Ionic liquid mediated Pd-free biaryls synthesis catalysed by *in-situ* generated nickel nano particles

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General Information: All starting materials and solvents were purchased from common commercial sources and were used without additional purification [($NiCl_2.6H_2O$, CAS No 7791-20-0, Merk), (1-methyl imidazole , CAS No 616-47-7, Sigma-Aldrich), ($NaBH_4$, CAS No 16940-66-2, Sigma-Aldrich), (1-chlorooctane, CAS No CAS RN: 111-85-3, TCI), (NaOH palletes, CAS No 1310-73-2 , Merk), toluene CAS No 108-88-3, Merk). To maintain palladium free environment, each and every apparatus such as glassware, spatula, round bottomed flask, magnetic bead used for the reaction is subjected to acid wash and oven dried. All reactions were carried out under atmospheric conditions and reported yields are all isolated yields. Aluminium sheets pre-coated with silica gel 60F254 (Merck) were used for thin layer chromatography (TLC) to visualize products under 254 nm UV light. Column chromatography was executed on silica gel (120–230 mesh) to obtain isolated yields. All ^{1}H-NMR spectra were recorded on 500 MHz and ^{13}C on 125 MHz spectrometer using TMS as an internal standard. Chemical shifts are reported in parts per million (ppm, δ). The Transmission Electron Microscope (TEM) analysis was performed by using JEOL JEM-F200 TEM model, Scanning Electron Microscopes (SEM) was performed by using FESEM, JEOL, JSM-7600F, X-Ray Photoelectron Spectrometer (XPS) analysis was performed by using ESCALAB Xi+ model, X-ray Diffraction (XRD) analysis was performed using Bruker D8 Advance model. Both ^{1}HNMR and ^{13}CNMR NMR Spectrometer were recorded on Bruker Advance 500MHz. Mass spectra are recorded on Thermo-Scientific Mass Spectrometer TSQ Endura model.

1. Synthesis of IL: 1-Methyl-3-octyl imidazolium chloride [OMIM][Cl]:

Equimolar mixture of 1-methylimidazole (10 g, 121.80 mmol) and 1-chlorooctane (18.11 g, 121.80 mmol) was stirred at 80 °C for near 10-15 h. After the accomplishment of the reaction, two distinct layers of liquids were found to be observed and IL layer was collected from that. Subsequently repeated wash of that layer was performed with ethyl acetate to remove excess 1-chlorooctane and residual viscous layer therefore obtained was [OMIM][Cl][1].

2. General experimental procedure for Suzuki reaction:

In a round bottomed flask, a mixture comprising with aryl halide (0.5 mmol, 1 equiv.), arylboronic acid (0.75 mmol, 1.5 equiv), nickel precursor (5 mol%), $NaBH_4$ (0.25 mmol, 0.5 equiv.), base (1 mmol, 2 equiv.) and IL (0.25 mmol, 0.5 equiv.) was stirred in toluene (1.5ml) for 5 h at 110 ºC as mention in **Scheme 4** in the manuscript. Consequently, the reaction solution was extracted three times with ethyl acetate (3 × 10 mL). The reaction mixture were purified by silica gel column chromatography using n-hexane/ethyl acetate (9:1 v/v) to get the desired

coupling products. The progress of the reaction was monitored by TLC. The products were characterized by ^{1}H NMR and LC-MS.

3. Additional analyses data

3.1 Average particle size distribution from HRTEM image

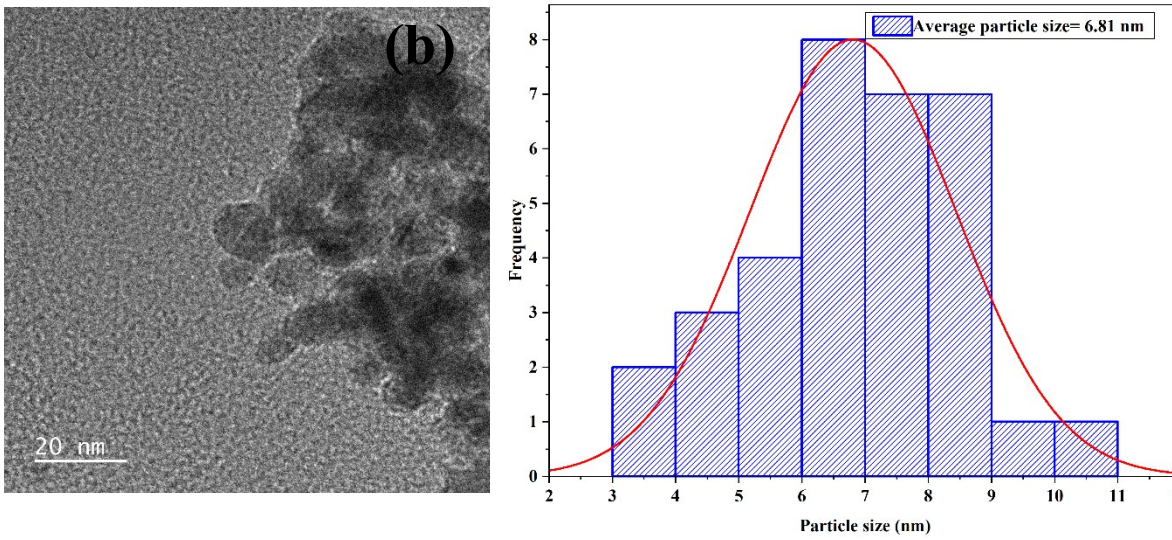


Figure S1: **(a)** High resolution transmission electron microscope (HRTEM) image of Ni NPs. **(b)** Average particle size distribution curve

3.2 d-spacing calculation of Ni NPs from SAED pattern

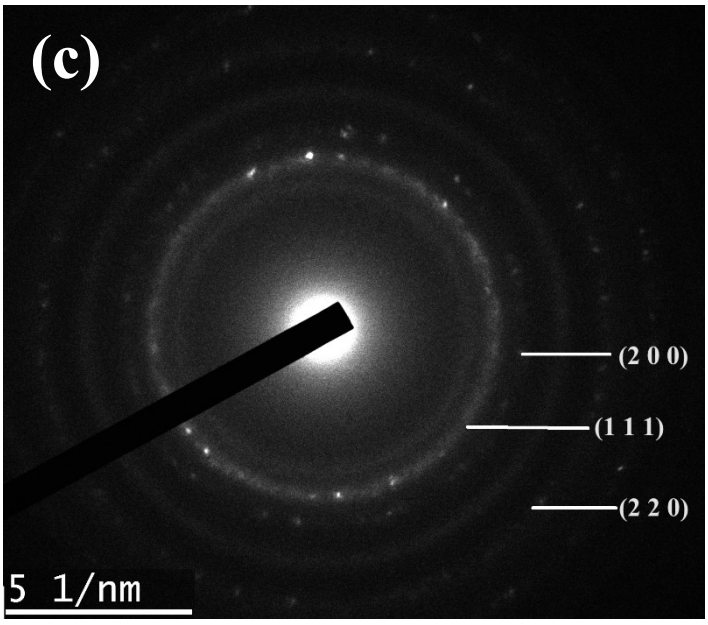
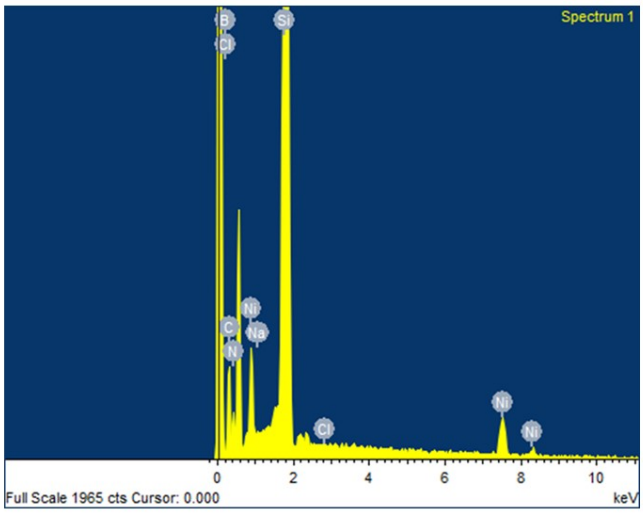


Fig. S2: **(c)** SAED pattern of Ni NPs.

Table S1: d-spacing calculation of Ni NPs from SAED pattern.

Sl. No.	1/D (nm^{-1})	1/r (nm^{-1})	r (nm)	d-spacing (Å)	(h k l)
1	9.127	4.5635	0.21913	2.19	(1 1 1)
2	10.587	5.2935	0.188911	1.88	(2 0 0)
3	15.53	7.765	0.128783	1.28	(2 2 0)

3.3: EDAX spectrum of the sample



Elements	Weight%	Atomic%
B K	323.37	86.44
C K	28.67	6.90
N K	16.13	3.33
Na K	0.07	0.01
Si K	31.83	3.27
Cl K	-0.01	0.00
Ni K	1.01	0.05

Fig. S3: EDAX spectrum of the sample.

3.4 Elemental mapping of the sample

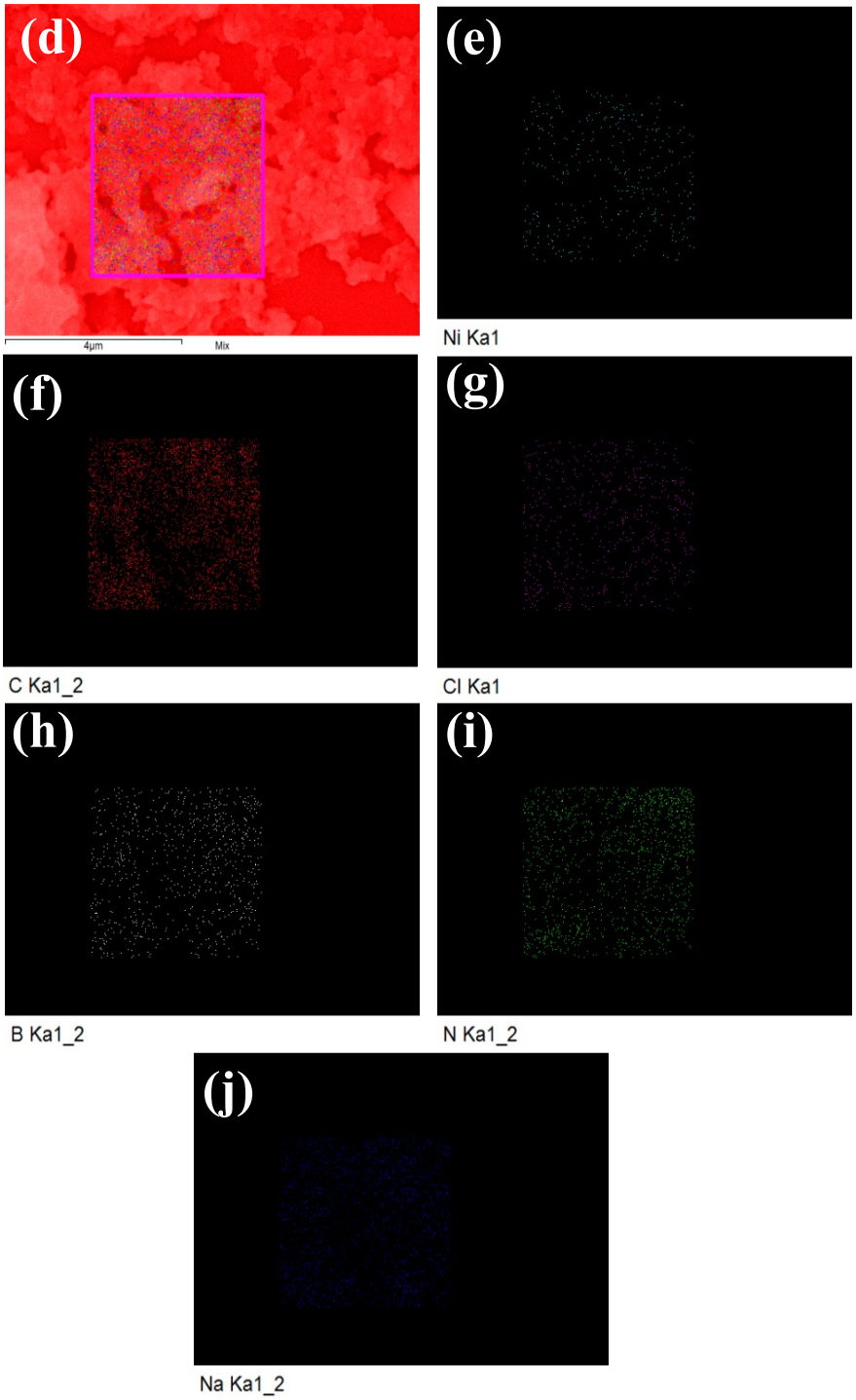


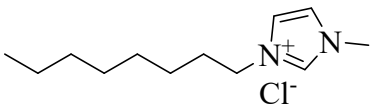
Figure S4: (d) Elemental mapping of the sample. (e), (f), (g), (h), (i) and (j) are showing elemental mappings of Ni, C, Cl, B, N & Na present in the sample respectively.

4. Salient features of the developed methodology compared to literature report:
A comparative study showing the advantages of this protocol over other reported Pd-free methods

Literature	Catalyst	Reaction conditions	Yield (%)	Substrate scope
Wu *et al.*[6] (2011)	Phosphine Dendrimer stabilized Nickel nanoparticles	THF/60 ºC/36 h	99	29 examples
Wang *et Al*[7] (2014)	$Ni(TFA)_2$/Ligand (PPh_3)	Imidazolium based ionic liquid : water (3:1)/ 80 ºC / 18 h	96.7	25 examples
Boit *et Al*[8] (2017)	$Ni(cod)_2$(5 mol%)/N-heterocyclic carbene (NHC) ligand (10 mol%)	Toluene/120 ºC /16 h (Prolonged time)	94	27 examples
Key *et al.*[9] (2019)	SiO2 supported nickel catalyst ([(2,2′:6′,2″-terpyridine-4′-benzoic acid)Ni(II)]Cl_2))	Dioxane/115 ºC /24 h	80	20 examples
Goldfogel *et al.*[10] (2022)	$NiCl_2.6H_2O$/ ligand (1′-bis(diphenylphosphino)ferrocene (DPPF))	Dimethylacetamide (DMAc) :methanol (9:1)/ 80 ºC 24 h	80	43 examples
This work	$NiCl_2.6H_2O$ (5 mol%)	Ionic liquid/$NaBH_4$/NaOH/ 110 ºC/5 h	95	42 examples

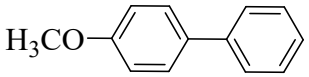
Characterization of the compounds:

1-methyl-3-octylimidazolium chloride



^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.62 (d, *J* = 12.2 Hz, 1H), 7.41 (s, 1H), 4.27 (d, *J* = 7.4 Hz, 2H), 4.09 (s, 3H), 1.94 – 1.71 (m, 2H), 1.24 (dd, *J* = 22.0, 15.3 Hz, 10H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.00, 123.62, 121.78, 50.05, 36.54, 31.60, 30.28, 28.92, 26.20, 22.50, 13.98.

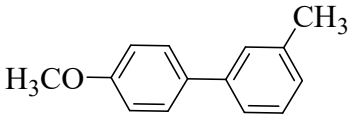
4-methoxy-1,1'-biphenyl (1)



White solid, mp- 49-51ºC, ^{1}H NMR (500 MHz, CDCl3) δ 7.43 (dd, J = 12.4, 8.0 Hz, 4H), 7.30 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 159.23, 140.86, 133.78, 128.83, 128.22, 126.80, 126.76, 114.30, 77.44, 77.18, 76.93, 55.38, 1.16. 19. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}O$ 185.09; Found 185.10

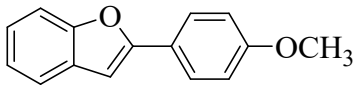
4'-methoxy-3-methyl-1,1'-biphenyl (4)



White solid, mp- 72-74ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.30 – 7.19 (m, 6H), 6.91 (d, 7.9 Hz, 2H), 3.78 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.62, 142.09, 140.31, 128.65, 128.18, 127.58, 127.28, 123.90, 122.89, 114.14, 55.46, 20.27. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}O$ 199.10; Found 199.12

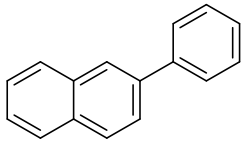
2-(4-methoxyphenyl)benzofuran (22)



White solid, mp- 146-148 ºC ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.54 (m, 3H), 7.01 (d, *J* = 8.6 Hz, 3H), 6.92 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.81, 161.79, 159.39, 130.26, 126.43, 123.76, 117.41, 114.29, 111.45, 111.00, 109.84, 99.68, 55.45. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}O_2$ 225.08; Found 225.09

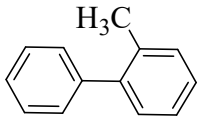
2-phenylnaphthalene (5)



White solid, mp- 94-96ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.96-7.89 (m, 3H), 7.77 (t, 3H), 7.53-7.40 (m, 5H).

^{13}C NMR (125 MHz, CDCl3) δ 128.88, 128.43, 128.22, 127.66, 127.45, 127.37, 126.31, 125.95, 125.82, 125.61. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{12}$ 205.09; Found 205.10

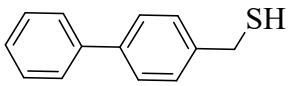
2-methyl-1,1'-biphenyl (6)



White solid, mp- 26-28 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 4H), 7.57-7.55 (m, 5H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.42, 140.53, 139.36, 132.19, 131.19, 129.62, 127.80, 126.96, 19.16. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}$ 169.09; Found 169.10

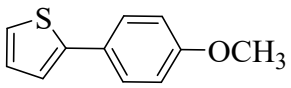
1,1'-biphenyl]-4-ylmethanethiol (14)



White solid, mp- 63-65 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 9H), 3.45 (m, 2H), 1.18 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.32, 138.63, 136.40, 135.01, 132.87, 130.29, 129.40, 128.67, 77.30, 77.05, 76.80, 34.89. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}S$ 201.06; Found 201.08

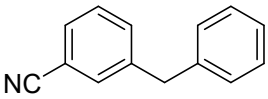
2-(4-methoxyphenyl)thiophene (21)



White solid, mp- 112-114ºC, ^{1}H NMR (500 MHz, CDCl3) δ 7.31 – 7.19 (m, 3H), 6.71 (d, J = 8.6 Hz, 2H), 3.71 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.72, 132.24, 130.77, 115.75, 112.83, 55.44. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}O$ 191.04; Found 191.06

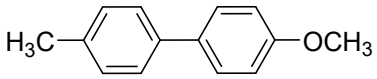
3-benzylbenzonitrile (13)



White solid, mp- 103-105 ºC, ^{1}H NMR (500 MHz, CDCl3) δ 7.75 (s, 1H), 7.56-7.42 (m, 5H), 7.19 – 6.80 (m, 12H), 4.11 (d, J = 6.2 Hz, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.39, 138.50, 133.28, 130.78, 127.25, 117.45, 111.79, 29.70. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}N$ 194.09; Found 194.10

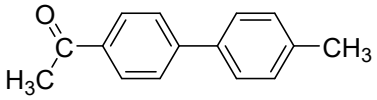
4-methoxy-4'-methyl-1,1'-biphenyl (7)



White solid, mp- 73-76 ºC, ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.50 (d, J = 36.4 Hz, 4H), 7.26 (d, J = 20.7 Hz, 2H), 6.97 (s, 2H), 3.85 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.99, 138.03, 136.43, 133.82, 129.51, 128.02, 126.65, 114.22, 55.42, 21.12. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}O$ 199.10; Found 199.11

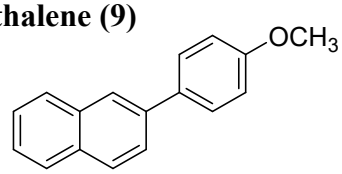
1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (10)



White solid, mp- 111-114 ºC, ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.03 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.43 (dt, J = 42.1, 7.4 Hz, 3H), 2.63 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (150 MHz, CHLOROFORM-D) δ 188.98, 145.15, 141.34, 136.79, 129.03, 129.00, 127.36, 127.31, 26.76. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}O$ 211.10; Found 211.11

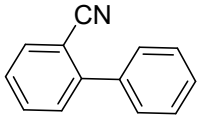
2-(4-methoxyphenyl)naphthalene (9)



White solid, mp- 139-141 ºC, ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.52-7.39 (d, *J* = 8.2 Hz, 9H), 6.97 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (150 MHz, CHLOROFORM-D) δ 159.49, 139.82, 132.58, 131.86, 128.38, 128.06, 120.86, 114.41, 55.45. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{14}O$ 235.10; Found 235.11

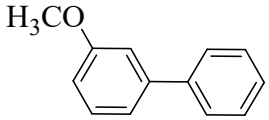
1,1'-biphenyl]-2-carbonitrile (11)



White solid, mp- 90-94 ºC, ^{1}H NMR (500 MHz, CDCl3) δ 7.77 (d, J = 7.8 Hz, 1H), 7.71-7.64 (m, 2H), 7.57-7.45 (m, 5H), 7.23 (d, J = 7.4 Hz, 1H).

^{13}C NMR (125 MHz, CDCl3) δ 134.03, 133.83, 132.86, 130.49, 130.07, 129.46, 128.76, 127.53, 127.12, 125.88. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{9}N$ 180.07; Found 185.10

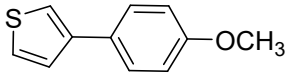
3-methoxy-1,1'-biphenyl (8)



Pale yellow solid, mp- 49-52 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.7 Hz, 2H), 7.50 – 7.19 (m, 5H), 6.96 (d, *J* = 5.5 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.00, 142.82, 141.15, 129.78, 128.77, 127.45, 127.24, 119.73, 112.96, 112.73, 55.32. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}O$ 185.09; Found 185.11

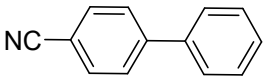
3-(4-methoxyphenyl)thiophene (18)



White solid, mp- 112-115 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.66 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.15, 141.75, 132.93, 127.74, 124.12, 114.18, 55.45. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}OS$ 191.04; Found 191.05

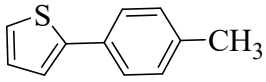
1,1'-biphenyl]-4-carbonitrile (16)



White solid, mp- 91-93 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 6H), 7.22 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.42, 142.10, 132.22, 126.57, 124.13, 120.96, 112.16. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N$ 180.07; Found 180.10

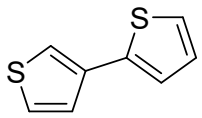
2-(p-tolyl)thiophene (19)



White solid, mp- 90-93 ºC, ^{1}H NMR (500 MHz, DMSO) δ 7.42 – 7.21 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 3H), 2.51 (s, 3H).

^{13}C NMR (125 MHz, DMSO) δ 152.65, 132.57, 130.13, 129.42, 127.98, 125.91, 122.40, 24.14. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{10}S$ 175.05; Found 175.06

2,3'-bithiophene (17)

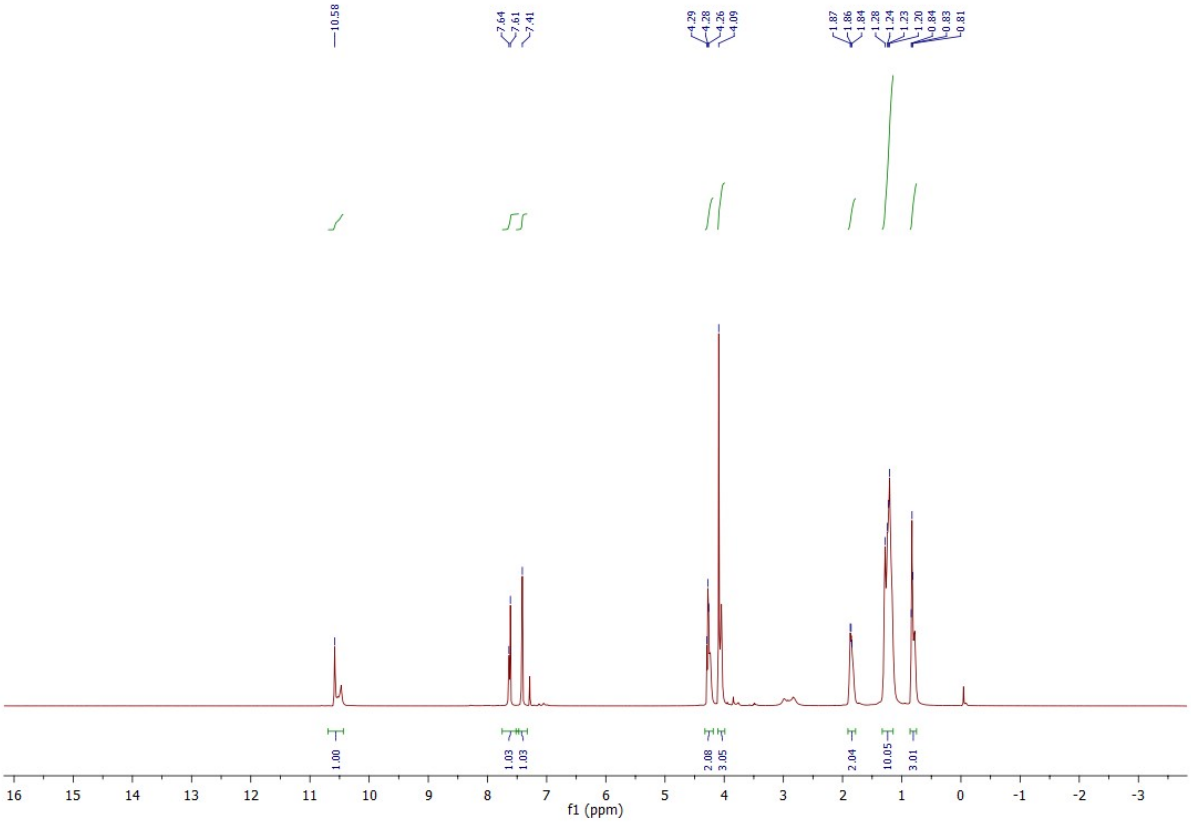


White solid, mp- 130-133 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 1H), 7.76-7.74 (m, 1H), 7.57 – 7.55 (m, 1H), 7.41 (d, *J*=8.8Hz, 2H), 6.82 (d, *J*=8.8Hz, 1H).

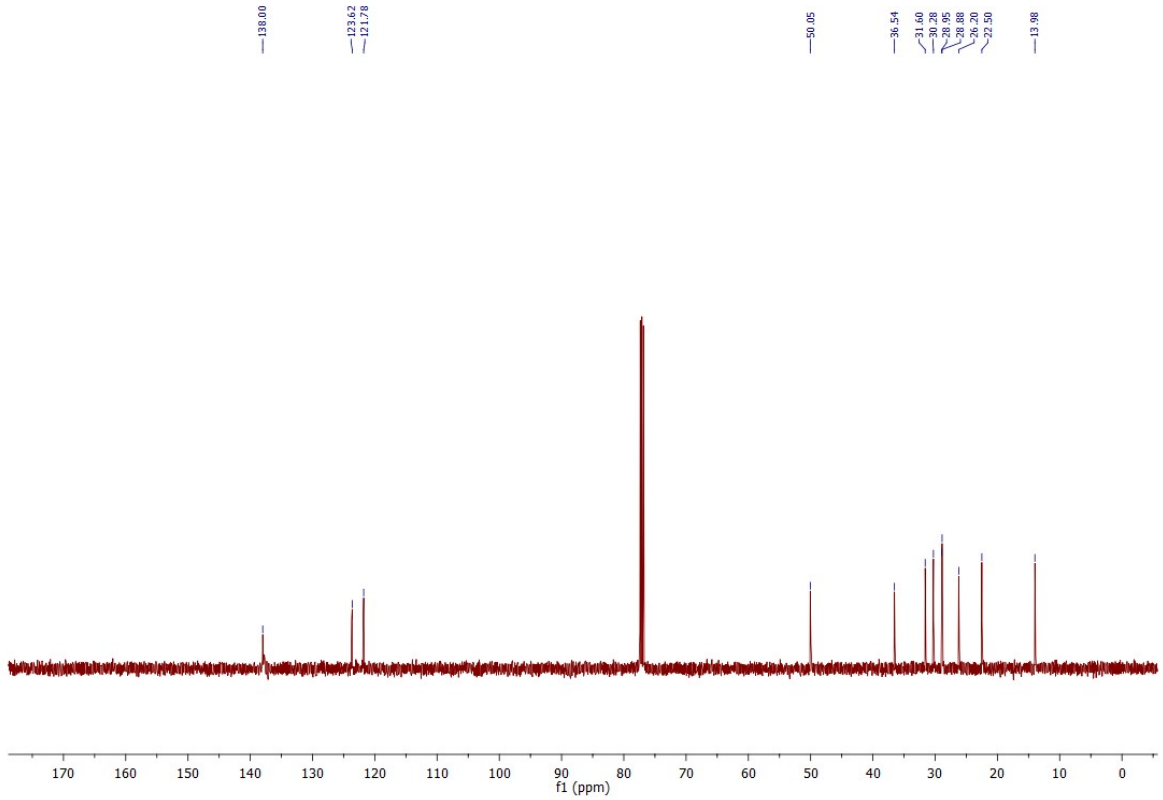
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.67, 137.87, 130.78, 130.51, 121.67.

MS (ESI) m/z: $[M+H]_+$ calcd for $C_8H_6S_2$ 167.10; Found 167.11

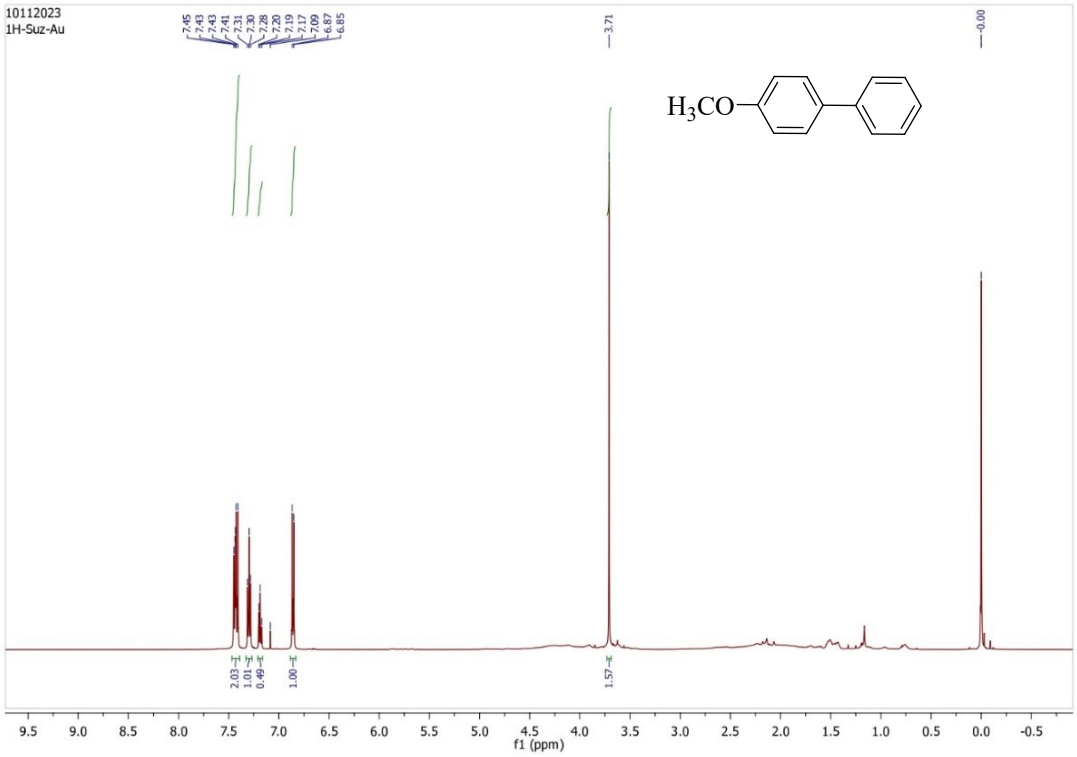
^{1}H NMR Spectrum of 1-methyl-3-octylimidazolium chloride



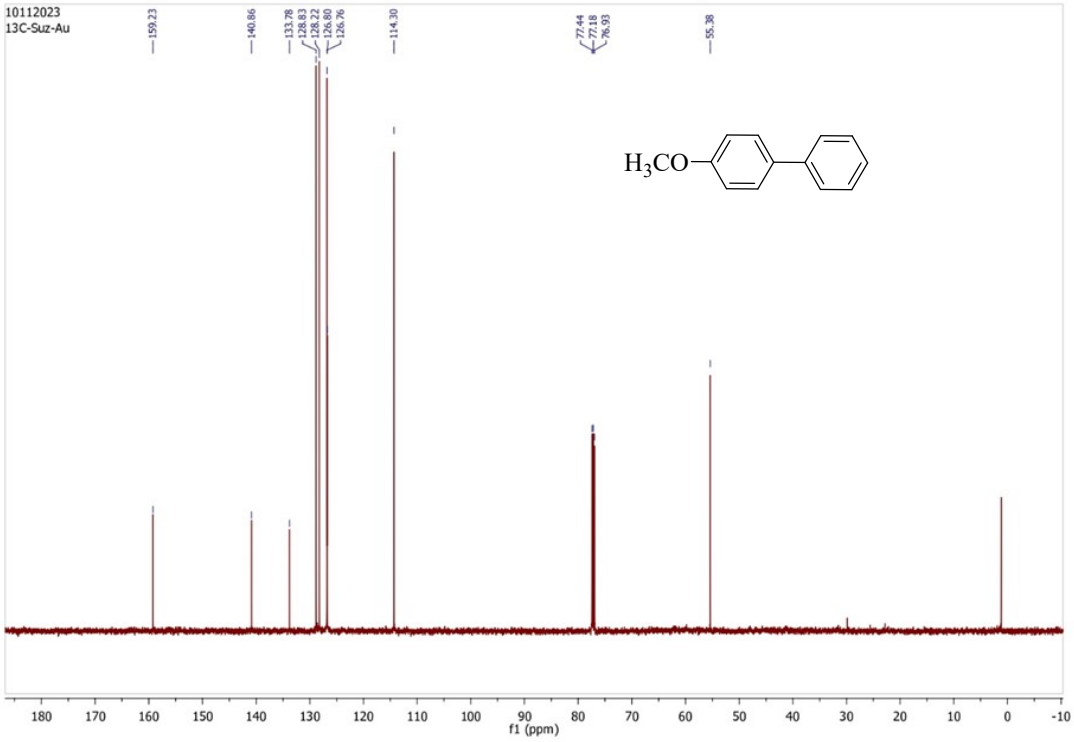
^{13}C NMR Spectrum of 1-methyl-3-octylimidazolium chloride



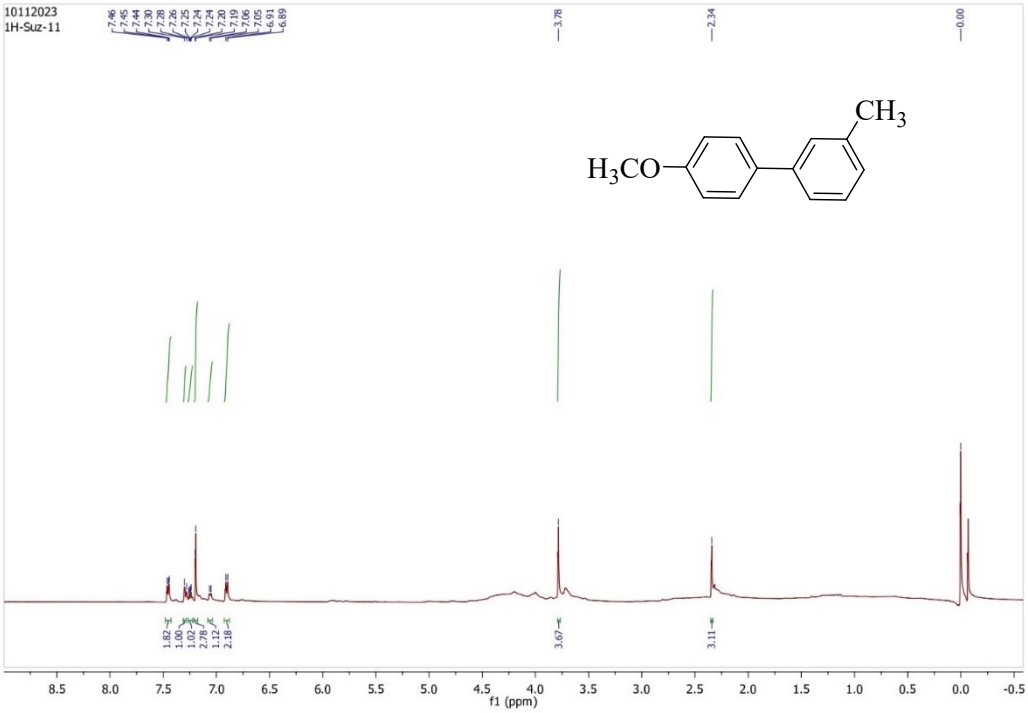
^{1}H NMR Spectrum of 4-methoxy-1, 1'-biphenyl (1)



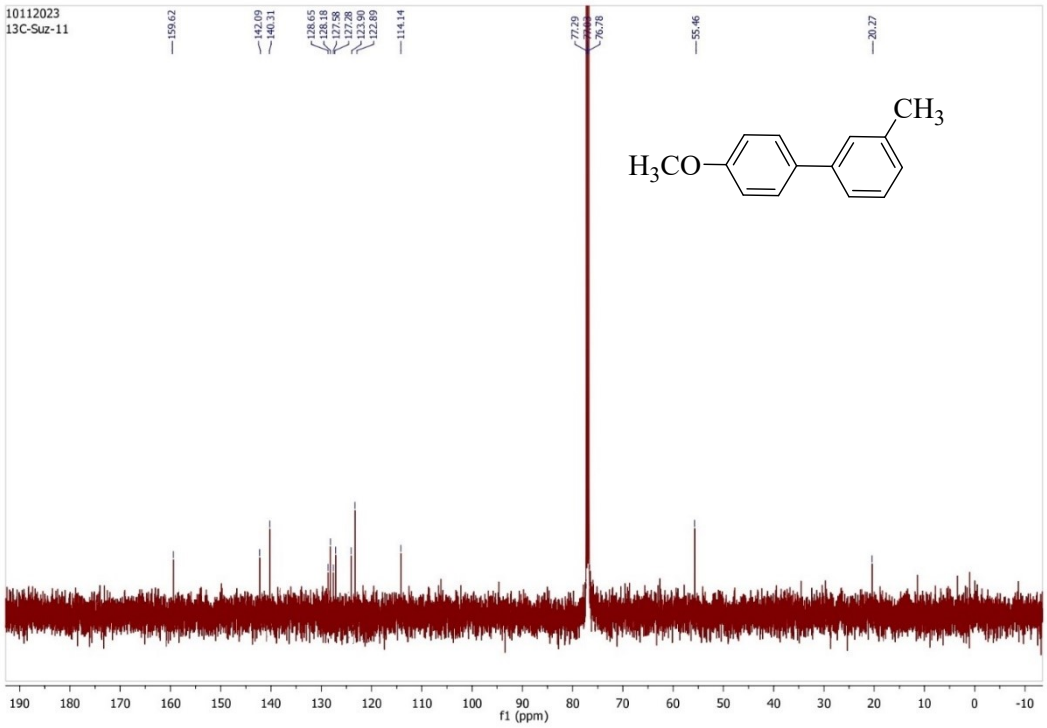
^{13}C NMR Spectrum of 4-methoxy-1,1'-biphenyl (1)



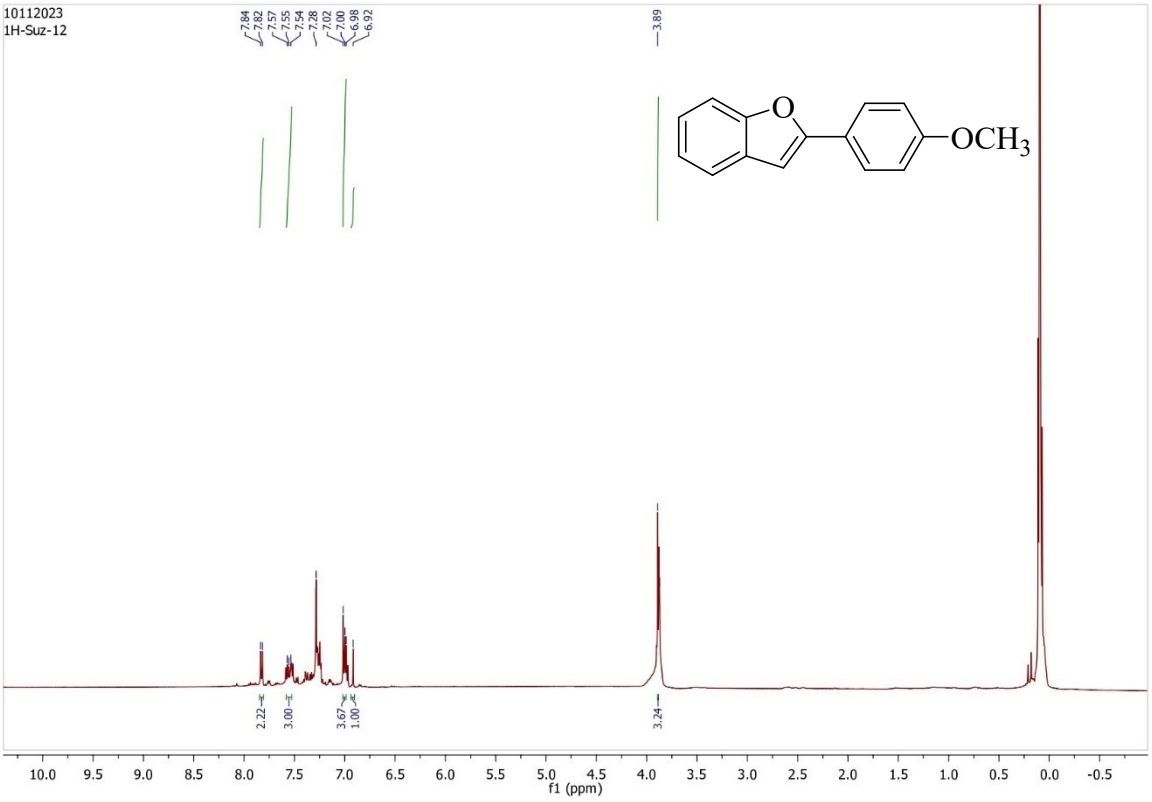
^{1}H NMR Spectrum of 4'-methoxy-3-methyl-1,1'-biphenyl (4)



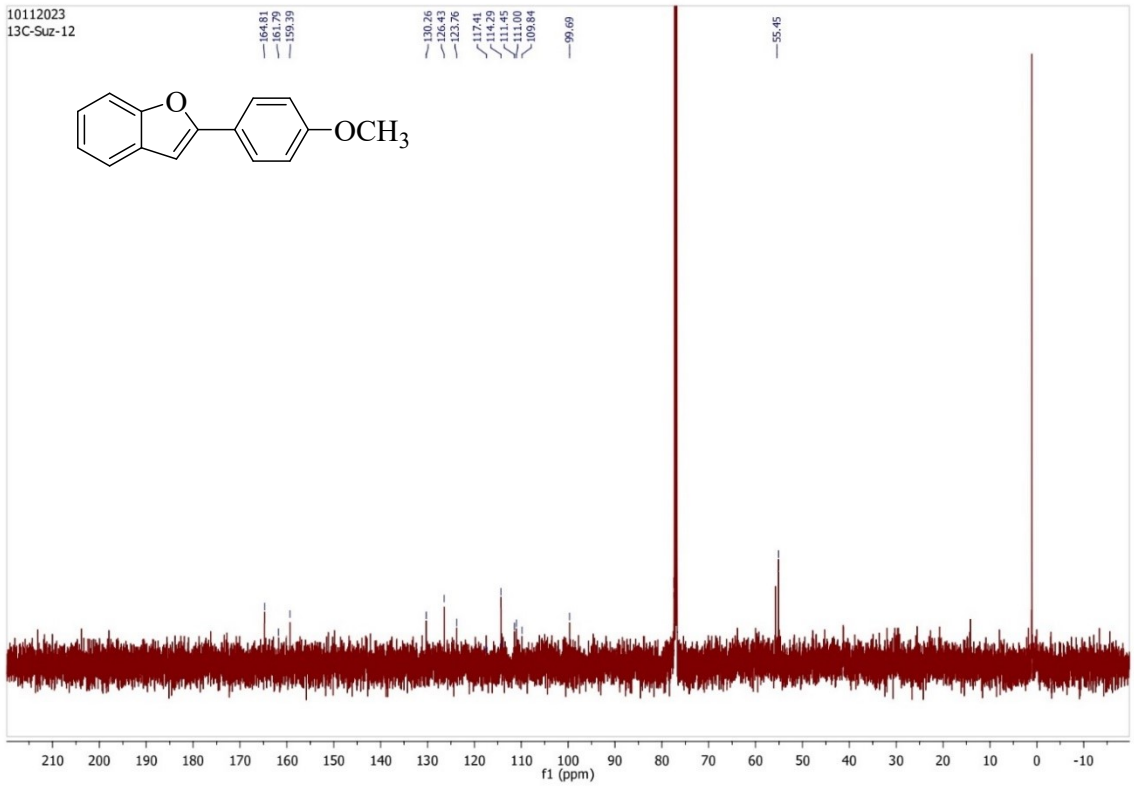
^{13}C NMR Spectrum of 4'-methoxy-3-methyl-1,1'-biphenyl (4)



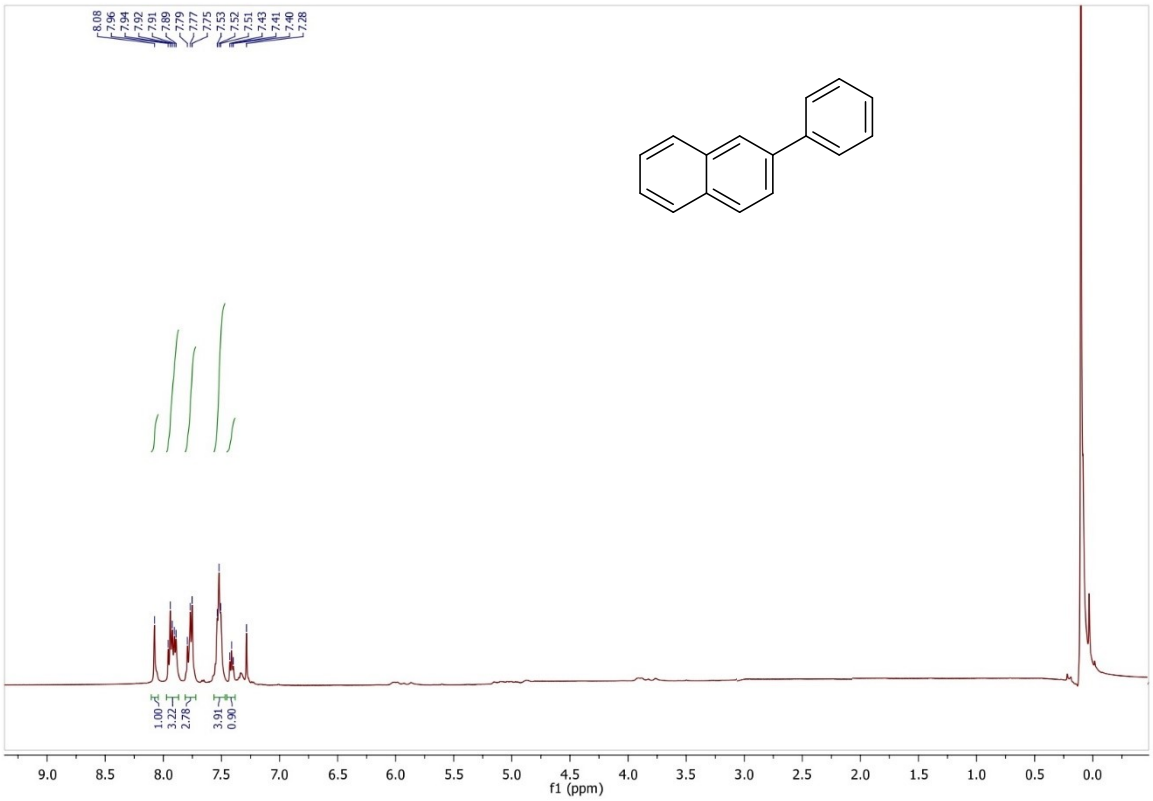
^{1}H NMR Spectrum of 2-(4-methoxyphenyl)benzofuran (22)



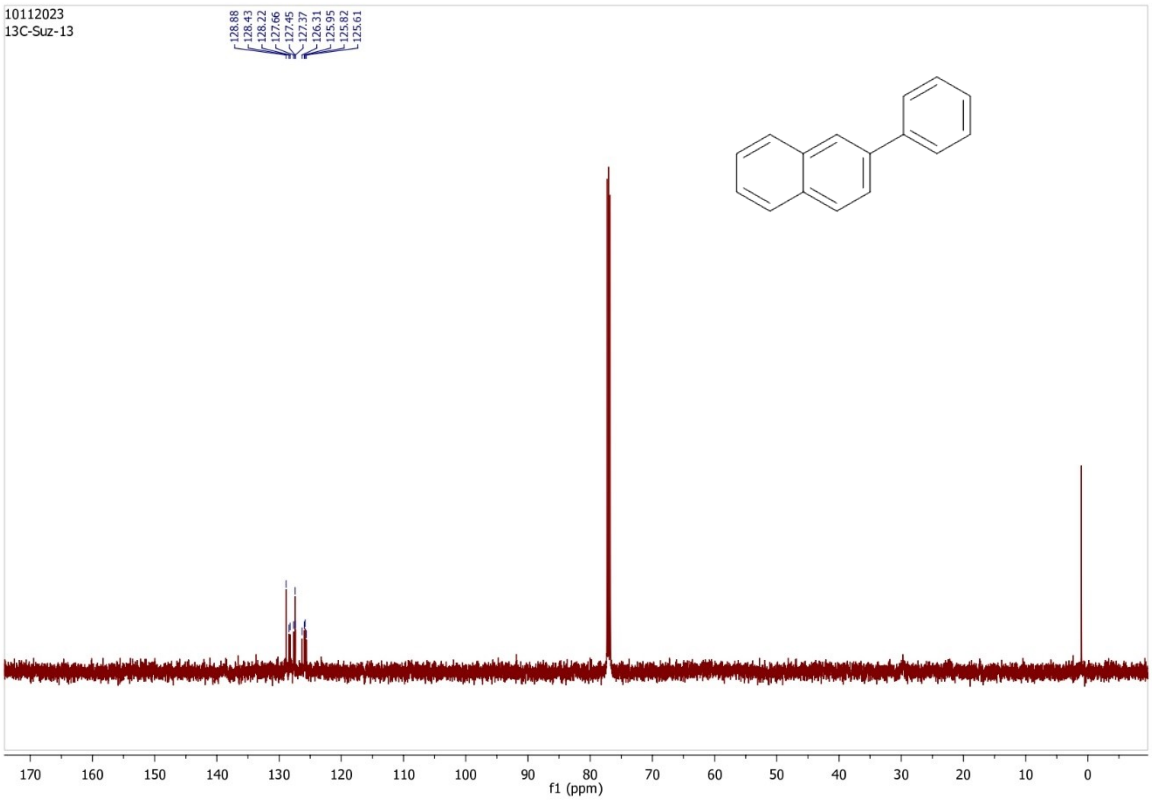
^{13}C NMR Spectrum of 2-(4-methoxyphenyl)benzofuran (22)



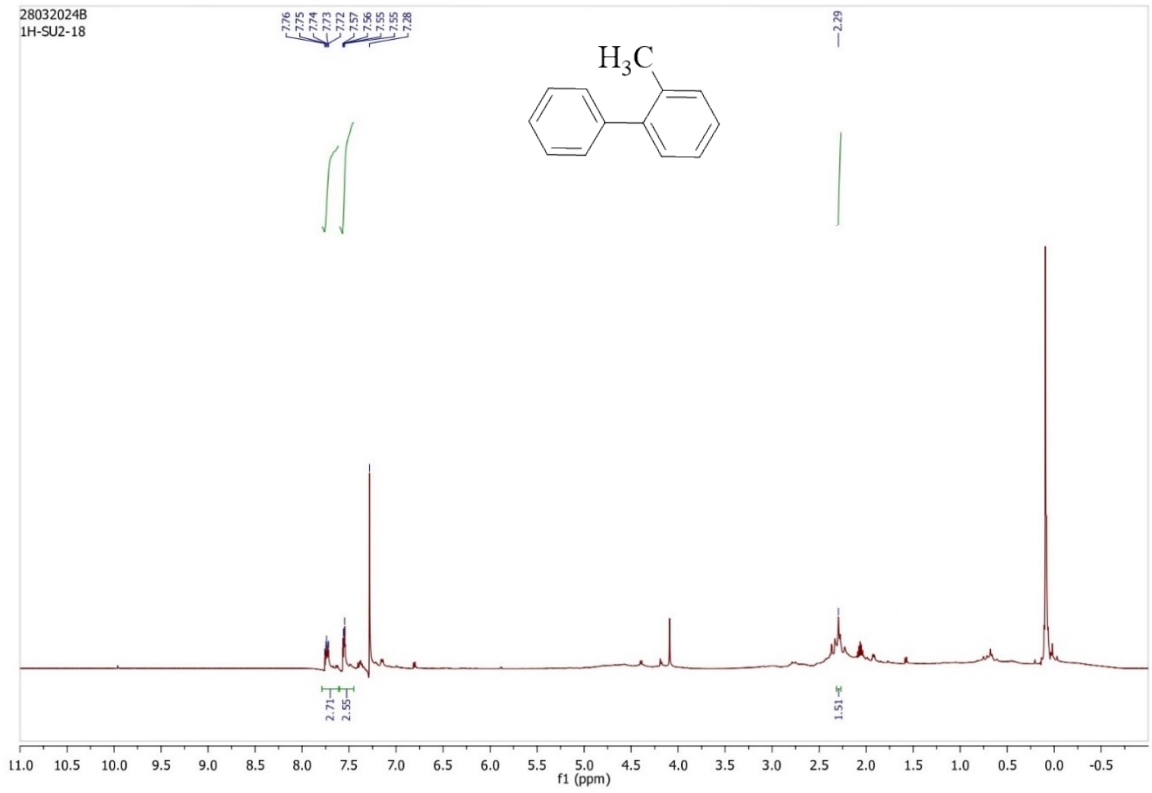
^{1}H NMR Spectrum of 2-phenylnaphthalene (5)



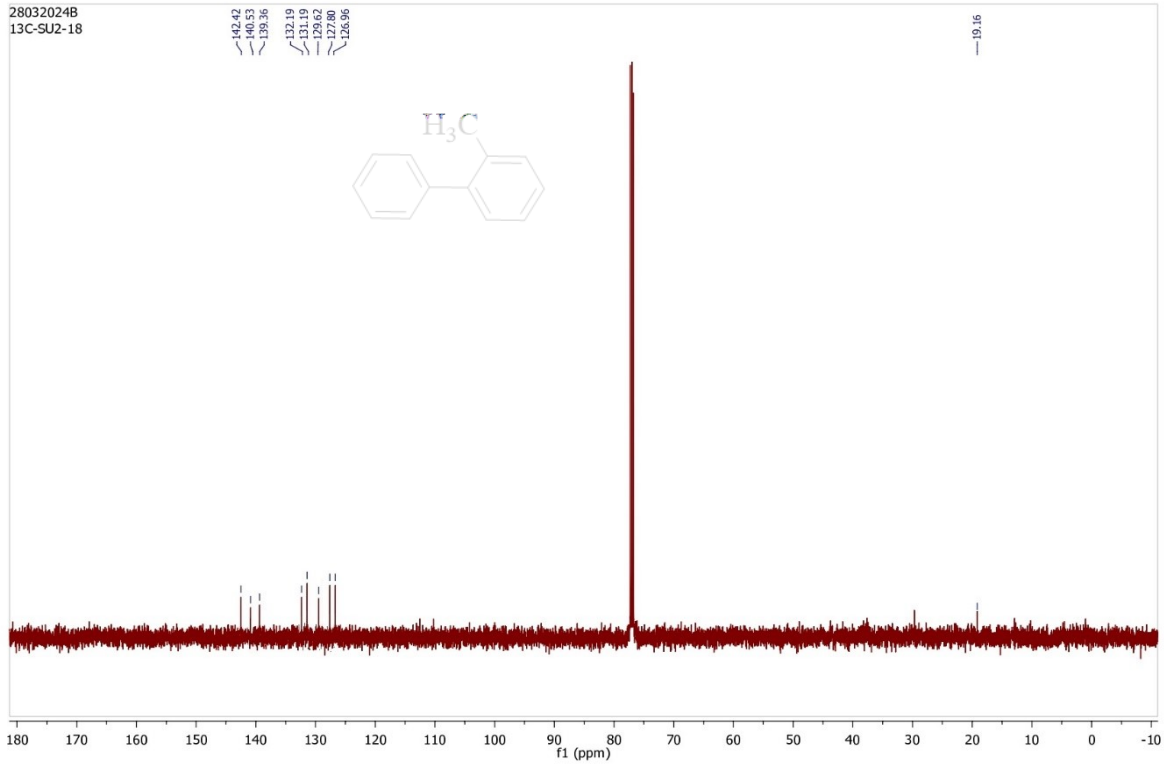
^{13}C NMR Spectrum of 2-phenylnaphthalene (5)



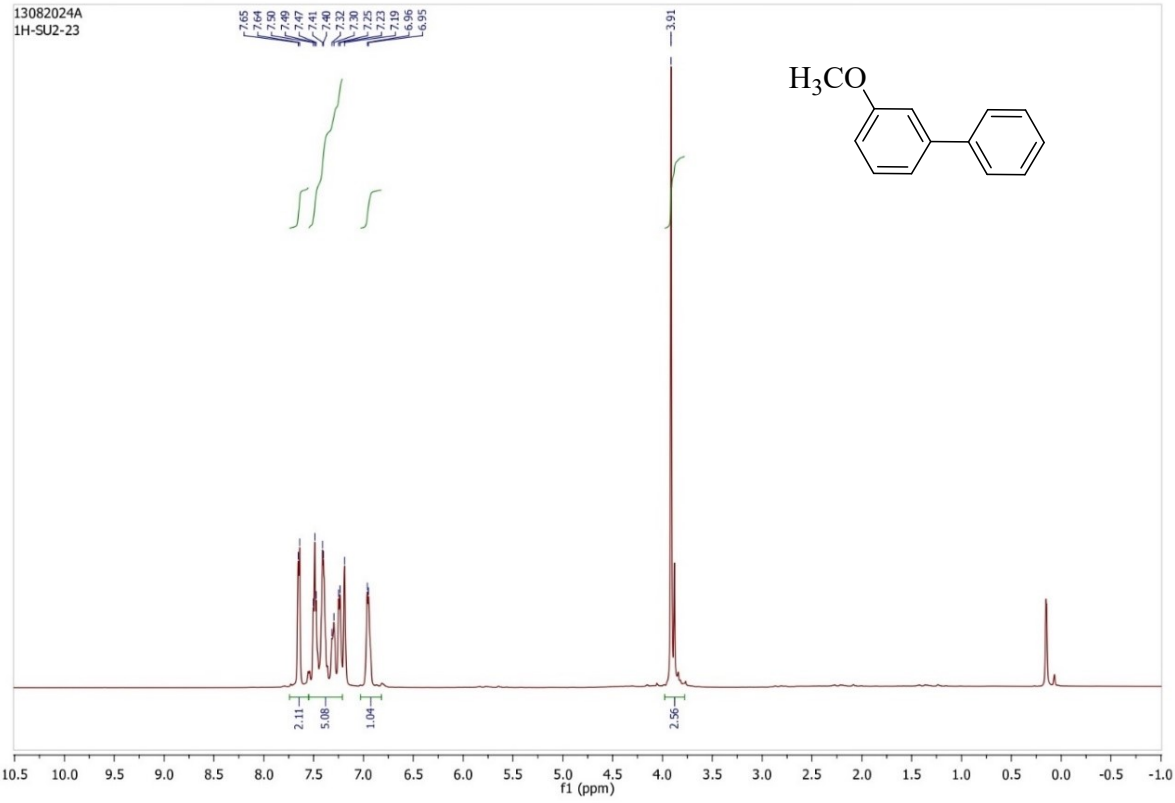
^{1}H NMR Spectrum of 2-methyl-1,1'-biphenyl (6)



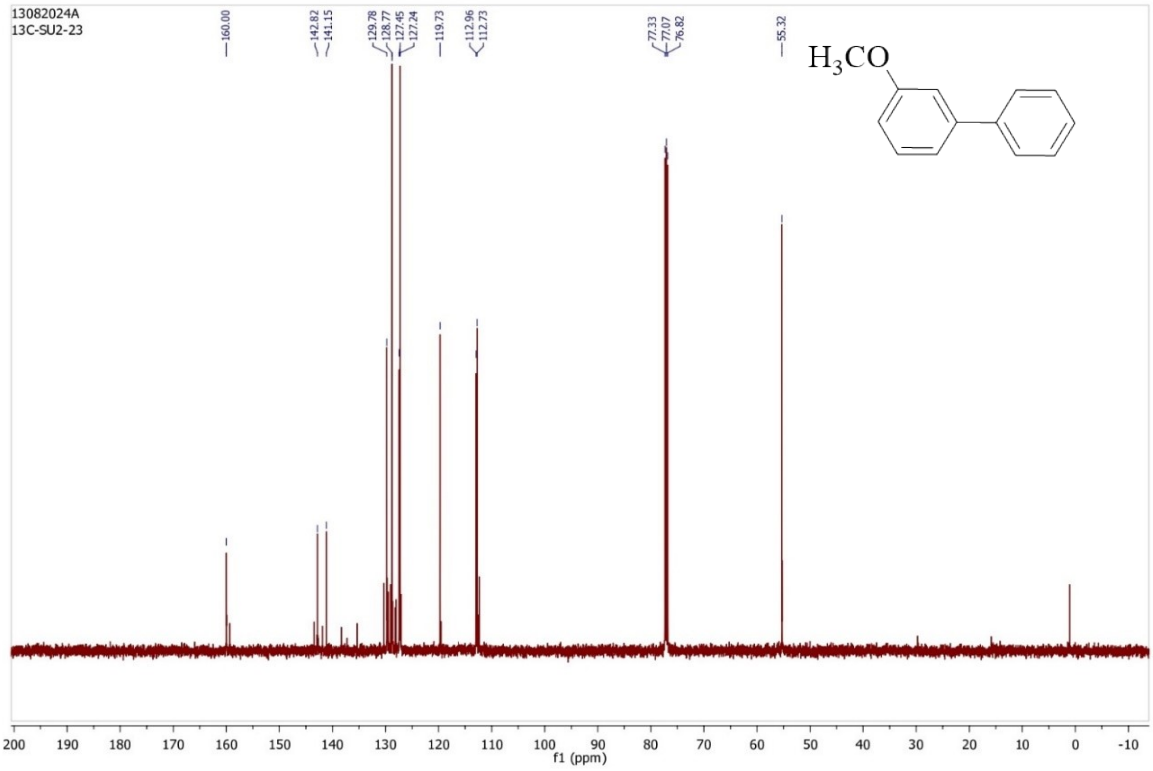
^{13}C NMR Spectrum of 2-methyl-1,1'-biphenyl (6)



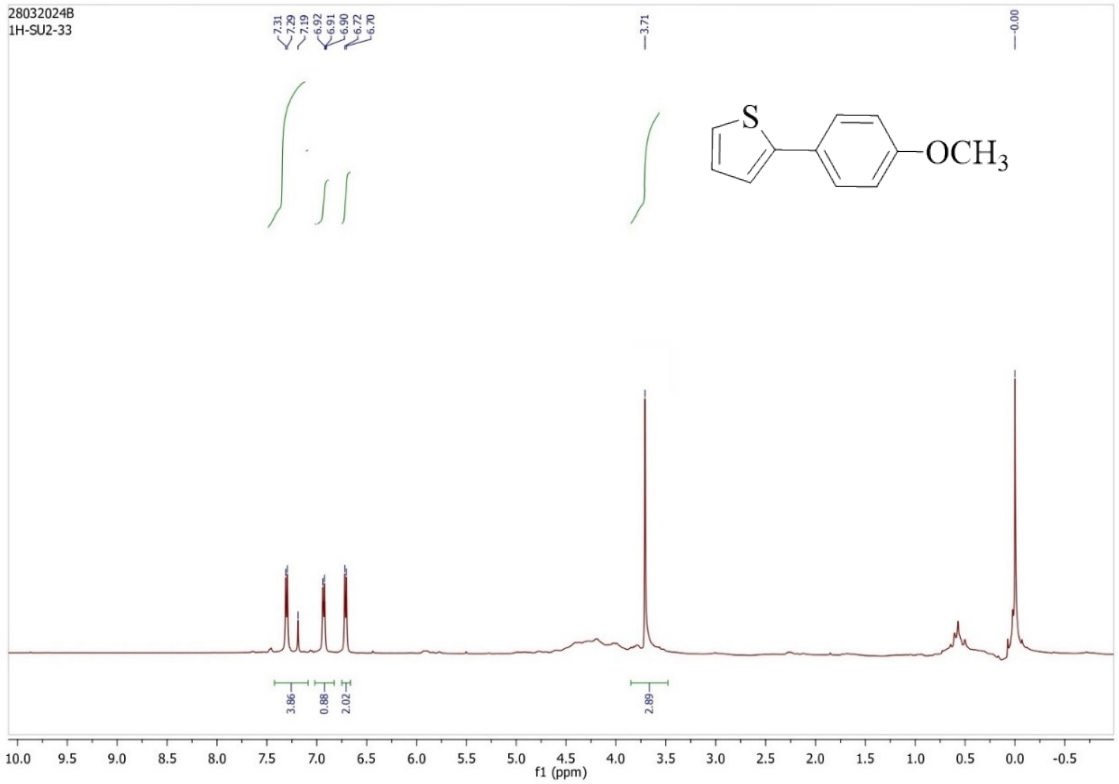
^{1}H NMR Spectrum of 3-methoxy-1,1'-biphenyl (8)



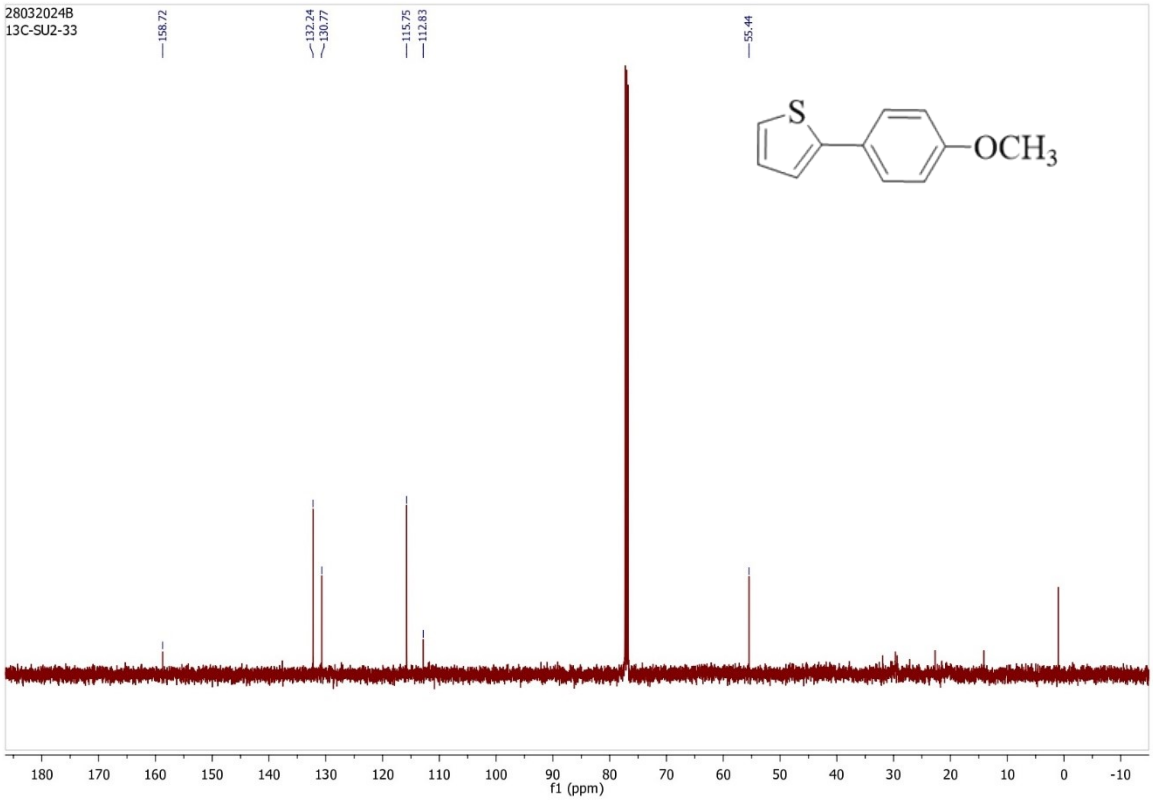
^{13}C NMR Spectrum of 3-methoxy-1,1'-biphenyl (8)



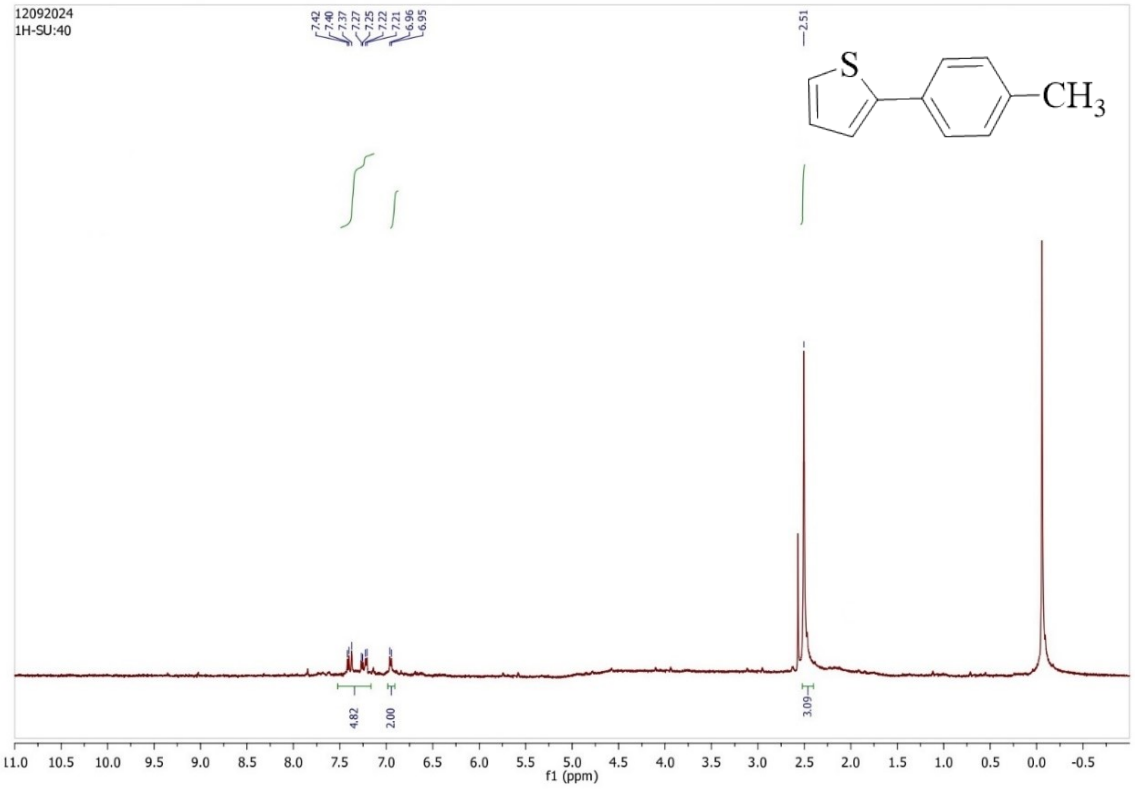
^{1}H NMR Spectrum of 2-(4-methoxyphenyl)thiophene (21)



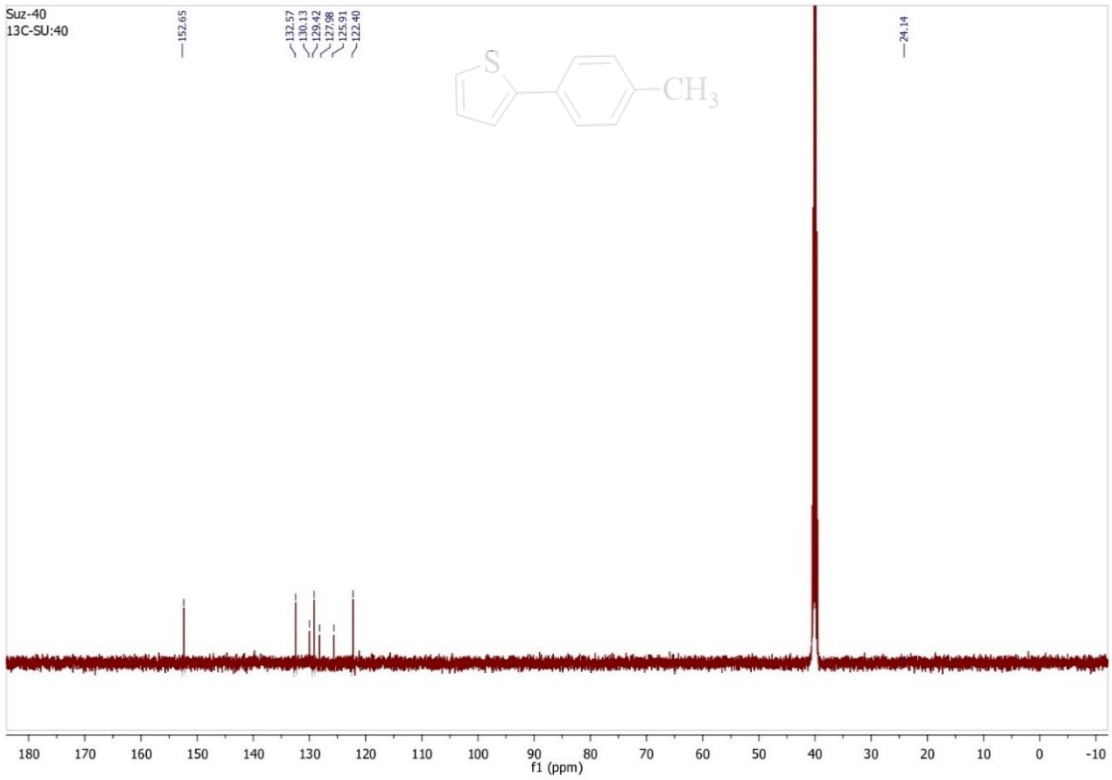
^{13}C NMR Spectrum of 2-(4-methoxyphenyl)thiophen (21)



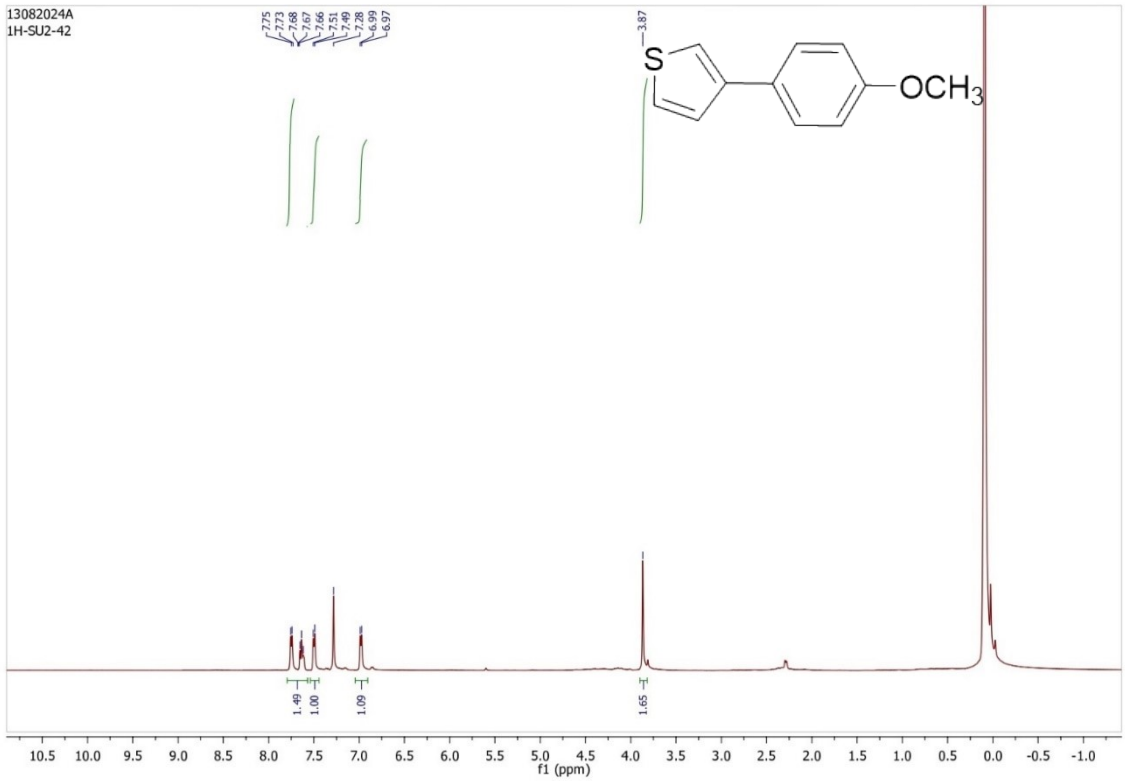
^{1}H NMR Spectrum of 2-(p-tolyl)thiophene (19)



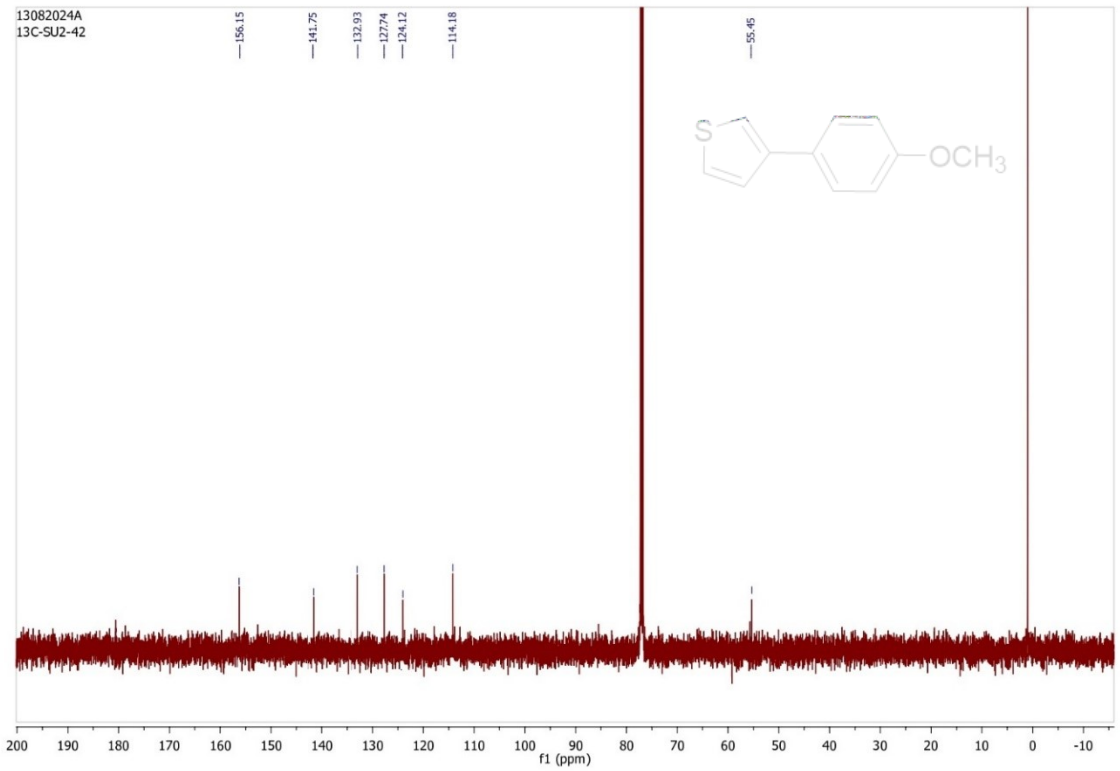
^{13}C NMR Spectrum of 2-(p-tolyl)thiophene (19)



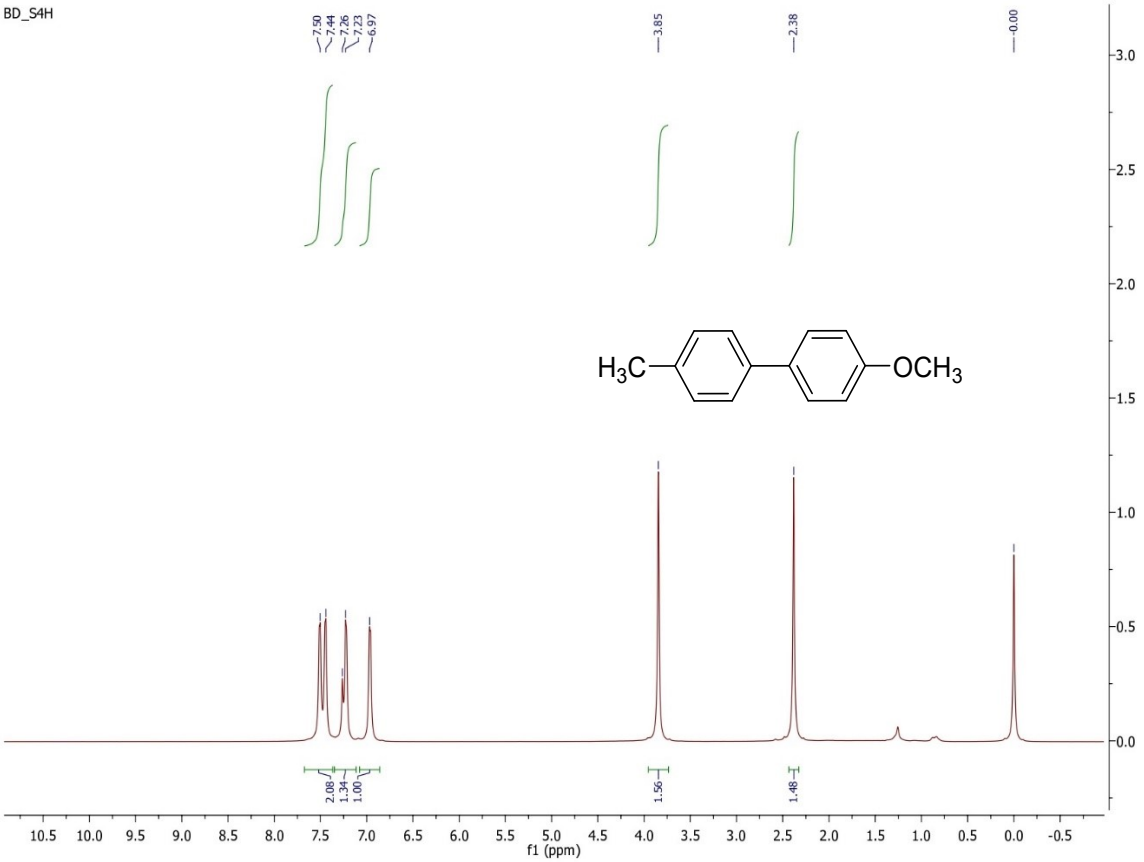
^{1}H NMR Spectrum of 3-(4-methoxyphenyl)thiophene (21)



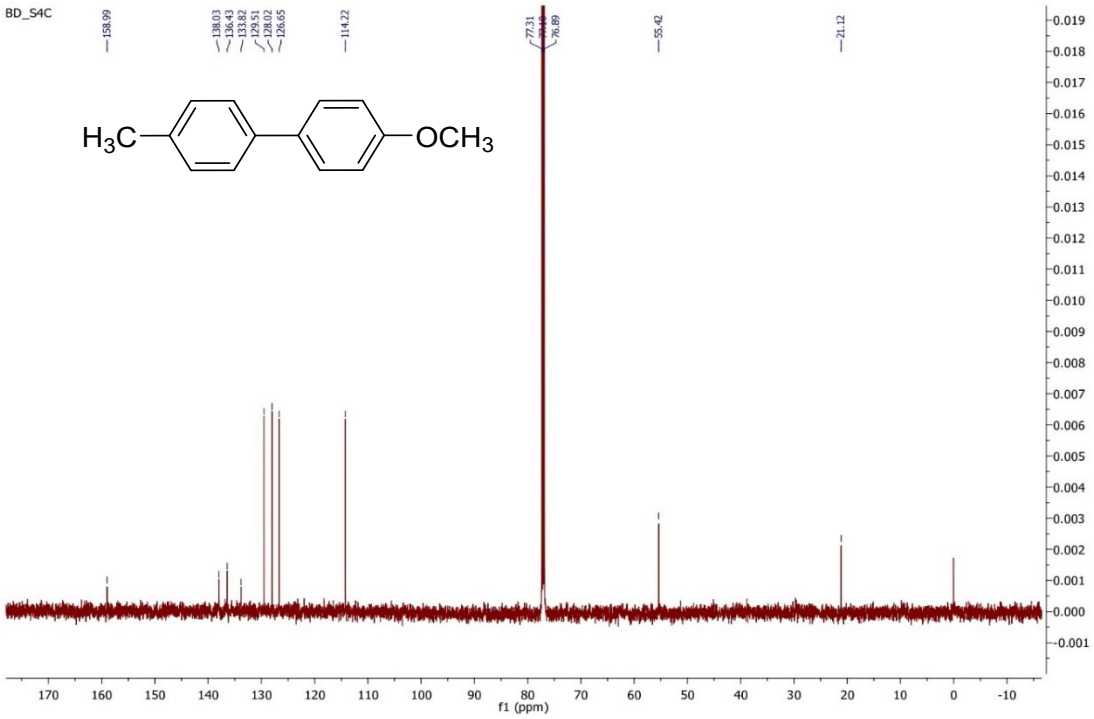
^{13}C NMR Spectrum of 3-(4-methoxyphenyl)thiophene (21)



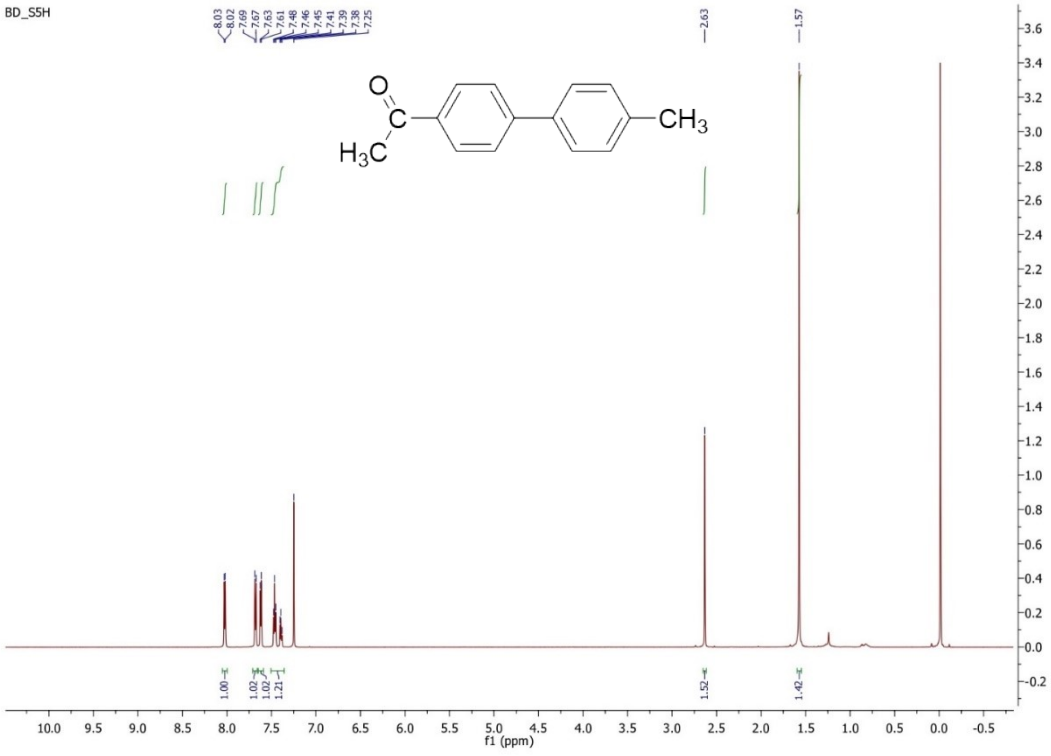
^{1}H NMR Spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl (7)



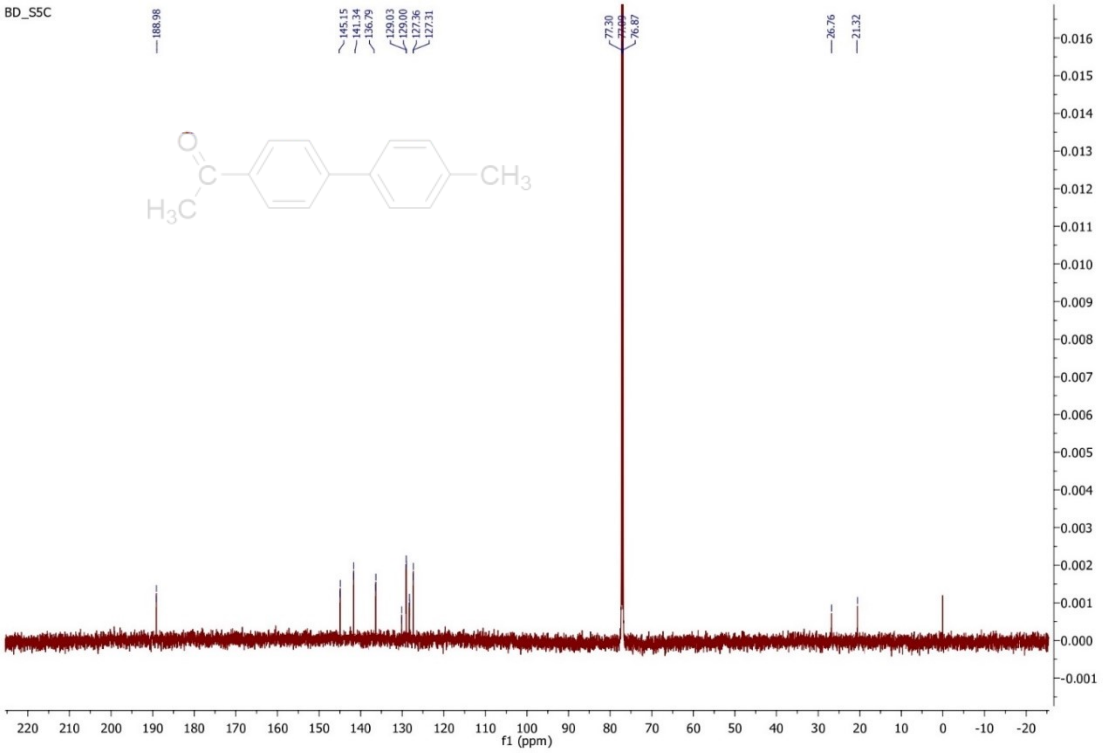
^{13}C NMR Spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl (7)



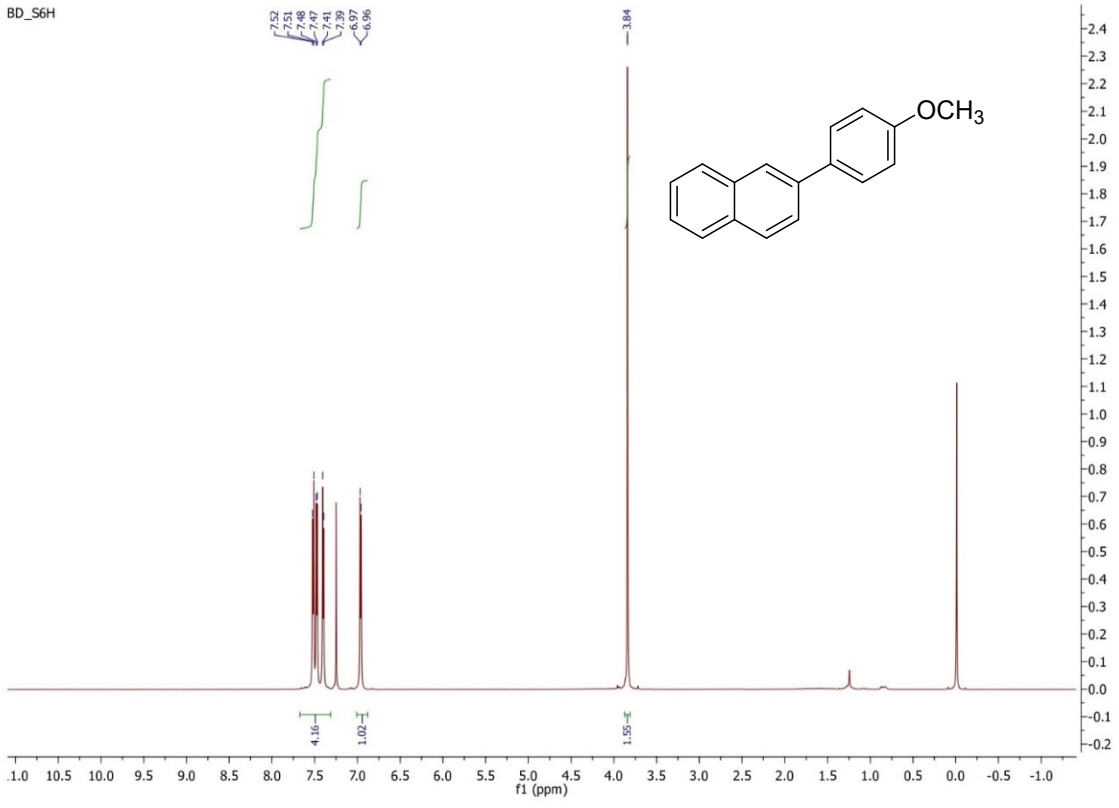
^{1}H NMR Spectrum of 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (10)



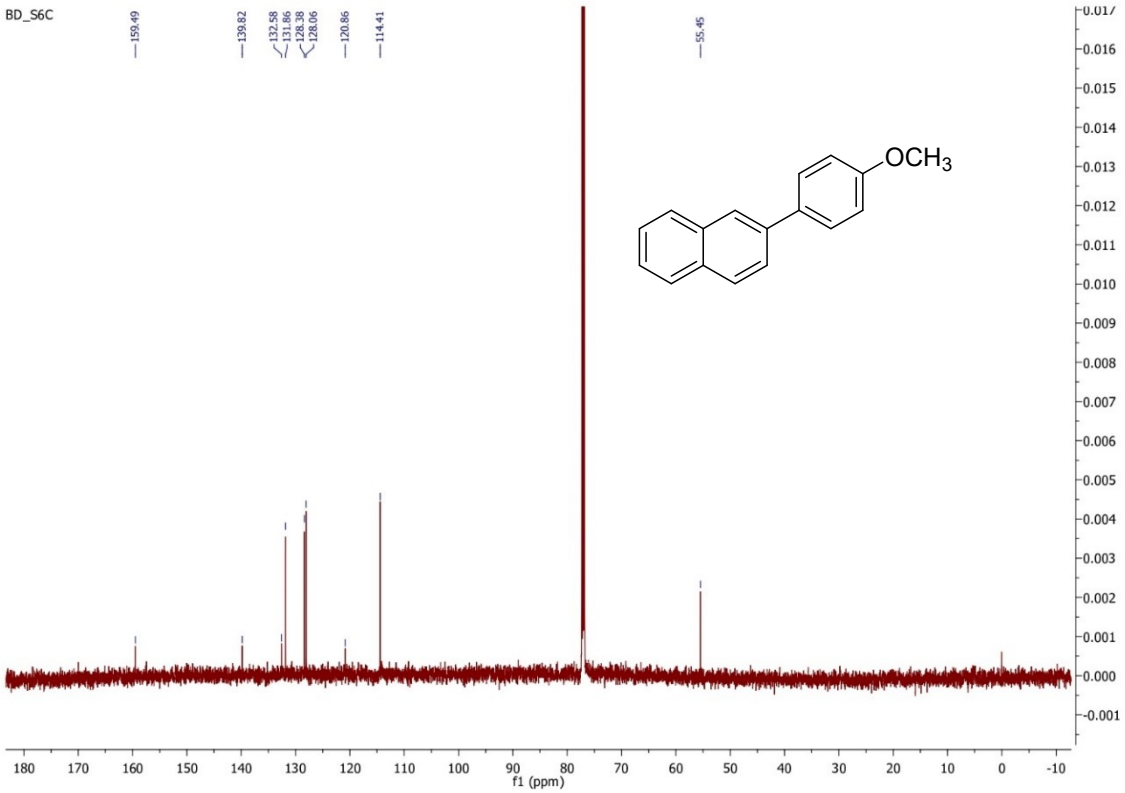
^{13}C NMR Spectrum of 1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (10)



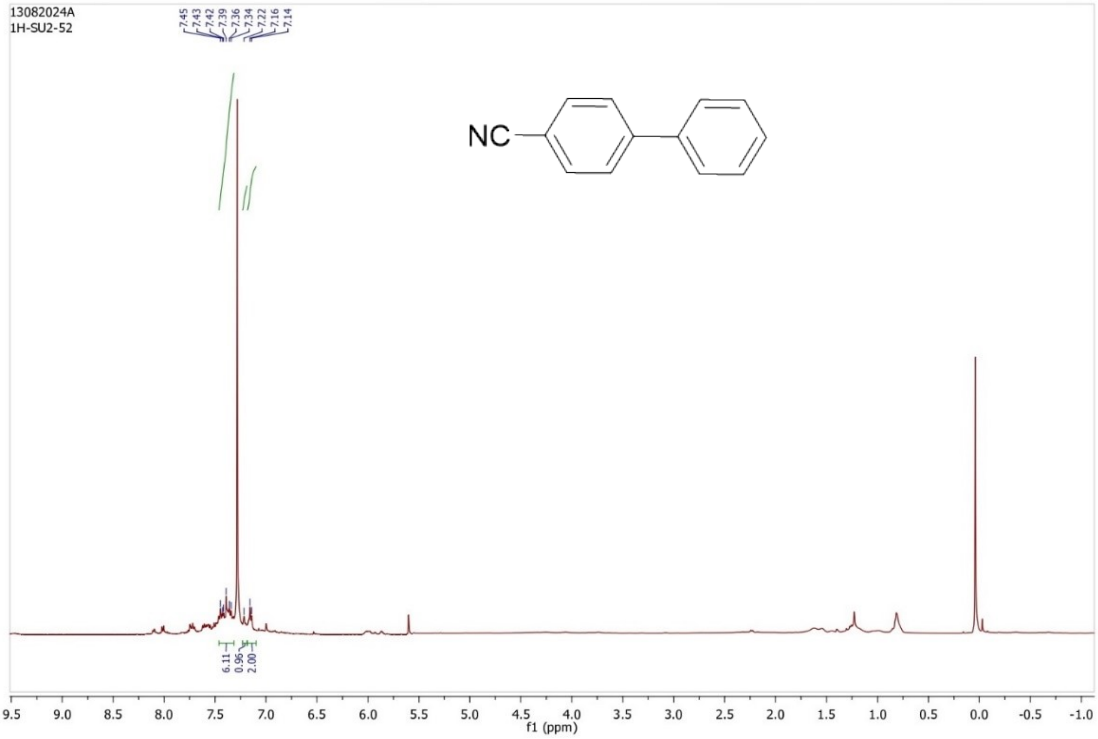
^{1}H NMR Spectrum of 2-(4-methoxyphenyl)naphthalene (9)



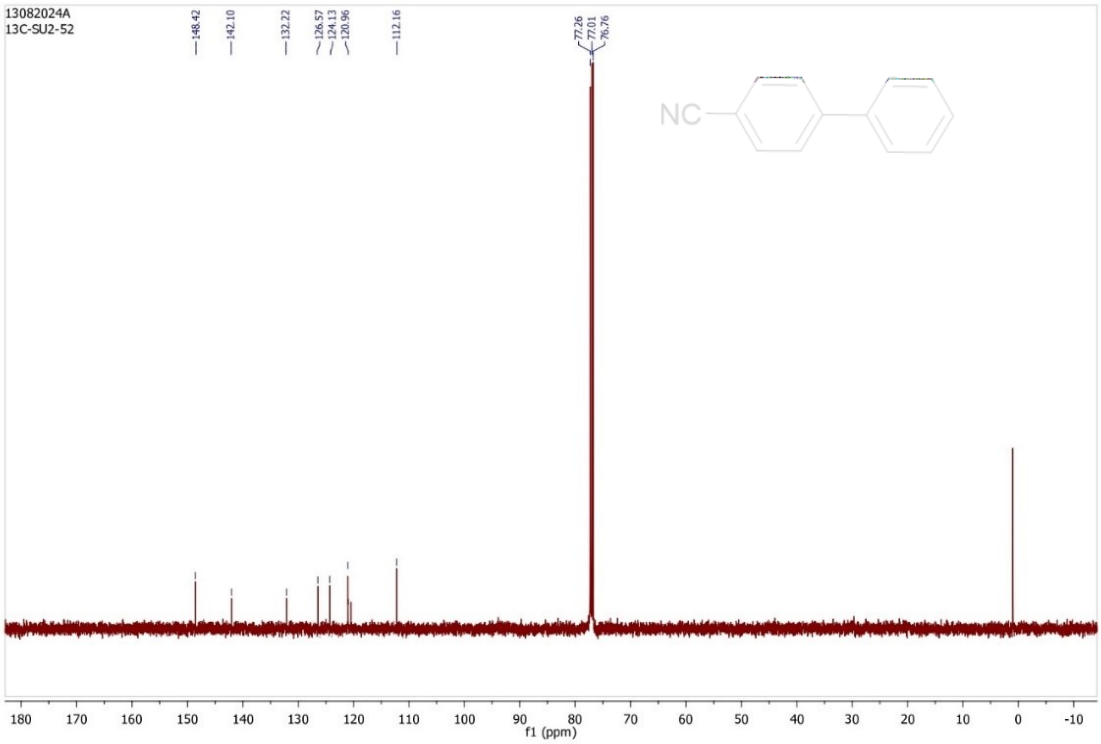
^{13}C NMR Spectrum of 2-(4-methoxyphenyl)naphthalene (9)



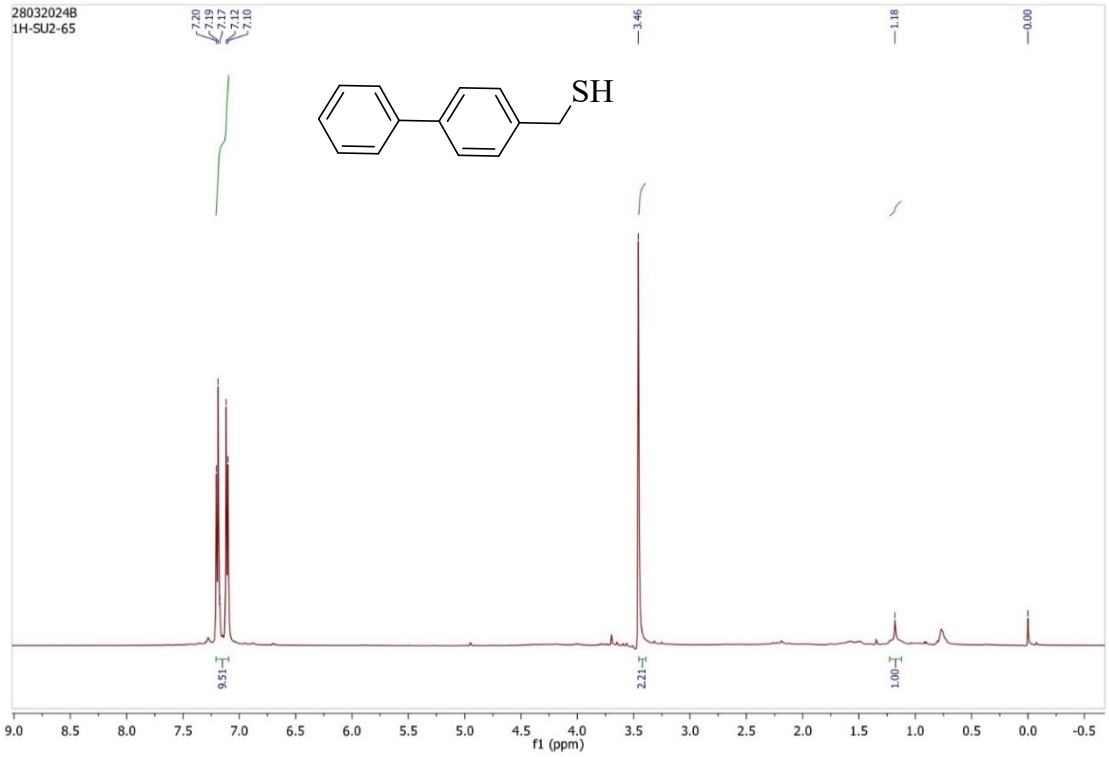
^{1}H NMR Spectrum of 1,1'-biphenyl]-4-carbonitrile (16)



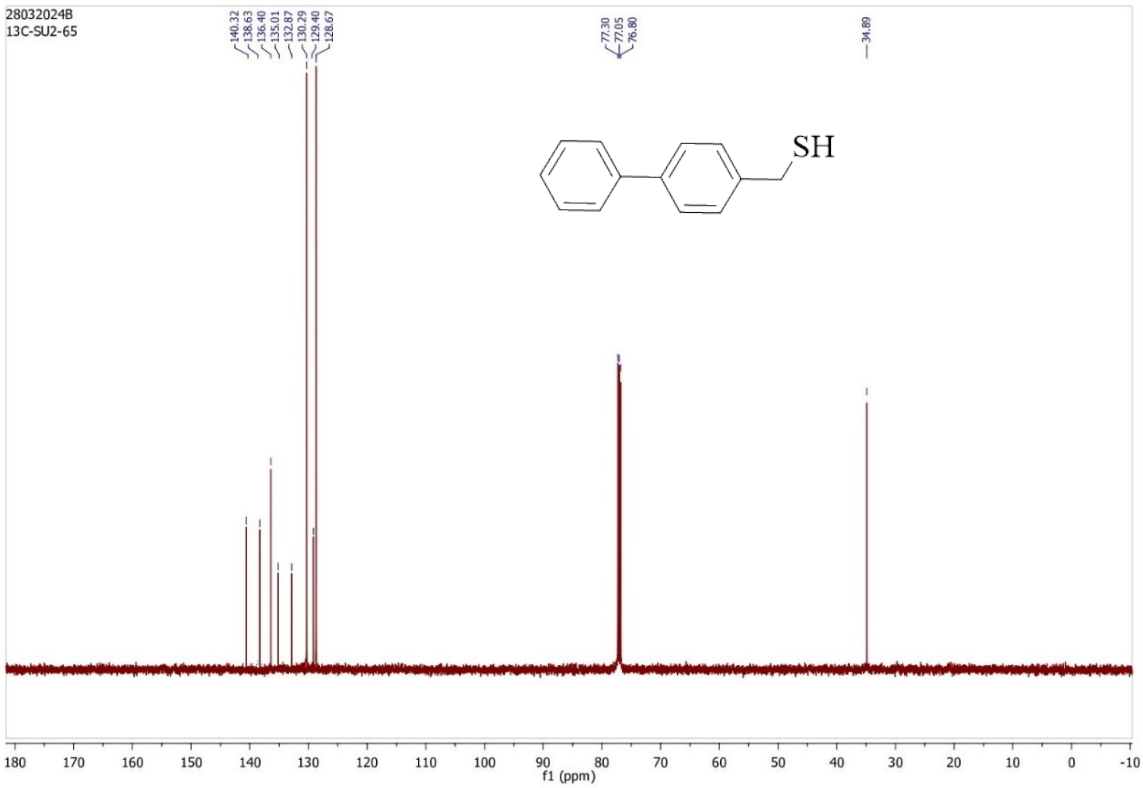
^{13}C NMR Spectrum of 1,1'-biphenyl-4-carbonitrile (16)



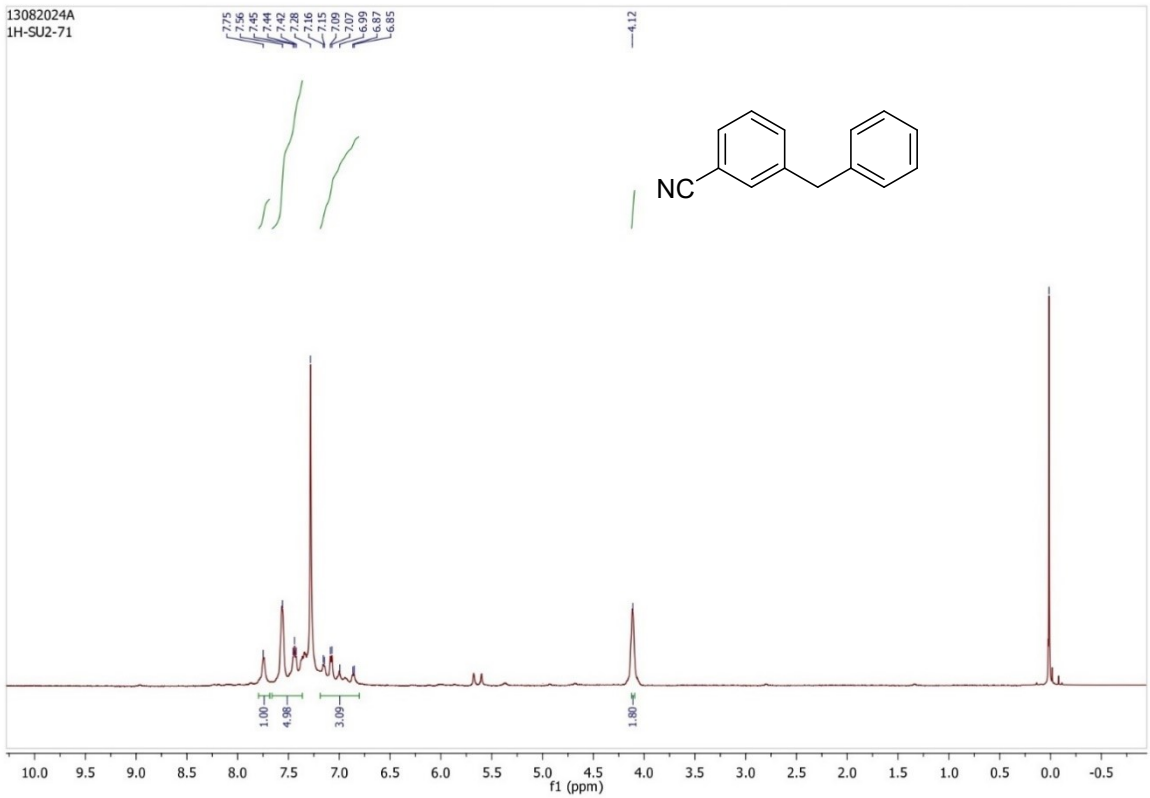
^{1}H NMR Spectrum of 1,1'-biphenyl]-4-ylmethanethiol (14)



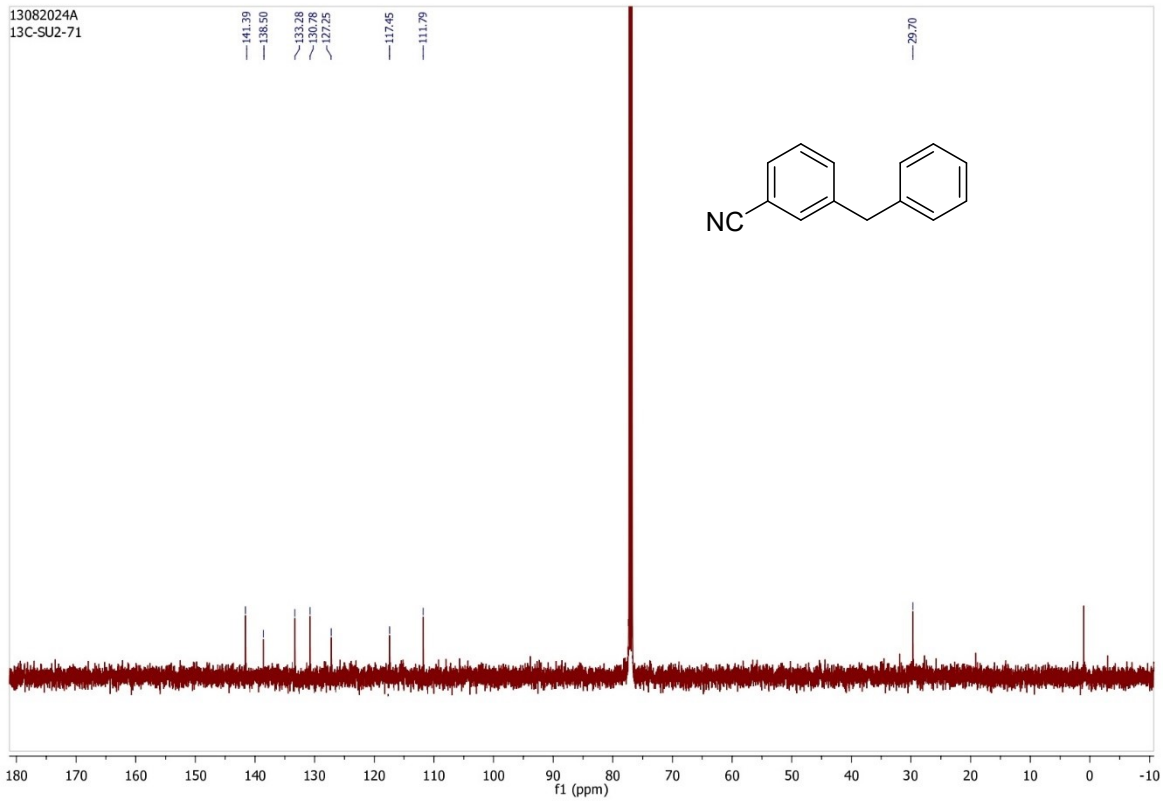
^{13}C NMR Spectrum of 1,1'-biphenyl-4-ylmethanethiol (14)



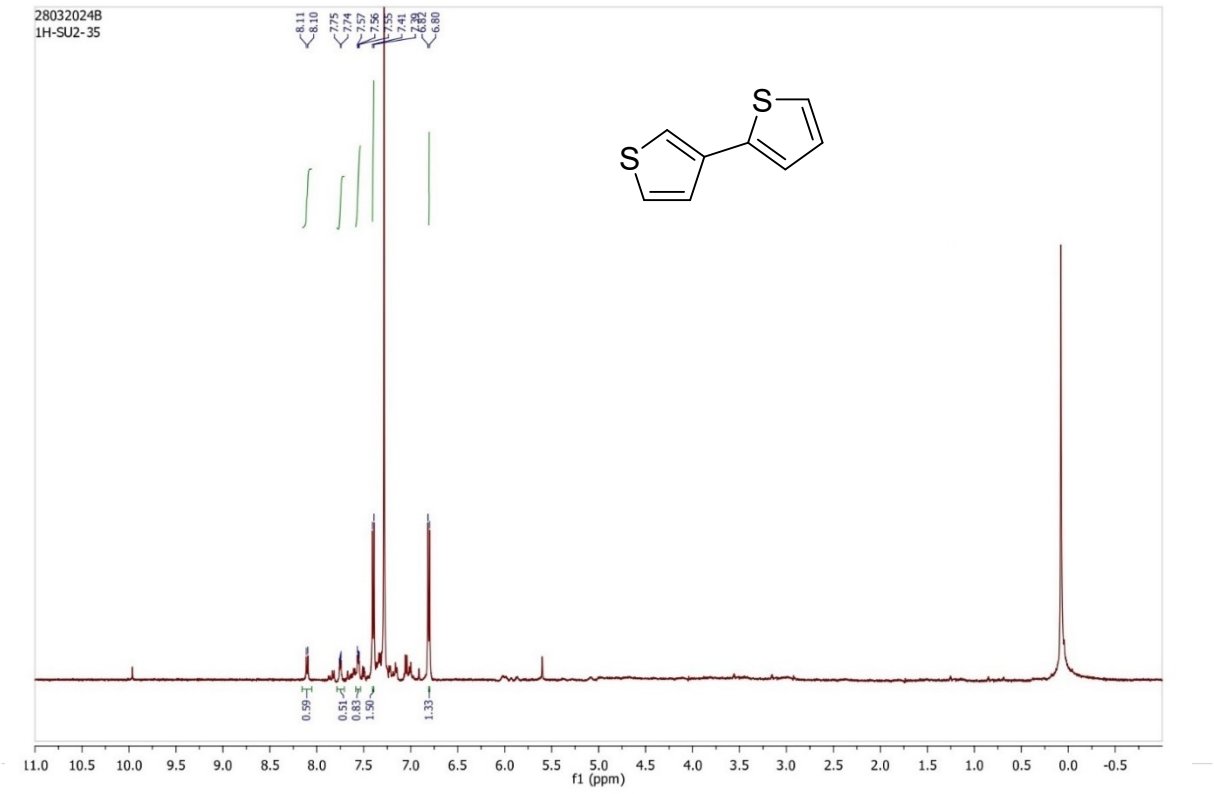
^{1}H NMR Spectrum of 3-benzylbenzonitrile (13)



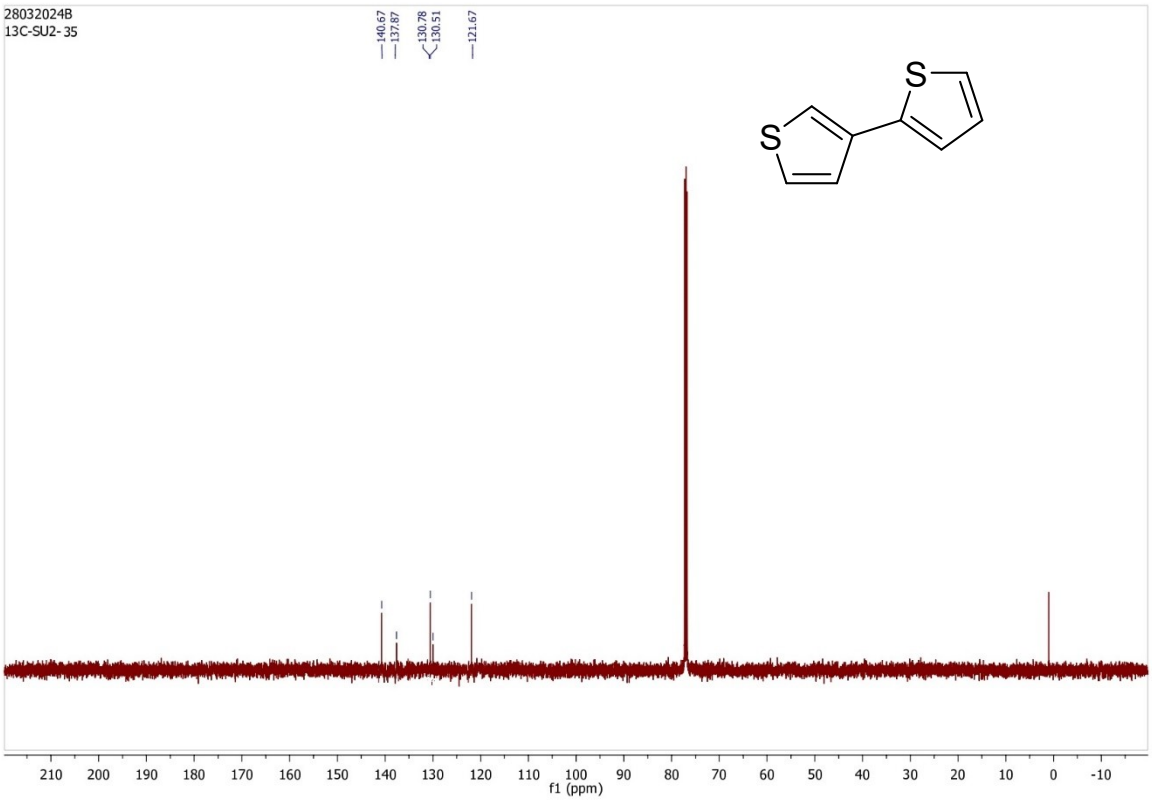
^{13}C NMR Spectrum of 3-benzylbenzonitrile (13)



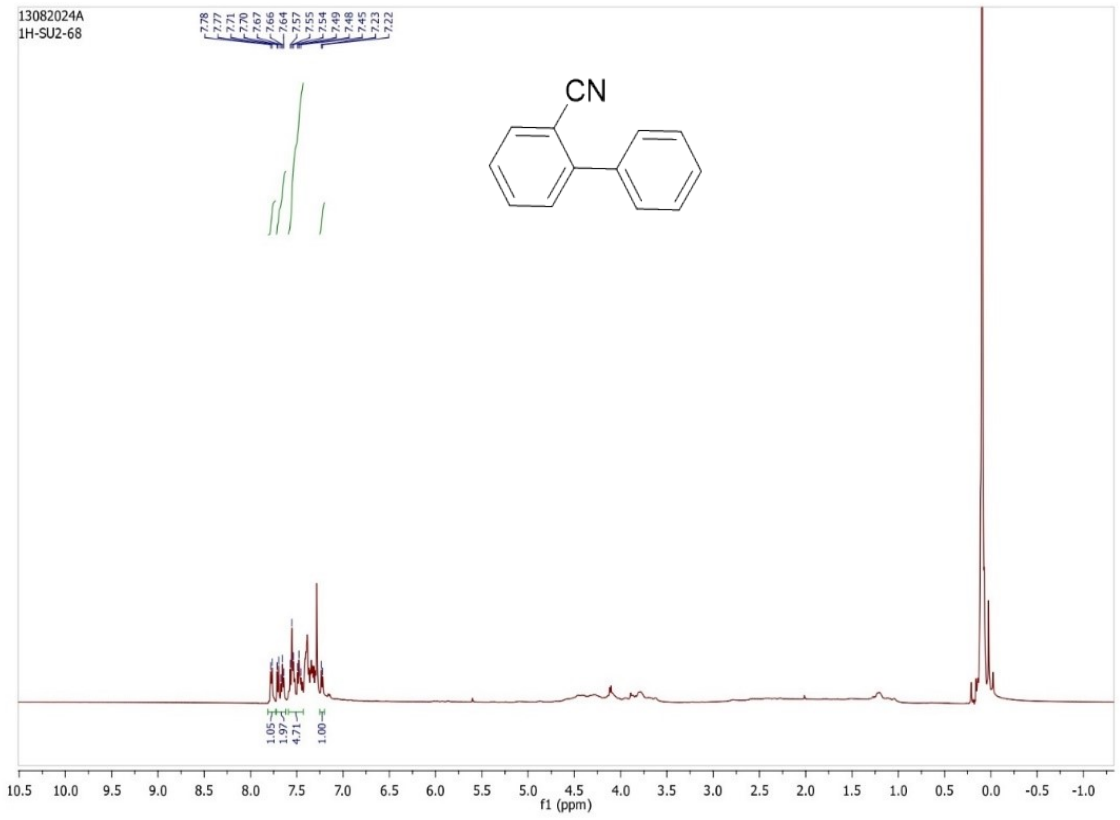
^{1}H NMR Spectrum of 2,3'-bithiophene (17)



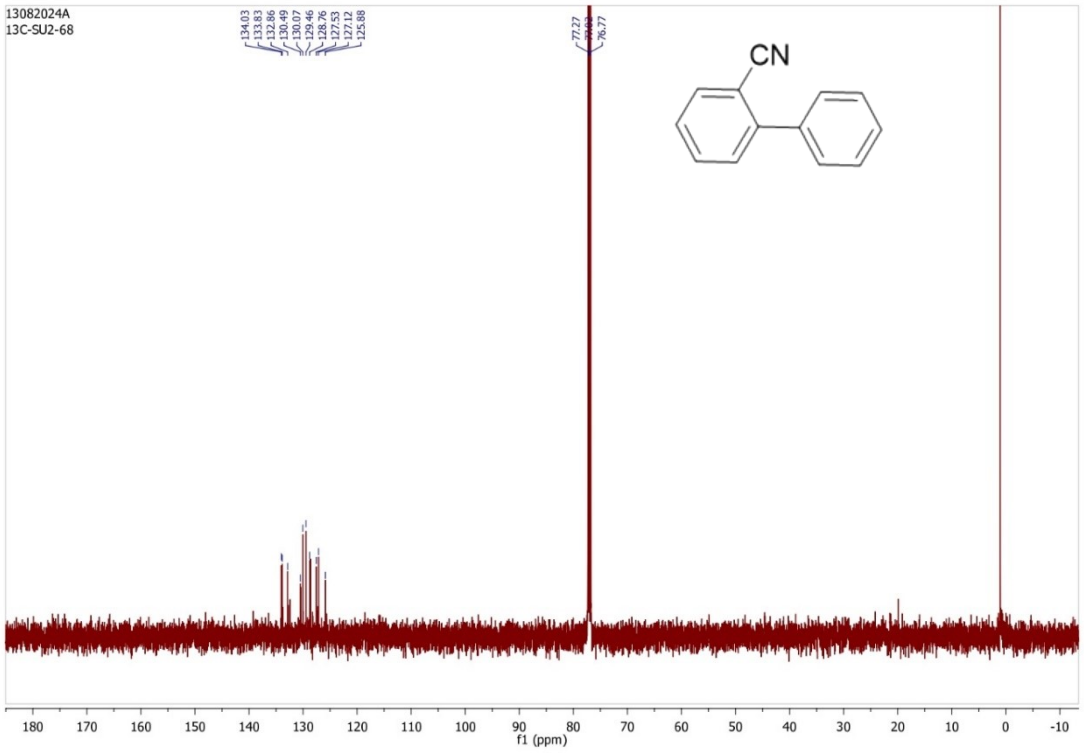
^{13}C NMR Spectrum of 2,3'-bithiophene (17)



^{1}H NMR Spectrum of 1,1'-biphenyl-2-carbonitrile (11)



^{13}C NMR Spectrum of 1,1'-biphenyl-2-carbonitrile (11)



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