Supplementary Information for

An efficient catalyst-free and chemoselective synthesis of azobenzenes from nitrobenzenes.

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Experimental section

Materials

All reagents were of analytical grade, purchased from M/S S. D. Fine Chemicals Pvt. Ltd., Sigma Aldrich and Alfa Aesar (NaOH, 99.99%). In addition, the purity of reagents was checked by GC and GC-MS analysis. The solvents were HPLC and AR grade. Especially ethanol was used after double distillation. All products were characterized by MS analysis (GC-MS Shimadzu QP 2010), LCMS, ^{13}C-NMR and ^{1}H-NMR analysis.

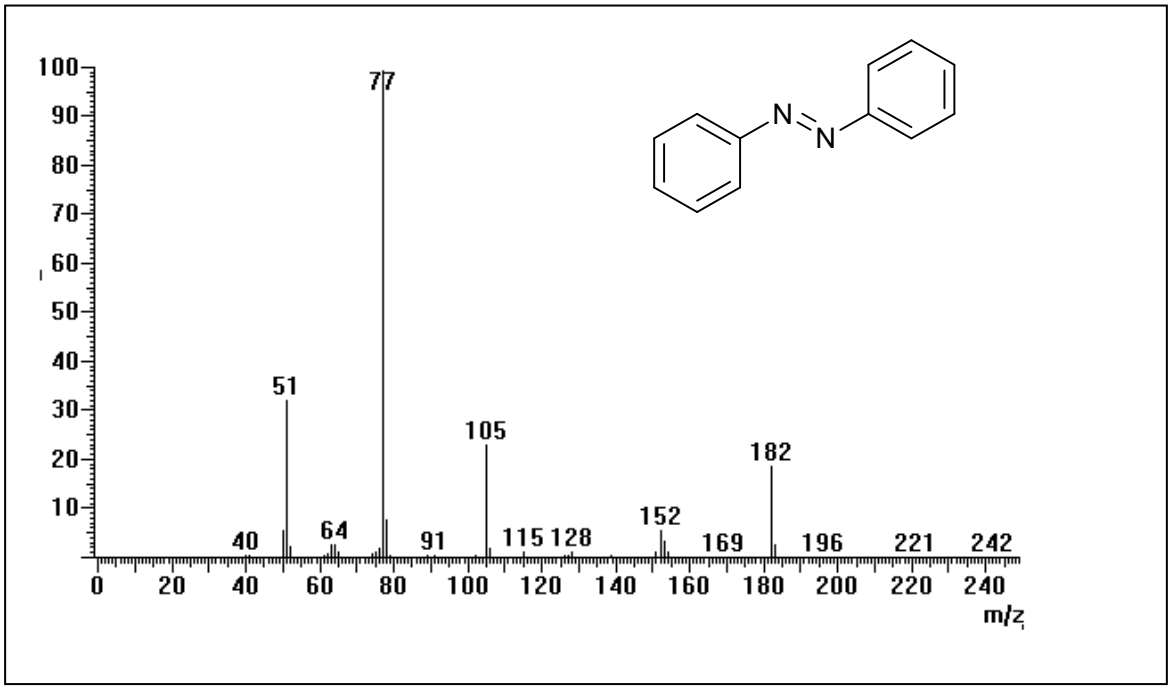
General procedure for the synthesis of azo compounds from substituted nitro compounds.

A mixture of substituted nitroarenes (1 mmol) and sodium hydroxide (3 mmol) in ethanol (1mL) was stirred at 80 °C temperature for 24 h, the progress of reaction which was monitored by TLC. After completion the reaction mixtures were concentrated under vacuum. The residue was taken in water. Further the reaction mixture was extracted with ethyl acetate (10 x 3mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to obtain crude product. The crude product was purified on silica gel column by using pet ether and ethyl acetate as solvent to get the pure product. The products were characterized by GC-MS and ^{1}H NMR.

The time course study was carried on GC with the specific time interval. The reaction mixture was subjected to work up after every 4h, and monitored on GC.

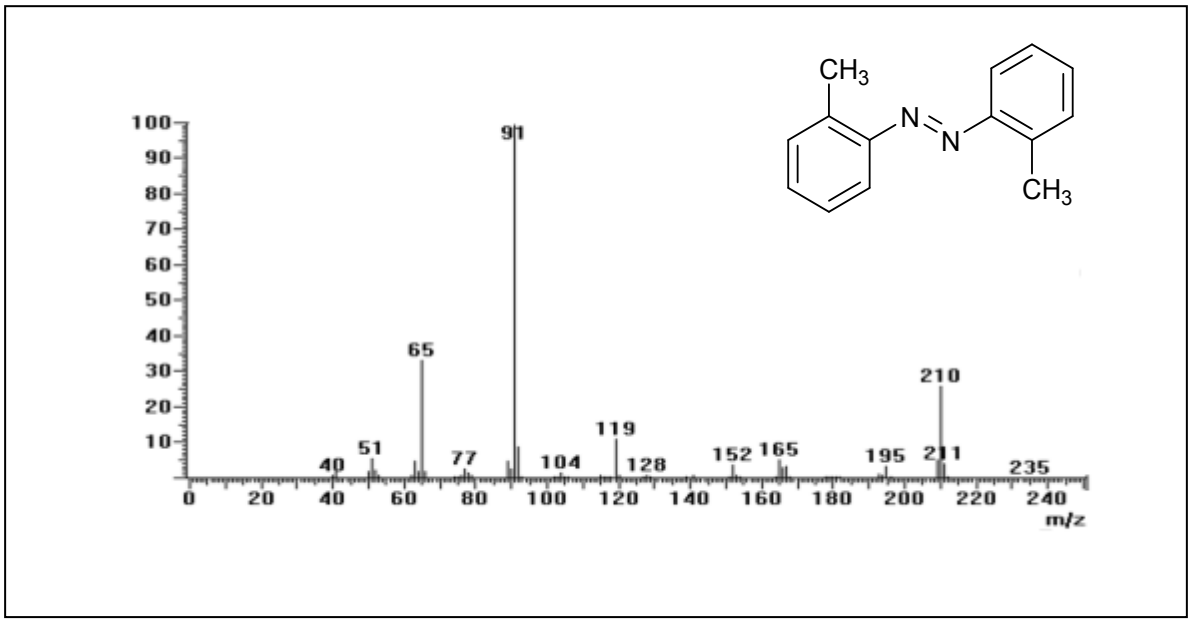
Characterization of products by mass spectra (EI, 70 eV):

1. **Azobenzene (Entry 1).**



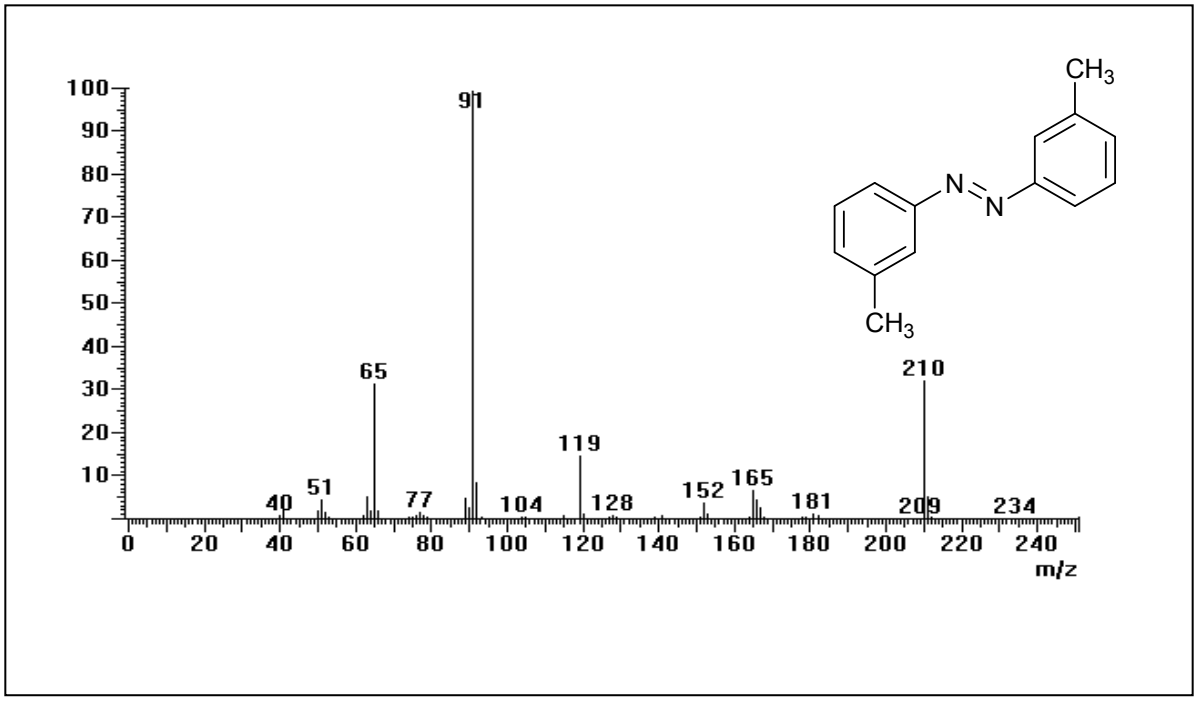
MS (m/z/rel.int.): 182(M^+): 51(31.7), 77(100), 105(22.9), 152(5.6), 182(17.6).

2. **1, 2-di-o-tolyldiazene (Entry 2).**



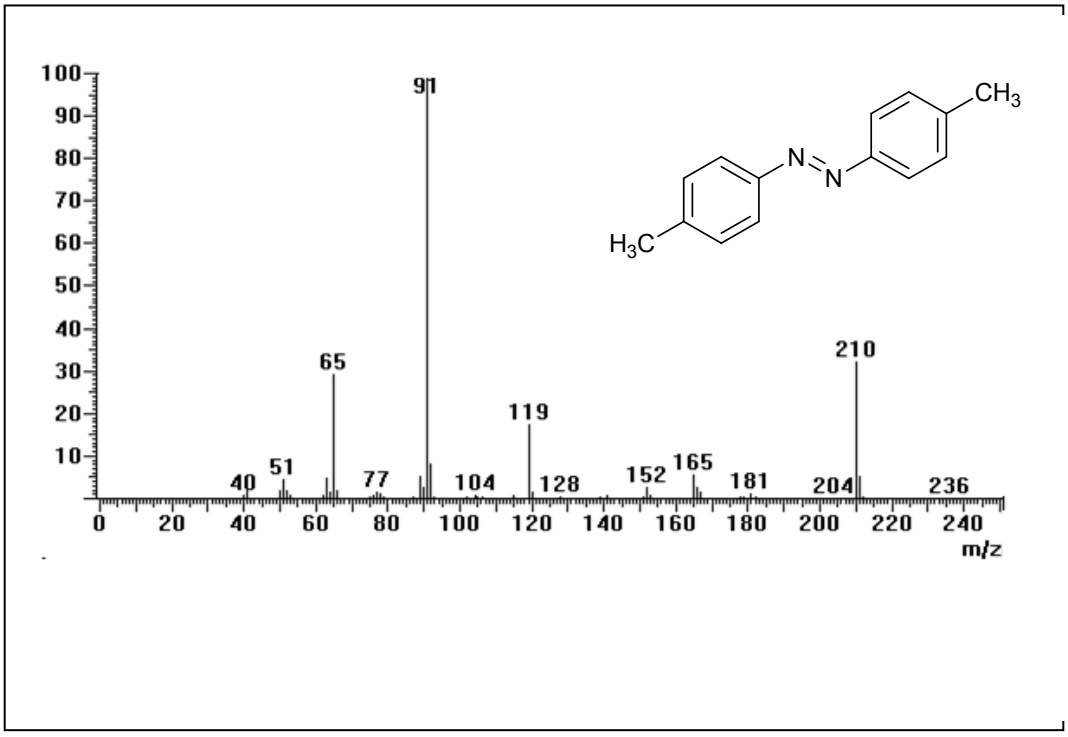
MS (m/z/rel.int.): 210(M^+): 51(5.4), 65(32.8), 91(100), 119(10.5), 165(4.9), 210(24.4).

3. 1, 2-di-m-tolyldiazene (Entry 3).



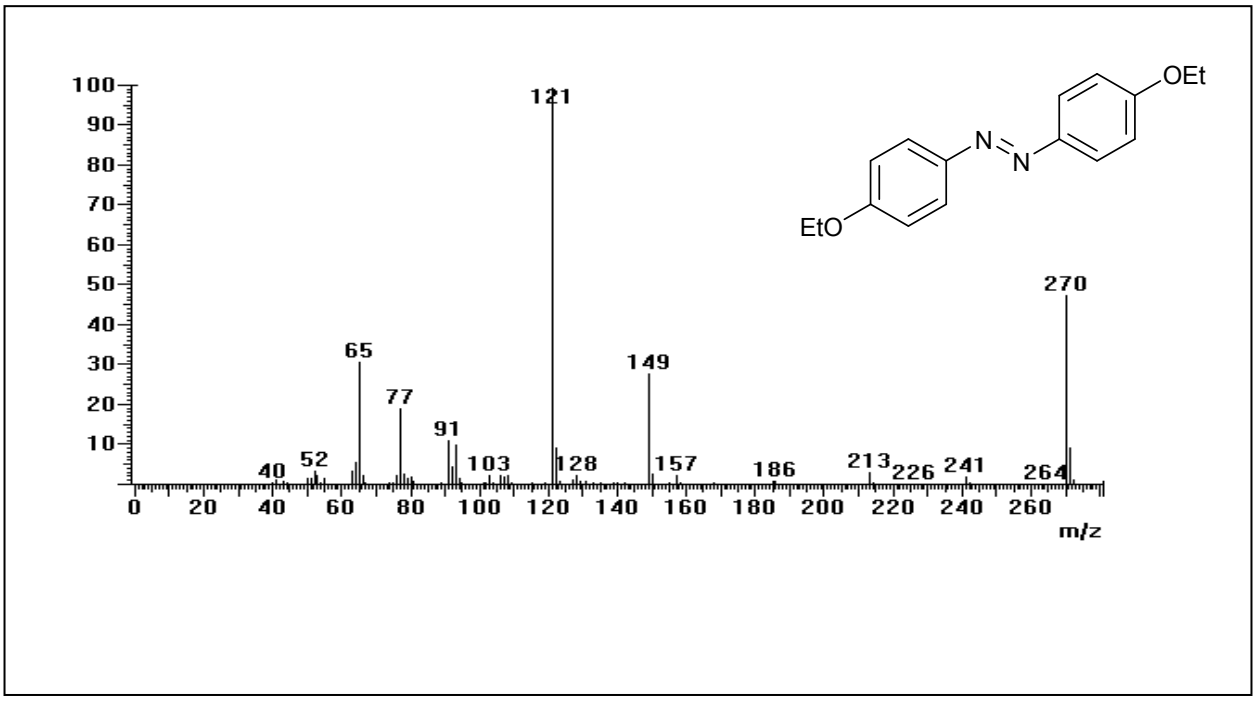
MS (m/z/rel.int.): 210(M^+): 51(4.2), 65(31.0), 91(100), 119(15.7), 165(7.0), 210(33.5).

4. 1, 2-di-p-tolyldiazene (Entry 4).



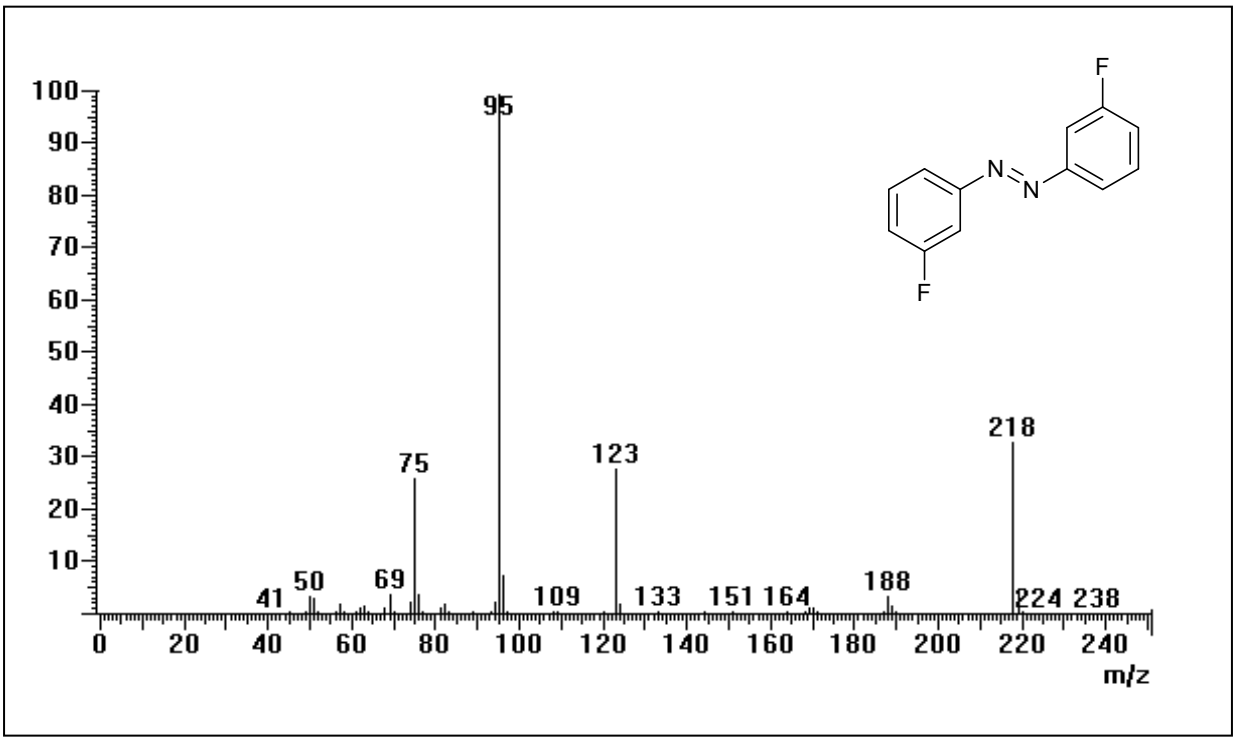
MS (m/z/rel.int.): 210(M^+): 51(4.8), 65(30.1), 91(100), 119(17.4), 165(5.3), 210(30.7).

5. 1, 2-Bis (4-ethoxyphenyl) diazene (Entry 5).



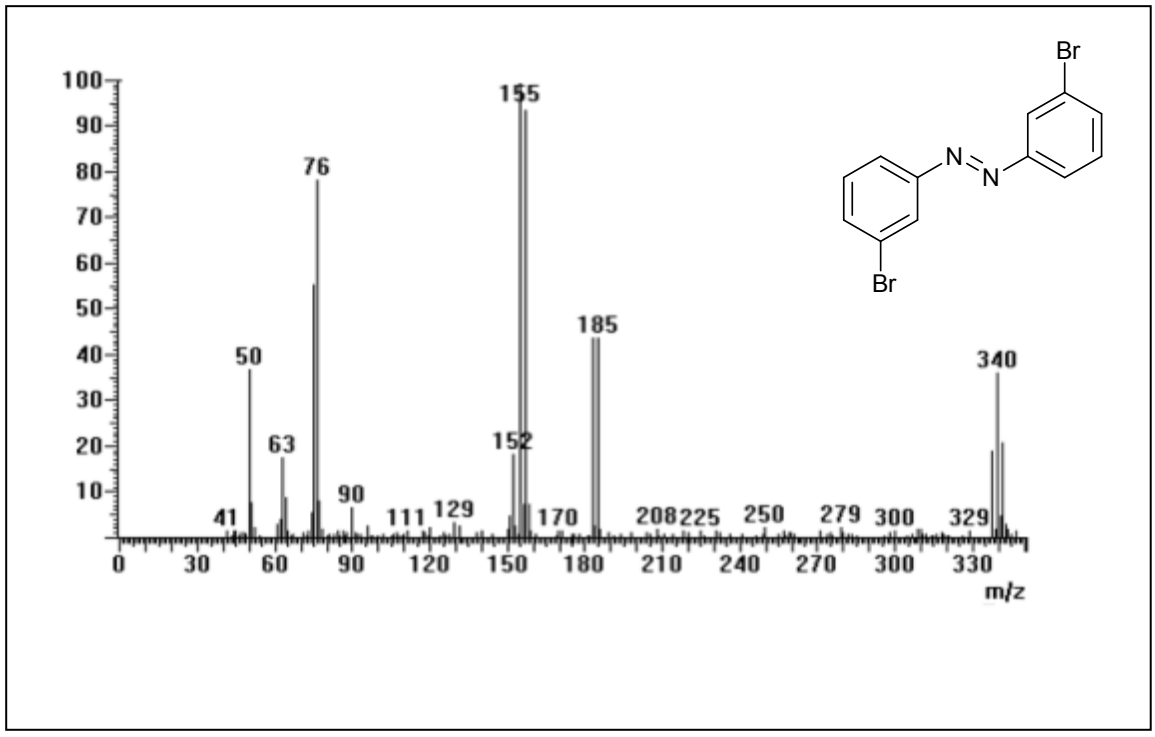
MS (m/z/rel.int.): 270(M^+): 65(31.4), 77(20.0), 91(11.0), 121(100), 149(27.8), 270(48.7).

6. 1, 2-Bis (3-fluorophenyl) diazene (Entry 6).



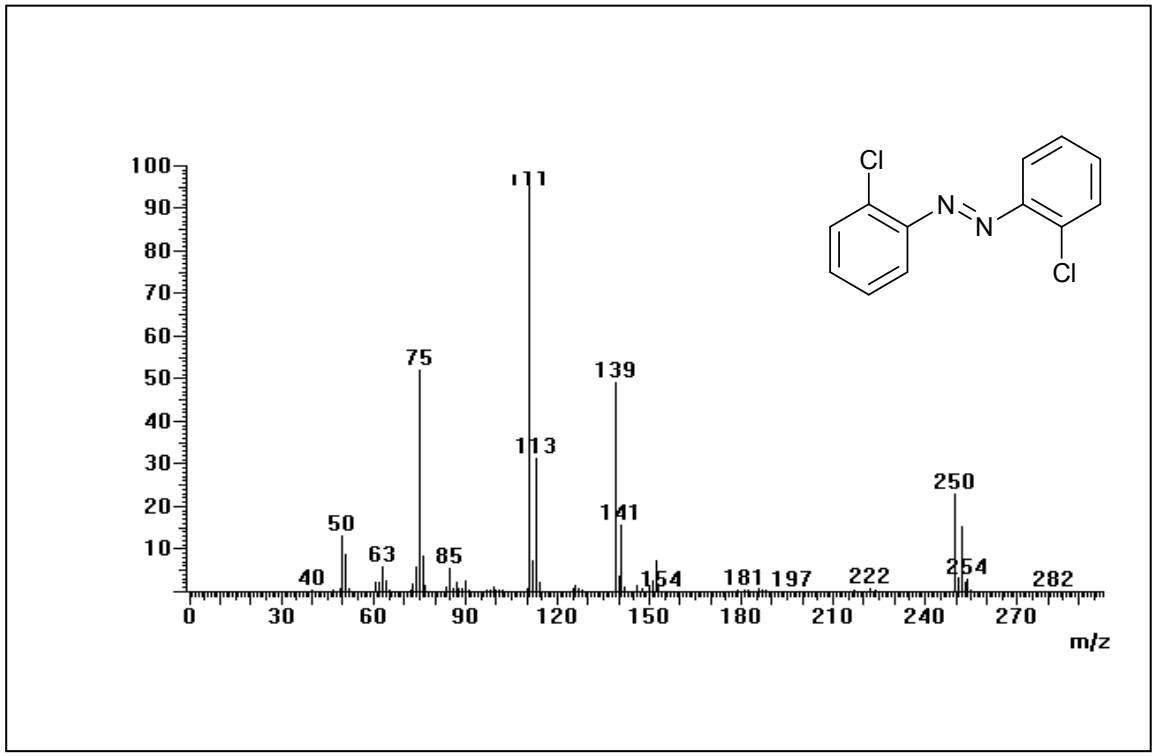
MS (m/z/rel.int.): 218(M^+): 50(2.9), 69(3.7), 75(25.1), 95(100), 123(27.2), 218(33.8)

7. 1, 2-Bis (3-bromophenyl) diazene (Entry 7).



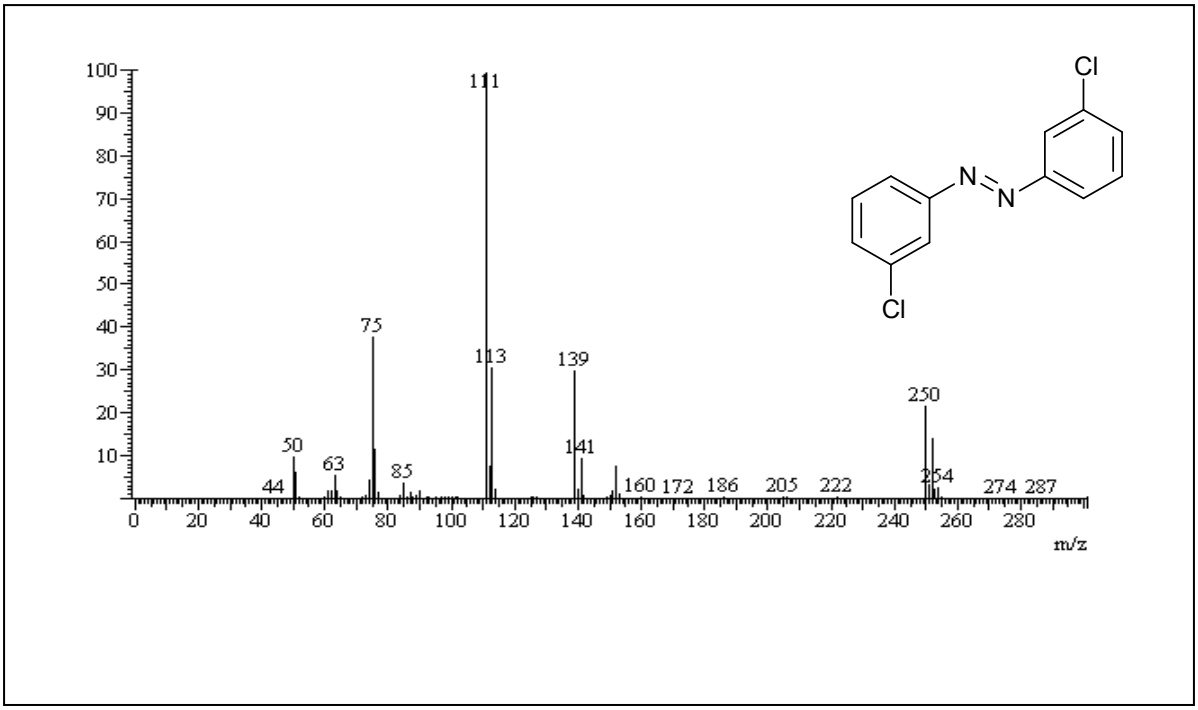
MS (m/z/rel.int.): 340(M^+): 50(40.1), 63(20.0), 76(77.9), 152(20.8), 155(100), 185(47.6), 338(17.6), 340(34.6).

8. 1, 2-Bis (2-chlorophenyl) diazene (Entry 8).



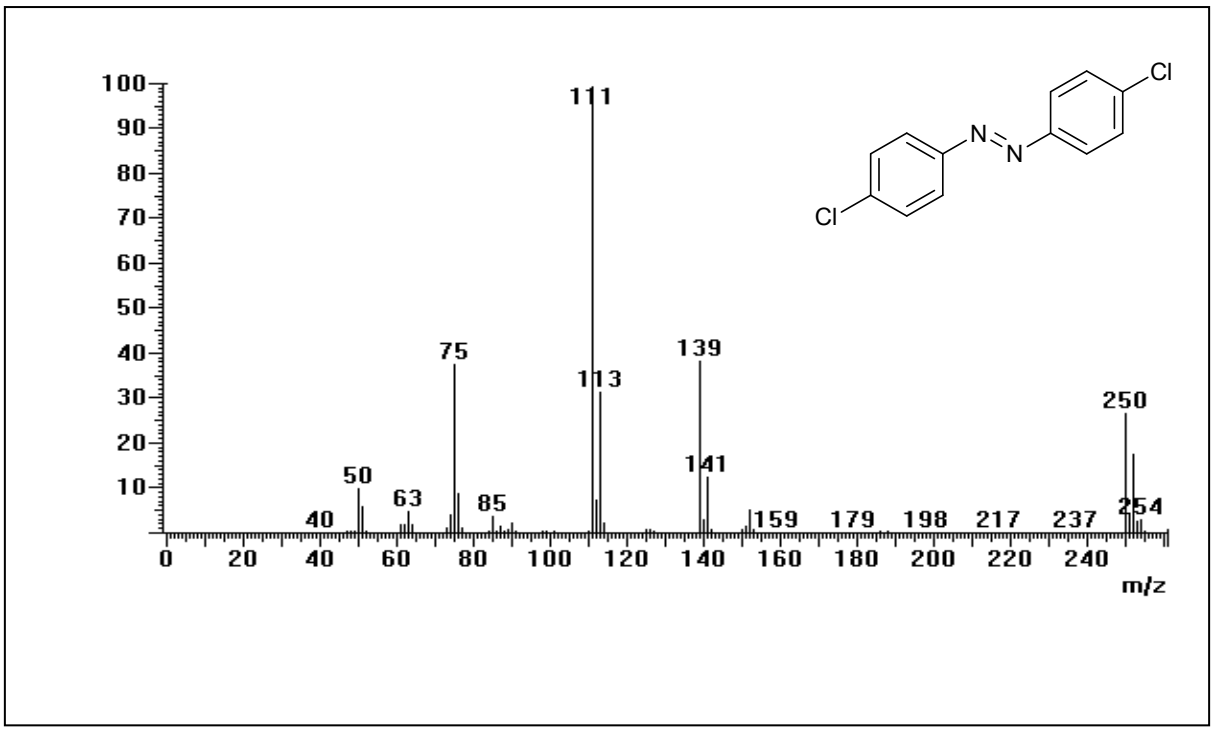
MS (m/z/rel.int.): 250(M^+): 50(13.0), 75(51.8), 111(100), 113(31.5), 139(49.0), 141(15.9), 250(23.0).

9. 1, 2-Bis (3-chlorophenyl) diazene (Entry 9).



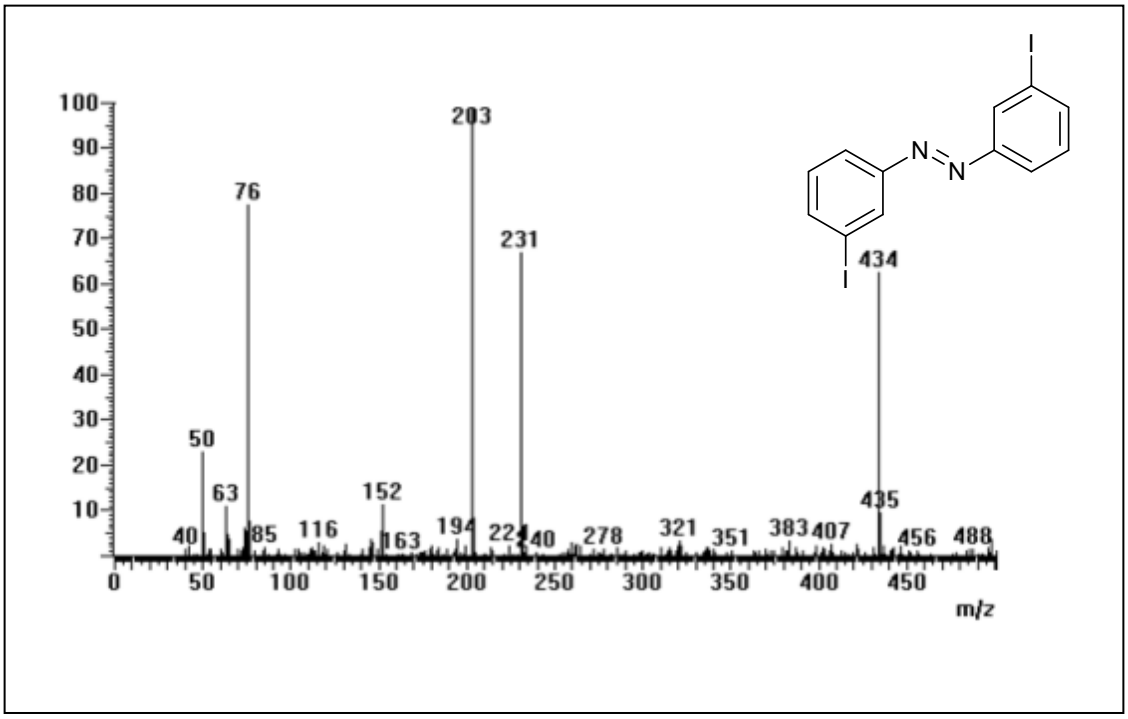
MS (m/z/rel.int.): 250(M^+): 50(10.7), 75(39.6), 111(100), 113(31.1), 139(29.6), 141(9.6), 250(20.1).

10. 1, 2-Bis (4-chlorophenyl) diazene (Entry 10).



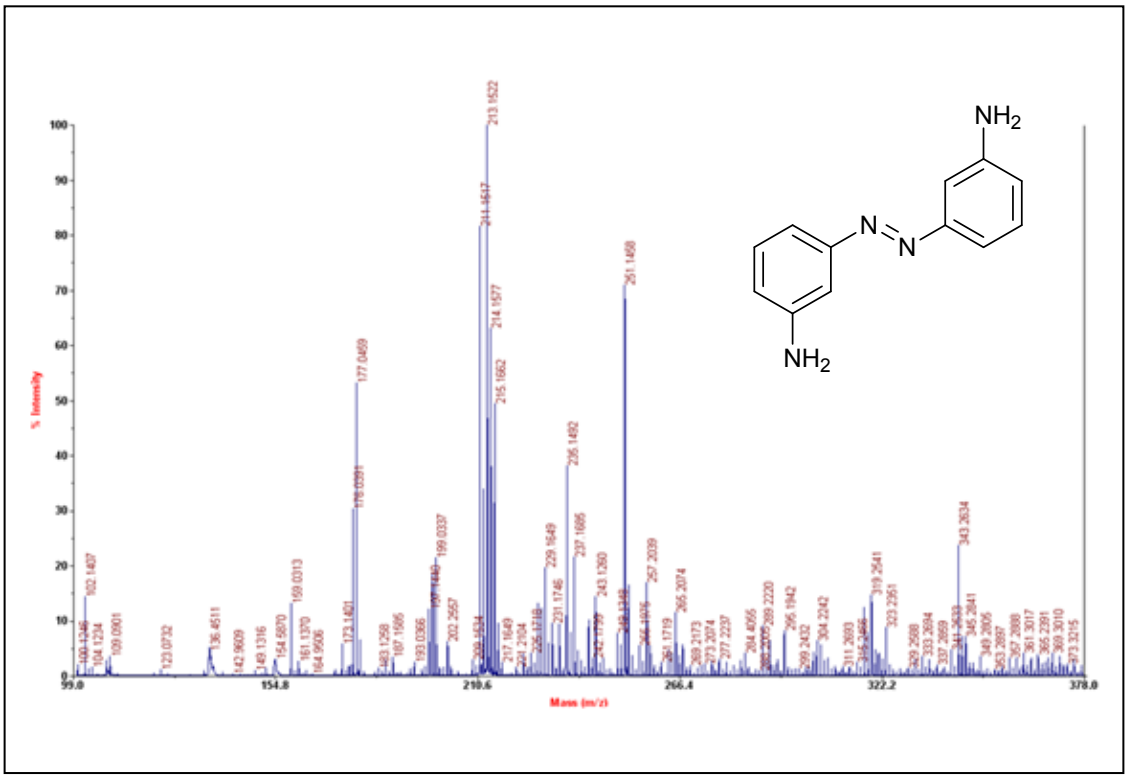
MS (m/z/rel.int.): 250(M^+): 50(11.0), 75(39.7), 111(100), 113(31.8), 139(37.4), 141(12.1), 250(23.3).

11. 1, 2-Bis (3-iodophenyl) diazene (Entry 11).

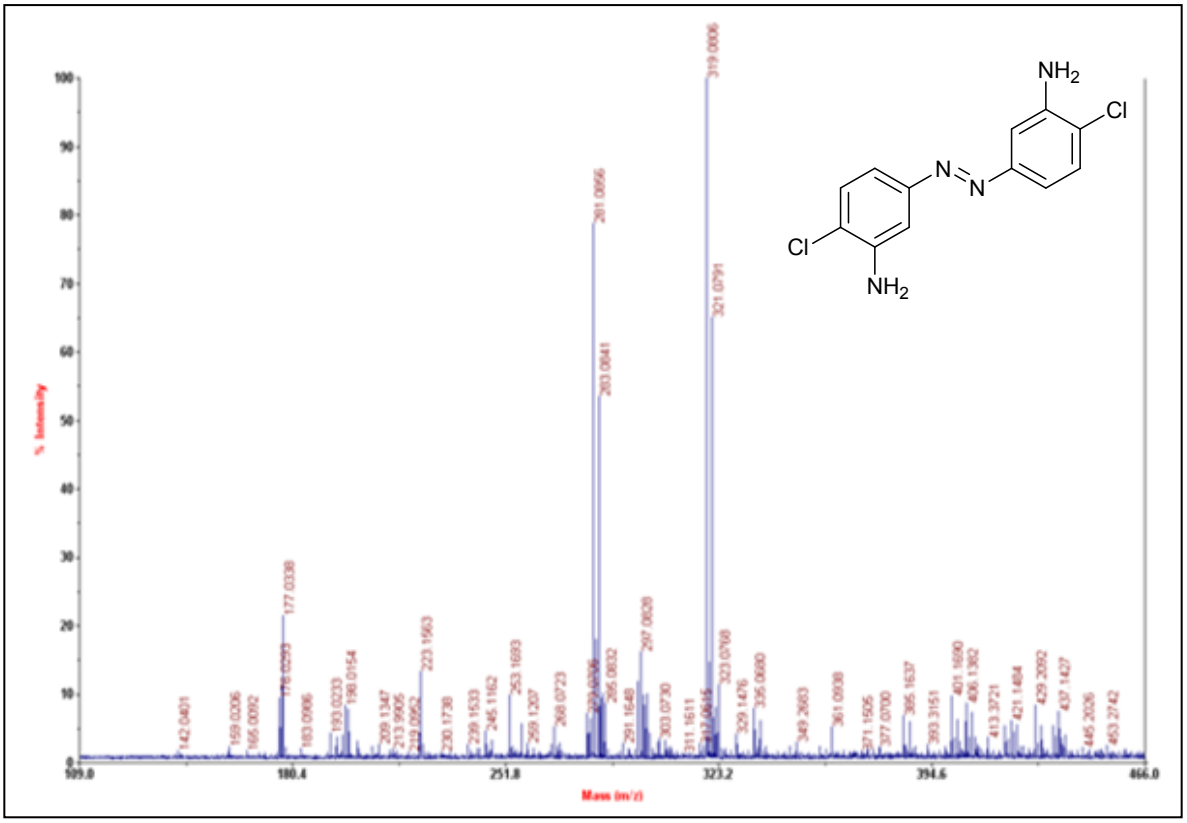


MS (m/z/rel.int.): 434(M^+): 50(32.7), 63(12.2), 76(100), 152(13.1), 203(88.6), 231(63.8), 434(49.3).

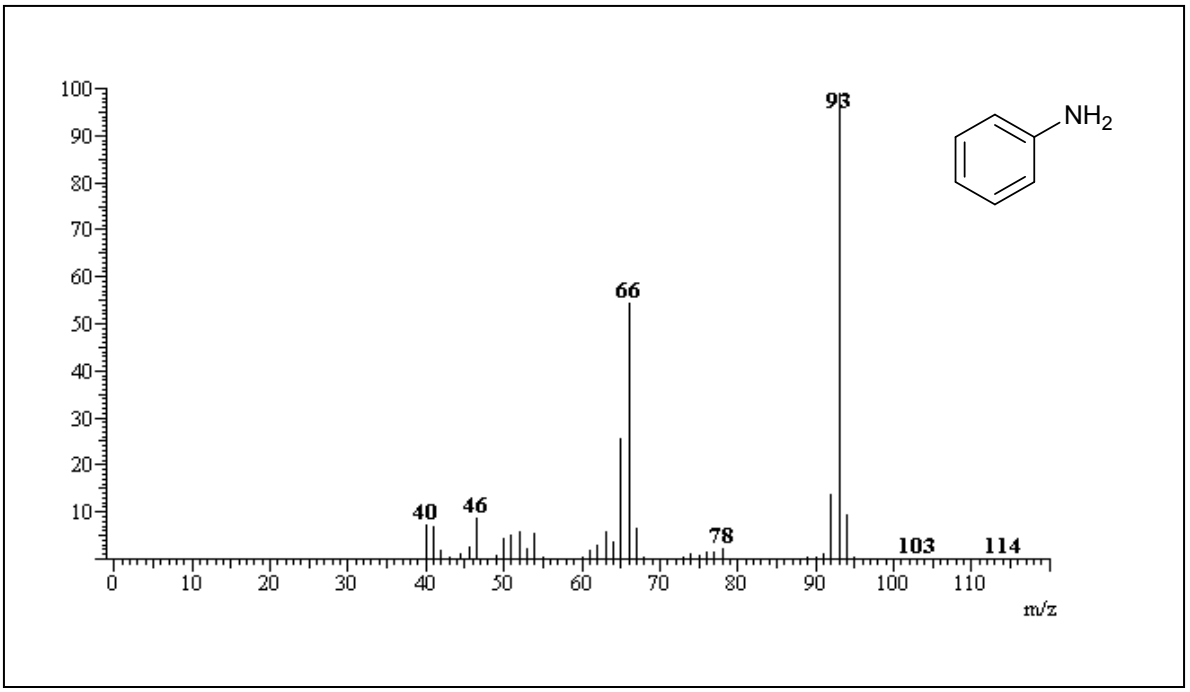
12. (E)-3,3'-(diazene-1,2-diyl)dianiline: M.W:212



13. (E)-5,5'-(diazene-1,2-diyl)bis(2-chloroaniline): M.W:281

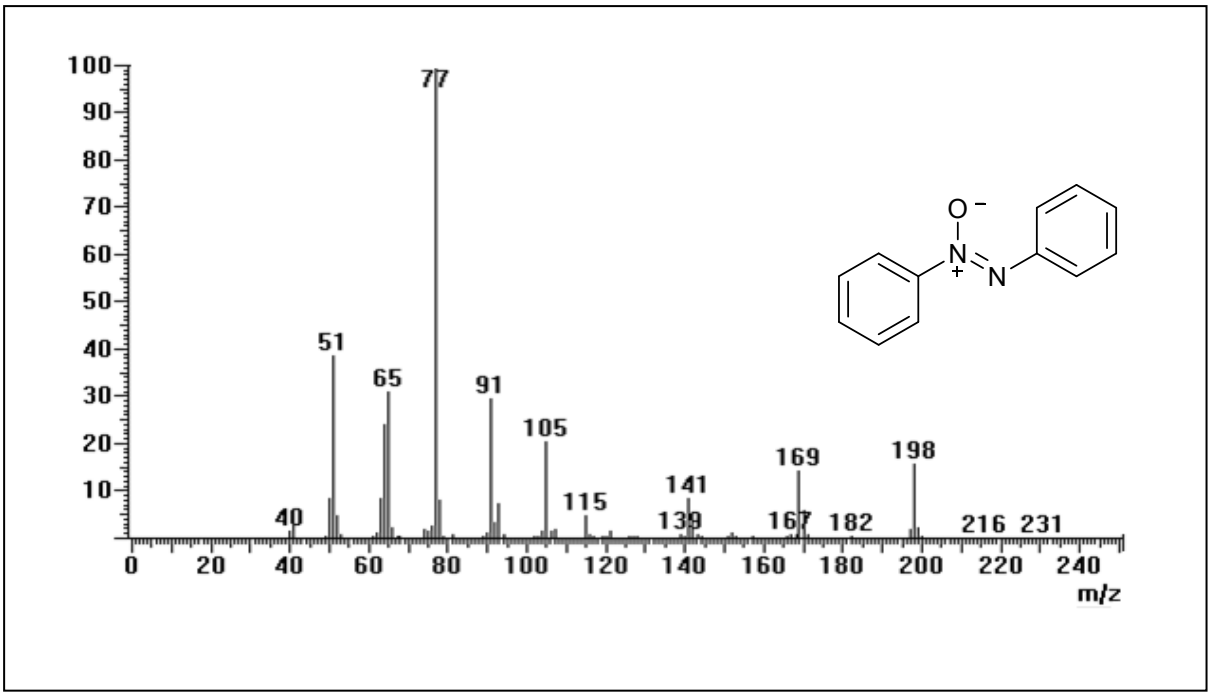


14. Aniline



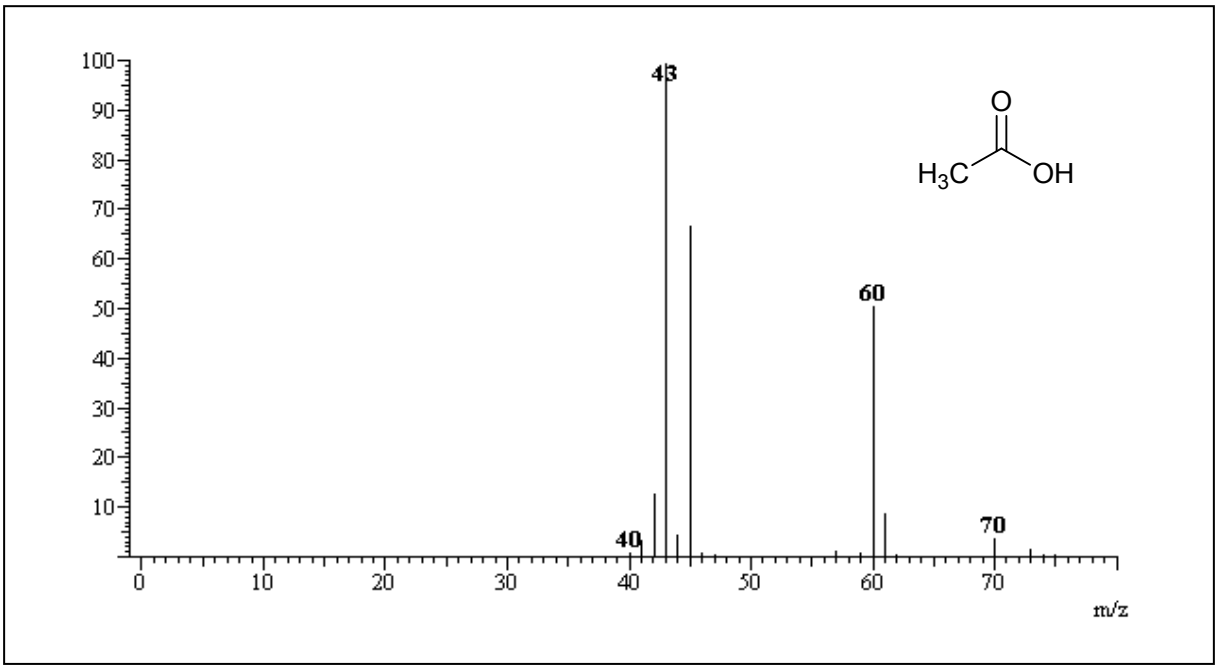
MS (m/z/rel.int.): 93(M^+): 46(7.1), 65(20.8), 66(47.0), 92(11.6), 93(100), 94(7.6).

15. Azoxybenzene



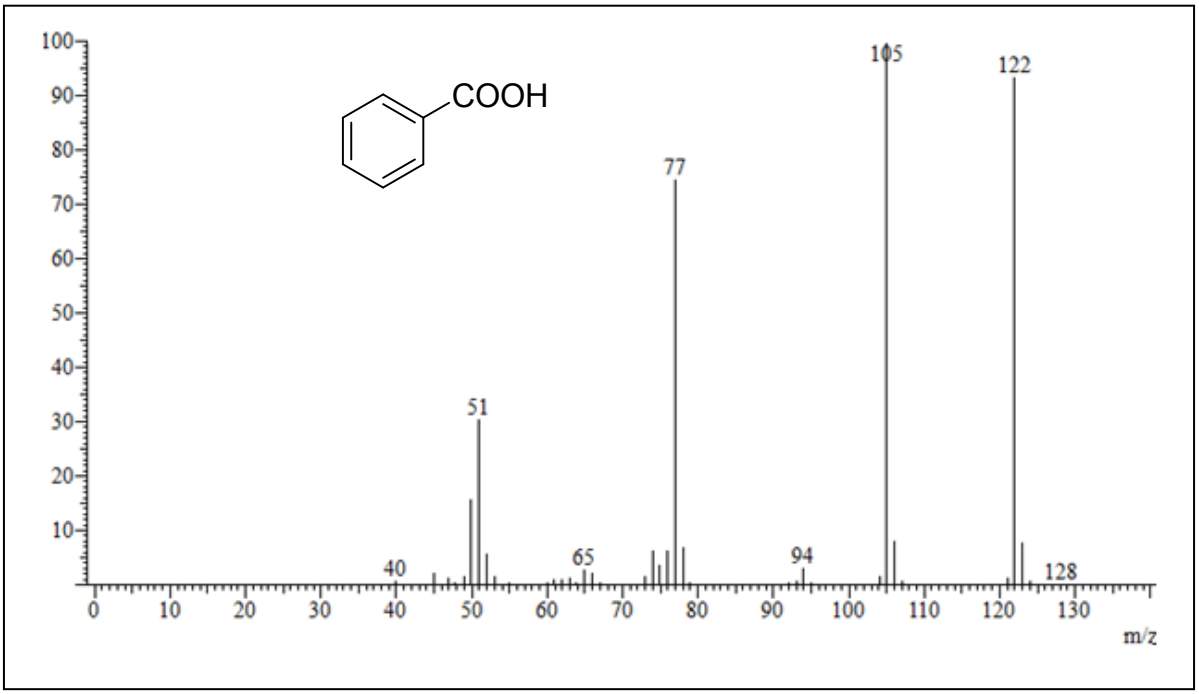
MS (m/z/rel.int.): 198(M^+): 51(37.0), 65(29.7), 77(100), 91(28.9), 105(20.1), 115(4.9), 141 (8.1), 169(14.2), 198(15.6).

16. Acetic acid



MS (m/z/rel.int.): 60(M^+): 42(13.4), 43(100), 45(66.8), 60(46.5), 61(8.7).

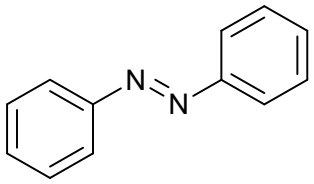
17. Benzoic acid



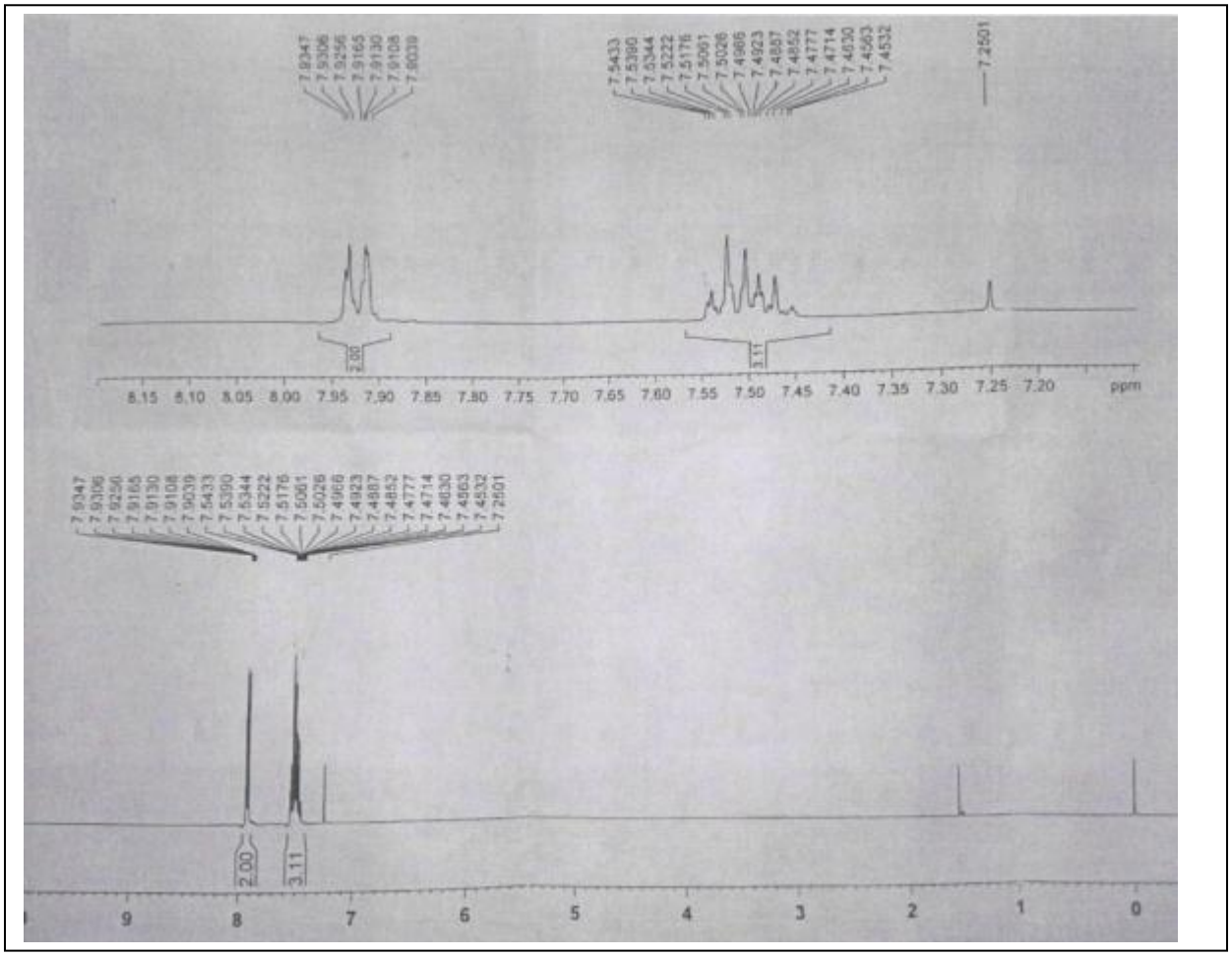
MS (m/z/rel.int.): 122(M^+): 50(15.8), 51(31.2), 77(71.7), 105(100), 122(90.9).

Characterization of products by ^{1}H NMR spectra:

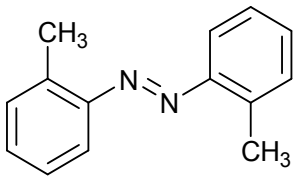
1. **Azobenzene (Entry 1).**



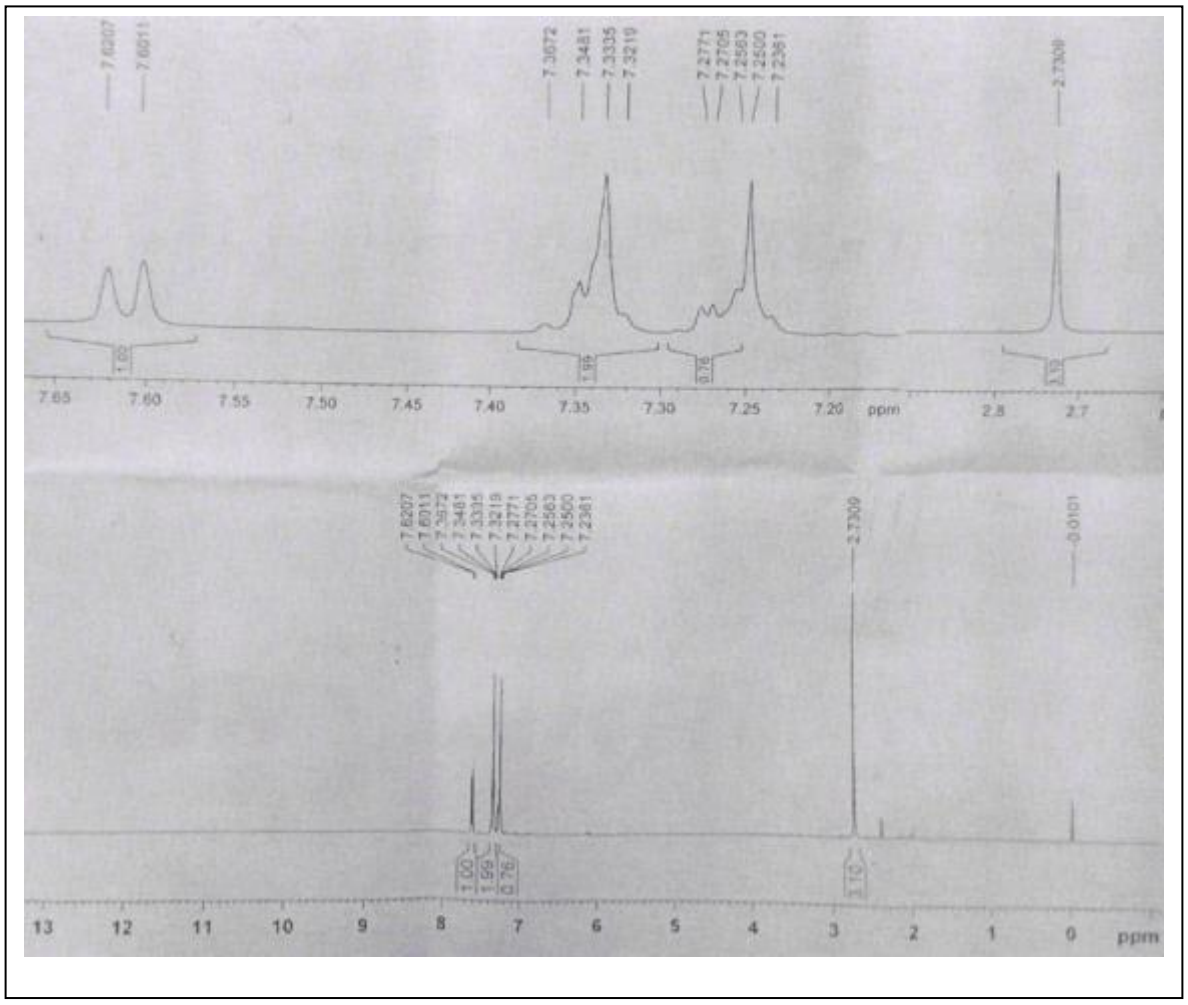
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.54 (m, 6H), 7.90-7.93 (m, 4H).



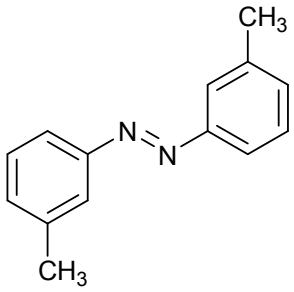
2. 1, 2-di-o-tolyldiazene (Entry 2).



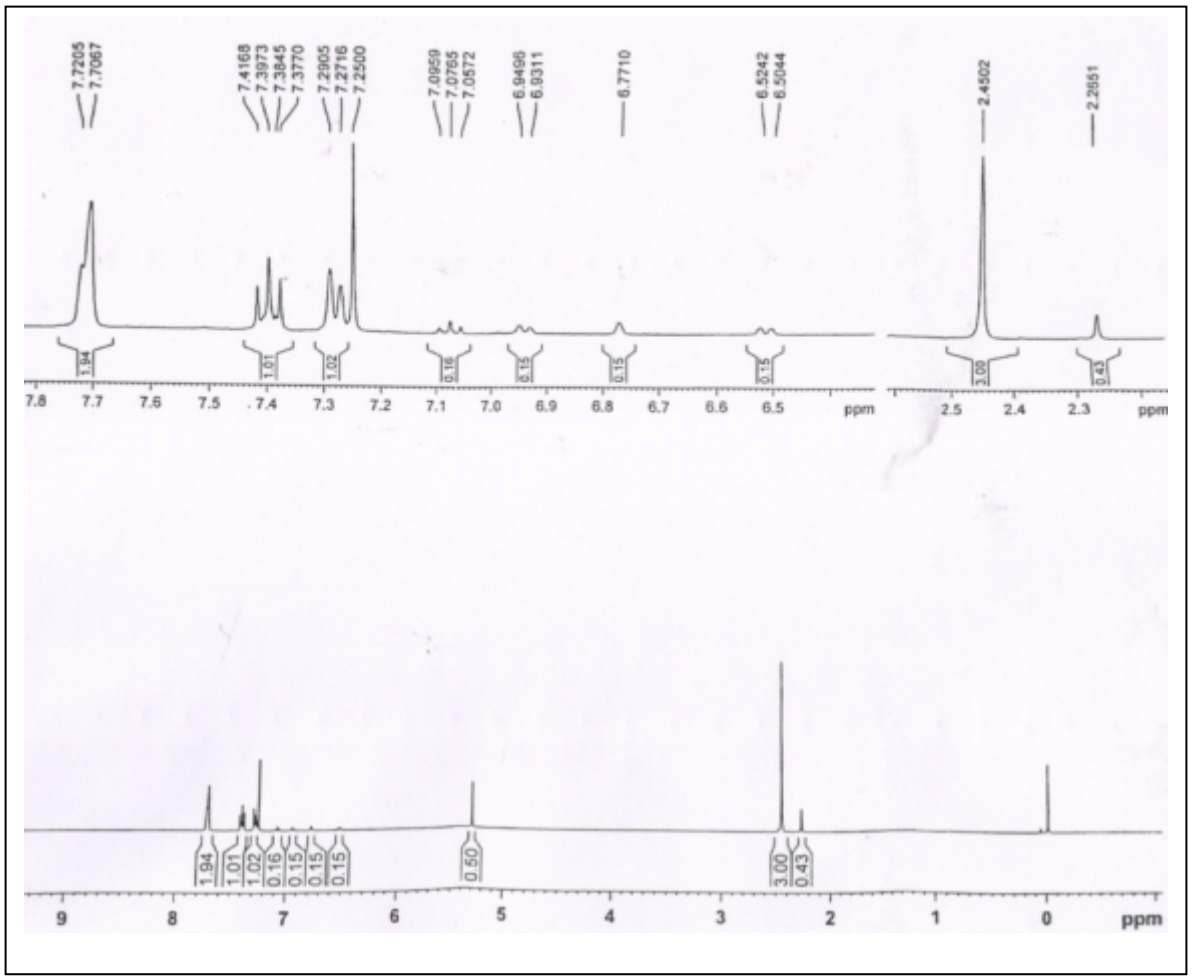
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (2H, d, J = 7.7 Hz), 7.23-7.36 (6H, m), 2.73ppm (6H, s).



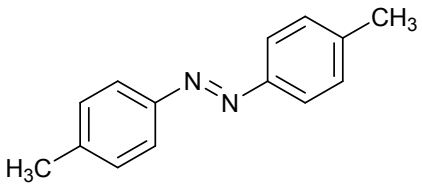
3. 1, 2-di-m-tolyldiazene (Entry 3).



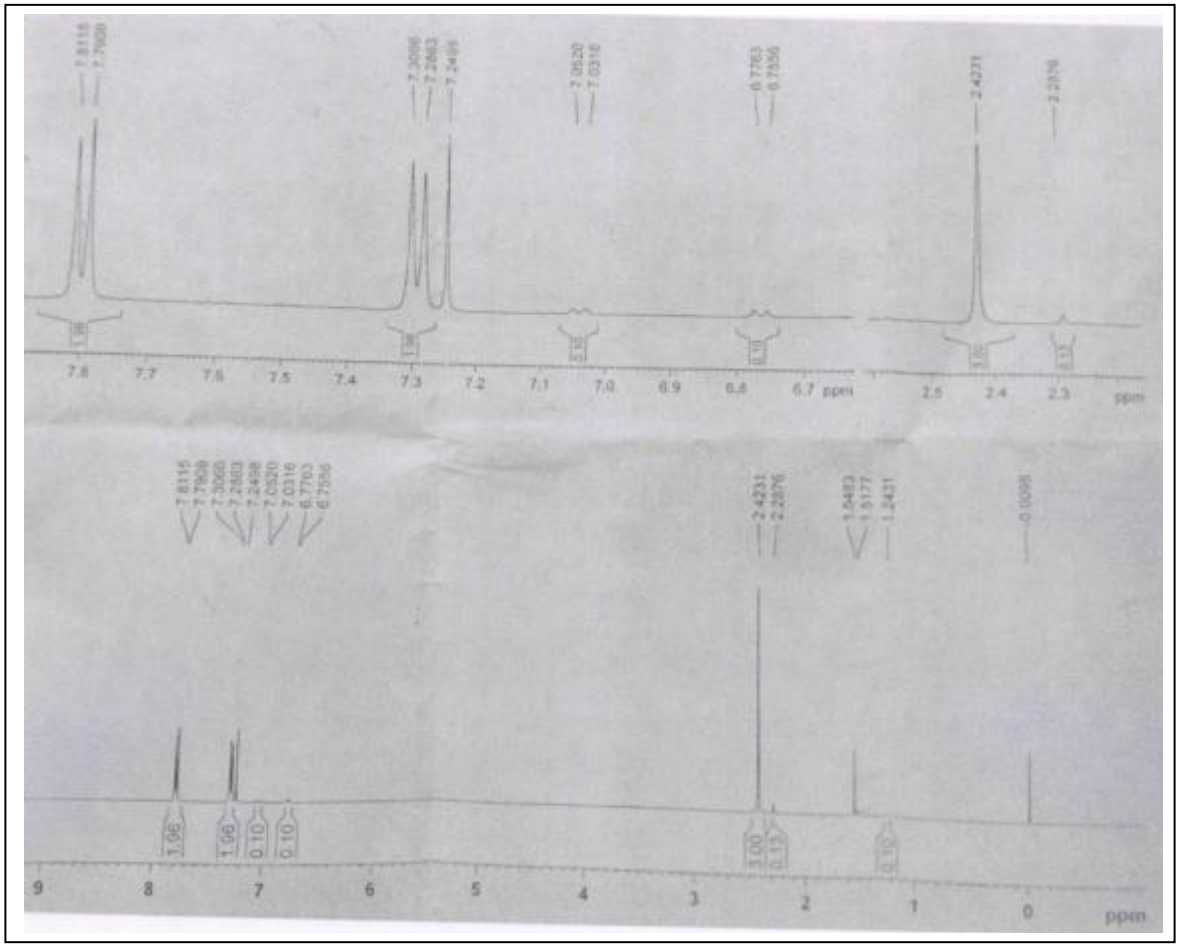
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.72 (4H, m), 7.37-7.39 (2H, t, J=7.9Hz), 7.28(2H, d, J=8.3Hz), 2.45ppm (6H, s).



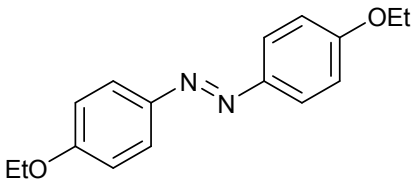
4. 1, 2-di-p-tolyldiazene (Entry 4).



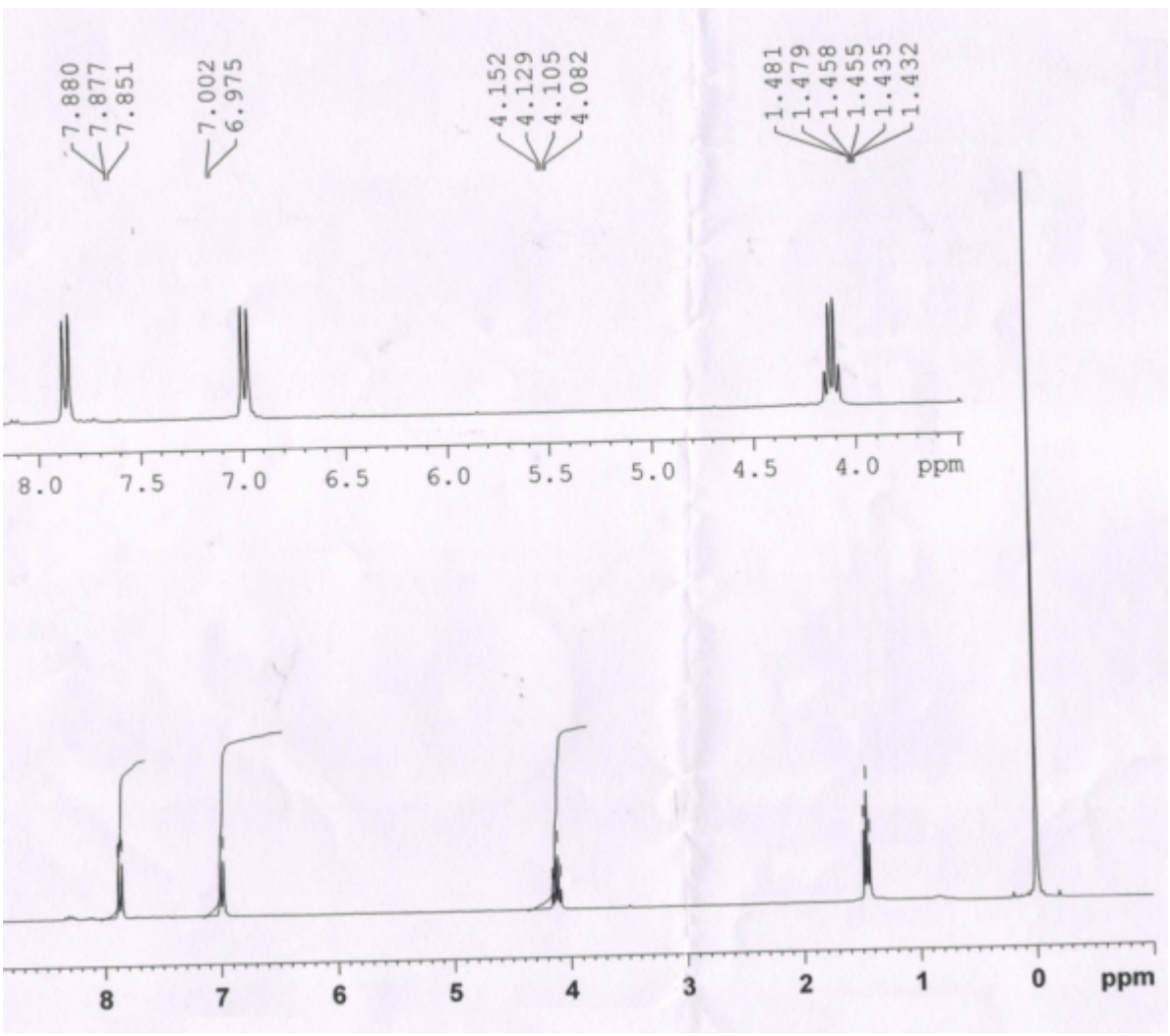
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (6H, s), 7.28-7.30 (4H, d, J=8.4Hz), 7.79-7.81(4H, d, J=8.4Hz).



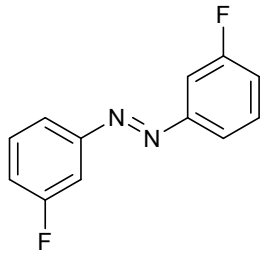
5. 1, 2-Bis (4-ethoxyphenyl) diazene (Entry 5).



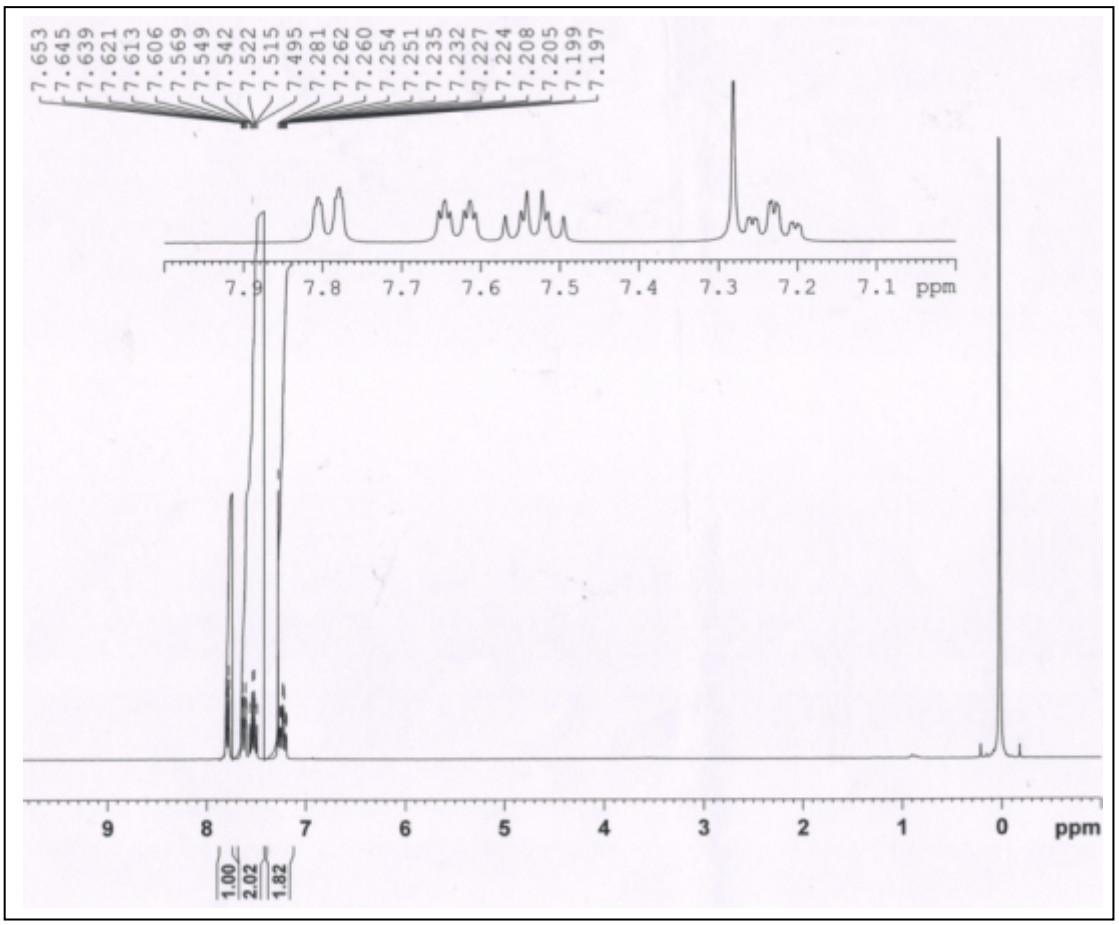
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.4 (6H, t, J=8Hz), 4.12 (4H, q, J=8Hz), 7.0 (4H, d, J=8.9Hz), 6.85 (4H, d, J=8.9Hz).



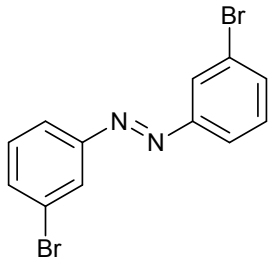
6. 1, 2-Bis (3-fluorophenyl) diazene (Entry 7).



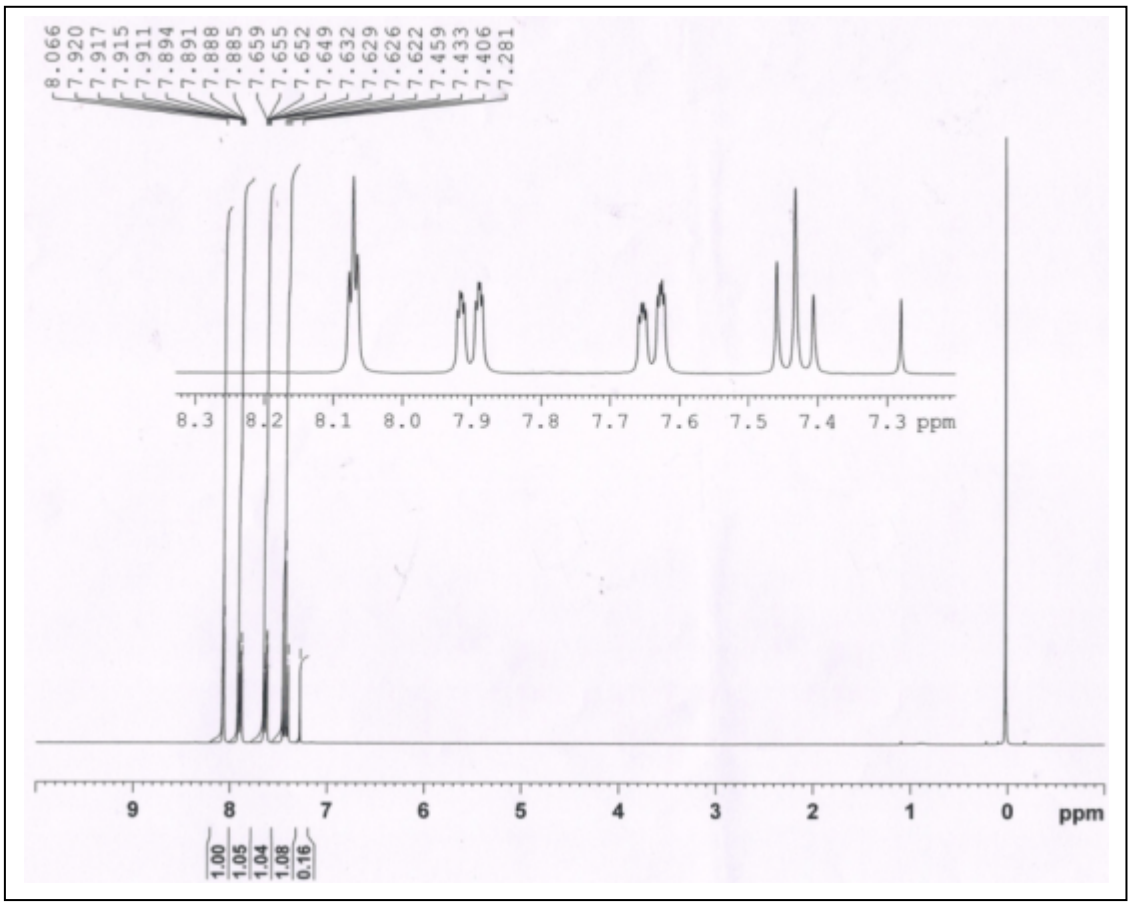
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19-7.29 (2H, m), 7.49-7.66 (4H, m), 7.79(2H, d).



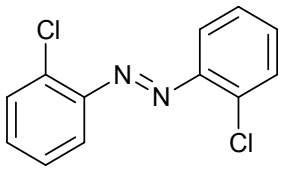
7. 1, 2-Bis (3-bromophenyl) diazene (Entry 7).



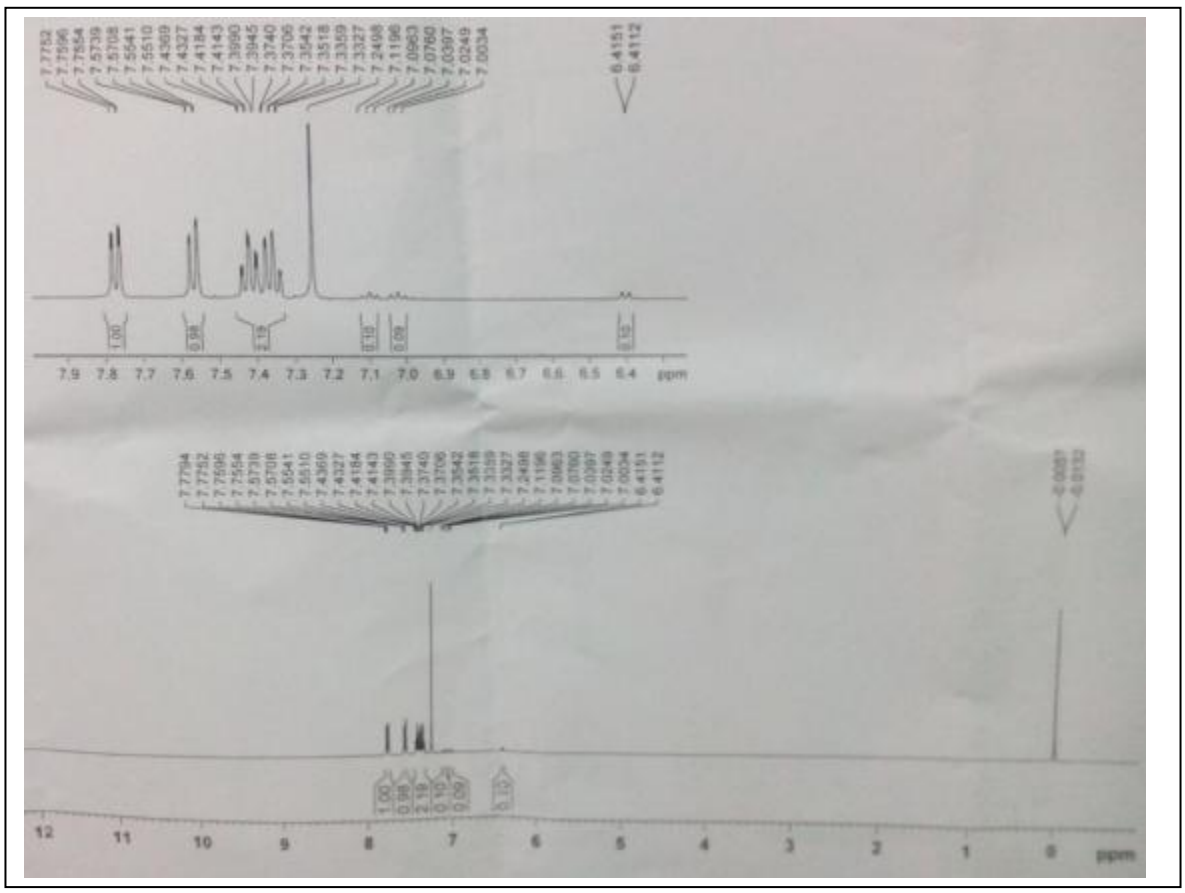
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09-8.05 (2H, m), 7.90 (2H, d, J=7.9Hz), 7.64 (2H, d, J=7.9Hz), 7.39-7.47 (2H, t, J=7.9Hz).



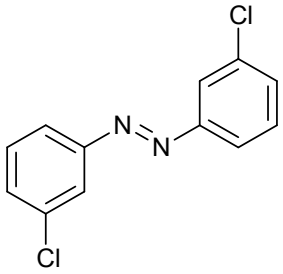
8. 1, 2-Bis (2-chlorophenyl) diazene (Entry 8).



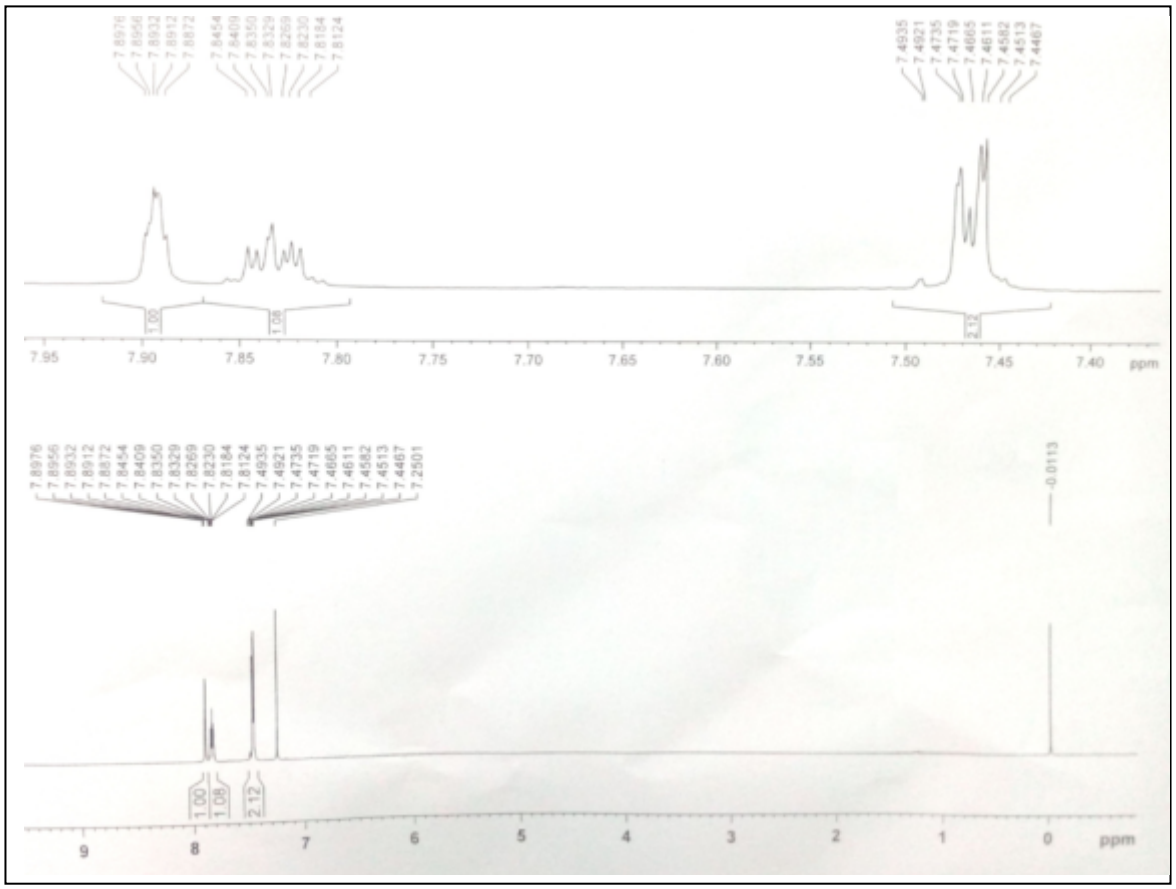
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (2H, d, J=7.7Hz), 7.55 (2H, d, J=7.7Hz), 7.43-7.33(4H, m).



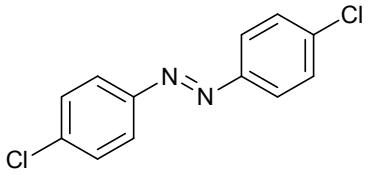
9. 1, 2-Bis (3-chlorophenyl) diazene (Entry 9).



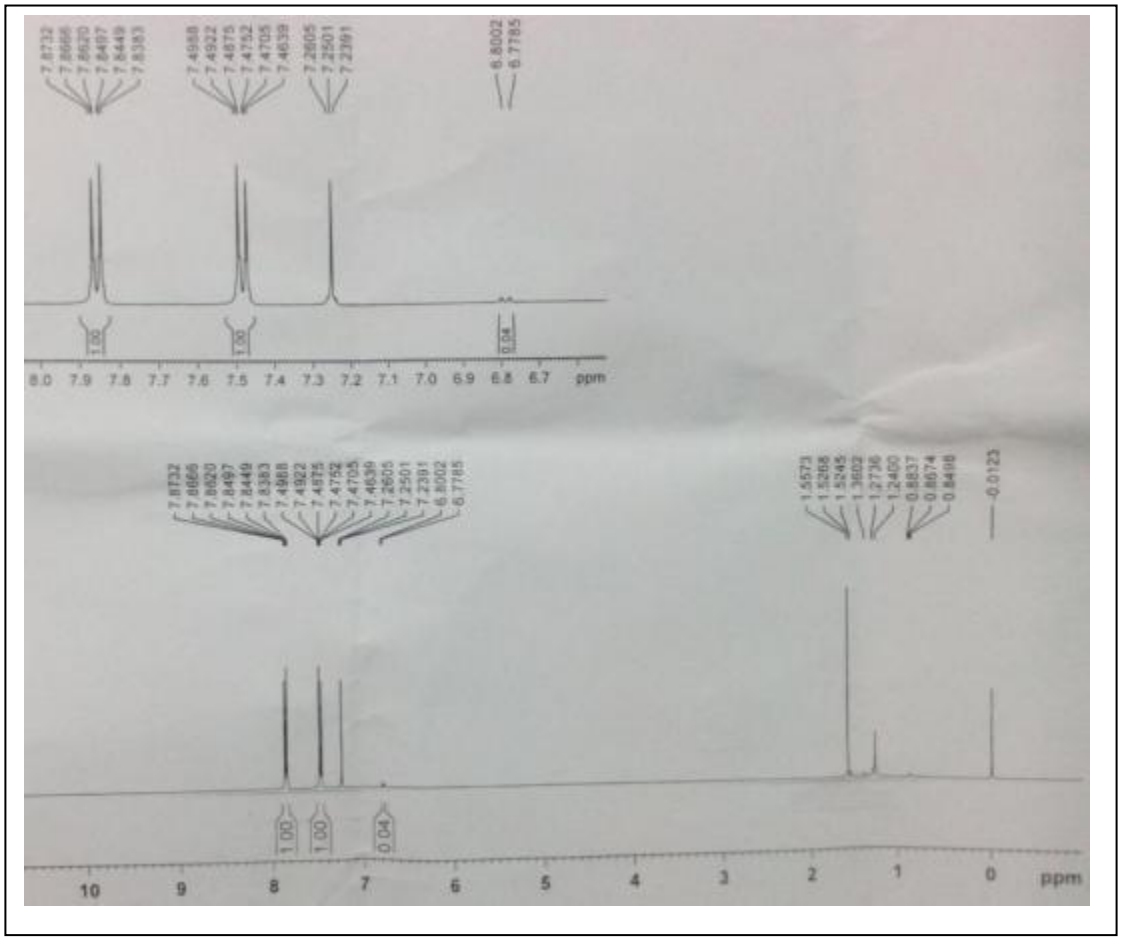
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.47 (4H, m), 7.81-7.86 (2H, m), 7.88-7.91 (2H,m).



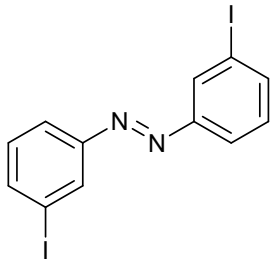
10. 1, 2-Bis (4-chlorophenyl) diazene (Entry 10).



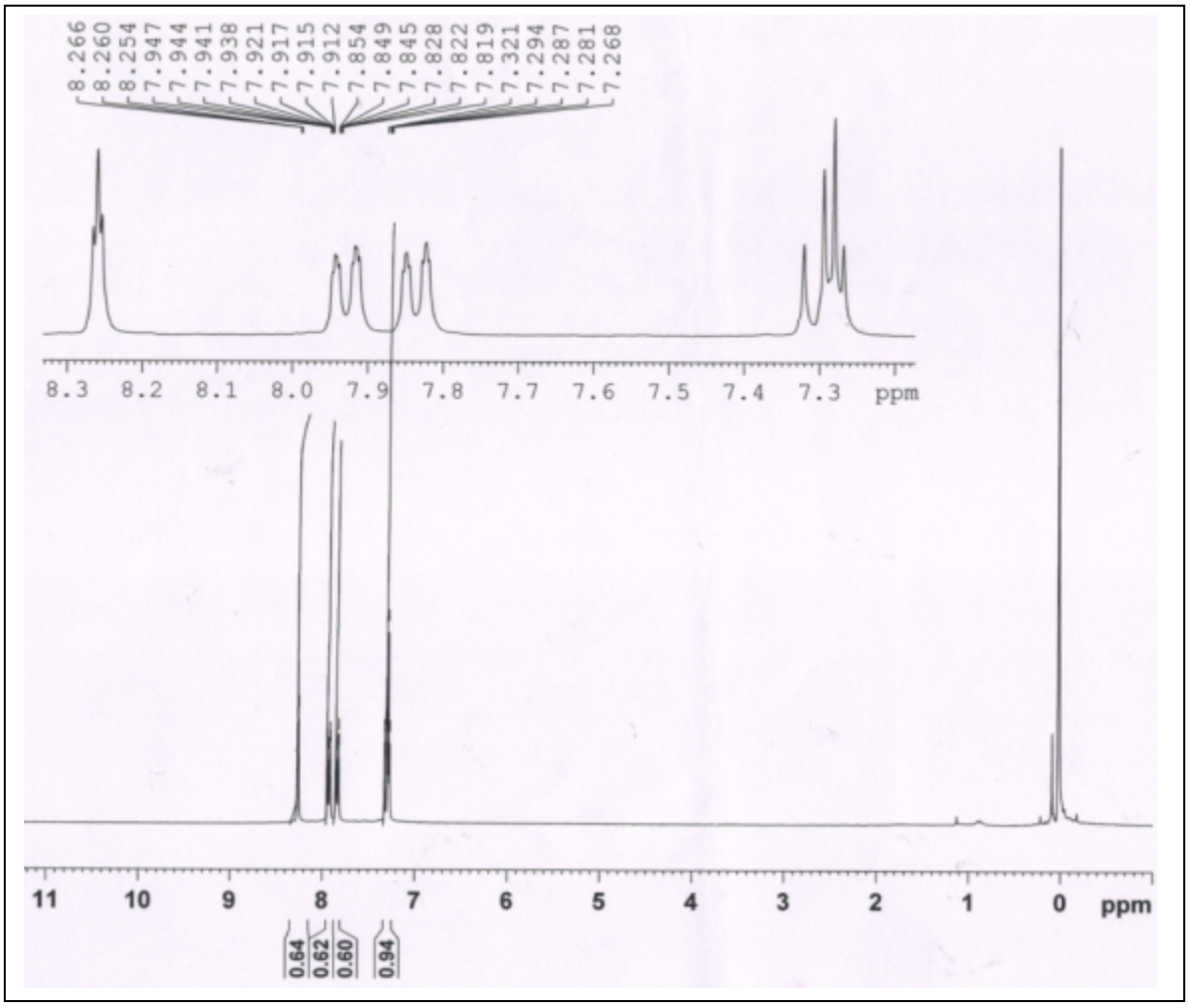
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.49 (4H, d, J=8.9Hz), 7.83-7.87 (4H, d, J=8.9Hz).



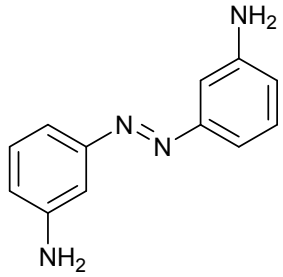
11. 1, 2-Bis (3-iodophenyl) diazene (Entry 11).



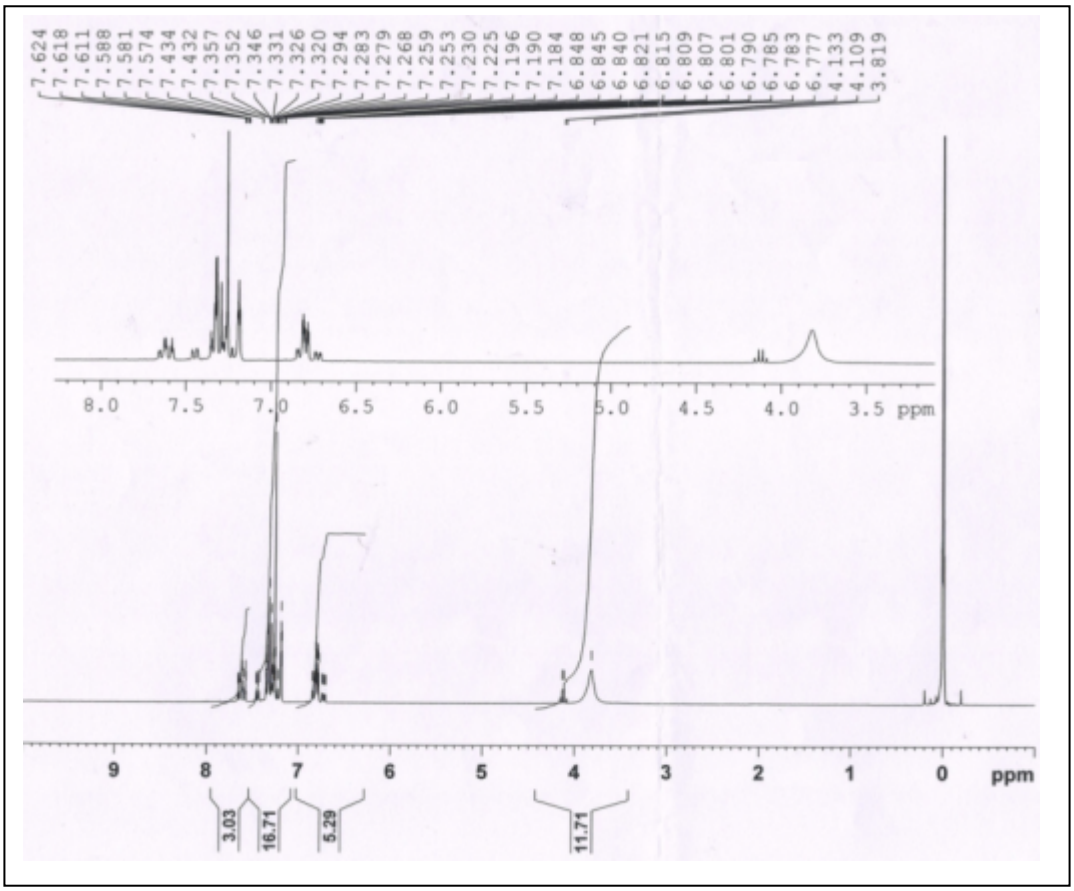
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (2H, m), 7.93 (2H, d, J=7.9Hz), 7.84 (2H, d, J=7.9Hz), 7.24-7.33 (2H, m).



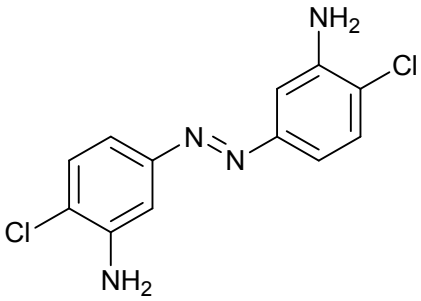
12. (E)-3,3'-(diazene-1,2-diyl)dianiline:



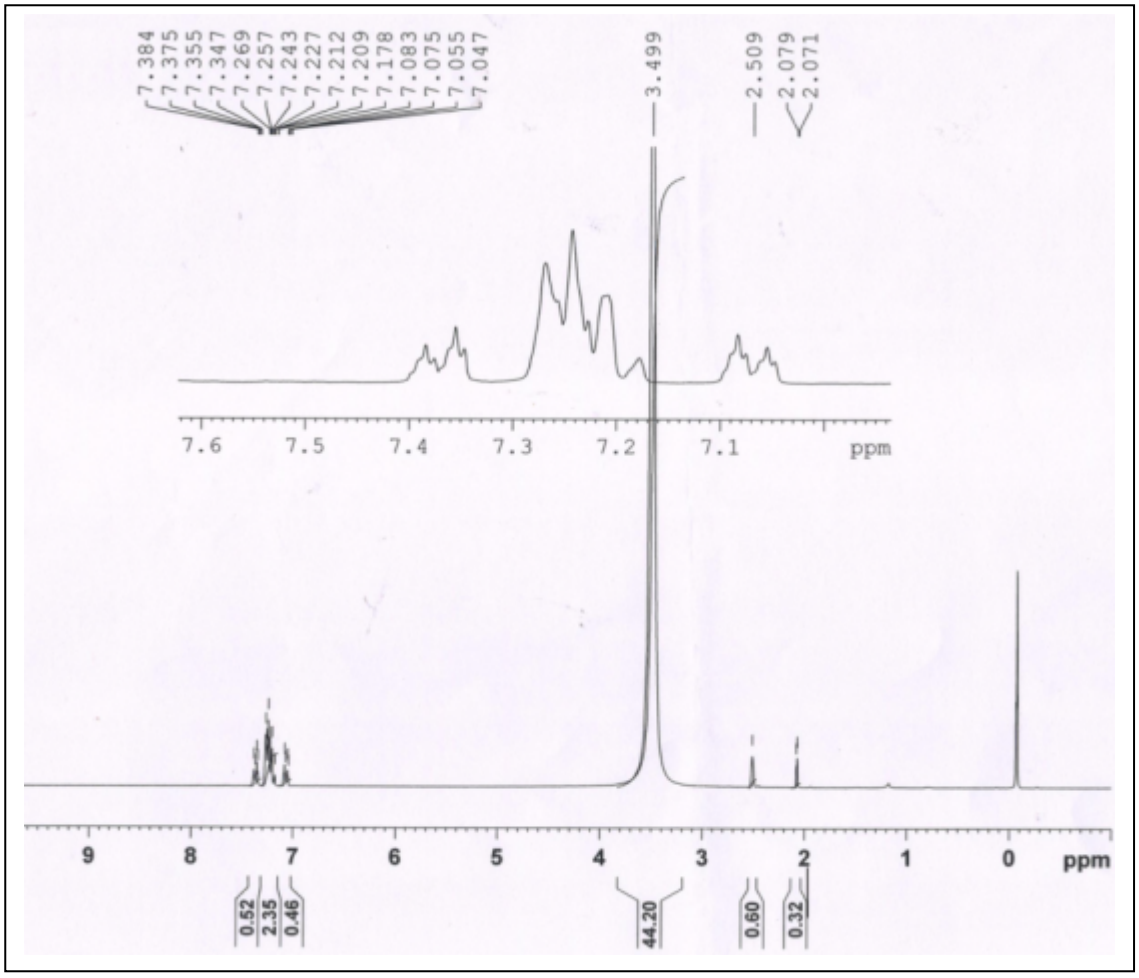
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.35 (6H, m), 6.77-6.84 (2H, m), 3.81(4H, s).



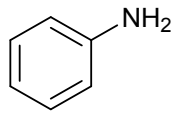
13. (E)-5,5'-(diazene-1,2-diyl)bis(2-chloroaniline):



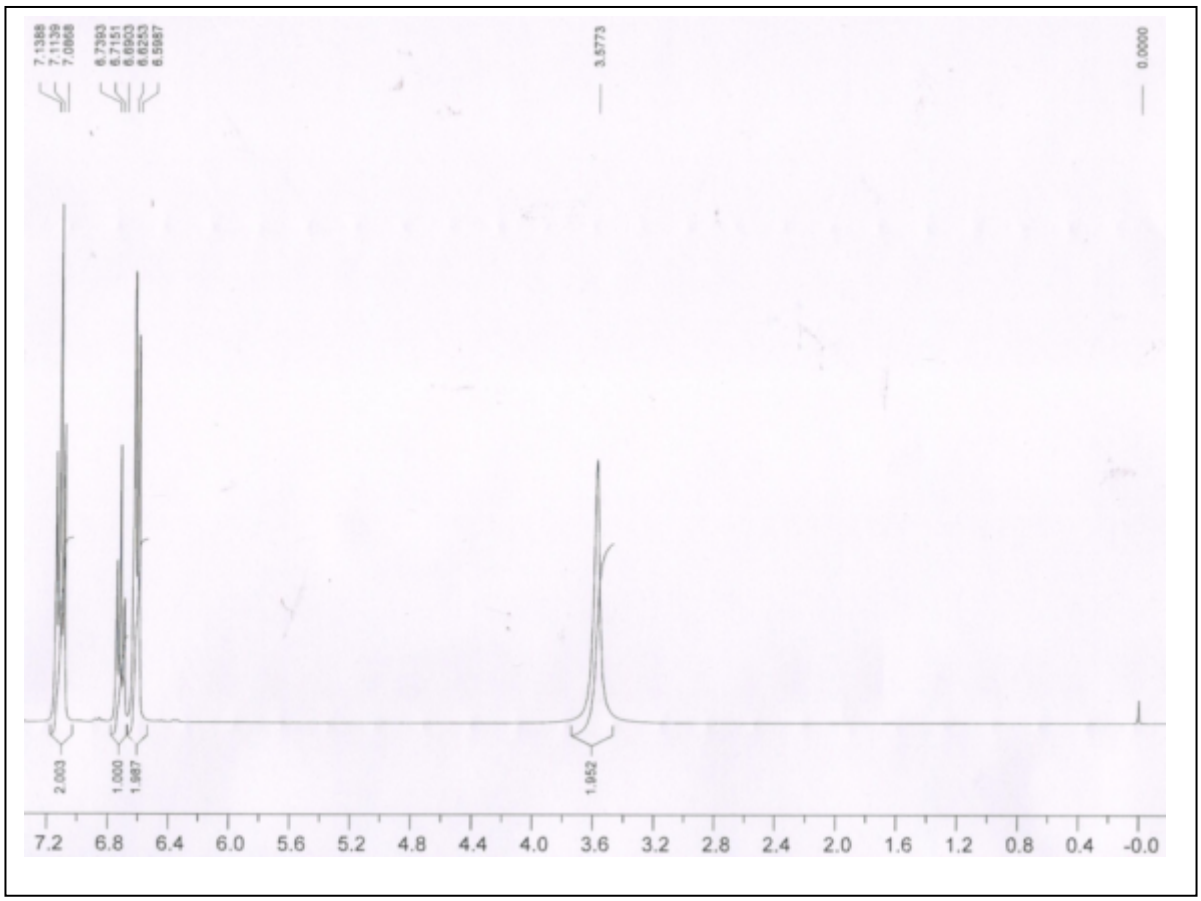
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.40 (2H, dt, J=7.5MHz), 7.17-7.29 (2H, m), 7.04-7.10(2H, dt, J=7.5MHz), 3.5 (4H, s).



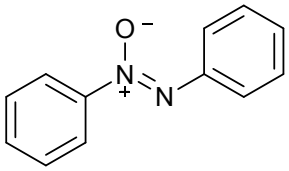
14. Aniline



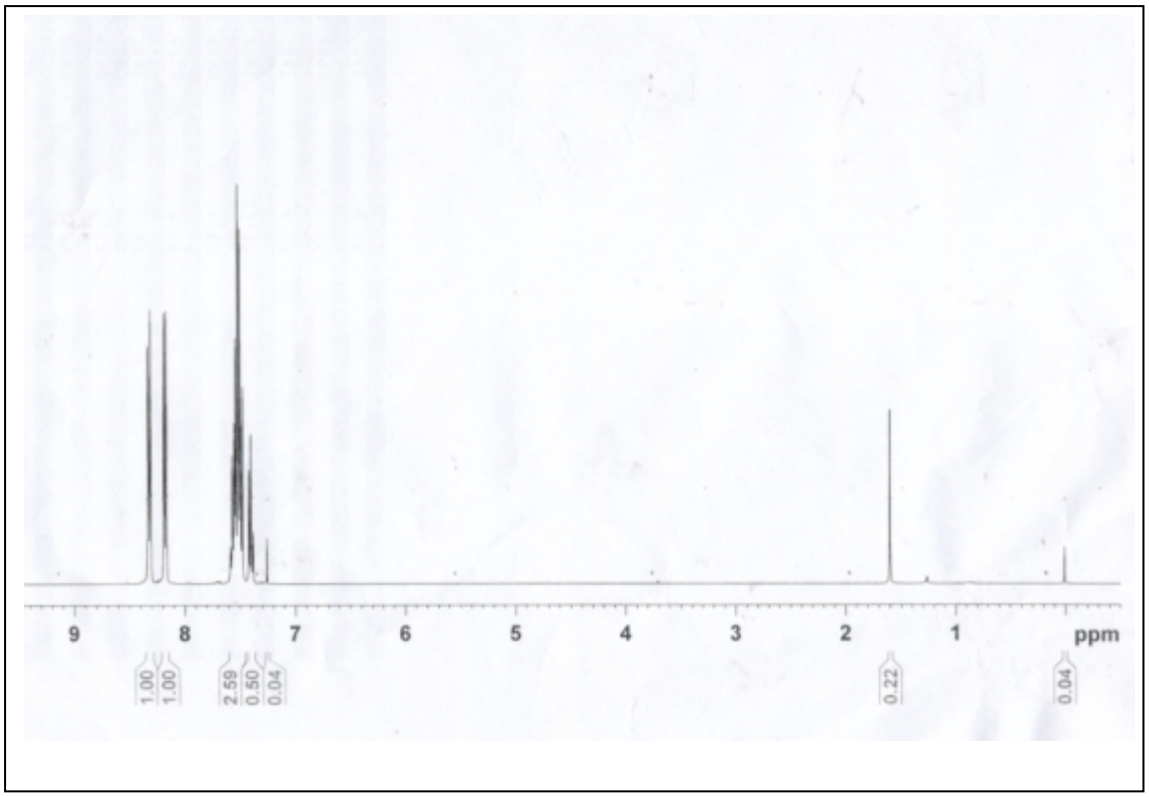
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.57(s, 2H), 6.59-6.62(m, 2H), 6.69-6.73(m, 1H), 7.08-7.13(m, 2H).



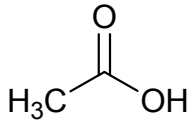
15. Azoxybenzene



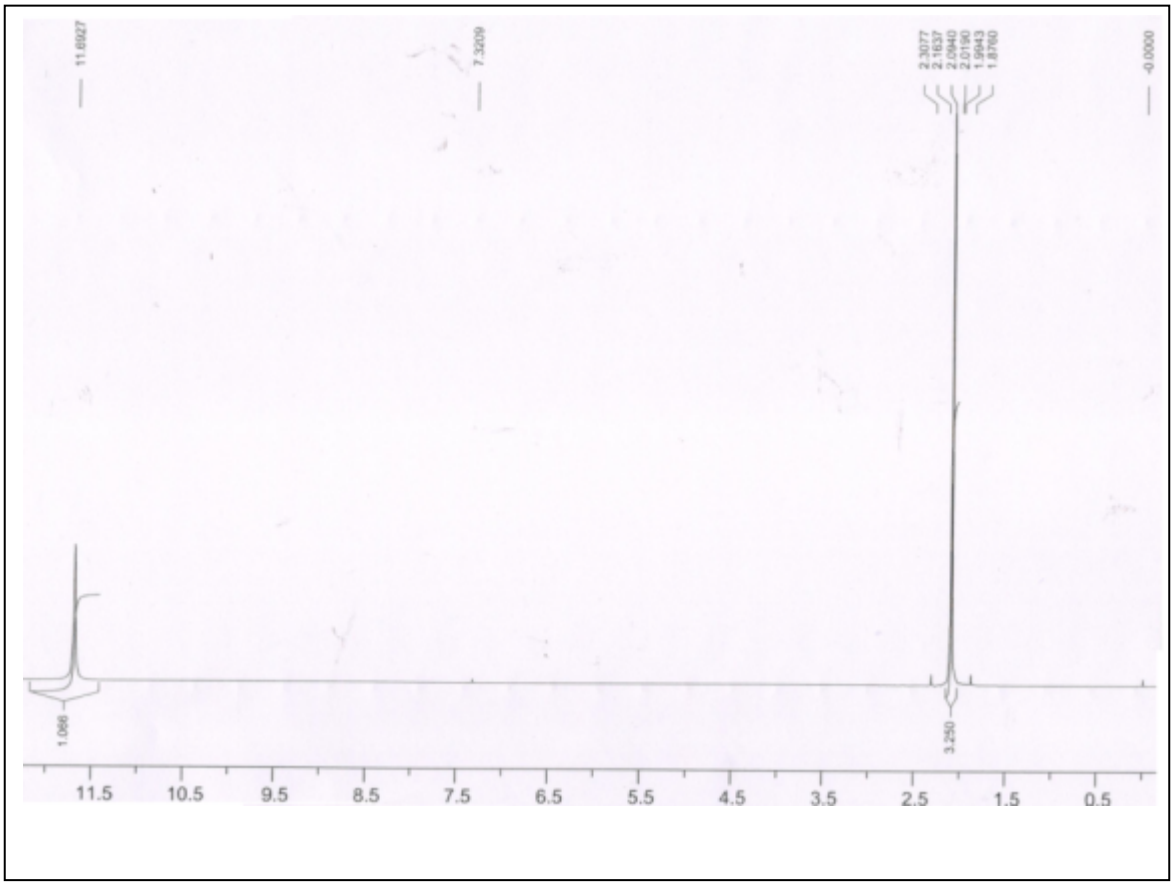
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (2H, d, J=8.2Hz), 8.15 (2H, d, J=8.3Hz), 7.58-7.36 (6H, m).



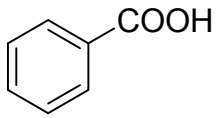
16. Acetic acid



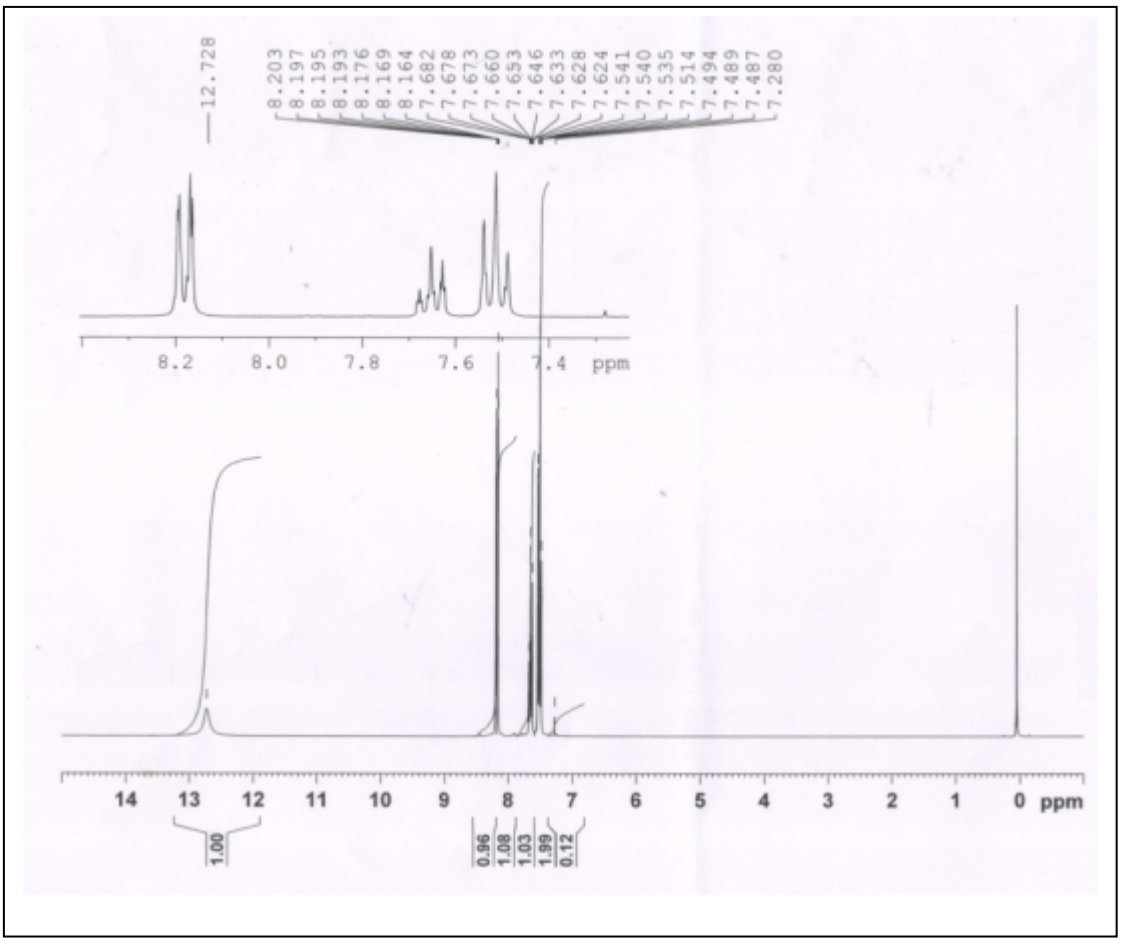
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09(s, 3H), 11.69(s, 1H).



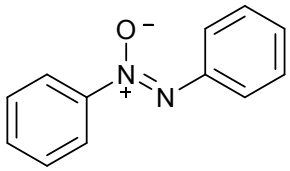
17. Benzoic acid



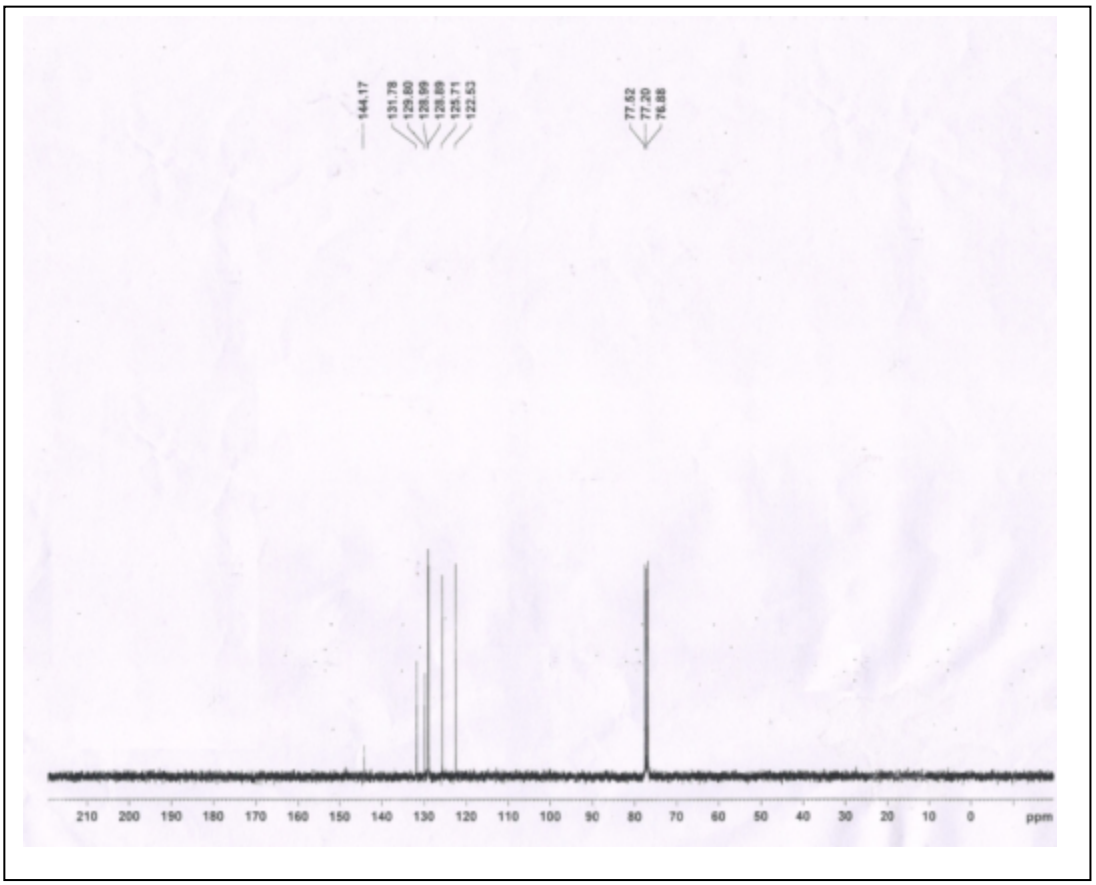
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.54(t, J=7.8Hz, 2H), 7.62-7.68(t, J=7.8Hz, 1H), 8.16-8.20(d, J=7.2Hz, 2H), 12.72(s, 1H).



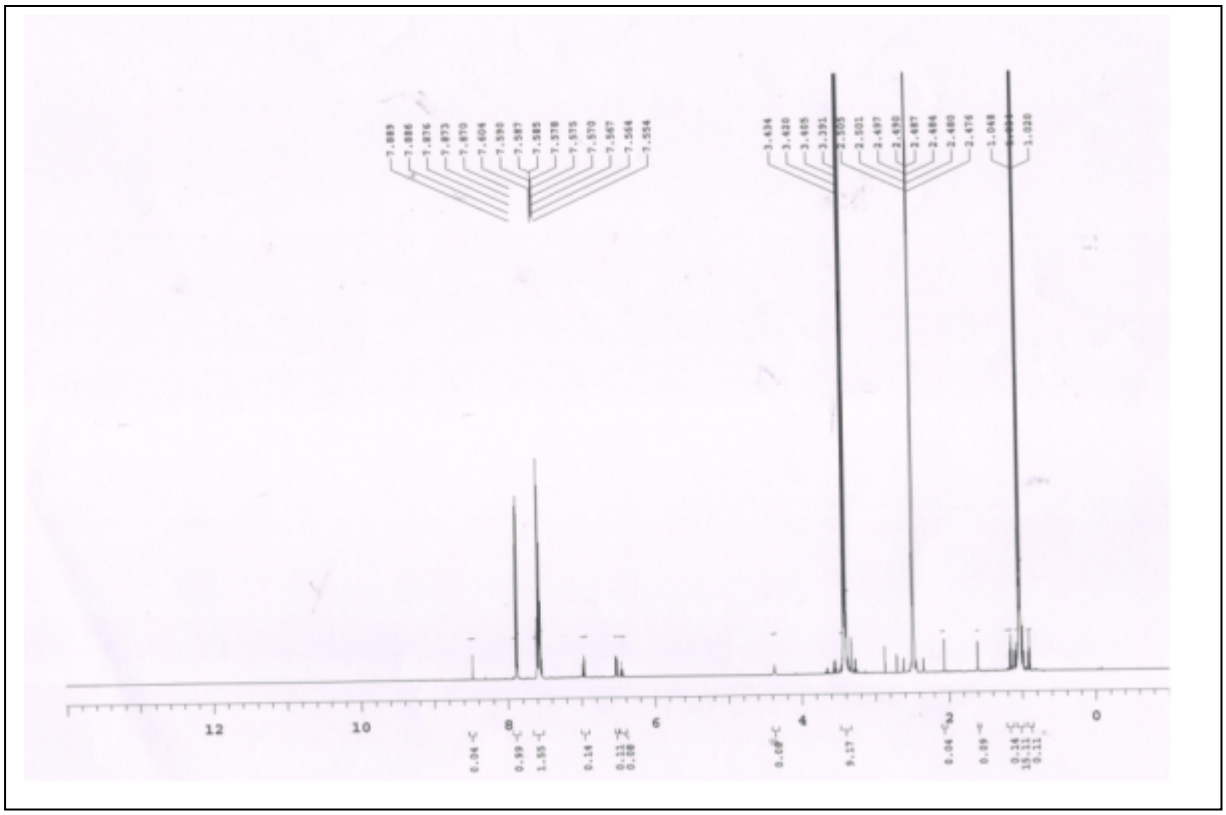
18. Azoxybenzene



^{13}C NMR (100 MHz, $CDCl_3$): δ 148.42, 144.17, 131.78, 129.80, 128.99, 128.89, 125.71, 122.53.



^{1}H NMR (DMSO, 500MHz) of crude mass of model reaction after 24h before work up:



FT-IR Spectra of (a) Standard sodium acetate, (b) Recovered sodium acetate from reaction mass: