Supplementary Information

Electro-Oxidative C(sp^2)-H/O-H Cross-Dehydrogenative Coupling of Phenols and Tertiary Anilines for Diaryl Ether Formation

Hongyang Tang, Simon Smolders, Yun li, Dirk E. De Vos* and Jannick Vercammen*

Centre for Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, Leuven, Belgium

*Correspondence to: dirk.devos@kuleuven.be (D.D.V.); Jannick.vercammen@kuleuven.be (J.V.).

Table of Contents

1. General Information

2. Cyclic Voltammetry

3. Procedures for the Electrolysis

4. Mechanism

5. Characterization Data for Products

6. NMR Spectra for New Compounds

7. References

1. General Information

Gas chromatography (GC) yields were determined using a Shimadzu GC-2014 equipped with a CP-SIL 8 CB column (Agilent, 60 m, 0.25 µm film thickness, 0.32 mm ID). Samples of 1 µl were injected automatically with an AOC-20s auto sampler and AOC-20i auto-injector aided by the GCsolution software bundle (version 2.44.00). Products were identified on an Agilent 6890 gas chromatograph equipped with a HP 1 MS column and coupled to a 5973 MSD mass spectrometer.

Column chromatography was performed on silica gel 60 A (0.060-0.200 mm, ACROS). The flash column chromatography was performed with silica gel (230-300 mesh). A mixture of petroleum ether and ethyl acetate in a ratio of 25/1, unless specified otherwise, was used as eluent mixture. Products were recrystallized using dichloromethane to assist in the removal of the eluent. Silica gel 60 sheets on Aluminum (F254, Merck, Darmstadt, Germany) were used for thin layer chromatography (TLC).

^{1}H, ^{13}C and ^{19}F NMR were recorded at room temperature, using a Bruker Avance 300 (300 MHz) equipped with a 5 mm BBO BB-^{1}H probe, a Bruker Avance III HD 400 (400 MHz) equipped with a 5 mm PABBO BB/^{19}F-^{1}H/D probe or a Bruker Avance II^{+} HD 600 (600 MHz) equipped with a 5 mm PABBO BB (31P-109Ag)-1H/D probe. As solvent, $CDCl_3$ was used in all cases.

Cyclic voltammetry (CV) curves were obtained on a Metrohm Autolab PGSTAT 302N electrochemical workstation and Nova 2.1 software. Solutions of **1a** (0.1 mmol) and/or **2a** (0.1 mmol) in HFIP/DCM = 6:4 (10 ml), $^{n}Bu_4NBF_4$ (0.1 mmol) (see SI) and $^{n}Bu_4NBF_4$ (1 mmol) as electrolyte were recorded at room temperature with a scan rate of 100 mV/s using a glassy carbon disk anode (diameter 1 mm), a platinum cathode (10 mm × 10 mm × 0.5 mm) and a Ferrocene reference electrode.

Electron paramagnetic resonance (EPR) spectra were recorded at room temperature on a Bruker 300E continuous wave spectrometer with a rectangular cavity and flat cell equipment. Data were analyzed and simulated using the EasySpin software package.[1] Solutions of **1a** (0.3 mmol) and/or **2a** (0.3 mmol) in 6 ml of HFIP/DCM (6:4) and $^{n}Bu_4NBF_4$ (0.15 mmol) as electrolyte were electrolyzed for 1 hour using a constant current of 5 mA with a carbon felt anode (20 mm × 10 mm × 2 mm, SIGRACELL®GFA 6 EA, obtained from SGL Carbon, Germany) and a Pt cathode (10 mm × 10 mm × 0.5 mm). A custom reactor (see Figure S2B), devoid of copper wiring, was designed to avoid any interference from copper. After electrolysis, the sample was transferred to a capillary and measured within 20 minutes.

2. Supplementary cyclic voltammetry

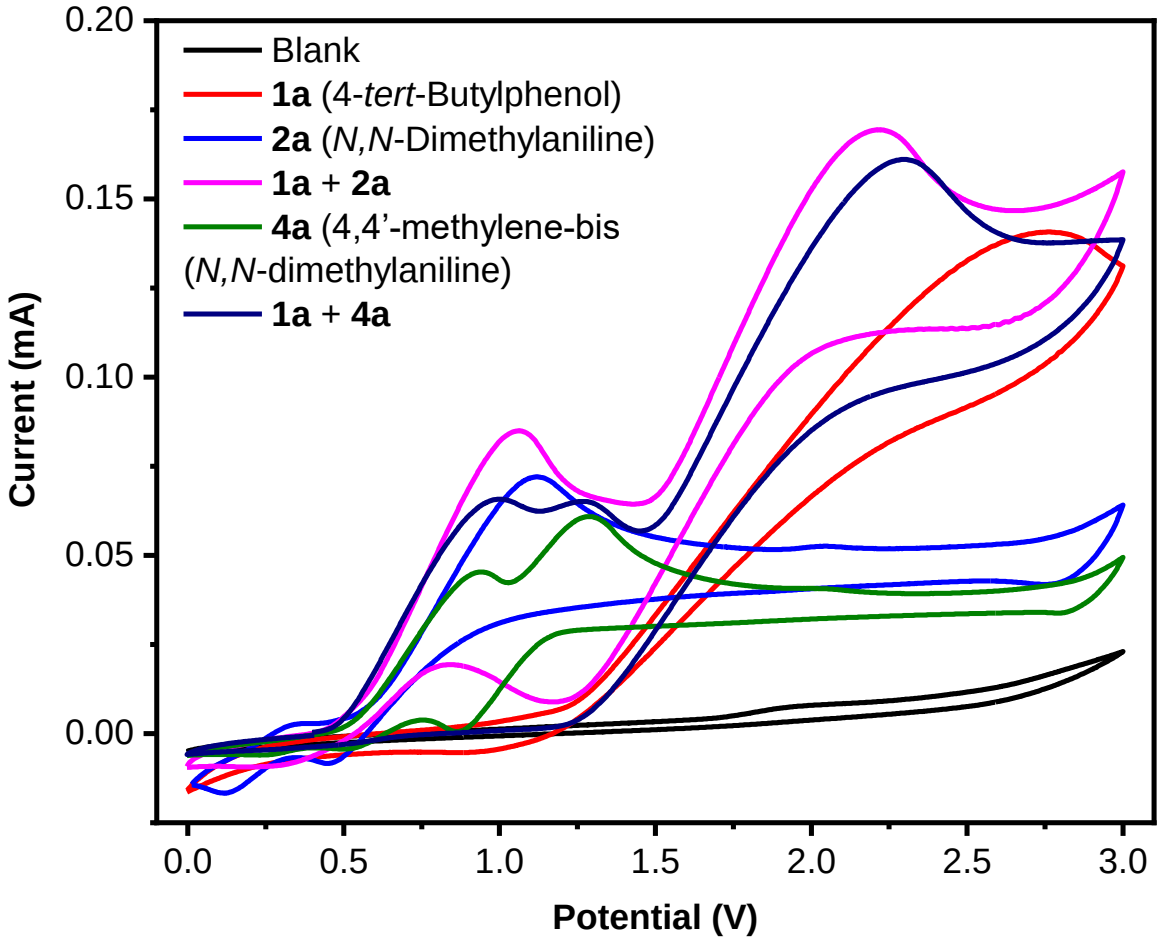


Figure S1. Additional cyclic voltammetry experiments at a lower concentration of supporting electrolyte $^{n}Bu_4NBF_4$ (0.1 mmol) on a glassy carbon anode (3 mm diameter), a platinum cathode and ferrocene reference electrode at 0.1 V s^{-1} under nitrogen. Experiments were conducted in a HFIP/DCM=6/4 solvent mixture.

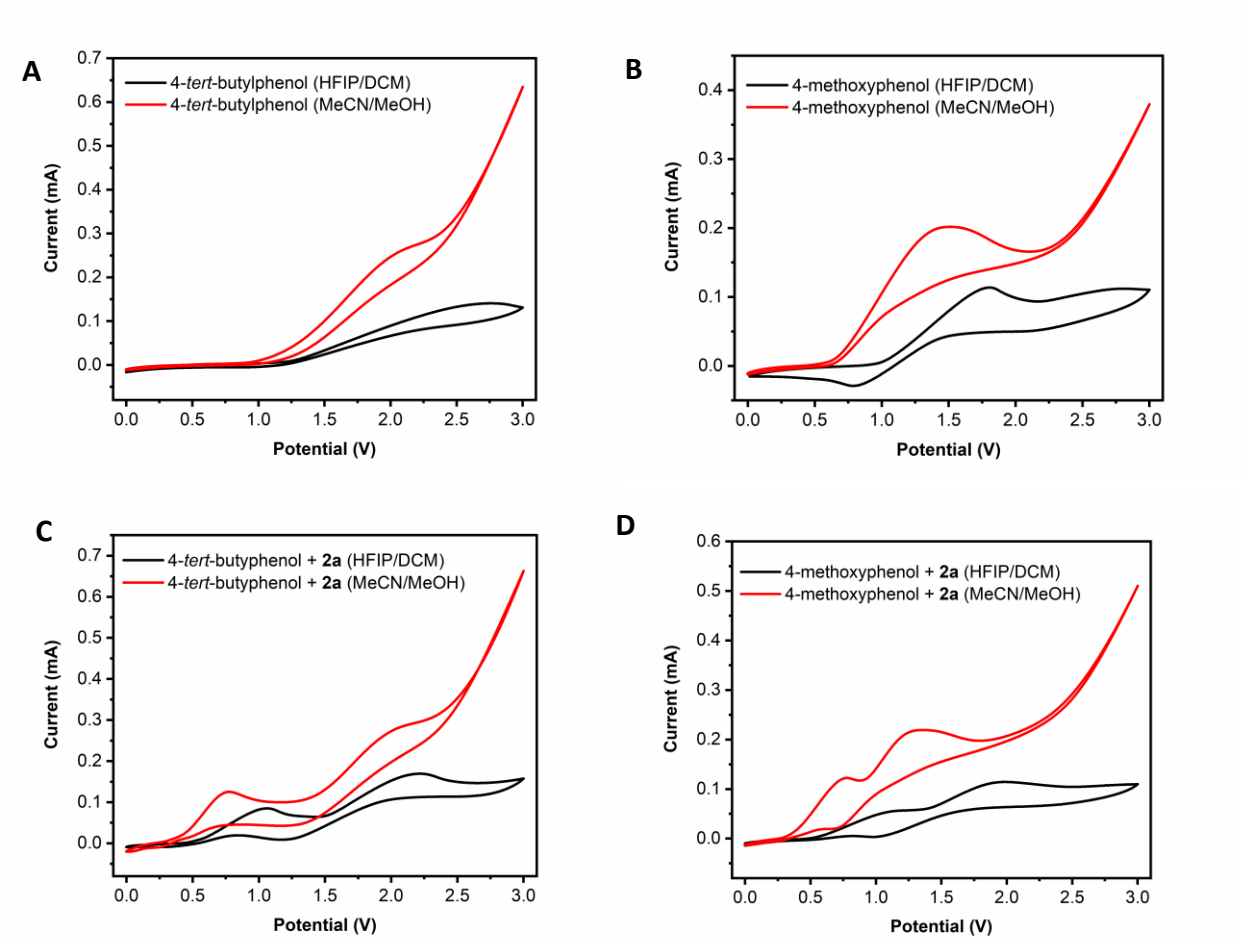


Figure S2. Additional cyclic voltammetry experiments on a glassy carbon anode (3 mm diameter), a platinum cathode and ferrocene reference electrode and $^{n}Bu_4NBF_4$ (0.1 mmol) as electrolyte at 0.1 V s^{-1} under nitrogen. Experiments were conducted both in a MeCN/MeOH solvent mixture (red lines) and a HFIP/DCM=6/4 solvent mixture (black lines). Following phenols were recorded; 4-tert-butylphenol (A,C), 4-methoxyphenol (B,D); both in the absence (A,B) and presence (C,D) of *N*,*N*-dimethylaniline.

3. Procedures for the diaryl ether formation

To a glass reactor (Figure S2A, made in campus glassworks, KULeuven), **1a** (0.3 mmol, 1 equiv), **2a** (0.3 mmol, 1 equiv), $^{n}Bu_4NBF_4$ (0.15 mmol, 0.5 equiv), HFIP (3.6 ml) and DCM (2.4 ml) were added. The reactor was equipped with a carbon felt as anode (20 mm × 10 mm × 2 mm, SIGRACELL®GFA 6 EA, obtained from SGL Carbon, Germany) and a nickel plate as cathode (20 mm × 10 mm × 1 mm, Goodfellow). The electrolysis was carried out at room temperature using a constant current of 5 mA until complete consumption of the substrate (monitored by TLC or GC). All reagents were obtained from commercial suppliers without further purification. A power supply of TENMA (72-10480) was used to control the current or potential.

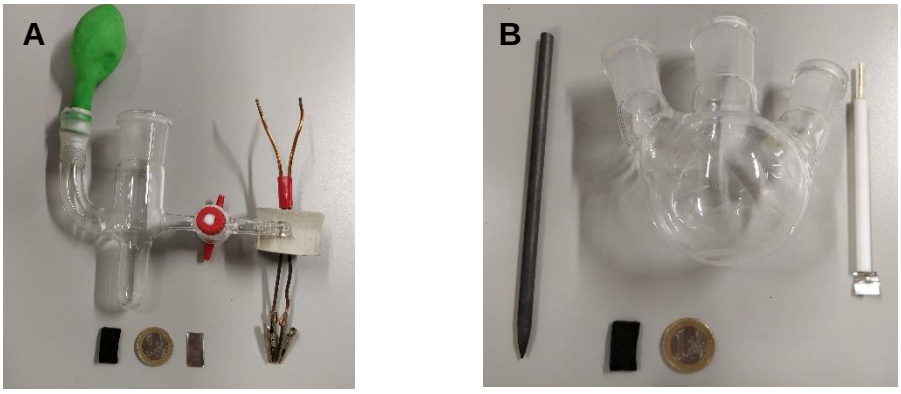


Figure S3. Glass reactors for the electrocatalytic formation of diarylethers (A) and for the electrolytic preparation for ePR measurements (B).

4. Mechanistic experiments

4.1 Reaction kinetics

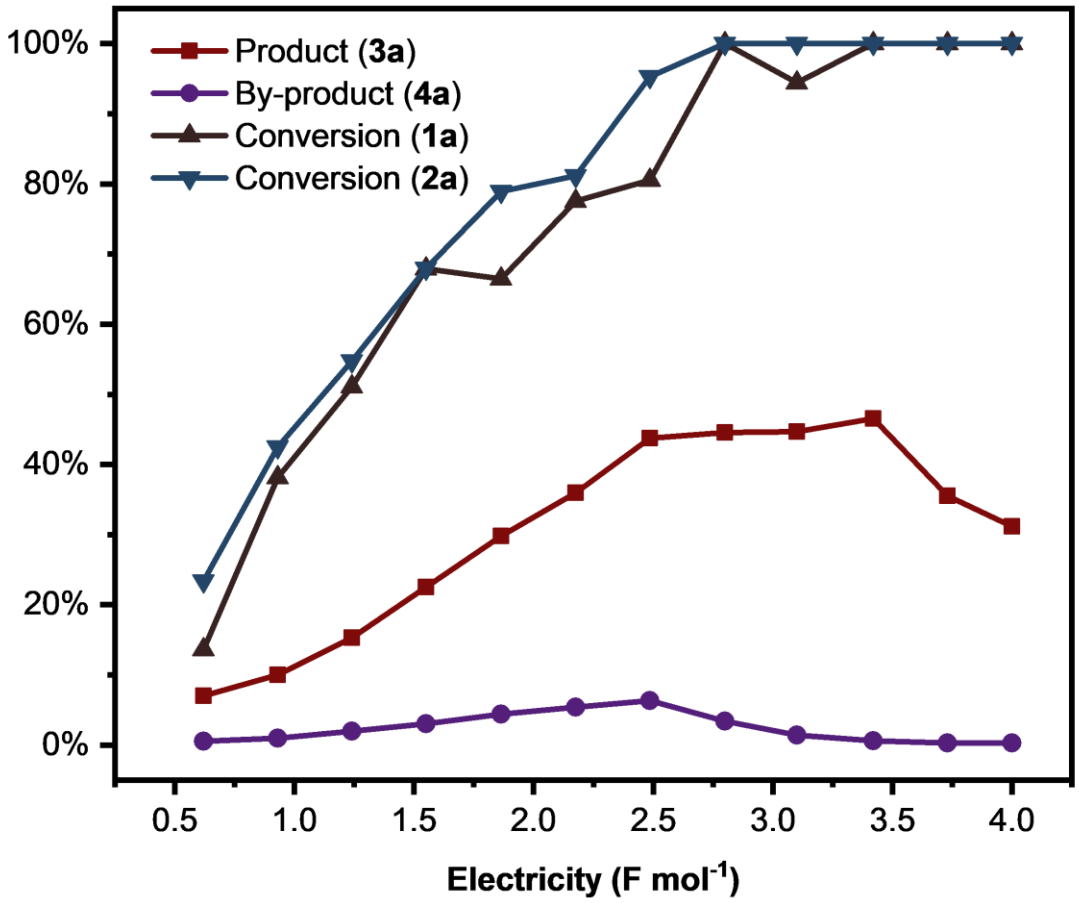
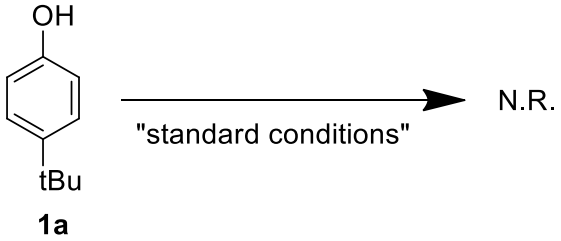


Figure S4. Reaction kinetics of electrocatalytic condensation of **1a** and **2a**. Reaction conditions: Carbon felt as anode and Nickel plate as cathode (10 mm x 10 mm x 1 mm), constant current at 5 mA, **1a** (0.3 mmol), **2a** (1 equiv, 0.3 mmol), $^{n}Bu_4NBF_4$ (0.5 equiv, 0.15 mmol), HFIP/DCM (6:4, 6 ml), room temperature, nitrogen; Yield determined by GC analysis using octane as the external standard. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, DCM = dichloromethane

4.2 Control experiments

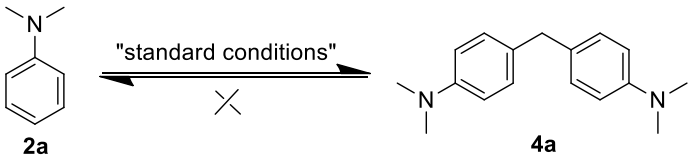
(1) Phenol experiments



1a

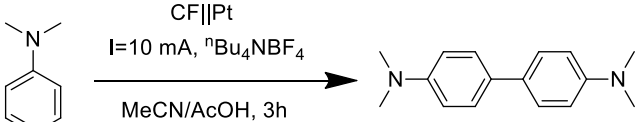
(2) *N,N*-dimethylaniline experiments

① *N,N*-dimethylaniline under our conditions with HFIP and DCM



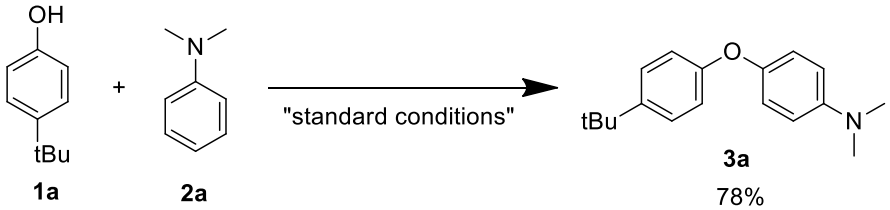
2a **4a**
13 %

② *N,N*-dimethylaniline under MeCN/AcOH

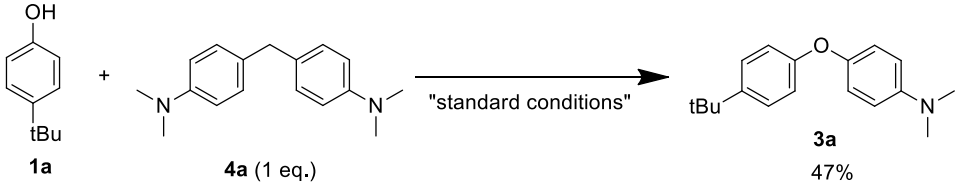


2a
6 %

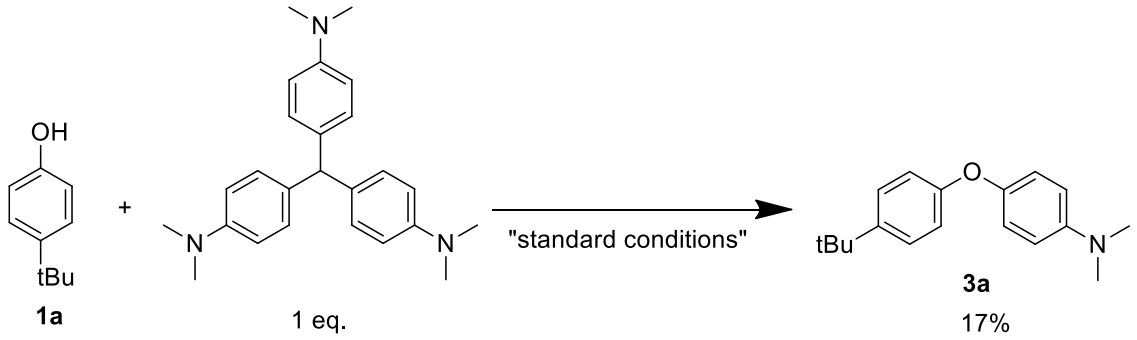
(3) Phenol and 4,4'-methylene-bis(*N,N*-dimethylaniline), 4,4',4''-Methylidynetris(*N,N*-dimethylaniline) experiments



1a **2a** **3a**
78%



1a **4a** (1 eq.) **3a**
47%



The substrate **1a** (0.3 mmol, 1 equiv), **2a** (0.3 mmol, 1 equiv), **4a** (0.3 mmol, 1 equiv) or 4,4',4''-Methylidynetris(*N,N*-dimethylaniline) (0.3 mmol), nBu_4NBF_4 (0.15 mmol, 0.5 equiv), HFIP (3.6 ml) and DCM (2.4 ml) were added respectively, then reacted under standard conditions. The yield of product **3a** was 78%, 47% and 17% respectively. In addition, the same solutions were stirred for two days without electricity, after which no conversion was observed. The color of the solution however changed depending on the employed aniline compound (Figure S4).

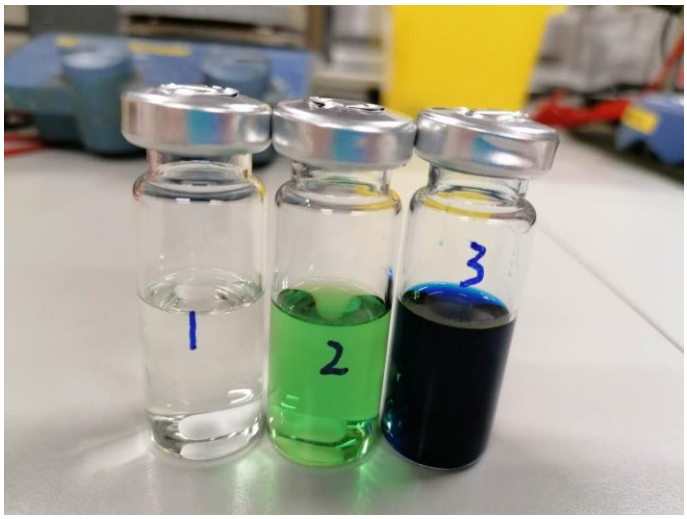
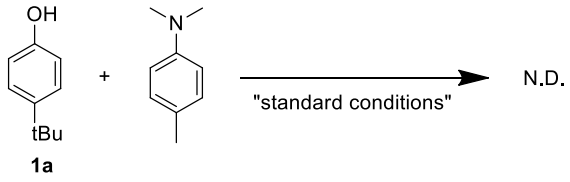


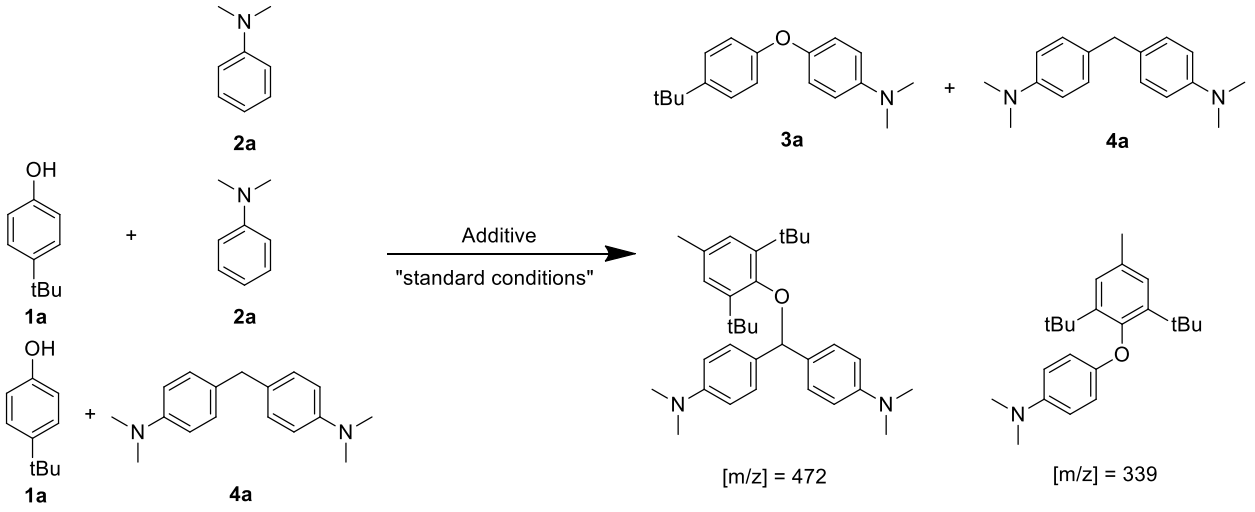
Figure S5. Solutions containing **2a** (1), **4a** (2) and 4,4',4''-Methylidynetris(*N,N*-dimethylaniline) (3) after two days of stirring at room temperature with **1a** (1 equiv), $^{n}Bu_4NBF_4$ (0.5 equiv), HFIP (3.6 ml) and DCM (2.4 ml).

(4) Phenol and *N,N*-dimethyl-*p*-toluidine



4.3 Radical trapping with butylated hydroxytoluene (BHT)

Table S1. Radical trapping experiment with BHT.[a]



Reactants	Yield		GC-MS signal	
	3a	**4a** [c]	[m/z]=472 [d]	[m/z]=339 [e]
2a	/	-[b]	Detected	Detected
1a + 2a	12%	-[b]	N.D.	Detected
1a + 4a	36%	9%	Detected	N.D.

[a]Reaction conditions: Carbon felt as anode and Nickel plate as cathode (10 mm x 10 mm x 1 mm), constant current of 5 mA, **1a** (0.3 mmol), **2a** or **4a** (1 equiv, 0.3 mmol), $^{n}Bu_4NBF_4$ (0.5 equiv, 0.15 mmol), BHT (1 equiv, 0.3 mmol), HFIP/DCM (6:4, 6 ml), room temperature, nitrogen, 5 h (3.1 F mol^{-1}). [b] GC yields could not be determined due to an overlap in retention times between the product of BHT and **1a**.[c] GC-MS (EI, 70 eV): *m/z* (rel int., %): 127.0 (6), 134.0 (17), 165.0 (7), 210.1 (30), 211.1 (5), 237.1 (16), 238.1 (5), 253.1 (79), **254.1 (100)**, 255.1 (18). [d] GC-MS (EI, 70 eV): *m/z* (rel int., %): 73.0 (14), 133.0 (10), 134.1 (31), 147.0 (8), 190.9 (9), 207.0 (65), 208.0 (14), 253.2 (12), 281.0 (29), 282.0 (9), 341.0 (8), 415.2 (11), 457.3 (21), **472.3 (100)**, 473.3 (37), 474.4 (6). [e] GC-MS (EI, 70 eV): *m/z* (rel int., %): 57.1 (6), 226.1 (21), 227.1 (5), 267.1 (5), 268.1 (28), 283.2 (100), 284.2 (22), **339.2 (9)**.

4.4 Chemical oxidants

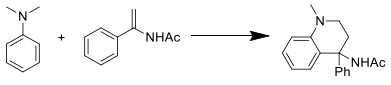
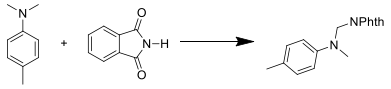
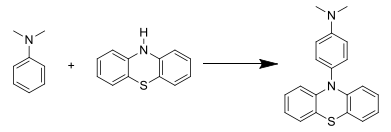
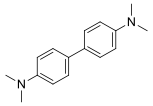
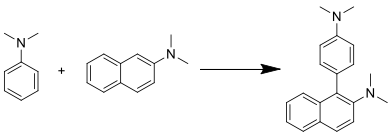
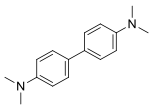
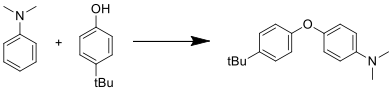
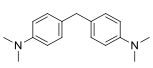
Table S2. Oxidative coupling of **1a** and **2a** with oxidants.[a]

Entry	Oxidant	**3a**	**4a**
1	None	<1%	1%
2	4 bar O_2	<1%	2%
3	8 bar O_2	<1%	2%
4	TBHP (70% in H_2O)	3%	12%
5	TBHP (70% in H_2O)[c]	1%	11%
6	TBEC	2%	12%
7	H_2O_2 (30% in water)	3%	24%
8	H_2O_2 (30% in water)[c]	<1%	5%
9[b]	H_2O_2 (30% in water)	<1%	<1%

[a]Reaction conditions: 0.1 mmol 4-*tert*-butylphenol, 0.1 mmol *N,N*-dimethylaniline, 0.11 mmol oxidant (1.1 equiv), 1.2 ml HFIP and 0.8 ml DCM, 80℃, 3 h, under N_2 unless stated otherwise. [b]40℃, 16 h. [c]10 µmol of TBAI was added.

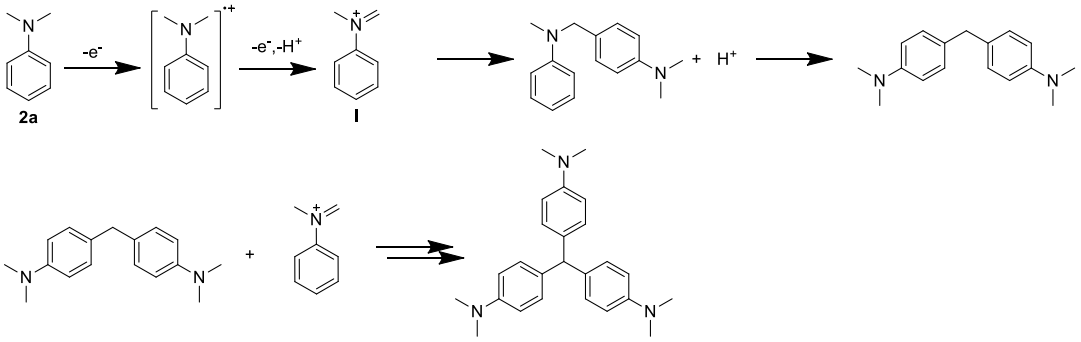
4.5 Comparison with previous work

Table S3. Summary of previous work

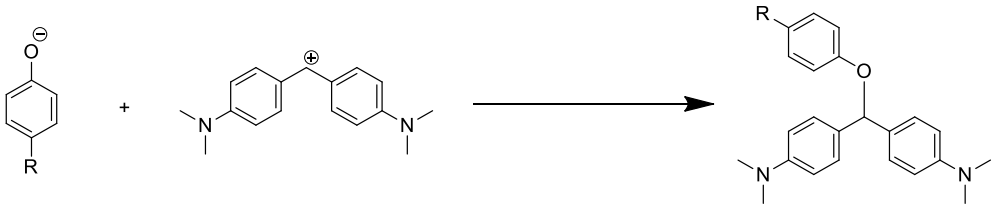
Entry	Year	Reaction	Electrode	Reaction Conditions	By-product	Ref.
1	2018		Pt||Pt	I=3 mA, 6h, MeCN/AcOH, $^{n}Bu_4NBF_4$	No by-product reported	2
2	2019		C||Pt	I=10 mA, 3 h, MeCN/AcOH, $^{n}Bu_4NBF_4$, 60 °C	No by-product reported	3
3	2019		C||Pt	I=7 mA, 2 h, MeCN/MeOH, $^{n}Bu_4NBF_4$		4
4	2020		C||Pt	I=5 mA, 4h, HFIP, $^{n}Bu_4NPF_6$		5
Our work			CF||Ni	I=5 mA, 6 h, $^{n}Bu_4NBF_4$, HFIP/DCM		

4.6 Reported mechanisms of possible side-reactions

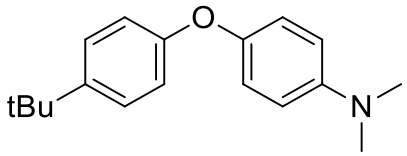
4.6.1 Electrochemical *N,N*-dimethylaniline formation[6]



4.6.1.1 Nucleophilic attack of phenol on *cation of 4a* [7,8]

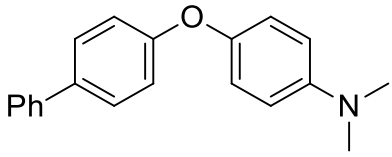


5. Characterization Data of Products



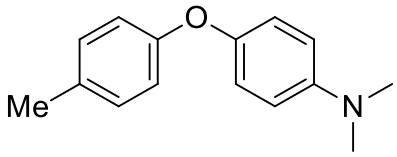
4-(4-(*tert*-butyl)phenoxy)-*N,N*-dimethylaniline (3aa): The desired pure product was obtained in 70% yield as a brown oil, 56.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.27 (m, 2H), 6.99 – 6.93 (m, 2H), 6.89 – 6.84 (m, 2H), 6.77 – 6.71 (m, 2H), 2.93 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.89, 153.38, 147.68, 129.09, 120.83, 119.27, 115.17, 114.21, 41.45, 34.94, 31.48.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 112.6 (10), 136.0 (14), 254.1 (63), 255.1 (11), 268.1 (6), 269.1 (100), 270.1 (20).



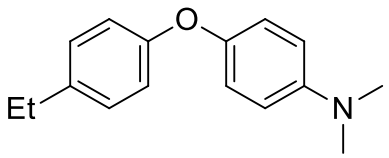
4-([1,1'-biphenyl]-4-yloxy)-*N,N*-dimethylaniline (3ab): The desired pure product was obtained in 59% yield as a white solid, 50.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.43 (t, *J*=7.7 Hz, 2H), 7.33 (t, *J*=7.3 Hz, 1H), 7.04 (t, *J*=2.4 Hz, 2H), 7.02 (t, *J*=2.3 Hz, 2H), 6.80 – 6.76 (m, 2H), 2.96 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.91, 147.91, 147.36, 140.91, 135.19, 128.90, 128.38, 127.00, 121.19, 114.13, 41.37.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (22), 152.0 (10), 274.1 (6), 288.1 (29), 289.1 (100), 290.1 (23).



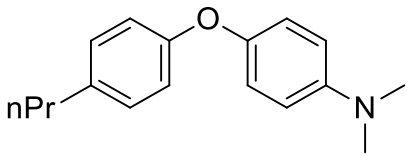
***N,N*-dimethyl-4-(*p*-tolyloxy)aniline (3ac):** The desired pure product was obtained in 38% yield as a yellow oil, 26.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (d, *J*=8.2 Hz, 2H), 6.98 – 6.91 (m, 2H), 6.87 – 6.79 (m, 2H), 6.79 – 6.68 (m, 2H), 2.93 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.86, 131.65, 130.16, 120.68, 117.52, 41.49, 20.77.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (23), 212.0 (9), 226.1 (47), 227.1 (100), 228.1 (16).



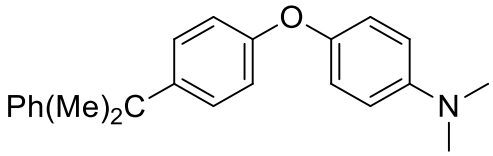
4-(4-ethylphenoxy)-*N,N*-dimethylaniline (3ad): The desired pure product was obtained in 40% yield as a brown oil, 29.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 – 7.08 (m, 2H), 6.99 – 6.93 (m, 2H), 6.90 – 6.84 (m, 2H), 6.77 – 6.72 (m, 2H), 2.93 (s, 6H), 2.61 (q, *J*=7.6 Hz, 2H), 1.23 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.03, 148.08, 147.59, 138.08, 128.94, 120.76, 117.43, 114.21, 28.25, 15.99.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (19), 226.0 (13), 240.1 (35), 241.1 (100), 242.1 (17).



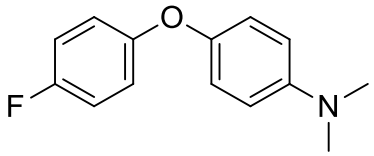
***N,N*-dimethyl-4-(4-propylphenoxy)aniline (3ae):** The desired pure product was obtained in 32% yield as a brown oil, 24.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 – 7.07 (m, 2H), 6.97 – 6.94 (m, 2H), 6.88 – 6.84 (m, 2H), 6.75 (d, *J*=9.0 Hz, 2H), 2.93 (s, 6H), 2.56 – 2.51 (m, 2H), 1.65 – 1.59 (m, 2H), 0.94 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.59, 129.56, 120.75, 117.38, 114.39, 41.58, 37.43, 24.92, 13.99.

GC-MS (EI, 70 Ev): *m/z* (rel int., %): 77.0 (5), 91.0 (5), 136.0 (15), 226.0 (30), 227.0 (5), 254.1 (19), 255.1 (100), 256.1 (19).



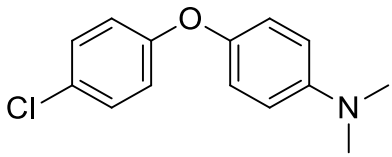
***N,N*-dimethyl-4-(4-(2-phenylpropan-2-yl)phenoxy)aniline (3af):** The desired pure product was obtained in 67% yield as a brown oil, 66.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 – 7.24 (m, 2H), 7.24 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 7.14 – 7.10 (m, 2H), 6.98 – 6.93 (m, 2H), 6.84 – 6.79 (m, 2H), 6.74 – 6.69 (m, 2H), 2.91 (s, 6H), 1.66 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.97, 150.94, 147.81, 147.61, 144.44, 128.15, 128.01, 126.91, 125.75, 120.99, 114.26, 77.62, 77.20, 76.78, 41.49, 31.06.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.1 (16), 316.2 (55), 317.2 (14), 330.3 (4), 331.2(100), 332.2 (26), 333.2 (4).



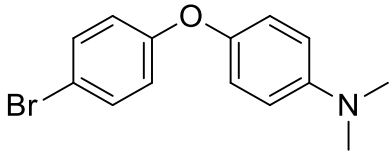
4-(4-fluorophenoxy)-*N,N*-dimethylaniline (3ae): The desired pure product was obtained in 52% yield as a brown solid, 36.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 – 6.95 (m, 2H), 6.95 – 6.91 (m, 2H), 6.91 – 6.86 (m, 2H), 6.77 – 6.71 (m, 2H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.06, 148.04, 147.79, 120.60, 118.78, 118.70, 116.22, 115.99, 114.17, 41.39; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -122.17.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (33), 215.0 (11), 230.0 (58), 231.0 (100), 232.0 (16).



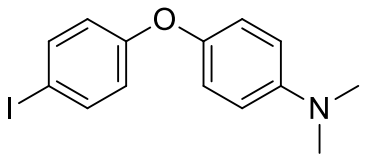
4-(4-chlorophenoxy)-*N,N*-dimethylaniline (3ah): The desired pure product was obtained in 58% yield as a yellow solid, 43.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.20 (m, 2H), 6.97 – 6.92 (m, 2H), 6.89 – 6.84 (m, 2H), 6.77 – 6.71 (m, 2H), 2.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.99, 147.08, 129.57, 126.95, 121.08, 118.48, 114.07, 41.31.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (39),231.0 (8), 246.0 (53), 247.0 (100), 248.0 (33), 249.1 (35).



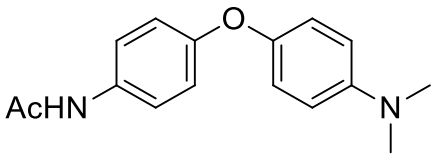
4-(4-bromophenoxy)-*N,N*-dimethylaniline (3ai): The desired pure product was obtained in 44% yield as a brown solid, 38.7 mg. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.29 – 7.20 (d, *J*=8.9 Hz, 2H), 6.97 (d, *J*=9.1 Hz, 2H), 6.88 (d, *J*=8.9 Hz, 2H), 6.76 (d, *J*=9.0 Hz, 2H), 2.96 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.55, 148.03, 146.91, 132.51, 121.12, 118.92, 114.04, 41.29.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.1 (51), 176.0 (8), 290.1 (45), 291.1 (100), 292.1 (58), 293.1 (99), 294.1 (15).



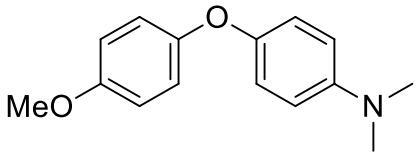
4-(4-iodophenoxy)-*N,N*-dimethylaniline (3aj): The desired pure product was obtained in 43% yield as a yellow solid, 44.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.52 (m, 2H), 6.98 – 6.91 (m, 2H), 6.76 – 6.71 (m, 2H), 6.71 – 6.67 (m, 2H), 2.94 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.44, 148.10, 146.73, 138.50, 121.20, 119.44, 114.04, 84.39, 41.29.

GC-MS (EI, 70 Ev): *m/z* (rel int., %): 76.0 (7), 136.0 (30), 212.0 (9), 337.9 (29), 338.9 (100), 292.1 (58), 339.9 (16).



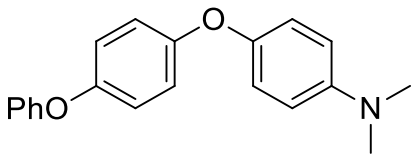
***N*-(4-(4-(dimethylamino)phenoxy)phenyl)acetamide (3ak):** The desired pure product was obtained in 64% yield as a blue crystal, 51.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (s, 1H), 7.41 – 7.36 (m, 2H), 6.95 – 6.90 (m, 2H), 6.88 (dd, *J*=9.4, 2.6 Hz, 2H), 6.76 – 6.70 (m, 2H), 2.92 (s, 6H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ =168.63, 155.64, 147.88, 147.64, 132.46, 121.99, 120.66, 117.87, 114.19, 41.42, 24.46.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (14), 227.1 (15), 228.0 (29), 256.1 (8), 269.1 (16), 270.1 (100), 271.1 (18).



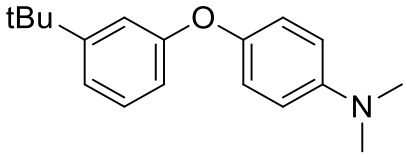
4-(4-methoxyphenoxy)-*N,N*-dimethylaniline (3al): The desired pure product was obtained in 21% yield as a brown oil, 15.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92 (t, *J*=2.3 Hz, 2H), 6.91 – 6.90 (m, 2H), 6.86 – 6.82 (m, 2H), 6.76 – 6.70 (m, 2H), 3.78 (s, 3H), 2.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.42, 149.05, 147.37, 119.94, 119.15, 114.81, 114.28, 55.83, 41.51.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (18), 228.0 (10), 242.1 (33), 243.0 (100), 244.1 (16).



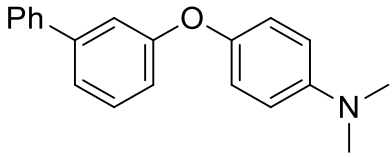
***N,N*-dimethyl-4-(4-phenoxyphenoxy)aniline (3am):** The desired pure product was obtained in 20% yield as a yellow oil, 63.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.28 (m, 2H), 7.06 (t, *J*=7.4 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.98 – 6.96 (m, 2H), 6.95 (d, *J*=2.3 Hz, 2H), 6.95 – 6.89 (m, 2H), 6.79 – 6.72 (m, 2H), 2.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.32, 155.06, 151.57, 147.70, 129.83, 122.84, 120.74, 120.65, 118.72, 118.08, 117.31, 114.21, 41.44.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 77.0 (8), 136.0 (17), 290.1 (6), 304.1(28), 305.1 (100), 306.1 (23).



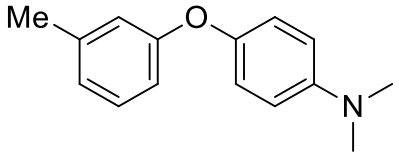
4-(3-(*tert*-butyl)phenoxy)-*N,N*-dimethylaniline (3an): The desired pure product was obtained in 53% yield as a yellow oil, 42.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (t, *J*=8.2 Hz, 1H), 7.06 (d, *J*=1.6 Hz, 1H), 7.06 – 7.02 (m, 1H), 7.00 – 6.94 (m, 2H), 6.78 – 6.71 (m, 2H), 6.71 – 6.66 (m, 1H), 2.94 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.89, 153.38, 147.68, 129.09, 120.83, 119.27, 115.17, 114.21, 41.45, 34.94, 31.48.

GC-MS (EI, 70 Ev): *m/z* (rel int., %): 121.0 (6), 136.0 (21), 239.1 (8), 254.1 (8), 268.1 (20), 269.1 (100), 270.1 (22).



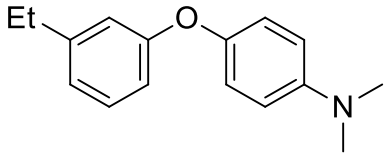
4-([1,1'-biphenyl]-3-yloxy)-*N,N*-dimethylaniline (3ao): The desired pure product was obtained in 47% yield as a brown oil, 40.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (dt, *J*=8.3, 2.3 Hz, 2H), 7.43 (t, *J*=7.5, 2H), 7.39 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 7.06 – 7.00 (m, 2H), 6.93 (ddd, *J*=8.1, 2.5, 0.9 Hz, 1H), 6.80 – 6.74 (m, 2H), 2.96 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.77, 147.49, 143.01, 140.94, 129.97, 128.89, 127.61, 121.11, 121.03, 116.14, 116.10, 77.62, 77.20, 76.78, 41.43.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (14), 152.0 (8), 288.1 (27), 289.1 (100), 290.1 (21).



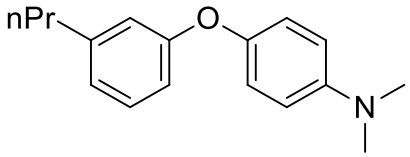
***N,N*-dimethyl-4-(*m*-tolyloxy)aniline (3ap):** The desired pure product was obtained in 31% yield as a red oil, 21.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (t, *J*=7.8 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.83 (d, *J*=7.5 Hz, 1H), 6.76 (s, 2H), 6.75 (d, *J*=4.3 Hz, 1H), 6.73 (d, *J*=3.6 Hz, 1H), 2.94 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.23, 147.75, 147.62, 139.81, 129.40, 122.96, 121.09, 118.00, 114.39, 114.15, 41.42, 21.62.

GC-MS (EI, 70 Ev): *m/z* (rel int., %): 65.0 (13), 91.0 (10), 108.0 (5), 136.0 (45),137.0 (4), 212.0 (9), 226.1 (46), 227.1 (100), 228.1 (17).



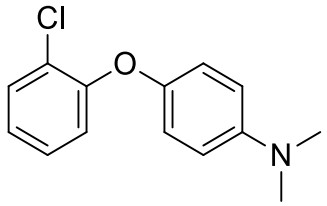
4-(3-ethylphenoxy)-*N,N*-dimethylaniline (3aq): The desired pure product was obtained in 18% yield as a brown oil, 12.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (t, *J*=7.9 Hz, 1H), 6.99 (d, *J*=2.3 Hz, 1H), 6.97 (d, *J*=2.3 Hz, 1H), 6.90 – 6.81 (m, 2H), 6.79 – 6.75 (m, 2H), 6.74 (d, *J*=3.5 Hz, 1H), 2.95 (s, 6H), 2.62 (q, *J*=7.6 Hz, 2H), 1.23 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.23, 147.70, 147.62, 146.25, 129.44, 121.73, 116.92, 114.49, 114.15, 41.41, 28.98, 15.66.

GC-MS (EI, 70 Ev): *m/z* (rel int., %): 77.0 (5), 136.0 (32), 226.0 (8), 240.1 (8), 241.1 (100), 242.1 (19).



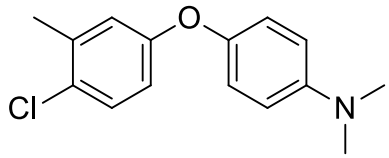
***N,N*-dimethyl-4-(3-propylphenoxy)aniline (3ar):** The desired pure product was obtained in 22% yield as a brown oil, 16.7 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (t, *J*=7.8 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.84 (d, *J*=7.5 Hz, 1H), 6.79 (s, 1H), 6.76 (q, *J*=4.9, 4.3 Hz, 2H), 6.73 (d, *J*=3.2 Hz, 1H), 2.94 (s, 6H), 2.57 – 2.50 (m, 2H), 1.65 – 1.59 (m, 2H), 0.94 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.14, 147.72, 144.71, 129.34, 122.40, 120.98, 114.60, 114.17, 41.43, 38.17, 24.62, 14.01.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 57.0 (10), 91.0 (5), 197.0 (8), 225.1 (100), 226.1 (14), 227.1 (34), 240.1 (17), 242.1 (5).



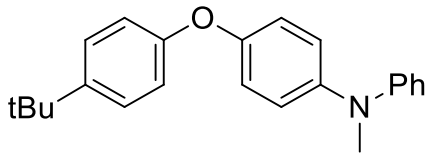
4-(2-chlorophenoxy)-*N,N*-dimethylaniline (3as): The desired pure product was obtained in 17% yield as a yellow oil, 12.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (dd, *J*=7.9, 1.6 Hz, 1H), 7.17 – 7.10 (m, 1H), 7.01 – 6.95 (m, 2H), 6.94 – 6.80 (m, 2H), 6.78 – 6.69 (m, 2H), 2.94 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.64, 147.91, 130.69, 124.30, 123.23, 120.52, 118.39, 114.12, 41.37.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 75.0 (6), 136.0 (43), 232.0 (6), 246.0 (51), 247.0 (100), 248.0 (31), 249.0 (33).



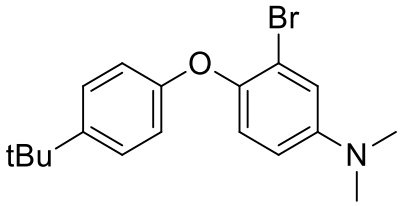
4-(4-chloro-3-methylphenoxy)-*N,N*-dimethylaniline (3at): The desired pure product was obtained in 71% yield as a red oil, 111.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, *J*=8.7 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.79 (d, *J*=2.9 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.69 – 6.66 (m, 1H), 2.91 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.78, 147.88, 147.22, 137.31, 129.82, 120.99, 119.60, 115.97, 114.01, 41.25, 20.37.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 136.0 (40), 246.0 (8), 260.0 (47), 261.0 (100), 262.0 (31), 263.0 (33).



4-(4-(*tert*-butyl)phenoxy)-*N*-methyl-*N*-phenylaniline (3ba): The desired pure product was obtained in 12% yield as a yellow oil, 12.3 mg. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.29 (d, *J*=7.7 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.13 (s, 2H), 7.01 – 6.93 (m, 2H), 6.90 (s, 1H), 6.84 (d, *J*=8.7 Hz, 2H), 6.77 – 6.61 (m, 2H), 2.94 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.23, 129.36, 126.67, 124.36, 121.44, 120.63, 120.08, 118.07, 40.41, 31.70.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 77.1 (6), 143.9 (14), 167.1 (11), 198.1 (19), 281.1 (6), 316.2 (38), 317.2 (10), 331.2 (100), 332.2 (26).



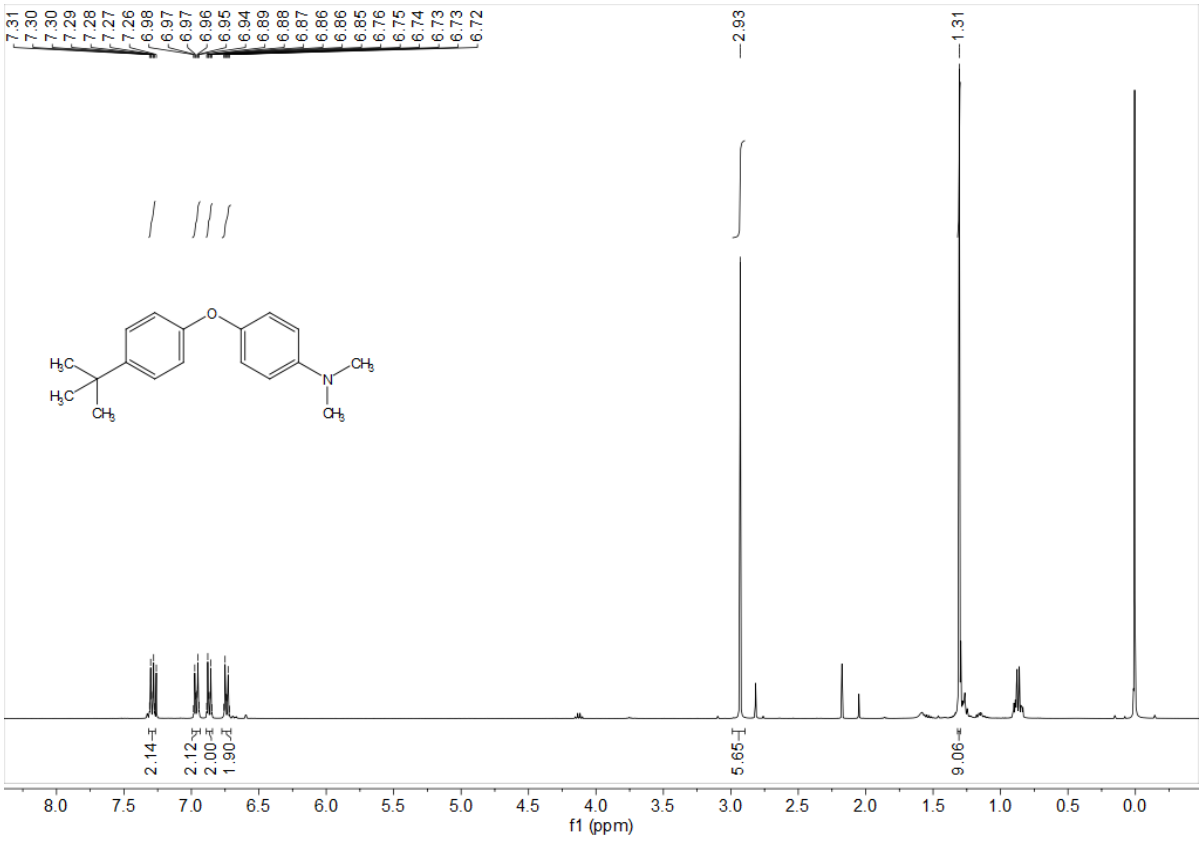
3-bromo-4-(4-(*tert*-butyl)phenoxy)-*N,N*-dimethylaniline (3ca): The desired pure product was obtained in 11% yield as a yellow oil, 11.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J*=2.2 Hz, 1H), 7.28 (d, *J*=2.1 Hz, 2H), 6.97 – 6.93 (m, 2H), 6.84 – 6.80 (m, 2H), 6.65 (dd, *J*=9.0, 3.0 Hz, 1H), 2.94 (s, 6H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.39, 148.66, 145.01, 143.75, 126.49, 122.87, 117.00, 116.83, 116.02, 112.99, 41.05, 34.36, 31.70.

GC-MS (EI, 70 eV): *m/z* (rel int., %): 151.1 (22), 179.1 (22), 180.1 (35), 181.1 (32), 301.1 (11), 317.1 (26), 333.1 (9), 348.2 (100), 349.2 (19).

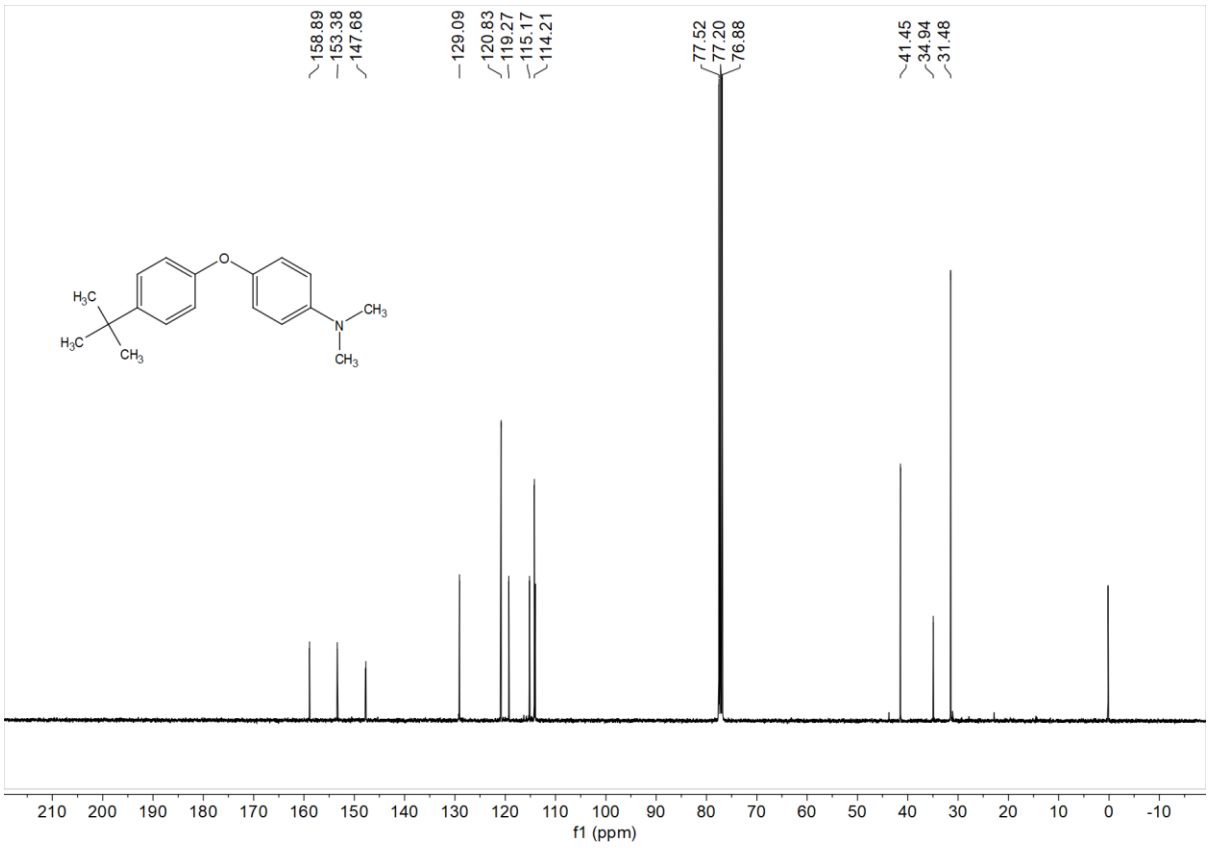
6. NMR Spectra of obtained products

Compound 3aa

^{1}H NMR

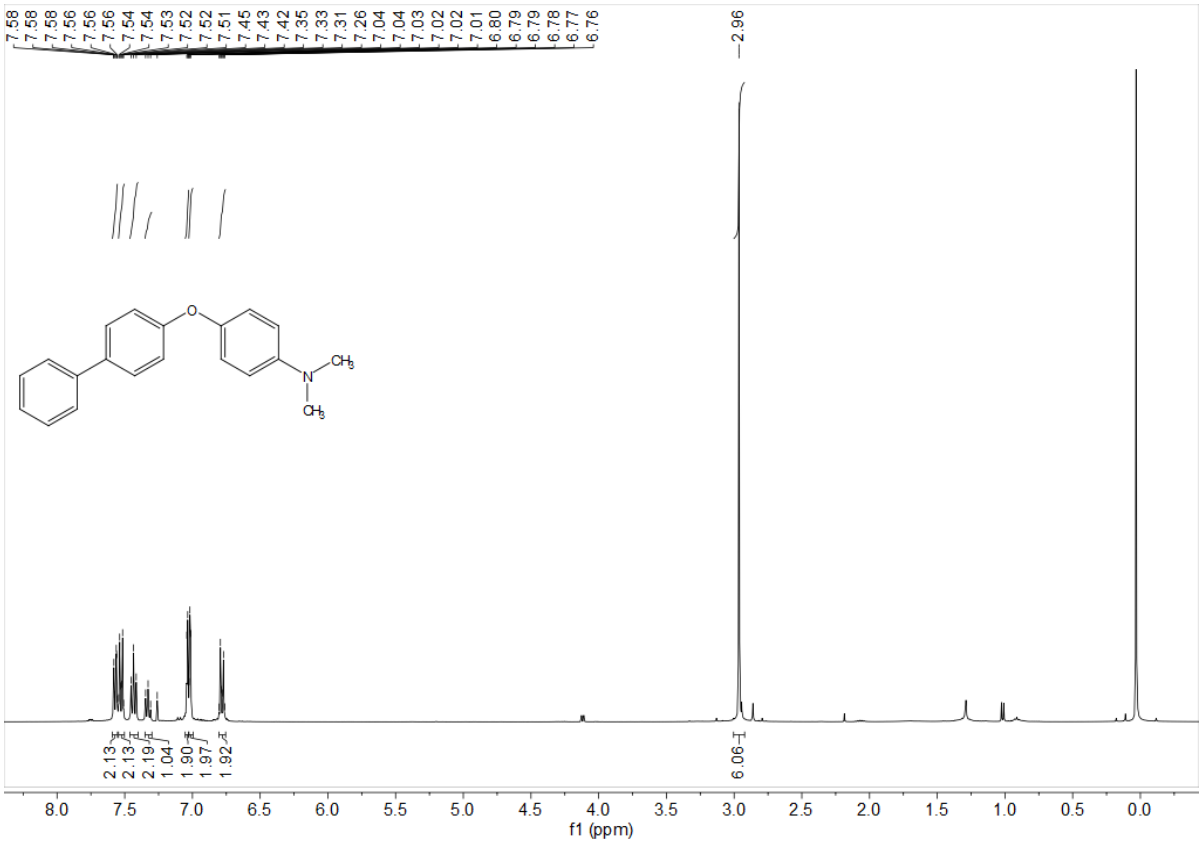


^{13}C NMR

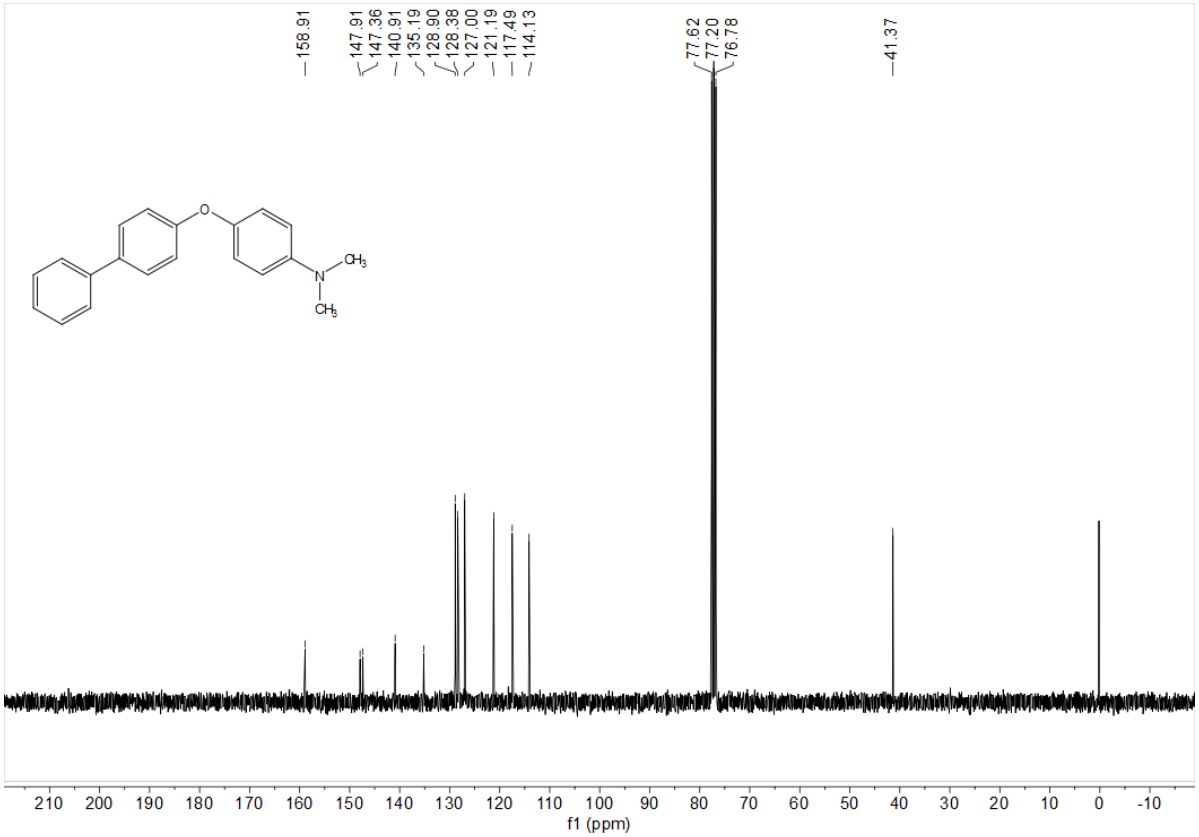

158.89
153.38
147.68
129.09
120.83
119.27
115.17
114.21
77.52
77.20
76.88
41.45
34.94
31.48
O
H3C
H3C
CH3
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ab

^{1}H NMR

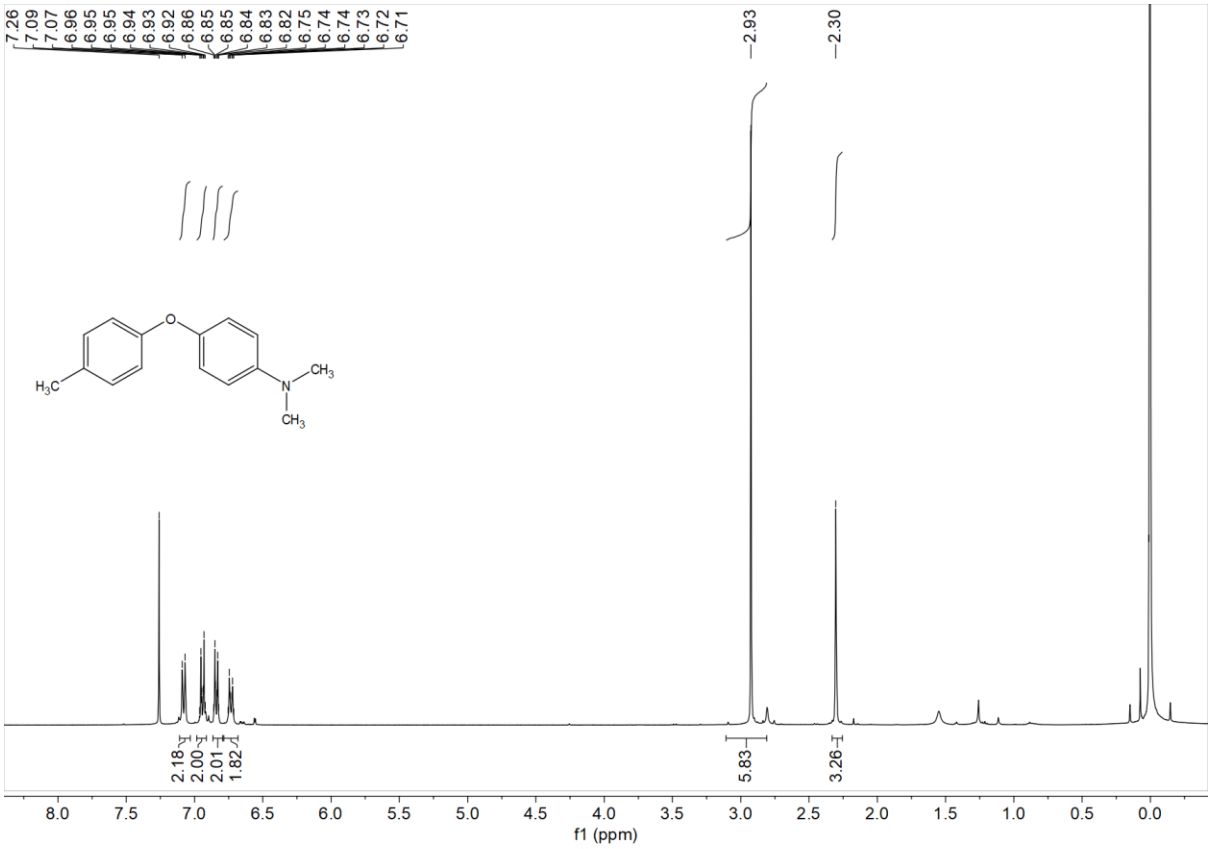


^{13}C NMR

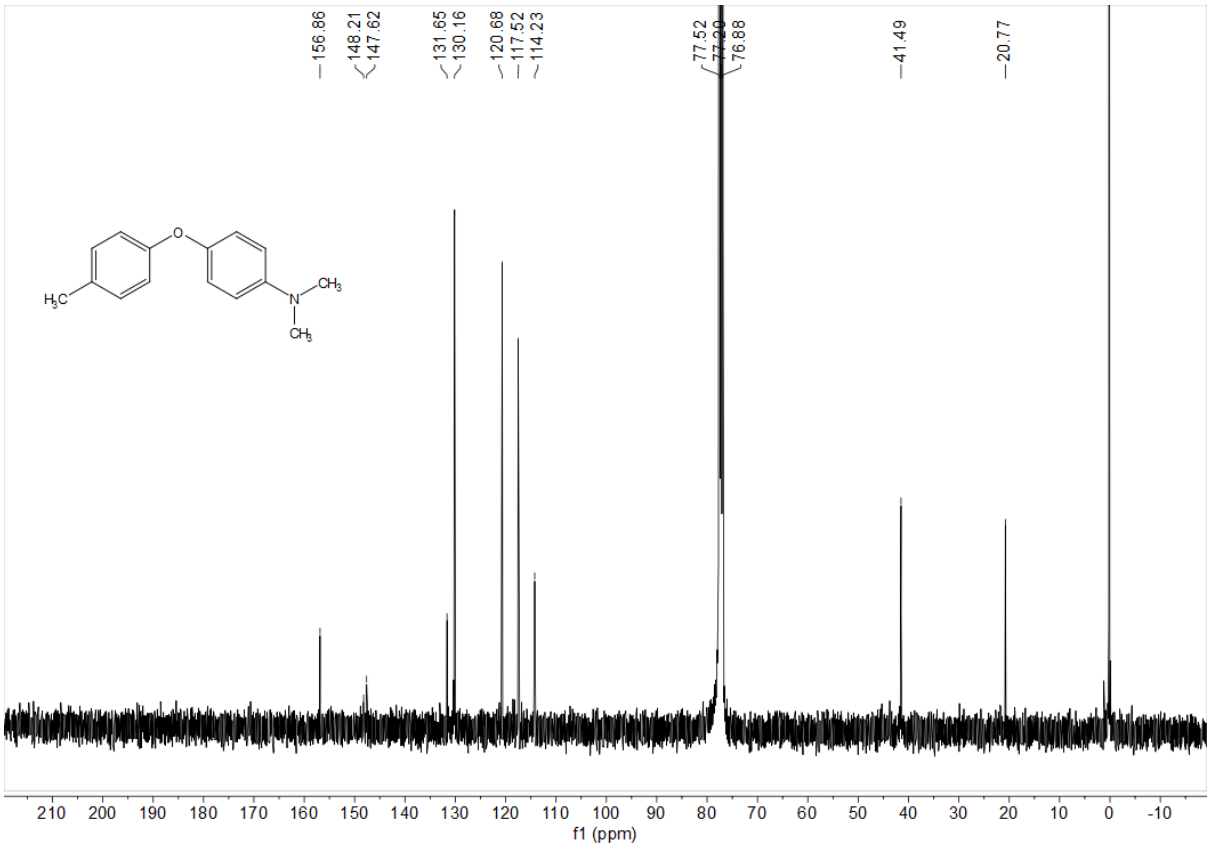

158.91
147.91
147.36
140.91
135.19
128.90
128.38
127.00
121.19
117.49
114.13
77.62
77.20
76.78
41.37
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ac

^{1}H NMR

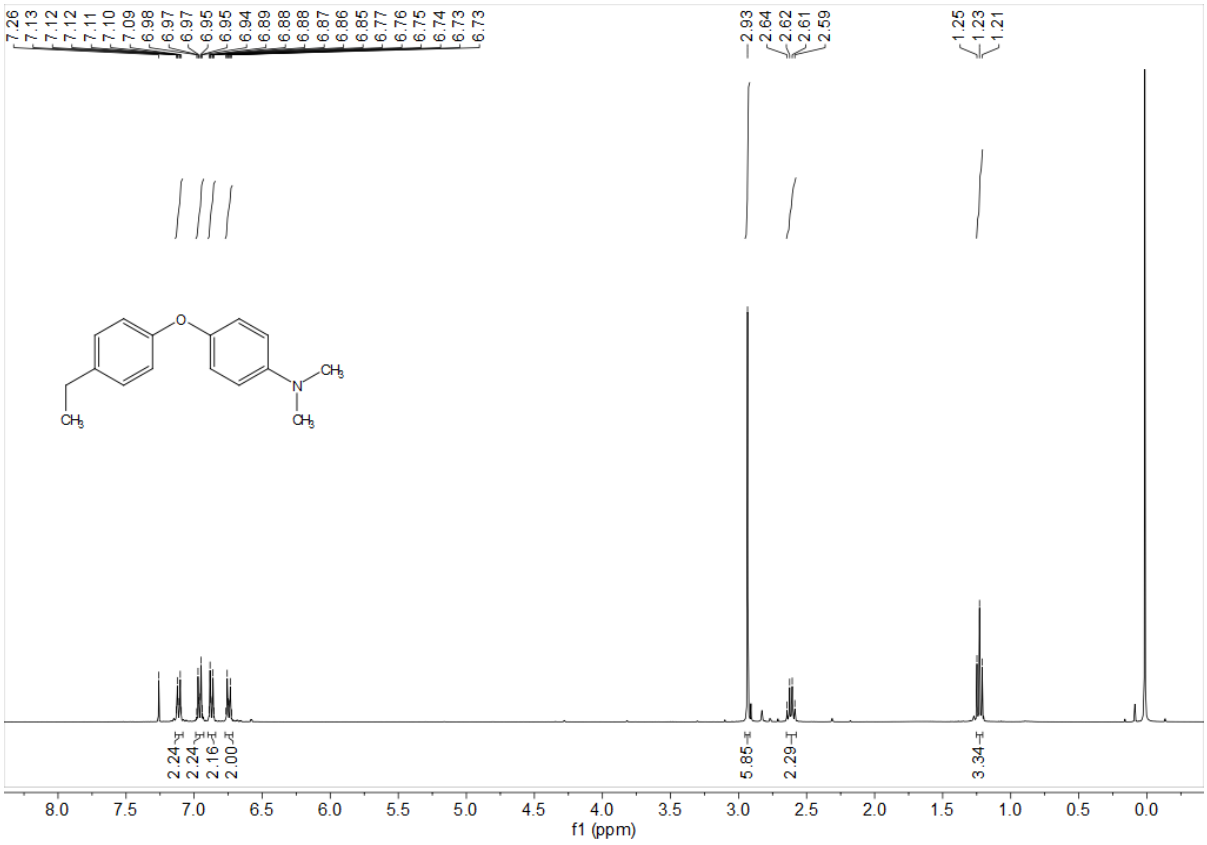


^{13}C NMR

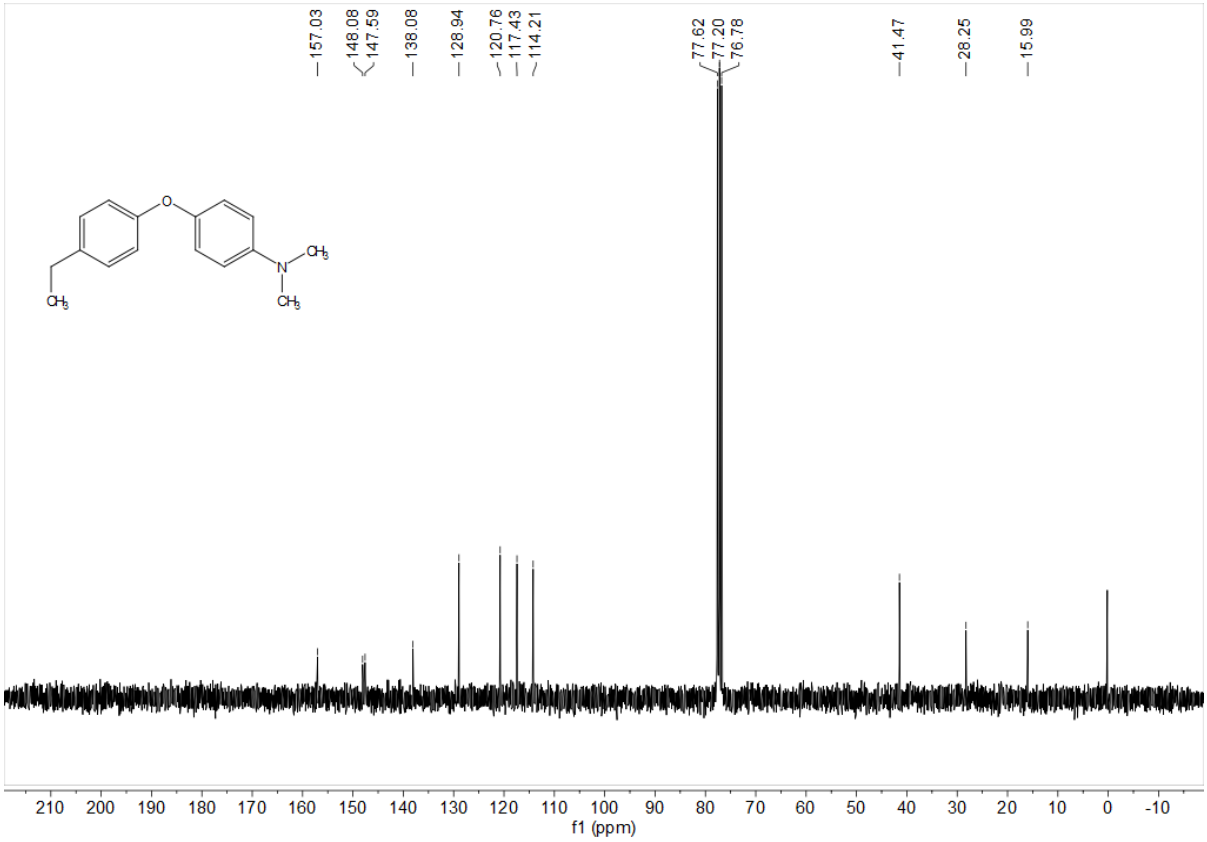

156.86
148.21
147.62
131.65
130.16
120.68
117.52
114.23
77.52
77.20
76.88
41.49
20.77
O
H3C
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ad

^{1}H NMR

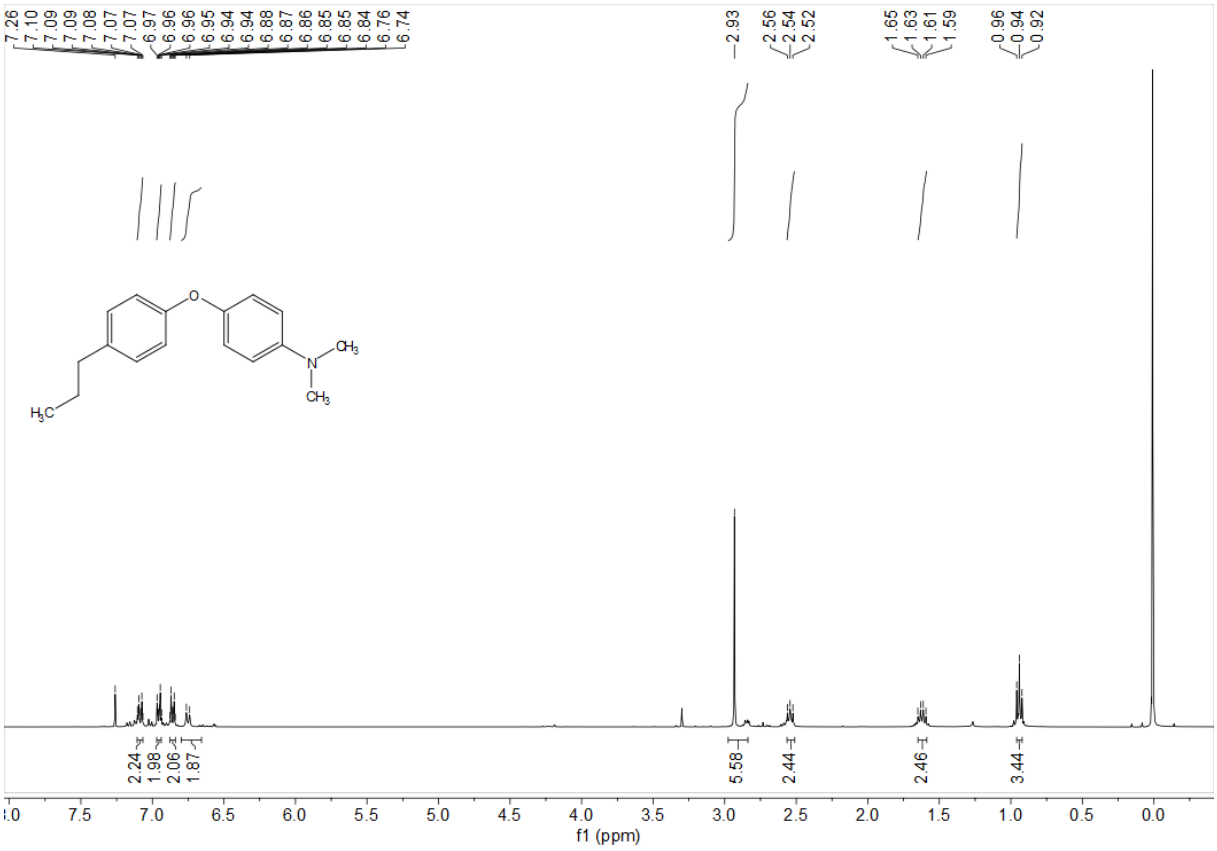


^{13}C NMR

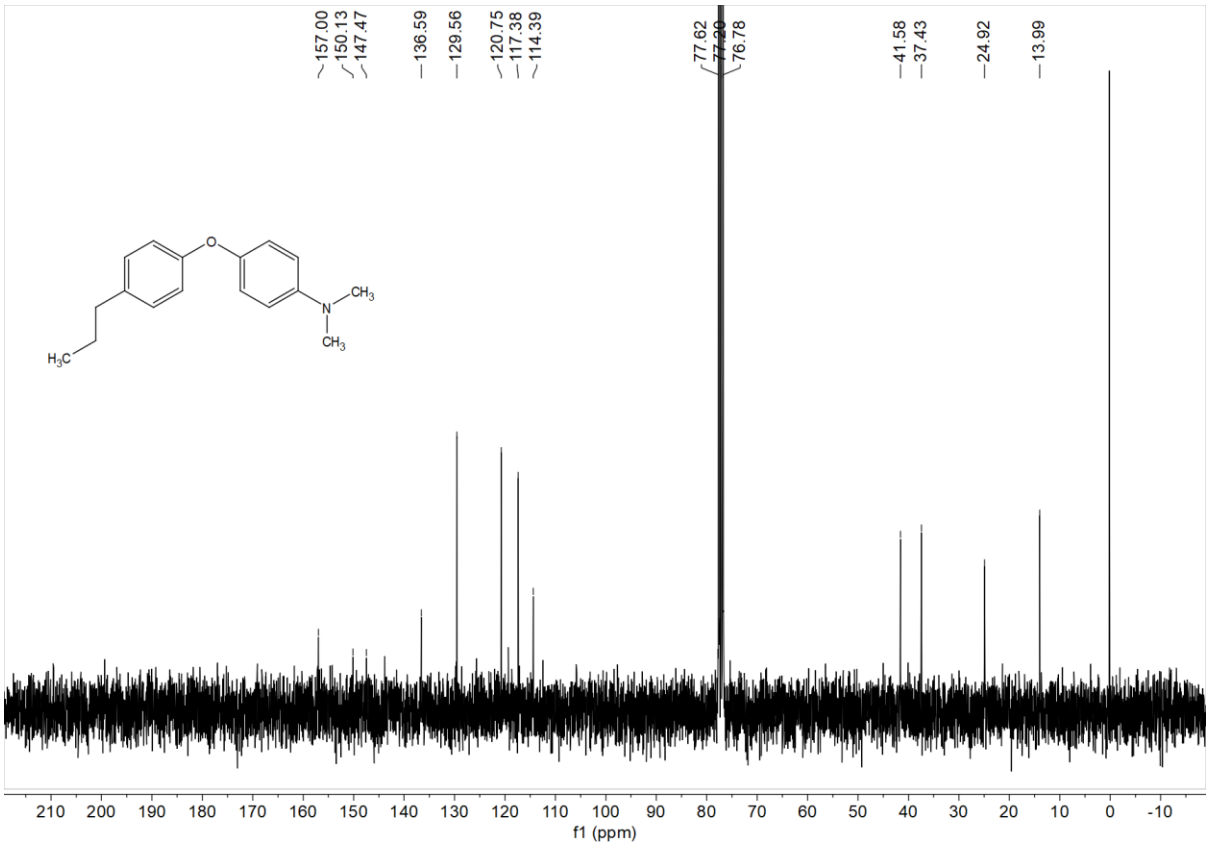

157.03
148.08
147.59
138.08
128.94
120.76
117.43
114.21
77.62
77.20
76.78
41.47
28.25
15.99
O
N
CH3
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ae

^{1}H NMR

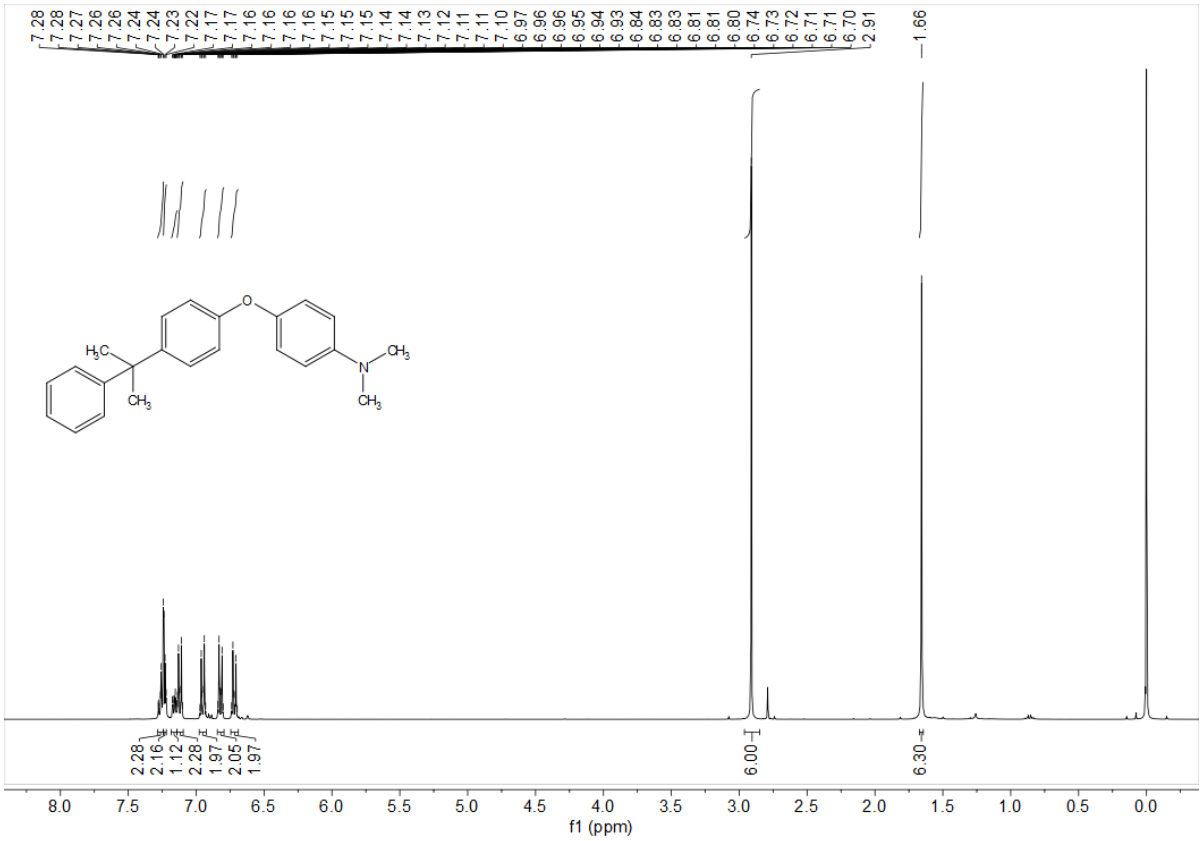


^{13}C NMR

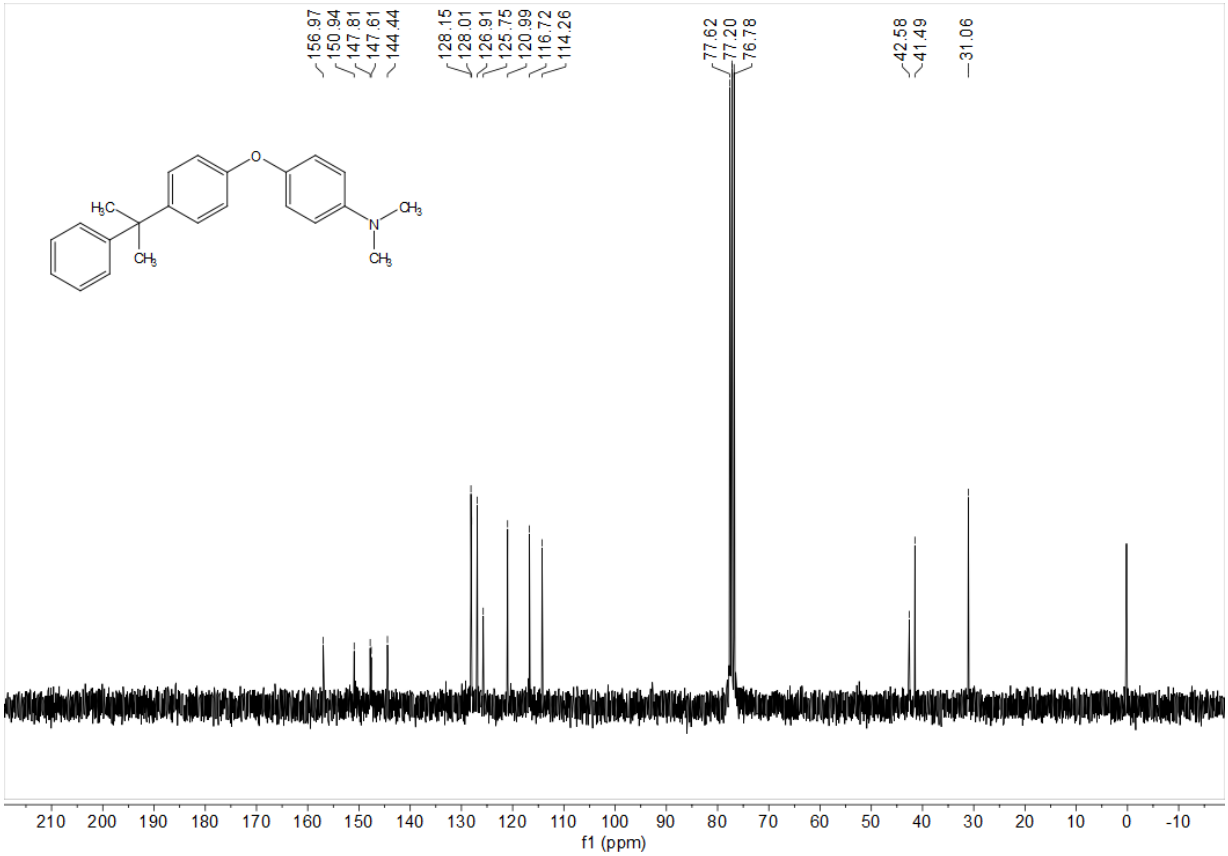

157.00
150.13
147.47
136.59
129.56
120.75
117.38
114.39
77.62
77.20
76.78
41.58
37.43
24.92
13.99
O
N
CH3
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3af

^{1}H NMR

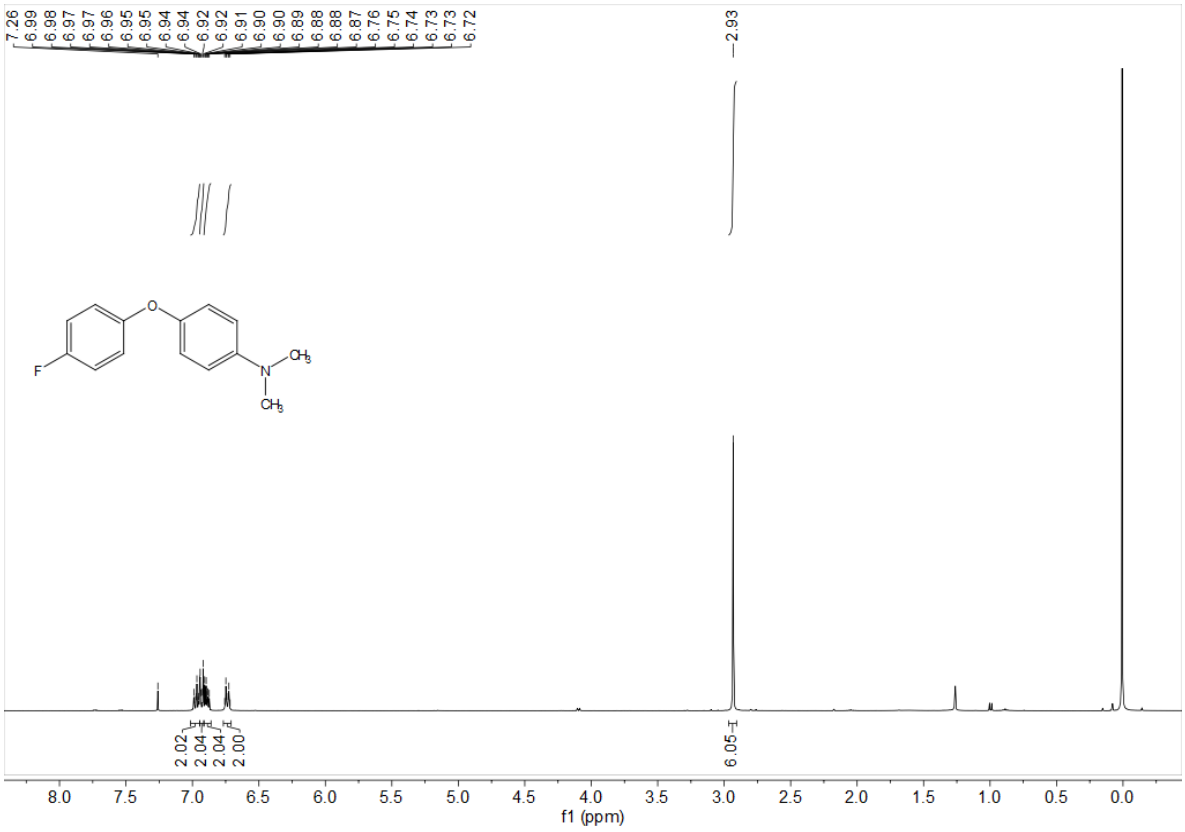


^{13}C NMR

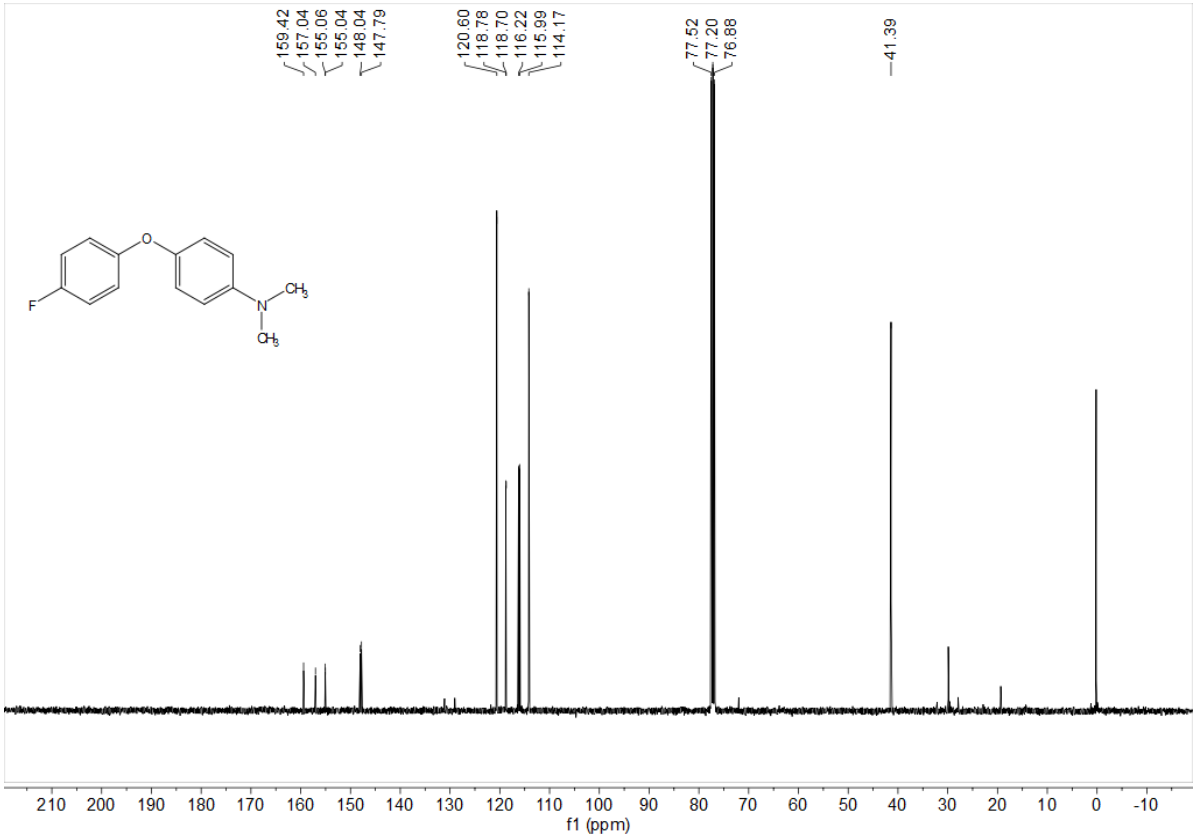

156.97
150.94
147.81
147.61
144.44
128.15
128.01
126.91
125.75
120.99
116.72
114.26
77.62
77.20
76.78
42.58
41.49
31.06
O
H3C
CH3
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ag

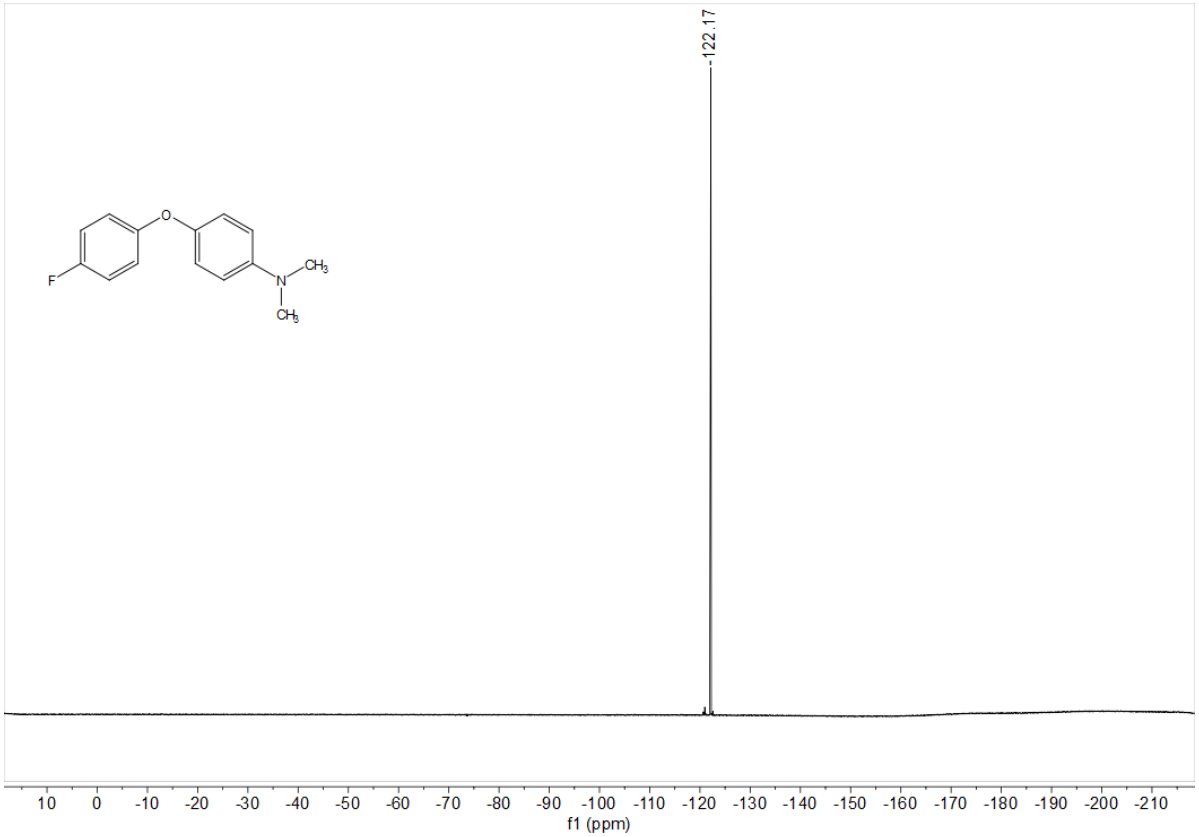
^{1}H NMR



^{13}C NMR

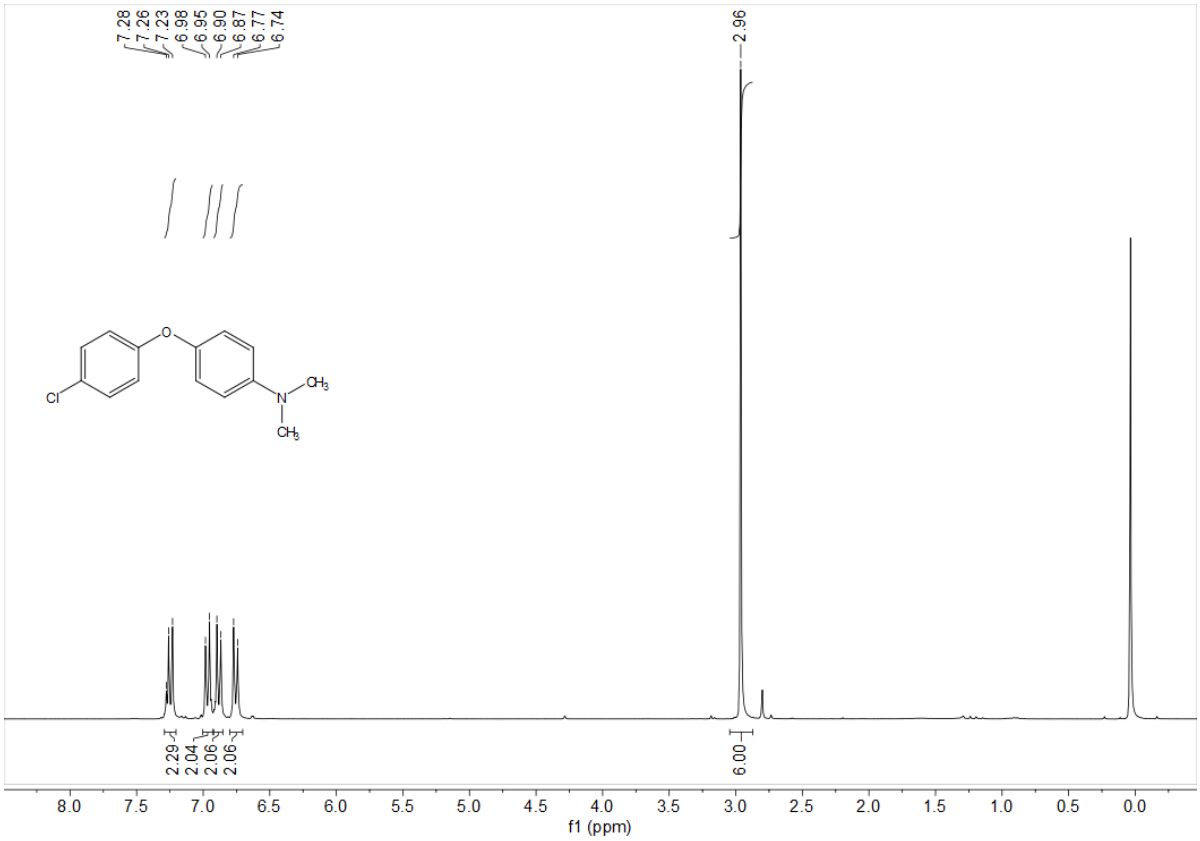

159.42
157.04
155.06
155.04
148.04
147.79
120.60
118.78
118.70
116.22
115.99
114.17
77.52
77.20
76.88
41.39
O
F
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR

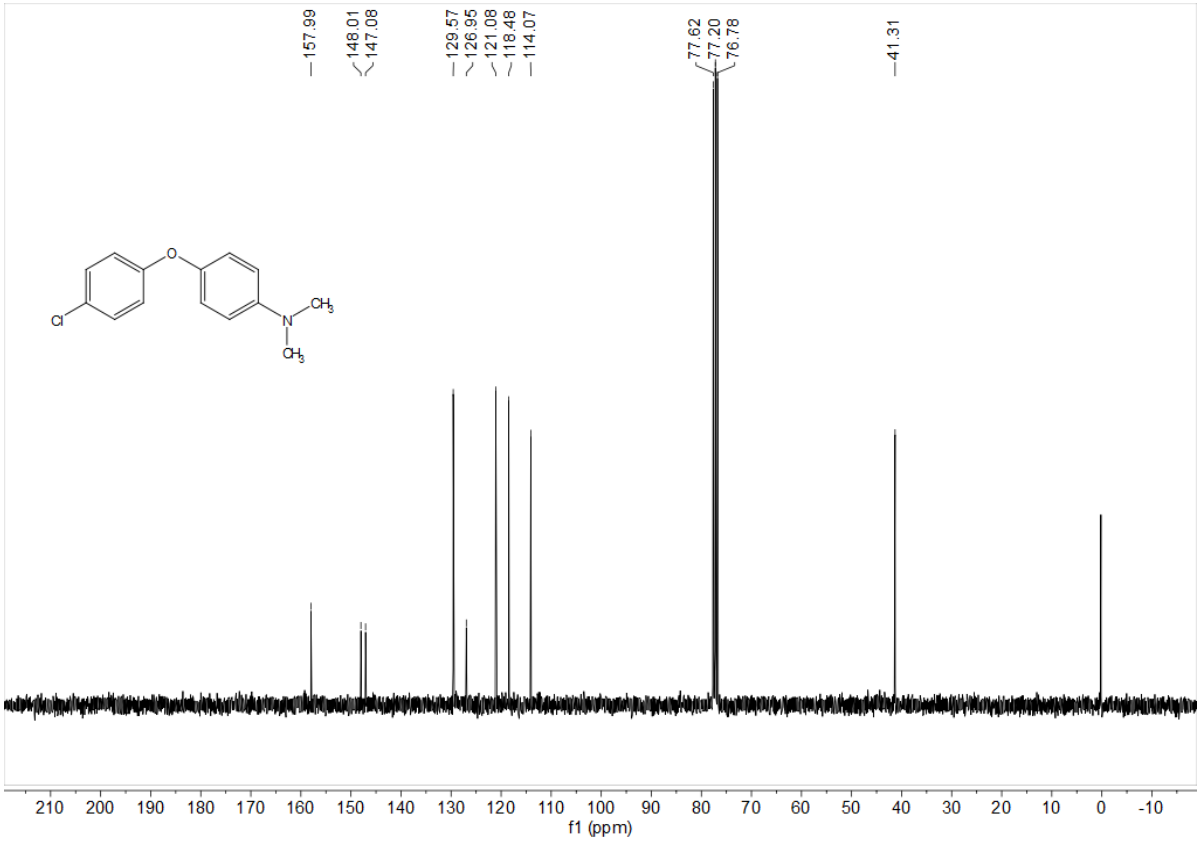

-122.17
F
O
N
CH3
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound 3ah

^{1}H NMR

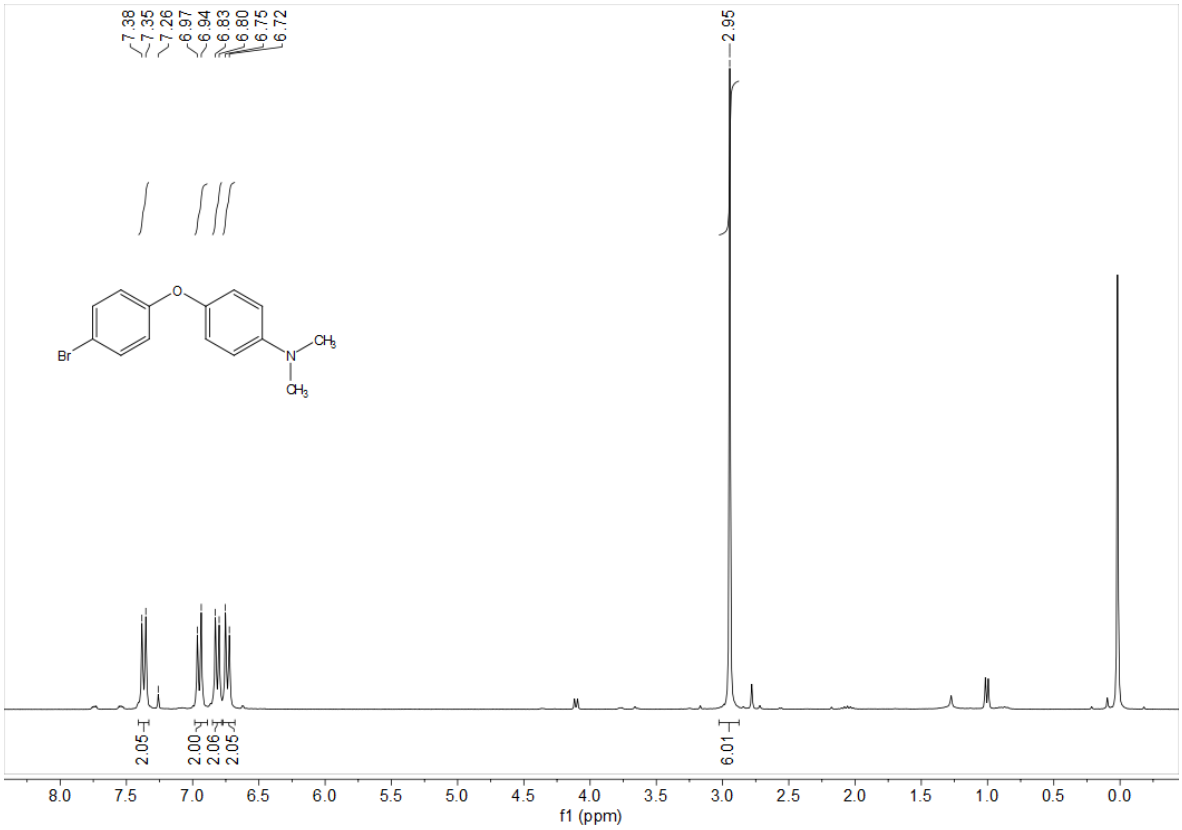


^{13}C NMR

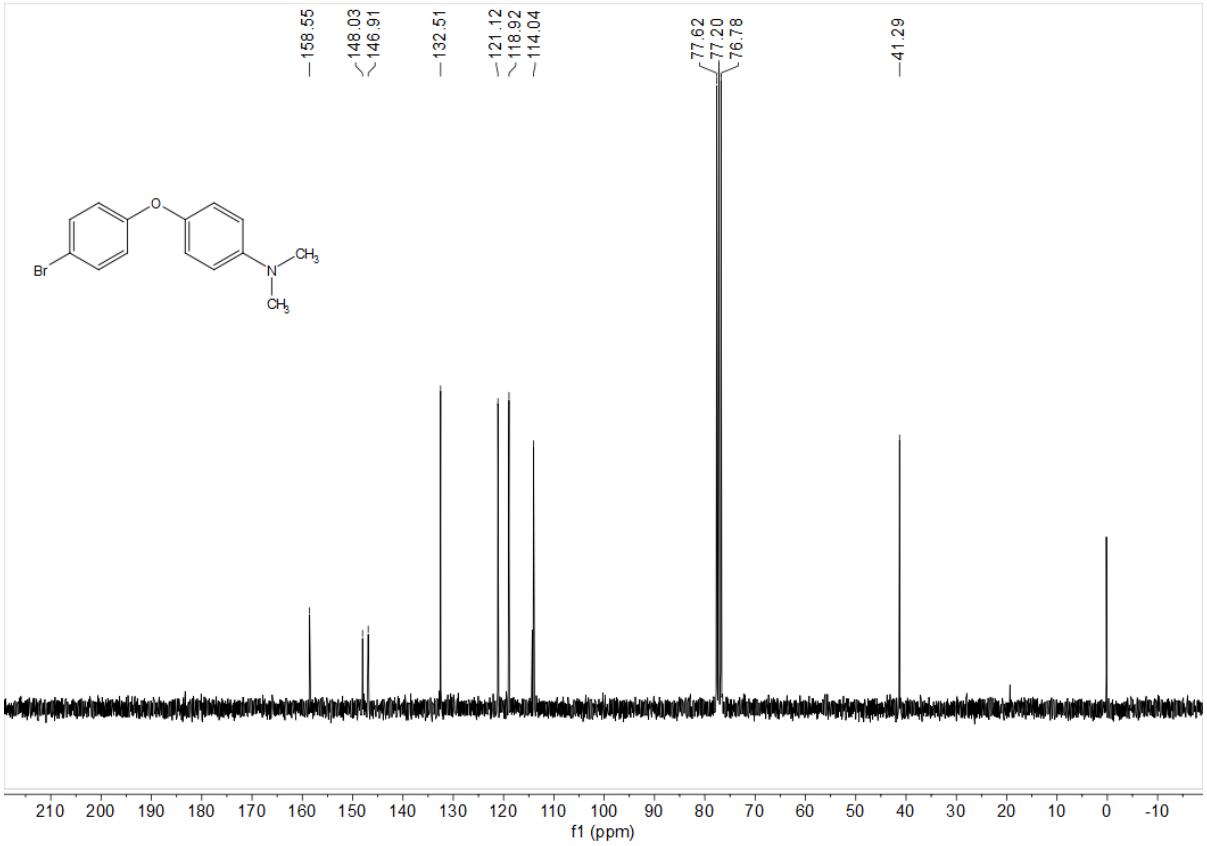

157.99
148.01
147.08
129.57
126.95
121.08
118.48
114.07
77.62
77.20
76.78
41.31
O
Cl
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ai

^{1}H NMR

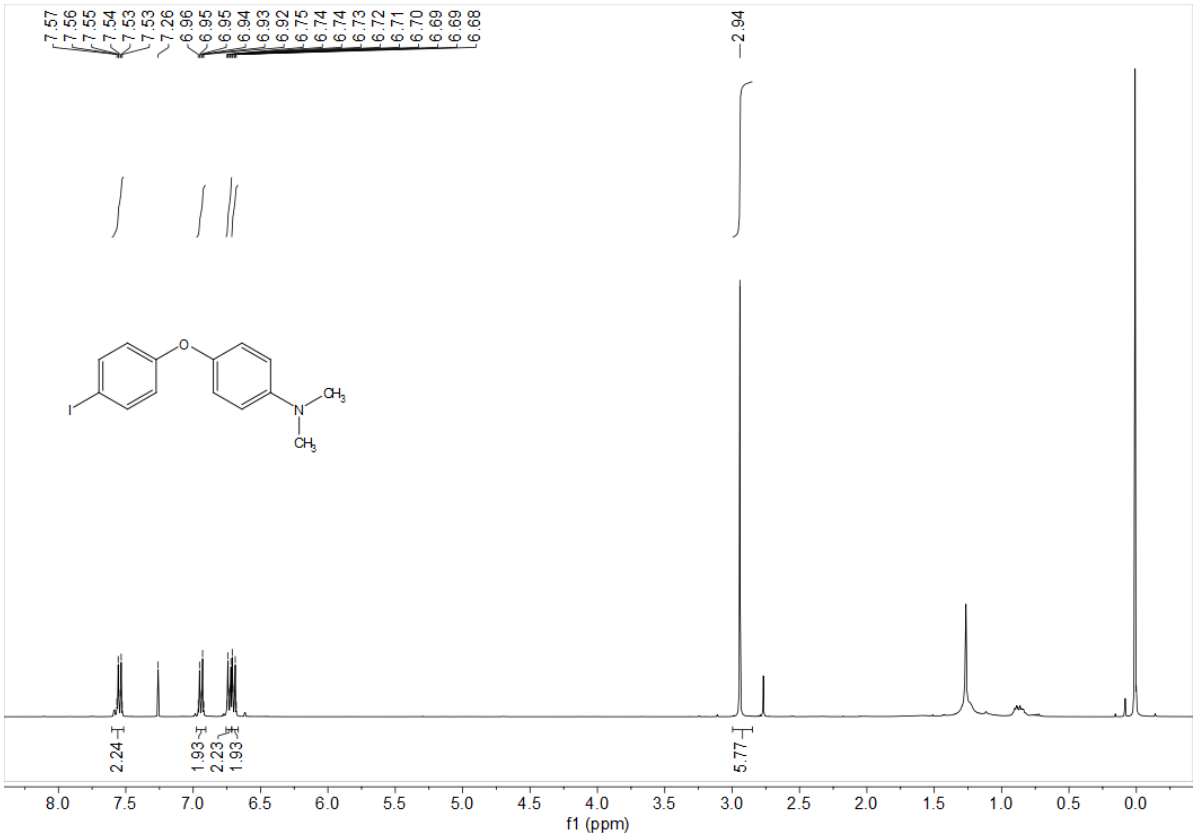


^{13}C NMR

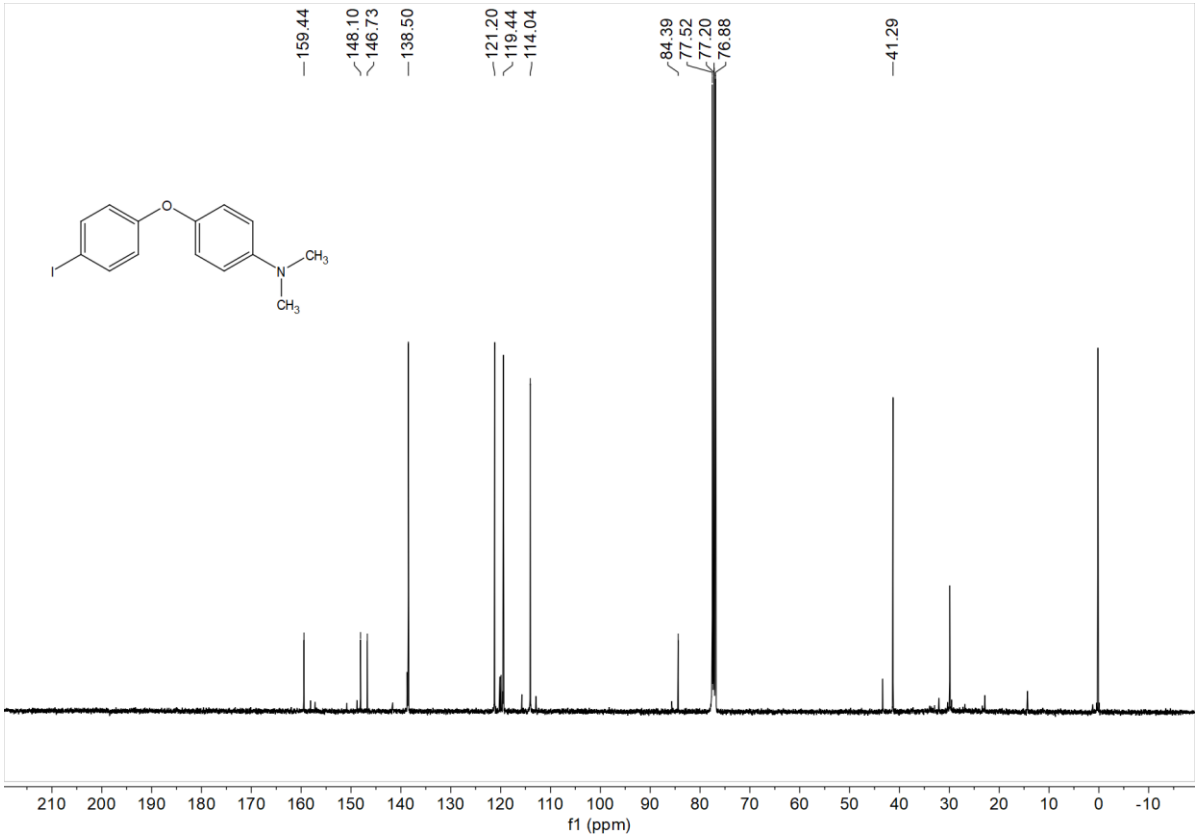

158.55
148.03
146.91
132.51
121.12
118.92
114.04
77.62
77.20
76.78
41.29
Br
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3aj

^{1}H NMR

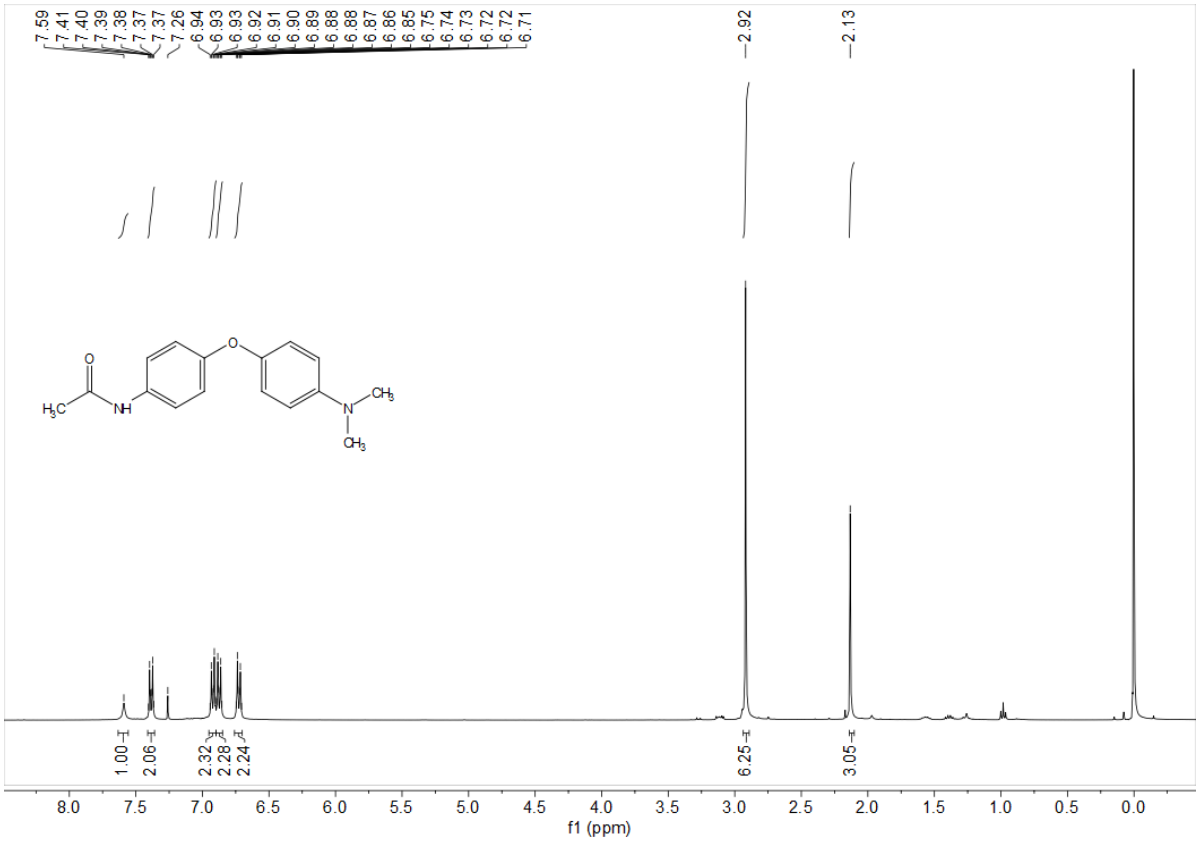


^{13}C NMR

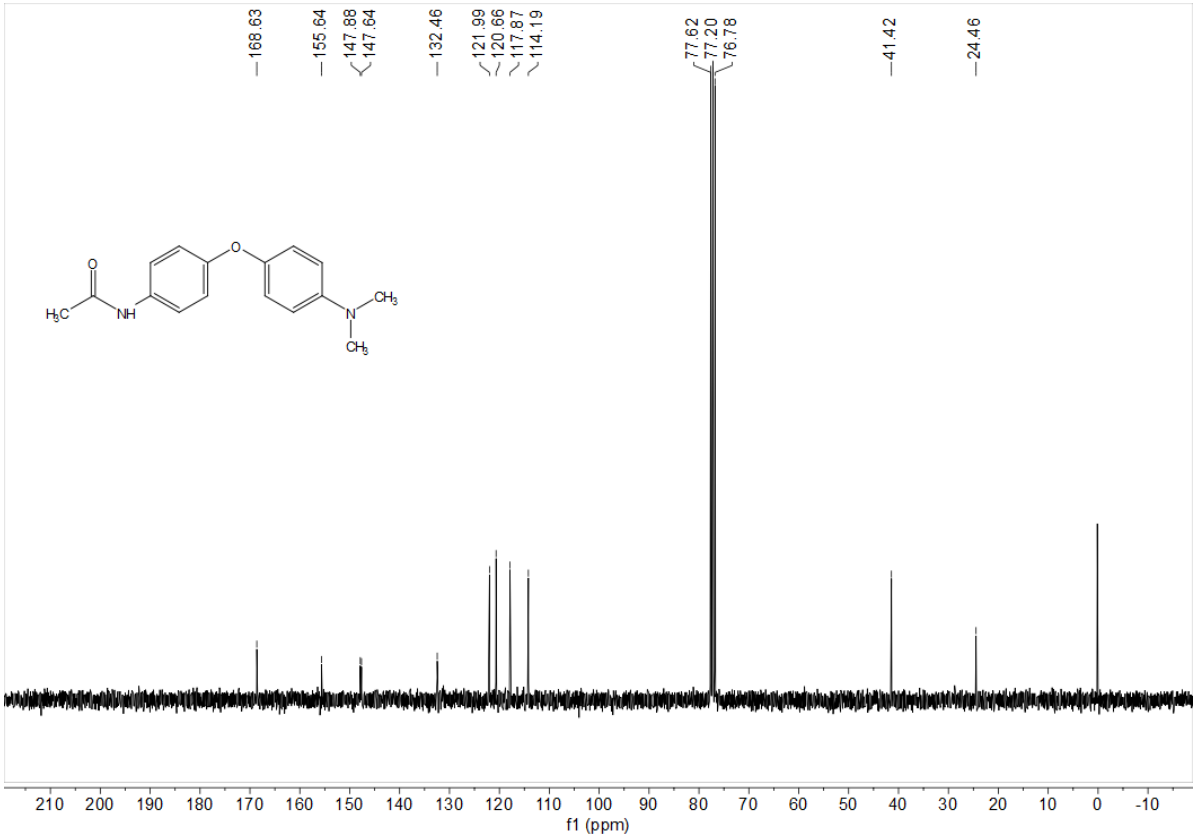

159.44
148.10
146.73
138.50
121.20
119.44
114.04
84.39
77.52
77.20
76.88
41.29
O
I
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ak

^{1}H NMR

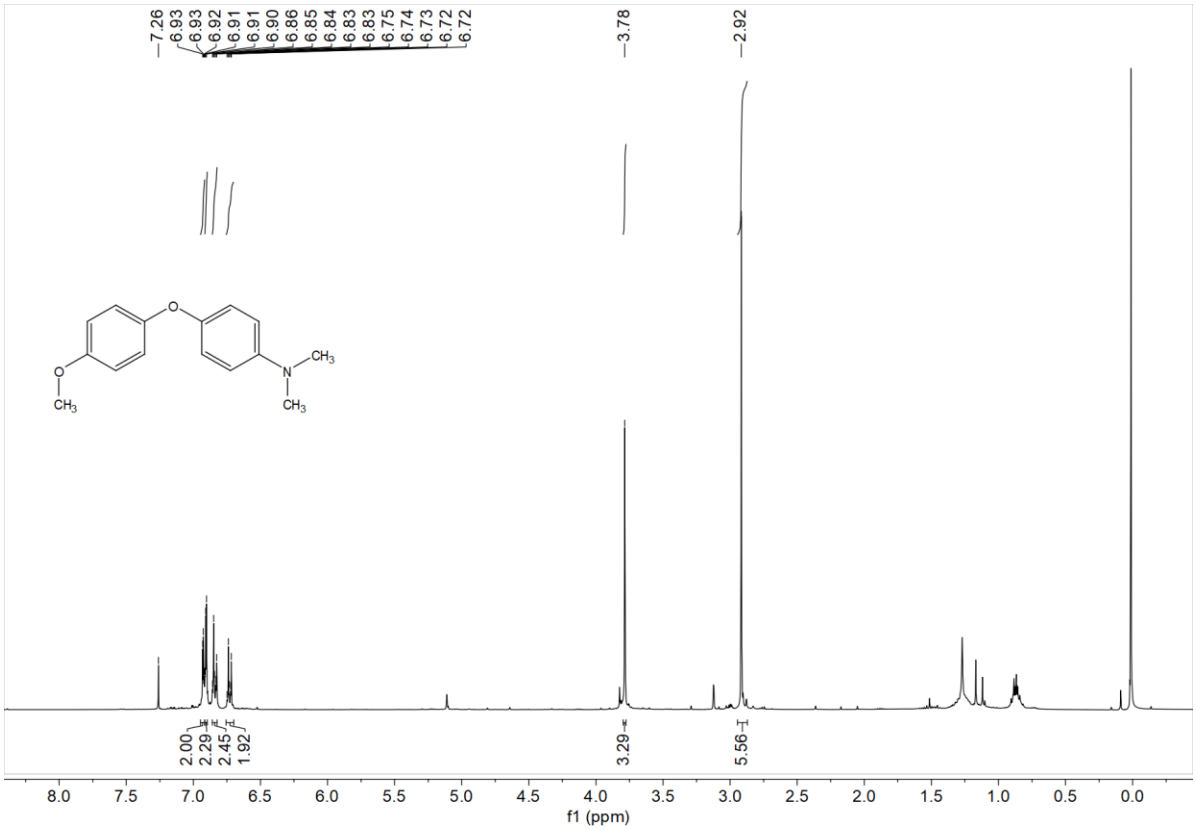


^{13}C NMR

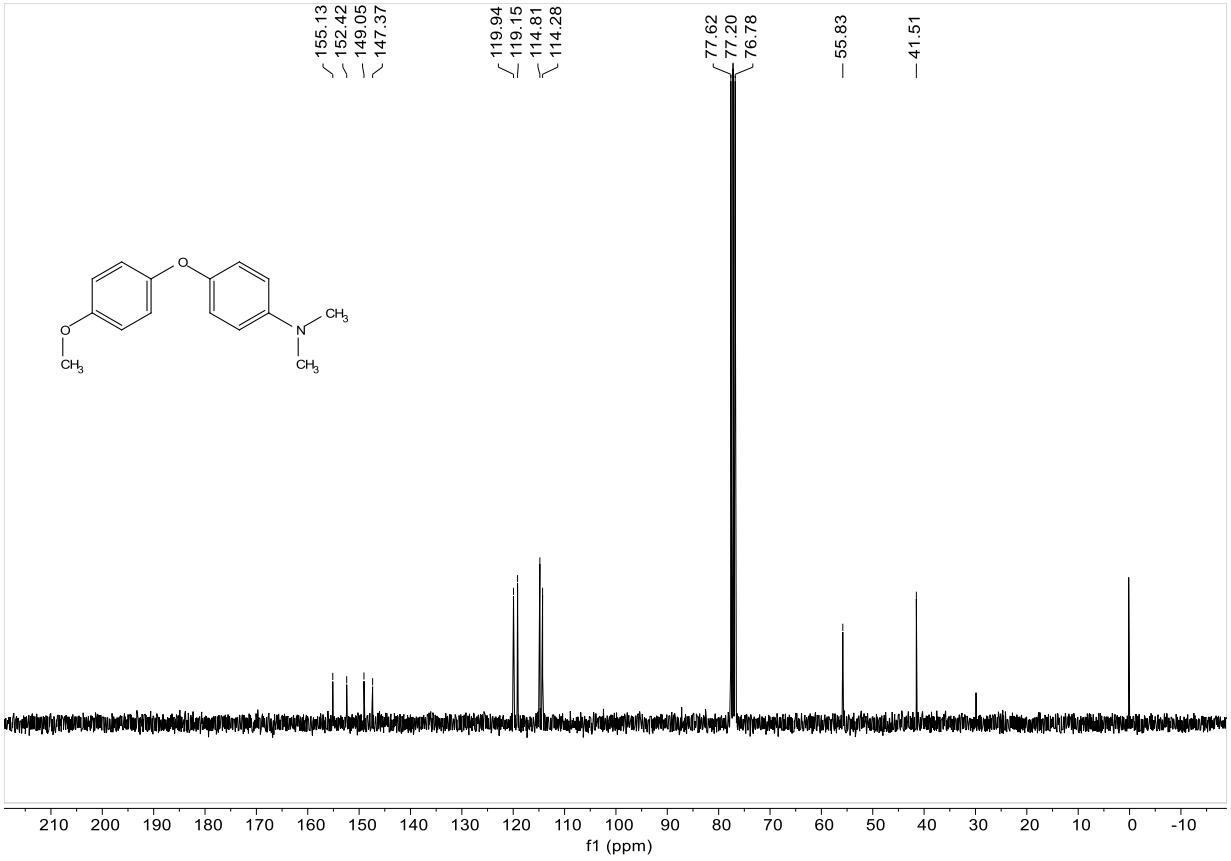

168.63
155.64
147.88
147.64
132.46
121.99
120.66
117.87
114.19
77.62
77.20
76.78
41.42
24.46
O
H3C
NH
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3al

^{1}H NMR

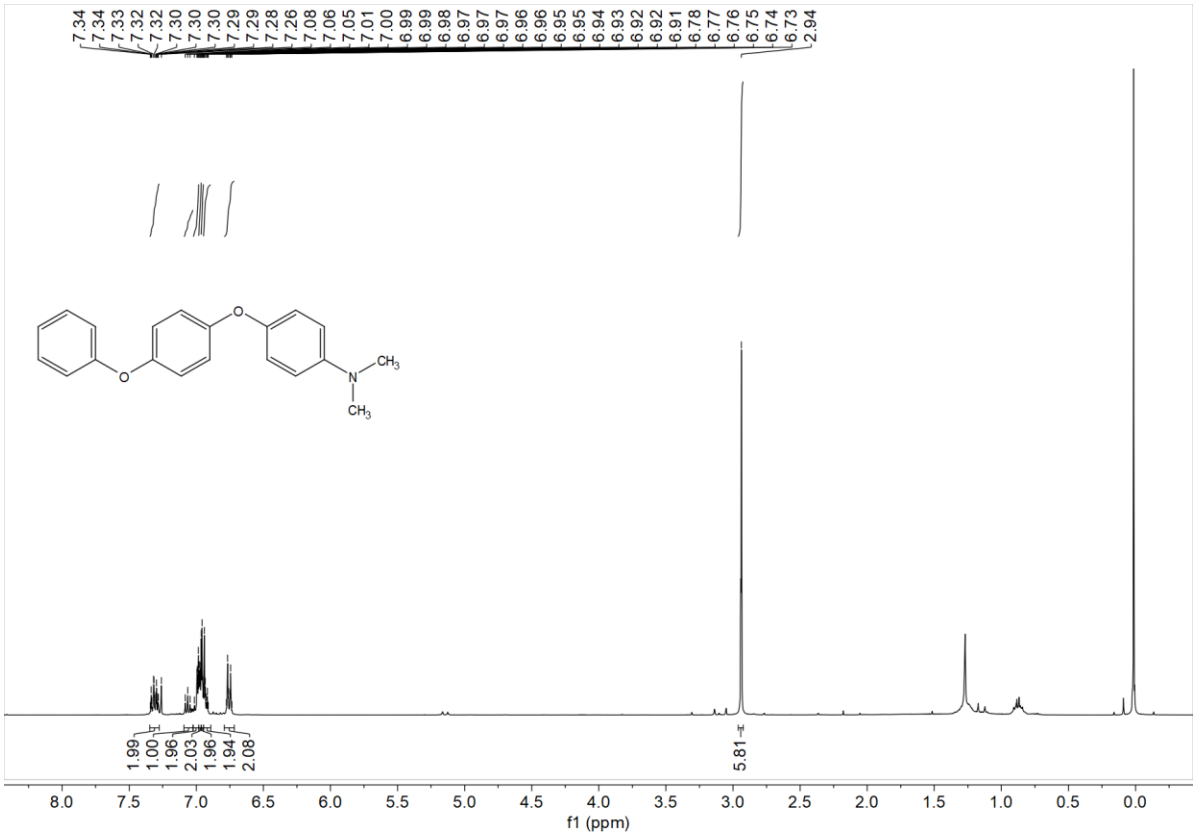


^{13}C NMR

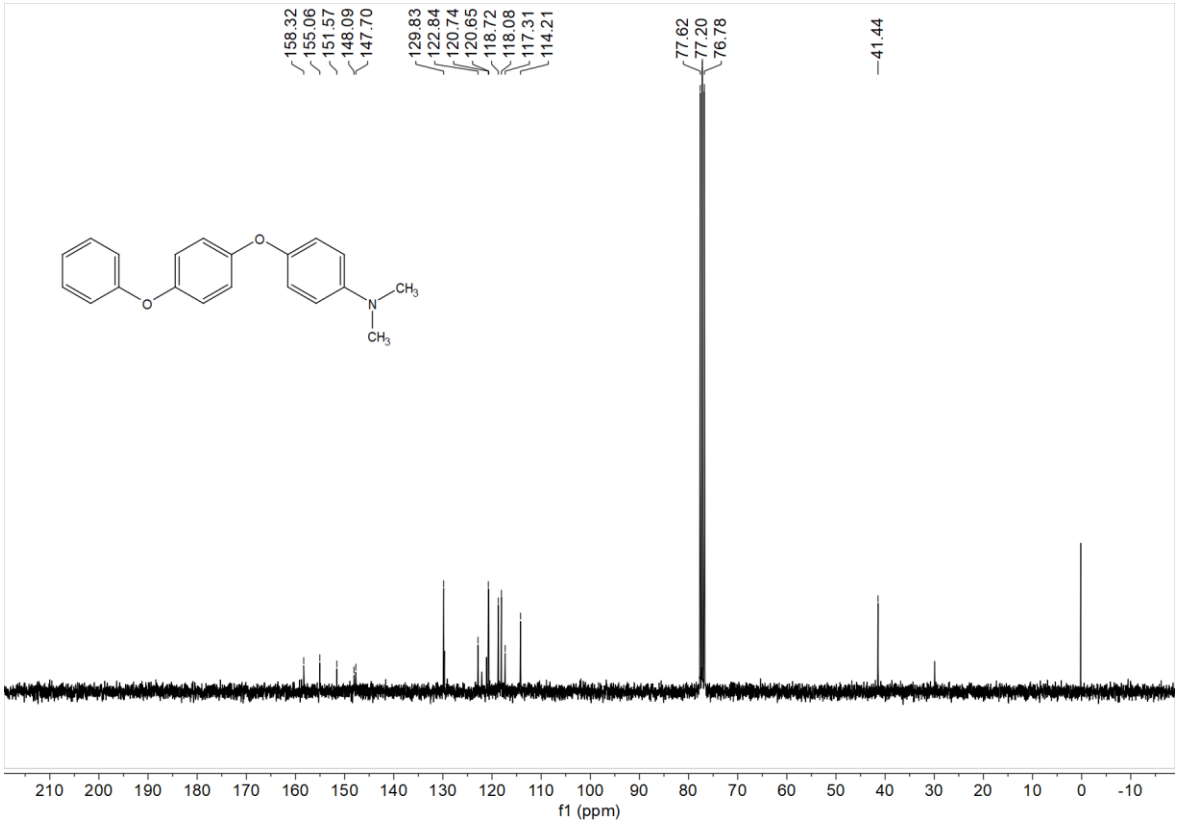

155.13
152.42
149.05
147.37
119.94
119.15
114.81
114.28
77.62
77.20
76.78
55.83
41.51
O
O
CH3
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3am

^{1}H NMR

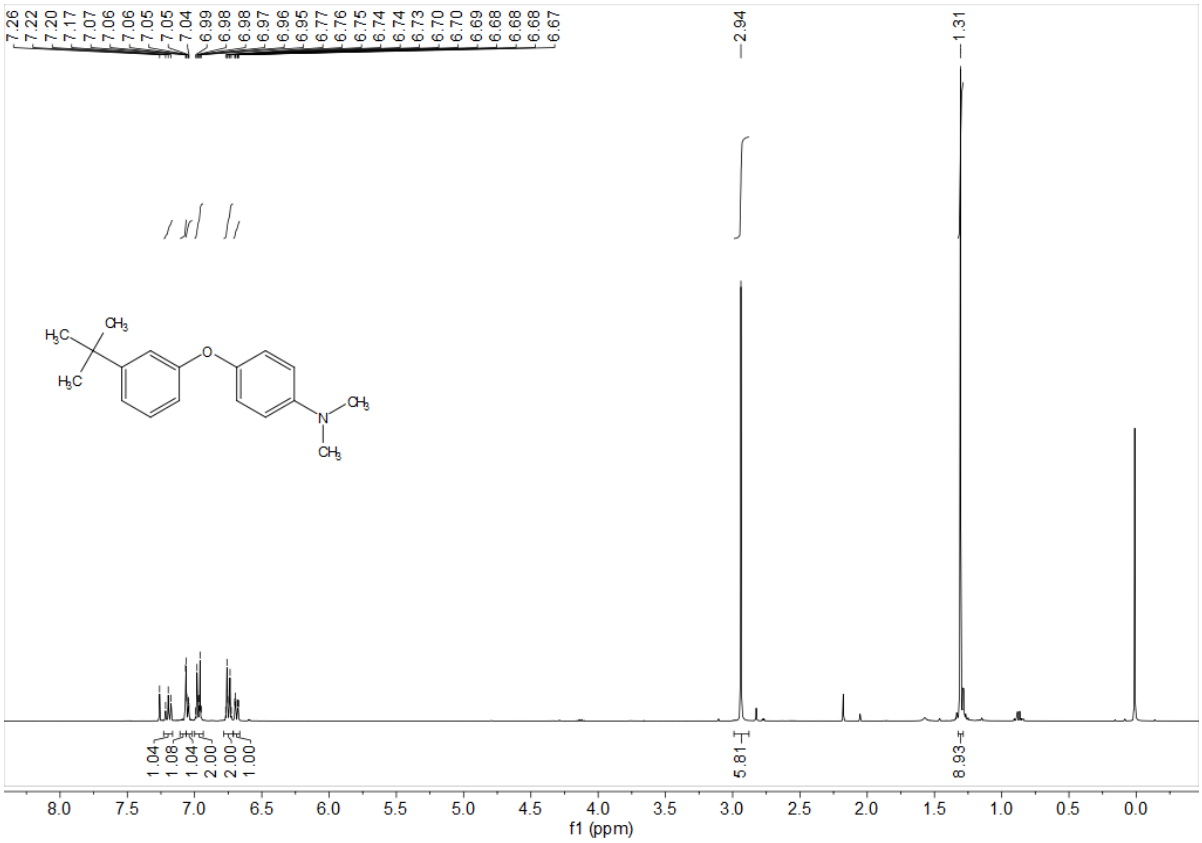


^{13}C NMR

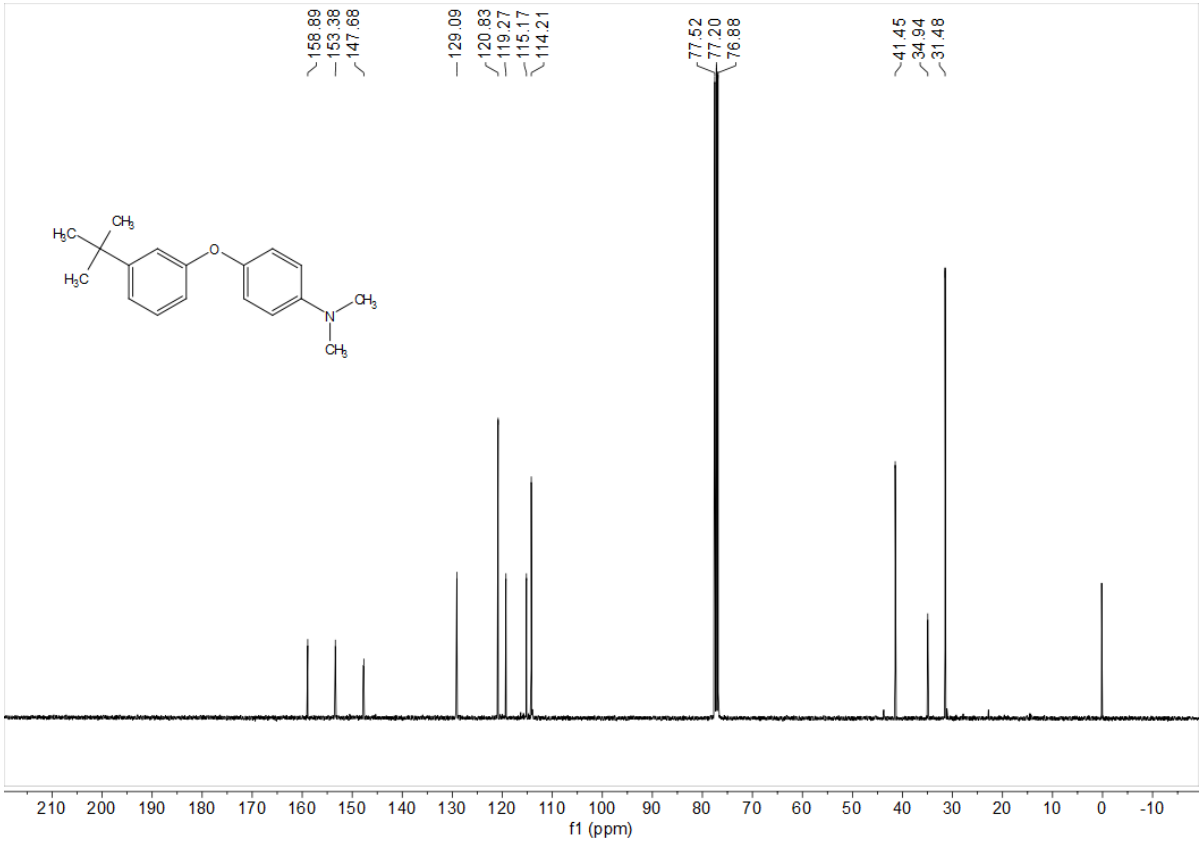

158.32
155.06
151.57
148.09
147.70
129.83
122.84
120.74
120.65
118.72
118.08
117.31
114.21
77.62
77.20
76.78
41.44
O
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3an

^{1}H NMR

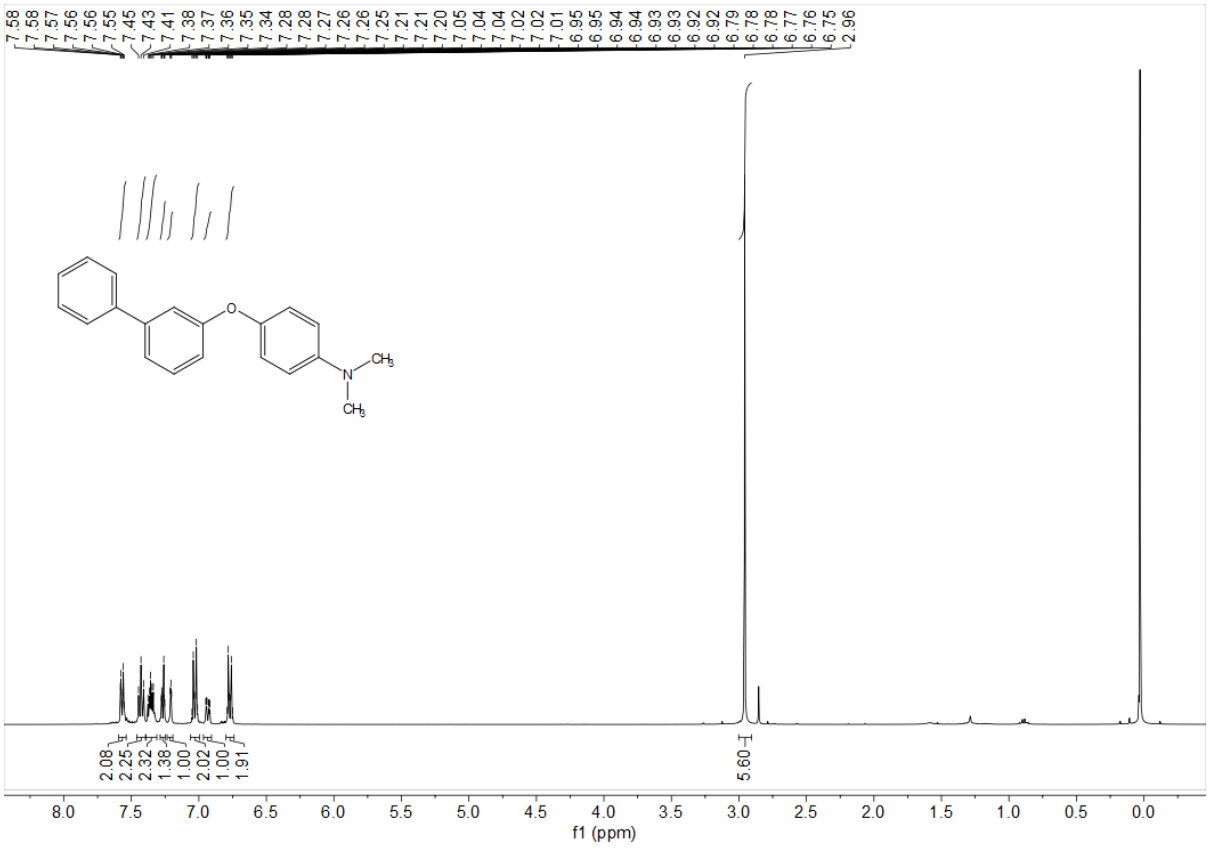


^{13}C NMR

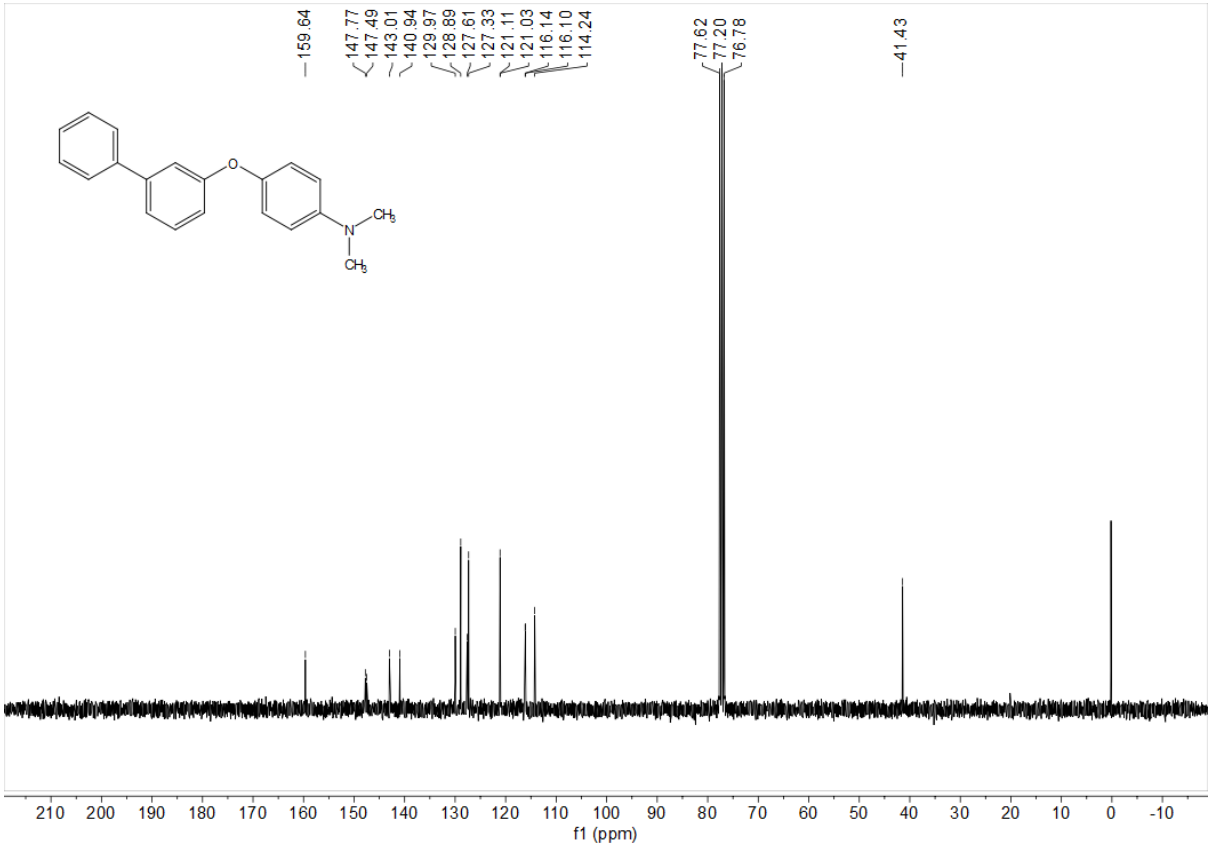

158.89
153.38
147.68
129.09
120.83
119.27
115.17
114.21
77.52
77.20
76.88
41.45
34.94
31.48
H3C
CH3
H3C
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ao

^{1}H NMR

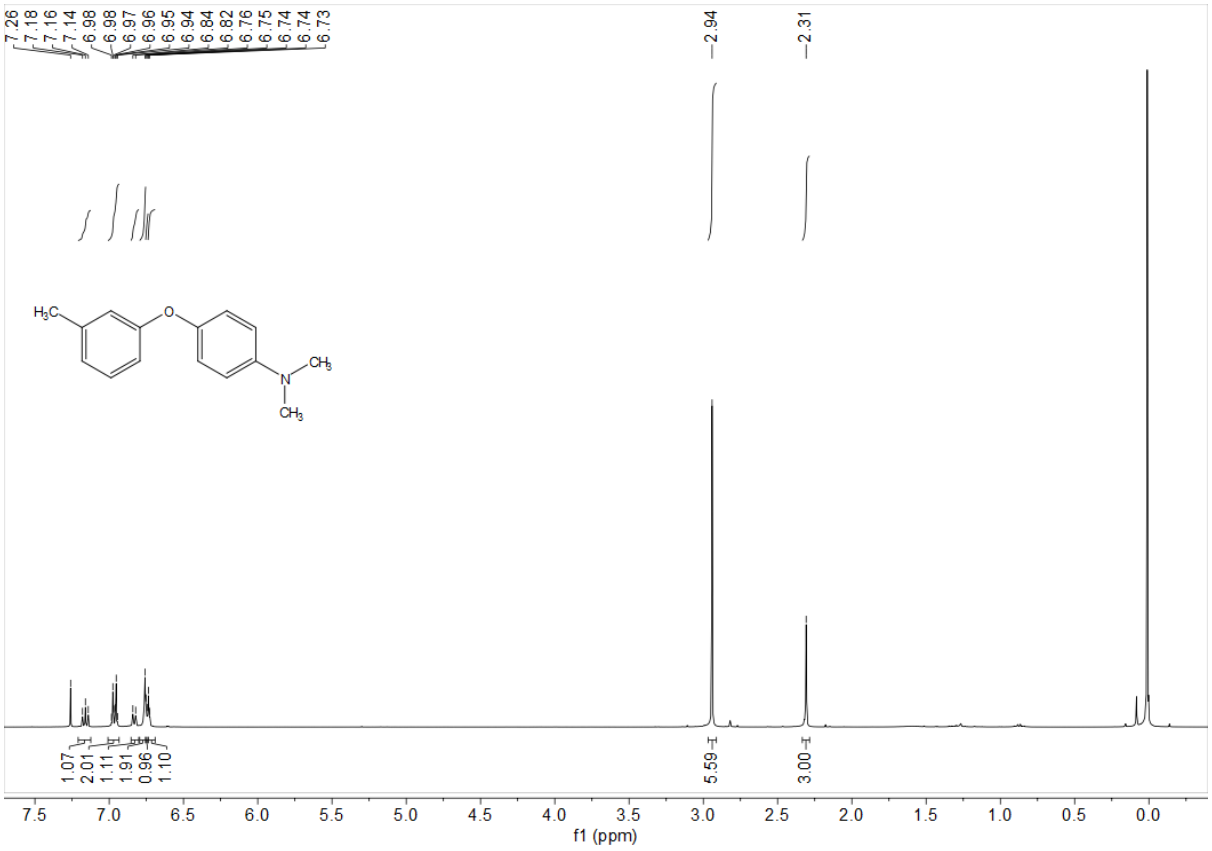


^{13}C NMR

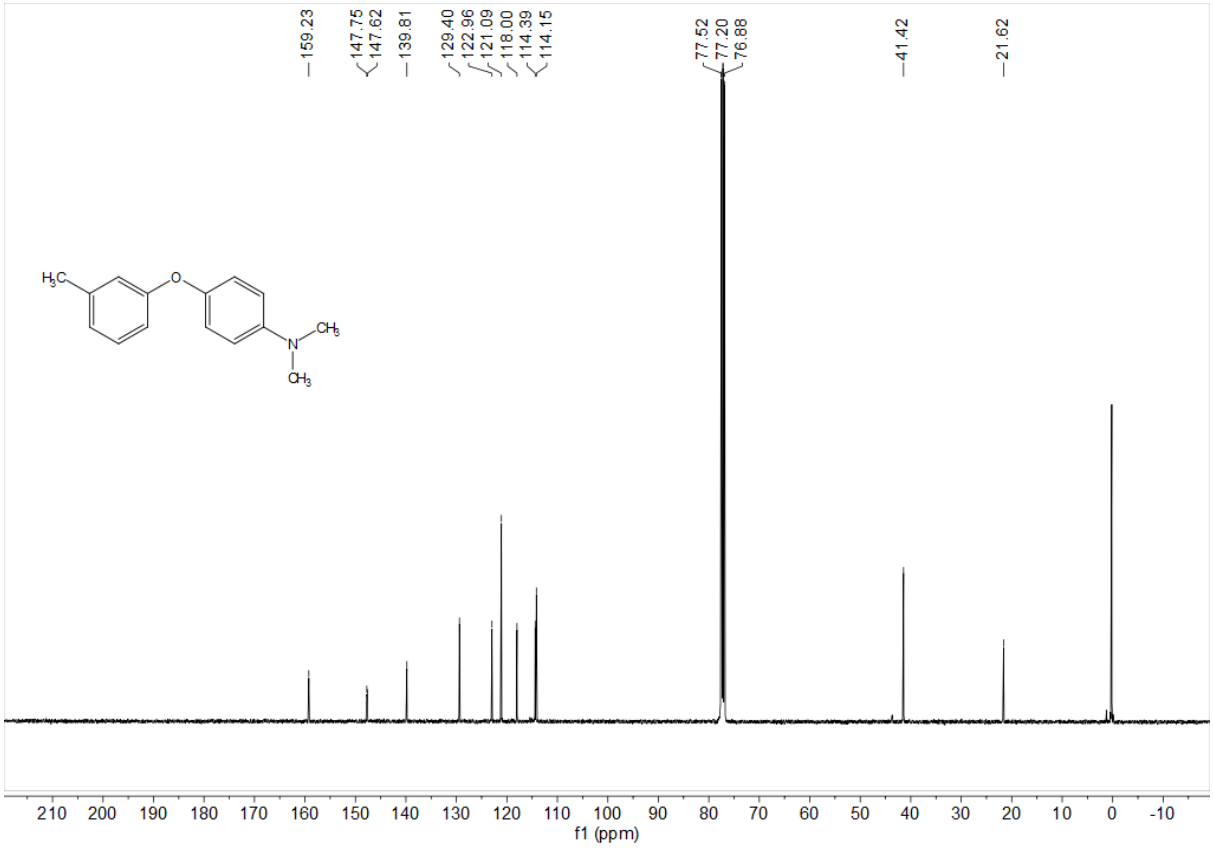

159.64
147.77
147.49
143.01
140.94
129.97
128.89
127.61
127.33
121.11
121.03
116.14
116.10
114.24
77.62
77.20
76.78
41.43
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ap

^{1}H NMR

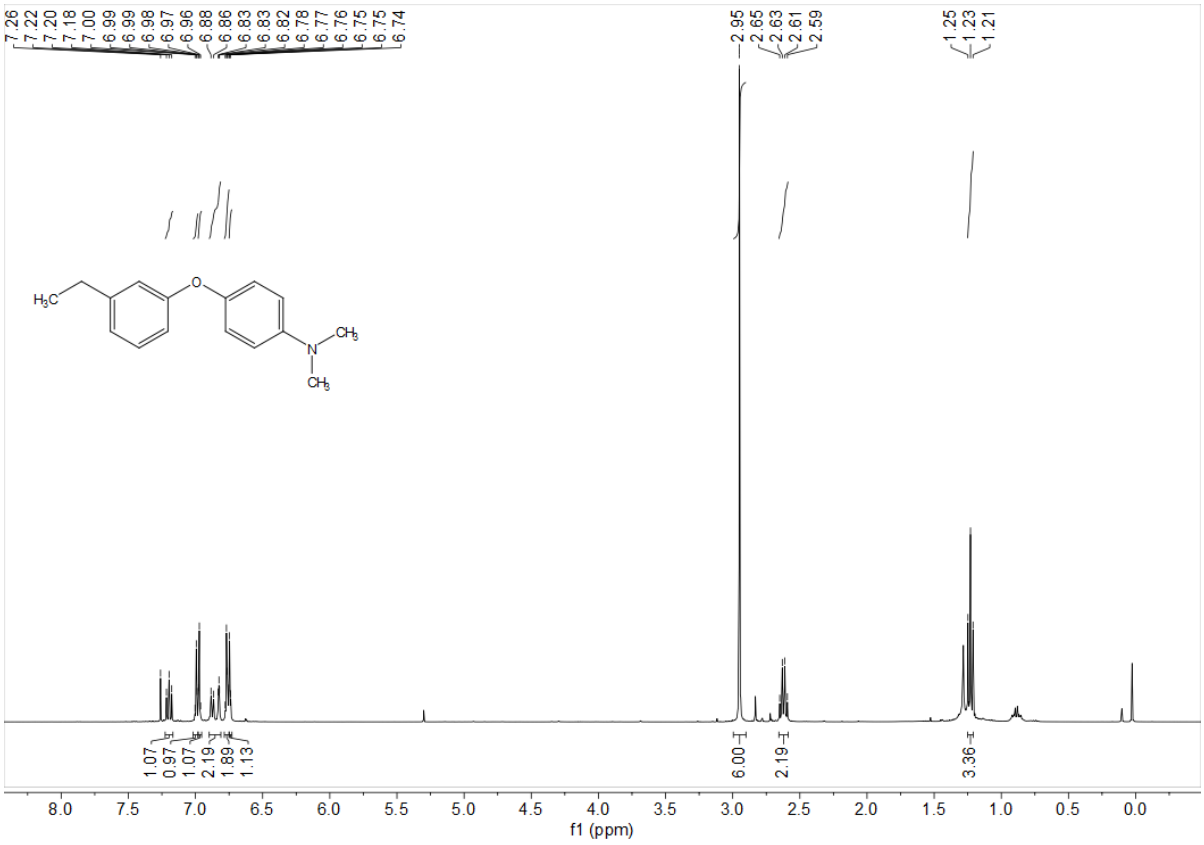


^{13}C NMR

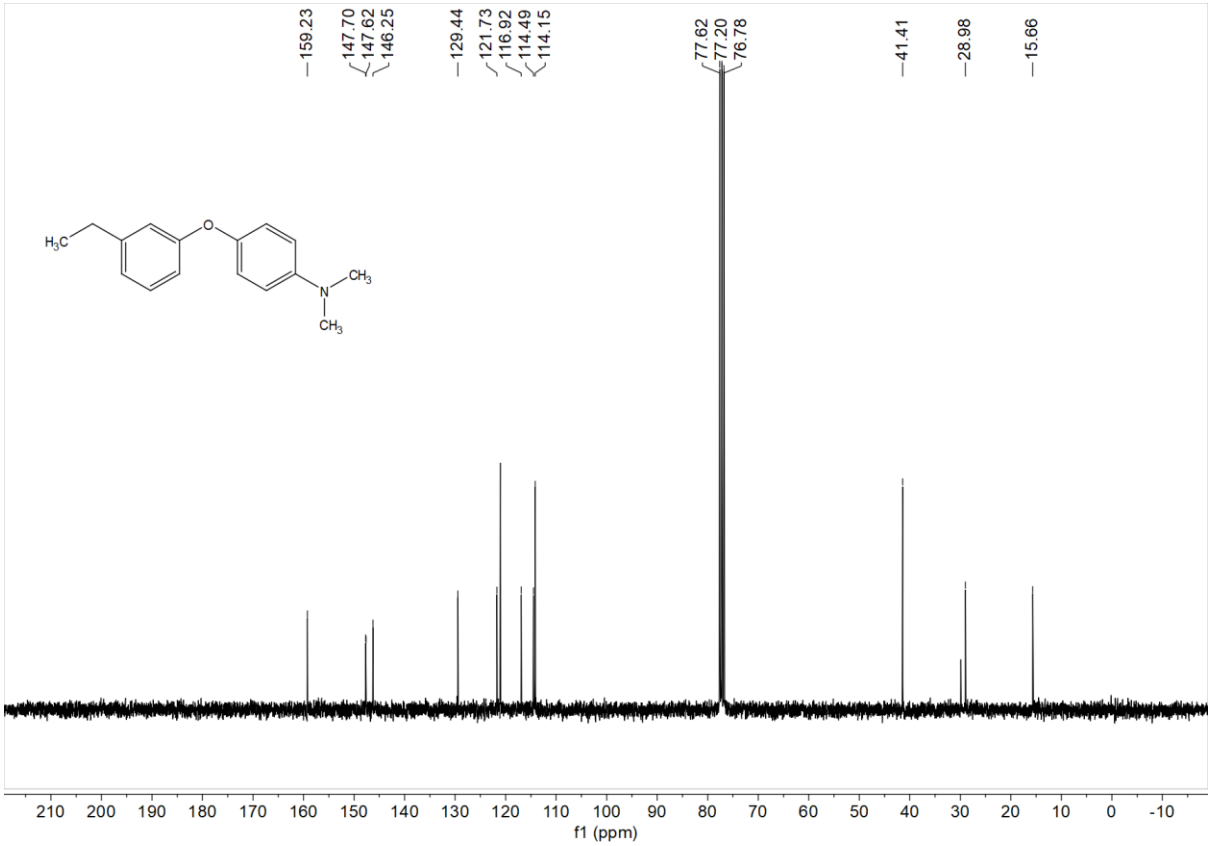

159.23
147.75
147.62
139.81
129.40
122.96
121.09
118.00
114.39
114.15
77.52
77.20
76.88
41.42
21.62
H3C
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3aq

^{1}H NMR

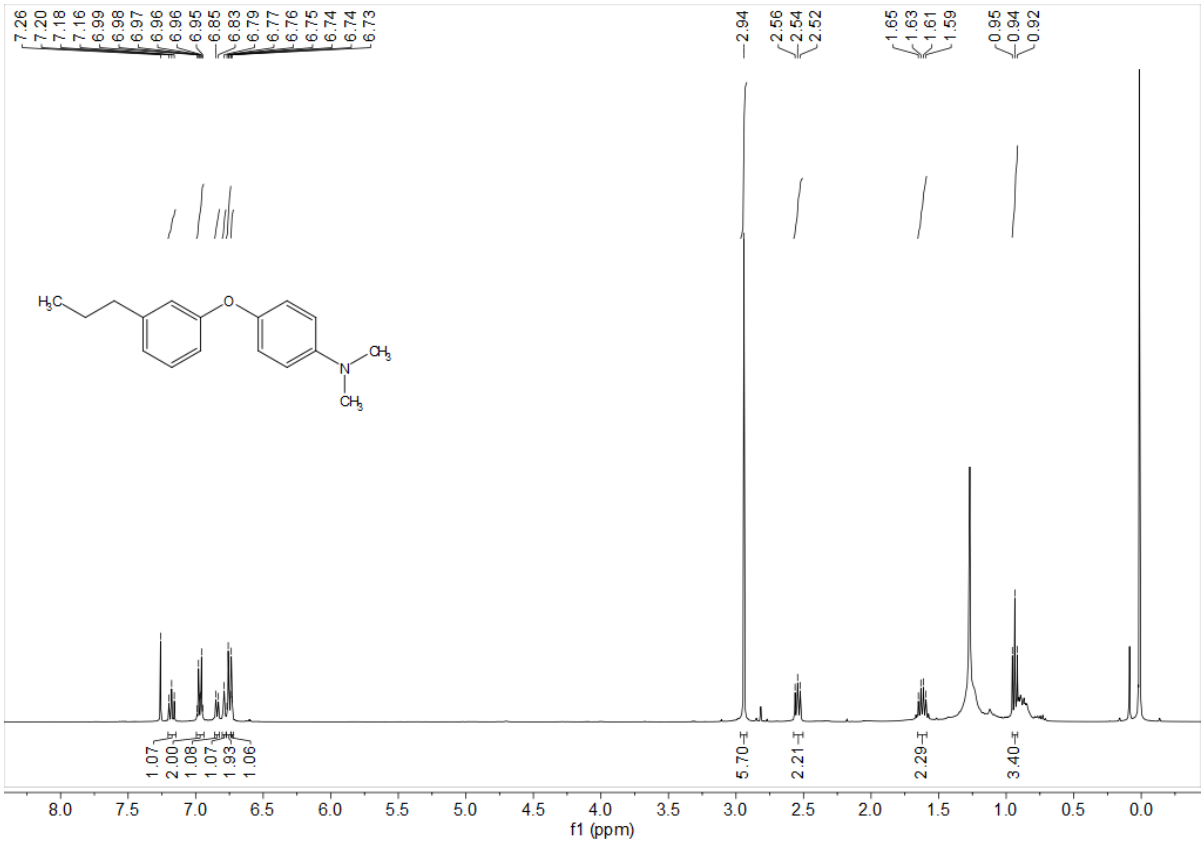


^{13}C NMR

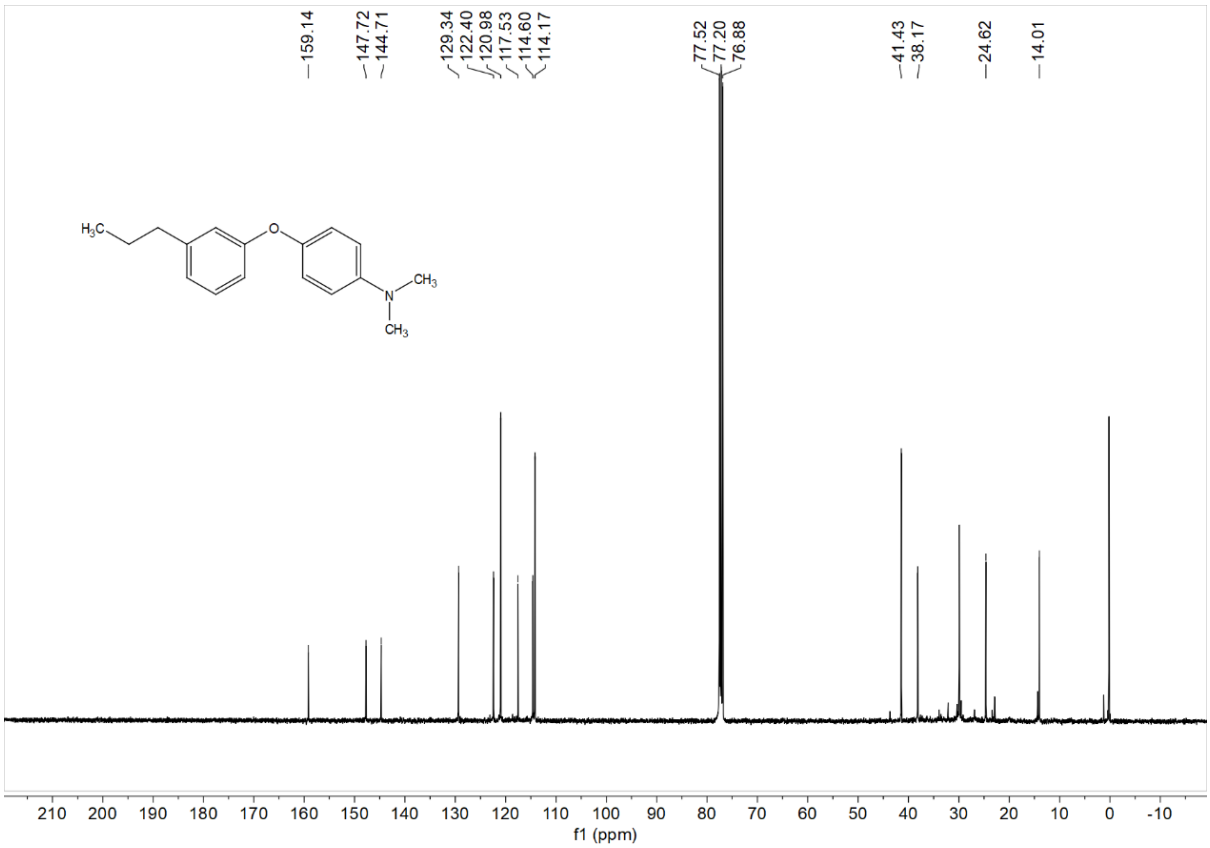

159.23
147.70
147.62
146.25
129.44
121.73
116.92
114.49
114.15
77.62
77.20
76.78
41.41
28.98
15.66
H3C
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ar

^{1}H NMR

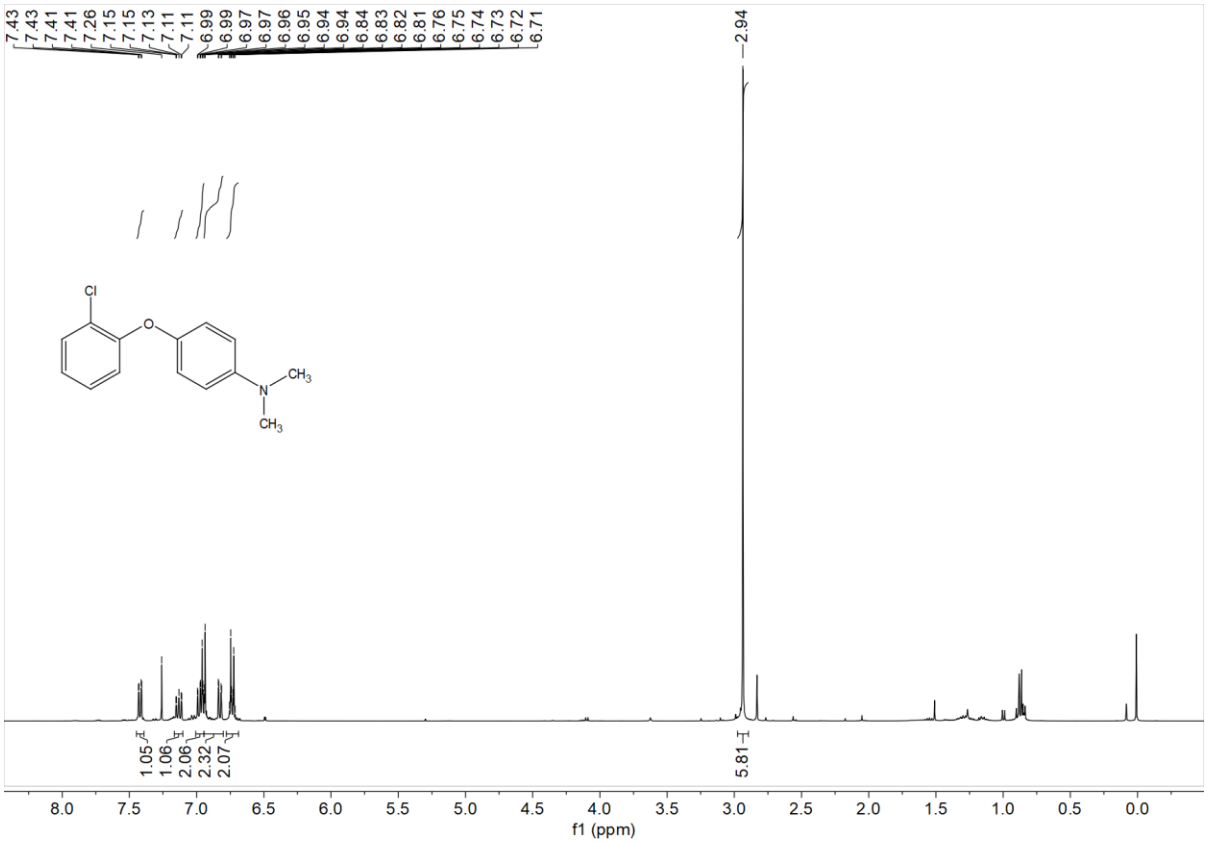


^{13}C NMR

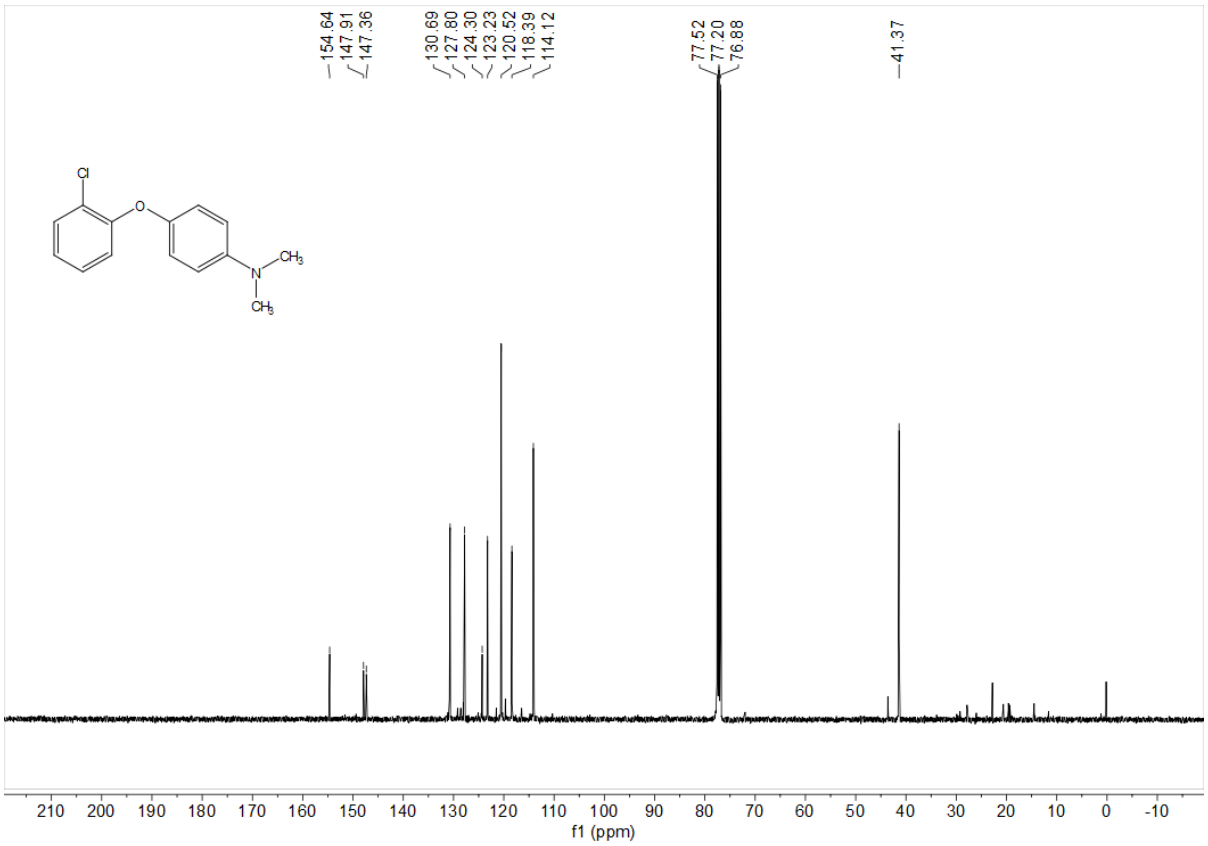

159.14
147.72
144.71
129.34
122.40
120.98
117.53
114.60
114.17
77.52
77.20
76.88
41.43
38.17
24.62
14.01
H3C
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3as

^{1}H NMR

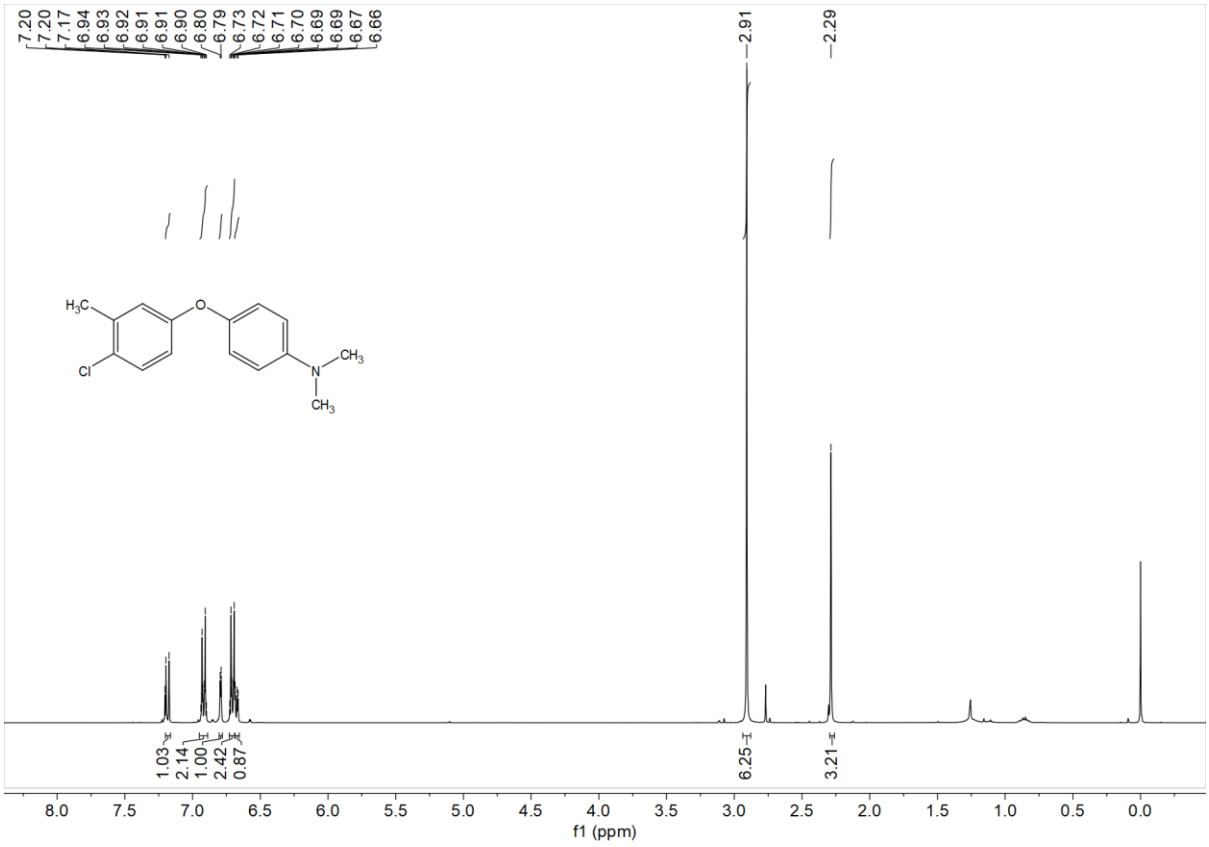


^{13}C NMR

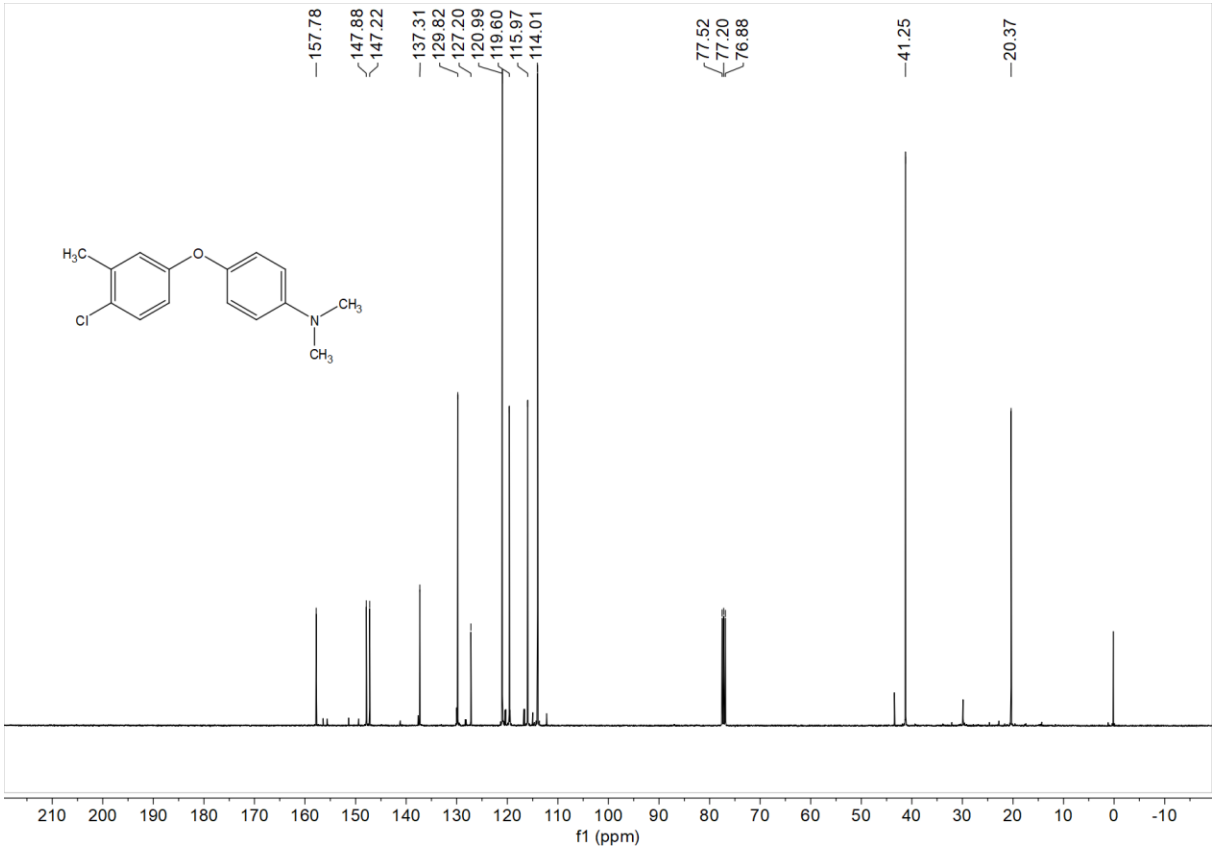

154.64
147.91
147.36
130.69
127.80
124.30
123.23
120.52
118.39
114.12
77.52
77.20
76.88
41.37
Cl
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3au

^{1}H NMR

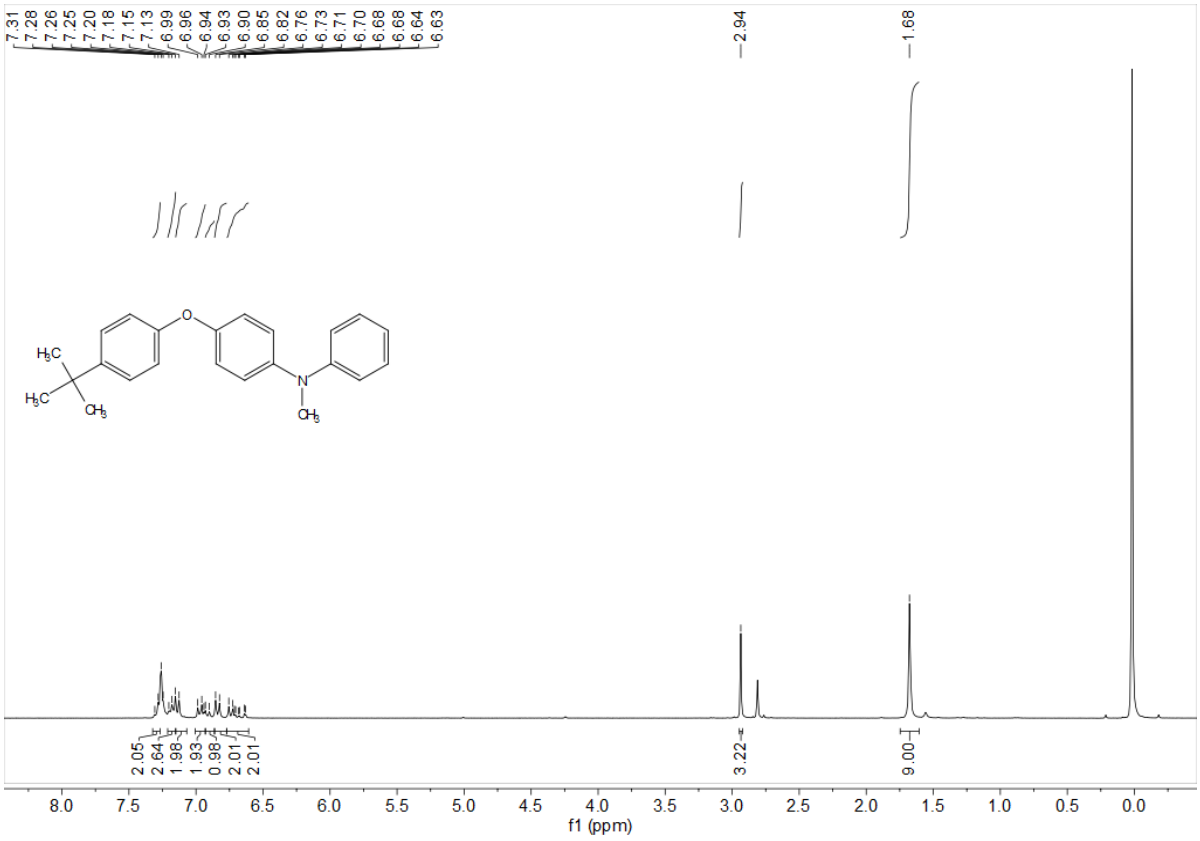


^{13}C NMR

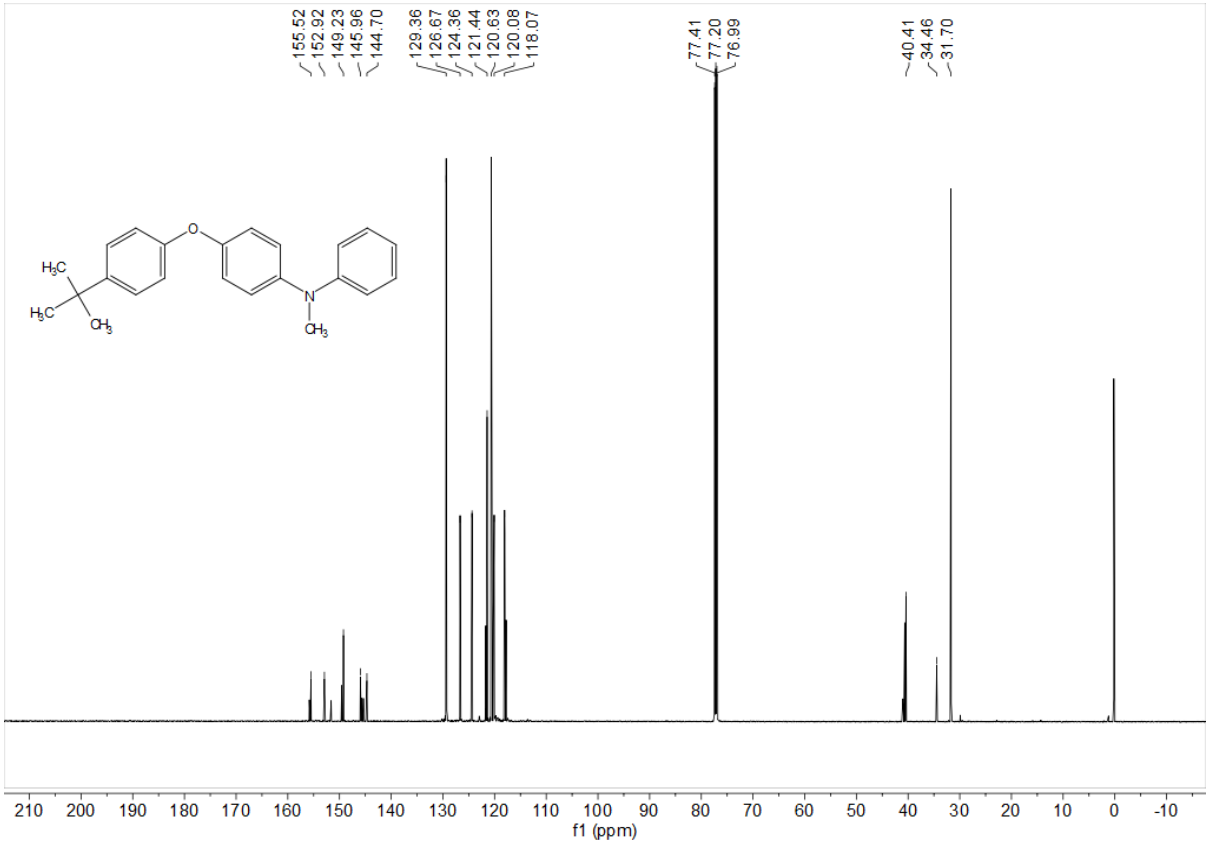

157.78
147.88
147.22
137.31
129.82
127.20
120.99
119.60
115.97
114.01
77.52
77.20
76.88
41.25
20.37
H3C
Cl
O
N
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ba

^{1}H NMR

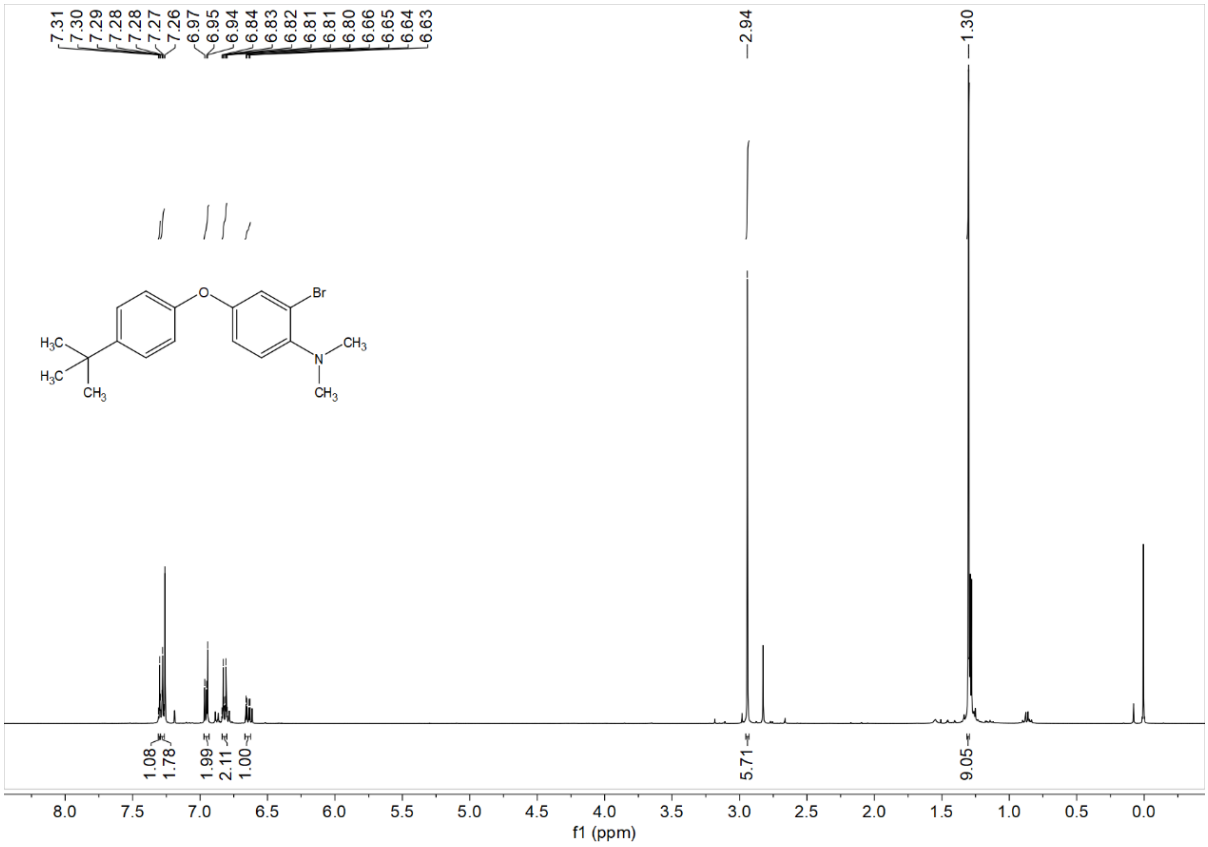


^{13}C NMR

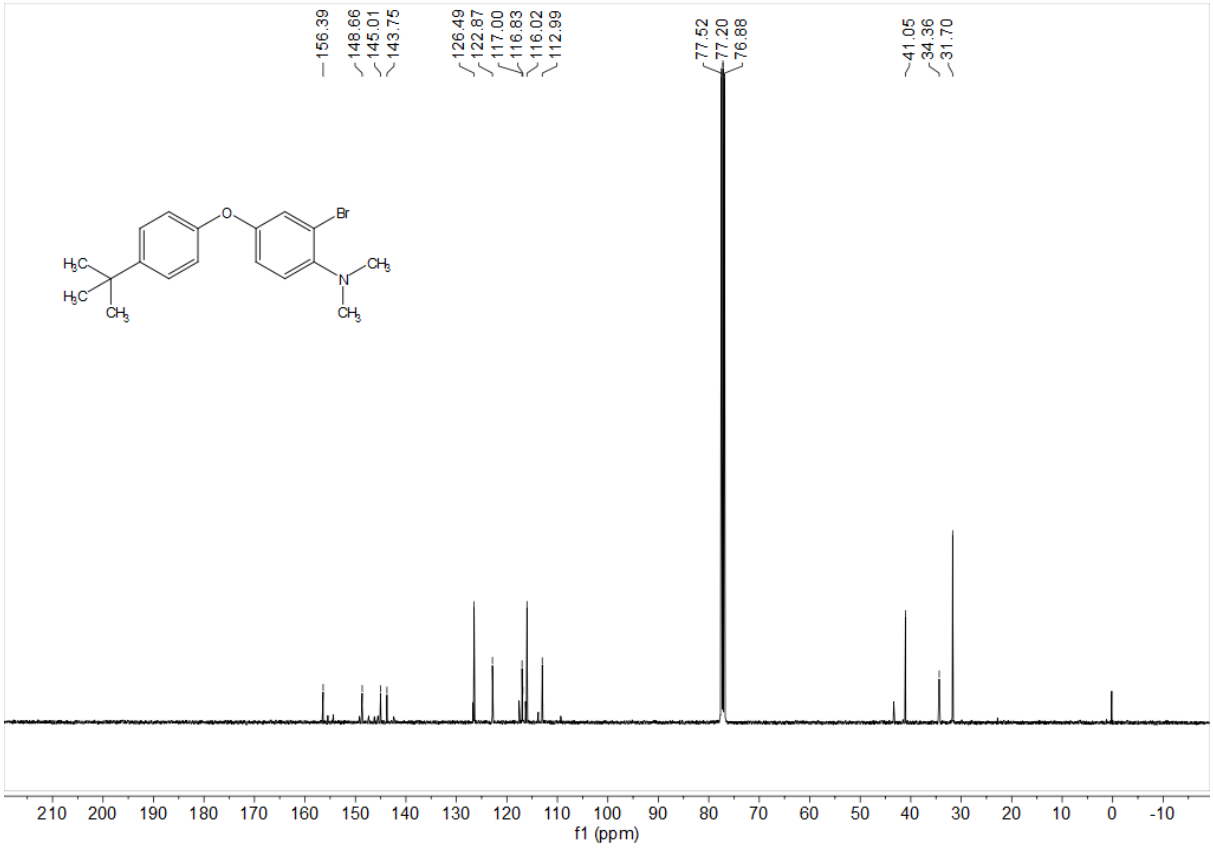

155.52
152.92
149.23
145.96
144.70
129.36
126.67
124.36
121.44
120.63
120.08
118.07
77.41
77.20
76.99
40.41
34.46
31.70
O
N
H3C
H3C
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3ca

^{1}H NMR



^{13}C NMR


156.39
148.66
145.01
143.75
126.49
122.87
117.00
116.83
116.02
112.99
77.52
77.20
76.88
41.05
34.36
31.70
Br
O
N
CH3
H3C
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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