Supporting Information

Electrochemical Oxidative Dehydrogenation Aromatization of cyclohex-2-enone and Amine to 1,4-Phenylenediamine

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Contents

General information……………………………………………………………………………………S2

Experimental procedures for the electrolysis…………………………………………………………S2

General procedure for the gram-scale reaction via anodic oxidation……………………………S4

Experimental of additional oxidant experiment………………………………………………………S5

Experimental of different current or reaction time experiment……………………………………S5

Experimental of online electrochemical mass spectra data…………………………………………S6

Verification experiments of intermediate 5……………………………………………………………S8

Electrochemical procedures for cyclic voltammetry ……………………………………………………S9

Detail descriptions for products………………………………………………………………………S12

References…………………………………………………………………………………………………S18

Copies of product NMR spectra…………………………………………………………………………S19

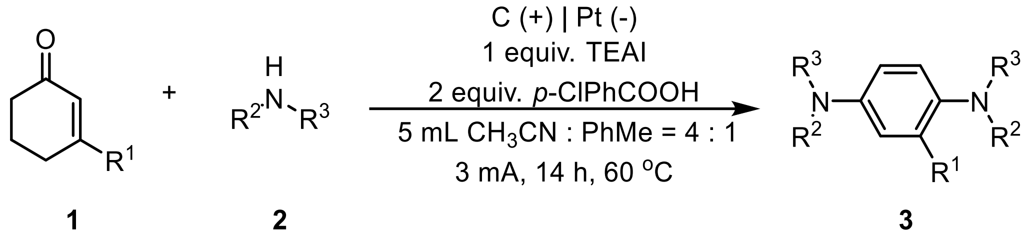
General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. The instrument for electrolysis was dual display potentiostat (XINRUI® DJS-292B) (made in China). Chronoamperometry and cyclic voltammograms were obtained on a CorrTest® CS2350H bipotentiostat. GC yields were recorded by SHIMADZU™ GC-2014 gas chromatography. Molecular weights of products were determined by SHIMADZU™ GCMS-QP2010 SE gas chromatgraphy mass spectrometrometry. Online Electrochemical mass spectra data were acquired by LTQ Velos Orbitrap Elite mass spectrometer (Thermo Fisher Scientific Co., Ltd., USA). All new compounds were characterized by High resolution mass spectra (HRMS). All undivided cells were purchased from Jiehengda® limited liability company (https://www.whjiehengda.com). All the electrochemical oxidations were performed in an oven-dried two-necked undivided cell equipped with a carbon felt anode (1.5 × 1.5 × 0. 30 cm^3) and a Pt plate cathode (1.5 × 0.75 × 0. 10 cm^3) unless otherwise noted. Unless otherwise noted, materials and solvents were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Flash chromatography columns were packed with 200-300 aluminium oxide neutral in petroleum (b.p. 60-90 °C). ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform, 39.60 ppm, dimethylsulfoxide), respectively.

Experimental procedures for the electrolysis

Figure S1. Reaction equipment

General procedures for electrochemical oxidative dehydrogenation aromatization of cyclohex-2-enone with amine:



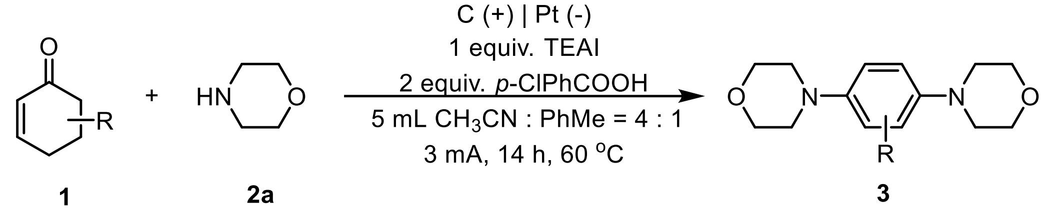
3a-3c, 3g-3h, 3k-3m, 3o-3q, 3z-3aa (condition A): In a 15 mL oven-dried two-necked undivided cell equipped with a stir bar, TEAI (77.2 mg, 0.3 mmol), *p*-ClPhCOOH (94.0 mg, 0.6 mmol) were added into the tube. The tube was equipped with carbon felt (1.5 × 1.5 × 0.30 cm^3) as the anode and Pt plate (1.5 × 0.75 × 0.10 cm^3) as the cathode and then charged with nitrogen to replace air atmosphere (purged three times). cyclohex-2-enone (0.30 mmol), **2** (1.80 mmol), MeCN (4.0 mL) and PhMe (1.0 mL) were added to the tube through a syringe. The mixtures were stirred at a constant current of 3.0 mA at 60 °C for 14 h ($J = 2.67$ mA·cm^2, 5.2 F·mol^{-1}). At the end of the reaction, the reaction was quenched by brine and extracted with EtOAc three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 aluminium oxide neutral (petroleum: EtOAc = 3:1).

3d-3f, 3i-3j, 3n, 3r-3y, 3ab (condition B): Otherwise above general procedure, *p*-ClPhCOOH (0.6 mmol) was replaced by TFA (0.6 mmol) and the mixtures were stirred at a constant current of 3.0 mA at 60 °C for 12 h ($J \approx 2.67$ mA·cm^2, 4.5 F·mol^{-1}).

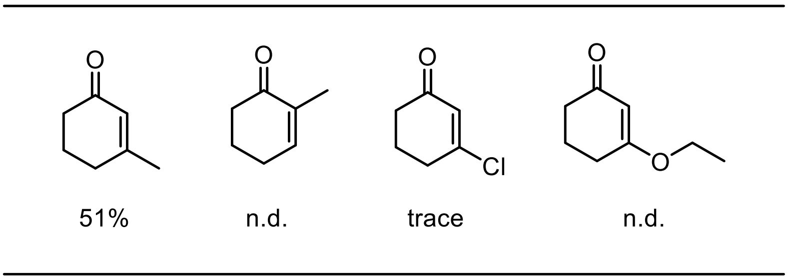
3ac (condition C): Otherwise above general procedure, TEAI (0.3 mmol) was replaced by TBAI (110.8 mg, 0.3 mmol) and the mixtures were stirred at a constant current of 3.0 mA at 60 °C for 12 h ($J \approx 2.67$ mA·cm^2, 4.5 F·mol^{-1}).

3ad (condition D): Otherwise above general procedure, 2-cyclohexen-1-one (0.3 mmol) was replaced by 3-methyl-2-cyclohexen-1-one (0.3 mmol), morpholine (1.80 mmol), *p*-ClPhCOOH (0.6 mmol) was replaced by TFA (0.6 mmol) and the mixtures were stirred at a constant current of 3.0 mA at 60 °C for 14 h ($J \approx 2.67$ mA·cm^2, 5.2 F·mol^{-1}).

General procedures for electrochemical oxidative dehydrogenation aromatization of cyclohex-2-enones with morpholine:

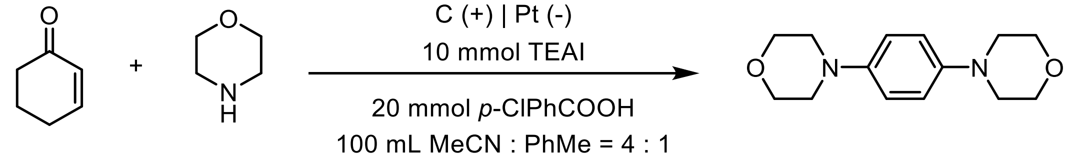


1 **2a** **3**



In a 15 mL oven-dried two-necked undivided cell equipped with a stir bar, TEAI (77.2 mg, 0.3 mmol), *p*-ClPhCOOH (94.0 mg, 0.6 mmol) were added into the tube. The tube was equipped with carbon felt (1.5 × 1.5 × 0.30 cm^3) as the anode and Pt plate (1.5 × 0.75 × 0.10 cm^3) as the cathode and then charged with nitrogen to replace air atmosphere (purged three times). **1** (0.30 mmol), **2a** (1.80 mmol), MeCN (4.0 mL) and PhMe (1.0 mL) were added to the tube through a syringe. The mixtures were stirred at a constant current of 3.0 mA at 60 °C for 14 h ($J = 2.67\ mA\cdot cm^2$, $5.2\ F\cdot mol^{-1}$). At the end of the reaction, the reaction was quenched by brine and extracted with EtOAc three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 aluminium oxide neutral (petroleum: EtOAc = 3:1).

General procedure for the gram-scale reaction via anodic oxidation:



1a 10 mmol **2a** 60 mmol **3a** 1.56g, 63%

In a 100 mL three-necked flask oven-dried beaker equipped with a stir bar, Et_4NI (2.57 g, 10 mmol), *p*-Cl-PhCOOH (3.13 g, 20 mmol) were added into the tube. The tube was equipped with carbon felt (3.0 × 2.0 × 0.30 cm^3) as the anode and Pt plate (3.0 × 1.5 × 0.10 cm^3) as the cathode. **1a** (10 mmol), **2a** (60 mmol), MeCN (80 mL) and PhMe (20 mL) were added to the flask. The mixtures were stirred at a constant current of 20.0 mA at 60 °C for 70 h ($J = 4.44\ mA\cdot cm^2$, $5.2\ F\cdot mol^{-1}$). At the end of the reaction, the reaction was quenched by brine and extracted with EtOAc three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 aluminium oxide neutral (petroleum: EtOAc = 3:1). The white solid (1.56 g) was obtained with 63% isolated yield.

Table of additional oxidant experiment

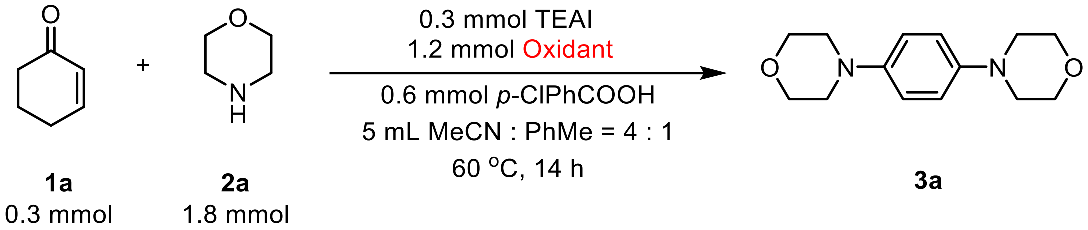


Table S1. Different oxidants

Entry	Oxidants	Yield
1	$(NH_4)_2S_2O_8$	n.d.
2	DTBP	Trace
3	TBHP	Trace
4	O_2 (1 atm)	10%

Reaction conditions: **1a** (0.30 mmol), **2a** (1.8 mmol), Et_4NI (0.3 mmol), *p*-ClPhCOOH (0.6 mmol), MeCN: PhMe= 4:1, 5 mL in a reaction tube.

Experimental of different current or reaction time experiment

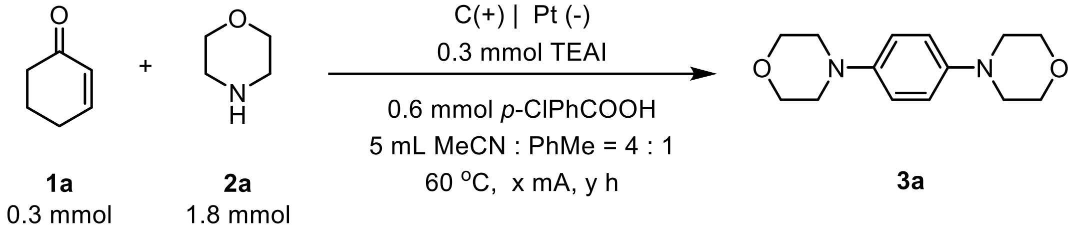
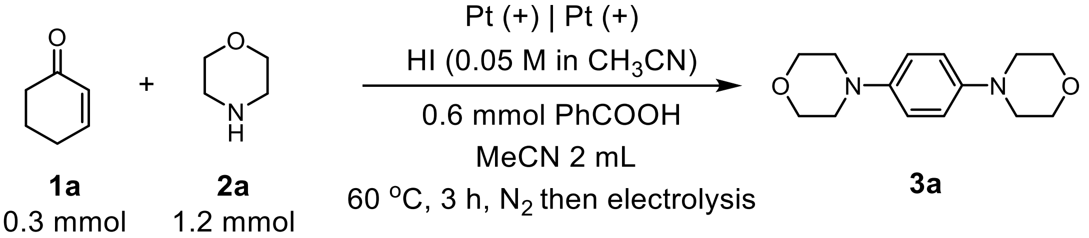


Table S2. Different current or reaction time

Entry	x mA, y h	Yield[a]	Faradaic efficiency
1	2 mA, 21 h	75%	57%
2	3 mA, 10 h	54%	57%
3	3 mA, 14 h	71%	42%
4	3 mA, 18 h	56%	43%
5	6 mA, 7 h	47%	36%

Reaction conditions: **1a** (0.30 mmol), **2a** (1.8 mmol), Et_4NI (0.3 mmol), *p*-Cl-PhCOOH (0.6 mmol), MeCN: PhMe= 4:1, 5 mL in a reaction tube. [a]Yield was determined by ^1H NMR using 1,3, 5-trimethoxybenzene as the internal standard.

Additional discussion of online electrochemical mass spectra data



In a 15 mL oven-dried two-necked undivided cell equipped with a stir bar, HI (0.05 M in CH_3CN), PhCOOH (73.3 mg, 0.6 mmol) were added into the tube. **1a** (0.3 mmol), **2a** (1.2 mmol), MeCN (2 mL) were added to the flask. Stir at 60 °C for 3 h and then cool to room temperature. Samples were taken for electrochemical on-line mass spectrometry test.

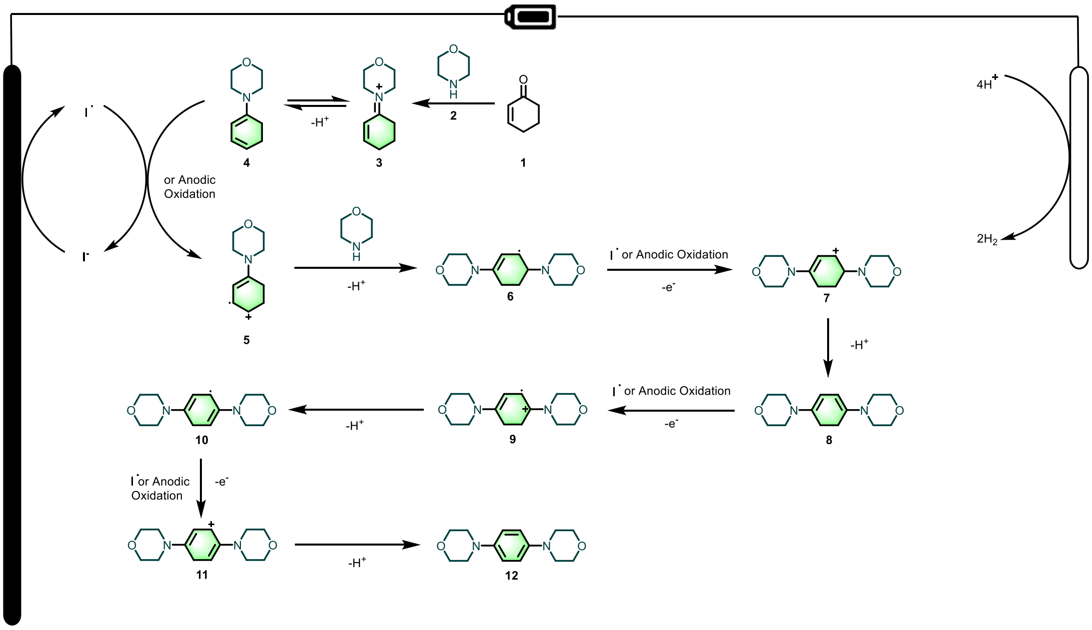
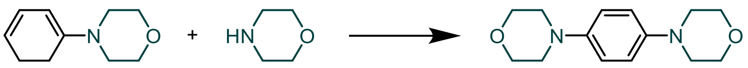
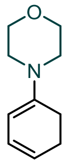


Figure S2. Proposed mechanism

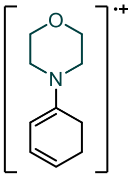


$[M+H]^+$
m/z 166.1226

$[M+H]^+$ *m/z* 249.1598



4



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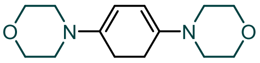


7

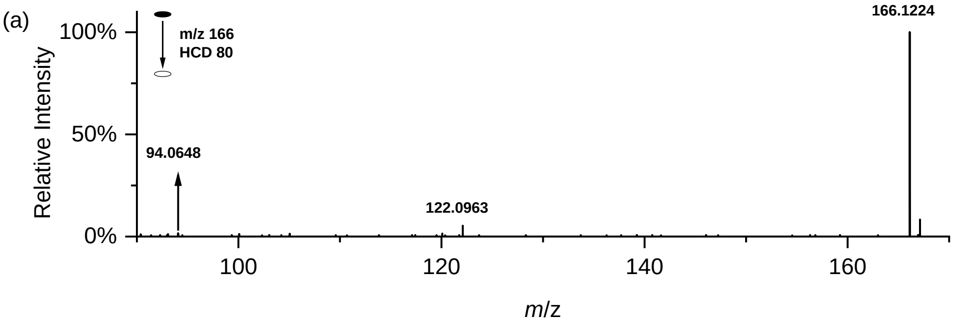
8

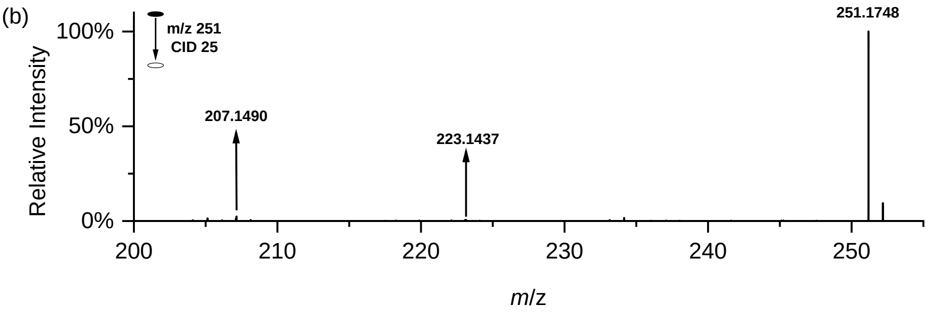
4: $[M+H]^+$ *m/z* 166.1226

5: *m/z* 165.1148

7: $[M+H]^+$ *m/z* 251.1754

8: $[M+H]^+$ *m/z* 249.1598





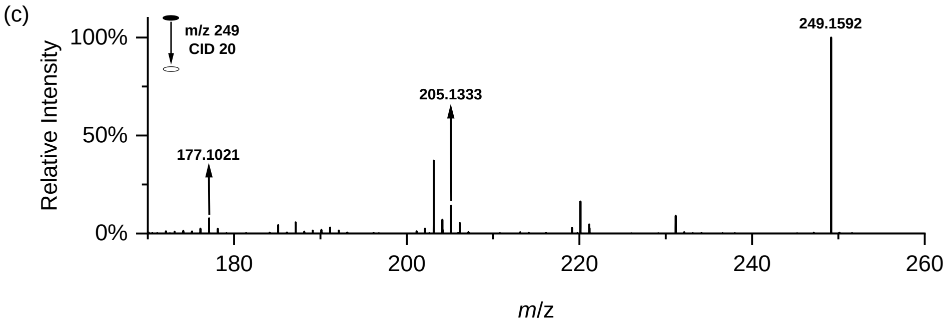
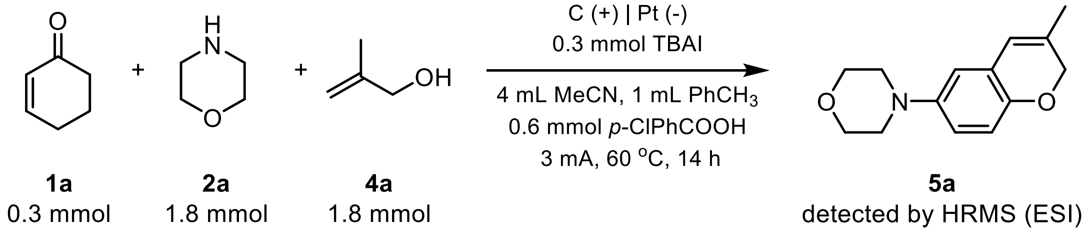


Figure S3. Monitoring during cyclohex-2-enone and morpholine. (a) High resolution tandem mass spectra of **4** (*m/z* 166.1224), (b) High resolution tandem mass spectra of **7** ([M]$^+$, *m/z* 251.1748), (c) High resolution tandem mass spectra of **8** ([M+H]$^+$, *m/z* 249.1592).

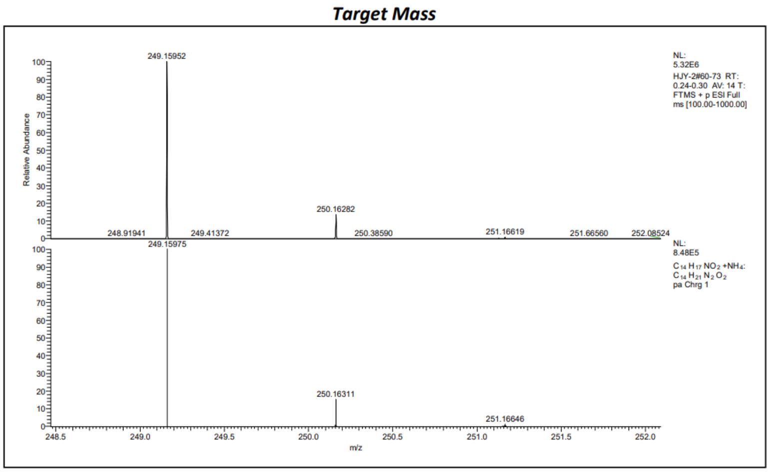
Table S3. Fragmentation ions from **4, 7, 8**.

No.	Measured Mass	Calculated Mass	Δppm	Chemical Formula	Fragment ion Molecular Formula
1	**166.1224**	166.1226	-1.2	$C_{10}H_{16}NO^+$	
2	122.0963	122.0964	-0.8	$C_8H_{12}N^{2+\bullet}$	$C_2H_4O^{2\bullet}$
3	94.0648	94.0651	-3.2	$C_6H_8N^{2+\bullet}$	$C_4H_8O^{2\bullet}$
4	**251.1748**	251.1754	-2.4	$C_{14}H_{23}N_2O_2^+$	
5	223.1437	223.1441	-1.8	$C_{12}H_{19}N_2O_2^{2+\bullet}$	$C_2H_4^{2\bullet}$
6	207.1490	207.1492	-1.0	$C_{12}H_{19}N_2O^{2+\bullet}$	$C_2H_4O^{2\bullet}$
7	**249.1592**	249.1598	-2.4	$C_{14}H_{21}N_2O_2^+$	
8	205.1333	205.1335	-1.0	$C_{12}H_{17}N_2O^{2+\bullet}$	$C_2H_4O^{2\bullet}$
9	177.1021	177.1022	-0.6	$C_{10}H_{13}N_2O^{2+\bullet}$	$C_4H_8O^{2\bullet}$

Verification experiments of intermediate 5



In a 15 mL oven-dried two-necked undivided cell equipped with a stir bar, ^{n}Et$_4$NI (77.2 mg, 0.3 mmol), 4-chlorobenzoic acid (94.0 mg, 0.6 mmol) were added into the tube. The tube was equipped with carbon felt (1.5 × 1.5 × 0.30 cm^3) as the anode and Pt plate (1.5 × 0.75 × 0.10 cm^3) as the cathode and then charged with nitrogen to replace air atmosphere (purged three times). **1a** (0.30 mmol), **2a** (1.80 mmol), **4a** (1.80 mmol), MeCN (4.0 mL) and PhMe (1.0 mL) were added to the tube through a syringe. Then the mixtures were stirred at a constant current of 3.0 mA at 60 °C for 14 h (J = 2.67 mA·cm^2, 5.2 F·mol^{-1}) and then cool to room temperature. Samples were taken for high resolution mass spectrometry test.



Target Mass

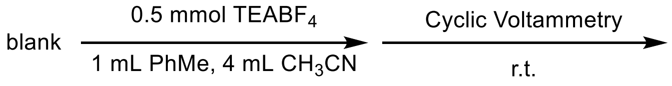
Formula:	*RDB:*	*Delta ppm:*	*Adduct ion:*
C14 H21 O2 N2	5.5	-0.941	M+NH4

Figure S4. HRMS result

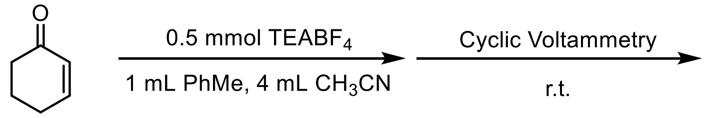
Electrochemical procedures for cyclic voltammetry

Cyclic voltammograms were obtained on a CHI 605E potentiostat at room temperature. ${}^{n}Et_4NBF_4$ (217.1 mg, 1.0 mmol) was used as the supporting electrolyte, with glassy carbon as working electrode (~7.0 mm^2) and a platinum wire (1.0 cm, spiral wire) as counter electrode, the scan rate was 100 mV/s. The scan range is between 0 V and 2 V.

a:

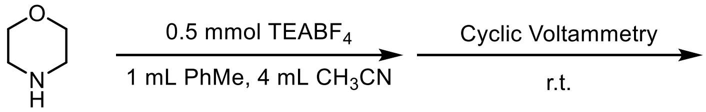


b:



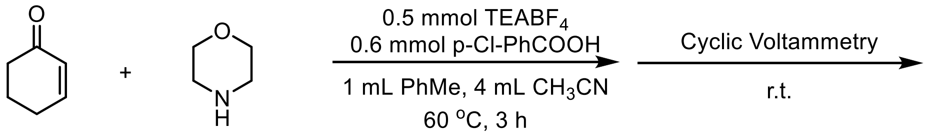
1a, 0.15 mmol

c:



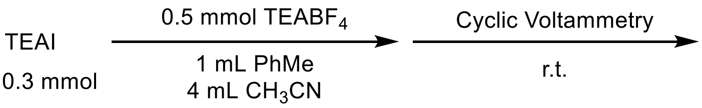
2a, 0.3 mmol

d:



1a, 0.3 mmol **2a**, 1.8 mmol

e:



3a, 0.3 mmol

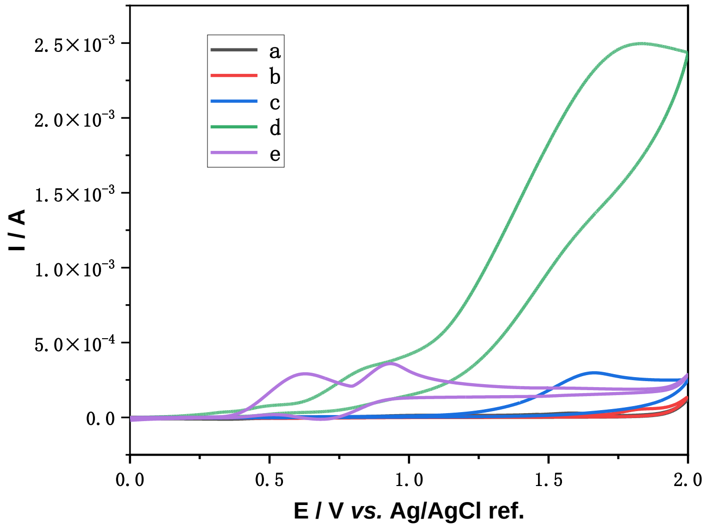
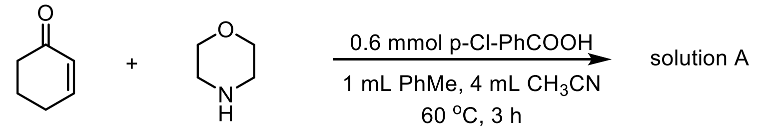


Figure S5. Cyclic voltammograms for different substrates.



1a, 0.3 mmol　**2a**, 1.8 mmol

a:　0.5 mmol $TEABF_4$ $\xrightarrow{\text{1 mL PhMe, 4 mL CH}_3\text{CN}}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

b:　0.4 mmol $TEABF_4$ + 0.1 mmol TEAI $\xrightarrow{\text{1 mL PhMe, 4 mL CH}_3\text{CN}}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

c:　1 mL solution A $\xrightarrow[\text{0.8 mL PhMe, 3.2 mL CH}_3\text{CN}]{\text{0.5 mmol TEABF}_4}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

d:　1 mL solution A $\xrightarrow[\text{0.8 mL PhMe, 3.2 mL CH}_3\text{CN}]{\text{0.4 mmol TEABF}_4\text{, 0.1 mmol TEAI}}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

e:　2 mL solution A $\xrightarrow[\text{0.6 mL PhMe, 2.4 mL CH}_3\text{CN}]{\text{0.4 mmol TEABF}_4\text{, 0.1 mmol TEAI}}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

f:　3 mL solution A $\xrightarrow[\text{0.4 mL PhMe, 1.6 mL CH}_3\text{CN}]{\text{0.4 mmol TEABF}_4\text{, 0.1 mmol TEAI}}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

g:　1 mL solution A $\xrightarrow[\text{0.8 mL PhMe, 3.2 mL CH}_3\text{CN}]{\text{0.5 mmol TEABF}_4\text{, 0.3 mmol I}_2}$ $\xrightarrow[\text{r.t.}]{\text{Cyclic Voltammetry}}$

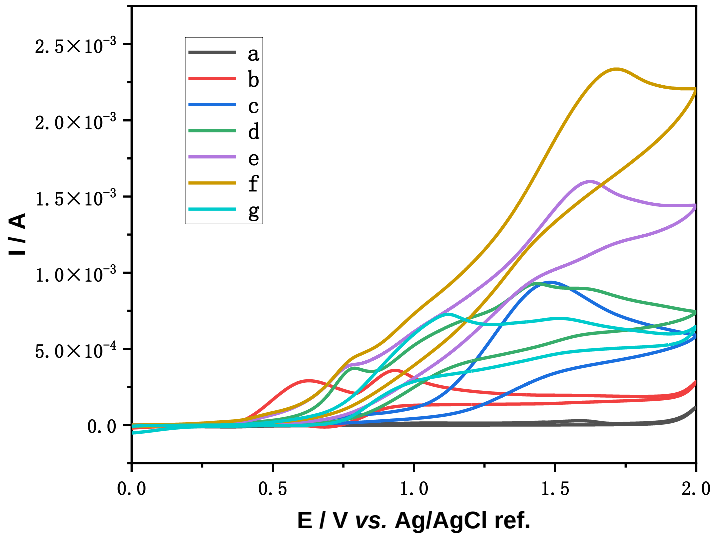
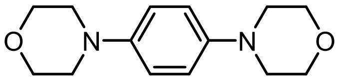


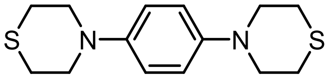
Figure S6. Cyclic voltammograms for the different concentration solution of 1a, 2a, and 4-chlorophenol with/without iodide

We further investigated the interaction between iodine and the intermediate under electrochemical conditions through cyclic voltammetry. In this CV graph, (d) exhibits a more pronounced peak current at 0.78 V compared to (c), suggesting that the addition of iodine may participate in and facilitate the oxidation process of the intermediate. Contrasting (d) with (e) and (f), the increase in peak current at 0.78 V implies that the species undergoing oxidation at the anode originate from intermediates formed after the reaction of pyrrolidine, 2-cyclohexen-1-one, and 4-chlorobenzoic acid. When compared to (d), (g) shows the disappearance of the oxidation peak at 0.78 V, indicating that I_2 can oxidize the reaction intermediate.

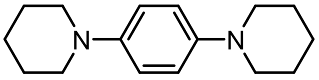
Detail descriptions for products



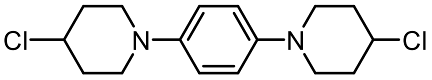
1,4-dimorpholinobenzene (3a)[1]: white solid was obtained with 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 4H), 3.89 – 3.82 (m, 8H), 3.10 – 3.03 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.35, 117.20, 66.89, 50.31.



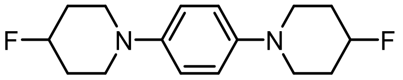
1,4-dithiomorpholinobenzene (3b): white solid was obtained with 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 4H), 3.72 – 3.15 (m, 8H), 2.89 – 2.48 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.13, 119.07, 53.19, 27.39. HRMS (ESI) calcd for $C_{14}H_{21}N_2S_2$ [M+H]$^+$: 281.1141 found: 281.1137.



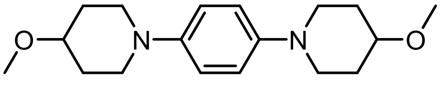
1,4-di(piperidin-1-yl)benzene (3c)[2]: colorless oil was obtained with 39% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 4H), 3.24 – 2.80 (m, 8H), 1.87 – 1.64 (m, 8H), 1.58 – 1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.25, 118.11, 51.94, 26.09, 24.21.



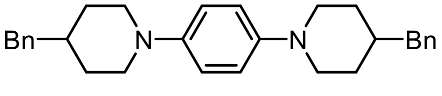
1,4-bis(4-chloropiperidin-1-yl)benzene (3d): white solid was obtained with 47% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 4H), 4.26 – 4.04 (m, 2H), 3.53 – 3.29 (m, 4H), 3.02 – 2.83 (m, 4H), 2.26 – 2.15 (m, 4H), 2.09 – 1.95 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.25, 118.20, 57.12, 48.62, 35.29. HRMS (ESI) calcd for $C_{16}H_{23}Cl_2N_2$ [M+H]$^+$: 313.1233 found: 313.1223.



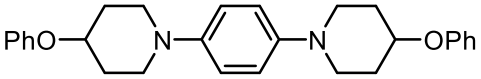
1,4-bis(4-fluoropiperidin-1-yl)benzene (3e): white solid was obtained with 38% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 4H), 5.00 – 4.79 (m, 1H), 4.77 – 4.54 (m, 1H), 3.42 – 3.18 (m, 4H), 3.10 – 2.94 (m, 4H), 2.24 – 1.80 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.37, 118.30, 89.21, 87.51, 47.14, 47.08, 31.47, 31.28. ^{19}F NMR (377 MHz, $CDCl_3$) δ -180.90. HRMS (ESI) calcd for $C_{16}H_{23}F_2N_2$ [M+H]$^+$: 281.1824 found: 281.1819.



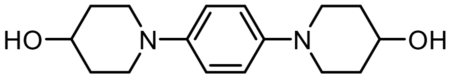
1,4-bis(4-methoxypiperidin-1-yl)benzene (3f): white solid was obtained with 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 4H), 3.37 (m, 12H), 2.85 – 2.76 (m, 4H), 2.06 – 1.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.41, 118.12, 76.15, 55.52, 48.52, 30.86. HRMS (ESI) calcd for $C_{18}H_{29}N_2O_2$ [M+H]$^+$: 305.2224 found: 305.2219.



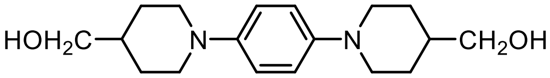
1,4-bis(4-benzylpiperidin-1-yl)benzene (3g): white solid was obtained with 51% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 4H), 7.21 – 7.13 (m, 6H), 6.86 (s, 4H), 3.54 – 3.27 (m, 4H), 2.72 – 2.36 (m, 8H), 1.73 (d, *J* = 12.9 Hz, 4H), 1.68 – 1.56 (m, 2H), 1.49 – 1.33 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.82, 140.55, 129.11, 128.15, 125.79, 118.10, 51.23, 43.17, 37.74, 32.26. HRMS (ESI) calcd for $C_{30}H_{37}N_2$ $[M+H]^+$: 429.2951 found: 429.2938.



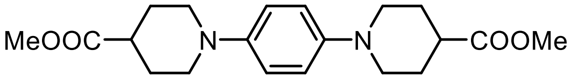
1,4-bis(4-phenoxypiperidin-1-yl)benzene (3h): white solid was obtained with 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 4H), 7.02 – 6.87 (m, 10H), 4.48 – 4.38 (m, 2H), 3.45 – 3.35 (m, 4H), 3.03 – 2.93 (m, 4H), 2.16 – 2.01 (m, 4H), 2.01 – 1.88 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.29, 145.40, 129.47, 120.80, 118.14, 116.08, 72.20, 47.95, 30.75. HRMS (ESI) calcd for $C_{28}H_{33}N_2O_2$ $[M+H]^+$: 429.2537 found: 429.2531.



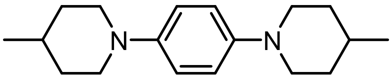
1,1'-(1,4-phenylene)bis(piperidin-4-ol) (3i): white solid was obtained with 53% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.80 (s, 4H), 4.64 (d, J = 4.2 Hz, 2H), 3.55 (td, J = 9.0, 4.4 Hz, 2H), 3.32 (dd, J = 11.6, 6.0 Hz, 4H), 2.72 – 2.61 (m, 4H), 1.85 – 1.74 (m, 4H), 1.54 – 1.40 (m, 4H).^{13}C NMR (101 MHz, DMSO-d_6) δ 144.73, 117.46, 66.22, 47.98, 34.26. HRMS (ESI) calcd for $C_{16}H_{25}N_2O_2$ $[M+H]^+$: 277.1911 found: 277.1911.



(1,4-phenylenebis(piperidine-1,4-diyl))dimethanol (3j): white solid was obtained with 51% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.81 (s, 4H), 4.47 (t, J = 5.3 Hz, 2H), 3.52 – 3.43 (m, 4H), 3.32 – 3.25 (m, 4H), 2.63 – 2.35 (m, 4H), 1.77 – 1.68 (m, 4H), 1.50 – 1.37 (m, 2H), 1.30 – 1.16 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.25, 117.57, 66.02, 50.23, 38.33, 28.79. HRMS (ESI) calcd for C18H29N2O2 $[M+H]^+$: 305.2224 found: 305.2219.

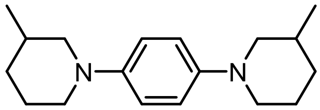


dibenzyl 4,4'-(1,4-phenylene)bis(piperazine-1-carboxylate) (3k): white solid was obtained with 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 4H), 3.70 (s, 6H), 3.54 – 3.45 (m, 4H), 2.68 (t, *J* = 11.7 Hz, 4H), 2.40 (m, *J* = 10.9, 3.5 Hz, 2H), 2.06 – 1.98 (m, 4H), 1.95 – 1.83 (m, 4H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.34, 145.64, 118.17, 51.62, 50.35, 40.79, 28.23. HRMS (ESI) calcd for $C_{20}H_{29}N_2O_4$ $[M+H]^+$: 361.2122 found: 361.2115.

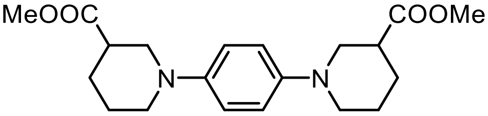


1,4-bis(4-methylpiperidin-1-yl)benzene (3l): white solid was obtained with 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 4H), 3.49 (m, J = 12.5, 3.4 Hz, 4H), 2.65 – 2.54 (m, 4H), 1.76 – 1.68 (m, 4H), 1.53 – 1.23 (m, 6H), 0.97 (d, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 118.06, 51.25, 34.39, 30.57, 21.87. HRMS (ESI) calcd for

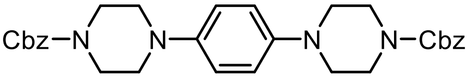
$C_{20}H_{29}N_2O_4$ [M+H]$^+$: 273.2325 found: 273.2322



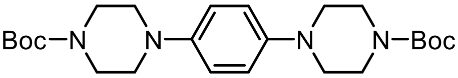
1,4-bis(3-methylpiperidin-1-yl)benzene (3m): white solid was obtained with 53% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 3.50 – 3.37 (m, 4H), 2.58 – 2.47 (m, 2H), 2.26 – 2.17 (m, 2H), 1.04 – 0.95 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.98, 118.17, 76.68, 59.26, 51.34, 32.81, 31.16, 25.62, 19.61. HRMS (ESI) calcd for $C_{18}H_{29}N_2$ [M+H]$^+$: 273.2325 found: 273.2319.



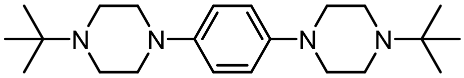
dimethyl 1,1'-(1,4-phenylene)bis(piperidine-3-carboxylate) (3n): white solid was obtained with 44% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 3.71 (s, 6H), 3.62 – 3.54 (m, 2H), 3.35 (d, *J* = 11.9 Hz, 2H), 2.91 (t, *J* = 10.8 Hz, 2H), 2.76 – 2.66 (m, 4H), 2.06 – 1.93 (m, 2H), 1.87 – 1.77 (m, 2H), 1.74 – 1.55 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.43, 145.69, 118.46, 53.34, 51.69, 51.06, 41.59, 26.75, 24.40. HRMS (ESI) calcd for $C_{20}H_{29}N_2O_4$ [M+H]$^+$: 361.2122 found: 361.2118.



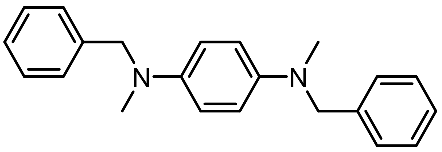
dibenzyl 4,4'-(1,4-phenylene)bis(piperazine-1-carboxylate) (3o): white solid was obtained with 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.08 (m, 10H), 6.88 (s, 4H), 5.15 (s, 4H), 3.79 – 3.31 (m, 8H), 3.02 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.03, 145.46, 136.48, 128.37, 128.25, 127.92, 127.78, 127.78, 127.71, 118.15, 67.05, 50.24, 43.70. HRMS (ESI) calcd for $C_{30}H_{35}N_4O_4$ [M+H]$^+$: 515.2653 found: 515.2639.



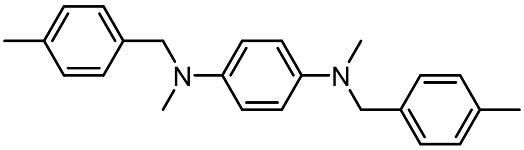
di-tert-butyl 4,4'-(1,4-phenylene)bis(piperazine-1-carboxylate) (3p): white solid was obtained with 55% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 3.57 (t, *J* = 5.1 Hz, 8H), 3.03 (d, *J* = 5.1 Hz, 8H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.68, 145.61, 118.18, 81.34, 50.40, 45.31, 29.86. HRMS (ESI) calcd for $C_{24}H_{39}N_4O_4$ [M+H]$^+$: 447.2966 found: 447.2959.



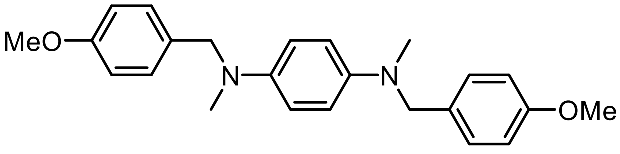
1,4-bis(4-(tert-butyl)piperazin-1-yl)benzene (3q): white solid was obtained with 47% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 4H), 3.11 (t, *J* = 4.8 Hz, 8H), 2.74 (t, *J* = 4.9 Hz, 8H), 1.11 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 117.49, 53.68, 50.89, 45.77, 25.79. HRMS (ESI) calcd for $C_{22}H_{38}N_4$ [M+H]$^+$: 359.3169 found: 359.3168.



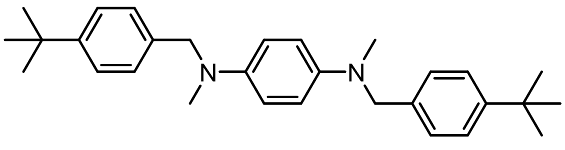
N1,N4-dibenzyl-N1,N4-dimethylbenzene-1,4-diamine (3r): white solid was obtained with 47% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.15 (m, 10H), 6.75 (s, 4H), 4.36 (s, 4H), 2.85 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 142.84, 139.49, 128.35, 127.23, 126.71, 115.07, 58.27, 38.99. HRMS (ESI) calcd for $C_{22}H_{25}N_2$ [M+H]$^+$: 317.2012 found: 317.2002.



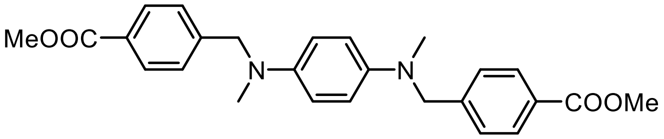
N1,N4-dimethyl-N1,N4-bis(4-methylbenzyl)benzene-1,4-diamine (3s): white solid was obtained with 45% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.06 (m, 8H), 6.75 (s, 4H), 4.32 (s, 6H), 2.83 (s, 6H), 2.31 (s, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.88, 136.24, 129.02, 127.24, 115.13, 58.02, 38.88, 21.04. HRMS (ESI) calcd for $C_{24}H_{29}N_2$ [M+H]$^+$: 345.2325 found: 345.2317.



N1,N4-bis(4-methoxybenzyl)-N1,N4-dimethylbenzene-1,4-diamine (3t): white solid was obtained with 45% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.13 (m, 4H), 6.87 – 6.79 (m, 4H), 6.77 (s, 4H), 4.30 (s, 4H), 3.77 (s, 6H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.44, 142.96, 131.32, 128.49, 115.33, 113.69, 57.75, 55.18, 38.80. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_2$ [M+H]$^+$: 371.2224 found: 377.2217.

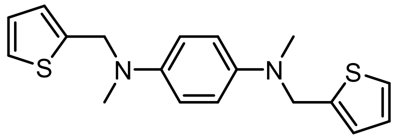


N1,N4-bis(4-(tert-butyl)benzyl)-N1,N4-dimethylbenzene-1,4-diamine (3u): white solid was obtained with 43% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.24 (m, 4H), 7.23 – 7.16 (m, 4H), 6.77 (s, 4H), 4.34 (s, 4H), 1.30 (s, 18H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.56, 142.94, 136.49, 126.95, 125.26, 115.04, 57.93, 38.96, 34.41, 31.39. HRMS (ESI) calcd for $C_{30}H_{41}N_2$ [M+H]$^+$: 429.3264 found: 429.3257.

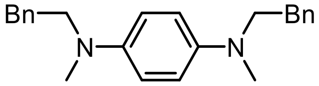


dimethyl 4,4'-((1,4-phenylenebis(methylazanediyl))bis(methylene))dibenzoate (3v): white solid was obtained with 47%

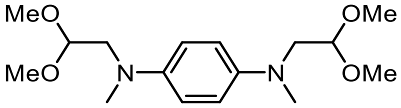
isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 4H), 7.33 (d, *J* = 8.3 Hz, 4H), 6.72 (s, 4H), 3.90 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 145.13, 142.61, 129.78, 128.75, 127.07, 115.04, 76.68, 58.12, 52.01, 39.30. HRMS (ESI) calcd for $C_{26}H_{29}N_2O_4$ [M+H]$^+$: 433.2122 found: 433.2116.



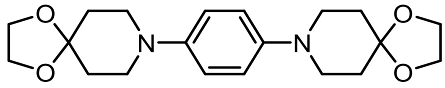
N1,N4-dimethyl-N1,N4-bis(thiophen-2-ylmethyl)benzene-1,4-diamine (3w): white solid was obtained with 33% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.0, 1.3 Hz, 2H), 7.00 – 6.90 (m, 2H), 6.90 – 6.86 (m, 2H), 6.82 (s, 4H), 4.54 (s, 4H), 2.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 142.30, 126.49, 125.06, 124.28, 115.95, 53.54, 38.70. HRMS (ESI) calcd for $C_{18}H_{21}N_2S_2$ [M+H]$^+$: 329.1141 found: 329.1131.



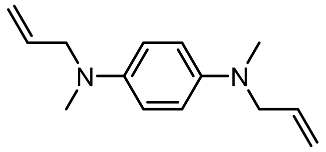
N1,N4-dimethyl-N1,N4-diphenethylbenzene-1,4-diamine (3x): colorless oil was obtained with 33% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 7.23 – 7.15 (m, 6H), 6.78 (s, 1H), 3.48 – 3.43 (m, 4H), 2.86 – 2.77 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.70, 140.13, 128.72, 128.39, 125.97, 115.25, 56.09, 39.19, 32.73. HRMS (ESI) calcd for $C_{24}H_{29}N_2$ [M+H]$^+$: 345.2325 found: 345.2315.



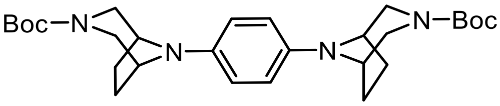
N1,N4-bis(2,2-dimethoxyethyl)-N1,N4-dimethylbenzene-1,4-diamine (3y): colorless oil was obtained with 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (s, 4H), 4.50 (t, *J* = 5.1 Hz, 2H), 3.39 (s, 12H), 3.36 – 3.32 (m, 4H), 2.94 – 2.89 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.20, 114.64, 103.38, 56.58, 54.32, 39.87. HRMS (ESI) calcd for $C_{16}H_{29}N_2O_4$ [M+H]$^+$: 313.2122 found: 313.2119.



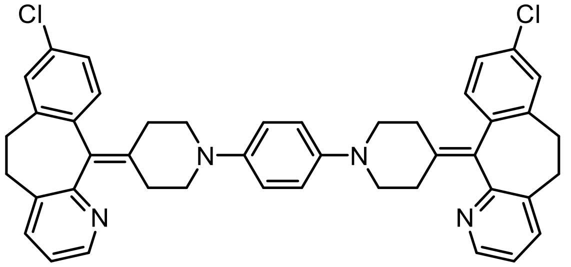
1,4-di(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)benzene (3z): white solid was obtained with 56% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 3.98 (s, 8H), 3.20 (t, *J* = 5.7 Hz, 8H), 1.85 (t, *J* = 5.8 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 118.28, 107.06, 64.22, 48.90, 34.73. HRMS (ESI) calcd for $C_{20}H_{29}N_2O_4$ [M+H]$^+$: 361.2122 found: 361.2111.



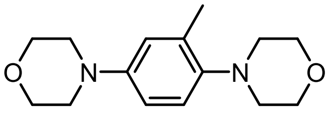
N1,N4-diallyl-N1,N4-dimethylbenzene-1,4-diamine (3aa): colorless oil was obtained with 30% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.75 (s, 4H), 5.86 (m, *J* = 17.3, 10.7, 5.5 Hz, 2H), 5.23 – 5.09 (m, 4H), 3.81 – 3.77 (m, 4H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.57, 134.71, 116.39, 115.35, 56.93, 38.77. HRMS (ESI) calcd for $C_{14}H_{21}N_2$ [M+H]$^+$: 217.1699 found: 217.1700.



di-tert-butyl 8,8'-(1,4-phenylene)(1R,1'R,5S,5'S)-bis(3,8-diazabicyclo[3.2.1]octane-3-carboxylate) (3ab): white soild was obtained with 56% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.74 (s, 4H), 4.05 (d, *J* = 21.1 Hz, 4H), 3.72 (d, *J* = 12.7 Hz, 2H), 3.58 (d, *J* = 12.7 Hz, 2H), 3.25 (dd, *J* = 34.6, 12.6 Hz, 4H), 2.00 – 1.95 (m, 4H), 1.79 (dd, *J* = 15.1, 7.4 Hz, 4H), 1.45 (s, 18H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.08, 139.39, 117.26, 79.49, 55.37, 55.15, 47.07, 45.83, 28.38, 26.75. HRMS (ESI) calcd for $C_{28}H_{43}N_4O_4$ [M+H]$^+$: 499.3279 found: 499.3270.



1,4-bis(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)benzene (3ac): white soild was obtained with 63% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (dd, J = 4.9, 1.7 Hz, 2H), 7.43 (dd, J = 7.8, 1.7 Hz, 2H), 7.21 – 7.05 (m, 8H), 6.86 (s, 4H), 3.48 – 3.30 (m, 8H), 2.90 – 2.73 (m, 8H), 2.72 – 2.60 (m, 2H), 2.60 – 2.40 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 157.45, 146.63, 139.53, 138.13 (d, J = 71.1 Hz), 137.28, 133.37, 132.97, 132.67, 130.77, 128.92, 126.01, 122.08, 118.13, 52.22, 52.11, 31.59 (d, J = 32.6 Hz), 30.85 (d, J = 25.7 Hz). HRMS (ESI) calcd for $C_{44}H_{41}N_4Cl_2$ [M+H]$^+$: 695.2703 found: 695.2683.



1,4-dimorpholino-2-methyl-benzene (3ad): white solid was obtained with 51% isolated yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (d, J = 8.6 Hz, 1H), 6.79 (d, J = 2.9 Hz, 1H), 6.74 (dd, J = 8.6, 3.0 Hz, 1H), 3.93 – 3.79 (m, 8H), 3.09 (dd, J = 5.8, 3.6 Hz, 4H), 2.88 – 2.81 (m, 4H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.52, 144.52, 133.81, 119.89, 118.92, 113.92, 67.51, 66.98, 52.62, 49.93, 17.96. HRMS (ESI) calcd for $C_{44}H_{41}N_4Cl_2$ $[M+H]^+$: 263.1754 found: 263.1755.

References

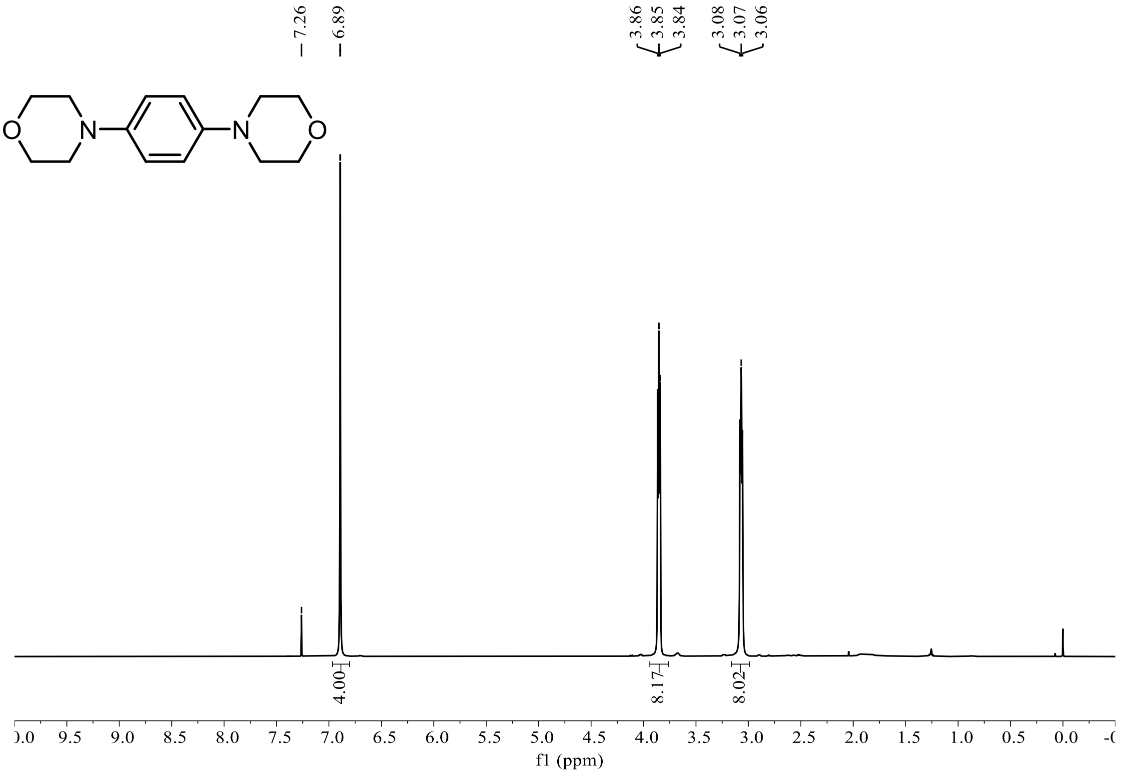
[1] A. Bismuto, T. Delcaillau, P. Müller and B. Morandi, *ACS Catal.*, 2020, **10**, 4630-4639.

[2] K. Chen, Q.-K. Kang, Y. Li, W.-Q. Wu, H. Zhu and H. Shi, *J. Am. Chem. Soc.*, 2022, **144**, 1144-1151.

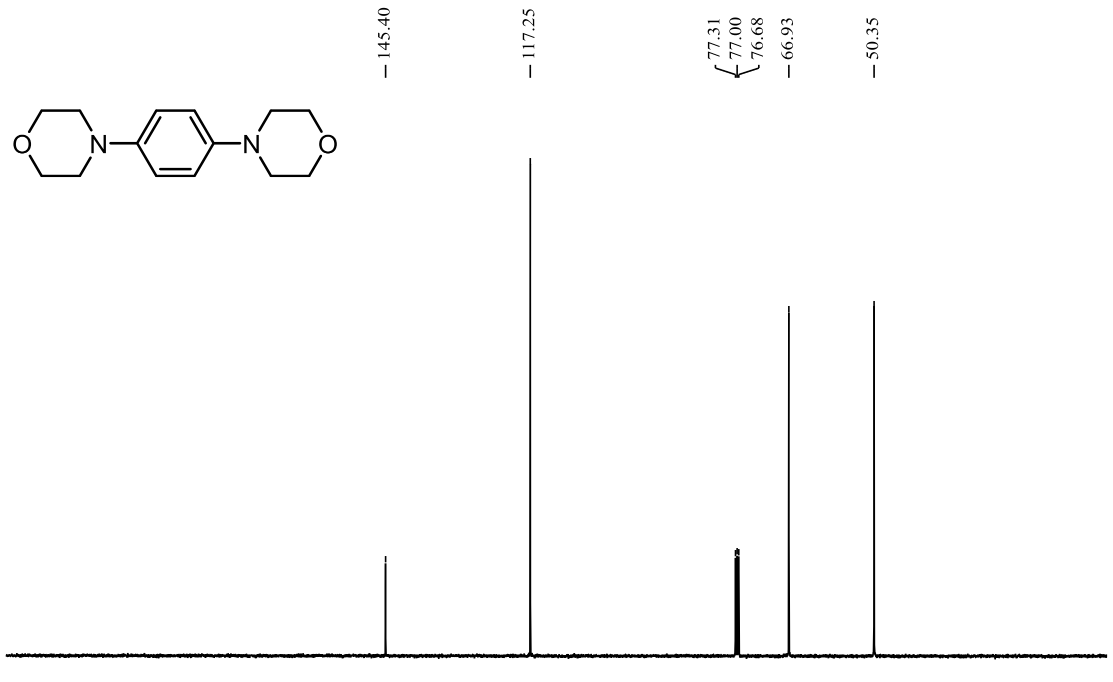
Copies of product NMR spectra

Spectrum of 3a

^{1}H NMR (400 MHz, CDCl$_3$)

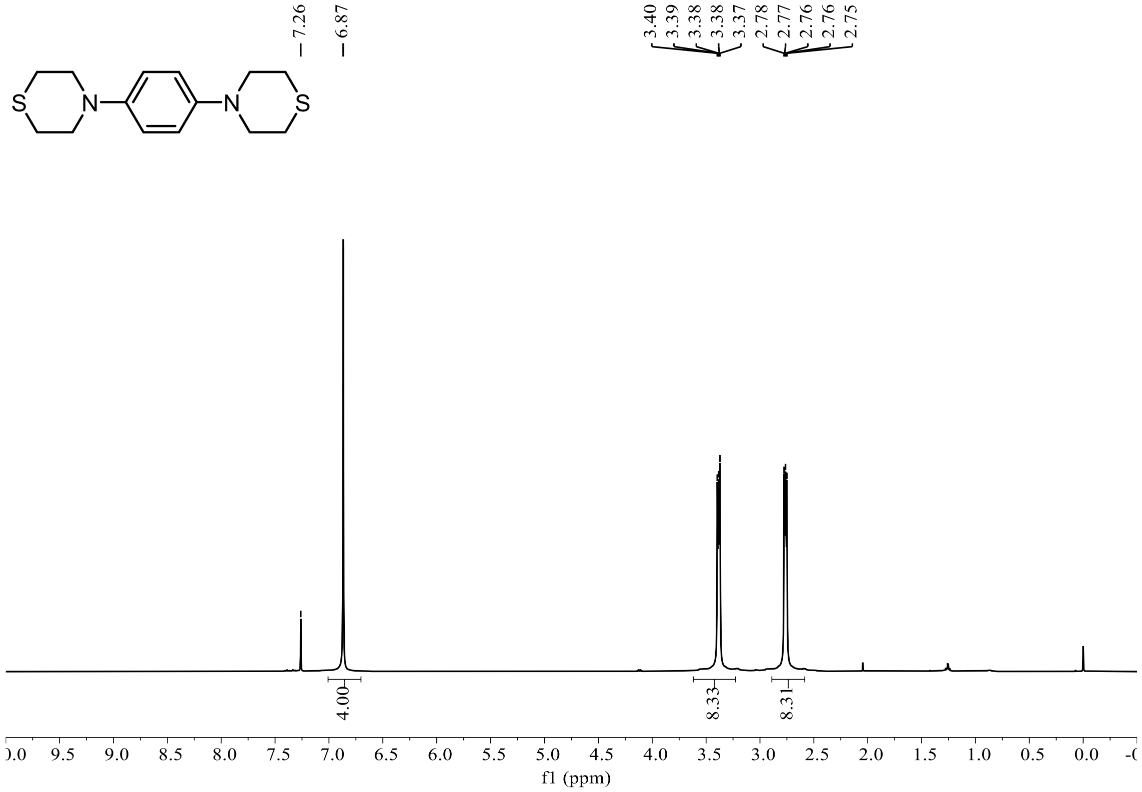


^{13}C NMR (101 MHz, CDCl$_3$)

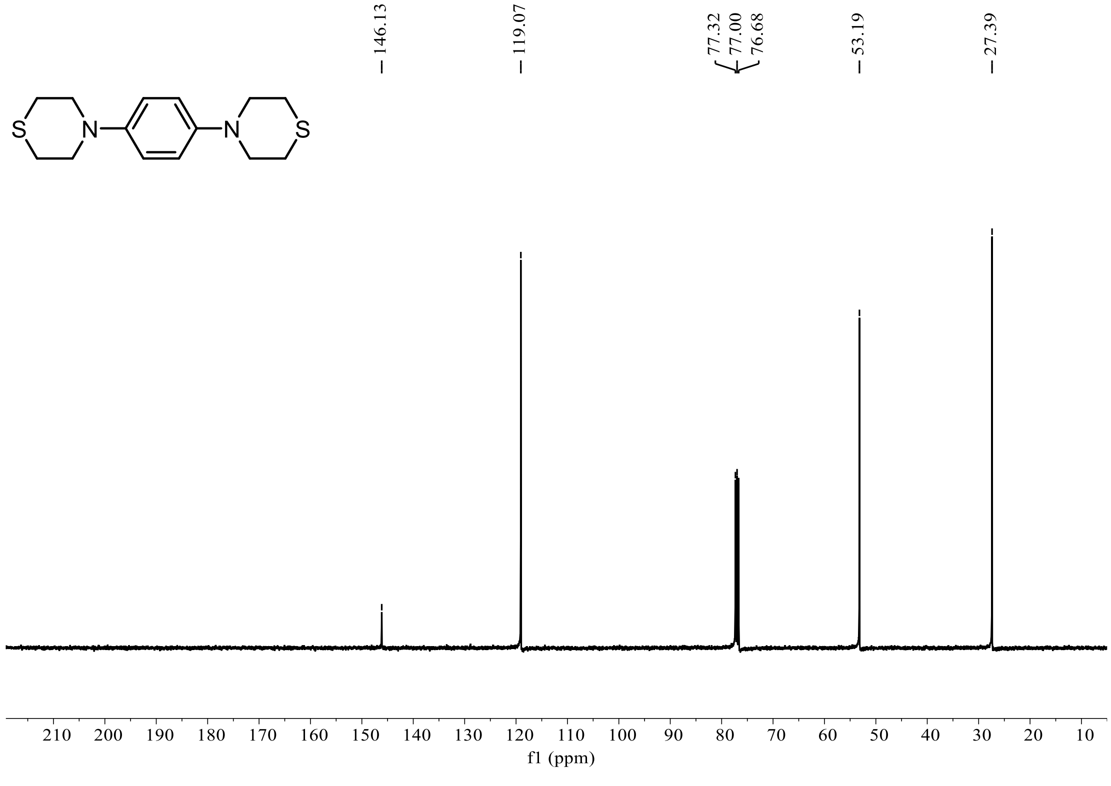


Spectrum of 3b

^{1}H NMR (400 MHz, CDCl$_3$)

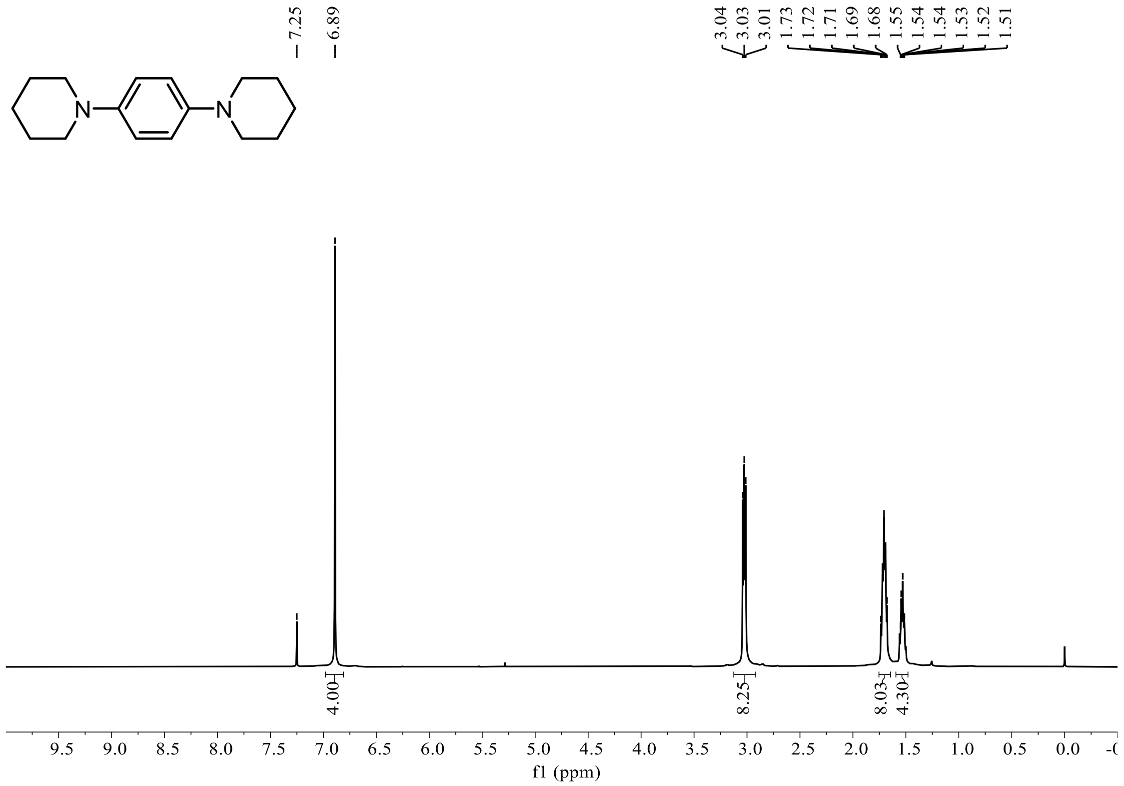


^{13}C NMR (101 MHz, CDCl$_3$)

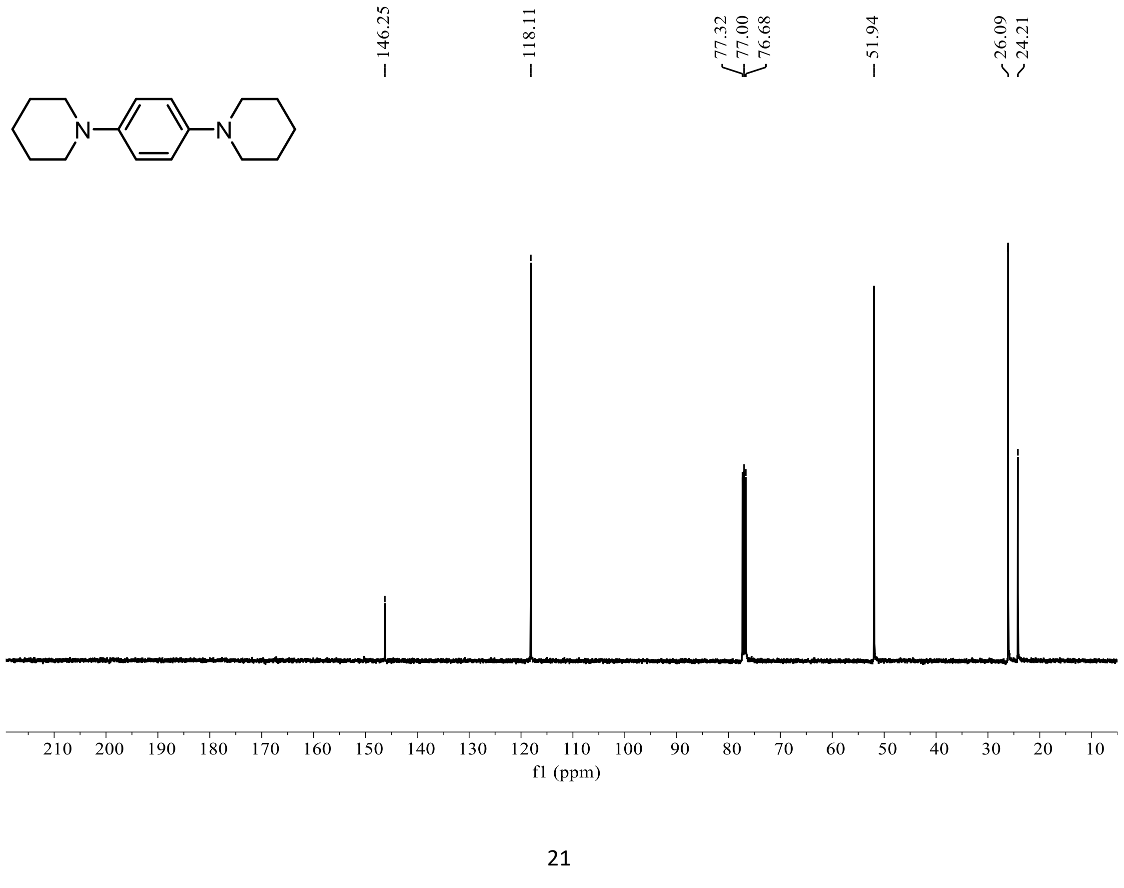


Spectrum of 3c

^{1}H NMR (400 MHz, CDCl$_3$)

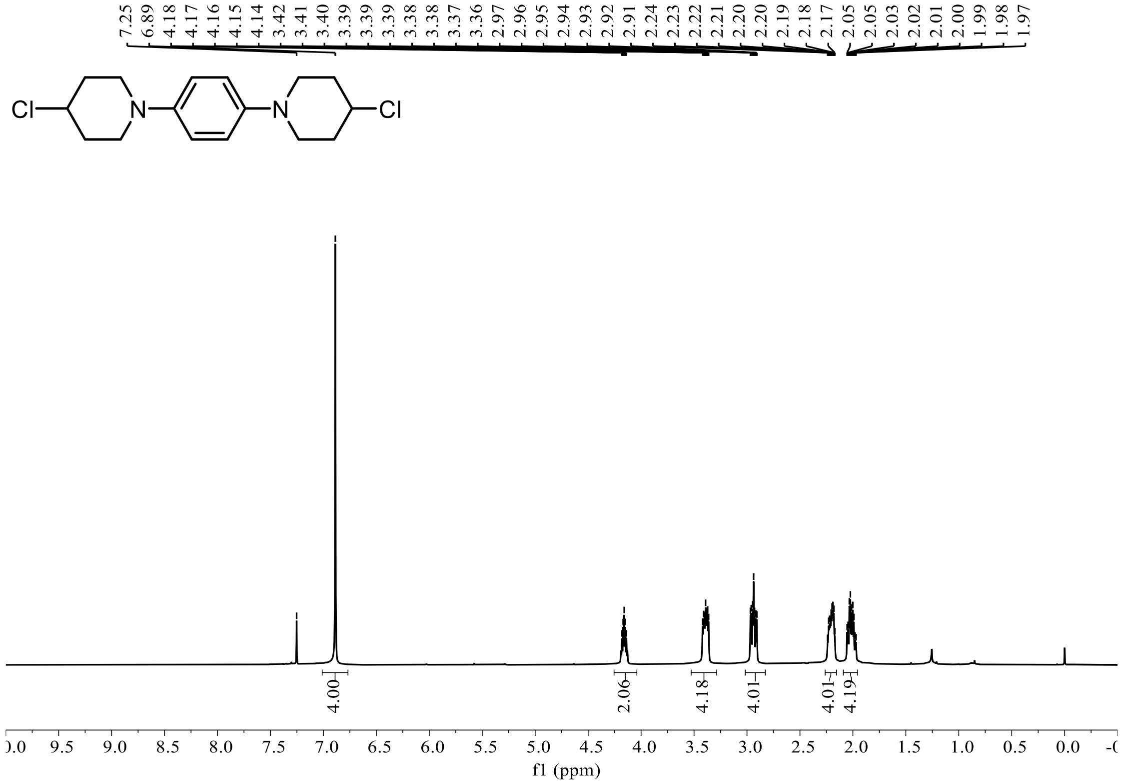


^{13}C NMR (101 MHz, CDCl$_3$)

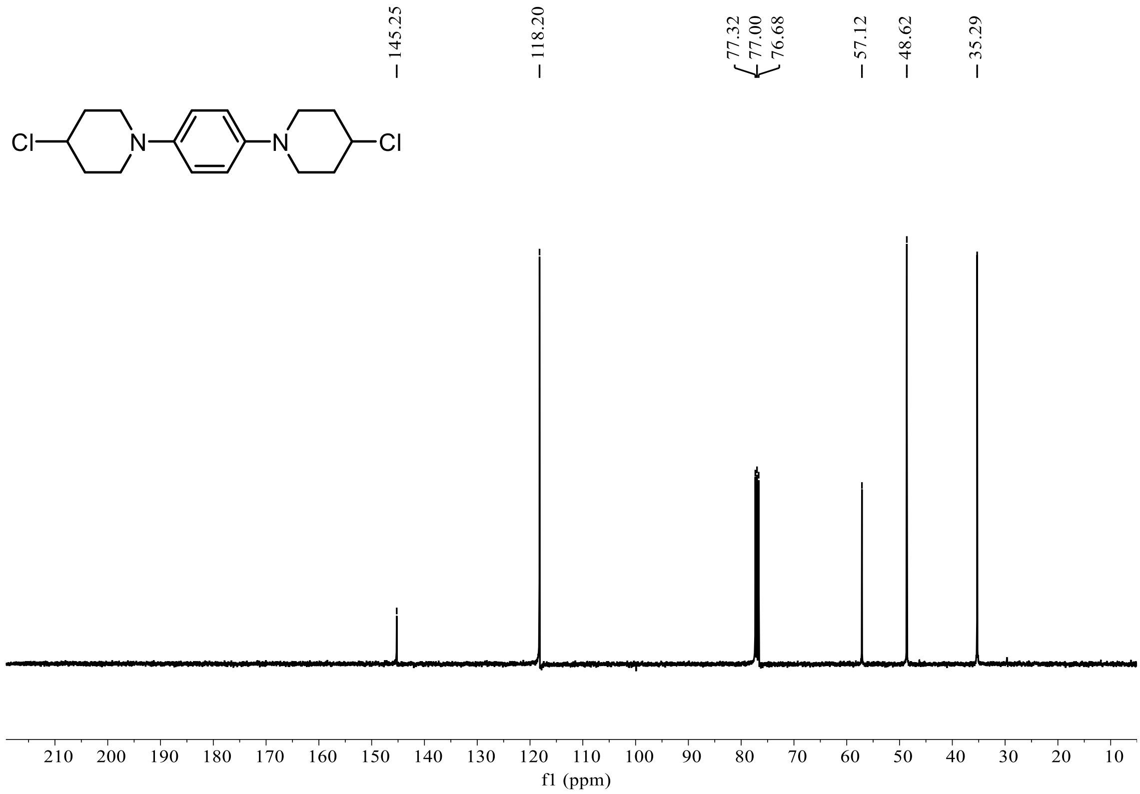


Spectrum of 3d

^{1}H NMR (400 MHz, CDCl$_3$)

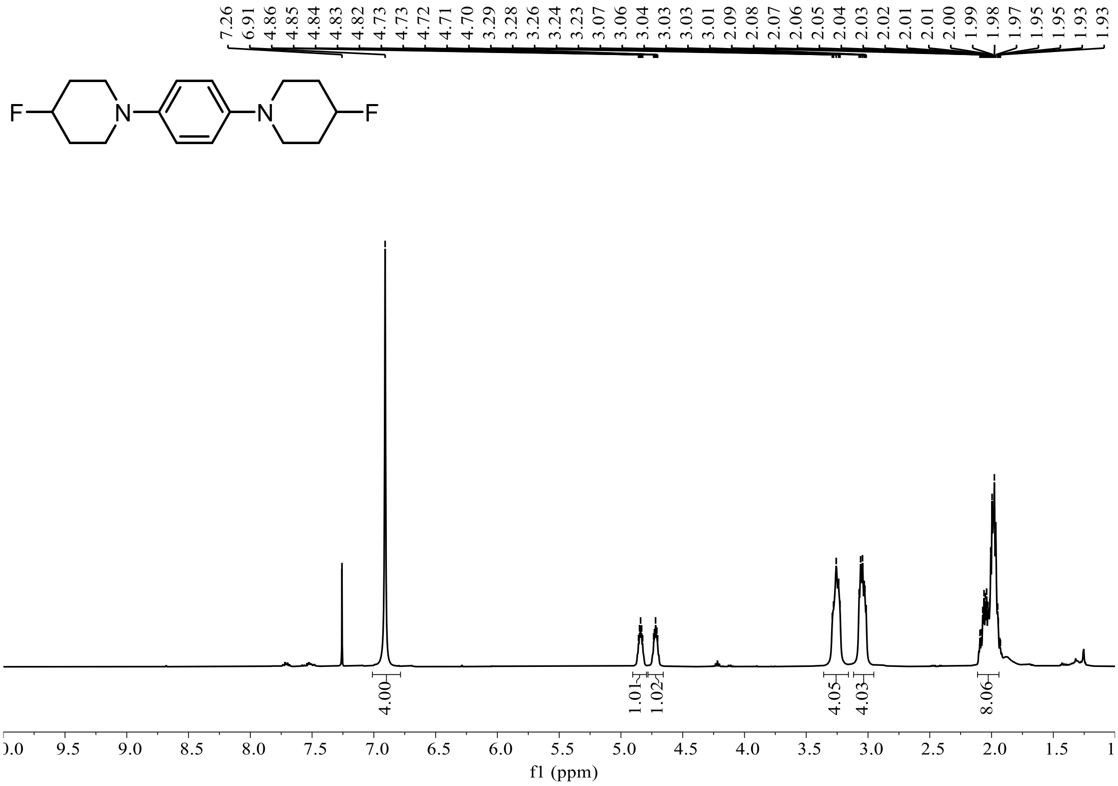


^{13}C NMR (101 MHz, CDCl$_3$)

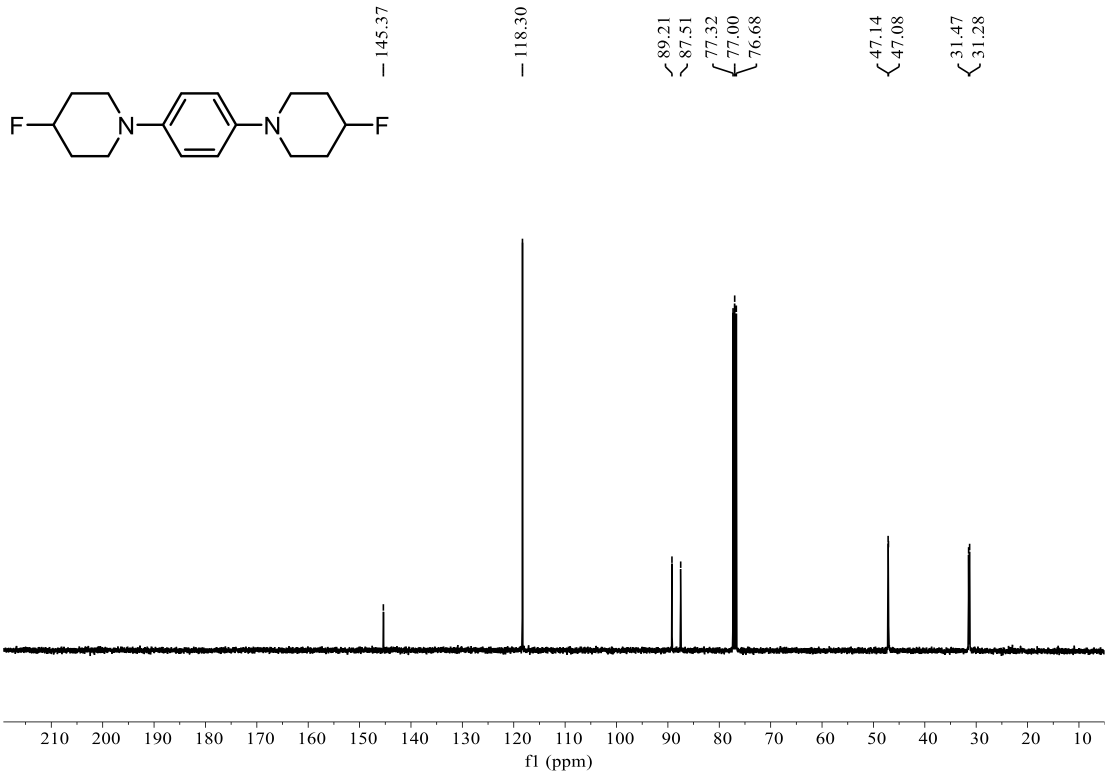


Spectrum of 3e

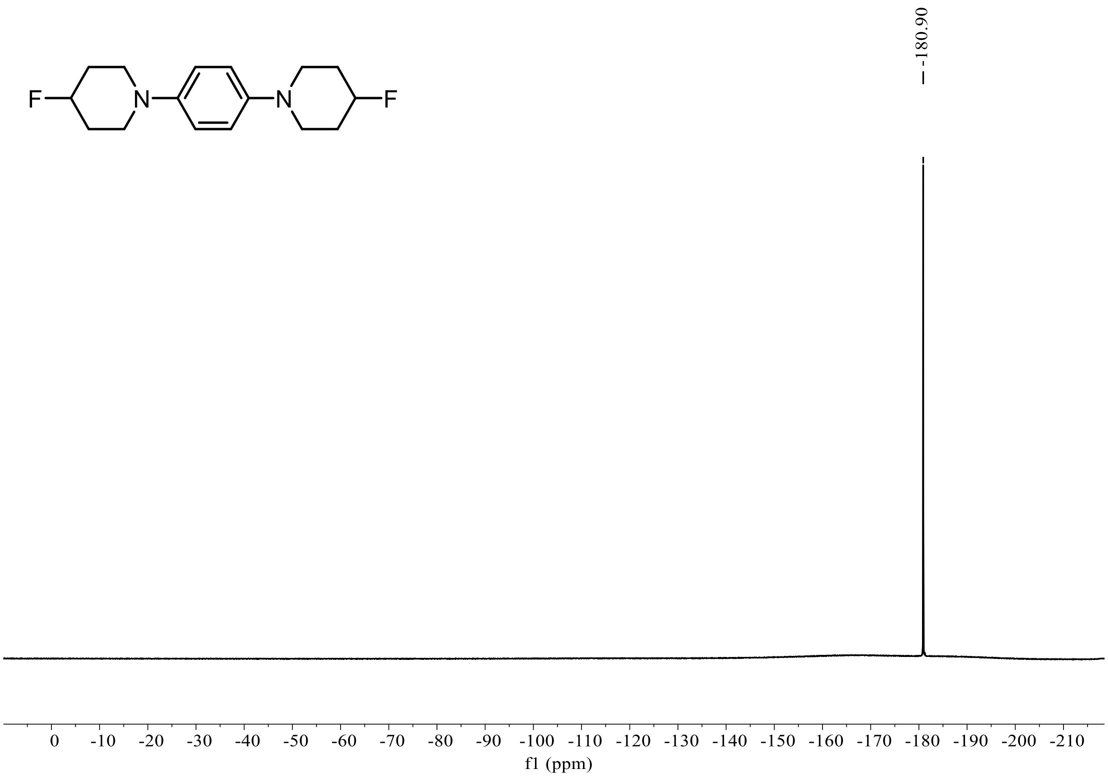
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)

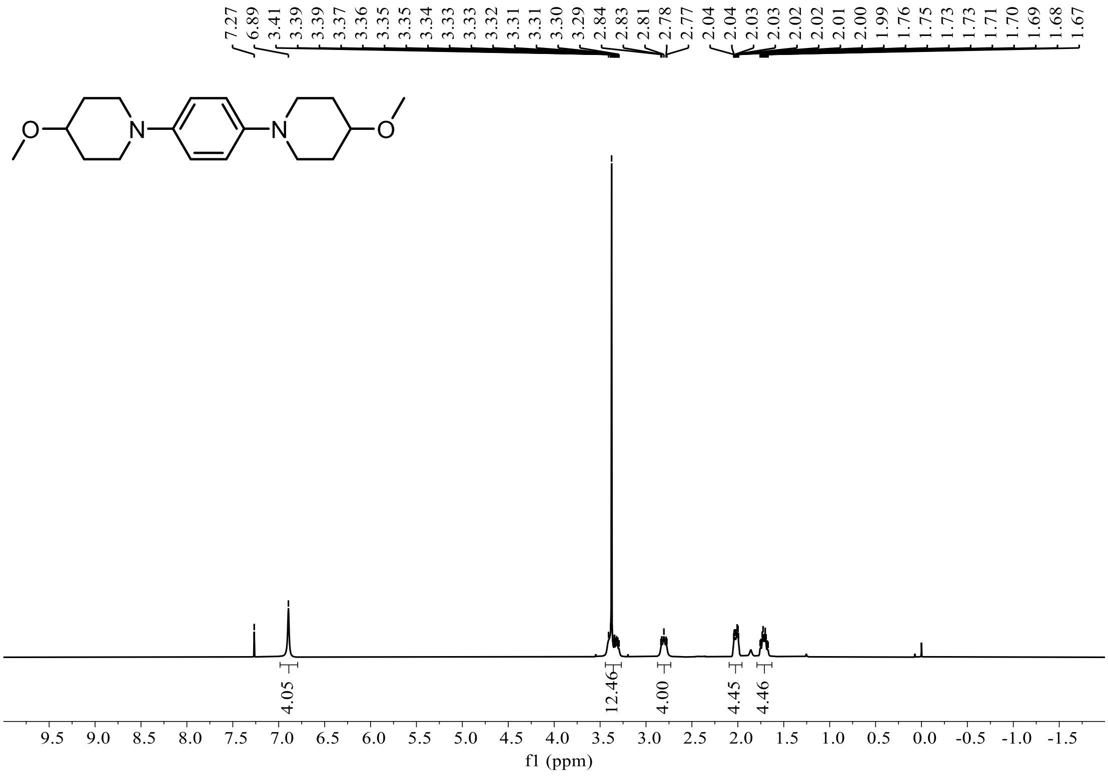


^{19}F NMR (377 MHz, CDCl$_3$)

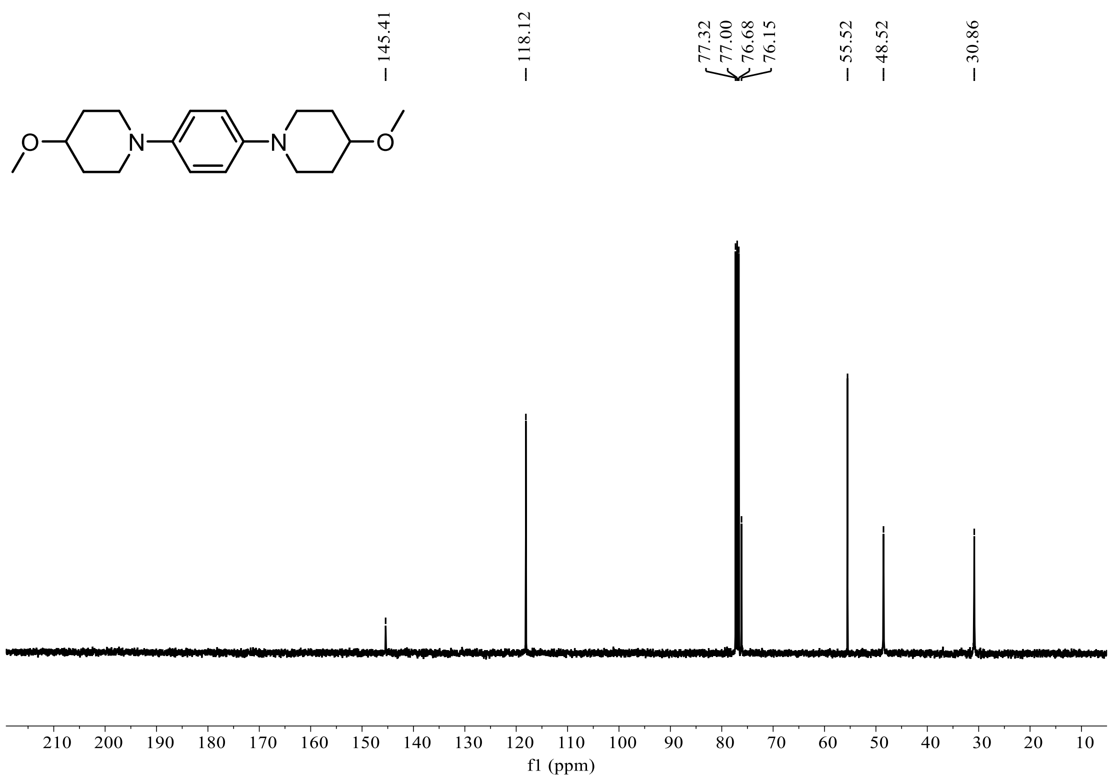


Spectrum of 3f

^{1}H NMR (400 MHz, CDCl$_3$)

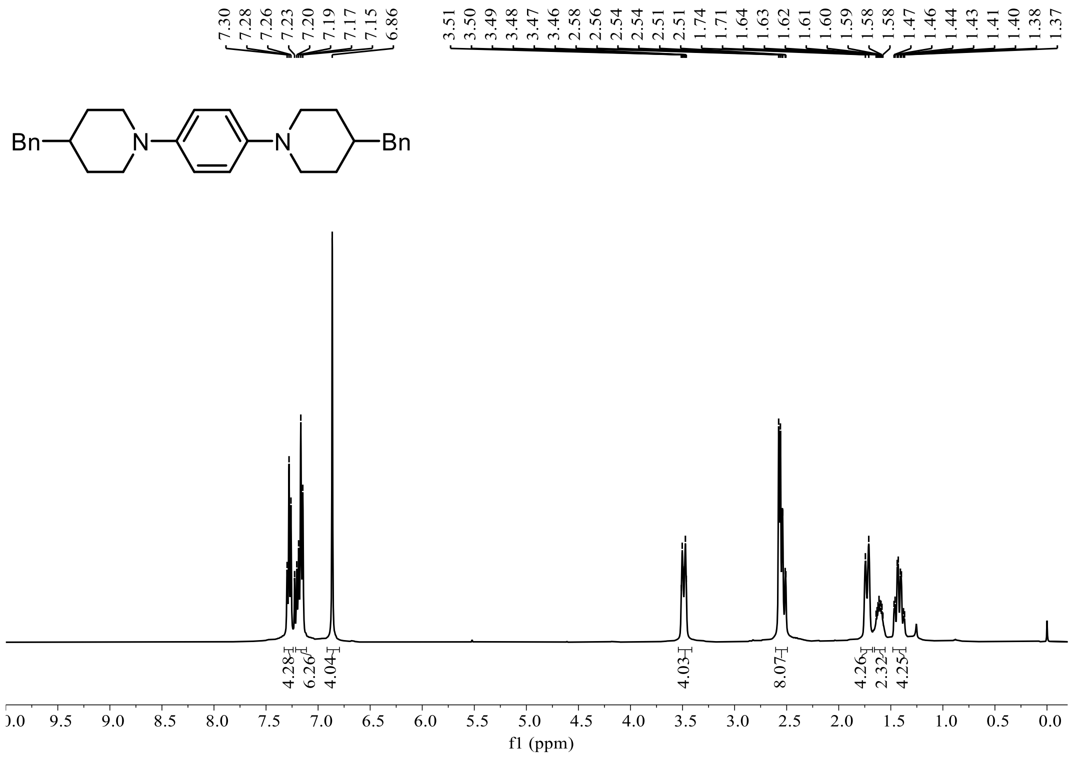


^{13}C NMR (101 MHz, CDCl$_3$)

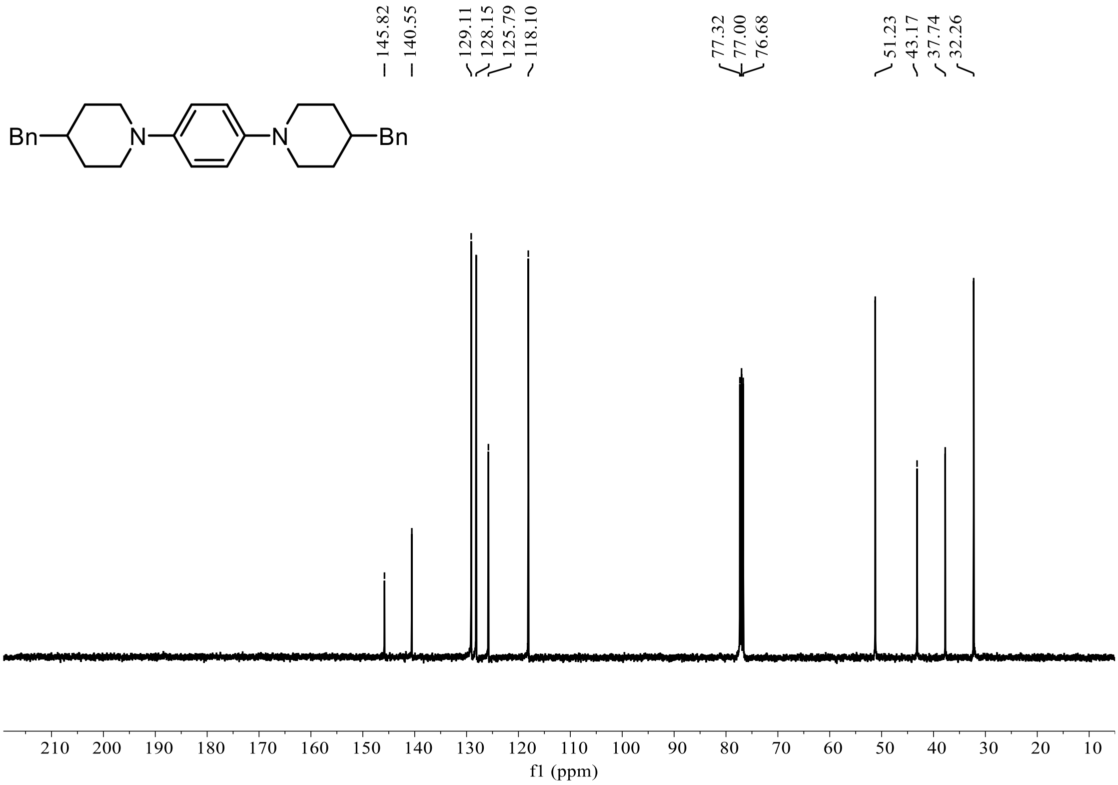


Spectrum of 3g

^{1}H NMR (400 MHz, CDCl$_3$)

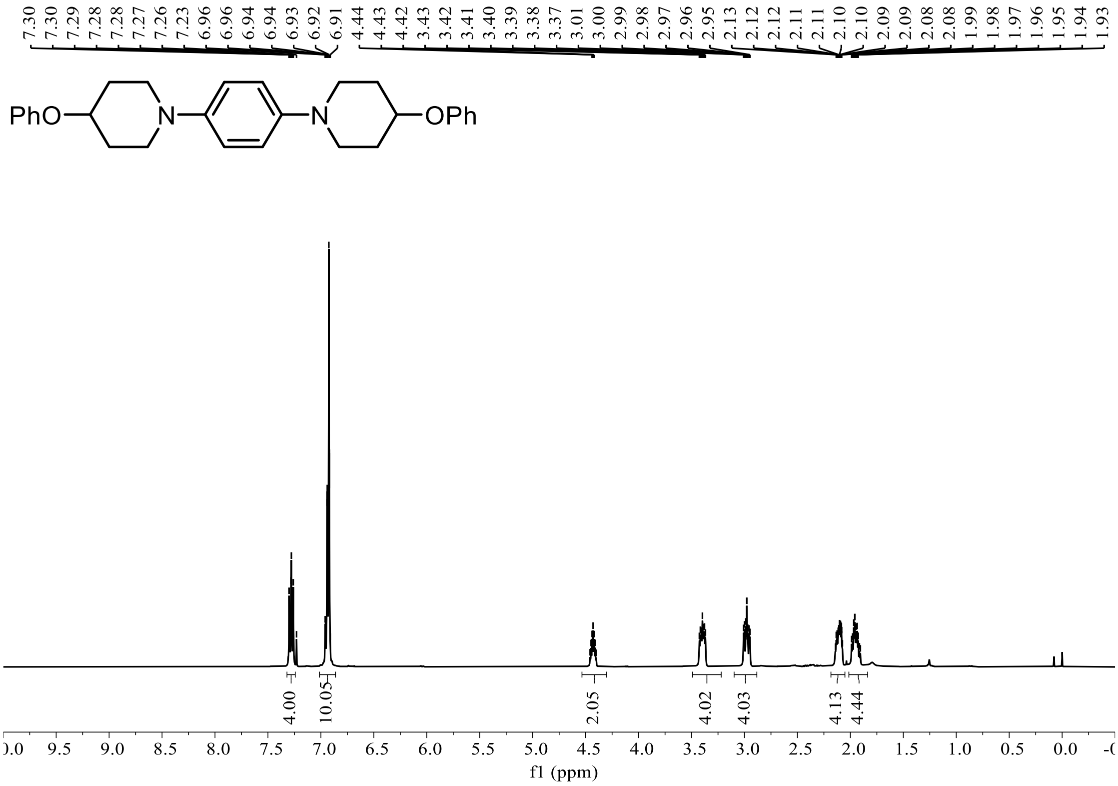


^{13}C NMR (101 MHz, CDCl$_3$)

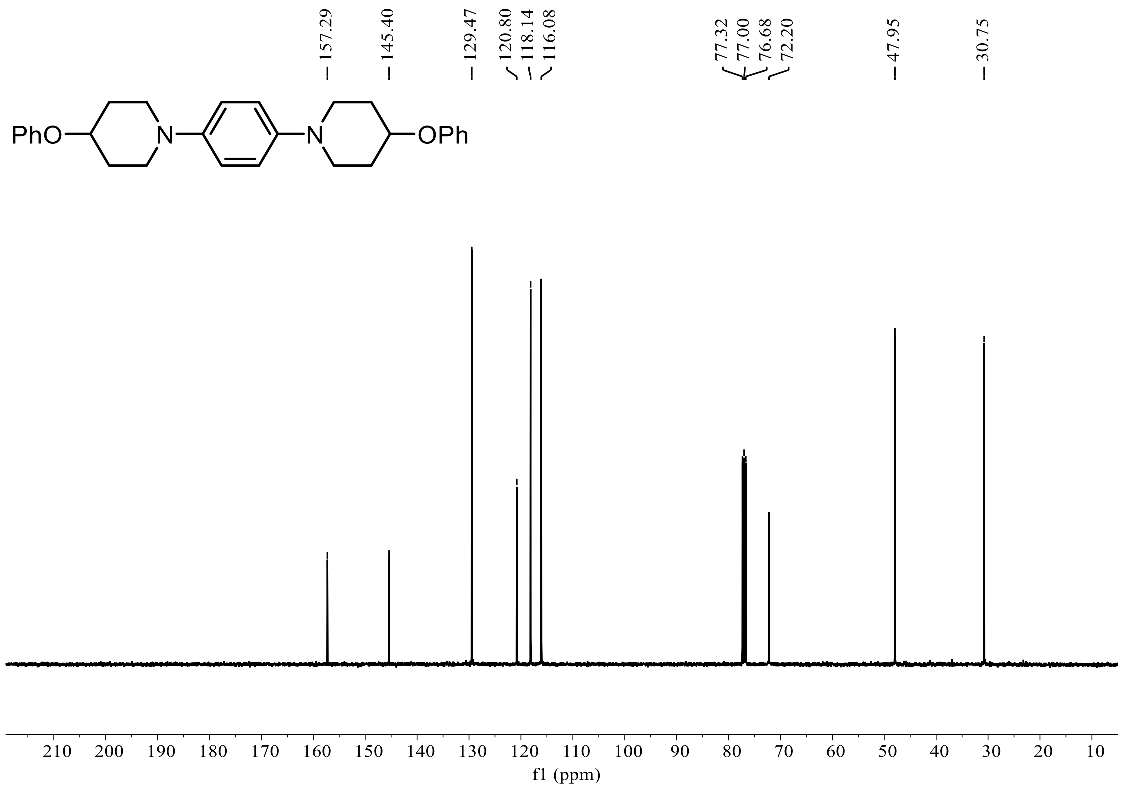


Spectrum of 3h

^{1}H NMR (400 MHz, CDCl$_3$)

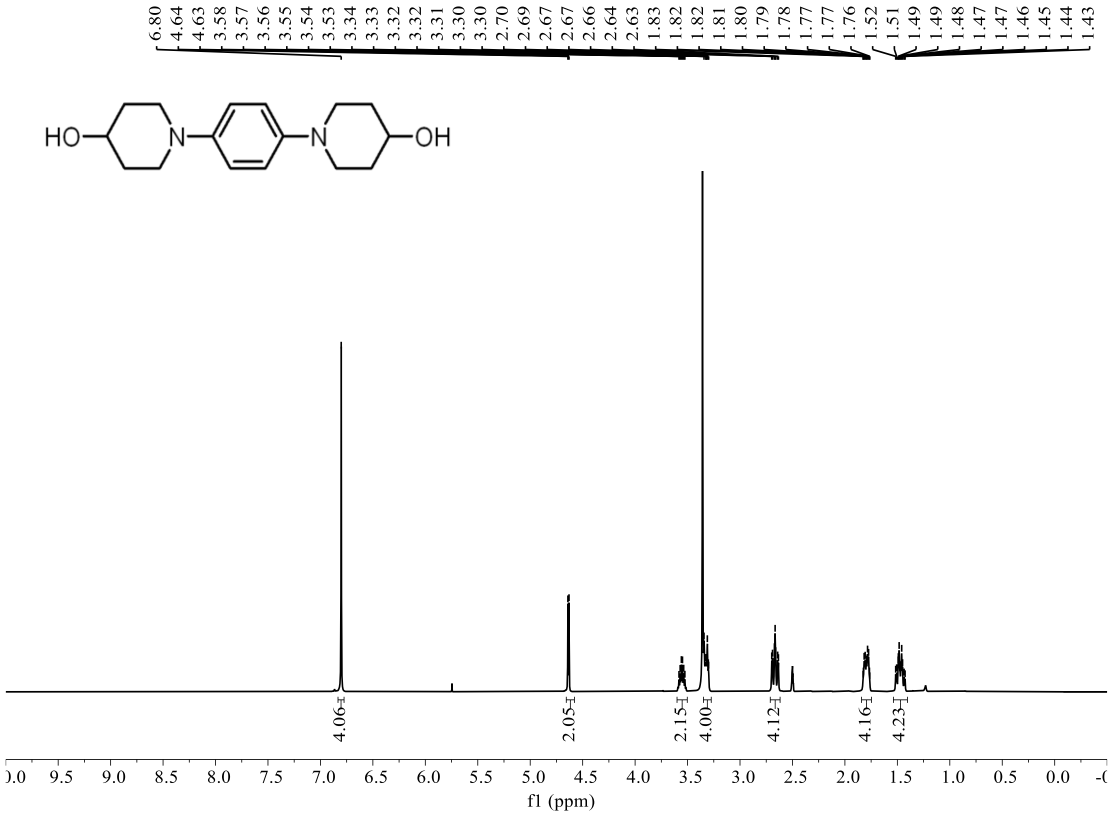


^{13}C NMR (101 MHz, $CDCl_3$)

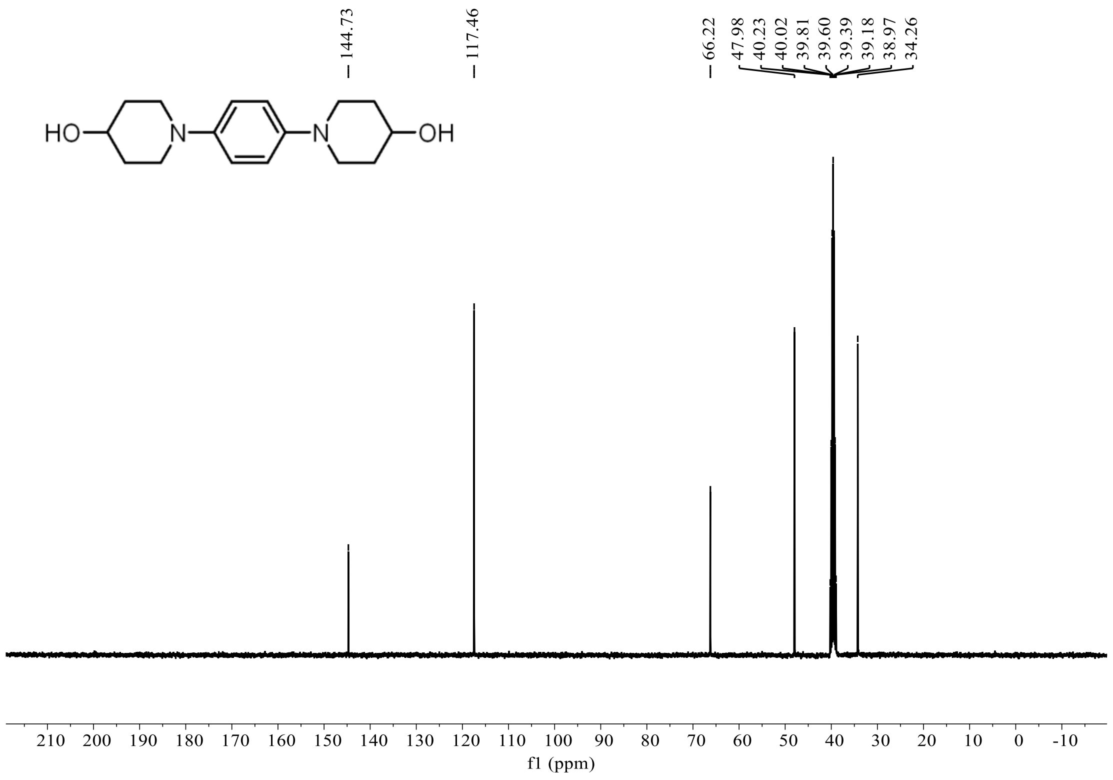


Spectrum of 3i

^1H NMR (400 MHz, DMSO-d_6)

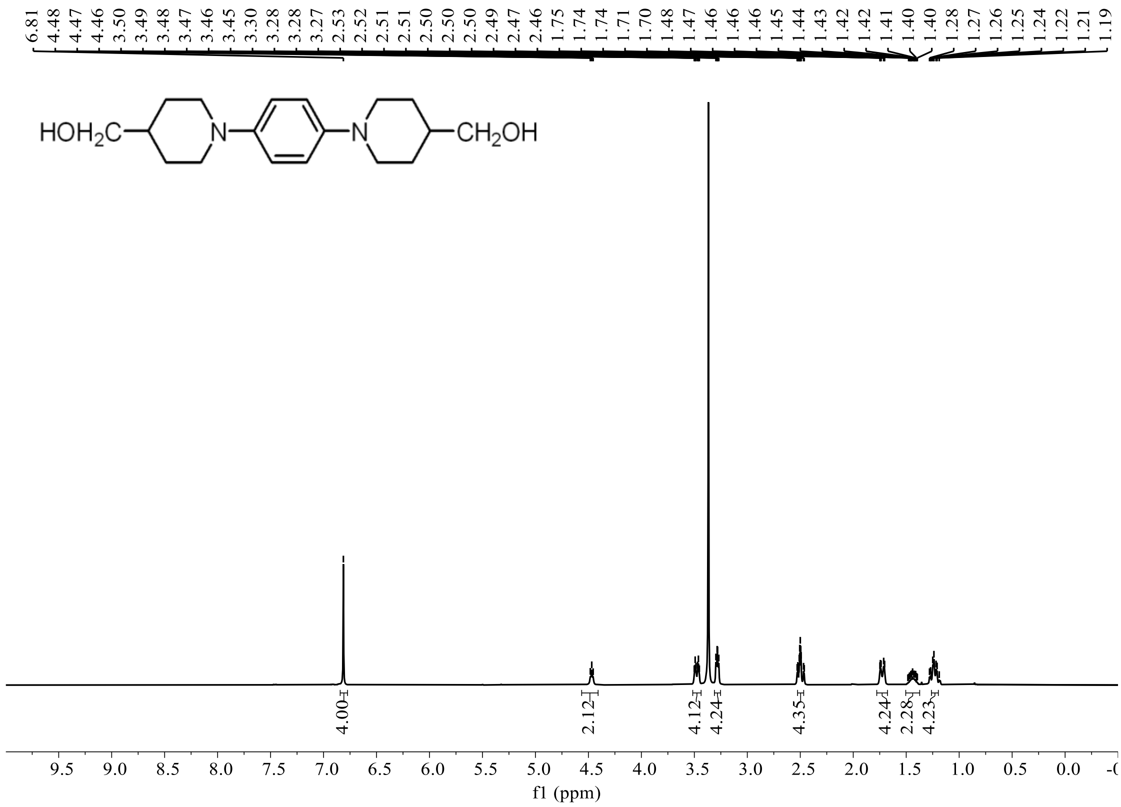


^{13}C NMR (101 MHz, DMSO-d_6)

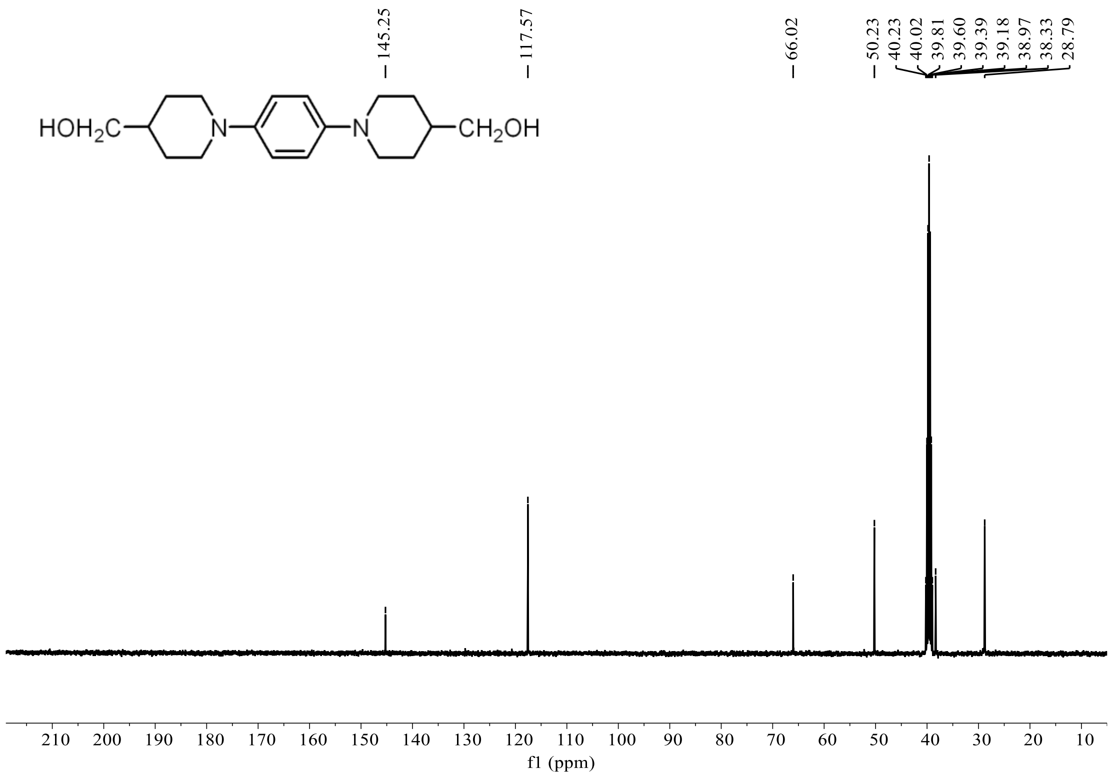


Spectrum of 3j

^{1}H NMR (400 MHz, DMSO-d_6)

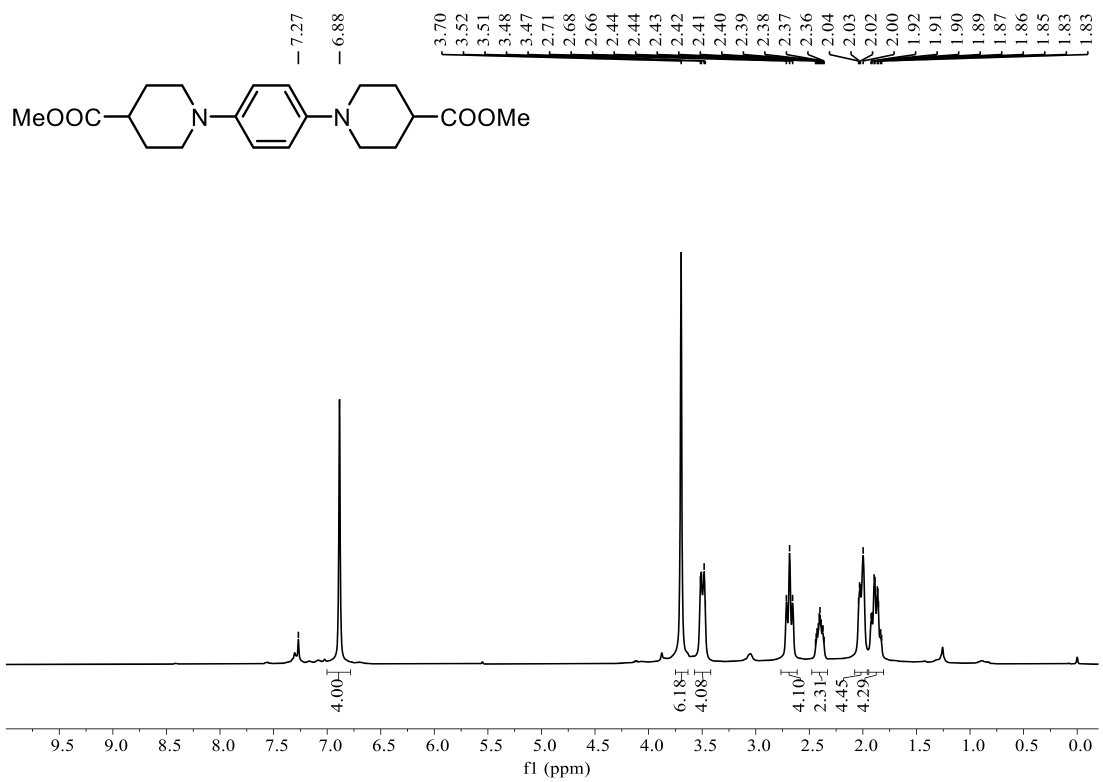


^{13}C NMR (101 MHz, DMSO-d_6)

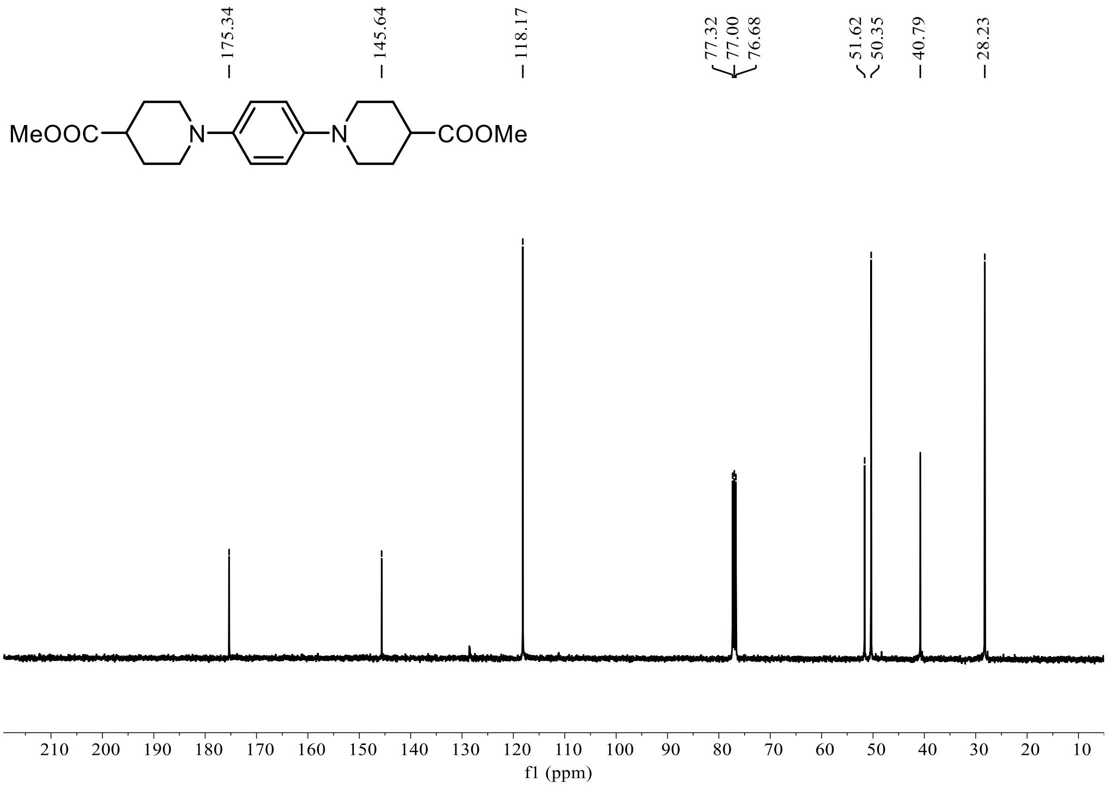


Spectrum of 3k

^{1}H NMR (400 MHz, CDCl$_3$)

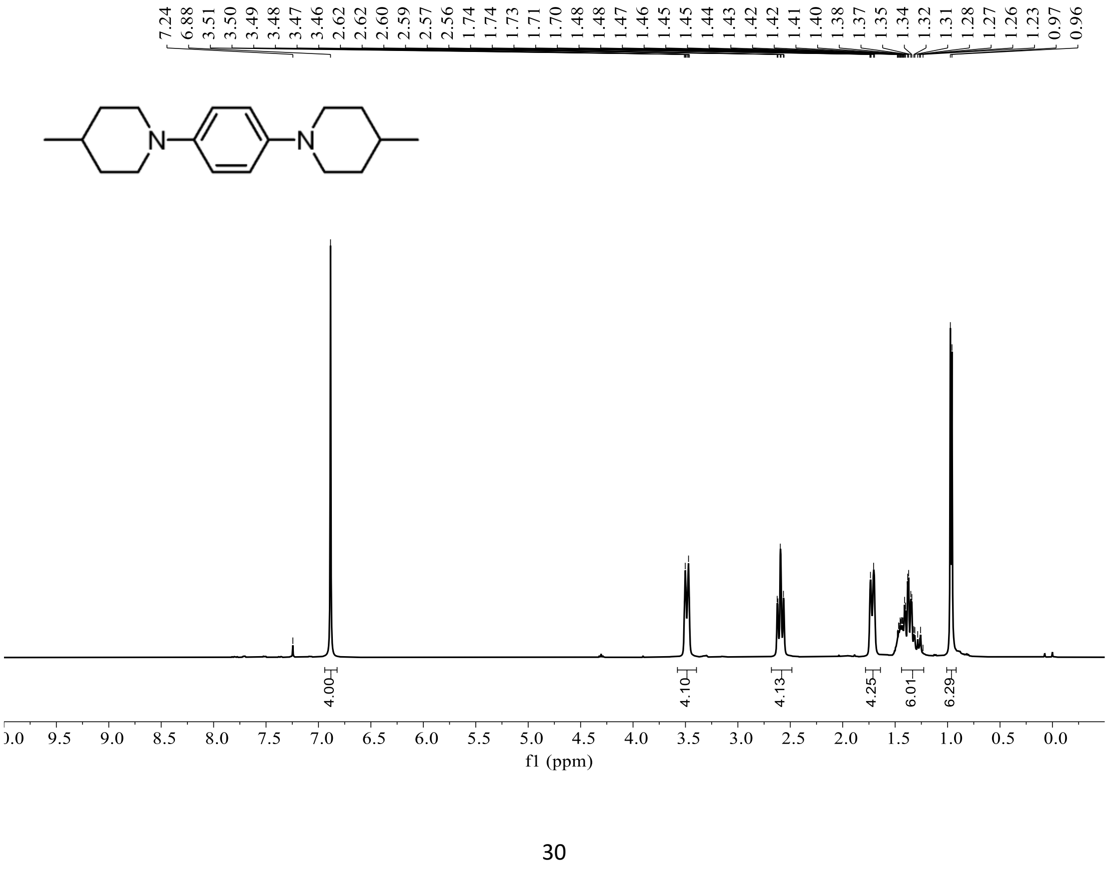


^{13}C NMR (101 MHz, $CDCl_3$)

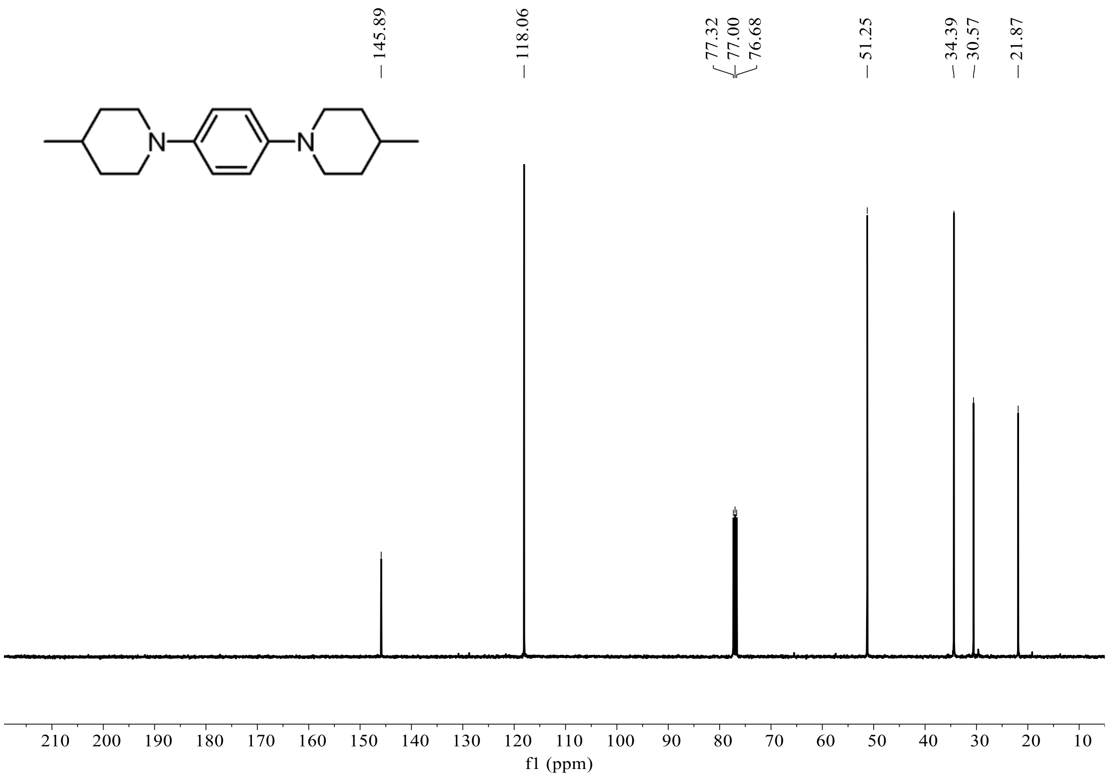


Spectrum of 3l

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3m

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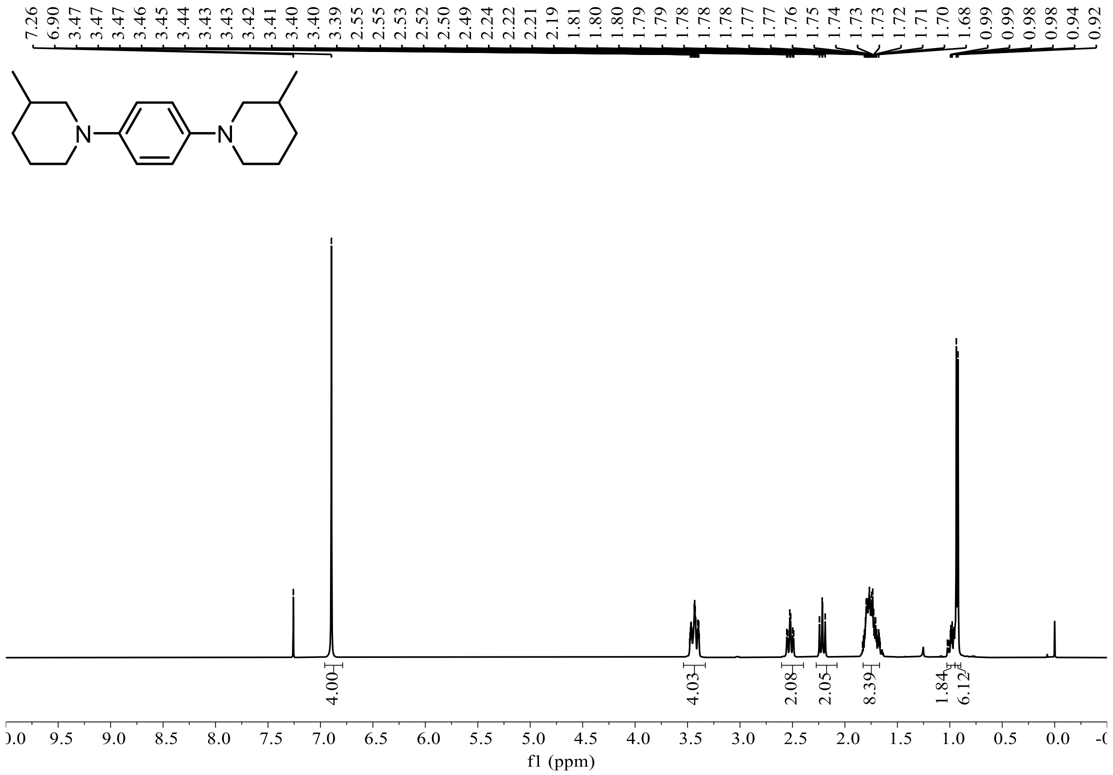
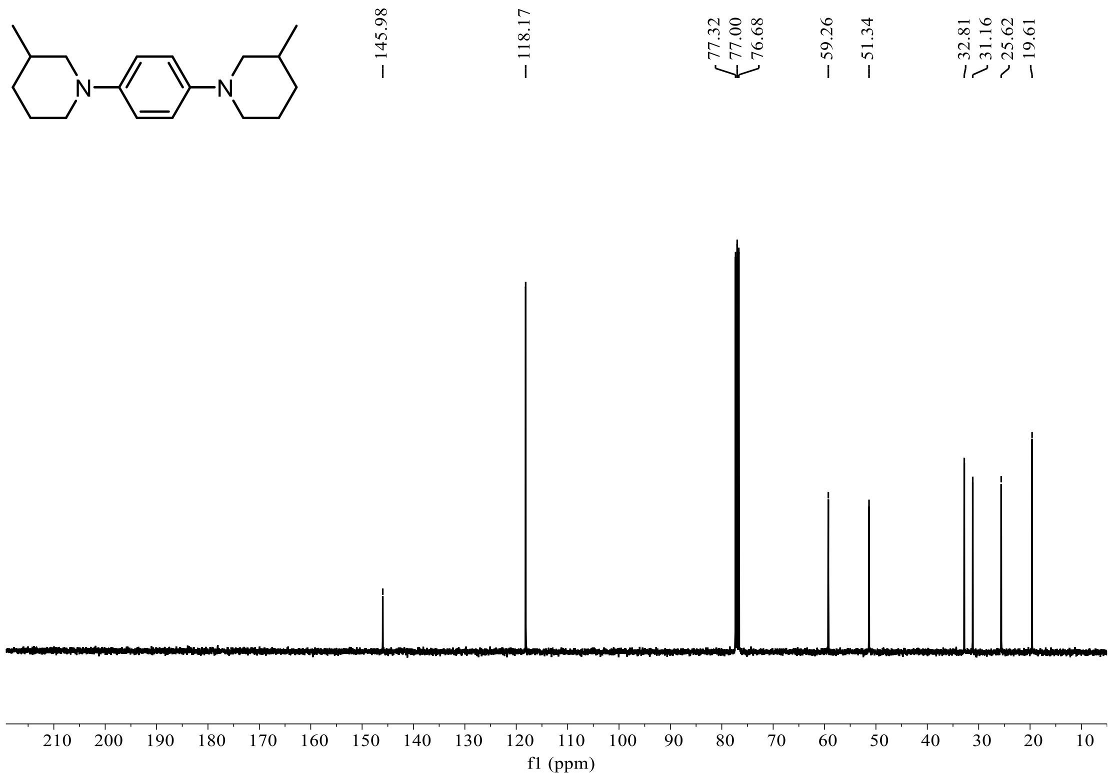
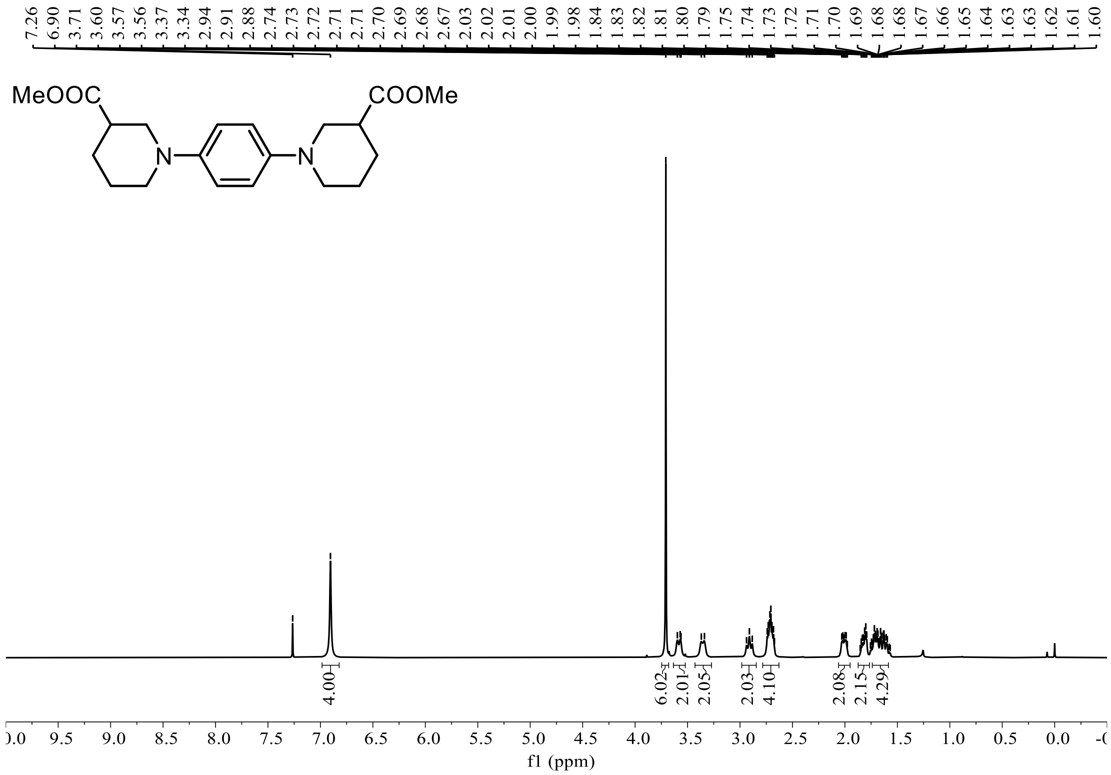


^{13}C NMR (101 MHz, CDCl$_3$)

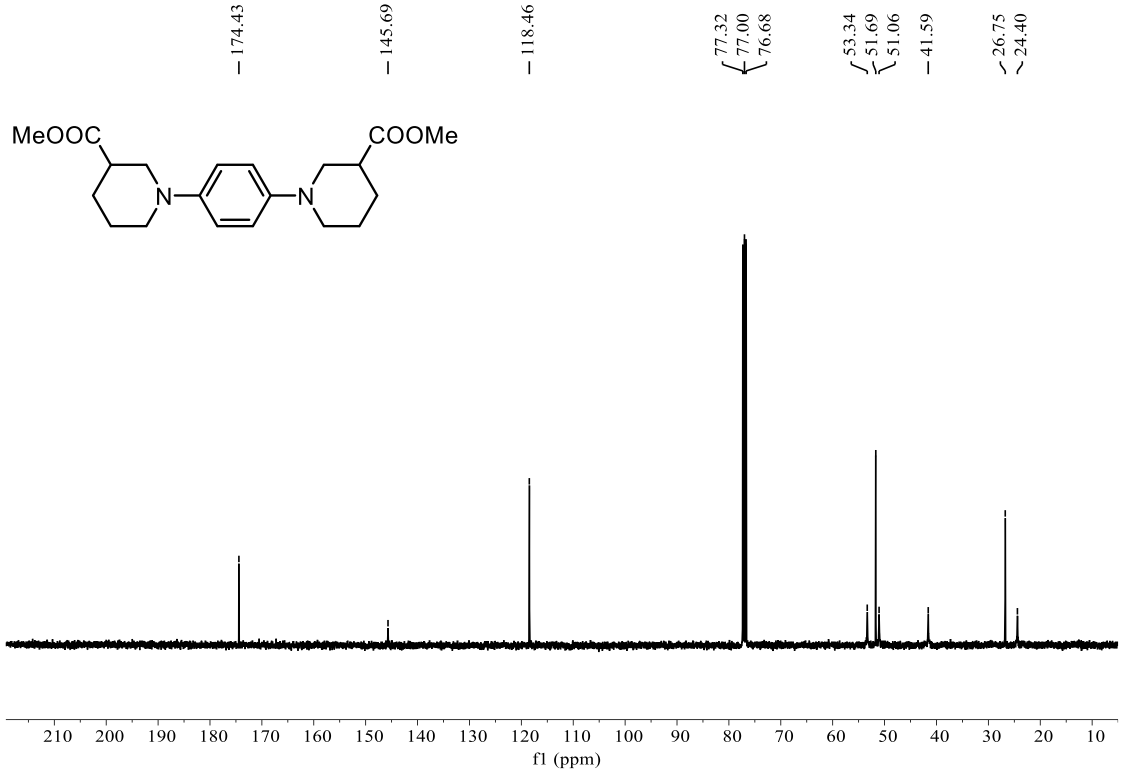


Spectrum of 3n

^{1}H NMR (400 MHz, CDCl$_3$)

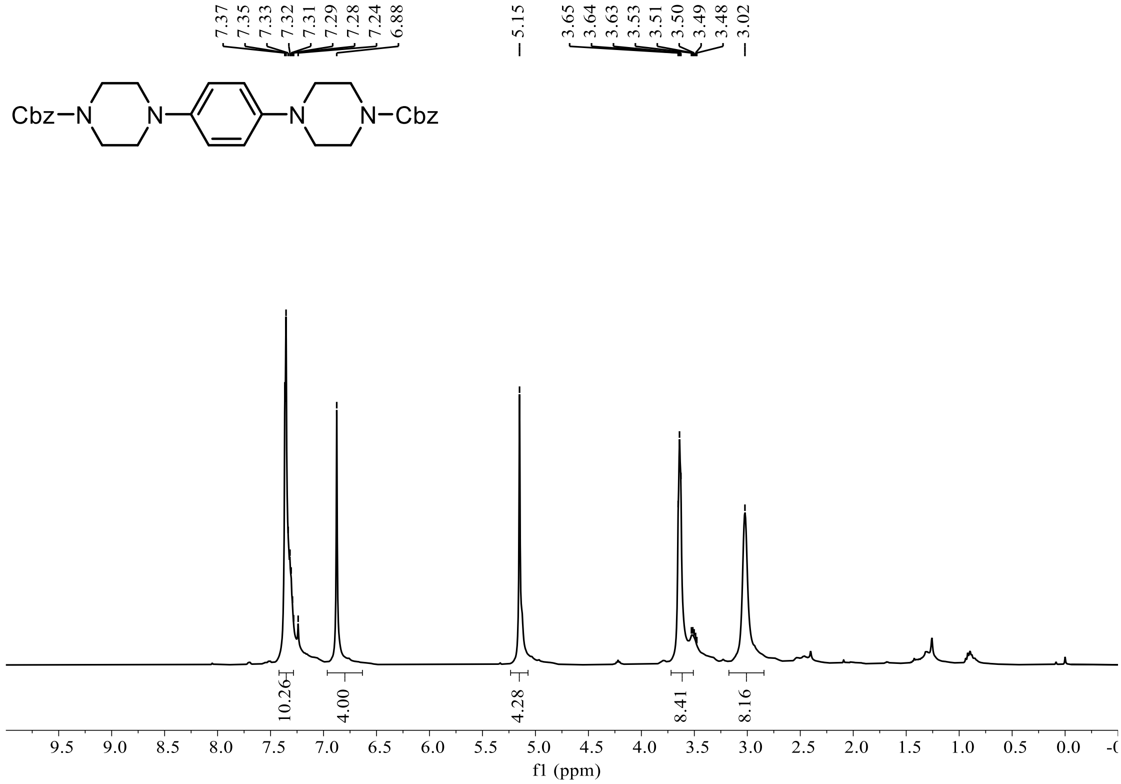


^{13}C NMR (101 MHz, CDCl$_3$)

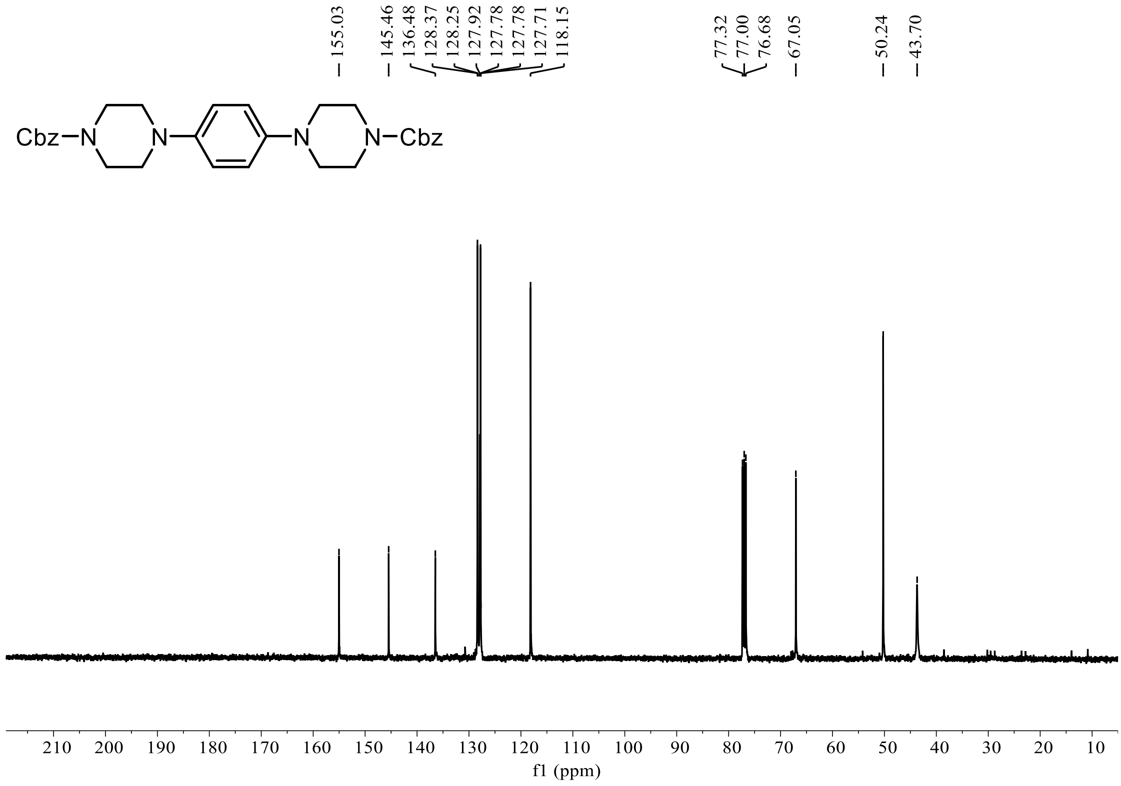


Spectrum of 3o

^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3p

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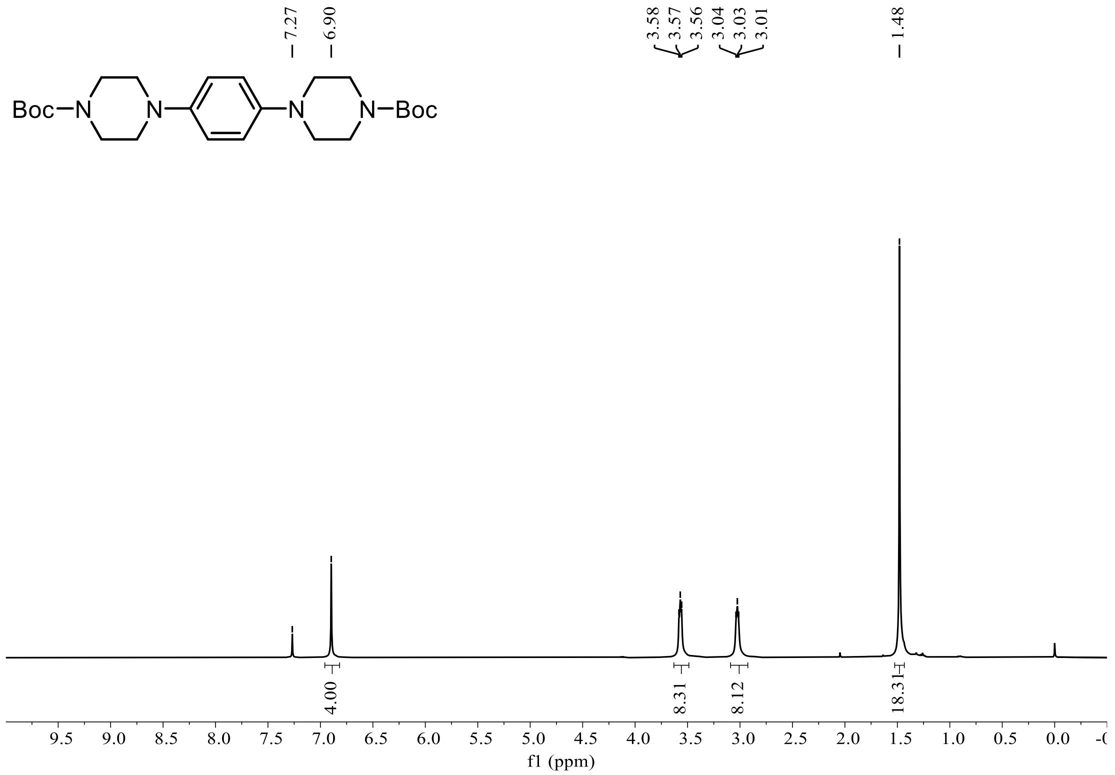
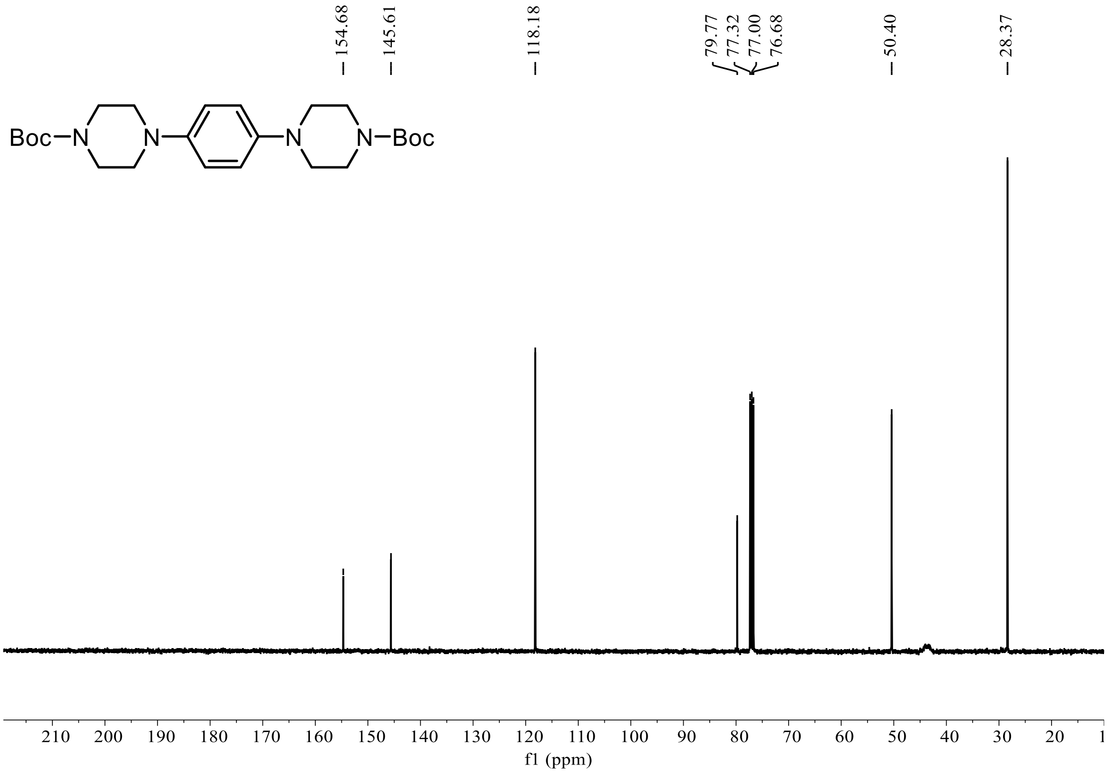


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3q

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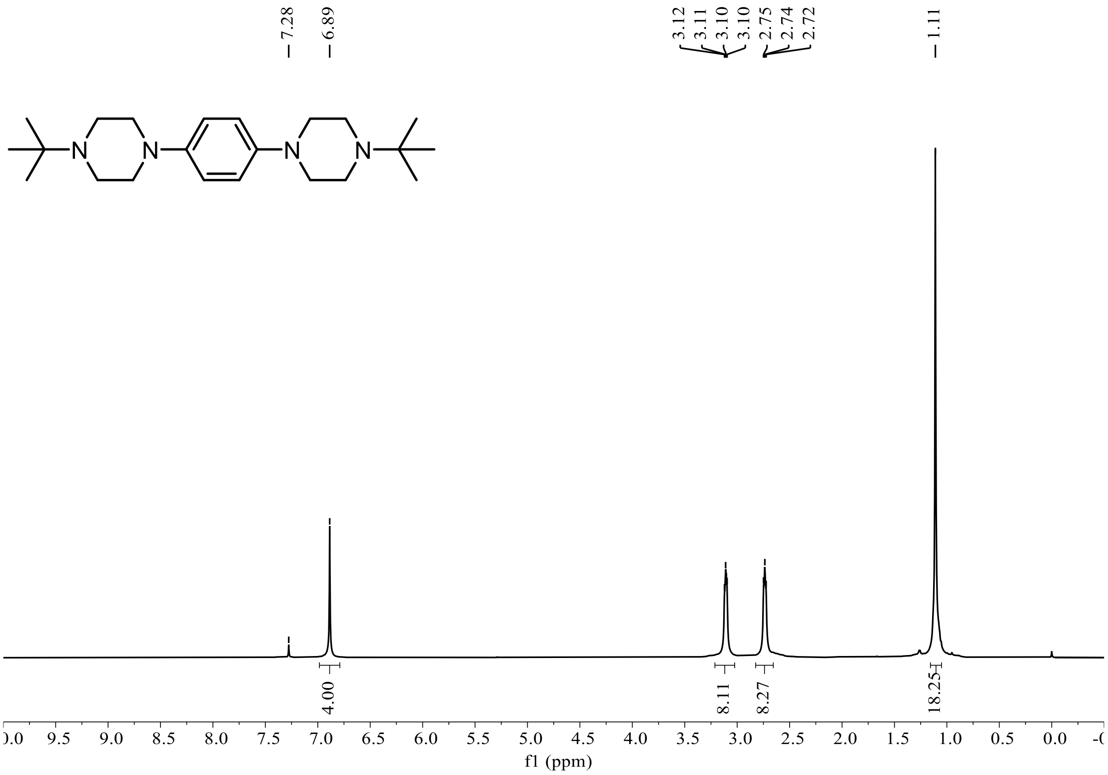
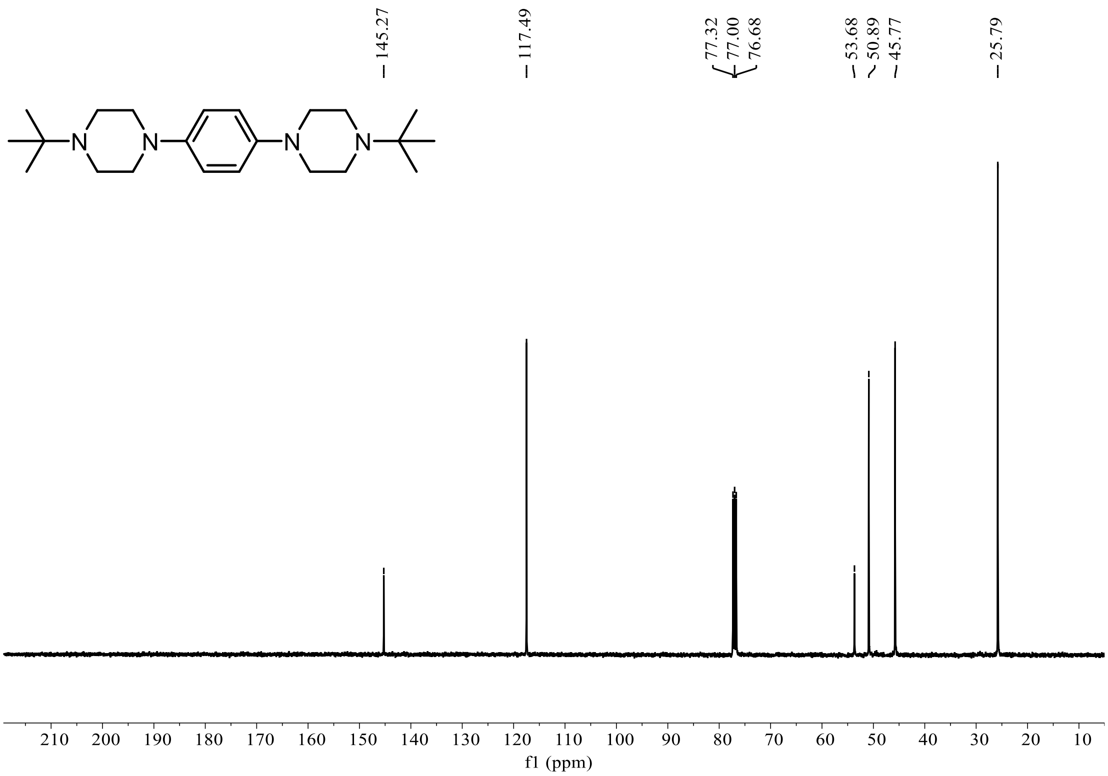
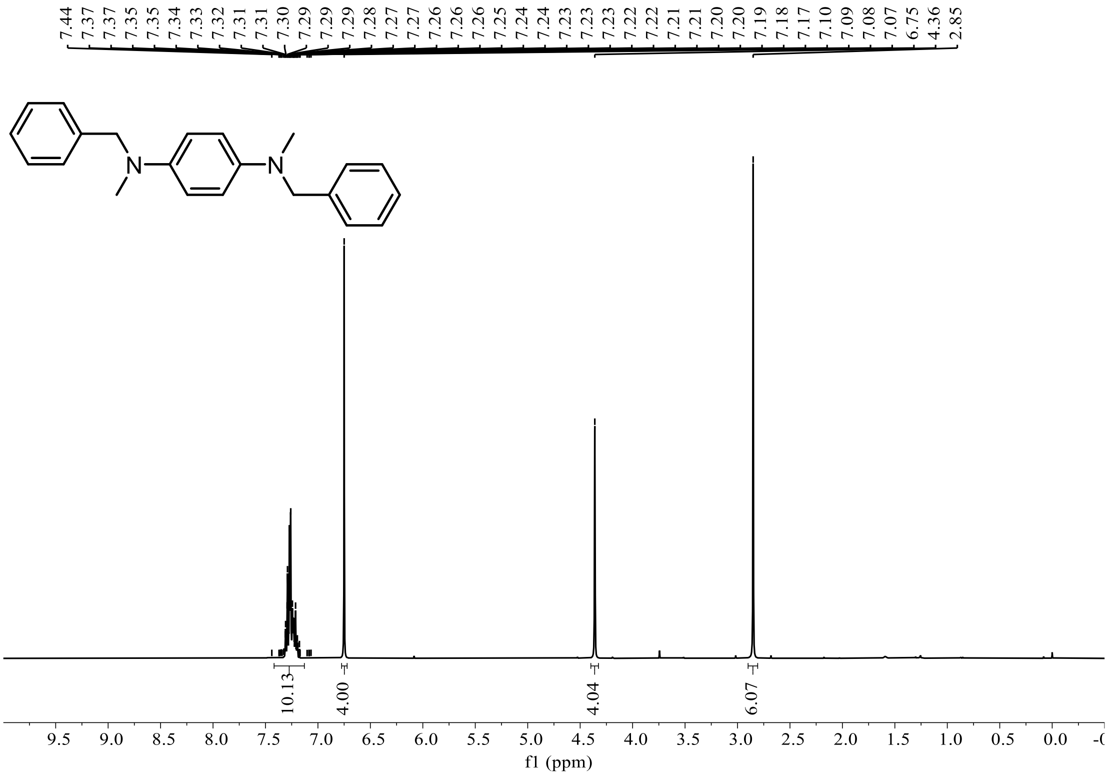


^{13}C NMR (101 MHz, $CDCl_3$)

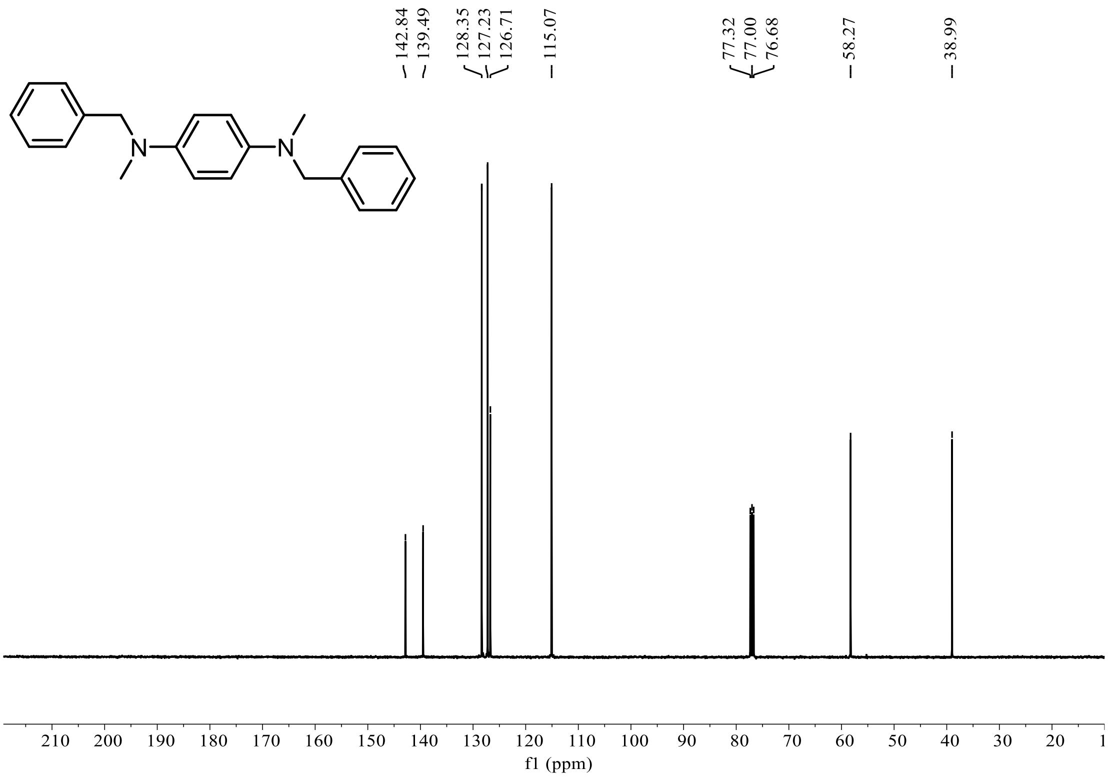


Spectrum of 3r

^1H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



Spectrum of 3s

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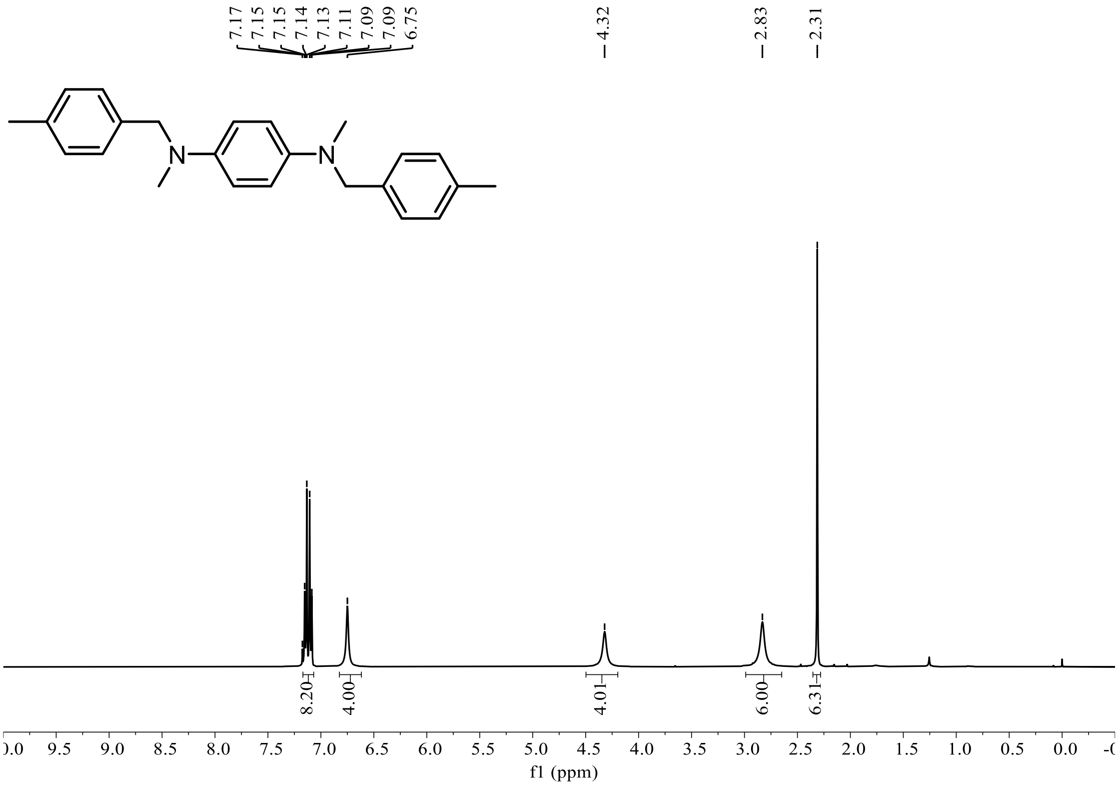
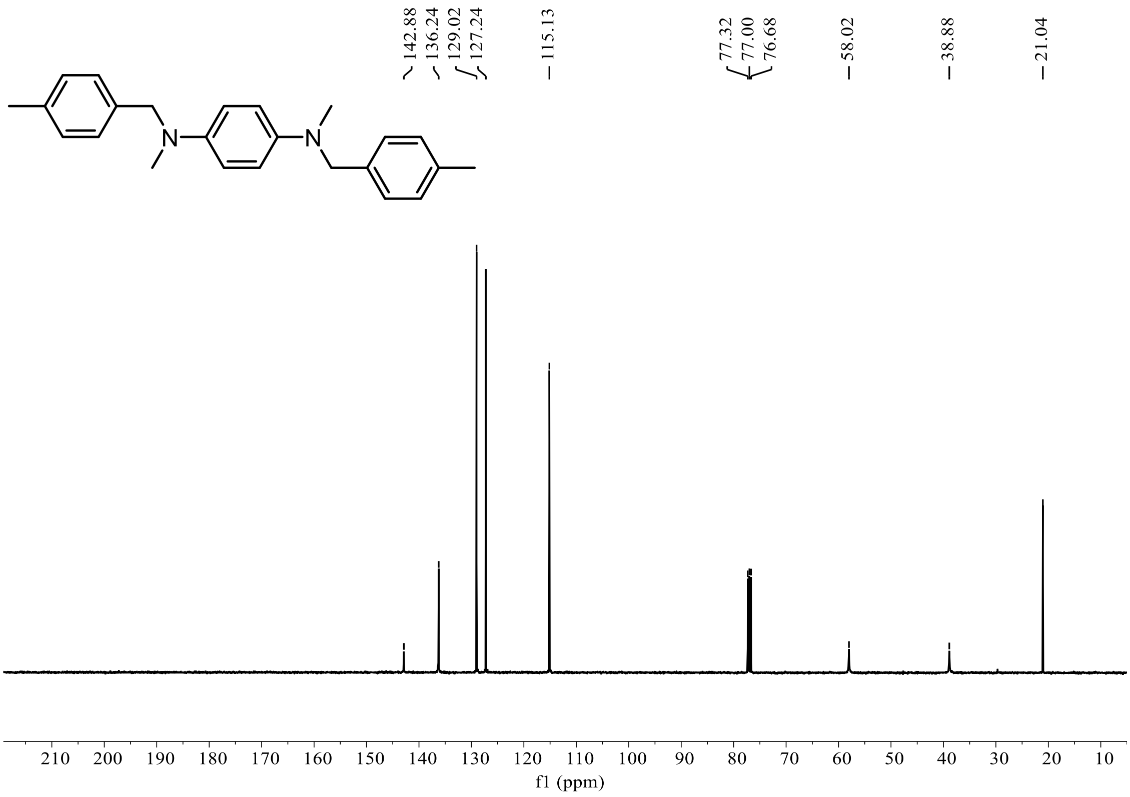


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3t

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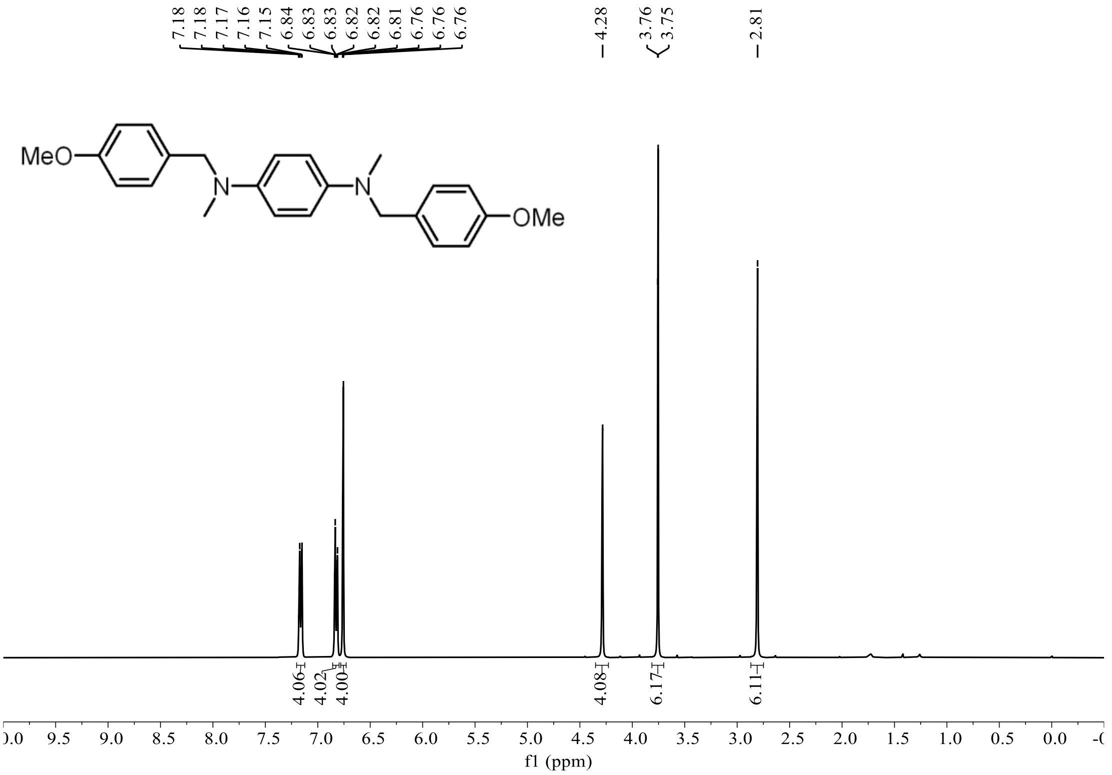
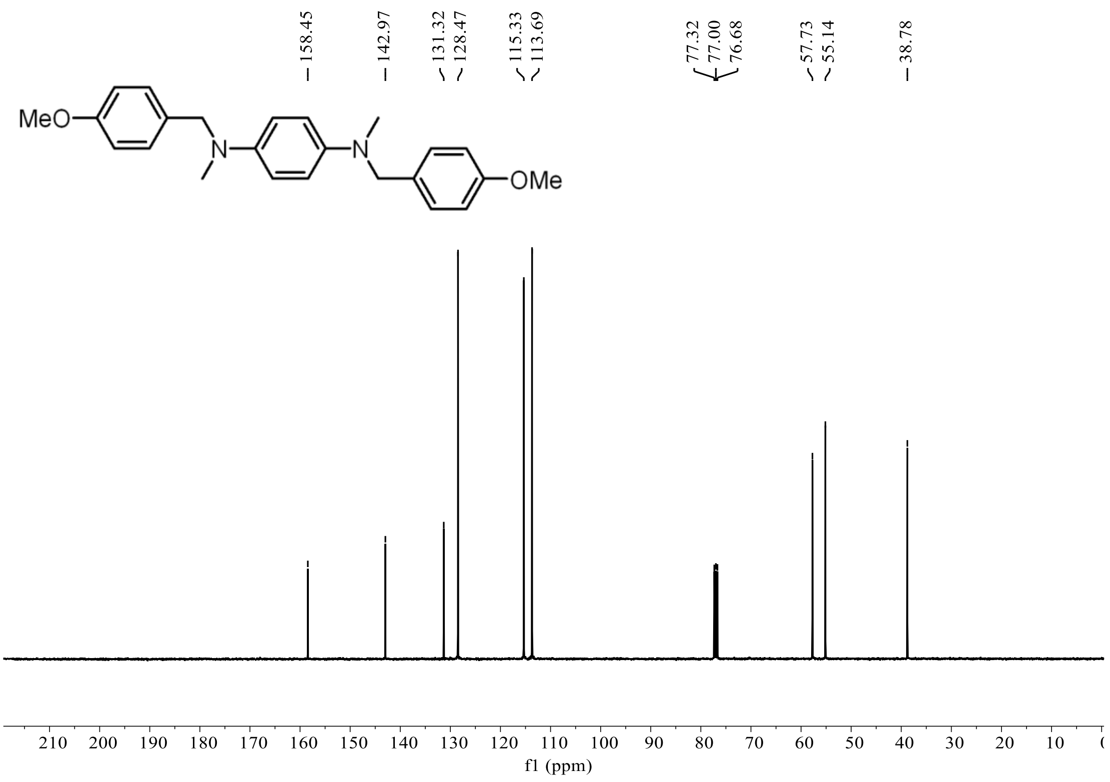


^{13}C NMR (101 MHz, $CDCl_3$)



Spectrum of 3u

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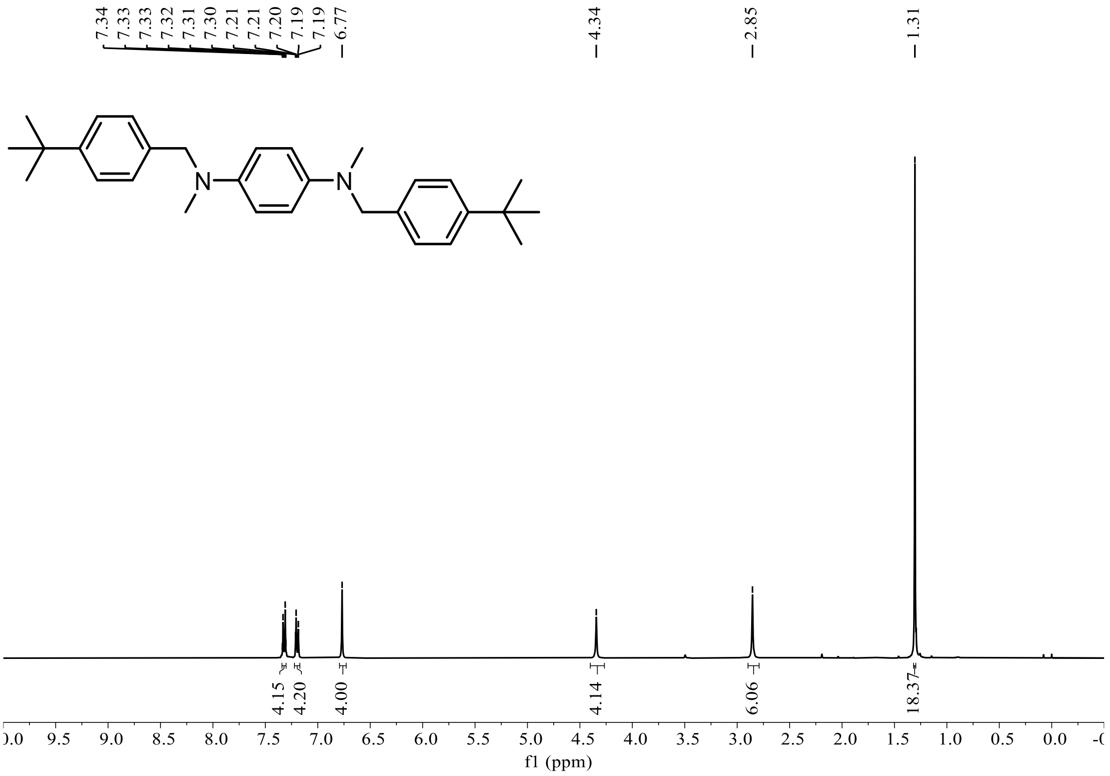
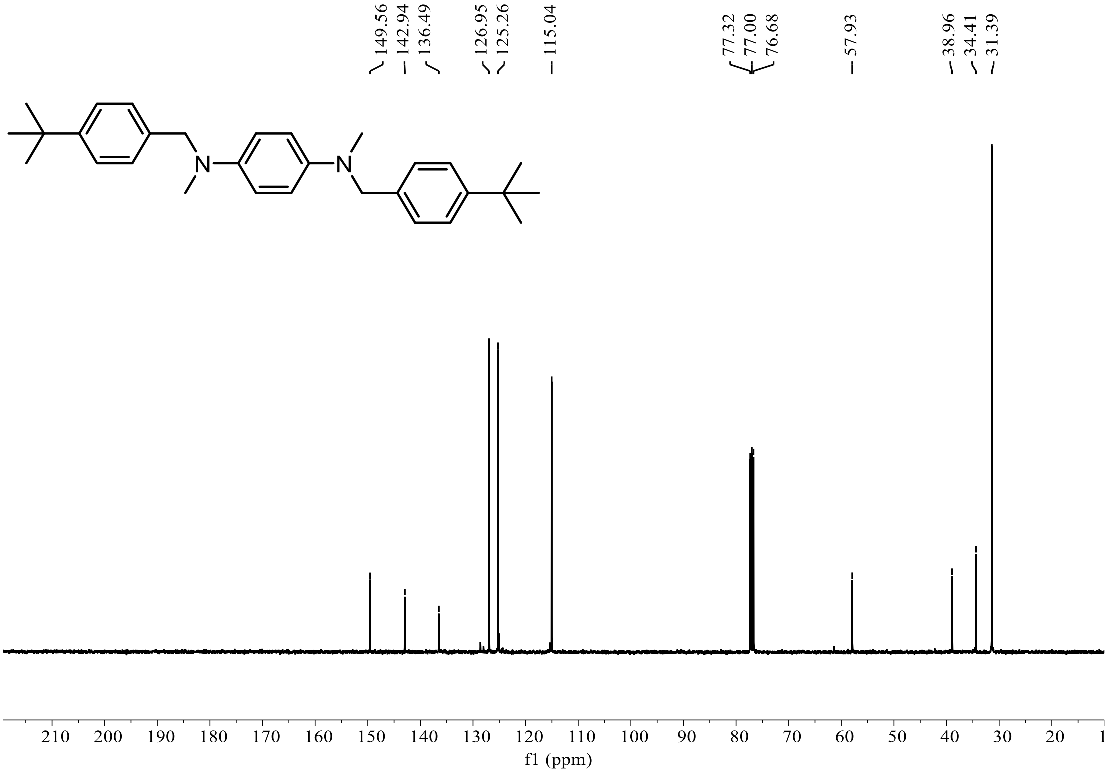


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3v

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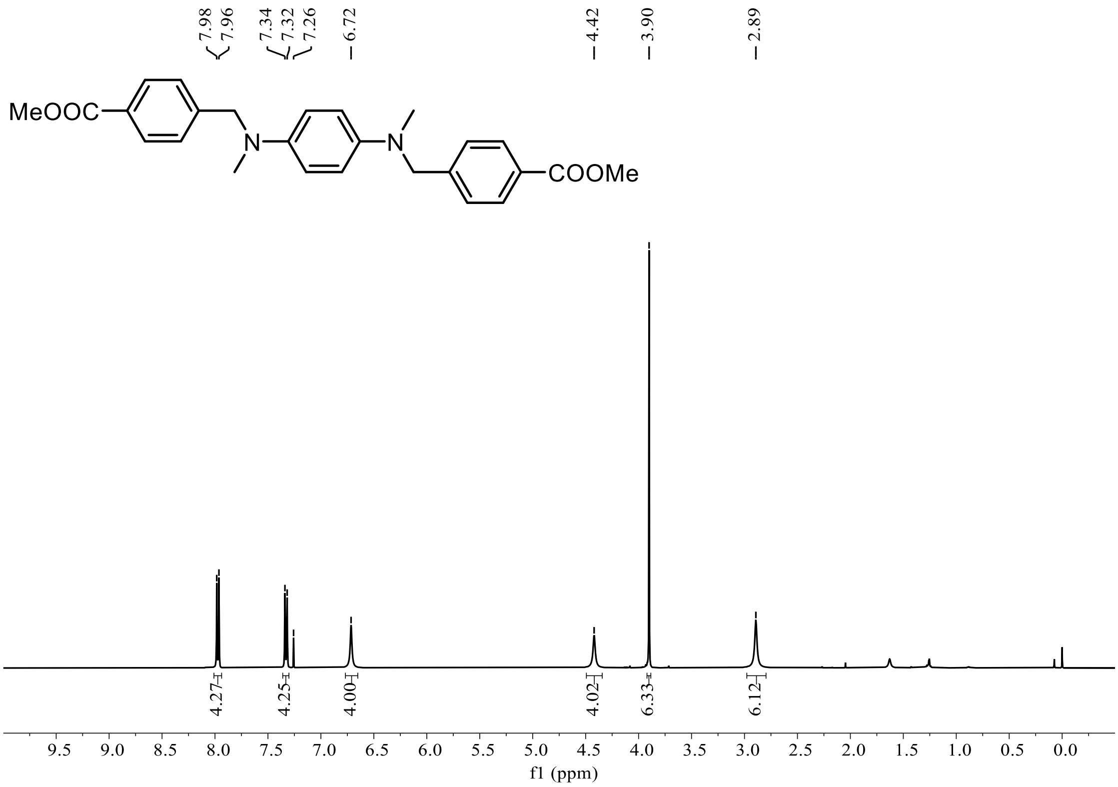
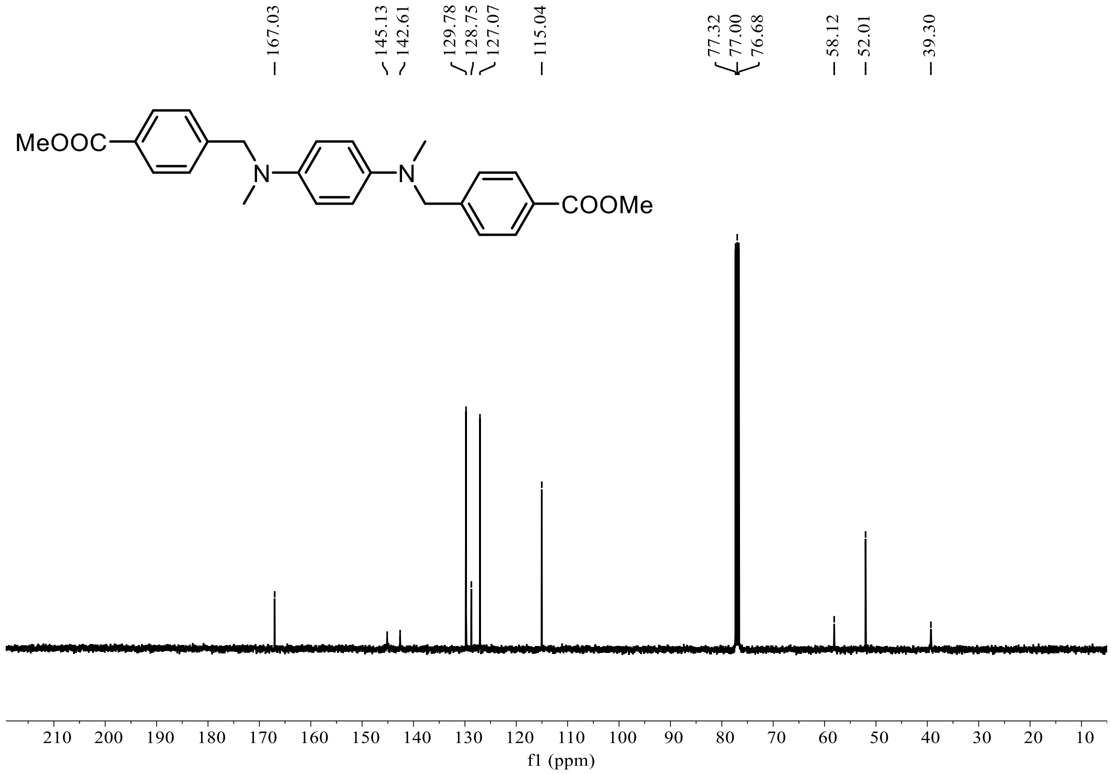


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3w

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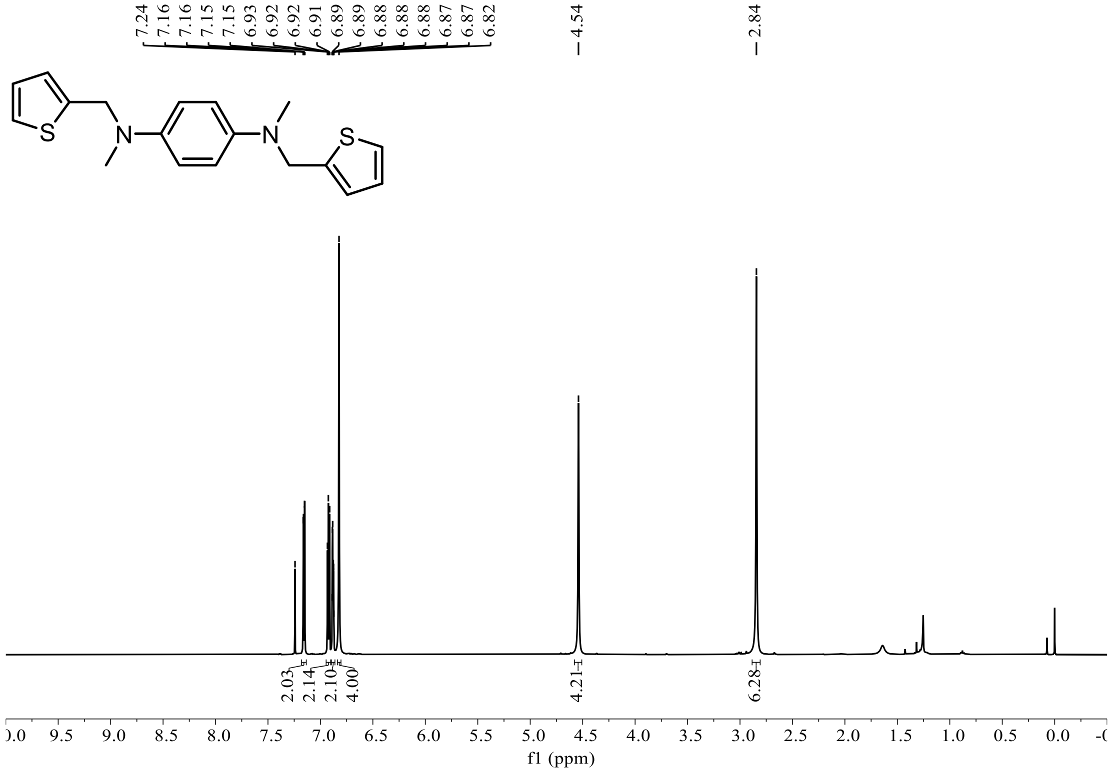
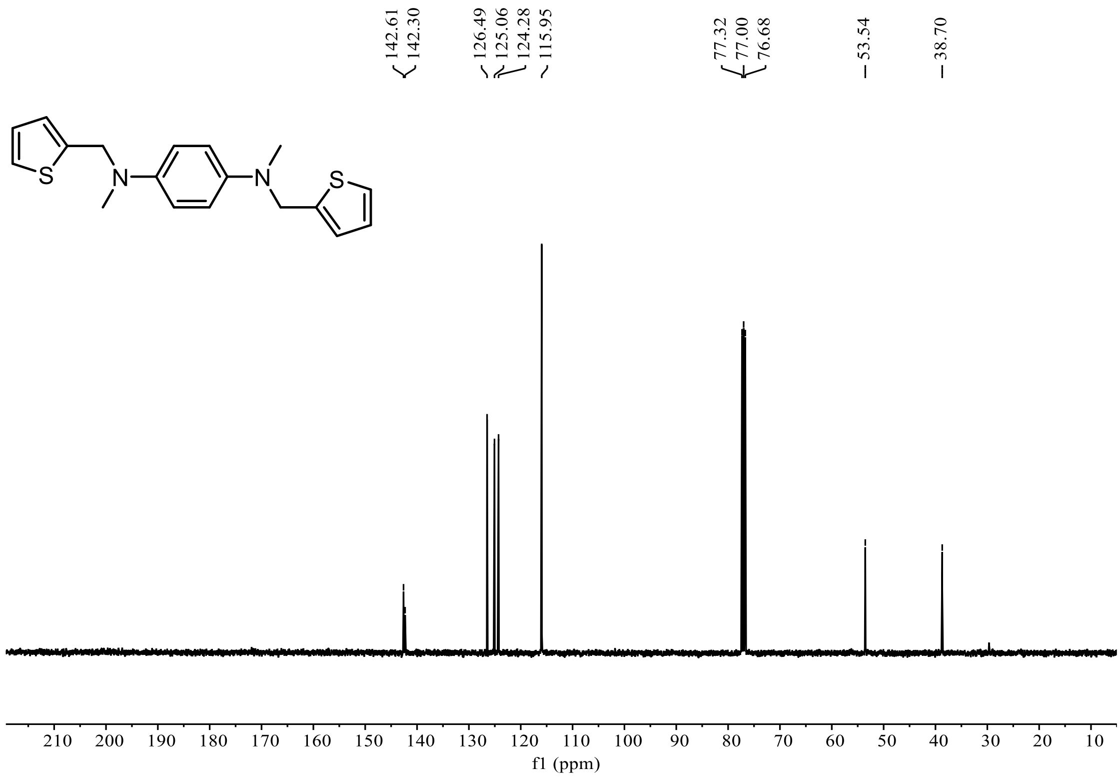


^{13}C NMR (101 MHz, $CDCl_3$)



Spectrum of 3x

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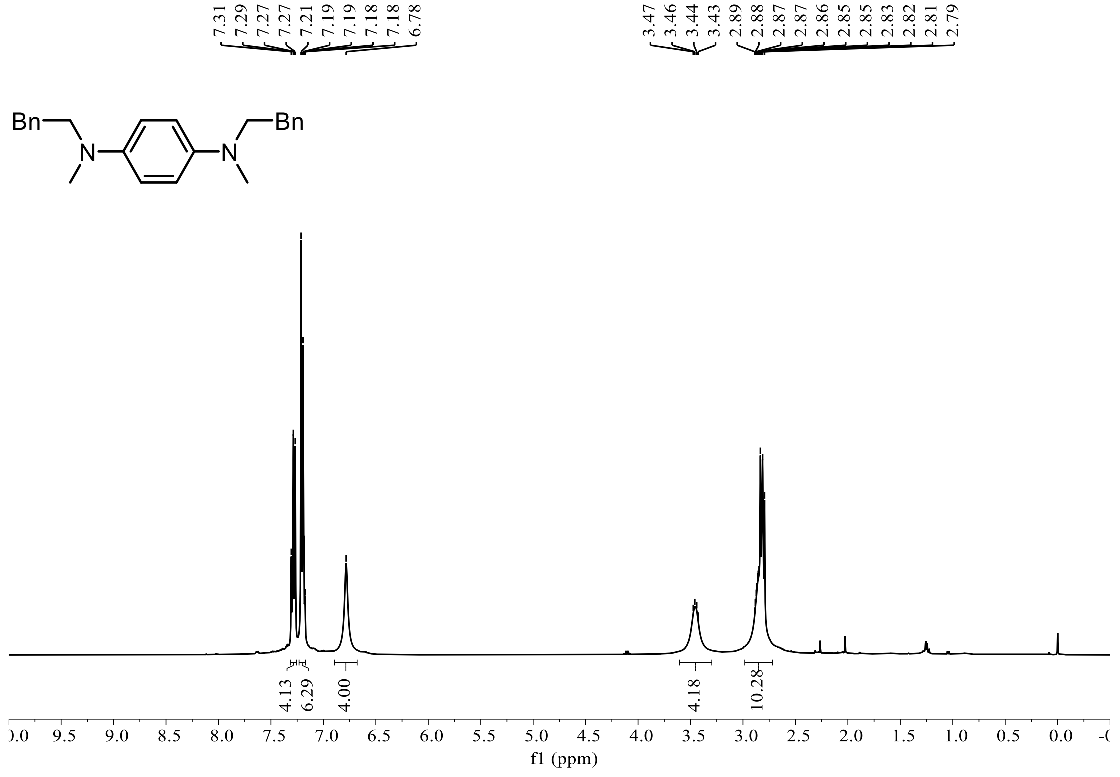
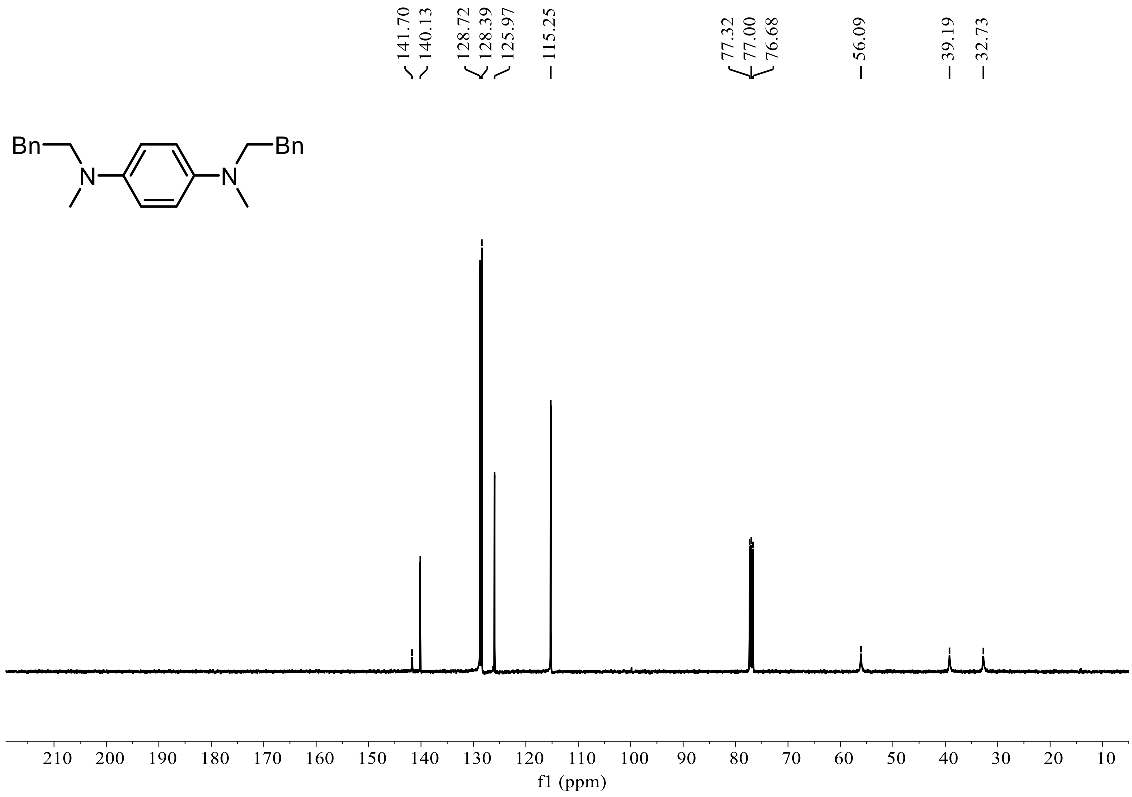


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3y

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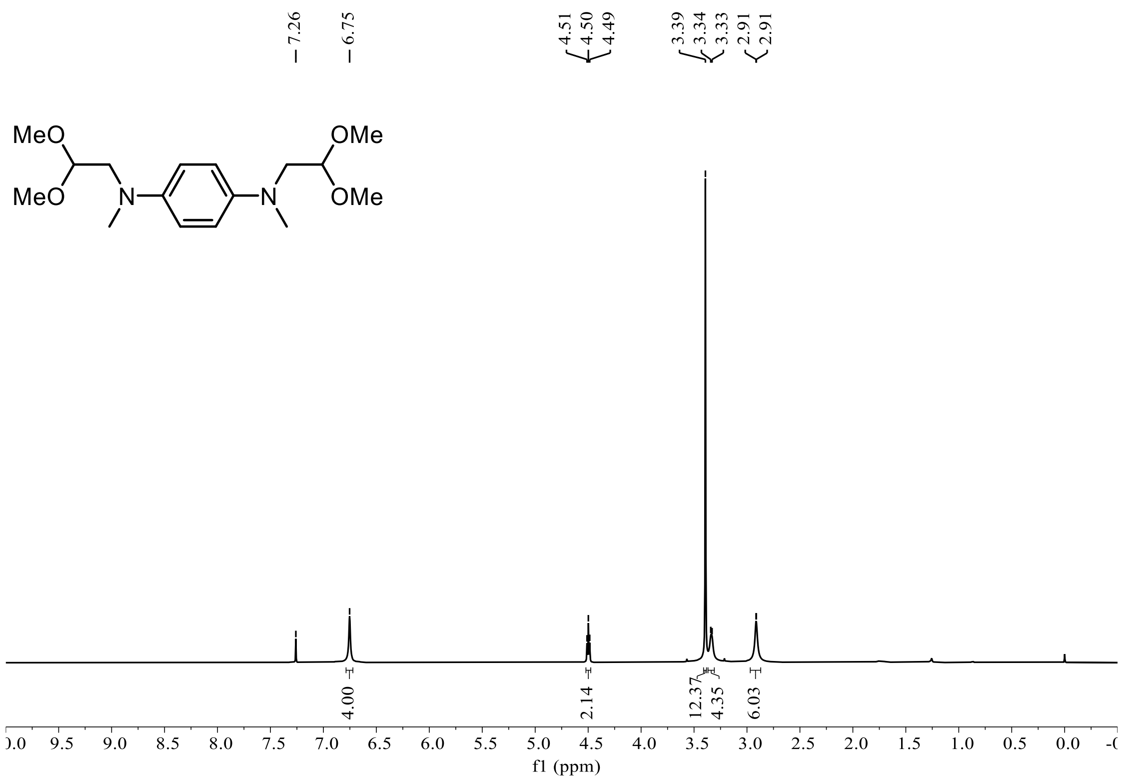
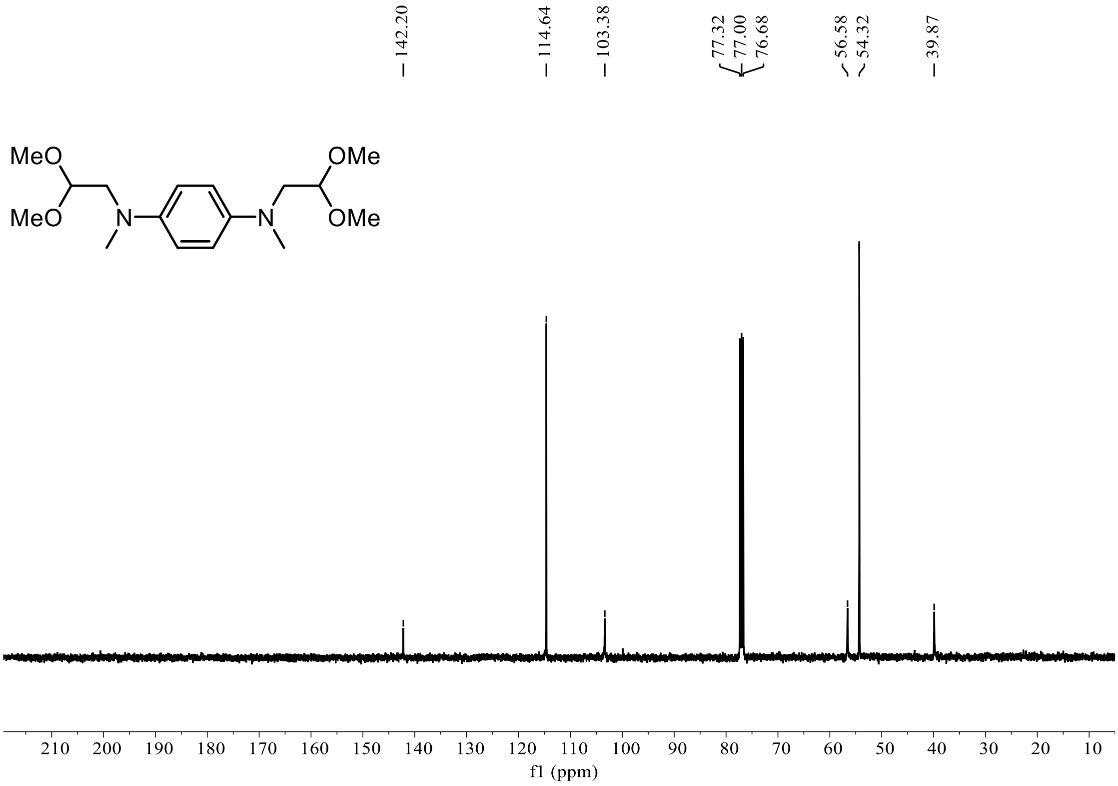


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3z

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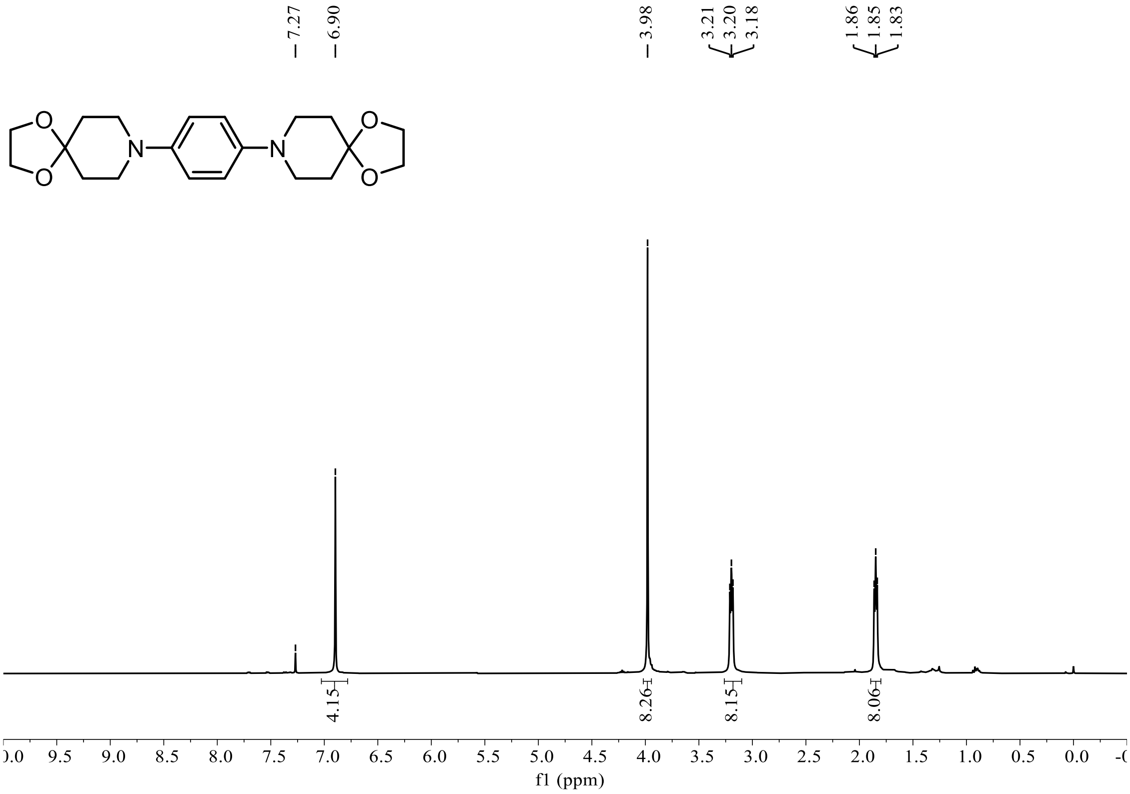
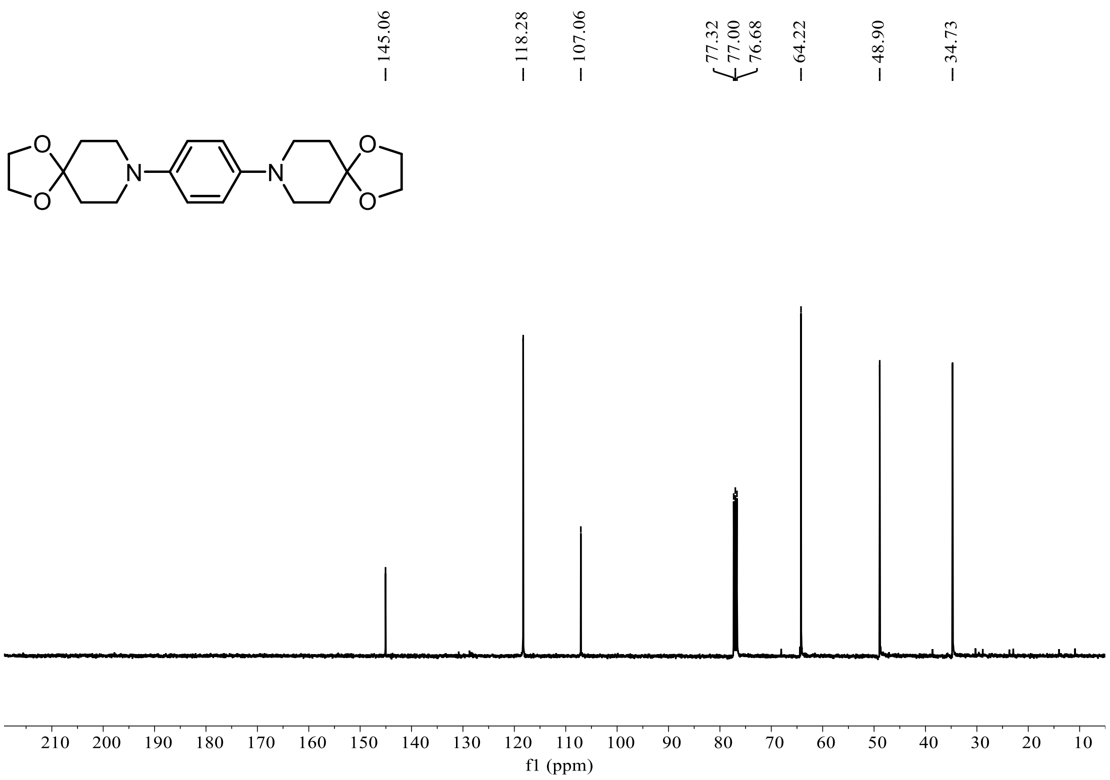
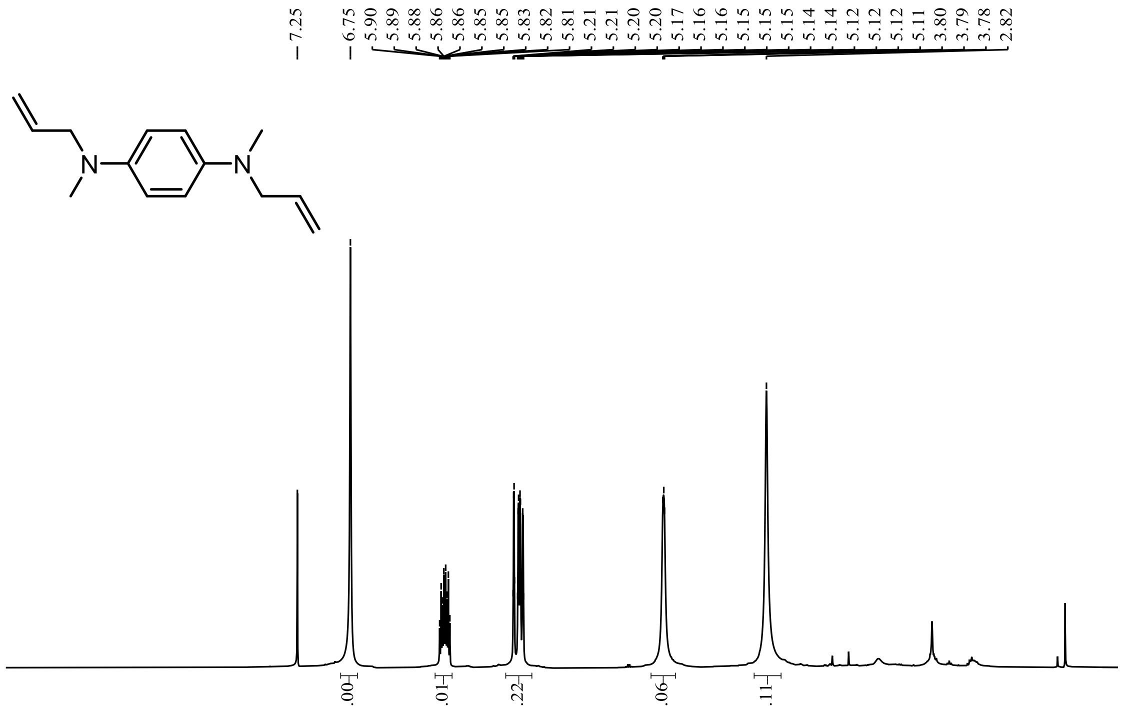


^{13}C NMR (101 MHz, CDCl$_3$)

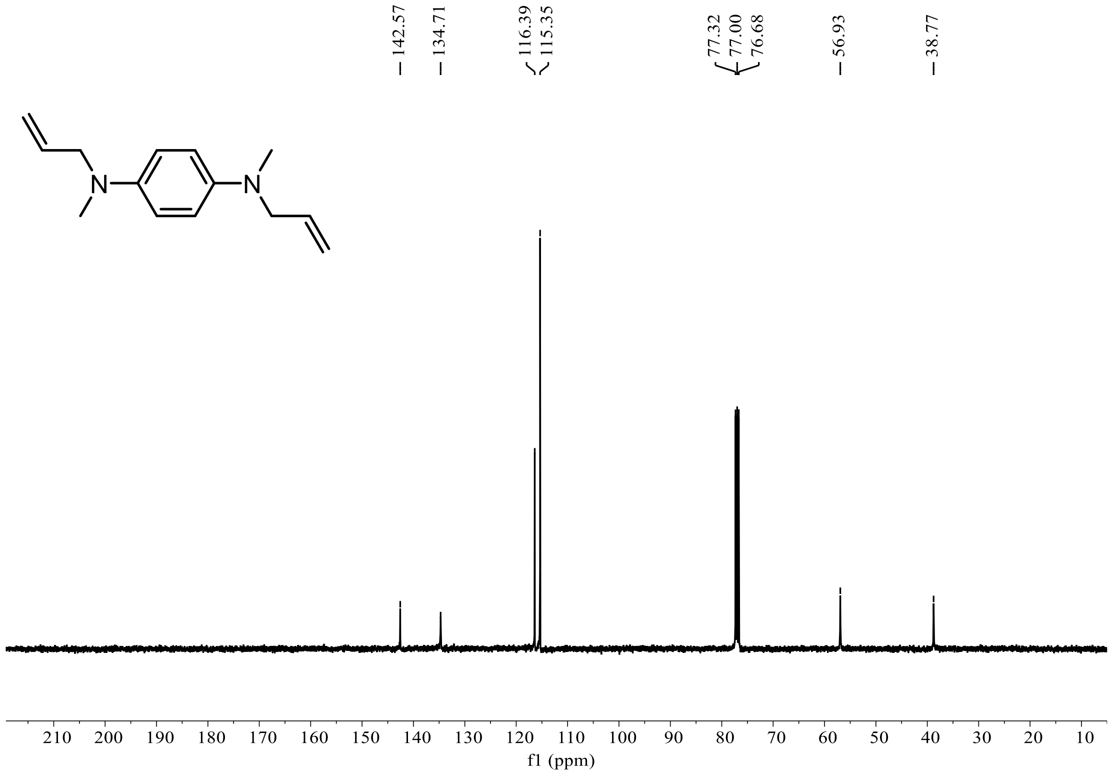


Spectrum of 3aa

^{1}H NMR (400 MHz, CDCl$_3$)

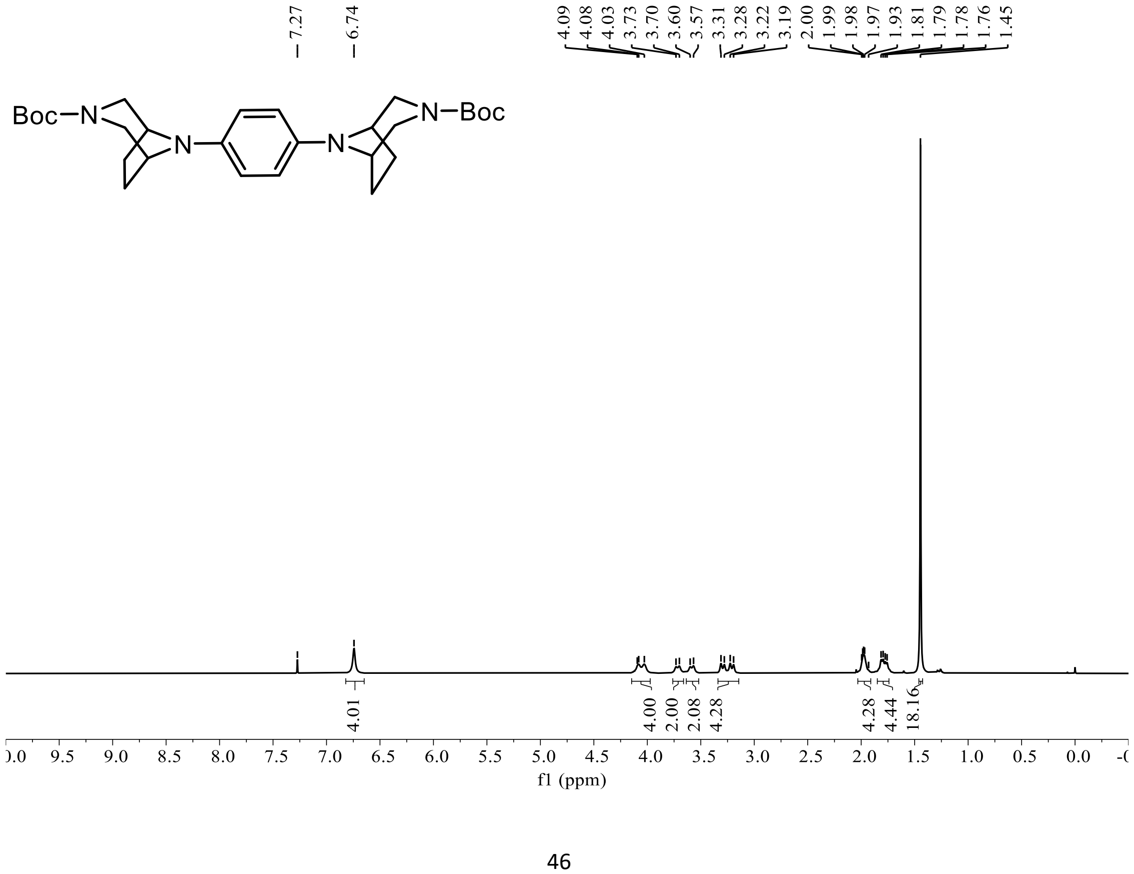


^{13}C NMR (101 MHz, CDCl$_3$)

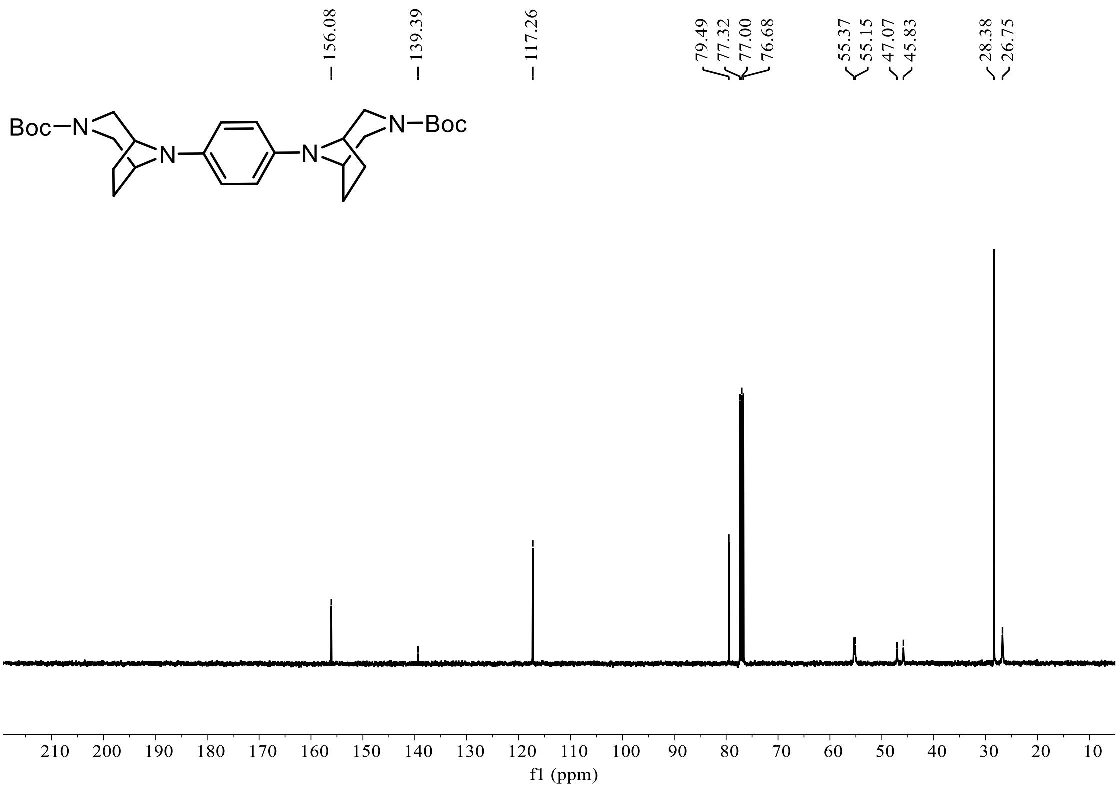


Spectrum of 3ab

^{1}H NMR (400 MHz, CDCl$_3$)

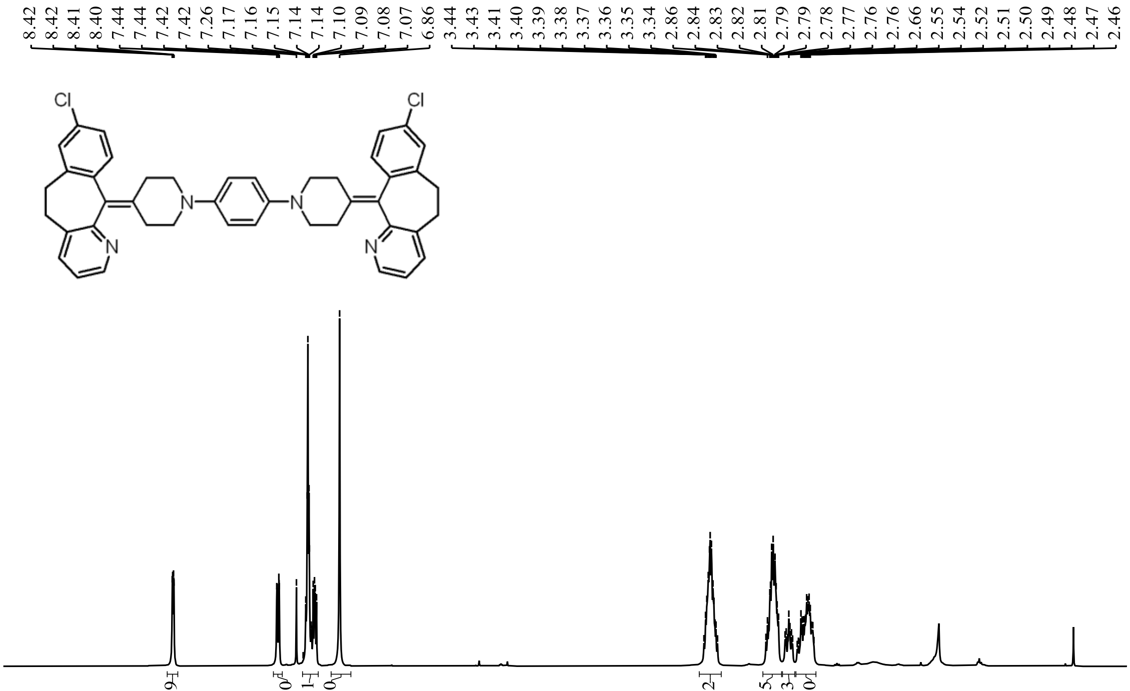


^{13}C NMR (101 MHz, CDCl$_3$)

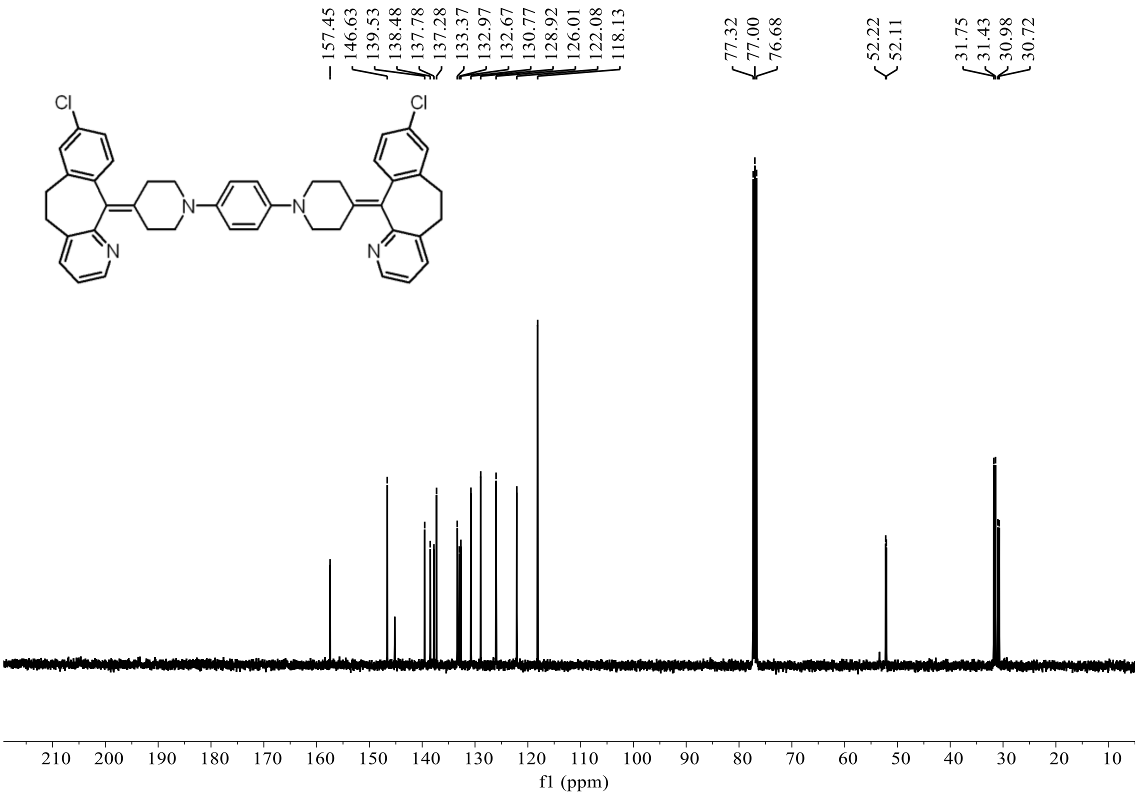


Spectrum of 3ac

^{1}H NMR (400 MHz, CDCl$_3$)

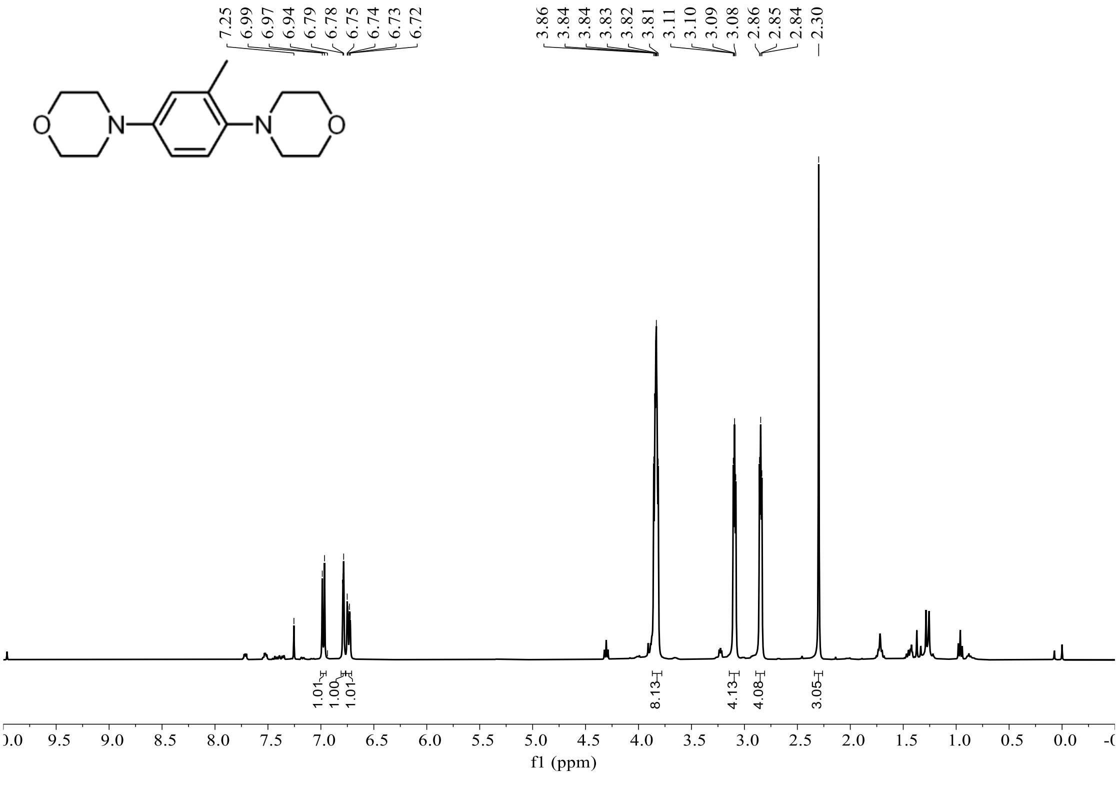


^{13}C NMR (101 MHz, CDCl$_3$)



Spectrum of 3ad

^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)