Synthesis of triphenylamines via ligand-free selective ring-opening of benzoxazoles or benzothiazoles under superparamagnetic nanoparticle catalysis

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Supporting Information

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 ^{o}C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 ^{o}C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM).

Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 80 kV. The $CuFe_2O_4$ sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 ^oC for 1 min; heated them from 100 ^oC to 280 ^oC at 40 ^oC/min; held them at 280 ^oC for 4.5 min. Inlet and detector temperatures were set constant at 280 ^oC. The GC yield was calculated using diphenyl ether as the internal standard. GC-MS analyses were analyzed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 50 ^oC for 2 min; heated samples from 50 to 280^oC at 10 ^oC/min and held them at 280 ^oC for 10 min. Inlet temperature was set constant at 280 oC. MS spectra were compared with the spectra gathered in the NIST library. The ^1H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

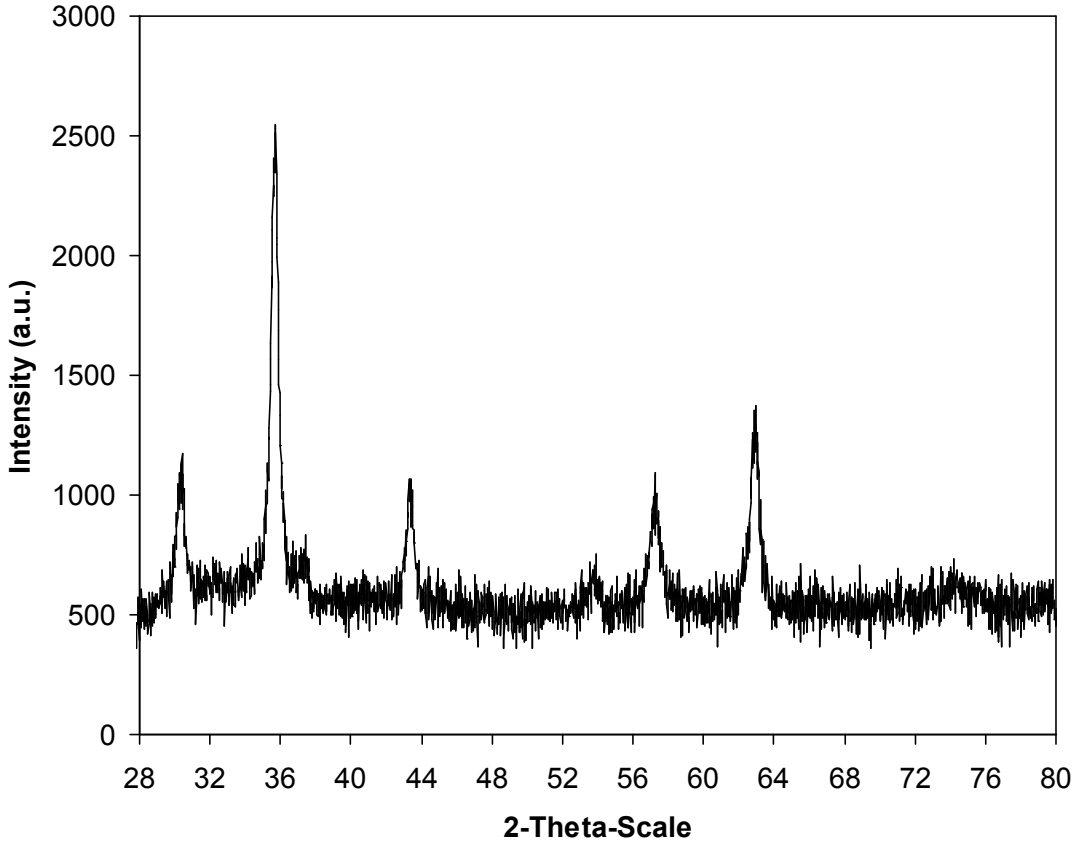

Fig. S1. X-ray powder diffractograms of the $CuFe_2O_4$ catalyst.

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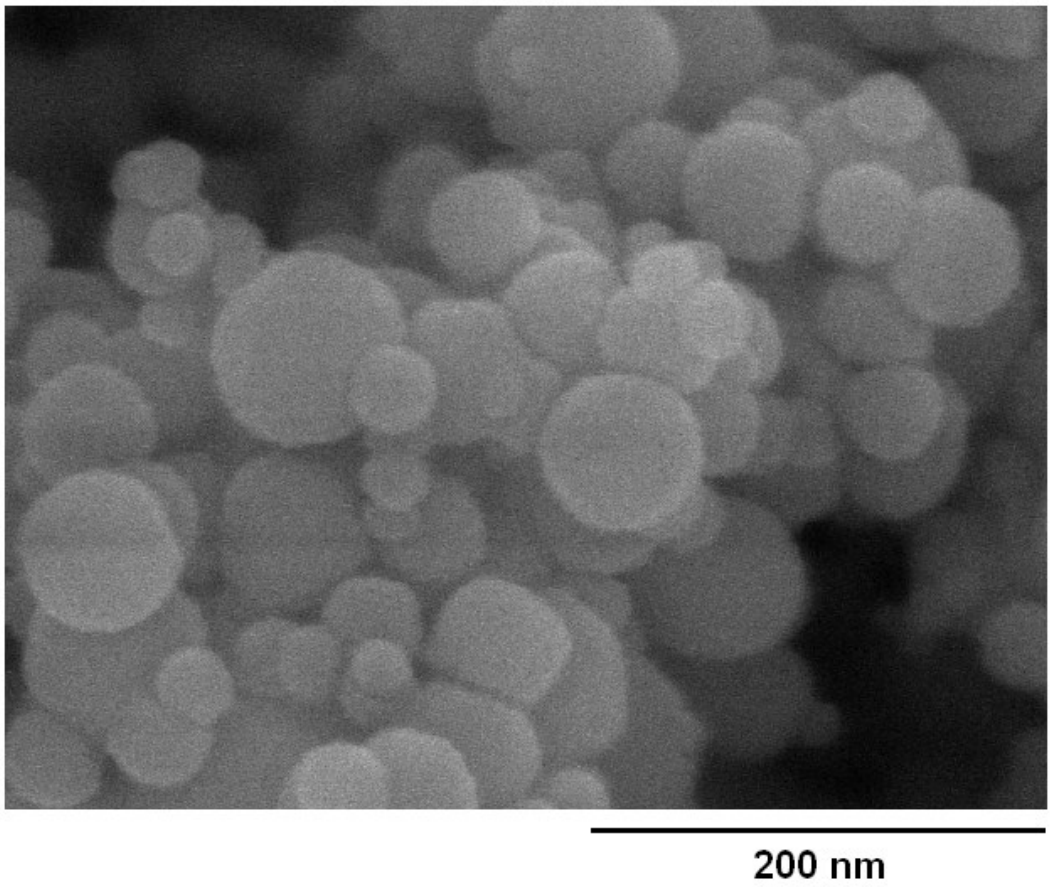


Fig. S2. SEM micrograph of the $CuFe_2O_4$ catalyst.

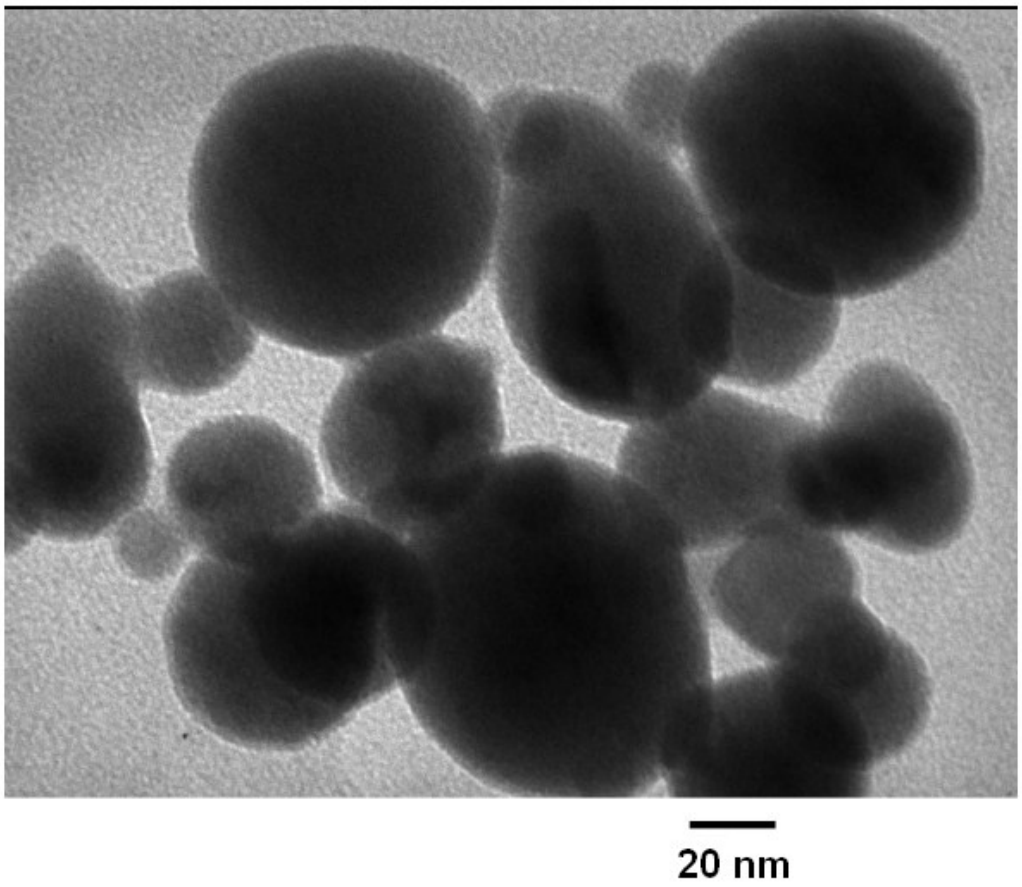


Fig. S3. TEM micrograph of the $CuFe_2O_4$ catalyst.

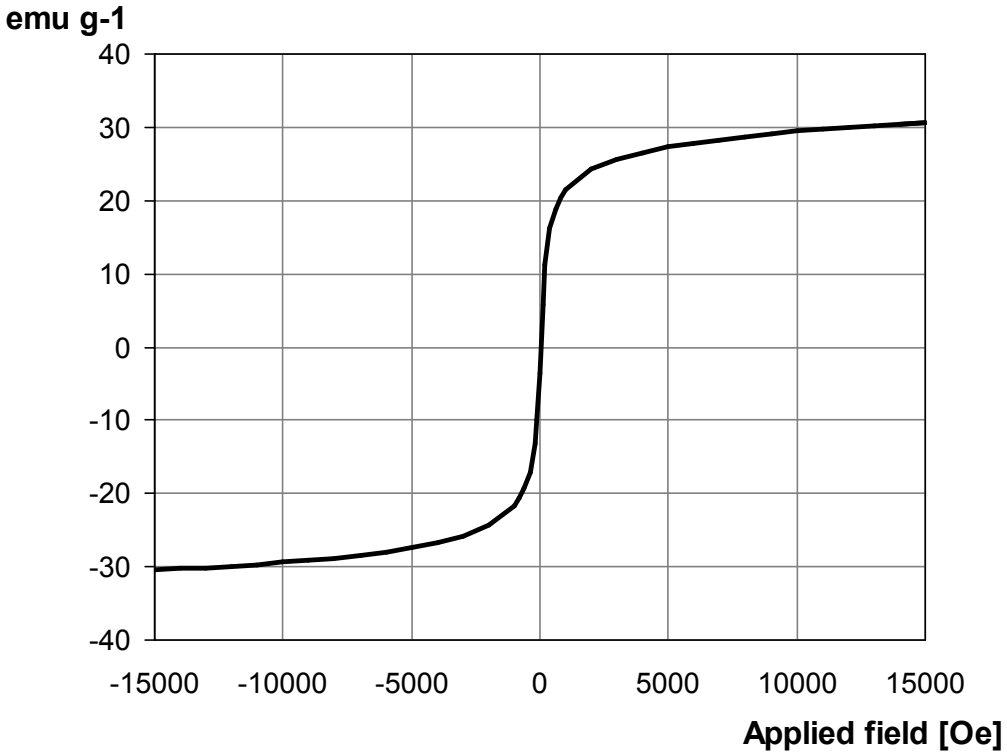


Fig. S4. Magnetization curves for the $CuFe_2O_4$ catalyst measured at room temperature.

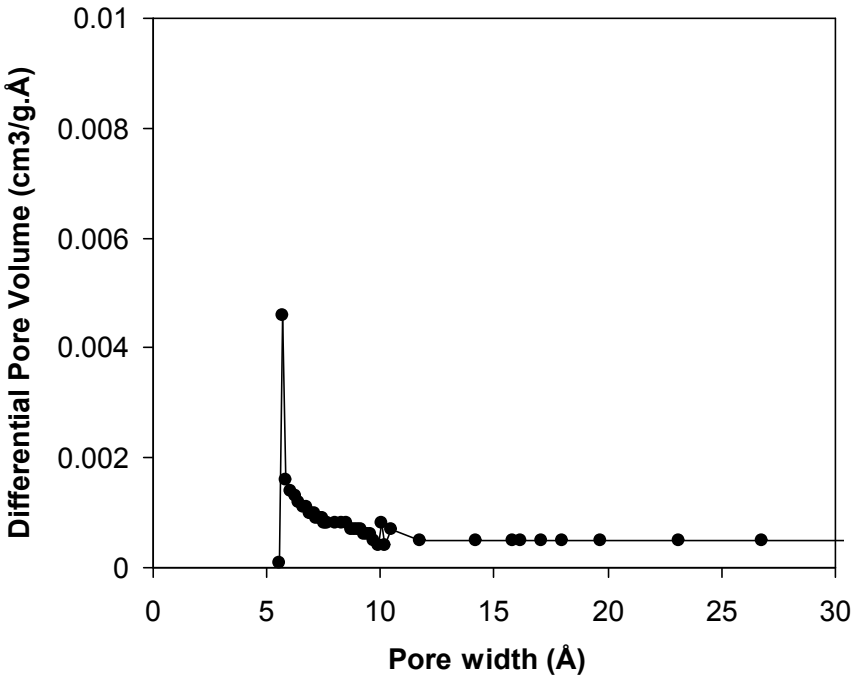


Fig. S5. Pore size distribution of the $CuFe_2O_4$ catalyst.

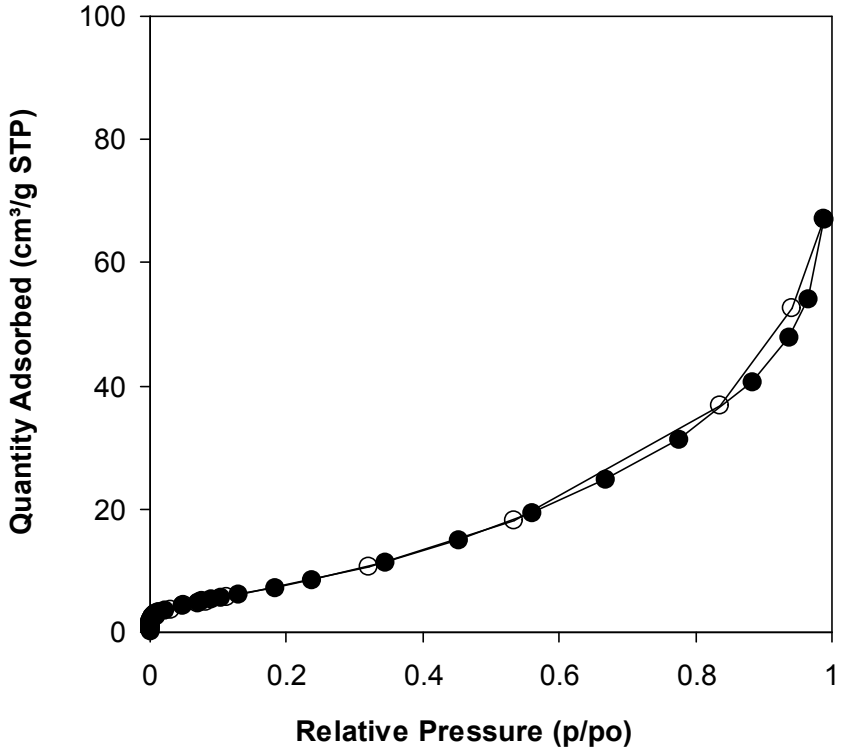


Fig. S6. Nitrogen adsorption/desorption isotherm of the $CuFe_2O_4$ catalyst. Adsorption data are shown as closed circles and desorption data as open circles.

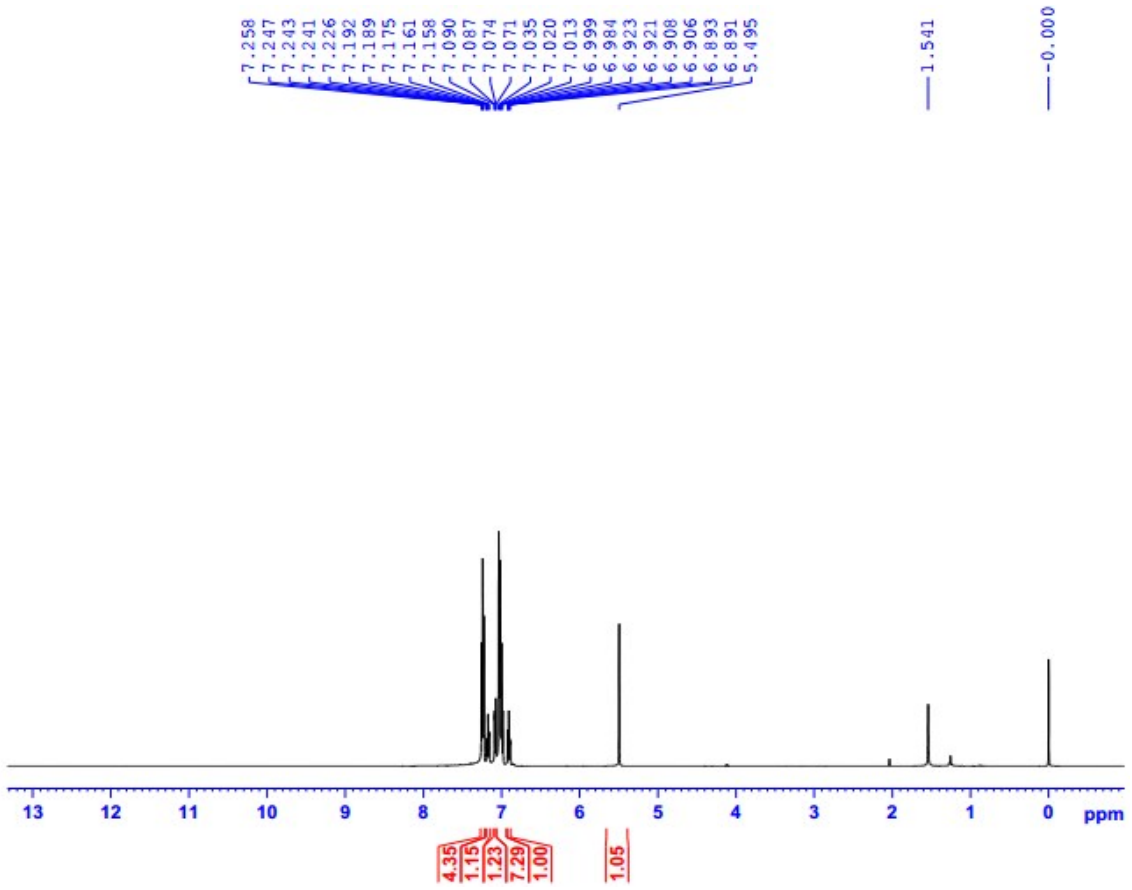


Fig. S7. ^{1}H-NMR spectra of 2-(diphenylamino)phenol.

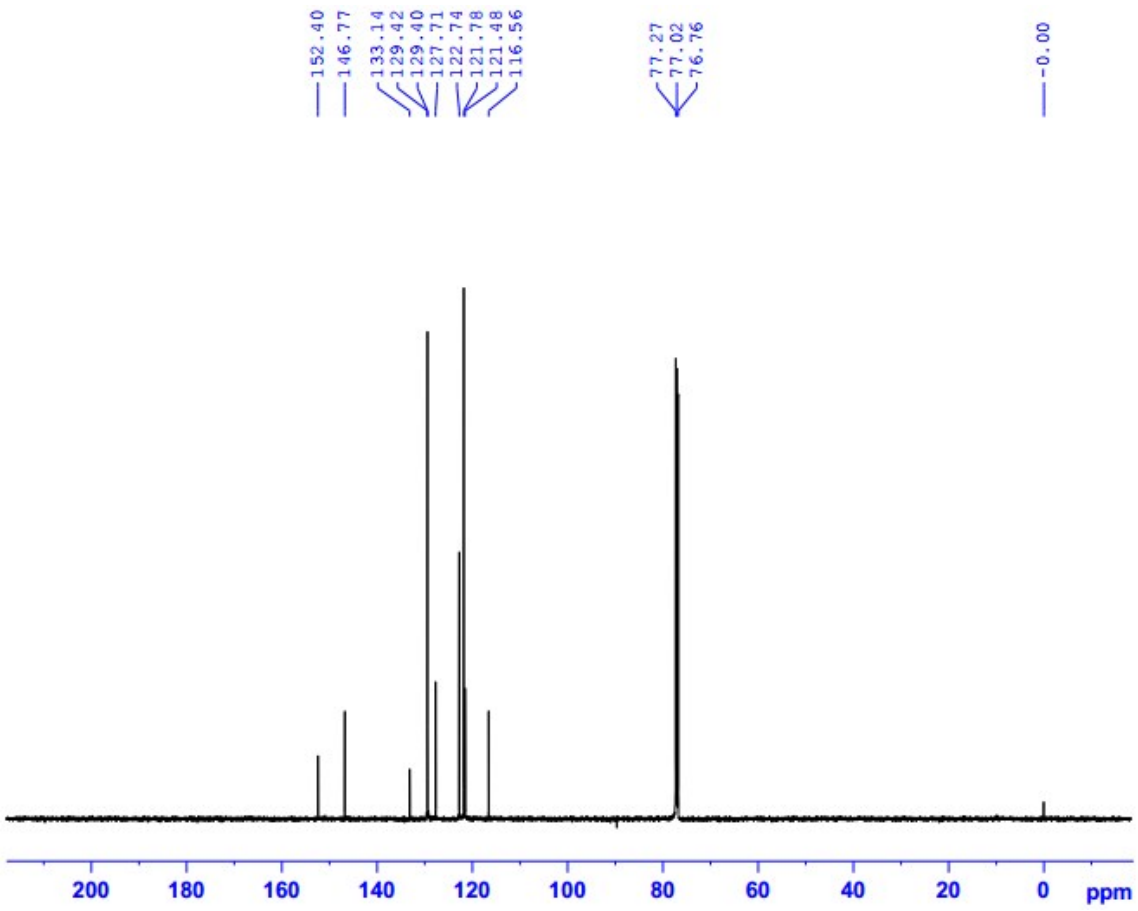
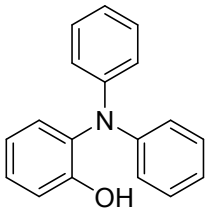


Fig. S8. ^{13}C-NMR spectra of 2-(diphenylamino)phenol.

Characterization data for 2-(diphenylamino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (cyclohexan/ethyl acetate = 15:1): white solid, 92% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 4H), 7.19 – 7.16 (m, 1H), 7.09 - 7.07 (dd, *J*= 6.5 Hz, 1H), 7.04 – 6.98 (m, 7H), 6.92 -

6.89 (m, 1H), 5.50 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 152.40, 146.77, 133.14, 129.42, 129.40, 127.71, 127.74, 121.78, 121.48, 116.56.

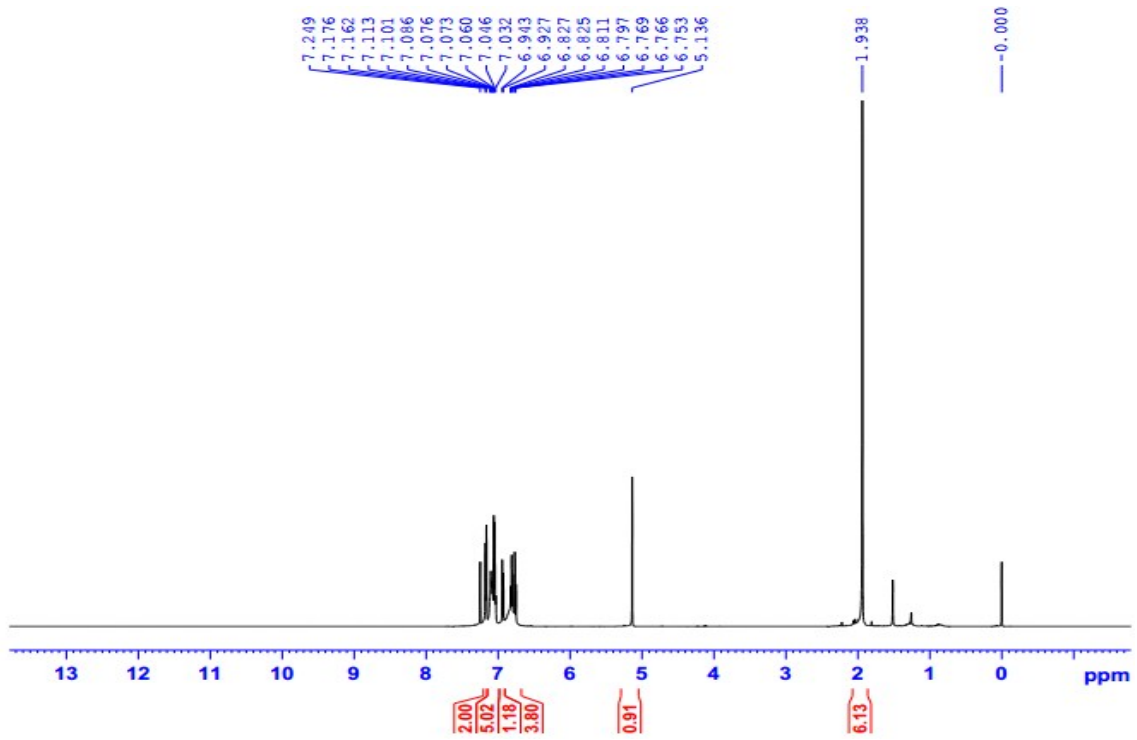


Fig. S9. ^{1}H-NMR spectra of 2-(di-o-tolylamino)phenol.

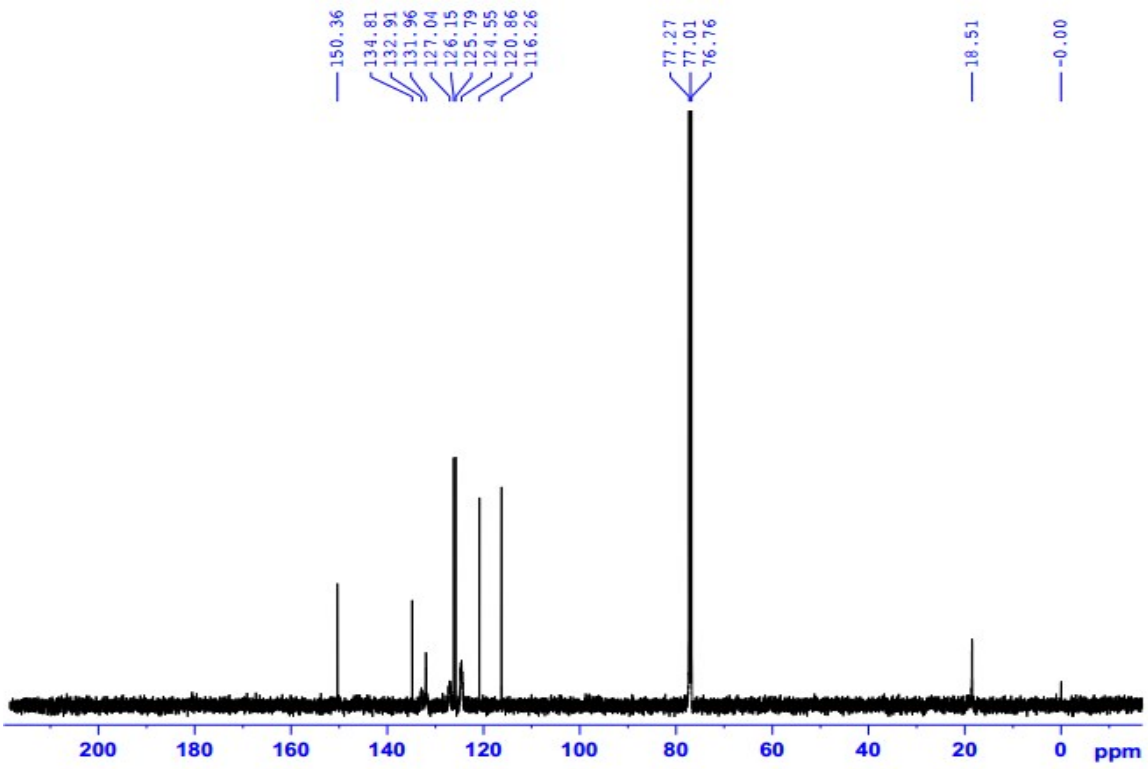
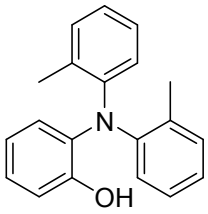


Fig. S10. ^{13}C-NMR spectra of 2-(di-o-tolylamino)phenol.

Characterization data for 2-(di-o-tolylamino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:8): yellow solid, 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J*= 7 Hz, 2H), 7.14 - 7.01 (m, 5H), 6.93 (d, *J*= 8 Hz, 1H), 6.84 - 6.74 (m, 4H), 5.14 (s, 1H), 1.94 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.36, 134.81, 132.91, 131.96, 127.04, 126.15, 125.79, 124.55, 120.86, 116.26, 18.51.

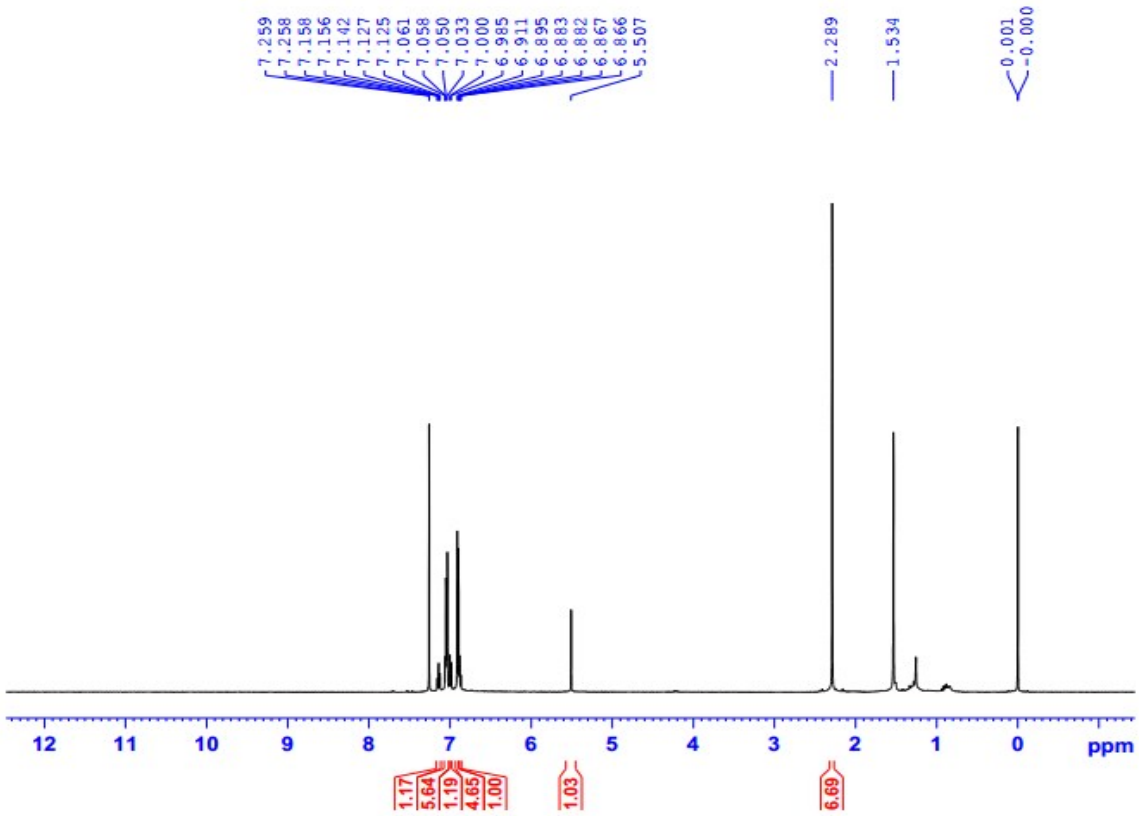


Fig. S11. ^{1}H-NMR spectra of 2-(di-*p*-tolylamino)phenol.

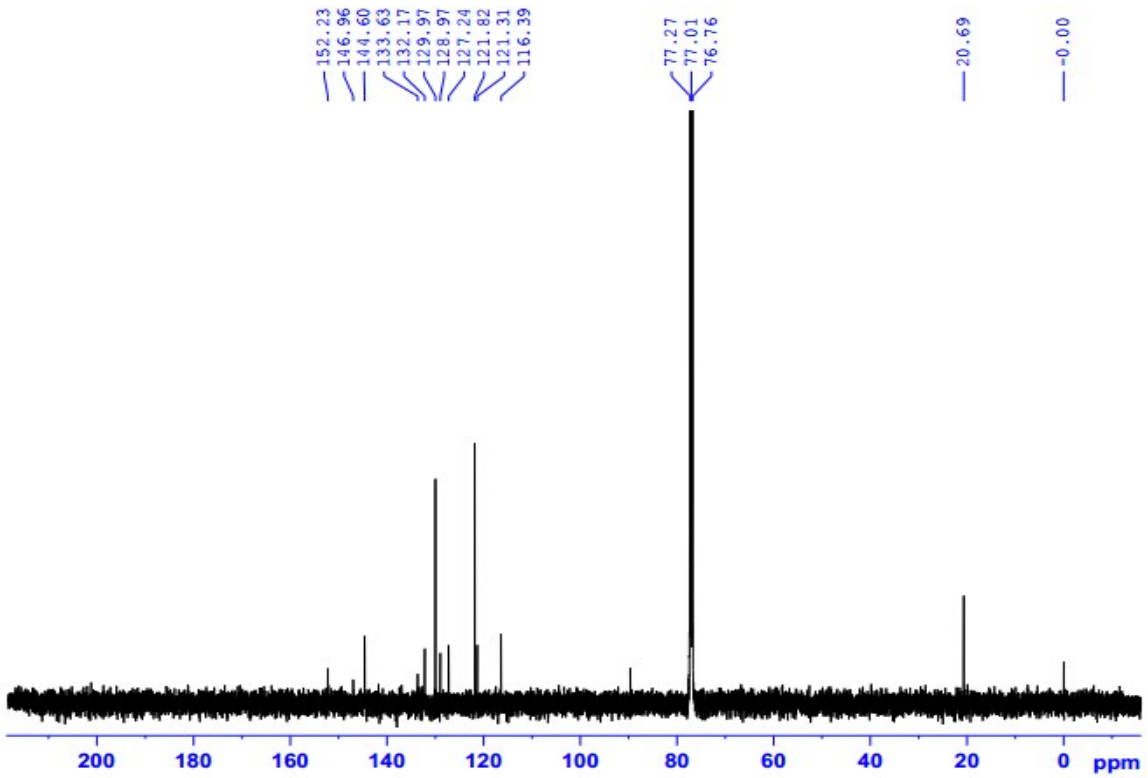
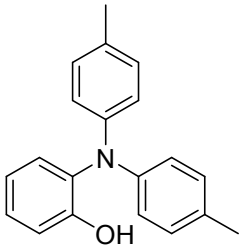


Fig. S12. ^{13}C-NMR spectra of 2-(di-*p*-tolylamino)phenol.

Characterization data for 2-(di-*p*-tolylamino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): light brown solid, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 - 7.12 (m, 1H), 7.06 - 7.03 (m, 5H), 6.92 (d, *J*= 7.5 Hz, 1H), 6.90 (d, *J*= 8 Hz, 4H), 6.88 - 6.86 (d, *J*= 7,5 Hz, 1H), 5.51 (s, 1H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.23, 144.96, 133.63, 132.17, 129.97, 128.97, 127.24, 121.82, 121.31, 116.39, 20.69.

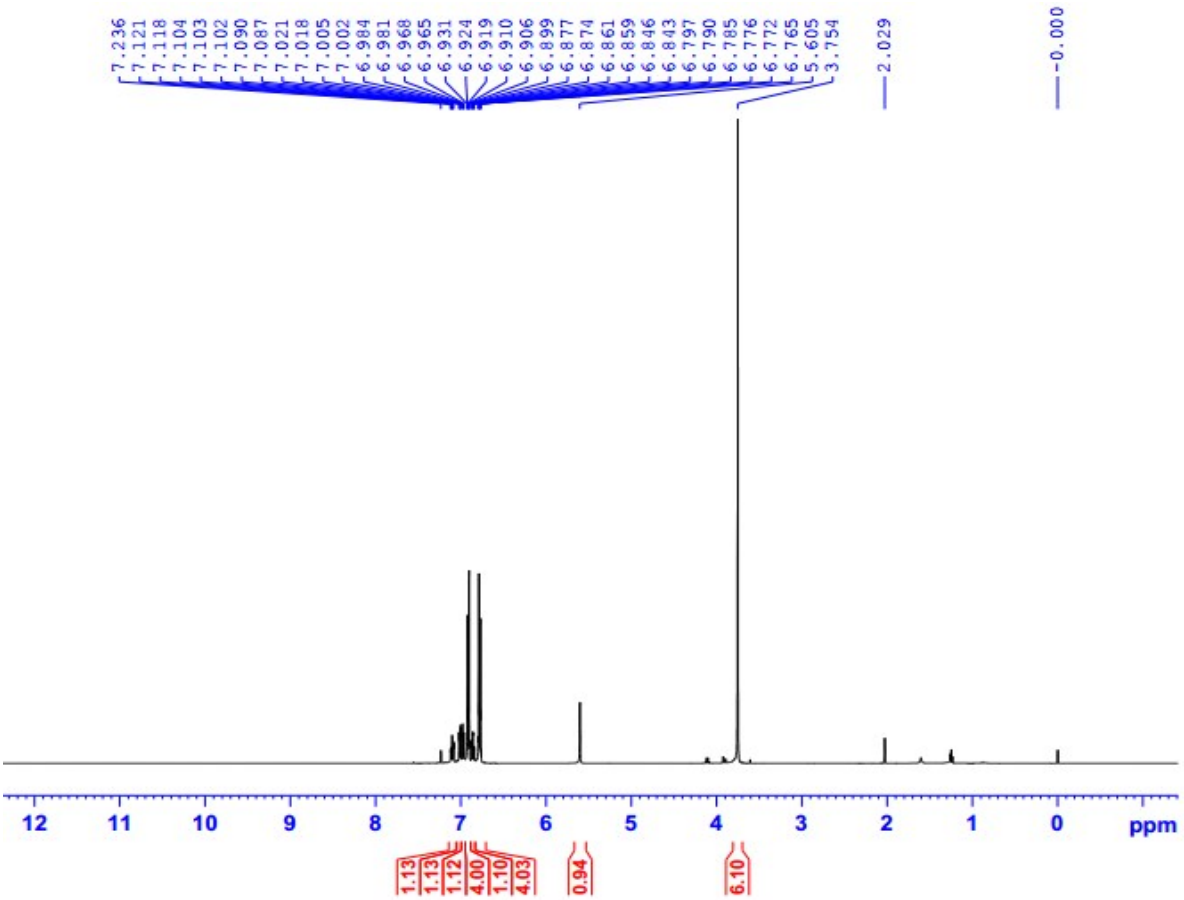


Fig. S13. ^{1}H-NMR spectra of 2-(bis(4-methoxyphenyl)amino)phenol.

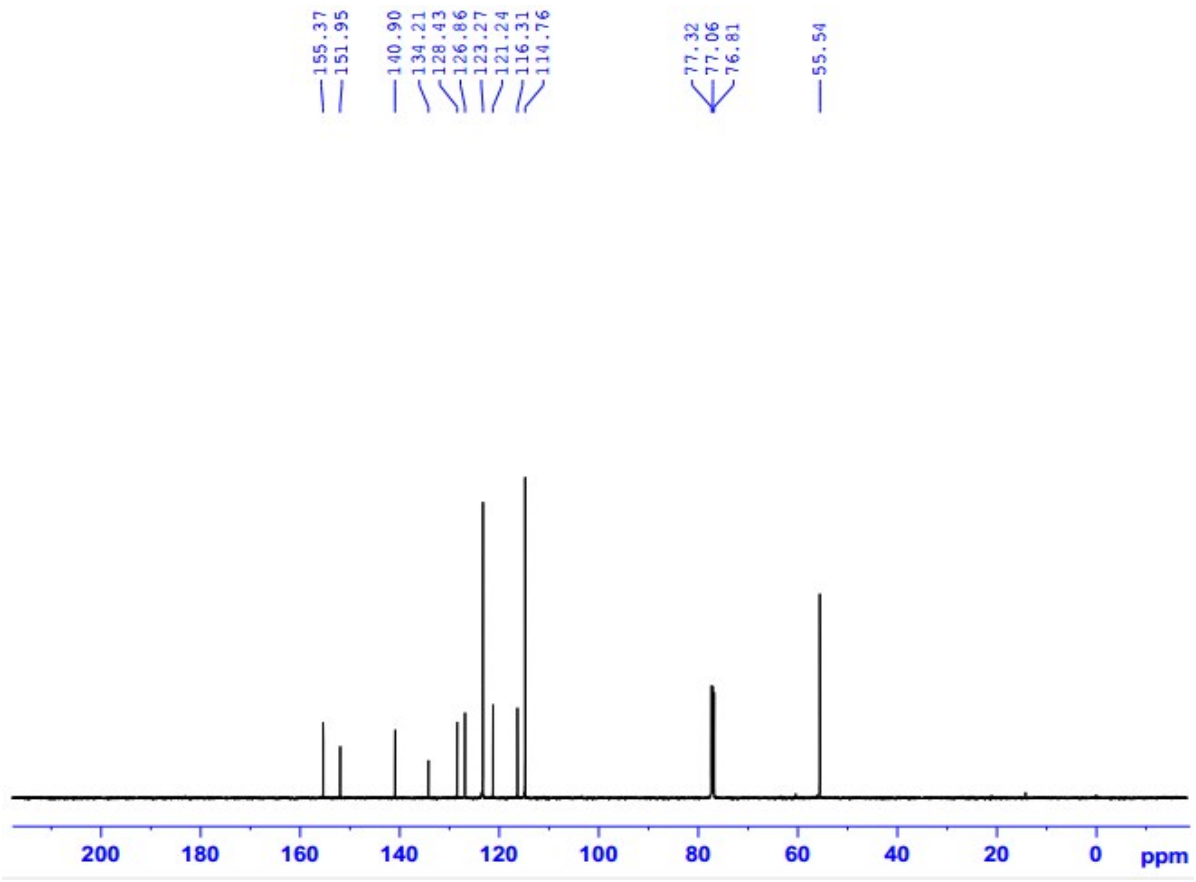
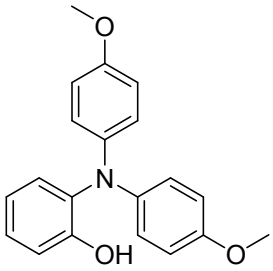


Fig. S14. ^{13}C-NMR spectra of 2-(bis(4-methoxyphenyl)amino)phenol.

Characterization data for 2-(bis(4-methoxyphenyl)amino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:3): yellow solid, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 - 7.08 (m, 1H), 7.03 - 6.99 (d, *J*= 6.5 Hz, 1H), 6.99-6.96 (d, *J*= 6 Hz, 1H), 6.94 - 6.89 (m, 4H), 6.88 - 6.84

(m, 1H), 6.81- 6.76 (m, 4H), 5.60 (s, 1H), 3.75 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.37, 151.95, 140.9, 134.21, 128.43, 126.86, 123.27 121.24, 116.31, 144.76, 55.54.

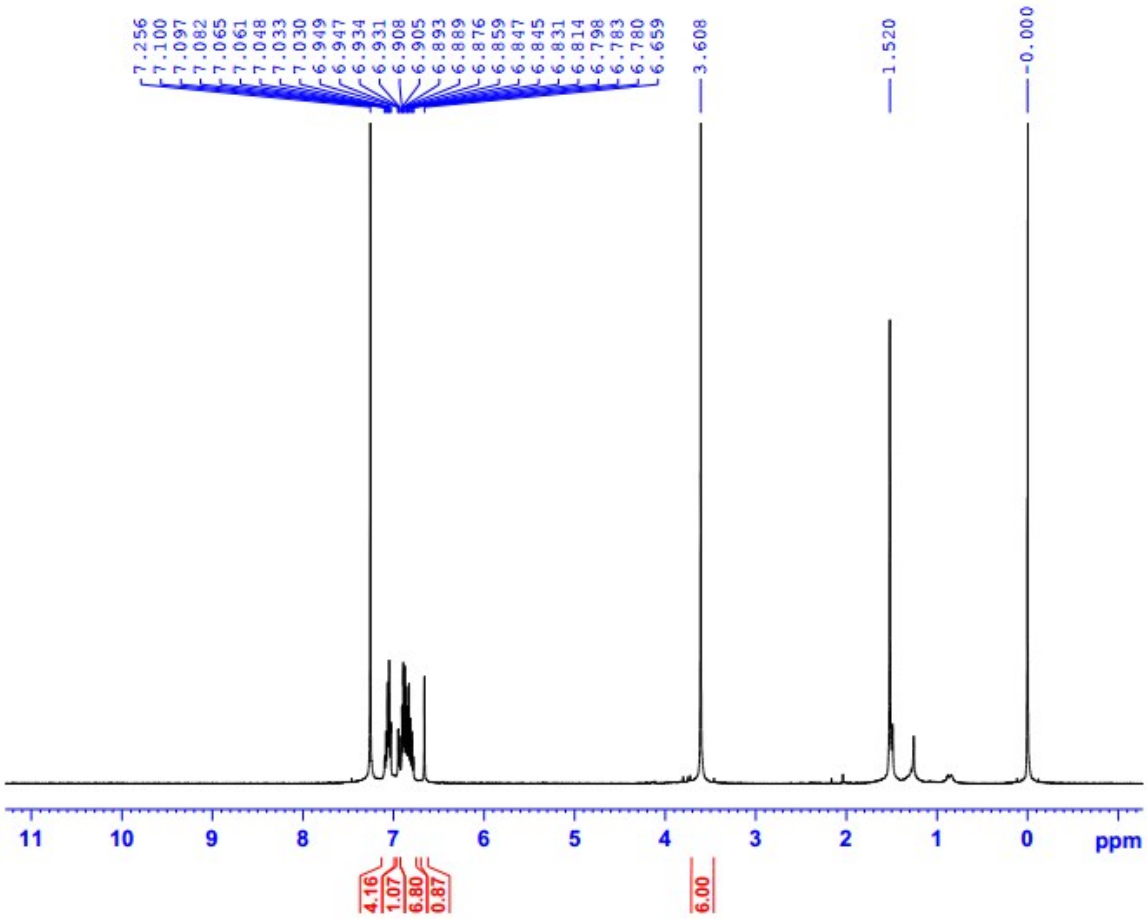


Fig. S15. ^{1}H-NMR spectra of 2-(bis(2-methoxyphenyl)amino)phenol.

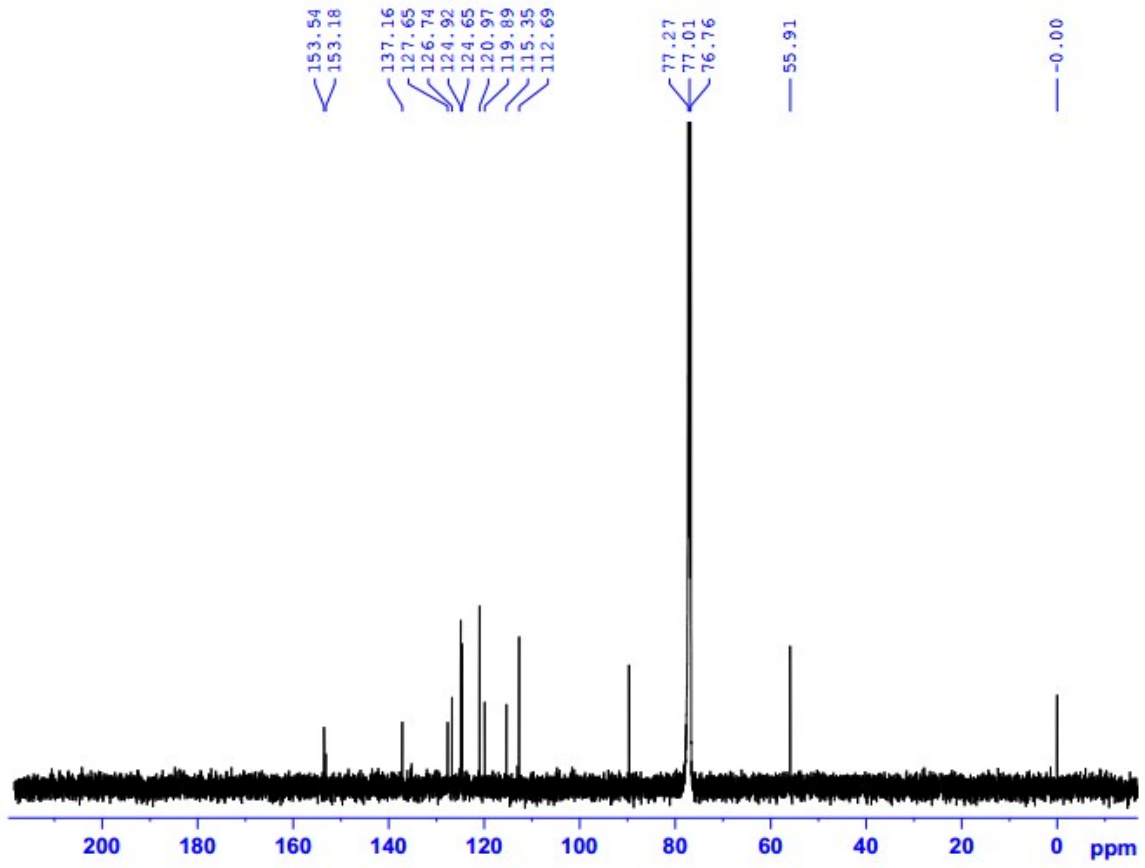
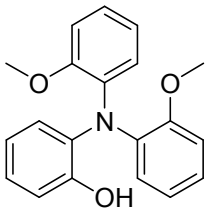


Fig. S16. ^{13}C-NMR spectra of 2-(bis(2-methoxyphenyl)amino)phenol.

Characterization data for 2-(bis(2-methoxyphenyl)amino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): yellow solid, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 - 7.03 (m, 4H), 6.95 - 6.93 (dd, *J*= 6.5 Hz, 1H), 6.91 - 6.78 (m, 7H), 6.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.54, 153.18, 137.16, 127.65, 126.74, 124.92, 124.65, 120.97, 119.89, 115.35, 112.69, 55.91.

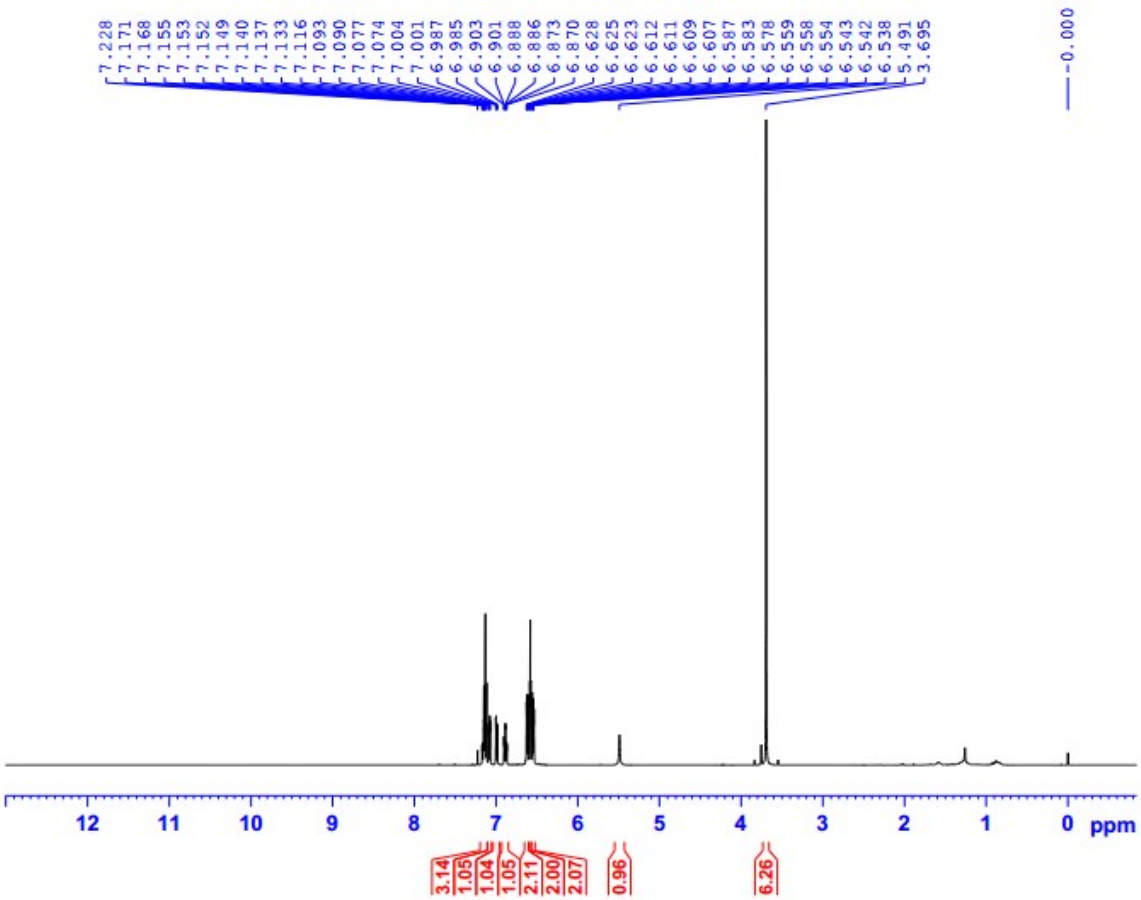


Fig. S17. ^{1}H-NMR spectra of 2-(bis(3-methoxyphenyl)amino)phenol.

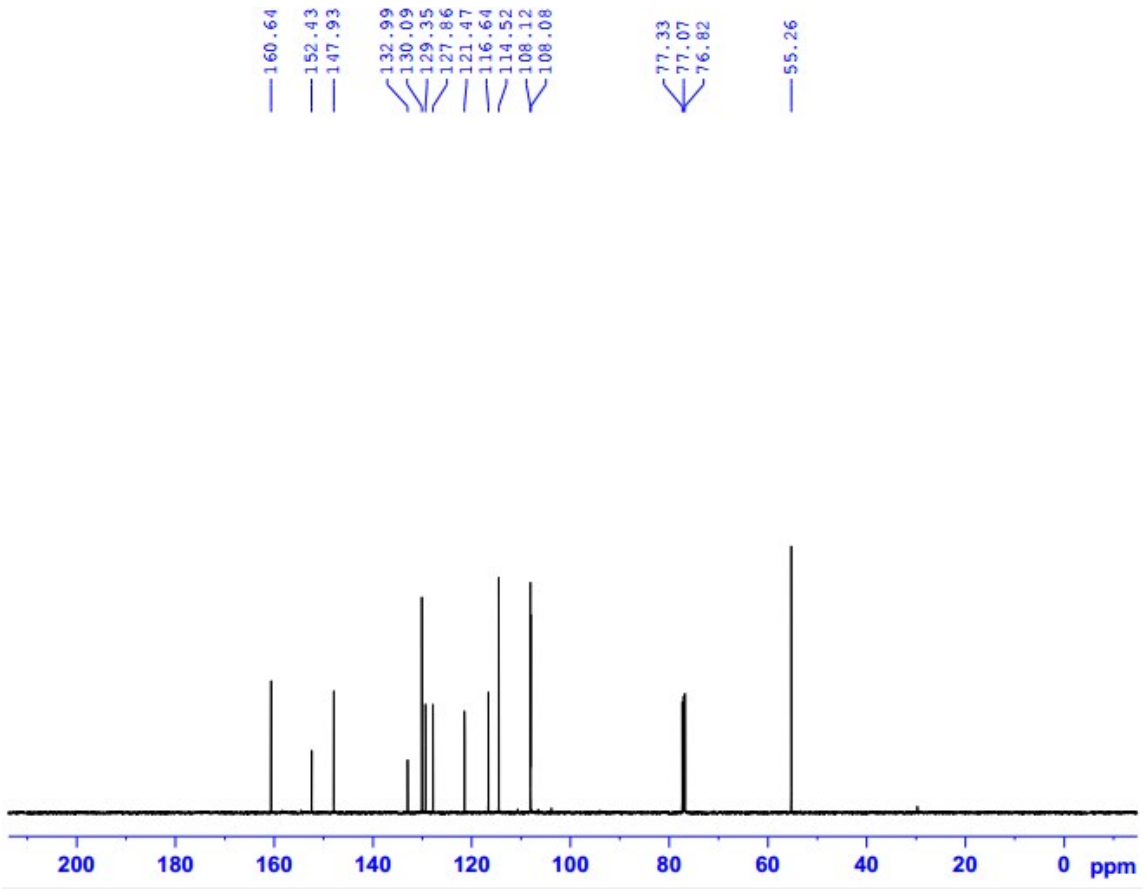
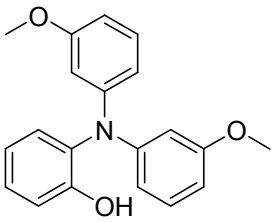


Fig. S18. ^{13}C-NMR spectra of 2-(bis(3-methoxyphenyl)amino)phenol.

Characterization data for 2-(bis(3-methoxyphenyl)amino)phenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:4): yellow solid, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 - 7.07 (m, 4H), 7.00 - 6.98 (dd, *J*= 7 Hz, 1H), 6.90 - 6.87 (m, 1H), 6,63 - 6,54 (m, 6H), 5.49 (s, 1H), 3.69 (s,

6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.64, 152.43, 147.93, 132.99, 130.09, 129.35, 127.86, 121.47, 116.64, 114.52, 108.12, 108.08, 55.26.

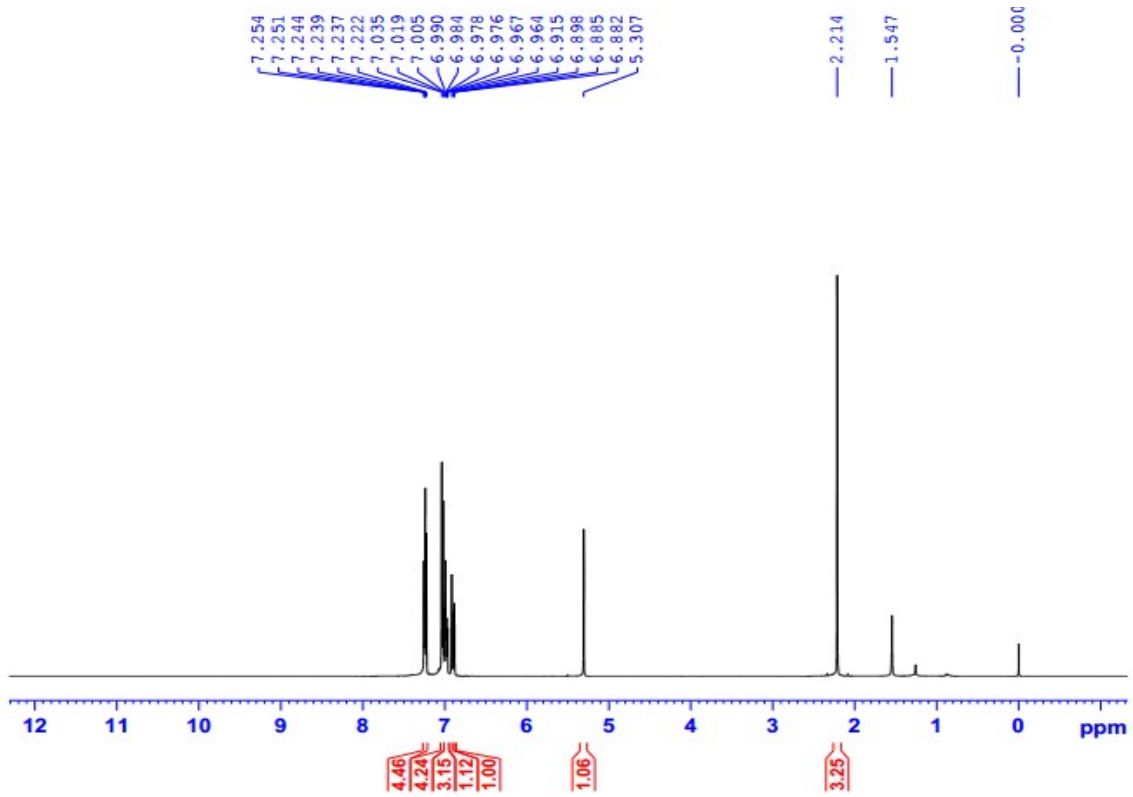


Fig. S19. ^{1}H-NMR spectra of 2-(diphenylamino)-4-methylphenol.

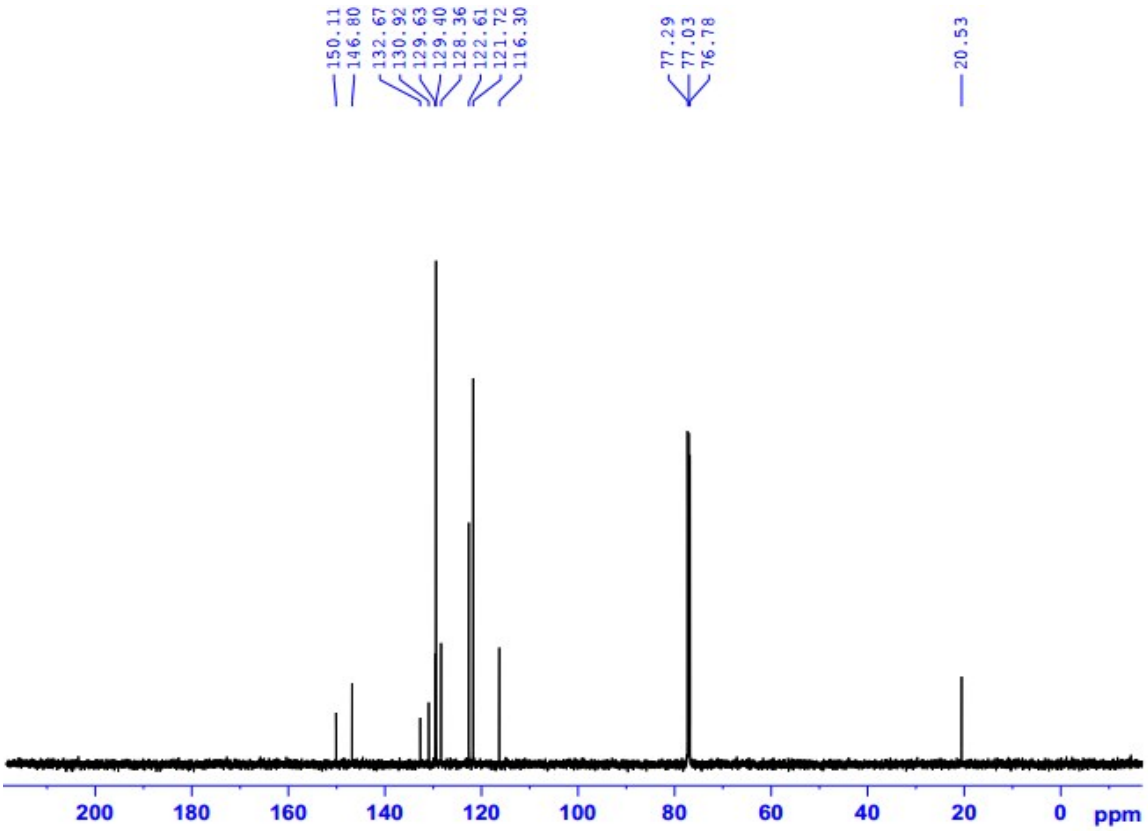
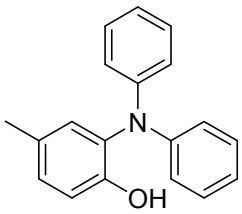


Fig. S20. ^{13}C-NMR spectra of 2-(diphenylamino)-4-methylphenol.

Characterization data for 2-(diphenylamino)-4-methylphenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:8): yellow iol, 86% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.25 - 7.22 (m, 4H), 7.03 (d, *J*= 7.5 Hz, 4H), 7.00 – 6.96 (m, 3H), 6.96 (d, *J*= 8.5 Hz, 1H), 6.88 (s, 1H), 5.31 (s, 1H), 2.21 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 150.11, 146.80, 132.67, 130.92, 129.63, 129.40, 128.36, 122.61, 121.72, 116.30.

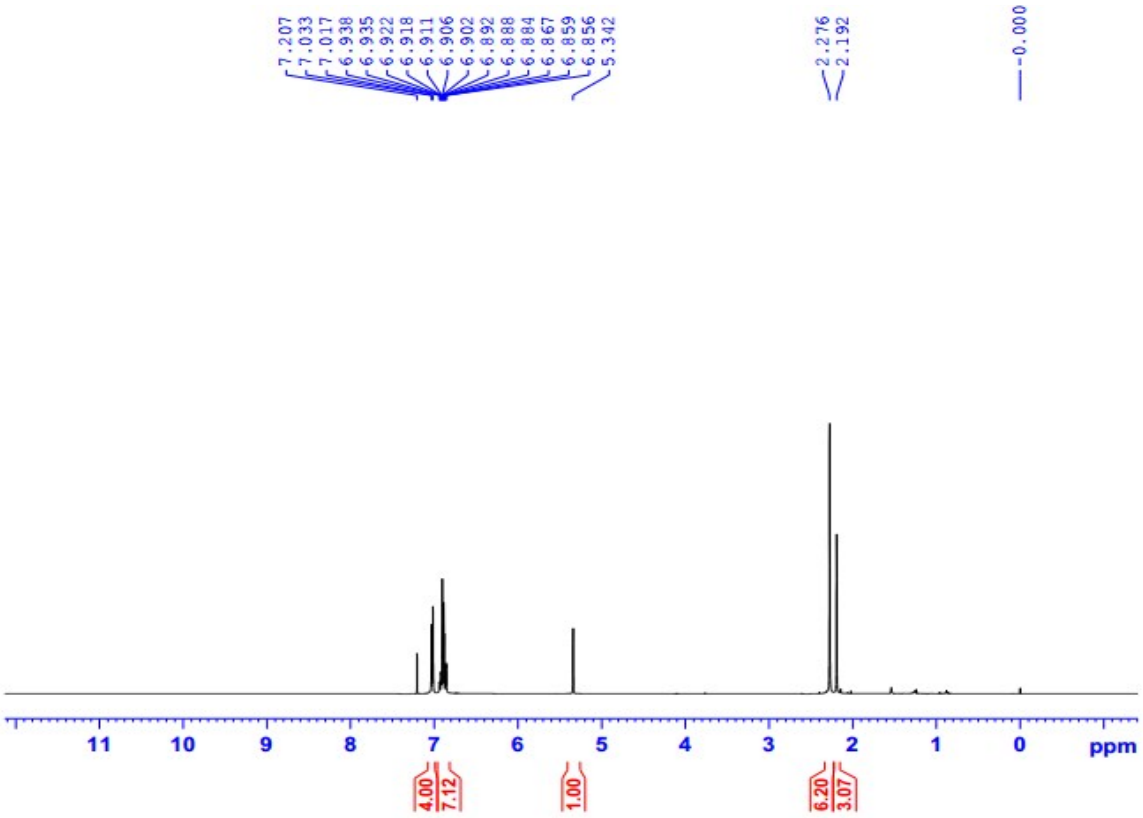


Fig. S21. ^{1}H-NMR spectra of 2-(di-*p*-tolylamino)-4-methylphenol.

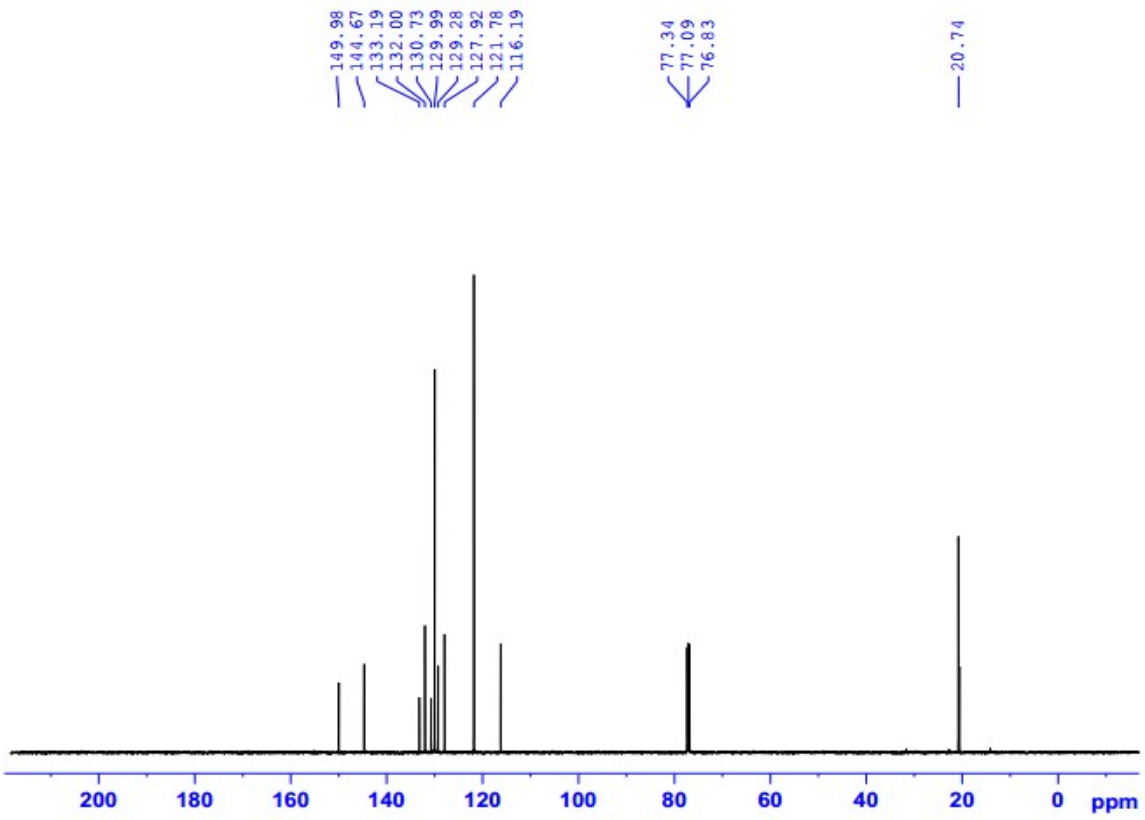
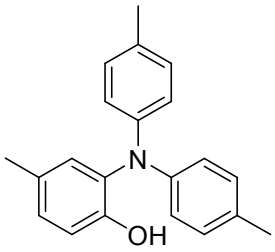


Fig. S22. ^{13}C-NMR spectra of 2-(di-*p*-tolylamino)-4-methylphenol.

Characterization data for 2-(di-*p*-tolylamino)-4-methylphenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): yellow iol, 88% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J*= 8 Hz, 4H), 6.94 – 6.86 (m, 7H), 5.34 (s, 1H), 2.28 (s, 3H), 2.19 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.98, 144.67, 133.19, 132.00, 130.73, 129.99, 129.28, 127.92, 121.78, 116.19.

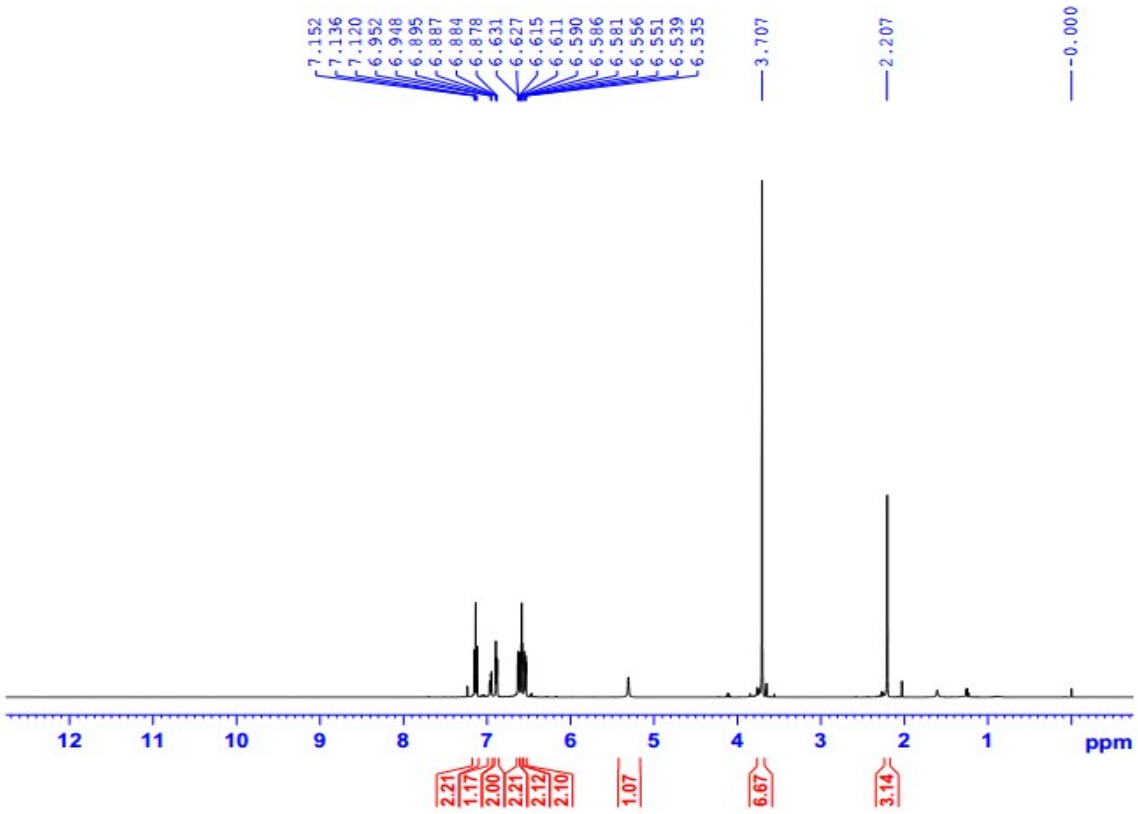


Fig. S23. ^{1}H-NMR spectra of 2-(bis(3-methoxyphenyl)amino)-4-methylphenol.

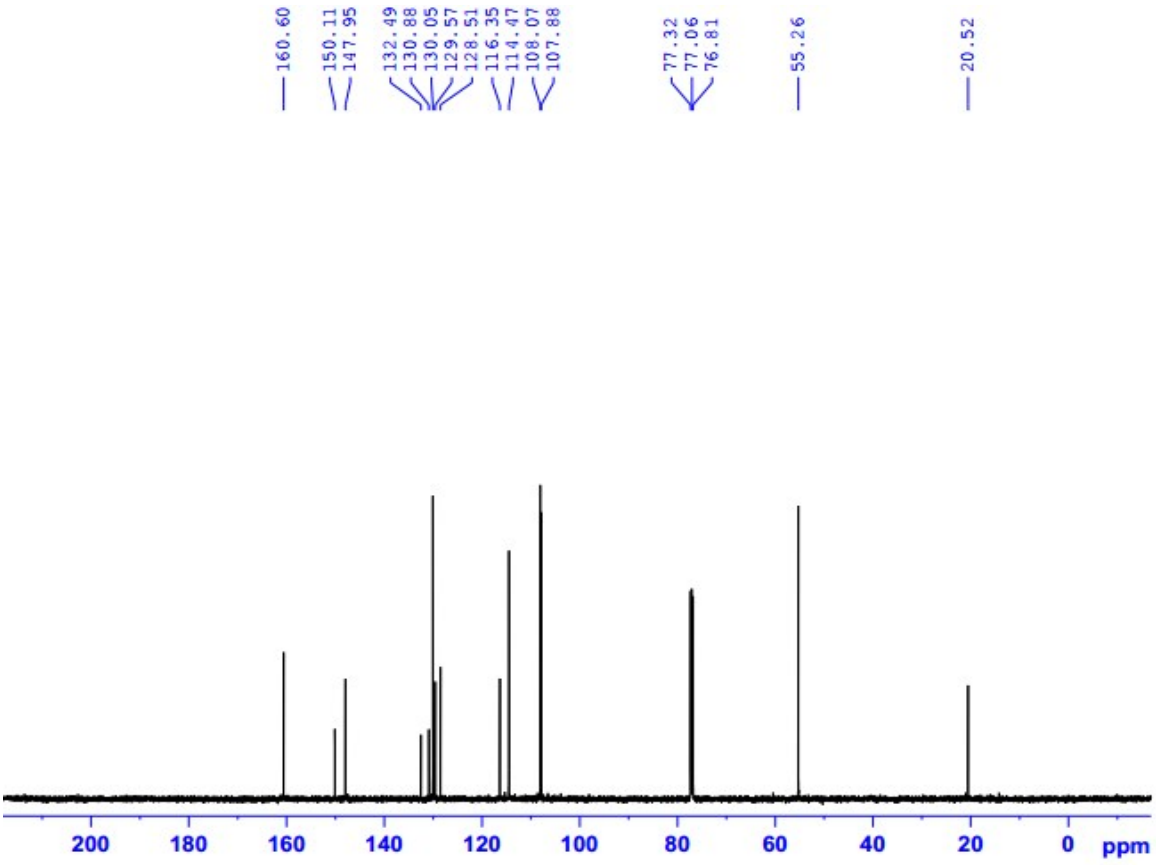
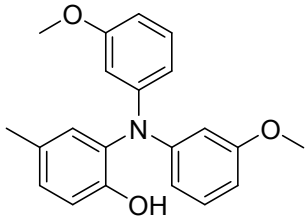


Fig. S24. ^{13}C-NMR spectra of 2-(bis(3-methoxyphenyl)amino)-4-methylphenol.

Characterization data for 2-(bis(3-methoxyphenyl)amino)-4-methylphenol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:8): yellow iol, 72% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J*= 8 Hz, 2H), 6.97 - 6.95 (m, 1H), 6.89 - 6.88 (m, 2H), 6.63 - 6.53 (m, 6H), 5.30 (s, 1H), 3.71 (s, 6H), 2.21 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 160.6, 150.11, 147.95, 132.49, 130.88, 130.05, 129.57, 128.51, 116.35, 114.47, 108.07, 107.88, 55.26.

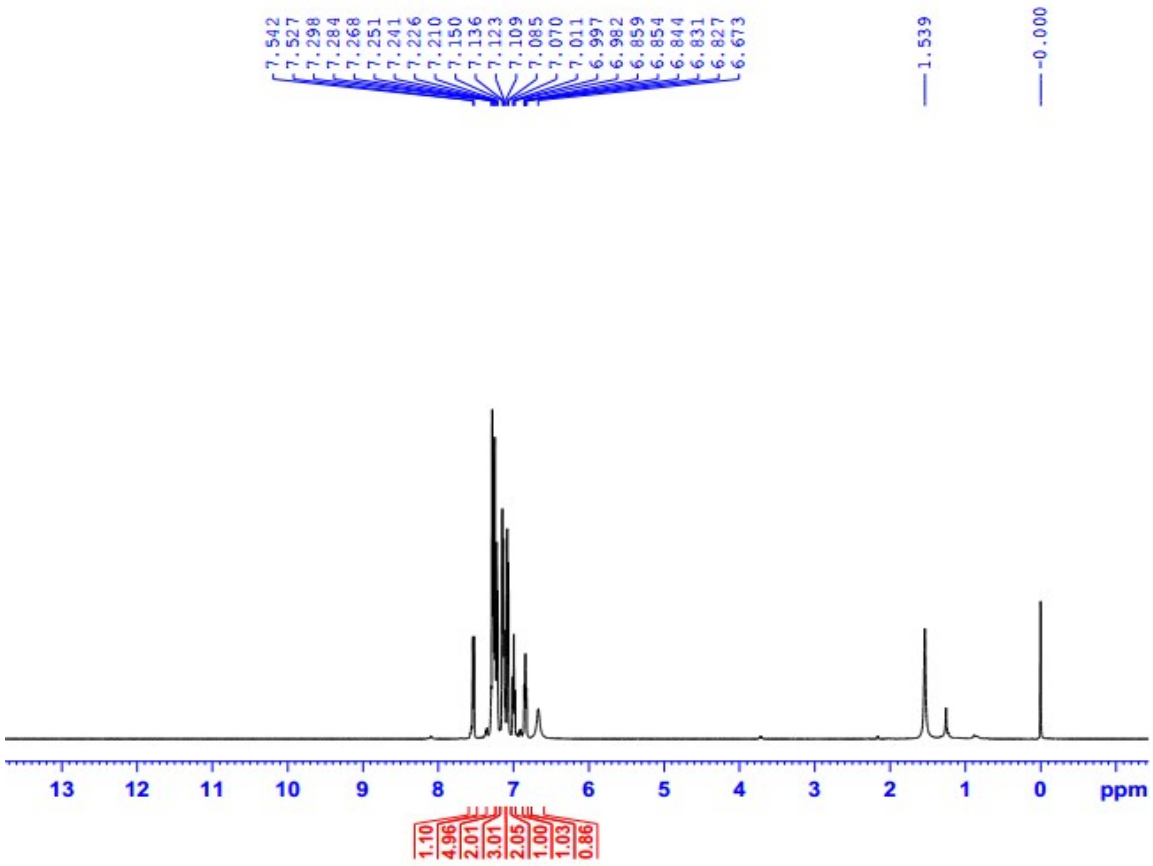


Fig. S25. ^{1}H-NMR spectra of 2-(diphenylamino)benzenethiol.

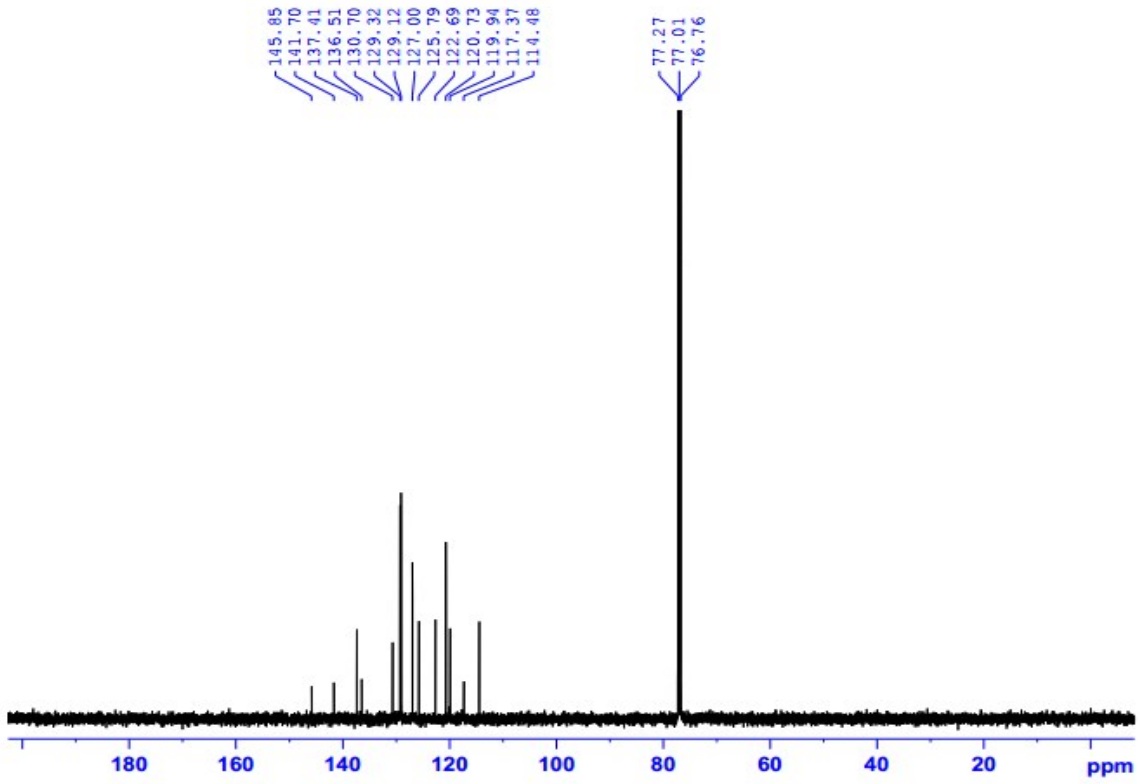
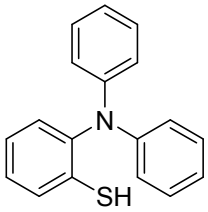


Fig. S26. ^{13}C-NMR spectra of 2-(diphenylamino)benzenethiol.

Characterization data for 2-(diphenylamino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:20): white solid, 79% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J*= 7.5 Hz, 1H), 7.29 - 7.21 (m, 6H), 7.15 – 7.07 (m, 5H), 7.00 (t, *J*= 7Hz, 1H), 6.86 - 6.827 (m, 1H), 6.67 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.85, 141.70, 137.41, 136.51, 130.70, 129.32, 129.12, 127.00, 125.79, 122.69, 120.73, 119.94, 117.37, 114.48.

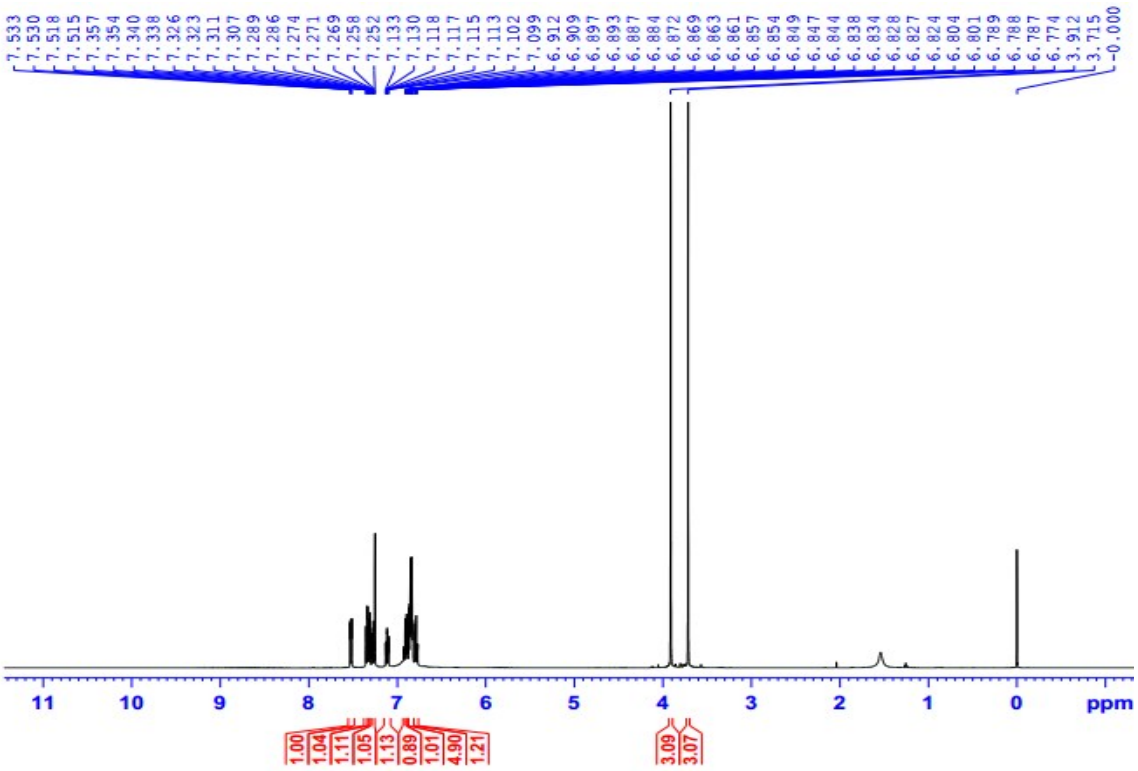


Fig. S27. ^{1}H-NMR spectra of 2-(bis(2-methoxyphenyl)amino)benzenethiol.

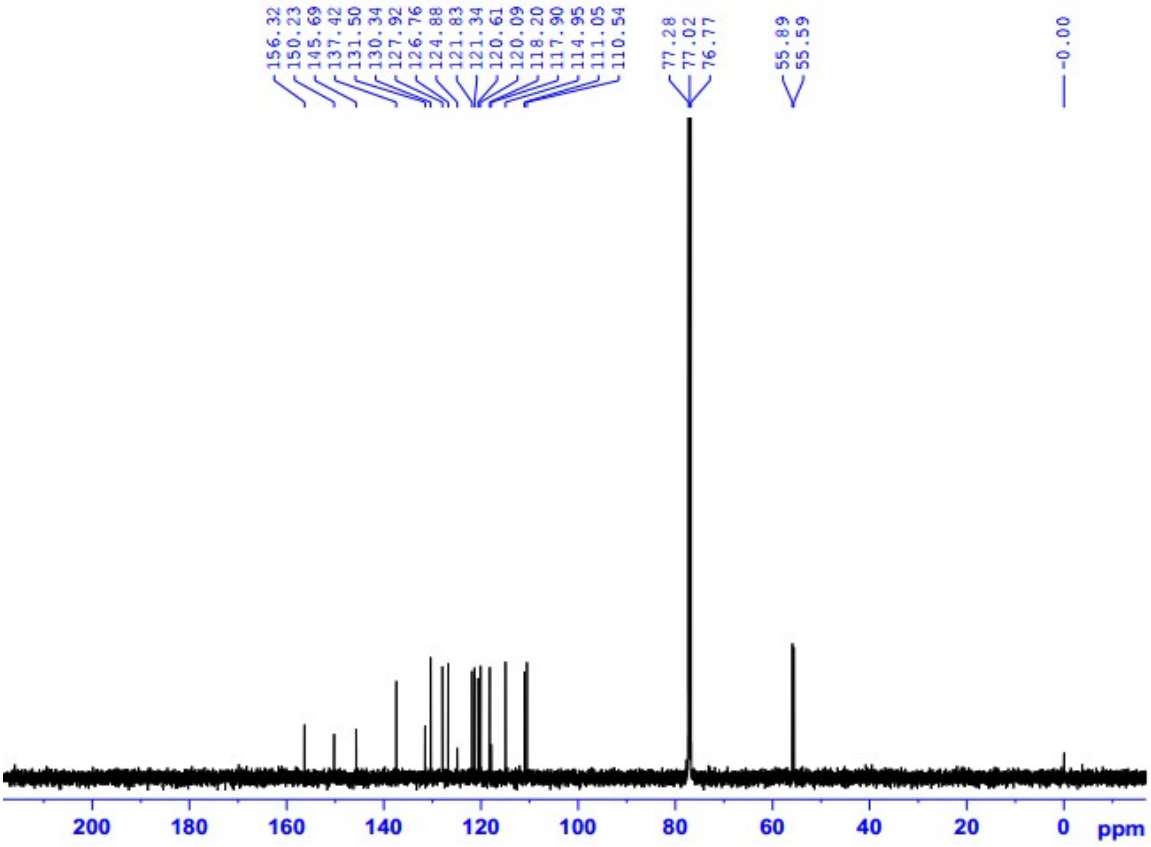
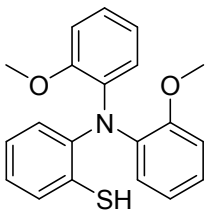


Fig. S28. ^{13}C-NMR spectra of 2-(bis(2-methoxyphenyl)amino)benzenethiol.

Characterization data for 2-(bis(2-methoxyphenyl)amino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): yellow oil, 85% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.55 - 7.50 (dd, *J*= 6Hz, 1H), 7.36 - 7.26 (m, 3H), 7.13- 7.099 (m, 1H), 6.93 - 6.78 (m, 8H), 3.91(s, 3H), 3.715(s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.32, 150.23, 145.69, 137.42, 131.50, 130.34, 127.92,

126.76, 124.88, 121.83, 121.34, 120.61, 120.09, 118.20, 117.90, 114.95, 111.05, 110.54, 55.89, 55.59.

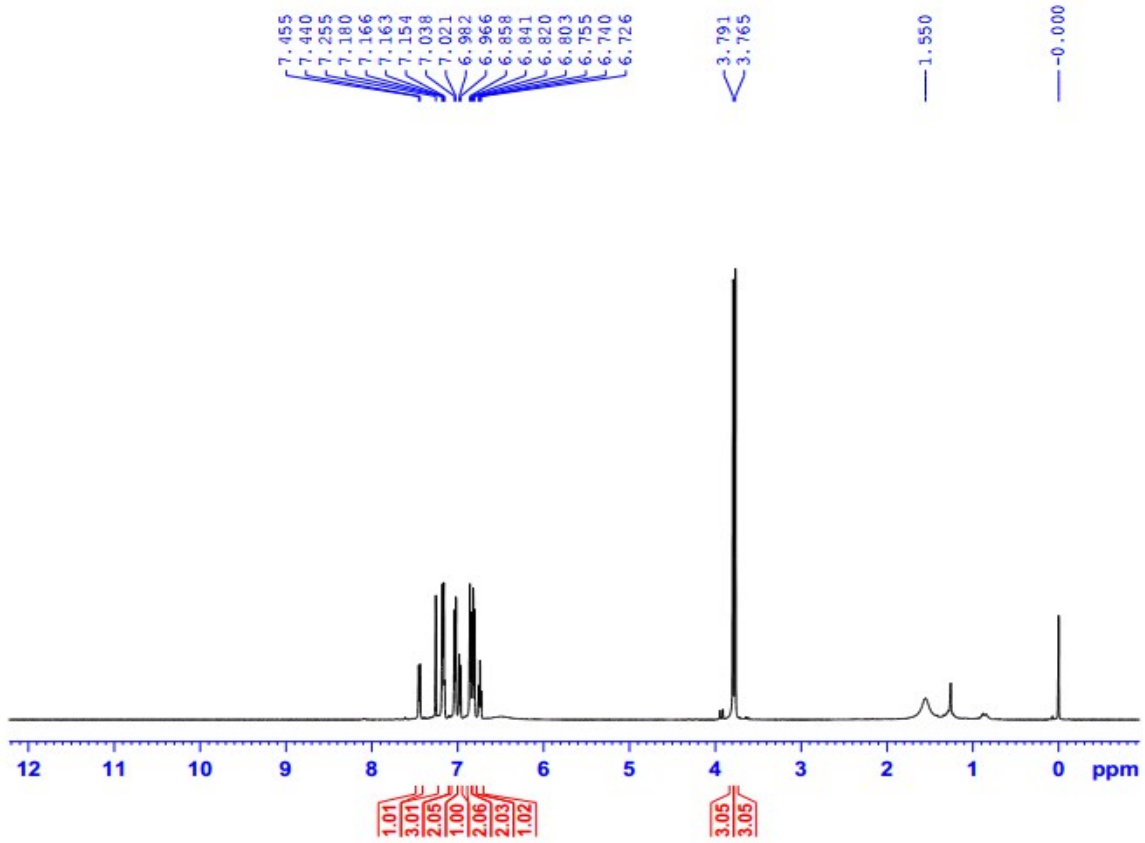


Fig. S29. ^{1}H-NMR spectra of 2-(bis(4-methoxyphenyl)amino)benzenethiol.

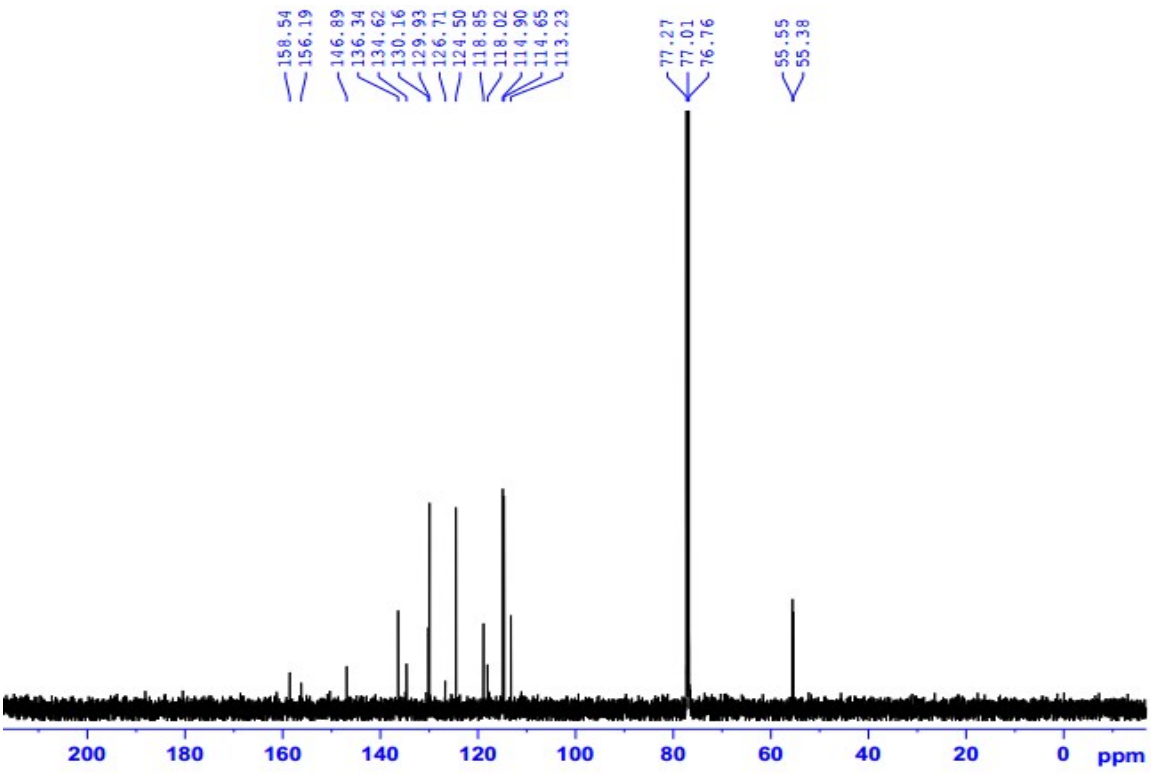
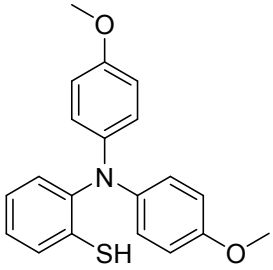


Fig. S30. ^{13}C-NMR spectra of 2-(bis(4-methoxyphenyl)amino)benzenethiol.

Characterization data for 2-(bis(4-methoxyphenyl)amino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:2): yellow oil, 84% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J*= 7.5 Hz, 1H), 7.18 - 7.15 (m, 3H), 7.03 (d, *J*= 8.5 Hz, 2H), 6.97 (d, *J*= 8Hz, 1H), 6.85 (d, *J*= 8.5 Hz, 2H), 6.81 (d, *J*= 8.5 Hz, 2H), 6.74 (t, *J*= 7.5 Hz, 1H), 3.79 (s, 3H), 3,76 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 158.54, 156.19, 146.89, 136.34, 134.62, 130.16, 129.93, 126.71, 124.50, 118.85, 118.02, 114.90, 114.65, 113.23, 55.55, 55.38.

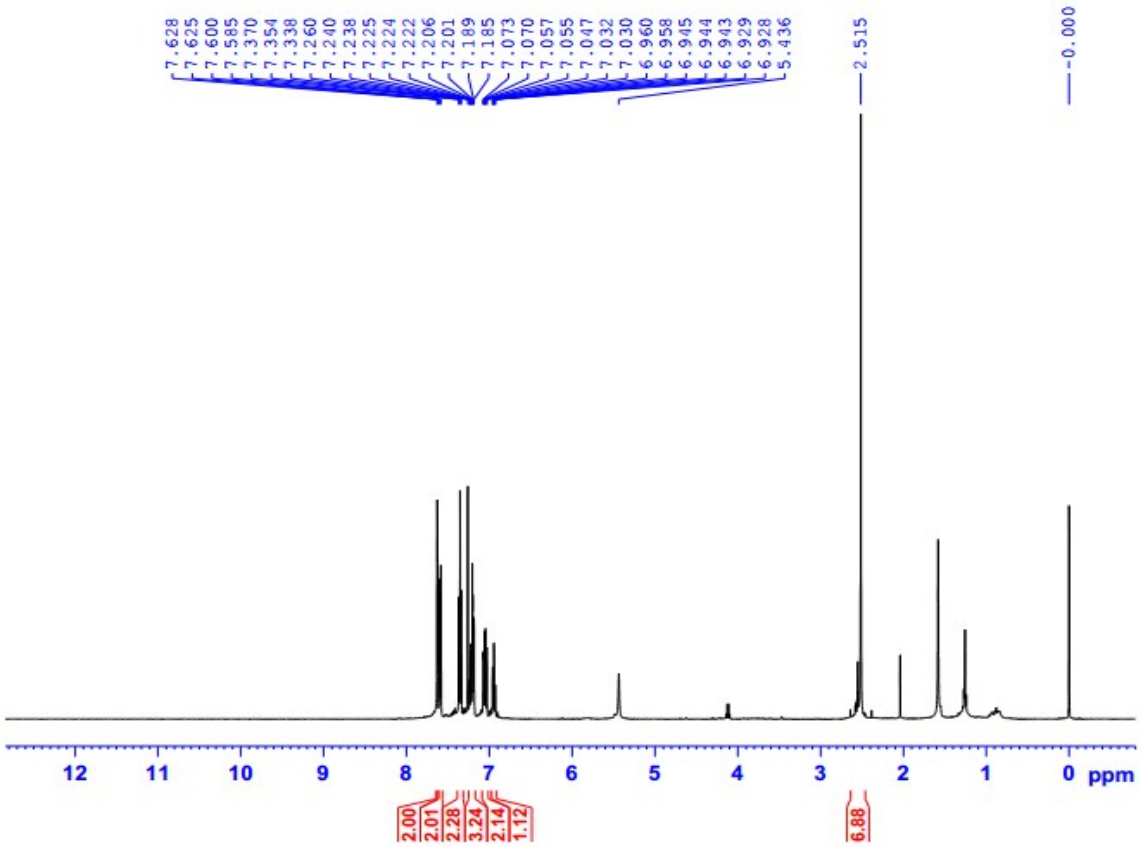


Fig. S31. ^{1}H-NMR spectra of 1,1'-(((2-hydroxyphenyl)azanediyl)bis(3,1-phenylene))diethanone.

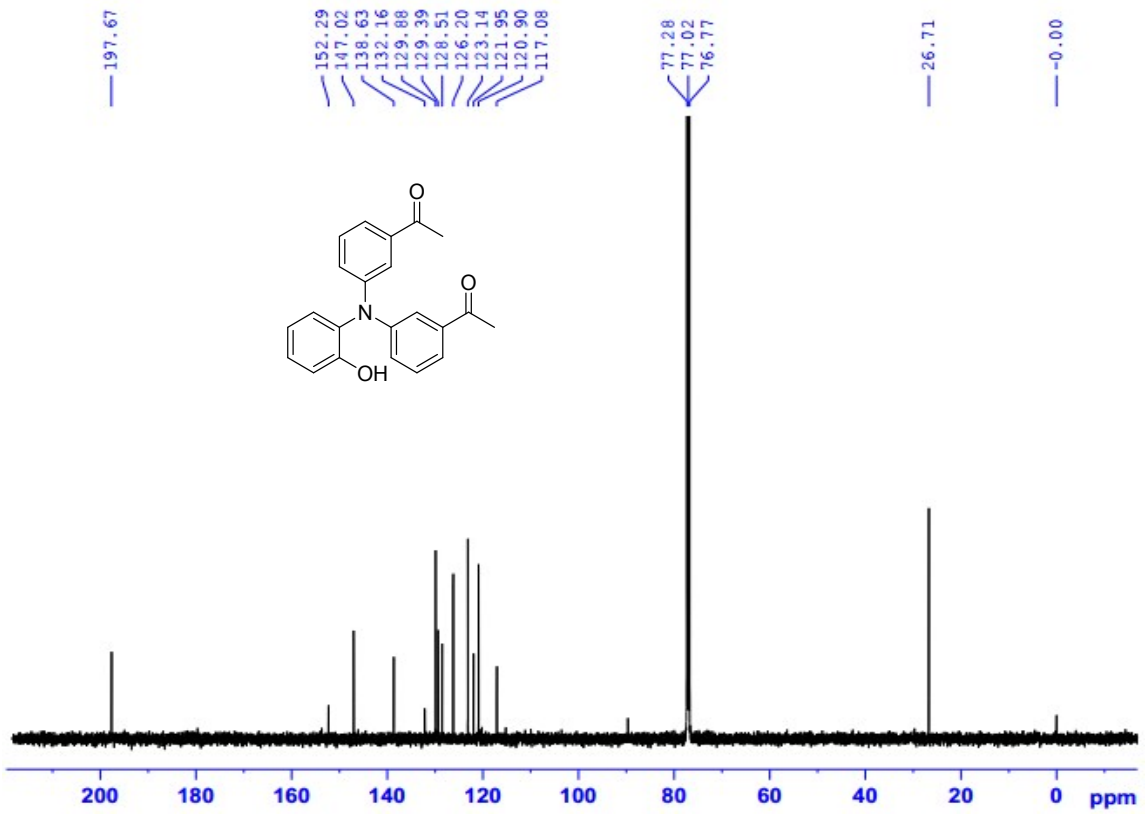
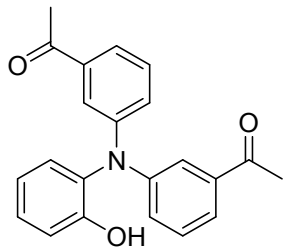


Fig. S32. ^{13}C-NMR spectra of 1,1'-(((2-hydroxyphenyl)azanediyl)bis(3,1-phenylene))diethanone.

Characterization data for 1,1'-(((2-hydroxyphenyl)azanediyl)bis(3,1-phenylene))diethanone.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:3): light orange solid, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 7.35 (t, *J*= 8 Hz, 2H), 7.24-7.18 (m, 3H), 7.07-7.03 (m, 2H), 6.96-6.93 (m, 1H), 5.44 (s, 1H), 2.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.67, 152.29, 147.02, 138.63, 132.16, 129.88, 129.39, 128.51, 126.20, 123.14, 121,95, 120.90, 117.08, 26.71.

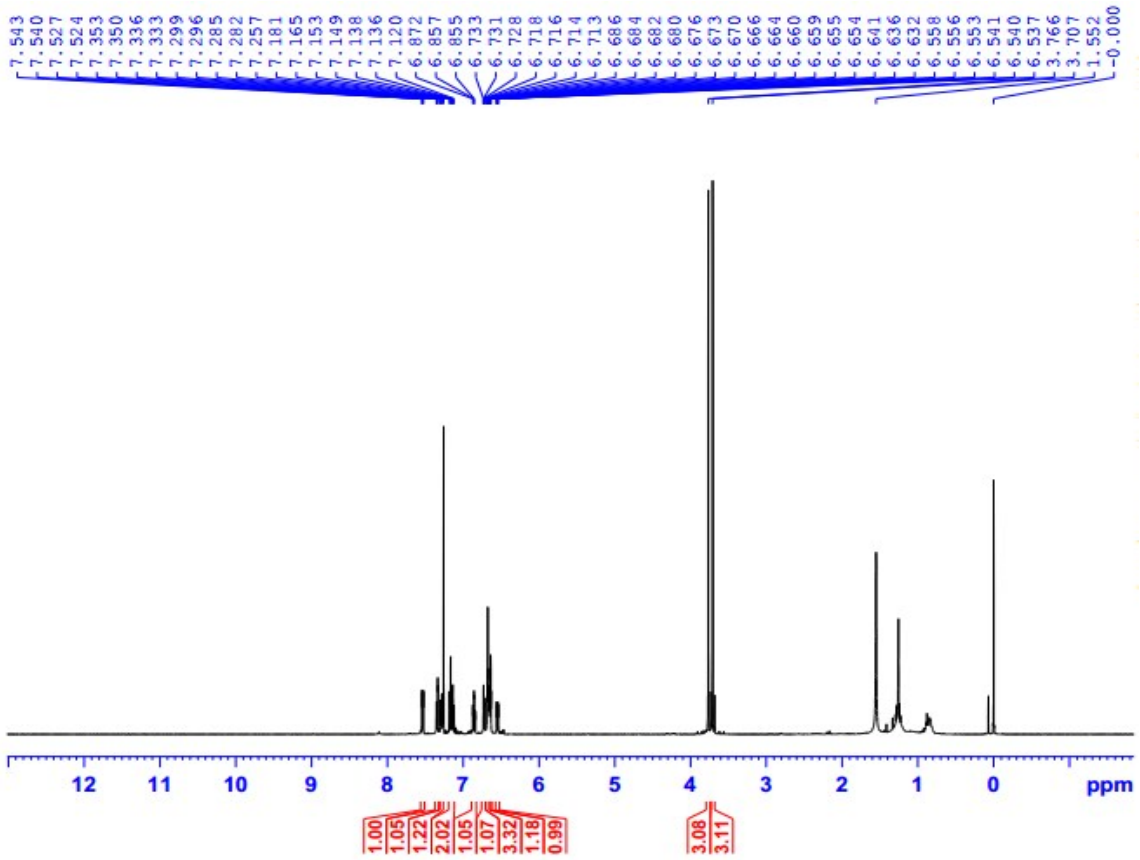


Fig. S33. ^{1}H-NMR spectra of 2-(bis(3-methoxyphenyl)amino)benzenethiol.

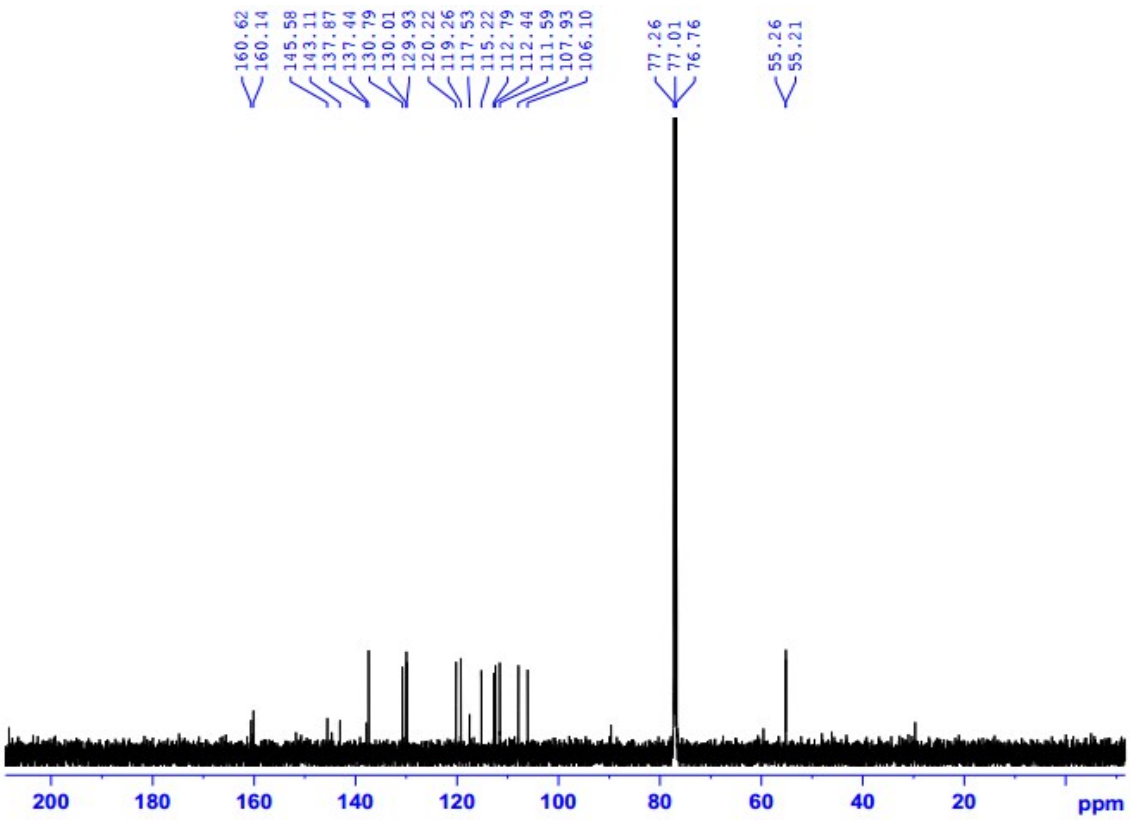
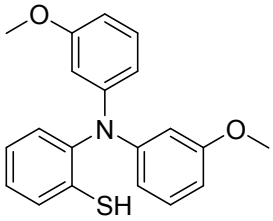


Fig. S34. ^{13}C-NMR spectra of 2-(bis(3-methoxyphenyl)amino)benzenethiol.

Characterization data for 2-(bis(3-methoxyphenyl)amino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): yellow oil, 68% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 - 7.52 (dd, J= 6.5Hz, 1H), 7.35 - 7.33 (dd, *J*= 7Hz, 1H), 7.30 - 7.26 (m, 1H), 7.18 - 7.12 (m, 2H), 6.87 - 6.84 (m, 1H), 6.73 - 6.63 (m, 5H), 6.56 - 6.53 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H); ^{13}C-NMR (125

MHz, $CDCl_3$) δ 160.62, 160.14, 145.58, 143.11, 137.87, 137.44, 130.79, 130.01, 129.93, 120.22, 119.26, 117.53, 115.22, 112.79, 112.44, 111.59, 107.93, 106.10, 55.26, 55.21.

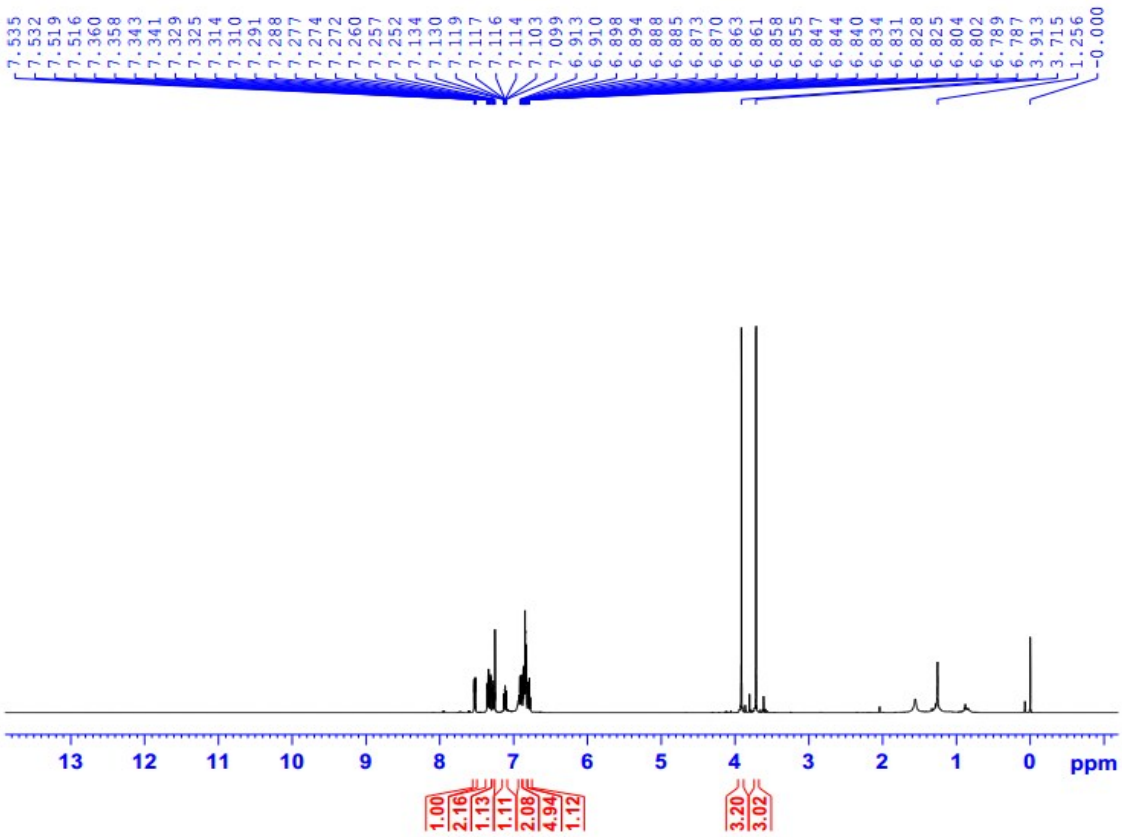


Fig. S35. ^{1}H-NMR spectra of 2-(bis(2-methoxyphenyl)amino)benzenethiol.

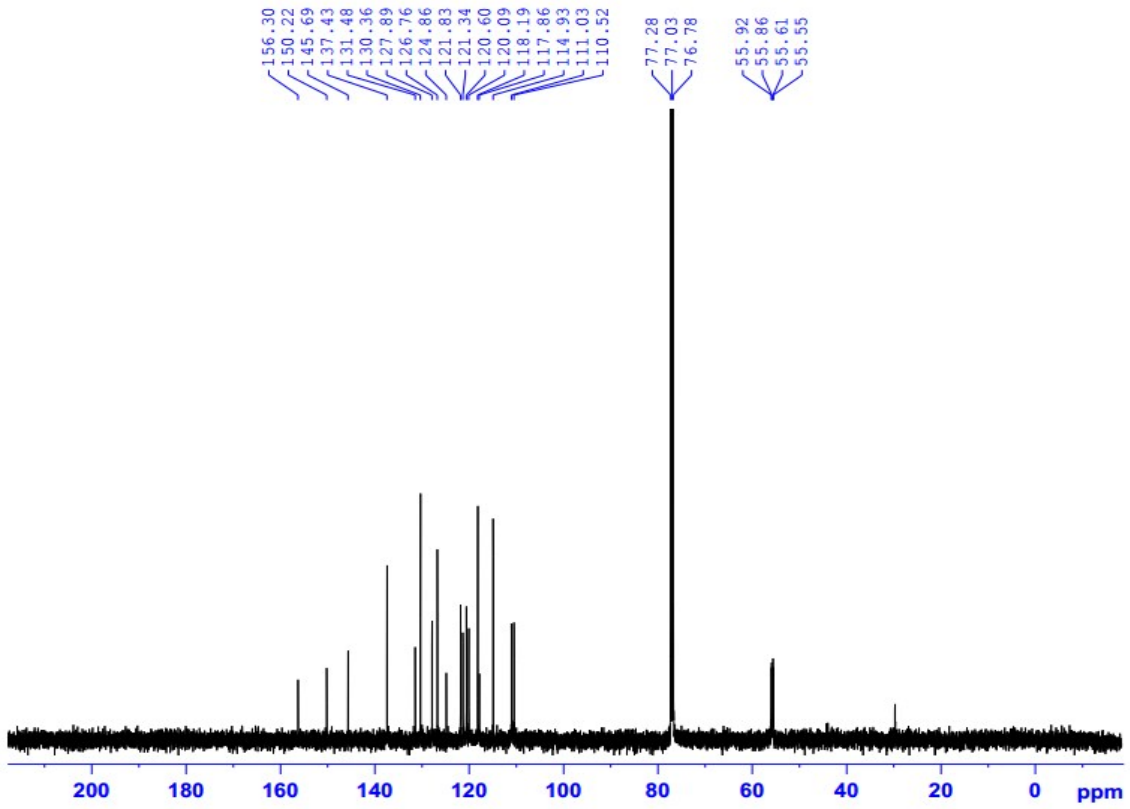
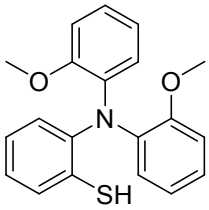


Fig. S36. ^{13}C-NMR spectra of 2-(bis(2-methoxyphenyl)amino)benzenethiol.

Characterization data for 2-(bis(2-methoxyphenyl)amino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:6): yellow oil, 77% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 - 7.52 (dd, *J*= 8Hz, 1H), 7.36 - 7.26 (m, 3H), 7.13- 7.099 (m, 1H), 6.93 - 6.77 (m, 8H), 3.91(s, 3H), 3.715(s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 156.30, 150.22, 145.69, 137.43, 131.48, 130.36, 127.89,

126.76, 124.86, 121.83, 121.34, 120.60, 120.09, 118.19, 117.86, 114.93, 111.03, 110.52, 55.89, 55.59.

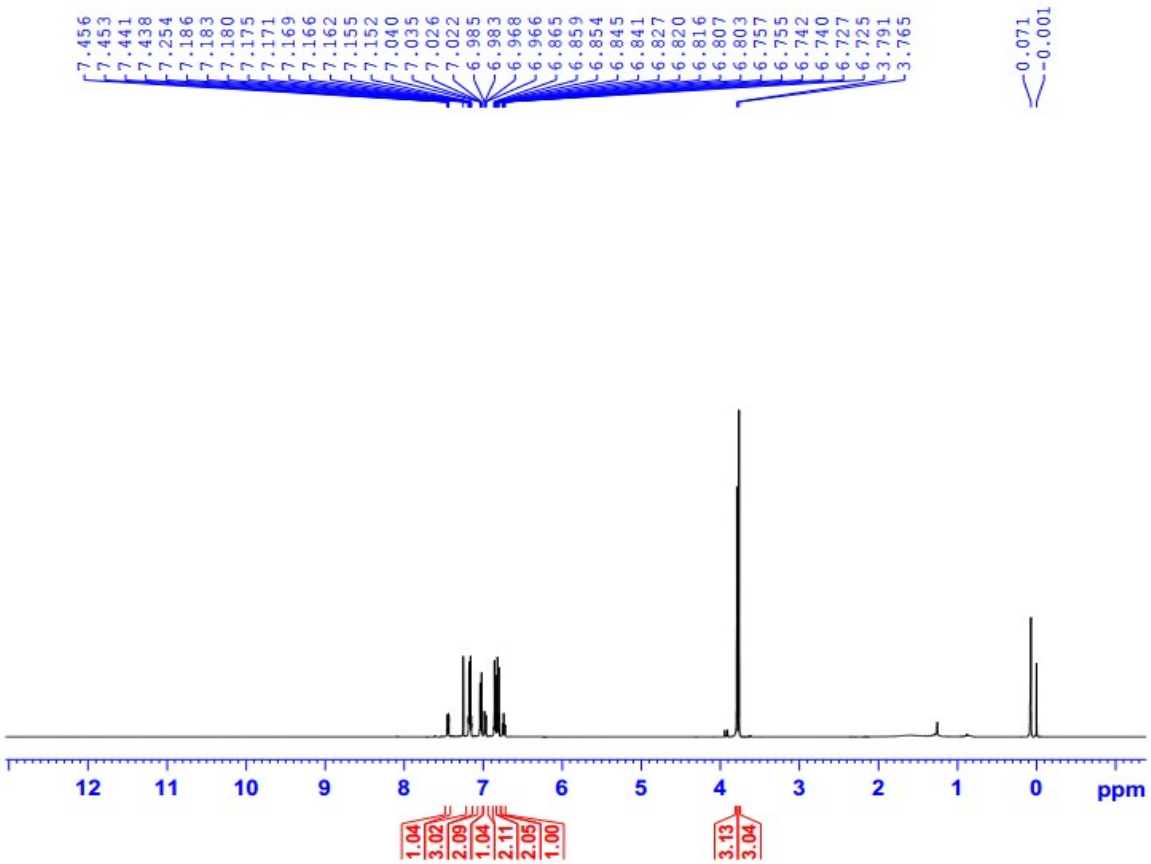


Fig. S37. ^{1}H-NMR spectra of 2-(bis(4-methoxyphenyl)amino)benzenethiol.

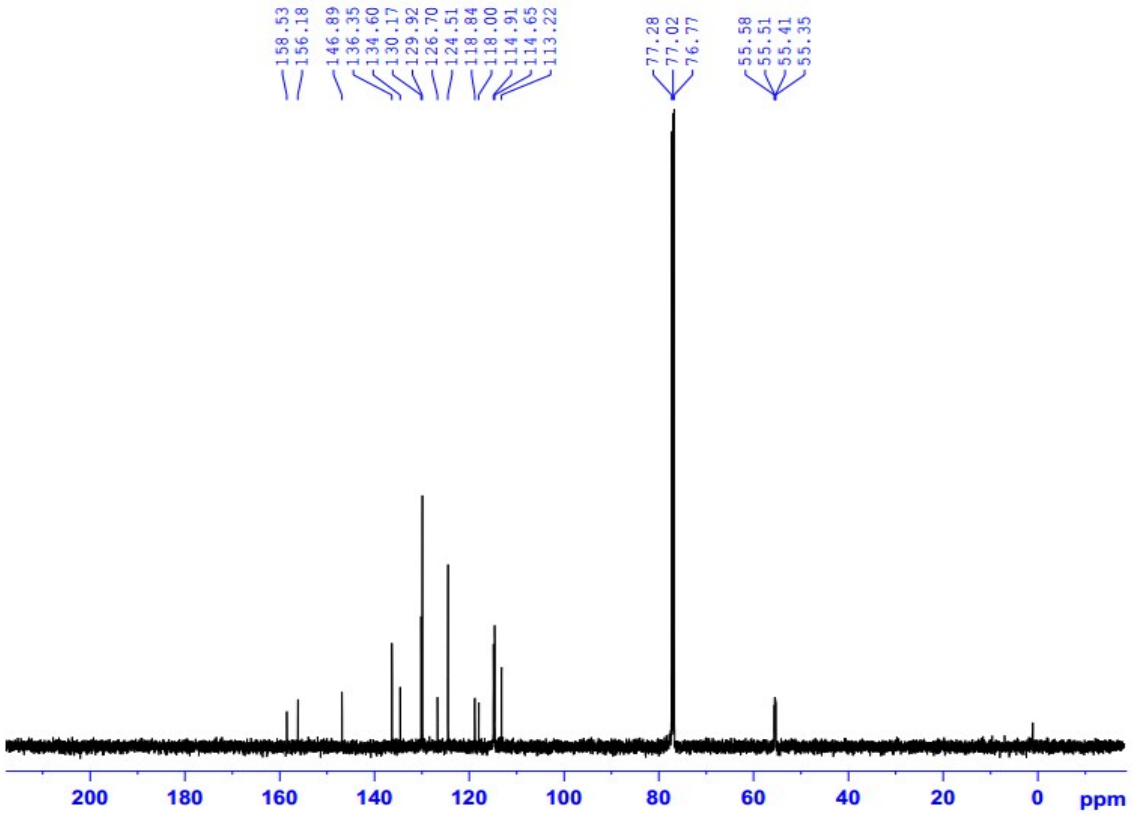
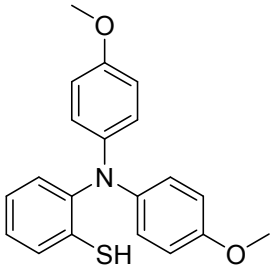


Fig. S38. ^{13}C-NMR spectra of 2-(bis(4-methoxyphenyl)amino)benzenethiol.

Characterization data for 2-(bis(4-methoxyphenyl)amino)benzenethiol.



Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexan = 1:2): yellow oil, 61% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.456 - 7.438 (dd, *J* = 7.5 Hz, 1H), 7.18 - 7.15 (m, 3H), 7.04 - 7.02 (dd, *J* = 7 Hz, 2H), 6.86- 6.72 (dd, *J* = 8.5Hz, 1H), 6.86 - 6.80 (m, 4H), 6.757 - 6.742 (ddd, *J* = 7.5Hz, 1H), 3.79 (s, 3H), 3,76 (s, 3H); ^{13}C-

NMR (125 MHz, $CDCl_3$) δ 158.53, 156.18, 146.89, 136.35, 134.60, 130.17, 129.92, 126.70, 124.51, 118.84, 118.00, 114.91, 114.65, 113.22, 55.55, 55.38.