Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Stable and Reusable Pd-nanoparticles Catalyzed Synthesis of Symmetrical and Unsymmetrical 1, 2-Dicarbonyl compounds

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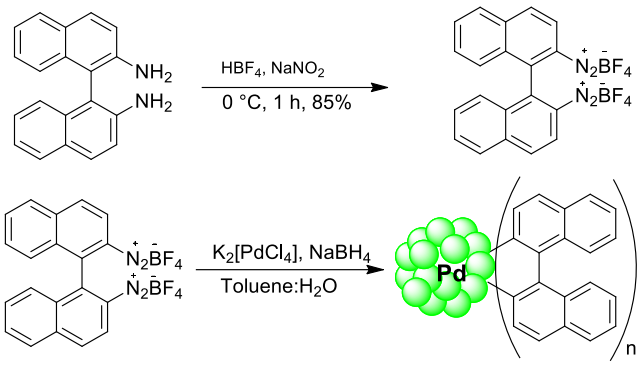
EXPERIMENTAL SECTION

1. General procedure for the synthesis of Pd-nanoparticles (Pd-BNP)[1]



1.1 Synthesis of Pd-nanoparticles (Pd-BNP)

Potassium tetrachloropalladate (326.5 mg, 1.0 mmol) in nanopure water (50 mL), 1,1'-binaphthyl, 2,2'-bis(diazonium tetrafluoroborate) (482.1 mg, 1.0 mmol), and toluene (50 ml) was added to a 250 mL round-bottomed flask. The reaction mixture was stirred vigorously for 1 h. After that, $NaBH_4$ (226.9 mg, 6.0 mmol) in water (2 mL) was added dropwise at room temperature to the solution, and the immediate color change to a dark greenish black signifies the formation of Pd-nanoparticles. The reaction mixture was stirred at room temperature for 2 h. The toluene layer was separated and washed with 0.5 M aq. H_2SO_4 (3 × 50 mL) and 0.5 M aq. $NaHCO_3$ (3 × 50 mL) to remove unreacted metal complexes. The residual solvent was removed using a rotary evaporator. The solid particles were suspended in ethanol (2 × 10 mL) and sonicated for 30 min. The suspension was centrifuged (4500 rpm, approximately 30 min.). The ethanol was removed, and the isolated mass was dried in vacuo to yield Pd-binaphthyl nanoparticles (Pd-BNP) as a black solid.

1.2 Typical procedure for synthesis of 1,1'-binaphthyl,-2,2' bis(diazoniumtetrafluoro borate)[1]

Sodium nitrite (1.2 g, 18.0 mmol) in 3 mL of water was added slowly to a stirred solution of (±)-BINAM (1.2 g, 4.0 mmol) and HBF_4 (45% in H_2O, 10 mL) at 0 °C. The reaction was then stirred at 0 °C for 30 minutes, followed by 30 minutes at room temperature. The resulting yellow precipitates were filtered using a Buchner funnel and washed with cold HBF_4 (2 × 5 mL), H_2O (2 × 10 mL), and EtOH (10 mL) to yield diazonium salt as a yellow solid (1.8 g).

2. Experimental procedure for recovery of the Pd-BNP catalyst[1]

To recover and reuse the Pd-BNP catalyst, the reaction was performed at a 1 mmol scale under the optimized reaction conditions using 1.0 equiv. of diphenyl acetylene **1a** as model substrate and Pd-BNP (3 mol %) as a catalyst in DMSO solvent under an oxygen atmosphere at 120 °C. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. EtOH (2 mL) was added to the reaction mixture and centrifuged. The liquid was decanted into a 50 mL conical flask. Again, 5 mL EtOH was added, centrifuged, and decanted into the same conical flask. This procedure was repeated two to three times. After that, the catalyst was washed with nanopore water (5 mL) and ethanol (5 mL) two to three times. Finally, the resulting solid residue (Pd-BNP) was dried under a vacuum. The dried catalyst was reused for a further catalytic cycle. The collected liquid was concentrated by reducing pressure. The resulting reaction mixture was purified by column chromatography on silica gel (hexanes: ethyl acetate) to afford **2a** as the desired product.

3. Experimental Procedure for hot filtration test[1]

Confirm that the reaction was catalyzed by a heterogeneous Pd-BNP catalyst and not by the leached homogeneous Pd. A hot centrifugation test was executed under the optimized reaction condition. Two separate reactions were carried out by using **1a** (0.5 mmol) and Pd-BNP (3 mol %) in DMSO solvent in an oven-dried reaction tube equipped with a magnetic pellet and stirred at 120 °C. After 7 h, one set of the reactions was removed and allowed to cool to room temperature. The solvent was removed, then ethanol was added, the reaction mixture was centrifuged, and the Pd-BNP catalyst was removed from the reaction mixture. This process was repeated several times sequentially, and the mother liquid, which is completely free from the catalyst, and the solvent were evaporated under a vacuum followed by flash column chromatography, which gave the desired product **2a** in a 30% yield. The remaining mother liquid, i.e., the Pd-BNP catalyst free-reaction mixture, was subjected to similar conditions for another 15 h. After 15 h, the reaction was stopped, and no improvement in the yield was observed, indicating no active catalyst was present to catalyze the further reaction. The same procedure was followed for another set of reactions.

4. Experimental Mercury poisoning experiment[1]

To confirm that the reaction was catalyzed by a heterogeneous Pd-BNP catalyst rather than leached homogeneous Pd, a Hg-poisoning test was performed.

Pd-BNP catalyst (3 mol%) and Hg (20.0 equiv.) in DMSO were stirred at room temperature for 1 h before adding diphenyl acetylene **1a** (0.5 mmol) and stirring at 120 °C. The formation of the desired product was not observed in the reaction.

In the second set of reactions, the addition of Hg (20.0 equiv.) at the same time as all other reagents: **1a** (0.5 mmol) and Pd-BNP (3 mol%) was observed to completely inhibit product formation. These experiments confirm that the Pd-BNP nanoparticle catalyst is a heterogeneous catalyst.

5. ^{1}H and ^{13}C spectra for symmetrical 1, 2-dicarbonyl compounds

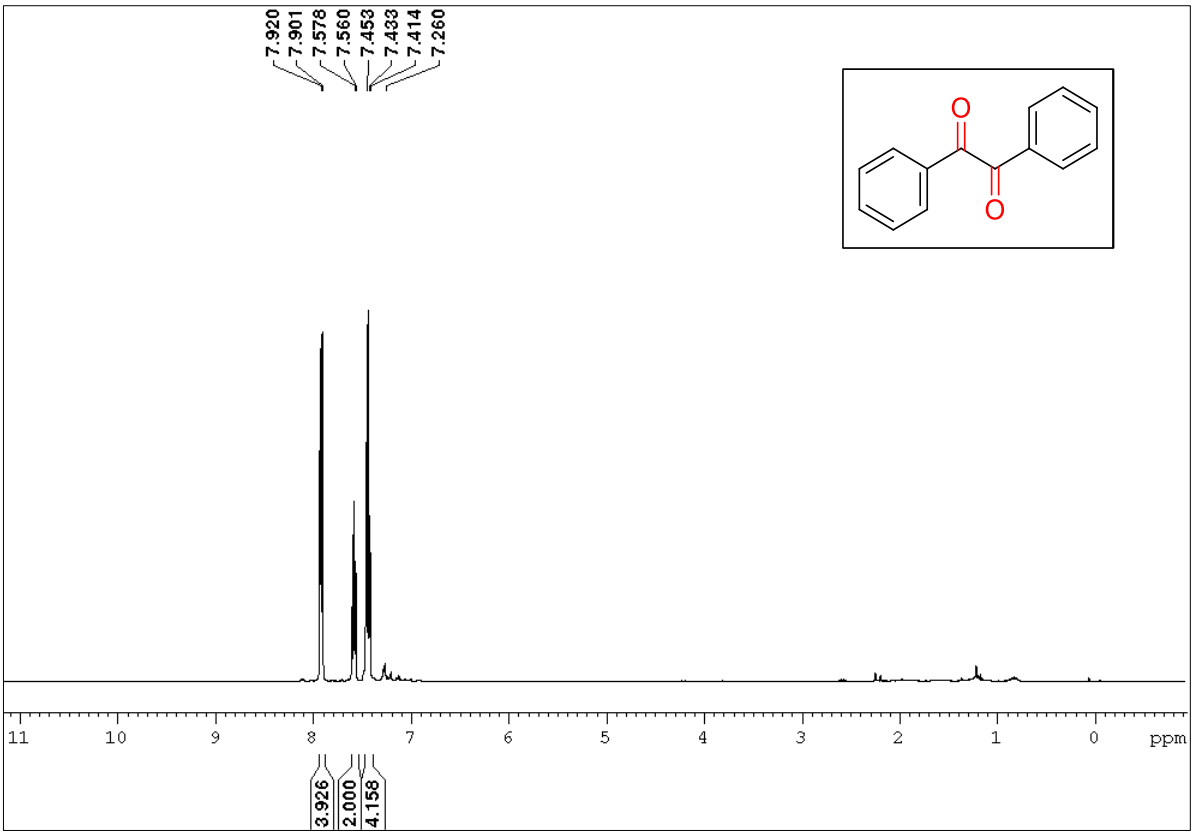


Figure 1: 400 MHz ^{1}H-NMR spectrum of **2a** in $CDCl_3$

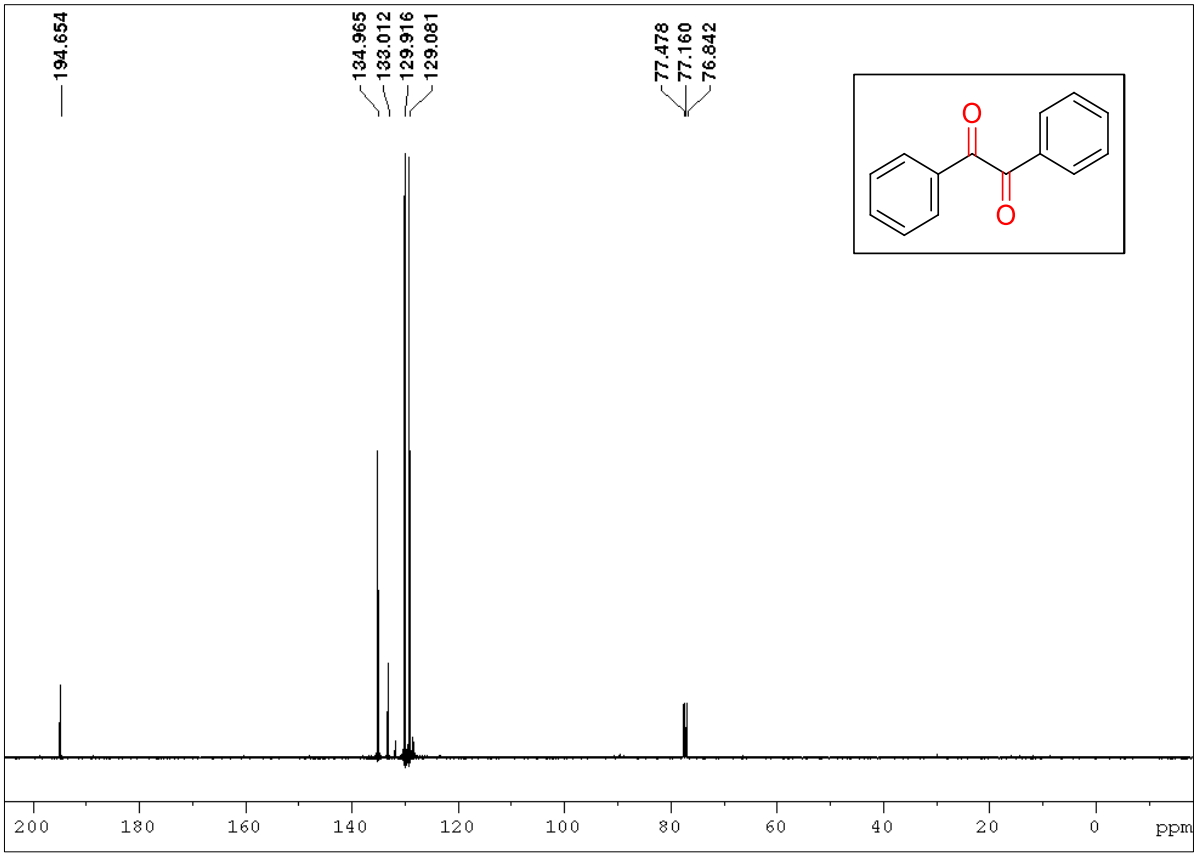


Figure 2:100 MHz ^{13}C-NMR spectrum of **2a** in $CDCl_3$

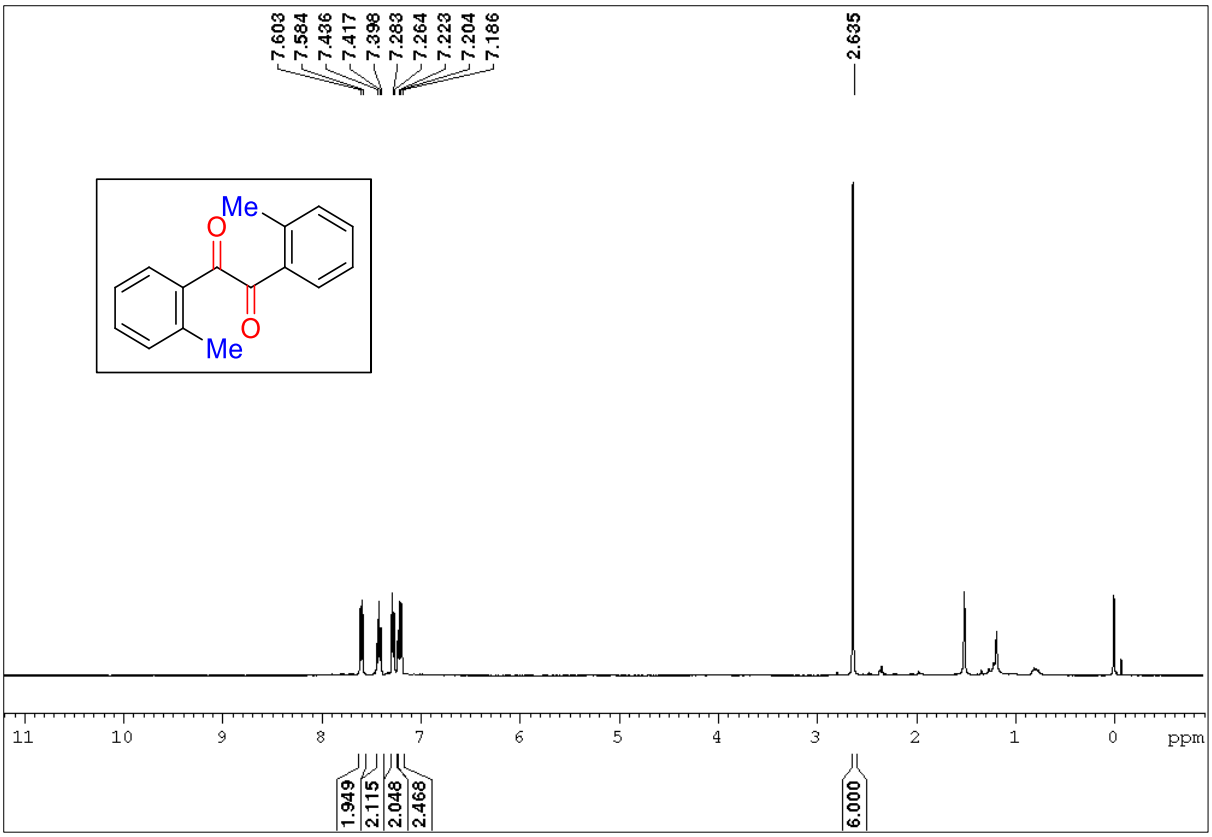


Figure 3: 400 MHz ^{1}H-NMR spectrum of **2b** in $CDCl_3$

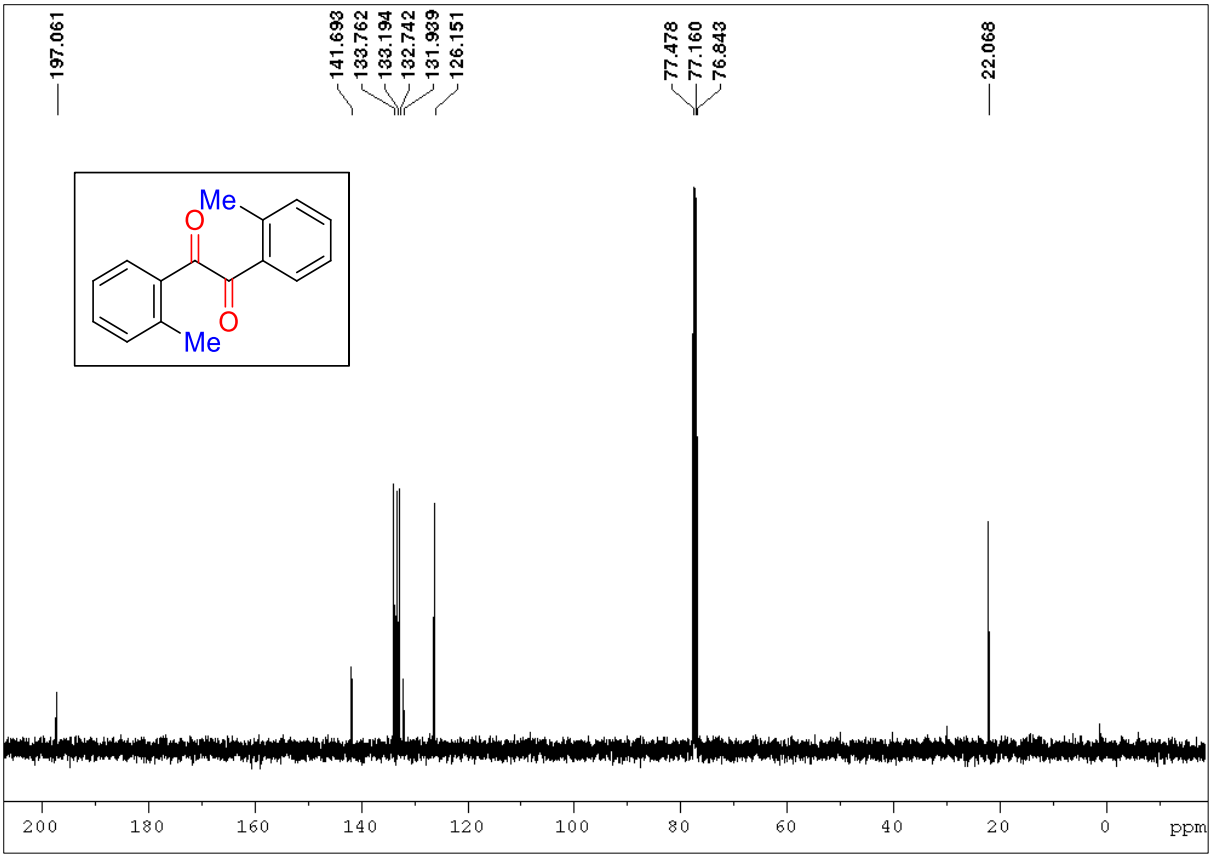


Figure 4: 100 MHz ^{13}C-NMR spectrum of **2b** in $CDCl_3$

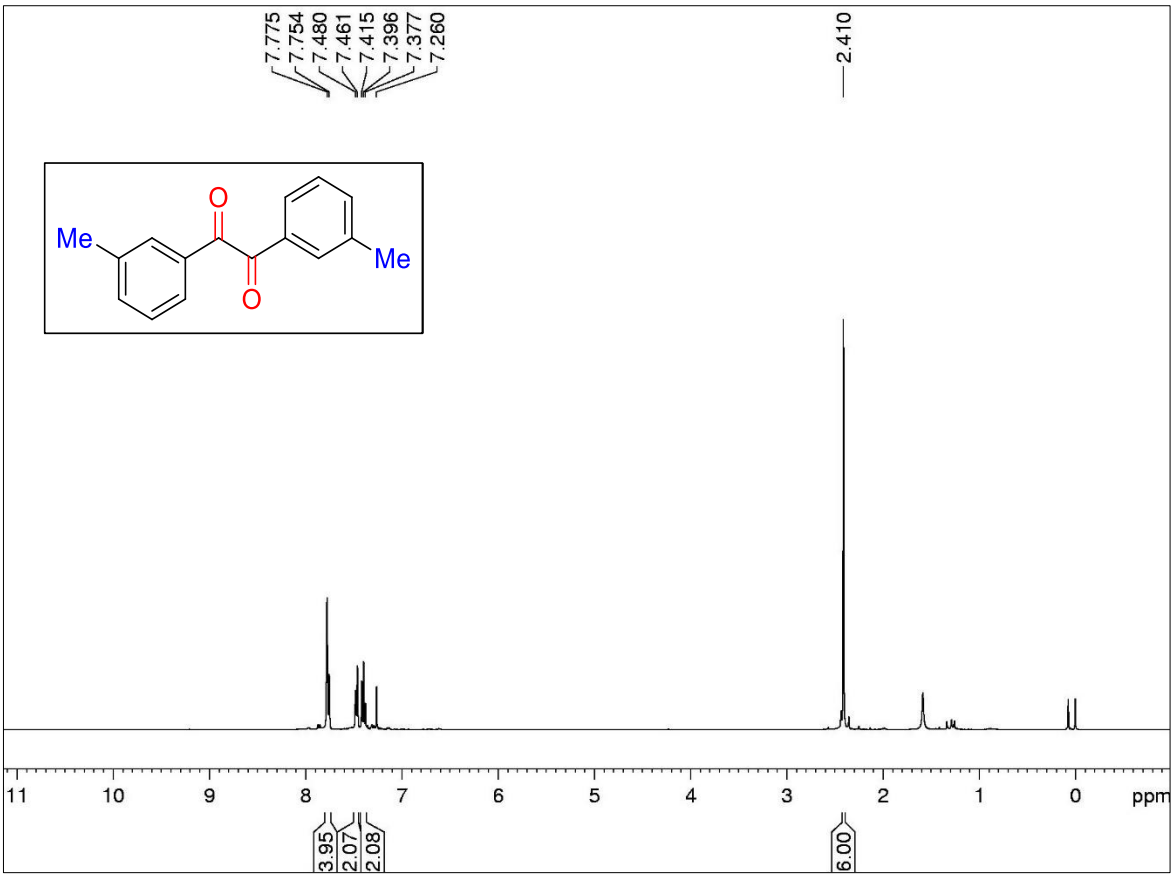


Figure 5: 400 MHz ^{1}H-NMR spectrum of **2c** in $CDCl_3$

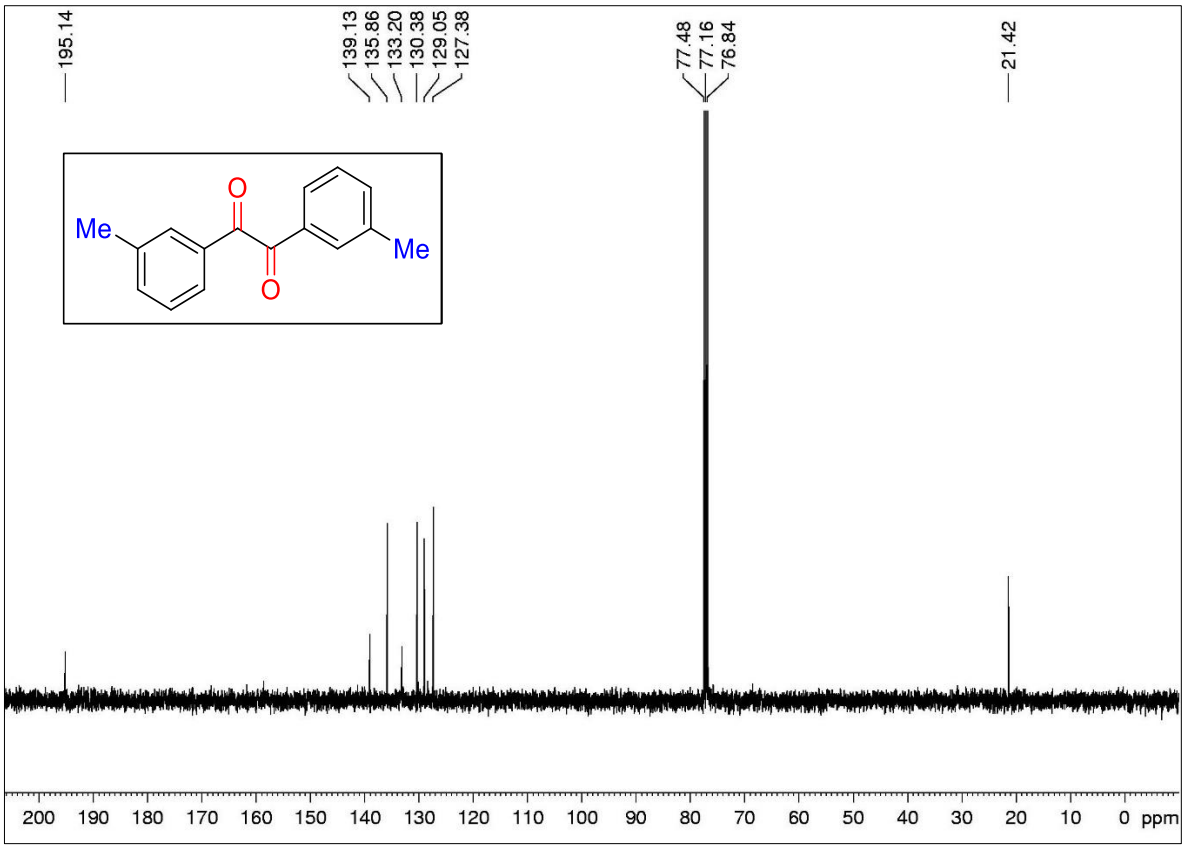


Figure 6: 100 MHz ^{13}C-NMR spectrum of **2c** in $CDCl_3$

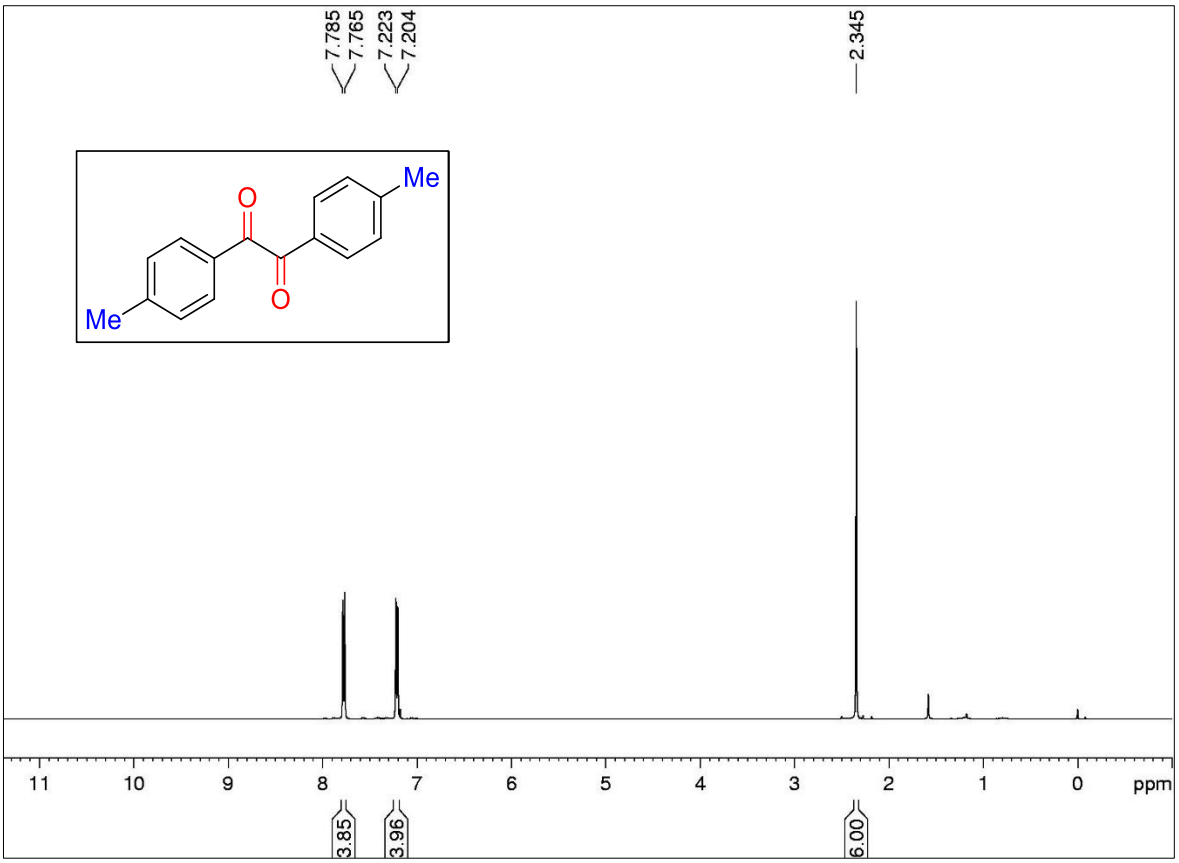


Figure 7: 400 MHz ^{1}H-NMR spectrum of **2d** in $CDCl_3$

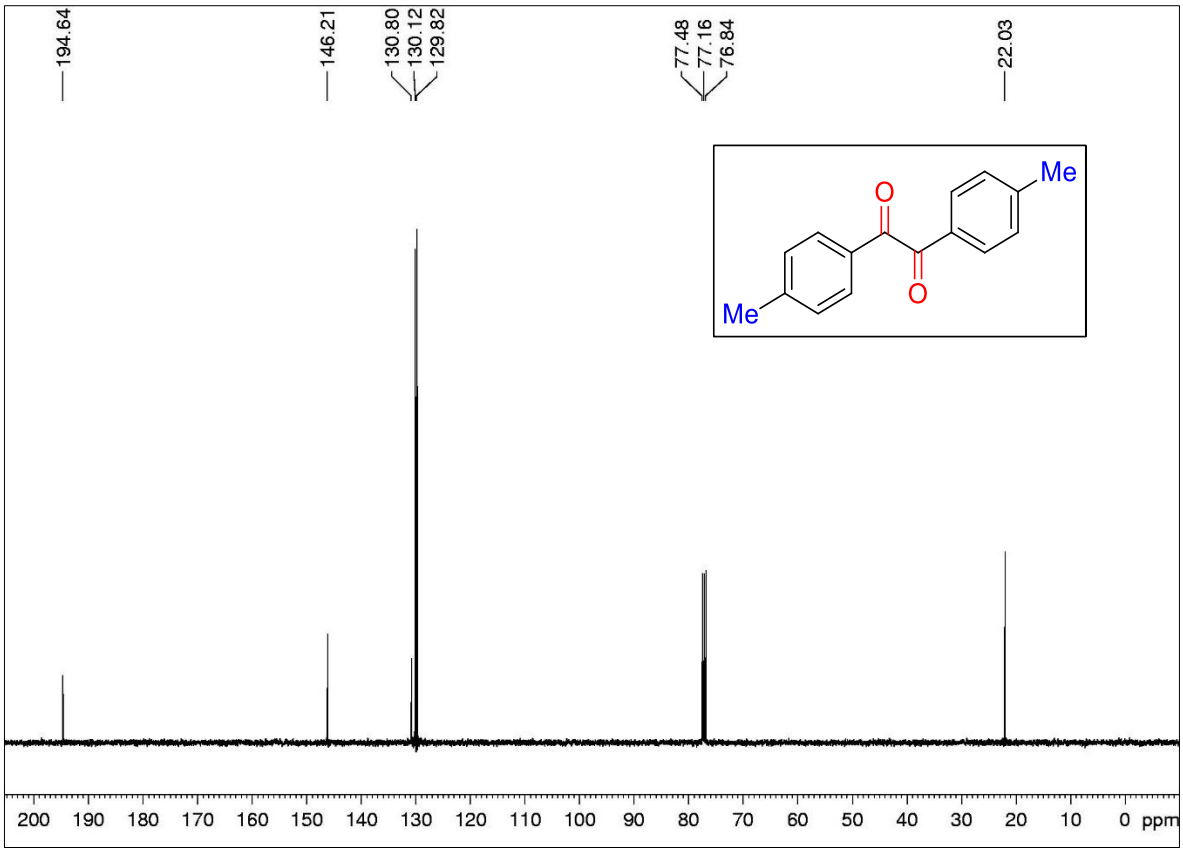


Figure 8: 100 MHz ^{13}C-NMR spectrum of **2d** in $CDCl_3$

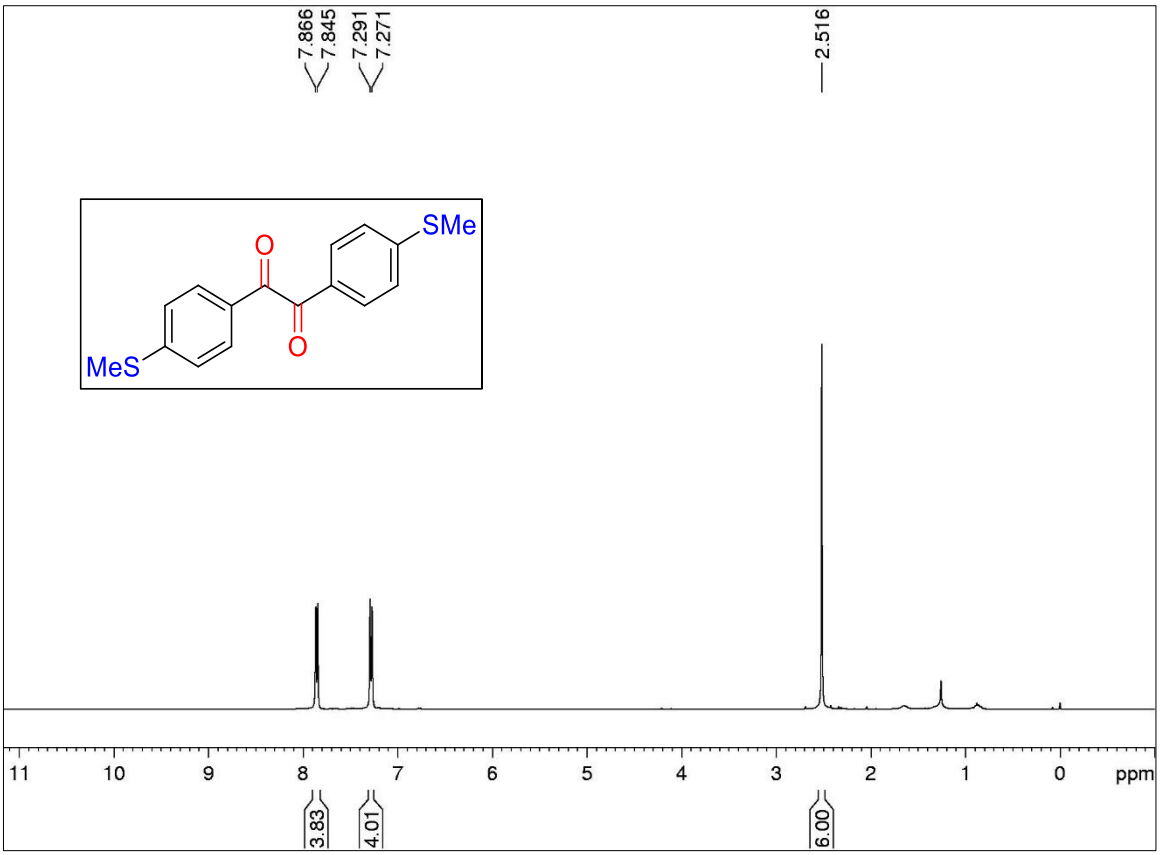


Figure 9: 400 MHz ^{1}H-NMR spectrum of **2e** in $CDCl_3$

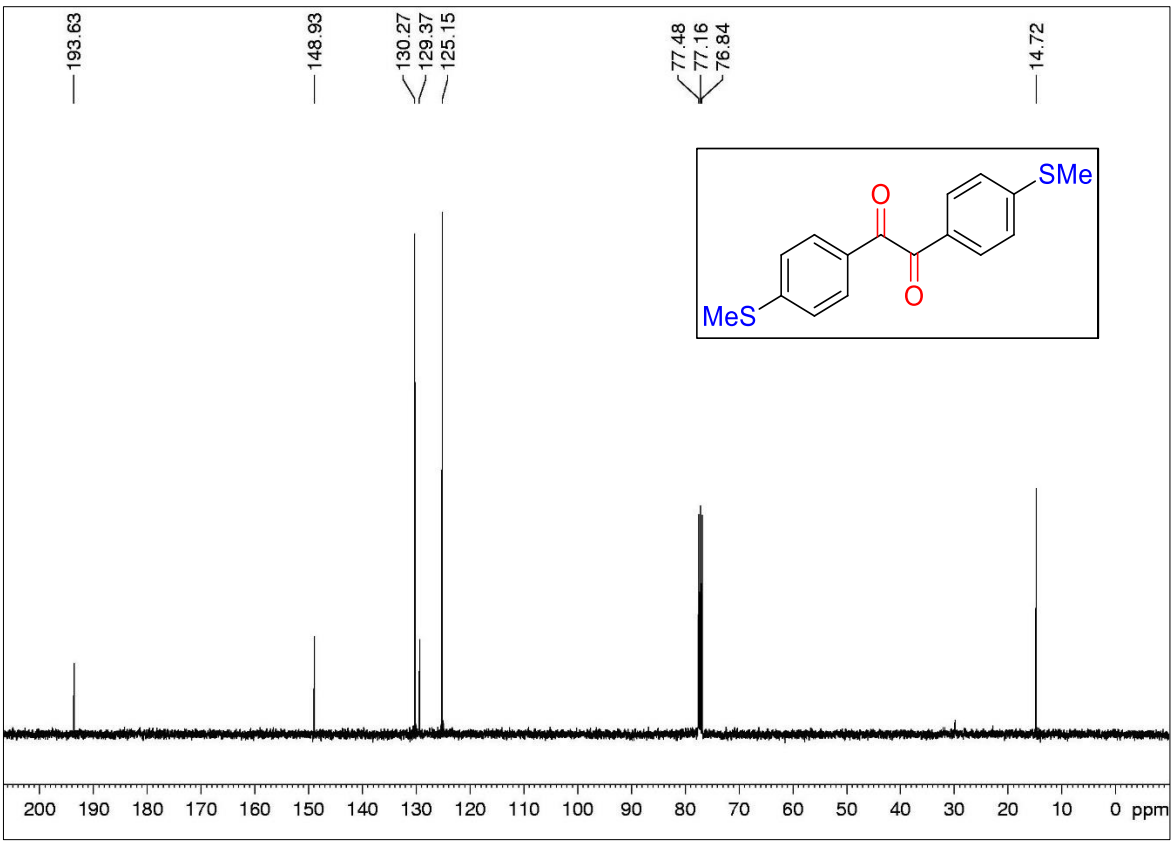


Figure 10: 100 MHz ^{13}C-NMR spectrum of **2e** in $CDCl_3$

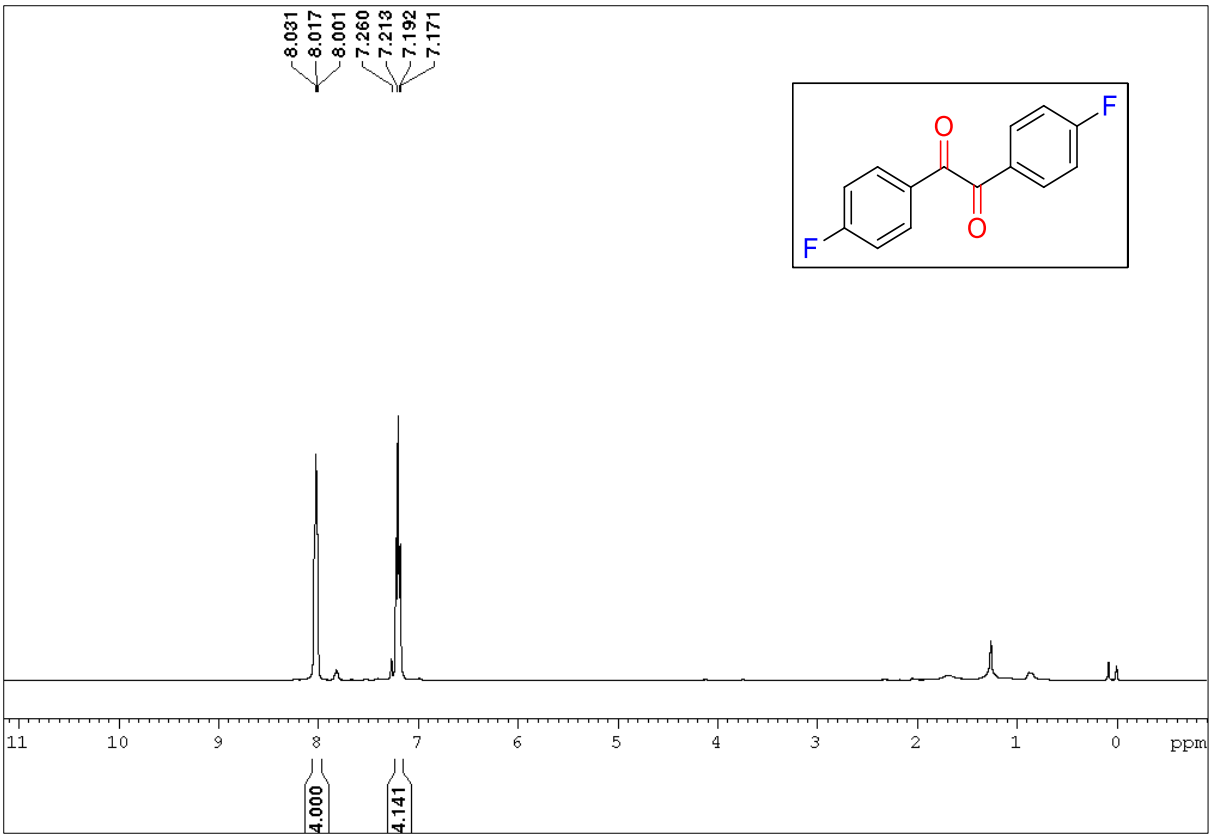


Figure 11: 400 MHz ^{1}H-NMR spectrum of **2f** in $CDCl_3$

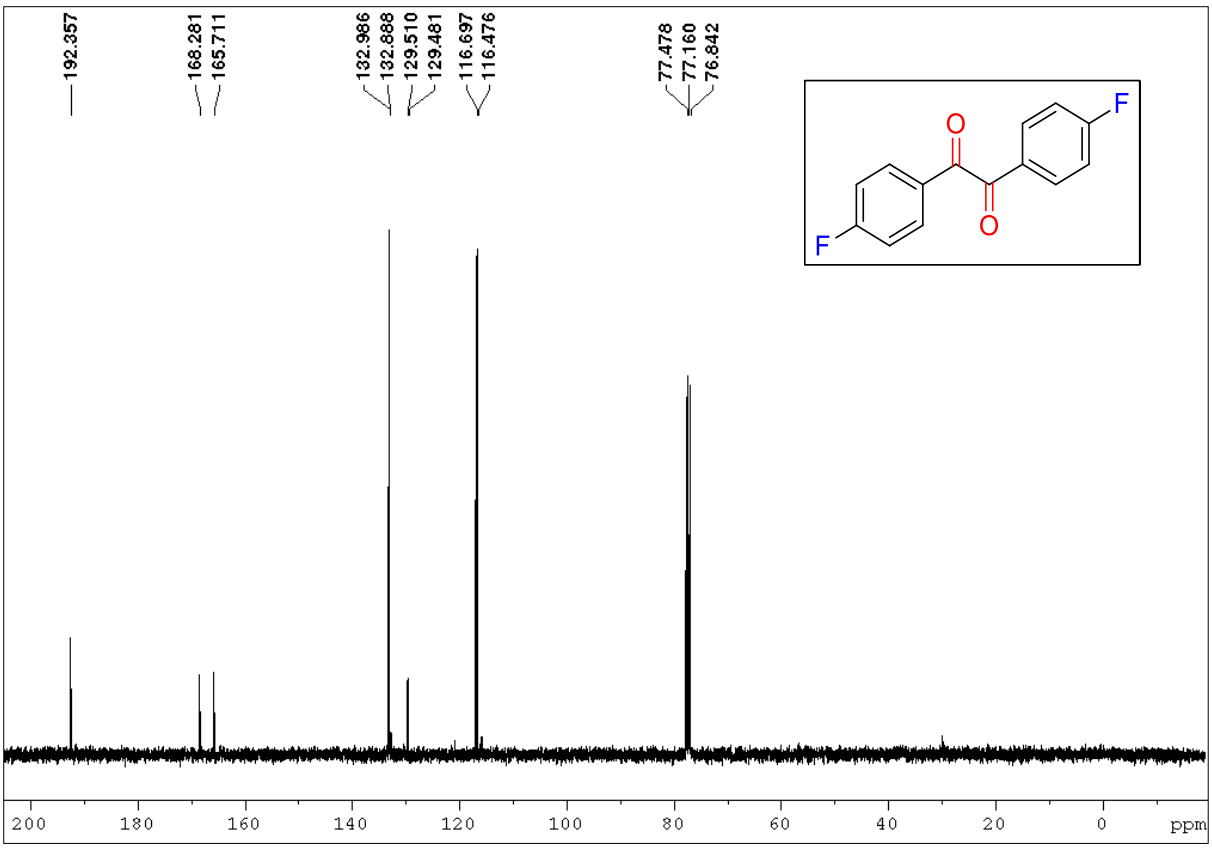


Figure 12: 100 MHz ^{13}C-NMR spectrum of **2f** in $CDCl_3$

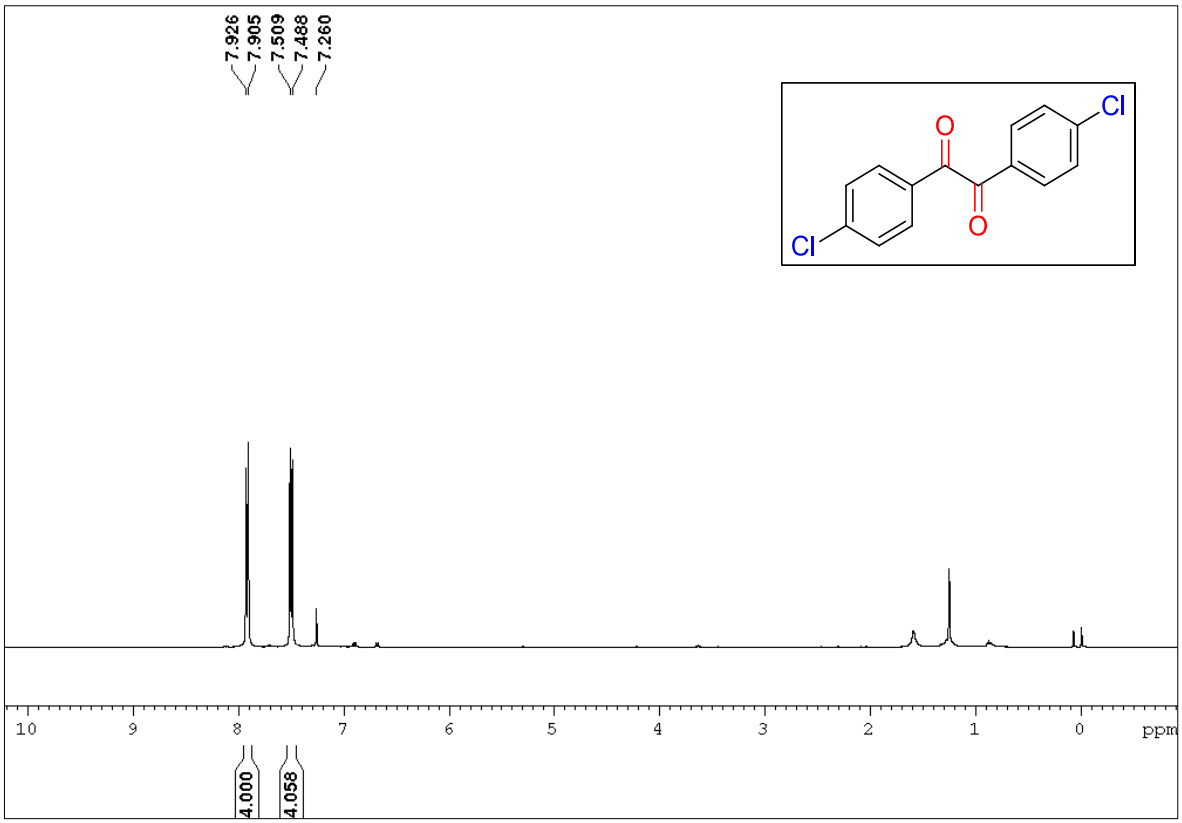


Figure 13: 400 MHz ^{1}H-NMR spectrum of **2g** in $CDCl_3$

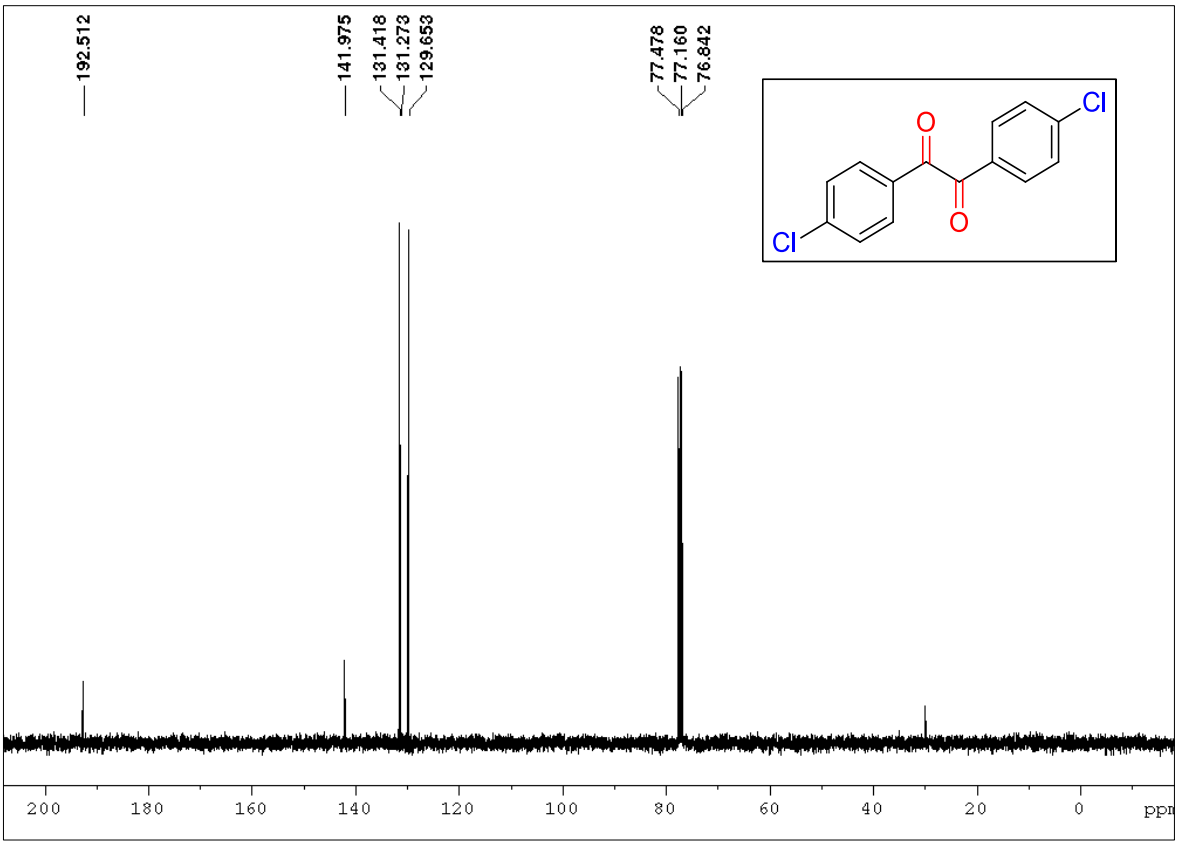


Figure 14: 100 MHz ^{13}C-NMR spectrum of **2g** in $CDCl_3$

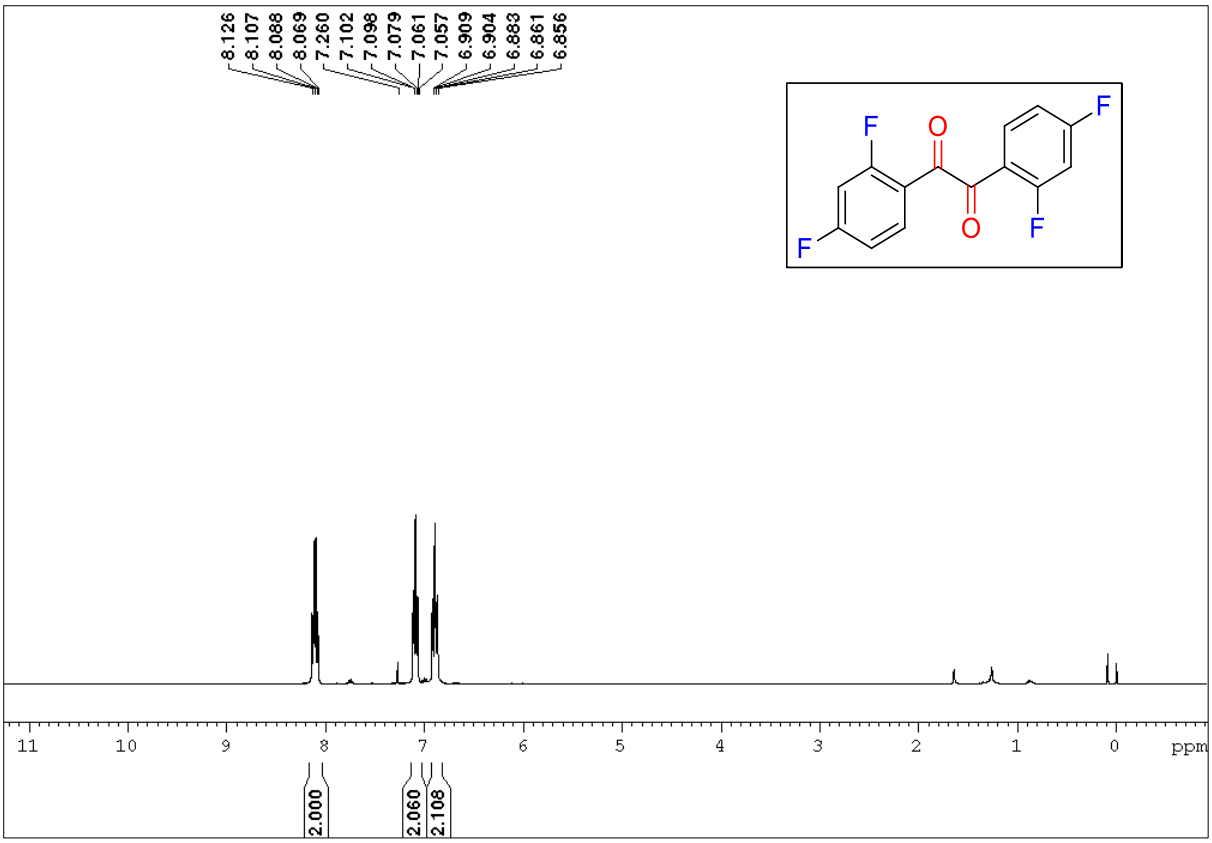


Figure 15: 400 MHz ^{1}H-NMR spectrum of **2h** in $CDCl_3$

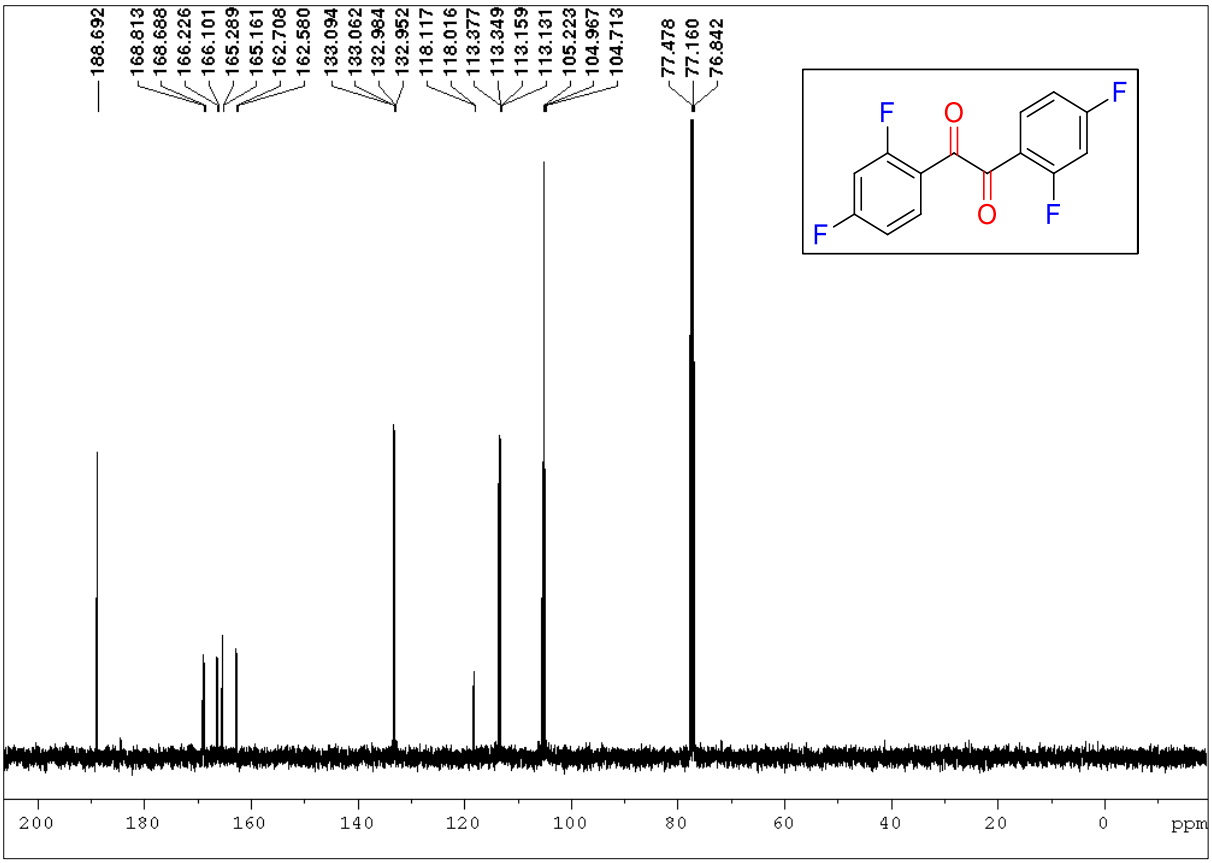


Figure 16: 100 MHz ^{13}C-NMR spectrum of **2h** in $CDCl_3$

6. ^{1}H and ^{13}C spectra for unsymmetrical 1, 2-dicarbonyl compounds

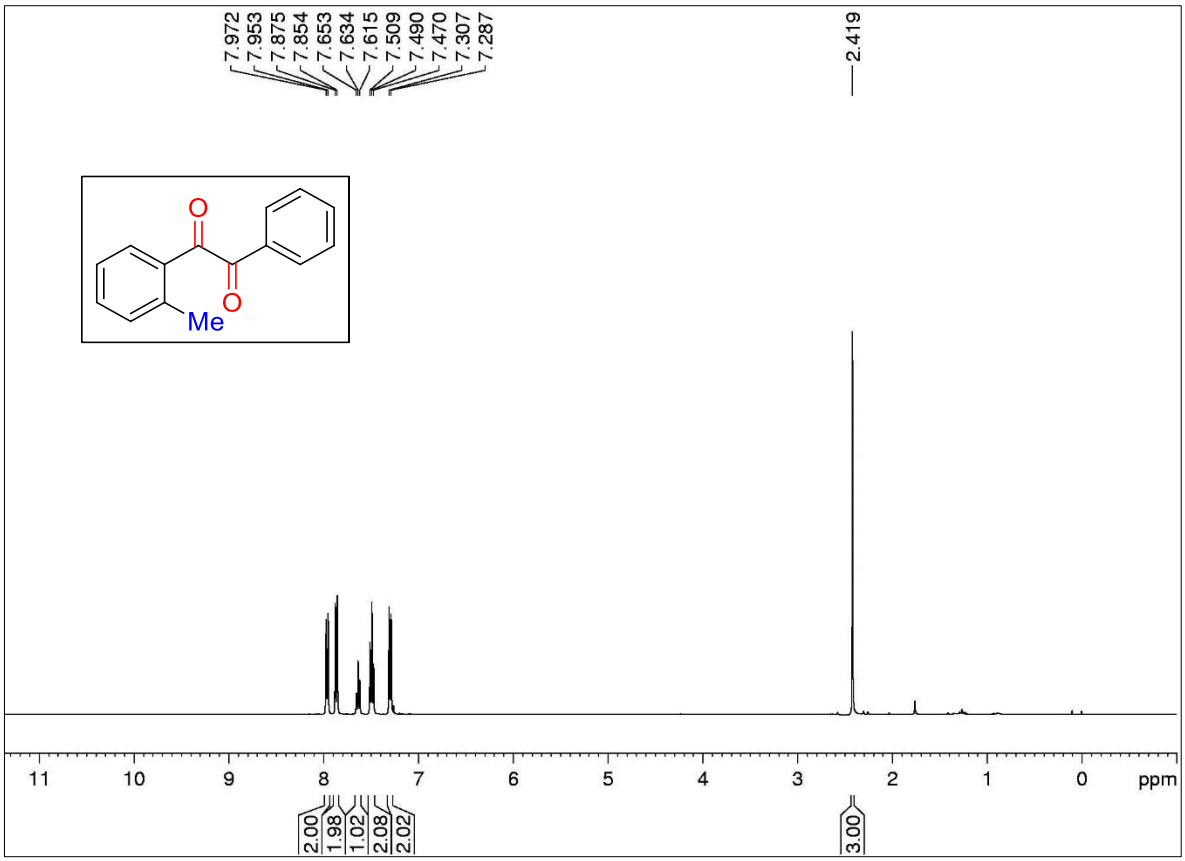


Figure 17: 400 MHz ^{1}H-NMR spectrum of **2i** in $CDCl_3$

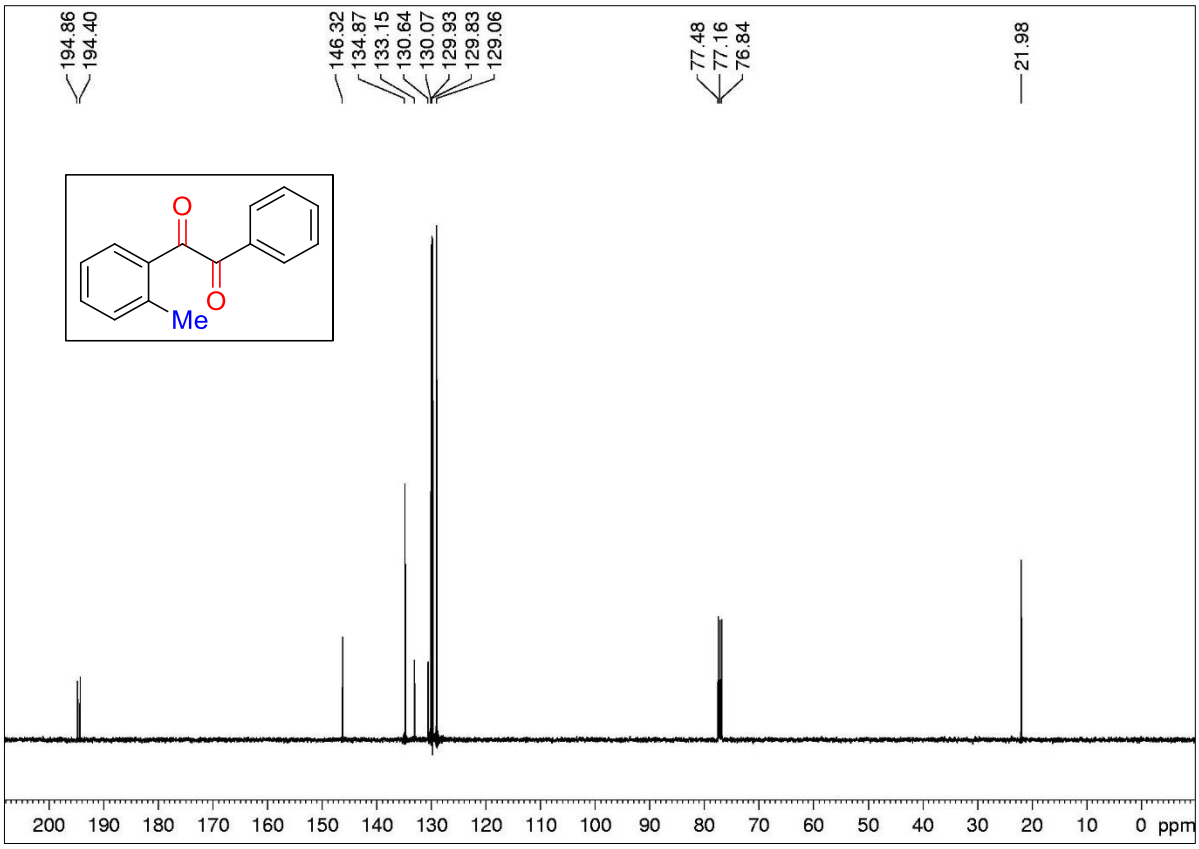


Figure 18: 100 MHz ^{13}C-NMR spectrum of **2i** in $CDCl_3$

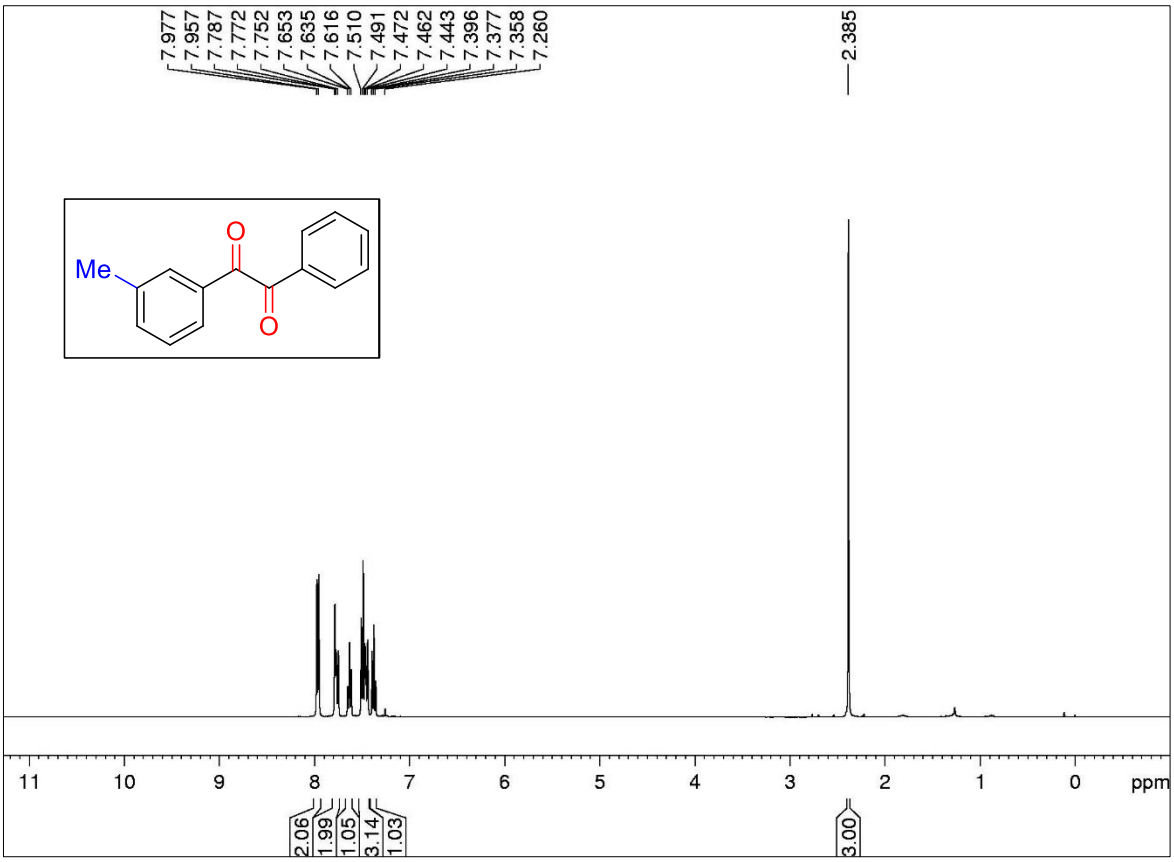


Figure 19: 400 MHz ^{1}H-NMR spectrum of **2j** in $CDCl_3$

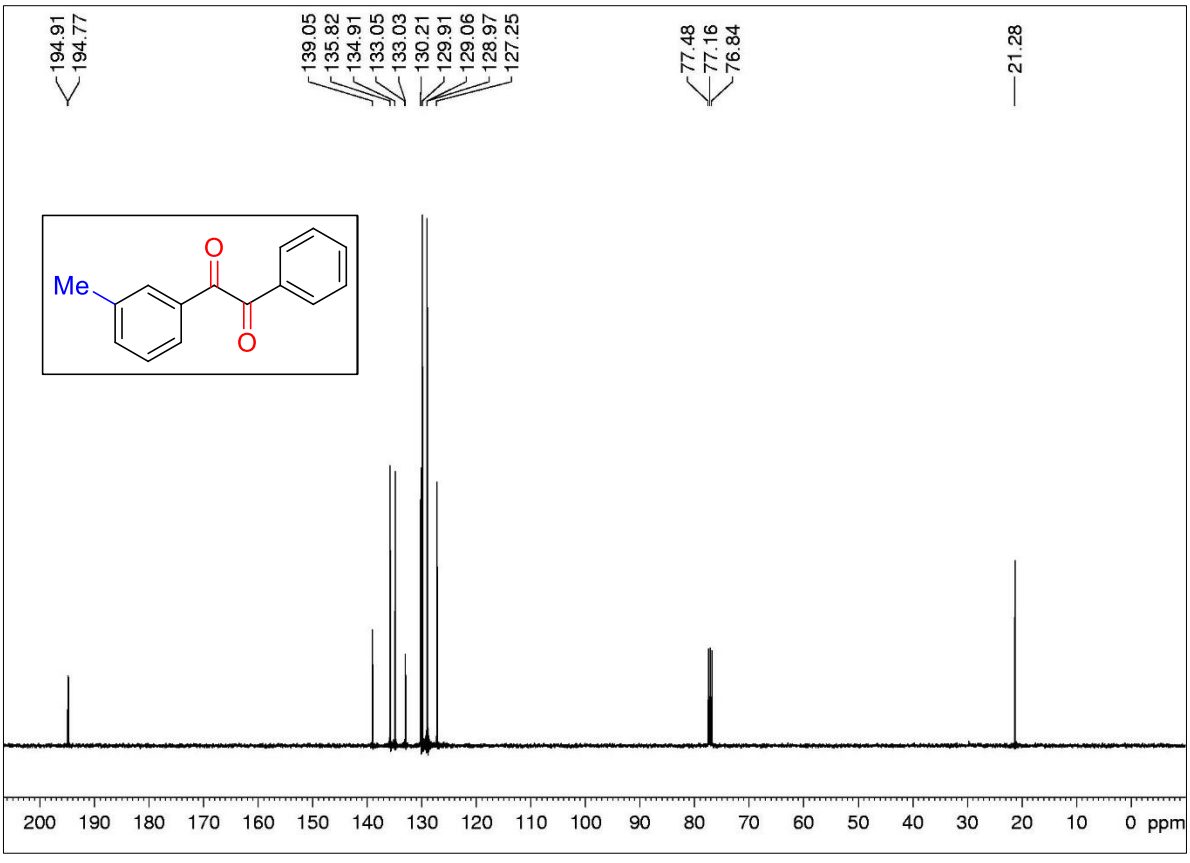


Figure 20: 100 MHz ^{13}C-NMR spectrum of **2j** in $CDCl_3$

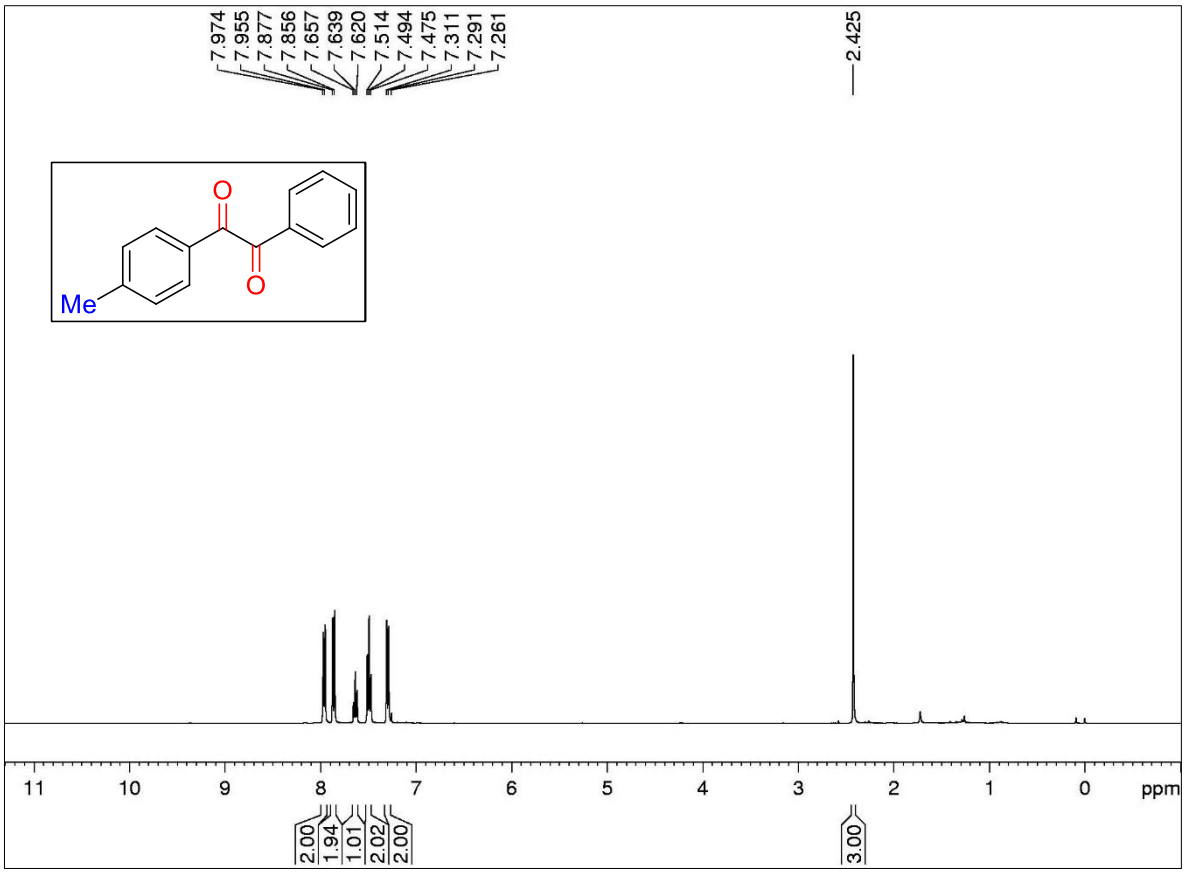


Figure 21: 400 MHz ^{1}H-NMR spectrum of **2k** in $CDCl_3$

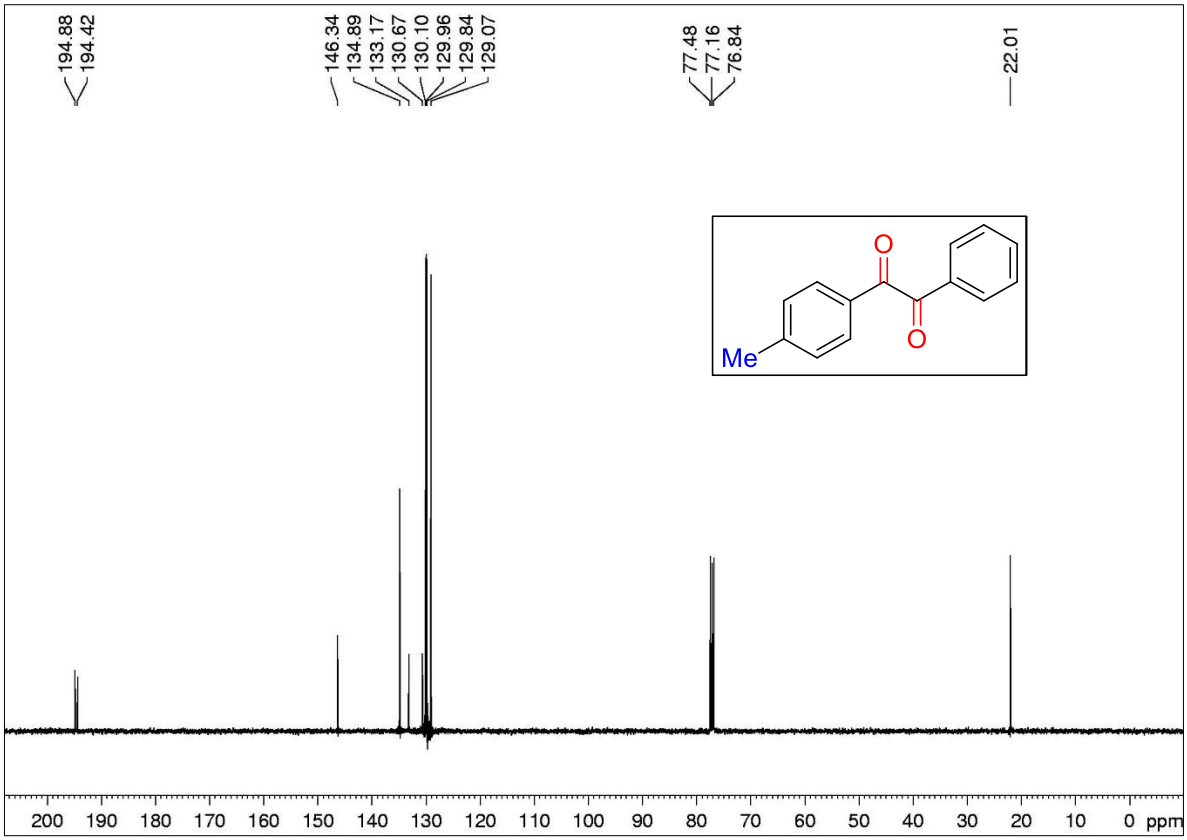


Figure 22: 100 MHz ^{13}C-NMR spectrum of **2k** in $CDCl_3$

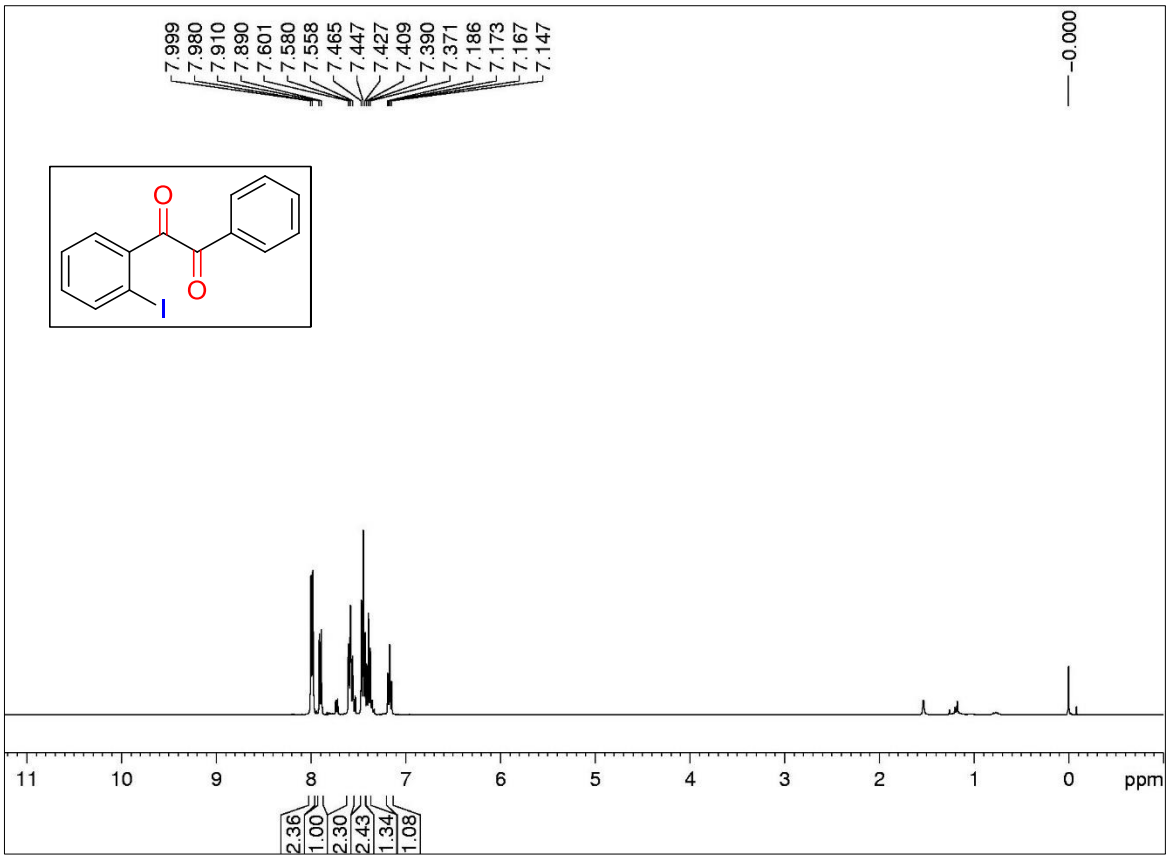


Figure 23: 400 MHz ^{1}H-NMR spectrum of **2l** in $CDCl_3$

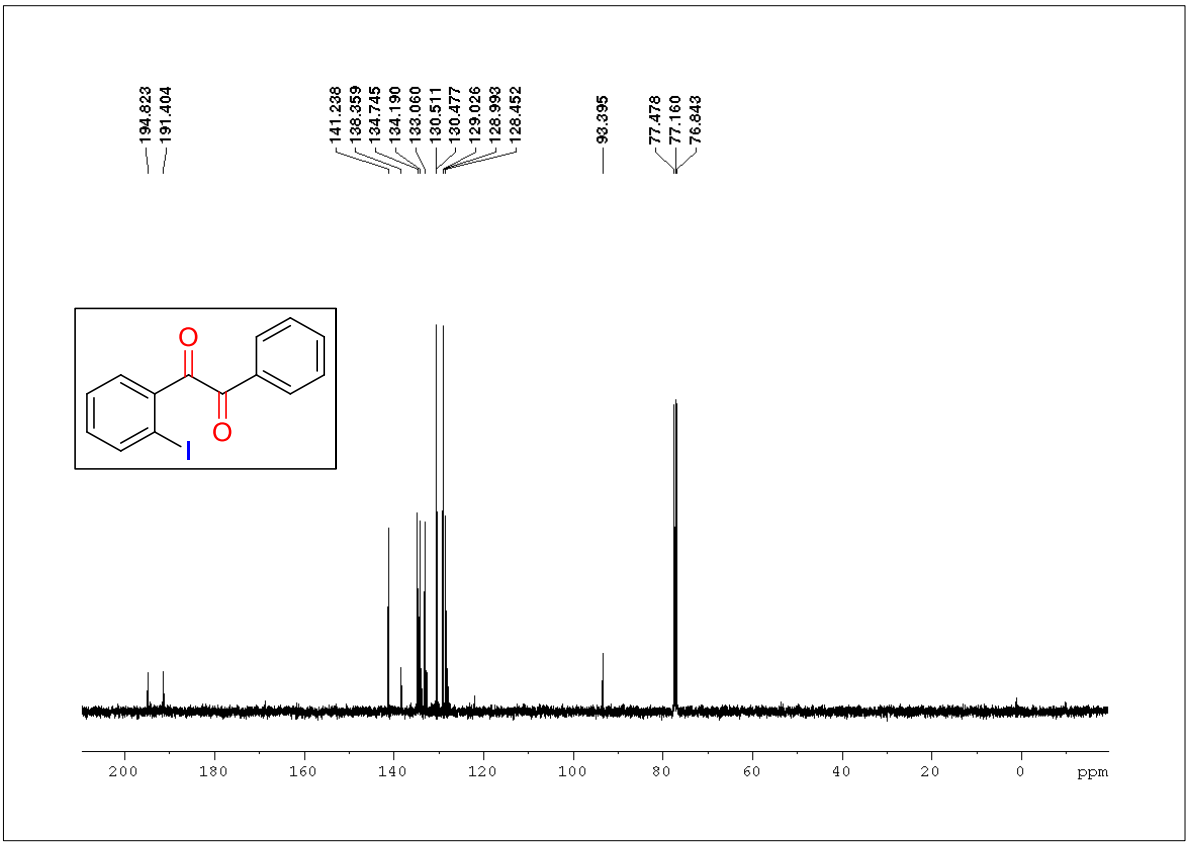


Figure 24: 100 MHz ^{13}C-NMR spectrum of **2l** in $CDCl_3$

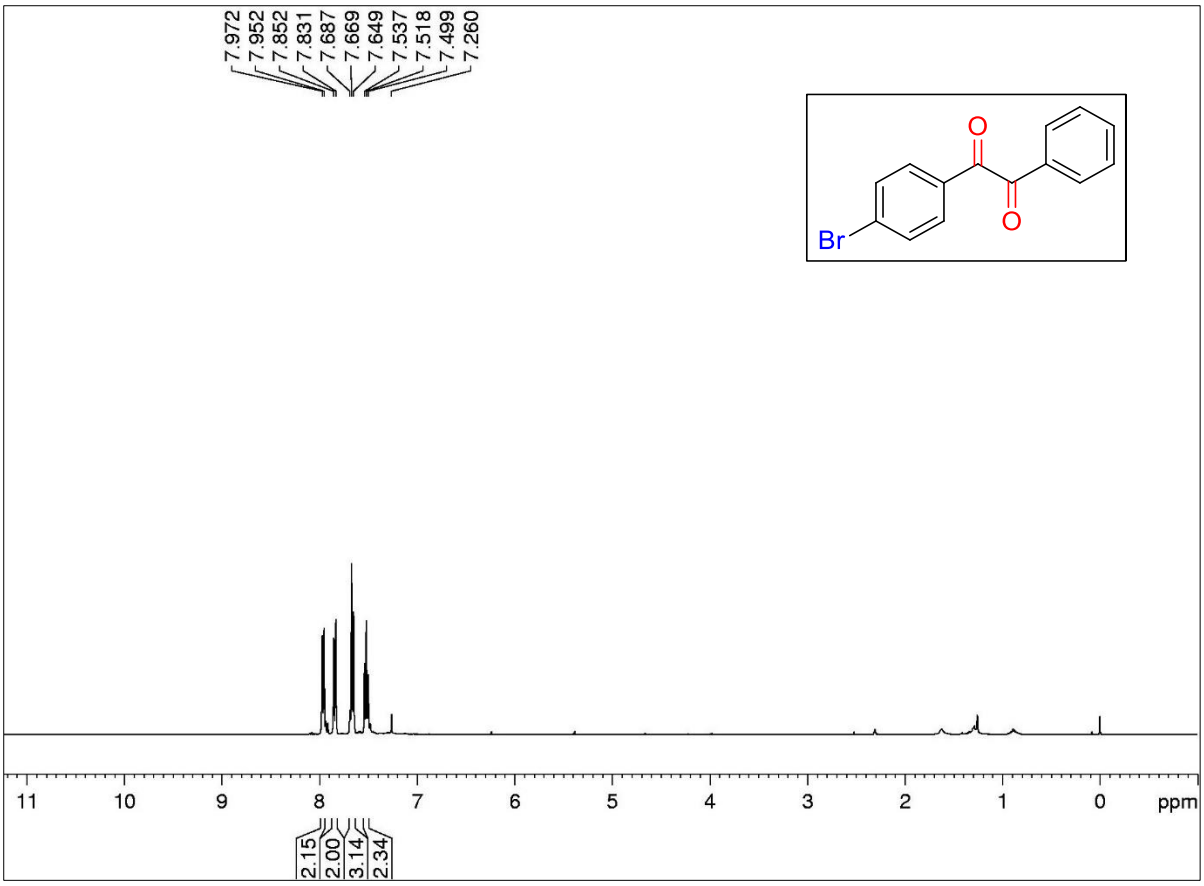


Figure 25: 400 MHz ^{1}H-NMR spectrum of **2m** in $CDCl_3$

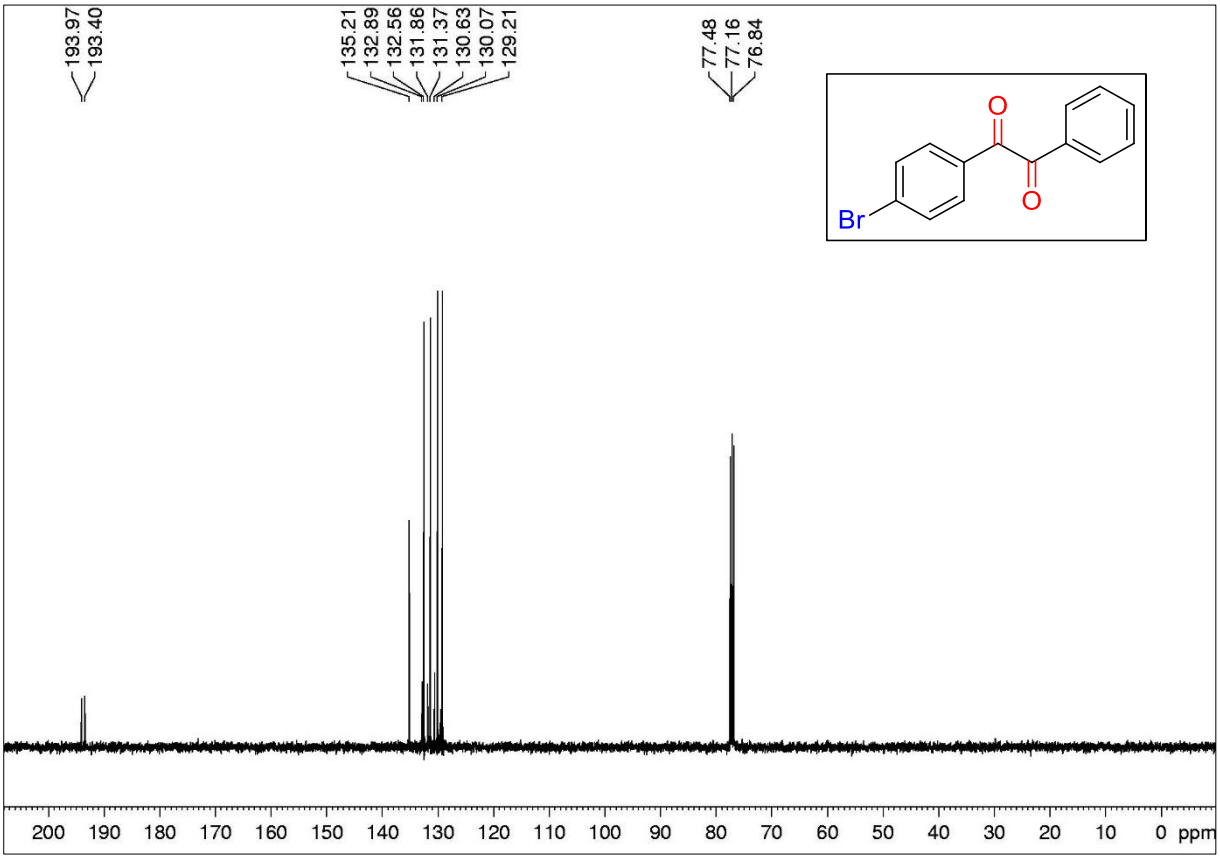


Figure 26: 100 MHz ^{13}C-NMR spectrum of **2m** in $CDCl_3$

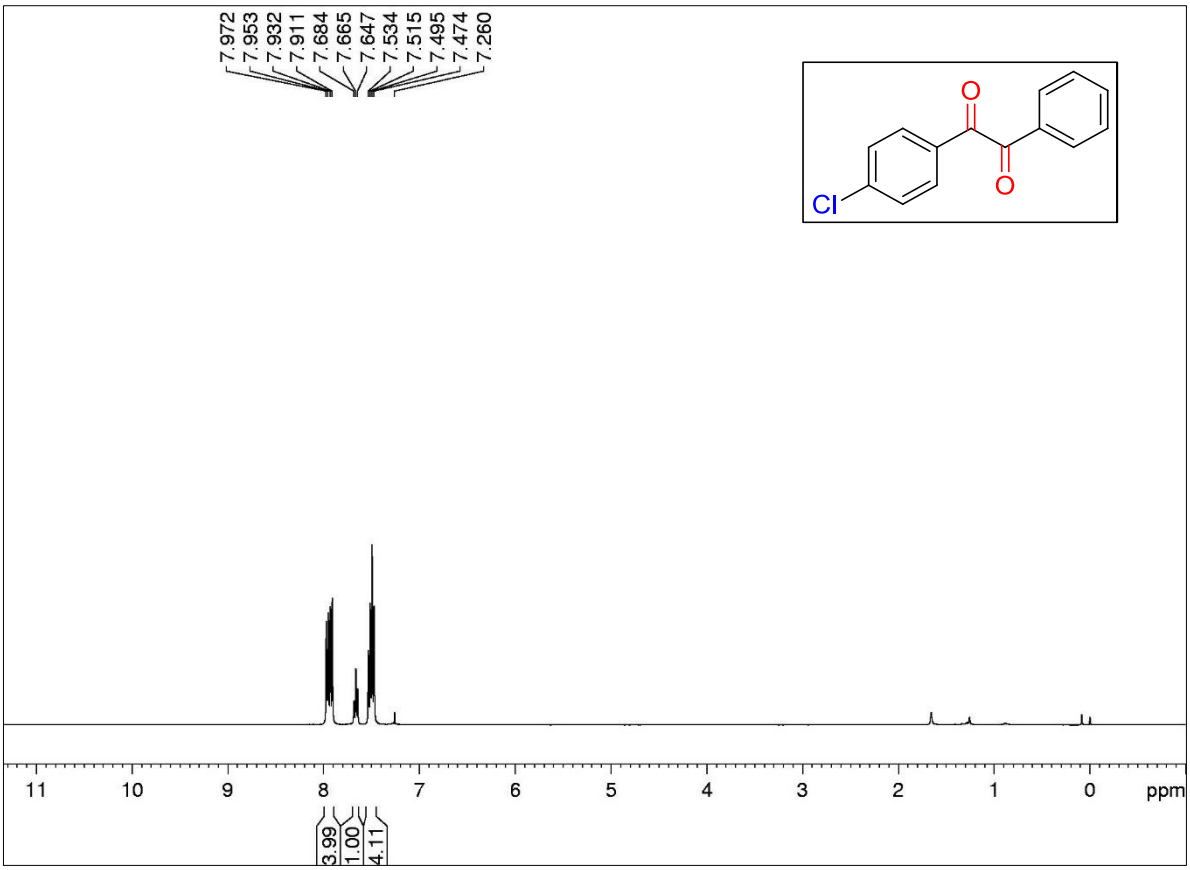


Figure 27: 400 MHz ^{1}H-NMR spectrum of **2n** in $CDCl_3$

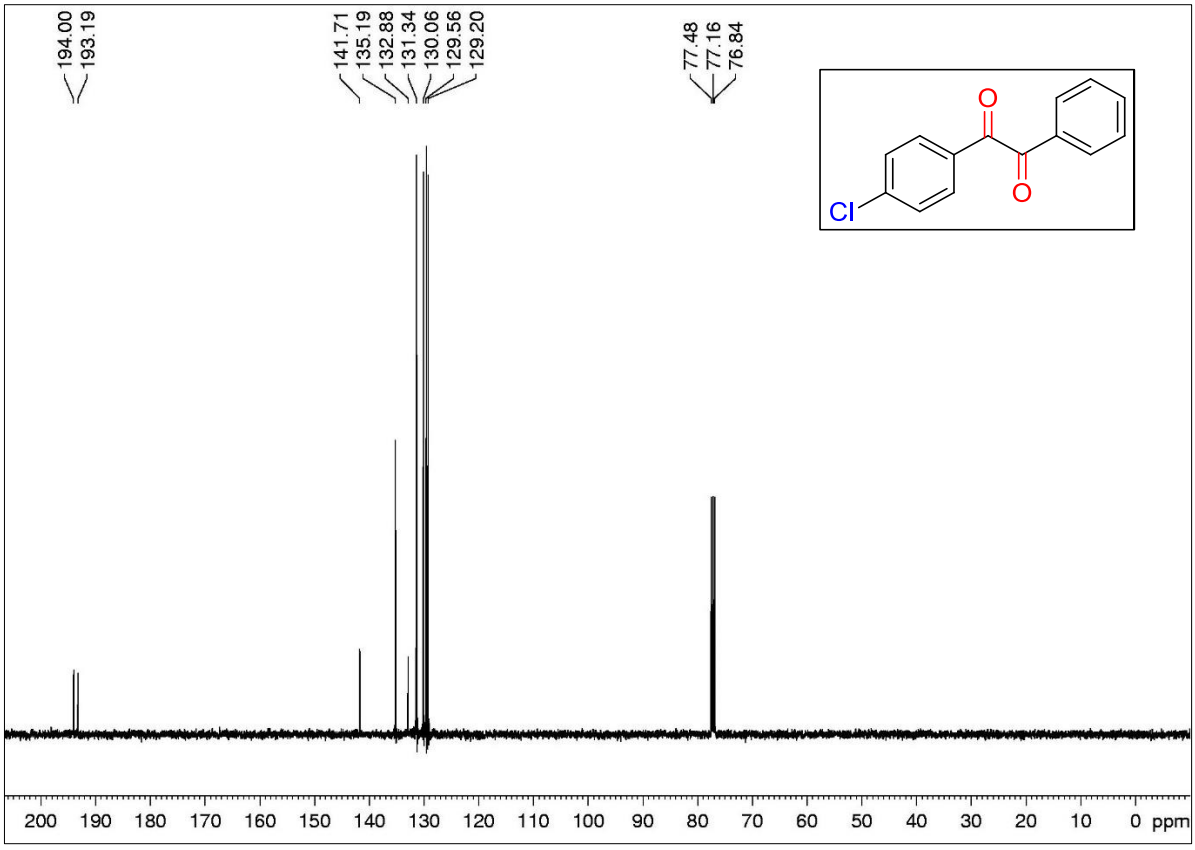


Figure 28: 100 MHz ^{13}C-NMR spectrum of **2n** in $CDCl_3$

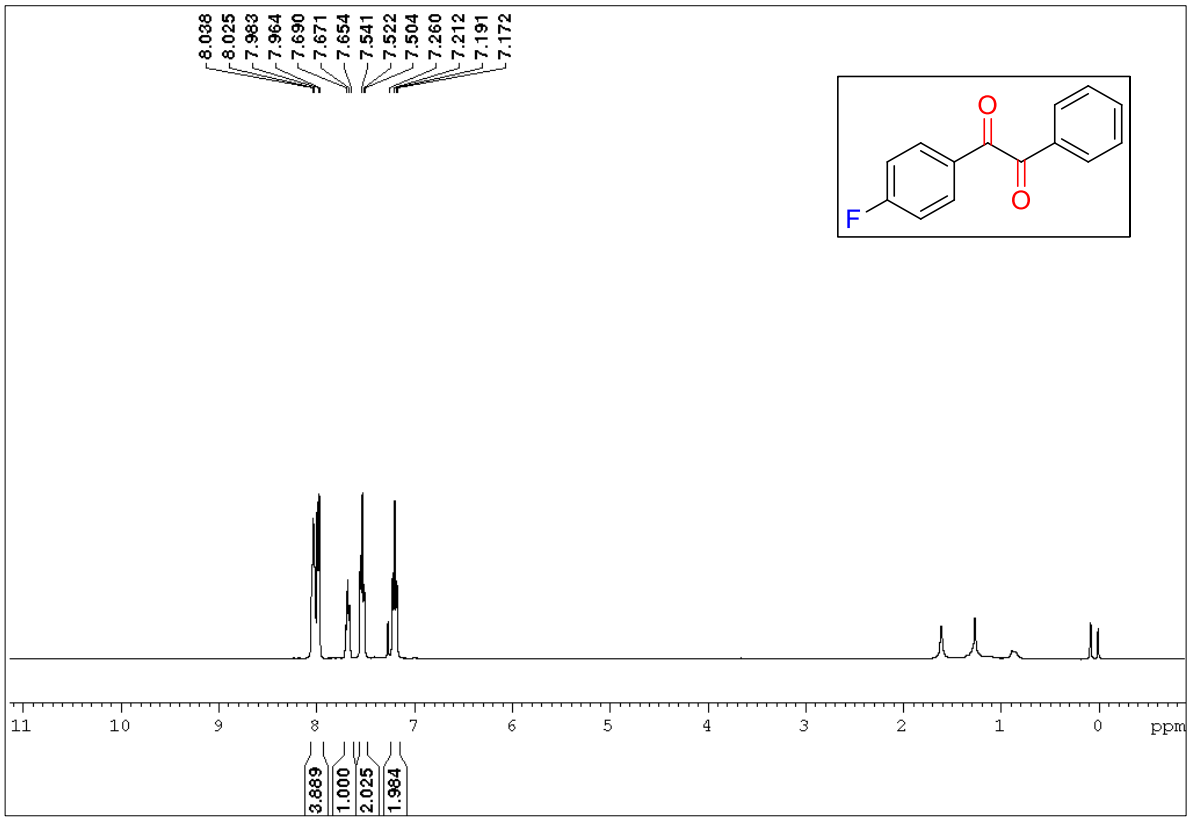


Figure 29: 400 MHz ^{1}H-NMR spectrum of **2o** in $CDCl_3$

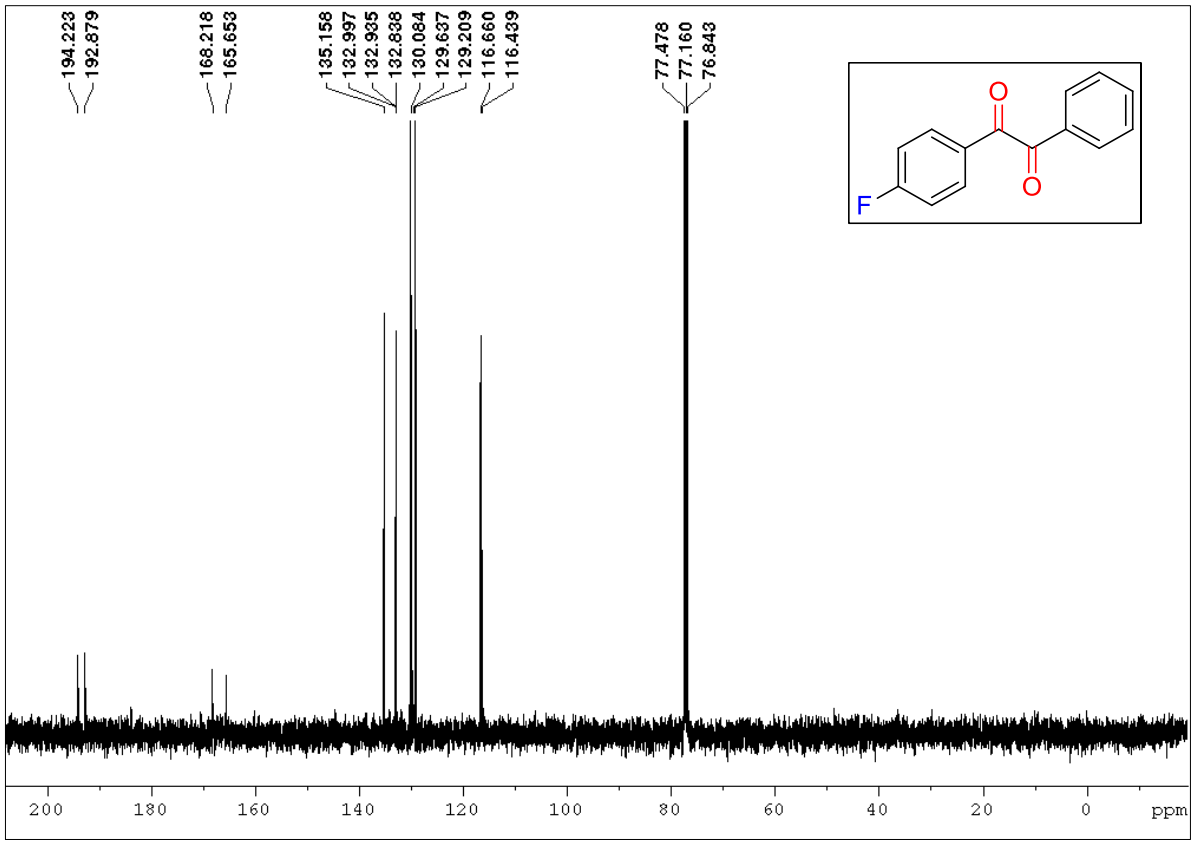


Figure 30: 100 MHz ^{13}C-NMR spectrum of **2o** in $CDCl_3$

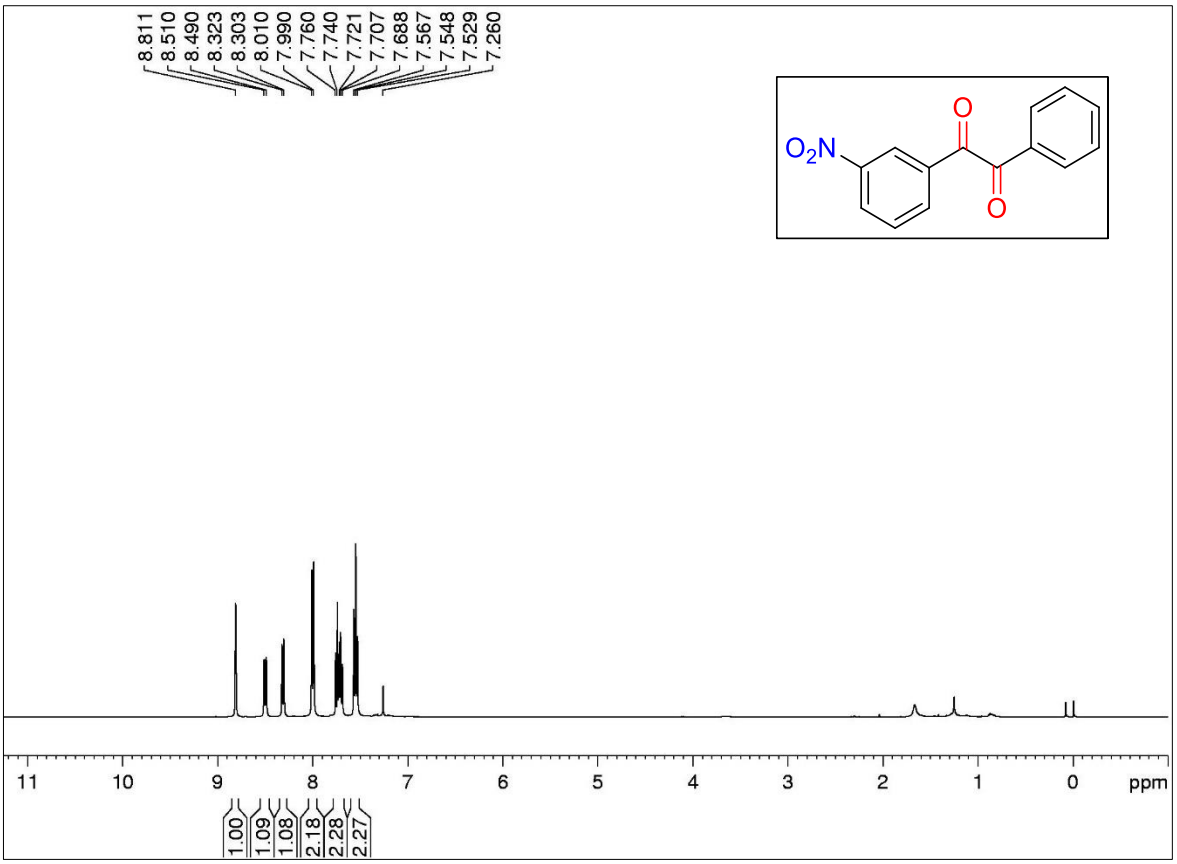


Figure 31: 400 MHz ^{1}H-NMR spectrum of **2p** in $CDCl_3$

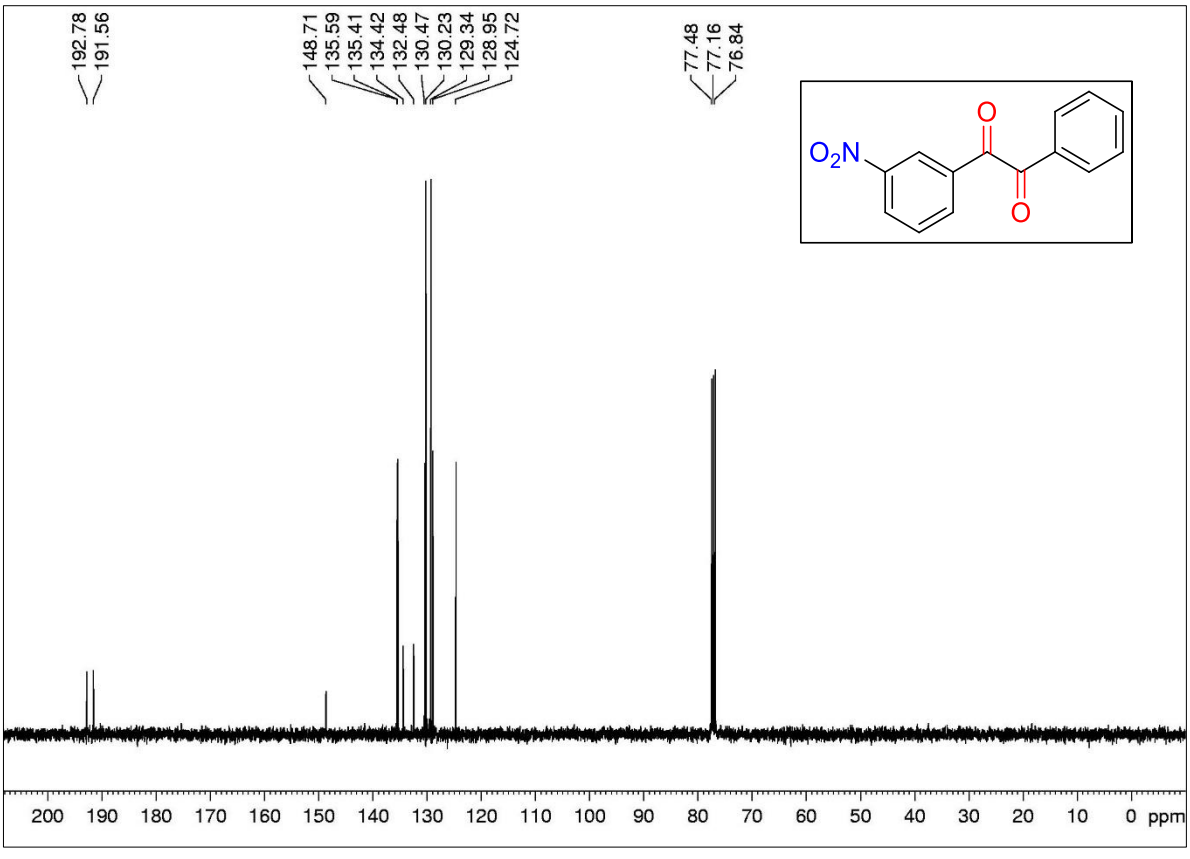


Figure 32: 100 MHz ^{13}C-NMR spectrum of **2p** in $CDCl_3$

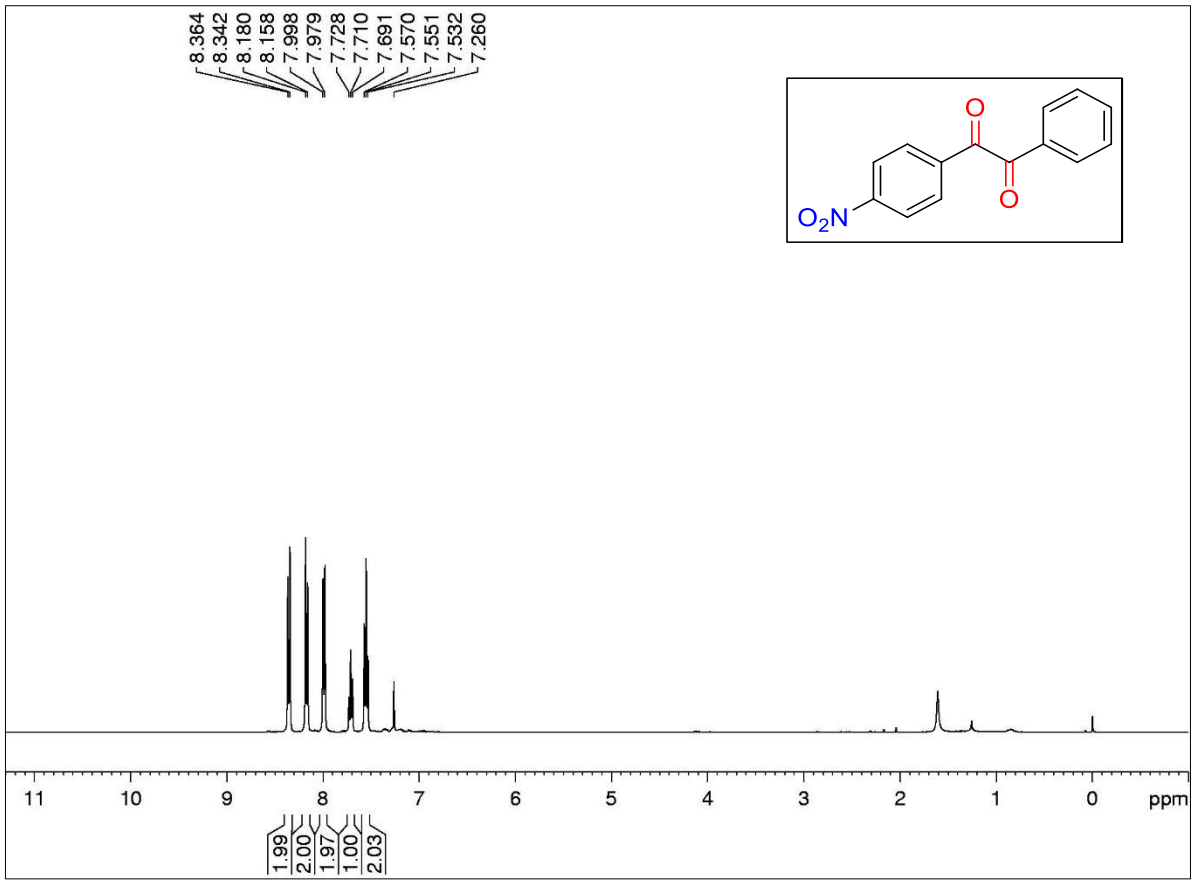


Figure 33: 400 MHz ^{1}H-NMR spectrum of **2q** in $CDCl_3$

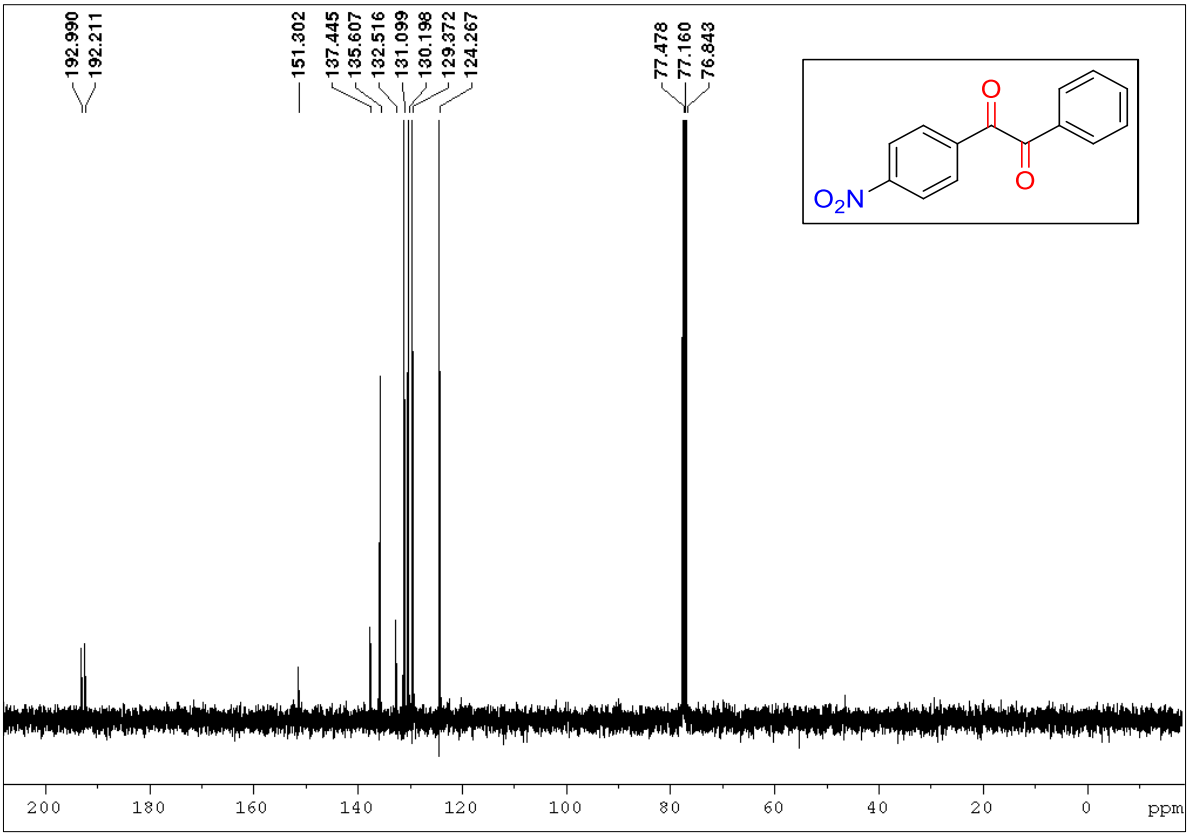


Figure 34: 100 MHz ^{13}C-NMR spectrum of **2q** in $CDCl_3$

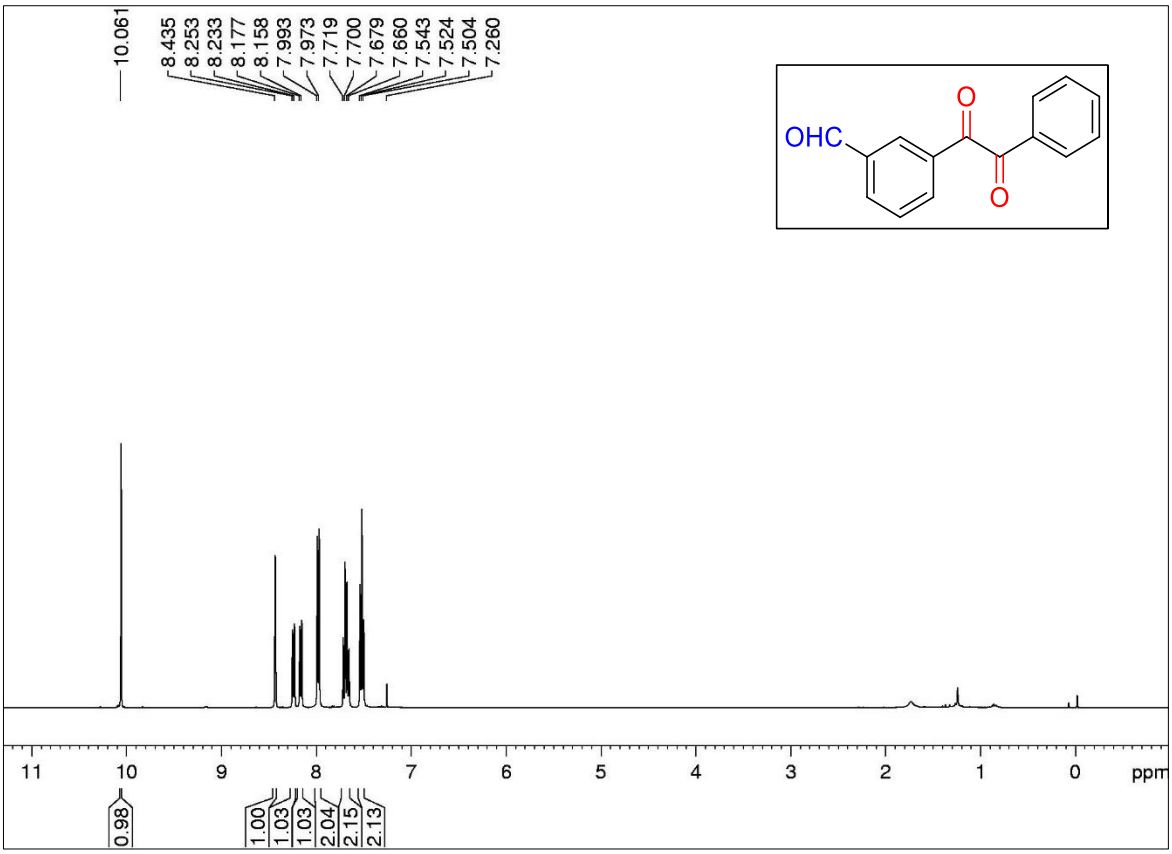


Figure 35: 400 MHz ^{1}H-NMR spectrum of **2r** in $CDCl_3$

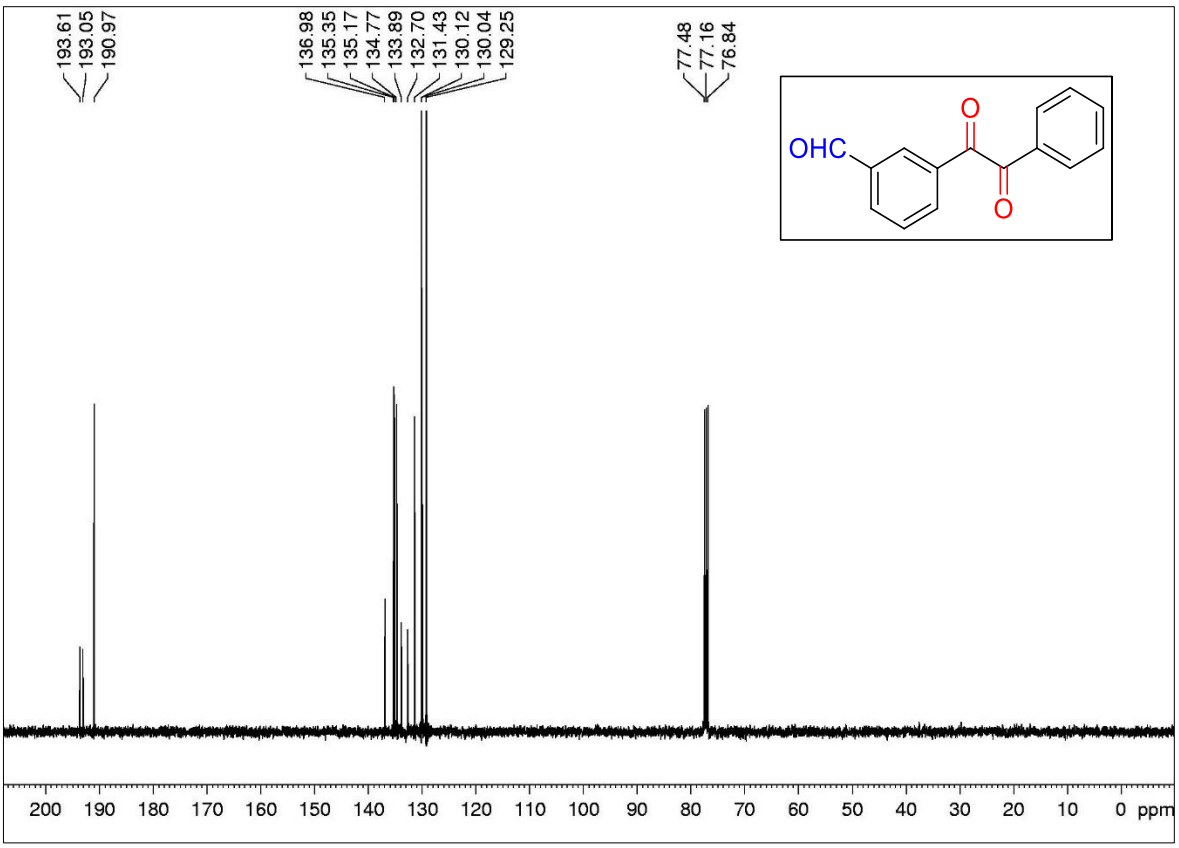


Figure 36: 100 MHz ^{13}C-NMR spectrum of **2r** in $CDCl_3$

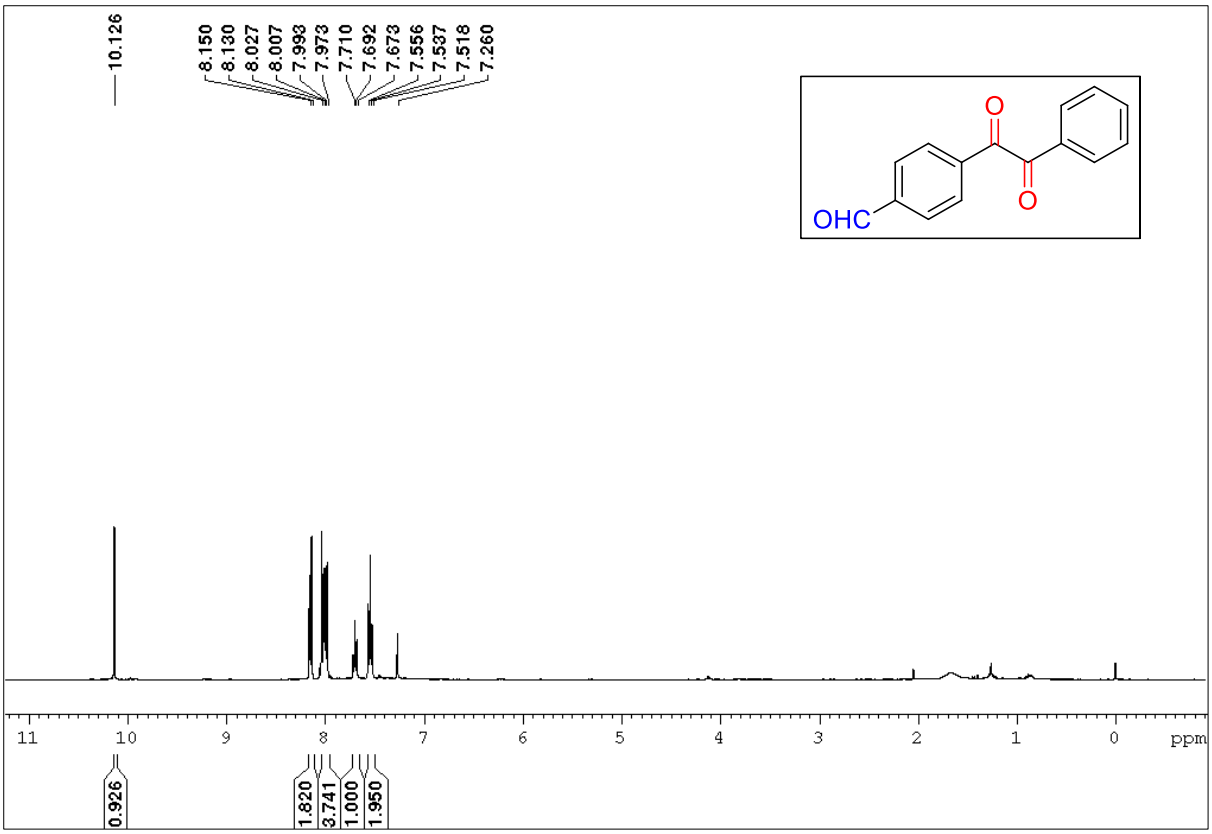


Figure 37: 400 MHz ^{1}H-NMR spectrum of **2s** in $CDCl_3$

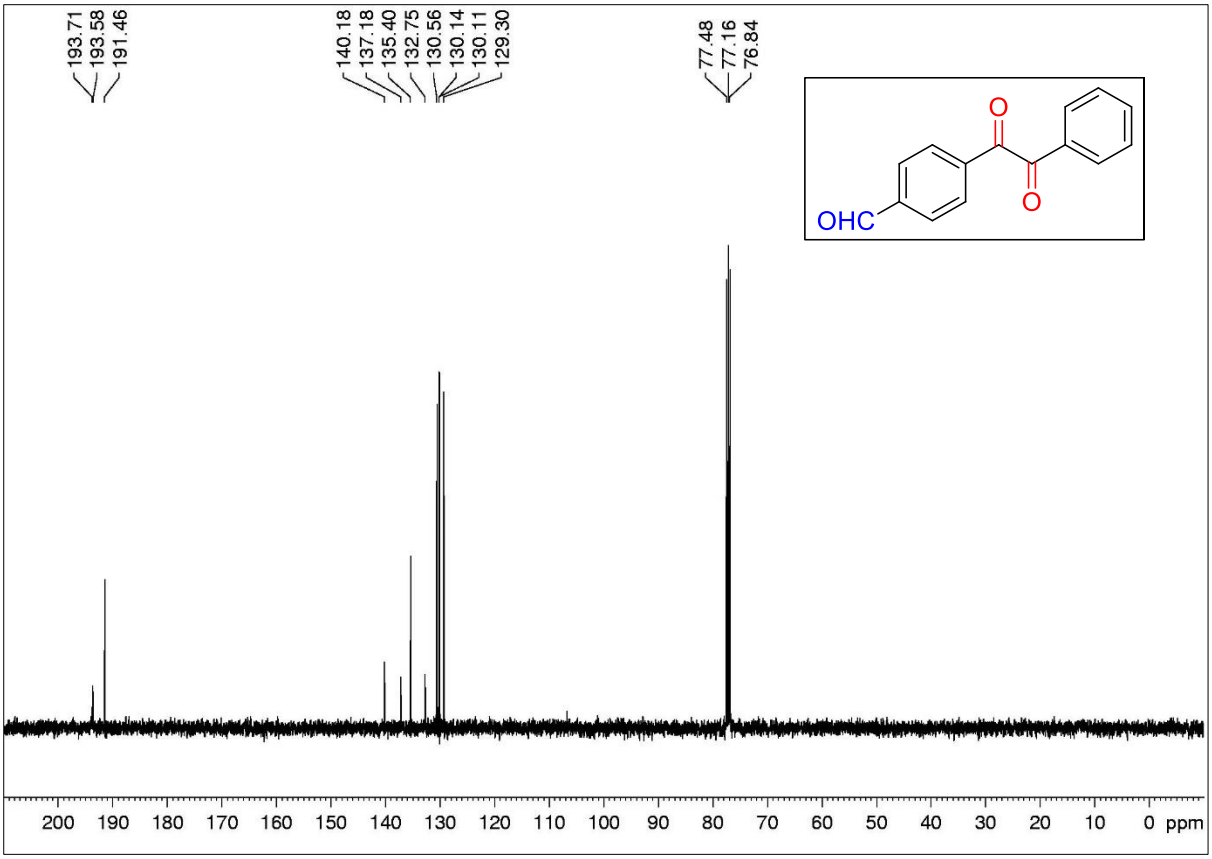


Figure 38: 100 MHz ^{13}C-NMR spectrum of **2s** in $CDCl_3$

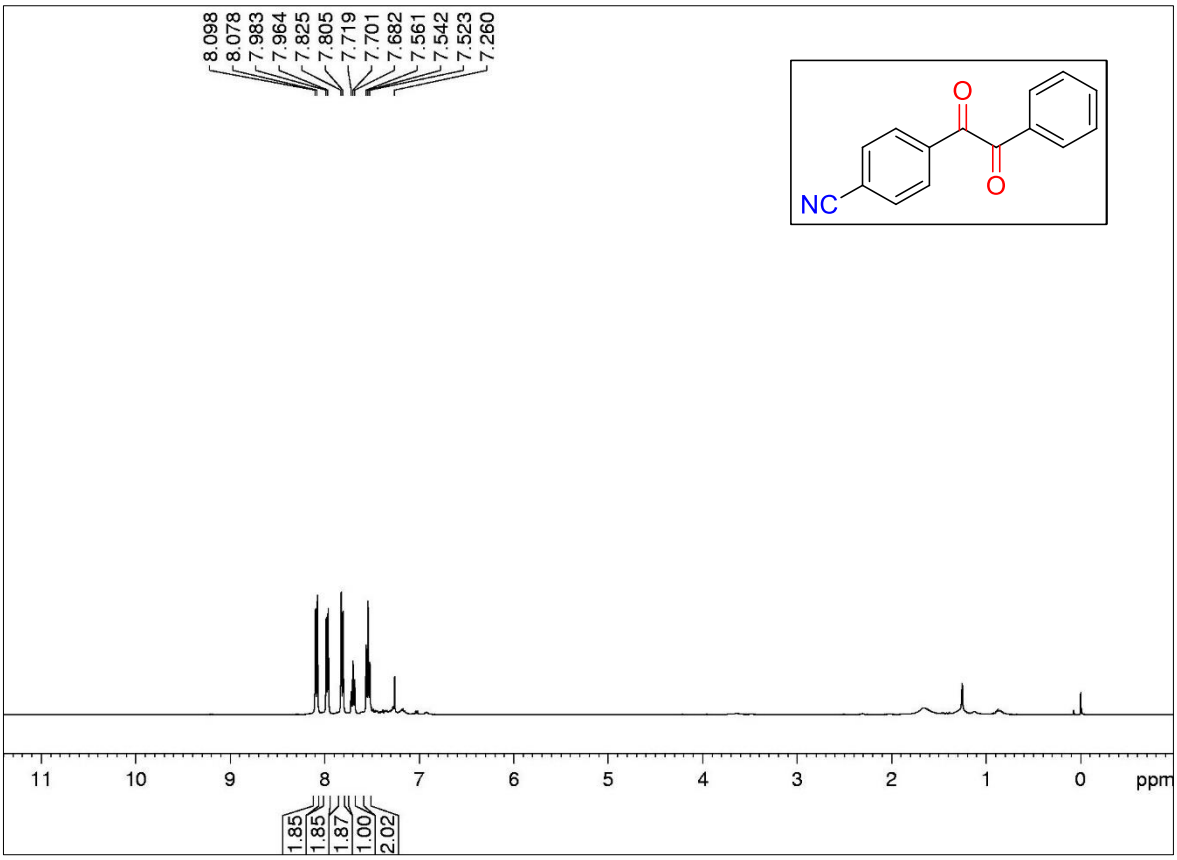


Figure 39: 400 MHz ^{1}H-NMR spectrum of **2t** in $CDCl_3$

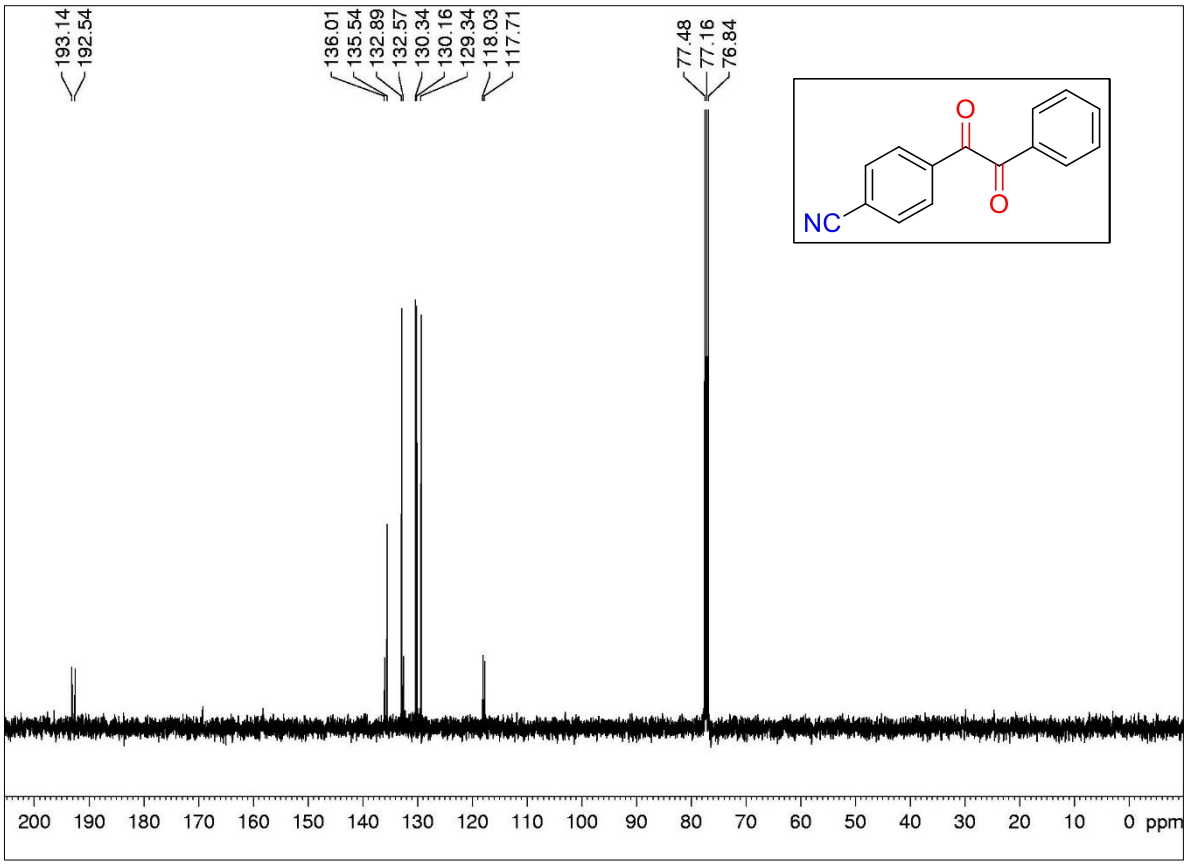


Figure 40: 100 MHz ^{13}C-NMR spectrum of **2t** in $CDCl_3$

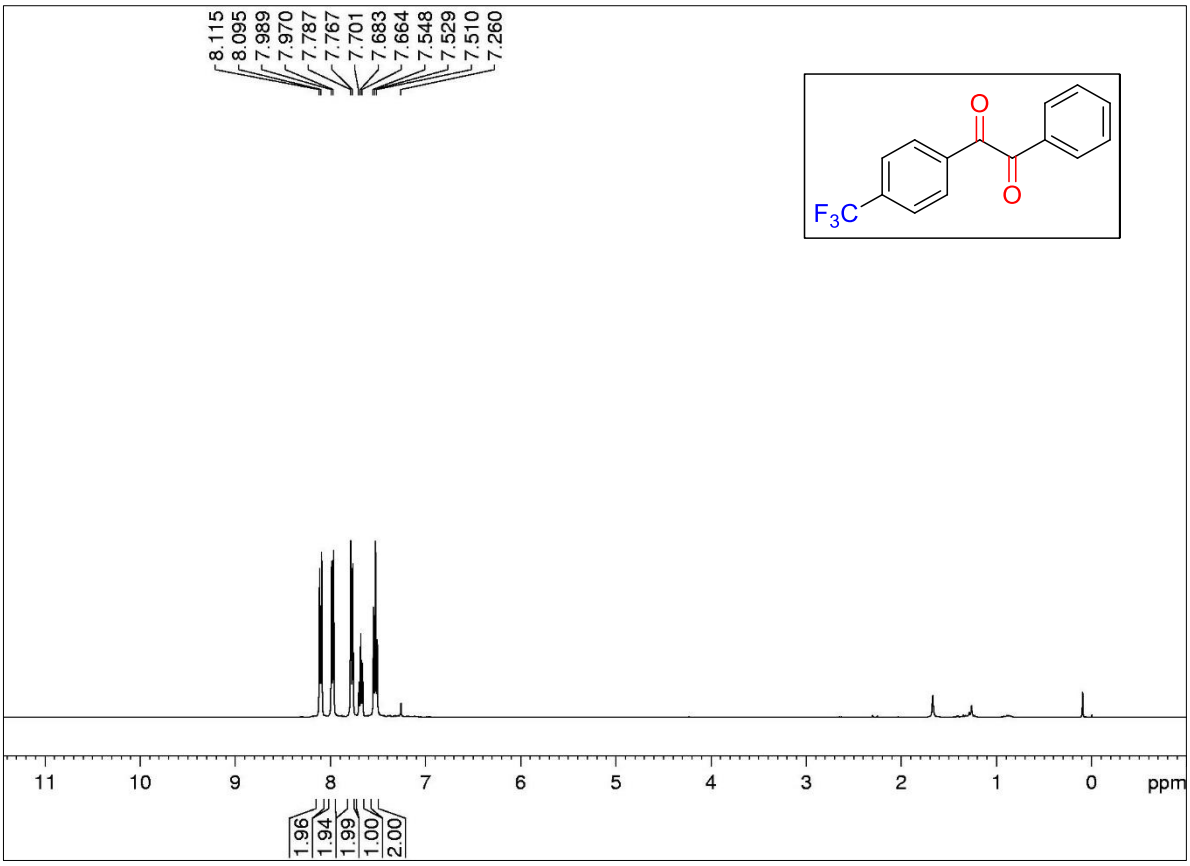


Figure 41: 400 MHz ^{1}H-NMR spectrum of **2u** in $CDCl_3$

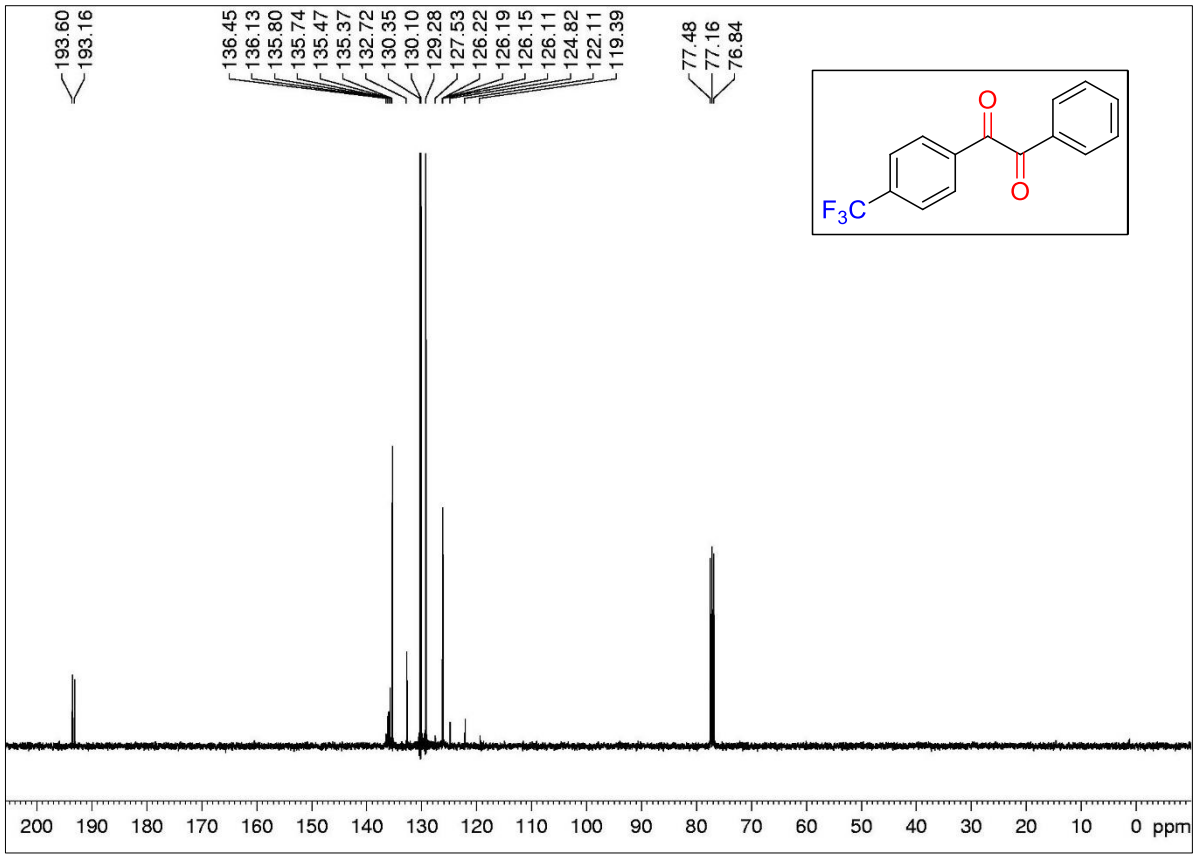


Figure 42: 100 MHz ^{13}C-NMR spectrum of **2u** in $CDCl_3$

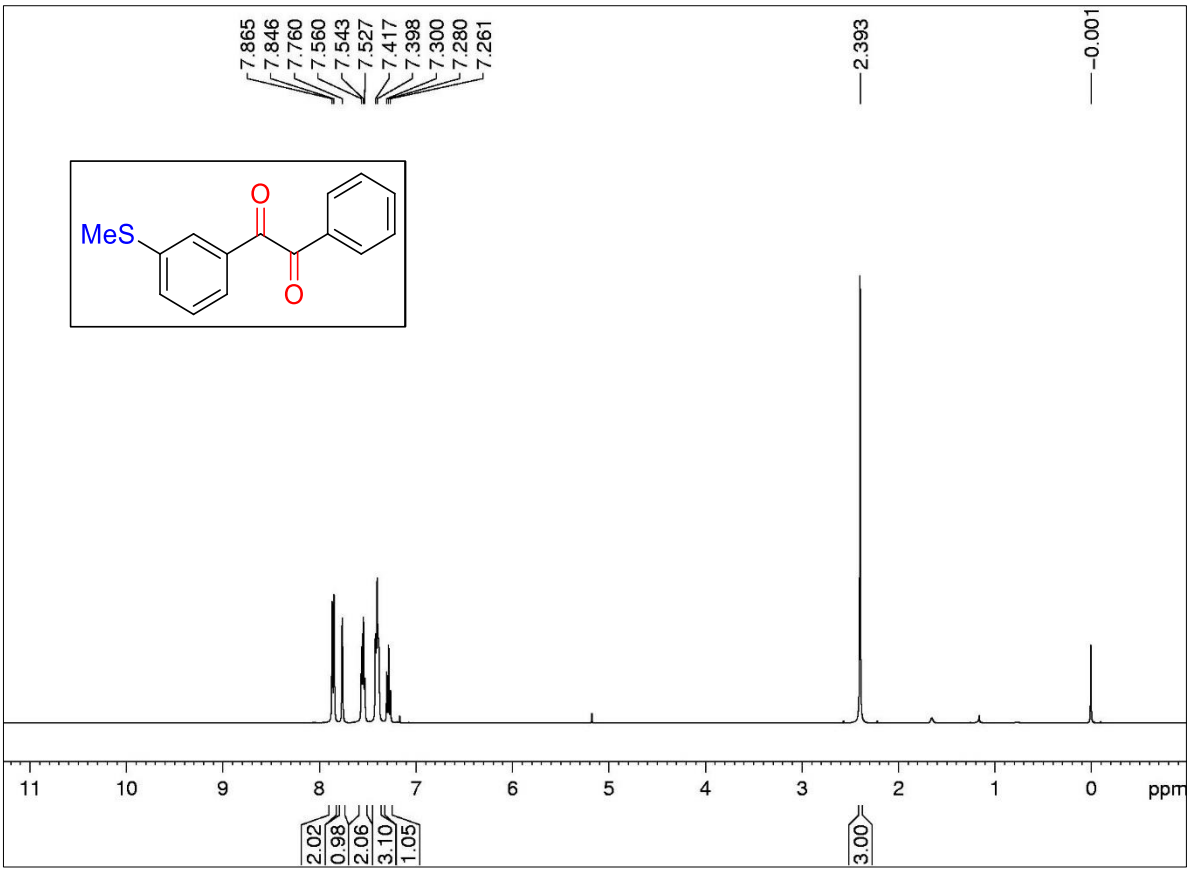


Figure 43: 400 MHz ^{1}H-NMR spectrum of **2v** in $CDCl_3$

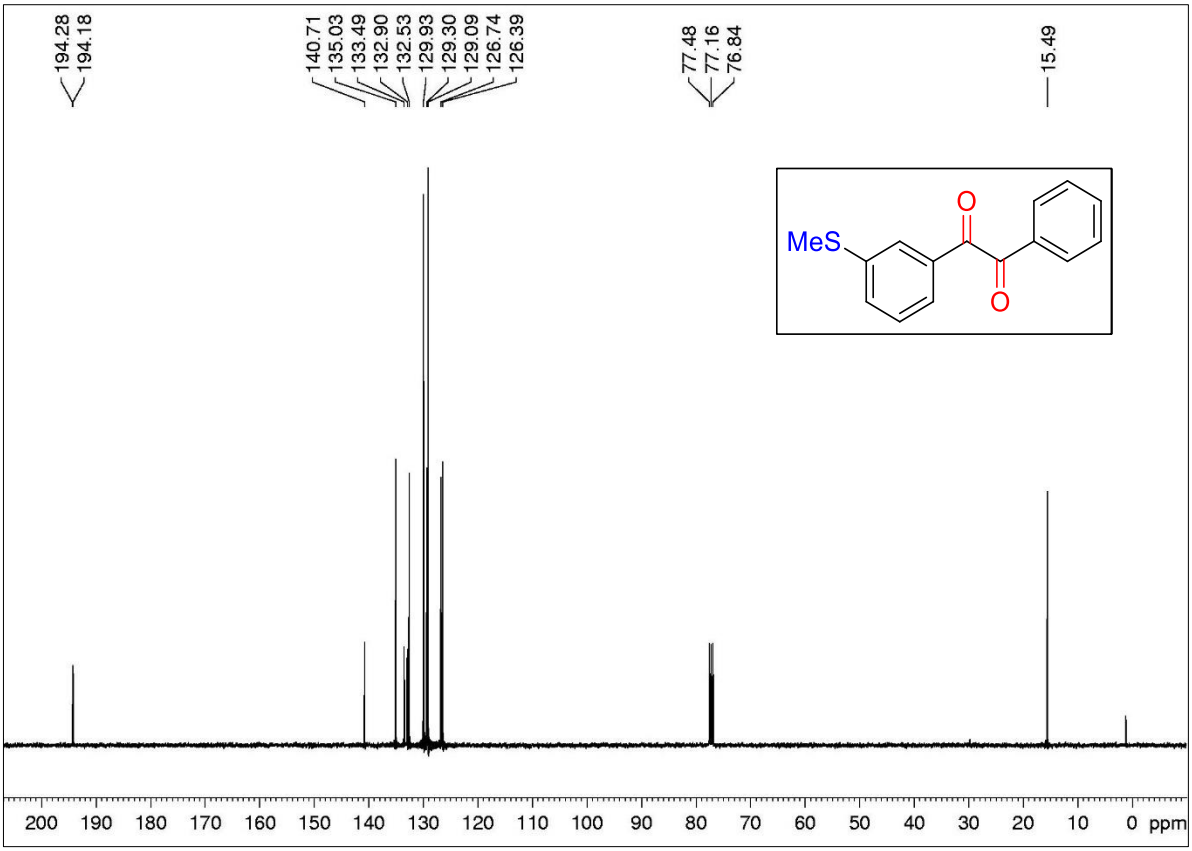


Figure 44: 100 MHz ^{13}C-NMR spectrum of **2v** in $CDCl_3$

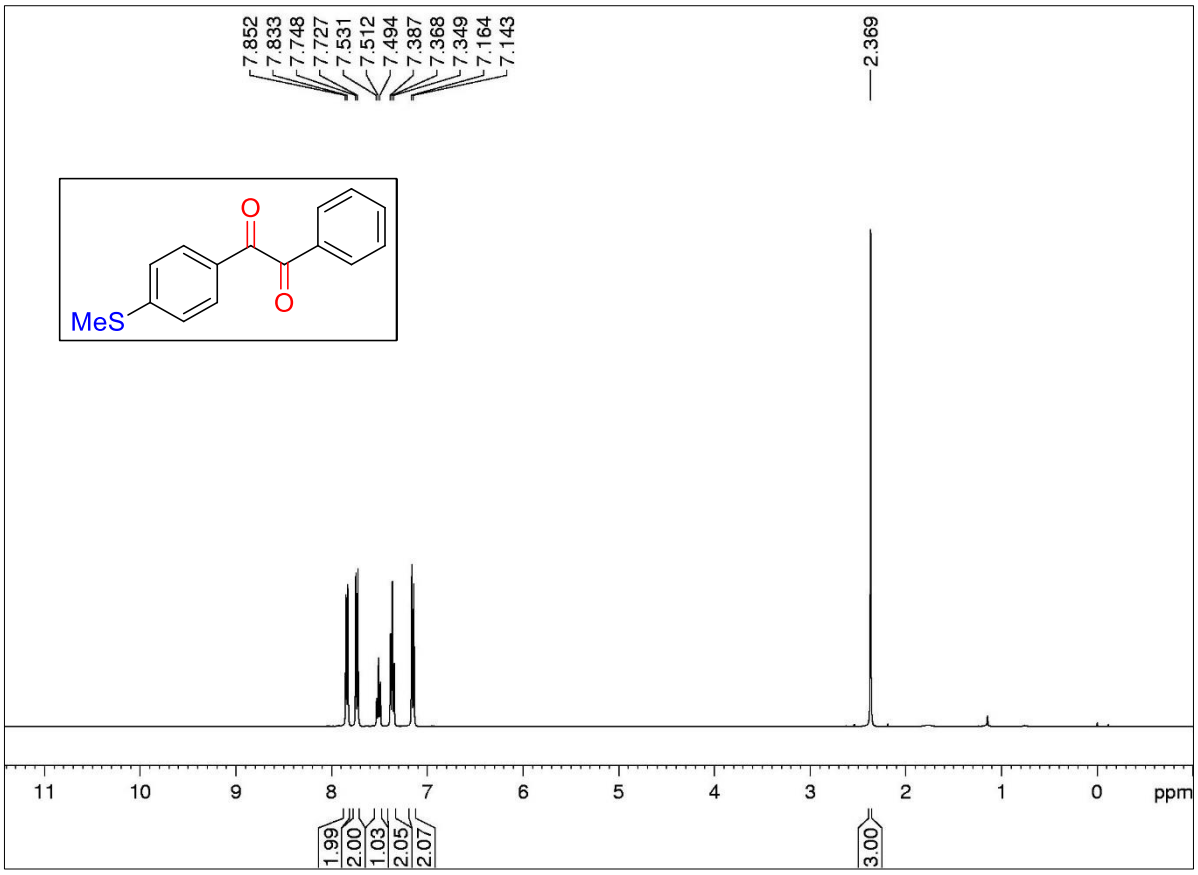


Figure 45: 400 MHz ^{1}H-NMR spectrum of **2w** in $CDCl_3$

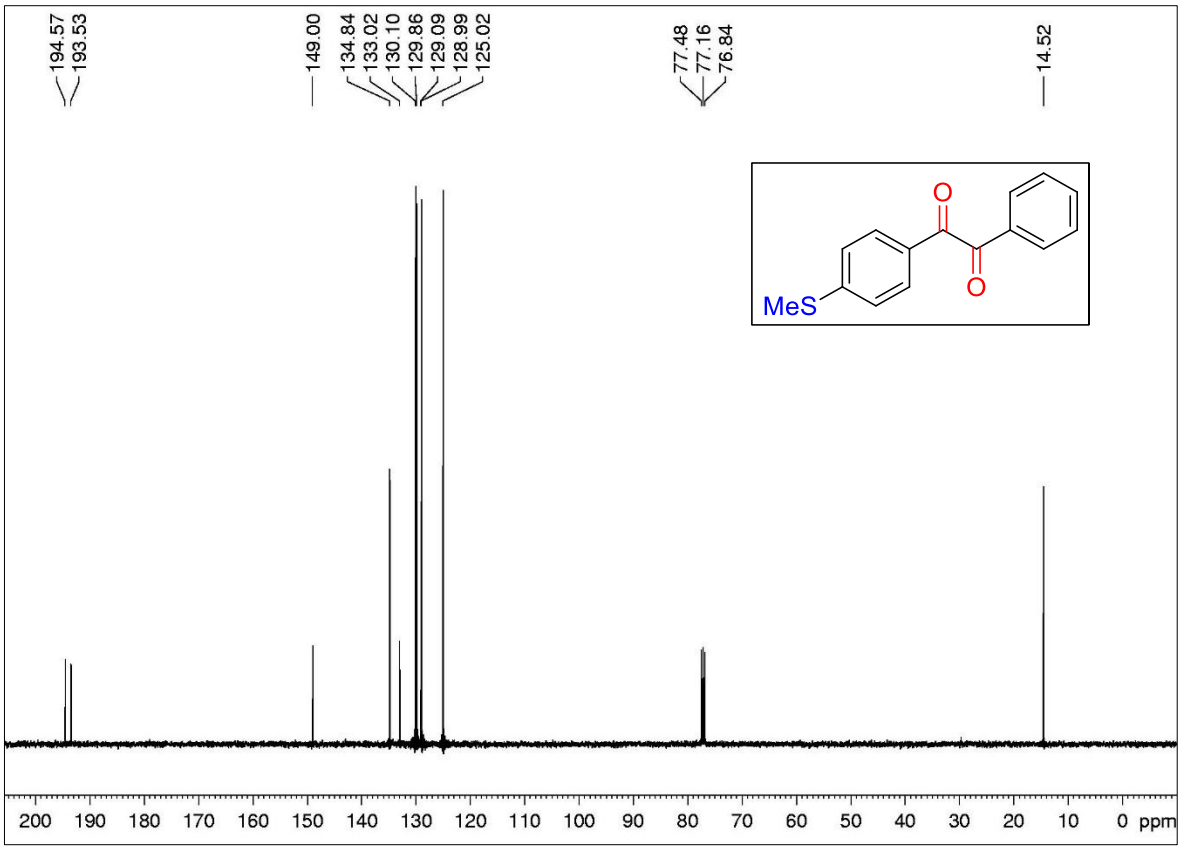


Figure 46: 100 MHz ^{13}C-NMR spectrum of **2w** in $CDCl_3$

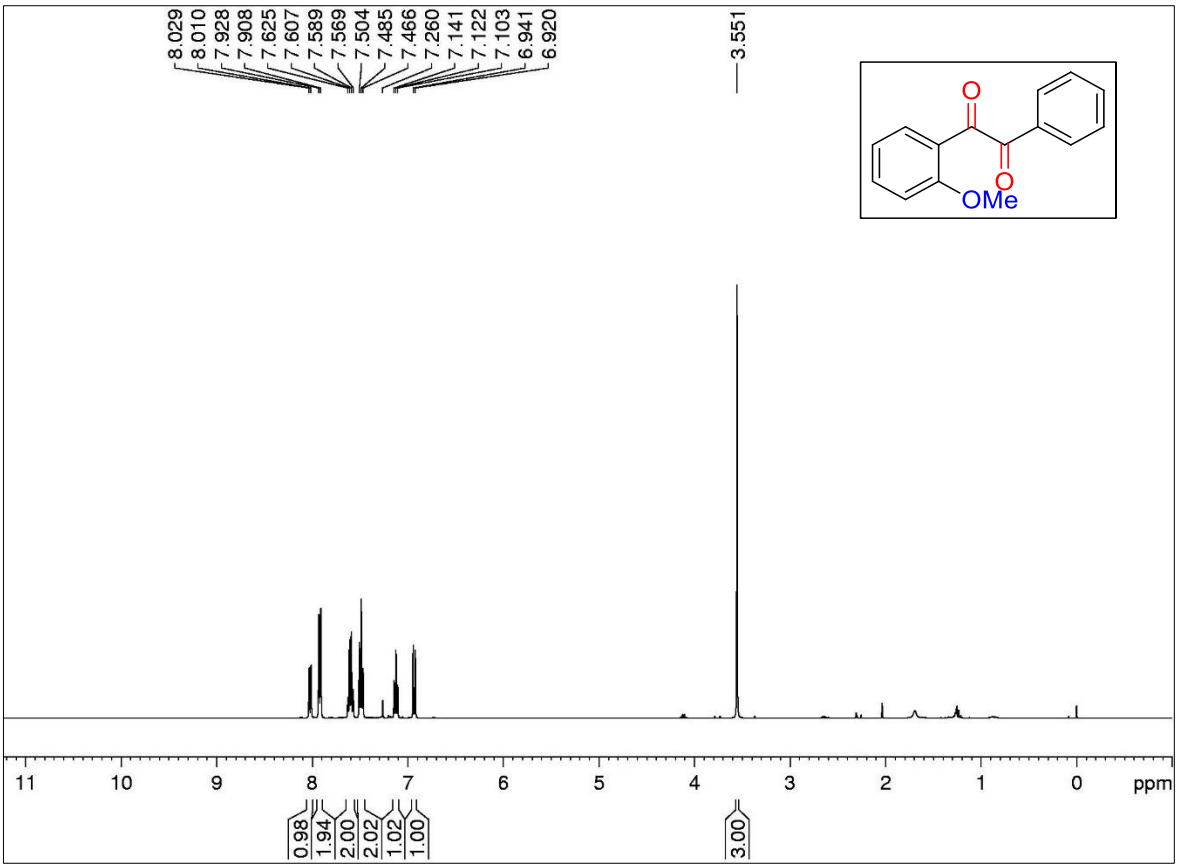


Figure 47: 400 MHz ^{1}H-NMR spectrum of **2x** in $CDCl_3$

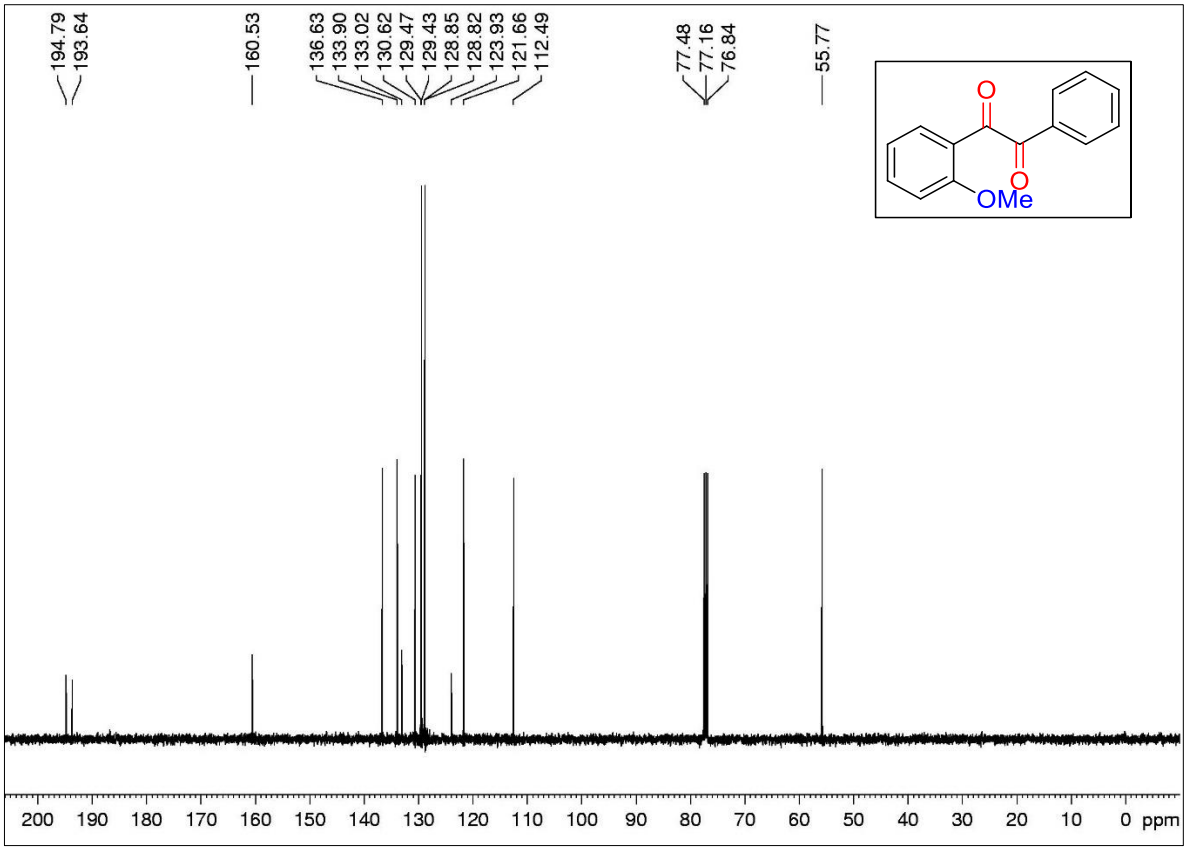


Figure 48: 100 MHz ^{13}C-NMR spectrum of **2x** in $CDCl_3$

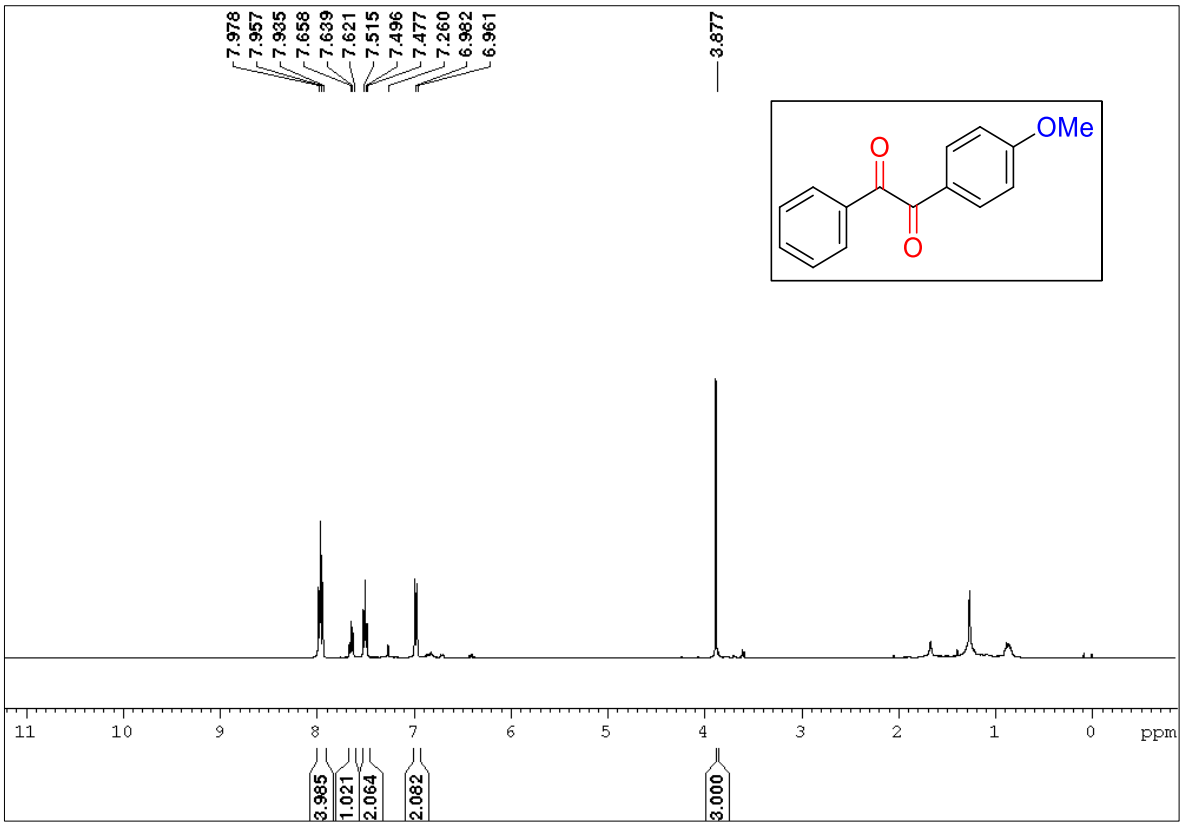


Figure 49: 400 MHz ^{1}H-NMR spectrum of **2y** in $CDCl_3$

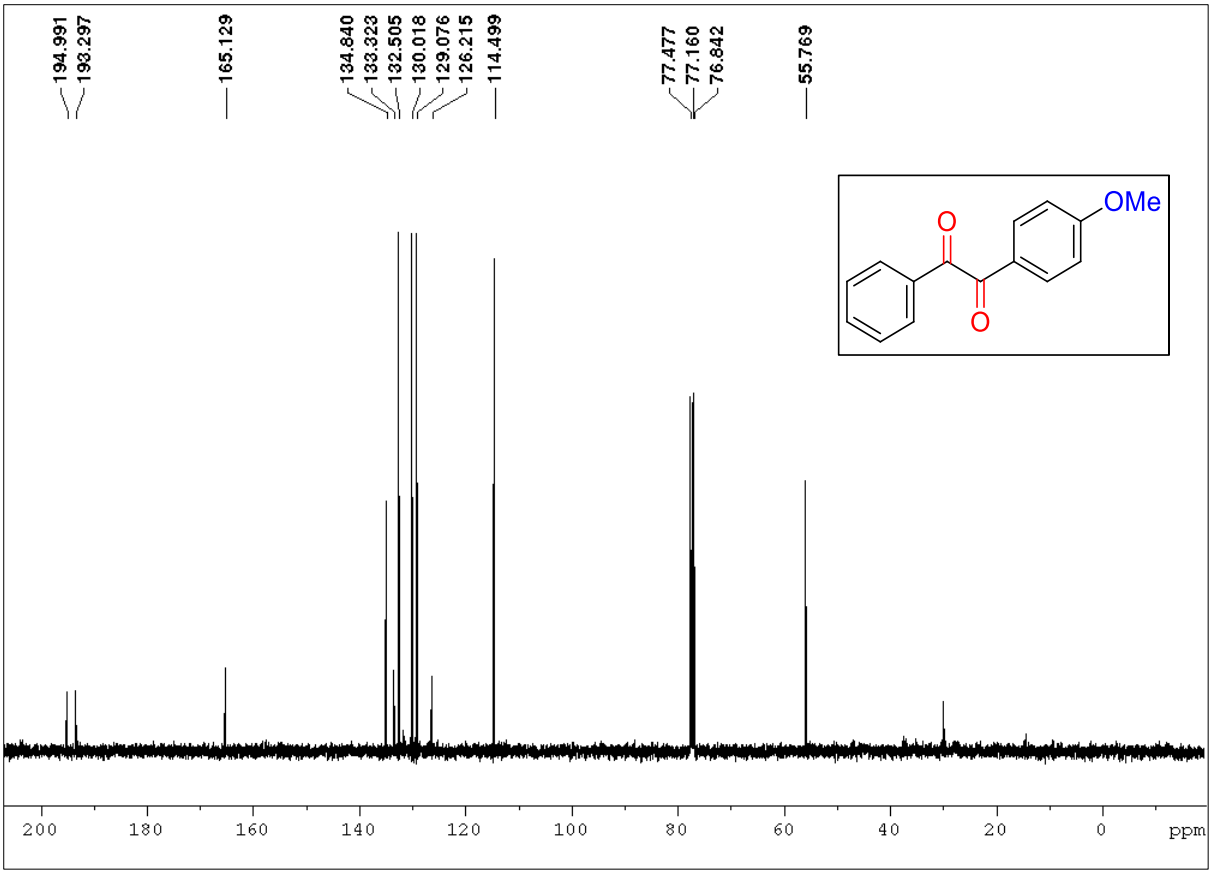


Figure 50: 100 MHz ^{13}C-NMR spectrum of **2y** in $CDCl_3$

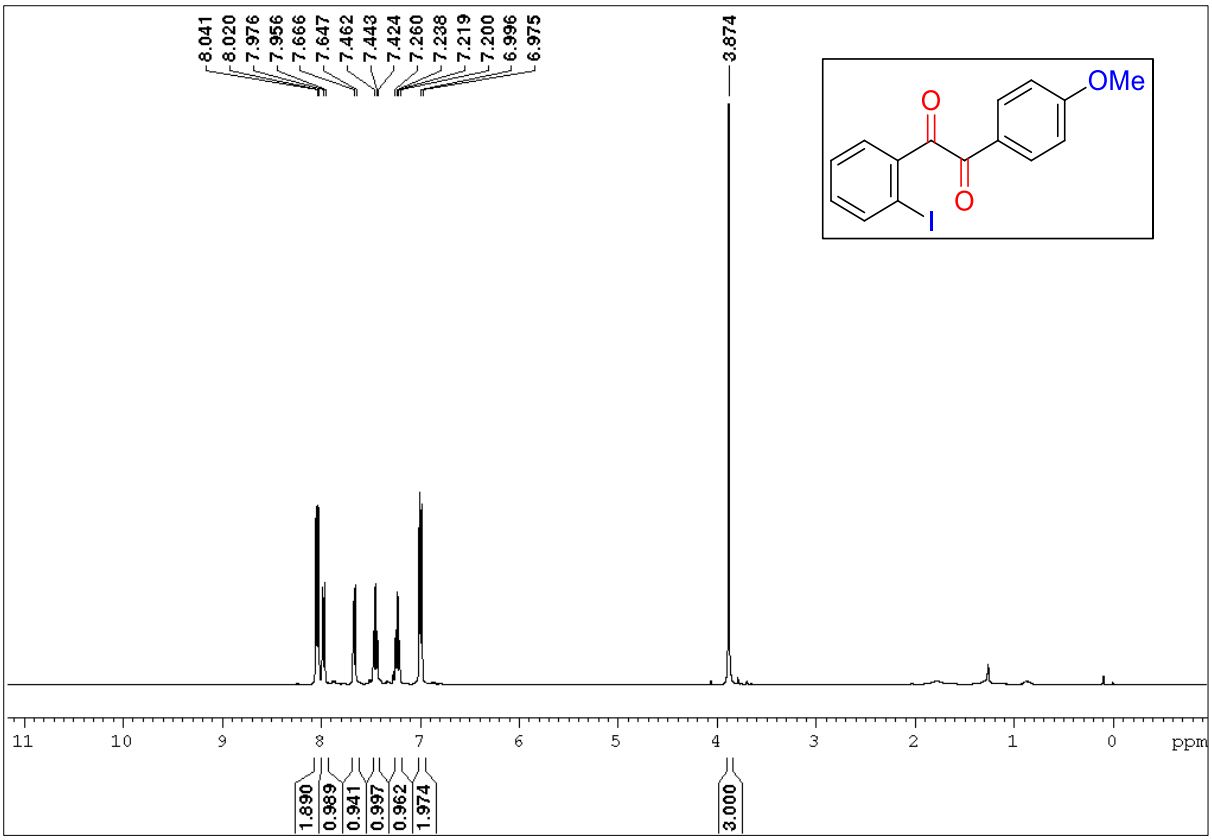


Figure 51: 400 MHz ^{1}H-NMR spectrum of **2z** in $CDCl_3$

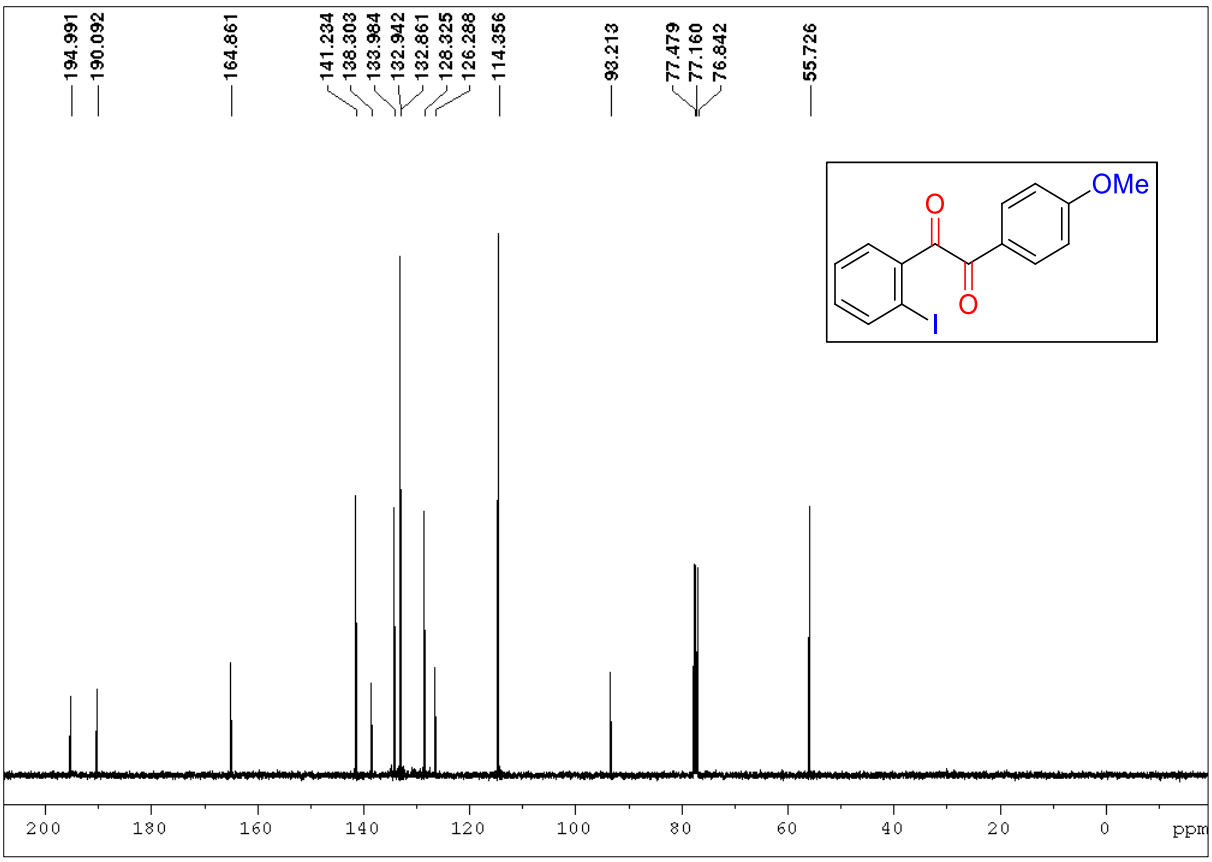


Figure 52: 100 MHz ^{13}C-NMR spectrum of **2z** in $CDCl_3$

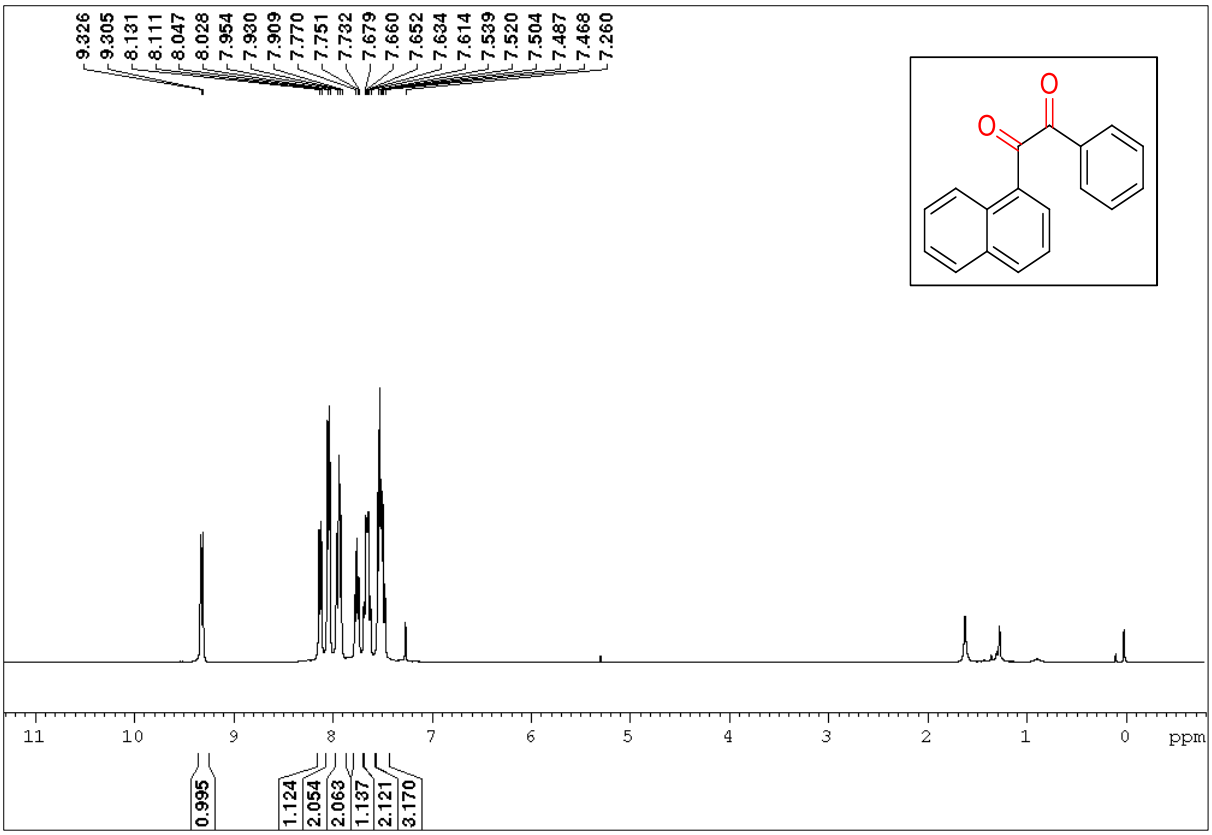


Figure 53: 400 MHz ^{1}H-NMR spectrum of **2aa** in $CDCl_3$

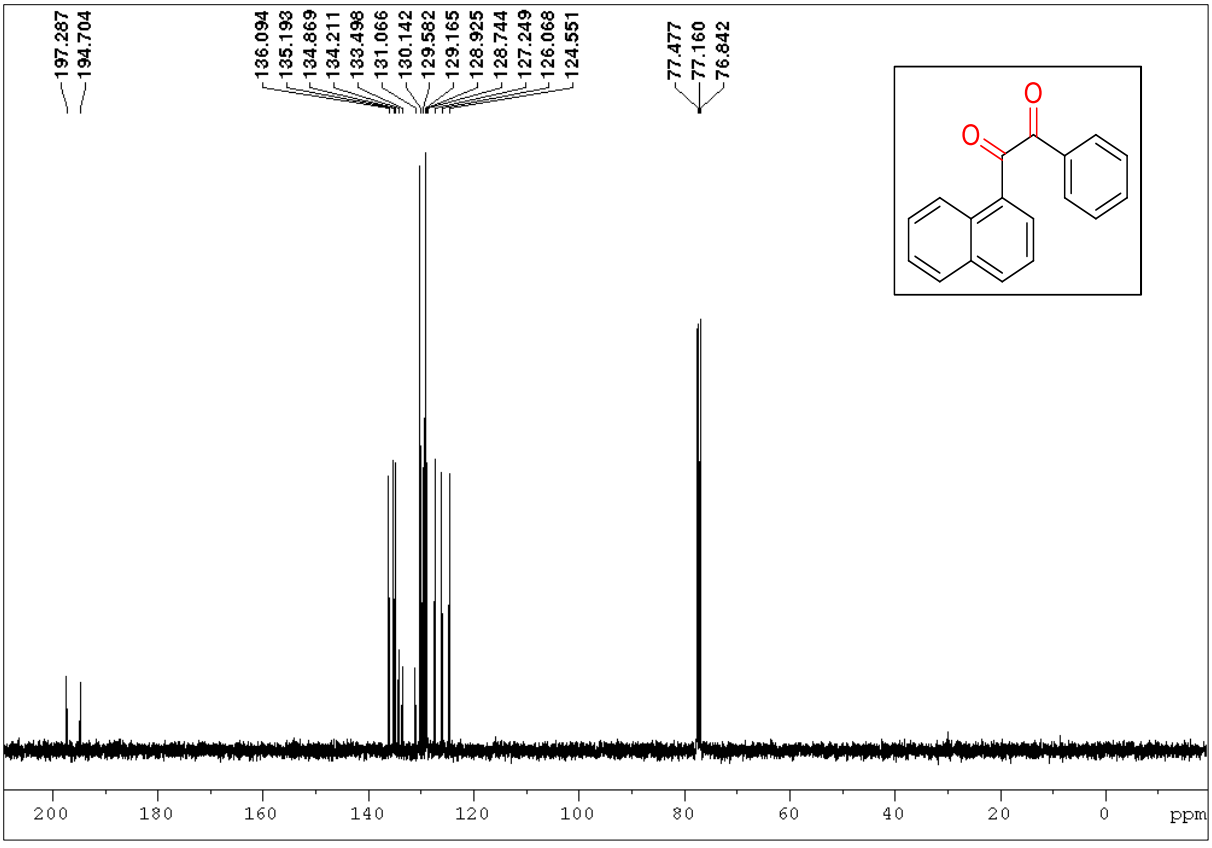


Figure 54: 100 MHz ^{13}C-NMR spectrum of **2aa** in $CDCl_3$

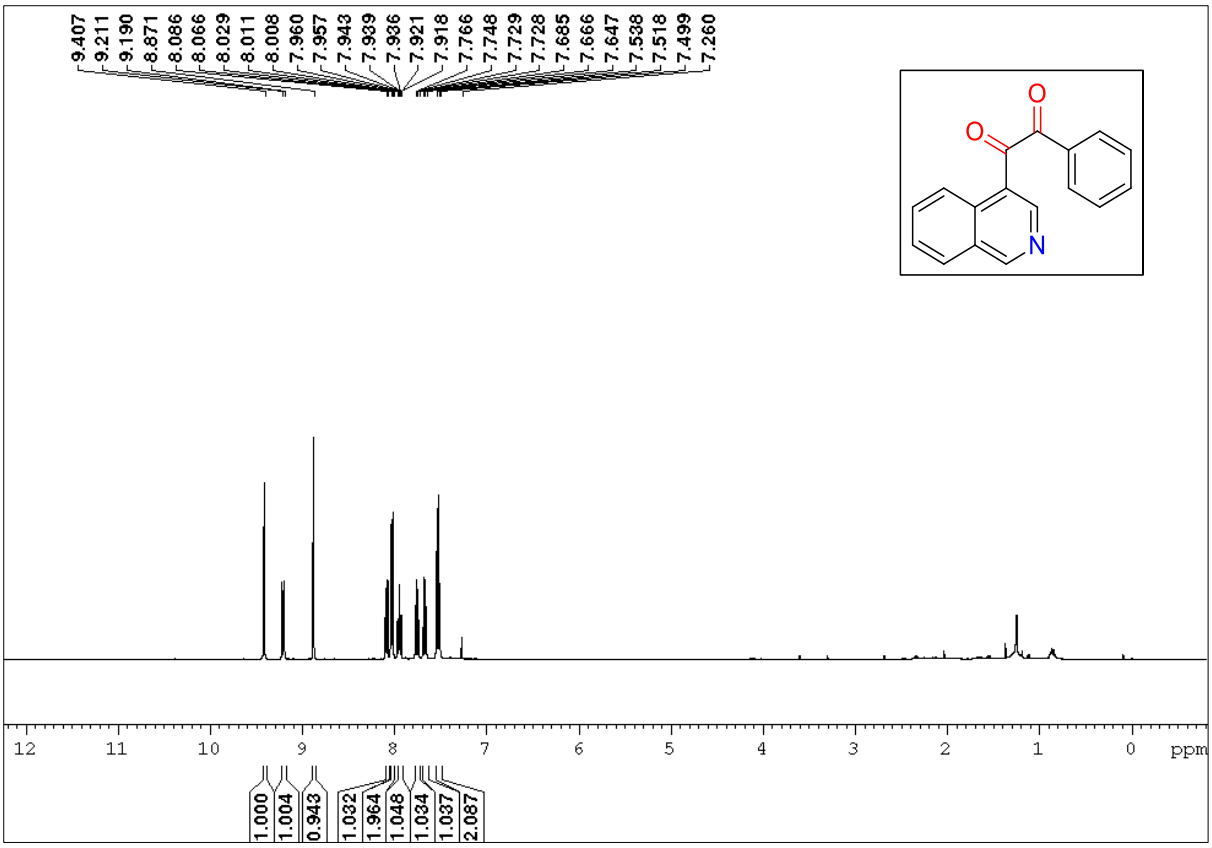


Figure 55: 400 MHz ^{1}H-NMR spectrum of **2ab** in $CDCl_3$

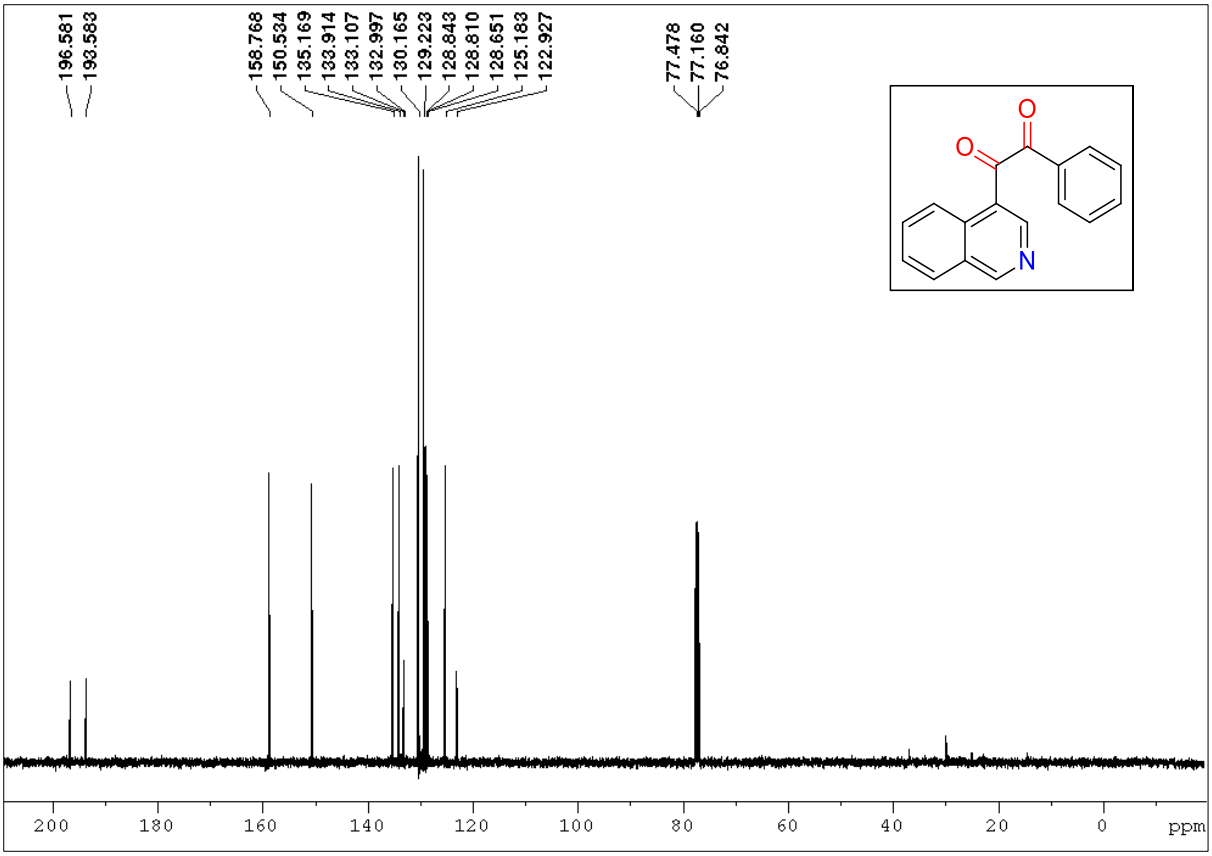


Figure 56: 100 MHz ^{13}C-NMR spectrum of **2ab** in $CDCl_3$

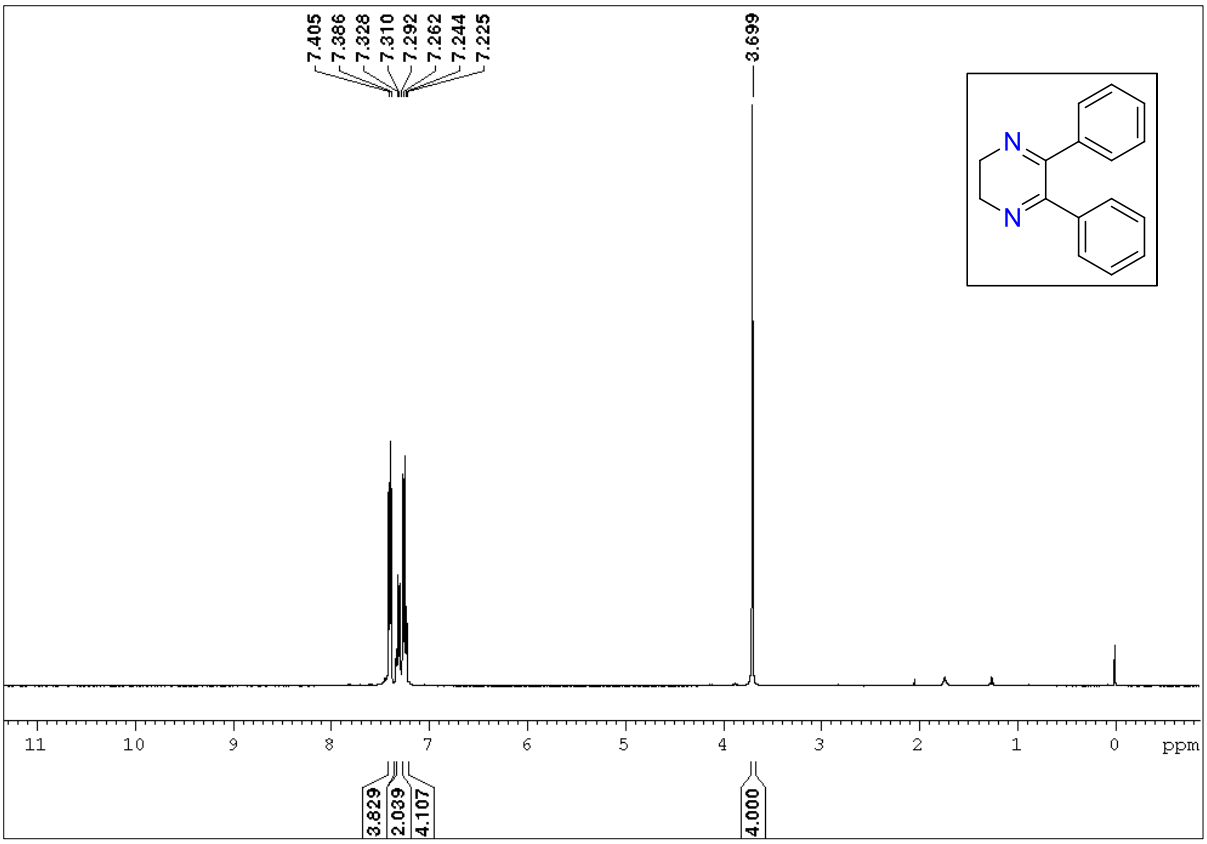


Figure 57: 400 MHz ^{1}H-NMR spectrum of **5** in $CDCl_3$

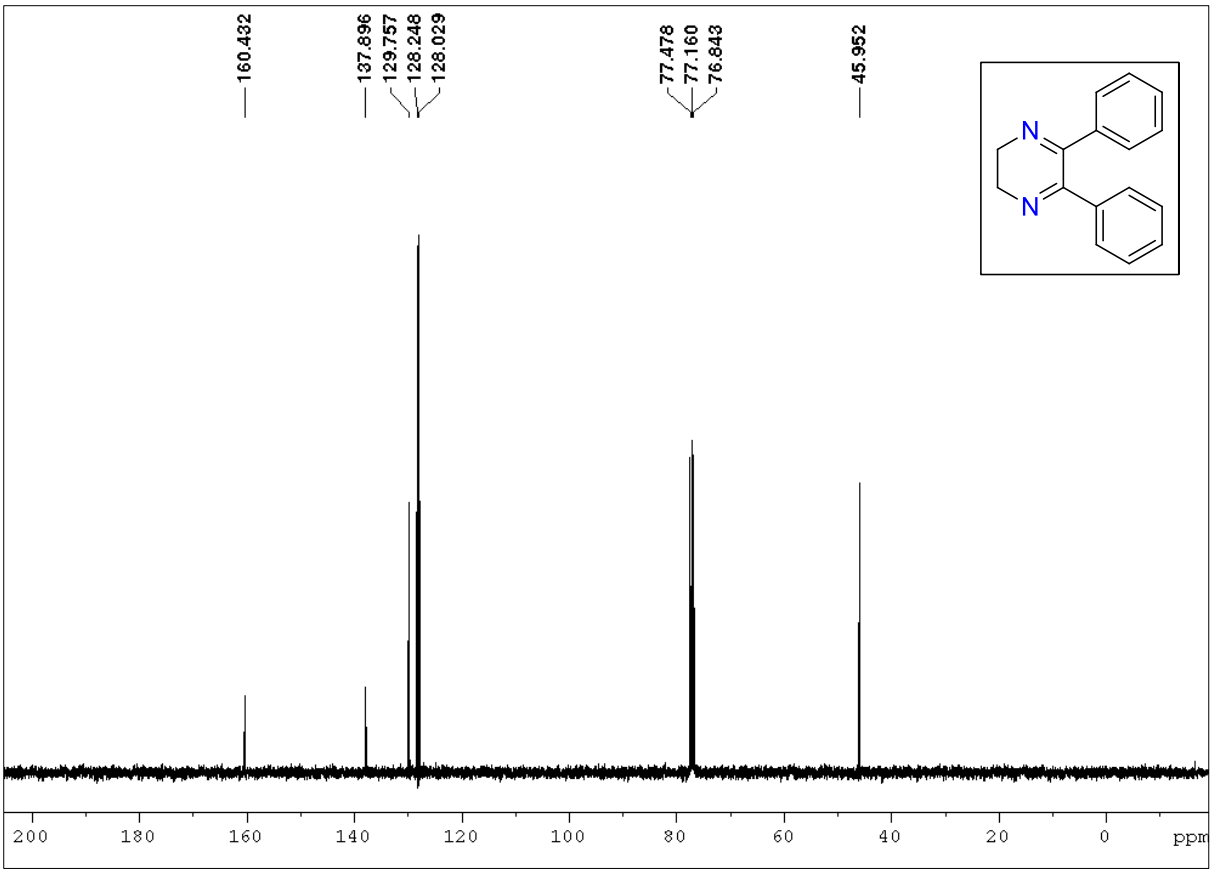


Figure 58: 100 MHz ^{13}C-NMR spectrum of **5** in $CDCl_3$

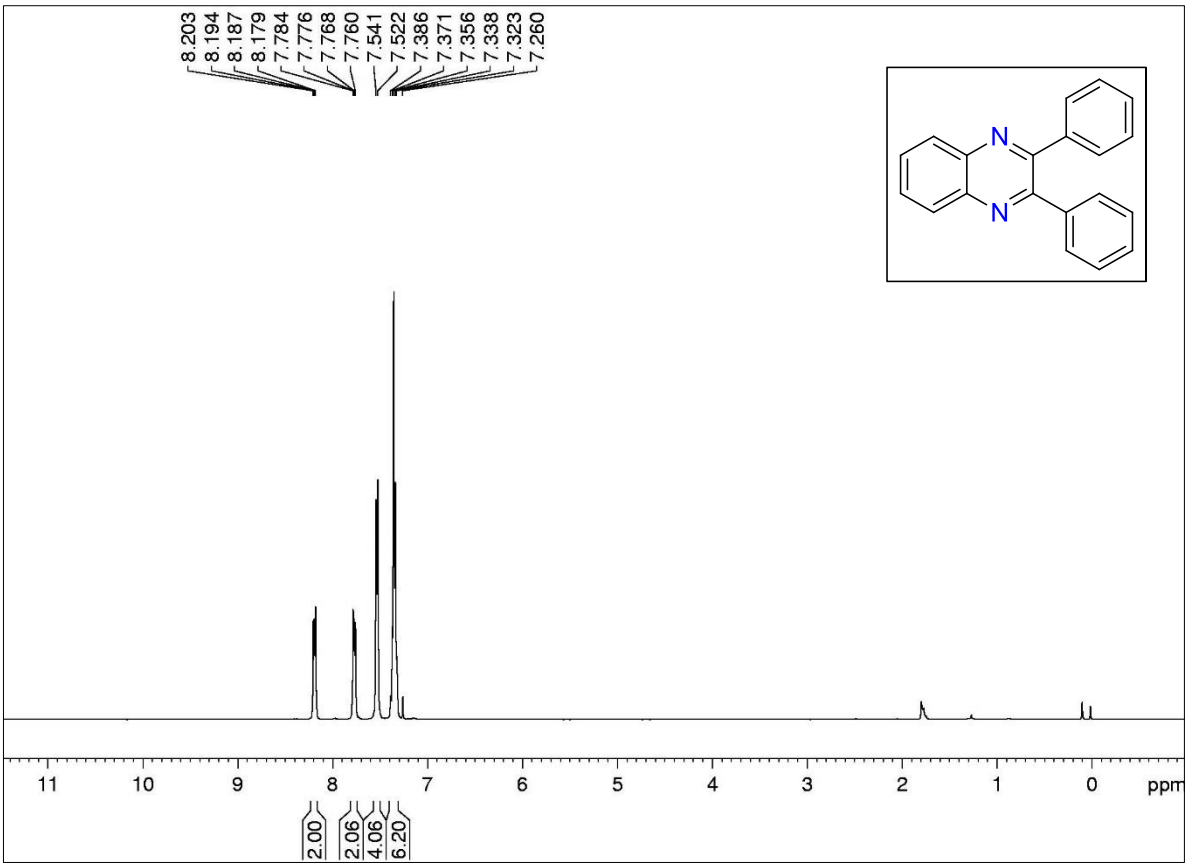


Figure 59: 400 MHz ^{1}H-NMR spectrum of **6** in $CDCl_3$

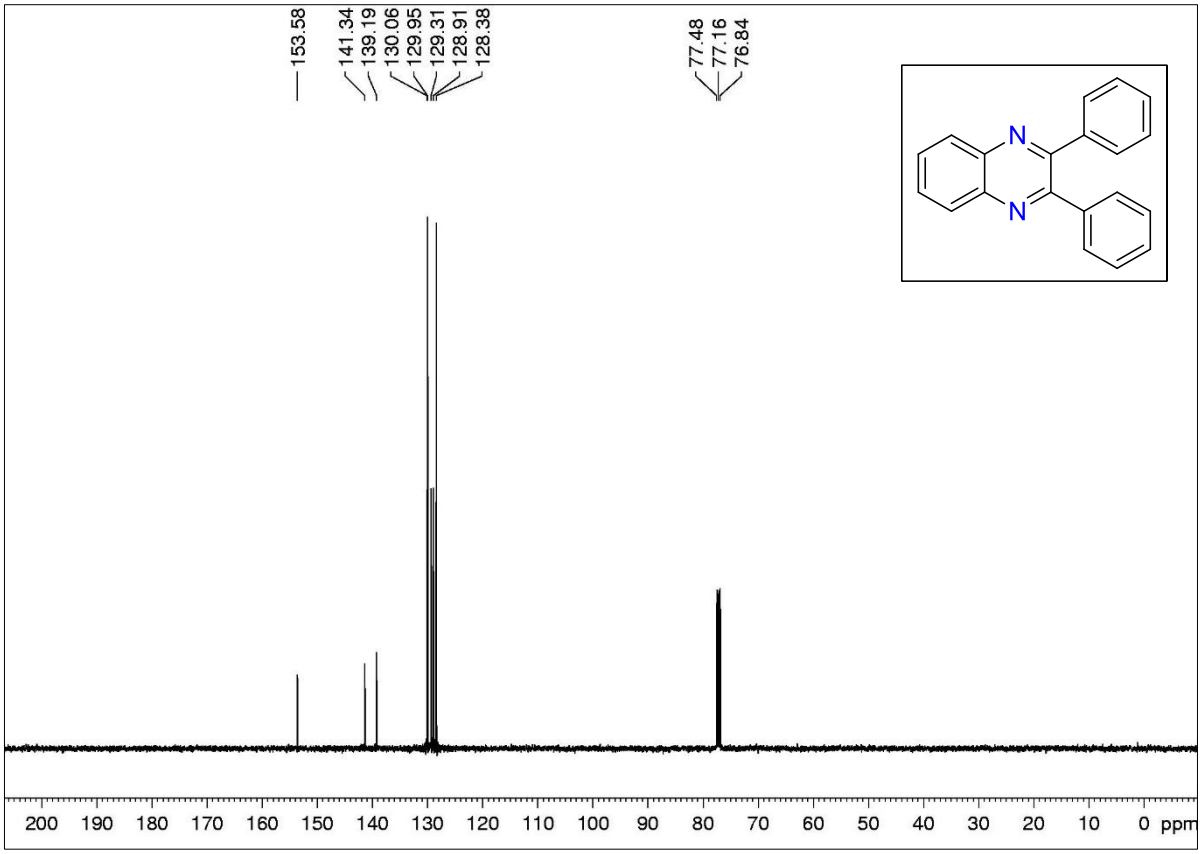


Figure 60:100 MHz ^{13}C-NMR spectrum of **6** in $CDCl_3$

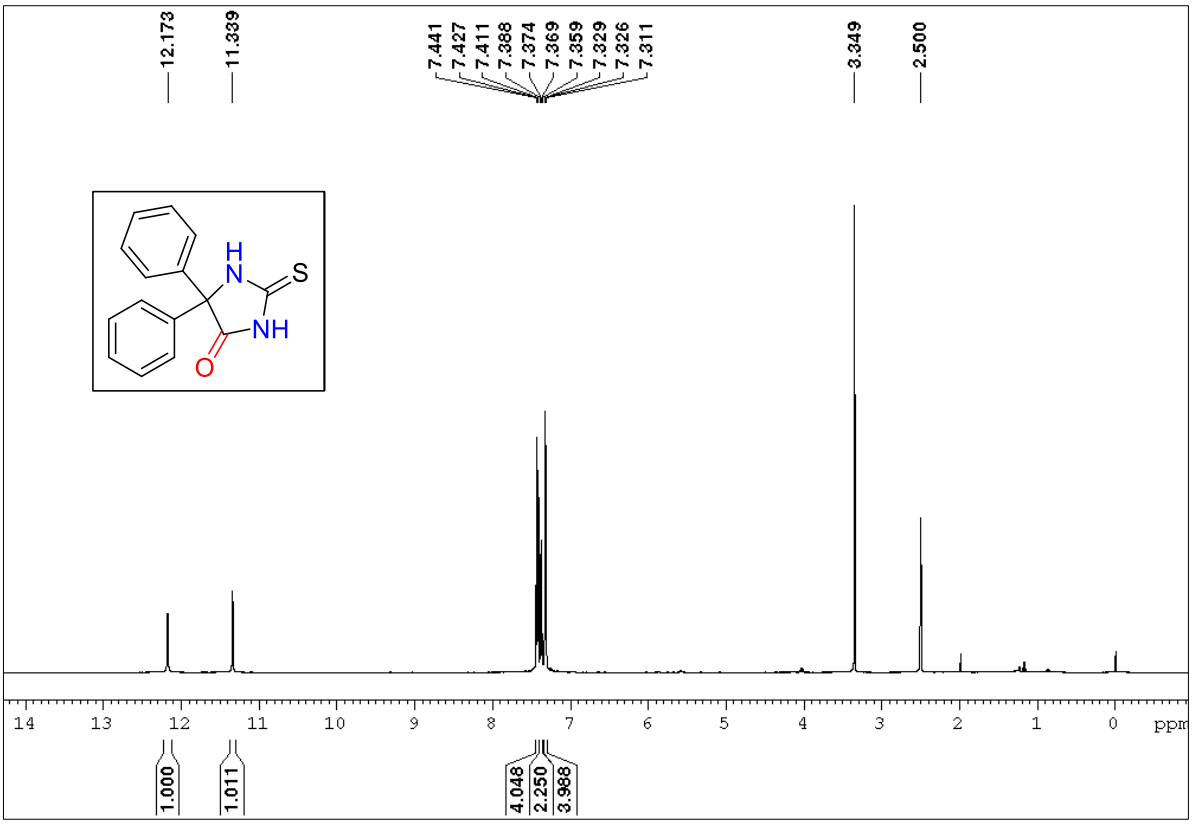


Figure 61: 400 MHz ^{1}H-NMR spectrum of **7** in DMSO-d_6

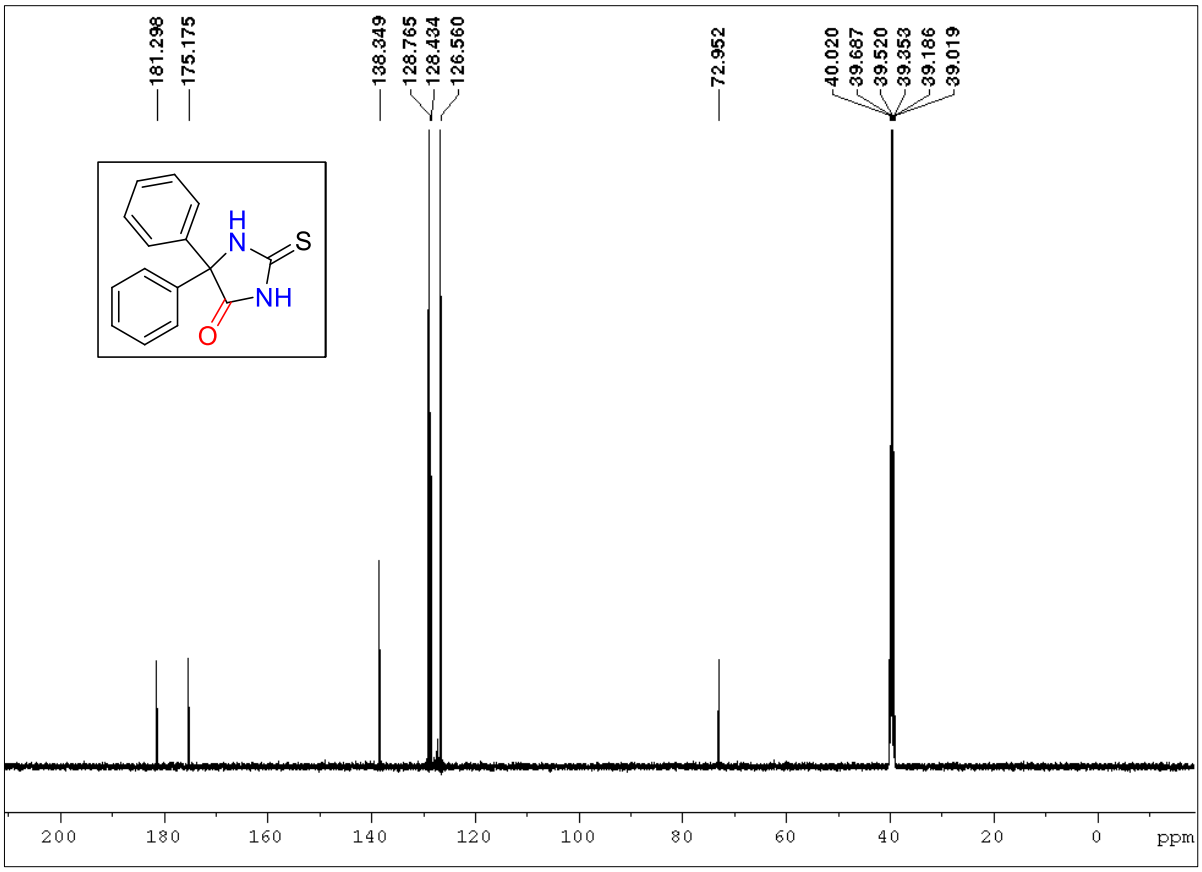


Figure 62:100 MHz ^{13}C-NMR spectrum of **7** in DMSO-d_6

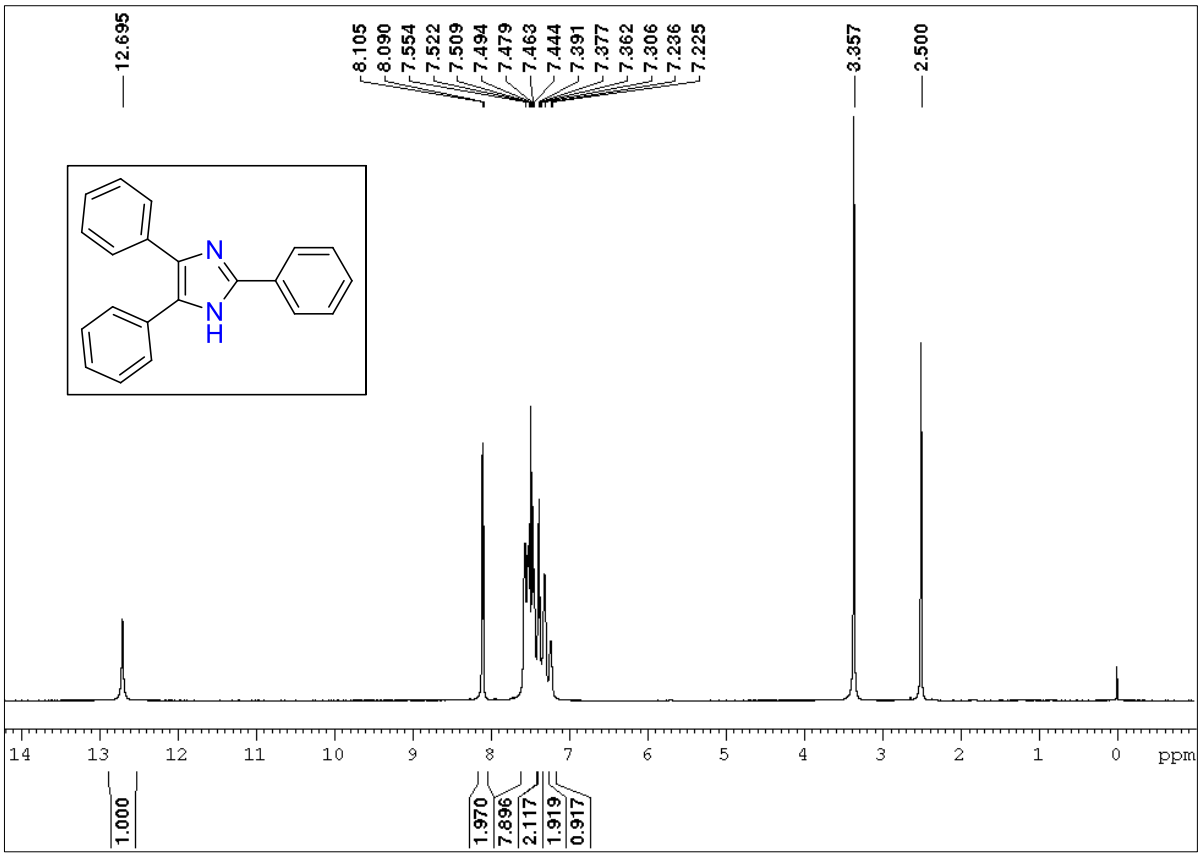


Figure 63: 400 MHz ^{1}H-NMR spectrum of **8** in DMSO-d_6

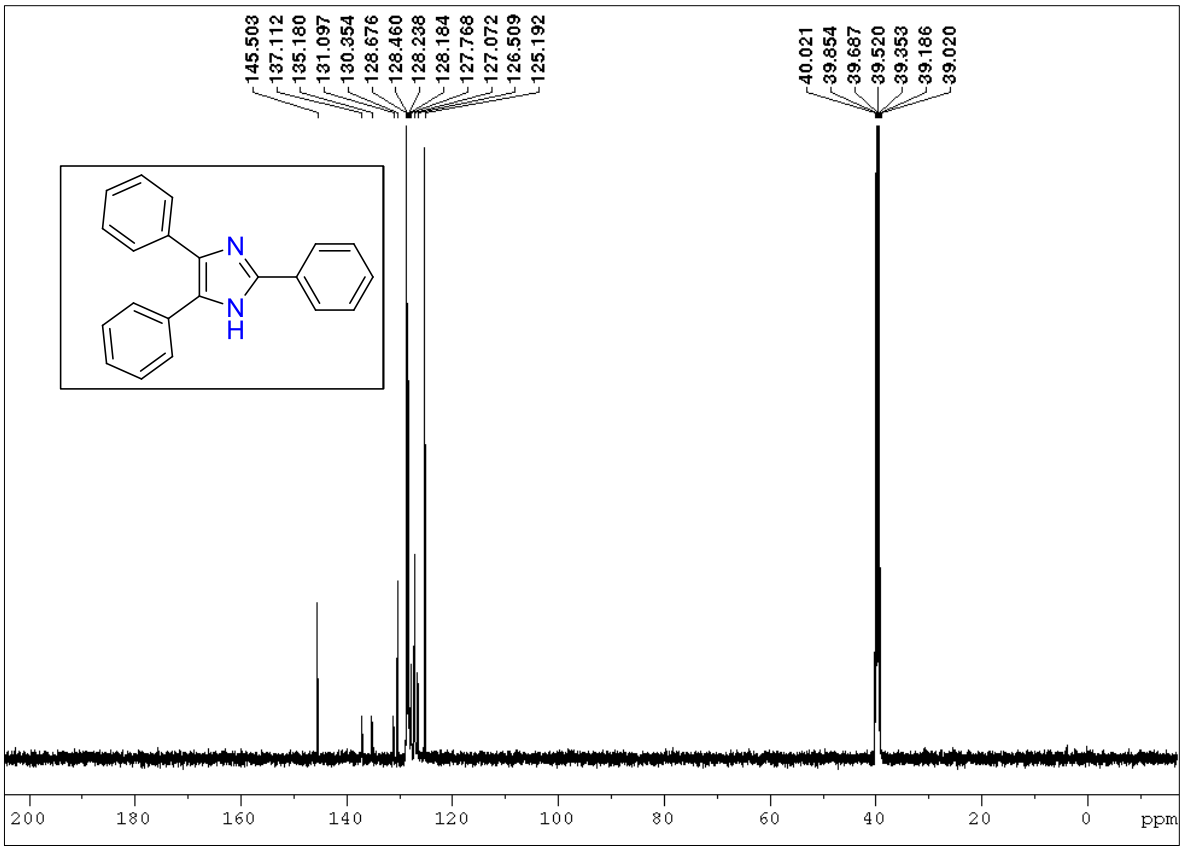


Figure 64:100 MHz ^{13}C-NMR spectrum of **8** in DMSO-d_6

7. ^{19}F-NMR spectras of 2u and 2h

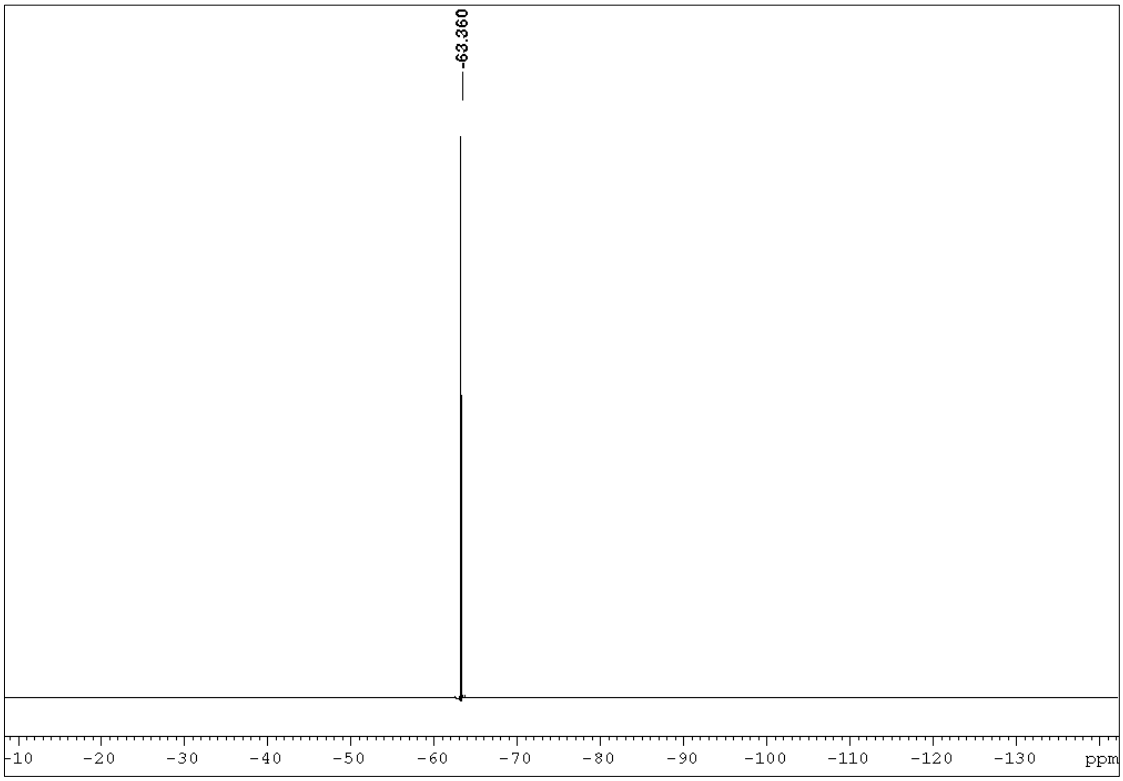


Figure 65: 470 MHz ^{19}F-NMR spectrum of **2u** in $CDCl_3$

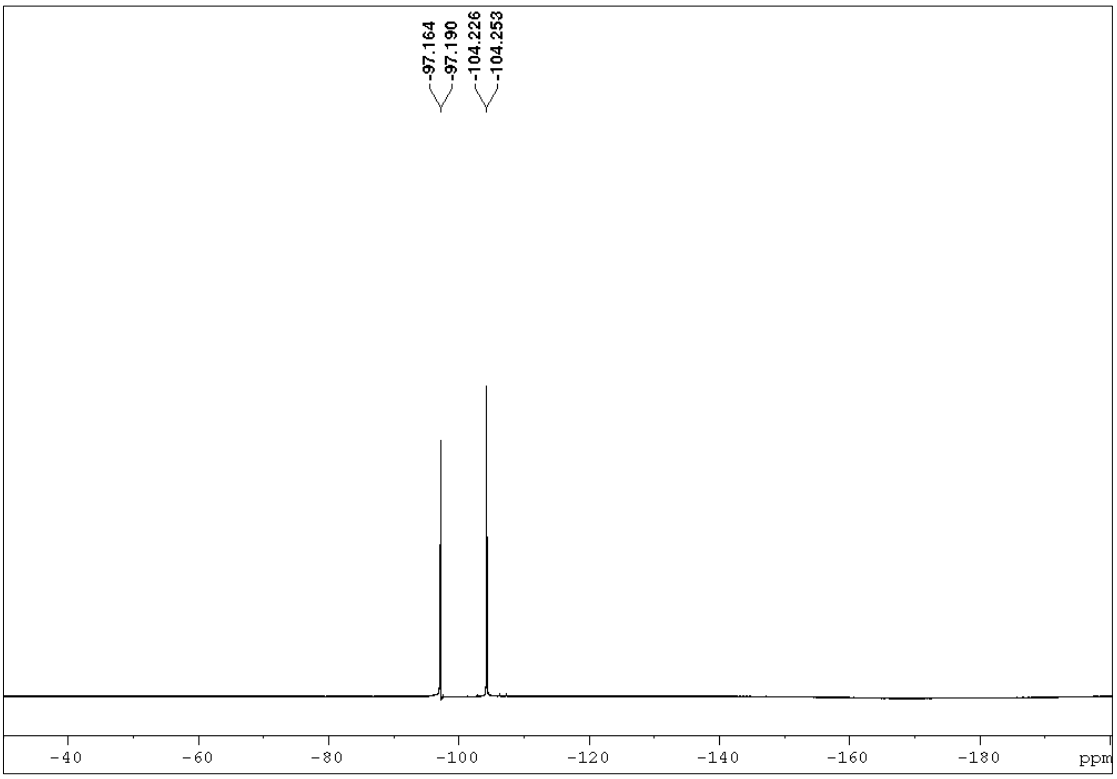


Figure 66: 470 MHz ^{19}F-NMR spectrum of **2h** in $CDCl_3$

8. References

1. D. Ganapathy, G. Sekar, Palladium nanoparticles stabilized by metal-carbon covalent bond: An efficient and reusable nanocatalyst in cross-coupling reactions, *Catal. Commun*., 2013, **39**, 50-54.