Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information

In-situ Palladium-Doped Conjugated Polymer Network for Visible and Natural Sunlight-Driven Suzuki Type Cross-Coupling Reaction at Room Temperature

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Calculation of Turn Over Number and Turn Over Frequency

For measuring the turnover number, we have performed a C-C cross-coupling reaction to calculate TON. The Pd content in CPN was measured by ICP-AES. The reaction was carried out by 9.2 mg CPN in a reaction mixture of 1 mmol 4-bromo benzonitrile, 1.2 mmol phenylboronic acid, and 2 mmol K_2CO_3 as a base in 3 ml (ethanol) solvent using 3Watt (0.05white LED. The reaction yield was 92%. The turnover number (TON) and turnover frequency (TOF) of the reaction were calculated as below:

TON = Number of moles of product / Number of moles of catalyst (Pd)
TOF = TON/time of reaction

For C-C cross-coupling reaction

TON = (0.92mmol) / 0.000125mmol (Pd content)
= 7360
TOF = TON/time = 7360 /4h = 1840 h^{-1}

Synthesis of monomer-

2, 7-Dibromofluorene –

Fluorene (0.831g, 5 mmol), NBS (3.601 g, 20.233 mmol), $FeCl_3$ (0.03232 g, 0.1992 mmol), and 20.328 mL of DMF was added and stirred at 90^0C temperature for 5 h in dark condition. The mixture was then washed with 3.5% HCl solution, $NaHCO_3$, water, and ethyl acetate. And recrystallized in ethanol then a white solid was obtained. The compound formation is confirmed by NMR (fig S1 ^1H NMR (500 MHz,) δ 7.64 (s, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 3.84 (s, 2H).

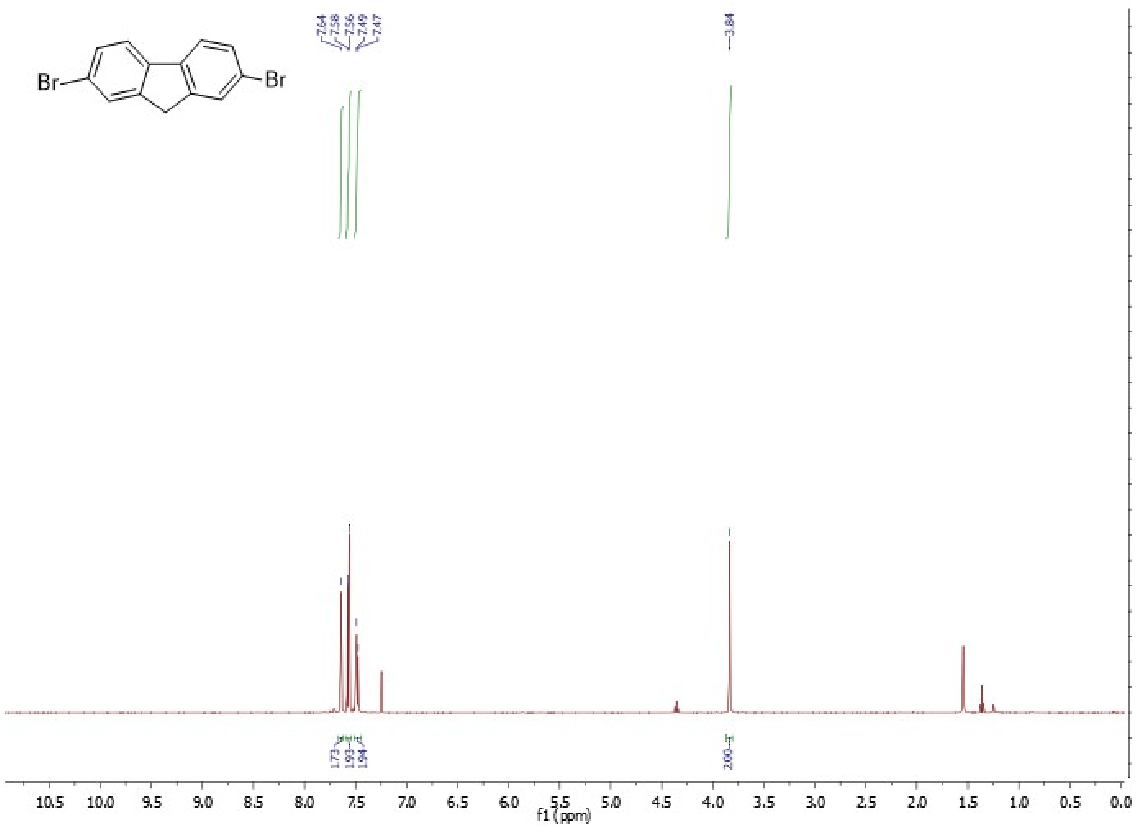


Fig. S1. ^{1}H NMR spectra of 2, 7-Dibromofluorene.

2, 7-Dibromofluorenone –

2, 7-Dibromofluorene ((1.62 g, 5 mmol), $K_2Cr_2O_7$ (1.716 g, 5.832 mmol) was stirred in 15 mL of acetic acid for 6 h at reflux temperature. After cooling to room temperature, the reaction solution was filtered. The filter solid was washed successively with acetic acid, water, and 5% hydrochloric acid to remove impurities. A yellow solid was obtained. The compound formation is confirmed by NMR (fig S2 ^{1}H NMR (500 MHz,) δ 7.76 (s, 2H), 7.69 – 7.55 (m, 2H), 7.40 (t, J = 21.6 Hz, 2H).

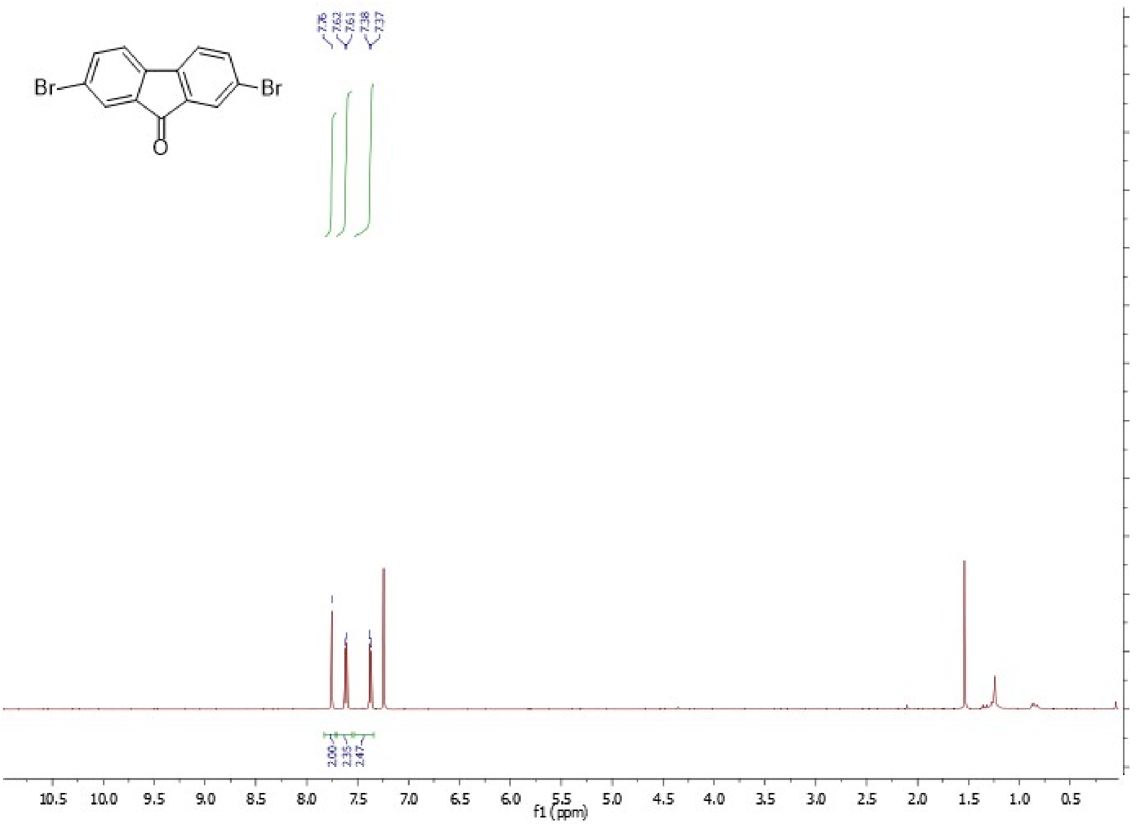


Fig. S2. ^{1}H NMR spectra of 2, 7-Dibromofluorenone.

1, 3, 5-Triazine phenylboronic acid-

In a 250 ml round bottle 4-cyanophenyl boronic acid (1g, 6.8 mmol) and triflic acid (6. 7 ml) and stirred overnight. The reaction mixture was diluted with cold water at vigorous stirring, then filter and wash with water. After washing white colour solid was obtained, and dried at 60^0 C in vacuum oven. The compound formation confirmed by NMR (Fig. S3) ^{1}H NMR (600 MHz, DMSO) δ 8.78 (d, J = 8.0 Hz, 6H), 8.37 (d, J = 27.2 Hz, 6H), 8.04 (dd, J = 94.6, 8.0 Hz, 6H).

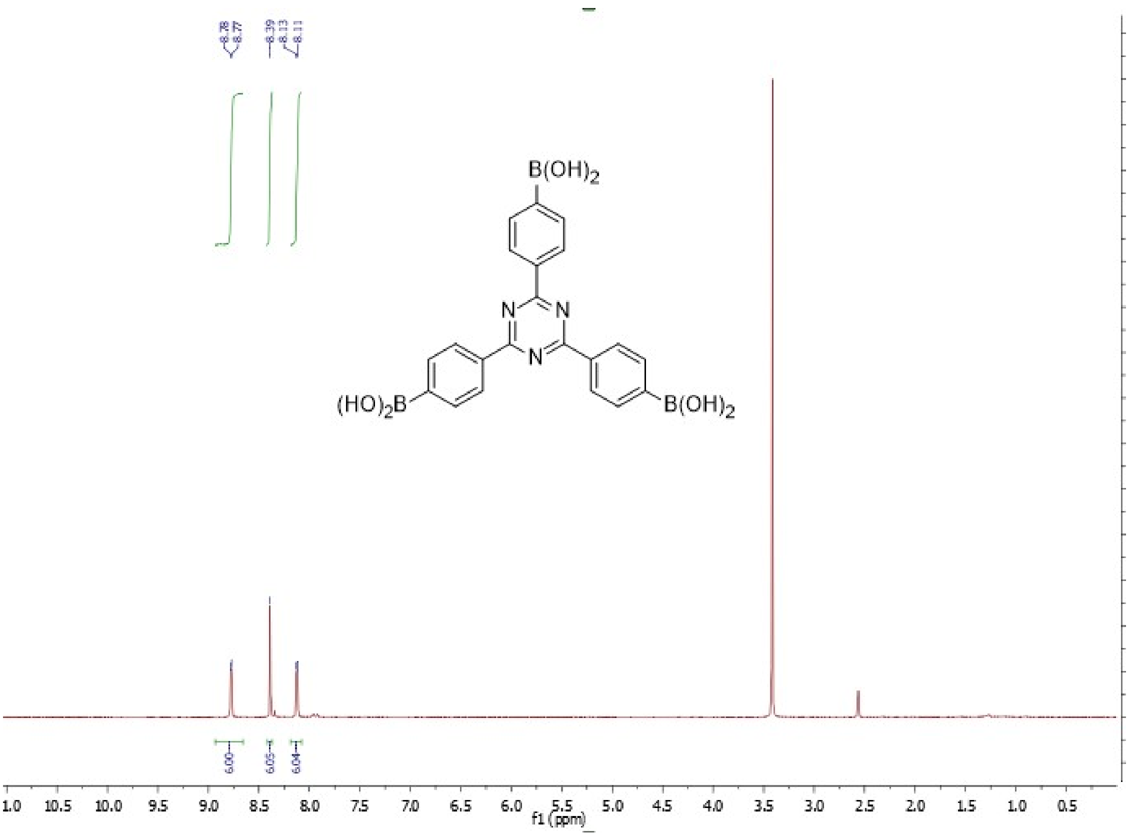


Fig. S3 ^{1}H NMR spectra of 1, 3, 5-Triazine phenylboronic acid.

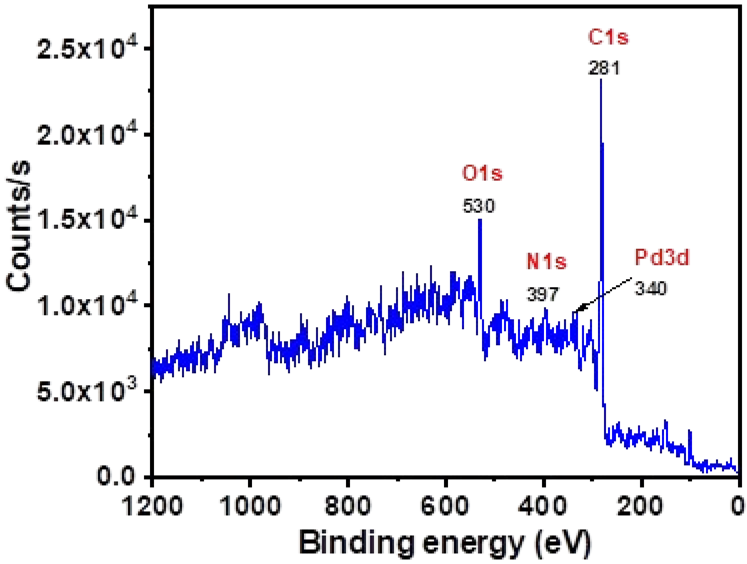


Fig. S4 XPS survey spectra of CPN without soxlet extraction (CPNWOSE)

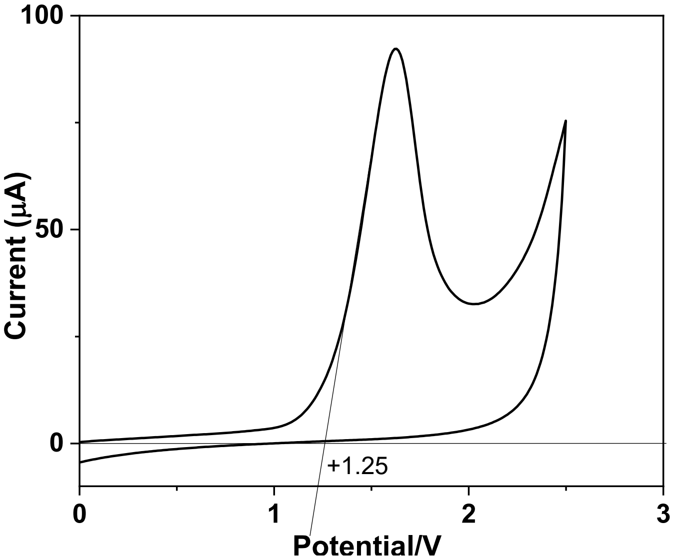


Fig. S5 Cyclic voltammetry of CPN deposited on glassy carbon electrodes. Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as the supporting electrolyte. The onset of oxidation is mentioned for each CV plot.

Quantum chemical calculations:

To understand the band gap and frontier energy levels, we have performed quantum chemical calculations at the B3LYP/6-31G(d,p) level of theory using the G09 suite of programs. We have also performed geometry optimization and frequency calculations to ensure stationary point geometry.

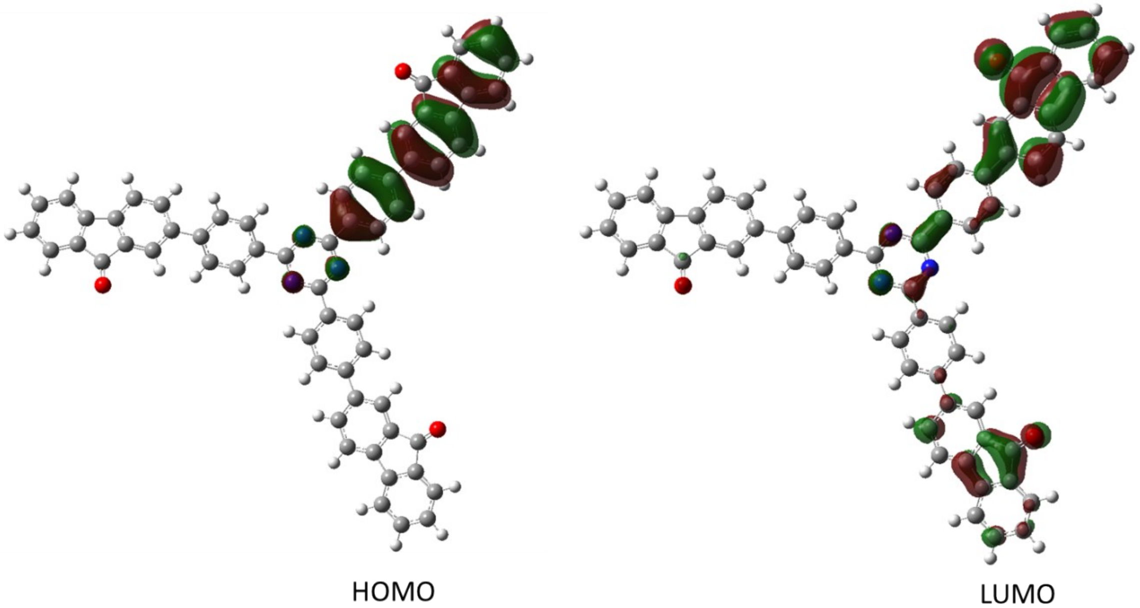


Fig. S6 Topographical representations of the HOMO and LUMO of CPN (top view)

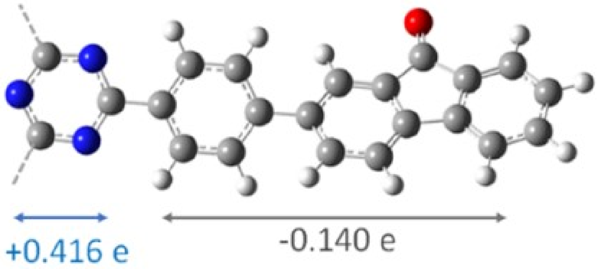


Fig. S7 Total Mulliken charge of triazine ring and one arm of the monomeric unit in CPN.

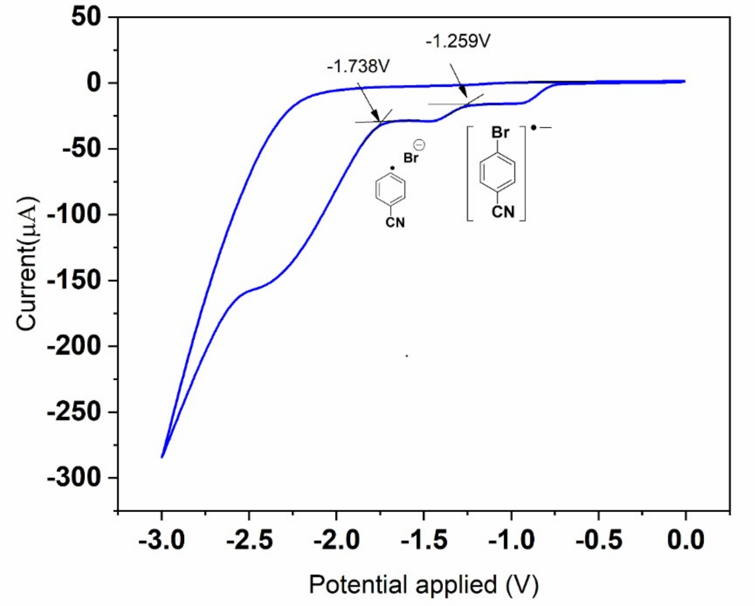
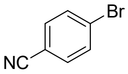
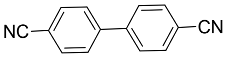
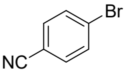
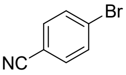
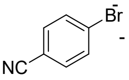
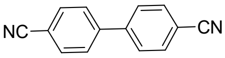
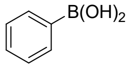
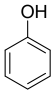
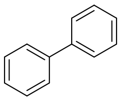
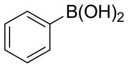
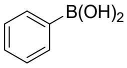
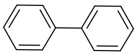
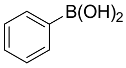


Fig. S8 Cyclic voltammetry of 4-bromobenzonitrile in solution (DCM) phase. Glassy carbon electrodes were used as the working electrode, Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in DCM as the supporting electrolyte. The onset of reduction is mentioned in the CV plot.

Table S1 Optimised conditions of C-C cross-coupling reaction.

Entry	Reactant	Reaction condition[a]	Product
1.		K_2CO_3, Ethanol, light	 25%
2.		Ethanol, light	no reaction
3	 -	K_2CO_3, Ethanol, electron quencher ($AgNO_3$), light	no reaction
4	 -	K_2CO_3, Ethanol, hole quencher (TEOA), light	 75%
5.		K_2CO_3, Ethanol, light	 11%  15%
6.		Ethanol, light	no reaction
7	 -	K_2CO_3, Ethanol, electron quencher ($AgNO_3$), light	 90%
8	 -	K_2CO_3, Ethanol, hole quencher (TEOA), light	no reaction

[a] Reaction time 6 hrs, catalyst 5 wt%, reactant 0.5 mol, white LED 3 Watt

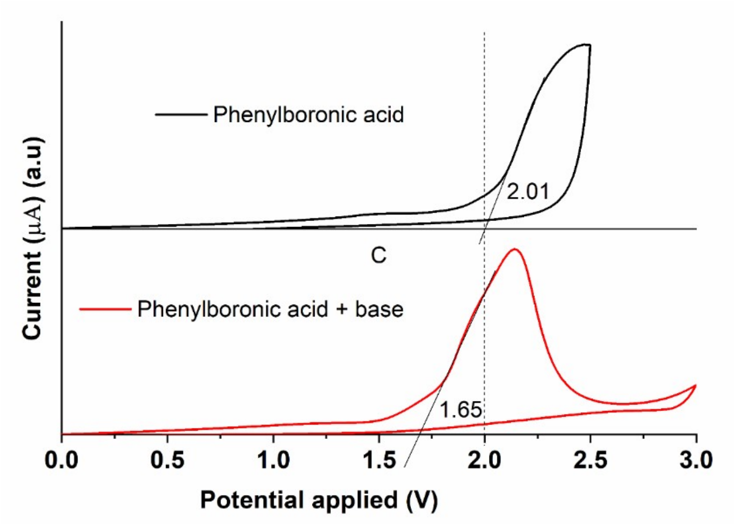


Fig. S9 Cyclic voltammetry of 4-bromobenzonitrile in solution (DCM) phase. Glassy carbon electrodes used as the working electrode, Platinum was used as the counter electrode, silver wire as a reference electrode, and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in DCM as the supporting electrolyte. The onset of oxidation is mentioned in the CV plot.

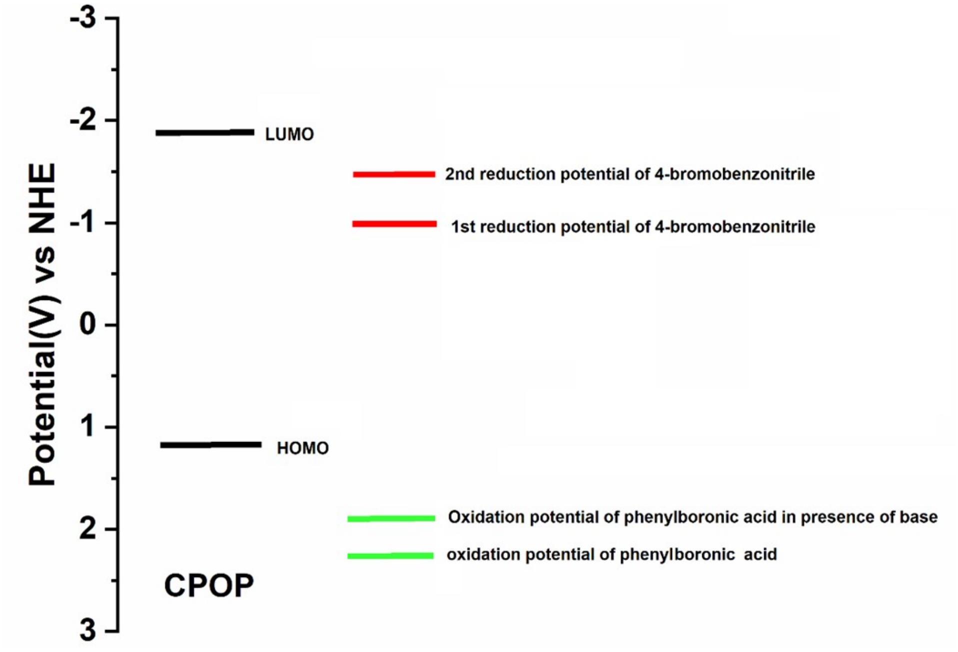
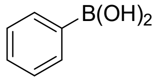
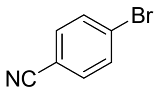
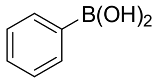
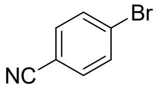
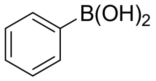
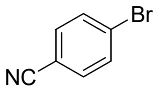
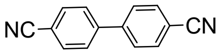
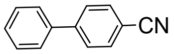
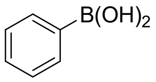
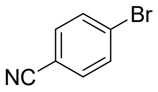
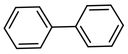
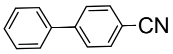
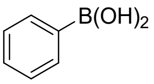
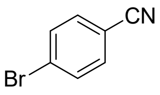
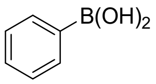
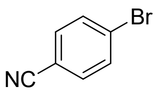
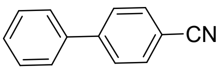


Fig. S10 Redox potential of 4-bromo benzonitrile and phenyl boronic acid compared to the HOMO and LUMO energy levels of CPN determined by cyclic voltammetry (vs. NHE).

Table S2. Role of base, light, hole, and electron.

Entry	Reactant 1	Reactant 2	Reaction condition[a]	Product
1.			Ethanol, K_2CO_3	no reaction
2.			Ethanol, light	no reaction
3			K_2CO_3, Ethanol, hole quencher (TEOA), light	 48%  10%
4			K_2CO_3, Ethanol, electron quencher ($AgNO_3$), light	 56%  13%
5			K_2CO_3, Ethanol, hole quencher (TEOA) and electron quencher($AgNO_3$), light	no reaction
6			K_2CO_3, Ethanol, radical quencher (benzoquinone), light	 9.3%

[a] Reaction time 6 hrs, catalyst 5 wt% phenylboronic acid 0.55 mmol, 4-bromobenzonitrile (0.5 mmol), solvent 3ml

NMR data analysis data of the coupled products are listed in Fig.…….

Biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 140.19, 127.70, 126.20, 126.12.

4-Methyl-1, 1-biphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.50 (t, J = 9.0 Hz, 1H), 7.39 (t, J = 13.3 Hz, 1H), 7.34 (dd, J = 16.6, 8.9 Hz, 1H), 7.25 (dt, J = 14.7, 7.5 Hz, 1H), 7.21 – 7.09 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 140.12, 137.32, 135.96, 128.44, 127.66, 126.20, 126.12, 125.93, 28.69.

4-phenylbenzonitrile- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.64 (t, J = 9.4 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 145.70, 139.24, 132.62, 129.13, 128.67, 127.76, 127.25, 118.96, 110.92.

4-phenyl benzaldehyde-^{1}H NMR (600 MHz, CDCl$_3$) δ 10.06 (s, 1H), 7.96 (t, J = 9.4 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 6.5 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 192.12, 147.17, 139.86, 135.37, 130.18, 129.04, 128.56, 127.72, 127.34.

2-amino-1, 1-biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 – 7.57 (m, 1H), 7.47 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 7.25 (dt, J = 13.8, 4.0 Hz, 1H), 7.05 (dt, J = 16.0, 9.6 Hz, 2H), 6.72 (t, J = 6.6 Hz, 1H), 6.65 (dd, J = 8.0, 0.7 Hz, 1H), 3.78 – 3.46 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 167.71, 143.57, 139.59, 132.29, 131.00, 130.48, 129.13, 128.90, 128.84, 128.53, 127.64, 127.19, 118.65, 115.64, 61.68.

4-acetyl biphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.04 (d, J = 7.1 Hz, 1H), 7.77 – 7.58 (m, 2H), 7.48 – 7.36 (m, 1H), 2.64 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 139.96, 135.50, 129.32, 128.46, 127.13, 26.99.

4-**Nitro biphenyl-** ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.62 (t, J = 7.9 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.48 – 7.41 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 147.66, 147.11, 138.79, 129.17, 128.93, 127.82, 127.40, 124.12.

4-methoxybiphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 7.54 (dd, J = 12.4, 8.1 Hz, 1H), 7.48 – 7.35 (m, 1H), 7.30 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 10.8 Hz, 1H), 3.85 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 158.93, 140.85, 133.80, 128.74, 128.18, 126.76, 126.68, 114.22, 55.36.

2-carboxylic acid-1, 1-biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 8.19 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 7.3 Hz, 1H), 7.49 (dd, J = 18.6, 11.2 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.12, 146.56, 139.91, 130.76, 128.93, 128.38, 127.86, 127.34, 29.64.

4-**chloro, 2-amino-1, 1-biphenyl-**^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 – 7.28 (m, 4H), 7.09 (td, J = 7.9, 1.5 Hz, 1H), 7.01 (dd, J = 7.6, 1.4 Hz, 1H), 6.75 (td, J = 7.5, 0.9 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 4.10 – 3.20 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.42, 137.94, 133.13, 130.49, 130.36, 129.01, 128.85, 126.35, 118.82, 115.77.

4-cyano, 4-methyl-1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 4H), 7.45 – 7.35 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.63, 138.77, 136.16, 132.58, 129.74, 127.48, 127.12, 119.06, 110.55, 21.19.

4-cyano, 4-carbaldehyde 1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.83 – 7.50 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.64, 144.93, 144.16, 136.15, 132.81, 130.45, 128.06, 127.94, 118.56, 112.18.

4-cyano, 2-amino-1, 1-biphenyl-^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (t, *J* = 10.5 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.61, 144.57, 143.38, 143.28, 132.92, 132.64, 130.25, 129.84, 129.65, 129.63, 127.98, 125.45, 119.03, 119.01, 118.90, 118.86, 116.13, 116.10, 110.82.

4-cyano, 4-nitro-1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.7 Hz, 2H), 7.79 (dd, *J* = 16.7, 6.0 Hz, 2H), 7.78 – 7.70 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.94, 145.40, 143.15, 132.93, 128.17, 128.11, 124.39, 118.36, 112.70.

4, 4-dicyano-1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 4H), 7.62 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.52, 131.88, 126.93, 117.40, 111.44.

4-methoxy, 4-methyl biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 3.75 (s, 1H), 2.29 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.95, 137.99, 136.37, 133.77, 133.51, 129.46, 127.97, 127.76, 126.60, 114.18, 55.36, 21.07.

4-methoxy, 4-cyano biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 30.3, 7.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.79 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.94, 137.98, 136.37, 133.77, 129.45, 127.97, 127.75, 126.60, 114.17, 55.18.

4-methoxy, 2-aniline ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.03 (dd, *J* = 18.3, 7.9 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 2H), 6.80 – 6.68 (m, 1H), 6.68 – 6.60 (m, 2H), 3.74 (s, 3H), 3.69 – 3.61 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.78, 143.59, 131.79, 130.53, 130.23, 128.23, 127.51, 118.78, 116.10, 115.65, 114.84, 114.26, 55.81, 55.35.

4-methoxy, 4-nitro-1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 6.99 (dd, *J* = 39.0, 7.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.32, 147.12, 146.48, 131.09, 128.58, 127.09, 124.16, 114.63, 55.44.

4, 4-dimethoxy-1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 32.4, 7.6 Hz, 4H), 6.97 (dd, *J* = 21.8, 7.6 Hz, 4H), 3.85 (d, *J* = 10.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.42, 132.26, 126.71, 113.14, 54.15.

4, 4-carbaldehyde 1, 1-biphenyl- ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.96, 146.11, 135.96, 130.65, 127.99.

4'-acetyl-[1,1 '-biphenyl]-4-carbonitrile- ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 2.66 (s, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.51, 144.33, 143.55, 136.92, 132.76, 129.14, 127.95, 127.47, 118.65, 111.92, 26.73.

3-chlorobiphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.61 – 7.50 (m, 1H), 7.47 – 7.37 (m, 1H), 7.37 – 7.23 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.13, 139.86, 134.71, 130.04, 128.95, 127.92, 127.35, 127.32, 127.17, 125.35.

3-chloro, 4-nitro-1, 1 biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 8.31 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 17.9 Hz, 1H), 7.57 – 7.46 (m, 1H), 7.46 – 7.36 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 147.49, 146.13, 140.59, 135.04, 130.42, 128.92, 127.91, 127.63, 125.57, 124.14.

3-chloro, 4-methyl biphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (dd, *J* = 33.7, 16.3 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.29 (dd, *J* = 17.8, 10.1 Hz, 2H), 7.26 – 7.17 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.05, 137.79, 136.96, 134.66, 129.99, 129.67, 127.12, 126.98, 125.13, 21.17.

3-chloro, 4-carbonitrirle biphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.25 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.18, 140.95, 135.08, 132.73, 130.41, 128.68, 127.75, 127.38, 127.36, 125.42, 118.71, 111.58, 111.56.

3-chloro, 4-acetyl-1, 1 biphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.46 – 7.37 (m, 1H), 7.37 – 7.24 (m, 1H), 2.57 (s, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.76, 144.65, 141.71, 136.54, 134.70, 130.21, 129.02, 128.36, 127.27, 125.37, 26.70.

3-chloro, 4-carboxaldehyde-1, 1 biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 10.07 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.62 (s, 1H), 7.57 – 7.47 (m, 1H), 7.47 – 7.34 (m, 2H).^{13}C NMR (151 MHz, CDCl$_3$) δ 191.83, 145.68, 141.56, 135.63, 134.99, 130.36, 130.28, 128.47, 127.74, 127.52, 125.54.

4-Acetyl, 4-methylbiphenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 9.1 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.13 (m, 1H), 2.63 (s, 1H), 2.41 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 196.82, 145.93, 130.84, 129.49, 128.80, 128.45, 128.42, 127.18, 126.86, 124.90, 28.67, 25.59, 19.35.
4-Acetyl, 4-nitro biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.75 (dd, *J* = 33.9, 7.7 Hz, 2H), 2.66 (s, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.29, 147.83, 146.11, 142.63, 136.81, 128.92, 127.61, 124.46, 26.51.

4, 4-diacetyl-1, 1-biphenyl-^{1}H NMR (600 MHz, CDCl$_3$) δ 8.41 – 8.21 (m, 1H), 8.20 – 8.01 (m, 1H), 2.74 – 2.67 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 196.42, 150.46, 141.39, 129.33, 123.87, 26.99.

Napthyl-1-phenyl- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.84 (dd, *J* = 18.2, 17.3 Hz, 3H), 7.63 – 7.30 (m, 9H).^{13}C NMR (151 MHz, CDCl$_3$) δ 140.88, 140.38, 133.92, 131.74, 130.19, 128.38, 127.75, 127.35, 127.05, 126.14, 125.88, 125.50.

Napthyl-1-Benzocarbonitrile- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.82 (dd, *J* = 17.8, 8.5 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.43 (dd, *J* = 15.9, 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 11.6 Hz, 1H).

Napthyl-1-(4-nitrobenzene) – ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.36 (d, *J* = 7.5 Hz, 1H), 7.98 – 7.89 (m, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.47 (dd, *J* = 14.1, 7.0 Hz, 1H), 7.42 (t, *J* = 11.0 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 147.70, 147.21, 137.80, 133.80, 130.95, 128.99, 128.59, 127.11, 126.76, 126.25, 125.34, 125.15, 123.61.

Napthyl-1-Benzaldehyde- ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.05 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.84 (dd, *J* = 20.7, 10.6 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.43 (m, 2H), 7.38 (dd, *J* = 16.7, 7.6 Hz, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 192.05, 147.28, 138.83, 135.34, 133.83, 131.13, 130.80, 129.77, 128.58, 128.51, 127.04, 126.53, 126.11, 125.48, 125.37.

Napthyl-1-(2-aminobenzene)- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (dd, *J* = 17.2, 8.2 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.52 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.47 (tt, *J* = 5.7, 2.8 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.24 (qd, *J* = 7.8, 3.4 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.80 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.75 – 2.99 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.19, 135.89, 132.77, 130.62, 130.15, 127.72, 127.27, 126.93, 126.54, 126.51, 125.22, 124.97, 124.90, 124.77, 117.34, 114.33.

2, 7-diphenyl-9H-fluorene- ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.79 (s, 2H), 7.65 (dd, *J* = 19.5, 7.6 Hz, 6H), 7.46 (t, *J* = 7.1 Hz, 4H), 7.36 (t, *J* = 7.1 Hz, 2H), 4.03 (s, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.16, 141.48, 140.63, 139.92, 128.80, 127.20, 126.12, 123.84, 120.22, 37.09.

3-phenyl thiophene-^{1}H NMR (600 MHz, CDCl$_3$) δ 7.53 (dd, *J* = 9.5, 8.0 Hz, 2H), 7.37 (dd, *J* = 9.7, 5.7 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 14.2, 6.8 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 127.78, 127.73, 126.23, 126.15, 125.44, 125.33, 125.17, 125.05, 119.24, 118.75.

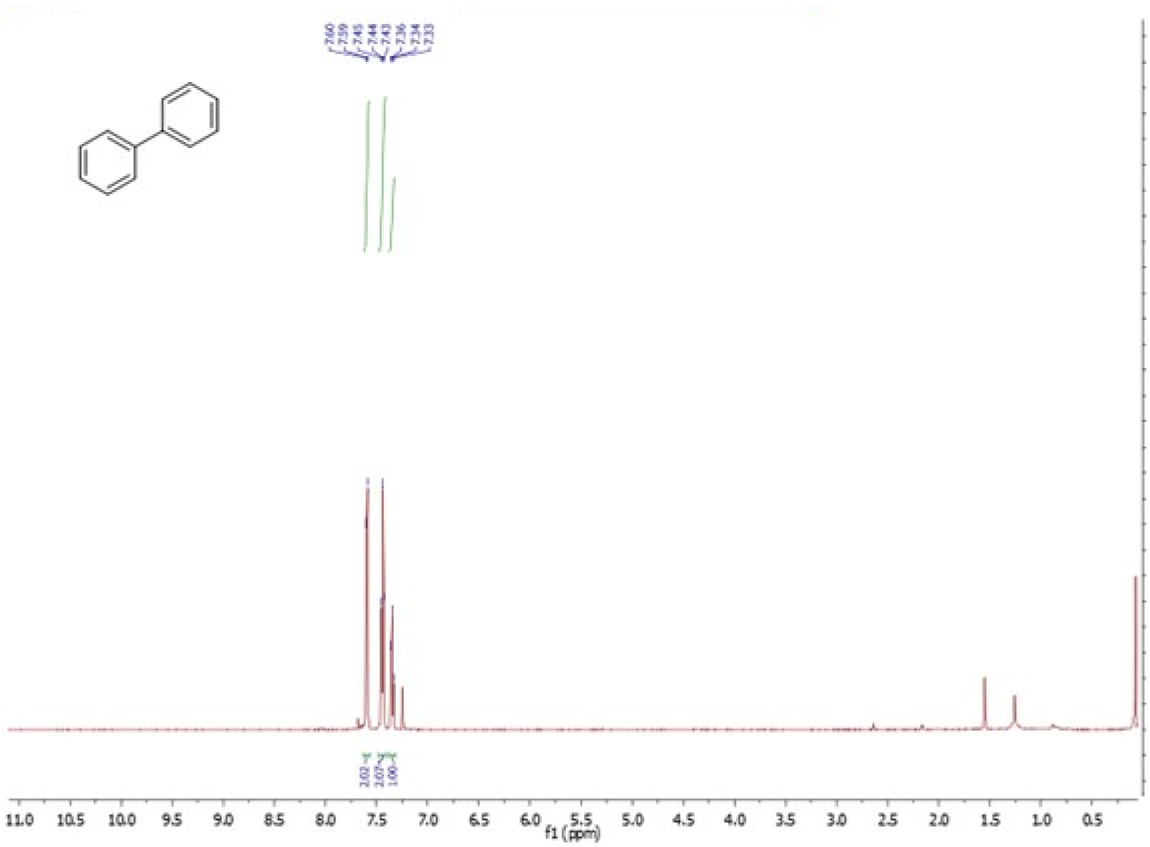


Fig. S11. ^{1}H NMR spectra of Biphenyl.

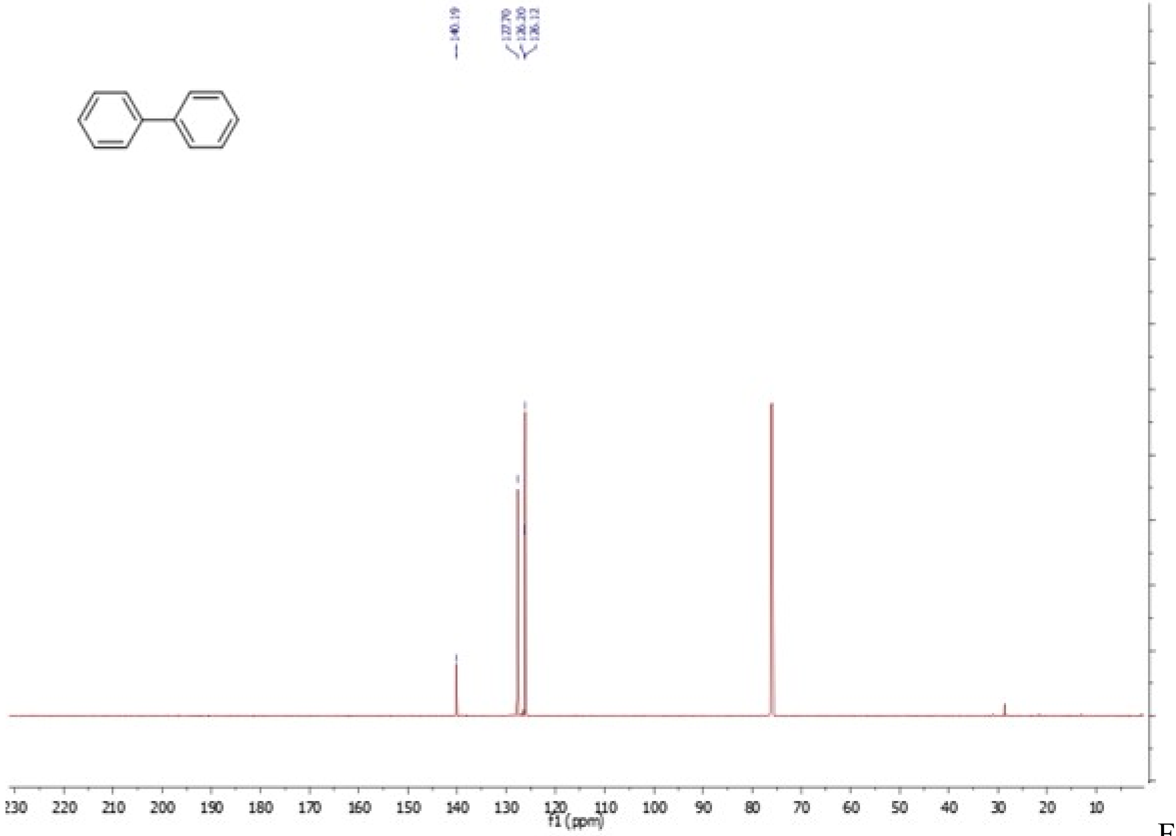


Fig. S12. ^{13}C NMR spectra of Biphenyl.

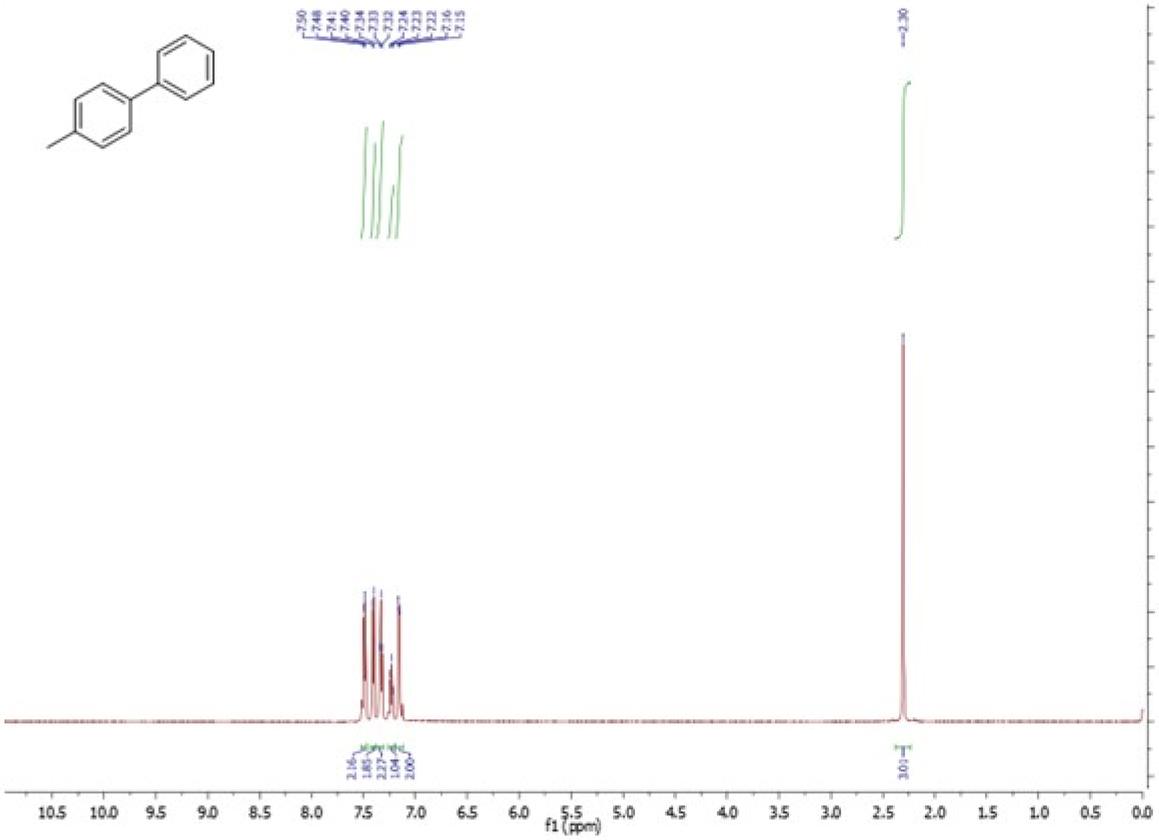


Fig. S13. ^{1}H NMR spectra of 4-methylbiphenyl.

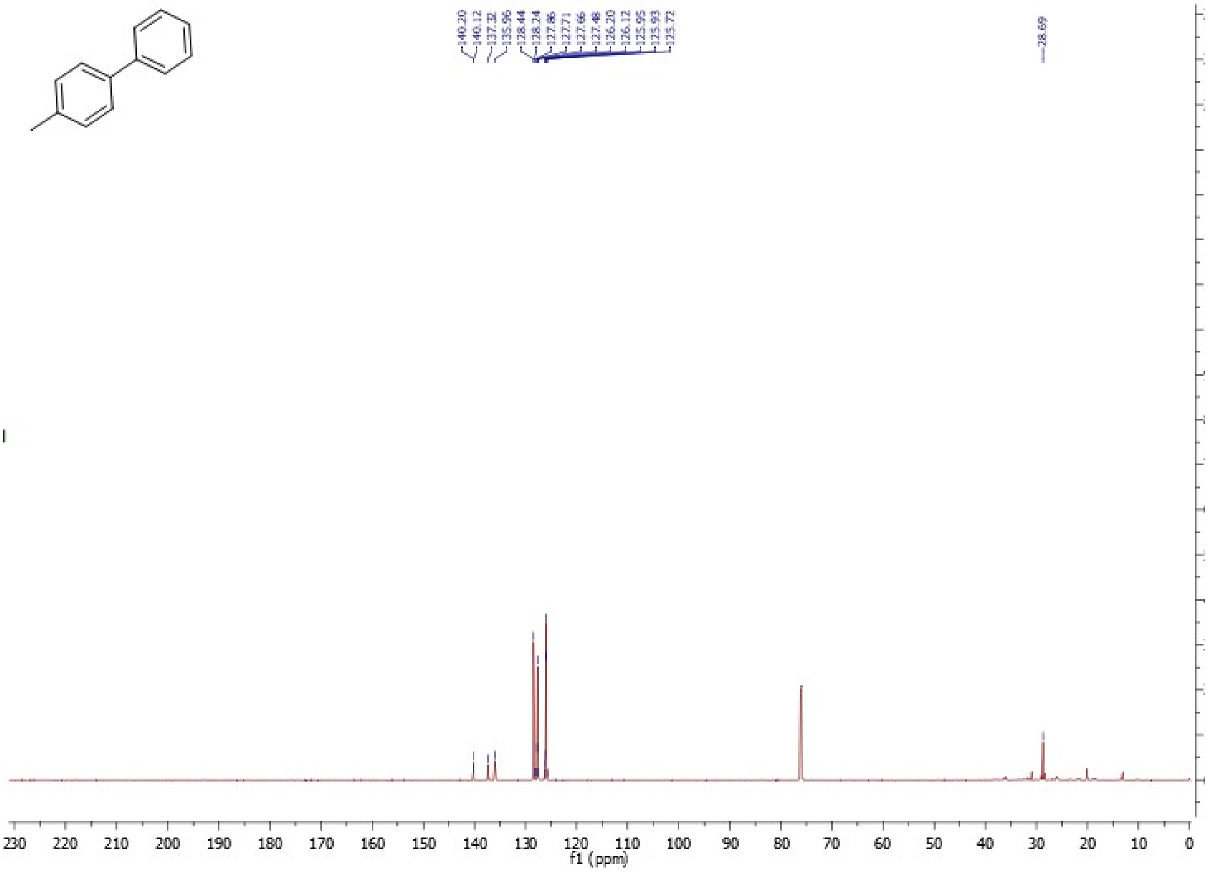


Fig. S14. ^{13}C NMR spectra of 4-methylbiphenyl.

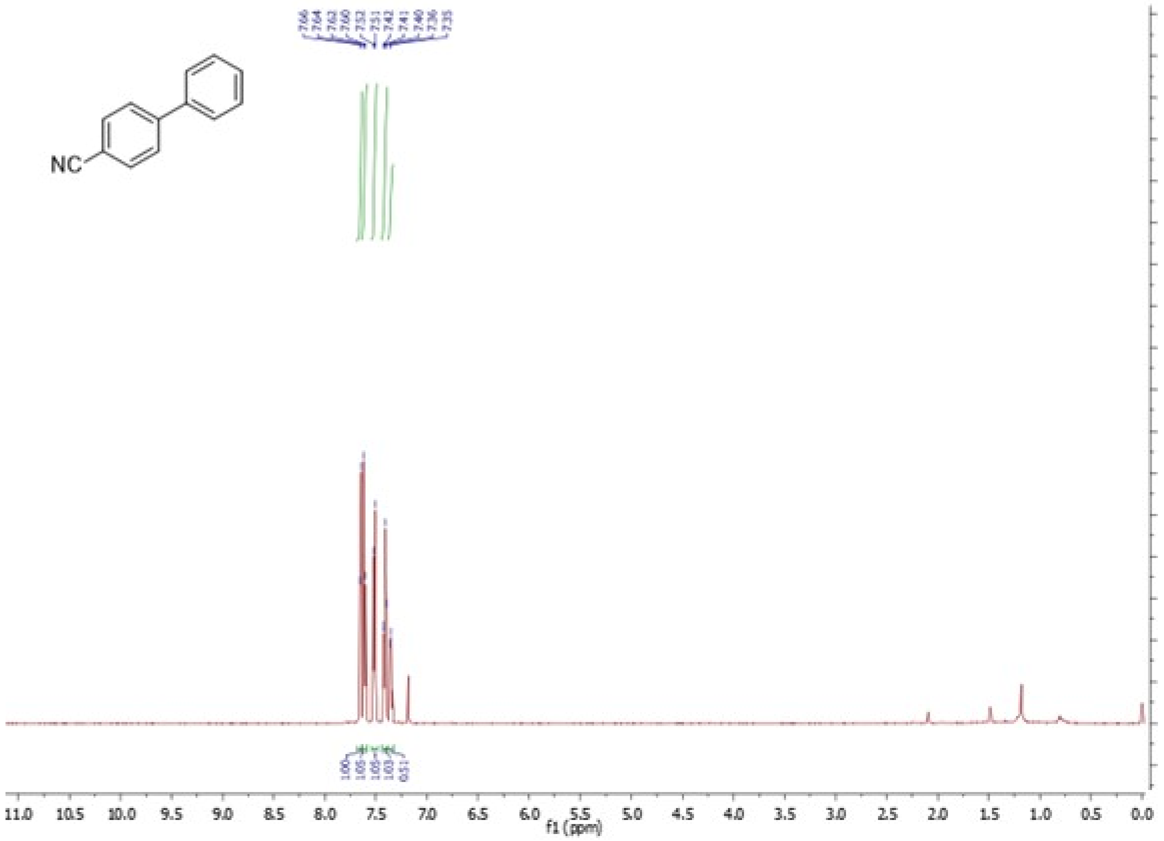


Fig. S15. ^{1}H NMR spectra of 4-phenylbenzonitrile.

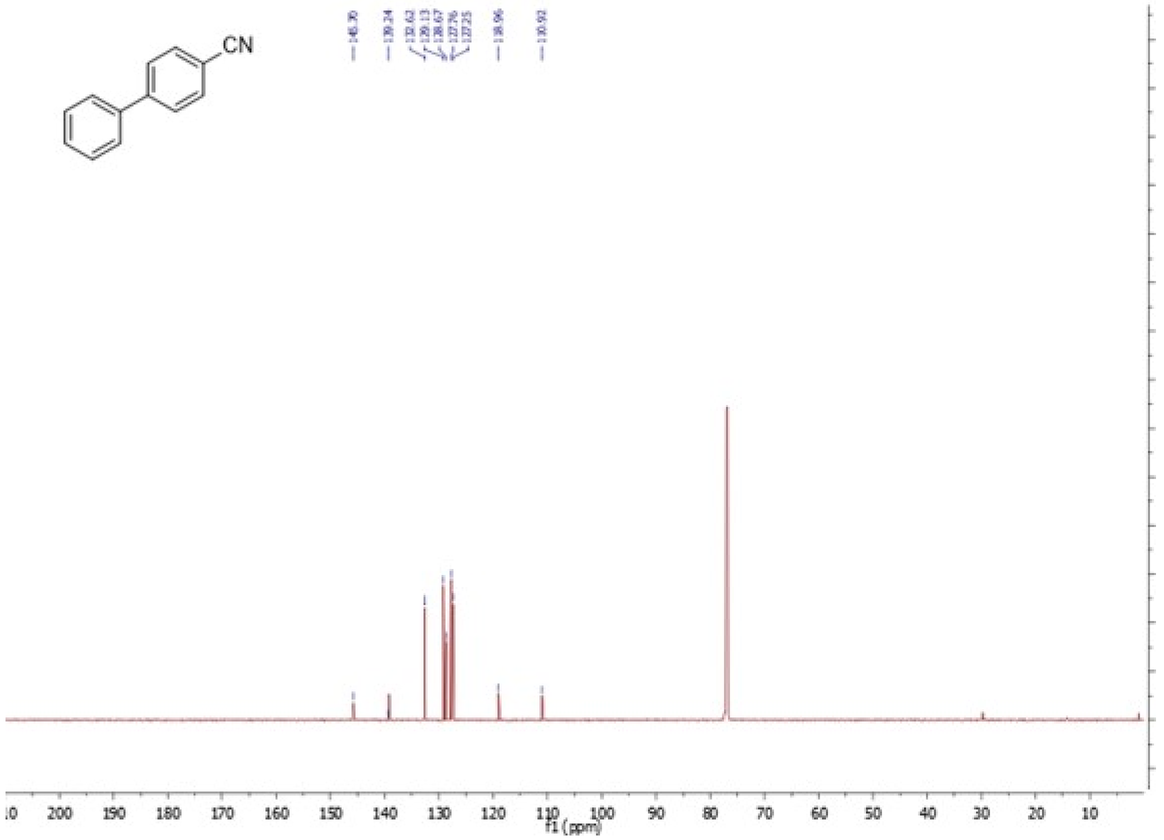


Fig. S16. ^{13}C NMR spectra of 4-phenylbenzonitrile.

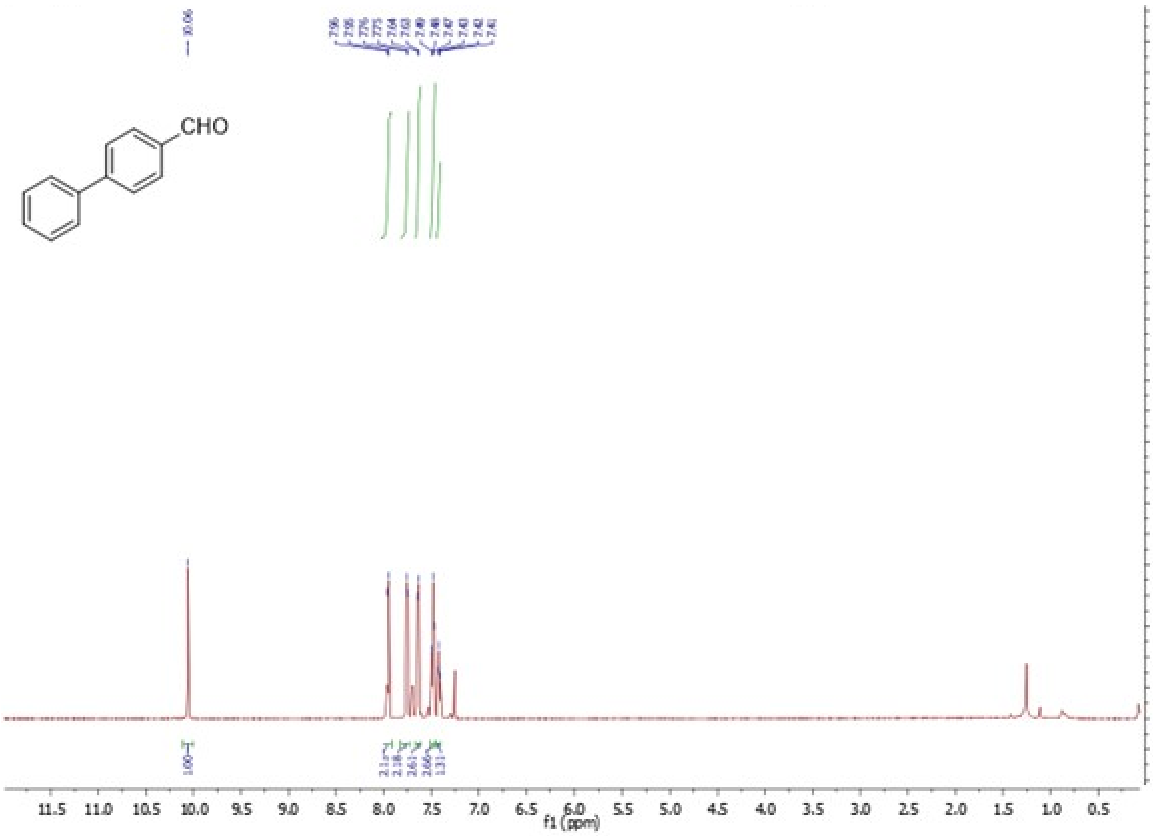


Fig. S17. ^{1}H NMR spectra of 4-phenylbenzaldehyde.

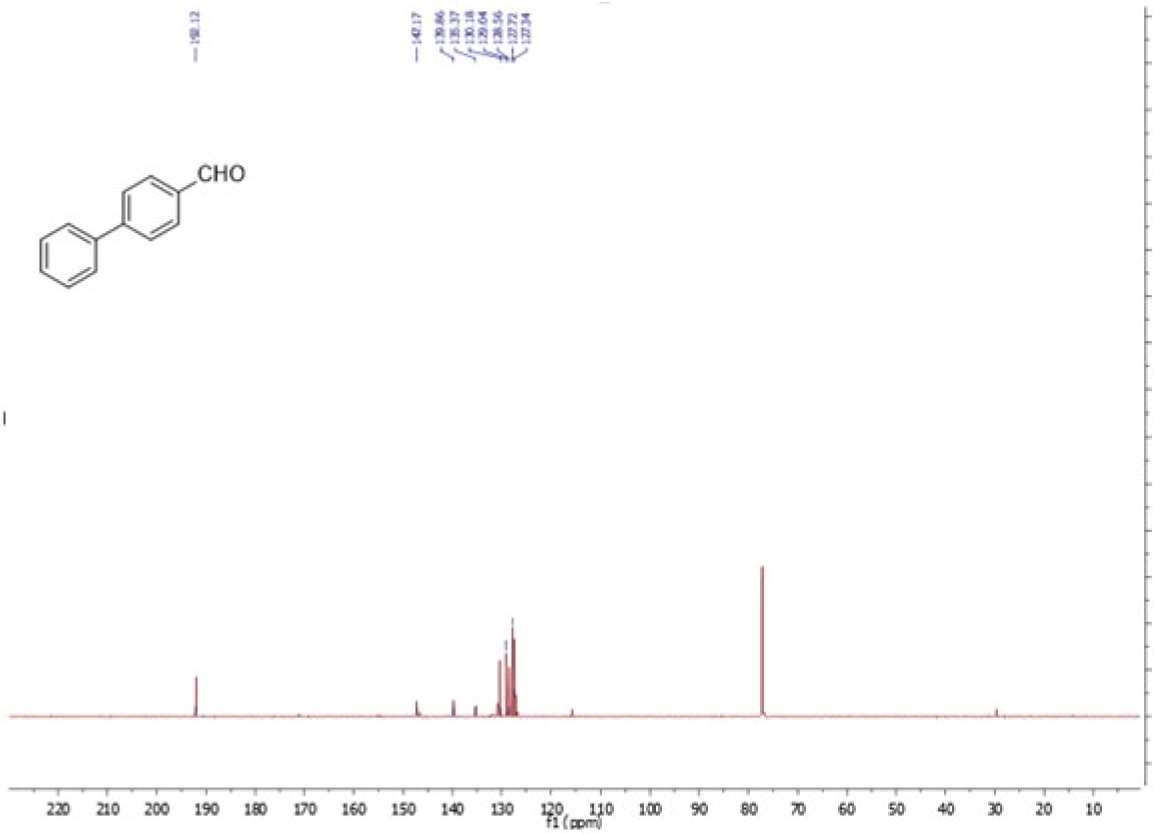


Fig. S18. ^{13}C NMR spectra of 4-phenylbenzaldehyde.

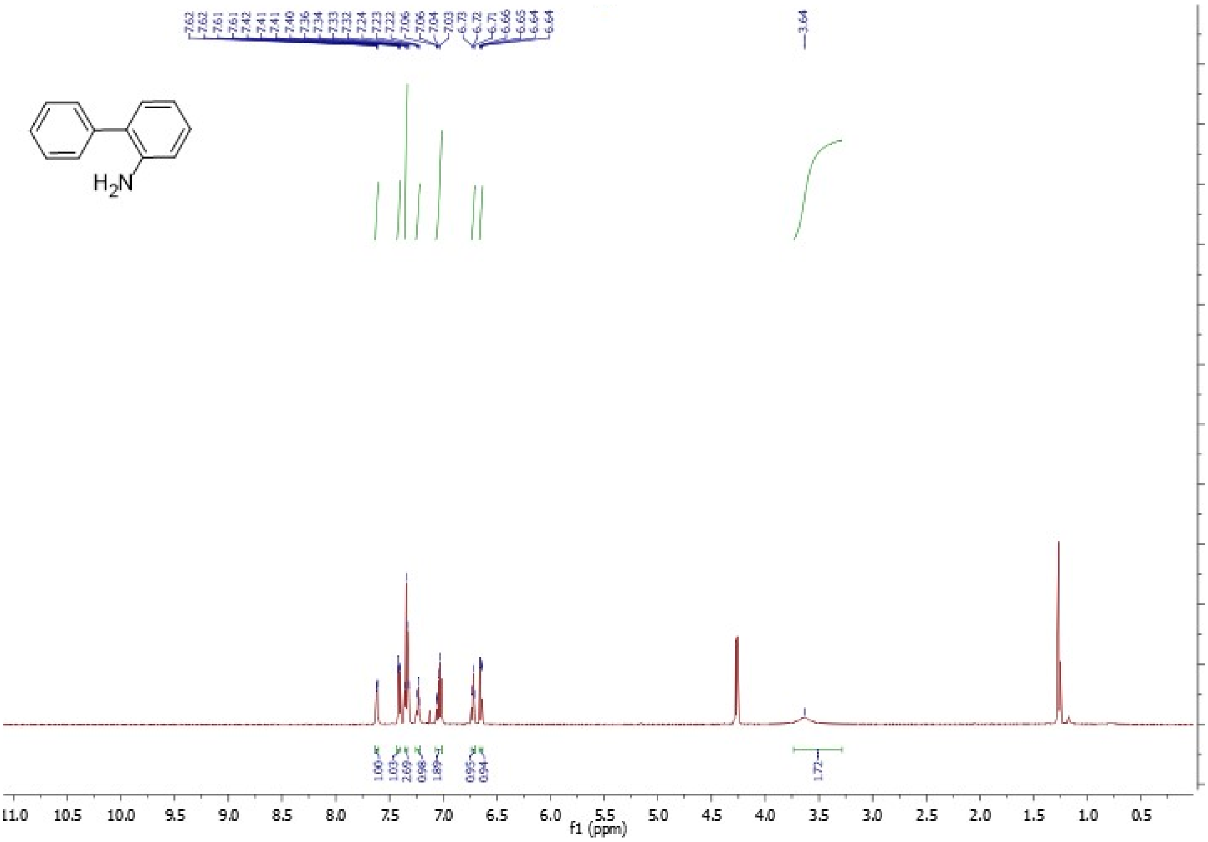


Fig. S19. ^{1}H NMR spectra of 2-amino-1, 1-biphenyl.

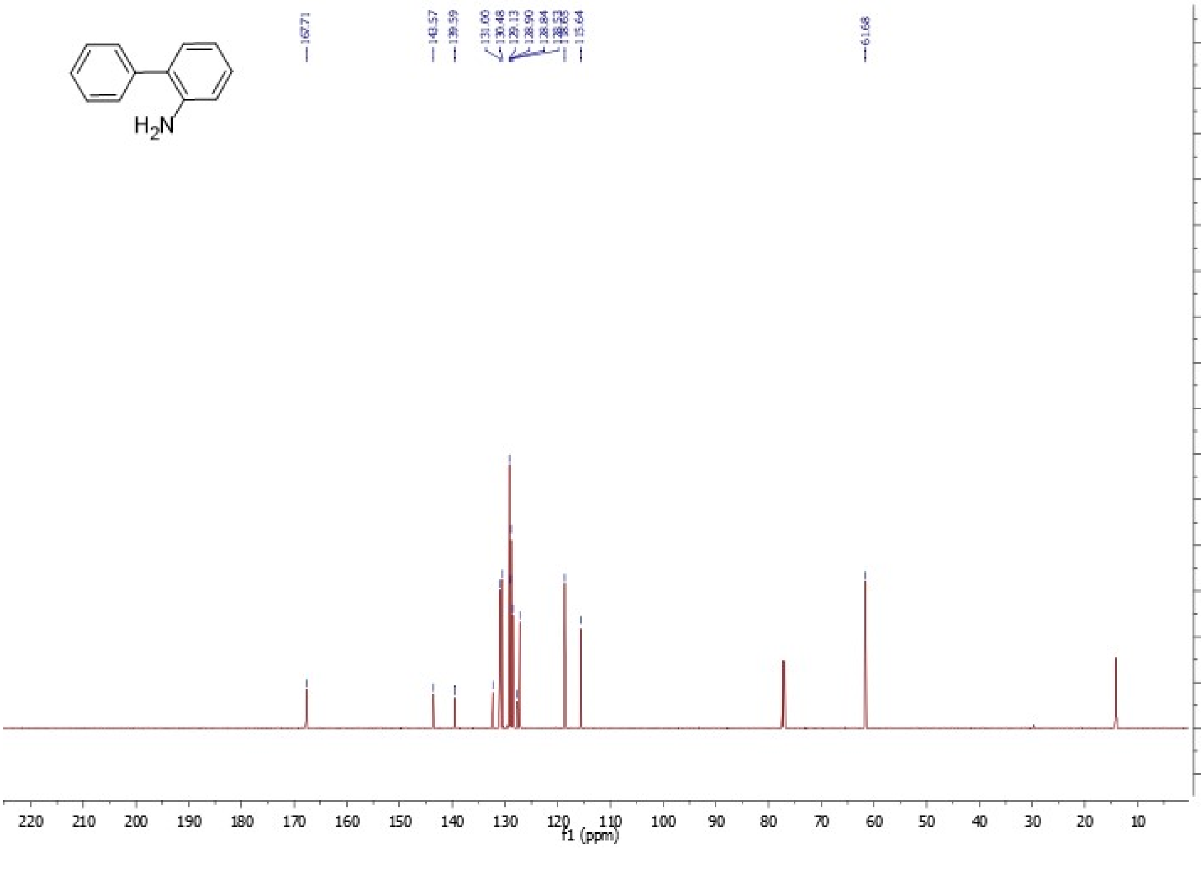


Fig. S20. ^{13}C NMR spectra of 2-amino-1, 1-biphenyl.

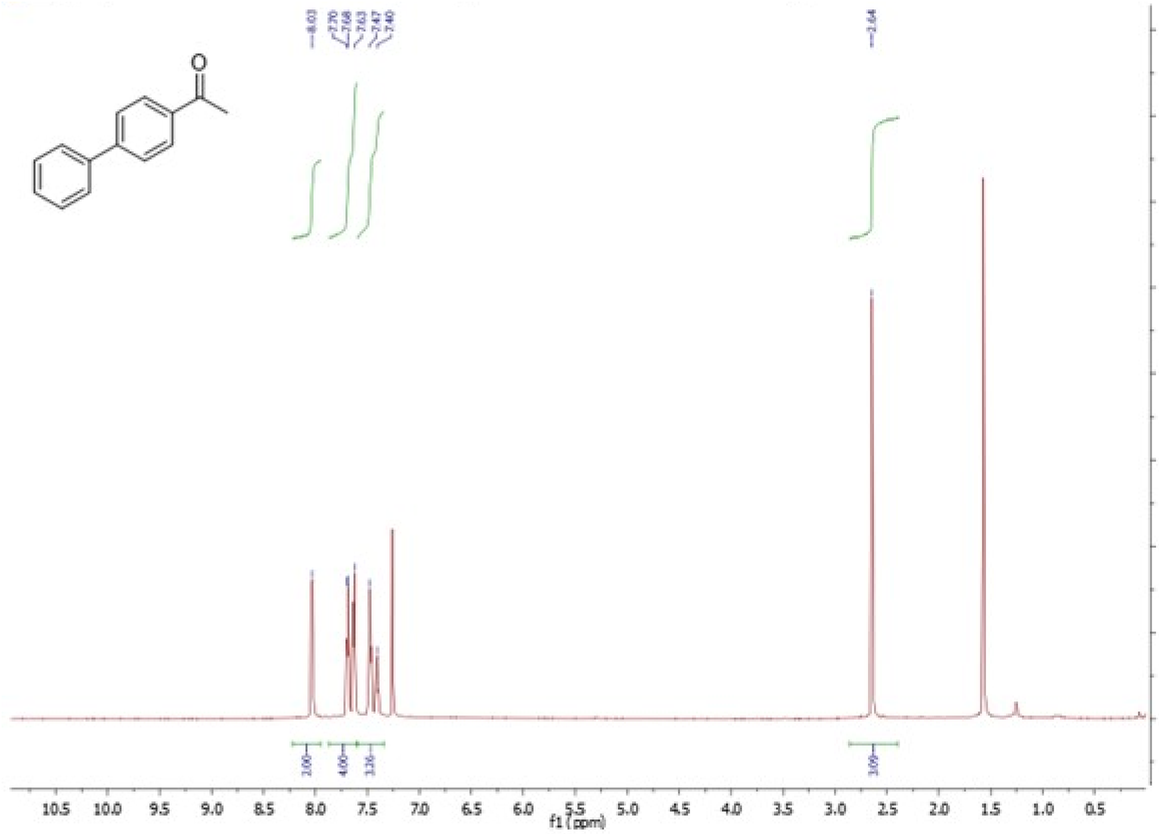


Fig. S21. ^{1}H NMR spectra of 4-acetyl-1, 1-biphenyl.

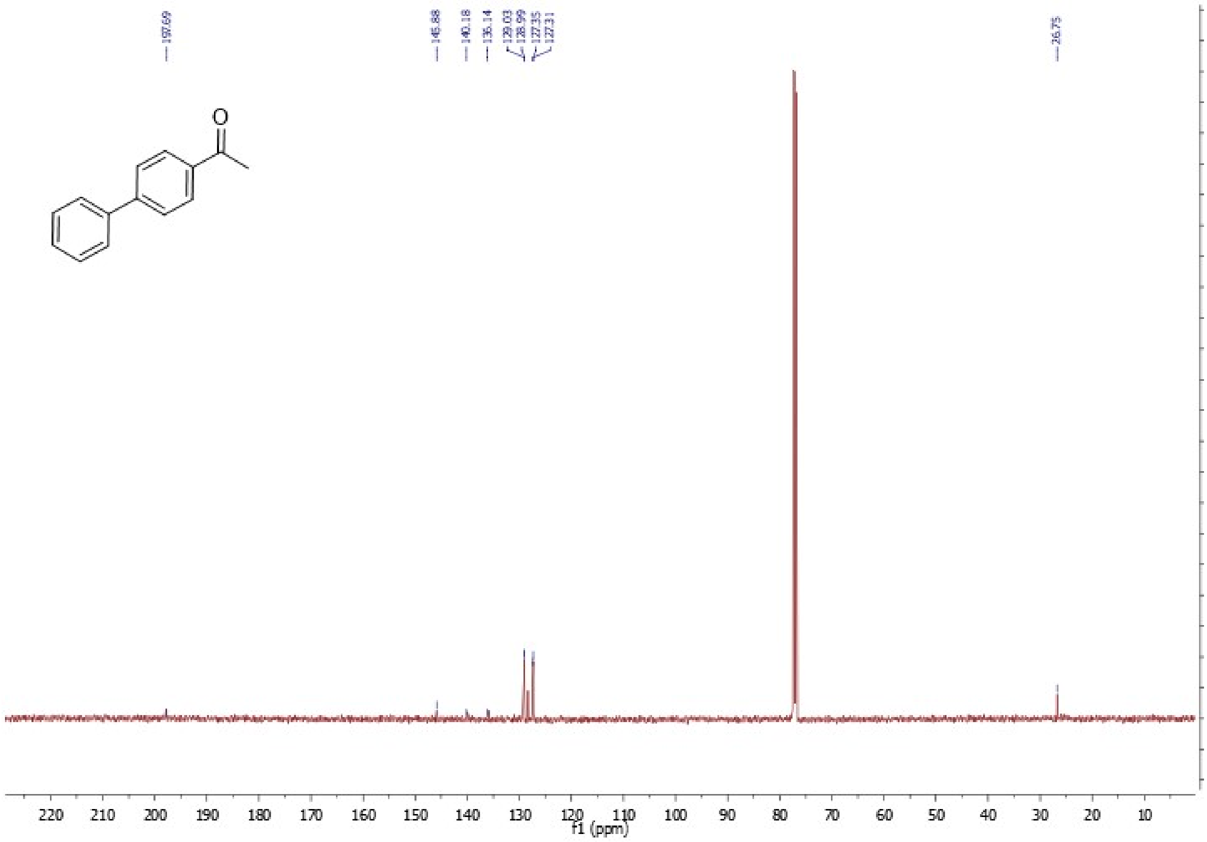


Fig. S22. ^{13}C NMR spectra of 4-acetyl-1, 1-biphenyl.

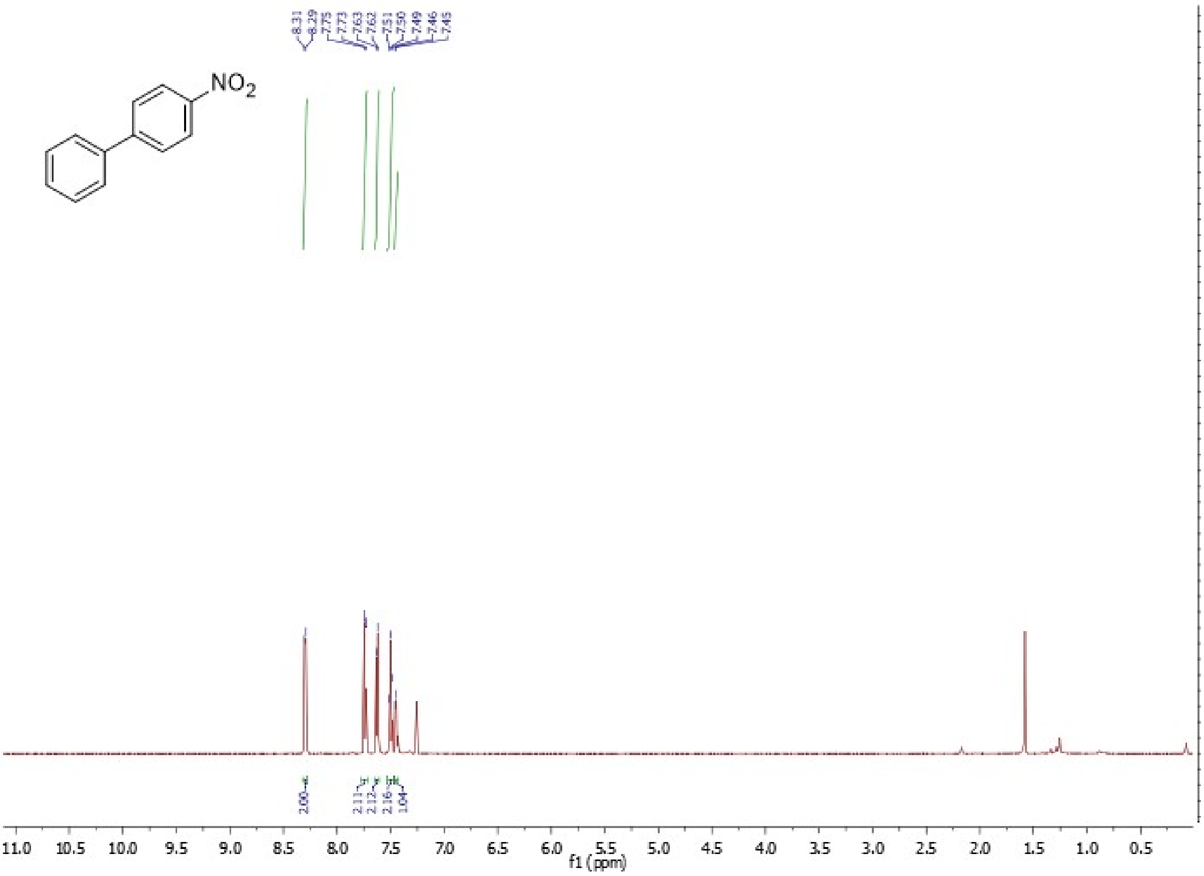


Fig. S23. ^{1}H NMR spectra of 4-nitrobiphenyl.

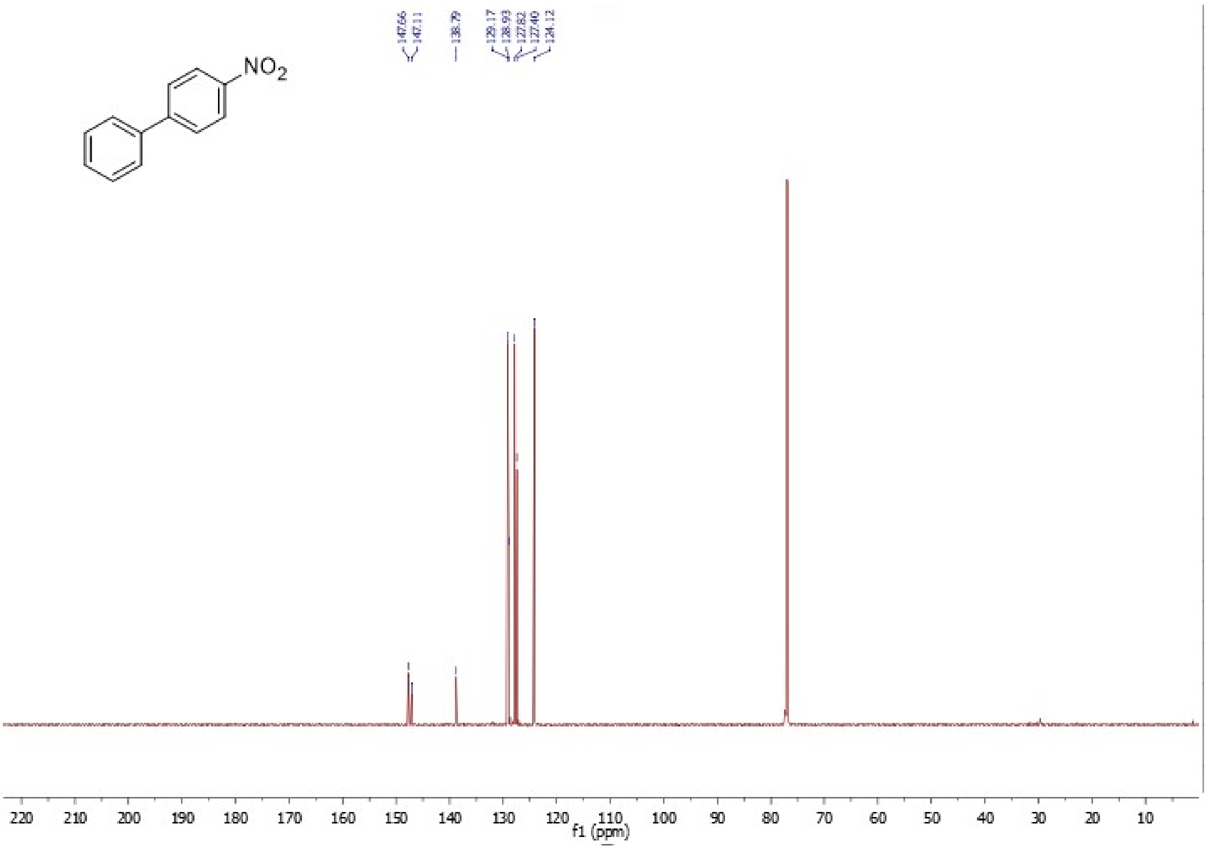


Fig. S24. ^{13}C NMR spectra of 4-nitrobiphenyl.

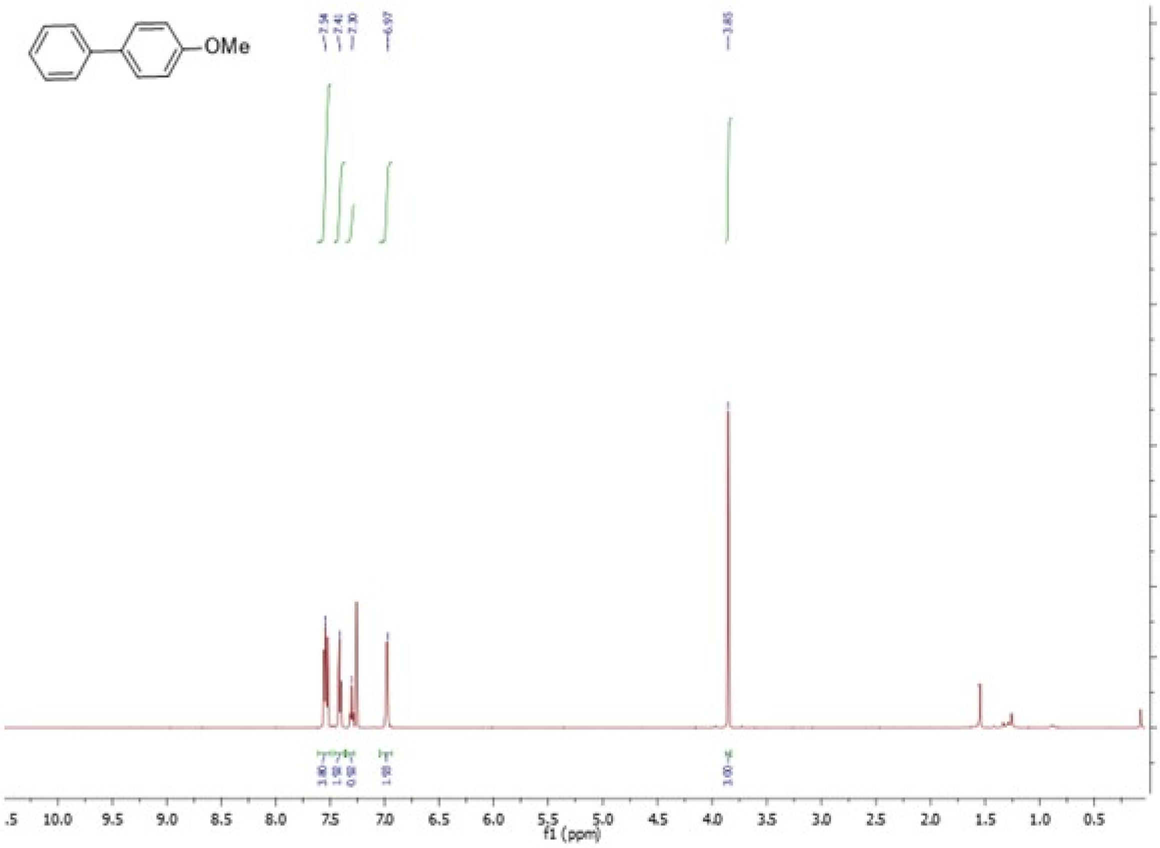


Fig. S25. ^{1}H NMR spectra of 4-methoxy biphenyl.

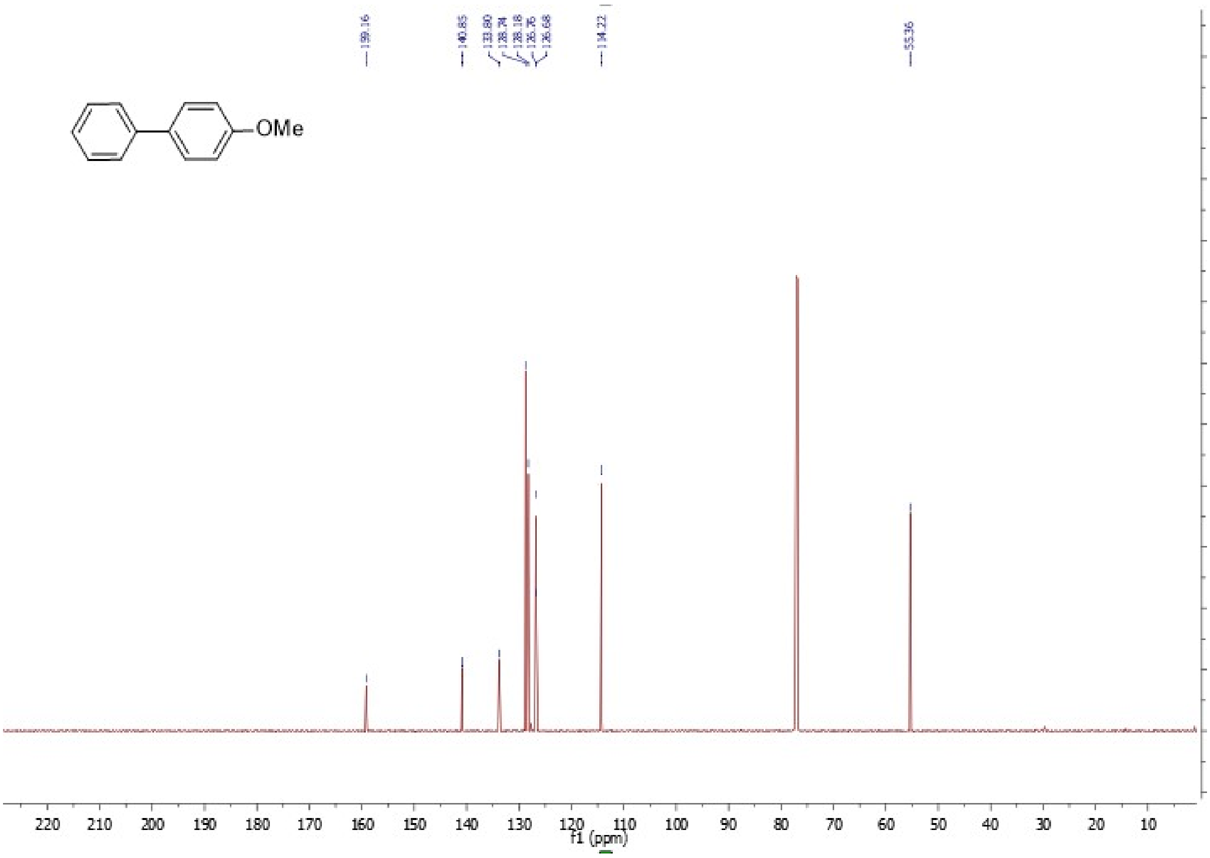


Fig. S26. ^{13}C NMR spectra of 4-methoxy biphenyl.

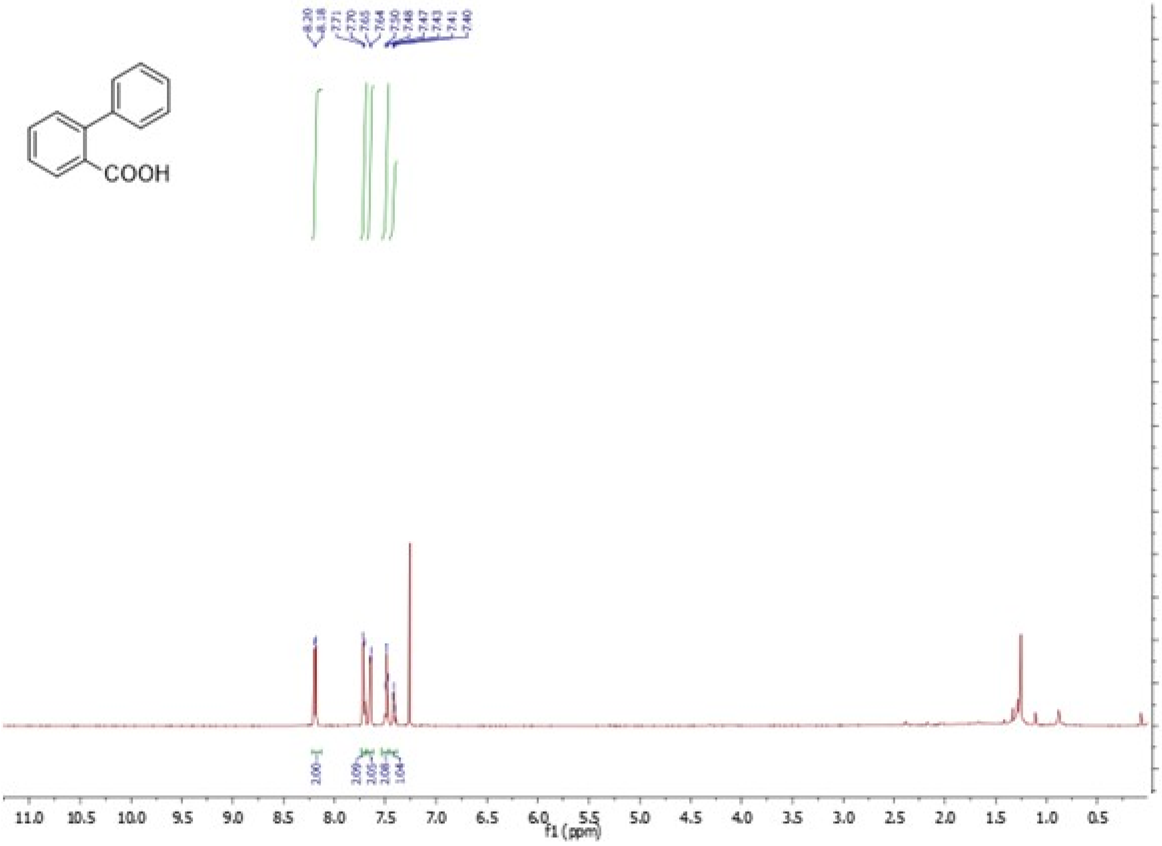


Fig. S27. ^{1}H NMR spectra of 2-carboxylic acid-1, 1-biphenyl.

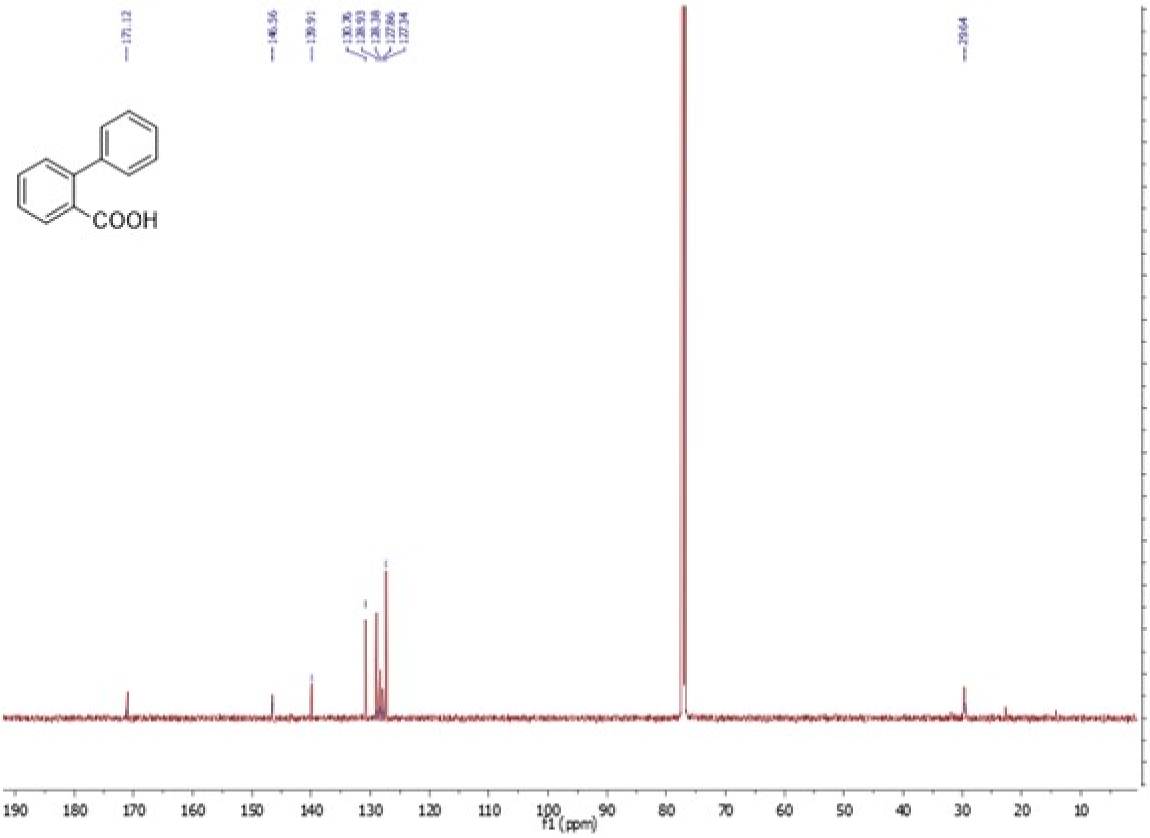


Fig. S28. ^{13}C NMR spectra of 2-carboxylic acid-1, 1-biphenyl.

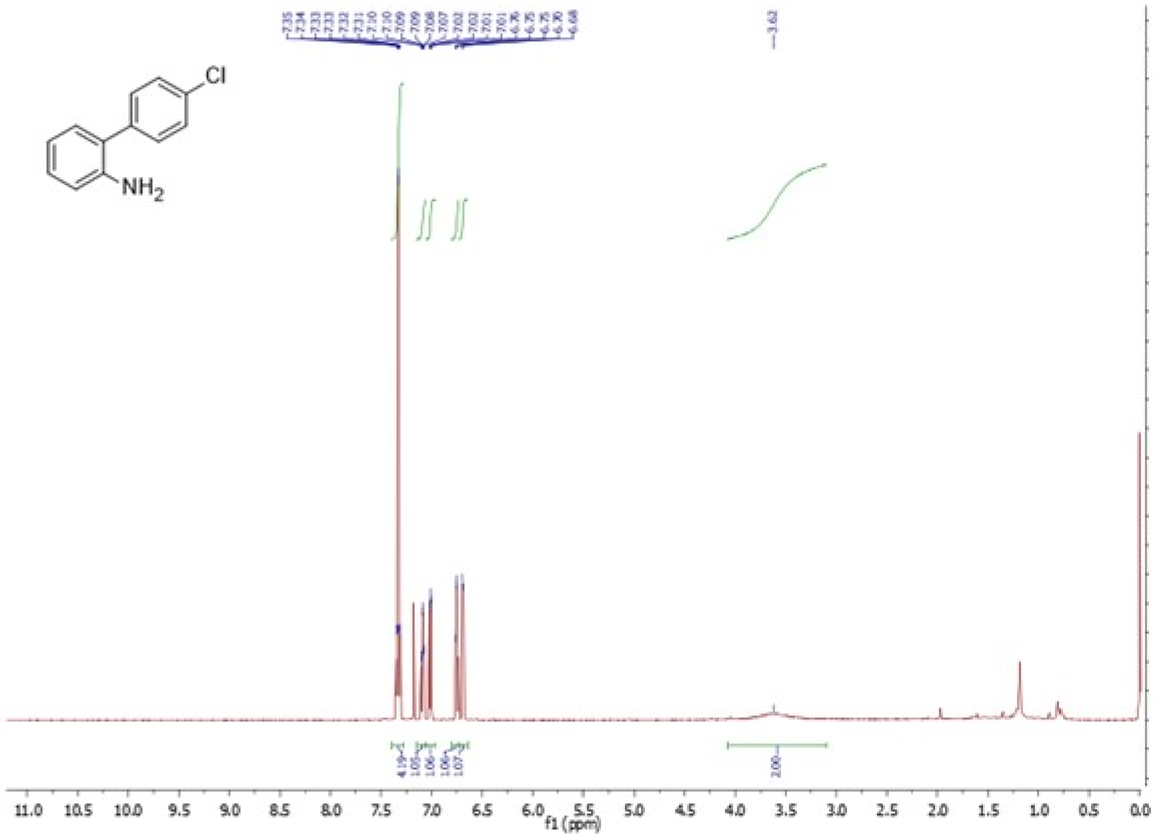


Fig. S29. ^{1}H NMR spectra of 4-chloro, 2-amino-1, 1-biphenyl.

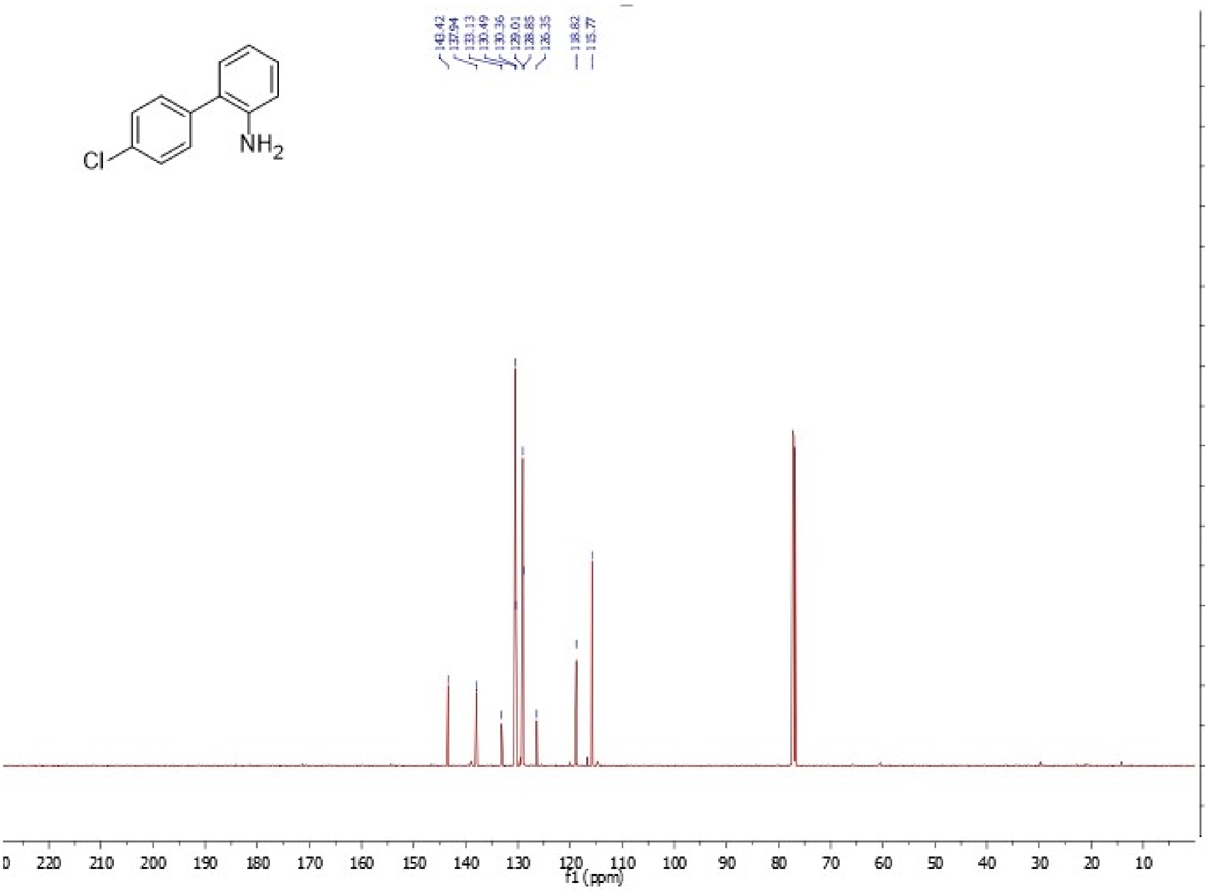


Fig. S30. ^{13}C NMR spectra of 4-chloro, 2-amino-1, 1-biphenyl.

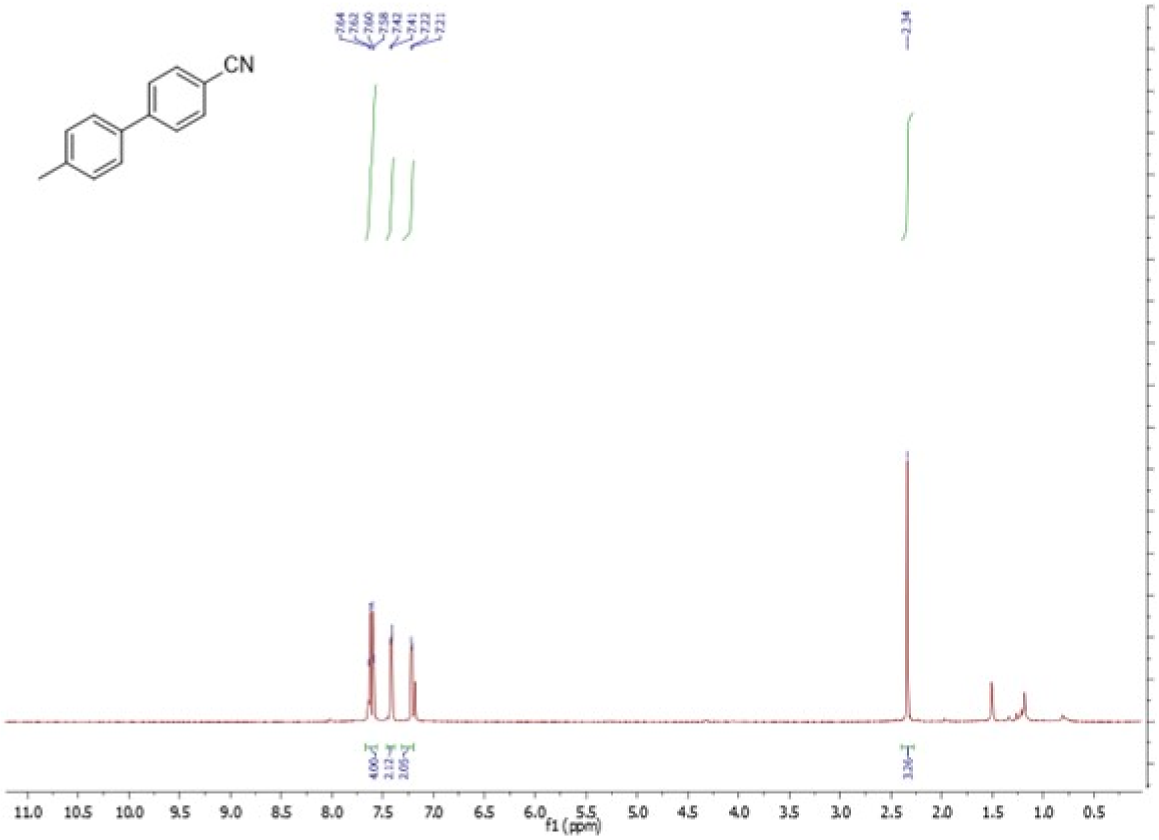


Fig. S31. ^{1}H NMR spectra of 4-cyano, 4-methyl-1, 1-biphenyl.

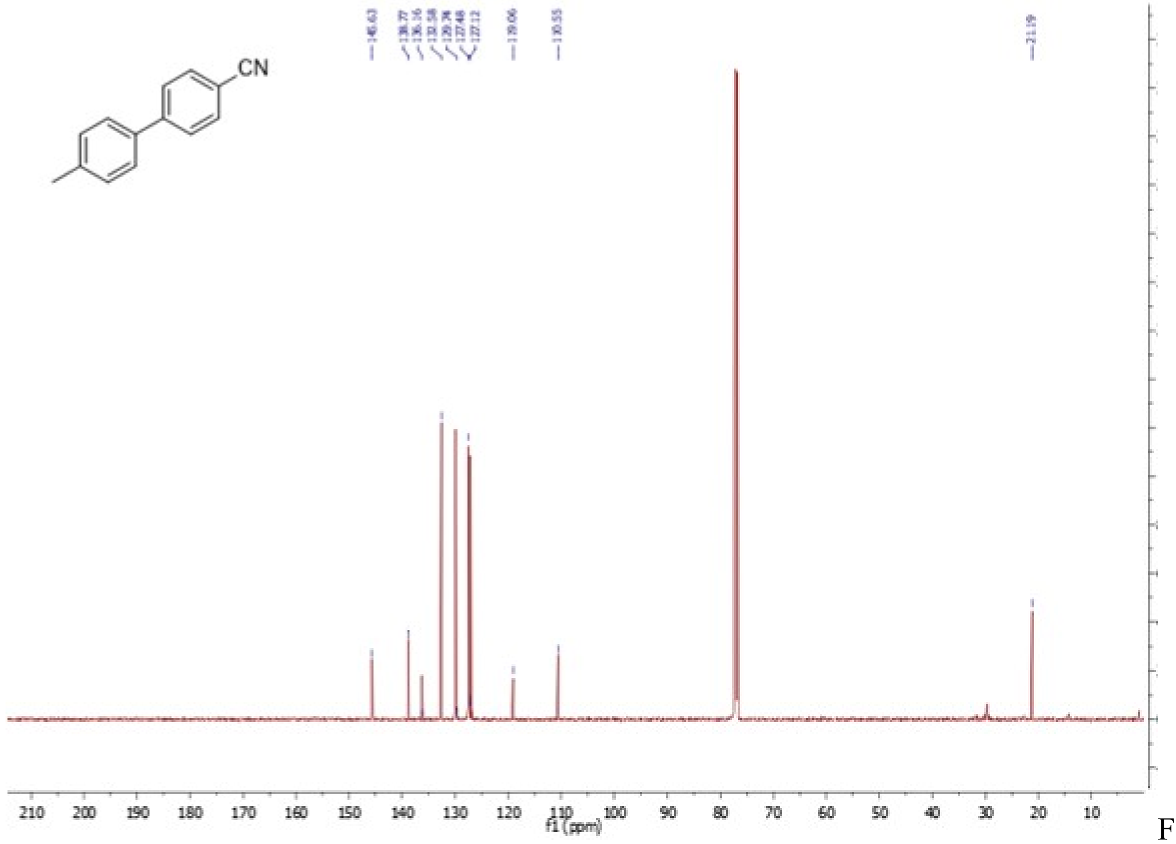


Fig. S32. ^{13}C NMR spectra of 4-cyano, 4-methyl-1, 1-biphenyl.

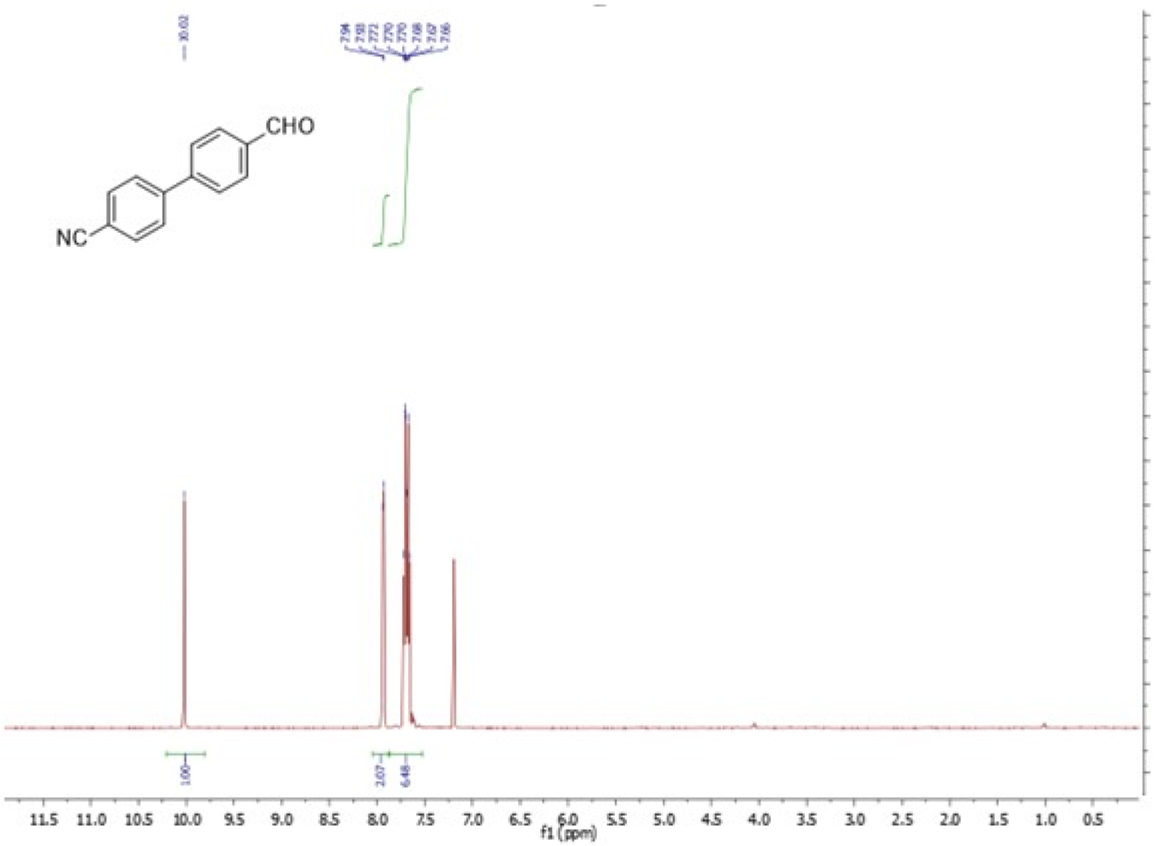


Fig. S33. ^{1}H NMR spectra of 4-cyano, 4-carbaldehyde-1, 1-biphenyl.

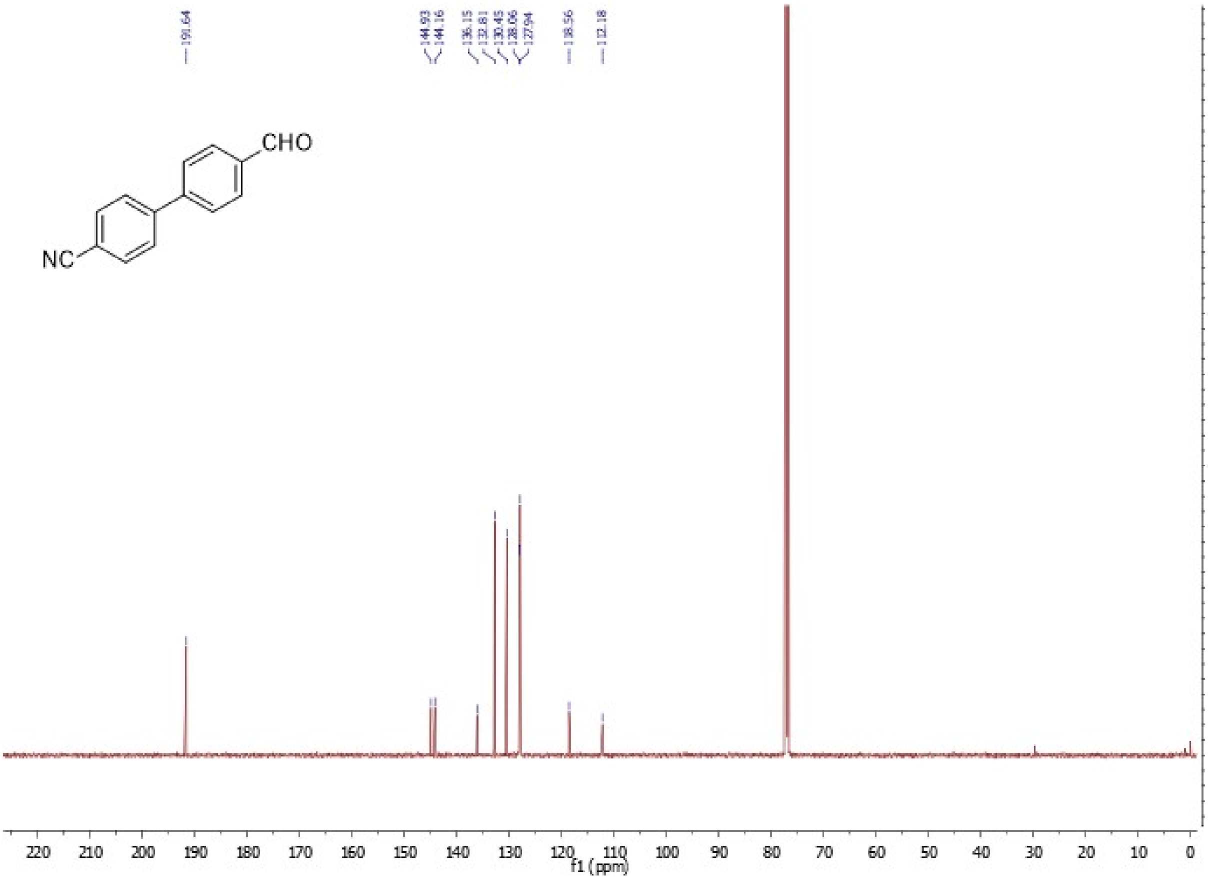


Fig. S34. ^{13}C NMR spectra of 4-cyano, 4-carbaldehyde-1, 1-biphenyl

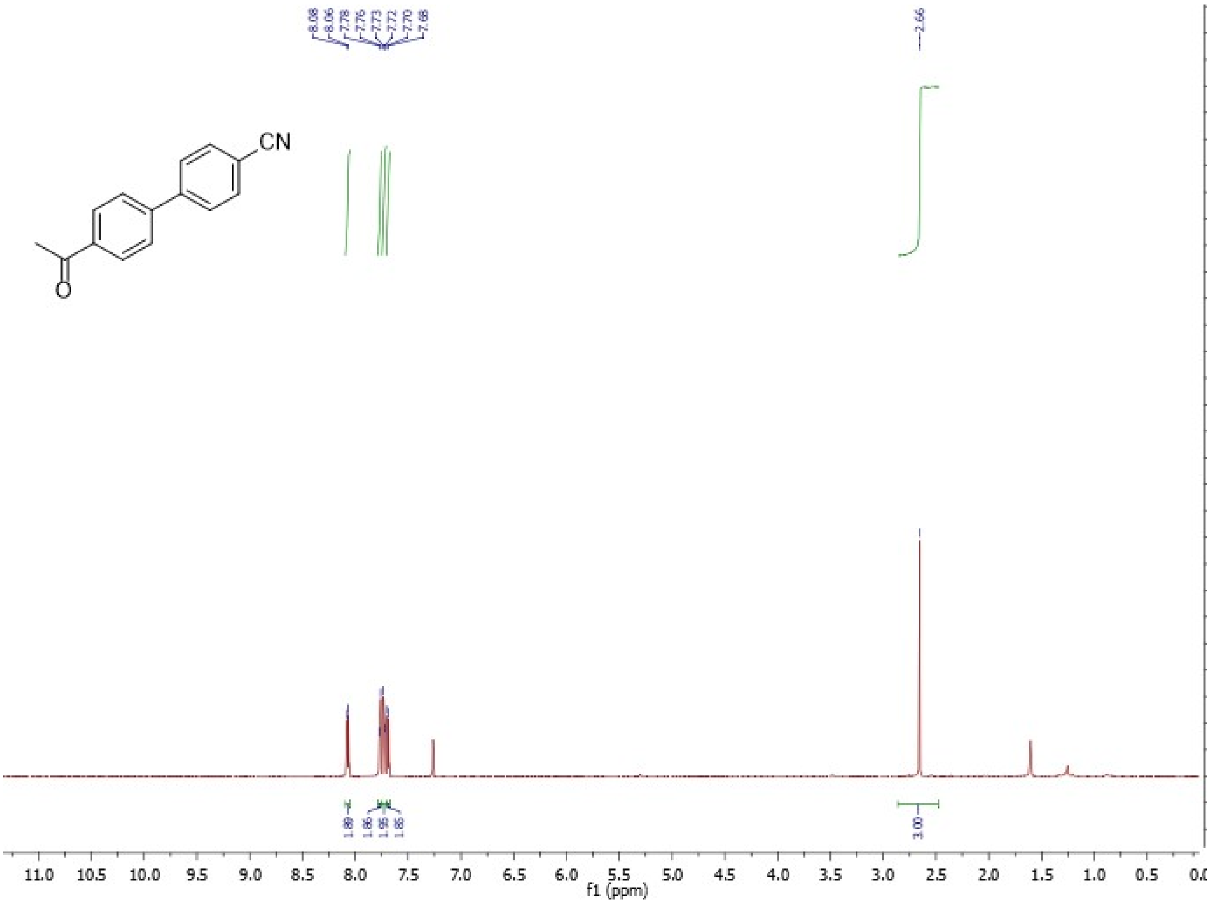


Fig. S35. ^{1}H NMR spectra of 4'-acetyl-[1,1'-biphenyl]-4-carbonitrile

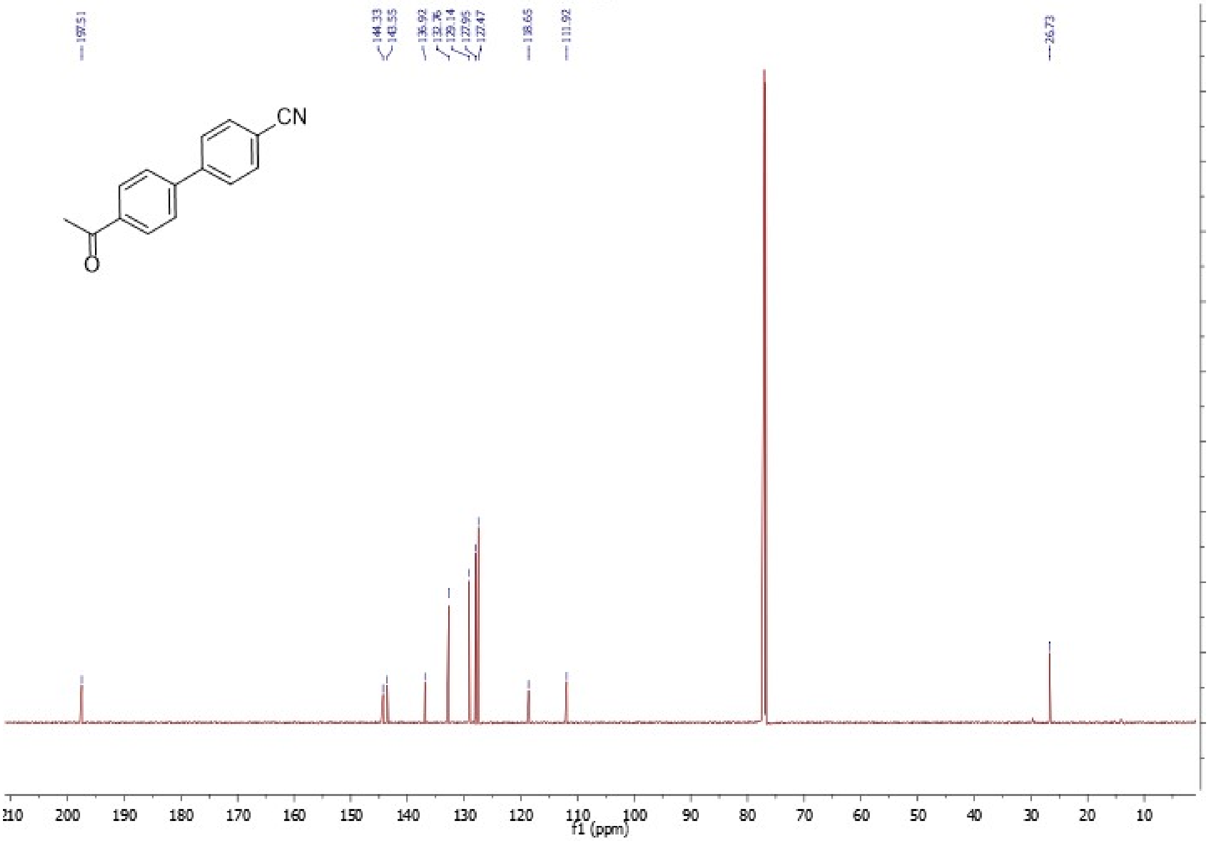


Fig. S36. ^{13}C NMR spectra of 4'-acetyl-[1, 1'-biphenyl]-4-carbonitrile

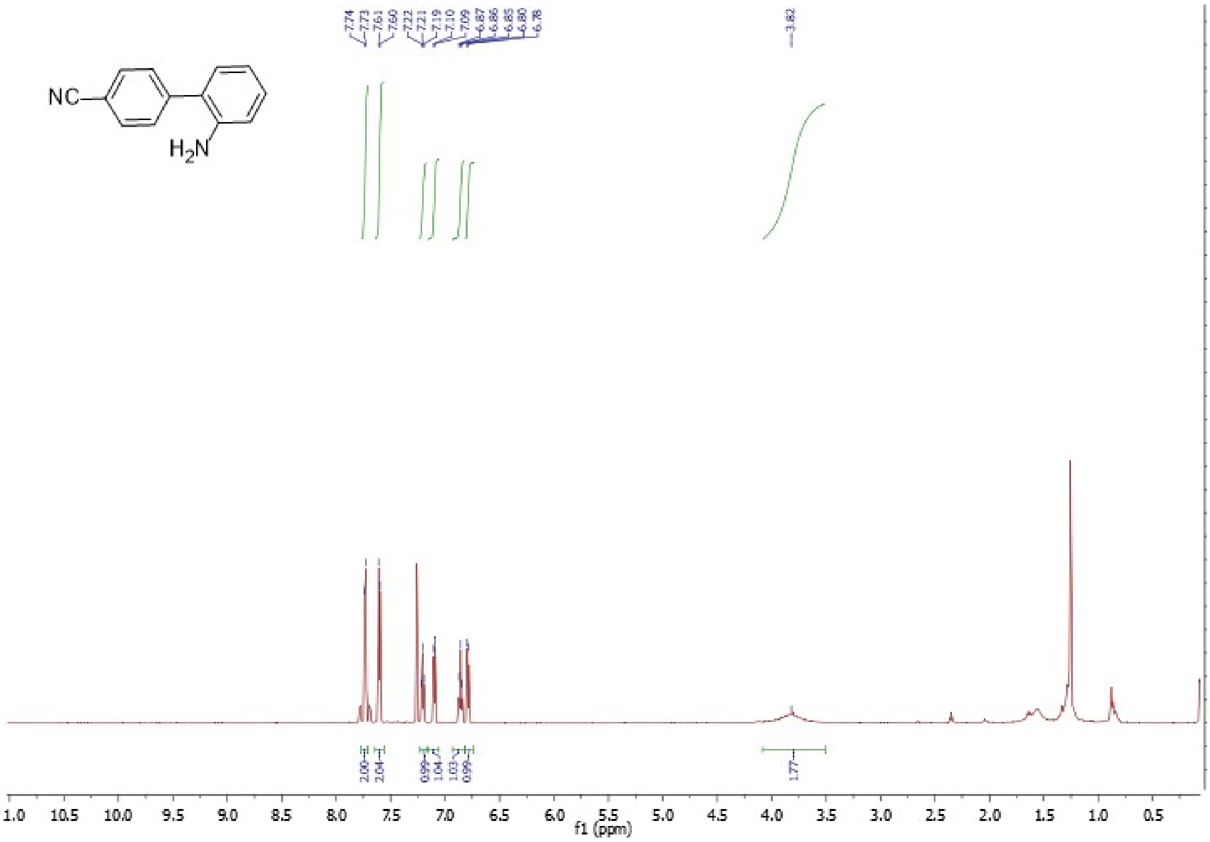


Fig. S37. ^{1}H NMR spectra of 4-cyano, 2-amino-1, 1-biphenyl.

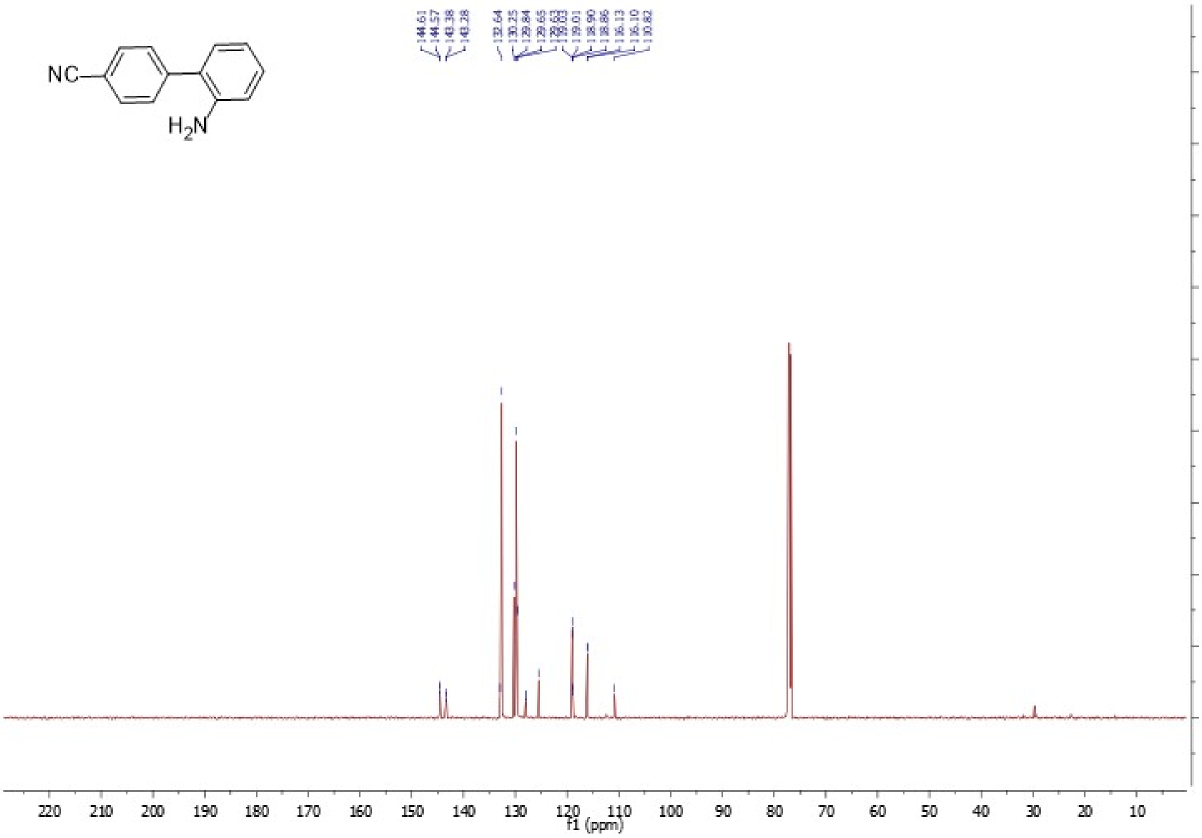


Fig. S38. ^{13}C NMR spectra of 4-cyano, 2-amino-1, 1-biphenyl.

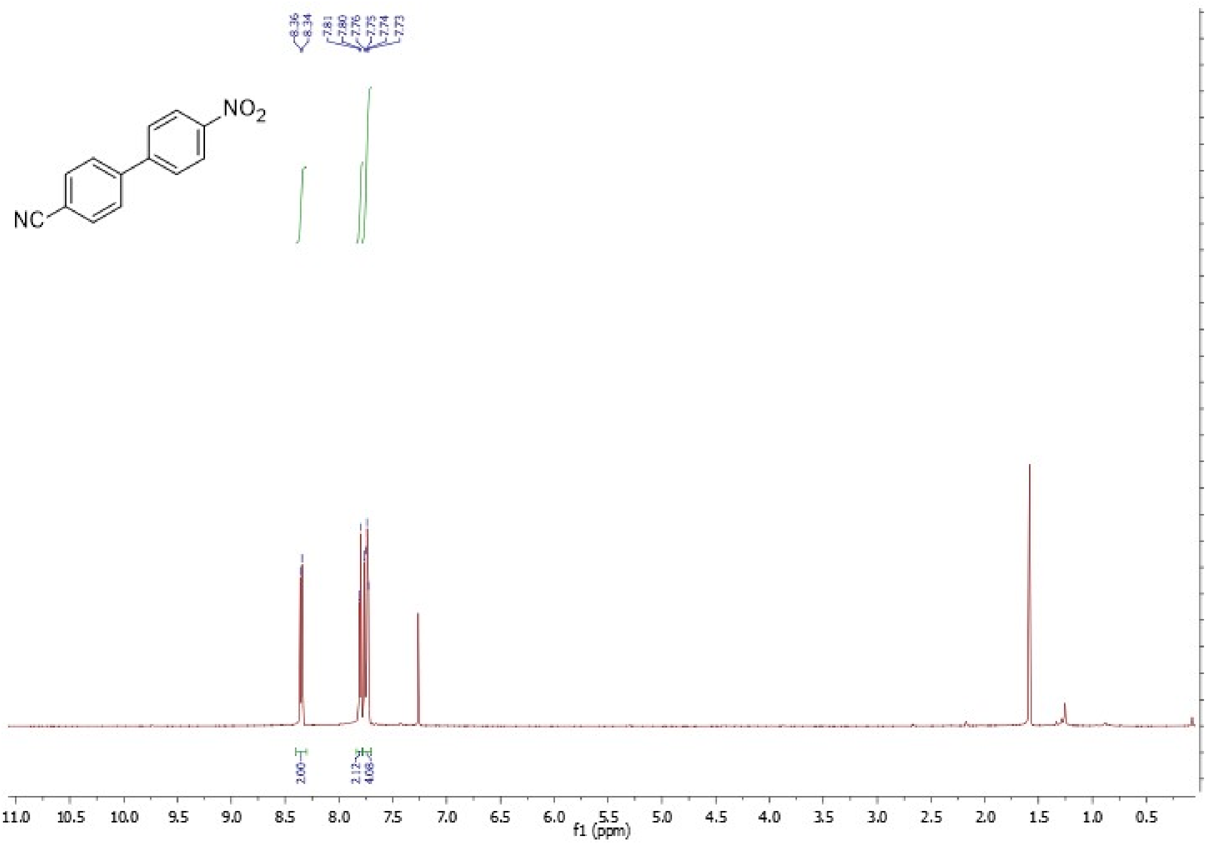


Fig. S39. ^{1}H NMR spectra of 4-cyano, 4-nitro-1, 1-biphenyl.

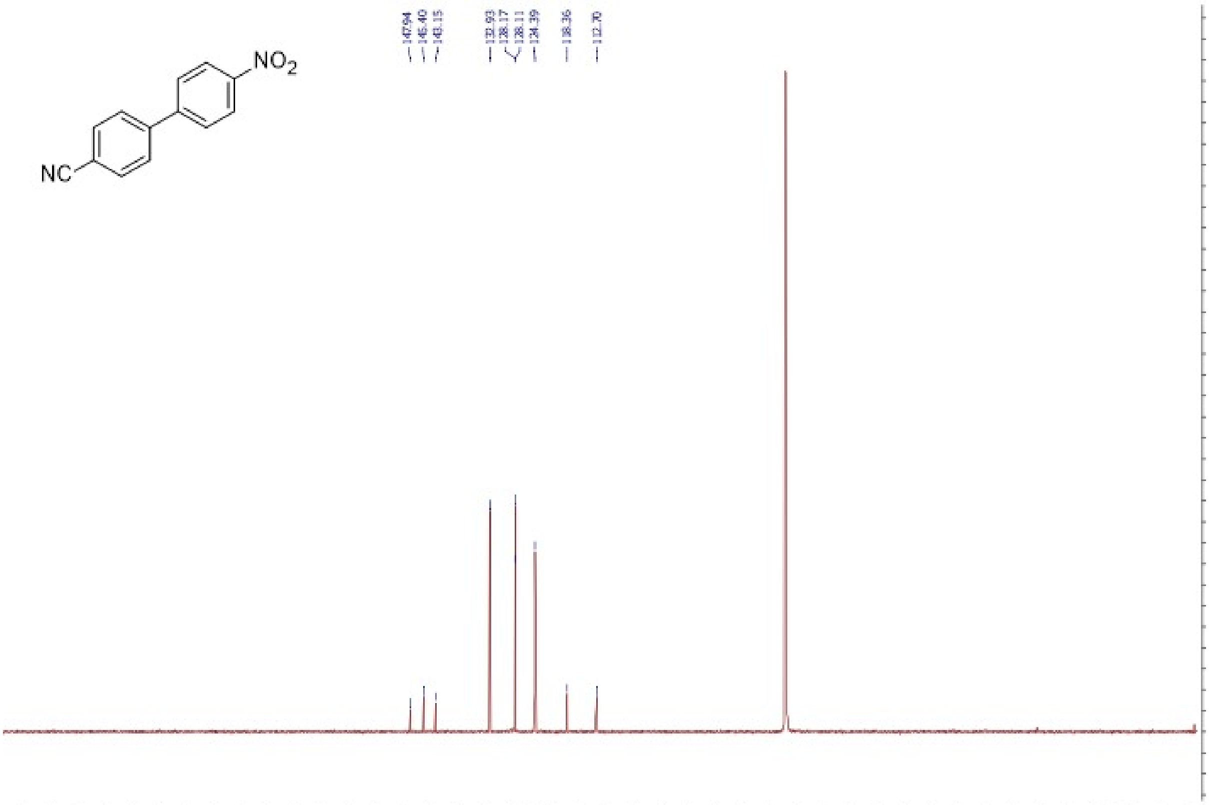


Fig. S40. ^{13}C NMR spectra of 4-cyano, 4-nitro-1, 1-biphenyl.

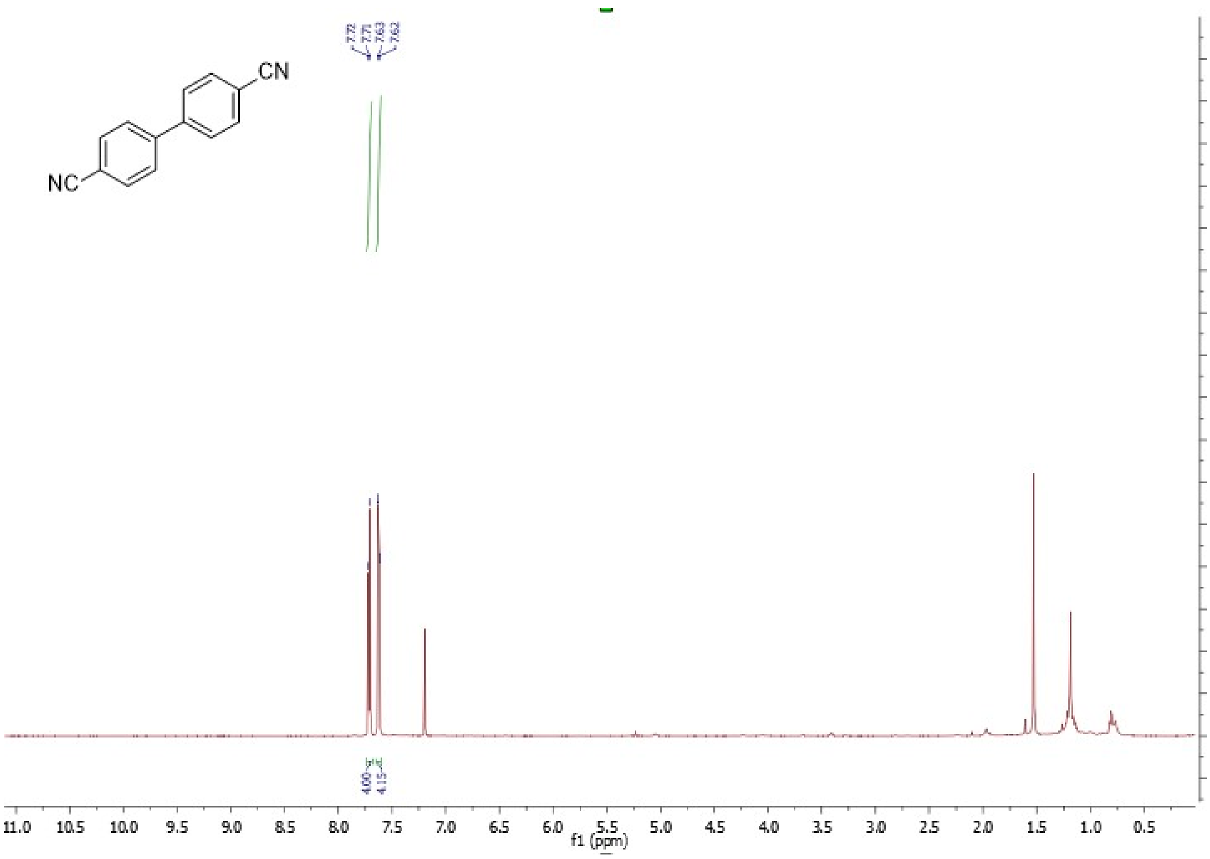


Fig.-S41. ^{1}H NMR spectra of 4, 4-dicyano-1, 1-biphenyl.

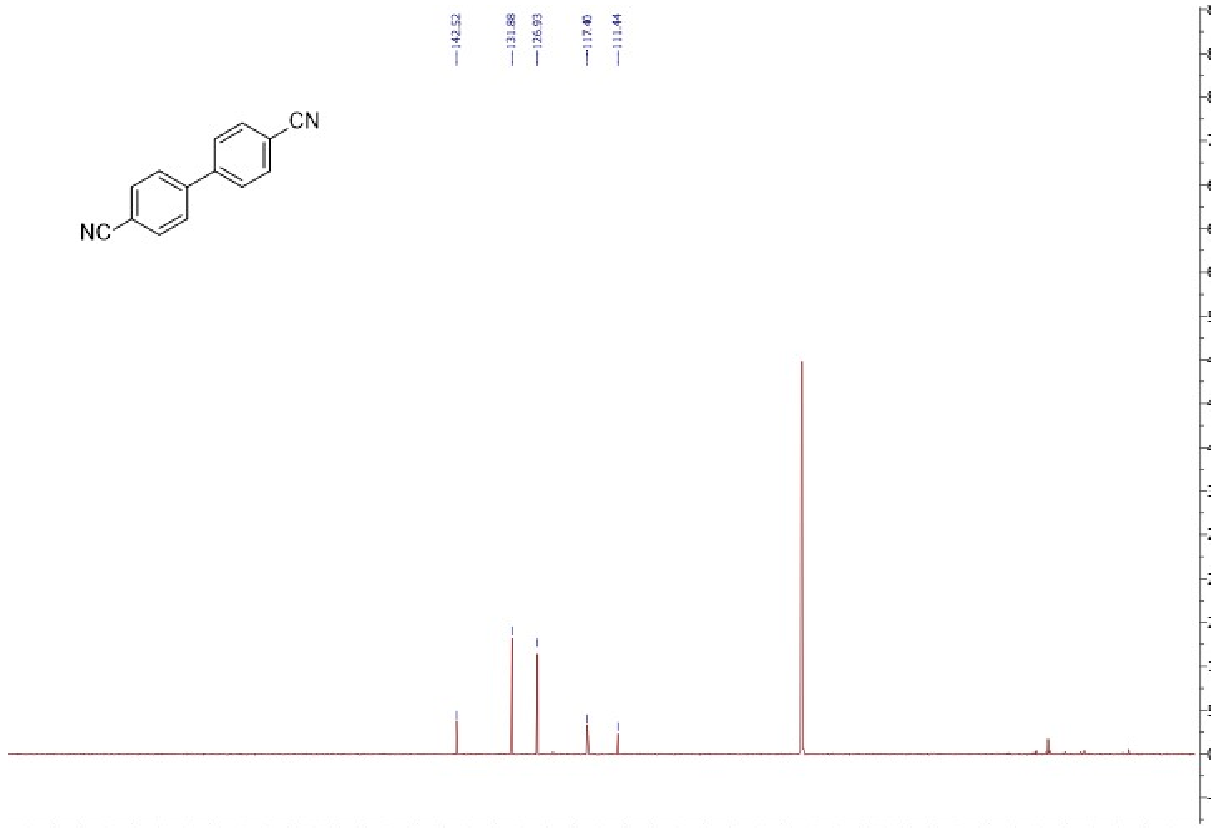


Fig. S42- ^{13}C NMR spectra of of 4, 4-dicyano-1, 1-biphenyl.

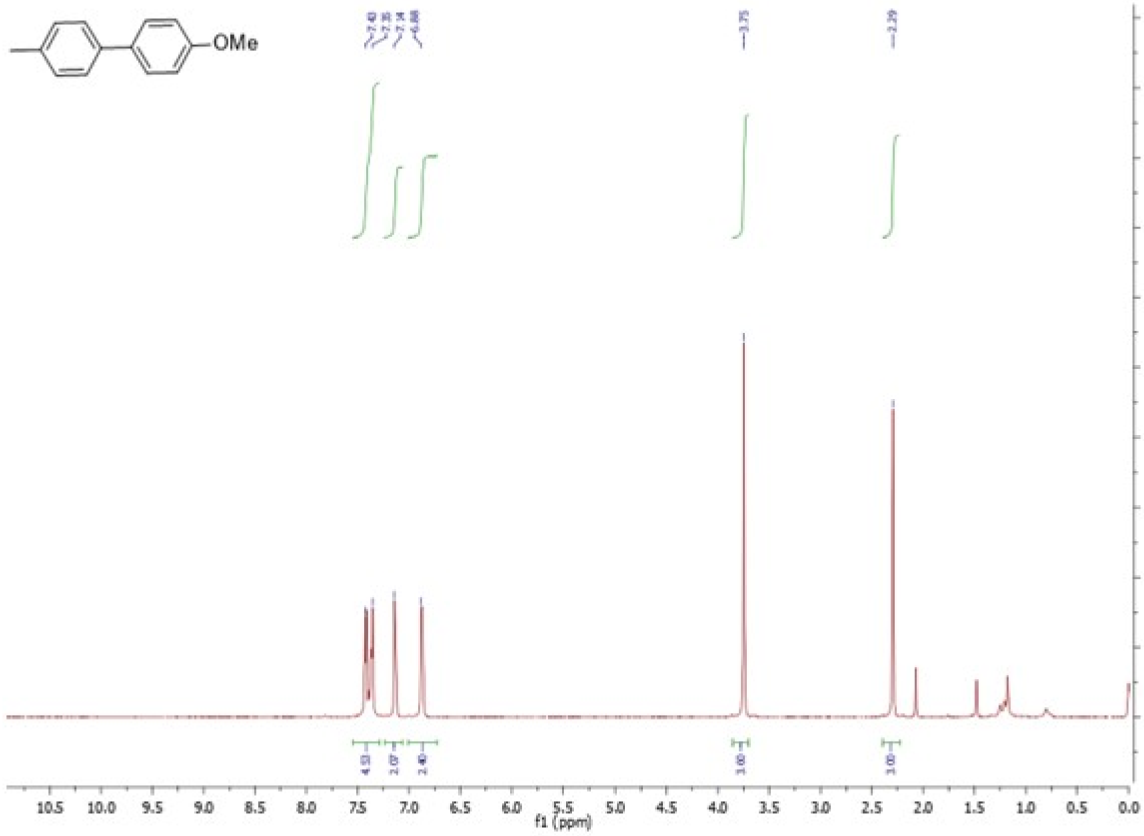


Fig. S43. ^{1}H NMR spectra of 4-methoxy, 4-methyl biphenyl.

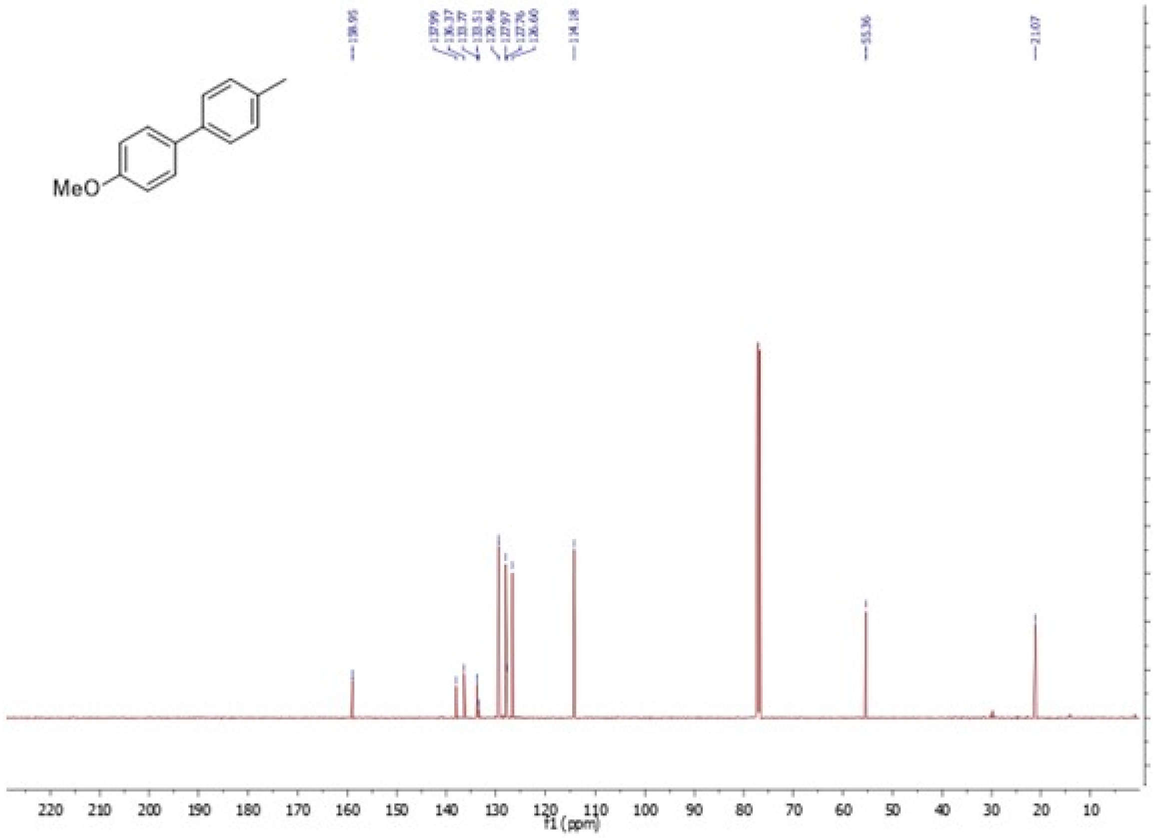


Fig. S44. ^{13}C NMR spectra of 4-methoxy, 4-methyl biphenyl.

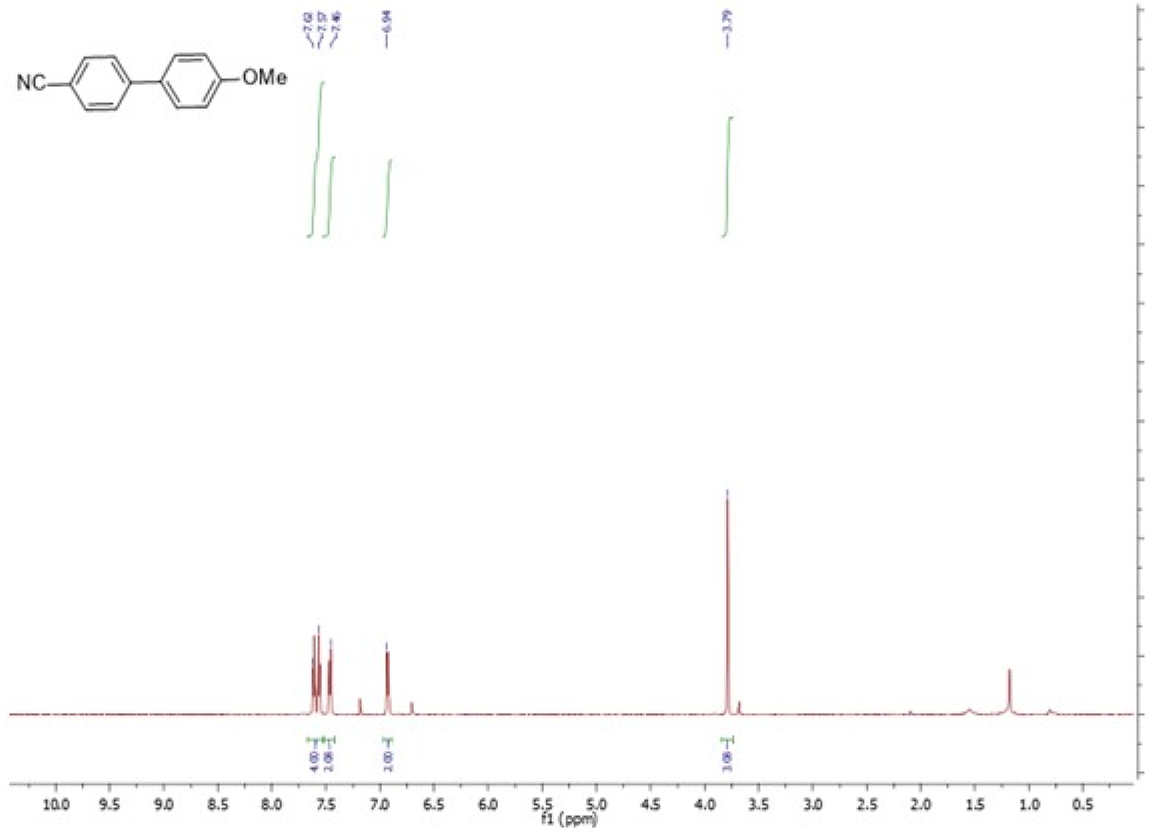


Fig. S45.^{1}H NMR spectra of 4-methoxy 4-cyano-1, 1-biphenyl.

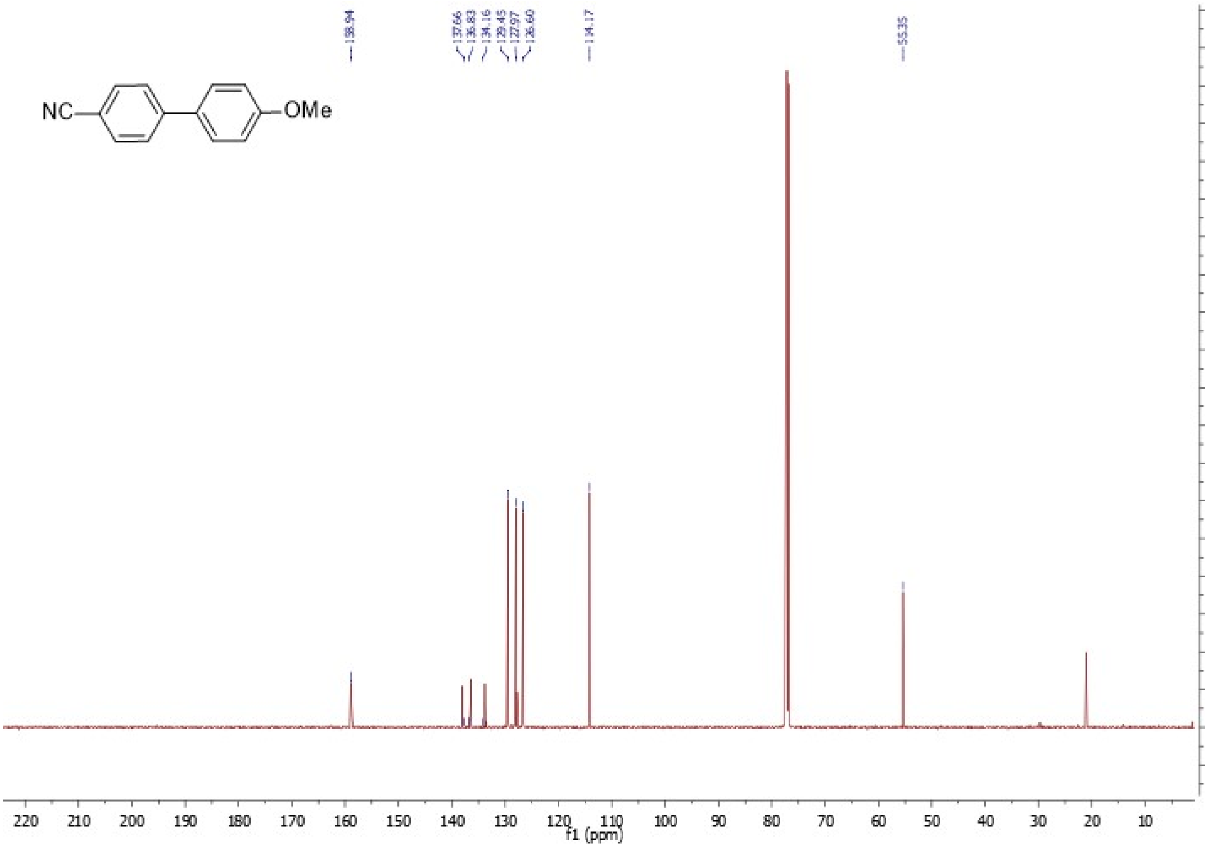


Fig. S46. ^{13}C NMR spectra of 4-methoxy 4-cyano-1, 1-biphenyl.

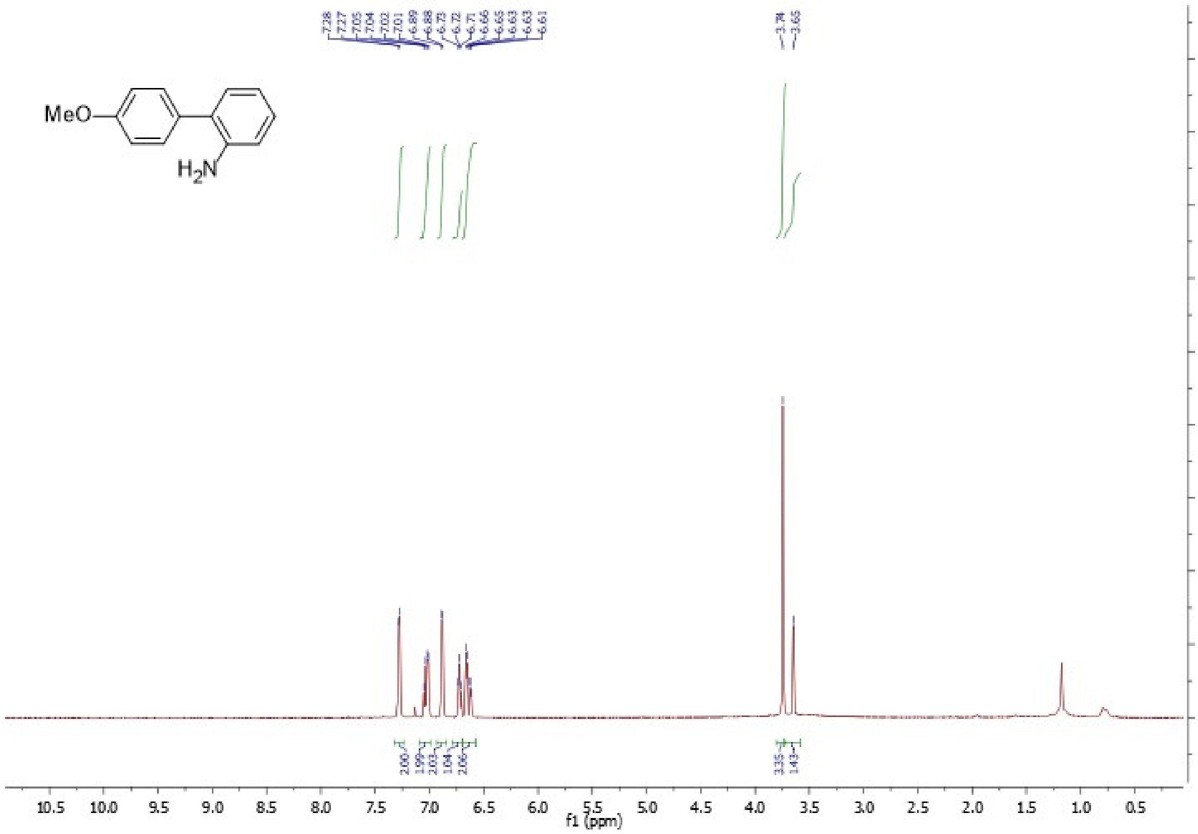


Fig. S47. ^{1}H NMR spectra of 4'-methoxy-[1,1'-biphenyl]-2-amine

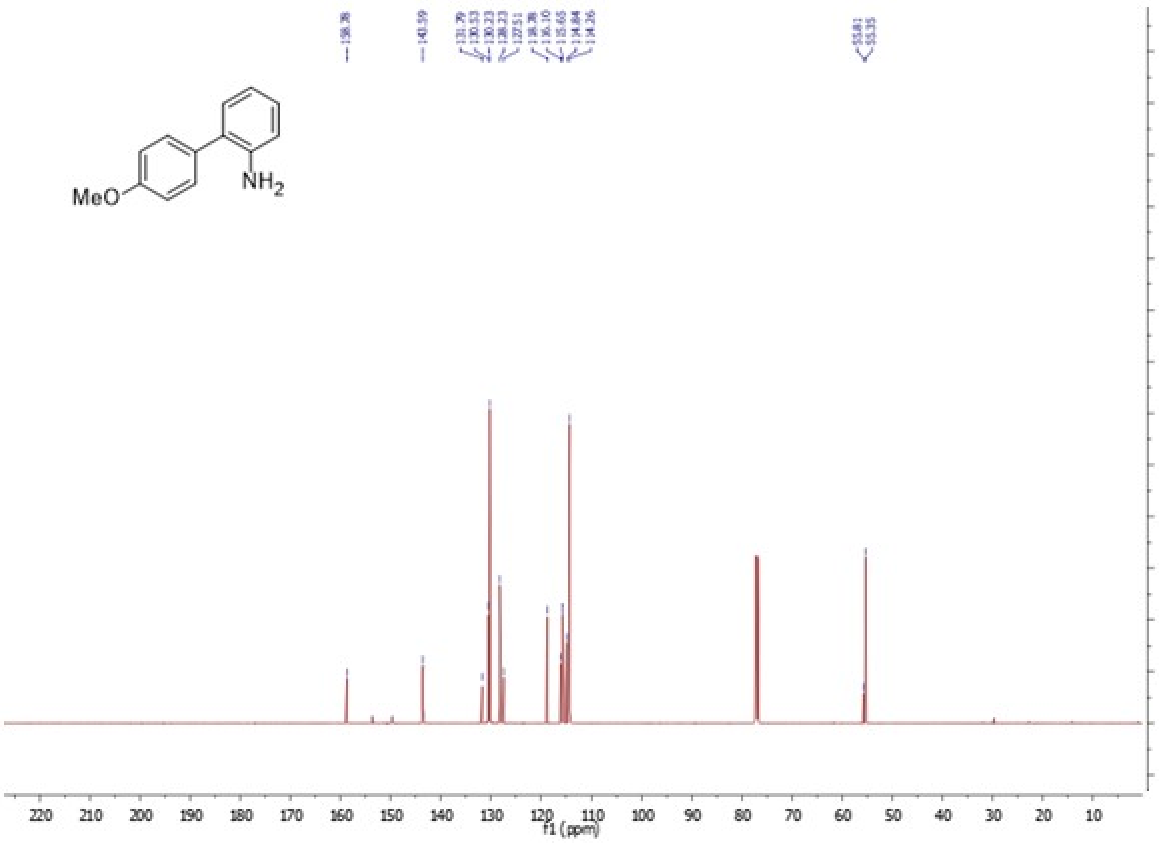


Fig. S48. ^{13}C NMR spectra of 4'-methoxy-[1, 1'-biphenyl]-2-amine

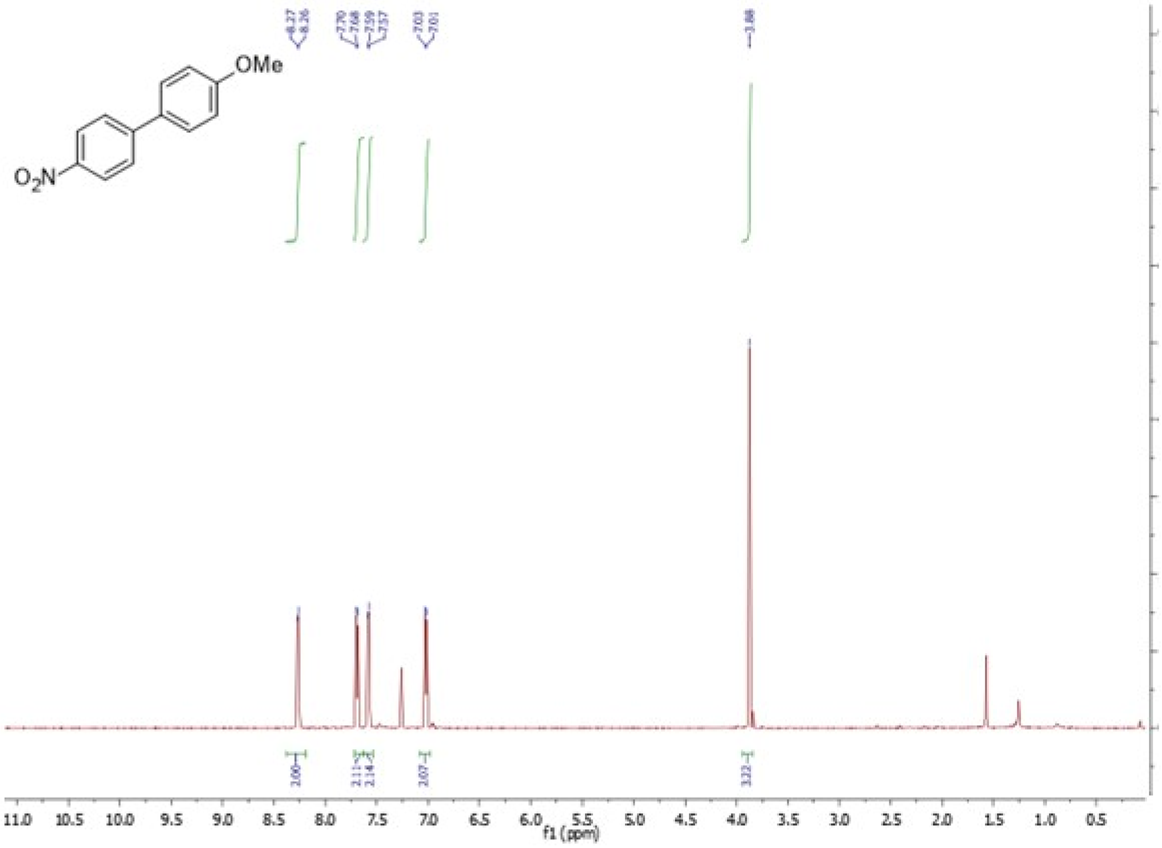


Fig. S49. ^{1}H NMR spectra of 4-methoxy-4'-nitro-1,1'-biphenyl

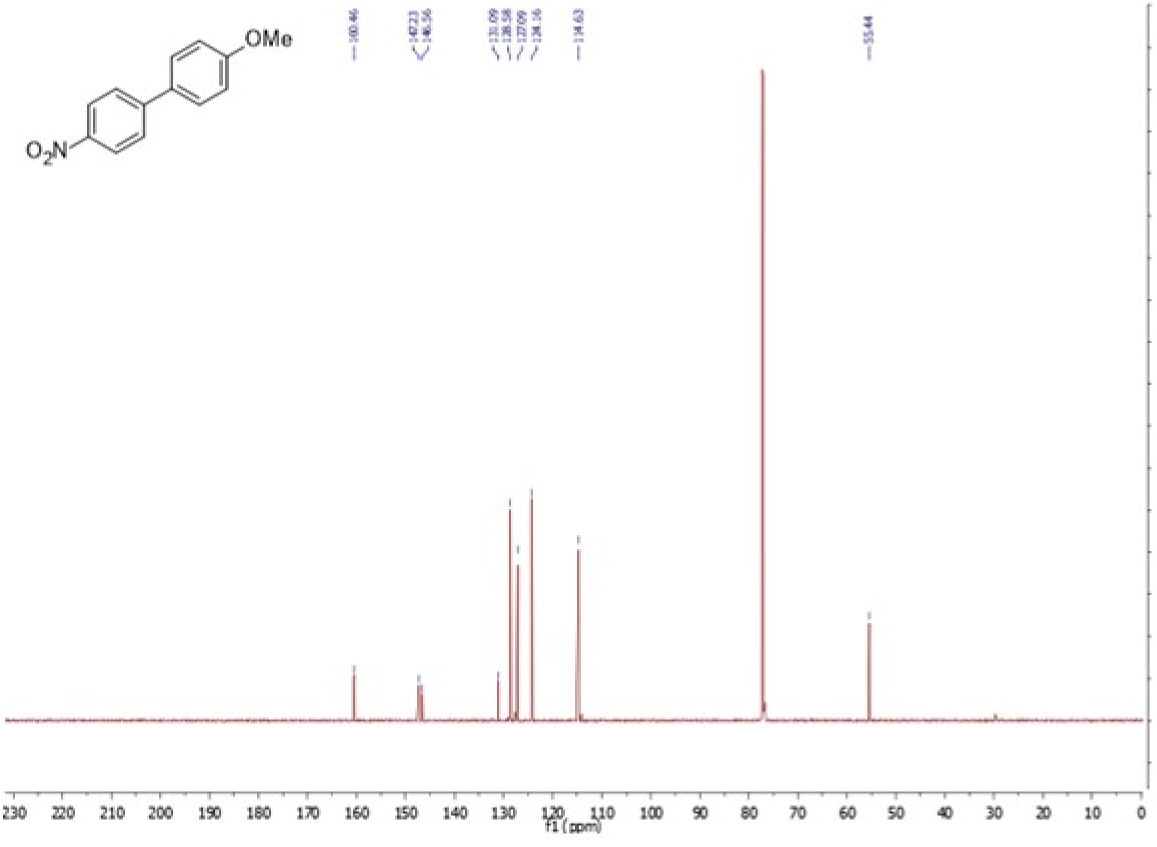


Fig. S50. ^{13}C NMR spectra of 4-methoxy-4'-nitro-1,1-biphenyl

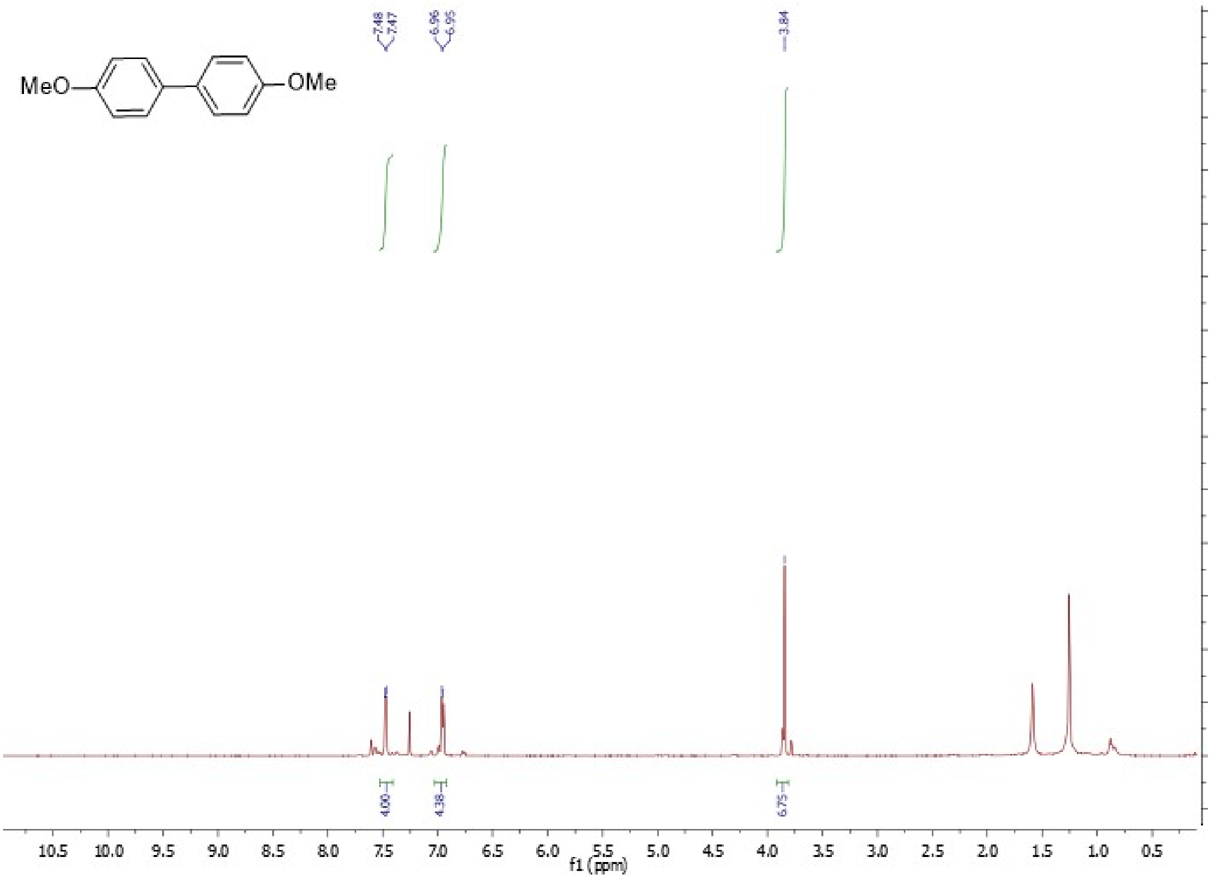


Fig. S51. ^{1}H NMR spectra of 4, 4'-dimethoxy-1, 1'-biphenyl

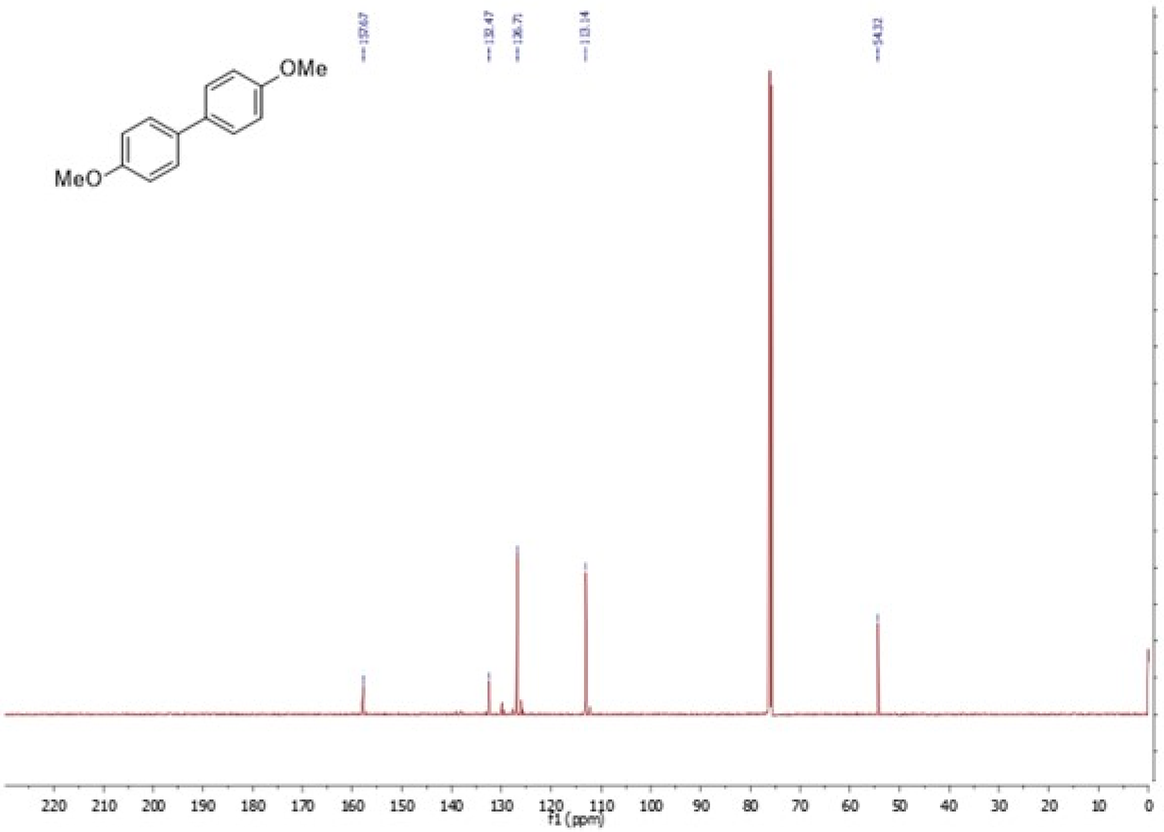


Fig. S52. ^{13}C NMR spectra of 4, 4'-dimethoxy-1, 1'-biphenyl

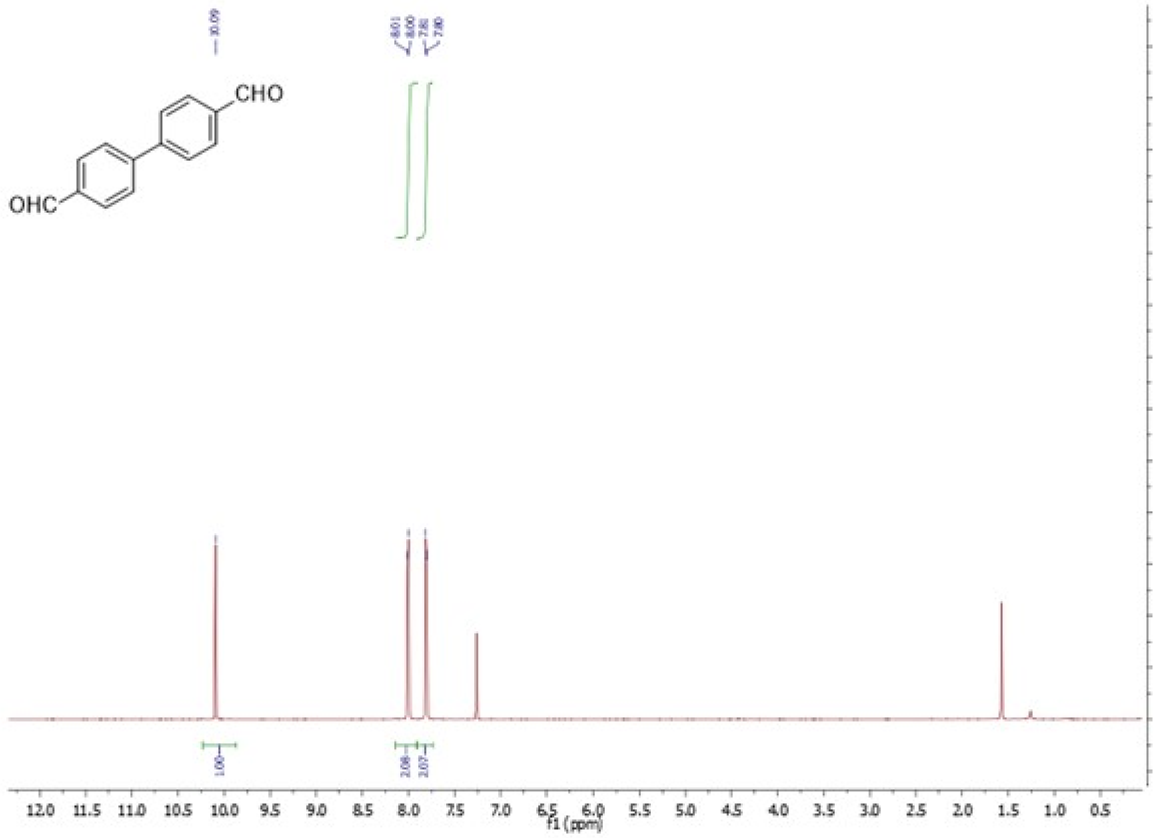


Fig. S53. ^{1}H NMR spectra of [1, 1'-biphenyl]-4, 4'-dicarbaldehyde

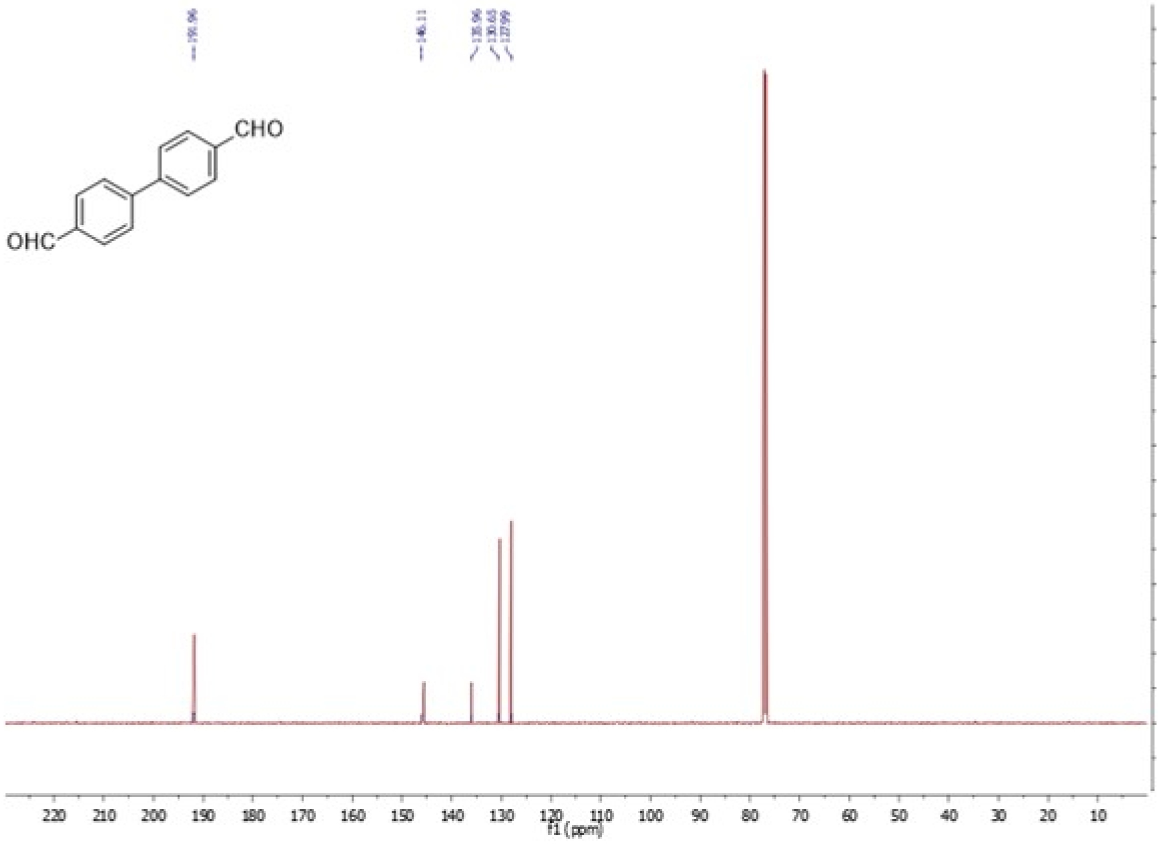


Fig. S54. ^{13}C NMR spectra of [1, 1'-biphenyl]-4, 4'-dicarbaldehyde

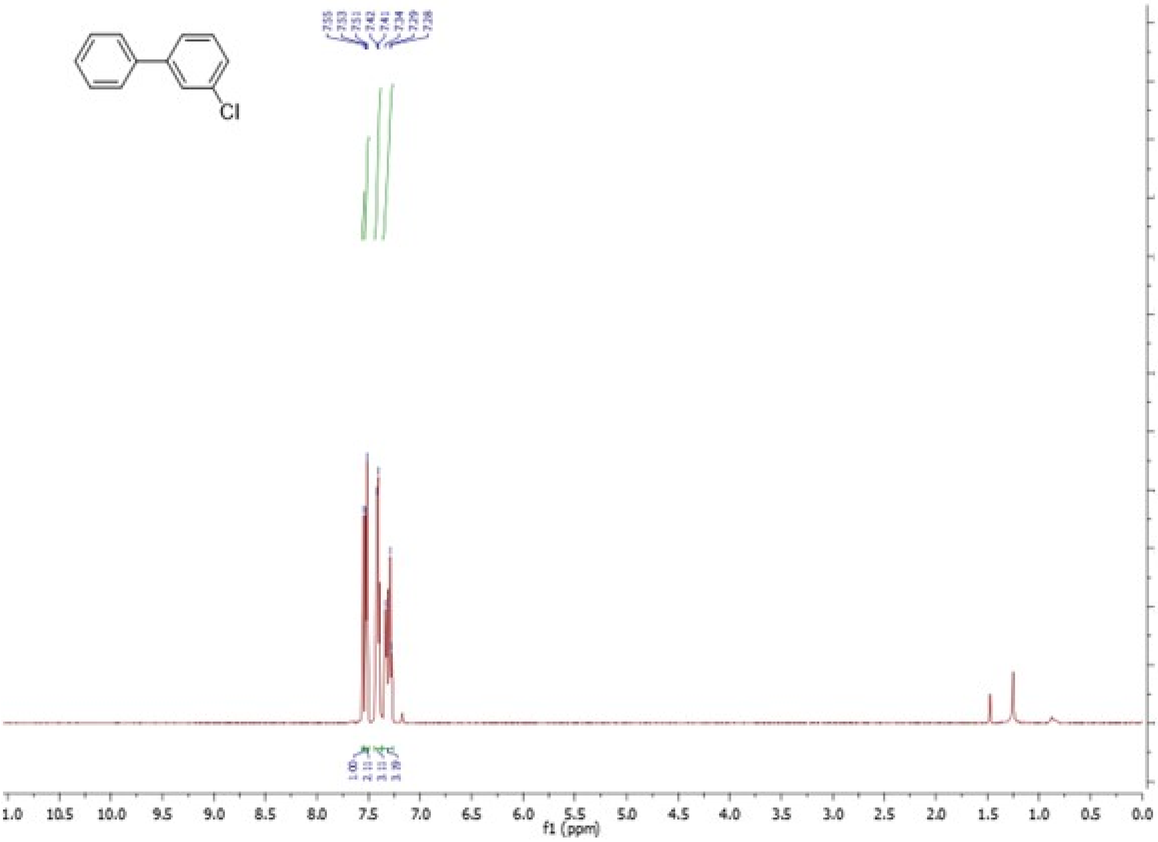


Fig. S55. ^{1}H NMR spectra of 3-chloro-1, 1'-biphenyl

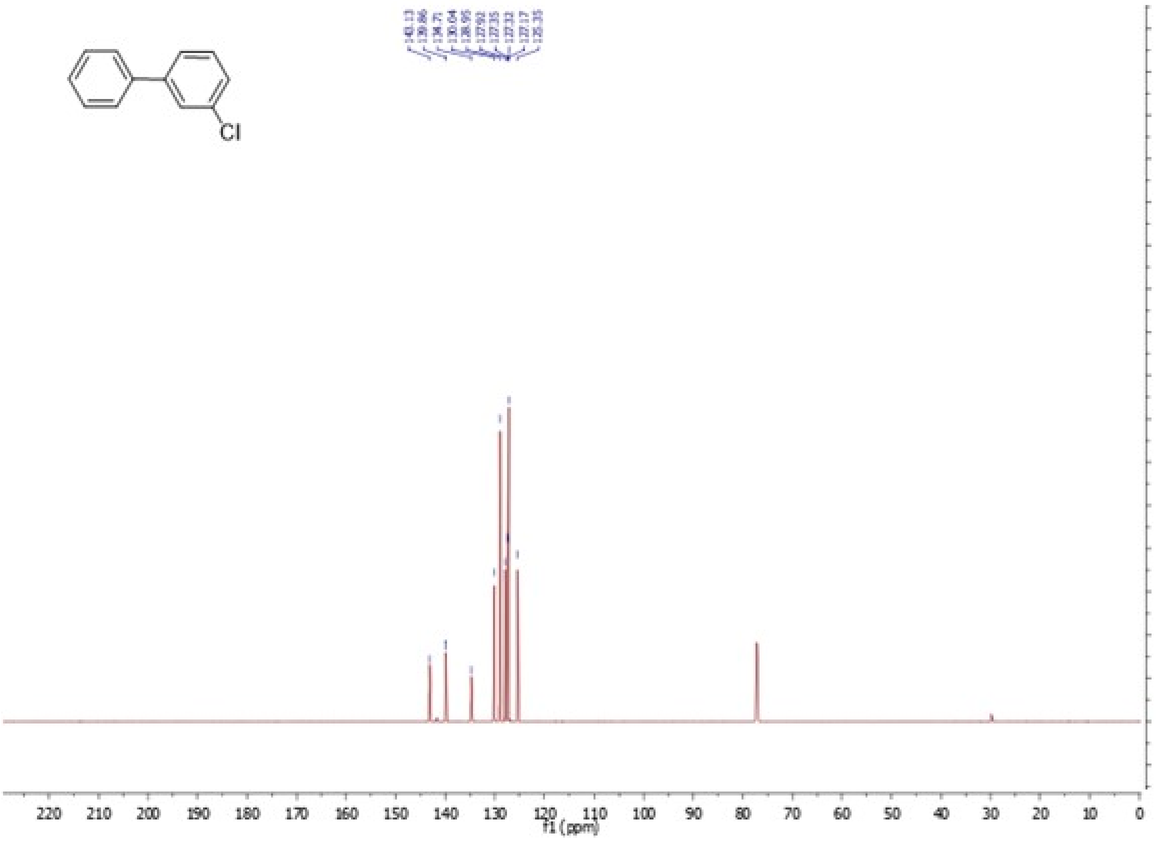


Fig. S56. ^{13}C NMR spectra of 3-chloro-1, 1'-biphenyl

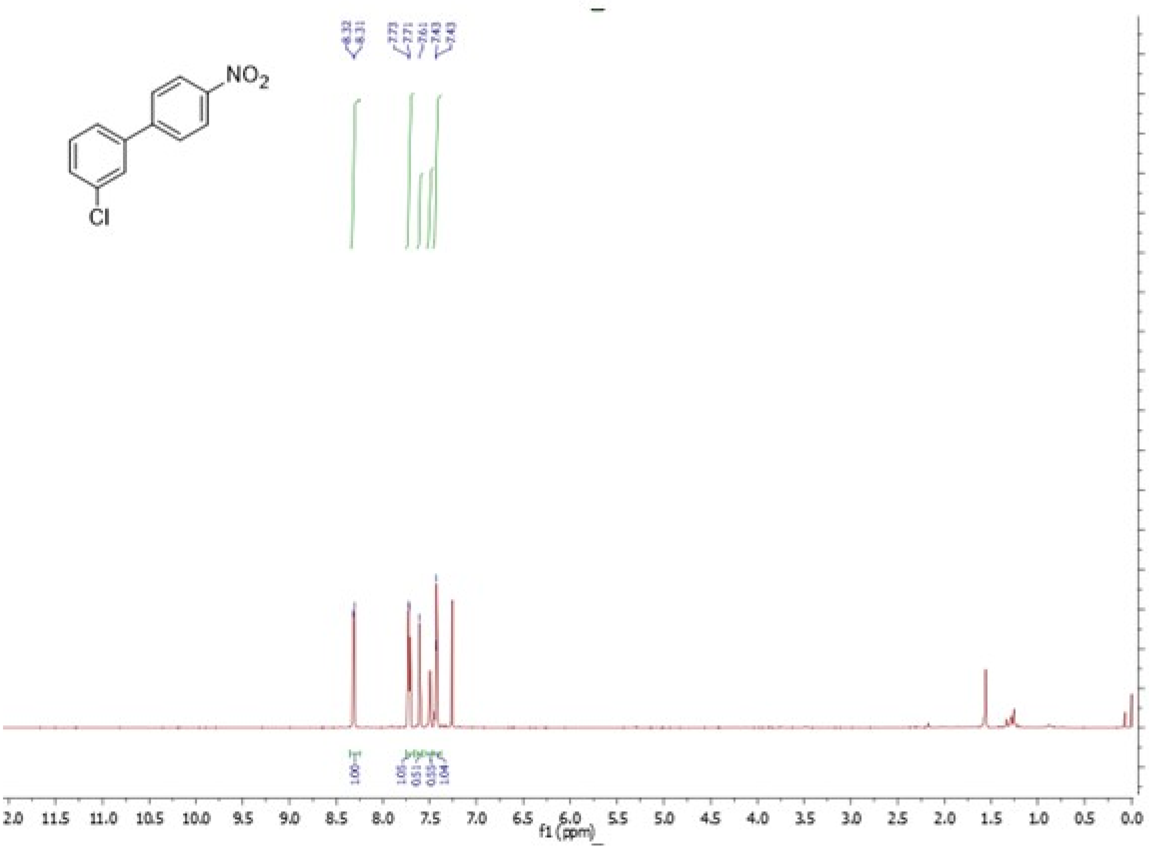


Fig. S57. ^{1}H NMR spectra of 3-chloro-4'-nitro-1, 1'-biphenyl

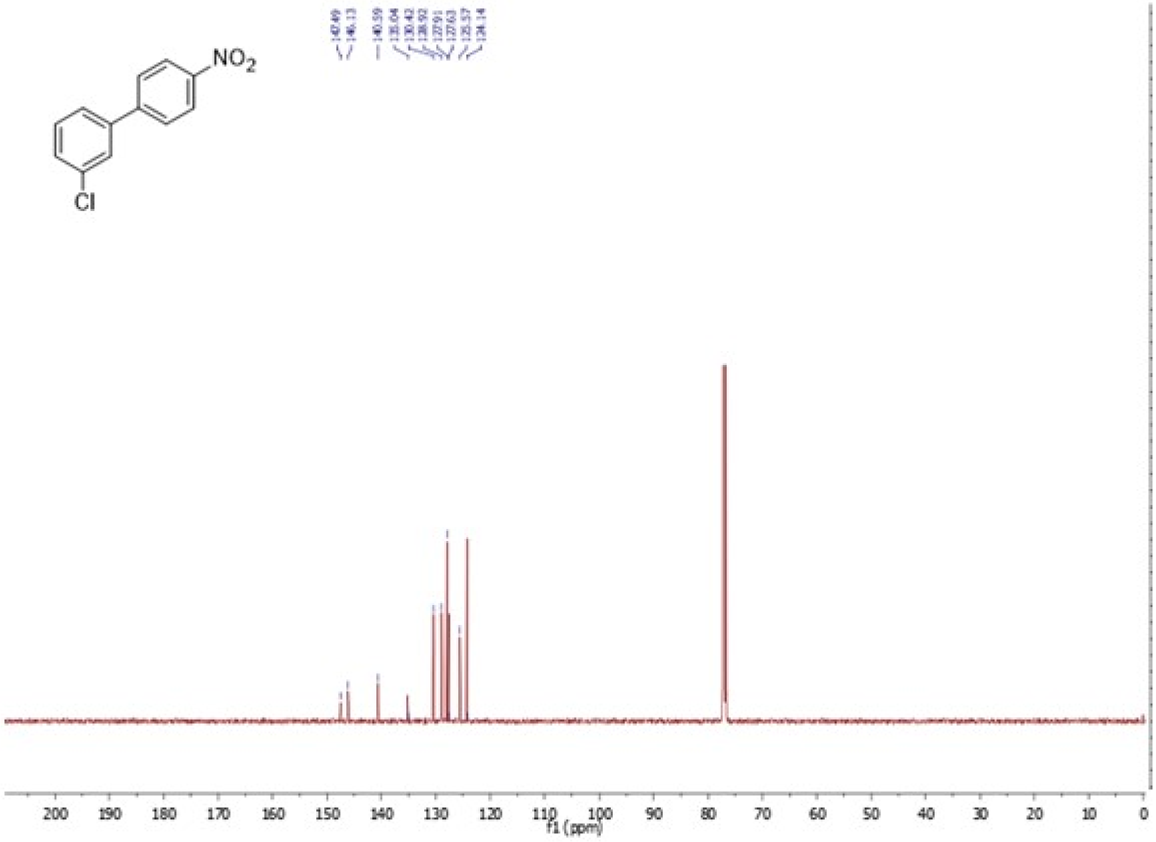


Fig. S58. ^{13}C NMR spectra of 3-chloro-4'-nitro-1, 1'-biphenyl

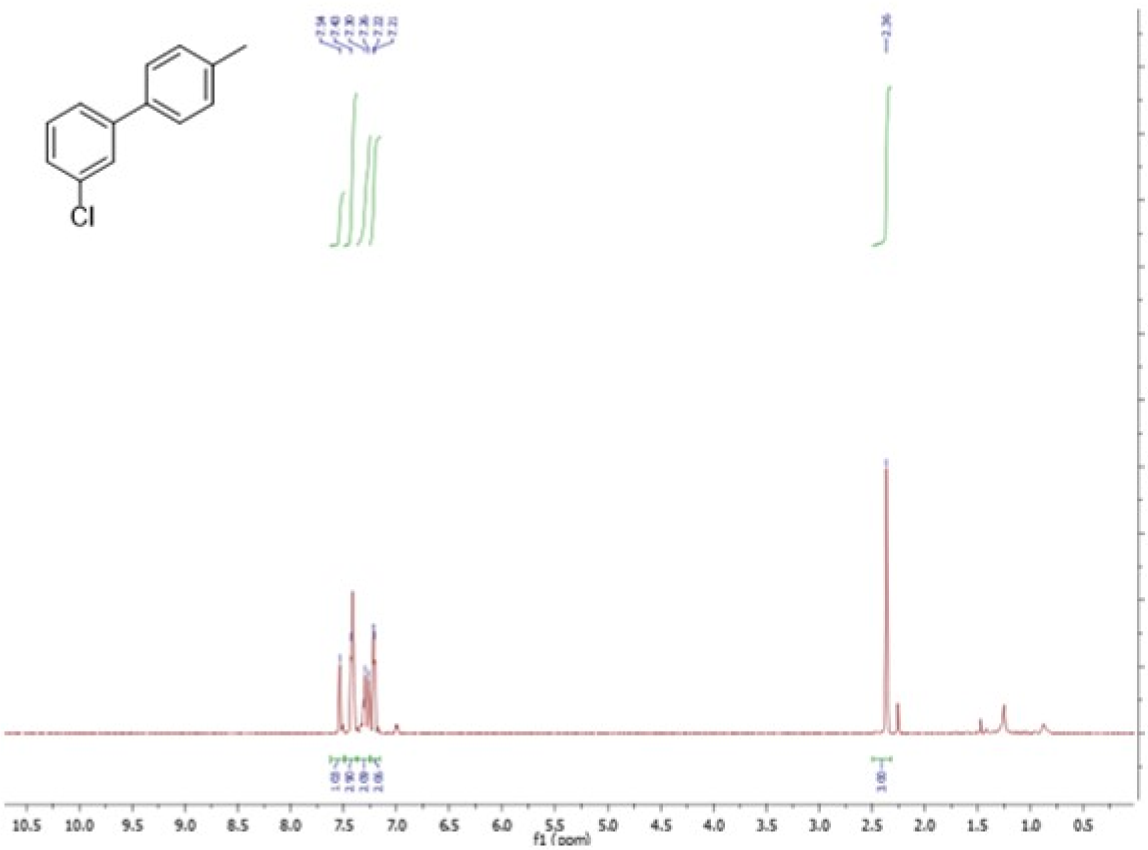


Fig.

Fig.S59. ^{1}H NMR spectra of 3-chloro-4'-methyl-1, 1'-biphenyl

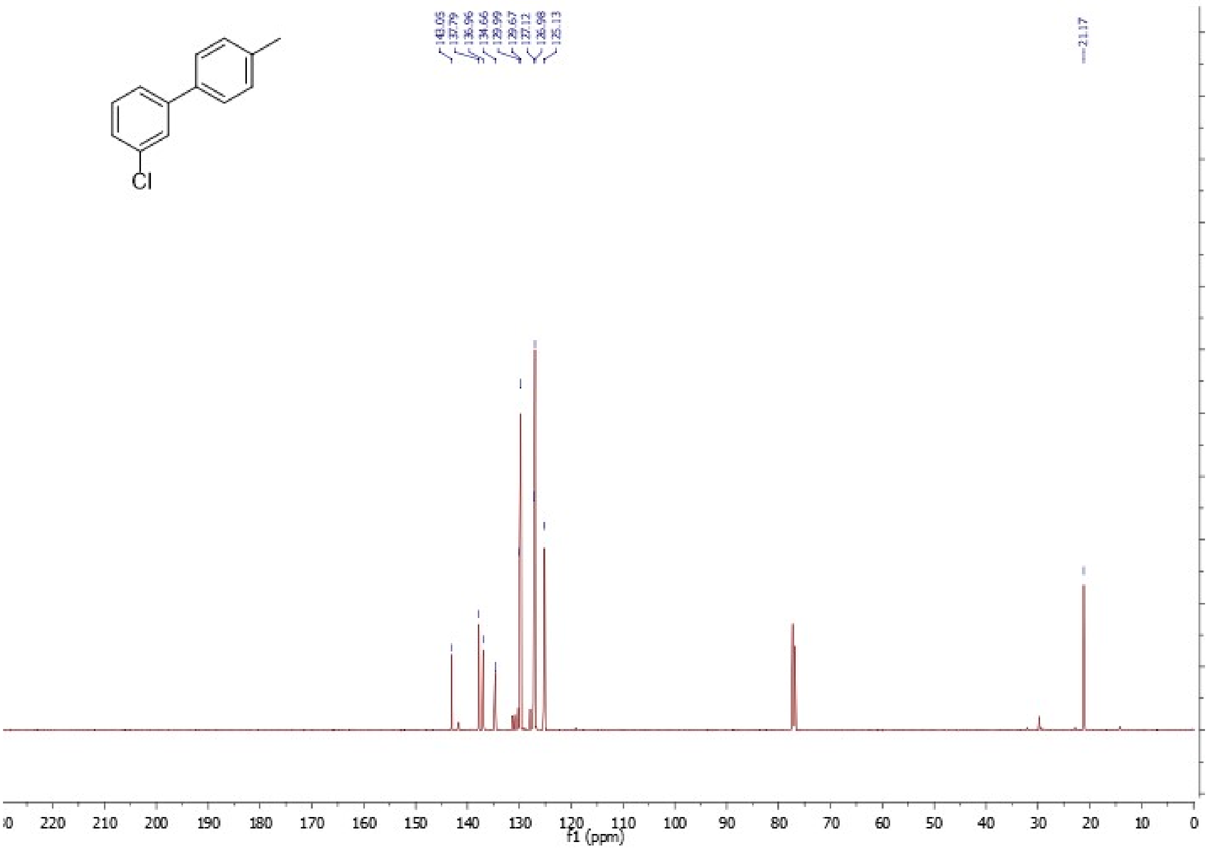


Fig. S60. ^{13}C NMR spectra of 3-chloro-4'-methyl-1, 1'-biphenyl

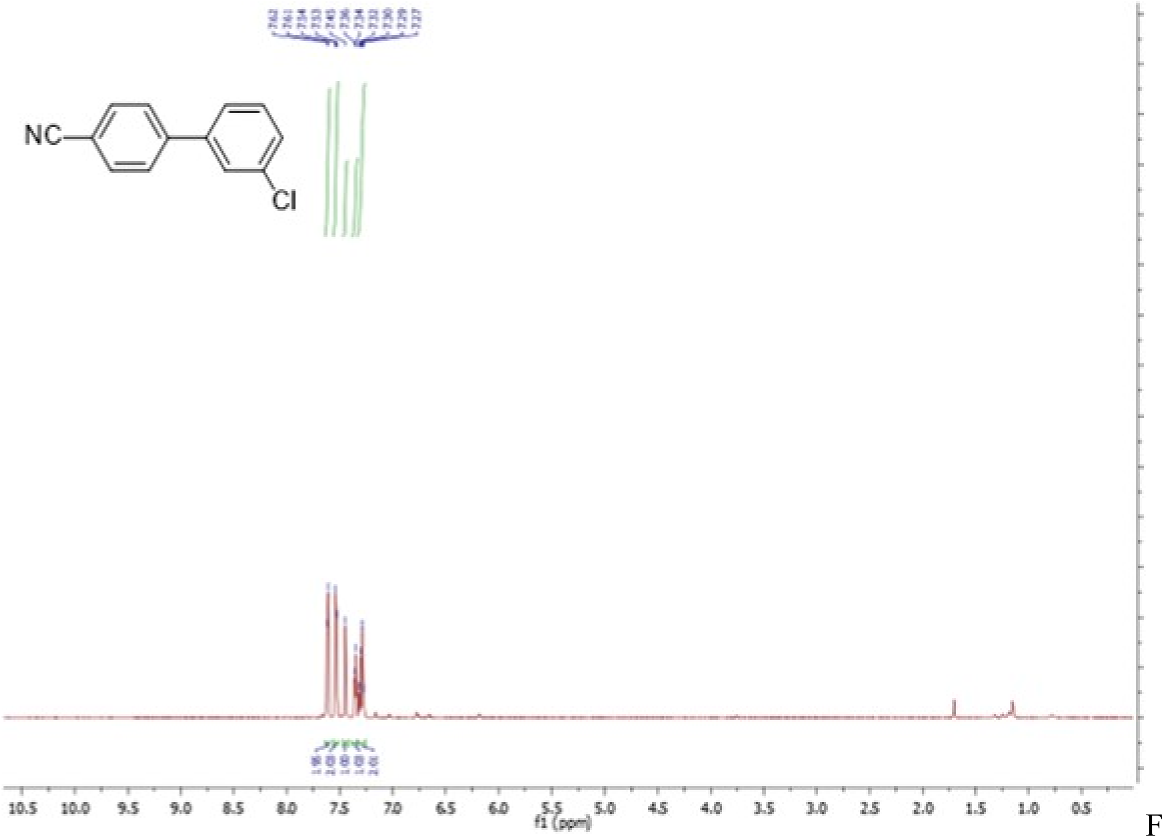


Fig. S61. ^{1}H NMR spectra of **3'-chloro-[1,1'-biphenyl]-4-carbonitrile**

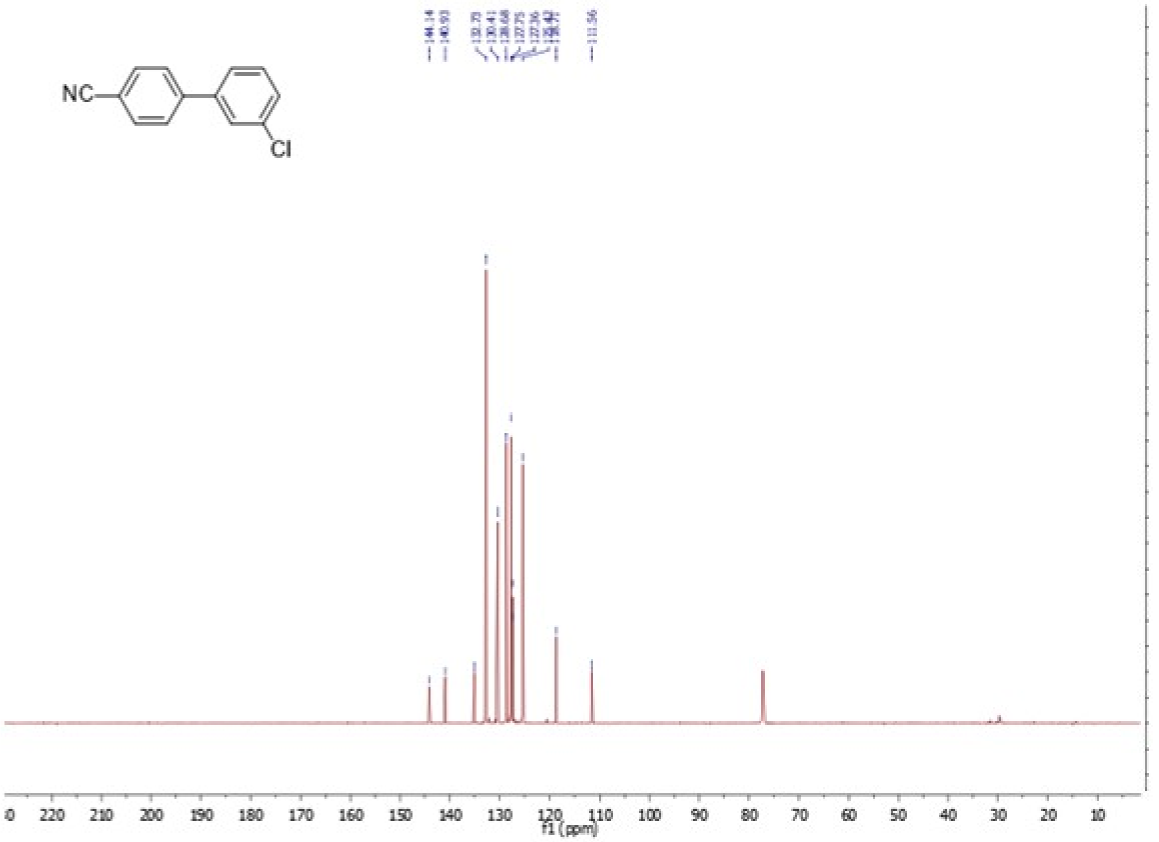


Fig. S62. ^{13}C NMR spectra of 3'-chloro-[1, 1'-biphenyl]-4-carbonitrile

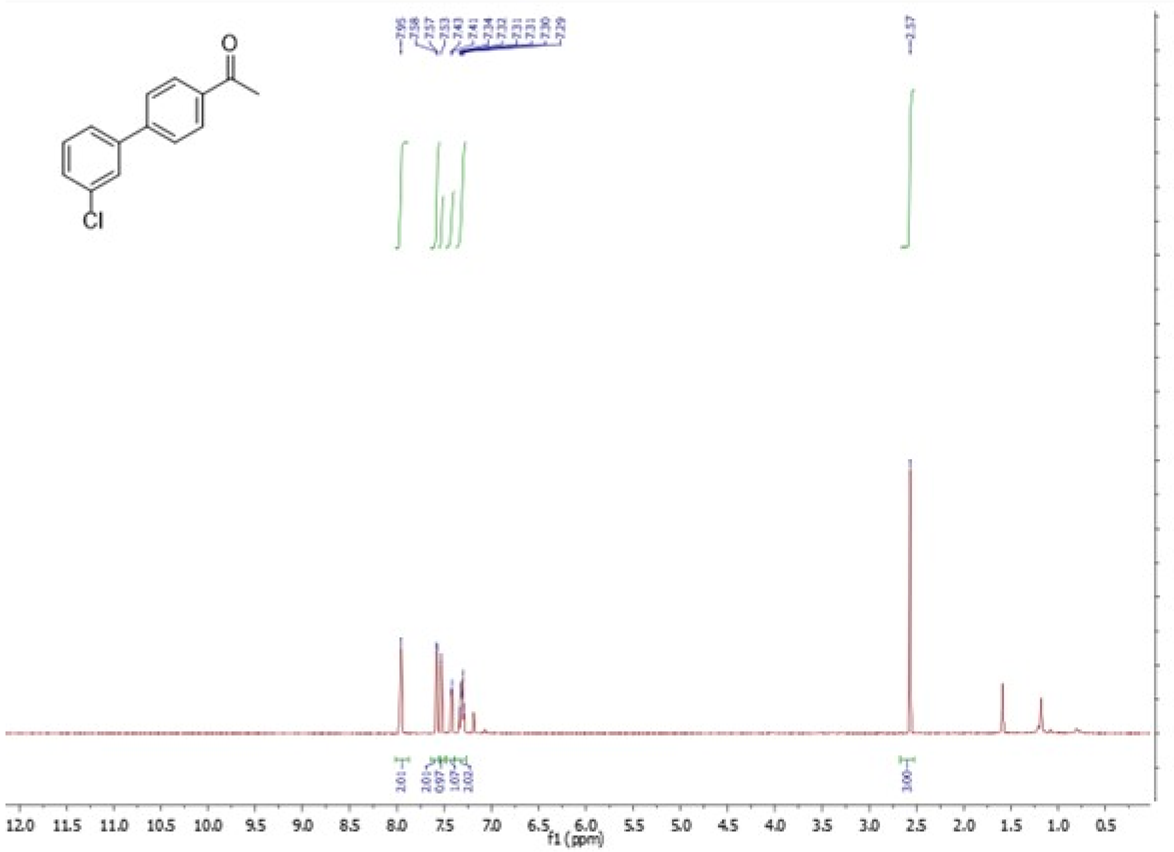


Fig. S63. ^1H NMR spectra of 1-(3'-chloro-[1, 1'-biphenyl]-4-yl) ethanone.

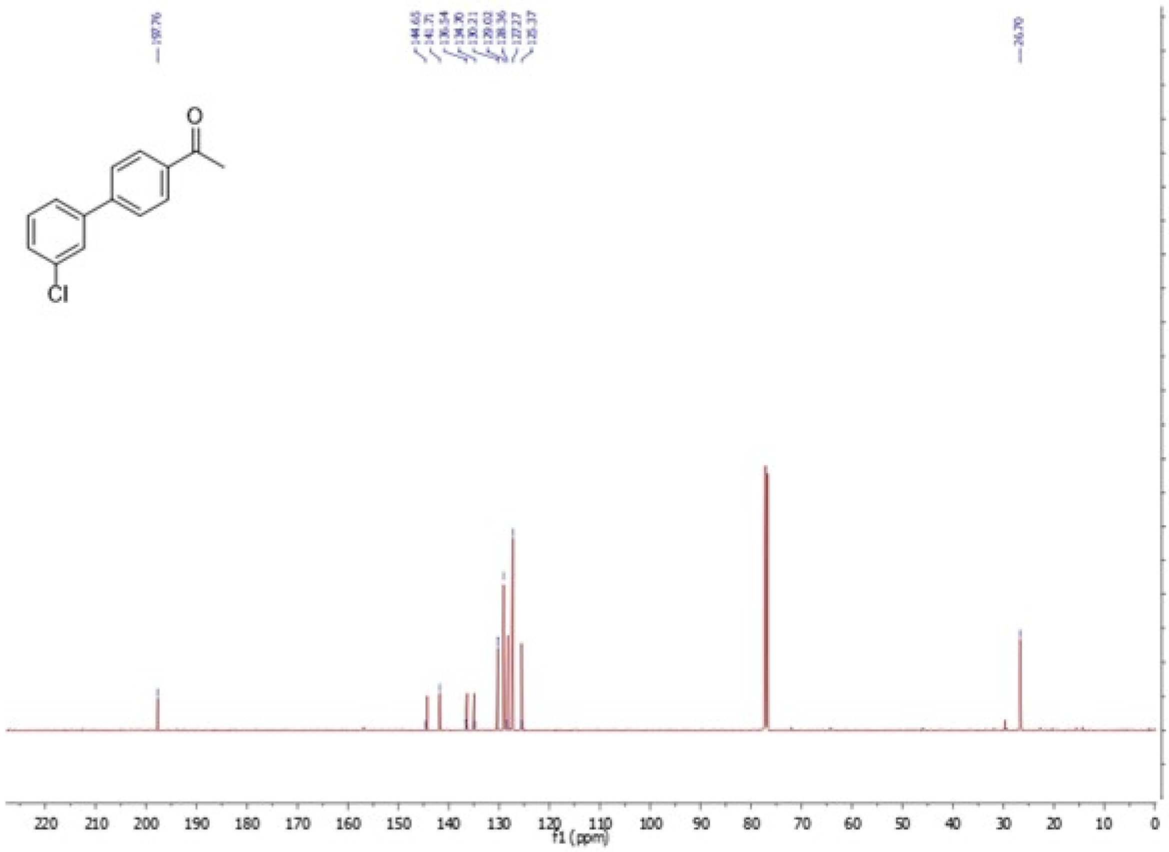


Fig. S64. ^{13}C NMR spectra of 1-(3'-chloro-[1, 1'-biphenyl]-4-yl) ethanone.

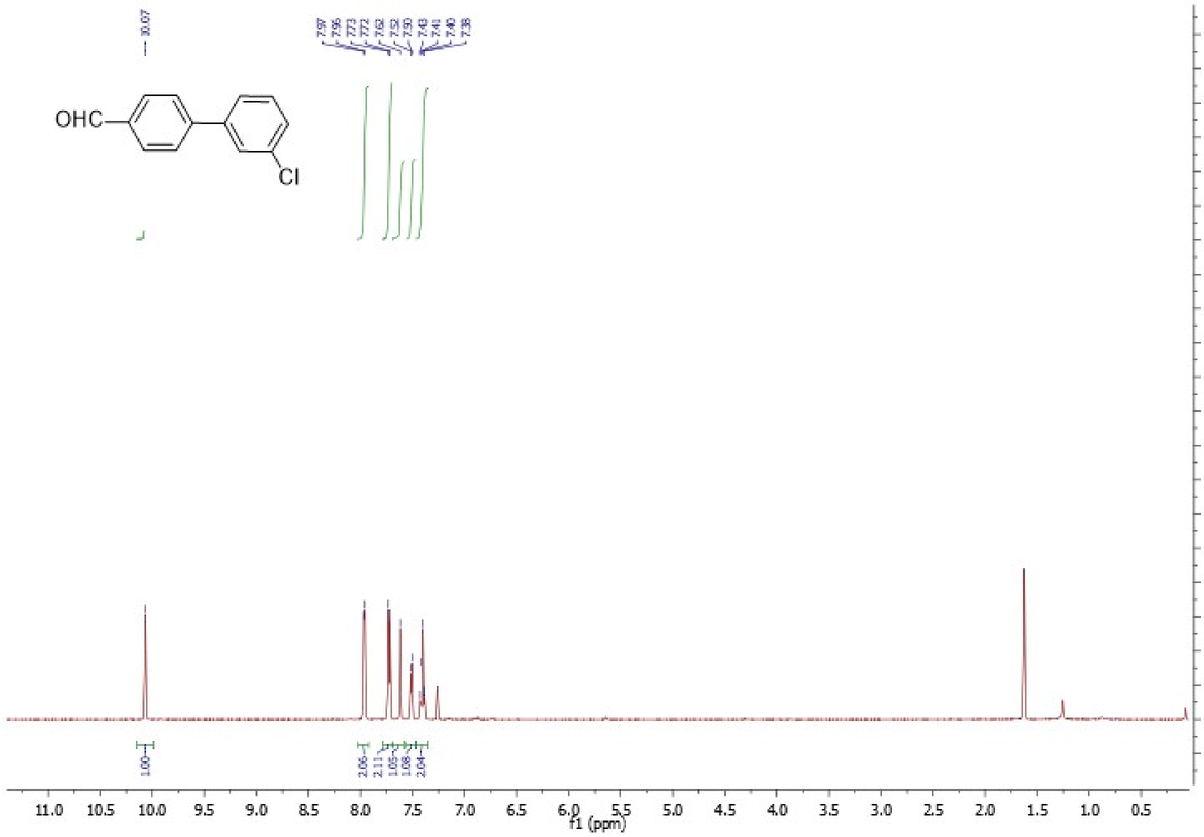


Fig. S65. ^{1}H NMR spectra of 3'-chloro-[1, 1'-biphenyl]-4-carbaldehyde.

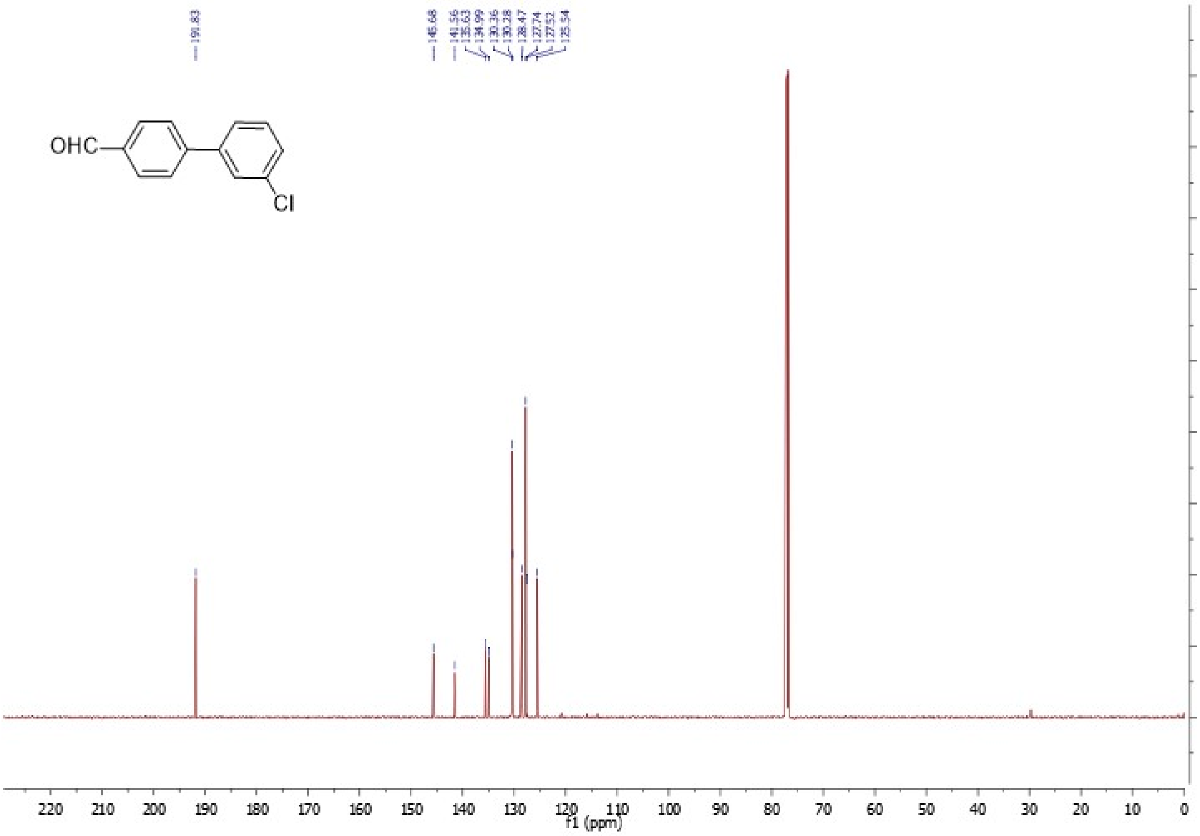


Fig. S66. ^{13}C NMR spectra of 3'-chloro-[1, 1'-biphenyl]-4-carbaldehyde

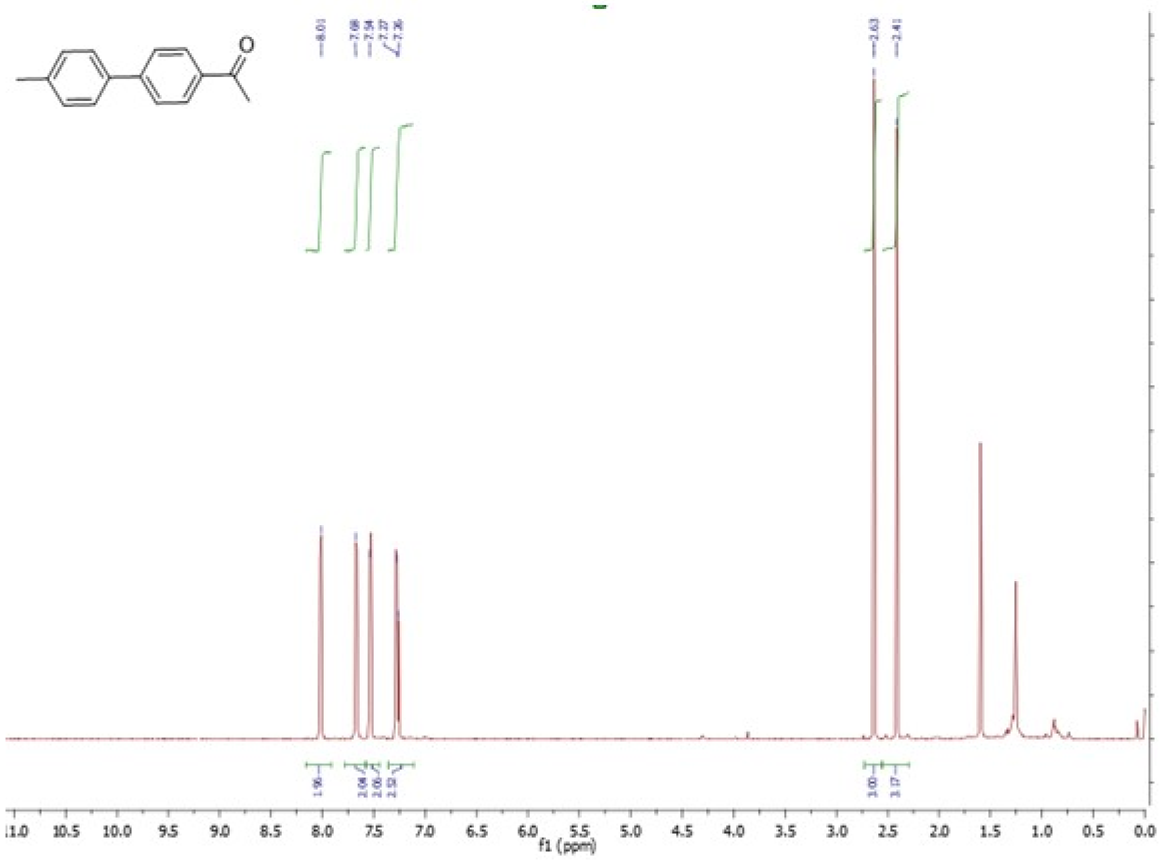


Fig. S67. ^{1}H NMR spectra of 1-(4'-methyl-[1, 1'-biphenyl]-4-yl)ethanone

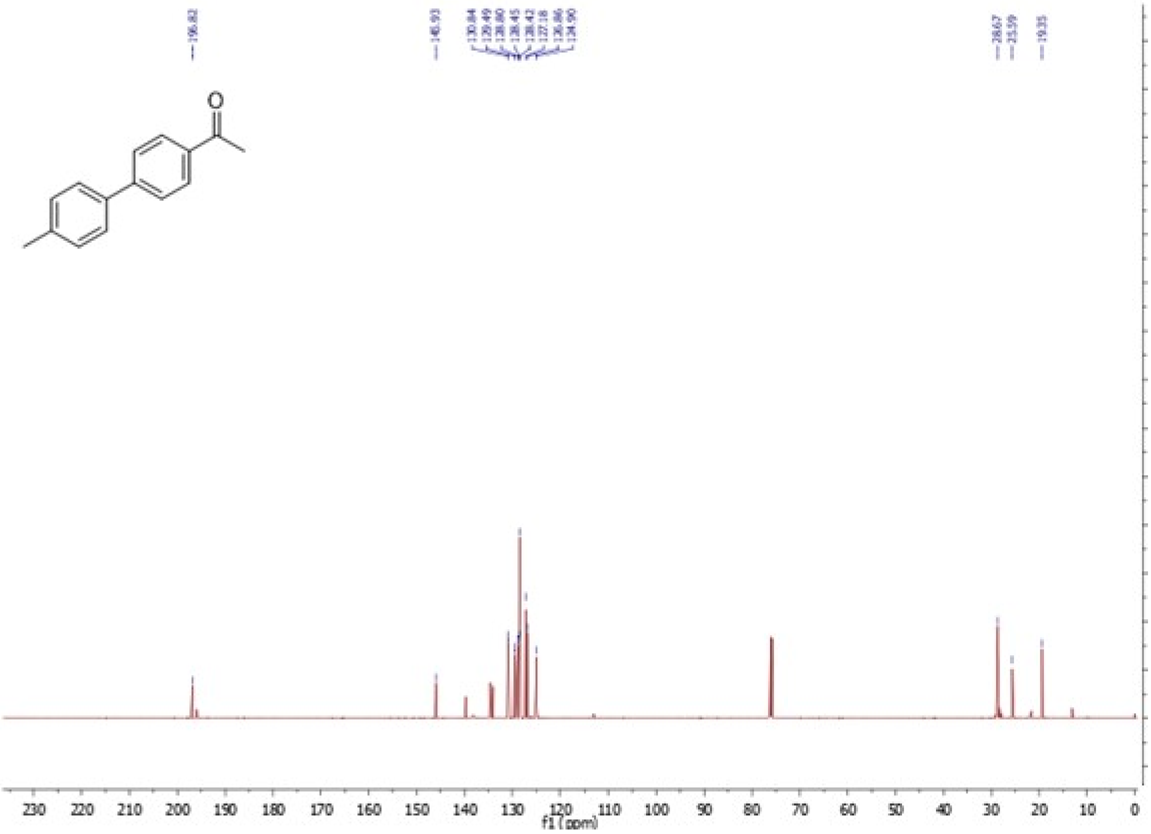


Fig. S68. ^{13}C NMR spectra of 1-(4'-methyl-[1, 1'-biphenyl]-4-yl)ethanone

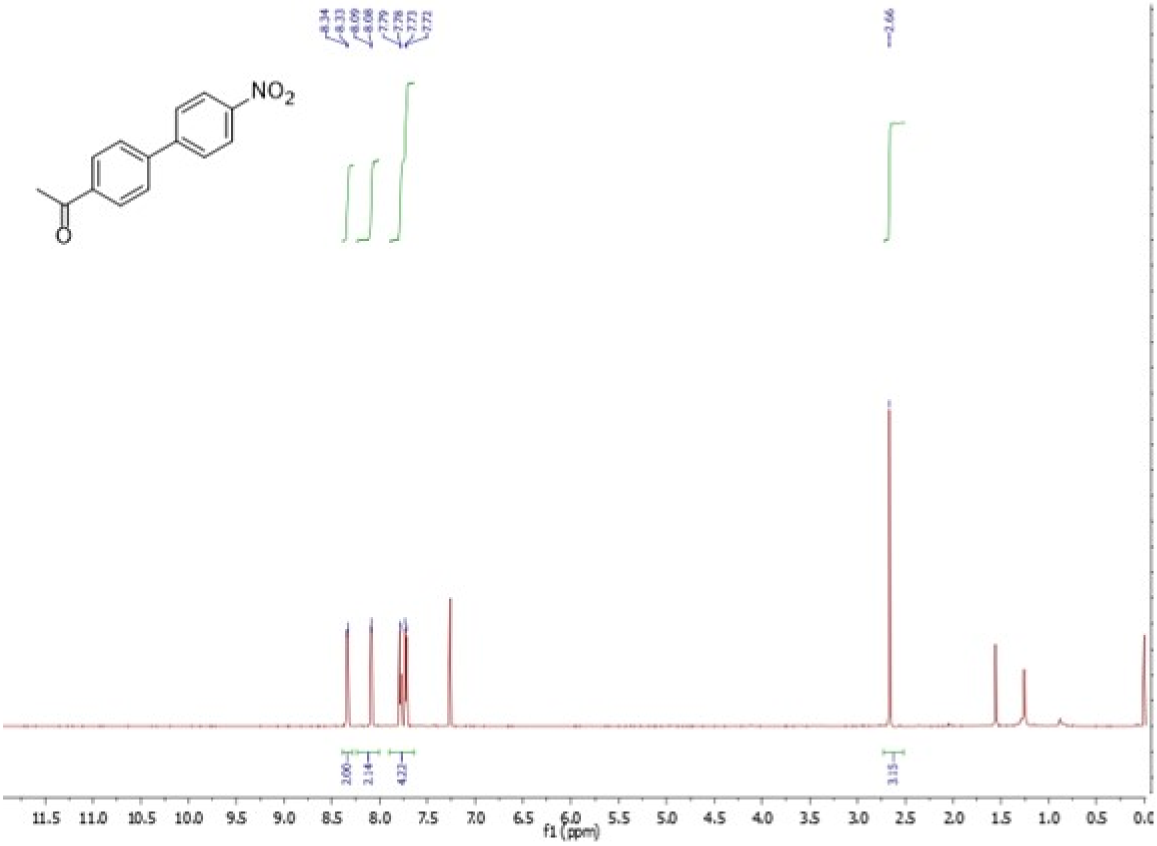


Fig. S69. ^{1}H NMR spectra of 1-(4'-nitro-[1, 1'-biphenyl]-4-yl)ethanone

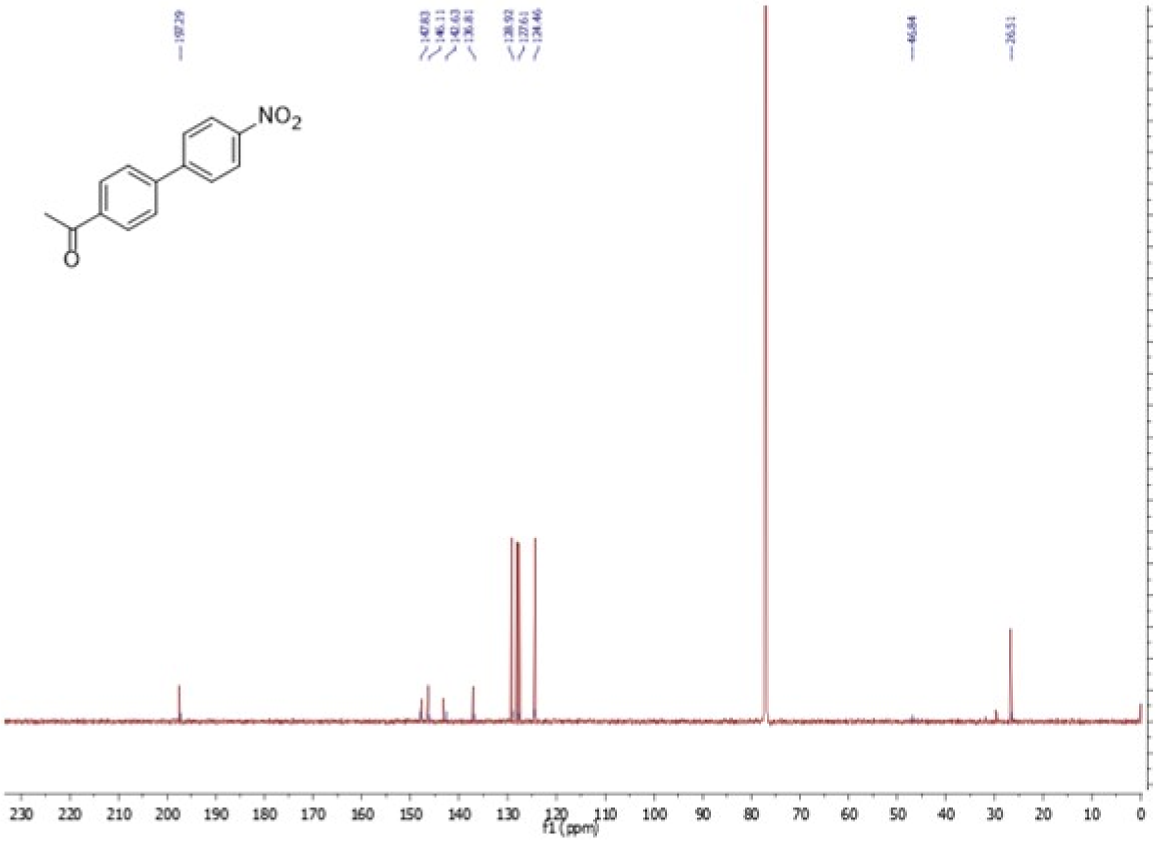


Fig. S70. ^{13}C NMR spectra of 1-(4'-nitro-[1, 1'-biphenyl]-4-yl)ethanone

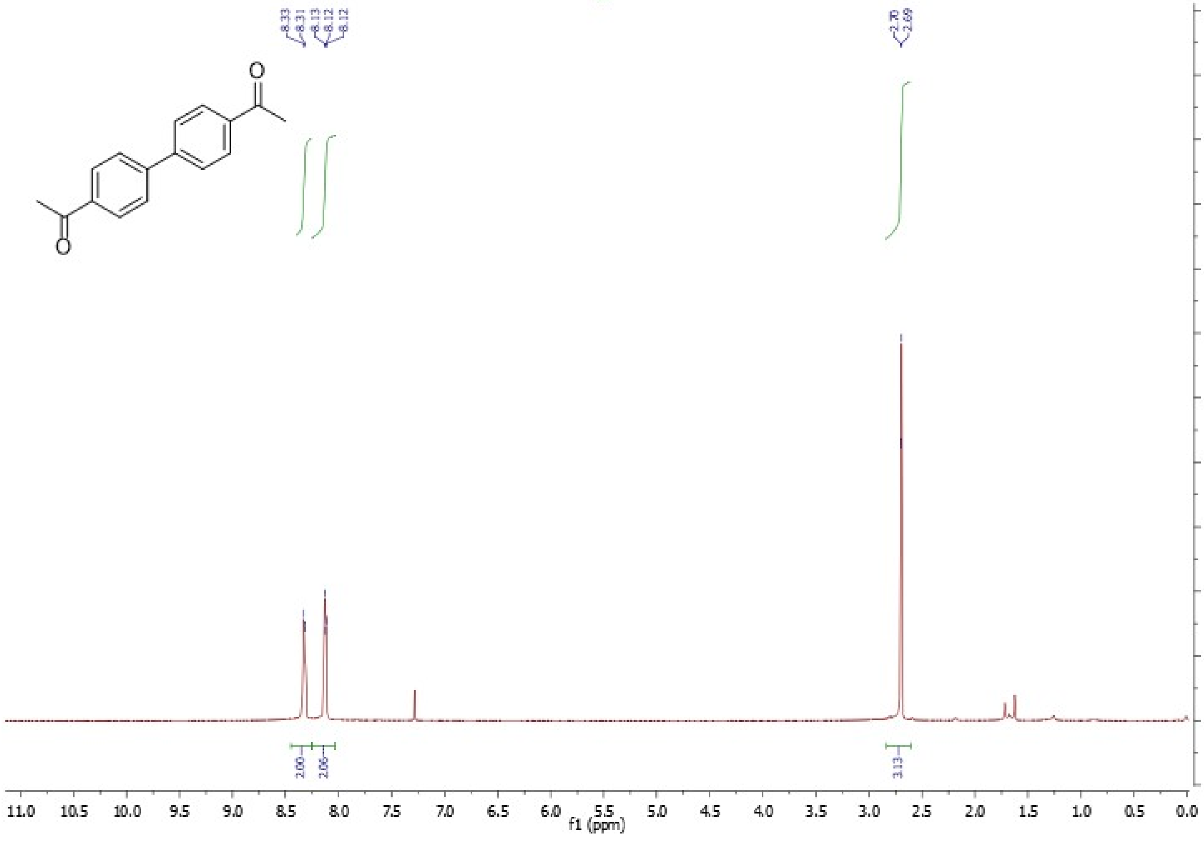


Fig.-S71. ^{1}H NMR spectra of 1, 1'-([1,1'-biphenyl]-4,4'-diyl)diethanone

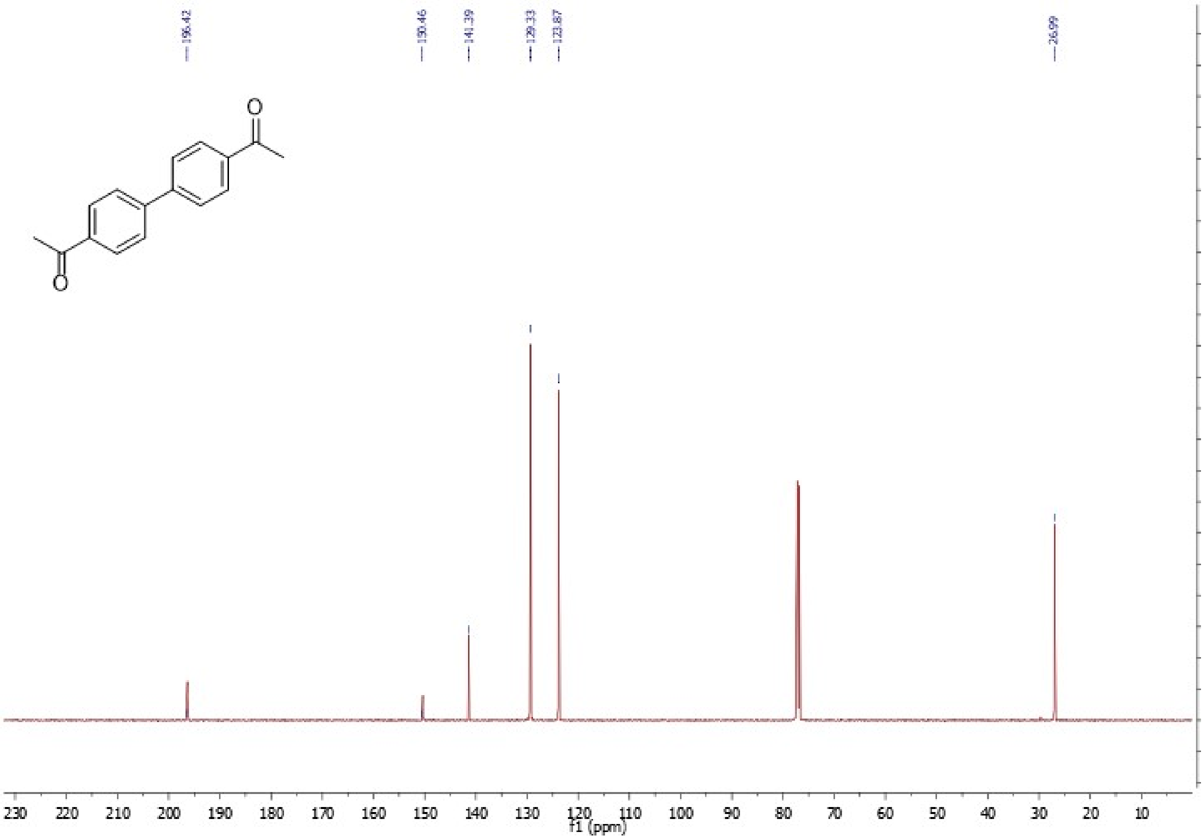


Fig.-S72. ^{13}C NMR spectra of 1, 1'-([1,1'-biphenyl]-4,4'-diyl)diethanone

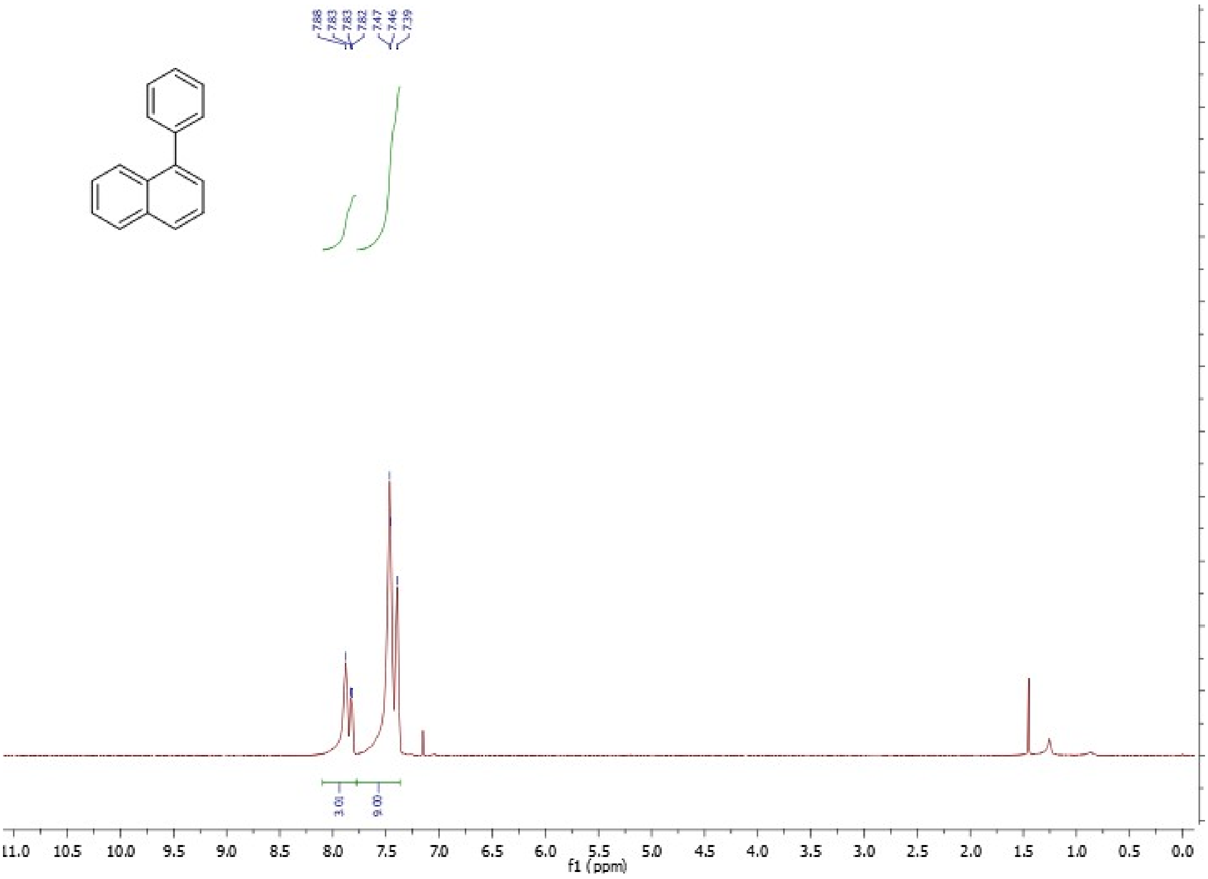


Fig. S73. ^{1}H NMR spectra of 1-phenylnaphthalene

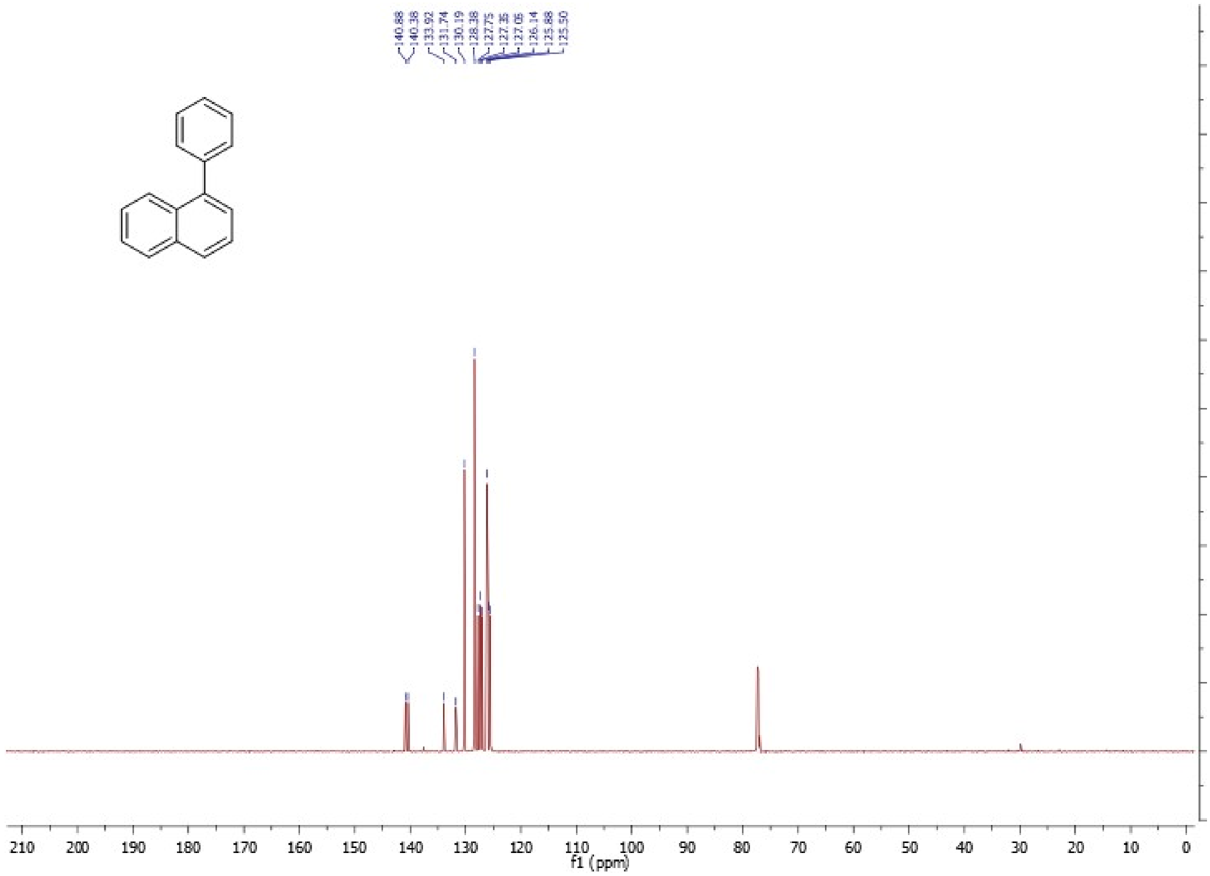


Fig. S74. ^{13}C NMR spectra of 1-phenyl naphthalene.

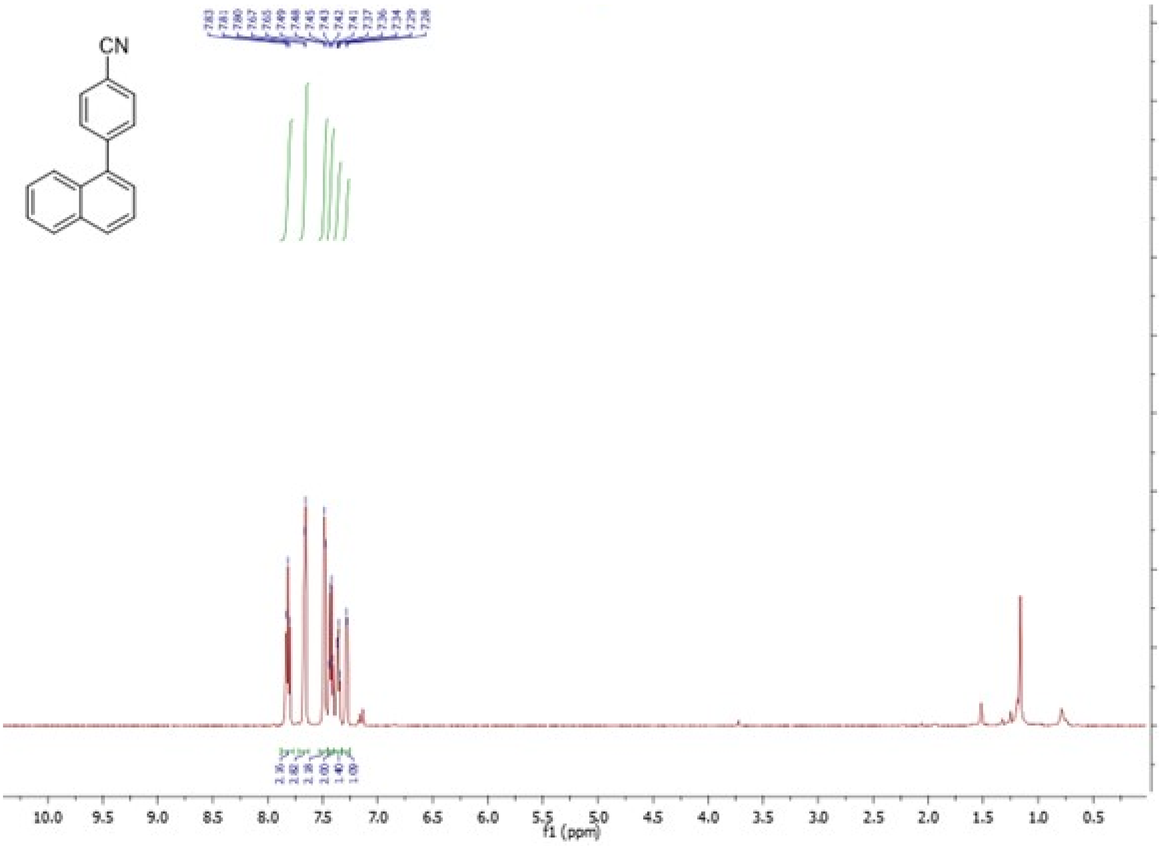


Fig. S75. ^{1}H NMR spectra of 4-(naphthalen-1-yl) benzonitrile.

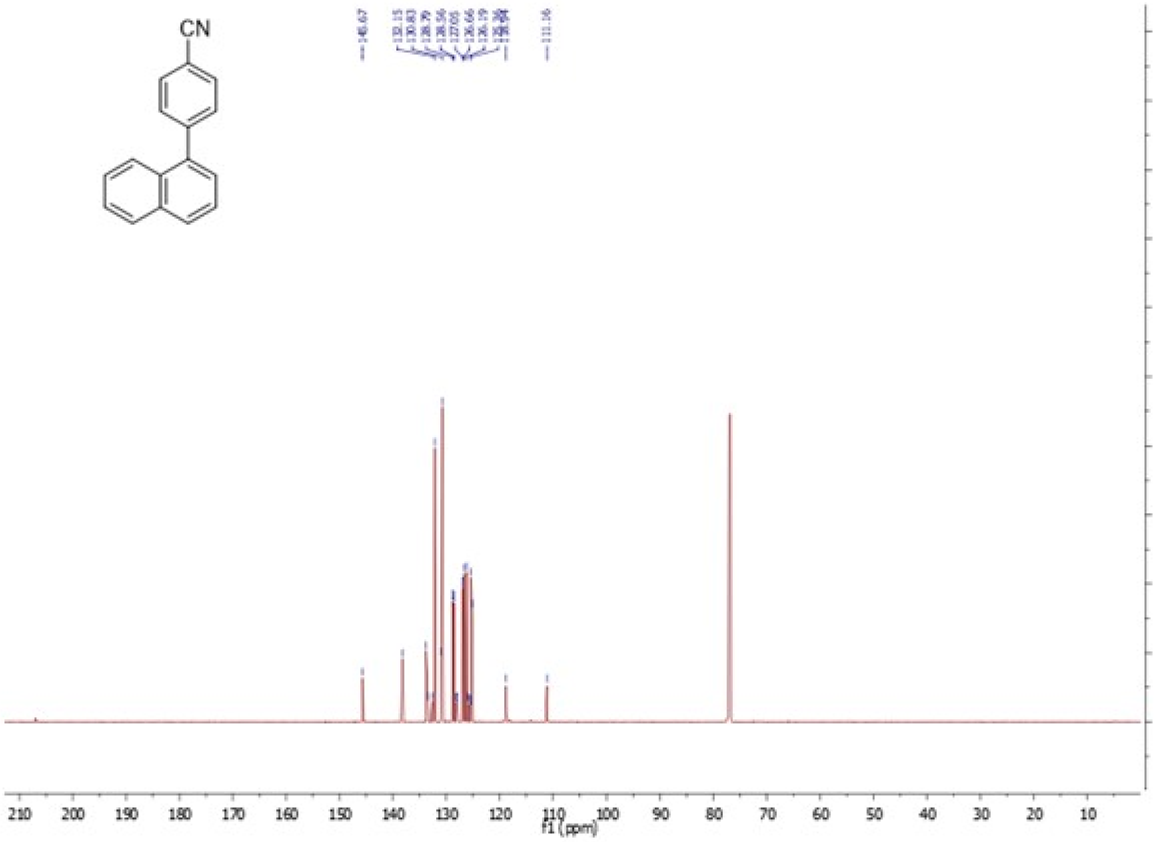


Fig. S76. ^{13}C NMR spectra of 4-(naphthalen-1-yl)benzonitrile

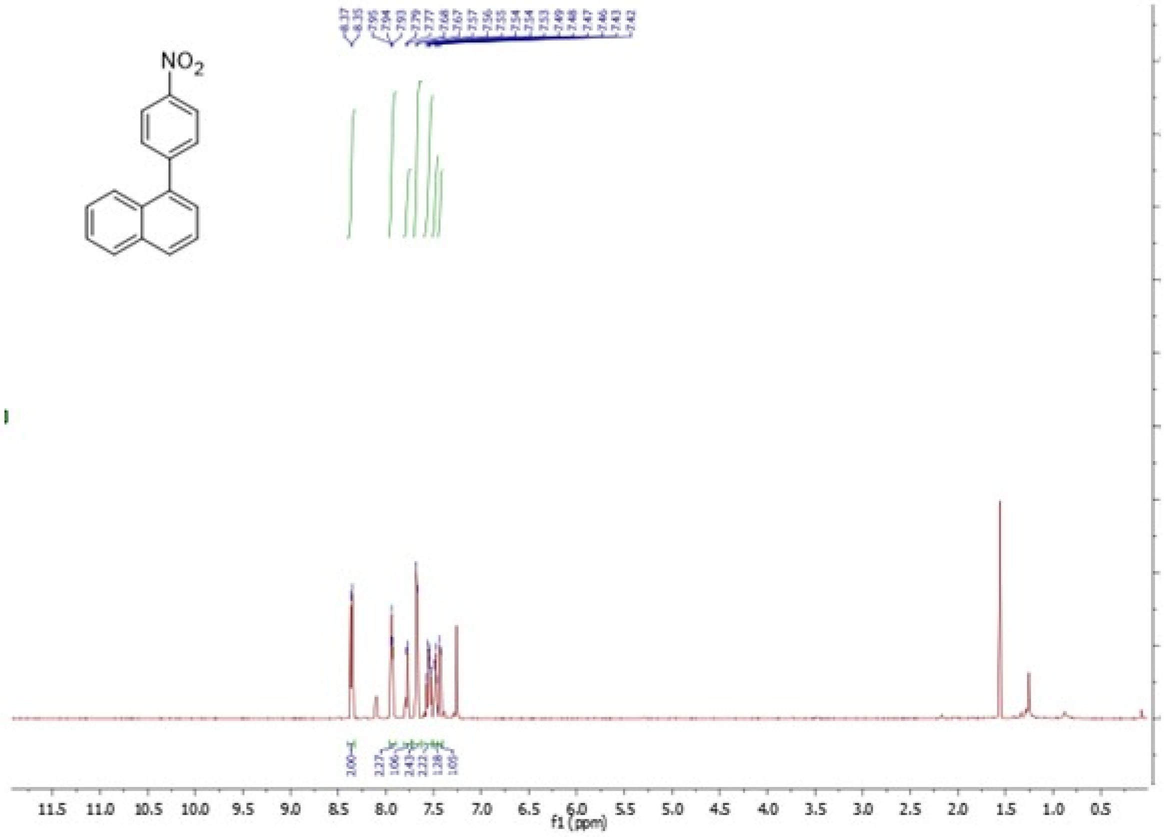


Fig. S77. ^{1}H NMR spectra of 1-(4-nitrophenyl) naphthalene

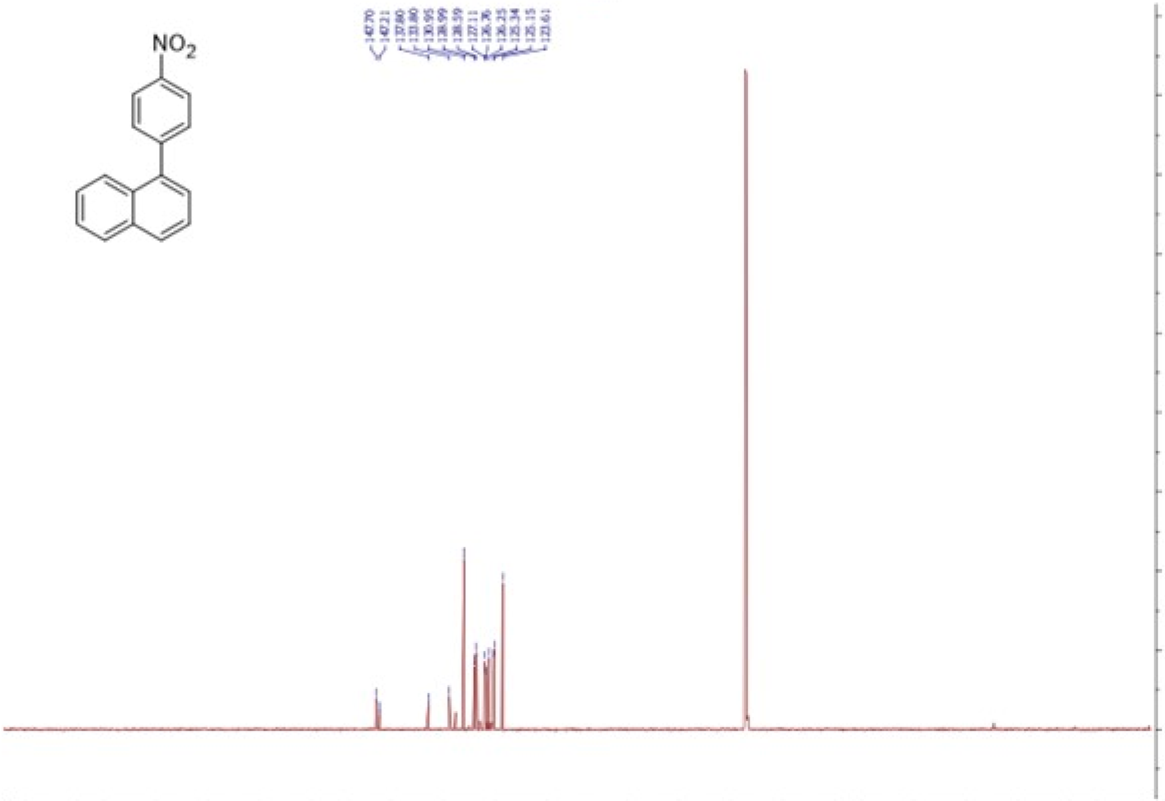


Fig. S78. ^{13}C NMR spectra of 1-(4-nitrophenyl) naphthalene.

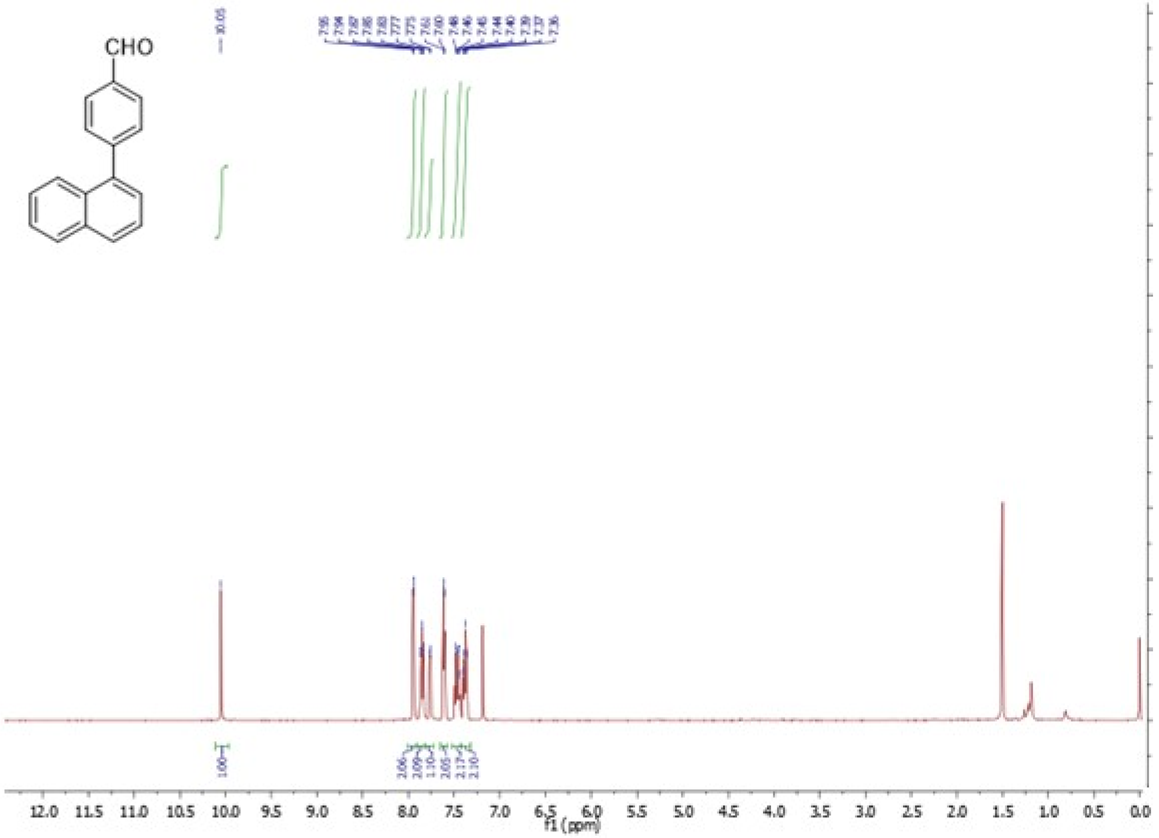


Fig. S79. ^{1}H NMR spectra of 4-(naphthalen-1-yl) benzaldehyde.

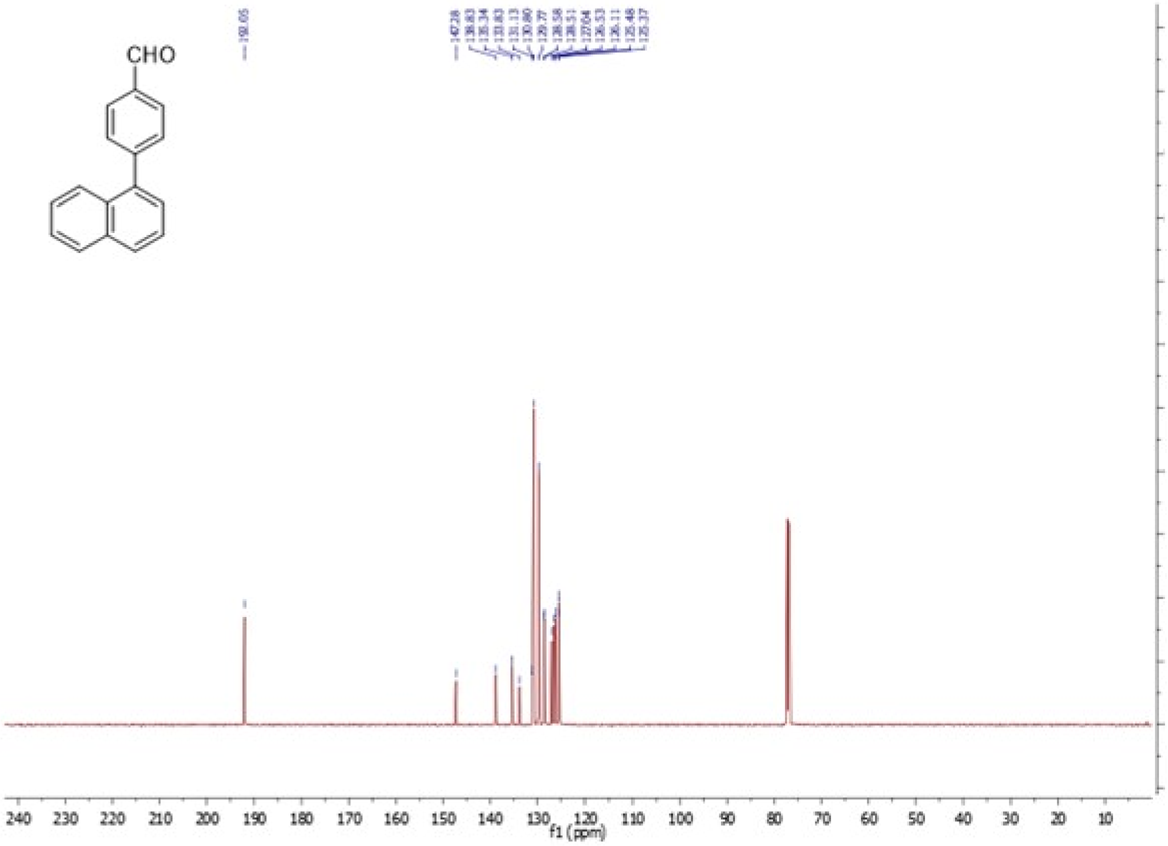


Fig. S80. ^{13}C NMR spectra of 4-(naphthalen-1-yl) benzaldehyde.

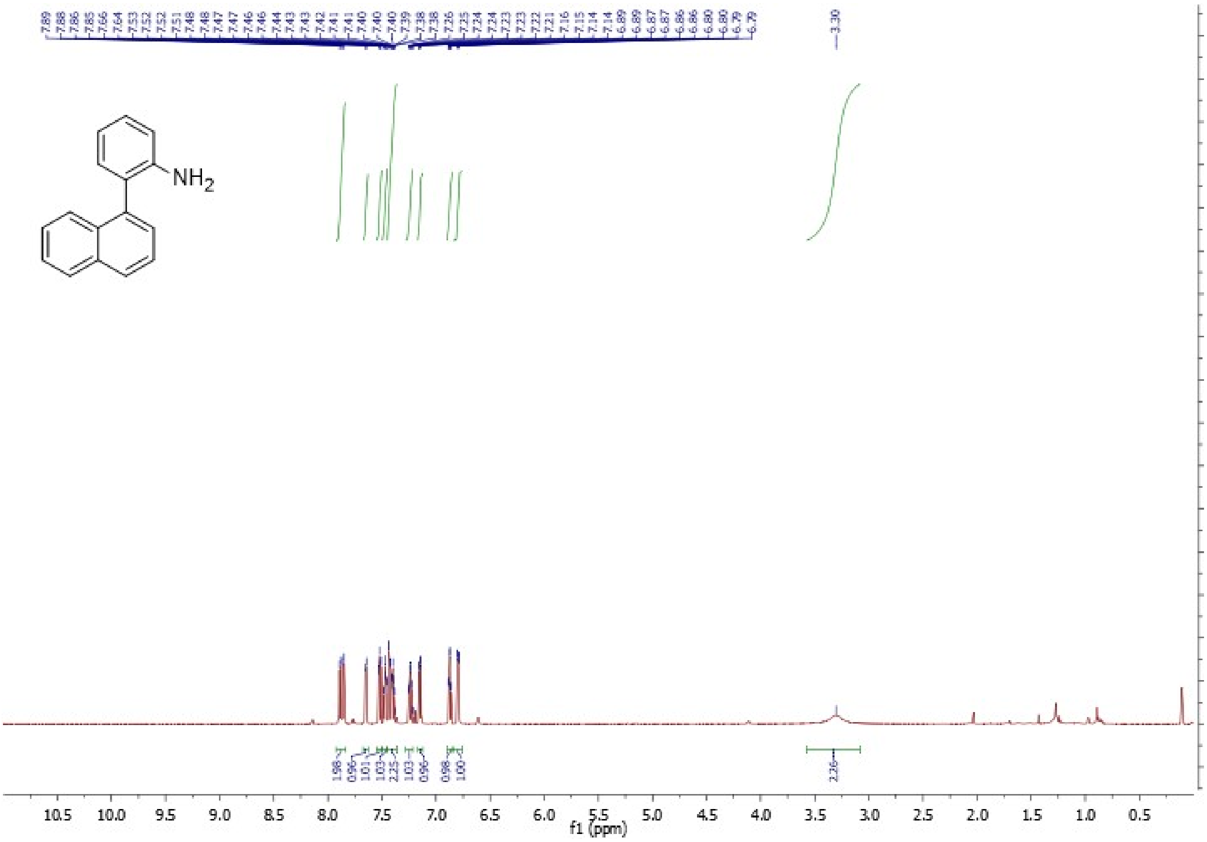


Fig. S81. ^{1}H NMR spectra of 2-(naphthalene-1-yl) aniline.

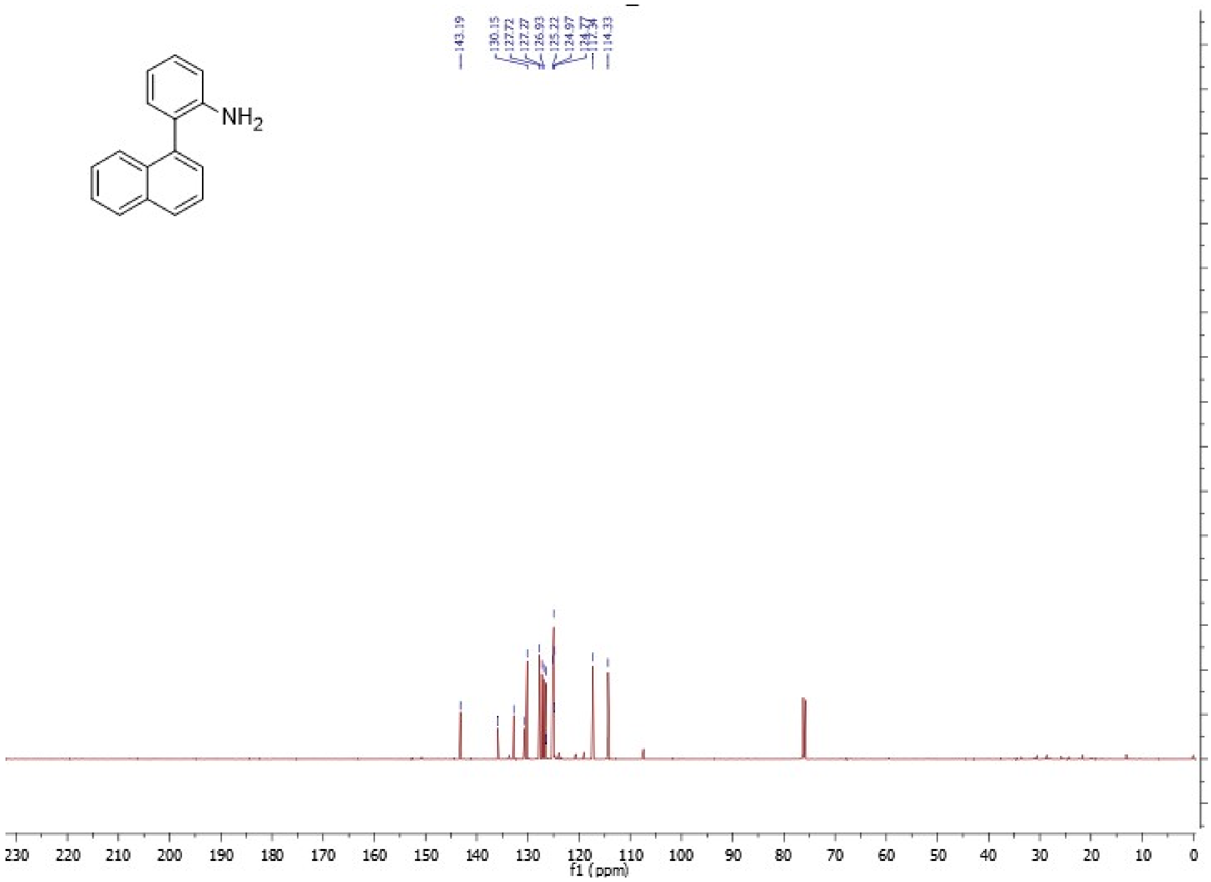


Fig. S82. ^{13}C NMR spectra of 2-(naphthalen-1-yl) aniline.

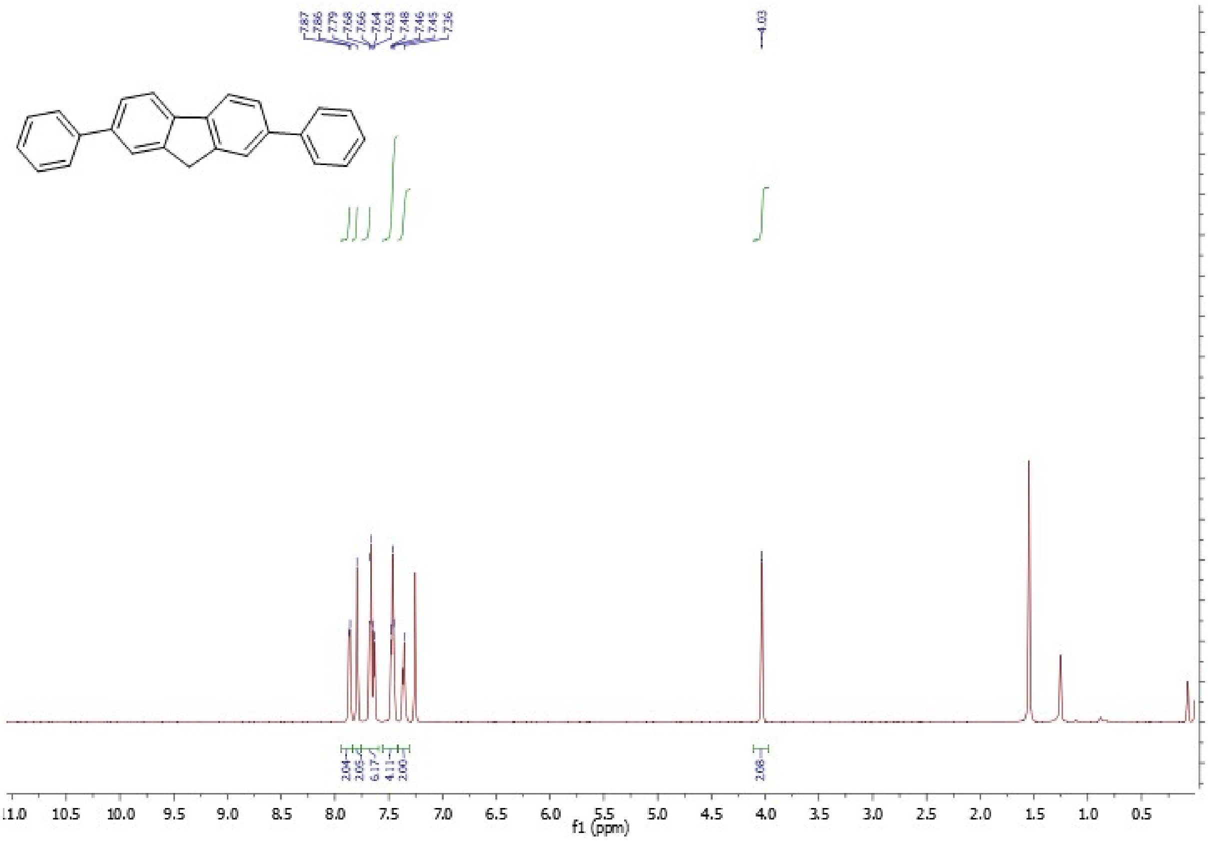


Fig. S83. ^{1}H NMR spectra of 2, 7-diphenyl-9H-fluorene.

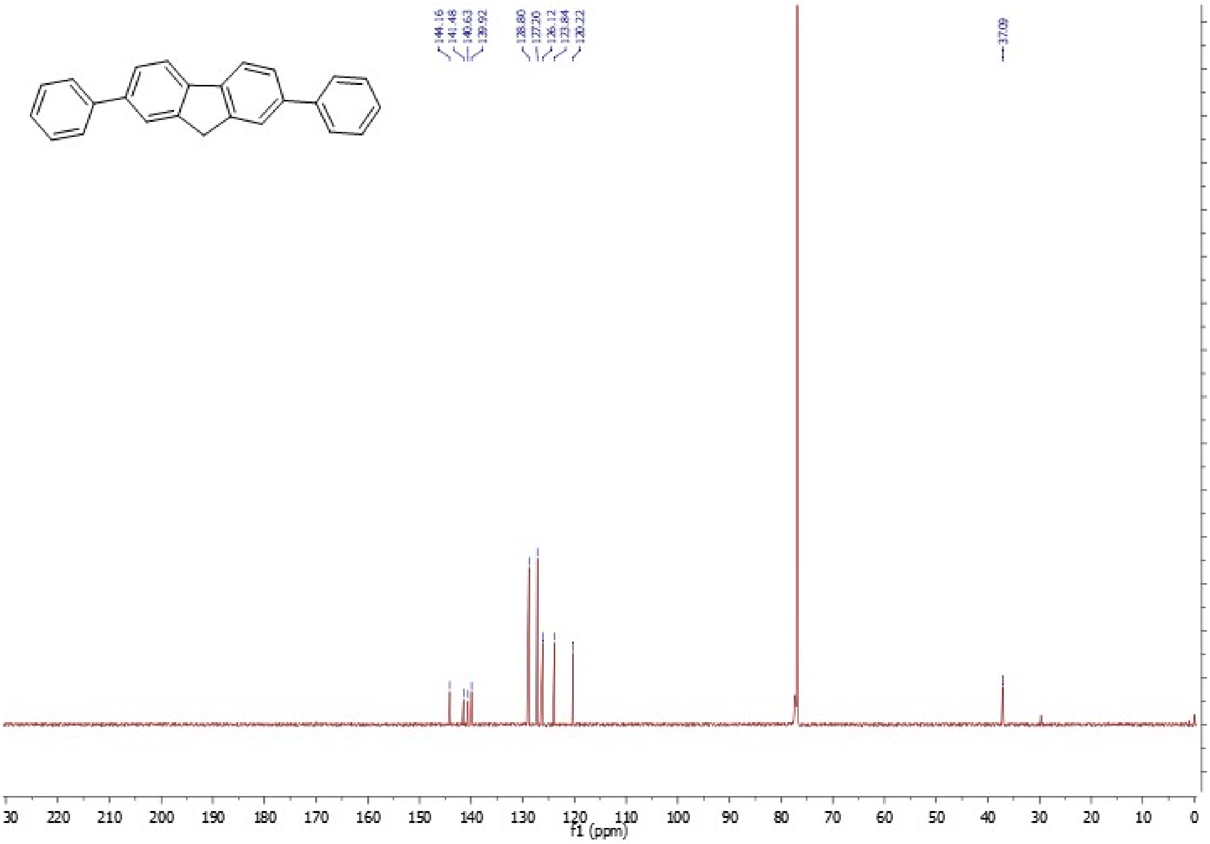


Fig. S84. ^{13}C NMR spectra of 2, 7-diphenyl-9H-fluorene.

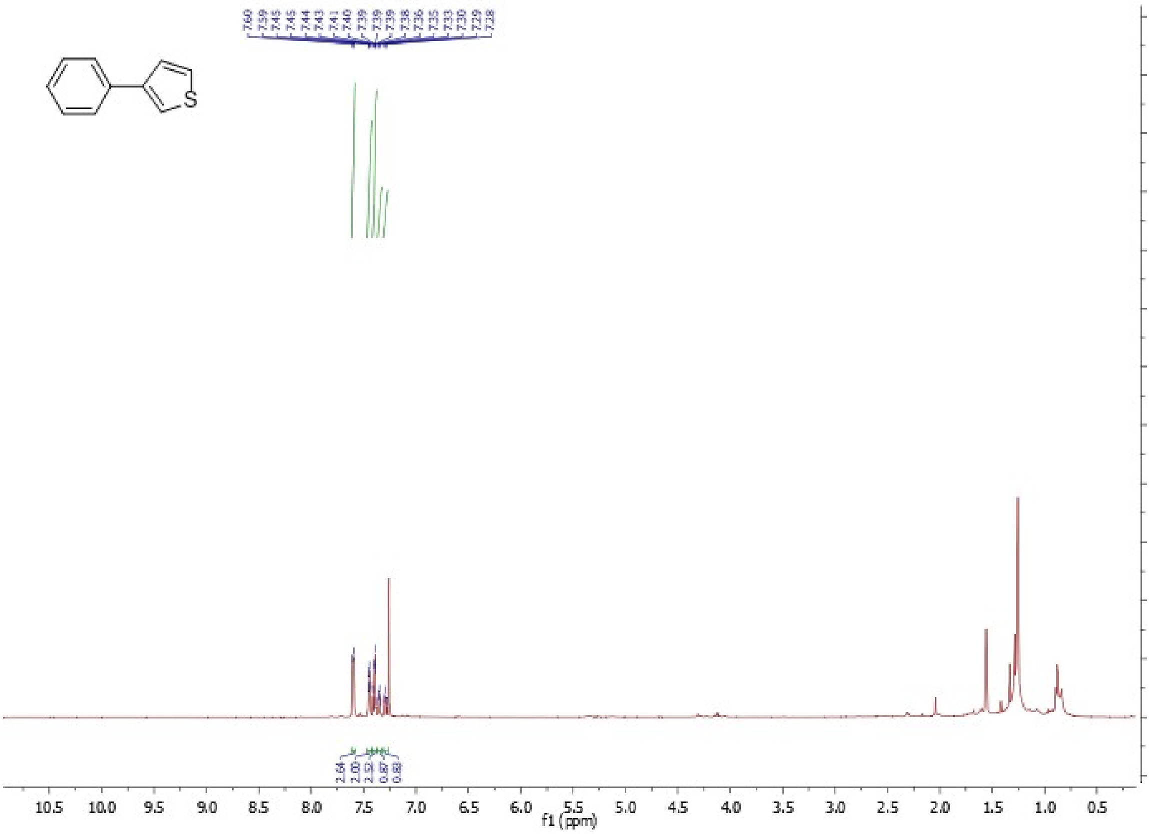


Fig. S85. ^{1}H NMR spectra of 3-phenyl thiophene.

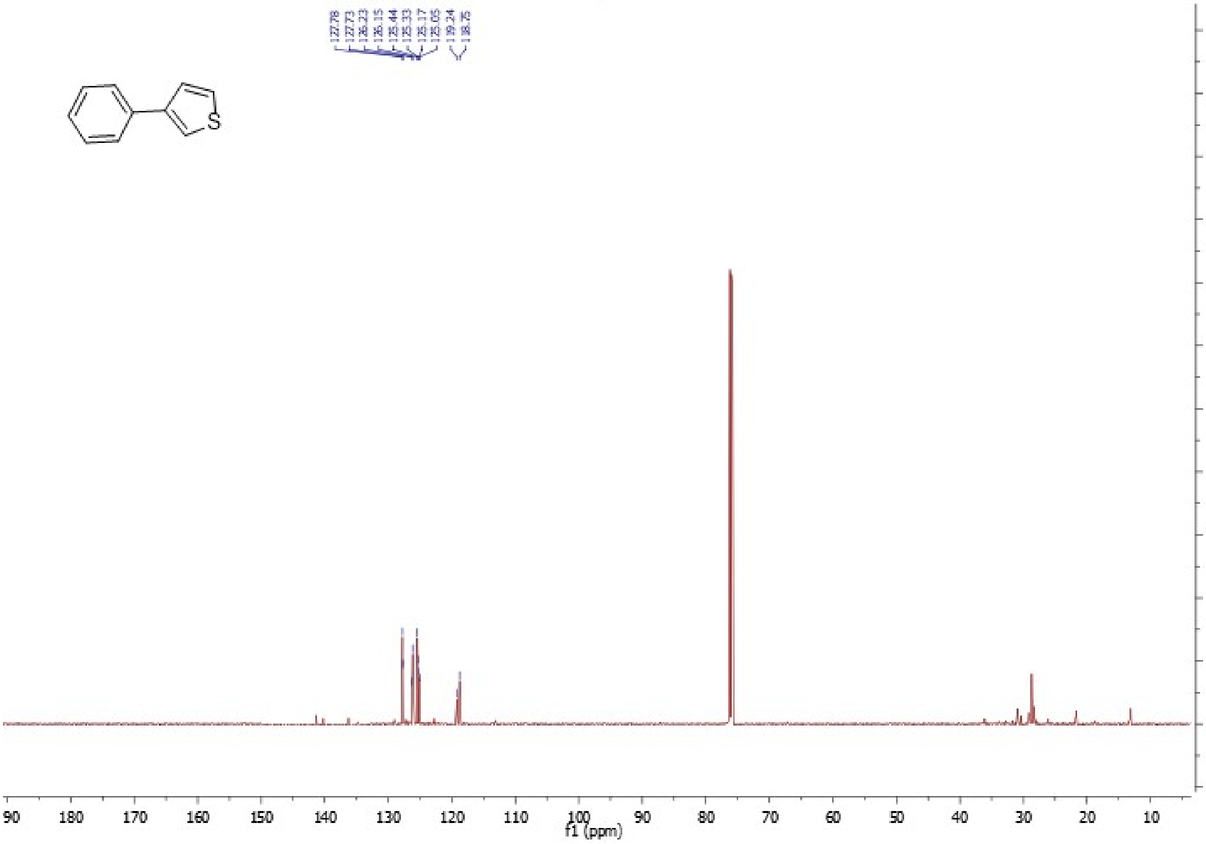
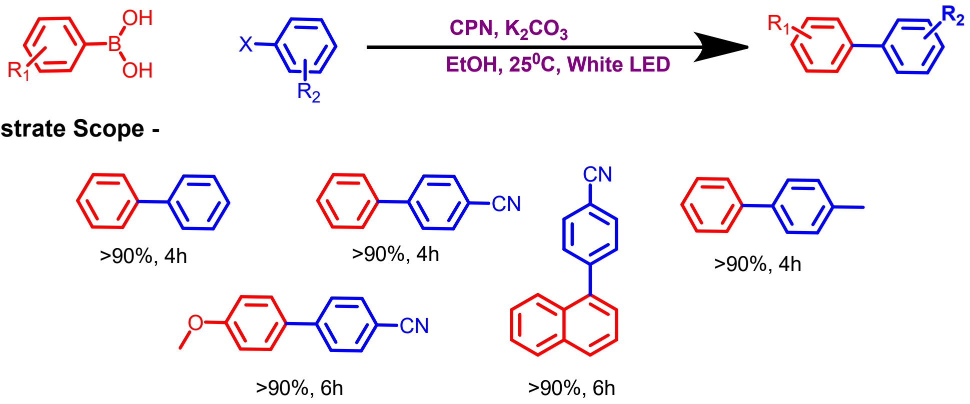


Fig. S86.^{13}C NMR spectra of 3-phenyl thiophene .

Table-S3 Comparison table of the CPN performance with previously reported catalyst towards C-C cross-coupling reaction.

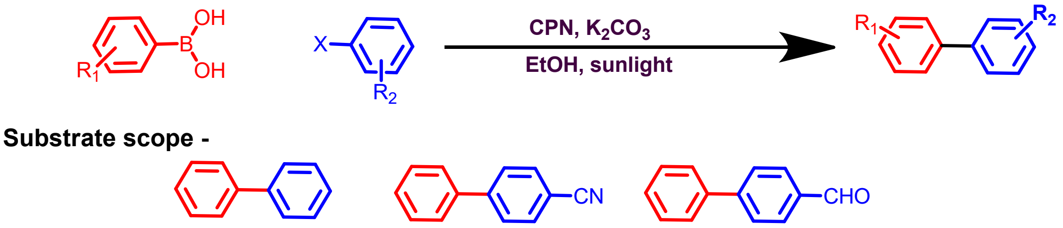
photocatalytic system	**Pd content/method of Pd loading**	**Reaction condition**	**Light source**	**Substrate Scope**	**TON / TOF (h^{-1})/conversion**	**Reference**
Pd-Azo-POP	0.3 mol%, Pd loaded ex-situ modification	EtOH/H_2O, $CsCO_3$	350 Watt Xenon lamp or Sunlight	19	TOF 2020.6 to 6533.3	S1
Pd@B-BO_3	3 wt%, Pd loaded ex-situ modification	DMF/H_2O, K_2CO_3	White LED Lamp (1.2 watt/cm^2)	8	Conversion 98%	S2
$NiFe_2O_4$@TiO_2 @PDA-Pd	5 wt% Pd loaded ex-situ modification	EtOH/H_2O, K_2CO_3	Sunlight	12	Conversion 98%	S3
St-MOP@Pd	0.14 mol% Pd loaded in-situ	MeOH, K_2CO_3	25^0C, White LED (0.98 mWatt/cm^2)	8	TON: 657 TOF: 219	S4
Alloy-1 photocatalysts (Au/Pd, 1:1.62)	1.43 wt% Pd loaded ex-situ modification	DMF/H_2O (3:1), K_2CO_3	White light LED, 0.5 W cm^{-2}	13	TON: 87 TOF: 14.5	S5
Pd−$BiVO_4$	0.002 equivalent,Pd loaded ex-situ modification	EtOH/H_2O (3:1), K_2CO_3	18Watt Blue LED,	40	TON:31200 TOF: 207	S6
Pd/CNP	0.5mol%, Pd loaded ex-situ modification	H_2O, K_3PO_4	Blue LED	31	TOF: 193	S7
Fe3O4@SiO2 @TiO2@Schiff base@Pd-(0)	0.159 wt%, Pd loaded ex-situ modification	K_2CO_3, PEG-400	Blue LED (20 W)	23	TOF: 5444 min^{-1}	S8
m-CNR-Pd	3 wt%, Pd loaded ex-situ modification	EtOH/H_2O, K_2CO_3	150 w Xenon lamp	16	Conversion 99%-	S9
CPN	**0.013 mol%**	**EtOH, K_2CO_3**	**3 Watt white LED light or sunlight**	**50**	TON: 7360 TOF: 1840	**This work**

Table S4. C-C cross-coupling reaction, maintaining at 25^{0}C, white LED.



[a] Reaction condition- Catalyst (5 wt%) arylboronic acid 0.55 mmol, arylhalide (0.5 mmol), base (1 mmol)solvent 3ml

Table S5 C-C cross-coupling reaction using CPN in sunlight



[a] Reaction condition- Catalyst (5 wt%) arylboronic acid 0.55 mmol, arylhalide (0.5 mmol), base (1 mmol)solvent 3ml, time-4h
Yield Conversion- >90%

Fig.S87. Synthesis of 1, 1-biphenyl, 4-carbonitrile in sunlight.

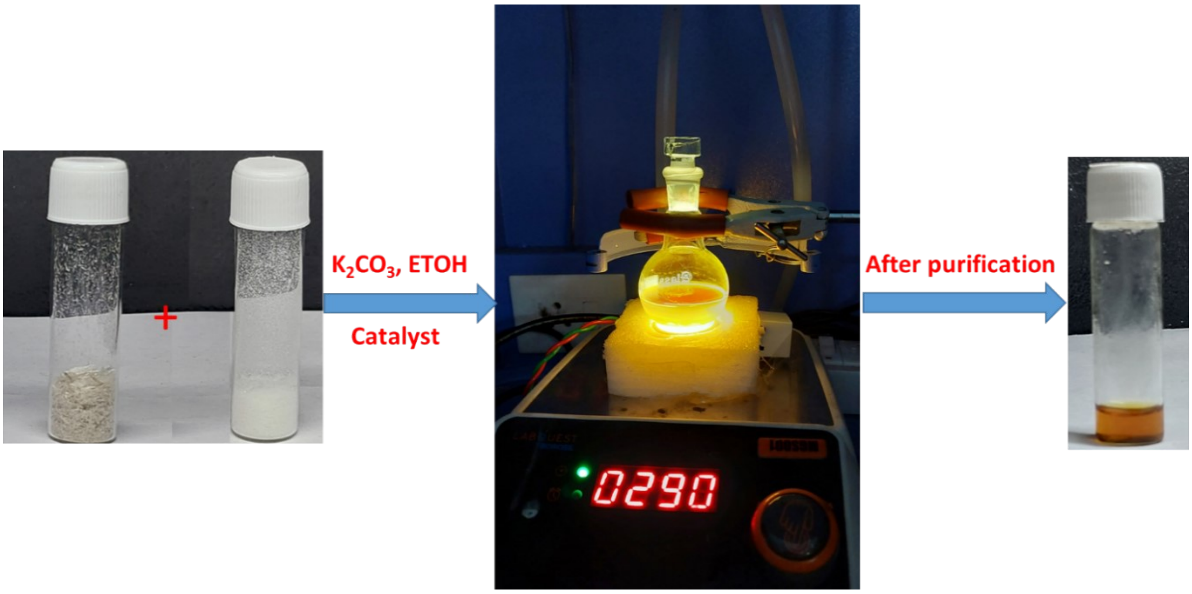


Fig.- S88. Gram scale synthesis of 4-chloro, 2-amino biphenyl in visible light.

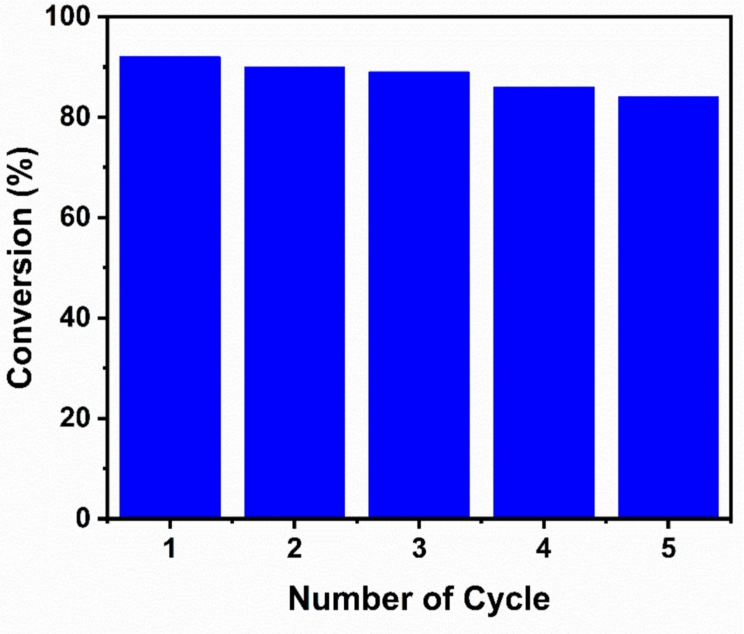


Fig. S89. Recyclability of catalyst, conversion obtained at 4 h reaction time in repeated runs of the C-C cross-coupling reaction of 4-bromobenzonitrile and phenylboronic acid using the same reaction condition.

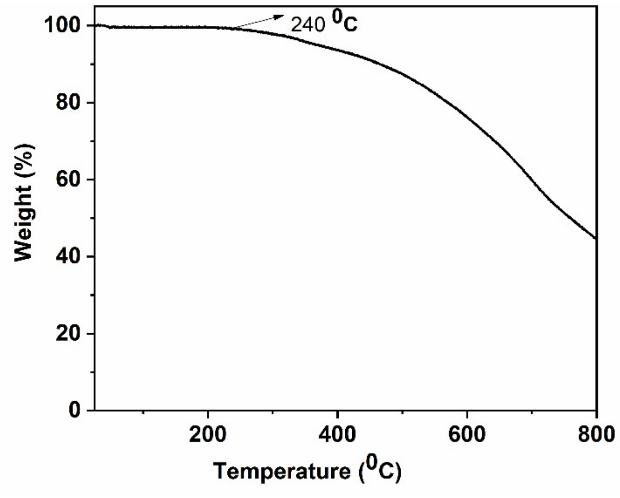


Fig. S90 TGA curve of Pd doped CPN

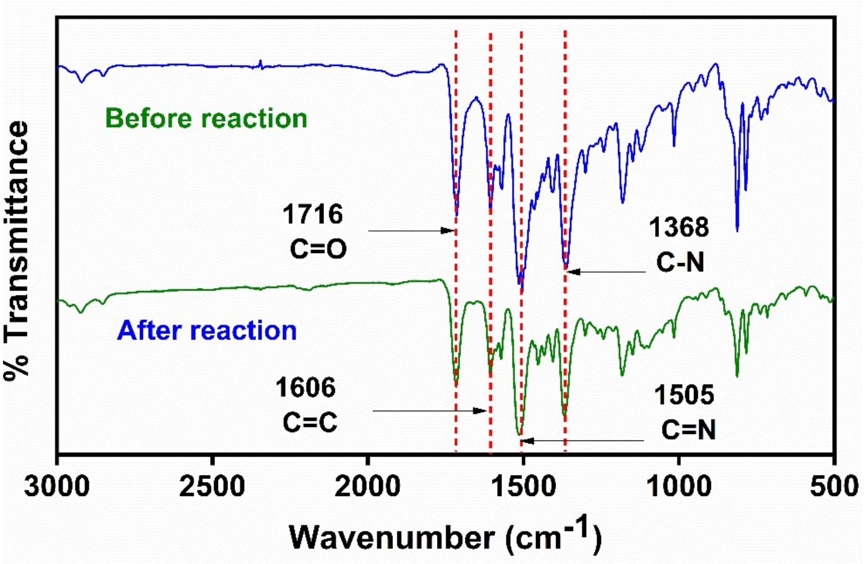


Fig. S91. Comparison of FTIR spectra of Pd doped CPN before and after reaction.

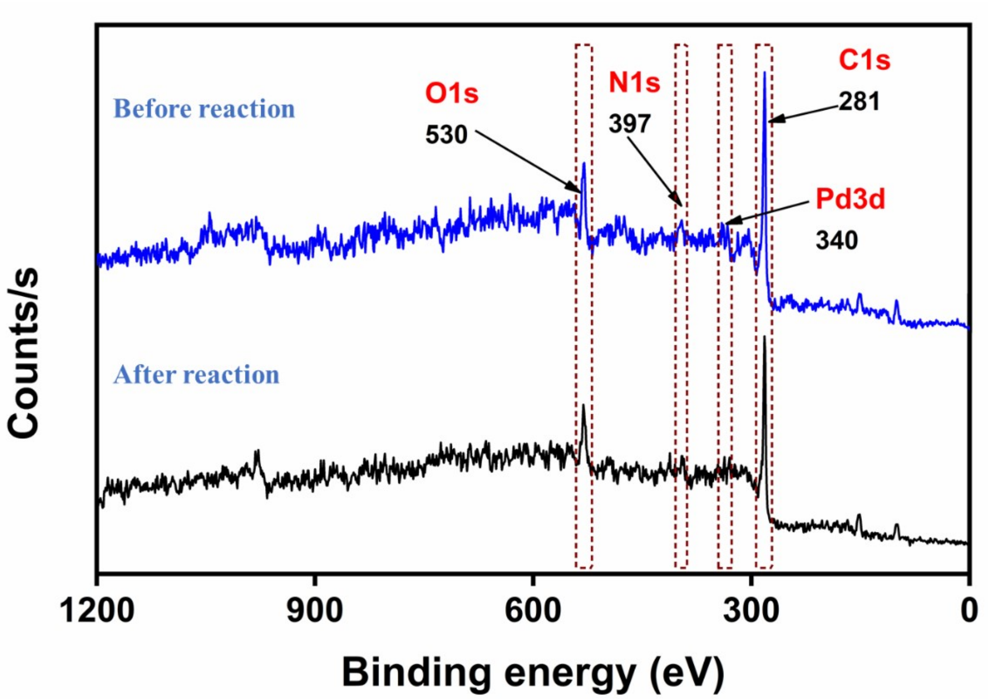


Fig. S92 Comparison of XPS Survey spectra of Pd doped CPN before and after the reaction.

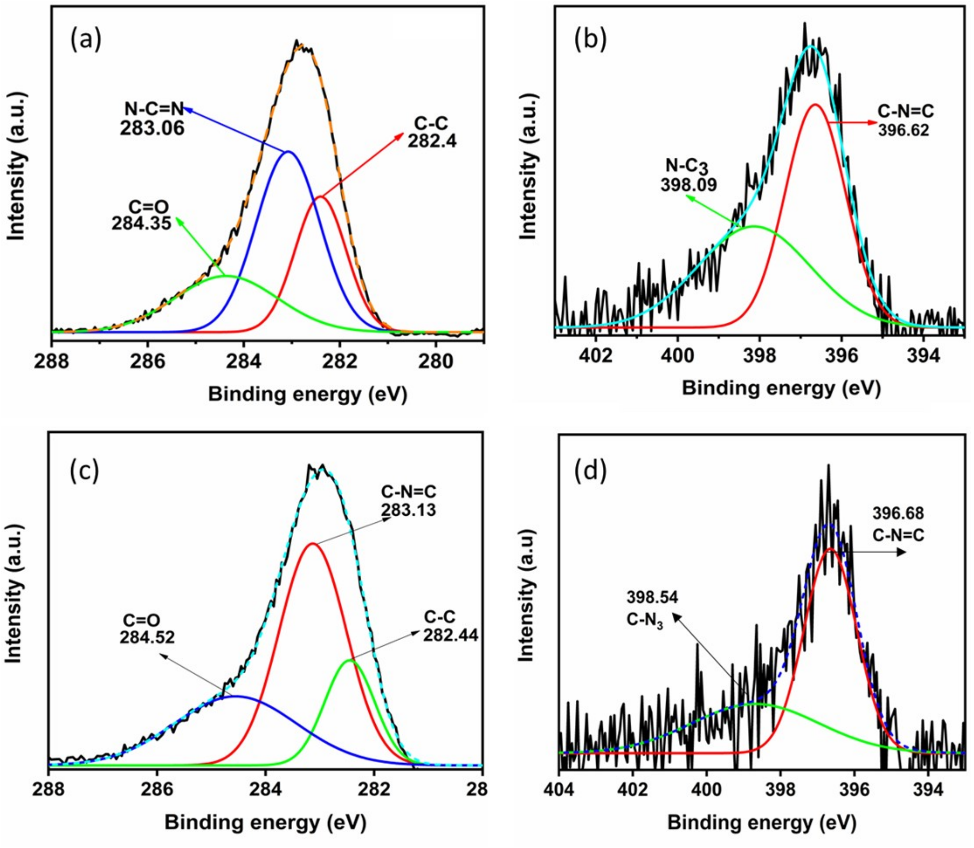


Fig. S93 (a & c) High resolution C1S spectra of Pd doped CPN, (a) before reaction (c) after reaction. (b &d) High resolution N1S spectra of Pd doped CPN, (b) before reaction and (d) after reaction.

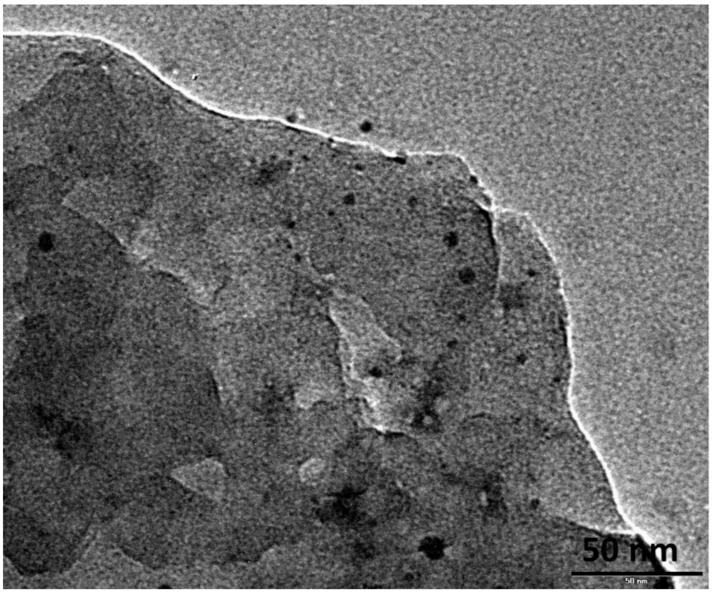


Fig. S94. TEM images of Pd doped CPN after use in reaction.

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