Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

for

Sulfoximinocarbonylation of aryl halides using heterogenous Pd/C catalyst

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Table of contents

1. General information

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. Pd/C was obtained from Sigma-Aldrich and used directly as received. Various aryl iodides, aryl bromides and substituted sulfides were purchased from Alfa-aesar and Sigma-Aldrich Company. *N*H-sulfoximines were prepared from commercially available sulphides using literature reported procedure.[1] All the reactions were carried out in temperature controlled IKA magnetic stirrers. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 400 MHz. ^{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). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), br s (broad single) and m (multiplet). Coupling constants, *J* are reported in Hertz. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using KBr (film). The wave numbers of recorded IR signals are quoted in cm^{-1}. GC-MS (EI) was recorded on Shimadzu GCMS- QP2010 Ultra using Restek-Rxi-5Sil MS (30 m, 0.25 mmID, 0.25 μm df) column. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

3. General procedure

3.1. General procedure for aroylation of *N*H-sulfoximines

Aryl iodide (0.5 mmol), *N*H-sulfoximine (0.75 mmol), Pd/C (5.3 mg, 1 mol%) and with K_2CO_3 (0.5 mmol) taken in an oven dried reaction tube equipped magnetic pellet and covered with septum. First the reaction tube was evacuated (10 min) and DMF (1 ml) was added, again it was evacuated (10 min). CO balloon is introduced and stirred at 60^{o}C until the completion of reaction (monitored by TLC). After completion of the reaction, it was allowed to cool to room temperature and extracted with ethyl acetate (3 X 5 mL), followed by brine solution. Then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (hexanes:ethyl acetate) to get *N*-aroylated sulfoximine **3**.

3. 2. Experimental procedure for recovery of the Pd/C catalyst

For recycling of Pd/C, the reaction was performed with 4-iodotoluene **1a** as substrate in 1.0 mmol scale in optimized reaction conditions such as *S*-methyl-*S*-phenyl-*N*H-sulfoximine **2a** (1.5 equiv), K_2CO_3 (1 equiv), and 2 mL DMF under CO balloon at 60 ^oC. After completion of the reaction, the reaction mixture was allowed to attain room temperature. Then ethyl acetate (5 mL) was added and centrifuged. The liquid decanted to a 50 mL conical flask. This procedure was repeated up to three times and decanted to the same conical flask. After that the catalyst was washed with nano pure water (5 mL) and methanol (5 mL). Finally, the resulting solid particles (Pd/C) 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*-aroylsulfoximine product **3a**.

Mercury Poisoning Test

Mercury poisoning test was also conducted to support that Pd/C is heterogeneous in the reaction medium. Pd/C (10.6 mg, 1 mol%), Hg (8.0 g, 40 mmol, 30 equiv.), 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 taken in oven dried reaction tube. The reaction tube was evacuated (10 min) and DMF (1 ml) was added, again it was evacuated (10 min) then CO balloon is introduced and stirred at 60^{o}C After 7 hours, the reaction mixture was allowed to cool to room temperature. Complete inhibition of the reaction was detected and even trace amount of product **3a** formation was not observed.

References

1. M. R. Yadav, R. K. Rit and A. K. Sahoo, *Chem. - Eur. J.*, 2012, **18**, 5541-5545.

4. ^{1}H and ^{13}C spectra for all compounds

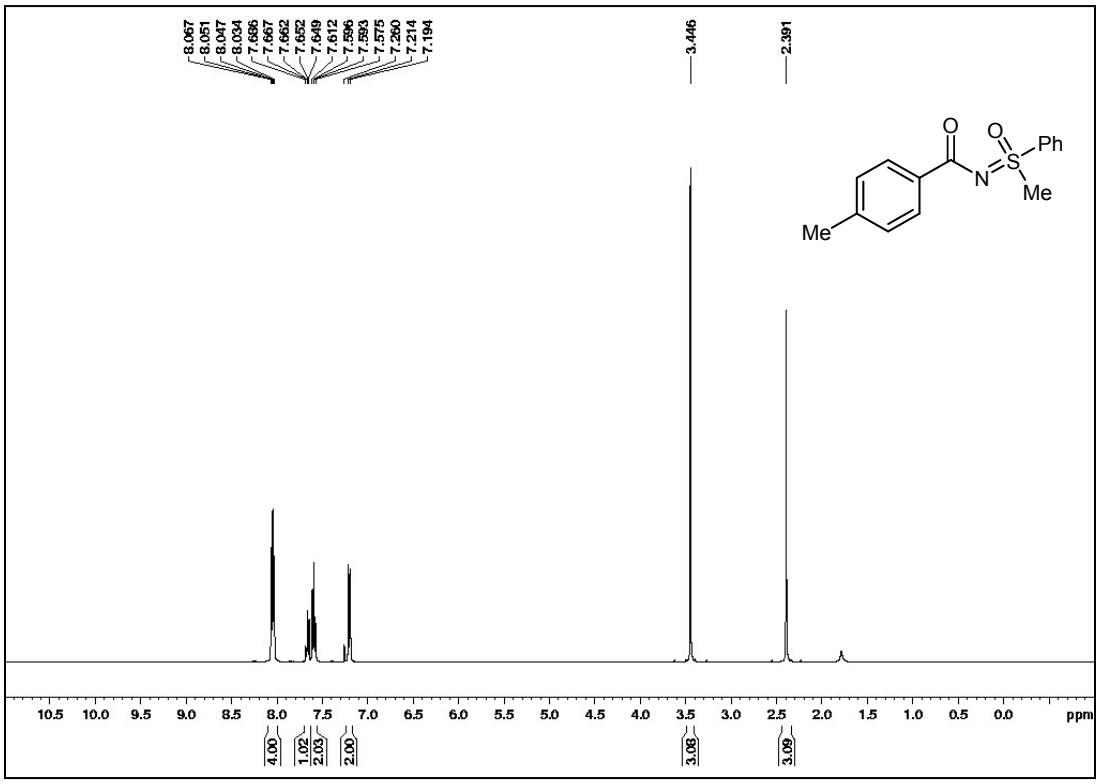


Figure 1: 400 MHz ^{1}H-NMR spectrum of **3a** in $CDCl_3$

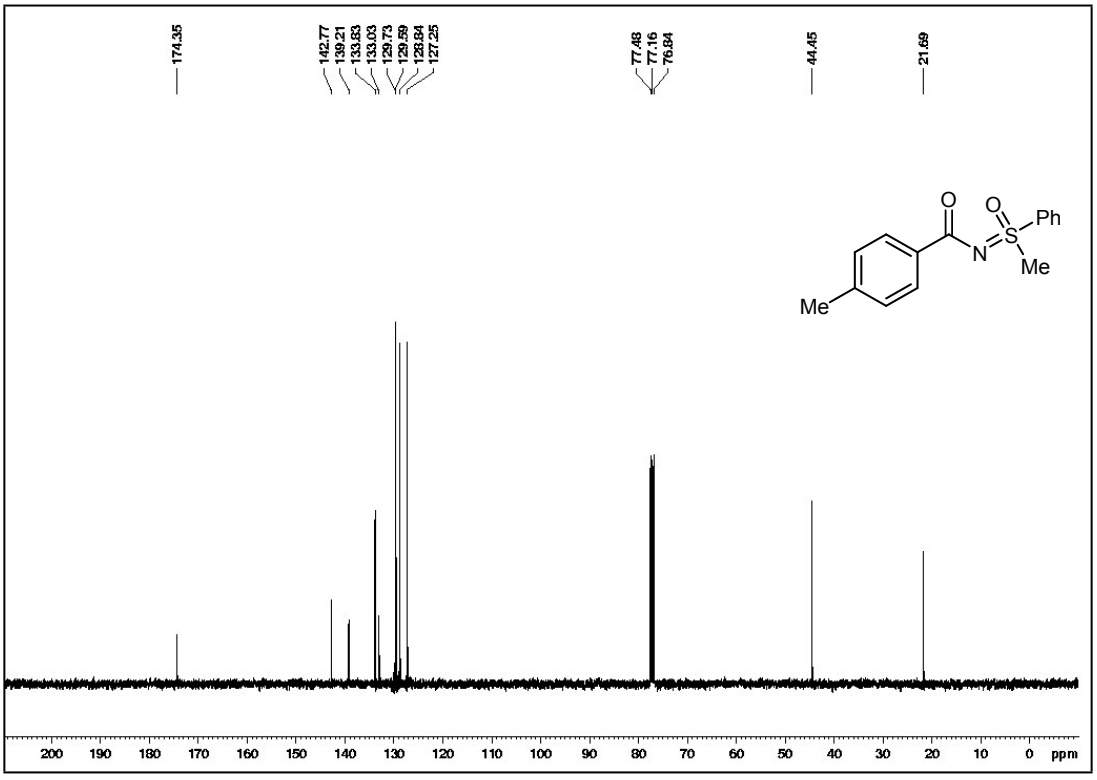


Figure 2: 100 MHz ^{13}C-NMR spectrum of **3a** in $CDCl_3$

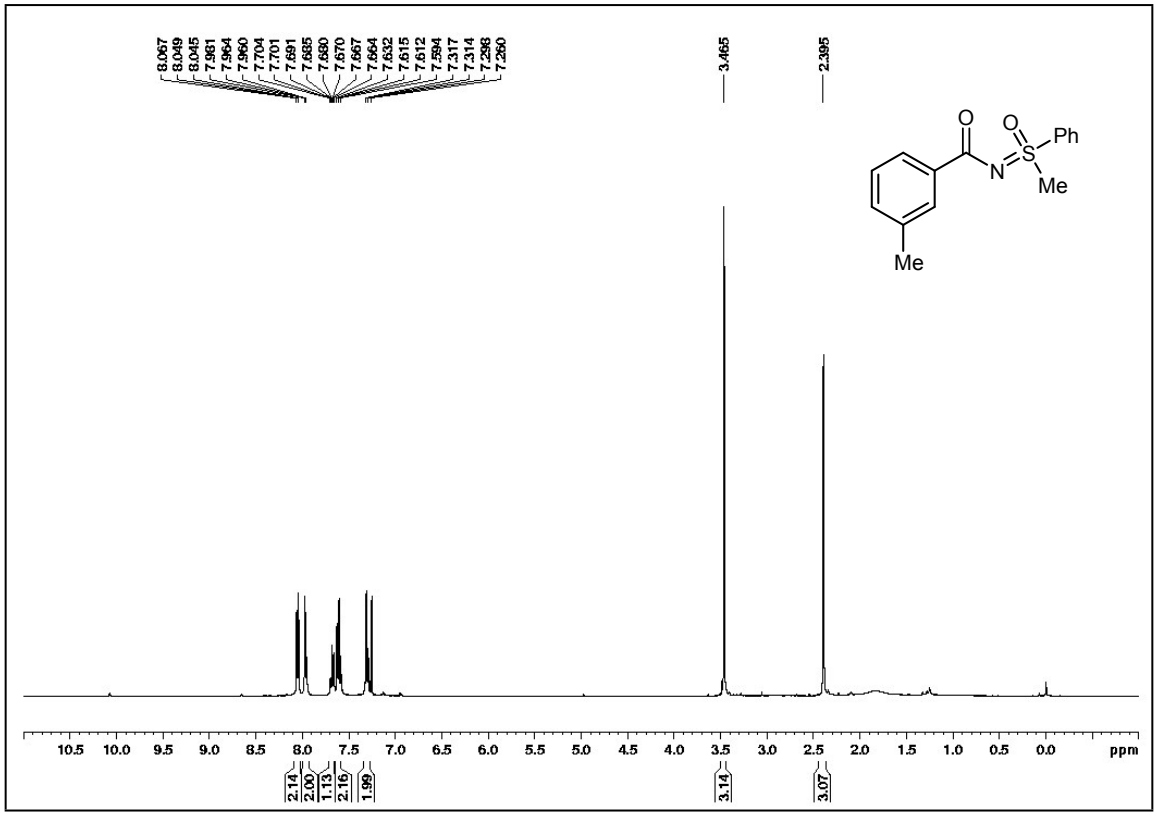


Figure 3: 400 MHz ^{1}H-NMR spectrum of **3b** in $CDCl_3$

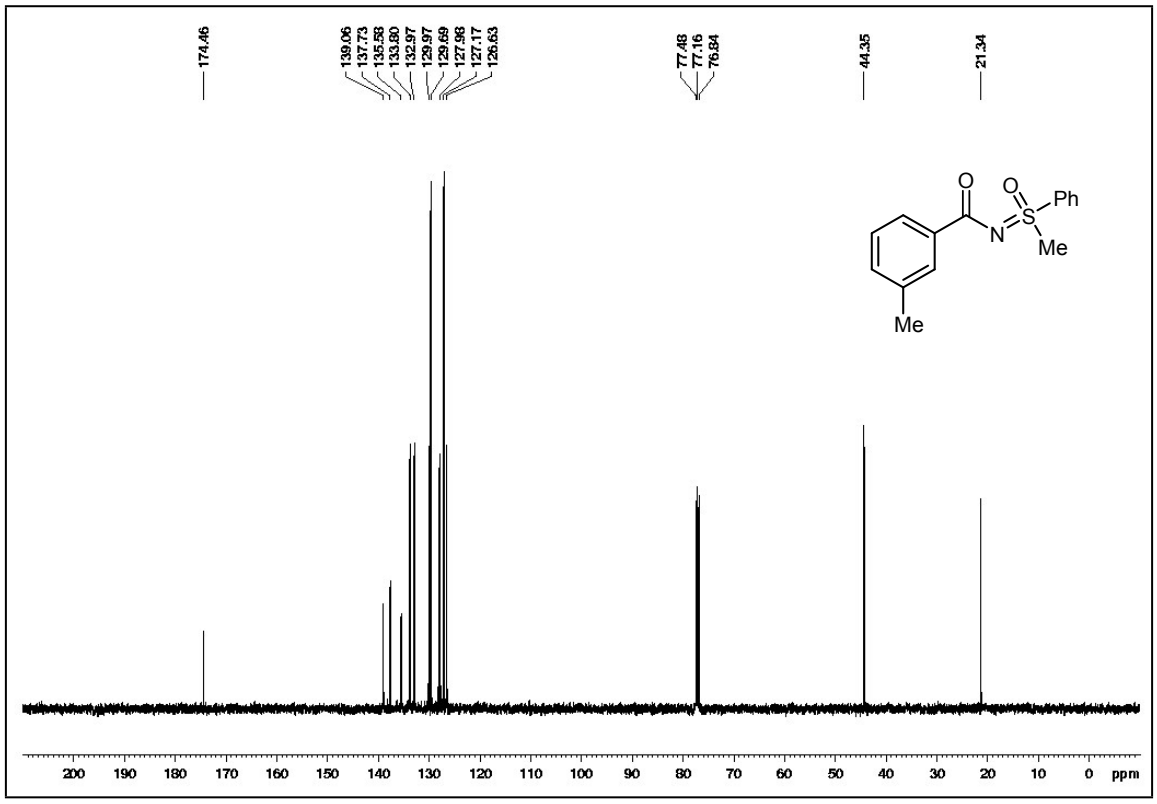


Figure 4: 100 MHz ^{13}C-NMR spectrum of **3b** in $CDCl_3$

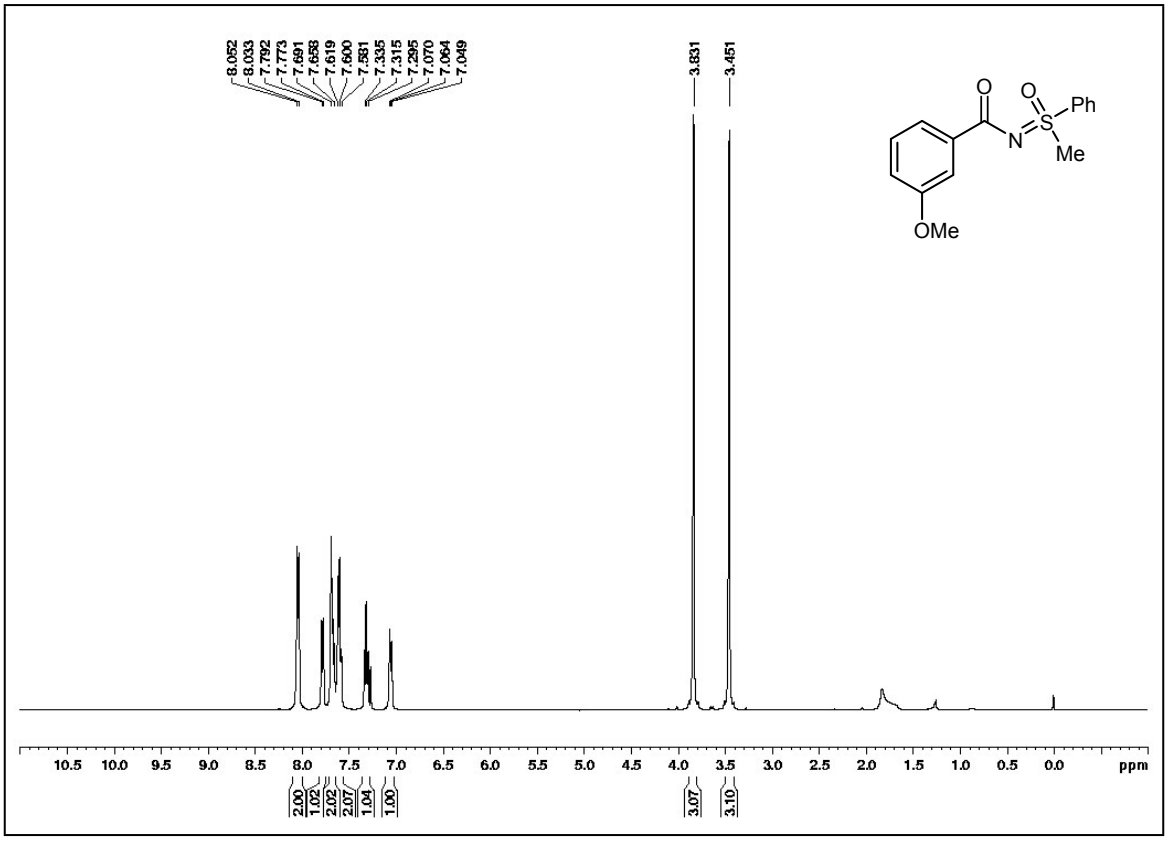


Figure 5: 400 MHz ^{1}H-NMR spectrum of **3c** in $CDCl_3$

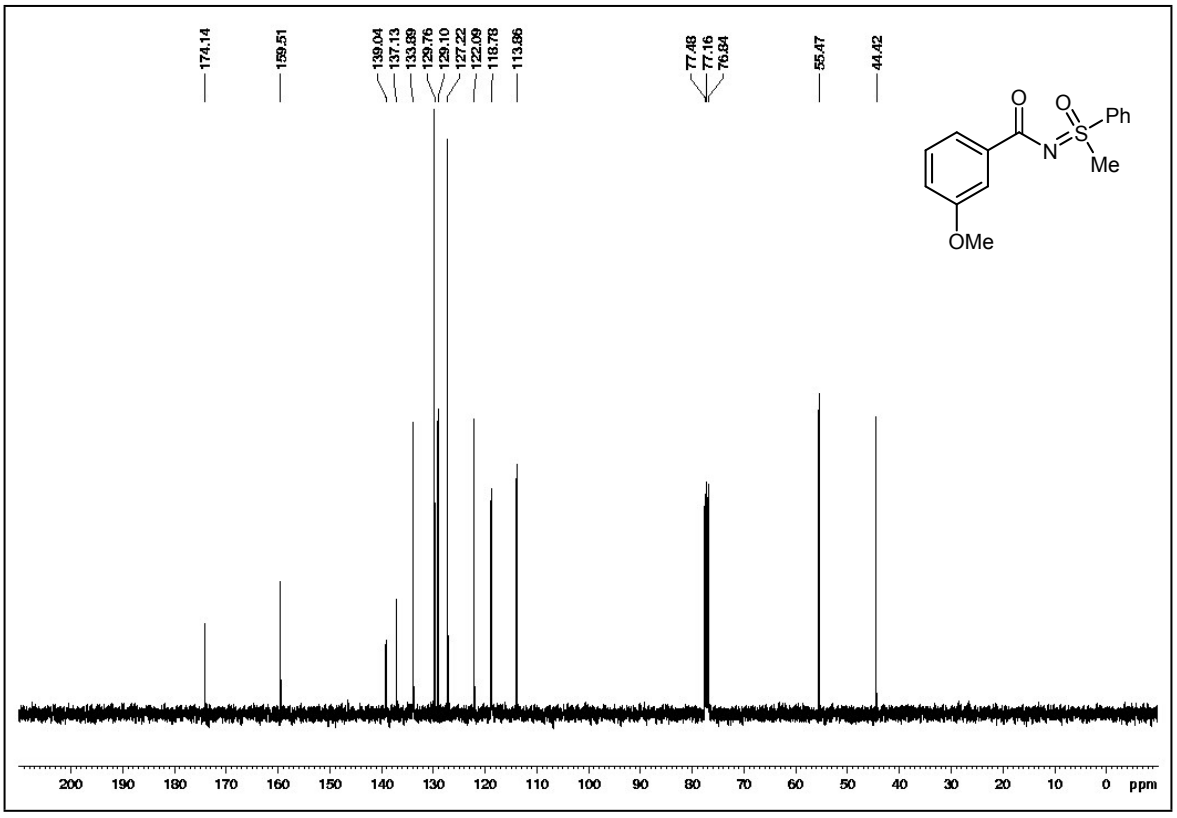


Figure 6: 100 MHz ^{13}C-NMR spectrum of **3c** in $CDCl_3$

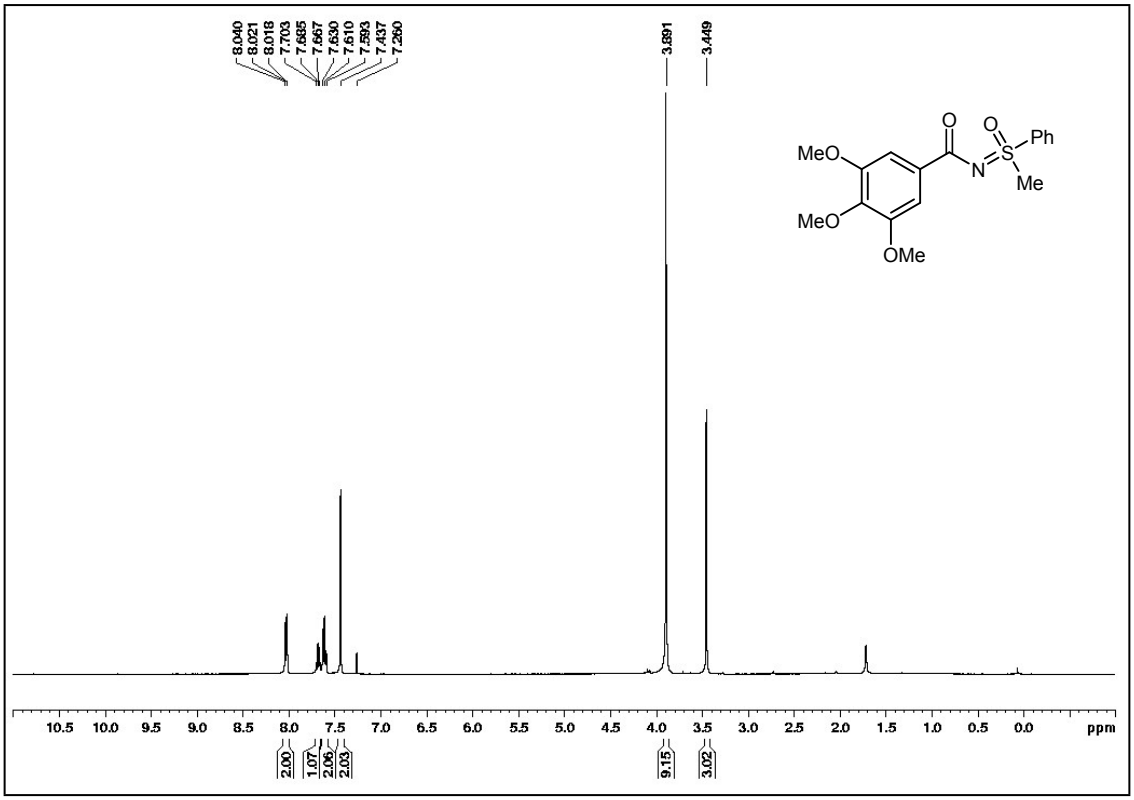


Figure 7: 400 MHz ^{1}H-NMR spectrum of **3d** in $CDCl_3$

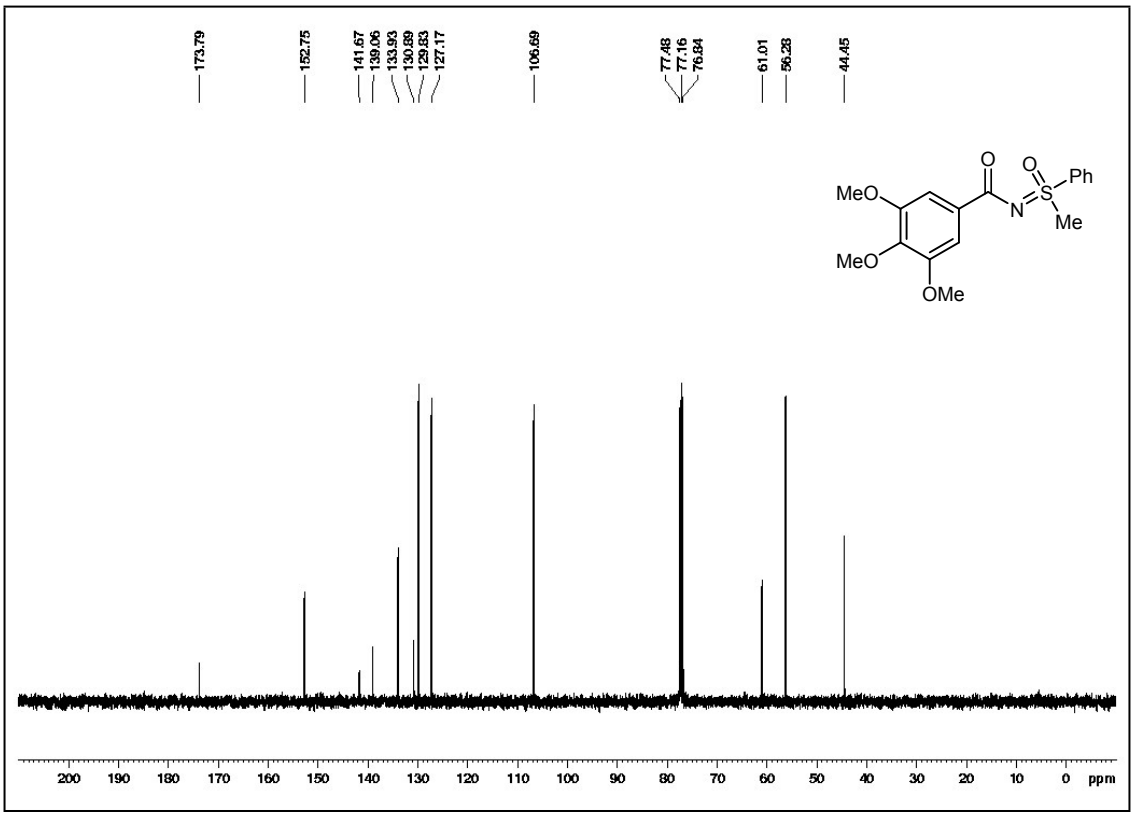


Figure 8: 100 MHz ^{13}C-NMR spectrum of **3d** in $CDCl_3$

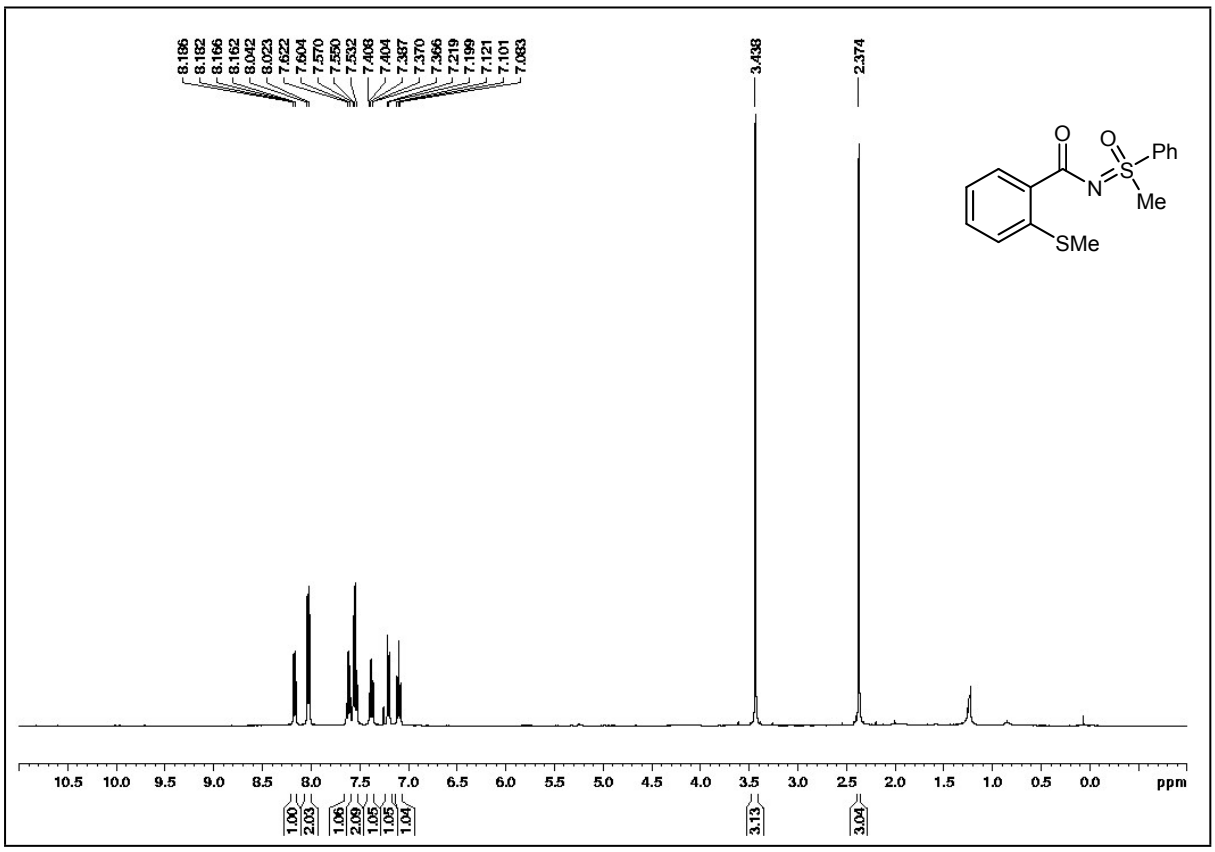


Figure 9: 400 MHz ^{1}H-NMR spectrum of **3e** in $CDCl_3$

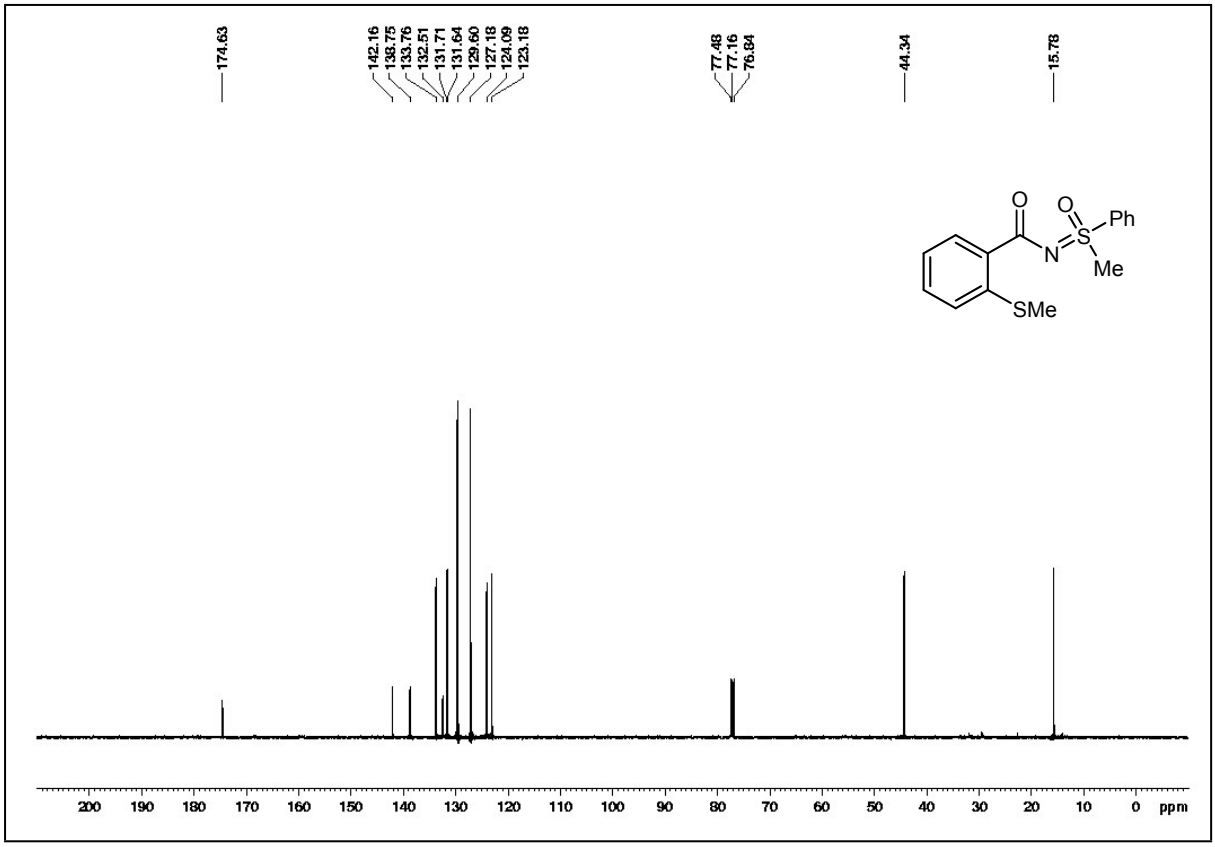


Figure 10: 100 MHz ^{13}C-NMR spectrum of **3e** in $CDCl_3$

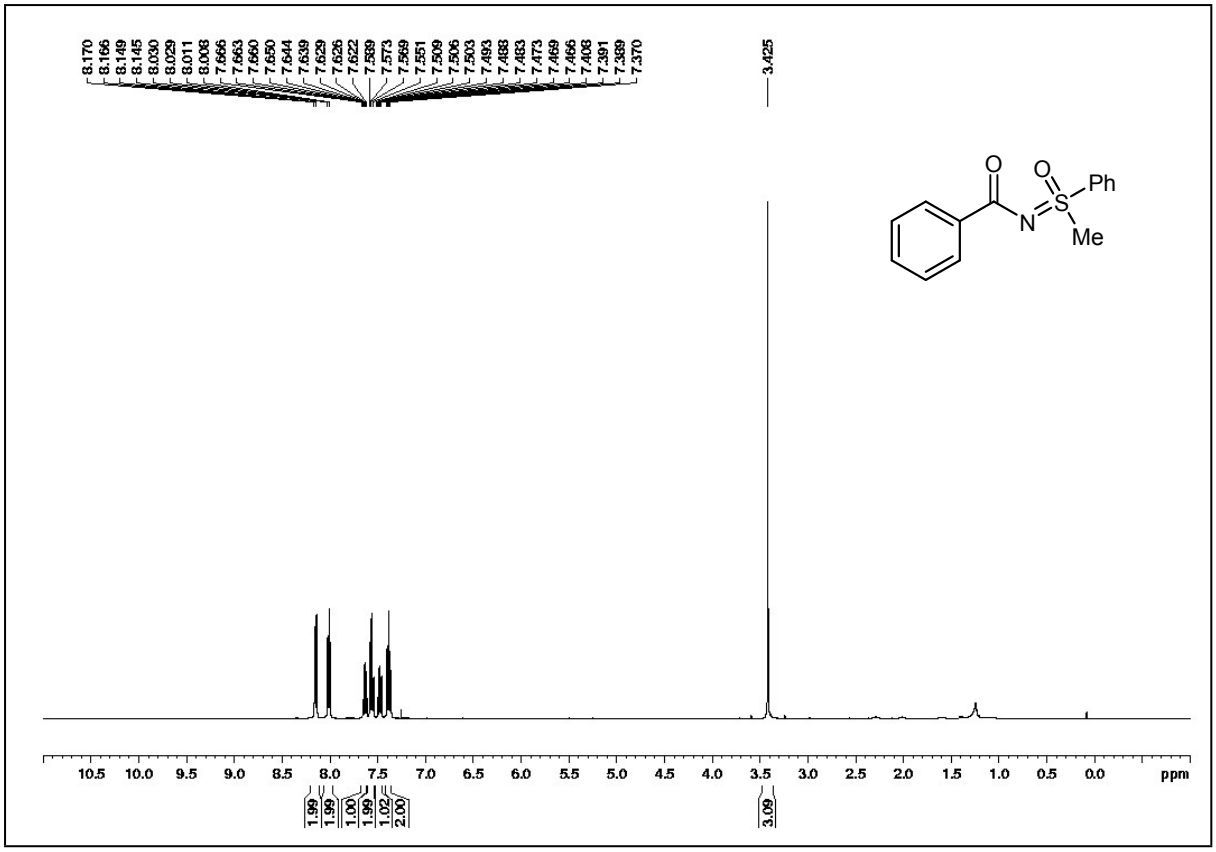


Figure 11: 400 MHz ^{1}H-NMR spectrum of **3f** in $CDCl_3$

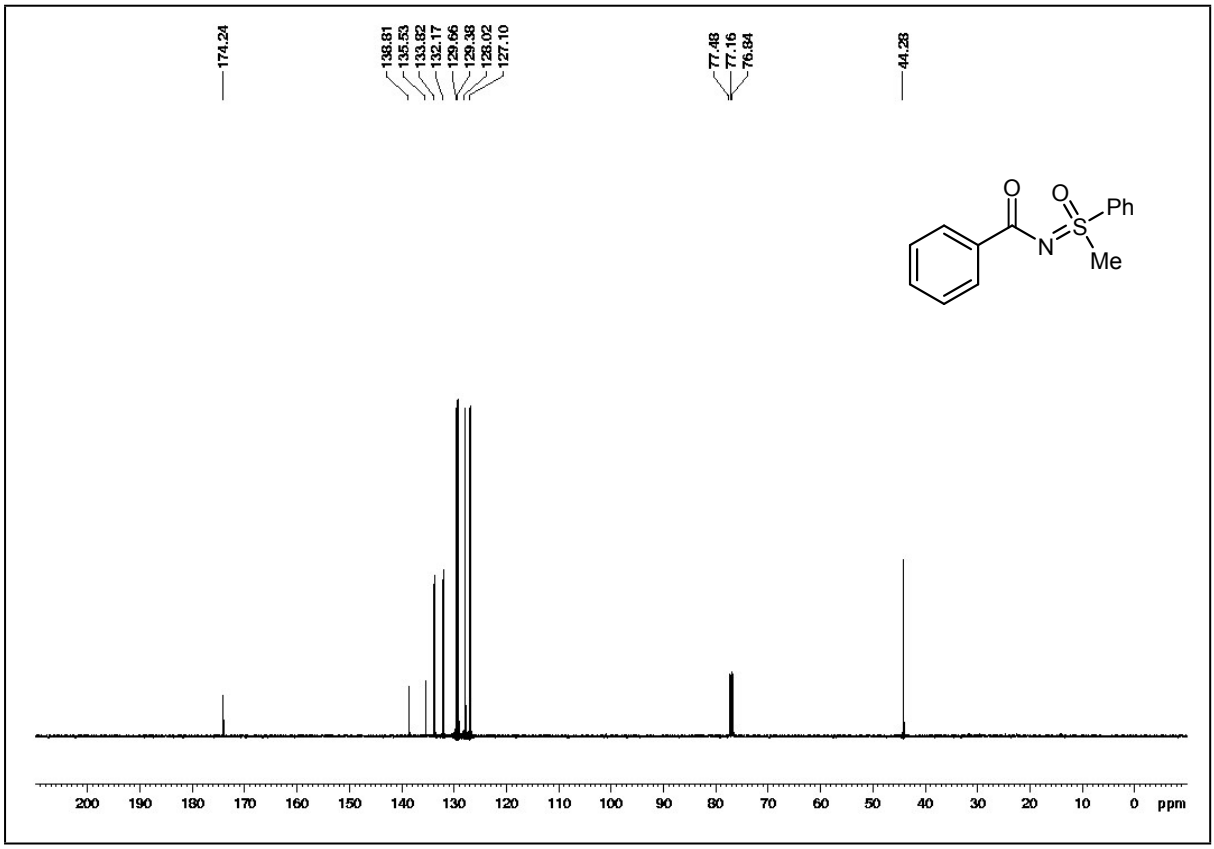


Figure 12: 100 MHz ^{13}C-NMR spectrum of **3f** in $CDCl_3$

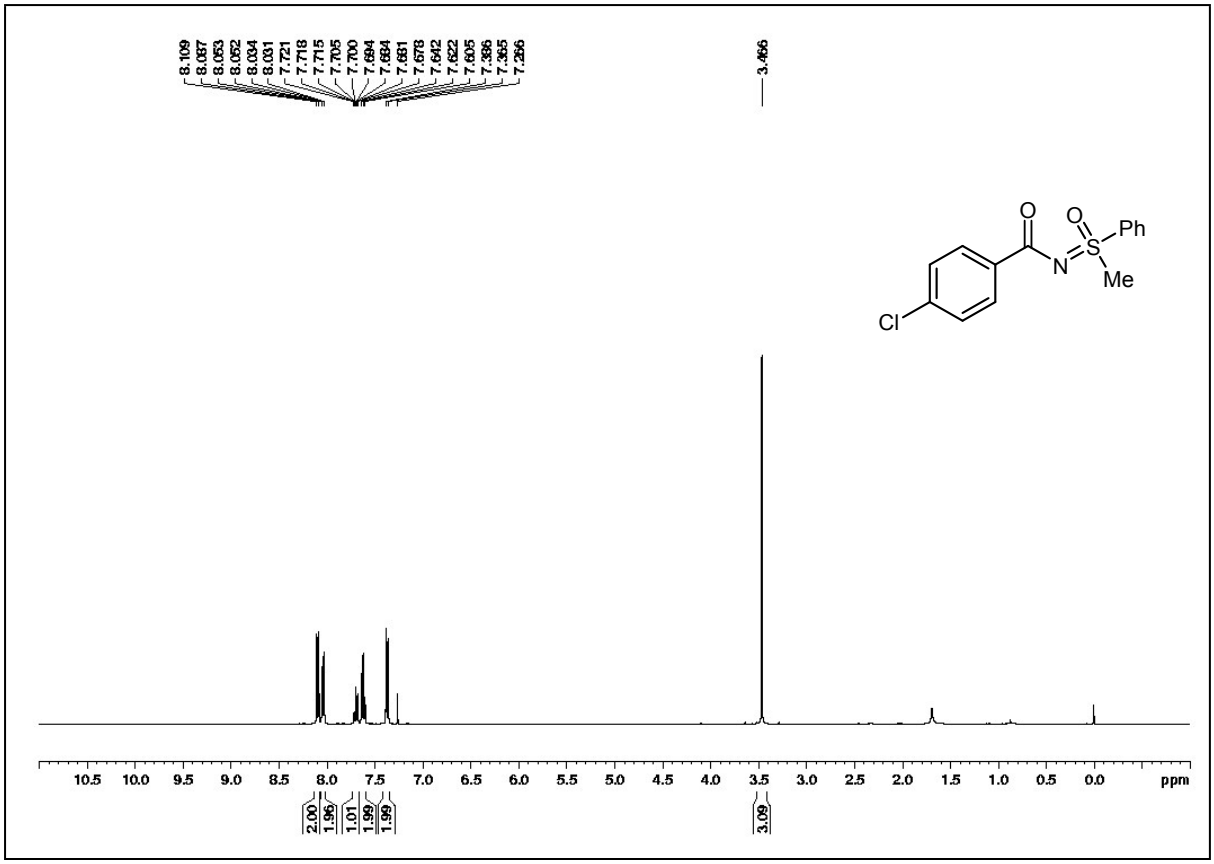


Figure 13: 400 MHz ^{1}H-NMR spectrum of **3g** in $CDCl_3$

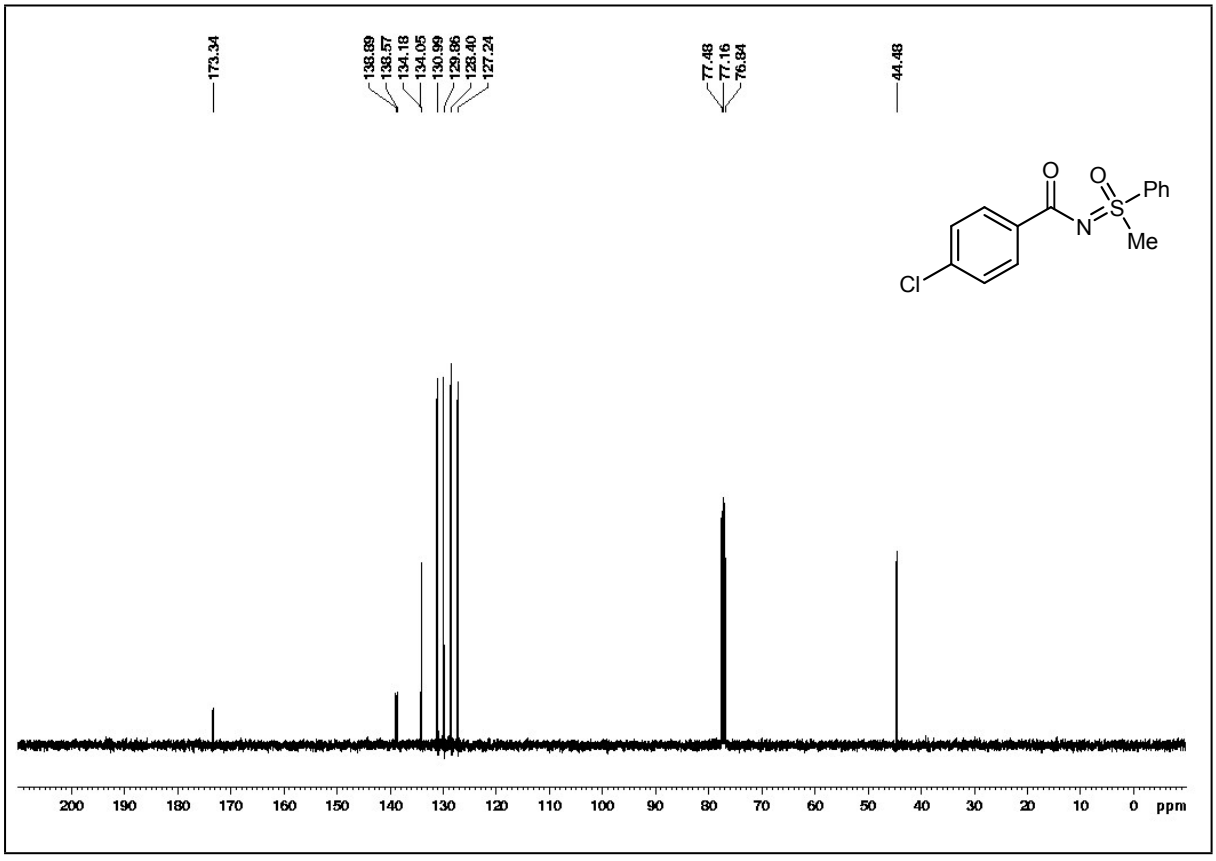


Figure 14: 100 MHz ^{13}C-NMR spectrum of **3g** in $CDCl_3$

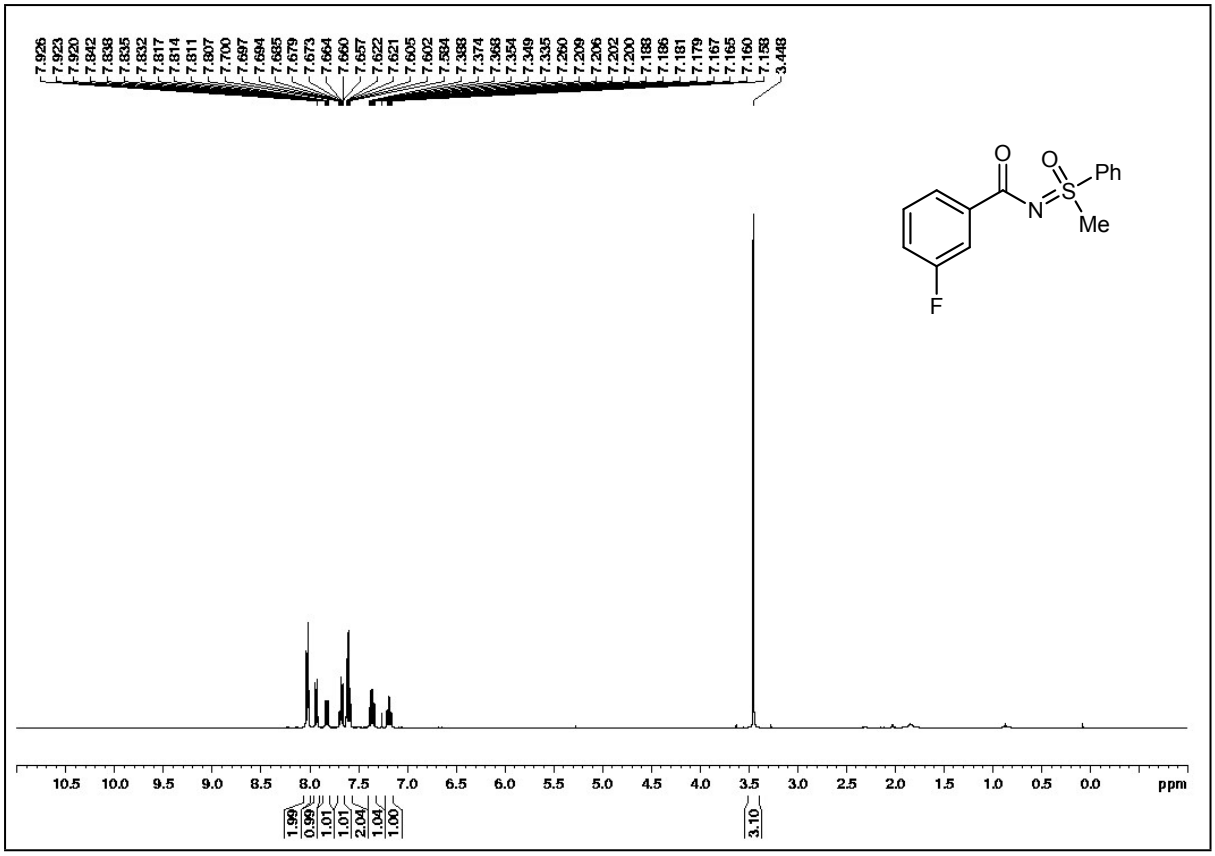


Figure 15: 400 MHz ^{1}H-NMR spectrum of **3h** in $CDCl_3$

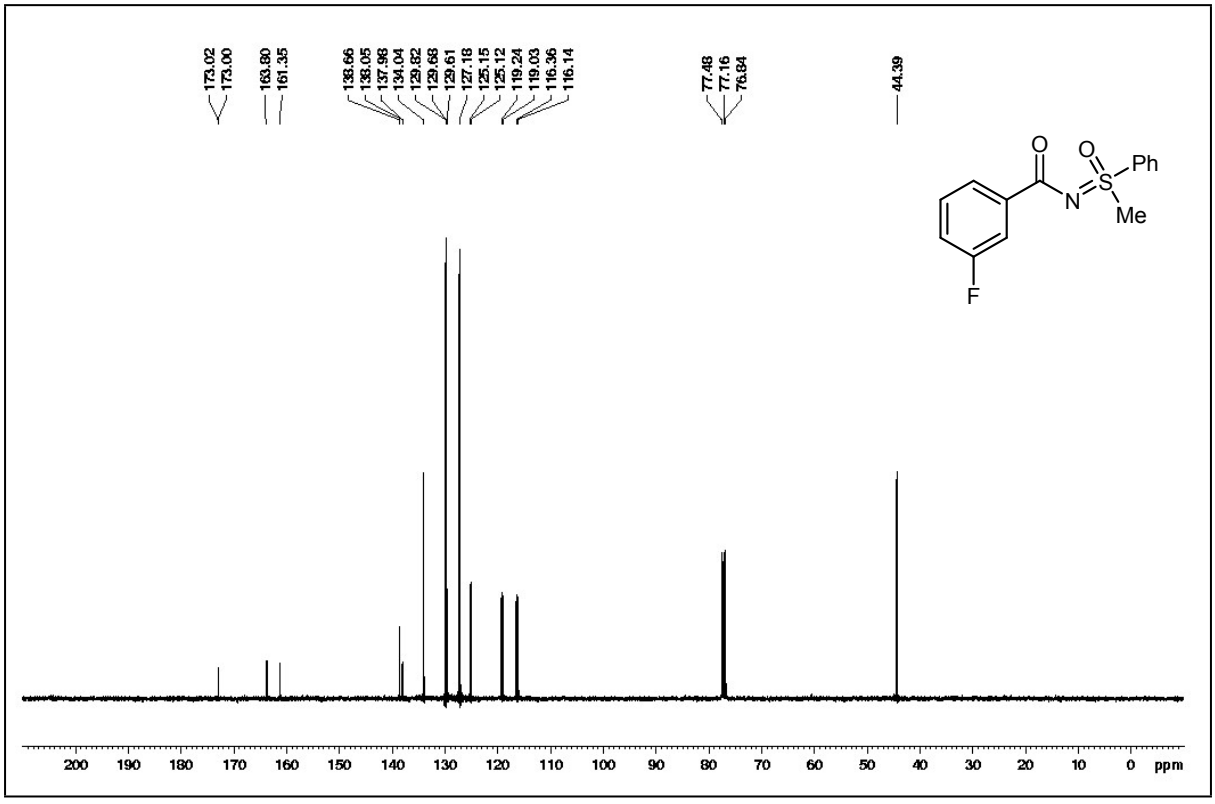


Figure 16: 100 MHz ^{13}C-NMR spectrum of **3h** in $CDCl_3$

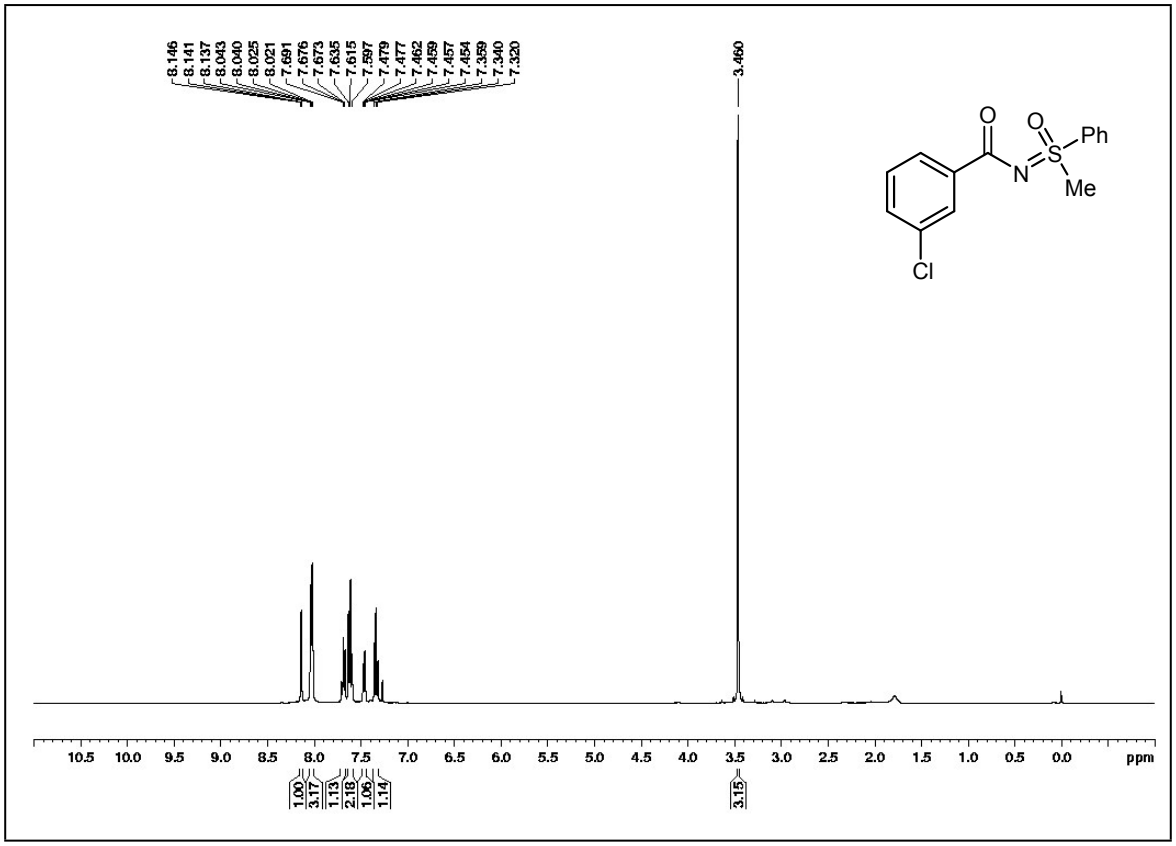


Figure 17: 400 MHz ^{1}H-NMR spectrum of **3i** in $CDCl_3$

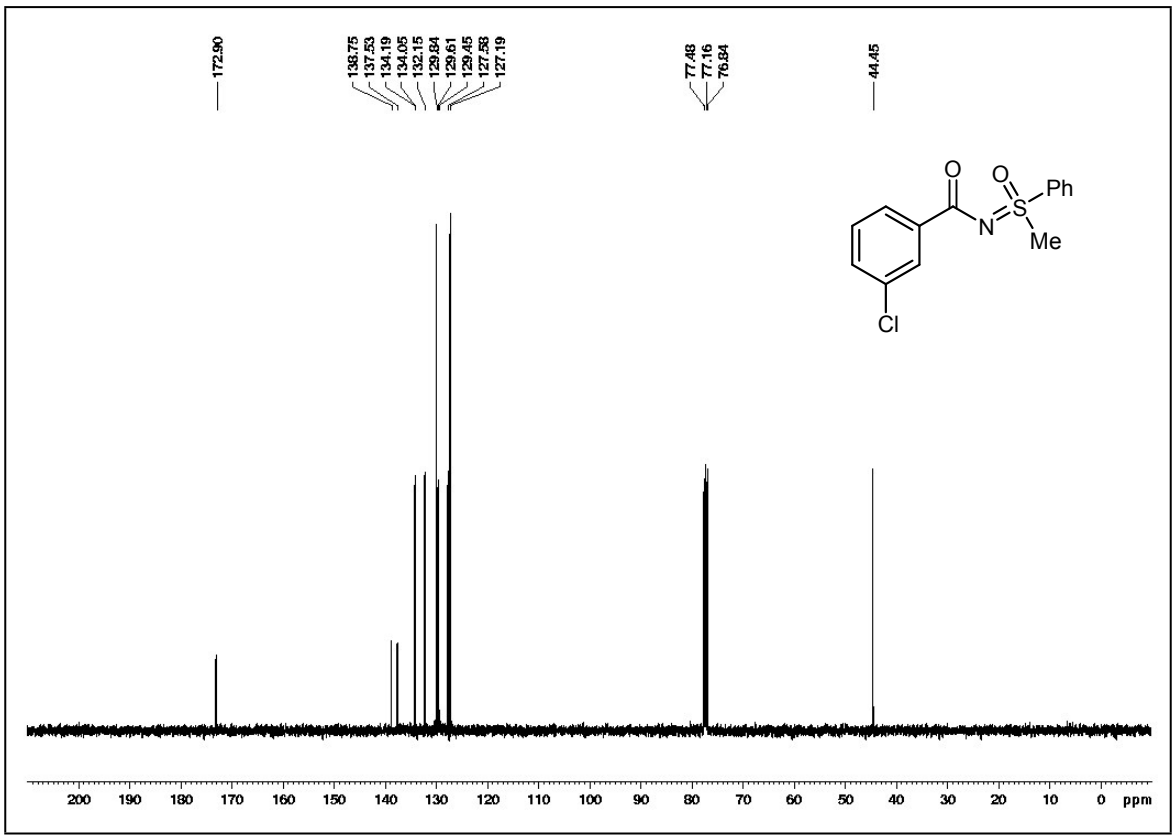


Figure 18: 100 MHz ^{13}C-NMR spectrum of **3i** in $CDCl_3$

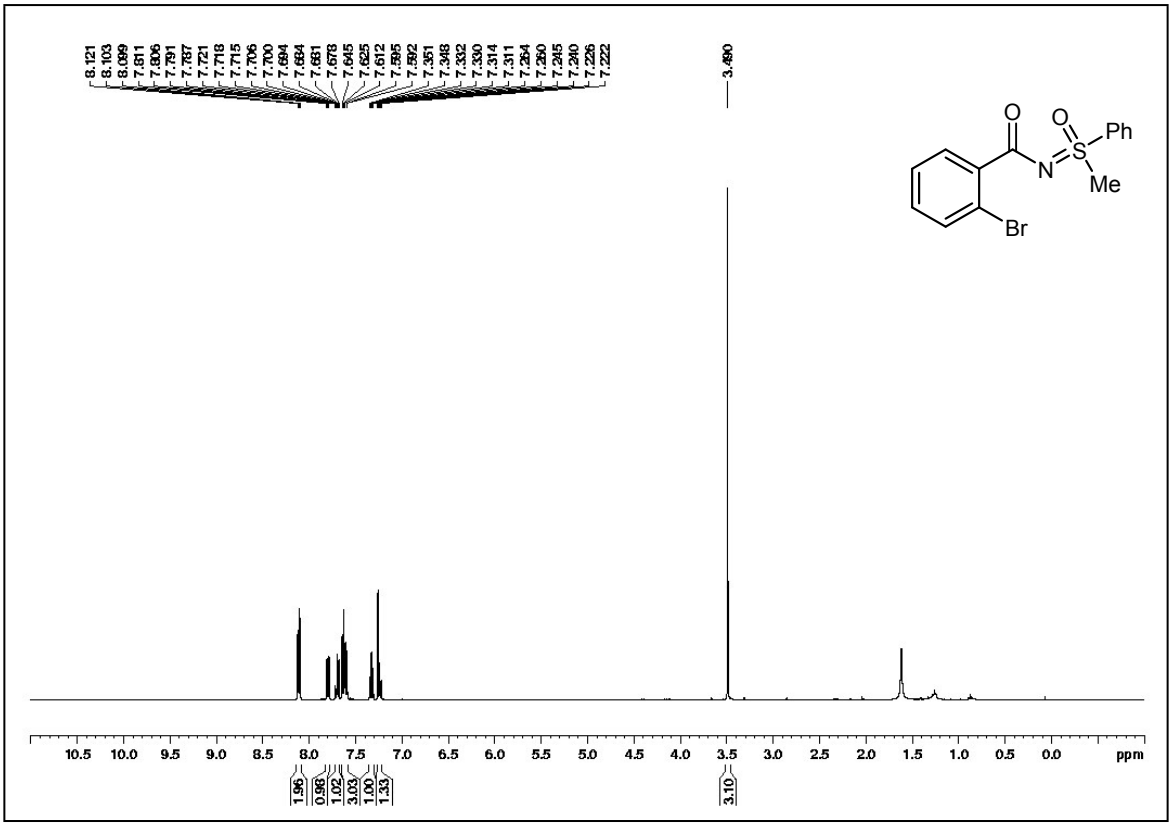


Figure 19: 400 MHz ^{1}H-NMR spectrum of **3j** in $CDCl_3$

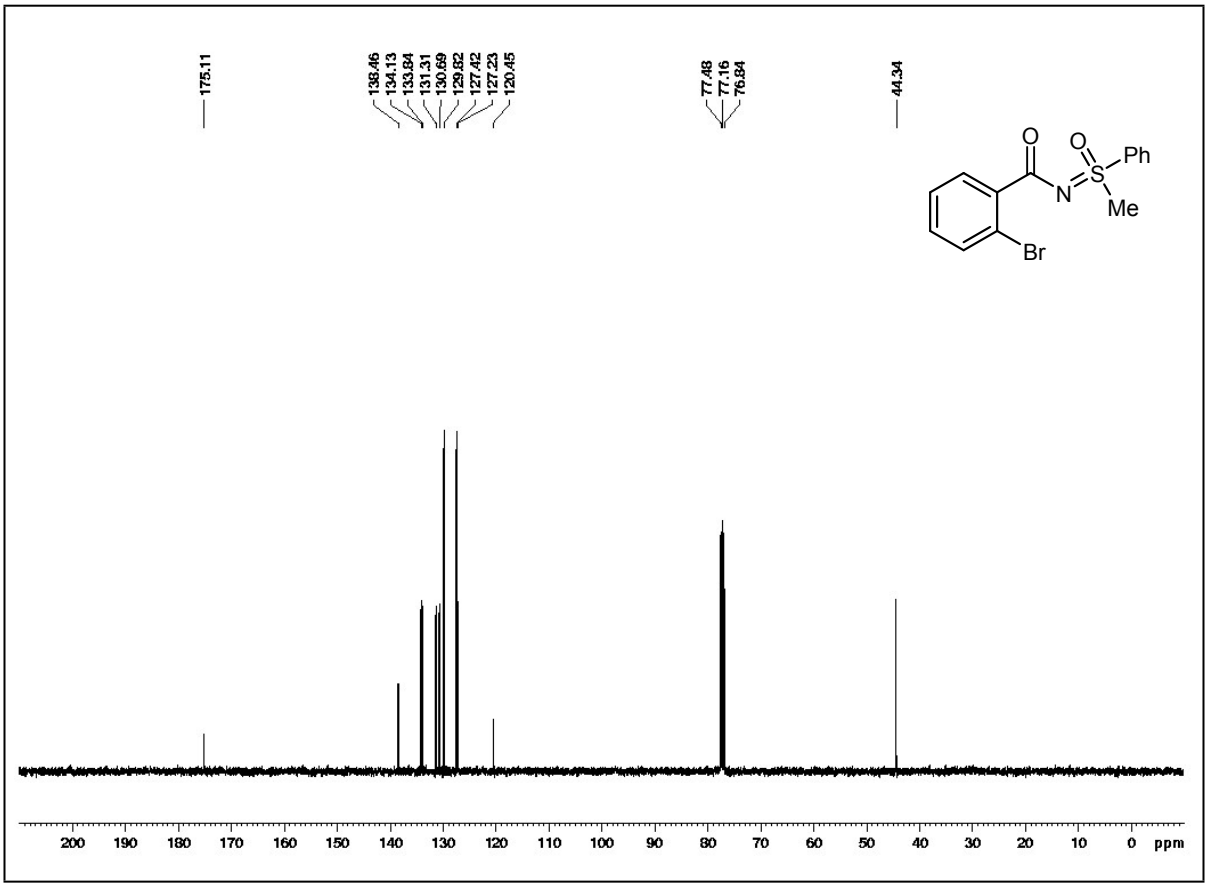


Figure 20: 100 MHz ^{13}C-NMR spectrum of **3j** in $CDCl_3$

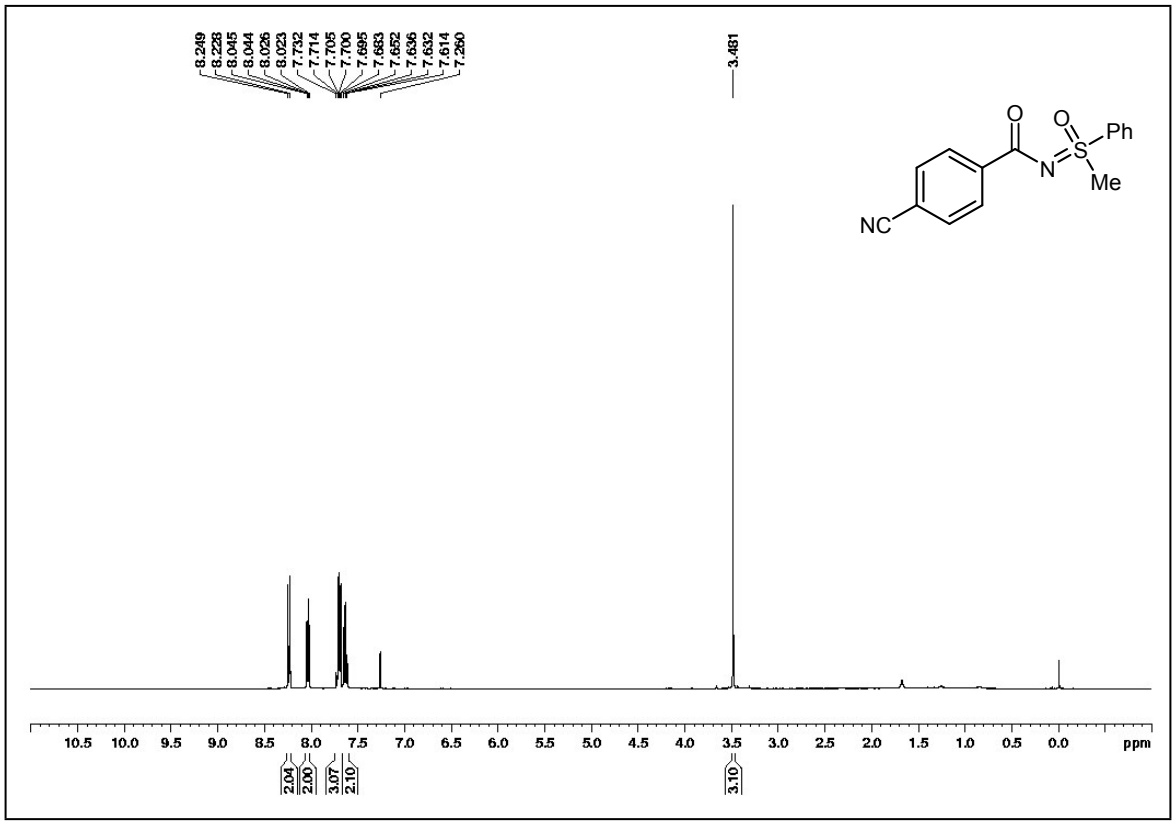


Figure 21: 400 MHz ^{1}H-NMR spectrum of **3k** in $CDCl_3$

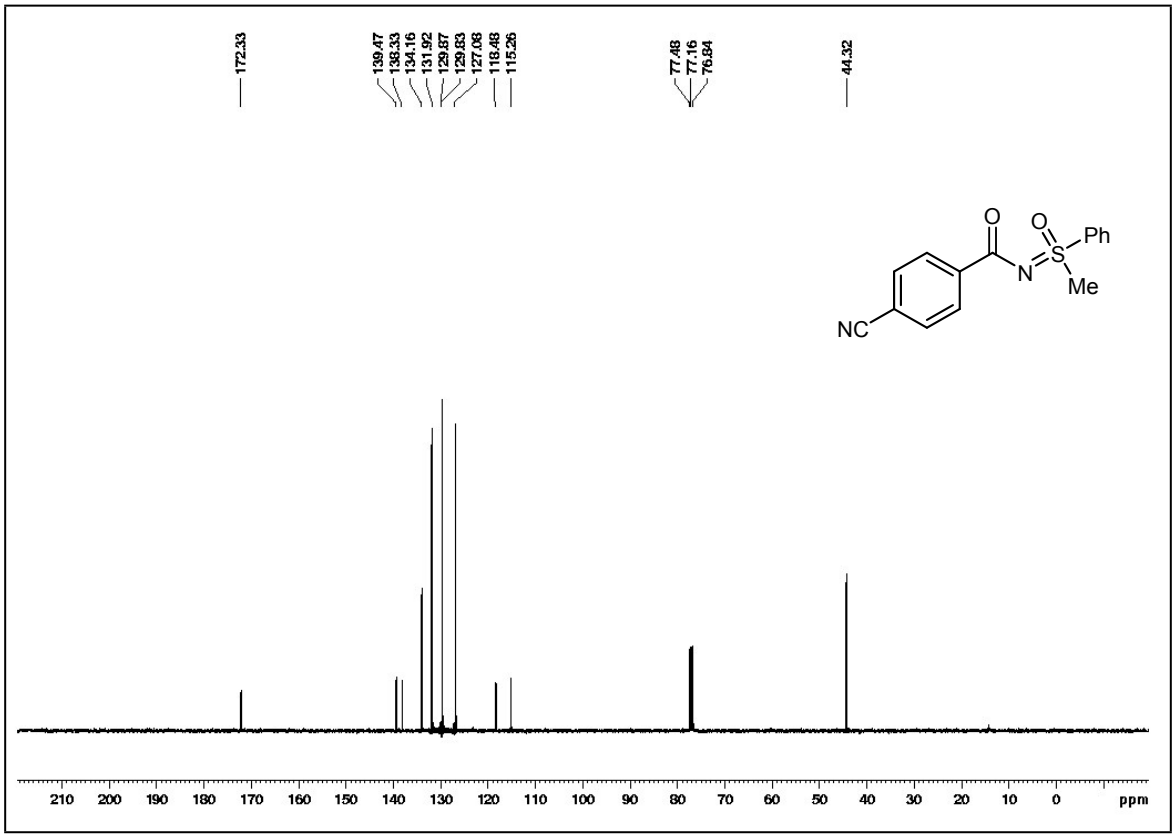
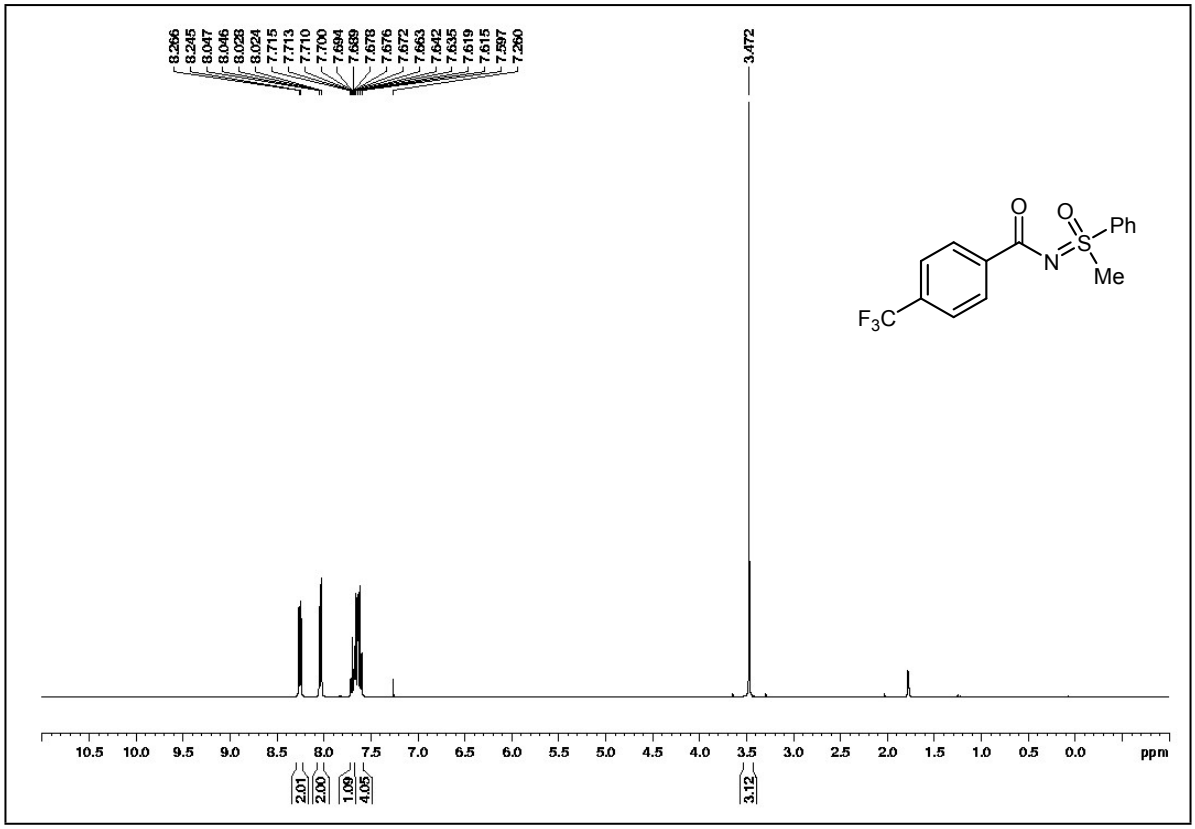


Figure 22: 100 MHz ^{13}C-NMR spectrum of **3k** in $CDCl_3$



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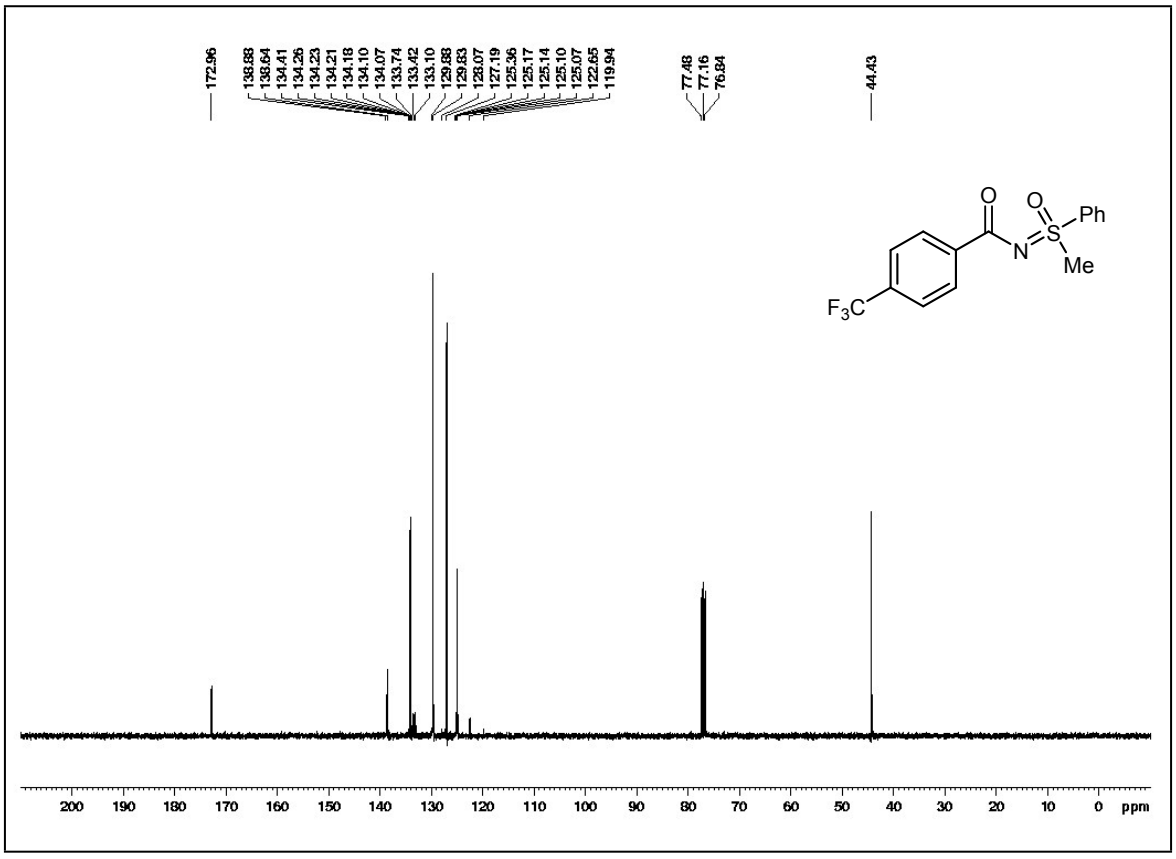

Figure 24: 100 MHz ^{13}C-NMR spectrum of **3l** in $CDCl_3$

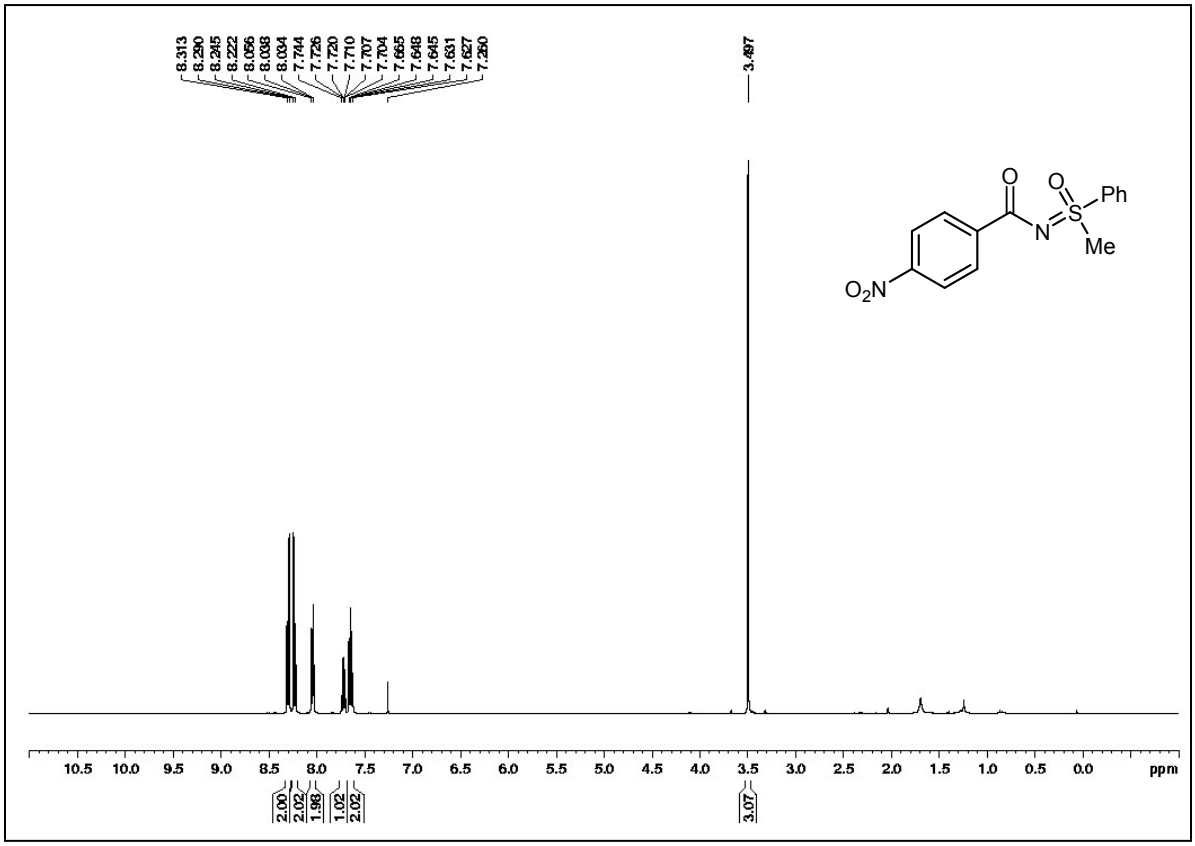

Figure 25: 400 MHz ^{1}H-NMR spectrum of **3m** in $CDCl_3$

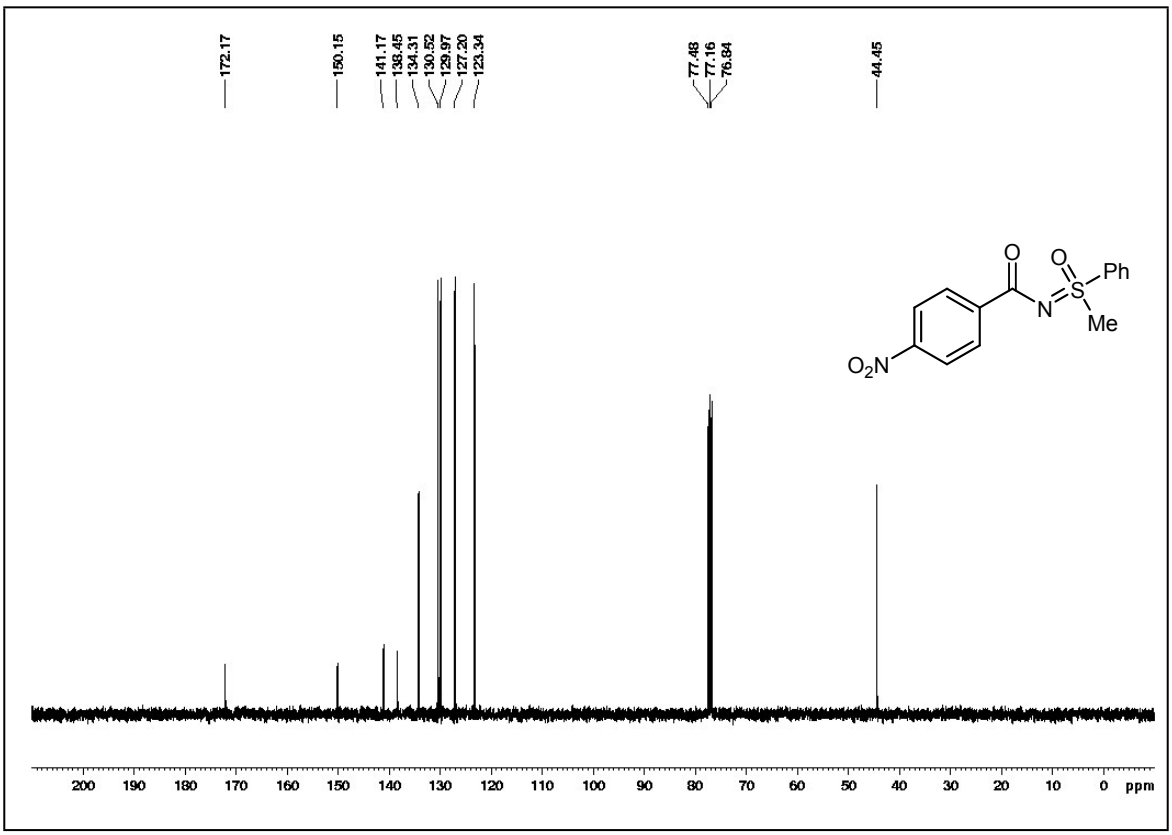

Figure 26: 100 MHz ^{13}C-NMR spectrum of **3m** in $CDCl_3$

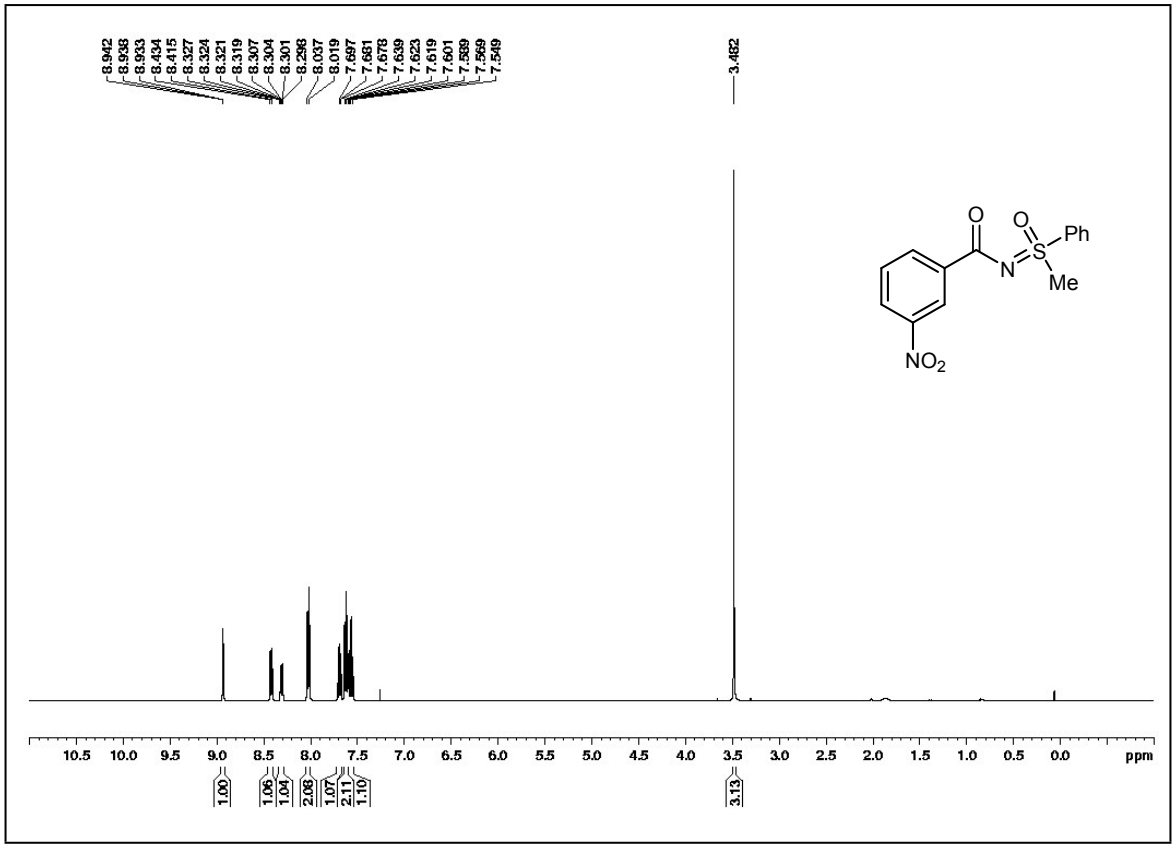

Figure 27: 400 MHz ^{1}H-NMR spectrum of **3n** in $CDCl_3$

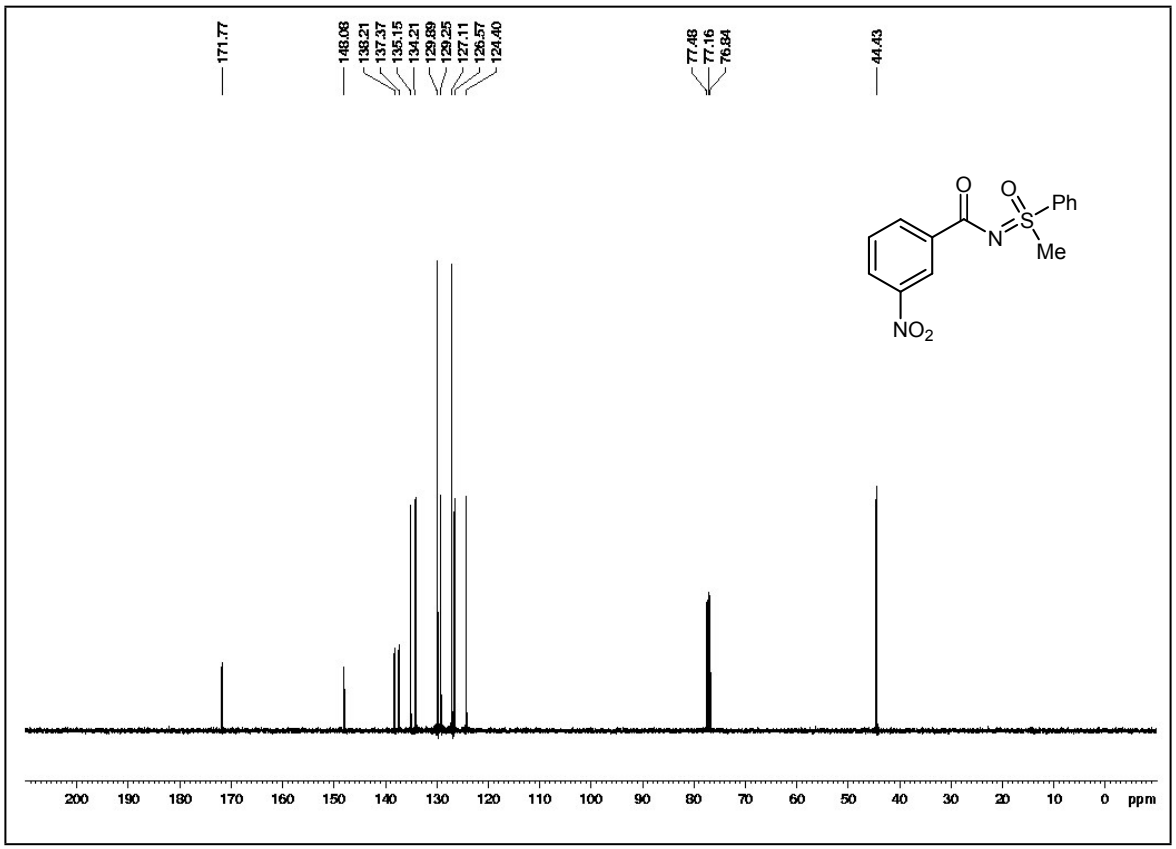

Figure 28: 100 MHz ^{13}C-NMR spectrum of **3n** in $CDCl_3$

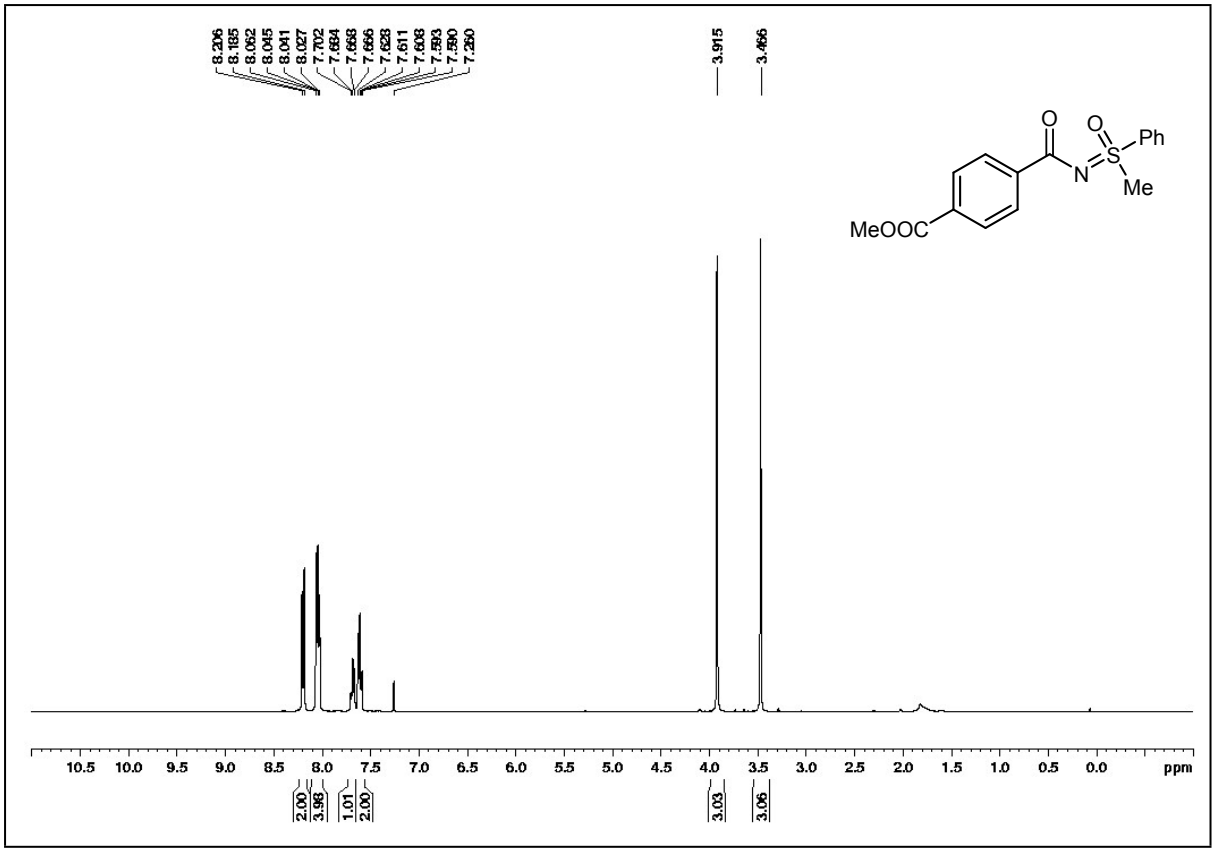

Figure 29: 400 MHz ^{1}H-NMR spectrum of **3o** in $CDCl_3$

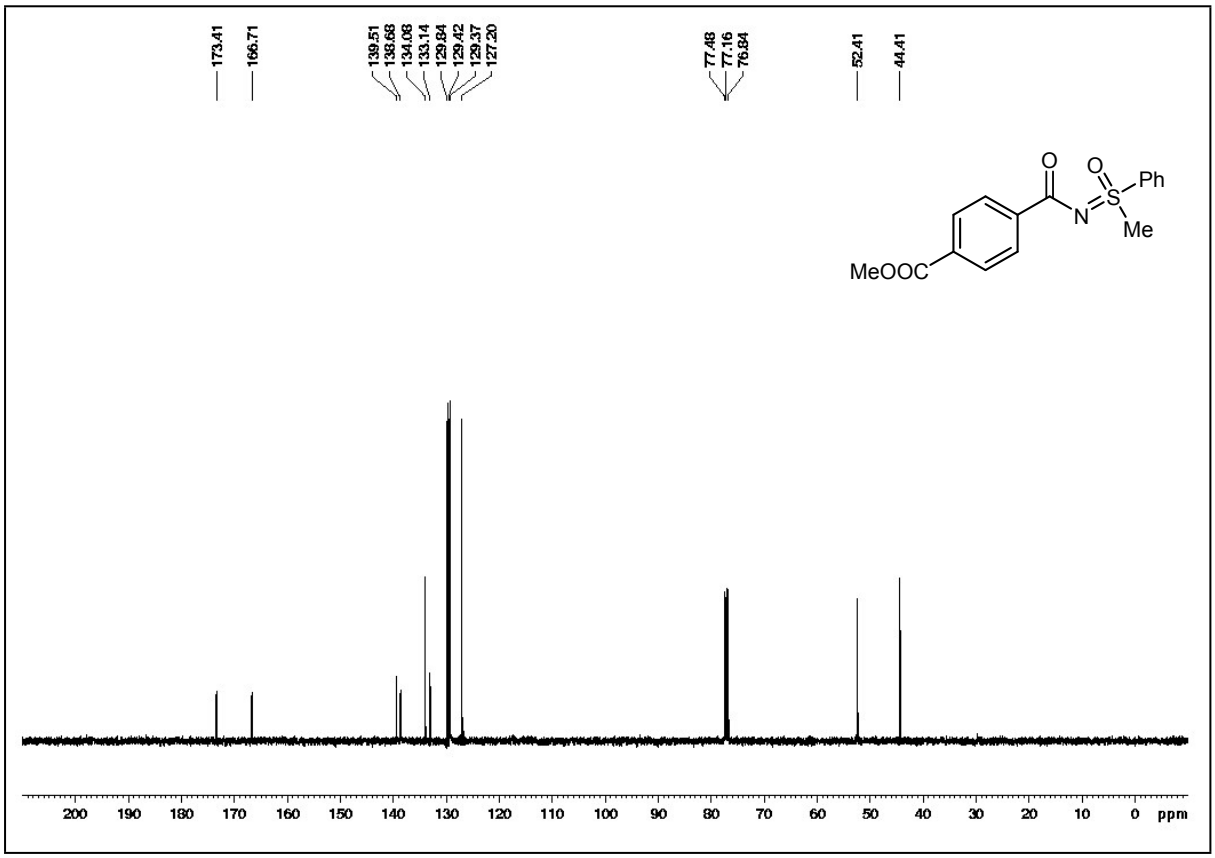

Figure 30: 100 MHz ^{13}C-NMR spectrum of **3o** in $CDCl_3$

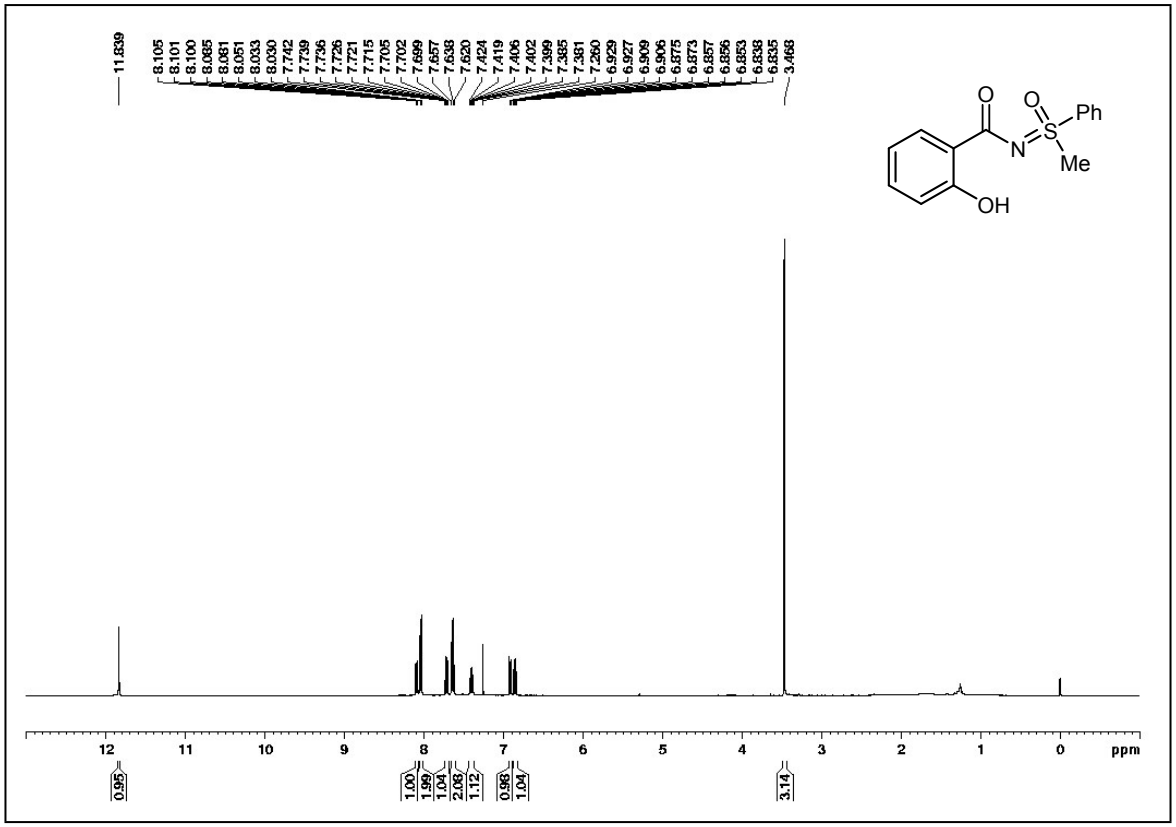

Figure 31: 400 MHz ^{1}H-NMR spectrum of **3p** in $CDCl_3$

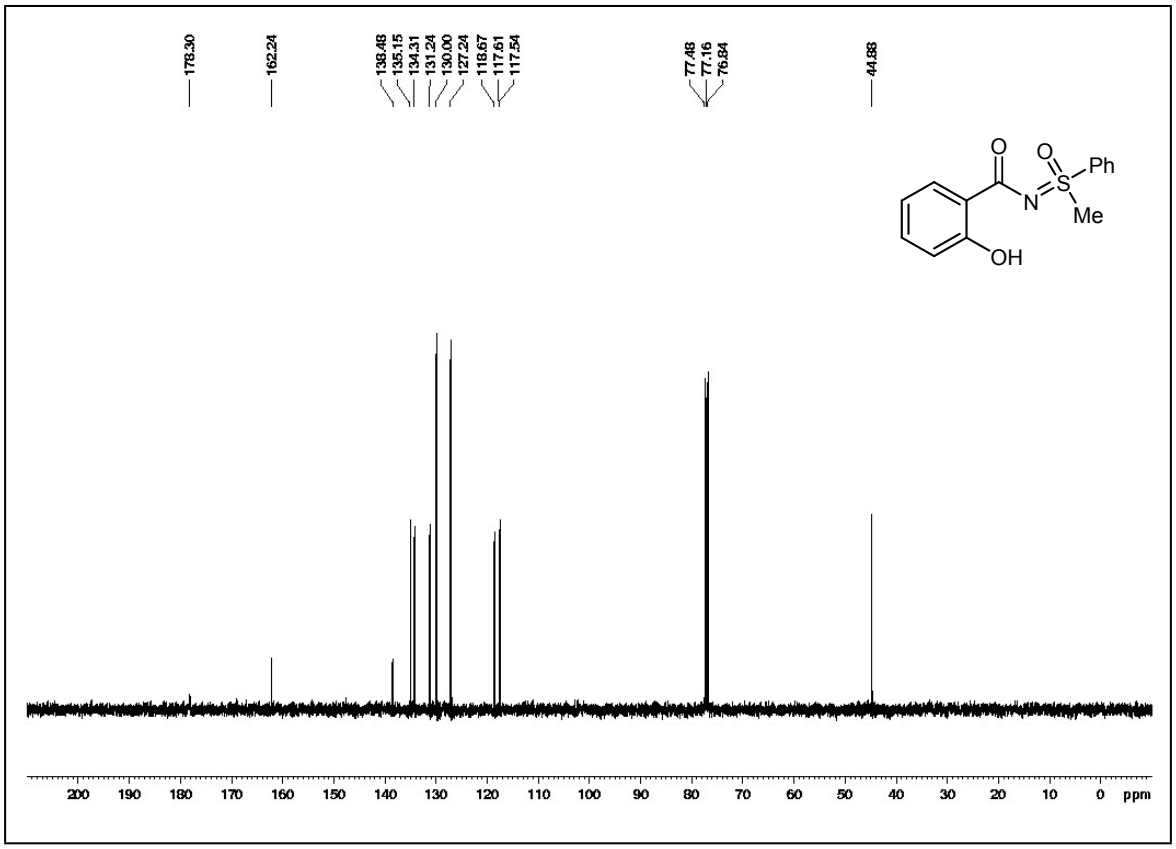

Figure 32: 100 MHz ^{13}C-NMR spectrum of **3p** in $CDCl_3$

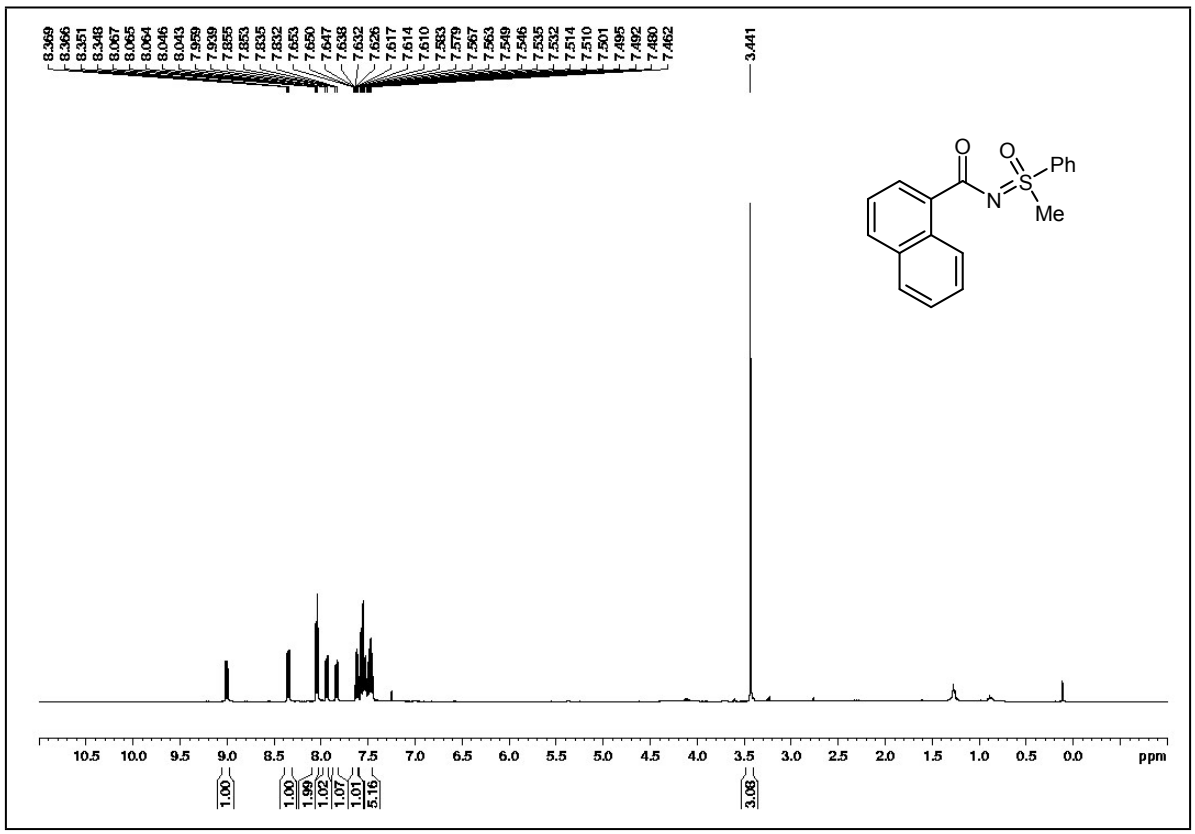

Figure 33: 400 MHz ^{1}H-NMR spectrum of **3q** in $CDCl_3$

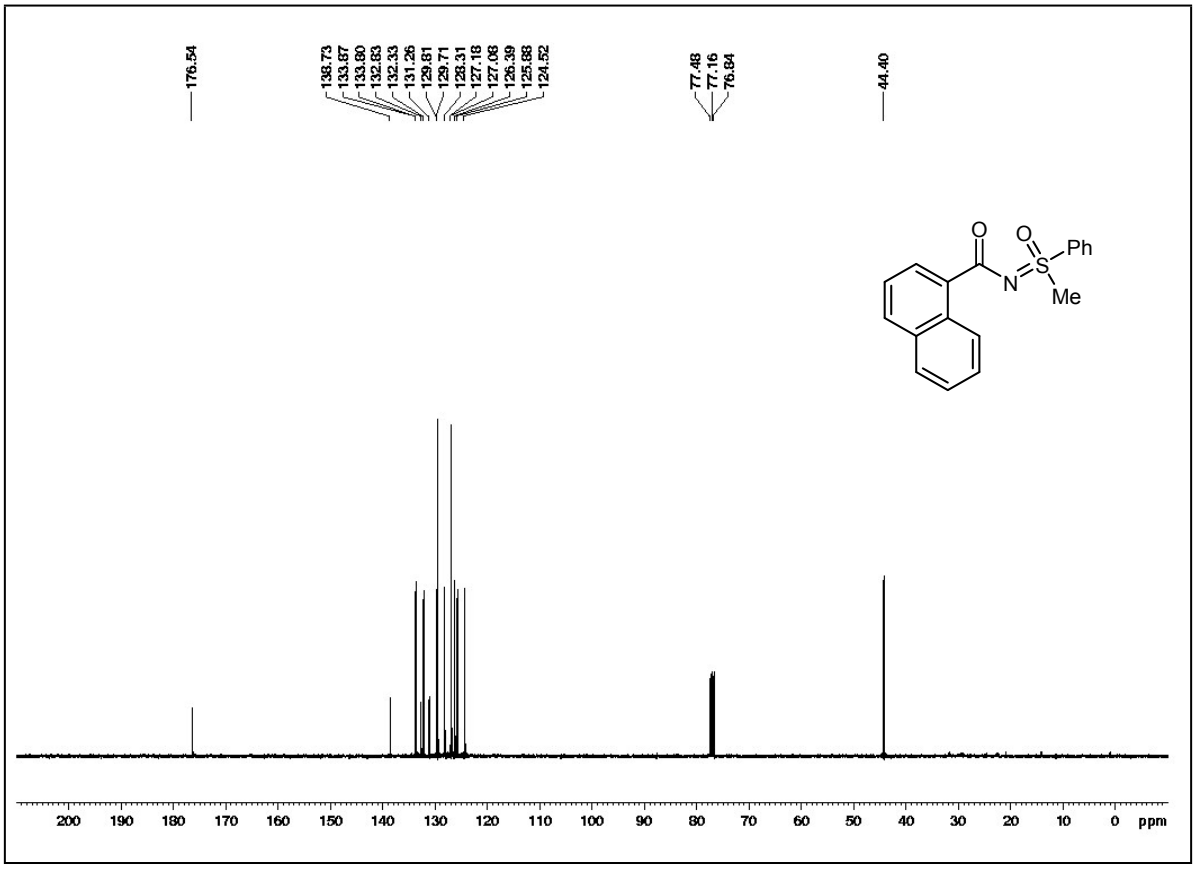

Figure 34: 100 MHz ^{13}C-NMR spectrum of **3q** in $CDCl_3$

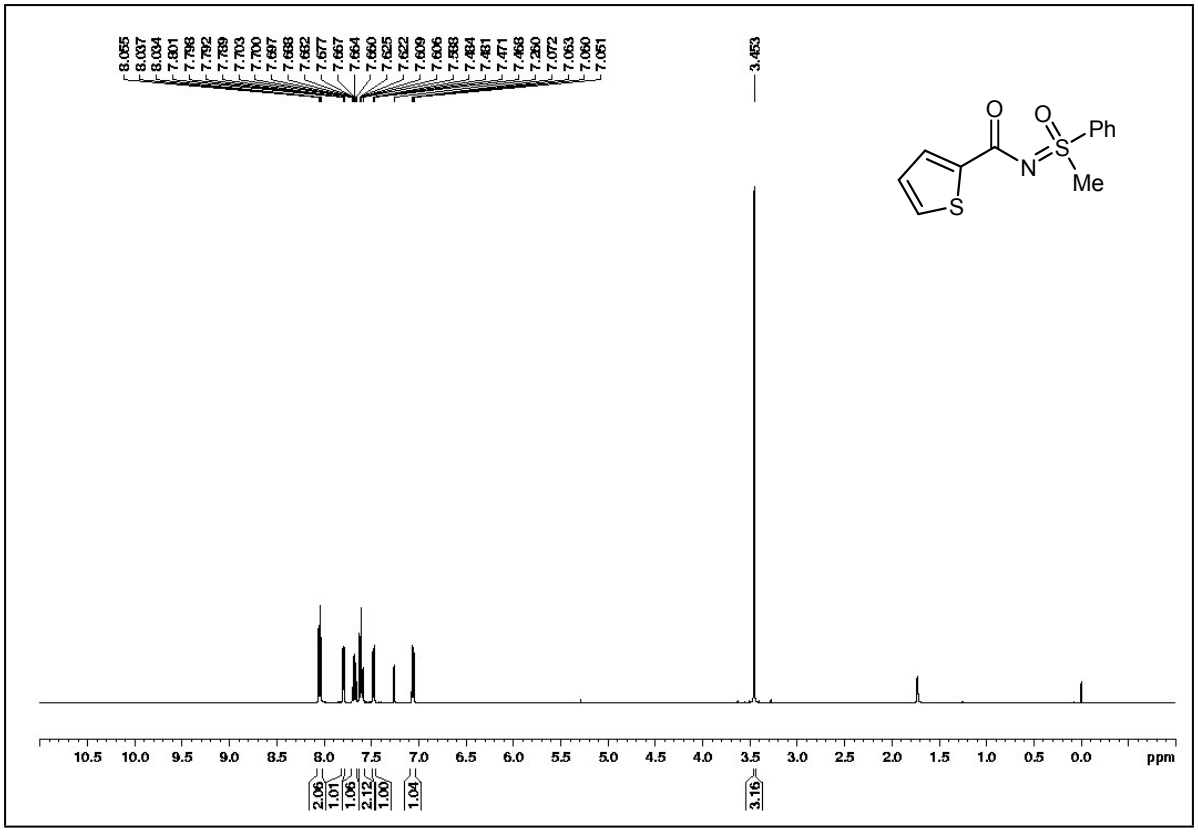

Figure 35: 400 MHz ^{1}H-NMR spectrum of **3r** in $CDCl_3$

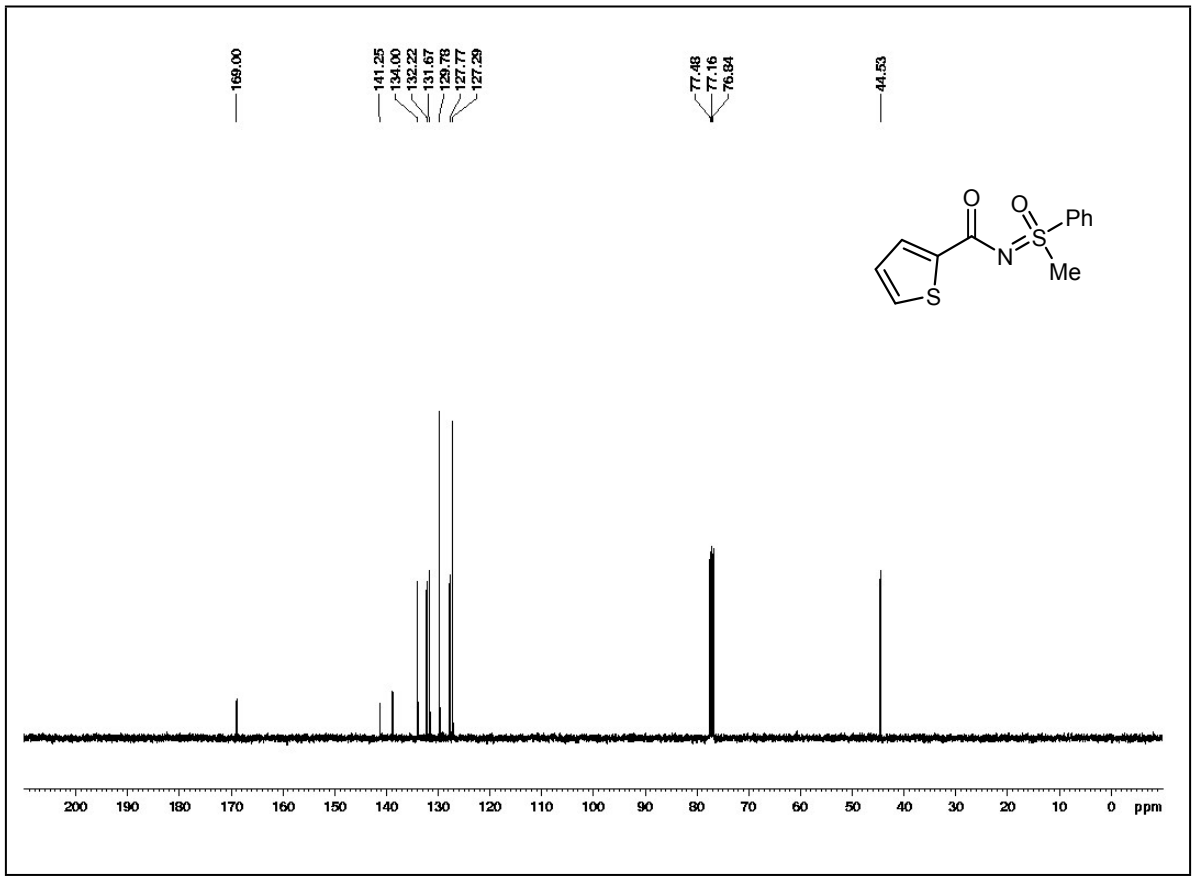

Figure 36: 100 MHz ^{13}C-NMR spectrum of **3r** in $CDCl_3$

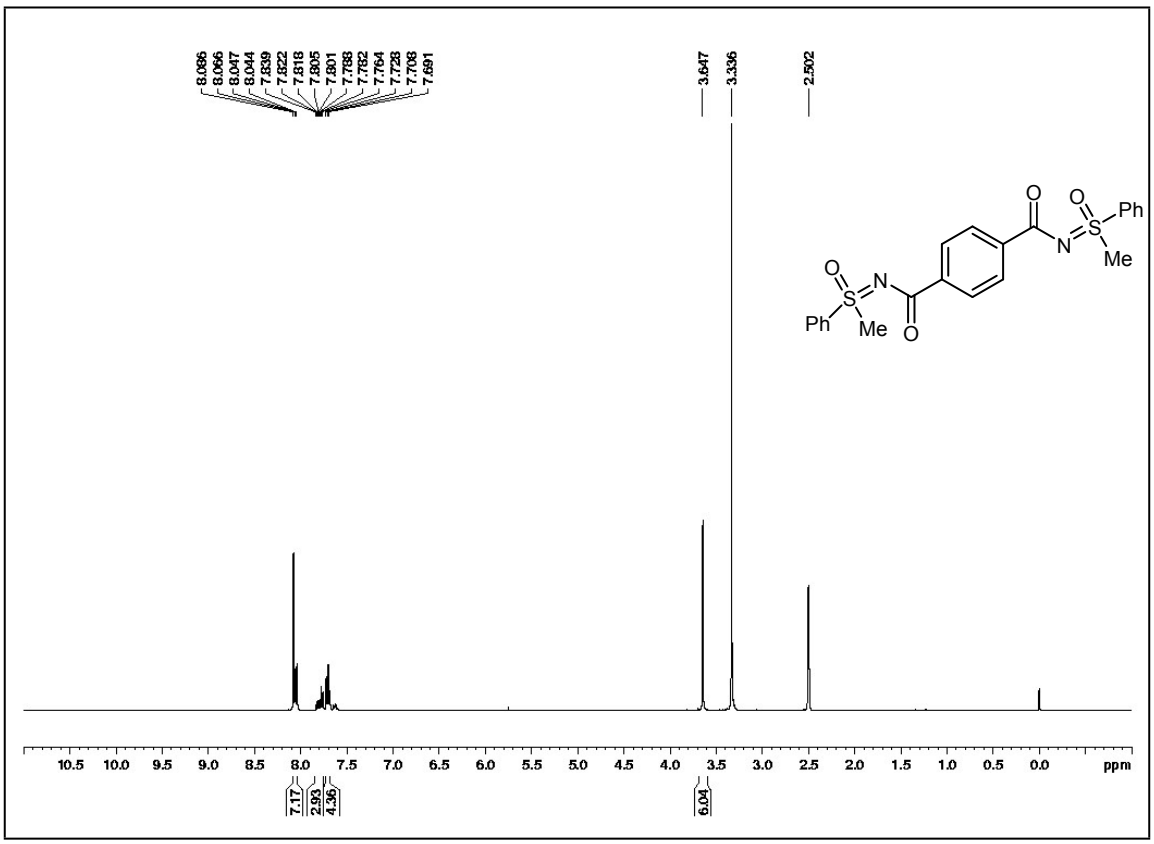

Figure 37: 400 MHz ^{1}H-NMR spectrum of **3s** in DMSO-d_6

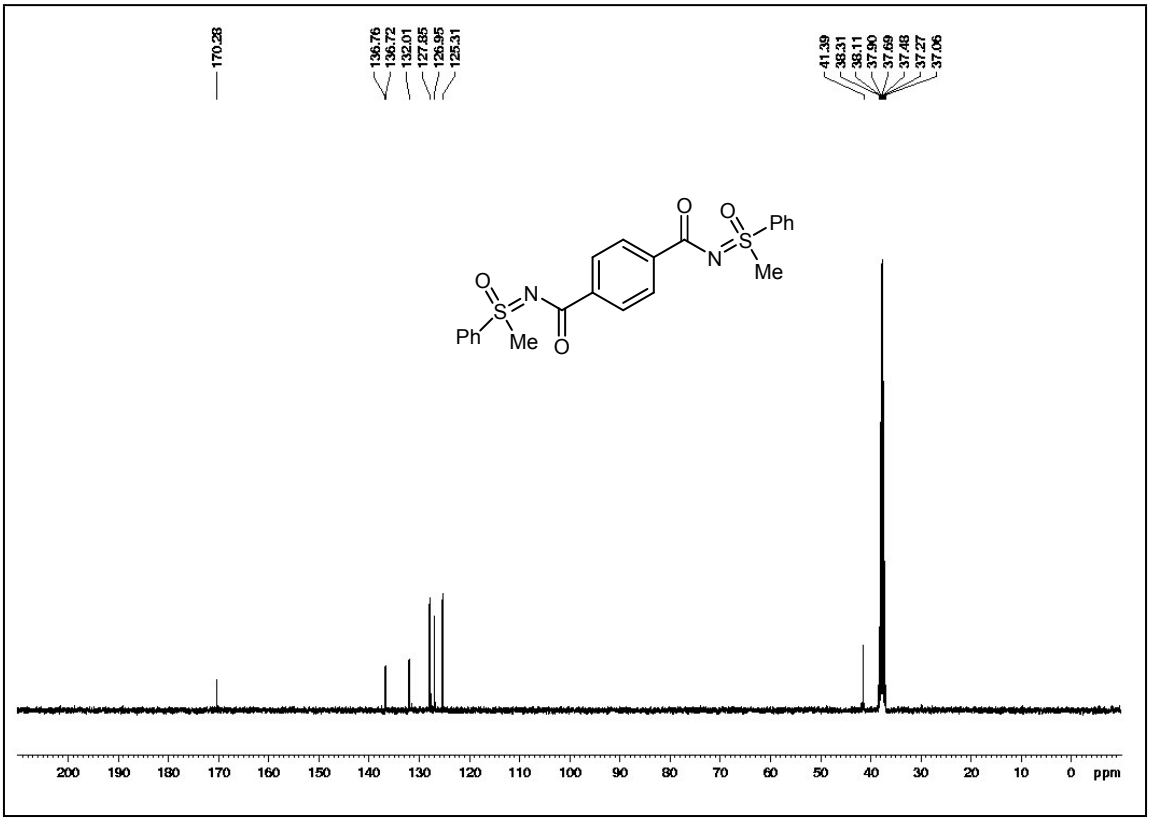

Figure 38: 100 MHz ^{13}C-NMR spectrum of **3s** in DMSO-d_6

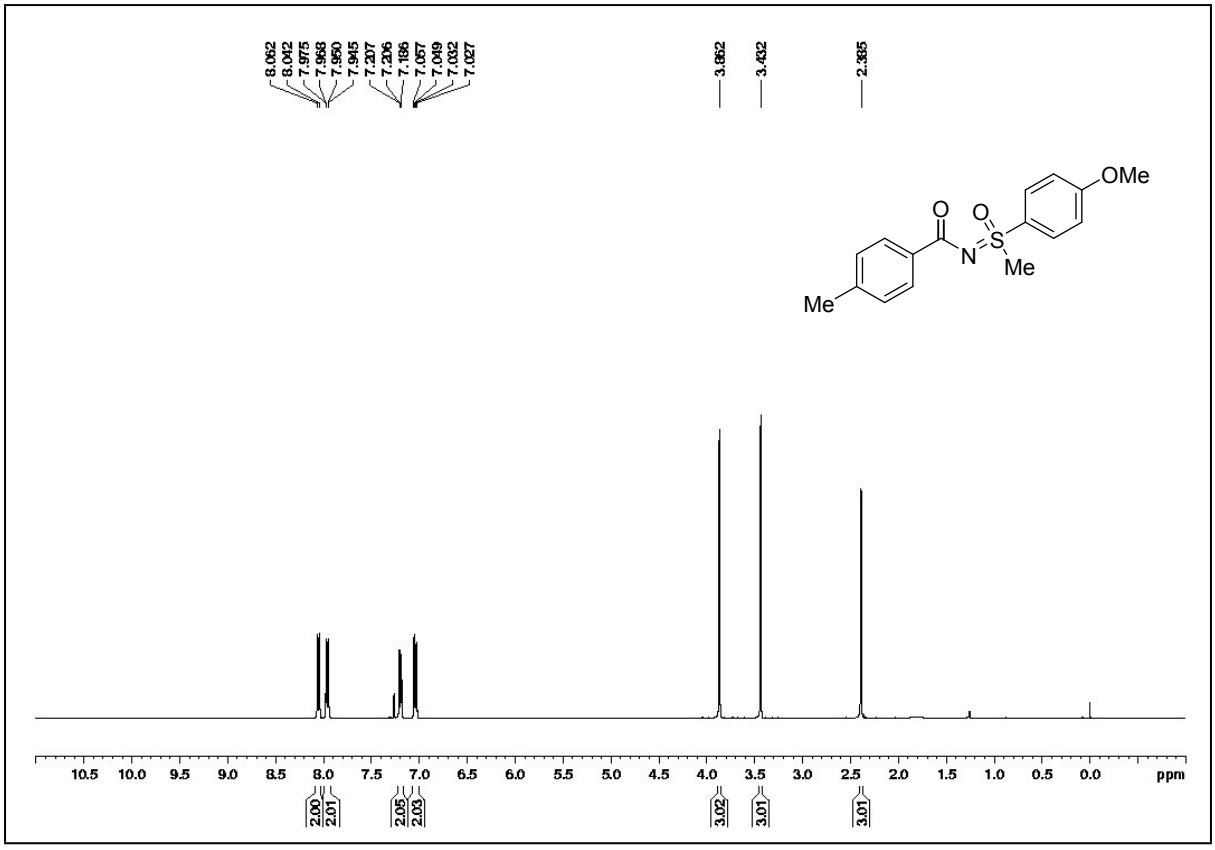

Figure 39: 400 MHz ^{1}H-NMR spectrum of **3t** in $CDCl_3$

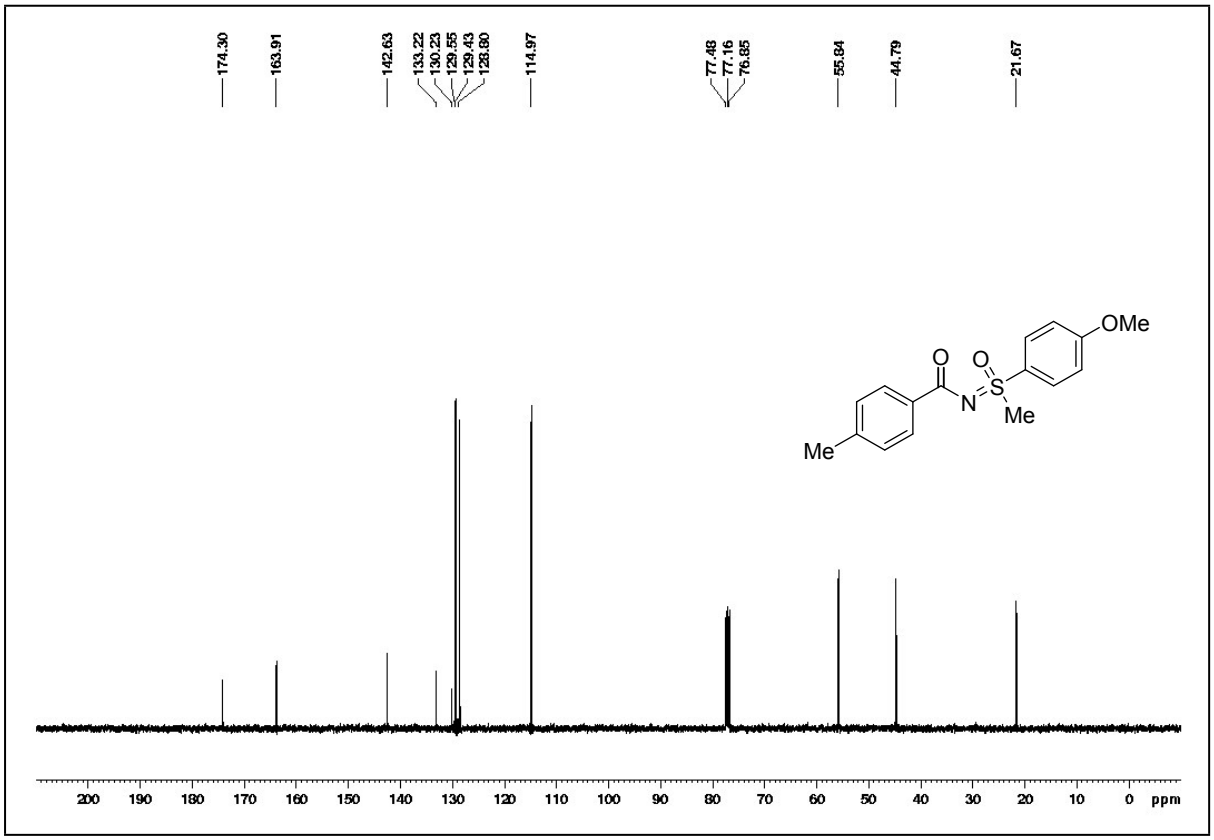

Figure 40: 100 MHz ^{13}C-NMR spectrum of **3t** in $CDCl_3$

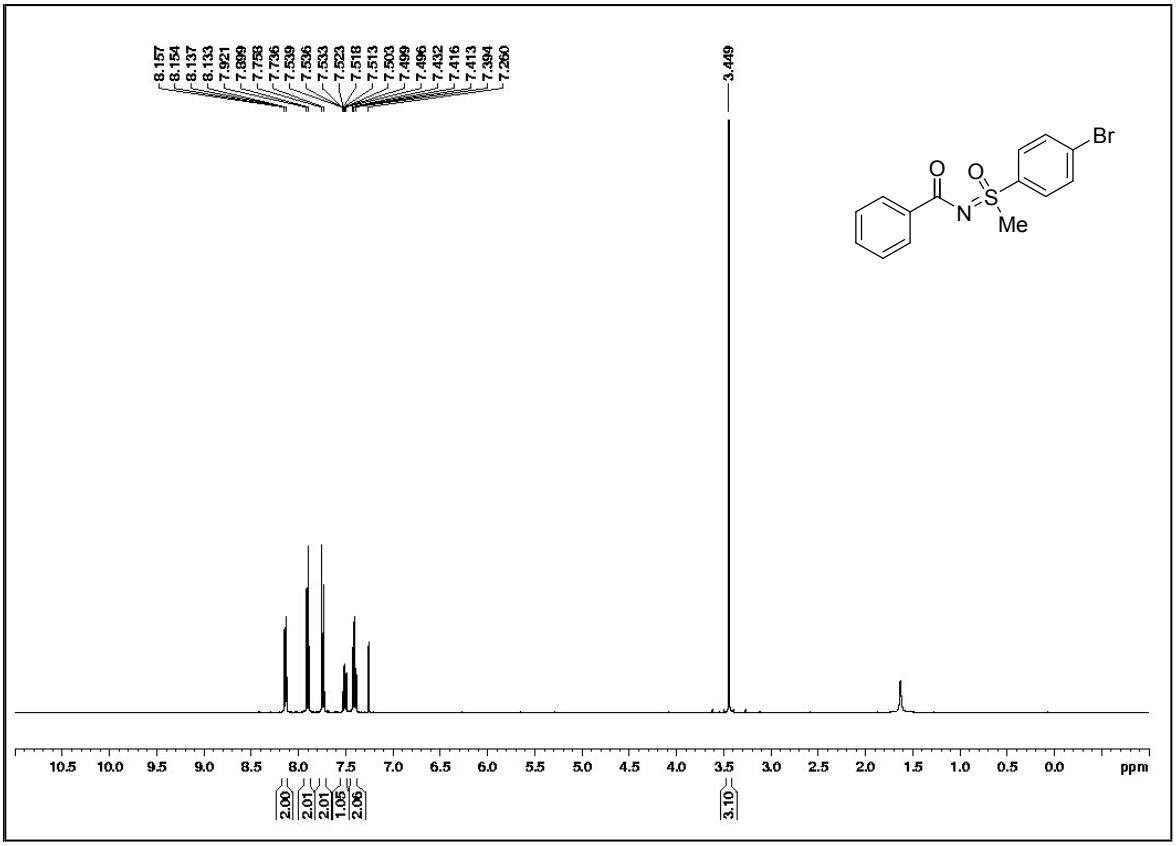

Figure 41: 400 MHz ^{1}H-NMR spectrum of **3u** in $CDCl_3$

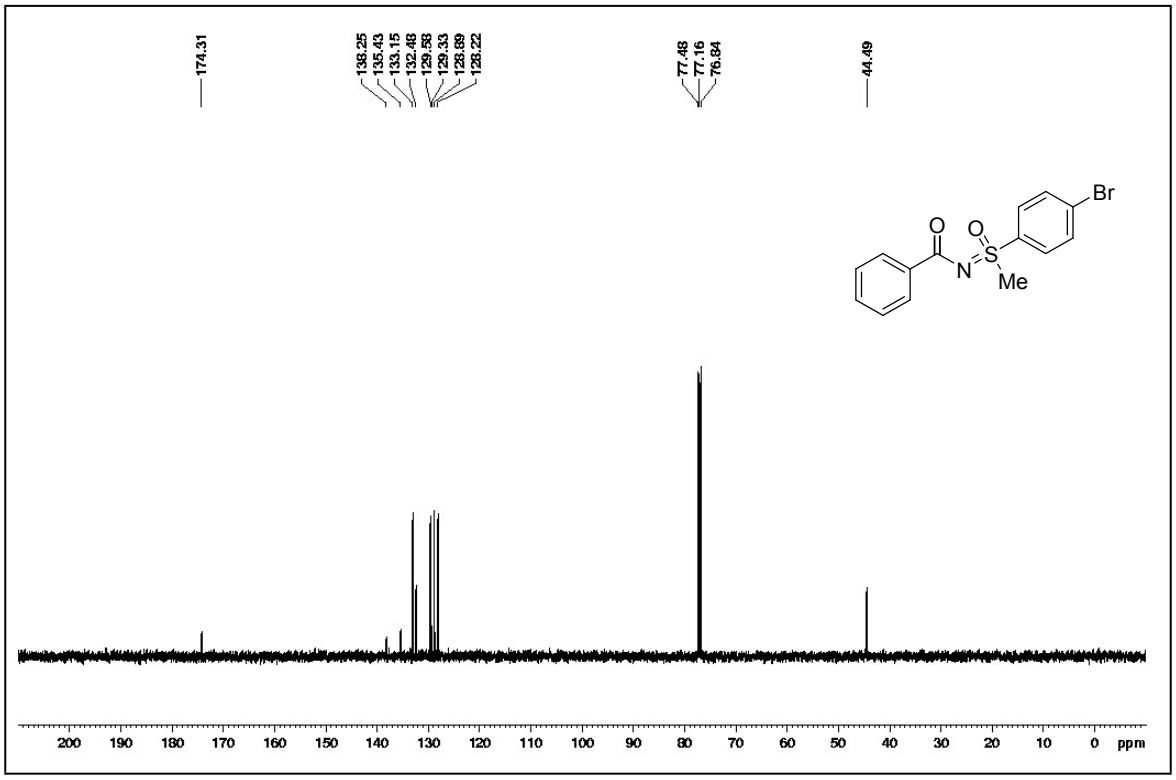

Figure 42: 100 MHz ^{13}C-NMR spectrum of **3u** in $CDCl_3$

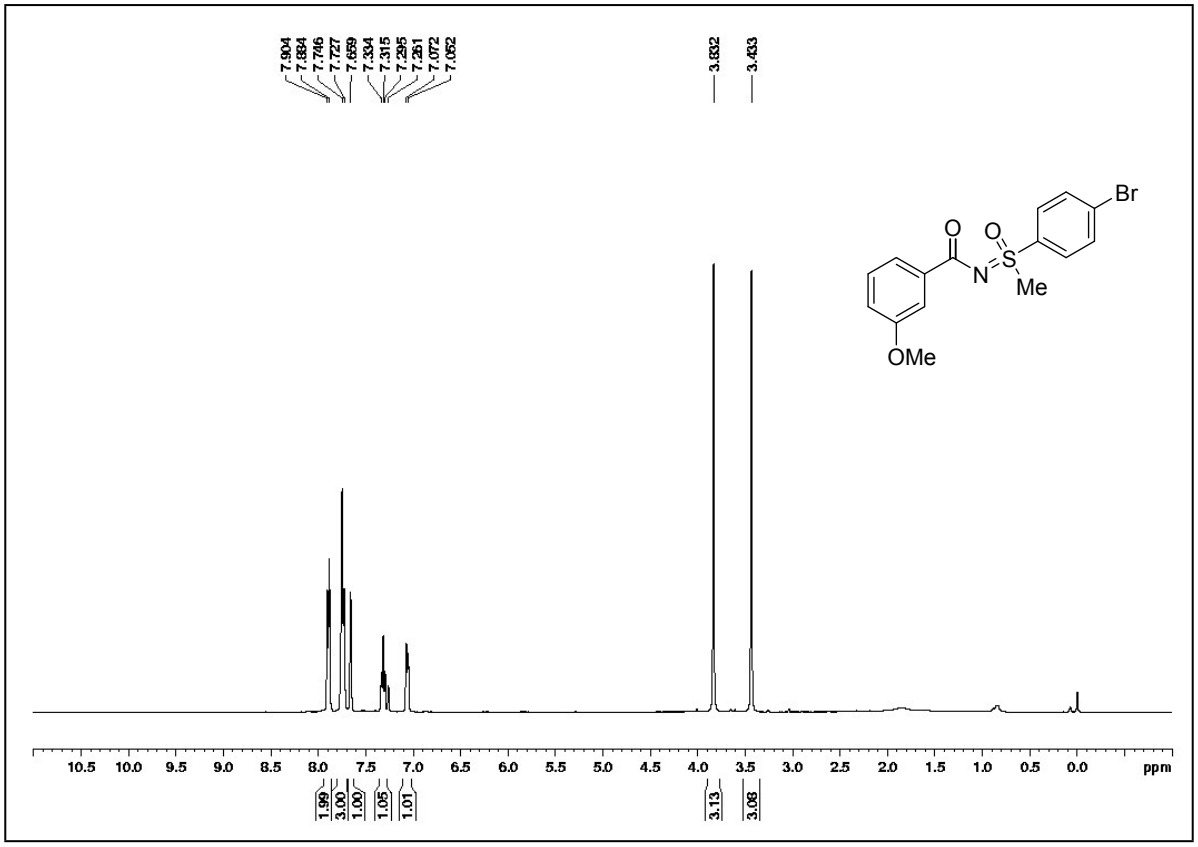

Figure 43: 400 MHz ^{1}H-NMR spectrum of **3v** in $CDCl_3$

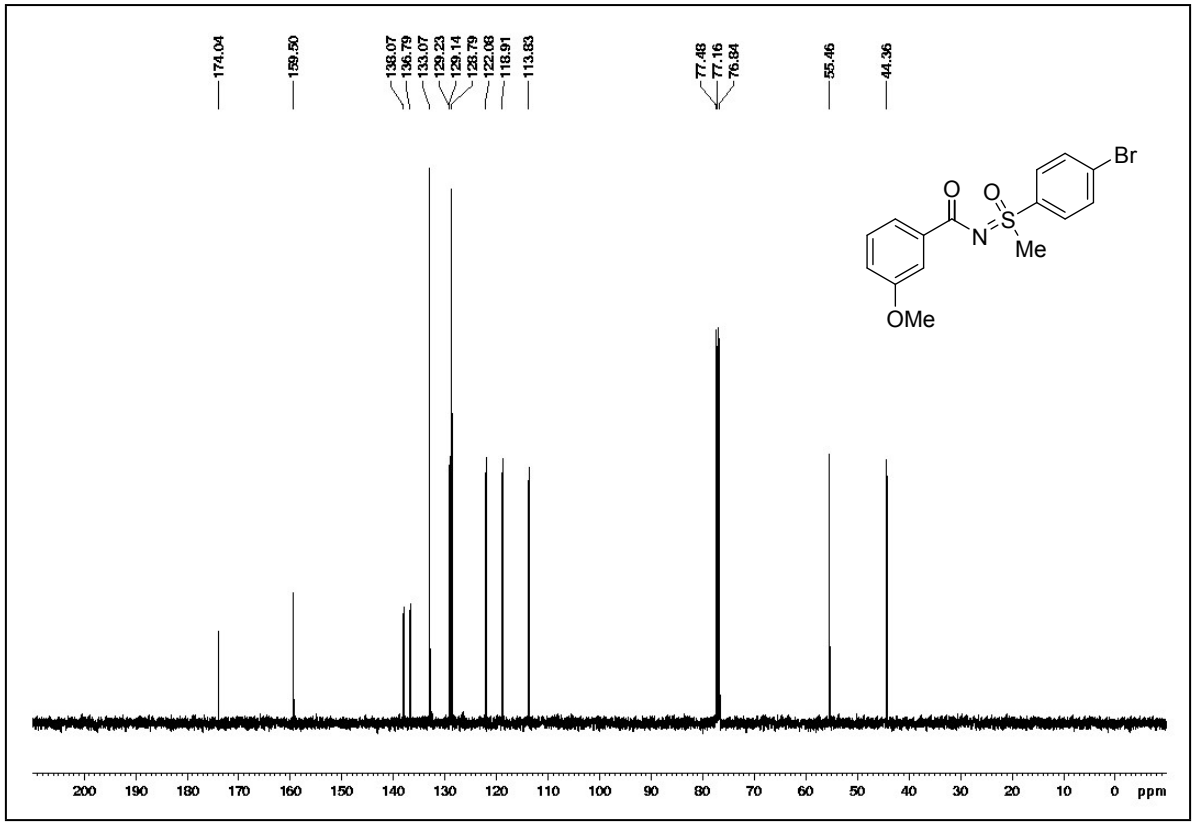

Figure 44: 100 MHz ^{13}C-NMR spectrum of **3v** in $CDCl_3$

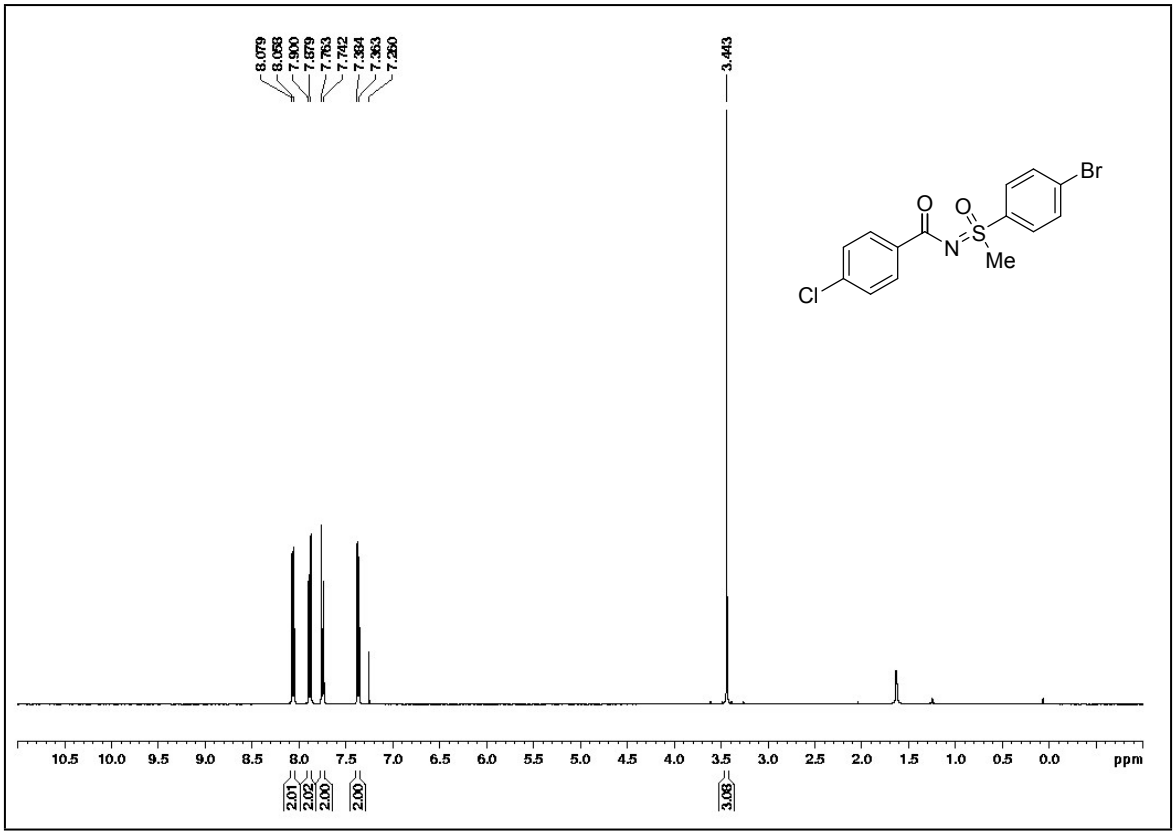

Figure 45: 400 MHz ^{1}H-NMR spectrum of **3w** in $CDCl_3$

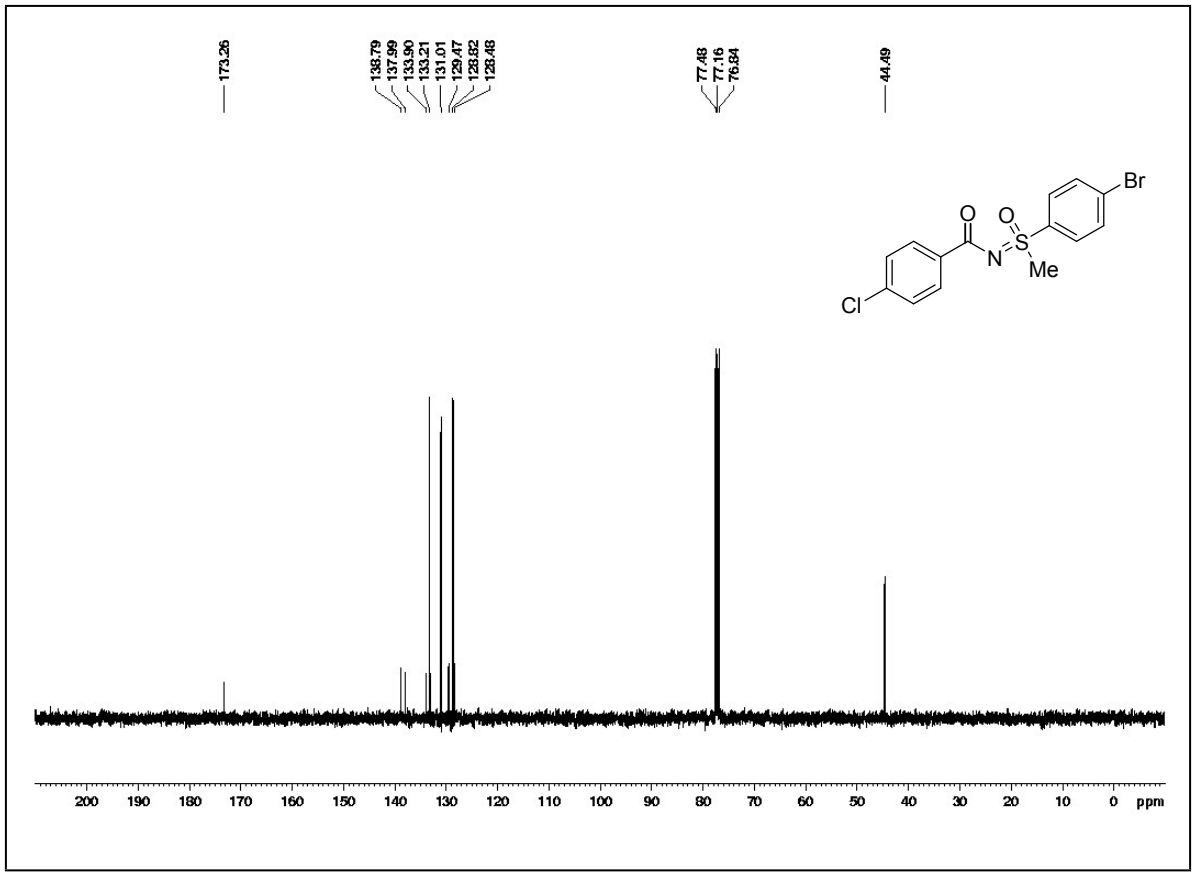

Figure 46: 100 MHz ^{13}C-NMR spectrum of **3w** in $CDCl_3$

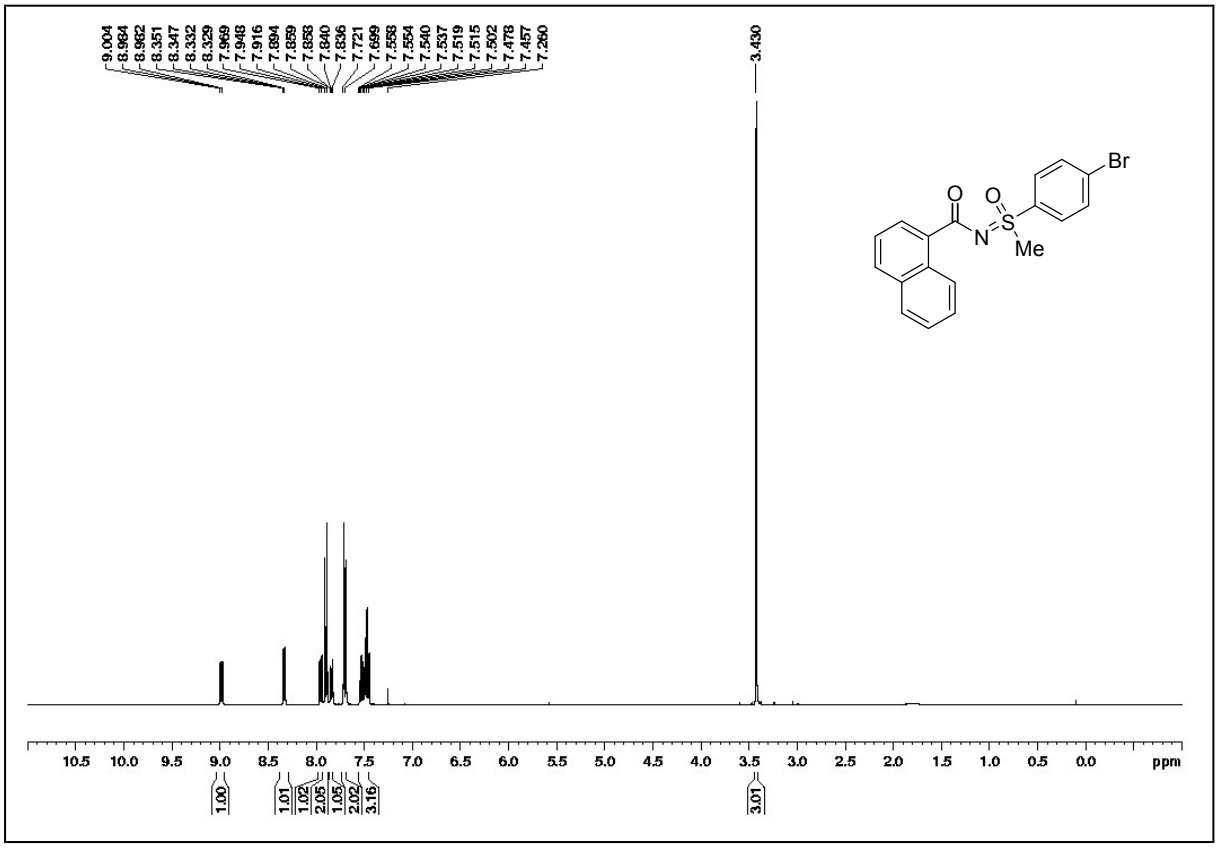

Figure 47: 400 MHz ^{1}H-NMR spectrum of **3x** in $CDCl_3$

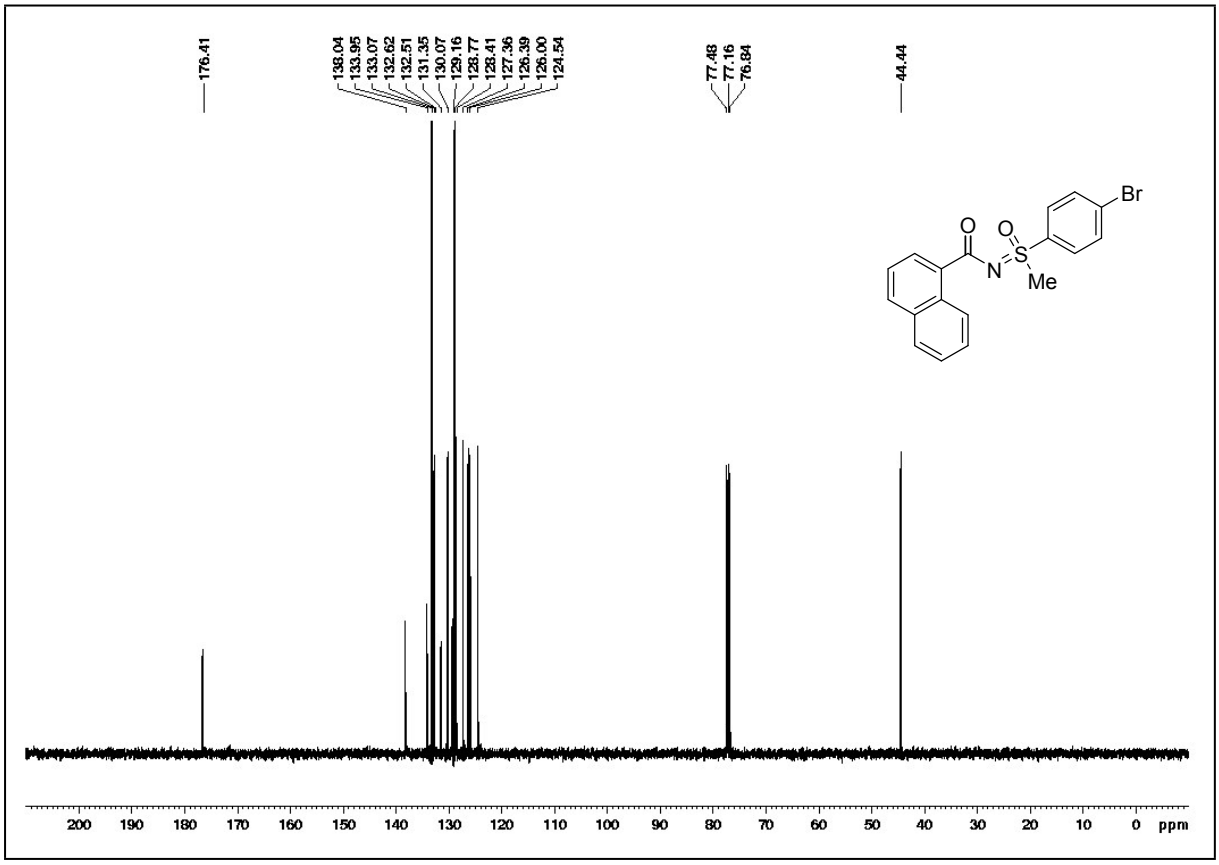

Figure 48: 100 MHz ^{13}C-NMR spectrum of **3x** in $CDCl_3$

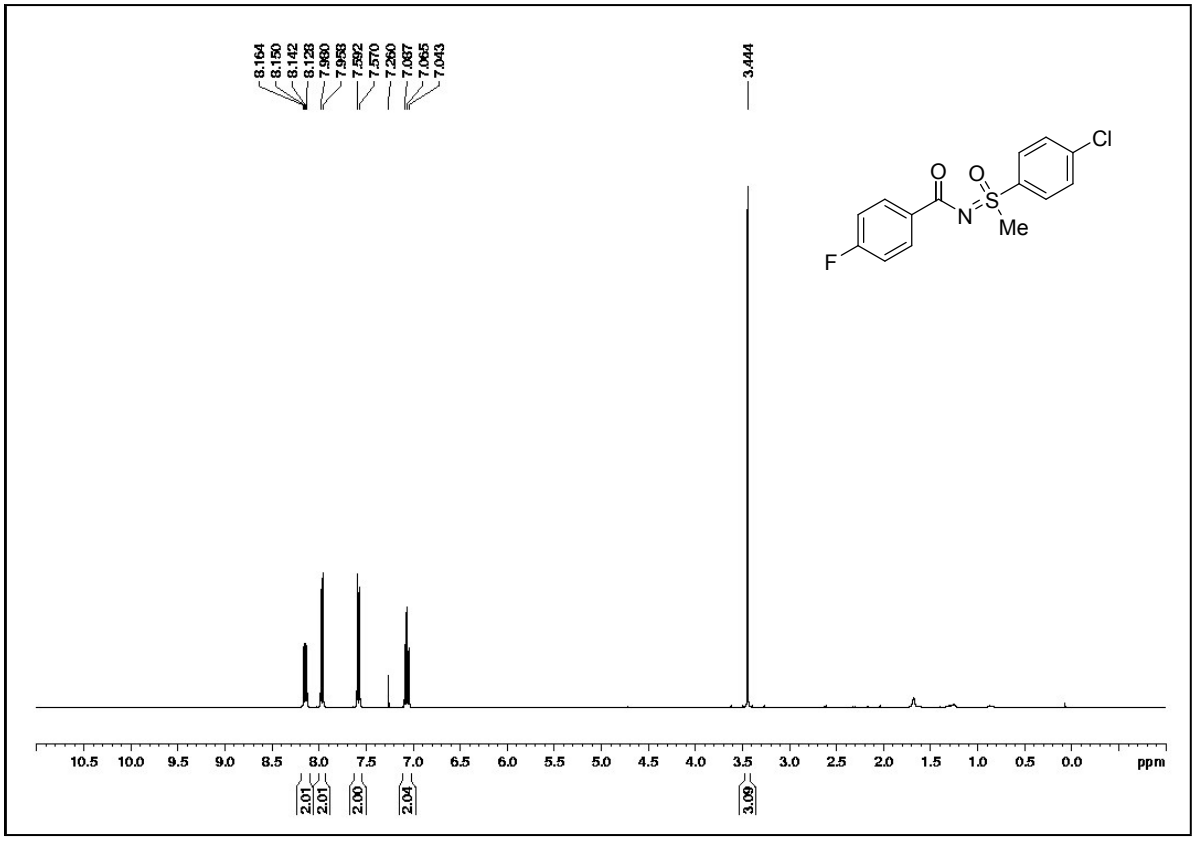

Figure 49: 500 MHz ^{1}H-NMR spectrum of **3y** in $CDCl_3$

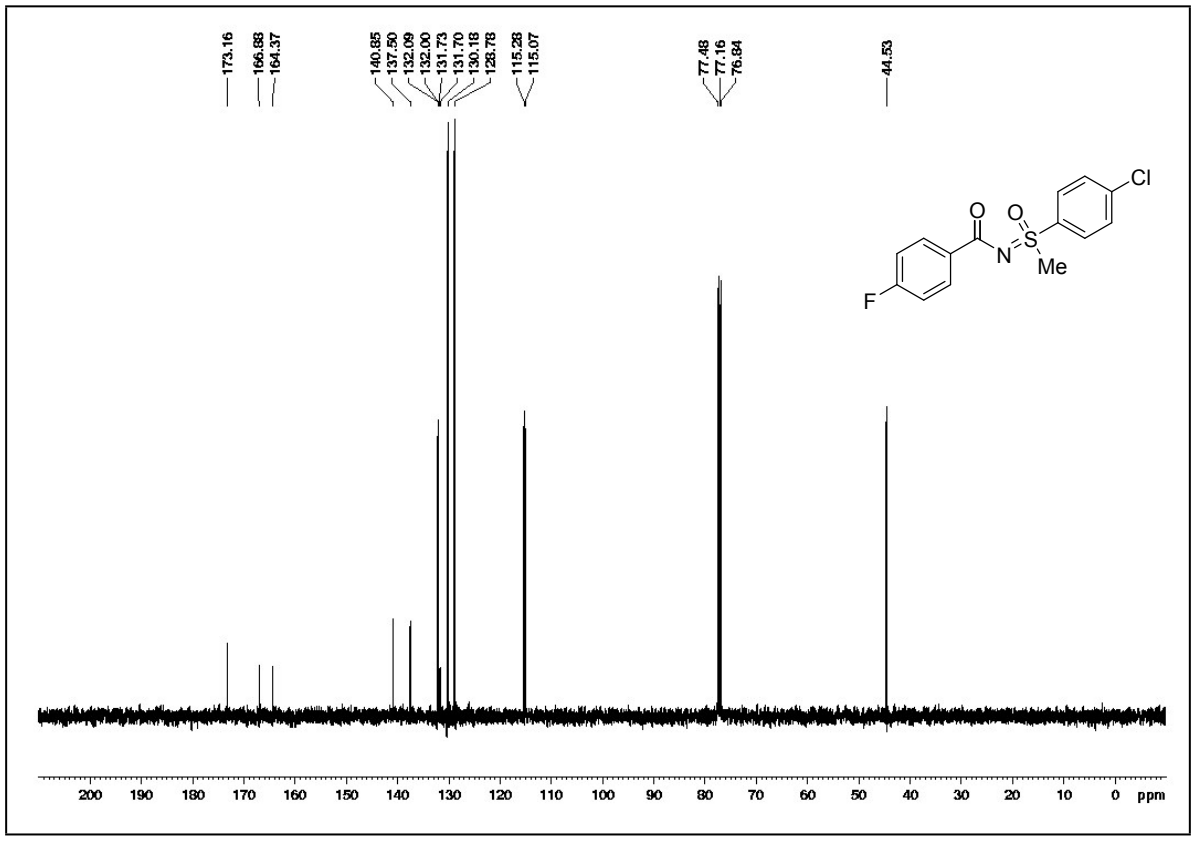

Figure 50: 125 MHz ^{13}C-NMR spectrum of **3y** in $CDCl_3$

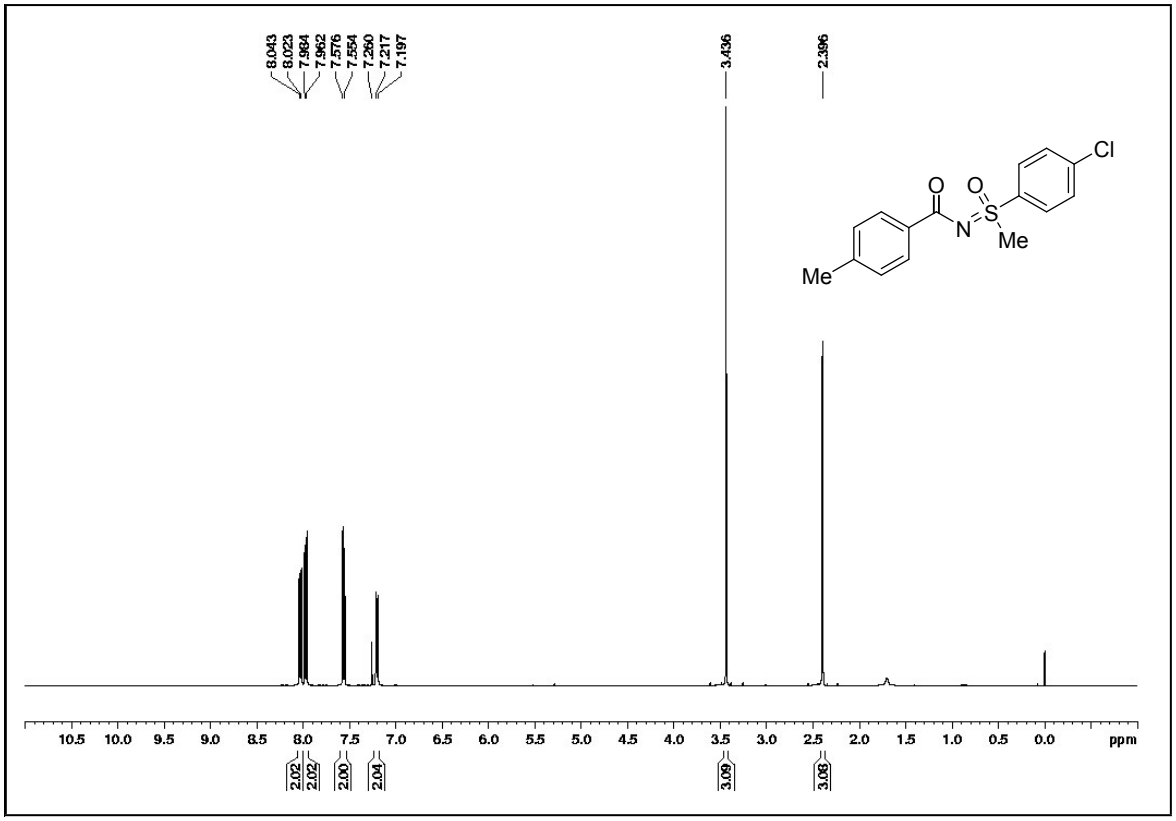

Figure 51: 400 MHz ^{1}H-NMR spectrum of **3z** in $CDCl_3$

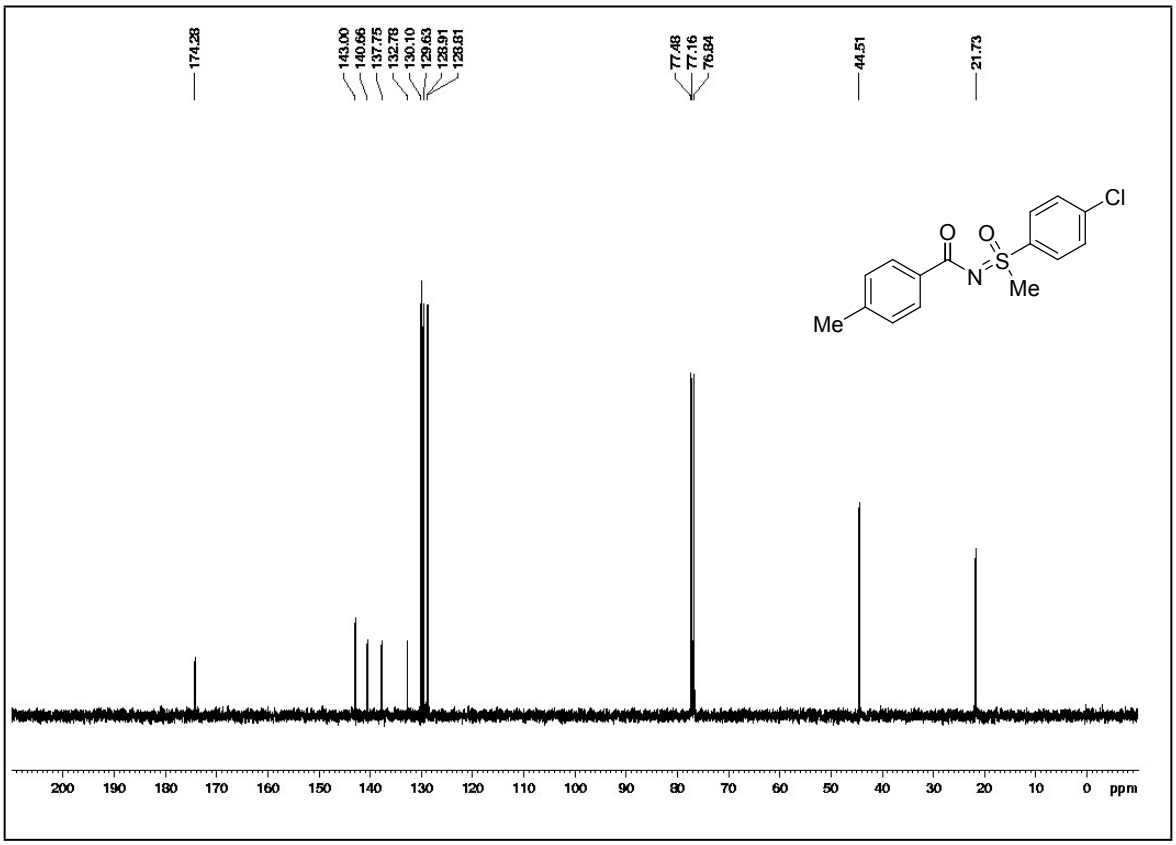

Figure 52: 100 MHz ^{13}C-NMR spectrum of **3z** in $CDCl_3$

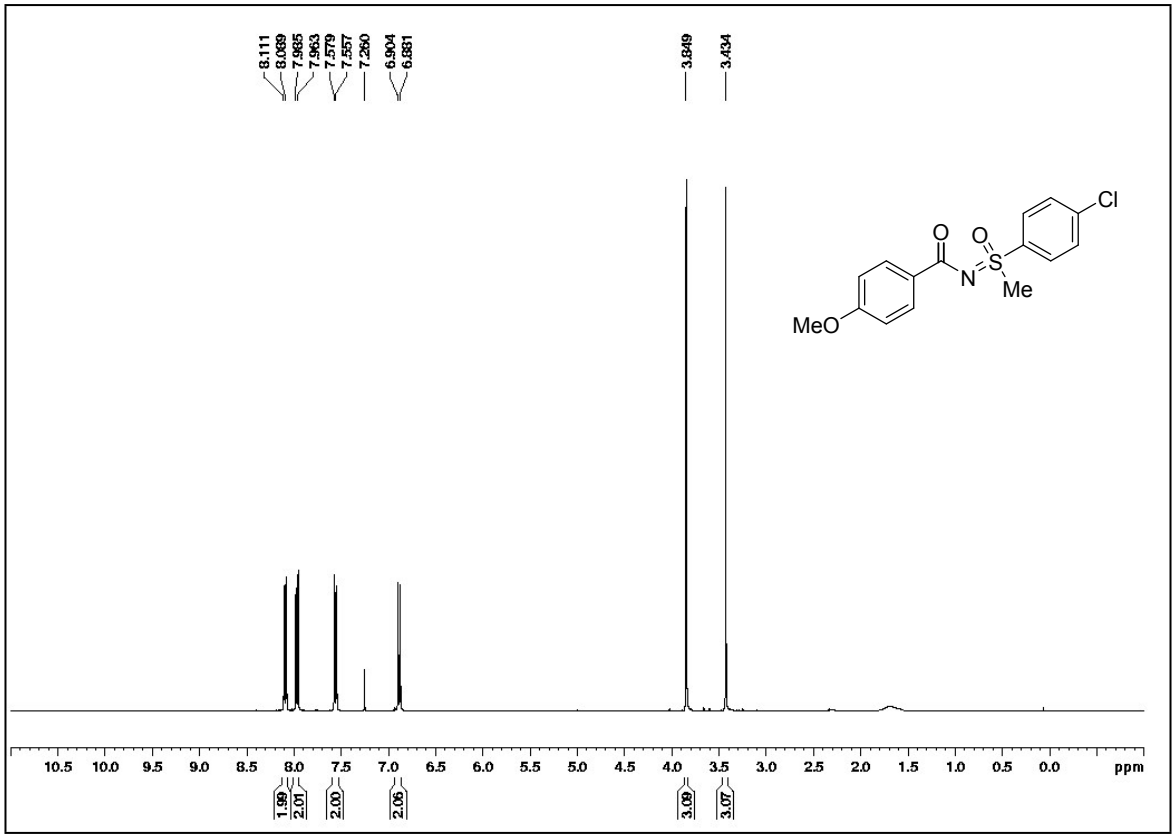

Figure 53: 400 MHz ^{1}H-NMR spectrum of **3aa** in $CDCl_3$

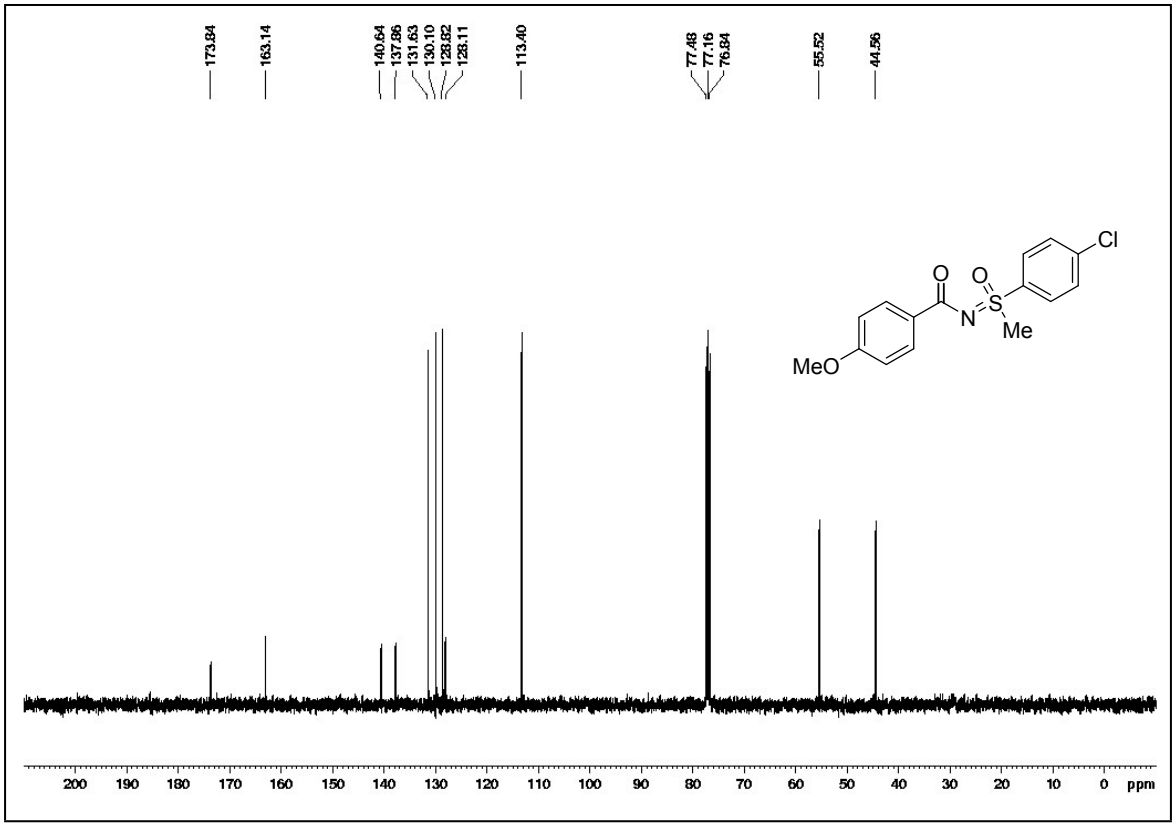

Figure 54: 100 MHz ^{13}C-NMR spectrum of **3aa** in $CDCl_3$

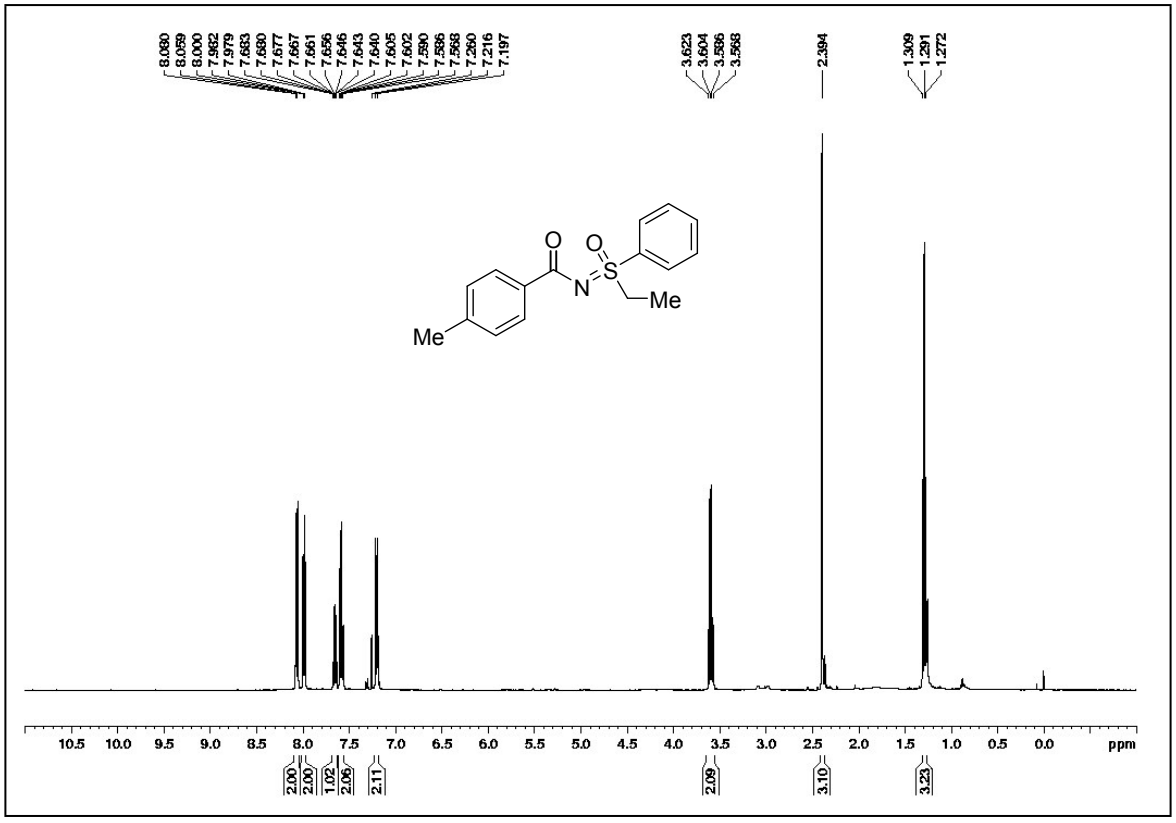

Figure 55: 400 MHz ^{1}H-NMR spectrum of **3ab** in $CDCl_3$

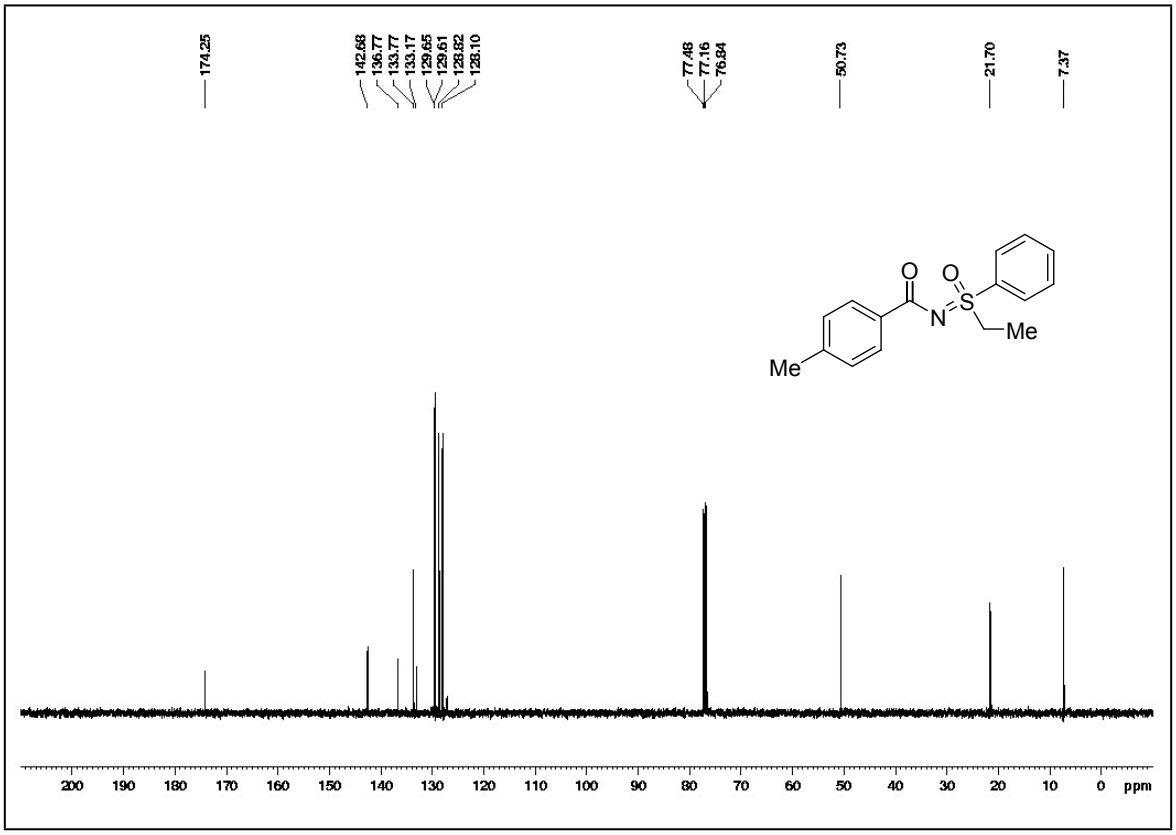

Figure 56: 100 MHz ^{13}C-NMR spectrum of **3ab** in $CDCl_3$