SUPPORTING INFORMATION

Transition-Metal-Free/ Boric Acid Catalysed Mechanochemical Synthesis of Symmetrical and Unsymmetrical Azobenzenes: A Sustainable Approach

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I. General Information

All the compounds were purchased from commercial suppliers and used without further purification. All the products were purified by column chromatography on silica gels (60−120 mesh, SRL, India). For TLC, Merck plates coated with silica gel 60, F254 were used. ^1H NMR and ^{13}C NMR were recorded using 400 MHz and 300 MHz, 100 MHz, 75 MHz respectively on Bruker AV 400 and 300 NMR spectrometer using TMS as internal standard. IR spectra were recorded on Film in the range 4000-500 cm^{-1} on Shimadzu FT-IR Spectrometer. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet), br (broad) and m (multiplate).

II. General procedure for the synthesis of symmetrical azobenzenes

The desired product of the model reaction was synthesized by grinding amine (1 mmol), oxone (0.5 mmol), and boric acid (10 mol%) together manually in a mortar and pestle at room temperature for 10 minutes under solvent-free conditions. The reaction progress was monitored by TLC using ethyl acetate and petroleum ether as the eluent system. After completion, the reaction mixture was extracted with ethyl acetate and washed repeatedly with water. The combined organic layer was then dried over anhydrous Na_2SO_3, concentrated, and the crude product was purified by column chromatography to obtain the pure solid compound. All the obtained compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy.

III. General procedure for the synthesis of unsymmetrical azobenzenes

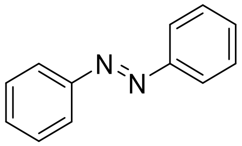
To obtain the desired product of the model reaction, p-toluidine (1 mmol), nitrosobenzene (1 mmol), and boric acid (10 mol%) were thoroughly ground together using a mortar and pestle at room temperature for 10 minutes under solvent-free conditions. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was extracted with ethyl acetate and water. The combined organic layer was dried over anhydrous Na_2SO_3, concentrated, and the resulting residue was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether as the eluent to yield the pure solid product. All the obtained products were characterized by ^1H NMR and ^{13}C NMR spectroscopy.

IV. Spectroscopic data of synthesized symmetrical azobenzenes

1.(*E*)-Azobenzene: [1-3] Yield = 82 %,

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.54-7.49 (m, 6H), 7.93 (d, *J* = 7.2 Hz, 4H);

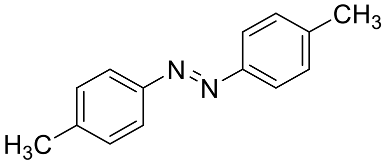
^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm):122.84, 129.10, 131.00, 152.62.



2. (*E*)-4,4′-Dimethylazobenzene: [1-3] Yield = 85 %,

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 2.32 (s, 6H), 7.19 (d, *J* = 8.1 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H);

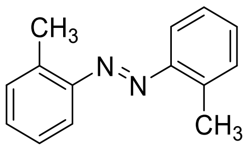
^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm): 122.75, 21.50, 129.73, 141.22, 150.82.



3. (*E*)-2,2′-Dimethylazobenzene: [1-3] Yield = 84%,

^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 2.28 (s, 6H), 7.20 (t, *J* = 7.2 Hz, 4H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.74 (s, 4H);

^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm): 18.48, 121.56, 128.62, 131.23, 142.78, 149.46.

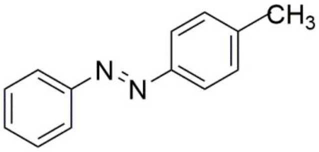


V. Spectroscopic data of synthesized unsymmetrical azobenzenes

1. (*E*)-1-(4-Methylphenyl)-2-phenyldiazene:[4] Yield = 80%,

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 2.44 (s, 3H), 7.3 (d, *J* = 8.0 Hz, 2H), 7.5 (d, *J* = 8.0 Hz, 3H), 7.8 (d, *J* = 8.2, 2H), 7.9 (d, *J* = 7.6, 2H);

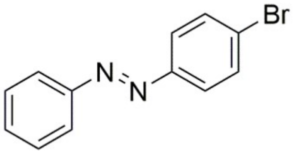
^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 22.69, 122.72, 122.85, 129.05, 129.74, 130.69, 141.56, 150.77, 152.74.



2. (*E*)-1-(4-bromophenyl)-2-phenyldiazene: [1,4] Yield = 72%,

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.54-7.48 (m, 3H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.92-7.90 (d, 2H);

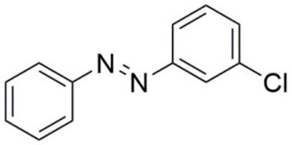
^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 122.95, 124.36, 125.36, 129.14, 131.31, 132.33, 151.37, 152.50.



3. (*E*)-1-(3-Chlorophenyl)-2-phenyldiazene: [1,4] Yield = 76%,

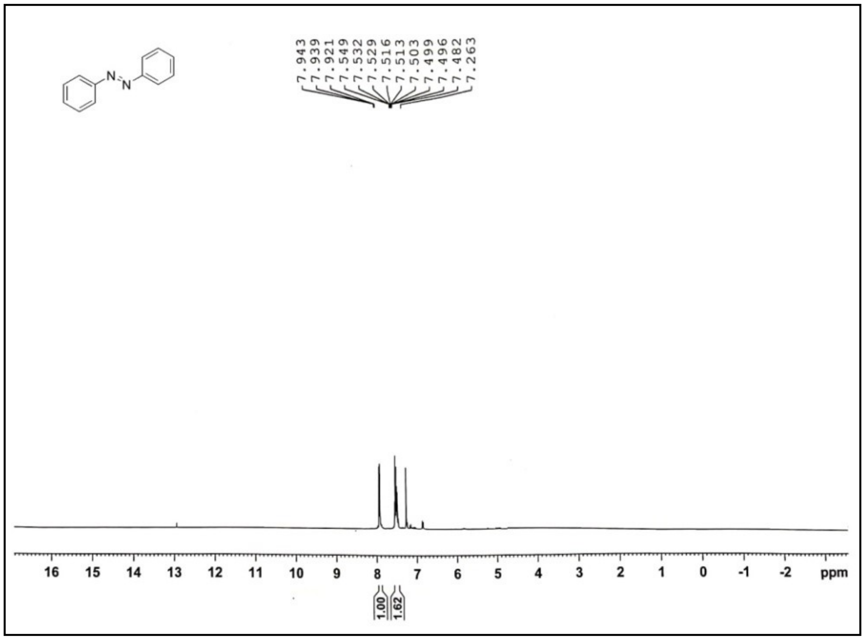
^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.92-7.90(m, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.54-7.48 (m, 3H), 7.65 (d, *J* = 8.8 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 121.84, 122.31, 123.04, 129.14, 130.09, 130.66, 131.47, 135.16, 152.42, 153.50.

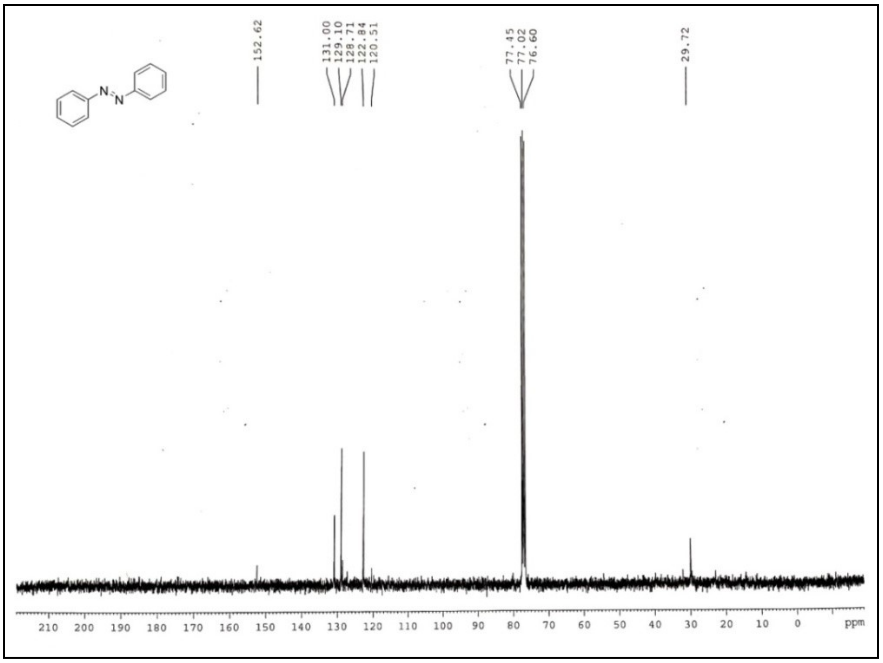


VI. Scanned copies of^{1}H and ^{13}C NMR spectra of symmetrical azobenzenes

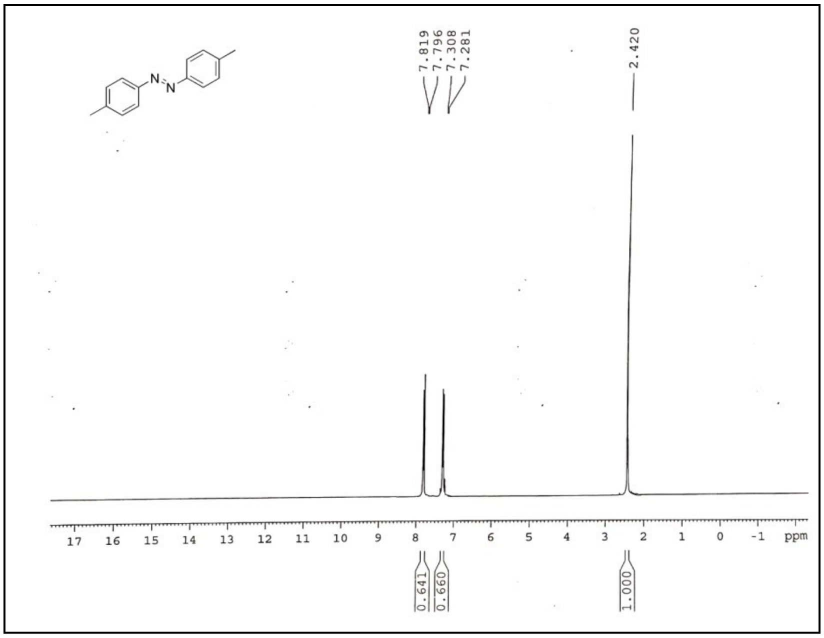
Scanned copy of ^{1}H NMR spectra of(*E*)-Azobenzene



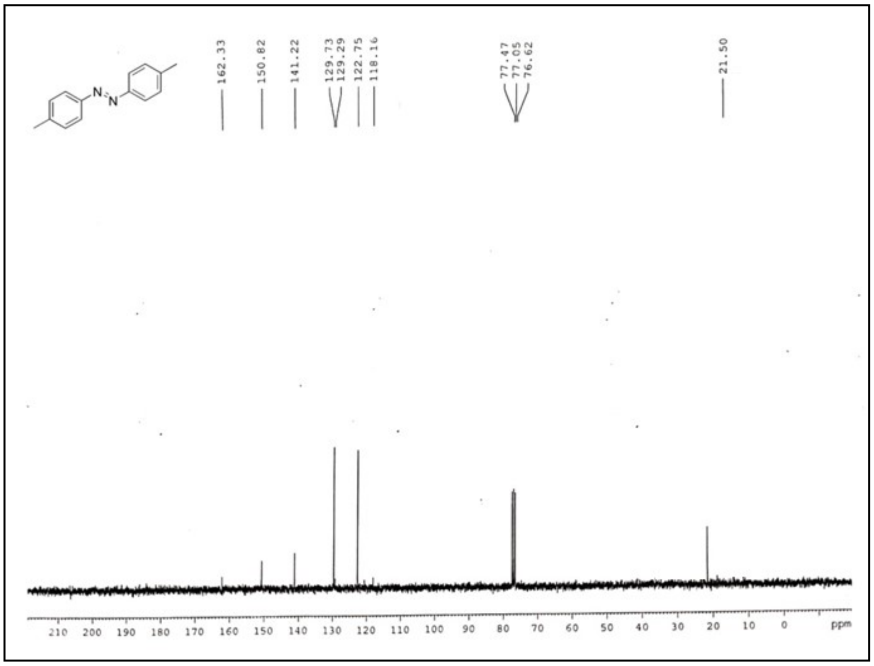
Scanned copy of ^{13}C NMR spectra of(*E*)-Azobenzene



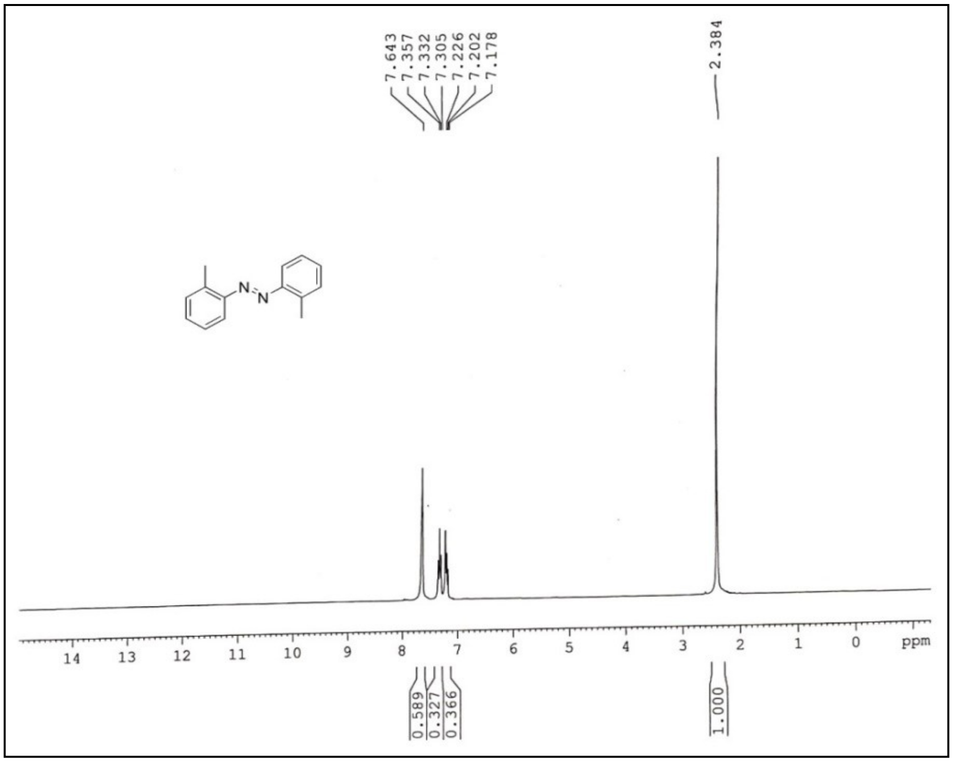
Scanned copy of ^{1}H NMR spectra of(*E*)-4,4′-Dimethylazobenzene



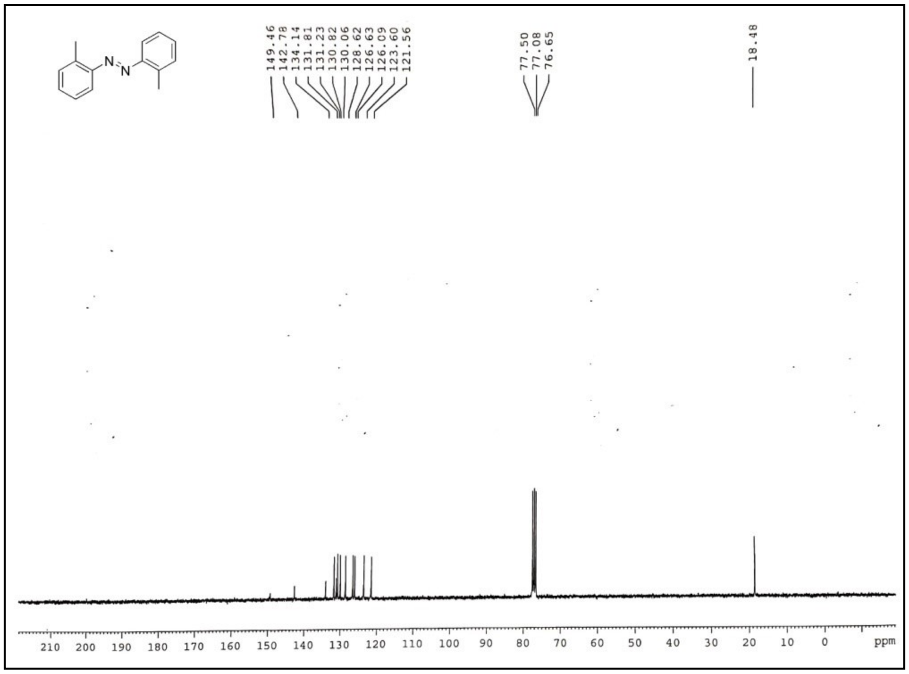
Scanned copy of ^{13}C NMR spectra of(*E*)-4,4′-Dimethylazobenzene



Scanned copy of ^{1}H NMR spectra of(*E*)-2,2′-Dimethylazobenzene

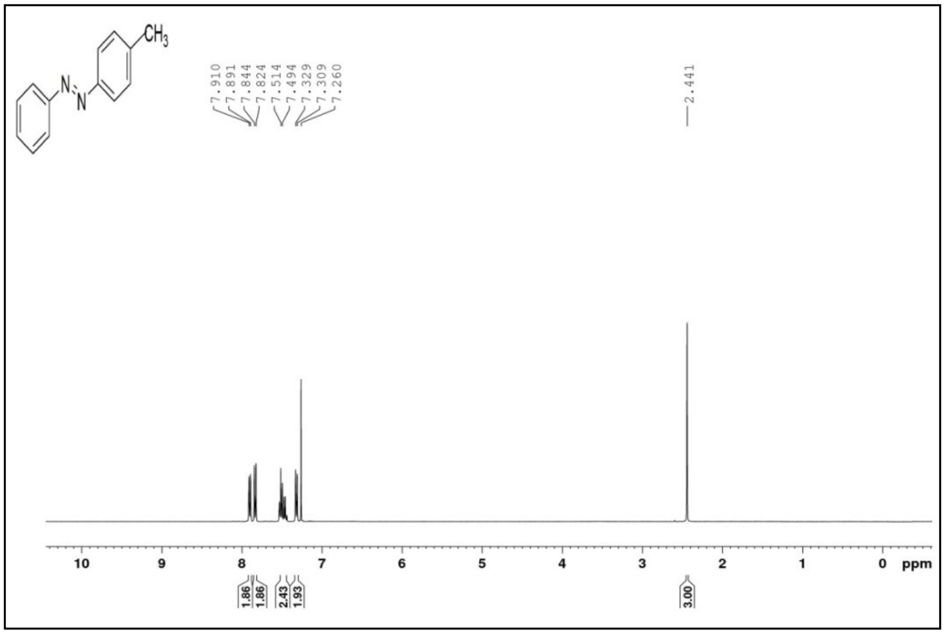


Scanned copy of ^{13}C NMR spectra of(*E*)-2,2′-Dimethylazobenzene

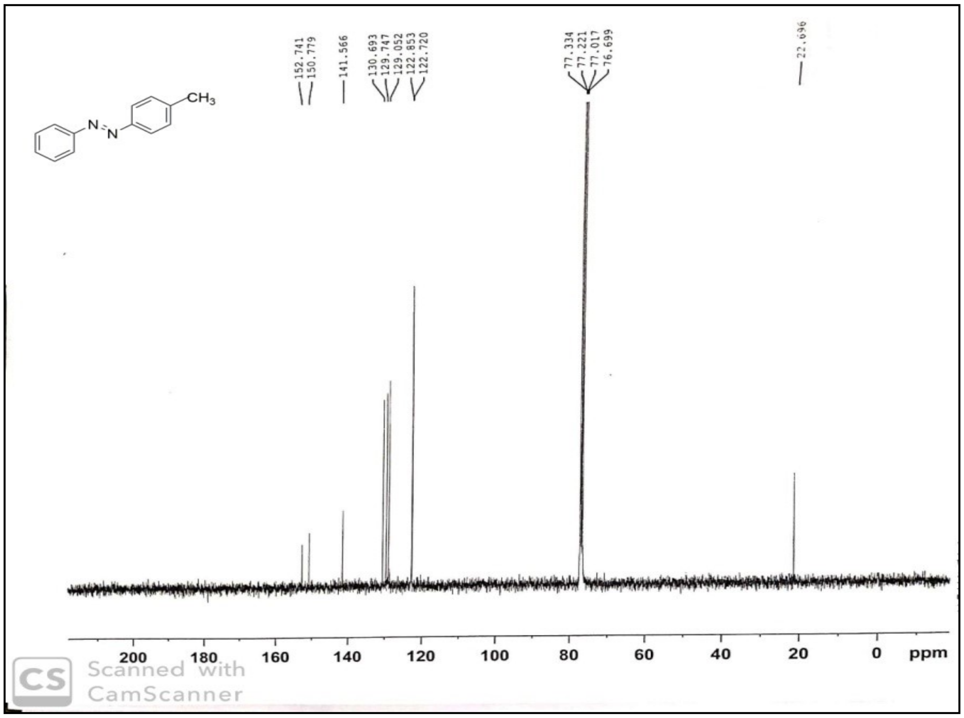


VII.Scanned copies of ^{1}H and^{13}C NMR spectra of unsymmetrical azobenzenes

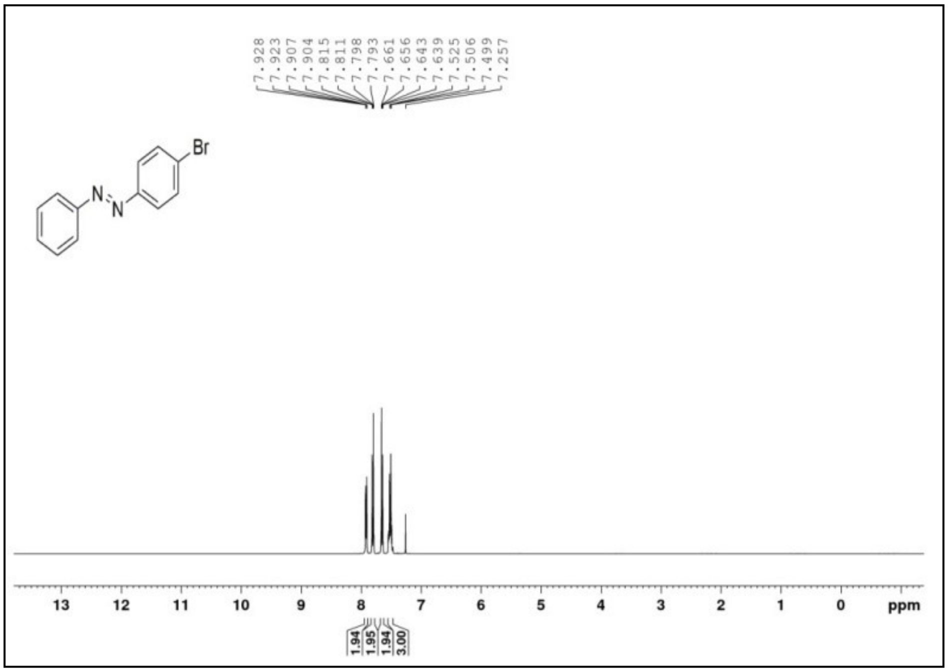
Scanned copy of ^{1}H NMR spectra of(*E*)-1-(4-Methylphenyl)-2-phenyldiazene



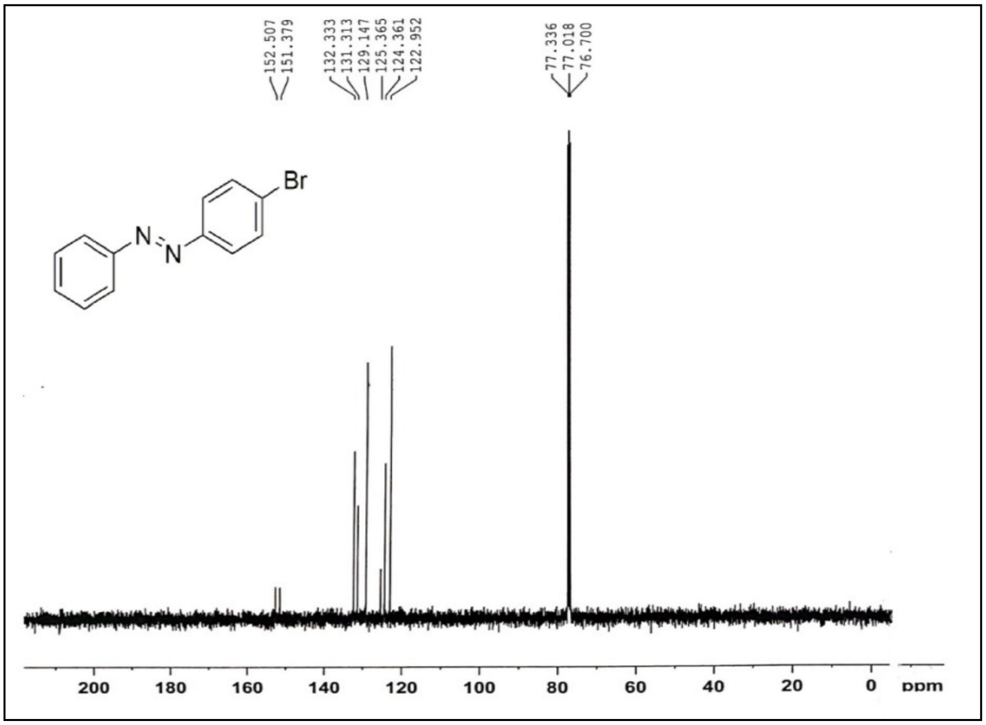
Scanned copy of ^{13}C NMR spectra of(*E*)-1-(4-Methylphenyl)-2-phenyldiazene



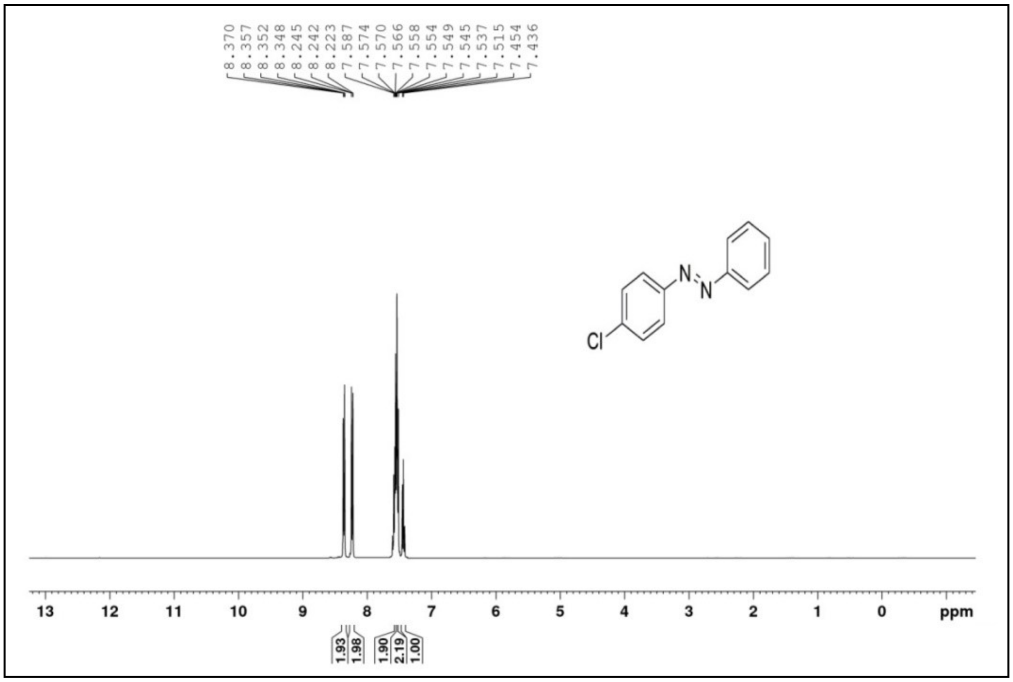
Scanned copy of ^{1}H NMR spectra of(*E*)-1-(4-bromophenyl)-2-phenyldiazene



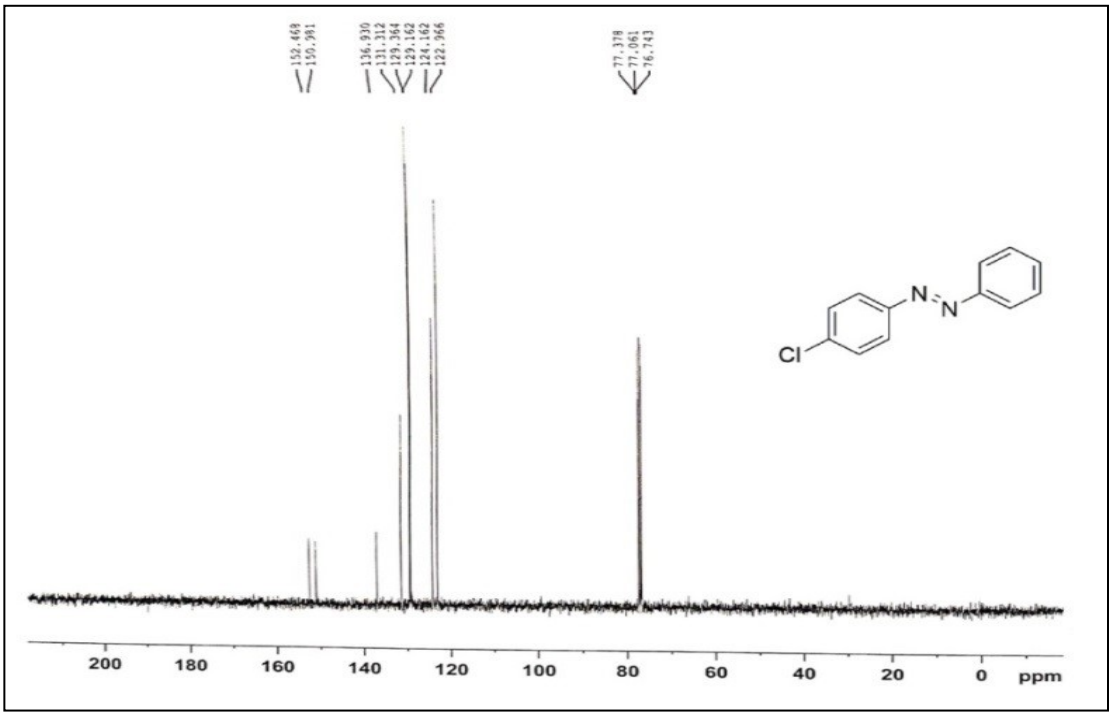
Scanned copy of ^{13}C NMR spectra of(*E*)-1-(4-bromophenyl)-2-phenyldiazene



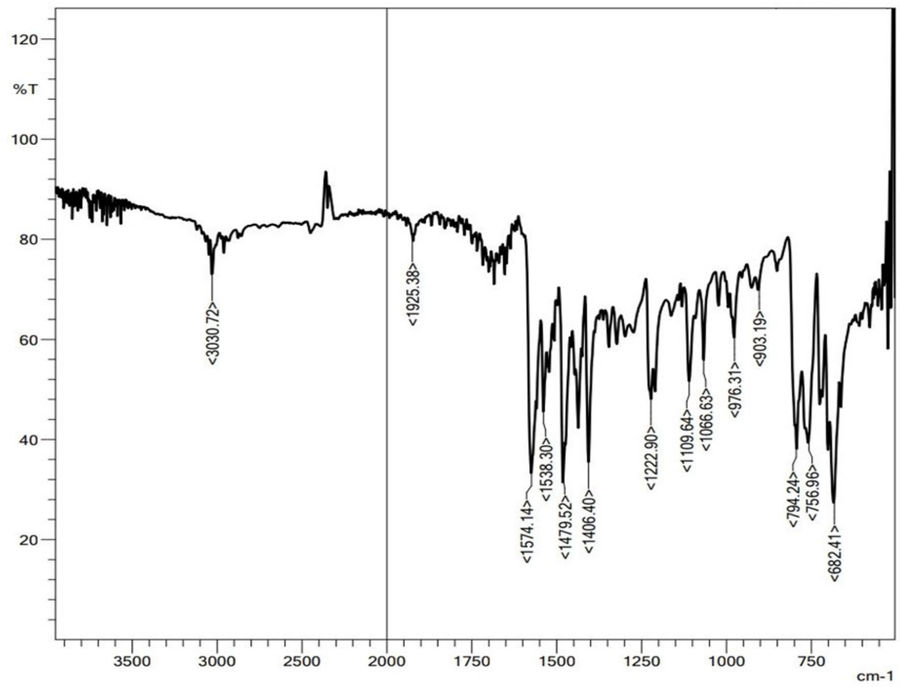
Scanned copy of ^{1}H NMR spectra of(*E*)-1-(3-Chlorophenyl)-2-phenyldiazene



Scanned copy of ^{13}C NMR spectra of(*E*)-1-(3-Chlorophenyl)-2-phenyldiazene



VIII. FT-IR spectra of Nitrosobenzene intermediate:



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[3] Á. Georgiádes, S. B. Ötvös and F. Fülöp, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 3388.

[4] M. Wang, J. Ma, M. Yu, Z. Zhang and F. Wang, *Catalysis Science & Technology*, 2016, **6**, 1940.