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Supporting Information

Palladium nanoparticles supported on reduced graphene oxide (Pd@rGO): an efficient heterogeneous catalyst for Suzuki-Miyaura, Heck-Matsuda and Double Suzuki-Miyaura cross-coupling reactions

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Experimental Section

All the necessary chemicals required were purchased from Sigma-Aldrich, Alfa Aesar and Spectrochem and utilized without further purification. IR spectra were recorded on a Bruker Alpha II system (υ_{max} in cm^{-1}) on KBr disk. ^{1}H NMR and ^{13}C NMR (400/500 MHz and 100/125 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in $CDCl_3$ (chemical shifts in δ with TMS as internal standard). GC-MS spectrum was recorded on Intuvo 9000GC System & 5977B GC/MSD, Agilent instrument. ESI-mass spectra were recorded on Xevo TQ-XS, Water Mass Spectrometer. Transmission Electron Microscope (TEM) and Energy Dispersive X-ray (EDX) analysis were recorded on JEM-2100, 200 kV, Jeol. Powder XRD was recorded on BRUKER AXS, D8 FOCUS instrument. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was carried out on Thermo Scientific^{TM} iCAP^{TM} 7600 instrument. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. Raman analysis was carried out on a Renishaw Basis Series with 514 lasers. X-Ray Photoelectron Spectroscopy (XPS) was performed using PHI 5000 VersaProbe III instrument.

Synthesis of Graphite Oxide (GO). GO was prepared according to the reported procedure from graphite powder.[1] Typically, 1 g of graphite powder and 0.5 g of sodium nitrate were added to 20 ml of concentrated H_2SO_4 (98%), and the mixture was kept in an ice-bath and stirred for 30 min. Next, 6 g of $KMnO_4$ was slowly added in portions over a period of 1 h, and the mixture was stirred again in ice-bath for another 1 h. The temperature of the mixture was then brought slowly to 35 ^{o}C (± 5 ^{o}C) and stirred for 1 h. After 1 h stirring, 20 ml of de-ionized water was added to the mixture and continued to stir at 35 ^{o}C (± 5 ^{o}C) for another 30 min. Finally, 180 ml of de-ionized water was added to the mixture followed by drop wise addition of H_2O_2 (30 %) which resulted in the formation bright yellow suspension. The synthesized graphite oxide was then collected by centrifugation, washed three times with water (3 × 30 ml) followed by ethanol (3 × 30 ml) and diethyl ether (3 × 30 ml). Finally, the obtained graphite oxide was dried in an oven at 40 ^{o}C for 24 h.

Synthesis of Pd@rGO. In a 250 ml round bottom flask, GO (1 g) was dispersed in DI water (100 ml) and ultrasonicated for 1 h at room temperature. After that, an aqueous solution of $PdCl_2$ (0.02 M, 5 ml) and NaCl (0.05 M, 5 ml) were added and the resulting reaction mixture was

further ultrasonicated at room temperature for another 1 h. Next, a freshly prepared aqueous solution of $NaBH_4$ (3 ml, 0.5 M) was added to the above suspension and stirred for 18 h at room temperature (25 ^oC). The prepared Pd@rGO catalyst was collected by centrifugation, filtration and washed three times with H_2O (3 × 30 ml) followed by ethanol (3 × 20 ml) and diethyl ether (3 × 10 ml). Finally, the obtained Pd@rGO catalyst was dried in an oven at 40 ^oC for 24 h.

General procedure for the synthesis of arenediazonium tetrafluoroborates.

An appropriate arylaniline (10 mmol) was dissolved in a mixture of hydrofluoroboric acid (3.4 ml) and distilled water (4 ml). The reaction mixture was cooled to 0 ^oC using an ice-water bath, and then aqueous solution of sodium nitrite (0.69 g in 1.5 ml of water) was added drop wise. After stirring for 40 min at 0-5 ^oC, the obtained precipitate was collected by filtration, dried and redissolved in a minimum amount of acetone. Then, the product was again precipitated by slow drop wise addition of diethyl ether with vigorous stirring. Finally, the product was filtered, washed several times with small portions of diethy ether, and dried under vacuum.

General procedure for the synthesis of biaryls (3a-3q) and terphenyl derivatives (5a-5f).

A mixture of arenediazonium tetrafluoroborate salt (**1**, 1.2 mmol), arylboronic acid (**2**, 1 mmol), and Pd@rGO (20 mg) in MeOH (5 ml) was stirred at 60 ^oC for the time indicated in **Table 2**. After completion of the reaction (TLC), the reaction mixture was cooled and the catalyst was removed by centrifugation followed by filtration. The recovered catalyst was washed with DCM (3 x 5 ml). The organic filtrate was concentrated and the resulting residue was purified by column chromatography over silica gel (60-120 mesh) by using ethylacetate in hexane (0-10 %) as eluent to obtain the pure products. To prepare the terphenyls, a mixture of 4-bromoarenediazonium tetrafluoroborate (1.2 mmol), arylboronic acid (**2**, 1 mmol), Pd@rGO (30 mg) and MeOH (5 ml) was stirred at 60 ^oC for 1 h. Next, aqueous Na_2CO_3 solution (2 M, 2 ml) and the second arylboronic acid (**4**, 1.2 mmol) were added slowly to the same reaction vessel and the reaction mixture was allowed to stir for another 6 h at 80 ^oC. The catalyst was then separated by centrifugation followed by filtration. The organic solvent was then removed from the filtrate by evaporation and the aqueous layer was extracted by dichloromethane (3 x 5 ml), washed with water (3 x 5 ml), brine (1 x 5 ml) and dried over anhydrous sodium sulphate. Finally, the

dichloromethane was removed and the crude product was purified by column chromatography (silica gel 60-120 mesh) by using ethylacetate in hexane as eluent to afford the desired products.

General procedure for the synthesis of cinnamates (7a-7i)

A mixture of arenediazonium tetrafluoroborate salt (**1,** 1.2 mmol), acrylate (**6**, 1 mmol) and Pd@rGO (25 mg) in MeOH (5 ml) was stirred at 50 ^{o}C for the time mentioned in **Table 4**. After completion of the reaction (TLC), the reaction mixture was cooled at room temperature and the catalyst was separated by centrifugation followed by filtration. The filtrate was concentrated to dryness by evaporation. Finally, the resulting residue was purified by column chromatography over silica gel (60-120 mesh) by using ethyl acetate and hexane as eluent to obtain the respective products.

Synthesis of 2-Amino-4'-Chlorobiphenyl (8)[13]

Typically, Fe powder (2.75 mmol), NH_4Cl (0.5 mmol) and H_2O (1 ml) were added to a solution of 4-chloro-2'-nitrobiphenyl (**3d,** 1 mmol) in EtOH (5 mL), and the resulting mixture was magnetically stirred for 1 h at 85 ^{o}C. After that, the reaction was cooled to room temperature and the organic solvent was removed from the reaction mixture. The aqueous layer was extracted by dichloromethane (3 x 5 ml), washed with water (3 x 5 ml), brine (1 x 5 ml) and dried over anhydrous sodium sulphate. Finally, the dichloromethane was removed and the crude product was purified by column chromatography (silica gel 60-120 mesh) by using ethyl acetate and hexane as eluent to afford the desired product **8**.

Synthesis of 2-chloronicotinoyl chloride (9)[4]

To a solution of chloronicotinic acid (1 mmol) in dry dichloromethane (5 ml), $(COCl)_2$ (2 mmol) and DMF (0.2 ml) were added and the mixture was stirred at 25 ^{o}C for 5 h under nitrogen atmosphere. After completion of the reaction, the solvent was removed under reduced pressure. Then, the crude product was used for the synthesis of boscalid without further purification.

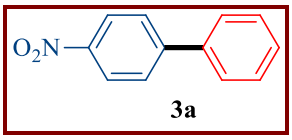
Synthesis of Boscalid (10)[4]

Typically, Et_3N (0.5 mmol) and 2-Amino-4'-Chlorobiphenyl (**8,** 0.5 mmol) were added to a solution of 2-chloronicotinoyl chloride (**9**, 0.75 mmol) in dry dichloromethane (3 ml) under N_2

atmosphere. The reaction mixture was then stirred at 30 °C for 8 h under N_2 atmosphere. After completion of the reaction time, 10 ml of water was added to the reaction mixture and extracted with dichloromethane (3 x 5 ml). The combined organic layers were washed with saturated solution of $NaHCO_3$ solution (1 x 10 ml) and dried over anhydrous sodium sulphate. The reaction mixture was then concentrated by evaporation and the crude product was purified by column chromatography (silica gel 60-120 mesh) by using ethyl acetate in hexane as eluent to afford the desired product **10**.

Characterization data for products.

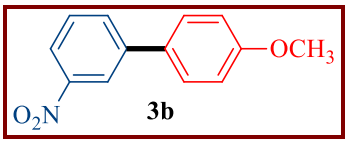
1. **4-nitro-1,1'-biphenyl (3a).**[2]



3a

White solid. IR (KBr): 1345, 1513, 2837, 2931, 3036, 3073 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.26 (m, 1H), 7.53-7.45 (m, 2H), 7.67 (t, *J* = 8 Hz, 2H), 7.78-7.74 (m, 2H), 8.34-8.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 124.1, 127.4, 127.8, 128.9, 129.1, 138.8, 147.5.

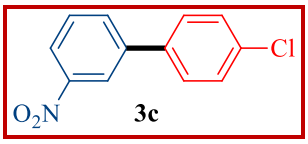
2. **4'-methoxy-3-nitro-1,1'-biphenyl (3b).**[3]



3b

Light yellow solid. IR (KBr): 1349, 1512, 1610, 2931, 2963, 3036, 3087 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.88 (s, 3H), 7.03 (d, *J* = 8 Hz, 2H), 7.60-7.56 (m, 3H), 7.88 (d, *J* = 8 Hz, 1H), 8.16-8.14 (m, 1H), 8.42-8.14 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.4, 114.5, 121.37, 121.39, 128.2, 129.6, 131.0, 132.5, 142.4, 148.7, 160.0. GC-MS (EI): *m/z* 229 $[M]^+$.

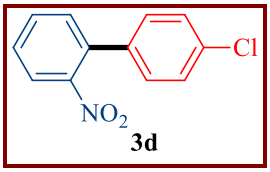
3. **4'-chloro-3-nitro-1,1'-biphenyl (3c).**



3c

Off white solid. IR (KBr): 1354, 1524, 2861, 2926, 3037 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, *J* = 12 Hz, 2H), 7.58 (d, *J* = 8 Hz, 2H), 7.65 (t, *J* = 8 Hz, 1H), 7.90 (d, *J* = 8 Hz, 1H), 8.23-8.21 (m, 1H), 8.43-8.42 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.8, 122.3, 128.4, 129.3, 129.9, 132.8, 134.8, 137.0, 141.6, 148.7.

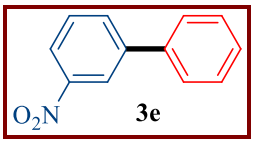
4. **4'-chloro-2-nitro-1,1'-biphenyl (3d).**[4]



3d

Yellow liquid. IR (KBr): 1354, 1524, 2860, 2924, 3086 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, *J* = 8 Hz, 2H), 7.42-7.39 (m, 3H), 7.53-7.49 (m, 1H), 7.65-7.61 (m, 1H), 7.90-7.87 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 124.2, 128.5, 128.9, 129.2, 131.8, 132.4, 134.5, 135.2, 135.9.

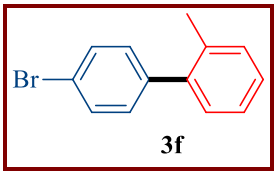
5. **3-nitro-1,1'-biphenyl (3e).**[2]



3e

White solid. IR (KBr): 1350, 1529, 2862, 2923, 3038, 3083 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.41 (m, 1H), 7.52 (t, *J* = 8 Hz, 2H), 7.64-7.59 (m, 3H), 7.93 (d, *J* = 8 Hz, 1H), 8.21-8.19 (m, 1H), 8.46-8.45 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.9, 122.0, 127.1, 128.5, 129.1, 129.7, 133.0, 138.6, 142.8, 148.7.

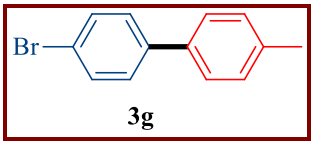
6. **4'-bromo-2-methyl-1,1'-biphenyl (3f).**



3f

Colourless liquid. IR (KBr): 1476, 2856, 2922, 3059 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20-7.17 (m, 3H), 7.24-7.21 (m, 1H), 7.27-7.26 (m, 2H), 7.54 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.9, 120.5, 125.4, 127.1, 129.1, 129.9, 130.4, 130.7, 134.7, 140.1, 140.3.

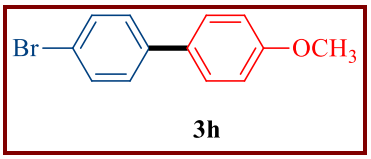
7. **4-bromo-4'-methyl-1,1'-biphenyl (3g).**[5]



3g

White solid. IR (KBr): 1478, 2853, 2914, 3054 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.59 (s, 3H), 7.46 (d, *J* = 8 Hz, 2H), 7.66-7.63 (m, 4H), 7.75 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.3, 121.3, 126.9, 128.7, 129.8, 131.9, 137.2, 137.6, 140.2.

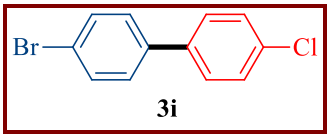
8. **4-bromo-4'-methoxy-1,1'-biphenyl (3h).**[5]



3h

White solid. IR (KBr): 1606, 2838, 2933, 2962, 3008 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.85 (s, 3H), 6.98 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8 Hz, 2H), 7.54-7.48 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.3, 114.3, 120.7, 127.9, 128.3, 131.7, 132.4, 139.7, 159.3.

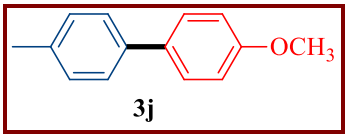
9. **4-bromo-4'-chloro-1,1'-biphenyl (3i).**



3i

White solid. IR (KBr): 1470, 1640, 2924, 2953, 3053 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44-7.42 (m, 4H), 7.51 (d, *J* = 8 Hz, 2H), 7.60 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.9, 128.20, 128.24, 128.53, 128.57, 129.06, 129.09, 132.0, 133.7, 133.8, 138.4, 138.9.

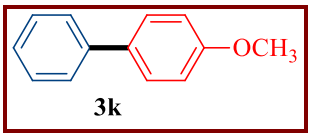
10. **4-methoxy-4'-methyl-1,1'-biphenyl (3j).**[6]



3j

White solid. IR (KBr): 1607, 2914, 2957, 3074 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 3H), 3.85 (s, 3H), 6.98 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.0, 55.3, 114.1, 126.5, 127.9, 129.4, 133.7, 136.3, 137.9, 158.9.

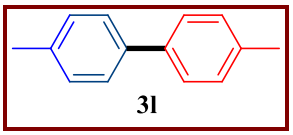
11. 4-methoxy-1,1'-biphenyl (3k).[3]



3k

White solid. IR (KBr): 1606, 2836, 2936, 2960, 3001, 3063 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 6.99 (d, *J* = 8 Hz, 2H), 7.32-7.29 (m, 1H), 7.44 (t, *J* = 8 Hz, 2H), 7.56 (t, *J* = 8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.3, 114.1, 126.6, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1.

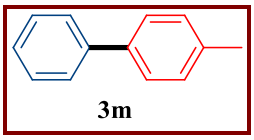
12. 4,4'-dimethyl-1,1'-biphenyl (3l).[6]



3l

White solid. IR (KBr): 1498, 2855, 2941, 2966, 3047 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 6H), 7.24 (d, *J* = 8 Hz, 4H), 7.49 (d, *J* = 8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.6, 126.3, 128.9, 136.2, 137.7.

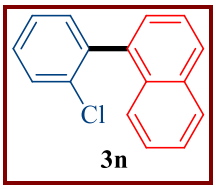
13. 4-methyl-1,1'-biphenyl (3m).[7]



3m

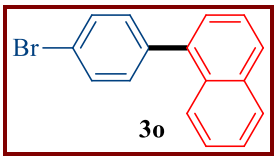
White solid. IR (KBr): 1497, 2857, 2916, 3025 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.39 (s, 3H), 7.26 (d, *J* = 8 Hz, 2H), 7.36-7.30 (m, 1H), 7.44 (t, *J* = 8 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 7.59 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.6, 126.3, 126.54, 126.56, 126.7, 126.8, 128.2, 128.3, 129.01, 129.05, 136.5, 137.8, 140.7.

14. 1-(2-chlorophenyl)naphthalene (3n).



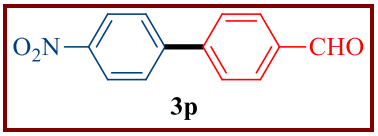
White solid. IR (KBr): 2851, 2922, 2954, 3056 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.42 (m, 5H), 7.61-7.52 (m, 4H), 7.96 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 125.2, 125.90, 125.92, 126.2, 126.6, 127.1, 128.2, 128.3, 128.9, 129.5, 131.6, 132.1, 133.4, 134.1, 137.4, 139.3.

15. 1-(4-bromophenyl)naphthalene (3o).



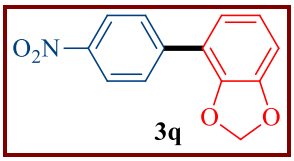
Colourless liquid. IR (KBr): 2851, 2922, 3045 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.35 (m, 4H), 7.53-7.48 (m, 2H), 7.62 (d, *J* = 8 Hz, 2H), 7.91-7.82 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.0, 124.9, 125.1, 125.4, 125.8, 126.4, 127.5, 127.9, 130.8, 130.9, 131.2, 133.3, 138.4, 139.1.

16. 4'-nitro-[1,1'-biphenyl]-4-carbaldehyde (3p).



Yellow solid. IR (KBr): 1343, 1567, 1697, 2726, 2825, 2927, 3070 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 8 Hz, 4H), 8.05 (d, *J* = 8 Hz, 2H), 8.37 (d, *J* = 8 Hz, 2H), 10.1 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 124.2, 128.1, 128.2, 130.4, 136.2, 144.5, 146.0, 147.7, 191.6.

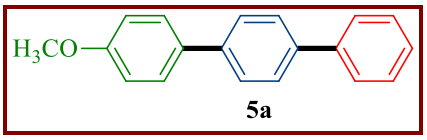
17. 4-(4-nitrophenyl)benzo[d][1,3]dioxole (3q).



3q

Yellow solid. IR (KBr): 1338, 1510, 2919, 2993 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.07 (s, 2H), 6.96 (d, *J* = 8 Hz, 1H), 7.15-7.11 (m, 2H), 7.68 (d, *J* = 8 Hz, 2H), 8.29 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 101.5, 107.6, 108.9, 121.4, 124.1, 127.3, 132.9, 146.7, 147.2, 148.51, 148.57.

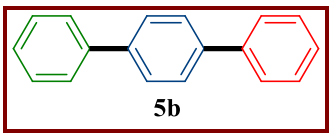
18. 4-methoxy-1,1':4',1''-terphenyl (5a).[8]



5a

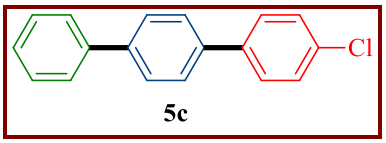
White solid. IR (KBr): 2923, 3001, 3063 $cm^{-1.}$ ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.87 (s, 3H), 7.01 (d, *J* = 8 Hz, 2H), 7.38 (t, *J* = 8 Hz, 1H), 7.48 (t, *J* = 8 Hz, 2H), 7.61-7.58 (m, 2H), 7.65-7.63 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 54.8, 113.8, 120.2, 126.50, 126.55, 126.9, 127.4, 127.5, 127.8, 128.3, 131.2, 131.9, 139.2, 158.9.

19. 1,1':4',1''-terphenyl (5b).[9]


5b

White solid. IR (KBr): 2924, 3032, 3058 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, *J* = 8 Hz, 2H), 7.42 (t, *J* = 8 Hz, 4H), 7.60-7.58 (m, 4H), 7.62 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 126.5, 126.8, 127.0, 128.3, 139.6, 140.2.

20. 4-chloro-1,1':4',1''-terphenyl (5c).[10]

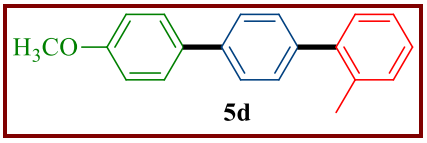


5c

White solid. IR (KBr): 2922, 3033 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.28 (m, 5H), 7.51 (d, *J* = 8 Hz, 2H), 7.62-7.56 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 126.5,

126.8, 126.9, 127.0, 127.1, 127.7, 128.33, 128.36, 128.4, 132.9, 138.3, 138.6, 139.9, 140.0.

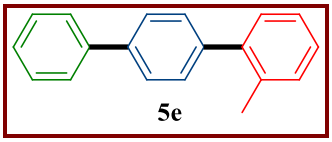
21. 4''-methoxy-2-methyl-1,1':4',1''-terphenyl (5d).



5d

White solid. IR (KBr): 1482, 2855, 2923, 2957 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.33 (s, 3H), 3.87 (s, 3H), 7.02 (d, *J* = 8 Hz, 2H), 7.30-7.26 (m, 4H), 7.39 (d, *J* = 8 Hz, 2H), 7.62-7.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.5, 55.3, 114.2, 125.8, 126.3, 127.2, 128.09, 129.6, 129.8, 130.3, 133.4, 135.4, 139.2, 140.3, 141.5, 159.2.

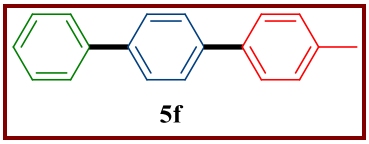
22. 2-methyl-1,1':4',1''-terphenyl (5e).



5e

White solid. IR (KBr): 1478, 2859, 2924, 2955, 3023 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.33 (s, 3H), 7.27 (brs, 3H), 7.47-7.33 (m, 6H), 7.65-7.63 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.7, 126.0, 127.0, 127.2, 127.4, 127.5, 129.0, 129.8, 130.0, 130.6, 135.6, 139.8, 141.0, 141.1, 141.6.

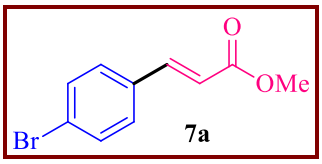
23. 4-methyl-1,1':4',1''-terphenyl (5f).[9]



5f

White solid. IR (KBr): 1483, 2858, 2916, 3029 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3H), 7.27 (d, *J* = 8 Hz, 2H), 7.37 (t, *J* = 8 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8 Hz, 2H), 7.66-7.63 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.3, 127.0, 127.2, 127.4, 127.6, 127.7, 129.0, 129.7, 137.3, 137.9, 140.0, 140.2, 140.9.

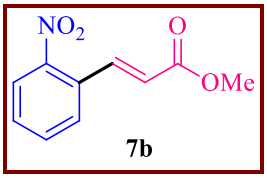
24. (E)-methyl 3-(4-bromophenyl)acrylate (7a).[4]



7a

White solid. IR (KBr): 1587, 1633, 1710, 2851, 2946, 2998, 3035, 3063 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.83 (s, 3H), 6.47 (d, *J* = 16 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.8, 118.4, 124.6, 129.4, 132.1, 133.2, 143.5, 167.2.

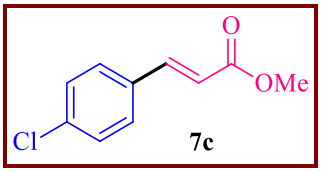
25. (E)-methyl 3-(2-nitrophenyl)acrylate (7b). [4]



7b

Light yellow solid. IR (KBr): 1346, 1520, 1636, 1719, 2953, 3024 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.80 (s, 3H), 6.35 (dd, *J* = 2.4 Hz, *J* = 16 Hz, 1H), 7.53-7.49 (m, 1H), 7.64-7.58 (m, 2H), 8.02 (d, *J* = 8 Hz, 1H), 8.11 (dd, *J* = 2.4 Hz, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.0, 122.8, 124.9, 129.1, 130.3, 130.6, 133.5, 140.2, 166.2.

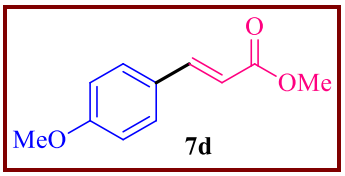
26. (E)-methyl 3-(4-chlorophenyl)acrylate (7c). [4]



7c

White solid. IR (KBr): 1318, 1632, 1706, 2837, 2949, 3001, 3036 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.83 (s, 3H), 6.45 (d, *J* = 16 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.8, 118.3, 129.20, 129.25, 132.8, 136.2, 143.4, 167.2.

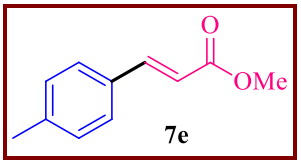
27. (E)-methyl 3-(4-methoxyphenyl)acrylate (7d). [4]



7d

White solid. IR (KBr): 1512, 1603, 1639, 1716, 2844, 2947, 3001 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.79 (s, 3H), 3.84 (s, 3H), 6.33 (d, *J* = 16 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.6, 55.4, 114.3, 115.2, 127.1, 129.7, 144.5, 161.4, 167.8.

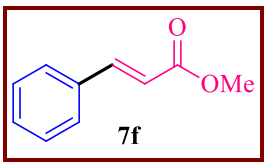
28. (E)-methyl 3-(p-tolyl)acrylate (7e). [11]



7e

White solid. IR (KBr): 1631, 1708, 2944, 3026, 3059 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.37 (s, 3H), 3.80 (s, 3H), 6.42 (d, *J* = 16 Hz, 1H), 7.20 (d, *J* = 8 Hz, 2H), 7.43 (d, *J* = 8 Hz, 2H), 7.69 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 51.6, 116.6, 128.0, 129.6, 131.6, 140.7, 144.9, 167.6.

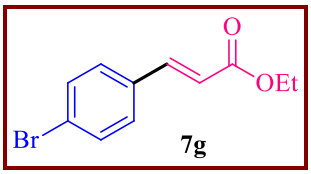
29. methyl cinnamate (7f). [11]



7f

White solid. IR (KBr): 1637, 1717, 2848, 2944, 2992, 3030 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.80 (s, 3H), 6.46 (d, *J* = 12 Hz, 1H), 7.39-7.37 (m, 3H), 7.53-7.51 (m, 2H), 7.71 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 51.7, 117.8, 128.0, 128.9, 130.3, 134.4, 144.9, 167.4.

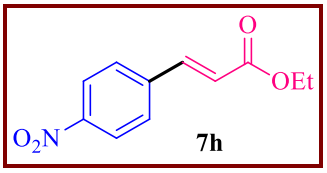
30. (E)-ethyl 3-(4-bromophenyl)acrylate (7g).



7g

Colourless liquid. IR (KBr): 1587, 1633, 1710, 2851, 2946, 2998, 3064 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.35 (t, *J* = 7.25 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 6.43 (d, *J* = 16 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.62 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.2, 60.6, 119.0, 124.4, 129.4, 132.1, 133.4, 143.1, 166.7.

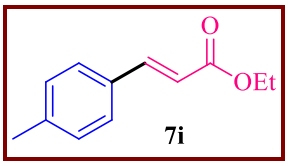
31. (E)-ethyl 3-(4-nitrophenyl)acrylate (7h).[12]



7h

White solid. IR (KBr): 1342, 1516, 1644, 1712, 2936, 3049 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 1.37 (t, *J* = 7.20 Hz, 3H), 4.32 (q, *J* = 7 Hz, 2H), 6.58 (d, *J* = 16 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 16.4 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 60.6, 119.0, 124.4, 129.4, 132.1, 133.4, 143.1, 166.7.

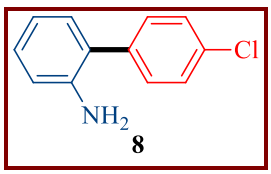
32. (E)-ethyl 3-(p-tolyl)acrylate (7i).[12]



7i

Light yellow liquid. IR (KBr): 1636, 1712, 2951, 3026 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.34 (t, *J* = 7 Hz, 3H), 2.36 (s, 3H), 4.27 (q, *J* = 7 Hz, 2H), 6.40 (d, *J* = 16 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.3, 21.4, 60.3, 117.2, 128.0, 129.6, 131.7, 140.6, 144.5, 167.1.

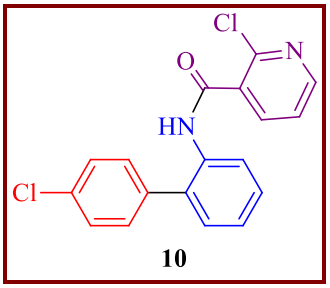
33. 2-Amino-4'-Chlorobiphenyl (8).[13]



8

Pale yellow solid. IR (KBr): 1479, 1615, 2924, 3055, 3361, 3444 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.83 (brs, 2H), 6.72 (d, *J* = 8 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H 7.11 (t, *J* = 7.6 Hz, 1H), 4.08 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 116.1, 119.2, 126.7, 128.8, 129.02, 130.4, 130.5, 133.1, 137.7, 142.7.

34. Boscalid (10).[4]



10

White solid. IR (KBr): 1661, 2854, 3025, 3229 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.26 (m, 2H), 7.37-7.33 (m, 3H), 7.48-7.42 (m, 3H), 8.15 (dd, *J* = 2 Hz, *J* = 7.6 Hz, 2H), 8.42 (d, *J* = 8 Hz, 1H), 8.46 (dd, *J* = 2 Hz, *J* = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 122.1, 122.9, 125.3, 128.9, 129.3, 130.2, 130.8, 131.0, 132.2, 134.3, 134.4, 136.2, 140.2, 146.7, 151.3, 162.5. ESI-MS: *m/z* 343, 345 (M^+).

5. ^{1}H and ^{13}C NMR Spectra

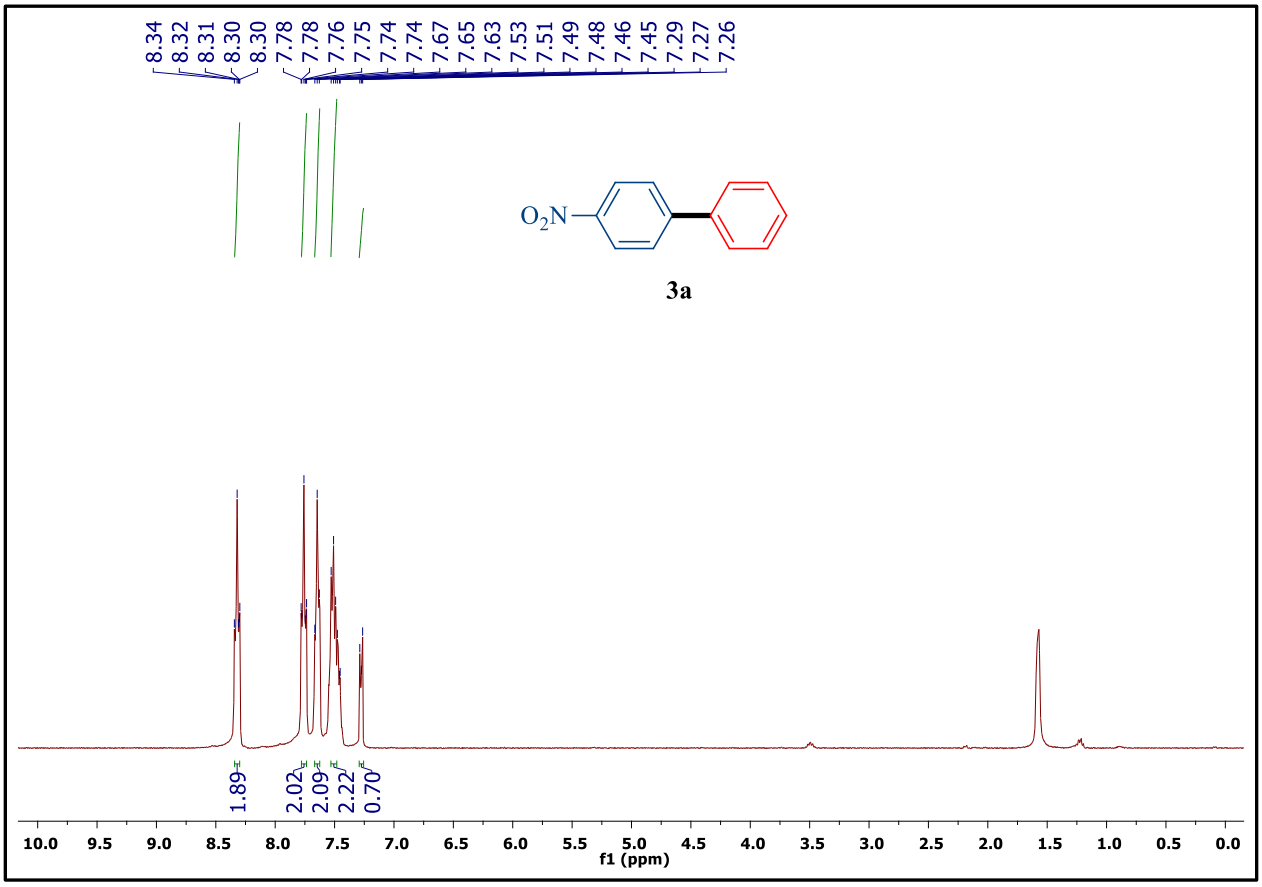


Figure S1. ^{1}H NMR spectra of **3a** in $CDCl_3$

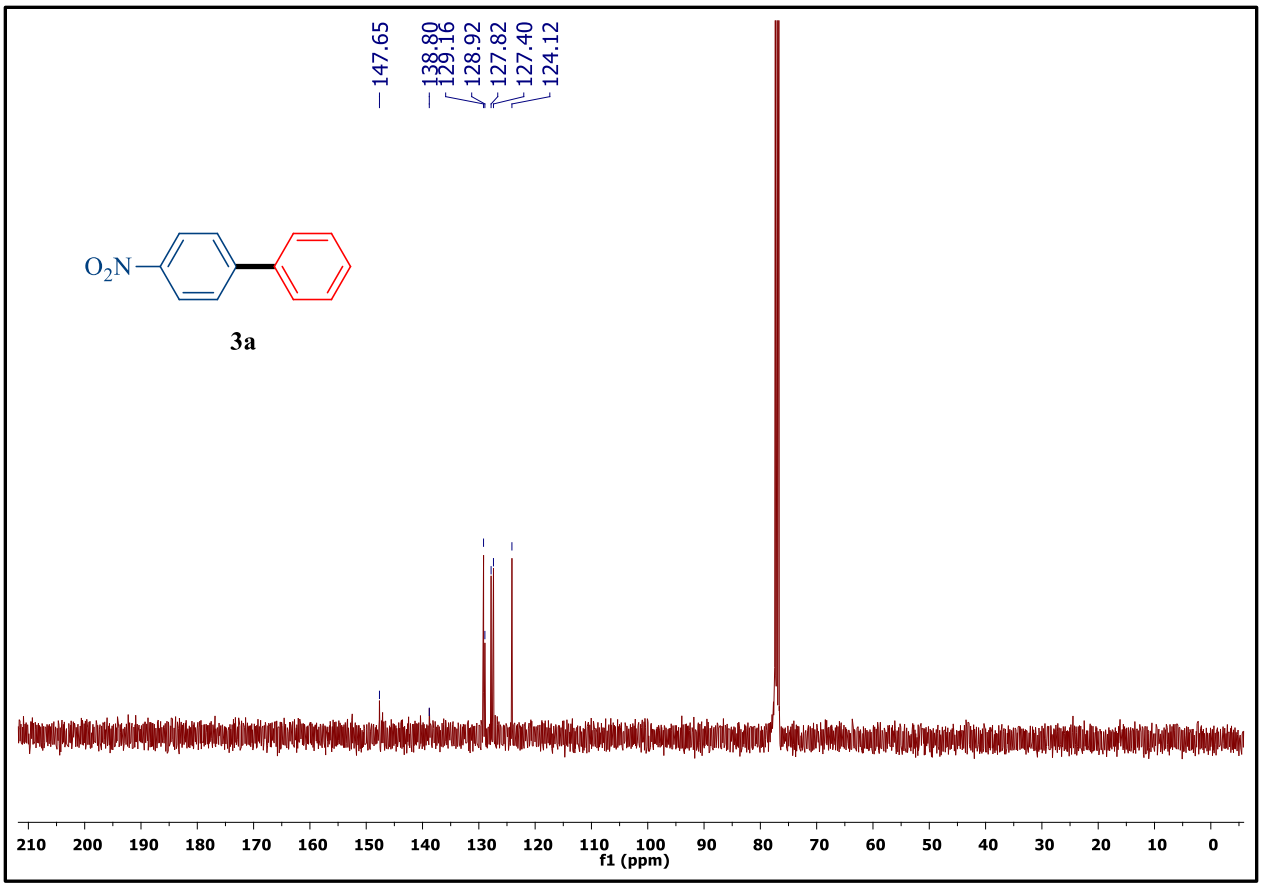


Figure S2. ^{13}C NMR spectra of **3a** in $CDCl_3$

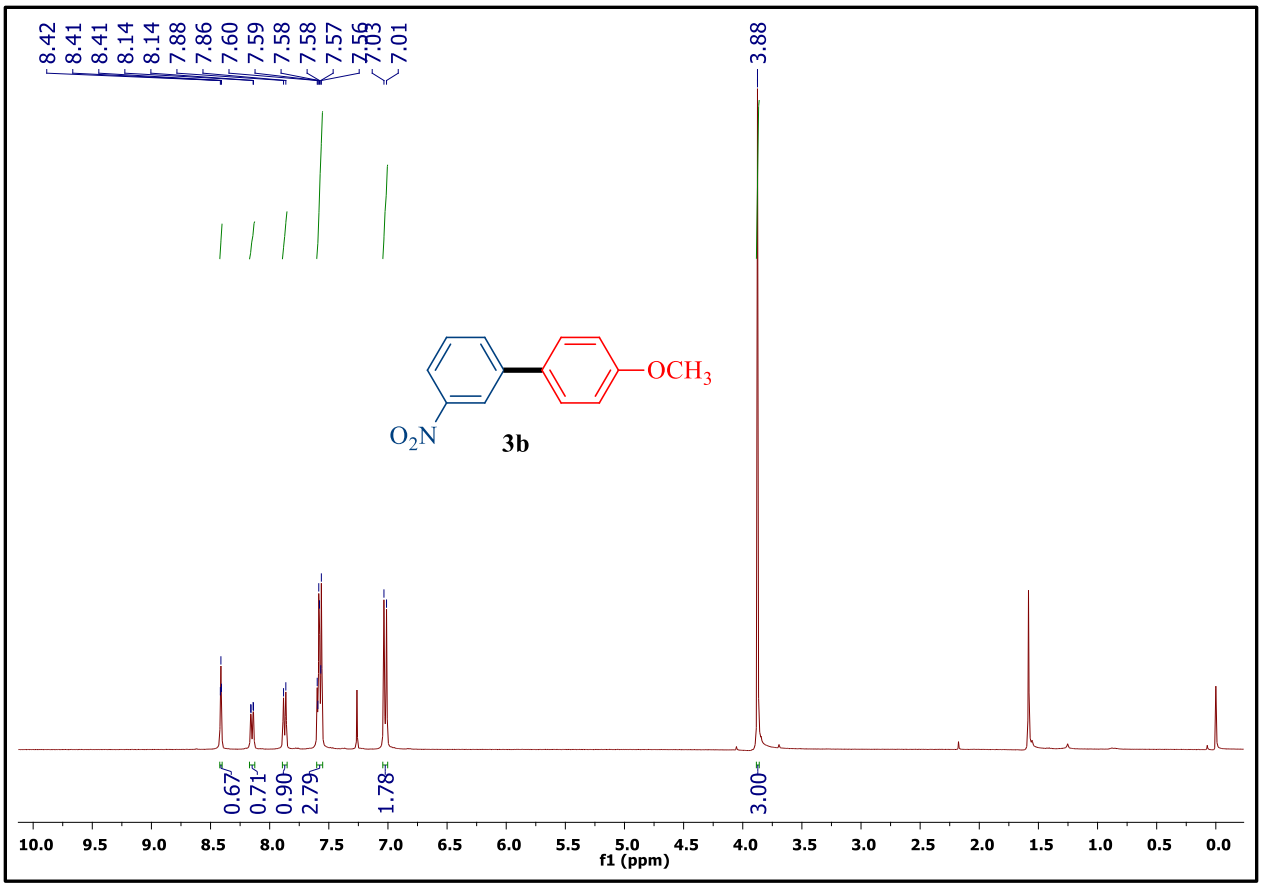


Figure S3. ^{1}H NMR spectra of **3b** in $CDCl_3$

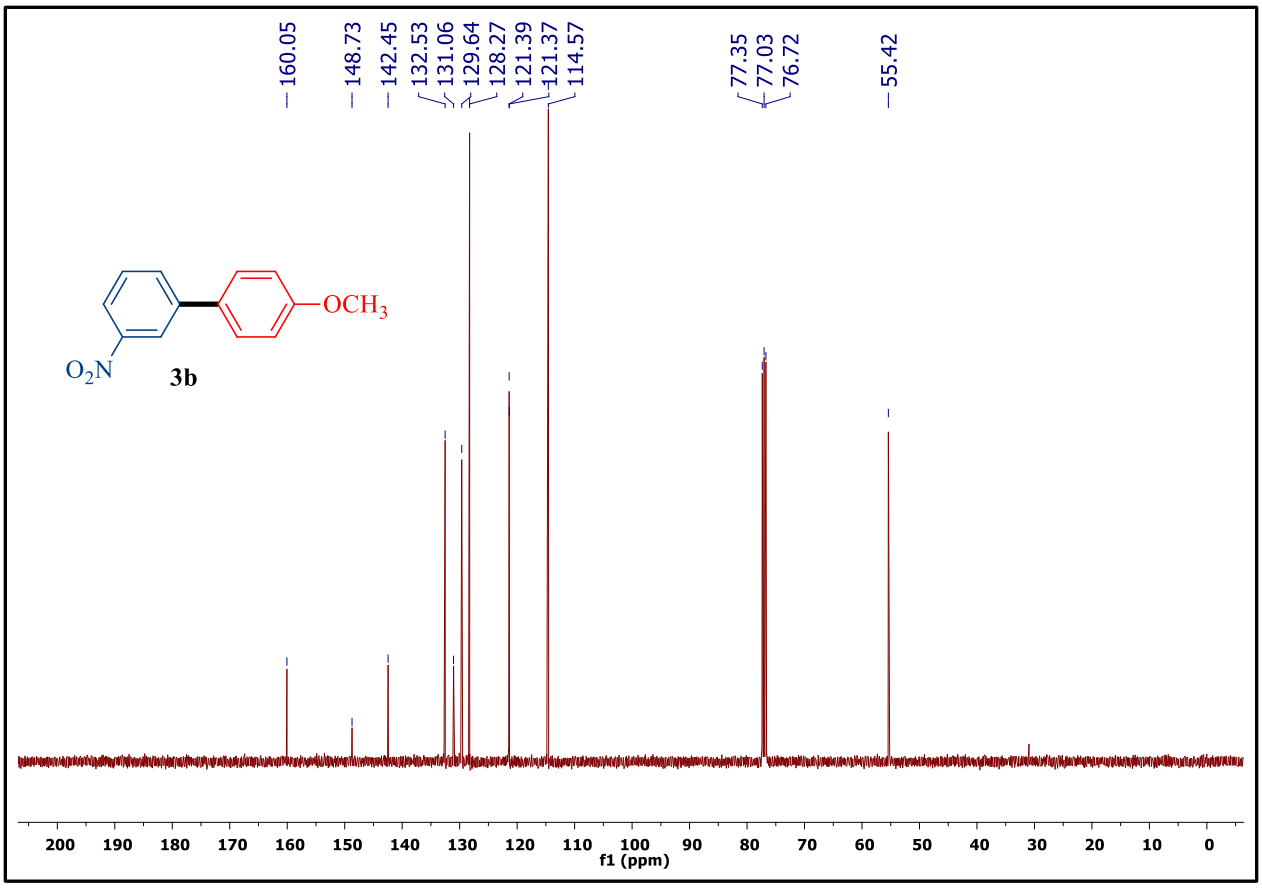


Figure S4. ^{13}C NMR spectra of **3b** in $CDCl_3$

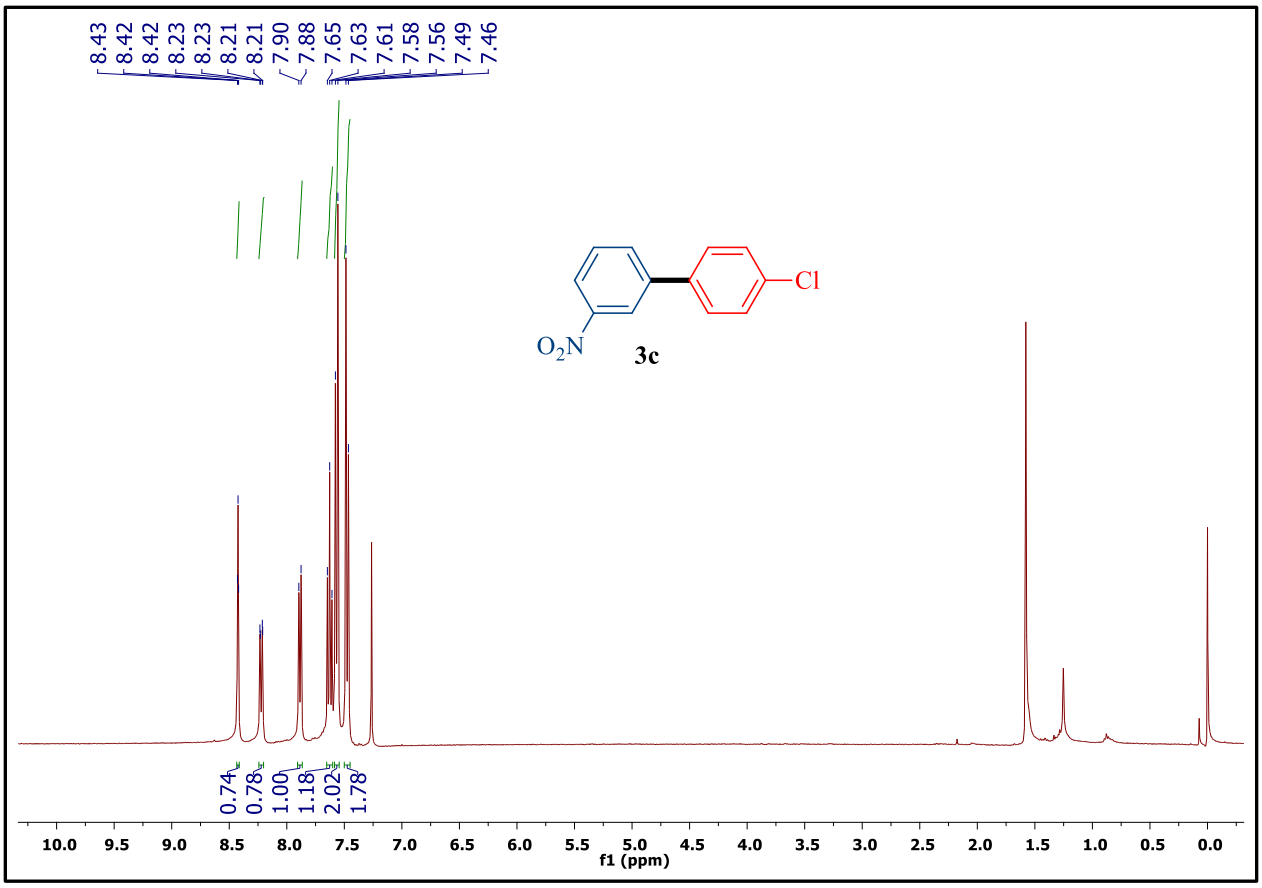


Figure S5. ^{1}H NMR spectra of **3c** in $CDCl_3$

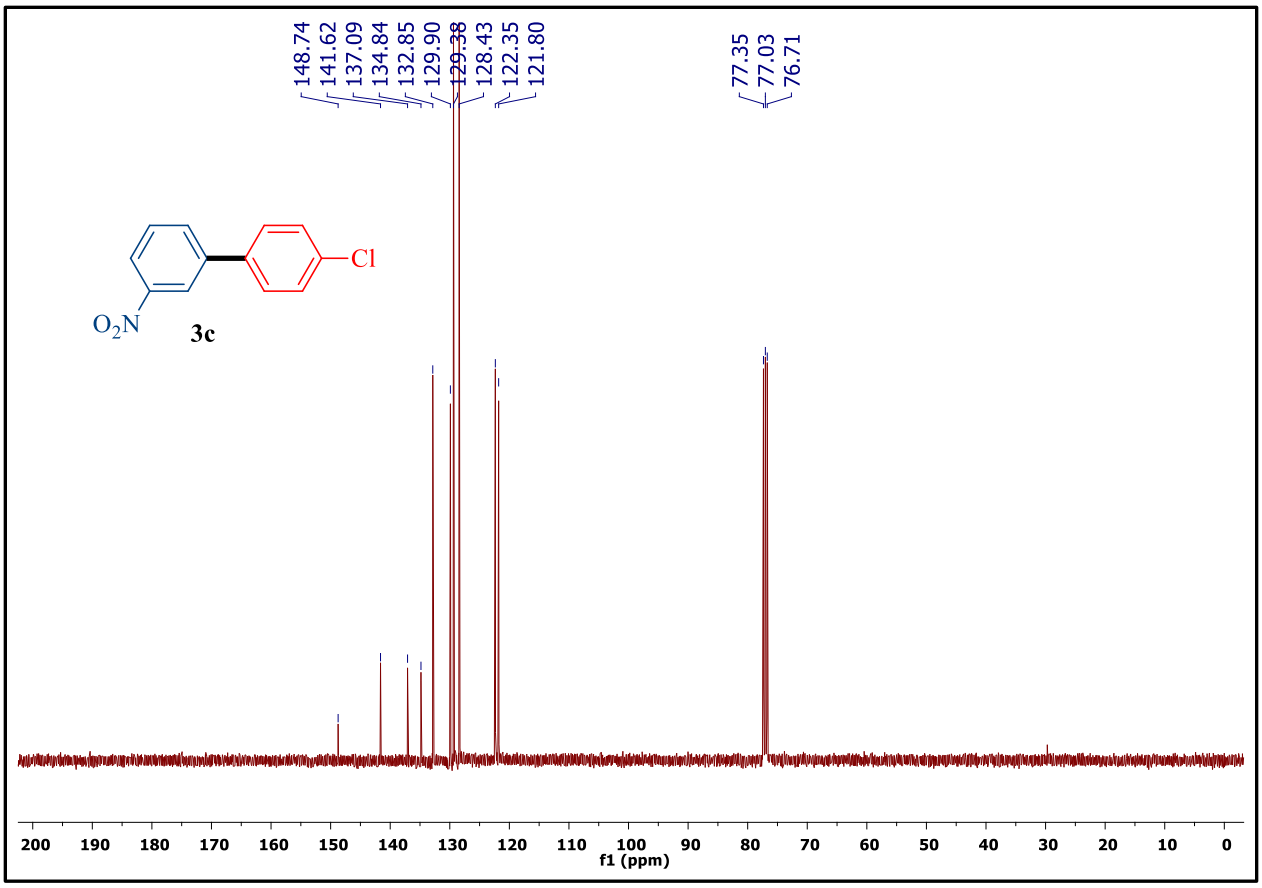


Figure S6. ^{13}C NMR spectra of **3c** in $CDCl_3$

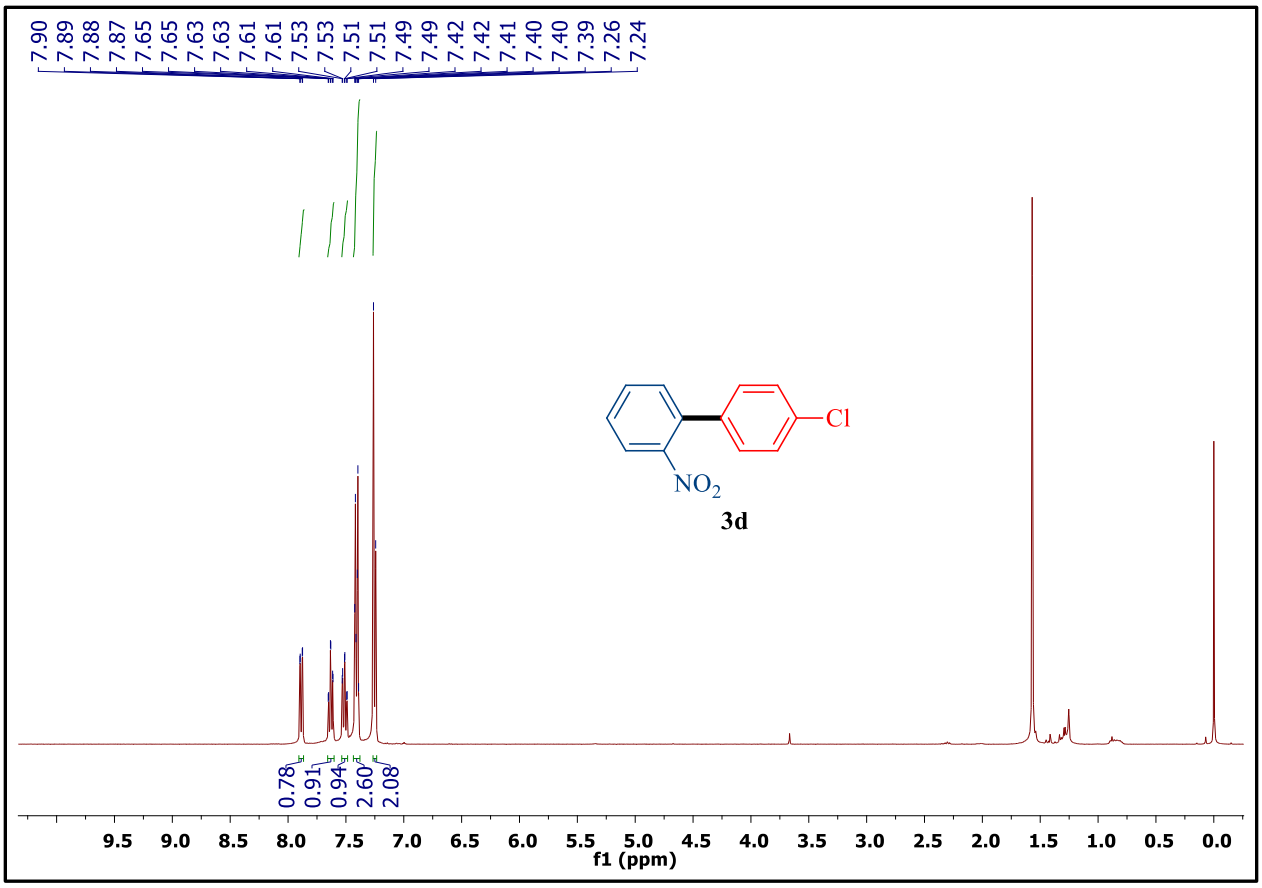


Figure S7. ^{1}H NMR spectra of **3d** in $CDCl_3$

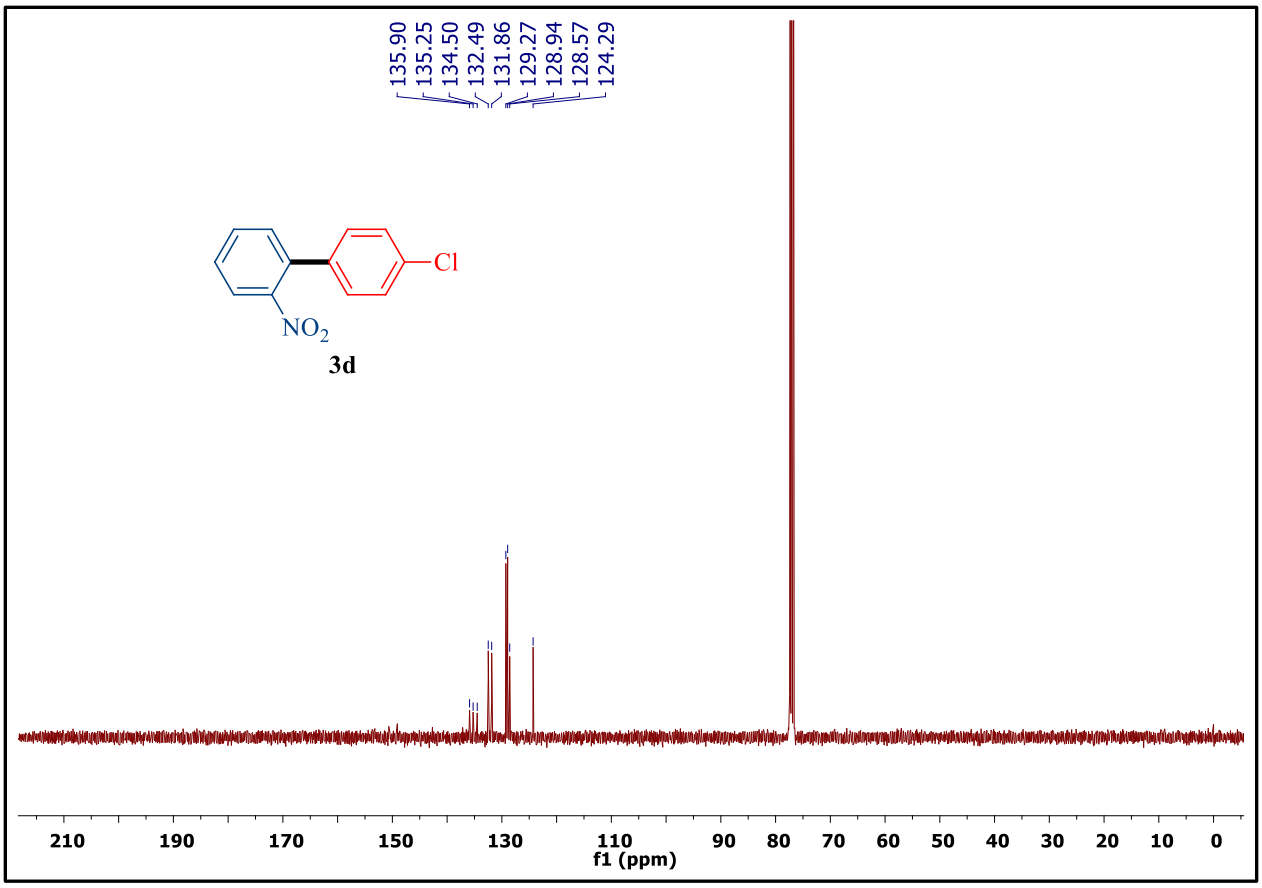


Figure S8. ^{13}C NMR spectra of **3d** in $CDCl_3$

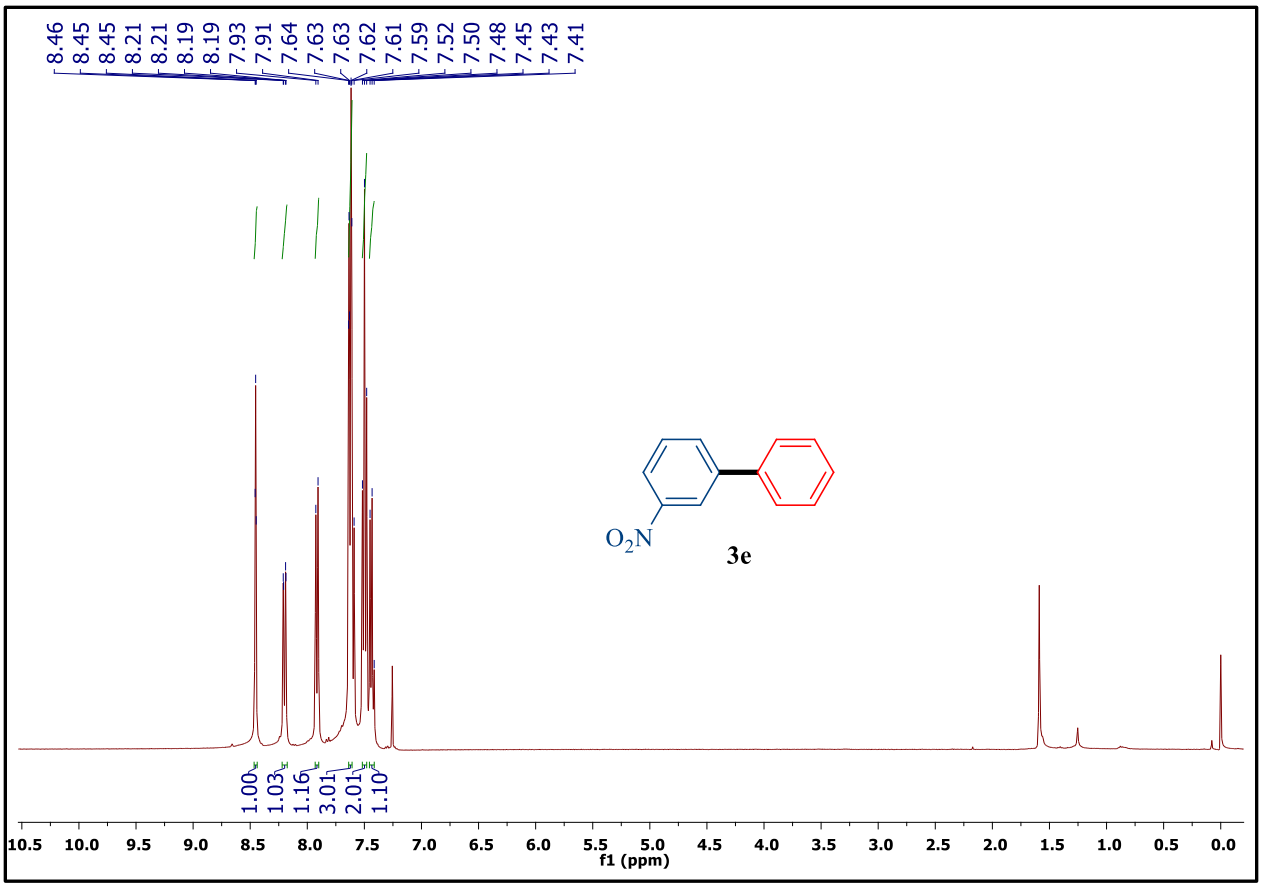


Figure S9. ^{1}H NMR spectra of **3e** in $CDCl_3$

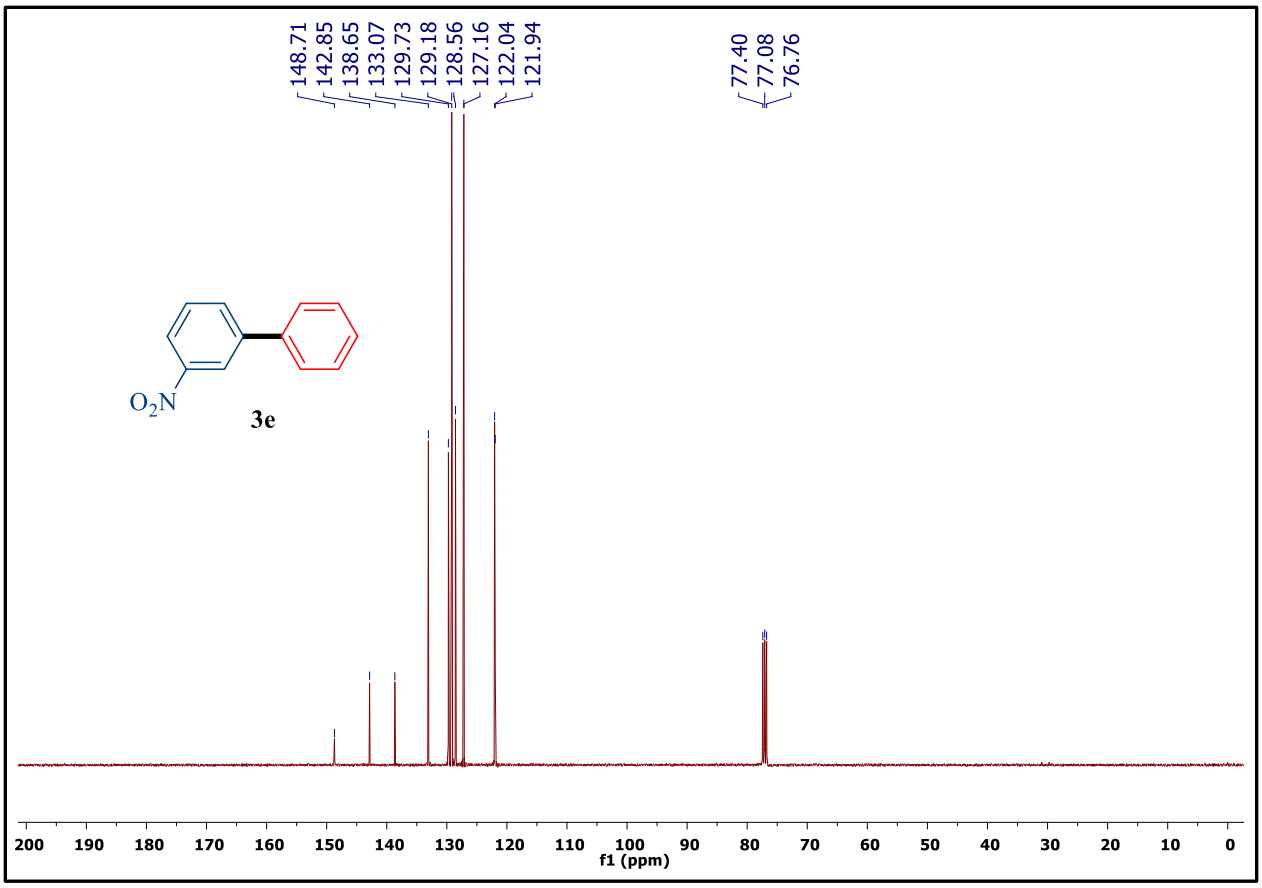


Figure S10. ^{13}C NMR spectra of **3e** in $CDCl_3$

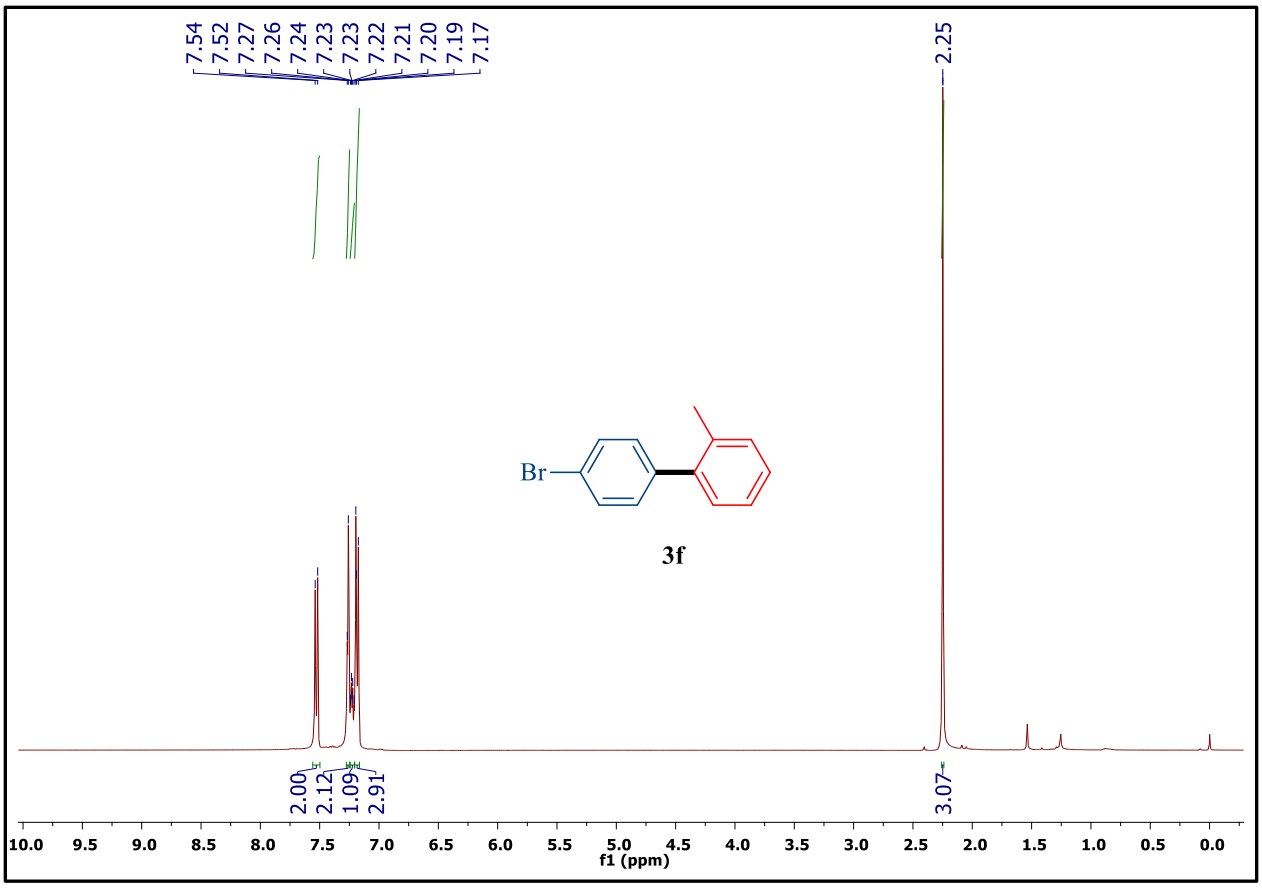


Figure S11. ^{1}H NMR spectra of **3f** in $CDCl_3$

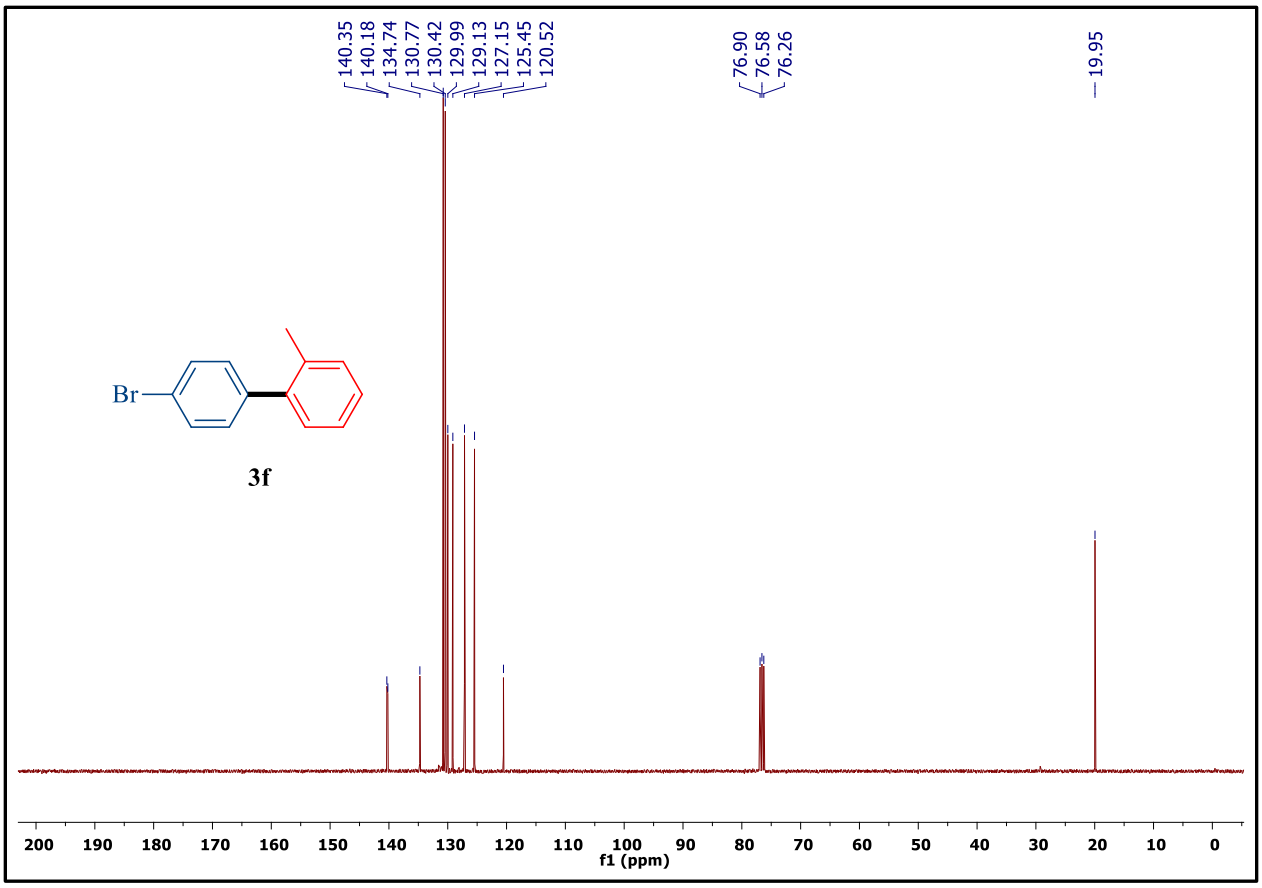


Figure S12. ^{13}C NMR spectra of **3f** in $CDCl_3$

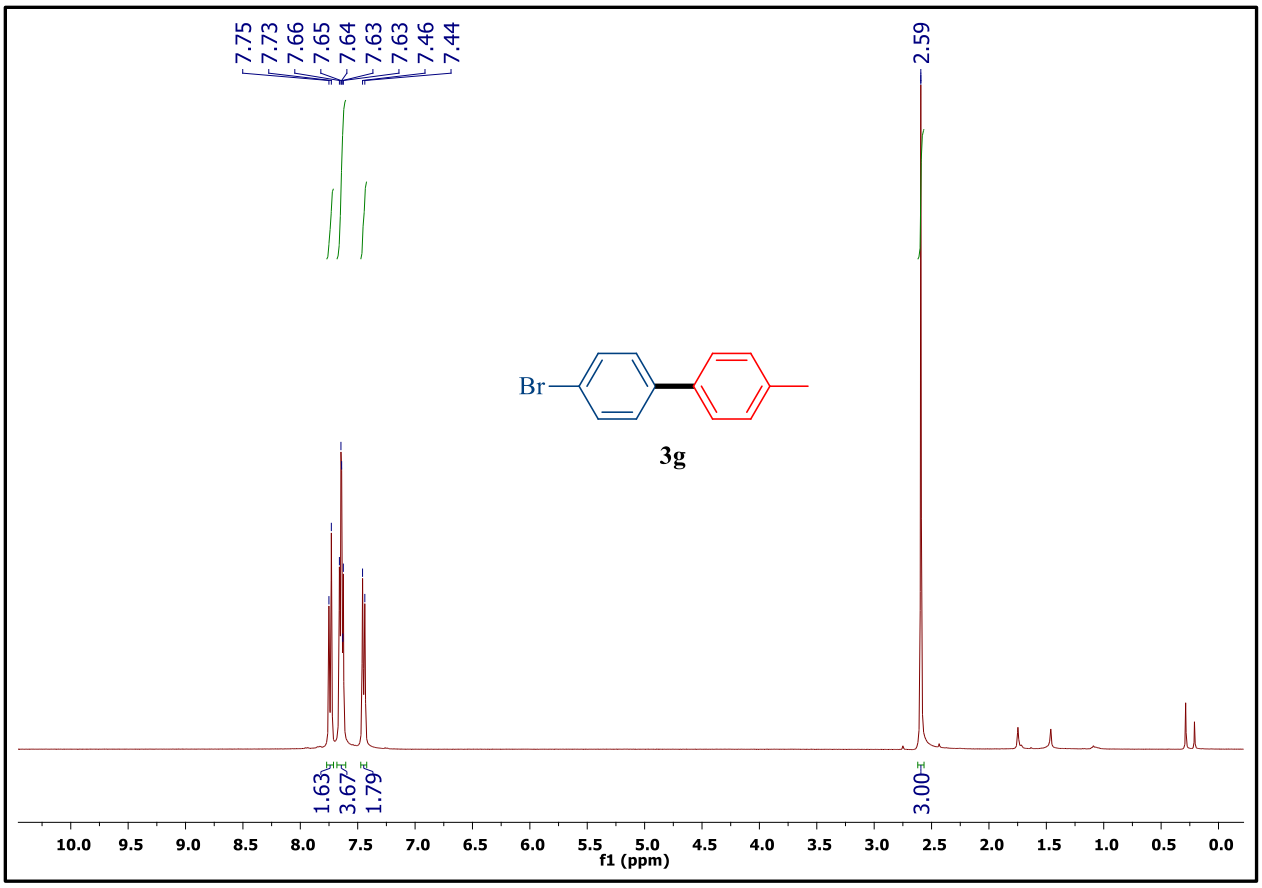


Figure S13. ^{1}H NMR spectra of **3g** in $CDCl_3$

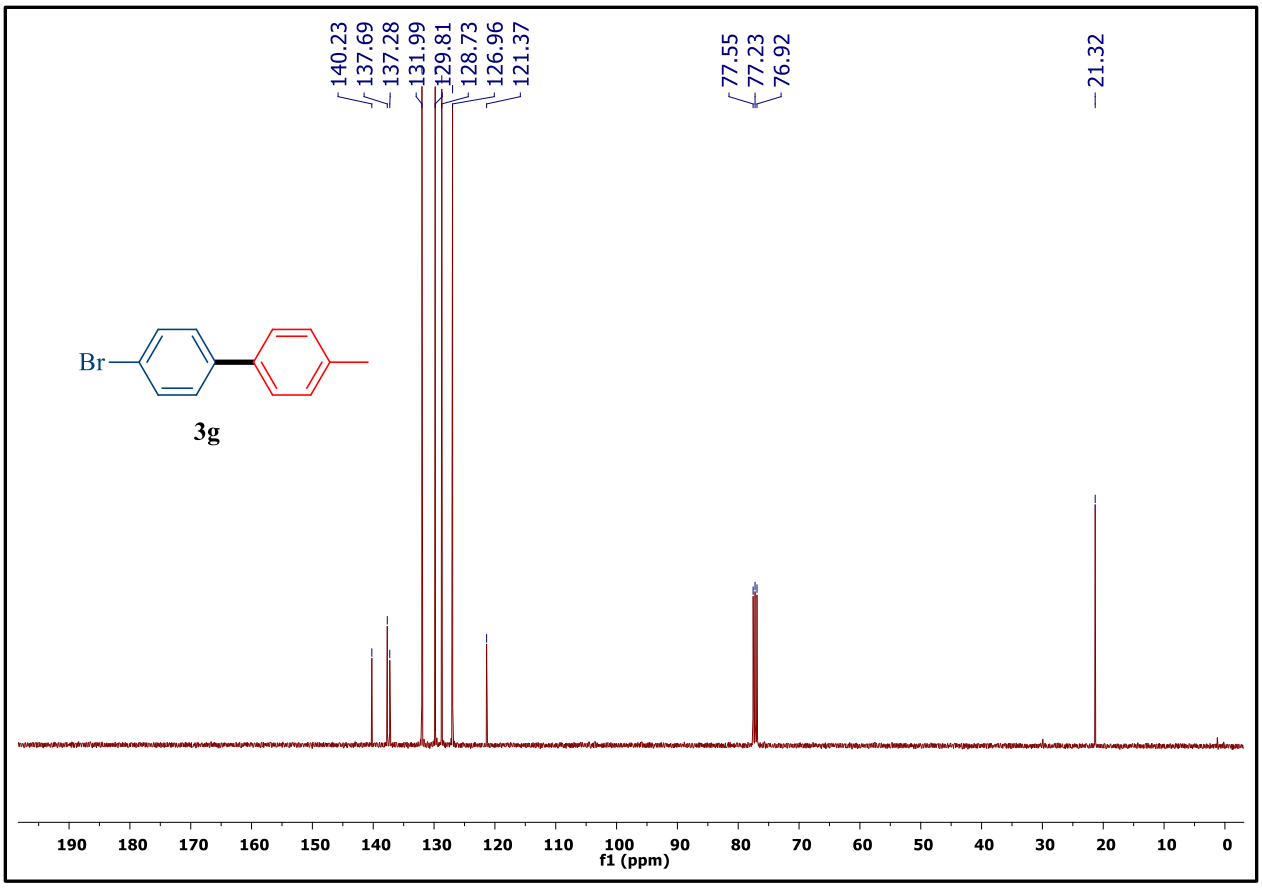


Figure S14. ^{13}C NMR spectra of **3g** in $CDCl_3$

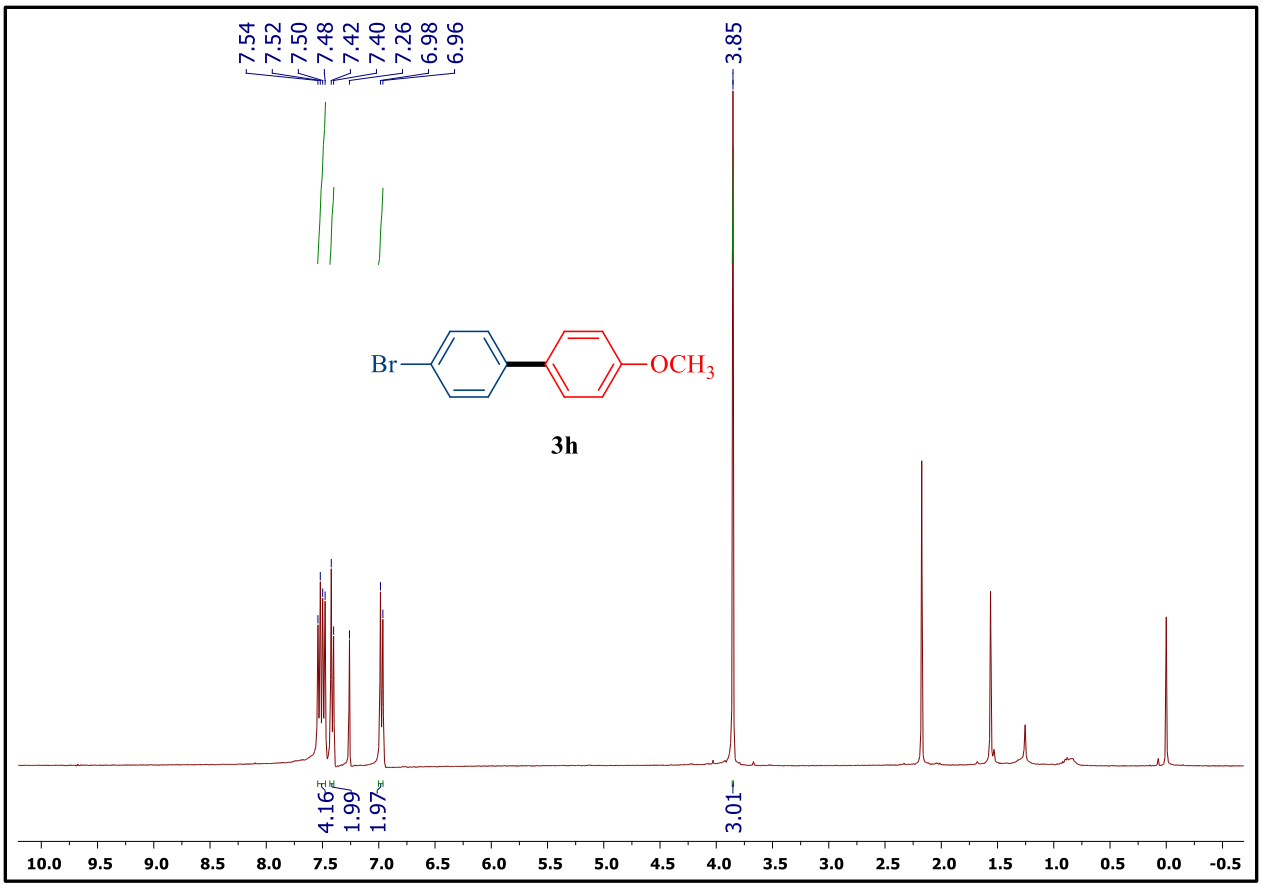


Figure S15. ^{1}H NMR spectra of **3h** in $CDCl_3$

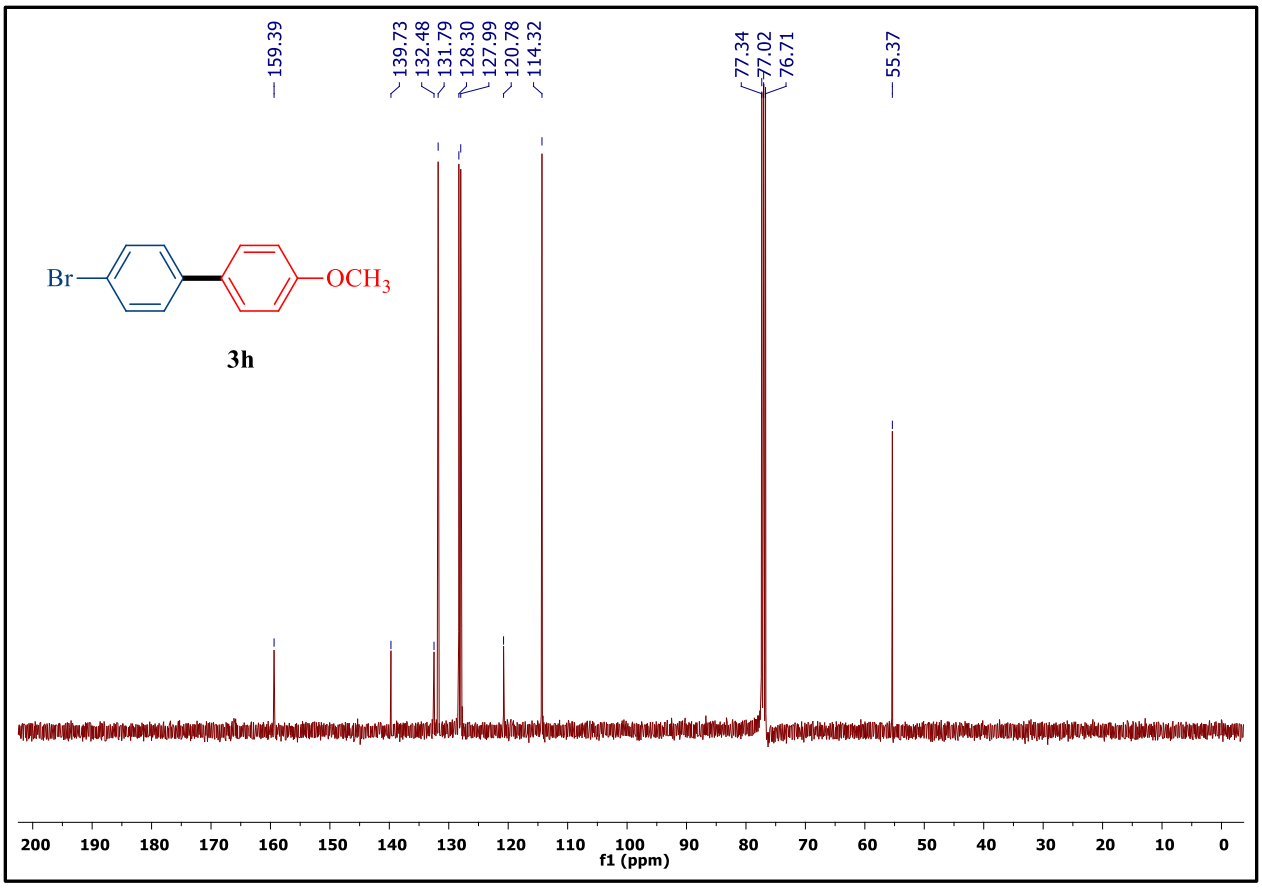


Figure S16. ^{13}C NMR spectra of **3h** in $CDCl_3$

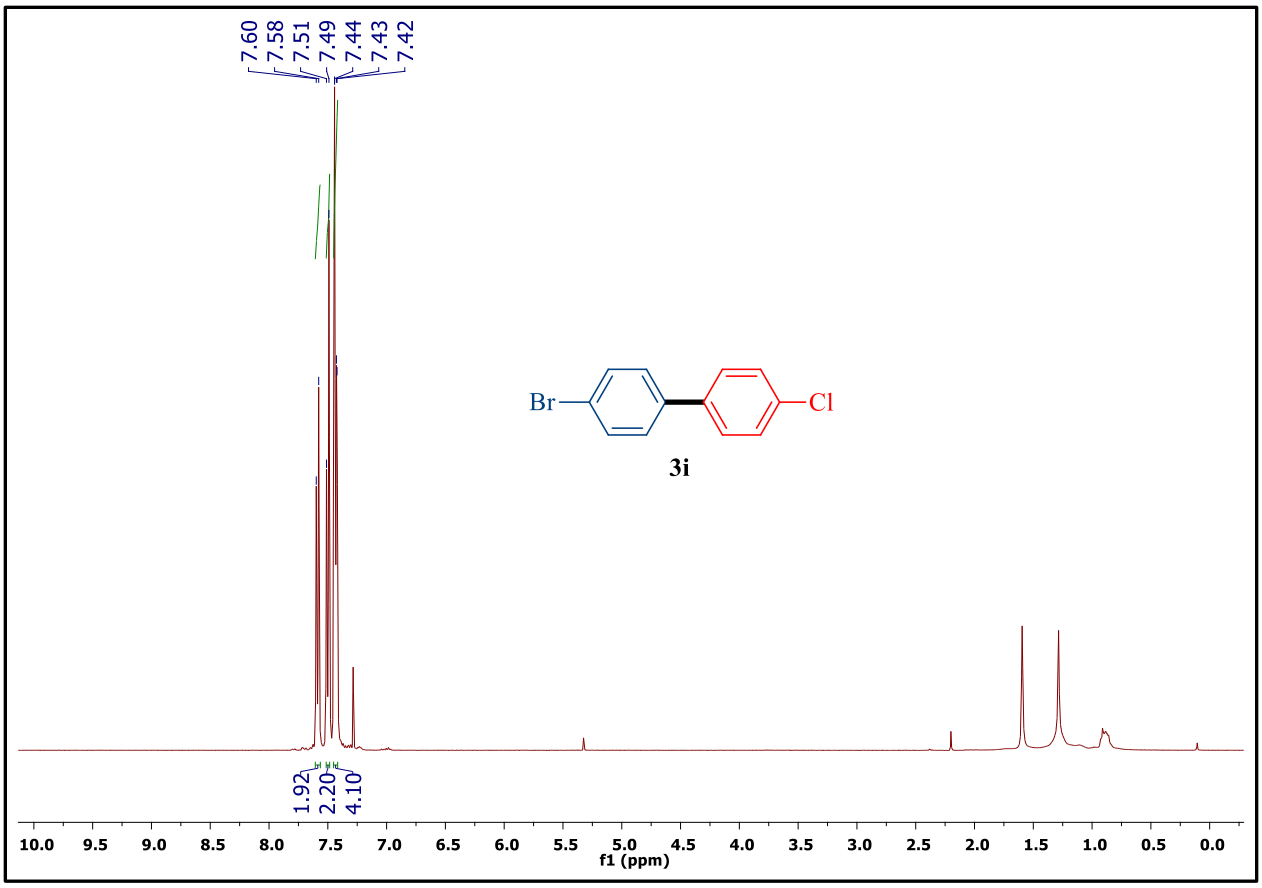


Figure S17. ^{1}H NMR spectra of **3i** in $CDCl_3$

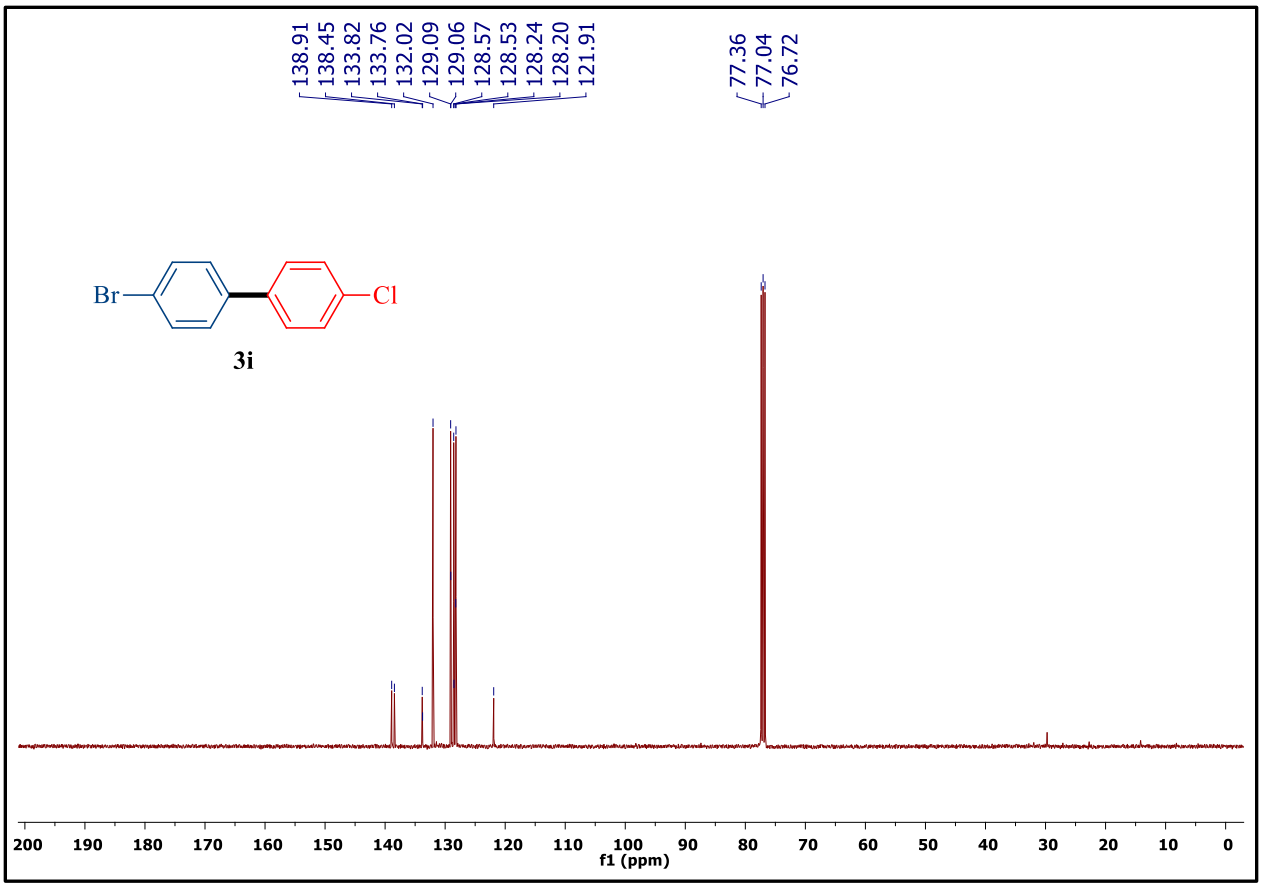


Figure S18. ^{13}C NMR spectra of **3i** in $CDCl_3$

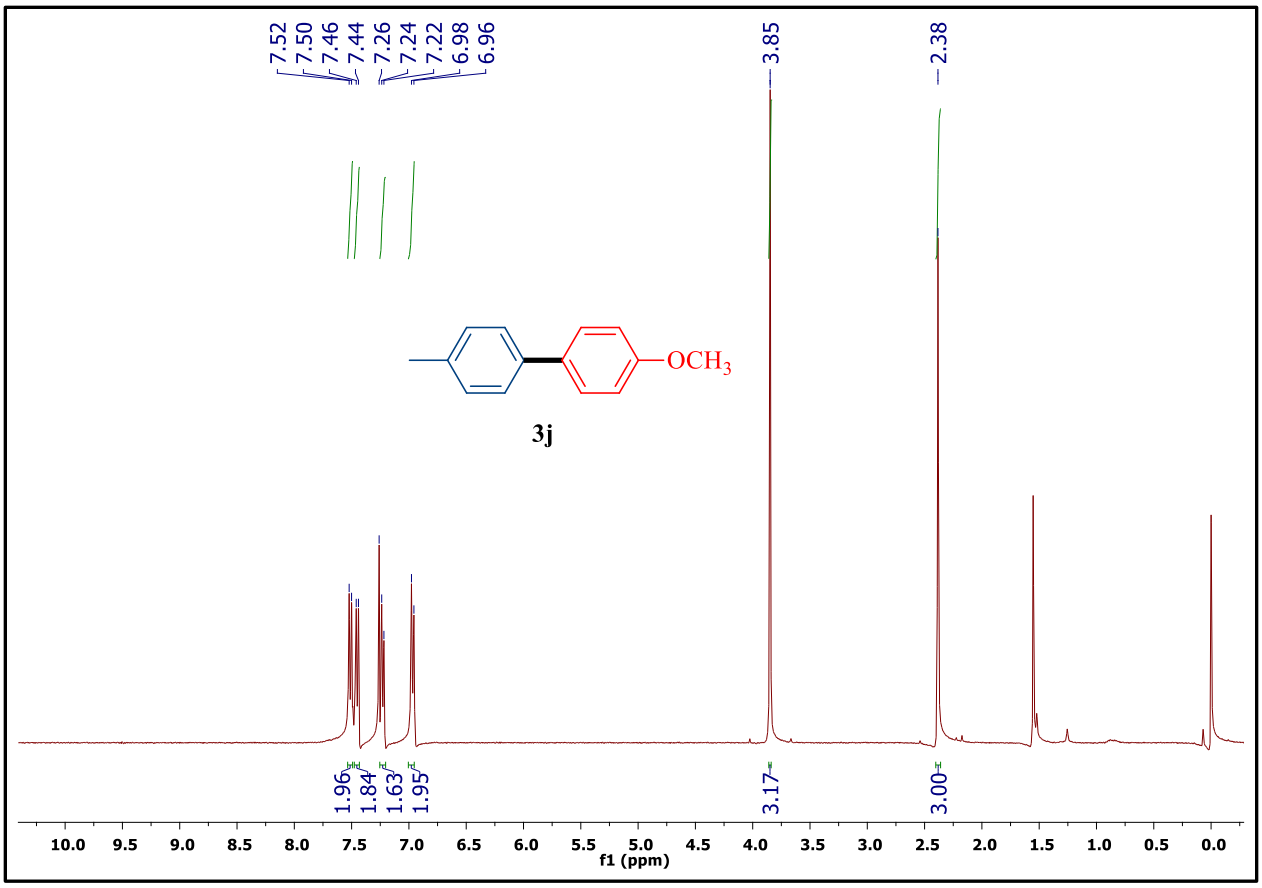


Figure S19. ^{1}H NMR spectra of **3j** in $CDCl_3$

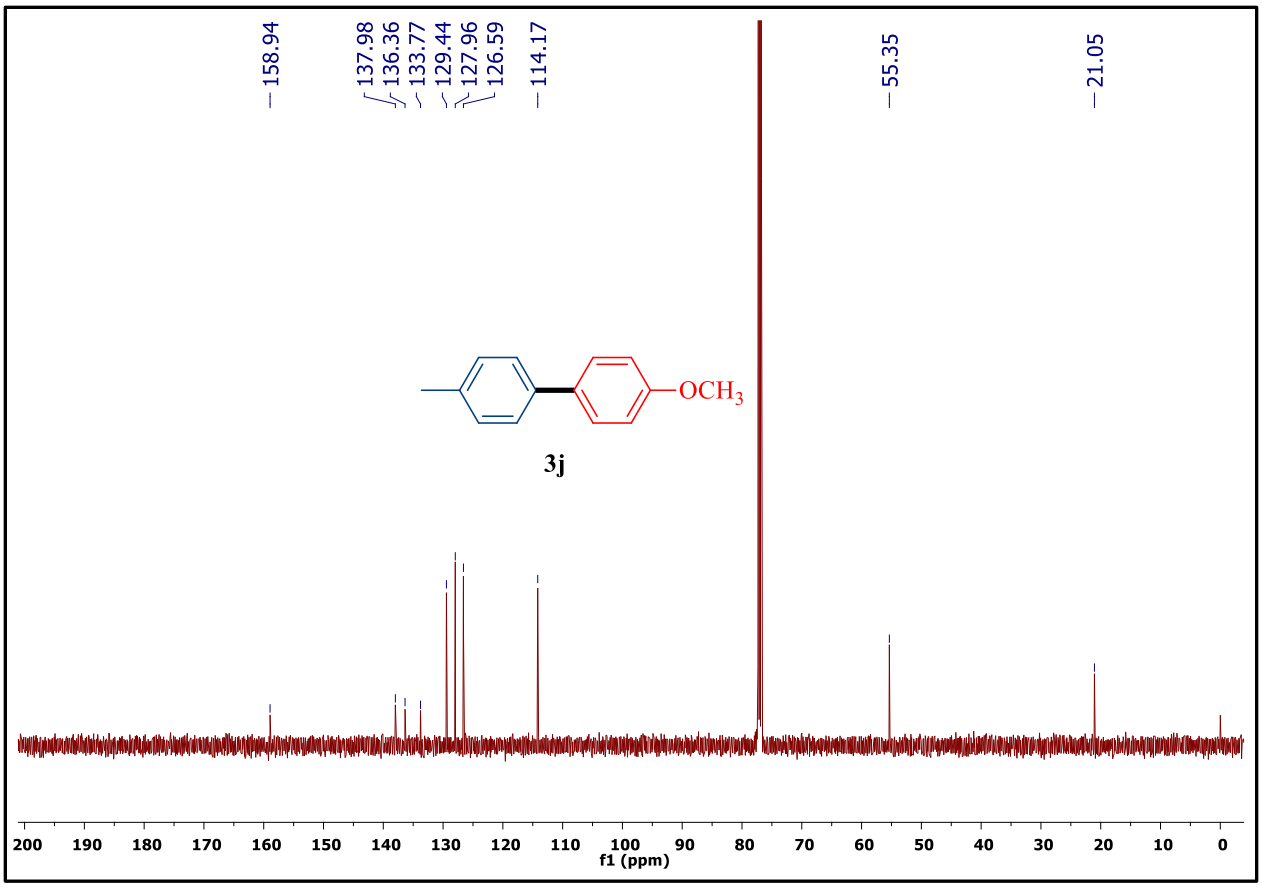


Figure S20. ^{13}C NMR spectra of **3j** in $CDCl_3$

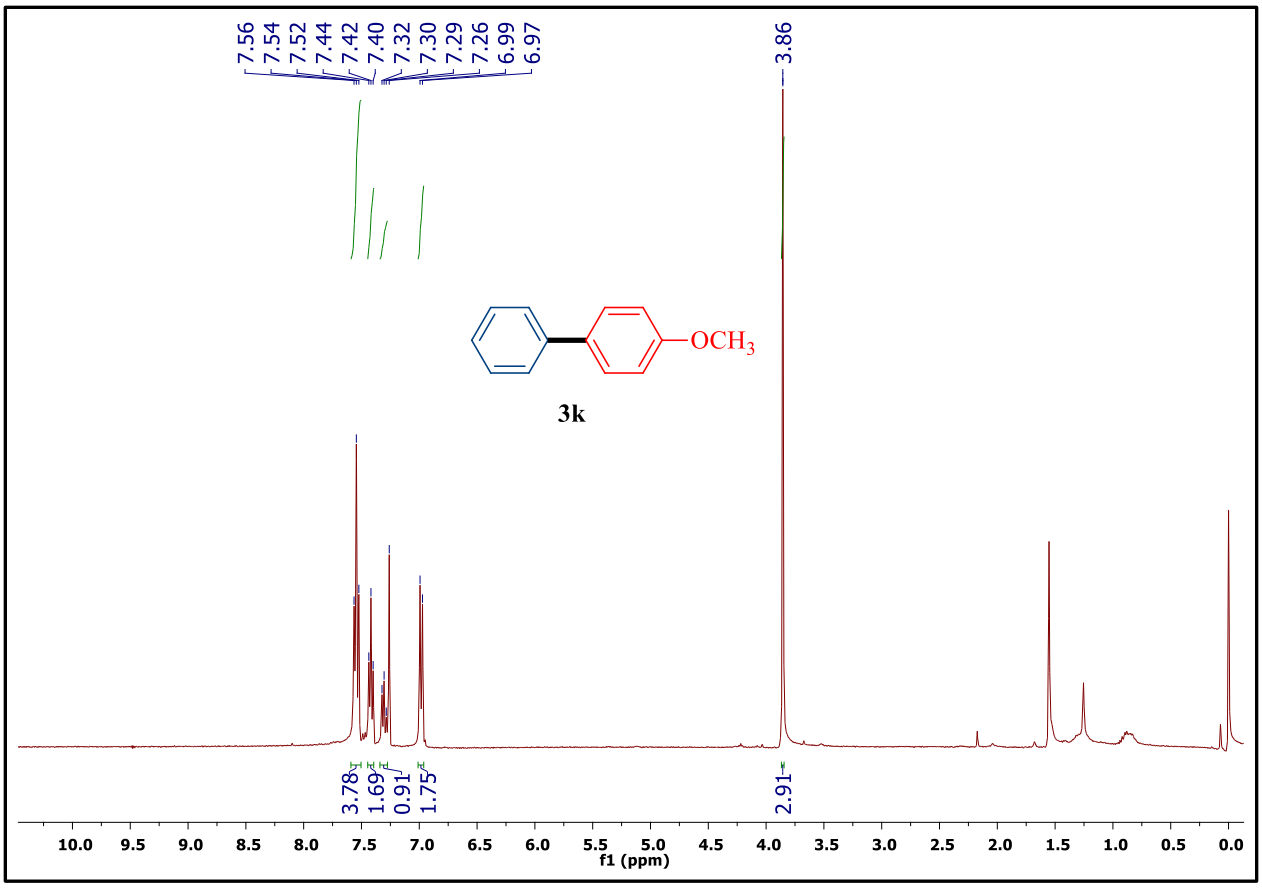


Figure S21. ^{1}H NMR spectra of **3k** in $CDCl_3$

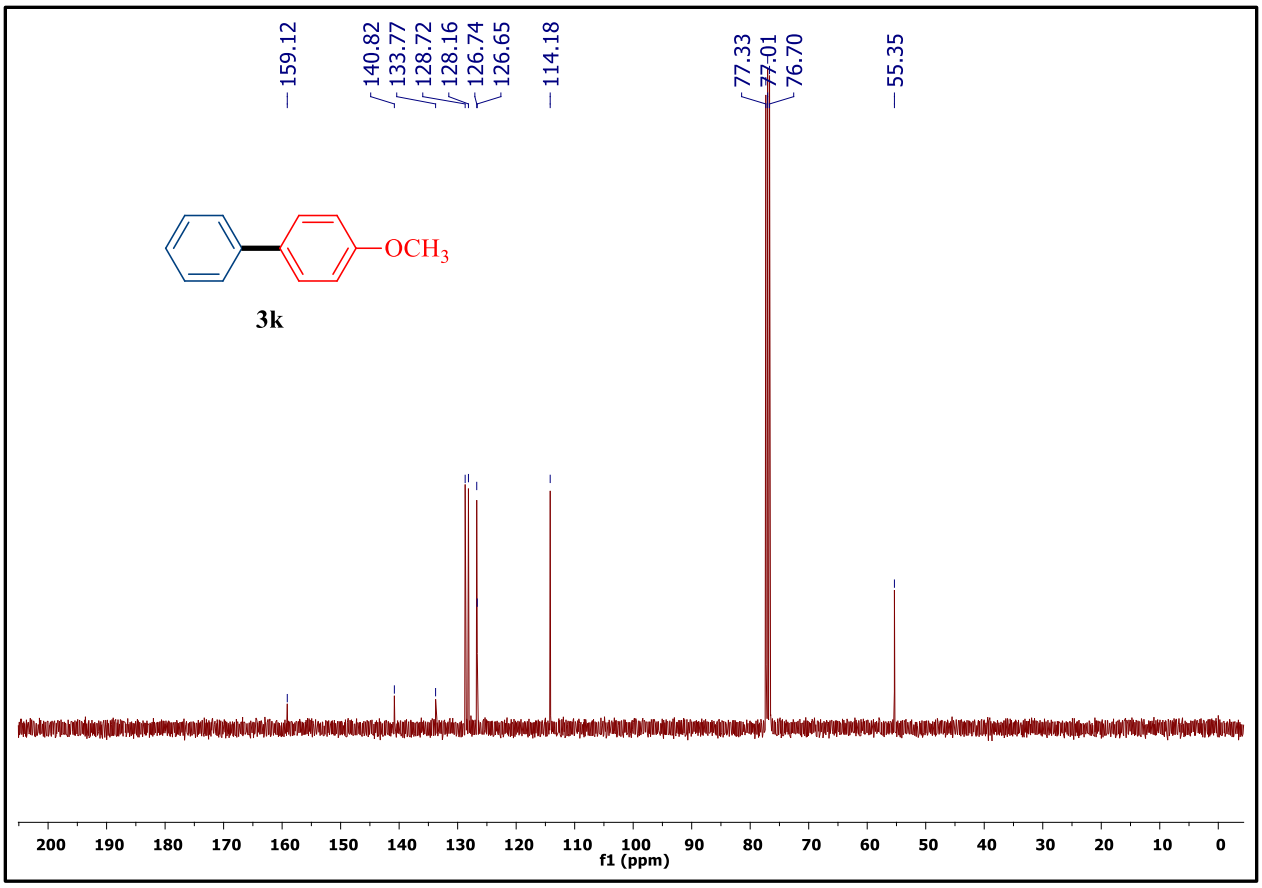


Figure S22. ^{13}C NMR spectra of **3k** in $CDCl_3$

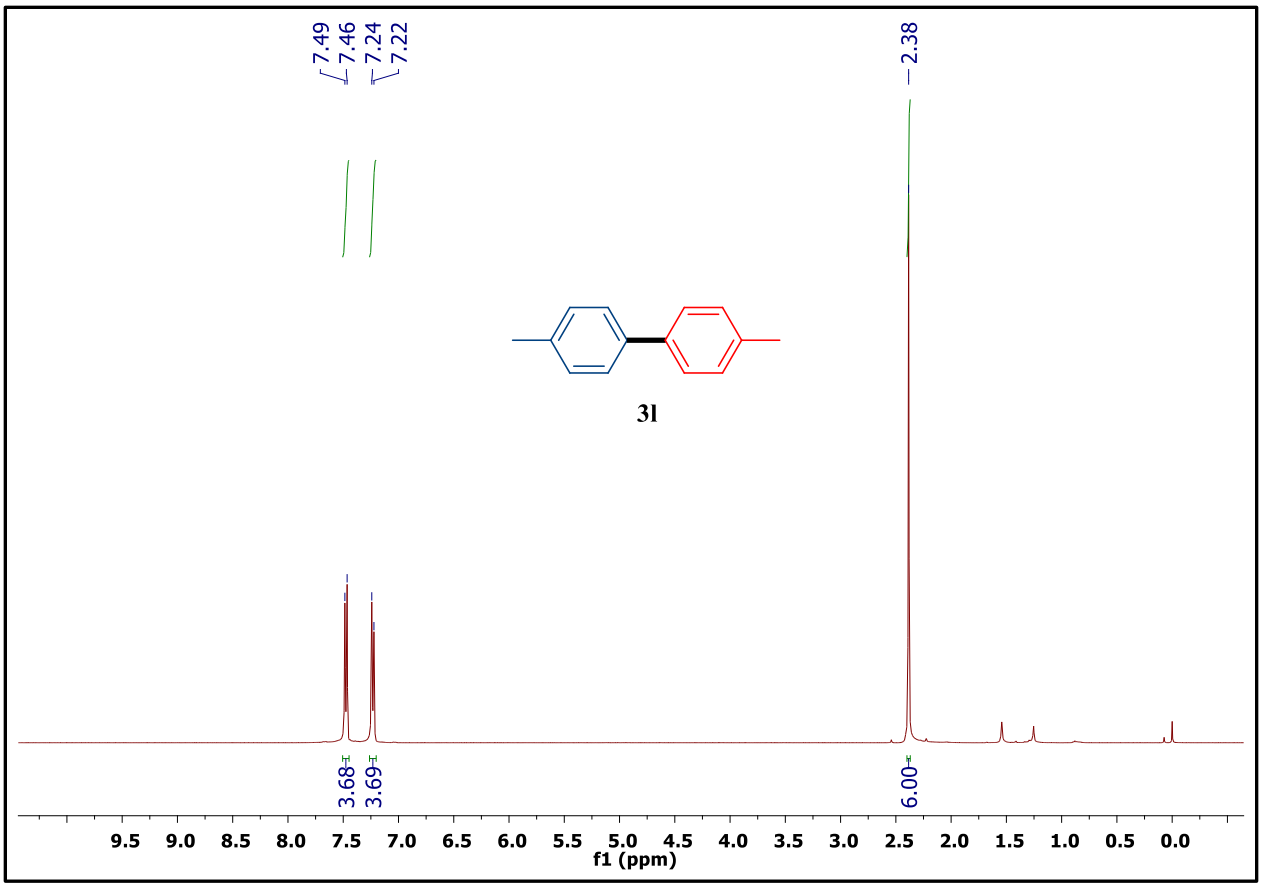


Figure S23. ^{1}H NMR spectra of **3l** in $CDCl_3$

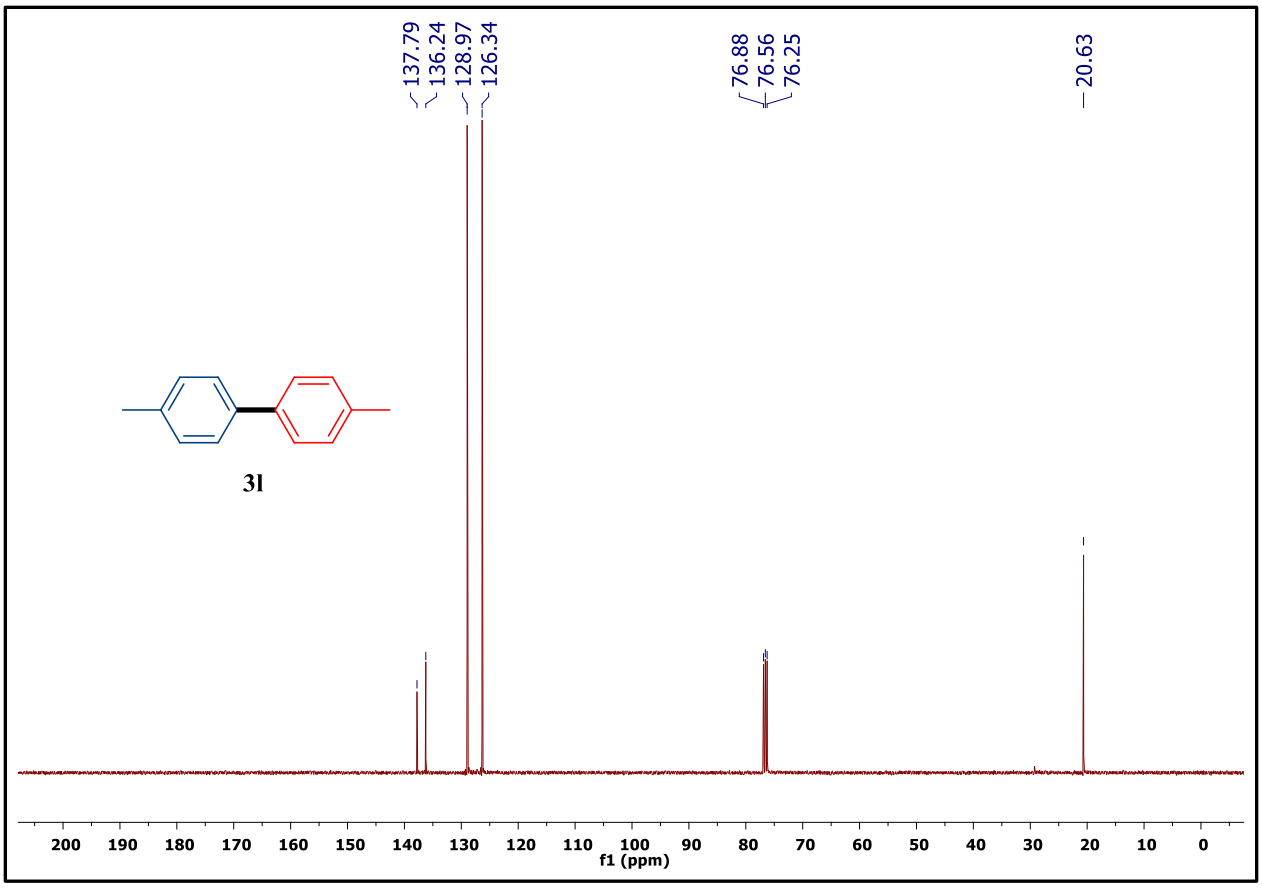


Figure S24. ^{13}C NMR spectra of **3l** in $CDCl_3$

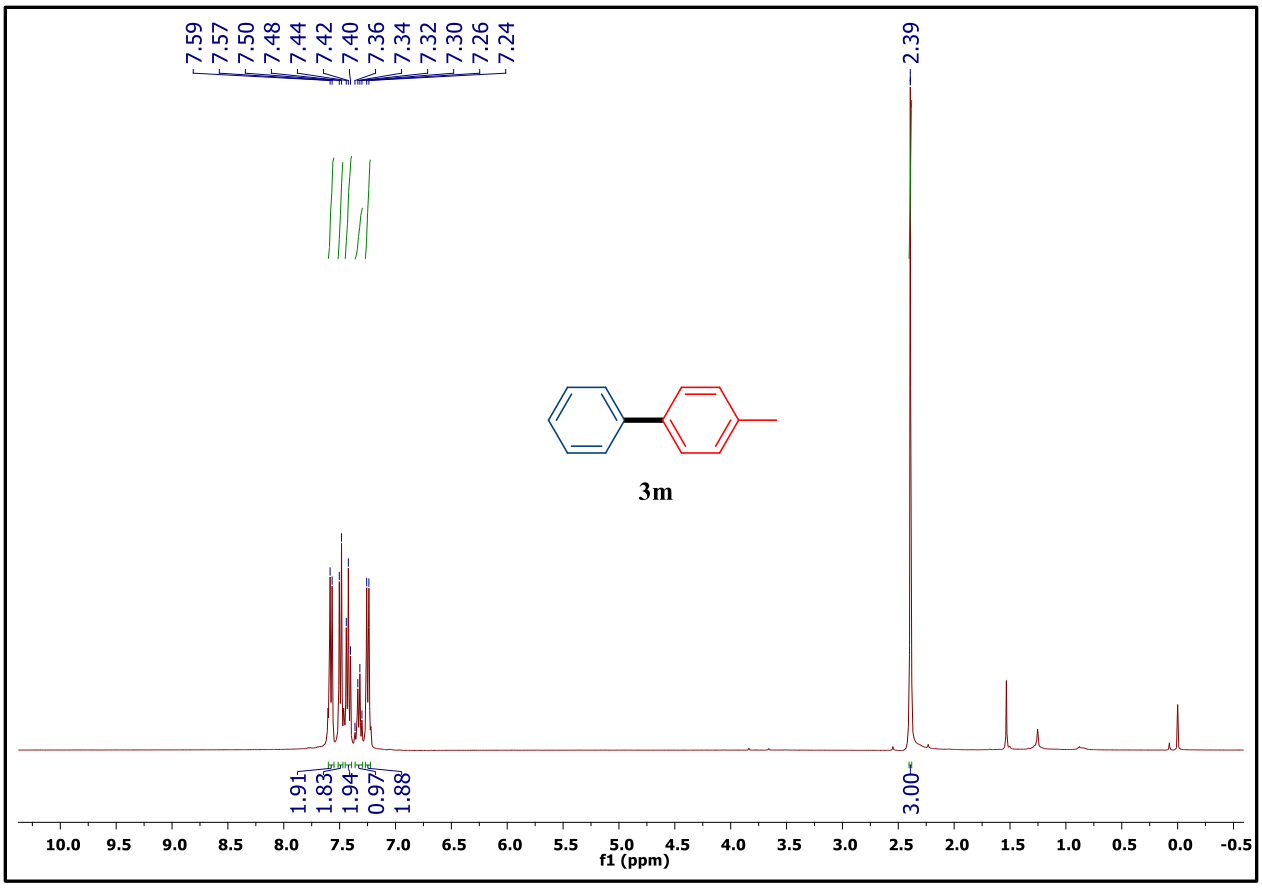


Figure S25. ^{1}H NMR spectra of **3m** in $CDCl_3$

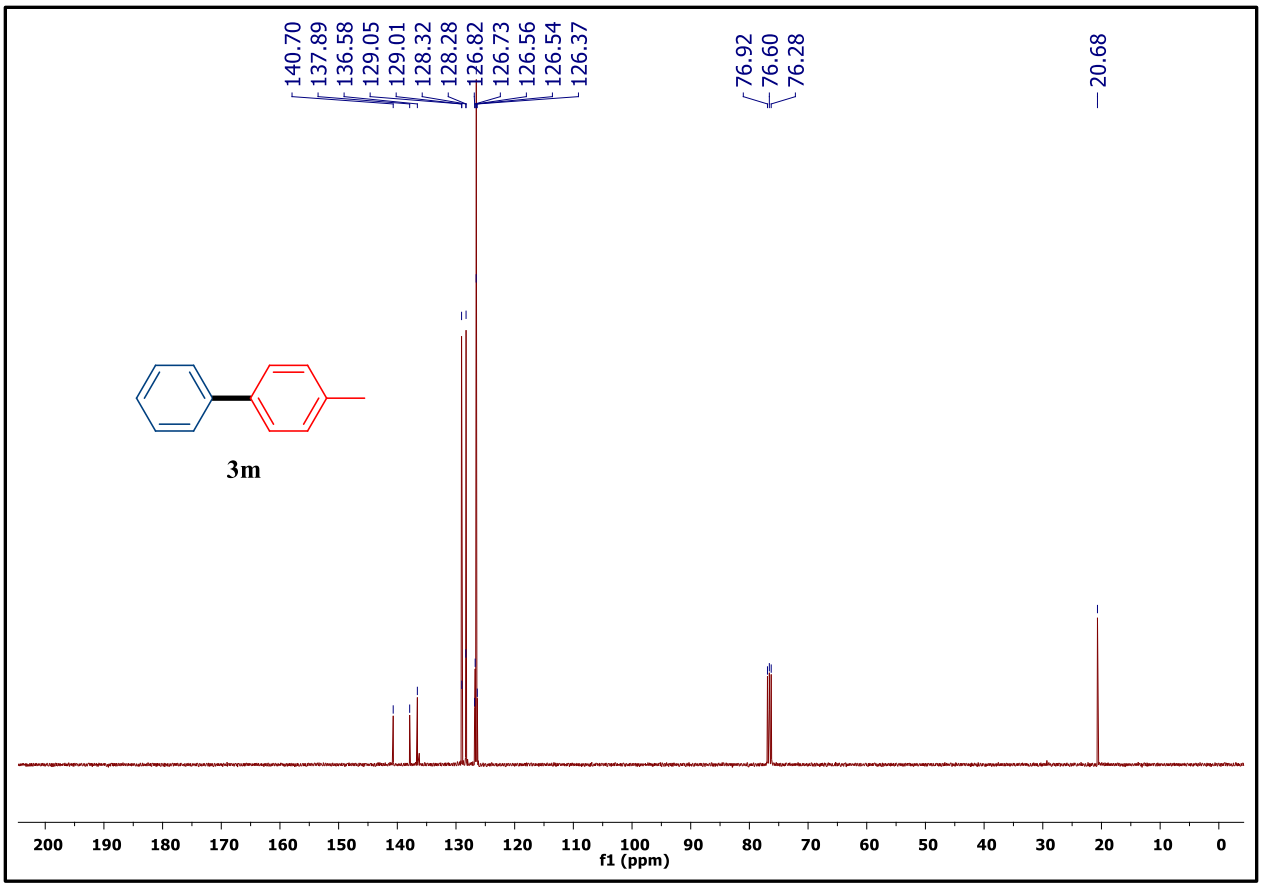


Figure S26. ^{13}C NMR spectra of **3m** in $CDCl_3$

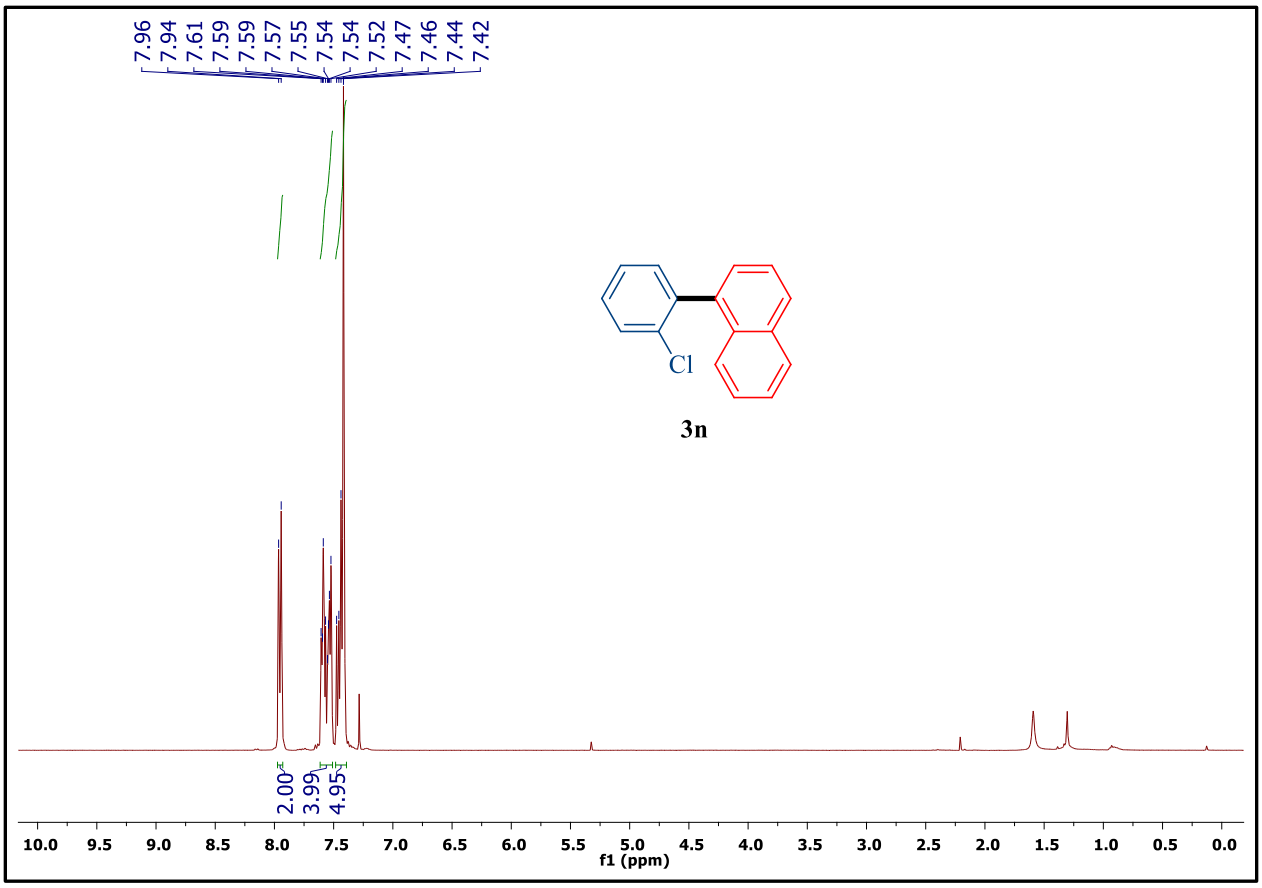


Figure S27. ^{1}H NMR spectra of **3n** in $CDCl_3$

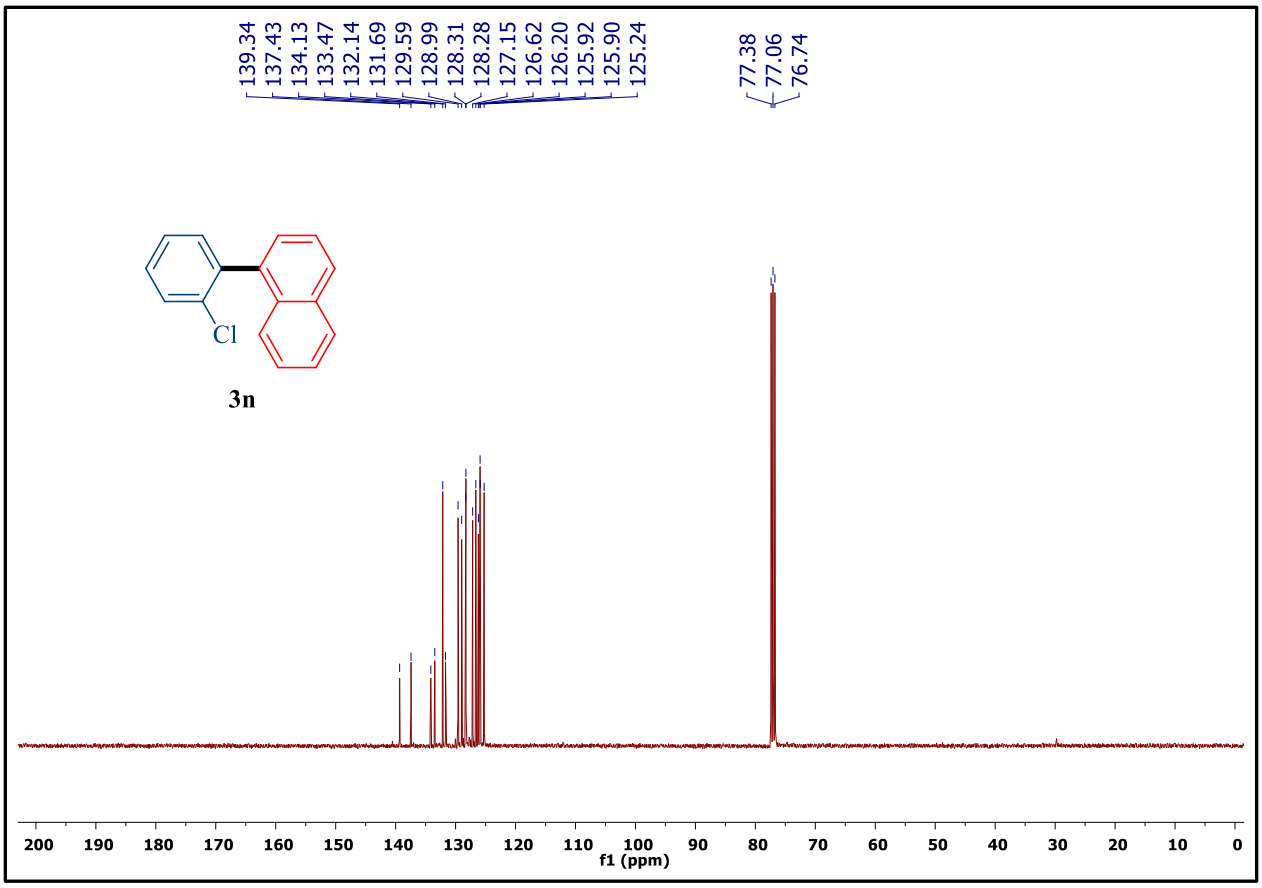


Figure S28. ^{13}C NMR spectra of **3n** in $CDCl_3$

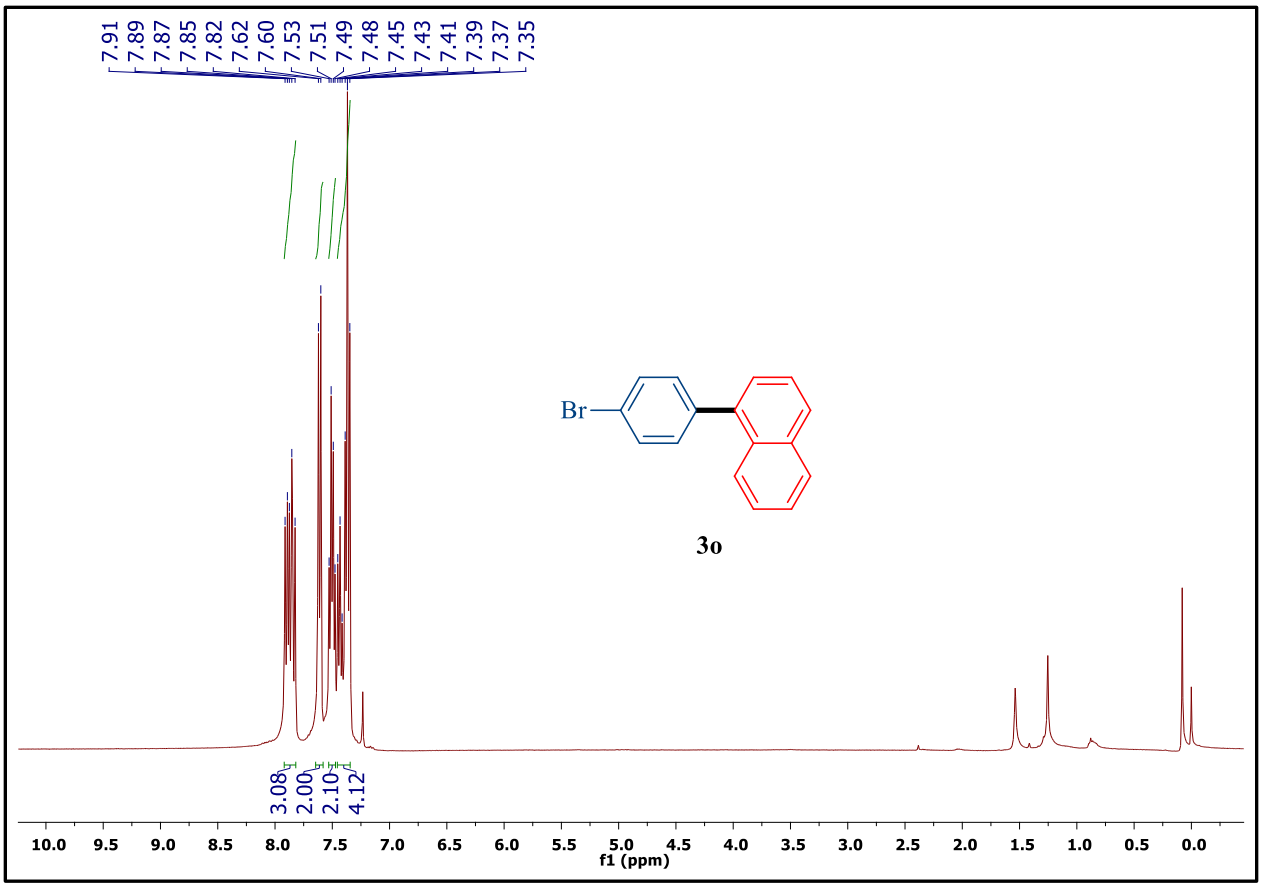


Figure S29. ^{1}H NMR spectra of **3o** in $CDCl_3$

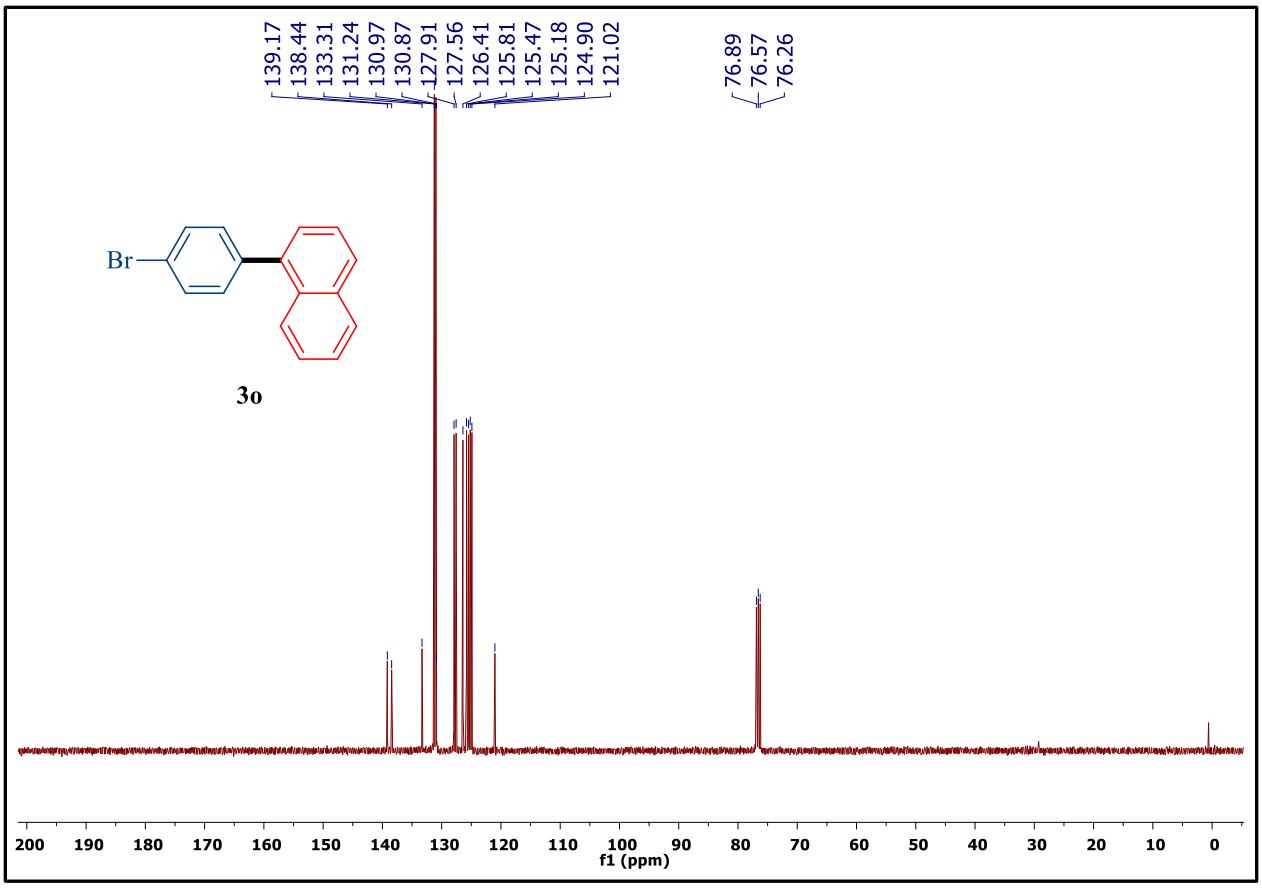


Figure S30. ^{13}C NMR spectra of **3o** in $CDCl_3$

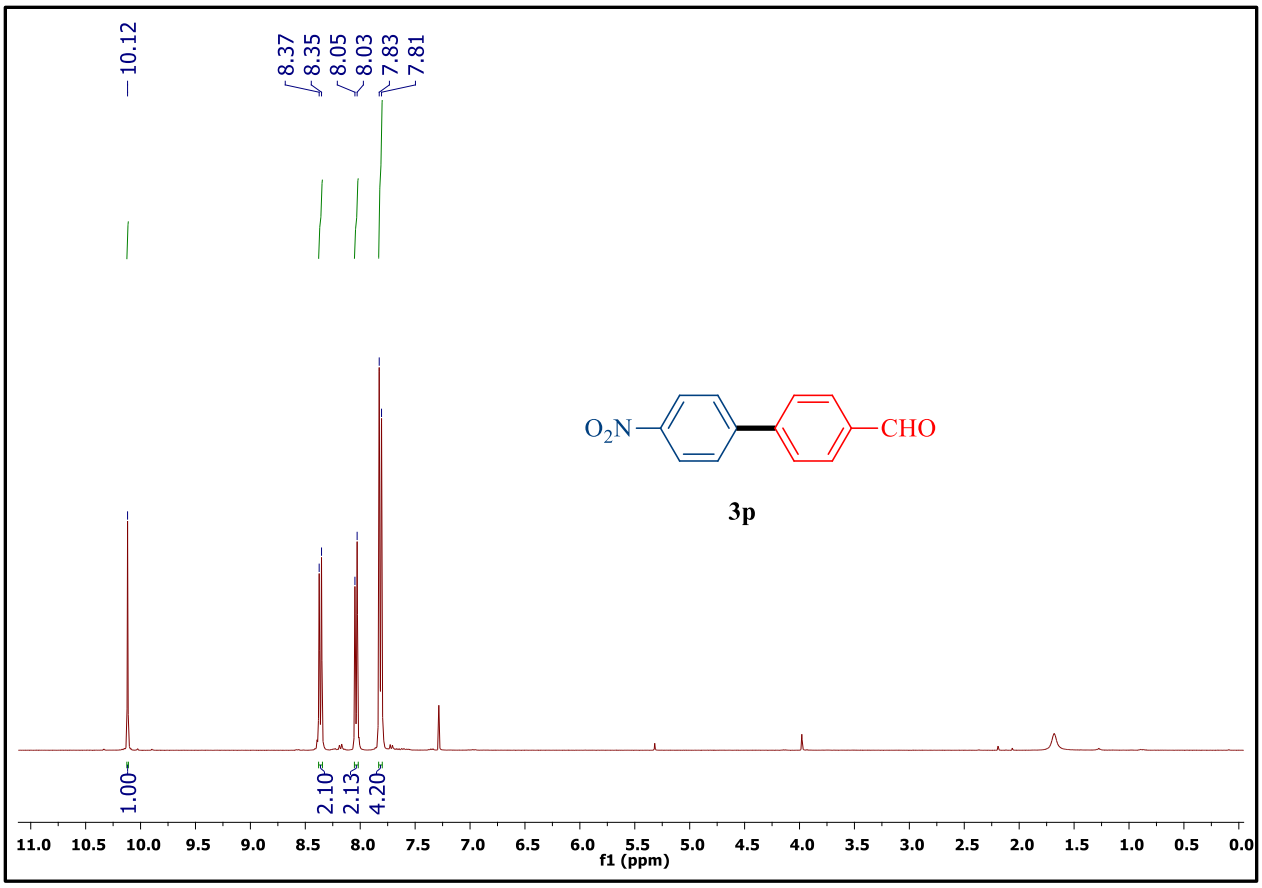


Figure S31. ^{1}H NMR spectra of **3q** in $CDCl_3$

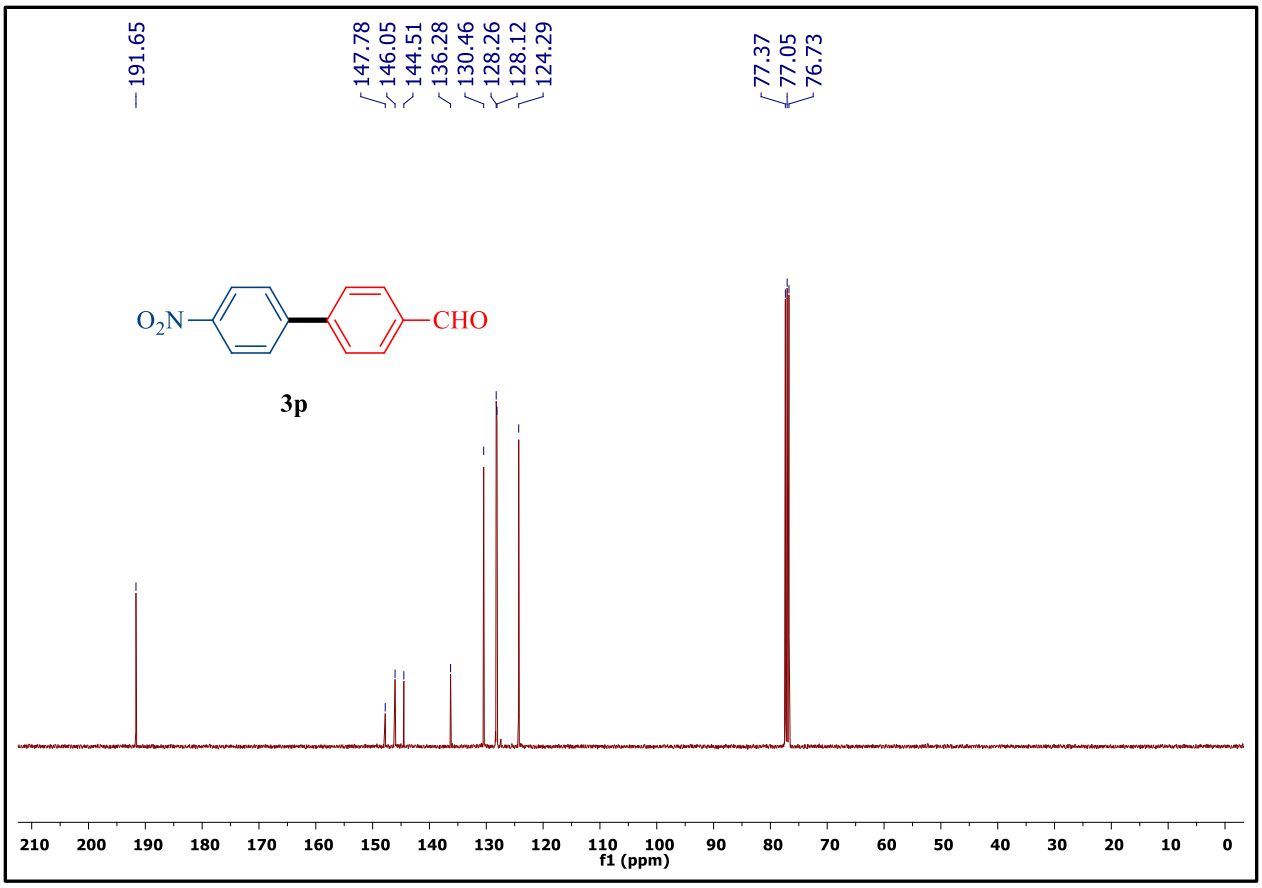


Figure S32. ^{13}C NMR spectra of **3q** in $CDCl_3$

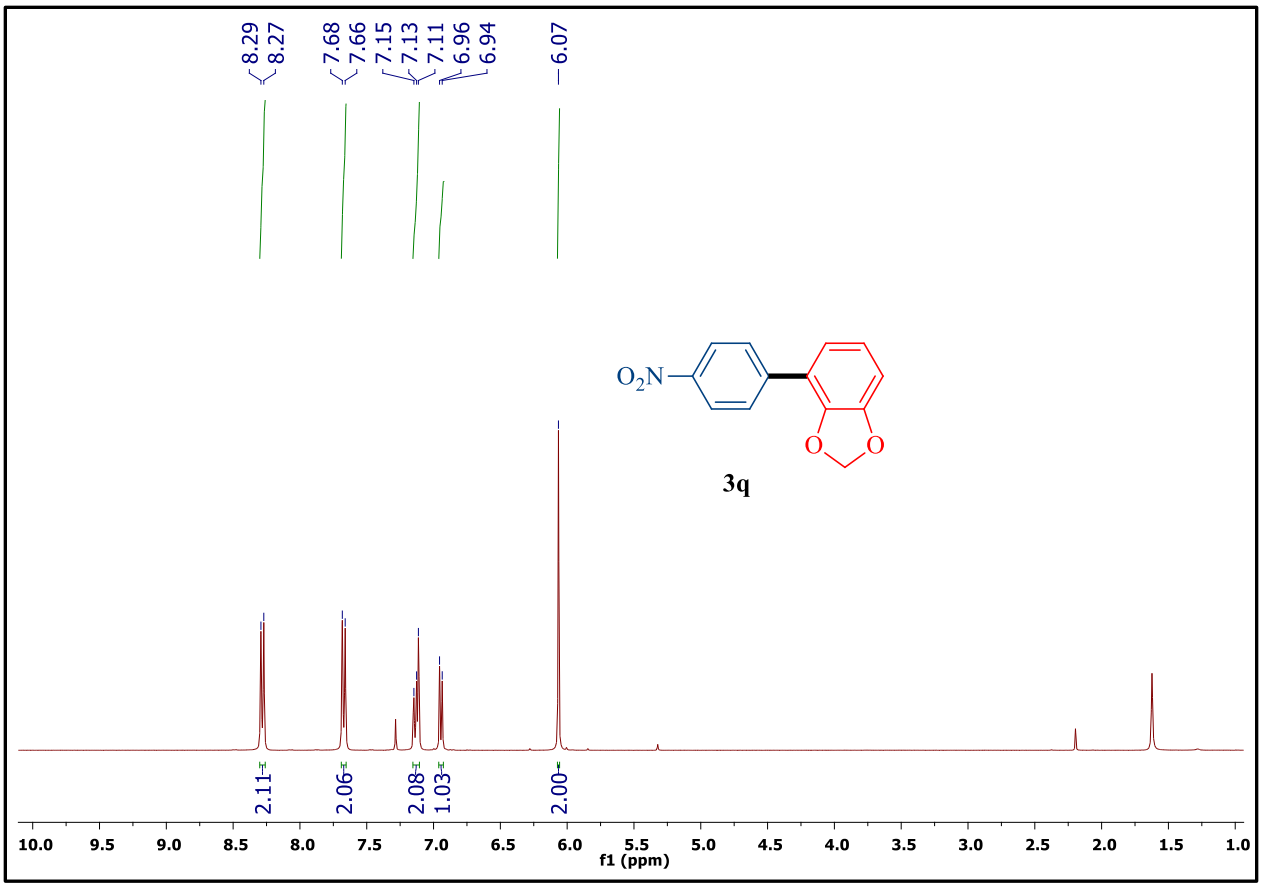


Figure S33. ^{1}H NMR spectra of **3q** in $CDCl_3$

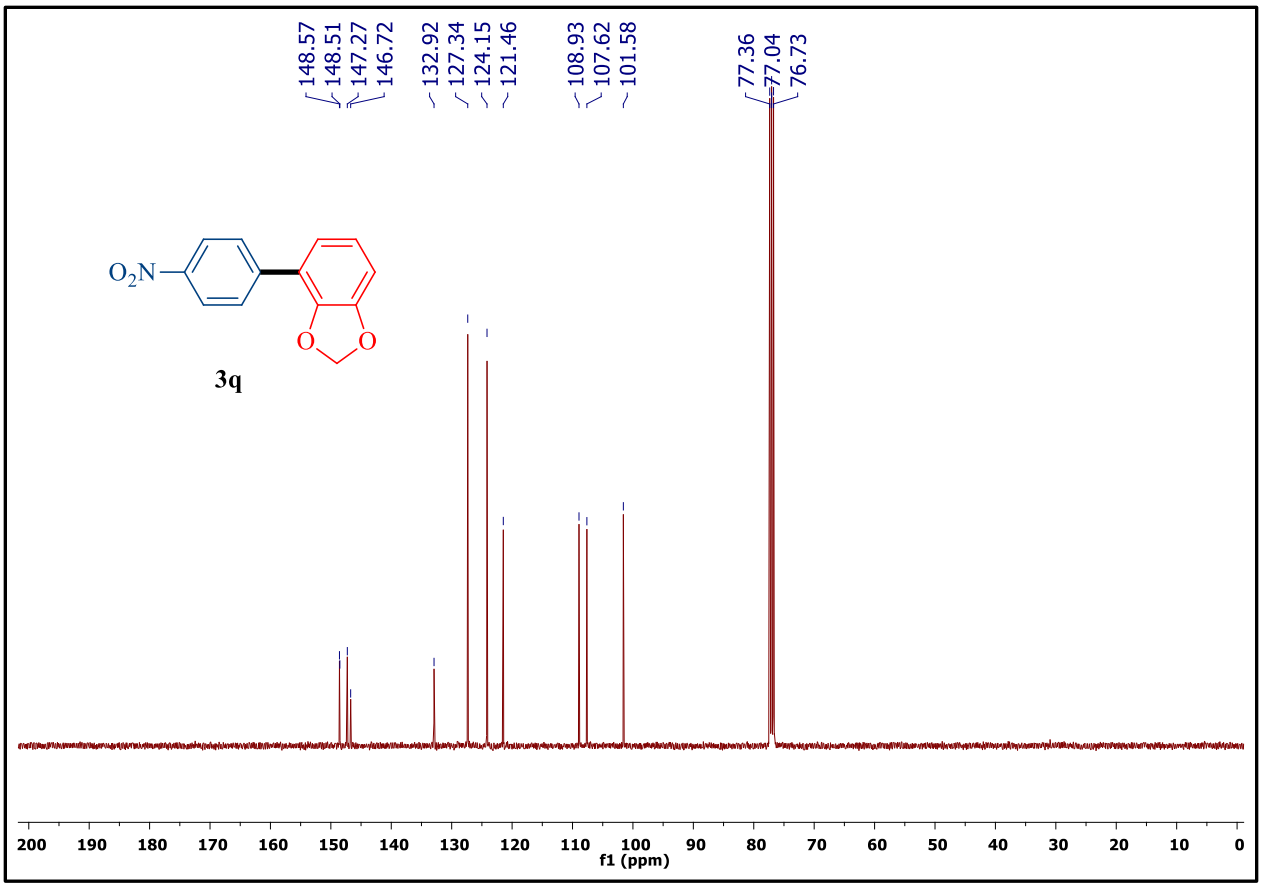


Figure S34. ^{13}C NMR spectra of **3q** in $CDCl_3$

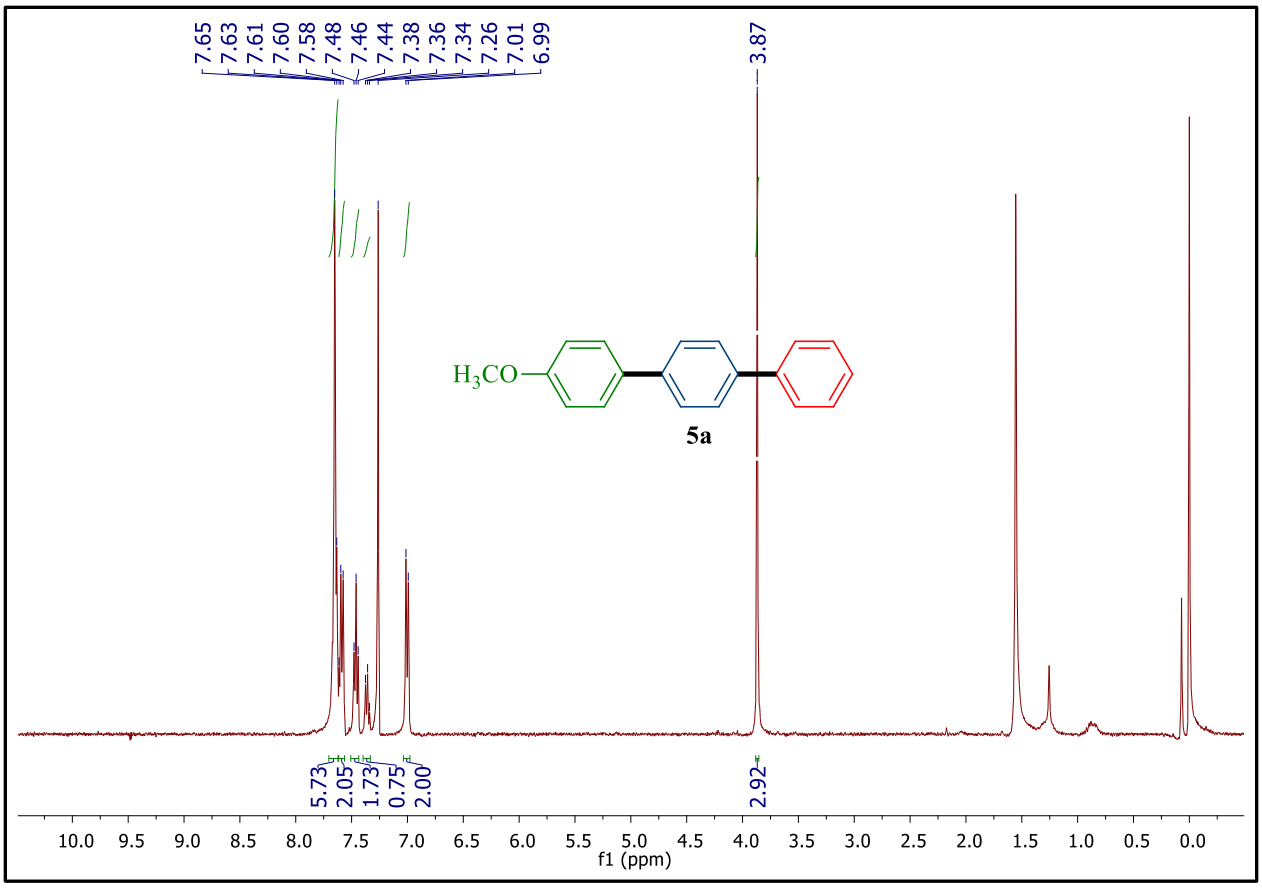


Figure S35. ^{1}H NMR spectra of **5a** in $CDCl_3$

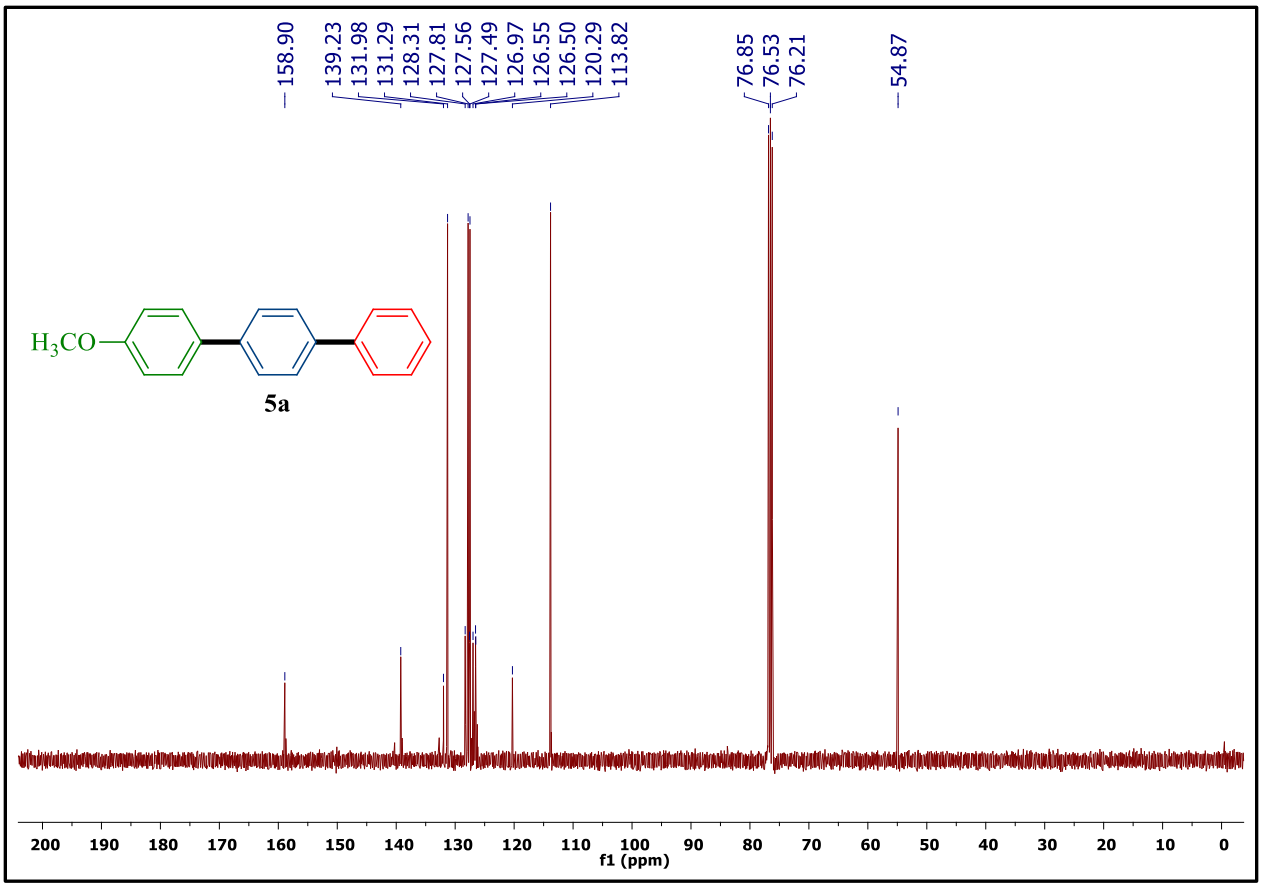


Figure S36. ^{13}C NMR spectra of **5a** in $CDCl_3$

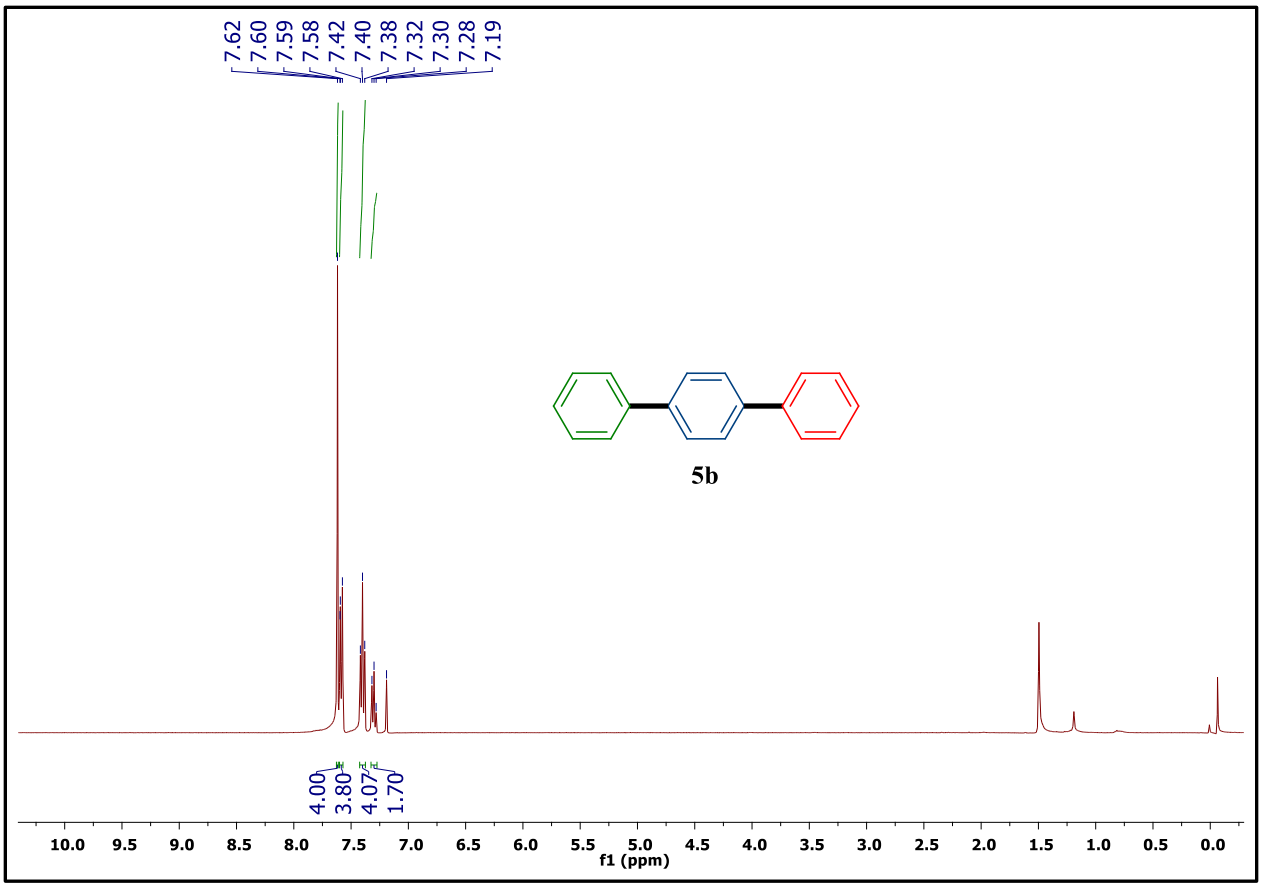


Figure S37. ^{1}H NMR spectra of **5b** in $CDCl_3$

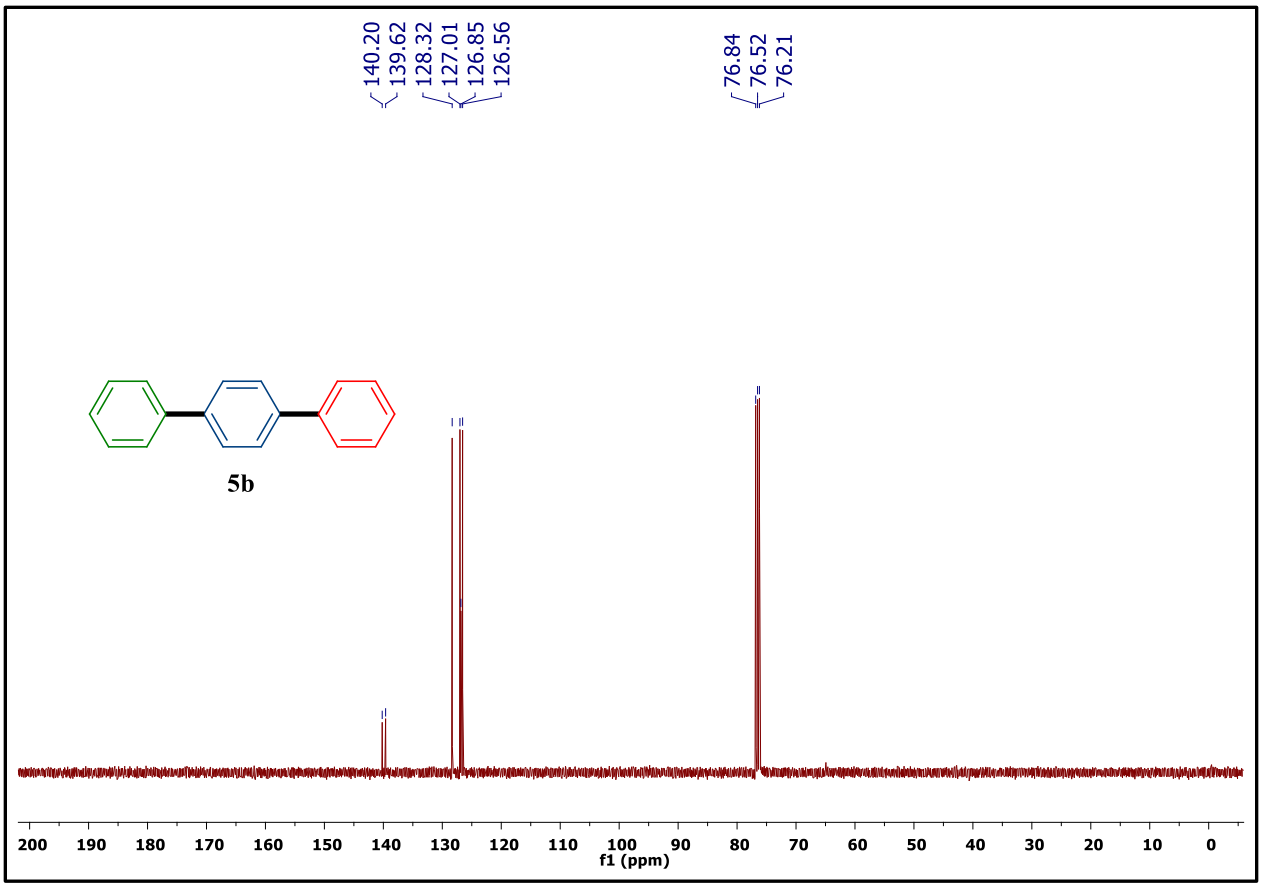


Figure S38. ^{13}C NMR spectra of **5b** in $CDCl_3$

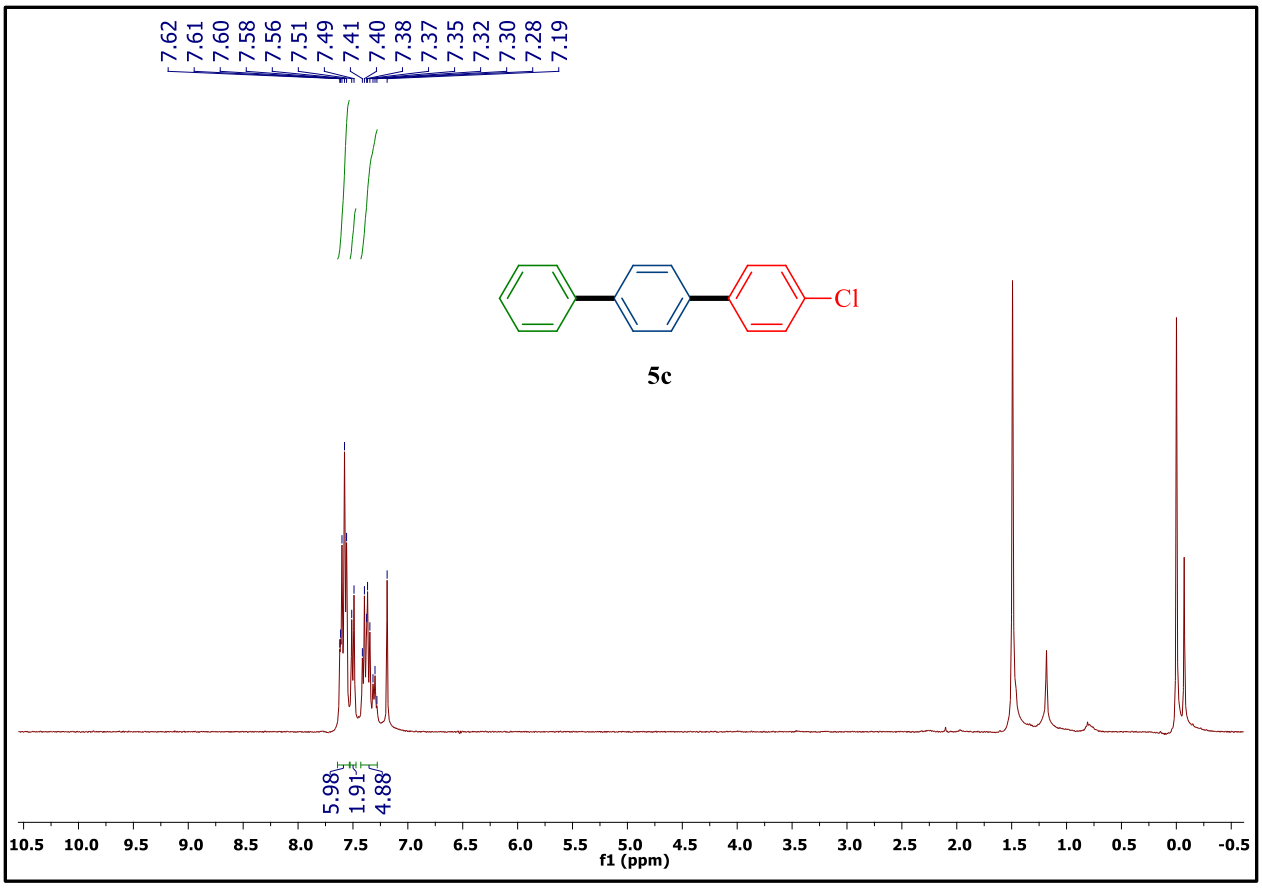


Figure S39. ^{1}H NMR spectra of **5c** in $CDCl_3$

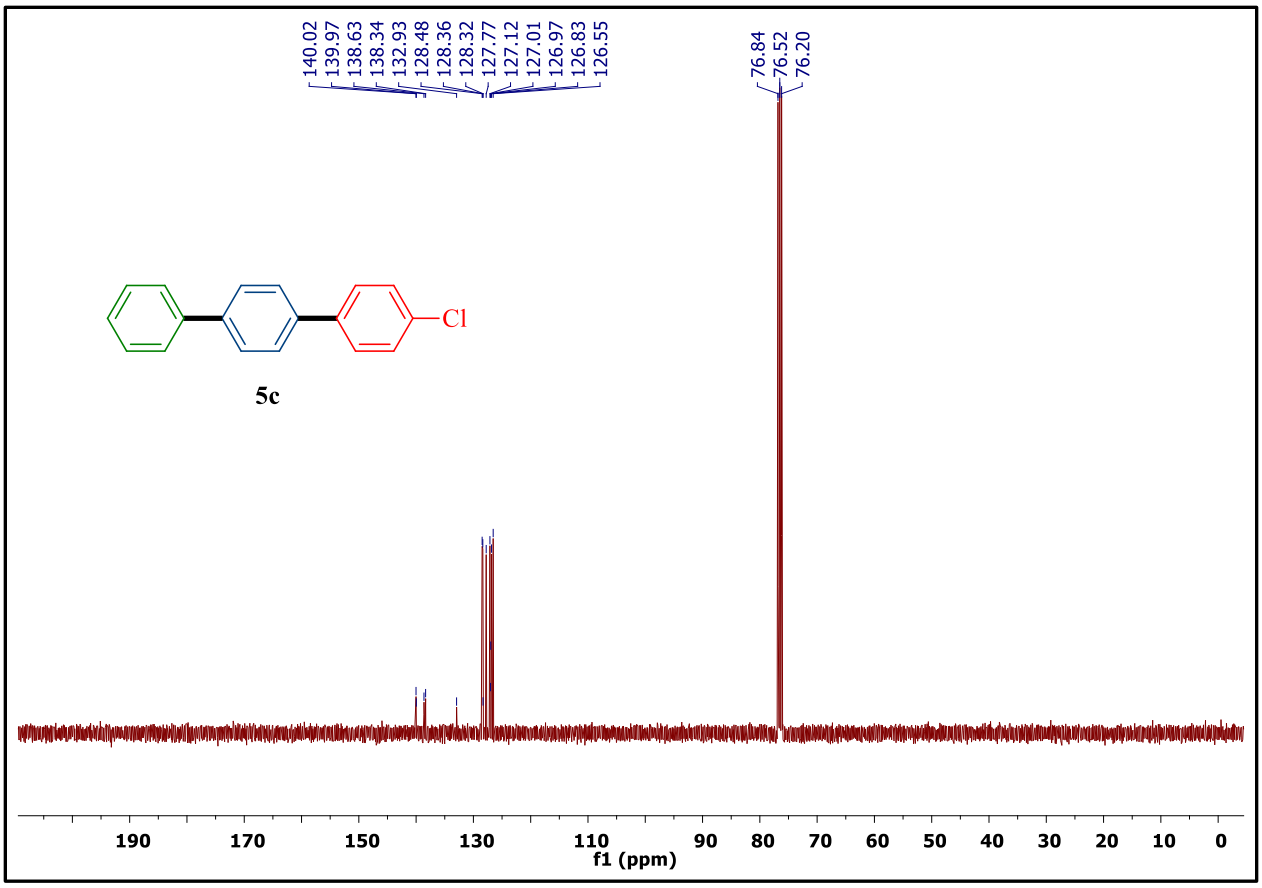


Figure S40. ^{13}C NMR spectra of **5c** in $CDCl_3$

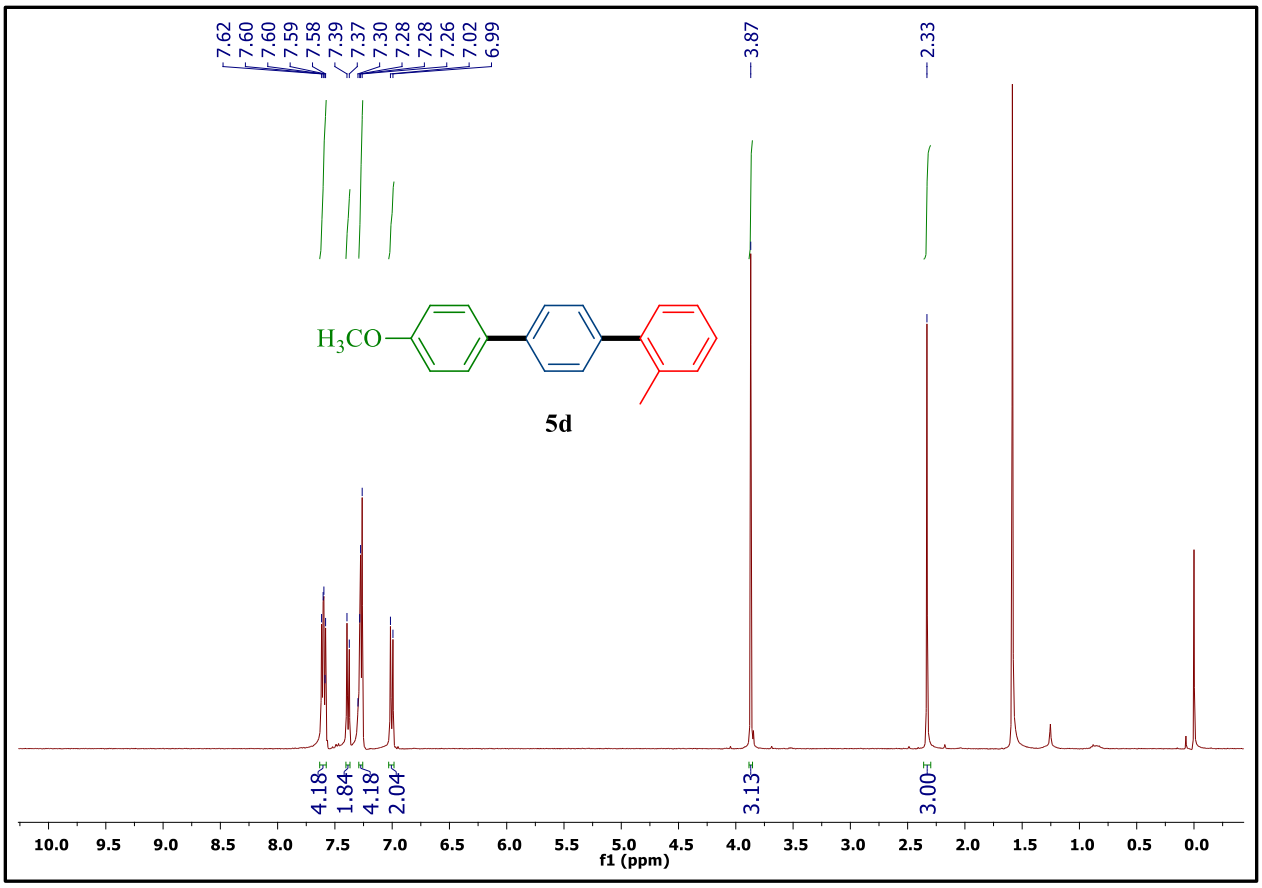


Figure S41. ^{1}H NMR spectra of **5d** in $CDCl_3$

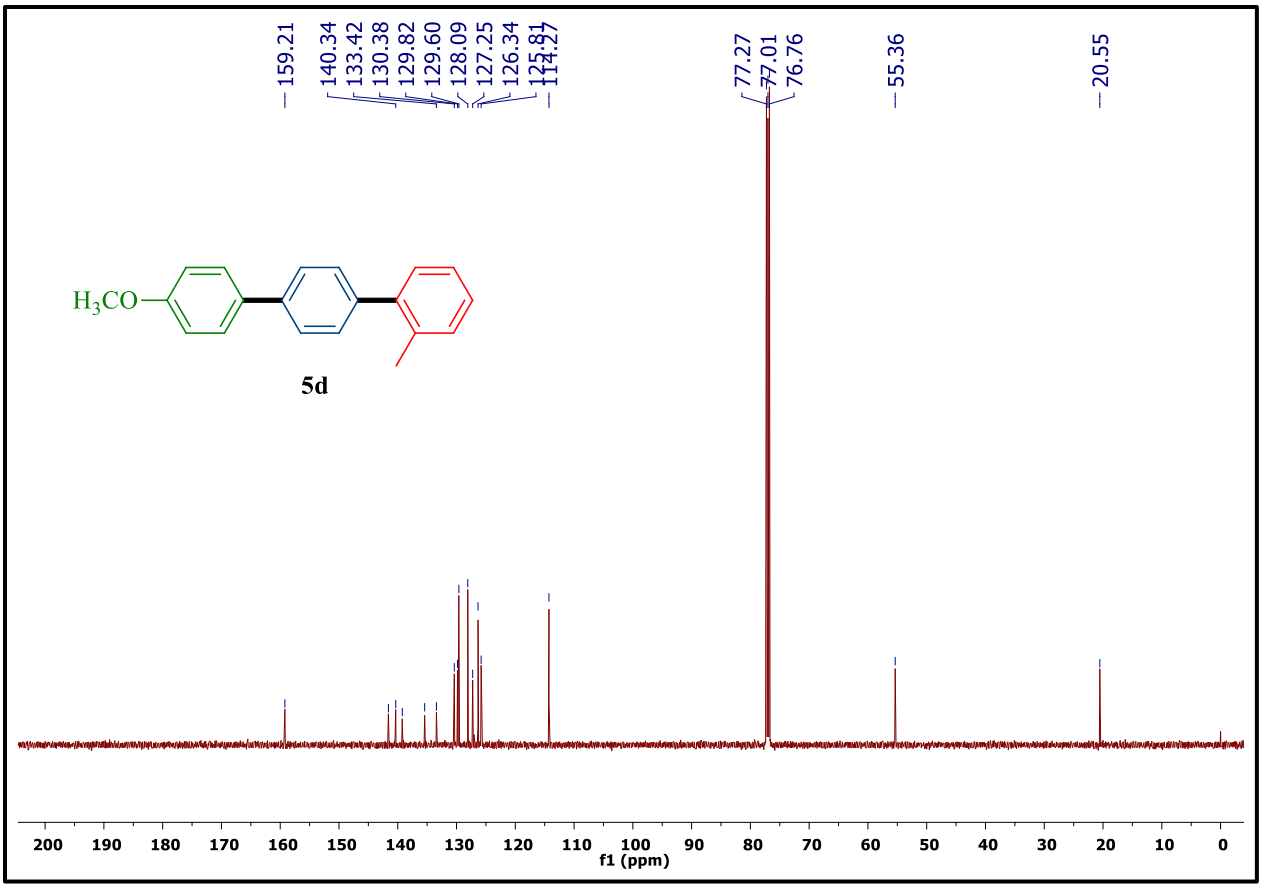


Figure S42. ^{1}H NMR spectra of **5d** in $CDCl_3$

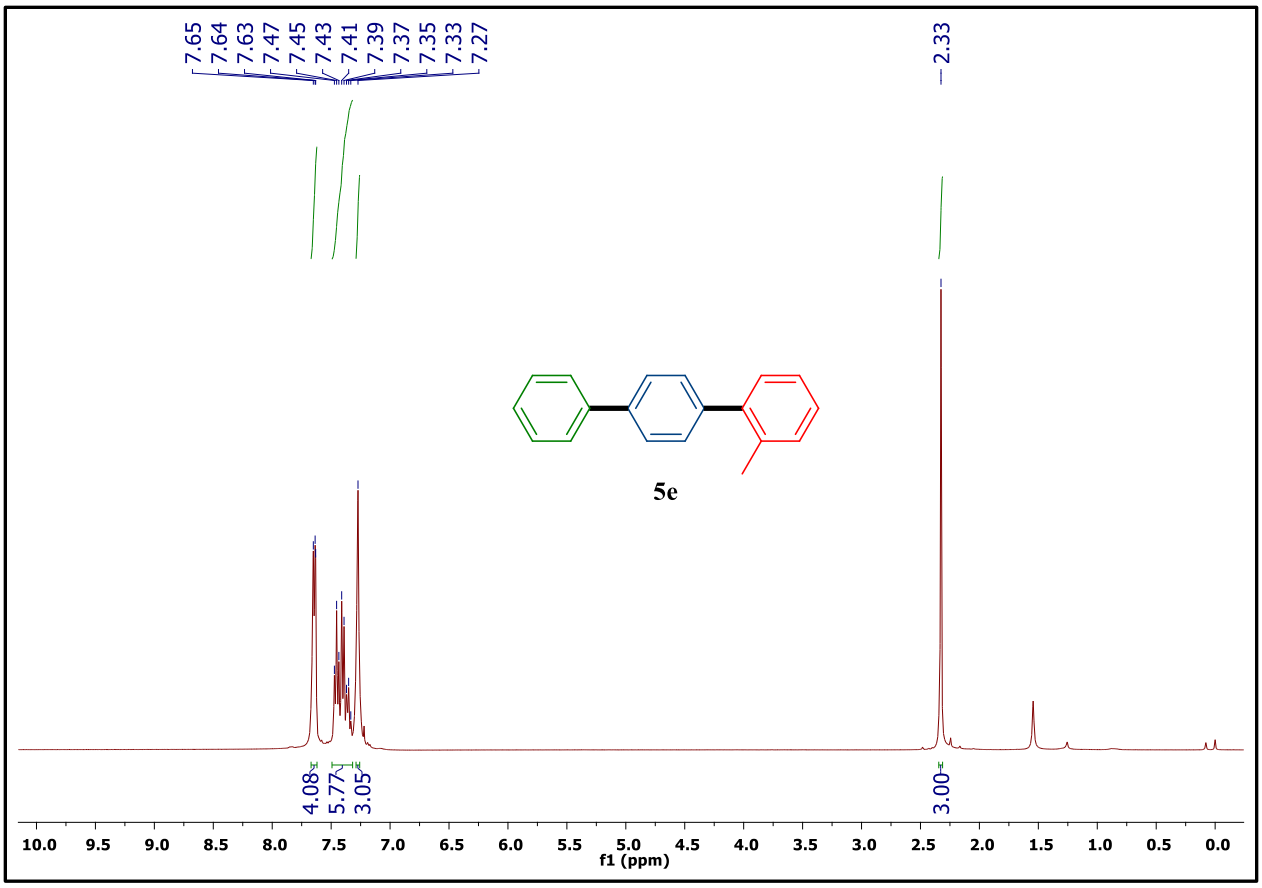


Figure S43. ^{1}H NMR spectra of **5e** in $CDCl_3$

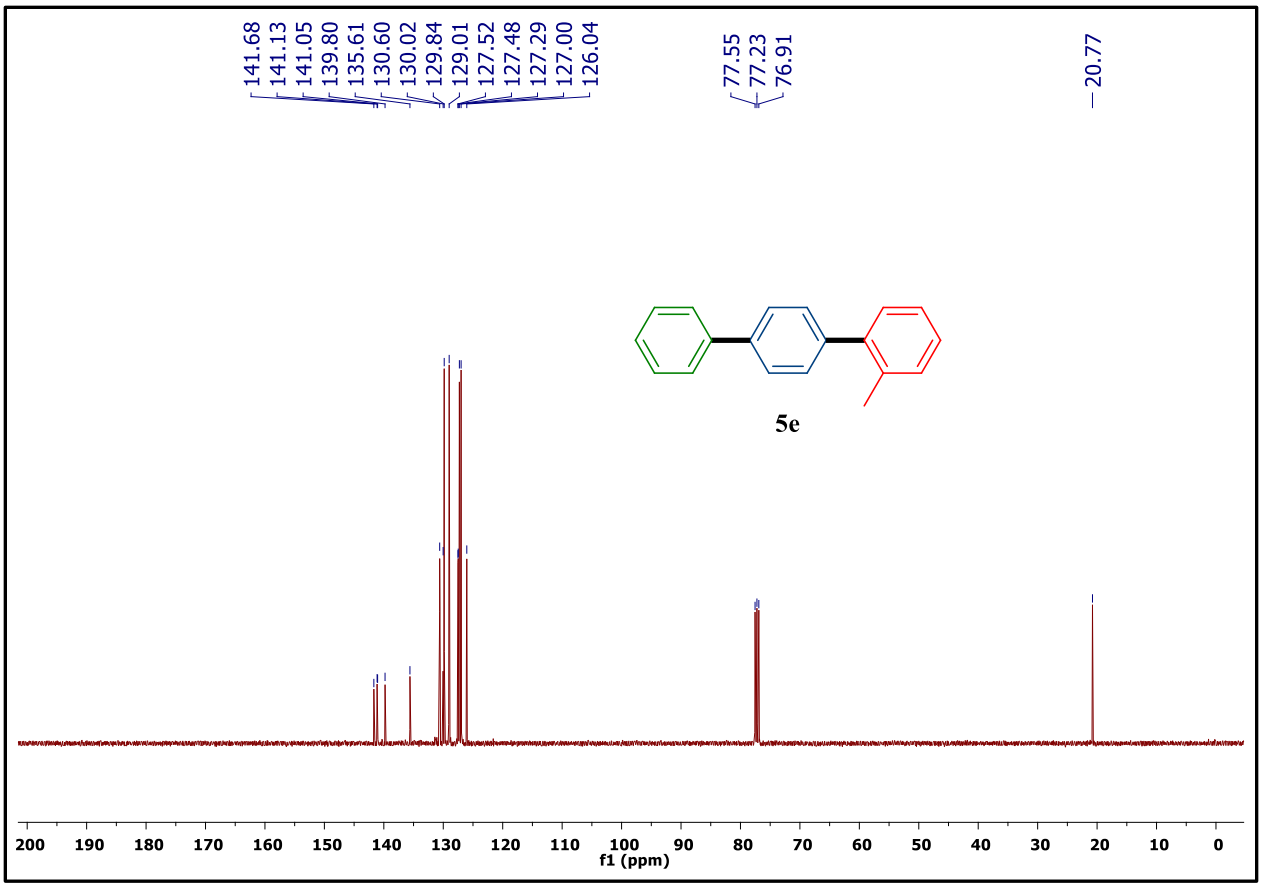


Figure S44. ^{13}C NMR spectra of **5e** in $CDCl_3$

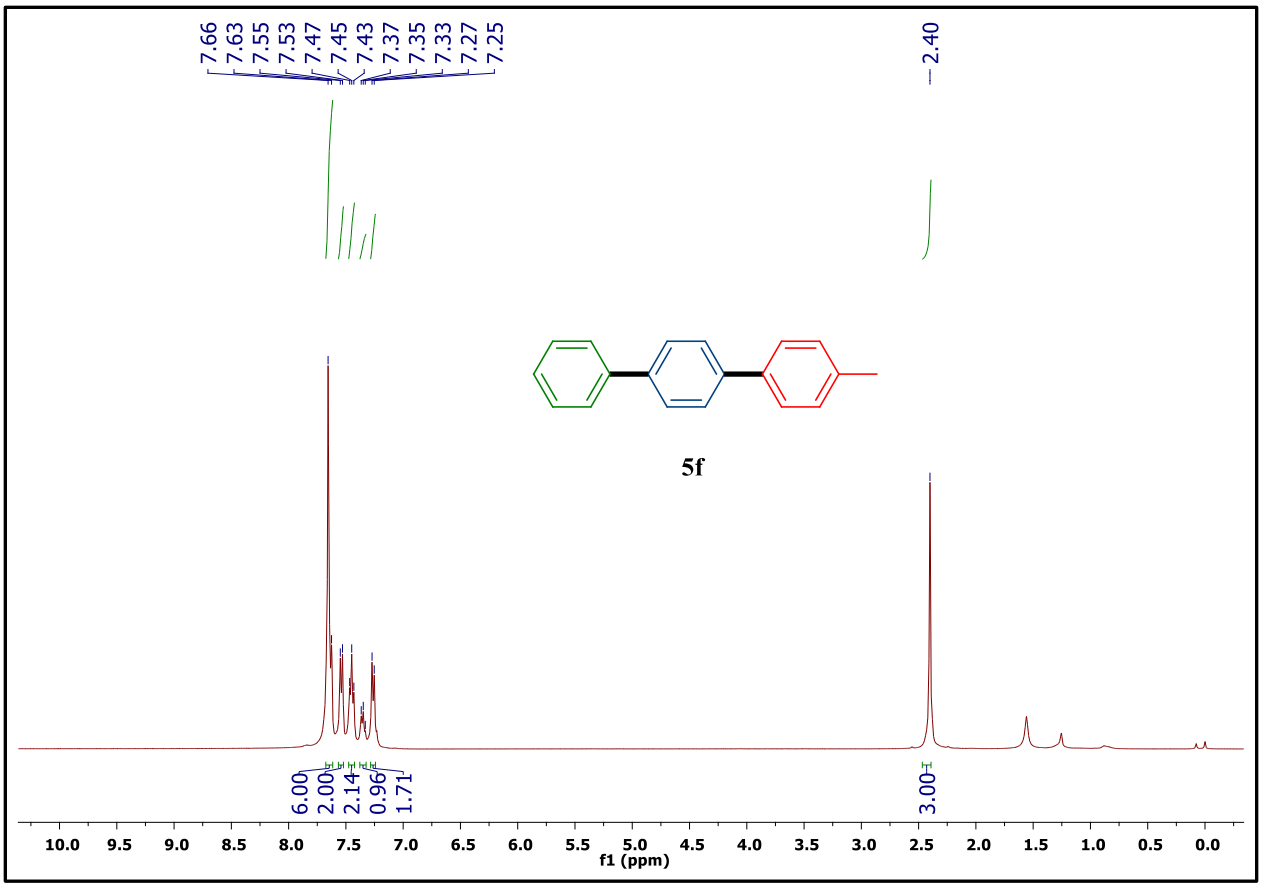


Figure S45. ^{1}H NMR spectra of **5f** in $CDCl_3$

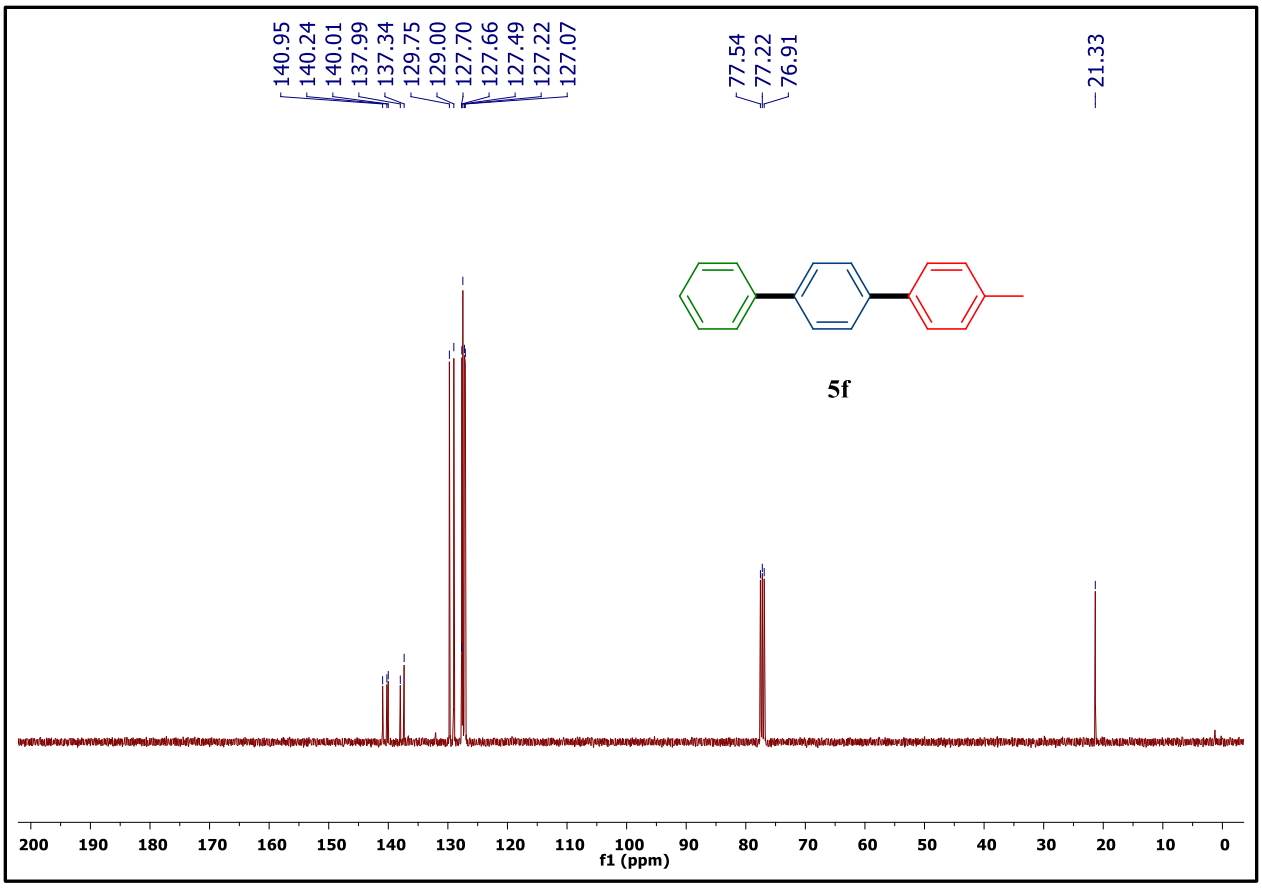


Figure S46. ^{13}C NMR spectra of **5f** in $CDCl_3$

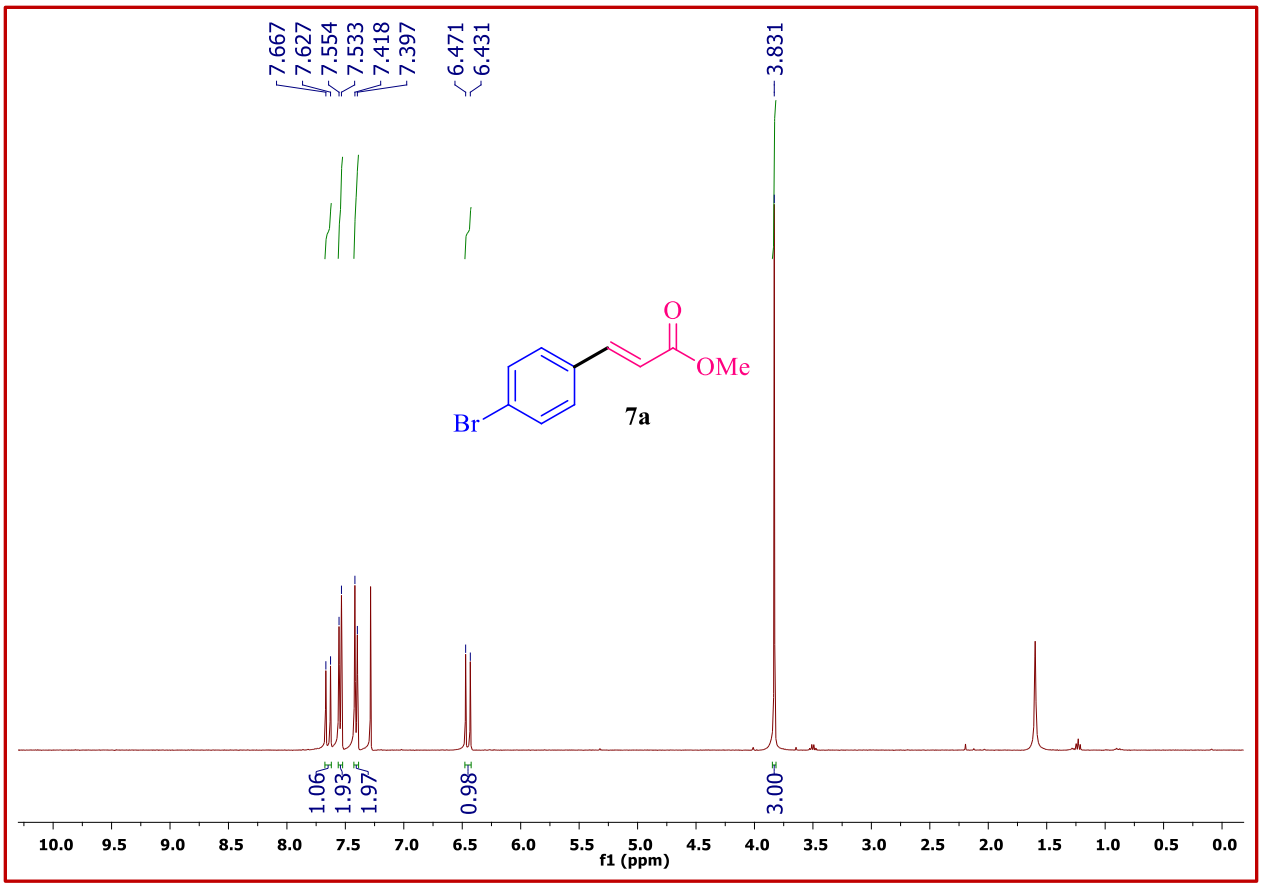


Figure S47. ^{1}H NMR spectra of **7a** in $CDCl_3$

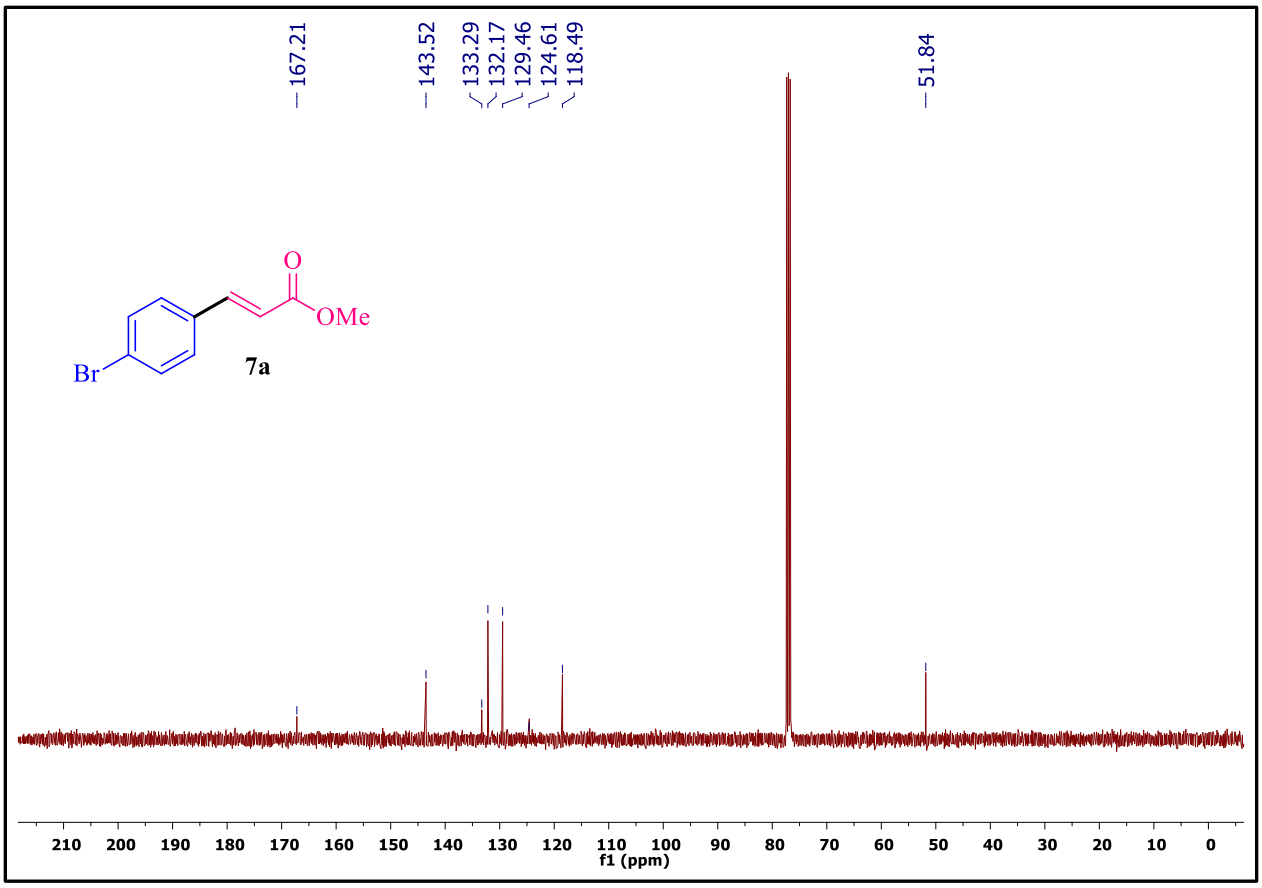


Figure S48. ^{13}C NMR spectra of **7a** in $CDCl_3$

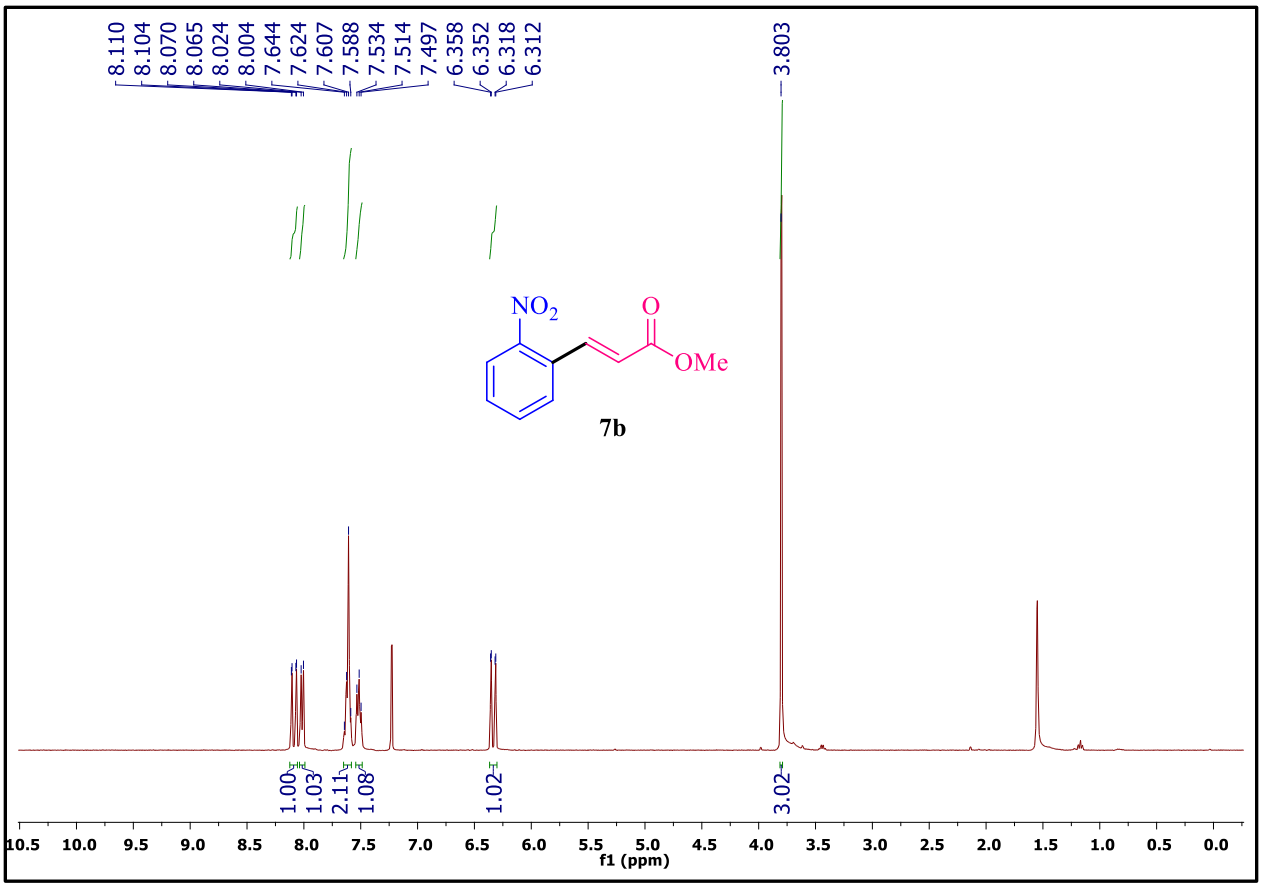


Figure S49. ^{1}H NMR spectra of **7b** in $CDCl_3$

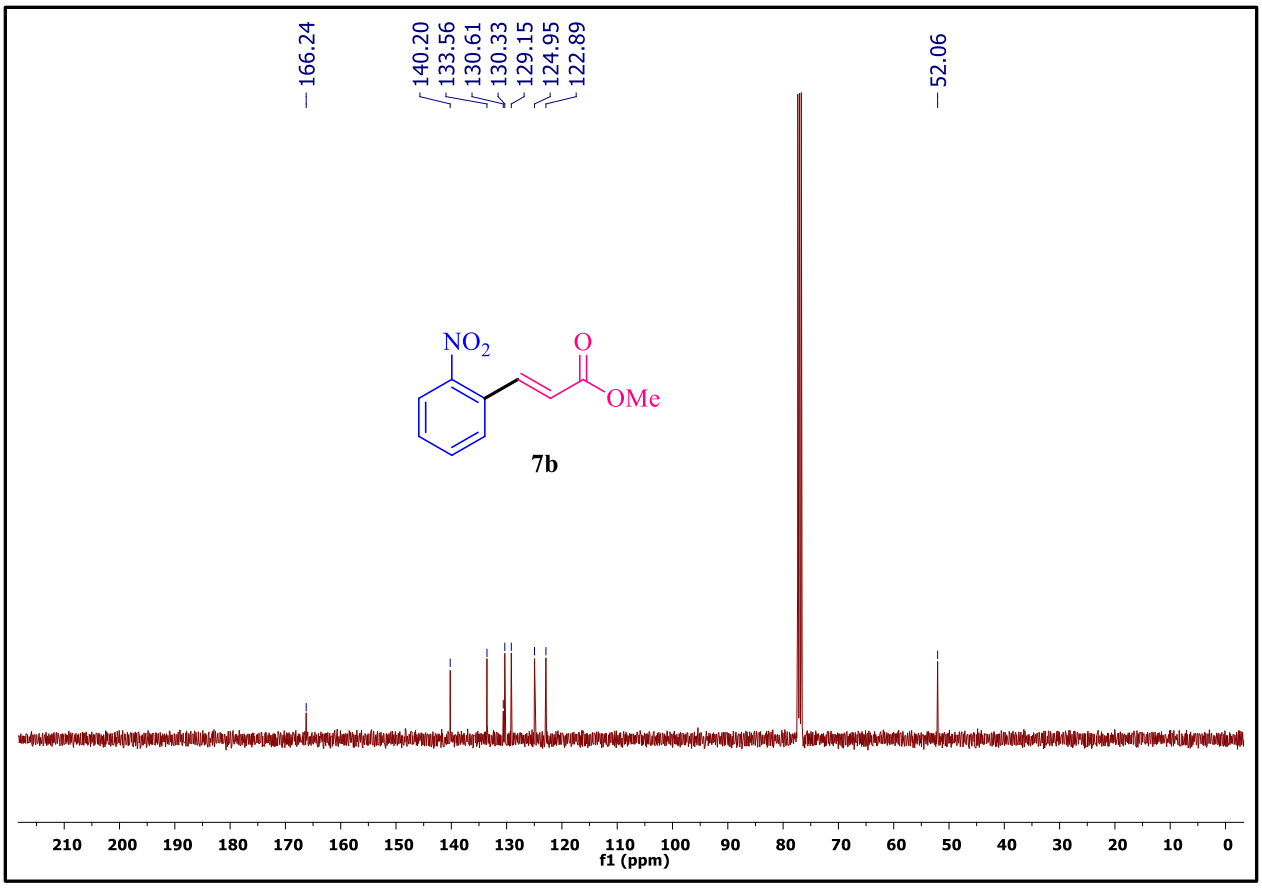


Figure S50. ^{13}C NMR spectra of **7b** in $CDCl_3$

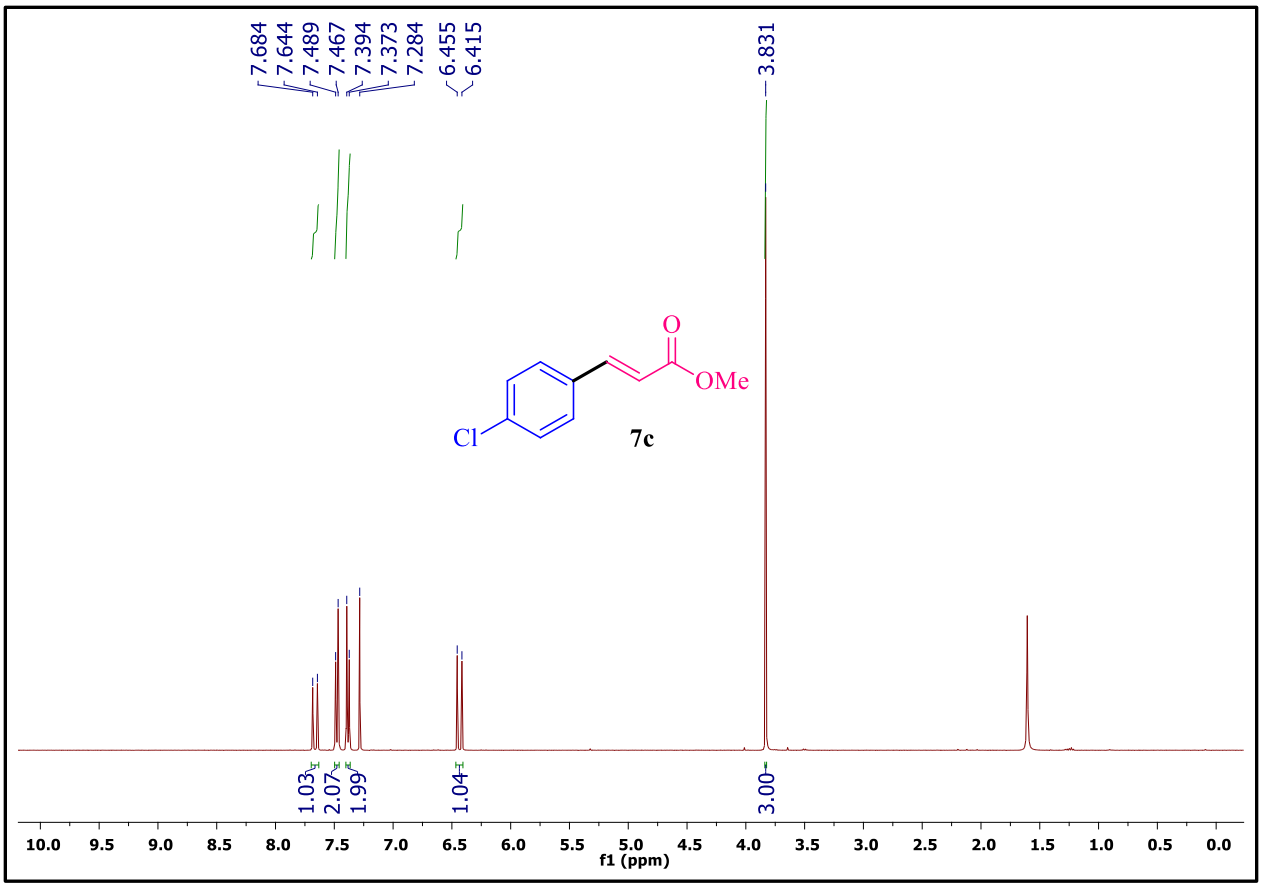


Figure S51. ^{1}H NMR spectra of **7c** in $CDCl_3$

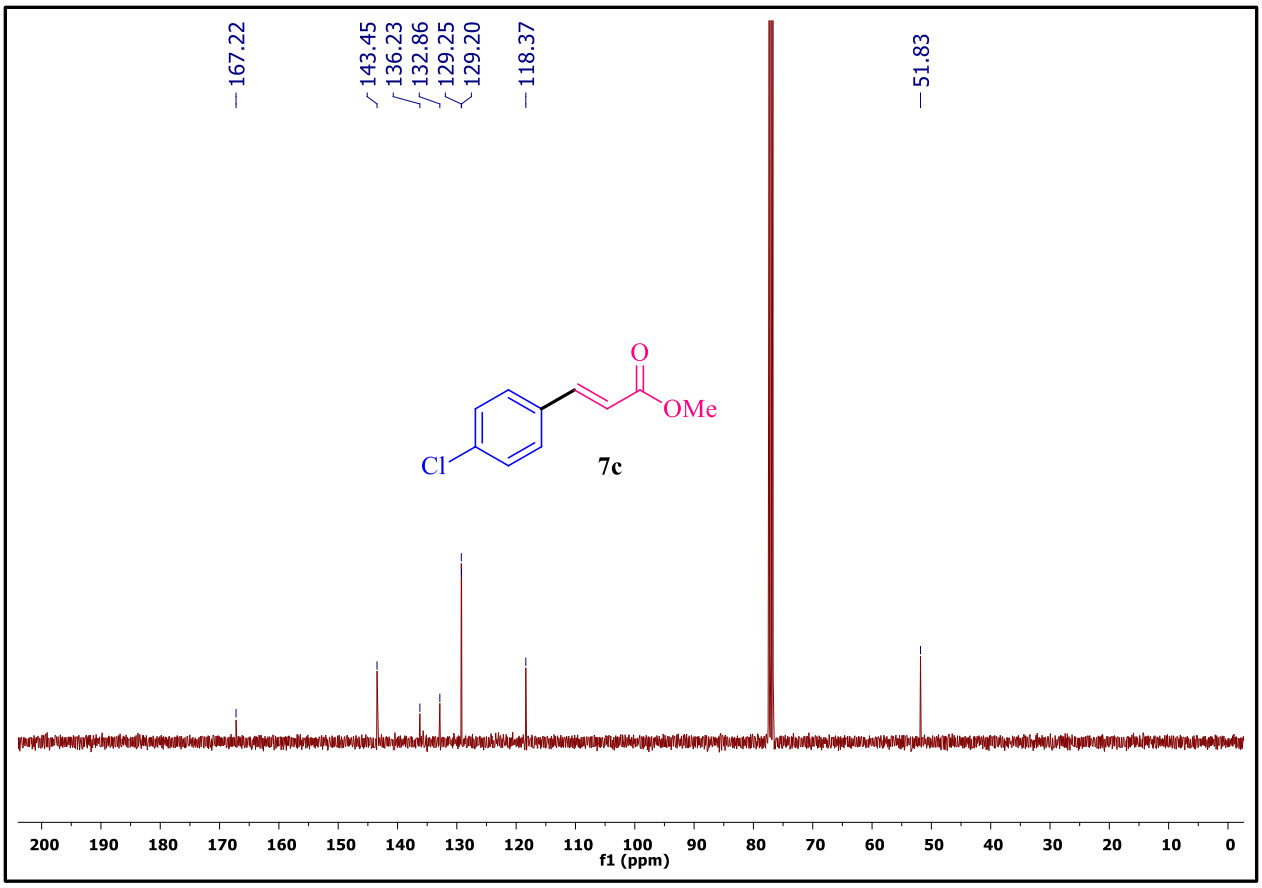


Figure S52. ^{13}C NMR spectra of **7c** in $CDCl_3$

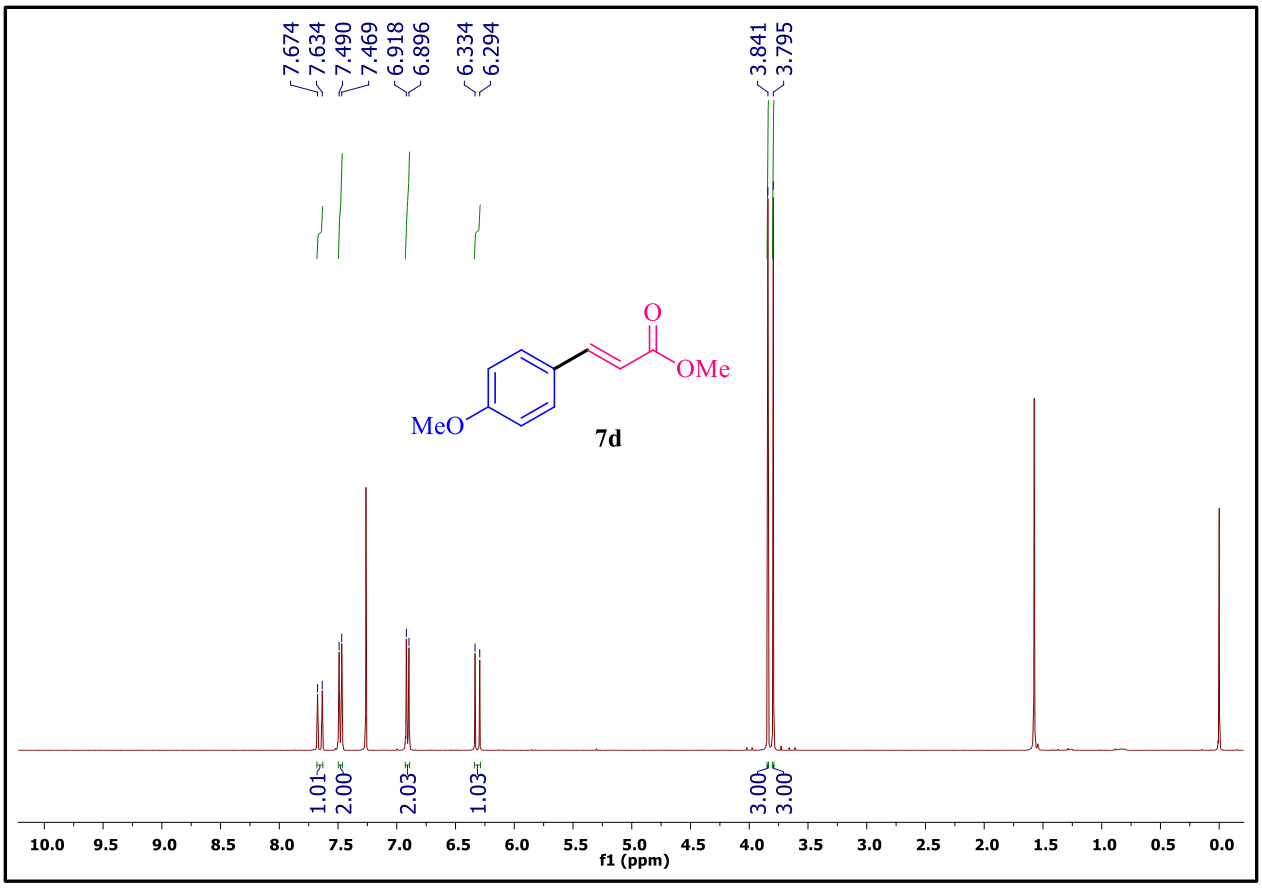


Figure S53. ^{1}H NMR spectra of **7d** in $CDCl_3$

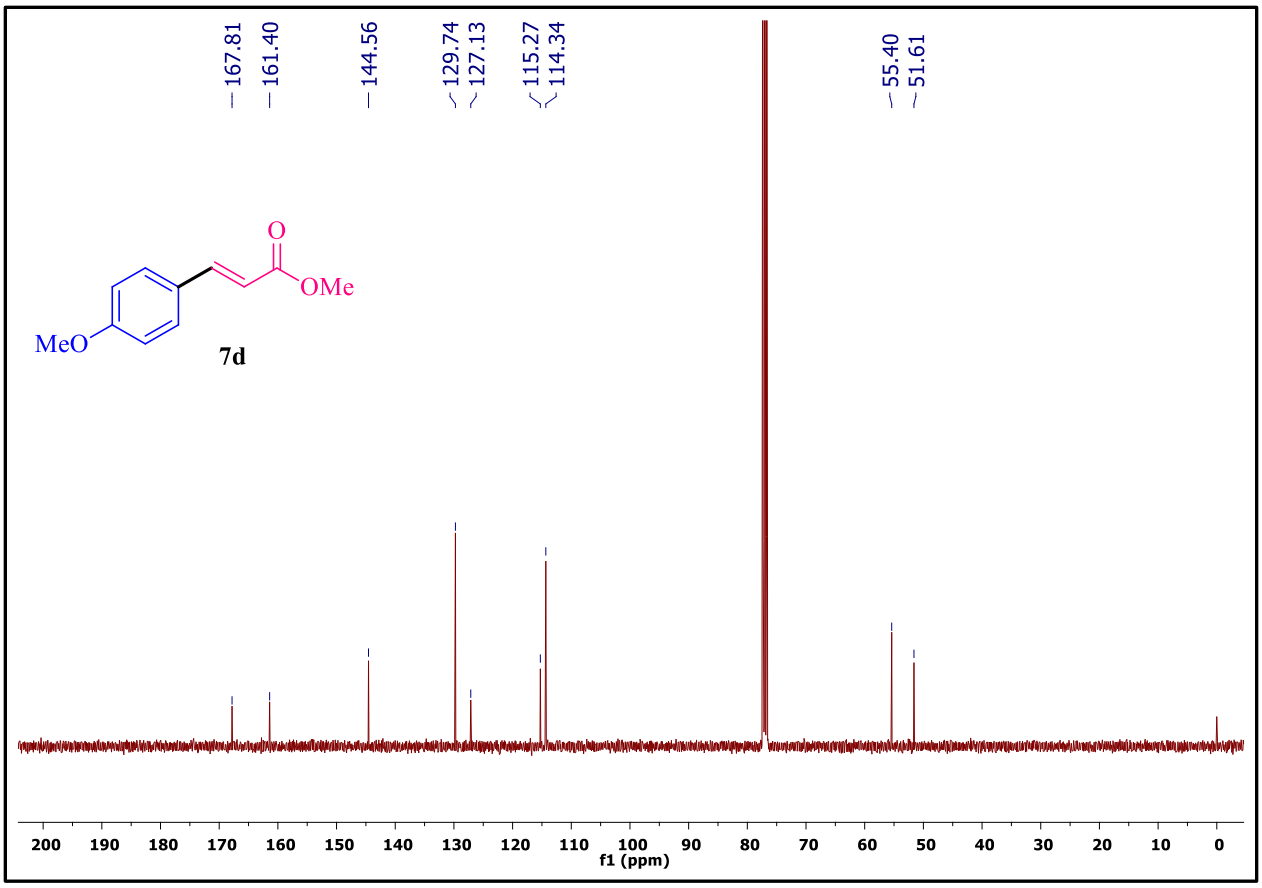


Figure S54. ^{13}C NMR spectra of **7d** in $CDCl_3$

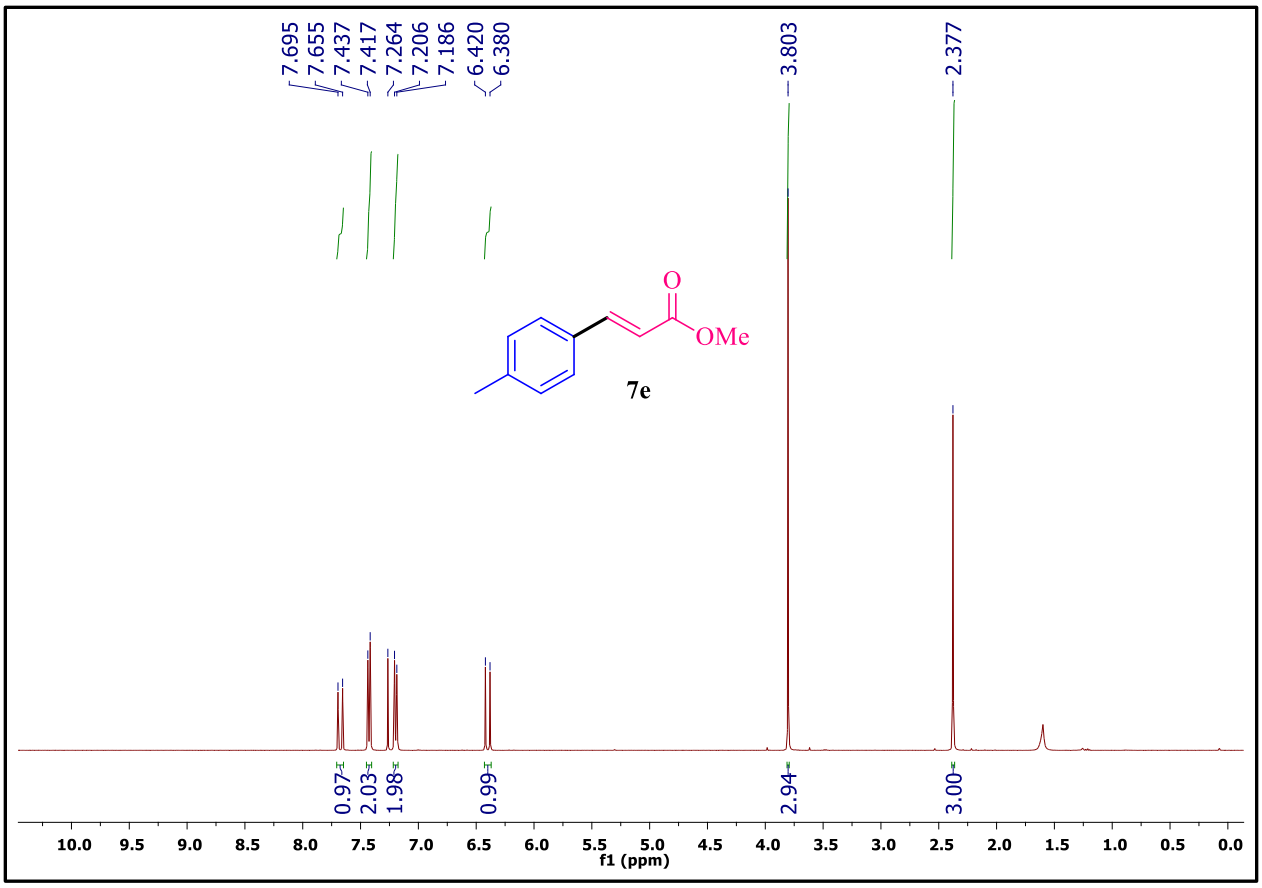


Figure S55. ^{1}H NMR spectra of **7e** in $CDCl_3$

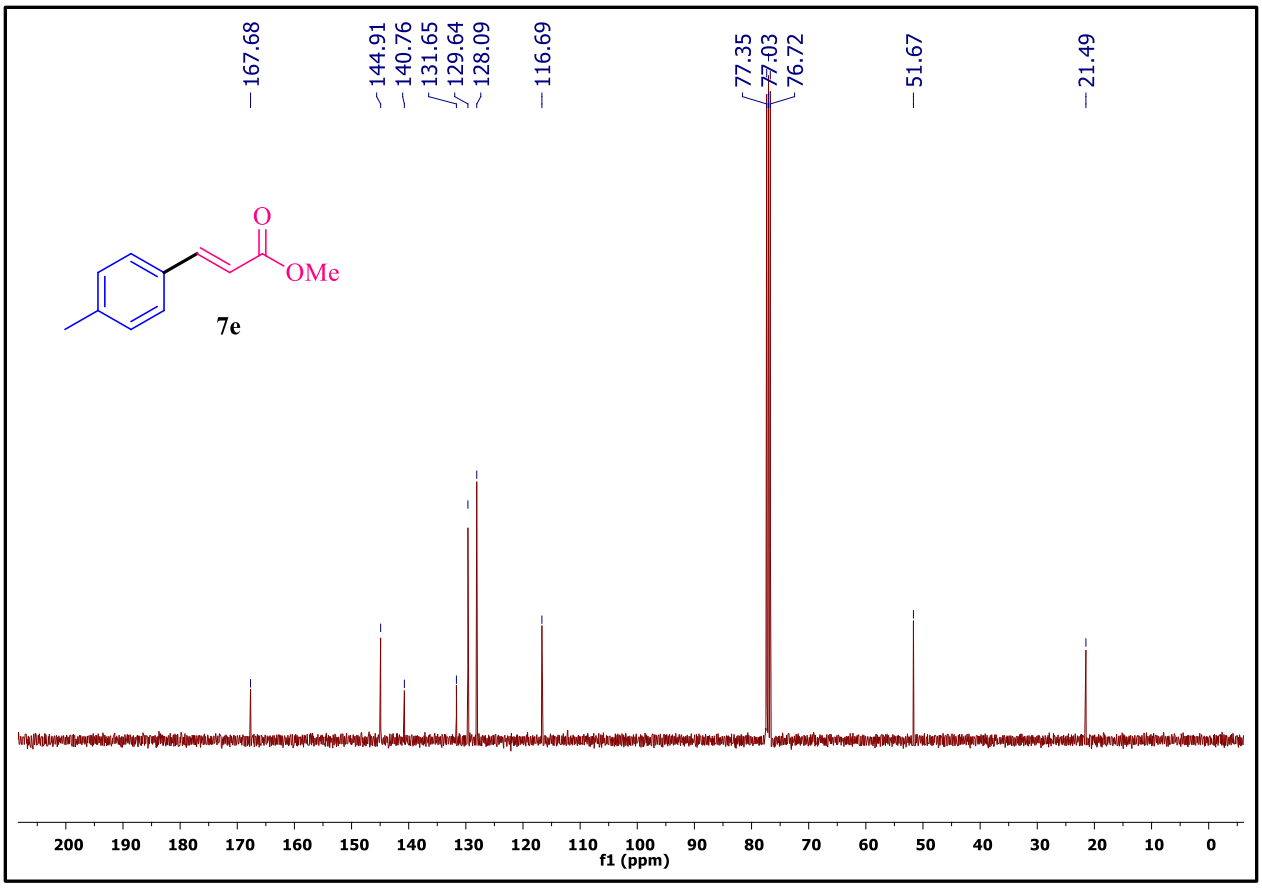


Figure S56. ^{13}C NMR spectra of **7e** in $CDCl_3$

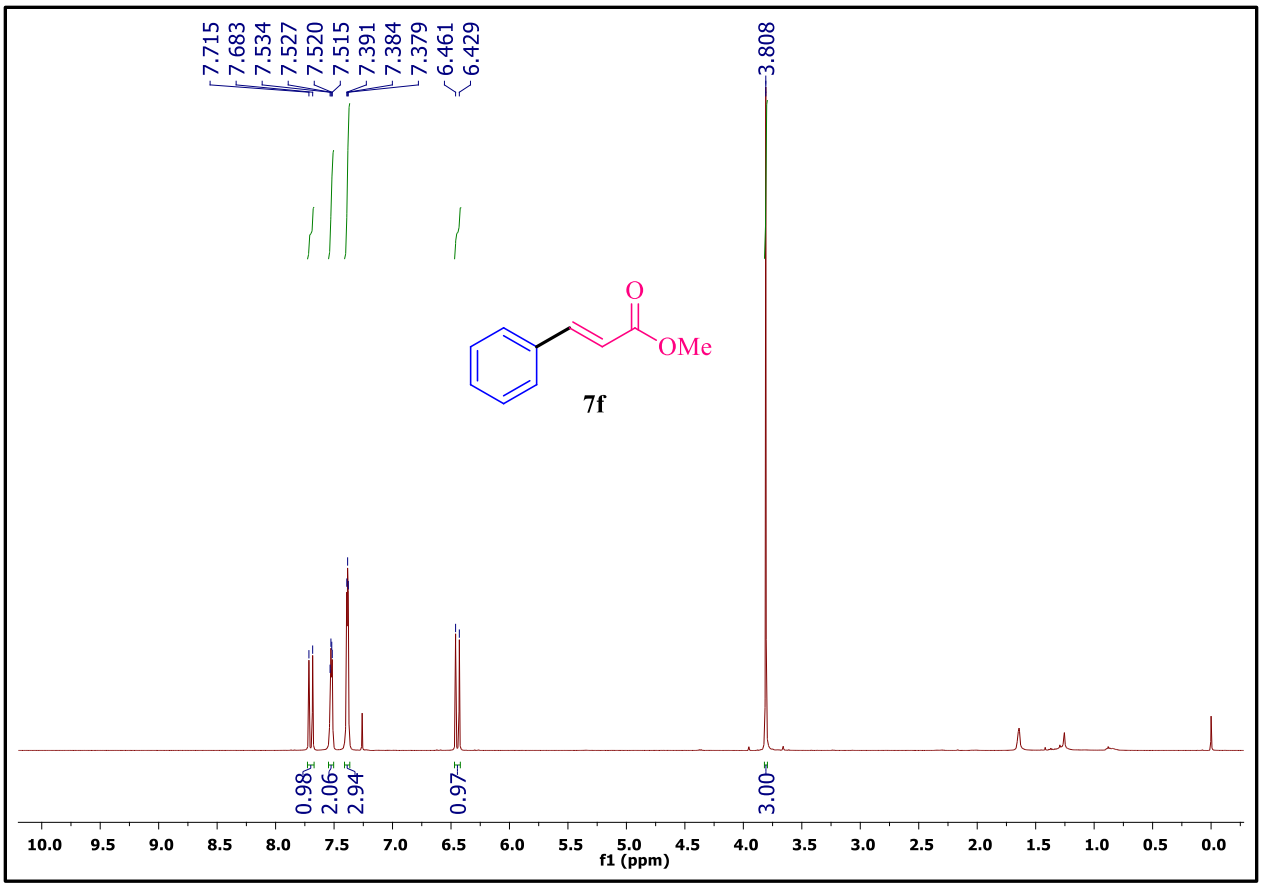


Figure S57. ^{1}H NMR spectra of **7f** in $CDCl_3$

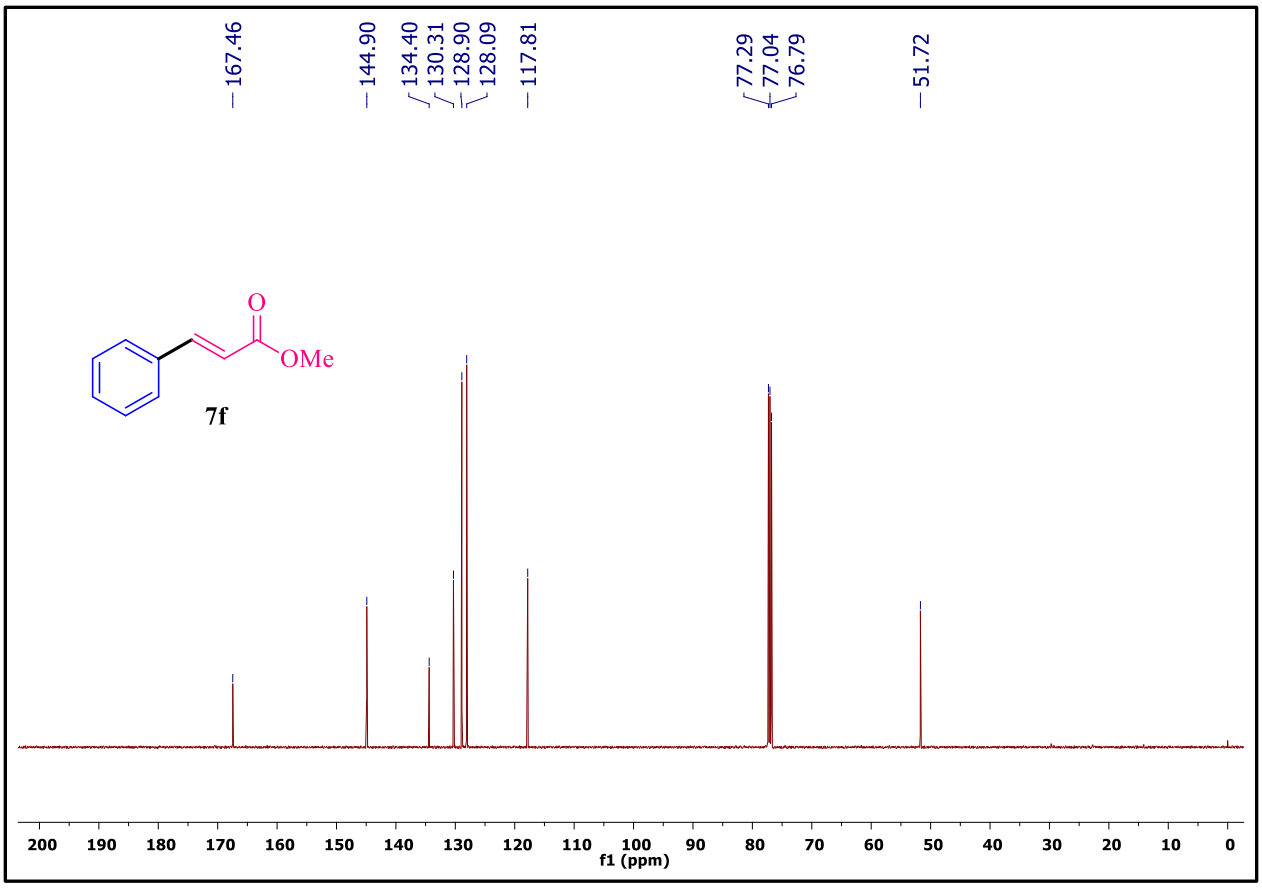


Figure S58. ^{13}C NMR spectra of **7f** in $CDCl_3$

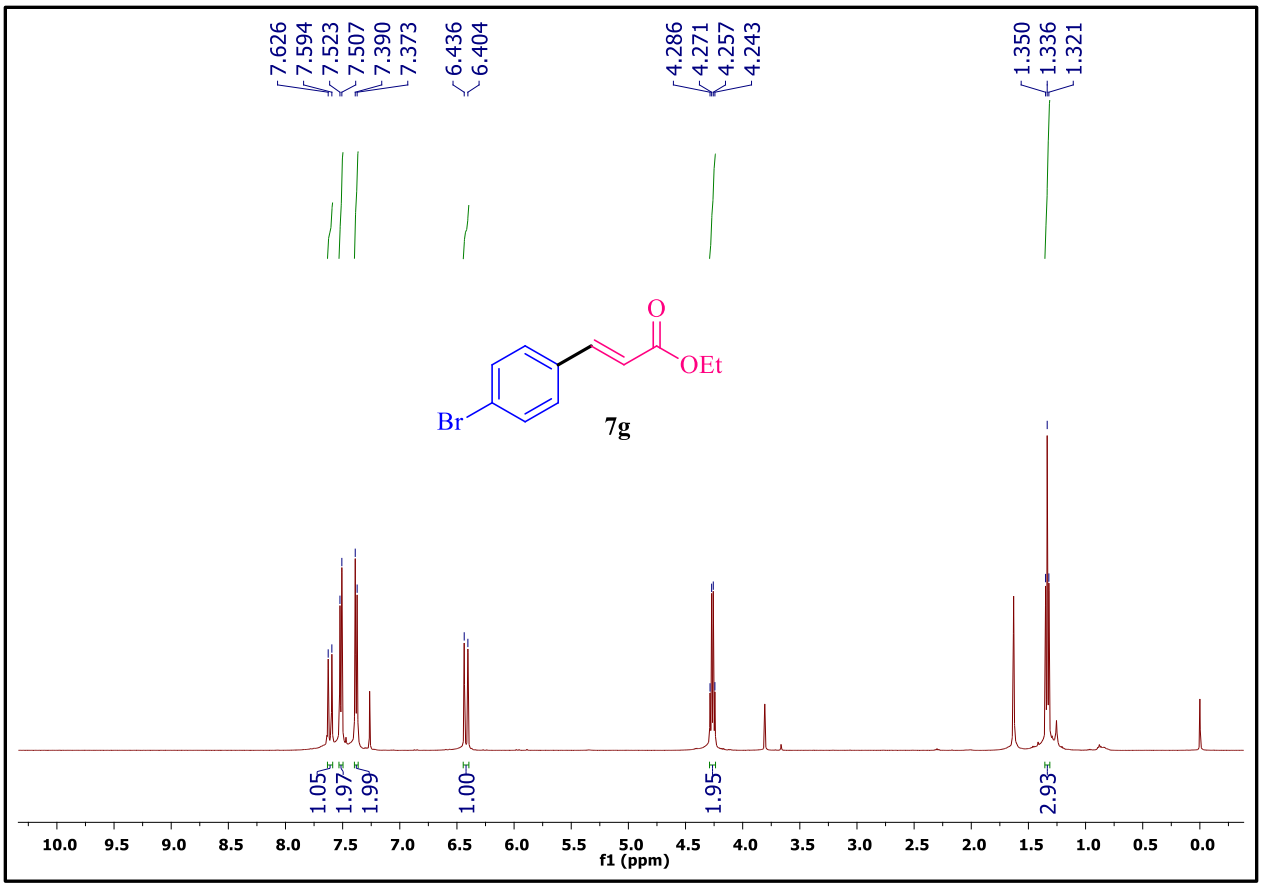


Figure S59. ^{1}H NMR spectra of **7g** in $CDCl_3$

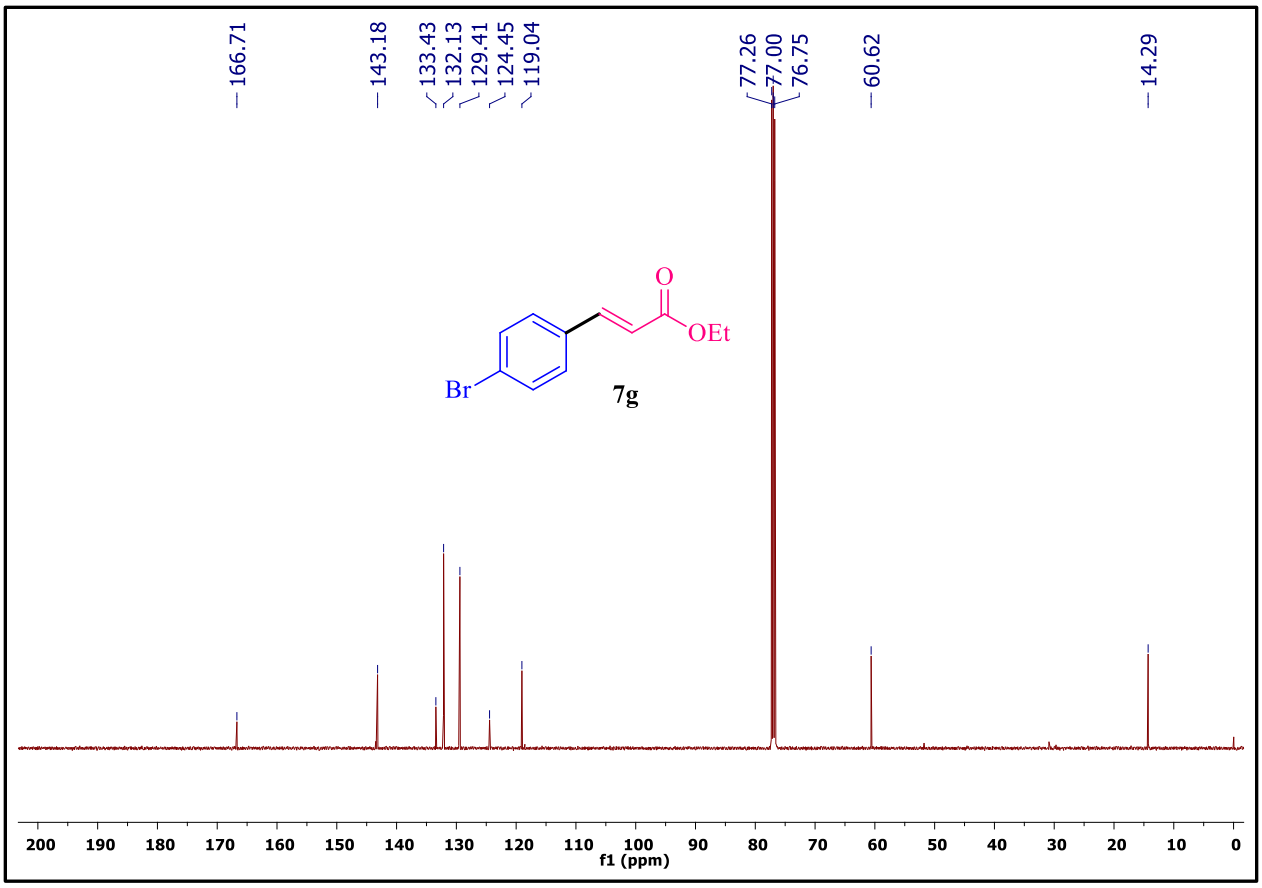


Figure S60. ^{13}C NMR spectra of **7g** in $CDCl_3$

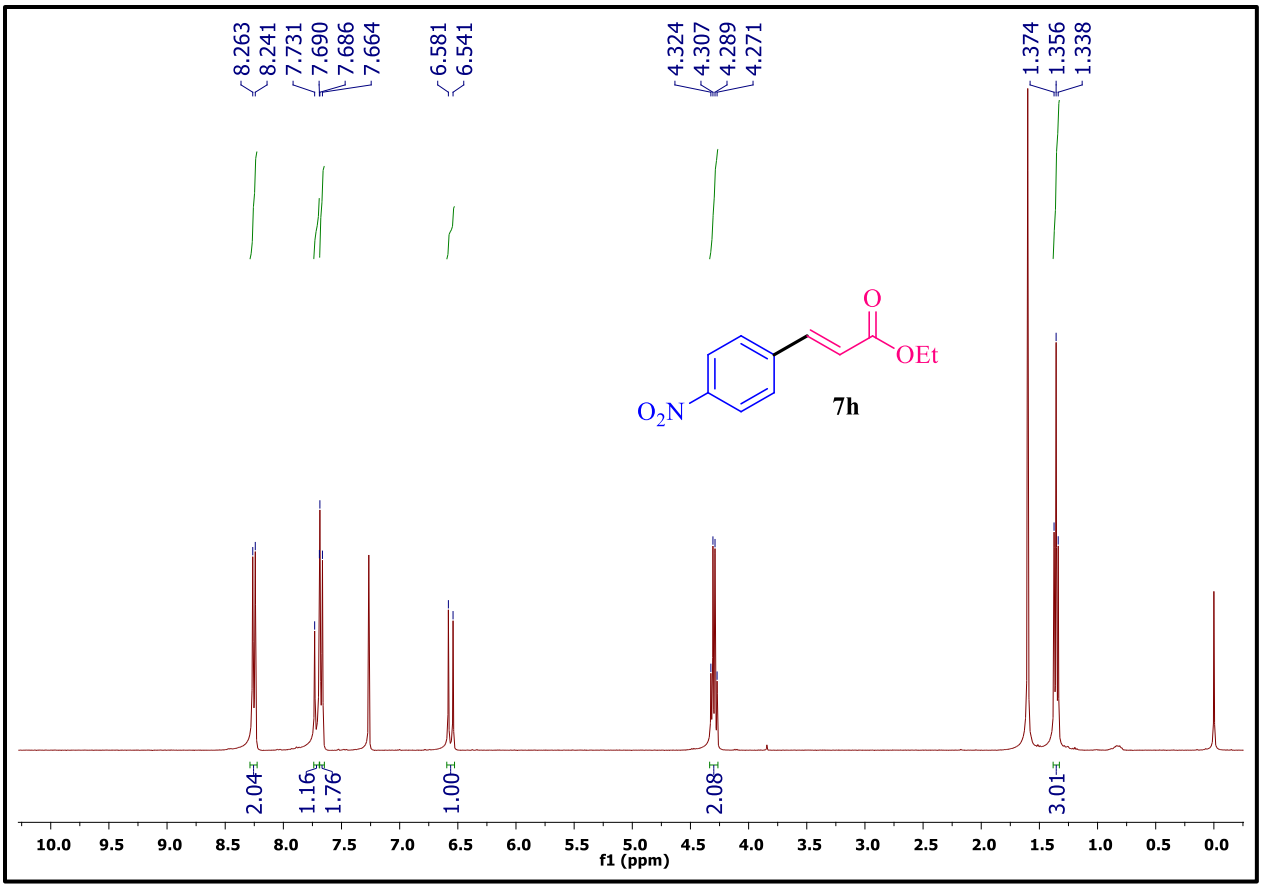


Figure S61. ^{1}H NMR spectra of **7h** in $CDCl_3$

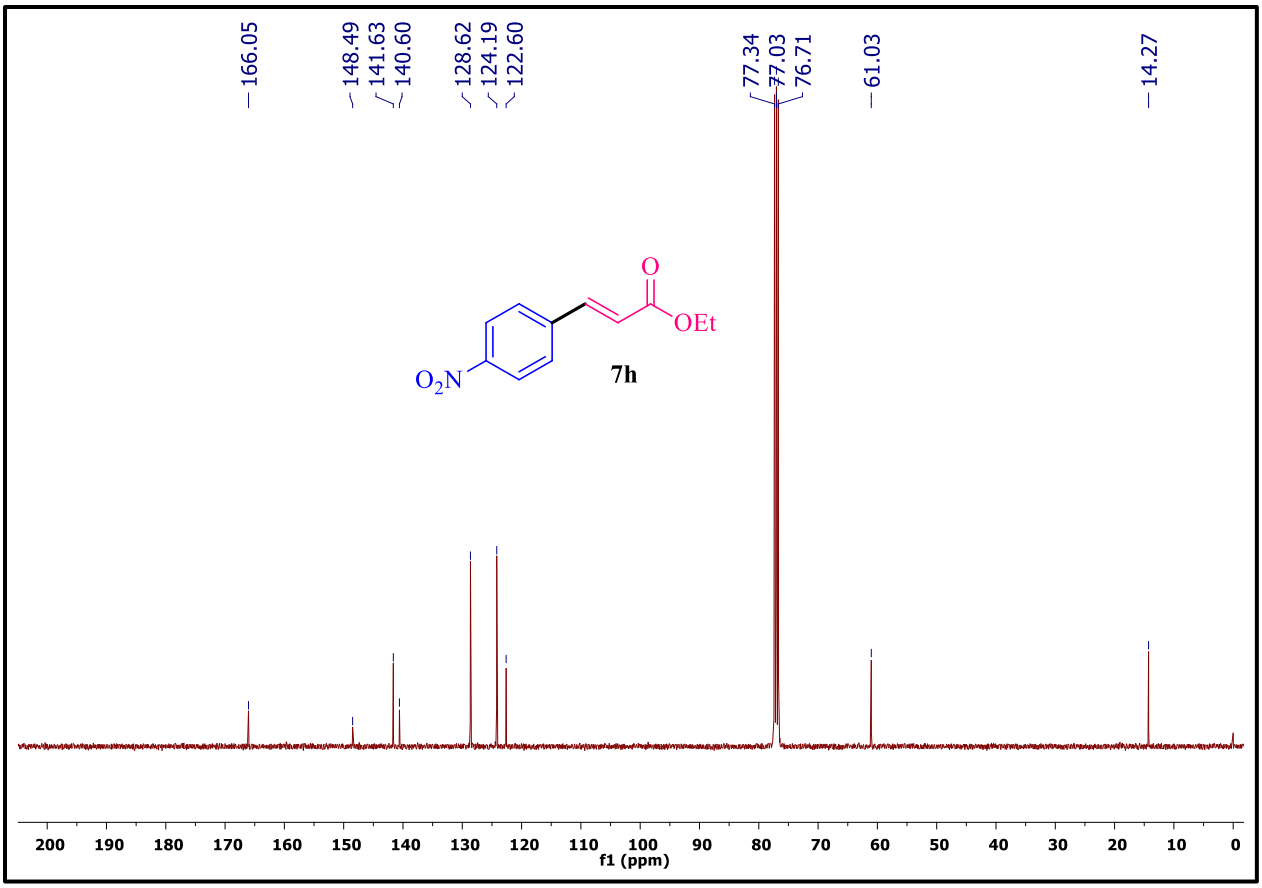


Figure S62. ^{13}C NMR spectra of **7h** in $CDCl_3$

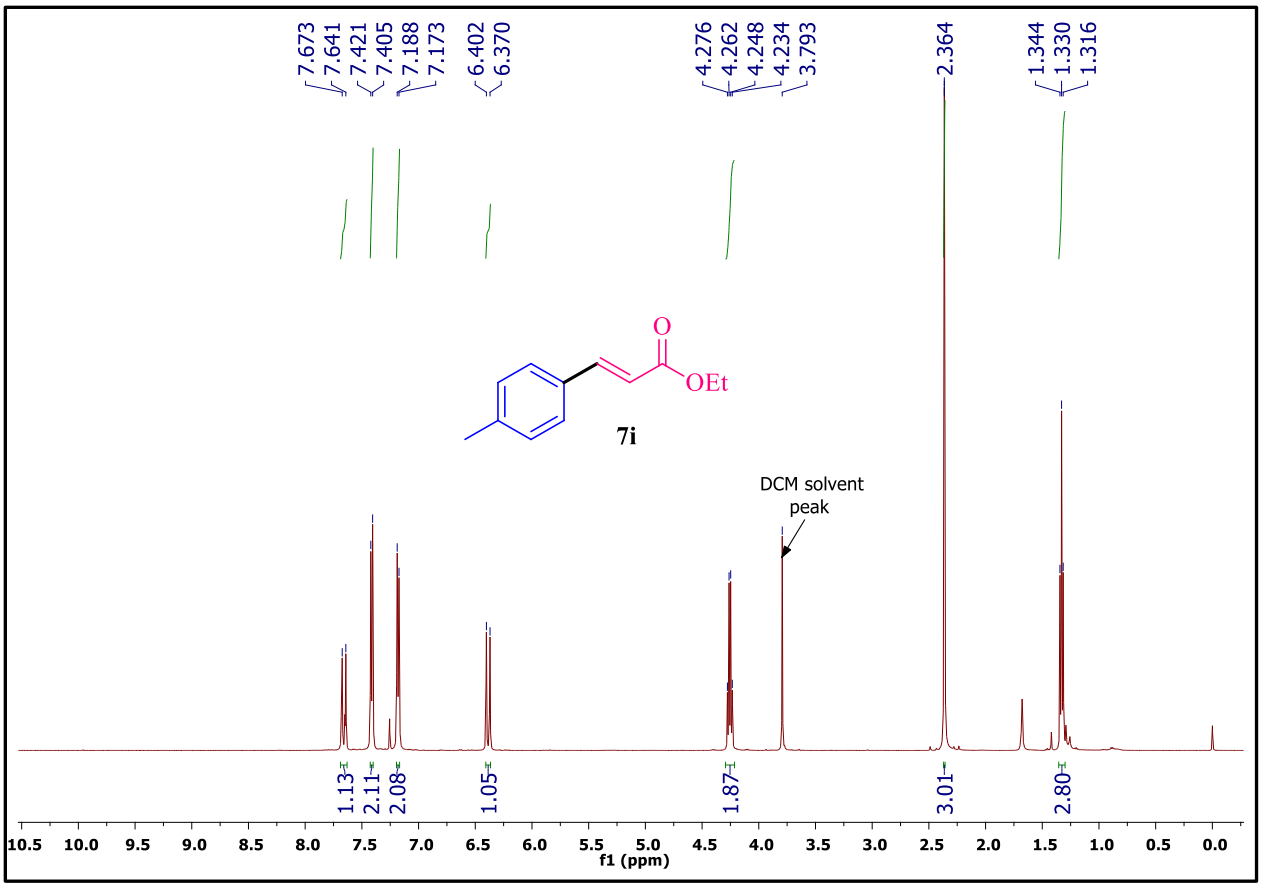


Figure S63. ^{1}H NMR spectra of **7i** in $CDCl_3$

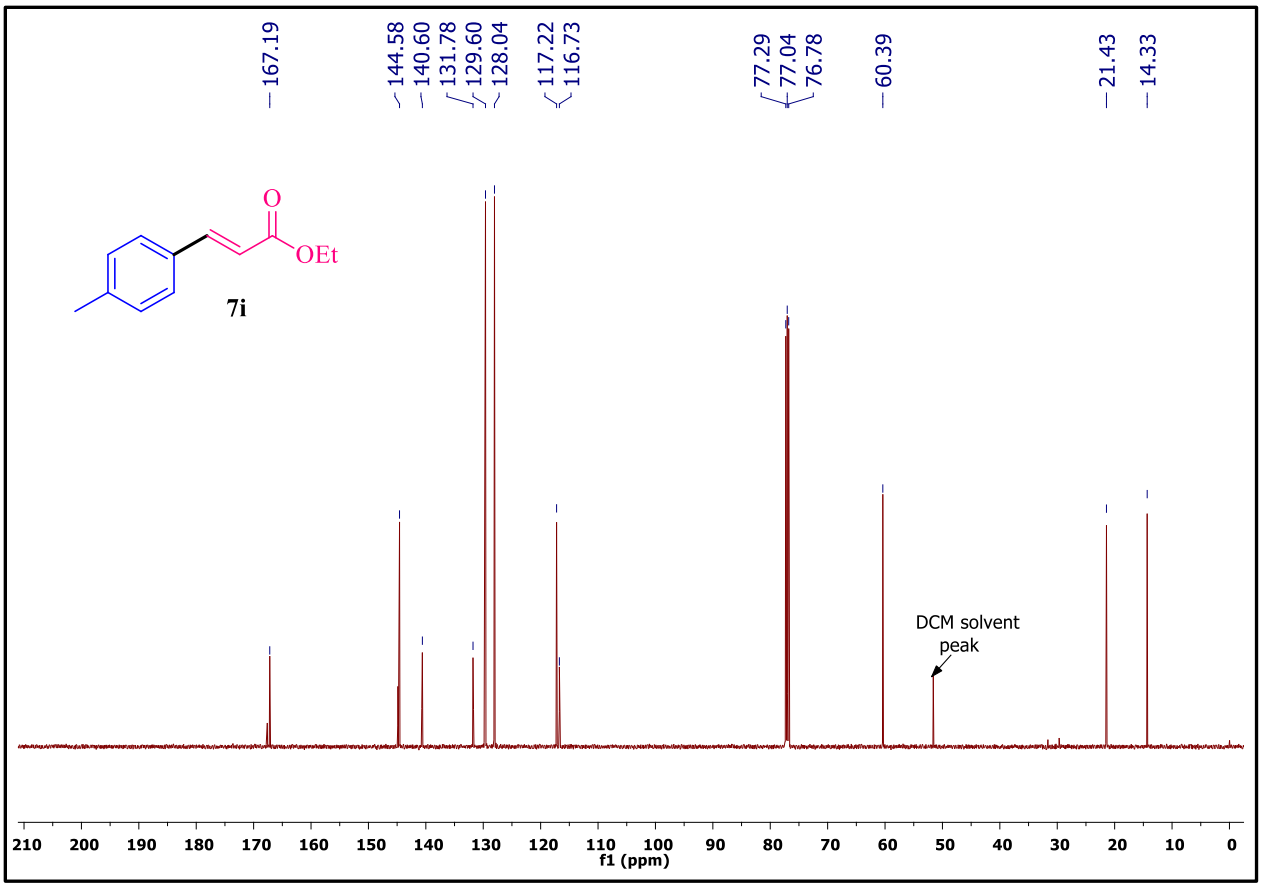


Figure S64. ^{13}C NMR spectra of **7i** in $CDCl_3$

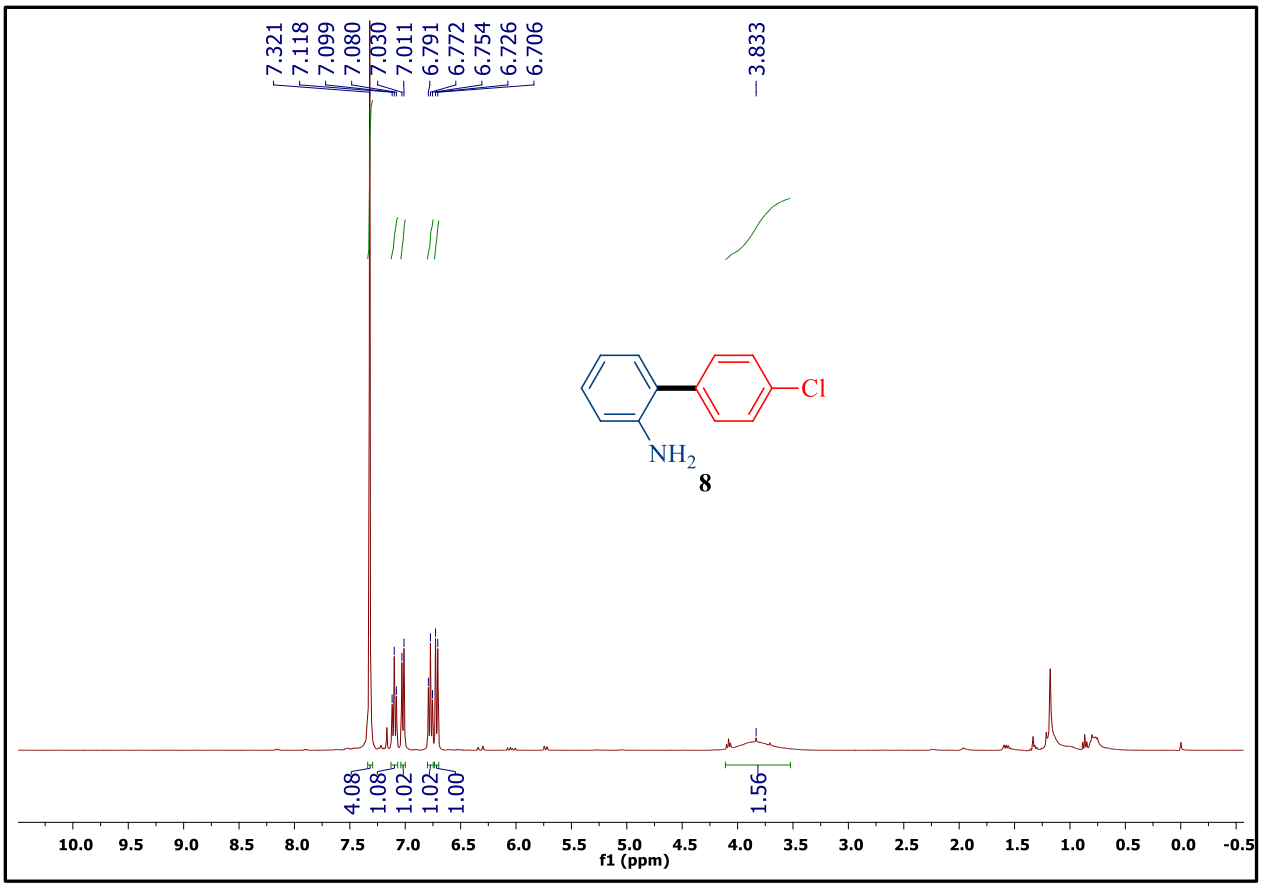


Figure S65. ^{1}H NMR spectra of **8** in $CDCl_3$

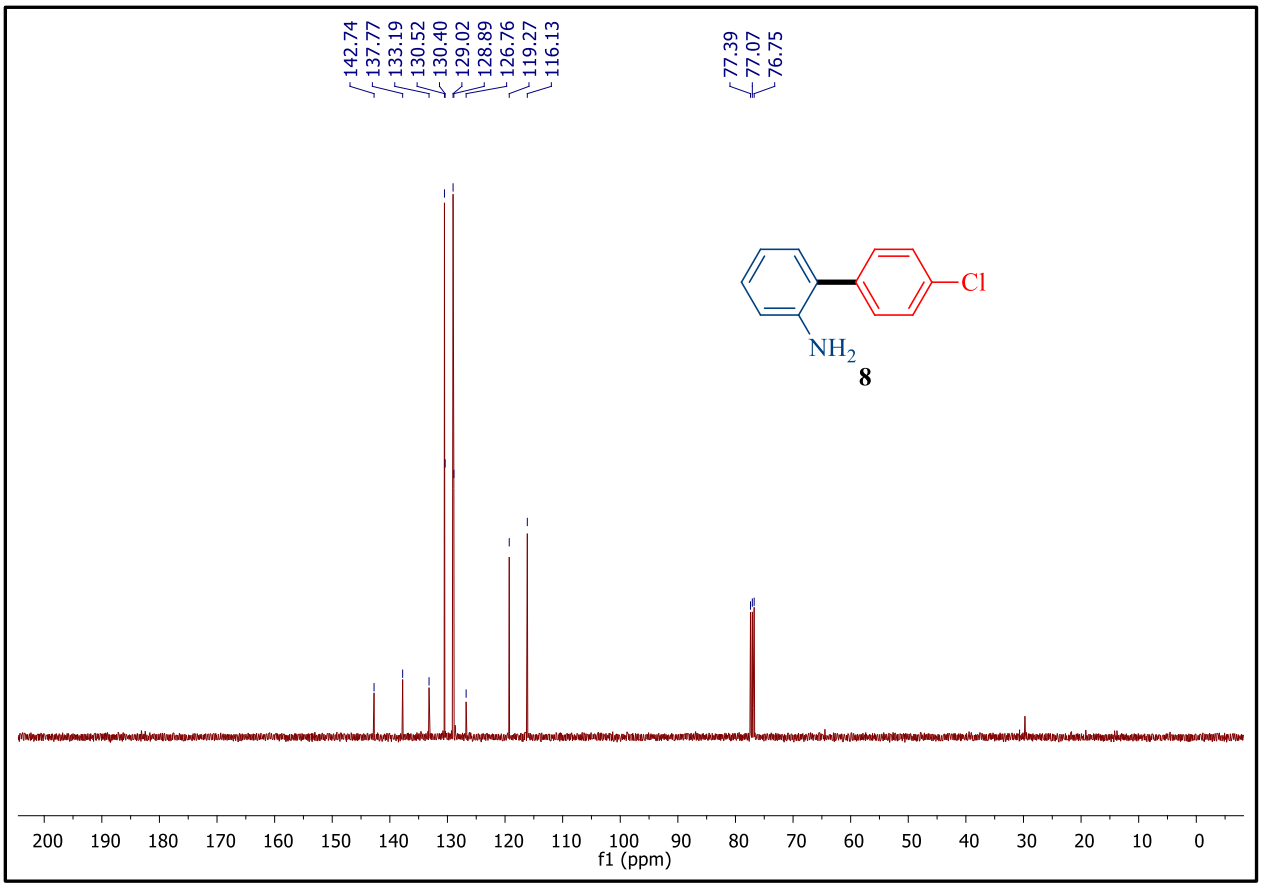


Figure S66. ^{13}C NMR spectra of **8** in $CDCl_3$

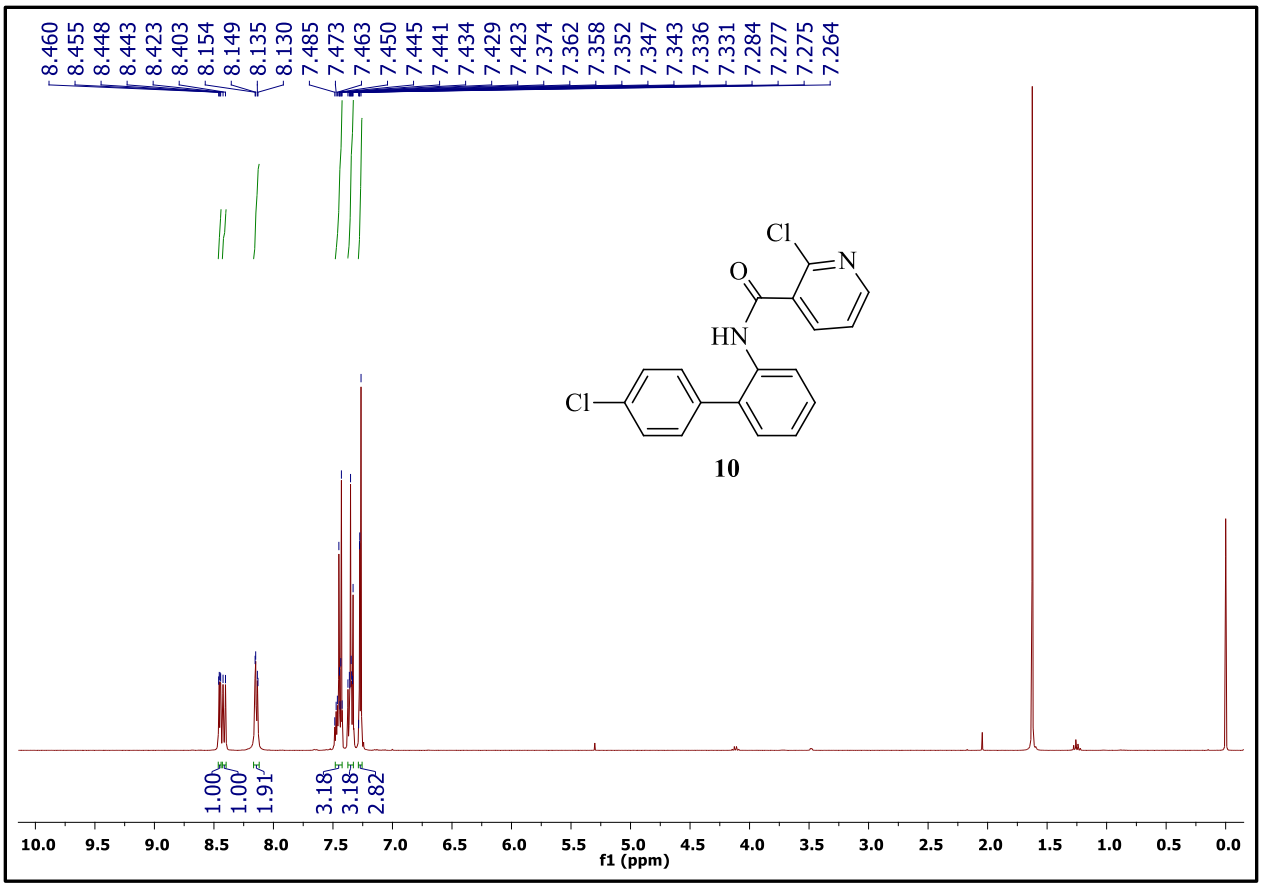


Figure S67. ^{1}H NMR spectra of **10** in $CDCl_3$

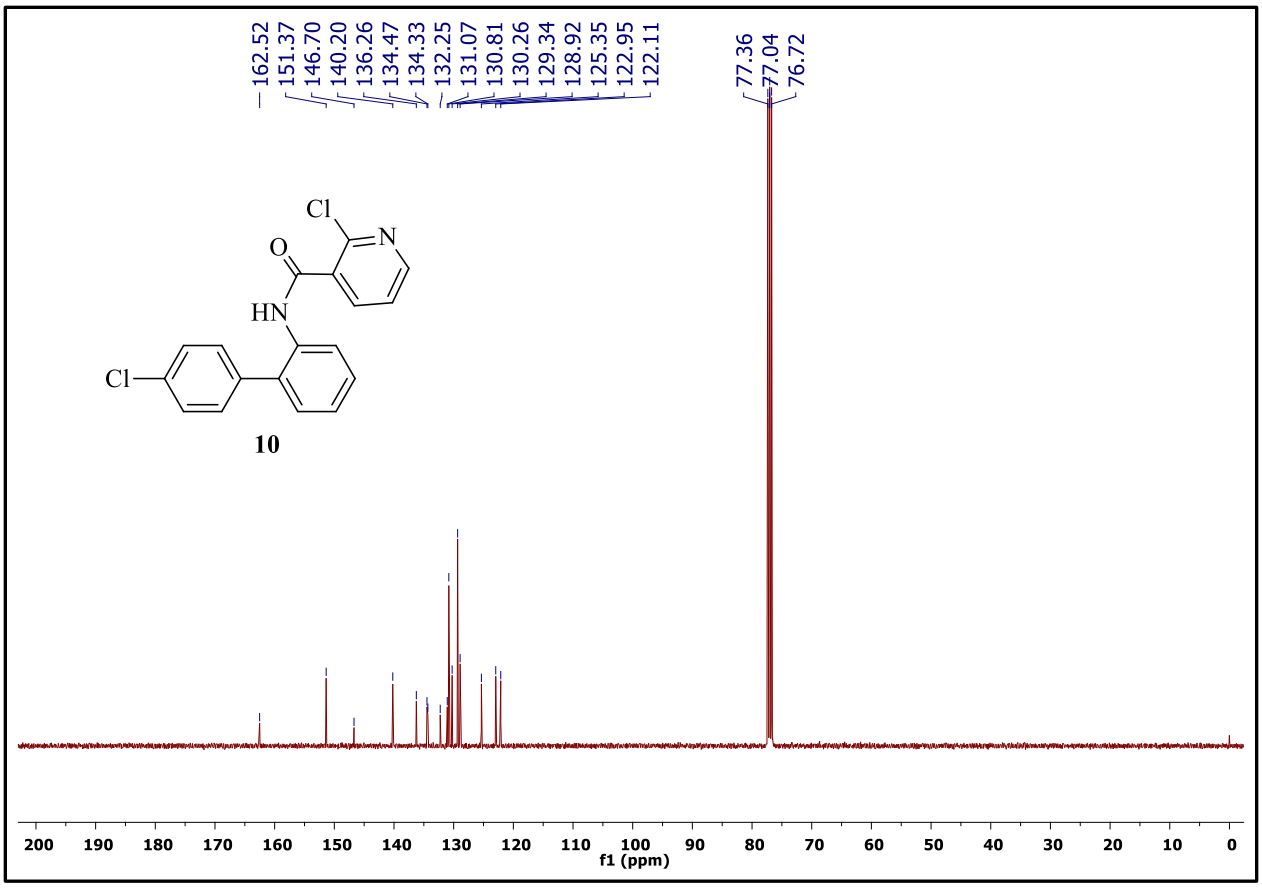


Figure S68. ^{13}C NMR spectra of **10** in $CDCl_3$

References

1 a) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80,** 1339; (b) K.-H. Liao, A. Mittal, S. Bose, C. Leighton, K. A. Khoyan and C. W. Macosko, *ACS Nano*, 2011, **5,** 1253-1258.

2 T. Zhu, X. Li, H. Chang, W. Gao and W. Wei, *Synlett*, 2016, **27,** 880-887.

3 F. Mo, Di. Qiu, Y. Jiang, Y. Zhang and J. Wang, *Tetrahedron Lett.*, 2011, **52,** 518-522.

4 N. Oger, E. L. Grognec and F.-X. Felpin, *ChemCatChem* 2015, **7,** 2085-2094.

5 L. S. Varnedoe, B. D. Angel, J. L. McClellan and J. M. Hanna, *Lett. Org. Chem.*, 2010, **7,** 1-6.

6 M. Gholinejad, *Appl. Organometal. Chem.*, 2013, **27,** 19-22.

7 B. Singh, R. Paira, G. Biswas, B. K. Shaw and S. K. Mandal, *Chem. Commun.*, 2018, **54,** 13220-13223.

8 X. Li, C. Liu, L. Wang, Q. Ye, X. Jin and Z. Jin, *Org. Biomol. Chem.*, 2018, **16,** 8719-8723.

9 C-H. Cho, H. Park, M.-A. Park, T-Y. Ryoo, Y.-S. Lee and K. Park, *Eur. J. Org. Chem.*, 2005, 3177-3181.

10 R. H. Taylor and F.-X. Felpin, *Org. Lett.*, 2007, **9,** 2911-2914.

11 M. Mirza-Aghayan, M. Mohammadi, A. Addad and R. Boukherroub, *Appl. Organometal. Chem.*, 2020, **34,** e5524.

12 W. Xu, C. Liu, D. Xiang, Q. Luo, Y. Shu, H. Lin, Y. Hu, Z. Zhang and Y. Ouyang, *RSC Adv.*, 2019, **9,** 34595-34600.

13 F.-X. Felpin, E. Fouquet and C. Zakri, *Adv. Synth. Catal.*, 2009, **351,** 649-655.