

A new Method for the Preparation of 1, 3, 5-Triarybenzenes Catalyzed by Nanoclinoptilolite/HDTMA

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1. General experimental details

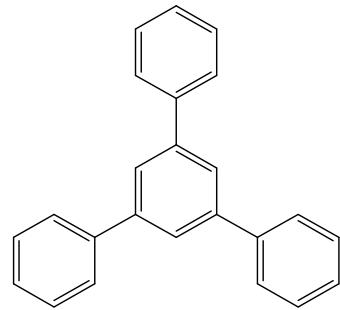
All reagents and starting materials were purchased from Merck and Fluka and were used without further purification. All solutions were prepared in double-distilled deionized water. products were known samples and were identified by comparison of their spectral and physical data with those previously reported. Progress of the reactions was monitored by TLC. Melting points were recorded on a Bamstead electrothermal type 9200 melting point apparatus. Fourier transform infrared (FT-IR) spectra were recorded on a 8700 Shimadzu Fourier-Transform spectrophotometer in the region of 250 to 4000 cm⁻¹ using KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 300-MHz instrument using CDCl₃ or DMSO-d₆ as the solvent with tetramethylsilane (TMS) as internal reference at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. All reactions were conducted under solvent free conditions.

1.1 General procedure:

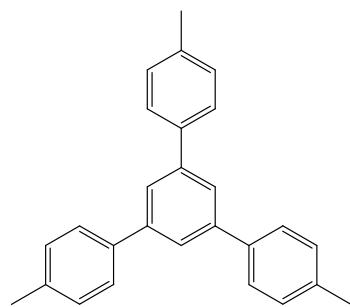
Acetophenone (1 mmol) and the surface modified nanoclinoptilolite (0.01 g) were added to a small test tube and the reaction mixture was stirred for 3 h at 100 °C. After completion of reaction, as indicated by TLC, hot ethanol was added to the reaction mixture and the insoluble catalyst was isolated via simple filtration. Water was the only by-product of the cyclotrimerization, which is added to its attractiveness. The filtrate was concentrated under reduced pressure, and finally the obtained crude product was re-crystallized from EtOH:H₂O (3:1).

2. Experimental characterization data for compounds

1, 3, 5-Triphenylbenzene (Table 6, entry 1): Light yellow solid; m. p. 171–173 °C. IR (KBr): $\nu_{\text{max}} = 3053, 1651, 1494, 1431, 1125, 758, 700 \text{ cm}^{-1}$. ^1H NMR (DMSO-d₆, 500 MHz): δ 7.88 (s, 3H), 7.87–7.86 (m, 6H), 7.52–7.49 (t, $J = 7.5 \text{ Hz}$, 6H), 7.43–7.40 (t, $J = 7.5 \text{ Hz}$, 3H). ^{13}C NMR (DMSO-d₆, 125 MHz): δ 141.6, 140.1, 128.9, 127.7, 127.2, 124.4.

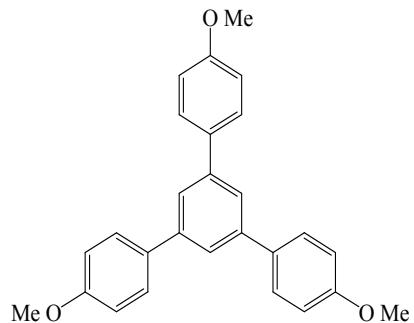


1, 3, 5-Tris(4-methylphenyl)benzene (Table 6, entry 4): White solid; m. p. 178–179°C. IR (KBr): $\nu_{\text{max}} = 3017, 2922, 1612, 1511, 1491, 1109, 812 \text{ cm}^{-1}$. ^1H NMR (CDCl₃, 500 MHz): δ 7.74 (s, 3H), 7.62 (d, $J = 8.0 \text{ Hz}$, 6H), 7.30 (d, $J = 7.5 \text{ Hz}$, 6H), 2.44 (s, 9H). ^{13}C NMR (CDCl₃, 125 MHz): 142.2, 138.3, 137.4, 129.4, 127.3, 124.7, 21.1.

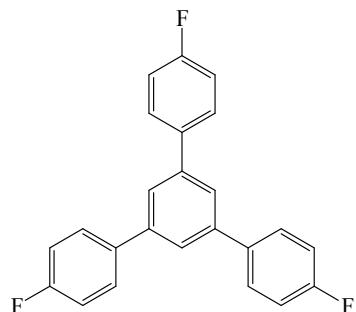


1, 3, 5-Tris(4-methoxyphenyl)benzene (Table 6, entry 2): White solid; m. p. 142–143 °C. IR (KBr): $\nu_{\text{max}} = 2953, 2918, 2848, 1598, 1460, 1378, 1263, 1097, 802 \text{ cm}^{-1}$. ^1H NMR (CDCl₃, 500

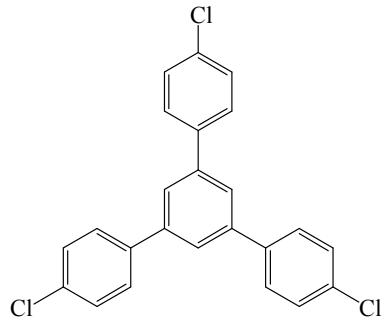
MHz): δ 7.59 (d, J = 9.0 Hz, 6H), 7.37 (s, 3H), 6.99 (d, J = 8.5 Hz, 6H), 3.86 (s, 9H). ^{13}C NMR (CDCl₃, 125 MHz): 159.7, 141.7, 134.0, 129.3, 122.7, 114.2, 55.9.



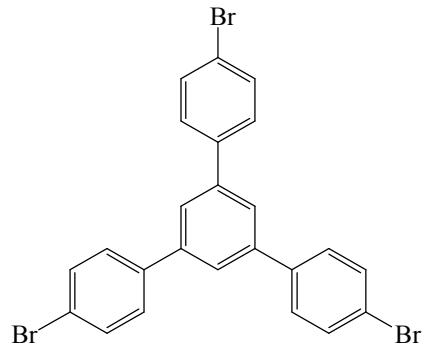
1, 3, 5-Tris(4-fluorophenyl)benzene (Table 6, entry 5): White solid; m. p. 238–240 °C. IR (KBr): ν_{max} = 3059, 1604, 1508, 1449, 1224, 1159, 825, 771 cm⁻¹. ^1H NMR (CDCl₃, 500 MHz): δ 7.67 (s, 3H), 7.61 (d, J = 8.5 Hz, 6H), 7.59 (d, J = 8.5 Hz, 6H). ^{13}C NMR (CDCl₃, 125 MHz): 161.7, 137.6, 132.4, 129.0 (d, J = 7.5 Hz), 125.3, 115.9 (d, J = 22.5 Hz).



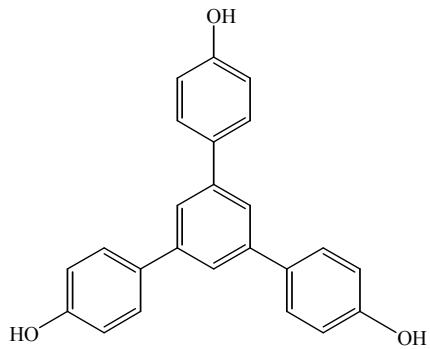
1, 3, 5-Tris(4-chlorophenyl) benzene (Table 6, entry 6): Light yellow solid; m. p. 247–249 °C. IR (KBr): ν_{max} = 3045, 1598, 1493, 1383, 1091, 1012, 815 cm⁻¹. ^1H NMR (CDCl₃, 500 MHz): δ 7.67 (s, 3H), 7.59 (d, J = 8.5 Hz, 6H), 7.44 (d, J = 8.5 Hz, 6H). ^{13}C NMR (CDCl₃, 125 MHz): 141.5, 139.4, 134.0, 129.6, 128.9, 125.1.



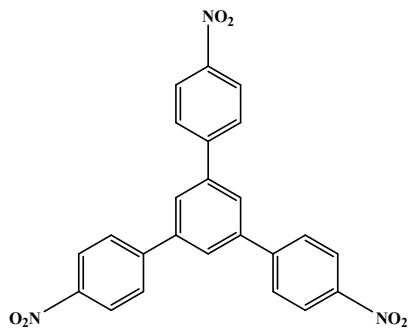
1, 3, 5-Tris(4-bromophenyl)benzene (Table 6, entry 7): White solid; m. p. 262–264 °C. IR (KBr): $\nu_{\text{max}} = 3043, 1595, 1489, 1379, 1075, 1007, 809 \text{ cm}^{-1}$. ^1H NMR (CDCl_3 , 500 MHz): δ 7.70(s, 3H), 7.62 (d, $J = 8.5 \text{ Hz}$, 6H), 7.56 (d, $J = 8.5 \text{ Hz}$, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): 141.7, 139.9, 132.3, 129.0, 125.2, 122.4.



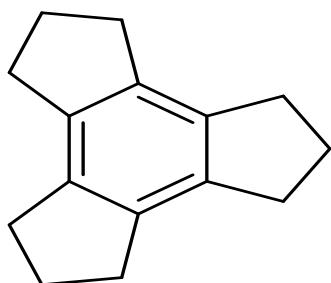
1, 3, 5-Tris(4-hydroxyphenyl)benzene (Table 6, entry 8): White solid; m. p. 237–239 °C. IR (KBr): $\nu_{\text{max}} = 2953, 2918, 2848, 1606, 1460, 1378, 1263, 1097, 802 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 3.81$ (s, 9H), 6.94–7.41 (m, 12H), 7.79 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 55.4, 114.3, 123.8, 128.3, 133.9, 141.8, 159.3.



1, 3, 5-Tris(4-nitrophenyl)benzene (Table 6, entry 3): White solid; m. p. 151–152 °C. IR (KBr): $\nu_{\text{max}} = 3043, 1595, 1489, 1379, 1085, 1007, 849 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 7.56$ (d, J 8.1 Hz, 6H), 7.62 (d, J 8.2 Hz, 6H), 7.70 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 122.3, 125.0, 128.9, 132.1, 139.7, 141.6.



Trindan (Table 6, entry 10): White solid; m. p. 95-98 °C . IR (KBr): $\nu_{\text{max}} = 2918, 2848, 1680, 1460, 1378, 1103, 957, 800$. ^1H NMR (500 MHz, CDCl_3): $\delta = 1.92\text{--}2.51$ (m, 6H), 2.49–3.21 (t, $J = 7.3$ Hz, 12 H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 25.6, 31.2, 137.6$.



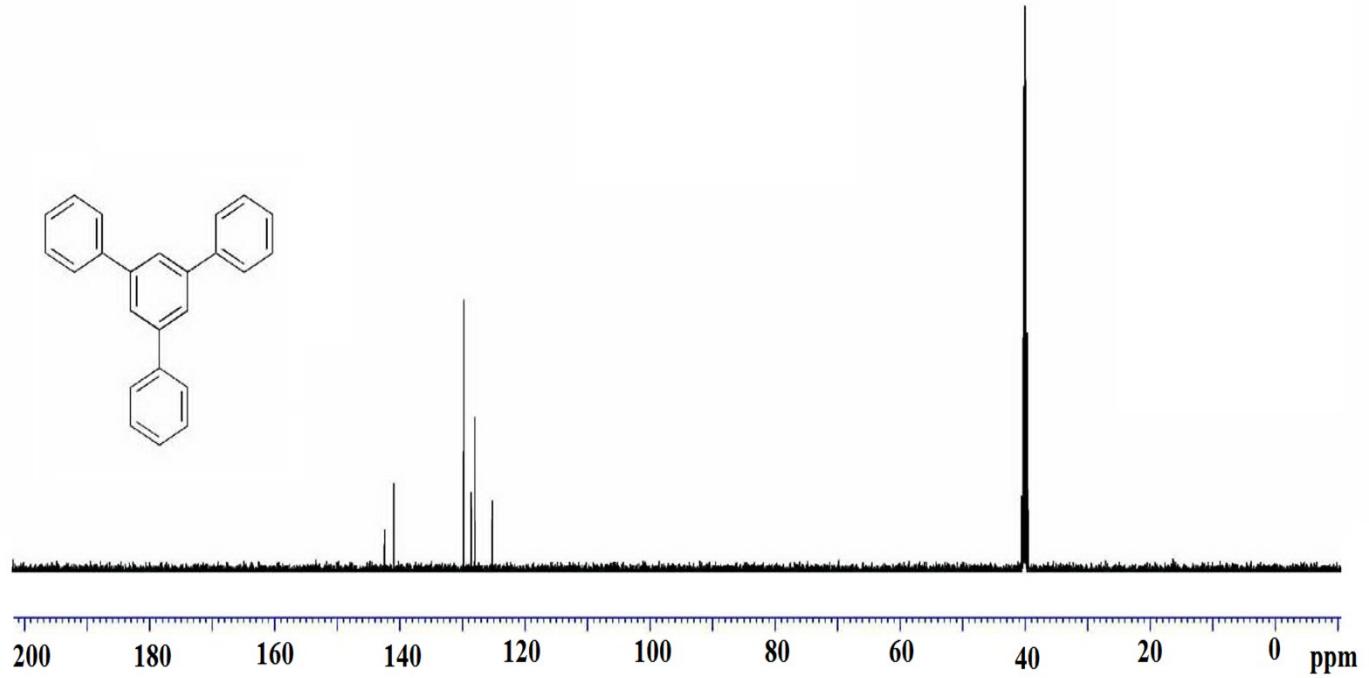


Fig. S1. ^{13}C -NMR spectrum of 1, 3, 5-triphenylbenzene.

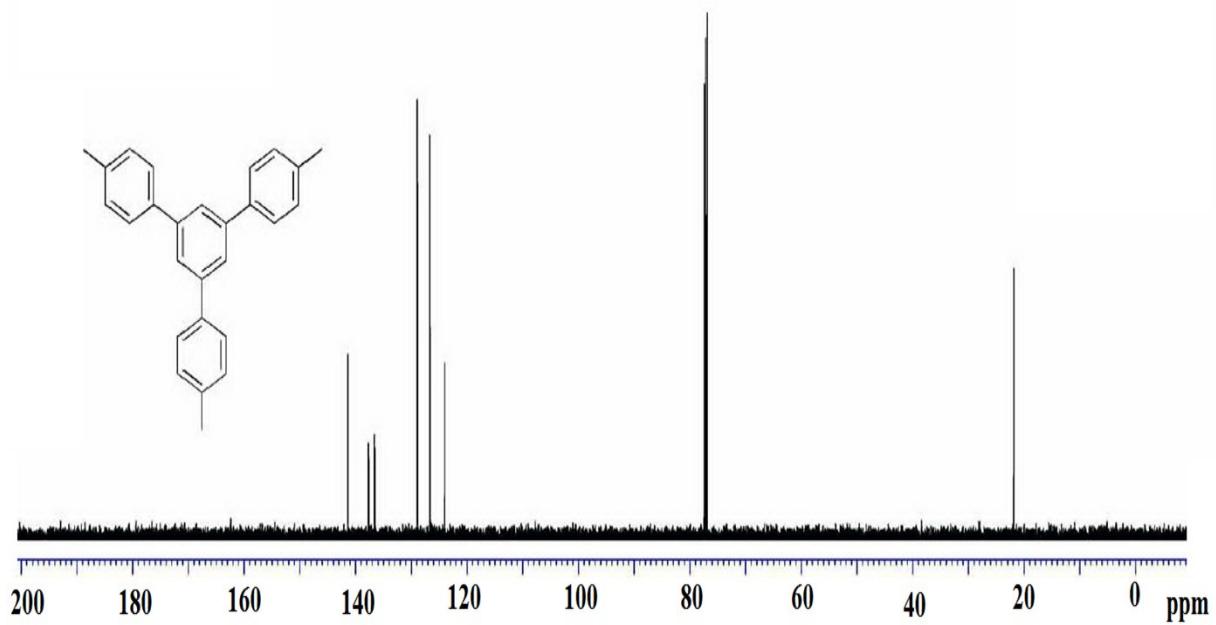


Fig. S2. ^{13}C -NMR spectrum of 1, 3, 5-tris(4-methylphenyl)benzene.

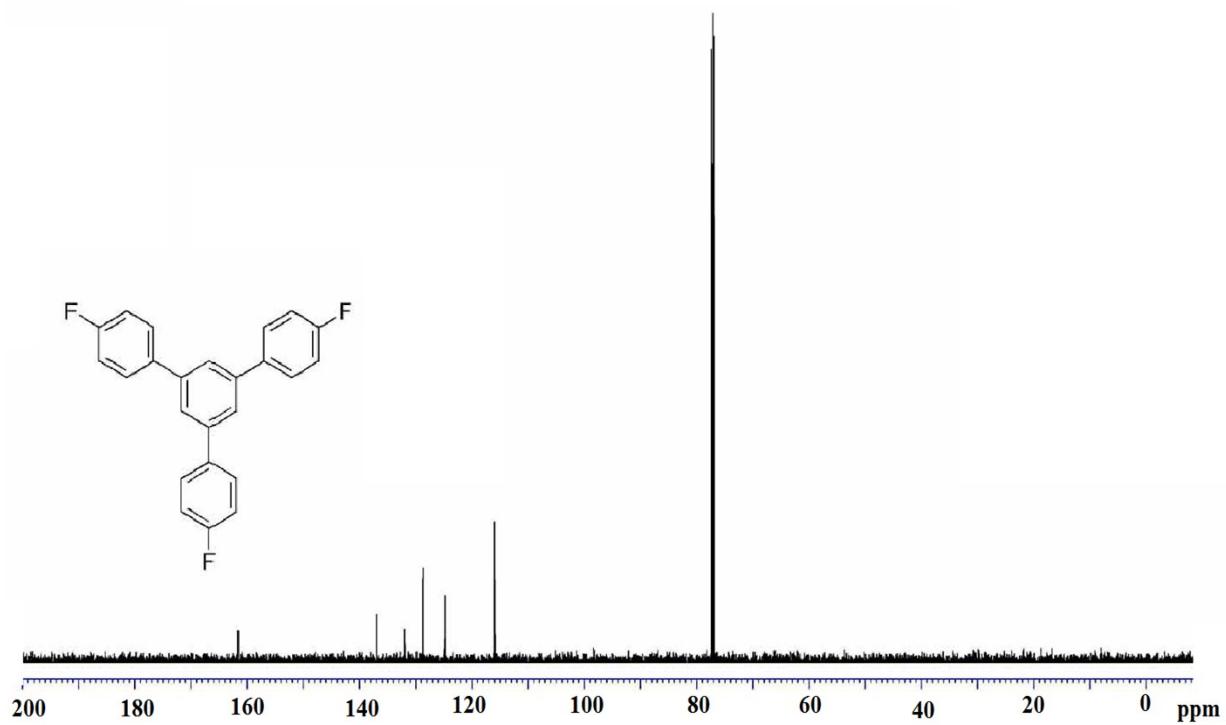


Fig. S3. ^{13}C -NMR spectrum of 1, 3, 5-tris(4-fluorophenyl)benzene.

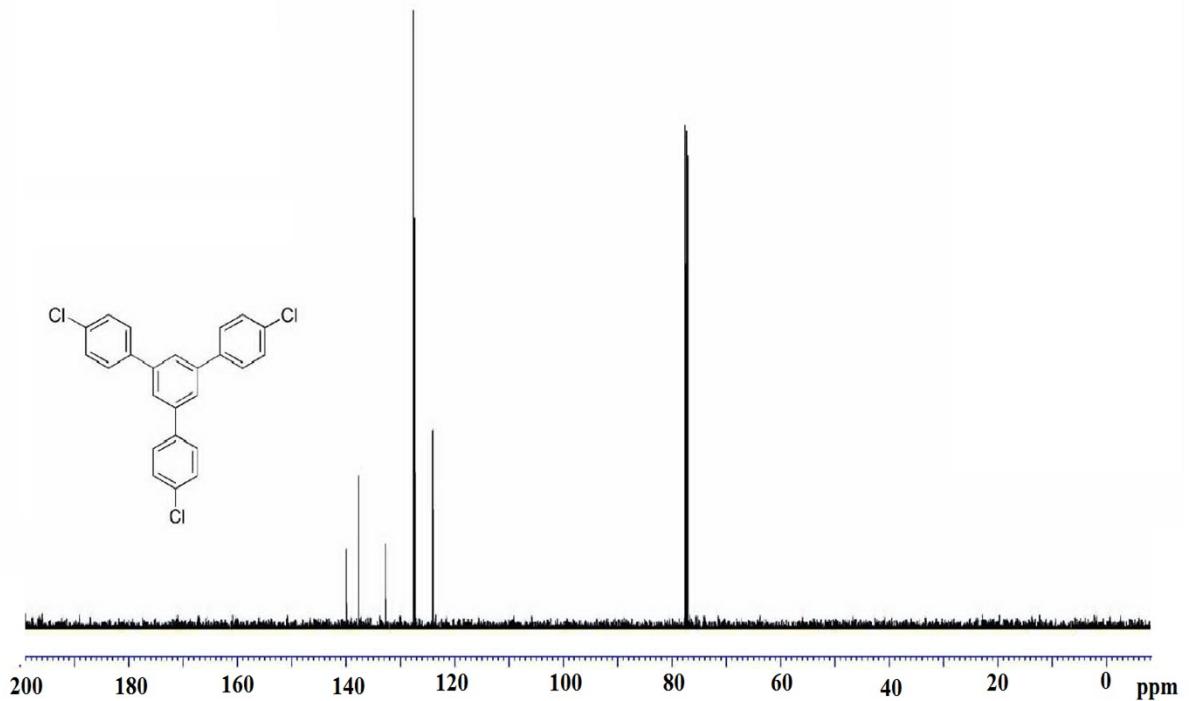


Fig. S4. ^{13}C -NMR spectrum of 1, 3, 5-tris(4-chlorophenyl)benzene.

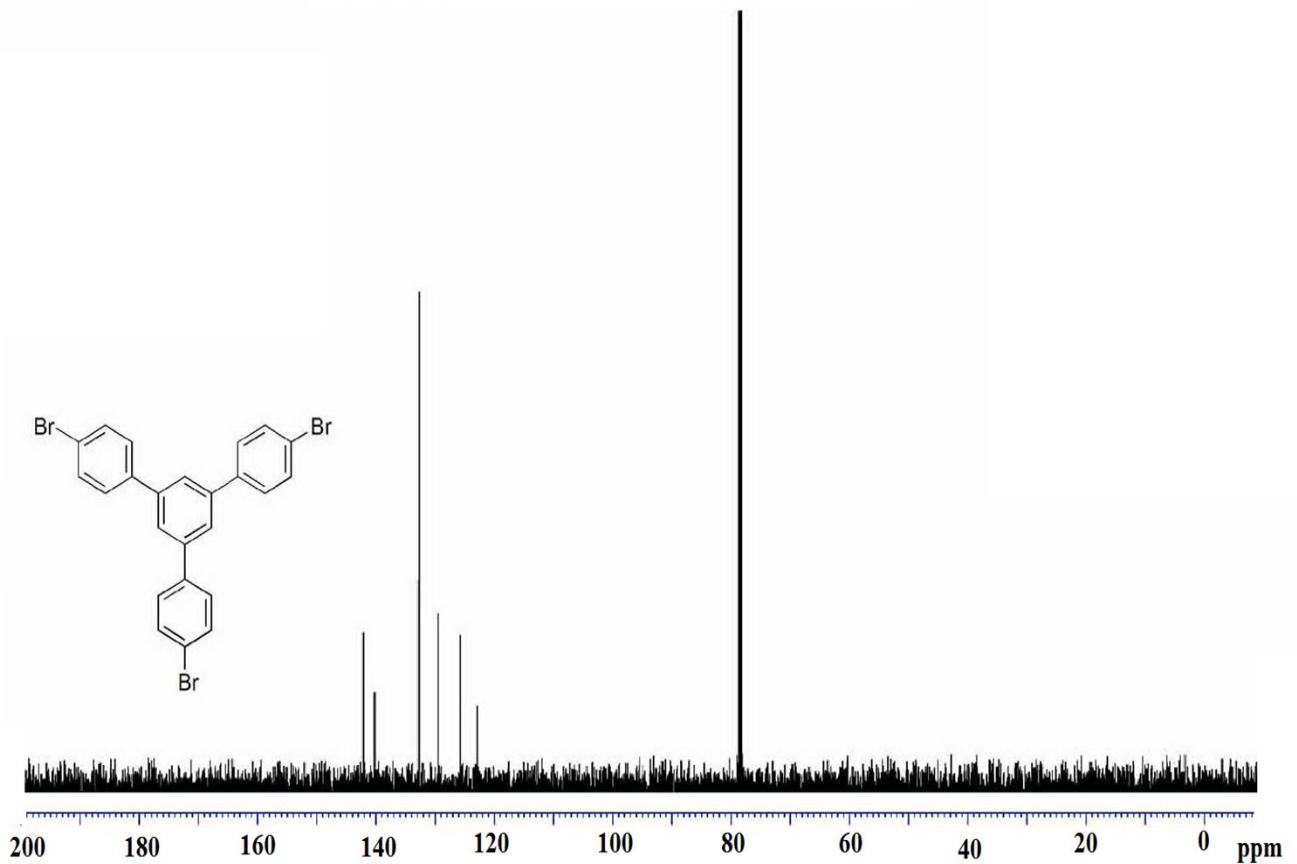


Fig. S5. ^{13}C -NMR spectrum of 1, 3, 5-tris(4-bromophenyl)benzene.

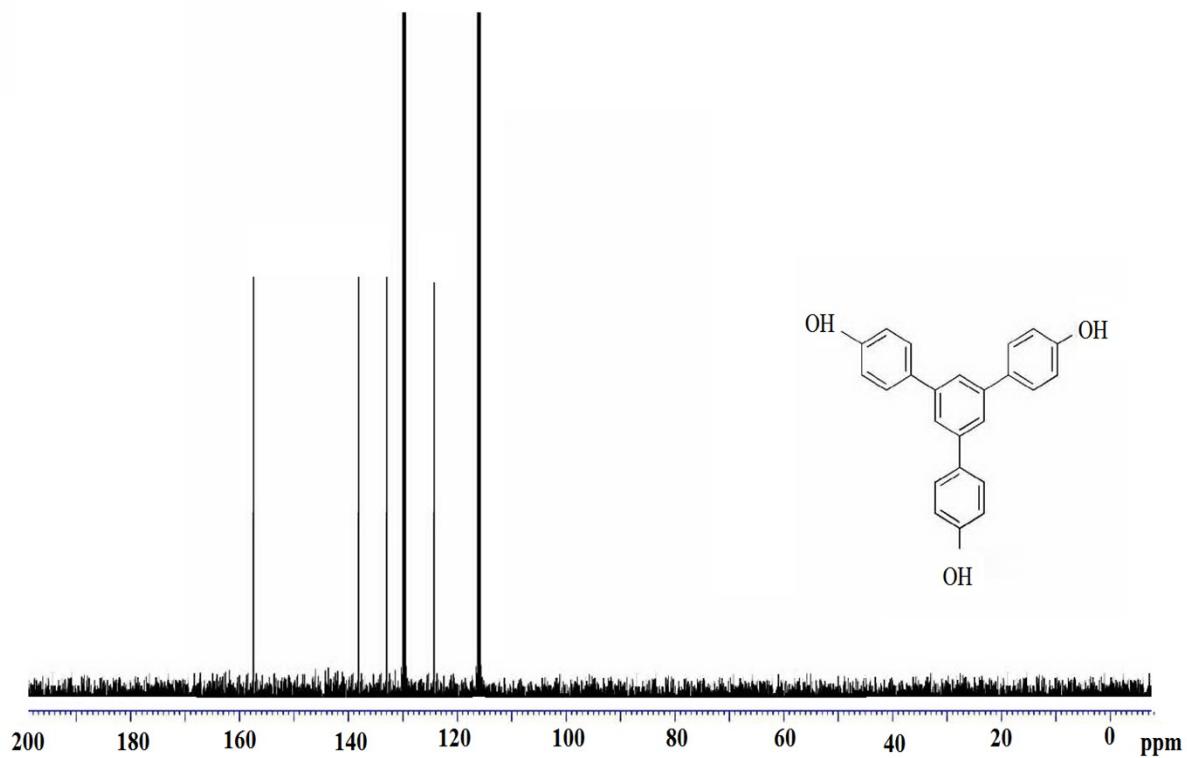


Fig. S6. ¹³C-NMR spectrum of 1, 3, 5-tris(4-hydroxyphenyl)benzene.

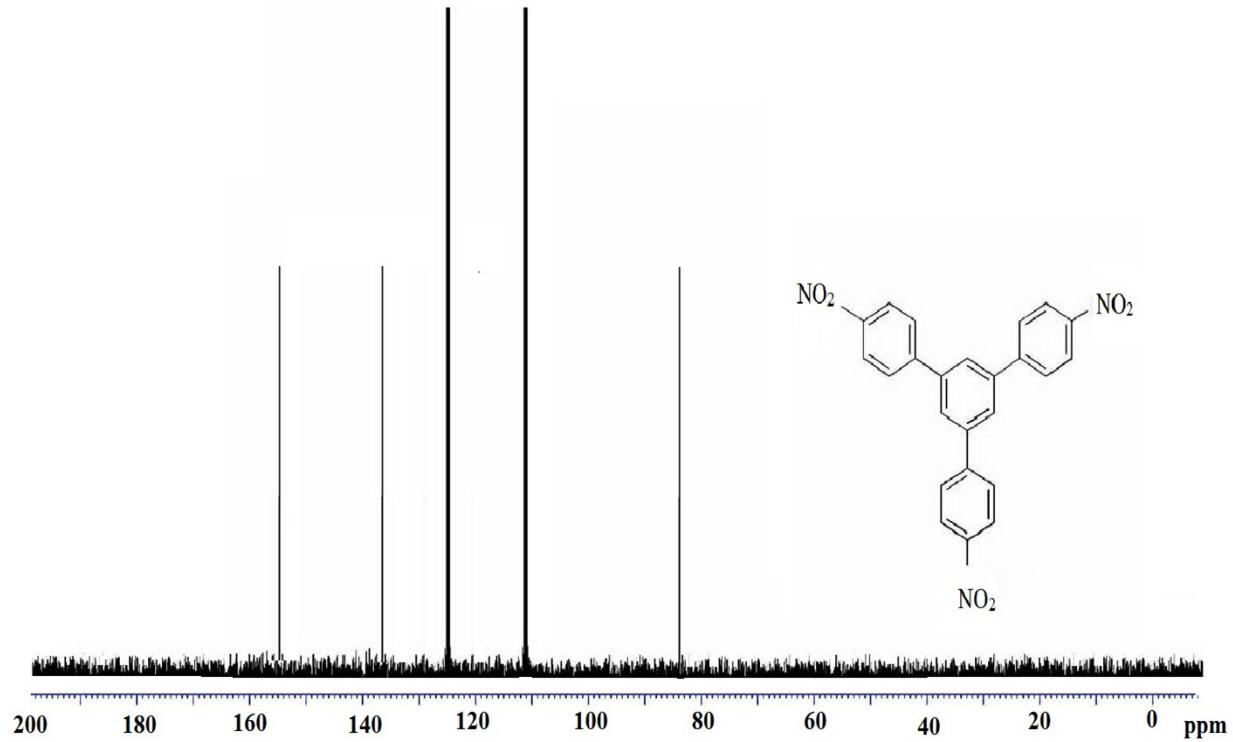


Fig. S7. ^{13}C -NMR spectrum of 1, 3, 5-tris(4-nitrophenyl)benzene.

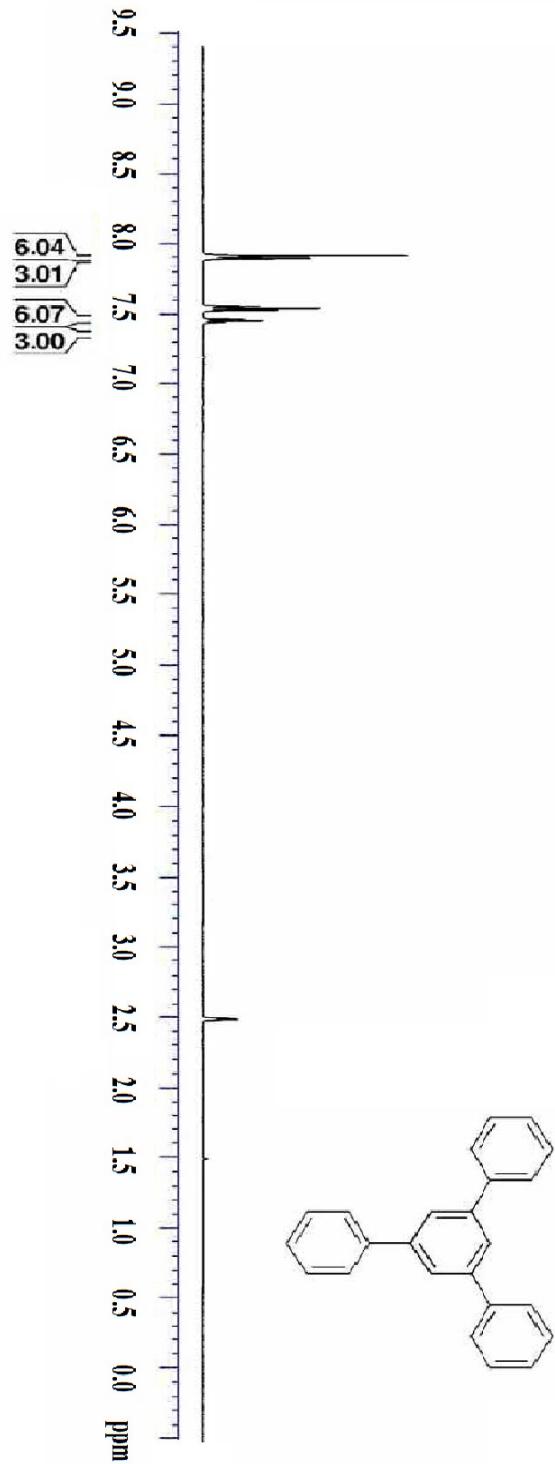


Fig. S8. ¹H-NMR spectrum of 1, 3, 5- triphenylbenzene.

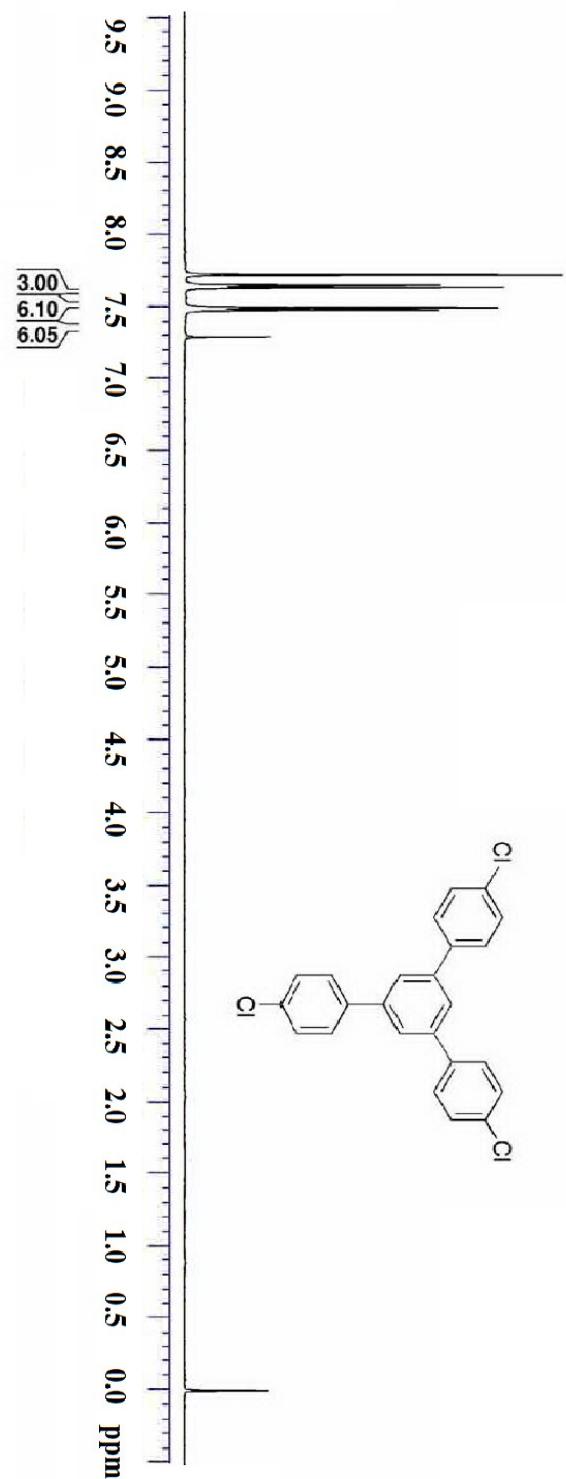


Fig. S9. ¹H-NMR spectrum of 1, 3, 5-tris(4-chlorophenyl)benzene.

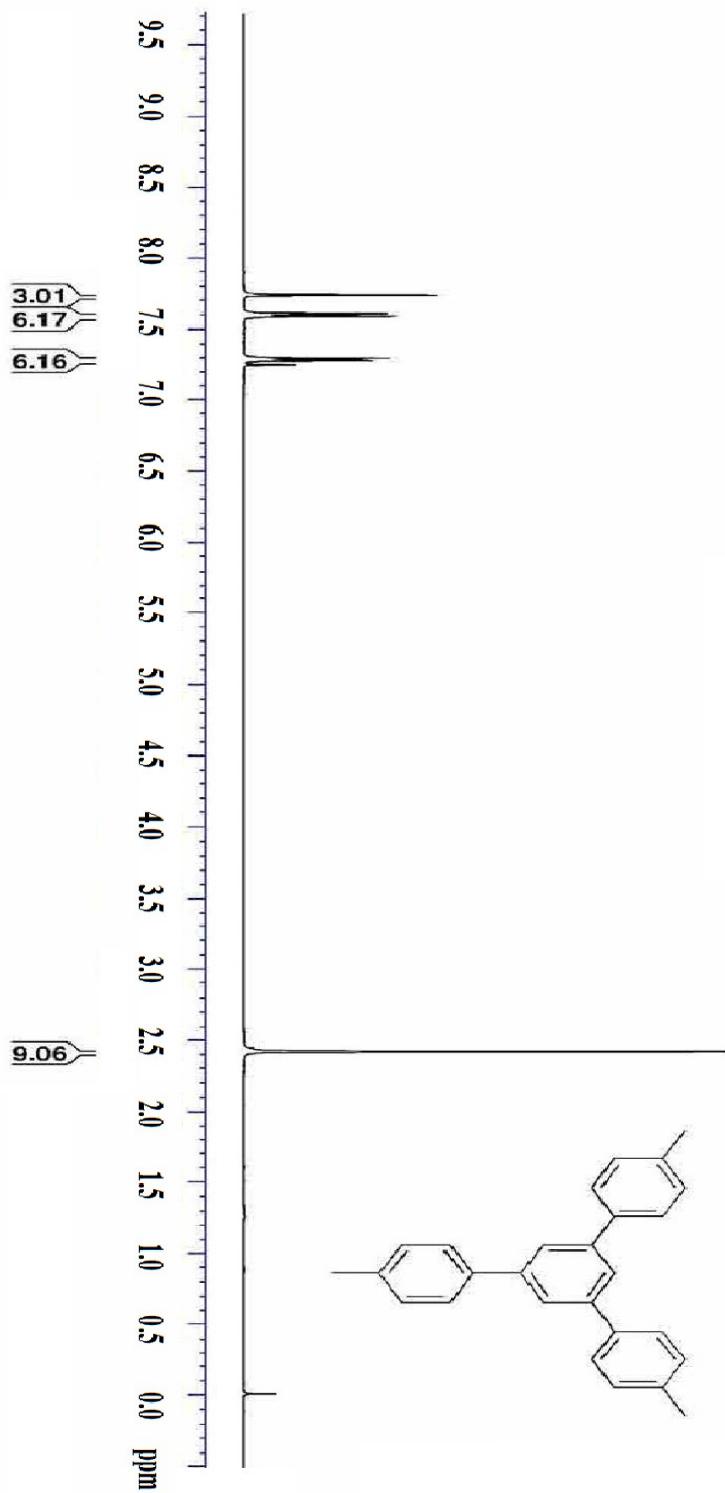


Fig. S10. ¹H-NMR spectrum of 1, 3, 5-tris(4-methylphenyl)benzene.

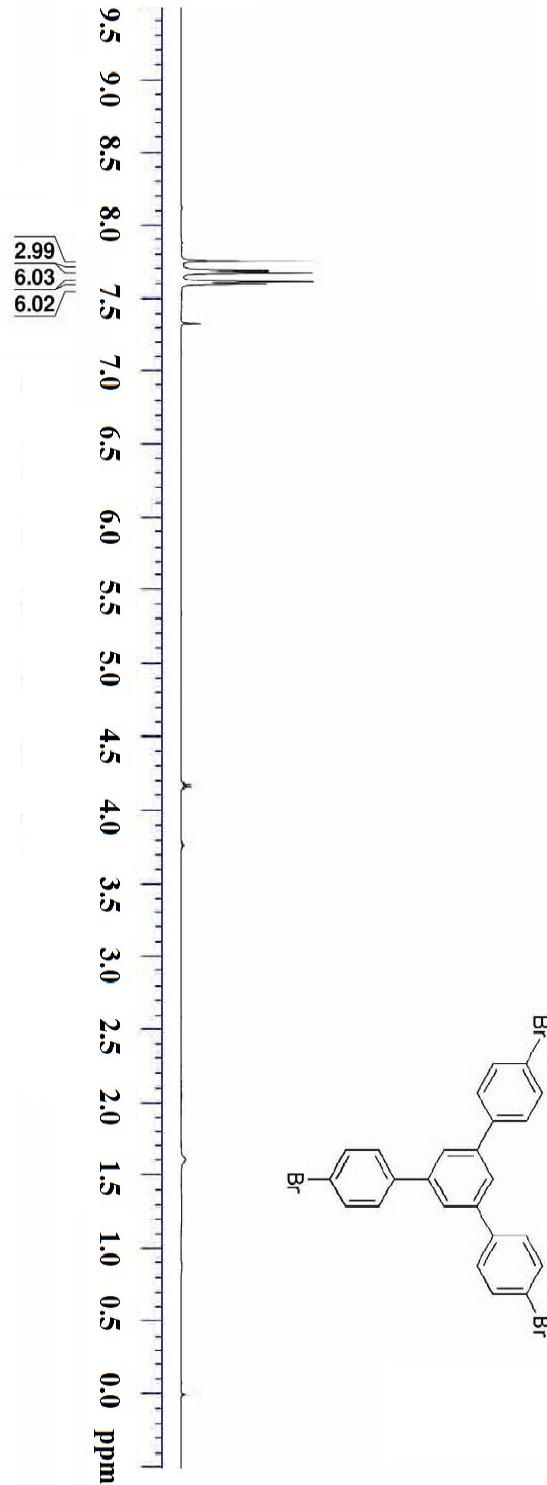


Fig. S11. ¹H-NMR spectrum of 1, 3, 5-tris(4-bromophenyl)benzene.

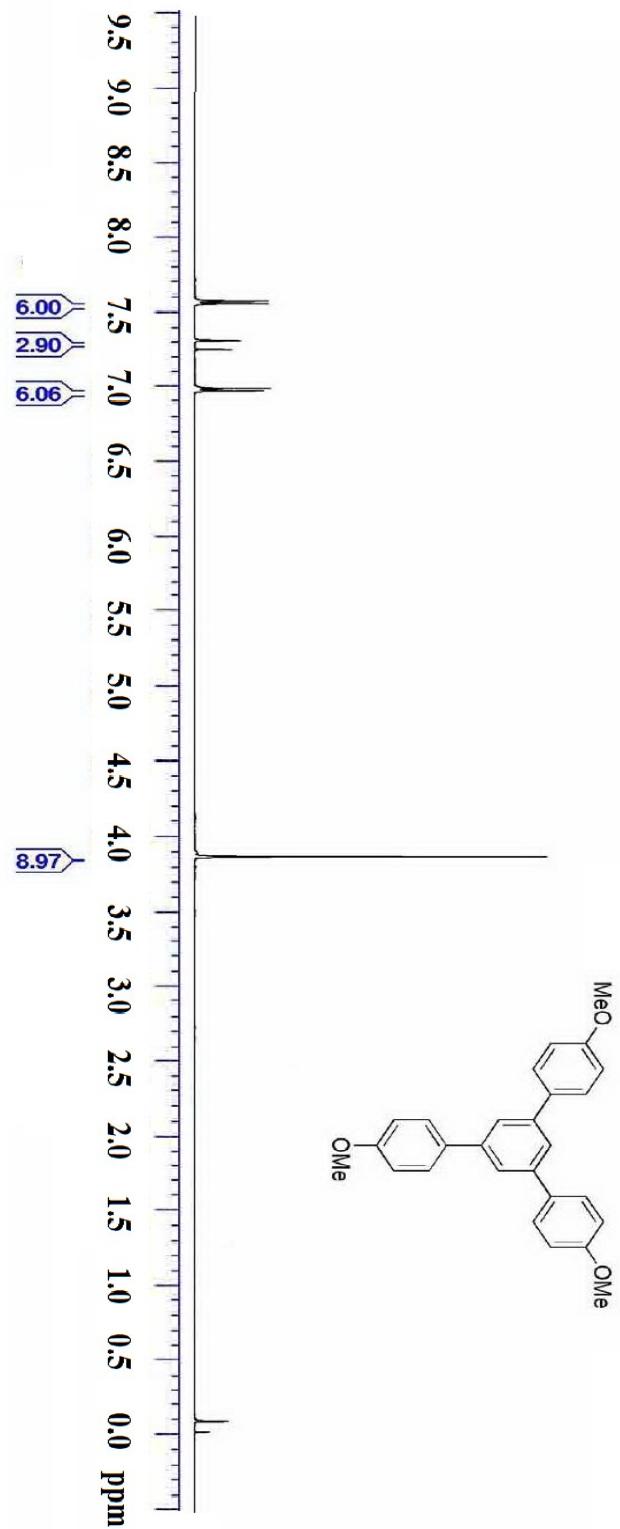


Fig. S12. ^1H -NMR spectrum of 1, 3, 5-tris(4-methoxyphenyl)benzene.

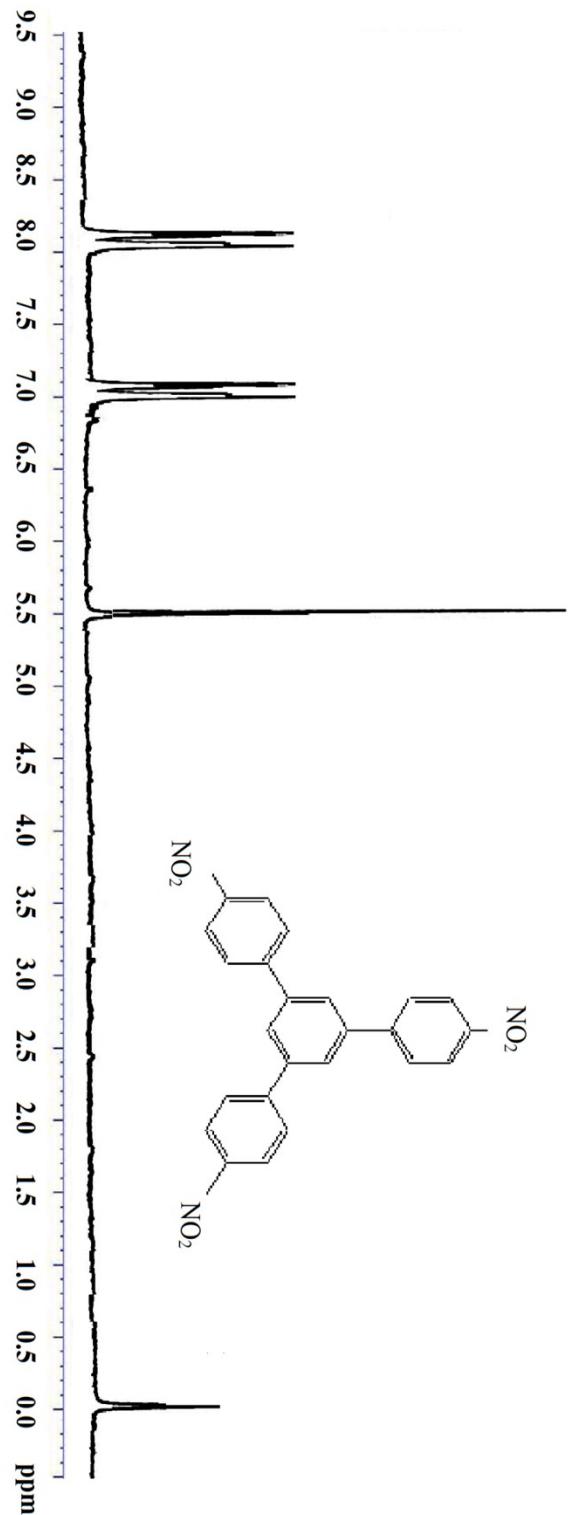


Fig. S13. ^1H -NMR spectrum of 1, 3, 5-tris(4-nitrophenyl)benzene.

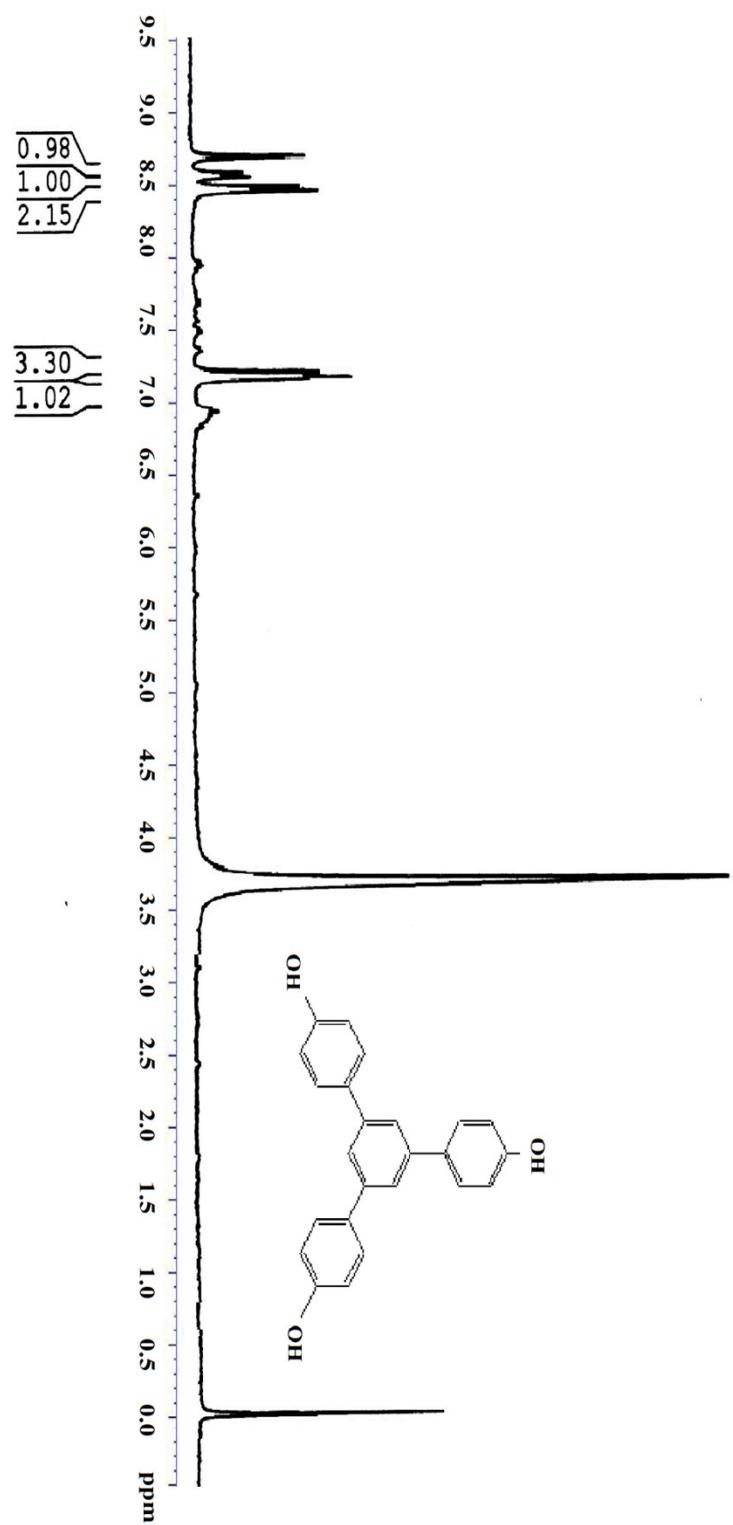


Fig. S14. ¹H-NMR spectrum of 1, 3, 5-tris(4-hydroxyphenyl)benzene.

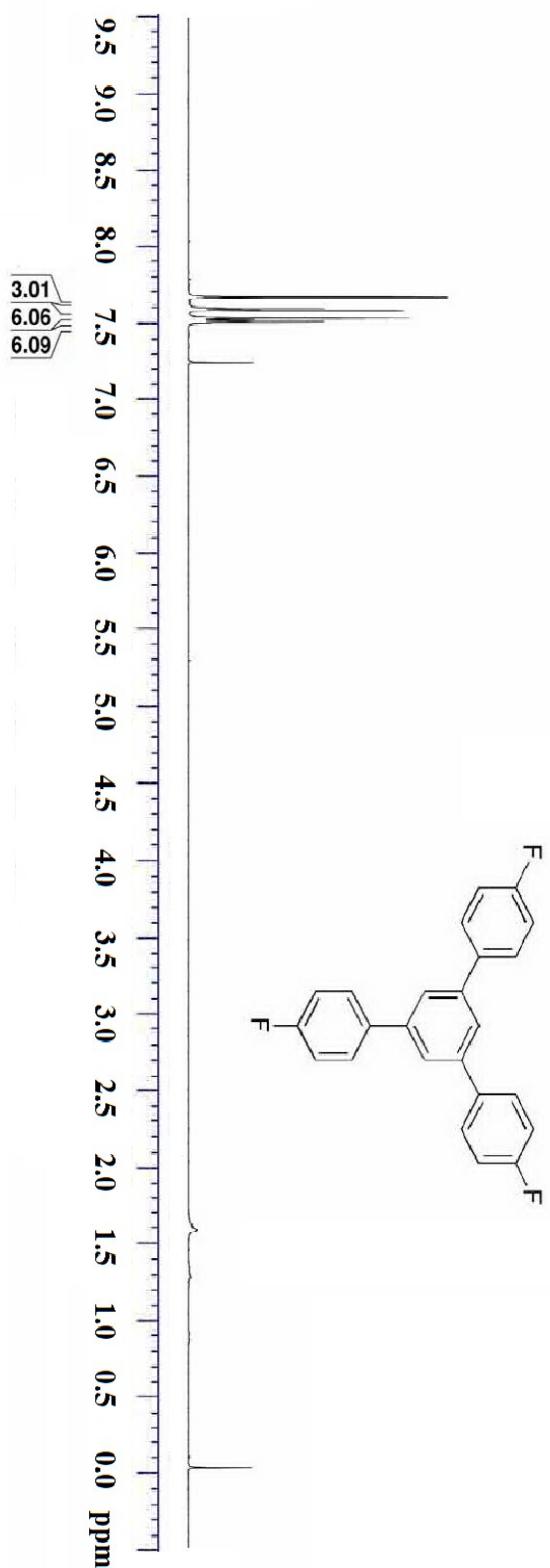


Fig. S15. ¹H-NMR spectrum of 1, 3, 5-tris(4-fluorophenyl)benzene.

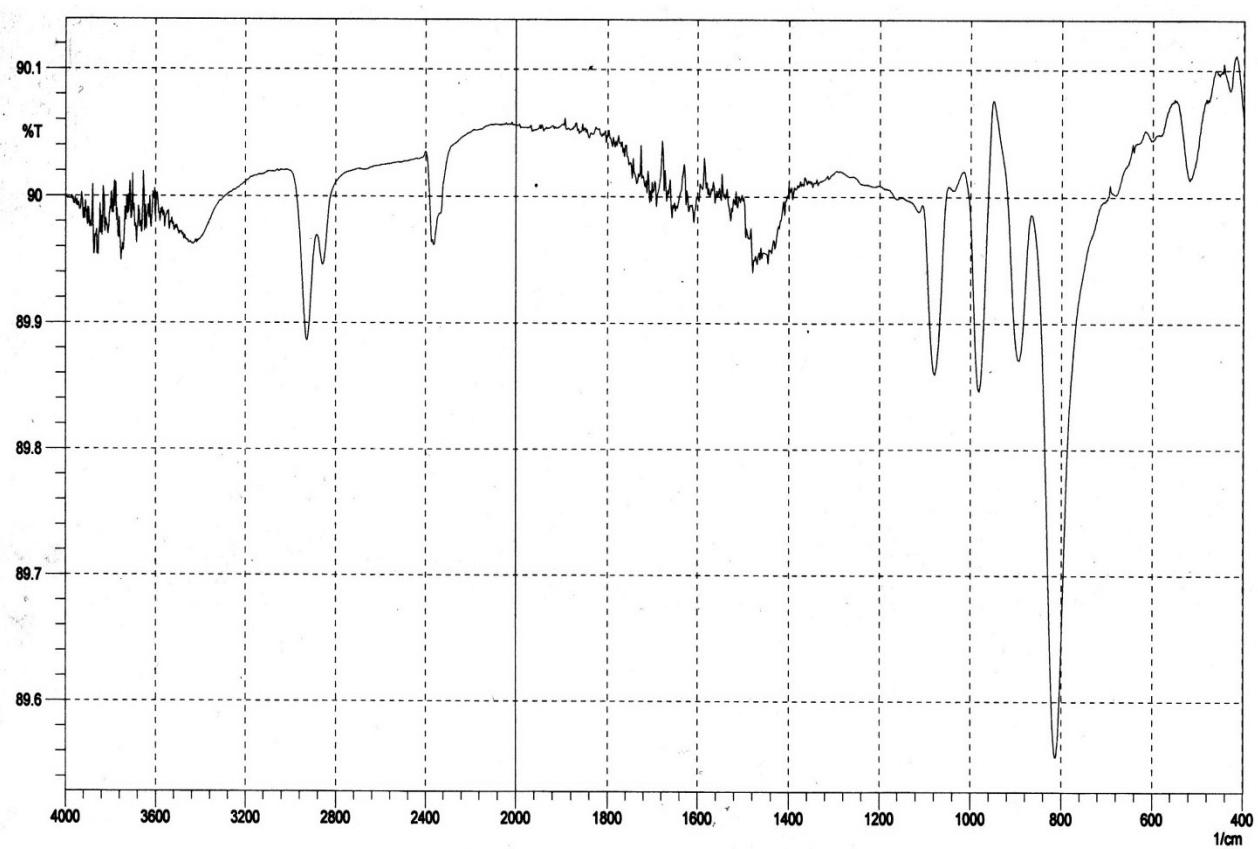


Fig. S16. FT-IR spectrum of 1, 3, 5-triphenylbenzene.

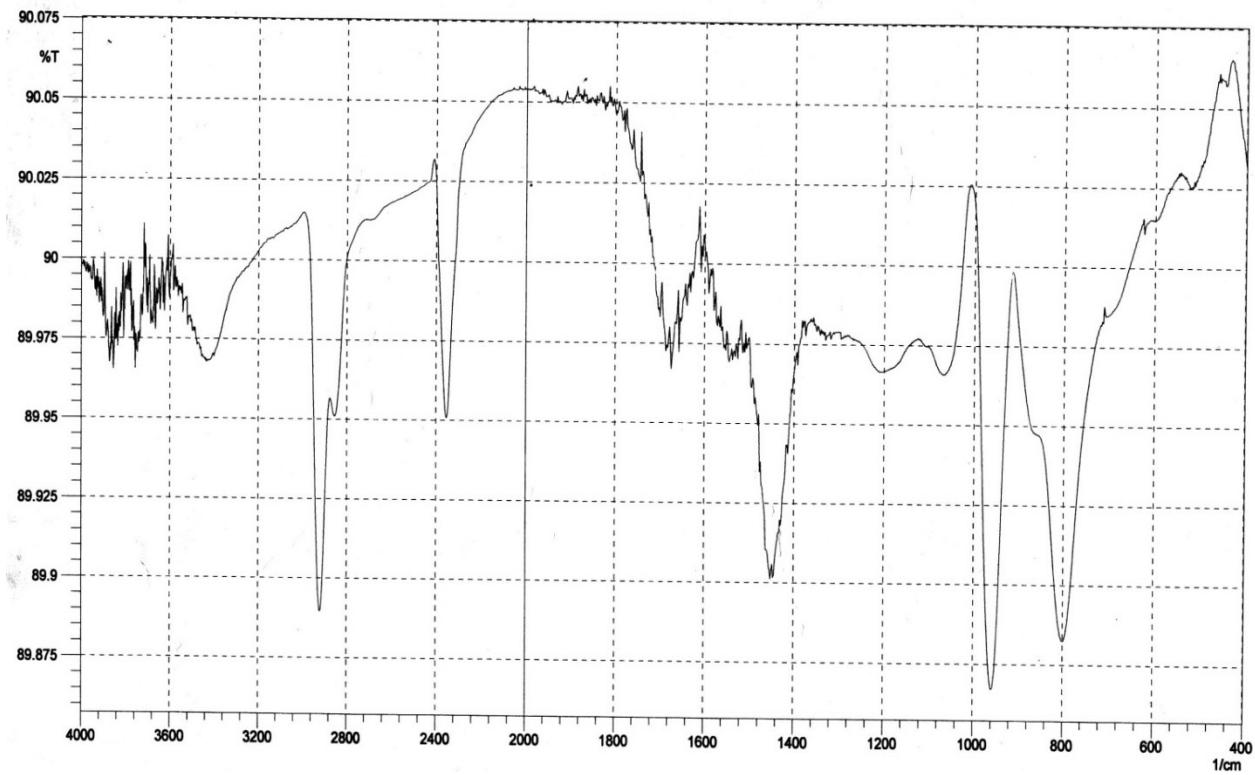


Fig. S17. FT-IR spectrum of trindan.

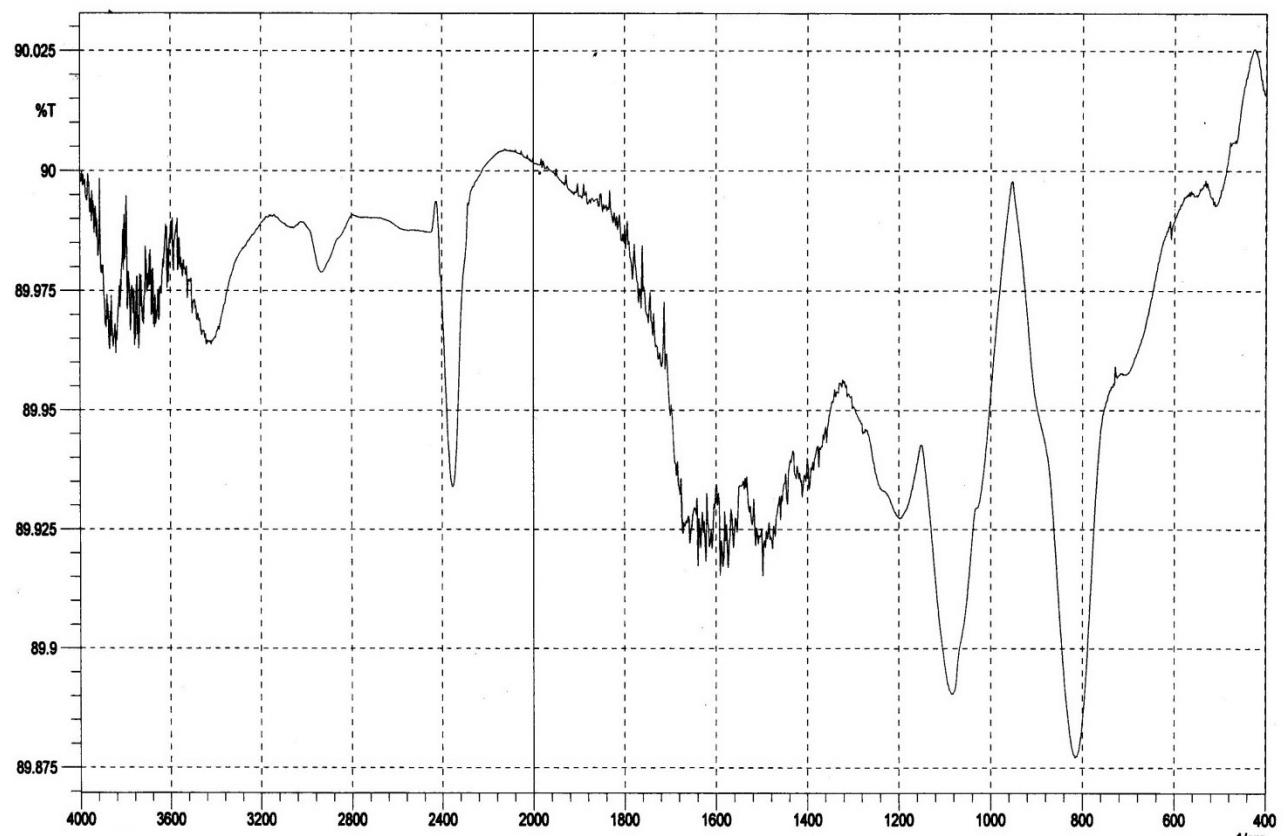


Fig. S18. FT-IR spectrum of 1, 3, 5-tris(4-chlorophenyl)benzene.

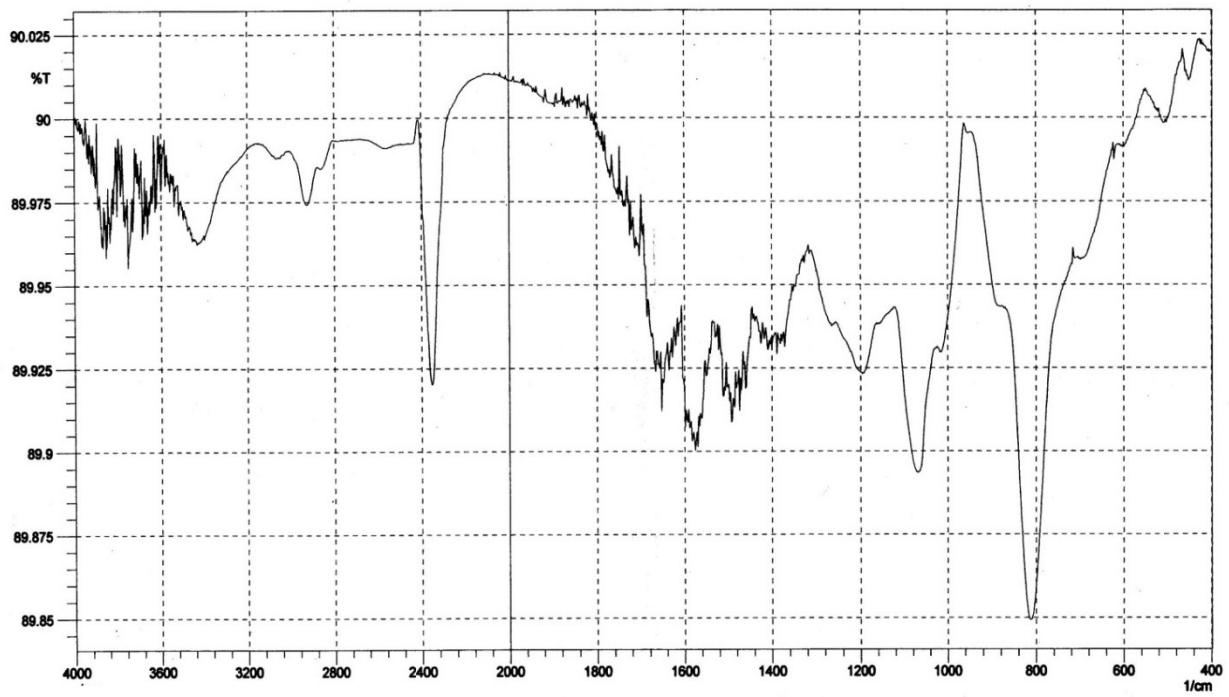


Fig. S19. FT-IR spectrum of 1, 3, 5-tris(4-bromophenyl)benzene.

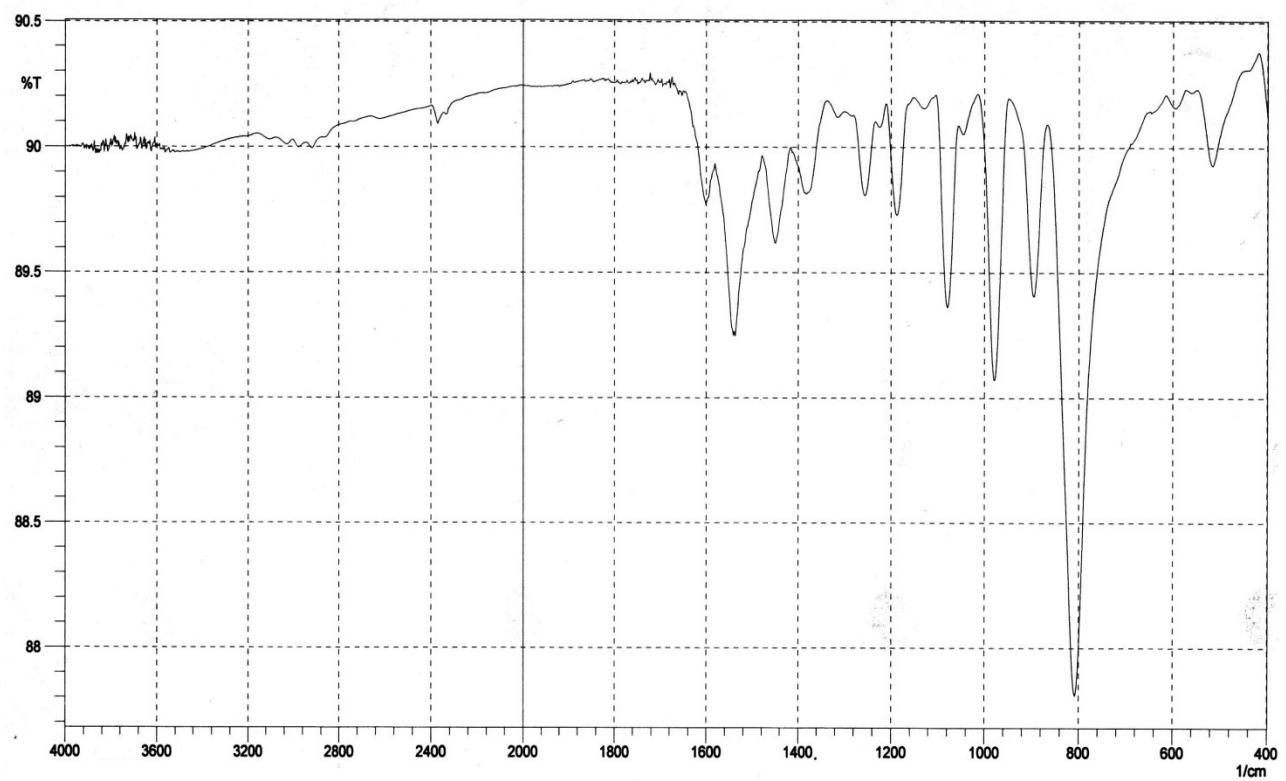


Fig. S20. FT-IR spectrum of 1, 3, 5-tris(4-fluorophenyl)benzene.

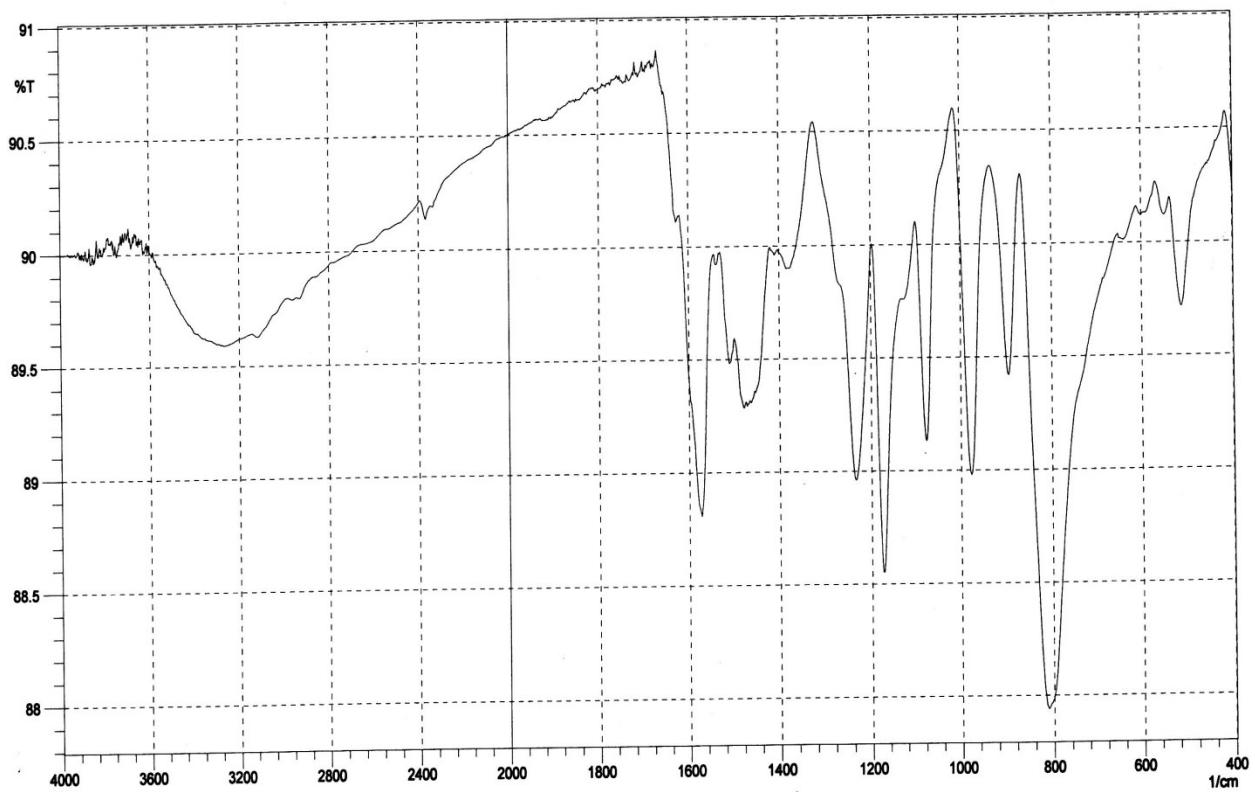


Fig. S21. FT-IR spectrum of 1, 3, 5-tris(4-hydroxyphenyl)benzene.

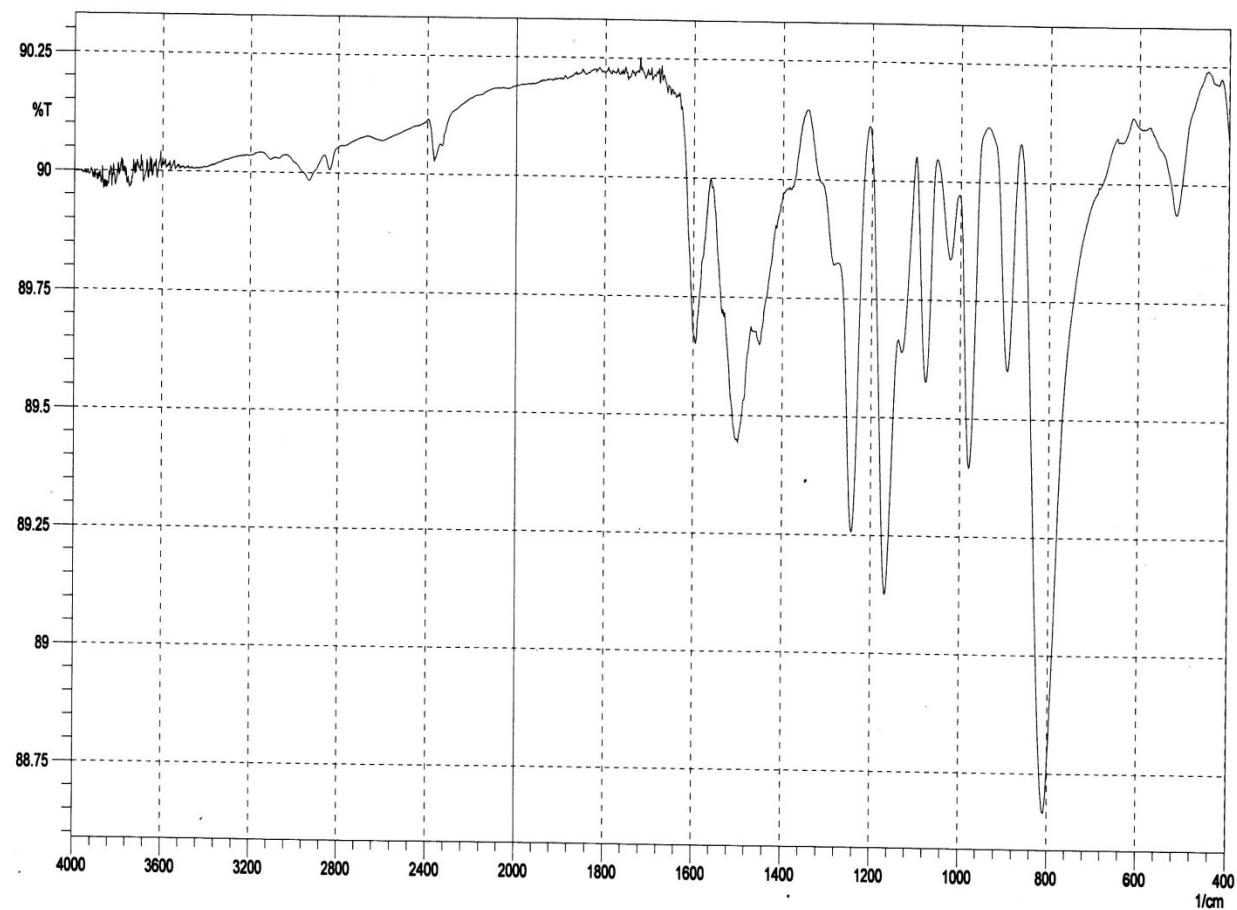


Fig. S22. FT-IR spectrum of 1,3,5-tris(4-methoxyphenyl)benzene.

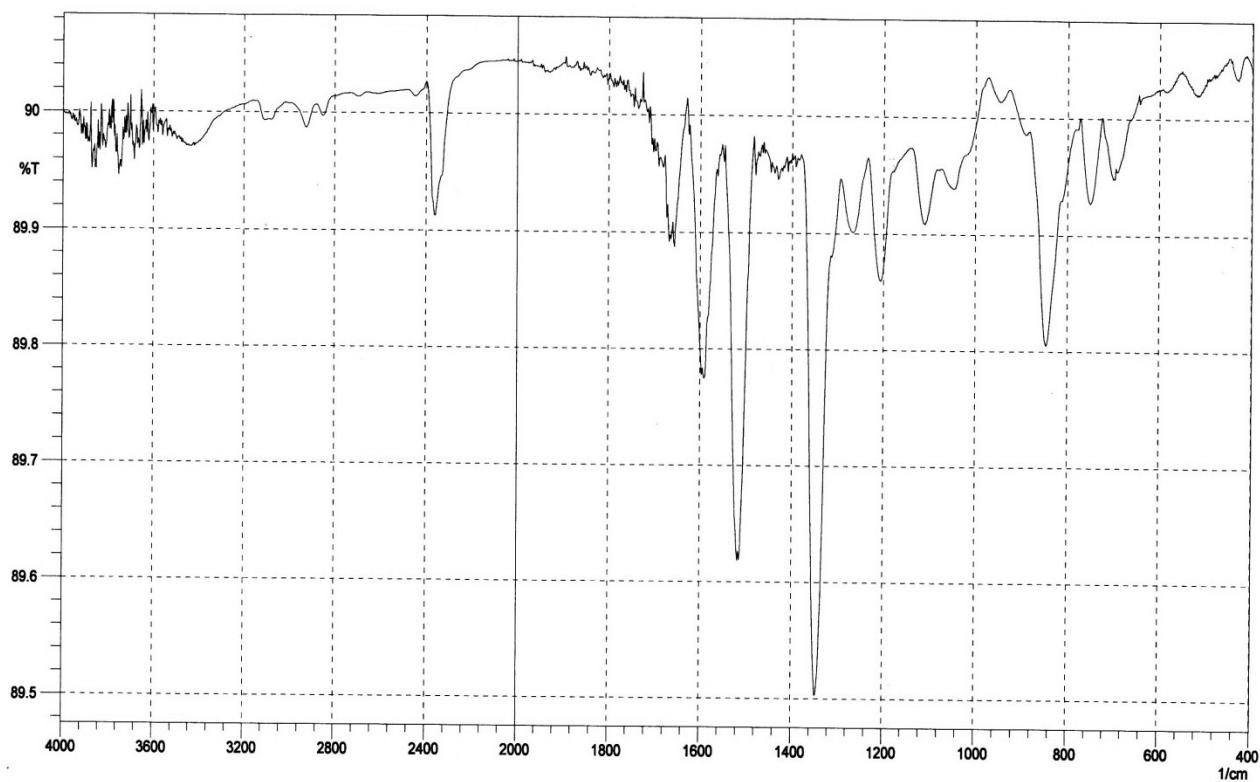


Fig. S23. FT-IR spectrum of 1, 3, 5-tris(4-nitrophenyl)benzene.

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