Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

Photo-Driven Synthesis of *N*-Sulfonyl Formamidines: A Catalyst- and Sensitizer-Free Approach

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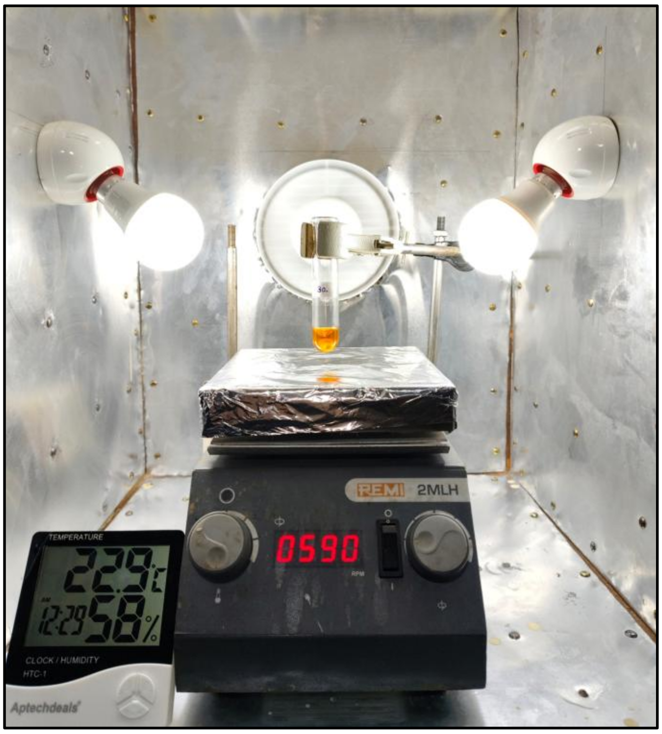
1. General Information

All the reactions were executed in an open atmosphere. The *N,N*-dibromoarylsulfonamides under consideration were readily synthesized as per literature procedures.[1–4] The formamides, however, were obtained from commercial sources. ^{1}H and ^{13}C{^{1}H} – NMR spectra were recorded on Bruker Ultrashield and Bruker Ascend 400 MHz spectrometers. Chemical shift values are reported in δ units relative to the tetramethylsilane (TMS) signal, an internal reference standard in $CDCl_3$, CD_3CN and DMSO-d6. Coupling constants for ^{1}H NMR were reported in Hz, while the multiplicities were indicated as follows: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet). The HRMS spectra were recorded on an Xevo XS QTof mass spectrometer. Chromatographic purification was carried out using flash chromatography over a manually packed column containing silica gel (230-400 mesh). UV-vis spectra were recorded using a UV-1800 (SHIMADZU) spectrophotometer over the range of 200 nm - 800 nm. Melting points were determined using a Relitech melting point apparatus.

2. About the Reaction Setup



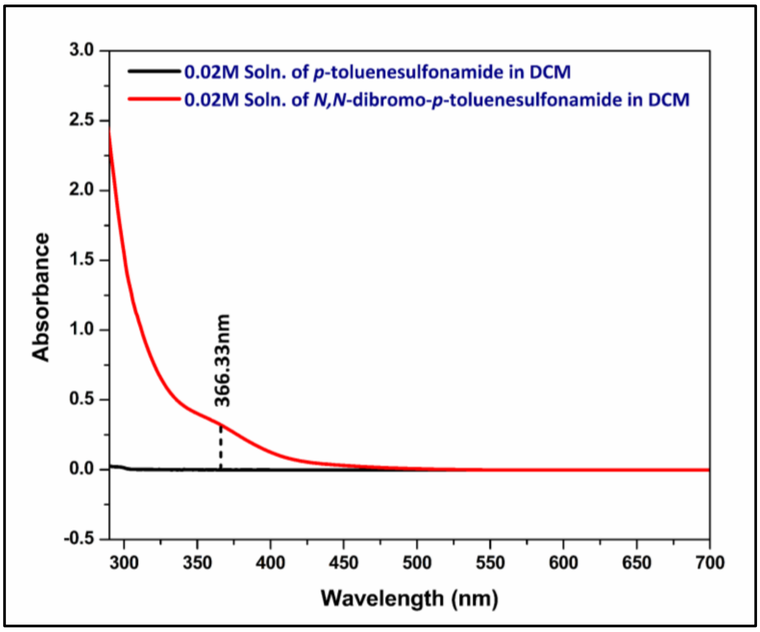
Supplementary Figure 1a: At the onset of the reaction.

Supplementary Figure 1b: On completion of the reaction.

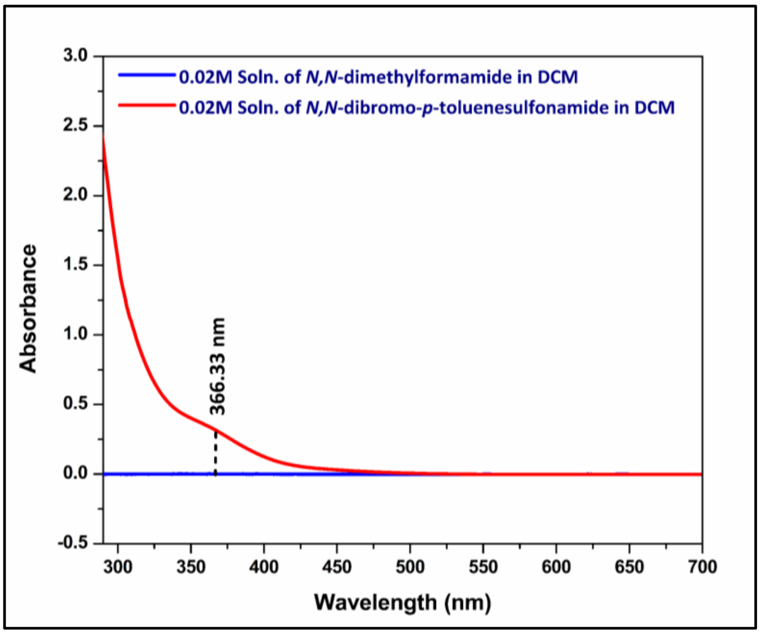
The reactions were performed in the photochemical reaction enclosure displayed in Supplementary Figure 1a & 1b. The irradiation chamber was meticulously designed to dispense reproducible, homogeneous and controlled irradiation throughout the reaction zone. The setup was equipped with two 9 W white LED bulbs. Reflective surfaces throughout the chamber interior were installed to amplify light scattering while minimizing irradiation gradients. Reaction vessels were carefully secured at a fixed and definite distance from both of the LEDs. Ambient temperature control and thorough ventilation were strictly maintained throughout the course of the reaction, as clearly evident from the above displayed images. The reaction mixture at the onset of the reaction appears to be pale yellow owing to the presence of unreacted *N,N*-dibromoarylsulfonamides. As the reaction progresses to completion, owing to the presence of free bromine radicals or other transient brominated species, the overall reaction mixture appears orange in colour.

3. UV-Vis Experiments

The experimental UV-Vis spectra for compound **1a**, **2a** and *p*-toluenesulfonamide were measured in a 0.02M solution in dichloromethane at room temperature. The corresponding spectra for each compound were recorded to study the comparative nature of absorbance due to the corresponding functionalities available in the compound.



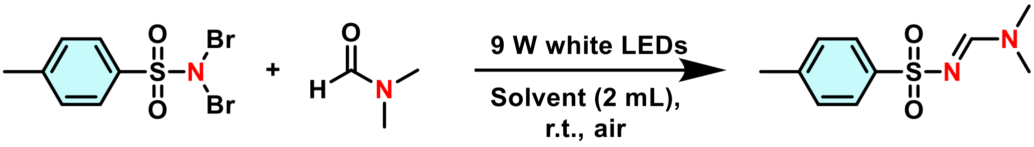
Supplementary Figure 2: Comparative UV-Vis spectra of *p*-toluenesulfonamide and *N,N*-dibromo-*p*-toluenesulfonamide **1a** in DCM.



Supplementary Figure 3: Comparative UV-Vis spectra of *N,N*-dimethyl formamide **2a** and *N,N*-dibromo-*p*-toluenesulfonamide **1a** in DCM.

4. Reaction Optimization

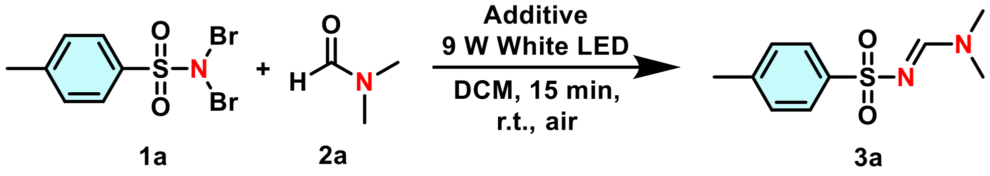
Supplementary Table 1: Optimization of reaction conditions[a]



Entry	Solvent	Variation in condition	Time	Yield (%)
1.	DCM	1.0 equiv of 2a	1 h	41
2.	DCM	2.0 equiv of 2a	1 h	63
3.	DCM	3.0 equiv of 2a	1 h	94
4.	THF	3.0 equiv of 2a	1 h	NR
5.	DCE	3.0 equiv of 2a	1 h	72
6.	1,4- Dioxane	3.0 equiv of 2a	1 h	Trace
7.	CH_3CN	3.0 equiv of 2a	1 h	28
8.	Diethyl ether	3.0 equiv of 2a	1 h	NR
9.	Toluene	3.0 equiv of 2a	1 h	22
10.	DCM	3.0 equiv of 2a	30 min	93
11.	**DCM**	**3.0 equiv of 2a**	**15 min**	**93**
13.	DCM	Under N_2 atmosphere	15 min	89
14.	DCM	Under Blue LED	15 min	Trace
15.	DCM	Under Darkness	15 min	NR
16.	DCM	15 W White LED	15 min	92

[a] Standard Reaction conditions: 1a (0.5 mmol), 2a (1.5 mmol), DCM (2 mL), r.t., using 9 W white LEDs for 15 min; Isolated yield.

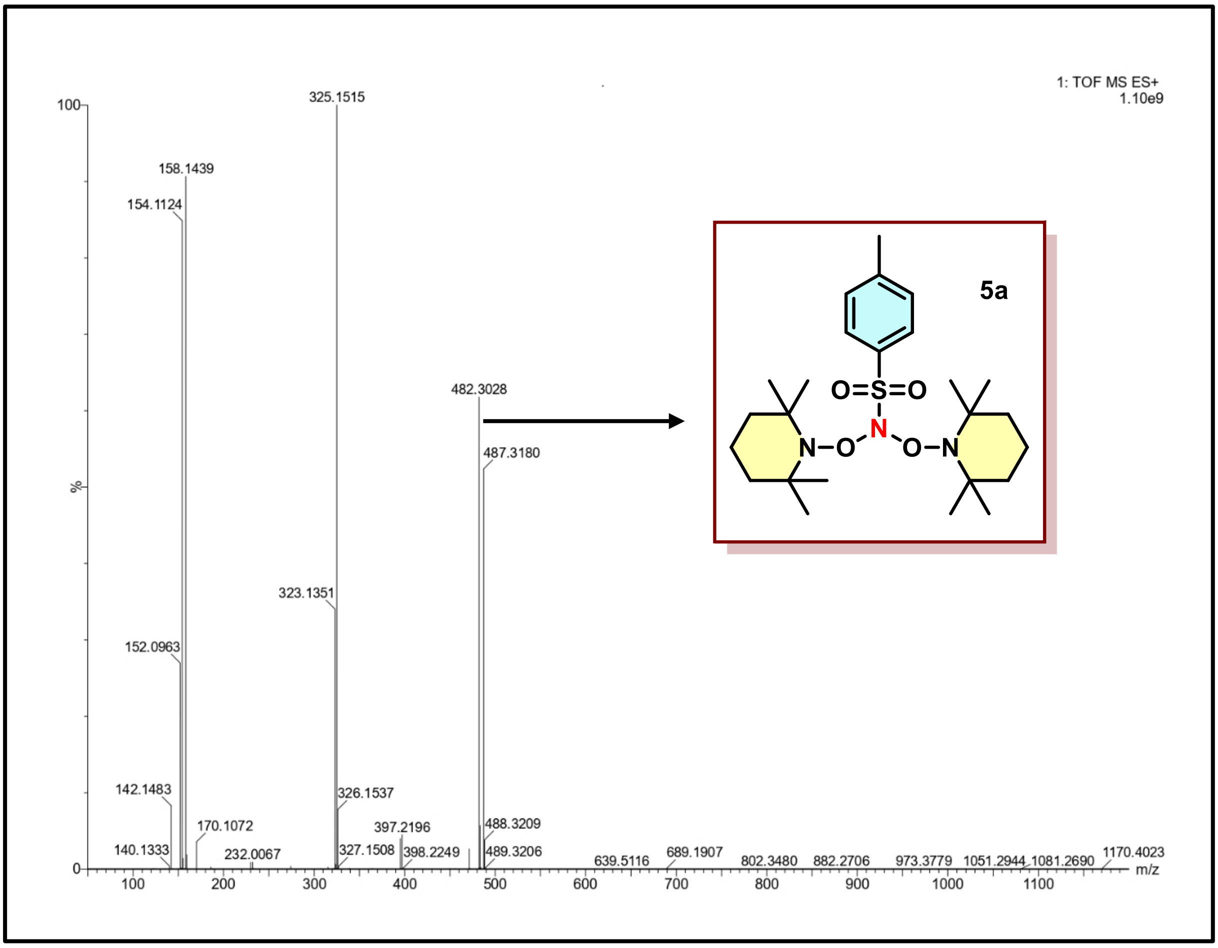
5. Control Experiments



Entry	Additive	Yield (%)
1	1.0 equiv of PPh_3	N.R.
2	0.1/ 0.5/ 1.0 equiv of TEMPO	53/ 31/ Trace
3	1.0 equiv of DMPO	N.R.
4	1.0 equiv of H_2O	20
5	1.0 equiv of MeOH	Trace

[a] Reaction conditions: 1a (0.5 mmol), 2a (1.5 mmol), DCM (2 mL), r.t., using 9 W white LEDs for 15 min; Isolated yield.

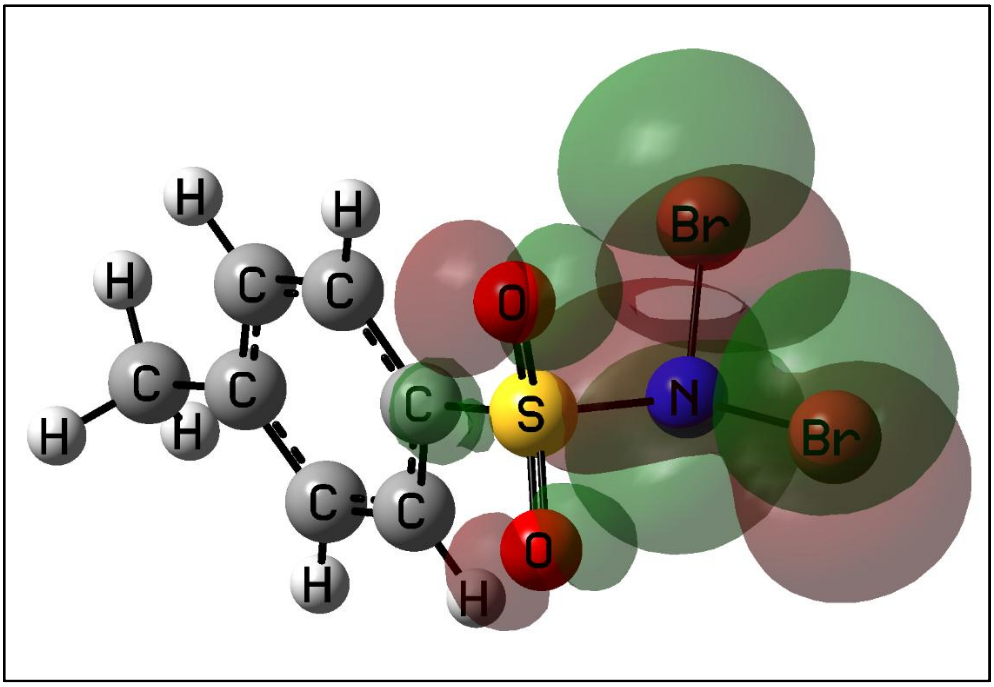
6. HRMS Spectra of 5a.



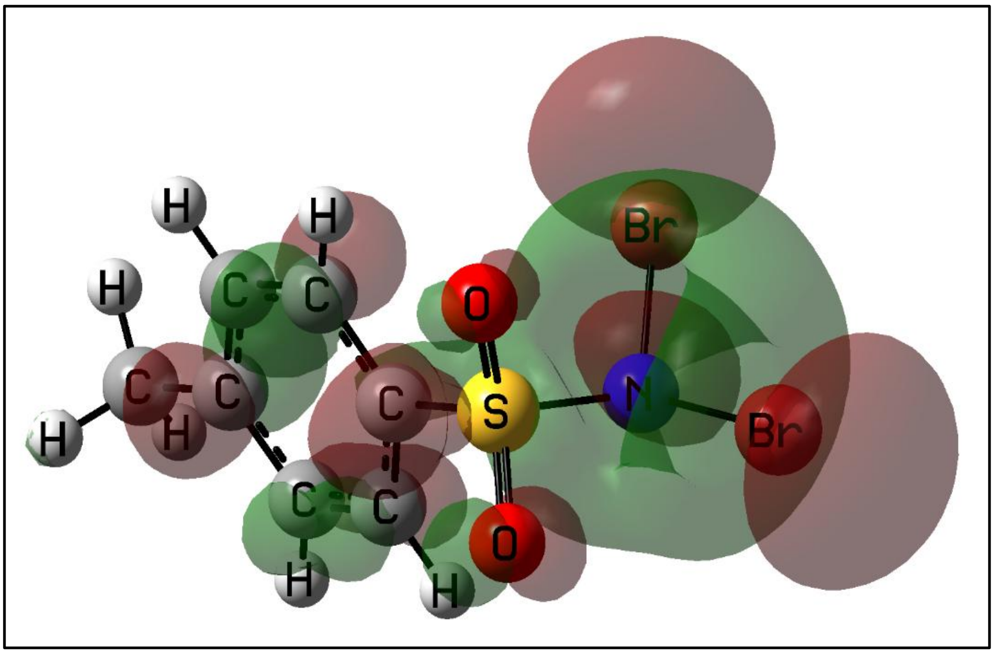
7. Computational Details

All calculations were performed using Gaussian09 program package.[5] The ground state solvent phase geometry optimization of the photoactive reactant **1a** has been carried out using density functional theory (DFT) method at the SMD(DCM)-B3LYP-D3/def2-SVP level of theory and DCM as the solvent. Further, time-dependent density functional theory (TD-DFT) operation was carried out for the photoactive reactant **1a** in order to study its absorption pattern under the same level of theory. The plots of the frontier molecular orbitals (FMOs) of the photoactive reactant **1a** were generated using Gauss View 5.0.9 software.

A. Frontier Molecular Orbitals of 1a.

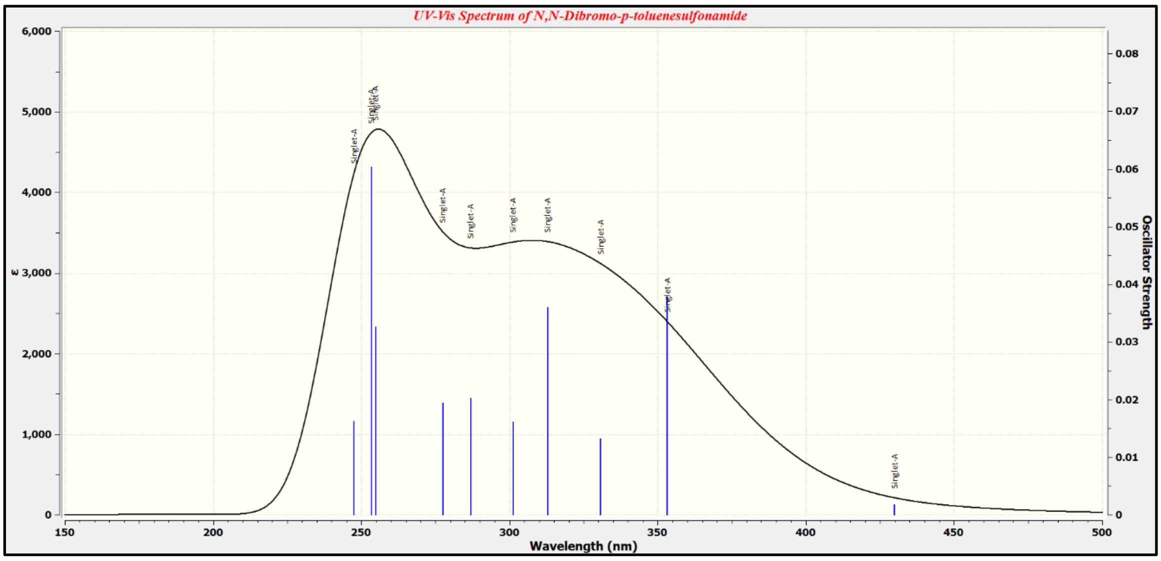


Supplementary Figure 4: HOMO of **1a.**



Supplementary Figure 5: LUMO of **1a**.

B. Computational Study of UV-Vis Spectra of 1a



Supplementary Figure 6: Calculated UV-Vis Spectrum of **1a.**

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.8838 eV **429.93 nm** f=0.0017 <S**2>=0.000

78 -> 80 0.19689

79 -> 80 0.67385

Excited State 2: Singlet-A 3.5100 eV **353.23 nm** f=0.0378 <S**2>=0.000

76 -> 80 -0.21652

78 -> 80 0.64161

79 -> 80 -0.18245

Excited State 3: Singlet-A 3.7483 eV **330.78 nm** f=0.0131 <S**2>=0.000

77 -> 80 0.69780

Excited State 4: Singlet-A 3.9630 eV **312.85 nm** f=0.0359 <S**2>=0.000

75 -> 80 -0.14203

76 -> 80 0.60745

78 -> 80 0.19187

79 -> 81 -0.22942

Excited State 5: Singlet-A 4.1154 eV **301.27 nm** f=0.0161 <S**2>=0.000

74 -> 80 0.13854

75 -> 80 0.56640

76 -> 80 0.22313

78 -> 81 0.10929

79 -> 81 0.27262

Excited State 6: Singlet-A 4.3212 eV **286.92 nm** f=0.0202 <S**2>=0.000

75 -> 80 -0.35991

76 -> 80 0.14096

78 -> 81 0.18605

79 -> 81 0.52871

79 -> 82 -0.12408

Excited State 7: Singlet-A 4.4679 eV **277.50 nm** f=0.0193 <S**2>=0.000

74 -> 80 0.67325

75 -> 80 -0.12489

Excited State 8: Singlet-A 4.8653 eV **254.83 nm** f=0.0325 <S**2>=0.000

73 -> 80 0.64654

76 -> 81 0.11083

78 -> 81 -0.17452

Excited State 9: Singlet-A 4.8925 eV **253.42 nm** f=0.0603 <S**2>=0.000

73 -> 80 0.23336

76 -> 81 -0.16316

78 -> 81 0.59457

78 -> 82 -0.11450

79 -> 81 -0.19573

Excited State 10: Singlet-A 5.0079 eV **247.58 nm** f=0.0162 <S**2>=0.000

77 -> 81 0.63072

78 -> 82 0.12282

78 -> 83 0.21594

79 -> 83 -0.11348

C. Coordinates of optimized structure of 1a

C	3.212956	0.719636	-1.264928
C	4.013999	-0.005010	-0.360872
C	3.462104	-0.384884	0.875590
C	2.146676	-0.063755	1.208468
C	1.899571	1.059126	-0.952609
C	1.383158	0.656226	0.285305
H	3.628129	1.021876	-2.229958

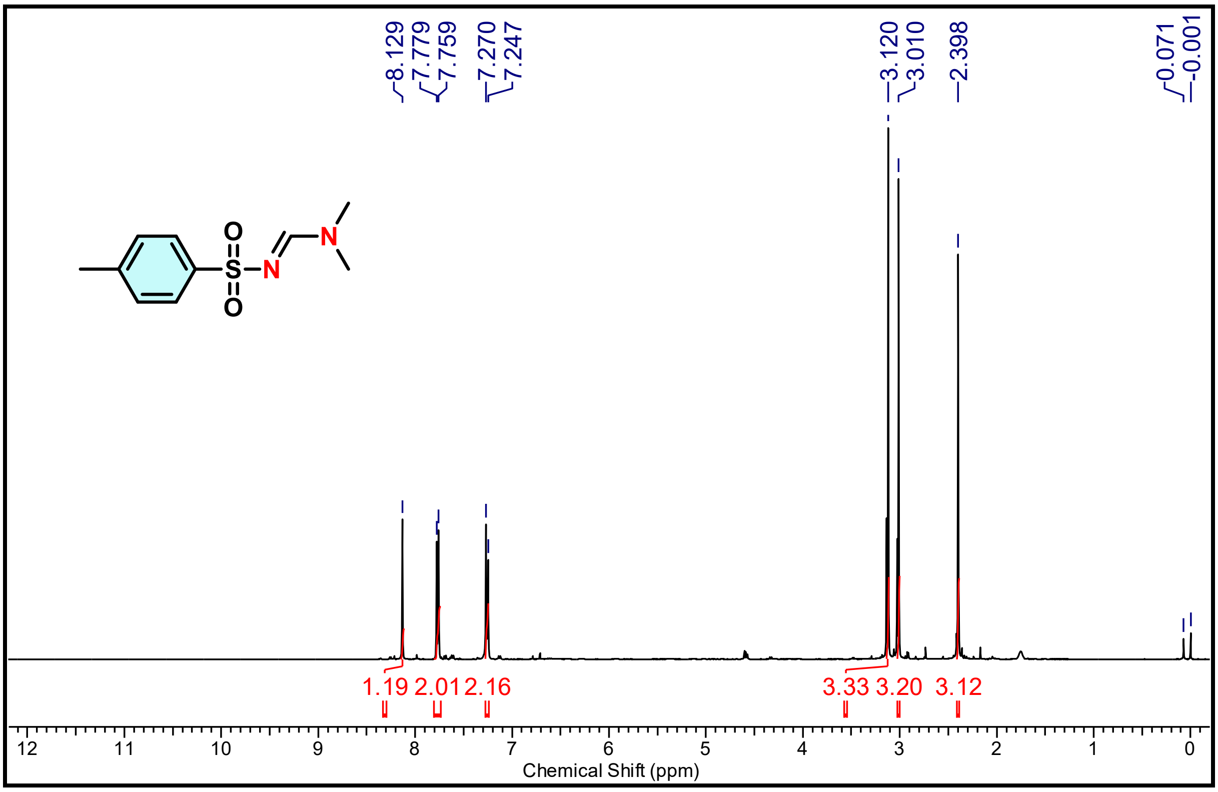
H	1.283222	1.622674	-1.655301
H	1.717563	-0.364378	2.165562
H	4.071443	-0.946015	1.588600
S	-0.292092	1.078557	0.685251
O	-0.593556	0.735209	2.073914
O	-0.630684	2.393779	0.142581
N	-1.131126	-0.041127	-0.463581
C	5.439760	-0.338635	-0.705683
H	5.552222	-0.562323	-1.777841
H	6.097582	0.520065	-0.482997
H	5.808366	-1.197136	-0.124964
Br	-3.006754	0.396629	-0.525765
Br	-0.853891	-1.880970	0.027319

8. References

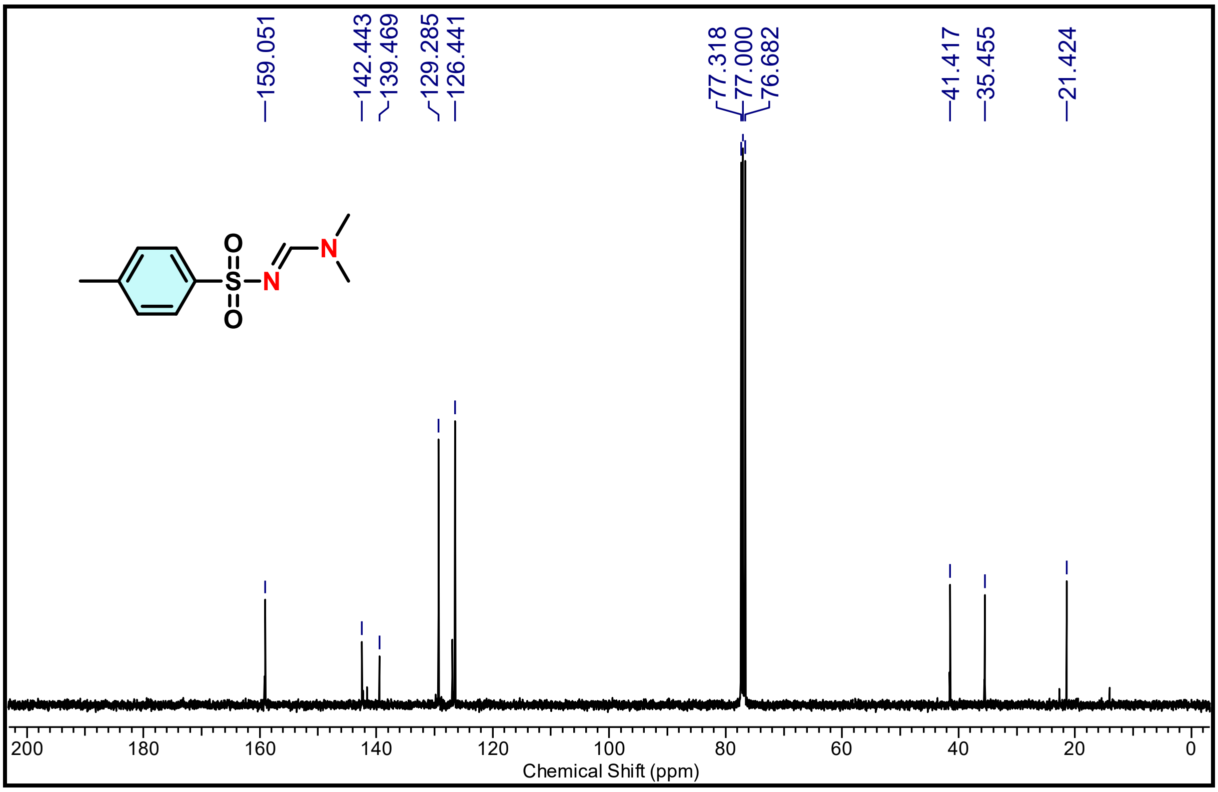
1. M. Tajbakhsh, A. Khazaei, M. S. Mahalli and R. G. Vaghi, *Phosphorus Sulfur Silicon Relat. Elem.*, 2004, **179**, 1159–1163.
2. A. Khazaei, A. Rostami, Z. Tanbakouchian and Z. Zinati, *Catal. Commun.*, 2006, **7**, 214–217.
3. P. Phukan, P. Chakraborty and D. Kataki, *J. Org. Chem.*, 2006, **71**, 7533–7537.
4. A. J. Borah and P. Phukan, *Chem. Commun.*, 2012, **48**, 5491.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 (version Revision D.01) Gaussian, Inc., Wallingford CT 2013.

9. Copy of ^{1}H & ^{13}C NMR Spectra of Products

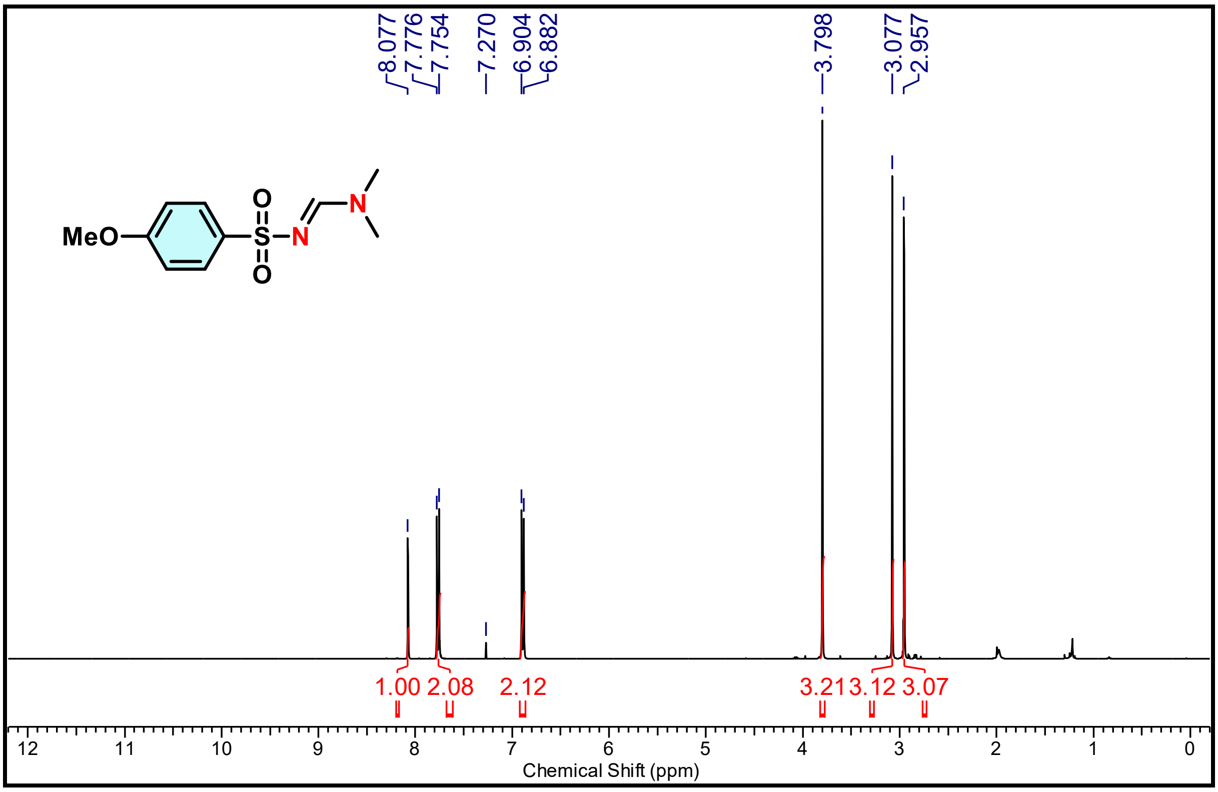
^{1}H spectra of **(3a)** (400 MHz, $CDCl_3$)



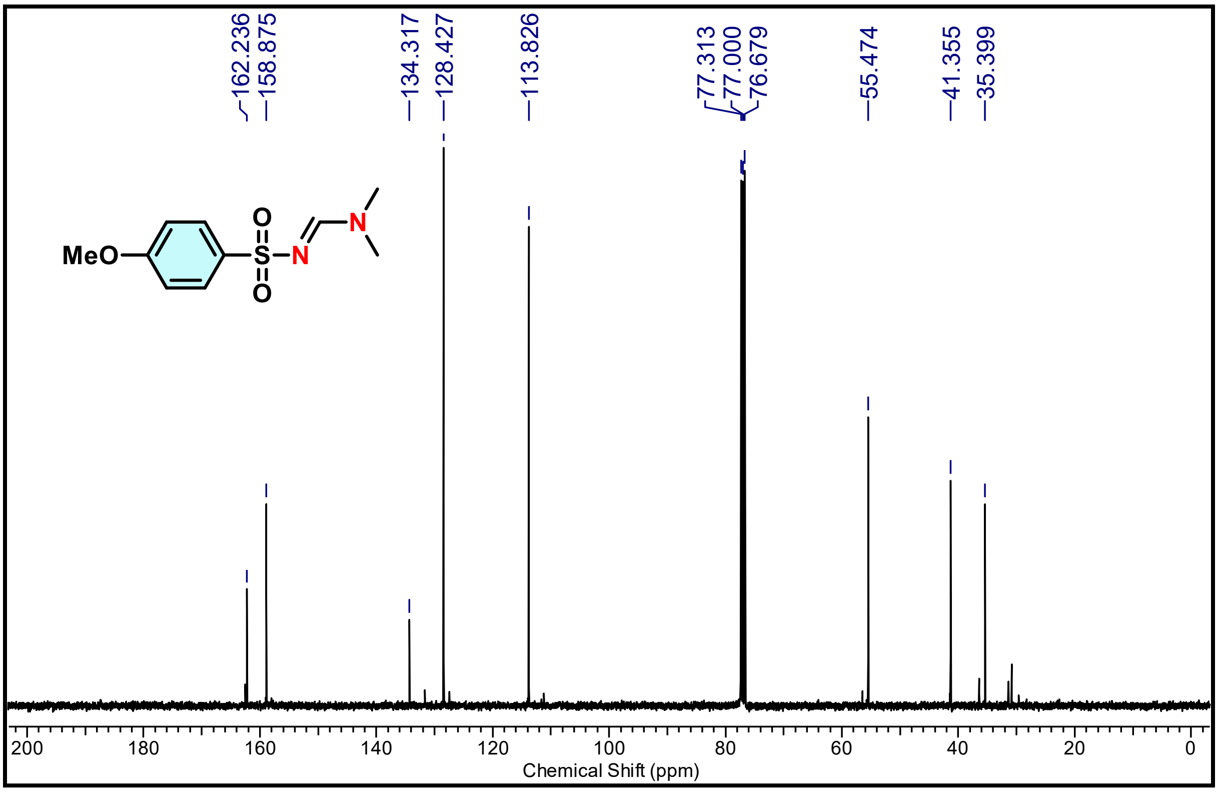
^{13}C spectra of **(3a)** (100 MHz, $CDCl_3$)



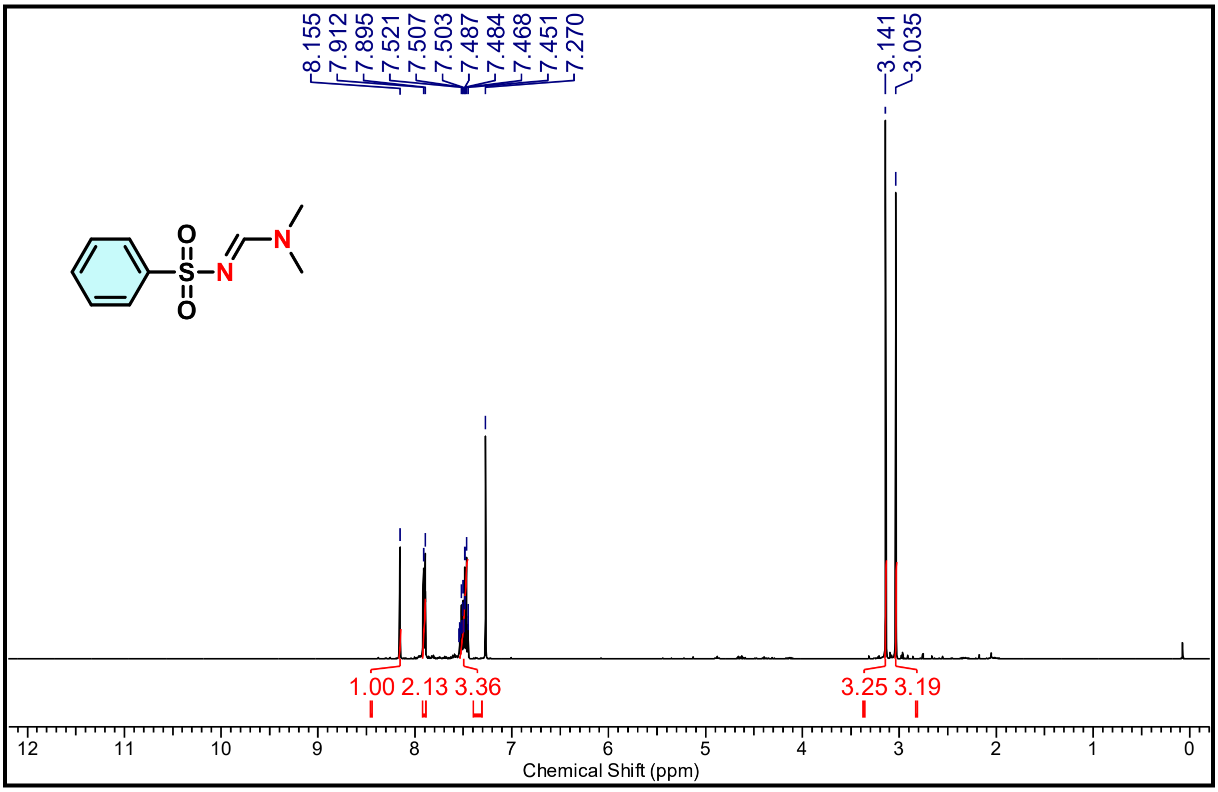
^{1}H spectra of **(3b)** (400 MHz, $CDCl_3$)



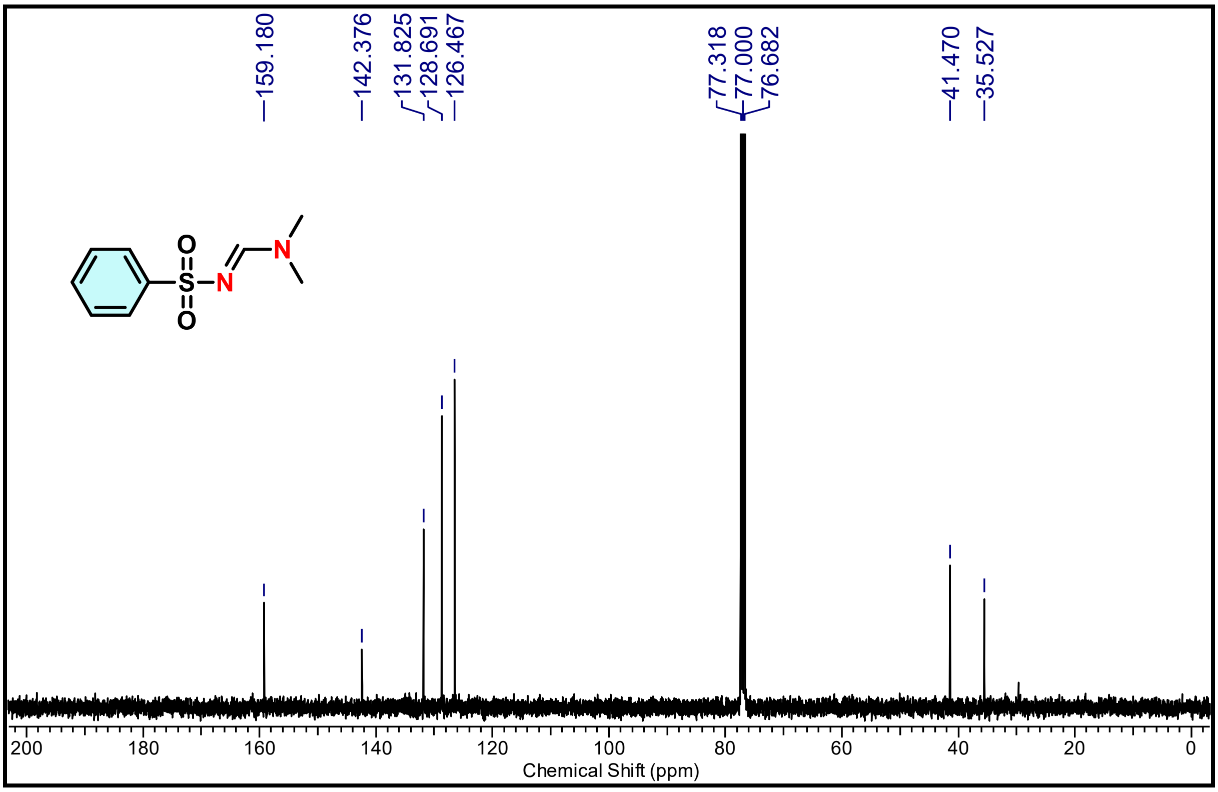
^{13}C spectra of **(3b)** (100 MHz, $CDCl_3$)



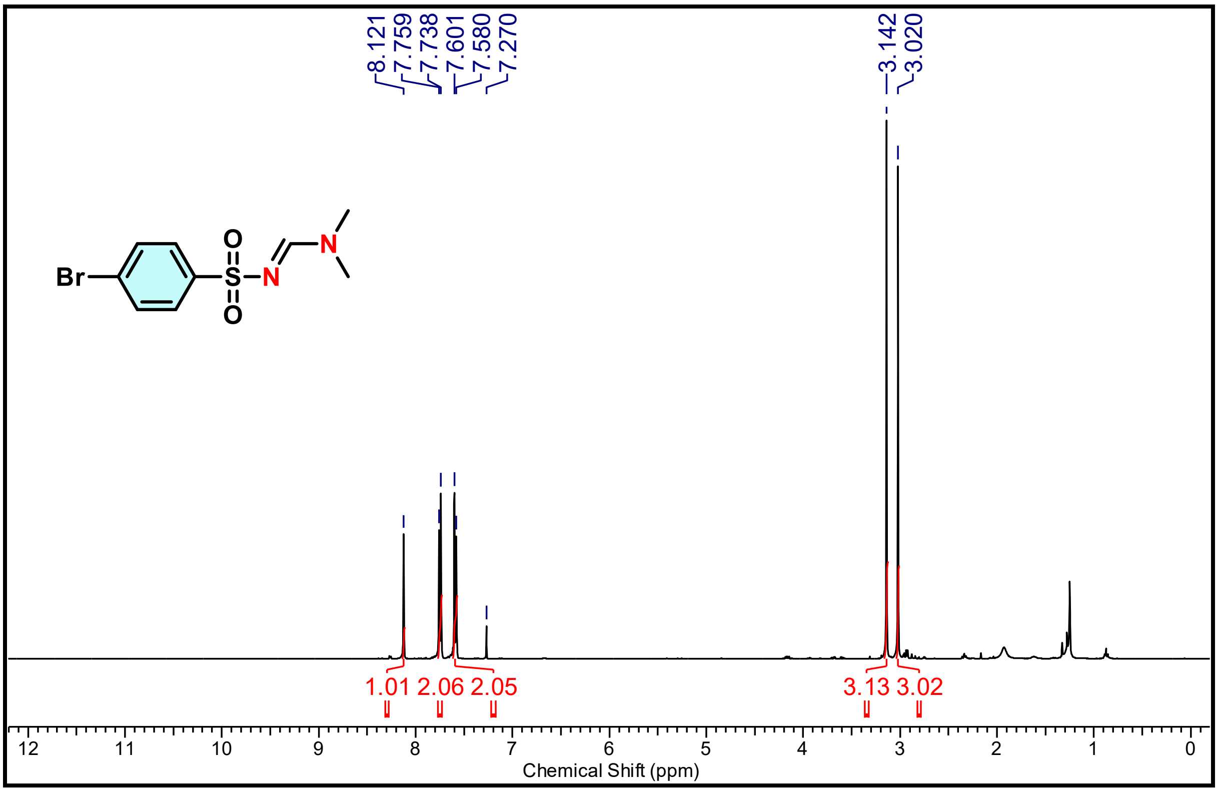
[1]H spectra of **(3c)** (400 MHz, $CDCl_3$)



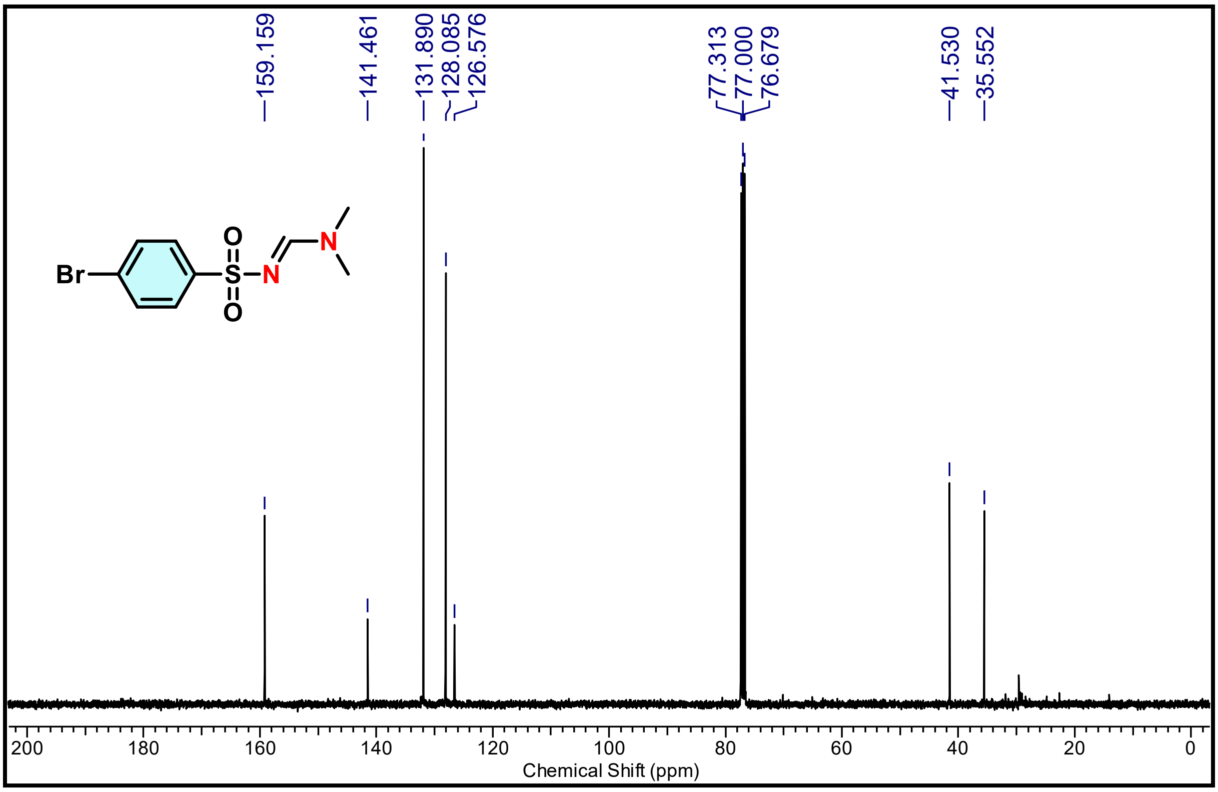
[13]C spectra of **(3c)** (100 MHz, $CDCl_3$)



^{1}H spectra of **(3d)** (400 MHz, $CDCl_3$)



^{13}C spectra of **(3d)** (100 MHz, $CDCl_3$)



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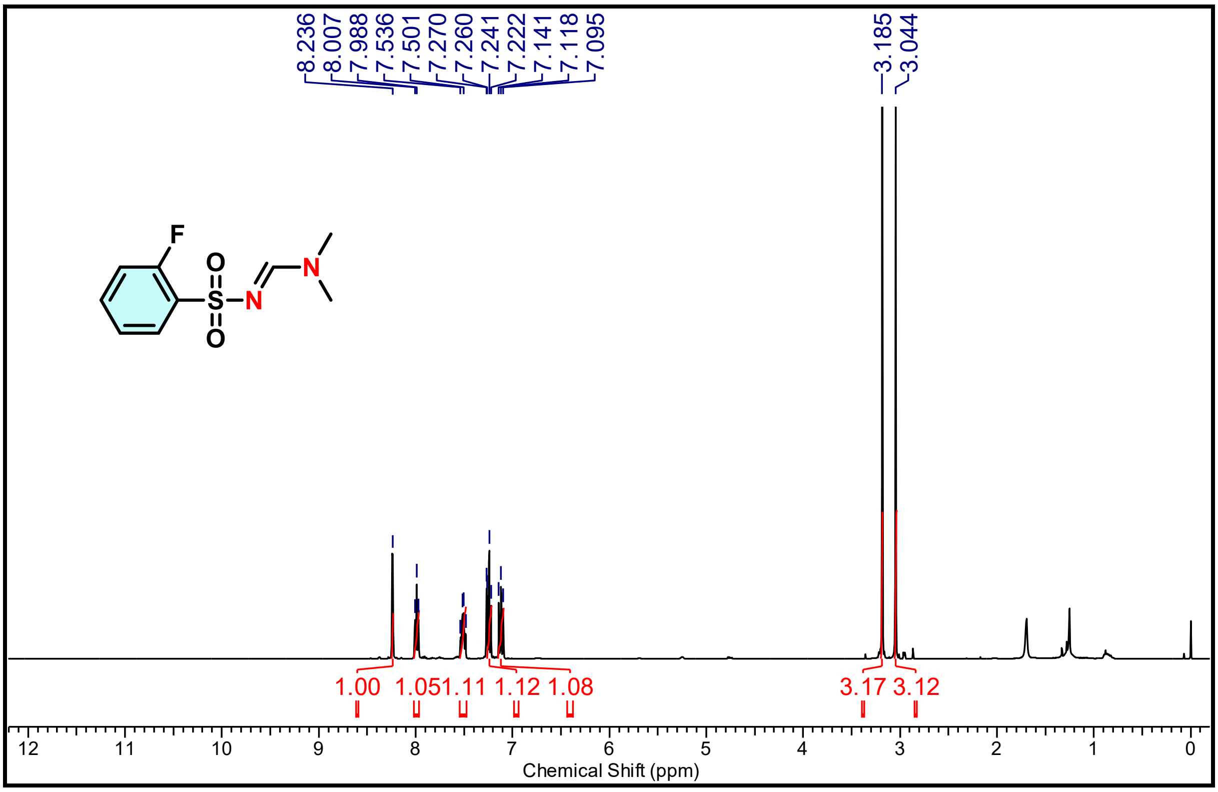

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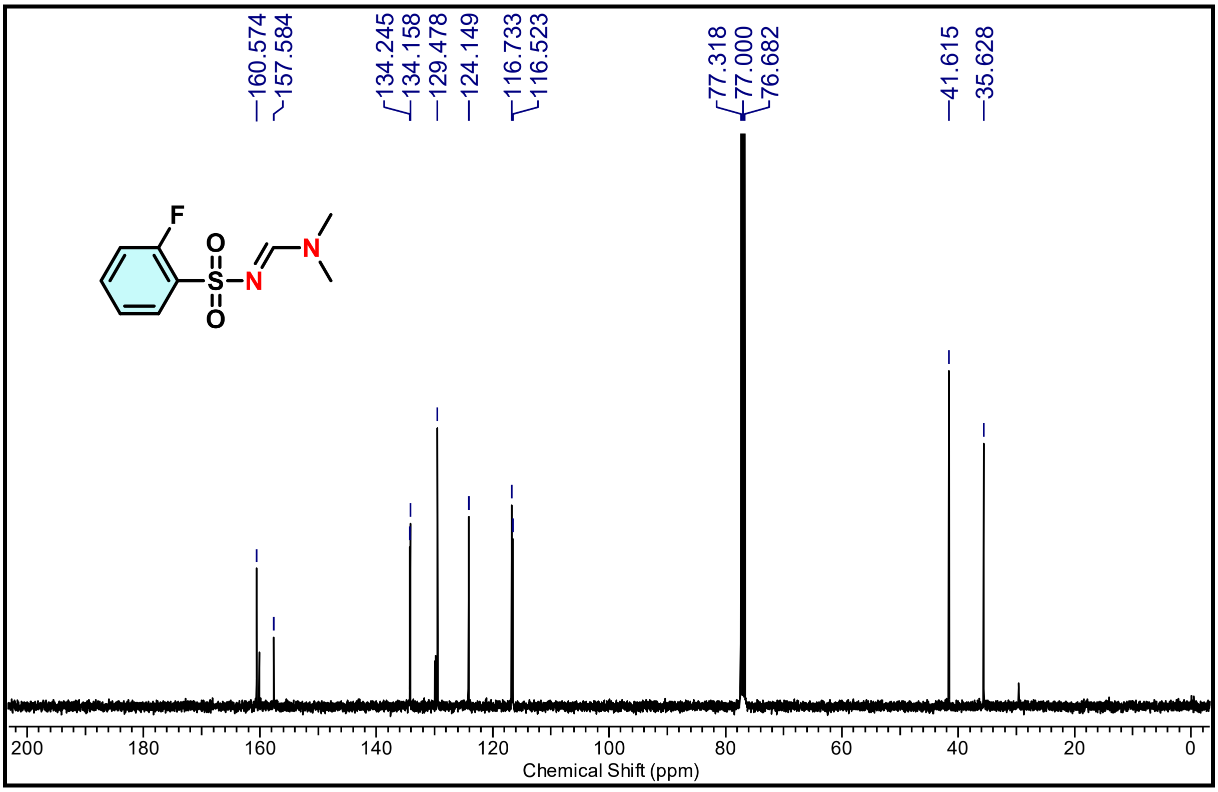
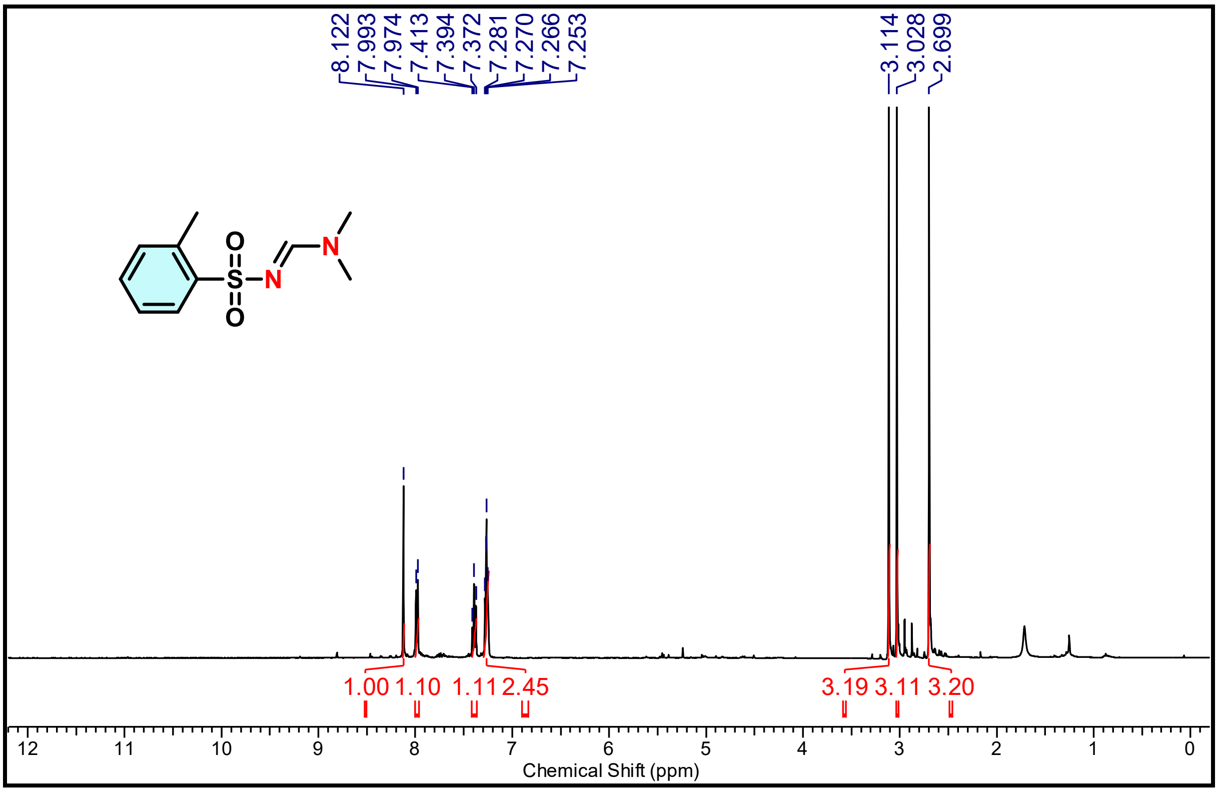


^{1}H spectra of **(3f)** (400 MHz, $CDCl_3$)



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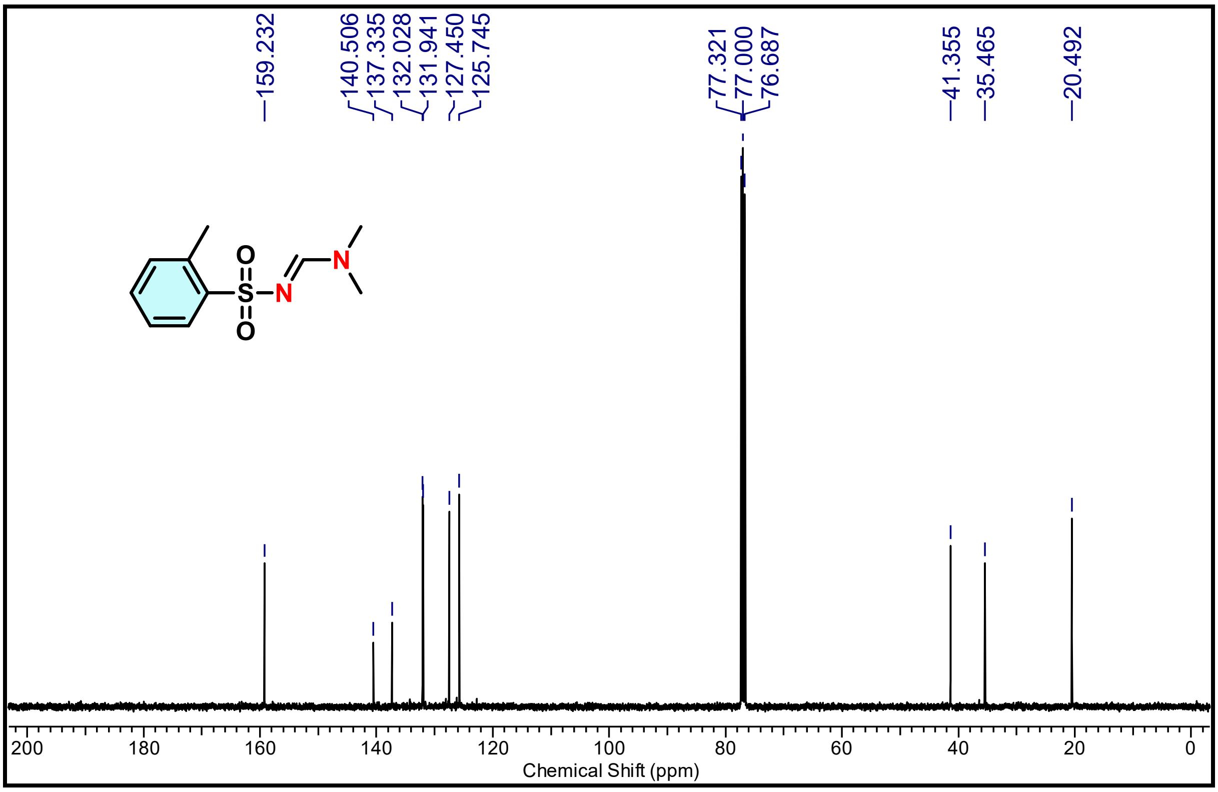
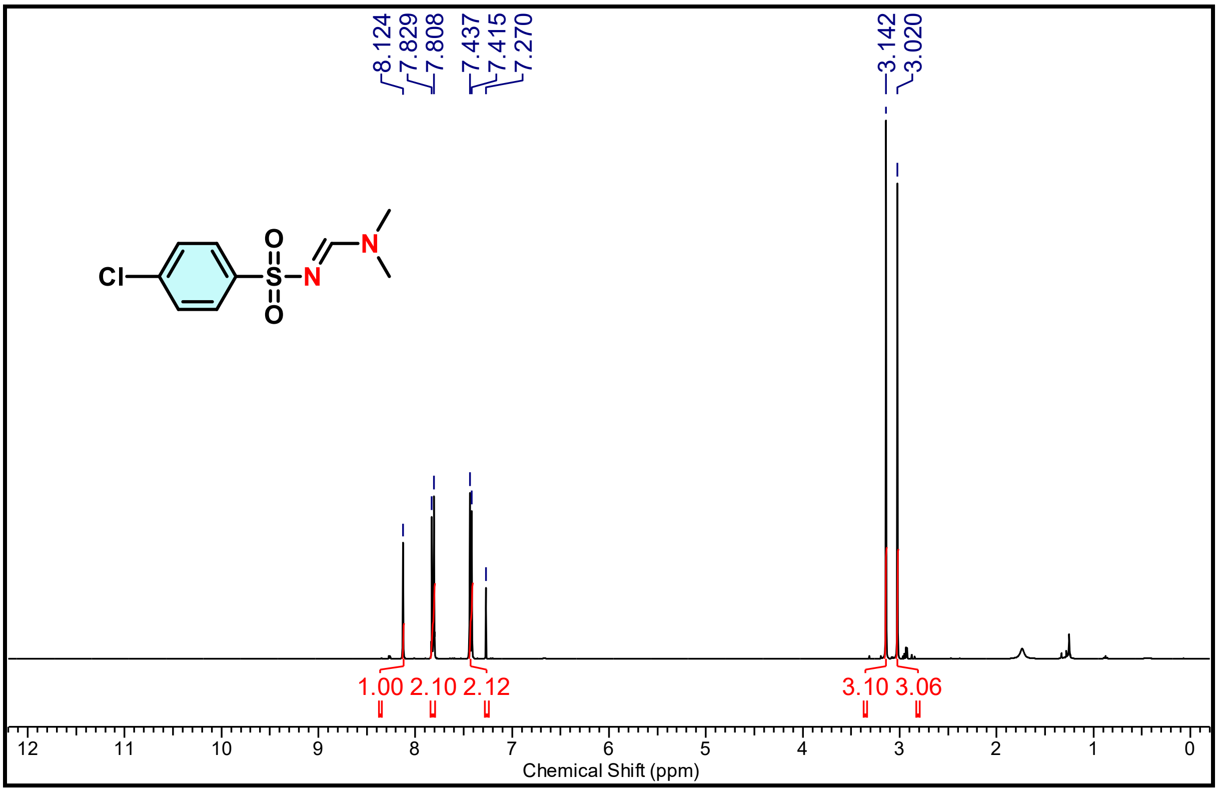
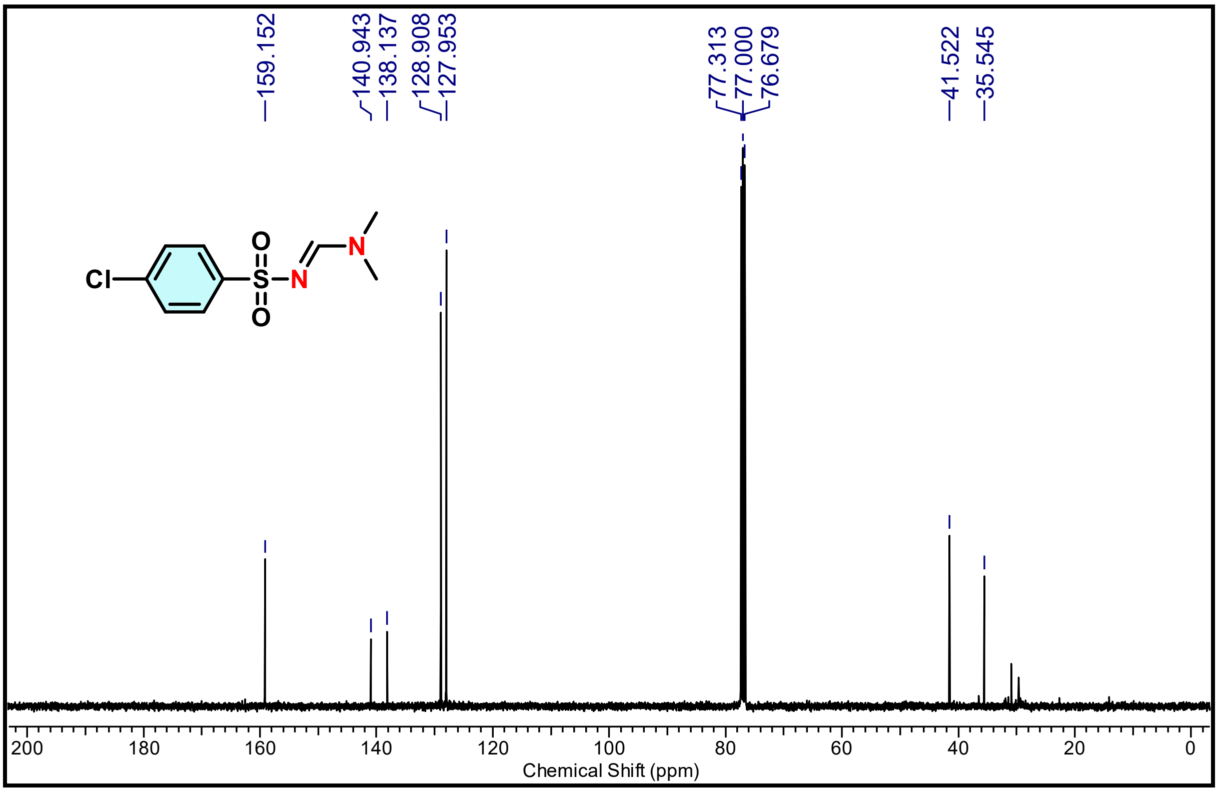


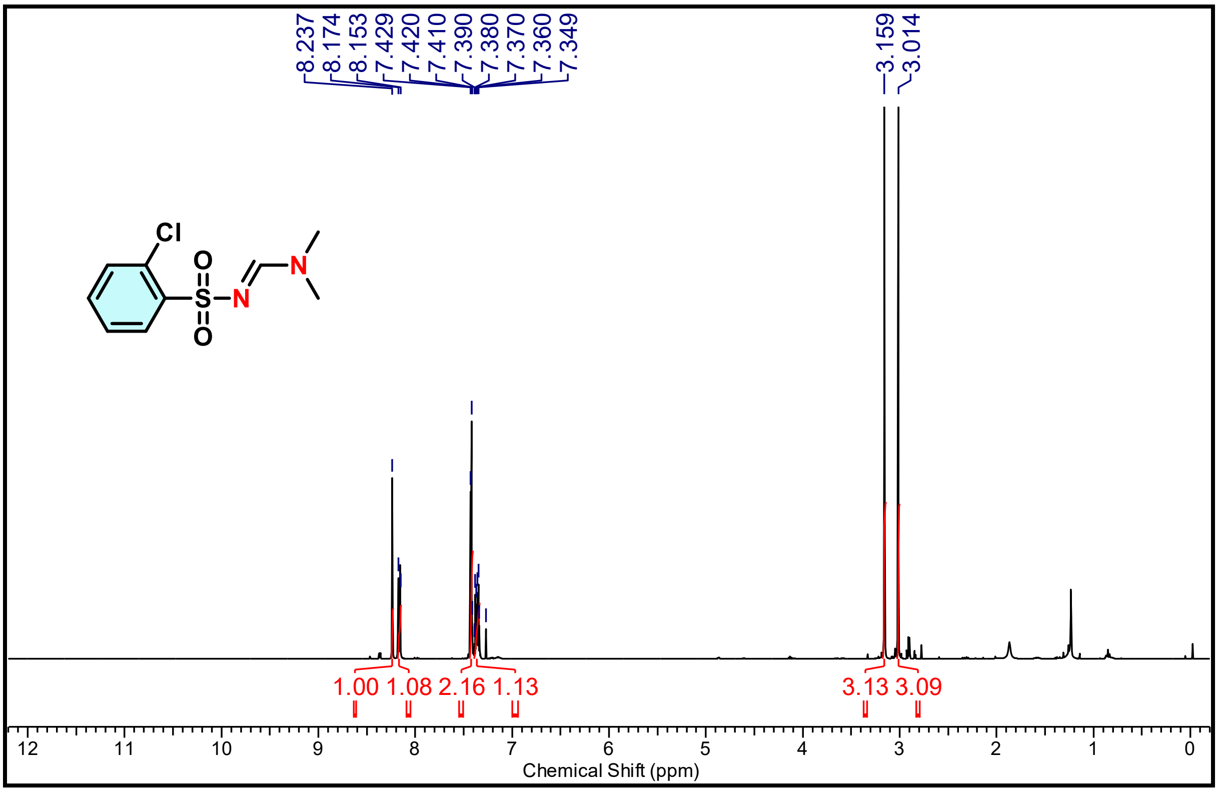
^{1}H spectra of **(3g)** (400 MHz, $CDCl_3$)



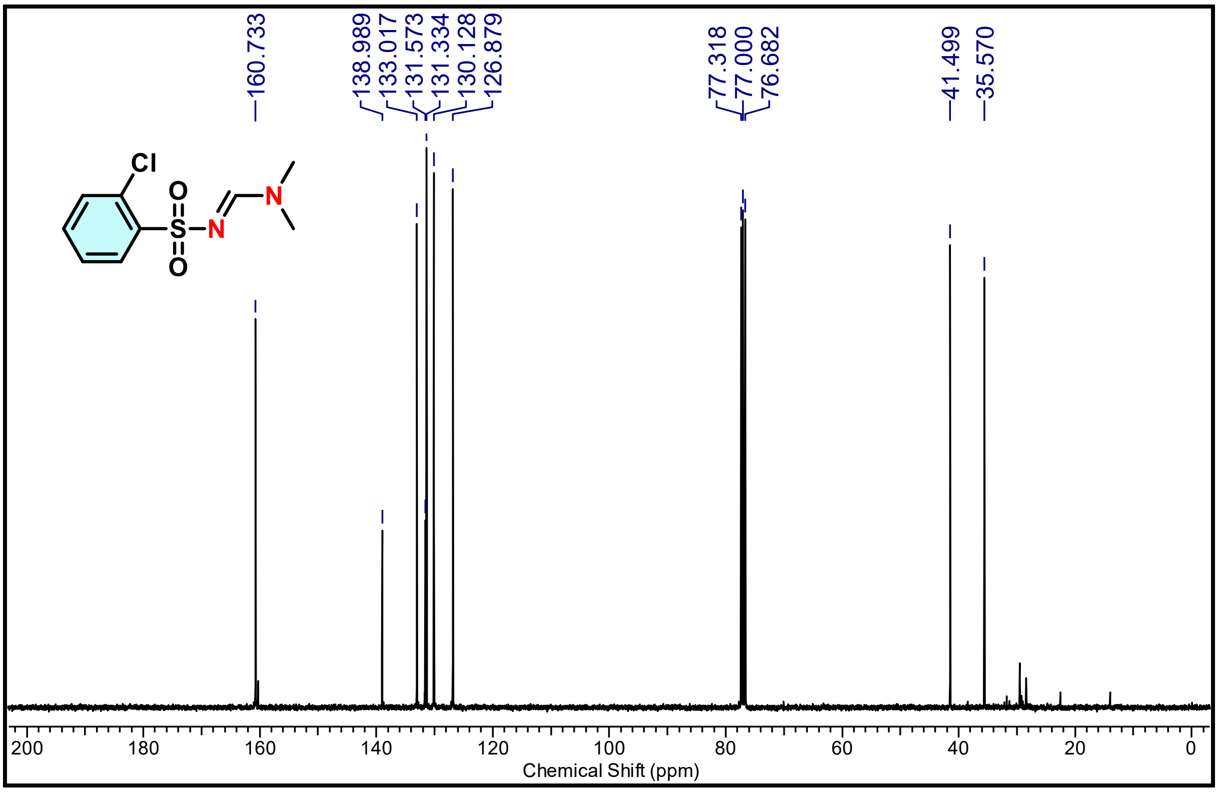
^{13}C spectra of **(3g)** (100 MHz, $CDCl_3$)



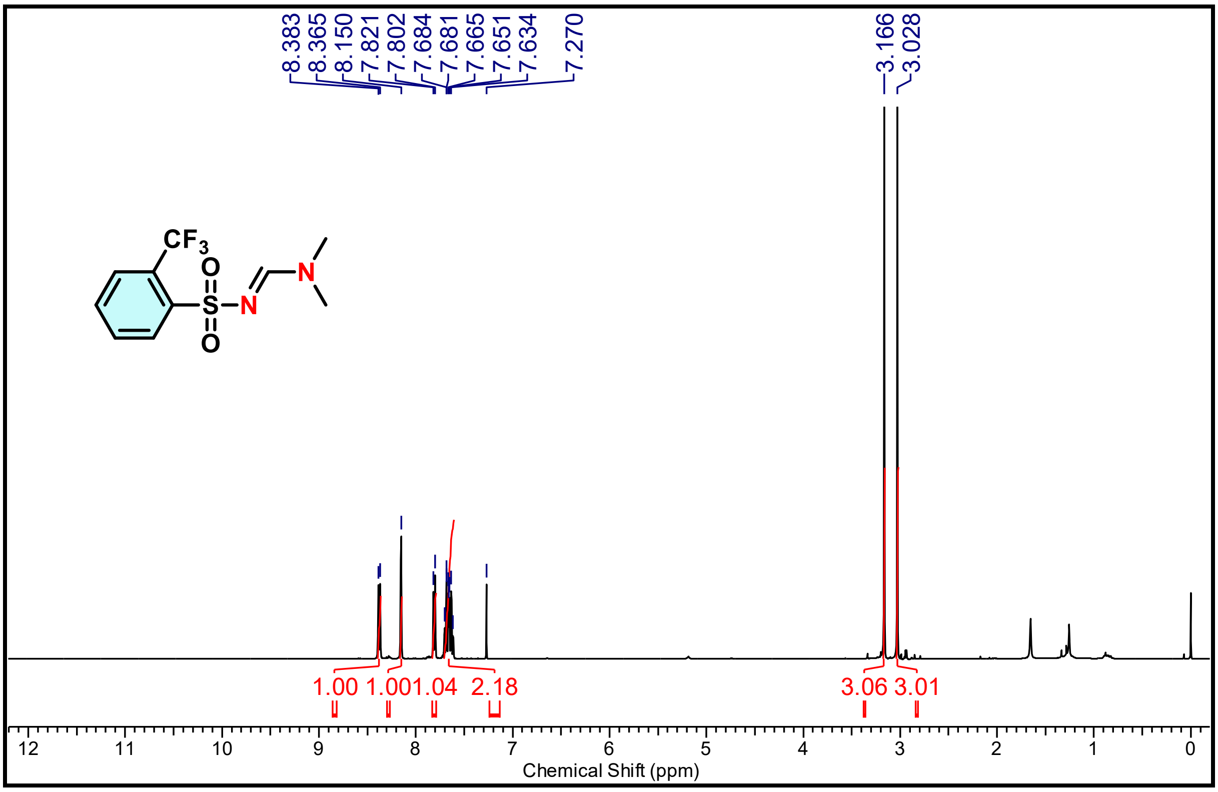
[1]H spectra of **(3h)** (400 MHz, $CDCl_3$)



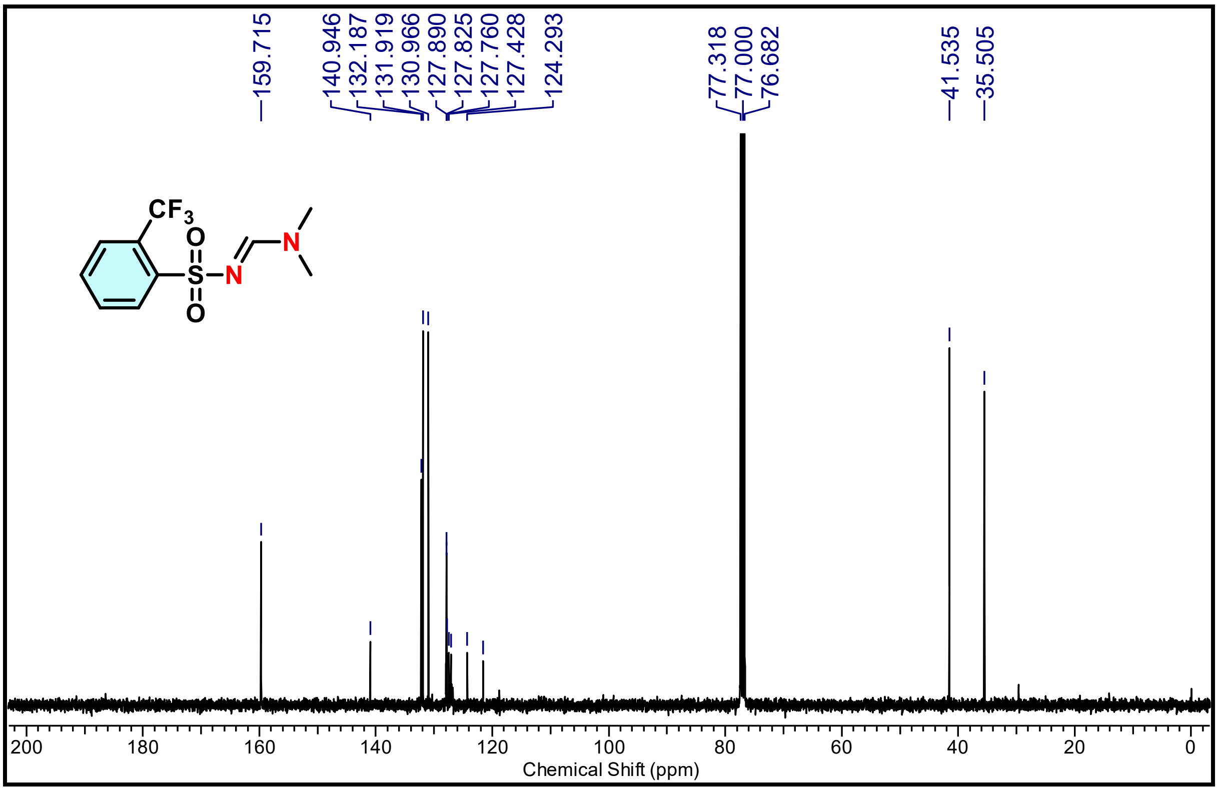
[13]C spectra of **(3h)** (100 MHz, $CDCl_3$)



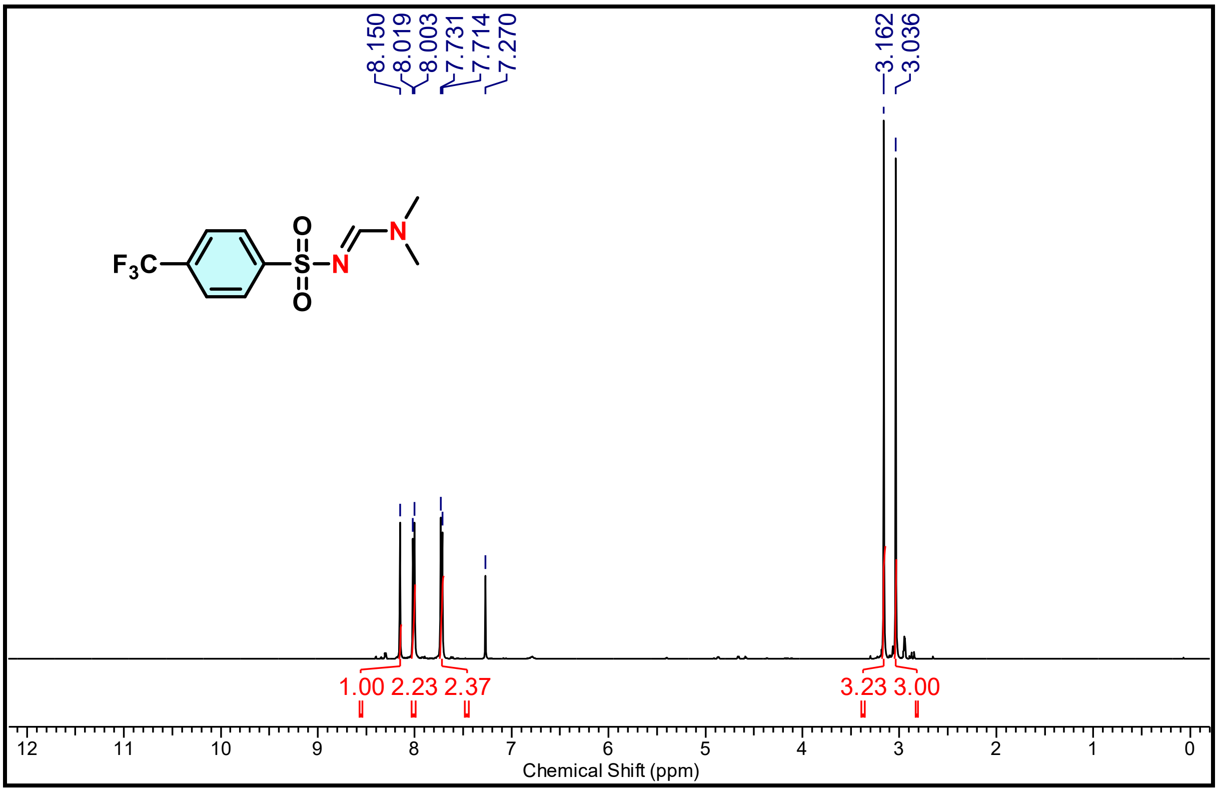
^{1}H spectra of **(3i)** (400 MHz, $CDCl_3$)



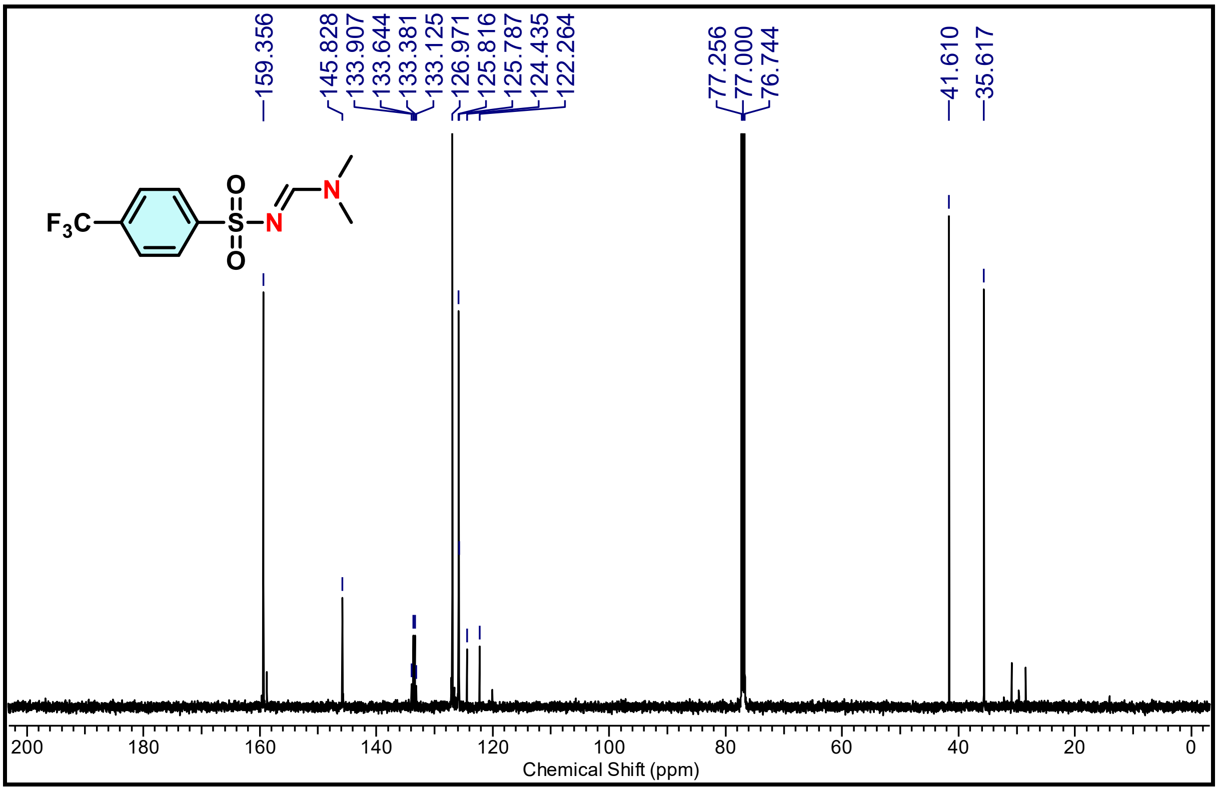
^{13}C spectra of **(3i)** (100 MHz, $CDCl_3$)



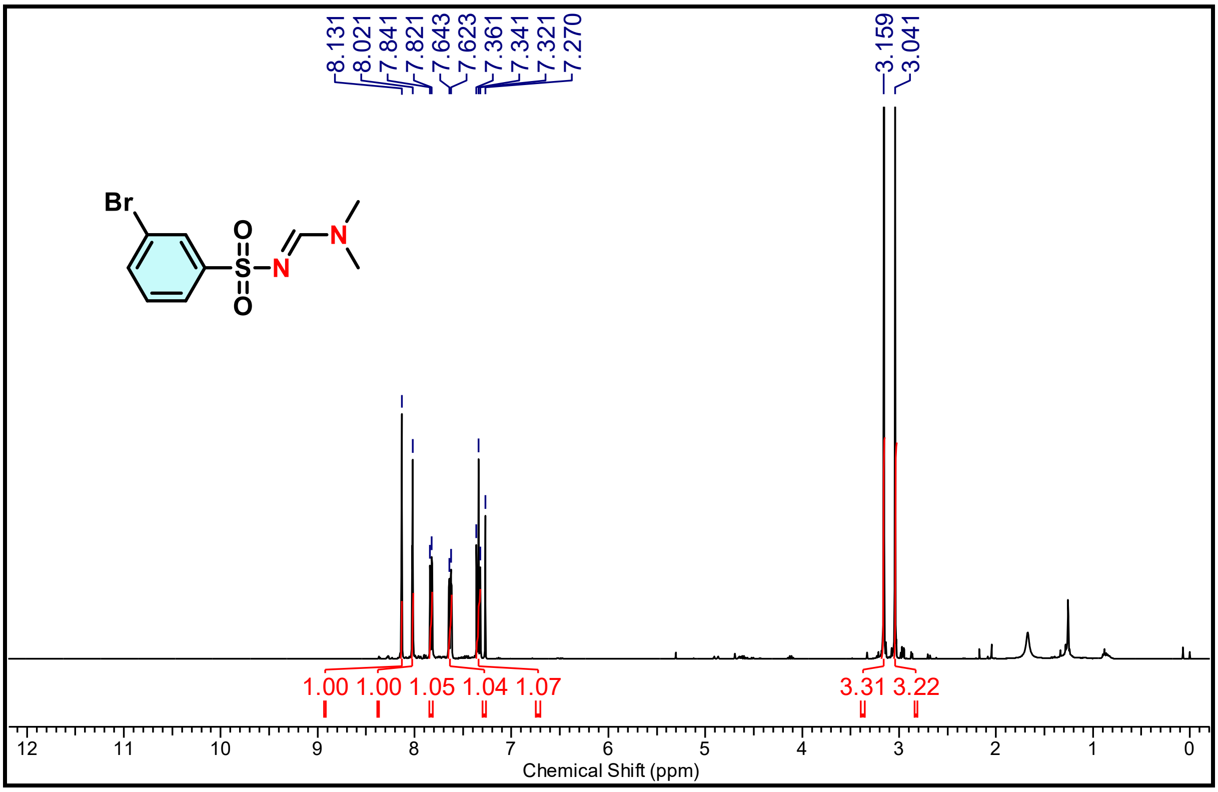
[1]H spectra of **(3j)** (400 MHz, $CDCl_3$)



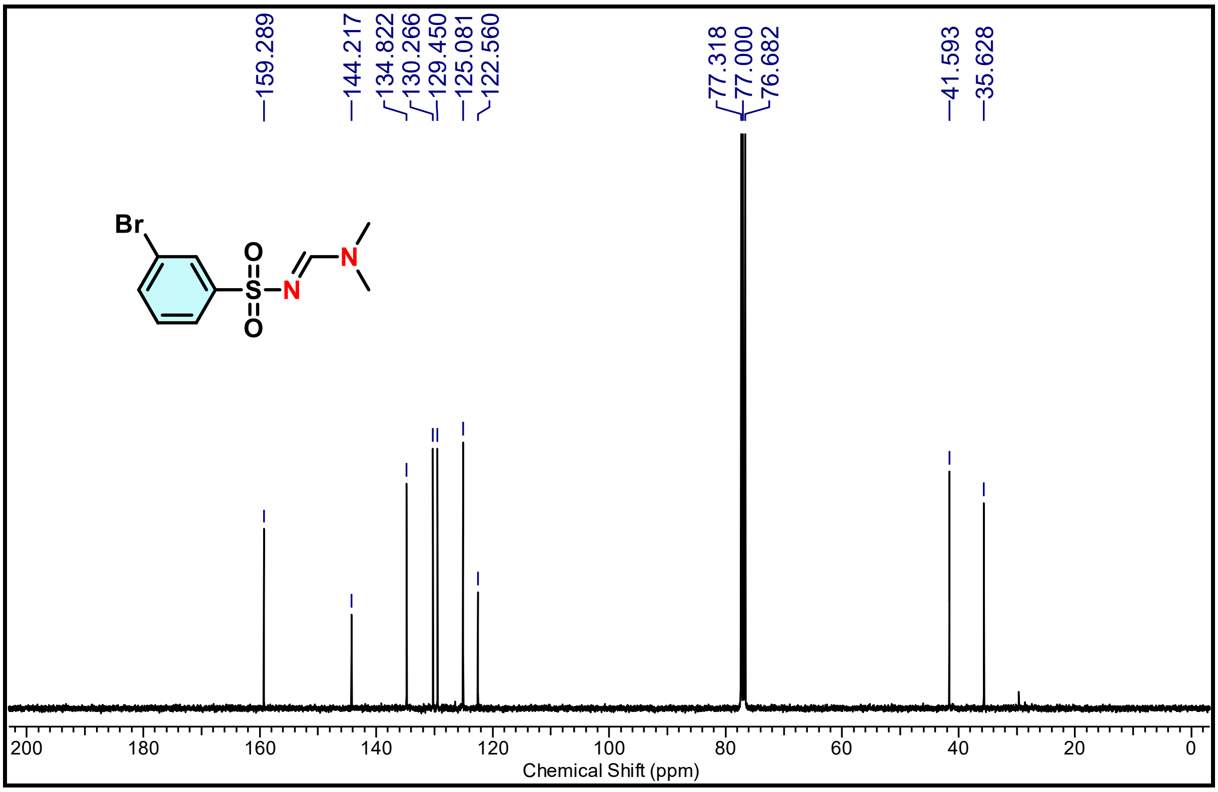
[13]C spectra of **(3j)** (100 MHz, $CDCl_3$)



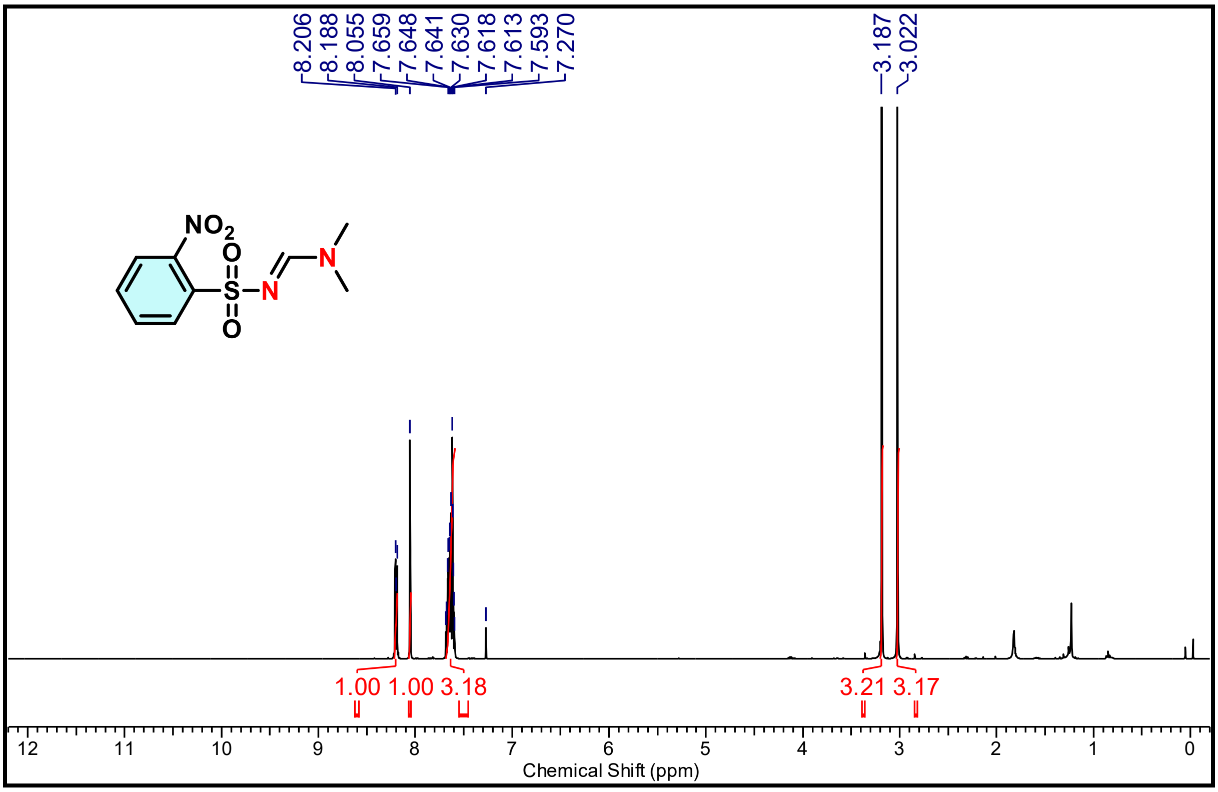
[1]H spectra of **(3k)** (400 MHz, $CDCl_3$)



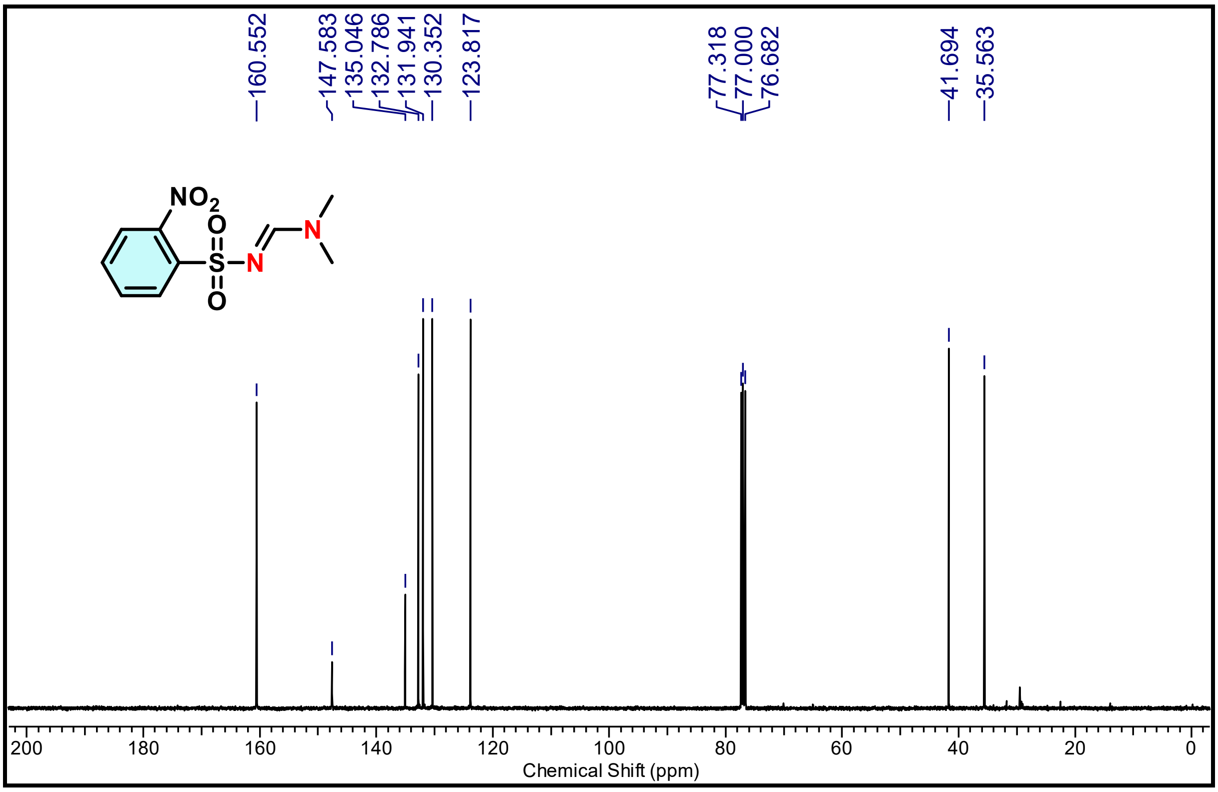
[13]C spectra of **(3k)** (100 MHz, $CDCl_3$)



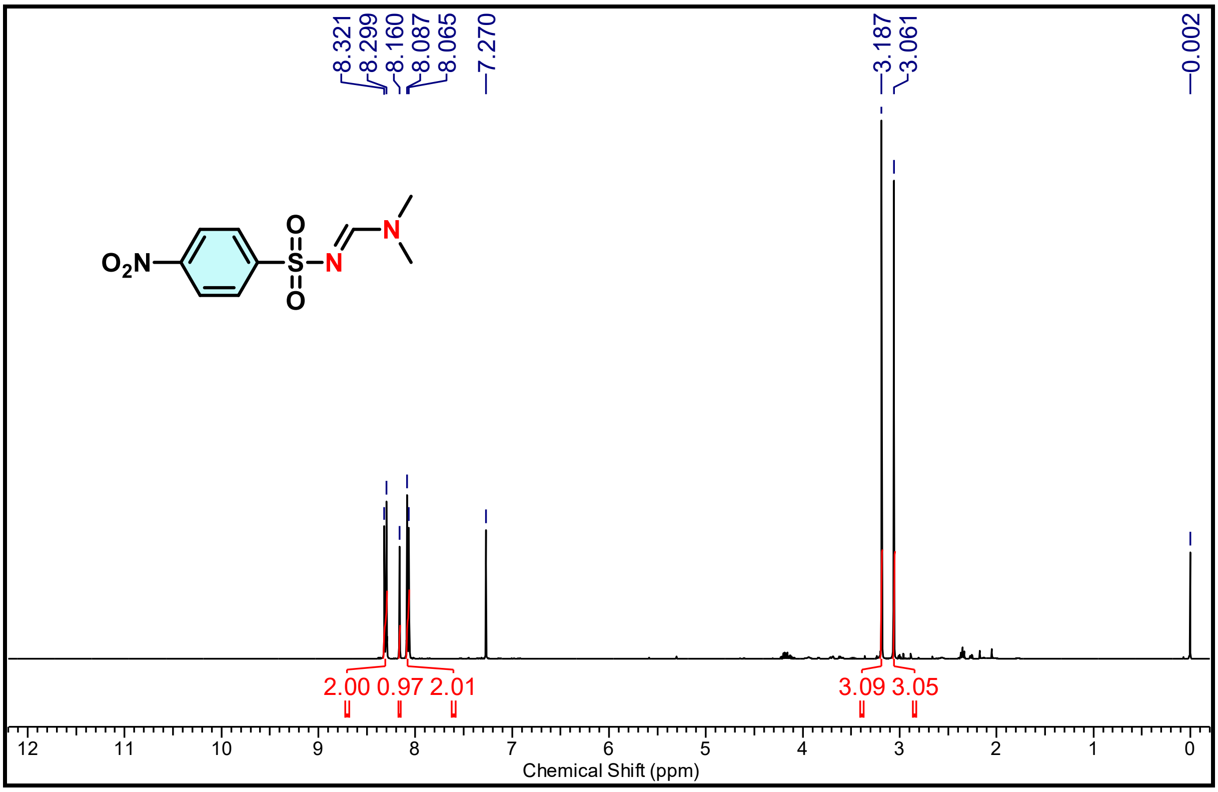
[1]H spectra of **(3l)** (400 MHz, $CDCl_3$)



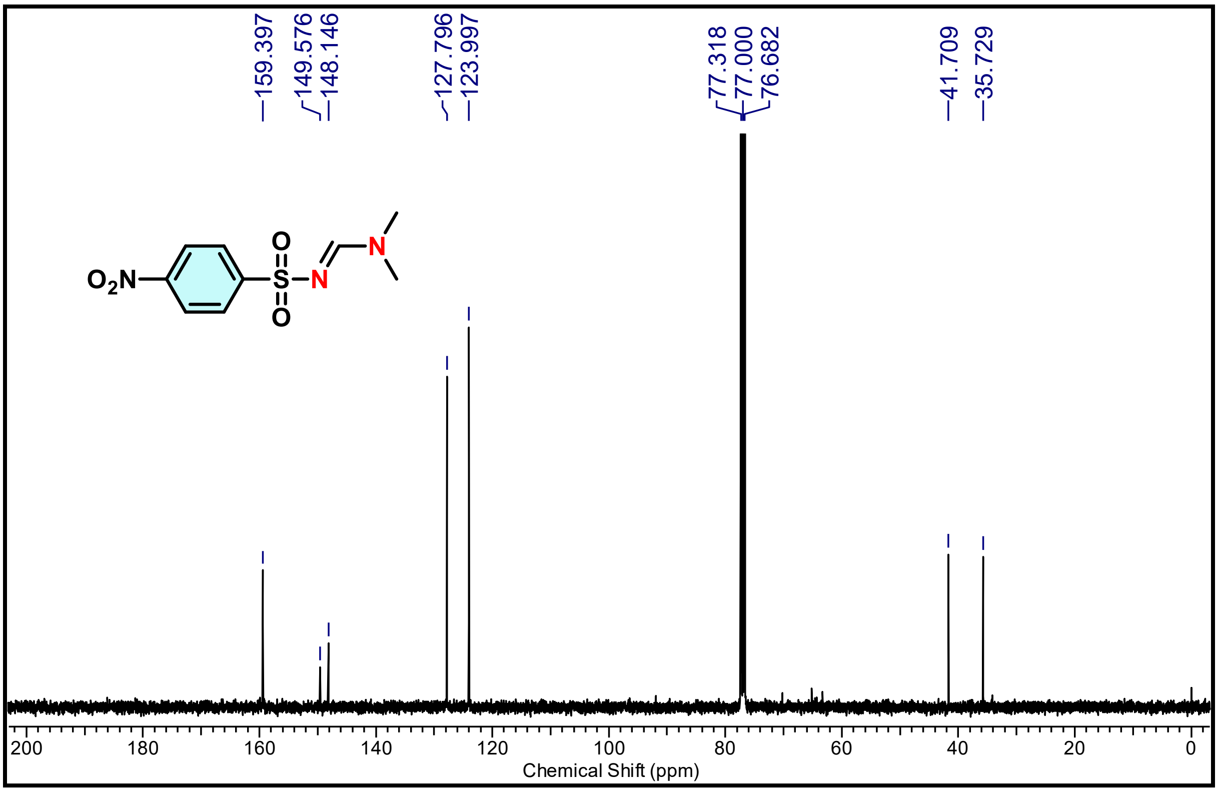
[13]C spectra of **(3l)** (100 MHz, $CDCl_3$)



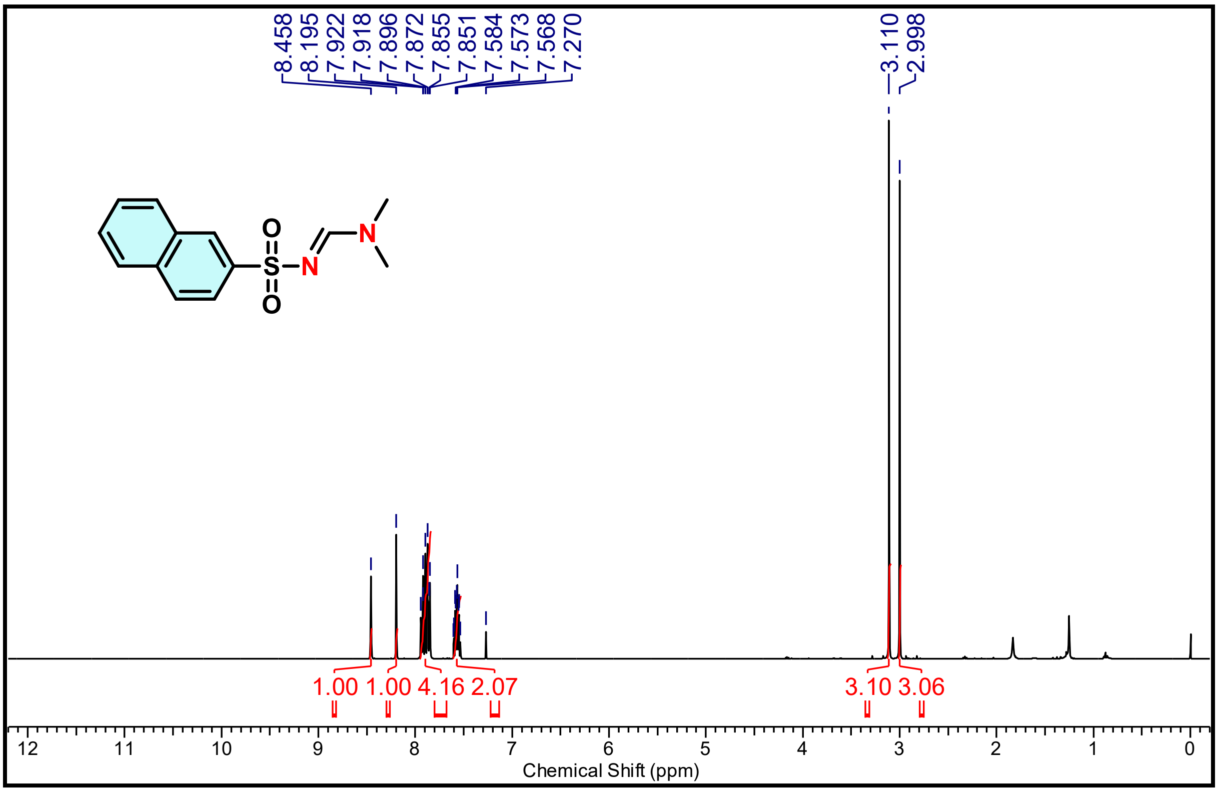
^{1}H spectra of **(3m)** (400 MHz, $CDCl_3$)



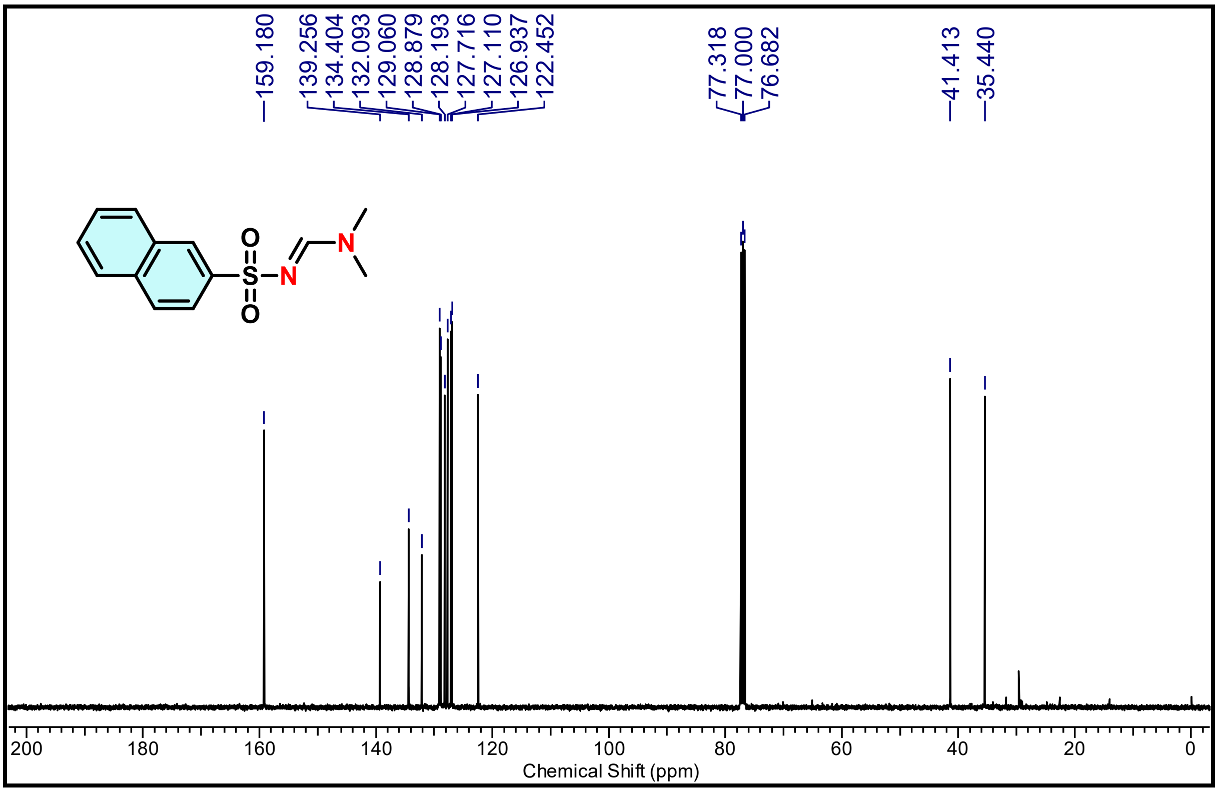
^{13}C spectra of **(3m)** (100 MHz, $CDCl_3$)



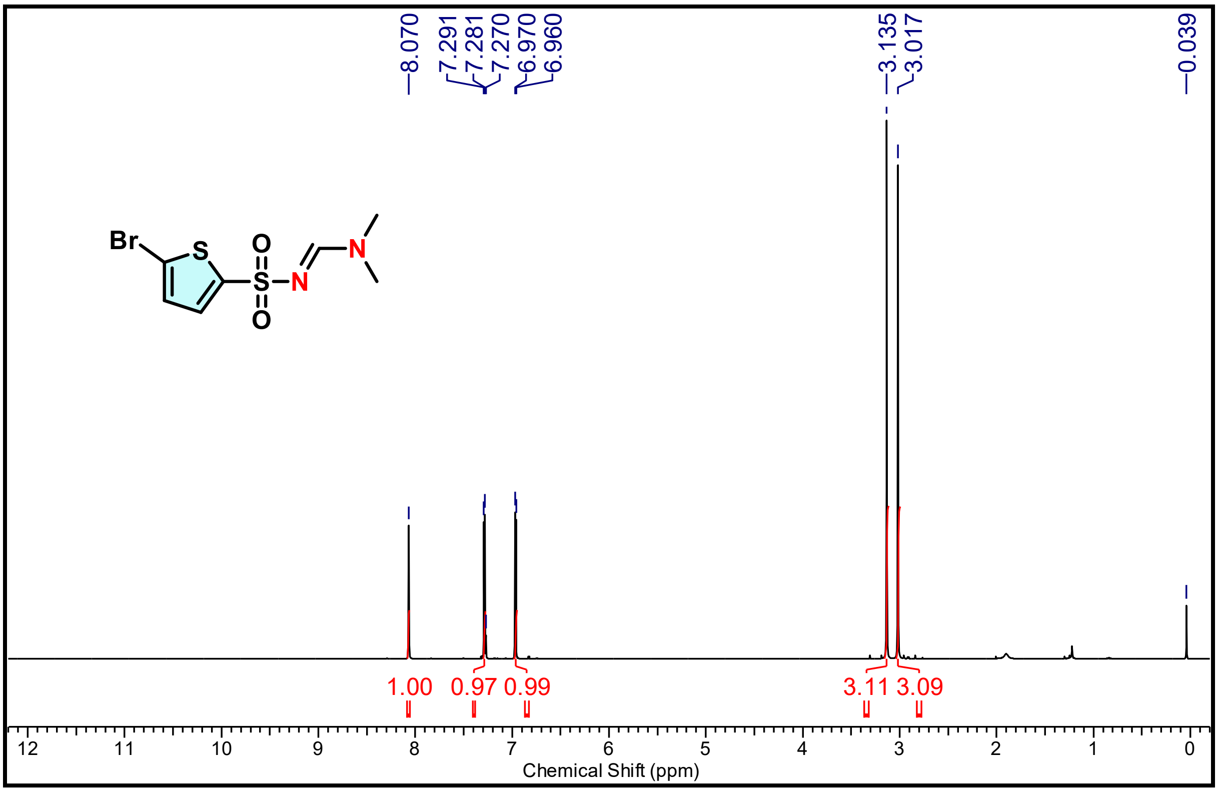
[1]H spectra of **(3n)** (400 MHz, $CDCl_3$)



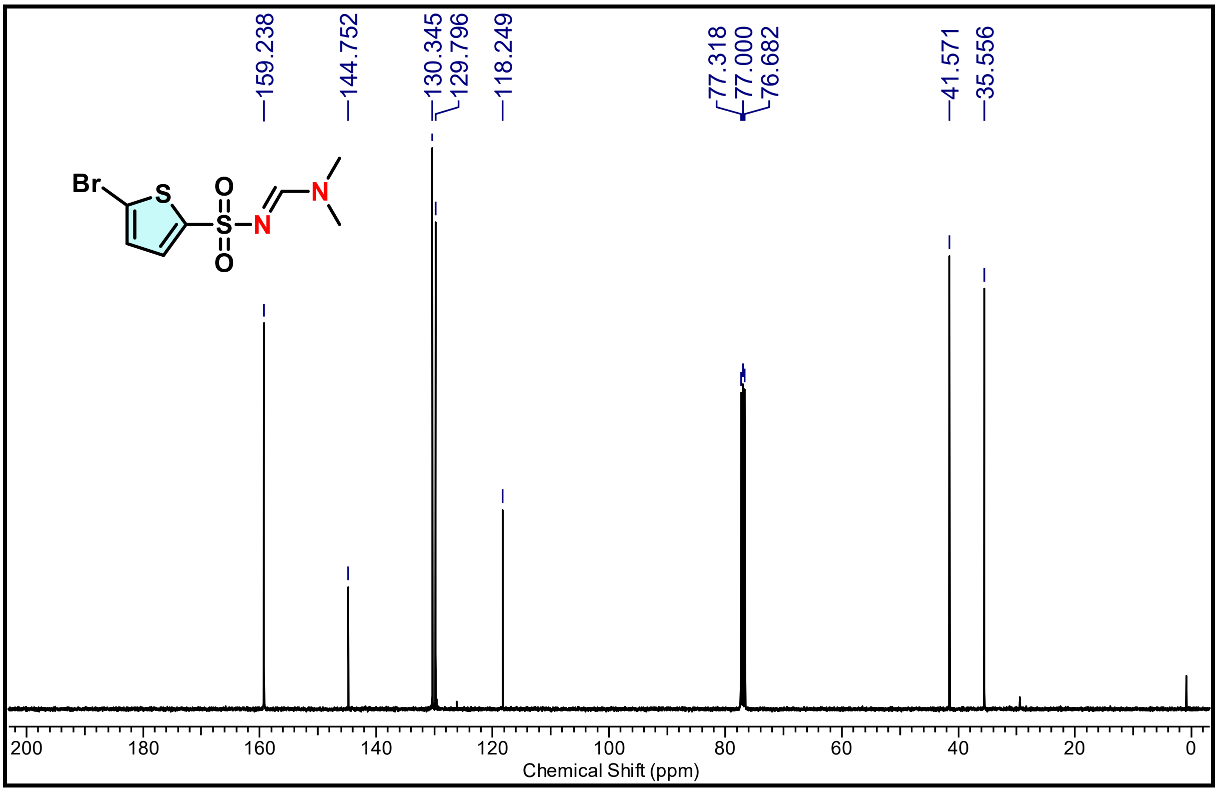
[13]C spectra of **(3n)** (100 MHz, $CDCl_3$)



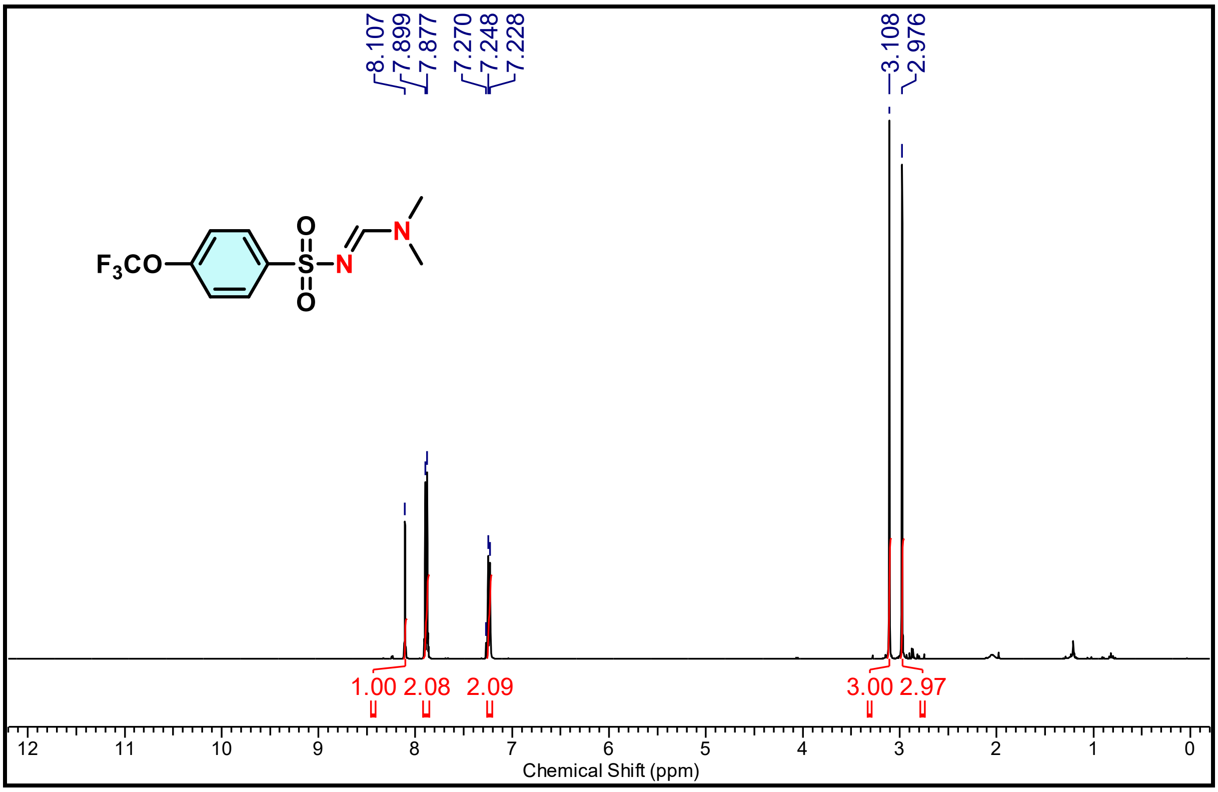
[1]H spectra of **(3o)** (400 MHz, $CDCl_3$)



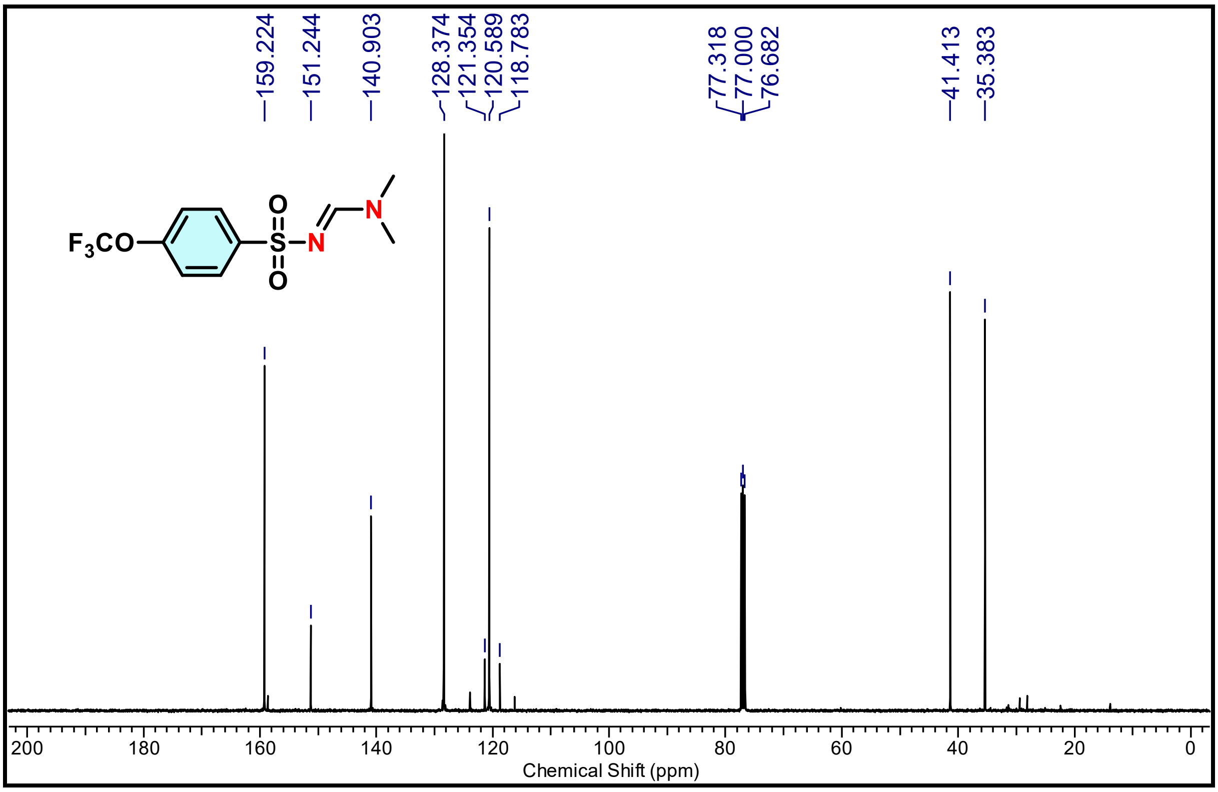
[13]C spectra of **(3o)** (100 MHz, $CDCl_3$)



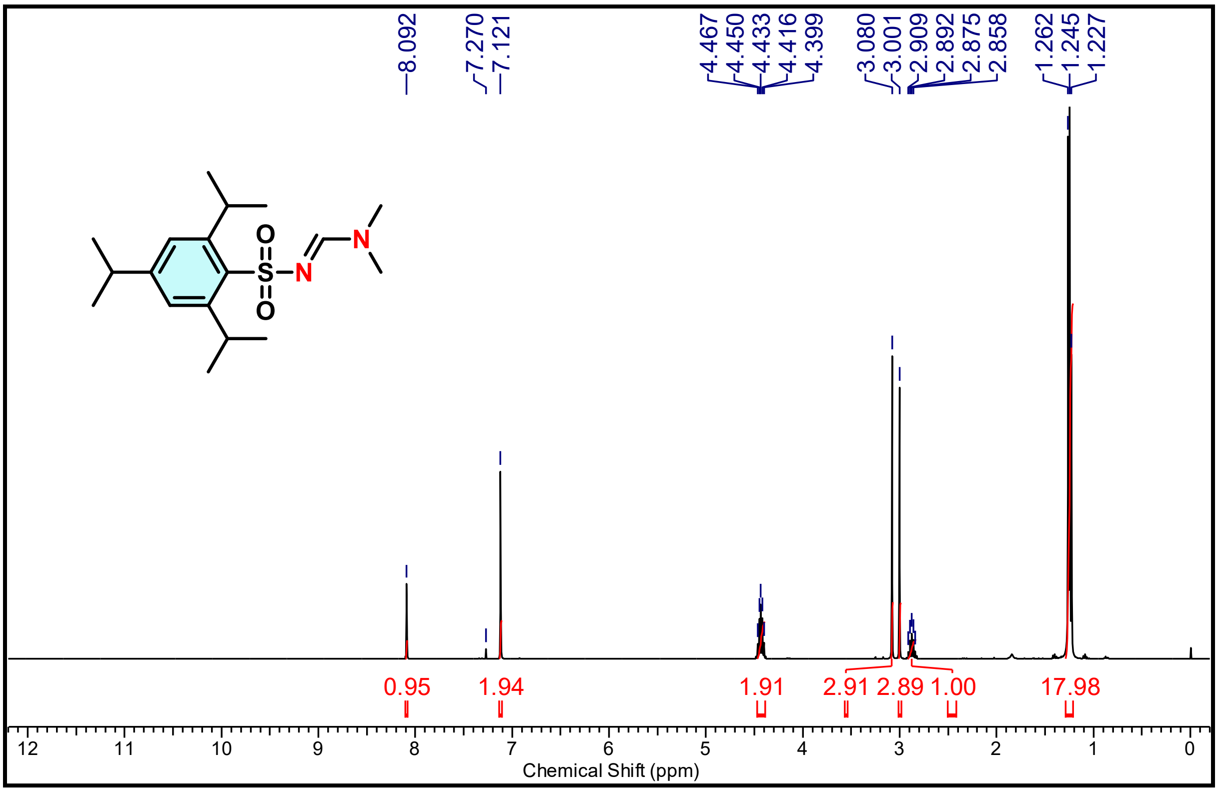
[1]H spectra of **(3p)** (400 MHz, $CDCl_3$)



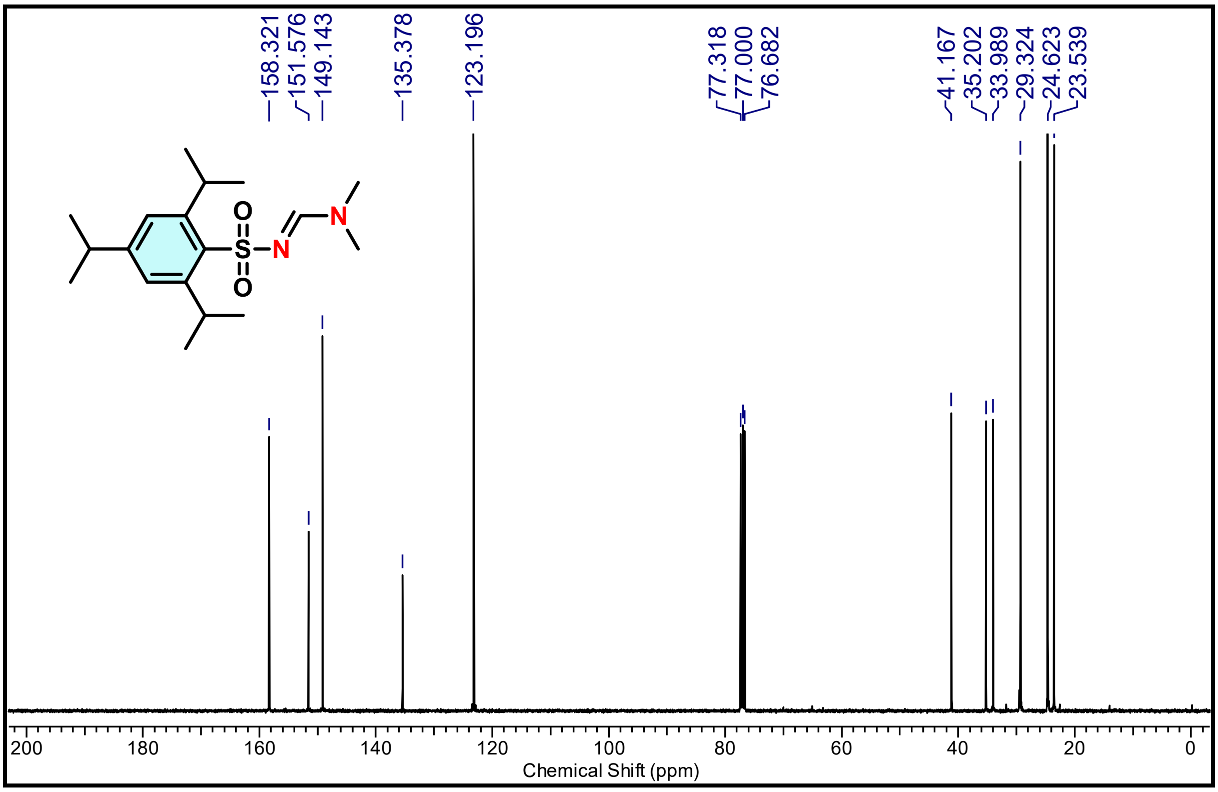
[13]C spectra of **(3p)** (100 MHz, $CDCl_3$)



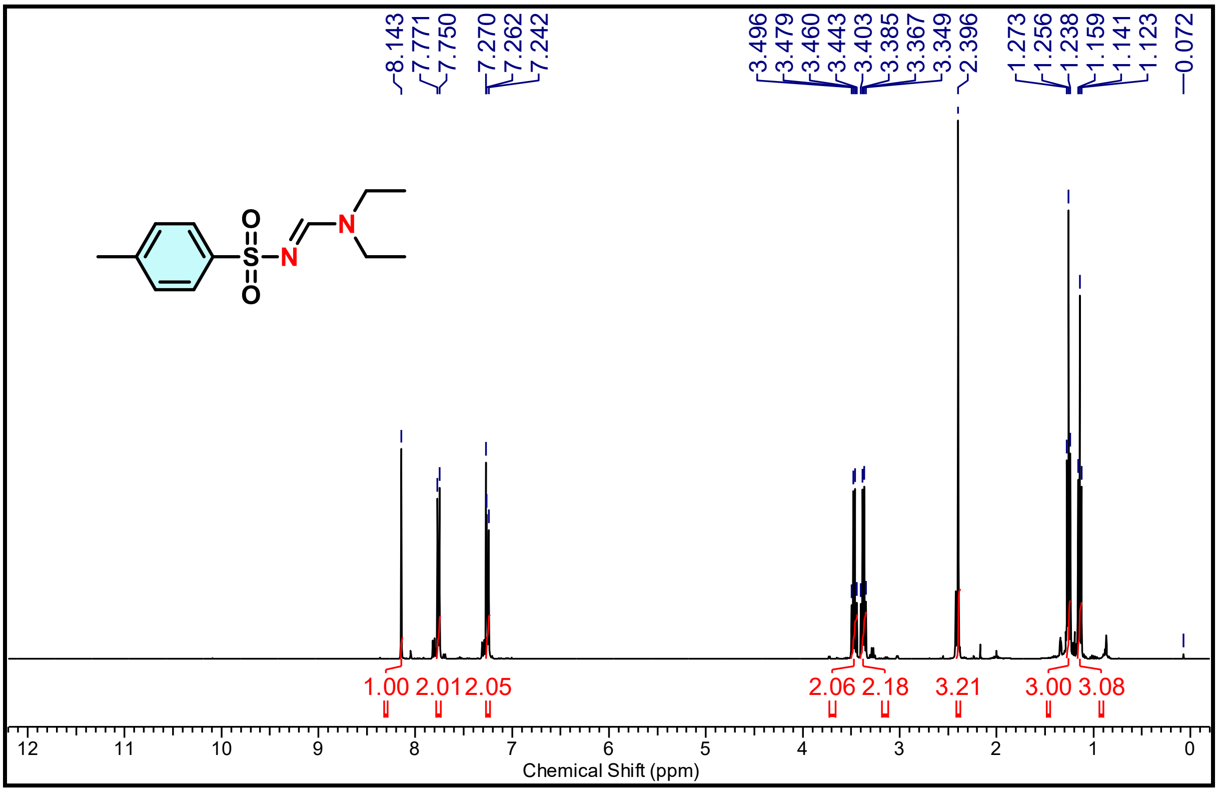
^{1}H spectra of **(3q)** (400 MHz, $CDCl_3$)



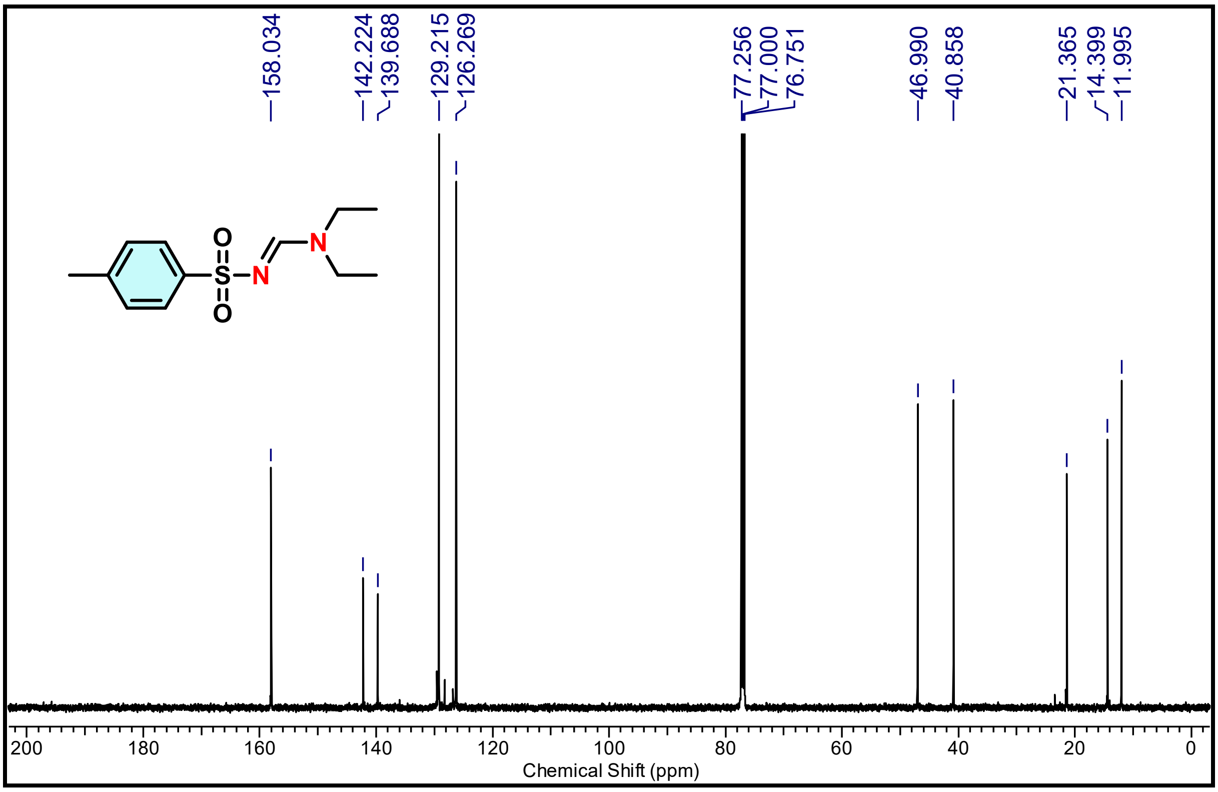
^{13}C spectra of **(3q)** (100 MHz, $CDCl_3$)



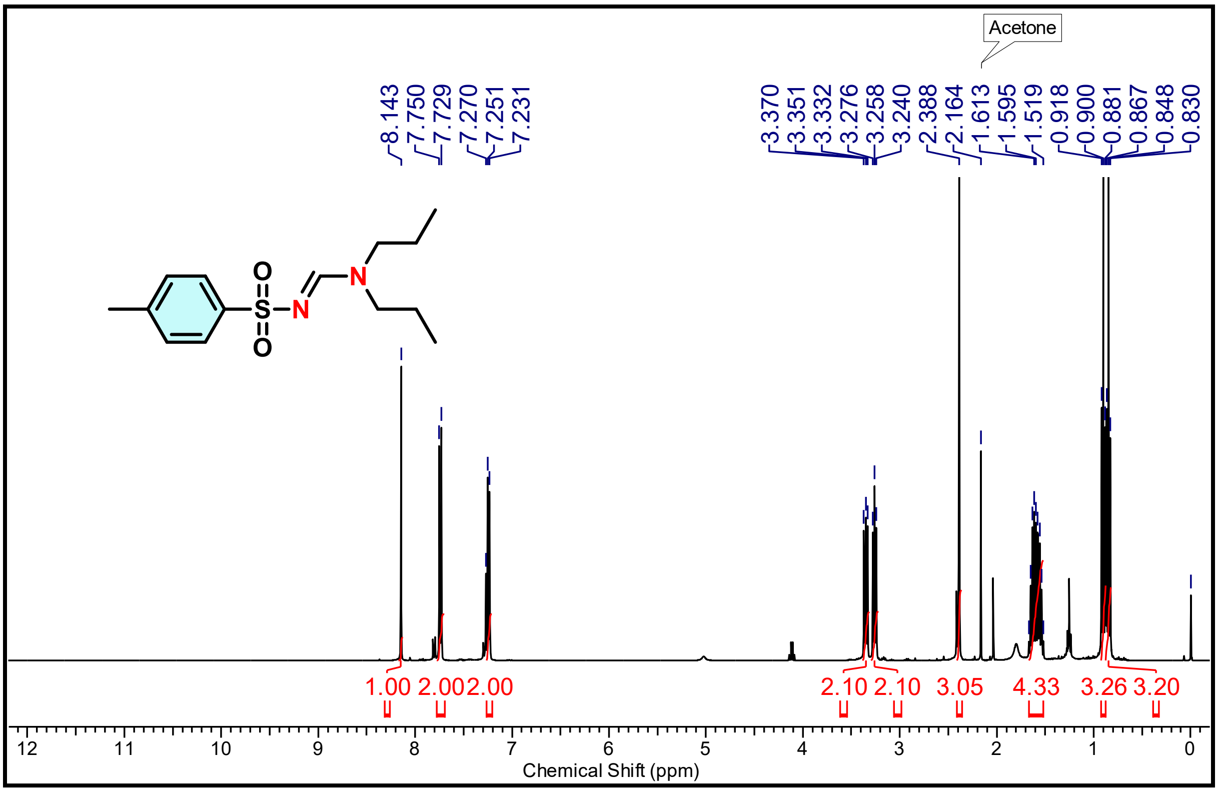
[1]H spectra of **(4a)** (400 MHz, $CDCl_3$)



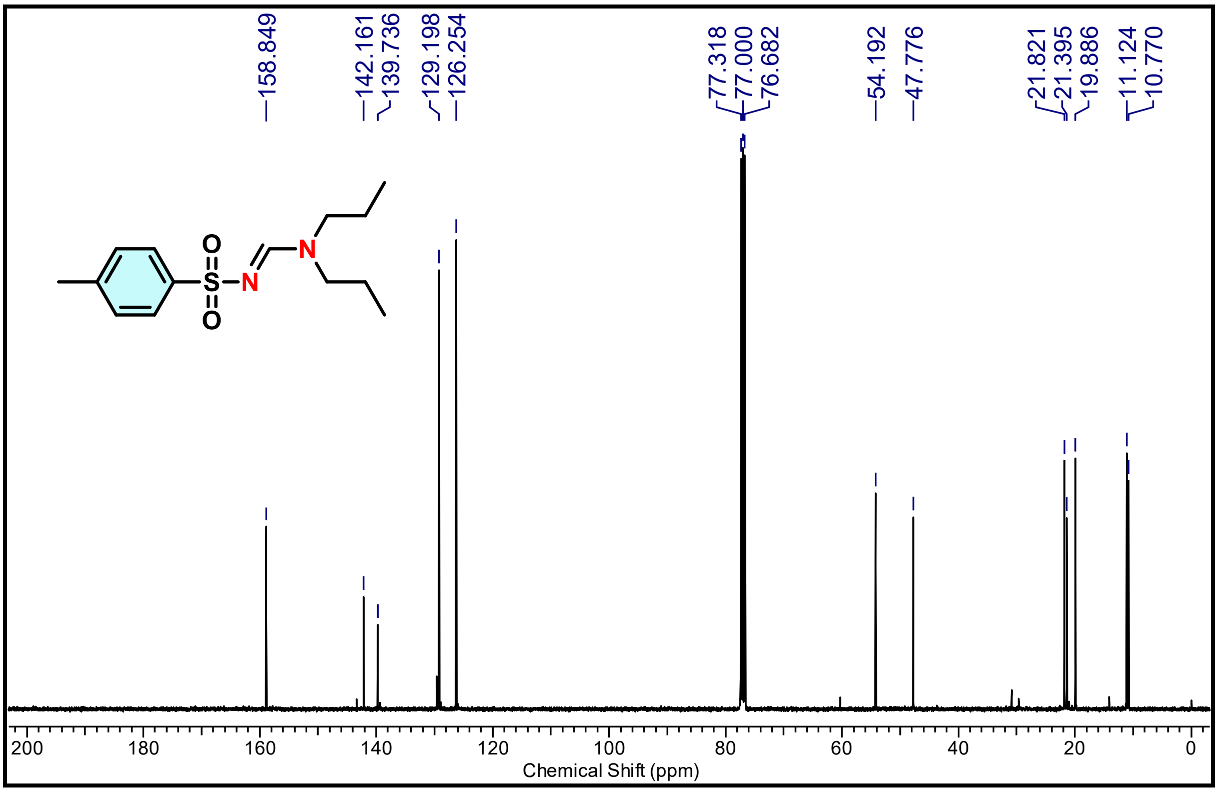
[13]C spectra of **(4a)** (100 MHz, $CDCl_3$)



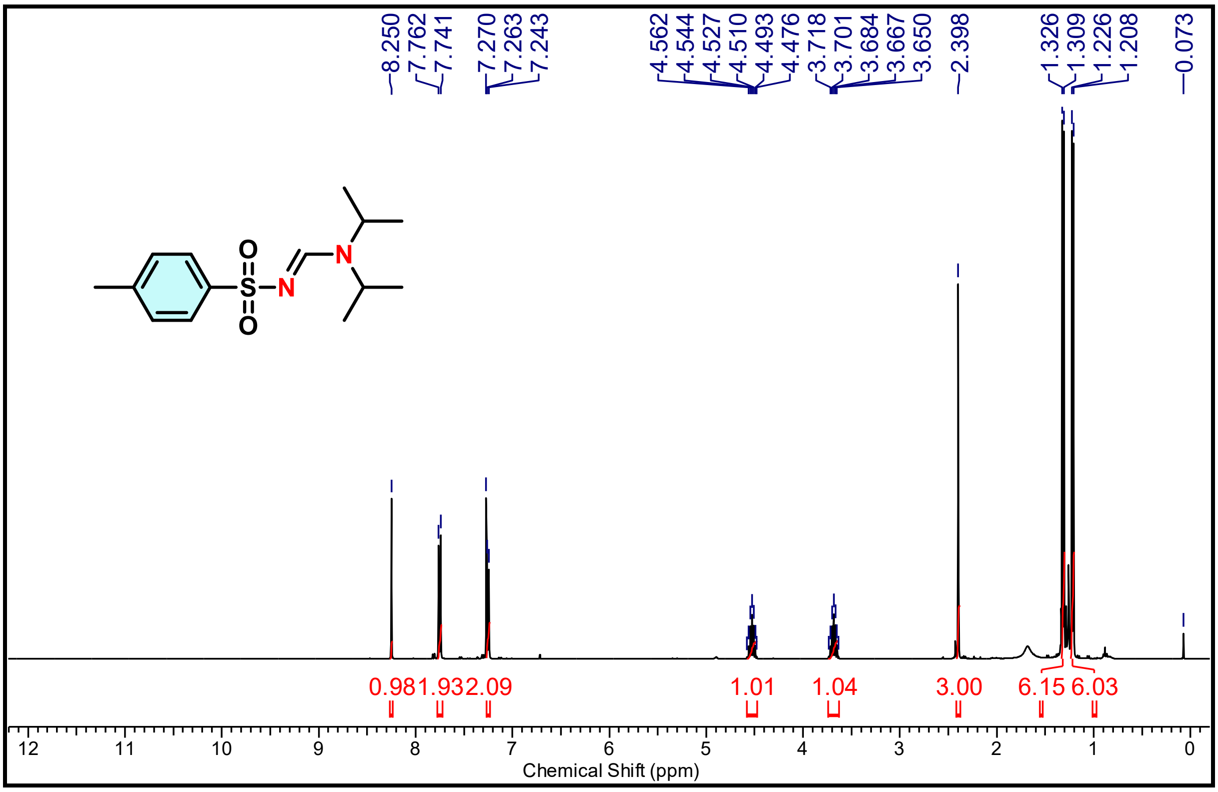
[1]H spectra of **(4b)** (400 MHz, $CDCl_3$)



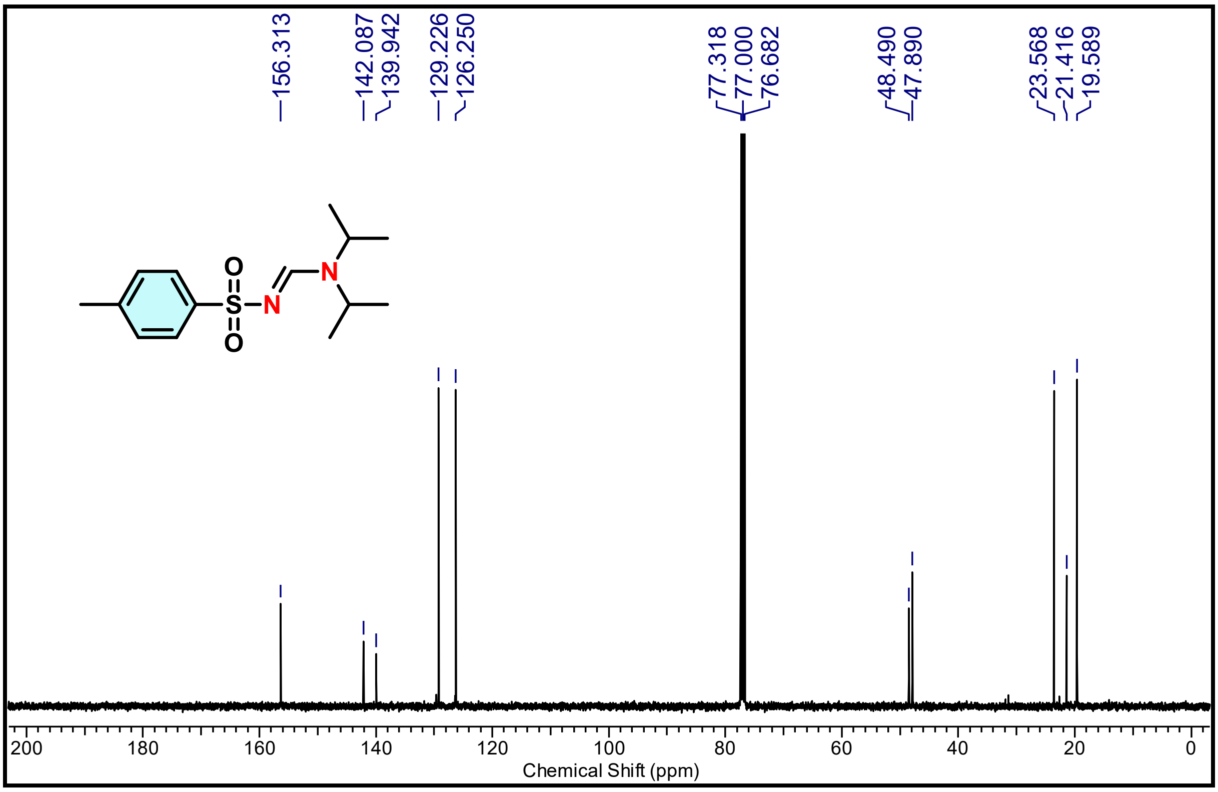
[13]C spectra of **(4b)** (100 MHz, $CDCl_3$)



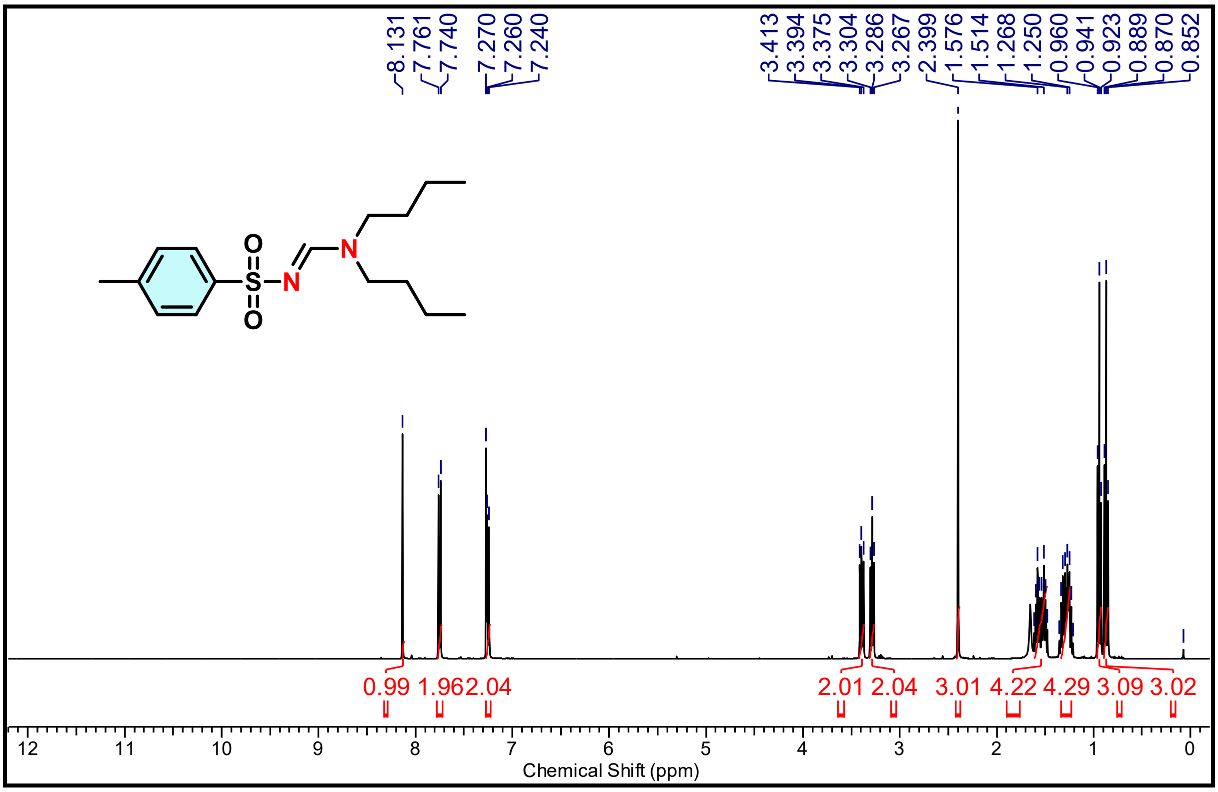
[1]H spectra of **(4c)** (400 MHz, $CDCl_3$)



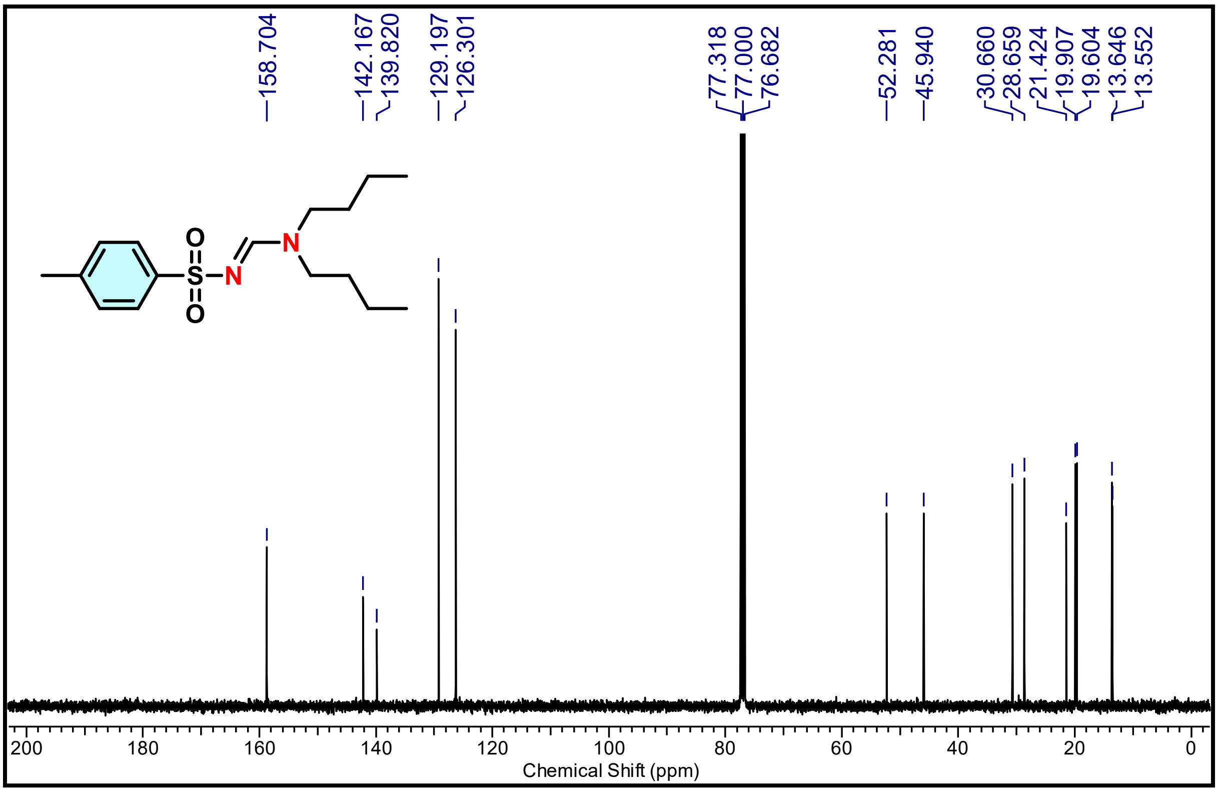
[13]C spectra of **(4c)** (100 MHz, $CDCl_3$)



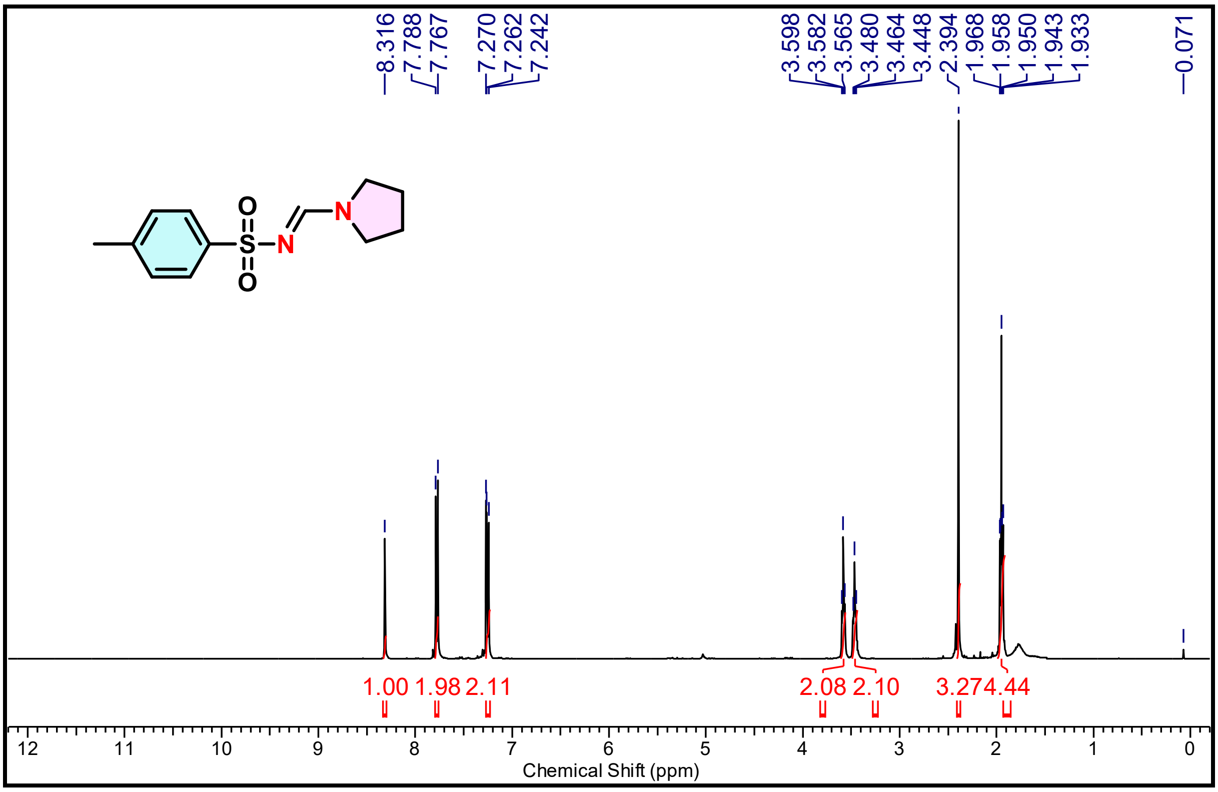
[1]H spectra of **(4d)** (400 MHz, $CDCl_3$)



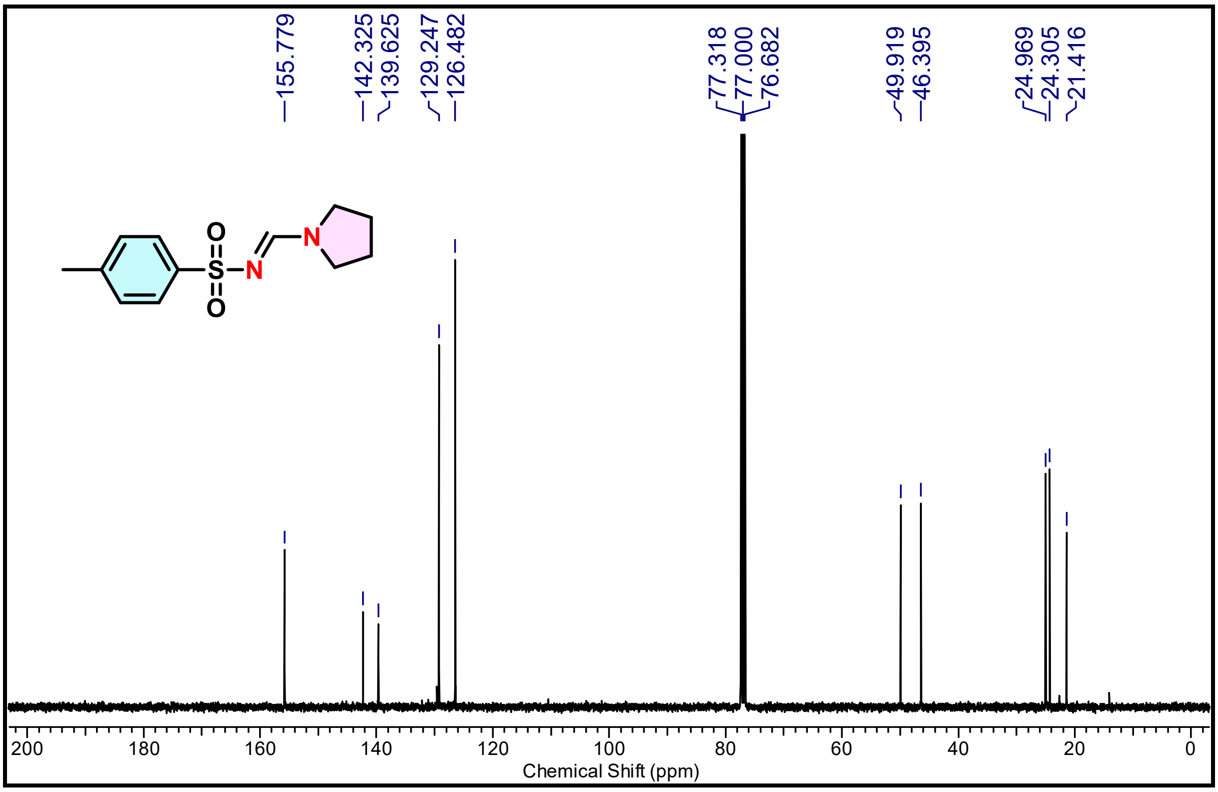
[13]C spectra of **(4d)** (100 MHz, $CDCl_3$)



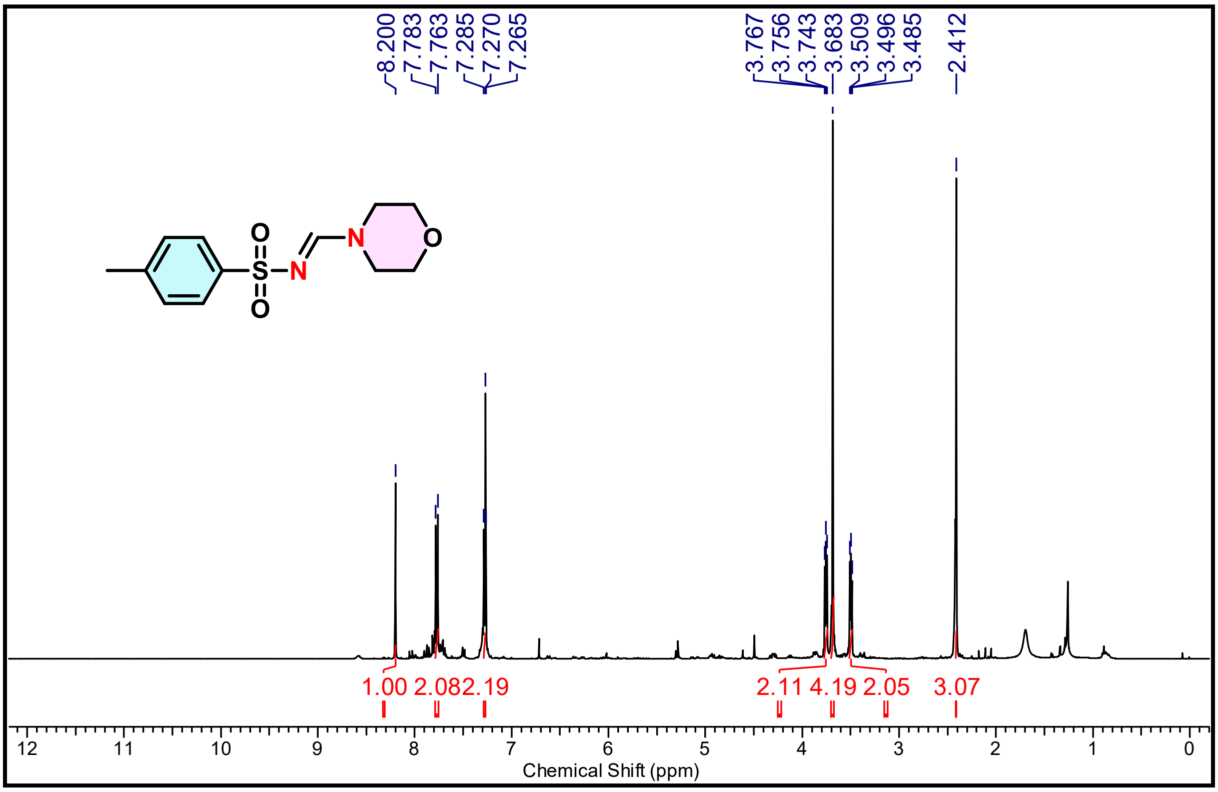
[1]H spectra of **(4e)** (400 MHz, $CDCl_3$)



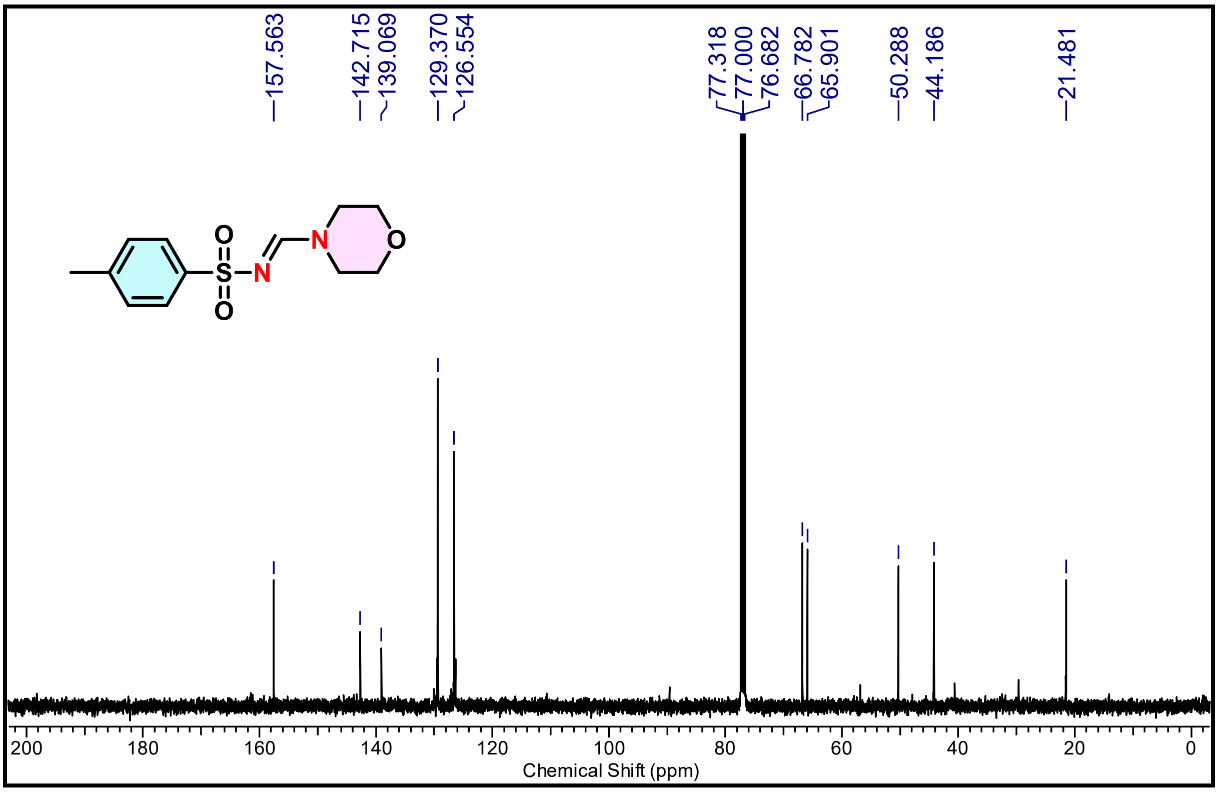
[13]C spectra of **(4e)** (100 MHz, $CDCl_3$)



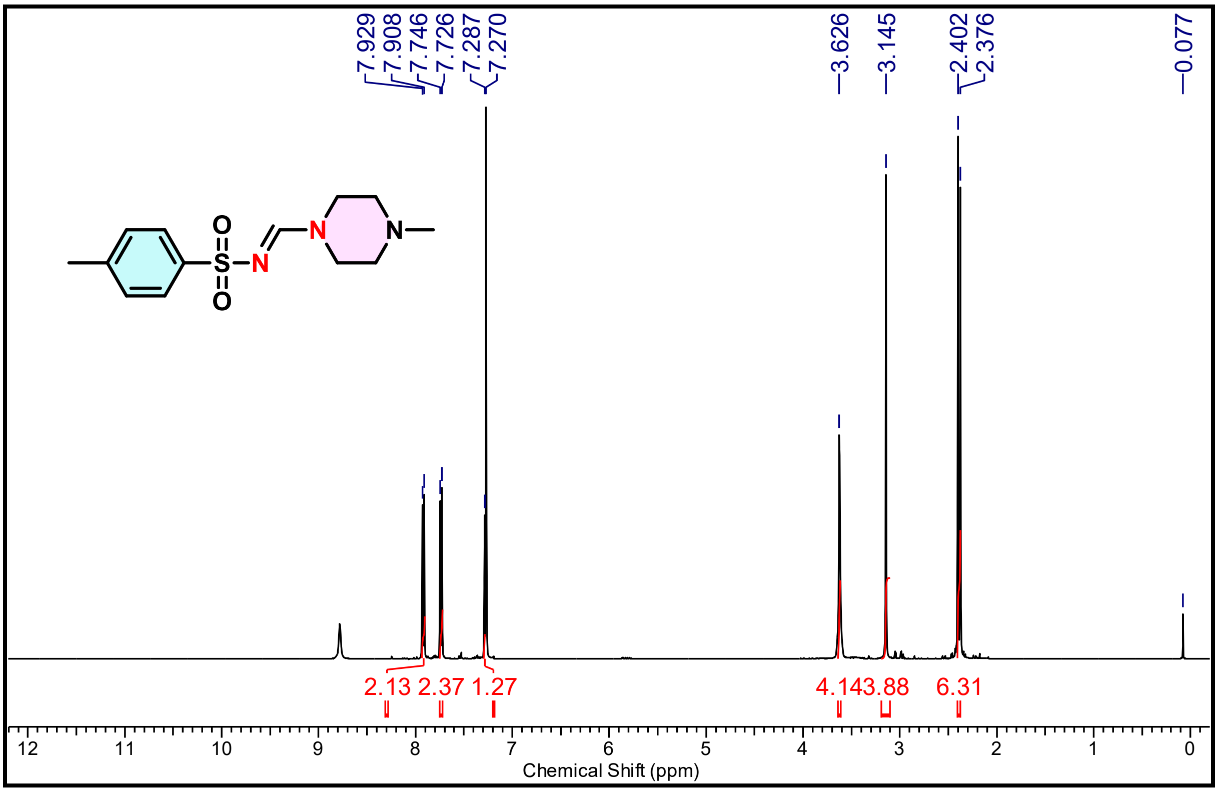
^{1}H spectra of **(4f)** (400 MHz, $CDCl_3$)



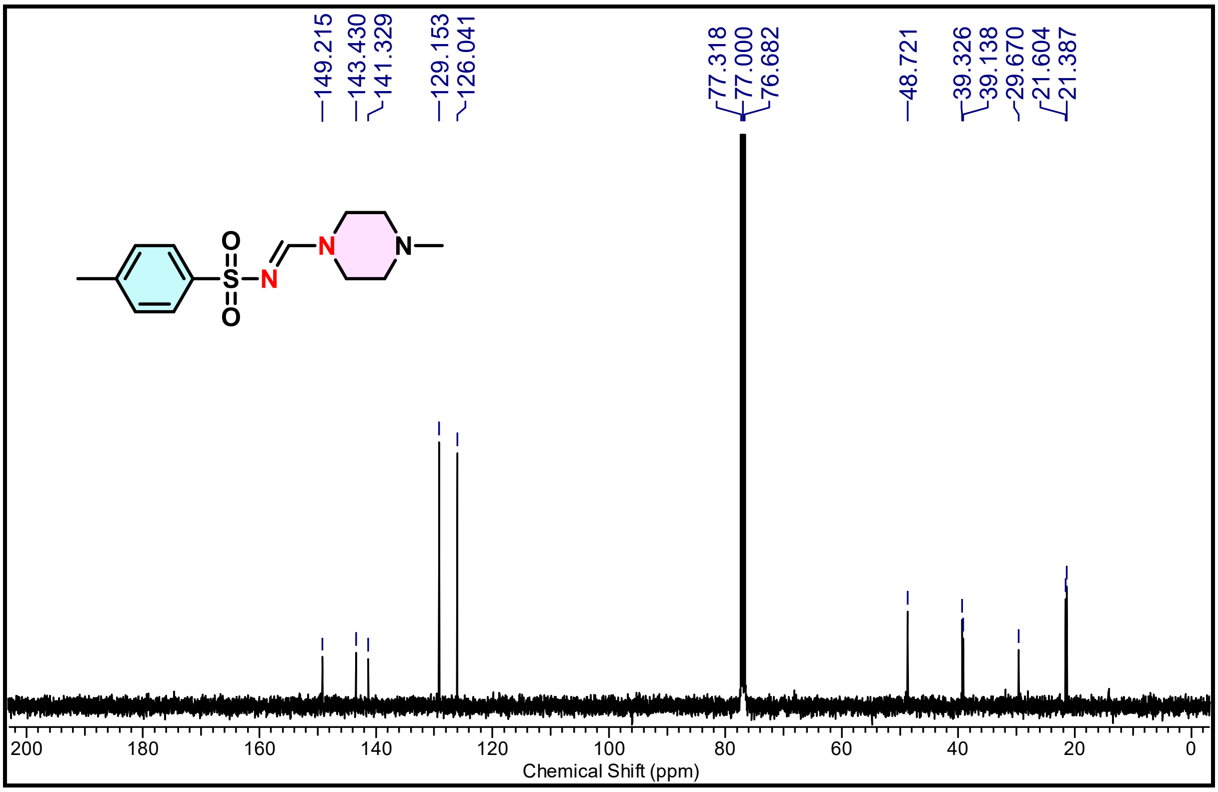
^{13}C spectra of **(4f)** (100 MHz, $CDCl_3$)



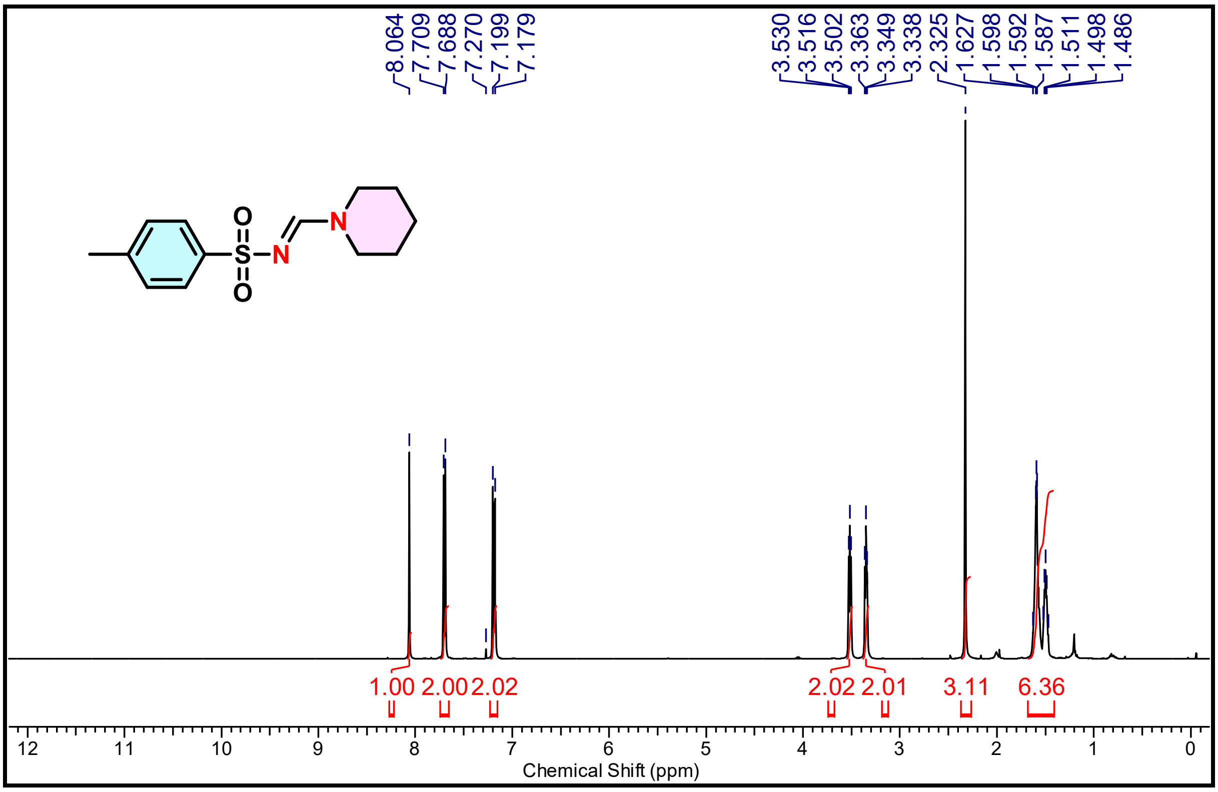
[1]H spectra of **(4g)** (400 MHz, $CDCl_3$)



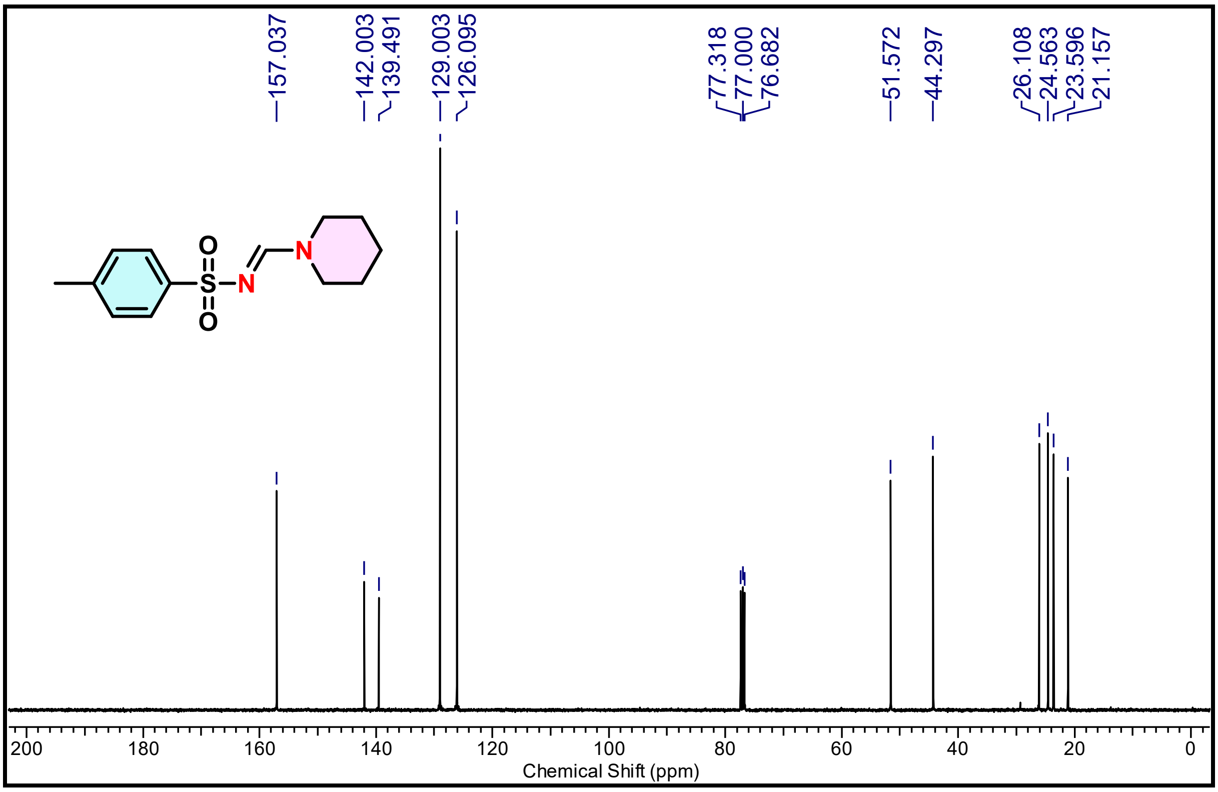
[13]C spectra of **(4g)** (100 MHz, $CDCl_3$)



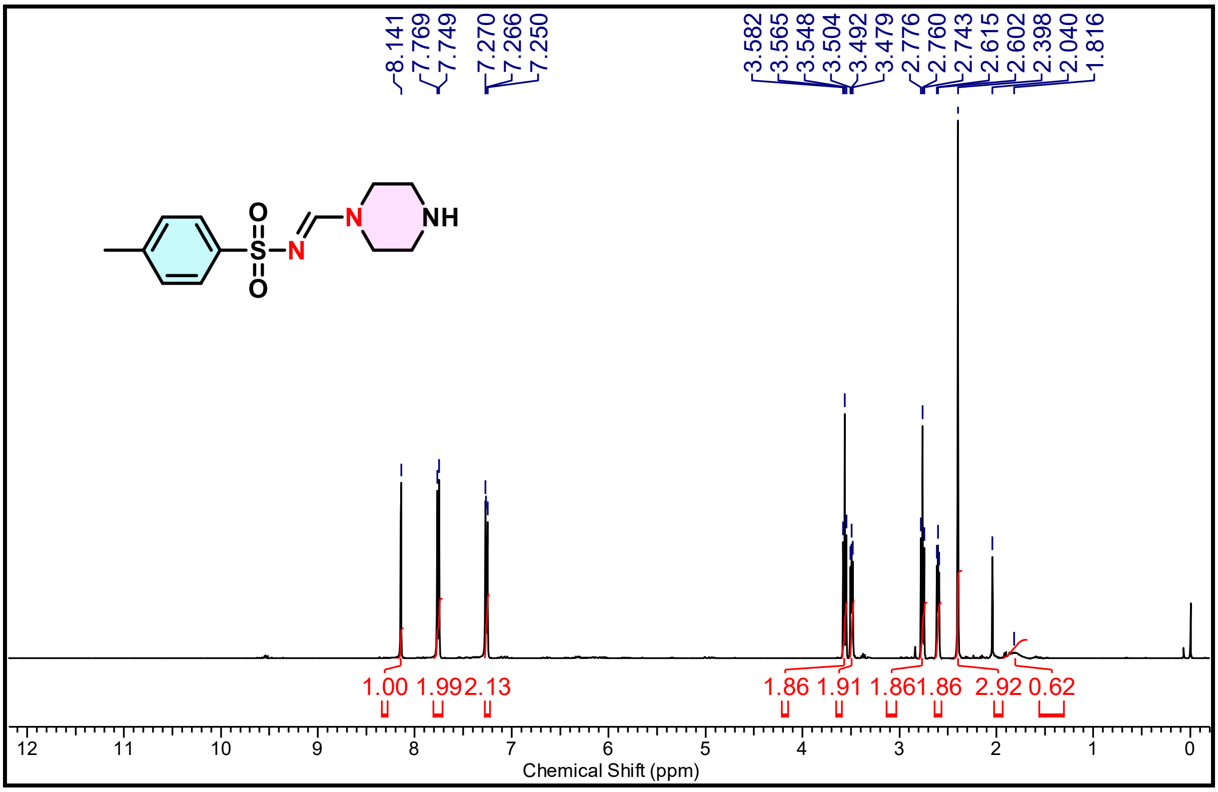
^{1}H spectra of **(4h)** (400 MHz, $CDCl_3$)



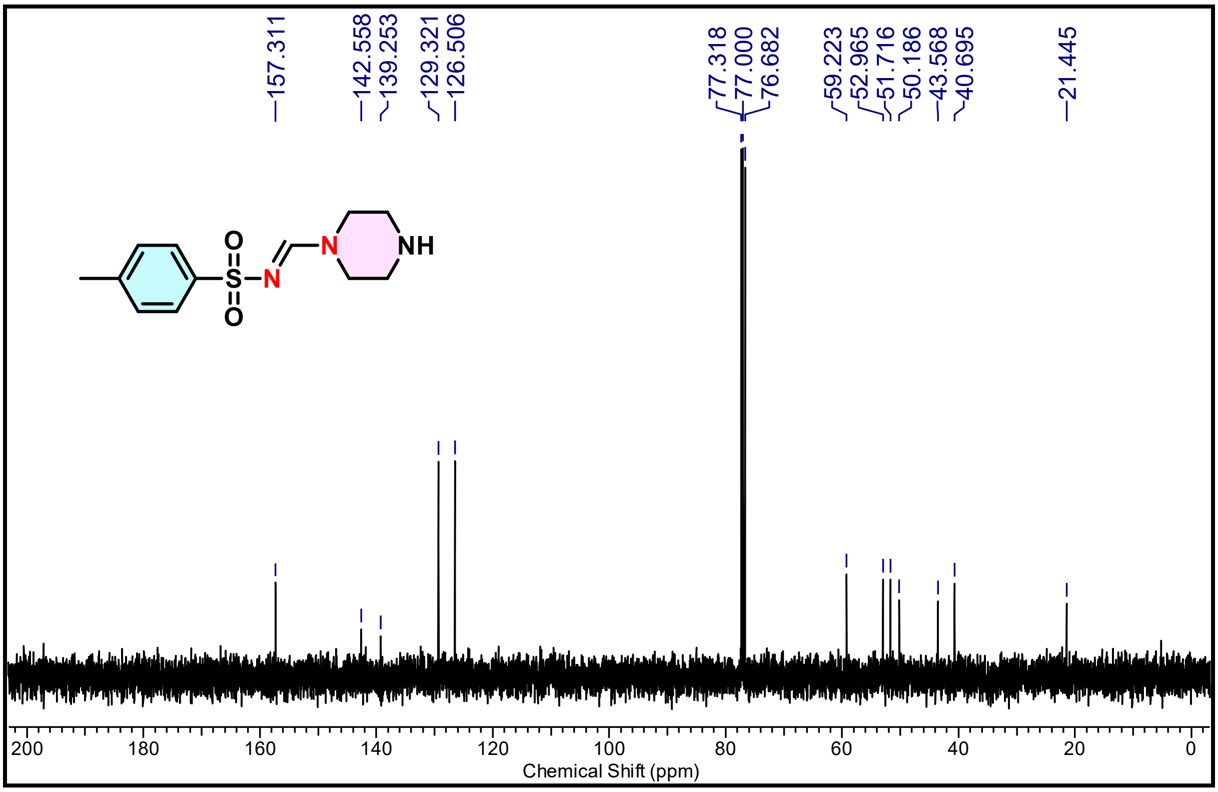
^{13}C spectra of **(4h)** (100 MHz, $CDCl_3$)



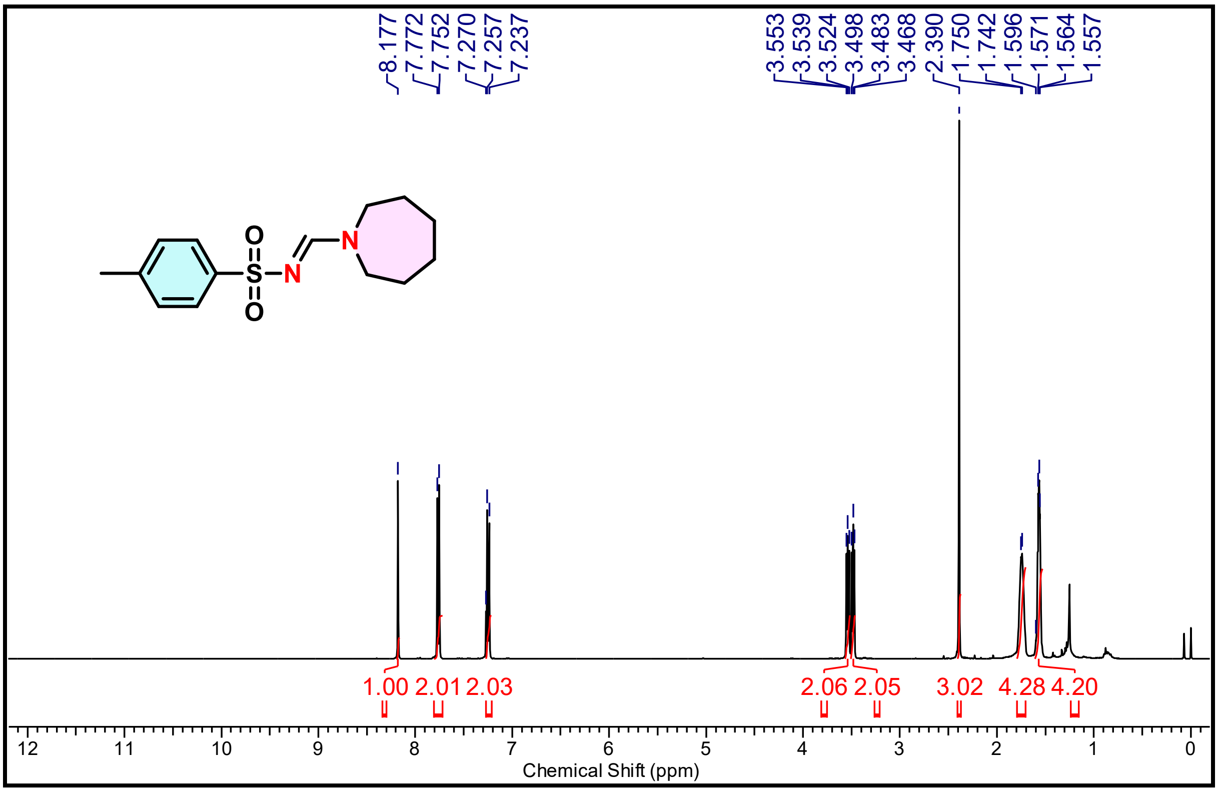
^{1}H spectra of **(4i)** (400 MHz, $CDCl_3$)



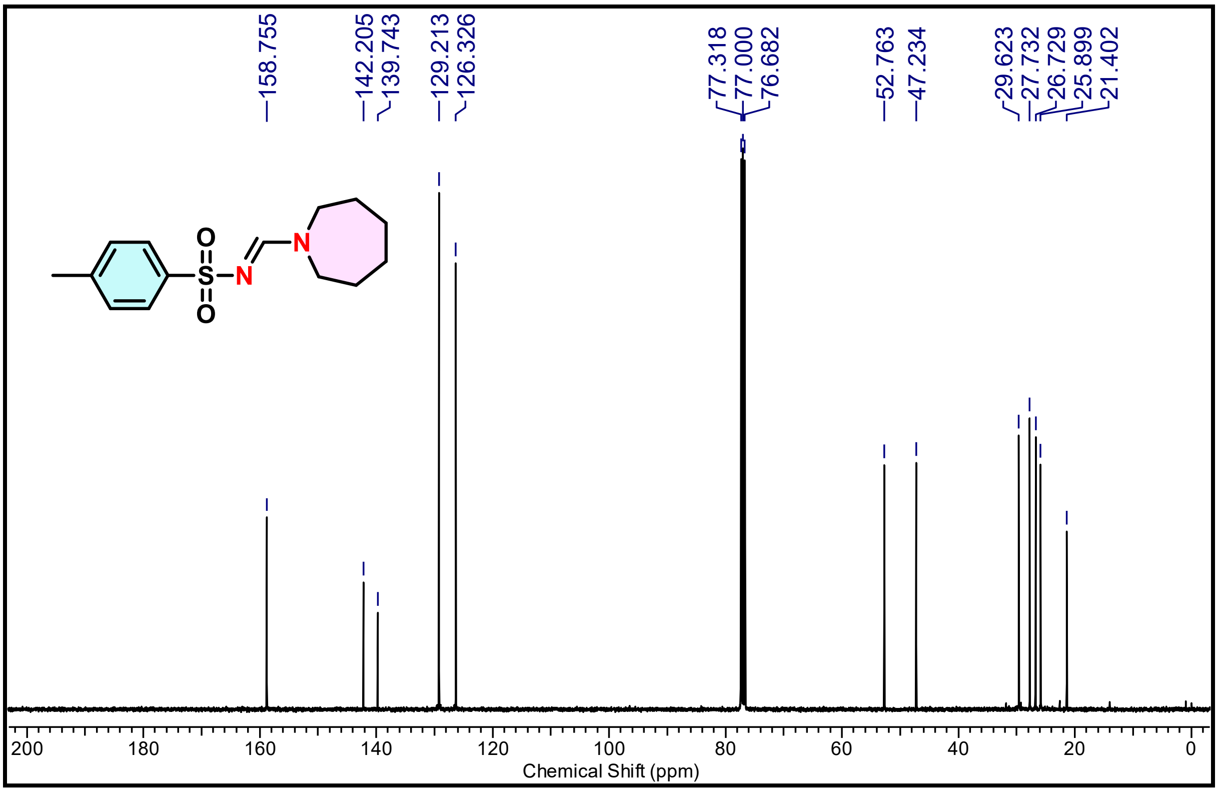
^{13}C spectra of **(4i)** (100 MHz, $CDCl_3$)



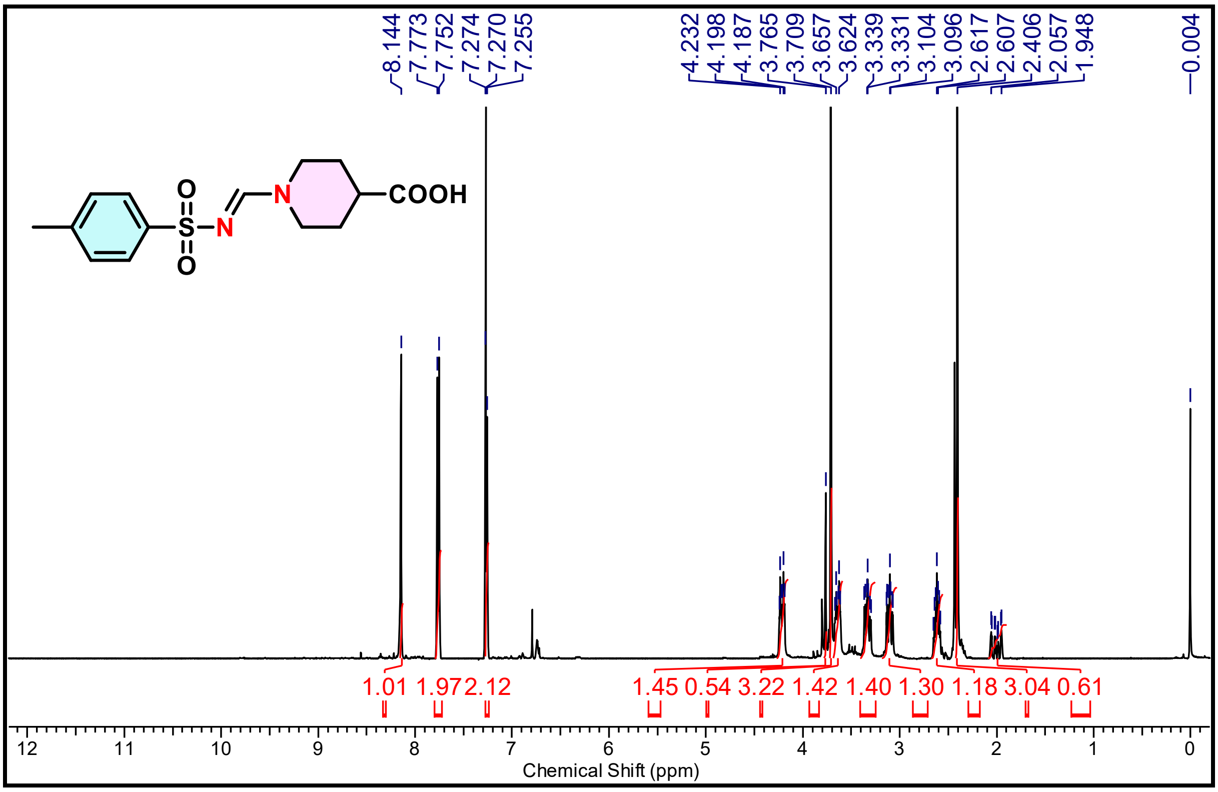
^{1}H spectra of **(4j)** (400 MHz, $CDCl_3$)



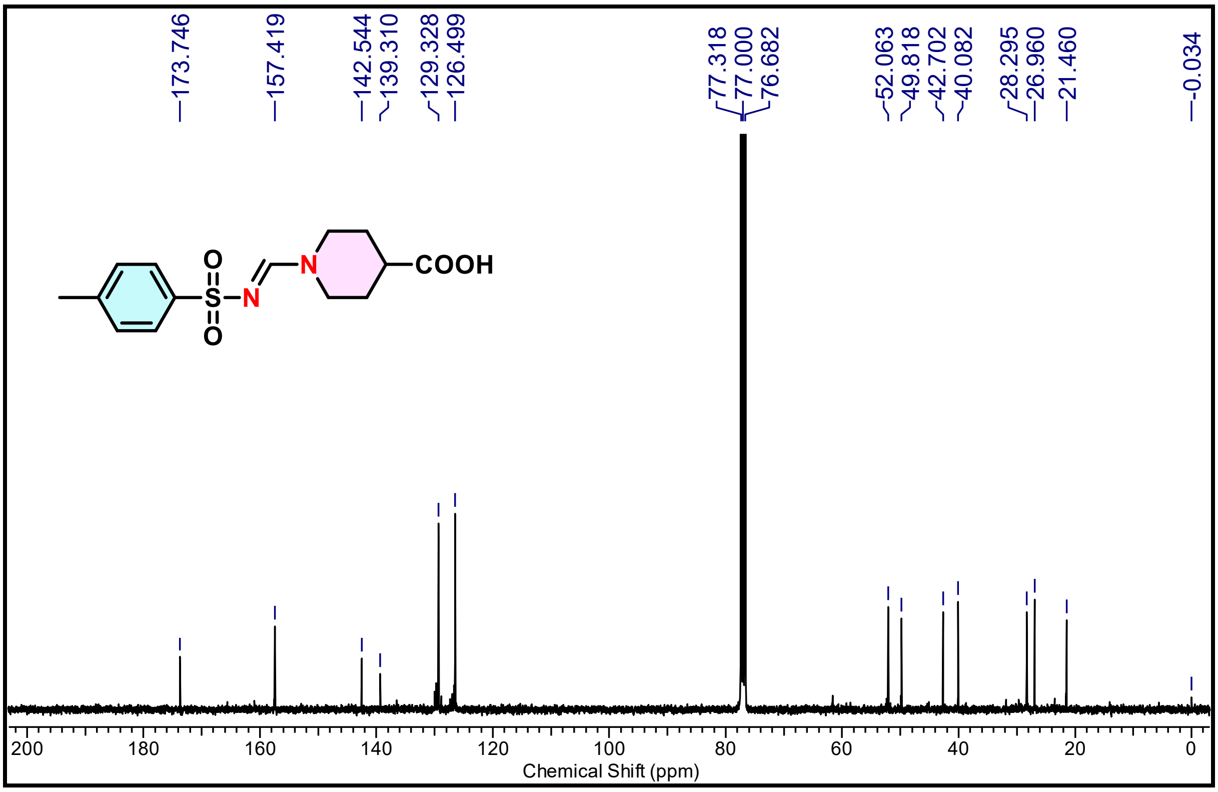
^{13}C spectra of **(4j)** (100 MHz, $CDCl_3$)



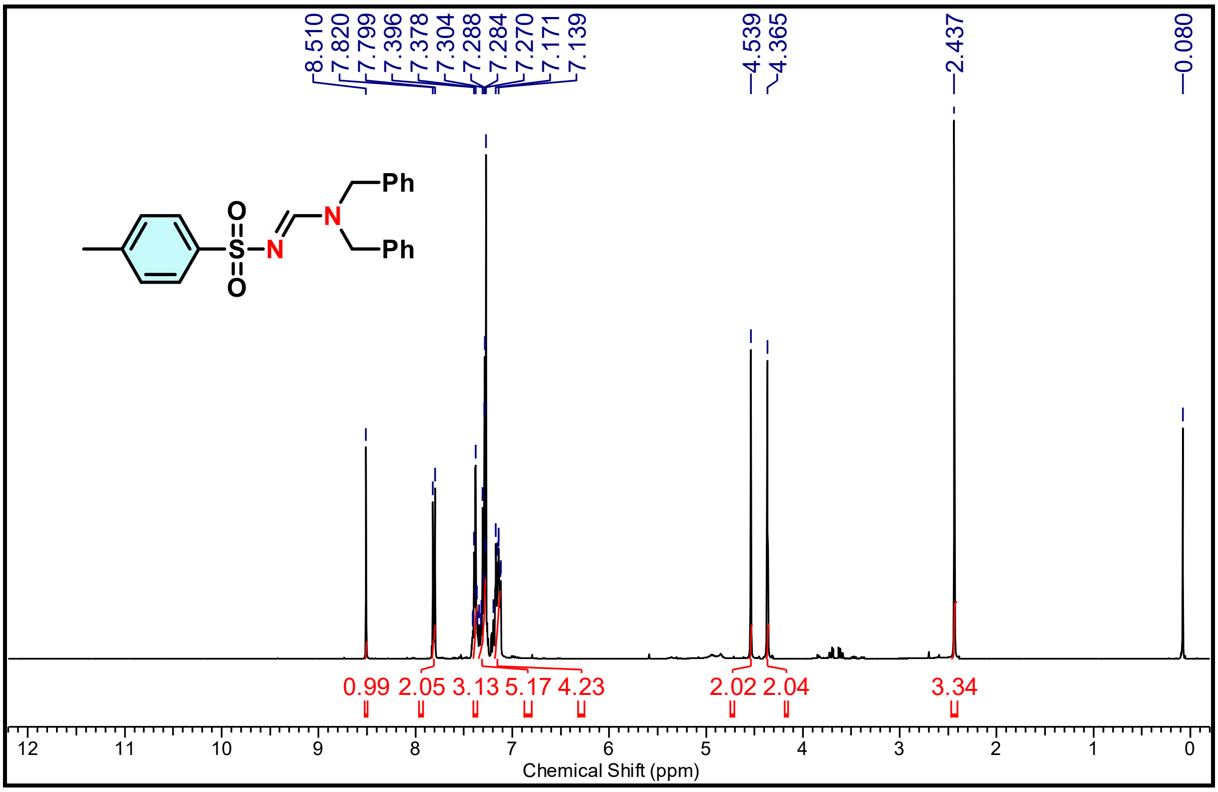
[1]H spectra of **(4k)** (400 MHz, $CDCl_3$)



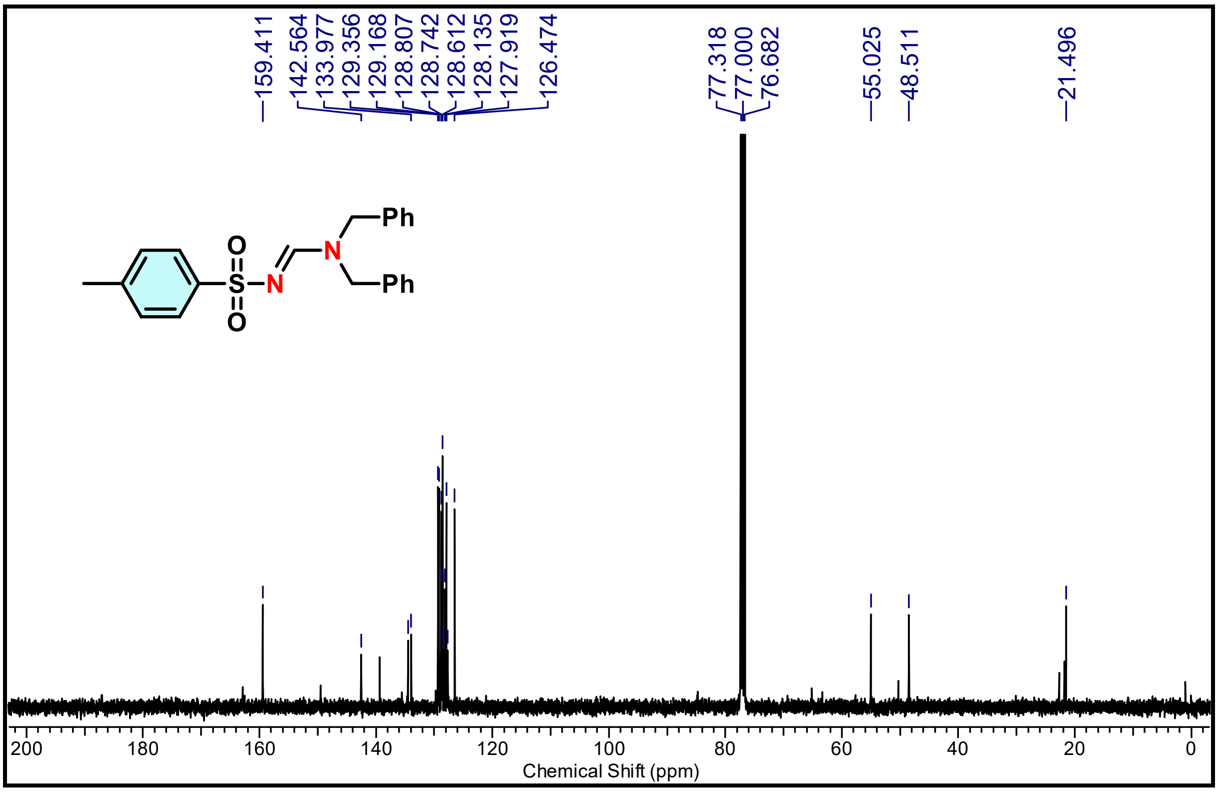
[13]C spectra of **(4k)** (100 MHz, $CDCl_3$)



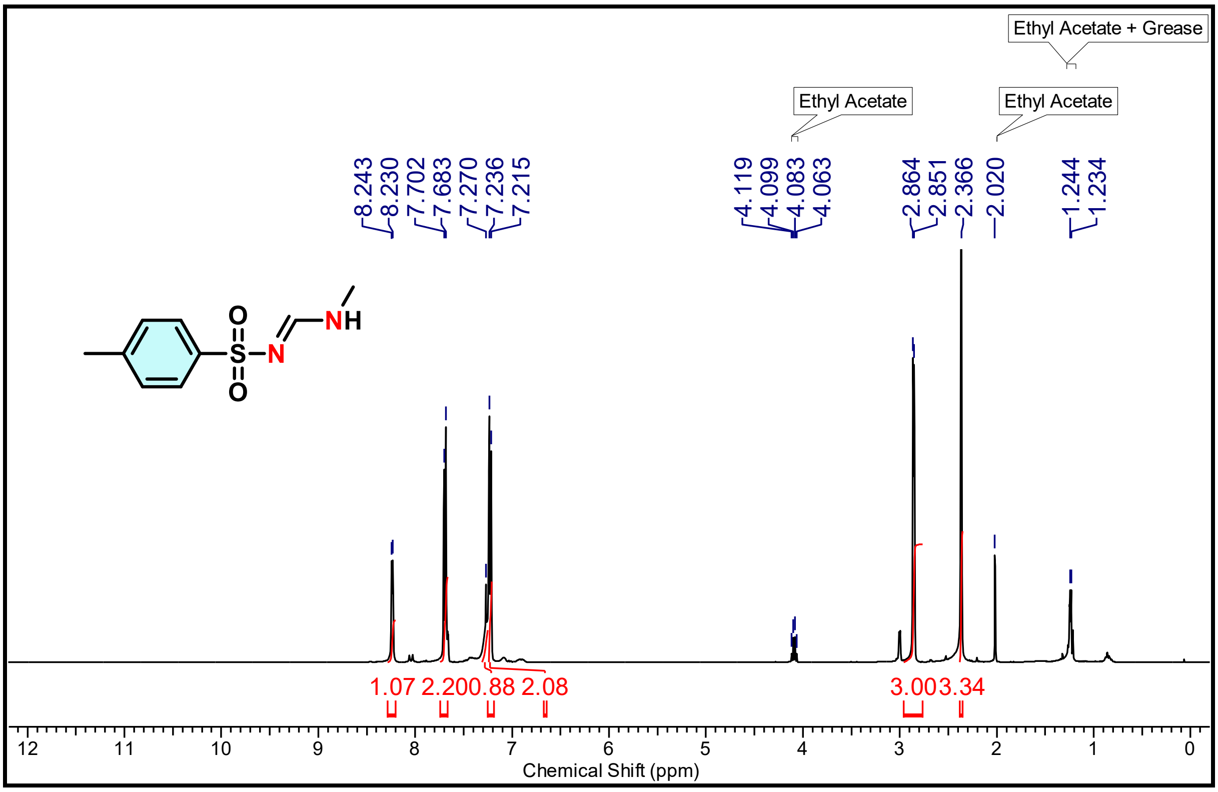
[1]H spectra of **(4l)** (400 MHz, $CDCl_3$)



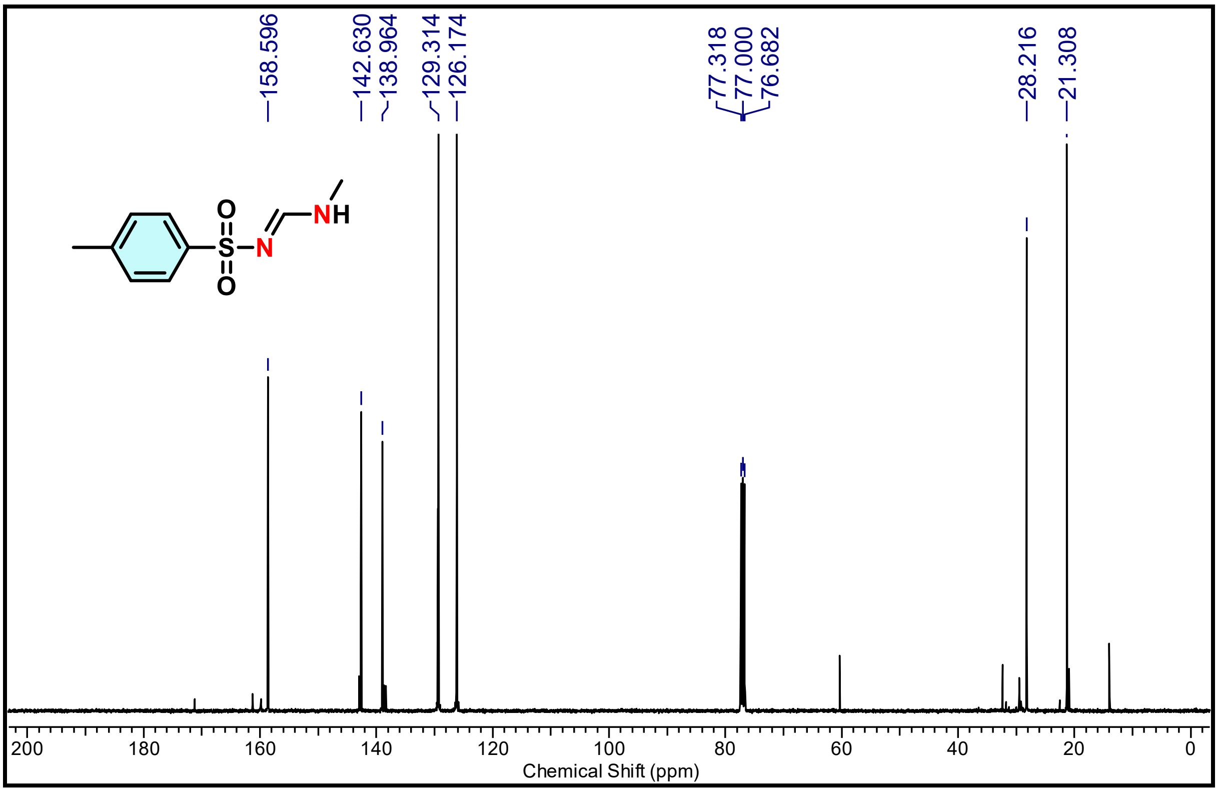
[13]C spectra of **(4l)** (100 MHz, $CDCl_3$)



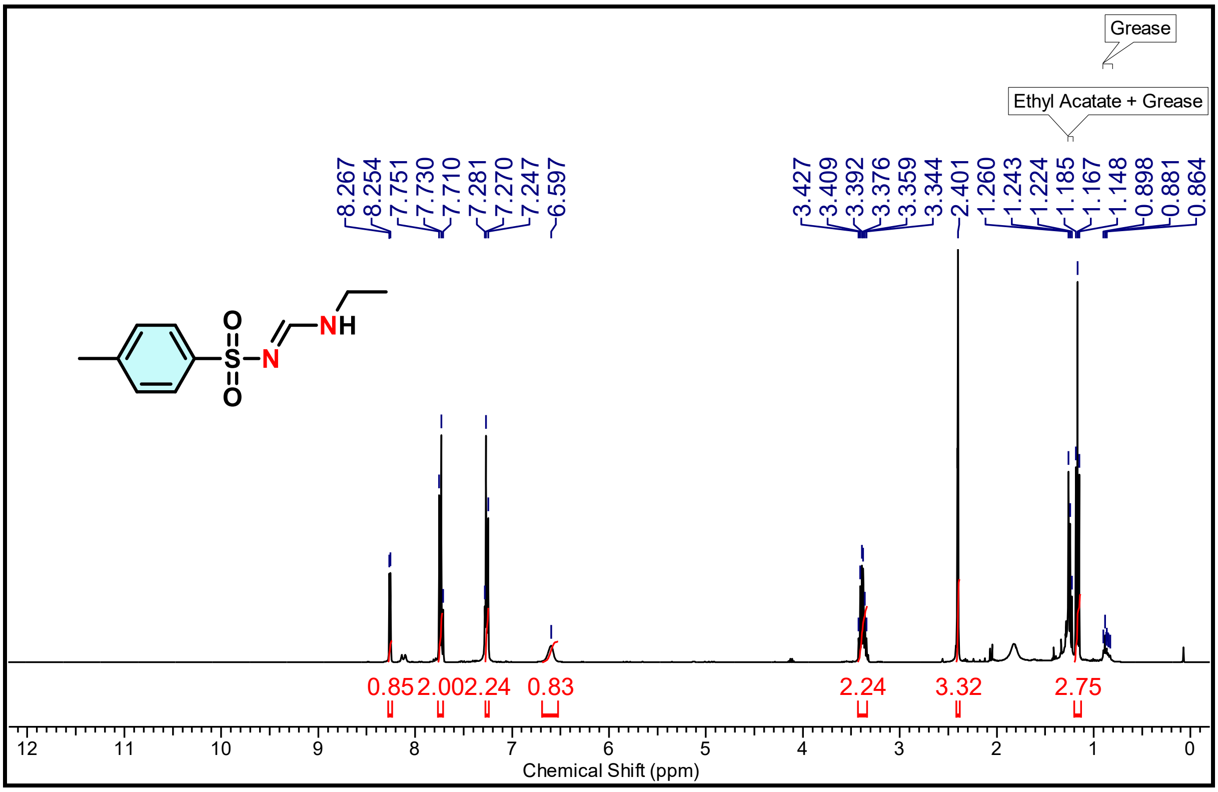
^{1}H spectra of **(4m)** (400 MHz, $CDCl_3$)



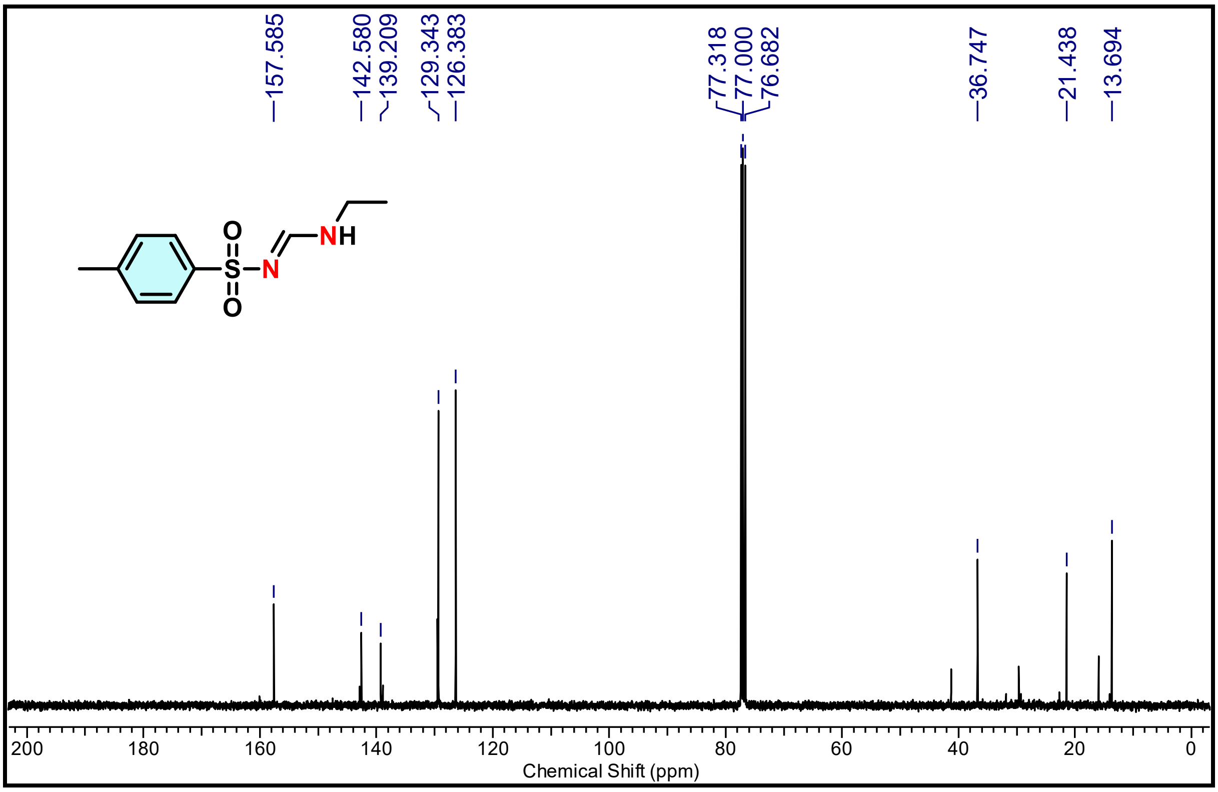
^{13}C spectra of **(4m)** (100 MHz, $CDCl_3$)



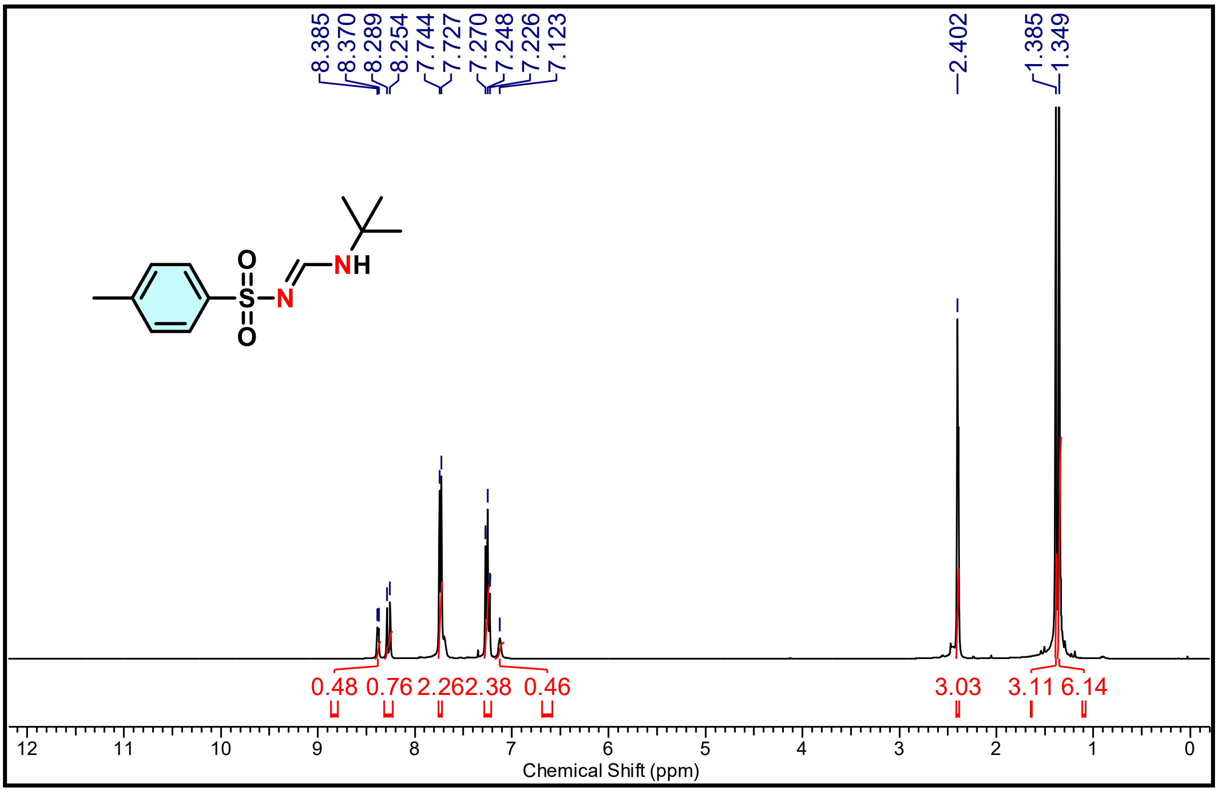
[1]H spectra of **(4n)** (400 MHz, $CDCl_3$)



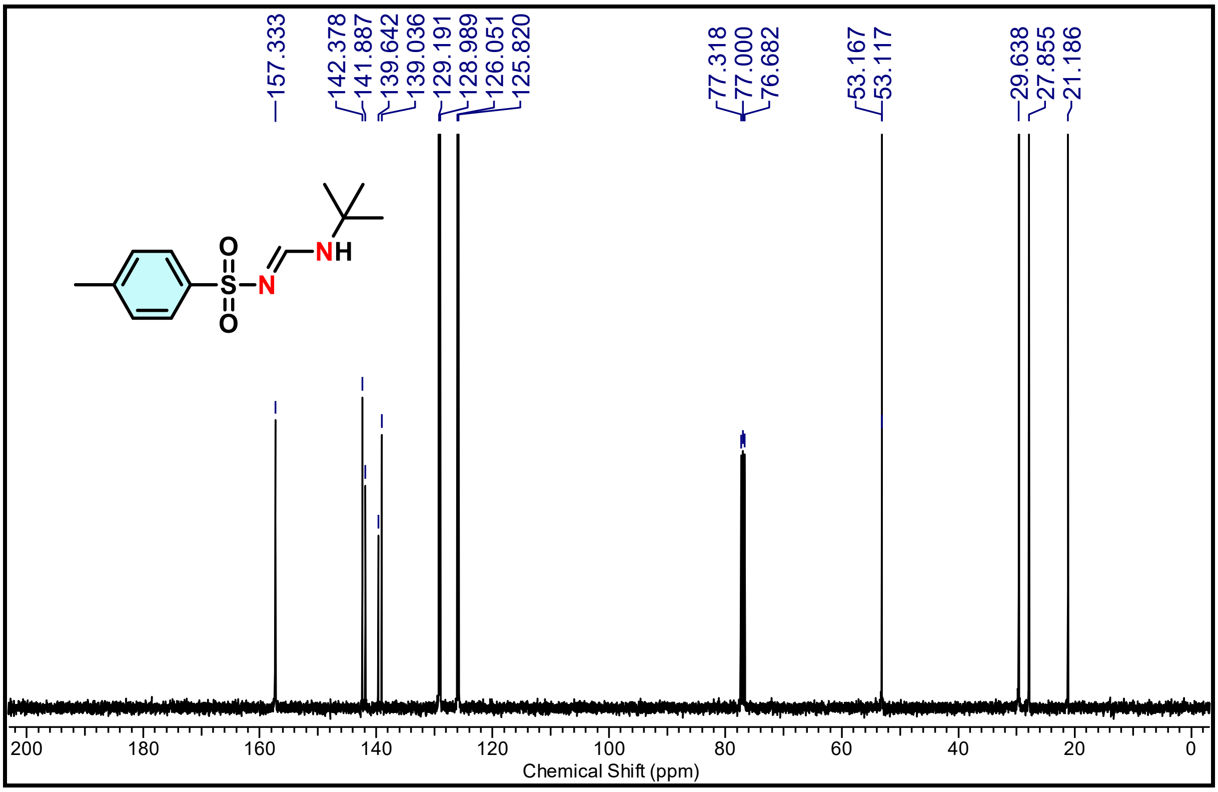
[13]C spectra of **(4n)** (100 MHz, $CDCl_3$)



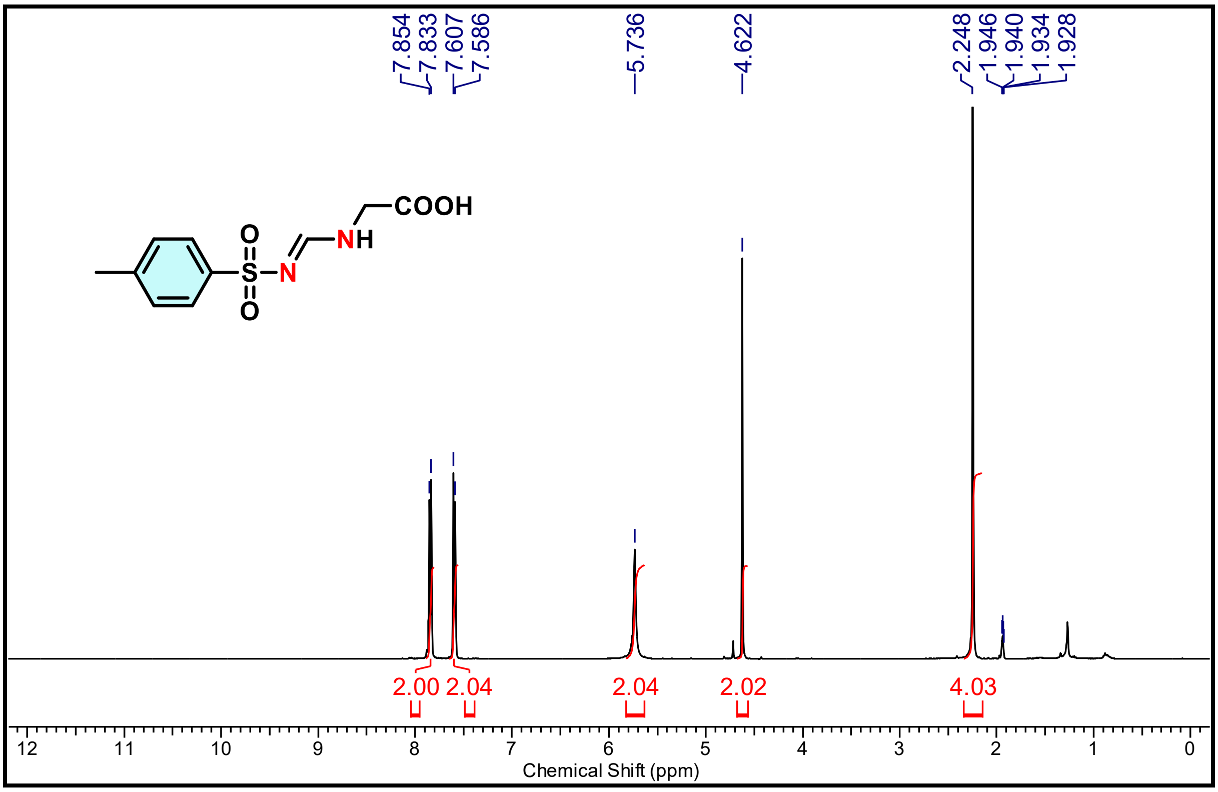
^{1}H spectra of **(4o)** (400 MHz, $CDCl_3$)



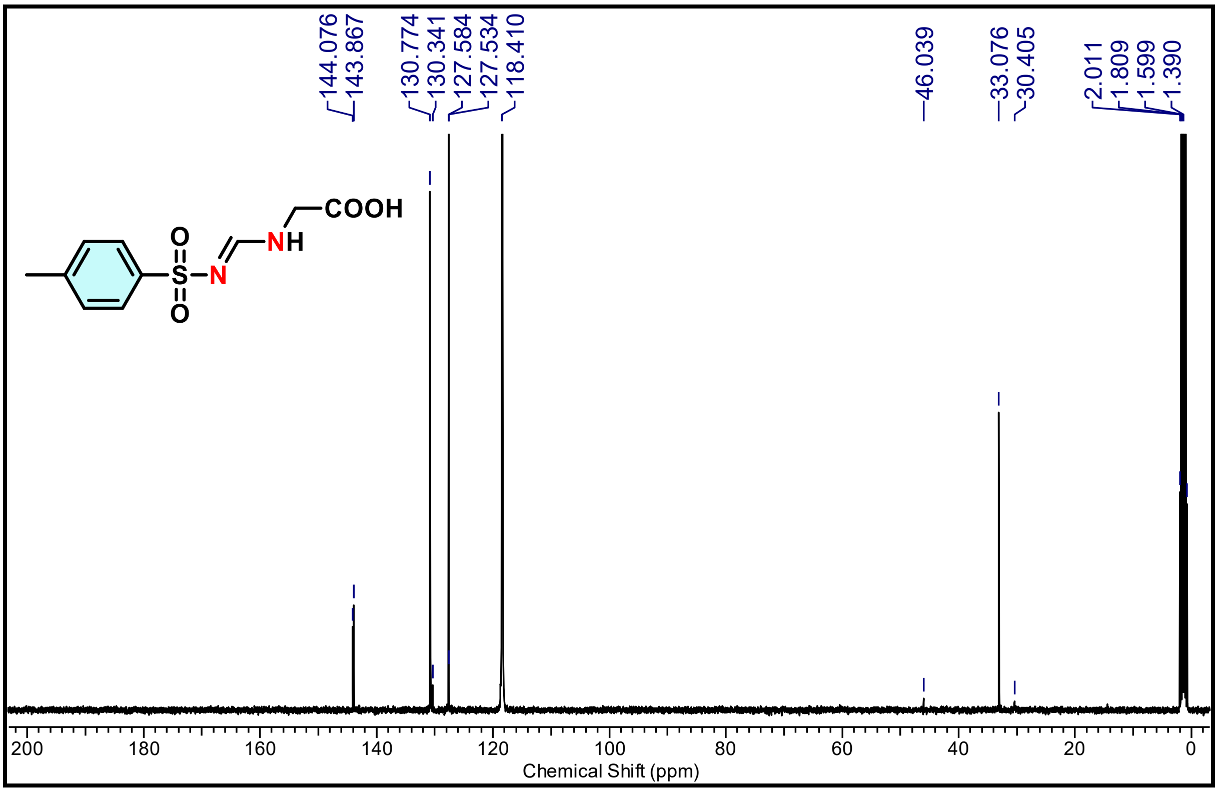
^{13}C spectra of **(4o)** (100 MHz, $CDCl_3$)



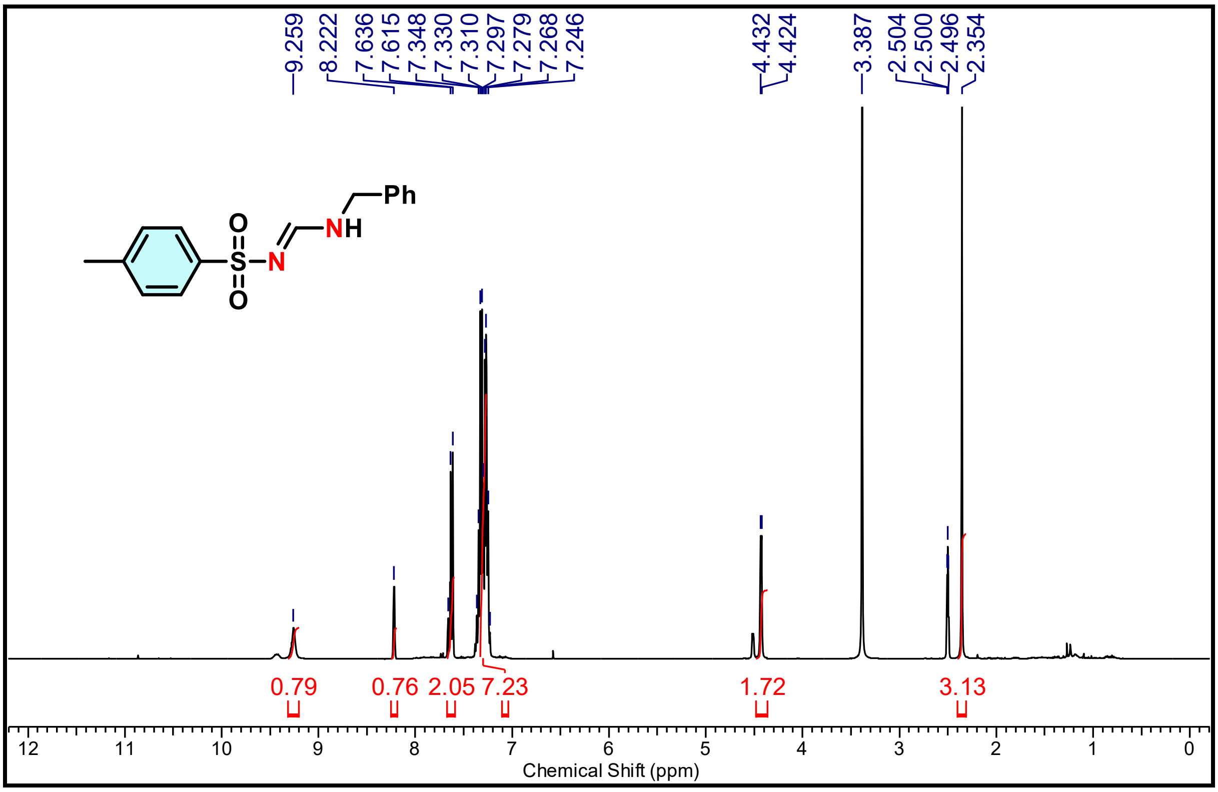
^1H spectra of **(4p)** (400 MHz, CD_3CN)



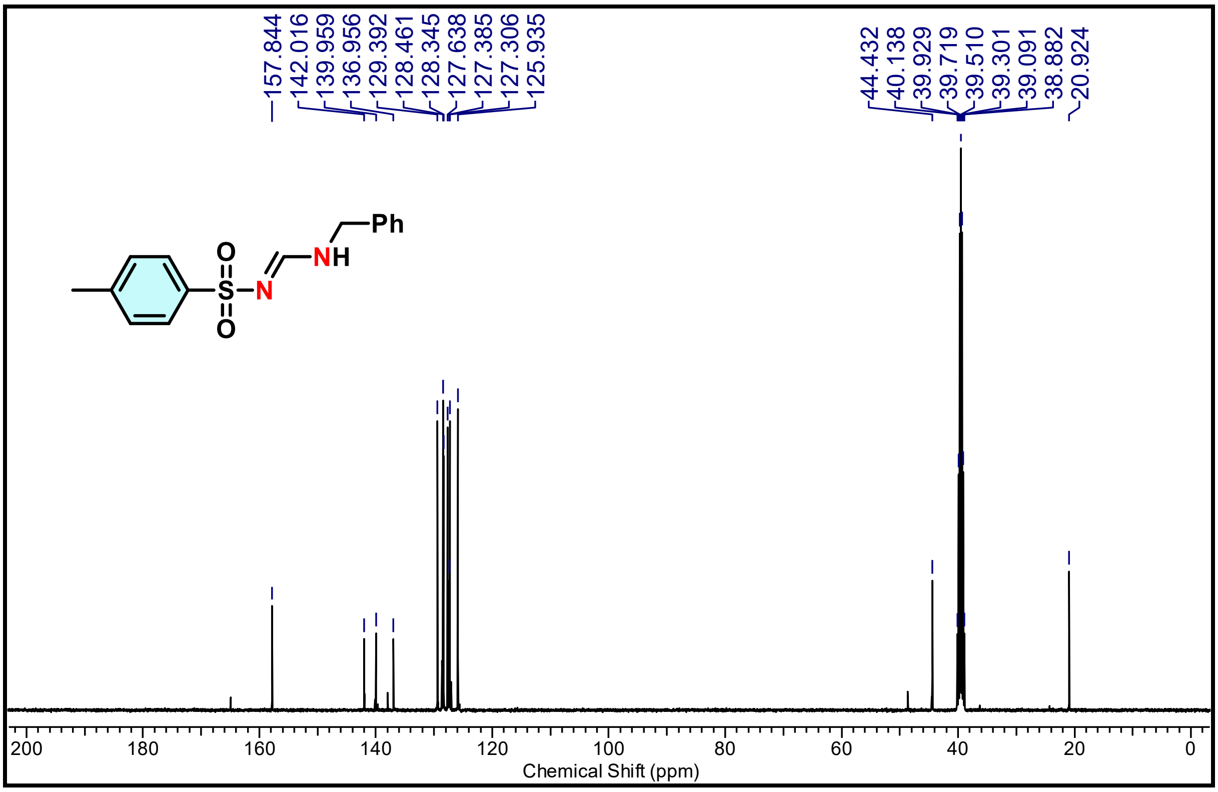
^{13}C spectra of **(4p)** (100 MHz, CD_3CN)



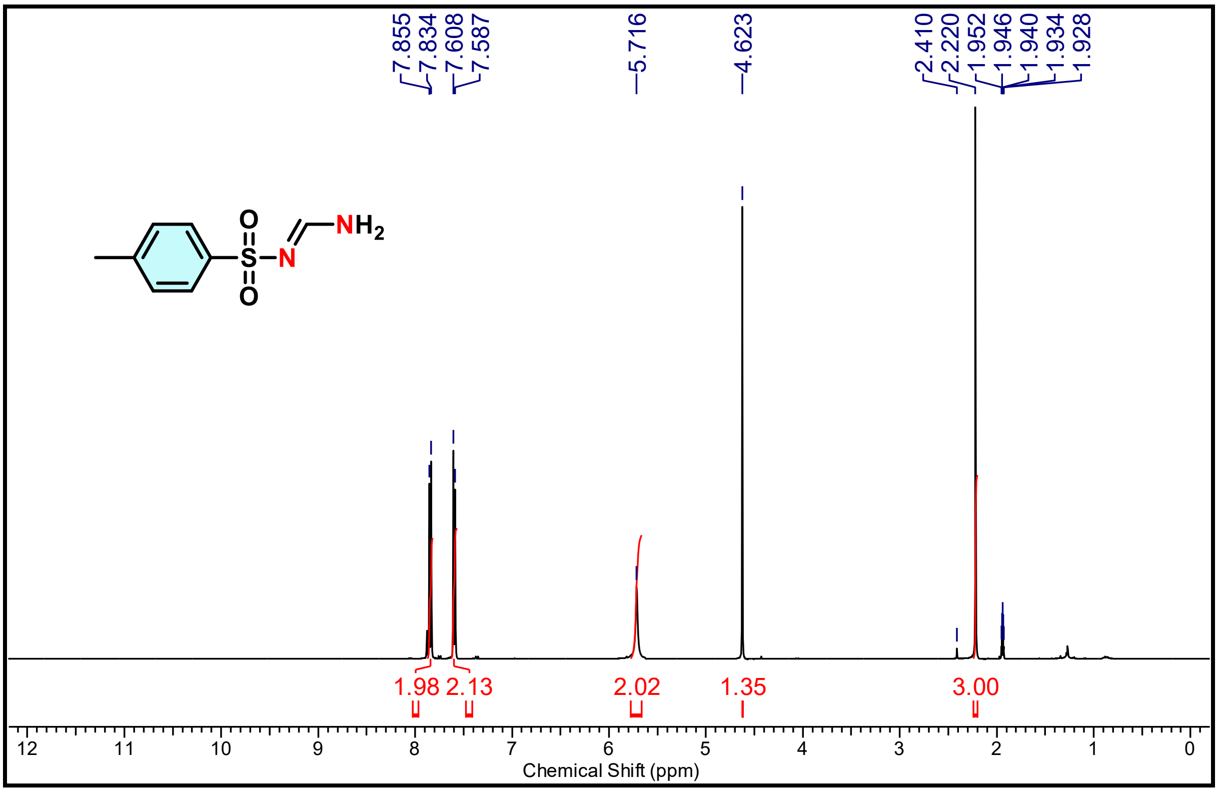
^{1}H spectra of **(4q)** (400 MHz, DMSO-d6)



^{13}C spectra of **(4q)** (100 MHz, DMSO-d6)



[1]H spectra of **(4r)** (400 MHz, CD_3CN)



[13]C spectra of **(4r)** (100 MHz, CD_3CN)