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Supporting Information

A highly water-dispersible/magnetically separable palladium catalyst based on Fe_3O_4@SiO_2 anchored TEG-imidazolium ionic liquid for the Suzuki-Miyaura coupling reaction in water

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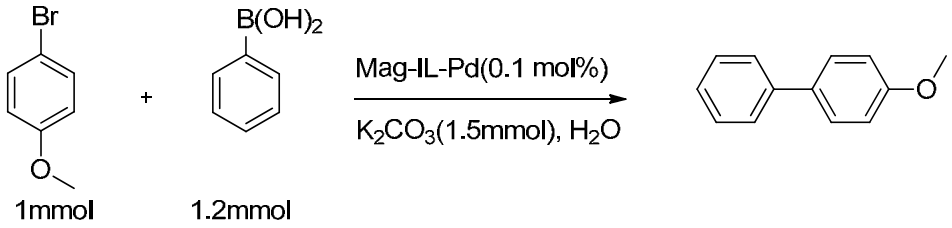
1- Optimizing of time and temperature in Suzuki reaction

Table S1: Optimizing of time and temperature in Suzuki reaction of 4-bromoanisol and phenyl boronic acid using **Mag-IL-Pd** catalyst



Entry	t(°C)	Time(h)	Yeild(%)[a]
1	60	6	52
2	60	8	65
3	60	10	80
4	**60**	**12**	**96**
5	75	6	80
6	75	8	88
7	75	10	77
8	75	12	77
9	90	6	94

[a] GC yields

2- Nitrogen adsorption-desorption isotherm of the prepared materials

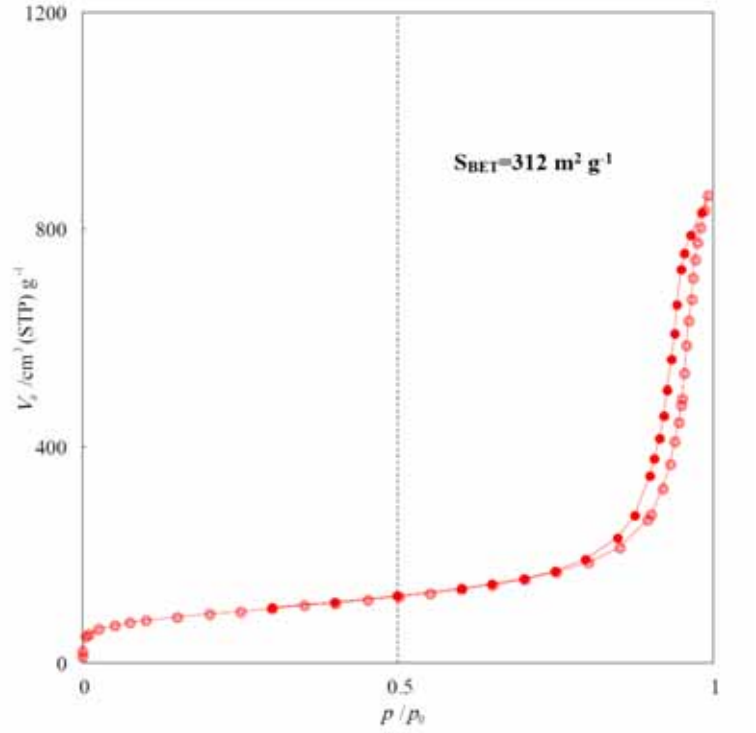


Fig S1 : Nitrogen adsorption-desorption isotherm of Fe_3O_4@SiO_2

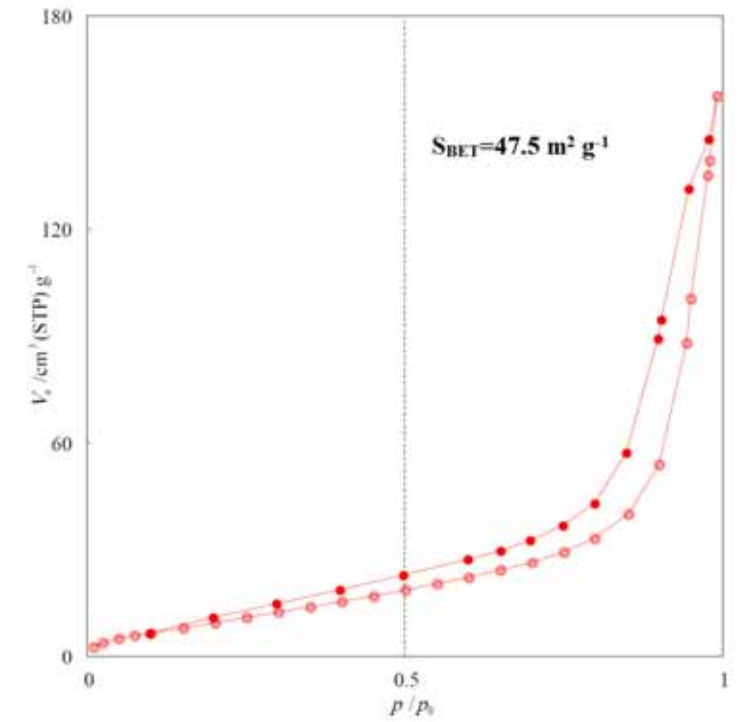


Fig S2 : Nitrogen adsorption-desorption isotherm of IL-functionalized Fe_3O_4@SiO_2

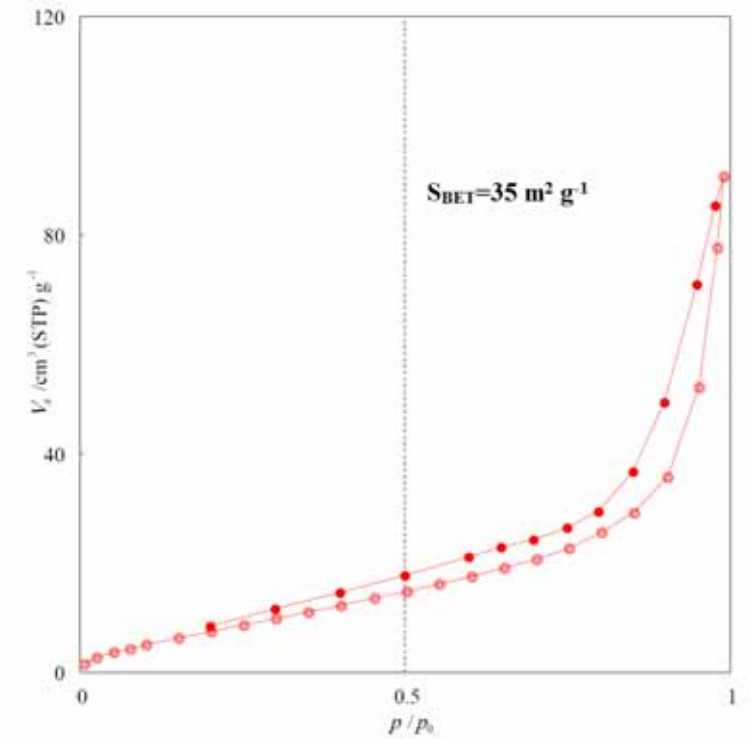


Fig S3 : Nitrogen adsorption-desorption isotherm of **Mag-IL-Pd**

3- TG/DTG analysis of the prepared materials

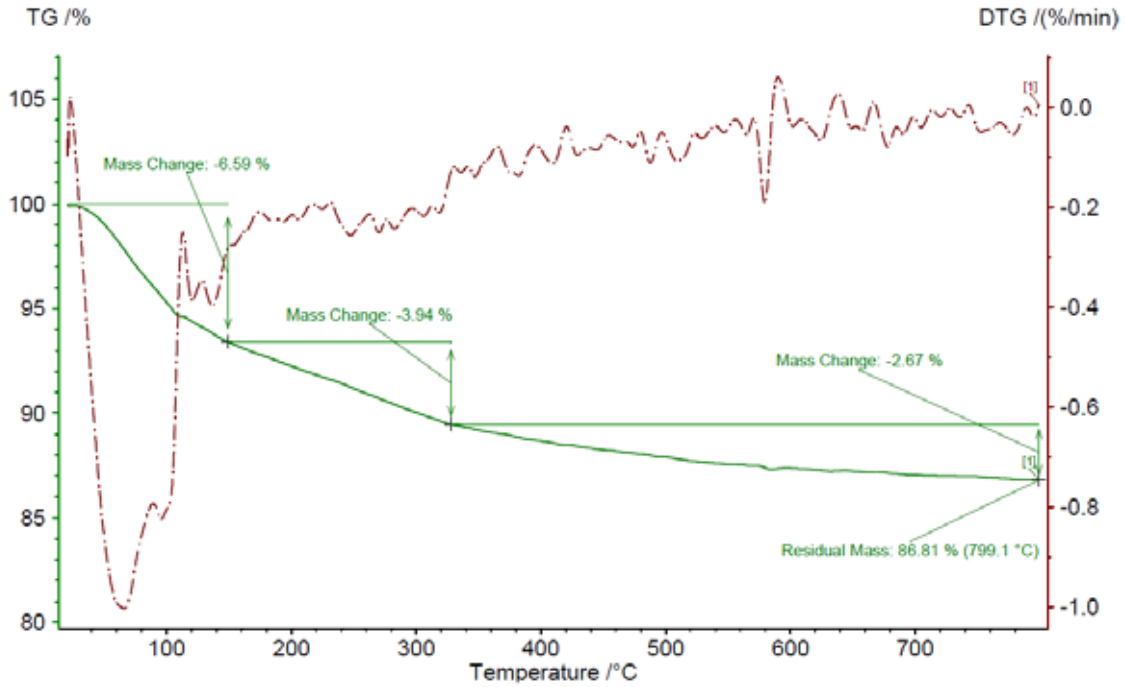


Fig. S4 : TG/DTG analysis of Fe_3O_4@SiO_2

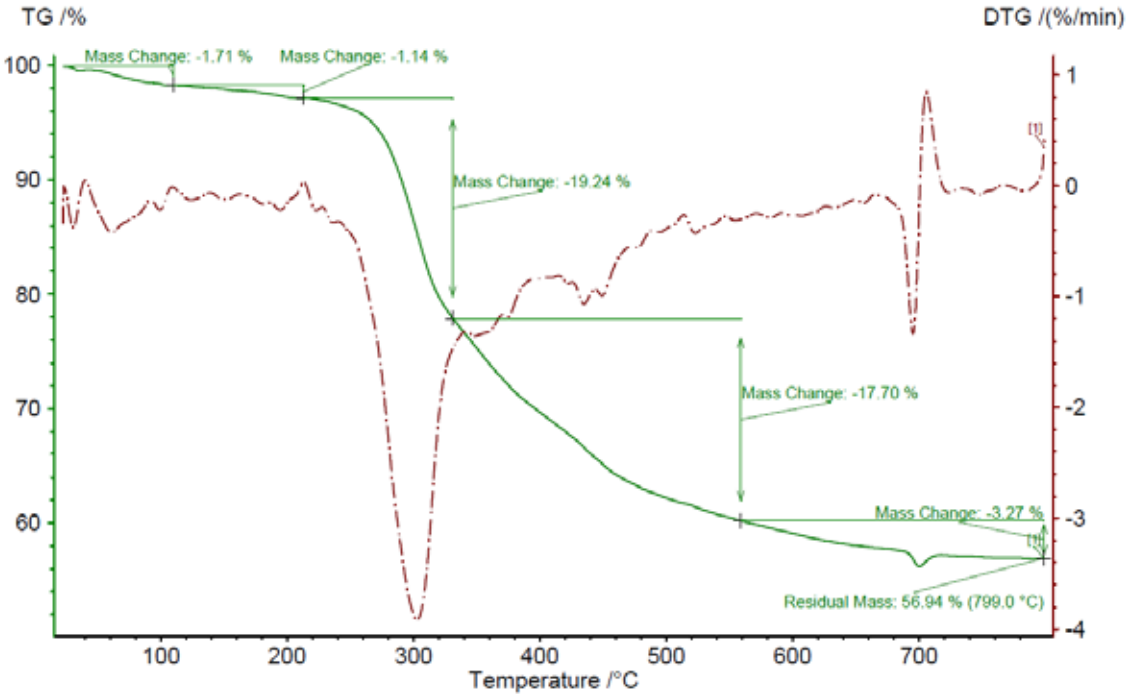


Fig. S5 TG/DTG analysis of IL-functionalized Fe_3O_4@SiO_2

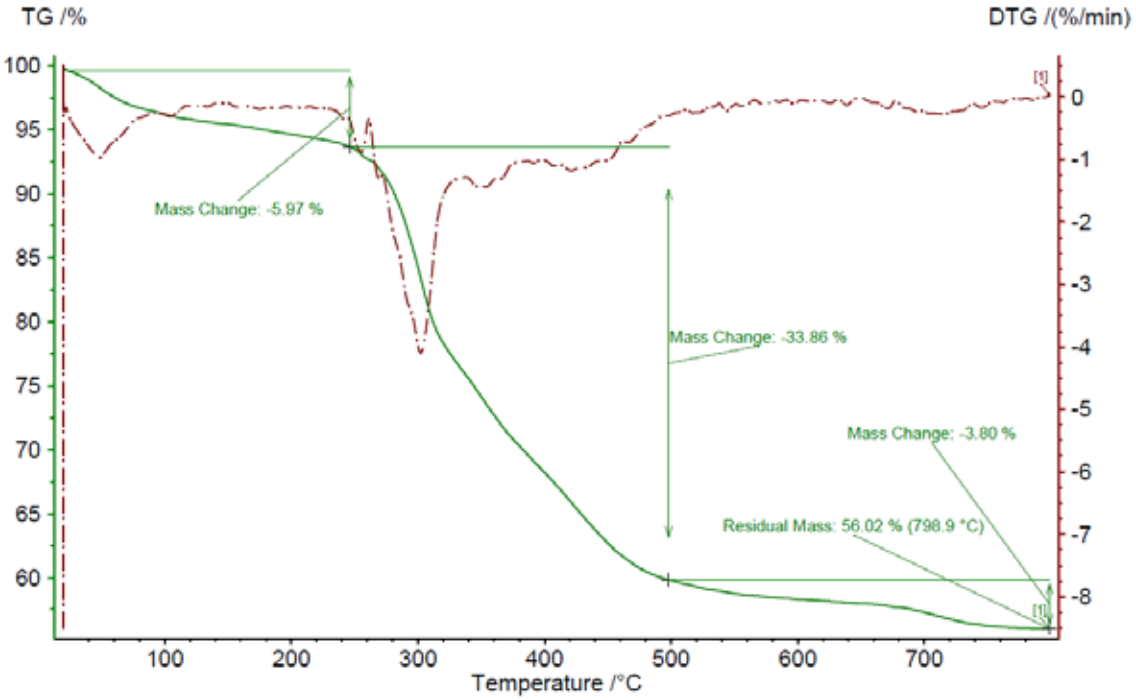


Fig. S6: TG/DTG analysis of **Mag-IL-Pd** catalyst

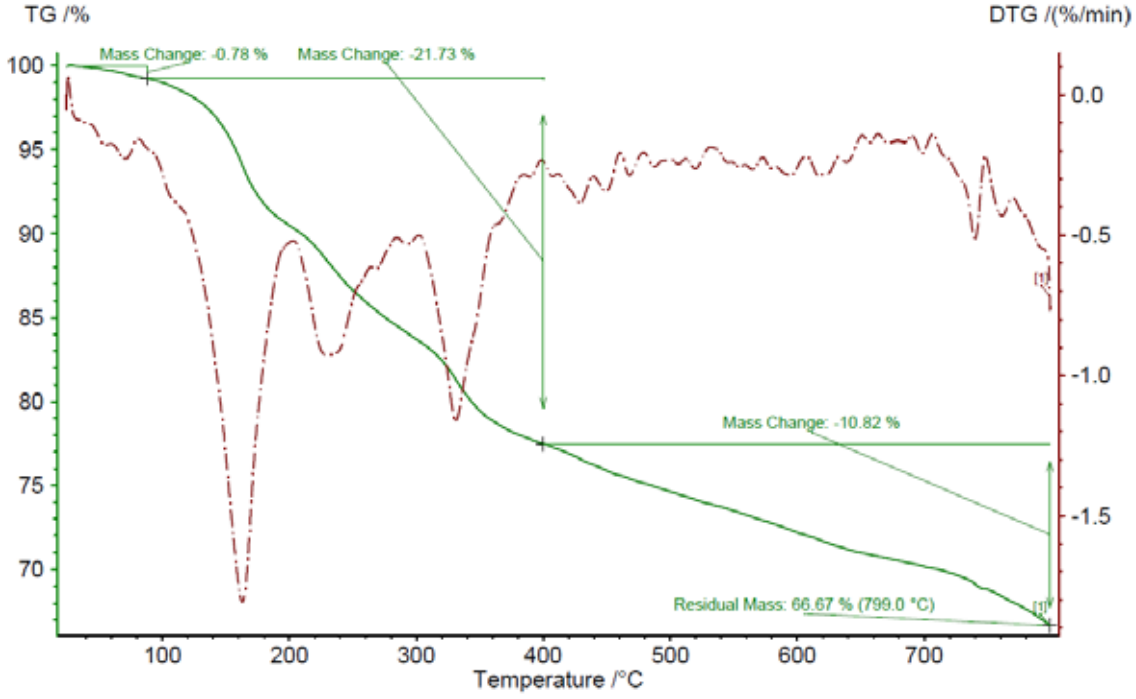


Fig. S7. TG/DTG analysis of the recycled **Mag-IL-Pd** catalyst

System

Temperature (°C):	25.0	**Zeta Runs:**	12
Count Rate (kcps):	322.2	**Measurement Position (mm):**	2.00
Cell Description:	Clear disposable zeta cell	**Attenuator:**	7

Results

			Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV):	45.9	**Peak 1:**	45.9	100.0	8.13
Zeta Deviation (mV):	8.13	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.269	**Peak 3:**	0.00	0.0	0.00

Result quality : Good

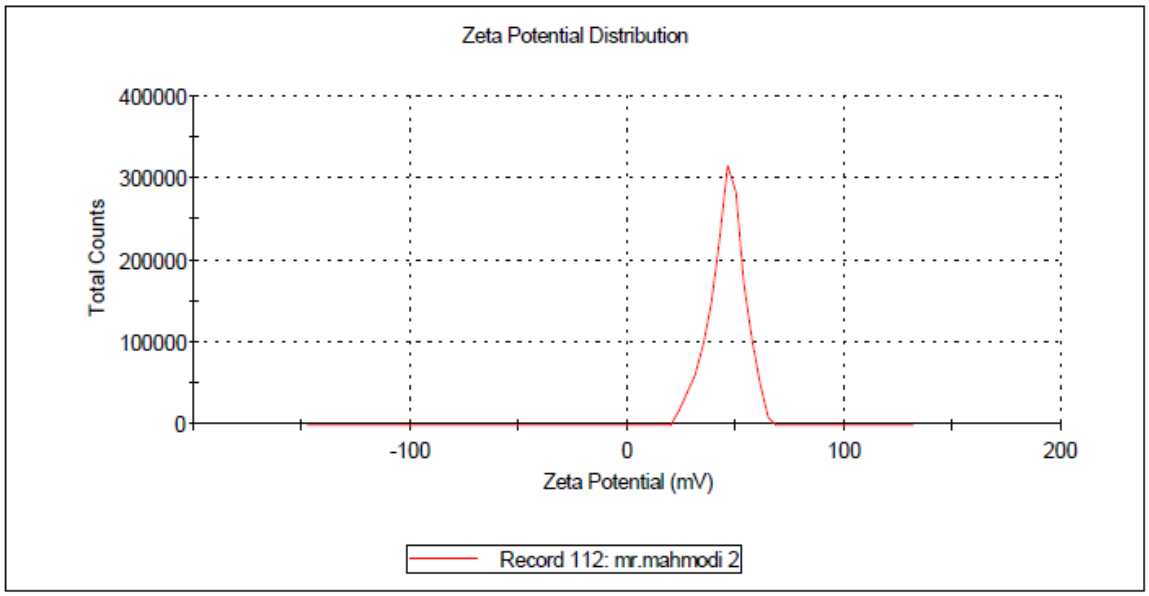


Fig. S8. Zeta potential analysis of the colloidal dispersion of **Mag-IL-Pd** catalyst in pure water after 5 min mixing before analysis

System

Temperature (°C):	25.0	**Zeta Runs:**	12
Count Rate (kcps):	73.2	**Measurement Position (mm):**	2.00
Cell Description:	Clear disposable zeta cell	**Attenuator:**	6

Results

			Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV):	41.1	**Peak 1:**	41.1	100.0	7.15
Zeta Deviation (mV):	7.15	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.316	**Peak 3:**	0.00	0.0	0.00

Result quality : Good

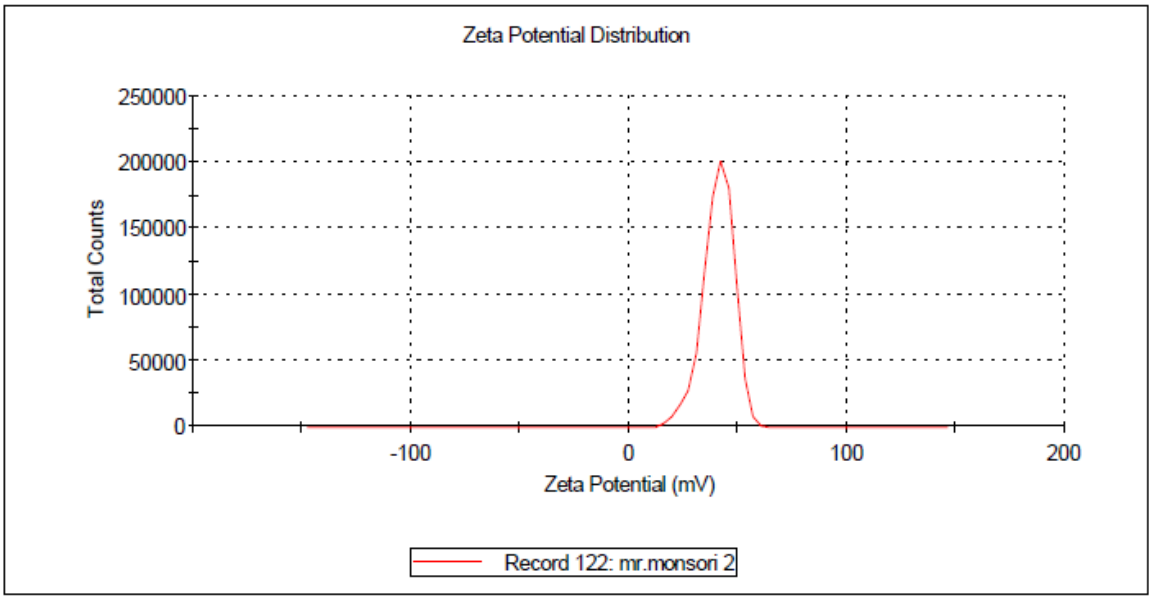
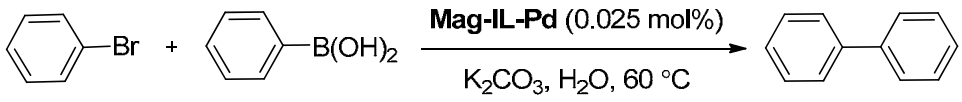


Fig. S9. Zeta potential analysis of the colloidal dispersion of **Mag-IL-Pd** catalyst in pure water after two days

Hg poisoning test results:



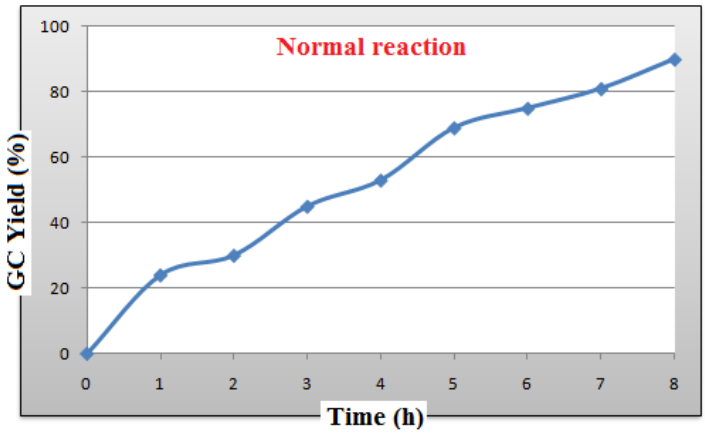


Fig. S10. Reaction condition: bromobenzene (3 mmol), phenylboronic acid (3.6 mmol), K_2CO_3 (4.5 mmol), **Mag-IL-Pd** (0.025 mol%), H_2O (5 mL), 60 °C, Ar atmosphere

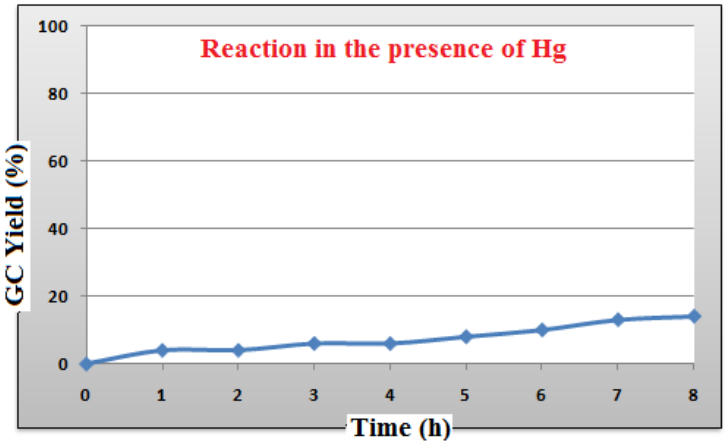


Fig. S11. Reaction condition: bromobenzene (3 mmol), phenylboronic acid (3.6 mmol), K_2CO_3 (4.5 mmol), **Mag-IL-Pd** (0.025 mol%), Hg (10 mol%), H_2O (5 mL), 60 °C, Ar atmosphere

The study of "induction period" for Suzuki reaction usin Mag-IL-Pd catalyst system in water:

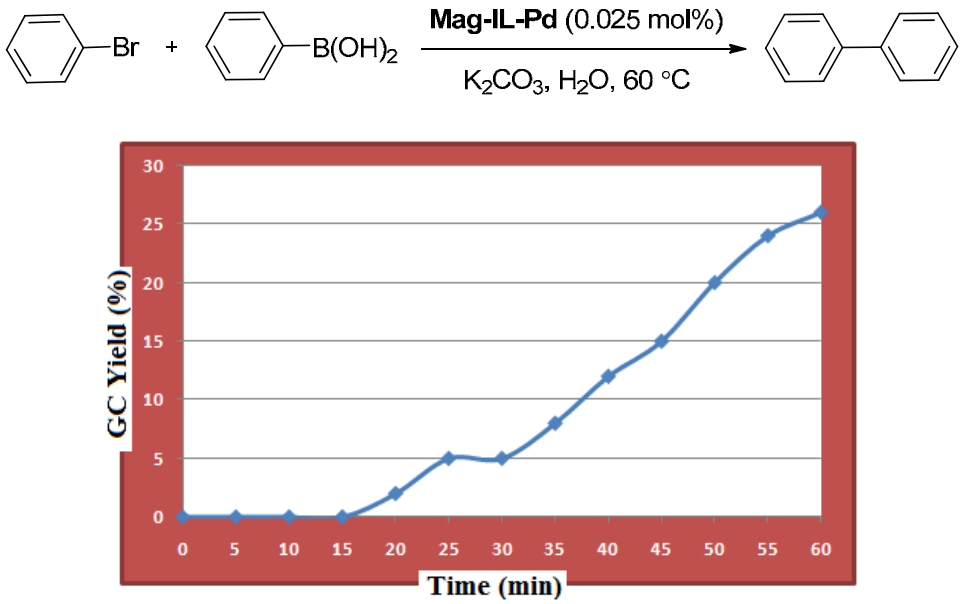
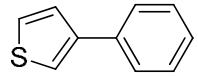


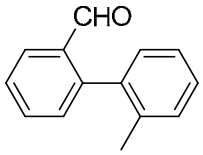
Fig. S12. Reaction condition: bromobenzene (3 mmol), phenylboronic acid (3.6 mmol), K_2CO_3 (4.5 mmol), Mag-IL-Pd (0.025 mol%), H_2O5 (mL), 60 °C, Ar atmosphere

4-^{1}H and ^{13}C NMR spectra of the products



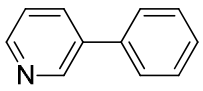
3-phenylthiophene

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.65 (d, *J*=1.2 Hz, 1H), 7.63 (d, *J*=1.2 Hz, 1H), 7.49 (m, 1H), 7.43-7.44 (m, 4H), 7.31-7.35 (m, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 142.39, 135.88, 128.83, 127.16, 126.48, 126.37, 126.22, 120.30.



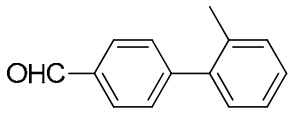
2'-methyl-[1,1'-biphenyl]-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=9.79 (s, 1H), 8.07 (dd, J_1=7.8 Hz, J_2=1.2Hz, 1H), 7.65-7.69 (td, J_1=7.4 Hz, J_2=1.2Hz, 1H), 7.53 (t, *J*=7.6Hz, 1H), 7.30-7.39 (m, 4H), 7.23 (d, *J*=7.2Hz, 1H), 2.14 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 192.34, 145.72, 137.52, 136.21, 133.85, 133.78, 130.80, 130.24, 130.13, 128.33, 127.87, 127.12, 125.73, 20.37.



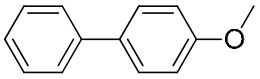
3-phenylpyridine

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.88 (d, *J*=1.6Hz, 1H), 8.60-8.62 (dd, J_1=4.6 Hz, J_2=1.2Hz, 1H), 7.86-7.88 (dd, J_1=6.2 Hz, J_2=1.6Hz, 1H), 7.59 (d, *J*=7.2Hz, 2H), 7.34-7.51 (m, 4H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 148.47, 148.33, 137.83, 136.65, 134.38, 129.11, 128.78, 128.13, 127.17, 123.58.



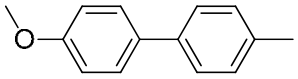
2'-methyl-[1,1'-biphenyl]-4-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=10.10 (s, 1H), 7.97 (d, *J*=8.4Hz, 2H), 7.53 (d, *J*=8.0Hz, 2H), 7.25-7.35 (m, 4H), 2.31 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS):192.05, 148.45, 140.60, 135.15, 134.97, 130.63, 129.96, 129.63, 129.51, 128.11, 126.03, 20.42.



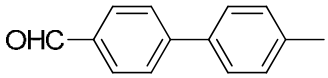
4-methoxy-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.58 (t, *J*=7.6Hz, 4H), 7.46 (t, *J*=7.6Hz, 2H), 7.34 (t, *J*=7.2Hz, 1H), 7.02 (d, *J*=8.8Hz, 2H), 3.89 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 159.16, 140.85, 133.80, 128.75, 128.18, 126.77, 126.68, 114.21, 55.37.



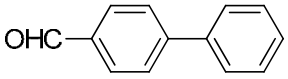
4-methoxy-4'-methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.54 (d, *J*=8.8Hz, 2H), 7.48 (d, *J*=8.0Hz, 2H), 7.27 (t, *J*=8.4Hz, 2H), 7.00 (d, *J*=8.8Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 158.95, 137.99, 136.39, 133.77, 129.47, 127.98, 126.61, 114.18, 55.37, 21.09.



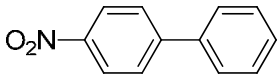
4'-methyl-[1,1'-biphenyl]-4-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=10.08 (s, 1H), 7.97 (d, *J*=8Hz, 2H), 7.77 (d, *J*=8Hz, 2H), 7.58 (d, *J*=8Hz, 2H), 7.32 (d, *J*=8Hz, 2H), 2.45 (s, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 191.98, 147.19, 138.57, 136.82, 134.99, 130.31, 129.78, 127.44, 127.23, 21.22.



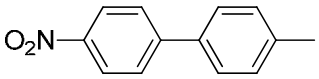
[1,1'-biphenyl]-4-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=10.09 (s, 1H), 7.99 (d, *J*=8.0Hz, 2H), 7.79 (d, *J*=8Hz, 2H), 7.67 (d, *J*=7.2Hz, 2H), 7.52 (t, *J*=6.8Hz, 2H), 7.45 (t, *J*=7.2Hz, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 191.94, 147.24, 139.75, 135.24, 130.29, 129.04, 128.50, 127.72, 127.39.



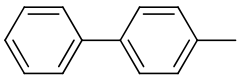
4-nitro-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.33 (d, *J*=8.8Hz, 2H), 7.77 (d, *J*=8.8Hz, 2H), 7.65-7.67 (m, 2H), 7.48-7.55 (m, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 147.66, 147.10, 138.80, 129.18, 128.94, 127.83, 127.42, 124.14.



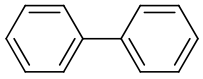
4-methyl-4'-nitro-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.31(d, *J*=8.8Hz, 2H), 7.75 (d, *J*=8.8Hz, 2H), 7.56 (d, *J*=8.0Hz, 2H), 7.33 (d, *J*=8.0Hz, 2H), 2.46 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 147.60, 146.86, 139.12, 135.87, 129.91, 127.51, 127.25, 124.13, 21.24.



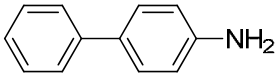
4-methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.73 (d, *J*=7.2Hz, 2H), 7.65(d, *J*=7.2Hz, 2H), 7.57 (t, *J*=6.8Hz, 2H), 7.47 (t, *J*=6.8Hz, 1H), 7.39 (d, *J*=7.2Hz, 2H), 2.54 (s, 3H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 141.30, 138.50, 137.13, 129.64, 128.86, 127.14, 127.12, 126.96, 21.24.



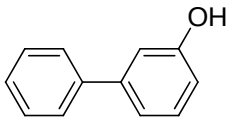
1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.66 (d, *J*=7.2Hz, 2H), 7.50 (t, *J*=7.2Hz, 2H), 7.41 (t, *J*=7.6Hz, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS):141.29, 128.80, 127.30, 127.22.



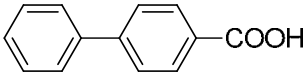
[1,1'-biphenyl]-4-amine

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.57 (t, *J*=8.0Hz, 2H), 7.41-7.56 (m, 4H), 7.19 (d, *J*=8.8Hz, 1H), 6.79 (d, *J*=8.0Hz, 2H), 3.75 (br, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 145.82, 141.17, 131.62, 128.67, 128.03, 126.42, 126.27, 115.39.



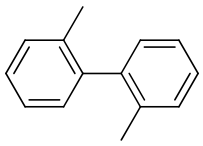
[1,1'-biphenyl]-3-ol

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.60-7.62 (m, 2H), 7.45-7.49 (m, 2H), 7.32-7.41 (m, 2H), 7.20-7.22 (m, 1H), 7.10 (t, *J*=2Hz, 1H), 6.84-6.87 (m, 1H), 4.89 (br, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 155.83, 143.06, 140.57, 130.03, 128.79, 127.52, 127.15, 119.84, 114.22, 114.13.



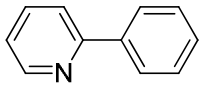
[1,1'-biphenyl]-4-carboxylic acid

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=11.66 (br, 1H), 8.22 (d, *J*=8.4Hz, 2H), 7.74(d, *J*=8.0Hz, 2H), 7.68 (d, *J*=7.2Hz, 2H), 7.52 (t, *J*=7.2Hz, 2H), 7.45 (t, *J*=7.2Hz, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 171.16, 146.56, 139.90, 130.78, 128.99, 128.33, 127.89, 127.36, 127.22.



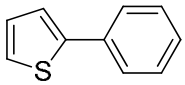
2,2'-dimethyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.32-7.39 (m, 6H), 7.23 (d, *J*=7.2Hz, 2H), 2.18 (s, 6H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 141.70, 135.90, 129.91, 129.39, 127.26, 125.65, 19.95.



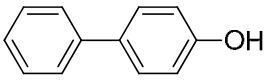
2-phenylpyridine

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.75 (d, *J*=4.4Hz, 1H), 8.02-8.04 (m, 2H), 7.76-7.82 (m, 2H), 7.52 (t, *J*=7.2Hz, 2H), 7.46 (t, *J*=7.2Hz, 1H), 7.26-7.28 (m, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 157.42, 149.56, 139.24, 136.94, 129.05, 128.80, 127.19, 126.97, 122.16, 120.68.



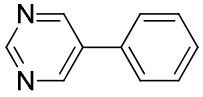
2-phenylthiophene

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.69 (d, *J*=7.2Hz, 2H), 7.45 (t, *J*=7.6Hz, 2H), 7.34-7.39 (m, 3H), 7.14-7.16 (m, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS):144.50, 134.47, 128.69, 128.08, 127.53, 126.02, 124.87, 123.15.



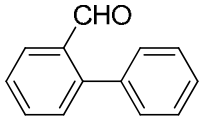
[1,1'-biphenyl]-4-ol

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.57 (d, *J*=7.2Hz, 2H), 7.52 (d, *J*=8.8Hz, 2H), 7.45 (t, *J*=7.2Hz, 2H), 7.34 (t, *J*=7.6Hz, 1H), 6.94 (d, *J*=8.4Hz, 2H), 4.83 (s, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 155.06, 140.77, 134.08, 128.76, 128.43, 126.75, 115.67.



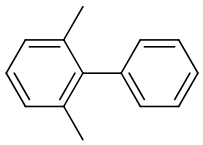
5-phenylpyrimidine

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=9.23 (s, 1H), 8.98 (s, 2H), 7.60-7.62 (m, 2H), 7.51-7.56 (m, 2H), 7.49 (t, *J*=2.4Hz, 1H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 157.49, 154.94, 134.36, 134.27, 129.46, 129.05, 127.02.



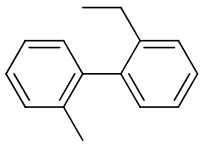
[1,1'-biphenyl]-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=10.01 (s, 1H), 8.05 (d, *J*=8.0Hz, 1H), 7.64-7.68 (m, 1H), 7.46-7.53 (m, 5H), 7.41-7.46 (m, 2H); ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): 192.44, 145.98, 137.75, 133.72, 133.60, 130.81, 130.13, 128.46, 128.15, 127.80, 127.57.



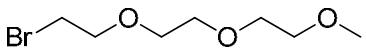
2,6-dimethyl-1,1'-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.46 (t, *J*=7.2 Hz, 2H), 7.38 (d, *J*=7.6 Hz, 1H), 7.14-7.21 (m, 5H), 2.07 (s, 6H).

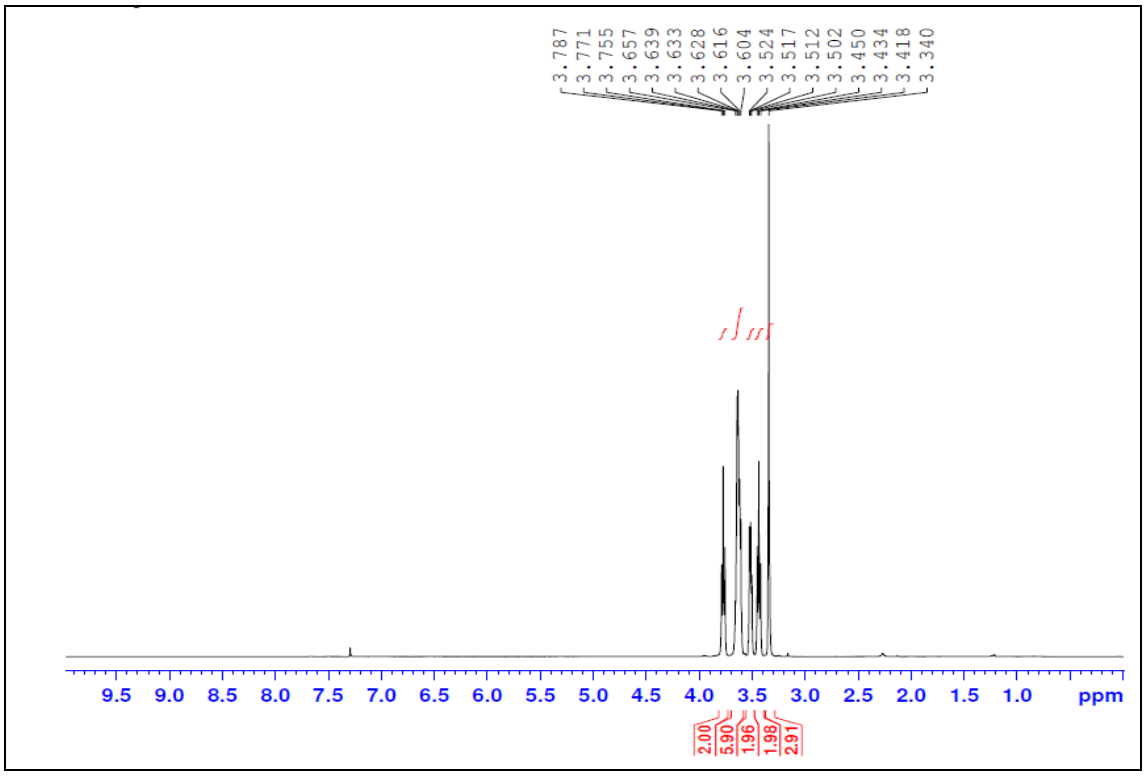


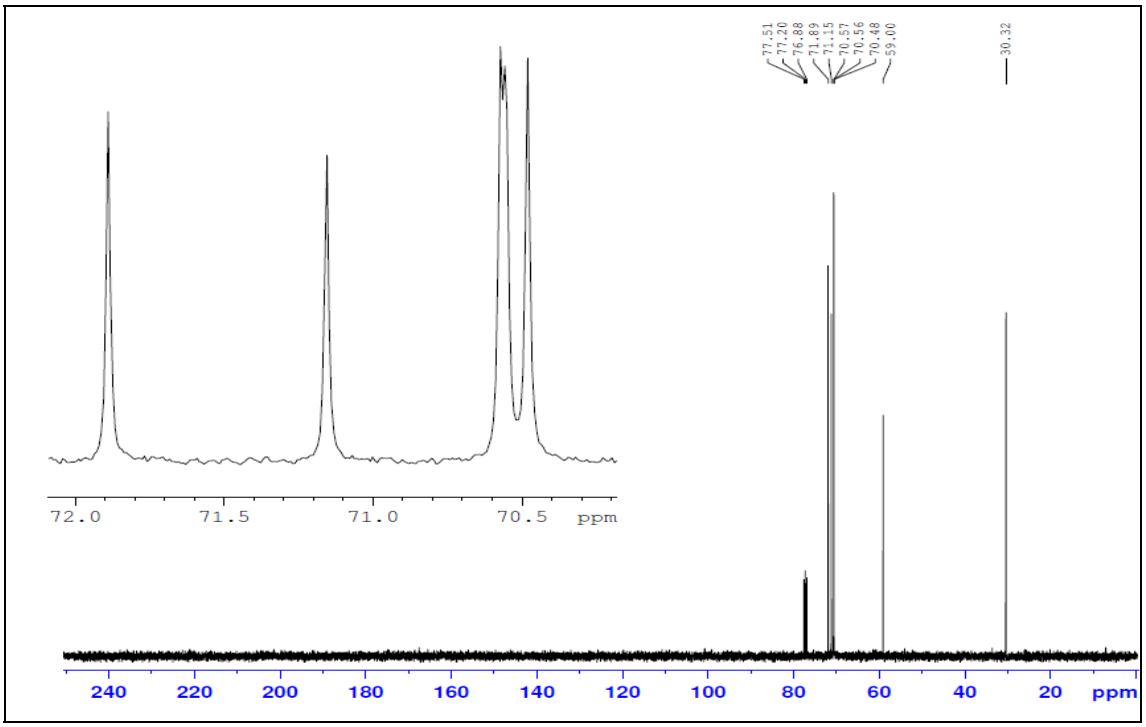
2-ethyl-2'-methyl-1,1'-biphenyl

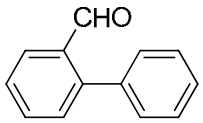
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ= 7.36 (d, *J*=4.0 Hz, 2H), 7.24-7.33 (m, 4H), 7.17 (d, *J*=7.2 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 1H), 2.33-2.52 (m, 2H), 2.10 (s, 3H), 1.08 (t, *J*=7.6 Hz, 3H); ^{13}C-NMR (63 MHz, CD_3COCD_3, 25 ºC, TMS): 14.7, 19.3, 25.9, 125.4, 125.6, 127.2, 127.5, 128.3, 129.3, 129.4, 129.8, 135.5, 140.9, 141.4, 141.6.



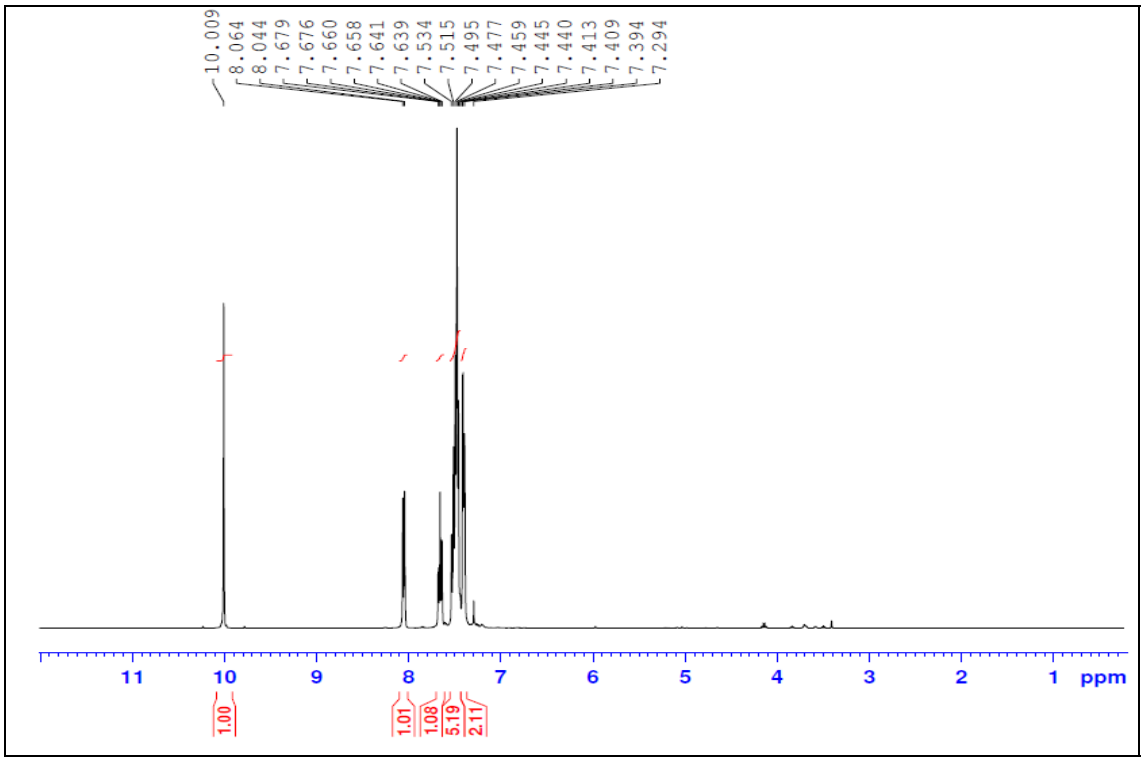
1-(2-(2-methoxyethoxy)ethoxy)-2- bromoethane

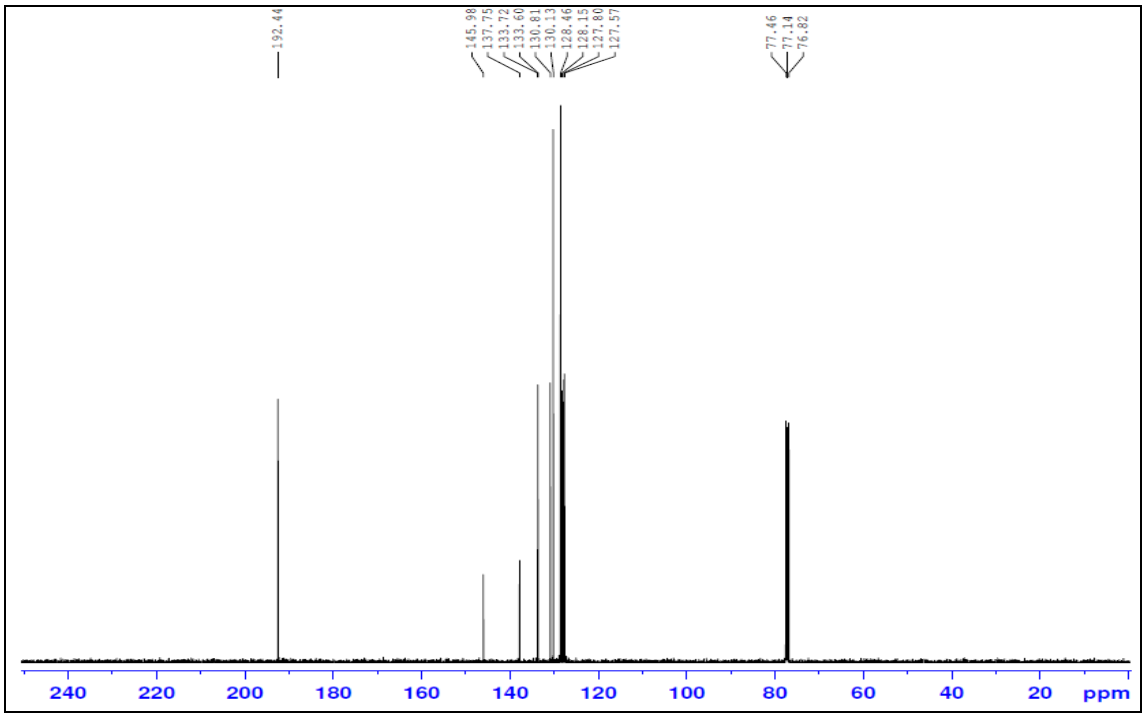


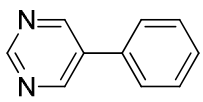




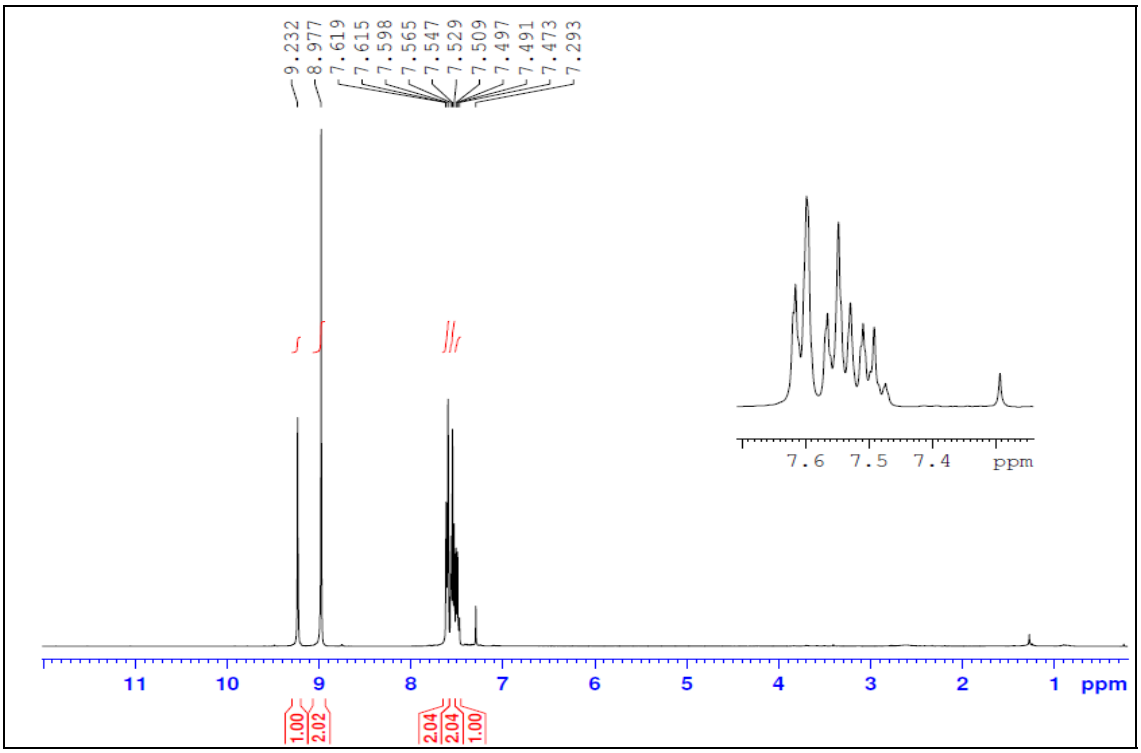
[1,1'-biphenyl]-2-carbaldehyde

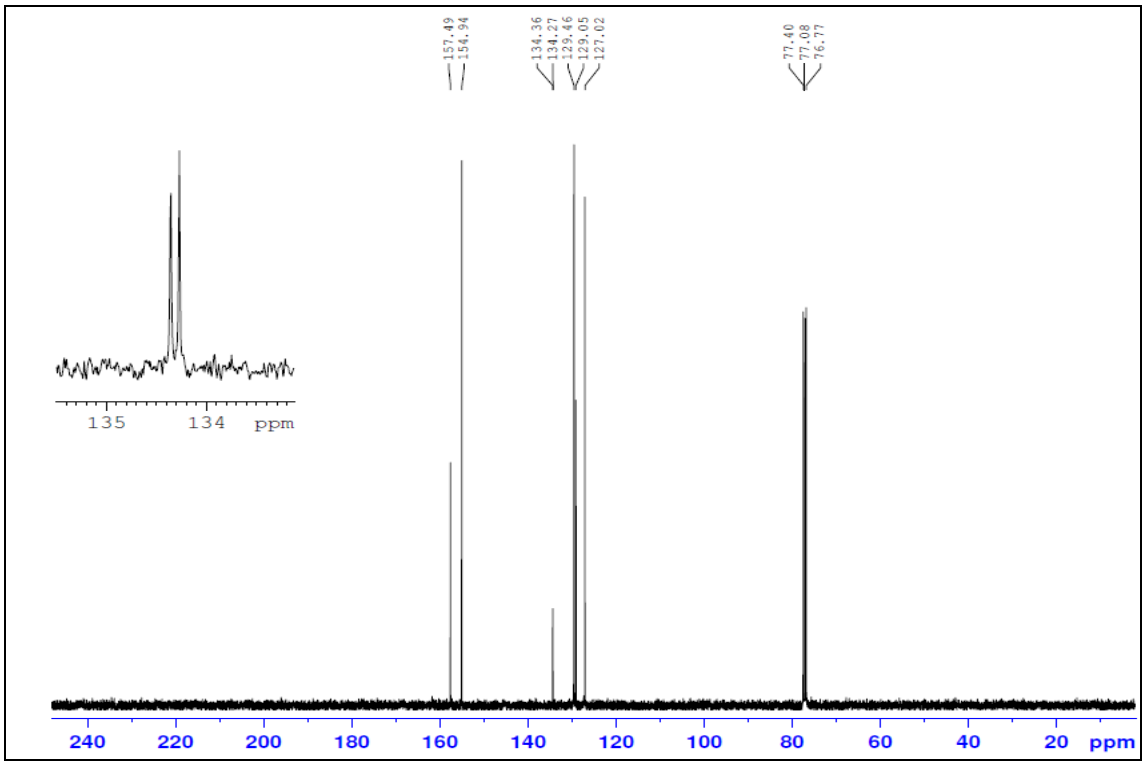


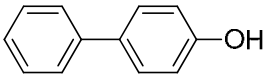




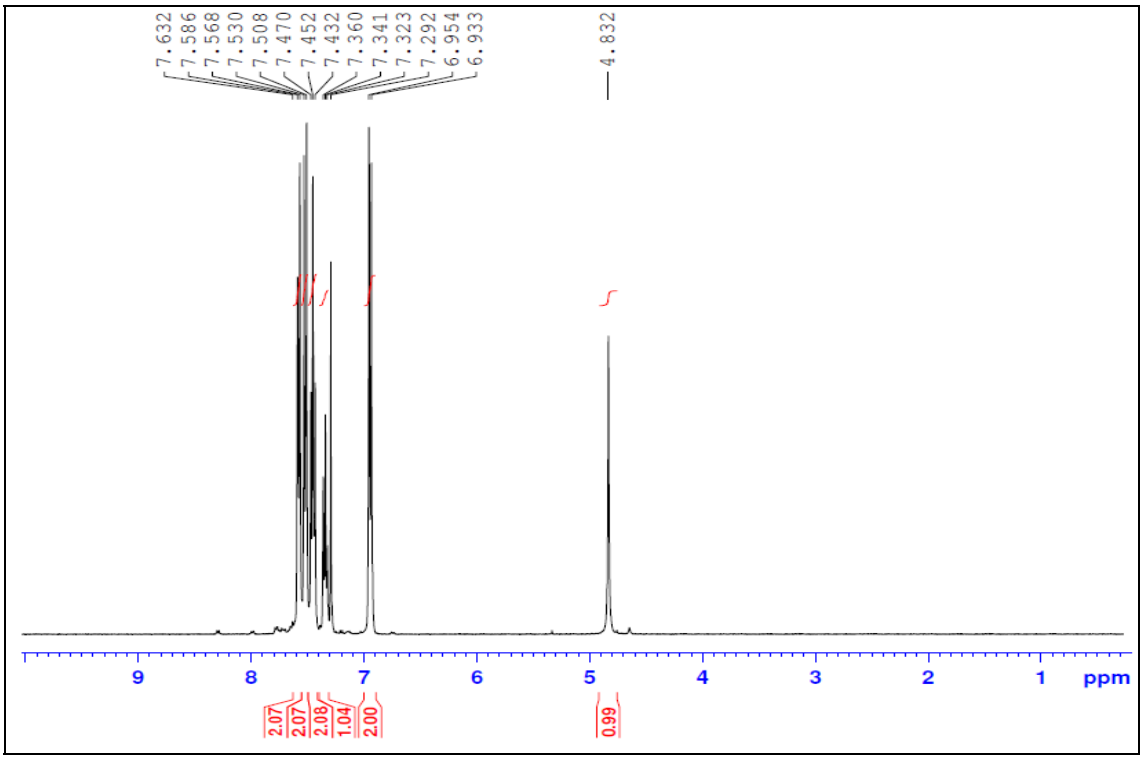
5-phenylpyrimidine

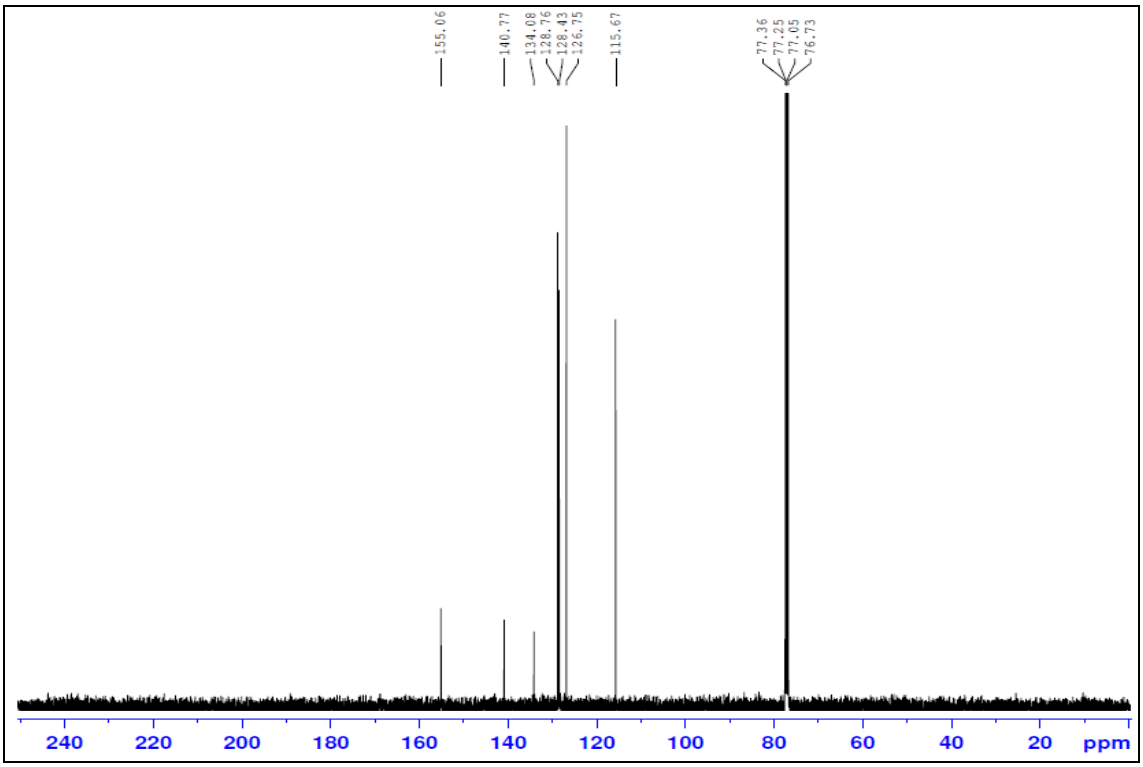


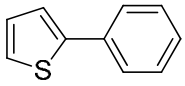




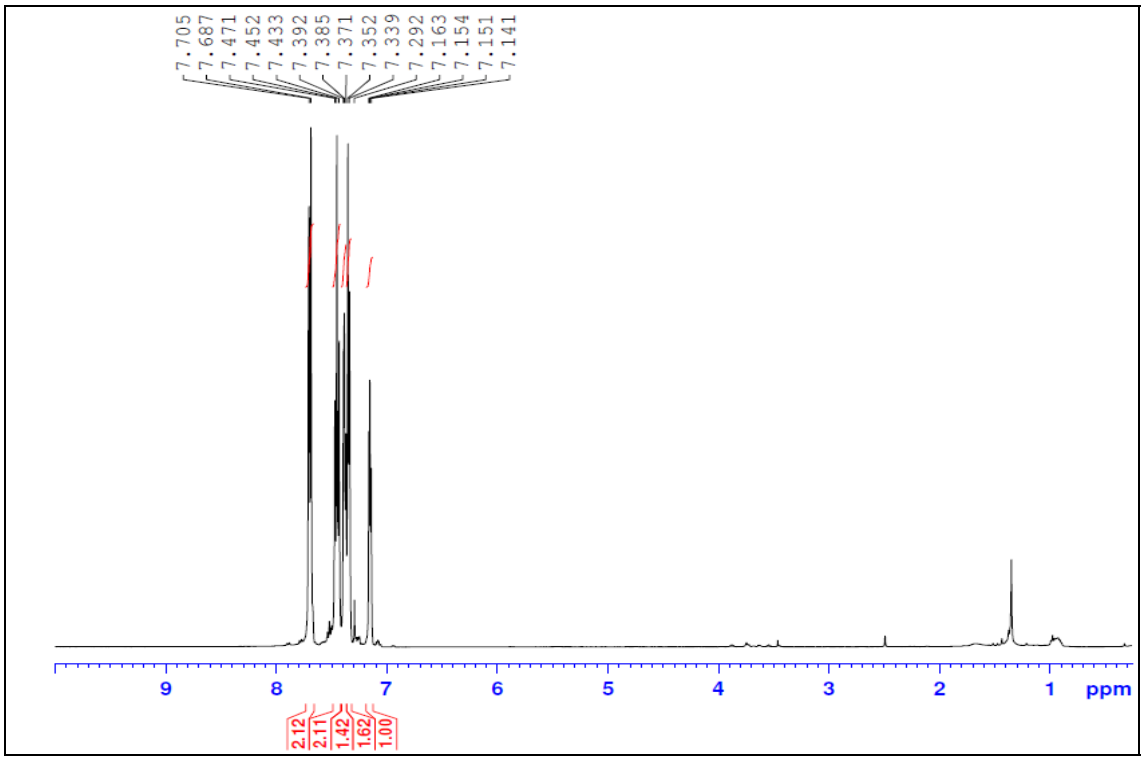
[1,1'-biphenyl]-4-ol

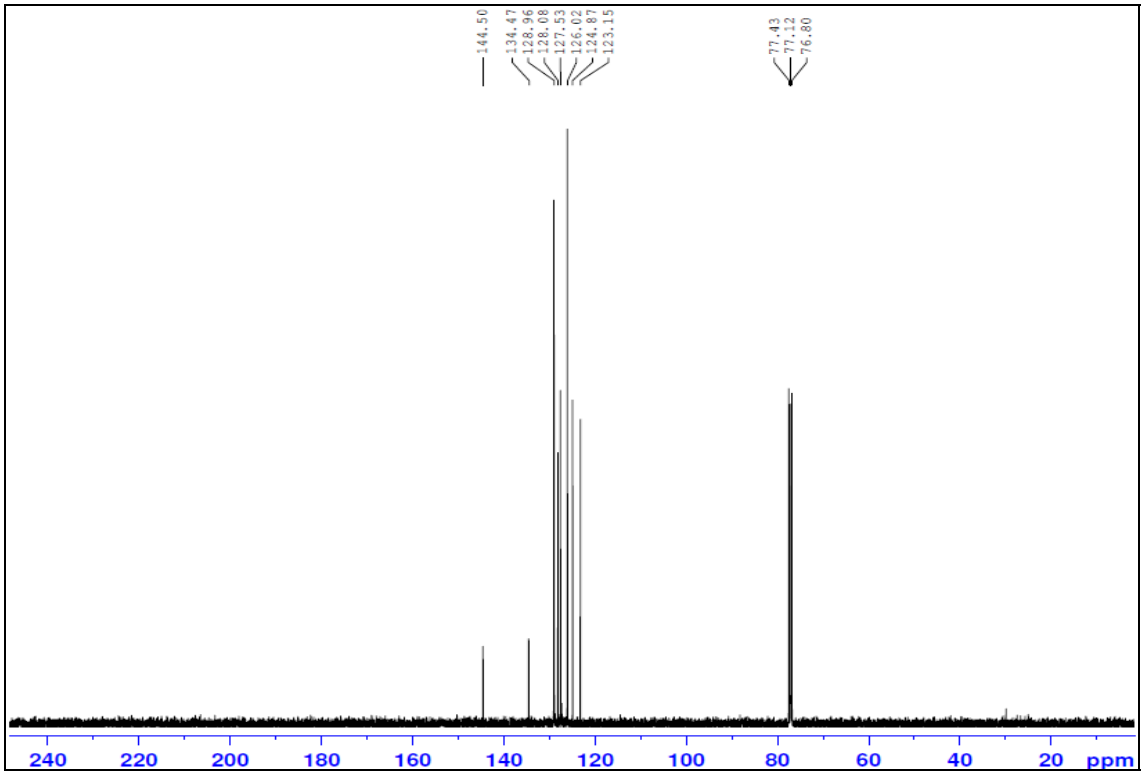


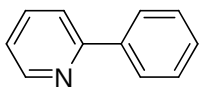




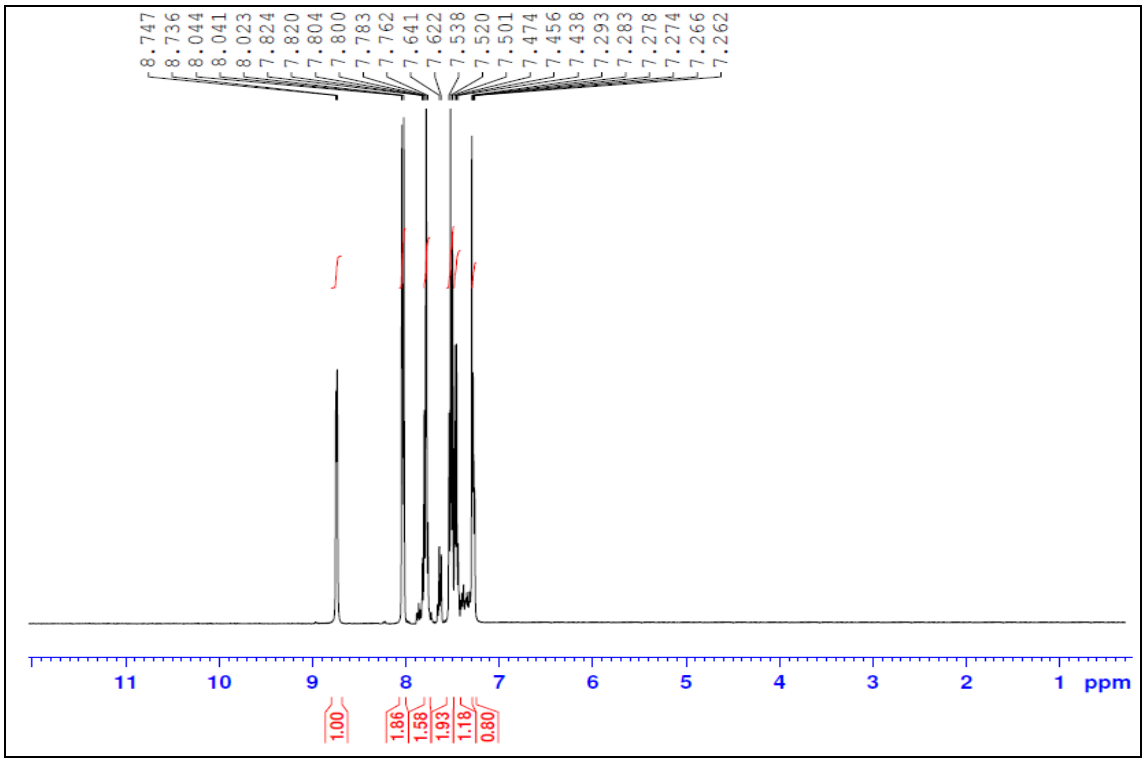
2-phenylthiophene







2-phenylpyridine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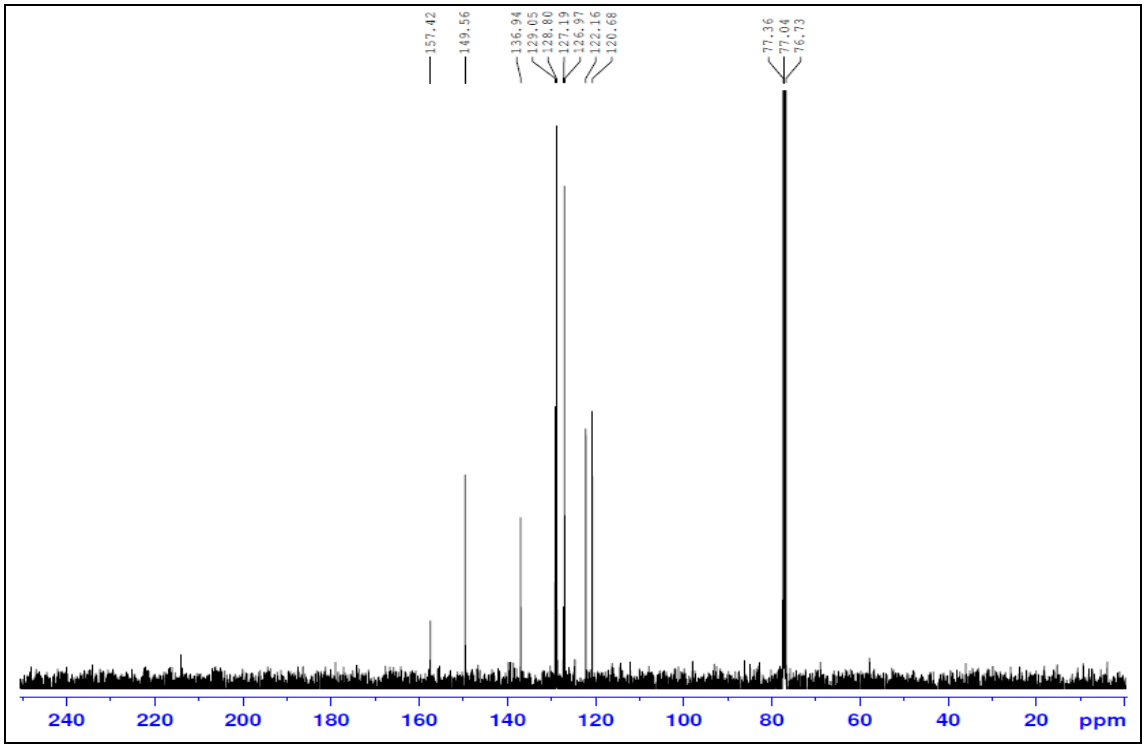
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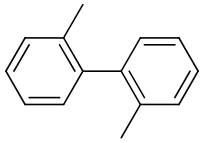
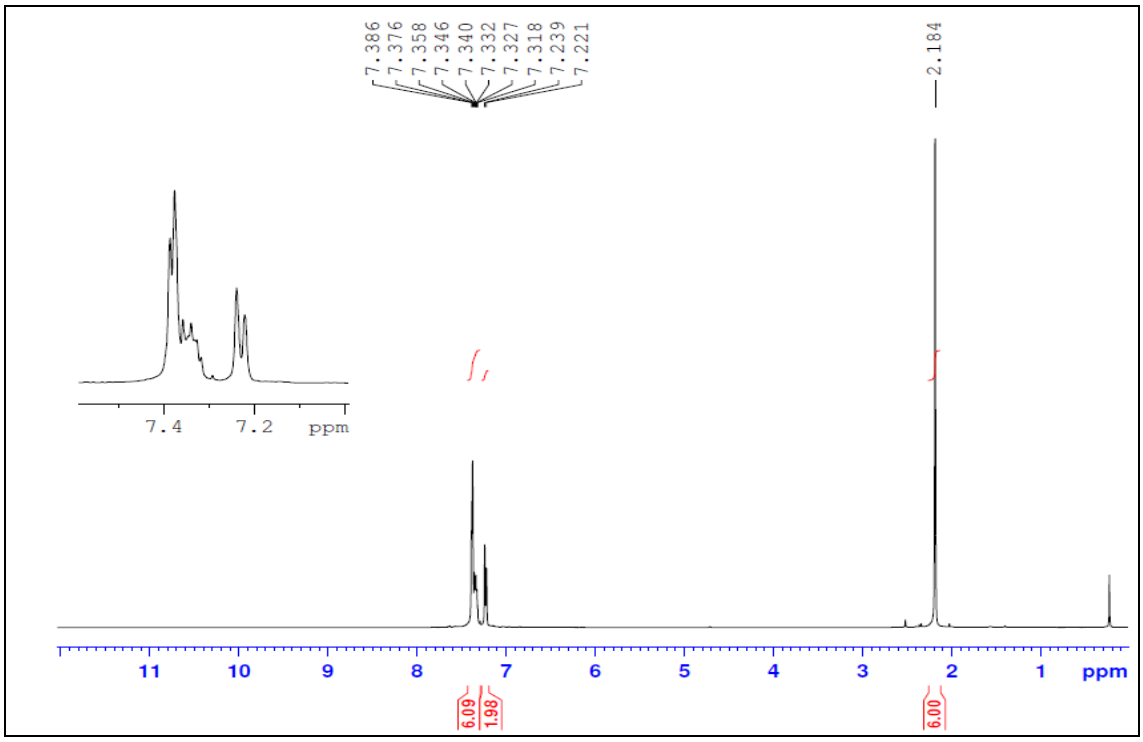
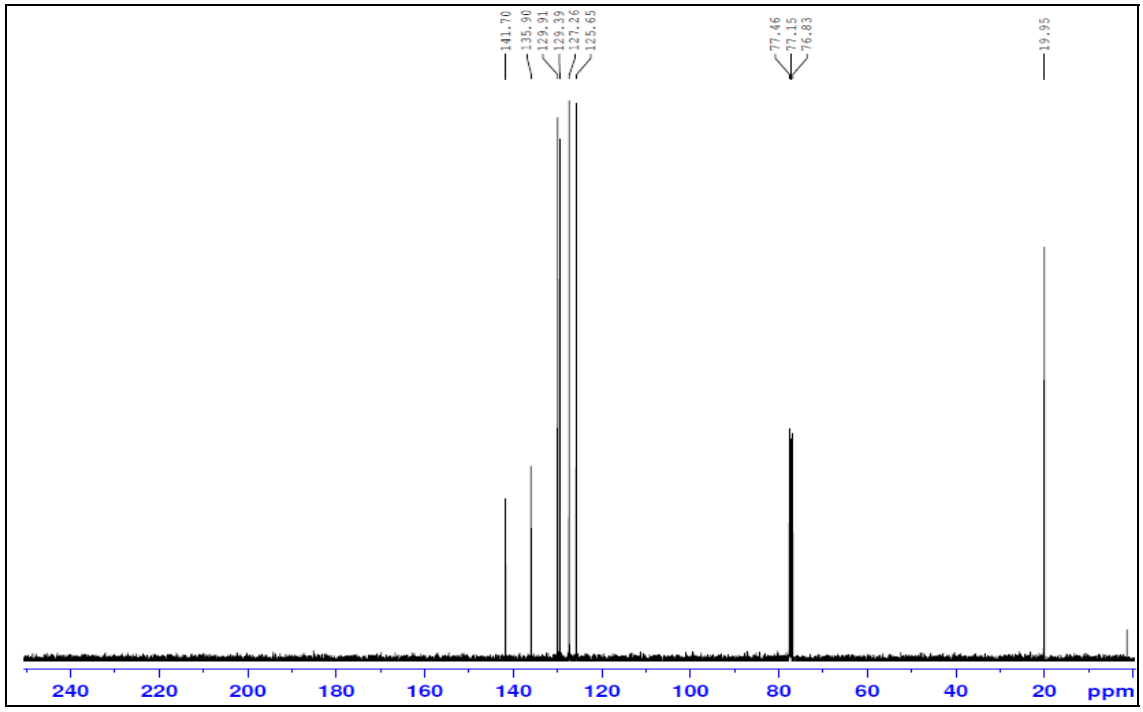
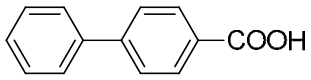


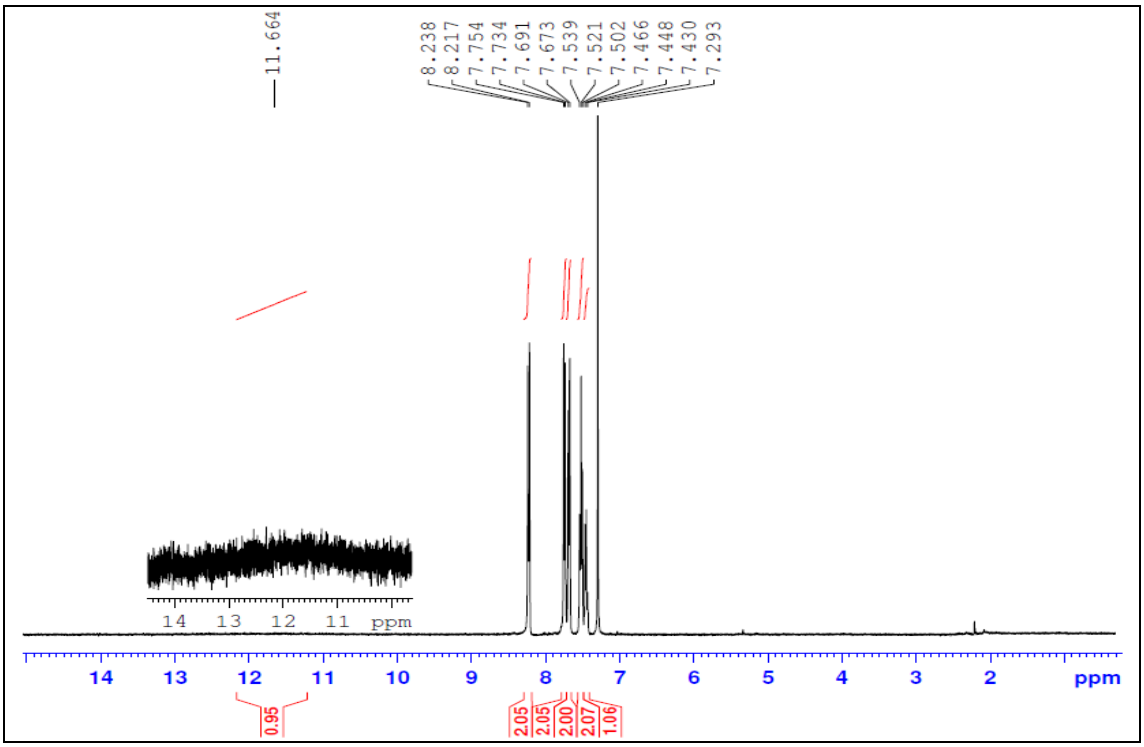
2,2'-dimethyl-1,1'-biphenyl

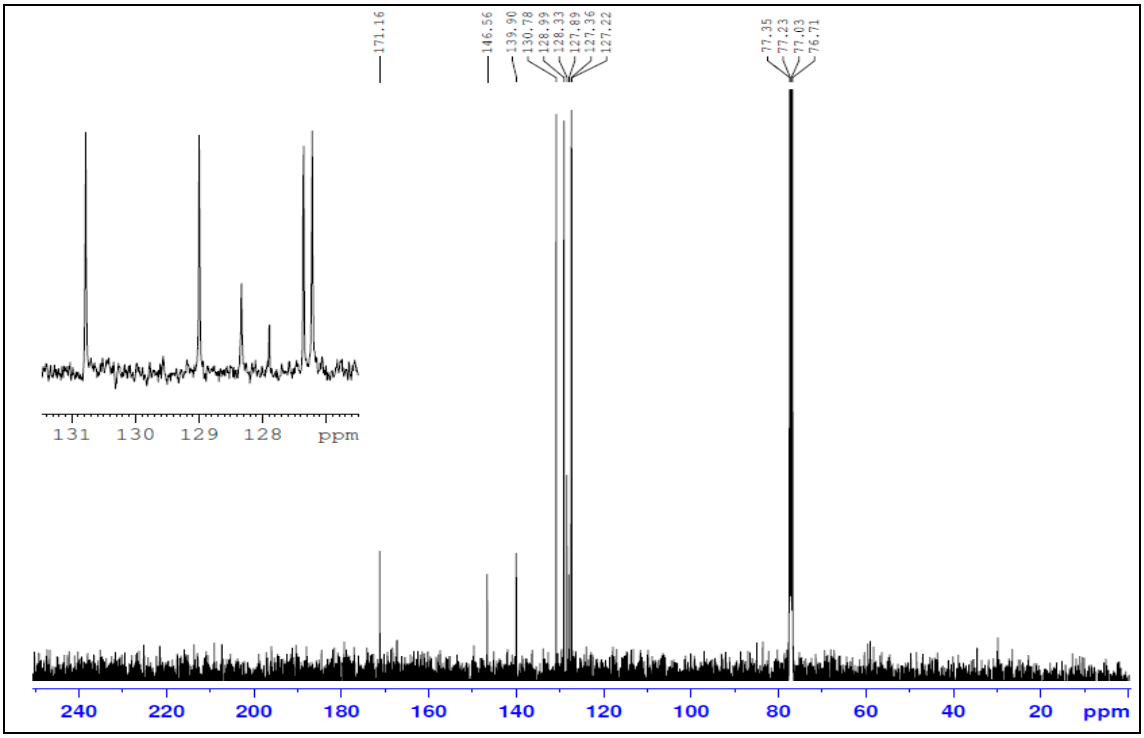


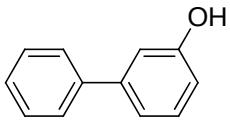




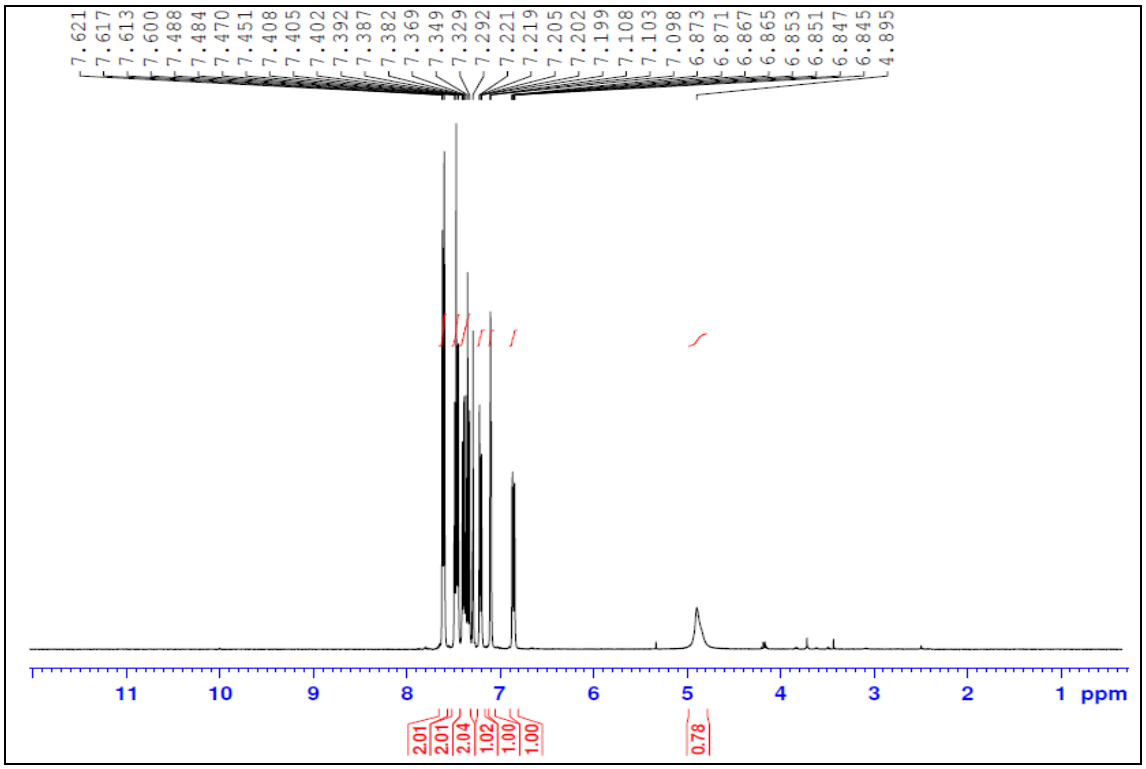
[1,1'-biphenyl]-4-carboxylic acid

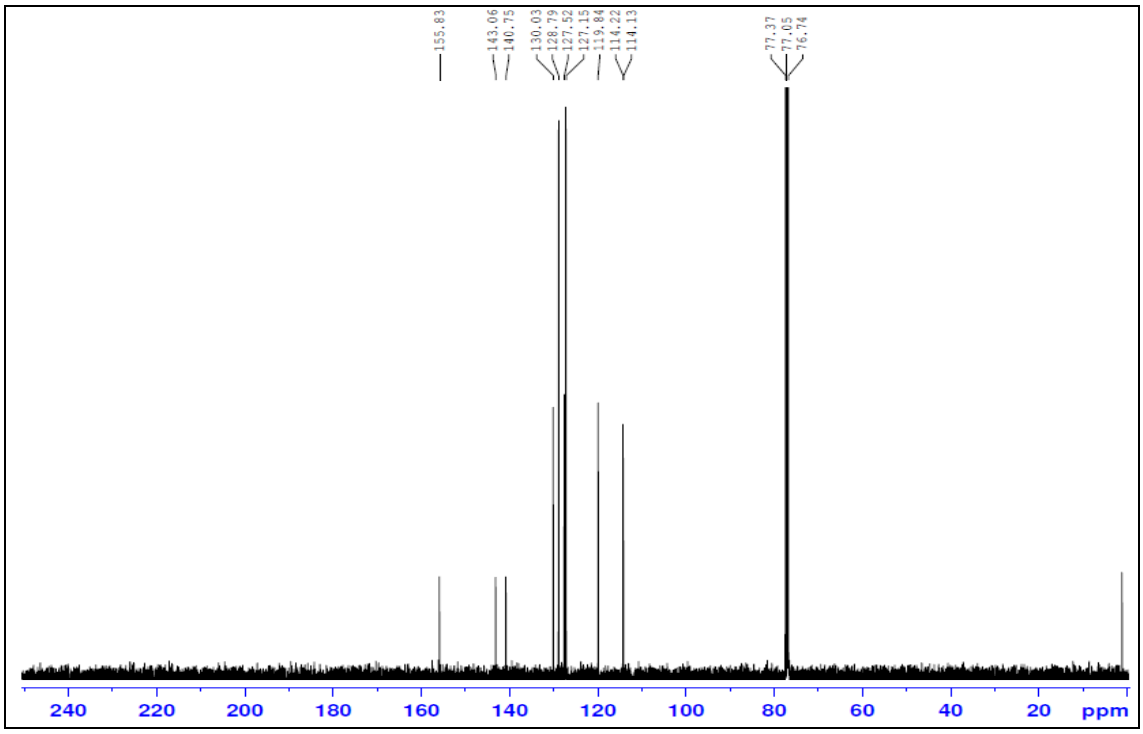


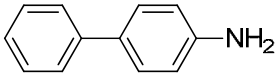




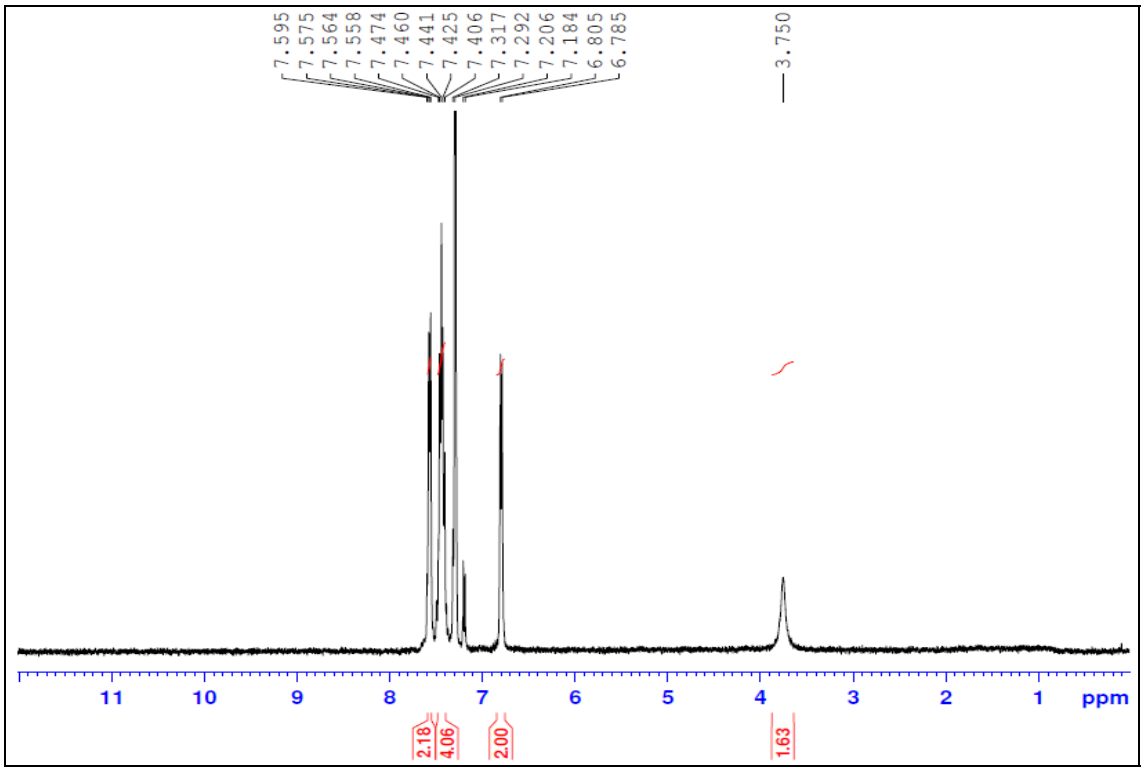
[1,1'-biphenyl]-3-ol

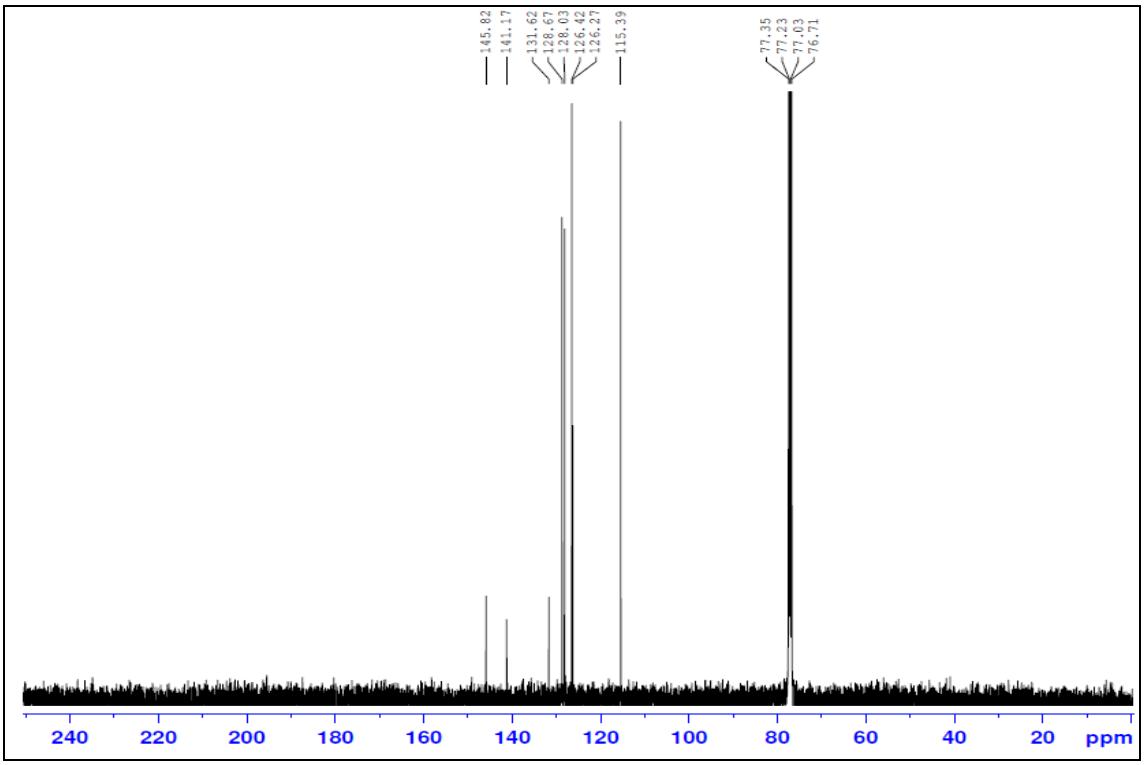


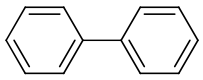




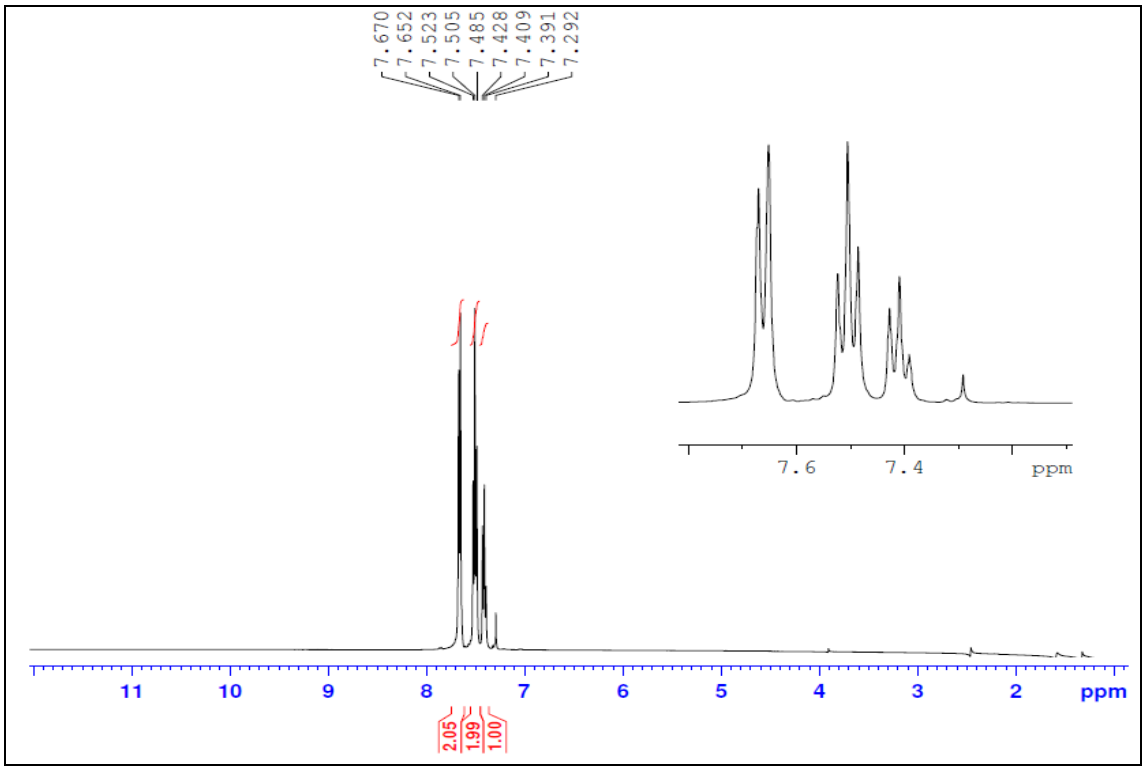
[1,1'-biphenyl]-4-amine







1,1'-biphenyl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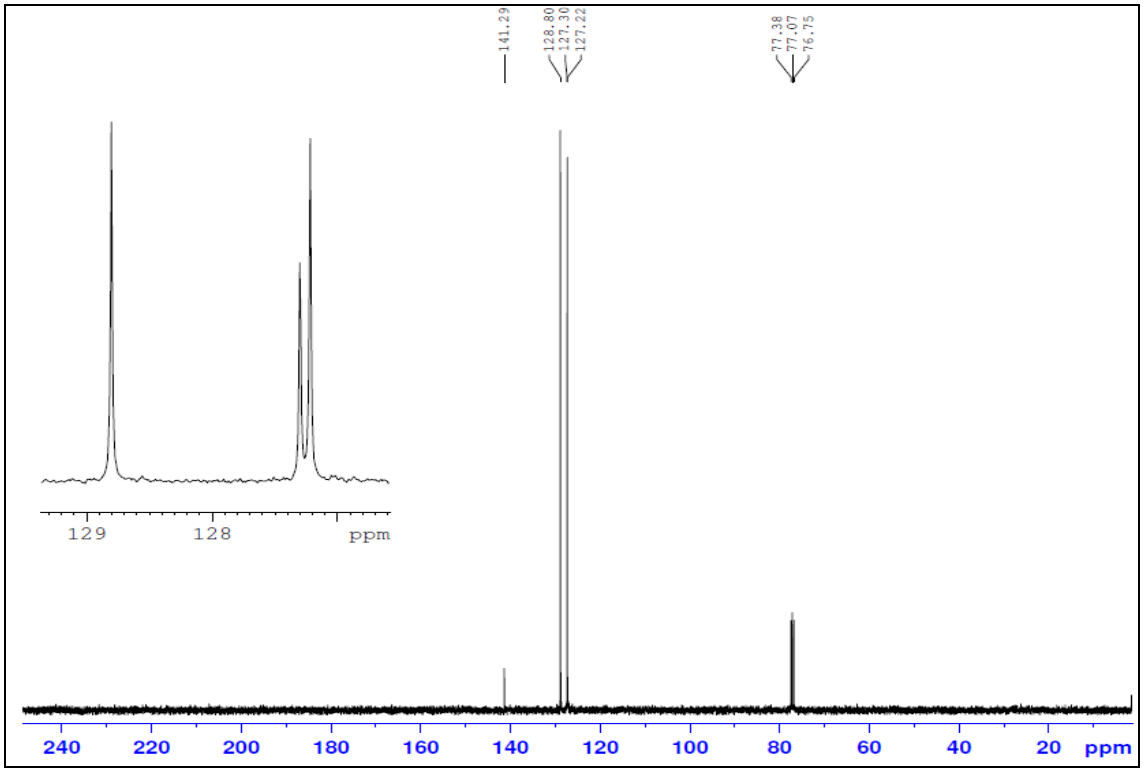
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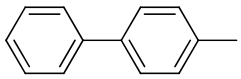
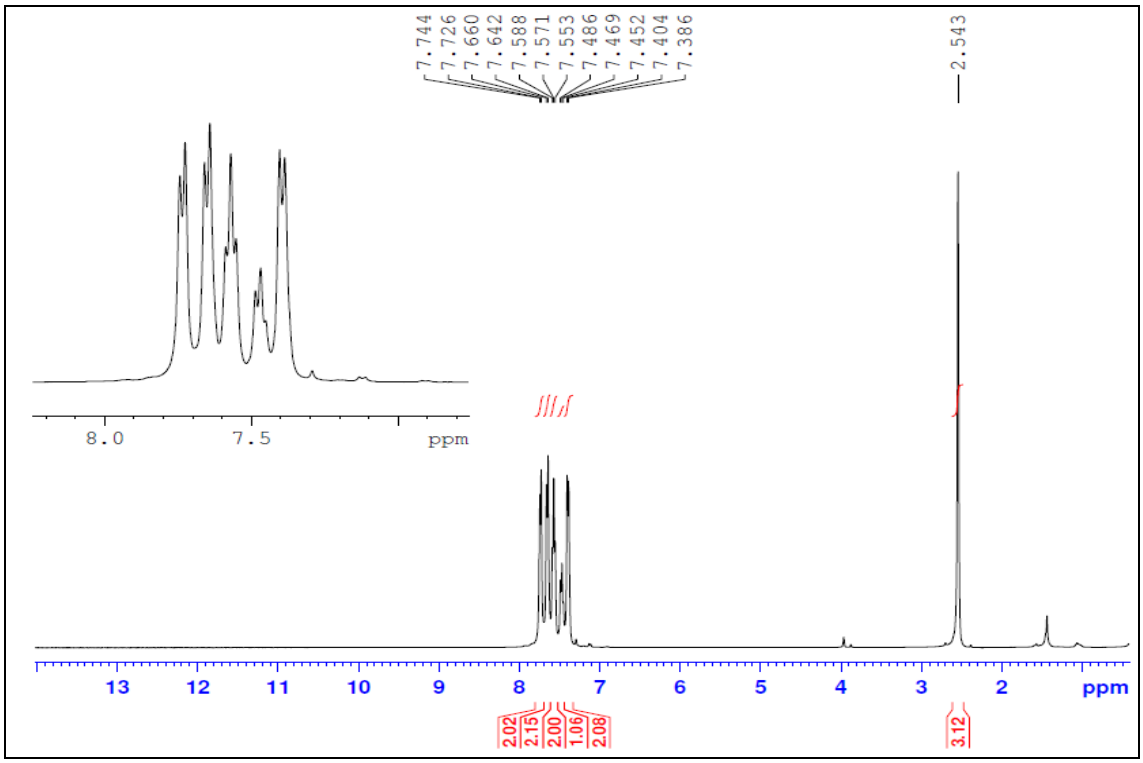
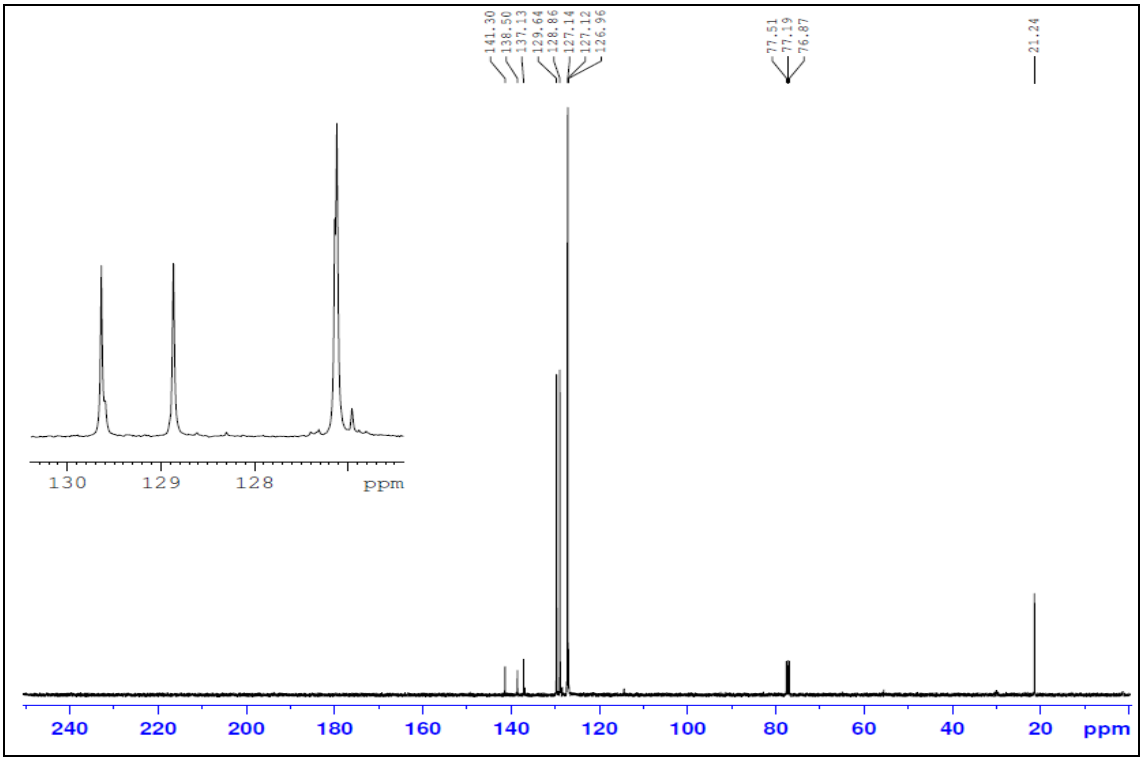
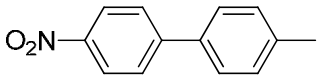


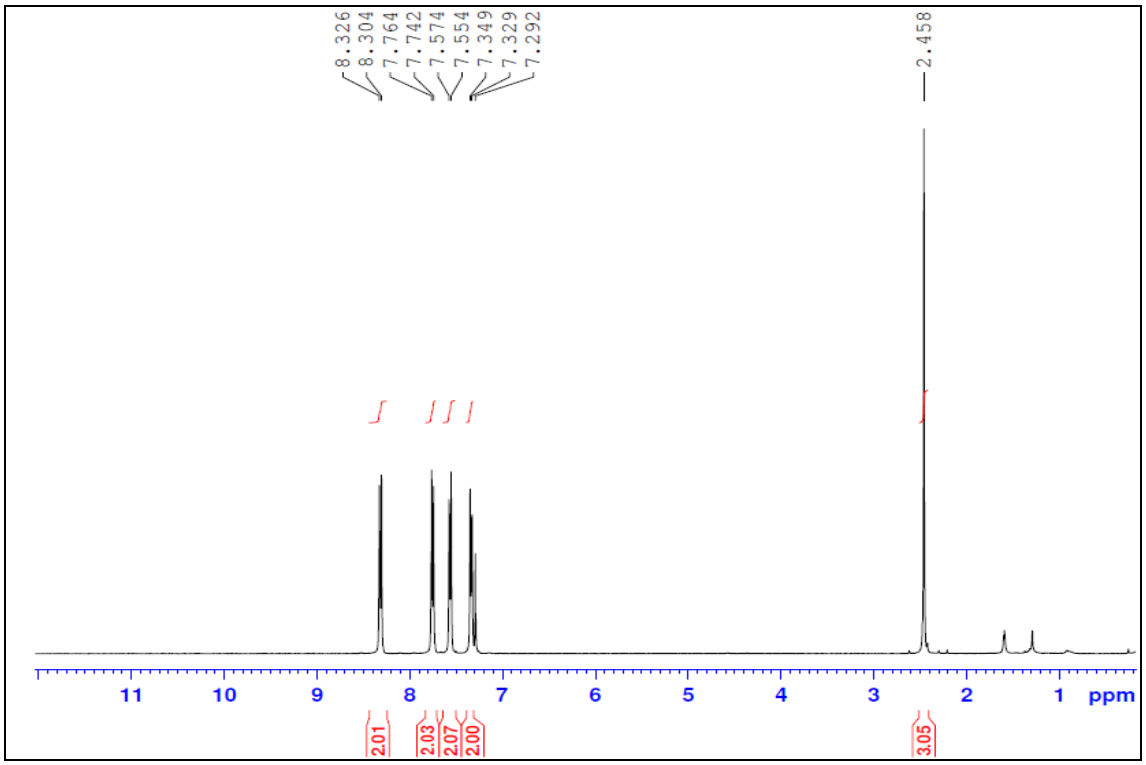
4-methyl-1,1'-biphenyl

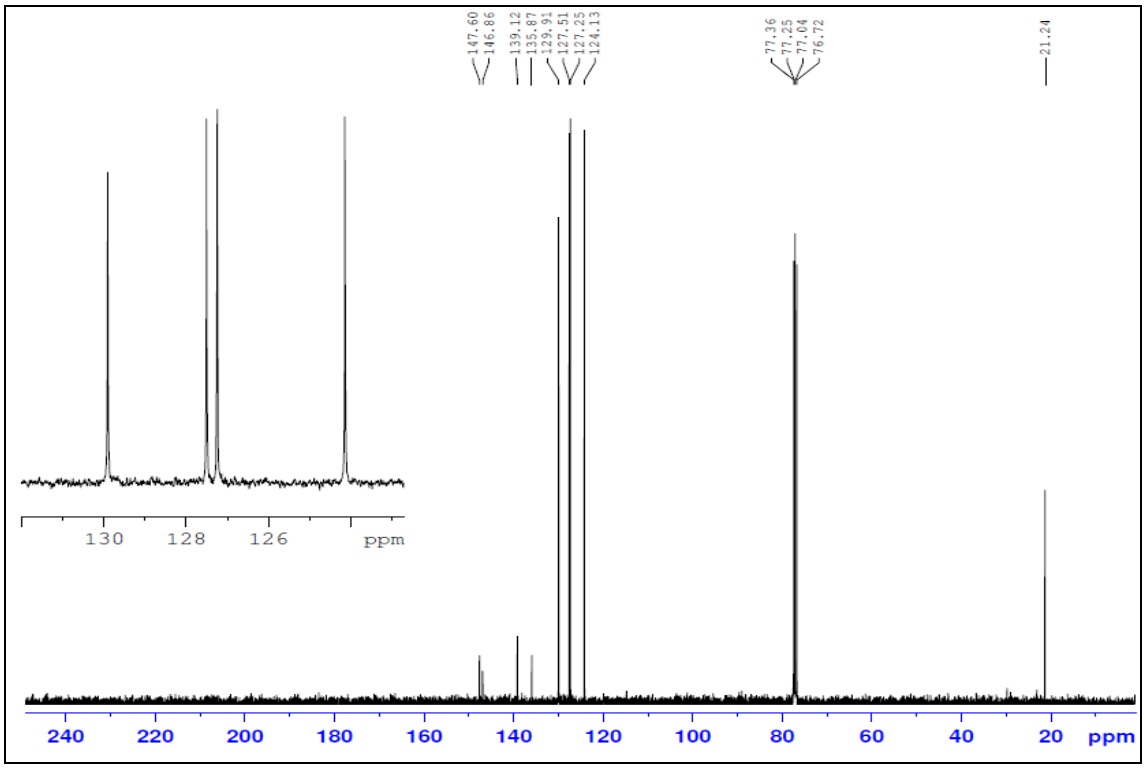


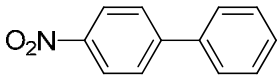




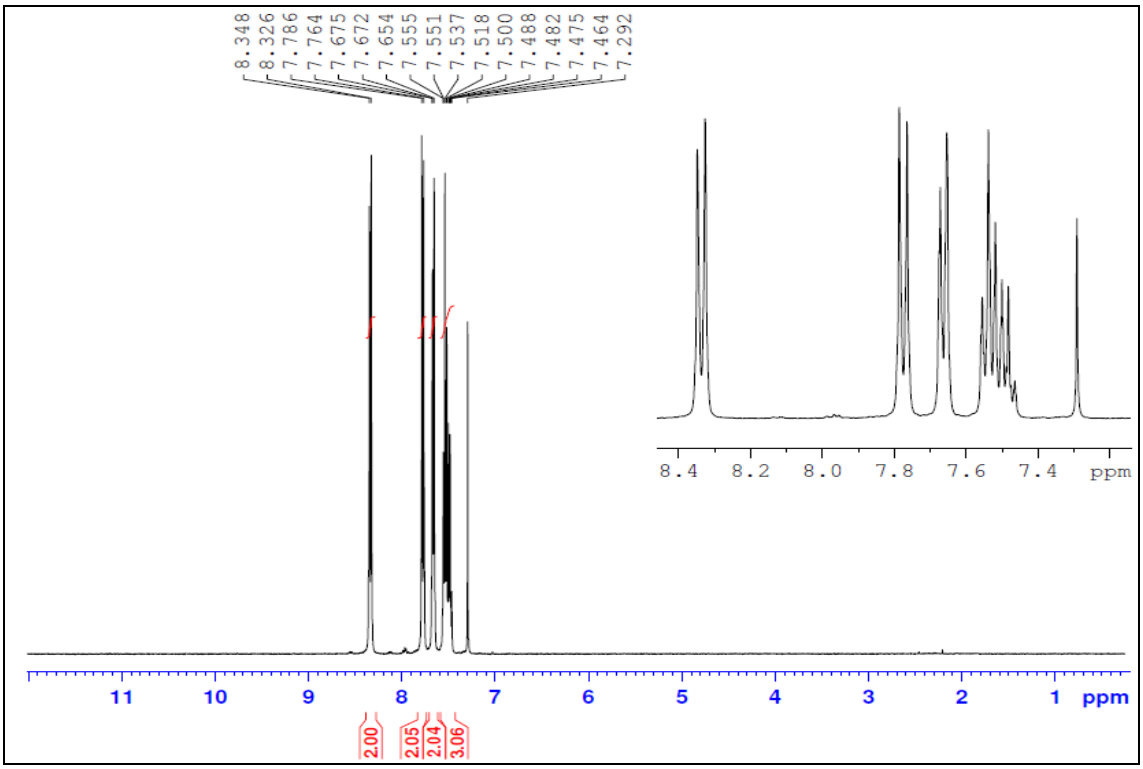
4-methyl-4'-nitro-1,1'-biphenyl

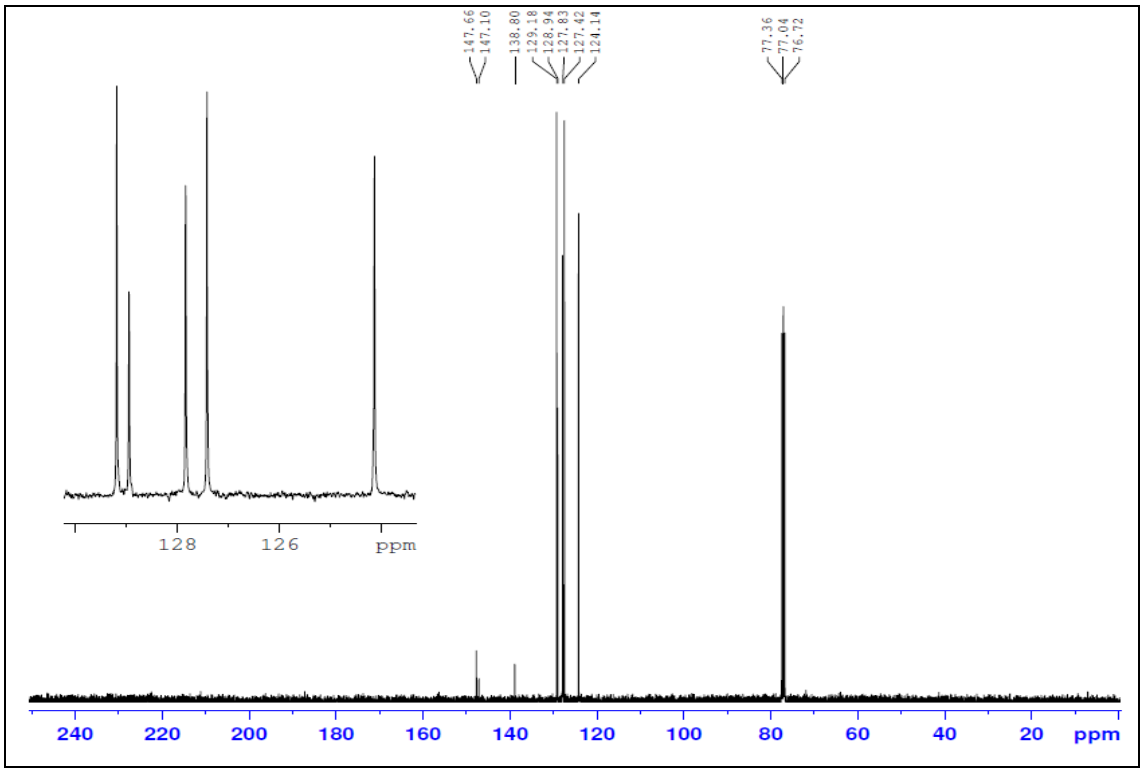


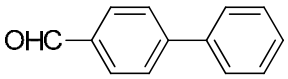




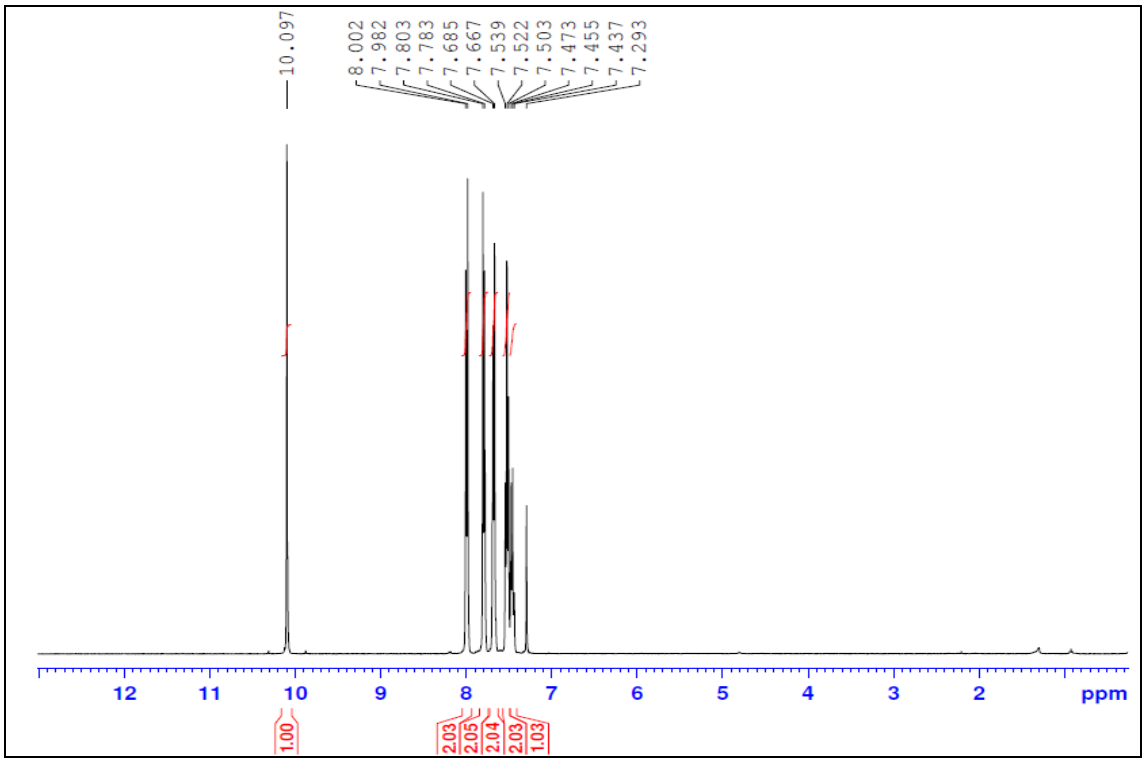
4-nitro-1,1'-biphenyl

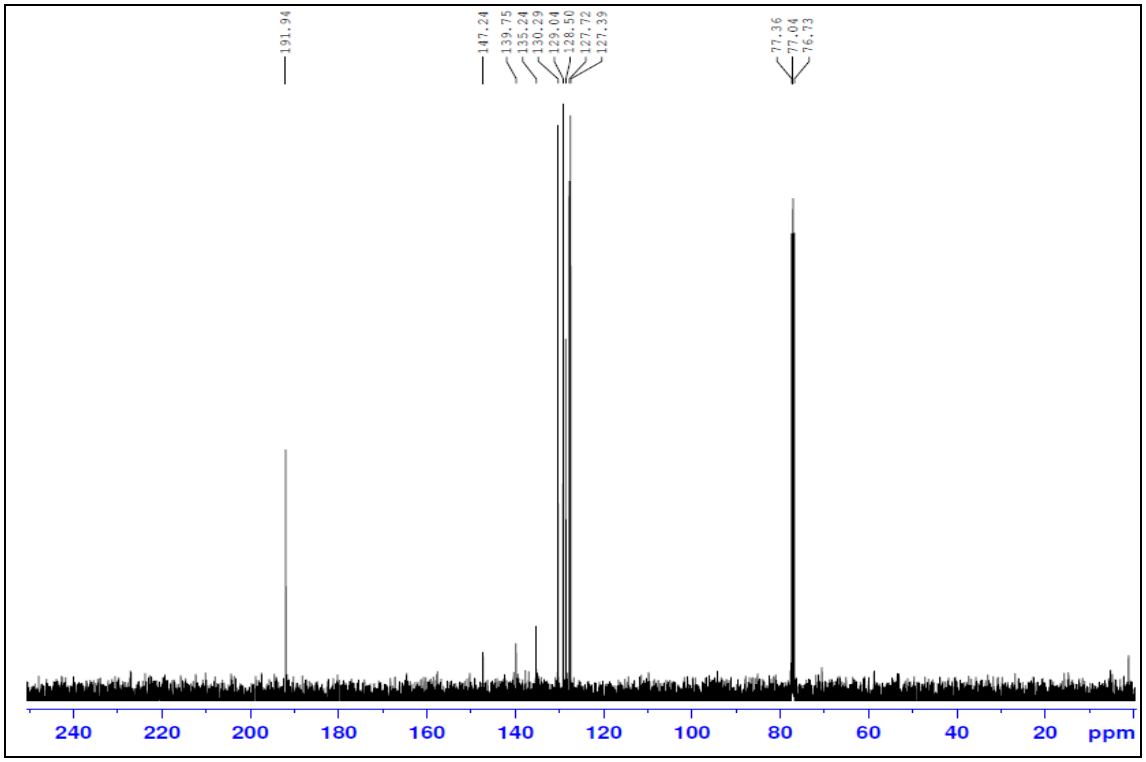


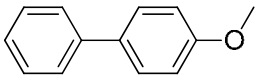




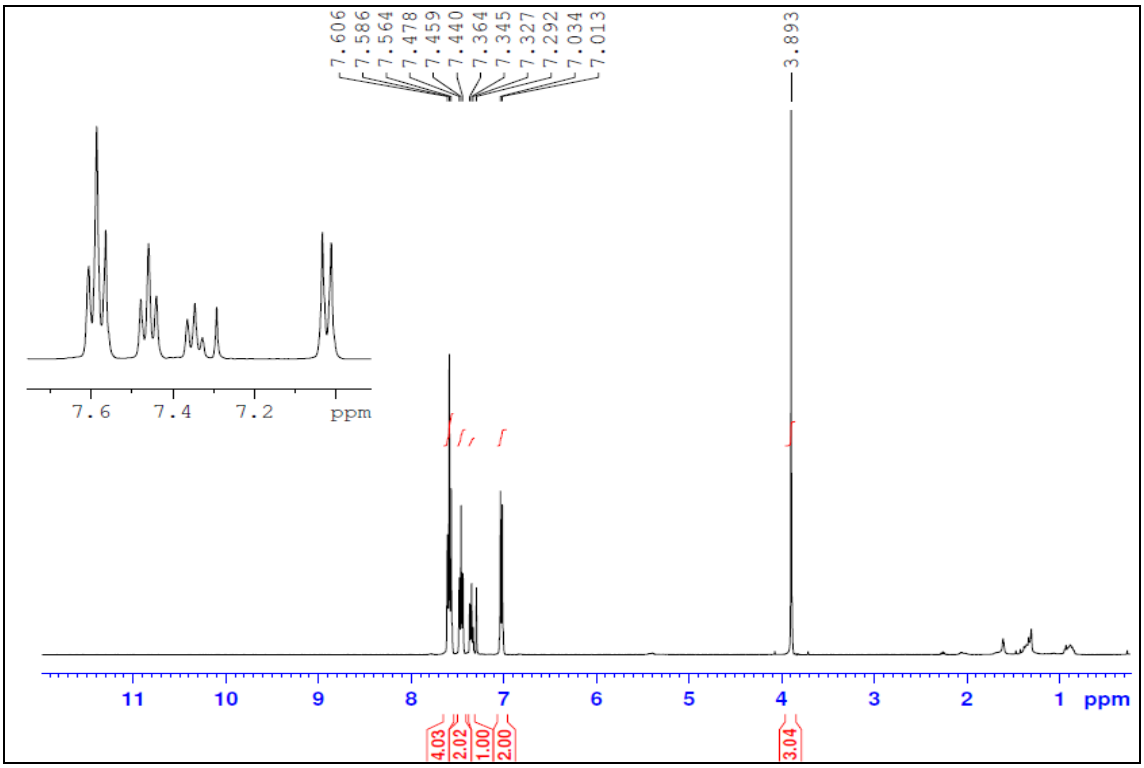
[1,1'-biphenyl]-4-carbaldehyde

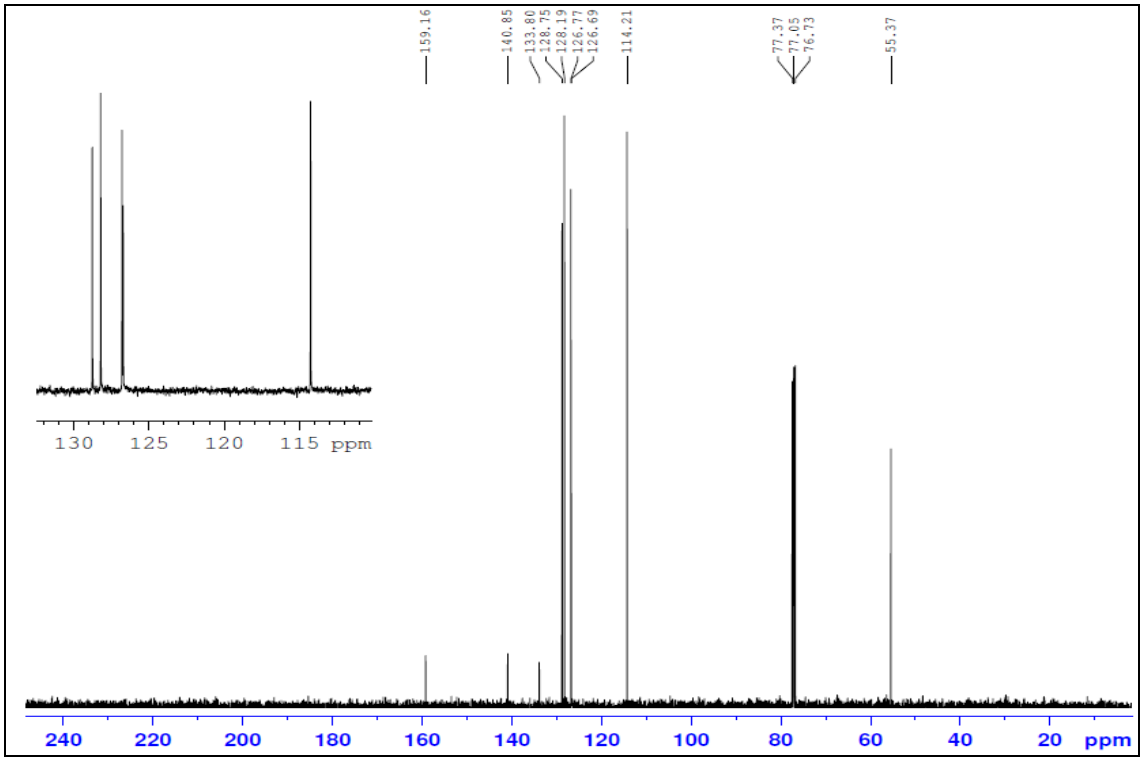


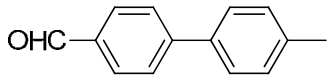




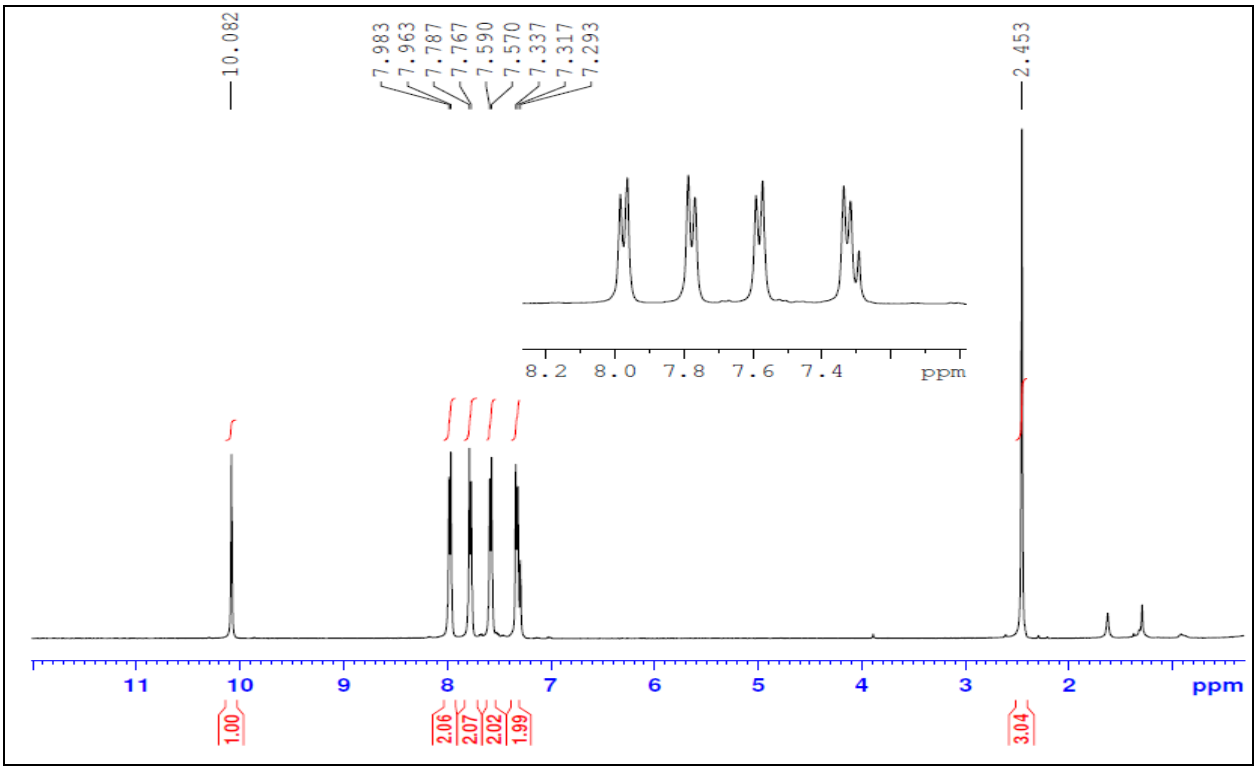
4-methoxy-1,1'-biphenyl

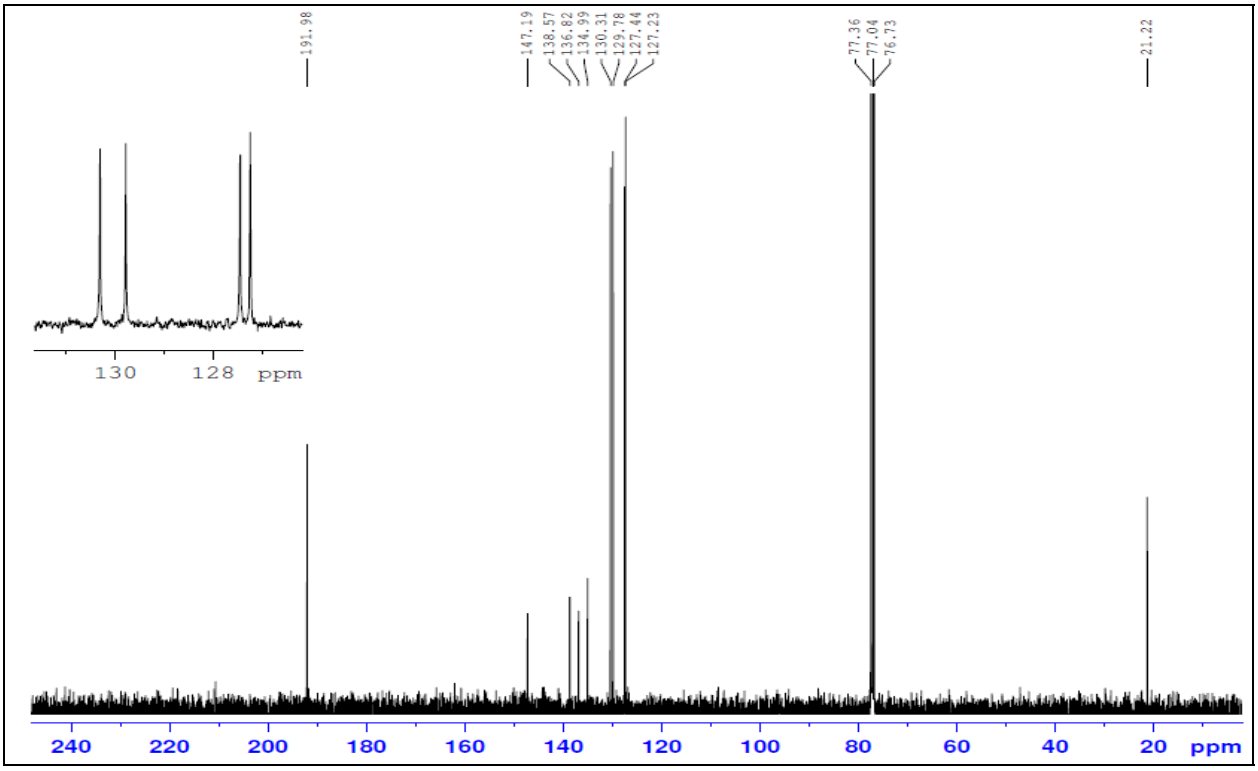


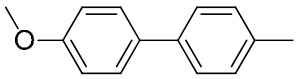




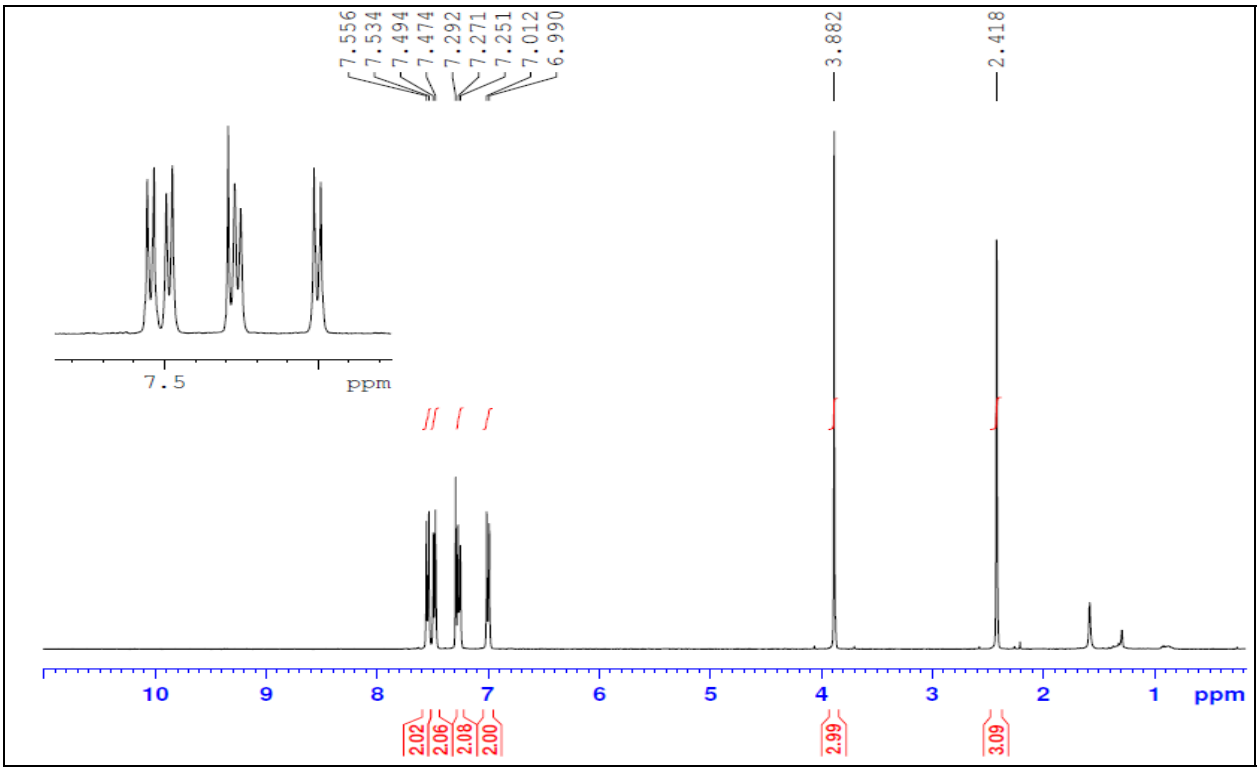
4'-methyl-[1,1'-biphenyl]-4-carbaldehyde

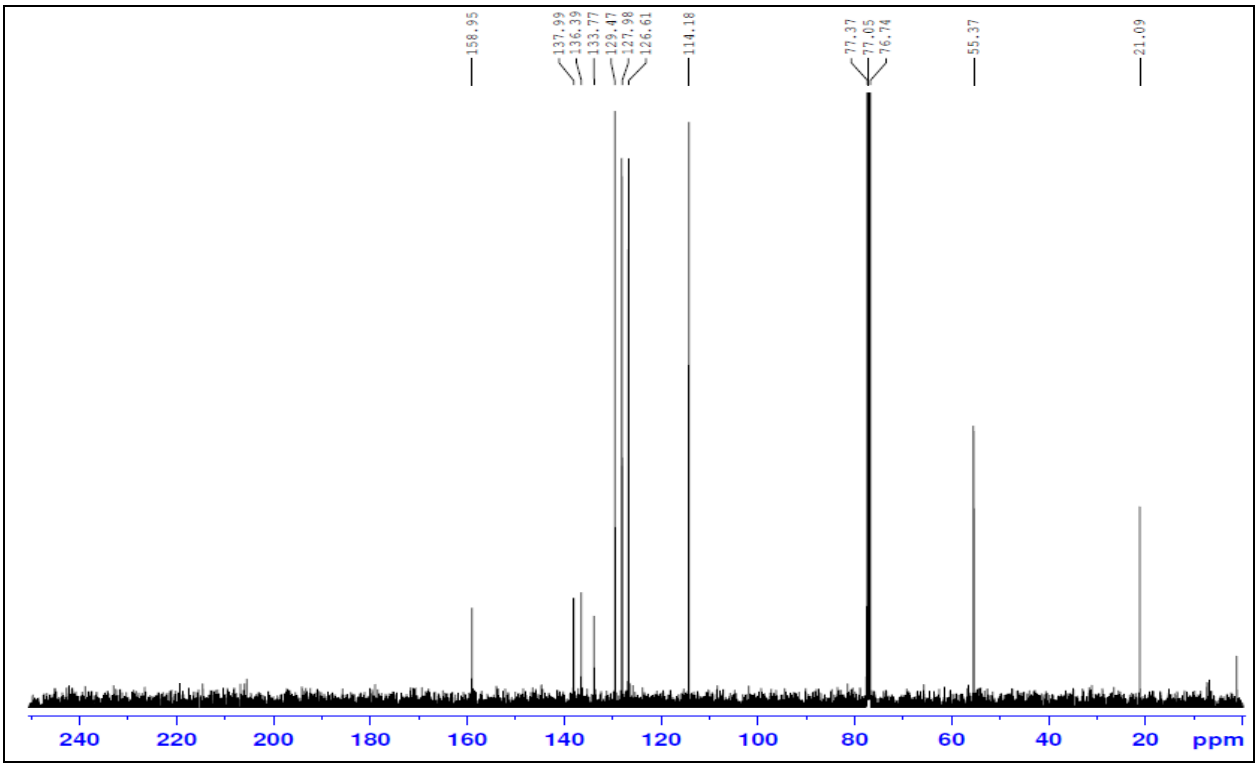


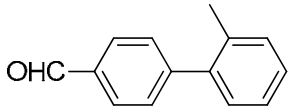




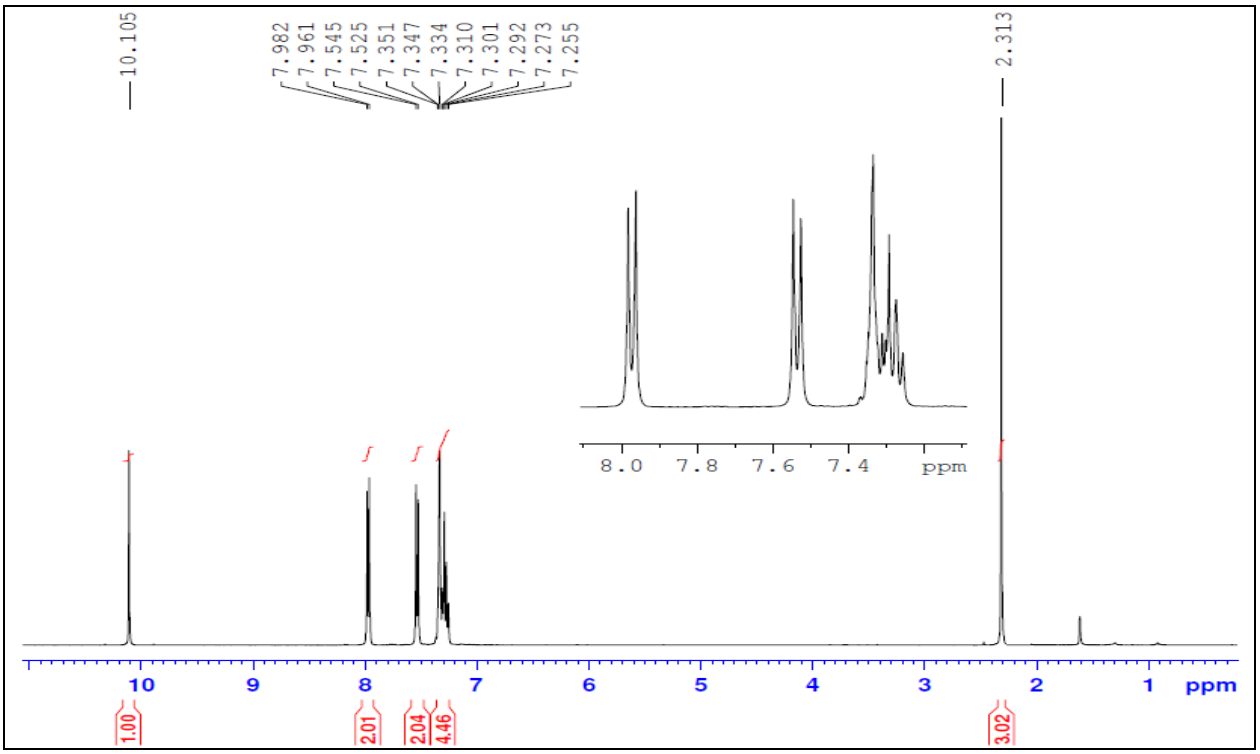
4-methoxy-4'-methyl-1,1'-biphenyl

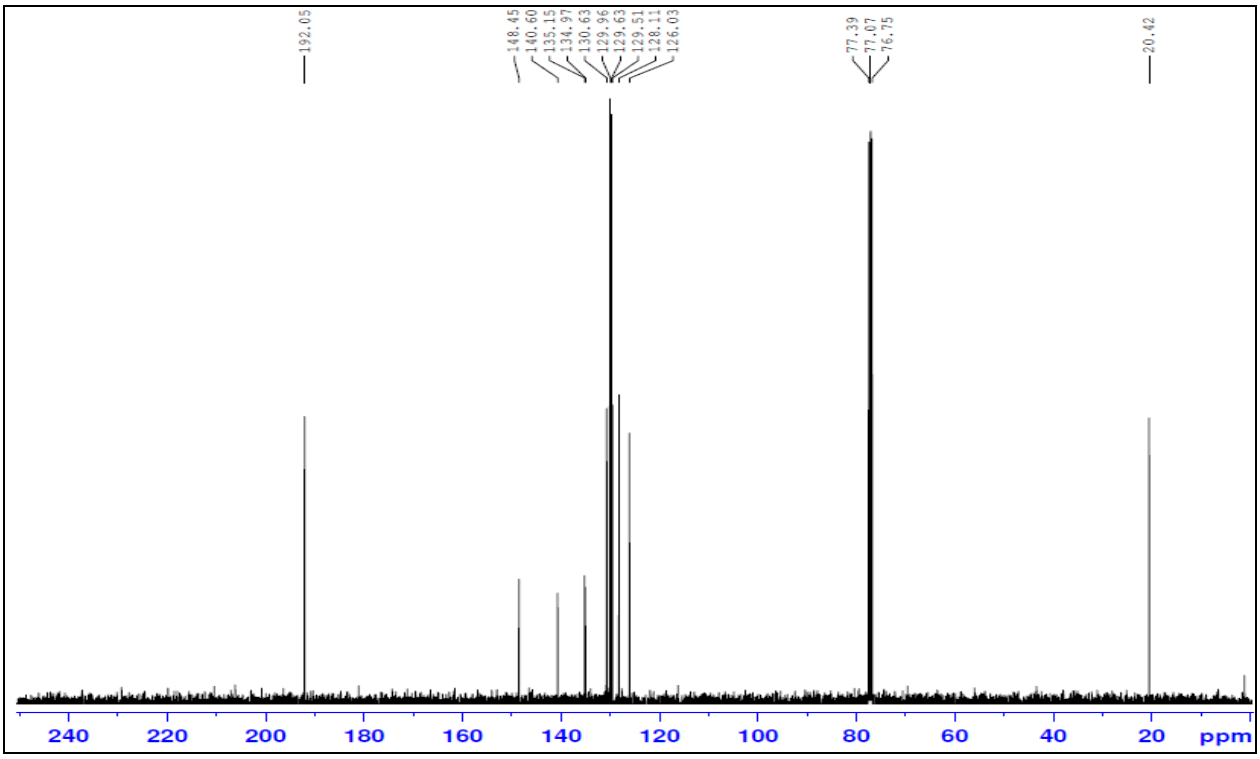


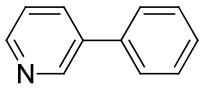




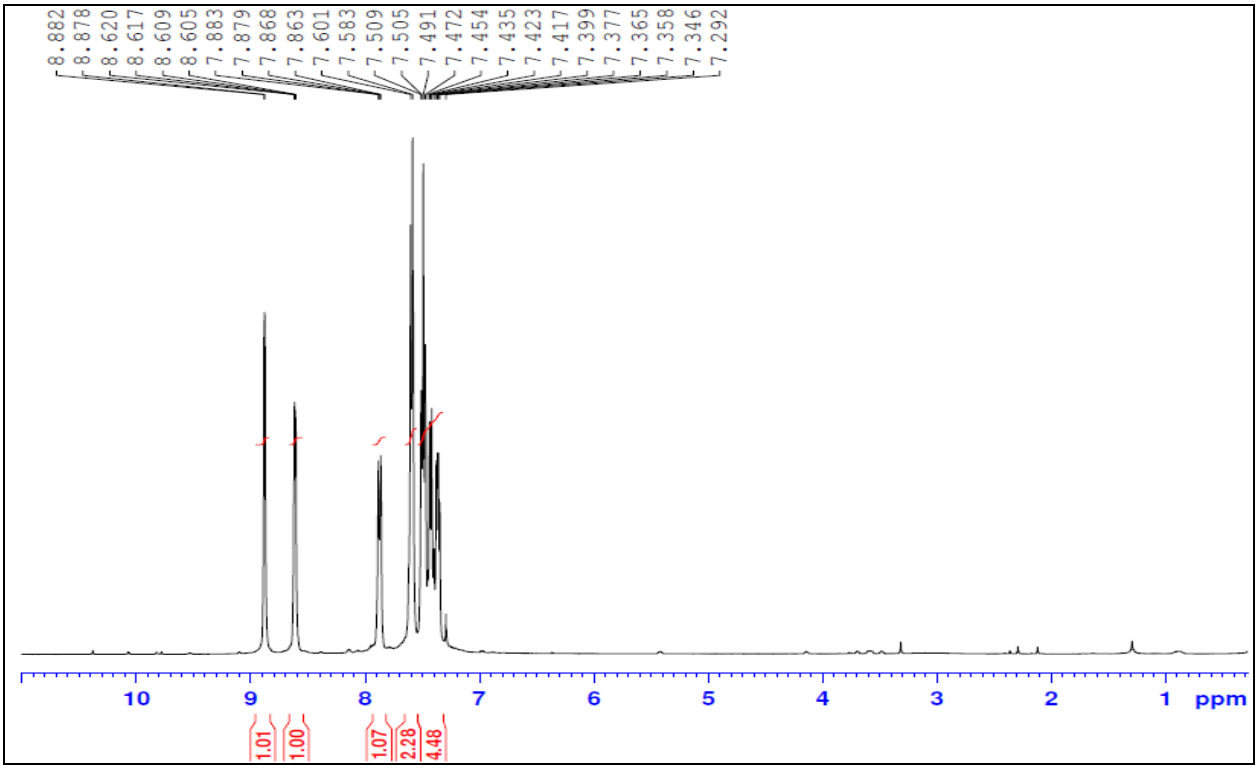
2'-methyl-[1,1'-biphenyl]-4-carbaldehyde

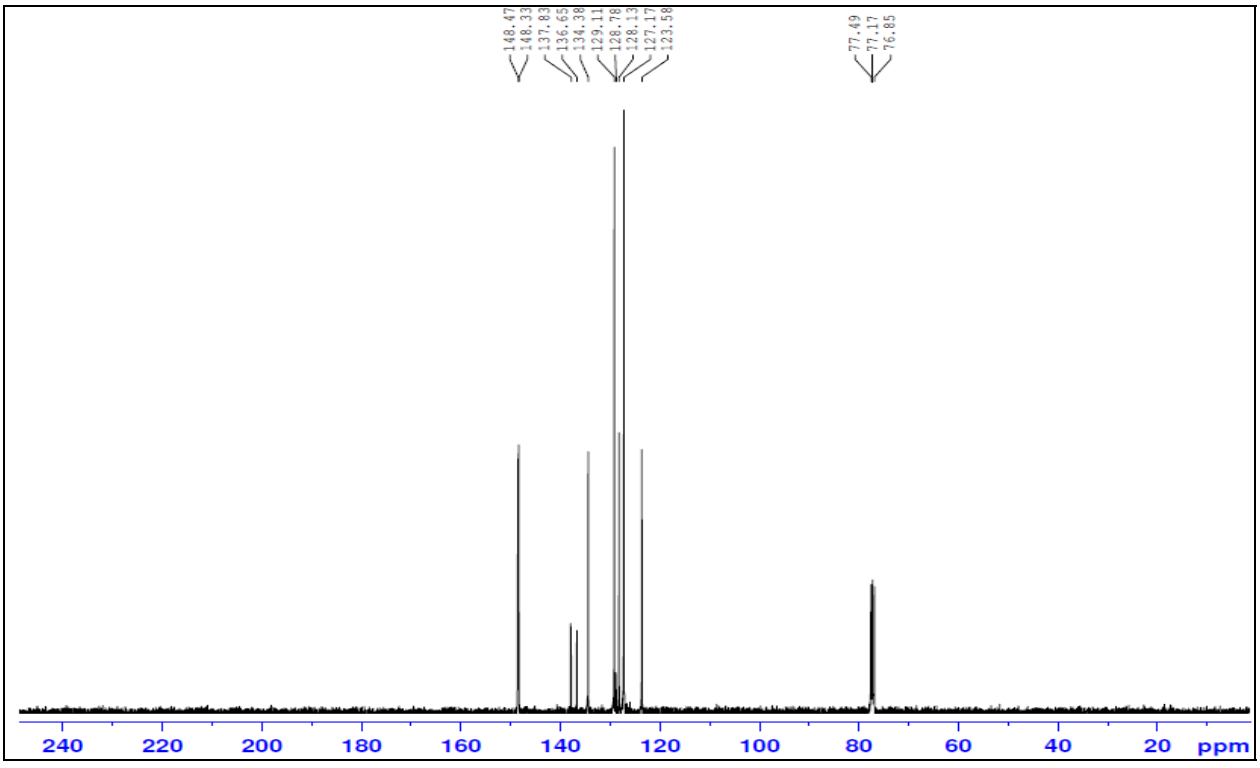


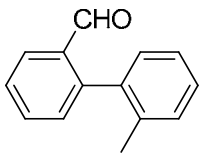




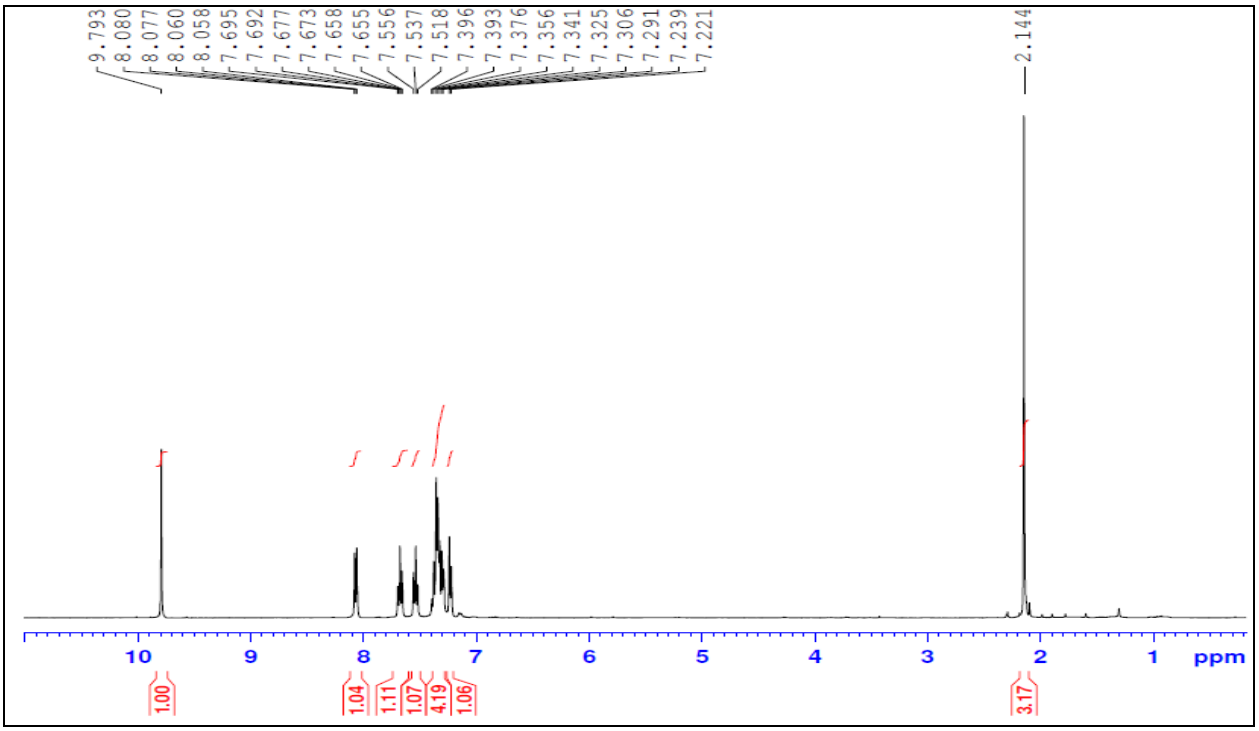
3-phenylpyridine

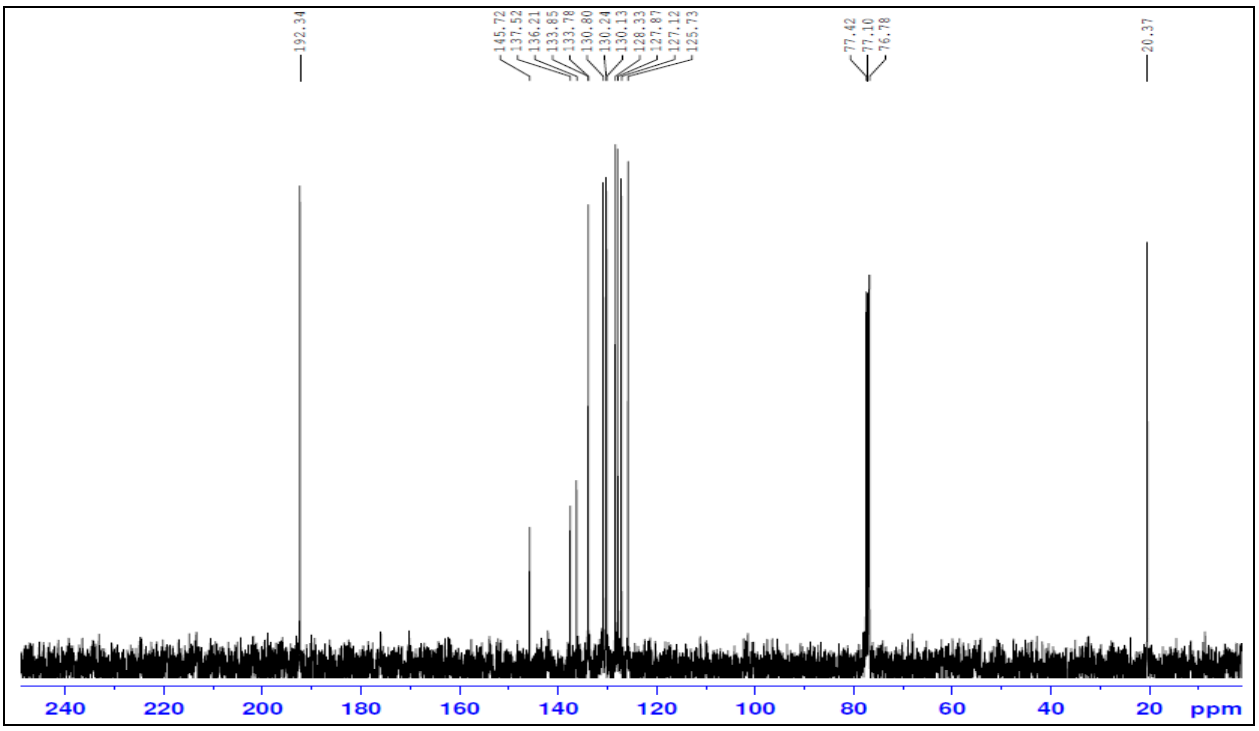


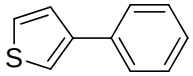




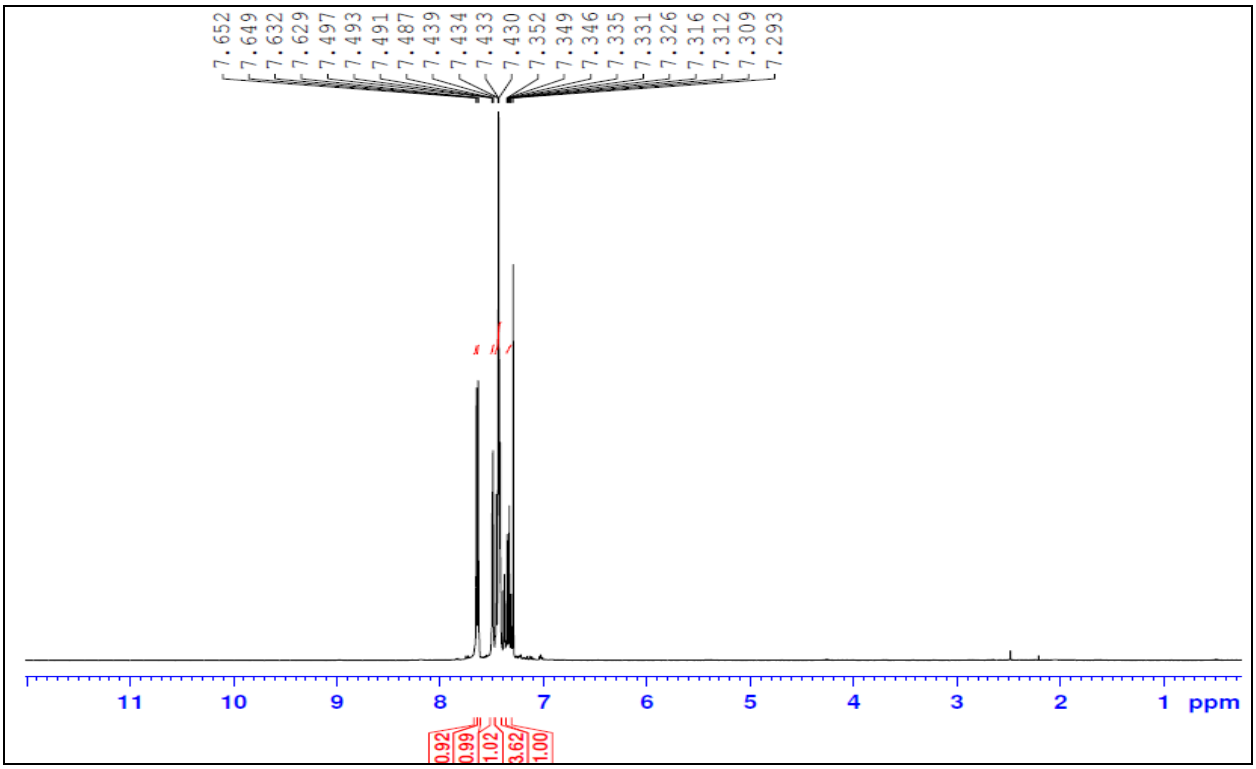
2'-methyl-[1,1'-biphenyl]-2-carbaldehyde

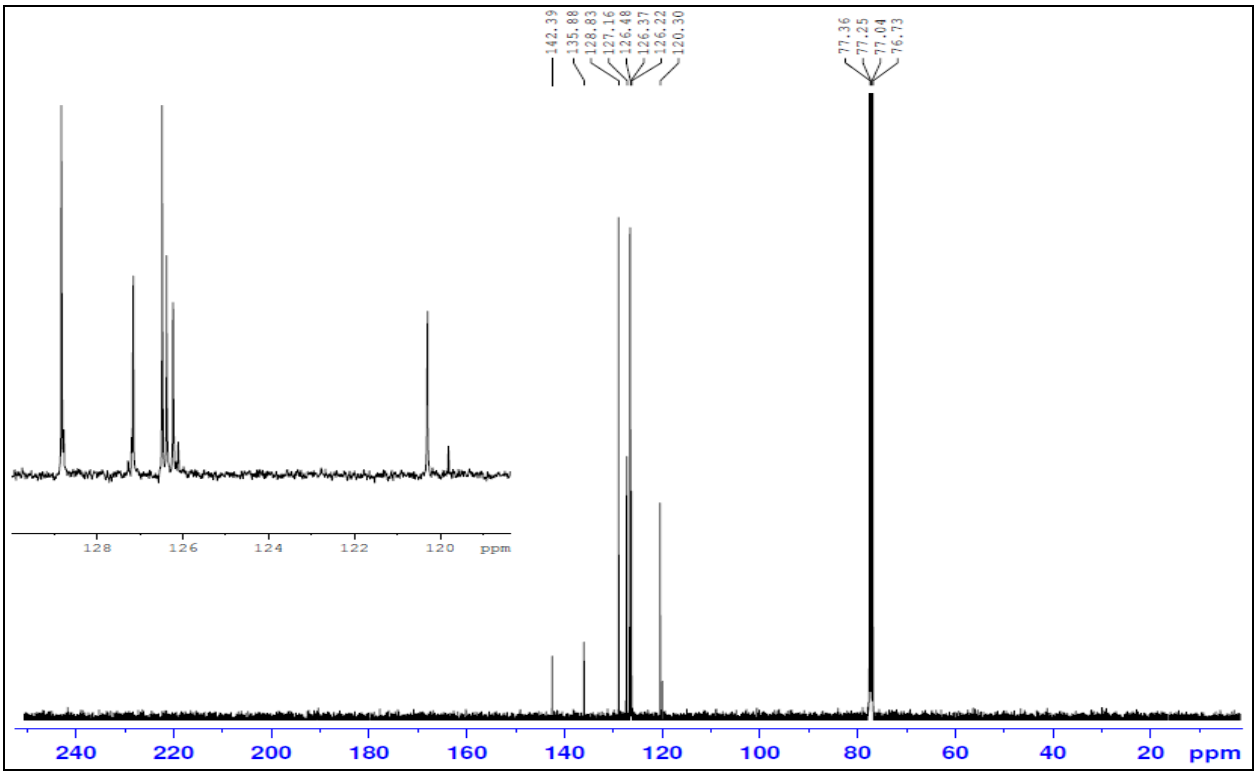


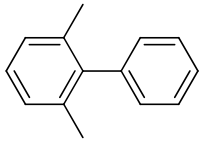




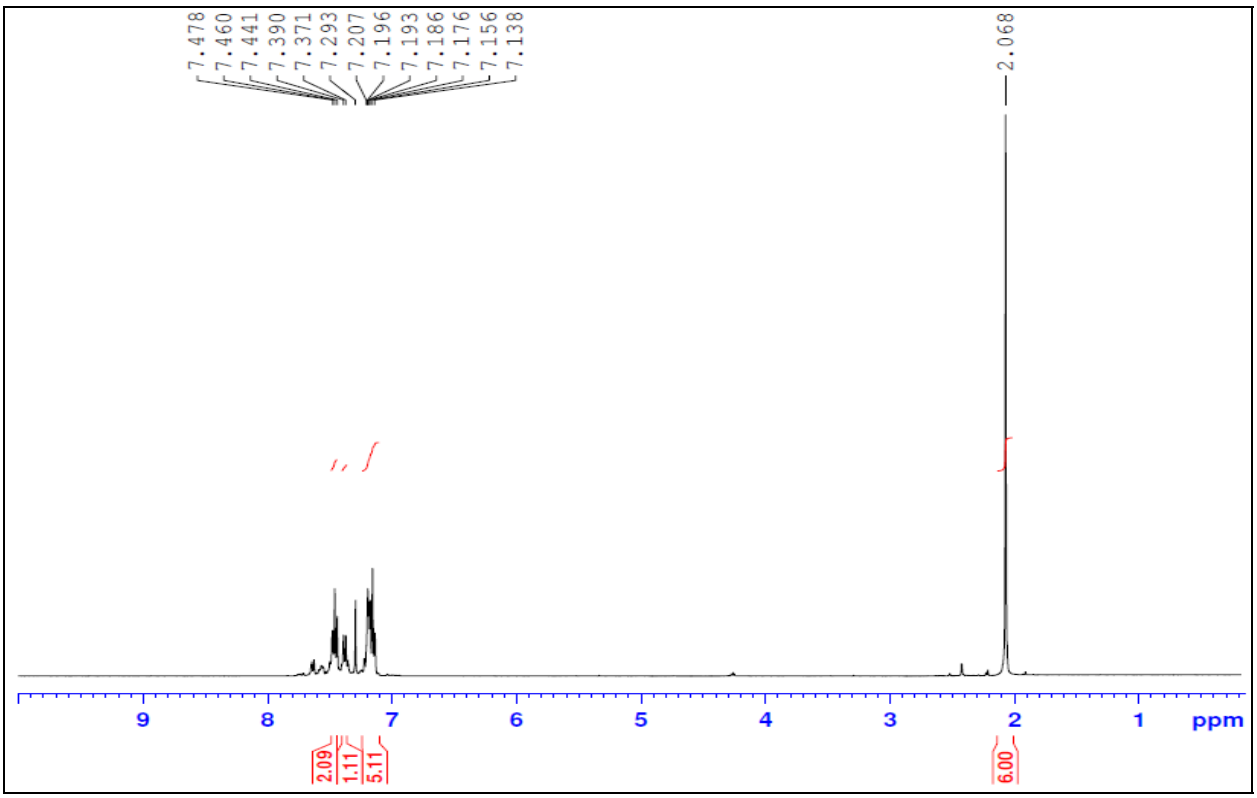
3-phenylthiophene

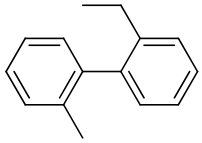






2,6-dimethyl-1,1'-biphenyl





2-ethyl-2'-methyl-1,1'-biphenyl