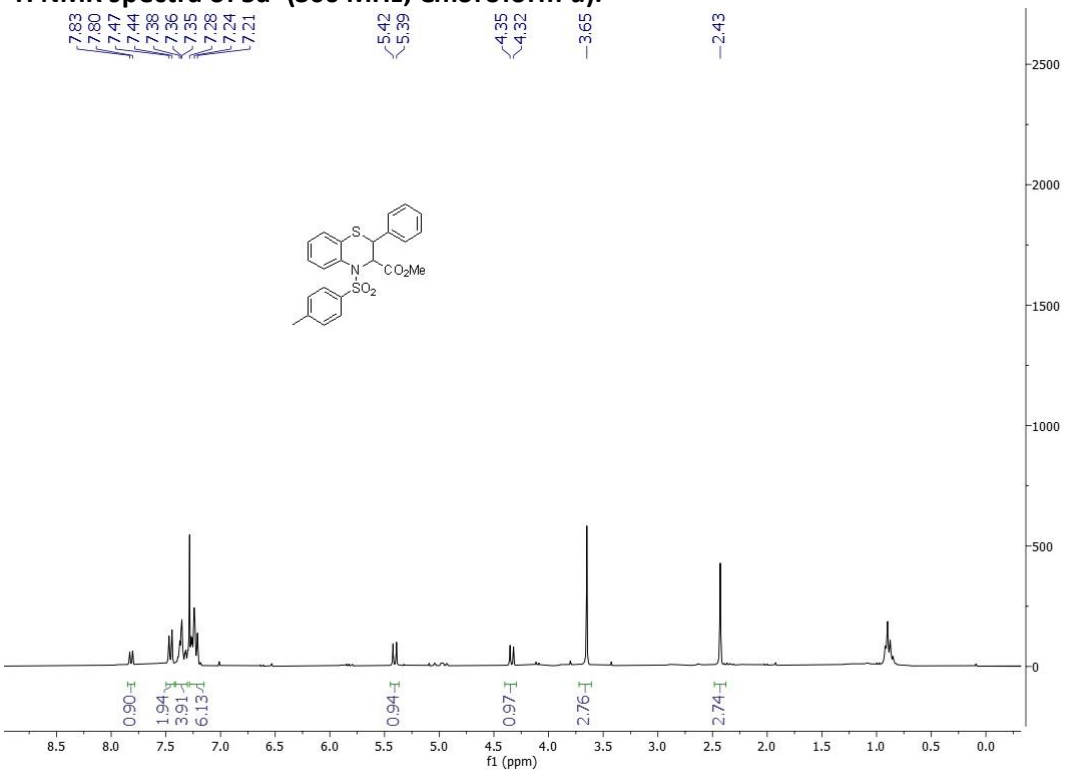
**$^{1}$H NMR spectra of 5a (300 MHz, Chloroform-*d*):**



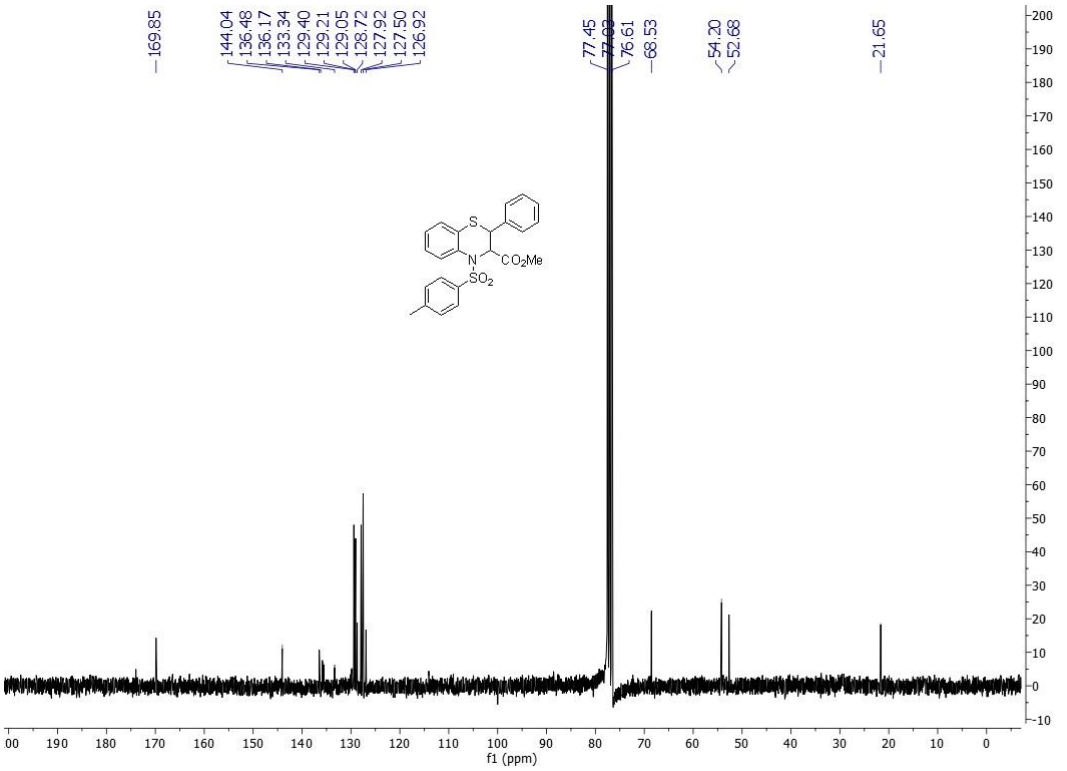

**$^{13}$C {1H} NMR spectra of 5a (75 MHz, Chloroform-*d*):**



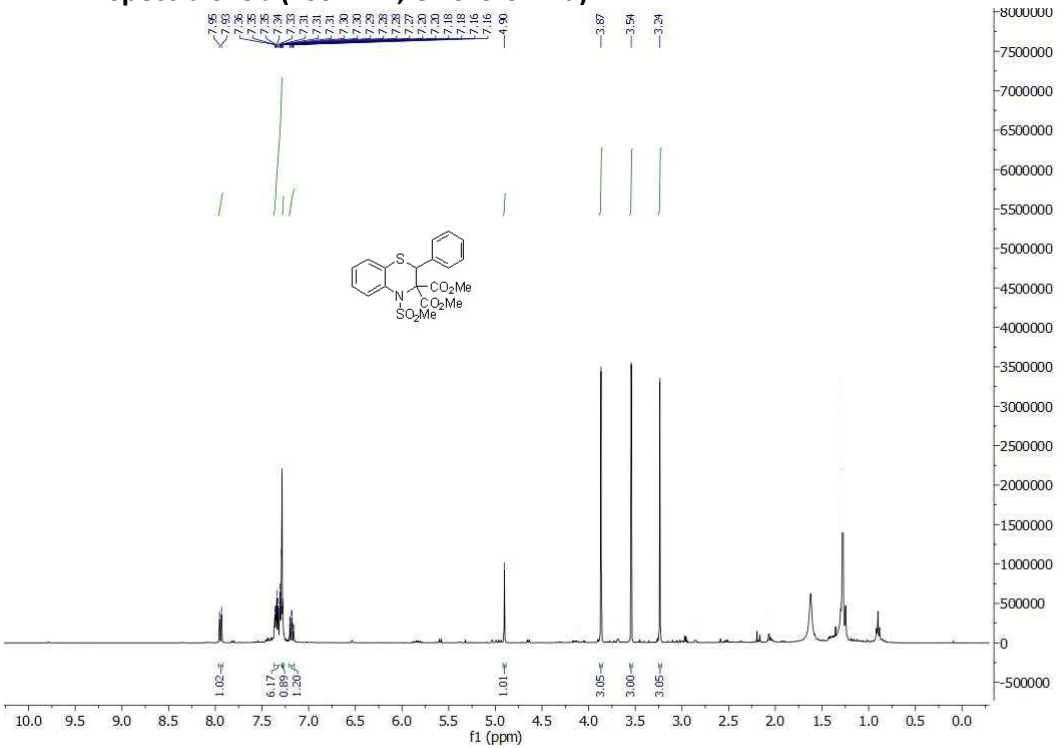
**$^{1}$H NMR spectra of 5a′ (300 MHz, Chloroform-*d*):**



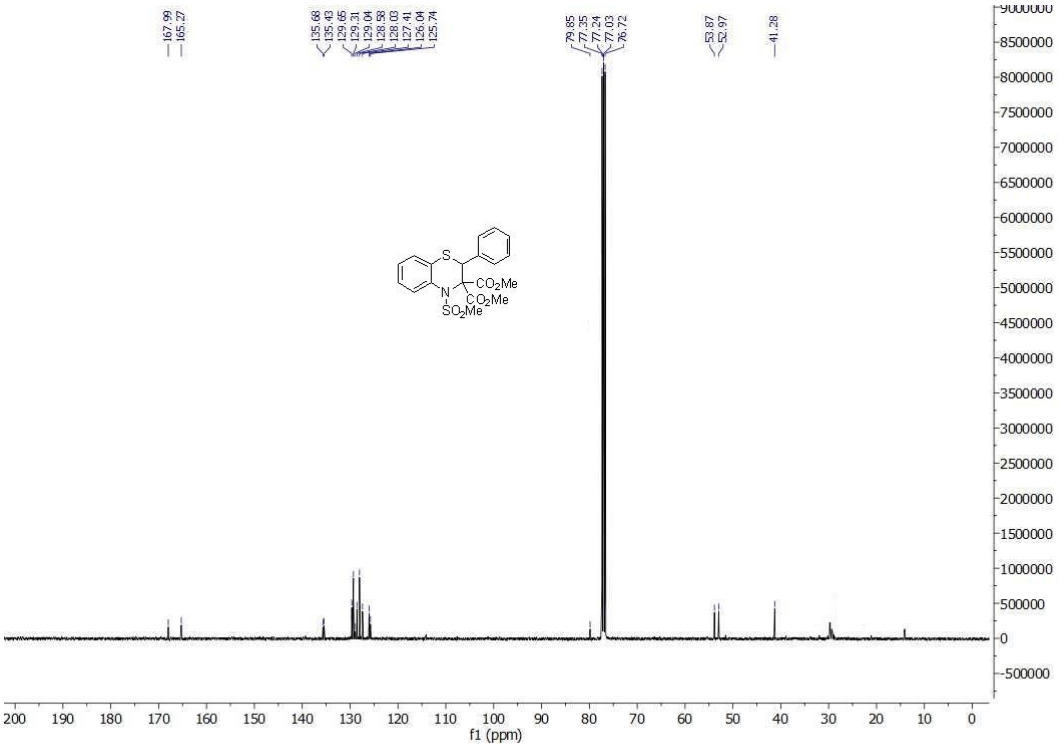

**$^{13}$C {1H} NMR spectra of 5a′ (75 MHz, Chloroform-*d*):**



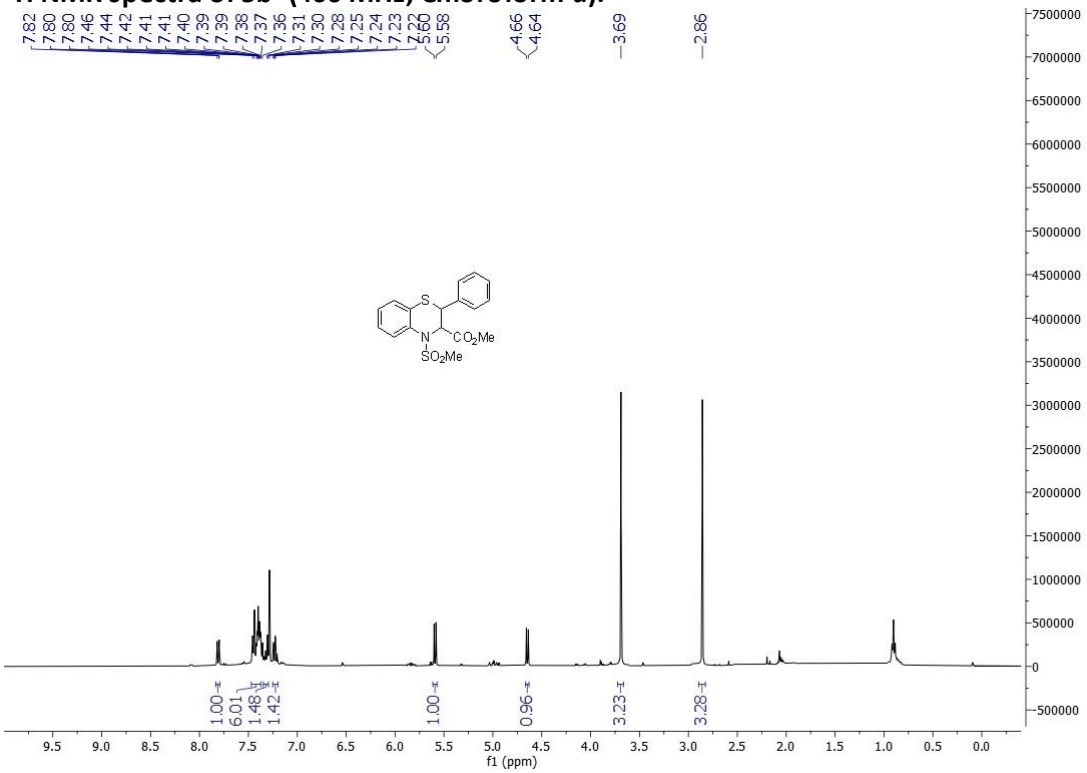
**$^{1}$H NMR spectra of 5b (400 MHz, Chloroform-*d*):**



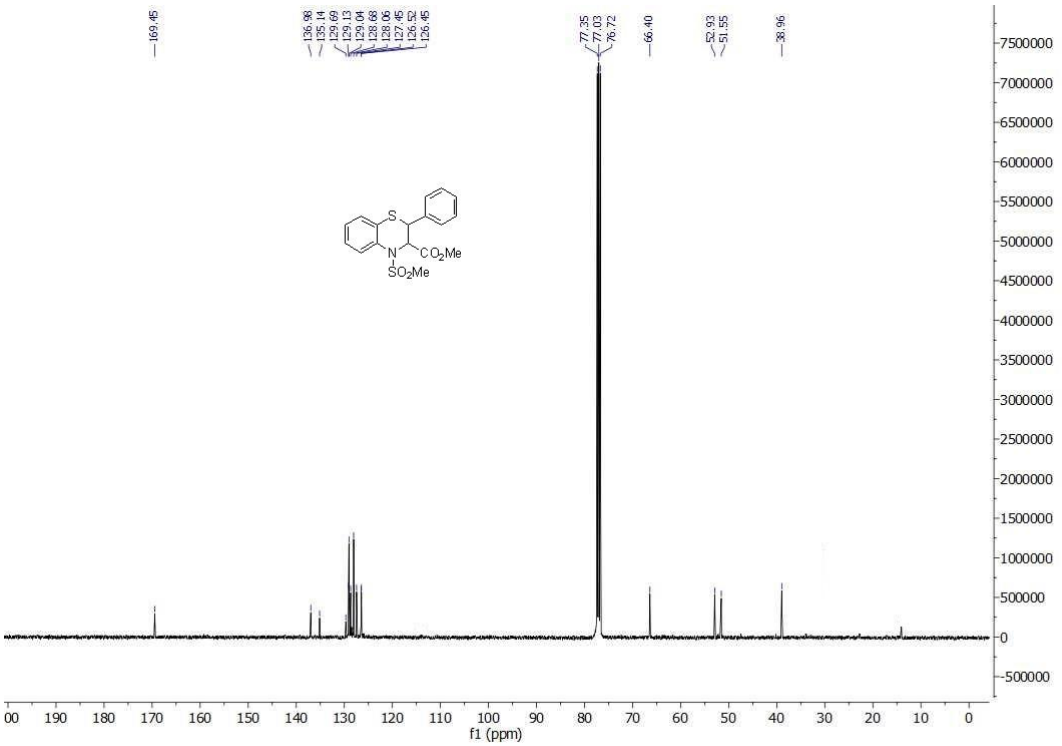

**$^{13}$C {1H} NMR spectra of 5b (100 MHz, Chloroform-*d*):**



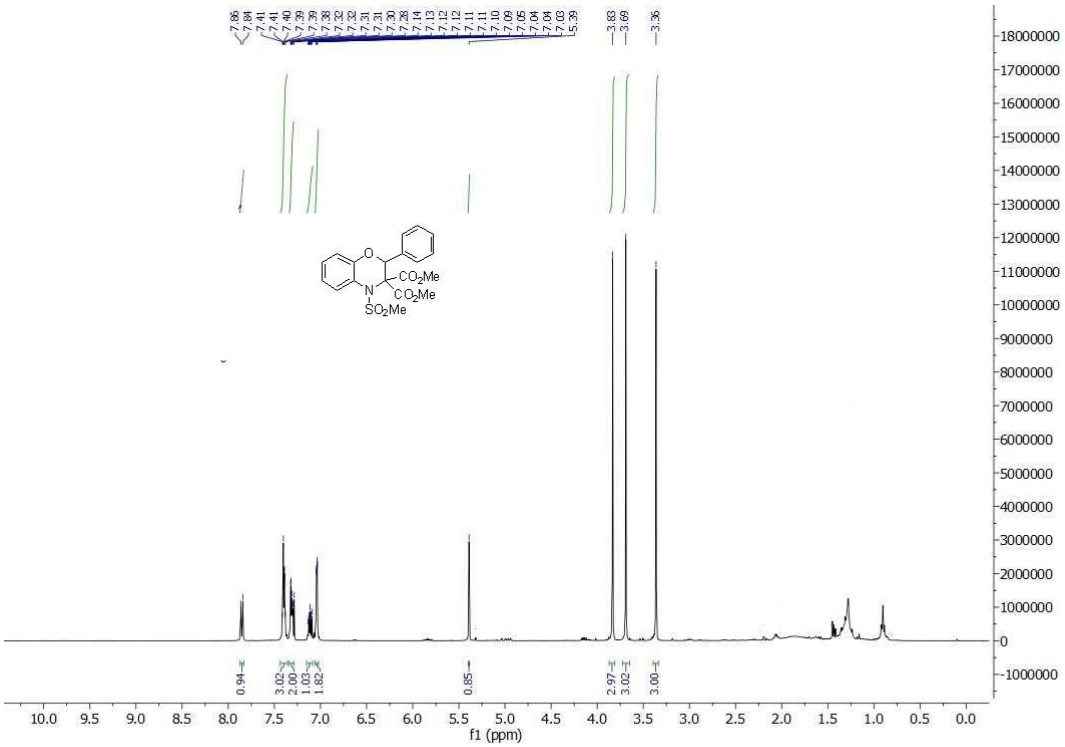
**$^{1}$H NMR spectra of 5b′ (400 MHz, Chloroform-*d*):**



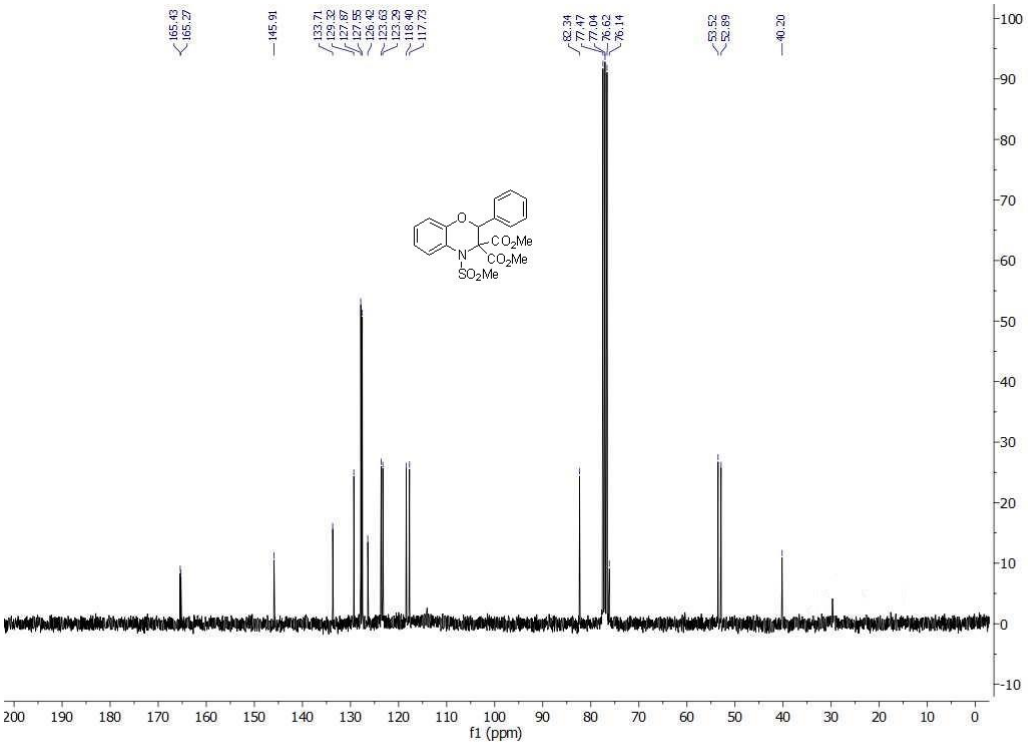

**$^{13}$C {1H} NMR spectra of 5b′ (100 MHz, Chloroform-*d*):**



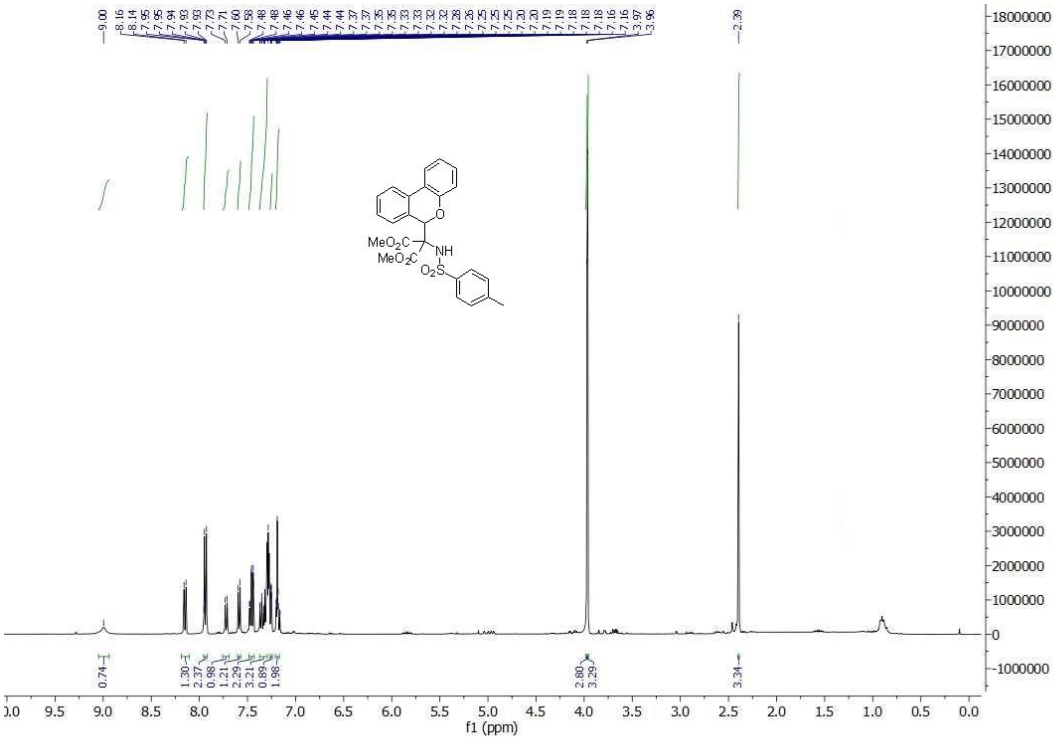
**$^{1}$H NMR spectra of 6a (400 MHz, Chloroform-*d*):**



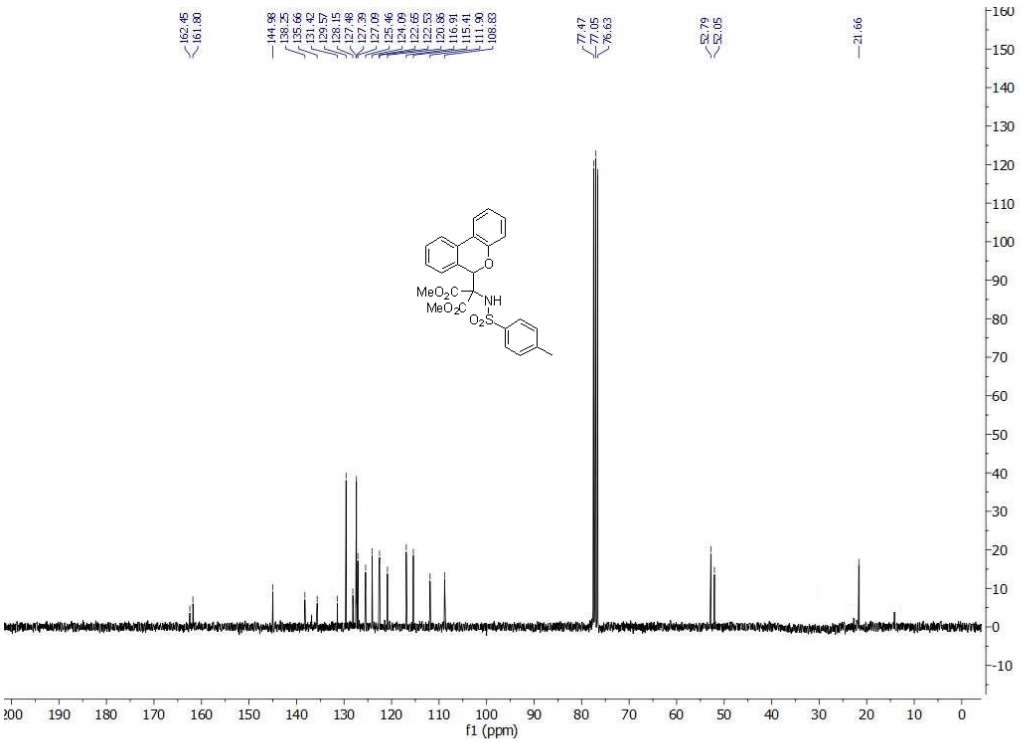

**$^{13}$C {1H} NMR spectra of 6a (75 MHz, Chloroform-*d*):**



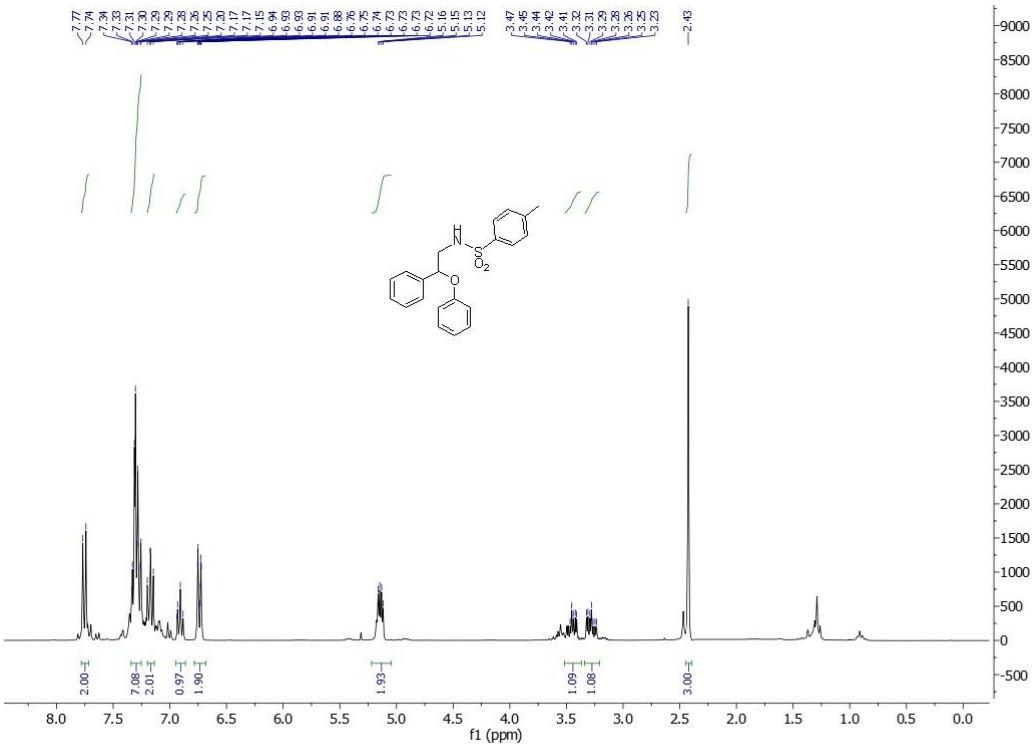
**$^{1}$H NMR spectra of 7a (400 MHz, Chloroform-*d*):**



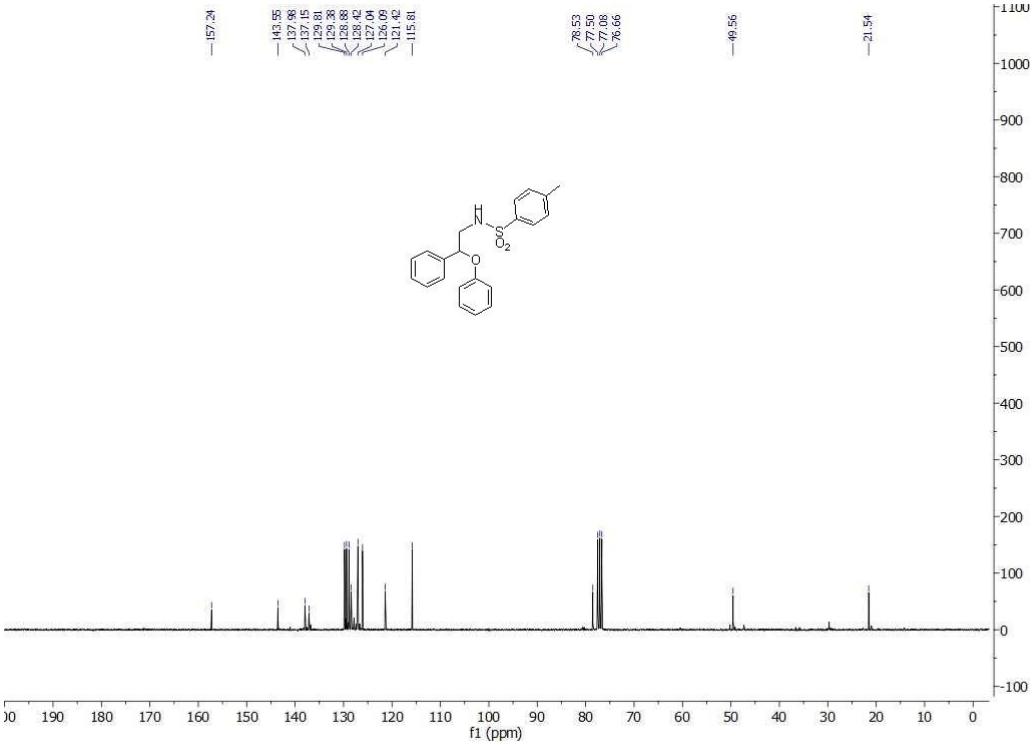
**$^{13}$C {1H} NMR spectra of 7a (75 MHz, Chloroform-*d*):**



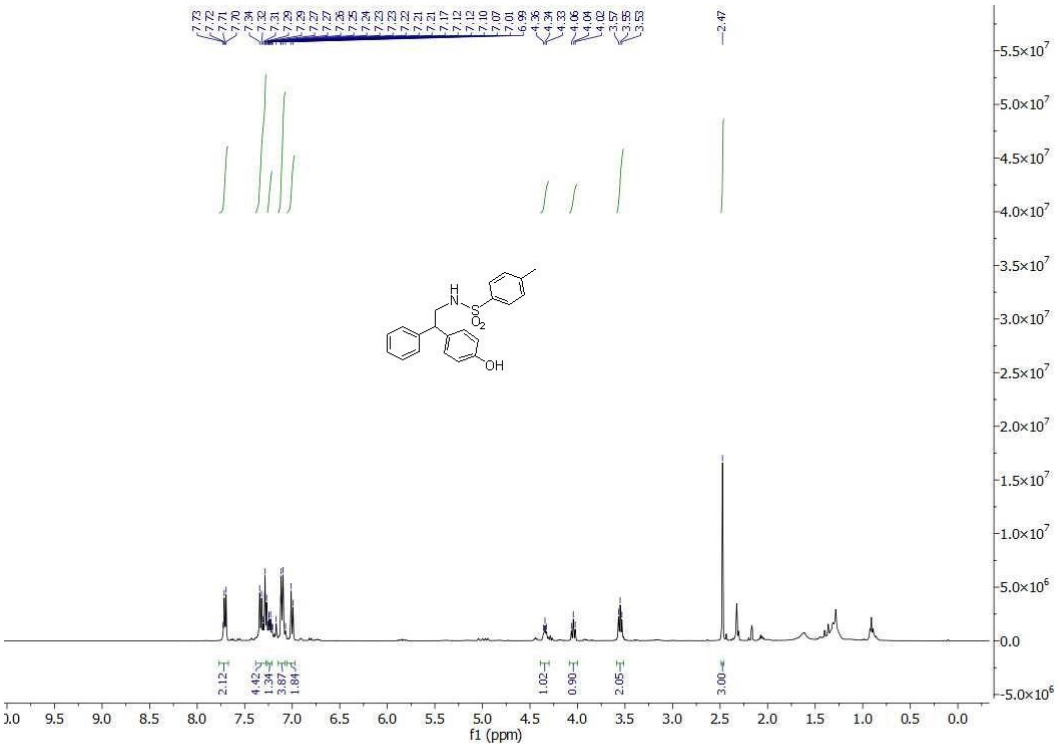
**$^{1}$H NMR spectra of 8a (300 MHz, Chloroform-*d*):**



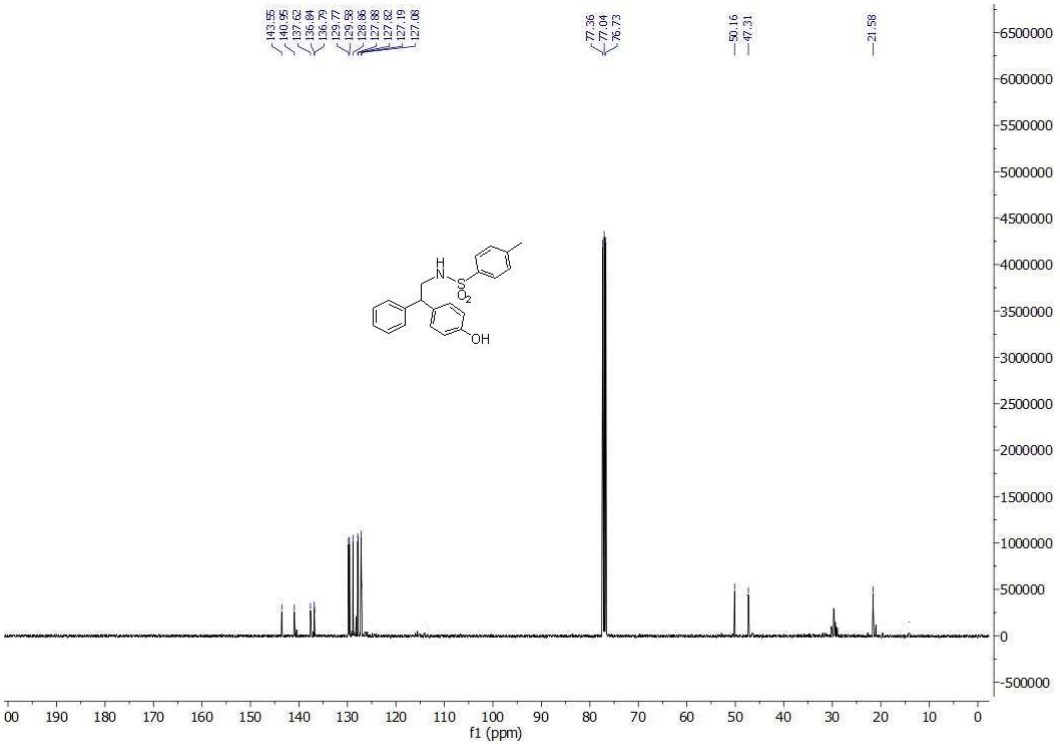

**$^{13}$C {1H} NMR spectra of 8a (75 MHz, Chloroform-*d*):**



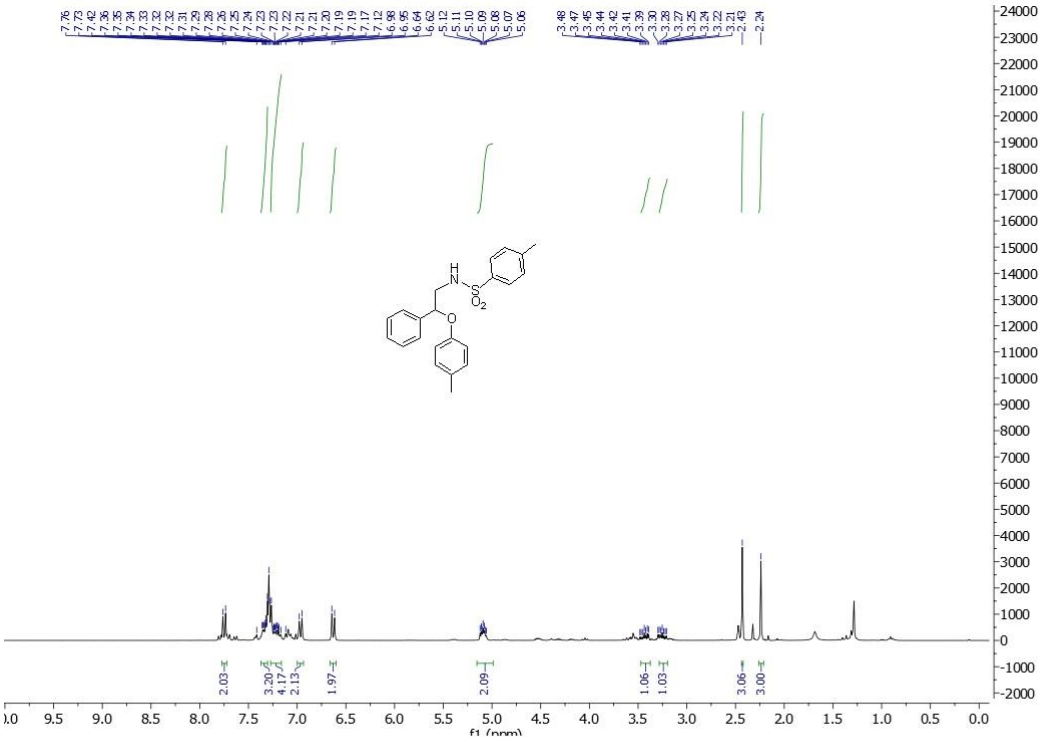
**$^{1}$H NMR spectra of 8a′ (400 MHz, Chloroform-*d*):**



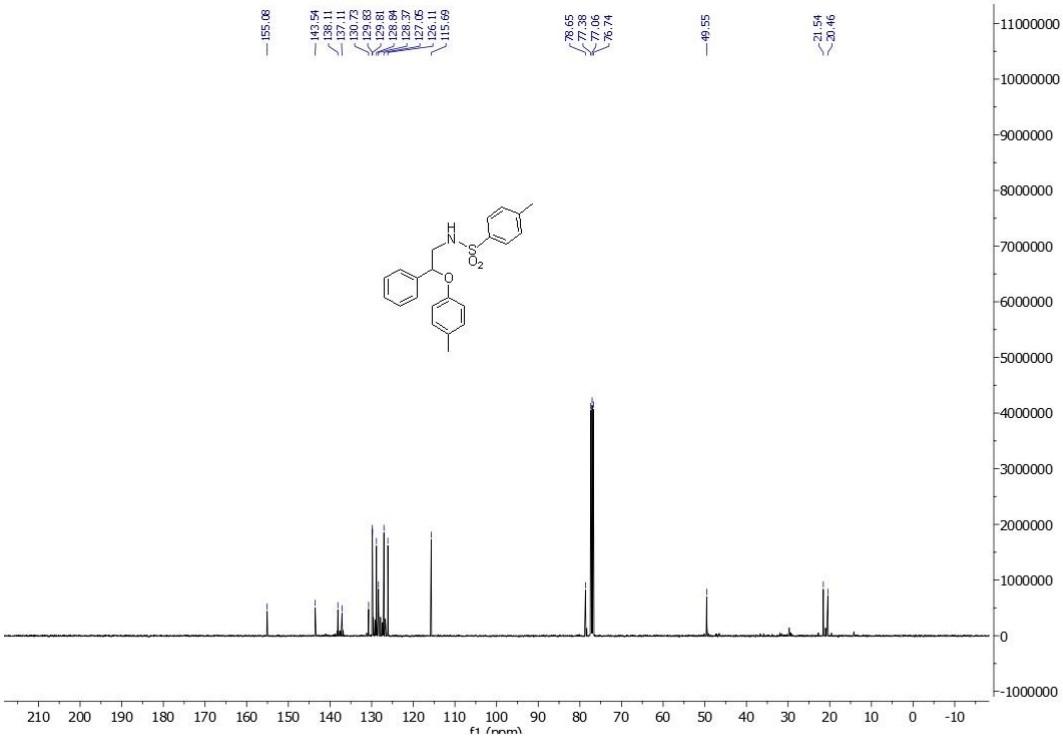

**$^{13}$C {1H} NMR spectra of 8a′ (100 MHz, Chloroform-*d*):**



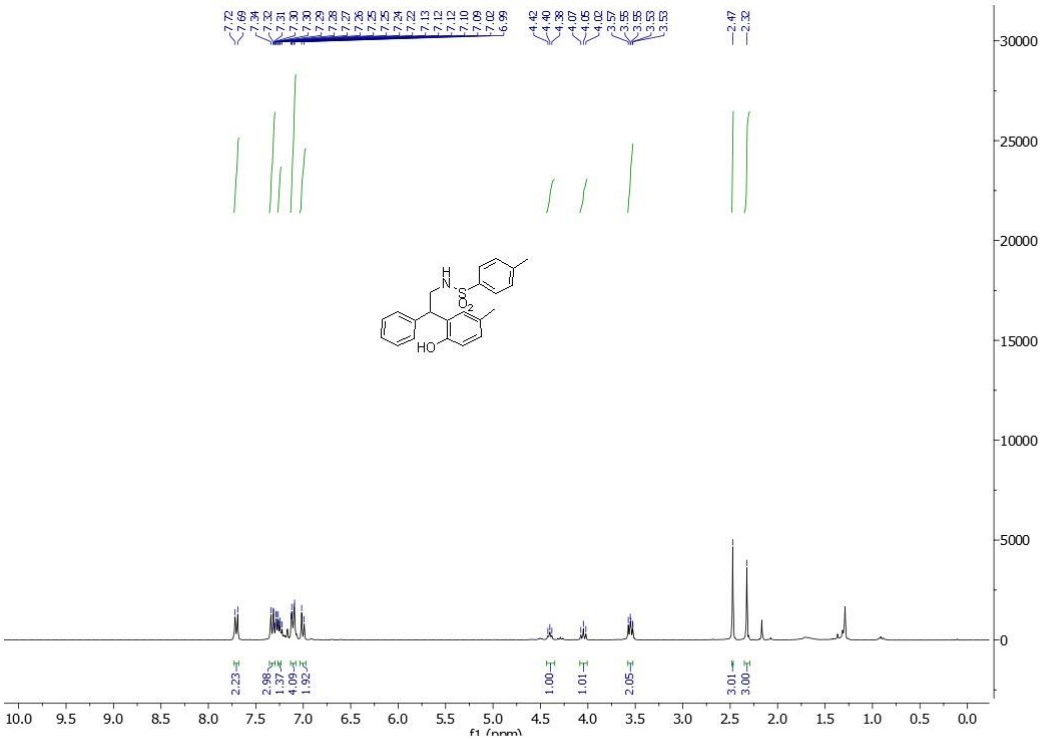
**$^{1}$H NMR spectra of 8b (300 MHz, Chloroform-*d*):**



**$^{13}$C {1H} NMR spectra of 8b (100 MHz, Chloroform-*d*):**



**$^{1}$H NMR spectra of 8b′ (300 MHz, Chloroform-*d*):**



**$^{13}$C {1H} NMR spectra of 8b′ (100 MHz, Chloroform-*d*):**