Supporting Information

Photo-assisted synthesis of Pd-Ag@CQD nanohybrid and its catalytic efficiency in promoting Suzuki-Miyaura cross coupling reaction under ligand-free and ambient conditions

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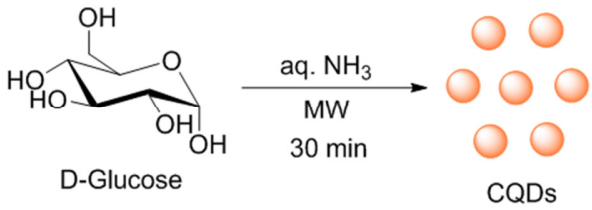
Preparation of carbon quantum dots (CQDs)

CQDs were prepared by a facile microwave-assisted hydrothermal process using glucose as an inexpensive, green andbio-based precursor (**Scheme S1**). In brief, 0.5g of glucose was dissolved in 50 mL of deionized water in a 100 mL conical flask. A few drops of aqueous ammonia (25%) were added to the solution flask and sealed with a cotton plug. The solution flask was transferred to a domestic microwave oven operating at 600 W for 30 min. The colour of the solution changed from colorless to dark brown, indicating the formation of CQDs. The as-formed CQDs were filtered andcentrifuged at 6000 rpm for 30 min to separate theparticle suspension. The water dispersed CQDs were collected, sonicated (acoustic power density 460 W/cm^2, 60 amplitude) for 10 min and stored under ambient conditions. The concentration of CQDs was 24 mg/mL.



Scheme S1 Microwave-assisted hydrothermal preparation of CQDs

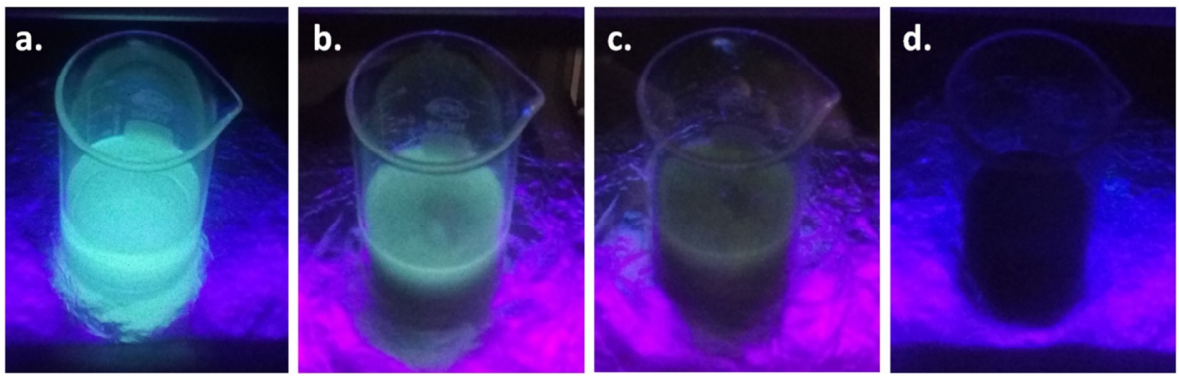


Figure S1 Images displaying the formation of Pd-Ag@CQD a) CQDs dispersion in water, b) immediately after addition of Pd and Ag precursors, c) after 30 min, d) after 60 min

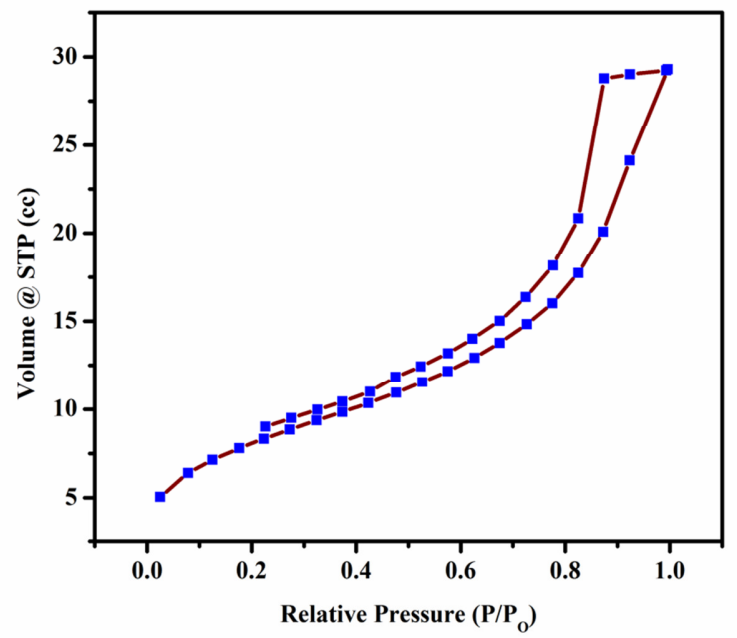


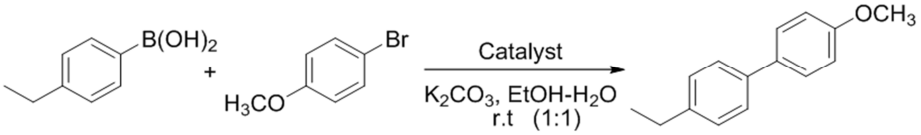
Figure 2 N_2 adsorption-desorption isotherm of Pd-Ag@CQD nanohybrid

Table S1 Synthesis of Pd-Ag@CQD under different conditions

Conditions	*Time (h)
UV light (365 nm)	1
Visible light	4
Dark	10

*As confirmed by UV-Visible spectroscopic study

Table S2 Catalyst reusability screening for Pd-Ag@CQD catalyzed Suzuki-Miyaura coupling reaction



Entry	Run	Time (h)	Yield (%)[b]
1	1st	1	94
2	2nd	1	94
3	3rd	1	93
4	4th	1	90
5	5th	1.1	87
6	6th	1.2	82

[b]Isolated yield

Calculation of mole ratio of Pd and Ag in the nanohybrid

Based on the EDX data,

wt% of Pd in the nanohybrid is17.72%, which is equivalent to 0.167 mole

wt% of Ag in the nanohybrid is 10.15%which is equivalent to 0.094 mole

Hence, the mole ratio of Pd and Ag in the nanohybrid is approximately 1.77:1.00.

Thus, the molar ratio of Pd: Ag: reactant (phenylboronic acid) is 8.8×10^{-2}:4.7×10^{-3}:8.2×10^{-1}.

Leaching experiment of Pd and Ag

In order to determine the leaching of Pd and Ag, the model reaction was emulated using 5 wt% of catalyst and the reaction mixture was analyzed by ICP after careful separation of the catalyst and product. The ICP analysis indicated the presence of less than 1 ppm leached Pd and Ag in the reaction medium (**Table S3**)

Table S3 Leached amount Pd and Ag by ICP

Element	Concentration in solution, mg/L (ppm)
^{106}Pd	0.871
^{107}Ag	0.520

Calculation of TON and TOF

Based on the EDX data,

wt% of Pd in the nanohybrid is 17.72%, which is equivalent to 0.167 mole

wt% of Ag in the nanohybrid is 10.15% which is equivalent to 0.094 mole

wt% of C in the nanohybrid is 42.35% which is equivalent to 3.52 mole

wt% of O in the nanohybrid is 29.78% which is equivalent to 1.86 mole

Total mole of catalyst used = 2.82×10^{-1}

Yield of the product is 94%

Mole of product produced is 2.257

Now, TON = (moles of product produced/moles of catalyst used)×(yield of the product)

and, TOF = TON/time

For example, in case of product **1d** (Entry No.5 of Table 2)

TON = (2.257 mol/0.282 mol) × 94 = 752.3

TOF = 752.3/60 min = 12.53 min^{-1}

Hot filtration test for heterogeneity of the catalyst

To test the heterogeneity of the catalyst, the model reactionwas again performed under the optimized reaction conditions and the yield monitored by GC. After 0.5 h, an isolated yield of 65% was obtained. After running for 0.5 h, the reaction mixture it was carefully filtered and the filtrate was allowed to react for an additional 12 h. However, no significant increase in the yield of the cross-coupled product was observed, which suggested the heterogeneity of the catalyst (**Figure S3**).

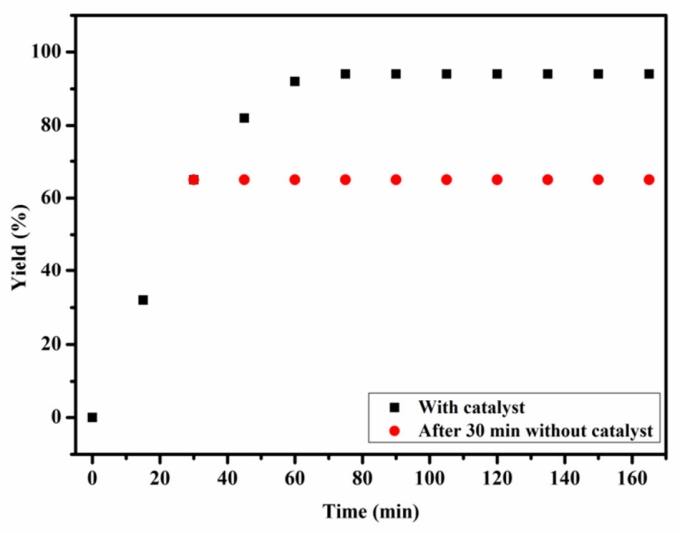
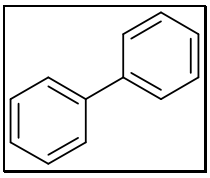


Figure S3 Hot filtration test for heterogeneity of the catalyst

NMR spectral analyses of Suzuki-Miyaura cross-coupling products

1,1'-biphenyl (**1a**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H(ppm) 7.62 (m, 4H), 7.47 (m, 4H), 7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 141.34, 128.88, 127.37, 127.29.

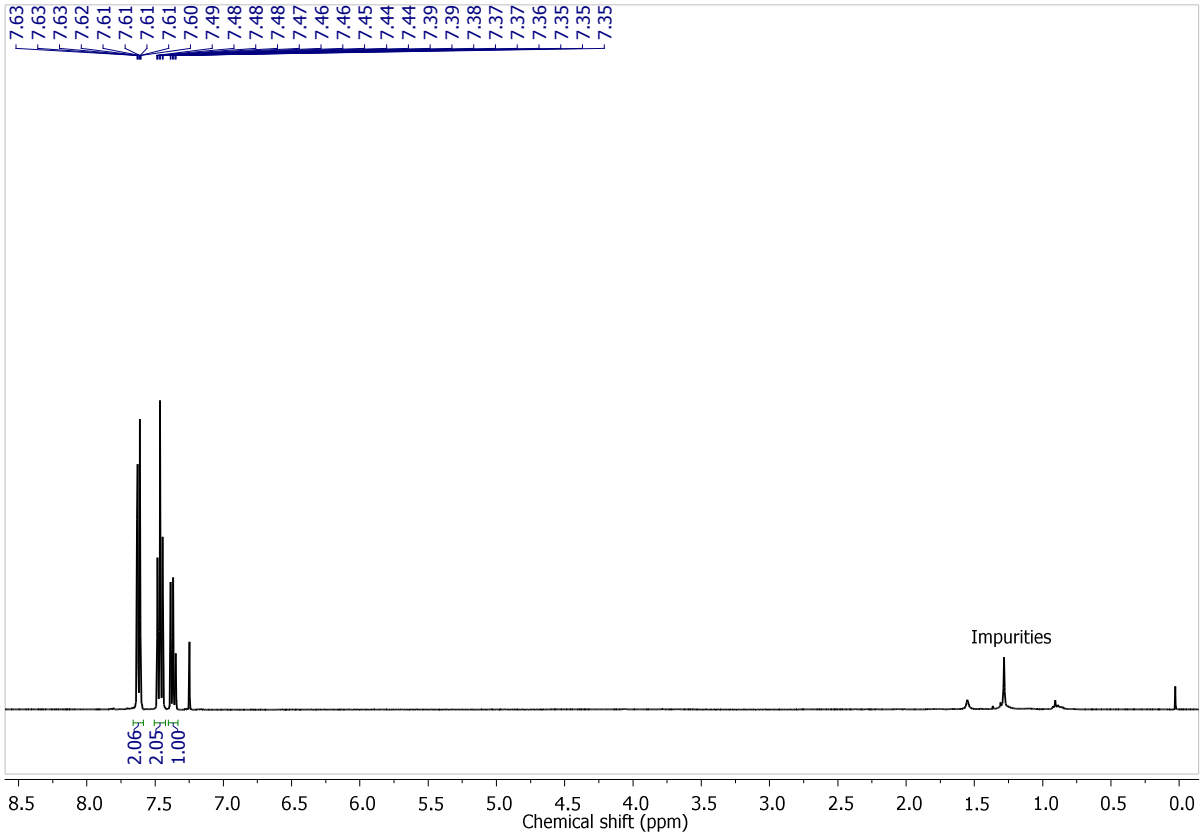


Figure S4a ^{1}H spectrum of **1a**

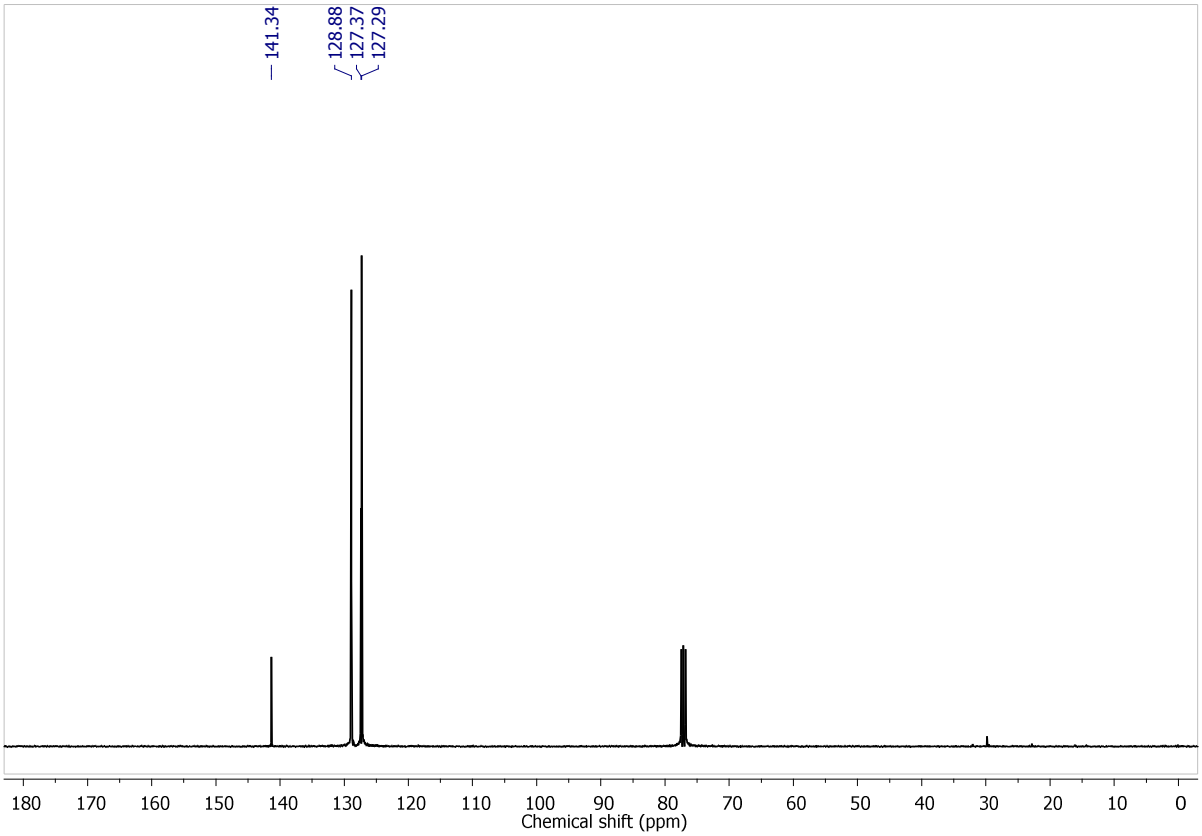
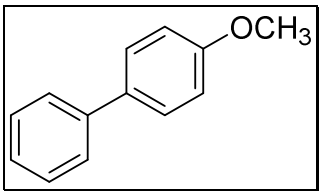


Figure S4b ^{13}C spectrum of **1a**

4-methoxy-1,1'-biphenyl (**1b**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.55 (t, J = 8 Hz, 4H), 7.42 (t, J =8 Hz, 2H), 7.32 (m, 1H) 6.99 (d, J = 8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 159.22, 140.91, 133.86, 128.83, 128.26, 128.27, 126.84, 126.76, 114.29, 55.44

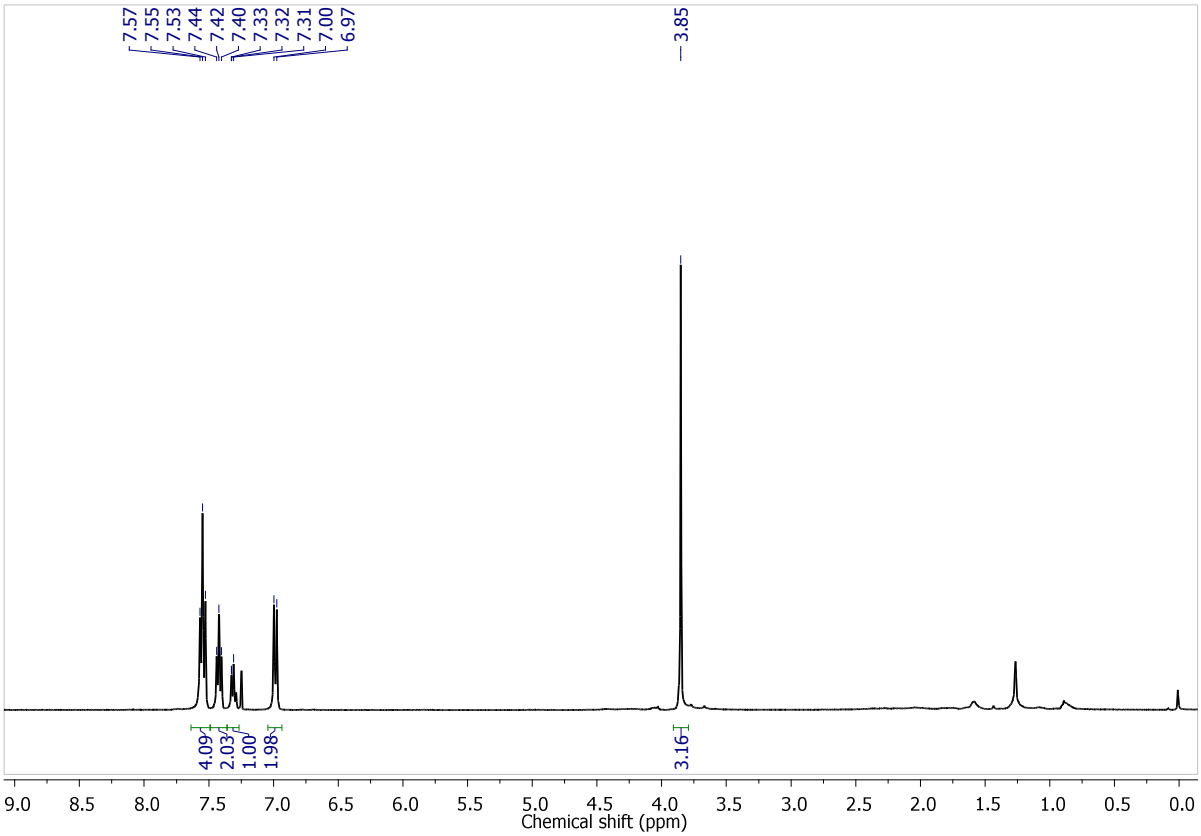


Figure S5a ^{1}H spectrum of **1b**

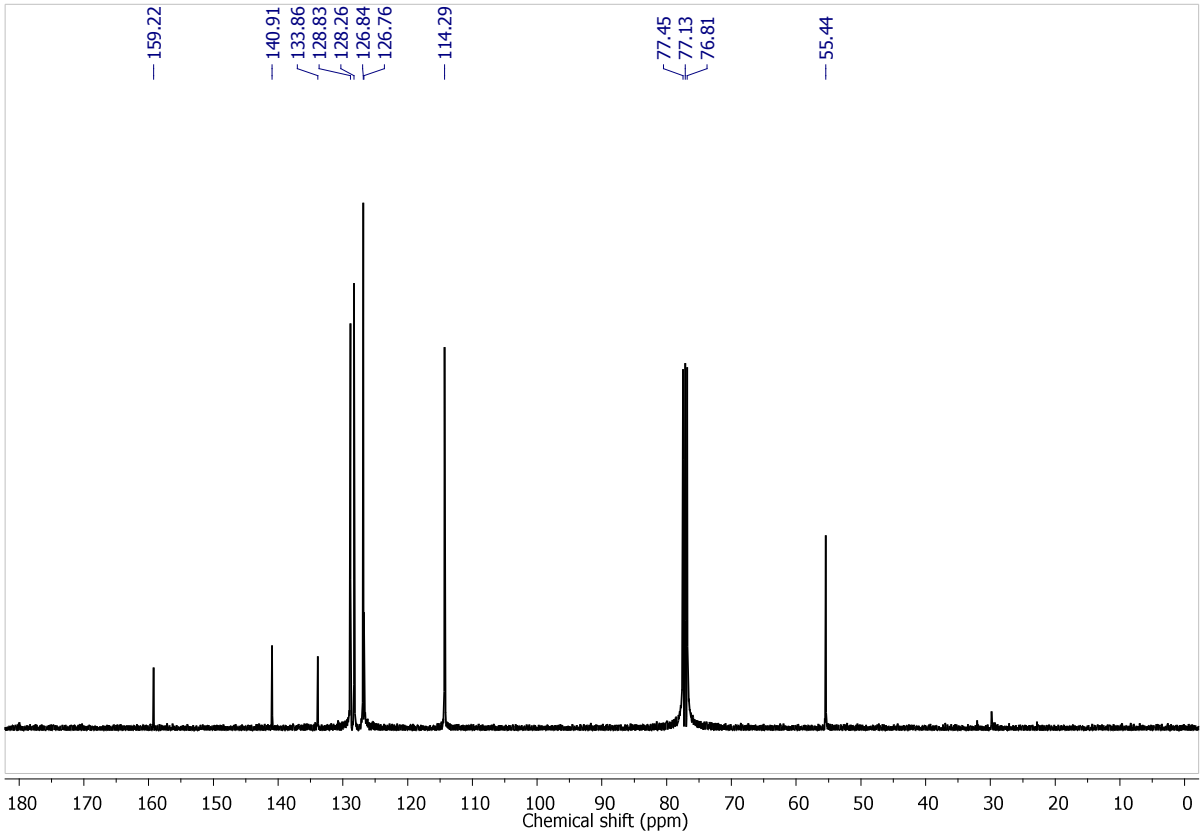
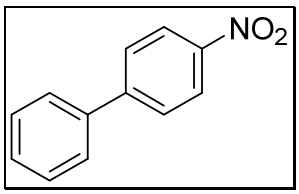


Figure S5b ^{13}C spectrum of **1b**

4-nitro-1,1'-biphenyl (**1c**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.30 (m, 1H), 7.91(m, 4H), 7.73 (m, 1H), 7.61 (m, 1H), 7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 147.71, 138.78, 138.74, 129.23, 128.99, 127.87, 127.46, 124.96, 124.94, 124.92, 124.18, 102.72, 100.00.

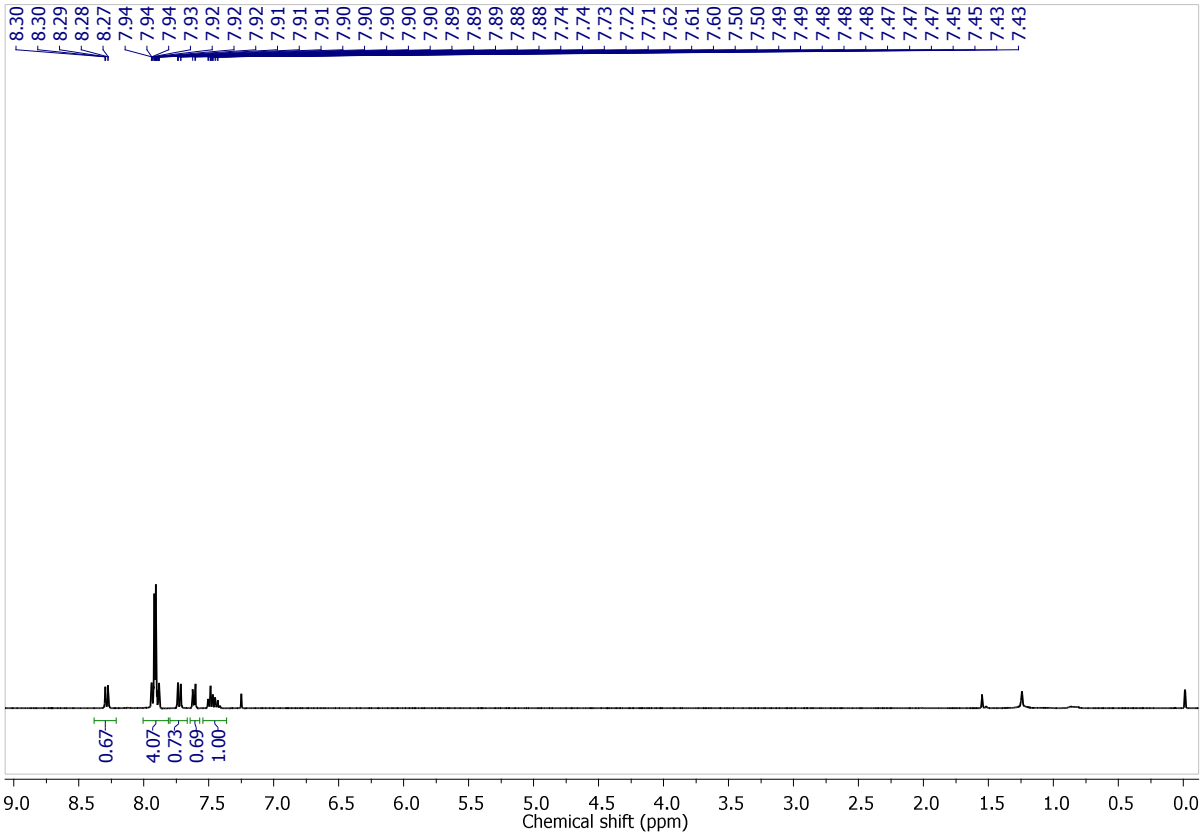


Figure S6a ^{1}H spectrum of **1c**

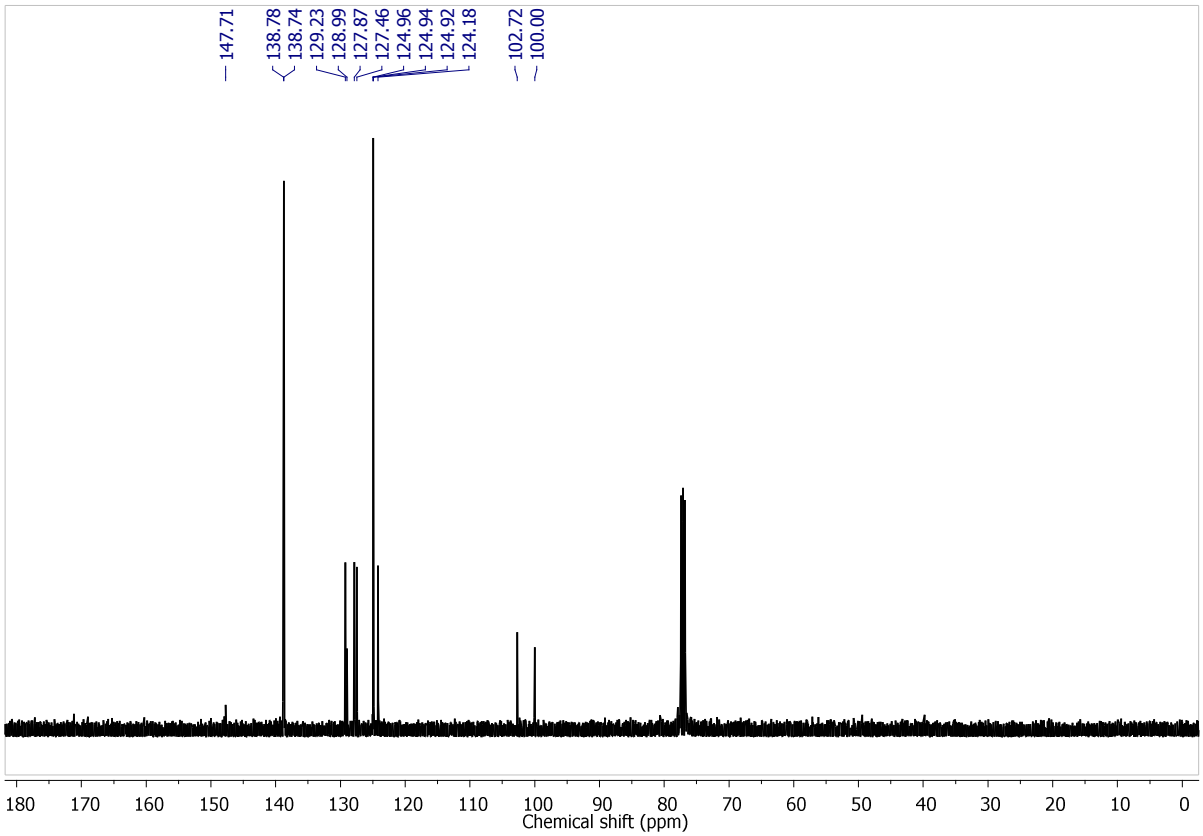
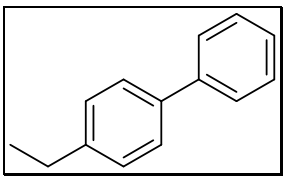


Figure S6b ^{13}C spectrum of **1c**

4-ethyl-1,1'-biphenyl (**1d**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.60 (m, 2H), 7.54 (m, 2H), 7.45 (m, 2H), 7.31 (m, 3H), 2.72 (q, J = 8 Hz, 2H), 1.30 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm)143.51, 141.30, 138.72, 128.83, 128.42, 127.20, 127.14, 127.09, 28.64, 15.75.

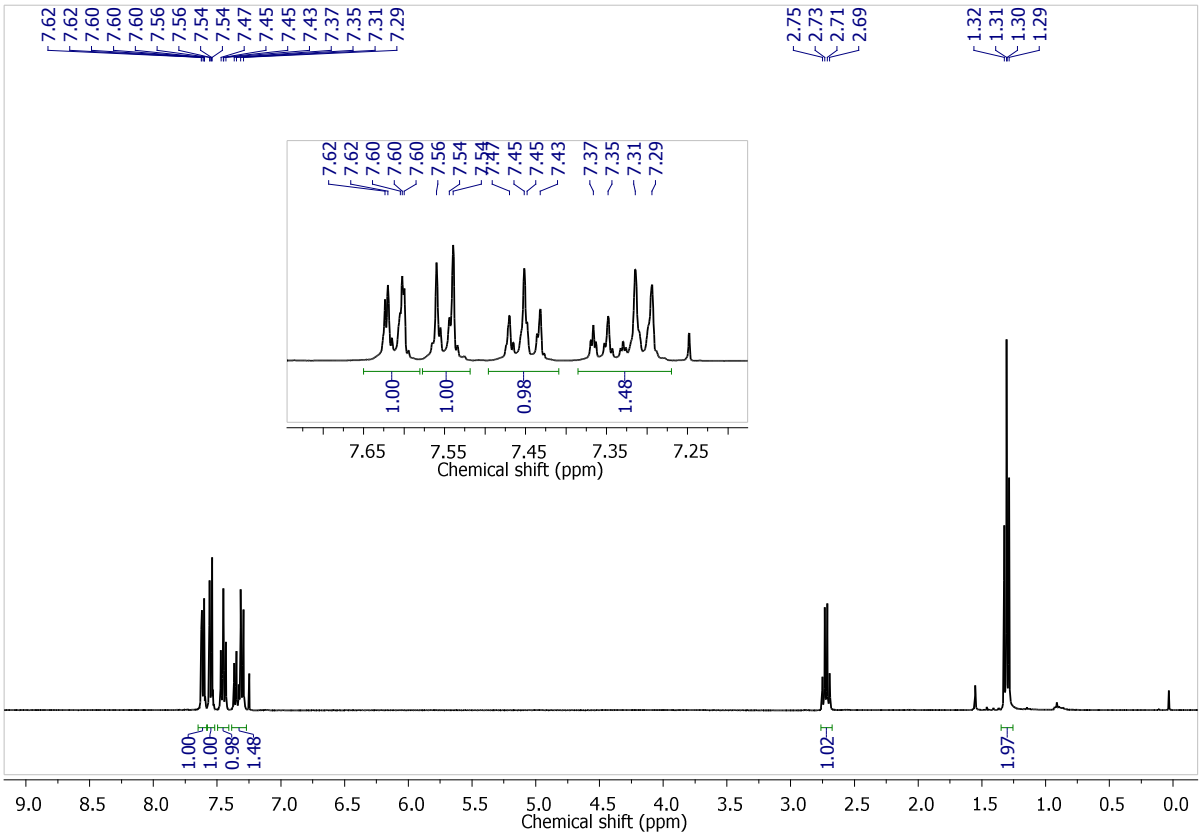


Figure S7a ^{1}H spectrum of **1d**

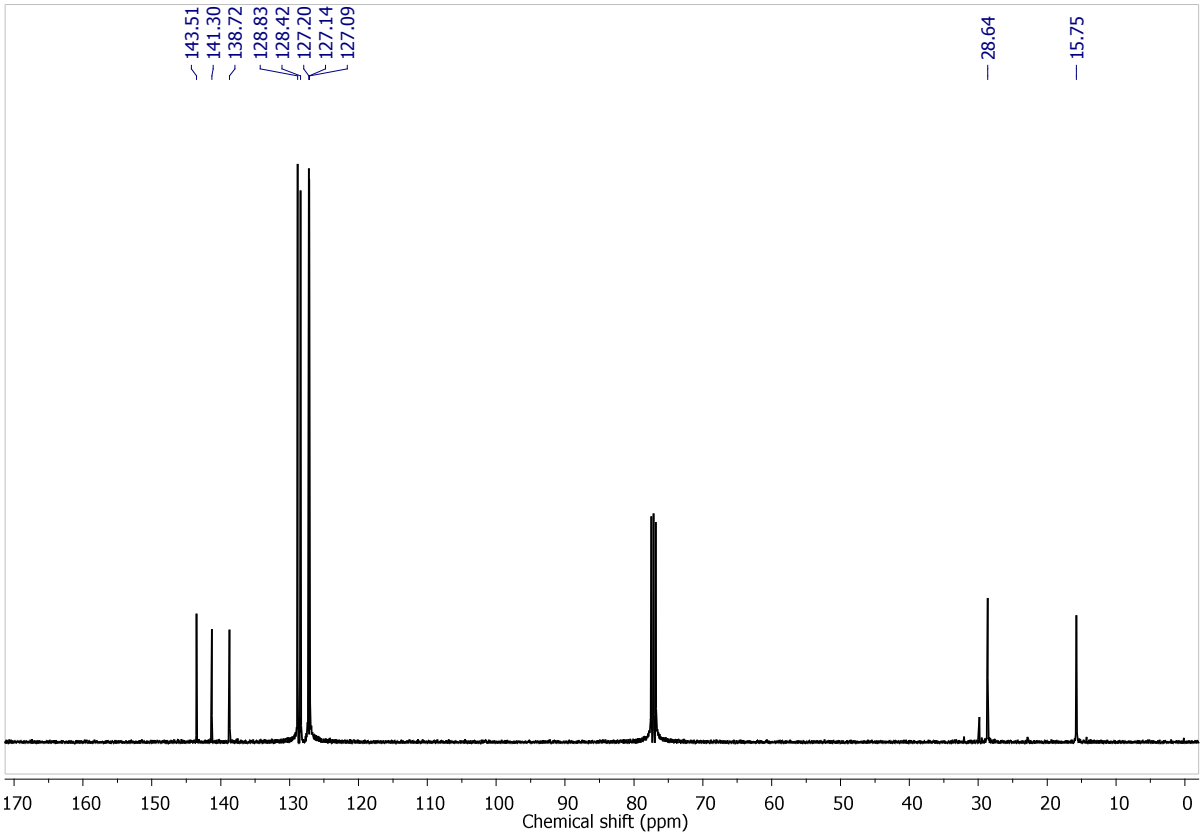
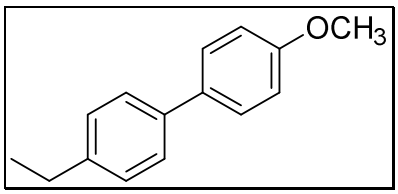


Figure S7b ^{13}C spectrum of **1d**

4-ethyl-4'-methoxy-1,1'-biphenyl (**1e**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.56 (m, 4H), 7.30 (d, J =8 Hz, 2H), 7.01 (m, 2H), 3.88 (s, 3H), 2.74 (q, J = 8 Hz, 2H), 1.33 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 159.01, 142.84, 138.31, 133.87, 128.33, 128.08, 128.08, 126.75, 114.23, 55.42, 28.56, 15.71

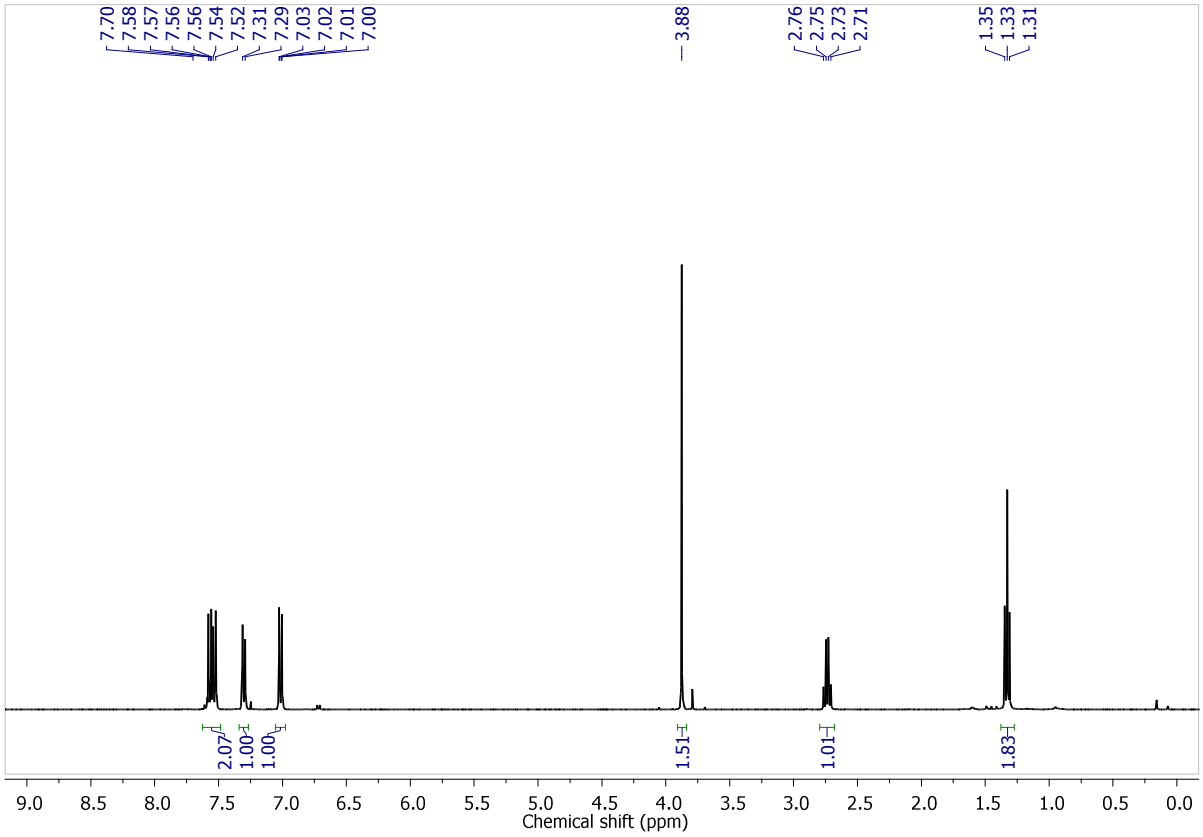


Figure S8a ^{1}H spectrum of **1e**

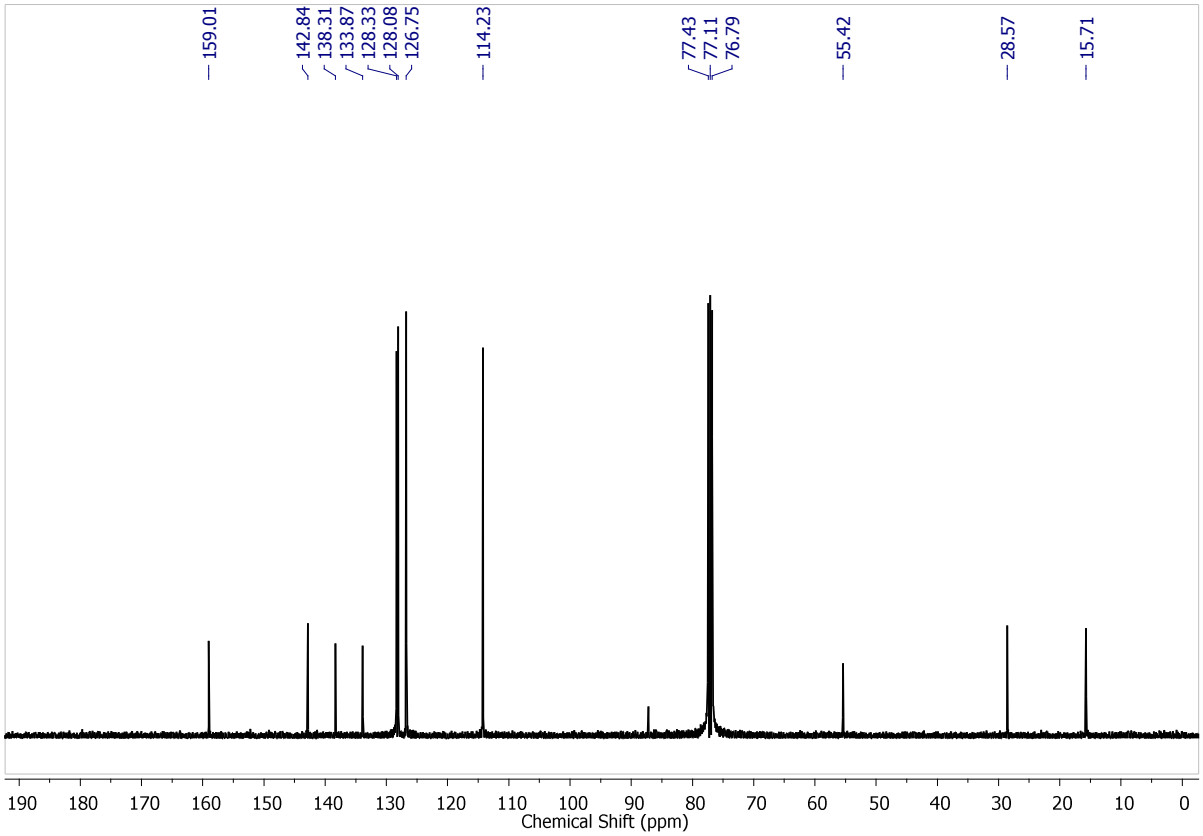
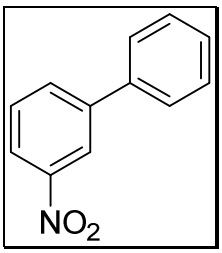


Figure S8b ^{13}C spectrum of **1e**

3-nitro-1,1'-biphenyl (**1f**)



^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.45 (s, 1H), 8.19 (d,*J* = 8 Hz, 1H), 7.91 (d,*J* = 8 Hz, 1H), 7.61 (m, 3H), 7.48 (m, 2H), 7.43 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ_C(ppm) 148.83, 142.97, 138.76, 133.12, 129.79, 129.25, 128.63, 127.25, 127.23, 122.12, 122.05.

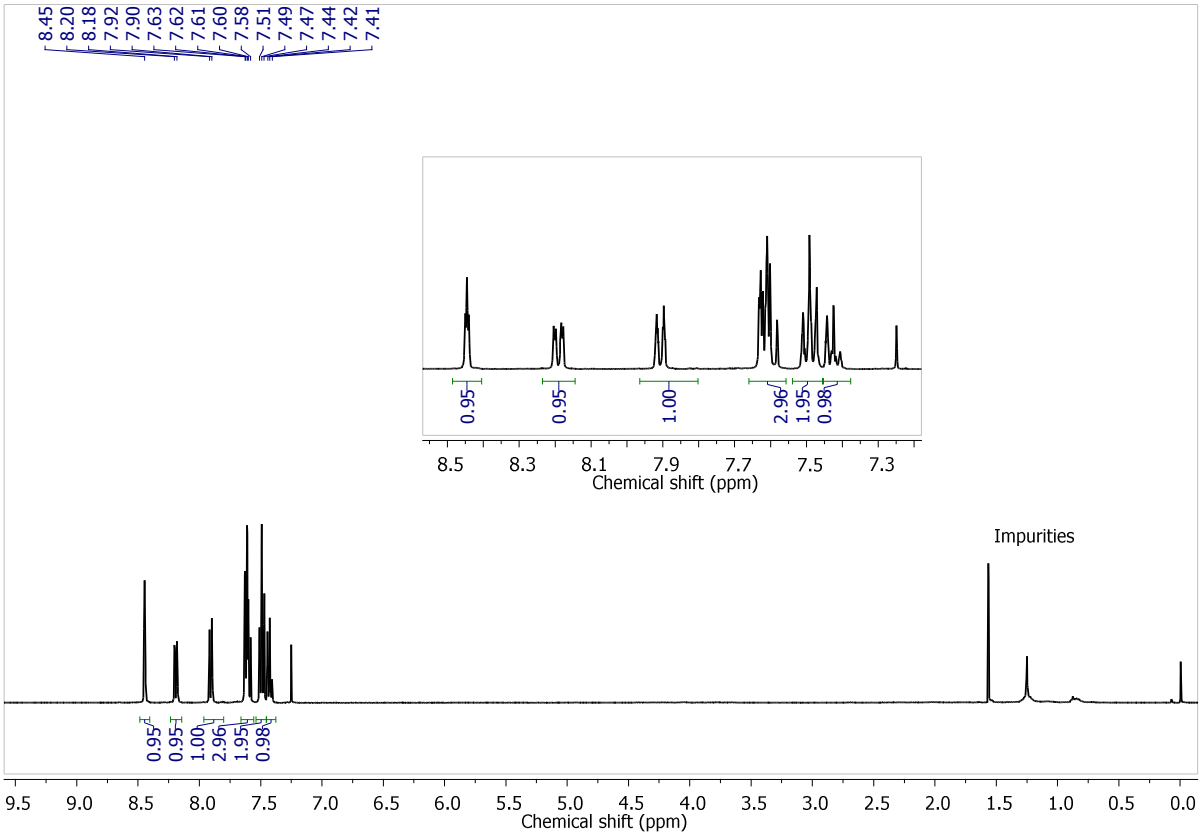


Figure S9a ^{1}H spectrum of **1f**

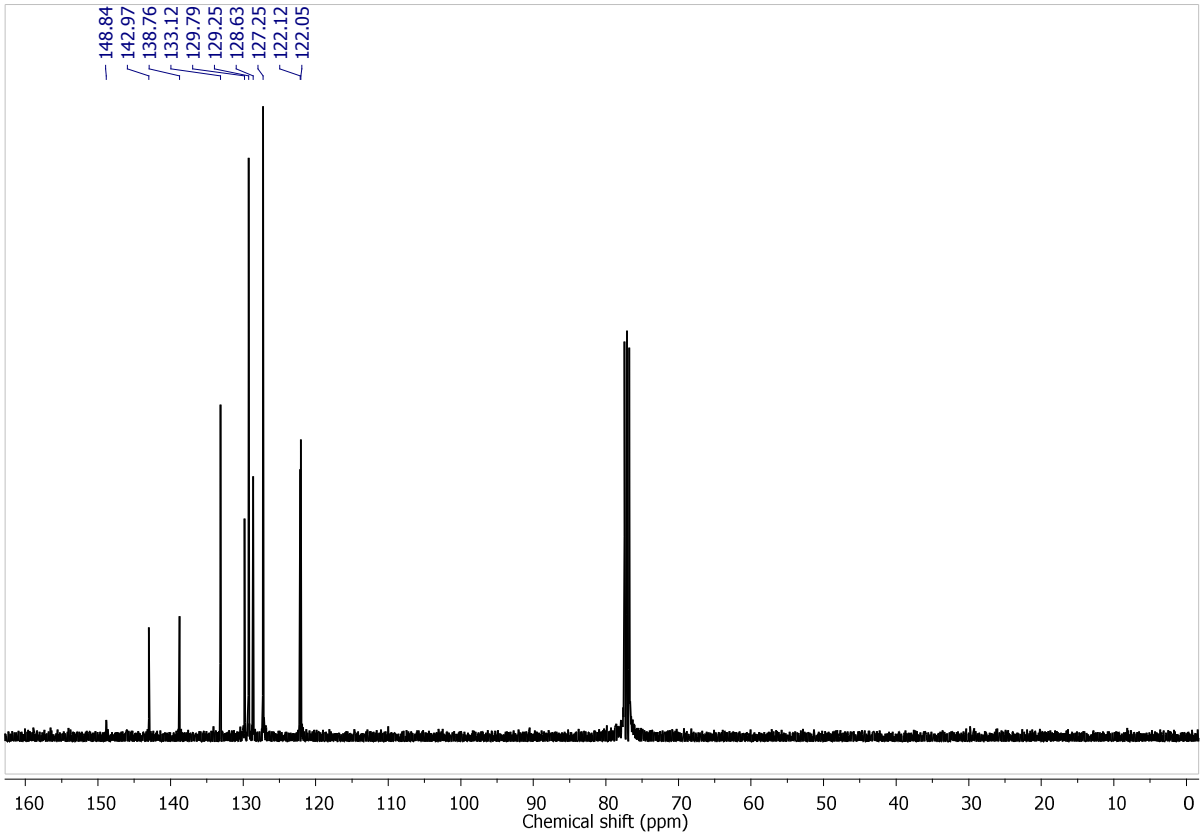
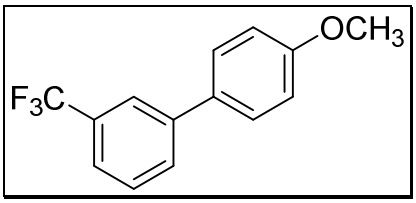


Figure S9b ^{13}C spectrum of **1f**

4'-methoxy-3-(trifluoromethyl)-1,1'-biphenyl (**1g**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)7.79 (s, 1H), 7.72 (d, J = 8 Hz, 1H), 7.53(m, 4H), 7.00 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 159.80, 141.68, 132.30, 131.66, 131.34, 131.02, 130.71, 130.01, 129.26, 128.33, 123.57, 123.53, 123.49, 123.39, 123.35, 123.31, 114.51, 55.44.

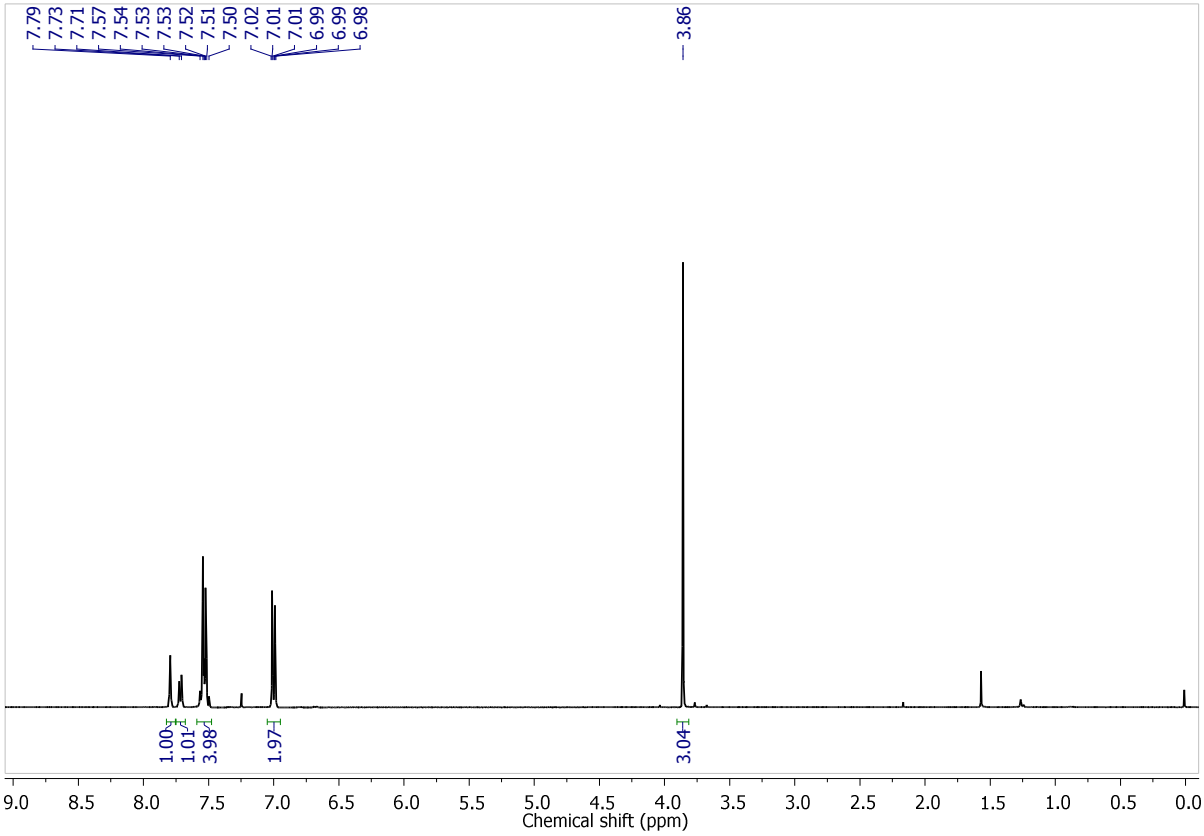


Figure S10a ^{1}H spectrum of **1g**

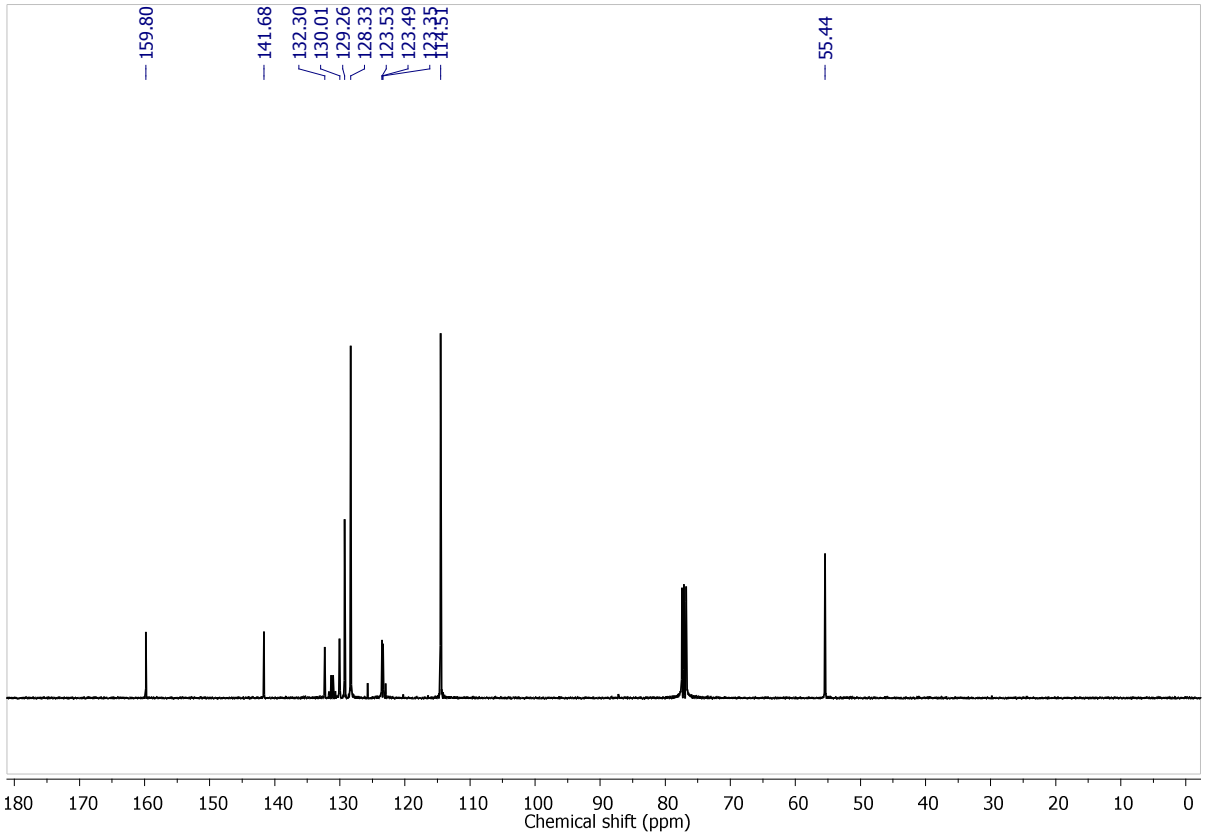
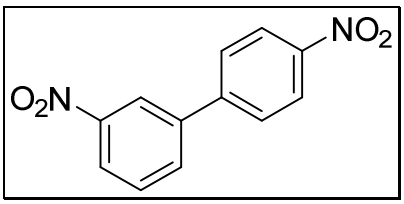


Figure S10b ^{13}C spectrum of **1g**

3,4'-nitro-1,1'-biphenyl (**1h**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 8.48 (s, 1H), 8.35 (m, 2H), 8.29 (m, 1H), 7.95 (m, 1H), 7.79 (m, 2H), 7.69 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, NMR (400 MHz, $CDCl_3$): δ_C (ppm)147.71, 138.74, 129.23, 128.99, 127.87, 127.46, 124.94, 124.92, 124.18, 102.72, 100.00.

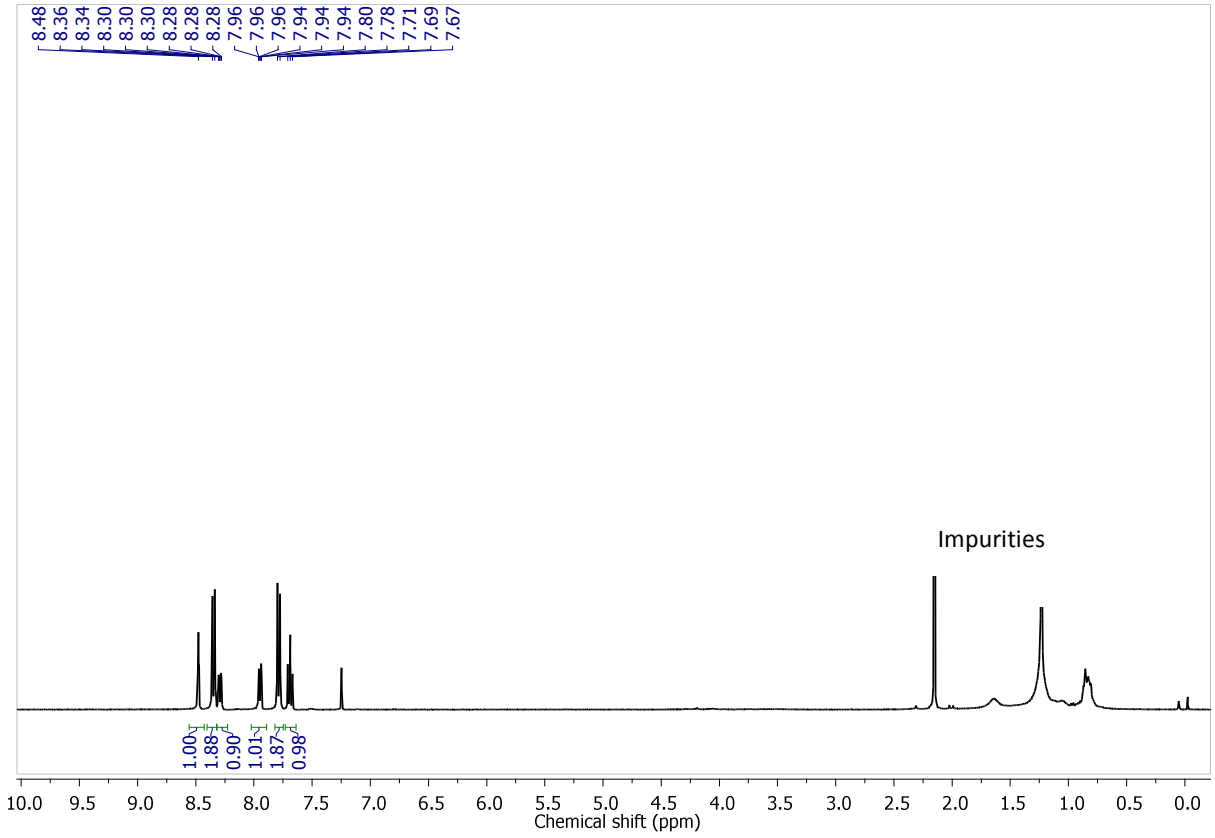


Figure S11a ^{1}H spectrum of **1h**

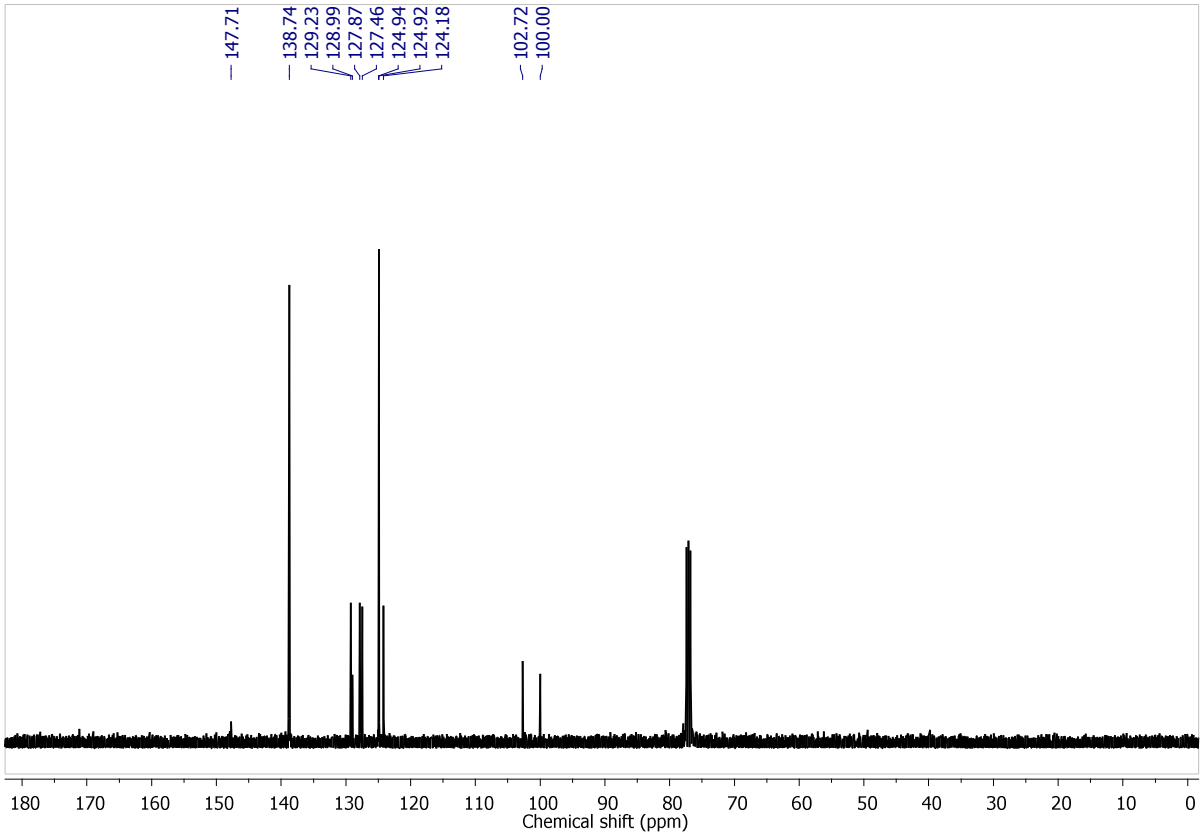
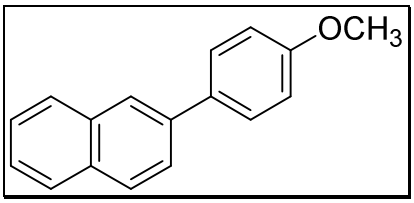


Figure S11b ^{13}C spectrum of **1h**

2-(4-methoxyphenyl)naphthalene(**1i**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.99 (s, 1H), 7.87 (m, 3H), 7.71 (dd, J =8 Hz, 1H), 7.65 (m, 2H), 7.47 (m, 2H), 7.02 (m,2H) 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 159.32, 133.83, 133.71, 132.39, 128.55, 128.52, 128.44, 128.14, 127.71, 126.33, 125.74, 125.53, 125.12, 114.40. 55.48

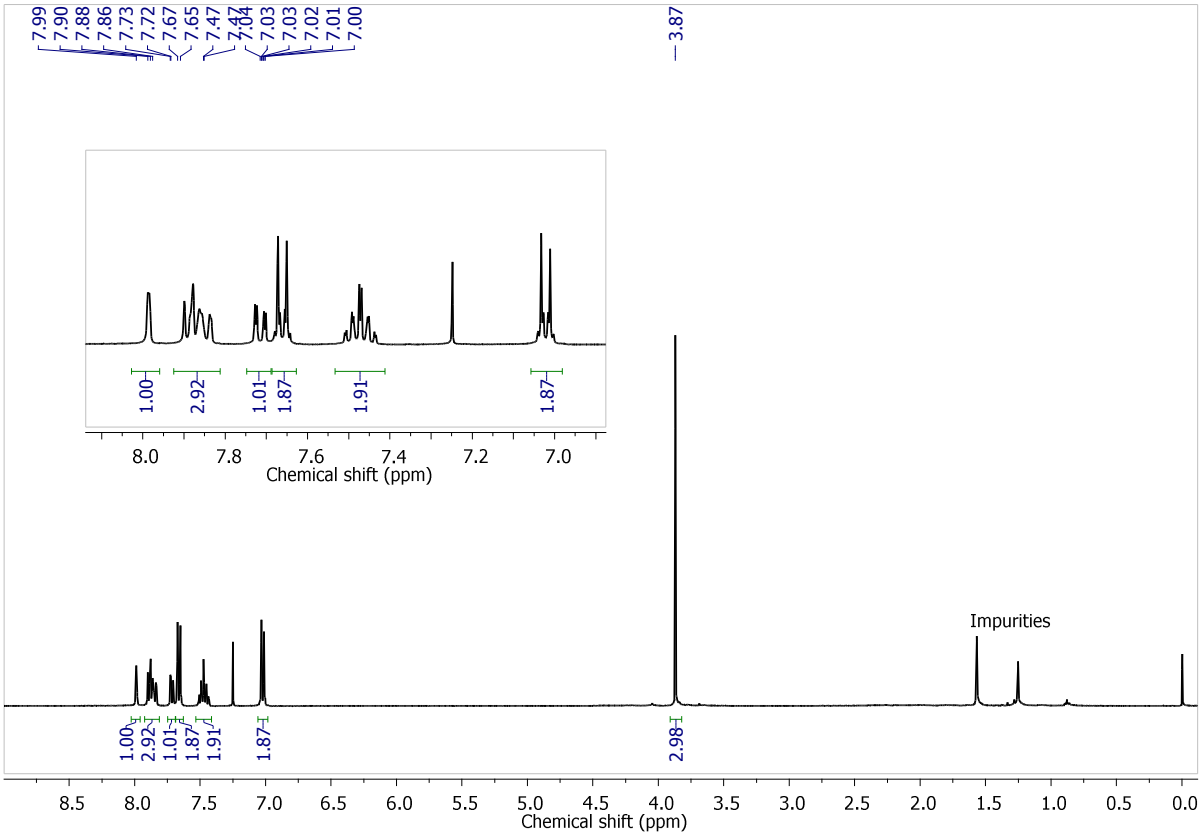


Figure S12a ^{1}H spectrum of **1i**

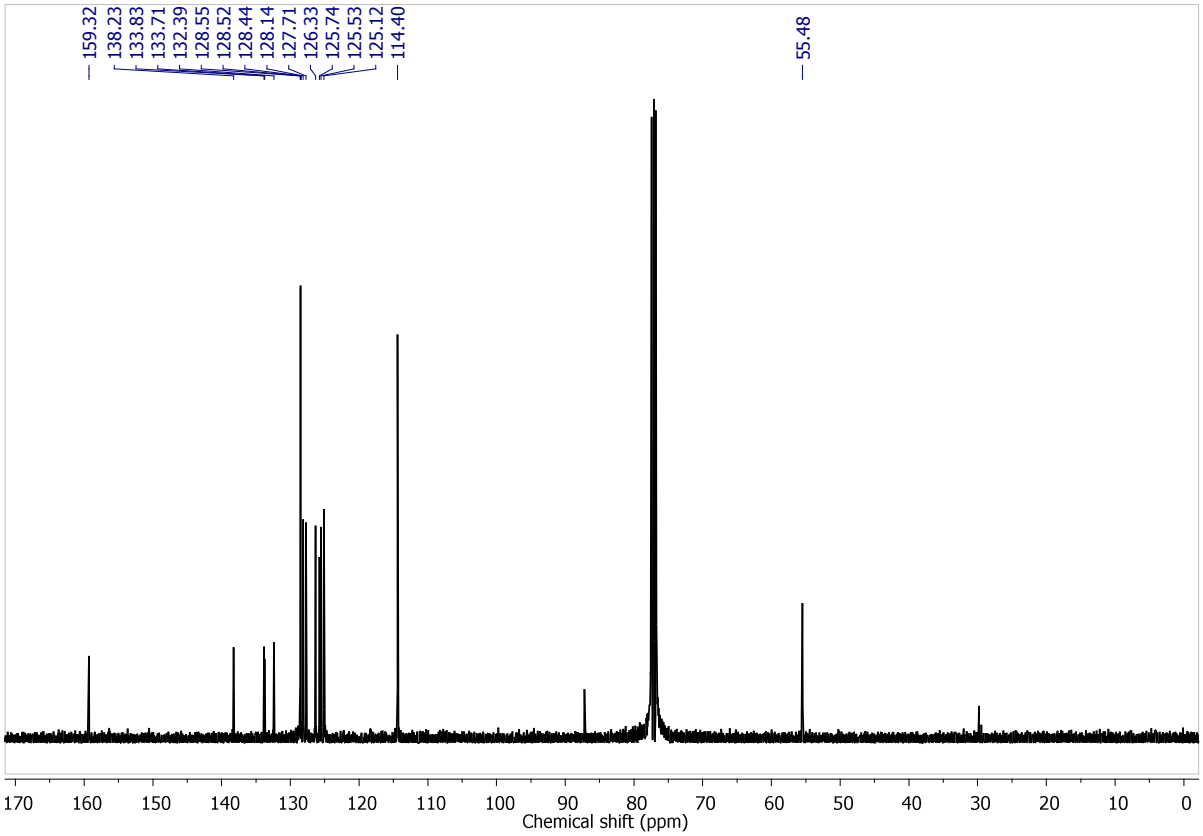
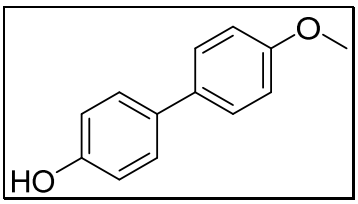


Figure S12b ^{13}C spectrum of **1i**

4'-methoxy-(1,1'-biphenyl)-4-ol (**1j)**



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.44 (m, 4H), 7.04 – 6.89 (m, 2H), 6.90 – 6.80 (m, 2H), 4.85 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 158.68, 154.57, 133.53, 133.51, 128.05, 127.73, 115.38, 114.17, 55.16.

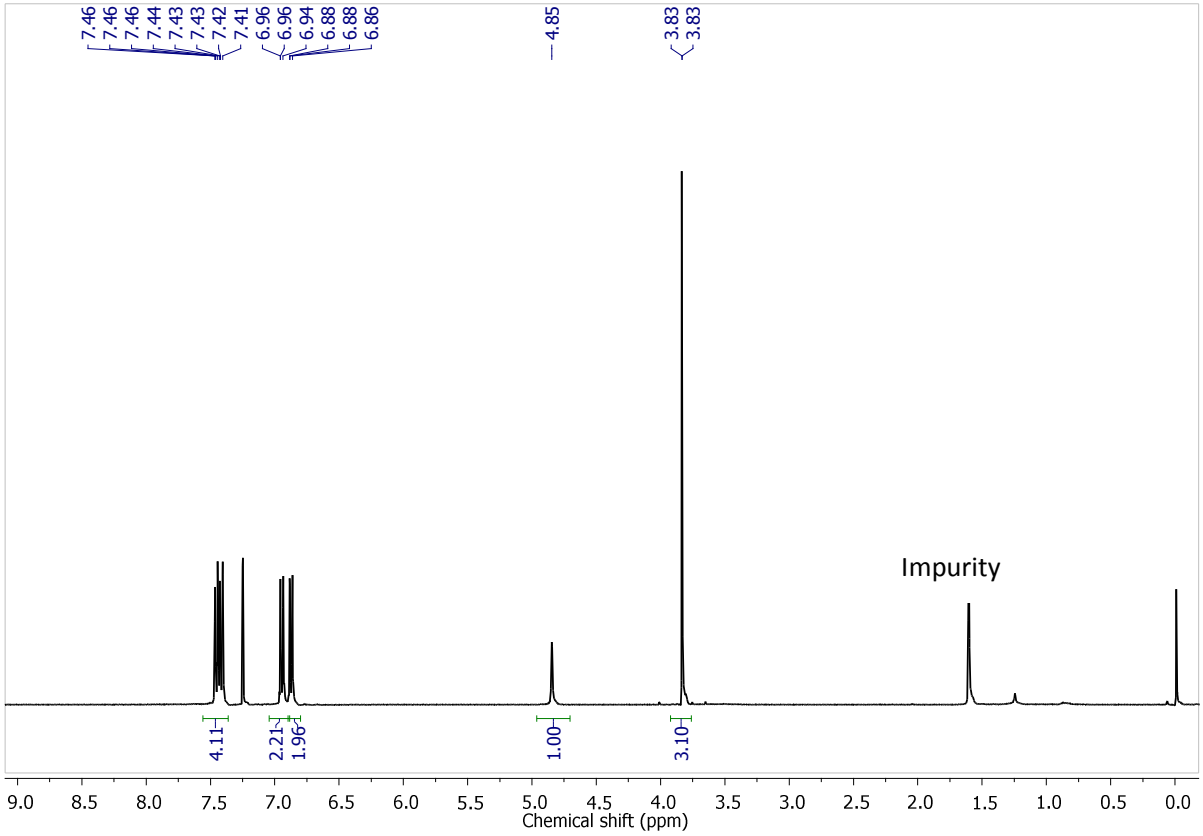


Figure S13a ^{1}H spectrum of **1j**

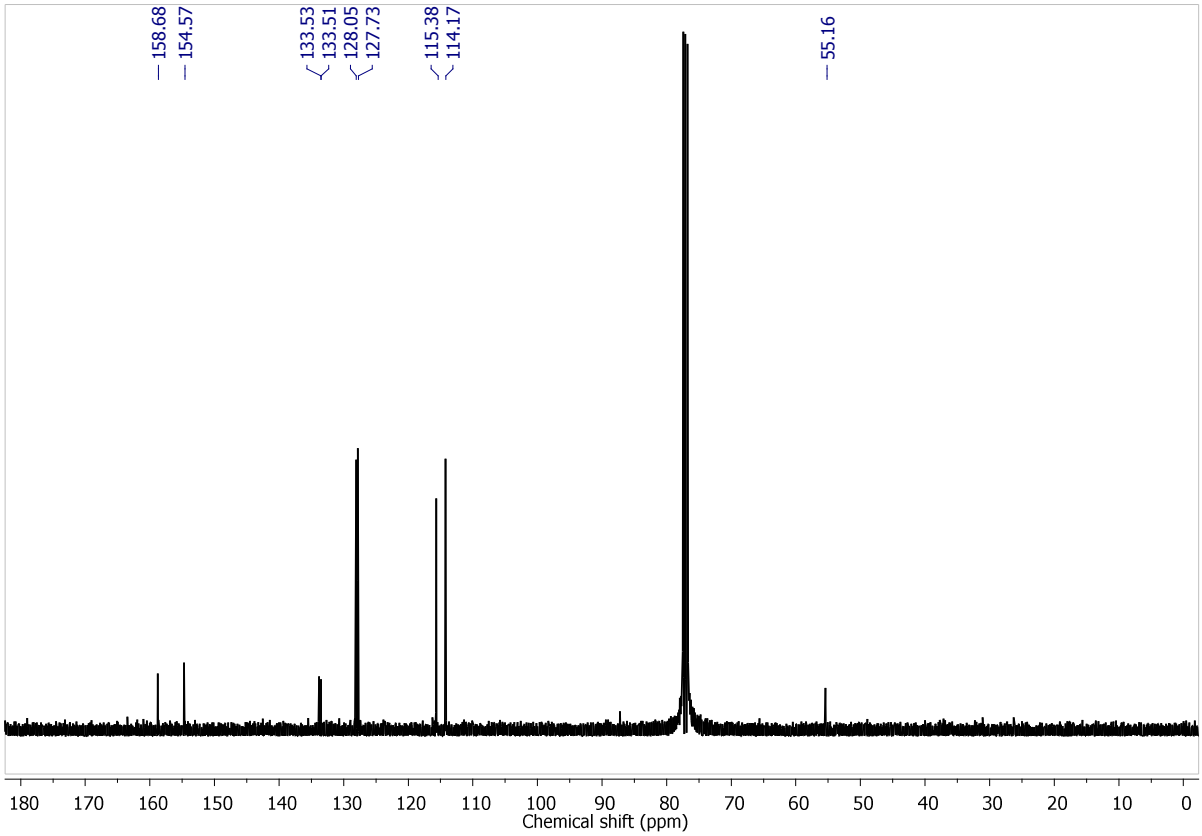
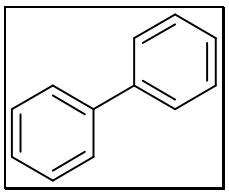


Figure S13b ^{13}C spectrum of **1j**

1,1'-biphenyl (**1k**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.61 (m, 4H), 7.46 (m, 4H), 7.37 (m, 2H)

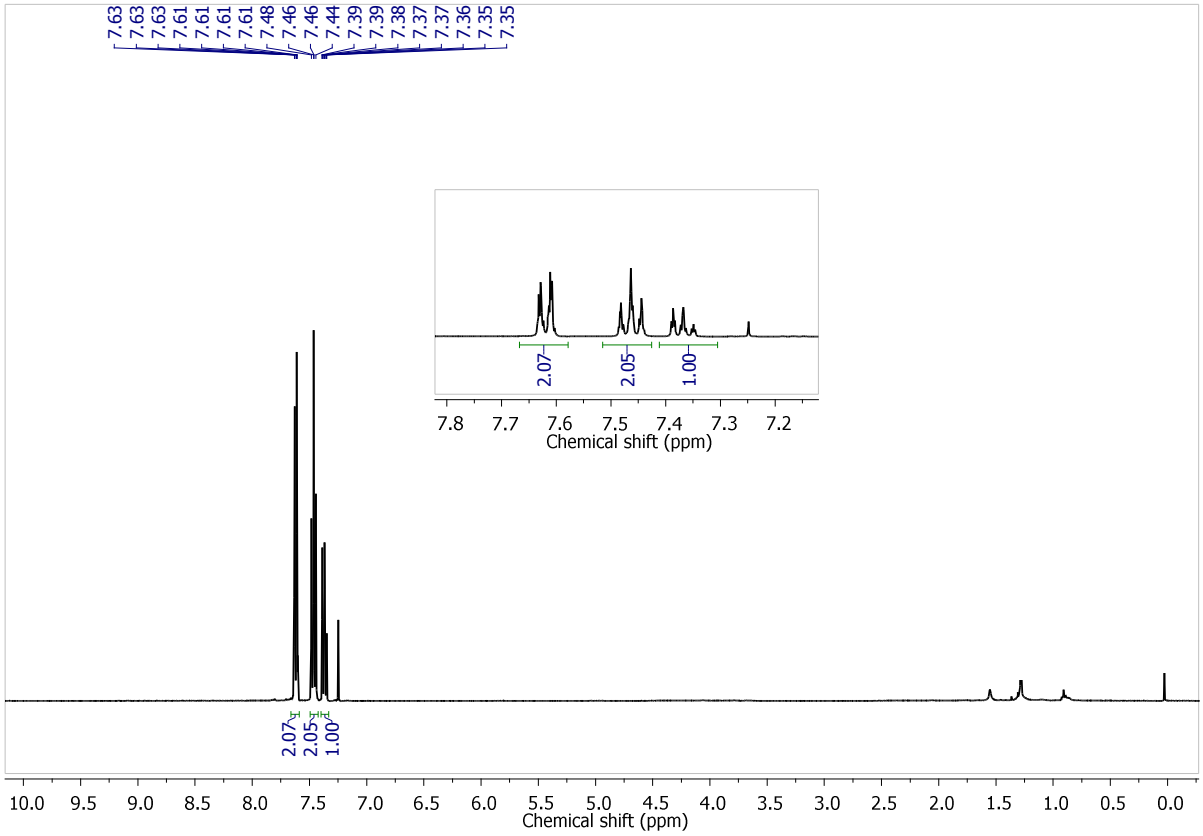
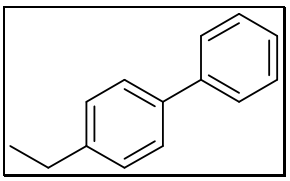


Figure S14 ^{1}H spectrum of **1k**

4-methoxy-1,1'-biphenyl (**1l**)



^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.57 (t, *J* = 8 Hz, 4H), 7.40 (t, *J* =8 Hz, 2H), 7.31 (m, 1H), 6.97 (d, *J* = 8 Hz, 2H), 3.85 (s, 3H)

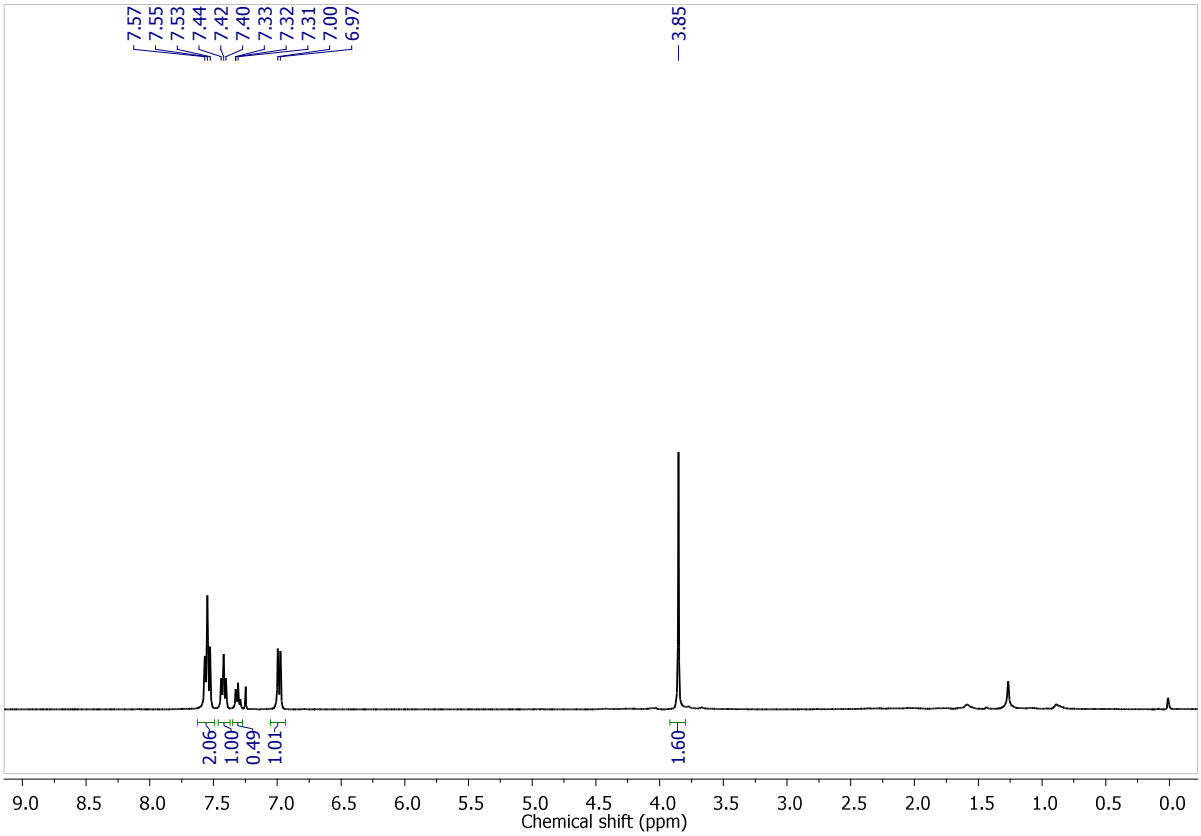


Figure S15 ^{1}H spectrum of **1l**