Supporting information

For

Palladium Nanoparticles Catalyzed Aroylation of *NH*-Sulfoximines with Aryl Iodides

Nidhi Sharma and Govindasamy Sekar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai,

Tamilnadu-600 036. India

gsekar@iitm.ac.in

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1. General consideration

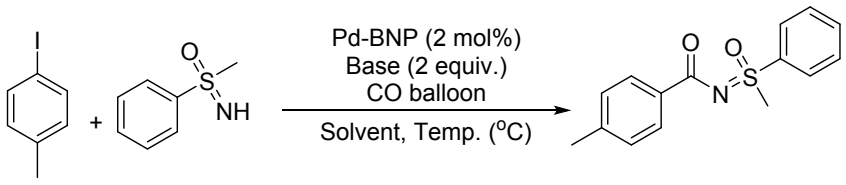
All reactions were carried out in reaction tubes under CO atmosphere. All the solvents used for the reactions were obtained from Fischer Scientific, India Pvt. Ltd. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra and used for column chromatography using hexanes and ethyl acetate mixture as eluent. K_2PdCl_4 (98%) and DABCO were obtained from Sigma-Aldrich and used directly as received. Various aryl iodides and substituted sulfides were purchased from Alfa-aesar and Sigma-Aldrich Company. (±)-BINAM was perchased from Gerchem Pvt. Ltd, Hyderabad, India and used as received. Other chemicals like $NaBH_4$ were purchased from Spectrochem Pvt. Ltd., Mumbai, India and K_2CO_3, Na_2CO_3, KOH were purchased from Fischer Scientific, India Pvt. Ltd. 1,1'-Binaphthyl,-2,2'-bis(diazoniumtetrafluoroborate) was prepared using literature procedure.[1] *N*H-sulfoximines were prepared from commercially available sulphides using literature reported procedure.[2] Nano pure water was obtained from Milli-Q Integral Water Purification System. All the reactions were carried out in temperature controlled IKA magnetic stirrers. ^{1}H, ^{13C} and ^{19}F NMR spectra were recorded on a Bruker 400 and 500 instruments. ^{1}H NMR spectra were reported relative to Me_4Si (δ 0.0 ppm) or residual $CDCl_3$ (δ 7.26 ppm) and DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm) and DMSO-d_6 (δ 39.51 ppm). ^{19}FNMR were reported relative to C_6F_6 (δ -164.9 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and were reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Optima 5300 DV was used to find the Pd content of the nanoparticles. Samples were prepared by digesting 20 mg of nanoparticles in 2.0 mL of H_2SO_4 using domestic microwave oven for 30 min. and the solutions was made upto 25 mL in standard flask. Pd emissions were detected at 340.458 nm under the flow condition.

HRTEM analysis of samples was performed using a JEM 2010 electron microscope. TEM analysis of the samples was done using carbon coated copper grids (nanoparticles in dichloromethane solutions). The instrument was operated at 200 kV.

2. Experimental conditions

2.1. Optimization of reaction parameters for Pd-BNP catalyzed Aroylation of *N*H-Sulfoximines[a]

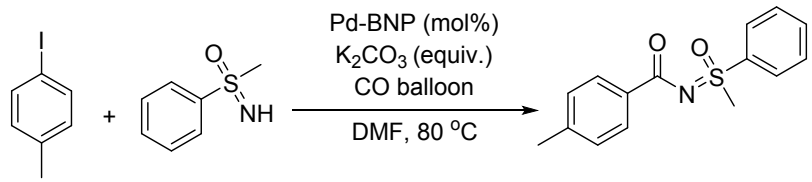


1a **2a** **3a**

Entry	Base	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	NEt_3	PhMe	110	36	39
2	KOH	PhMe	110	48	NR
3	NaOH	PhMe	110	48	NR
4	DBU	PhMe	110	36	45
5	NaH	PhMe	110	24	trace
6	NaO^tBu	PhMe	110	24	21
7	K_2CO_3	PhMe	110	24	92
8	K_2CO_3	PhMe	100	48	60
9	K_2CO_3	1,4-Dioxane	100	15	45
10	K_2CO_3	Xylene	100	38	54
11	K_2CO_3	DMF	100	7	89
12	K_2CO_3	DMF	80	7	91
13	K_2CO_3	DMF	60	18	67

[a]Reaction conditions: 0.5 mmol of **1a**, 1.0 mmol of **2a** and solvent (3 mL) was used.
[b]Isolated yield

2.2. Quantitative optimization of reaction parameters Aroylation of *N*H-Sulfoximines[a]



1a **2a** **3a**

Entry	**2a** (equiv.)	K_2CO_3 (equiv.)	Pd-BNP (mol%)	Time (h)	Yield (%)[b]
1	2.0	2.0	2.0	7	91
2	2.0	1.5	2.0	7	90
3	2.0	1.0	2.0	8	92
4	2.0	0.5	2.0	24	59
5	2.0	1.0	1.5	8	93
6	2.0	1.0	1.0	10	93
7	2.0	1.0	0.5	12	72
8	1.5	1.0	1.0	10	94
9	1.2	1.0	1.0	14	77
10	1.0	1.0	1.0	19	76

[a]Reaction conditions: 0.5 mmol of **1a** and DMF (1 mL) was used; [b]Isolated yield

2.3. Typical experimental procedure for Aroylaion of *NH*-Sulfoximines

Aryl iodide (0.5 mmol), *NH*-sulfoximine (0.75 mmol), Pd-BNP catalyst (5.3 mg, 1 mol%) and K_2CO_3 (69 mg, 1 equiv.) was taken in an oven dried reaction tube equipped with magnetic pellet and capped with septum. The reaction tube was evacuated and DMF (1 mL) was added. Reaction tube was again evacuated and refilled with CO using balloon and stirred at 80 °C until completion of the reaction and monitored by TLC. After completion of the reaction, the reaction mixture was then allowed to cool to room temperature and extracted with ethyl acetate (3 × 10 mL), followed by brine solution. Then the organic phase was dried over Na_2SO_4 and concentrated in vacuum. The resulting reaction mixture was purified by column chromatography on silica gel (hexanes: ethyl acetate) to get *N*-Aroylated sulfoximine product **3**.

3. Experimental procedure for recovery of the Pd-BNP catalyst

For recyclability of Pd-BNP, the reaction was repeated with 4-iodotoluene **1a** as substrate in 3.0 mmol scale retaining the same conditions such as *S*-methyl-*S*-phenyl-*N*H-sulfoximine **2a** (1.5 equiv.), K_2CO_3 (1 equiv.), and 3 mL DMF under CO atmosphere (CO balloon) at 80 ^oC, except using the recovered catalyst. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Ethyl acetate (5 mL) was added and centrifuged. The liquid then decanted to a 50 mL conical flask. Again ethyl acetate (5 mL) was added and centrifuged and decanted to the same conical flask, this procedure was repeated upto two to three times. After that the catalyst was washed with nano pure water (5 mL) and ethanol (5 mL). Finally, the resulting solid particles (Pd-BNP) dried under vacuum. The dried catalyst was reused for further catalytic cycle. The collected liquid was extracted with ethyl acetate (3 × 10 mL), followed by brine solution. Then the organic phase was dried over Na_2SO_4 and concentrated in vacuum. The resulting reaction mixture was purified by column chromatography on silica gel (hexanes: ethyl acetate) to get *N*-Aroylated sulfoximine product **3a**.

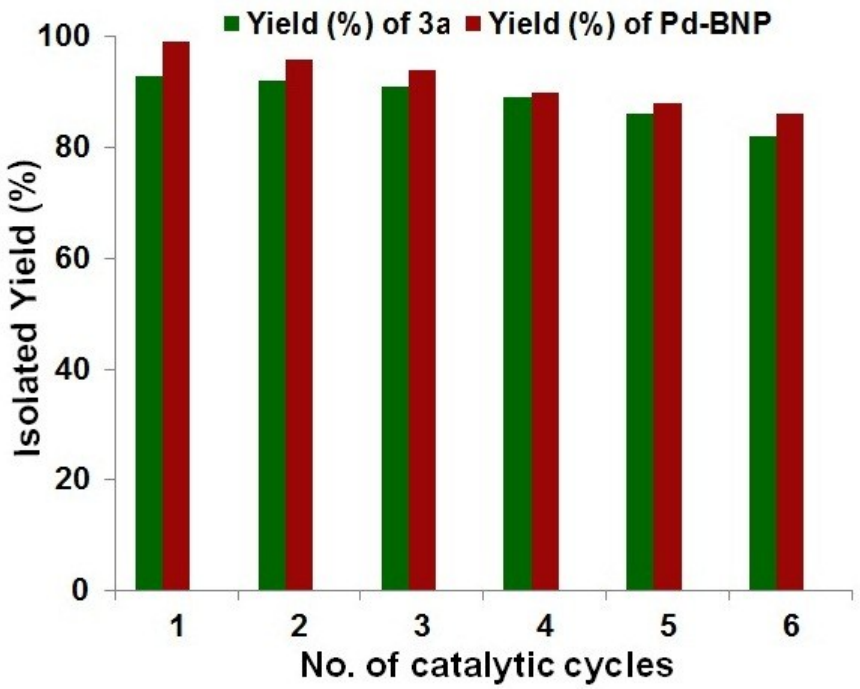


Figure1. Recycling of the Pd-BNP catalyst

4. HRTEM images of Pd-BNP catalyst:

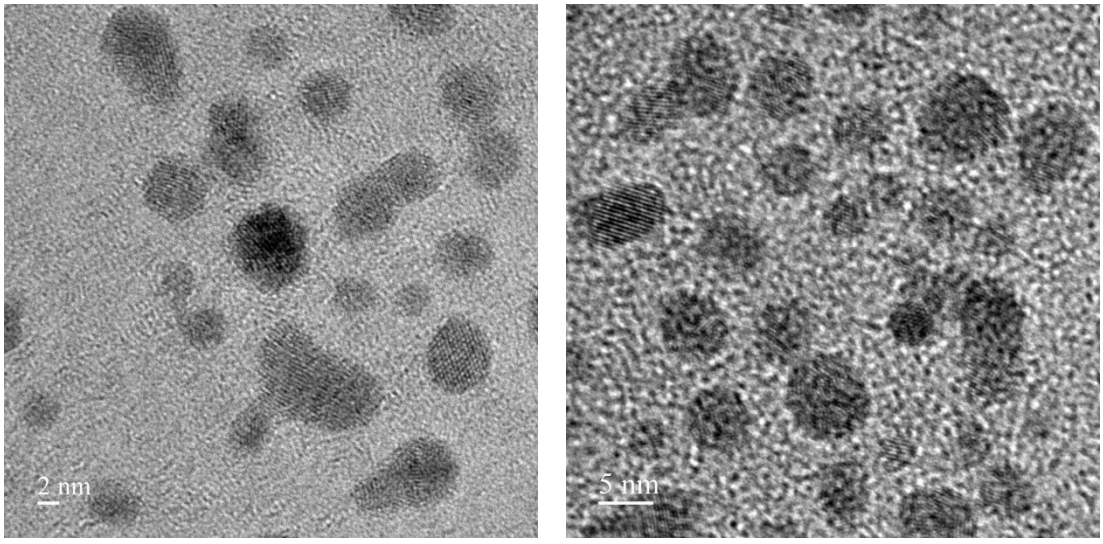


Figure 2. HR-TEM images of Pd-BNP catalyst before the catalytic cycle

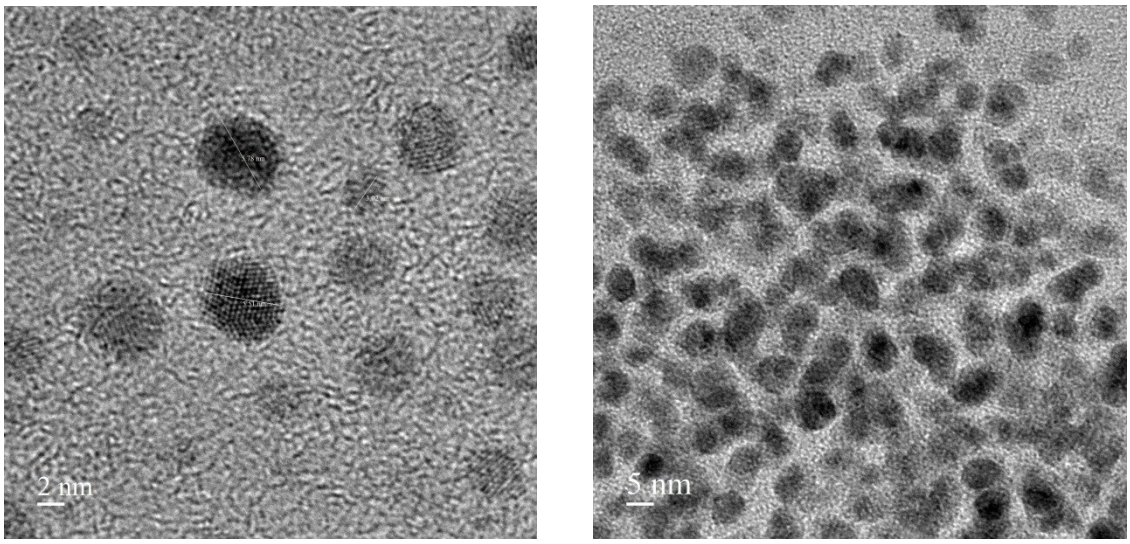


Figure 3: HR-TEM images of Pd-BNP catalyst after the sixth catalytic cycle

5. Mercury Poisoning Test

Mercury poisoning test was also conducted to support that the *N*-aroylation reaction of *NH*-sulfoximines were catalyzed by Pd-BNP catalyst not by the leached Pd. It is known that the reactions catalyzed by noble metals were inhibited by mercury through amalgamation.

First Pd-BNP catalyst (10.64 mg, 1 mol%) and Hg (8.0 g, 40 mmol, 30 equiv.) in 3 mL of DMF was stirred for 2 hours at room temperature. 4-Iodotoluene **1a** (218 mg, 1.0 mmol, 1.0 equiv.)), *S*-methyl-*S*-phenyl-sulfoximine **2a** (232.83 mg, 1.5 mmol, 1.5 equiv.) were then added to the reaction tube. Reaction tube was was evacuated and refilled with CO using balloon and stirred at 80 ^{o}C. After 10 hours, the reaction mixture was allowed to cool to room temperature. Complete inhibition of the reaction was observed and even trace amount of product **3a** formation was not observed.

These results suggested that Pd-BNP catalyst is heterogeneous in nature.

6. References:

1) M. Barbero, S. Bazzi, S. Cadamuro, S. Dughera, C. Magistris, P. Venturello, *Synlett* 2010, 1803.
2) M. R. Yadav, R. K. Rit, , A. K. Sahoo, *Chem. - Eur. J.* 2012, **18**, 5541.
3) D. Ganapathy, G. Sekar, *Catal. Commun.* 2013, **39**, 50.

7. ^{1}H ,^{13}C and ^{19}F spectra for all compounds

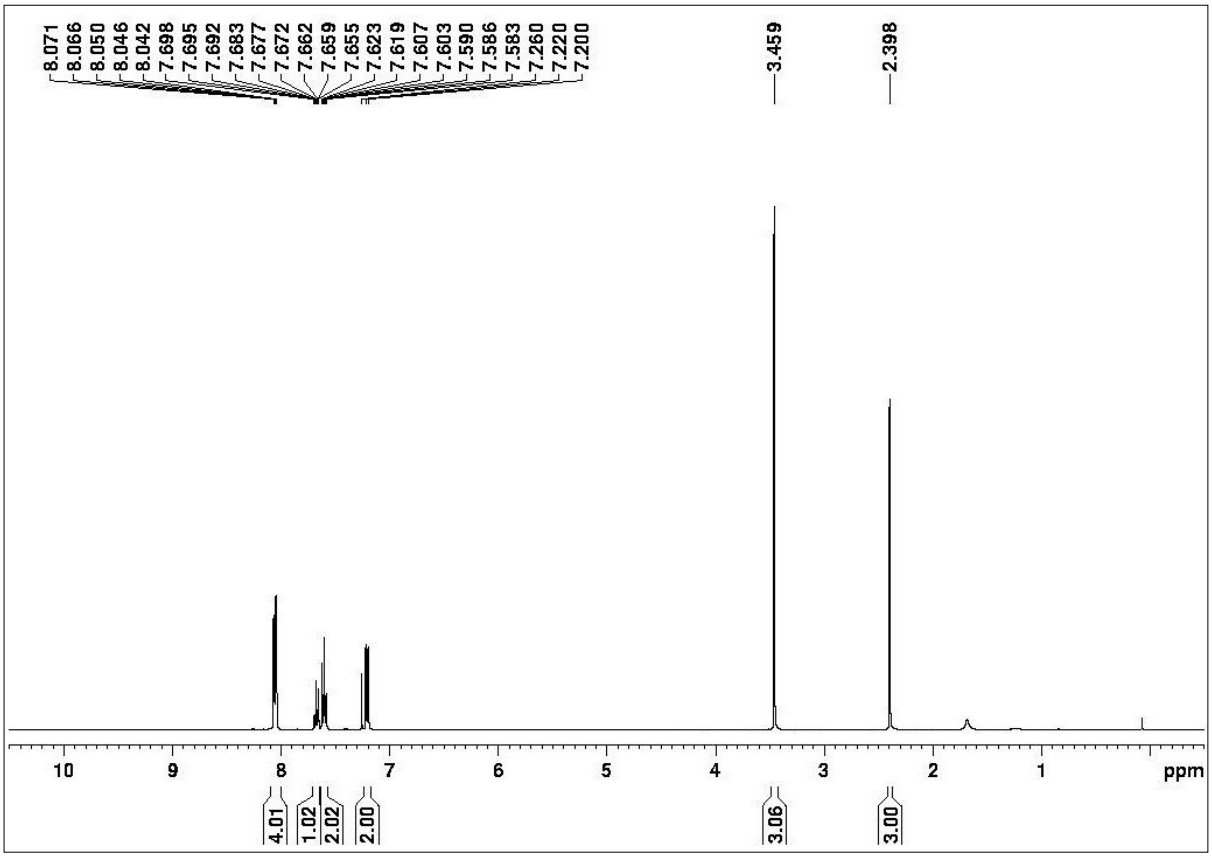


Figure 4: 400 MHz ^{1}H-NMR spectrum of **3a** in $CDCl_3$

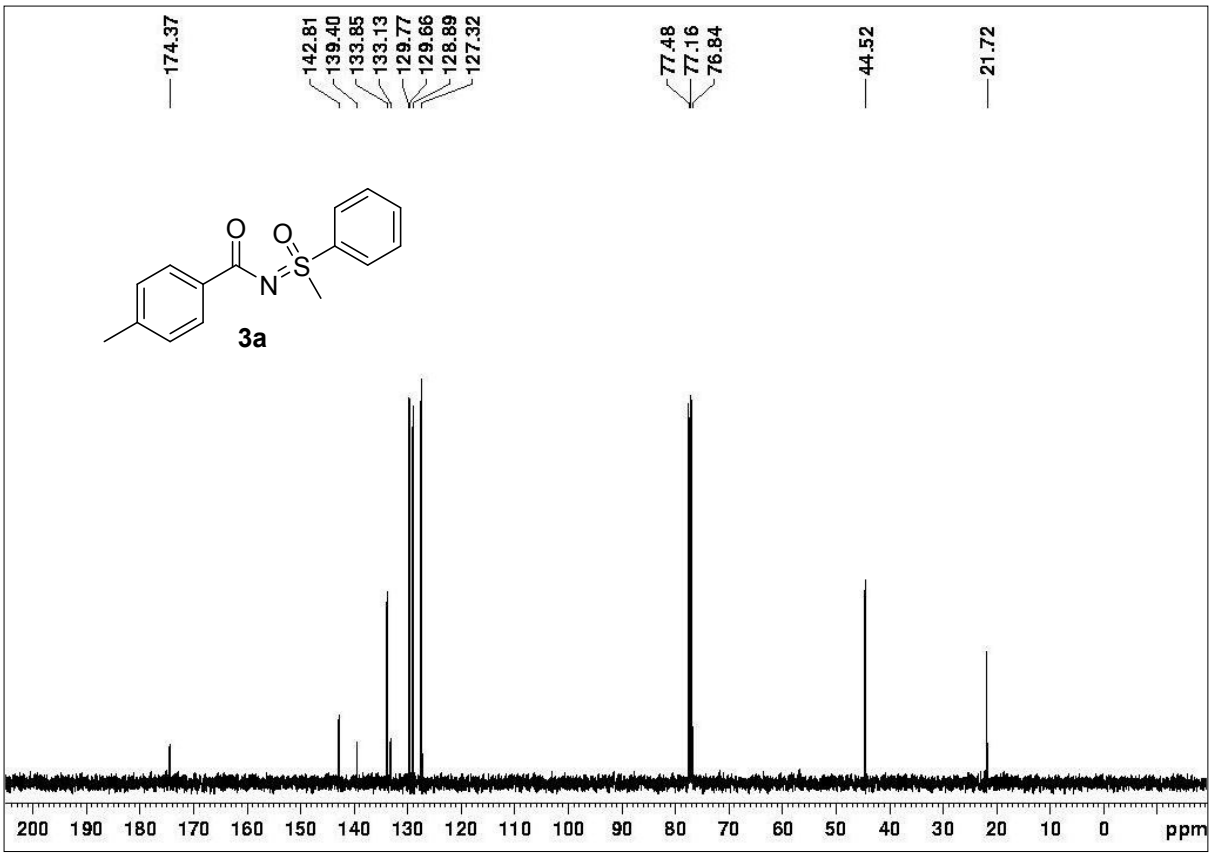


Figure 5: 100 MHz ^{13}C-NMR spectrum of **3a** in $CDCl_3$

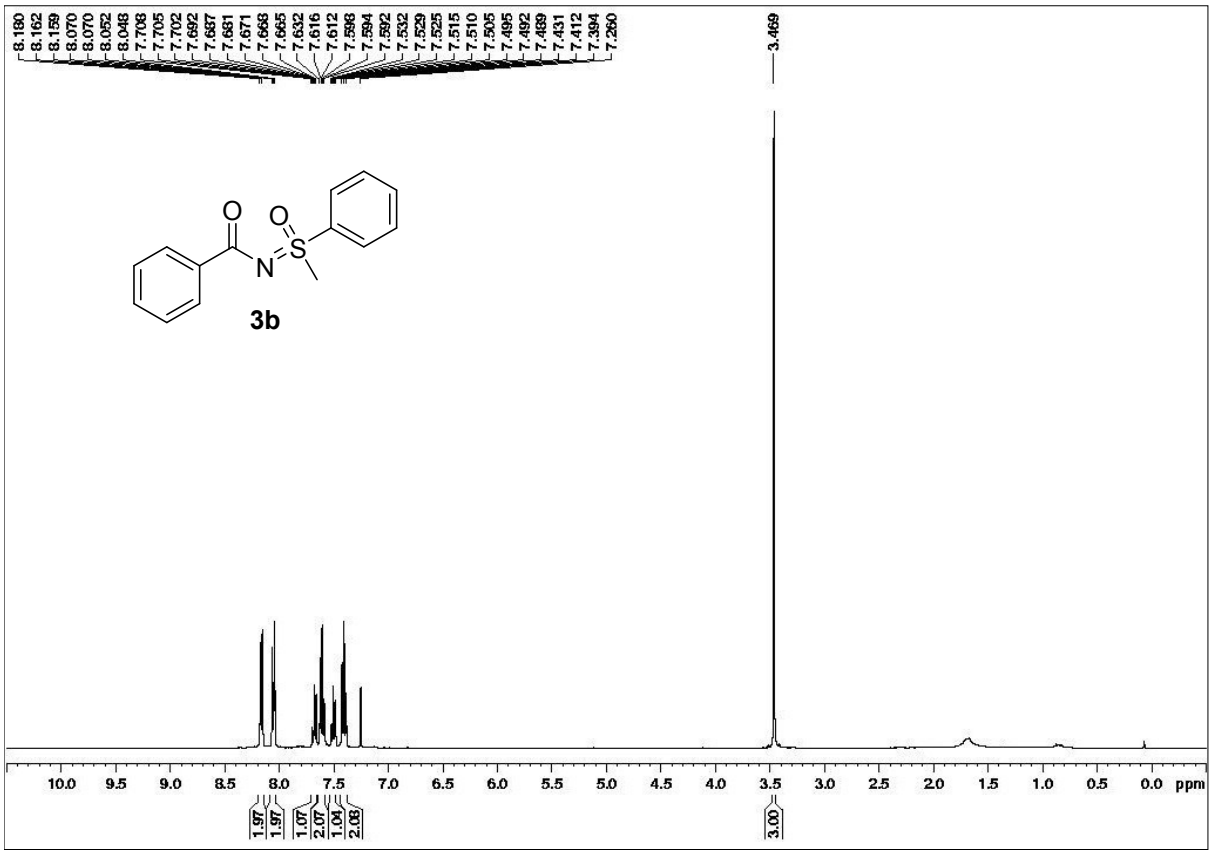


Figure 6: 400 MHz ^{1}H-NMR spectrum of **3b** in $CDCl_3$

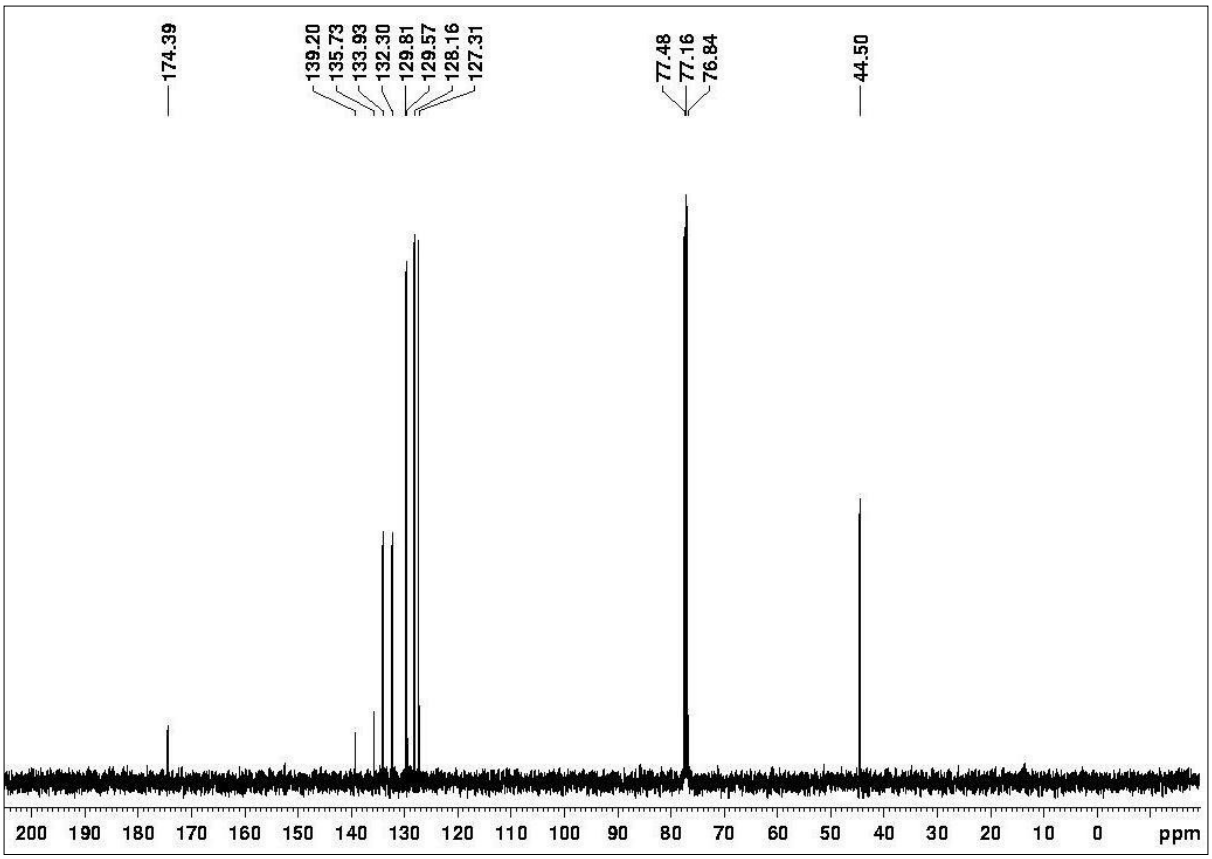


Figure 7: 100 MHz ^{13}C-NMR spectrum of **3b** in $CDCl_3$

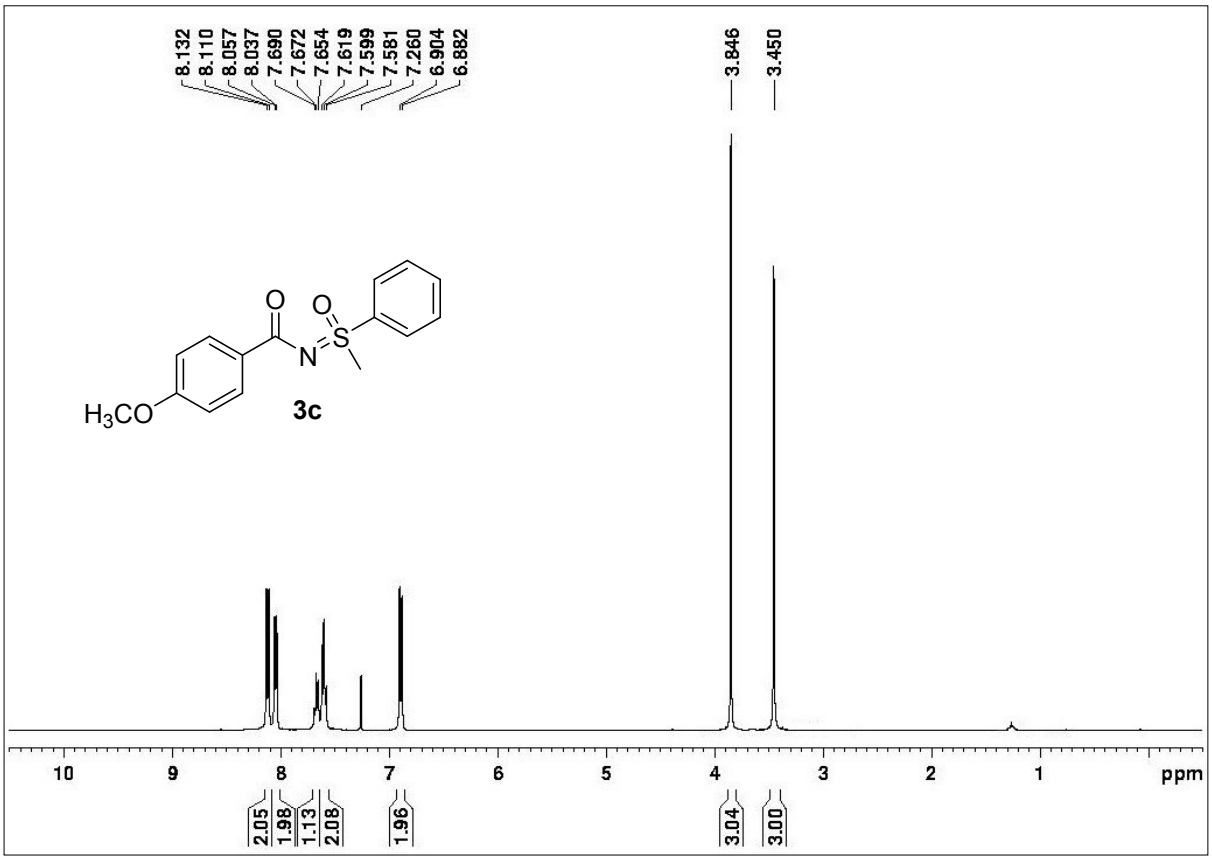


Figure 8: 400 MHz ^{1}H-NMR spectrum of **3c** in $CDCl_3$

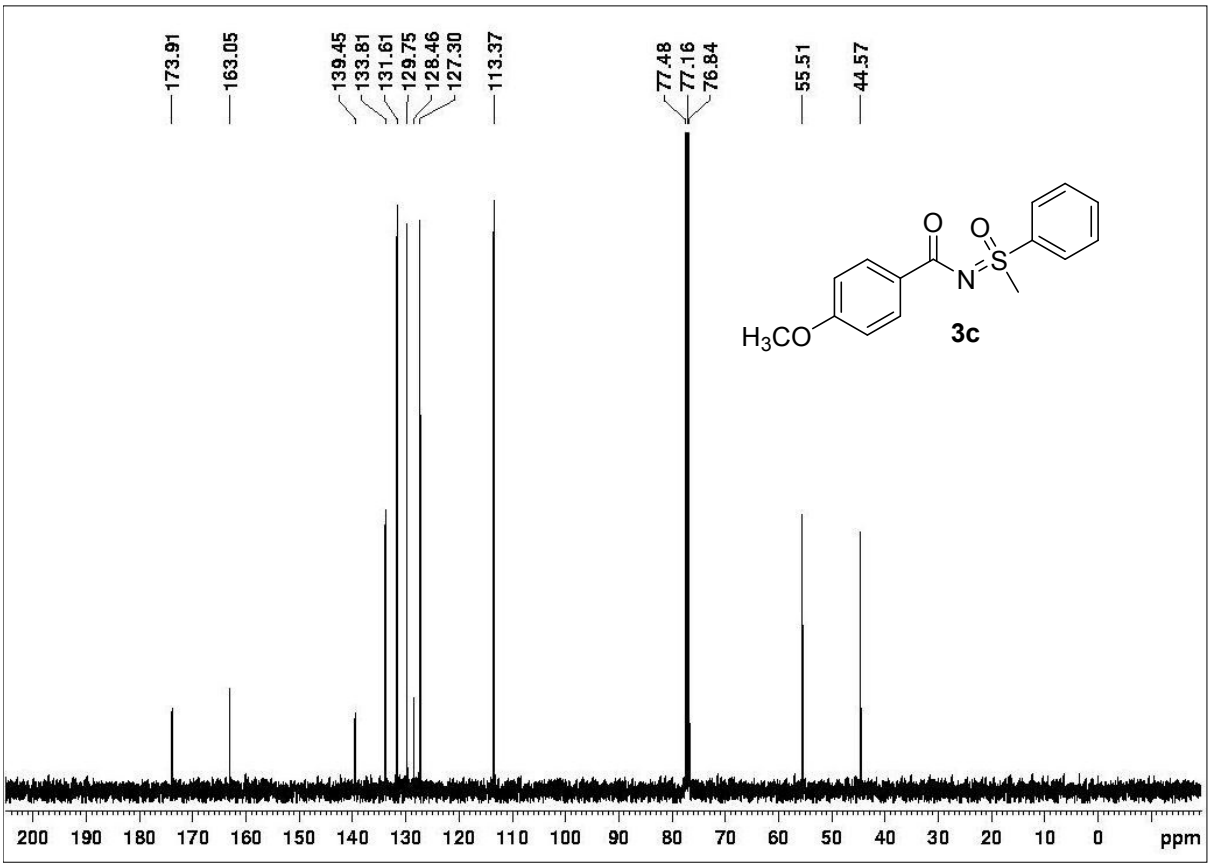


Figure 9: 100 MHz ^{13}C-NMR spectrum of **3c** in $CDCl_3$

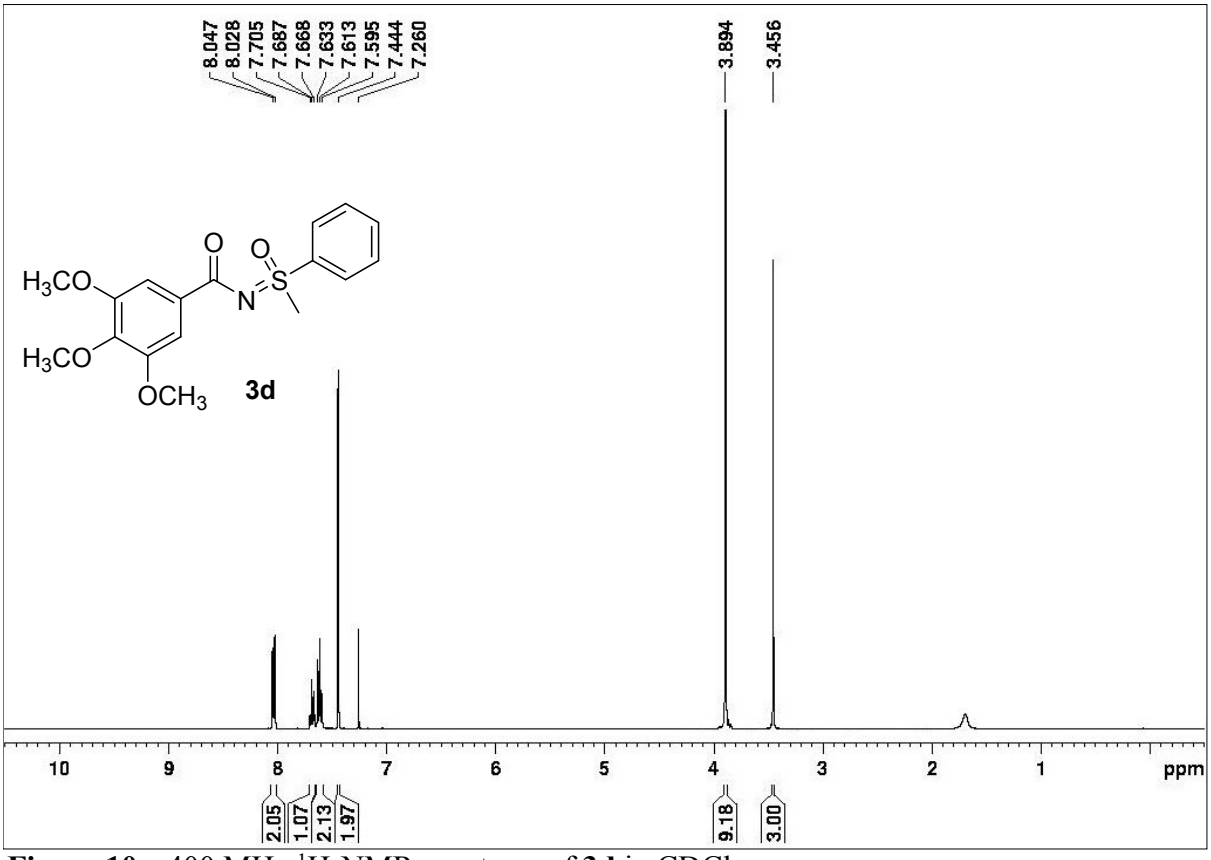


Figure 10: 400 MHz ^{1}H-NMR spectrum of **3d** in $CDCl_3$

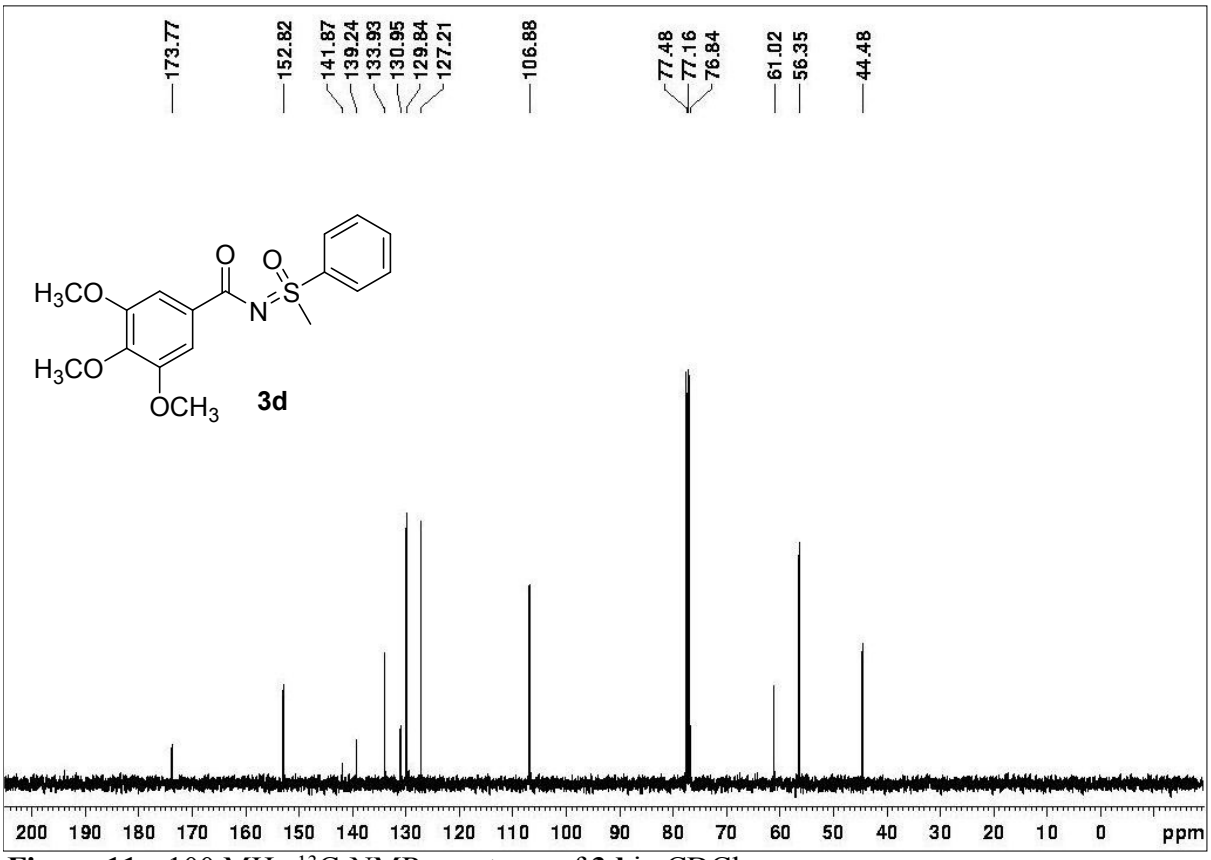


Figure 11: 100 MHz ^{13}C-NMR spectrum of **3d** in $CDCl_3$

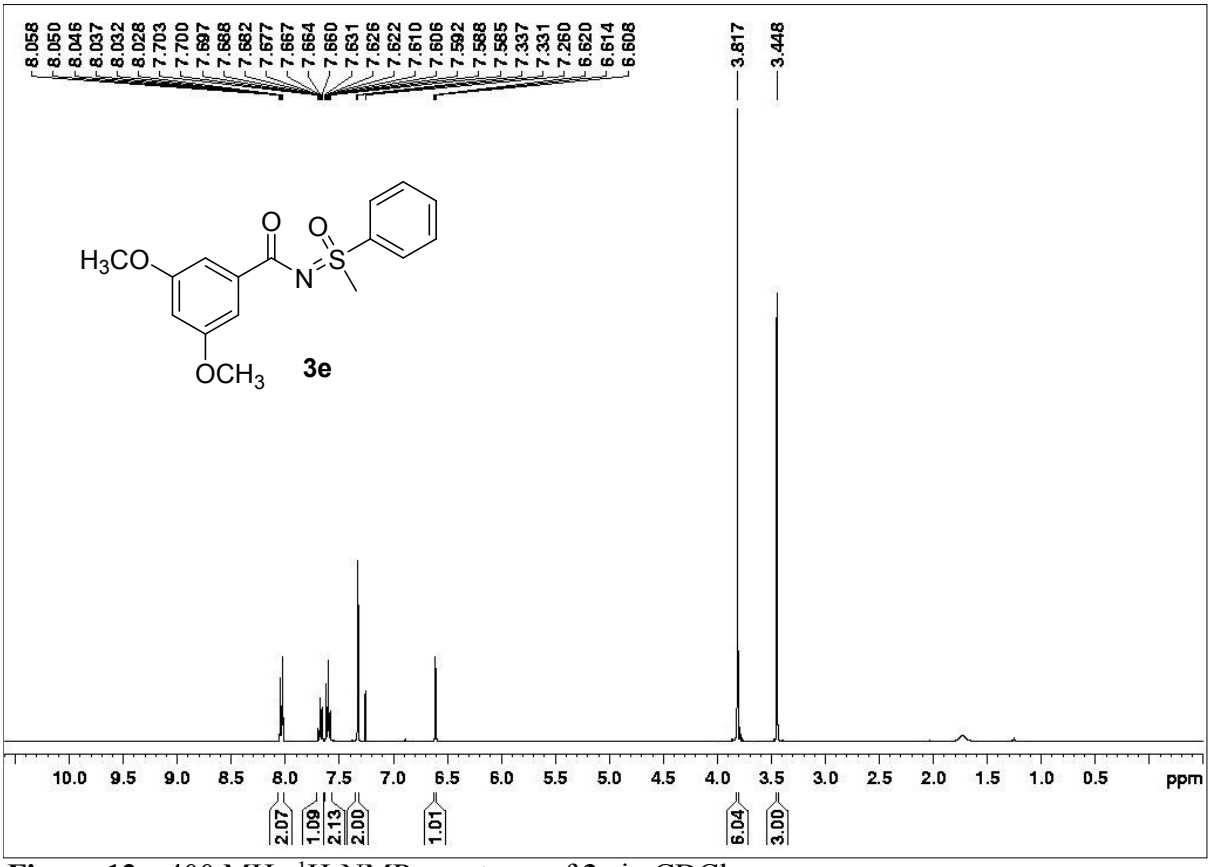


Figure 12: 400 MHz ^{1}H-NMR spectrum of **3e** in $CDCl_3$

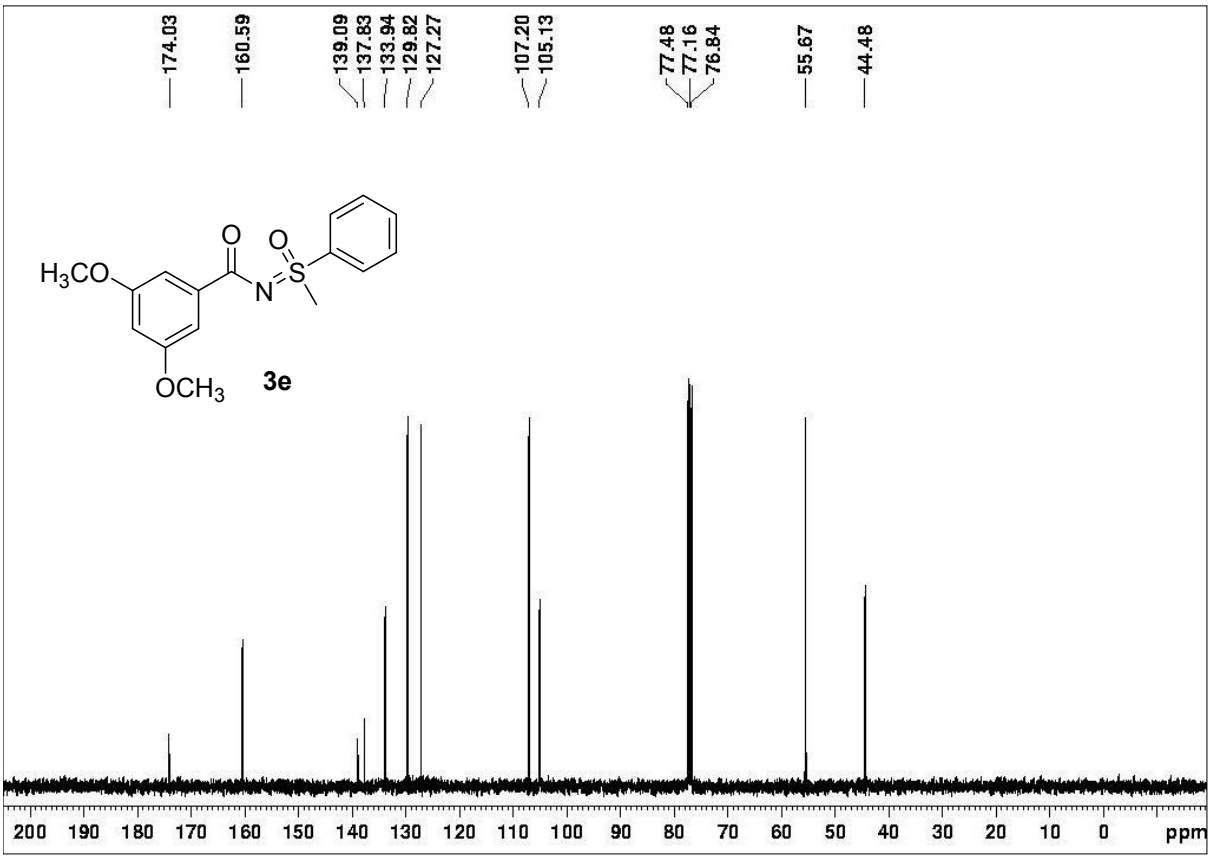


Figure 13: 100 MHz ^{13}C-NMR spectrum of **3e** in $CDCl_3$

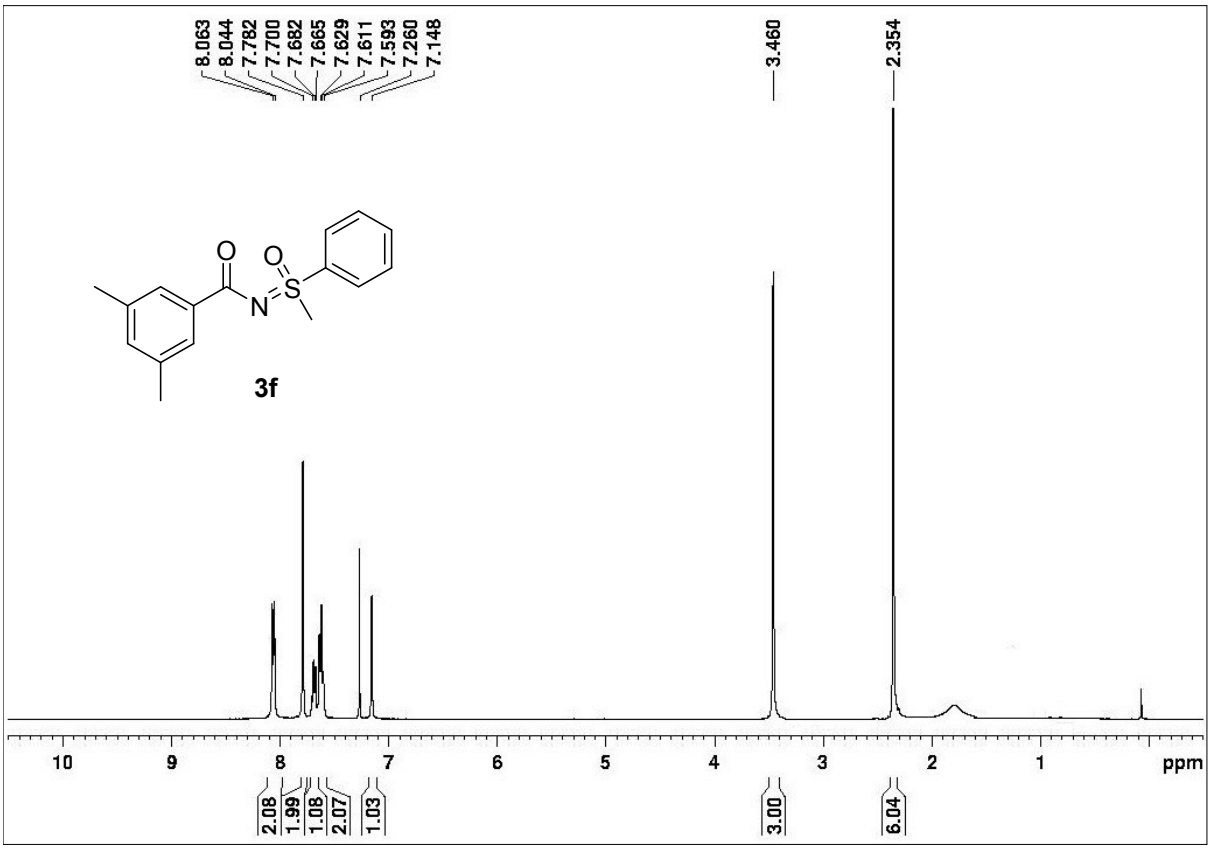


Figure 14: 400 MHz ^{1}H-NMR spectrum of **3f** in $CDCl_3$

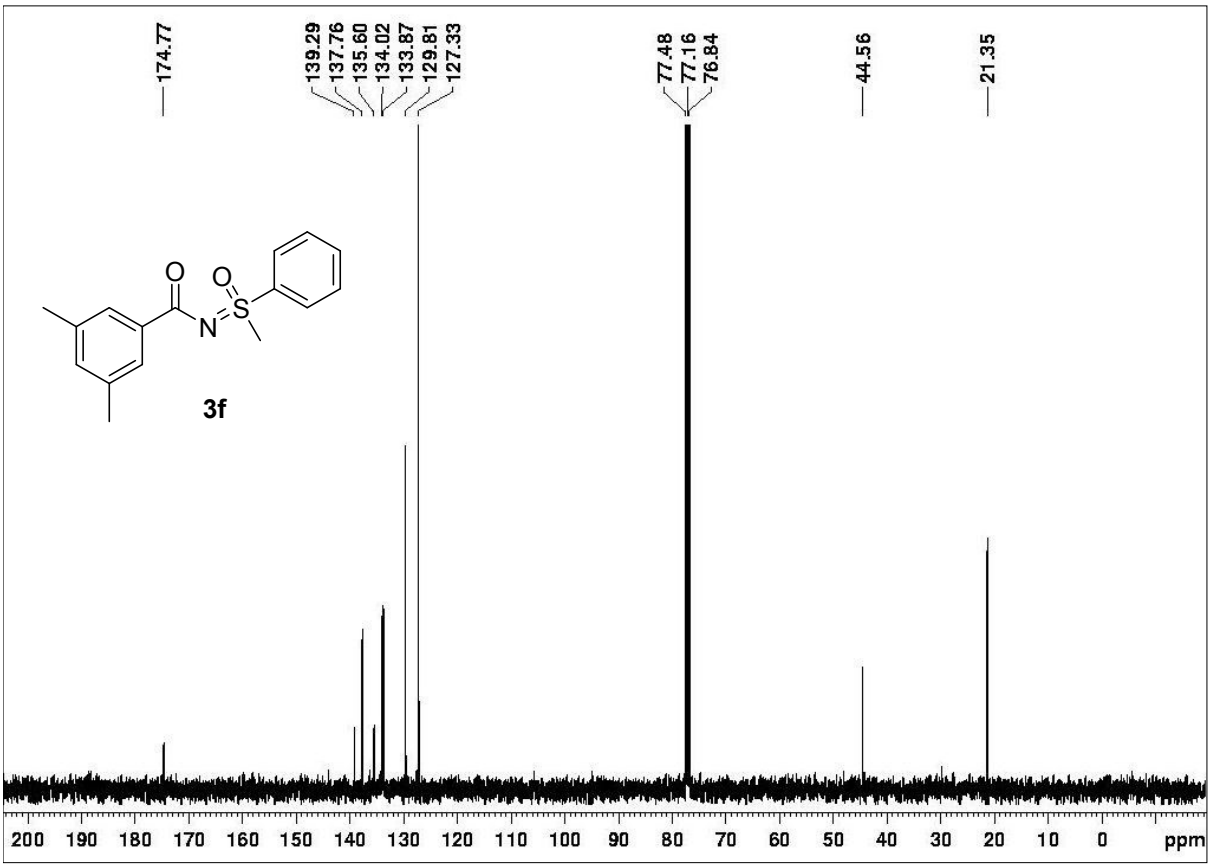


Figure 15: 100 MHz ^{13}C-NMR spectrum of **3f** in $CDCl_3$

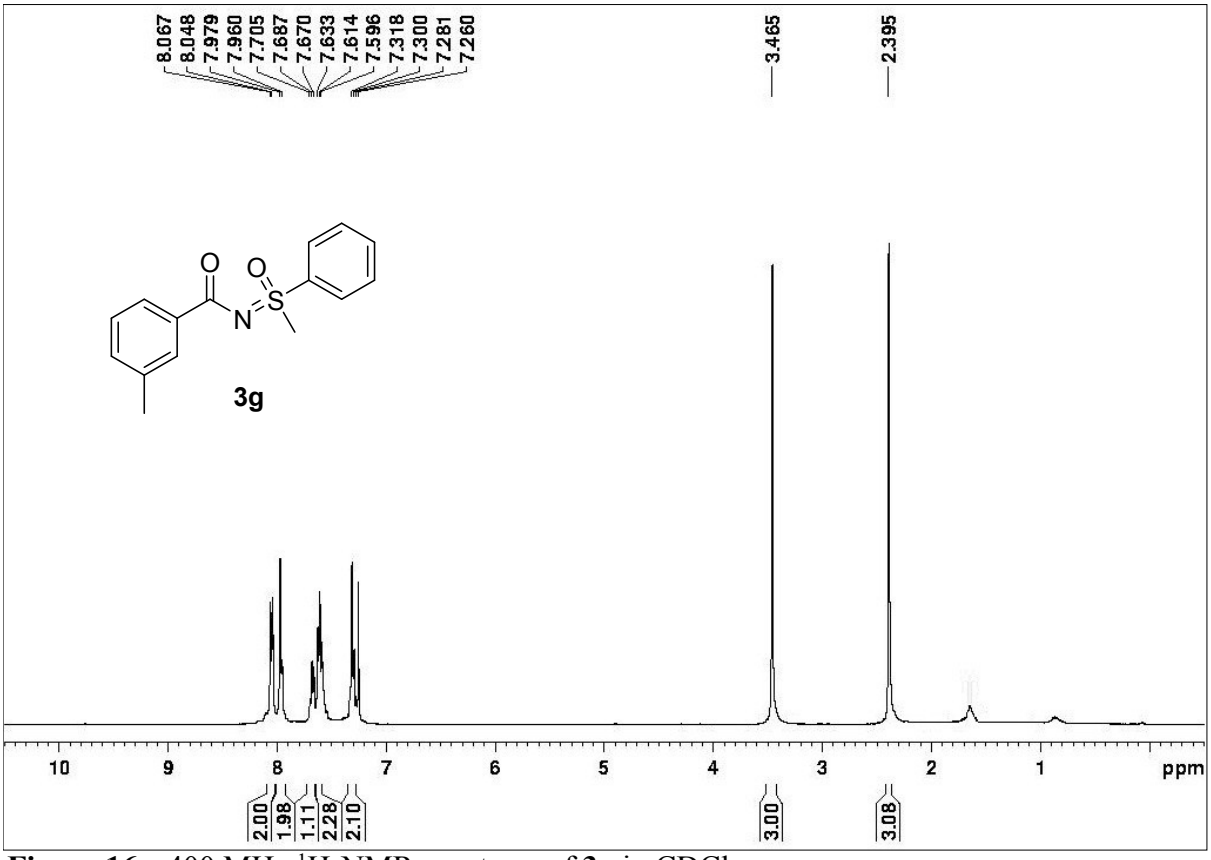


Figure 16: 400 MHz ^{1}H-NMR spectrum of **3g** in $CDCl_3$

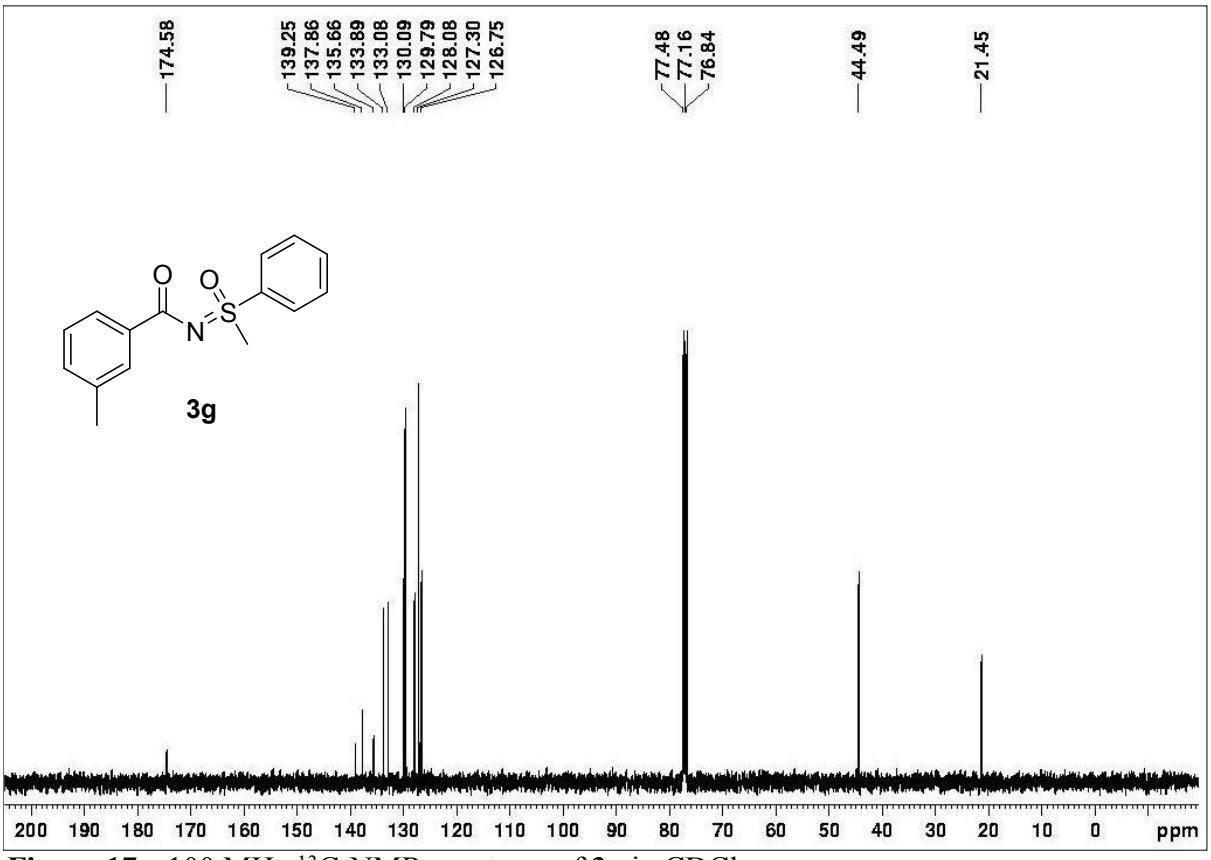


Figure 17: 100 MHz ^{13}C-NMR spectrum of **3g** in $CDCl_3$

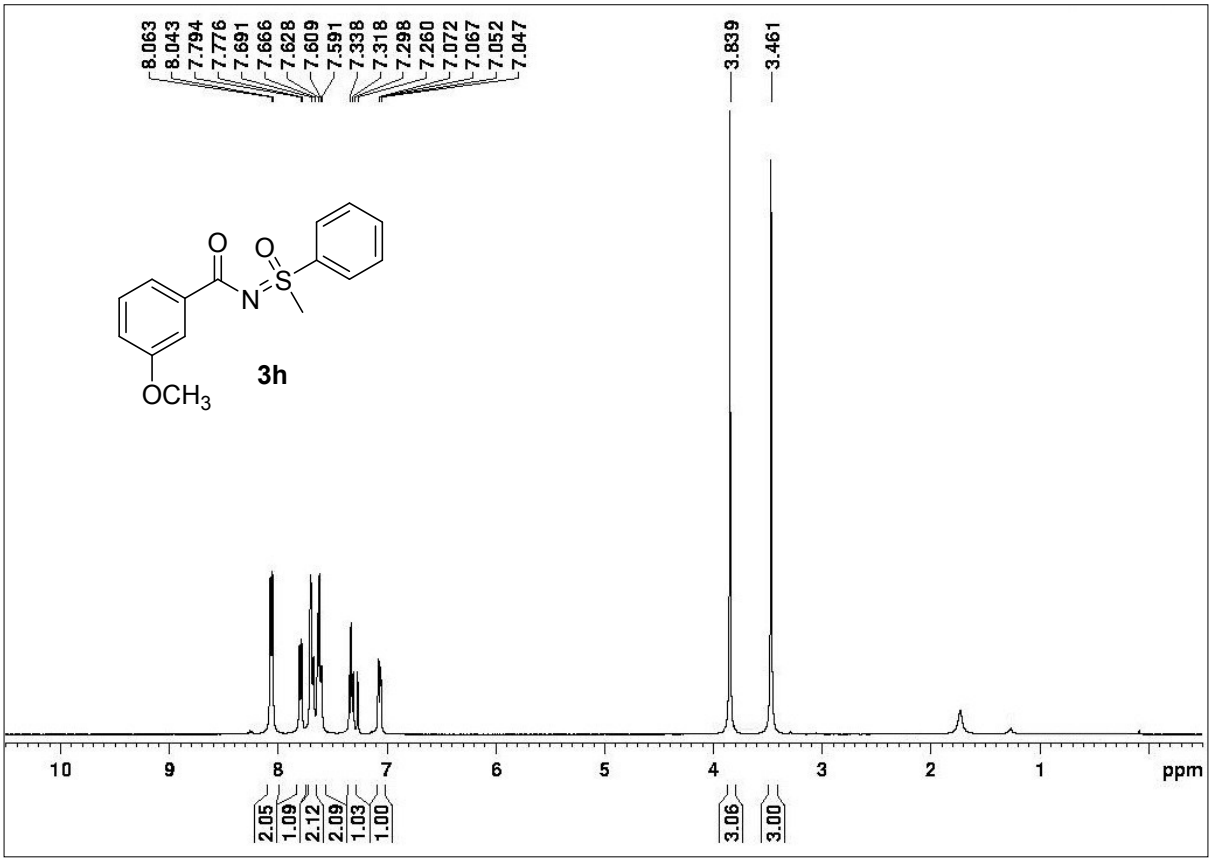


Figure 18: 400 MHz ^{1}H-NMR spectrum of **3h** in $CDCl_3$

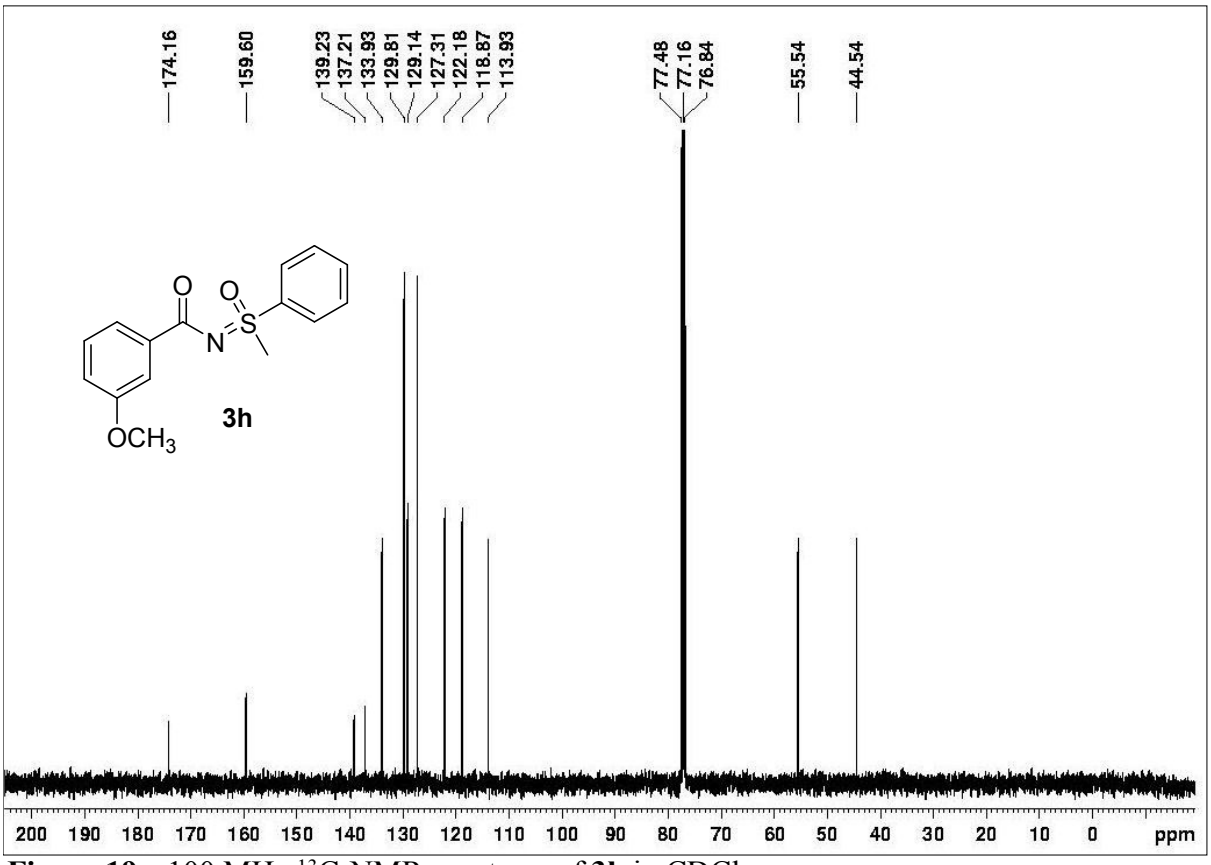


Figure 19: 100 MHz ^{13}C-NMR spectrum of **3h** in $CDCl_3$

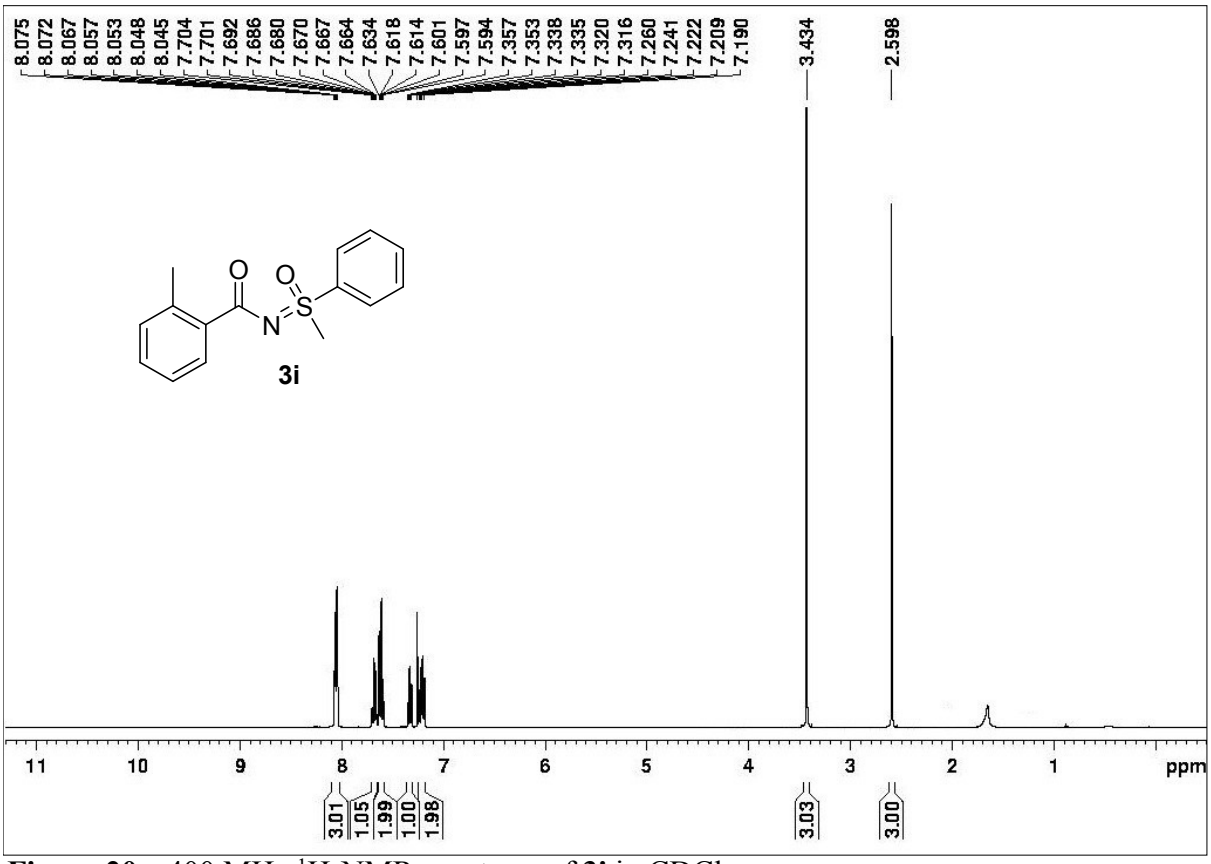


Figure 20: 400 MHz ^{1}H-NMR spectrum of **3i** in $CDCl_3$

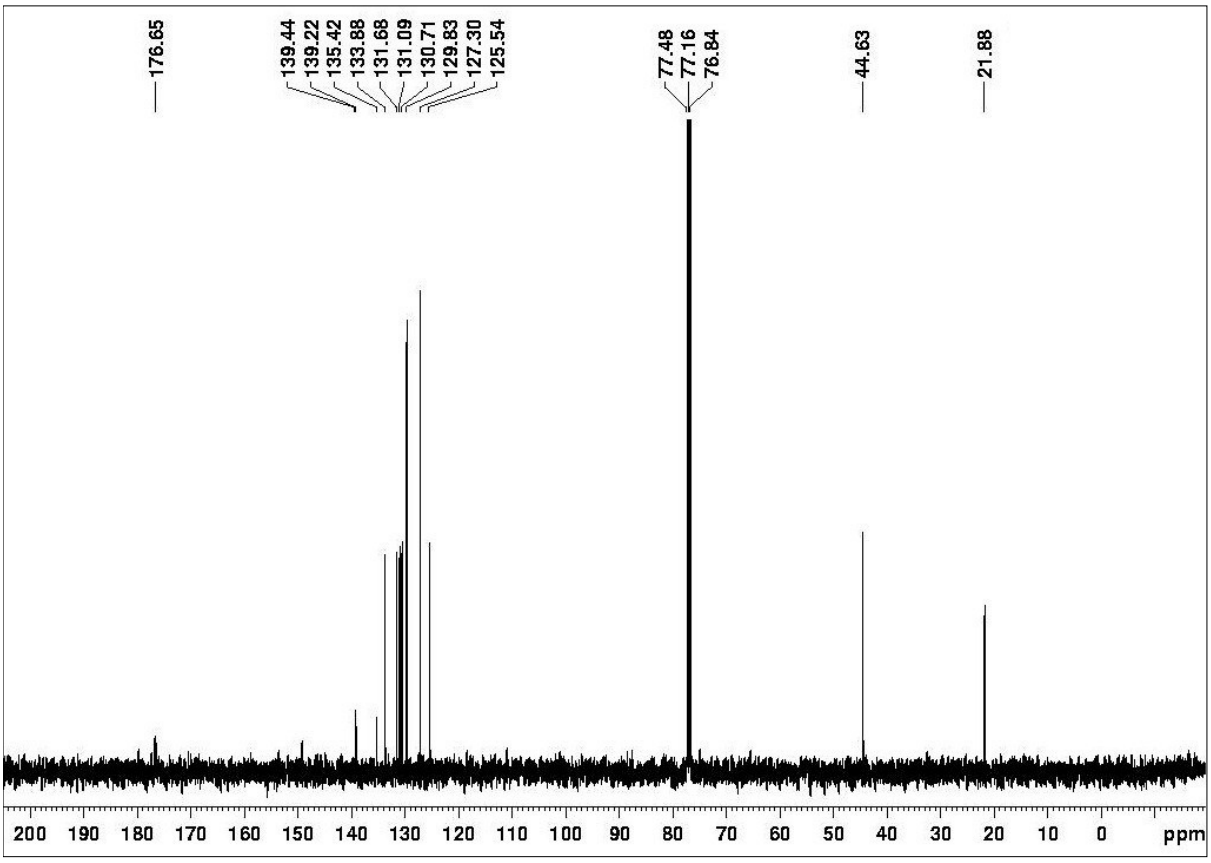


Figure 21: 100 MHz ^{13}C-NMR spectrum of **3i** in $CDCl_3$

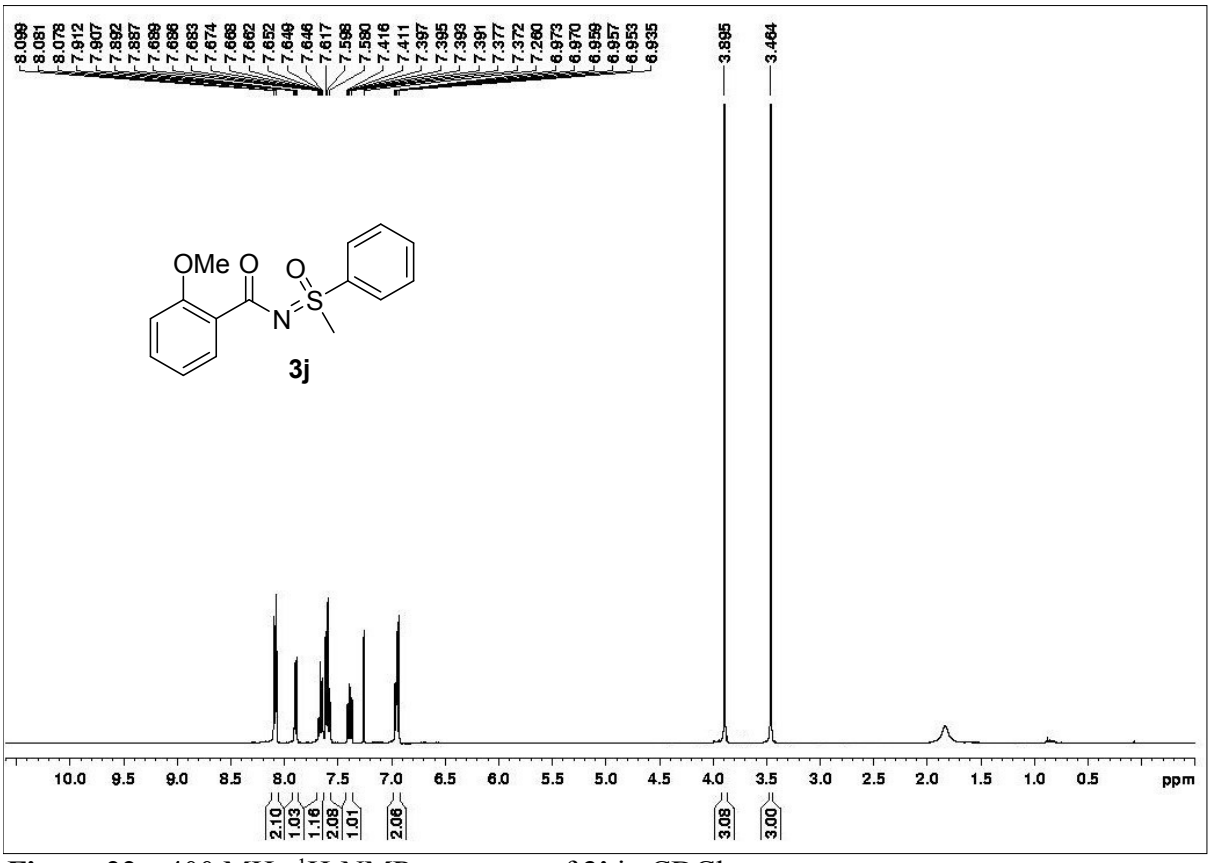


Figure 22: 400 MHz ^{1}H-NMR spectrum of **3j** in $CDCl_3$

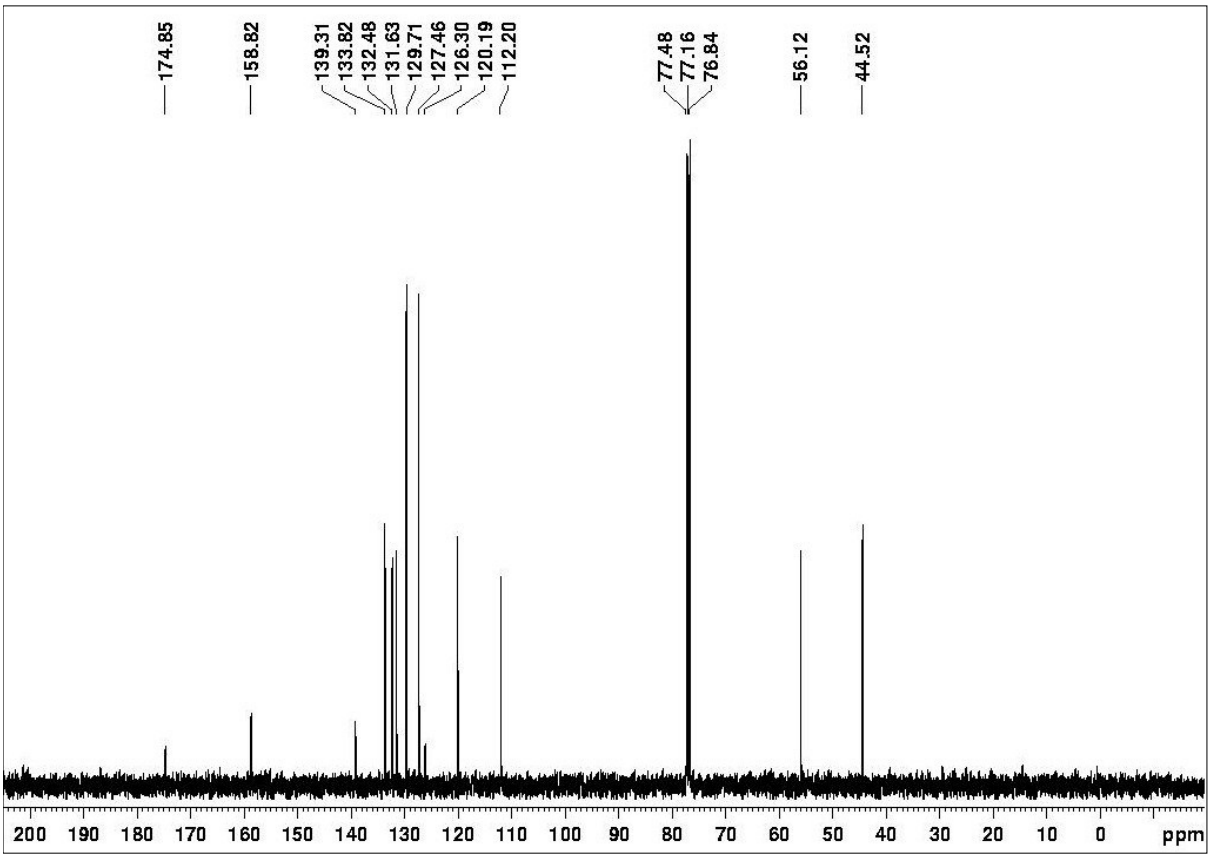


Figure 23: 100 MHz ^{13}C-NMR spectrum of **3j** in $CDCl_3$

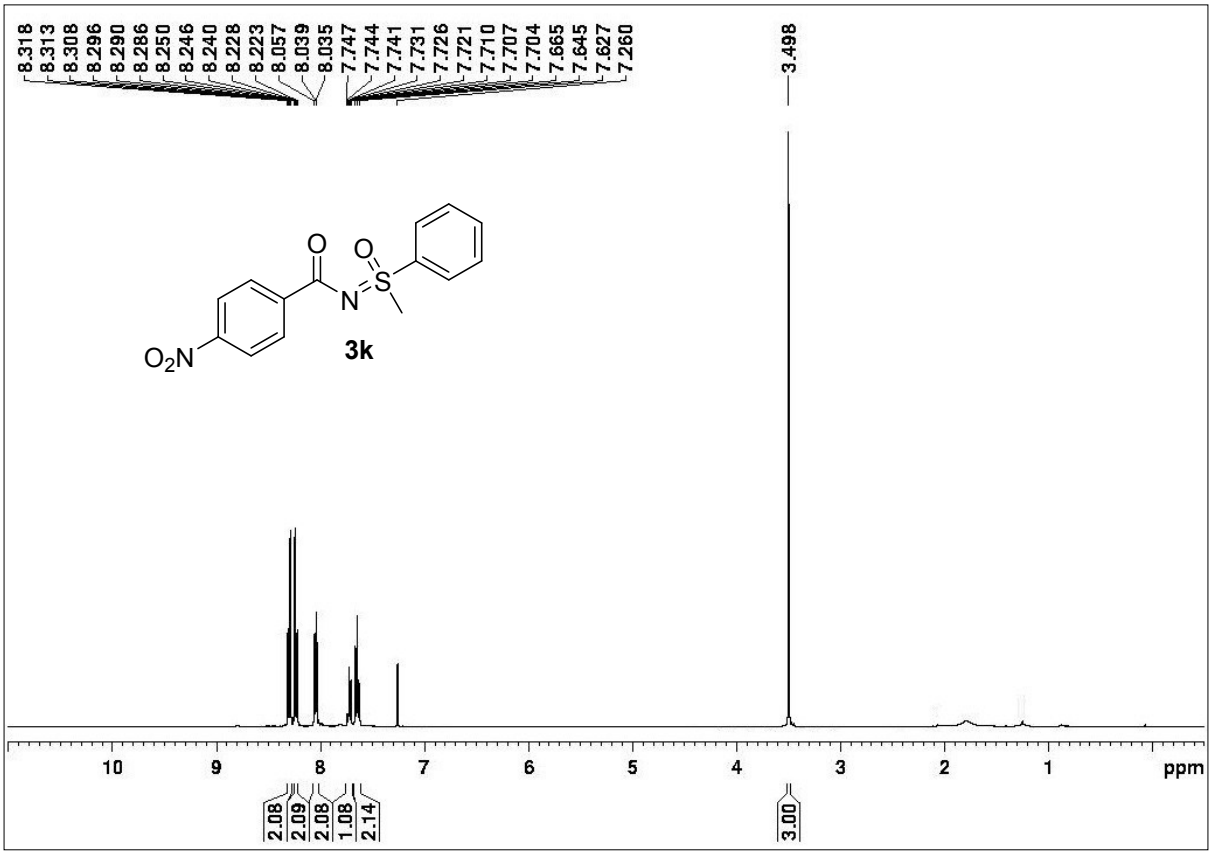


Figure 24: 400 MHz ^{1}H-NMR spectrum of **3k** in $CDCl_3$

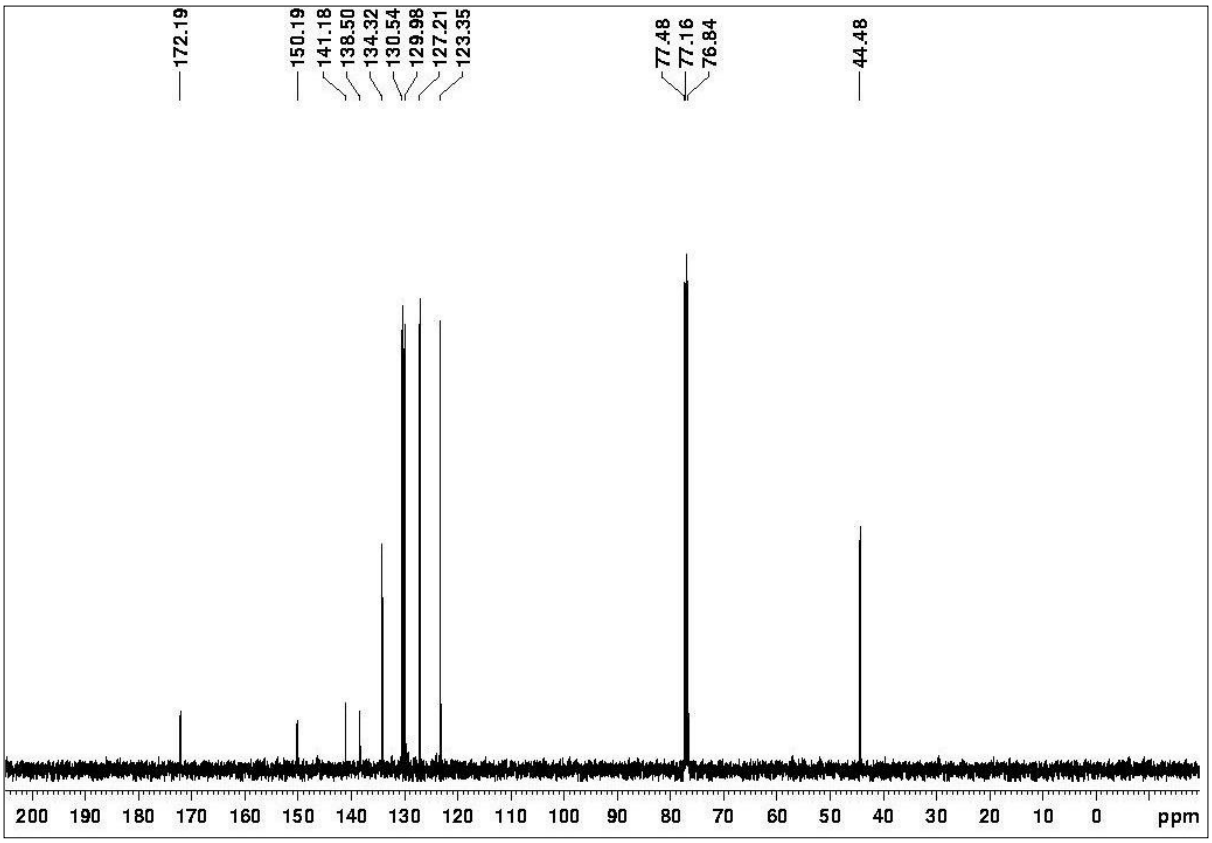


Figure 25: 100 MHz ^{13}C-NMR spectrum of **3k** in $CDCl_3$

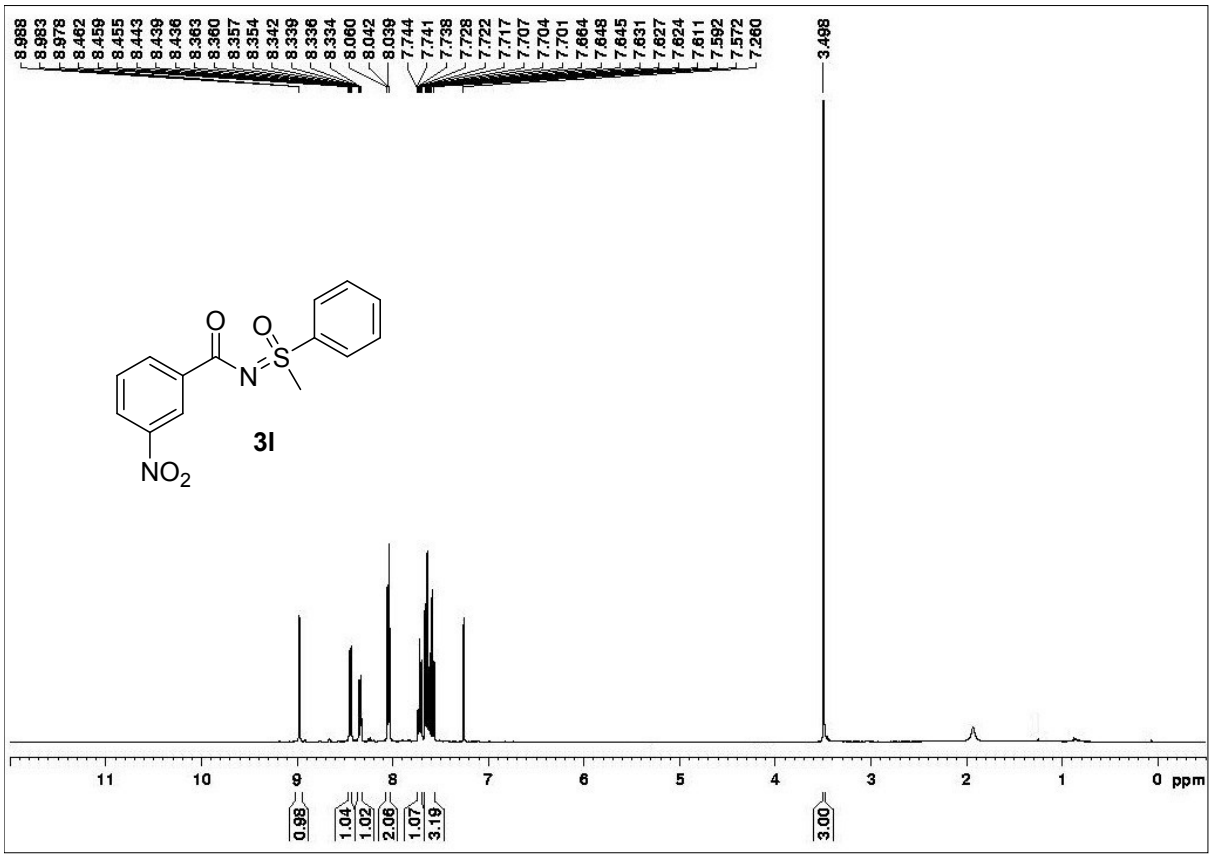


Figure 26: 400 MHz ^{1}H-NMR spectrum of **3l** in $CDCl_3$

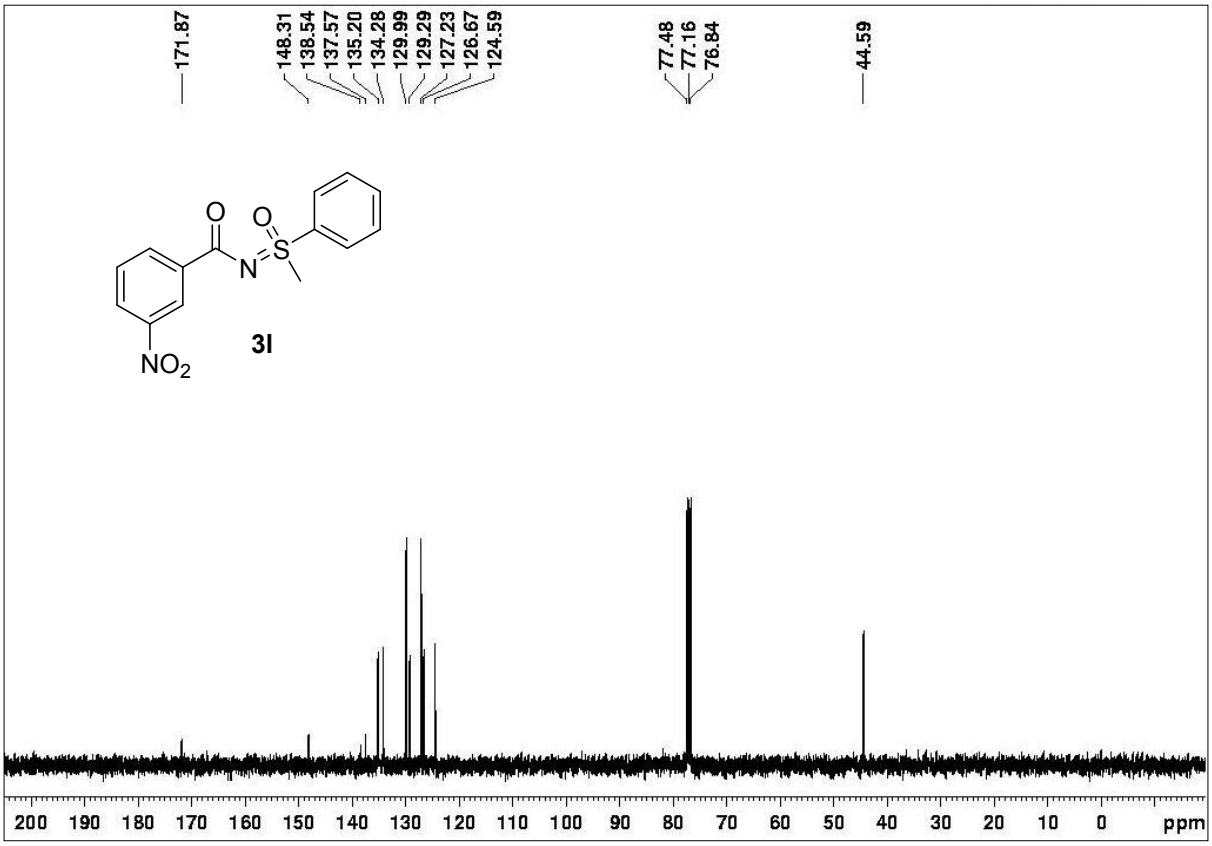


Figure 27: 100 MHz ^{13}C-NMR spectrum of **3l** in $CDCl_3$

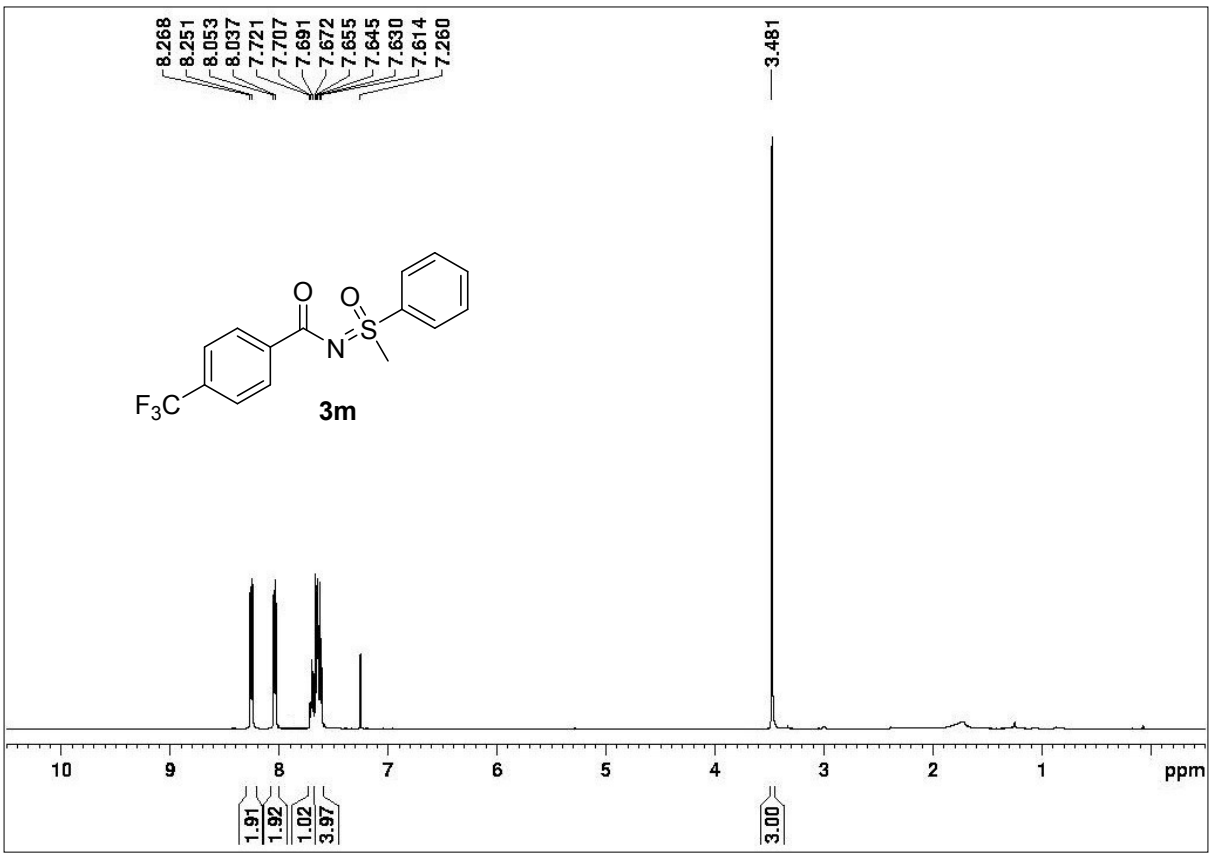


Figure 28: 500 MHz ^{1}H-NMR spectrum of **3m** in $CDCl_3$

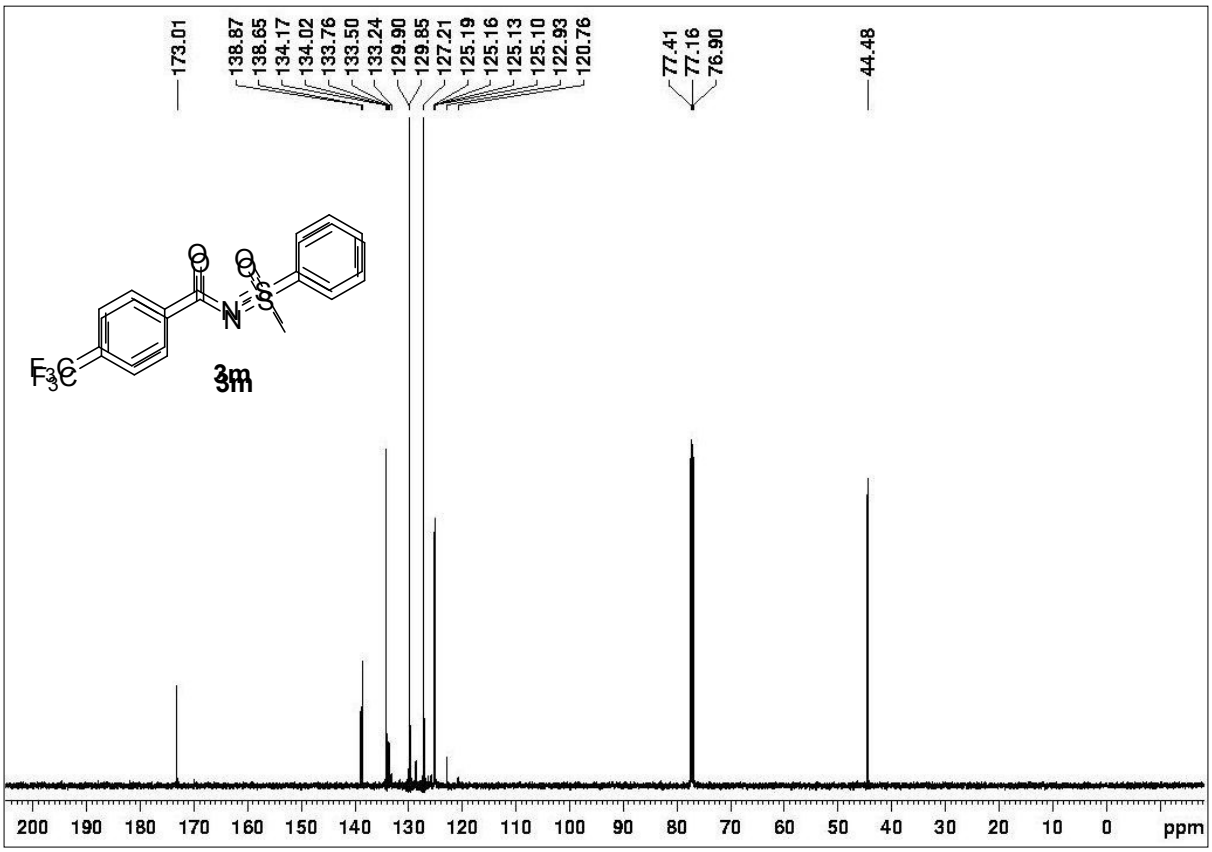


Figure 29: 125 MHz ^{13}C-NMR spectrum of **3m** in $CDCl_3$

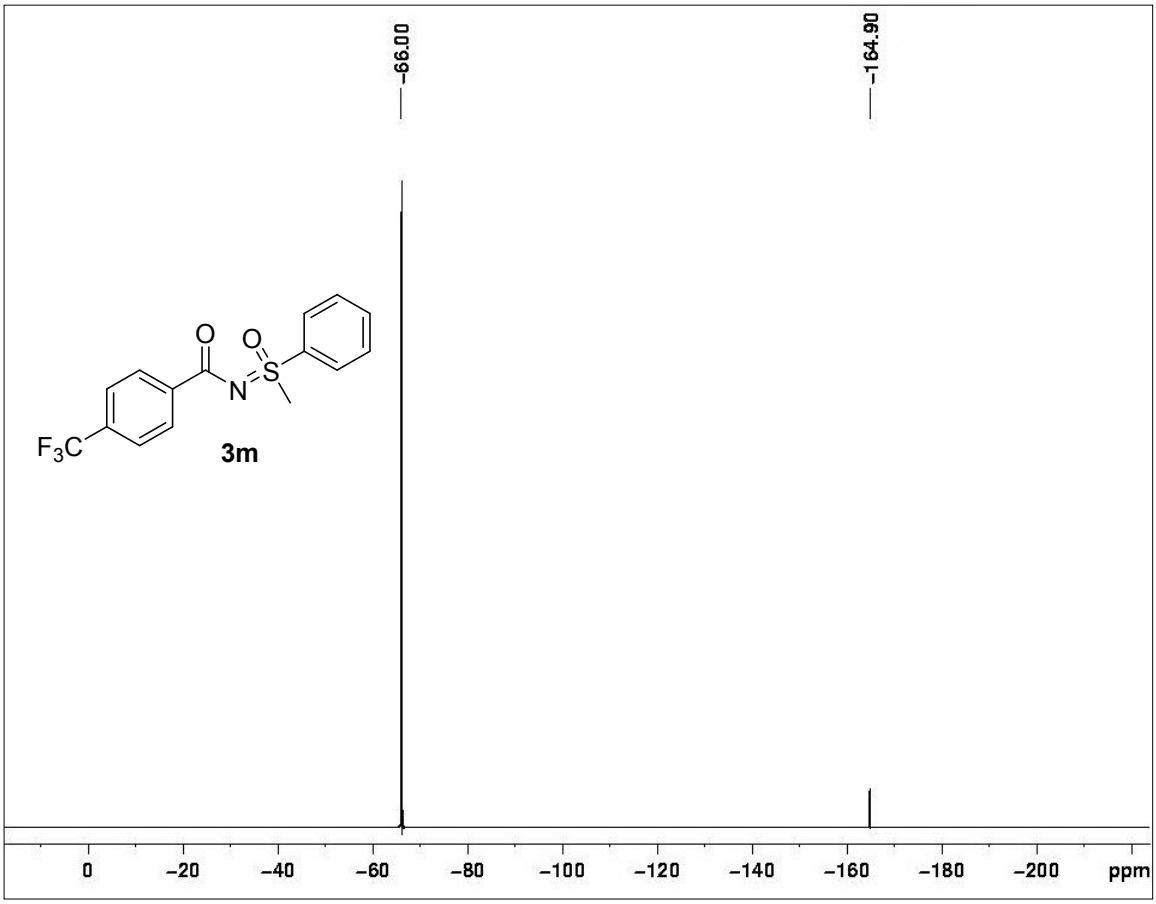


Figure 30: 470 MHz ^{19}F-NMR spectrum of **3m** in $CDCl_3$

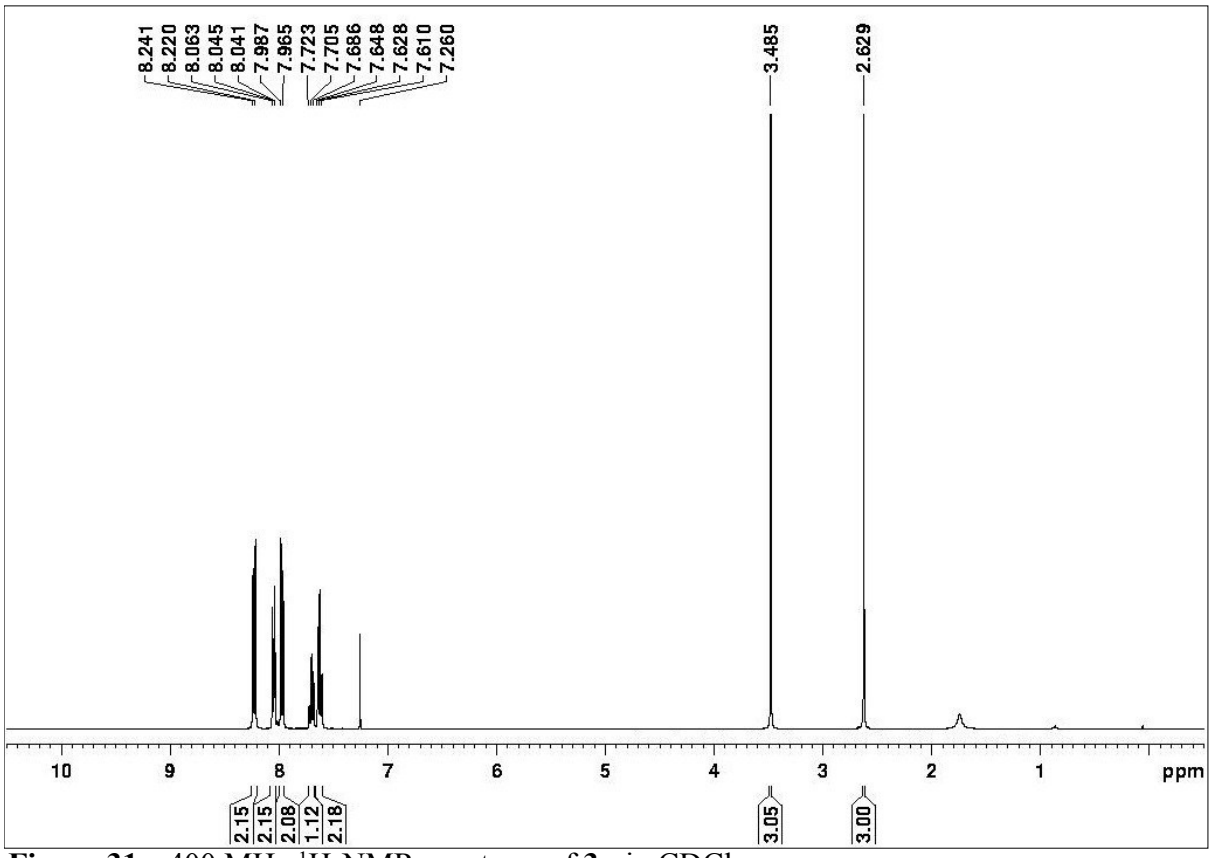


Figure 31: 400 MHz ^{1}H-NMR spectrum of **3n** in $CDCl_3$

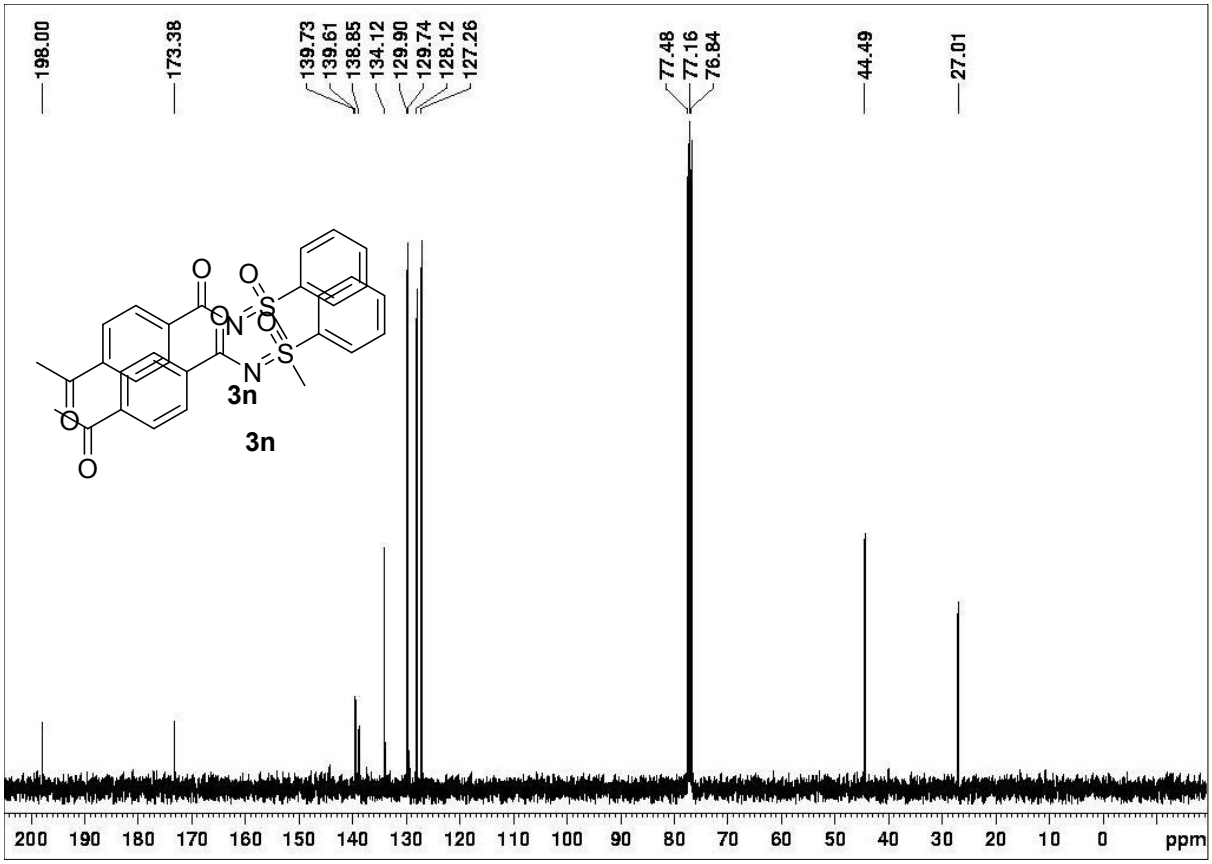


Figure 32: 100 MHz ^{13}C-NMR spectrum of **3n** in $CDCl_3$

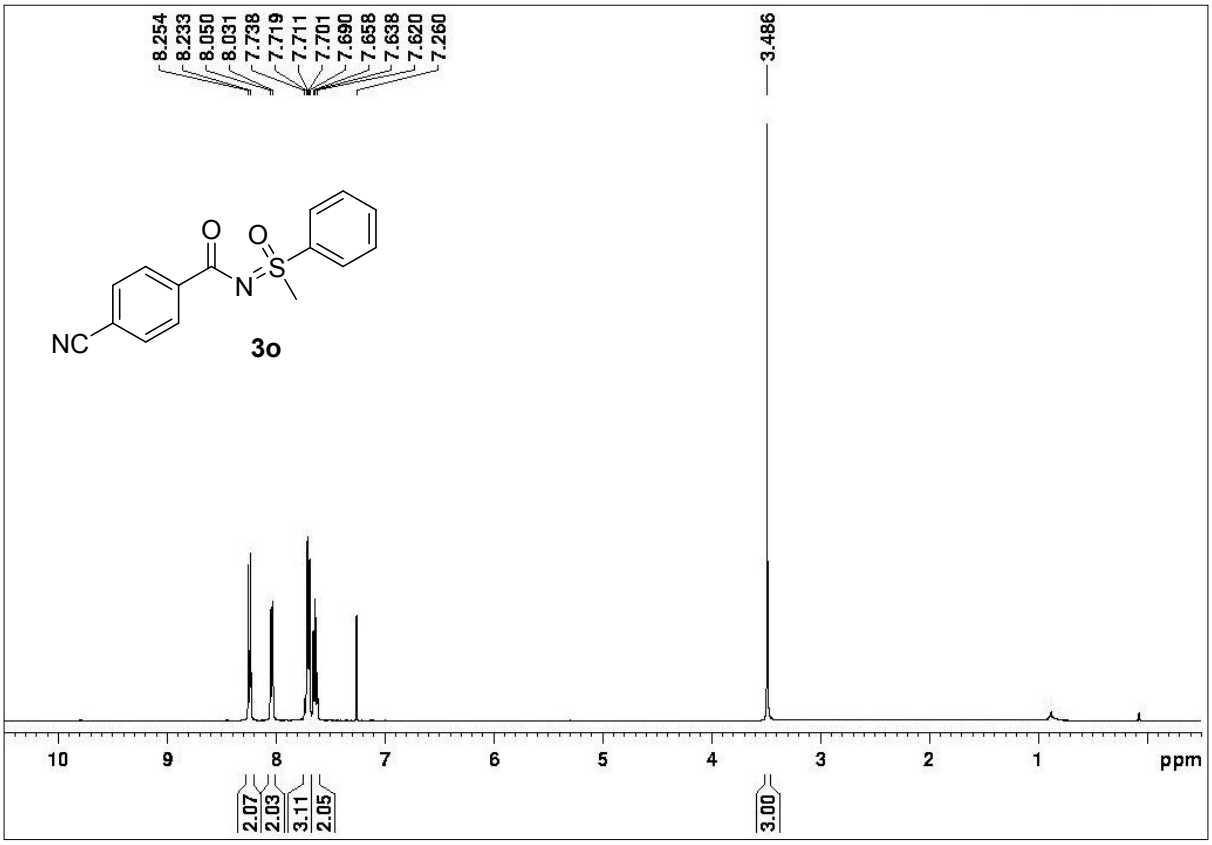


Figure 33: 400 MHz ^{1}H-NMR spectrum of **3o** in $CDCl_3$

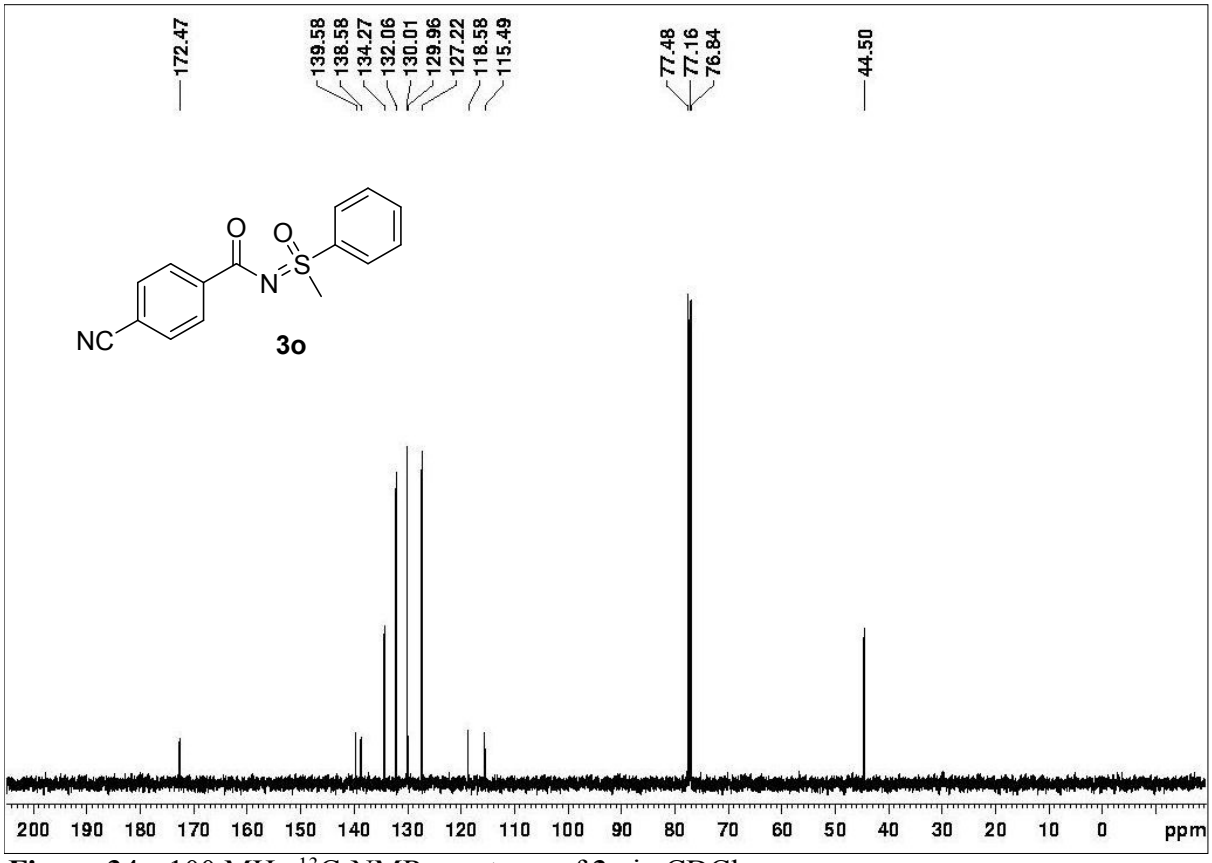


Figure 34: 100 MHz ^{13}C-NMR spectrum of **3o** in $CDCl_3$

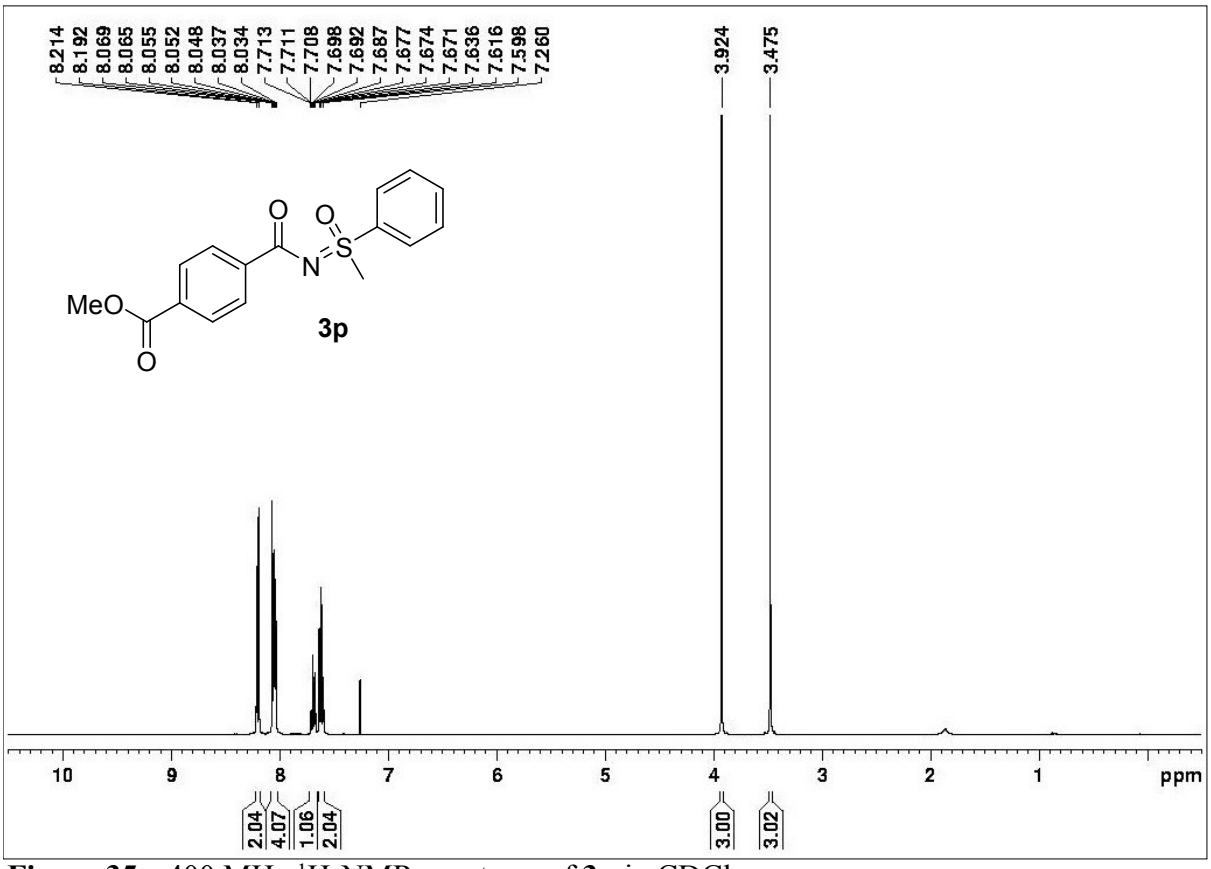


Figure 35: 400 MHz ^{1}H-NMR spectrum of **3p** in $CDCl_3$

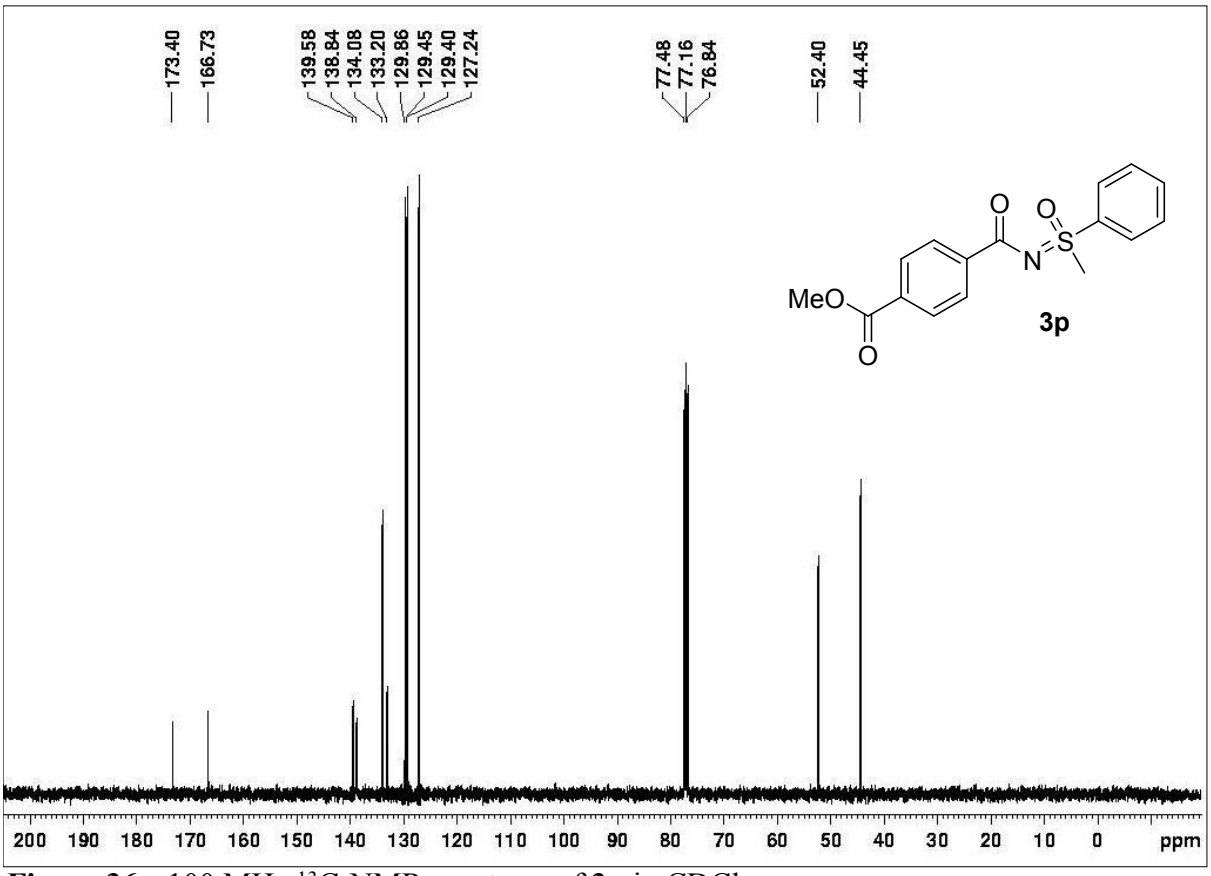


Figure 36: 100 MHz ^{13}C-NMR spectrum of **3p** in $CDCl_3$

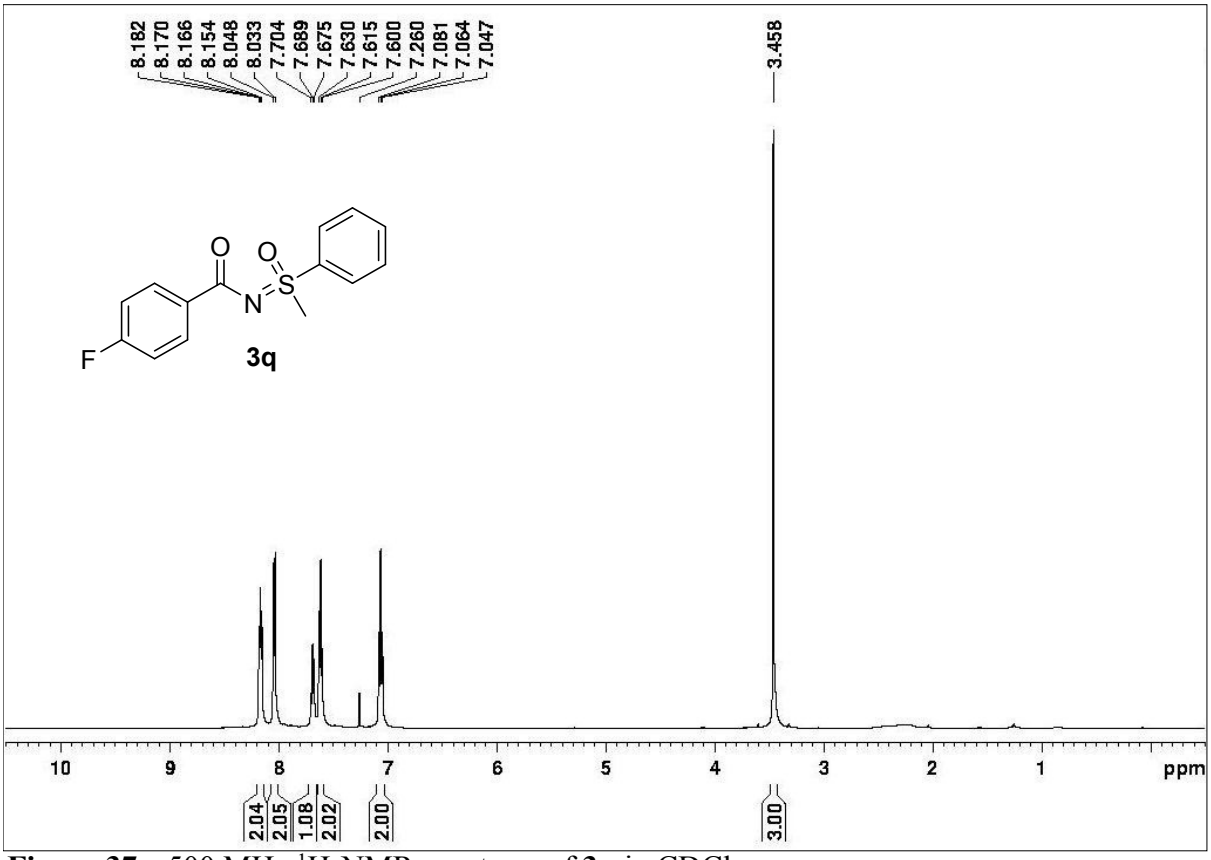


Figure 37: 500 MHz ^{1}H-NMR spectrum of **3q** in $CDCl_3$

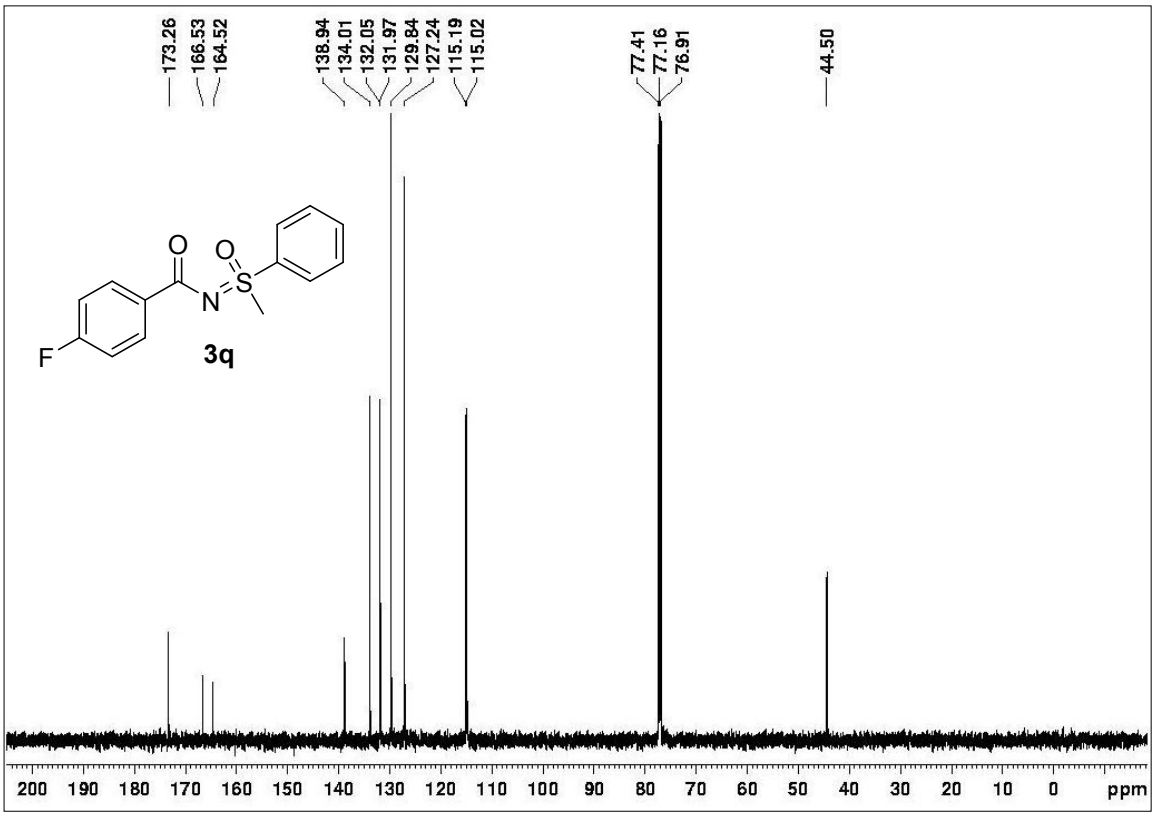


Figure 38: 125 MHz ^{13}C-NMR spectrum of **3q** in $CDCl_3$

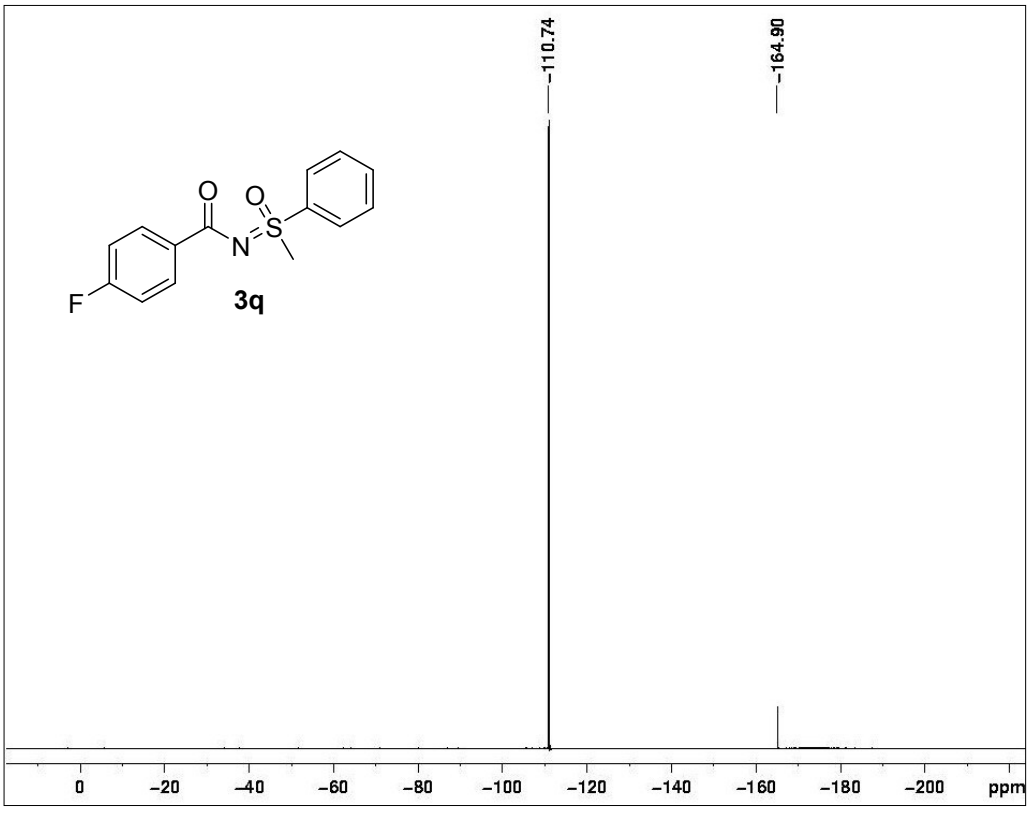


Figure 39: 470 MHz ^{19}F-NMR spectrum of **3q** in $CDCl_3$

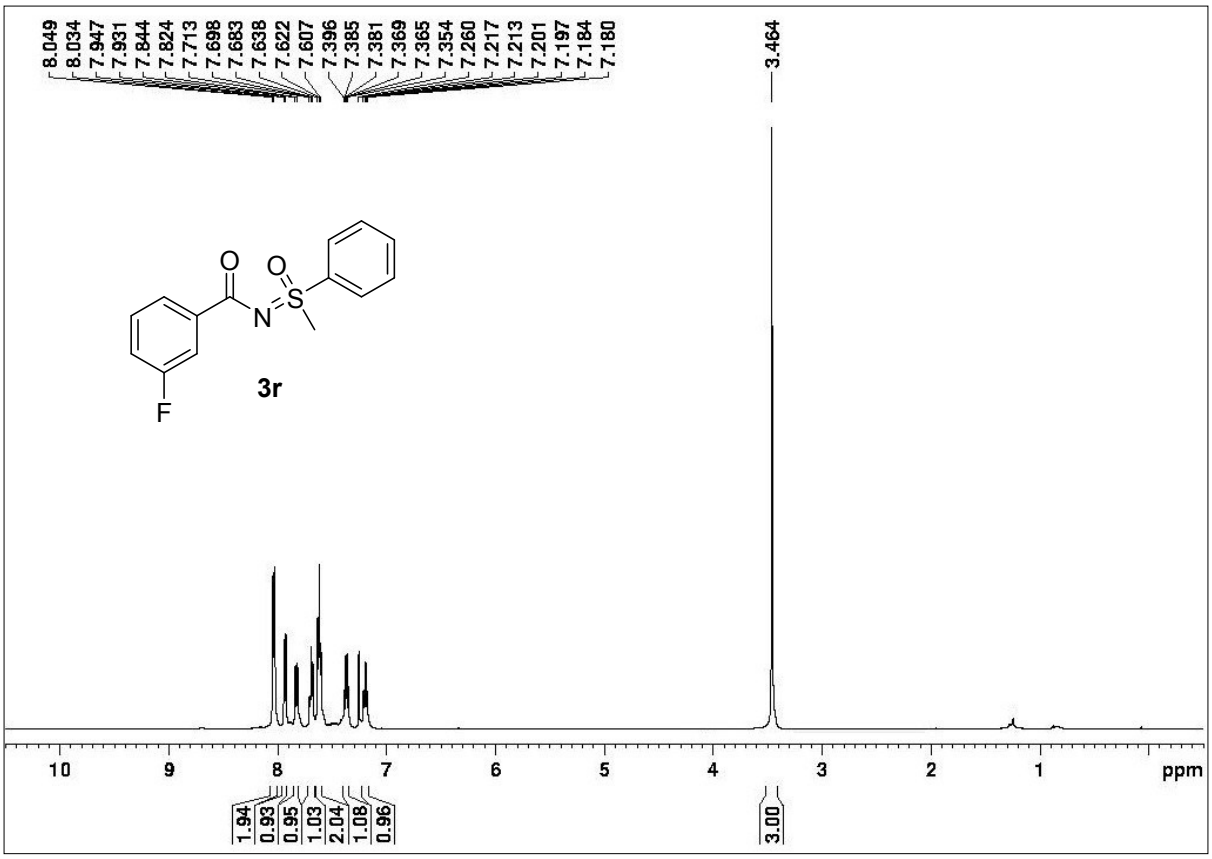


Figure 40: 500 MHz ^{1}H-NMR spectrum of **3r** in $CDCl_3$

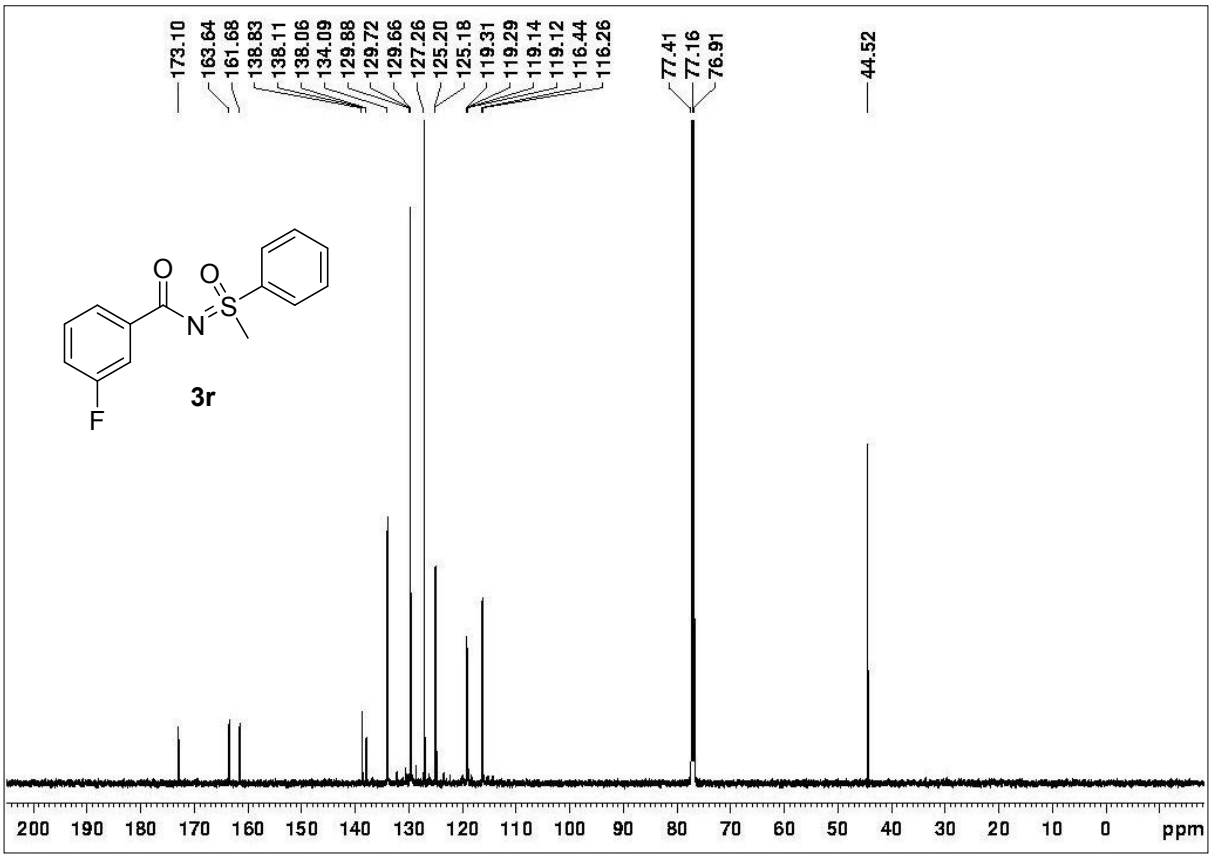


Figure 41: 125 MHz ^{13}C-NMR spectrum of **3r** in $CDCl_3$

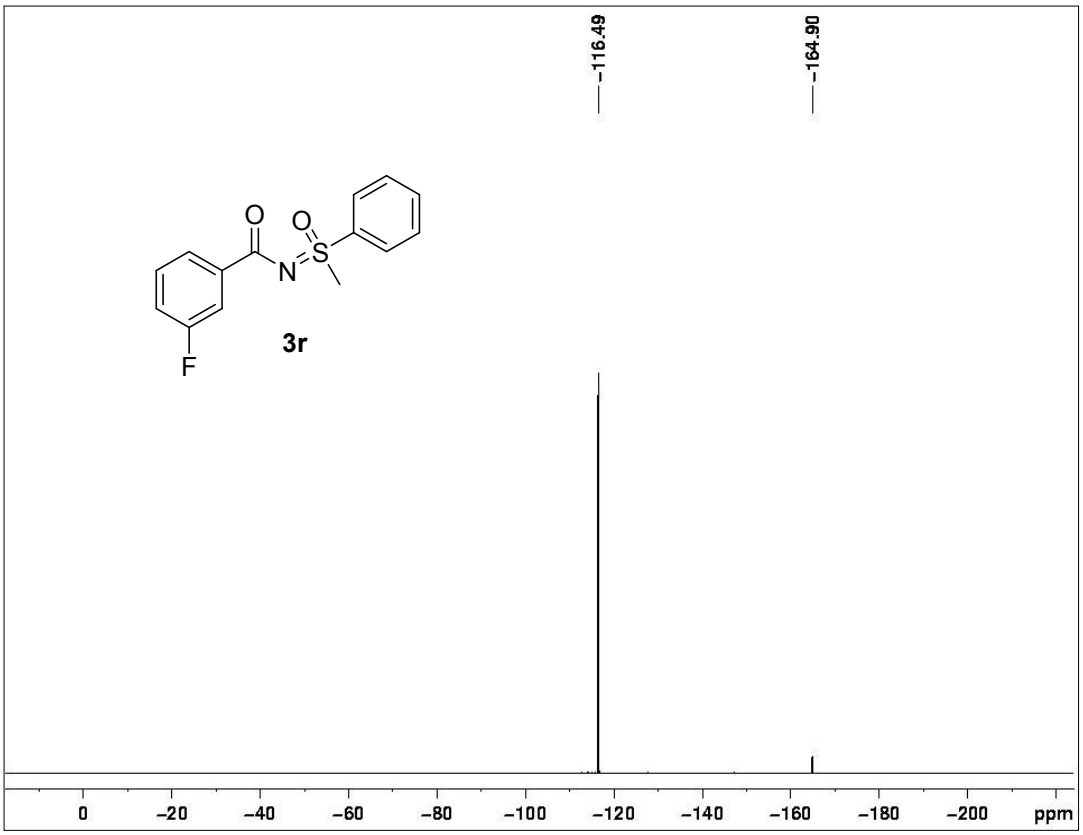


Figure 42: 470 MHz ^{19}F-NMR spectrum of **3r** in $CDCl_3$

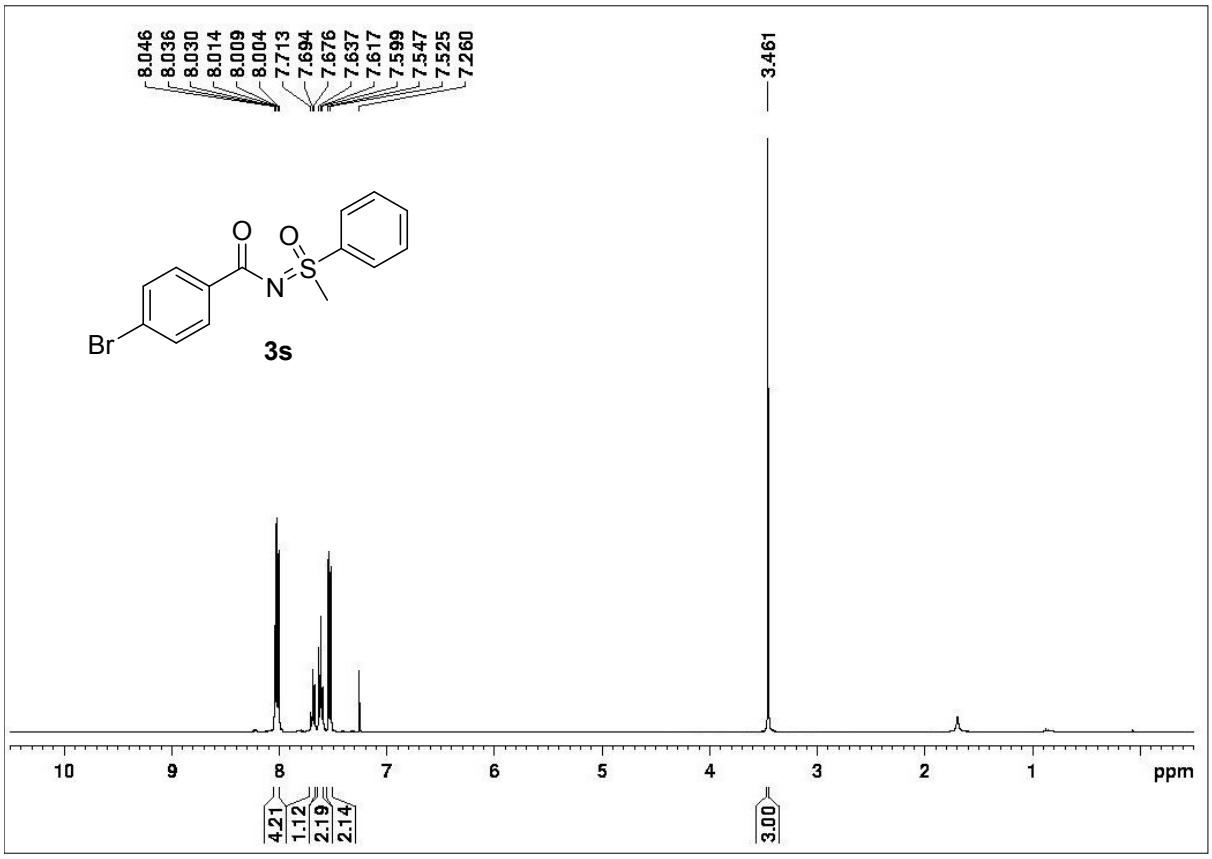


Figure 43: 400 MHz ^{1}H-NMR spectrum of **3s** in $CDCl_3$

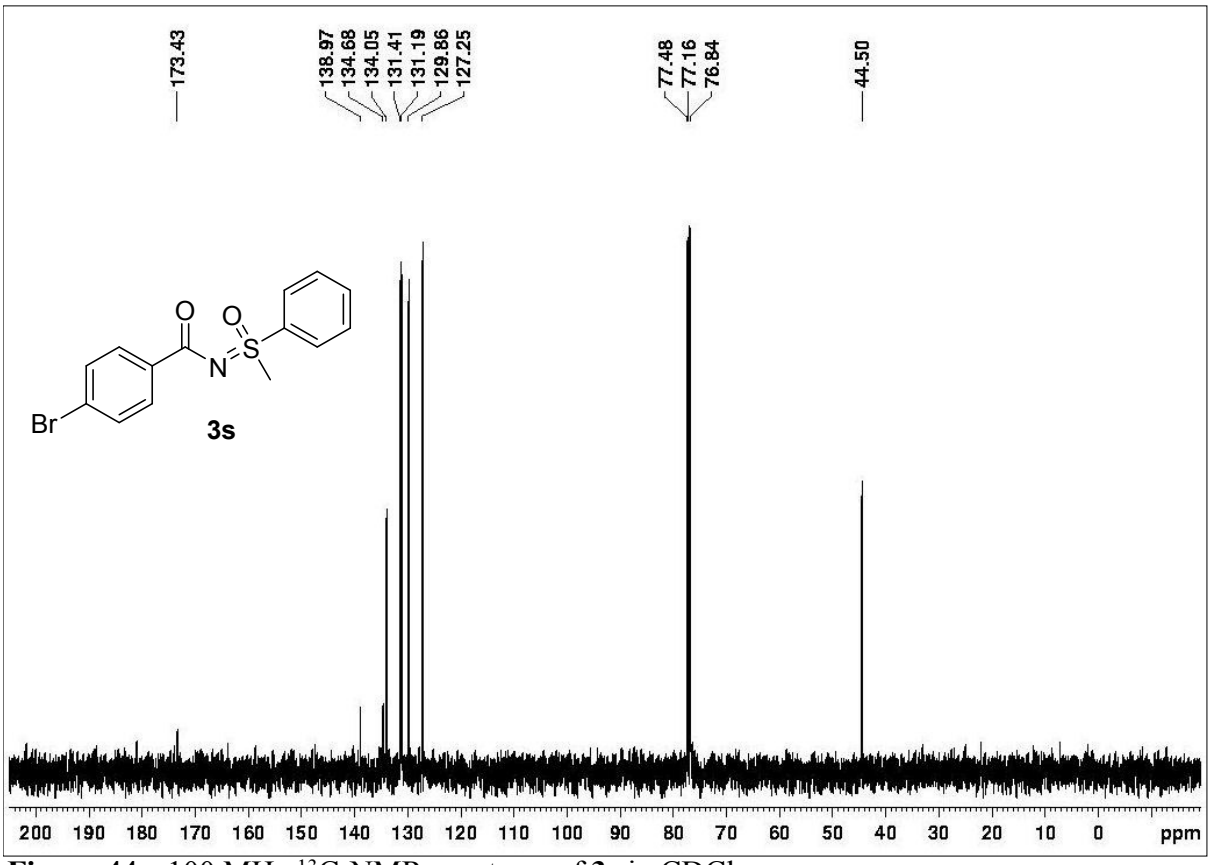


Figure 44: 100 MHz ^{13}C-NMR spectrum of **3s** in $CDCl_3$

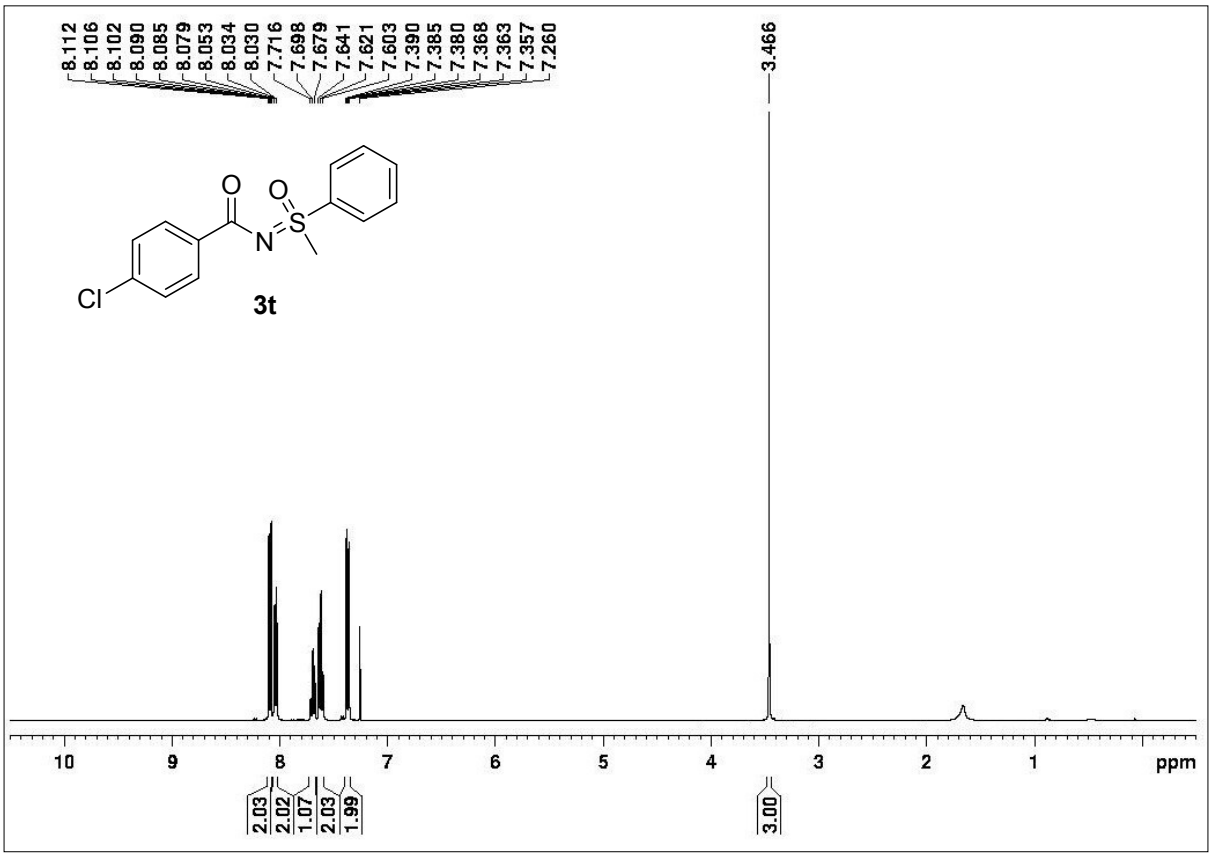


Figure 45: 400 MHz ^{1}H-NMR spectrum of **3t** in $CDCl_3$

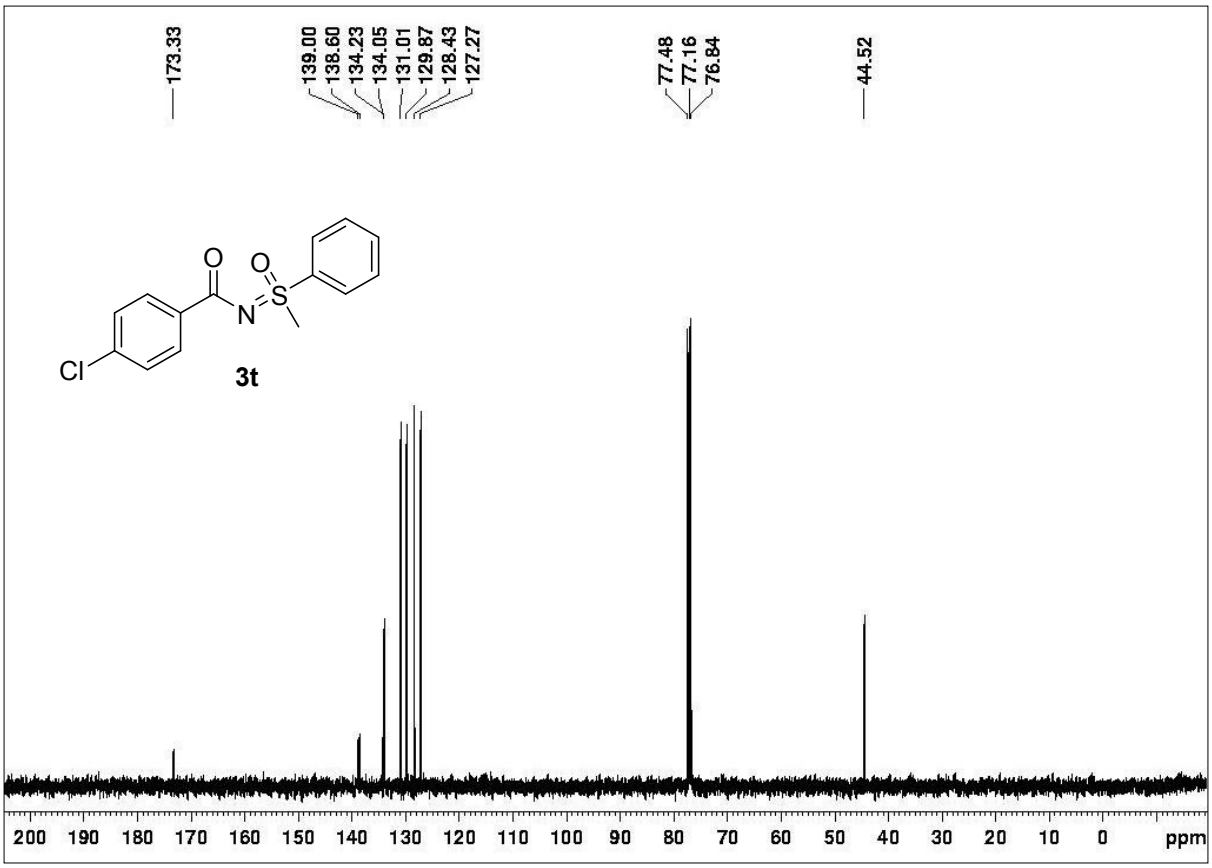


Figure 46: 100 MHz ^{13}C-NMR spectrum of **3t** in $CDCl_3$

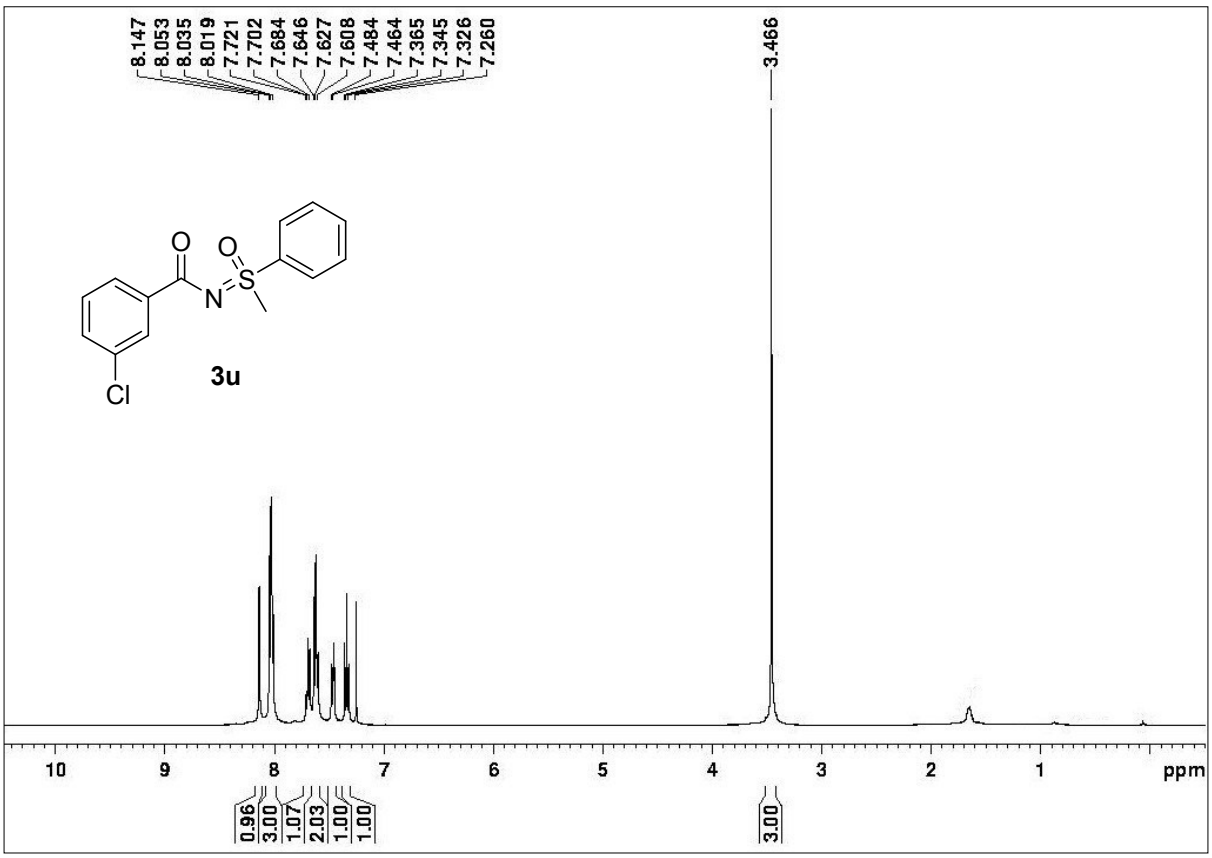


Figure 47: 400 MHz ^{1}H-NMR spectrum of **3u** in $CDCl_3$

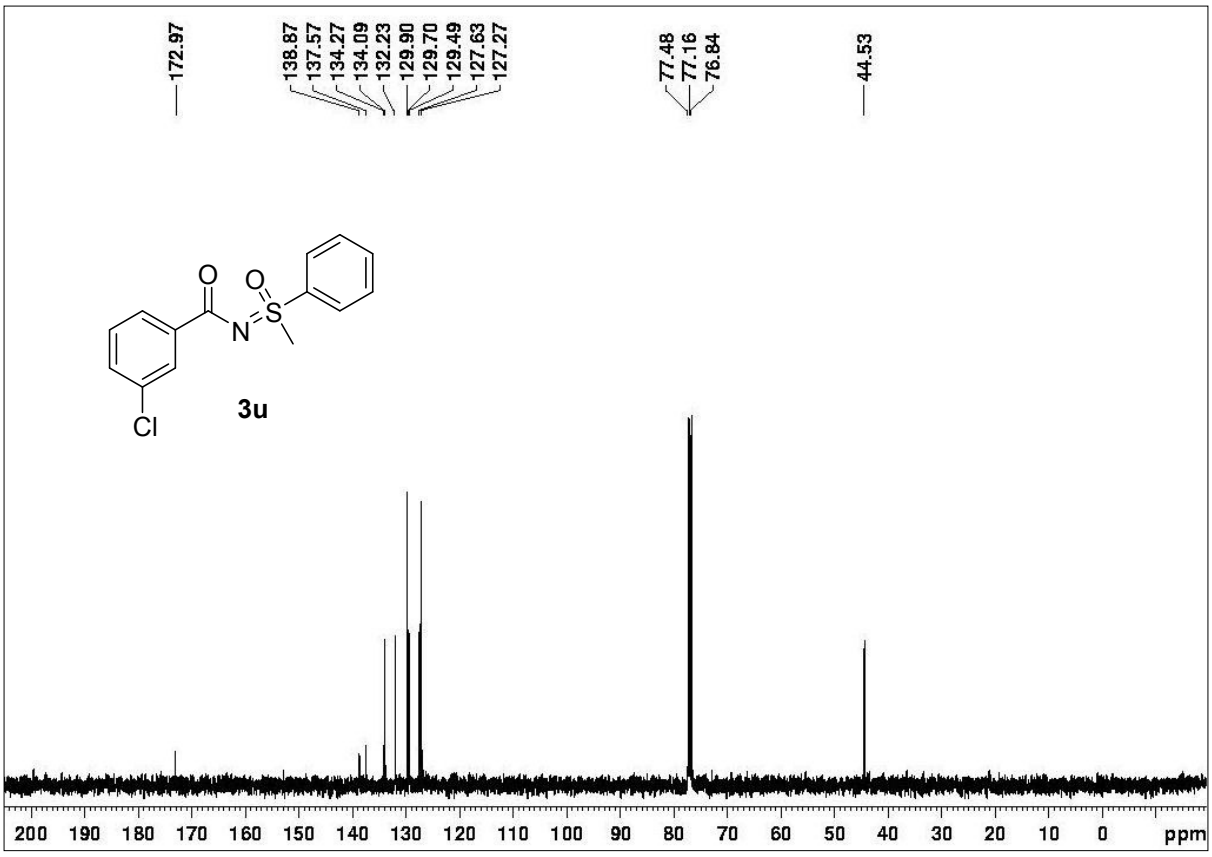


Figure 48: 100 MHz ^{13}C-NMR spectrum of **3u** in $CDCl_3$

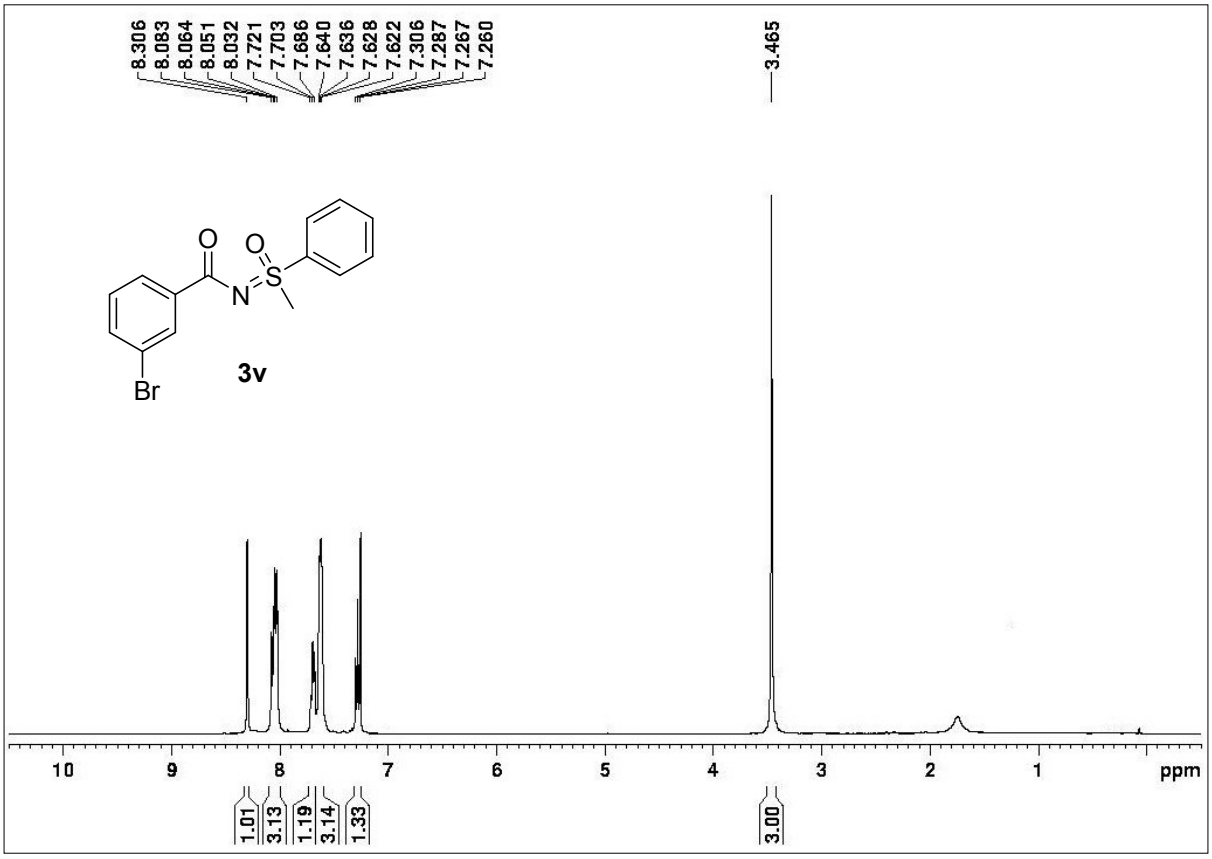


Figure 49: 400 MHz ^{1}H-NMR spectrum of **3v** in $CDCl_3$

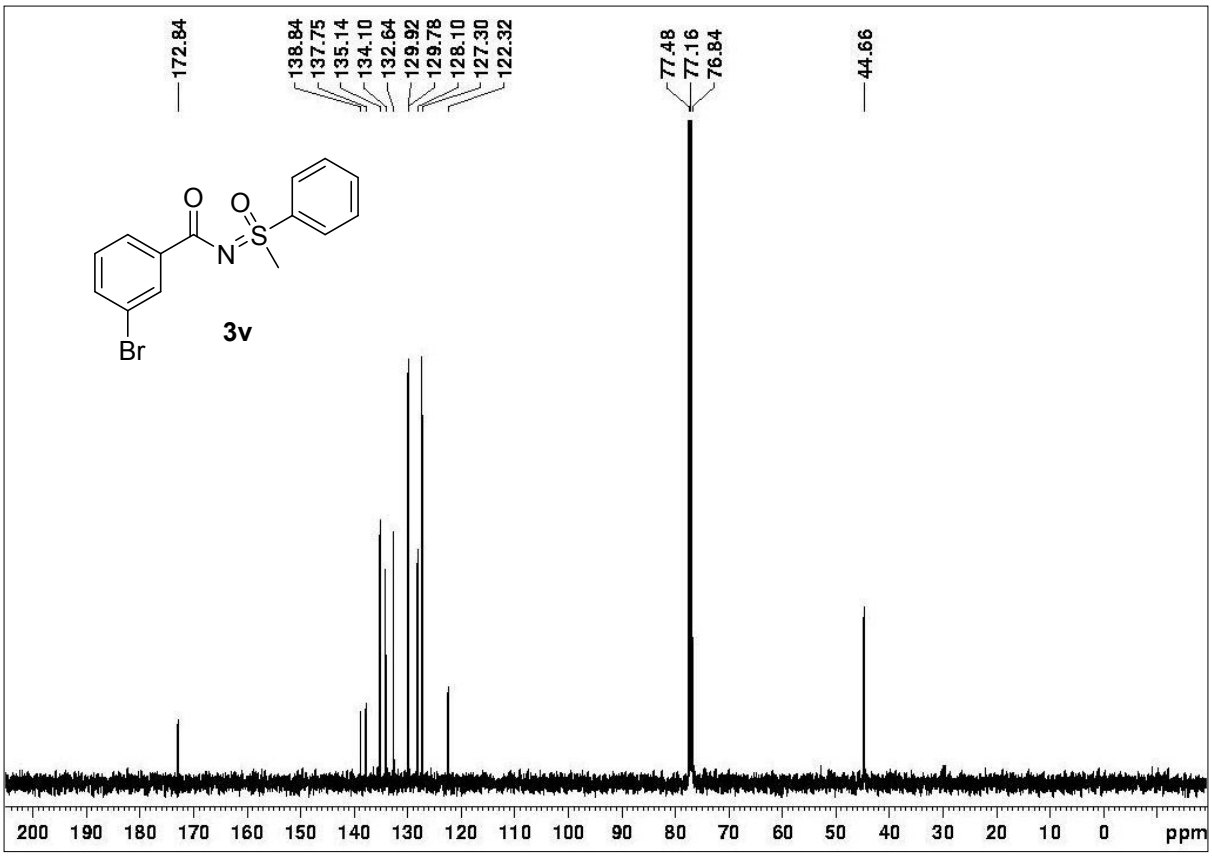


Figure 50: 100 MHz ^{13}C-NMR spectrum of **3v** in $CDCl_3$

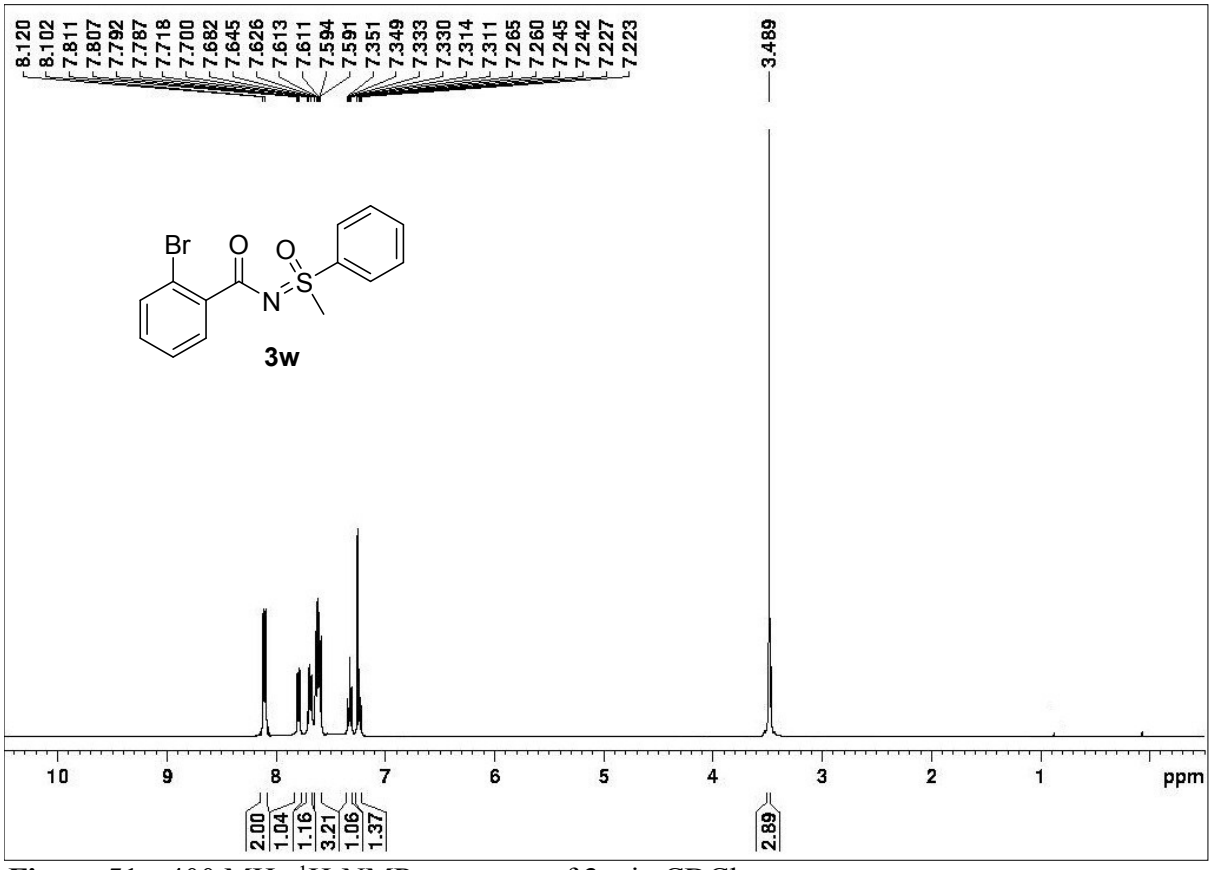


Figure 51: 400 MHz ^{1}H-NMR spectrum of **3w** in $CDCl_3$

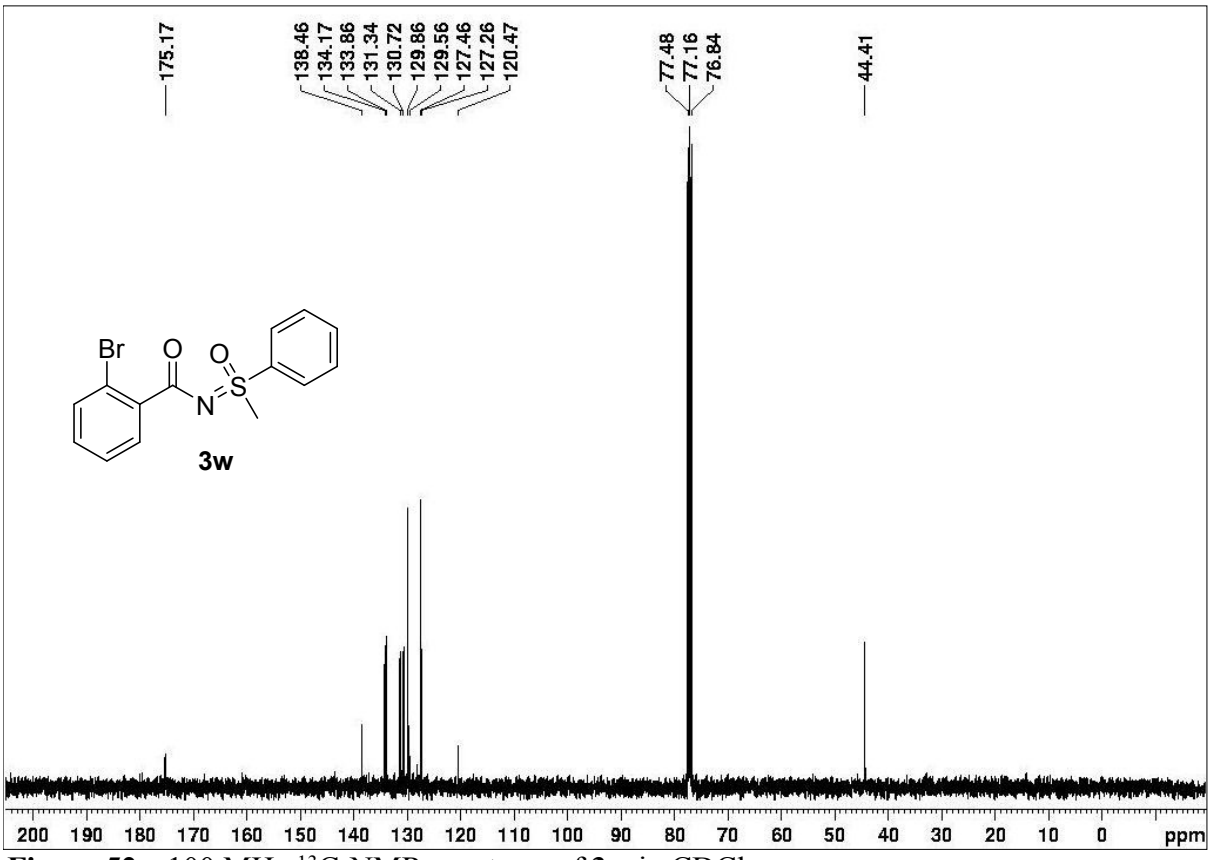


Figure 52: 100 MHz ^{13}C-NMR spectrum of **3w** in $CDCl_3$

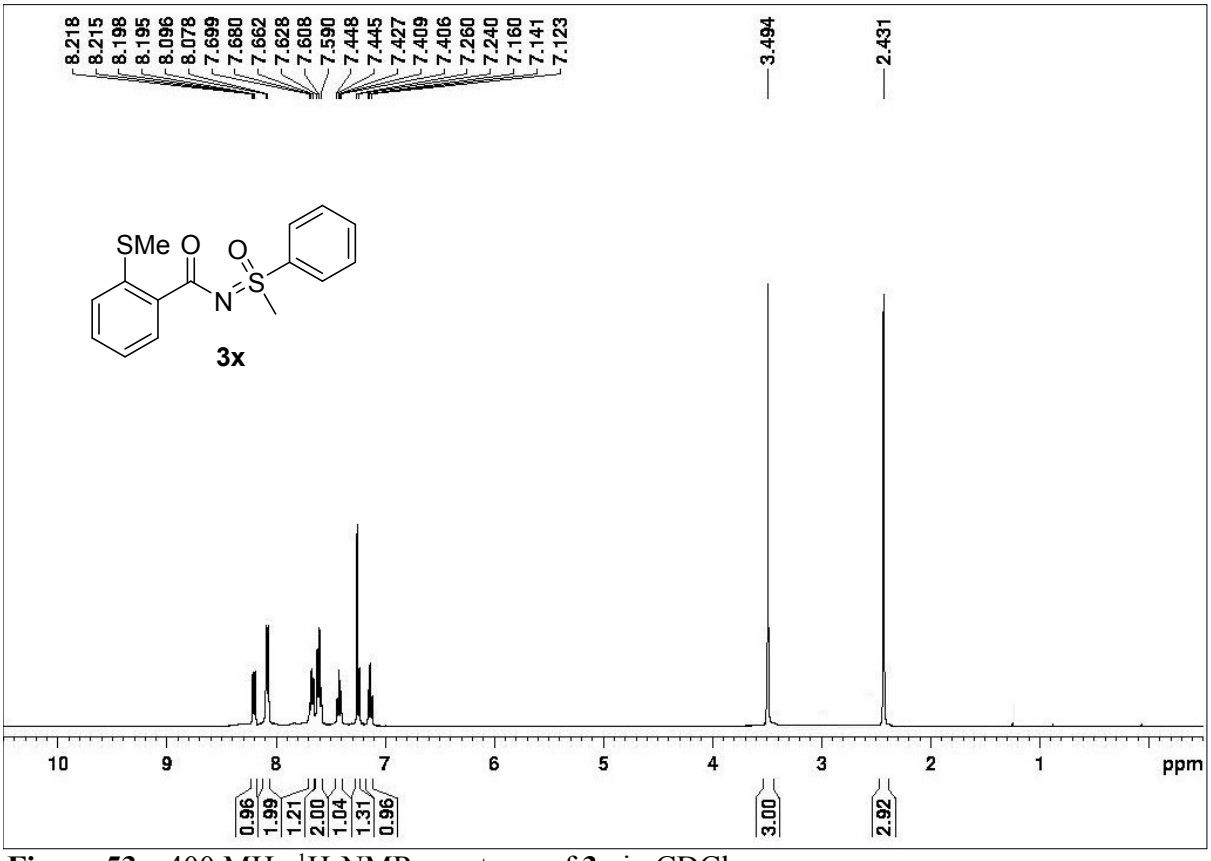


Figure 53: 400 MHz ^{1}H-NMR spectrum of **3x** in $CDCl_3$

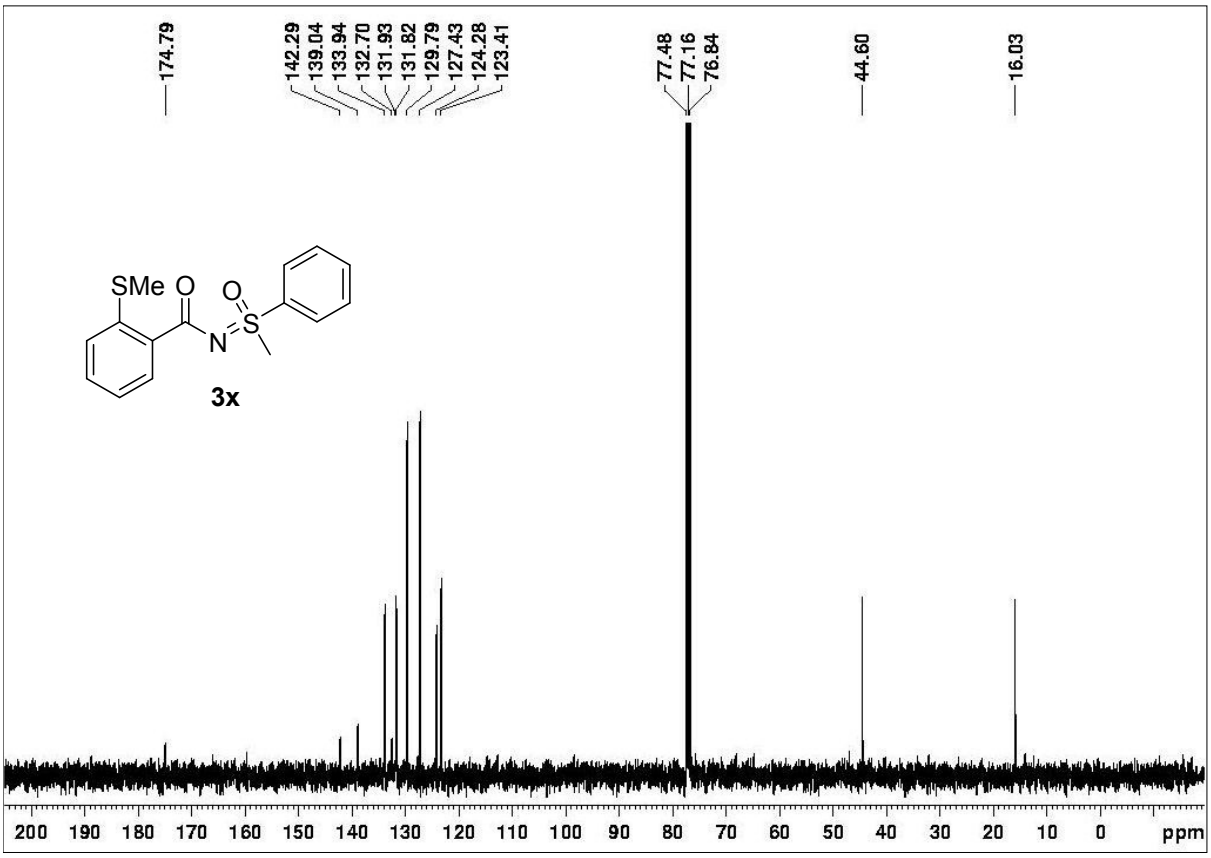


Figure 54: 100 MHz ^{13}C-NMR spectrum of **3x** in $CDCl_3$

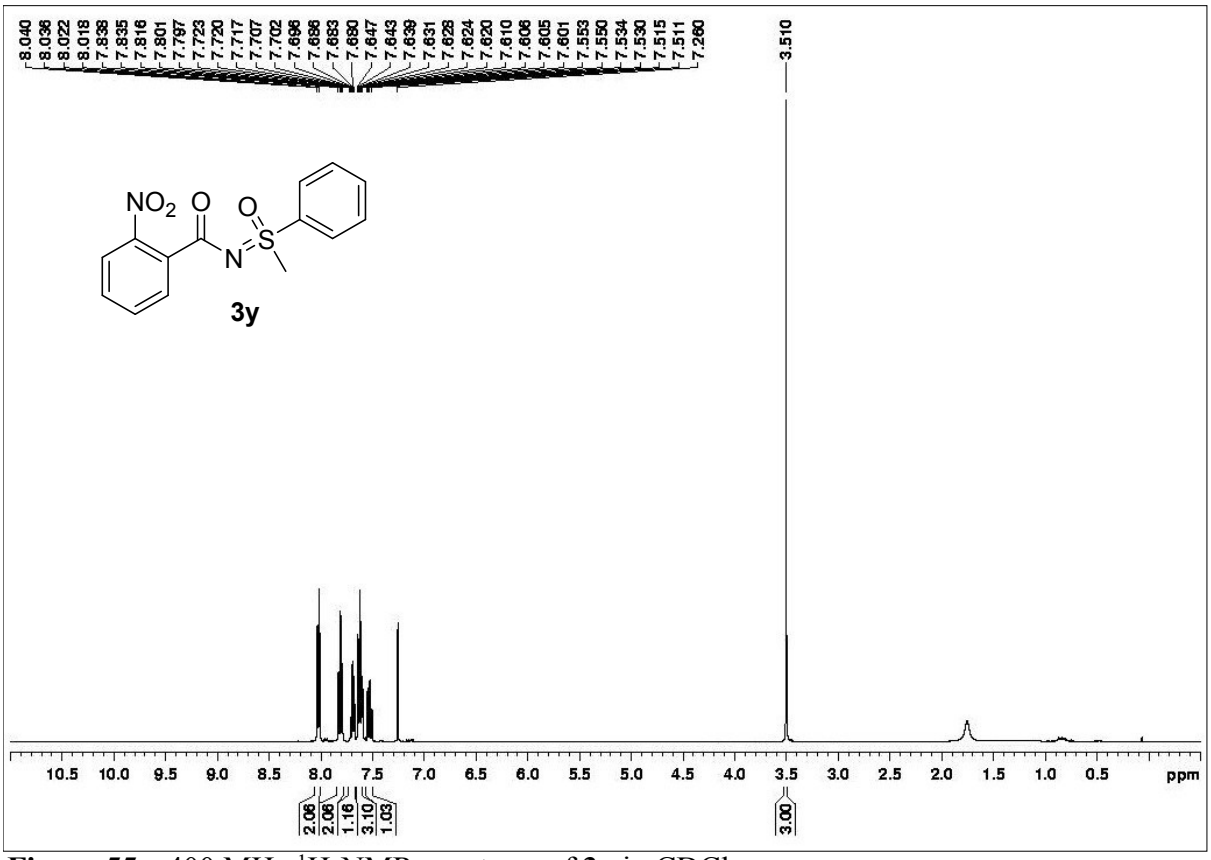


Figure 55: 400 MHz ^{1}H-NMR spectrum of **3y** in $CDCl_3$

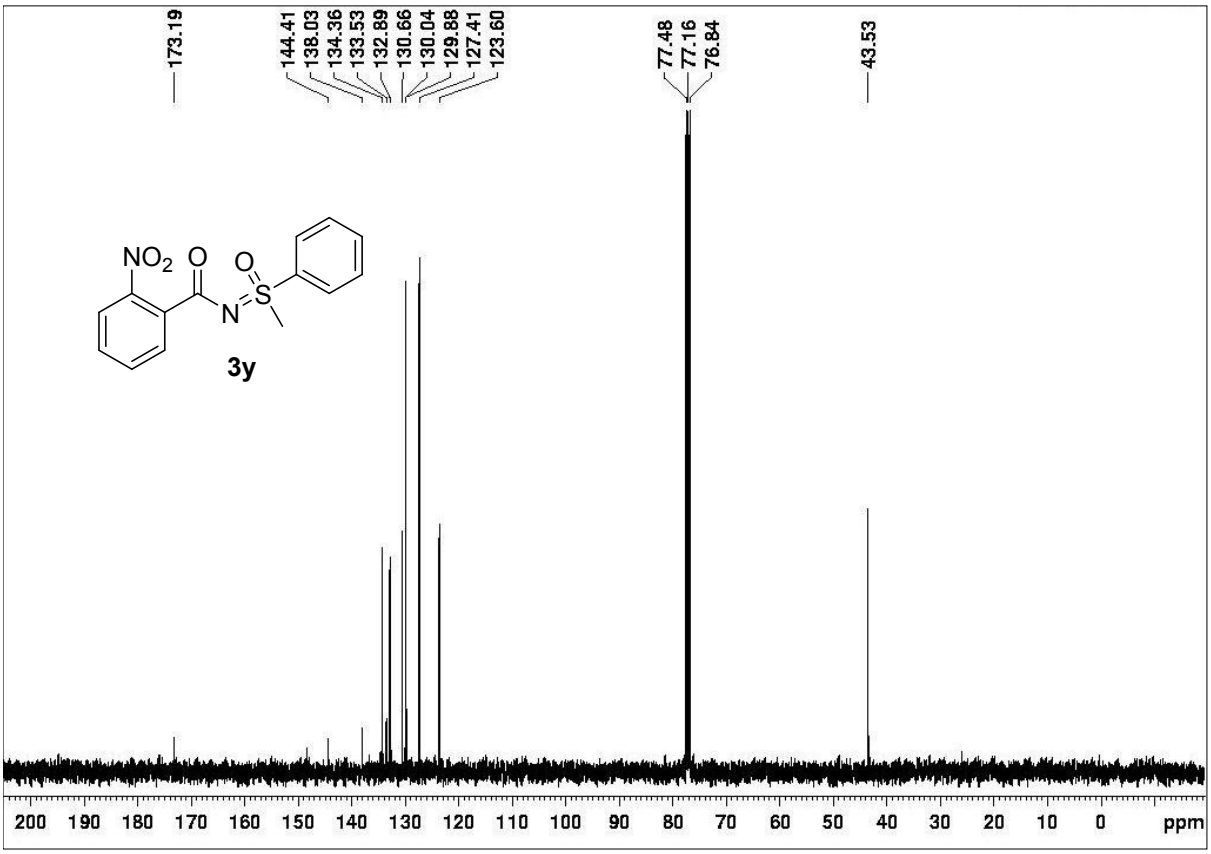


Figure 56: 100 MHz ^{13}C-NMR spectrum of **3y** in $CDCl_3$

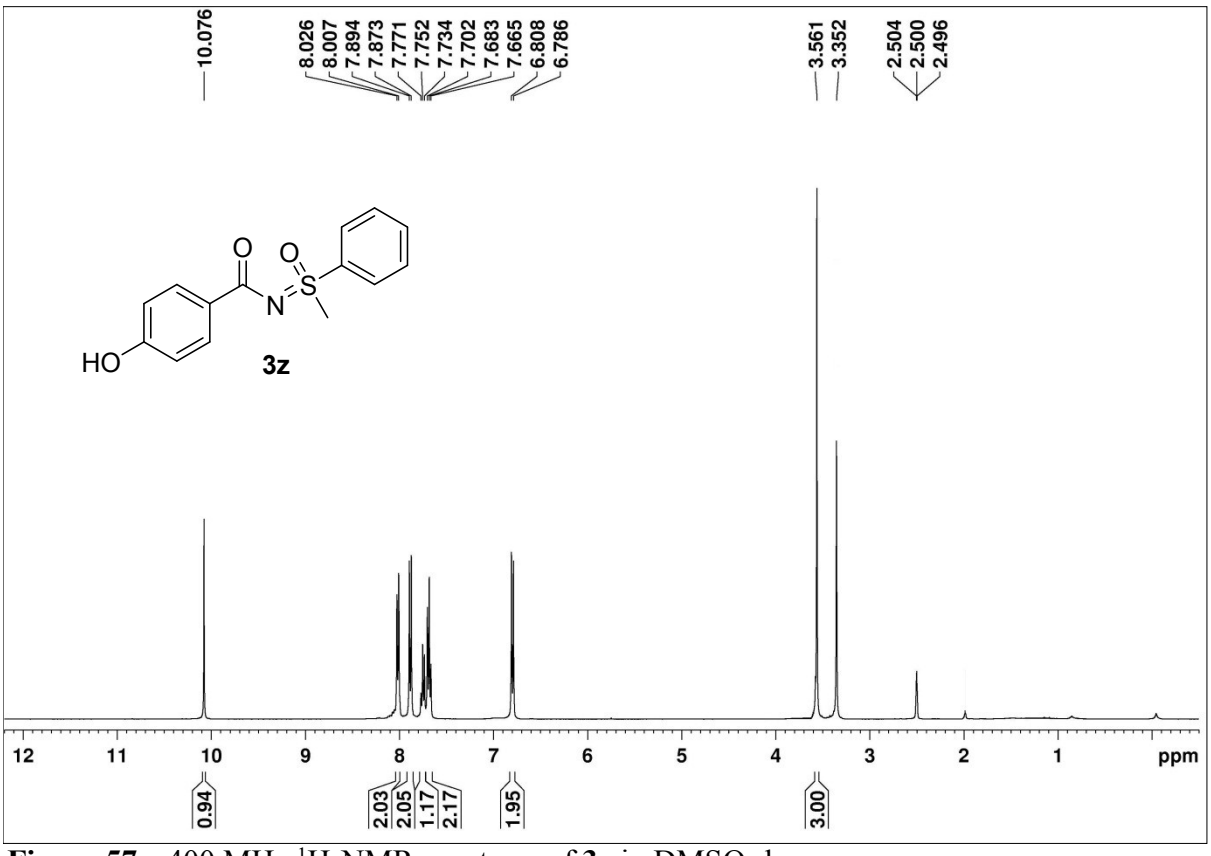


Figure 57: 400 MHz ^{1}H-NMR spectrum of **3z** in DMSO-d_6

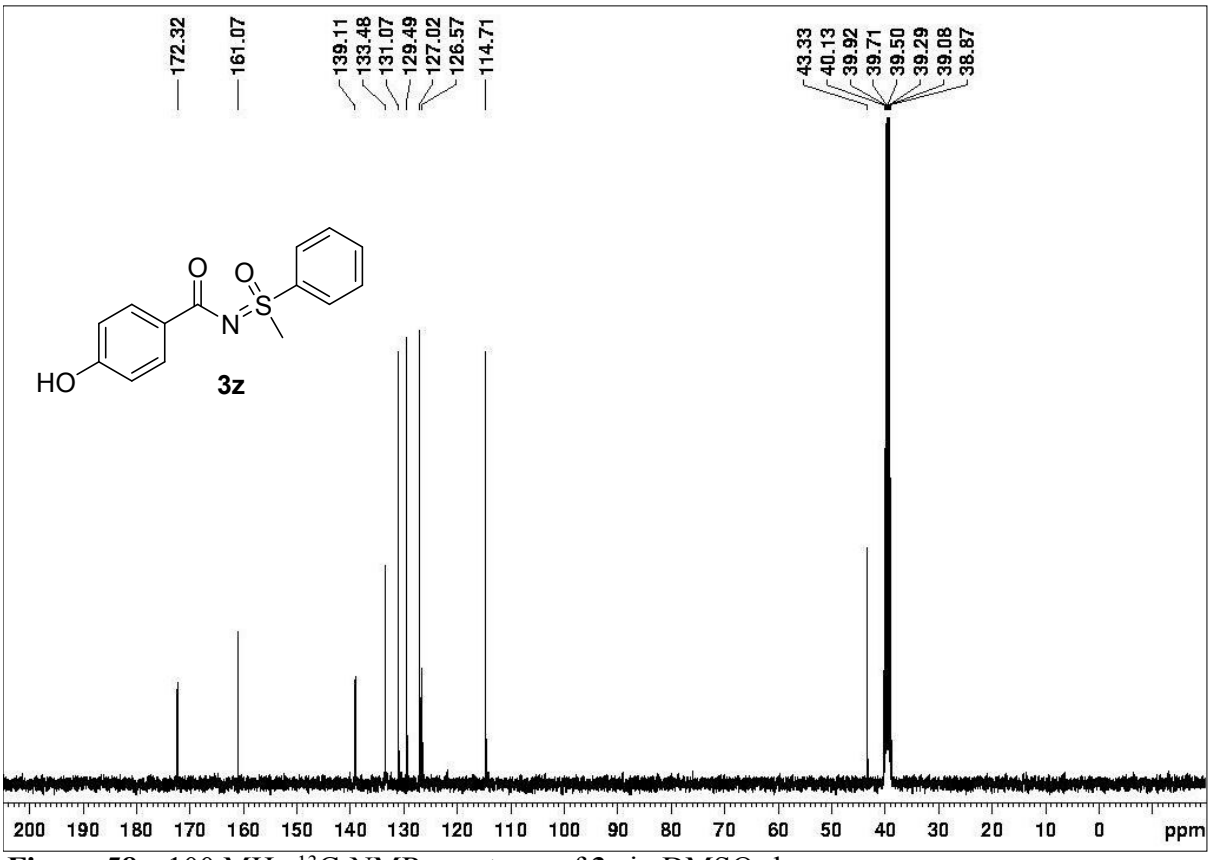


Figure 58: 100 MHz ^{13}C-NMR spectrum of **3z** in DMSO-d_6

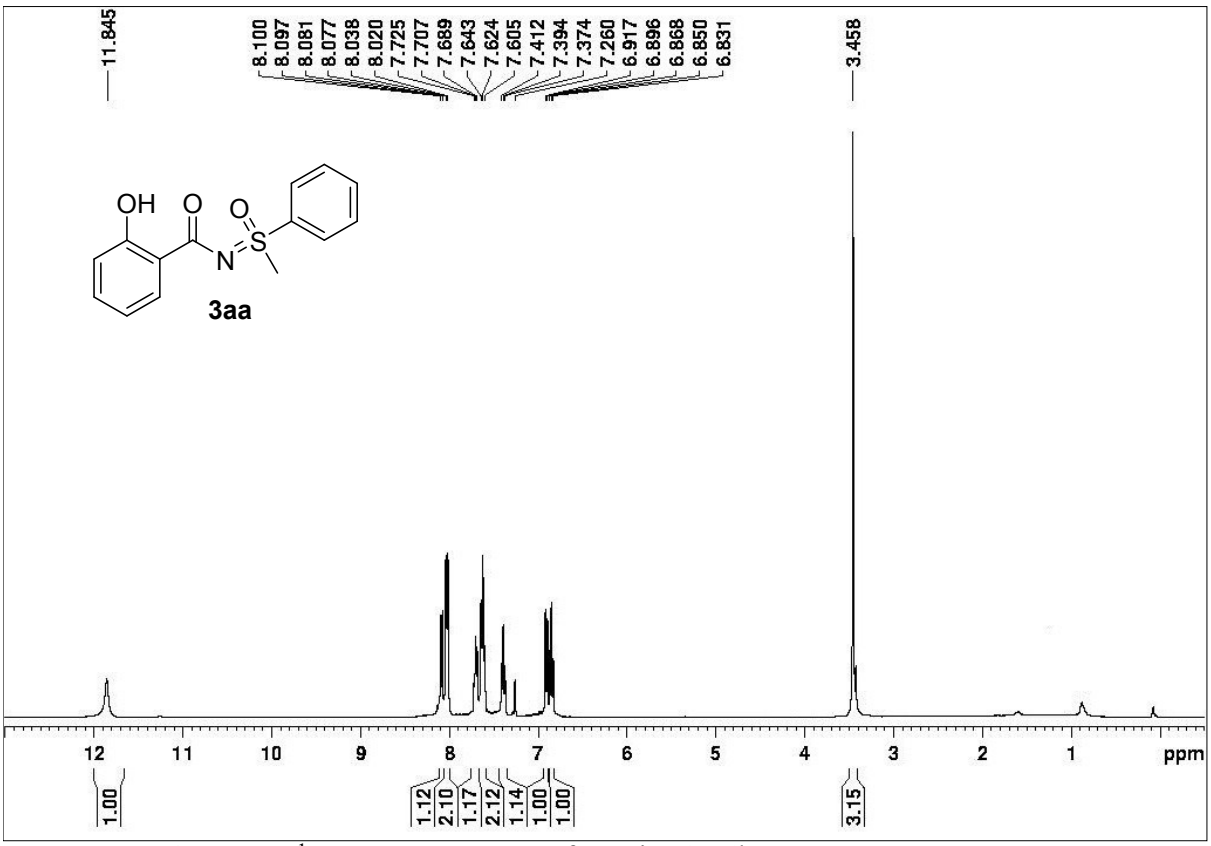


Figure 59: 400 MHz ^{1}H-NMR spectrum of **3aa** in $CDCl_3$

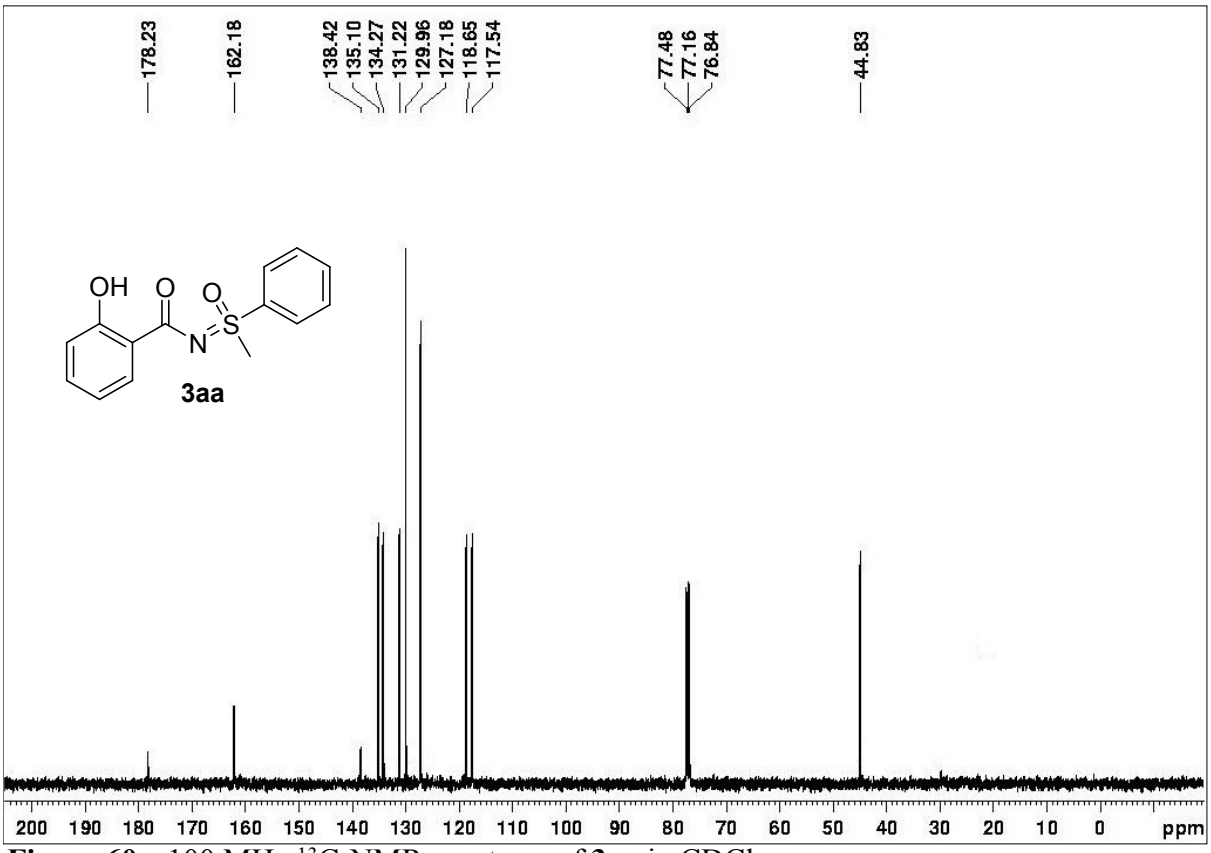


Figure 60: 100 MHz ^{13}C-NMR spectrum of **3aa** in $CDCl_3$

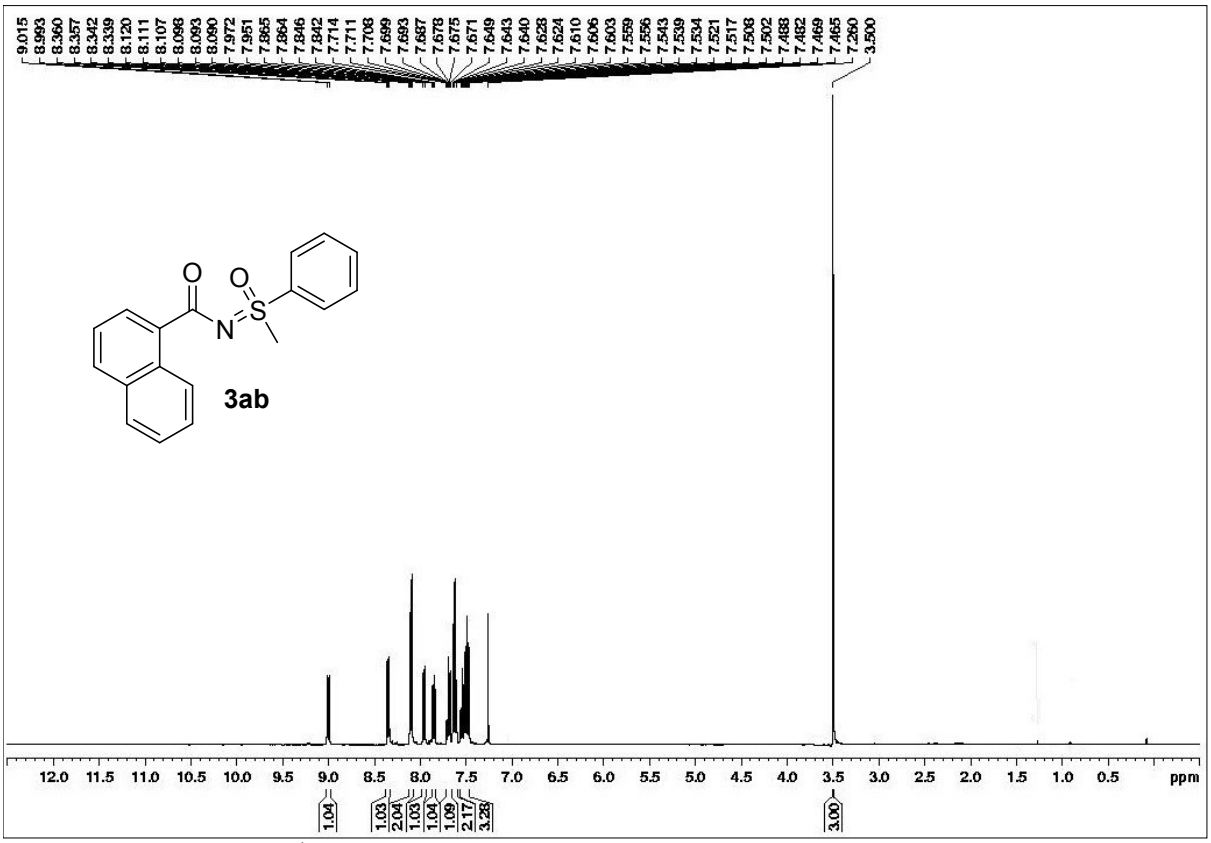


Figure 61: 400 MHz ^{1}H-NMR spectrum of **3ab** in $CDCl_3$

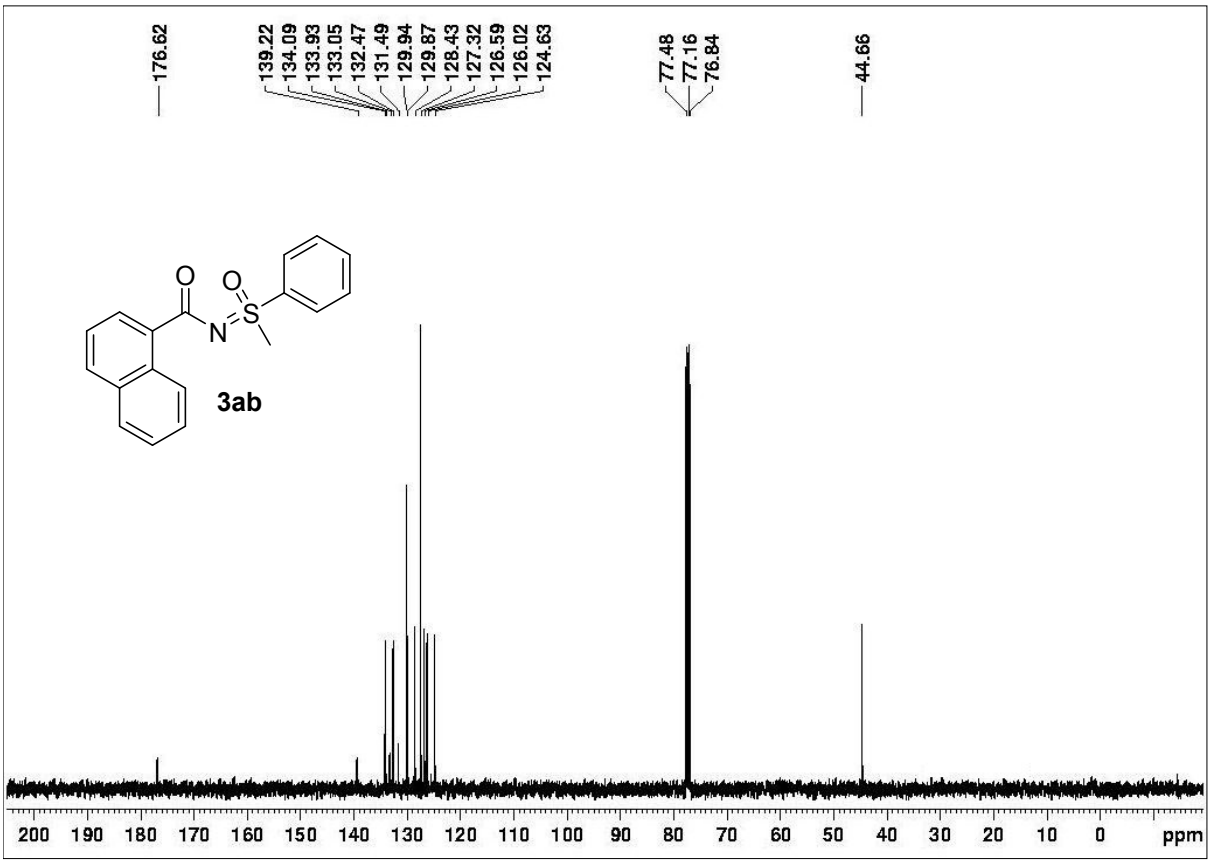


Figure 62: 100 MHz ^{13}C-NMR spectrum of **3ab** in $CDCl_3$

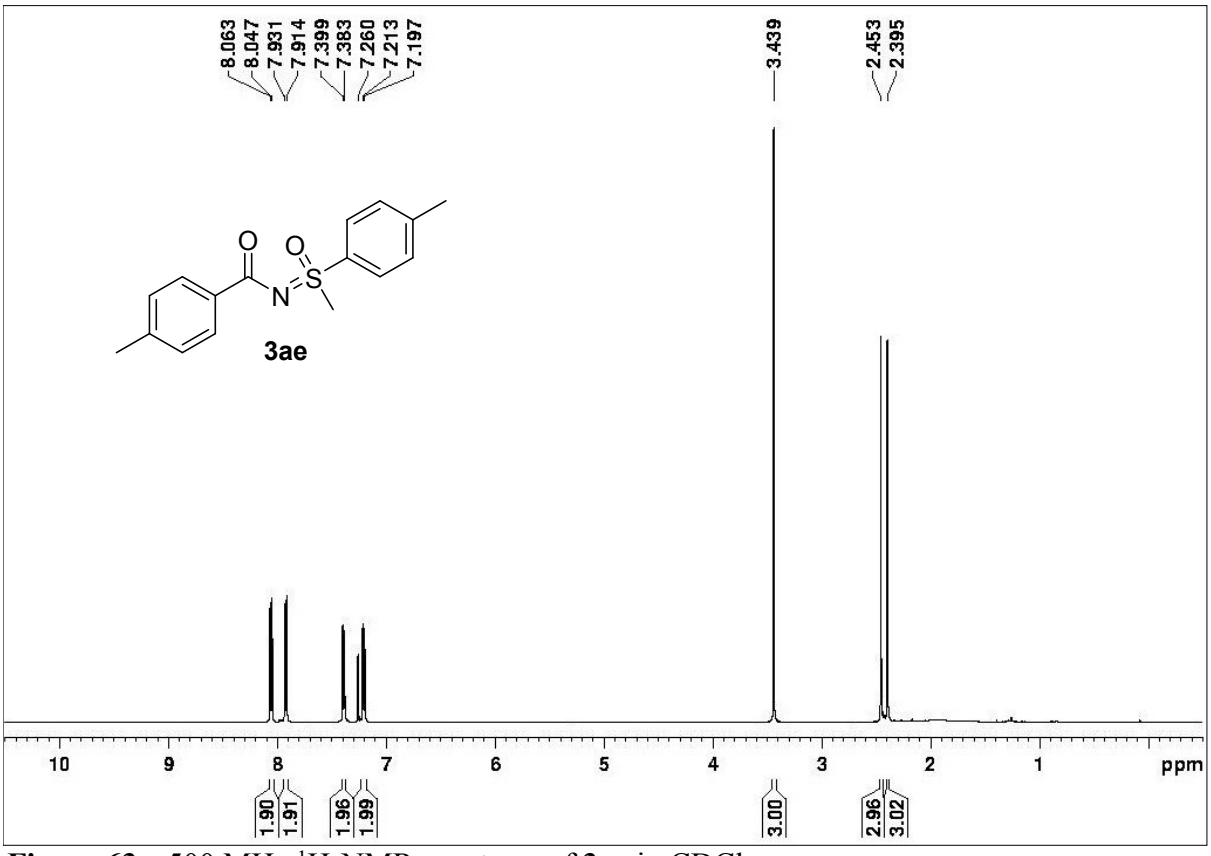


Figure 63: 500 MHz ^{1}H-NMR spectrum of **3ae** in $CDCl_3$

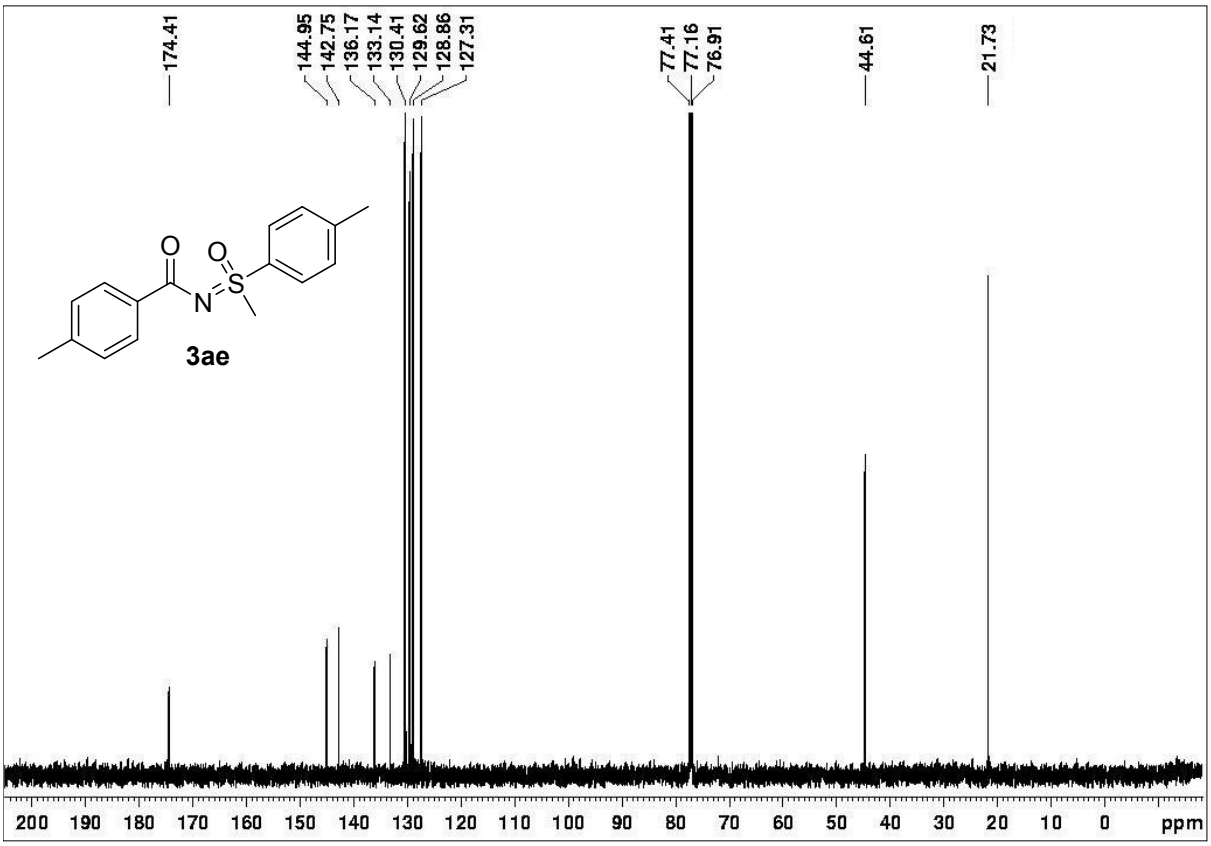


Figure 64: 125 MHz ^{13}C-NMR spectrum of **3ae** in $CDCl_3$

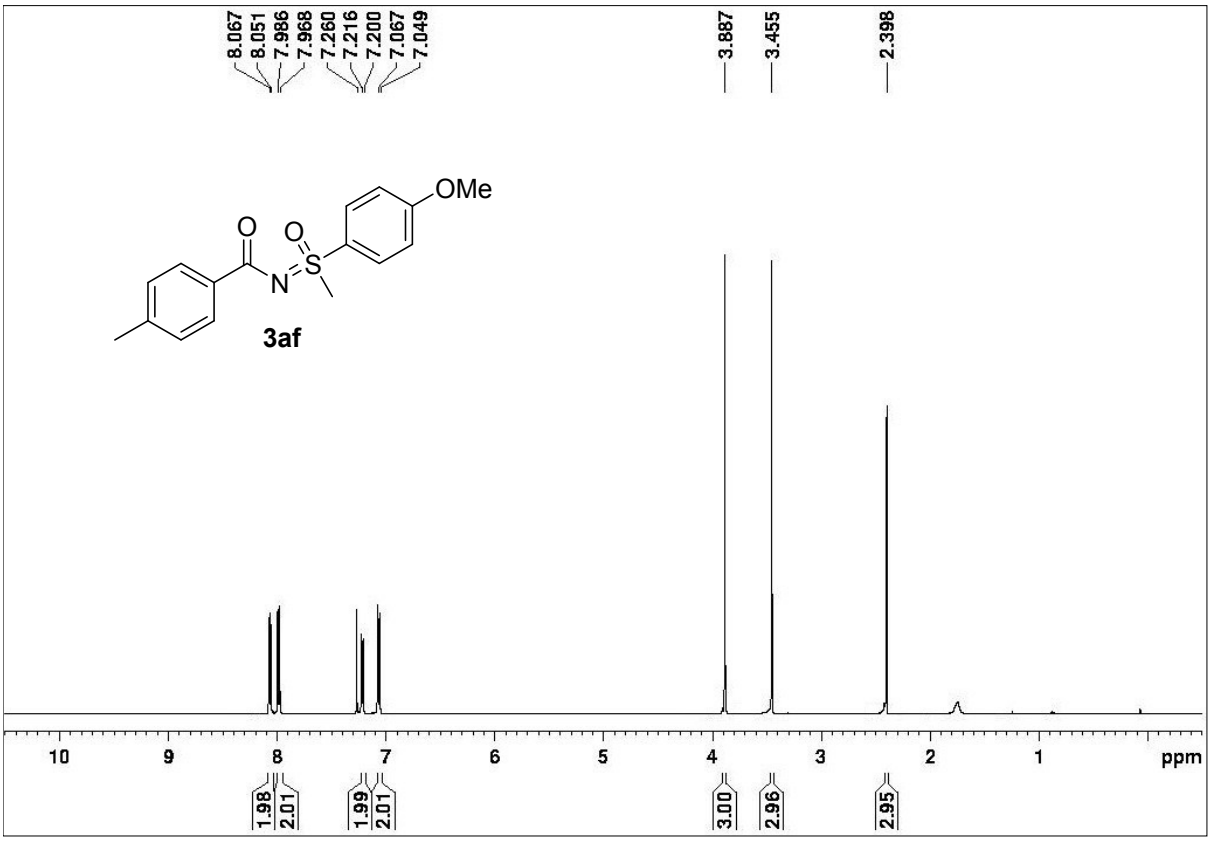


Figure 65: 500 MHz ^{1}H-NMR spectrum of **3af** in $CDCl_3$

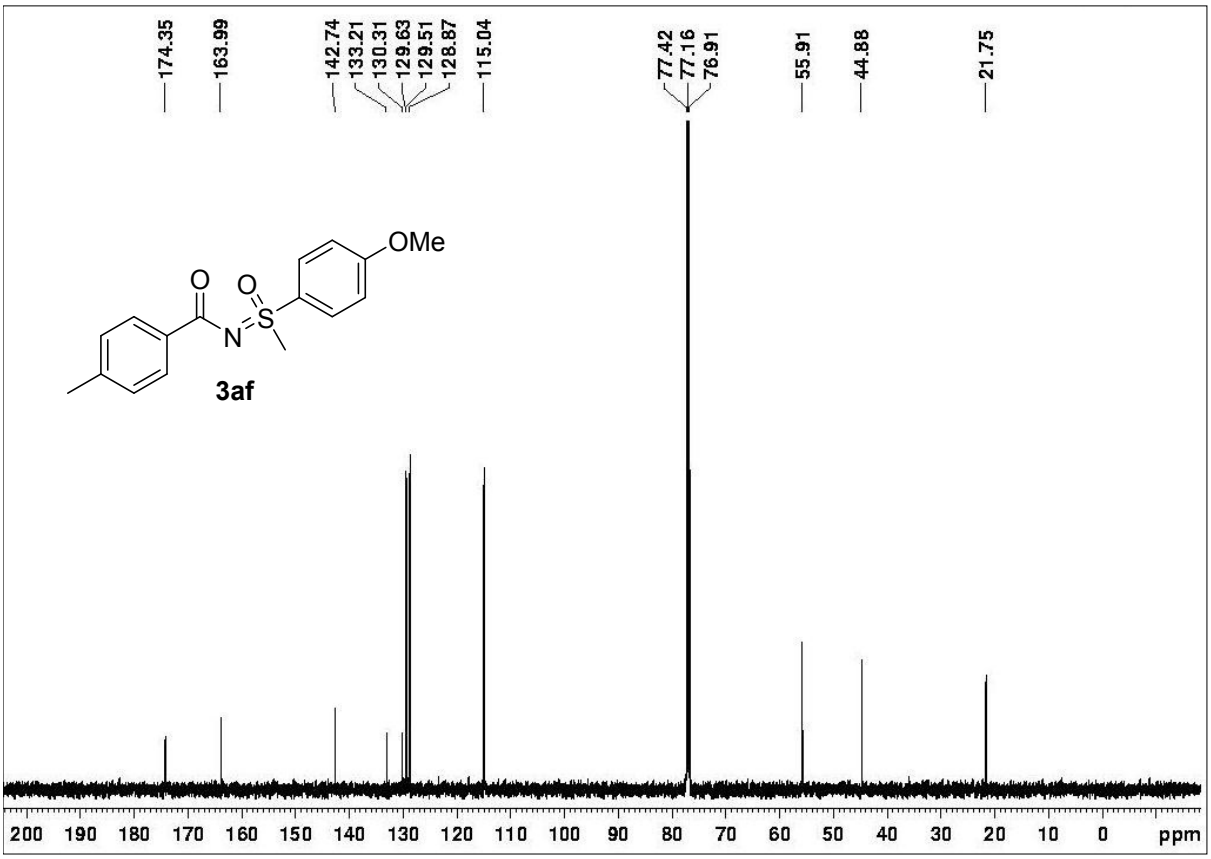


Figure 66: 125 MHz ^{13}C-NMR spectrum of **3af** in $CDCl_3$

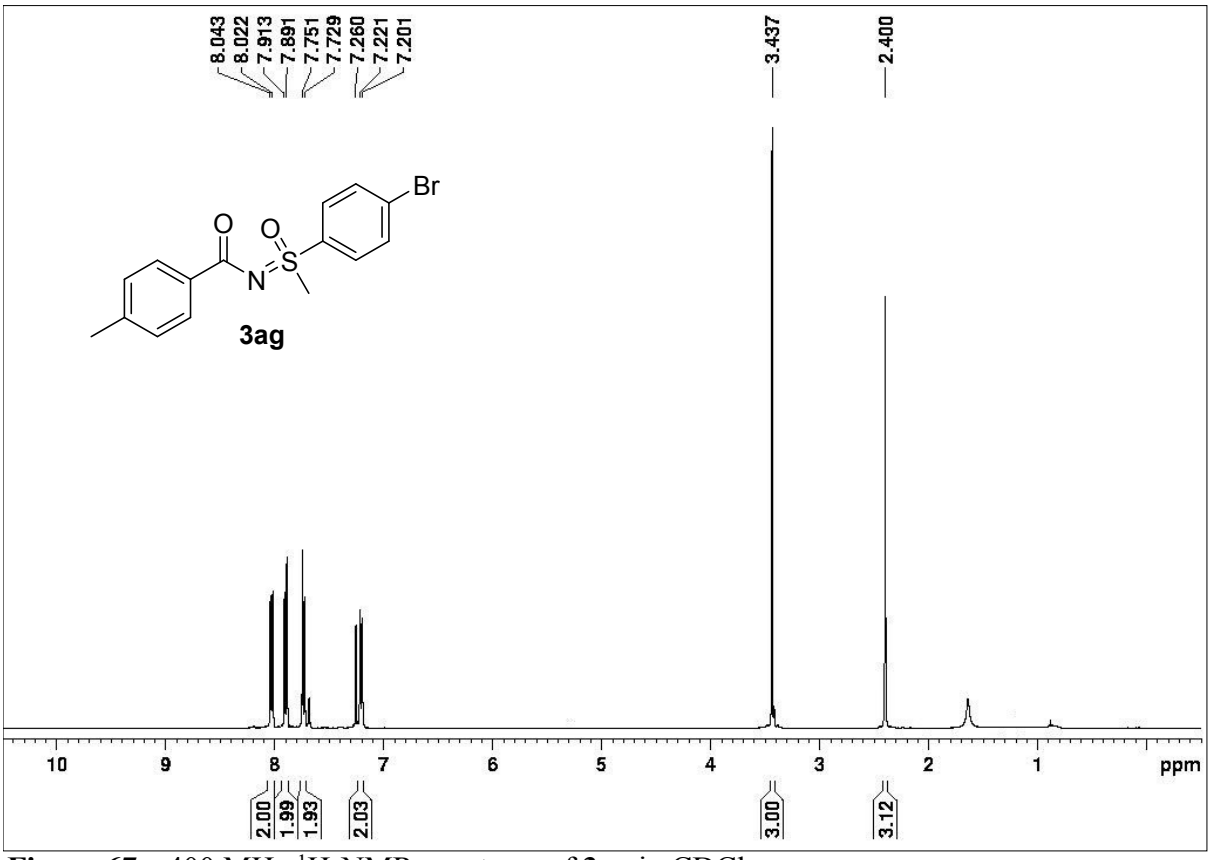


Figure 67: 400 MHz ^{1}H-NMR spectrum of **3ag** in $CDCl_3$

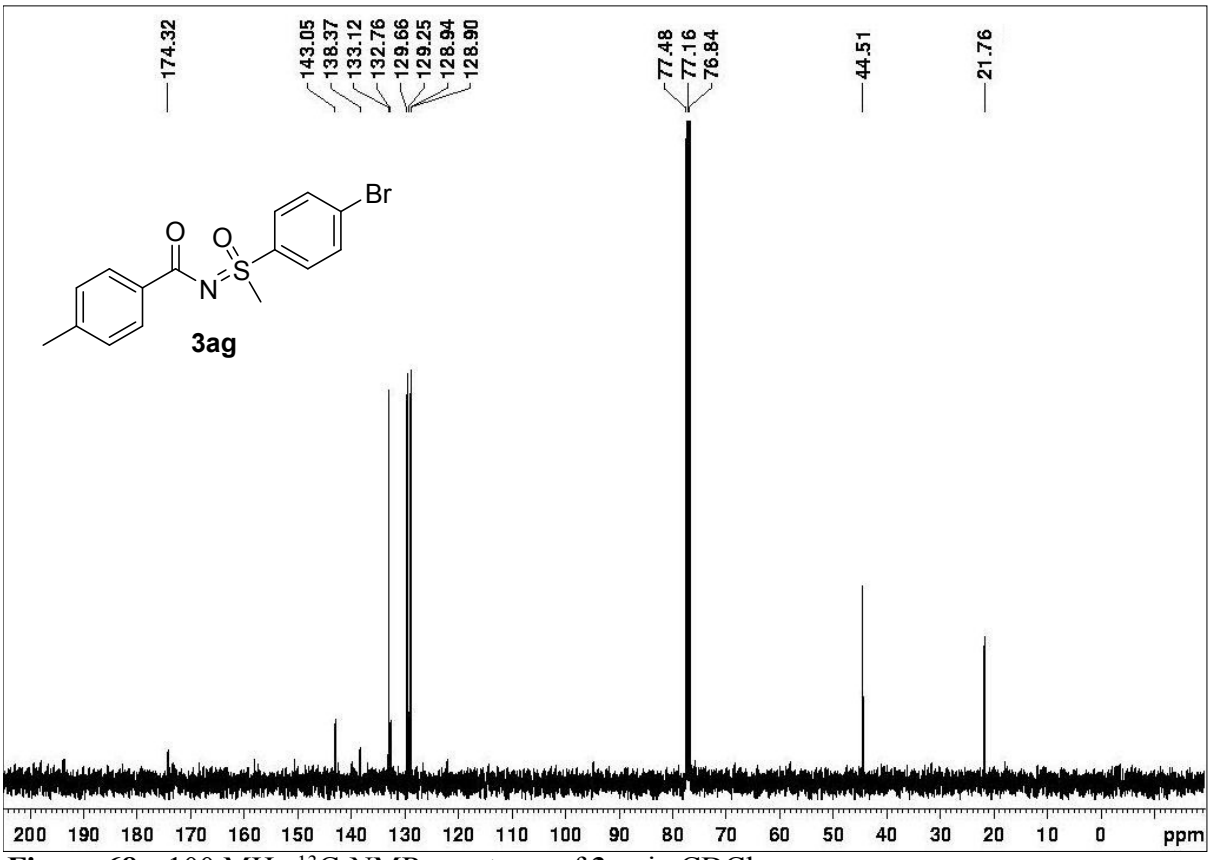


Figure 68: 100 MHz ^{13}C-NMR spectrum of **3ag** in $CDCl_3$

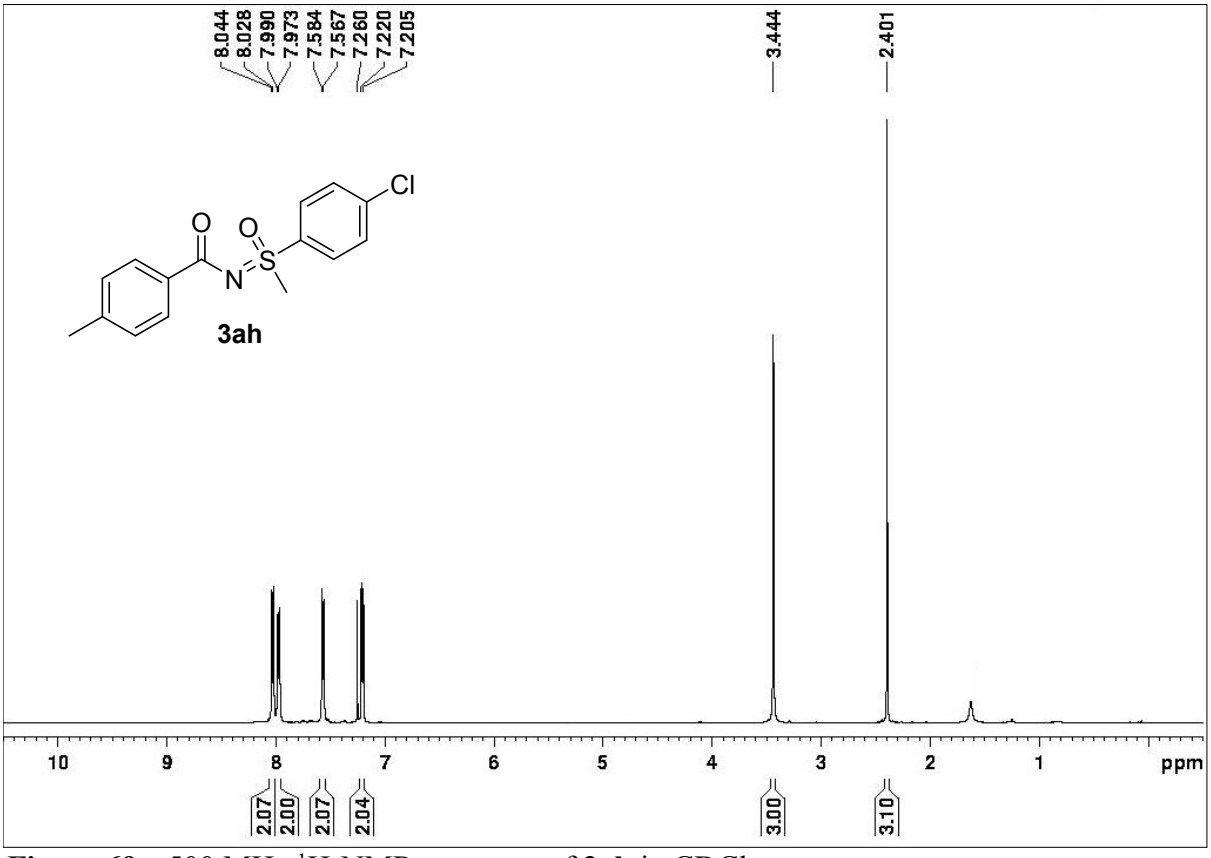


Figure 69: 500 MHz ^{1}H-NMR spectrum of **3ah** in $CDCl_3$

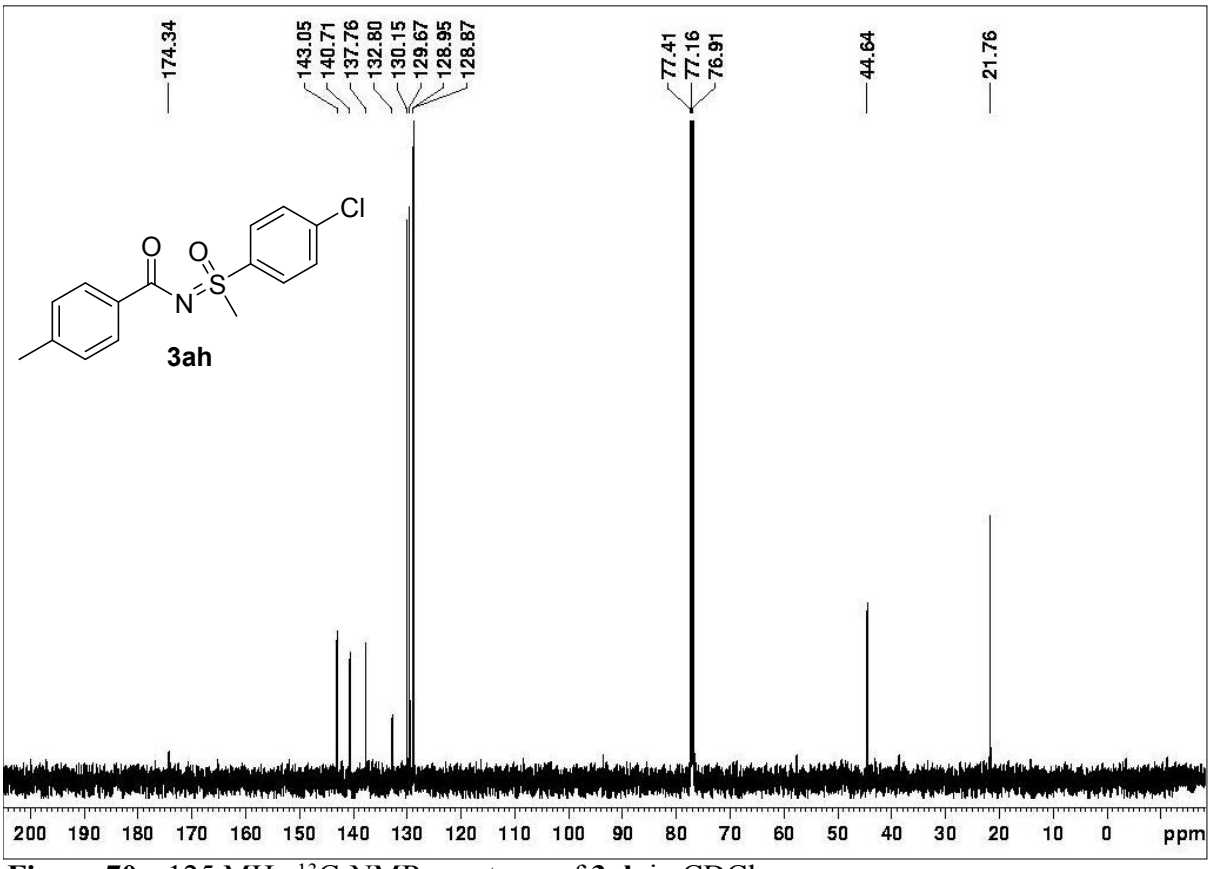


Figure 70: 125 MHz ^{13}C-NMR spectrum of **3ah** in $CDCl_3$

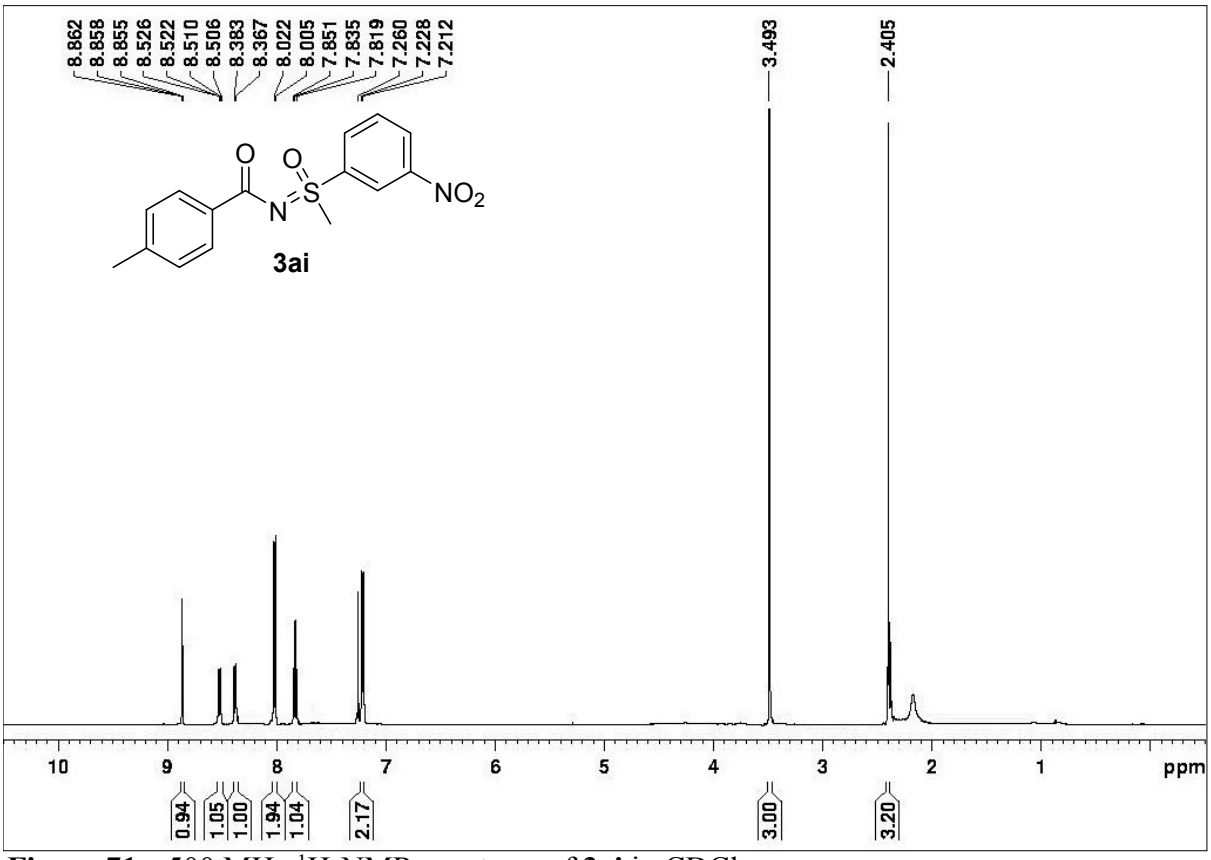


Figure 71: 500 MHz ^{1}H-NMR spectrum of **3ai** in $CDCl_3$

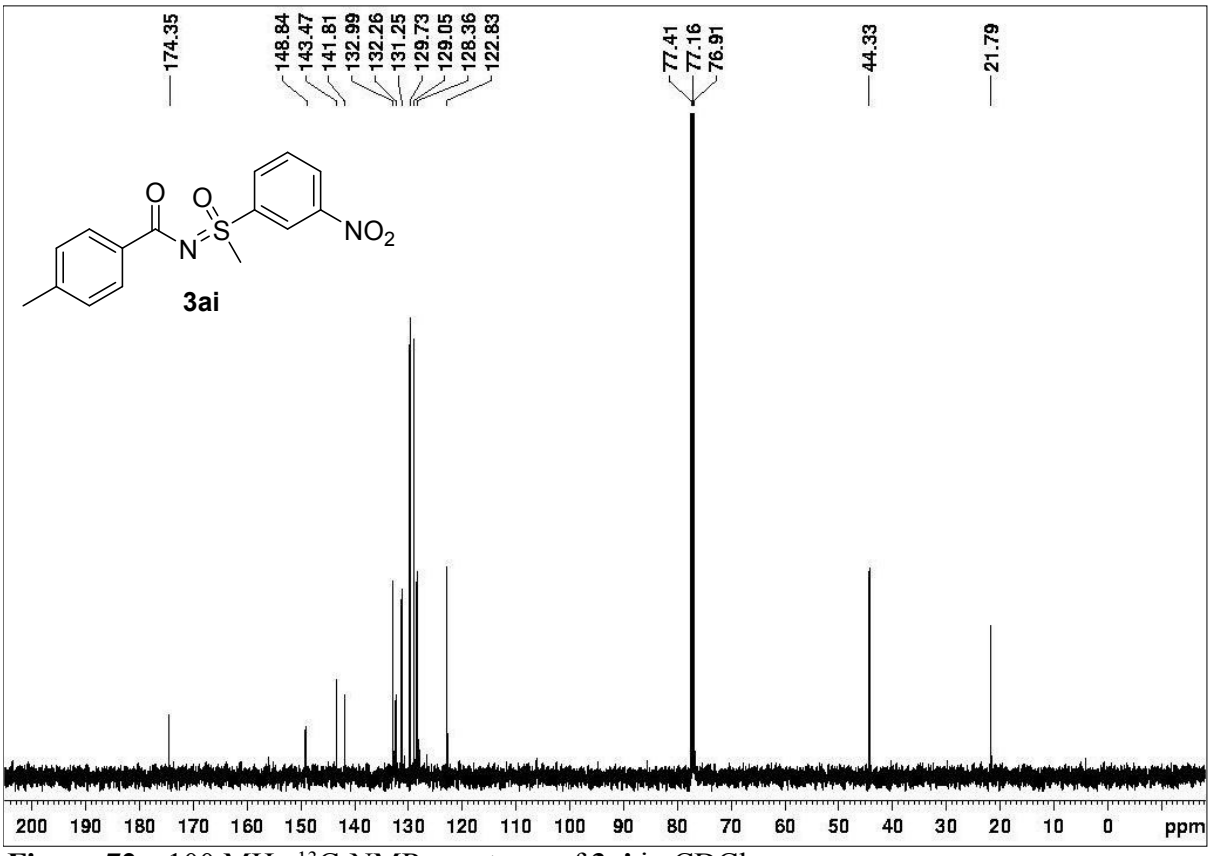


Figure 72: 100 MHz ^{13}C-NMR spectrum of **3ai** in $CDCl_3$

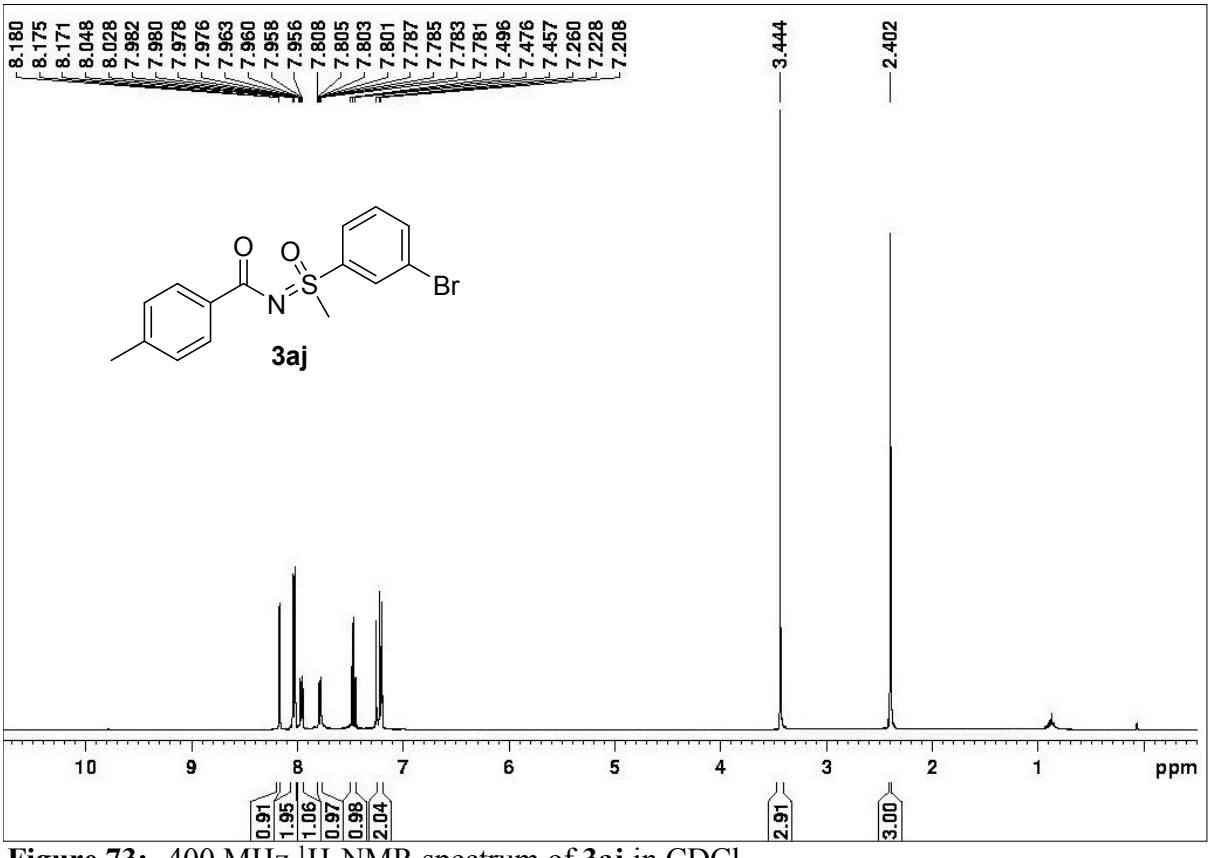


Figure 73: 400 MHz ^{1}H-NMR spectrum of **3aj** in $CDCl_3$

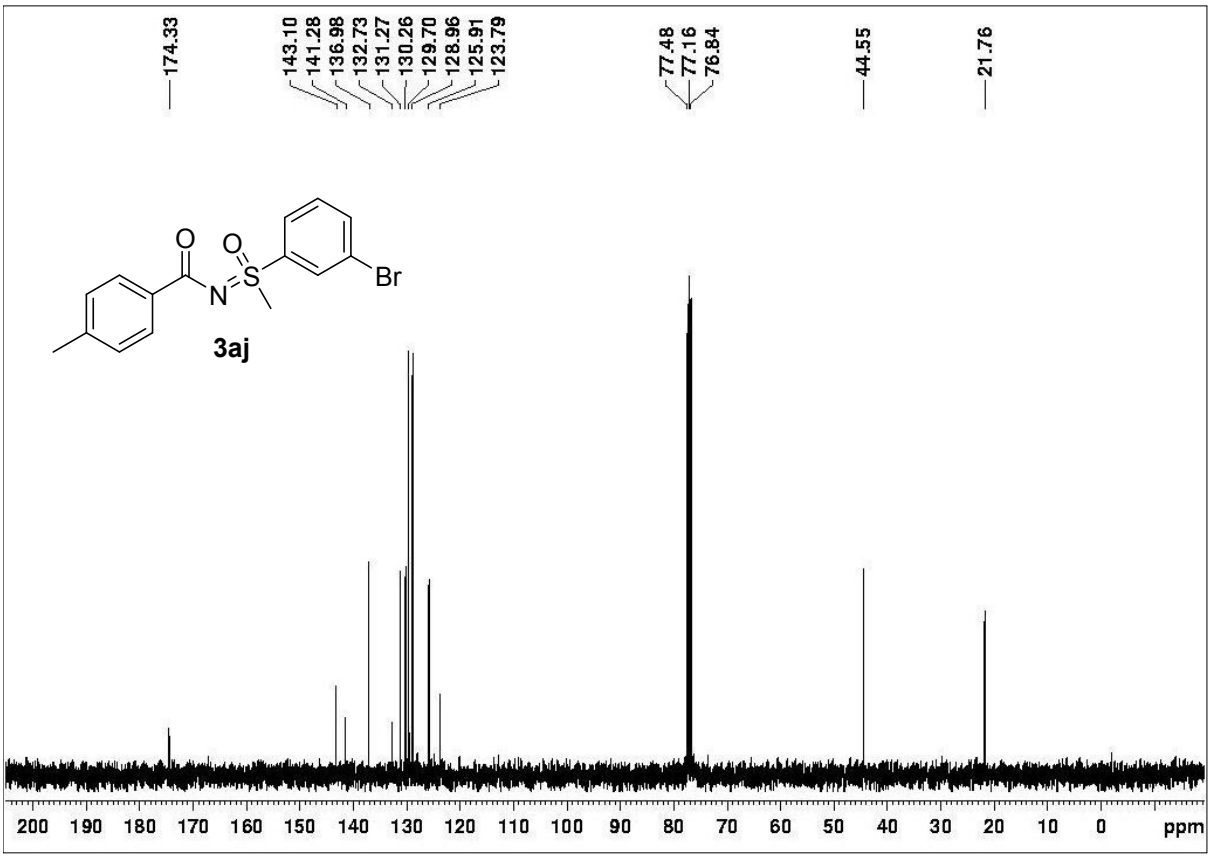


Figure 74: 100 MHz ^{13}C-NMR spectrum of **3aj** in $CDCl_3$

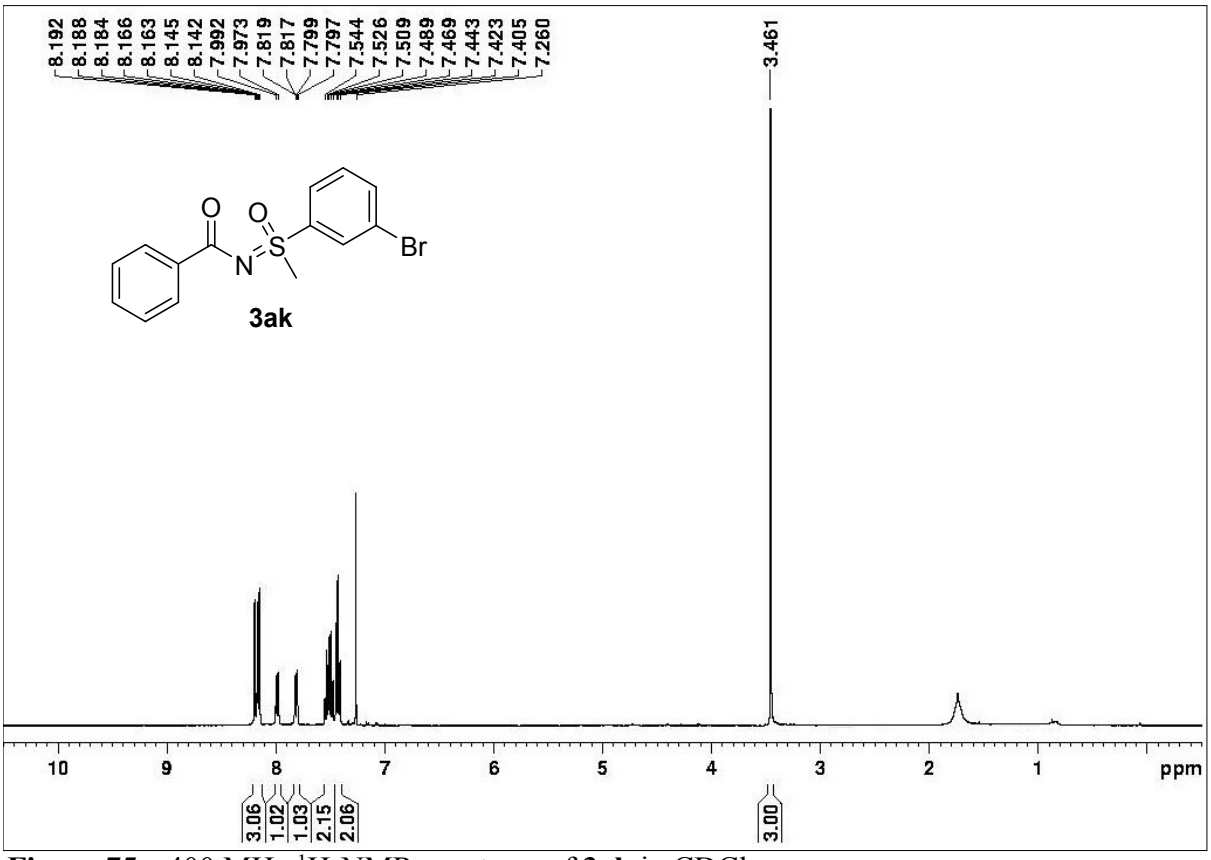


Figure 75: 400 MHz ^{1}H-NMR spectrum of **3ak** in $CDCl_3$

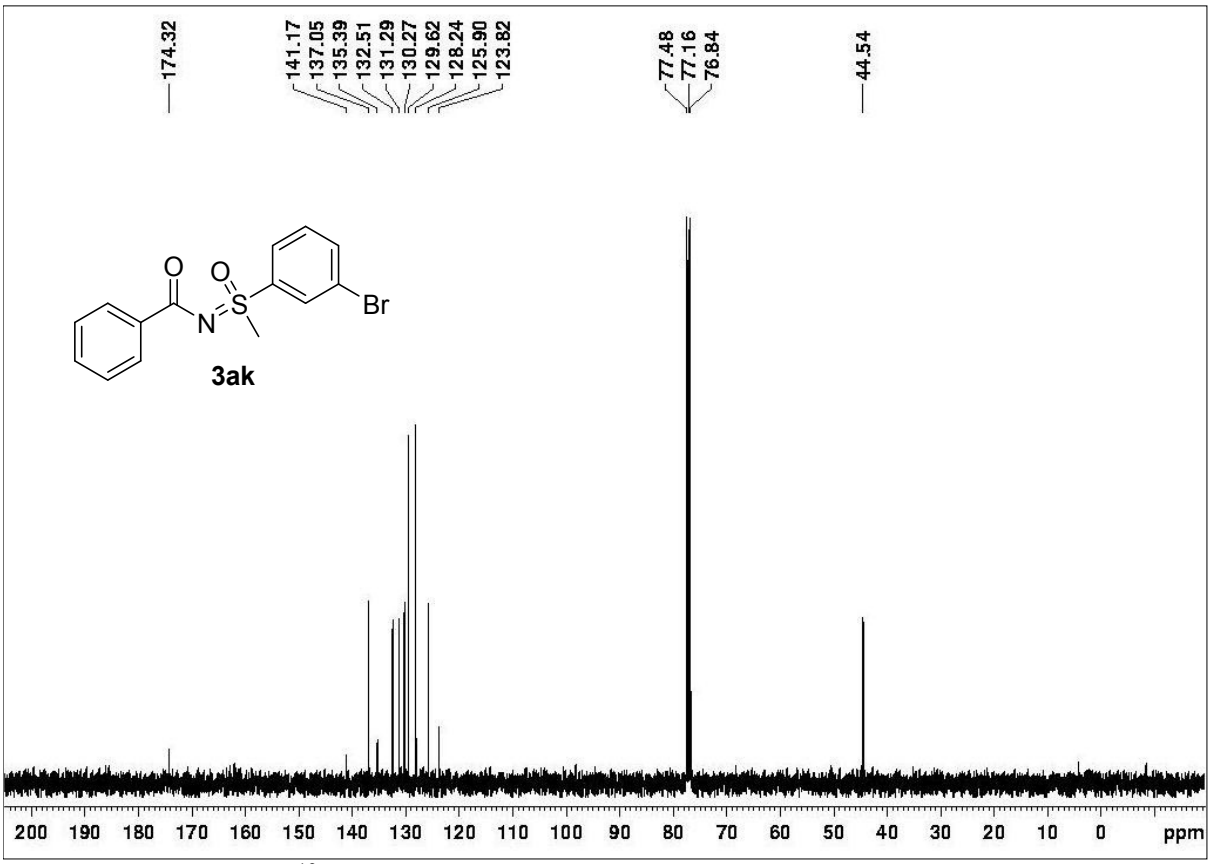


Figure 76: 100 MHz ^{13}C-NMR spectrum of **3ak** in $CDCl_3$

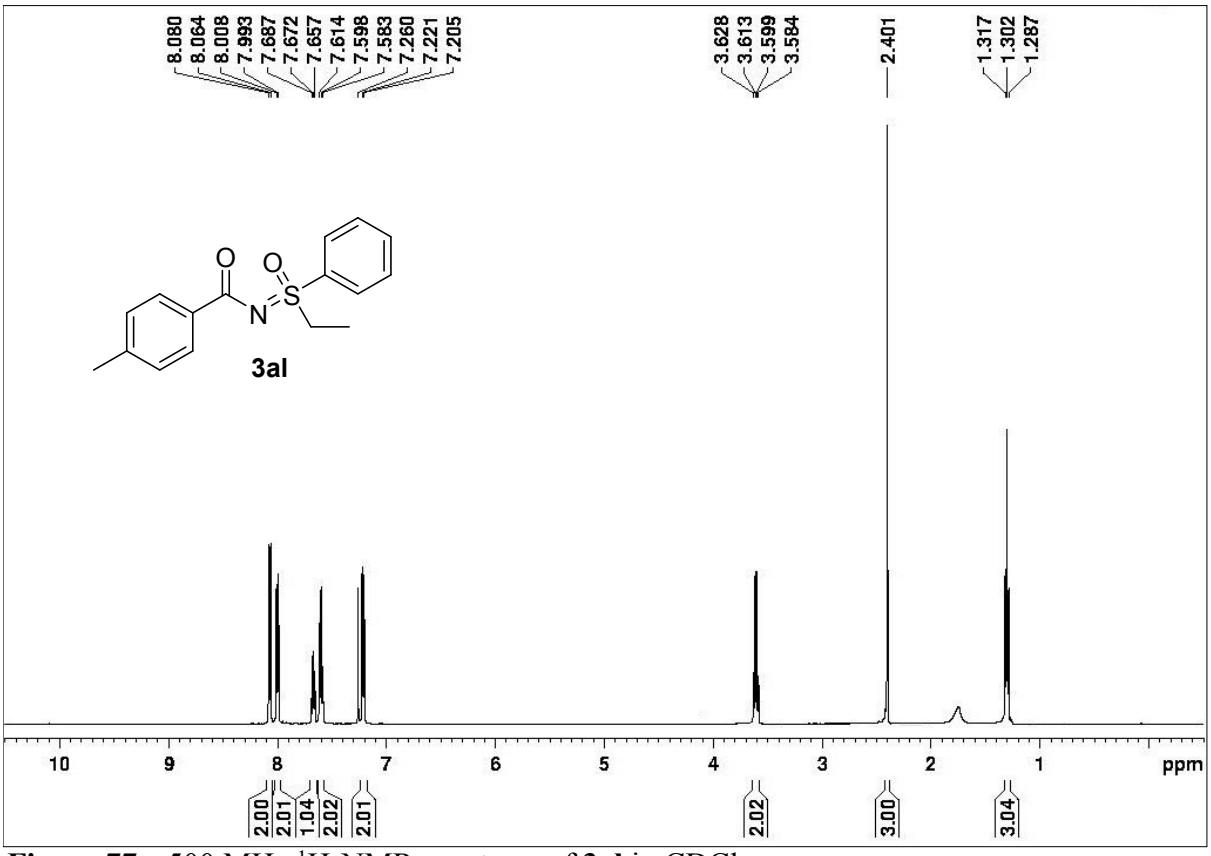


Figure 77: 500 MHz ^{1}H-NMR spectrum of **3al** in $CDCl_3$

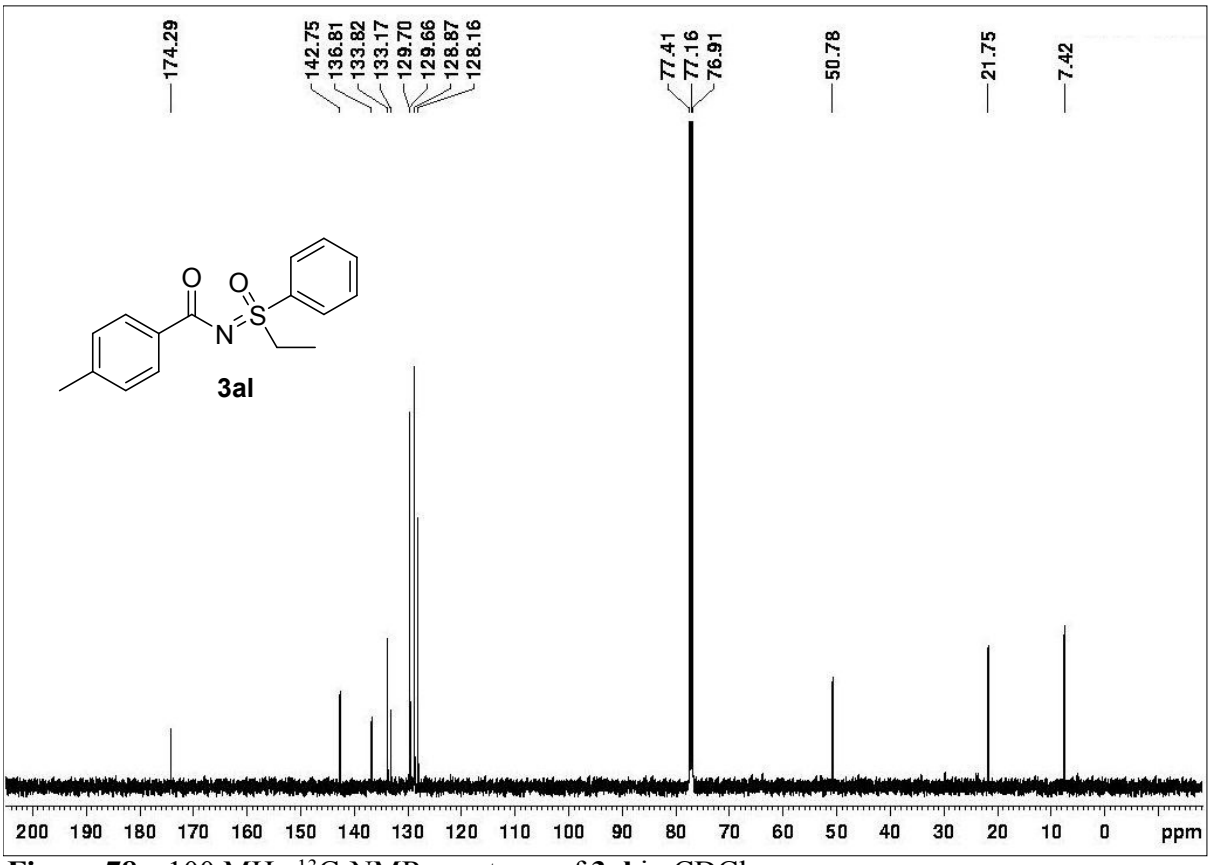


Figure 78: 100 MHz ^{13}C-NMR spectrum of **3al** in $CDCl_3$

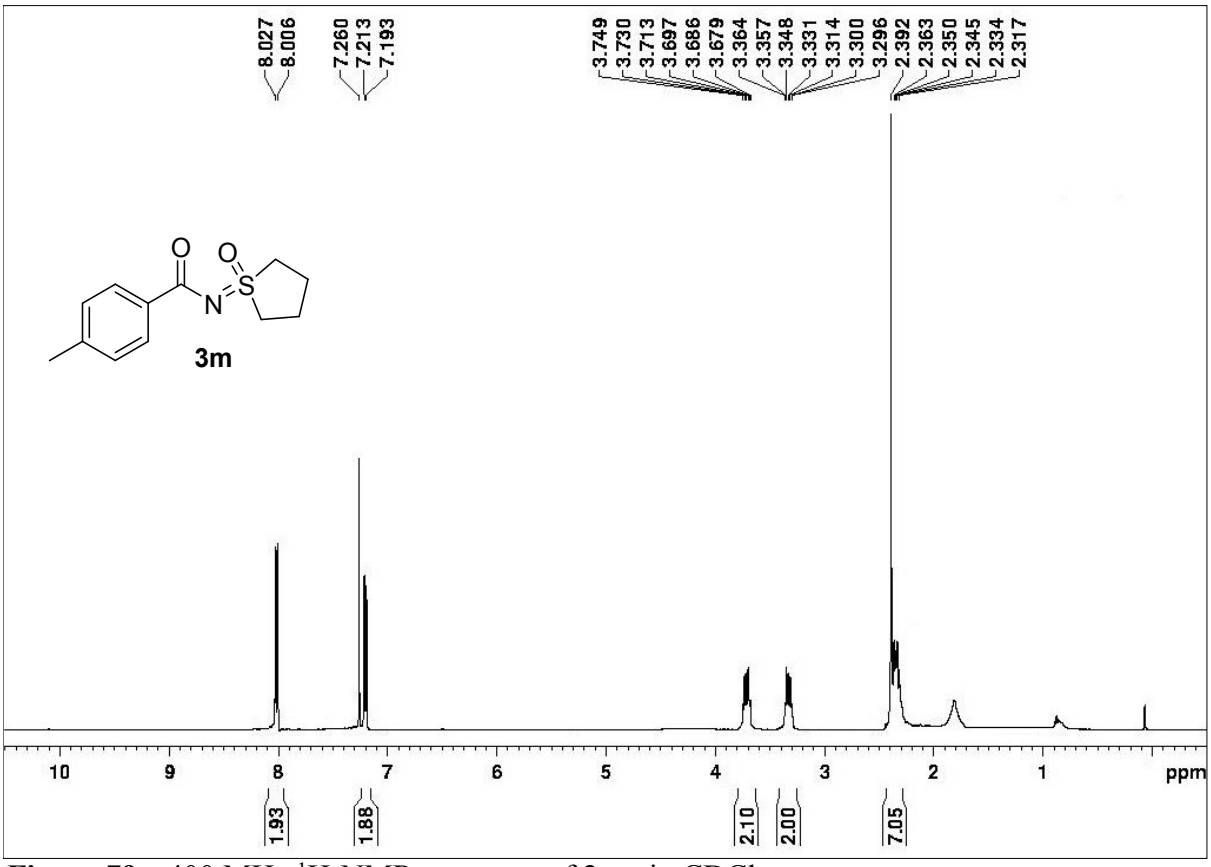


Figure 79: 400 MHz ^{1}H-NMR spectrum of **3am** in $CDCl_3$

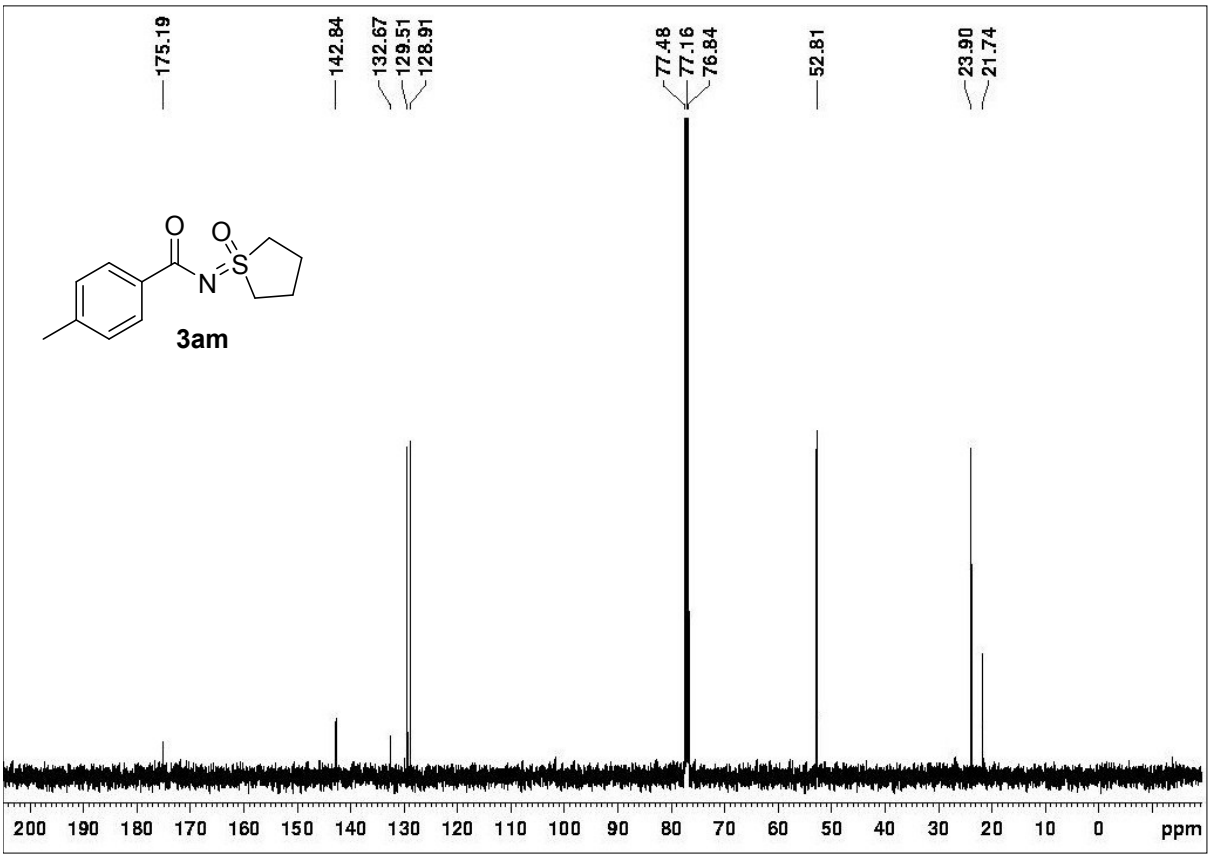


Figure 80: 100 MHz ^{13}C-NMR spectrum of **3am** in $CDCl_3$

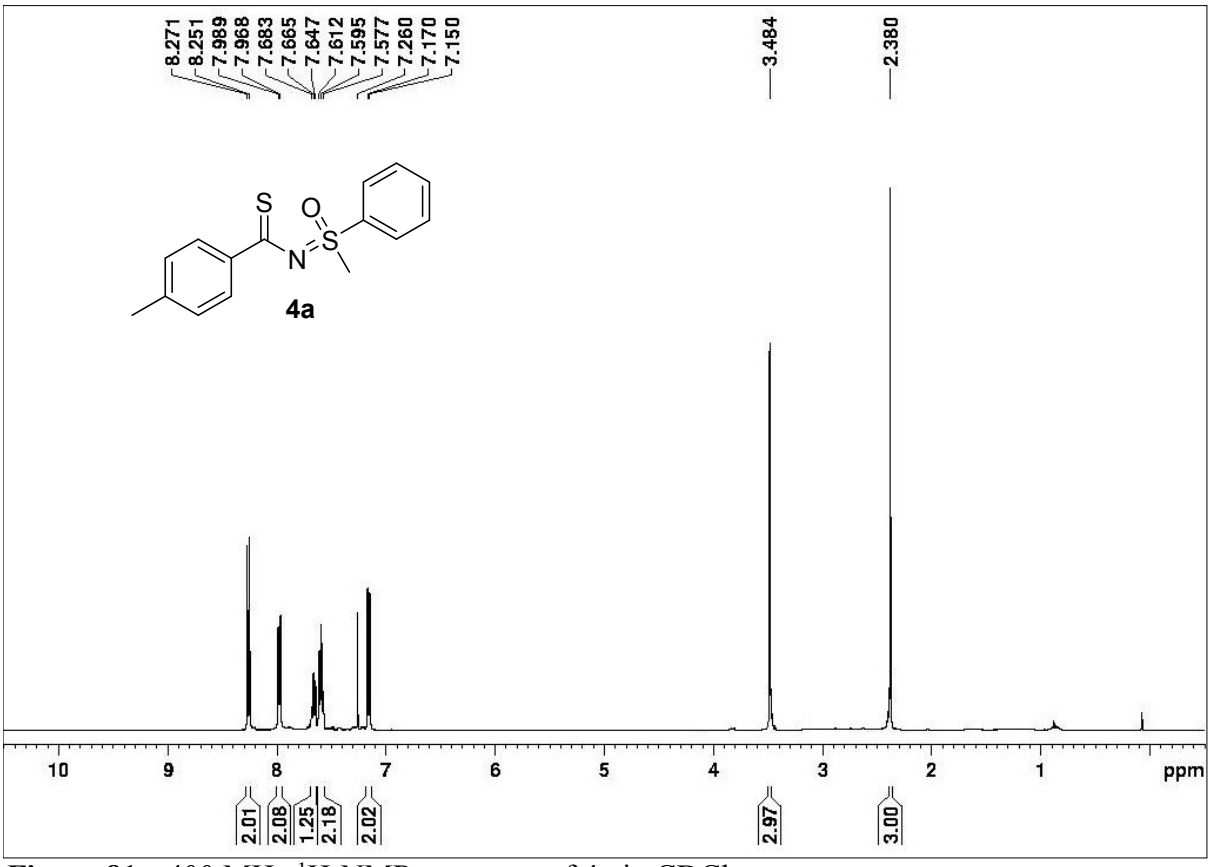


Figure 81: 400 MHz ^{1}H-NMR spectrum of **4a** in $CDCl_3$

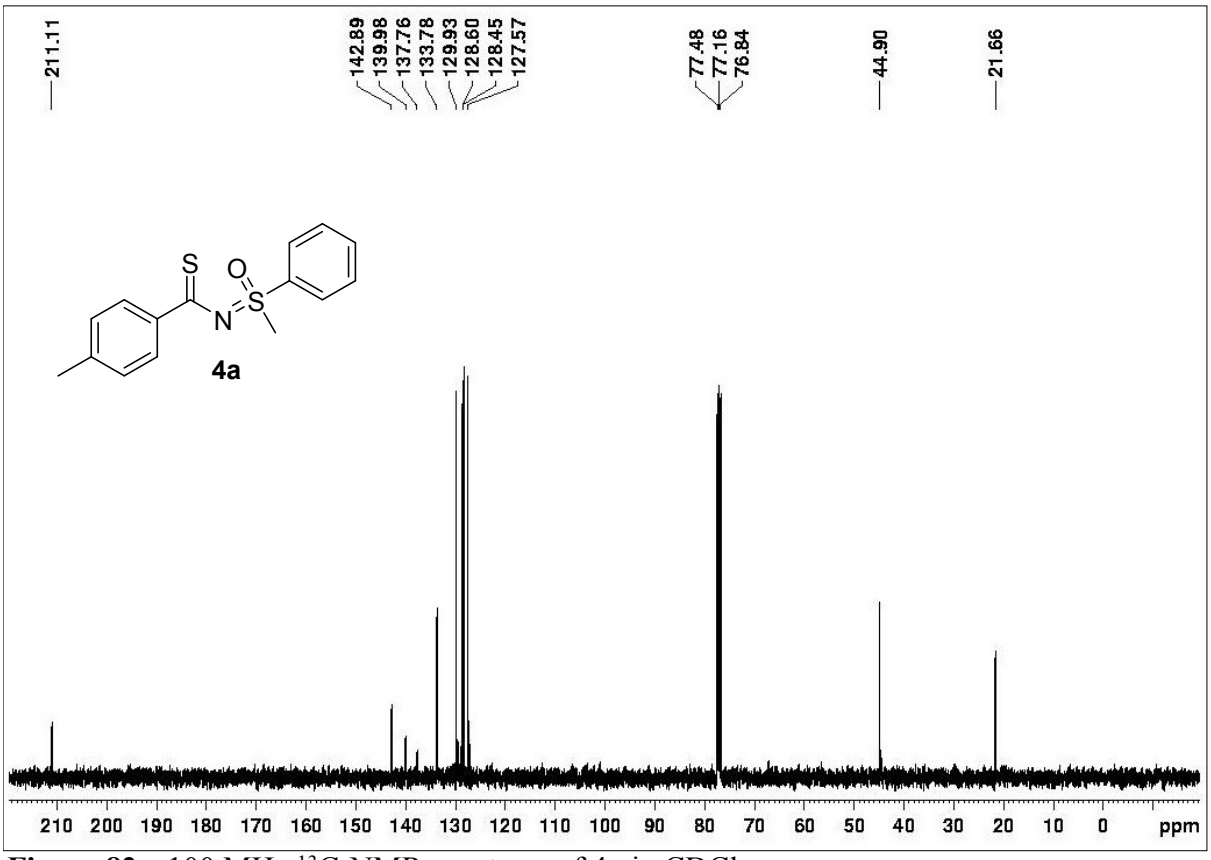


Figure 82: 100 MHz ^{13}C-NMR spectrum of **4a** in $CDCl_3$