**Supplementary Information for:**

# Palladium Nanoparticles Embedded on Thiourea-Modified Chitosan: A Green and Sustainable Heterogeneous Catalyst for Suzuki Reaction in Water

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## Contents

**General Methods**

Absorbance spectroscopy was carried out using a UV-Vis., JASCO V-550 double beam spectrophotometer. Readings were taken at a wavelength range of 250–600 nm. FT-IR analyses were performed using shimandzu FT-IR-410 spectrometer in the range of 4000–400 $cm^{-1}$. The solid samples were dried and mixed with KBr to form pellets. The XRD pattern of the catalyst samples is measured using a Cu Kα radiation at room temperature. HR-TEM images were taken by JEOL-JEM-2100, High Resolution Transmission Electron Microscopy (HR-TEM). NMR spectra are registered on NMR spectrometer operating at 300 MHz for $^{1}H$ and 75 MHz for $^{13}C$. All $^{1}H$-NMR and $^{13}C$-NMR spectra are measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm. Purifications of biaryl products by column chromatography are performed on silica gel 60-120 mesh.

**Experimental details**

**a) Preparation of thiourea modified chitosan (TMC)**

A mixture of 16.1 g (0.1 mol) chitosan powder, 15.2 g (0.2 mol) ammonium thiocyanate and 150 mL ethanol in a three-neck flask with a magnetic stirring was refluxed for 12 h. After cooling down to room temperature, the precipitate was collected by filtration and repeatedly washed with ethanol, and then was dissolved in 500 mL of 1% (v/v) acetic acid solution. By adding 10% (w/v) NaOH solution into the solution and filtrating, the precipitate was collected and successfully washed with water and finally dried to give 16.5 g of thiourea modified chitosan. FT-IR spectra of chitosan and TMC are shown in figure S3 in SI.

**b) Green synthesis of PdNPs supported on TMC**

Increasing the concentrations of EA, from 0.1 eq to 0.5 eq (0.1 mmol to 0.5 mmol) in distilled water at pH=7 were prepared and immediately added with 1eq (1 mmol) of palladium (II) acetate solution. The samples were allowed to heat at 50 °C for 3 h, occurrence of color changed from orange red to brown black then UV-Vis., absorption spectroscopy was

recorded. This is the preliminary observations to conform the formation of Pd(0) in water which shown in figure 1. TMC was prepare as reported in literature available and characterized by FT-IR spectroscopy we took 1 g TMC with 100 mL of 0.1 % (v/v) acetic acid and palladium(II) acetate (1 mmol) stirred well for 5 min to the formation of Pd(II)/TMC complex at RT then added 0.5 mmol of fixed concentration of EA in distilled water at 50 °C for 3 h with constant stirring brown black color precipitate were formed contains PdNPs/TMC solid, at which they were filtered, and washed prior to characterized as well as catalyzed for Suzuki reaction in water.

**c) Typical procedures for Suzuki cross-coupling reaction**

PdNPs/TMC (20 mg), aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol) $K_2CO_3$ (3.0 mmol), water (3mL) are taken in reaction tube. The tube is heated on a preheated oil bath at a given temperature and magnetically stirred under atmospheric pressure. After the reaction was completed, the mixture was cooled to room temperature. Subsequently, the product and catalyst was filtered from the reaction mixture and washed three times with water (3 x 10 mL). Then the solid biaryl product was washed with diethyl ether and the organic phase is dried over $Na_2SO_4$. After evaporation of solvent the compound was analyzed by $^{1}H$ & $^{13}C$-NMR.

The reusability of PdNPs/TMC for Suzuki reaction was carried out by taking, iodobenzene (0.06 mL, 0.5 mmol), phenylboronic acid (0.06 g, 0.5 mmol) and $K_2CO_3$ (0.27 g, 2 mmol) in a reaction tube containing the PdNPs/TMC heterogeneous catayst (0.02 g) in water (2 mL) at 80 °C. After completion of the reaction, the reaction mixture was cooled to room temperature to give a dark solid mass of the catalyst. The resulting mass compound was washed with diethyl ether. The ethereal phase was separated and the resulting dark gray solid catalyst mass was used for another batch of the reaction.

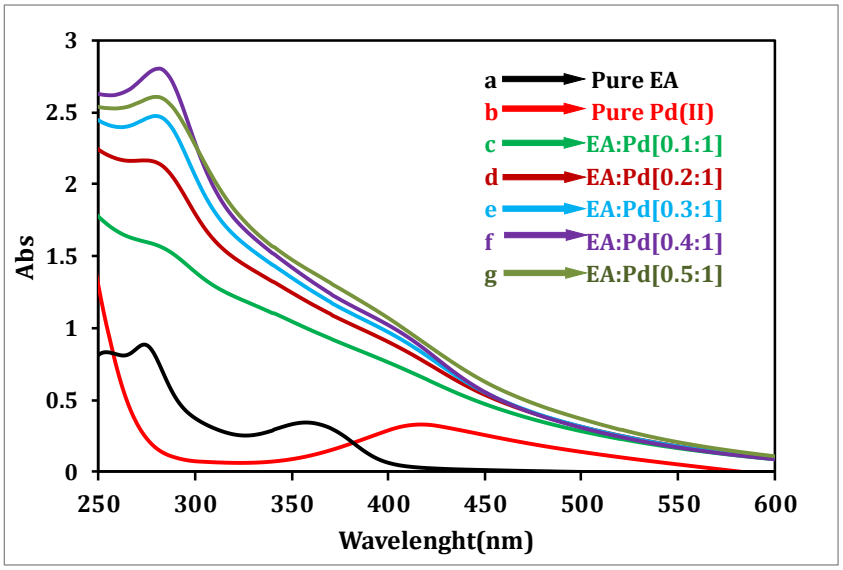


**Figure S1** UV-Vis., absorption spectra of PdNPs using EA as a green reducing agent. a) EA (0.5 mmol, 0.151 g); b) $Pd(OAc)_2$ (1 mmol, 0.224 g); 'c to g' increasing concentration of EA from (0.1-0.5 equiv.) in water at 50 ºC.

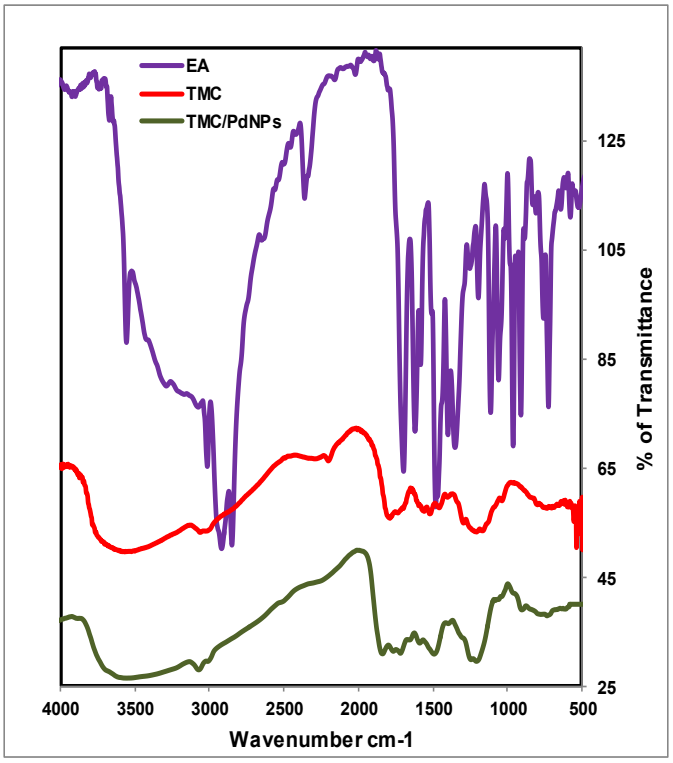


**Figure S2** FT-IR spectra of a) pure EA b) TMC c) PdNPs/TMC.

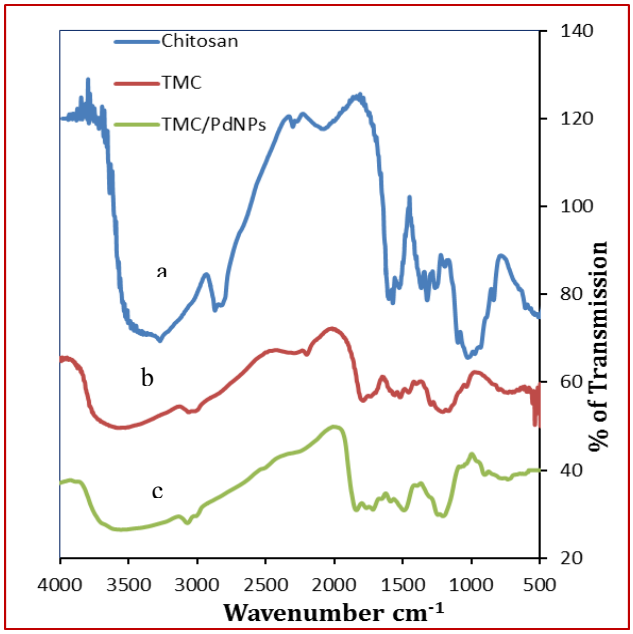


**Figure S3** FT-IR spectra of pure a) chitosan b) TMC c) TMC/PdNPs heterogeneous catalyst.

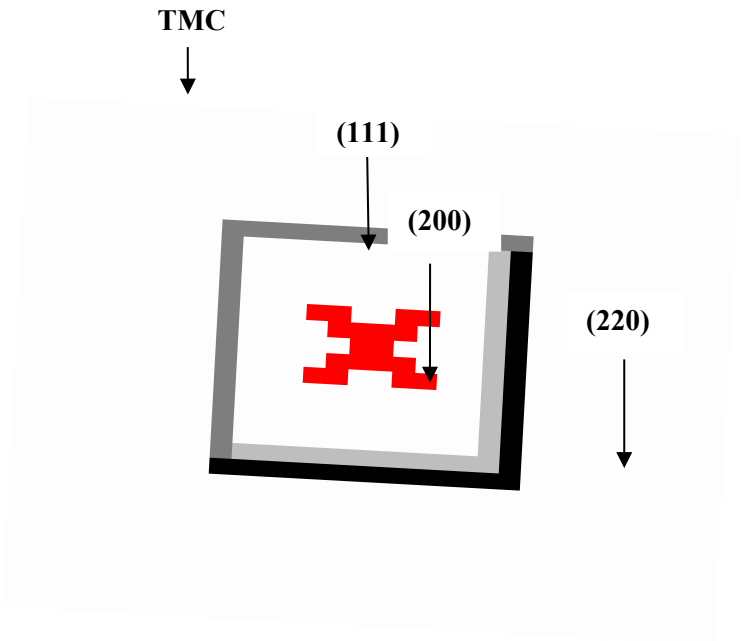


**Figure S4** XRD pattern of PdNPs/TMC catalyst

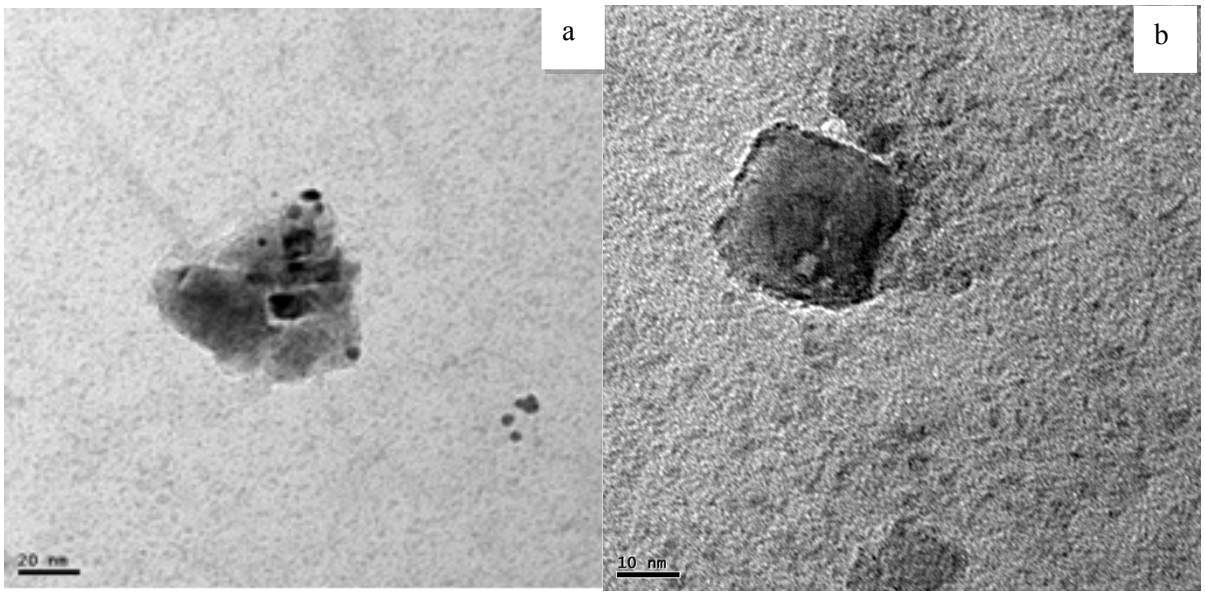


**Figure S5** a) TEM image of cubical and spherical shaped PdNPs observed on TMC solid surface (scale 20 nm).

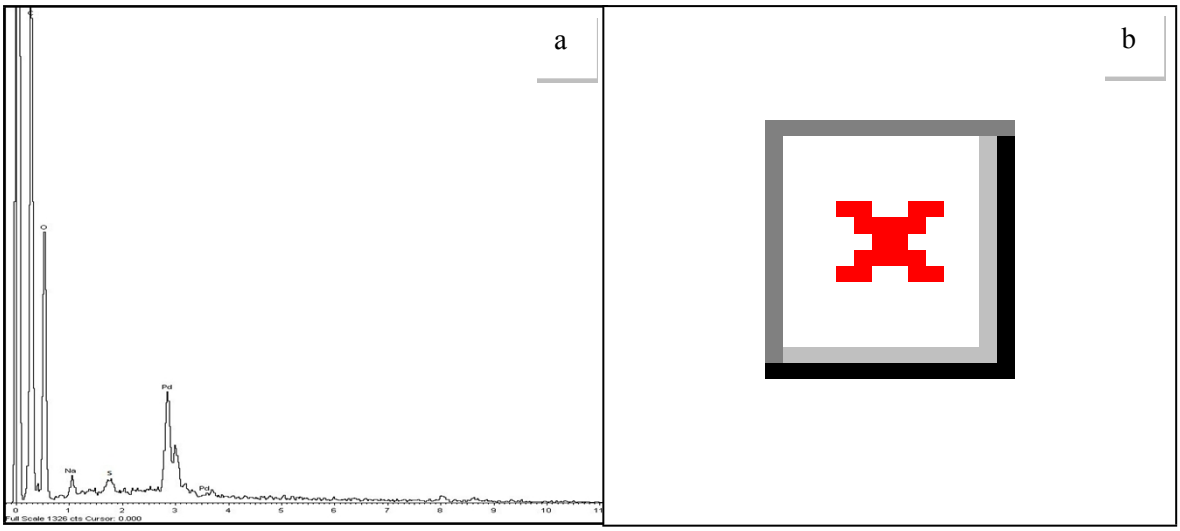


**Figure S6** a) HR-TEM image of single cube (scale 10 nm). c) EDX spectra of the freshly prepared PdNPs/TMC. d) EDX spectra of PdNPs/TMC catalyst after reused.

## $^{1}H$ and $^{13}C$-NMR Characterisation data

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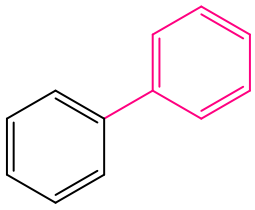
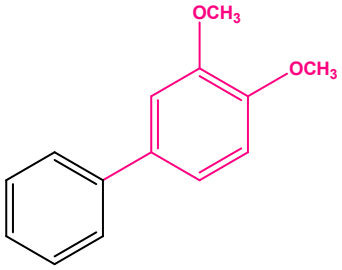
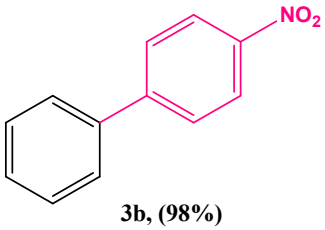
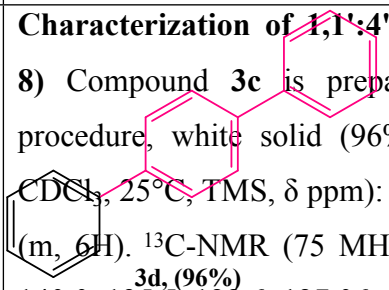
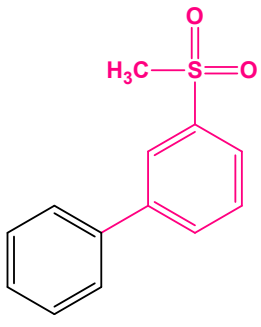
|  3, (99%) | **Characterization of 1, 1'-biphenyl, (Table 2, entry 1)** Compound **3** is prepared according to the general procedure, white solid (99% yield). $^{1}H$-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 7.60 (d, 4H), 7.45 (d, 4H), 7.35 (m, 2H). $^{13}C$-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 127.1, 127.2, 128.7, 141.24. |
|  3a, (98%) | **Characterization of 3, 4-dimethoxy-1, 1'-biphenyl, (Table 2, entry 4)** Compound **3a** is prepared according to the general procedure, white solid (98% yield). $^{1}H$-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 3.92(s, 6H), 6.94 (s, 1H), 6.92 (d, 1H), 7.30 (d, 1H), 7.32 (d, 2H), 7.42 (t, 2H), 7.55(m, 1H). $^{13}C$-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 55.8, 110.3, 111.4, 119.27, 126.7, 128.6, 134.1, 140.01, 140.5, 149.1. |
|  3b, (98%) | **Characterization of 3-nitro-1, 1'-biphenyl, (Table 2, entry 6)** Compound **3b** is prepared according to the general procedure, light yellow solid (98% yield). $^{1}H$-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 8.35 (m, 2H), 7.75(m, 2H), 7.52(m, 2H), 7.42(m, 3H). $^{13}C$-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 124.0, 124.7, 127.7, 128.8, 129.0, 144.9, 147.5. |
|  3d, (96%) | **Characterization of 1,1':4',1''-terphenyl, (Table 2, entry 8)** Compound **3c** is prepared according to the general procedure, white solid (96% yield). $^{1}H$-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 7.26 (m, 4H), 7.36 (m, 4H), 7.65 (m, 6H). $^{13}C$-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 140.0, 135.5, 128.6, 127.06, 101.0, 108.4. |
|  3d, (91%) | **Characterization of 3-(methylsulfonyl)-1,1'-biphenyl, (Table 2, entry 9)** Compound **3d** is prepared according to the |

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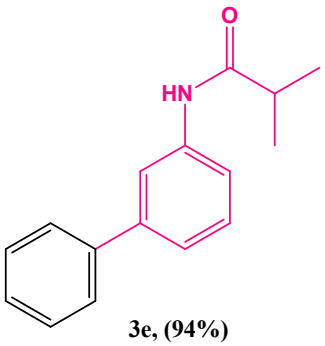
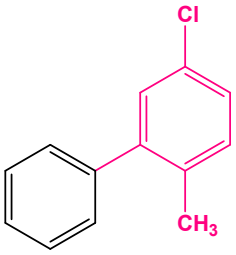
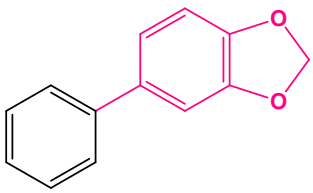
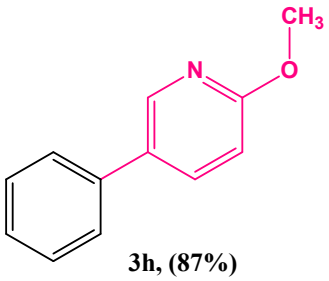
| | general procedure, white solid (91% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 3.07 (s, 3H), 8.24 (s, 1H), 8.14 (d, 1H), 8.00(m, 1H), 7.8 (m, 1H), 7.5 (m, 5H). $^{13}$C-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 44.50, 125.7, 127.2, 128.4, 129.8, 132.2, 130.2, 138.9, 142.6. |
|  <br>**3e, (94%)** | **Characterization of N-([1,1'-biphenyl]-3-yl)isobutyramide, (Table 2, entry 11)** Compound **3e** is prepared according to the general procedure, white solid (94% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 3.13(sep, 1H), 1.5 (d, 6H), 8.2 (s, 1H), 7.15(d, 1H), 7.21 (d, 1H), 7.55 (d, 1H), 7.3-7.4 (m, 5H). $^{13}$C-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 21.5, 38.2, 129.2, 127.1, 127.9, 128.6, 138.2, 141.2, 11.3, 169.9. |
|  <br>**3f, (80%)** | **Characterization of 5-chloro-2-methyl-1,1'-biphenyl, (Table 2, entry 13)** Compound **3f** is prepared according to the general procedure, white solid (80% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 2.1(s, 3H), 7.14 (s, 1H), 7.25(d, 1H), 7.10 (d, 1H), 7.31-7.6 (m, 5H). $^{13}$C-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 21.7, 126.0, 126.5, 126.9, 127.3, 127.8, 128.17, 128.37, 128.68, 137.32. |
|  <br>**3g, (90%)** | **Characterization of 5-phenylbenzo[d][1,3]dioxole, (Table 2, entry 14)** Compound **3g** is prepared according to the general procedure, white solid (90% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 5.94(s, 2H), 6.92 (d, 1H), 7.10(d, 1H), 7.15 (s, 1H), 7.3-7.5 (m, 5H). $^{13}$C-NMR (75 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 101.0, 107.58, 108.47, 127.2, 128.1, 128.7, 129.57, 131.3, 131.5, 133.78, 140.72, 143.52. |
|  <br>**3h, (87%)** | **Characterization of 2-methoxy-5-phenylpyridine, (Table 2, entry 15)** Compound **3h** is prepared according to the general procedure, white solid (87% yield). $^{1}$H-NMR (300 |

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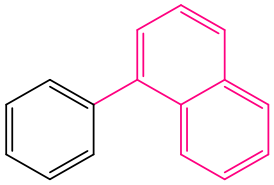
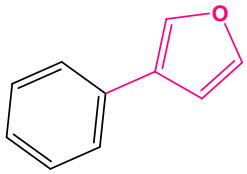
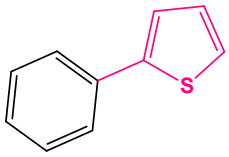
| | MHz, $CDCl_3$, 25°C, TMS, δ ppm): 3.85(s, 3H), 5.94 (s, 1H), 6.85(d, 1H), 7.0 (d, 1H), 7.20-7.56 (m, 5H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 55.83, 101.03, 107.5, 120.5, 126.7, 127.16, 128.64, 135.52, 146.99, 140.05. |
|  **3i, (97%)** | **Characterization of 1-phenylnaphthalene, (Table 2, entry 16)** Compound **3i** is prepared according to the general procedure, white solid (97% yield). $^{1}$H-NMR (400 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 7.07 (t, 1H), 7.80(d, 1H), 7.85 (d, 1H), 8.20 (d, 2H), 7.28 (t, 1H), 8.30 (d, 1H), 7.78 (t, 1H), 7.50 (m, 5H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 126.34, 126.73, 127.35, 127.42, 127.97, 128.59, 128.96, 131.55, 132.55, 133.39, 134.79, 149.48. |
|   **3k, (84%)** | **Characterization of 3-phenylfuran, (Table 2, entry 19)** Compound **3k** is prepared according to the general procedure, white solid (84% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 6.61 (d, 1H), 7.15 (d, 1H), 7.25 (d, 1H), 7.34 (m, 5H), 8.12 (s, 1H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 120.6, 124.8, 126.2, 127.60, 128.37, 128.61, 129.25, 142.53. |
|   **3l, (92%)** | **Characterization of 3-phenylthiophene, (Table 2, entry 21)** Compound **3l** is prepared according to the general procedure, white solid (92% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 7.59 (s, 1H), 7.15 (d, 1H), 7.21 (d, 1H), 7.32 (m, 5H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 110.36, 115.22, 123.1, 127.5, 128.7, 132.99, 137.05, 143.30. |

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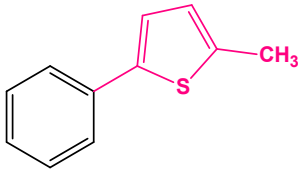
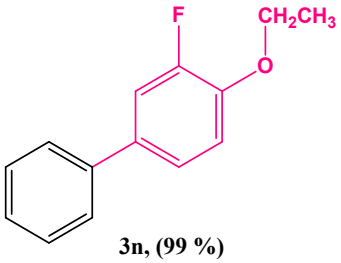
|  <br>**3m, (91%)** | **Characterization of 2-methyl-5-phenylthiophene, (Table 2, entry 22)** Compound **3m** is prepared according to the general procedure, white solid (91% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 1.25 (s, 3H), 7.10 (d, 1H), 7.34 (d, 1H), 7.97 (t, 1H) 7.43 (t, 2H), 7.59 (d, 2H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 29.52, 110.36, 115.2, 123.15, 126.95, 127.10, 128.3, 132.9, 137.9, 143.30. |
|  <br>**3n, (99 %)** | **Characterization of 4-ethoxy-3-fluoro-1,1'-biphenyl, (Table 2, entry 23)** Compound **3n** is prepared according to the general procedure, white solid (99% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 4.13(q, 2H), 1.46 (t, 3H), 7.21 (s, 1H), 7.50 (d, 1H), 7.60 (d, 1H), 7.33 (m, 5H). $^{13}$C-NMR (100 MHz, $CDCl_3$, 25°C, TMS, δ ppm): 14.56, 64.64, 114.5, 122.3, 126.3, 127.06, 128.65, 133.97, 139.43, 146.15, 150.99, 154.24. |

# $^{1}$H & $^{13}$C-NMR spectra

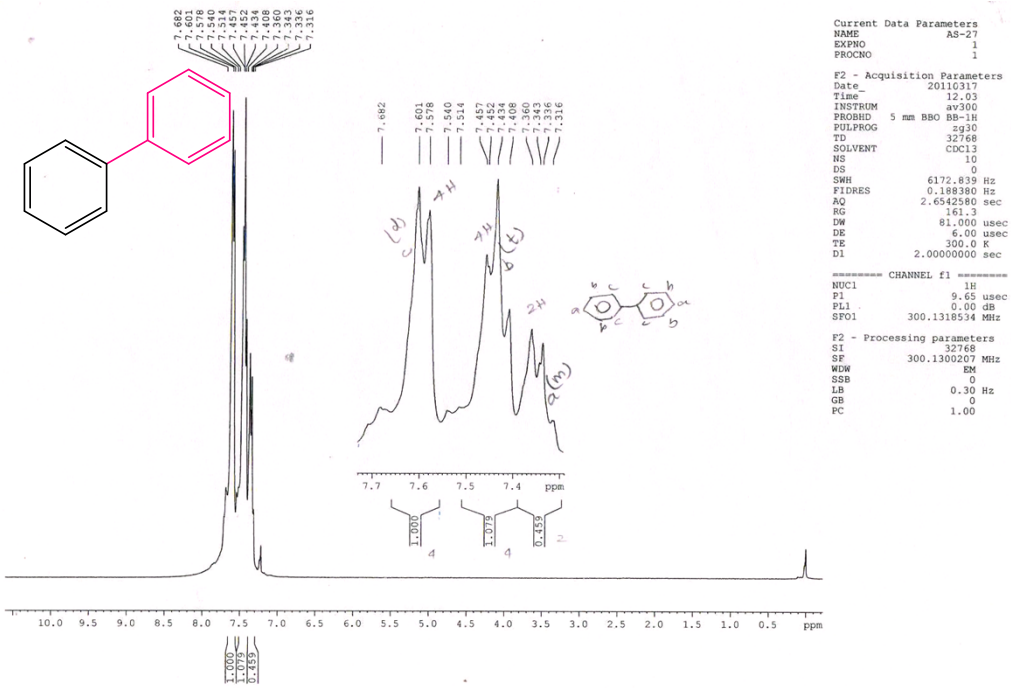



**Figure S6** $^{1}$H-NMR spectrum of 1,1'-biphenyl **3** (Table 2)

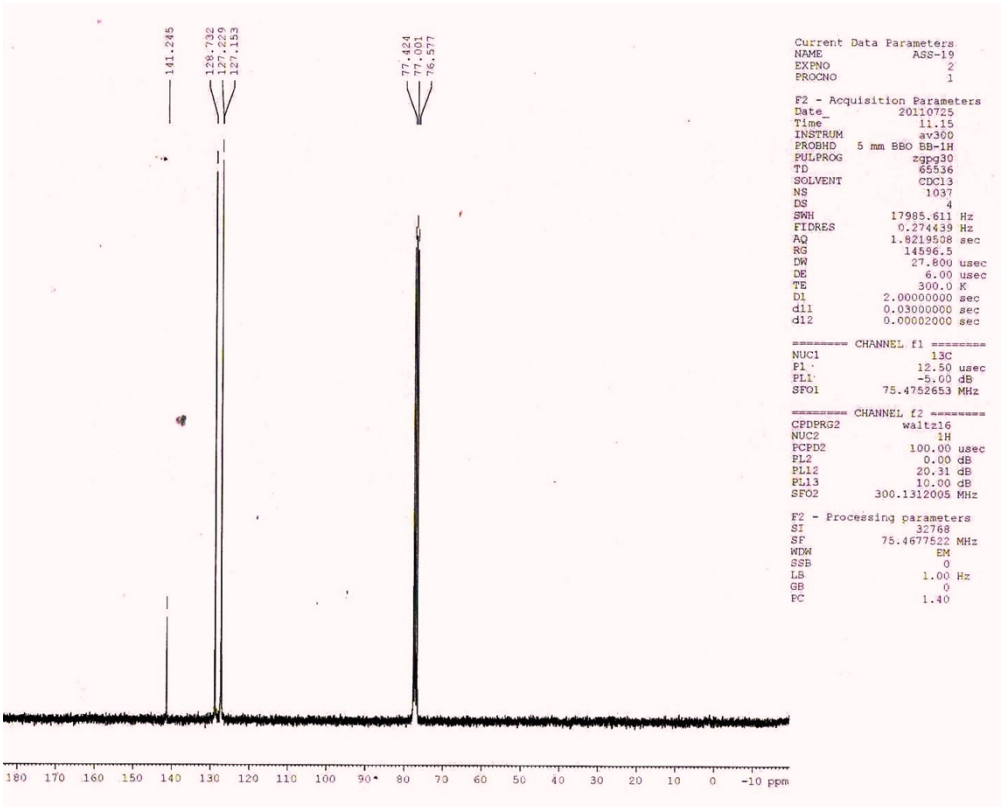



**Figure S7** $^{13}$C-NMR spectrum of 1,1'-biphenyl **3** (Table 2)

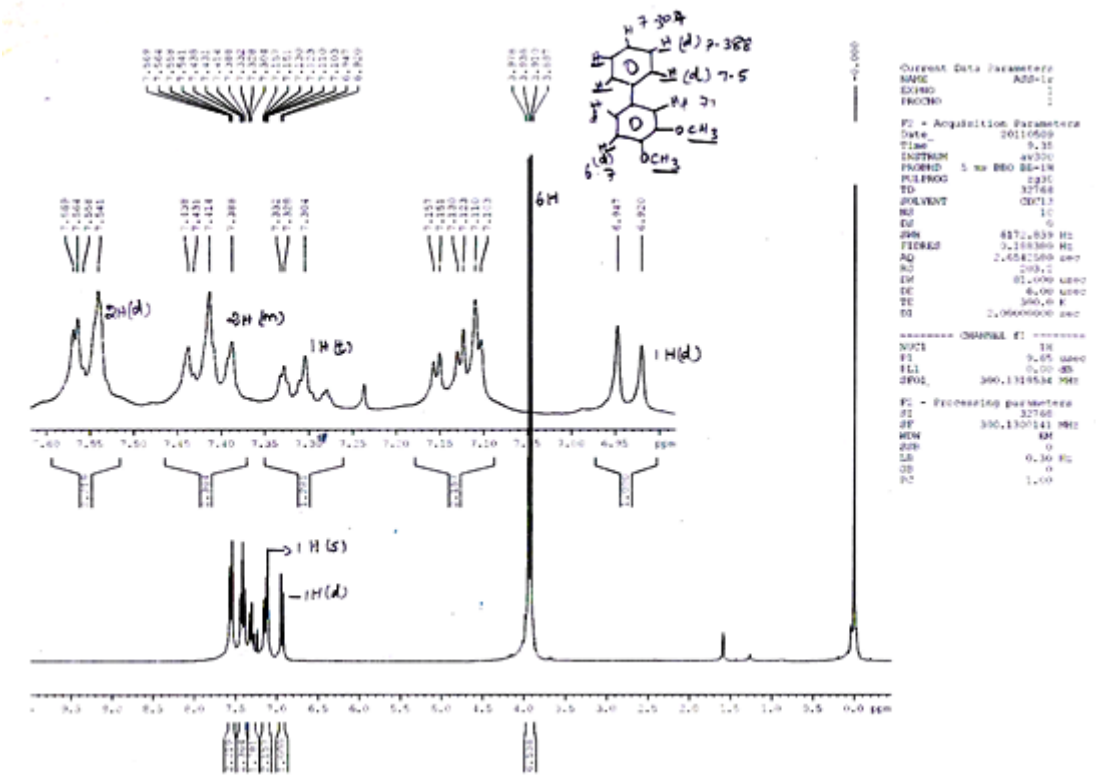


**Figure S8** [1]H-NMR spectrum of 3,4-dimethoxy-1,1'-biphenyl **3a** (Table 2)

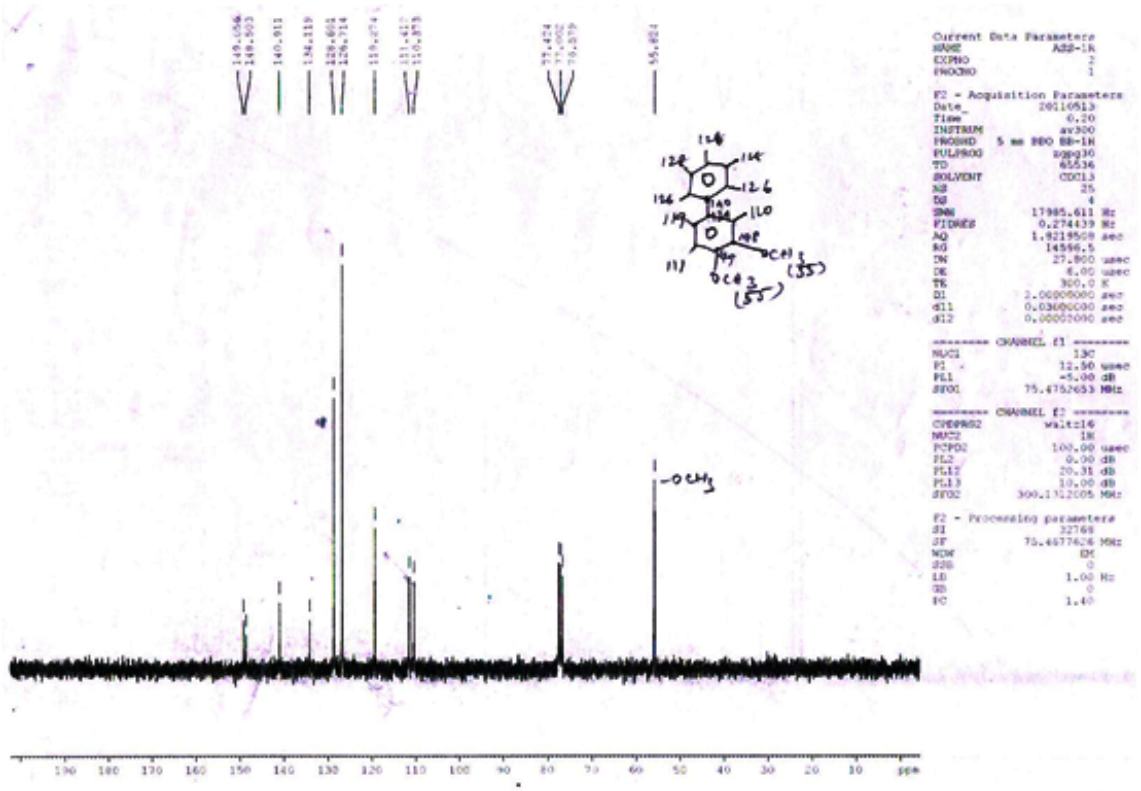


**Figure S9** [13]C-NMR spectrum of 3,4-dimethoxy-1,1'-biphenyl **3a** (Table 2)

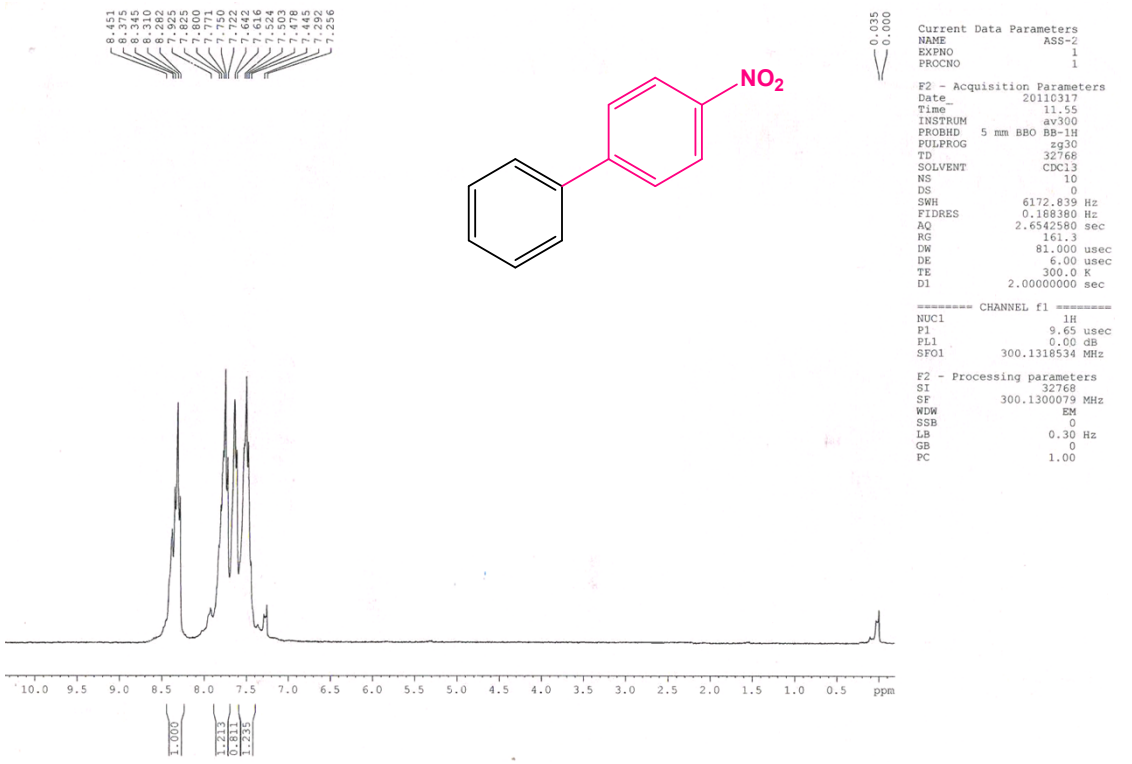



**Figure S10** [1]H-NMR spectrum of 3-nitro-1,1'-biphenyl **3b** (Table 2)

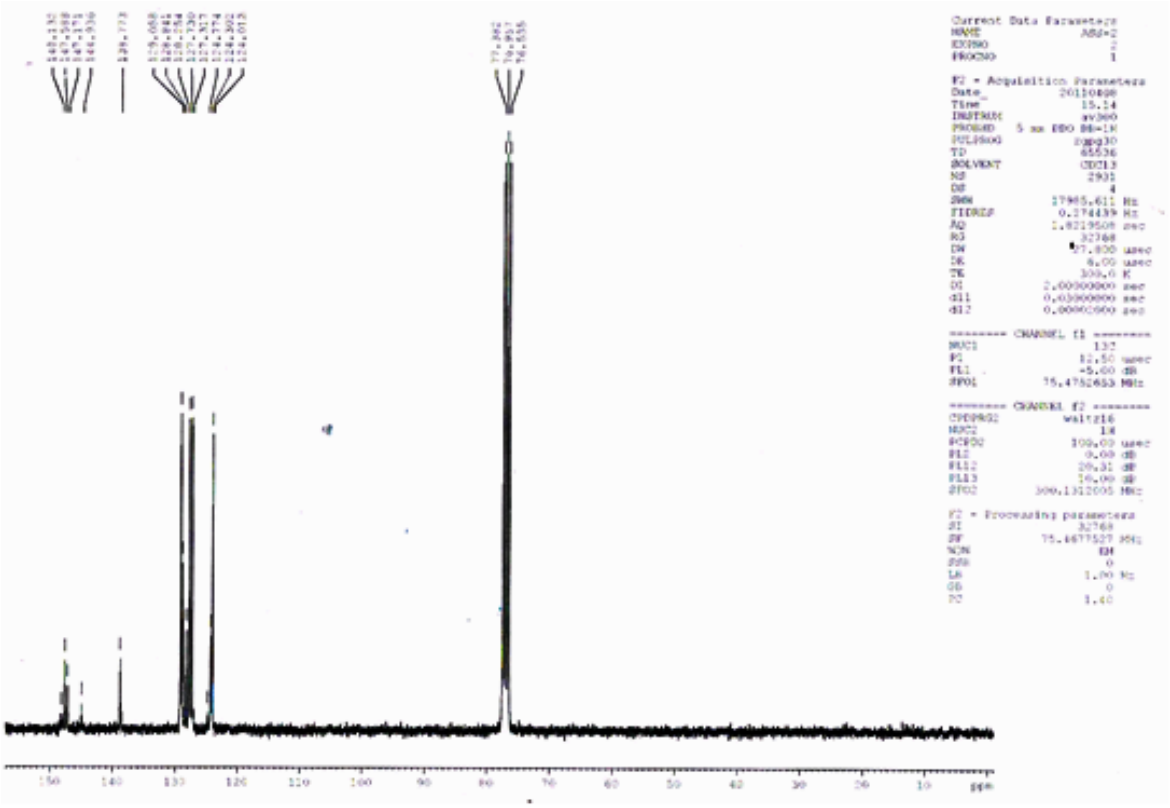


**Figure S11** [13]C-NMR spectrum of 3-nitro-1,1'-biphenyl **3b** (Table 2)

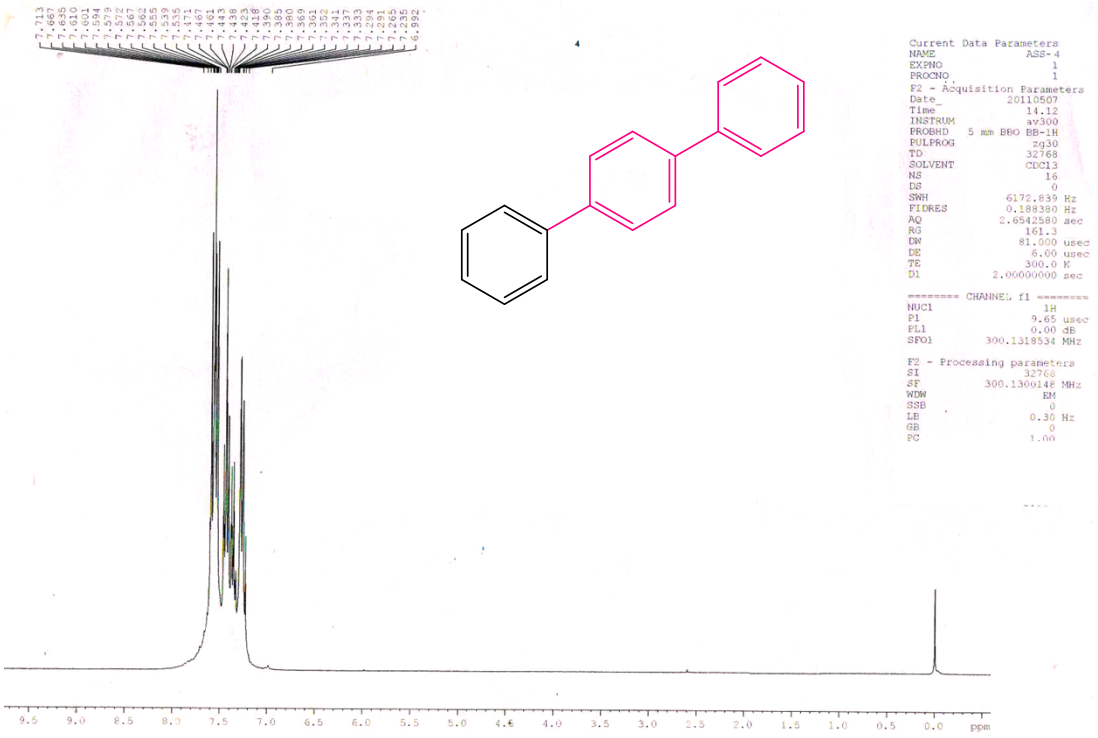


**Figure S11** $^{13}$C-NMR spectrum of 1,1':4',1"-terphenyl **3c** (Table 2)

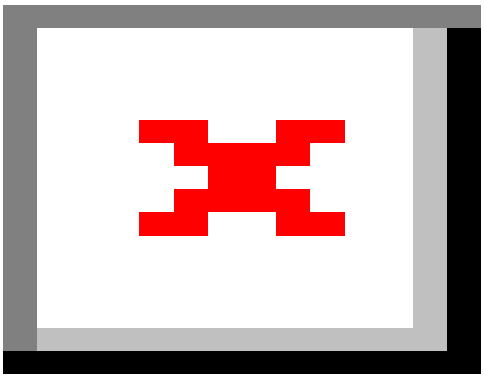


**Figure S12** $^{13}$C-NMR spectrum of 1,1':4',1"-terphenyl **3c** (Table 2)

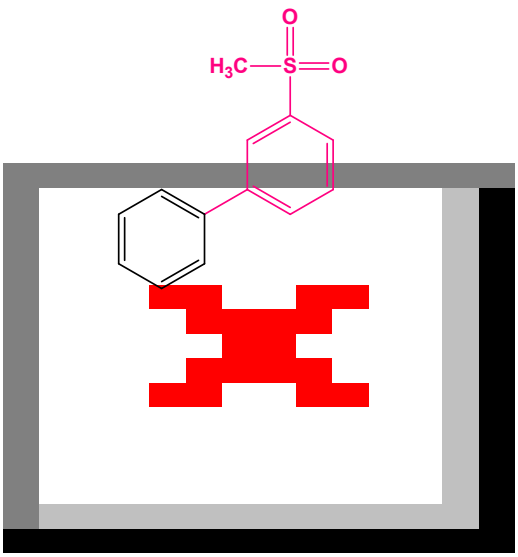



**Figure S13** $^{1}$H-NMR spectrum of 3-(methylsulfonyl)-1,1'-biphenyl **3d** (Table 2)

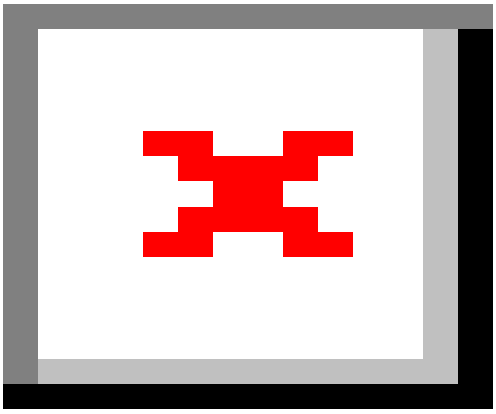


**Figure S14** $^{13}$C-NMR spectrum of 3-(methylsulfonyl)-1,1'-biphenyl **3d** (Table 2)

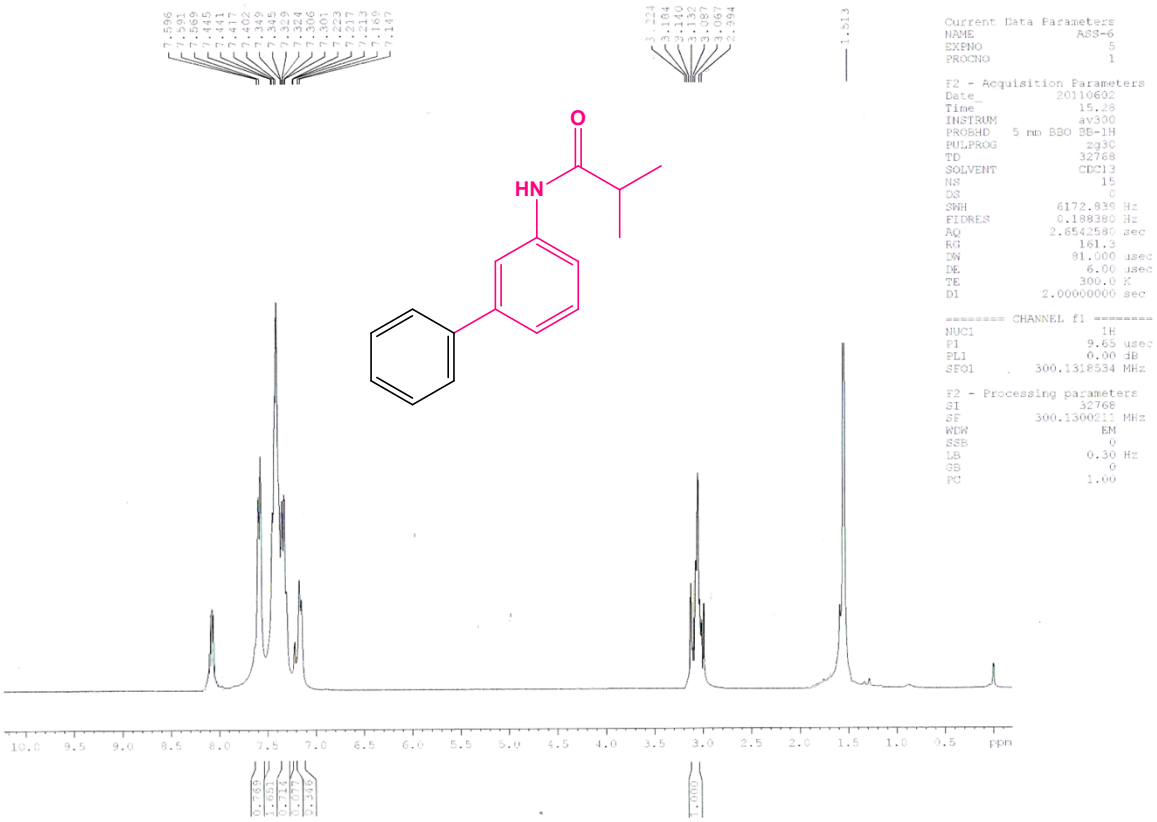



**Figure S15** [1]H-NMR spectrum of N-([1,1'-biphenyl]-3-yl)isobutyramide **3e** (Table 2)

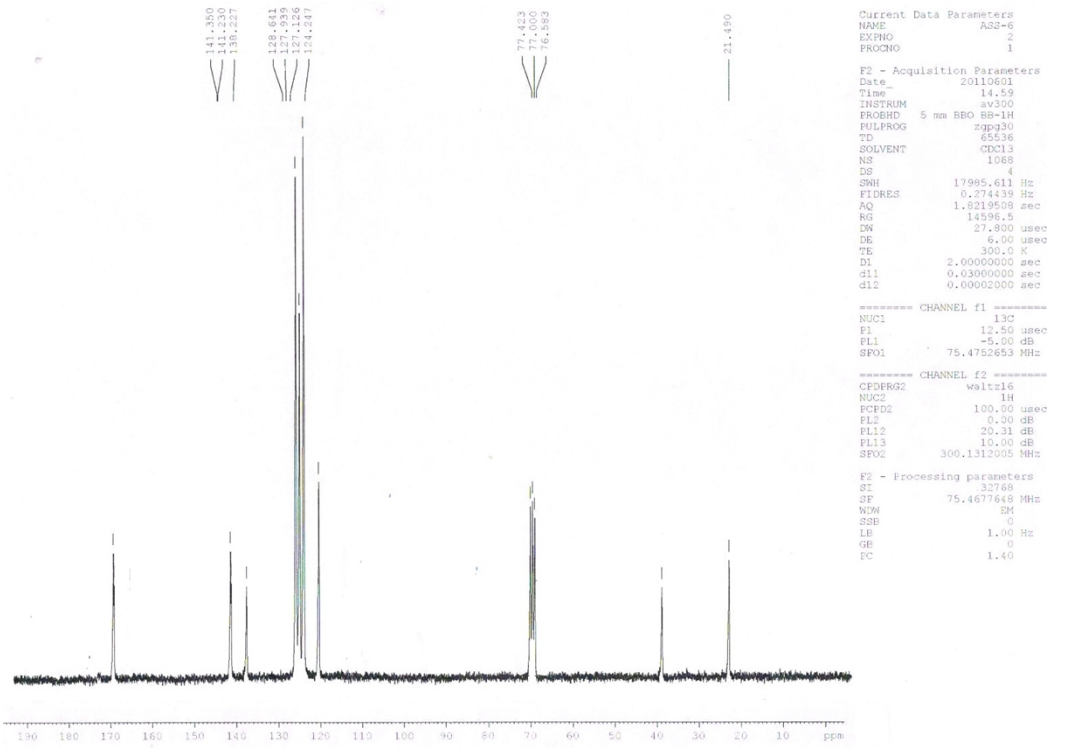


**Figure S16** [13]C-NMR spectrum of N-([1,1'-biphenyl]-3-yl)isobutyramide **3e** (Table 2)

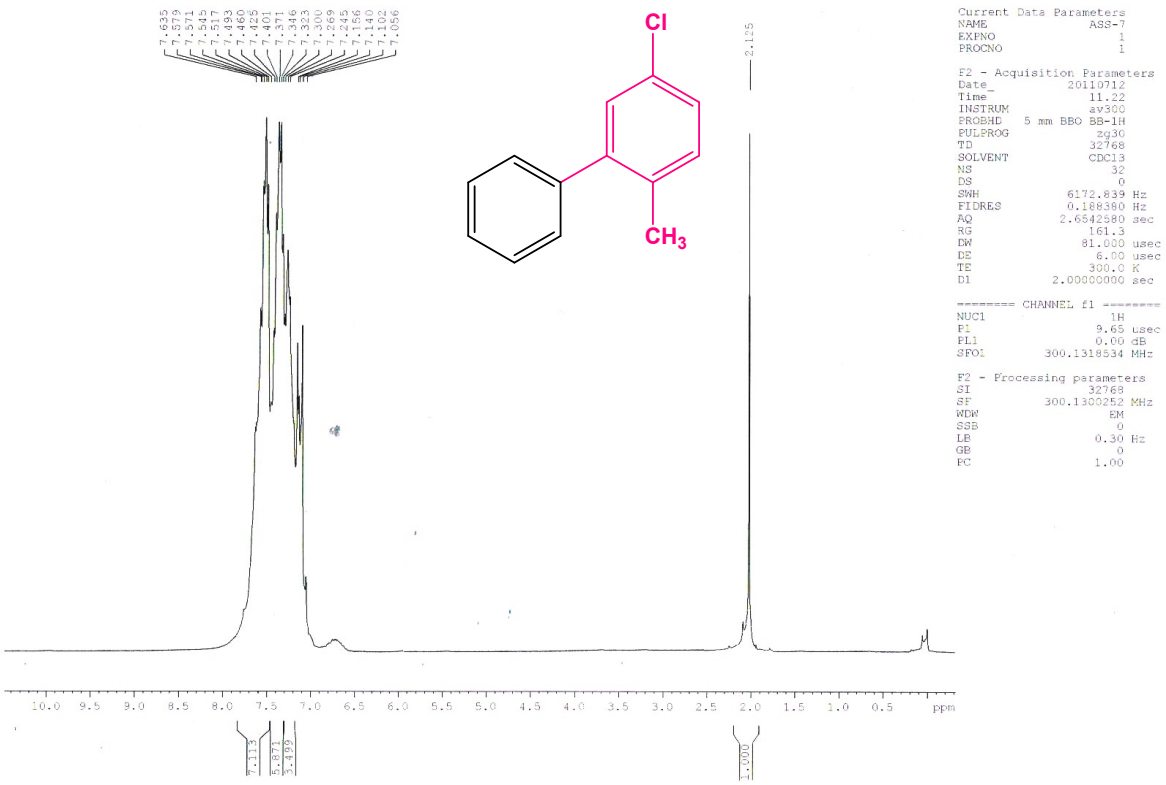



**Figure S17** $^{1}$H-NMR spectrum of 5-chloro-2-methyl-1,1'-biphenyl **3f** (Table 2)

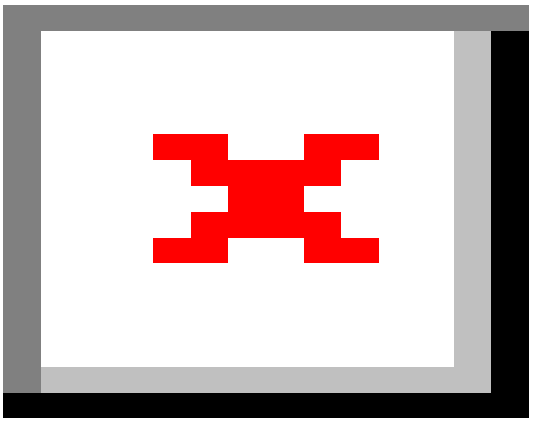


**Figure S18** $^{13}$C-NMR spectrum of 5-chloro-2-methyl-1,1'-biphenyl **3f** (Table 2)

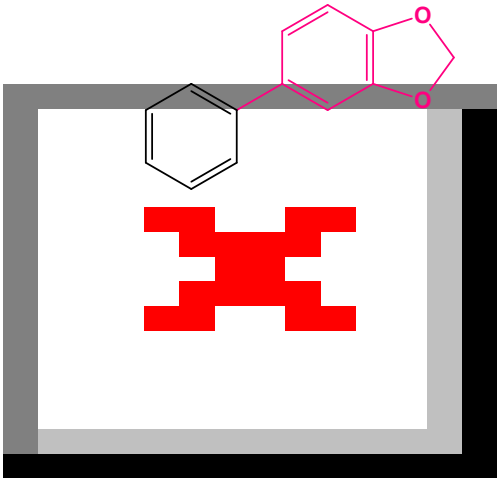



**Figure S19** $^{1}$H-NMR spectrum of 5-phenylbenzo[d][1,3]dioxole **3g** (Table 2)

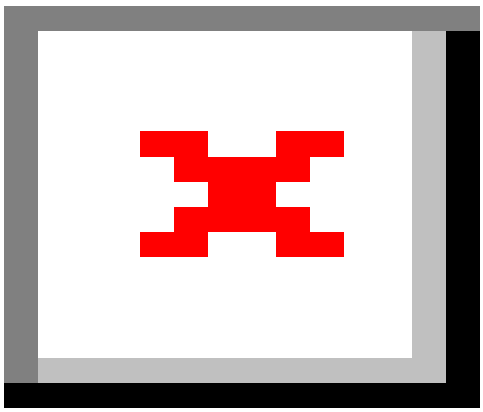


**Figure S20** $^{13}$C-NMR spectrum of 5-phenylbenzo[d][1,3]dioxole **3g** (Table 2)

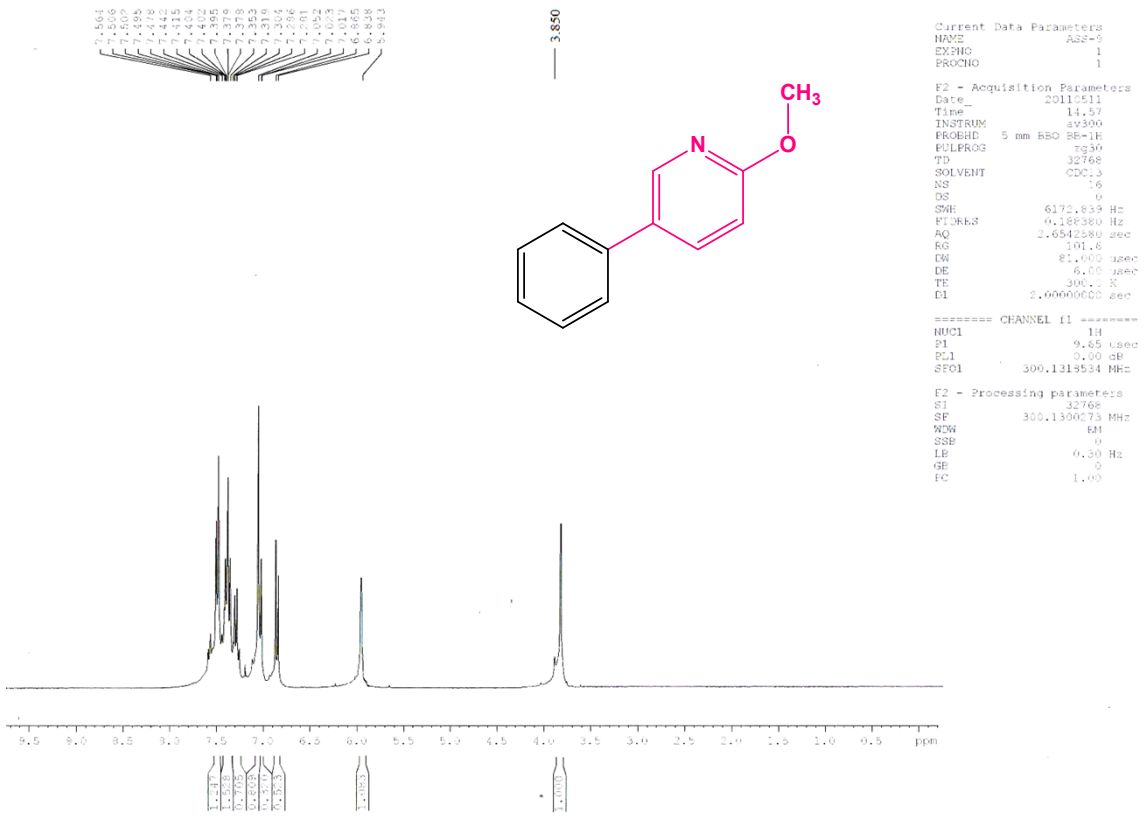



**Figure S21** [1]H-NMR spectrum of 2-methoxy-5-phenylpyridine **3h** (Table 2)

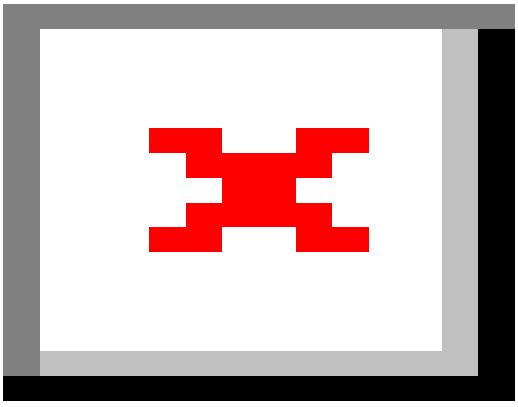


**Figure S22** [13]C-NMR spectrum of 2-methoxy-5-phenylpyridine **3h** (Table 2)

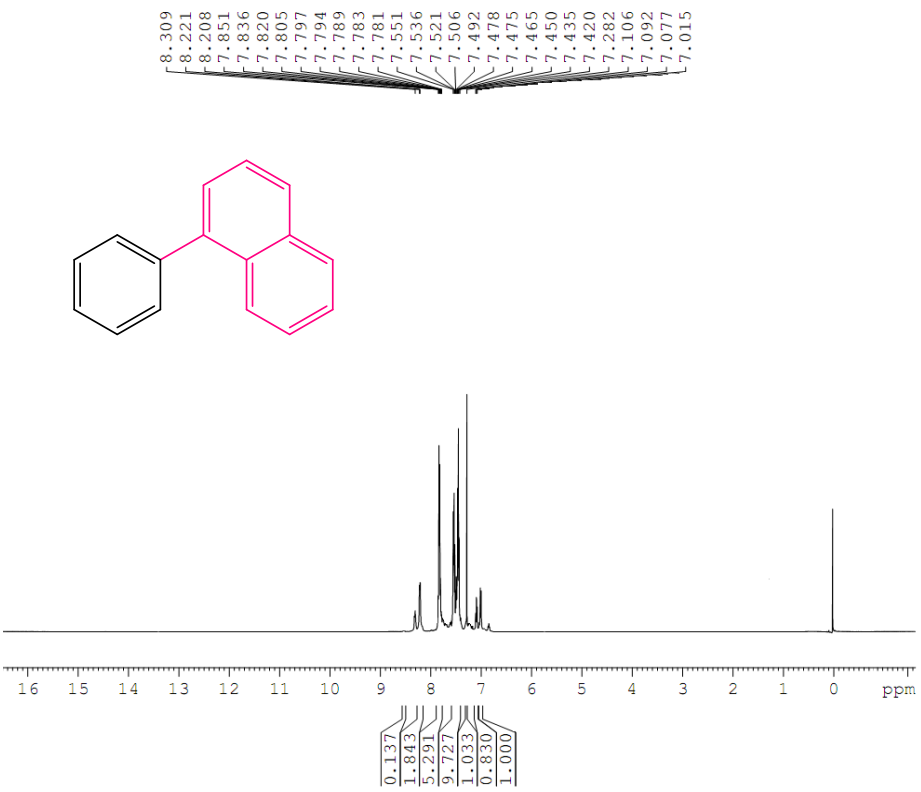



**Figure S23** $^{13}$C-NMR spectrum of 1-phenylnaphthalene **3i** (Table 2)

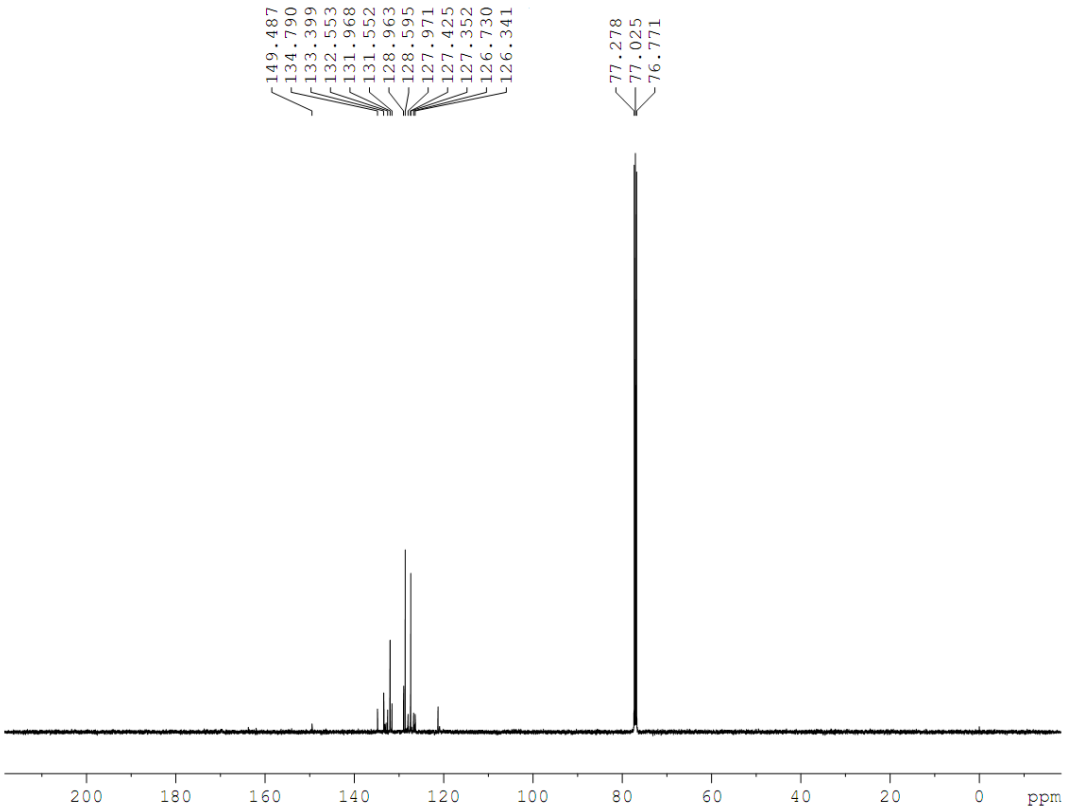



**Figure S24** $^{13}$C-NMR spectrum of 1-phenylnaphthalene **3i** (Table 2)

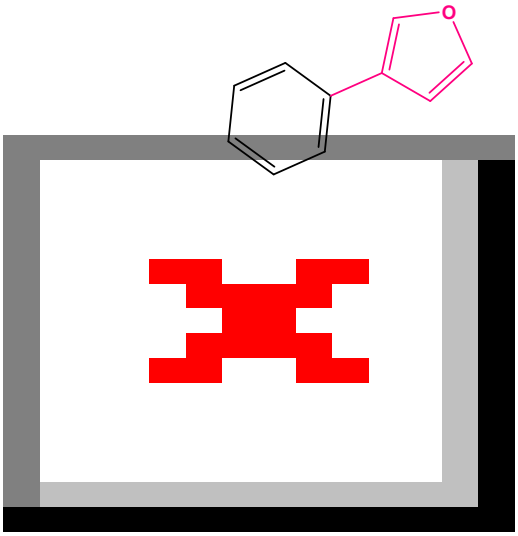


**Figure S25** $^{13}$C-NMR spectrum of 3-phenylfuran **3k** (Table 2)

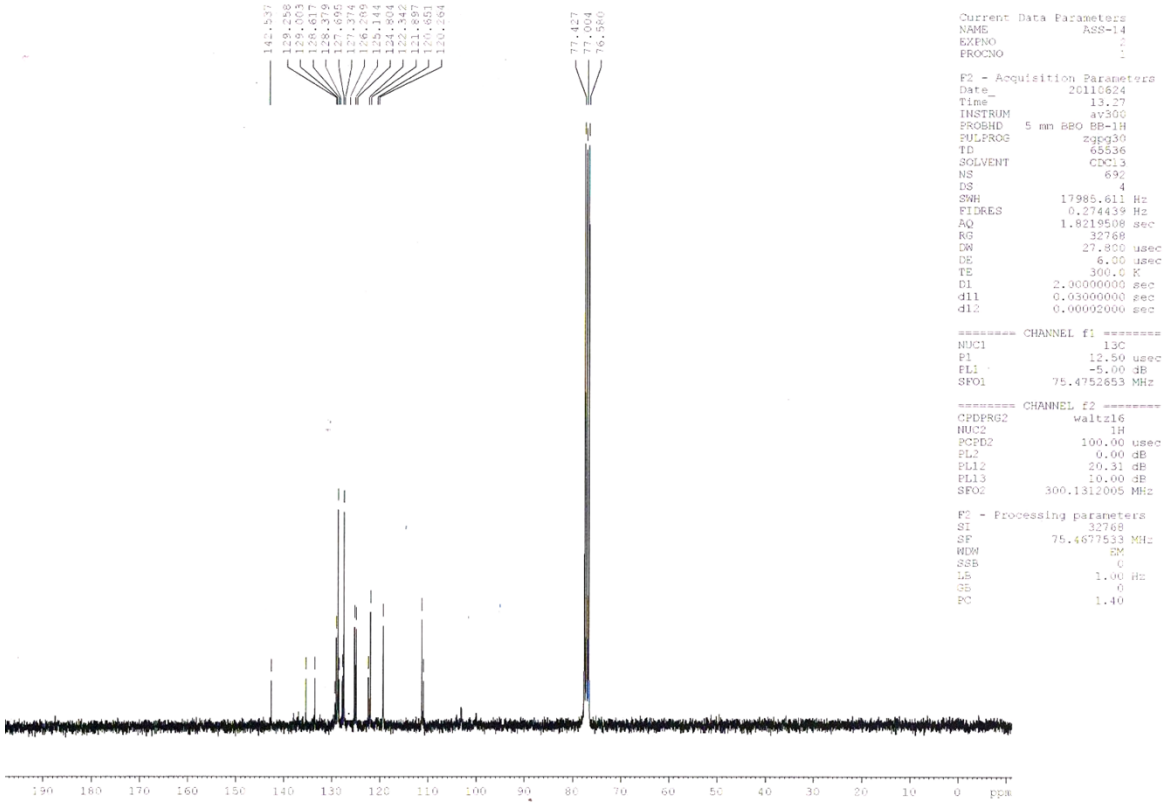



**Figure S26** $^{13}$C-NMR spectrum of 3-phenylfuran **3k** (Table 2)

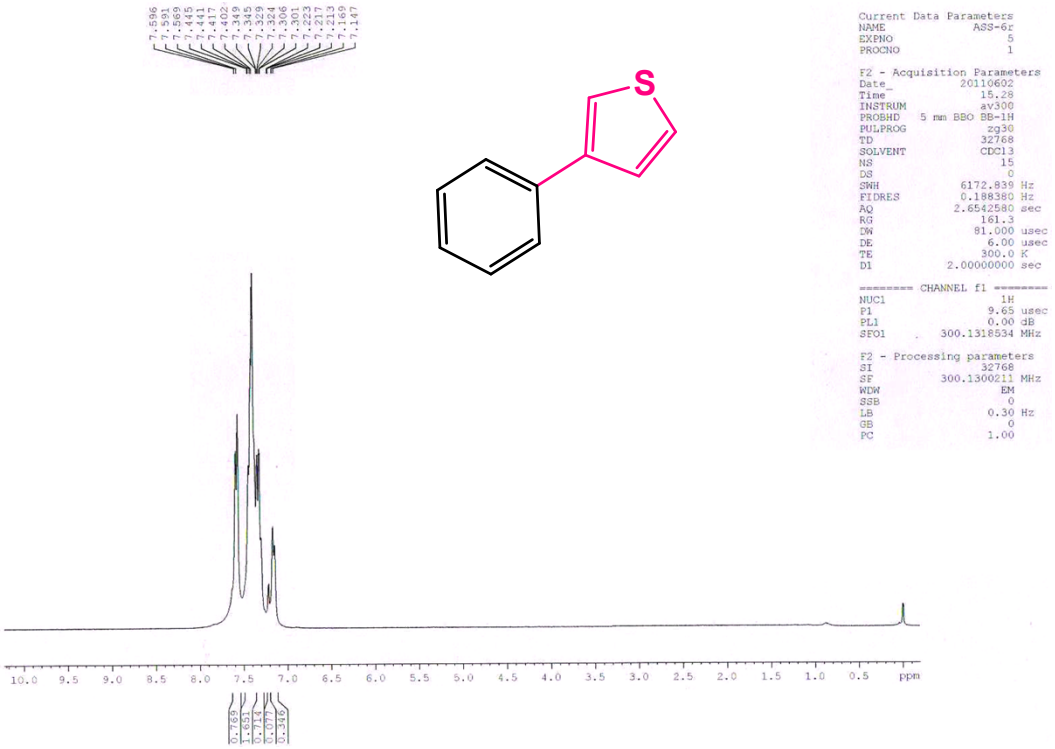



**Figure S27** $^{13}$C-NMR spectrum of 3-phenylthiophene **3l** (Table 2)

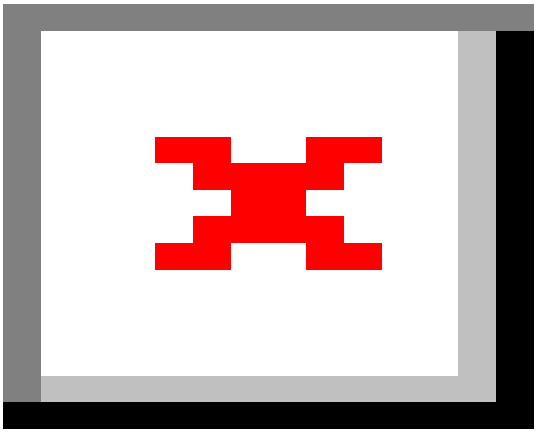


**Figure S28** $^{13}$C-NMR spectrum of 3-phenylthiophene **3l** (Table 2)

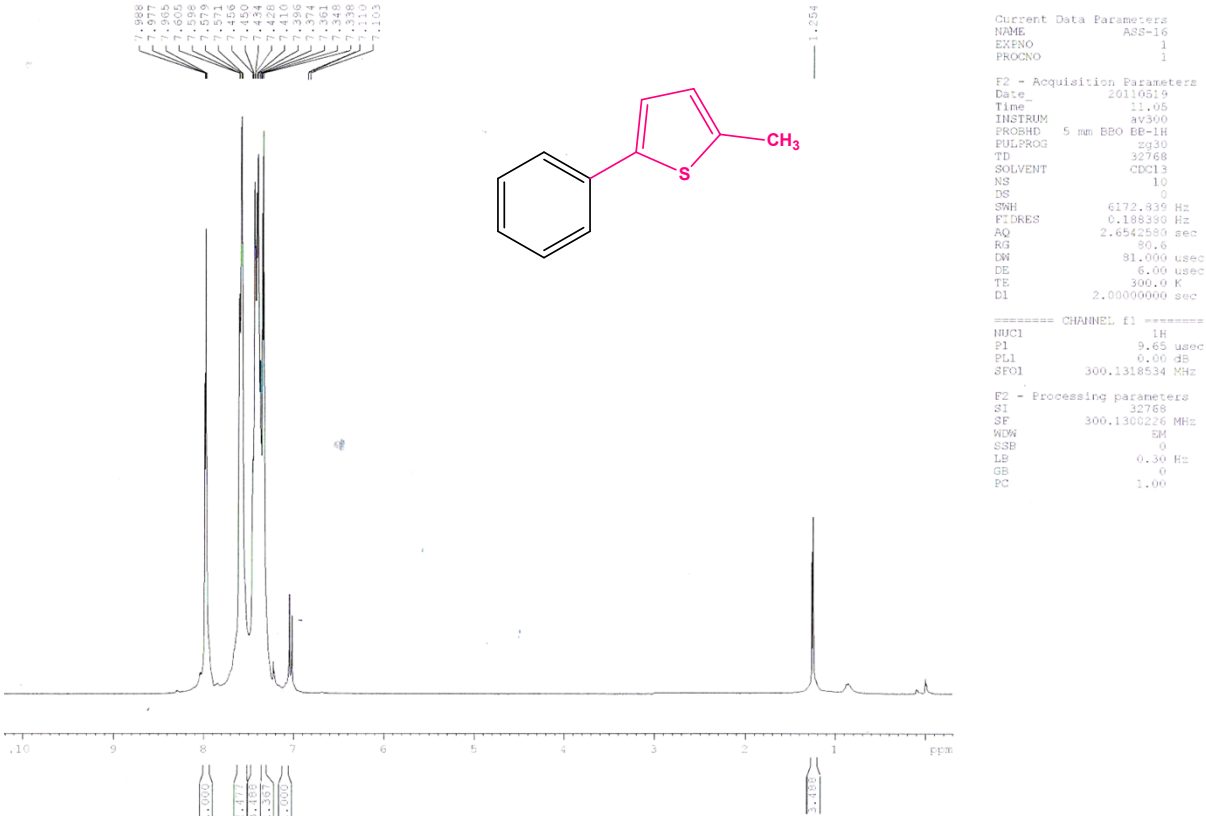



**Figure S29** $^{13}$C-NMR spectrum of 2-methyl-5-phenylthiophene **3m** (Table 2)

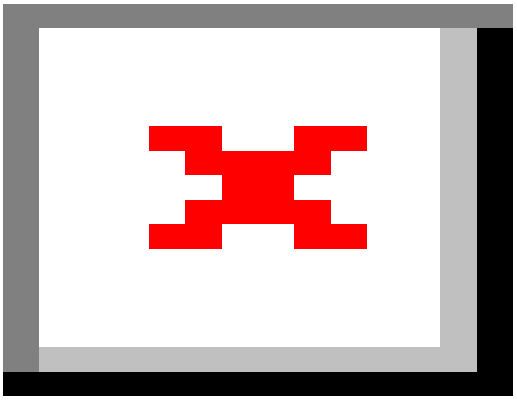


**Figure S30** $^{13}$C-NMR spectrum of 2-methyl-5-phenylthiophene **3m** (Table 2)

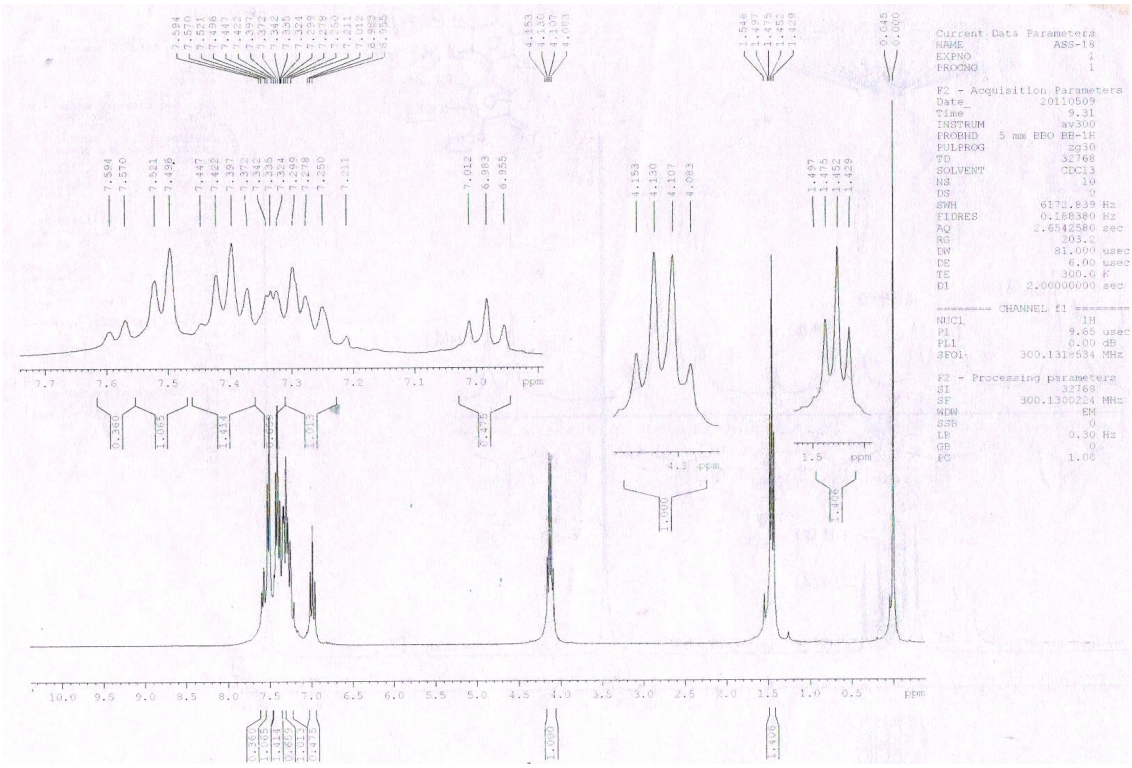


**Figure S31** $^{1}$H-NMR spectrum of 4-ethoxy-3-fluoro-1,1'-biphenyl **3n** (Table 2)

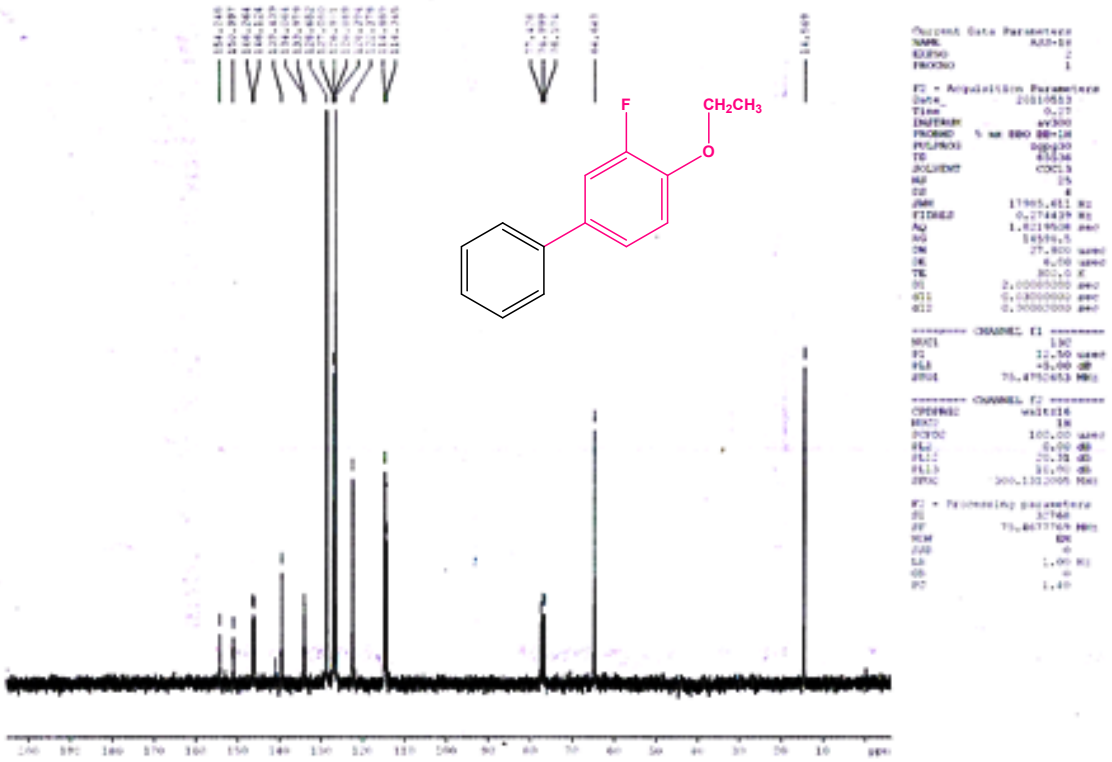



**Figure S32** $^{13}$C-NMR spectrum of 4-ethoxy-3-fluoro-1,1'-biphenyl **3n** (Table 2)