Supporting Information for

Simultaneous pore confinement and sidewall modification of a N-rich COF with Pd(II): an efficient and sustainable heterogeneous catalyst for cross-coupling reactions

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Table of Contents Page no.

Section S1

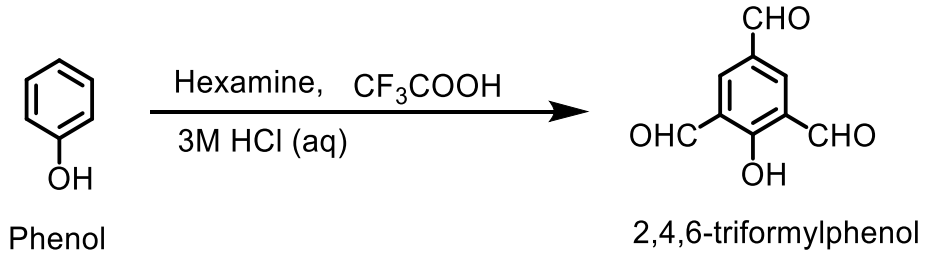
Instruments, methods and physical measurements

FTIR spectra were recorded using a PerkinElmer Spectrum 400 FTIR spectrophotometer. Data was collected using the ATR mode. Solid state NMR spectra were recorded on JEOL 500 MHz NMR spectrometer. Carbon chemical shifts are expressed in ppm (δ scale). In liquid state Bruker 400 MHz NMR/ JEOL 500 MHz NMR spectrometer were used $CDCl_3$/DMSO-d_6 as a NMR solvent to collect the data and dibromomethane used as an internal standard to calculate the NMR yield. SEM images were obtained using a Carl Zeiss ultra plus Field Emission Scanning Electron Microscope (FE-SEM). EDX-Mapping ware performed in the Zeiss-EDAX. The morphology of the COFs was characterized by transmission electron microscopy (TEM) using a FEI TECNAI G2 F20-ST instrument operated at an accelerating voltage of 200 kV. The COF powder was dispersed in ethanol and drop-cast onto carbon-coated copper grids. The grids were then dried under an infrared lamp before imaging. Thermogravimetric analysis (TGA) was performed by using a Perkin Elmer STA 6000 analyzer in the temperature range of 30−600 °C, under a nitrogen atmosphere and at a heating rate of 10°C/min. Powder X-ray diffraction (PXRD) patterns were recorded on Empyrean Malvern PANalytical diffractometer using Cu Kα radiation (α =1.5406 Å), with a scan speed of 2°/min. Surface area of the samples were measured using Quantachrome Autosorb instrument (Quantachrome, USA) with extra-high purity gases (99.9999%)**.** Prior to surface area analysis, the samples were activated by heating them at 120 °C for 12h. The resulting samples were subjected to gas adsorption measurements (P/P_0 range from 0 to 1 atm) at 77 K. The Brunauer-Emmett-Teller (BET) model was utilized to calculate the specific surface areas. The pore size distributions were derived from the sorption curves by using the non-local density functional theory. X-ray photoelectron spectroscopy (XPS) measurements for oxidation state and binding energy analysis were conducted either at beamline BL-14, Indus-2, RRCAT, Indore, or using the Thermo Scientific NEXSA Surface Analysis system at IIT Mandi. ICP-AES analysis was carried out using a SPECTRO Analytical Instruments GmbH, Germany (Model: ARCOS, Simultaneous ICP Spectrometer) at SAIF facility, IIT Bombay.

Section S2

1.1 Raw Materials and Synthesis of the monomers: All reagents were purchased from commercial suppliers (Sigma-Aldrich, TCI Chemicals, CDH Chemicals, and Alfa Aesar) depending on their availability and used without further purification unless stated otherwise. phenol trialdehyde (TFP) were synthesized according to a literature reported protocol.[1] 5-Amino-2-cyanopyridine was procured from Sigma Aldrich. 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine) was synthesized using the previously reported procedure.[2] Detailed synthetic procedures are mentioned in Section S2. The COFs are reported herein are synthesized according to the previously reported or slightly modified procedures mentioned in section 1.2.[2] All the other reagents, starting materials and solvents were purchased locally and were used as obtained without further purification.

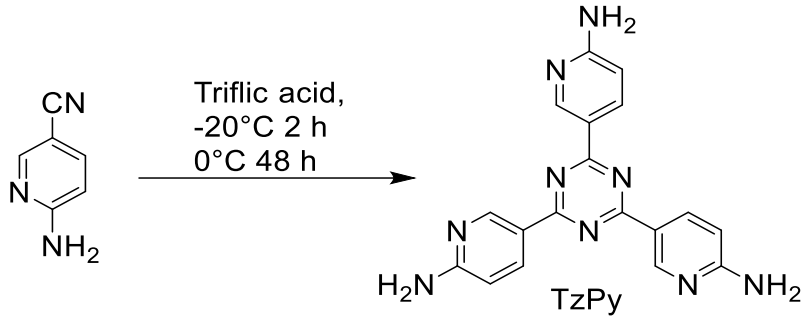
Synthesis of phenol aldehyde (TFP)[1, 2]



Phenol 2,4,6-triformylphenol

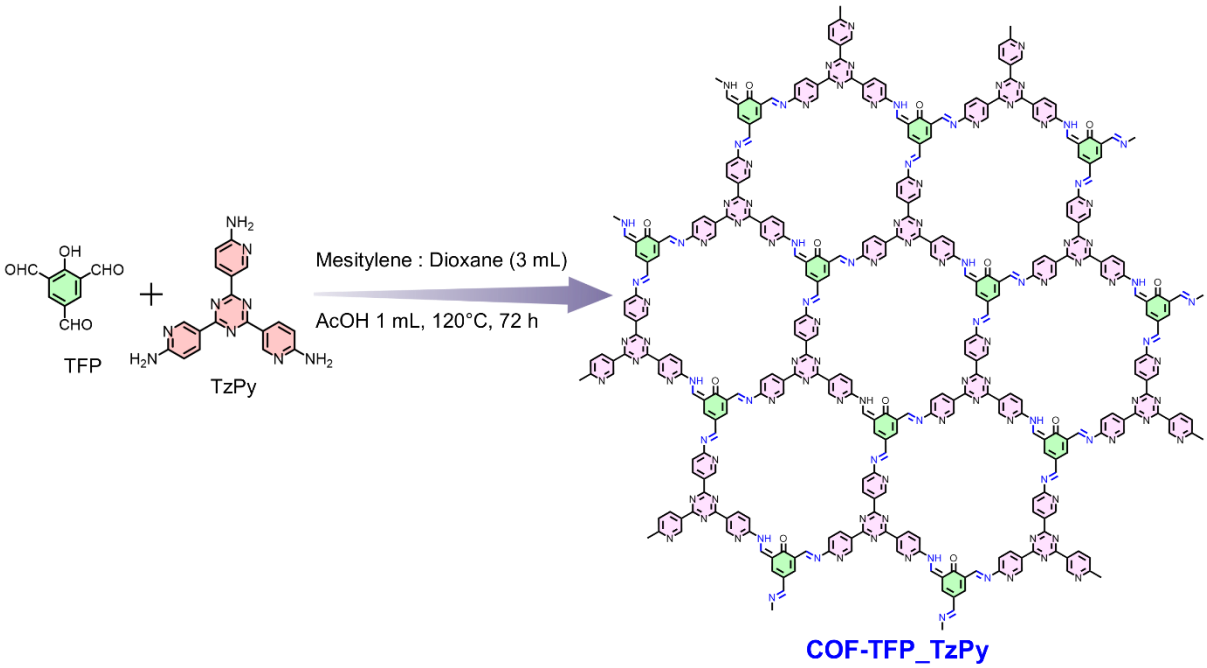
A mixture of phenol (1 g, 10.6 mmol) and hexamethylenetetramine (3.23 g, 23.04 mmol) were dissolved in 15 mL trifluoroacetic acid (TFA) under an argon atmosphere. The reaction mixture was refluxed at 130 °C for 16 h, and then heated to 150 °C for additional 3h. Subsequently, the reaction mixture was cooled to 100 °C and treated with 20 ml 3M HCl. After the addition of HCl, we observed the formation of a yellow precipitate within 5 minutes. Reaction was heated for additional 30 min at 100 °C. The crude products thus obtained were filtered and washed with ethanol until the filtrate was clear. The desired product was obtained as a powder after drying in oven at 60 °C for several hours (yield 41%).

Synthesis of 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine) (TzPy)[2, 3]



In a typical synthesis, 1.544 g (13.076 mmol) 6-Amino-3-pyridinecarbonitrile was taken in a round bottom flask at -20 ºC. Then 8 mL (88.8 mmol) CF_3SO_3H was added drop wise for 20 minutes. The resulting mixture was stirred for 24 h at room temperature in an inert atmosphere. Subsequently, the reaction mixture was quenched with distilled water and was neutralized by adding 2M NaOH solution until the pH was 7. At this pH, a pale yellow precipitate was observed which with further increase in pH it turns white. This white precipitate was filtered off and washed several times with distilled water (yield 70%).

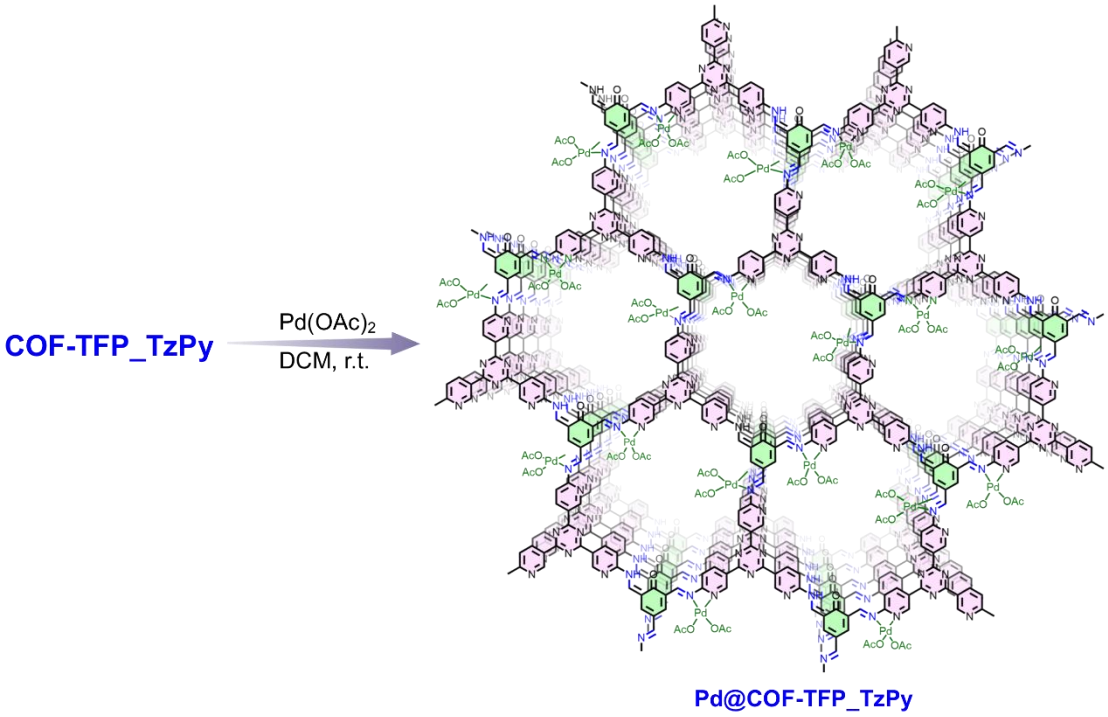
1.2 Synthesis of the **COF-TFP-TzPy[2, 3]**



TFP (25 mg, 0.14 mmol) and TzPy (49 mg, 0.14 mmol) were dissolved in a mixture of 1,4-dioxane and mesitylene (3 mL, v/v 1:1) and filled into a 15 mL glass vial. An aqueous solution of glacial acetic acid (1mL) was then added to the tube and ultrasonicated for 1 minute. The glass vial was then sealed with teflon tape. The reaction mixture was heated at 120 °C for 3

days and a reddish precipitate was observed. The product was separated by filtration and washed with large volumes of organic solvent. After further Soxhlet purification with THF and methanol for 24 h, the final product was dried in a vacuum oven at 110 °C for 24 h and used for further analysis (yield 83%).

Synthesis of the Pd@COF-TFP_TzPy



Palladium acetate (50 mg) was dissolved in 50 mL of dichloromethane, and then COF-TFP-TzPy (500 mg) was added. The mixture was kept stirring for 24 h at room temperature. The resulting solid was isolated by centrifugation, washed with dichloromethane using Soxhlet extraction for 24 h, and then dried at 80 °C under vacuum for 24 h to yield Pd@COF-TFP-TzPy as a red-coloured. The Pd content was 4.859 % as determined by ICP-AES.

Section S3

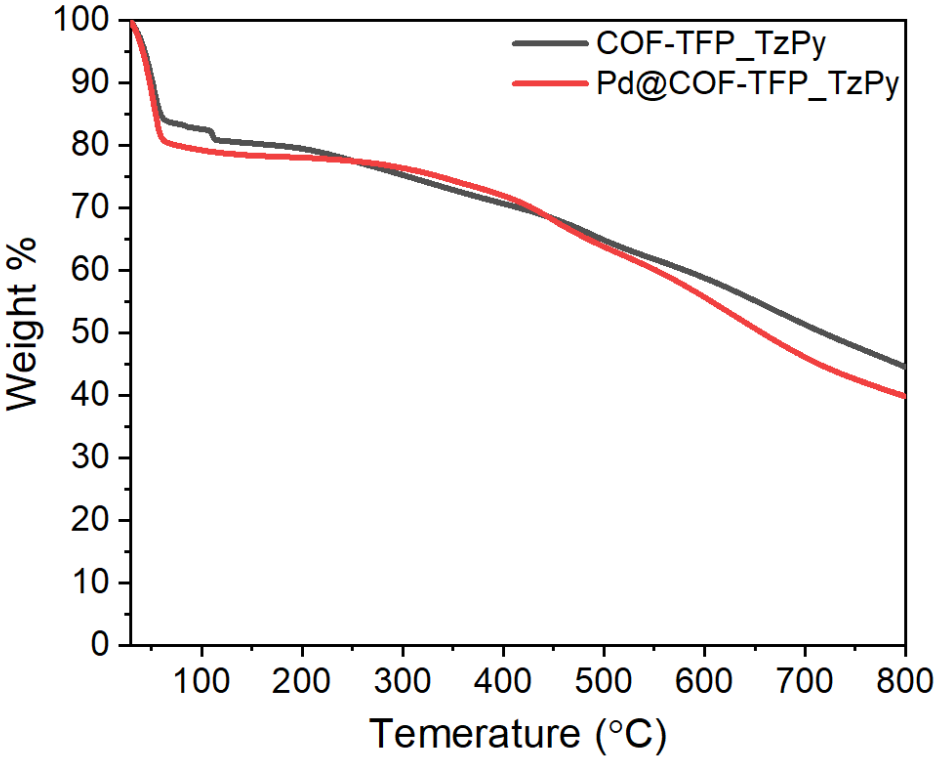


Figure-S1: TGA analysis of COF-TFP_TzPy and Pd@ COF-TFP_TzPy

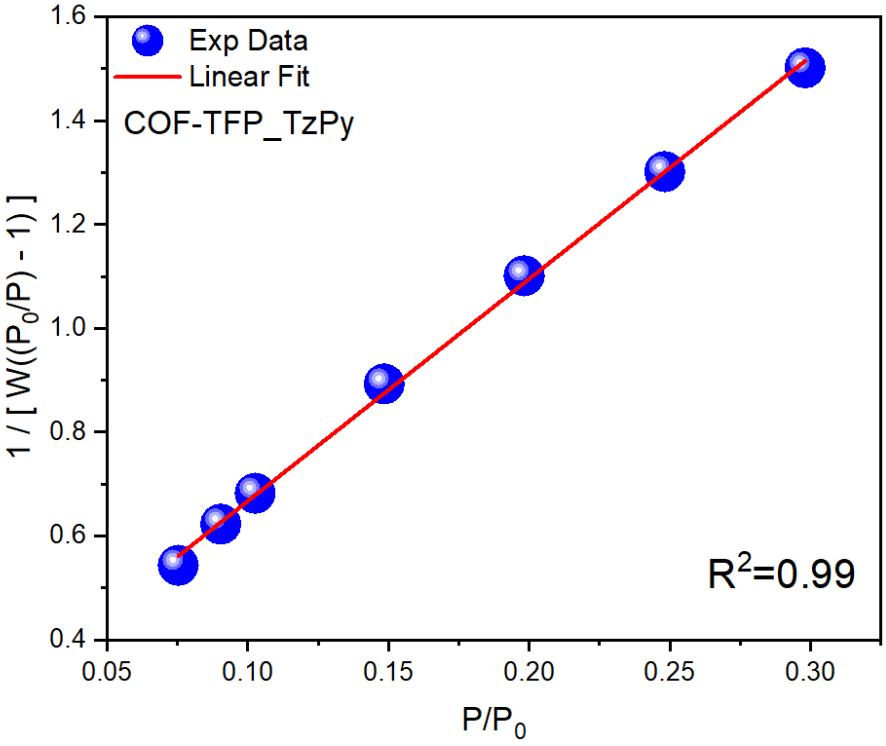


Figure-S2: BET plot of COF-TFP_TzPy

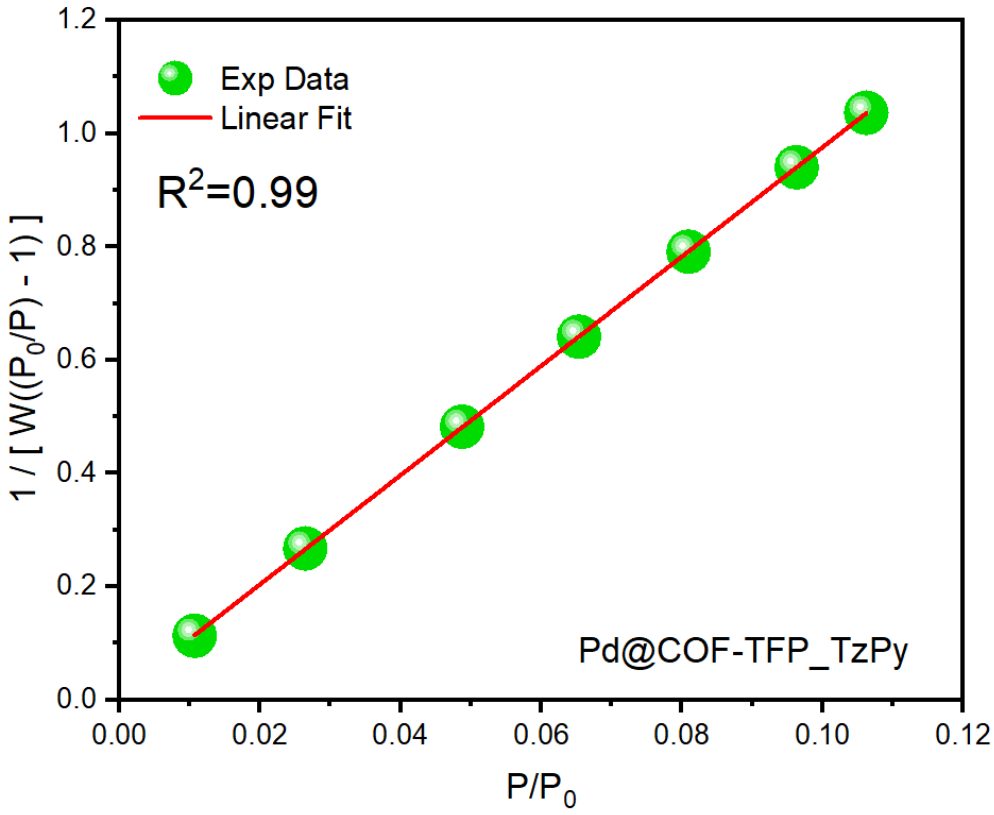


Figure-S3: BET plot of Pd@COF-TFP_TzPy

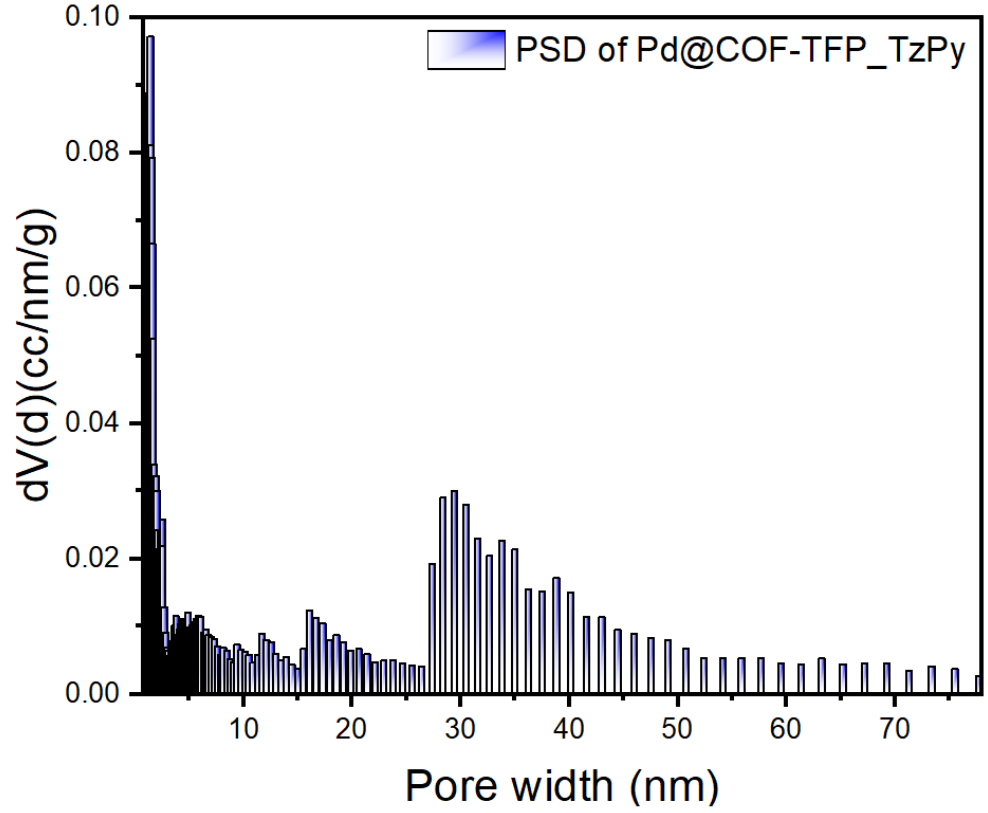


Figure-S4: Pore size distribution plot of COF-TFP_TzPy

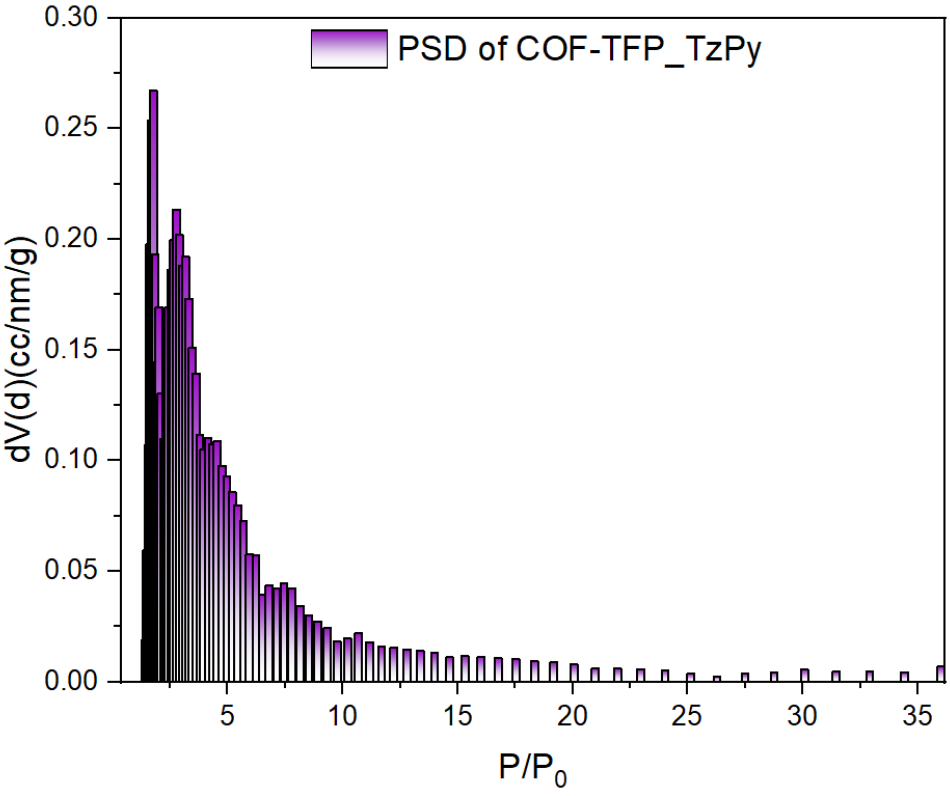


Figure-S5: Pore size distribution plot of Pd@COF-TFP_TzPy

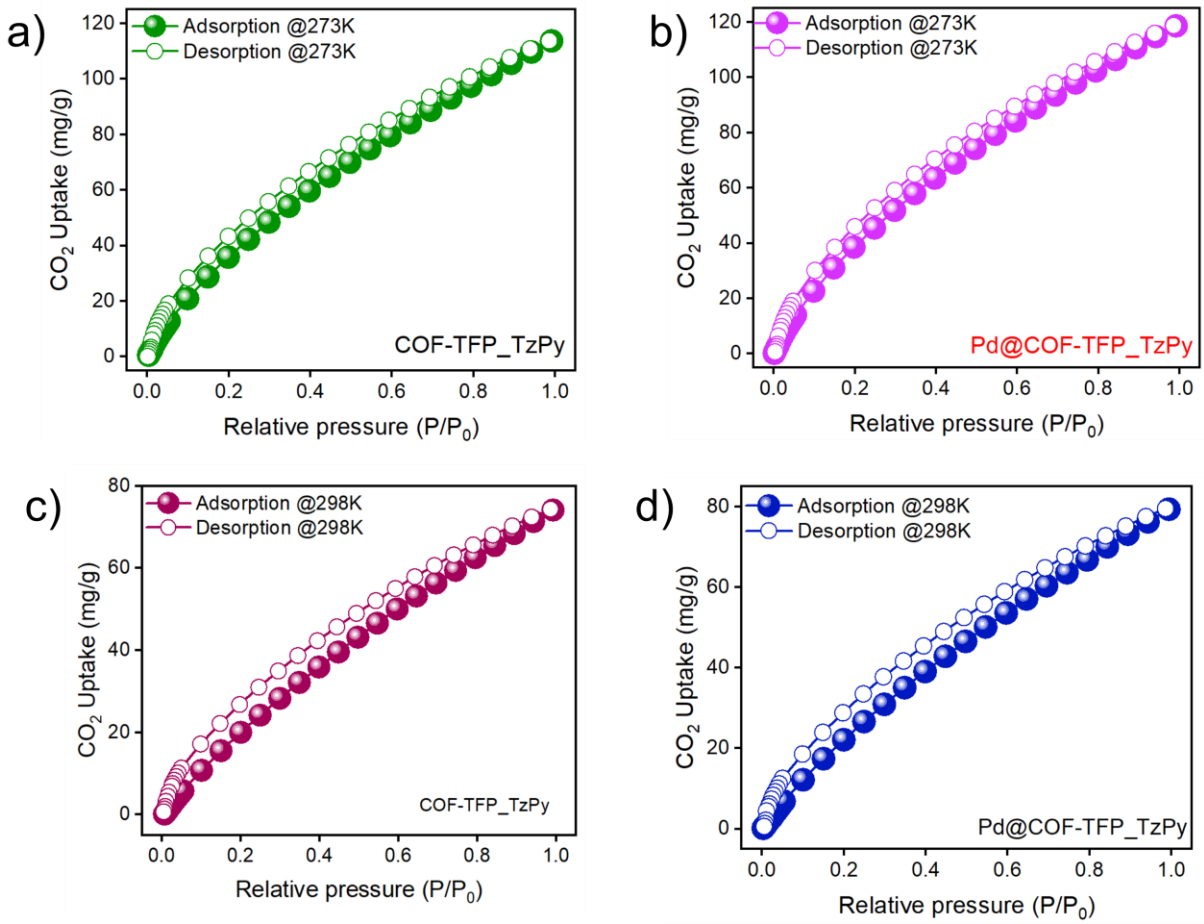


Figure-S6: CO_2 uptake isotherms of the COF-TFP_TzPy and Pd@COF-TFP_TzPy

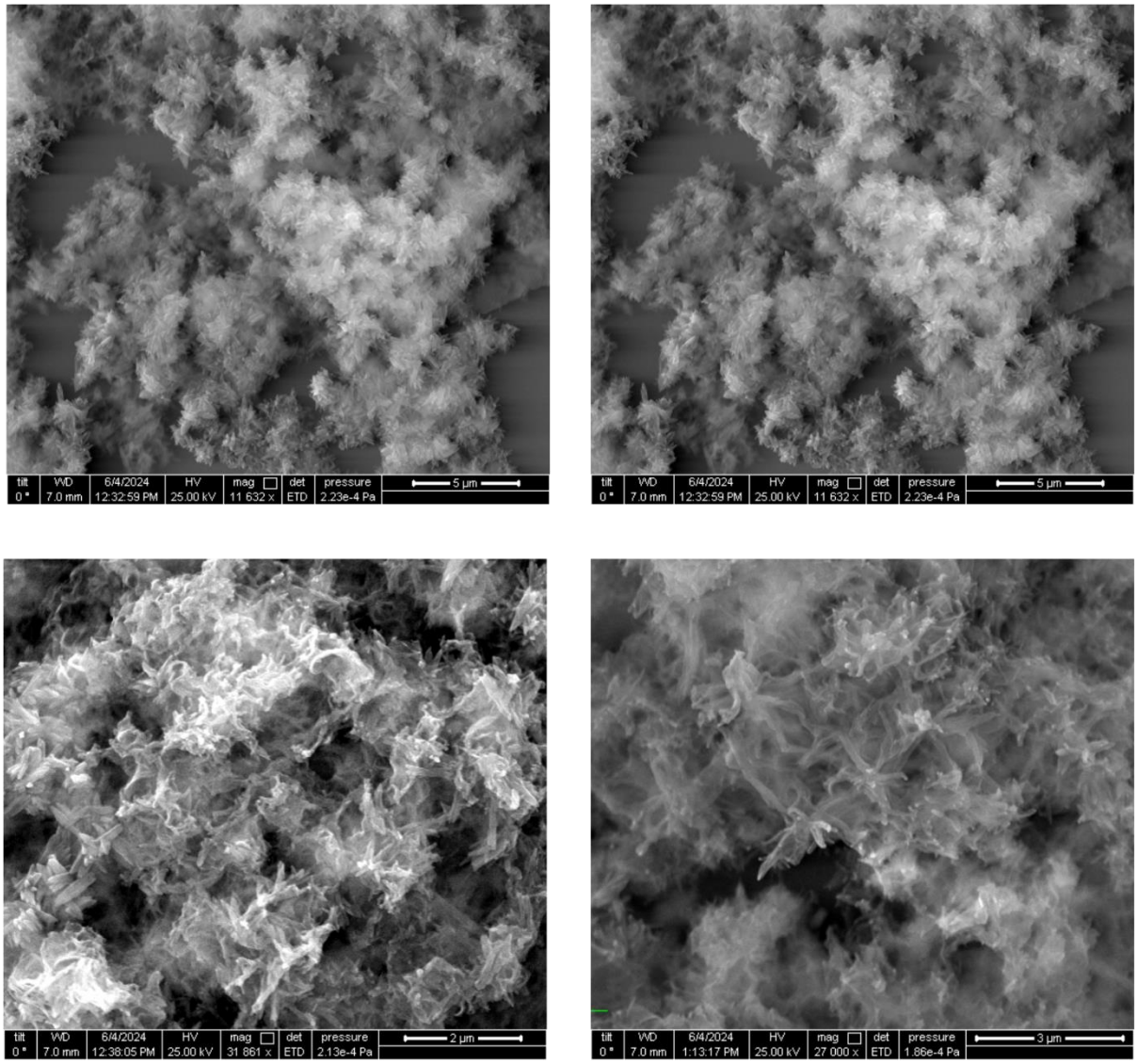


Figure-S7 – FE-SEM images of COF-TFP_TzPy

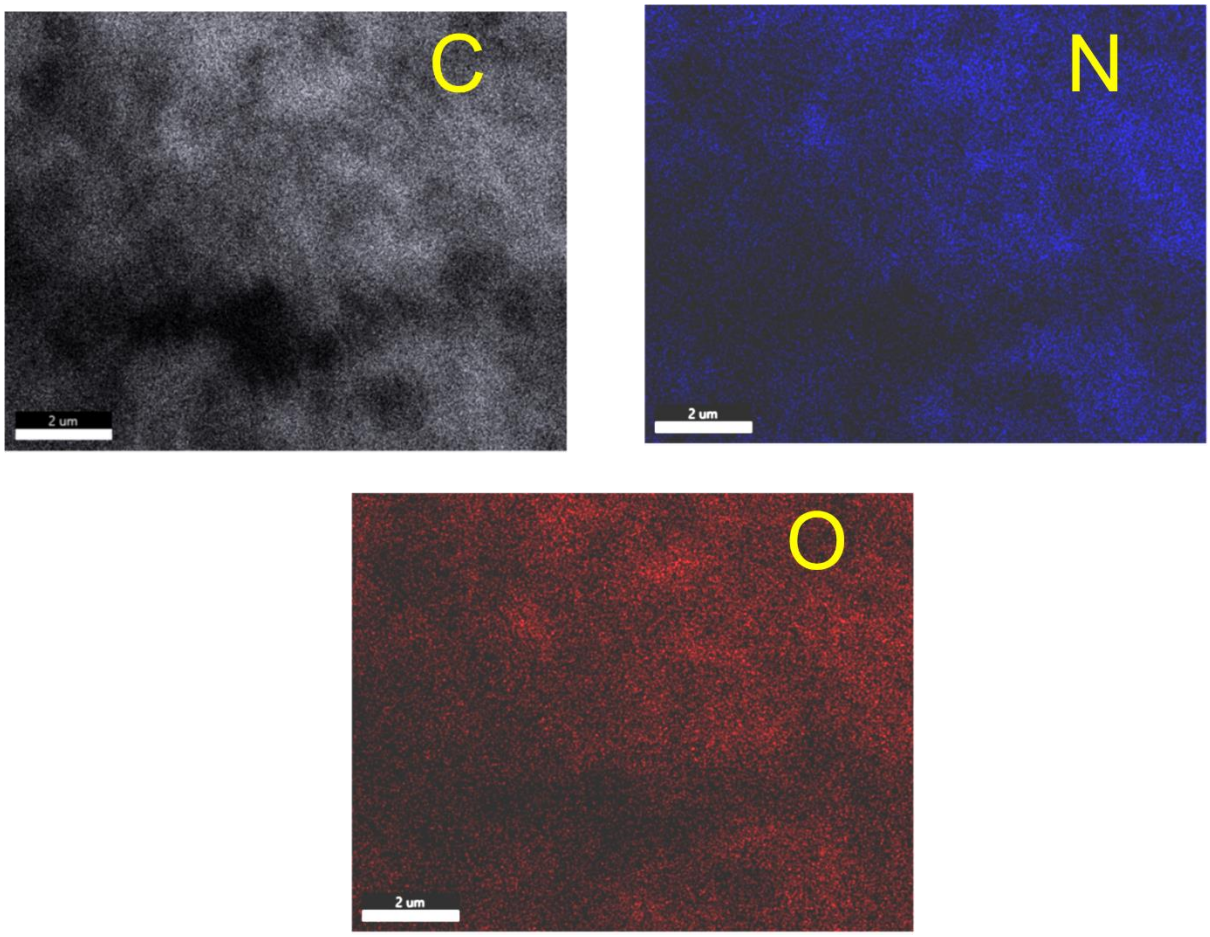
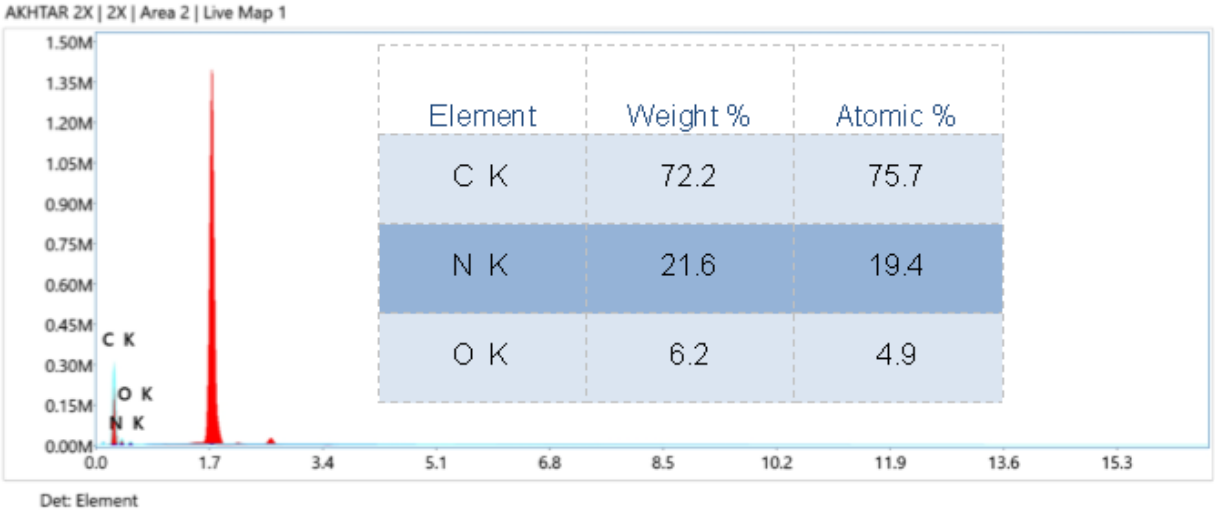
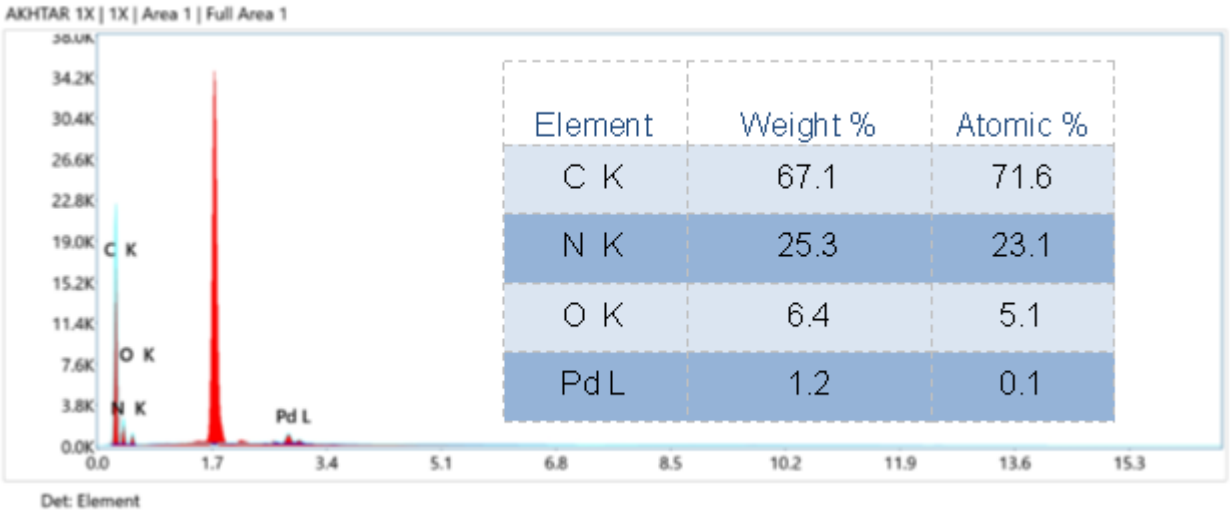


Figure-S8 – Elemental Mapping of COF-TFP_TzPy



Element	Weight %	Atomic %
C K	72.2	75.7
N K	21.6	19.4
O K	6.2	4.9

Figure-S9 – EDX analysis of COF-TFP_TzPy



Element	Weight %	Atomic %
C K	67.1	71.6
N K	25.3	23.1
O K	6.4	5.1
Pd L	1.2	0.1

Figure-S10 – EDX analysis of Pd@COF-TFP_TzPy

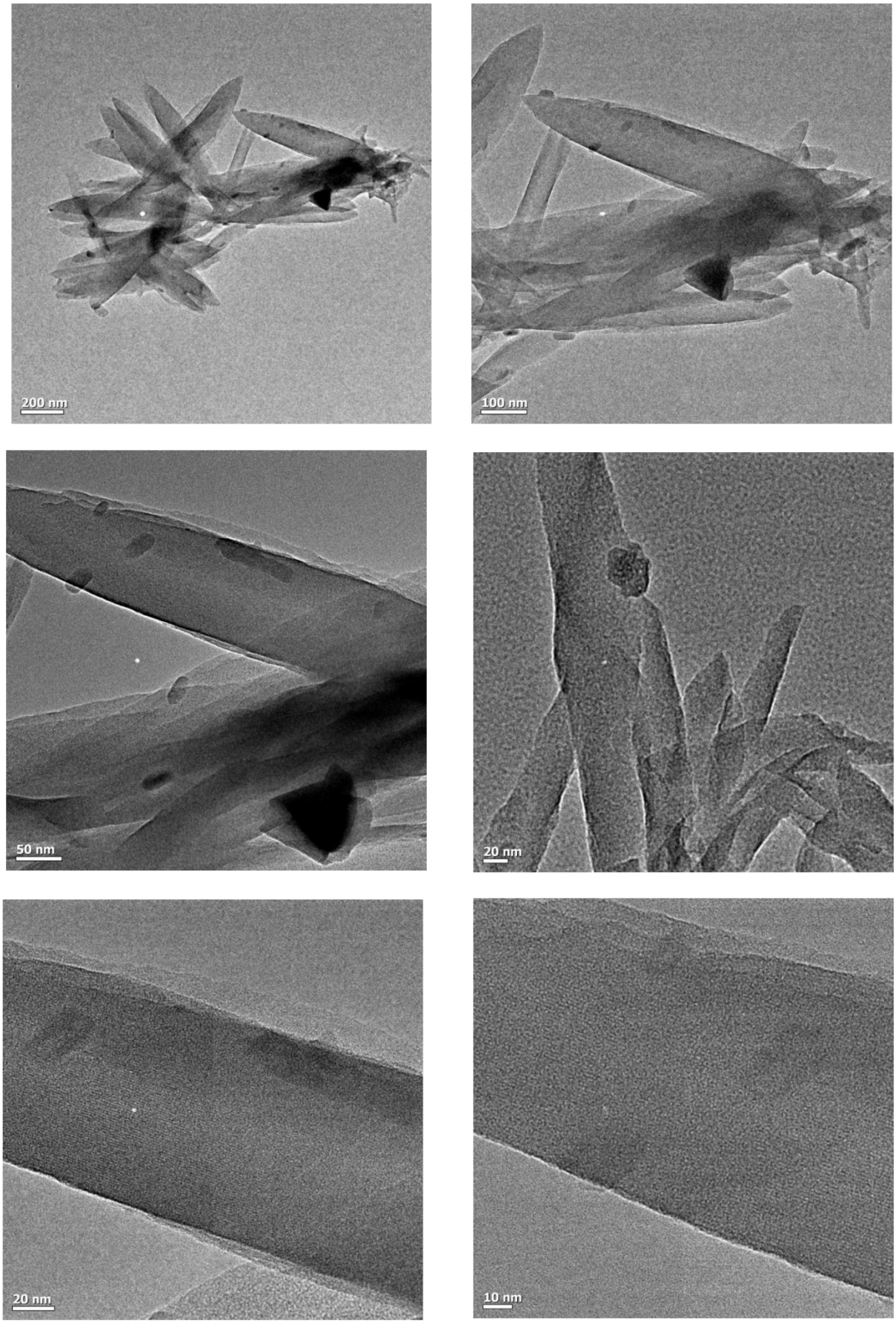


Figure-S11 – TEM and HR-TEM images of COF-TFP_TzPy

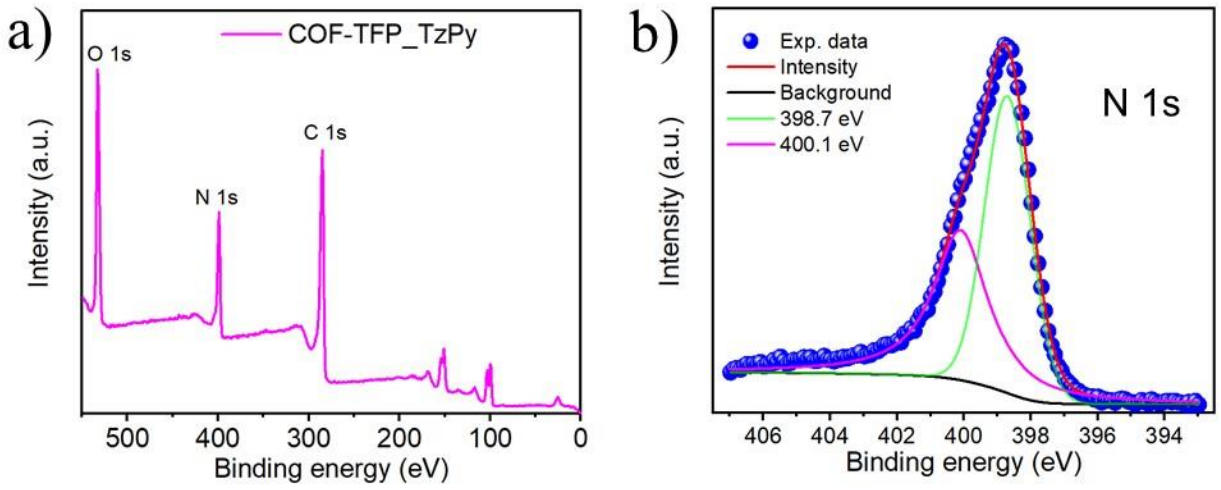


Figure S12 – XPS analysis of COF-TFP_TzPy (b) HR-XPS of N1s spectrum

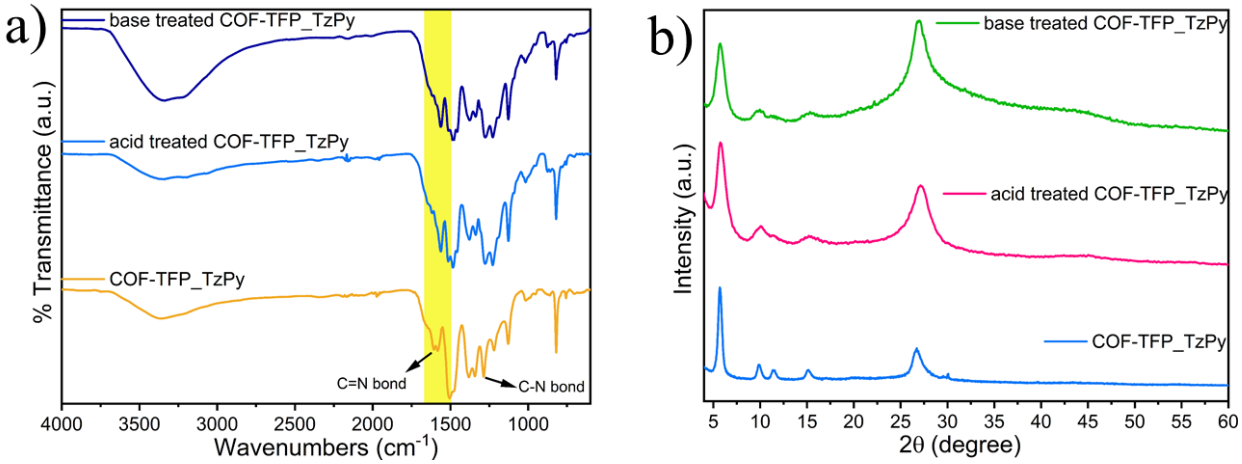


Figure S13 – Acid and Base stability of the COF characterized with (a) FT-IR Spectra (b) P-XRD Patterns

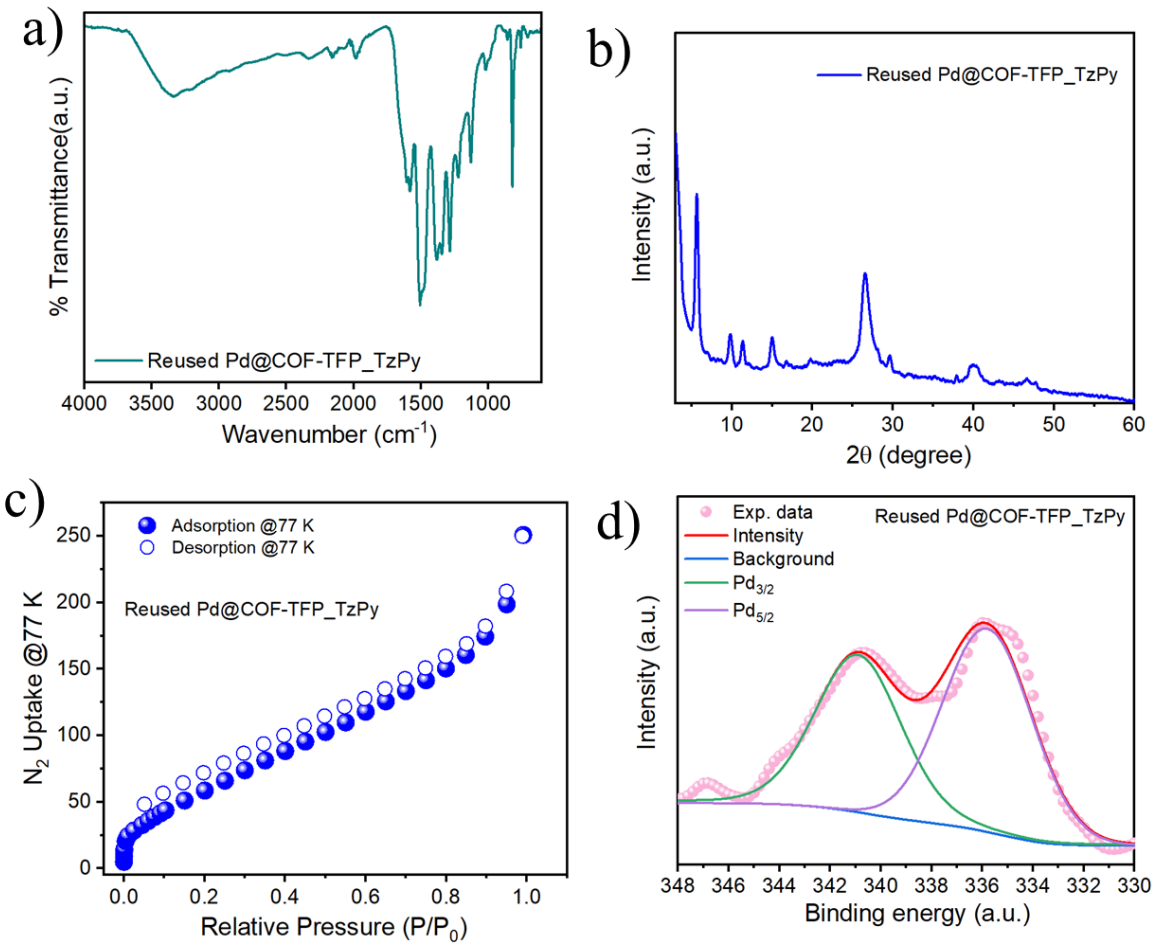


Figure S14 – Characterization of Reused Pd COF-TFP_TzPy (a) FT-IR spectrum (b) P-XRD patterns (c) N_2 gas isotherm at 77 K(d) XPS spectra of Pd 3d

Section S4

General procedure for Suzuki–Miyaura coupling (SMC) reaction

To an oven-dried reaction flask, sequentially added aryl boronic acid (0.6 mmol), base (0.6 mmol), aryl halide (0.4 mmol), and the catalyst (0.56 mol % Pd@COF-TFP_TzPy, 5 mg), followed by the addition of 4 mL EtOH-H_2O (1:1) solvent mixture. The reaction mixture was then stirred at room temperature (RT) for three hours. The reaction was monitored by TLC. After completion, the reaction mixture was filtered off to separate the catalyst. Then, the organic phase was extracted with DCM, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was then purified by column chromatography on silica gel.

General procedure for the Heck coupling reaction

To an oven-dried pressure tube. sequentially added styrene (0.8 mmol), Et_3N (0.8 mmol), aryl halide (0.4 mmol), and the catalyst (0.56 mol% of Pd@COF-TFP_TzPy, 5 mg), followed by the addition of DMF (2 mL) solvent mixture. The reaction mixture was then stirred at 120 °C for the 12 hours. The reaction was monitored by TLC, and after completion, the organic phase was extracted with DCM, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was then purified by column chromatography on silica gel.

General procedure for Sonogashira coupling reaction.

To an oven-dried, pressure tube, sequentially added phenylacetylene (0.6 mmol), diisopropylamine (0.8 mmol), aryl halide (0.4 mmol), CuI (0.14 mmol) and the catalyst (0.56 mol% of Pd@COF-TFP_TzPy, 5 mg), followed by the addition of acetonitrile (2mL) solvent mixture. The reaction mixture was then stirred at 90 °C for the 12 h. The reaction was monitored by TLC, and after completion, the organic phase was extracted with DCM, dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was then purified by column chromatography on silica gel.

Procedure for scale-up synthesis

To an oven-dried reaction flask, sequentially added phenylboronic acid (7.5 mmol), base (7.5 mmol), Iodotoluene (5 mmol), and the catalyst (Pd@COF-TFP-TzPy, 25 mg), followed by the addition of 50 mL EtOH-H_2O (1:1) solvent mixture. The reaction mixture was then stirred at room temperature (RT) for the designated time. The reaction was monitored by TLC. After completion, the reaction mixture was centrifuged to separate the catalyst. Then, the organic phase was extracted with DCM, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was then purified by column chromatography on silica gel using hexane as eluent. The desired product was isolated in a 94% yield (795 mg).

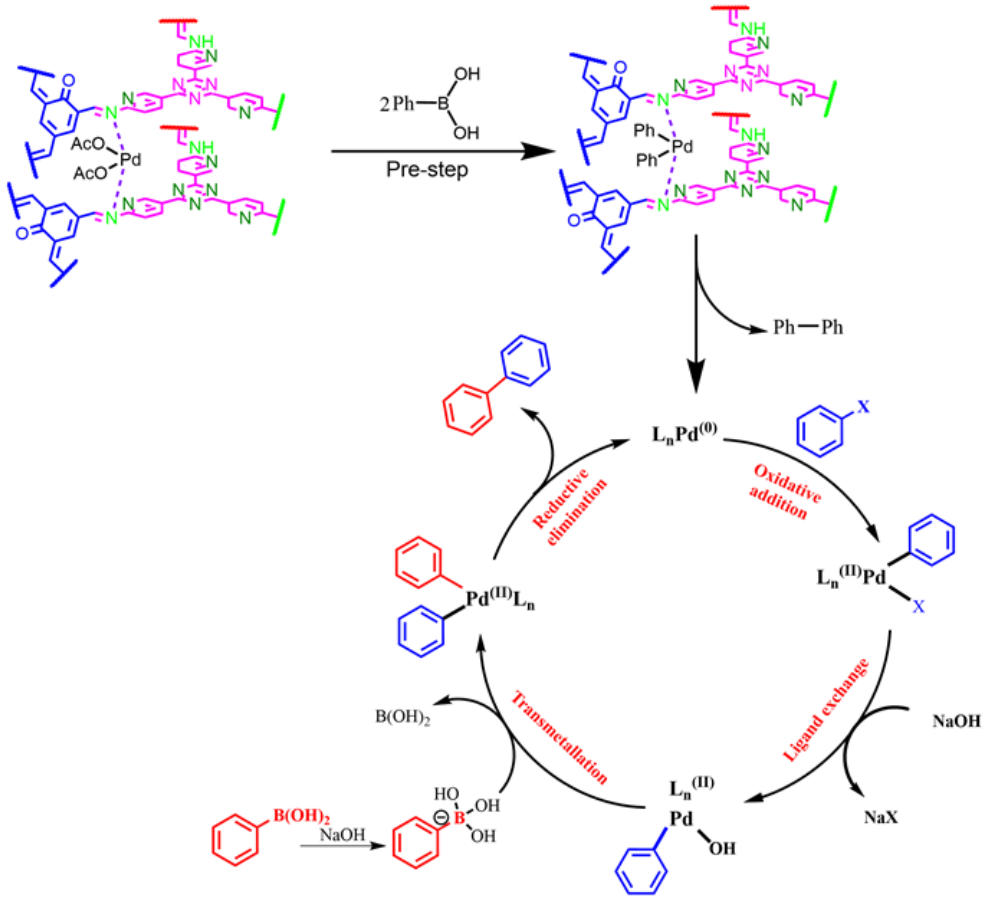
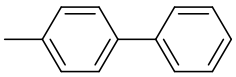


Figure S15. Plausible mechanism for the Pd@COF-TFP_TzPy catalysed Suzuki-Miyaura Cross Coupling (SMC) reaction. [4]

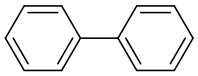
Notes - In this manuscript, we have provided spectral data for only one compound in cases where the compounds have similar structures.

Experimental data

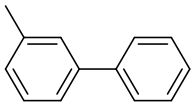
4-methyl-1,1'-biphenyl (3a)


The compound was isolated as a white solid (63.1 mg, 90% yield); R_f (Hexane)= 0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.43 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.33 (s, 1H), 7.28 – 7.24 (m, 2H), 2.40 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0, 129.5, 128.7, 127.0 (d, *J* = 2.8 Hz), 21.1.

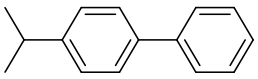
1,1'-biphenyl (3b)


The compound was isolated as a white solid (55.1 mg, 91% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 4H), 7.38 – 7.32 (m, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 141.2, 128.7, 127.2.

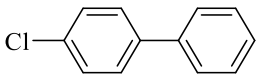
3-methyl-1,1'-biphenyl (3c)


The compound was isolated as a viscous liquid (60.3 mg, 89% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, *J* = 6.9, 3.0, 1.6 Hz, 2H), 7.46 (m, *J* = 8.6, 2.0 Hz, 4H), 7.38 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.23 – 7.19 (m, 1H), 2.47 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 141.2, 138.2, 128.6, 128.0, 127.1, 124.2, 21.5.

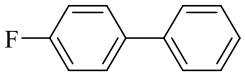
4-isopropyl-1,1'-biphenyl (3d)


The compound was isolated as a viscous liquid (59.0 mg, 76% yield); R_f (Hexane)=0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.56 – 7.52 (m, 2H), 7.44 (t, 2H), 7.36 – 7.29 (m, 3H), 2.97 (q, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 6H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.0, 141.1, 138.7, 128.7, 127.1, 127.0, 126.9, 126.8, 33.8, 24.0.

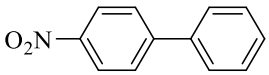
4-chloro-1,1'-biphenyl (3e)


The compound was isolated as a white solid (67.3 mg, 89% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.47 – 7.35 (m, 5H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 140.0, 139.6, 133.3, 128.9, 128.4, 127.6, 127.0.

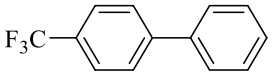
4-fluoro-1,1'-biphenyl (3f)


The compound was isolated as a white solid (62.0 mg, 91% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.14 (t, *J* = 8.7 Hz, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$ δ 162.4 (d, $^1J_{C-F}$ = 246.1 Hz), 140.2, 137.3, 128.8, 128.7 (d, $^3J_{C-F}$ = 8.0 Hz), 127.1 (d, $^2J_{C-F}$ = 30.1 Hz), 115.7, 115.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.7.

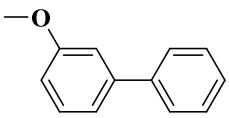
4-nitro-1,1'-biphenyl (3g)


The compound was isolated as a viscous liquid (73.5 mg, 92% yield); R_f (Hexane)=0.3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.44 (m, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 147.7, 147.1, 138.8, 129.3, 127.9, 127.5, 124.2.

4-(trifluoromethyl)-1,1'-biphenyl (3h)

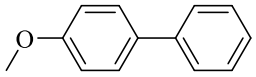

The compound was isolated as a white solid (63.2 mg, 71% yield); R_f (Hexane)=0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.63 – 7.58 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 144.8, 139.9 129.1 (q, $^2J_{C-F}$ = 32 Hz), 128.3, 127.4, 125.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.2.

3-methoxy-1,1'-biphenyl (3i)


The compound was isolated as a viscous liquid (59.87 mg, 82% yield); R_f (Hexane)=0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H),

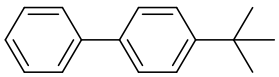
7.41 – 7.36 (m, 2H), 7.21 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.16 (t, *J* = 2.1 Hz, 1H), 6.93 (m, *J* = 8.4, 2.7, 0.8 Hz, 1H), 3.89 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 159.9, 142.7, 141.1, 129.7, 128.7, 127.2, 119.6, 112.9, 112.6, 55.2.

4-methoxy-1,1'-biphenyl (3j)

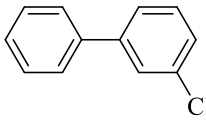


The compound was isolated as a white solid (69.2 mg, 94% yield); R_f (Hexane)=0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.31 (t, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 159.2, 140.9, 133.9, 128.8, 128.3, 126.8, 114.3, 55.4.

4-(tert-butyl)-1,1'-biphenyl (3n)

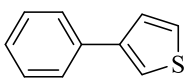

The compound was isolated as a white solid (62.4 mg, 76% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.41 (m, 4H), 7.36 – 7.32 (m, 1H), 1.38 (s, 9H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 150.4, 141.2, 138.4, 128.8, 127.2, 126.9, 125.8, 31.5.

3-chloro-1,1'-biphenyl (3q)



The compound was isolated as a colorless liquid (65.0 mg, 89% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 3H), 7.48 – 7.42 (m, 3H), 7.40 – 7.34 (m, 2H), 7.31 (m, *J* = 8.0, 2.1, 1.2 Hz, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 143.2, 139.9, 134.7, 130.1, 129.0, 128.0, 127.2, 125.4.

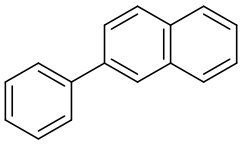
3-phenylthiophene (3s)



The compound was isolated as a white solid (45.6 mg, 71% yield); R_f (Hexane)=0.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.38 (t, 2H), 7.34 – 7.23

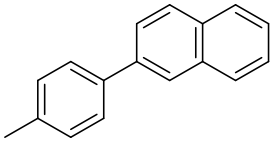
(m, 3H), 7.11 – 7.05 (m, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.4, 134.3, 128.9, 128.0, 127.4, 125.9, 124.8, 123.0.

2-phenylnaphthalene (3t)



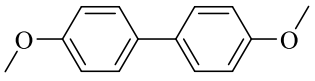
The compound was isolated as a white solid (77.2 mg, 97% yield); R_f (Hexane)=0.7; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 1H), 7.95 – 7.85 (m, 3H), 7.79 – 7.72 (m, 3H), 7.54 – 7.47 (m, 4H), 7.40 (d, *J* = 7.4 Hz, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.2, 138.7, 133.8, 132.7, 128.5, 128.3, 127.8, 127.5, 126.4, 126.0, 125.9, 125.7.

2-(p-tolyl)naphthalene (3u)



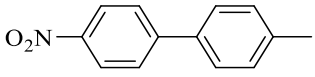
The compound was isolated as a white solid (83.3 mg, 95% yield); R_f (Hexane)=0.6; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.93 – 7.83 (m, 3H), 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.48 (td, *J* = 7.7, 1.5 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.5, 138.2, 137.1, 133.7, 132.5, 129.6, 128.3, 128.1, 127.6, 127.2, 126.2, 125.7, 125.5, 21.1.

4,4'-dimethoxy-1,1'-biphenyl (3v)



The compound was isolated as a white solid (63.2 mg, 74% yield); R_f (Hexane)=0.4; ^1H NMR (500 MHz $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 4H), 6.97 (d, *J* = 8.7 Hz, 4H), 3.84 (s, 6H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.8, 133.6, 127.8, 114.3, 55.4.

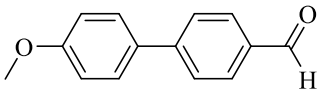
4-methyl-4'-nitro-1,1'-biphenyl (3w)



The compound was isolated as a white solid (74.8 mg, 88% yield); R_f (Hexane)=0.3; ^1H NMR (400 MHz $CDCl_3$) δ 8.3 (d, *J* = 8.9 Hz, 2H), 7.7 (d, *J* = 8.8 Hz, 2H),

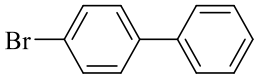
7.5 (d, *J* = 8.2 Hz, 12H), 7.3 (d, *J* = 7.9 Hz, 2H), 2.4 (s, 3H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 146.8, 139.1, 135.8, 129.9, 127.4, 127.2, 124.1, 21.2.

4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (3x)



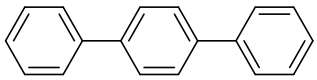
The compound was isolated as a white solid (25.1 mg, 30% yield); R_f (Hexane)=0.3; ^1H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 191.9, 160.1, 146.8, 134.6, 132.0, 130.3, 128.5, 127.0, 114.4, 55.4.

4-bromo-1,1'-biphenyl (3y)

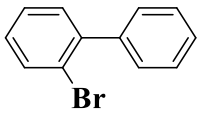


The compound was isolated as a white solid (66.1 mg, 71% yield); R_f (Hexane)=0.7; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (m, *J* = 7.8, 5.5 Hz, 4H), 7.48 – 7.42 (m, 4H), 7.37 (m, *J* = 7.3 Hz, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.13, 140.00, 131.85, 128.88, 128.73, 127.63, 126.93, 121.52.

1,1':4',1''-terphenyl (3y')

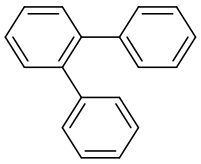

The compound was isolated as a white solid (23.2 mg, 25% yield); R_f (Hexane)=0.6; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.68 – 7.64 (m, 4H), 7.47 (m, *J* = 8.4, 7.0 Hz, 4H), 7.40 – 7.35 (m, 2H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.69, 140.11, 128.80, 127.48, 127.33, 127.03.

2-bromo-1,1'-biphenyl (3z)



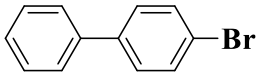
The compound was isolated as a white solid (51.3 mg, 66% yield); R_f (Hexane)=0.7; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.37 – 7.31 (m, 2H), 7.20 (m, *J* = 8.0, 7.0, 2.2 Hz, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.7, 141.2, 133.2, 131.4, 129.5, 128.8, 128.1, 127.7, 127.5, 122.7.

1,1':2',1''-terphenyl (3z')



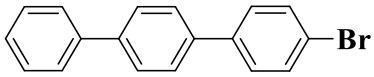
The compound was isolated as a white solid (20.6 mg, 22% yield); R_f (Hexane)=0.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.6 Hz, 4H), 7.24 – 7.19 (m, 6H), 7.16 (dd, *J* = 7.5, 2.0 Hz, 4H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 141.5, 140.5, 130.6, 129.9, 127.8, 127.4, 126.4.

4-bromo-1,1'-biphenyl (3aa)



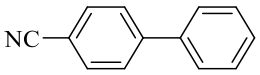
The compound was isolated as a white solid (59.9 mg, 65% yield); R_f (Hexane)=0.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (td, *J* = 5.6, 2.6 Hz, 4H), 7.49 – 7.43 (m, 4H), 7.41 – 7.36 (m, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 140.0, 131.8, 128.8, 127.62, 126.9, 121.5.

4-bromo-1,1':4',1''-terphenyl (3aa')



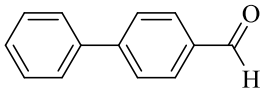
The compound was isolated as a white solid (19.2 mg, 16% yield); R_f (Hexane)=0.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.56 (m, 8H), 7.54 – 7.42 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 140.6, 139.7, 138.9, 132.0, 129.0, 128.7, 127.7, 127.4, 127.1, 121.7.

[1,1'-biphenyl]-4-carbonitrile (3ac)



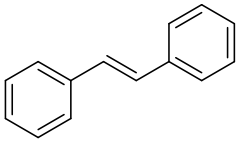
The compound was isolated as a white solid (66.7 mg, 94% yield); (Hexane /ethyl acetate=20:1)=0.3; ^{1}H NMR (400 MHz $CDCl_3$) δ 7.7 (q, *J* = 8.1 Hz, 4H), 7.6 (d, *J* = 7.0 Hz, 2H), 7.5 – 7.4 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 145.6, 139.1, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.8.

[1,1'-biphenyl]-4-carbaldehyde (3ae)

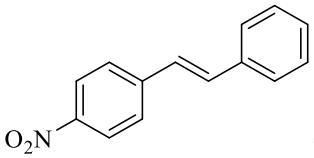


The compound was isolated as a white solid (59.4 mg, 81% yield); R_f (Hexane)=0.3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.47 – 7.39 (m, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 192.1, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

(E)-1,2-diphenylethene (6a)

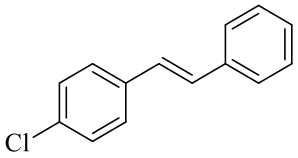

The compound was isolated as a white solid (63.7 mg, 89 % yield); R_f (Hexane)=0.5) . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m *J* = 8.0, 1.3 Hz, 4H), 7.37 (m, *J* = 7.8, 1.2 Hz, 4H), 7.30 – 7.24 (m, 2H), 7.14 – 7.11 (s, 2H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 137.3, 128.7, 127.6, 126.5.

(E)-1-nitro-4-styrylbenzene (6b)



The compound was isolated as a white solid (80.7 mg, 90 % yield); R_f (Hexane)=0.5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.42 – 7.30 (m, 3H), 7.29 – 7.22 (m, 2H), 7.13 (d, *J* = 16.3 Hz, 1H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 146.7, 143.8, 136.1, 133.3, 128.8 (d, *J* = 6.5 Hz), 127.0, 126.8, 126.2, 124.1.

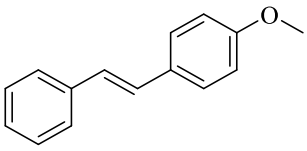
(E)-1-chloro-4-styrylbenzene (6c)



The compound was isolated as a white solid (69.0 mg, 82 % yield); R_f (Hexane)=0.5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 2H),

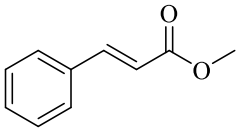
7.40 – 7.24 (m, 5H), 7.06 (d, *J* = 4.3 Hz, 2H) ^{13}C{1H} NMR (125 MHz, CDCl3) δ 137.1, 136.0, 133.3, 129.4, 129.0, 128.8, 128.0, 127.8, 127.5, 126.7.

(E)-1-methoxy-4-styrylbenzene (6d)



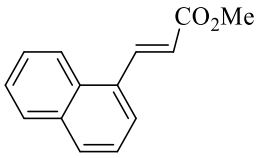
The compound was isolated as a white solid (55.7 mg, 67 % yield); R_f (Hexane)=0.3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.5 – 7.5 (m, 2H), 7.5 (d, *J* = 8.7 Hz, 2H), 7.3 (t, *J* = 7.7 Hz, 2H), 7.3 – 7.2 (m, 1H), 7.1 (d, *J* = 16.3 Hz, 1H), 7.0 (d, *J* = 16.3 Hz, 1H), 6.9 (d, *J* = 8.8 Hz, 2H), 3.8 (s, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ δ 159.4, 137.8, 130.3, 128.8, 128.3, 127.8, 127.3, 126.7, 126.4, 114.3, 55.4.

methyl cinnamate (6e)



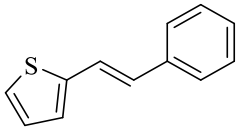
The compound was isolated as a white solid (60.9 mg, 95 % yield); R_f (Hexane)=0.5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.43 – 7.32 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.79 (d, *J* = 1.1 Hz, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 167.4, 144.8, 134.3, 130.2, 128.8, 128.0, 117.7, 51.6.

methyl (Z)-3-(naphthalen-1-yl)acrylate (6f)



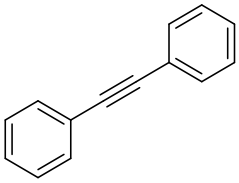
The compound was isolated as a white solid (60.9 mg, 95 % yield); R_f (Hexane)=0.5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 15.7 Hz, 1H), 8.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.97 – 7.81 (m, 2H), 7.74 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.62 – 7.44 (m, 3H), 6.53 (d, *J* = 15.8 Hz, 1H), 3.85 (s, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 167.5, 142.0, 133.8, 131.8, 131.5, 130.7, 128.8, 127.0, 126.3, 125.6, 125.1, 123.5, 120.5, 51.9.

(E)-2-styrylthiophene (6g)



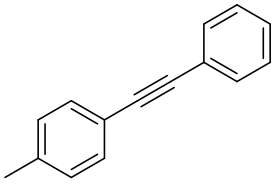
The compound was isolated as a white solid (60.9 mg, 67% yield; R_f (Hexane)=0.5). ^{1}H NMR (500 MHz, $CDCl_3$ δ 7.5 – 7.4 (m, 2H), 7.3 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.3 – 7.2 (m, 2H), 7.2 – 7.2 (m, 1H), 7.1 – 7.0 (m, 1H), 7.0 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.9 (d, *J* = 16.1 Hz, 1H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 143.0, 137.1, 128.8, 128.4, 127.7, 126.4, 126.2, 124.4, 121.9.

1,2-diphenylethyne (8a)



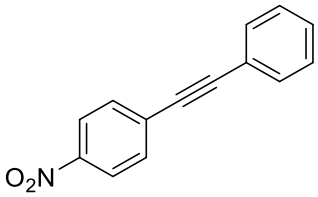
The compound was isolated as a white solid (57.0 mg, 81 % yield); R_f (Hexane)=0.7). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6 – 7.5 (m, 4H), 7.4 – 7.3 (m, 6H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 132.6, 131.7, 129.3, 128.4 (d, *J* = 11.0 Hz), 123.4, 89.5.

1-methyl-4-(phenylethynyl)benzene (8b)



The compound was isolated as a white solid (67.78 mg, 88 % yield); R_f (Hexane)=0.7). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.5 – 7.5 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 3H), 7.2 – 7.1 (m, 2H), 2.4 (s, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 138.5, 132.6, 131.6 (d, *J* = 6.1 Hz), 129.2, 128.4, 128.2, 123.6, 120.3, 89.7, 88.8, 21.6.

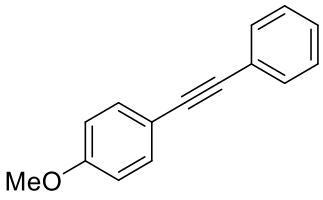
1-nitro-4-(phenylethynyl)benzene (8c)



The compound was isolated as a white solid (86.74 mg, 98 % yield); R_f (Hexane)=0.3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.2 (d, *J* = 8.5 Hz, 2H), 7.6 (d, *J* = 8.5 Hz,

2H), 7.6 – 7.5 (m, 2H), 7.4 (d, *J* = 2.0 Hz, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 147.1, 132.4, 132.0, 130.4, 129.4, 128.7, 123.7, 122.2, 94.8, 87.7.

1-methoxy-4-(phenylethynyl)benzene (8d)



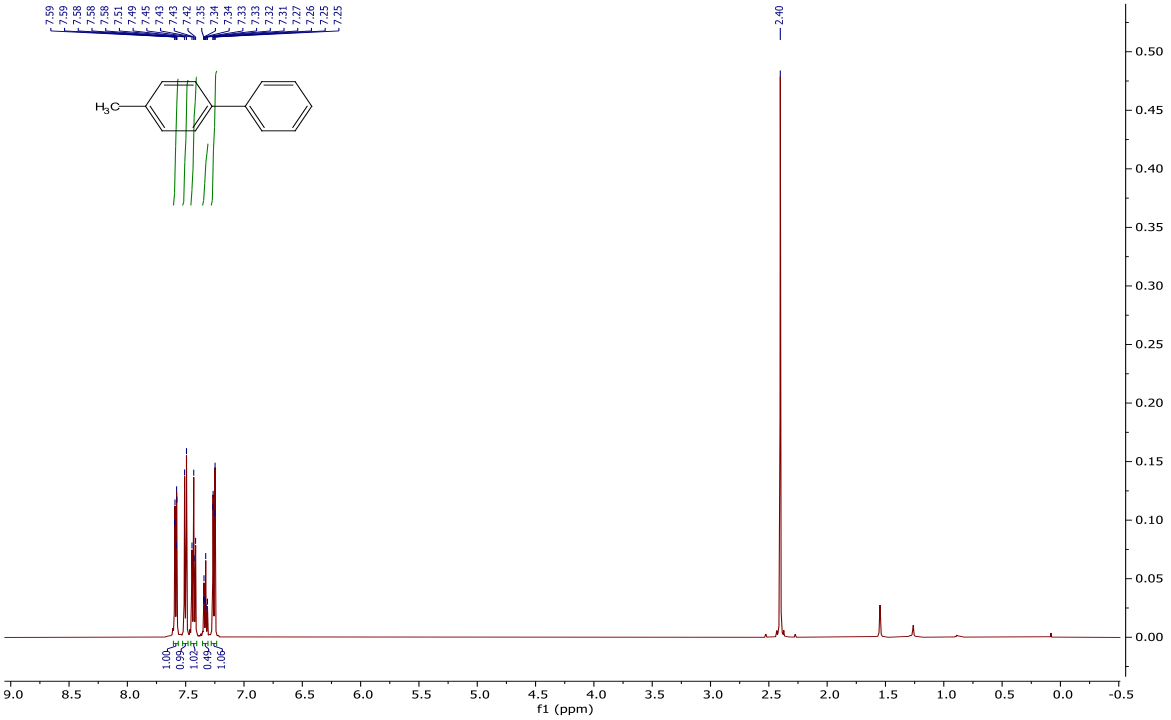
The compound was isolated as a white solid (56.78 mg, 69 % yield); R_f (Hexane)=0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 – 7.4 (m, 4H), 7.4 – 7.3 (m, 3H), 6.9 (d, *J* = 8.8 Hz, 2H), 3.8 (s, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 159.6, 133.0, 131.4, 128.3, 127.9, 115.3, 114.0, 89.3, 88.0, 55.3.

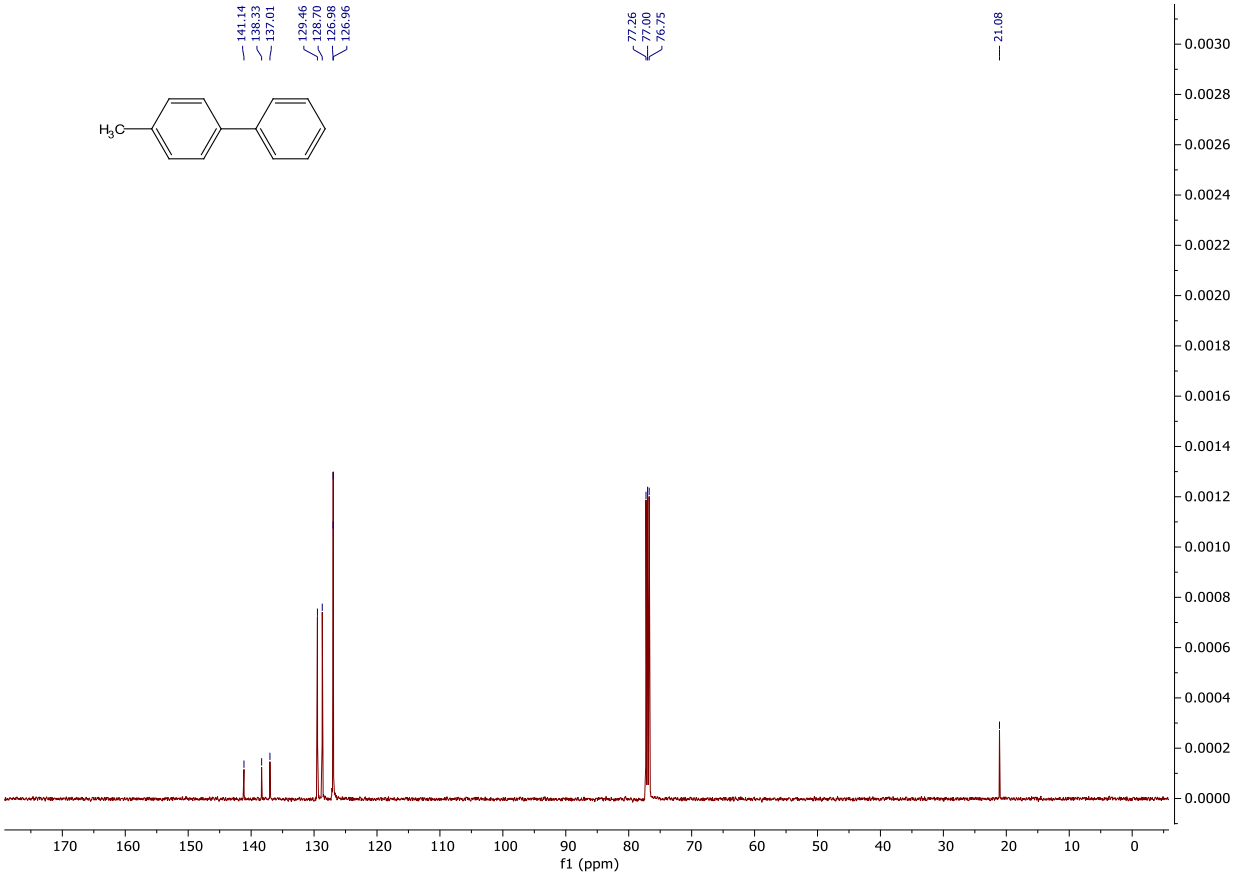
Comparison table-T1

Catalyst	Mol % Pd	Reaction Conditions	Time (h)	Yield (%)	Reference
Pd@COF-TFP_TzPy	**0.56**	**NaOH, EtOH-H_2O, 25°C**	**3**	**94**	***This Work***
Pd-CM-phos	1.0	K_3PO4, tBuOH, 110°C	18	97	*J. Org. Chem.* **2010**, *75*, 15, 5109–5112.
Fe_3O_4@PUNP-Pd	0.1	K_2CO_3, H_2O, 90 °C	1	98	Green Chem. **2013,** *15*, 3429– 3437.
Pd NPs	0.08	K_2CO_3, H_2O, 25–100 °C	5	83	*Chem. Mater.* **2015**, *27*, 6, 1921–1924.
Pd/*PN*-CeO_2	0.5	DMF-H_2O, K_2CO_3 ,30 °C	0.5	98.1	ACS Catal. **2015**, *5*, 11, 6481–6488.
[($PhSCH_2CH_2SePh$)$PdCl_2$]	1.0	K_2CO_3, DMF/H_2O, 100 °C	12	77	Dalton Trans. **2015**, *44*, 6600– 6612.
PDA/Pd NPs	3.0	DMF-H_2O, K_2CO_3, 25°C, Visible light	2	95	Catal. Sci. Technol**. 2016**,*6*, 1764-1771.
WS2/Pd NPs	0.45	EtOH-H_2O, K_2CO_3, 25°C, Visible light	3	92	J. Am. Chem. Soc. **2017**,*139*, 14767−14774.
Pd-MNPSS	0.36	K_2CO_3, H_2O, 100 °C	4	90	ACS Sustainable Chem. Eng**. 2018**, *6*, 1, 1456–1467.
Pd@COF-NHC	0.5	H_2O/EtOH, K_2CO_3, 25°C	5	94	GreenChem. **2019**, *21*, 5267.
Y_3Pd_2	40.0	K_2CO_3, H_2O,30°C	12	98.1	Nat. Commun. **2019**, *10*, 5653.
RH_P-Si-NH_2-Pd(0)	1.0	EtOH:H_2O(1:1), K_2CO_3, 70°C	1	98	Sci Rep. **2020,** *10*, 6407.
$(BICAAC)_2PdCl_2$	4.0	DMA, K_2CO_3, 110°C	6	82	*Inorg. Chem.* **2021**, *60*, 9, 6209–6217.
Pd/SF	3.8	H_2O/EtOH, K_2CO_3, 100°C	3	70	Eur. J. Org. Chem**. 2022**, 2022, e202101567.
UiO-66-NH2@cyanuric chloride@guanidine@Pd-NPs	0.09	H_2O, K_2CO_3, 60°C	0.3	99	ACS Omega **2023**, *8*, 16395.
mPAN-Pd	2.0	K_2CO_3, H_2O, 80°C	10	81	ChemistrySelect **2023**, *8*, e202204374
[Pd(IPr)(cin)Cl]	5.0	*t*-BuONa, THF, 65 °C	15	98	*Org. Lett.* **2024**, *26*, 11, 2309–2314.
Pd/Meso-FAU(Na^+)	0.1	TPAOH,H_2O/EtOH, 80°C	0.33	98	Ind. Eng. Chem. Res. **2024**, *63*, 24, 10532–10543

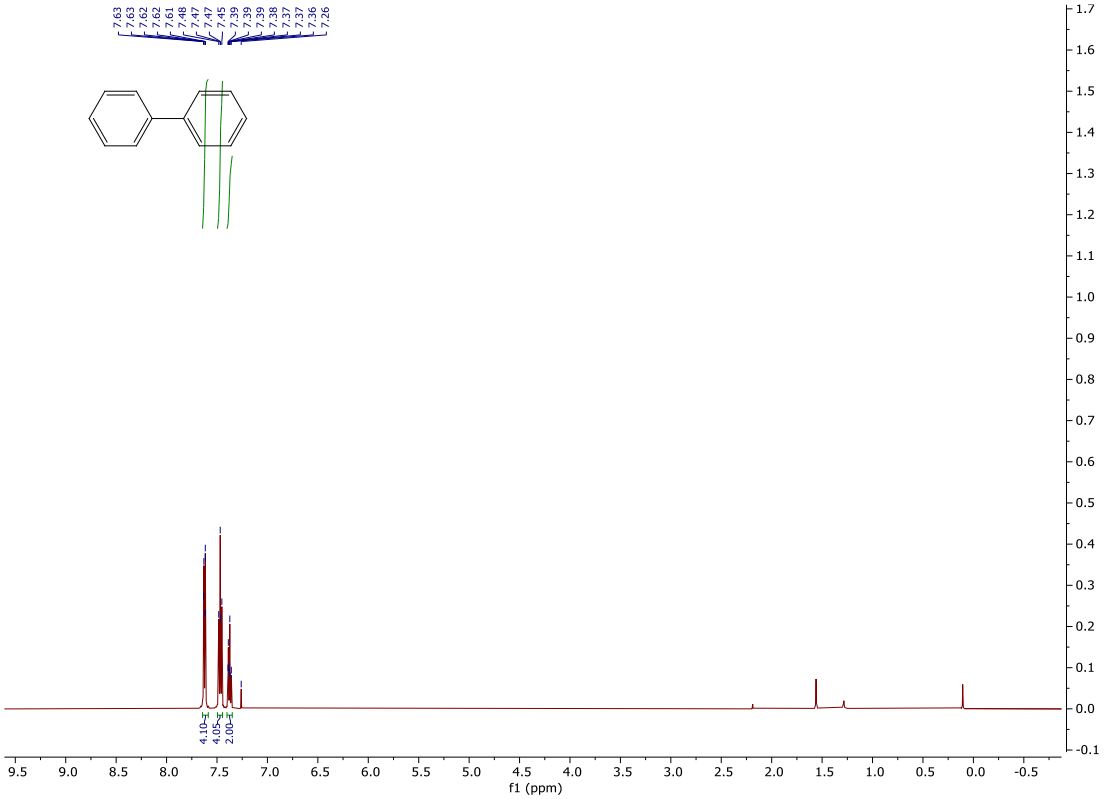
(1) Hassan, A.; Alam, A.; Ansari, M.; Das, N. Hydroxy functionalized triptycene based covalent organic polymers for ultra-high radioactive iodine uptake. *Chemical Engineering Journal* **2022**, *427*, 130950. DOI: https://doi.org/10.1016/j.cej.2021.130950.
(2) Fajal, S.; Majumder, D.; Mandal, W.; Let, S.; Dam, G. K.; Shirolkar, M. M.; Ghosh, S. K. Unraveling mechanistic insights into covalent organic frameworks for highly efficient sequestration of organic iodides from simulated nuclear waste. *Journal of Materials Chemistry A* **2023**, *11* (48), 26580-26591, 10.1039/D3TA04995G. DOI: 10.1039/D3TA04995G.
(3) Haldar, S.; Kushwaha, R.; Maity, R.; Vaidhyanathan, R. Pyridine-Rich Covalent Organic Frameworks as High-Performance Solid-State Supercapacitors. *ACS Materials Letters* **2019**, *1* (4), 490-497. DOI: 10.1021/acsmaterialslett.9b00222.
(4) Chen, T.; Pang, Y.; Ali, S. H.; Chen, L.; Li, Y.; Yan, X.; Wang, B. Efficient catalysis of Pd (II) supported by thiourea covalent organic framework in Suzuki coupling reaction. *Molecular Catalysis* **2024**, *558*, 114045. DOI: https://doi.org/10.1016/j.mcat.2024.114045.

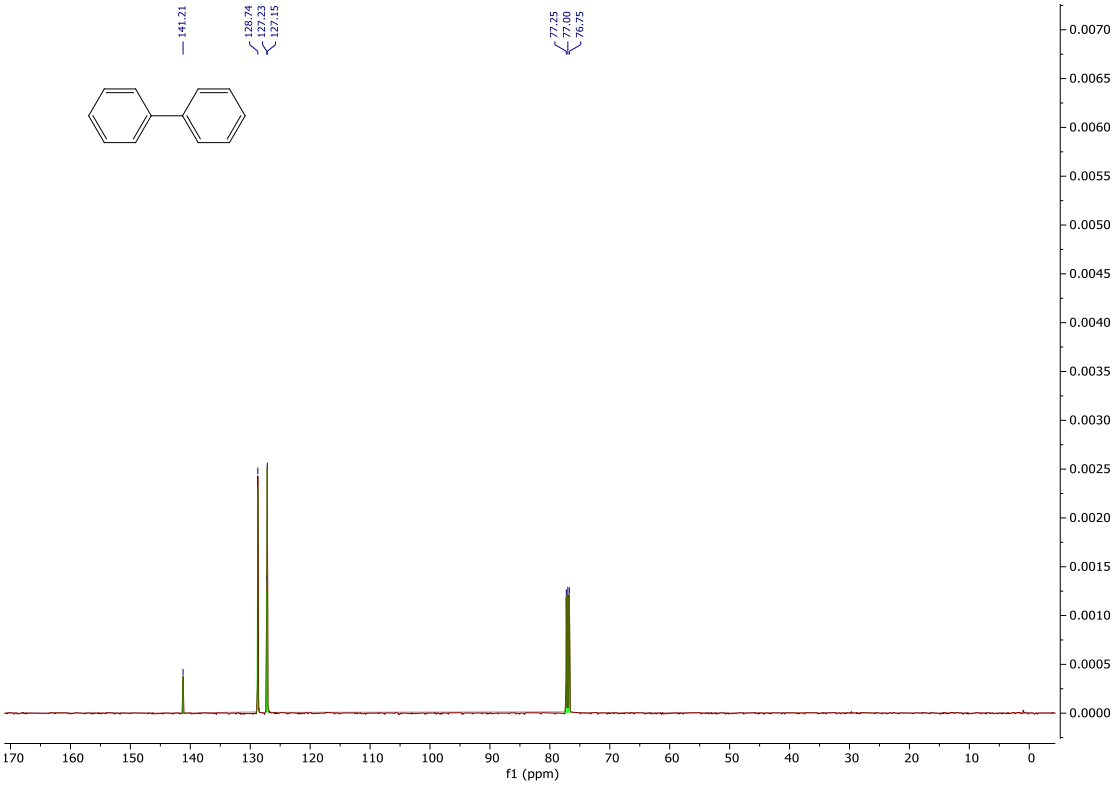
^{1}H(500 MHz) and $^{13}C\{1H\}$(125 MHz) spectra of 3a, 3m, 3x in $CDCl_3$



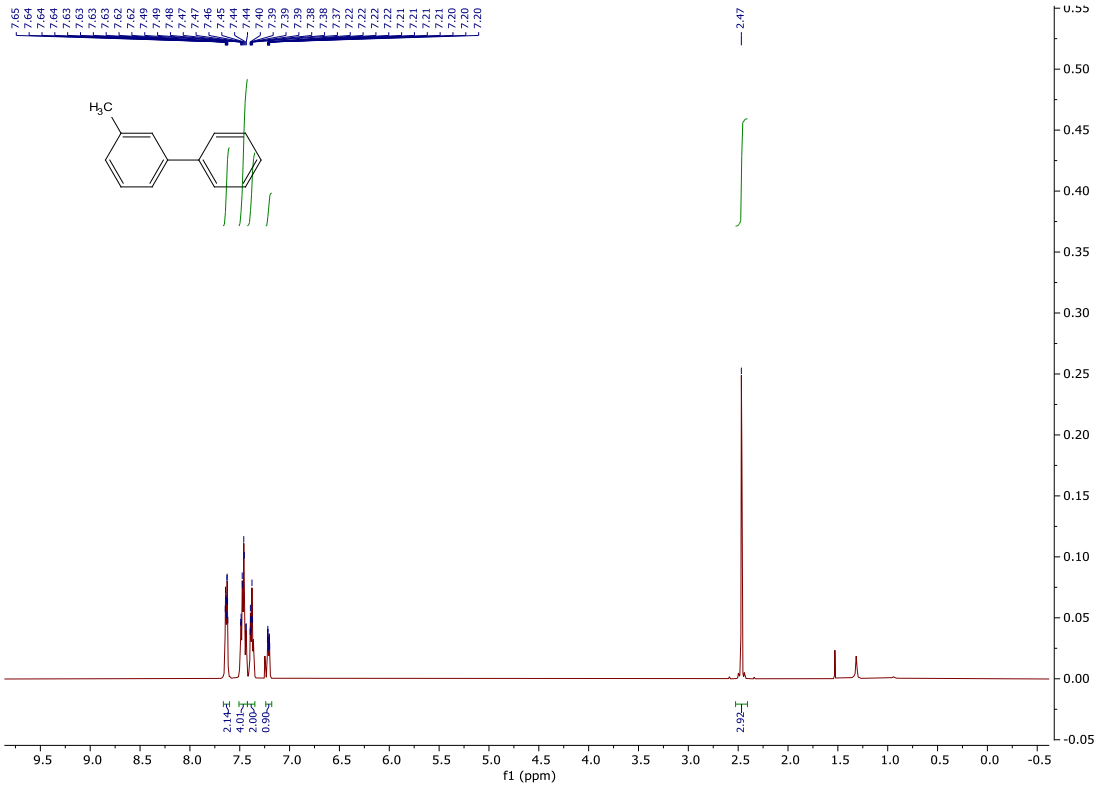


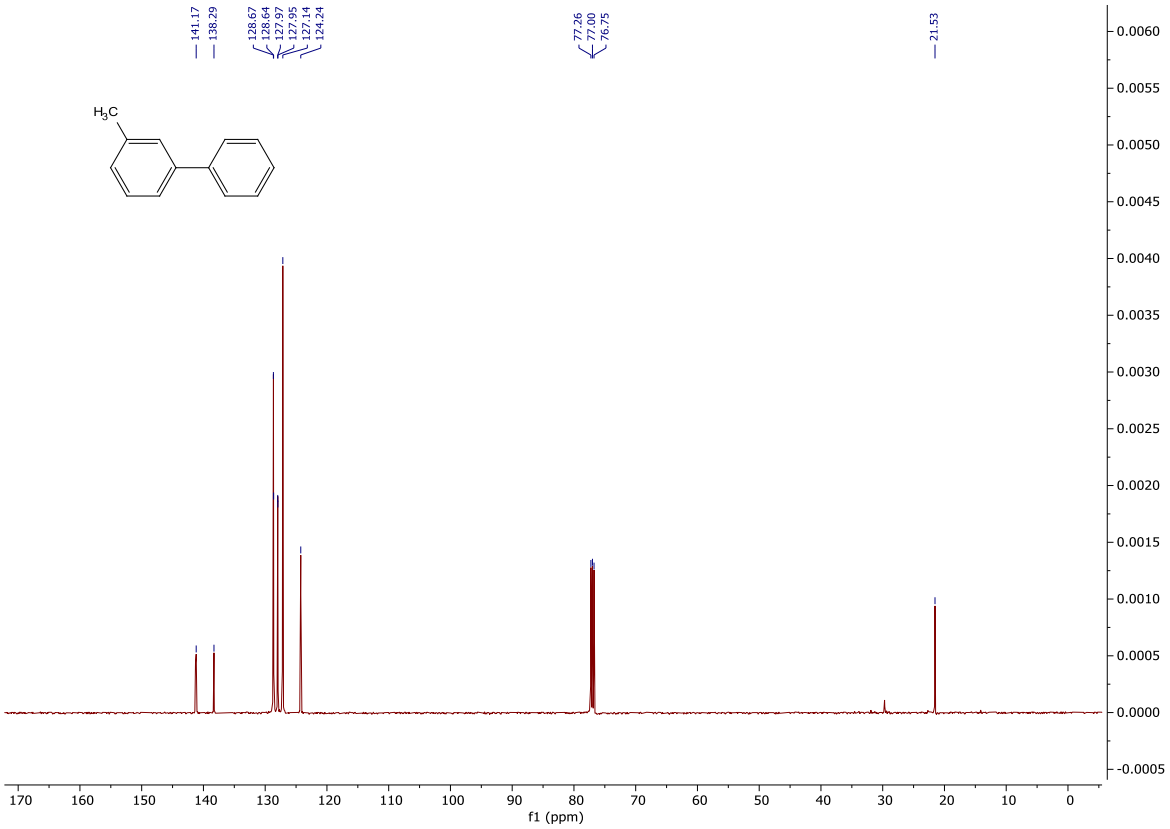
^{1}H (500 MHz) and ^{13}C{1H}(125 MHz) spectra of 3b in $CDCl_3$:



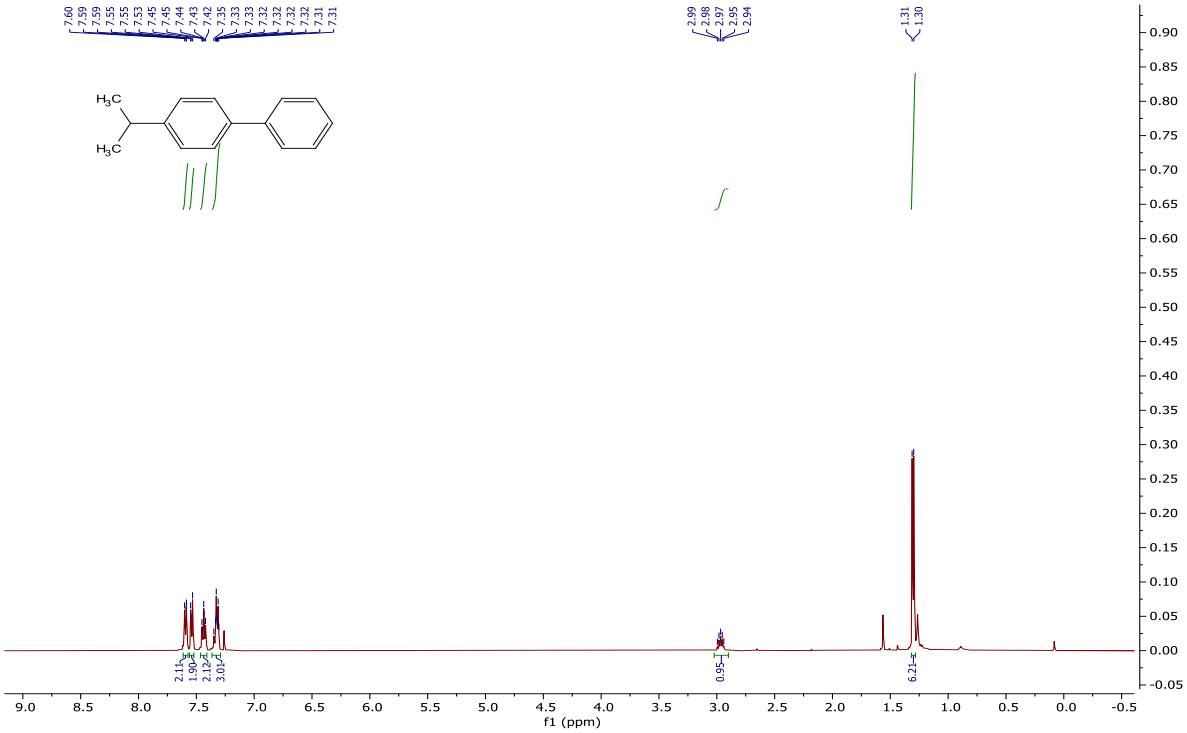


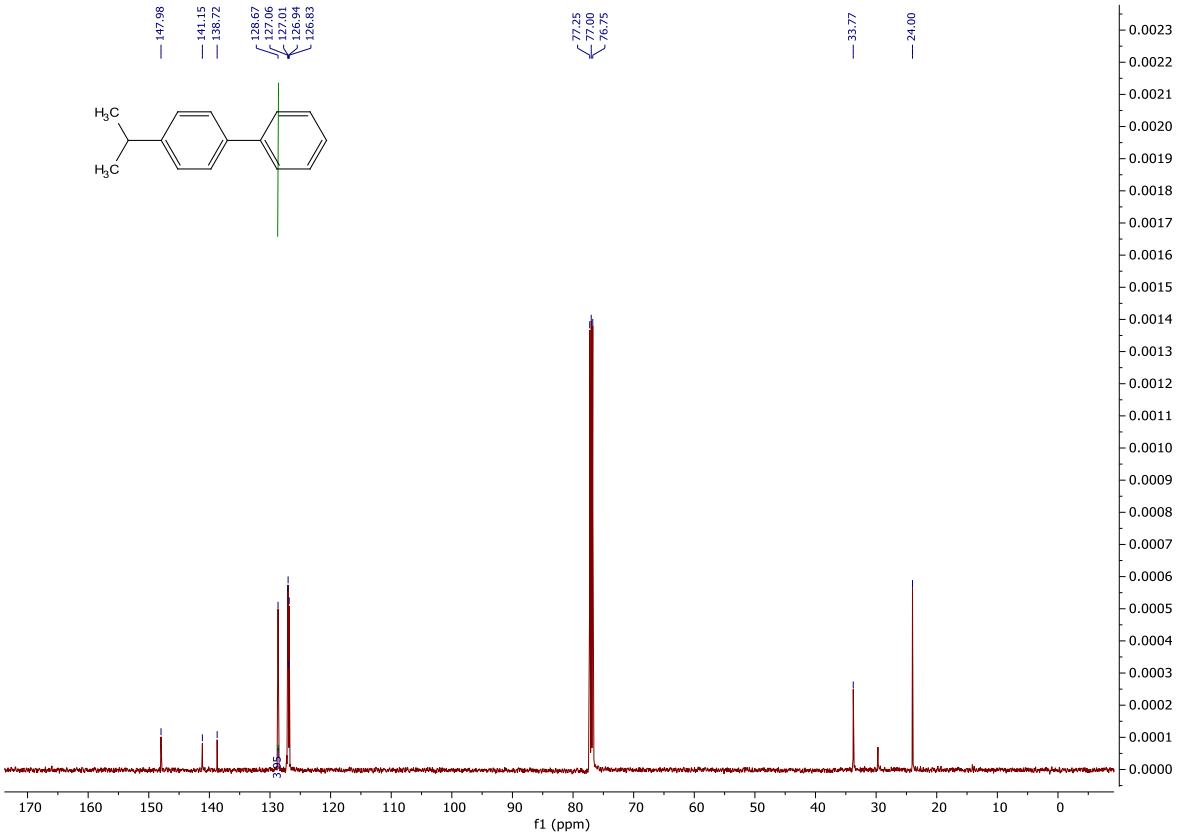
^{1}H(500 MHz) and $^{13}C\{1H\}$(125 MHz) spectra of 3c in $CDCl_3$:



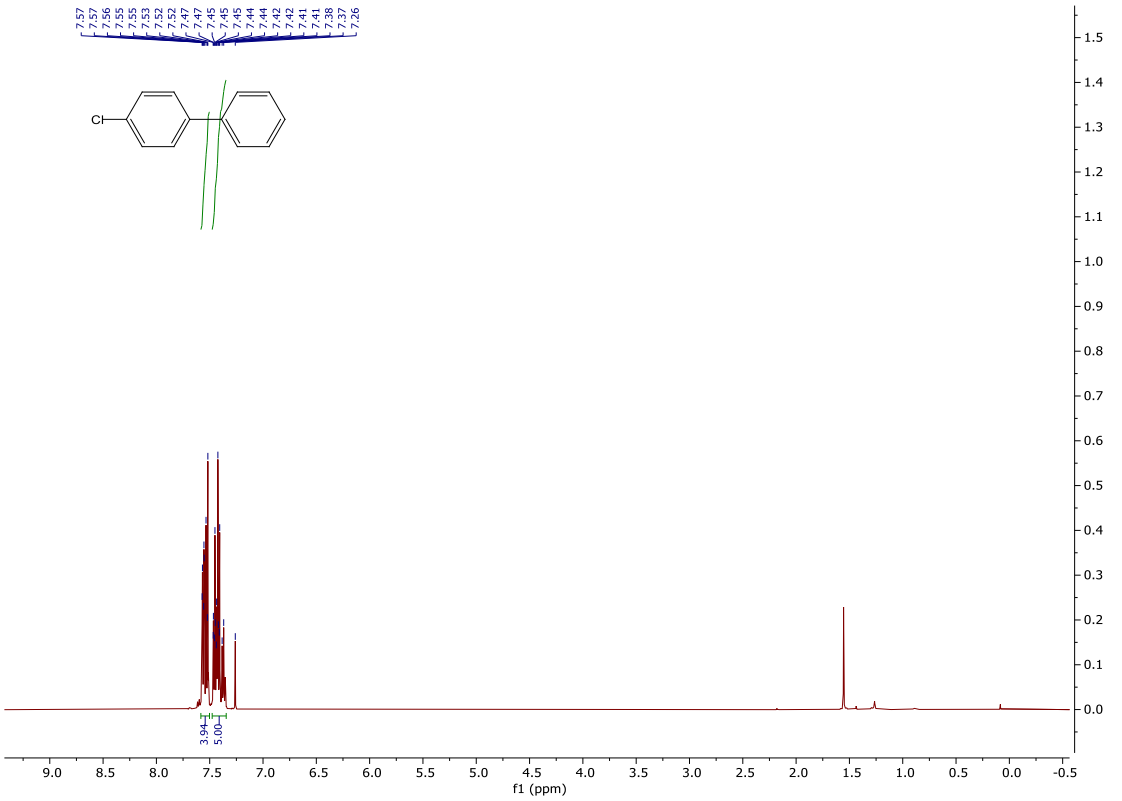


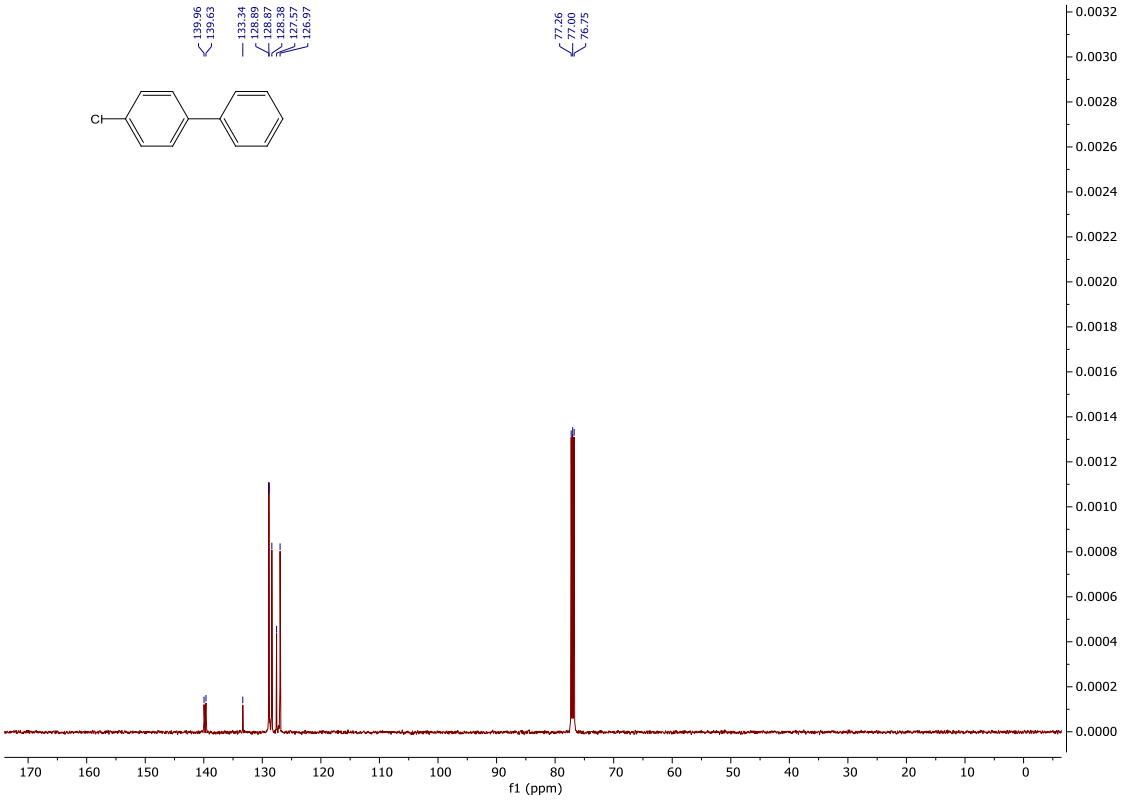
^{1}H(500 MHz) and ^{13}C{1H}(125 MHz) spectra of 3d in $CDCl_3$:



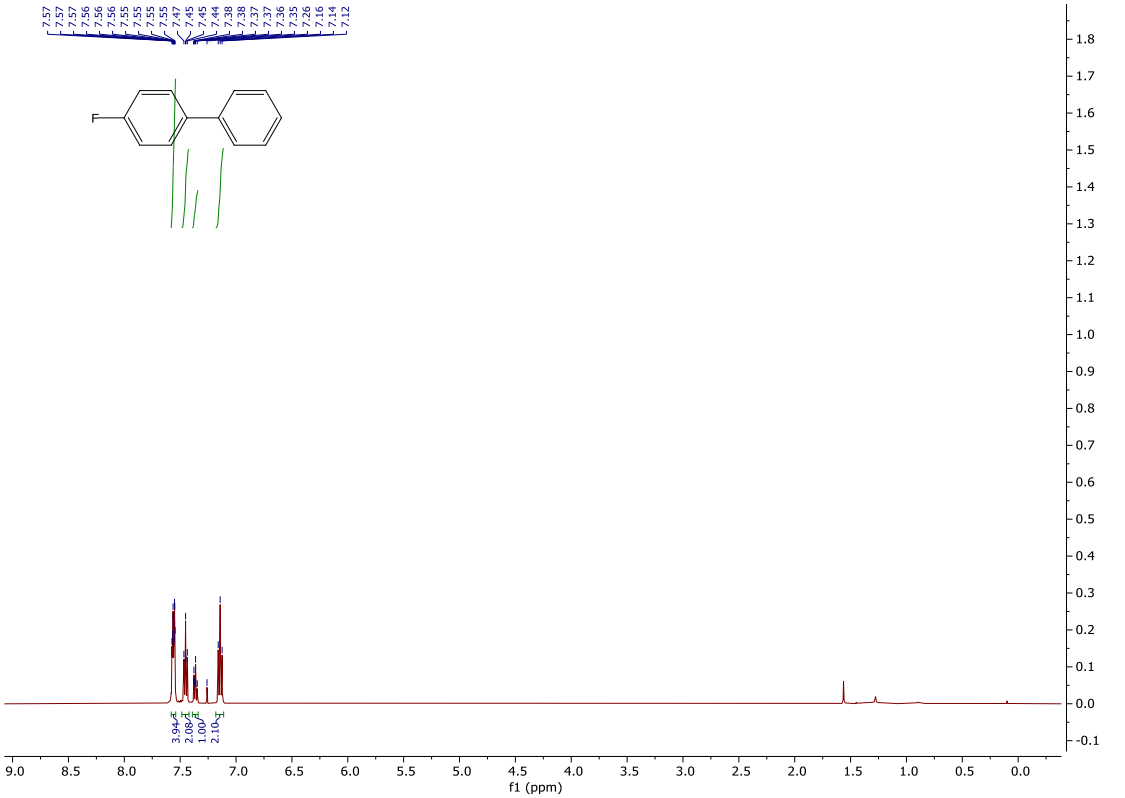


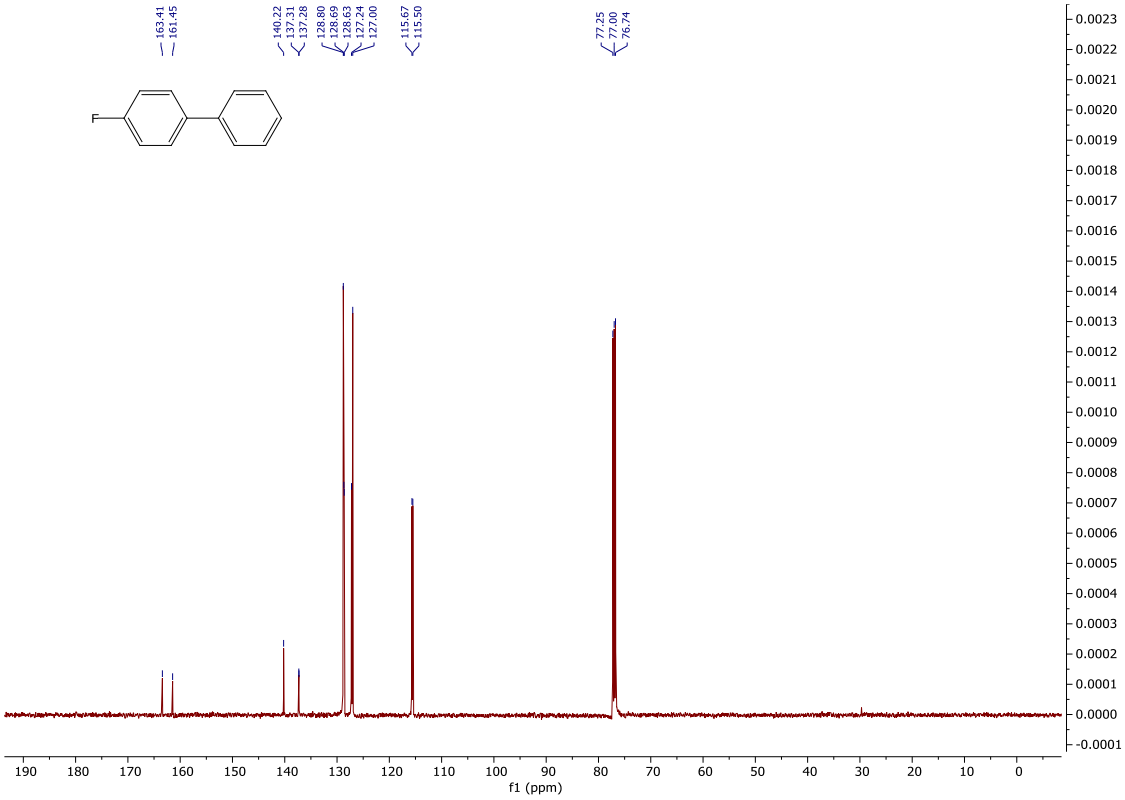
^{1}H(500 MHz) and ^{13}C{1H}(125 MHz) spectra of 3e, 3r in $CDCl_3$:

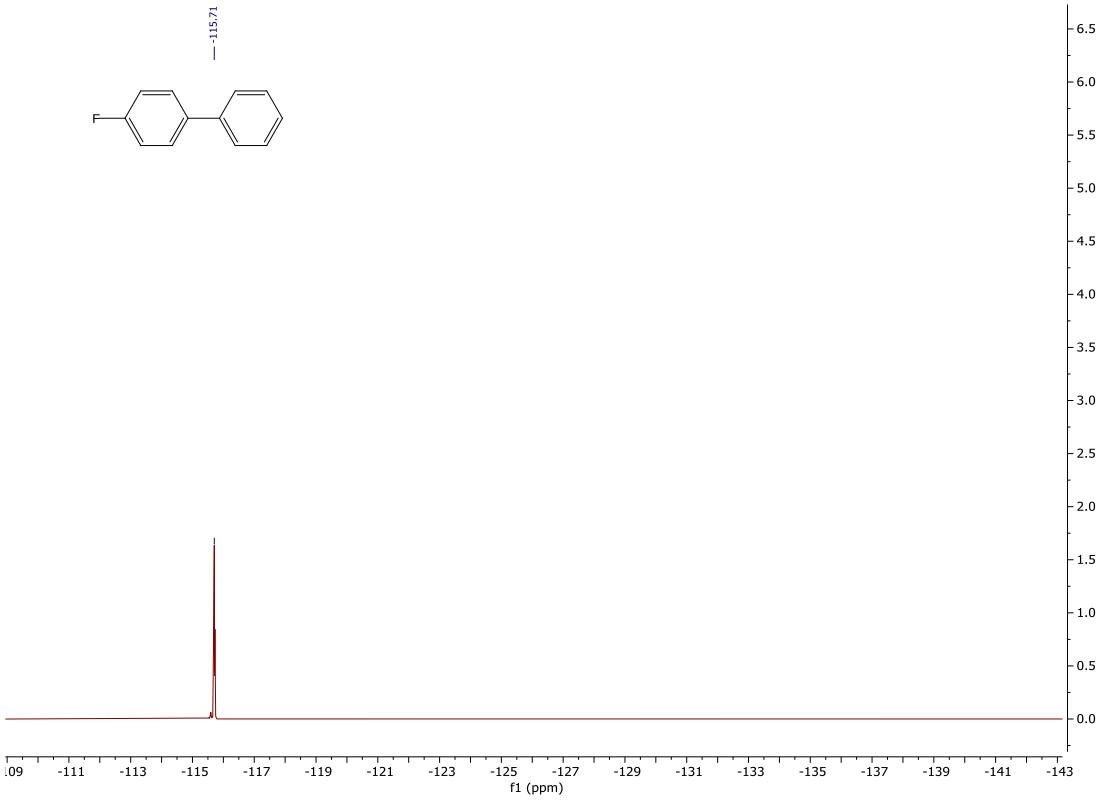




^{1}H (500 MHz), ^{13}C{1H}(125 MHz) and ^{19}F(471 MHz) spectra of 3f, 3p in $CDCl_3$:



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F
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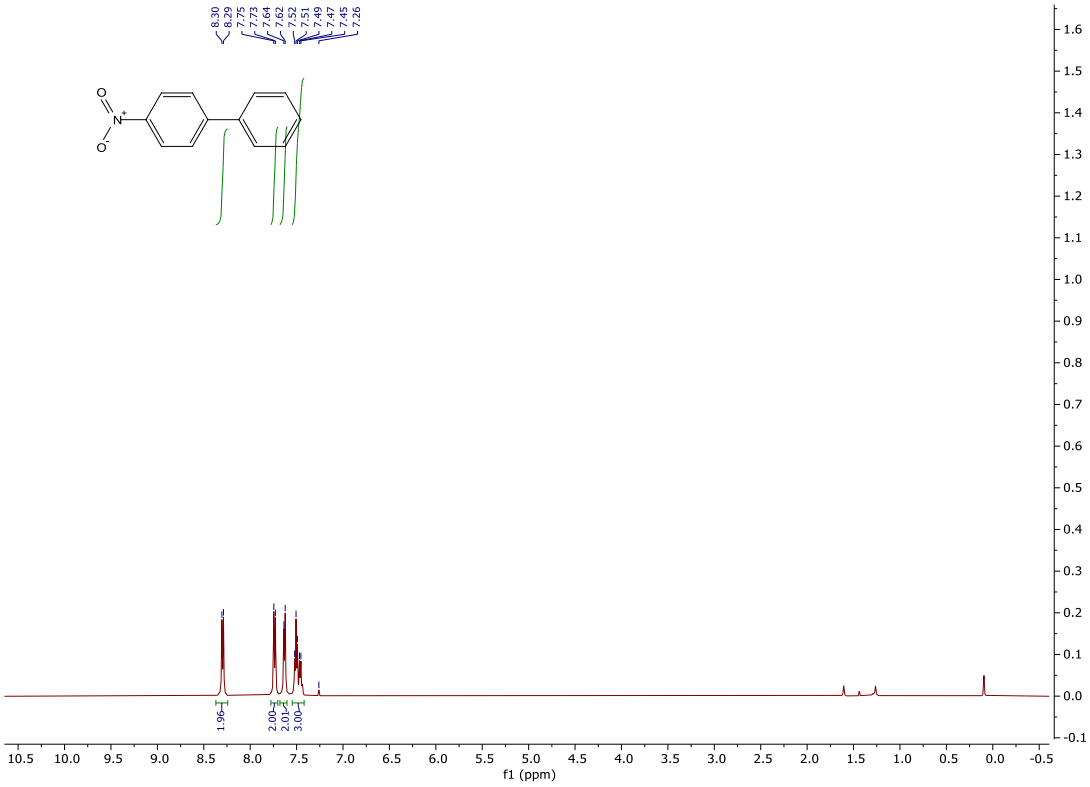
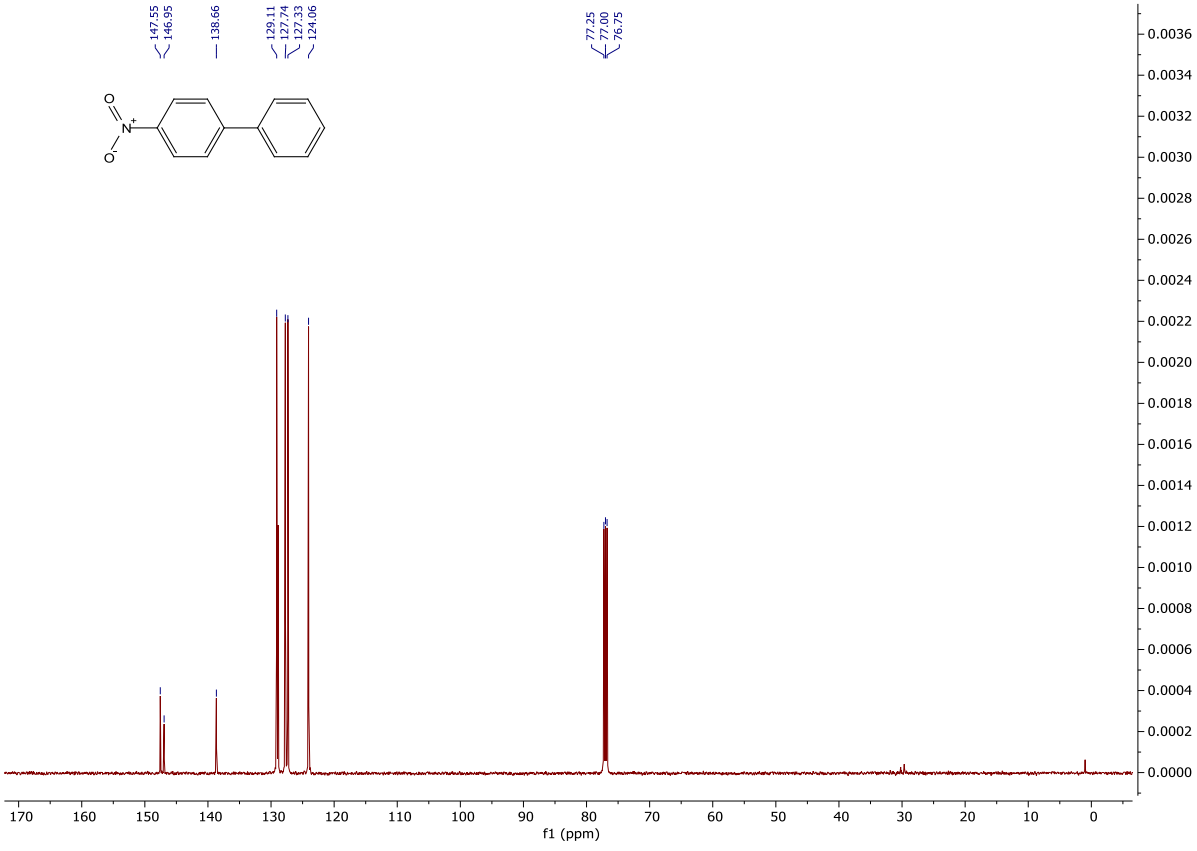
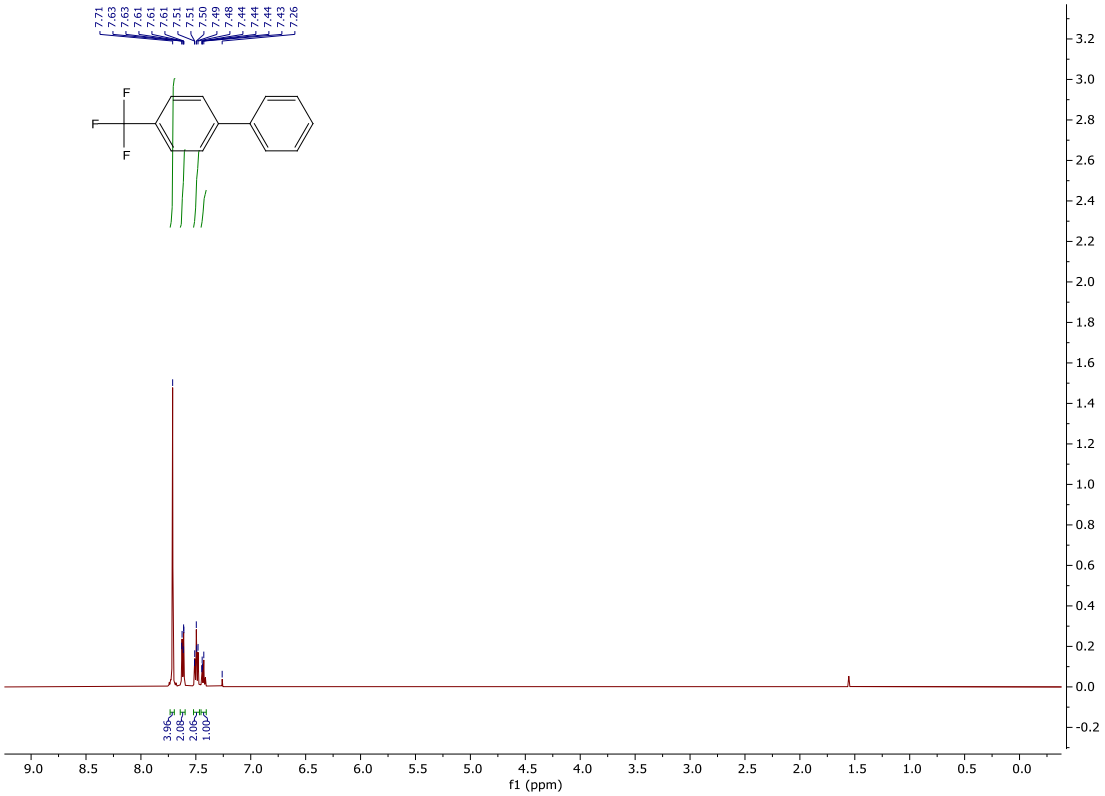
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
f1 (ppm)

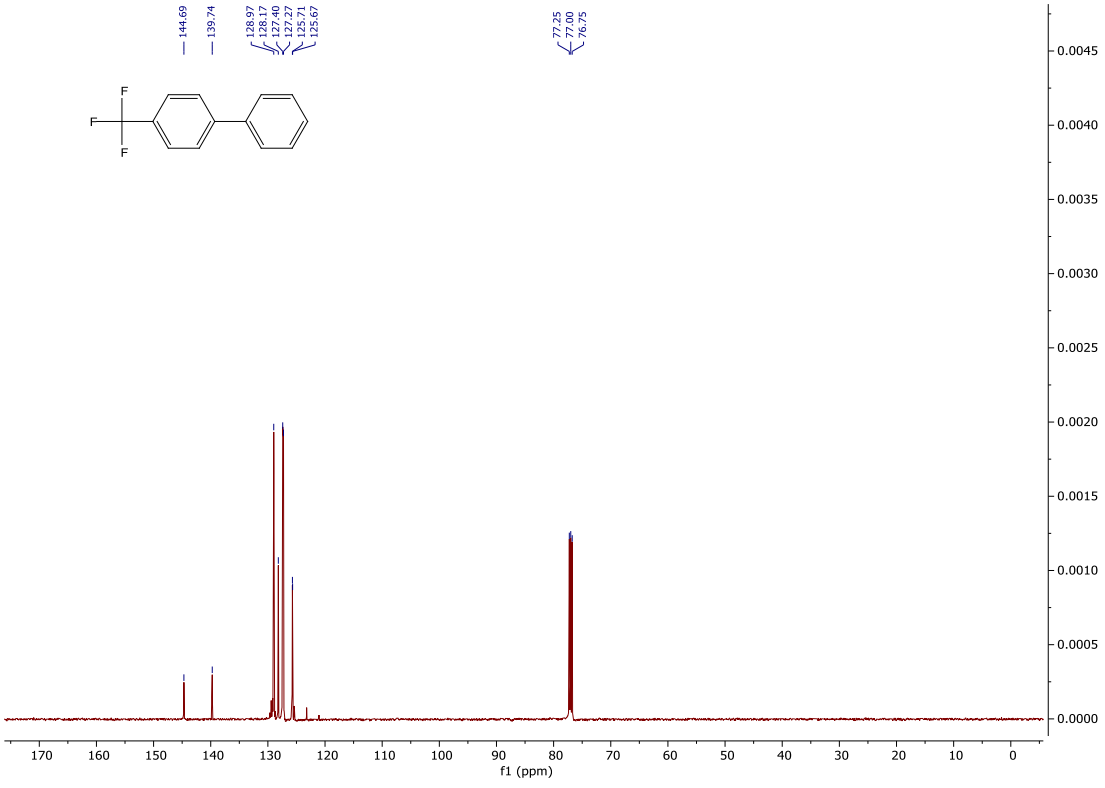
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3g in $CDCl_3$:

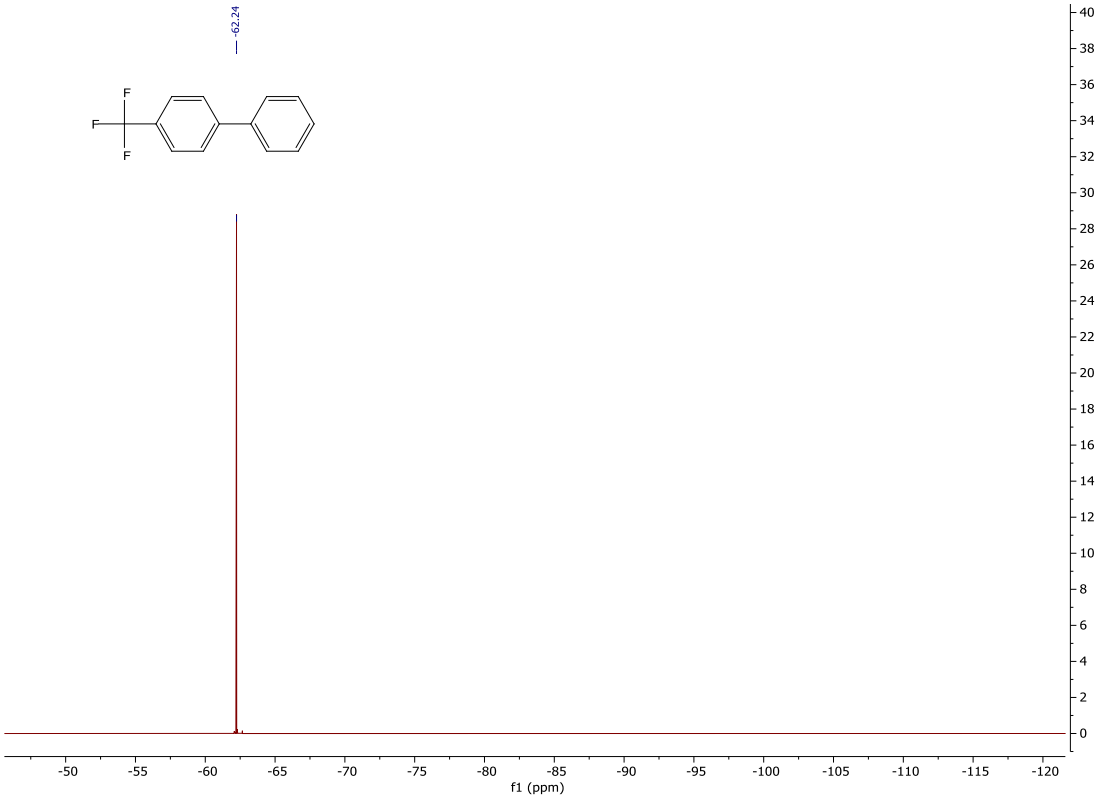




^{1}H(500 MHz),^{13}C{1H}(125 MHz) and ^{19}F(471 MHz) spectra of 3h, 3o in $CDCl_3$:



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F
40
38
36
34
32
30
28
26
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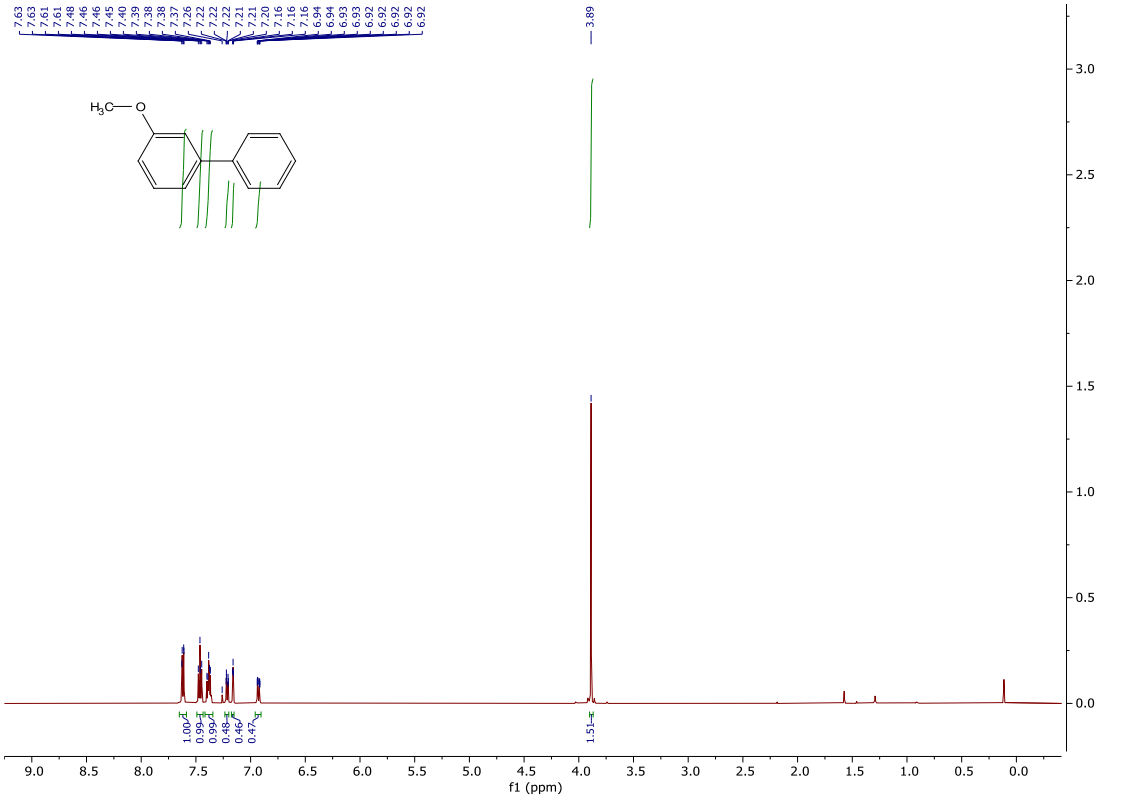
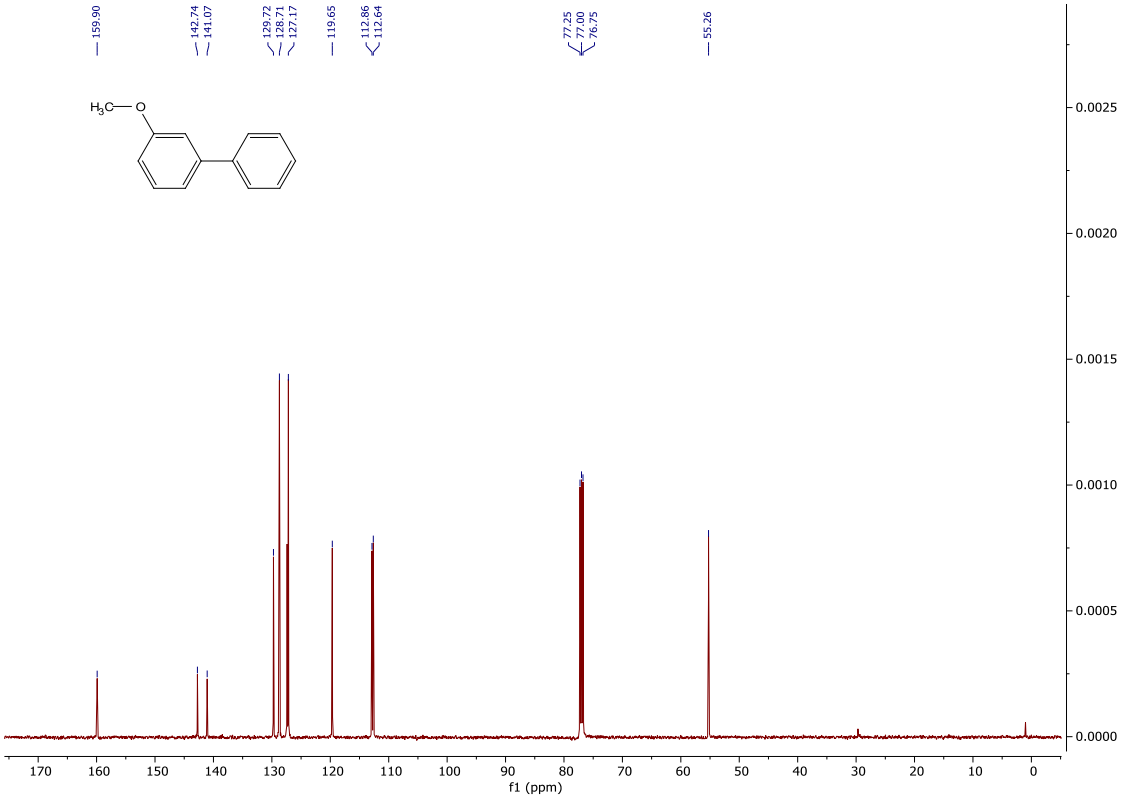
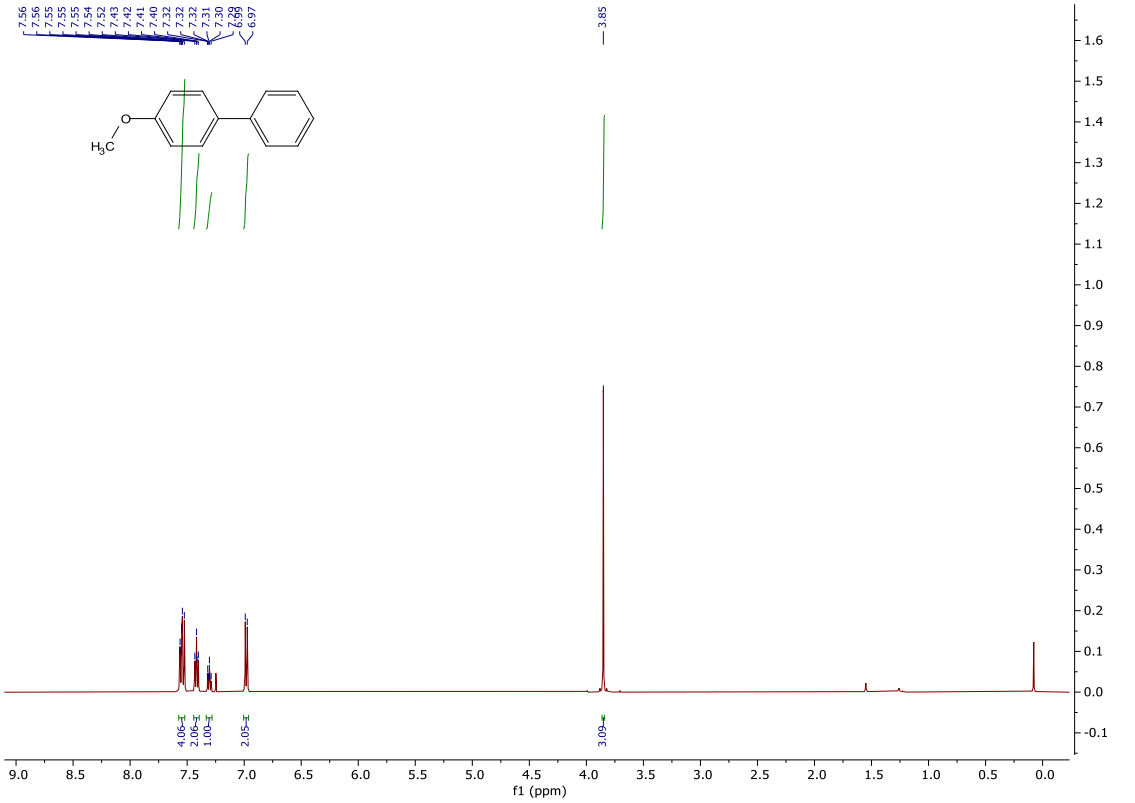
22
20
18
16
14
12
10
8
6
4
2
0
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
f1 (ppm)

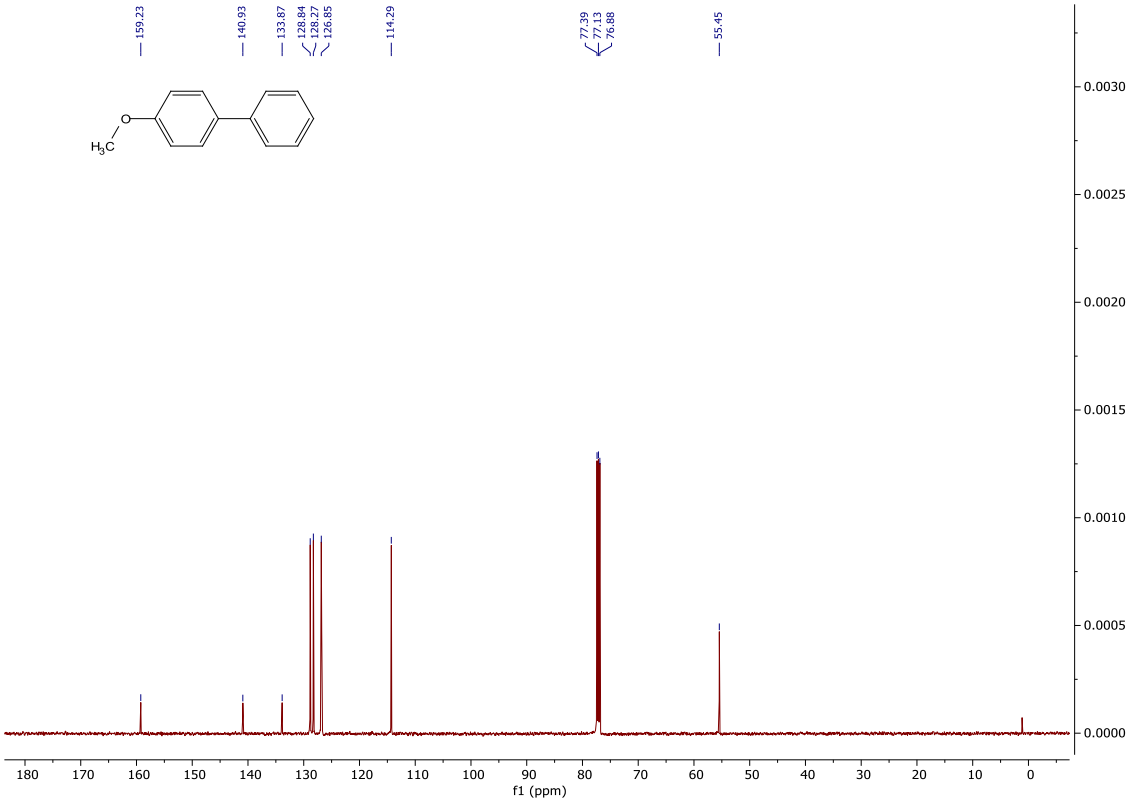
^{1}H(500 MHz) and $^{13}C\{1H\}$(125 MHz) spectra of 3i, 3l in $CDCl_3$



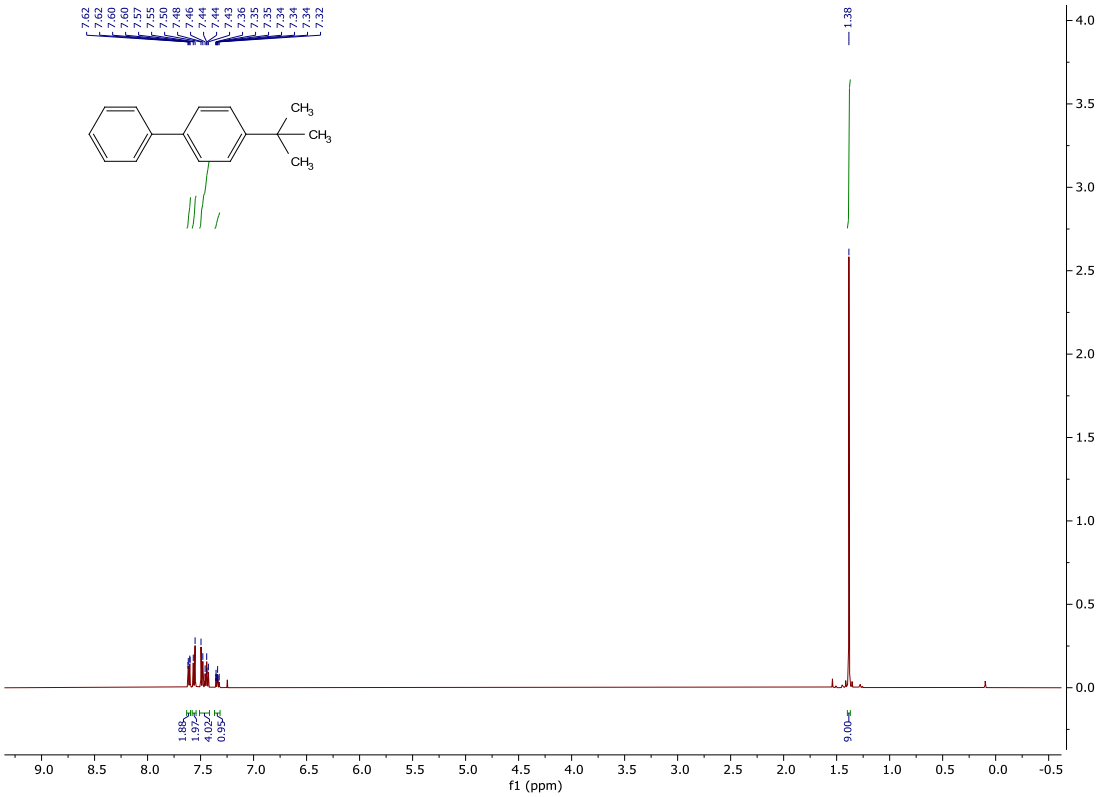


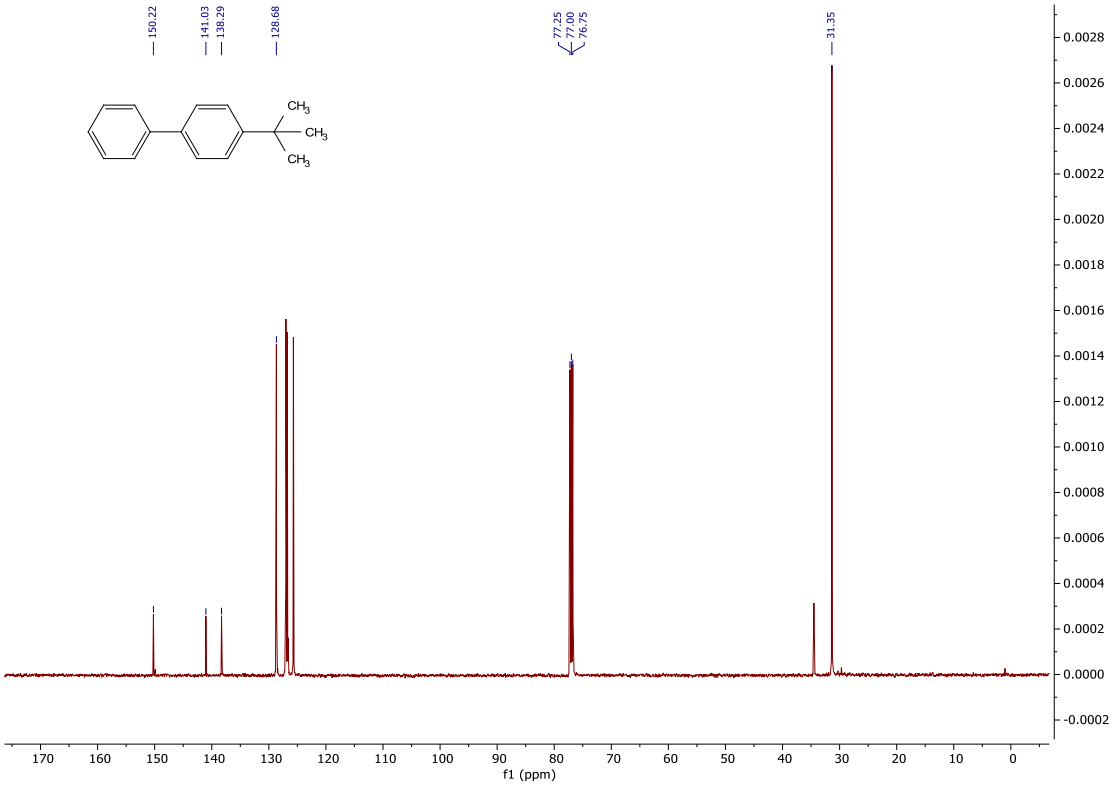
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3j, 3k, 3w in $CDCl_3$:



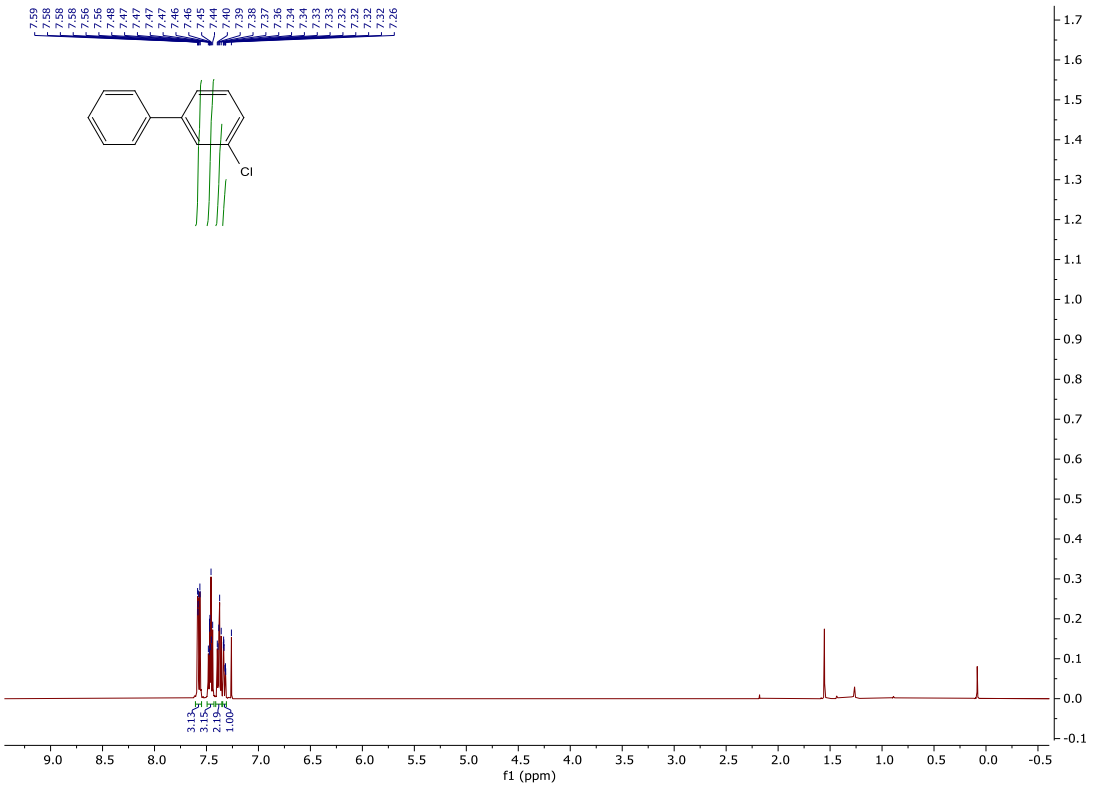


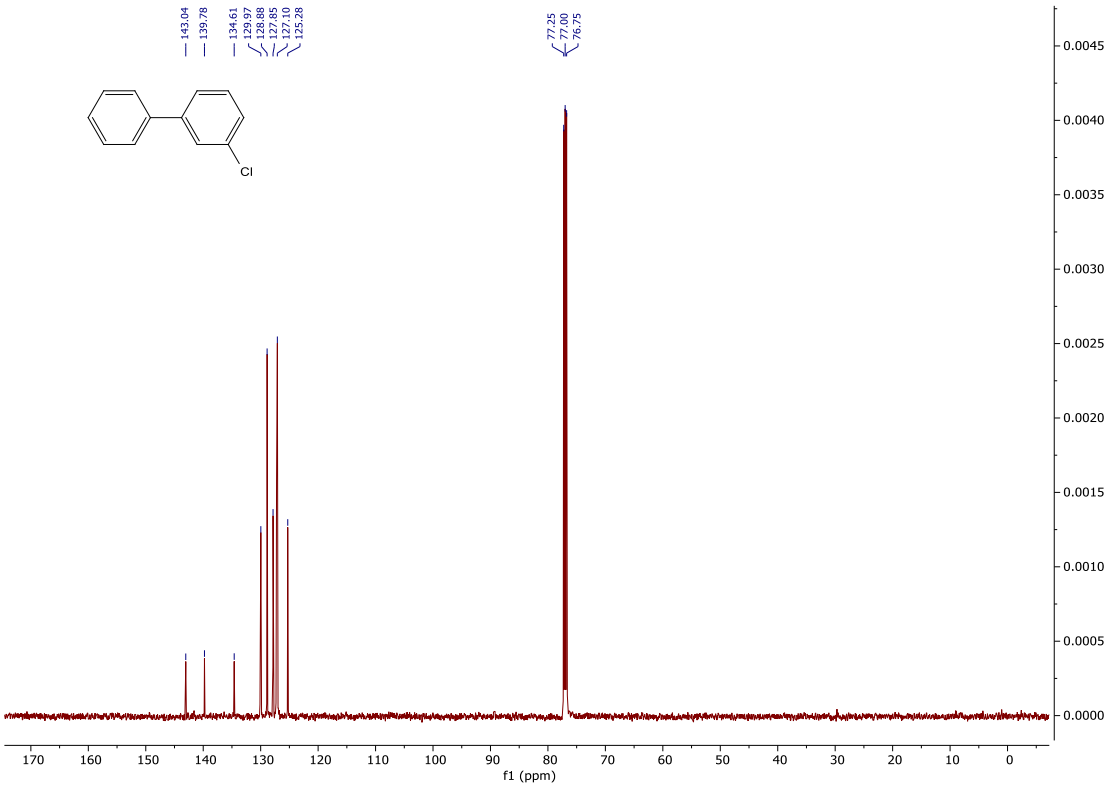
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3n in $CDCl_3$:



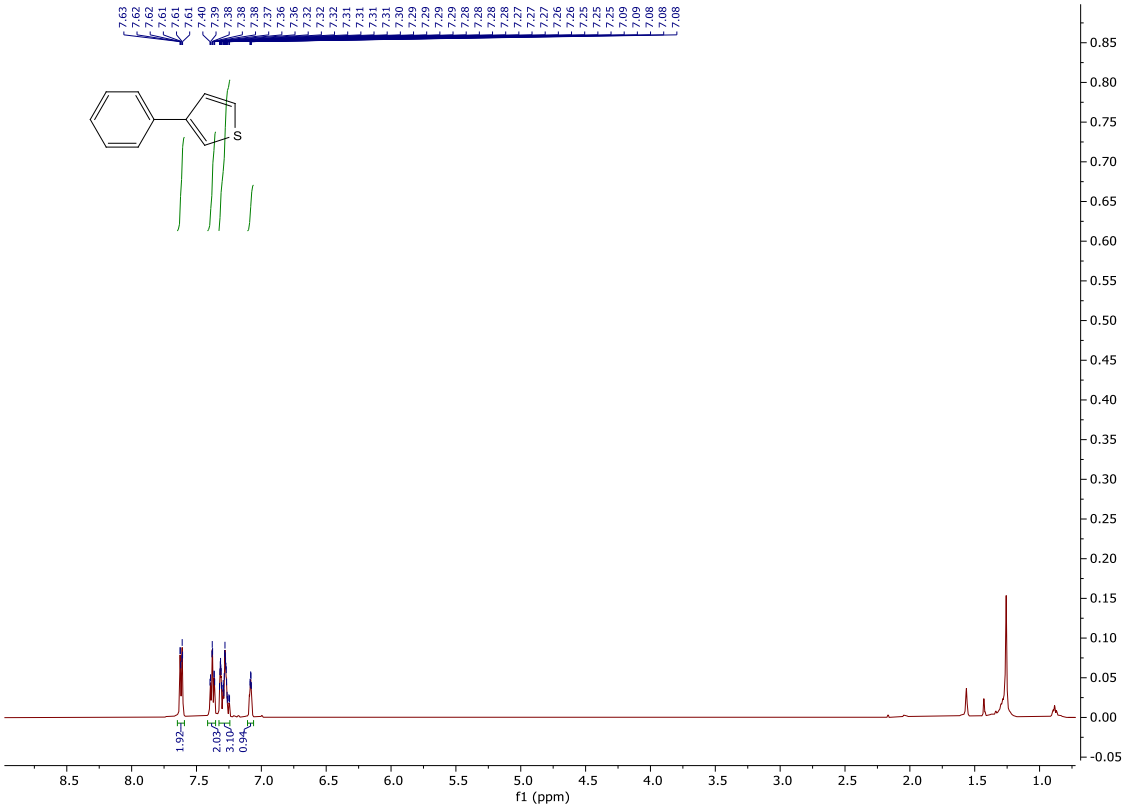


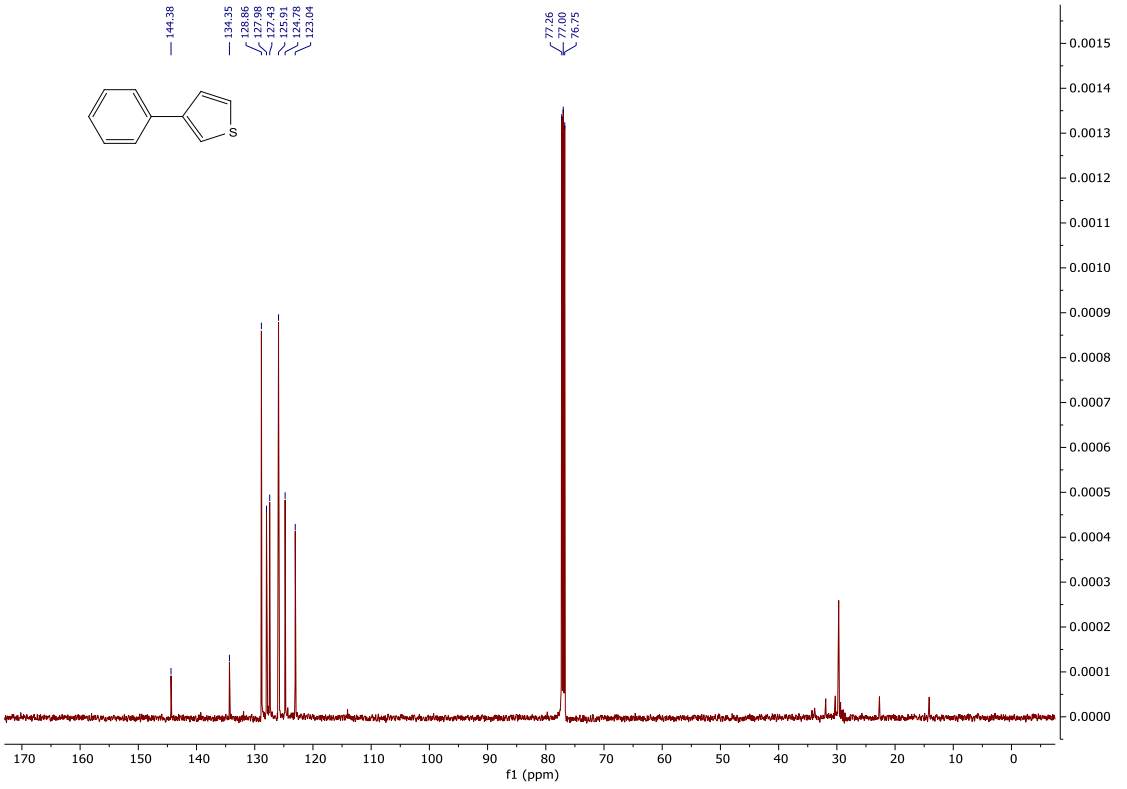
^{1}H(500 MHz) and $^{13}C\{1H\}$(125 MHz) spectra of 3q in $CDCl_3$:



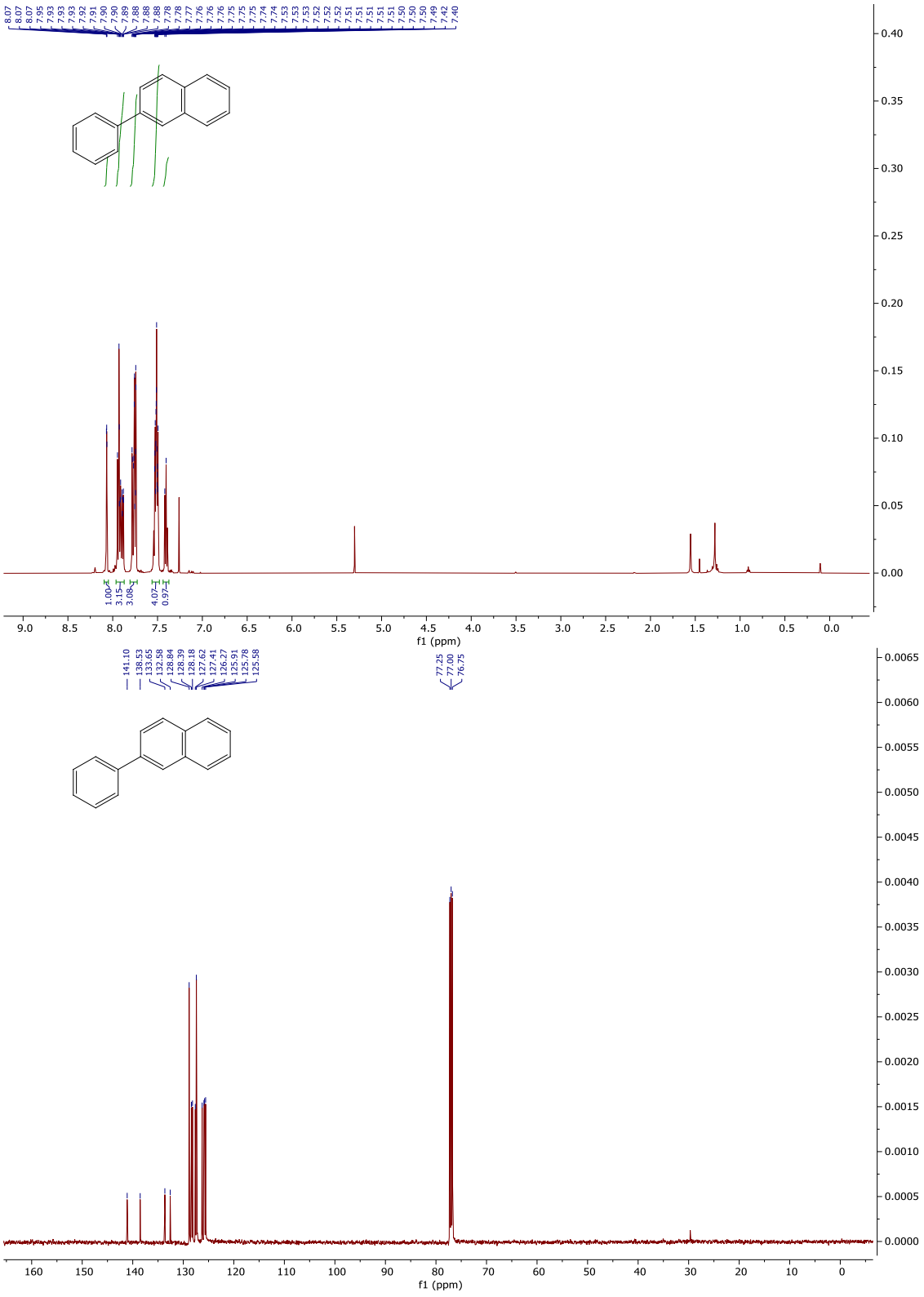


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3s in $CDCl_3$:

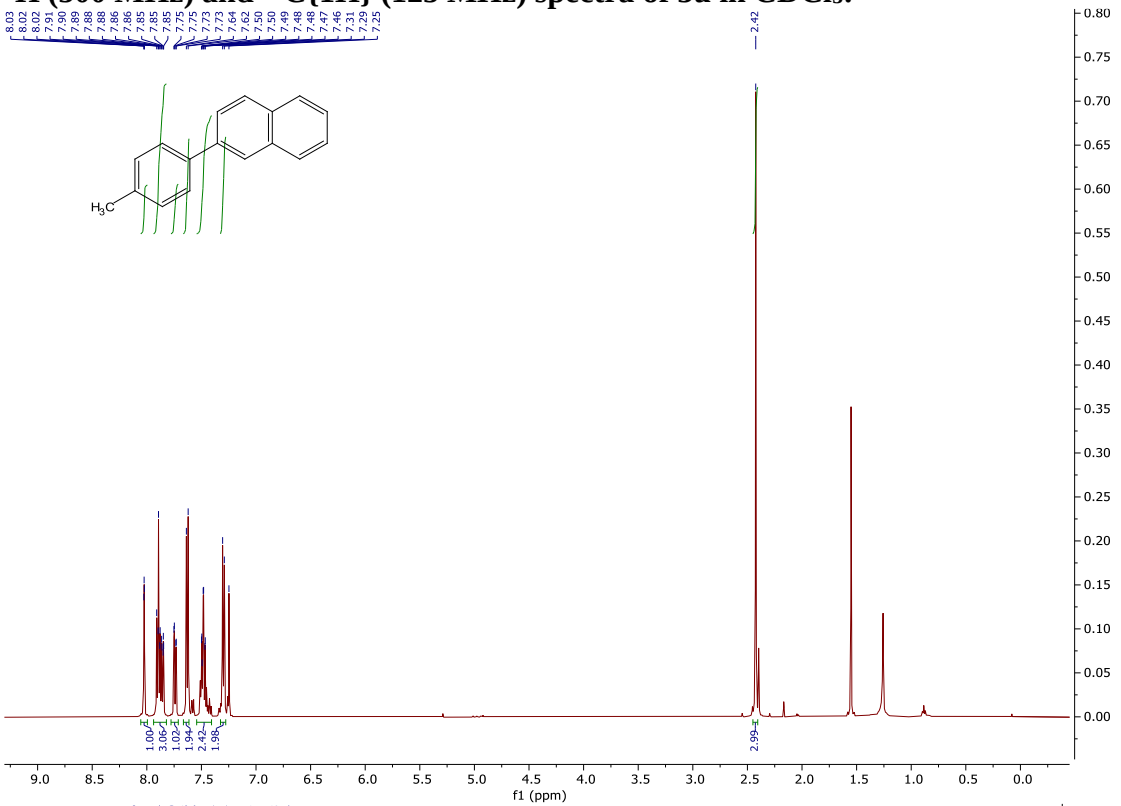


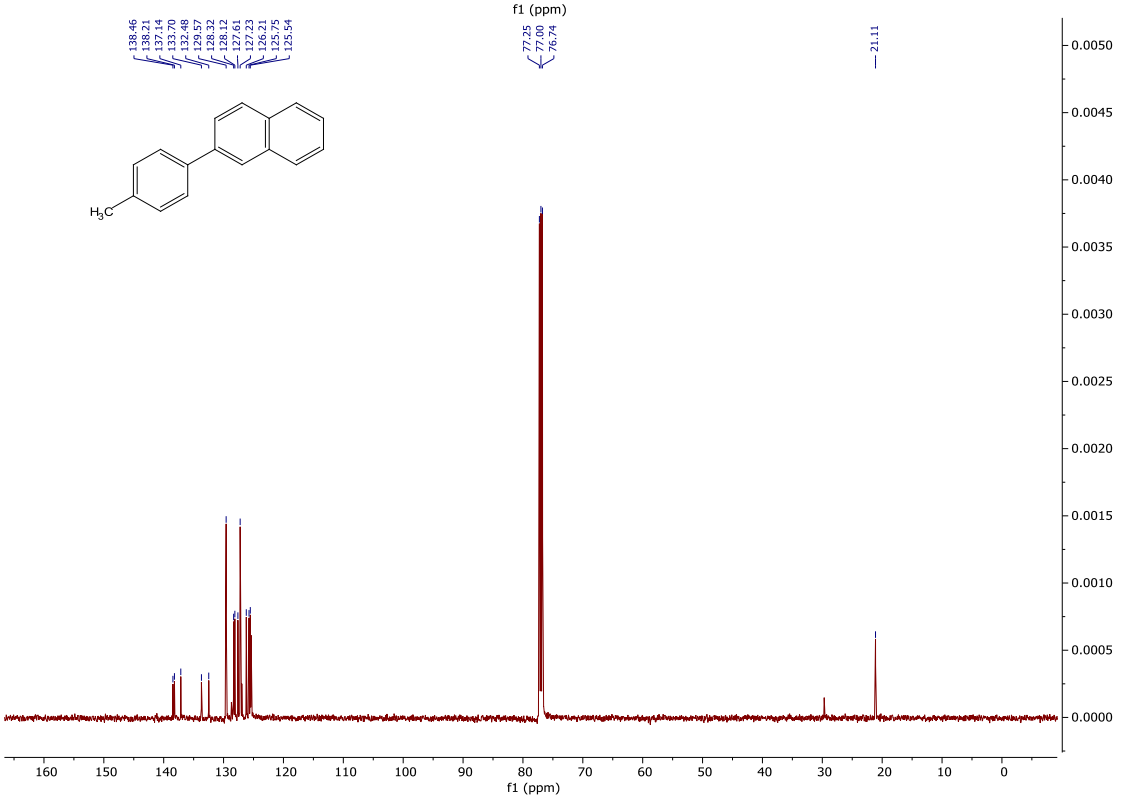


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3t in $CDCl_3$:

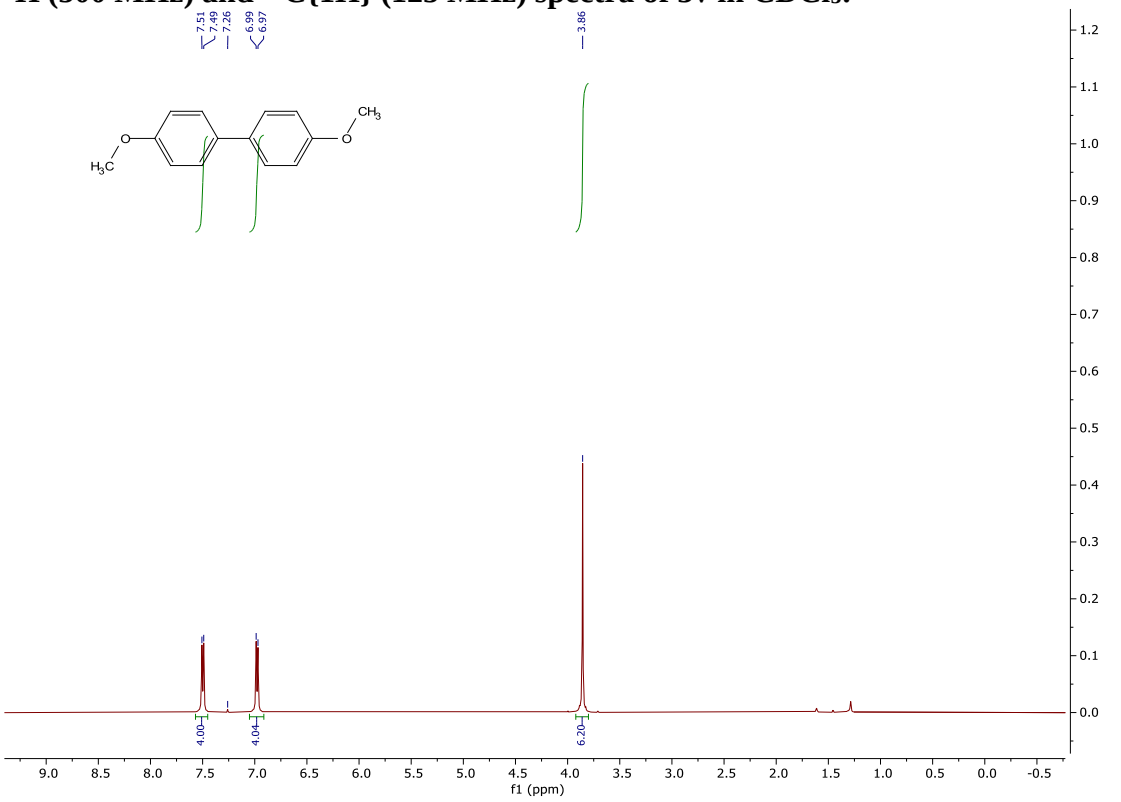


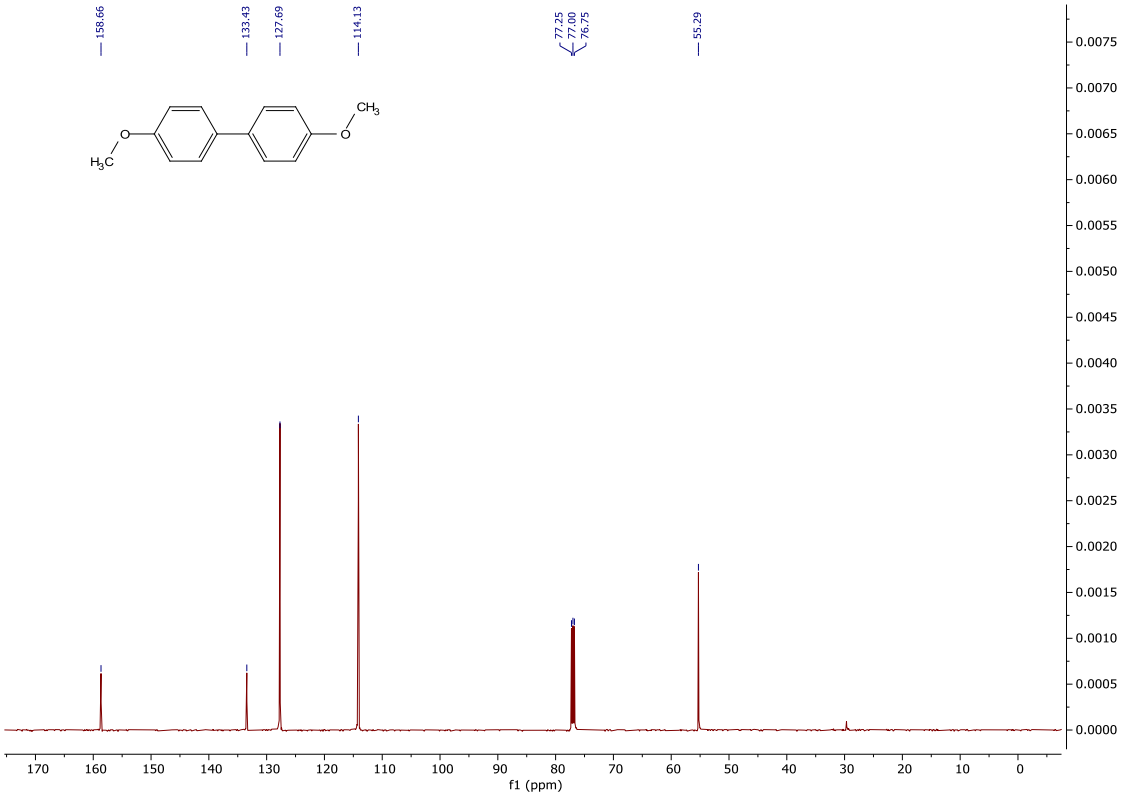
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3u in $CDCl_3$:



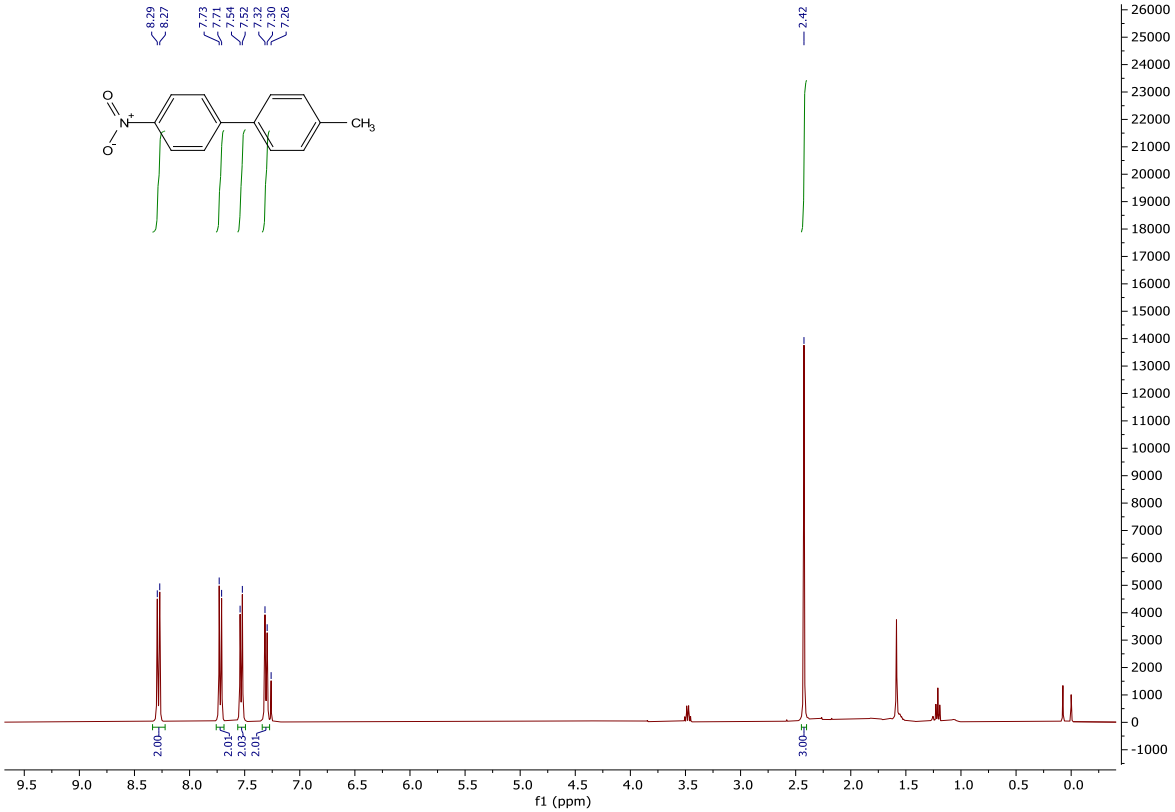


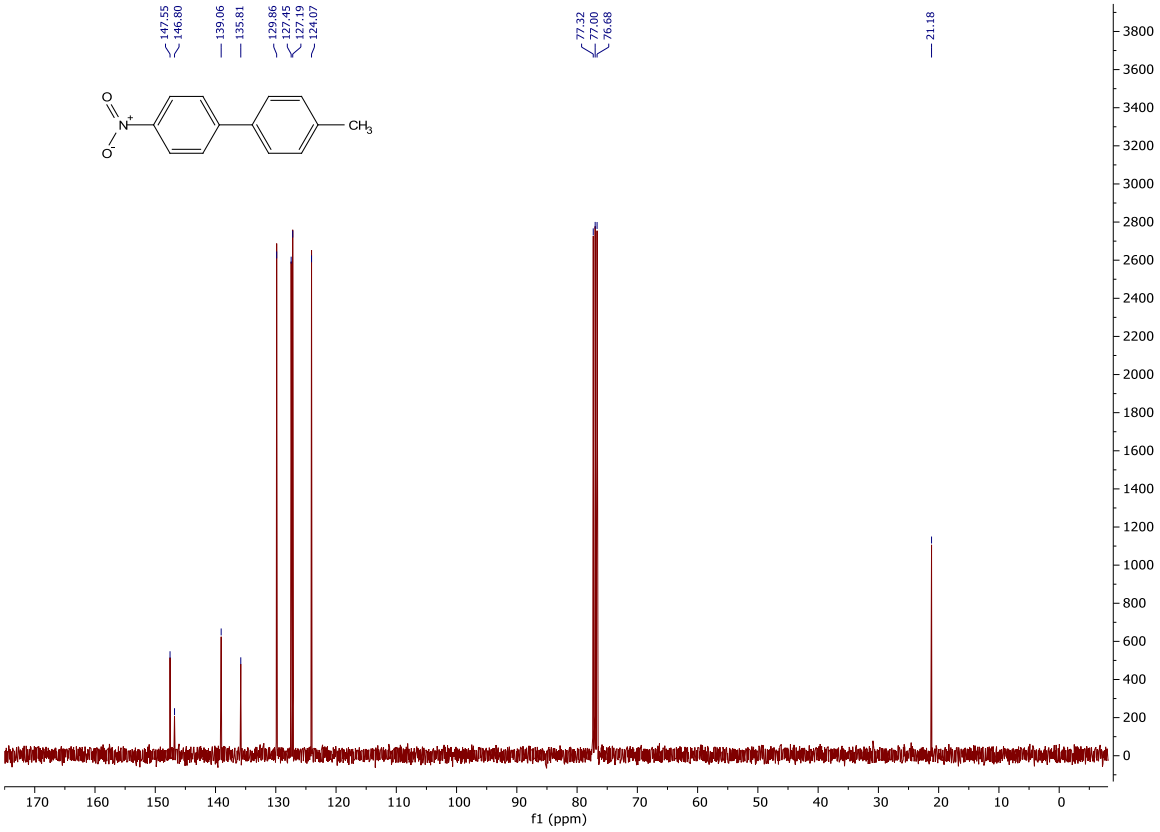
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3v in $CDCl_3$:



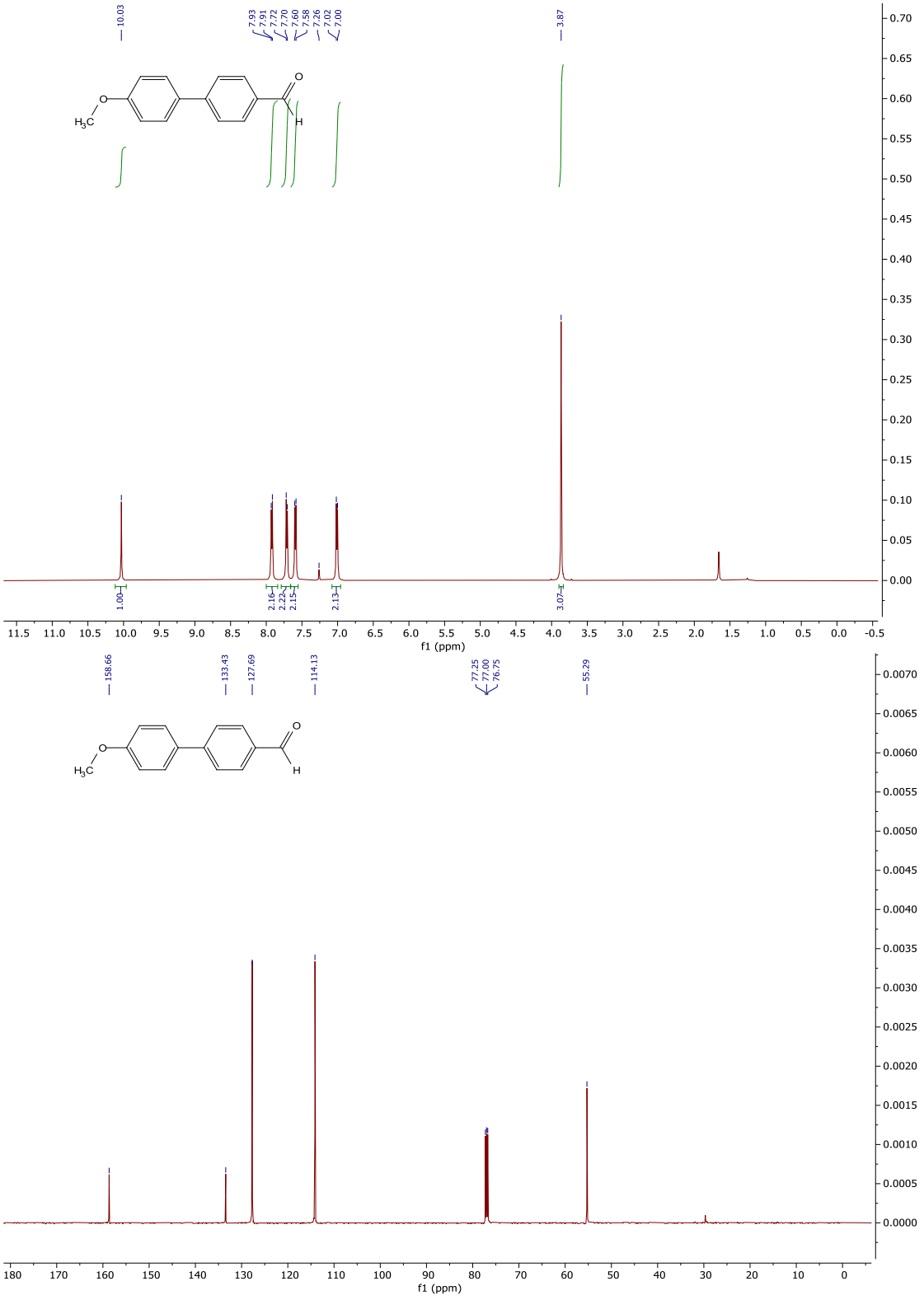


^{1}H (400 MHz) and ^{13}C{1H} (100 MHz) spectra of 3w in $CDCl_3$:

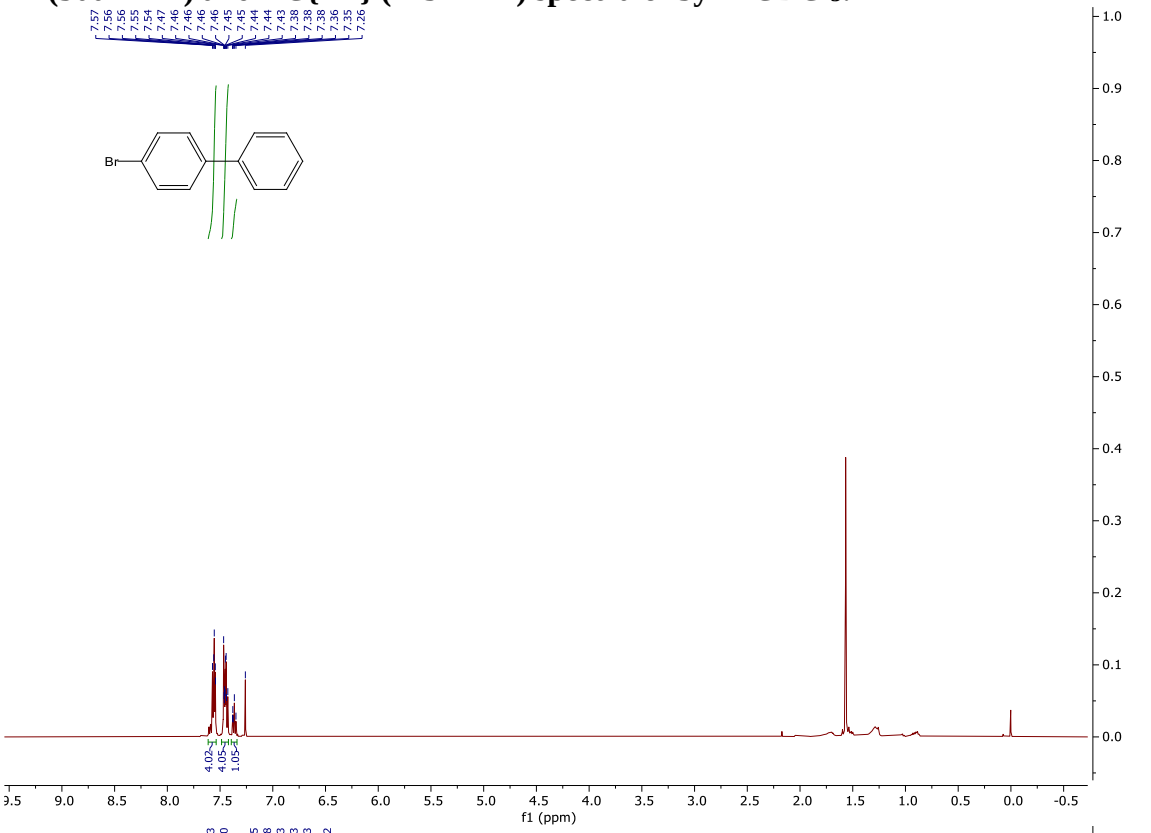


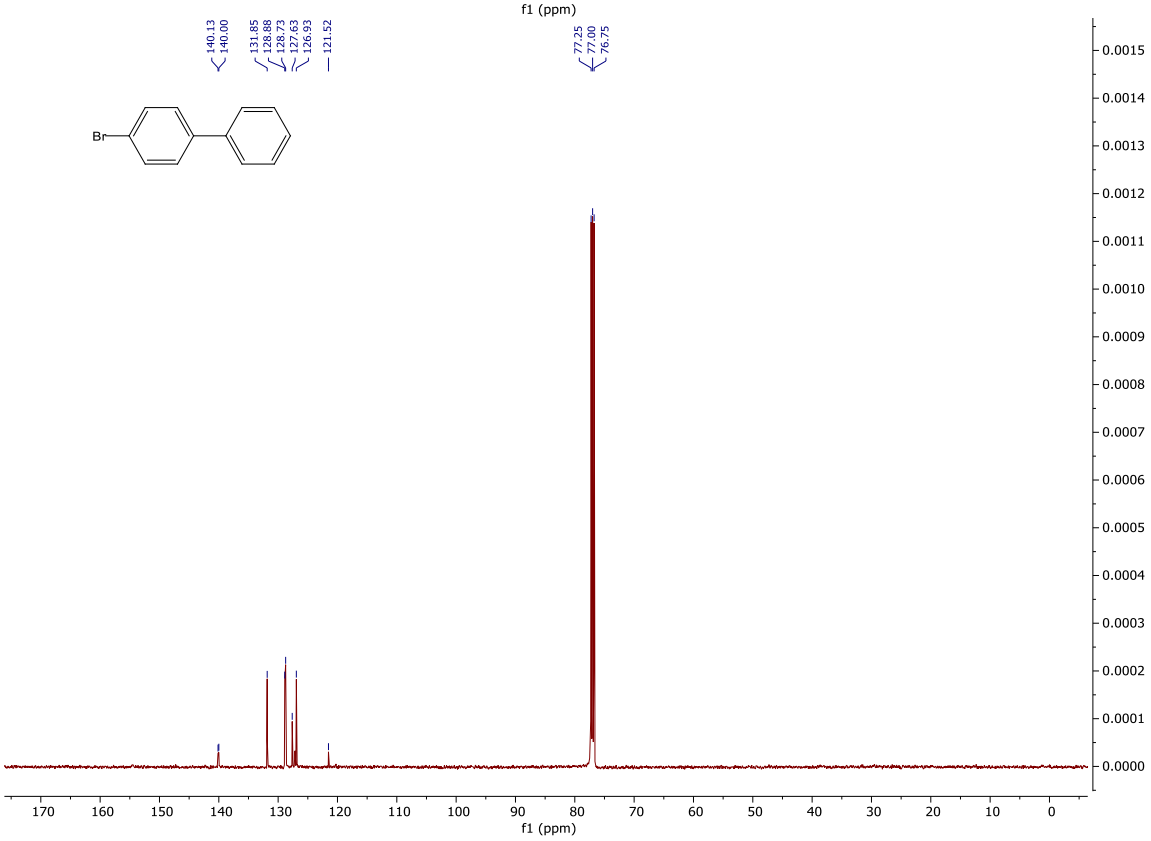


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3x in $CDCl_3$:

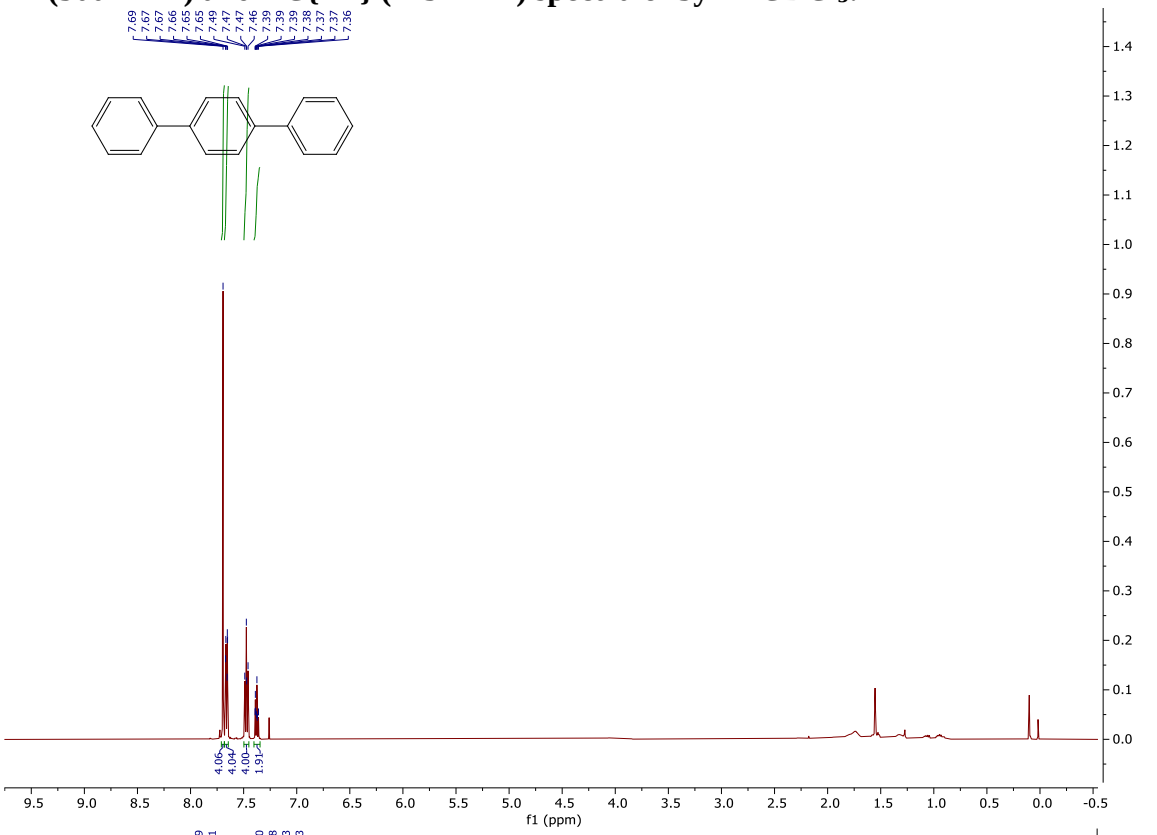


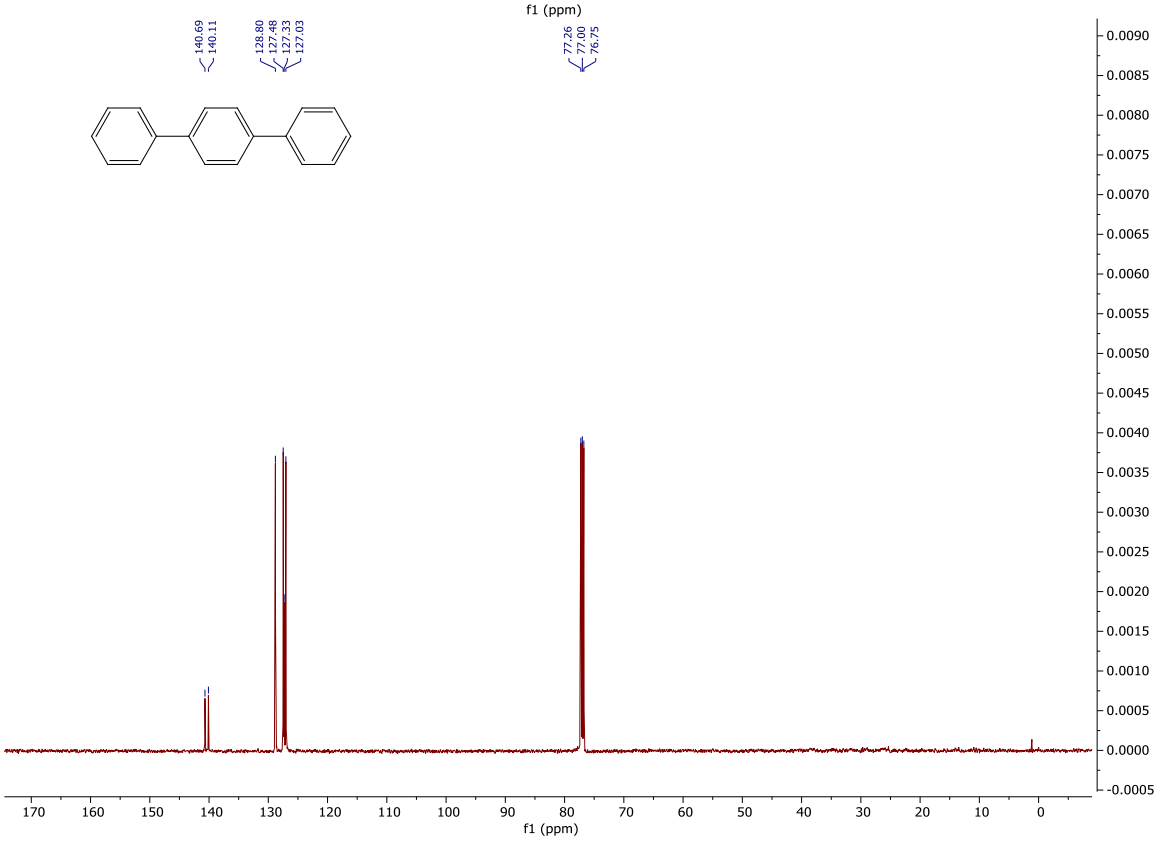
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3y in $CDCl_3$:



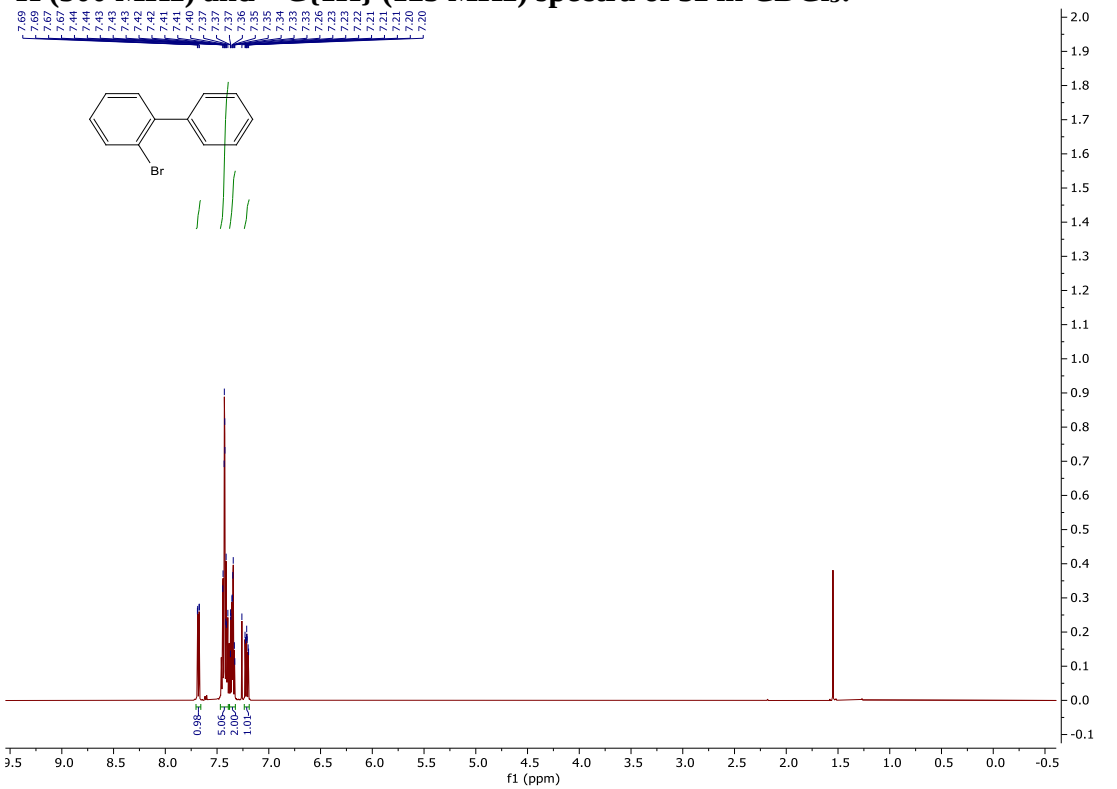


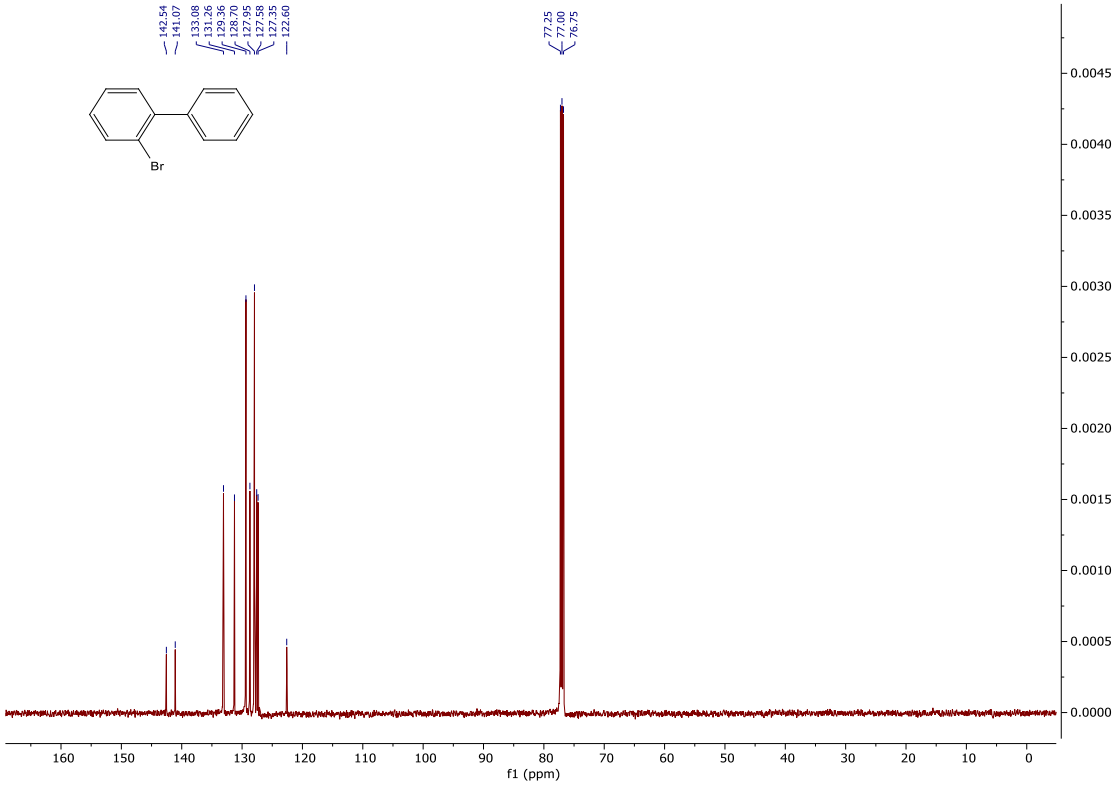
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3y' in $CDCl_3$:



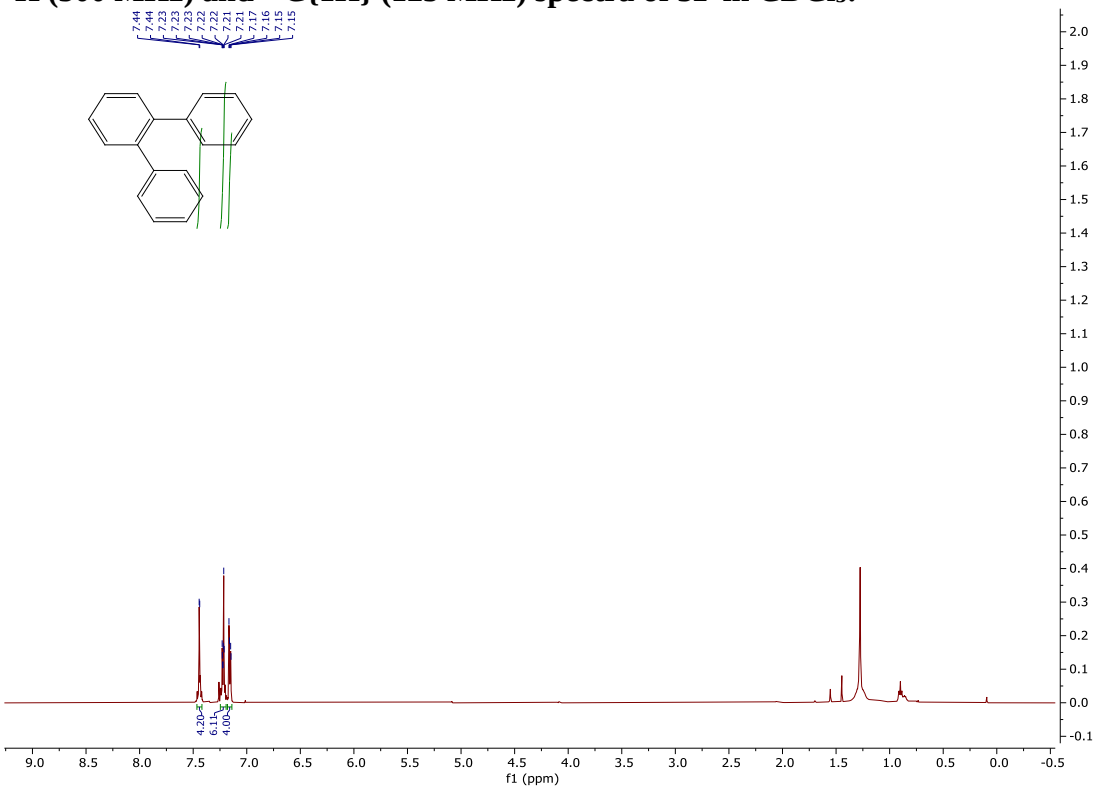


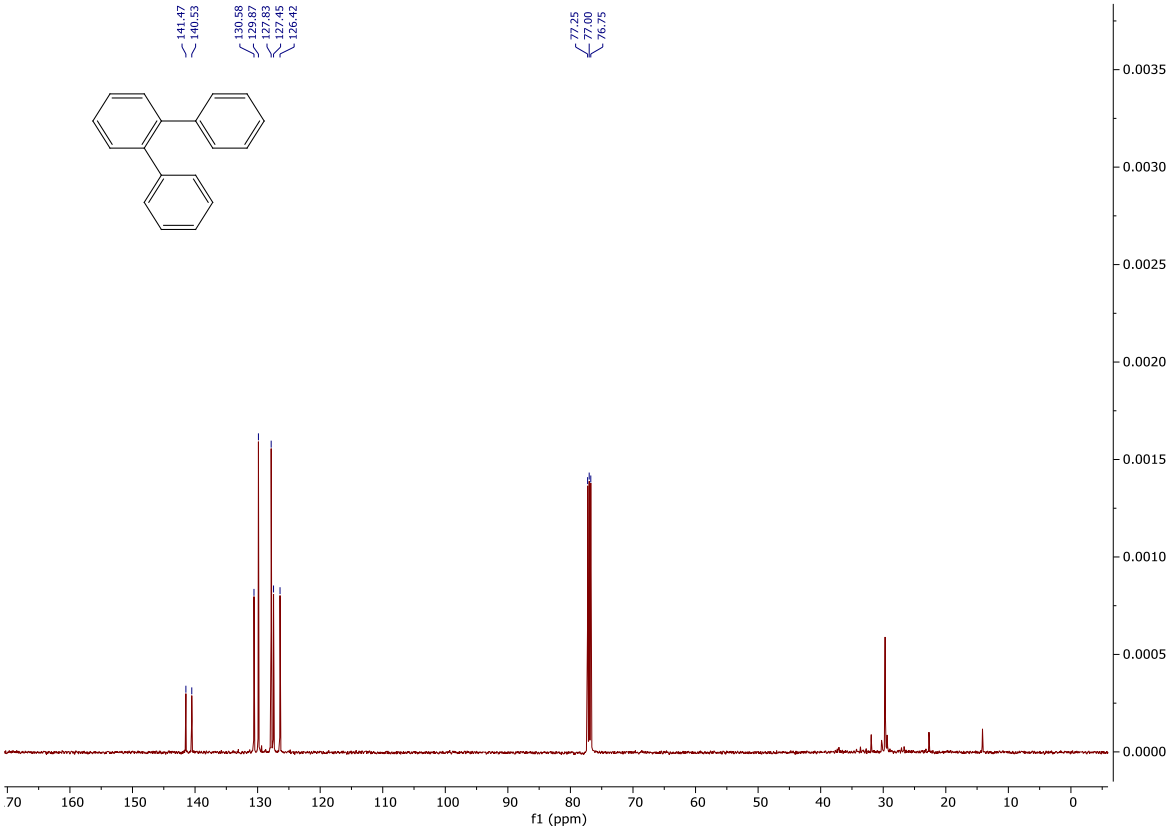
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3z in $CDCl_3$:



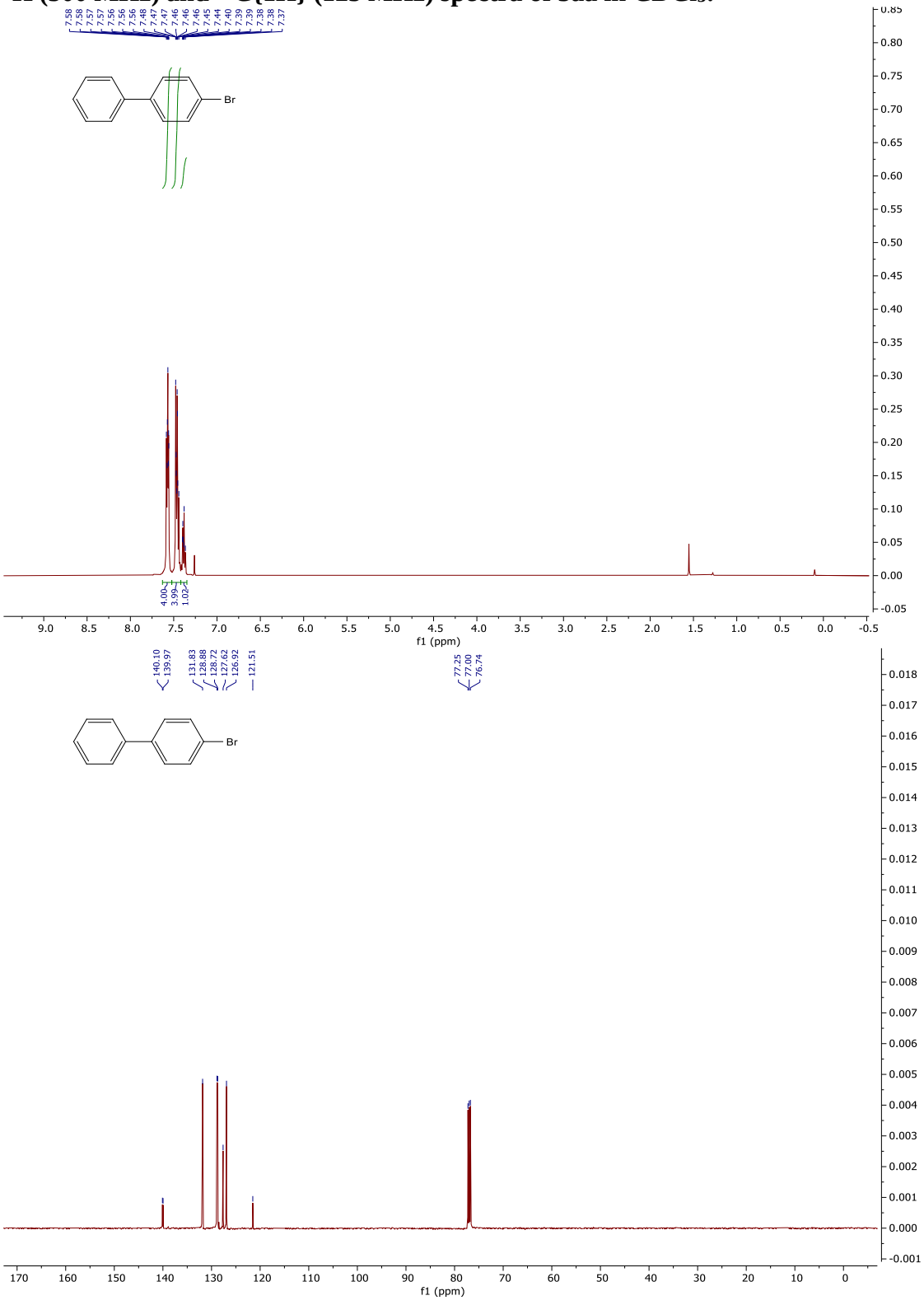


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3z' in $CDCl_3$:

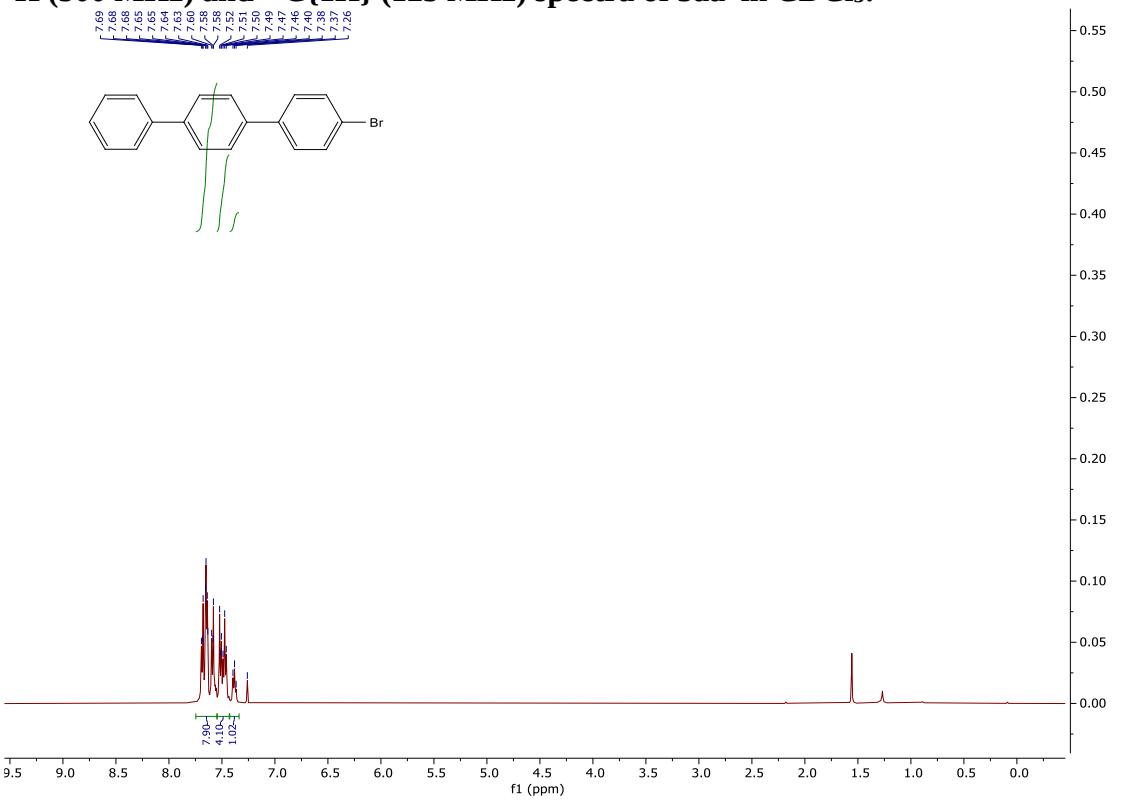


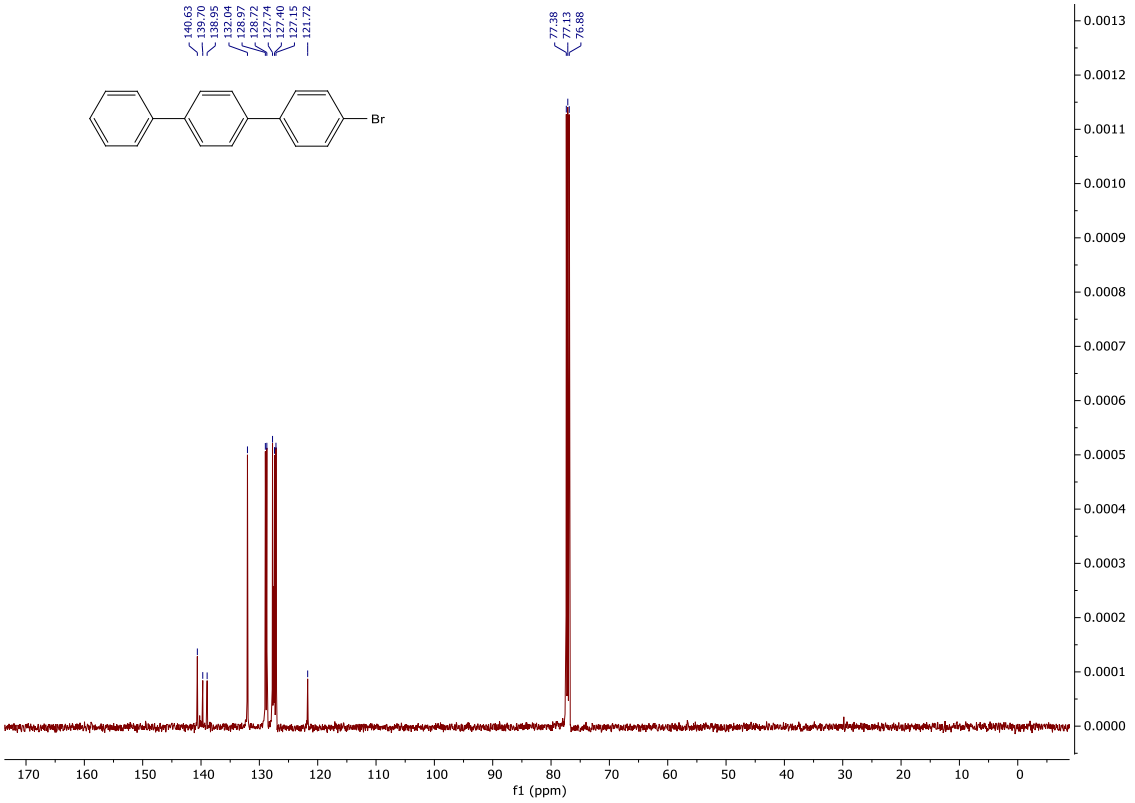


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3aa in $CDCl_3$:

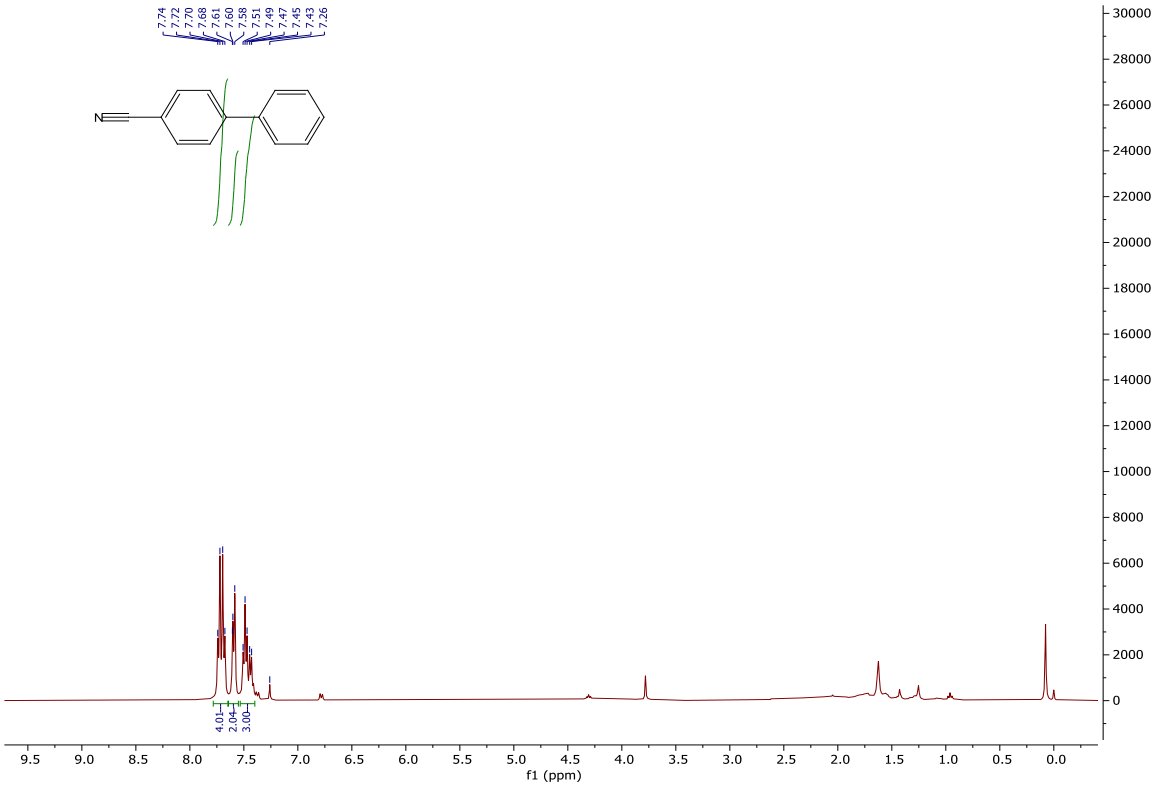


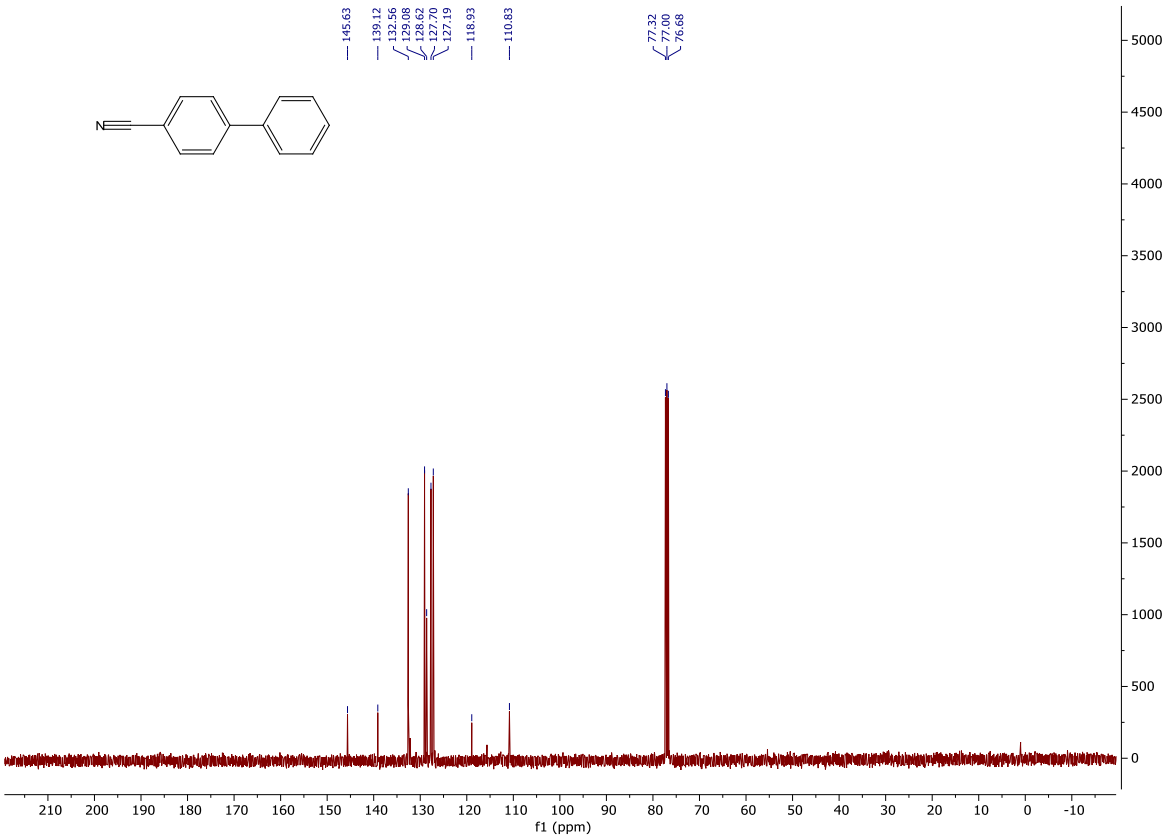
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 3aa' in $CDCl_3$:



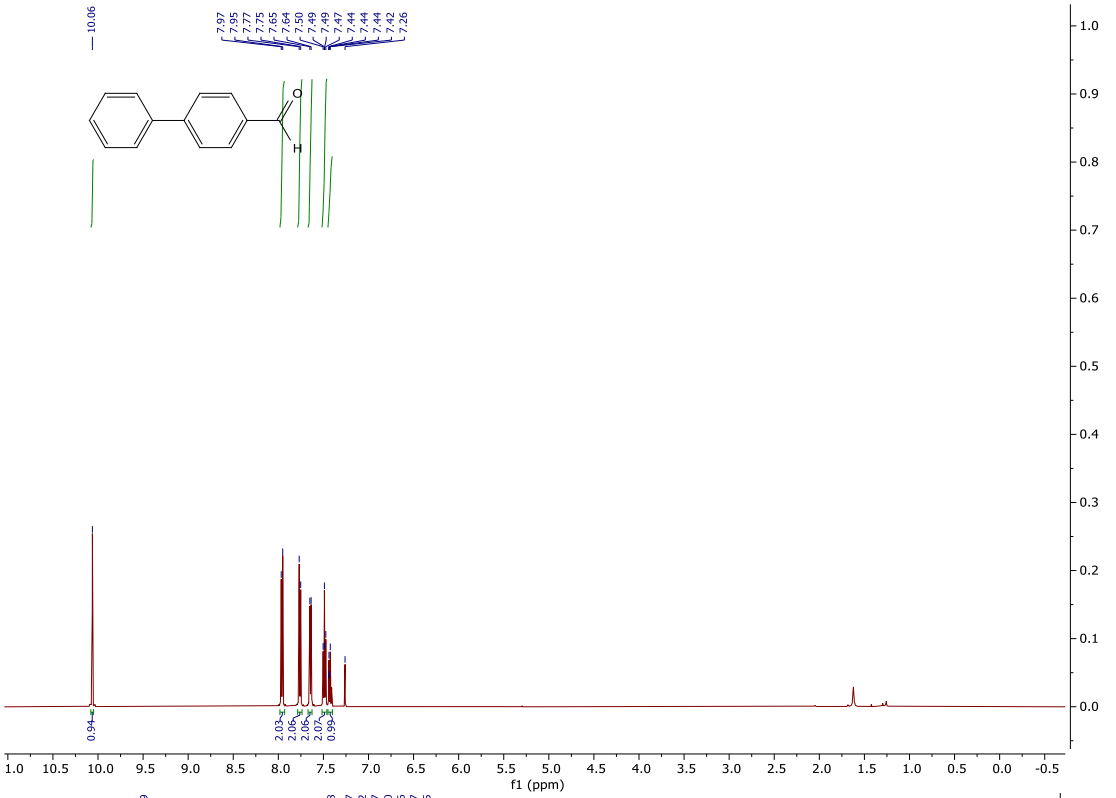


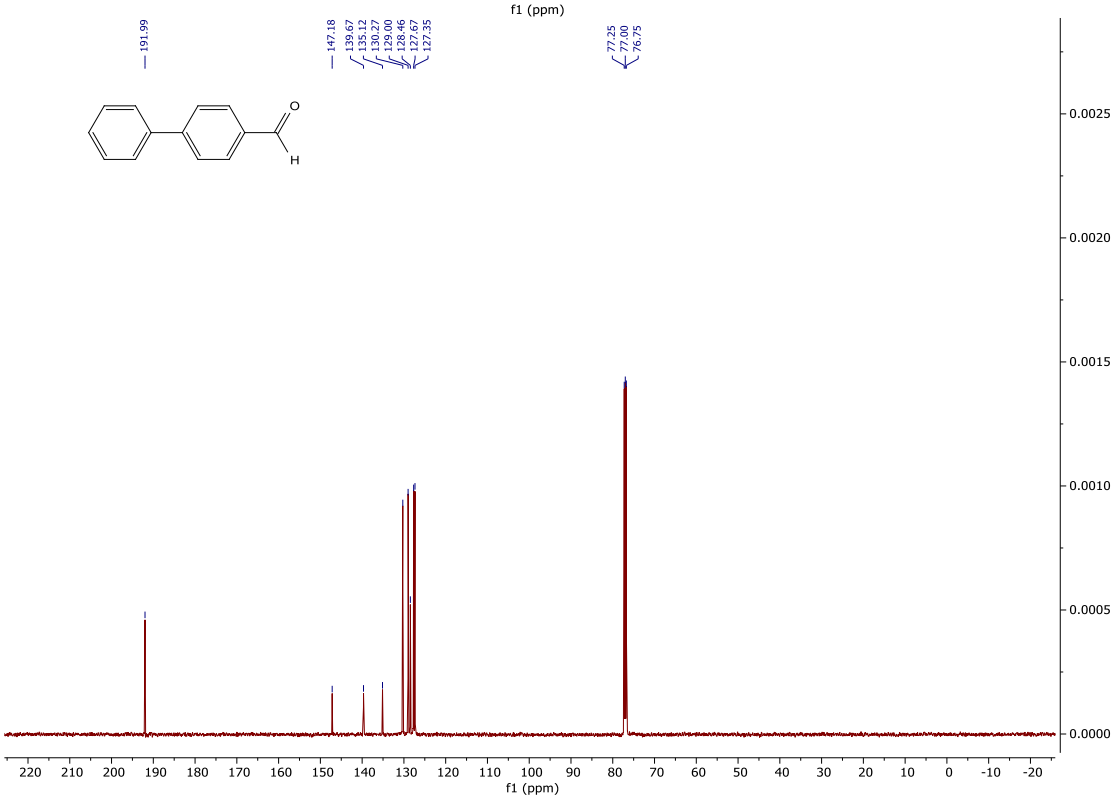
^{1}H (400 MHz) and ^{13}C{1H} (100 MHz) spectra of 3ac in $CDCl_3$:



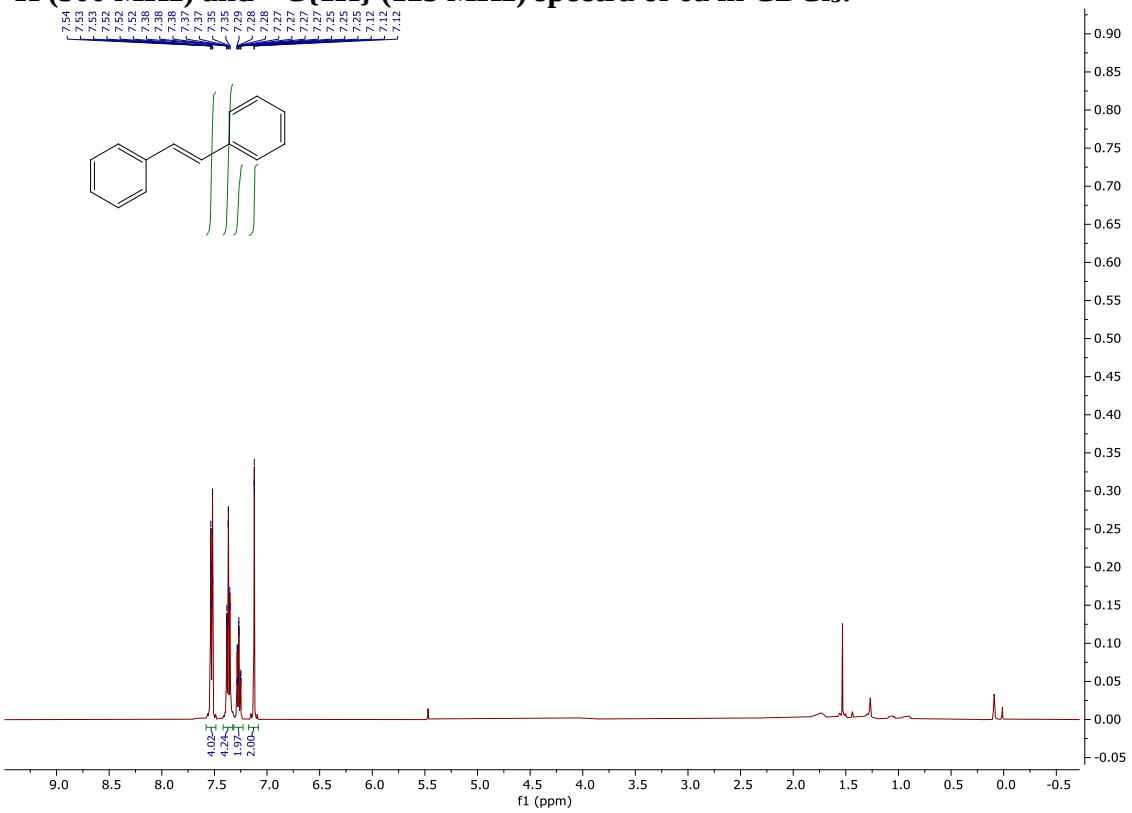


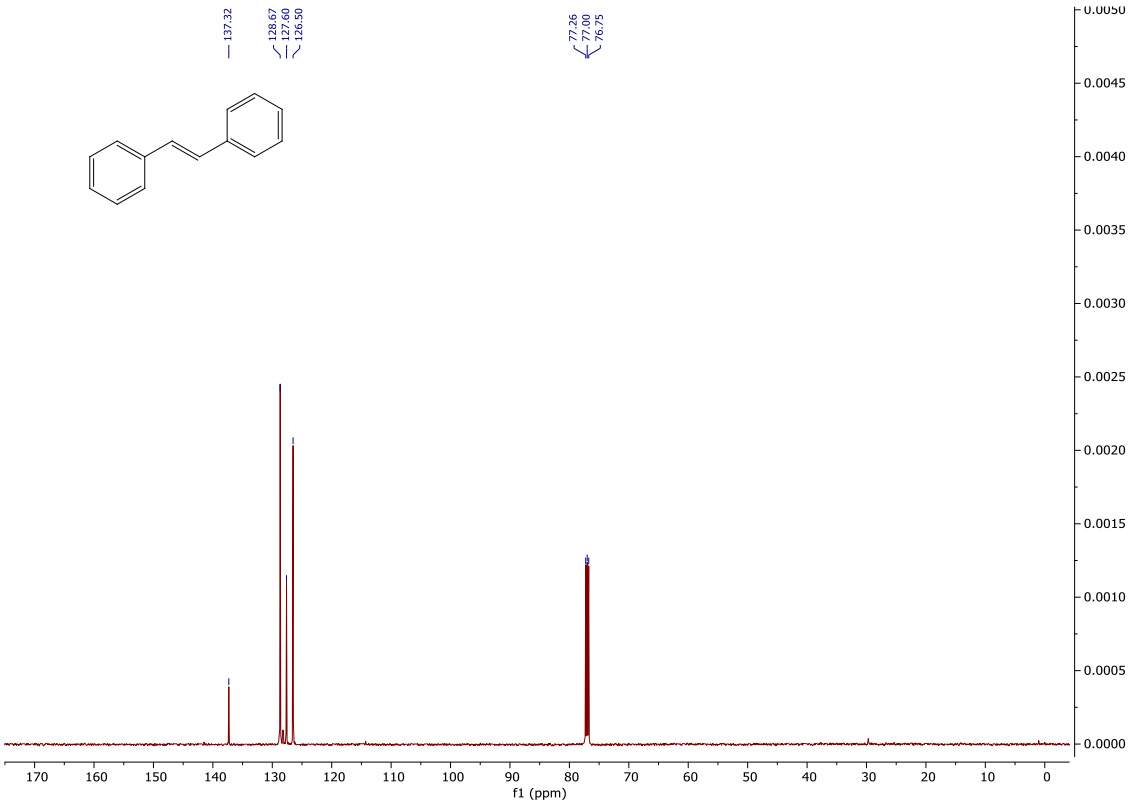
^{1}H (500 MHz) and $^{13}C\{1H\}$ (125 MHz) spectra of 3ae in $CDCl_3$:



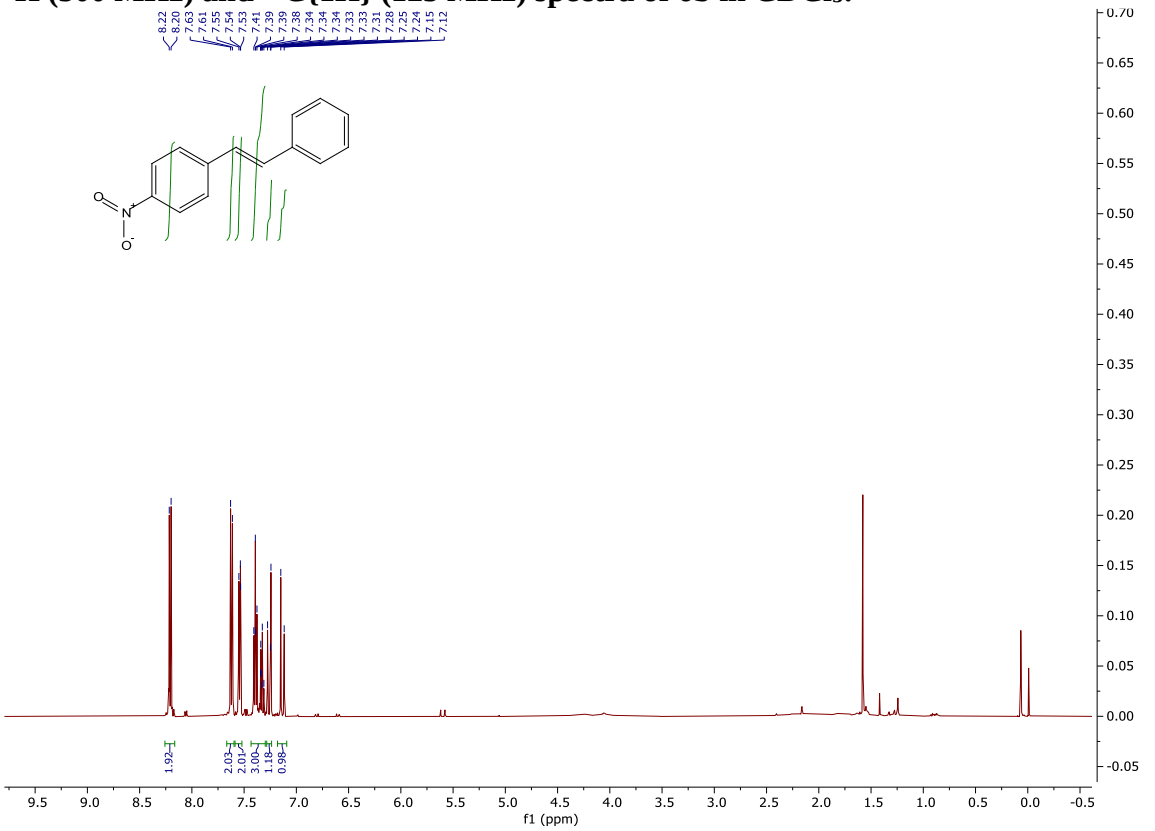


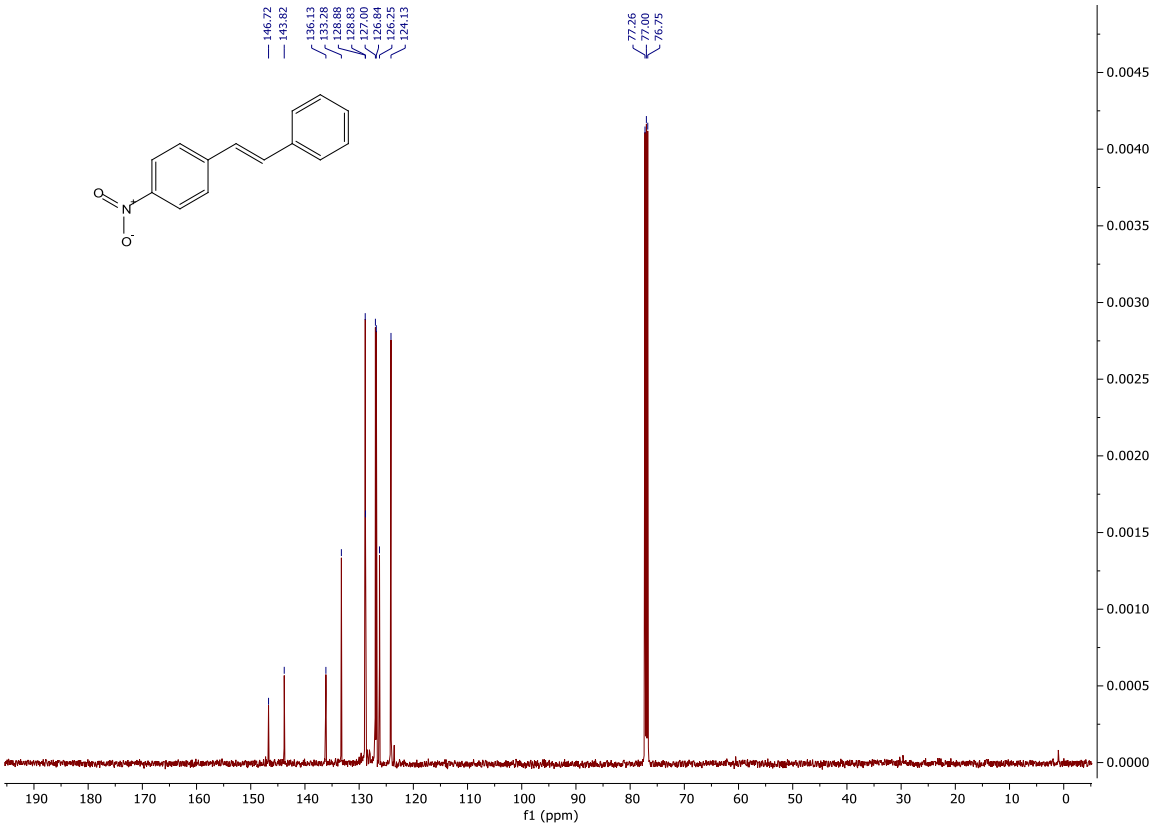
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6a in $CDCl_3$:



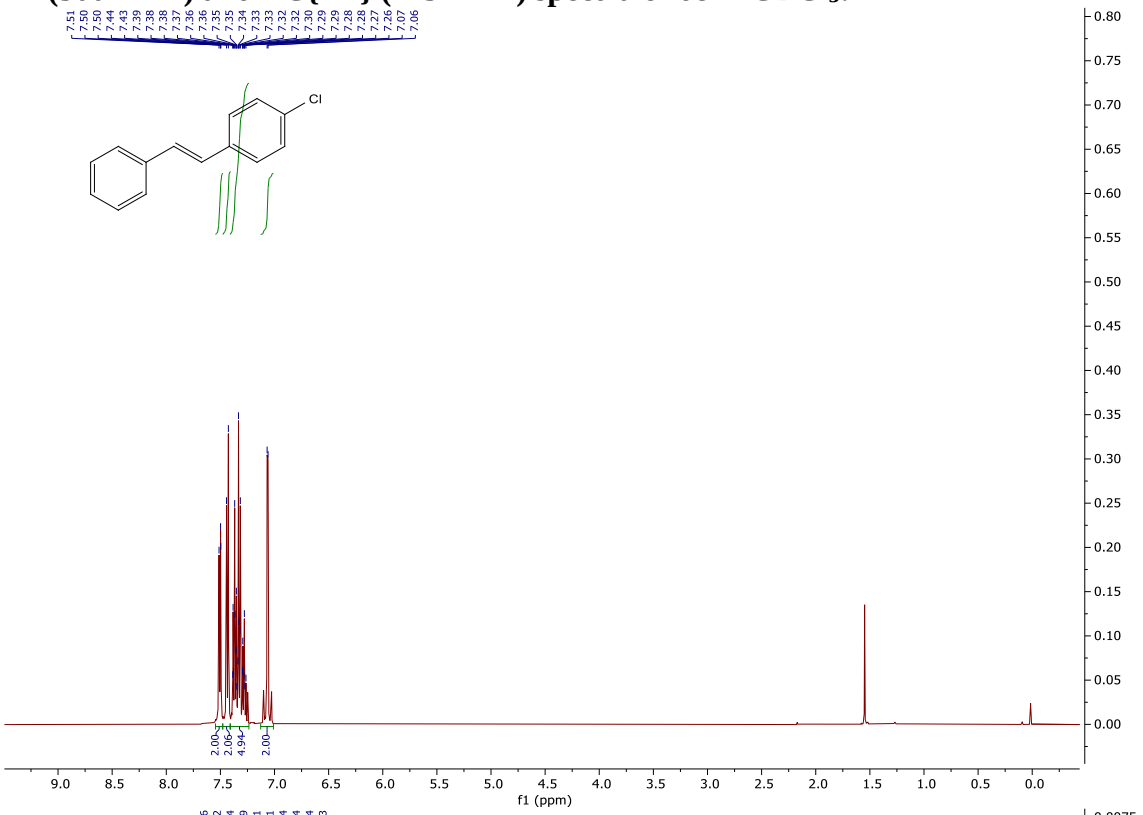


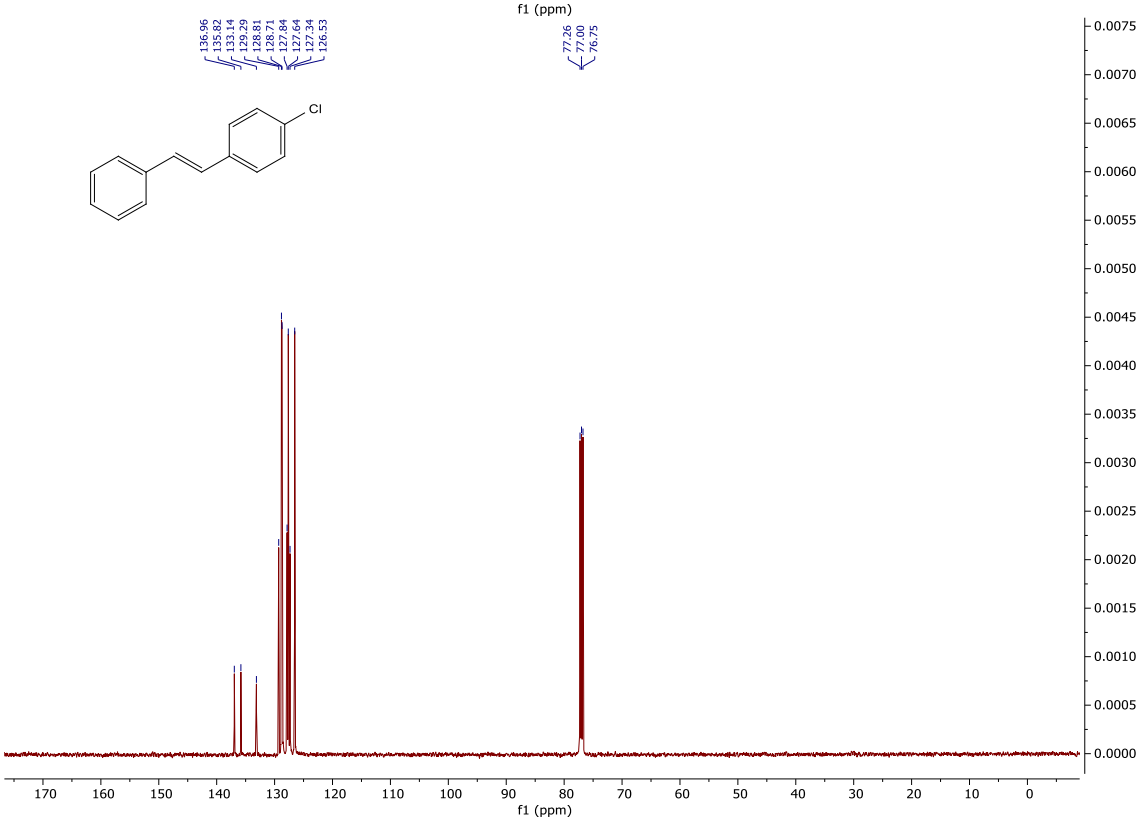
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6b in $CDCl_3$:



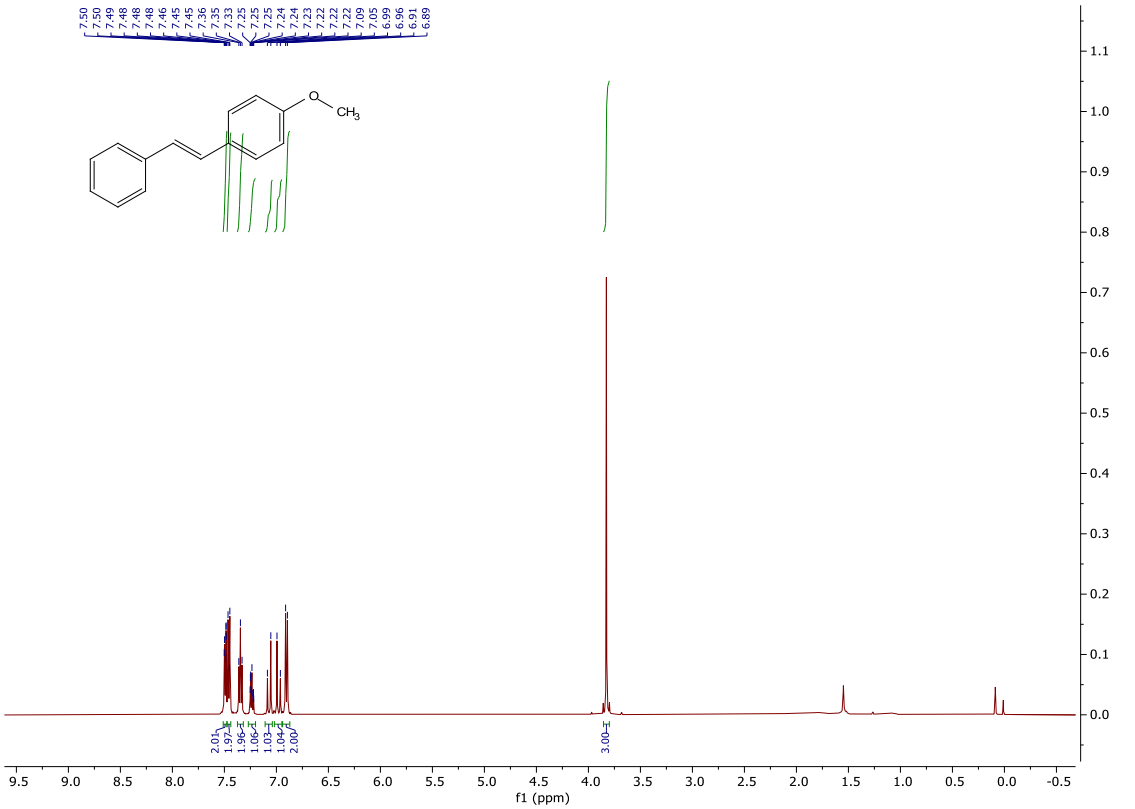


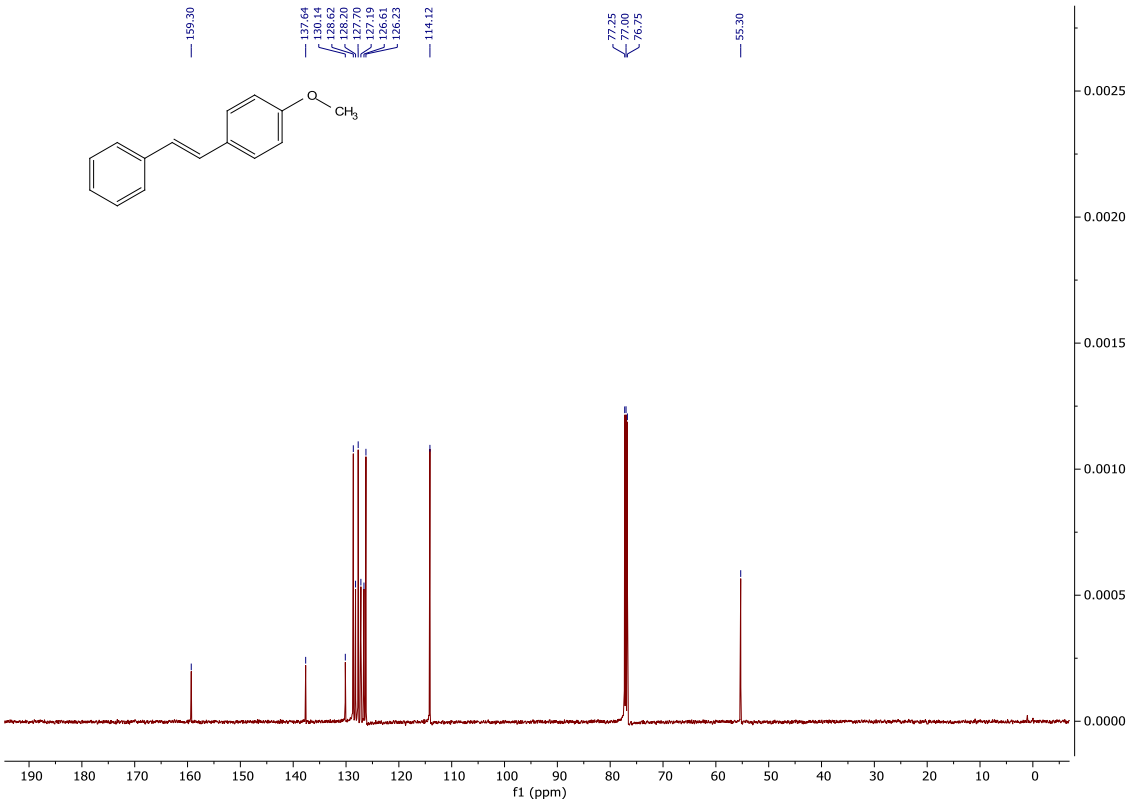
^{1}H (500 MHz) and $^{13}C\{1H\}$ (125 MHz) spectra of 6c in $CDCl_3$:



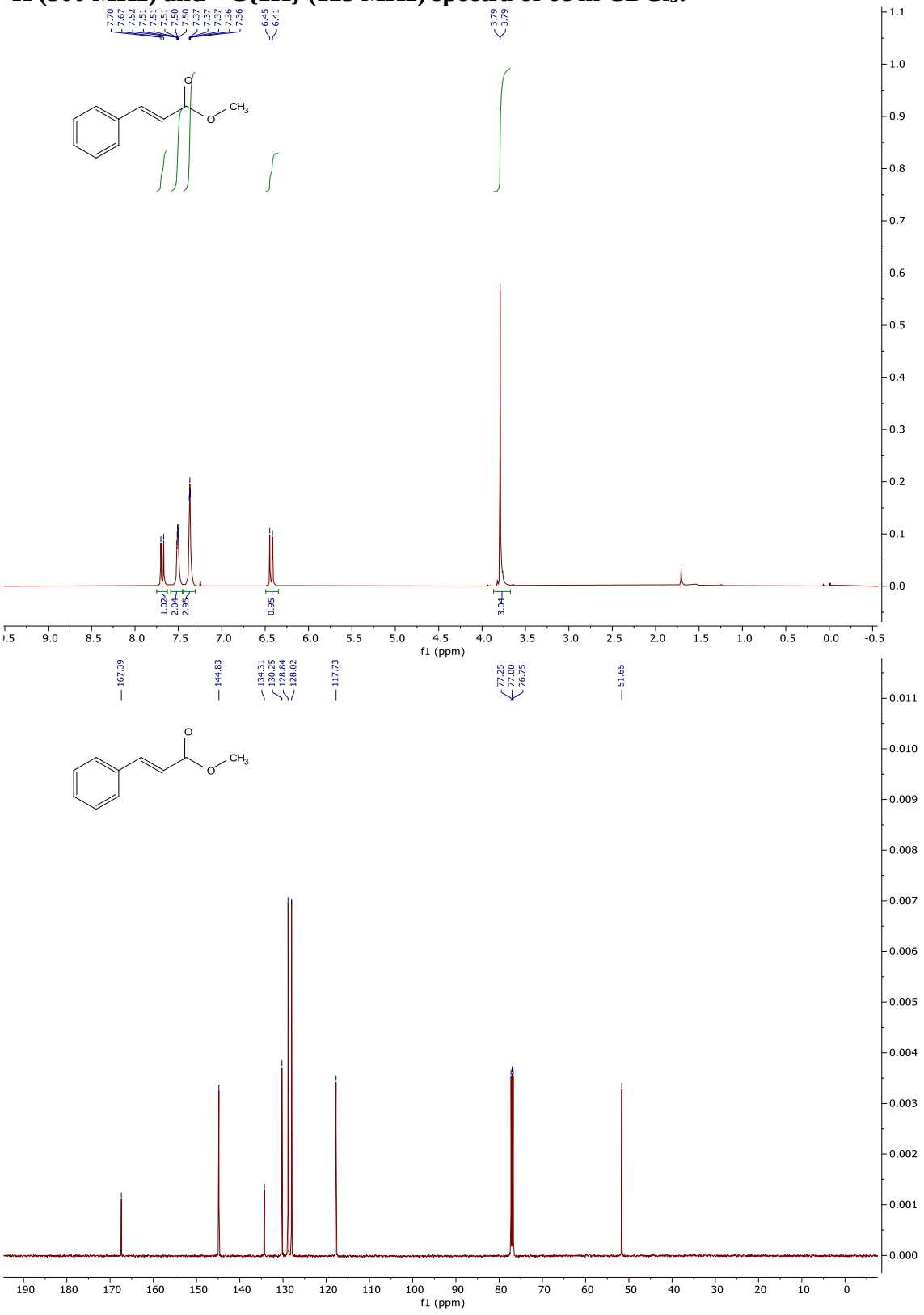


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6d in $CDCl_3$:

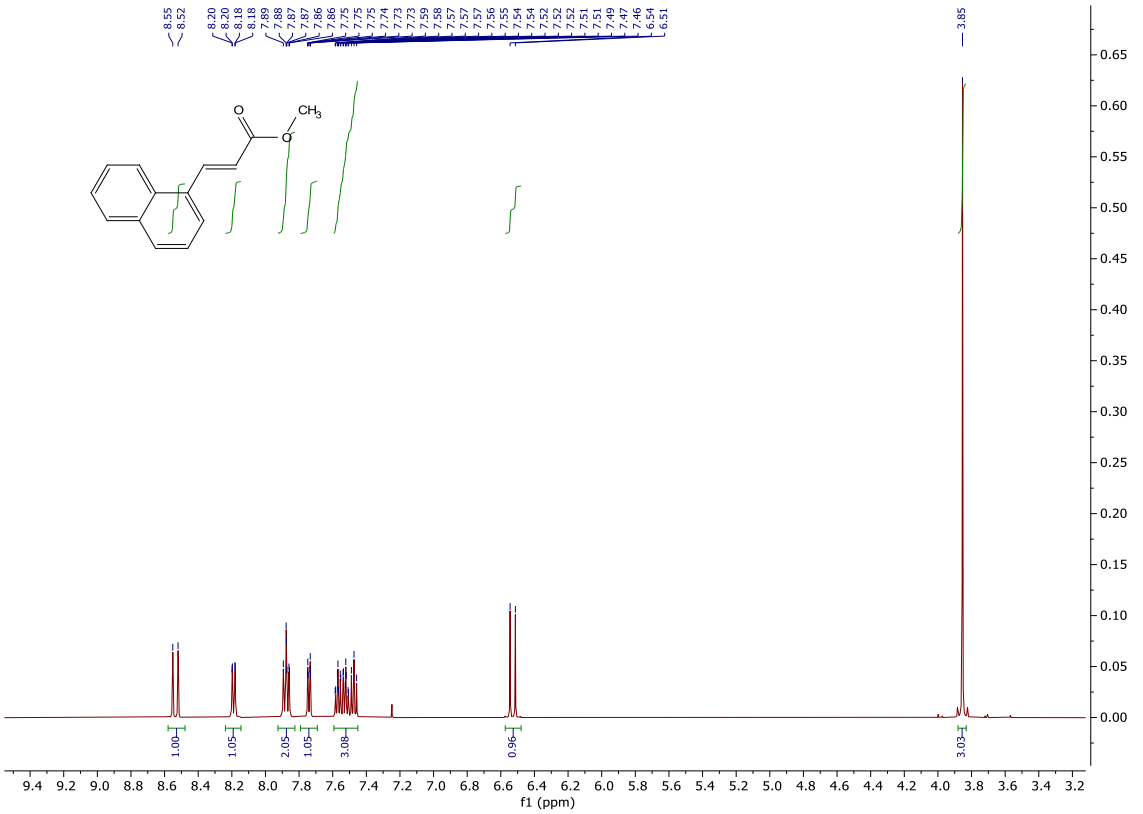


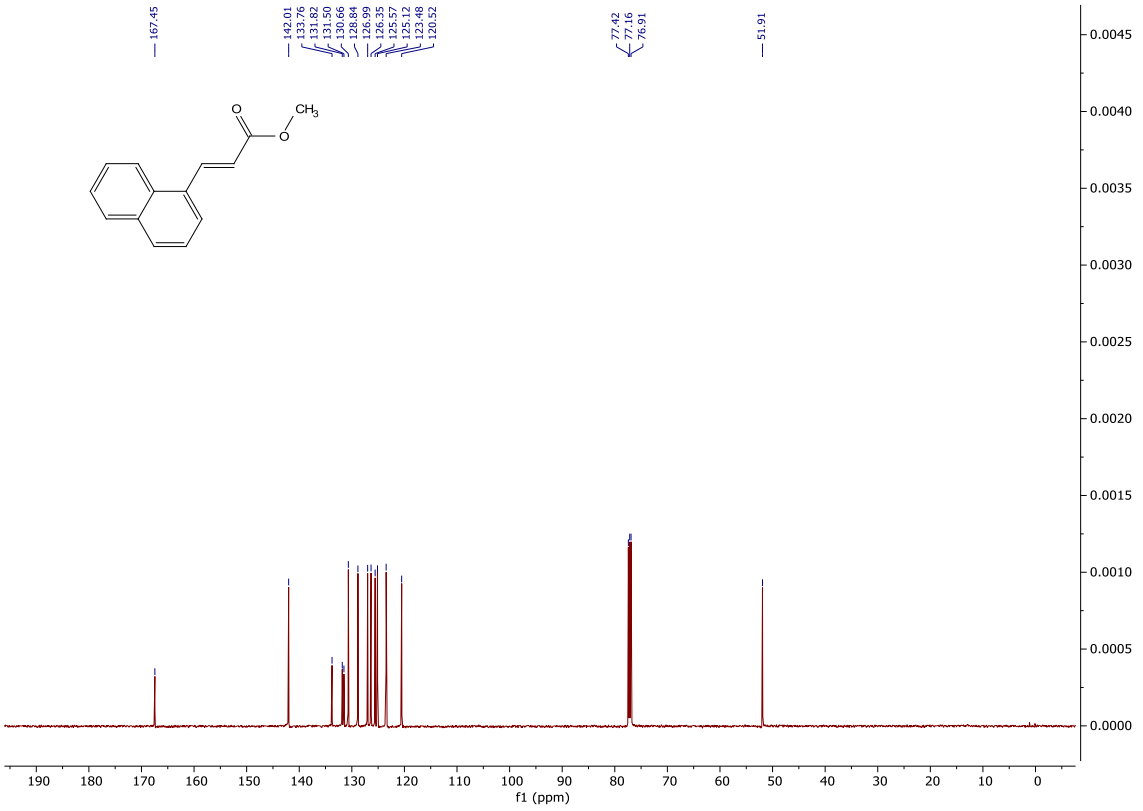


^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6e in $CDCl_3$:

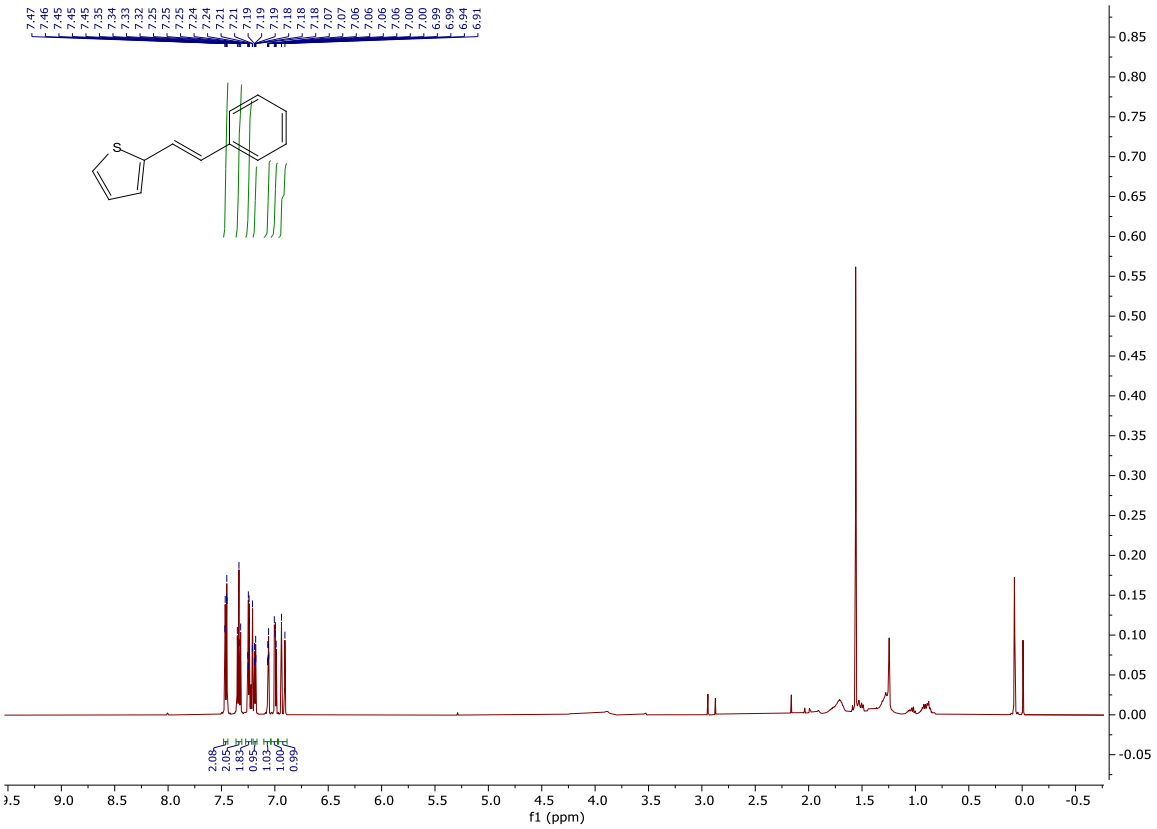


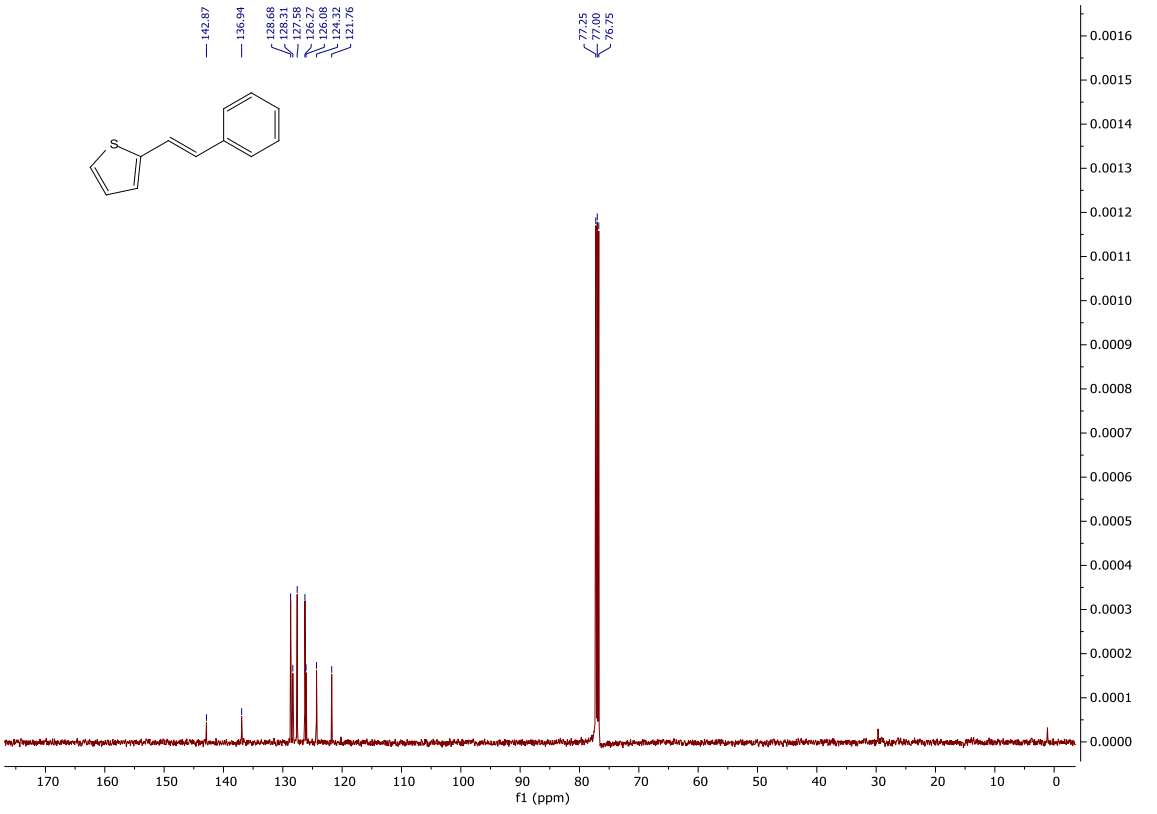
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6f in $CDCl_3$:



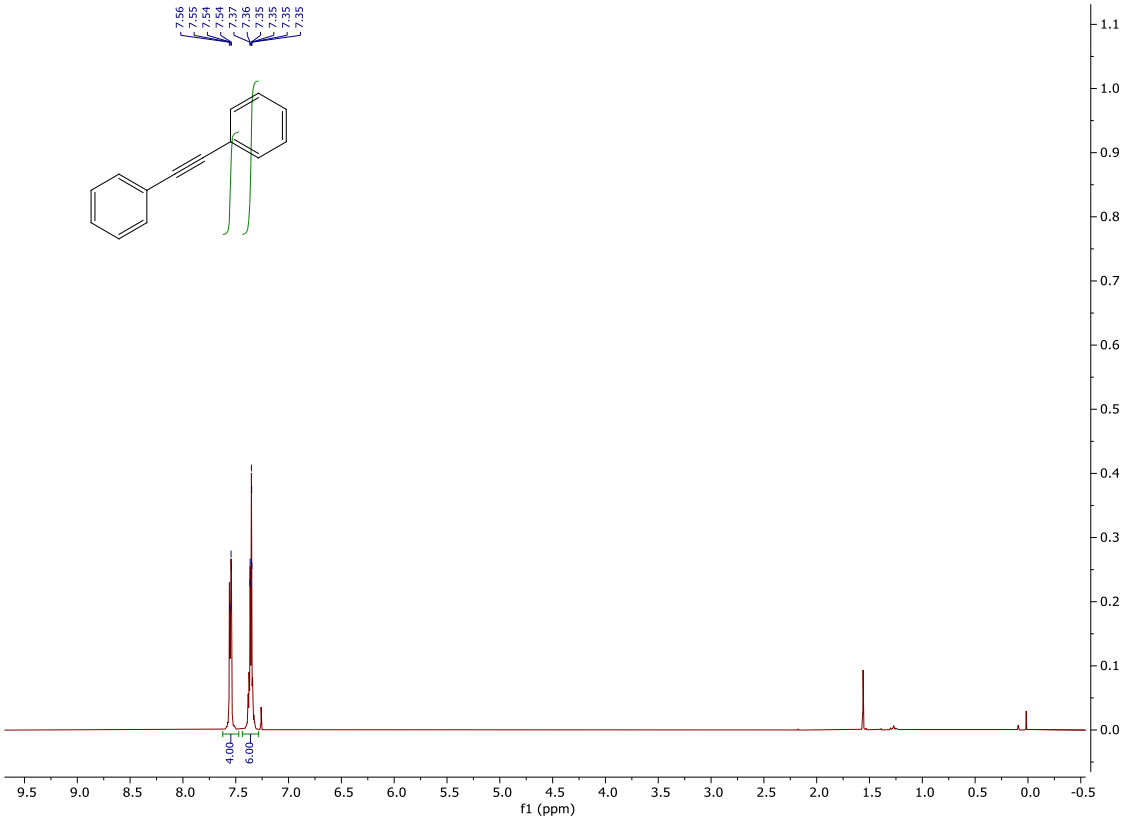


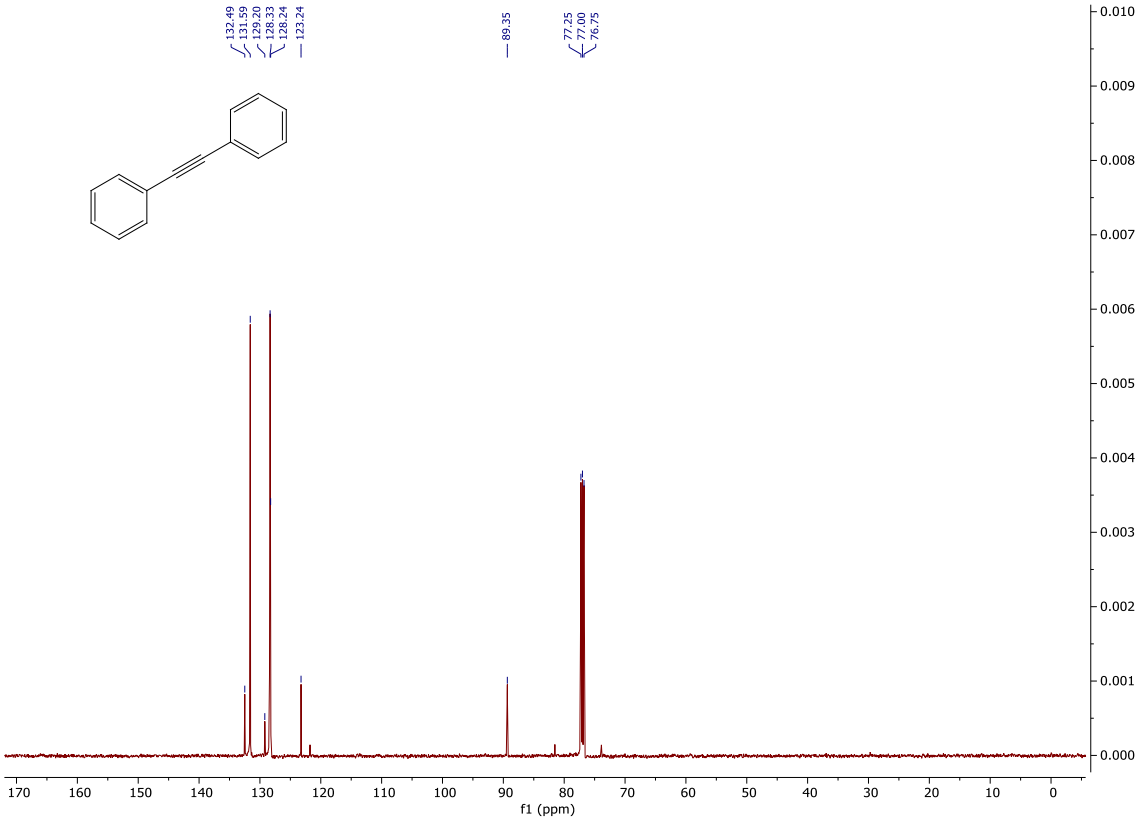
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 6g in $CDCl_3$:



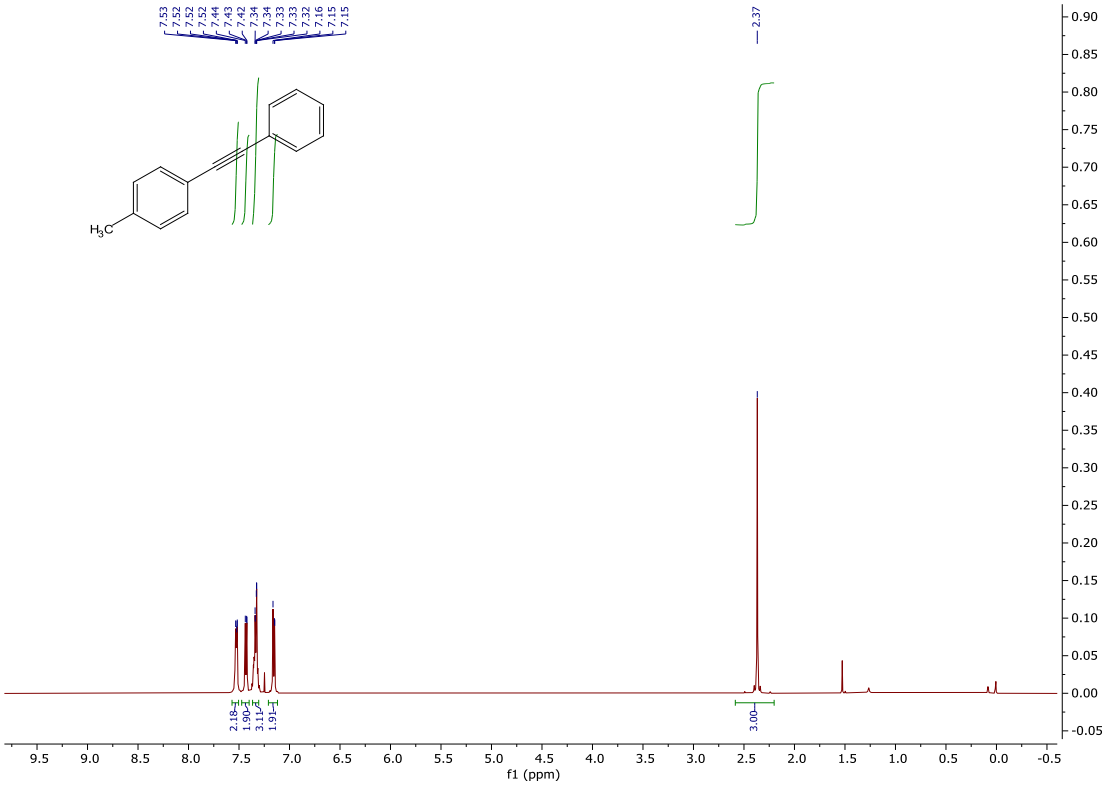


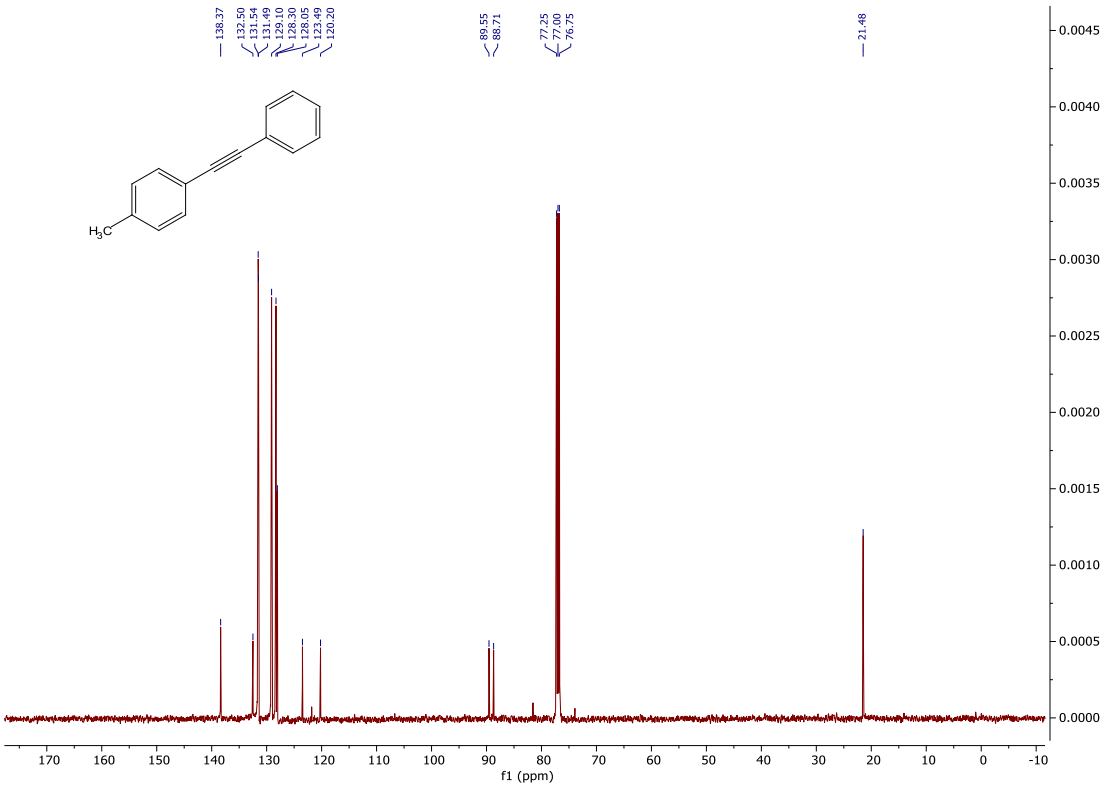
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 8a in $CDCl_3$:



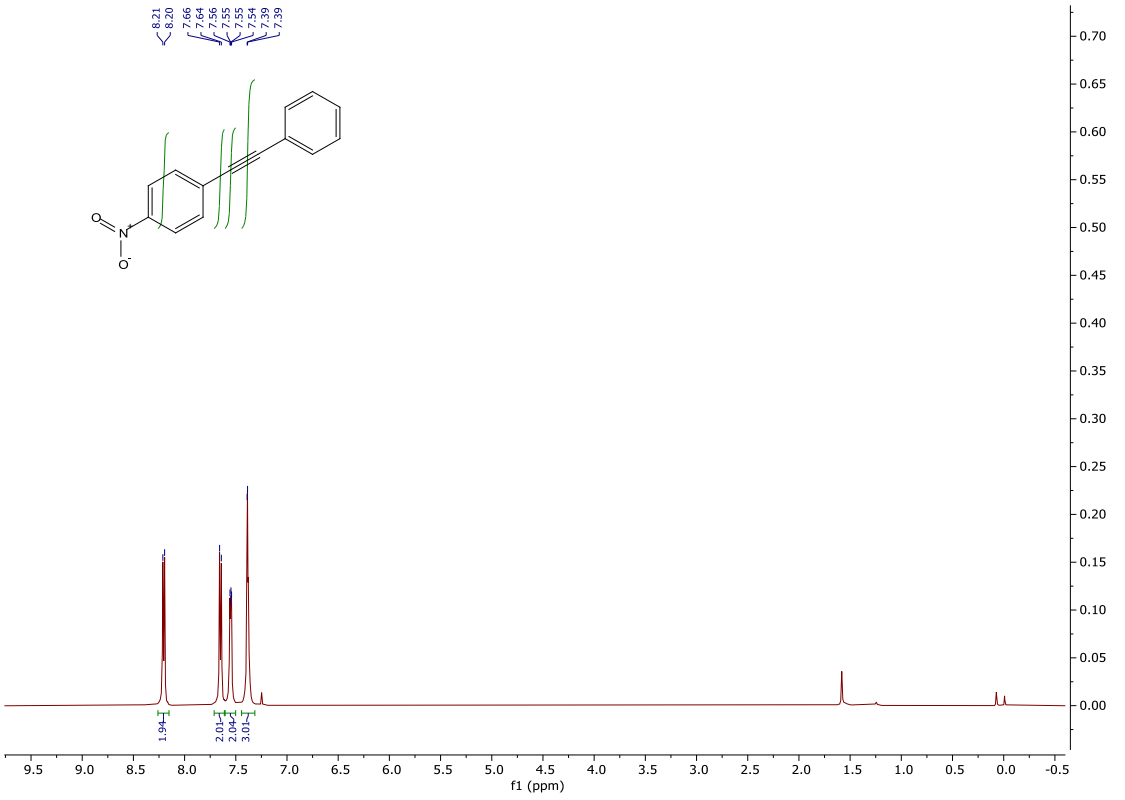


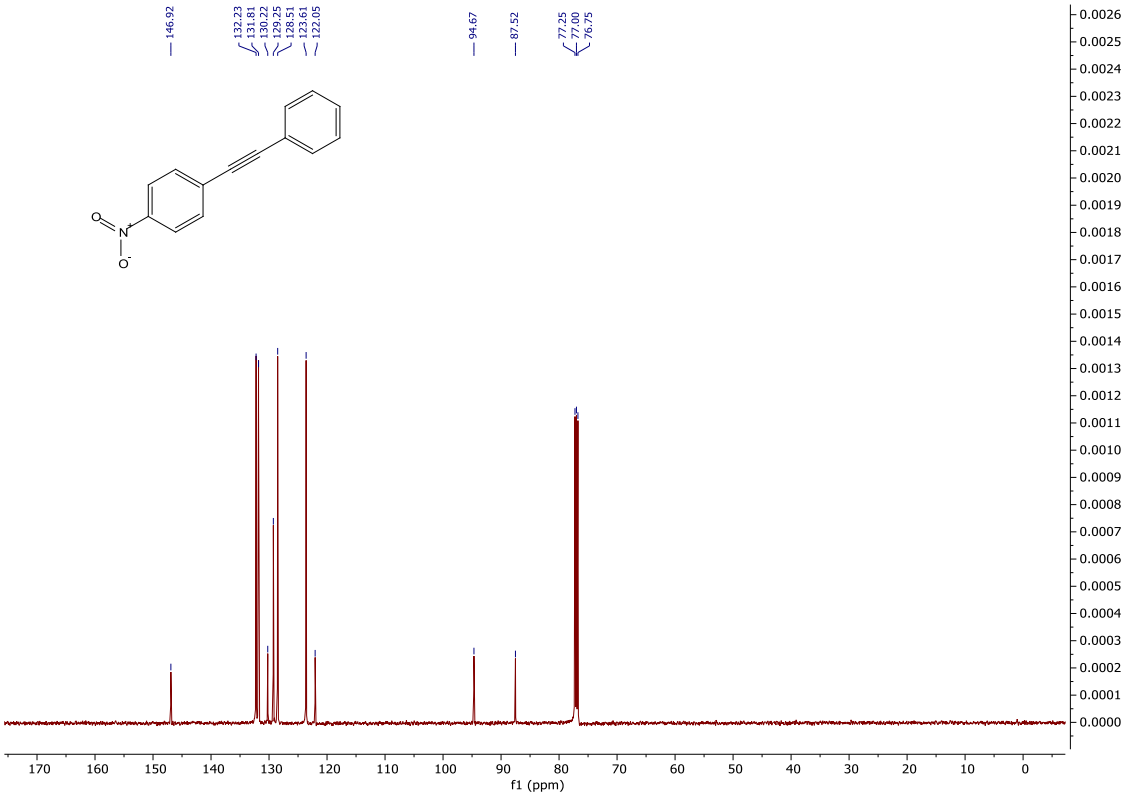
^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 8b in $CDCl_3$:





^{1}H (500 MHz) and ^{13}C{1H} (125 MHz) spectra of 8c in $CDCl_3$:





^{1}H (400 MHz) and ^{13}C{1H} (125 MHz) spectra of 8d in $CDCl_3$: