Electronic Supplementary Material (ESI) for RSC Advances.

A Triazine-Phosphite Polymeric Ligand Bearing Cagelike P,N-Ligation Sites: As an Efficient ligand in Nickel-catalyzed Amination of Aryl Chlorides and Phenols

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Outline

1- Figure 1S: The color and powder state of TPPM

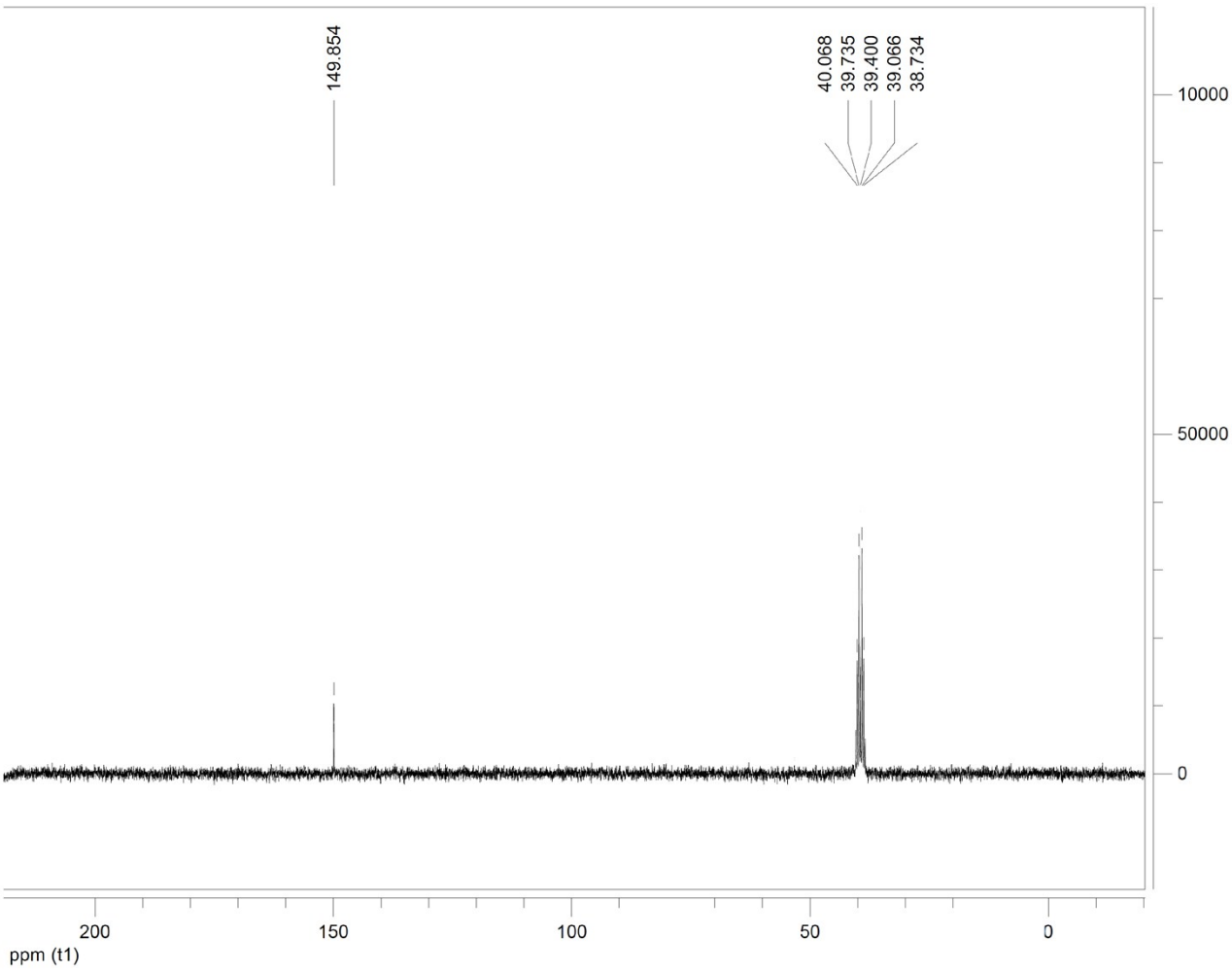
Cyanuric acid

+

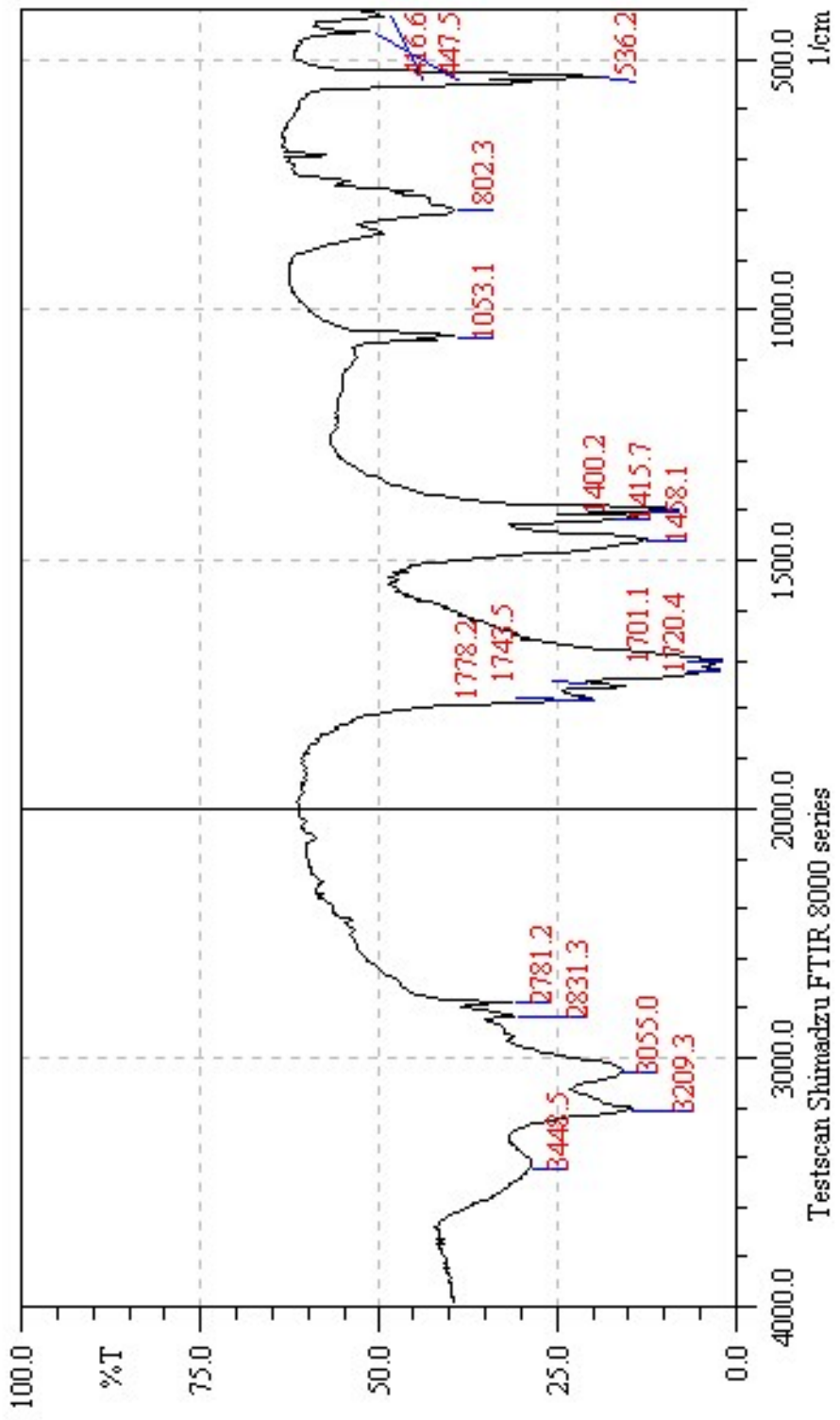
trichlorophosphine (PCl_3)

TPC

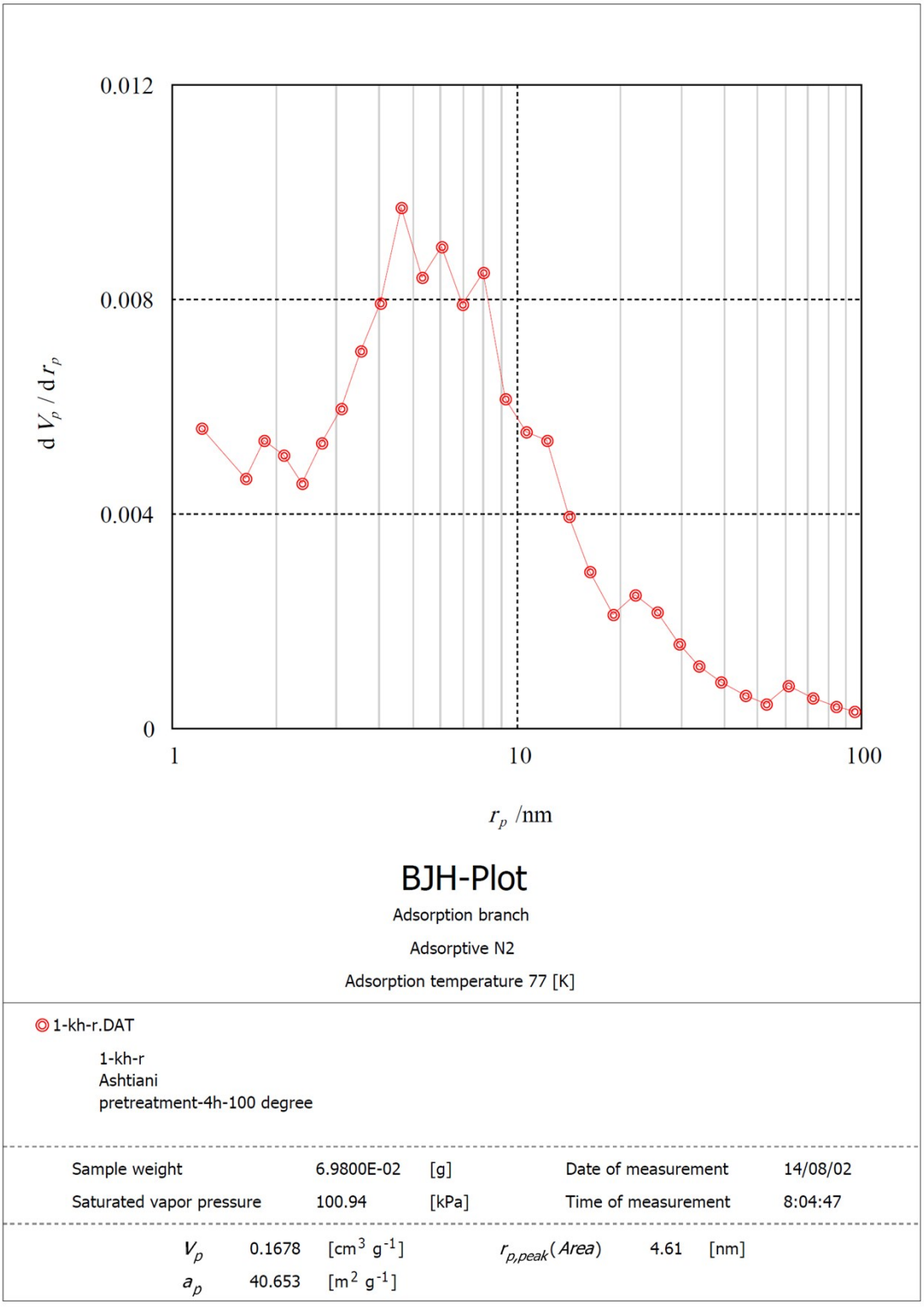
2- Figure 2S: The ^{13}C NMR of TPPM



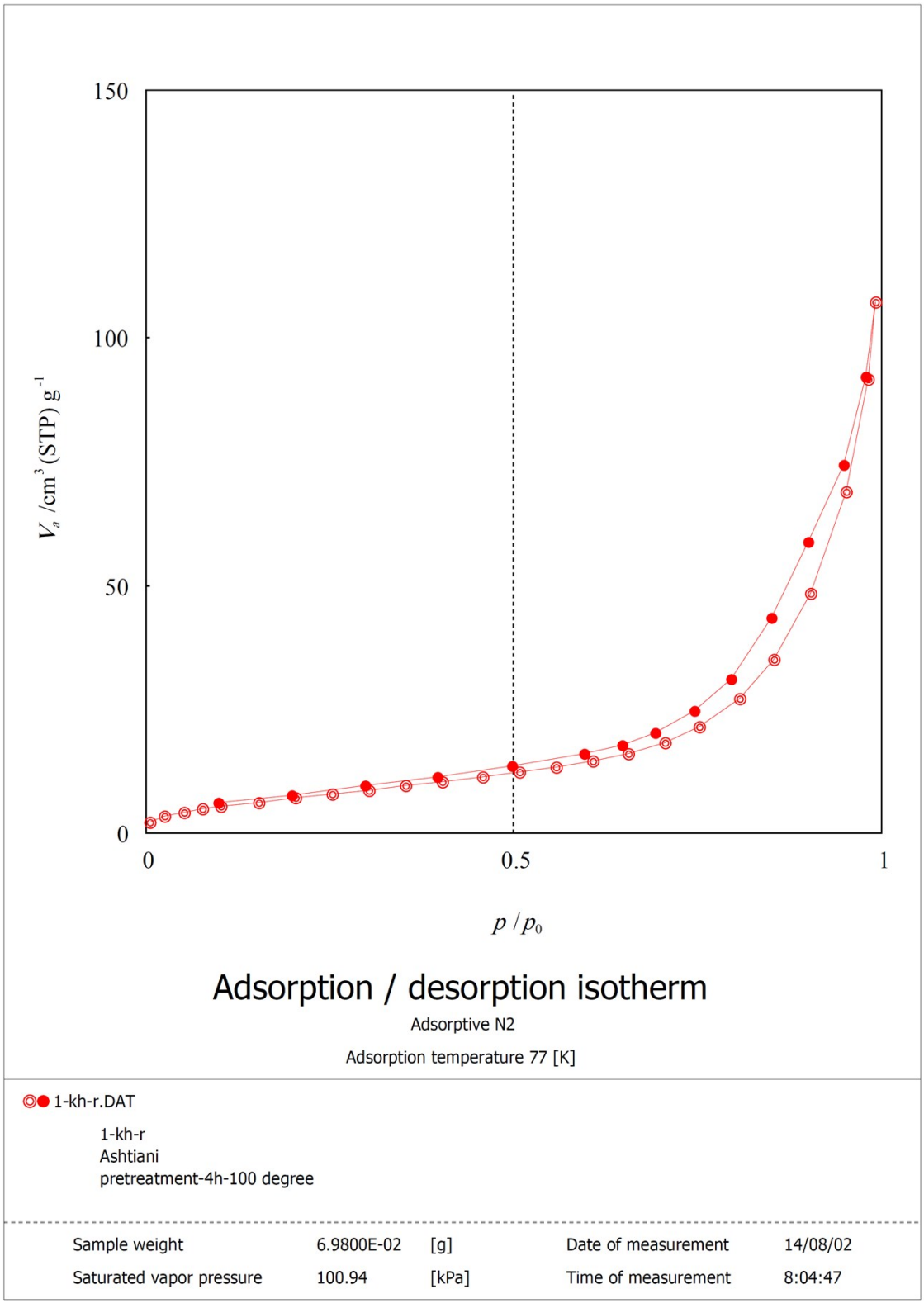
3- Figure 3S: The FT-IR of TPPM



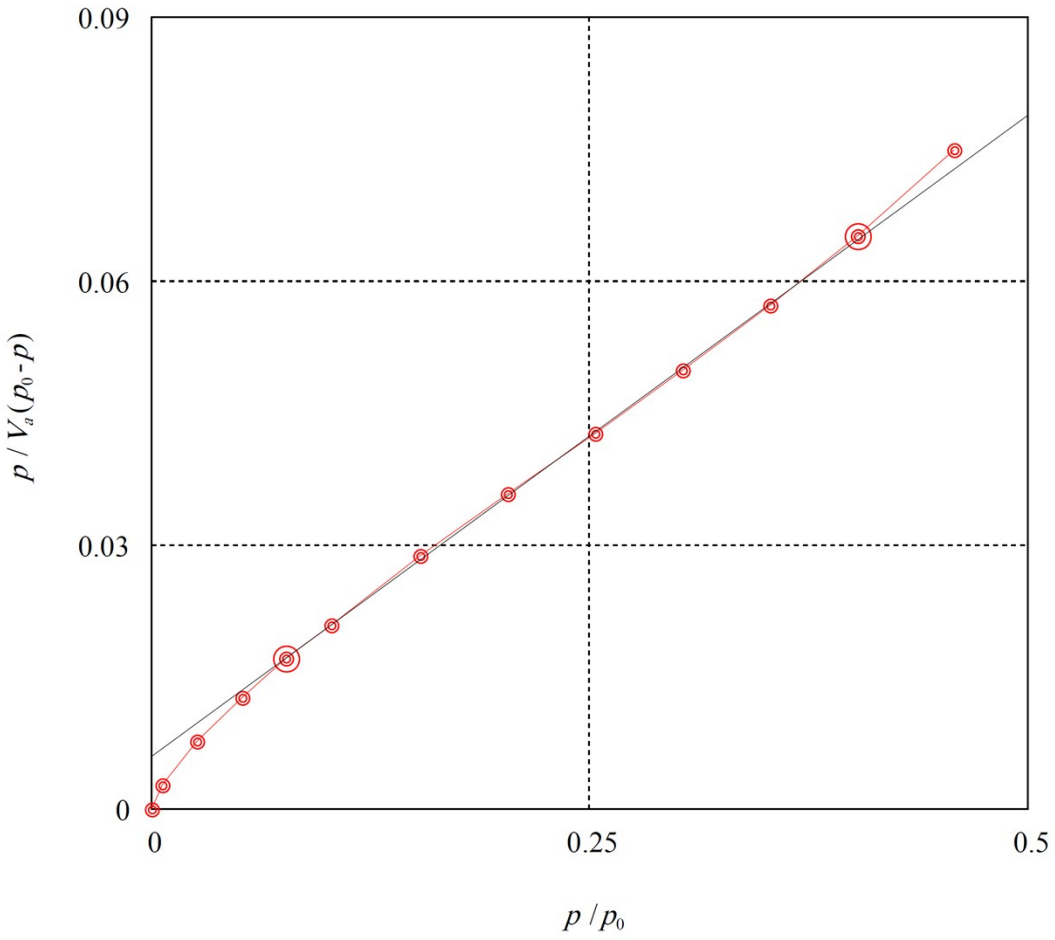
4- Figure 4S: BJH-plot of TPPM



5- Figure 5S: N2-adsorption-desorption curve of TPPM



6- Figure 6S: BET-plot of TPPM



BET-Plot

Adsorptive N2

Adsorption temperature 77 [K]

◎ 1-kh-r.DAT

1-kh-r
Ashtiani
pretreatment-4h-100 degree

Sample weight	6.9800E-02	[g]	Date of measurement	14/08/02	
Saturated vapor pressure	100.94	[kPa]	Time of measurement	8:04:47	

V_m	6.5951	[cm^3(STP) g^{-1}]	$a_{s,BET}$	2.8705E+01	[m^2 g^{-1}]
C	24.950		Total pore volume(p/p_0=0.990)	0.1632	[cm^3 g^{-1}]
Mean pore diameter	22.737	[nm]			

2. Experimental section

2.2. General

Chemicals were purchased from Fluka and Aldrich chemical companies and all reagents and solvents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded on a Brucker Avance DPX-250 spectrometer and ^{31}P NMR (on a BruckerAvance Yaris-400 spectrometer) in deuterated chloroform ($CDCl_3$) and deuterated dimethylsulfoxide (DMSO-d_6) solutions with tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in ppm (δ), and coupling constants in Hz (*J*). X-ray diffraction (XRD, D8, Advance, Bruker, axs) and Fourier-transform infrared (FT-IR) spectroscopy with a Shimadzu FTIR-8300 spectrophotometer, was employed for characterization of the catalysts and products. Melting points were determined in open capillary tubes using a Barnstead electro-thermal 9100 BZ circulating oil melting point apparatus .The scanning electron micrograph (SEM) for materials were obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the catalyst. The reaction monitoring was carried out on silica gel analytical sheets and column chromatography was carried out on column of silica gel. Thin layer chromatography was carried out on silica gel 254 analytical sheets obtained from Fluka.

2.3. Synthesis of triazine-phosphite compound (TPPM)

Into a canonical flask 20.0 mmol of cyanuric acid (which previously highly powdered) is added to a 60 mmol of $(n\text{-Pr})_3N$ and permit it to stir for 1h at 60-80 °C. Then, the reaction mixture was cooled down to room temperature. Afterward, 20.0 mmol of PCl_3 is added to the reaction mixture drop wise under argon gas. Then the reaction temperature increased to 80 °C and is stirred for 12h under argon gas. The obtained crude yellow product was washed with water (2 x 25 mL). After drying it was washed with ethyl acetate (2 x 20 mL) in order to remove the un-reacted organic starting materials. To obtain a high

uniform powder it was stirred in a mixture of EtOAc and *n*-hexane (1:1) for 1h at room temperature. After drying in oven the TPPM was obtained as a yellow powder.

2.4. General procedure for Ni-catalyzed synthesis of anilines from aryl chlorides and 2,4,6-triaryloxy-1,3,5-triazines (TAT) using TPPM as ligand

Aryl chloride (1.0 mmol) or 2,4,6-triaryloxy-1,3,5-triazine (0.35 mmol), $(NH_4)_2SO_4$ (3 mmol), $Ni(COD)_2$ (10.0 mol%), sodium *tert*-butoxide (1.5 mmol, 0.144), TPPM (50 mg) and PEG-200 (2.0 mL) was placed in a 25 mL flask equipped with a magnetic stirring bar and heated at 100 °C under nitrogen gas. The reaction was then monitored by TLC until the consumption of aryl halide was detected. After completion of the reaction 5 mL of water and 5 mL of EtOAc were added to the reaction mixture. The organic solution was extracted and dried over anhydrous Na_2SO_4. After removing of organic solvent the crude product was obtained. For further purification the chromatography technique was used.

3. Spectral data for synthesized compounds

3.1. Aniline (CAS No. 62-53-3) (3a)

The general procedure afforded 81 mg (88%) of the title compound. The spectral data was compared with the literature.[1]

3.2. *p*-Toluidine (CAS No. 106-49-0) (3b)

The general procedure afforded 91 mg (85%) of the title compound. The melting point (44.5-46 °C) and spectral data were gree with commercially available material.[1]

3.3. 4-Isopropylaniline (CAS No. 99-88-7) (3c)

The general procedure afforded 109 mg (81%) of the title compound. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.35 (d, J = 7.5 Hz, 6H), 2.87-3.03 (m, 1H), 3.61 (brs, 2H), 6.73 (d, J = 10 Hz, 2H), 7.16 (d, J = 10 Hz, 2H).

[1] - N. Iranpoor, F. Panahi, Adv. Synth. Catal. 2014, 356, 3067 – 3073

3.4. 2-Ethylaniline (CAS No. 578-54-1) (3d)

The general procedure afforded 95 mg (79%) of the title compound. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.37-1.46 (m, 3H), 2.63-2.68 (m, 2H), 3.71 (brs, 2H), 6.77-6.82 (m, 1H), 6.92-6.97 (m, 1H), 7.18-7.25 (m, 2H).

3.5. 2,4,6-Trimethylaniline (CAS No. 88-05-1) (3e)

The general procedure afforded 97 mg (72%) of the title compound. The spectral data were gree with commercially available material and litrature.[1]

3.6. 3-Methoxyaniline (CAS No. 536-90-3) (3f)

The general procedure afforded 108 mg (88%) of the title compound. The spectral data was compared with the literature.[1]

3.7. 4-Methoxyaniline (CAS No. 104-94-9) (3g)

The general procedure afforded 104 mg (85%) of the title compound. The melting point (57-58 °C) and spectral data were gree with commercially available material.[1]

3.8. 3,4-Dimethoxyaniline (CAS No. 6315-89-5) (3h)

The general procedure afforded 137 mg (90%) of the title compound. The melting point (86-88 °C) and spectral data were gree with commercially available material. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.34 (brs, 2H), 3.80 (s, 3H), 3.82 (s, 3H), 6.19-6.32 (m, 2H), 6.66-6.70 (m, 1H), 7.23-7.27 (m, 1H).

3.9. 3-Nitroaniline (CAS No. 99-09-2) (3i)

The general procedure afforded 124 mg (90%) of the title compound. The melting point (113-115 °C) and spectral data were gree with commercially available material.[1]

3.10. 2-Nitroaniline (CAS No. 88-74-4) (3j)

The general procedure afforded 114 mg (83%) of the title compound. The melting point (72-74 °C) and spectral data were gree with commercially available material. ^{1}H NMR

(250 MHz, $CDCl_3$): δ (ppm) = 6.12 (brs, 2H), 6.63-6.71 (m, 1H), 6.79-6.83 (m, 1H), 7.30-7.37 (m, 1H), 8.06-8.10 (m, 1H).

3.11. 4-Aminobenzonitrile (CAS No. 873-74-5) (3k)

The general procedure afforded 108 mg (92%) of the title compound. The melting point (84-86 °C) and spectral data were gree with commercially available material.[1]

3.12. 4'-Aminoacetophenone (CAS No. 99-92-3) (3l)

The general procedure afforded 115 mg (85%) of the title compound. The melting point (105-108 °C) and spectral data were gree with commercially available material. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.47 (s, 3H), 4.32 (brs, 2H), 6.60 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H).

3.13. 3-Aminopyridine (CAS No. 462-08-8) (3m)

The general procedure afforded 81 mg (87%) of the title compound. The melting point (63-65 °C) and spectral data were gree with commercially available material.

3.14. Acridine-9-amine (CAS No. 90-45-9) (3n)

The general procedure afforded 174 mg (90%) of the title compound. The melting point (298-300 °C) and spectral data were gree with commercially available material. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 5.58 (brs, 2H), 7.38-7.45 (m, 2H), 7.67-7.74 (m, 2H), 7.92 (d, J = 7.5 Hz, 2H), 8.07 (d, J = 7.5 Hz, 2H).

3.15. Benzo[d][1,3]dioxol-5-amine (CAS No. 14268-66-7) (3o)

The general procedure afforded 117 mg (86%) of the title compound. The melting point (38-40 °C) and spectral data were gree with commercially available material. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.00 (brs, 2H), 3.44 (s, 2H), 5.42-5.86 (m, 2H), 6.26-6.54 (m, 1H).

3.16. Naphthalen-1-amine (CAS No. 134-32-7) (3p)

The general procedure afforded 121 mg (85%) of the title compound. The spectral data was compared with the literature.[1]

3.17. 2-Aminoanthracene-9,10-dione (CAS No. 117-79-3) (3q)

The general procedure afforded 182 mg (82%) of the title compound. The melting point (292-293.5 °C) and spectral data were gree with commercially available material.

3.18. 4-(*p*-Tolyloxy)aniline (CAS No. 41295-20-9) (3r)

The general procedure afforded 175 mg (88%) of the title compound. The melting point (121-123 °C) and spectral data were gree with commercially available material. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.33 (s, 3H), 3.55 (brs, 2H), 6.67 (d, J = 7.5 Hz, 2H), 6.85-6.90 (m, 4H), 7.11 (d, J = 10 Hz, 2H).

3.19. 1-Phenyl-*1H*-indene (4a)

Yield: 92% (177 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.68-6.71 (m, 1H), 7.15-7.27 (m, 3H), 7.33-7.41 (m, 2H), 7.50-7.60 (m, 4H), 7.68-7.73 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 103.6, 110.5, 120.4, 121.2, 122.4, 124.4, 126.5, 128.0, 129.3, 129.6, 135.9, 139.9.

3.20. 1-*p*-Tolyl-*1H*-indole (4b)

Yield: 88% (182 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.36 (s, 3H), 6.59-6.62 (m, 1H), 7.05-7.49 (m, 8H), 7.59-7.64 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 21.0, 103.1, 110.5, 120.1, 121.0, 122.2, 124.3, 128.1, 129.1, 130.1, 136.3, 143.8.

3.21. 9-Phenyl-*9H*-carbazole (4c)

Yield: 85% (206 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.16-7.42 (m, 7H), 7.47-7.57 (m, 4H), 8.06-8.09 (m, 2H).

^{13}C NMR (62.5 MHz, CDCl3): δ (ppm) = 109.7, 119.8, 120.3, 123.3, 125.9, 127.1, 127.4, 129.8, 137.7, 140.9.

3.22. 2-Methyl-1-*p*-tolyl-*1H*-imidazole (4d)

Yield: 82% (141 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.34 (s, 3H), 2.41 (s, 3H), 6.99 (d, *J* = 10 Hz, 2H), 7.14-7.28 (m, 4H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 13.6, 21.1, 115.6, 125.3, 127.3, 130.0, 133.9, 138.2, 143.1.

3.23. 1-(4-Methoxyphenyl)-2-methyl-*1H*-imidazole (4e)

Yield: 80% (150 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.37(s, 3H), 3.80 (s, 3H), 6.90- 6.95 (m, 3H), 7.11-7.26 (m, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 14.1, 55.6, 114.6, 114.9, 126.8, 127.7, 136.9, 137.3, 160.8.

3.24.1-(4-Methoxyphenyl)-*1H*-benzo[d]imidazole (4f)

Yield: 80% (179 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.89 (s, 3H), 7.06-7.11 (m, 2H), 7.24-7.50 (m, 6H), 7.93 (brs, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) =55.6, 114.9, 115.1, 120.3, 122.9, 123.7, 125.8, 135.2, 136.8, 140.6, 142.8, 161.2.

3.25. 2-(*1H*-Pyrrol-1-yl)pyridine (4g)

Yield: 76% (109 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.35-6.38 (m, 2H), 7.07-7.17 (m, 1H), 7.24-7.33 (m, 1H), 7.51-7.54 (m, 2H), 7.69-7.77 (m, 1H), 8.41-8.44 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 111.3, 111.4, 118.0, 120.1, 138.5, 148.7, 159.5.

3.26. 1-(4-Methoxyphenyl)-*1H*-pyrrole-2-carbaldehyde (4h)

Yield: 80% (161 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.76 (s, 3H), 6.25 (s, 1H), 6.86-7.26 (m, 6H), 9.49 (s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 55.5, 114.6, 114.9, 119.7, 122.2, 126.9, 129.3, 139.6, 160.3, 174.9.

3.27. Triphenylamine (4i)

Yield: 84% (205 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.87-6.94 (m, 3H), 6.98-7.02 (m, 6H), 7.10-7.18 (m, 6H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 122.7, 124.2, 129.2, 142.8.

3.28. *N*-Dodecylbenzenamine (4j)

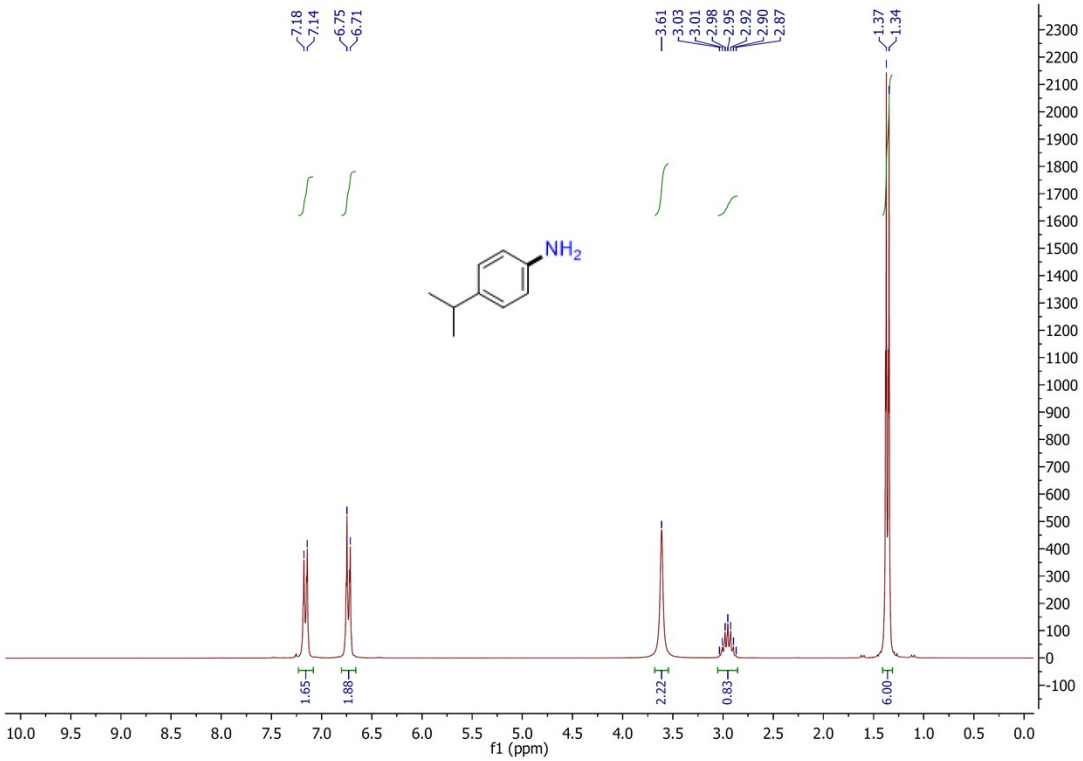
Yield: 76% (198 mg).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.80 (t, J = 7.5 Hz, 3H), 1.17 (brs, 18H), 1.41-1.52 (m, 2H), 3.94 (t, J = 7.5 Hz, 2H), 4.39 (t, J = 7.5 Hz, 1H), 7.29- 7.48 (m, 5H).

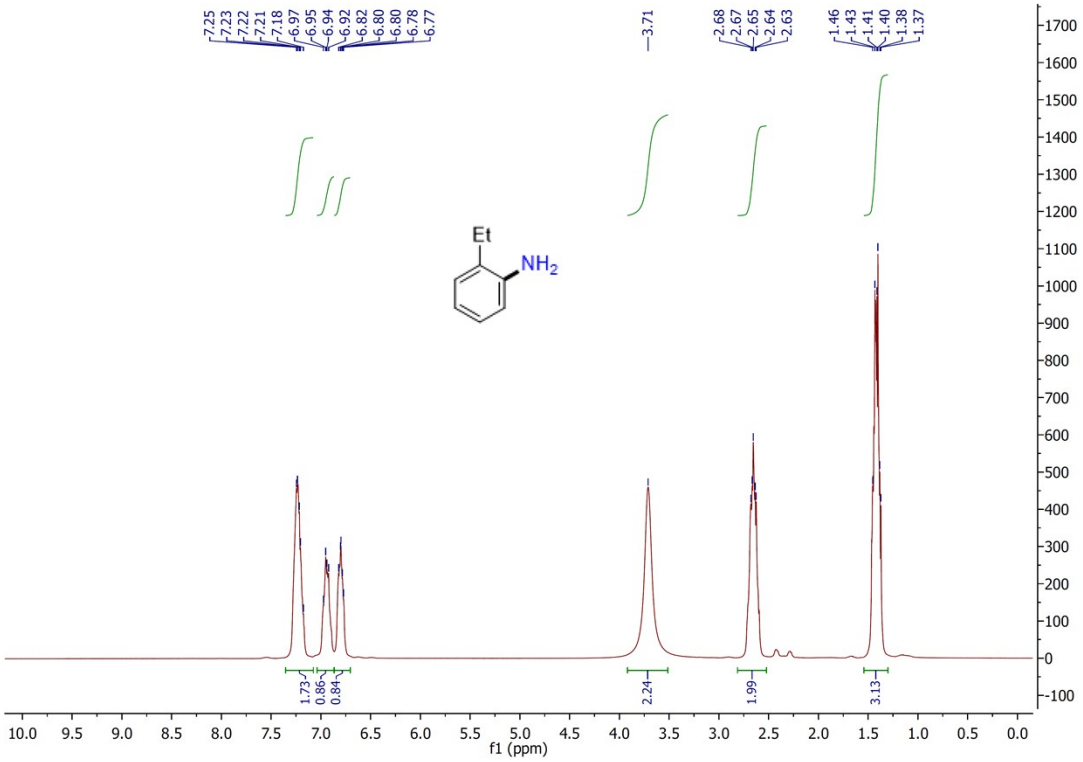
^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 14.1, 22.7, 26.4, 29.1, 29.6, 31.9, 32.5, 43.9, 119.6, 127.3, 129.5, 145.7.

4. Copy of ^{1}HNMR & ^{13}CNMR of synthesized compounds

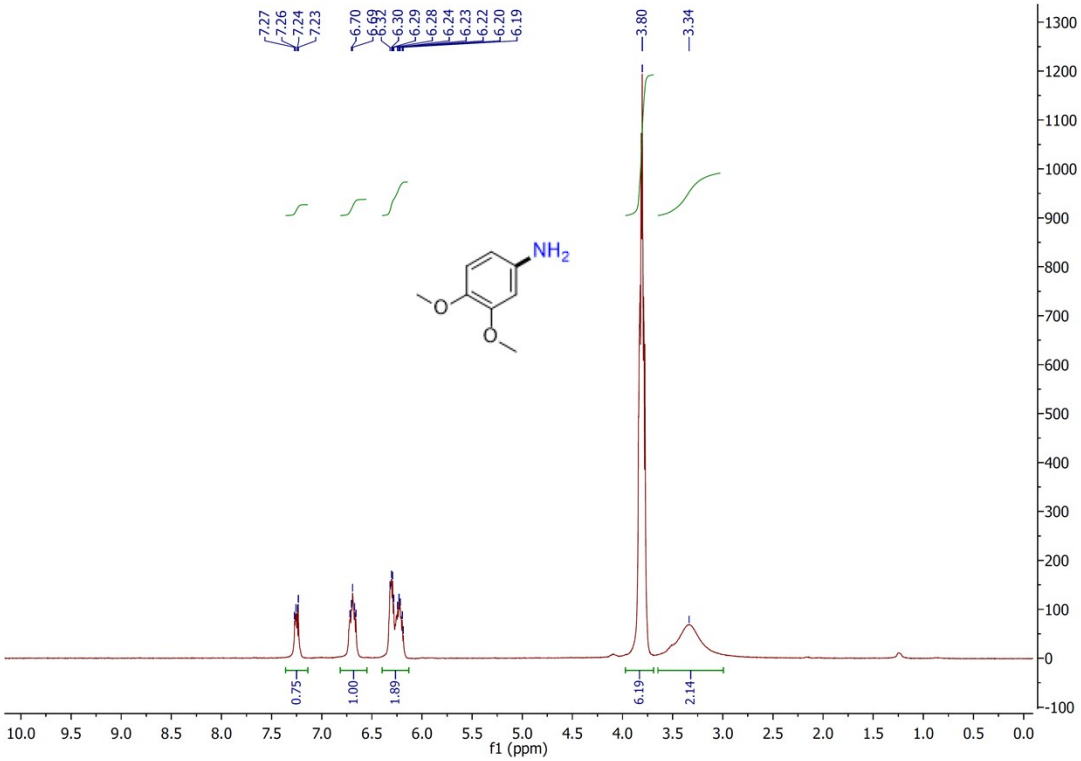
4.1. 4-Isopropylaniline (3c)



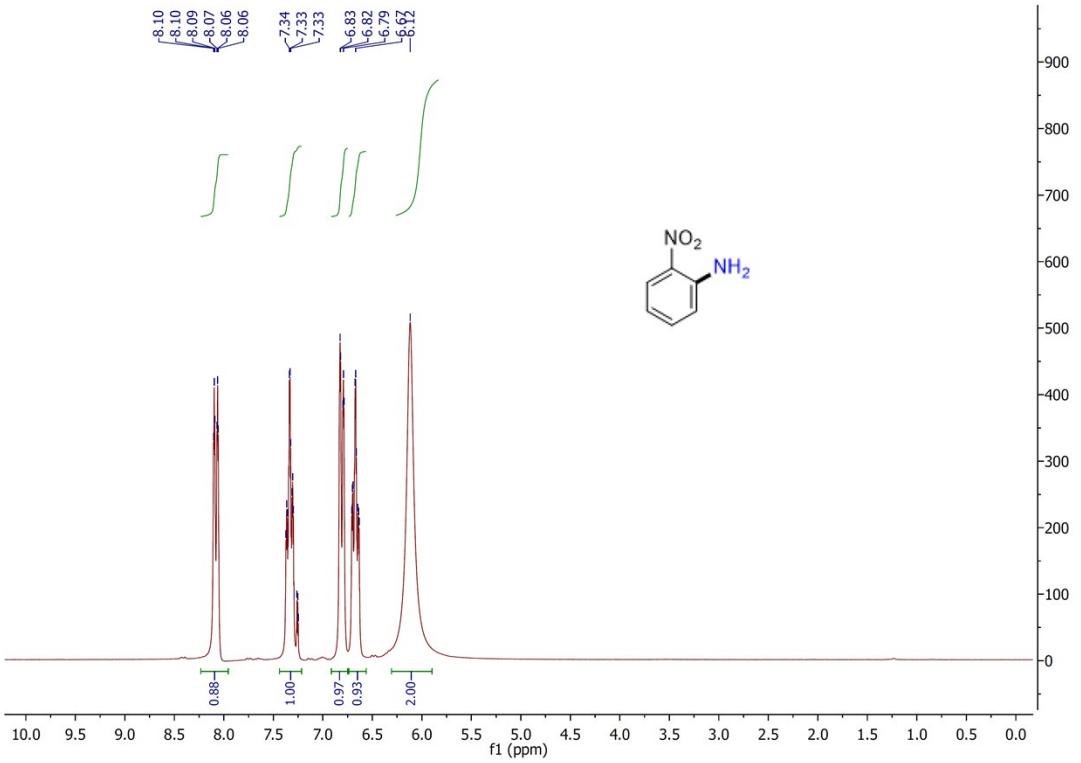
4.2. 2-Ethylaniline (3d)



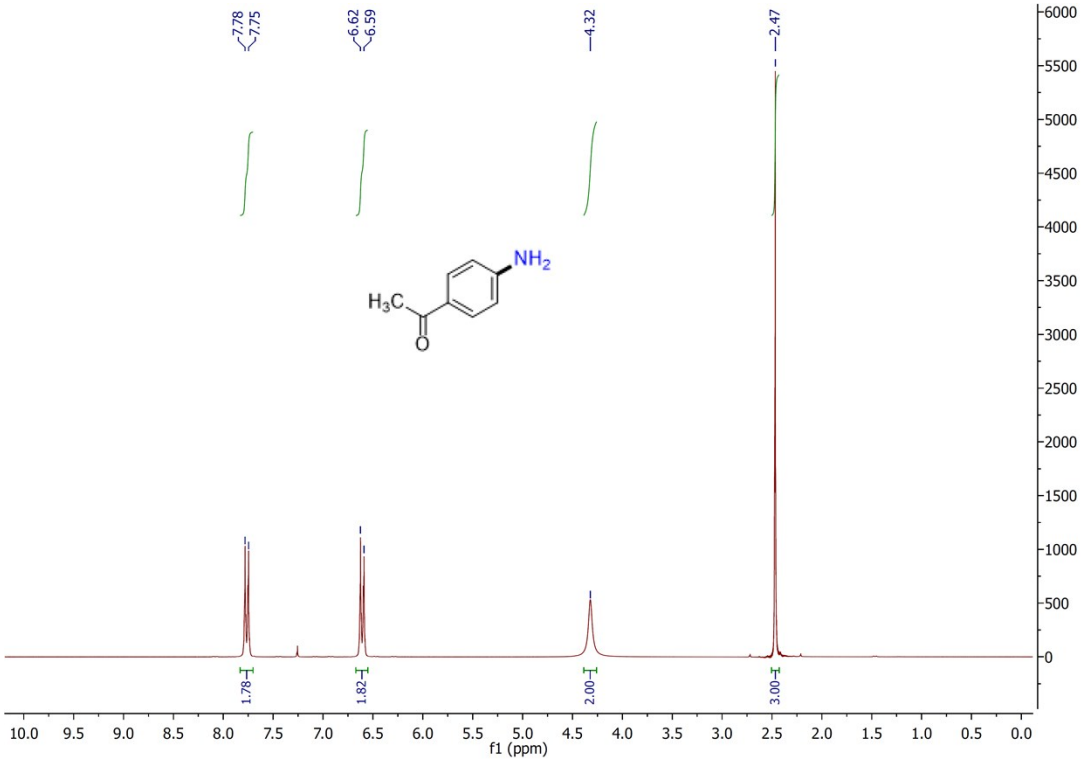
4.3. 3,4-Dimethoxyaniline (3h)



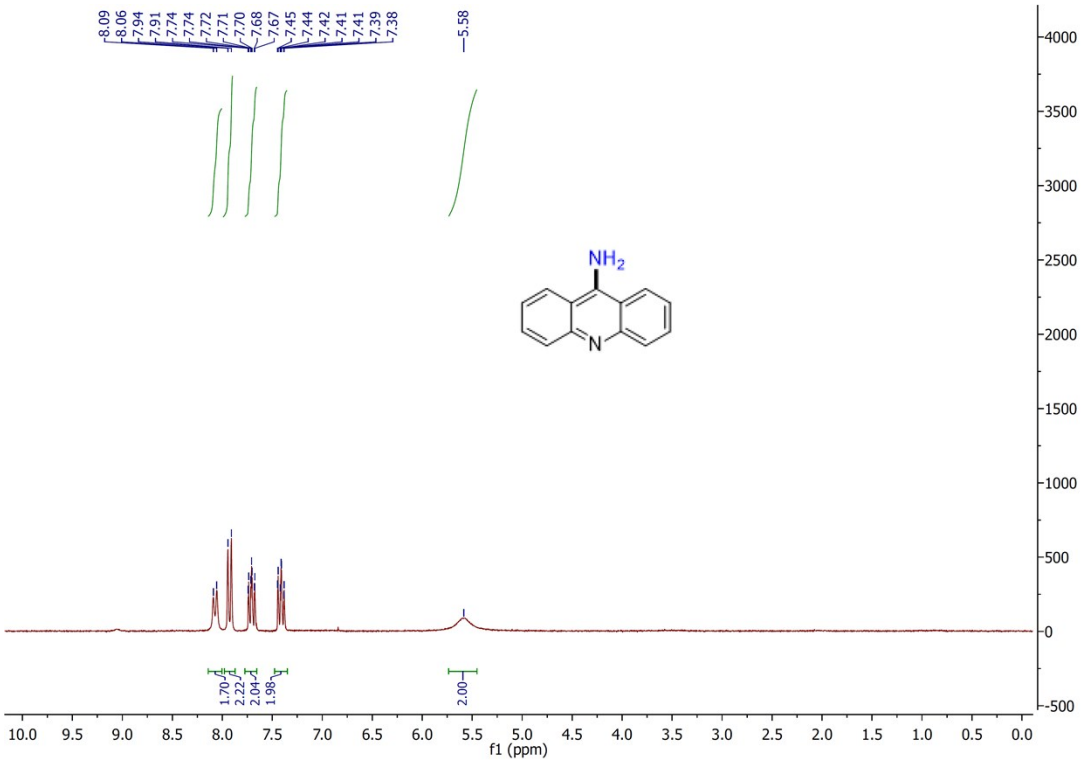
4.4. 2-Nitroaniline (3j)



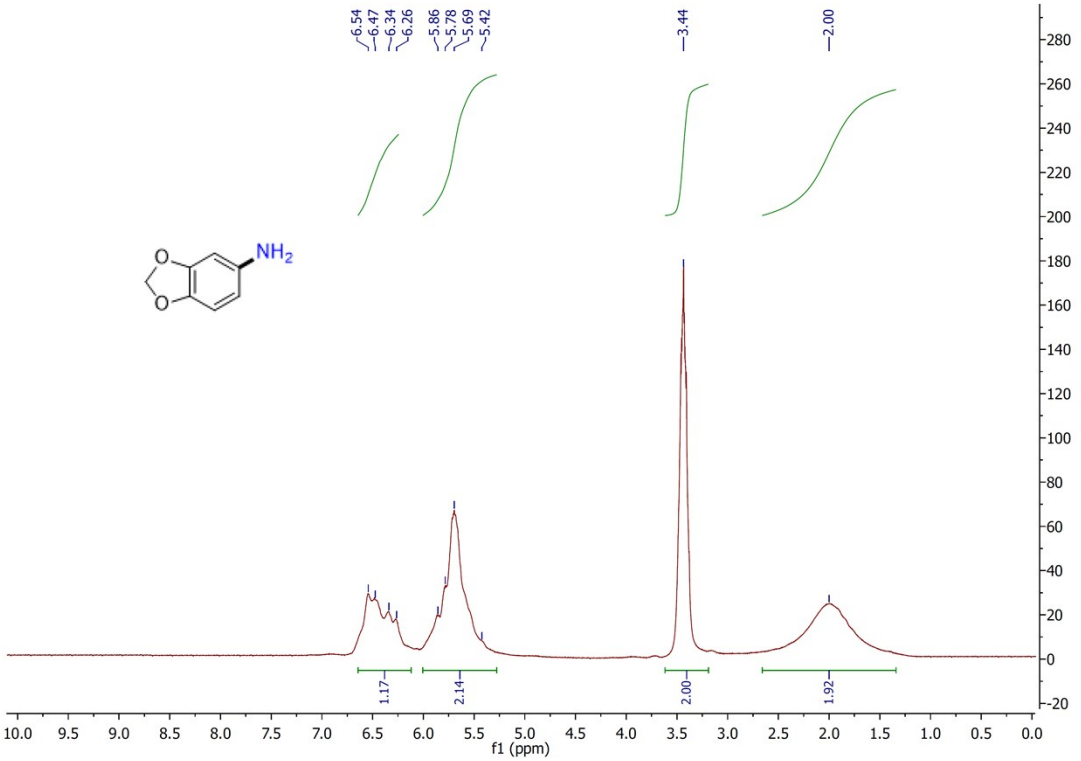
4.5. 4‘-Aminoacetophenone (3l)



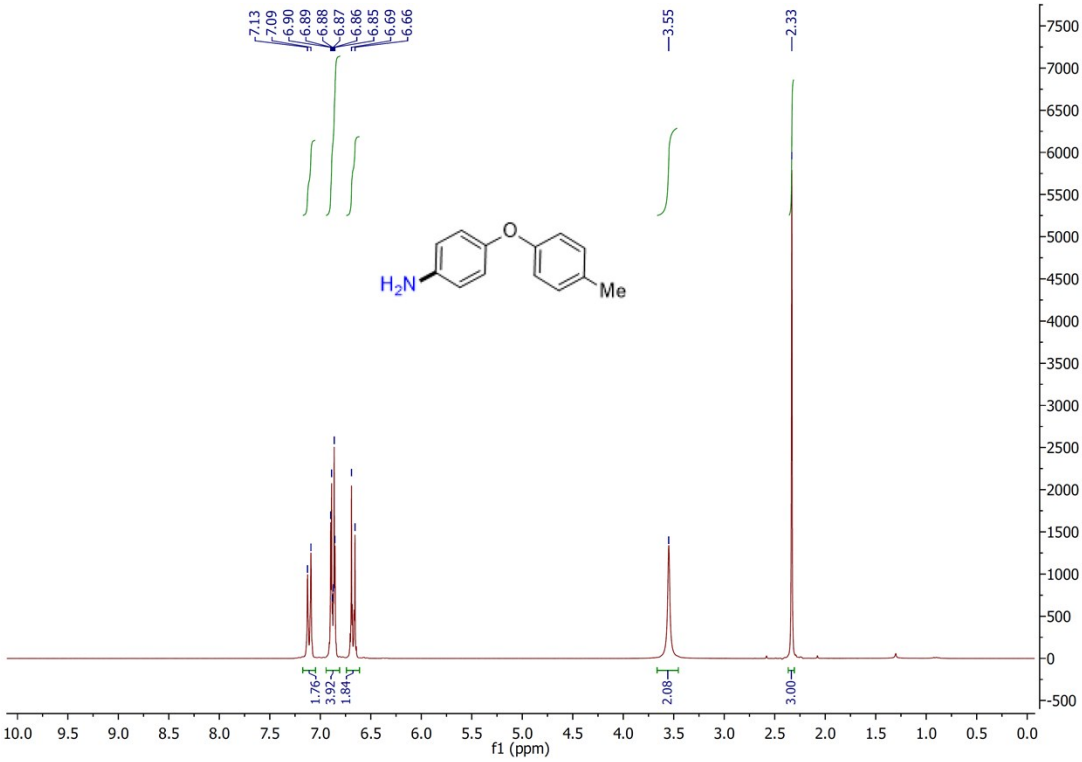
4.6. Acridine-9-amine (3n)



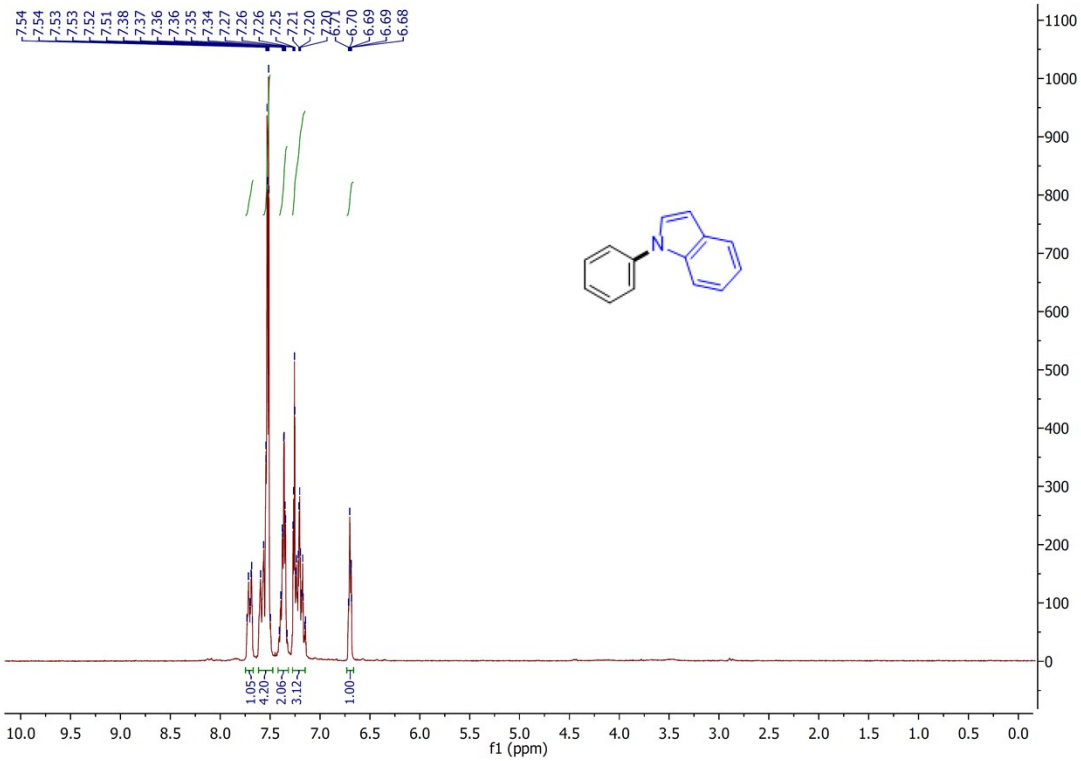
4.7. Benzo[d][1,3]dioxol-5-amine (3o)

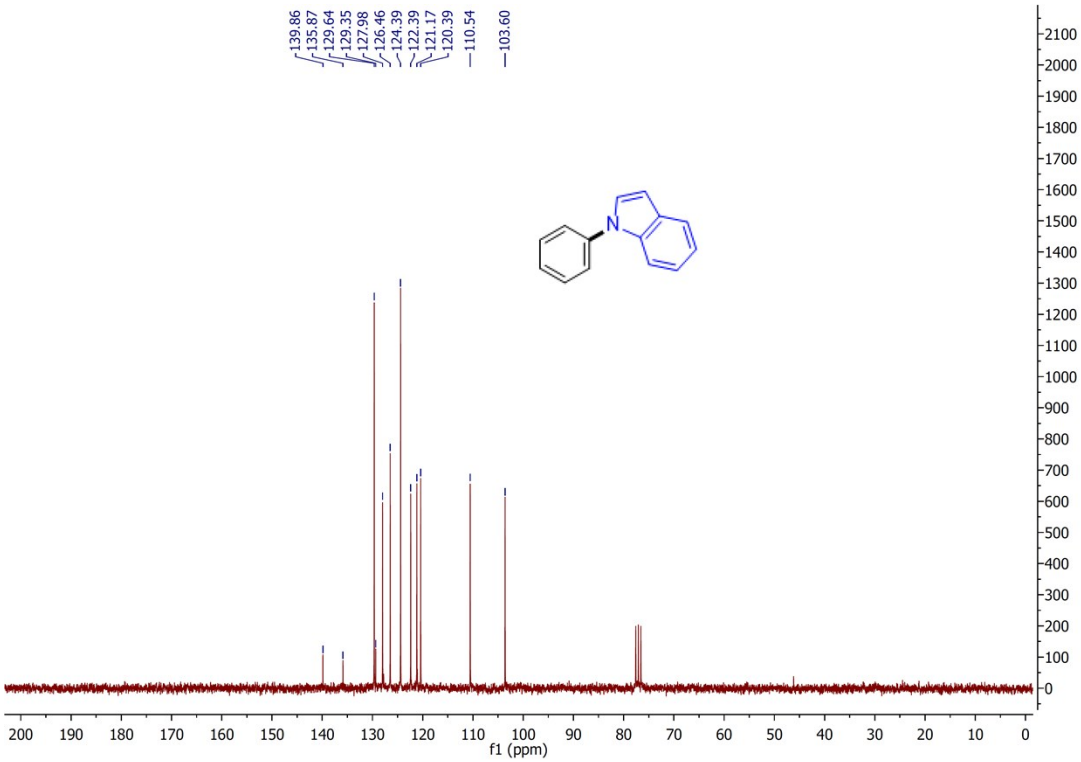


4.8. 4-(*p*-Tolyloxy)aniline (3r)

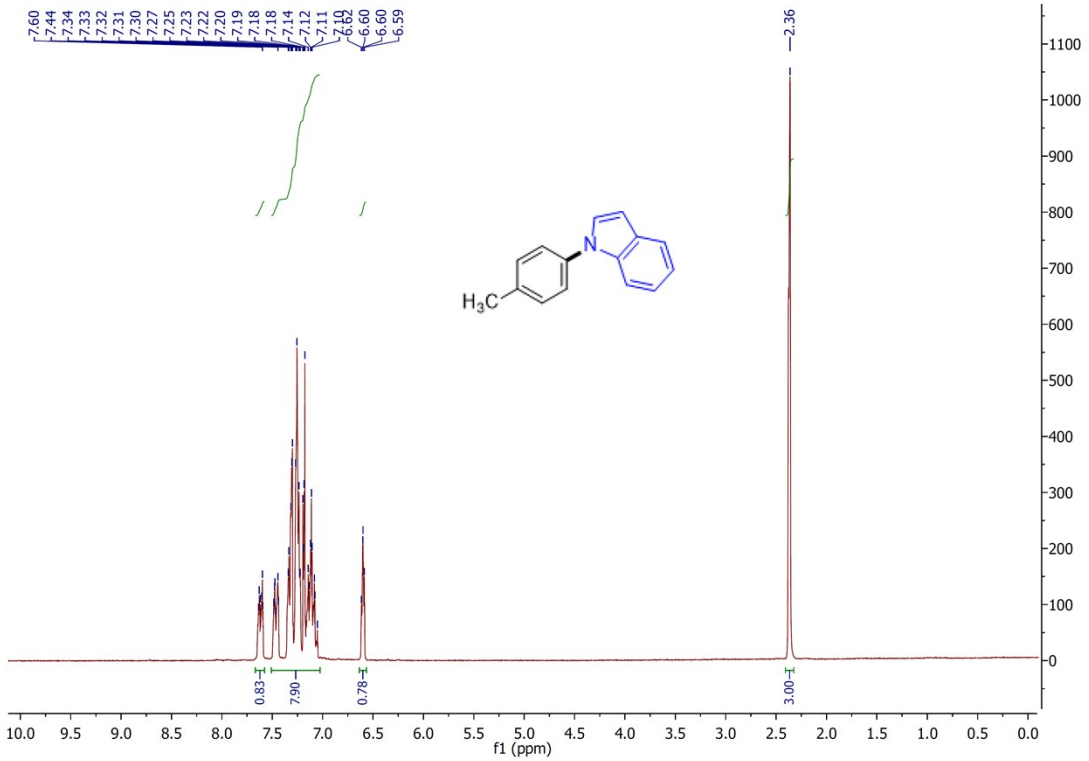


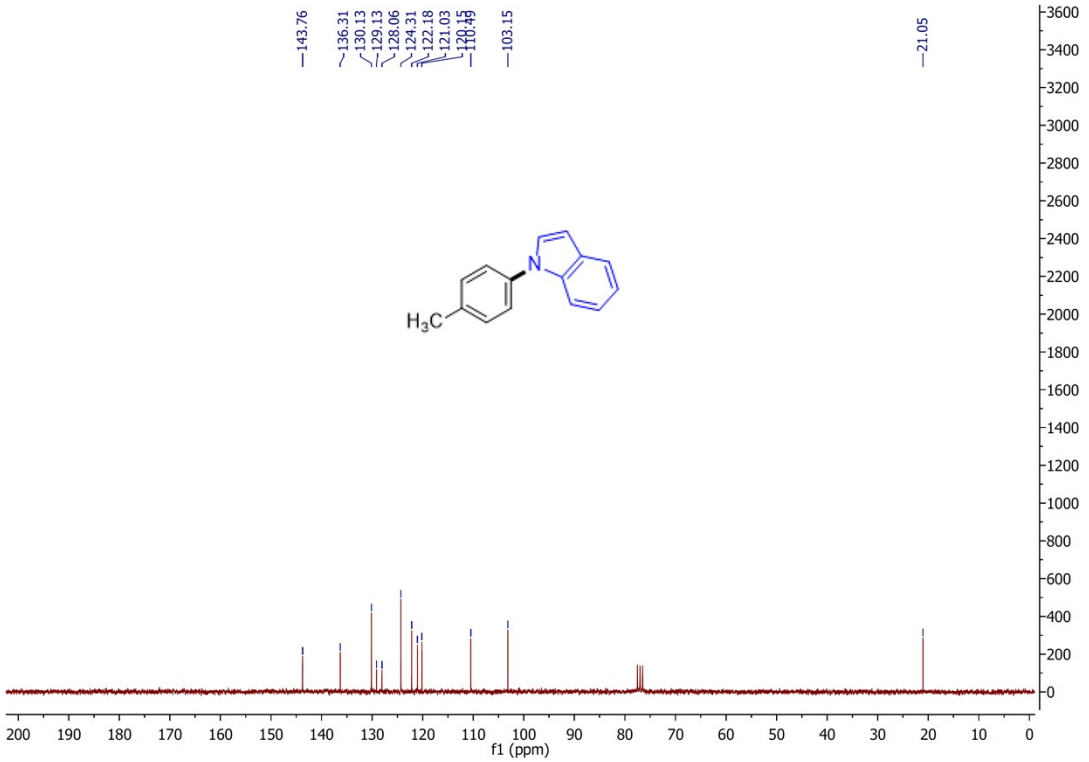
4.9. 1-Phenyl-*1H*-indene (4a)



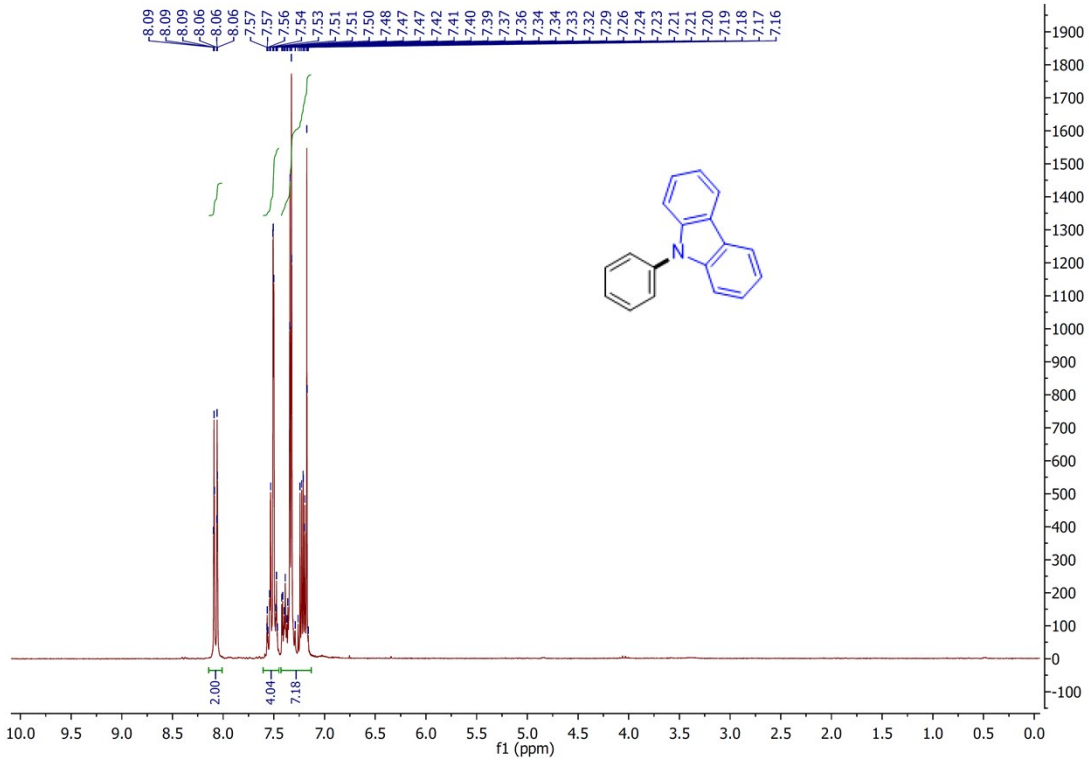


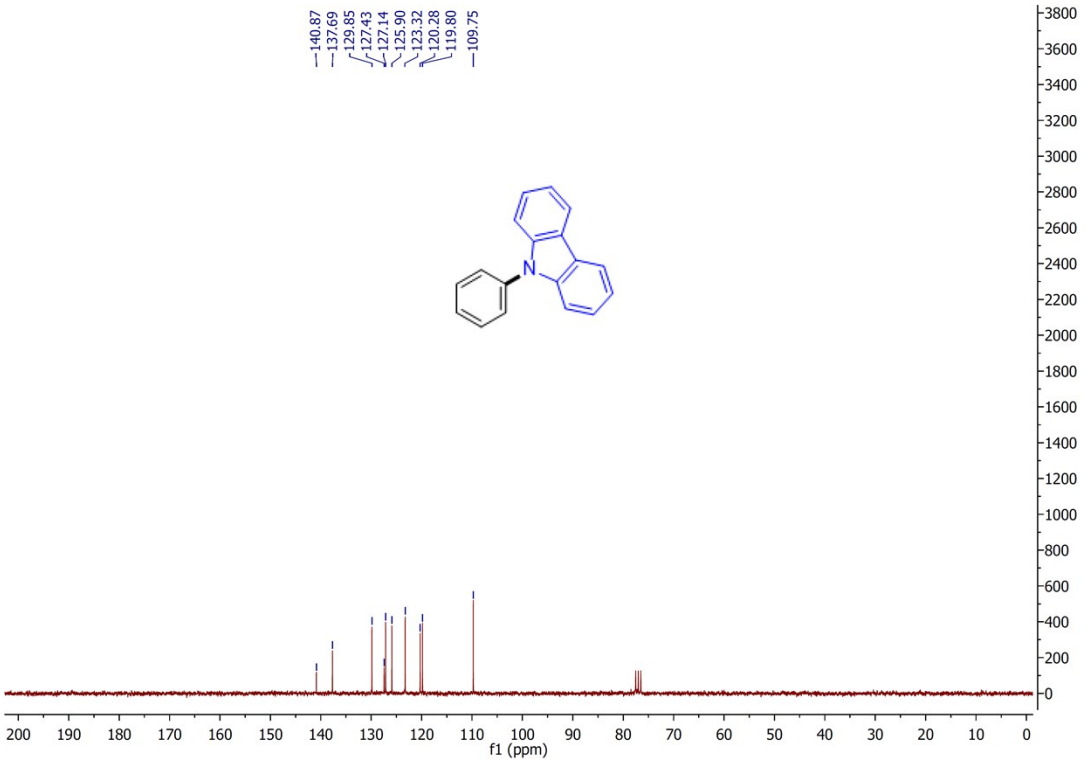
4.10. 1-*p*-Tolyl-*1H*-indole (4b)



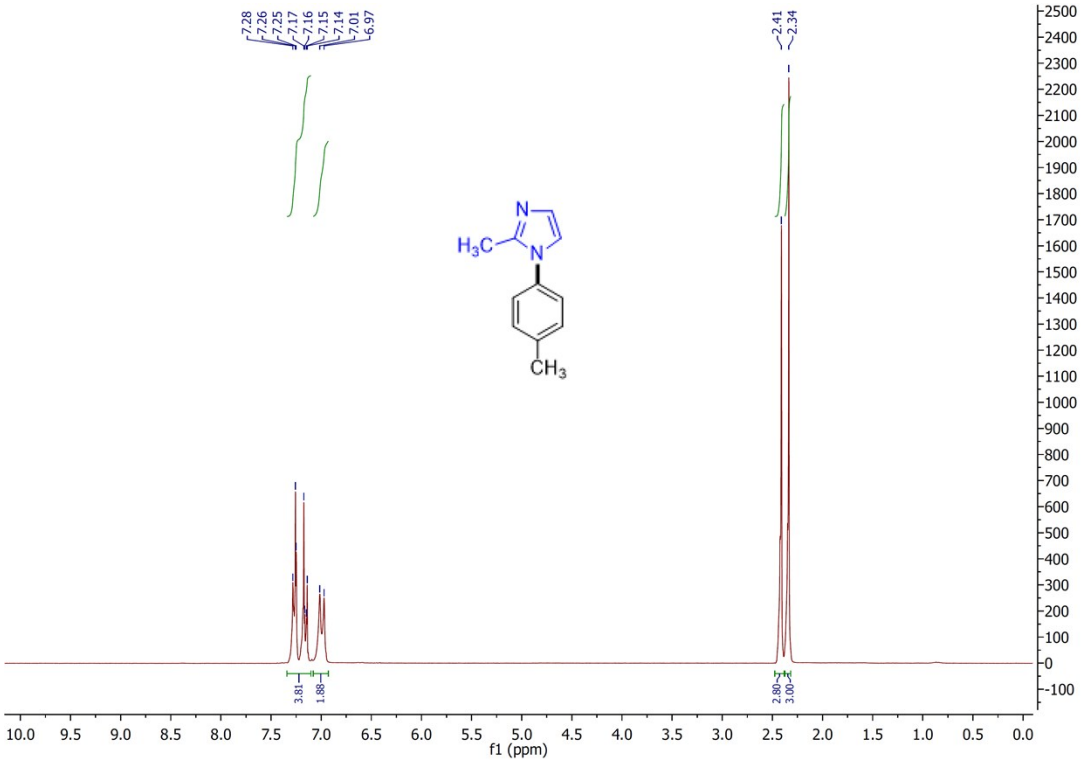


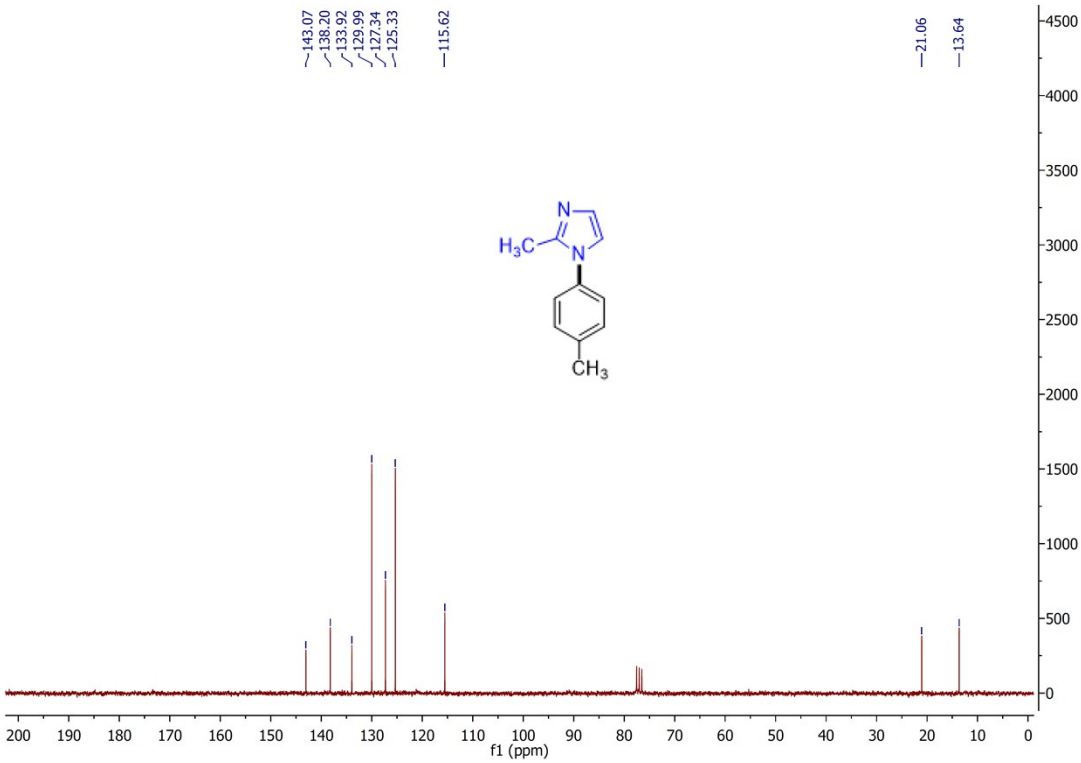
4.11. 9-Phenyl-*9H*-carbazole (4c)



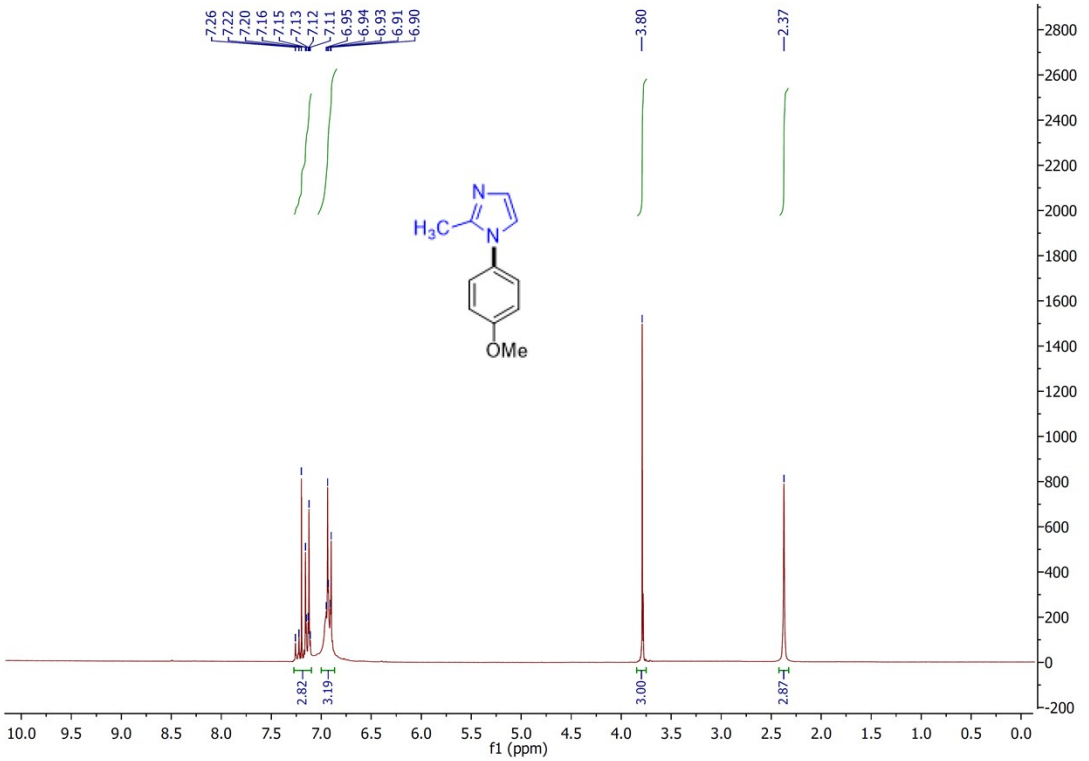


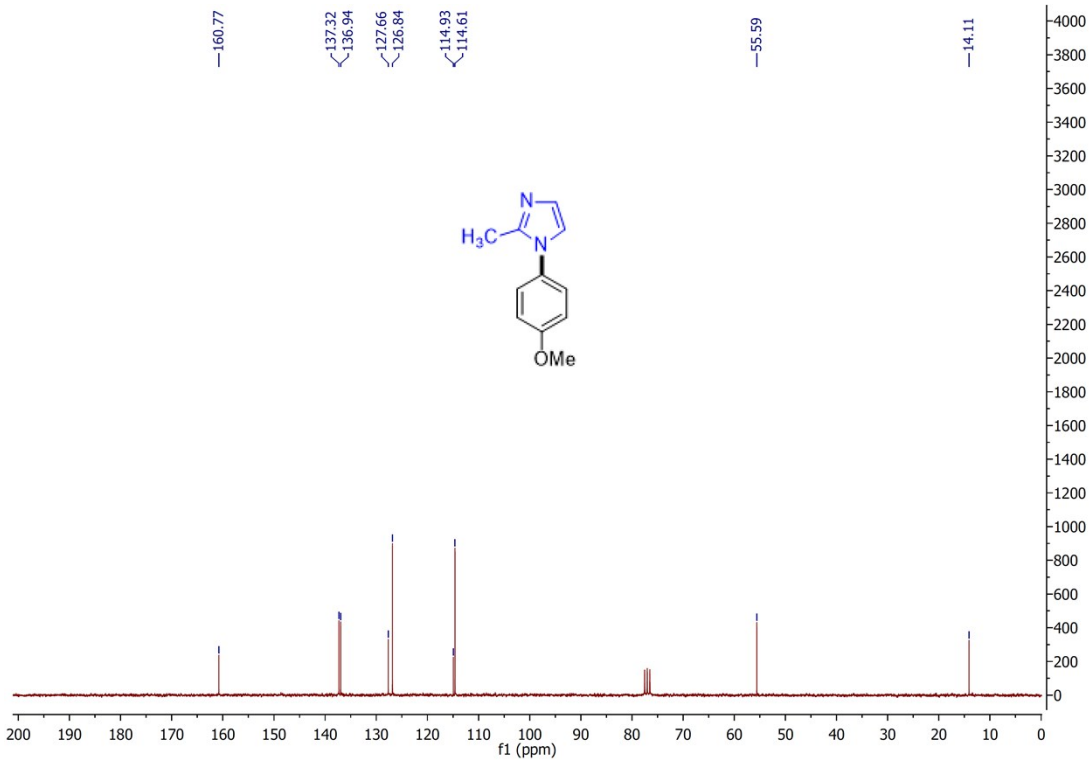
4.12. 2-Methyl-1-*p*-tolyl-*1H*-imidazole (4d)



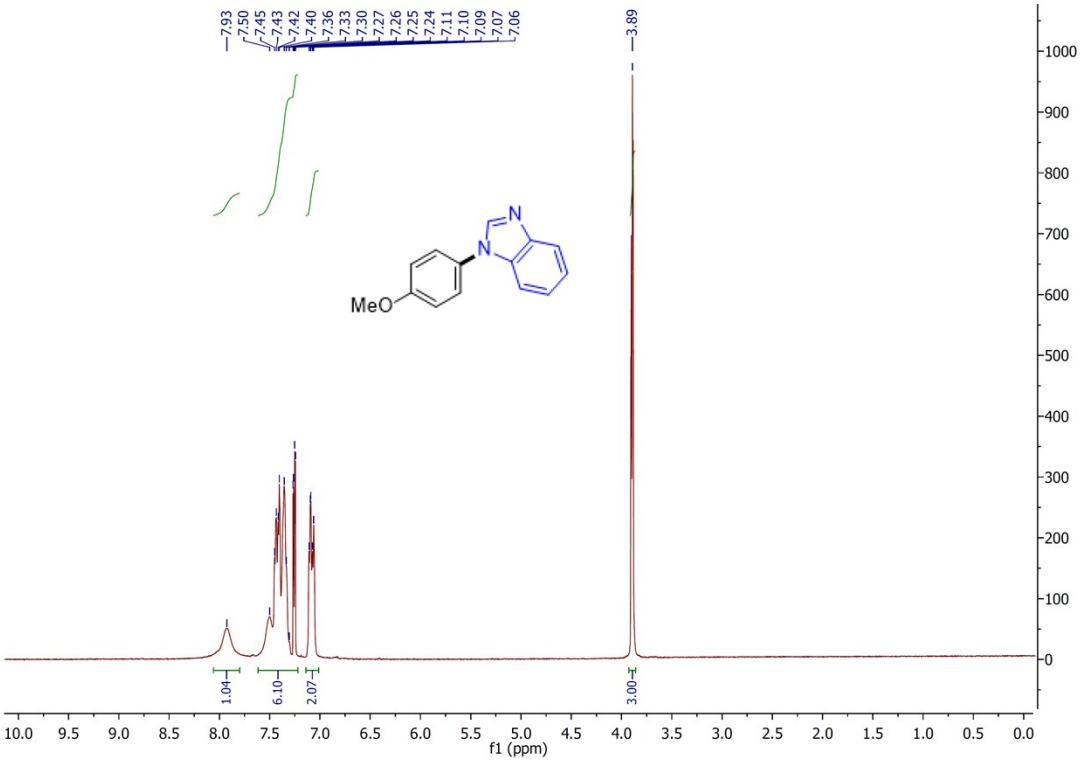


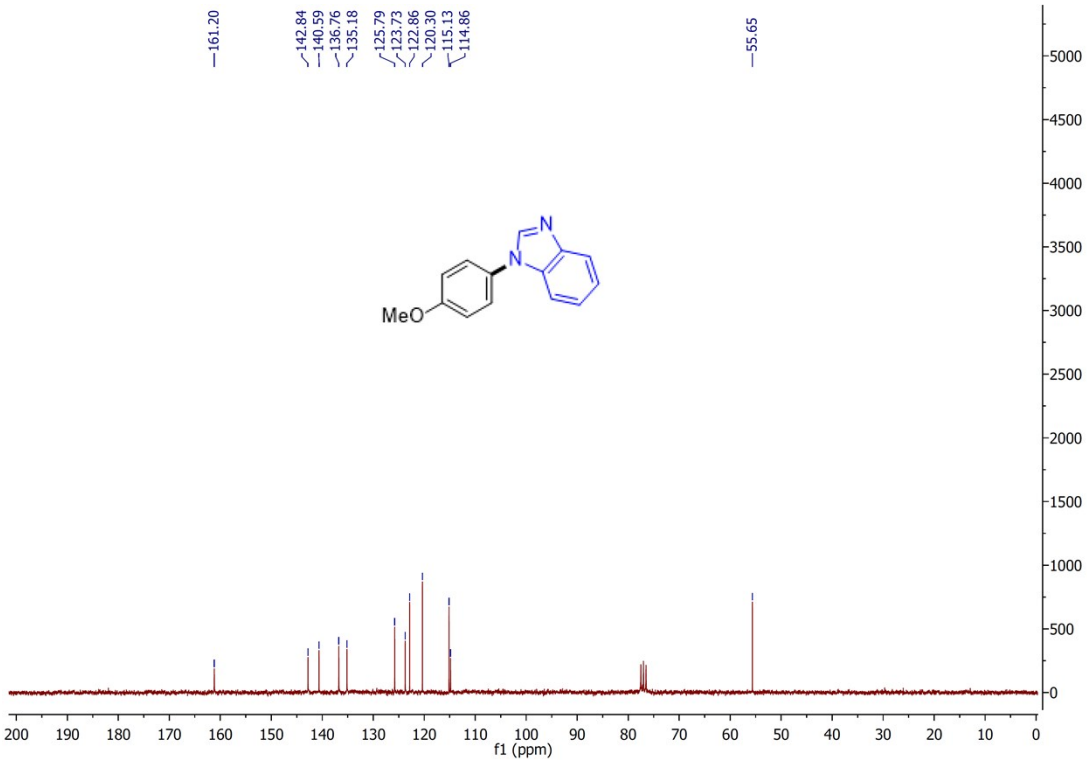
4.13. 1-(4-Methoxyphenyl)-2-methyl-*1H*-imidazole (4e)



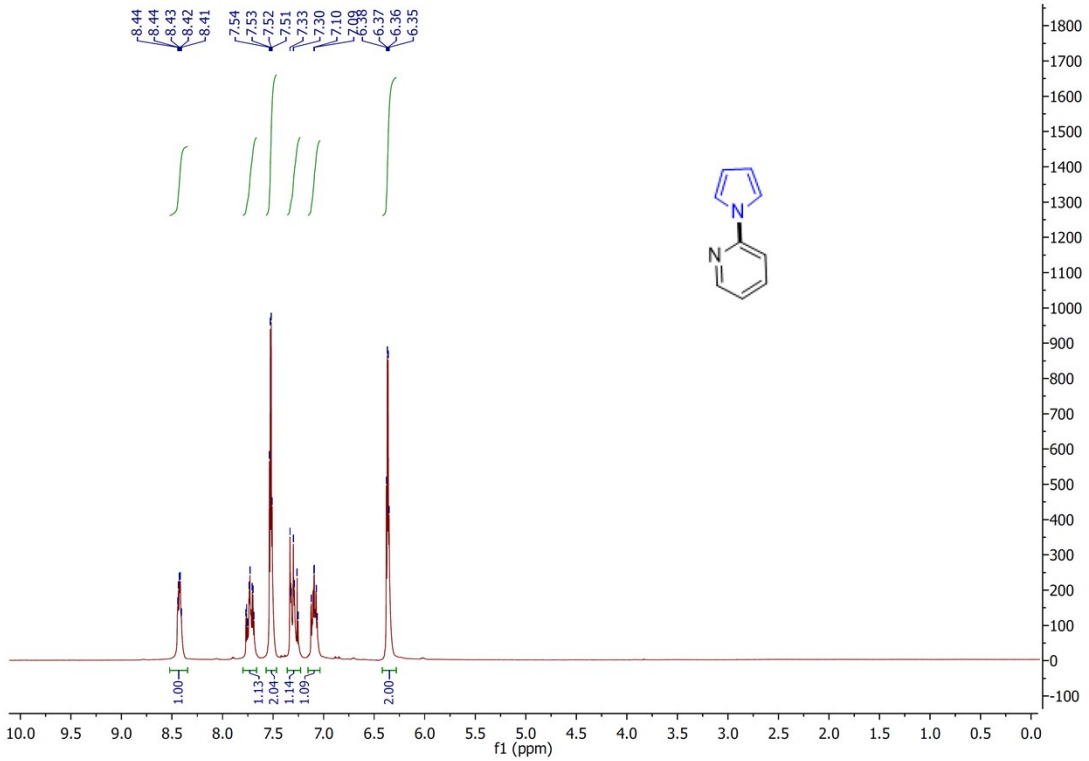


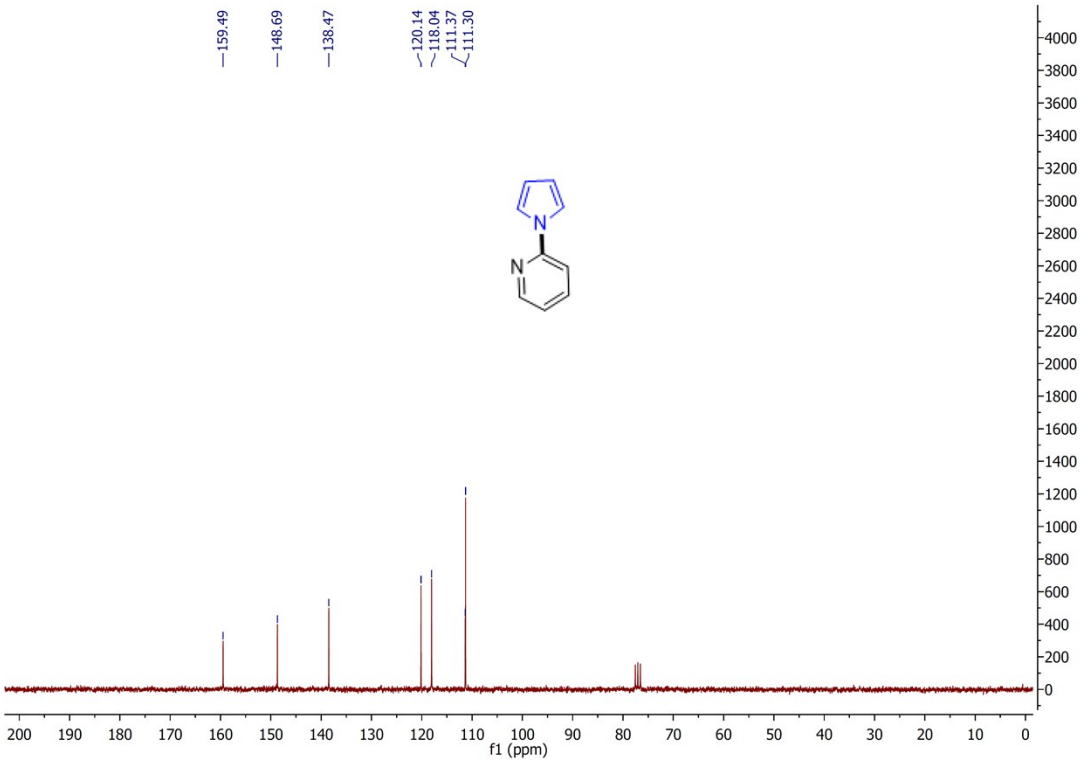
4.14.1-(4-Methoxyphenyl)-*1H*-benzo[d]imidazole (4f)



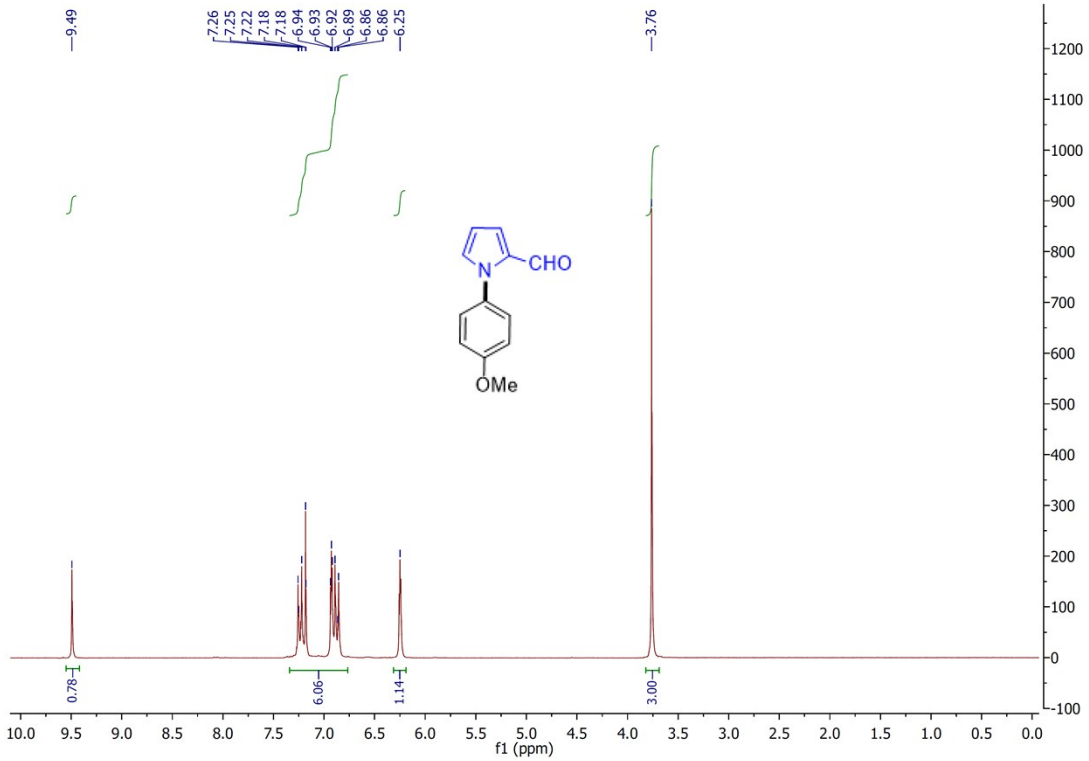


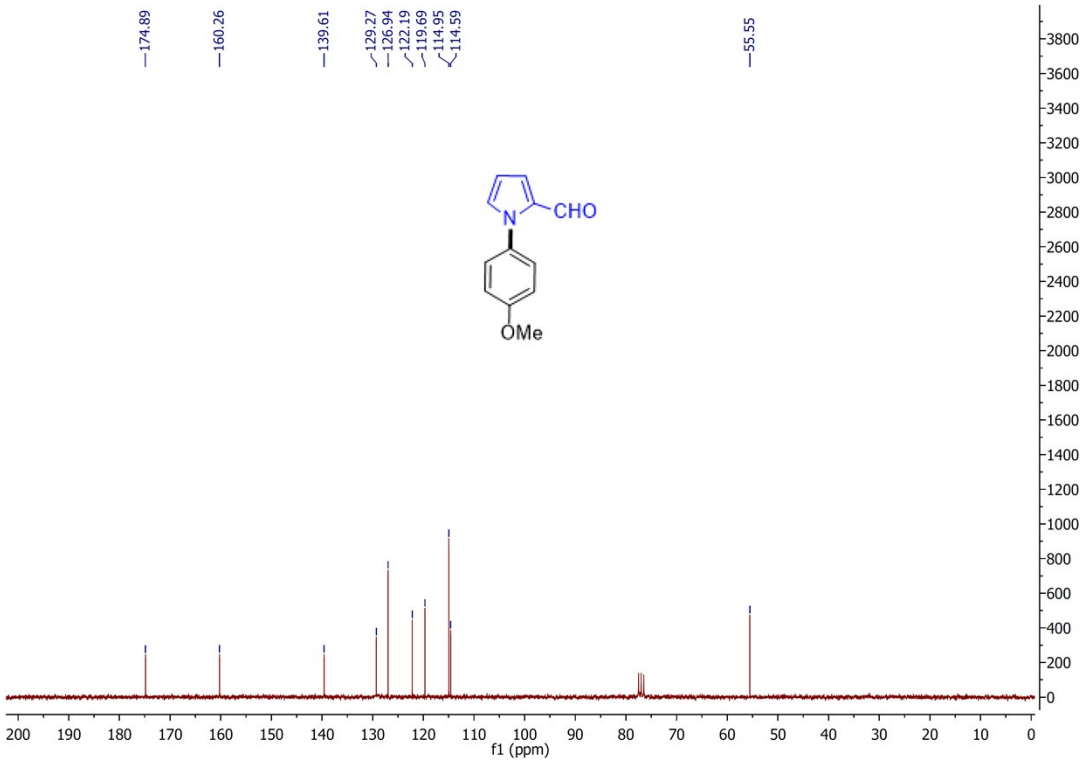
4.15. 2-(*1H*-Pyrrol-1-yl)pyridine (4g)



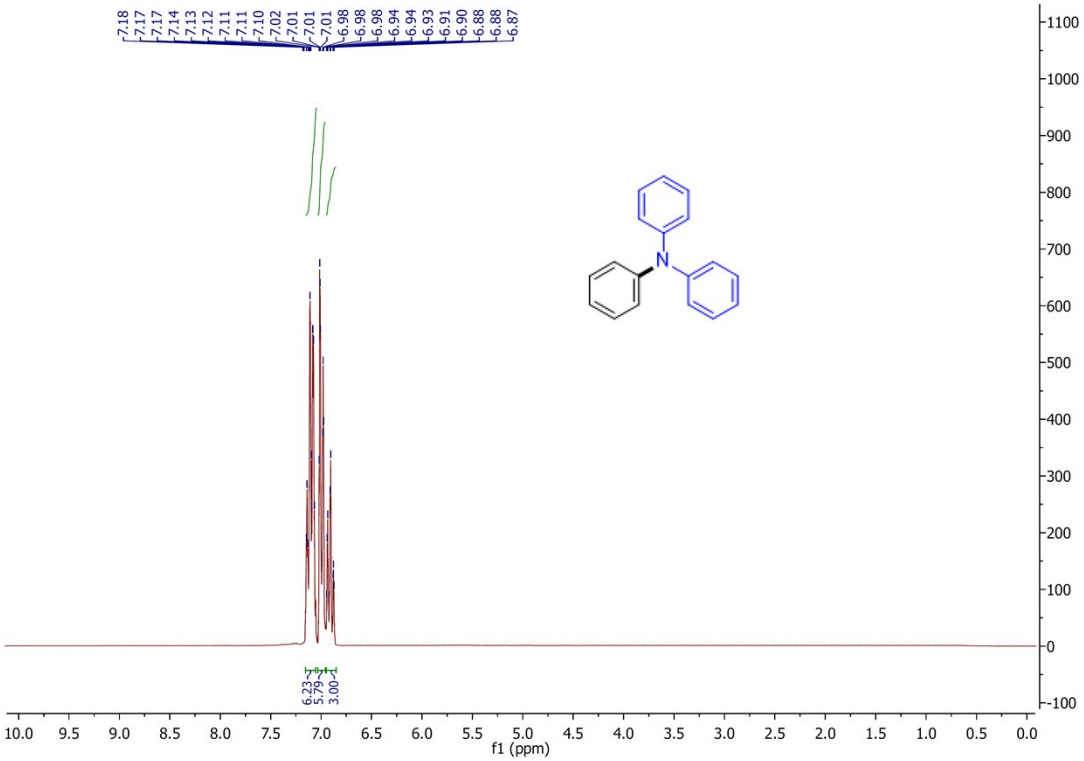


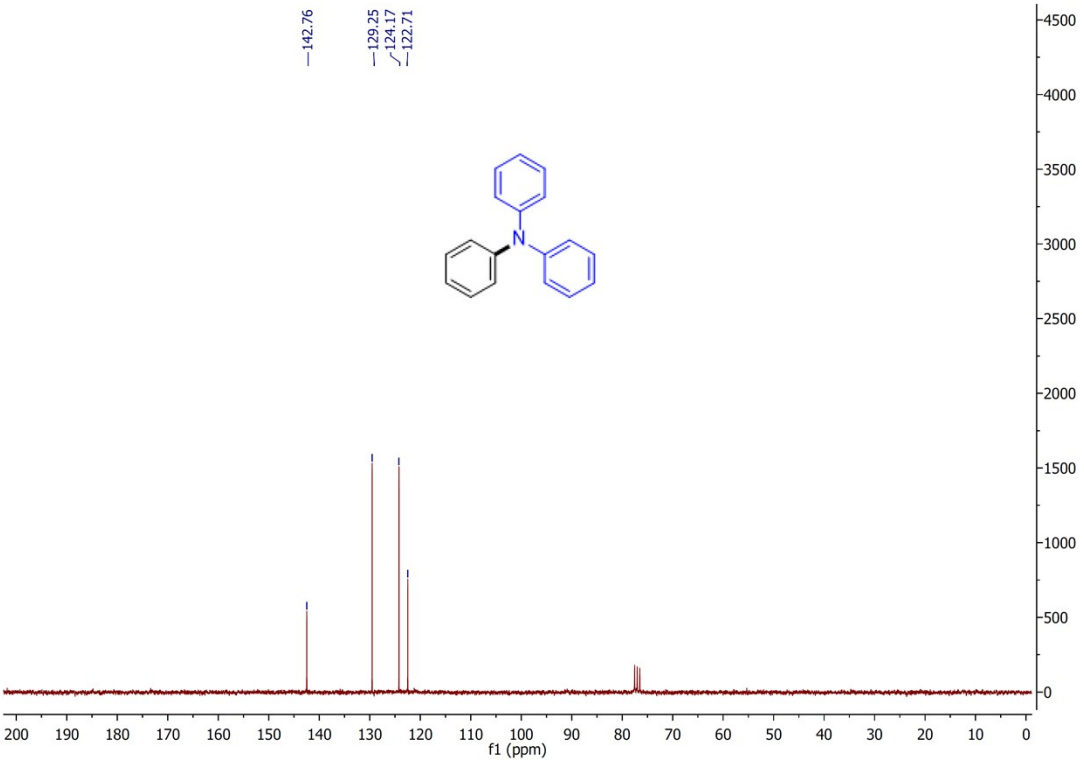
4.16. 1-(4-Methoxyphenyl)-*1H*-pyrrole-2-carbaldehyde (4h)





4.17. Triphenylamine (4i)





4.18. *N*-Dodecylbenzenamine (4j)