Supporting Information

Palladium-loading ceramic membrane catalyzed flow-through Suzuki-Miyaura reaction

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I. General information

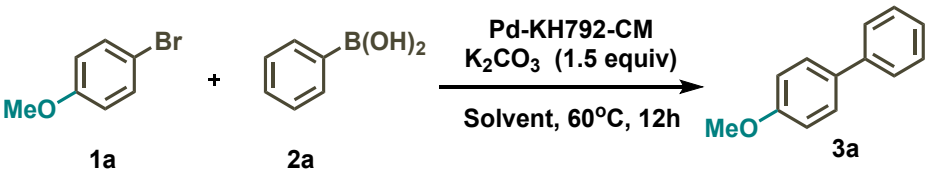
Unless otherwise noted, all reagents were used as received from commercial suppliers. Reactions were monitored by thin-layer chromatography (TLC). TLC plates were visualized with UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm) or SiliCycle silica gel F60 (0.040-0.063 mm). The dilute solvents usually used Ethyl Acetate/Petroleum Ether, which was abbreviated as EA/PE. ^{1}H NMR spectra were acquired on Jeol 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvent ($CDCl_3$: δ 7.26, DMSO-d_6: δ 8.32). ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16, DMSO-d_6: δ 39.60). Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra. GCMS analysis was performed on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was performed on a ThermoFinnigan LCQ Fleet MS spectrometer. Gas chromatographic (GC) analysis was performed on a SHIMADZU GC-2010 plus instrument equipped with an FID detector and an Agilent J & W GC column DB-5MS-UI.

The morphologies of the catalytic membranes were obtained by a field-emission scanning electron microscope (FESEM, Hitachi S-4800II). The contents of Pd were determined from inductively coupled plasma emission spectroscopy (ICP-AES, Optima2000DV). An FEI Tecnai G2 F30S-Twin transmission electron microscope was used to obtain high-resolution transmission electron microscopy (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images and elemental mappings. The element composition and chemical state of the samples were characterized by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 spectrometer equipped with a monochromatized Al KR radiation. The mechanical flexure strength of membrane was determined with three-point bending method using universal testing machine (CMT-6203, Meister Industrial Systems Co., Ltd., China).

II. Condition Optimization for the Model Reaction

General Procedure: A flowthrough catalytic membrane reactor was designed and constructed based on the as-fabricated catalytic membrane. Typically, aryl halides (1.0 equiv, 1.0 mmol), phenylboronic acids (1.5 equiv, 1.5 mmol), K_2CO_3 (1.5 equiv, 1.5 mmol) and EtOH (20 mL) were charged to the catalytic membrane reactor. Then the reactor was put in a pre-warmed 60°C oil bath. The reaction mixture was forced through the catalytic membrane with the aid of a pump (50mL/min). After 12 hours, the reaction mixture was cooled to room temperature and filtered out with a pump, then washed the reactor with ethyl acetate. The organics were extracted using ethyl acetate and the combined extracts were concentrated to obtain the crude product. The reaction progress was monitored by TLC as well as gas chromatography (GC). After 12 hours, the tube was cooled to room temperature, then 100 μL dodecane was added in the tube. After filtering, the filtrate was subjected to GC analysis to determine the conversion of aryl bromide **1a,** and calibrated GC yield of the product.

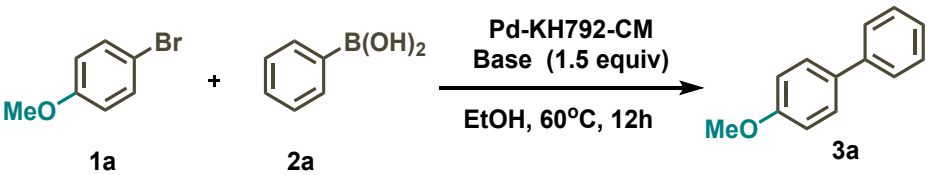
Table S1 Effect of Solvents



1a 2a 3a

Entry	Solvent	Aryl bromide (**1a**)/Conversion (%)	Yield (%)
1	**EtOH**	**99**	**88**
2	CH_3CN	45	45
3	Toluene	73	73
4	H_2O	15	15
5	DMF	38	38
6	DME	19	17
7	$PhCF_3$	62	60
8	THF	0	0
9	Dioxane	0	0

Table S2 Effect of Base

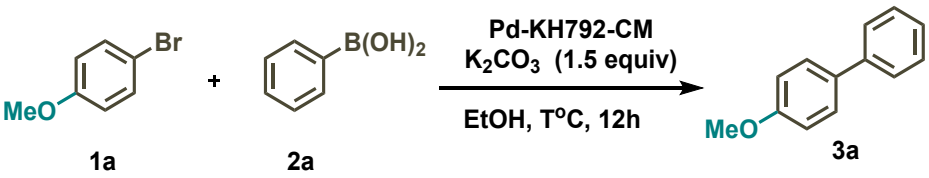


1a 2a 3a

Entry	Base	Aryl bromide (**1a**)/Conversion (%)	Yield (%)
1	**K_2CO_3**	**99**	**88**

2	Na_2CO_3	99	87
3	Cs_2CO_3	99	82
4	K_3PO_4	99	82
5	Na_3PO_4	99	86
6	NaOH	20	12
7	KOH	99	43
8	Et_3N	99	63

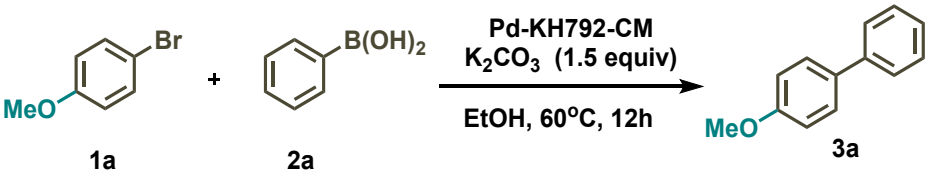
Table S3 Effect of Temperature



1a 2a 3a

Entry	T (℃)	Aryl bromide (**1a**) /Conversion (%)	Yield (%)
1	**70**	**99**	**93**
2	**60**	**99**	**88**
3	50	95	80
4	40	91	70
5	rt	87	66

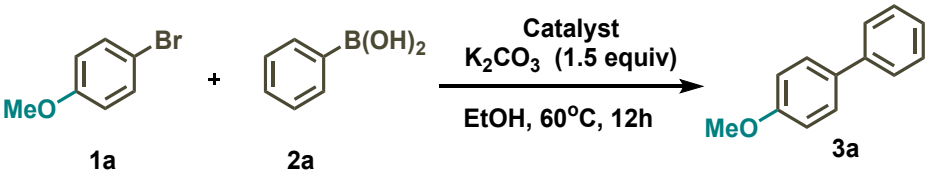
Table S4 Effect of Boronic acids



1a 2a 3a

Entry	Boronic acids (equiv)	Aryl bromide (**1a**) /Conversion (%)	Yield (%)
1	**1.5**	**99**	**88**
2	1.3	88	83
3	1.0	71	68

Table S5 Effect of Catalysts

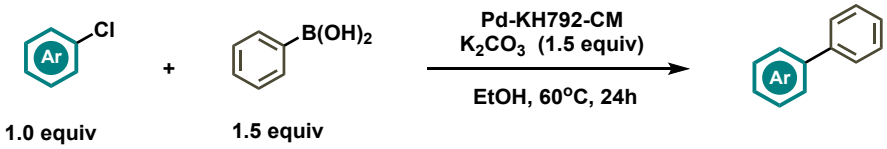


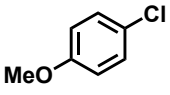
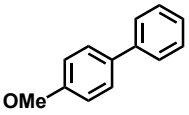
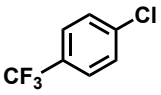
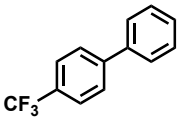
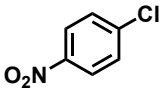
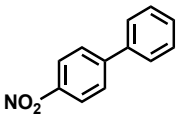
1a 2a 3a

Entry	Catalyst	Aryl bromide (**1a**)	Yield (%)

		/Conversion (%)	
1	No Catalyst	0	0
2	CM	0	0
3	KH792-CM	0	0
4	**Pd-KH792-CM**	**99**	**88**

Table S6 Aryl chloride scope of the flow-through Suzuki-Miyaura Reaction



Entry	ArCl	Product	Yield (%)
1			68
2			82
3			61

III. Experimental apparatus and Characterization

Initially, the ceramic membrane was submerged in bubbling water for 10 h, followed by drying in a stove at 110°C for 12 h. The steps of modification and impregnation were then conducted to prepare palladium-N-[3-(trimethoxysilyl)propyl] ethylenediamine-Ceramic Membrane (named as Pd-KH792-CM). The detailed procedure was described as following: Firstly, the ceramic membrane was submerged in 50 mL dichloromethane solution of 6 g/L N-[3-(trimethoxysilyl)propyl] ethylenediamine (KH792) at 25°C for 60 minutes. Subsequently, the modified ceramic membrane was washed with ethanol to eliminate unreacted KH792 and dried at room temperature (named as KH792-CM). Then, the modified membrane film was impregnated with 0.04 mol/L $Pd(OAc)_2$ arrangement in 50 mL acetone at 30°C for 12 hours. Finally, the Pd-loading ceramic membrane (named as Pd-KH792-CM) was entirely cleaned with acetone and dried at 25°C.

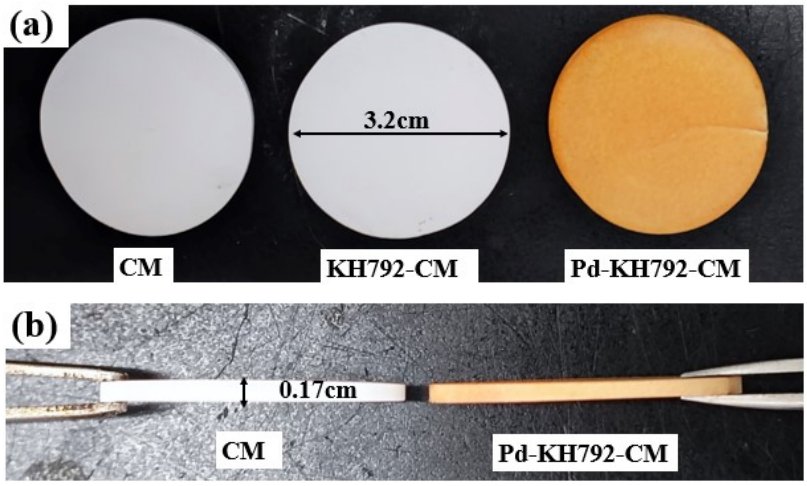


Figure S1. Digital photo of ceramic membrane (a) the front (b) the side.

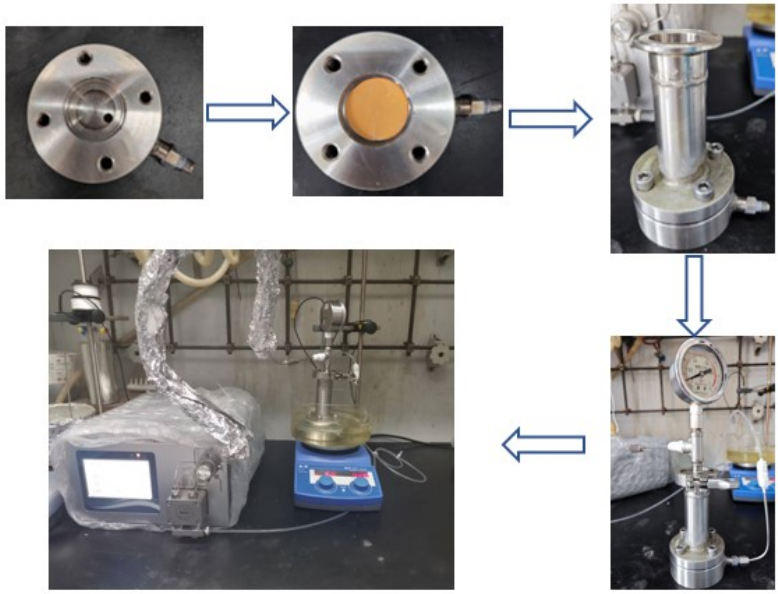


Figure S2 The installation process of experimental setup.

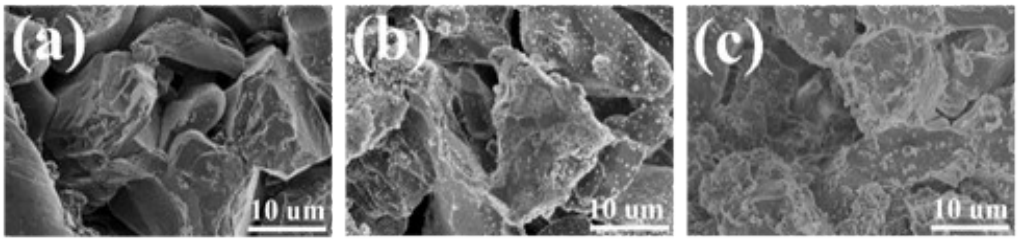


Figure S3 Surface FESEM images of (a) CM, (b) KH792-CM, (c) Pd-KH792-CM.

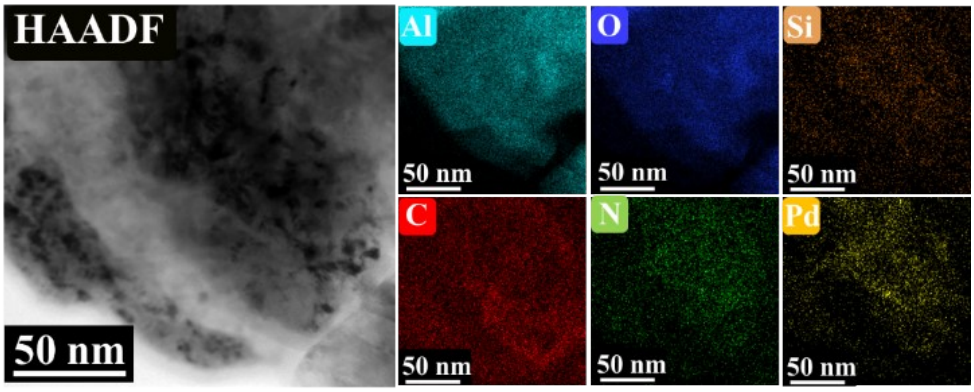


Figure S4. HAADF-STEM image and corresponding elemental mapping images of Pd-KH792-CM.

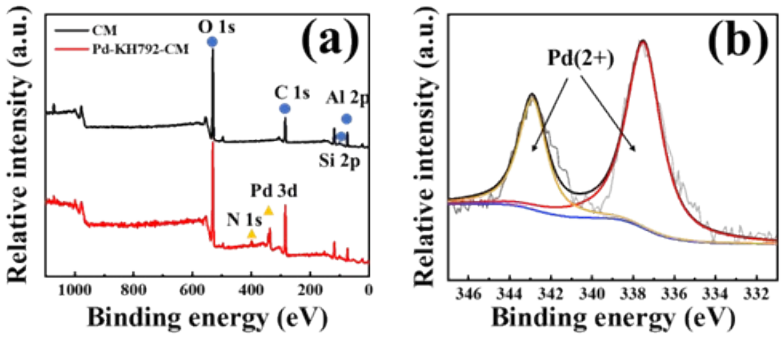


Figure S5. XPS survey spectra of (a) CM and Pd-KH792-CM, (b) Pd 3d of Pd-KH792-CM.

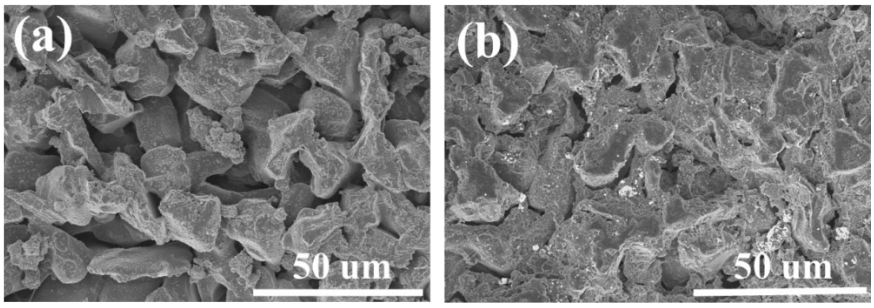


Figure S6. SEM of catalytic membrane(a) fresh; (b) recovered.

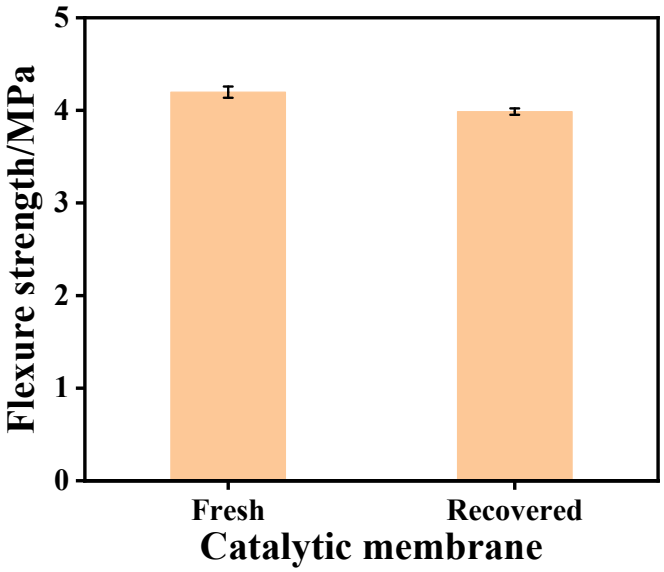


Figure S7. The flexure strength of membrane catalytic membrane.

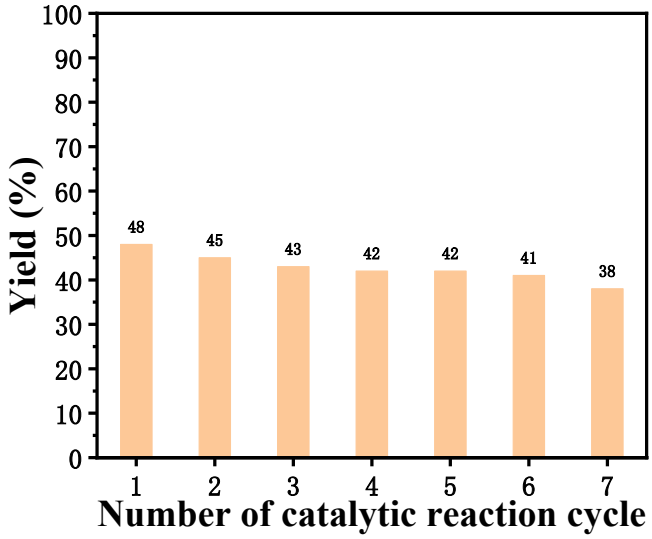


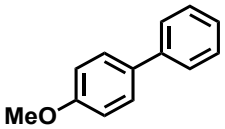
Figure S8. Recyclability chat of the Pd-KH792-CM catalyzed Suzuki-Miyaura reaction (Conversion < 50%).

Table S7. The Pd content of catalytic membrane and reaction mixture via ICP-OES analysis.

Samples	Pd content (mg)	Pd content (mg/cm^2)	Pd content (mol%)
Pd-KH792-CM	2.00	0.25	1.89
1st cycle	2.00	0.25	1.89
8st cycle	1.97	0.25	1.86
Reaction mixture after cycle	0.0	-	-

IV. Suzuki cross-coupling reactions

General Procedure: A flowthrough catalytic membrane reactor was designed and constructed based on the as-fabricated catalytic membrane. The reactor is composed of three parts, the membrane is placed at the bottom, a storage tank in the middle and a circulating feed port at the top. In addition, there is a pump for mixture circulation. Typically, ArX (1.0 equiv, 1.0 mmol), phenylboronic acids (1.5 equiv, 1.5 mmol), K_2CO_3 (1.5 equiv, 1.5 mmol) and EtOH (20 mL) were charged to the catalytic membrane reactor. Then the reactor was put in a pre-warmed 60^{o}C oil bath. The reaction mixture was forced through the catalytic membrane with the aid of a pump (50mL/min). After 12 hours (for aryl chlorides was 24 hours), the reaction mixture was cooled to room temperature and filtered out with a pump, then washed the reactor with ethyl acetate. The organics were extracted using ethyl acetate and the combined extracts were concentrated to obtain the crude product. The reaction progress was monitored by TLC as well as gas chromatography (GC). The crude product obtained after filtration and concentration in vacuo was purified by column chromatography with petroleum ether and ethyl acetate as eluents to afford the pure product. The structure of the pure product was determined by ^{1}H and ^{13}C NMR spectroscopy.

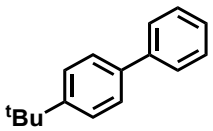


4-methoxy-1,1'-biphenyl (3a) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=50:1) as white solid (X=Br, 162.1 mg, 88%; X=Cl, 125.1 mg, 68%). The spectral data agreed closely with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 4H), 7.44-7.40 (m, 2H), 7.33-7.29 (m, 1H), 7.01-6.97 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.27, 140.96, 133.91, 128.87, 128.30, 126.89, 126.80, 114.33, 55.49.

GCMS (EI): calcd. for $C_{13}H_{12}O$ 184.09, found: 184.06.

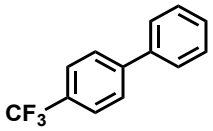


4-(tert-butyl)-1,1'-biphenyl (3b) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE as eluent) as white solid (151.2 mg, 72%). The spectral data agreed closely with those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.56-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.46-7.42 (m, 2H), 7.35-7.32 (m, 1H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.39, 141.20, 138.46, 128.90, 128.84, 127.39, 127.31, 127.17, 126.93, 125.86, 34.67, 31.51.

GCMS (EI): calcd. for $C_{16}H_{18}$ 210.14, found: 210.10.



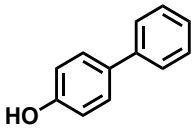
4-(trifluoromethyl)-1,1'-biphenyl (3c) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE as eluent) as yellow oil (X=Br, 188.7 mg, 85%; X=Cl, 182.1 mg, 82%). The spectral data agreed closely with those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.67-7.64 (m, 2H), 7.56-7.51 (m, 2H), 7.50-7.45 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.87, 139.91, 129.62, 129.13, 128.89, 128.33, 127.57, 127.43, 125.85 (q, J = 3.75 Hz), 123.10.

^{19}F NMR (376 MHz, CDCl3): δ -62.27 .

GCMS (EI): calcd. for $C_{13}H_9F_3$ 222.07, found: 222.04.

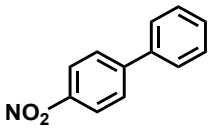


[1,1'-biphenyl]-4-ol (3d) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=15:1) as white solid (149.8 mg, 88%). The spectral data agreed closely with those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.53 (m, 2H), 7.51–7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.34-7.29 (m, 1H), 6.93-6.90 (m, 2H), 4.90 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.17, 140.88, 134.17, 128.87, 128.54, 126.86, 115.77.

GCMS (EI): calcd. for $C_{12}H_{10}O$ 170.07, found: 170.07.

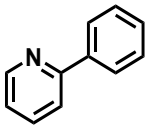


4-nitro-1,1'-biphenyl (3e) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=10:1) as white solid (X=Br, 167.3 mg, 84%; X=Cl, 121.4, 61%). The spectral data agreed closely with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.29 (m, 2H), 7.76-7.72 (m, 2H), 7.64-7.61 (m, 2H), 7.53-7.43 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.77, 147.22, 138.91, 129.30, 129.06, 127.94, 127.53, 124.25.

GCMS (EI): calcd. for $C_{12}H_9NO_2$ 199.06, found: 199.03.

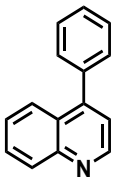


2-phenylpyridine (3f) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=10:1) as white solid (122.6 mg, 79%). The spectral data agreed closely with those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71-8.69 (m, 1H), 8.02-7.99 (m, 2H), 7.75-7.70 (m, 2H), 7.50-7.40 (m, 3H), 7.24-7.18 (m, 1H)..

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.55, 149.76, 139.48, 136.86, 129.05, 128.85, 127.01, 122.20, 120.68.

GCMS (EI): calcd. for $C_{11}H_9N$ 155.07, found: 155.07.

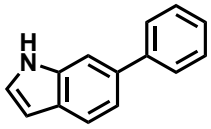


4-phenylquinoline (3g) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=5:1) as white solid (182.7 mg, 89%). The spectral data agreed closely with those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, *J* = 4.48 Hz, 1H), 8.19 (d, *J* = 8.48 Hz, 1H), 7.94-7.91 (m, 1H), 7.75-7.70 (m, 1H), 7.55-7.47 (m, 6H), 7.33 (d, *J* = 4.32 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.08, 148.76, 148.61, 138.08, 129.93, 129.65, 129.44, 128.68, 128.54, 126.85, 126.74, 125.98, 121.44.

GCMS (EI): calcd. for $C_{15}H_{11}N$ 205.09, found: 205.08.

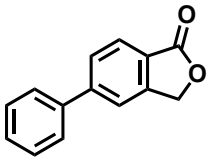


6-phenyl-1H-indole (3h) The reaction was conducted according to general procedure . The product was purified by column chromatography (PE: EA=5:1) as yellow oil (162.3 mg, 84%). The spectral data agreed closely with those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15(s, 1H),7.90 (s, 1H), 7.70-7.67 (m, 2H), 7.50 – 7.45 (m, 4H), 7.36-7.32 (m, 1H), 7.24 (t, *J* = 2.76 Hz, 1H), 6.64 (t, *J* = 3.00 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.64, 135.38, 133.49, 128.76, 128.46, 127.51, 126.45, 125.00, 122.00, 119.35, 111.38, 103.08.

GCMS (EI): calcd. for $C_{14}H_{11}N$ 193.09, found: 193.09.

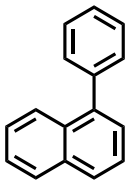


5-phenylisobenzofuran-1(3H)-one (3i) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=8:1) as white solid (176.5 mg, 84%). The spectral data agreed closely with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 1H),7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.61-7.58 (m, 2H), 7.50-7.40 (m, 3H), 5.34 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.12, 147.59, 147.50, 139.79, 129.23, 128.76, 128.59, 127.65, 126.20, 124.61, 120.71, 69.75.

GCMS (EI): calcd. for $C_{14}H_{10}O_2$ 210.07, found: 210.04.

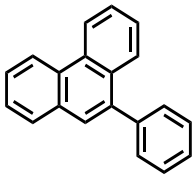


1-phenylnaphthalene (3j) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=5:1) as white solid (173.6 mg, 85%). The spectral data agreed closely with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.89 (d, *J* = 8.48 Hz, 1H), 7.57-7.50 (m, 6H), 7.48-7.44 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.88, 140.38, 133.92, 131.74, 130.21, 128.39, 127.76, 127.37, 127.06, 126.16, 125.90, 125.52.

GCMS (EI): calcd. for $C_{16}H_{12}$ 204.09, found: 204.12.



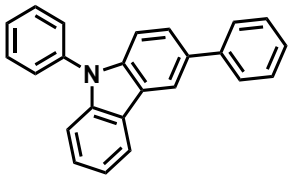
9-phenylphenanthrene (3k) 95% The reaction was conducted according to general

procedure. The product was purified by column chromatography (PE: EA=9:1) as white solid (241.6 mg, 95%). The spectral data agreed closely with those reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* =8.36 Hz, 1H), 8.74 (d, *J* =8.68 Hz, 1H), 7.95-7.90 (m, 2H), 7.70-7.61 (m, 4H), 7.58-7.45 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.86, 138.92, 131.61, 131.18, 130.69, 130.15, 130.01, 128.74, 128.39, 127.62, 127.44, 126.99, 126.92, 126.66, 126.59, 126.54, 123.00, 122.61.

GCMS (EI): calcd. for $C_{20}H_{14}$ 254.11, found: 254.11.

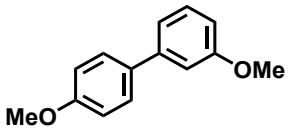


3,9-diphenyl-9H-carbazole (3l) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=9:1) as white solid (274.7 mg, 86%). The spectral data agreed closely with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 1.72 Hz, 1H), 8.21-8.19 (m, 1H), 7.74-7.71 (m, 2H), 7.68-7.58 (m, 5H), 7.51-7.43 (m, 6H), 7.38-7.29 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.12, 141.45, 140.48, 137.76, 133.60, 130.05, 128.92, 127.63, 127.47, 127.18, 126.70, 126.26, 125.62, 123.99, 123.59, 120.50, 120.19, 118.95, 110.14, 110.05.

GCMS (EI): calcd. for $C_{24}H_{17}N$ 319.14, found: 319.15.



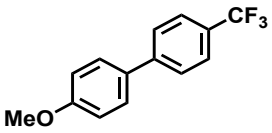
3,4'-dimethoxy-1,1'-biphenyl (4a) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=20:1) as white solid (190.7 mg, 89%). The spectral data agreed closely with those reported in

the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.34 (t, *J* = 7.88 Hz, 1H), 7.17-7.13 (m, 1H), 7.10-7.09 (m, 1H), 7.00-6.97 (m, 2H), 6.88-6.85 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.05, 159.37, 142.49, 133.73, 129.84, 128.33, 119.42, 114.29, 112.64, 112.14, 55.48, 55.41.

GCMS (EI): calcd. for $C_{14}H_{14}O_2$ 214.10, found: 214.07.



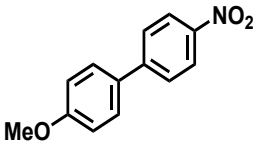
4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (4b) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=50:1) as white solid (226.9 mg, 90%). The spectral data agreed closely with those reported in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.63 (m, 4H), 7.57-7.52 (m, 2H), 7.03-6.99 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.97, 144.42, 132.31, 128.97, 128.65, 128.50, 127.01, 125.82 (q, *J* = 3.82 Hz), 123.17, 114.55, 55.52.

^{19}F NMR (376 MHz, CDCl3): δ -62.20.

GCMS (EI): calcd. for $C_{14}H_{11}F_3O$ 252.08, found: 252.04.



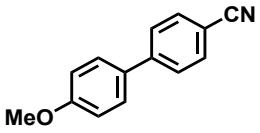
4-methoxy-4'-nitro-1,1'-biphenyl (4c) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=5:1) as yellow solid (188.0 mg, 82%). The spectral data agreed closely with those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.25 (m, 2H), 7.71-7.68 (m, 2H), 7.60-7.57 (m,

2H), 7.04-7.00 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.58, 147.36, 146.68, 131.22, 128.72, 127.23, 124.30, 114.75, 55.58.

GCMS (EI): calcd. for $C_{13}H_{11}NO_3$ 229.07, found: 229.04.

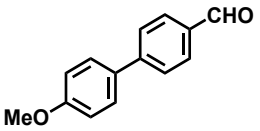


4-methoxy-4'-nitro-1,1'-biphenyl (4d) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=20:1) as white solid (192.5 mg, 84%). The spectral data agreed closely with those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 2H), 7.65-7.63 (m, 2H), 7.55-7.52 (m, 2H), 7.02-7.00 (m, 2H) , 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.34, 145.37, 132.72, 131.65, 128.51, 127.26, 119.25, 114.69, 110.24, 55.54.

GCMS (EI): calcd. for $C_{14}H_{11}NO$ 209.08, found: 209.06.

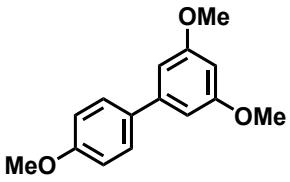


4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (4e) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=10:1) as light-yellow solid (186.8 mg, 88%). The spectral data agreed closely with those reported in the literature.[11]

1H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.94-7.91 (m, 2H), 7.73-7.71 (m, 2H), 7.61-7.58 (m, 2H), 7.03-6.99 (m, 2H), 3.87 (s, 3H).

13C NMR (100 MHz, $CDCl_3$): δ 192.07, 160.24, 146.92, 134.79, 132.18, 130.47, 128.64, 127.19, 114.60, 55.53.

GCMS (EI): calcd. for $C_{14}H_{12}O_2$ 212.08, found: 212.08.

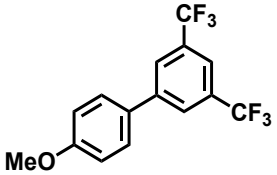


3,4',5-trimethoxy-1,1'-biphenyl (4f) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=10:1) as white solid (222.1 mg, 91%). The spectral data agreed closely with those reported in the literature.[12]

1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.00-6.96 (m, 2H), 6.72 (d, *J* = 2.32Hz, 2H), 6.45 (t, *J* = 2.28Hz, 1H), 3.86 (s, 9H).

13C NMR (100 MHz, $CDCl_3$): δ 161.15, 159.45, 143.17, 133.78, 128.31, 114.22, 105.16, 98.78, 55.49, 55.44.

GCMS (EI): calcd. for $C_{15}H_{16}O_3$ 244.11, found: 244.06.



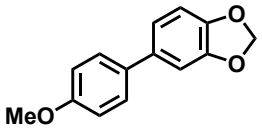
4'-methoxy-3,5-bis(trifluoromethyl)-1,1'-biphenyl (4g) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=50:1) as yellow liquid (252.8 mg, 79%). The spectral data agreed closely with those reported in the literature.[13]

1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.80 (s, 1H), 7.57-7.54 (m, 2H), 7.05-7.01 (m, 2H), 3.88 (s, 3H).

13C NMR (100 MHz, $CDCl_3$): δ 160.45, 143.01, 132.14 (d, *J* = 32.5 Hz), 130.75, 128.53, 126.80, 123.57 (d, *J* = 270.6 Hz), 120.35, 114.82, 55.58.

^{19}F NMR (376 MHz, CDCl3): δ -62.64 .

GCMS (EI): calcd. for $C_{15}H_{10}F_6O$ 320.06, found: 320.04.

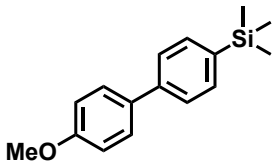


5-(4-methoxyphenyl)benzo[d][1,3]dioxole (4h) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=5:1) as white solid (173.3 mg, 76%). The spectral data agreed closely with those reported in the literature.[14]

1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (m, 2H), 7.04-6.94 (m, 4H), 6.88-6.85 (m, 1H), 5.99 (s, 2H), 3.85 (s, 3H).

13C NMR (100 MHz, $CDCl_3$): δ 158.98, 148.17, 146.70, 135.42, 133.68, 128.02,, 120.20, 114.27, 108.66, 107.51, 101.19, 55.46.

GCMS (EI): calcd. for $C_{14}H_{12}O_3$ 228.08, found: 228.01.

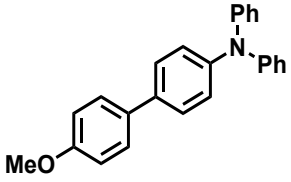


(4'-methoxy-[1,1'-biphenyl]-4-yl)trimethylsilane (4i) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=50:1) as white solid (210.0 mg, 82%). The spectral data agreed closely with those reported in the literature.[14]

1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.55 (m, 6H), 7.01-6.99 (m, 2H), 3.86 (s, 3H), 0.32 (s, 9H).

13C NMR (100 MHz, $CDCl_3$): δ 159.33, 141.34, 138.58, 133.95, 128.31, 126.22, 114.33, 55.47, -0.93.

GCMS (EI): calcd. for $C_{16}H_{20}OSi$ 256.13, found: 256.11.



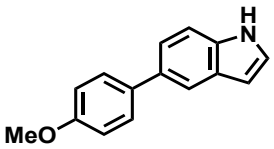
4'-methoxy-N,N-diphenyl-[1,1'-biphenyl]-4-amine (4j) The reaction was conducted

according to general procedure. The product was purified by column chromatography (PE: EA=20:1) as white solid (281.2 mg, 80%). The spectral data agreed closely with those reported in the literature.[11]

1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.47-7.43 (m, 2H), 7.30-7.25 (m, 4H), 7.17-7.13 (m, 6H), 7.06-6.96 (m, 4H), 3.86 (s, 3H).

13C NMR (100 MHz, $CDCl_3$): δ 158.93, 147.88, 146.71, 135.11, 133.38, 129.37, 127.81, 127.47, 124.35, 122.88, 114.30, 55.45.

GCMS (EI): calcd. for $C_{25}H_{21}NO$ 351.16, found: 351.12.

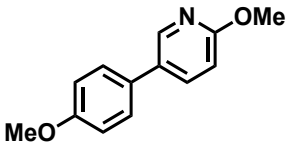


4-methoxy-4'-nitro-1,1'-biphenyl (4k) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=50:1) as yellow solid (178.8 mg, 78%). The spectral data agreed closely with those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.81 (s, 1H), 7.60-7.56 (m, 2H), 7.46-7.40 (m, 2H), 7.25-7.23 (m, 1H), 7.01-6.98 (m, 2H), 6.61-6.59 (m, 1H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.59, 135.34, 135.12, 133.22, 128.47, 124.91, 121.84, 118.88, 114.23, 111.30, 103.04, 55.49.

GCMS (EI): calcd. for $C_{15}H_{13}NO$ 256.13, found: 256.11.



2-methoxy-5-(4-methoxyphenyl)pyridine (4l) The reaction was conducted according to general procedure. The product was purified by column chromatography (PE: EA=20:1) as white solid (174.2 mg, 81%). The spectral data agreed closely with those reported in the literature.[16]

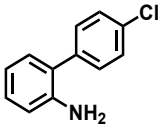
1H NMR (400 MHz, $CDCl_3$): δ 8.35-8.34 (m, 1H), 7.74 (dd, J = 8.6, 2.64Hz, 1H), 7.46-

7.44 (m, 2H), 7.00-6.96 (m, 2H), 6.81-6.79 (m, 1H),3.97 (s, 3H), 3.85 (s, 3H).

13C NMR (100 MHz, $CDCl_3$): δ 163.31, 159.28, 144.59, 137.34, 130.52, 129.93, 127.87, 114.54, 110.85, 55.48, 53.65.

GCMS (EI): calcd. for $C_{13}H_{13}NO_2$ 215.09, found: 215.09.

Drug molecules

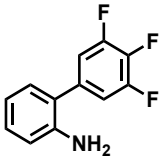


Boscalid intermediate: The reaction was conducted according to general procedure A. The product was purified by column chromatography (PE: EA=30:1) as colorless oil (166.5mg, 82%). The spectral data agreed closely with those reported in the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 4H), 7.21-7.16 (m, 1H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.85 (td, *J* = 7.5, 1.2 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.61 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.52, 138.02, 133.22, 130.59, 130.46, 129.60, 129.12, 128.96, 126.43, 118.91, 116.78, 115.86.

GCMS (EI): calcd. for $C_{12}H_{10}ClN$ 203.05, found:203.01.



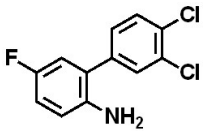
Fluxapyroxad intermediate: The reaction was conducted according to general procedure A. The product was purified by column chromatography (PE: EA=30:1) as colorless oil (174.0 mg, 78%). The spectral data agreed closely with those reported in the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.18 (m, 1H), 7.16-7.07 (m, 3H), 6.87-6.88 (m, 1H), 6.79-6.77 (m, 1H), 3.76 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.74, 150.25 (d, *J* = 10.0 Hz), 143.39, 140.30, 137.81, 135.60 (d, *J* = 5.0 Hz),130.31, 129.61, 119.04, 116.12, 113.37 (d, *J* = 5.7 Hz).

^{19}F NMR (376 MHz, CDCl3): δ -133.76, -162.05.

GCMS (EI): calcd. for $C_{12}H_8F_3N$ 223.06, found:223.04.



Bixafen intermediate: The reaction was conducted according to general procedure A. The product was purified by column chromatography (PE: EA=30:1) as colorless oil (206.5mg, 81%). The spectral data agreed closely with those reported in the literature.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.31-7.28(m, 1H), 6.92-6.87 (m, 1H), 6.83-6.80 (m, 1H), 6.73-6.68 (m, 1H), 3.59 (s, 2H).

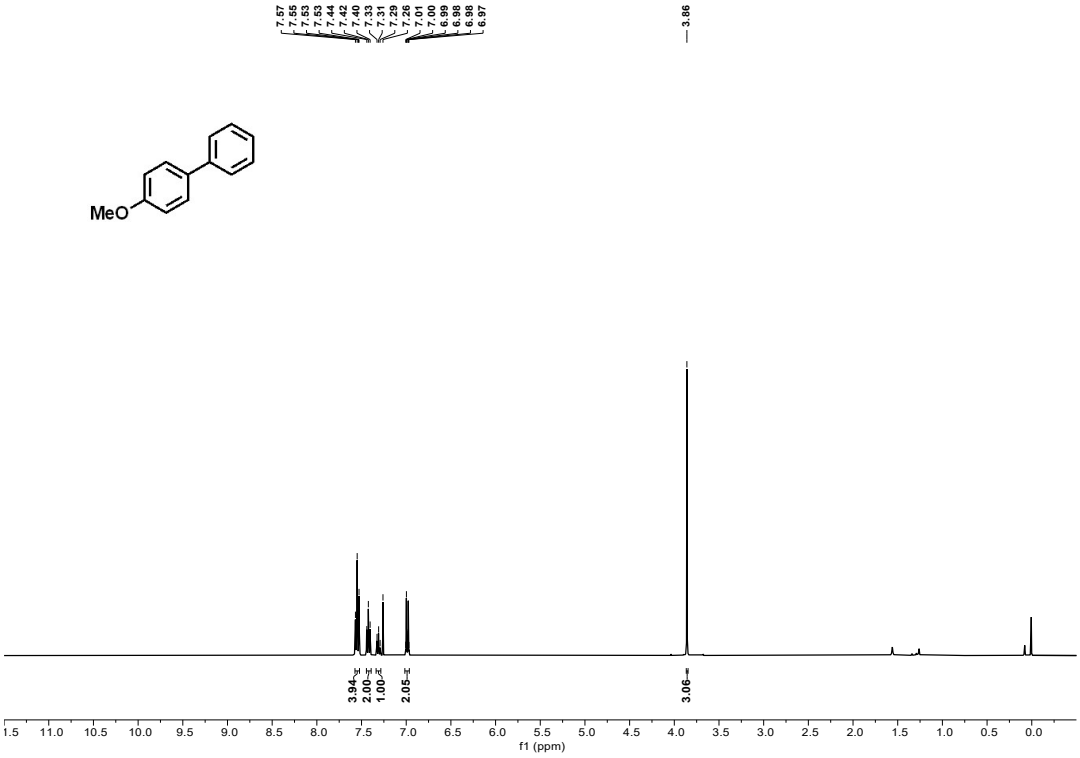
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.56, 155.21, 139.62, 138.63, 133.17, 131.94, 131.03 (d, J = 2.3 Hz), 128.47, 126.00 (d, J = 7.2 Hz), 116.98 (d, J = 7.6 Hz), 116.57 (d, J = 22.7 Hz), 115.92 (d, J = 22.4 Hz).

^{19}F NMR (376 MHz, CDCl3): δ -125.98.

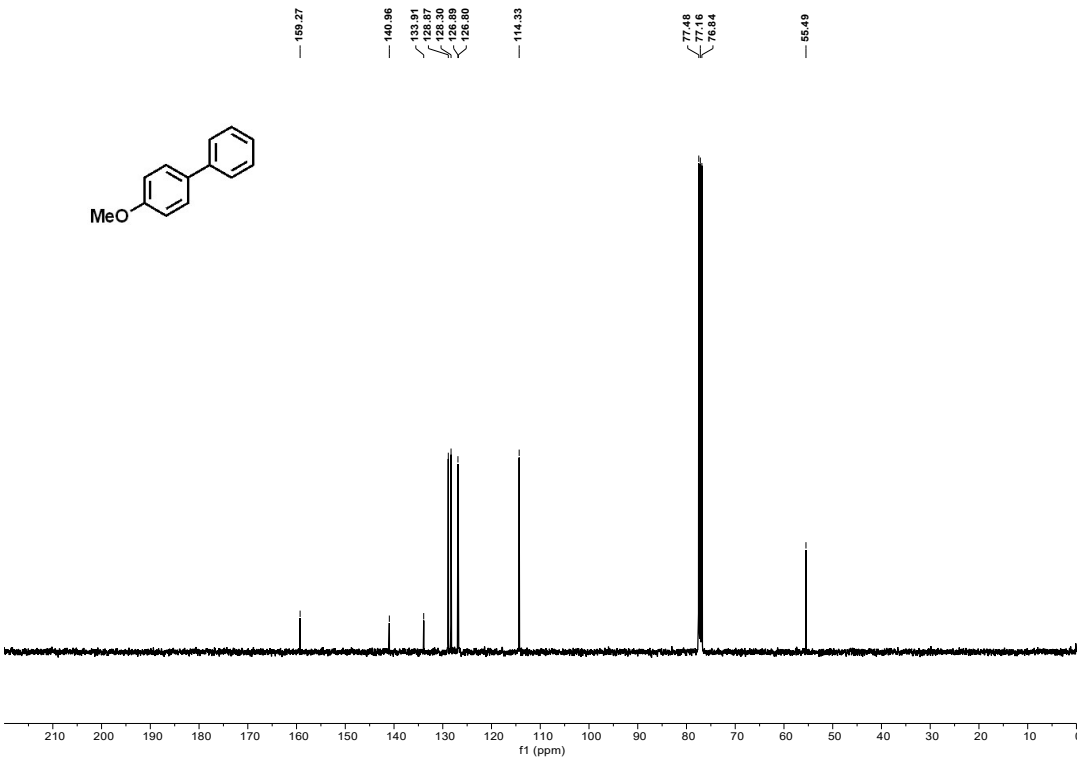
GCMS (EI): calcd. for $C_{12}H_8Cl_2FN$ 255.00, found:254.99.

V. NMR spectra

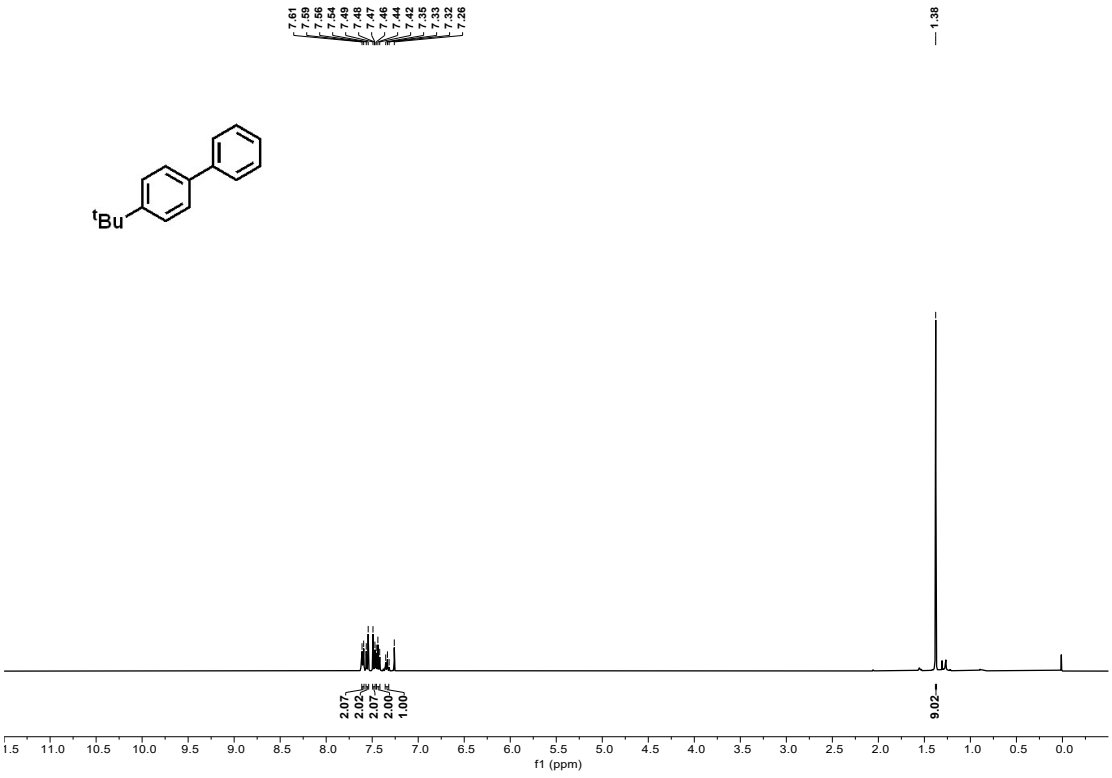
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**



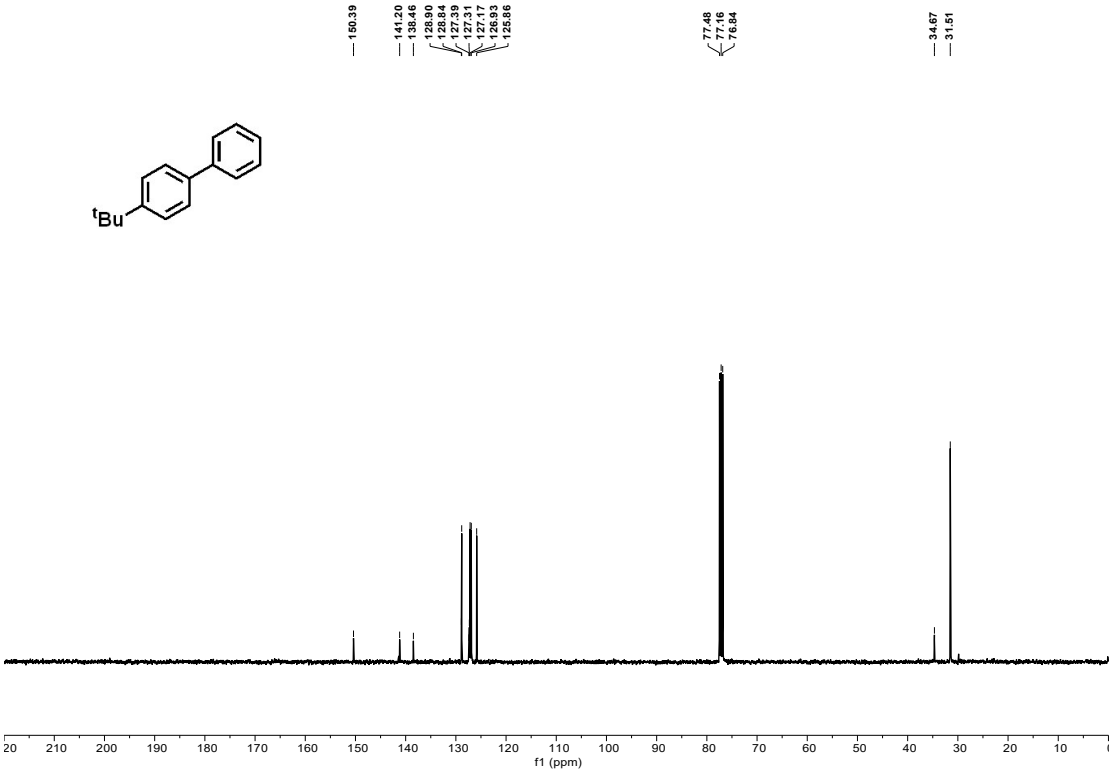
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3a**



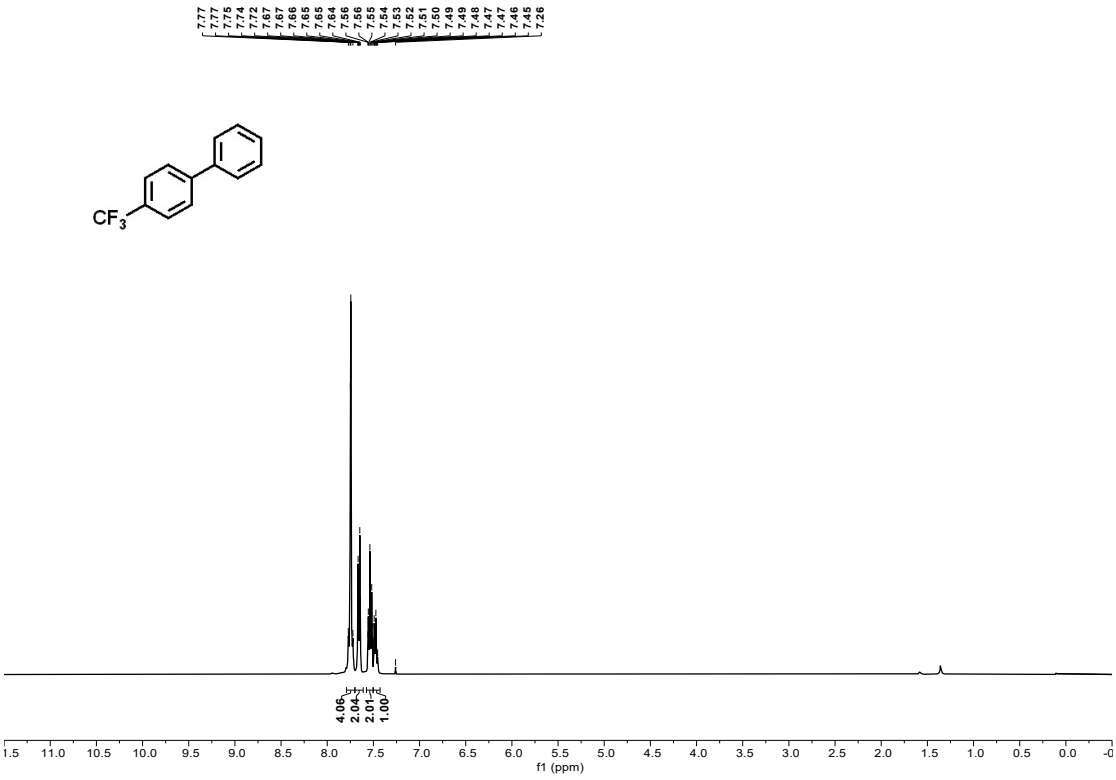
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3b**



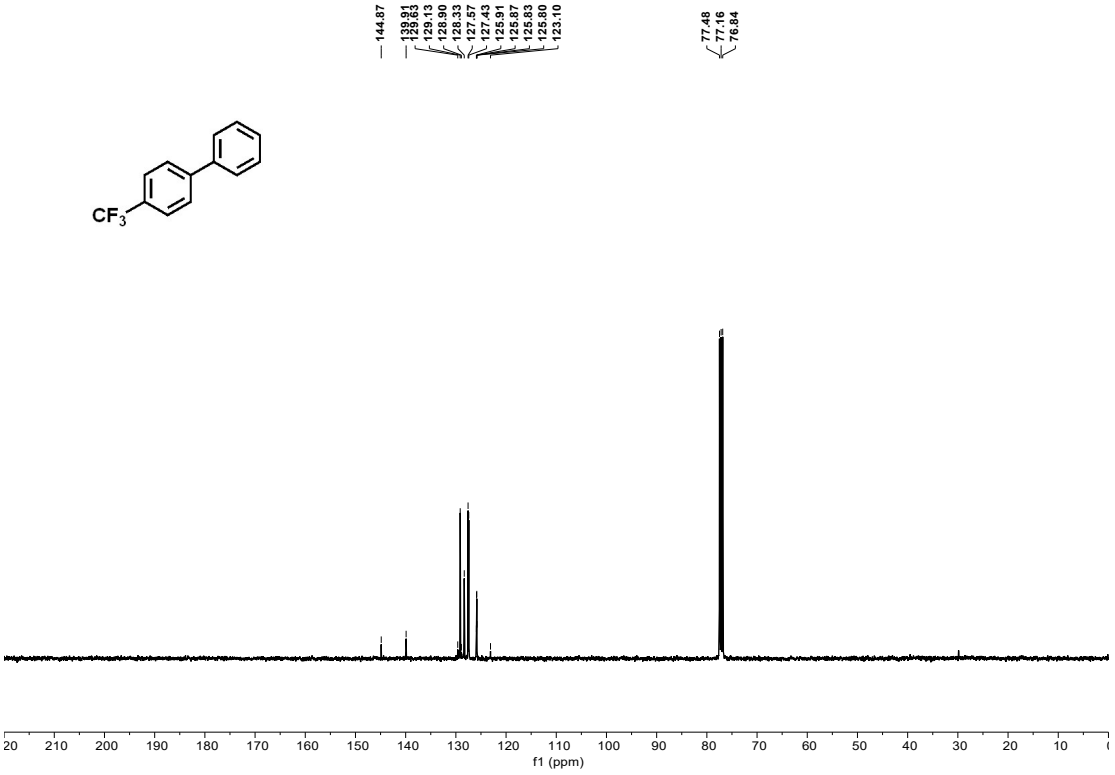
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3b**



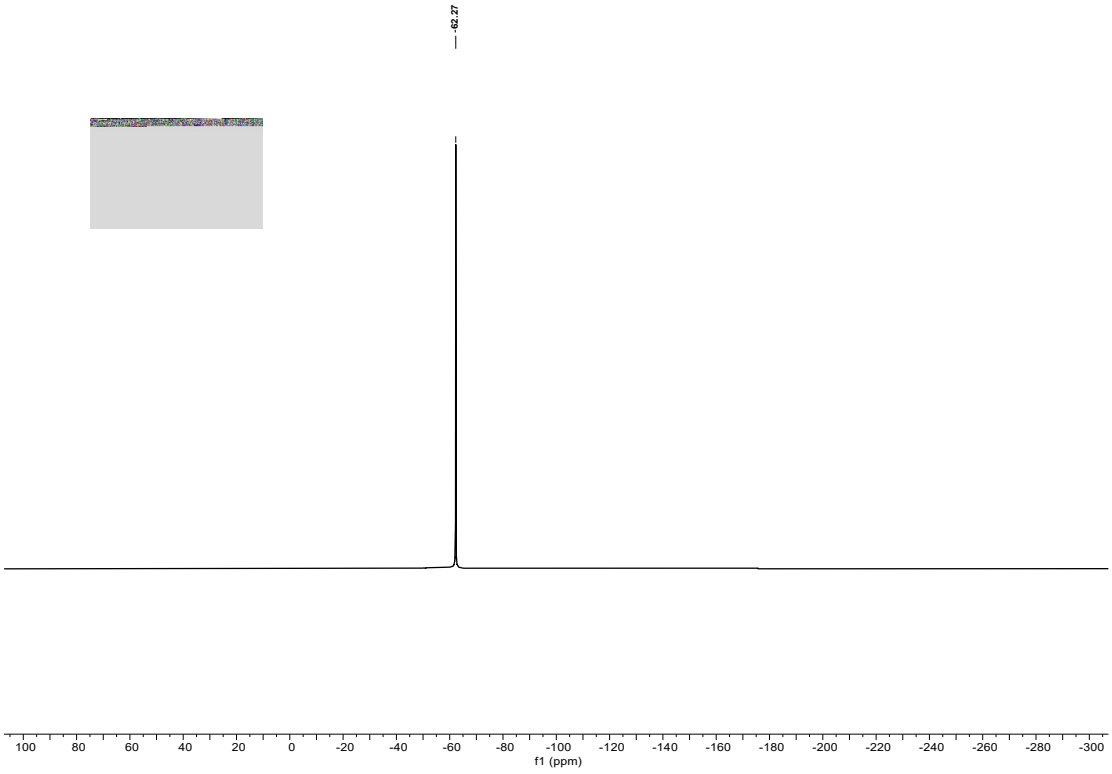
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3c**



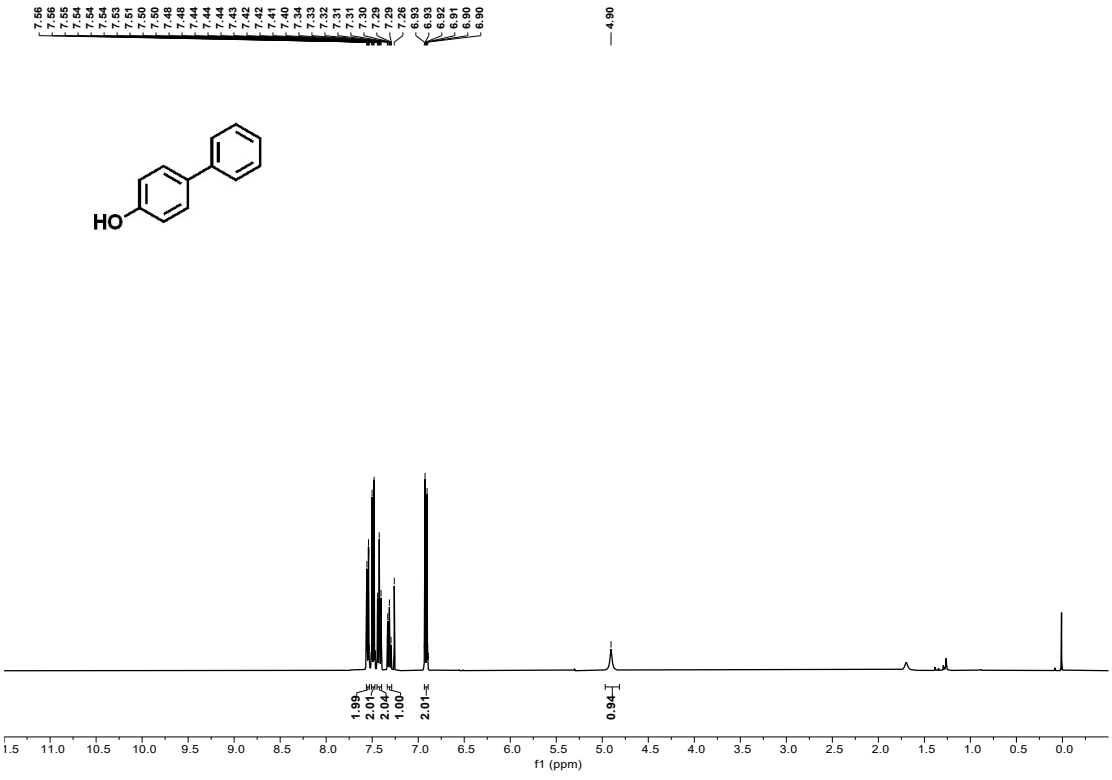
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3c**



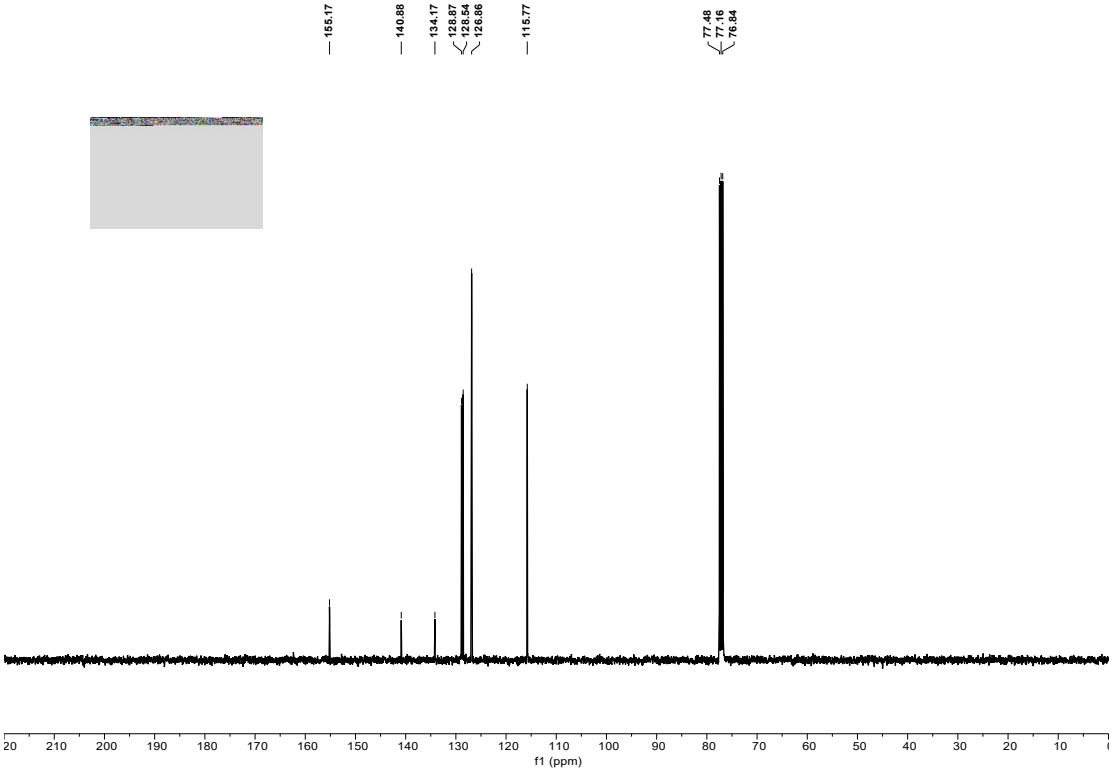
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3c**



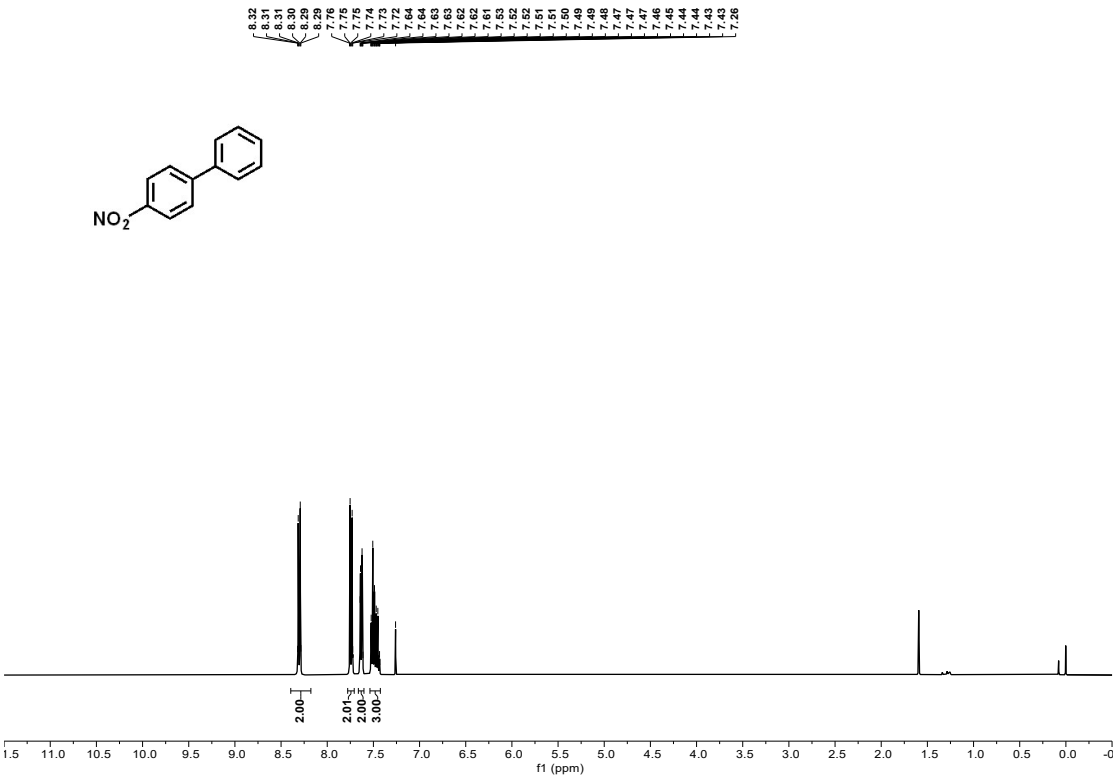
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3d**



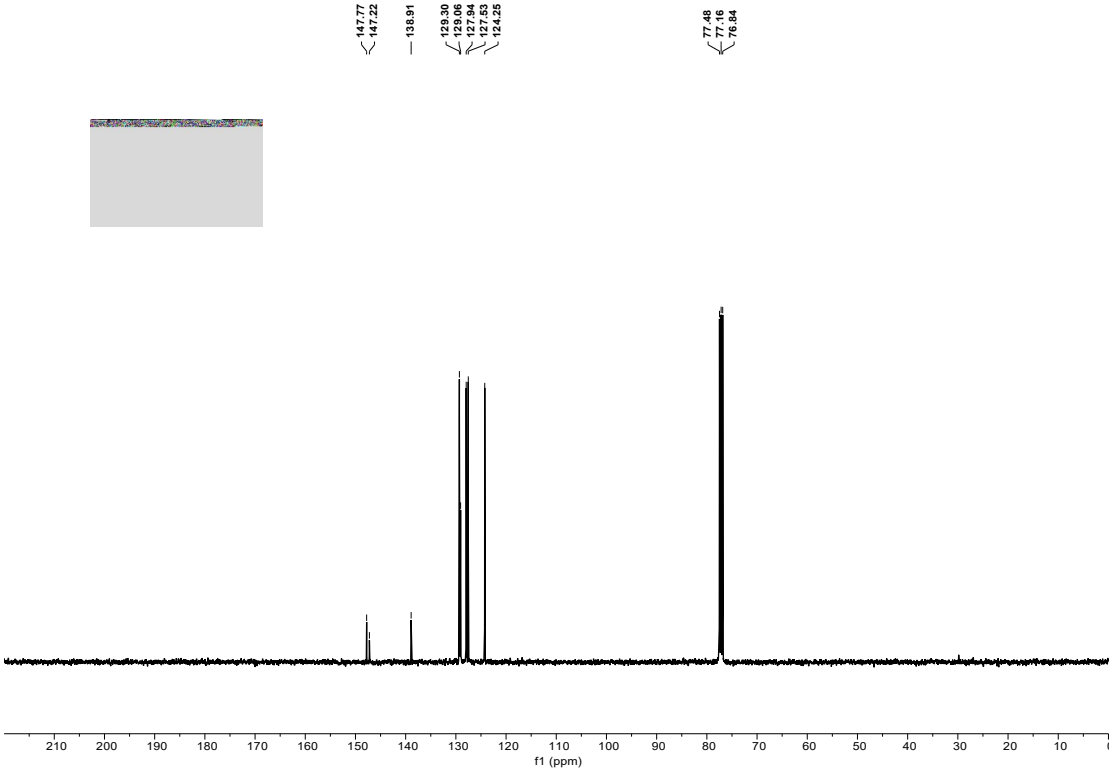
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3d**



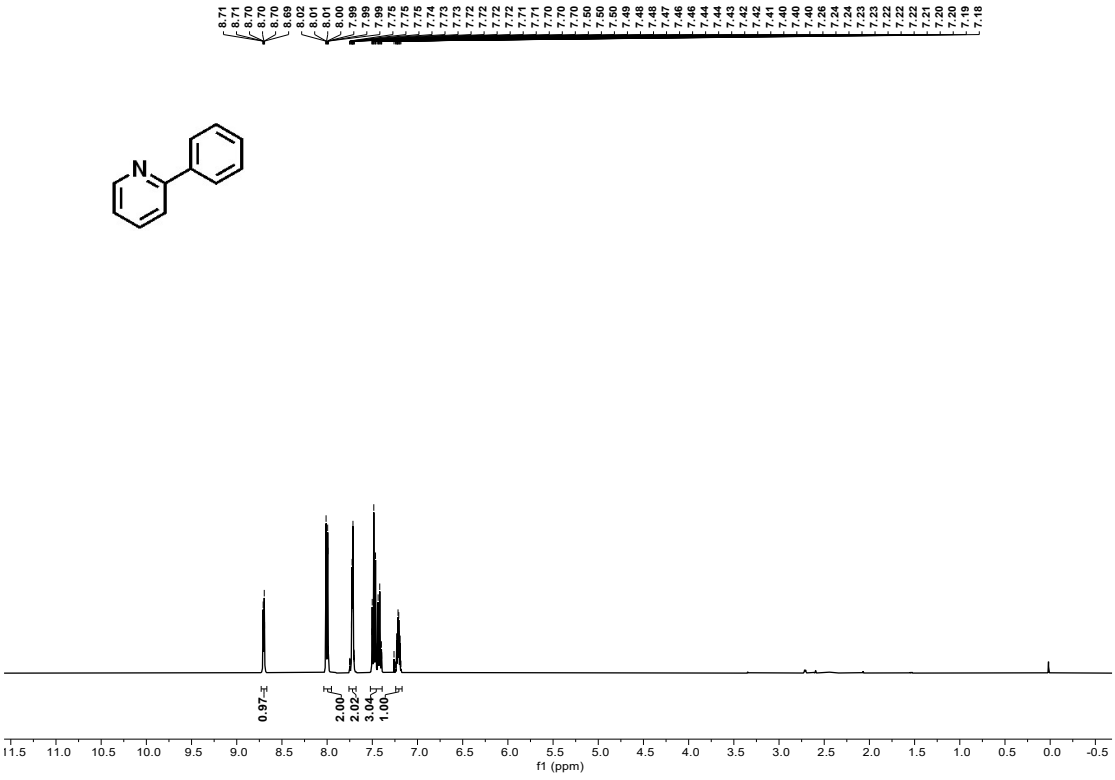
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3e**



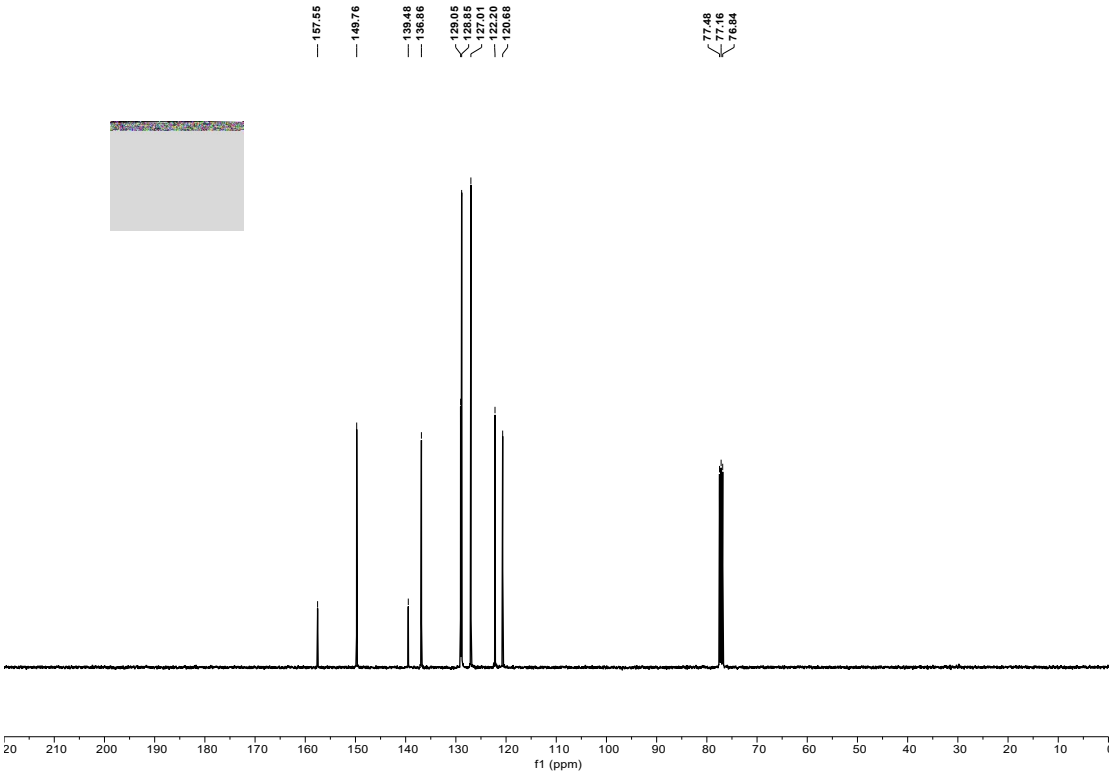
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3e**



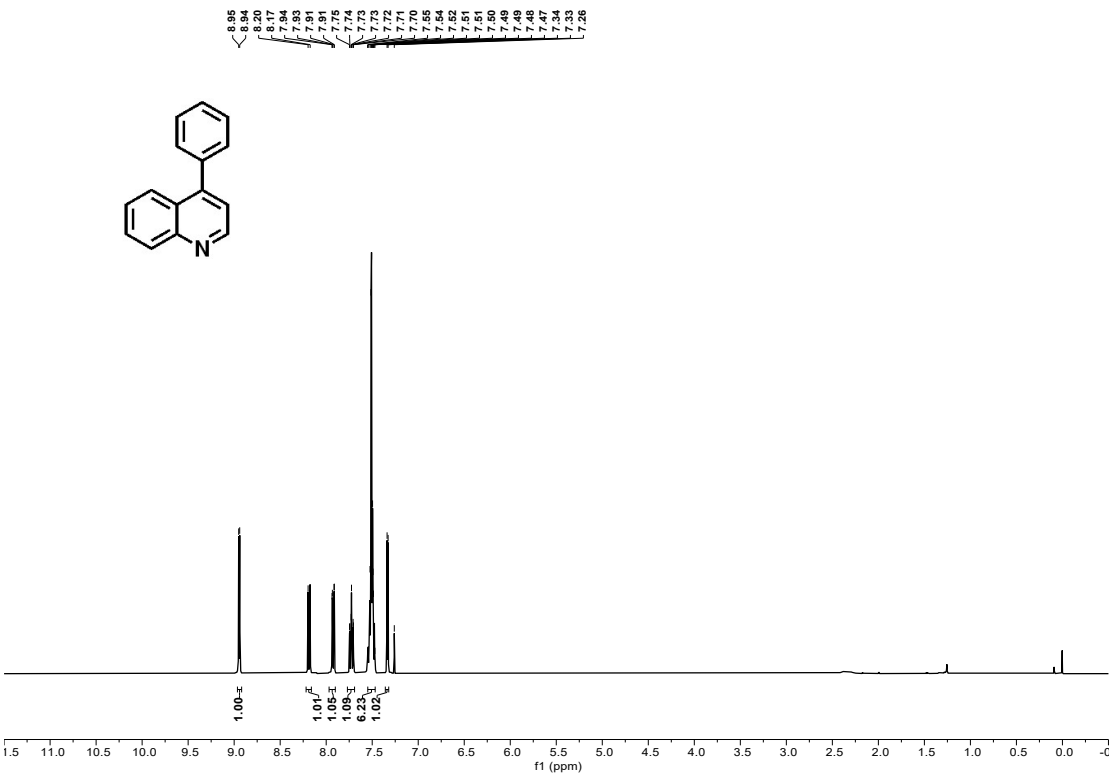
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**



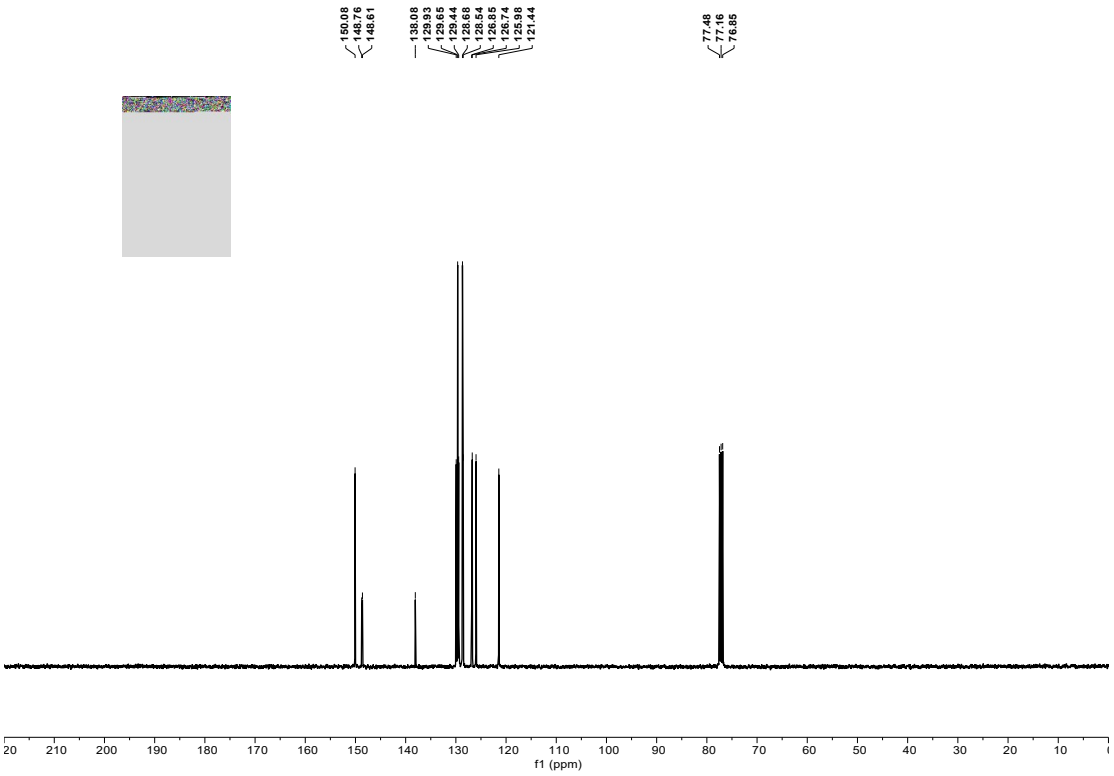
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3f**



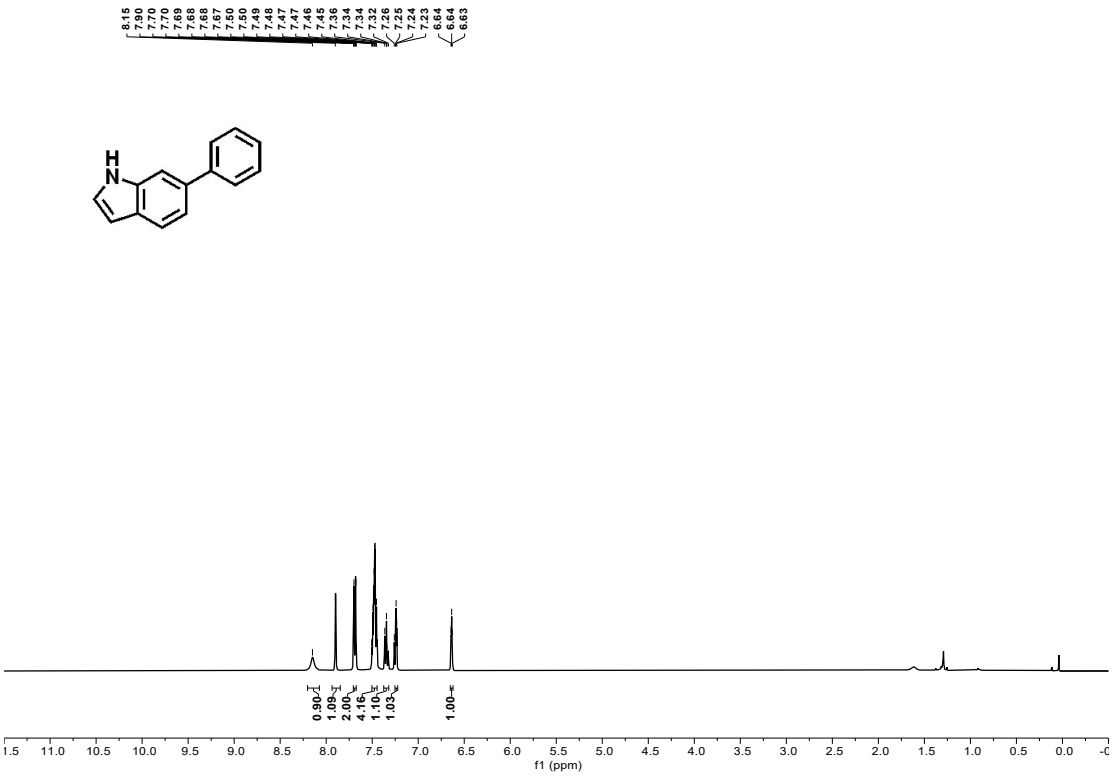
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3g**



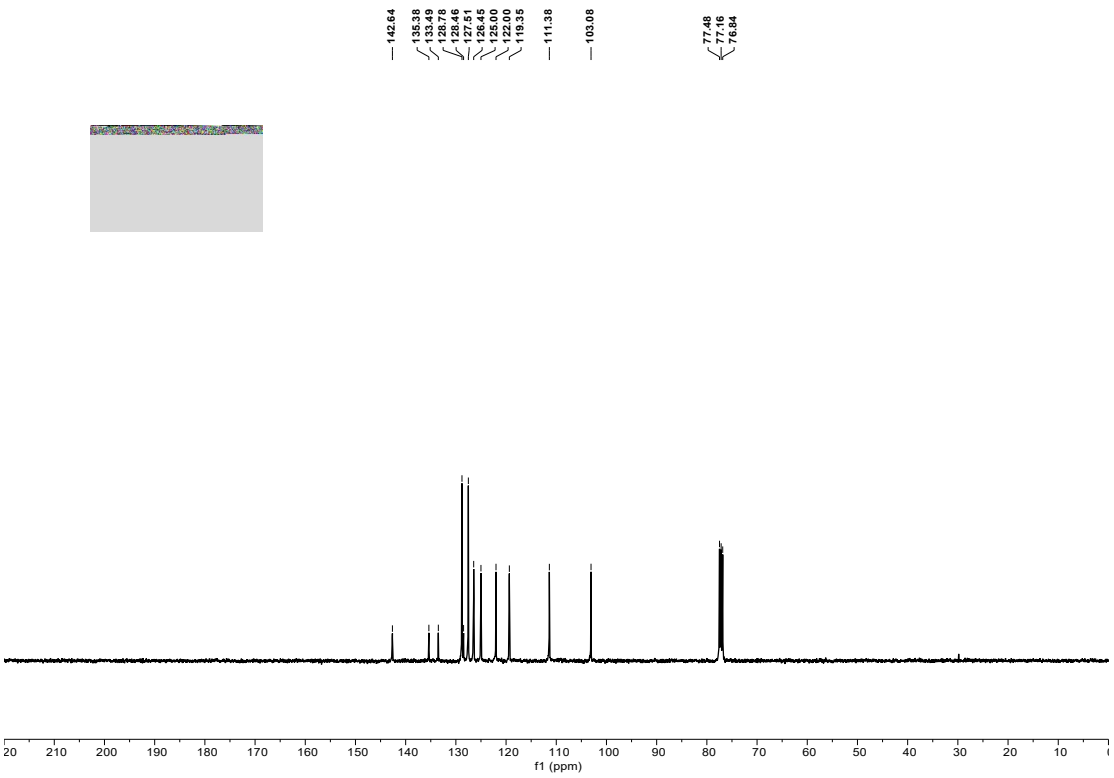
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3g**



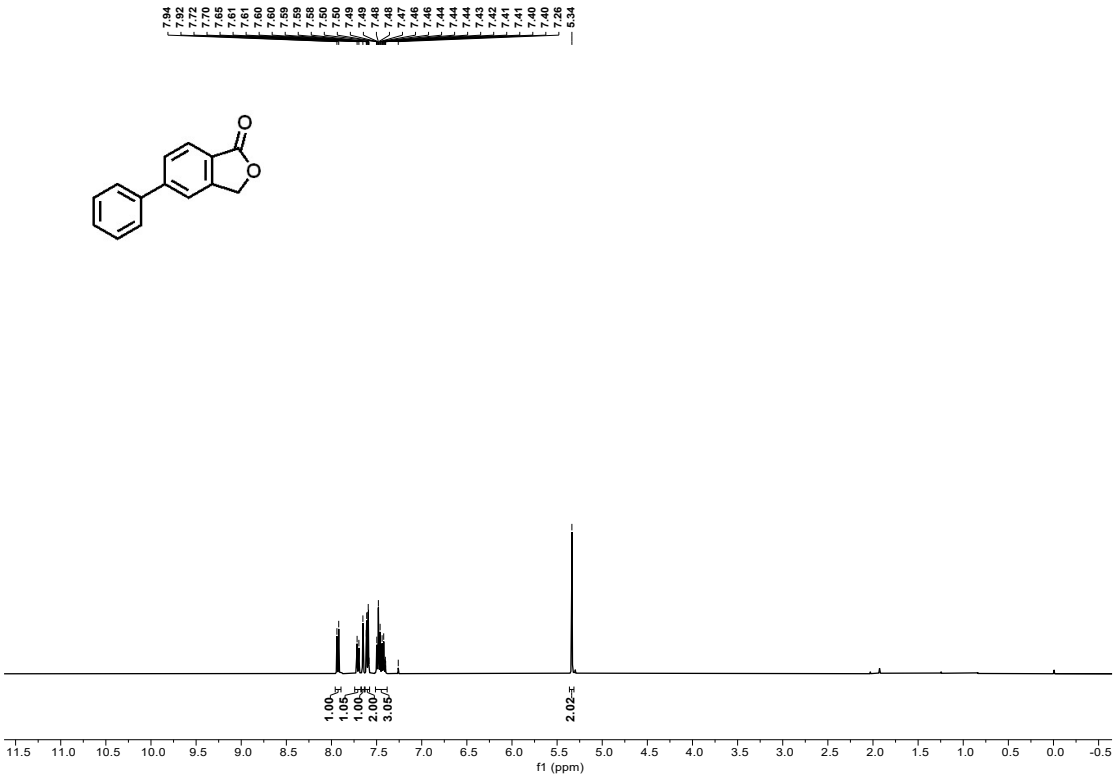
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



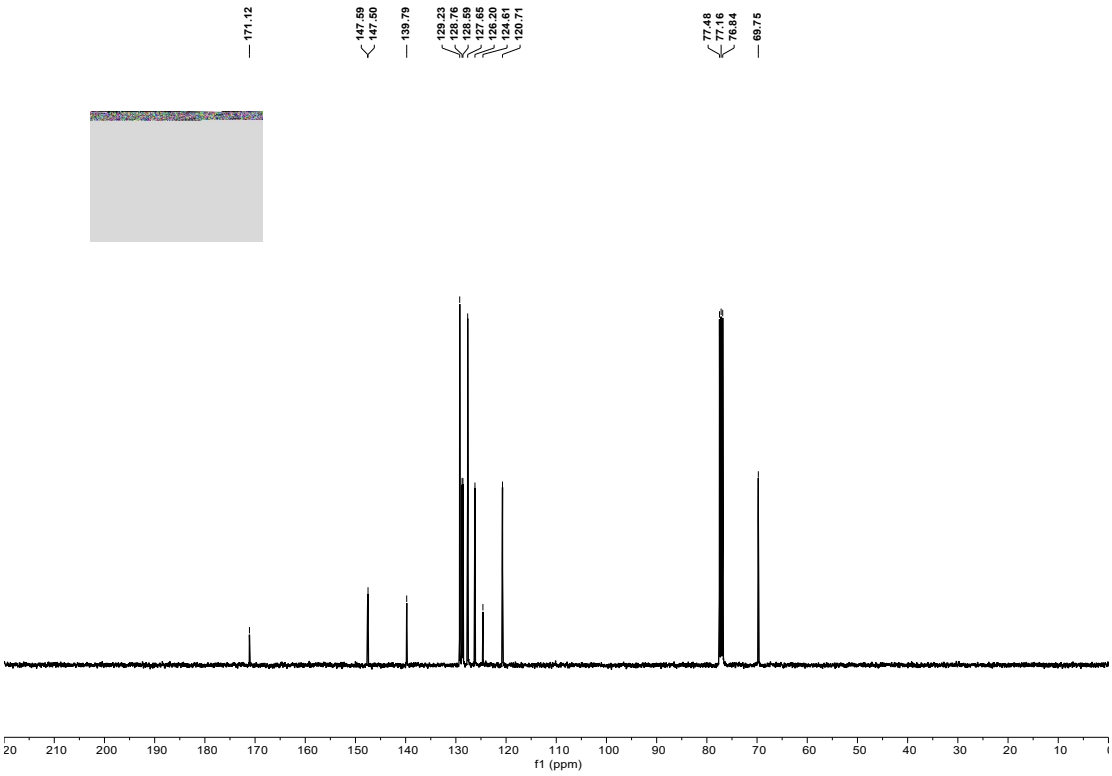
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3h**



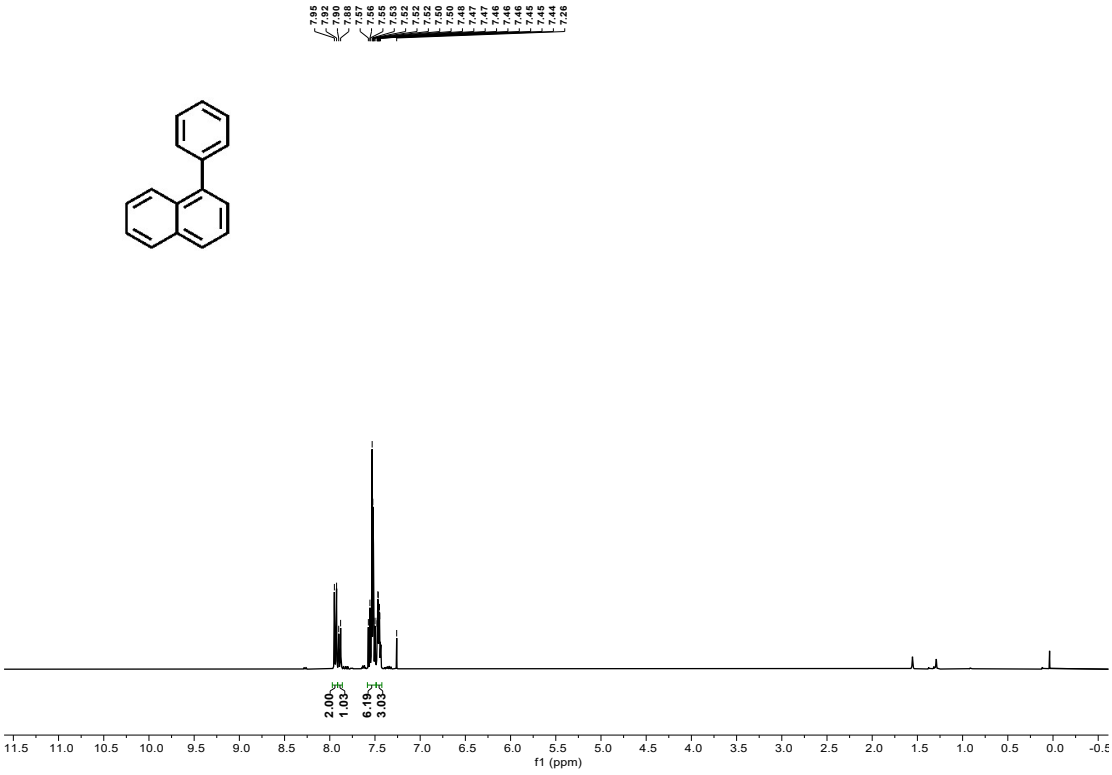
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3i**



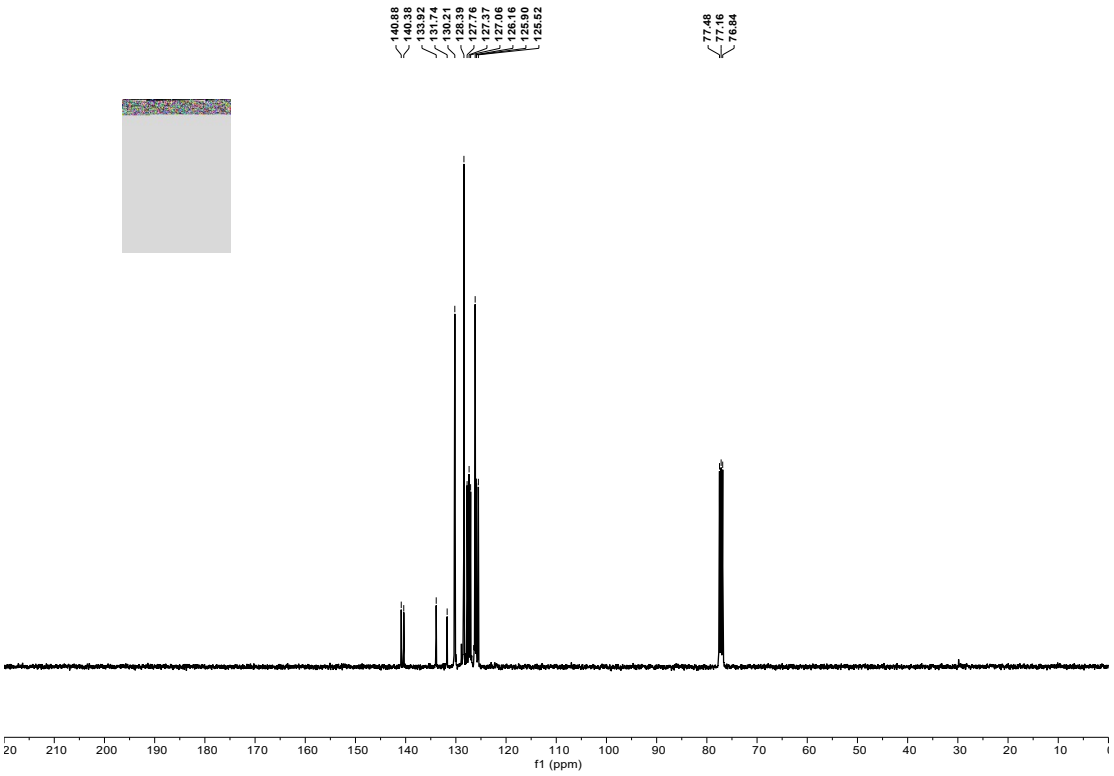
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3i**



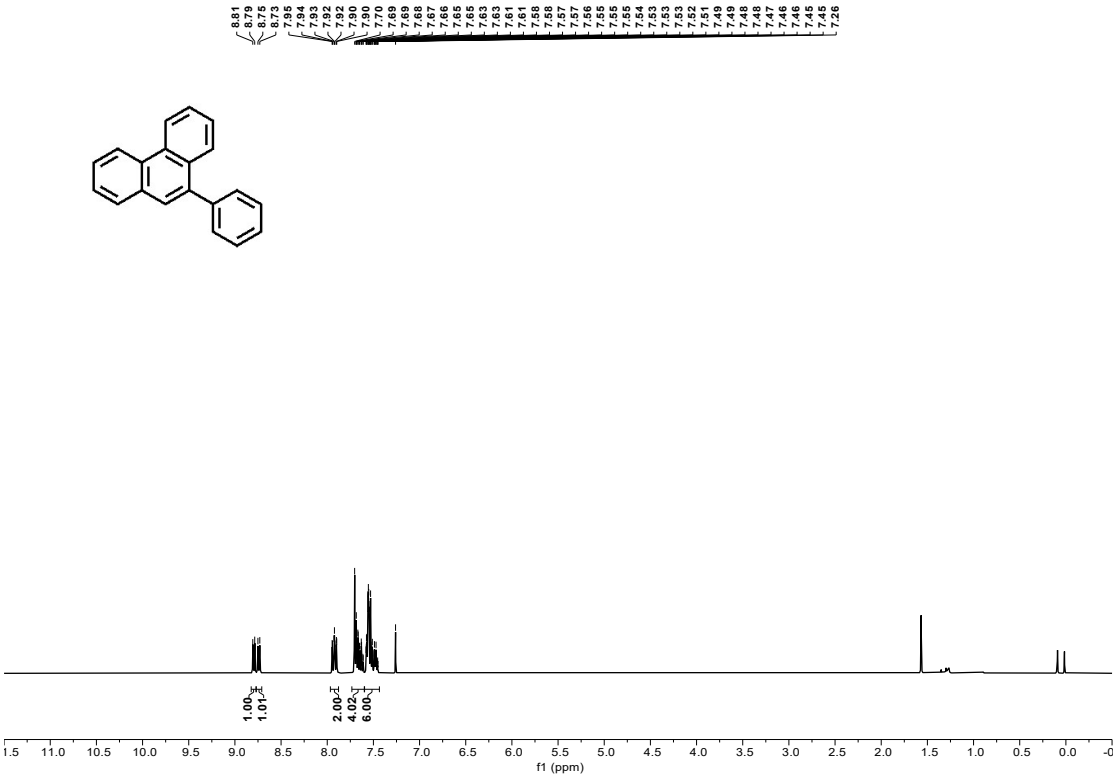
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3j**



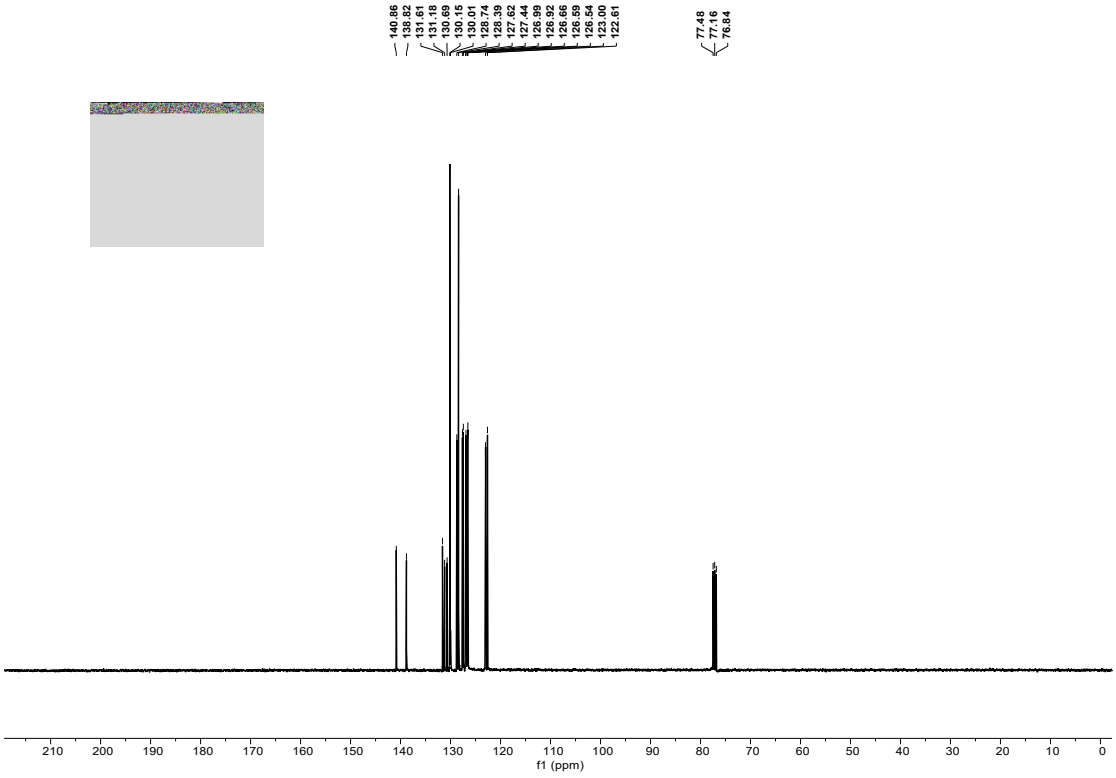
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3j**



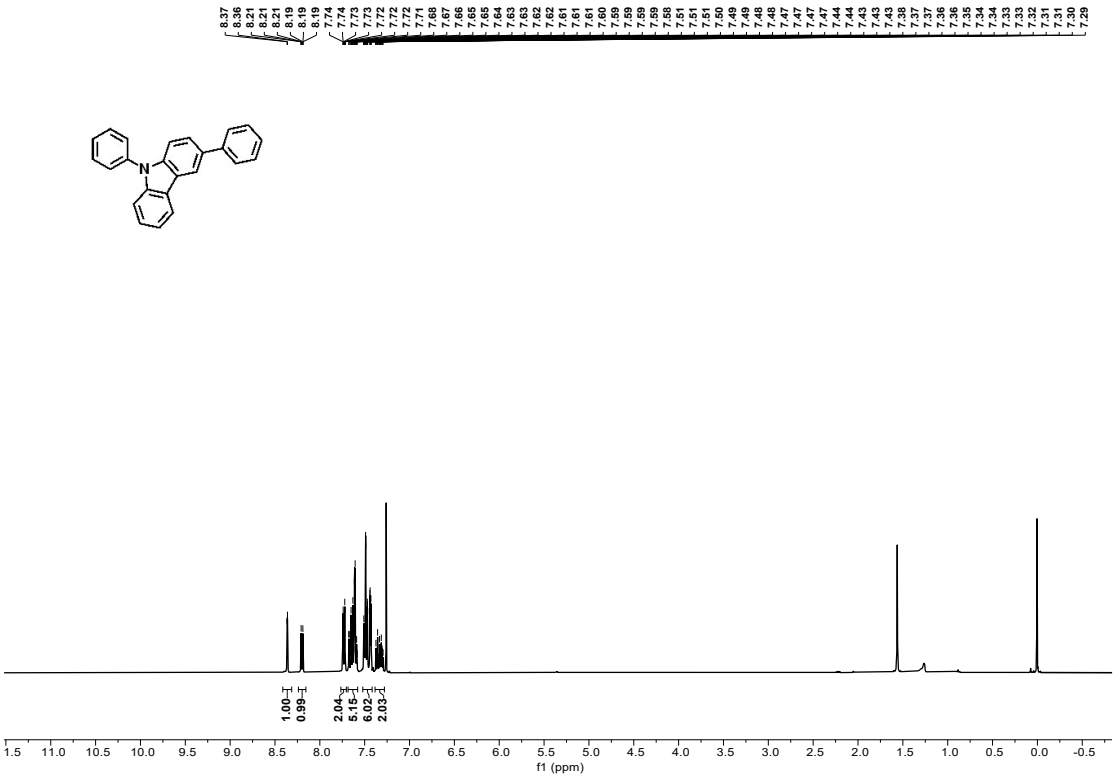
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3k**



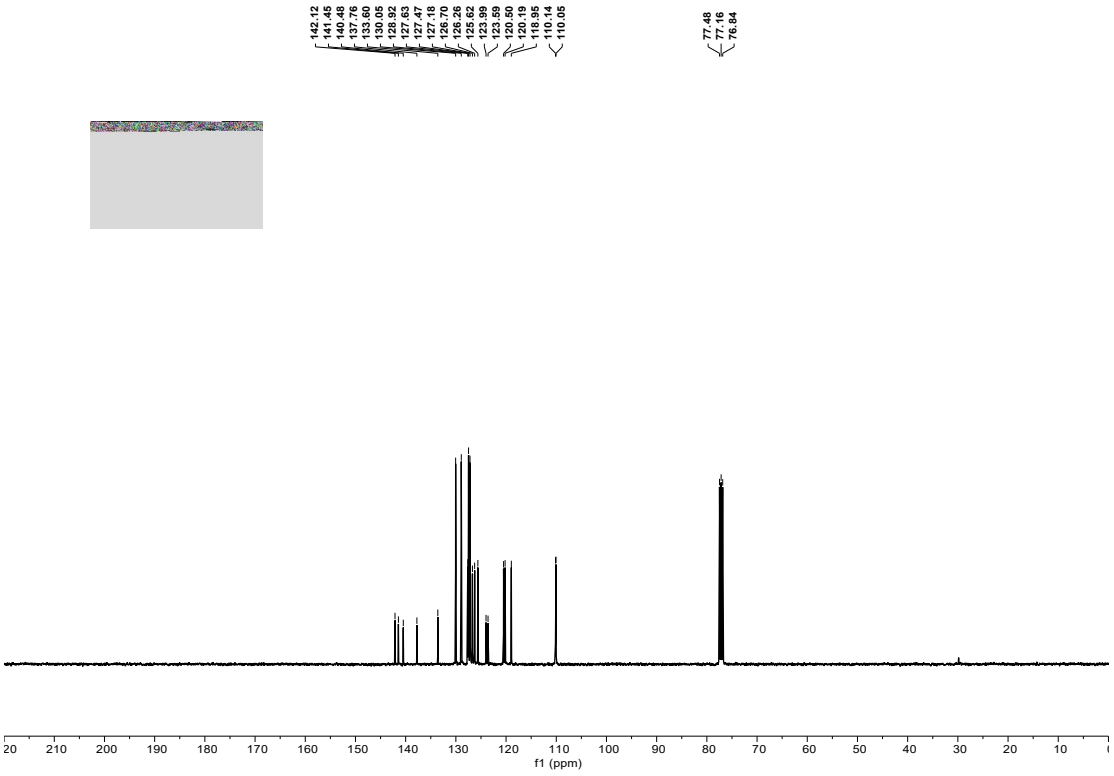
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3k**



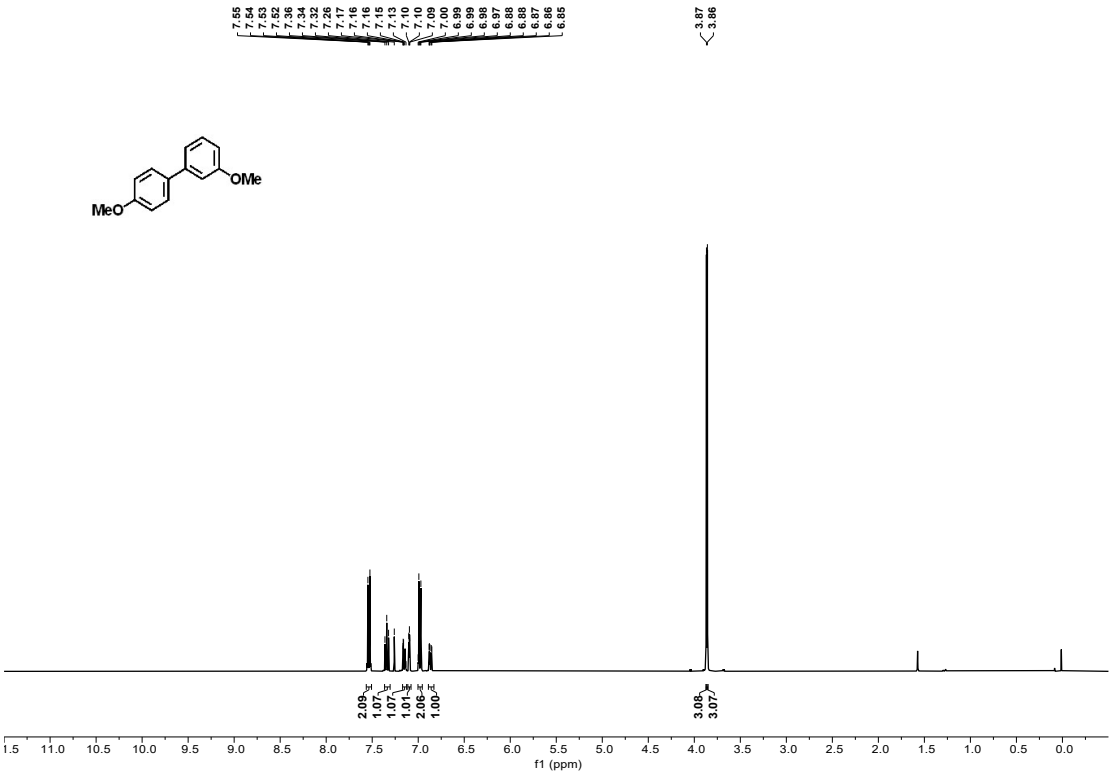
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3l**



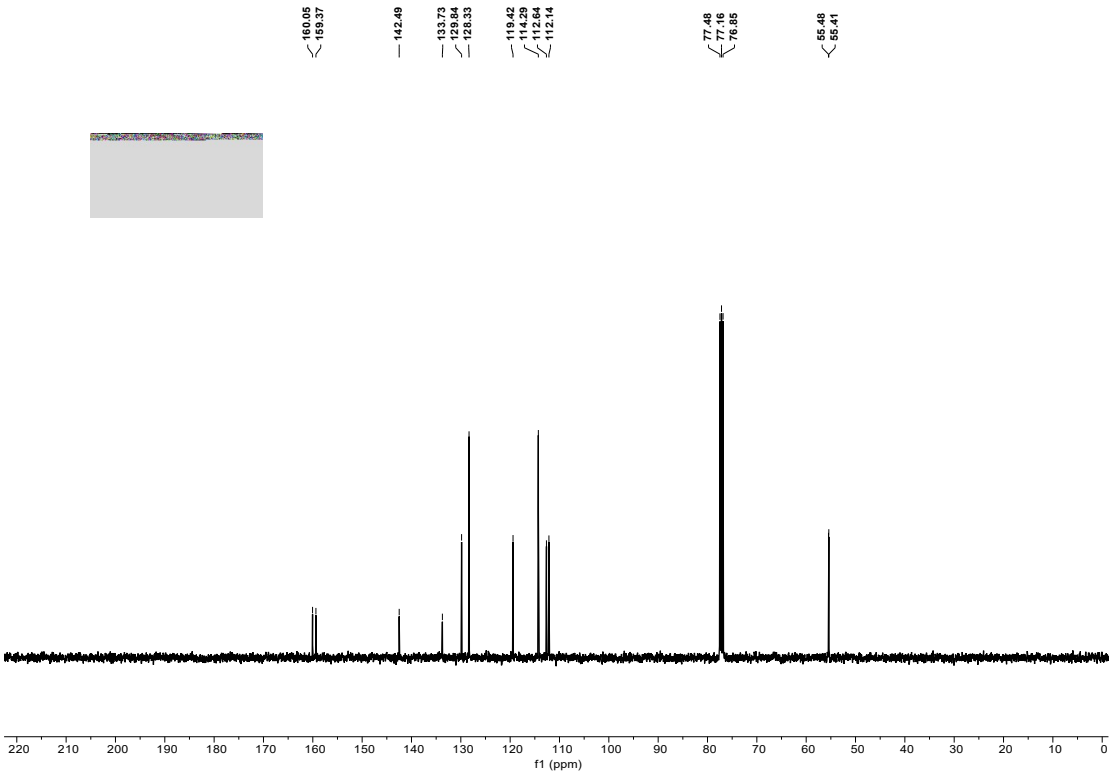
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3l**



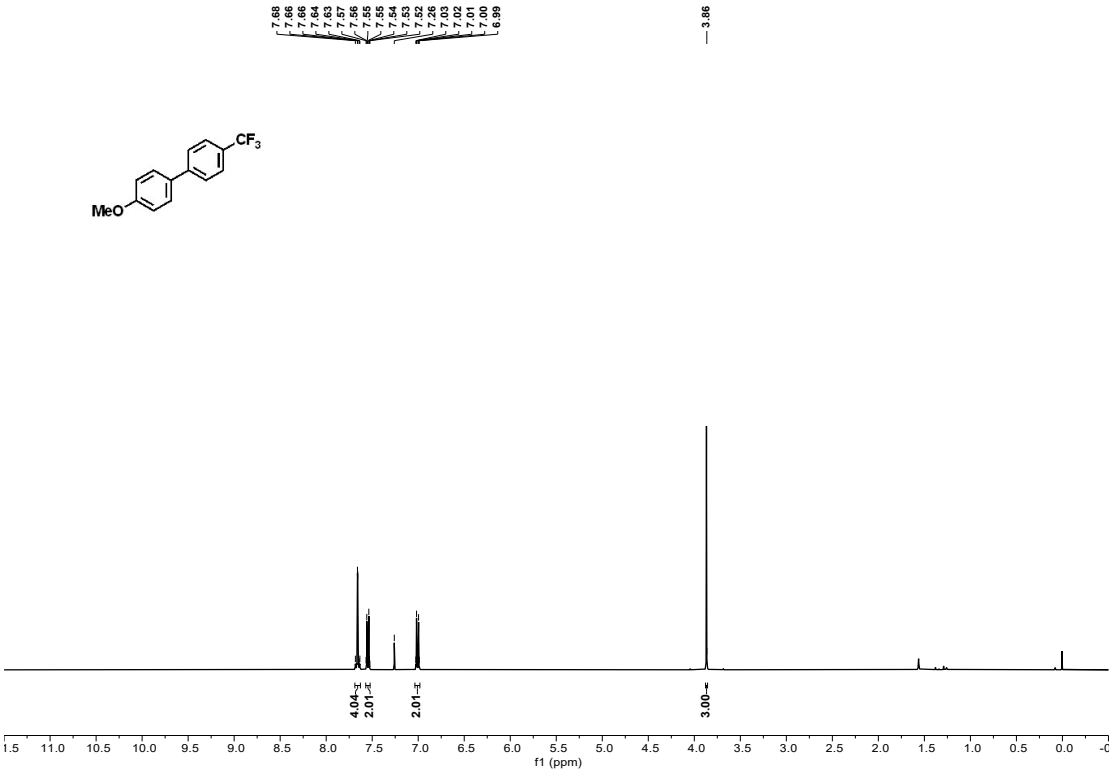
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4a**



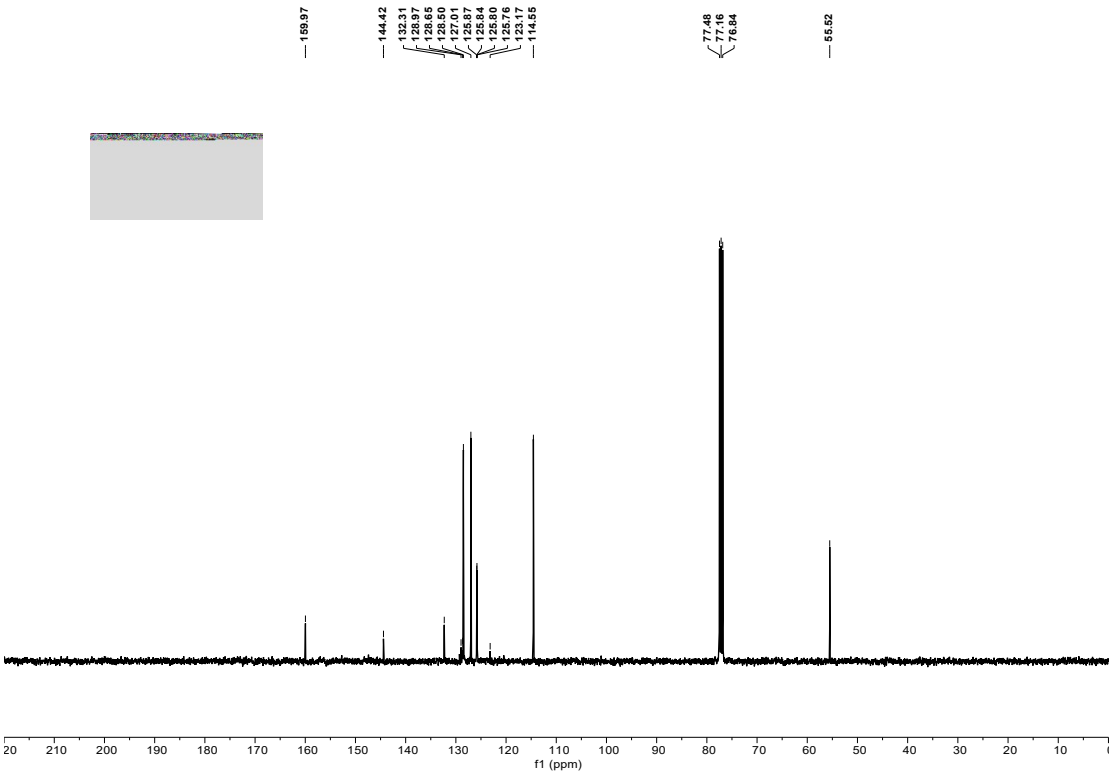
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4a**



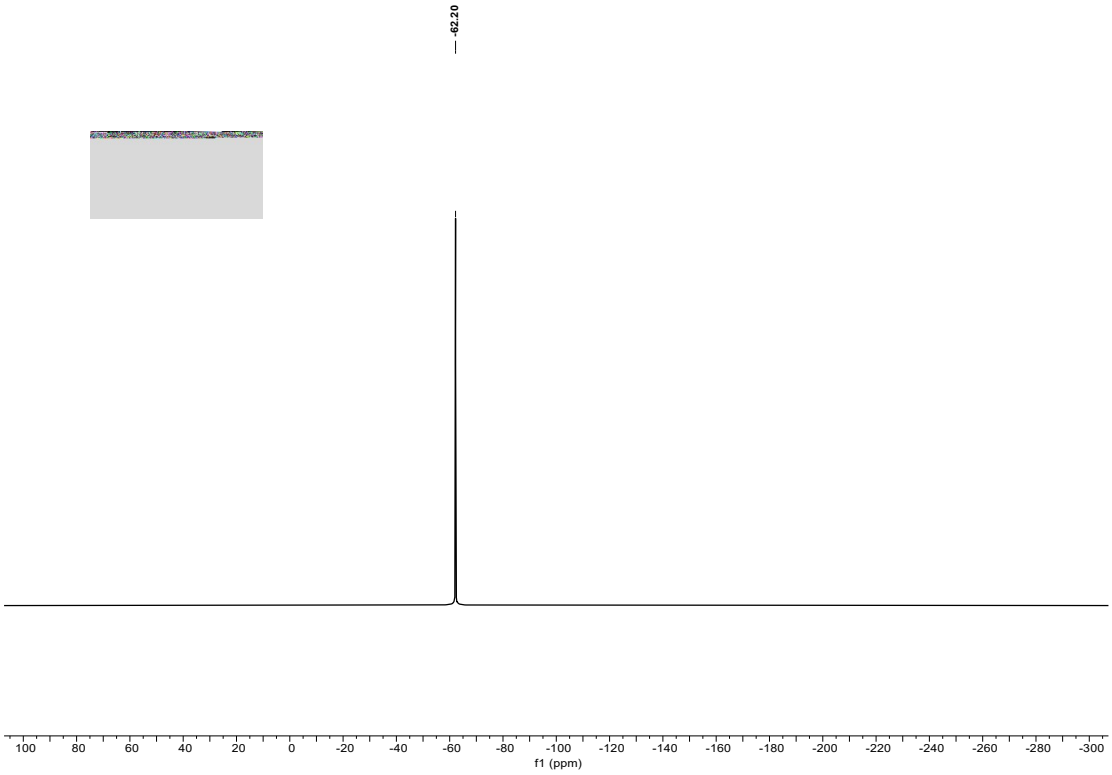
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4b**



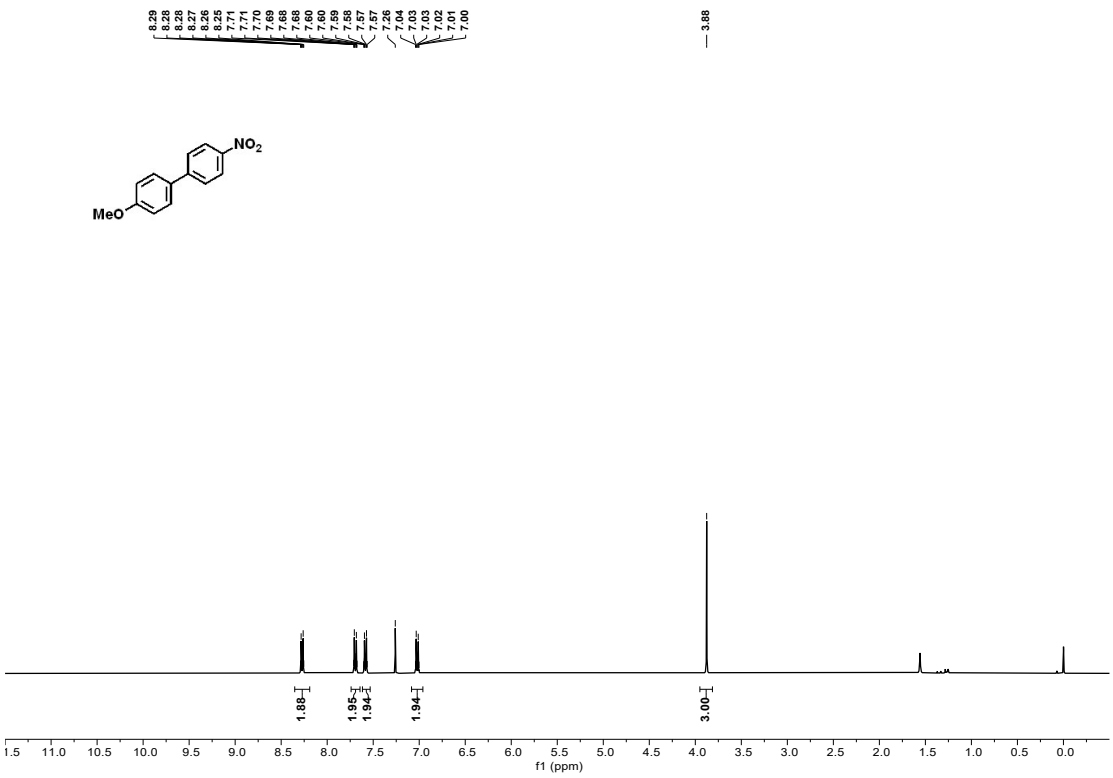
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4b**



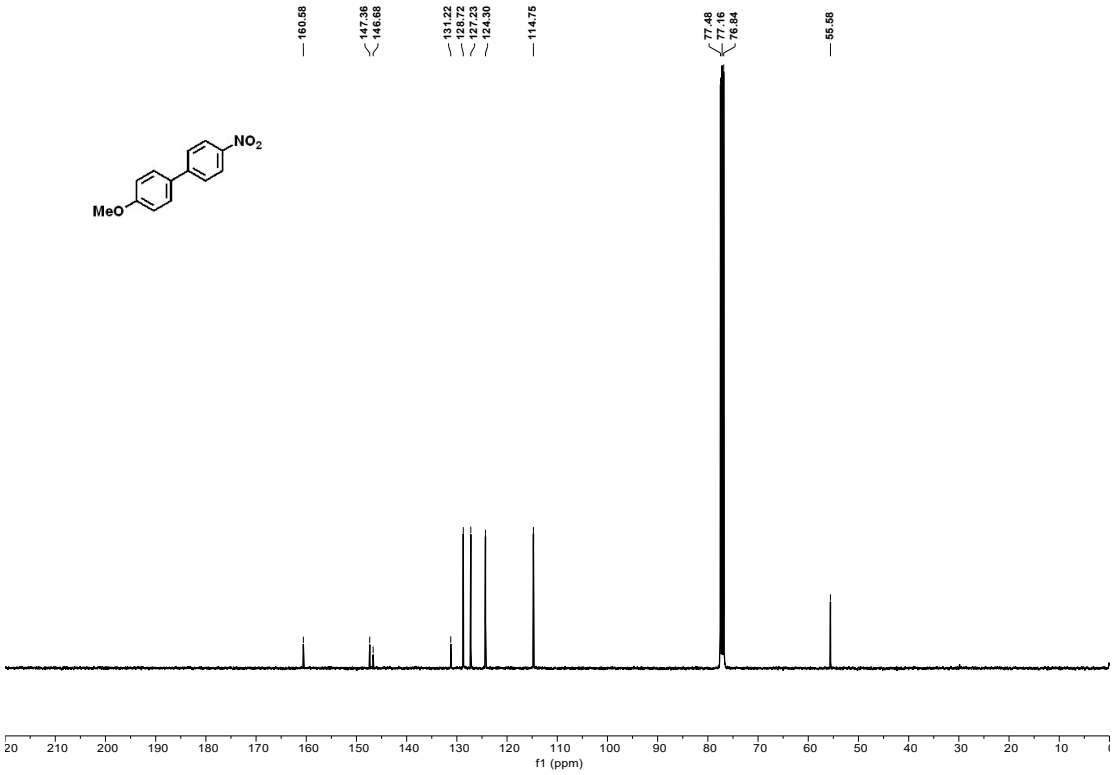
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4b**



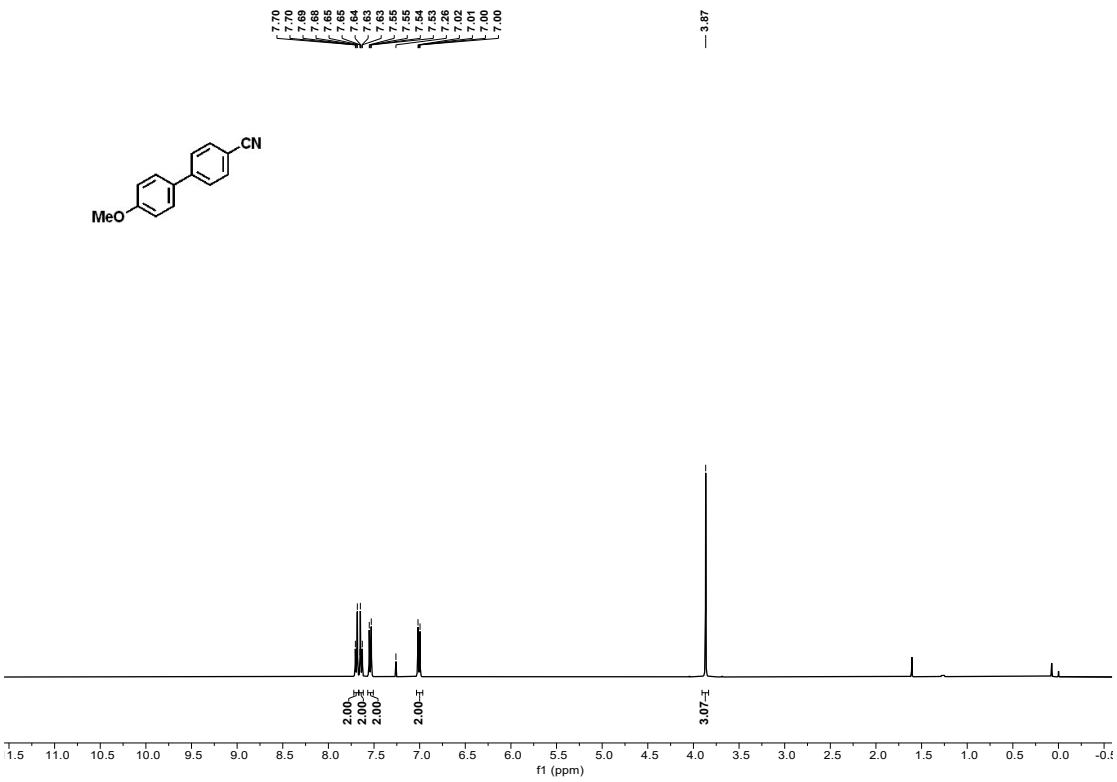
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4c**



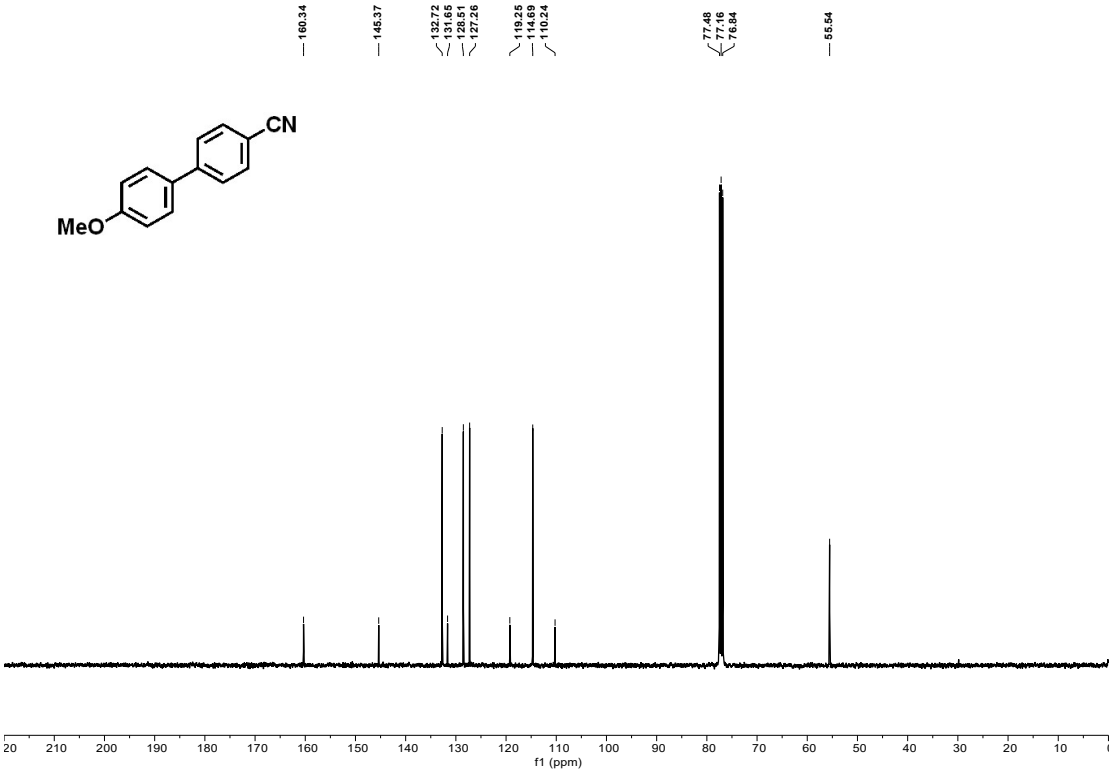
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4c**



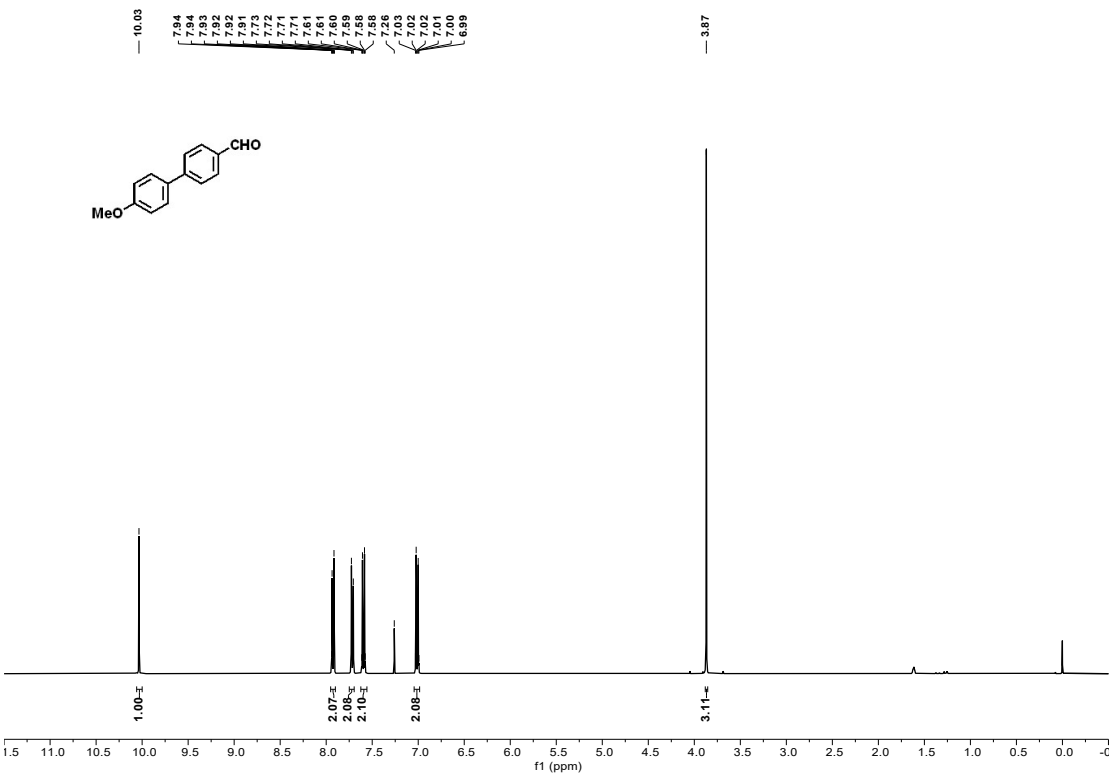
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4d**



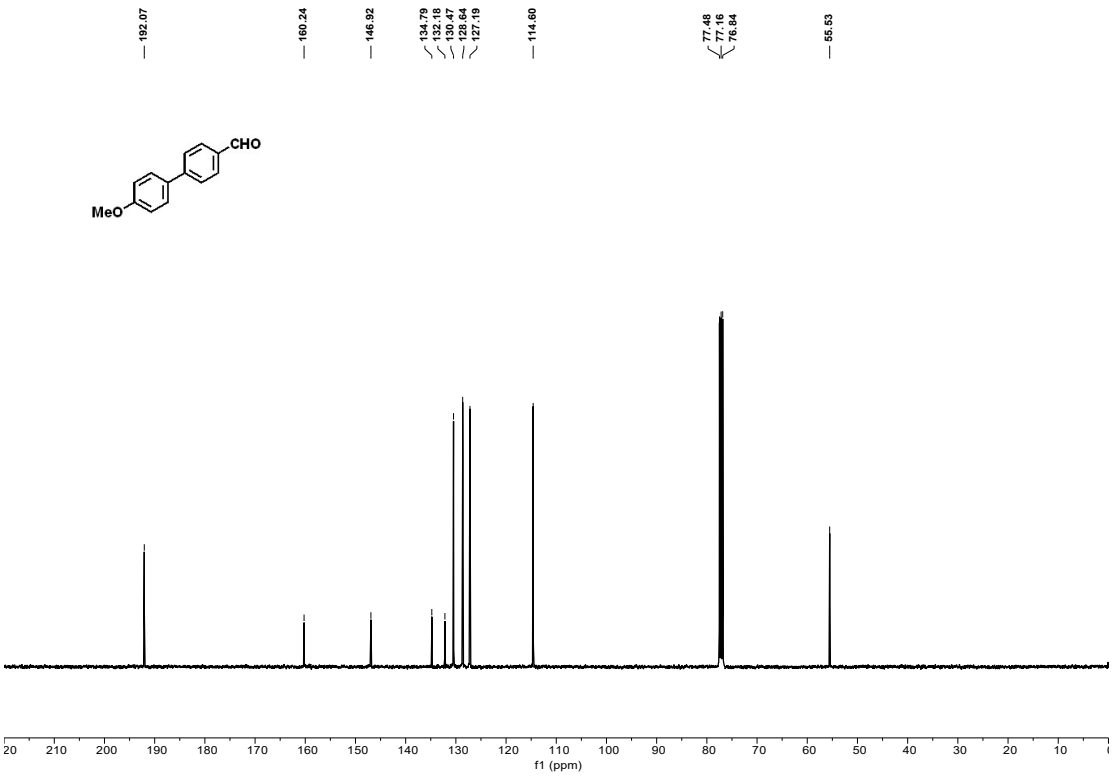
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4d**



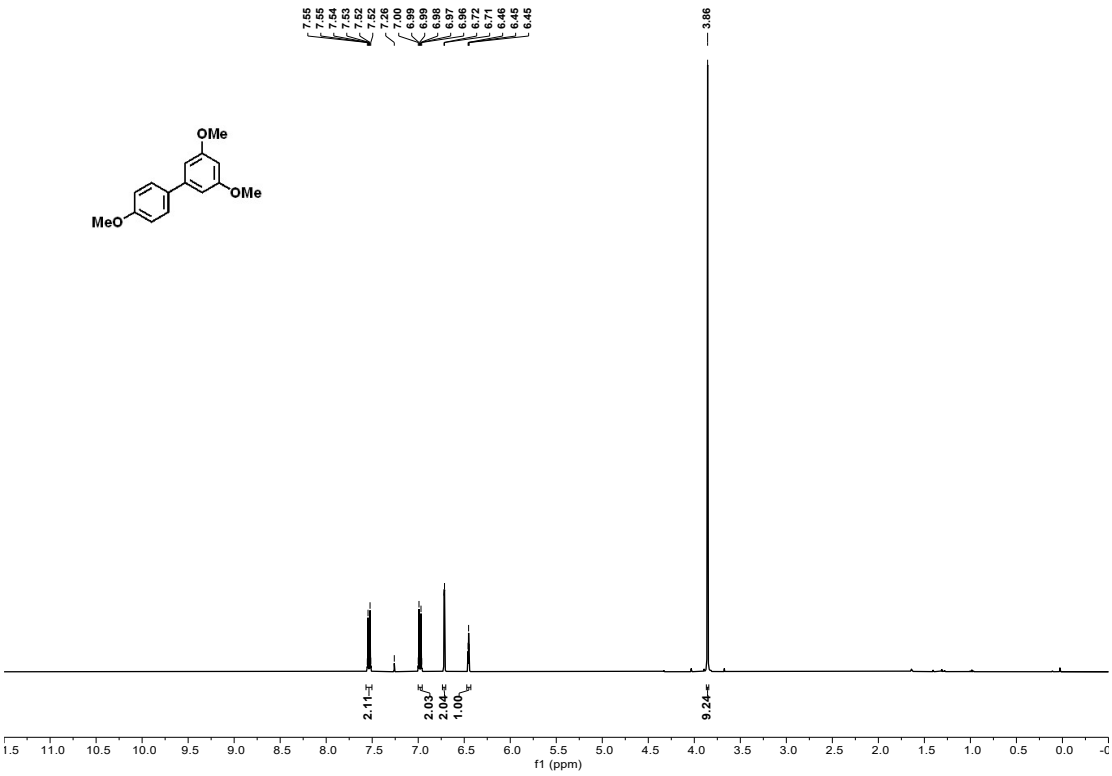
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4e**



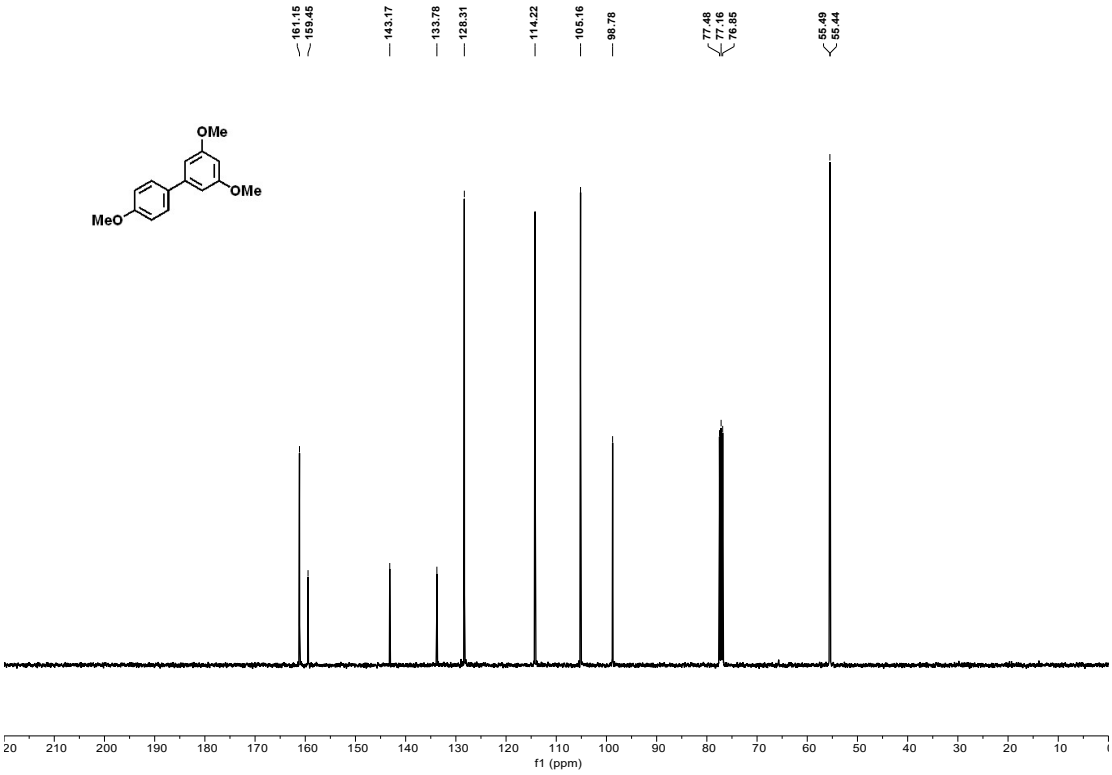
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4e**



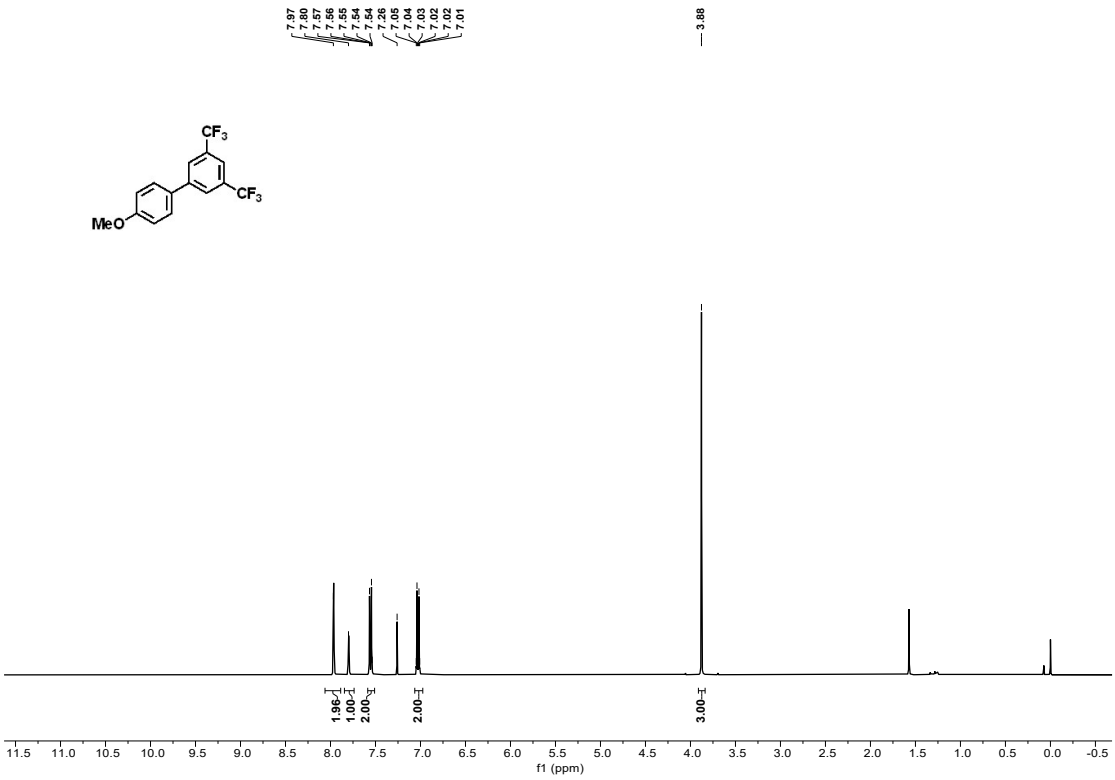
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4f**



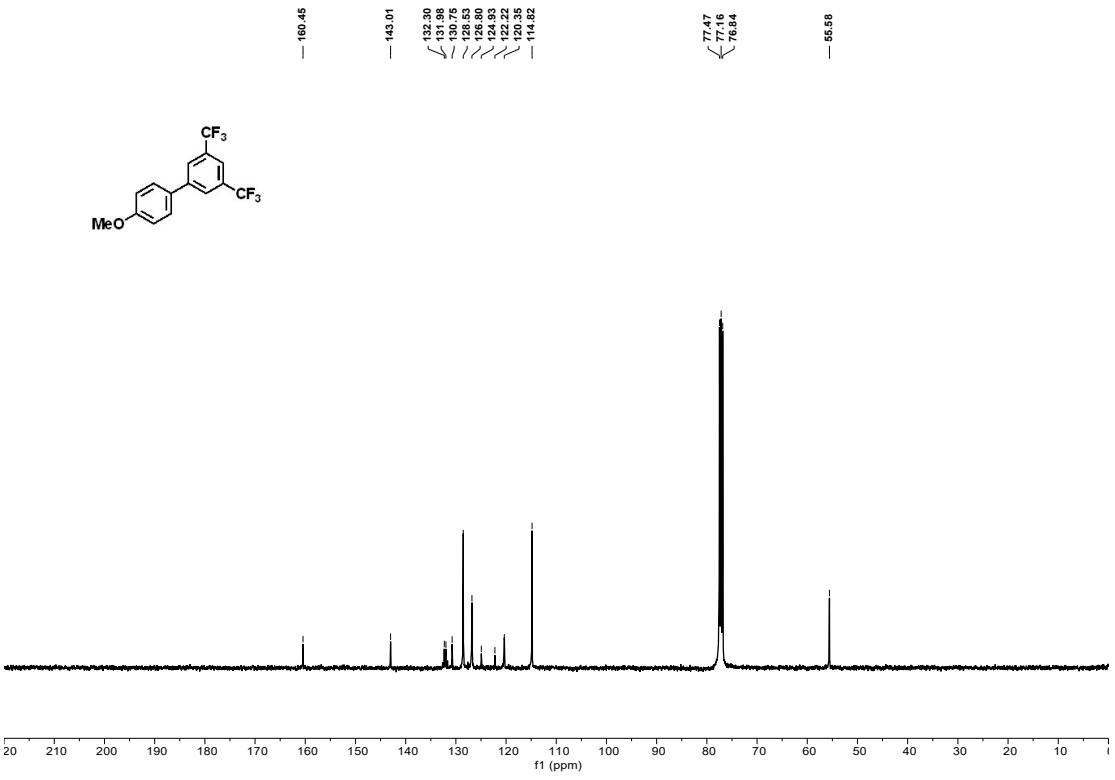
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4f**



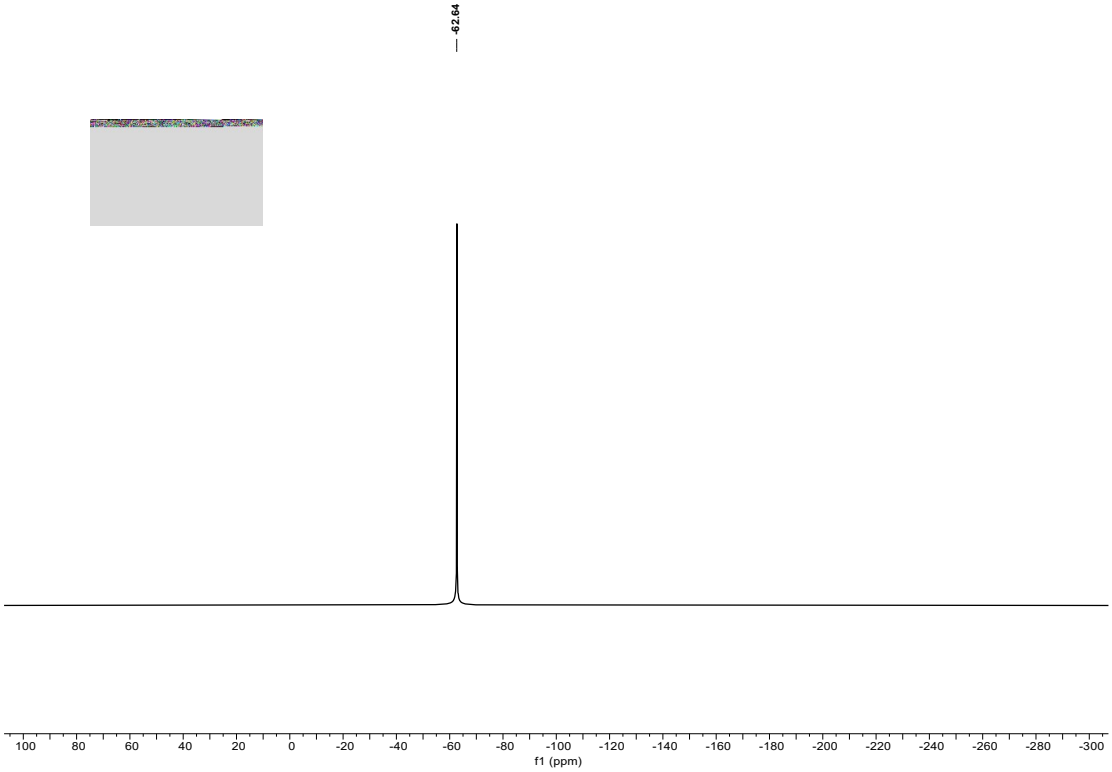
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4g**



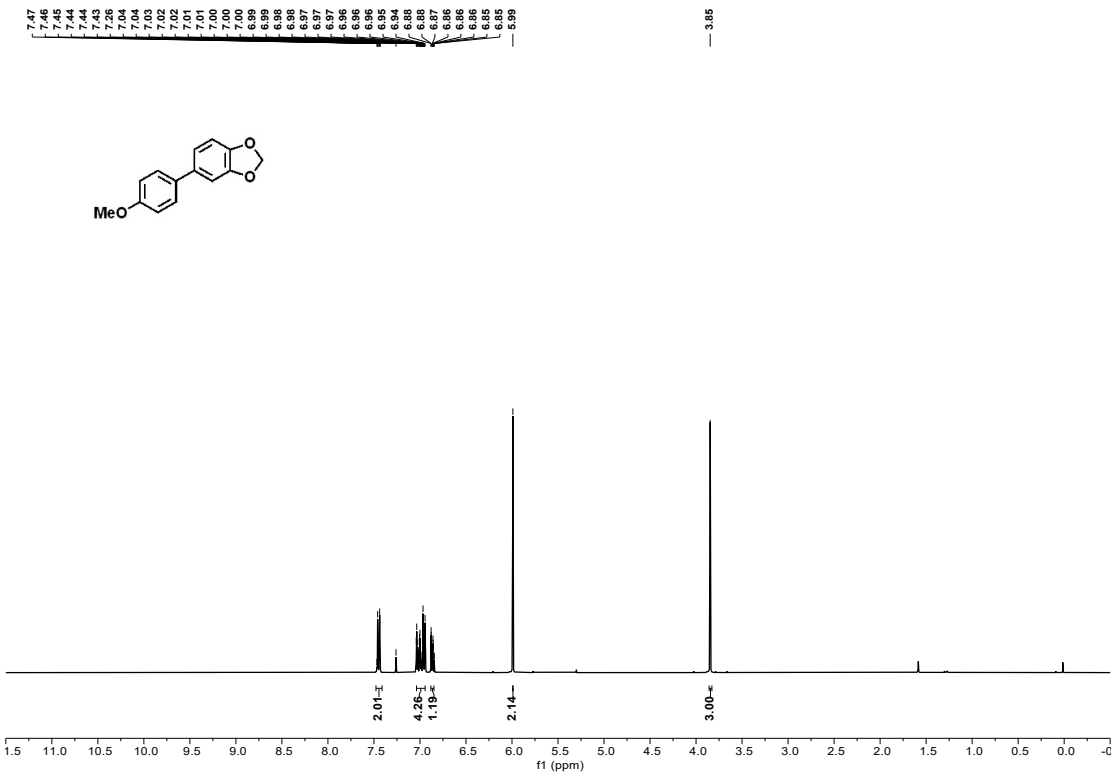
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4g**



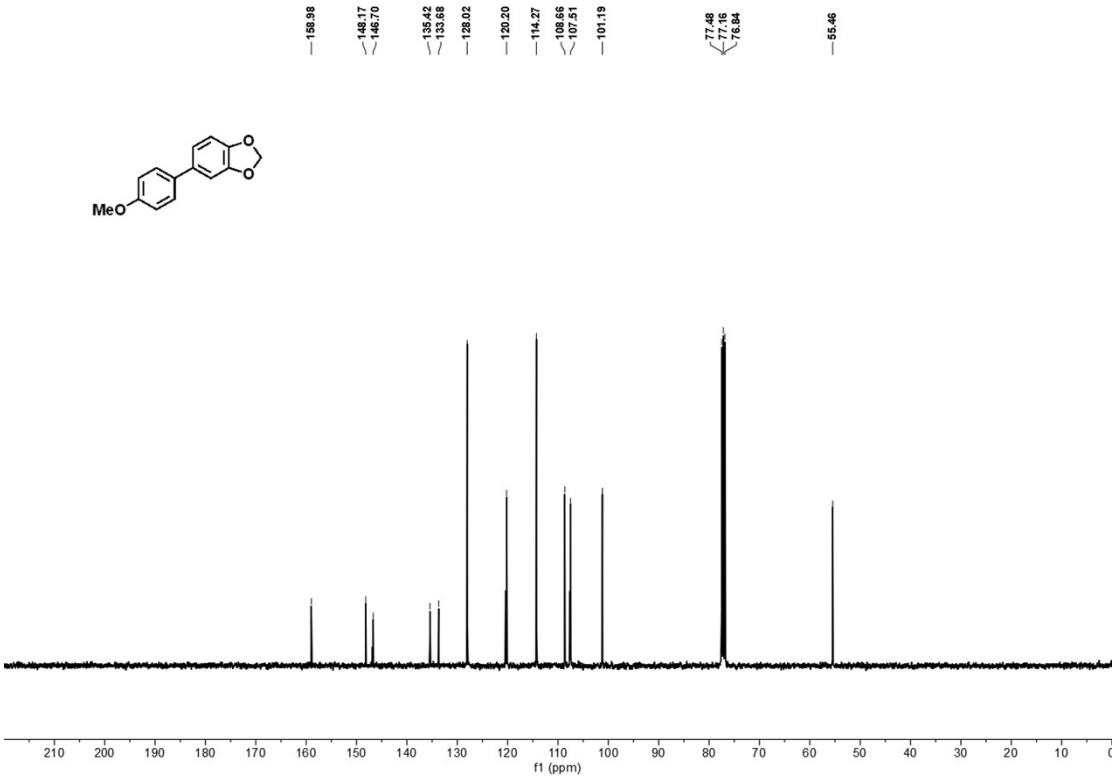
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4g**



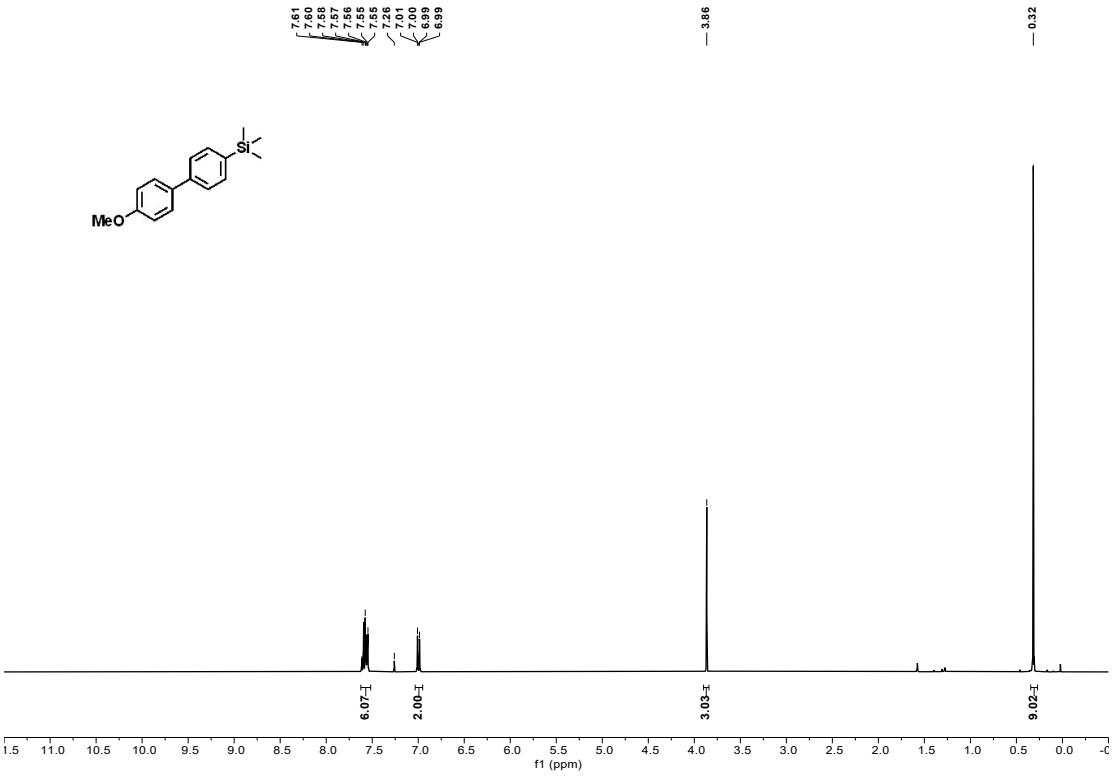
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4h**



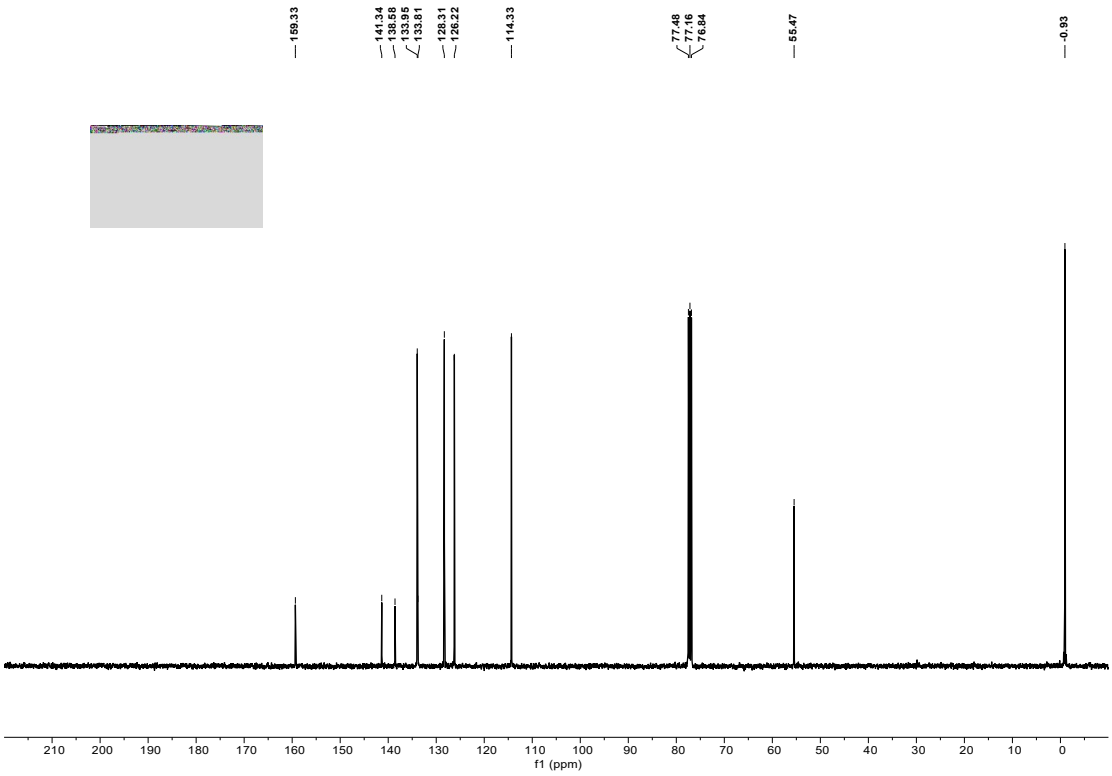
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4h**



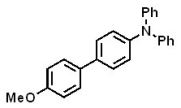
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4i**

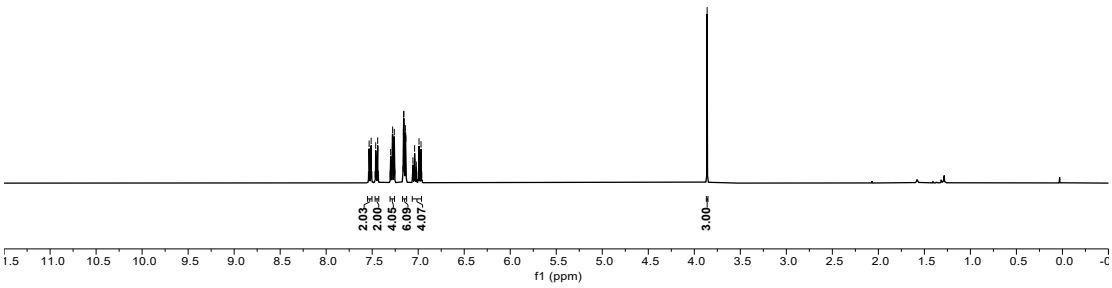


^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4i**

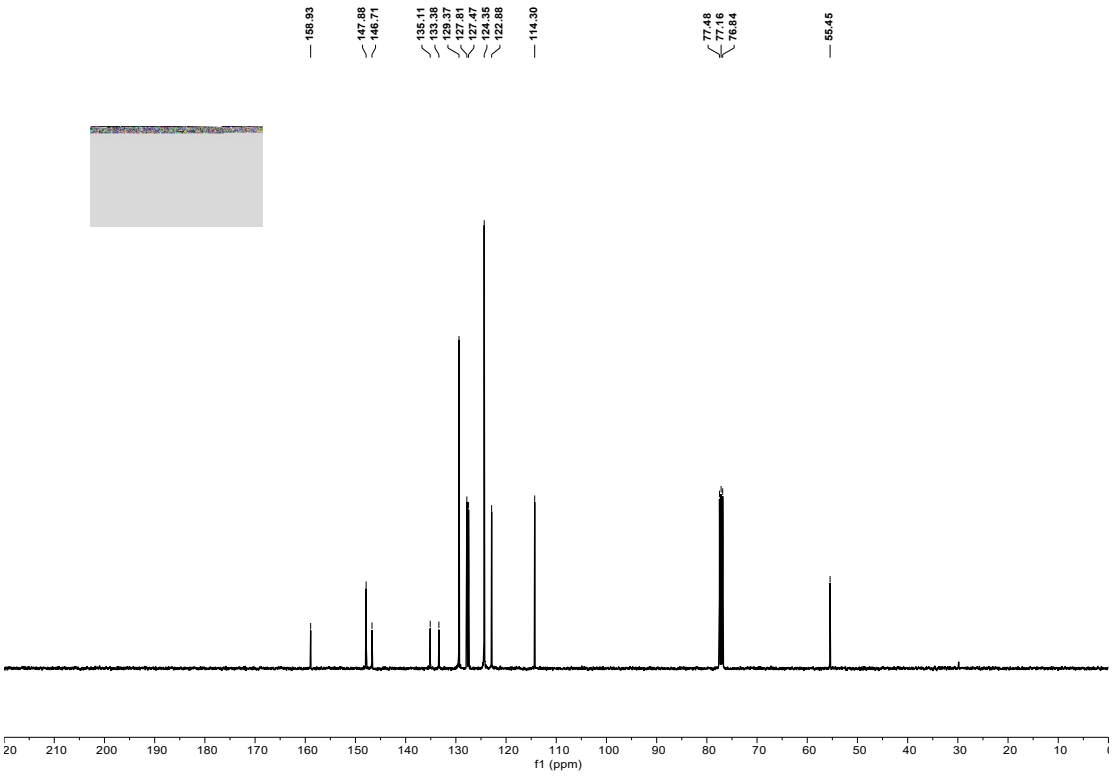


^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4j**

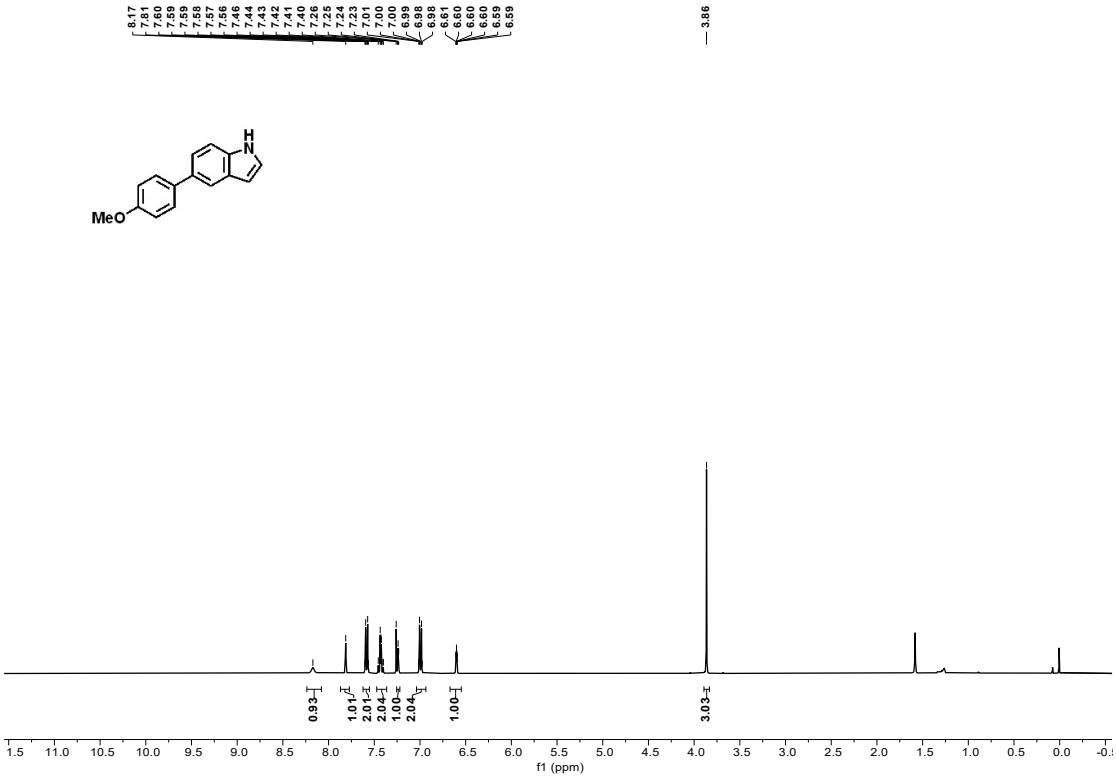




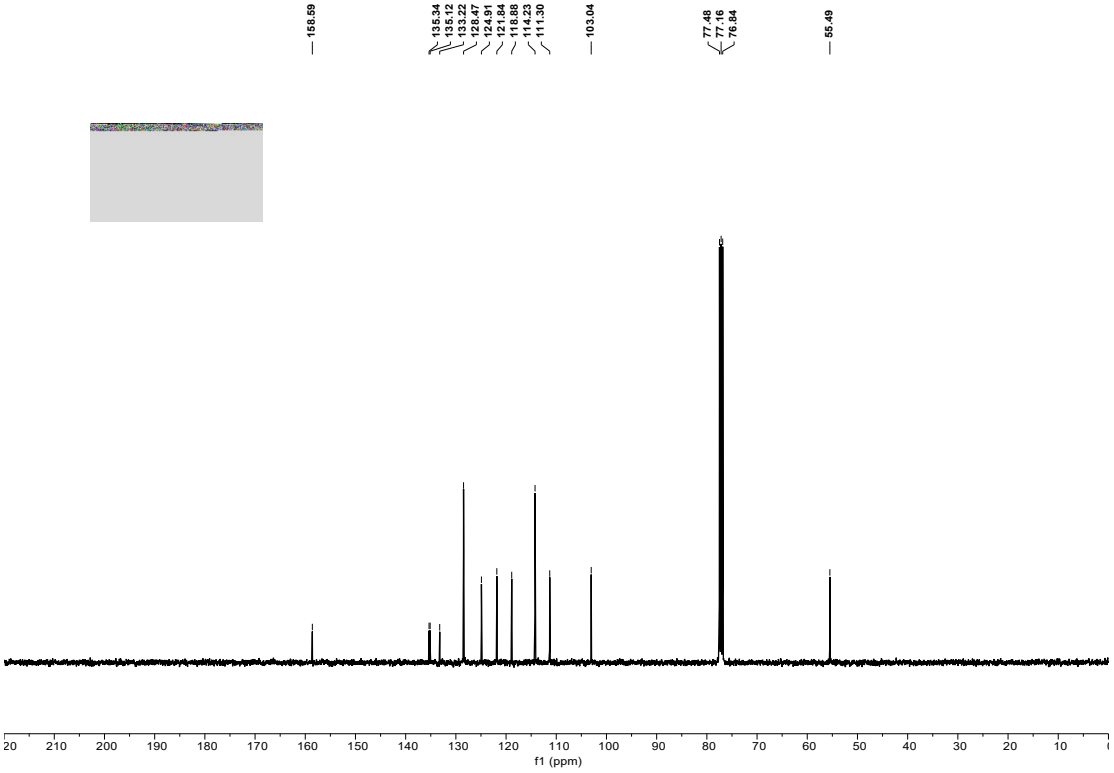
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4j**



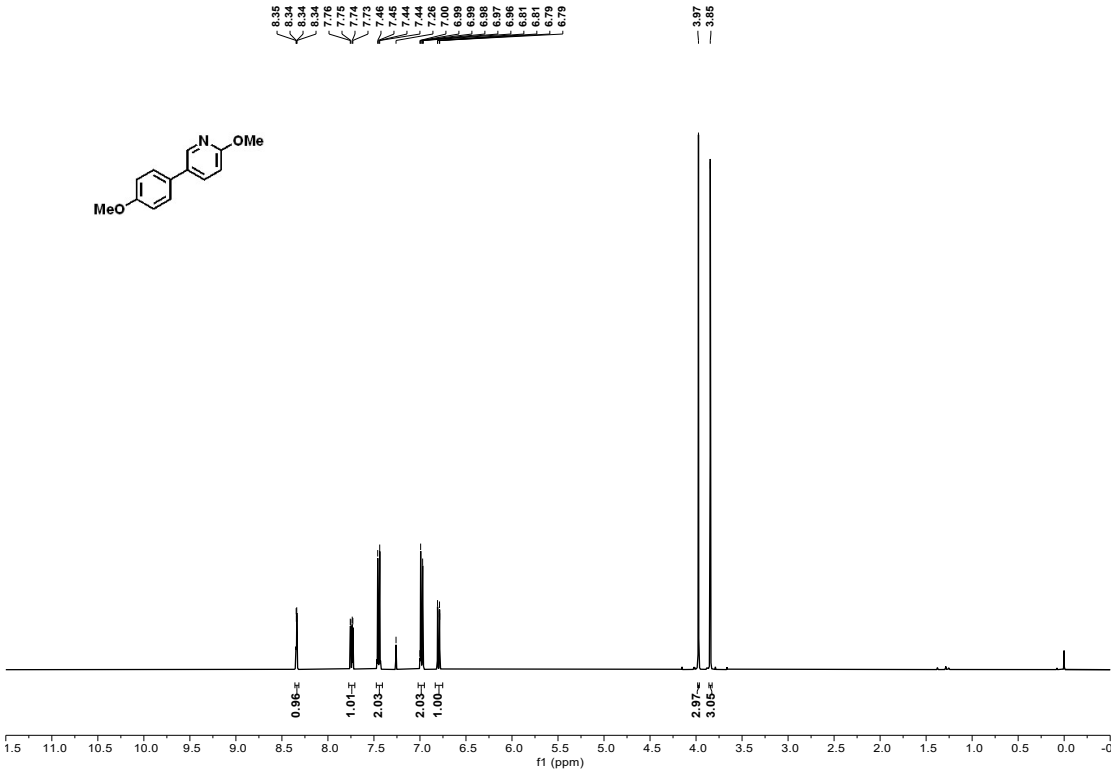
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4k**



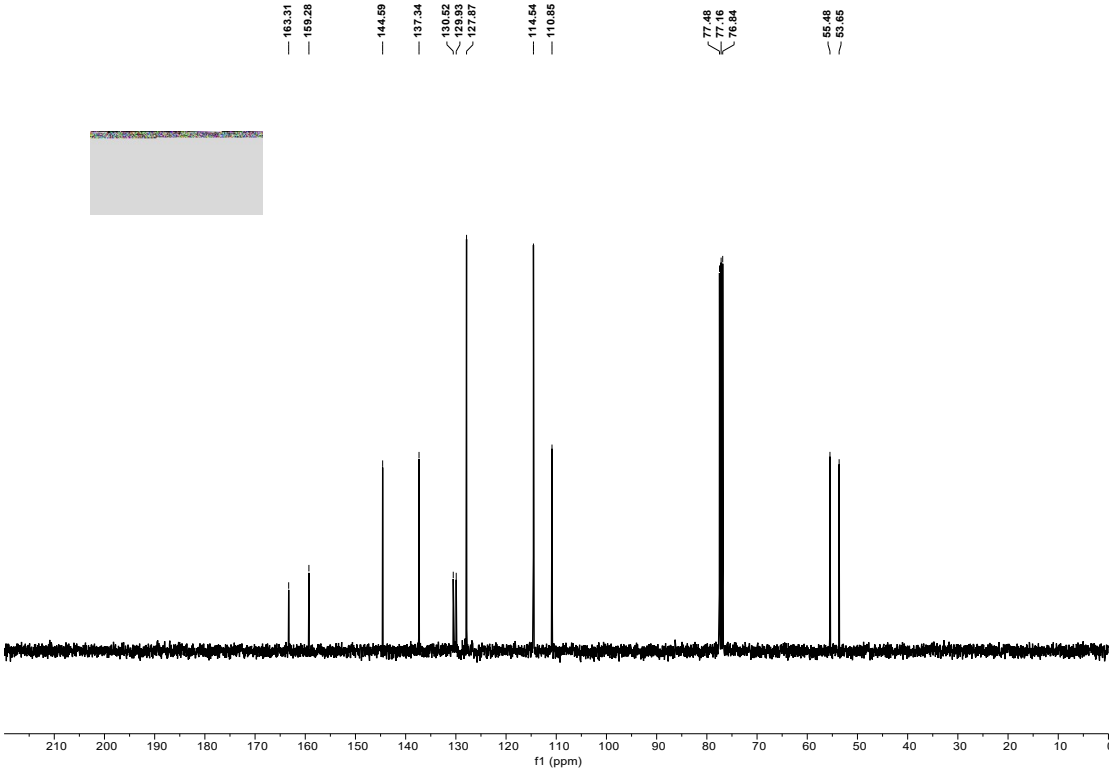
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4k**



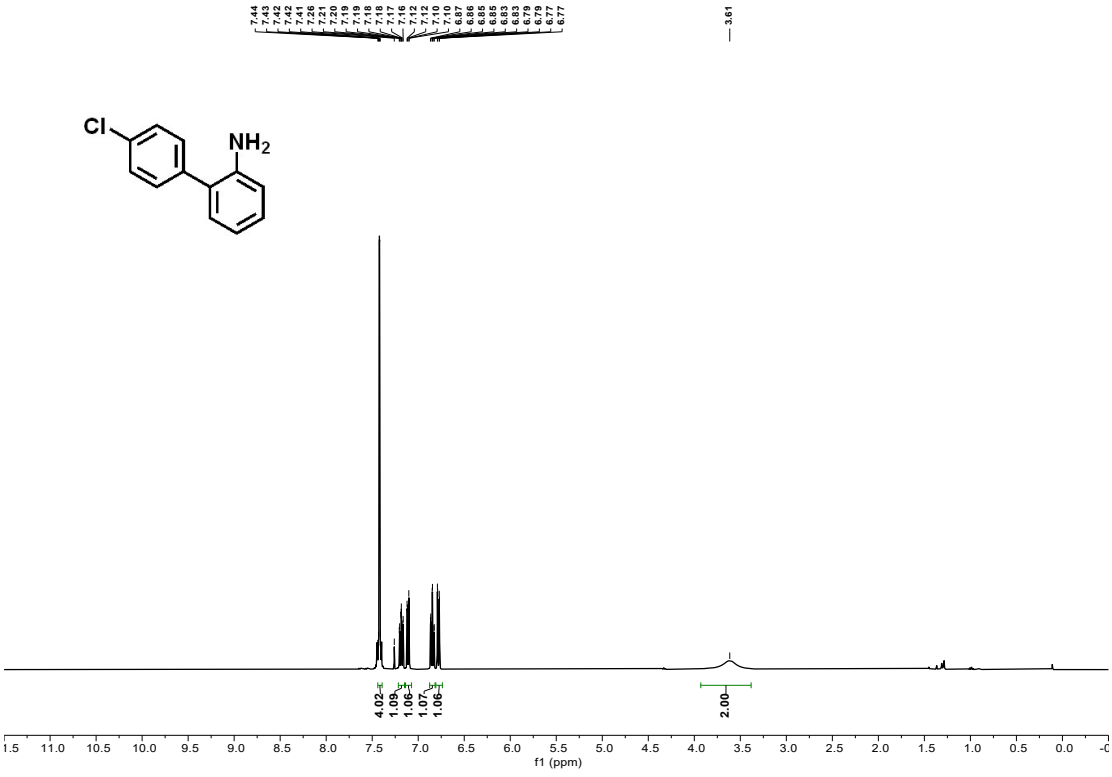
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4l**



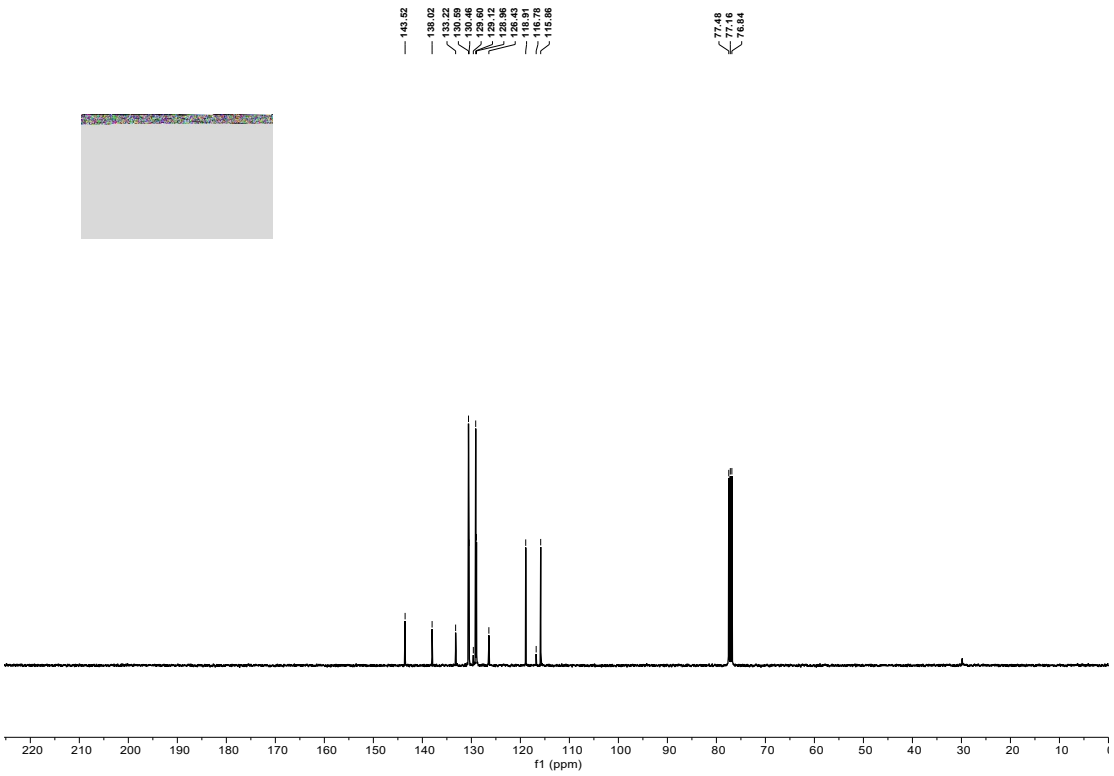
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **4l**



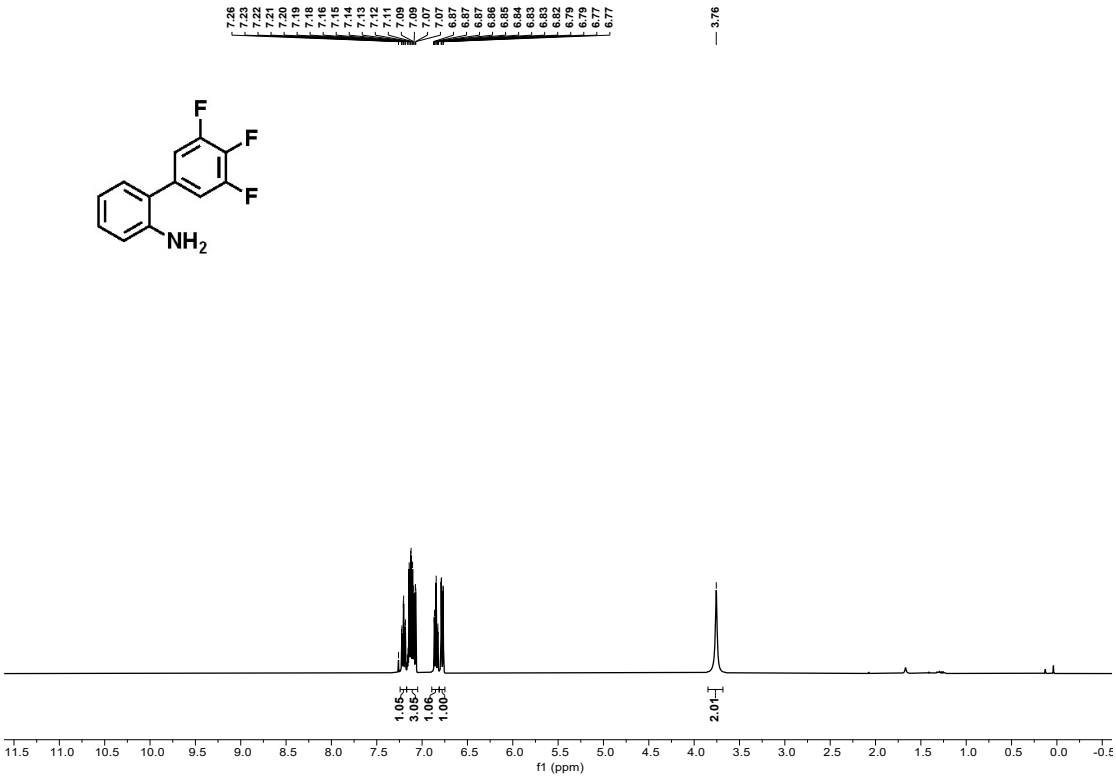
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **Boscalid intermediate**



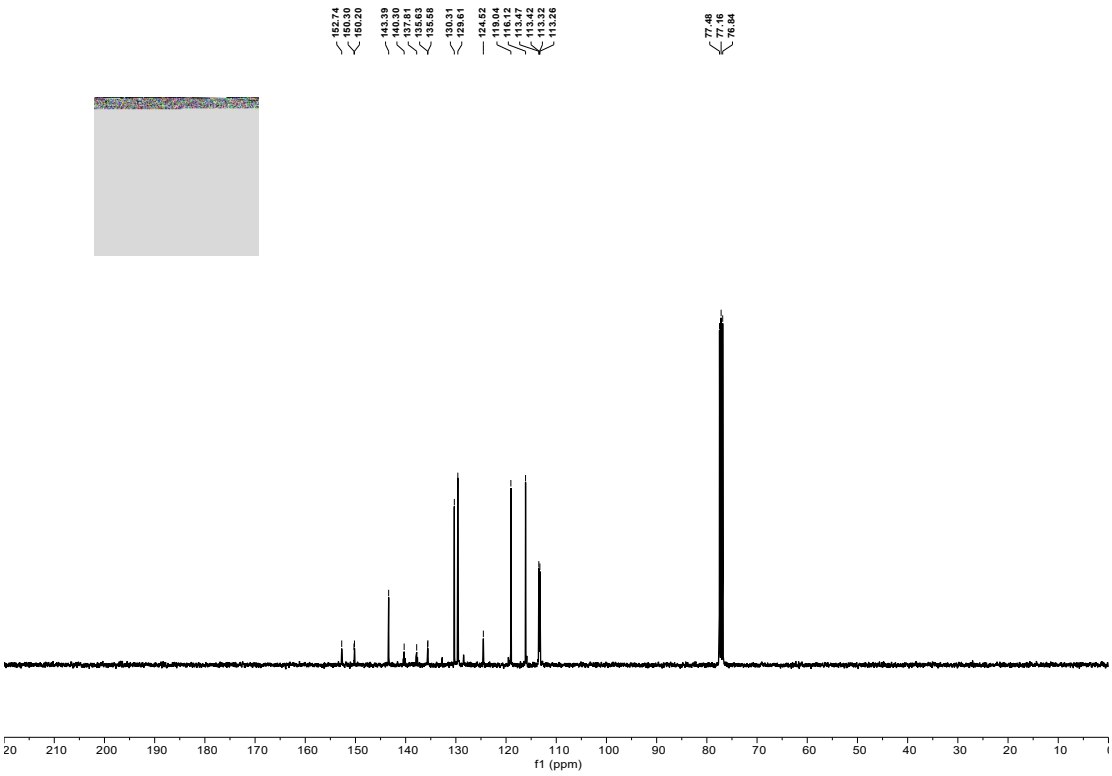
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **Boscalid intermediate**



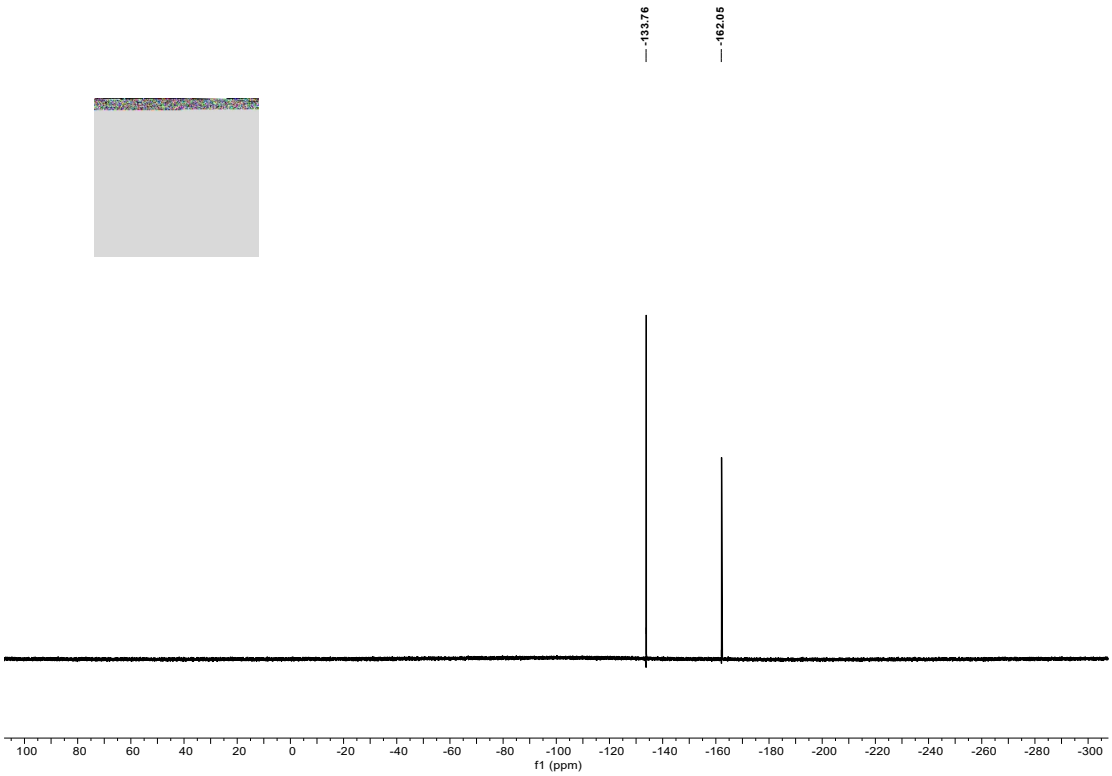
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **Fluxapyroxad intermediate**



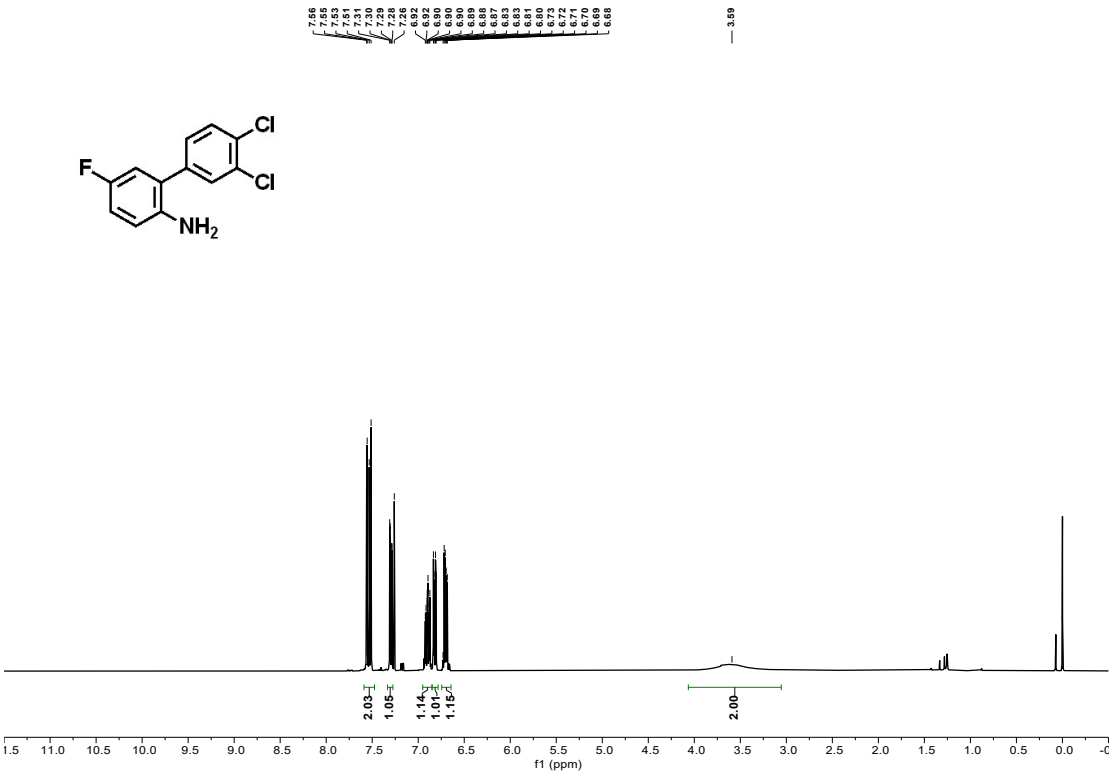
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **Fluxapyroxad intermediate**



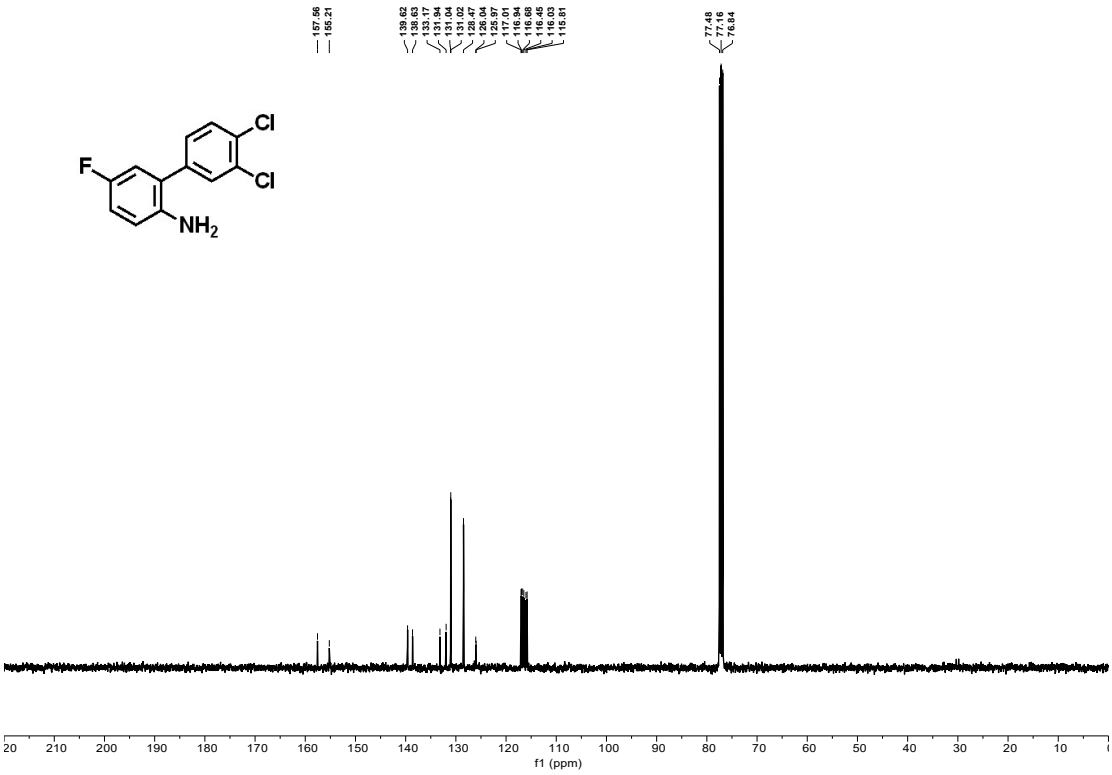
^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **Fluxapyroxad intermediate**



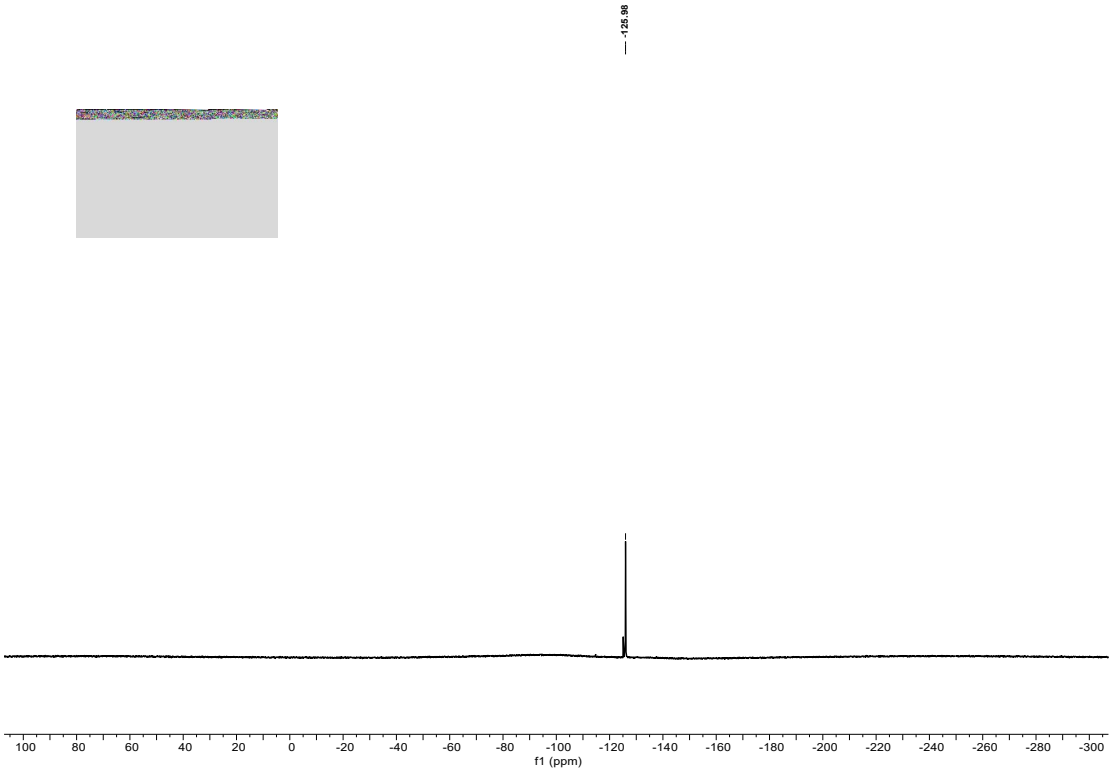
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **Bixafen intermediate**



^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **Bixafen intermediate**



^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **Bixafen intermediate**


-125.98
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

VI. References

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