

Supplemental Information

Co(dppbsa)-catalyzed reductive *N,N*-Dimethylation of nitroaromatics with CO₂ and hydrosilane

Shuang-Shuang Ma^{a,b,1}, Rui Sun^{a,b,1}, Zi-Heng Zhang^{c,d,1}, Peng-Xin Guan^{a,b}, Jin-Qing Lin^d, Chun-Shan Li^{a,b,*}, and Bao-Hua Xu^{a,c,*}

^a Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institution of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

^b College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China.

^c School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China.

^d College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, China.

¹ These authors contribute this article equally.

* Corresponding Authors:

Bao-Hua Xu, Email: bhxu@bit.edu.cn

Chun-Shan Li, Email: csli@ipe.ac.cn

Table of Contents

1.	General information.....	S3
2.	Synthesis of cobalt complex catalysts	S4
3.	Reaction condition optimization	S10
4.	General procedure for <i>N,N</i> -Dimethylation of nitroarenes with CO ₂ and Characterization of Products 2.....	S11
5.	General procedure for scale-up reaction.....	S16
6.	General procedure for Reduction reaction of nitroarenes and Characterization of Products 3.....	S17
7.	The time-course plots for the reaction of intermediates	S22
8.	Detection of Cp*	S22
9.	GC-MS analysis of 6a and 7a before and after hydrolysis	S22
10.	NMR Spectra	S23
11.	Hydrosilylation of CO ₂	S70
12.	References	S74

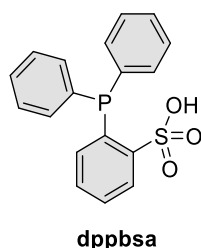
1. General information

All commercial reagents were purchased from Beijing Innochem Science & Technology co., LTD without further purification, and were used without further purification unless otherwise stated. Toluene was dried and distilled under argon prior to use. All reactions were done under argon using standard glove-box and the solvents were dried before use unless otherwise noted. In particular, the Schlenk techniques were used in synthesis of the cobalt catalyst. All catalytic reactions were carried out in 25 mL autoclaves (Wuzhou Dingchuang (Beijing) Technology Co., Ltd.). The autoclaves were made from stainless steel and an insert (Teflon) was also used to avoid cross-contaminations with metals from previous runs in the autoclave. ESI-MS analysis was performed on a Bruker time of flight mass spectrometer micro TOF-Q II using an electrospray ionization (ESI) source. NMR spectra were recorded on a Bruker ASCEND spectrometer (^1H , 600 MHz; $^{13}\text{C}\{^1\text{H}\}$, 151 MHz; ^{31}P , 243 MHz). ^1H NMR, ^{13}C NMR and ^{31}P NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constants (J) are reported in Hz and relative integrations are reported. Column chromatography was performed using silica gel (200-300 mesh). Analytical TLC was done using pre-coated silica gel 60 F254 plates. GC analysis was performed using Aglient GC-7890B equipped with a capillary column (DB-FFAP, 30 m \times 0.32 mm) using a flame ionization detector. GC-MS was performed using GCMS-QP2020 with Rtx-5MS (30 m \times 0.25 mm) column.

Data collections were performed at 180 K on Rigaku diffractometer, using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by SHELXTL or Olex program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compound Co(dppbsa) is summarized in following tables. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: CCDC 2149710 (Co(dppbsa)). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

2. Synthesis of cobalt complex catalysts

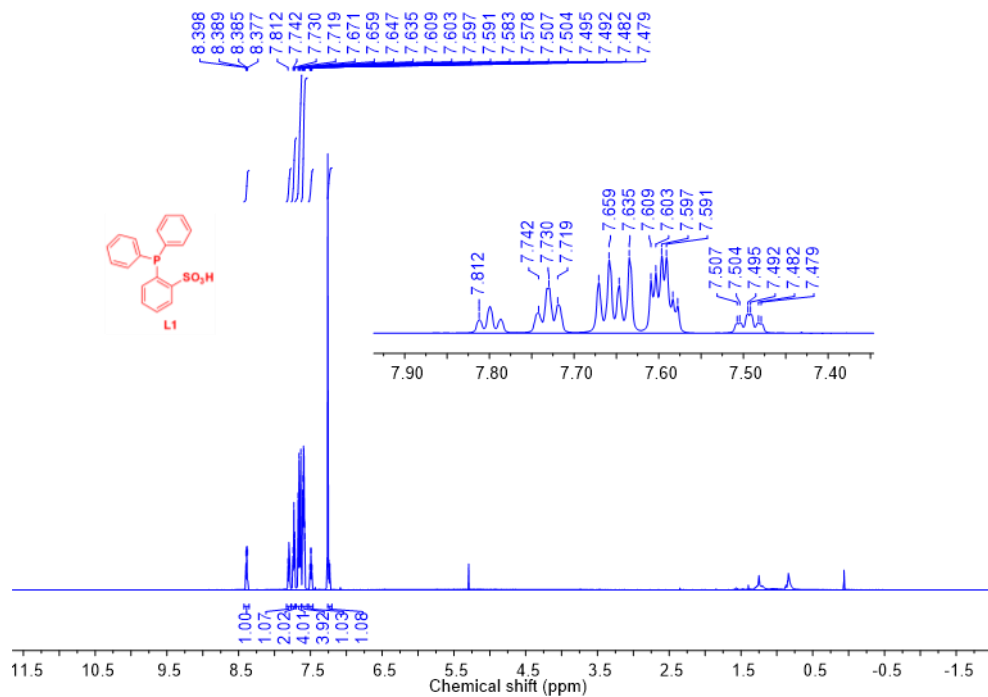
2.1. Synthesis of 2-(diphenylphosphaneyl)benzenesulfonic acid (dppbsa)¹



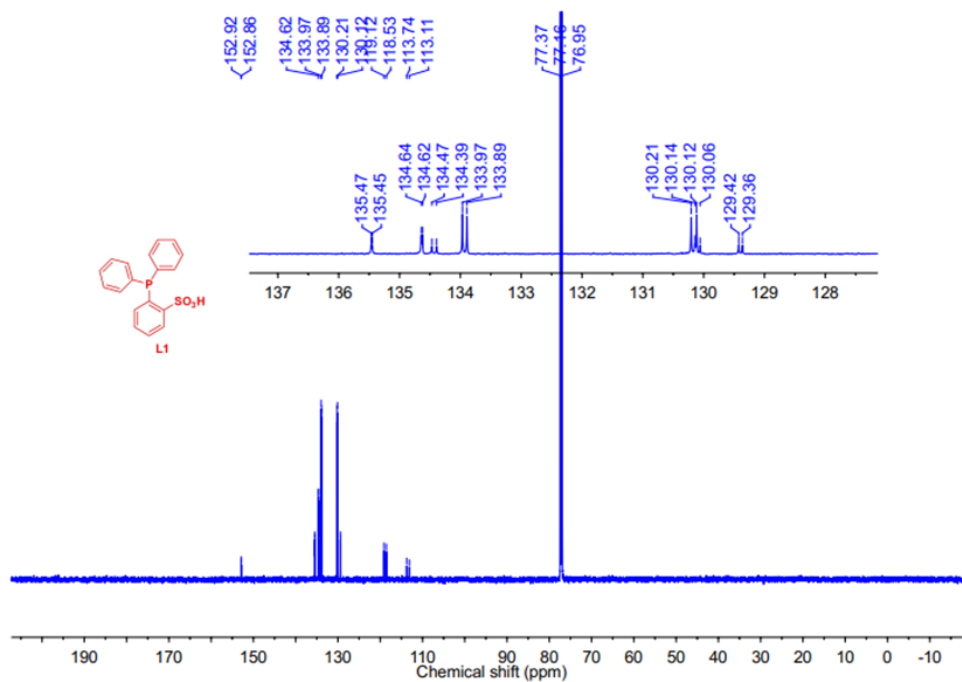
2-(diphenylphosphaneyl)benzenesulfonic acid was prepared according to the reported literature procedure^[1].

Under protection of argon, dry benzenesulfonic acid (1.580 g, 10 mmol) and THF (30 mL) were added in a 100 mL Schlenk tube equipped with a Teflon stopcock

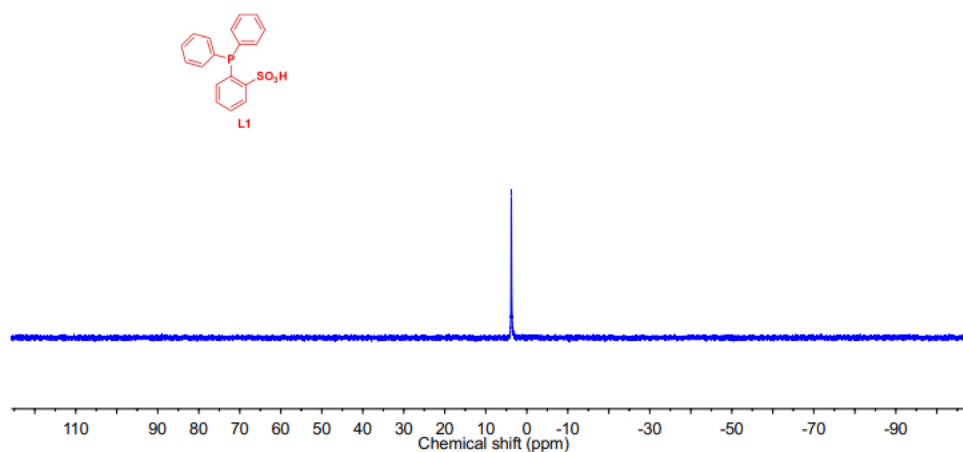
and a magnetic stirring bar. *n*-BuLi (2.5 M solution in hexane, 8.0 mL, 20 mmol) was added dropwise to the mixture at -78 °C over 10 min. The mixture was stirring at 25 °C for 45 minutes and then cooled at -78 °C. a solution of bis(phenyl)chlorophosphane (2.200 g, 10 mmol) in THF (10 mL) was added at -78 °C over 30 min. After stirring for 12 h at room temperature, the solvent was removed in vacuo to leave a white solid. The solid was dissolved in dichloromethane (40 mL) and extracted with acidic water (2 mL of concentrated HCl in 30 mL of water), and then twice with degassed water (30 mL). The organic layers were dried over MgSO₄ evaporated under vacuum to yield a pale white solid. The solid was recrystallized from dichloromethane/*n*-hexane followed by concentration under vacuum to afford a white powder (*dppbsa*) in 65% yield. ¹H NMR (600 MHz, 298K, CDCl₃): δ = 8.39 (m, 1H), 7.80 (m, 1H), 7.73 (m, 2H), 7.66 (m, 2H), 7.64 (m, 2H), 7.59 (m, 4H), 7.49 (m, 1H), 7.25 (m, 1H), N.O. (-SO₃H). ¹³C{¹H} NMR (151 MHz, 298K, CDCl₃): δ = 152.9 (*J*_{PC} = 8.9 Hz, *i*-Ph-SO₃H), 135.5 (*J*_{PC} = 3.2 Hz, *i*-Ph), 134.6 (*J*_{PC} = 3.0 Hz, 2×*i*-Ph), 134.5, 134.4, 134.0, 133.9, 130.2, 130.1(4), 130.1(1), 130.0(5), 129.4(2), 129.3(6), 119.1, 118.5, 113.7, 113.1 (Ph). ³¹P{¹H} NMR (243 MHz, 298K, CDCl₃): δ = 3.8. HRMS (ESI) *m/z* calcd for C₁₈H₁₅O₃NaPS⁺ (M+Na)⁺, 365.03717; Found: 365.0368.



¹H NMR (600 MHz, 298K, CDCl₃) of dppbsa

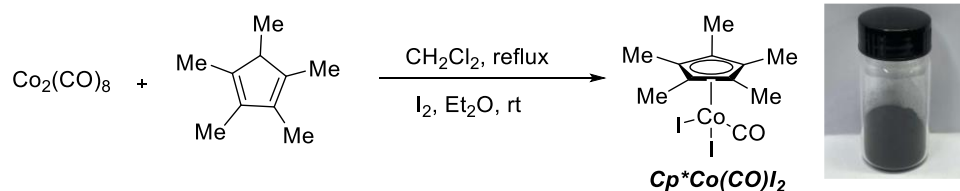


¹³C{¹H} NMR (151 MHz, 298K, CDCl₃) of dppbsa

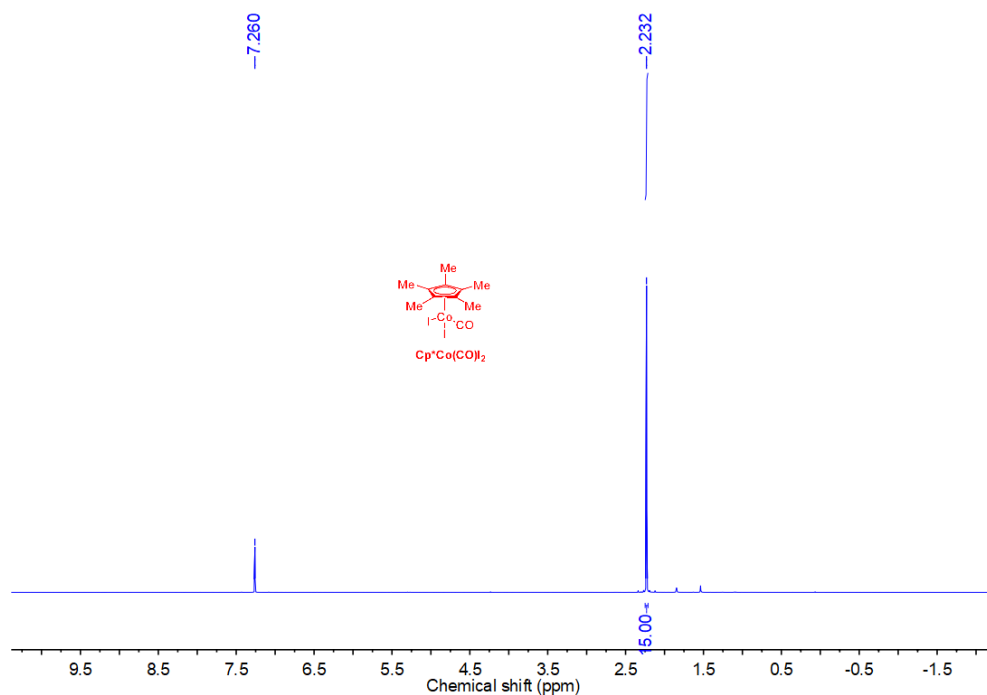


$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 298K, CDCl_3) of dppbsa

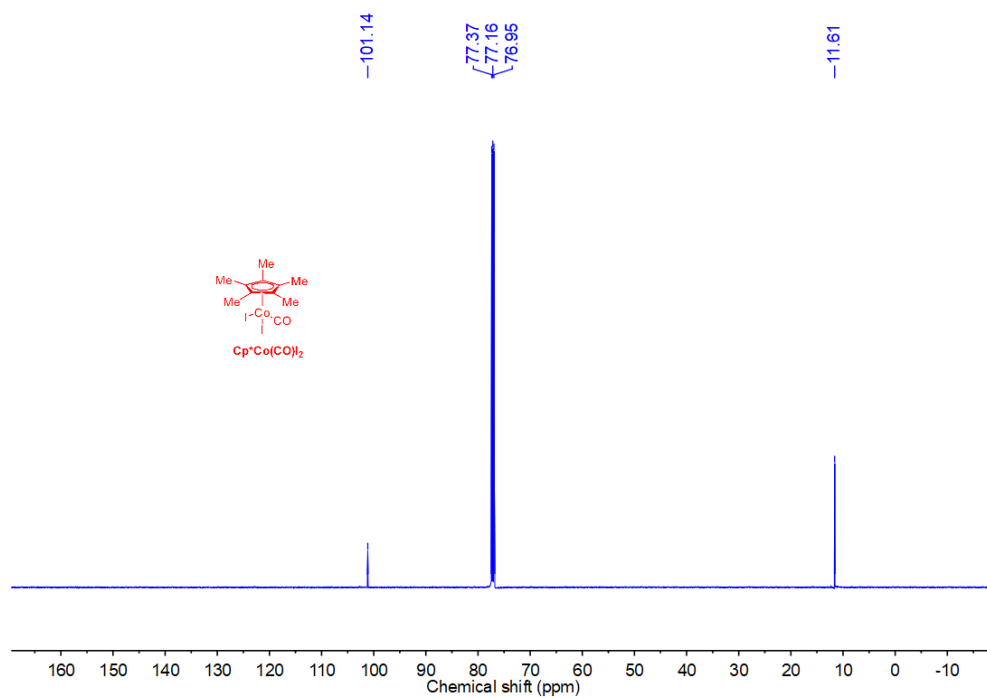
2.2. Synthesis of cobalt precursor ($\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$)



Cobalt precursor ($\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$) was prepared according to the reported literature procedure^[1]. Under protection of argon, to a well-dried 100 mL Schlenk tube were successively added $\text{Co}_2(\text{CO})_8$ (1.0 g, 2.92 mmol), degassed CH_2Cl_2 (20 mL) and pentamethylcyclopentadiene (1.11 mL, 7.08 mmol). The mixture was refluxed at 60 °C under argon stream for 6 h and then cooled to room temperature. The solvent was removed in vacuo. The residue was dissolved in degassed Et_2O (10 mL) and then iodine (1.8 g, 7.1 mmol) in degassed Et_2O (50 mL) was added drop wise at room temperature with stirring. (Caution: During the addition, the mixture was refluxed due to the exothermic reaction and CO gas evolution was observed.) After the mixture was stirred at room temperature for 4 h, the solvent was evaporated. Resulting residue was purified by silica gel column chromatography (n-hexane then $\text{CH}_2\text{Cl}_2/\text{n-hexane} = 4/1$) to afford deep purple crystalline solid (2.1 g, 75% yield). ^1H NMR (600 MHz, 298K, CDCl_3): $\delta = 2.23$ (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 298K, CDCl_3): $\delta = 101.2, 11.6$.

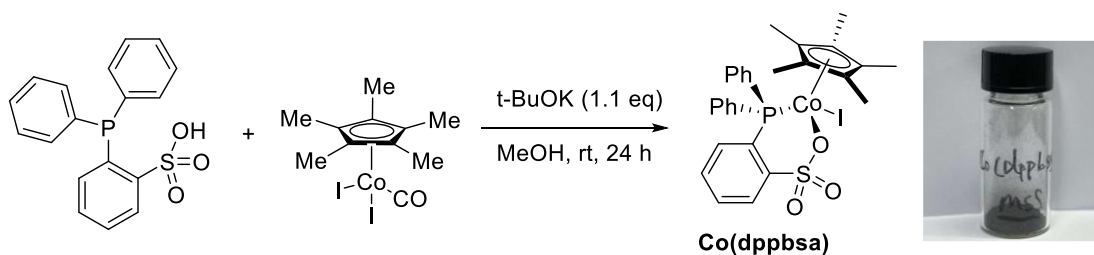


^1H NMR (600 MHz, 298K, CDCl_3) of $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$

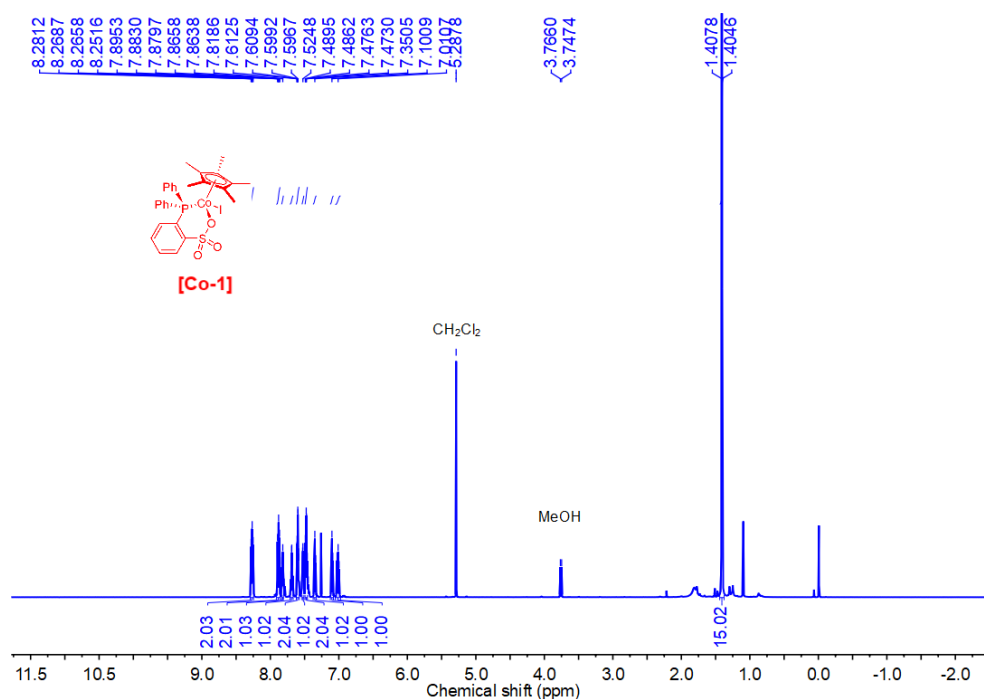


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 298K, CDCl_3) of $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$

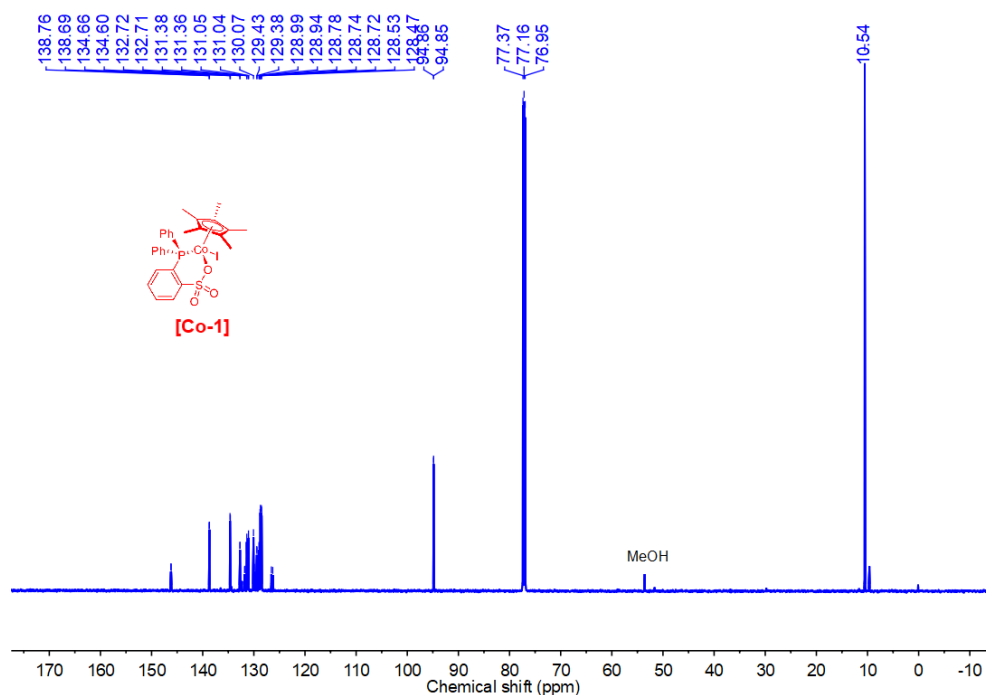
2.3. Synthesis, structure and characterisation of complex $\text{Co}(\text{dppbsa})$



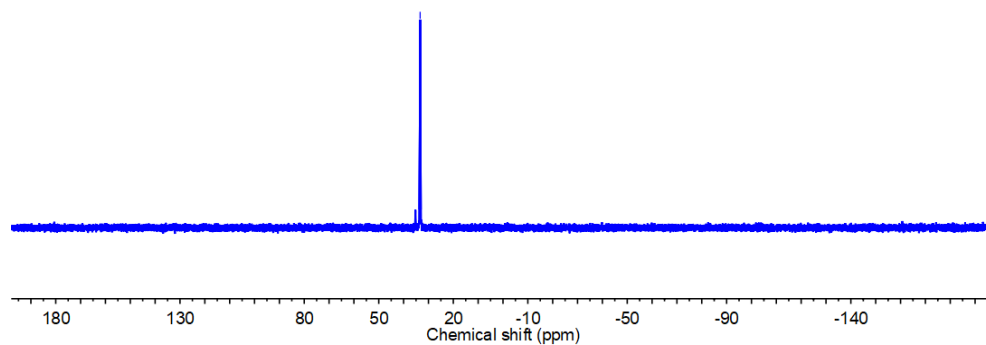
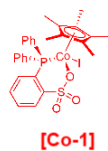
General procedure for the preparation of cobalt complex: Under protection of argon, 2-(diphenylphosphanyl)benzenesulfonic acid (dppbsa) (3.42 g, 10 mmol, 1.0 equiv.) and t-BuOK (1.47 g, 12 mmol, 1.2 equiv.) were added to a 250 mL Schlenk tube equipped with a magnetic stirring bar. Degassed dried MeOH (100 mL, Water \leq 50 ppm) was added and the solution was stirred for 1 h at room temperature which generated a clear colorless solution. To this solution $Cp^*Co(CO)I_2$ (4.78 g, 10 mmol, 1.0 equiv.) was added. After stirring for 24 h, MeOH was evaporated, and then the crude was dissolved in 30 ml of CH_2Cl_2 . The solution was filtered by diatomite to remove the inorganic salt. The filtrate was concentrated under reduced pressure to give a dark green solid residue. The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with MeOH/ CH_2Cl_2 = 1:50 to give the product Co(dppbsa) as dark blue solid in 42% yields. **1H NMR** (600 MHz, 298 K, $CDCl_3$): δ = 8.27 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.88 (t, $^3J_{HH}$ = 9.6 Hz, 2H), 7.82 (m, 1H), 7.69 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.60 (td, $^3J_{HH}$ = 7.8, 1.8 Hz, 2H), 7.53 (m, 1H), 7.47 (m, 2H), 7.35 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.01 (t, $^3J_{HH}$ = 9.0 Hz, 1H), 1.41 (d, $^3J_{HH}$ = 1.8 Hz, 15H, Me). **$^{13}C\{^1H\}$ NMR** (151 MHz, 298K, $CDCl_3$): δ = 146.2 (J_{PC} = 11.2 Hz), 138.7 (J_{PC} = 10.4 Hz), 134.6 (J_{PC} = 9.0 Hz), 132.7 (J_{PC} = 2.2 Hz), 131.8 (J_{PC} = 9.5 Hz), 131.4 (J_{PC} = 2.0 Hz), 131.0 (J_{PC} = 2.0 Hz), 130.1 (J_{PC} = 11.6 Hz), 129.4 (J_{PC} = 6.7 Hz), 128.9 (J_{PC} = 6.7 Hz), 128.7 (J_{PC} = 9.7 Hz), 128.5 (J_{PC} = 9.7 Hz), 126.6, 126.3, 94.9 (J_{PC} = 2.3 Hz, CH), 10.5 (Me). **$^{31}P\{^1H\}$ NMR** (243 MHz, 298K, $CDCl_3$): δ = 33.4. **HRMS** (ESI) m/z calcd for $C_{28}H_{29}CoO_3PS^+$ (M-D) $^+$, 535.09015; Found: 535.0851.



^1H NMR (600 MHz, 298 K, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 298K, CDCl_3)



$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, 298K, CDCl_3)

X-ray crystal structure analysis of $\text{Co}(\text{dppb})\cdot\text{CH}_2\text{Cl}_2$: formula $\text{C}_{29}\text{H}_{31}\text{Cl}_2\text{CoIO}_3\text{PS}$, $M = 747.30$, black block $0.36 \times 0.05 \times 0.03$ mm, $a = 10.7008(4)$, $b = 13.6759(3)$, $c = 11.2342(5)$ Å, $\alpha = 90$, $\beta = 113.510(5)$, $\gamma = 90$, $V = 1507.58(11)$ Å³, $\rho_{\text{calc}} = 1.646\text{g}/\text{cm}^3$, $\mu = 1.922$ mm⁻¹, Semi-empirical absorption correction ($0.59189 \leq T \leq 1.00000$), $Z = 2$, monoclinic, space group $P2_1/n$, $\lambda = 0.71073$ Å, $T = 180.00(10)$ K, ω and ϕ scans, 7272 reflections collected (\pm

$h, \pm k, \pm l$), 358 refined parameters, $R = 0.0403$, $wR^2 = 0.0883$, max. (min.), hydrogen atoms calculated and refined as riding atoms.

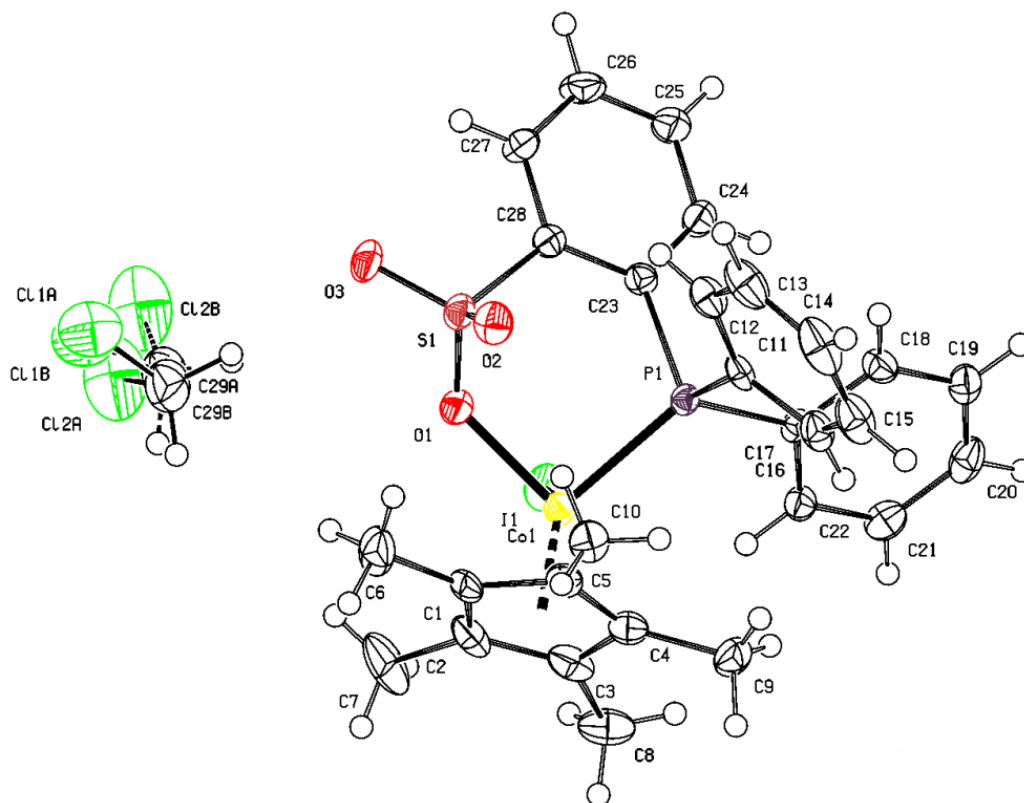
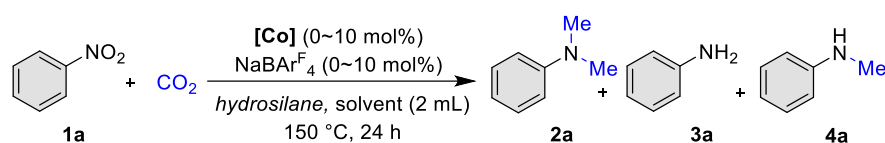


Figure S1. Co(dppbsa)·CH₂Cl₂ from the X-ray single crystal structure.

3. Reaction condition optimization

Table S1. Screening of the reaction conditions^a



Entry ^a	[Co] (mol%)	<i>Hydrosilane (equiv.)</i>		CO ₂ (MPa)	Additive (mol%)	solvent	Conv. (%)	Yield ^[b] (%)		
		<i>PhSiH₃</i>	<i>Si-H</i>					2a	3a	4a
1	5	6	-	3	-	toluene	100	35	24	4
2	5	10	-	3	-	toluene	100	41	20	3
3	5	11	-	3	-	toluene	100	41	20	3
4	5	15	-	3	-	toluene	100	40	15	5
5	5	16	-	3	-	toluene	100	40	52	5
6	5	10	-	3	-	THF	100	19	25	5
7	5	10	-	3	-	CH ₃ CN	25	5	10	0
8	5	10	-	3	-	DMSO	20	10	5	0
9	5	10	-	3	-	DMAC	30	14	10	0
10	5	-	<i>Et₃SiH</i> (10)	3	-	toluene	22	16	0	4
11	5	-	<i>Et₃SiH</i> (33)	3	-	toluene	37	24	8	2

12	5	-	<i>TMDSO</i> (10)	3	-	toluene	47	14	5	15
13	5	-	<i>(EtO)₃SiH</i> (10)	3	-	toluene	0	0	0	0
14	5	-	<i>Ph₂SiH₂</i> (10)	3	-	toluene	79	18	35	0
15	5	-	<i>PMHS</i> (80)	3	-	toluene	42	32	4	0
16	5	6	<i>PMHS</i> (5)	3	-	toluene	100	45	40	2
17	5	6	<i>PMHS</i> (10)	3	-	toluene	100	56	41	0
18	5	6	<i>PMHS</i> (20)	3	-	toluene	100	52	39	0
19	5	6	<i>PMHS</i> (40)	3	-	toluene	100	56	35	2
20	5	6	<i>PMHS</i> (80)	3	-	toluene	100	69	20	5
21	5	8	<i>PMHS</i> (80)	3	-	toluene	100	72	23	0
22	5	10	<i>PMHS</i> (80)	3	-	toluene	100	71	20	0
23	5	15	<i>PMHS</i> (80)	3	-	toluene	81	50	39	3
24	5	6	<i>TMDSO</i> (10)	3	-	toluene	100	59	30	2
25	5	6	<i>Ph₂SiH₂</i> (10)	3	-	toluene	100	55	30	5
26	5	6	<i>Et₃SiH</i> (10)	3	-	toluene	100	74	15	0
27	5	6	<i>Et₃SiH</i> (15)	3	-	toluene	100	85	4	0
28	5	6	<i>Et₃SiH</i> (25)	3	-	toluene	100	78	15	0
29	5	6	<i>Et₃SiH</i> (15)	2	-	toluene	100	63	18	5
30	5	6	<i>Et₃SiH</i> (15)	5	-	toluene	100	70	20	2
31 ^c	5	6	<i>Et₃SiH</i> (15)	3	-	toluene	83	50	20	8
32 ^d	5	6	<i>Et₃SiH</i> (15)	3	-	toluene	100	34	18	12
33	0	6	<i>Et₃SiH</i> (15)	3	-	toluene	0	0	0	0
34 ^e	0	6	<i>Et₃SiH</i> (15)	3	-	toluene	65	28	20	10

^[a] Reaction condition: **1a** (0.2 mmol), CO₂ (0~5 MPa), [Co] (0~10 mol%), NaBAR^F₄ (5 mol%), hydrosilane (x equiv.), solvent (2 mL), at 150 °C for 24 h, under argon. ^[b] determined by GC analysis using biphenyl as the internal standard. ^[c] 130 °C. ^[d] without NaBAR^F₄. ^[e] Cp*Co(CO)I₂ (5 mol%) was added in reaction. PMHS = (poly(methylhydrosiloxane), MW = 1900), TMDSO = 1,1,3,3-tetramethyldisiloxane. DMSO = dimethyl sulfoxide, DMAC = *N,N*-dimethylacetamide.

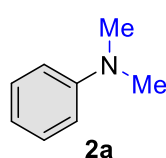
4. General procedure for *N,N*-Dimethylation of nitroarenes with CO₂ and Characterization of Products 2

Under protection of argon, nitroarenes (0.2 mmol, 1.0 equiv.), Co(dppbsa) (5 mol%), NaBAR^F₄ (5 mol%), PhSiH₃ (1.2 mmol, 6.0 equiv.), Et₃SiH (3.0 mmol, 15.0 equiv.) and 2 mL of toluene were charged in a 25 mL autoclave with magnetic bar, subsequently charged with CO₂ (3 MPa). The mixture was stirred at the desired temperature (150 °C) for a 24 h. After the desired reaction time, the reaction mixture was allowed to cool to room temperature. The distribution of the product was determined by GC and GC-MS analysis using biphenyl as an internal standard. The solvent was removed under vacuum and then the product was further purified by flash column chromatography on silica gel to obtain the desired product.



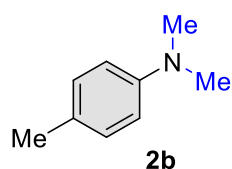
Figure S2. 25-mL autoclaves (Wuzhou Dingchuang (Beijing) Technology Co., Ltd.)

***N,N*-dimethylaniline (2a)**



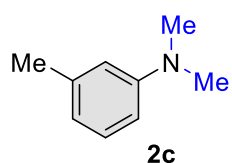
Isolated yield: 75%, (petroleum ether/ethyl acetate = 50:1); Brown liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.31 (m, 2H), 6.81 (m, 3H), 3.01 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 150.7, 129.1, 116.7, 112.7, 40.8. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{12}\text{N}^+$ ($\text{M}+\text{H}$) $^+$: 122.0964; found: 122.0956.

***N,N*,4-trimethylaniline (2b)**



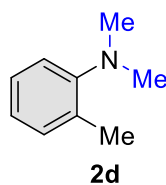
Isolated yield: 80%, (petroleum ether/ethyl acetate = 50:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.07 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 2H), 6.71 (d, $^3J_{\text{HH}}$ = 8.44 Hz, 2H), 2.92 (s, 6H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 148.9, 129.7, 126.3, 113.4, 41.2, 20.3. HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{14}\text{N}^+$ ($\text{M}+\text{H}$) $^+$: 136.1121; found: 136.1127.

***N,N*,3-trimethylaniline (2c)**



Isolated yield: 75%, (petroleum ether/ethyl acetate = 50:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.22 (m, 1H), 6.65 (m, 3H), 3.00 (s, 6H), 2.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 150.8, 138.78, 129.0, 117.7, 113.5, 110.0, 40.8, 22.0. HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{14}\text{N}^+$ ($\text{M}+\text{H}$) $^+$: 136.1121; found: 136.1118.

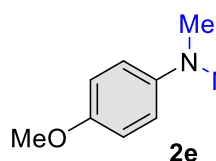
***N,N*,2-trimethylaniline (2d)**



Isolated yield: 71%, (petroleum ether/ethyl acetate = 50:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.41 (t, $^3J_{\text{HH}}$ = 6.8 Hz, 2H), 7.29 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 1H), 7.21 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 1H), 2.95 (s, 6H), 2.61 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 152.7, 132.1, 131.1, 126.4, 122.6, 118.4, 44.2, 18.3. HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{14}\text{N}^+$ ($\text{M}+\text{H}$) $^+$: 136.1121; found:

136.1122.

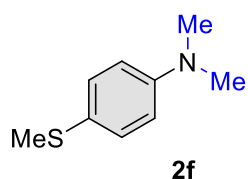
4-methoxy-*N,N*-dimethylaniline (2e)



Isolated yield: 81%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 6.85 (m, 2H), 6.78 (d, ³J_{HH} = 8.3 Hz, 2H), 3.77 (s, 3H), 2.87 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 152.1, 145.6, 115.0, 114.7, 55.7, 41.9.

HRMS (ESI) m/z calcd for C₉H₁₄NO⁺ (M+H)⁺: 152.1070; found: 152.1064.

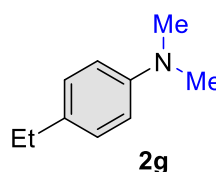
N,N-dimethyl-4-(methylthio)aniline (2f)



Isolated yield: 73%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.26 (m, 2H), 6.66 (d, ³J_{HH} = 8.1 Hz, 2H), 2.91 (s, 6H), 2.39 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 131.3, 124.9, 123.8, 113.1, 40.5, 19.1.

HRMS (ESI) m/z calcd for C₉H₁₄NS⁺ (M+H)⁺: 168.0842; found: 168.0841.

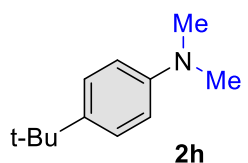
4-ethyl-*N,N*-dimethylaniline (2g)



Isolated yield: 81%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.08 (d, ³J_{HH} = 9.3 Hz, 2H), 6.71 (d, ³J_{HH} = 8.2 Hz, 2H), 2.90 (s, 6H), 2.56 (q, ³J_{HH} = 7.3 Hz, 2H), 1.20 (t, ³J_{HH} = 7.9 Hz, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298

K): δ = 149.1, 128.5, 123.8, 113.3, 41.1, 27.9, 16.0. HRMS (ESI) m/z calcd for C₁₀H₁₆N⁺ (M+H)⁺: 150.1277; found: 150.1268.

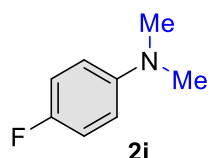
4-(tert-butyl)-*N,N*-dimethylaniline (2h)



Isolated yield: 80%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.26 (d, ³J_{HH} = 8.5 Hz, 2H), 6.71 (d, ³J_{HH} = 8.5 Hz, 2H), 2.90 (s, 6H), 1.29 (m, 9H). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 148.6, 139.5, 125.9, 112.6, 40.9,

33.8, 31.6. HRMS (ESI) m/z calcd for C₁₂H₂₀N⁺ (M+H)⁺: 178.1590; found: 178.1586.

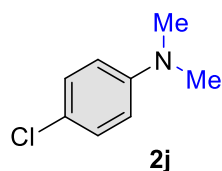
4-fluoro-*N,N*-dimethylaniline (2i)



Isolated yield: 67%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 6.96 (m, 2H), 6.70 (m, 2H), 2.91 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K): δ = 155.7, 147.7, 115.5, 114.1, 41.5. HRMS (ESI) m/z calcd for C₈H₁₀FN⁺ (M+H)⁺:

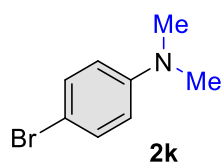
140.0870; found: 140.0868.

4-chloro-*N,N*-dimethylaniline (2j)



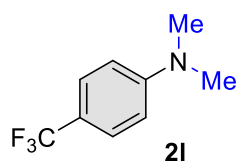
Isolated yield: 69%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): $\delta = 7.17$ (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.65 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 2.93 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): $\delta = 149.3, 128.9, 121.6, 113.8, 40.8$. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{11}\text{ClN}^+$ ($\text{M}+\text{H}^+$): 156.0575; found: 156.0574.

4-bromo-*N,N*-dimethylaniline (2k)



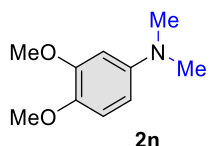
Isolated yield: 72%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): $\delta = 7.31$ (d, $^3J_{\text{HH}} = 9.1$ Hz, 2H), 6.61 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 2.93 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): $\delta = 149.5, 131.8, 114.3, 108.9, 40.8$. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{11}\text{BrN}^+$ ($\text{M}+\text{H}^+$): 200.0064; found: 200.0048.

N,N-dimethyl-4-(trifluoromethyl)aniline (2l)



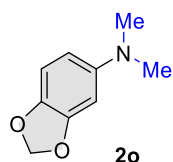
Isolated yield: 62%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): $\delta = 8.46$ (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H), 8.23 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H), 7.82 (d, $^3J_{\text{HH}} = 9.0$ Hz, 1H), 7.76 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 0.63 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): $\delta = 128.9, 126.4, 125.8, 123.2, 6.8, 4.8$. HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{11}\text{F}_3\text{N}^+$ ($\text{M}+\text{H}^+$): 190.0838; found: 190.0837.

3,4-dimethoxy-*N,N*-dimethylaniline (2n)



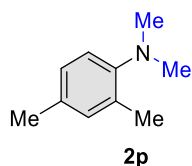
Isolated yield: 85%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): $\delta = 6.80$ (d, $^3J_{\text{HH}} = 8.7$ Hz, 1H), 6.42 (d, $^3J_{\text{HH}} = 2.1$ Hz, 1H), 6.29 (d, $^3J_{\text{HH}} = 8.7, 3.5$ Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.88 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): $\delta = 149.8, 146.4, 141.6, 113.0, 104.9, 99.6, 56.7, 55.9, 41.8$. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{15}\text{NaO}_2\text{N}^+$ ($\text{M}+\text{Na}^+$): 204.0995; found: 204.0994.

N,N-dimethylbenzo[*d*][1,3]dioxol-5-amine (2o)



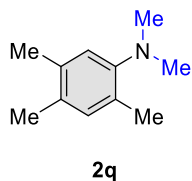
Isolated yield: 80%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): $\delta = 6.63$ (d, $^3J_{\text{HH}} = 9.1$ Hz, 1H), 6.34 (d, $^3J_{\text{HH}} = 2.1$ Hz, 1H), 6.09 (dd, $^3J_{\text{HH}} = 9.4, 2.8$ Hz, 1H), 5.77 (s, 2H), 2.77 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): $\delta = 147.3, 146.1, 138.4, 107.2, 104.2, 99.5, 95.4, 40.8$. HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_{11}\text{NNaO}_2\text{N}^+$ ($\text{M}+\text{Na}^+$): 188.0682; found: 188.0674.

N,N,2,4-tetramethylaniline (2p)



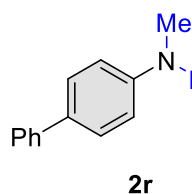
Isolated yield: 83%, (petroleum ether/ethyl acetate = 30:1); Yellow liquid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.82 (d, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.03 (d, $^3J_{\text{HH}} = 9.4$ Hz, 1H), 6.88 (d, $^3J_{\text{HH}} = 12.3$ Hz, 1H), 2.54 (m, 6H), 2.23 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 144.2, 133.9, 133.5, 127.6, 125.0, 118.4, 44.6, 21.3, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{15}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 172.1097; found: 172.1088.

N,N,2,4,5-pentamethylaniline (**2q**)



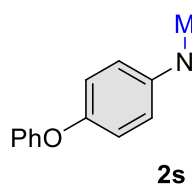
Isolated yield: 86%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 6.86 (s, 1H), 6.75 (s, 1H), 2.59 (s, 6H), 2.19 (m, 3H), 2.14 (m, 3H), 2.1 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 134.3, 132.6, 130.6, 129.4, 127.6, 119.9, 44.6, 19.6, 19.0, 17.7. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{17}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 186.1253; found: 186.1249.

N,N-dimethyl-[1,1'-biphenyl]-4-amine (**2r**)



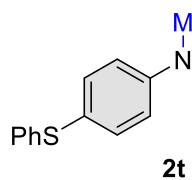
Isolated yield: 84%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.56 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 7.52 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 7.40 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 7.28 (s, 1H), 6.83 (s, 2H), 3.00 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 129.3, 129.0, 128.7, 127.9, 127.9, 127.5, 126.4, 126.1, 124.2, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 220.1097; found: 220.1089.

N,N-dimethyl-4-phenoxyaniline (**2s**)



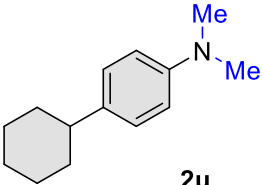
Isolated yield: 89%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.20 (m, 2H), 6.93 (t, $^3J_{\text{HH}} = 7.0$ Hz, 1H), 6.89 (m, 2H), 6.86 (s, 2H), 6.83 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 2.86 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 159.2, 147.7, 147.4, 129.6, 122.1, 121.0, 117.3, 114.1, 41.4. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NaNO}^+$ ($\text{M}+\text{Na}$) $^+$: 236.1046; found: 236.1042.

N,N-dimethyl-4-(phenylthio)aniline (**2t**)

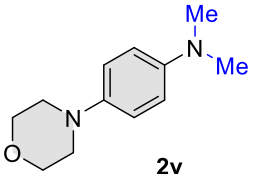


Isolated yield: 81%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.40 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 7.20 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 7.12 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 7.09 (t, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 6.72 (d, $^3J_{\text{HH}} = 9.3$ Hz, 2H), 3.00 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 136.2, 134.9, 130.1, 128.8, 127.0, 125.1, 124.1, 113.1, 40.4. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NaNS}^+$ ($\text{M}+\text{Na}$) $^+$: 252.0817; found: 152.0814.

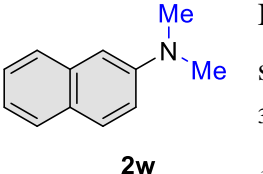
4-cyclohexyl-*N,N*-dimethylaniline (**2u**)


 Isolated yield: 86%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.01 (d, $^3J_{\text{HH}}$ = 8.9 Hz, 2H), 6.63 (t, $^3J_{\text{HH}}$ = 8.9 Hz, 2H), 2.83 (s, 6H), 2.33 (m, 1H), 1.75 (m, 4H), 1.30 (m, 4H), 1.20 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 149.1, 136.7, 127.4, 113.1, 43.6, 41.0, 34.8, 27.1, 26.3. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{21}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 226.1566; found: 226.1569.

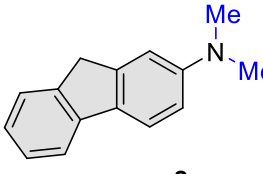
N,N-dimethyl-4-morpholinoaniline (**2v**)


 Isolated yield: 82%, (petroleum ether/ethyl acetate = 10:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 6.84 (m, 4H), 3.86 (m, 4H), 2.97 (m, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 145.9, 143.3, 118.0, 114.6, 67.2, 51.1, 41.6. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{18}\text{ONaNa}_2^+$ ($\text{M}+\text{Na}$) $^+$: 229.1311; found: 229.1316.

N,N-dimethylnaphthalen-2-amine (**2w**)

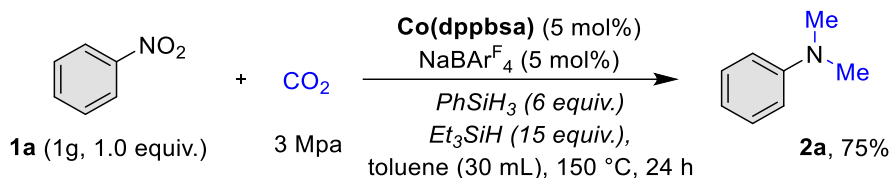

 Isolated yield: 70%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.67 (m, 2H), 7.64 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 1H), 7.35 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 1H), 7.19 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 1H), 7.14 (d, $^3J_{\text{HH}}$ = 8.7 Hz, 1H), 6.91 (s, 1H), 3.01 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 148.7, 135.0, 128.7, 127.6, 127.0, 126.3, 126.3, 122.2, 116.5, 106.6, 41.0. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 194.0940; found: 194.0948.

N,N-dimethyl-9*H*-fluoren-2-amine (**2x**)


 Isolated yield: 79%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 7.65 (d, $^3J_{\text{HH}}$ = 7.9 Hz, 2H), 7.48 (d, $^3J_{\text{HH}}$ = 7.2 Hz, 1H), 7.33 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 1H), 7.19 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 1H), 6.97 (s, 1H), 6.80 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 1H), 3.87 (s, 2H), 3.03 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K): δ = 150.3, 145.1, 142.4, 131.3, 130.0, 126.7, 124.9, 124.7, 120.5, 118.6, 111.8, 109.4, 41.2, 37.2. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NaN}^+$ ($\text{M}+\text{Na}$) $^+$: 232.1097; found: 232.1087.

5. General procedure for scale-up reaction

Scheme S1



6. General procedure for Reduction reaction of nitroarenes and Characterization of Products 3

Under protection of argon, nitroarenes (0.2 mmol, 1.0 equiv.), Co(dppbsa) (5 mol%), NaBARF₄ (5 mol%), Et₂SiH₂ (3.0 equiv.) and 0.5 mL of toluene were charged in an oven-dried 25 mL screw-cap vial equipped with a magnetic stir bar. The reaction was sealed and removed from the glove box, placed on a matching metal module and heated, the reflux cooling device was turned on, the speed and temperature parameters were set, and at the end of a certain time the reaction was completed, the reaction tube was cooled to room temperature, slowly opened and 15 mL of ethyl acetate was added to dilute the reaction solution, filtered through a short silica gel column, 1 mL of filtrate was taken for GC, GC-MS for quantitative and qualitative analysis, and the rest was used for rotary evaporator. The crude product was concentrated, dissolved in solvent with anhydrous ether and finally passed through dry HCl gas to obtain a white flocculent precipitate, which was centrifuged and dried to obtain the arylamine in the form of a chloride salt, the separation yield was calculated by weighing, tested by dissolution with DMSO-d₆ and analysed by NMR.

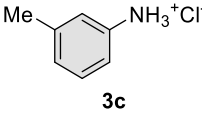
Benzenaminium chloride (**3a**·HCl)

Isolated yield: 89%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 8.66 (s, 3H), 7.27 (t, ³J_{HH} = 7.8 Hz, 2H), 7.04 (d, ³J_{HH} = 7.2 Hz, 2H), 7.00 (t, ³J_{HH} = 7.3 Hz, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): δ = 139.1, 129.2, 122.5, 119.1. HRMS (ESI) m/z calcd for C₆H₈N⁺ (M-Cl)⁺: 94.0651; found: 94.0654.

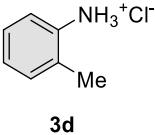
4-methylbenzenaminium chloride (**3b**·HCl)

Isolated yield: 88%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.40 (s, 3H), 7.29 (s, 4H), 2.32 (s, 3H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): δ = 137.3, 129.9, 129.0, 122.9, 20.5. HRMS (ESI) m/z calcd for C₇H₁₀N⁺ (M-Cl)⁺: 108.0808; found: 108.0809.

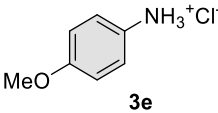
3-methylbenzenaminium chloride (**3c**·HCl)

 Isolated yield: 84%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 10.17 (s, 3H), 7.36 (s, 1H), 7.21 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 1H), 7.16 (m, 2H), 2.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 139.3, 131.9, 129.5, 128.3, 123.1, 119.9, 20.7. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_{10}\text{N}^+$ (M-Cl) $^+$: 108.0808; found: 108.0804.

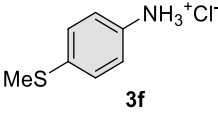
2-methylbenzenaminium chloride (**3d**·HCl)

 Isolated yield: 81%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 10.33 (s, 3H), 7.47 (s, 1H), 7.32 (d, $^3J_{\text{HH}}$ = 7.6 Hz, 1H), 7.29 (m, 2H), 2.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 132.4, 131.7, 131.3, 128.4, 127.4, 123.7, 17.6. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_{10}\text{N}^+$ (M-Cl) $^+$: 108.0808; found: 108.0807.

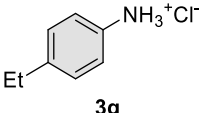
4-methoxybenzenaminium chloride (**3e**·HCl)

 Isolated yield: 86%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 7.80 (s, 3H), 6.90 (s, 2H), 6.82 (m, 2H), 3.69 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 154.4, 133.8, 119.3, 114.6, 55.3. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_{10}\text{NO}^+$ (M-Cl) $^+$: 124.0757; found: 124.0758.

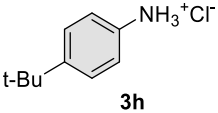
4-(methylthio)benzenaminium chloride (**3f**·HCl)

 Isolated yield: 79%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 10.56 (s, 3H), 7.37 (s, 4H), 2.49 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 138.2, 128.5, 126.7, 123.8, 14.7. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_{10}\text{NS}^+$ (M-Cl) $^+$: 140.0529; found: 140.0530.

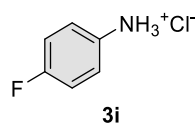
4-(methylthio)benzenaminium chloride (**3g**·HCl)

 Isolated yield: 81%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 7.38 (s, 3H), 7.01 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H), 6.79 (d, $^3J_{\text{HH}}$ = 8.4 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 140.5, 136.0, 128.8, 117.8, 27.9, 16.3. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{12}\text{N}^+$ (M-Cl) $^+$: 122.0964; found: 122.0958.

4-(tert-butyl)benzenaminium chloride (**3h**·HCl)

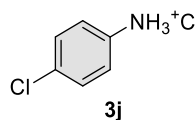
 Isolated yield: 87%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): δ = 10.52 (s, 3H), 7.50 (d, $^3J_{\text{HH}}$ = 8.6 Hz, 2H), 7.35 (d, $^3J_{\text{HH}}$ = 8.6 Hz, 2H), 1.28 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): δ = 150.5, 129.1, 126.3, 122.8, 34.3, 30.9. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{16}\text{N}^+$ (M-Cl) $^+$: 150.1277; found: 150.1274.

4-fluorobenzenaminium chloride (**3i**·HCl)



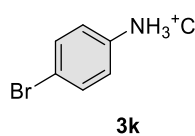
Isolated yield: 65%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 10.43$ (s, 3H), 7.45 (m, 2H), 7.33 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 13\text{C}$ NMR (151 MHz, DMSO) δ 161.2 ($^1J_{\text{CF}} = 245.2$ Hz), 128.4, 125.2, 116.6. HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_7\text{FN}^+$ ($\text{M}-\text{Cl}^-$) $^+$: 112.0557; found: 112.0558.

4-chlorobenzenaminium chloride (**3j**·HCl)



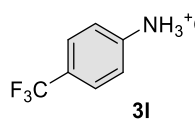
Isolated yield: 72%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 10.05$ (s, 3H), 7.51 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 7.37 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 132.4, 131.3, 129.5, 124.4$. HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_7\text{ClN}^+$ ($\text{M}-\text{Cl}^-$) $^+$: 128.0262; found: 128.0264.

4-bromobenzenaminium chloride (**3k**·HCl)



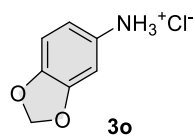
Isolated yield: 83%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 9.91$ (s, 3H), 7.65 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 7.31 (d, $^3J_{\text{HH}} = 8.9$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 132.8, 132.4, 124.6, 119.4$. HRMS (ESI) m/z calcd for $\text{C}_6\text{H}_7\text{BrN}^+$ ($\text{M}-\text{Cl}^-$) $^+$: 171.9756; found: 171.9754.

4-(trifluoromethyl)benzenaminium chloride (**3l**·HCl)



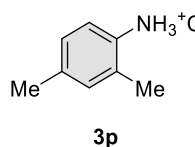
Isolated yield: 62%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 8.76$ (s, 3H), 7.61 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 7.18 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 126.5, 125.5, 123.7, 118.9, 117.1$. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_7\text{F}_3\text{N}^+$ ($\text{M}-\text{Cl}^-$) $^+$: 162.0525; found: 162.0524.

Chloridebenzo[*d*][1,3]dioxol-5-aminium chloride (**3o**·HCl)



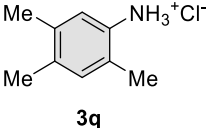
Isolated yield: 80%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 10.44$ (s, 3H), 7.00 (m, 2H), 6.91 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 6.10 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 147.7, 146.8, 125.34, 116.4, 108.5, 104.4, 101.9$. HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_8\text{NO}_2^+$ ($\text{M}-\text{Cl}^-$) $^+$: 138.0550; found: 138.0554.

2,4-dimethylbenzenaminium chloride (**3p**·HCl)

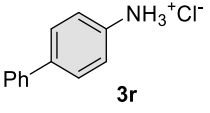


Isolated yield: 79%, White solid; ^1H NMR (600 MHz, DMSO- d_6 , 298 K): $\delta = 10.36$ (s, 3H), 7.38 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.13 (s, 1H), 7.08 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K): $\delta = 137.3, 131.6, 131.6, 127.7, 127.1, 123.0, 20.2, 16.9$. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{12}\text{N}^+$ ($\text{M}-\text{Cl}^-$) $^+$: 122.0964; found: 122.0969.

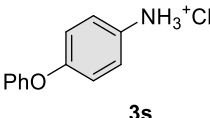
2,4,5-trimethylbenzenaminium chloride (**3q**·HCl)


3q Isolated yield: 77%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.03 (s, 3H), 6.90 (s, 1H), 6.74 (s, 1H), 1.97 (s, 3H), 1.85 (s, 6H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 136.1, 134.7, 132.2, 128.9, 127.8, 124.1, 18.8, 18.7, 16.5. HRMS (ESI) m/z calcd for C₉H₁₄N⁺ (M-Cl⁻)⁺: 136.1121; found: 136.1124.

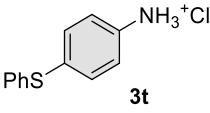
[1,1'-biphenyl]-4-aminium chloride (**3r·HCl**)


3r Isolated yield: 82%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.49 (s, 3H), 7.77 (d, ³J_{HH} = 8.5 Hz, 2H), 7.68 (d, ³J_{HH} = 7.6 Hz, 2H), 7.49 (t, ³J_{HH} = 8.5 Hz, 4H), 7.39 (t, ³J_{HH} = 6.9 Hz, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 139.9, 139.5, 132.2, 129.5, 128.3, 128.2, 127.2, 124.0. HRMS (ESI) m/z calcd for C₁₂H₁₂N⁺ (M-Cl⁻)⁺: 170.0964; found: 170.0968.

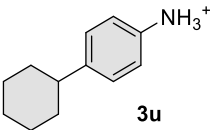
4-phenoxybenzenaminium chloride (**3s·HCl**)


3s Isolated yield: 80%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.38 (s, 3H), 7.41 (m, 4H), 7.18 (d, ³J_{HH} = 7.6 Hz, 1H), 7.11 (t, ³J_{HH} = 8.6 Hz, 2H), 7.04 (t, ³J_{HH} = 7.5 Hz, 2H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 156.7, 156.5, 130.7, 127.7, 125.3, 124.3, 119.9, 119.3. HRMS (ESI) m/z calcd for C₁₂H₁₂NO⁺ (M-Cl⁻)⁺: 186.0913; found: 186.0915.

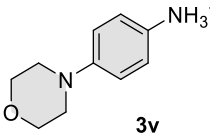
4-(phenylthio)benzenaminium chloride (**3t·HCl**)


3t Isolated yield: 76%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 9.80 (s, 3H), 7.37 (m, 4H), 7.31 (m, 5H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 134.7, 133.6, 132.4, 131.9, 130.5, 129.6, 127.5, 123.1. HRMS (ESI) m/z calcd for C₁₂H₁₂NS⁺ (M-Cl⁻)⁺: 202.0685; found: 202.0682.

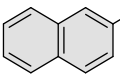
4-cyclohexylbenzenaminium chloride (**3u·HCl**)


3u Isolated yield: 90%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.25 (s, 3H), 7.30 (m, 4H), 2.52 (m, 1H), 1.77 (t, ³J_{HH} = 10.8 Hz, 4H), 1.70 (d, ³J_{HH} = 12.5 Hz, 1H), 1.37 (m, 4H), 1.23 (m, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 147.4, 129.5, 127.8, 123.0, 43.2, 33.8, 26.2, 25.4. HRMS (ESI) m/z calcd for C₁₂H₁₈N⁺ (M-Cl⁻)⁺: 176.1434; found: 176.1438.

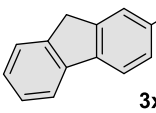
4-morpholinobenzenaminium chloride (**3v·HCl**)


3v Isolated yield: 81%, Purple solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.38 (s, 3H), 7.38 (s, 4H), 3.88 (s, 4H), 3.29 (s, 4H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 132.1, 125.1, 124.5, 118.6, 65.5, 50.7. HRMS (ESI) m/z calcd for C₁₀H₁₅N₂O⁺ (M-Cl⁻)⁺: 179.1179; found: 179.1167.

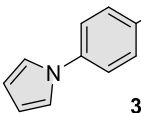
Naphthalen-2-aminium chloride (**3w·HCl**)


Nc1ccc2ccccc2c1.[NH3+].[Cl-]
3w Isolated yield: 82%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.32 (s, 3H), 8.04 (d, ³J_{HH} = 8.5 Hz, 1H), 7.98 (d, ³J_{HH} = 7.1 Hz, 2H), 7.92 (d, ³J_{HH} = 2.8 Hz, 1H), 7.58 (m, 2H), 7.51 (d, ³J_{HH} = 7.8 Hz, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 147.4, 129.5, 127.8, 123.0, 43.2, 33.8, 26.2, 25.4. HRMS (ESI) m/z calcd for C₁₀H₁₀N⁺ (M-Cl)⁺: 144.0808; found: 144.0806.

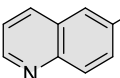
9H-fluoren-2-aminium chloride (3x·HCl)


Nc1ccc2c3ccccc3c2c1.[NH3+].[Cl-]
3x Isolated yield: 89%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.41 (s, 3H), 8.00 (d, ³J_{HH} = 8.5 Hz, 1H), 7.93 (d, ³J_{HH} = 7.8 Hz, 1H), 7.61 (d, ³J_{HH} = 7.2 Hz, 2H), 7.41 (t, ³J_{HH} = 7.2 Hz, 2H), 7.36 (t, ³J_{HH} = 6.7 Hz, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 145.0, 143.6, 141.2, 140.4, 131.0, 127.7, 127.4, 125.7, 122.2, 121.4, 120.84, 120.4, 37.0. HRMS (ESI) m/z calcd for C₁₃H₁₂N⁺ (M-Cl)⁺: 182.0964; found: 182.0968.

4-(1H-pyrrol-1-yl)benzenaminium chloride (3y·HCl)


Nc1ccc(cc1)N2C=CC=C2.[NH3+].[Cl-]
3y Isolated yield: 83%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 10.36 (s, 3H), 7.68 (d, ³J_{HH} = 8.4 Hz, 2H), 7.46 (d, ³J_{HH} = 8.8 Hz, 2H), 7.37 (t, ³J_{HH} = 2.2 Hz, 2H), 6.82 (t, ³J_{HH} = 1.8 Hz, 2H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 138.9, 129.2, 124.1, 120.1, 119.0, 110.7. HRMS (ESI) m/z calcd for C₁₀H₁₁N⁺ (M-Cl)⁺: 159.0917; found: 159.0914.

quinolin-6-aminium chloride (3z·HCl)


Nc1ccc2nc3ccccc3c2c1.[NH3+].[Cl-]
3z Isolated yield: 79%, White solid; ¹H NMR (600 MHz, DMSO-d₆, 298 K): δ = 8.82 (s, 2H), 8.24 (d, ³J_{HH} = 8.6 Hz, 1H), 7.84 (d, ³J_{HH} = 6.5 Hz, 1H), 7.64 (t, ³J_{HH} = 9.3 Hz, 1H), 7.28 (s, 1H). ¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K): 147.2, 142.7, 138.8, 131.9, 130.8, 126.8, 121.9, 121.5. HRMS (ESI) m/z calcd for C₉H₉N⁺ (M-Cl)⁺: 145.0760; found: 145.0764.

7. The time-course plots for the reaction of intermediates

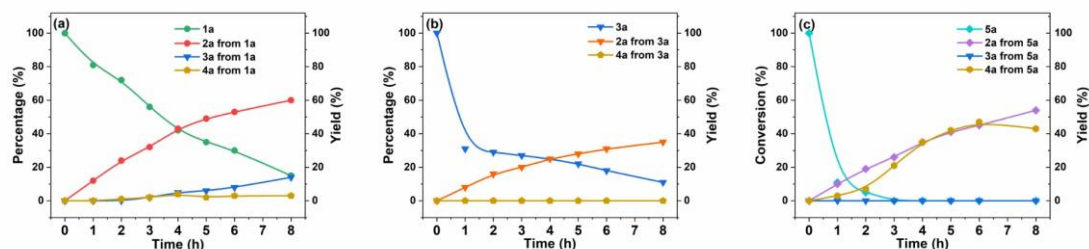
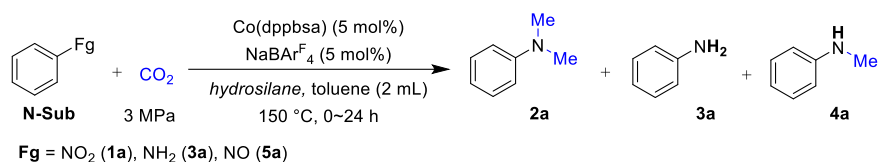


Figure S3. The time-course plots for the reaction of intermediate.

8. Detection of Cp*

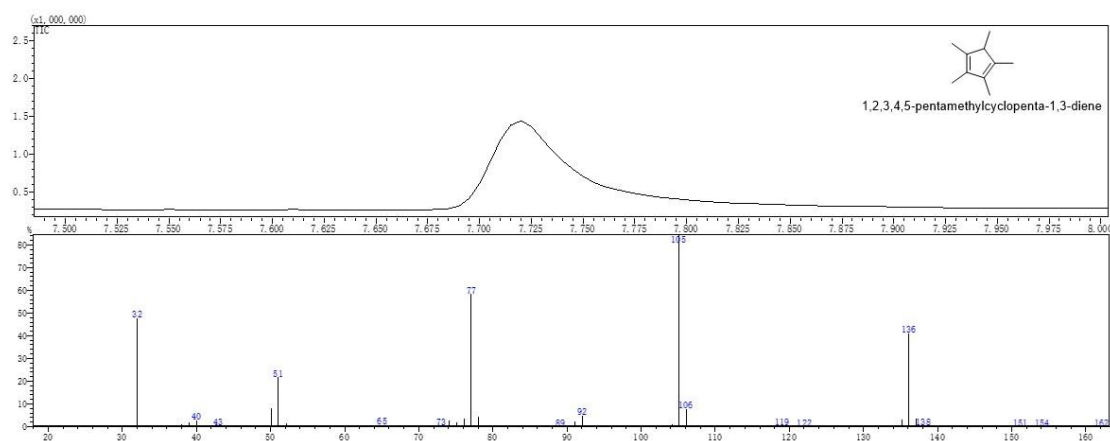


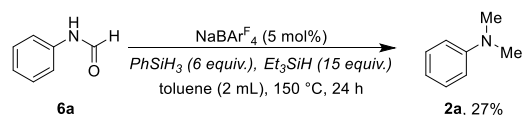
Figure S4. Cp* was detected by GC-MS analysis in the evaluation of catalytic performance.

9. GC-MS analysis of 6a and 7a before and after hydrolysis

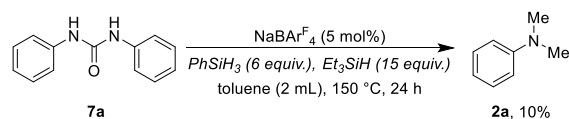
General procedure for hydrolysis. The reaction was quenched with 10% NaOH (5 mL) and methanol (5 mL) solution, stirred at 70 °C overnight. A sample of the mixture was analyzed by GC-MS.

Scheme S2. The performance of 6a and 7a under NaBAR₄^F

(a) The performance of 6a under NaBAR₄^F



(b) The performance of 7a under NaBAR₄^F



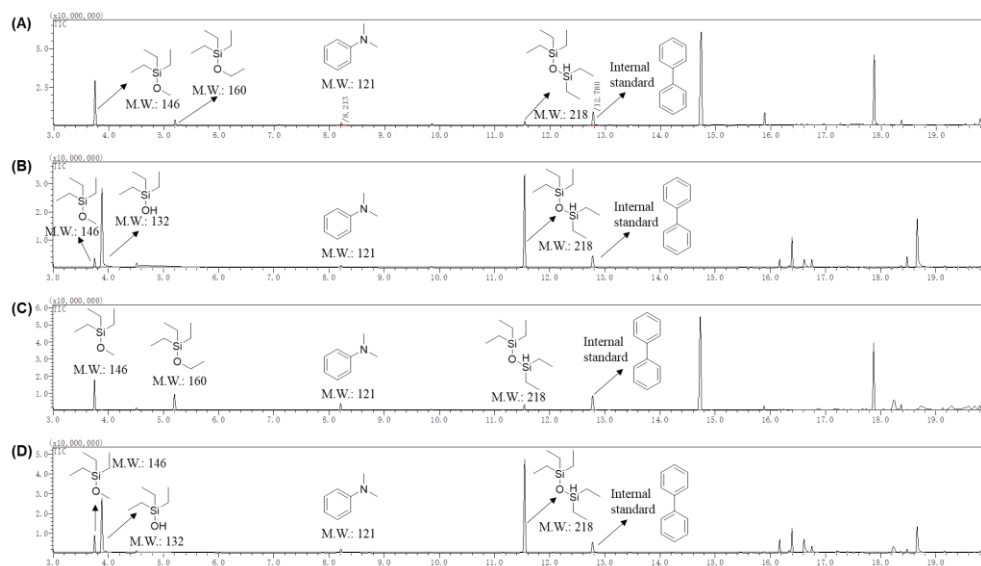
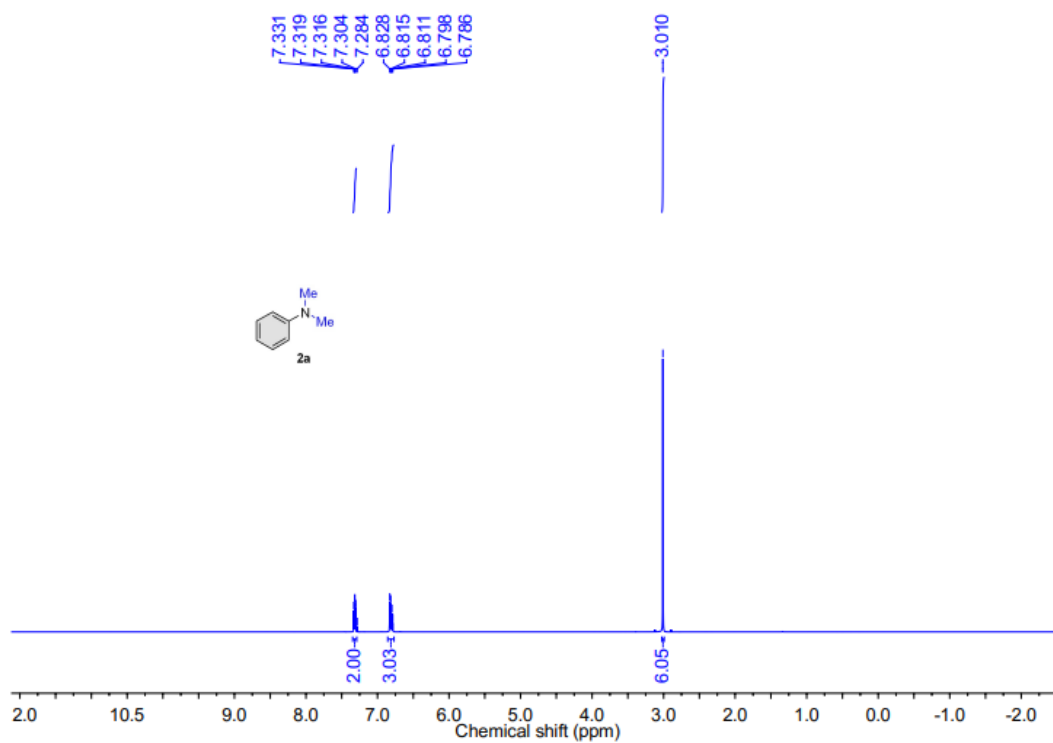
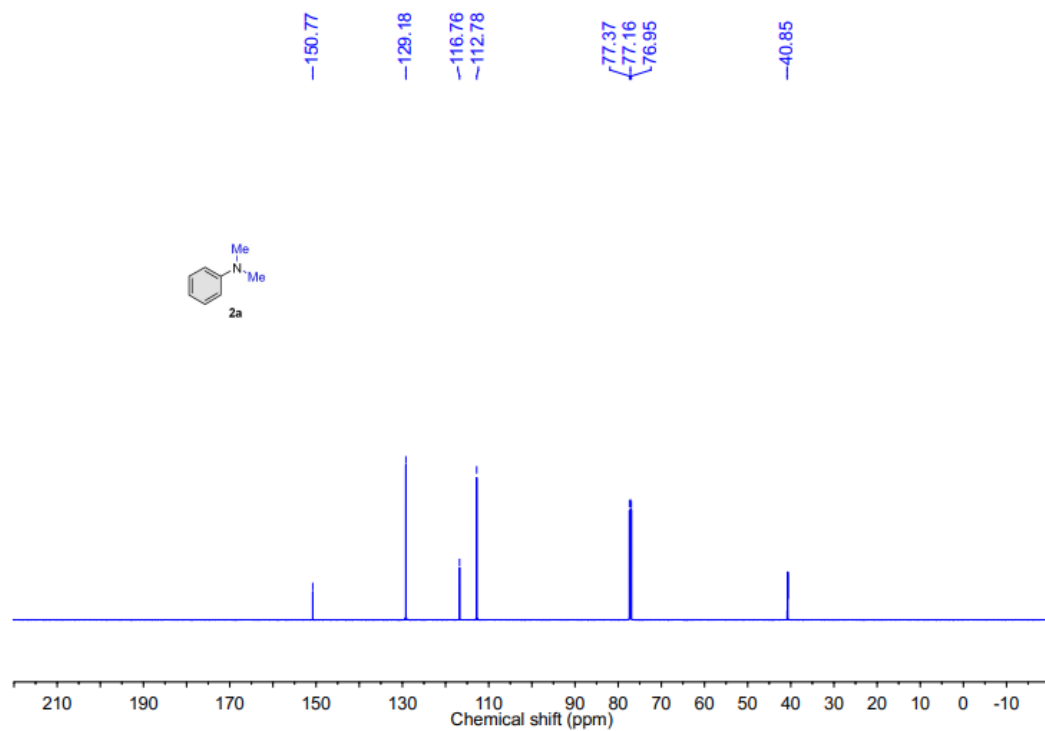


Figure S5. (A) GC-MS analysis of Scheme S2a before hydrolysis. (B) GC-MS analysis of Scheme S2a after hydrolysis. (C) GC-MS analysis of Scheme S2b before hydrolysis. (D) GC-MS analysis of Scheme S2b after hydrolysis.

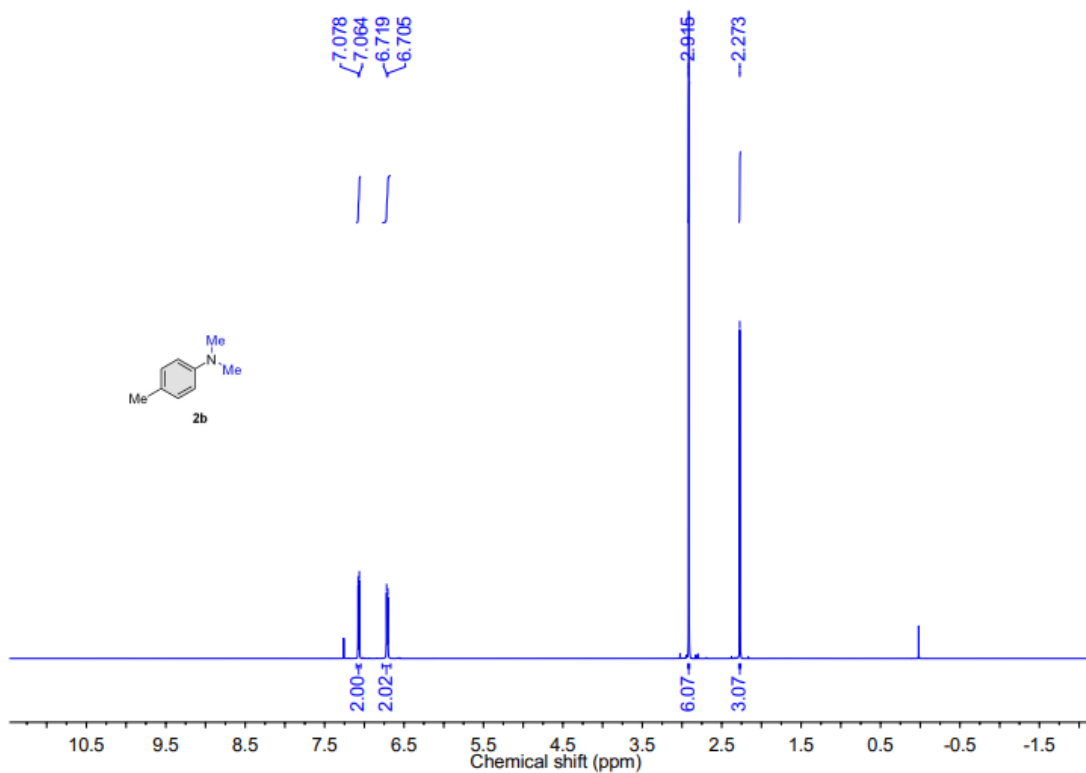
10. NMR Spectra



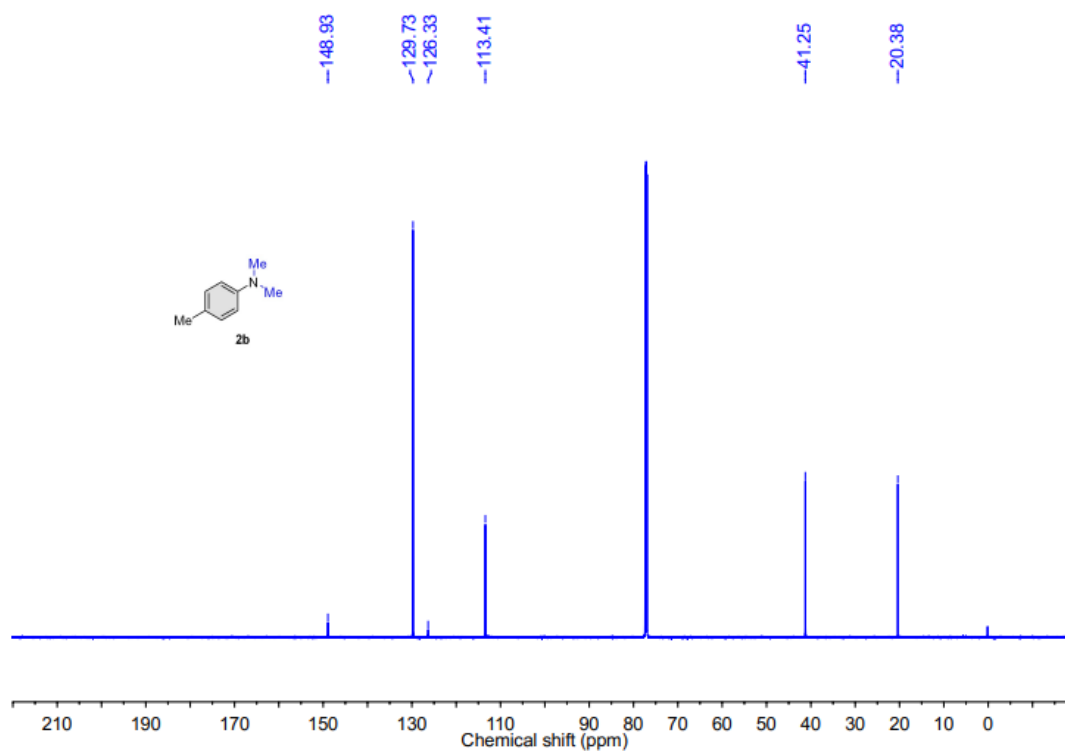
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2a**



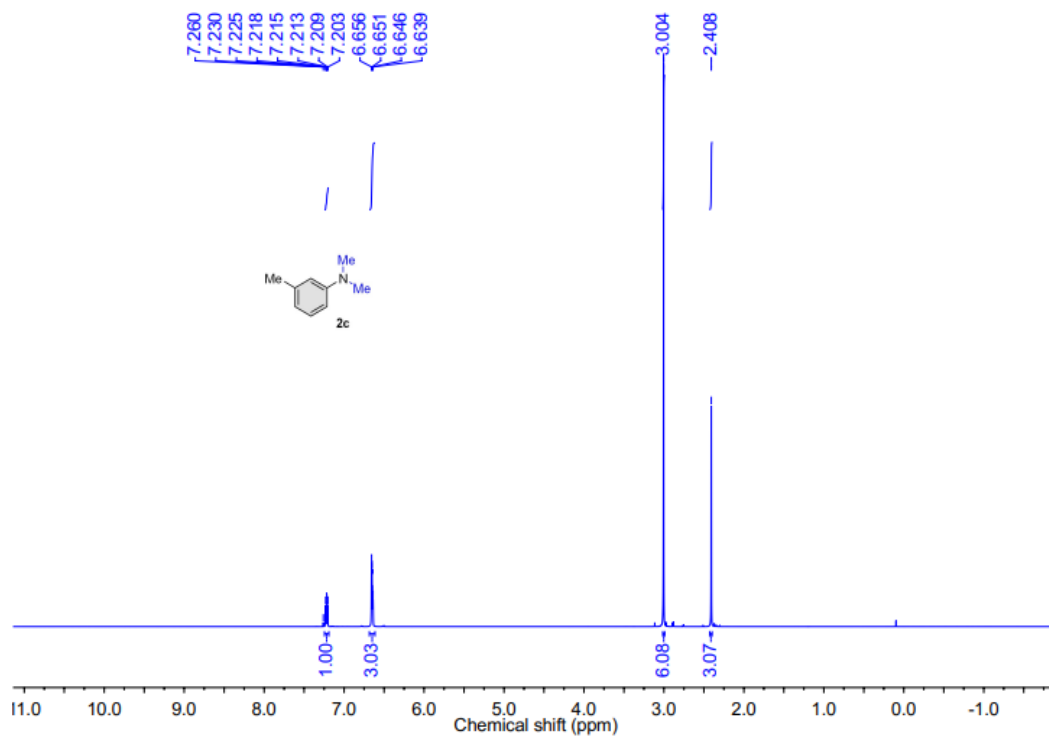
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2a**



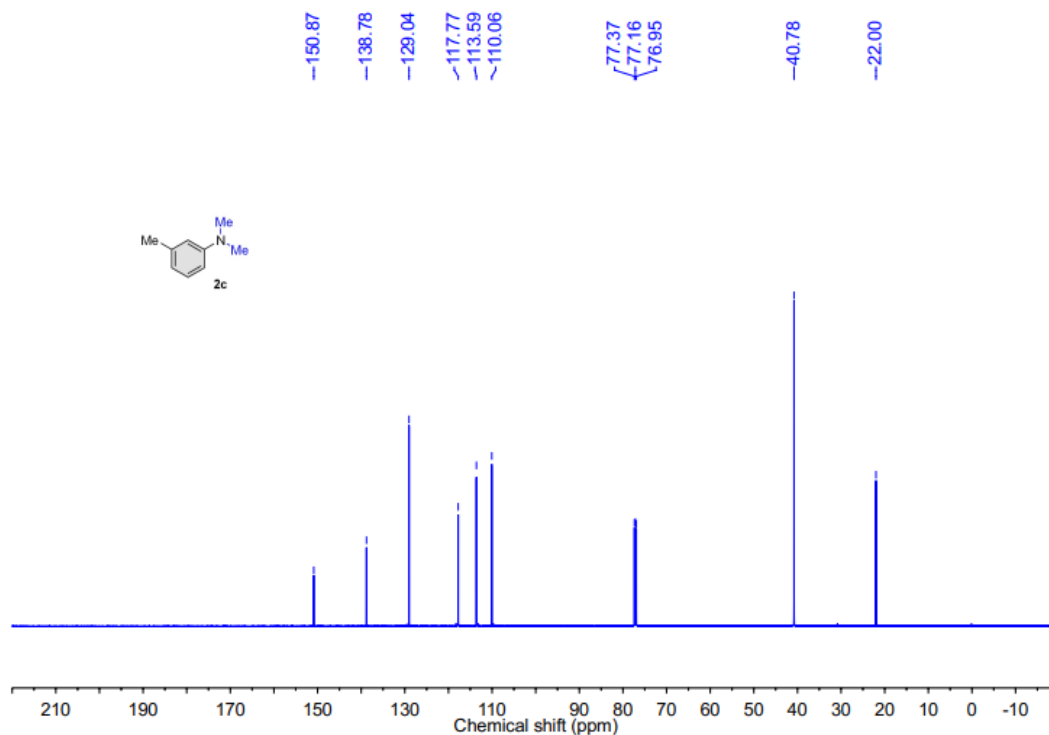
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2b**



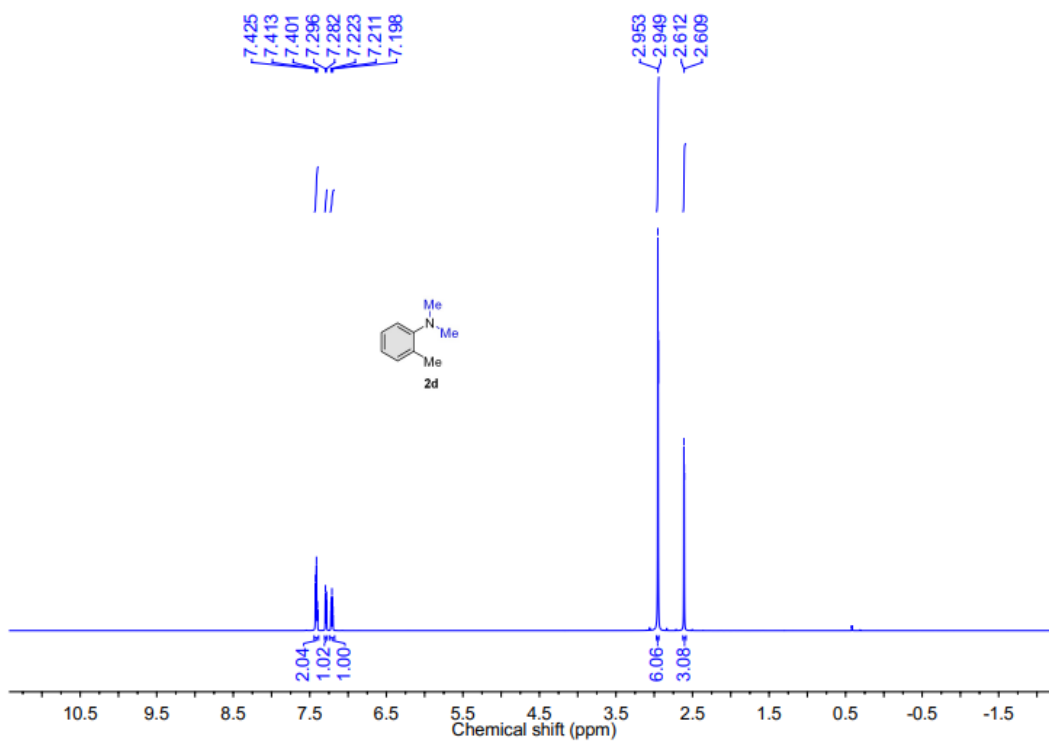
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2b**



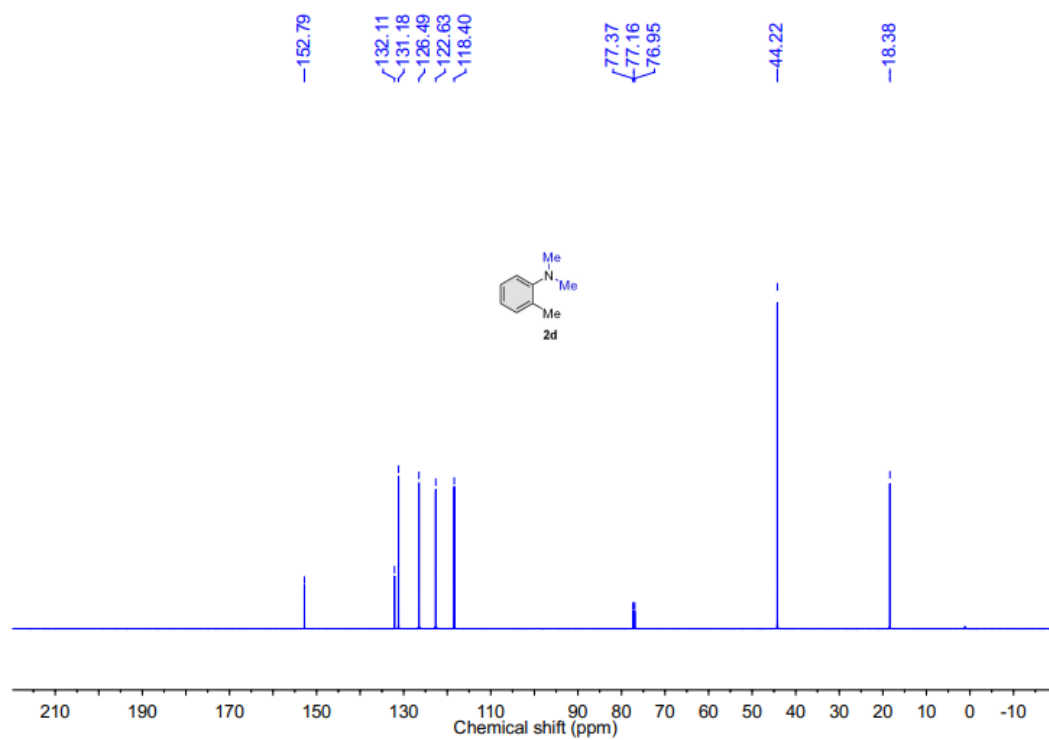
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2c**



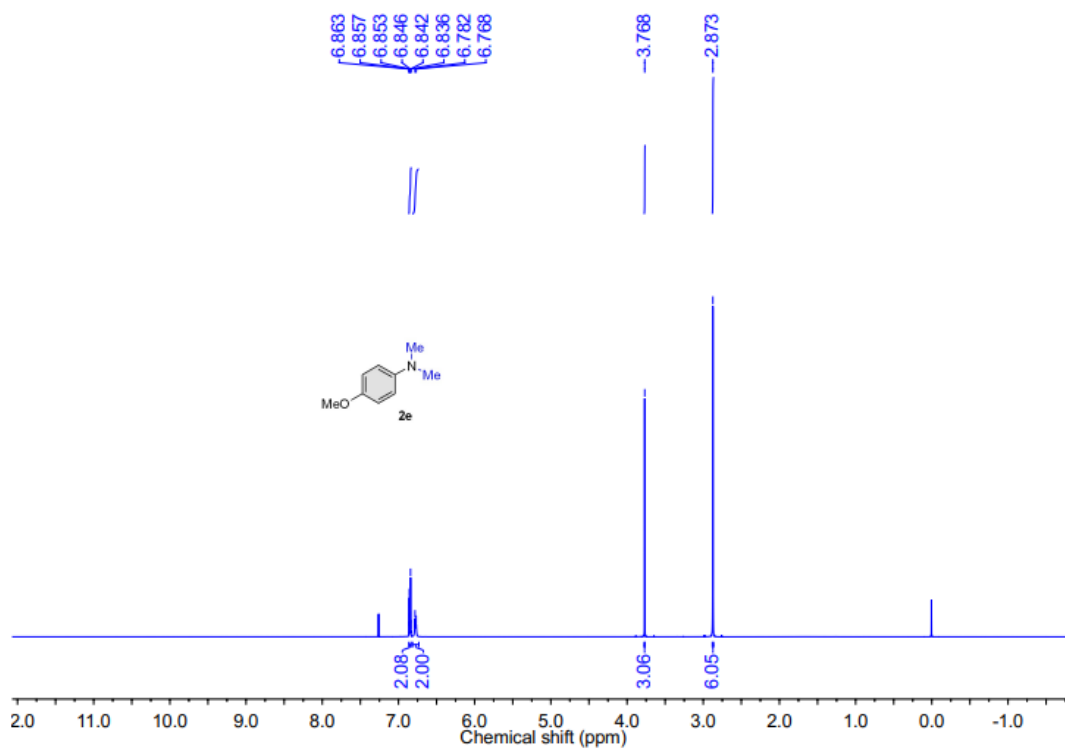
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2c**



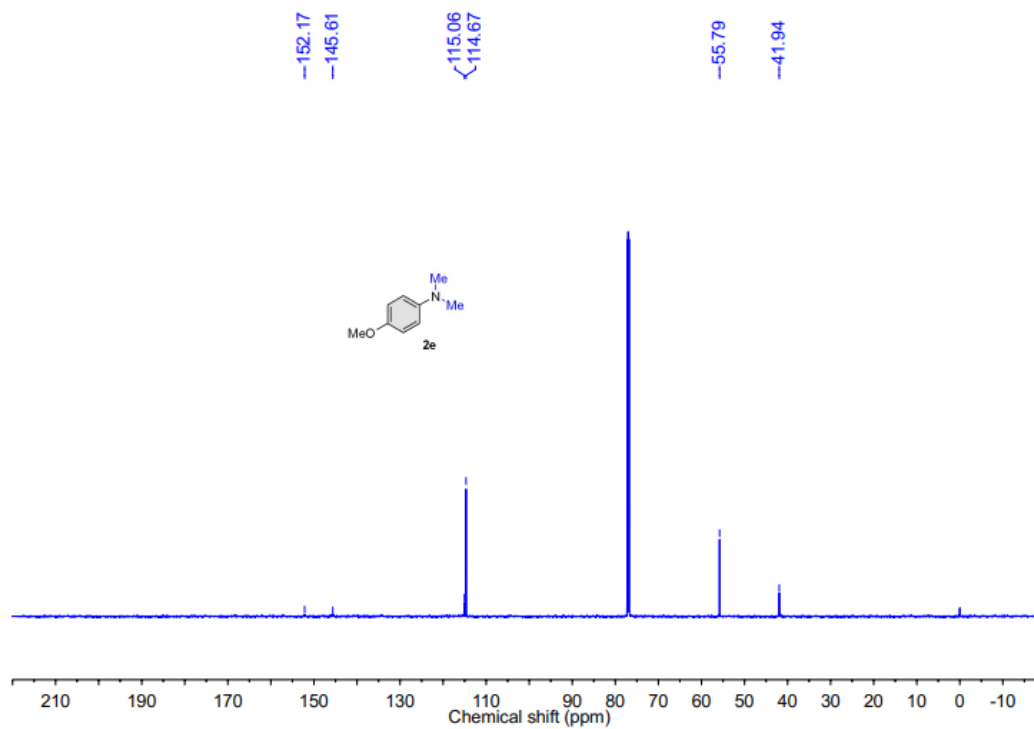
$^1\text{H NMR}$ (600 MHz, CDCl_3 , 298 K) of **2d**



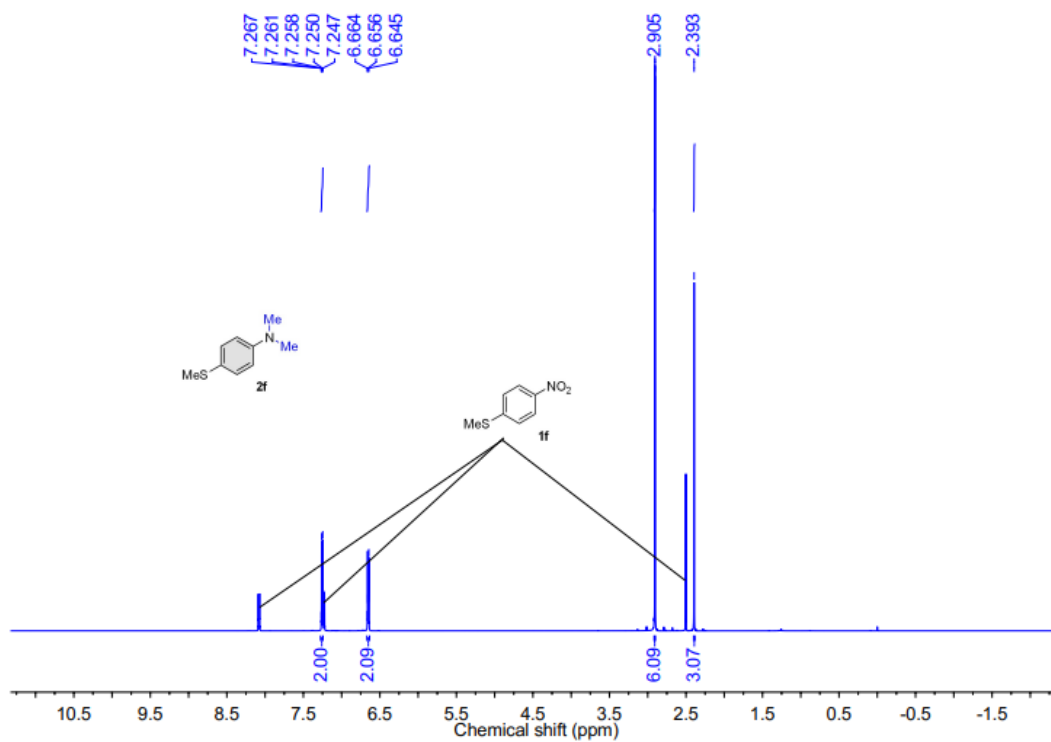
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2d**



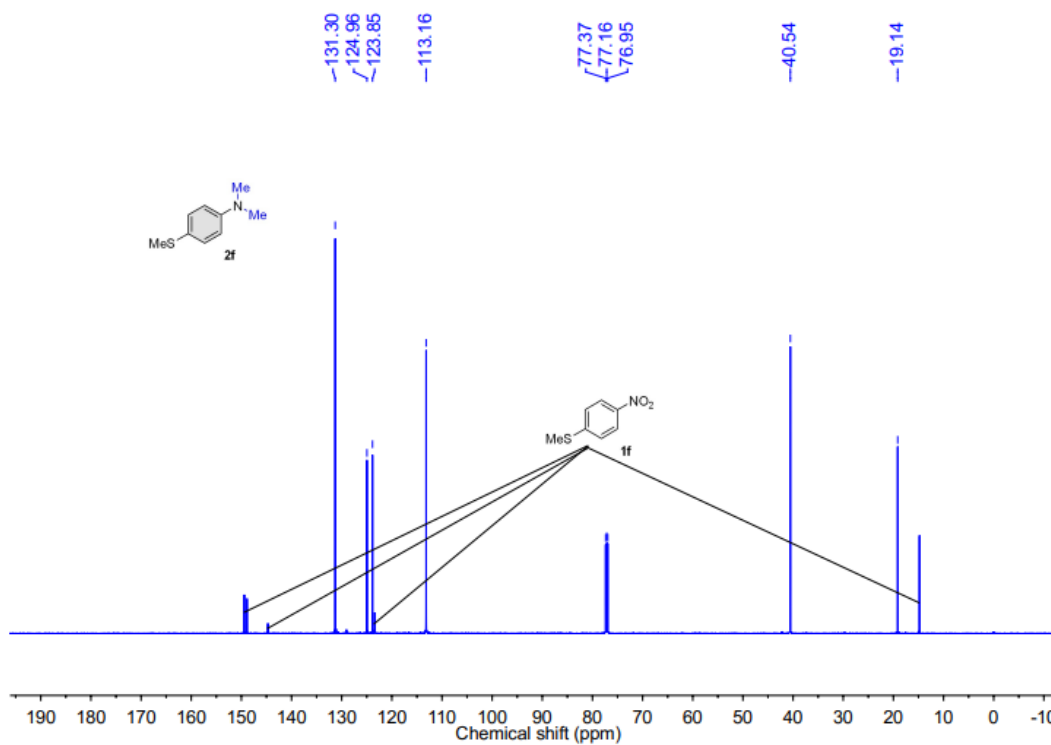
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2e**



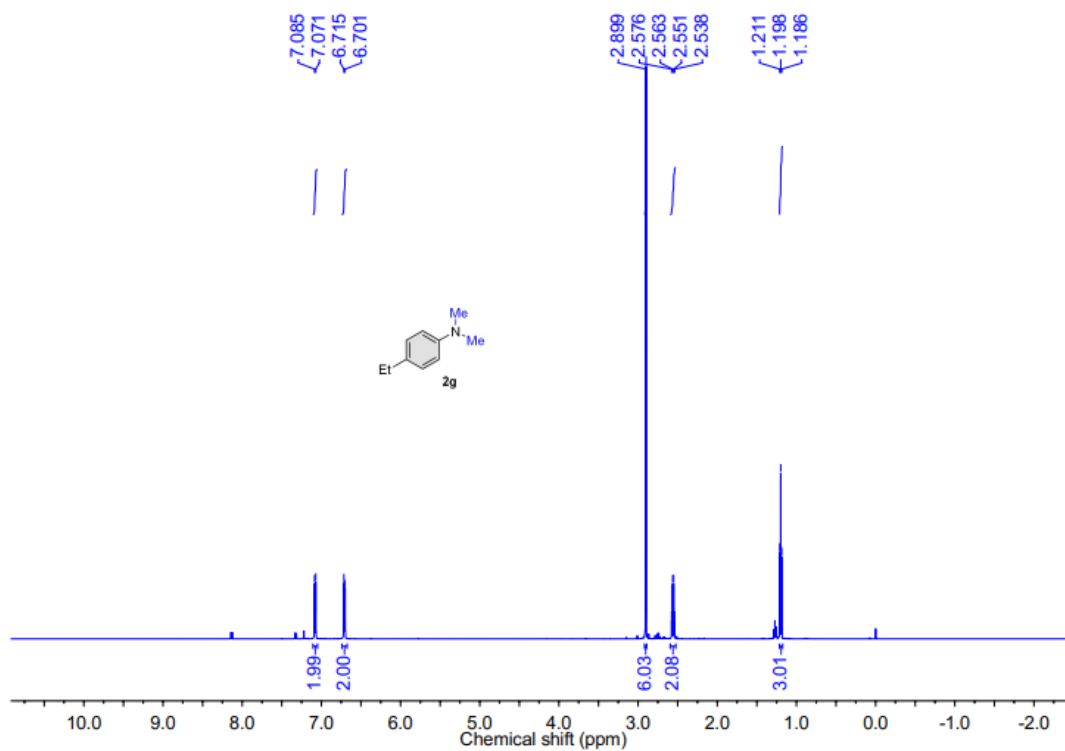
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2e**



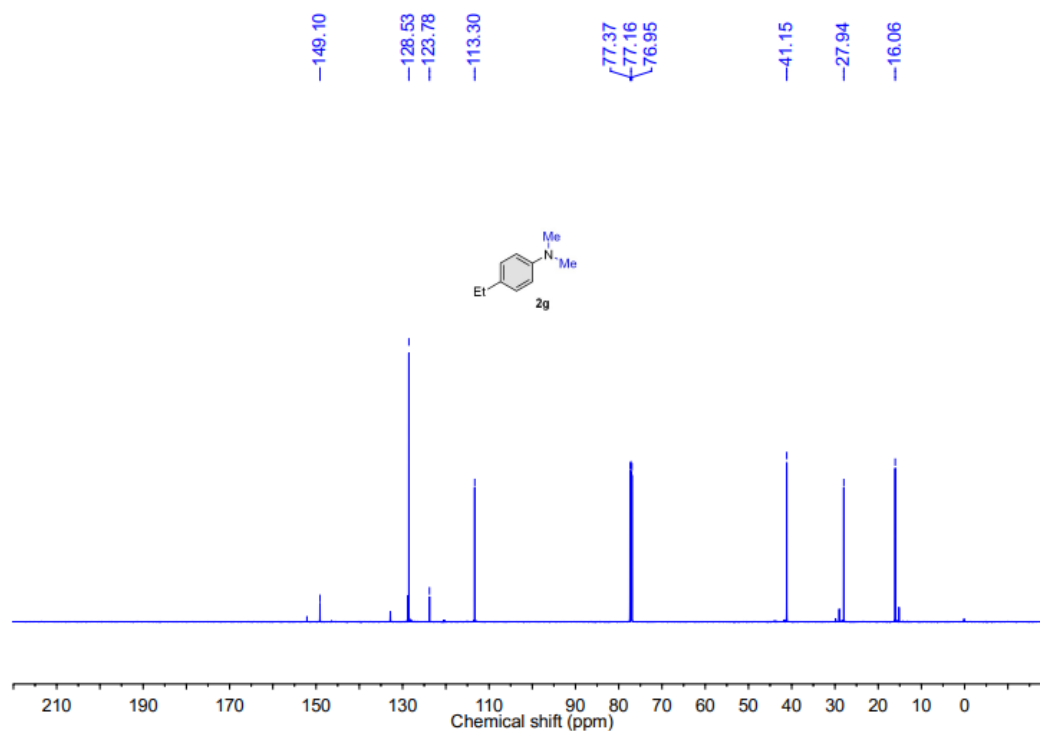
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2f**



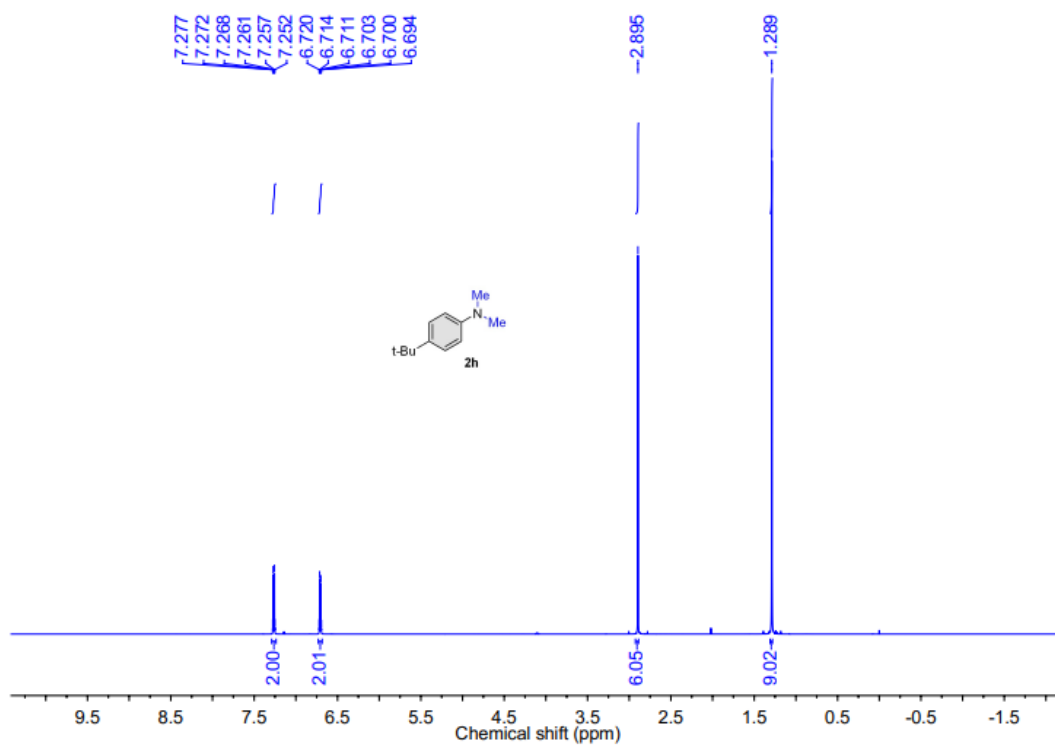
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2f**



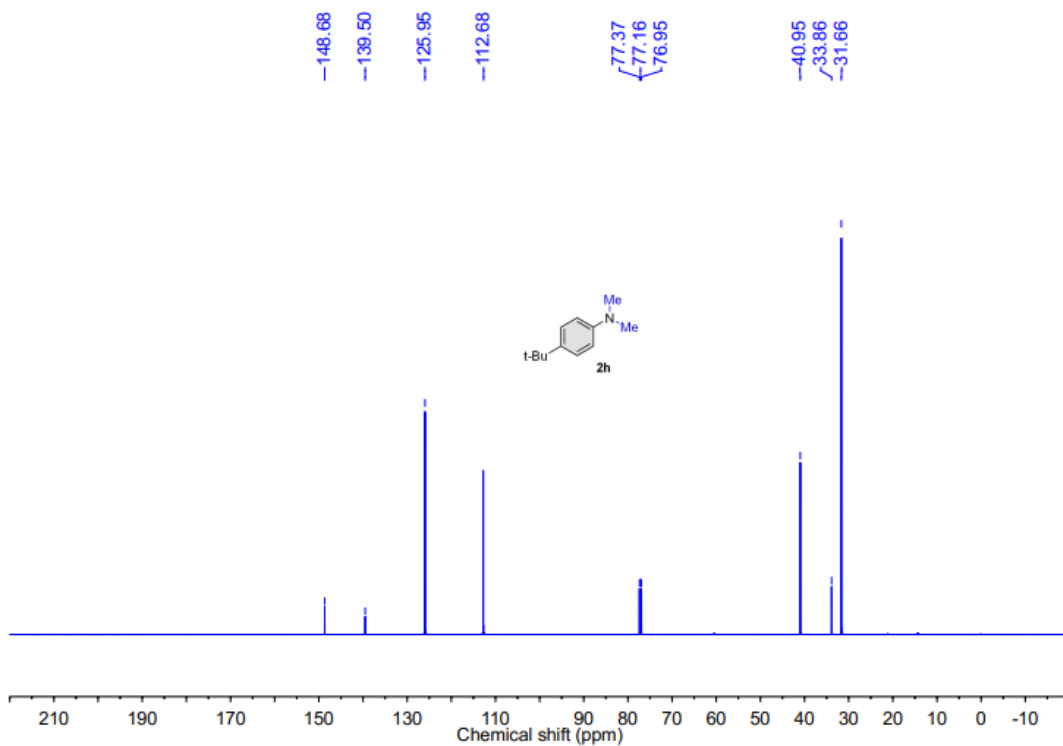
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2g**



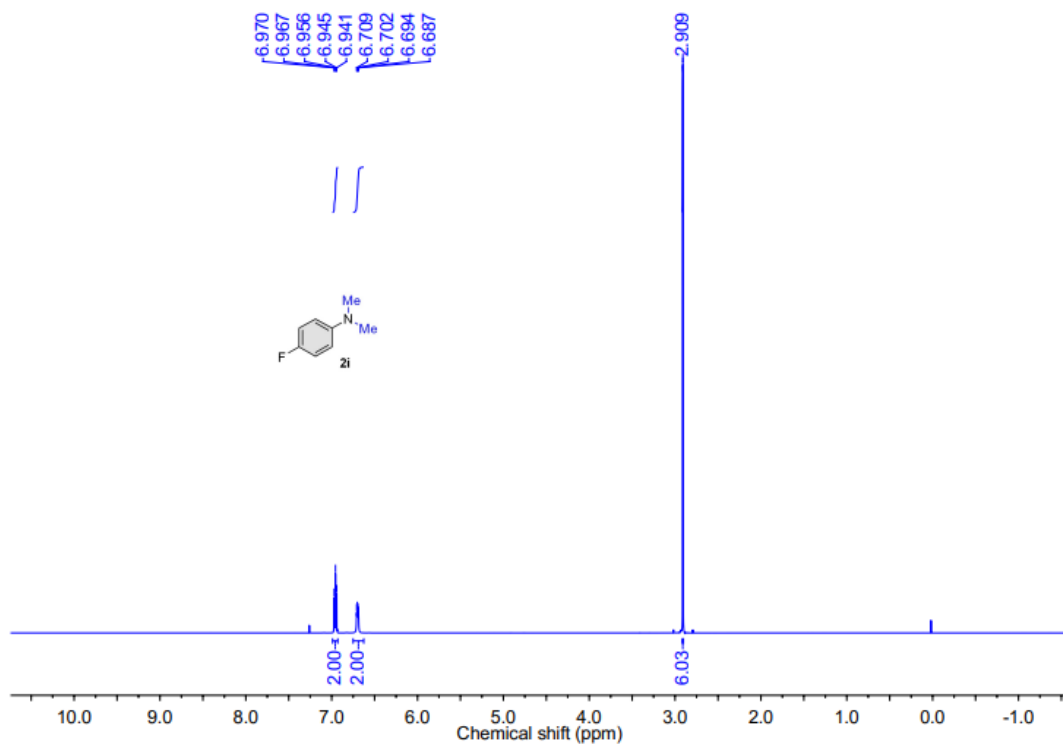
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2g**



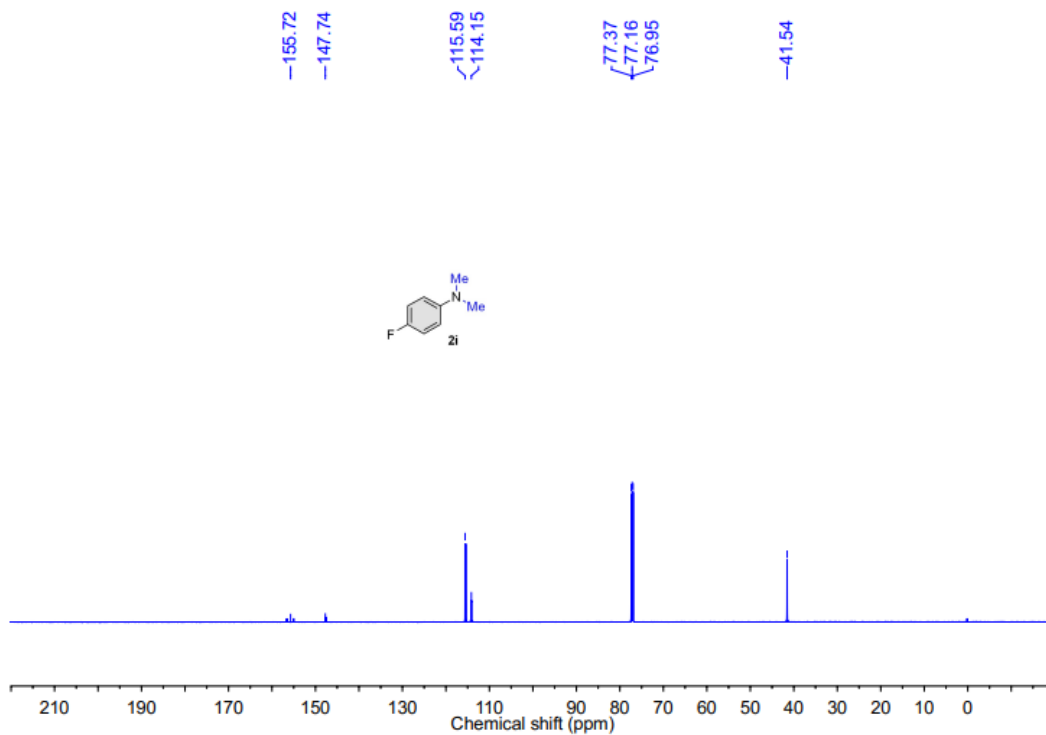
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2h**



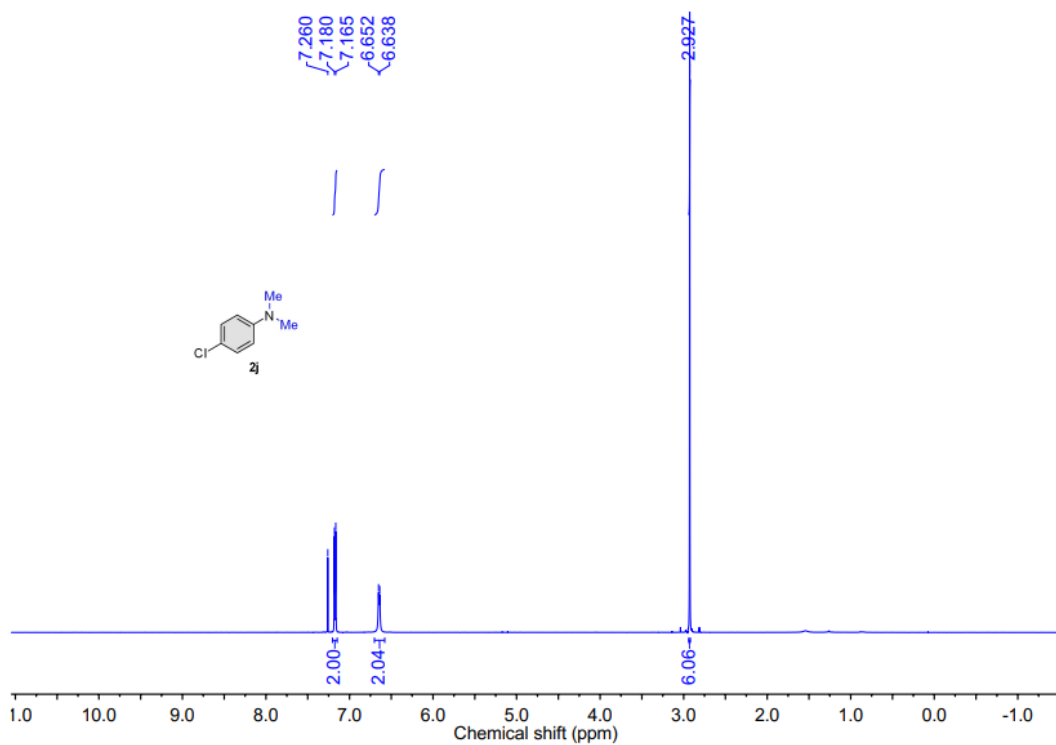
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2h**



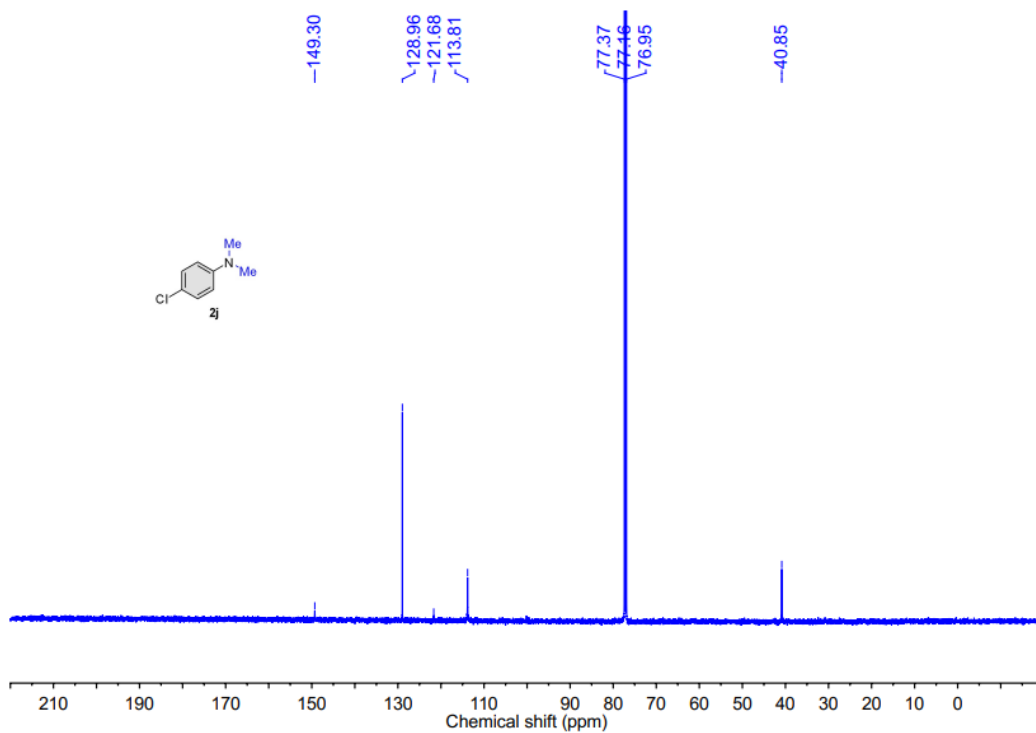
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2i**



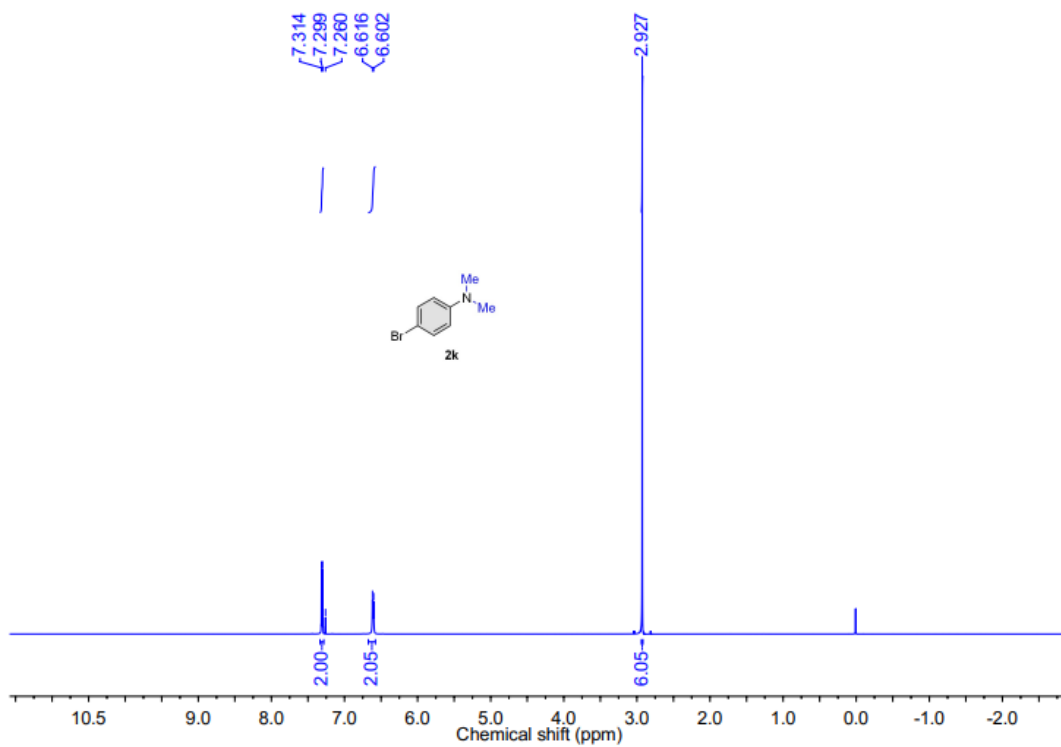
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2i**



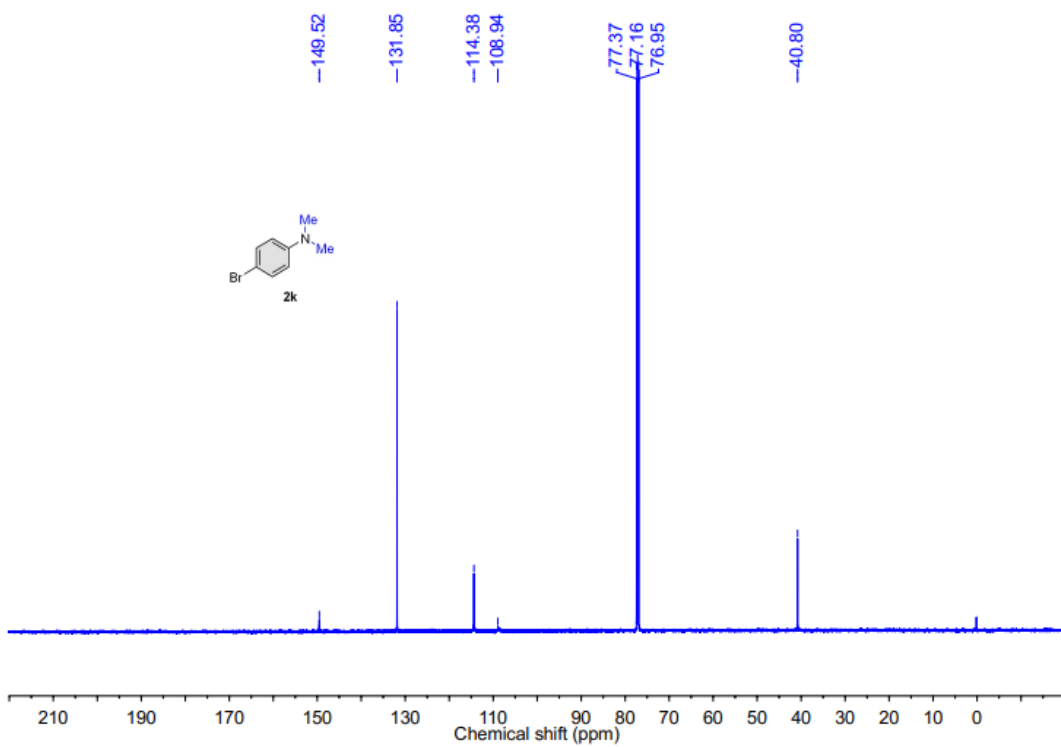
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2j**



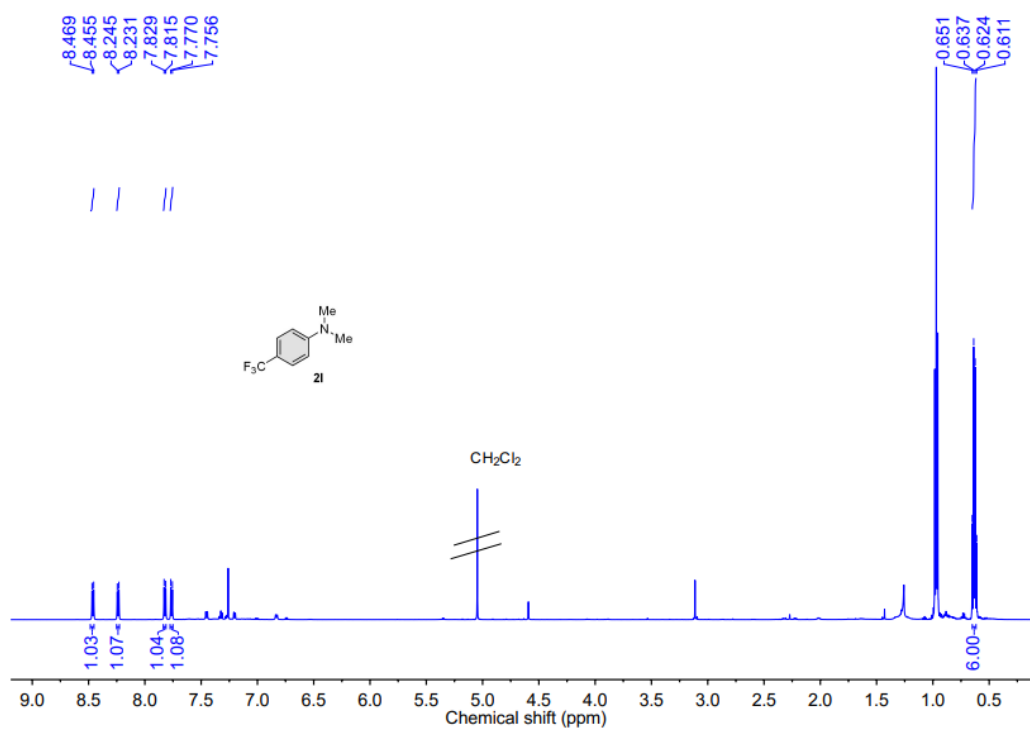
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2j**



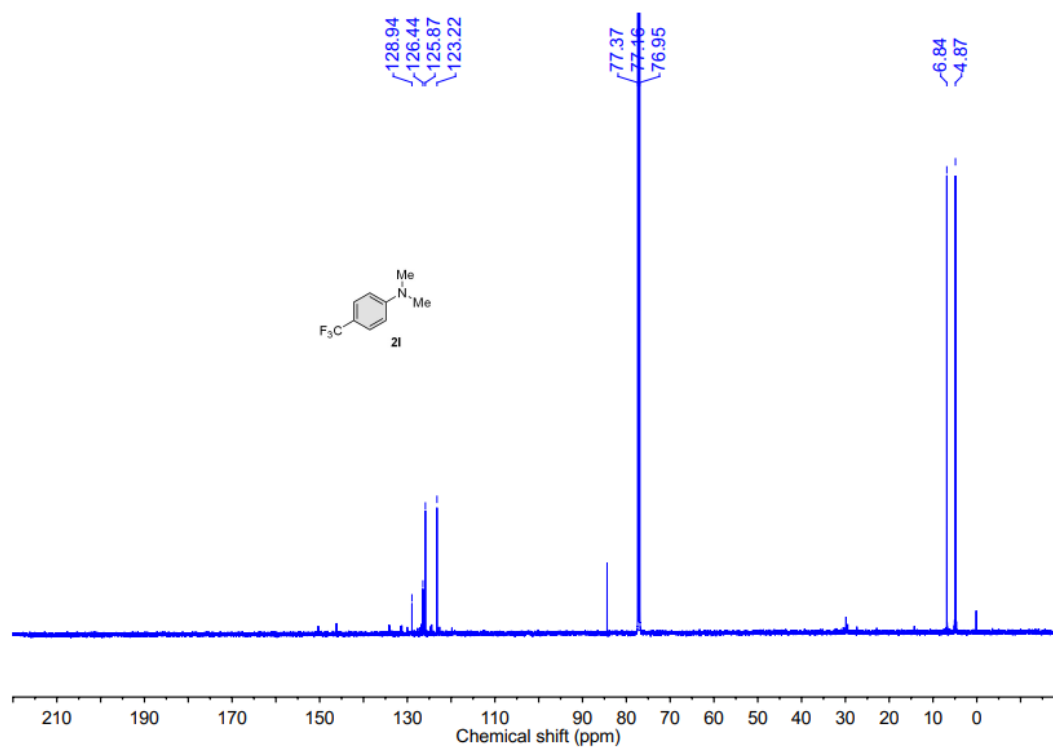
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2k**



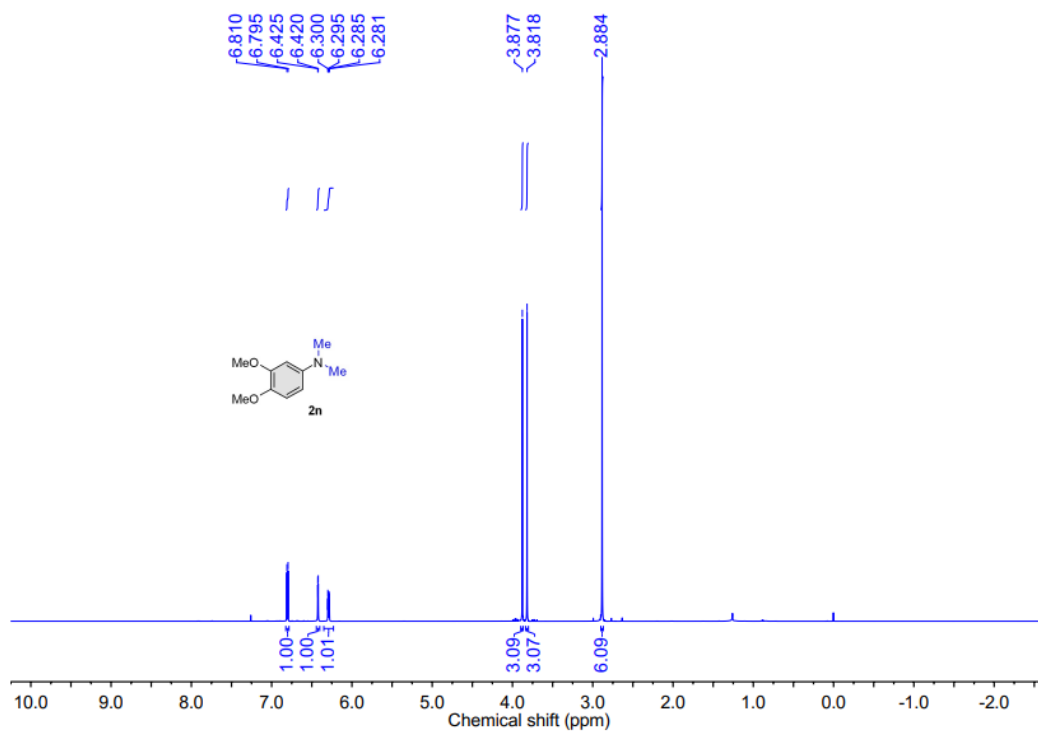
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2k**



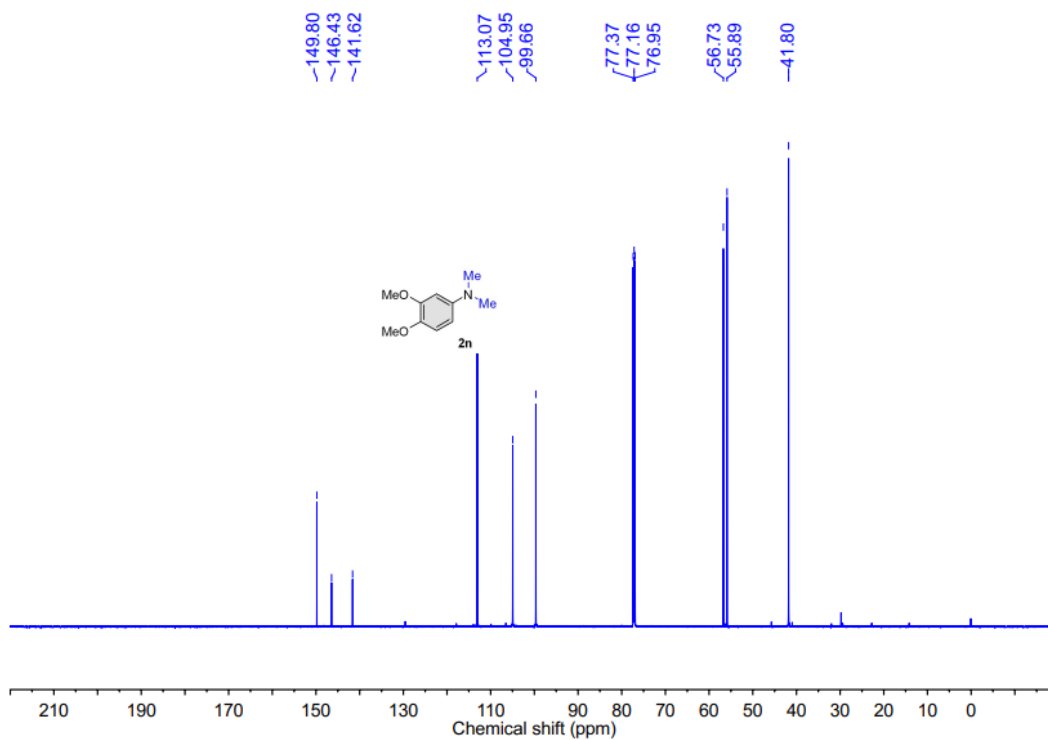
¹H NMR (600 MHz, CDCl₃, 298 K) of **2I**



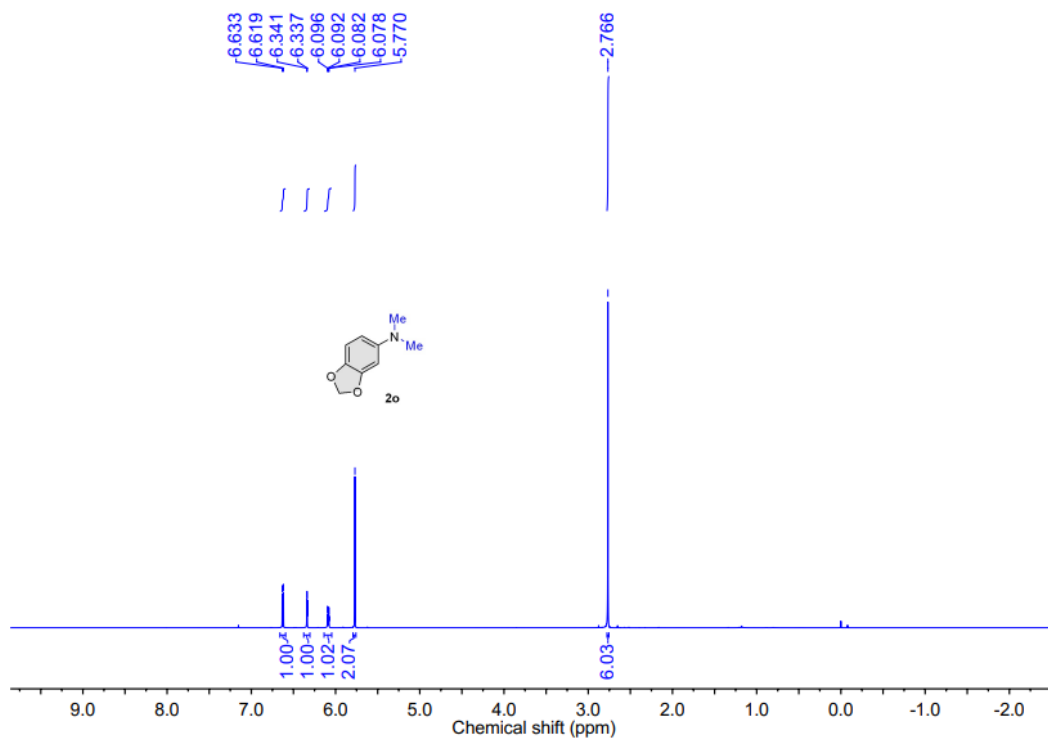
¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K) of **2I**



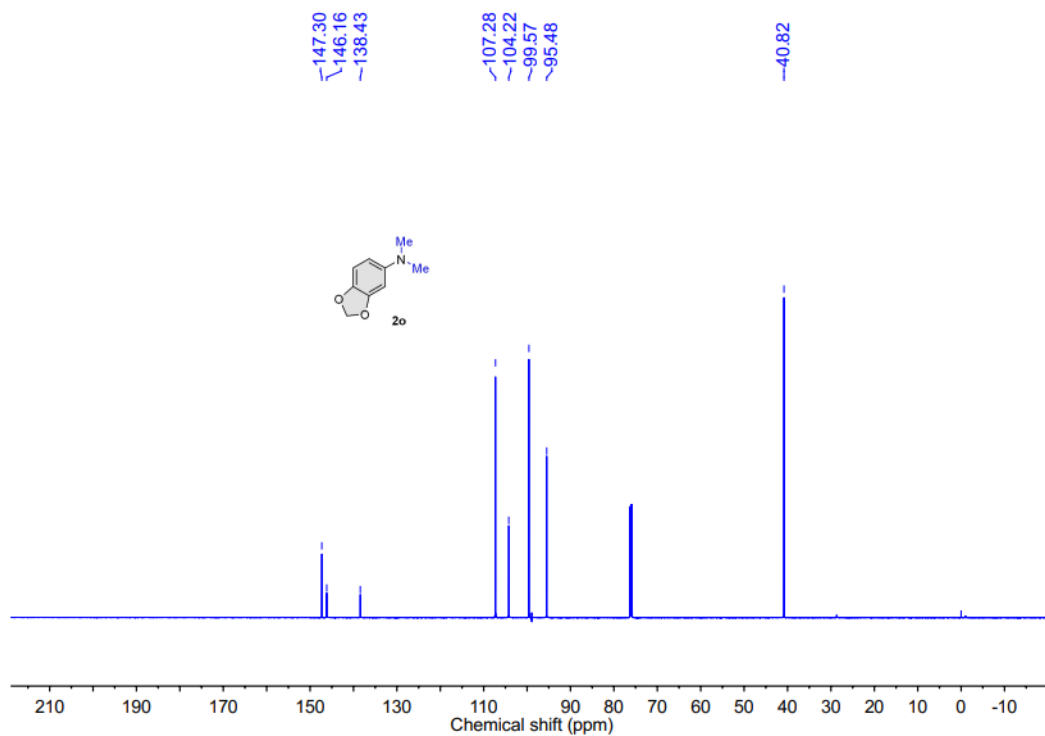
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2n**



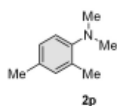
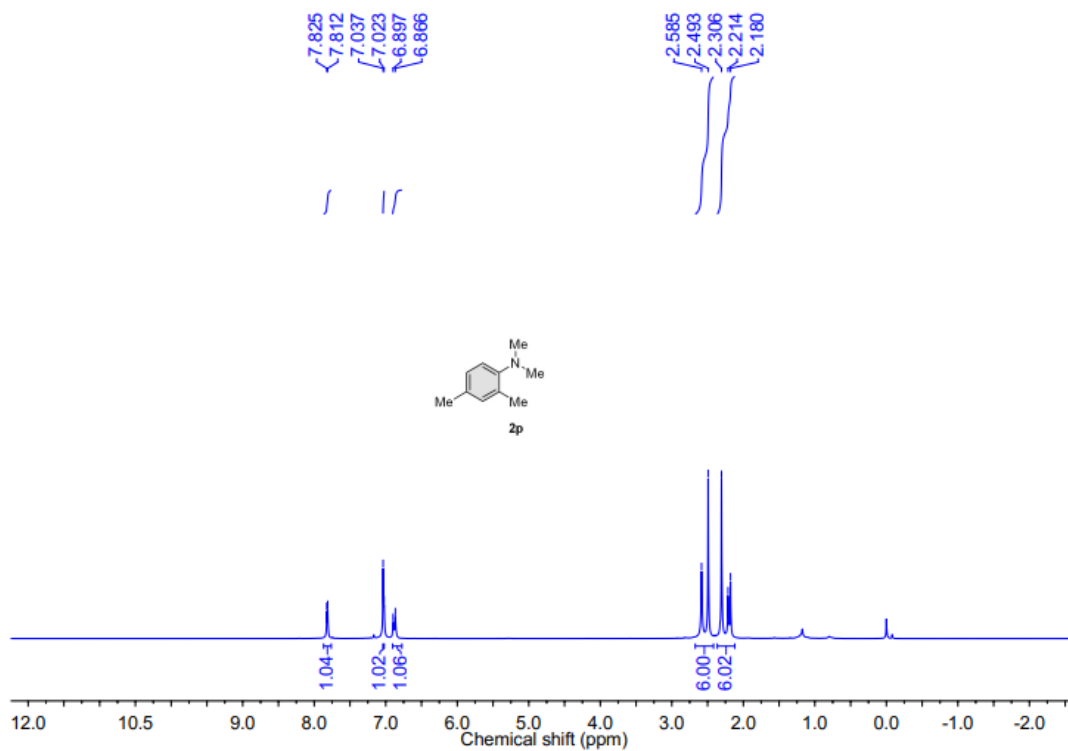
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2n**



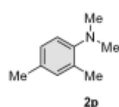
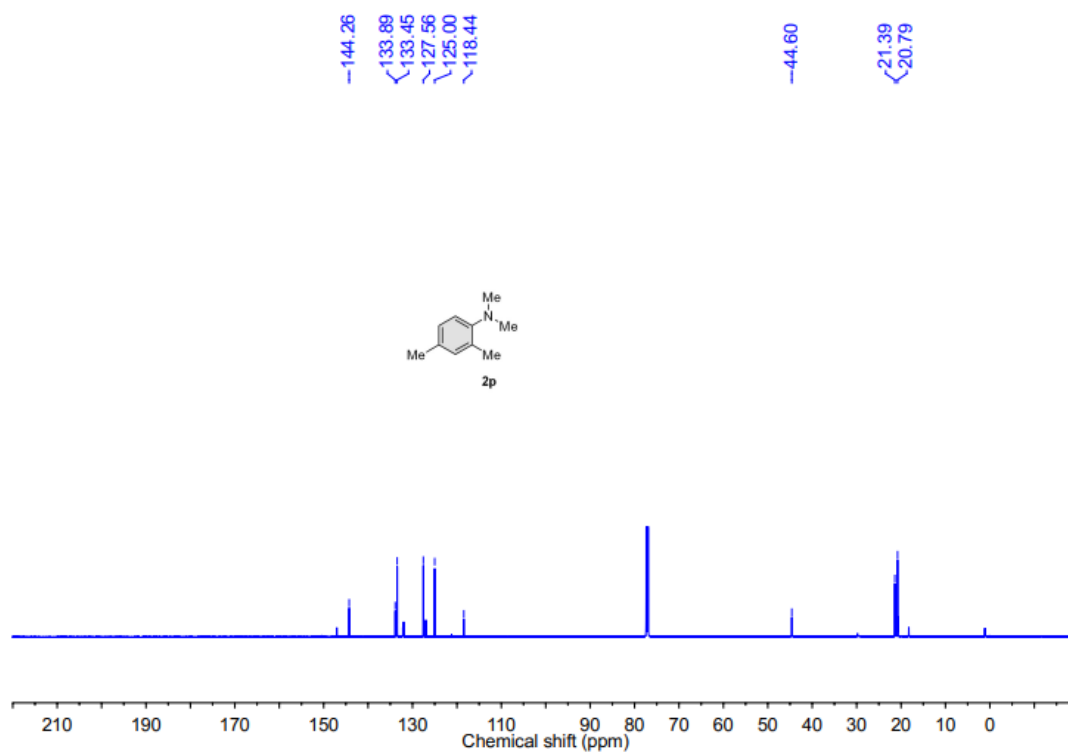
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2o**



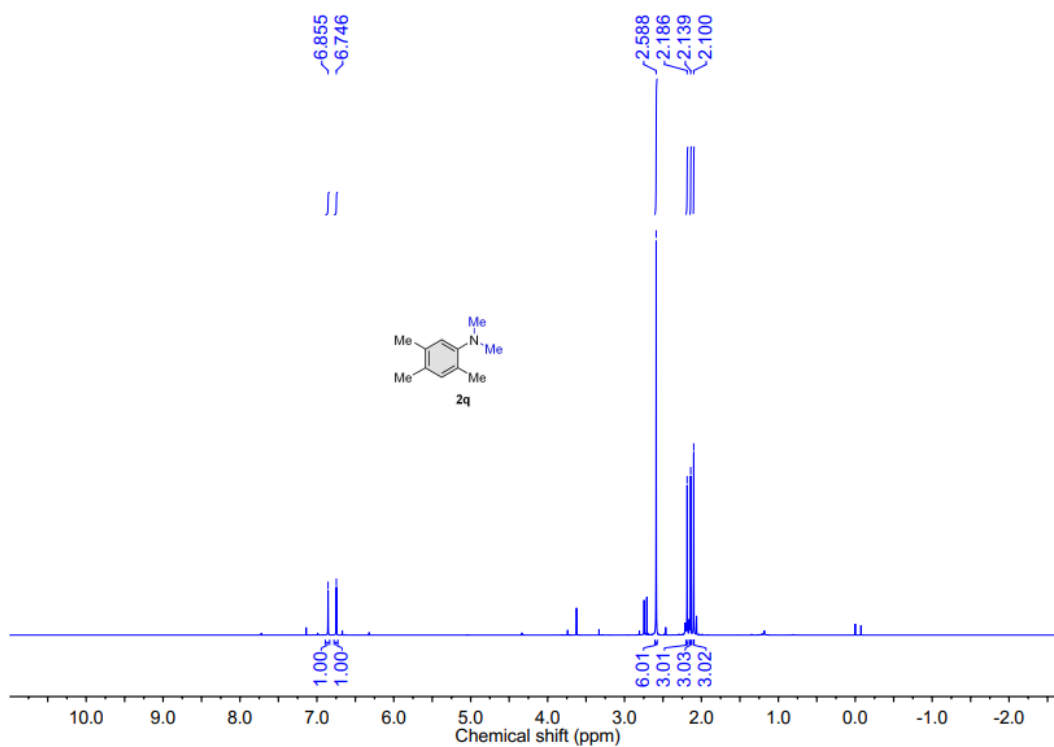
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2o**



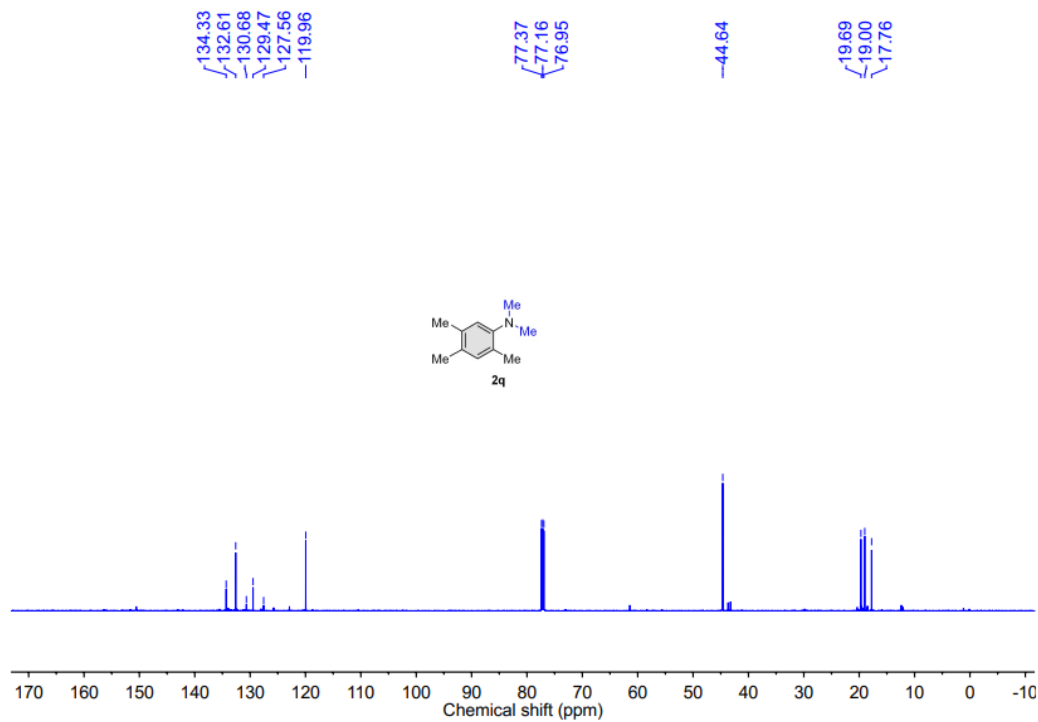
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2p**



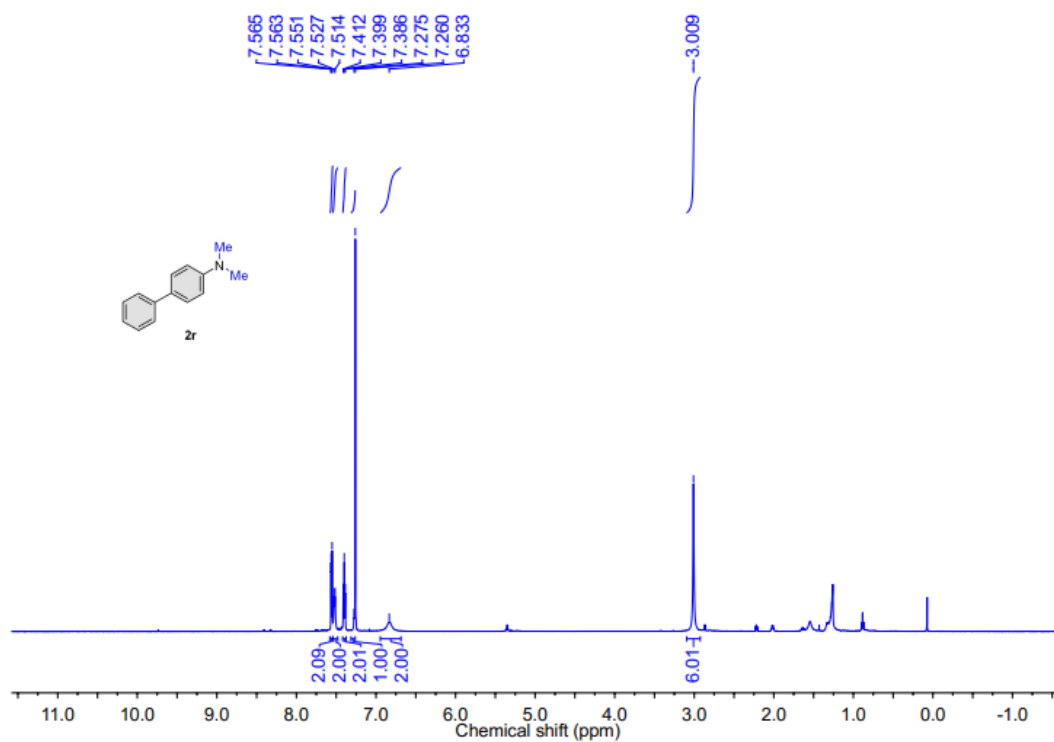
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2p**



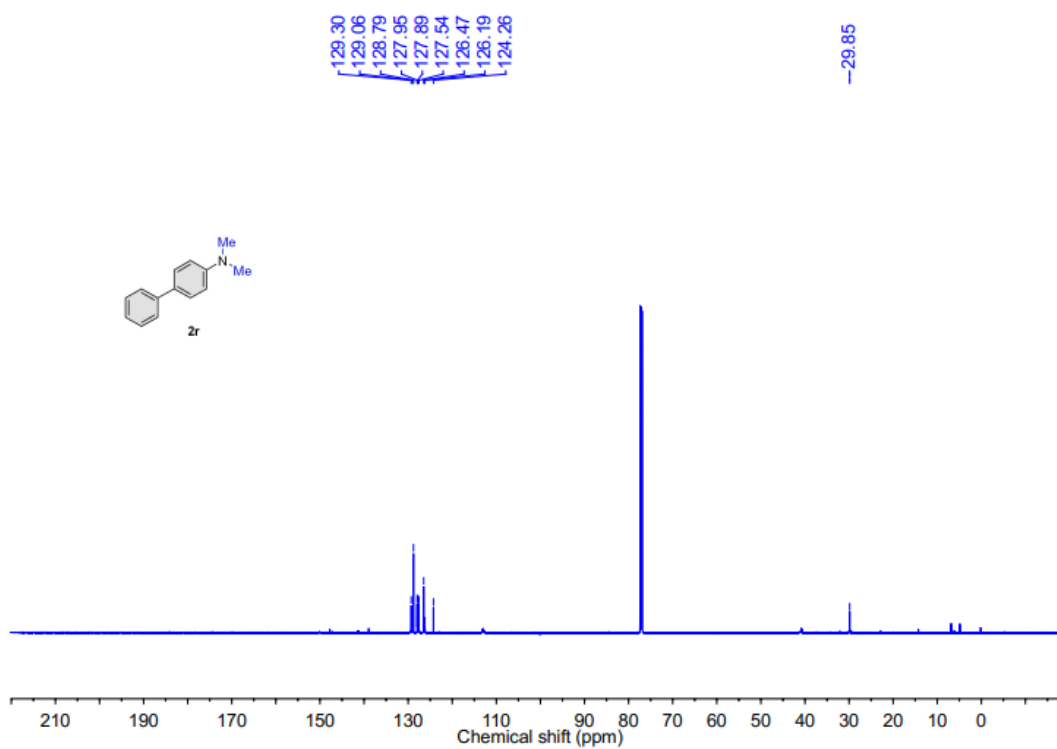
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2q**



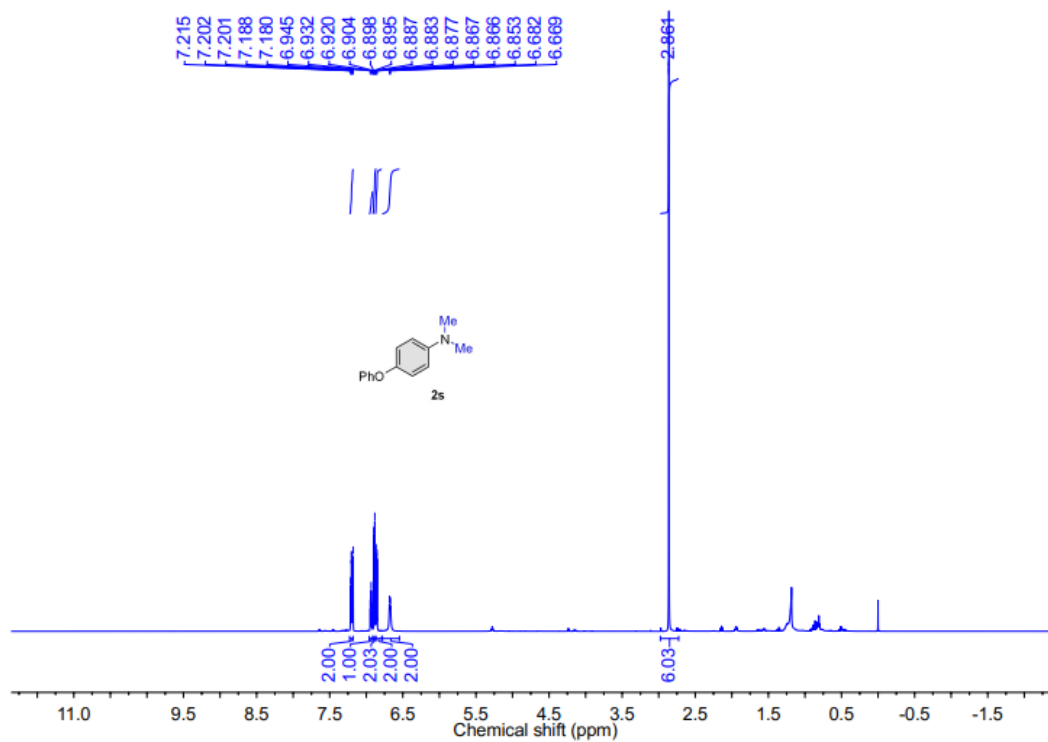
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2q**



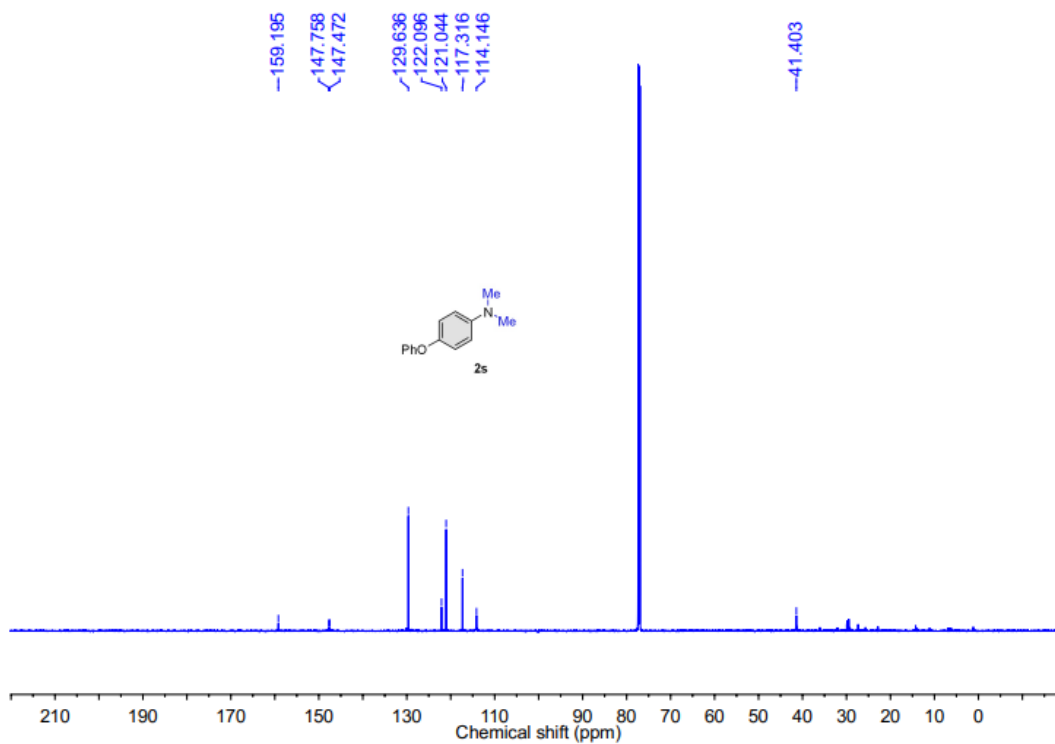
¹H NMR (600 MHz, CDCl₃, 298 K) of **2r**



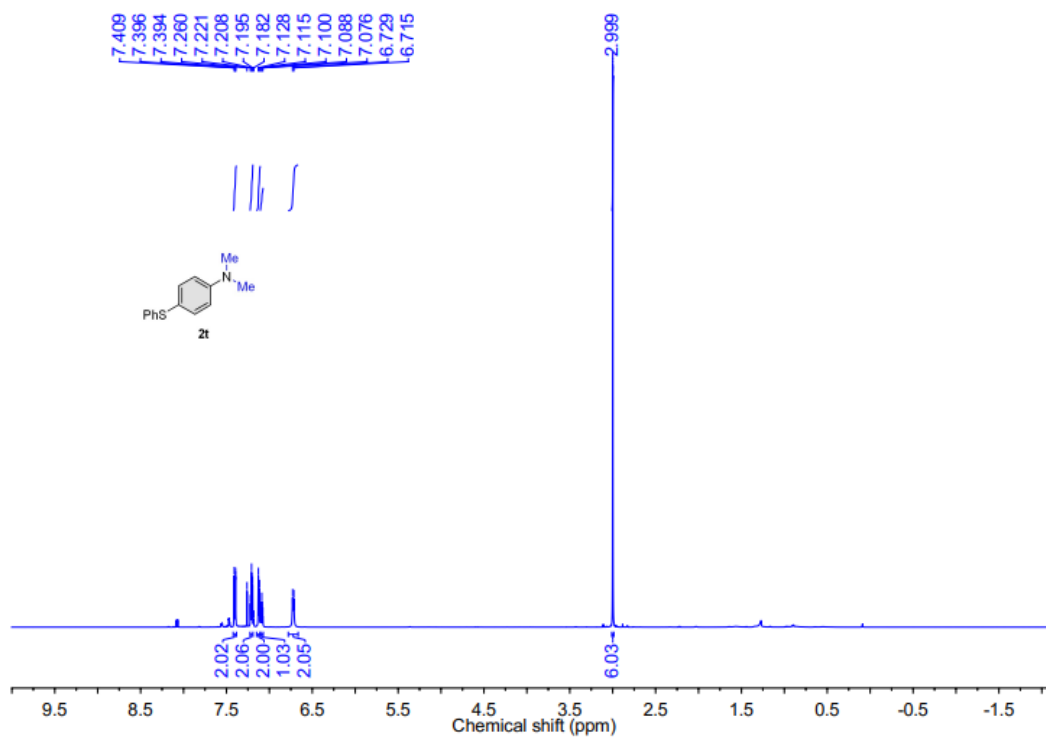
¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K) of **2r**



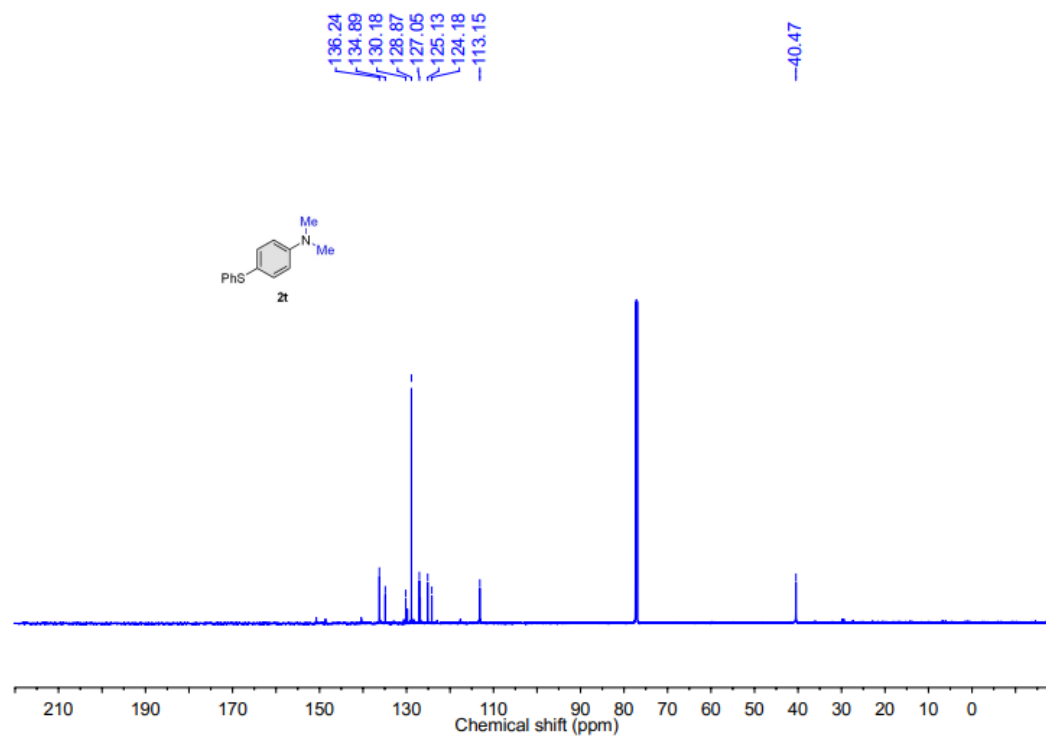
¹H NMR (600 MHz, CDCl₃, 298 K) of **2s**



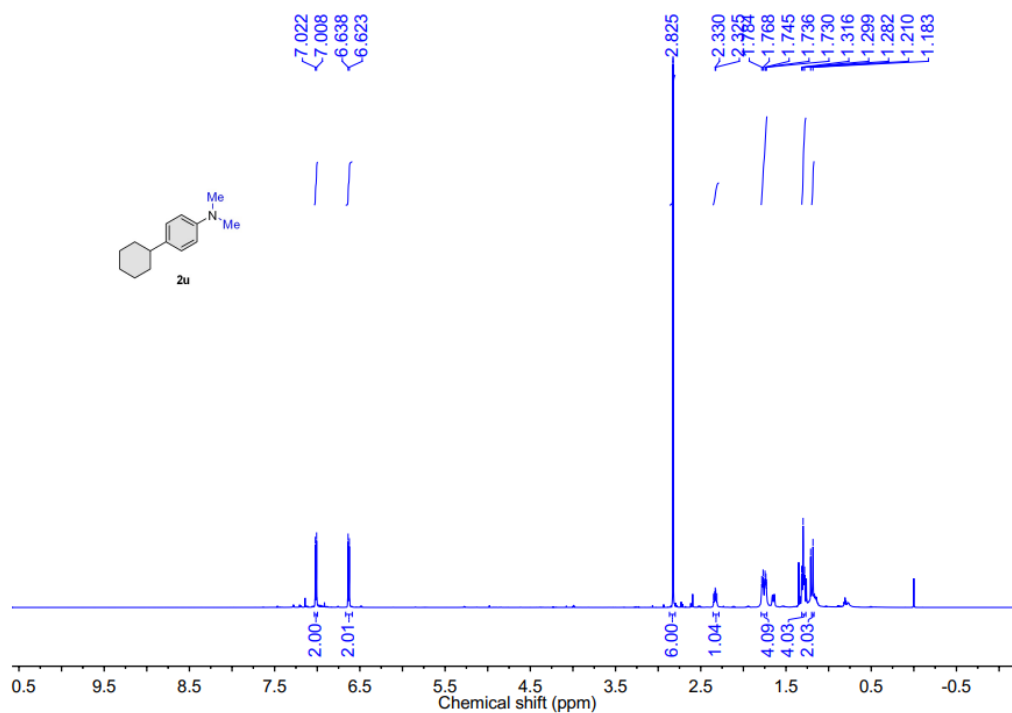
¹³C {¹H} NMR (151 MHz, CDCl₃, 298 K) of **2s**



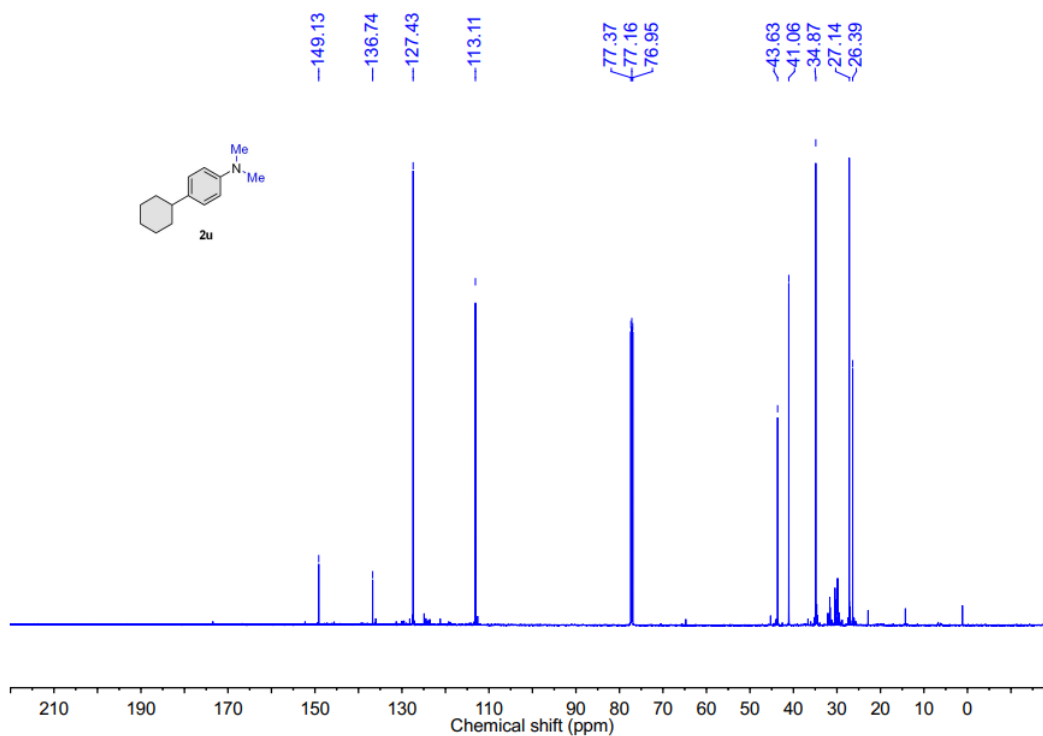
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2t**



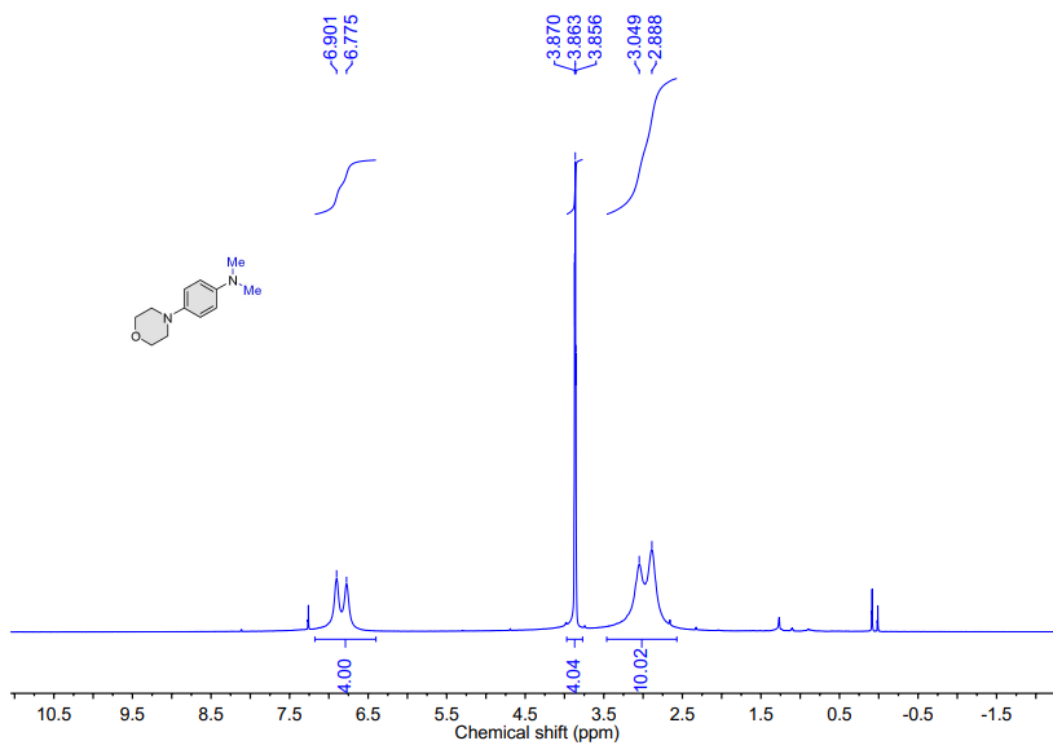
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2t**



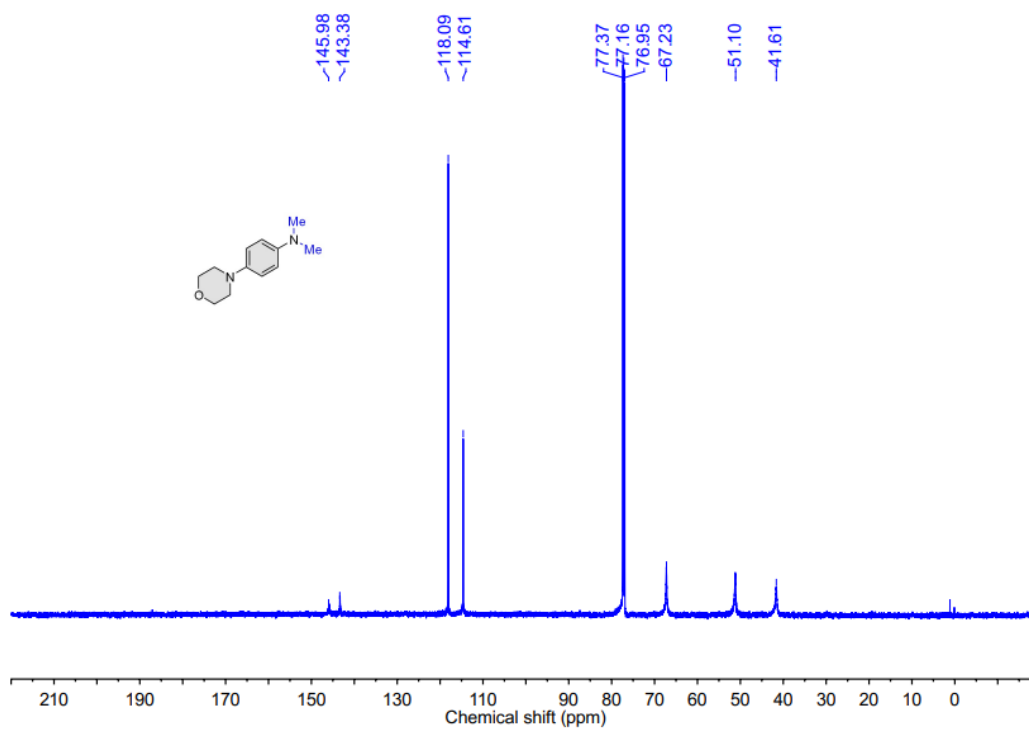
¹H NMR (600 MHz, CDCl₃, 298 K) of **2u**



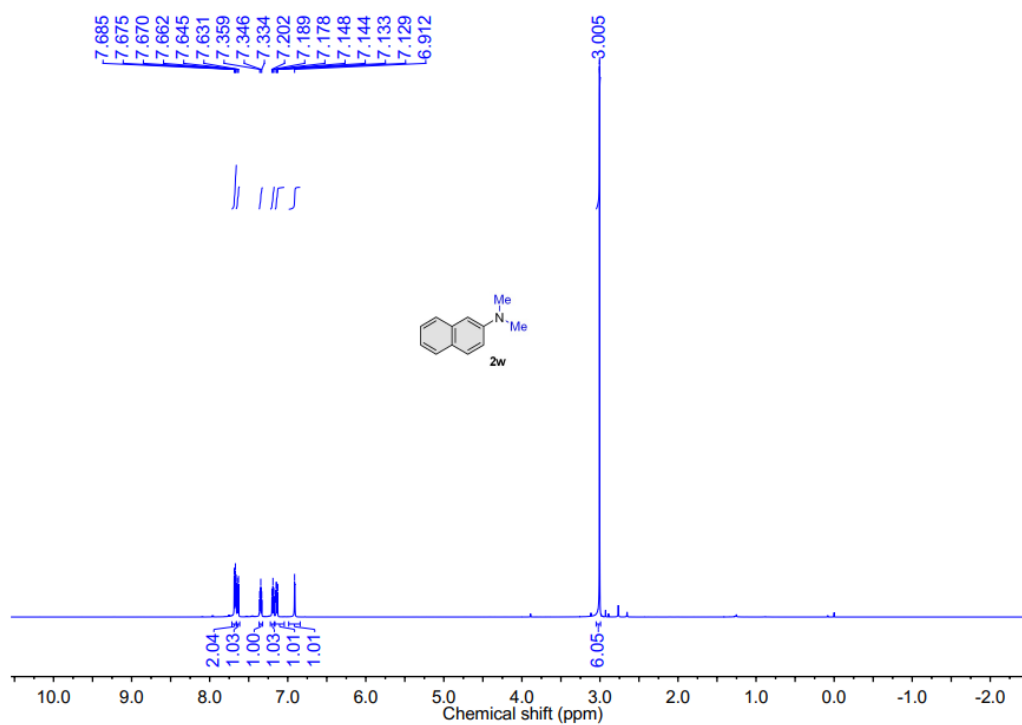
¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K) of **2u**



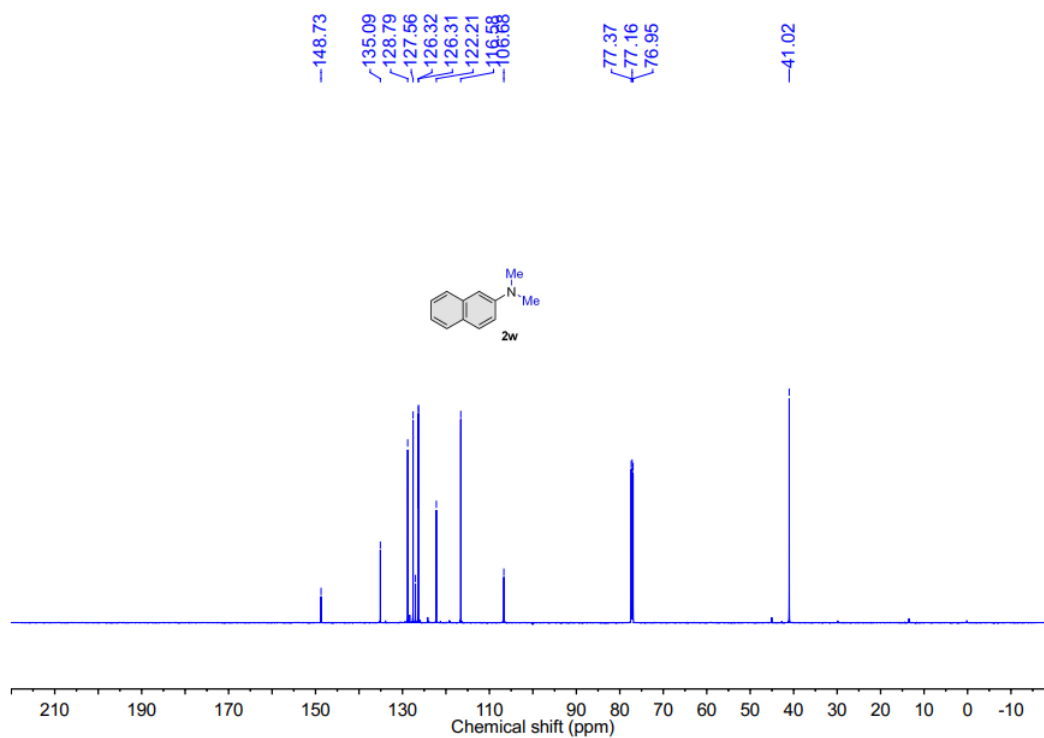
¹H NMR (600 MHz, CDCl₃, 298 K) of **2v**



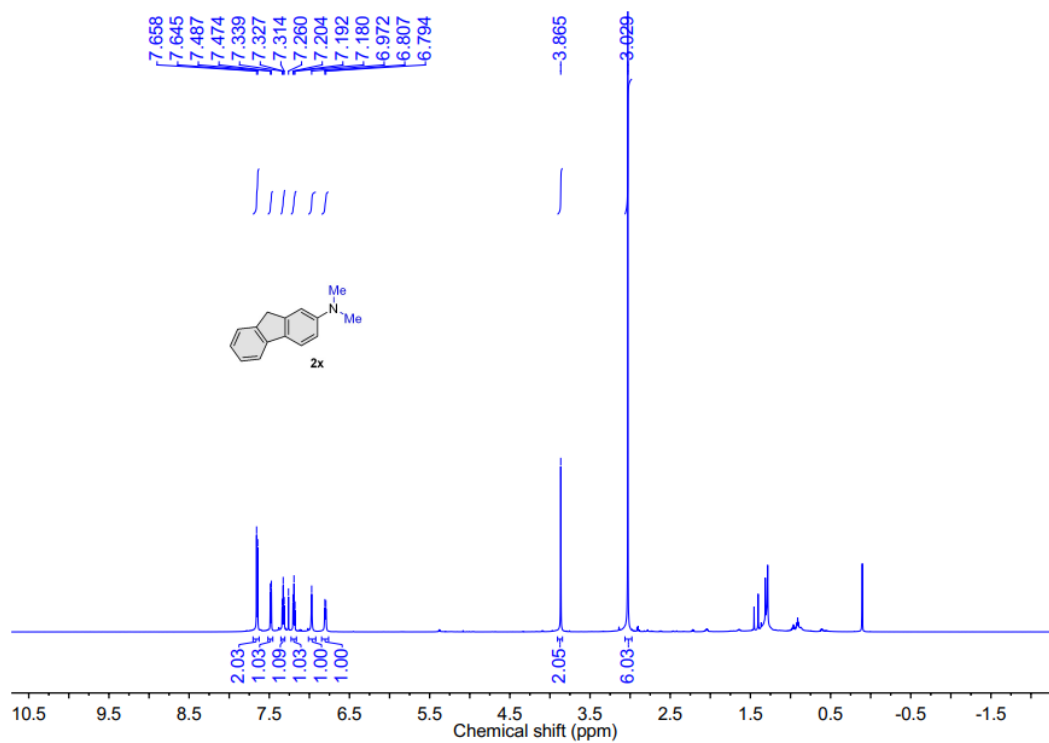
¹³C{¹H} NMR (151 MHz, CDCl₃, 298 K) of **2v**



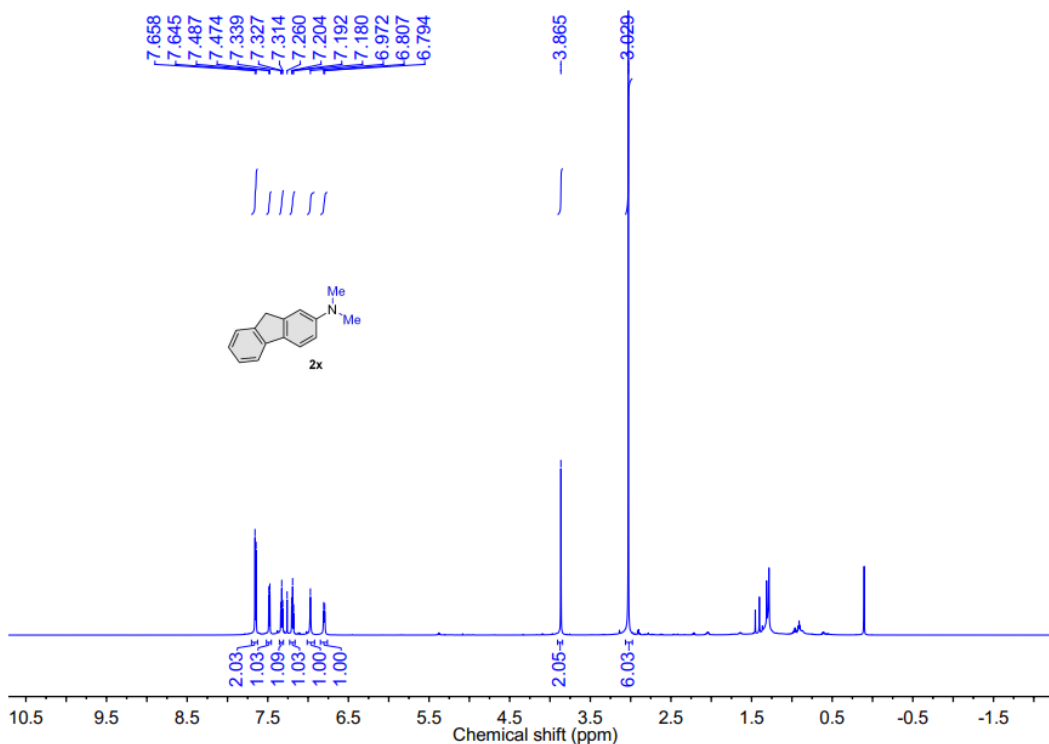
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2w**



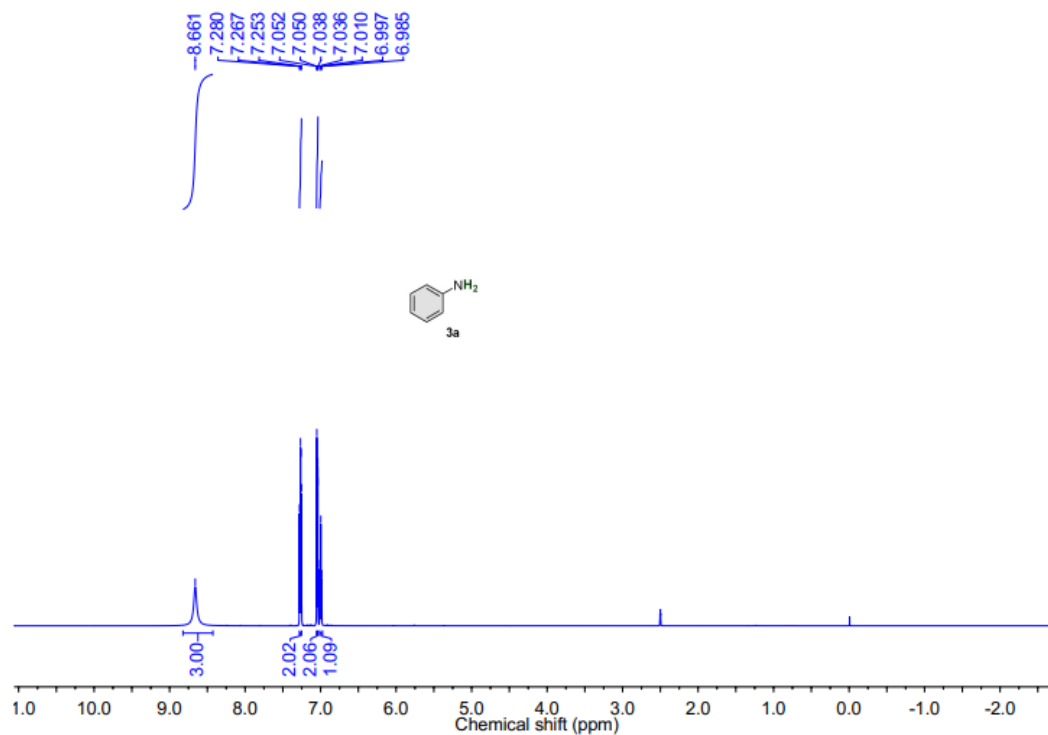
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2w**



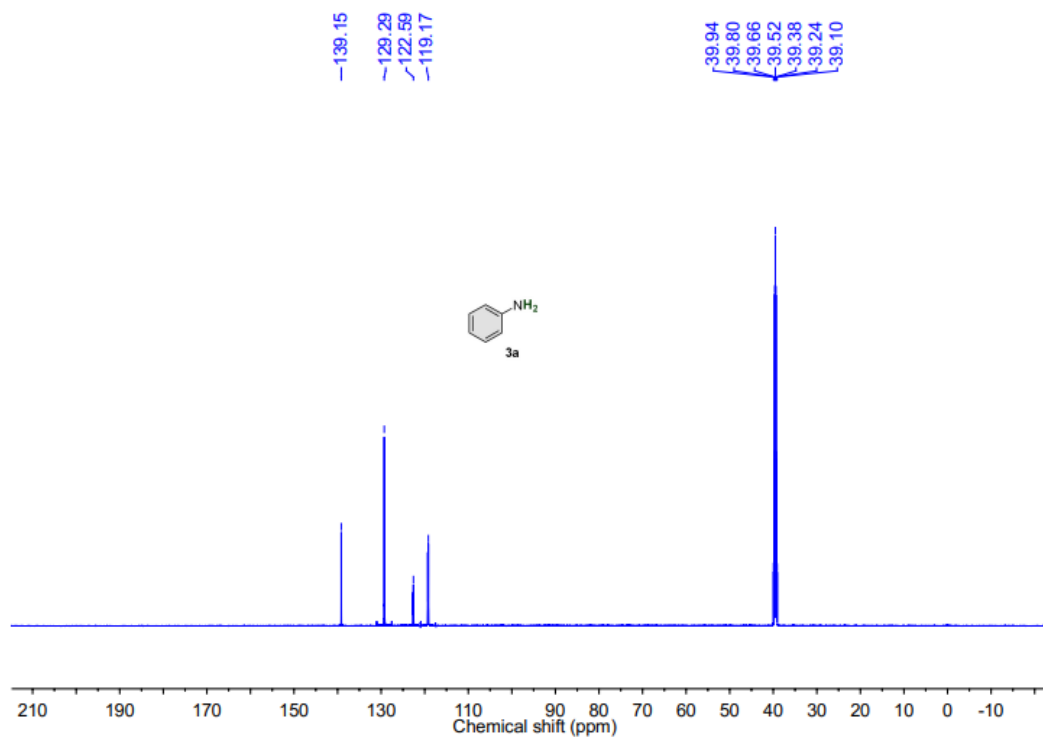
^1H NMR (600 MHz, CDCl_3 , 298 K) of **2x**



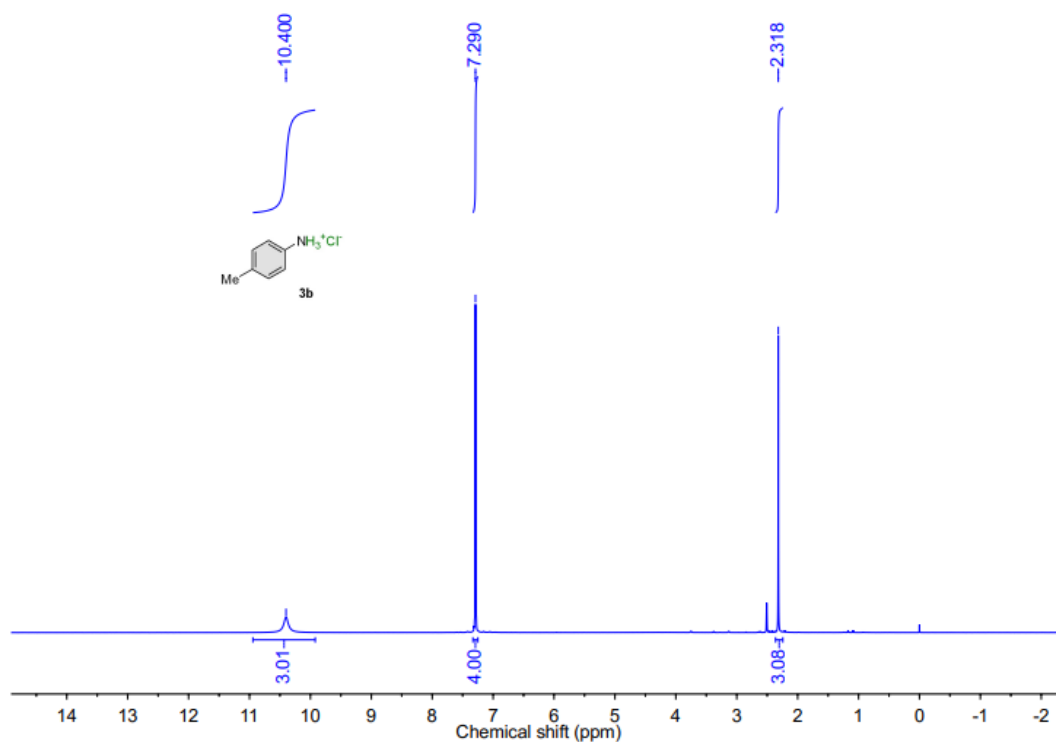
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , 298 K) of **2x**



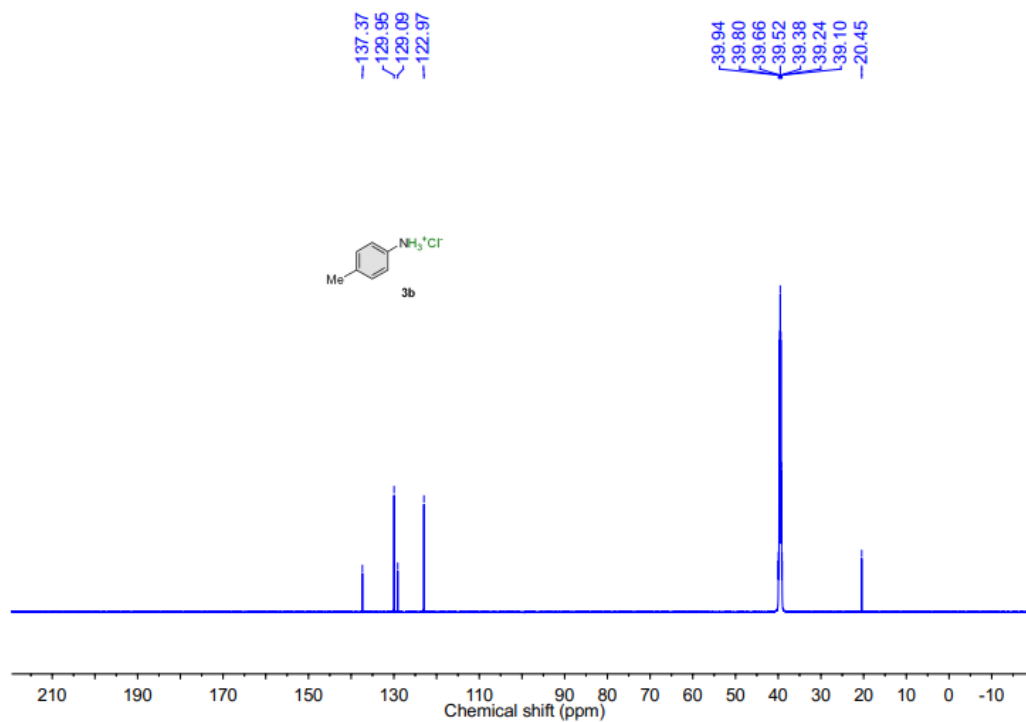
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3a**·HCl



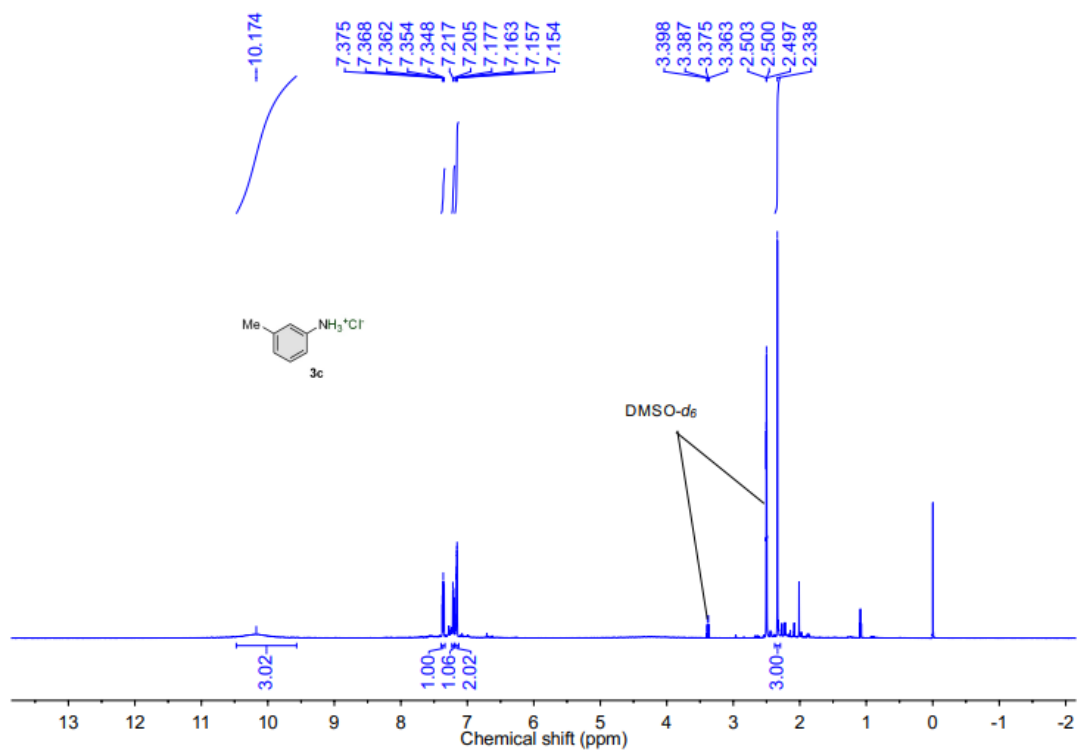
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3a**·HCl



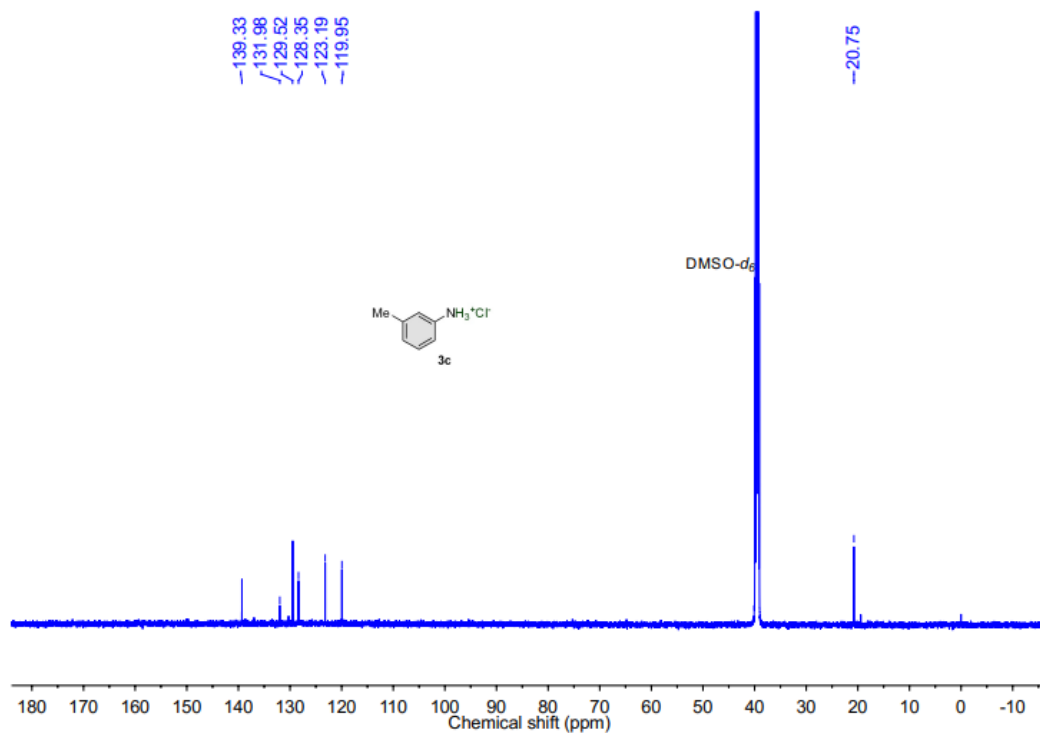
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3b**·HCl



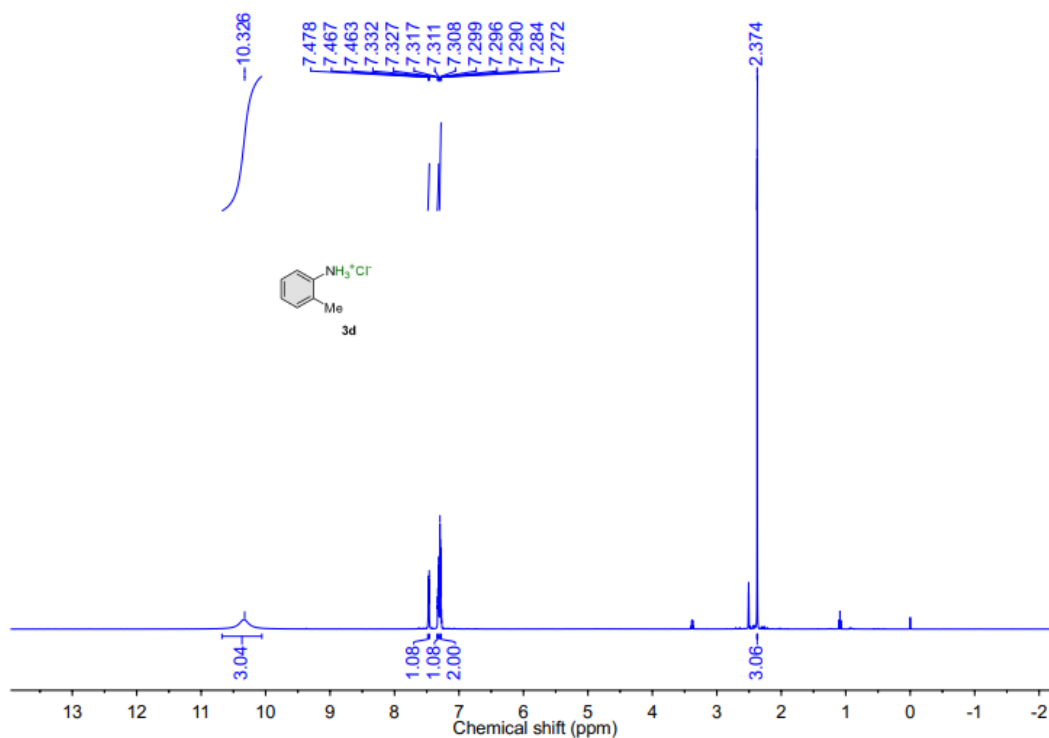
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3b**·HCl



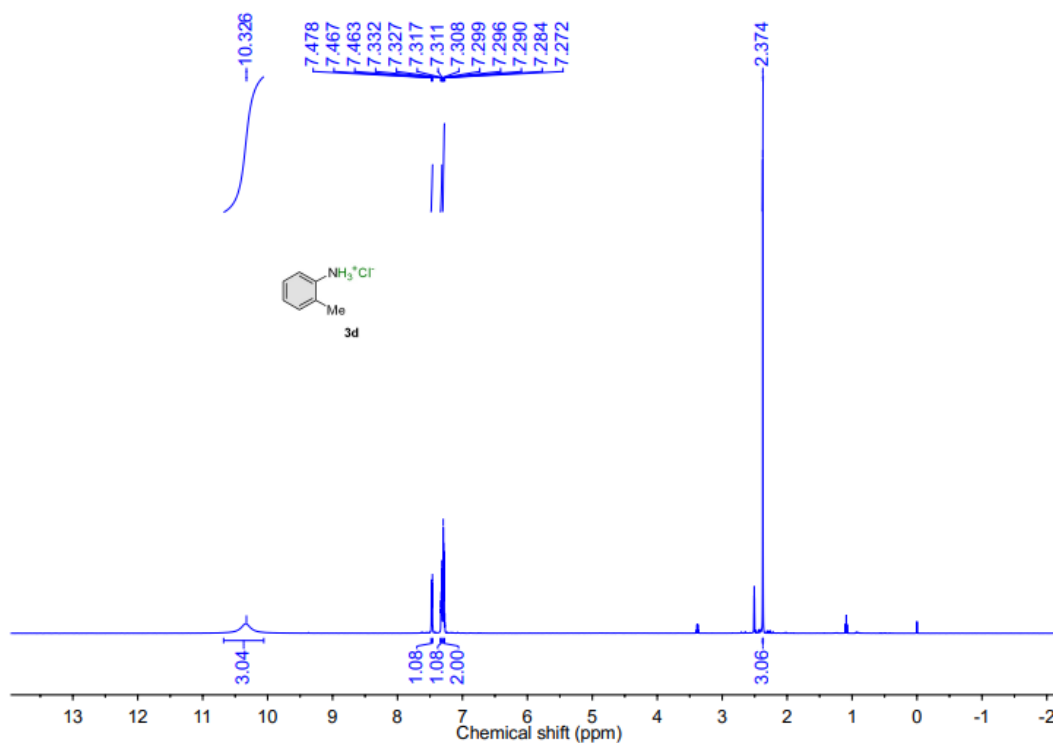
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3c**·HCl



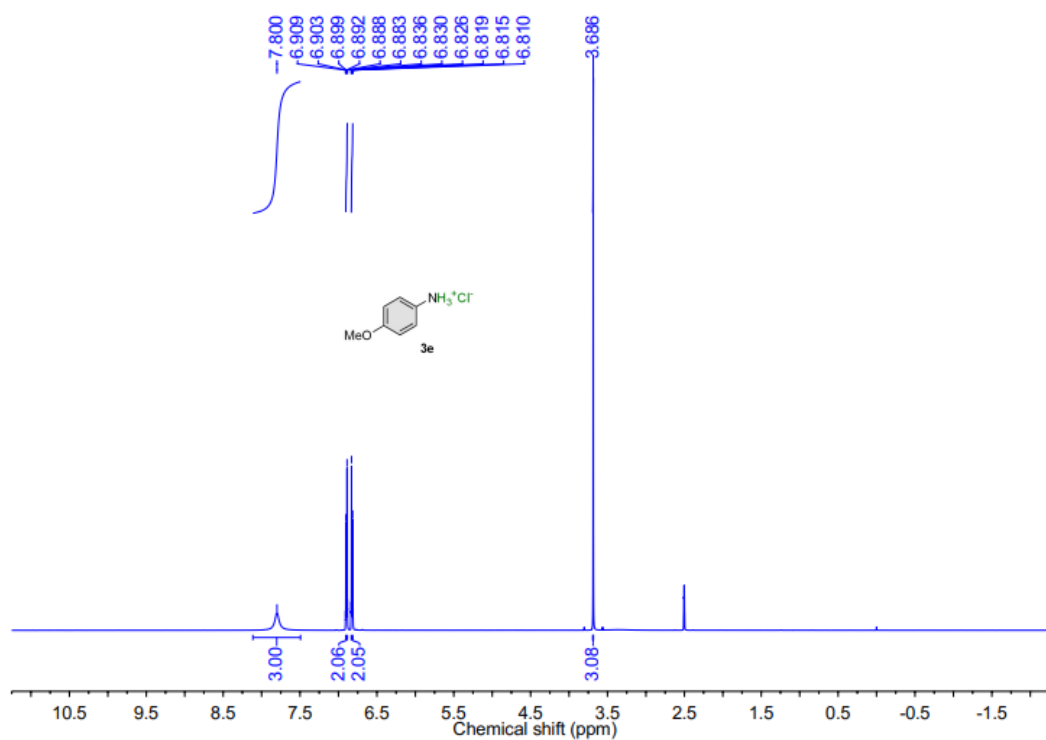
^{13}C { ^1H } NMR (151 MHz, DMSO- d_6 , 298 K) of **3c**·HCl



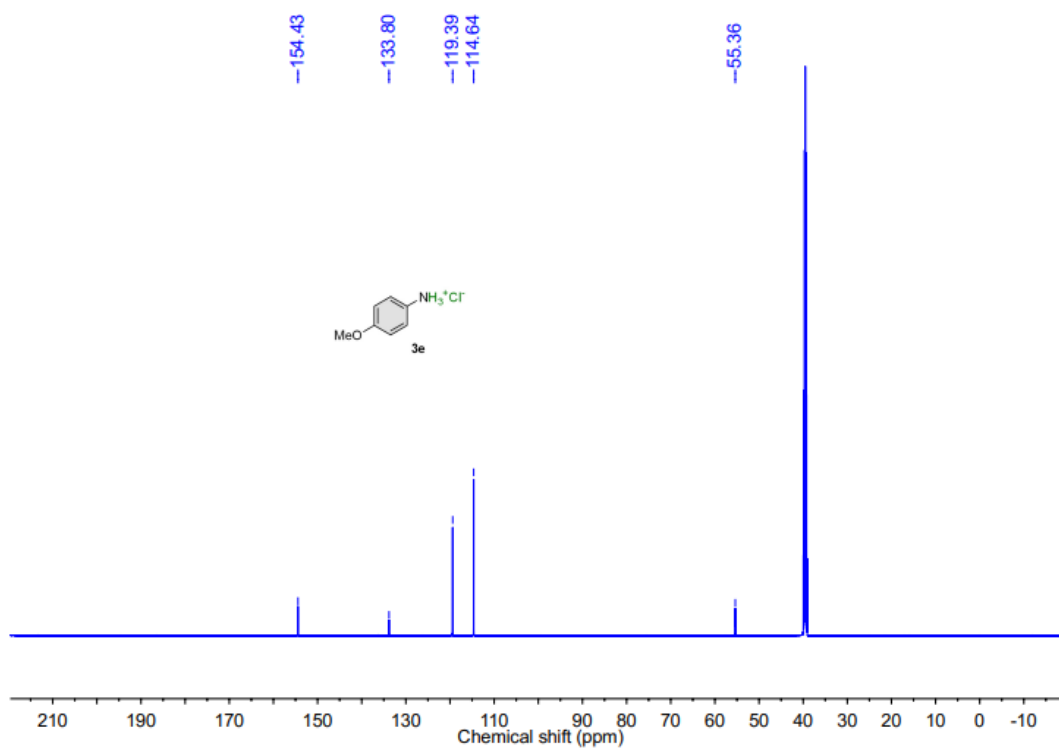
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3d**·HCl



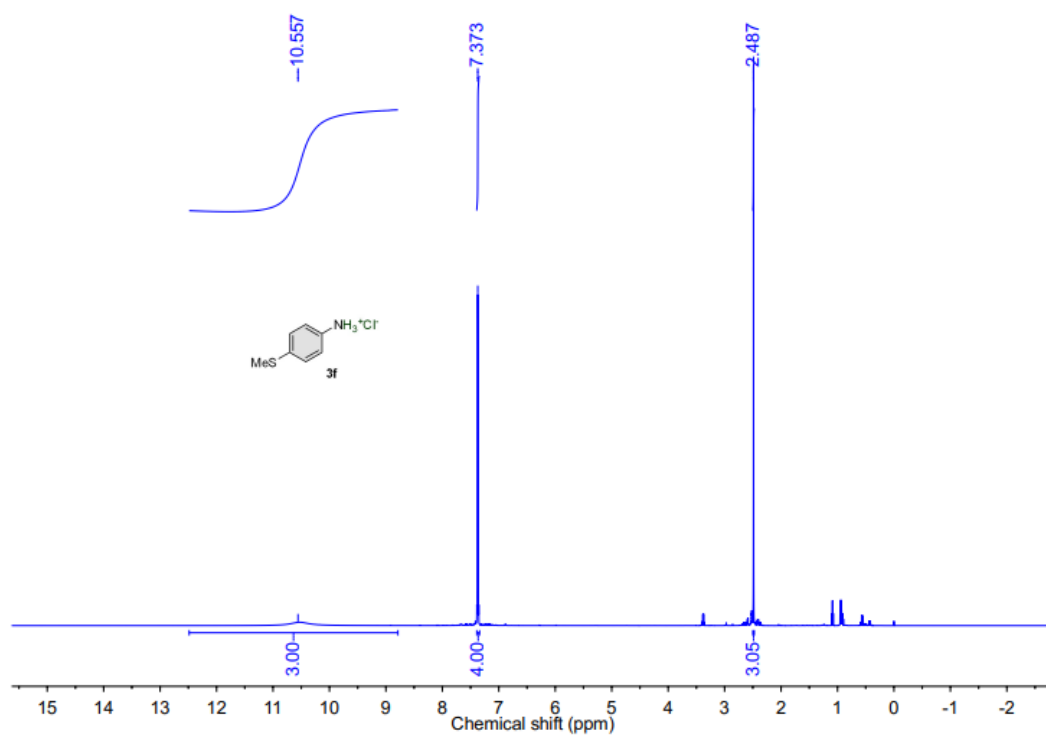
¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3d**·HCl



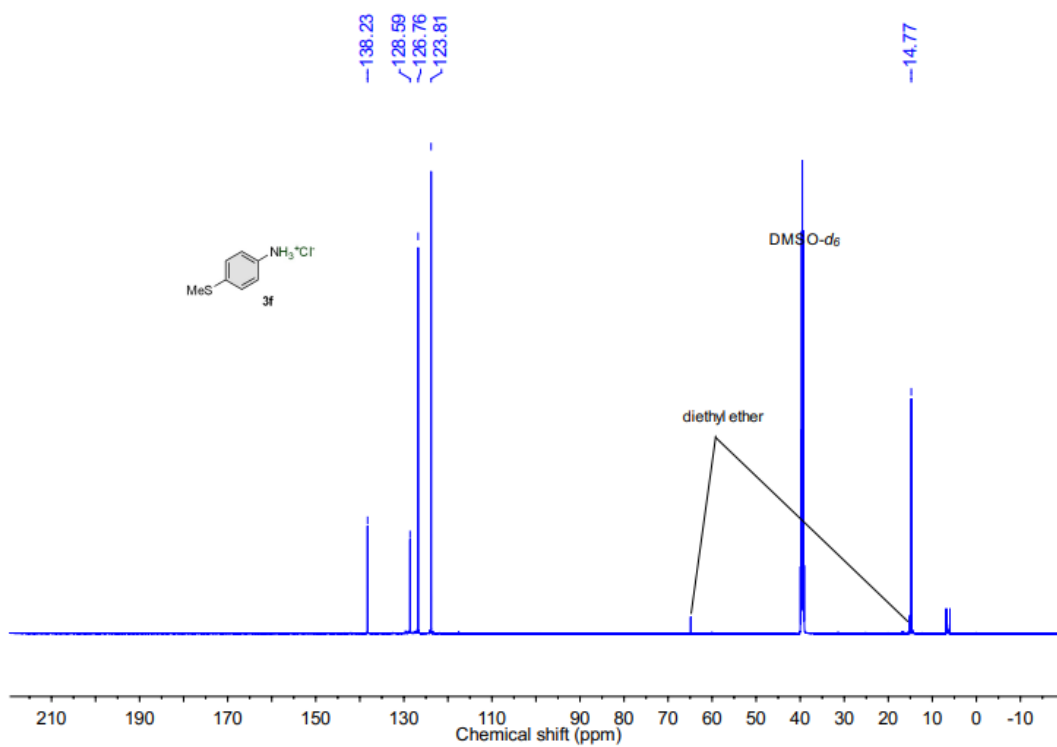
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3e·HCl**



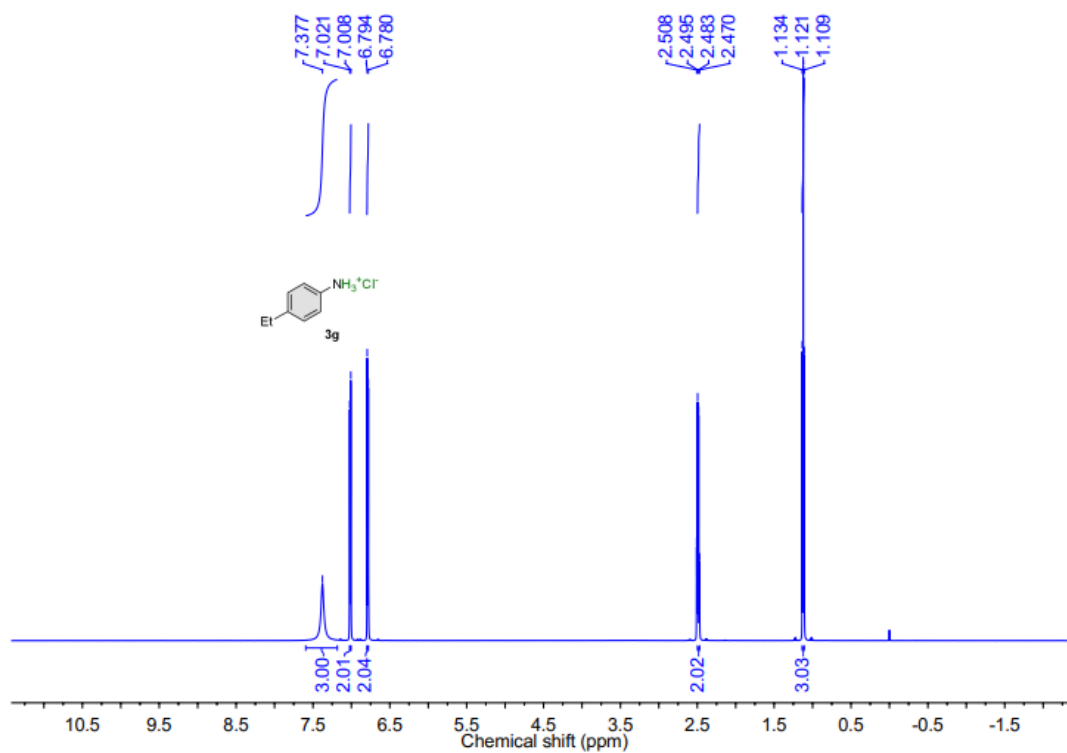
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3e·HCl**



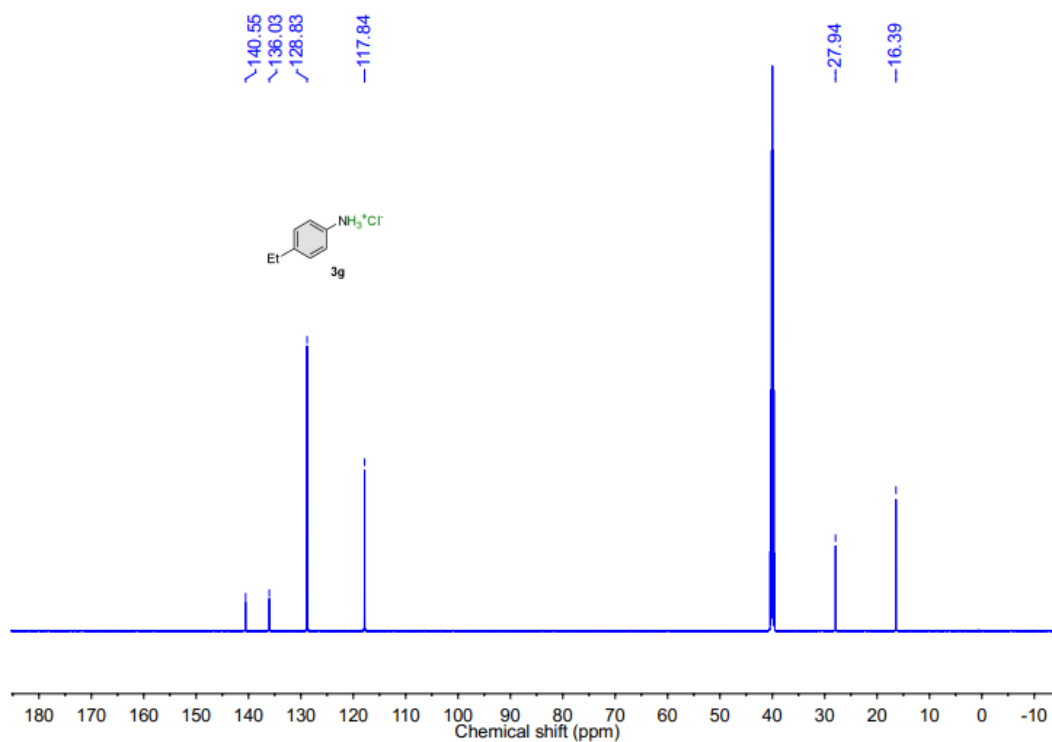
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3f**·HCl



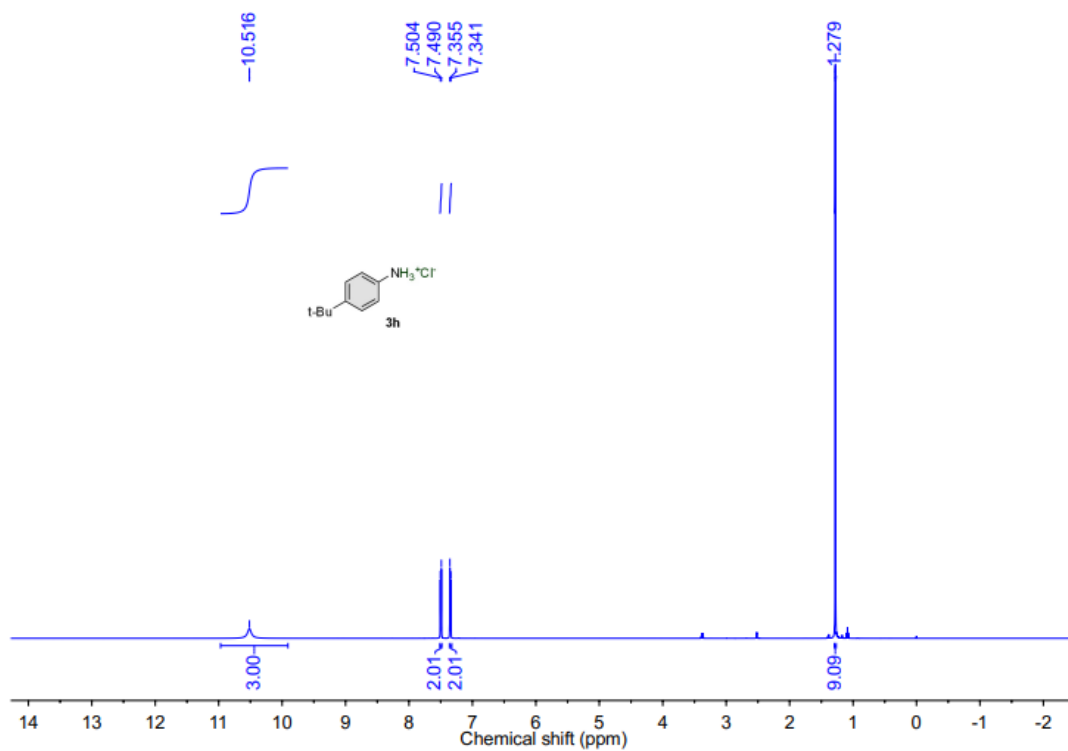
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3f**·HCl



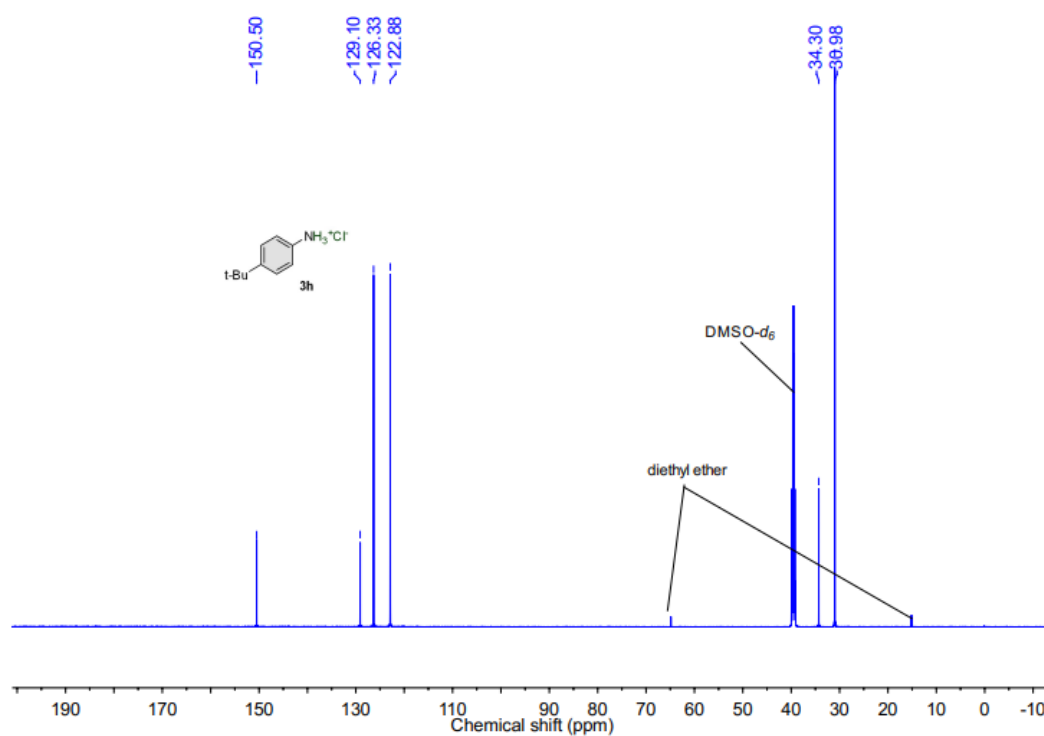
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3g·HCl**



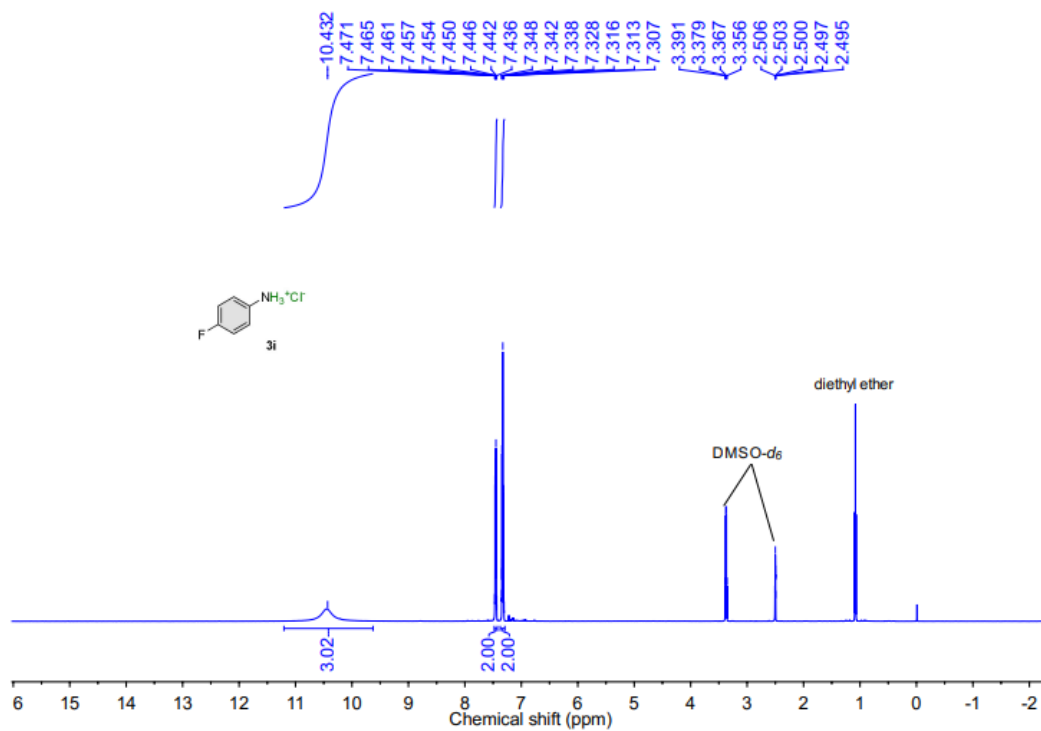
¹³C {¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3g·HCl**



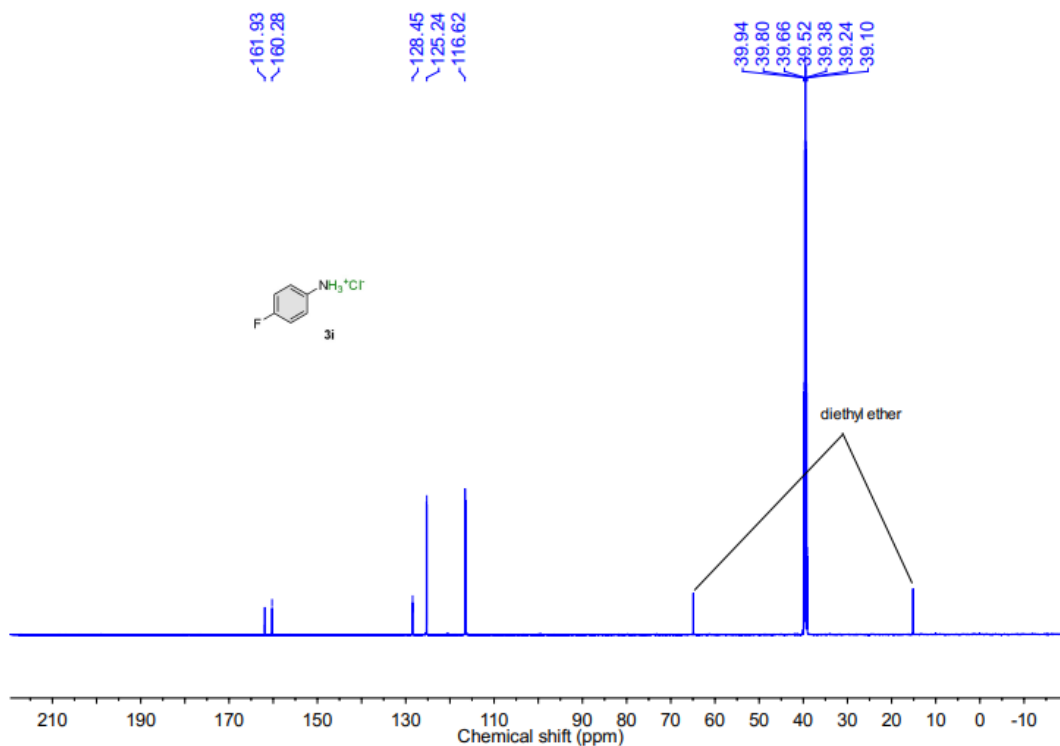
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3h**·HCl



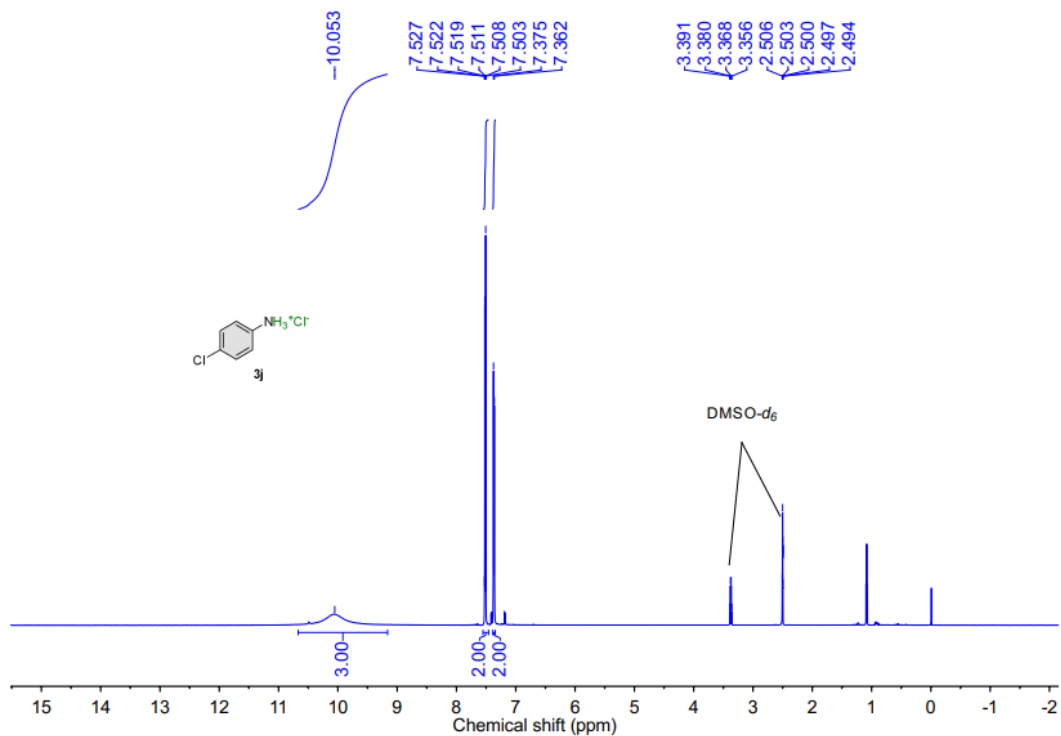
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3h**·HCl



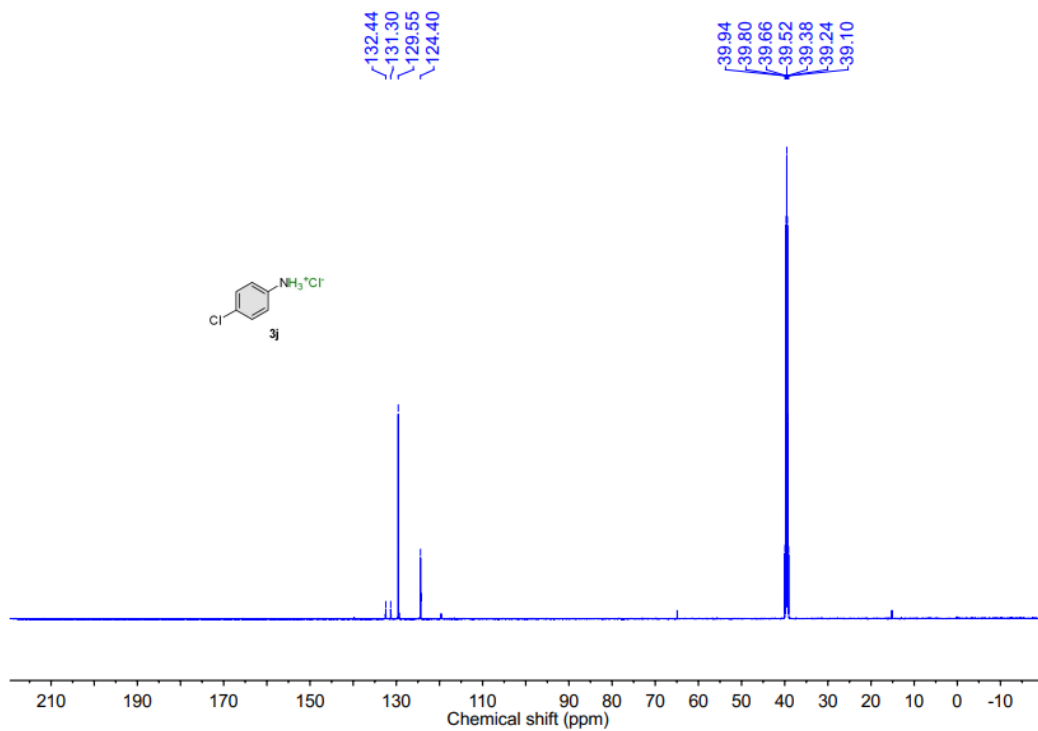
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3i**·HCl



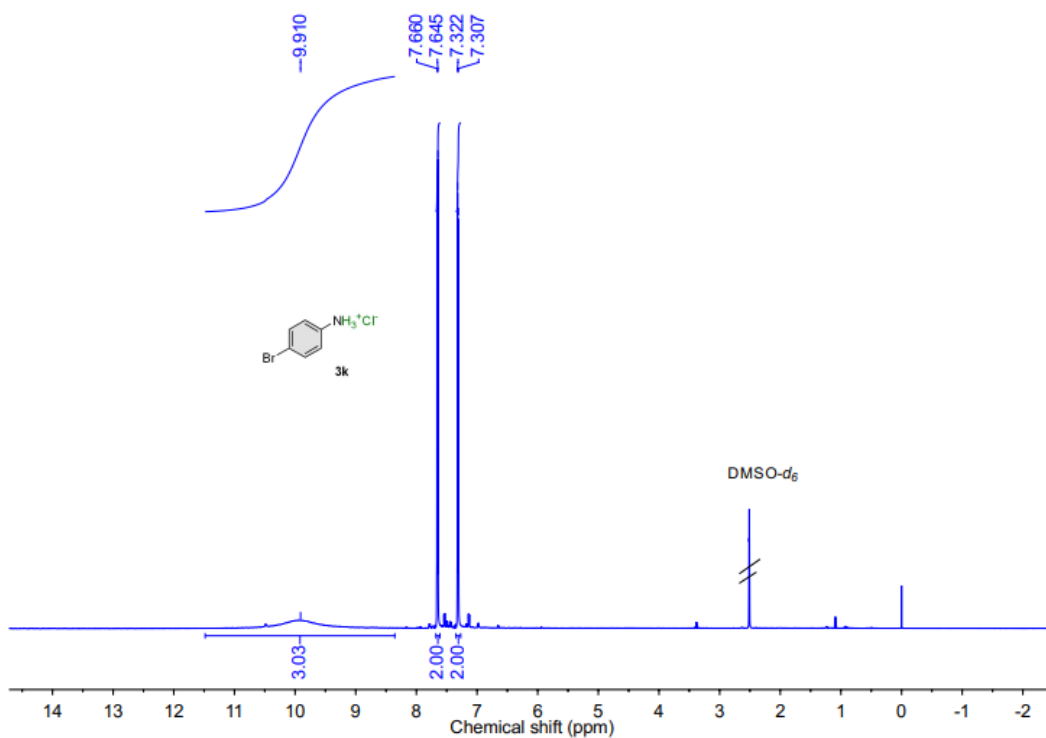
¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3i**·HCl



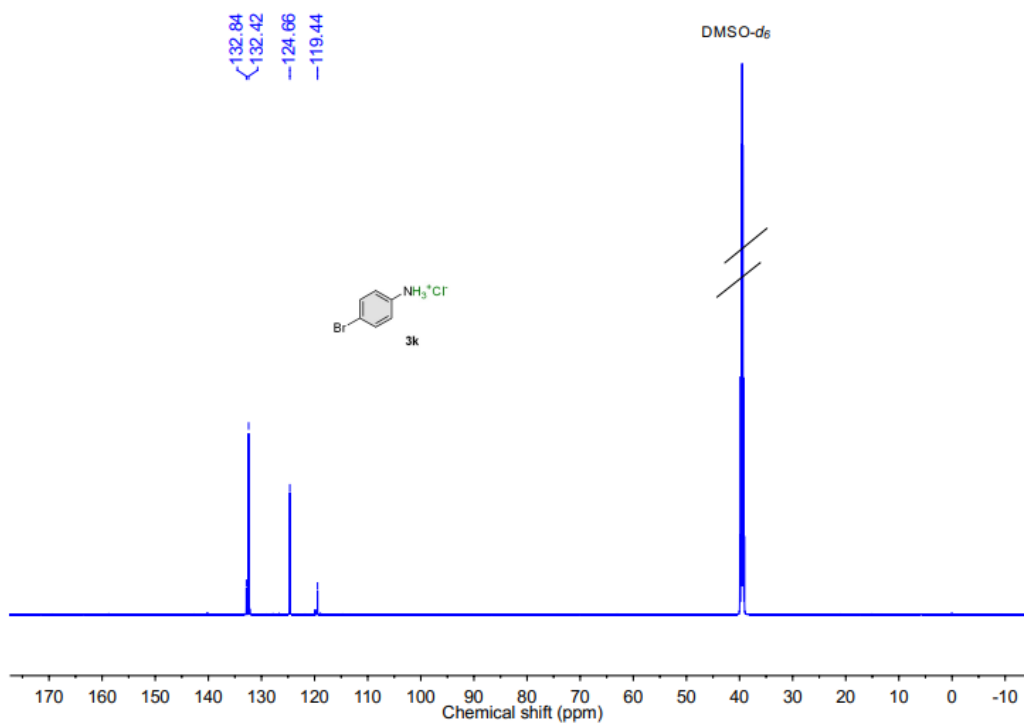
$^1\text{H NMR}$ (600 MHz, DMSO-d_6 , 298 K) of **3j**·HCl



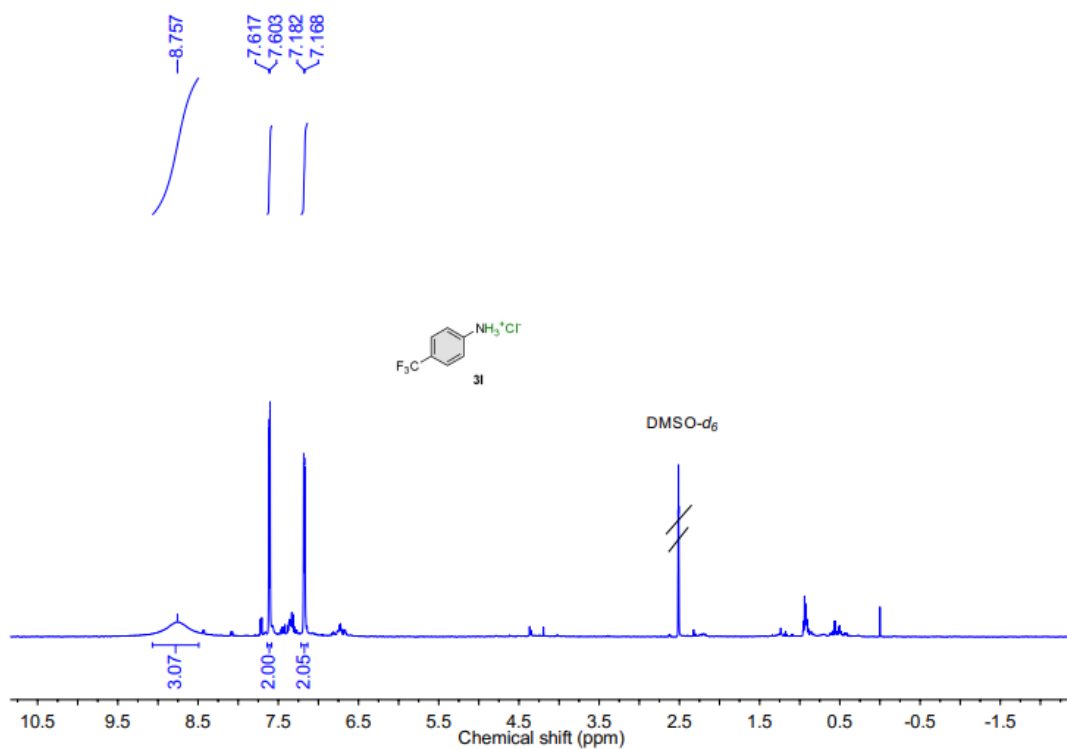
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO-d_6 , 298 K) of **3j**·HCl



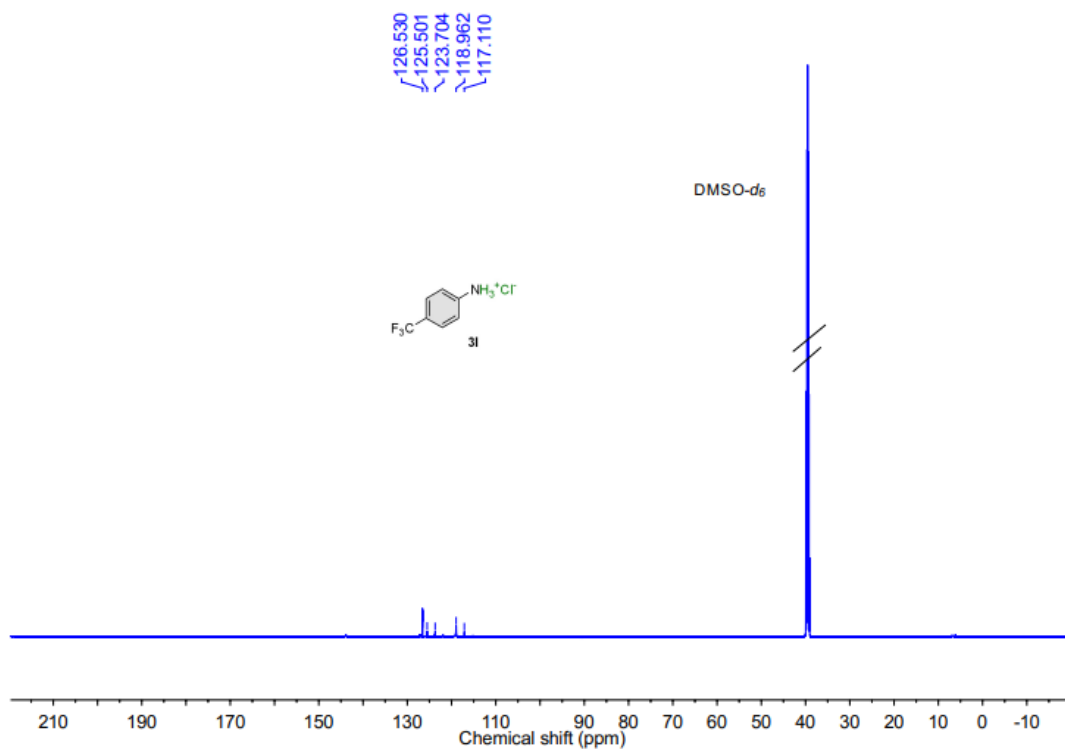
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3k**·HCl



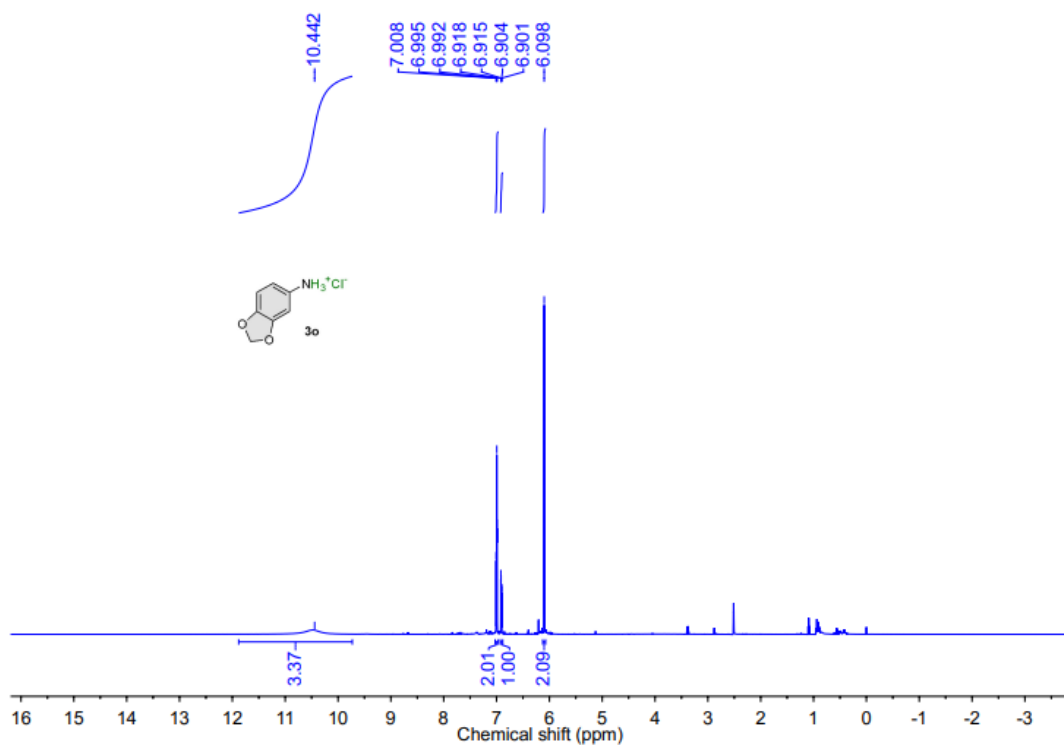
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3k**·HCl



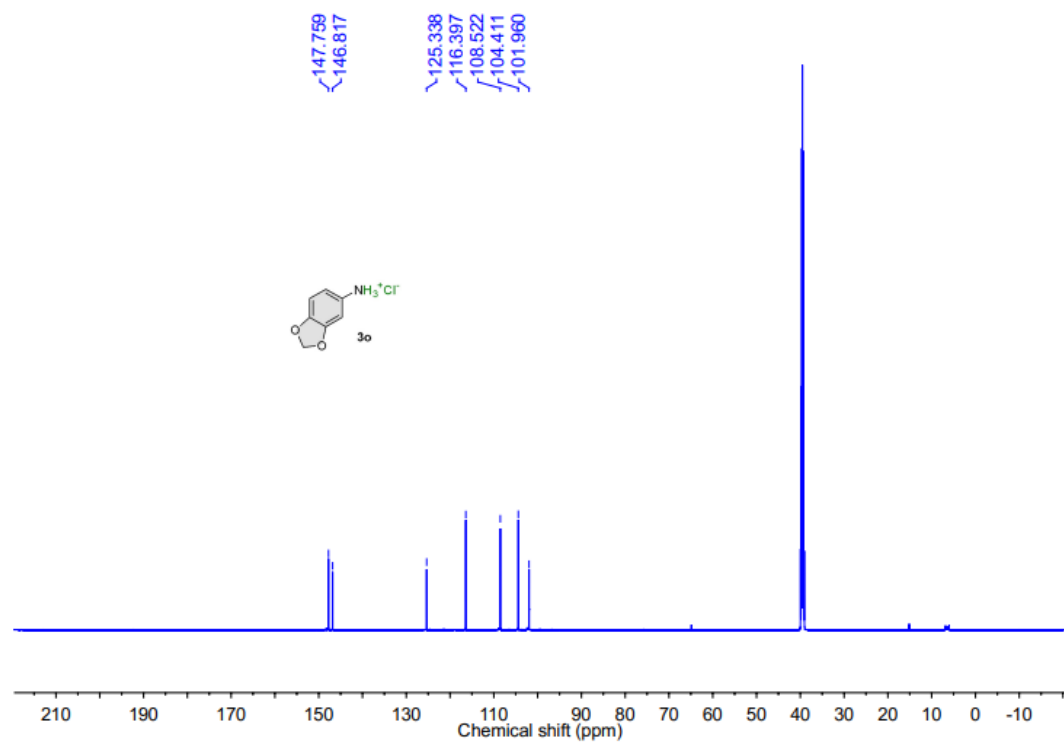
$^1\text{H NMR}$ (600 MHz, DMSO-d_6 , 298 K) of **31**·**HCl**



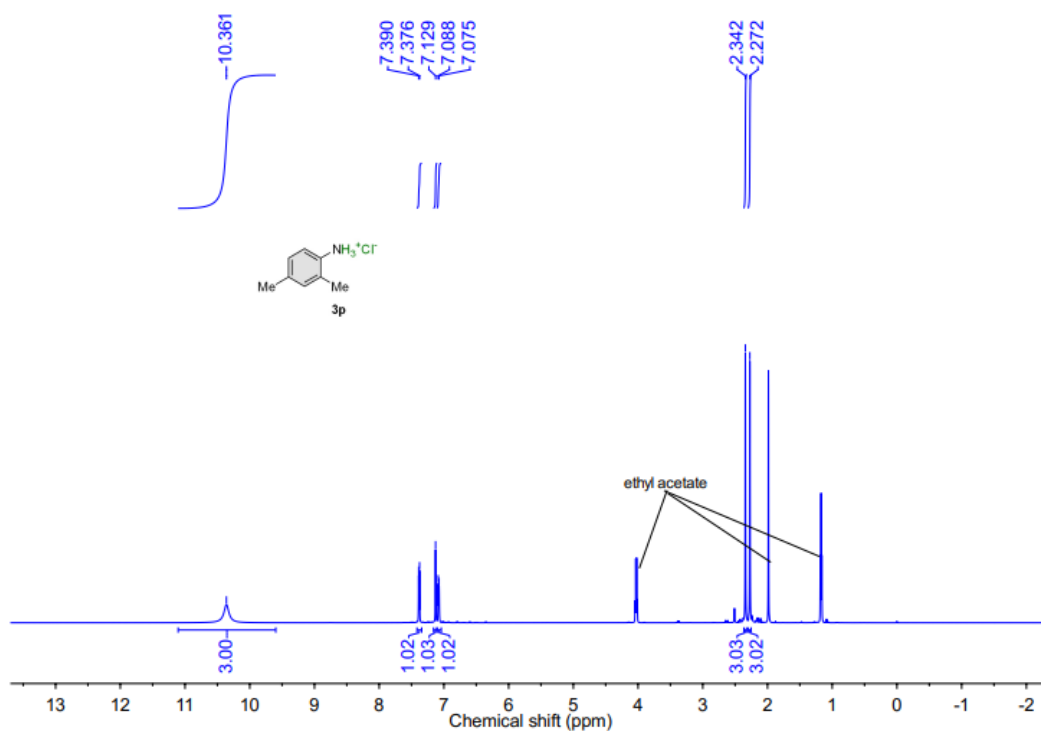
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO-d_6 , 298 K) of **31**·**HCl**



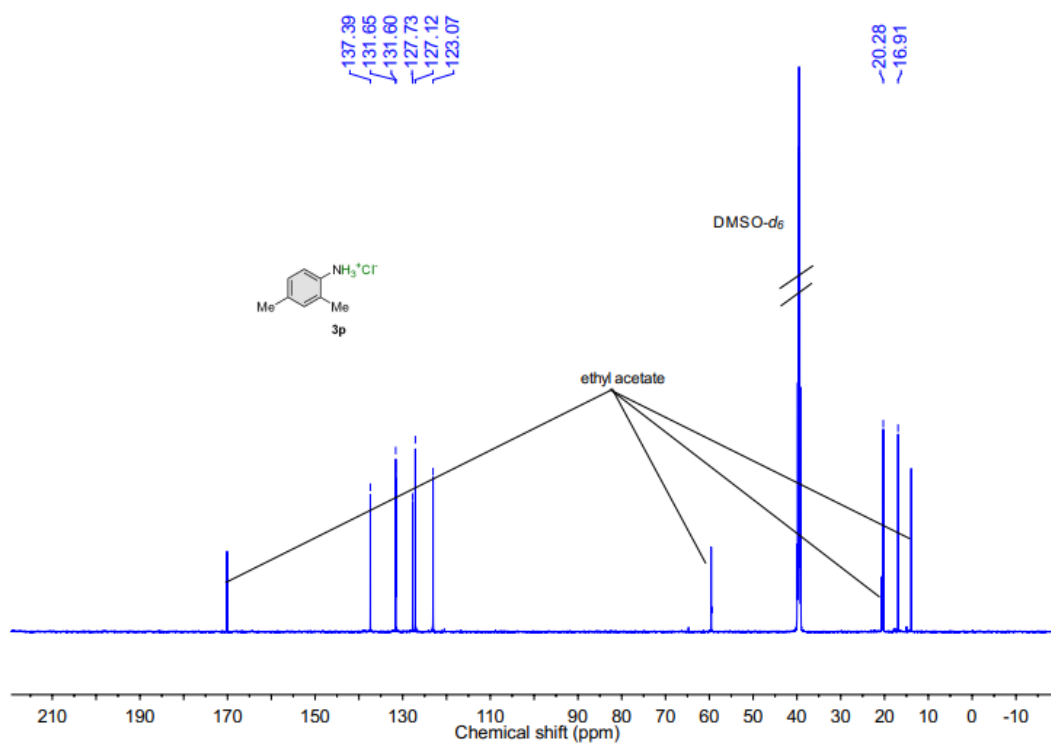
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3o**·HCl



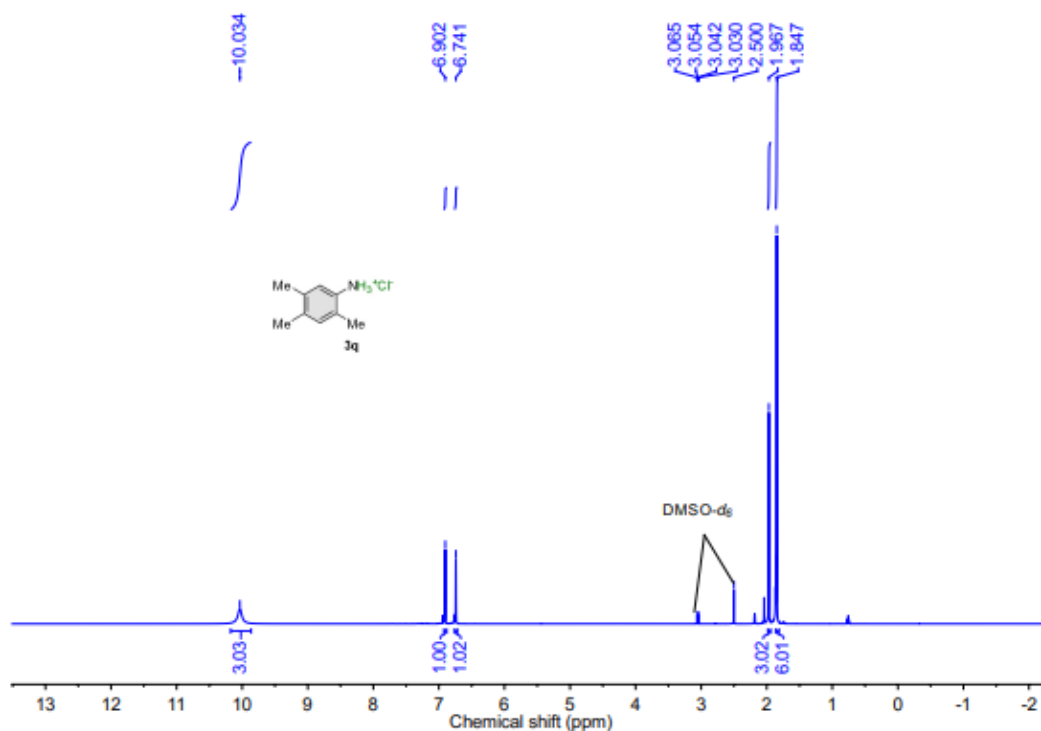
¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3o**·HCl



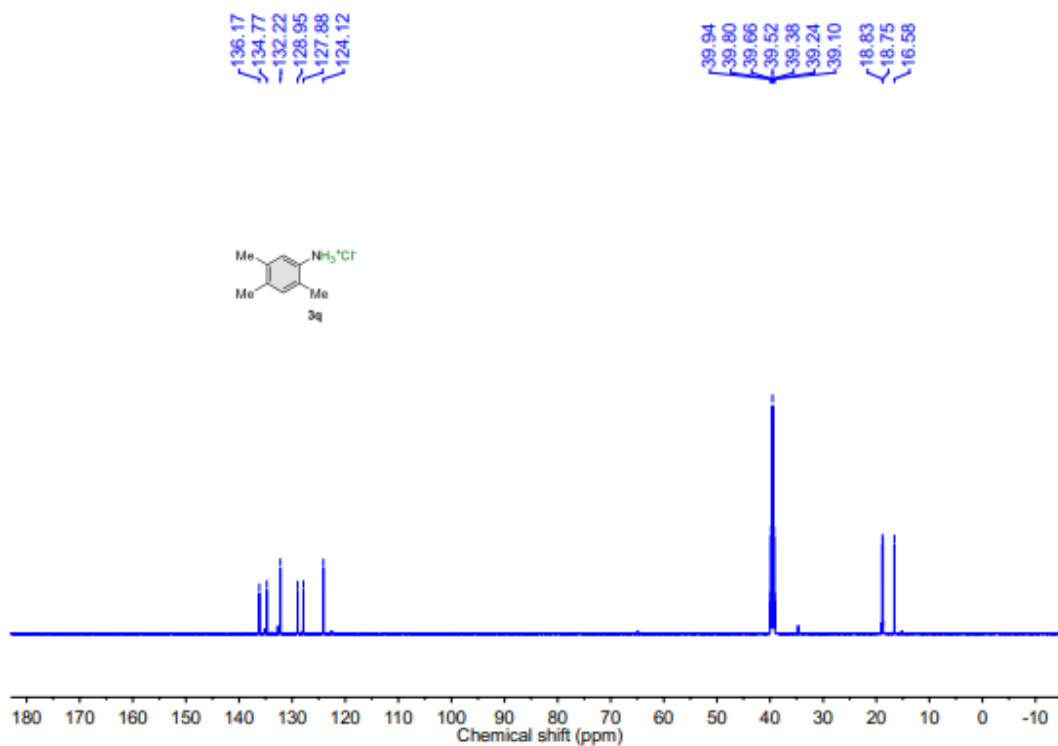
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3p**·HCl



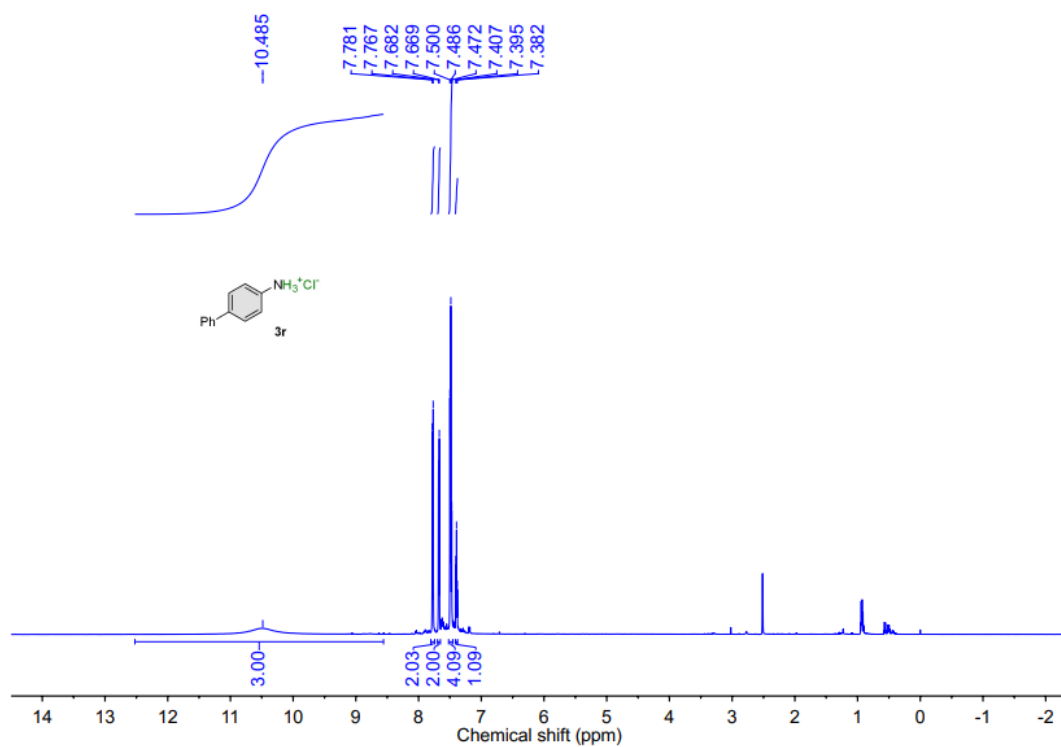
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3p**·HCl



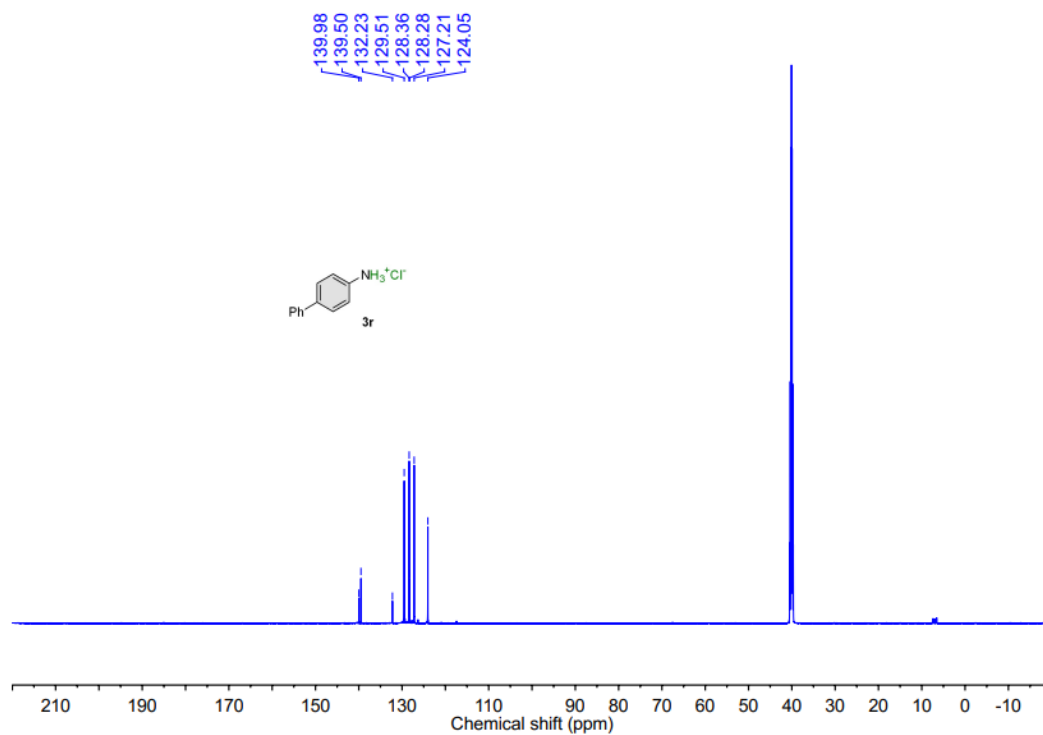
$^1\text{H NMR}$ (600 MHz, DMSO-d_6 , 298 K) of **3q**·HCl



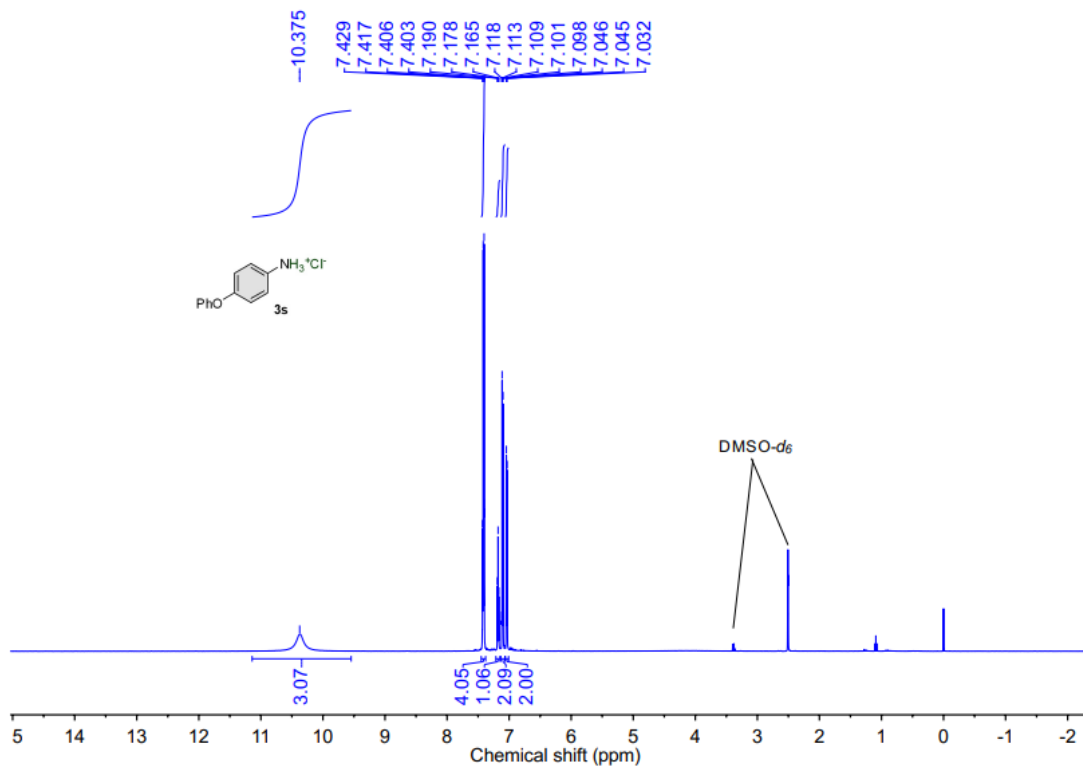
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO-d_6 , 298 K) of **3q**·HCl



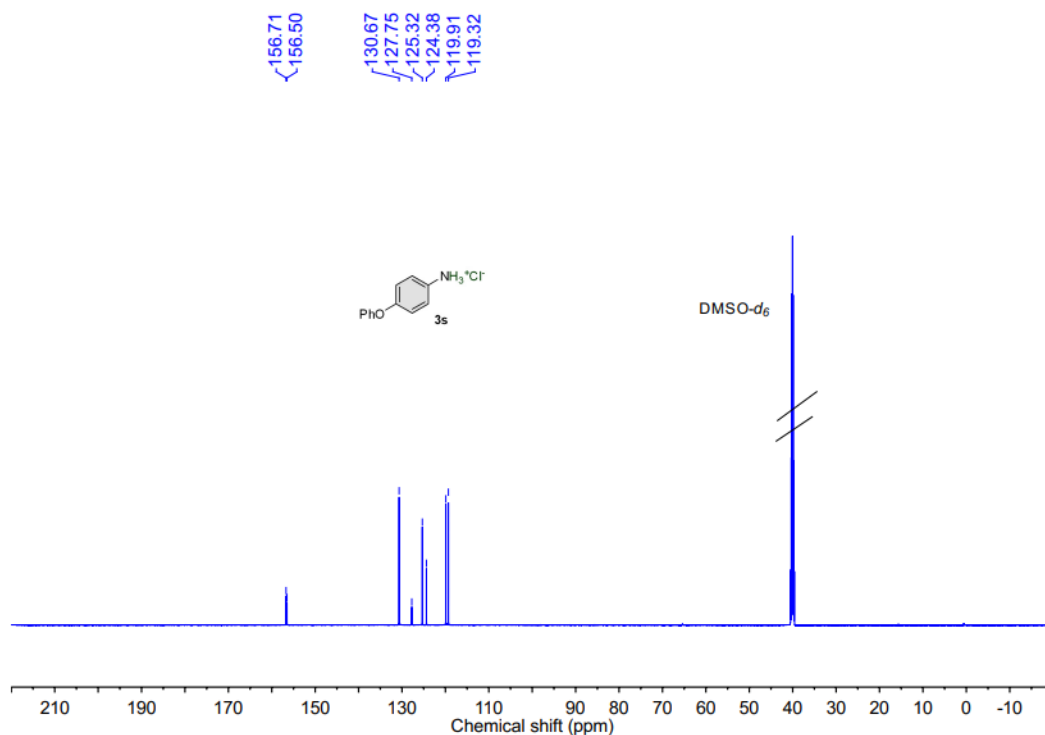
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3r**·HCl



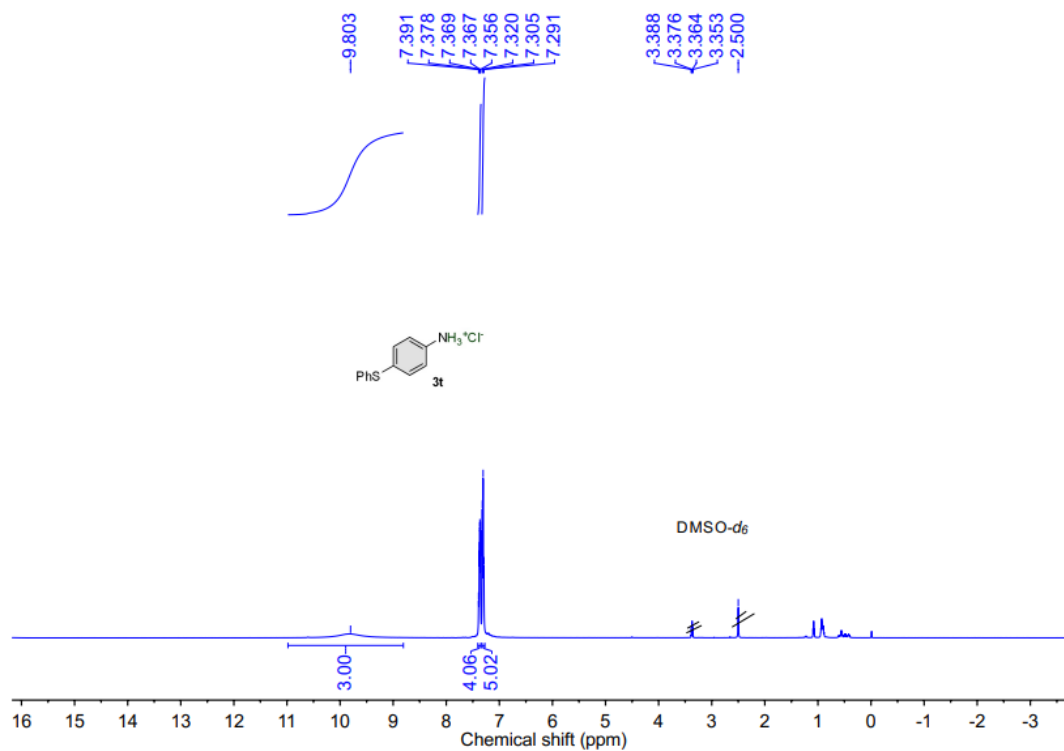
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3r**·HCl



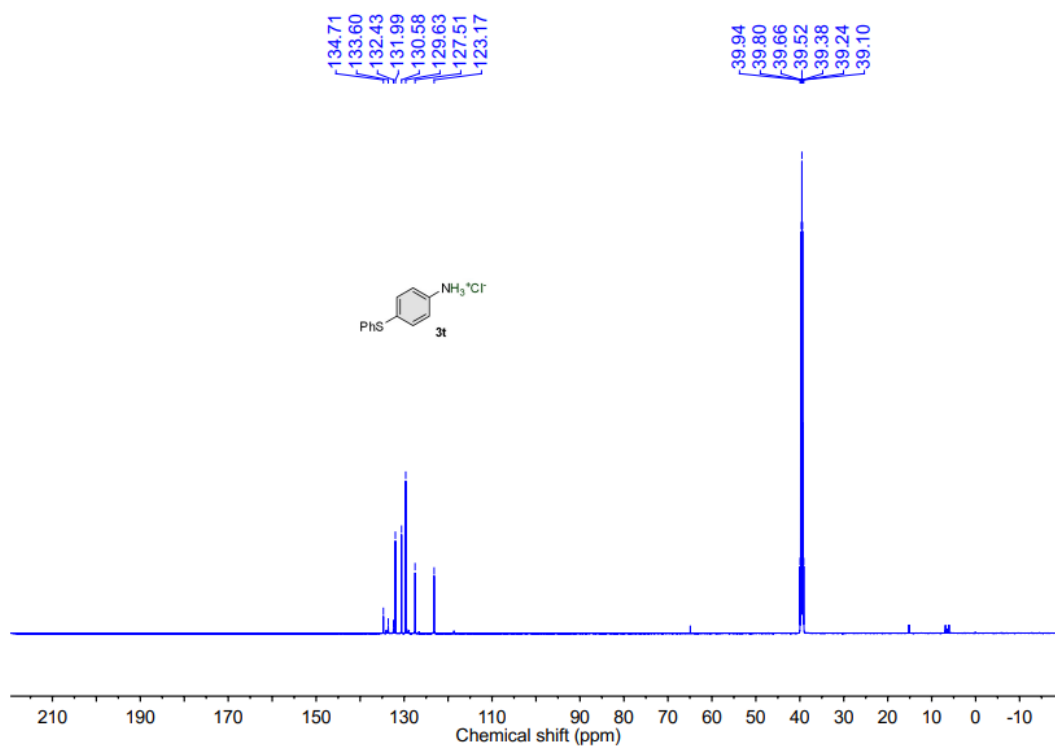
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3s·HCl**



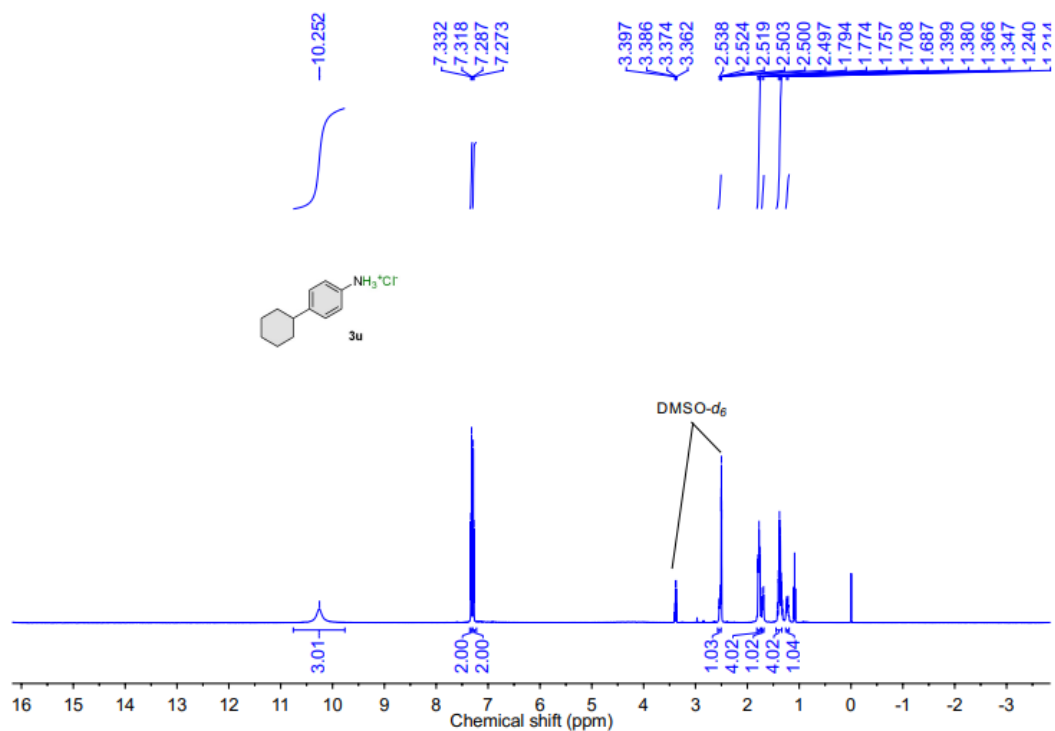
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3s·HCl**



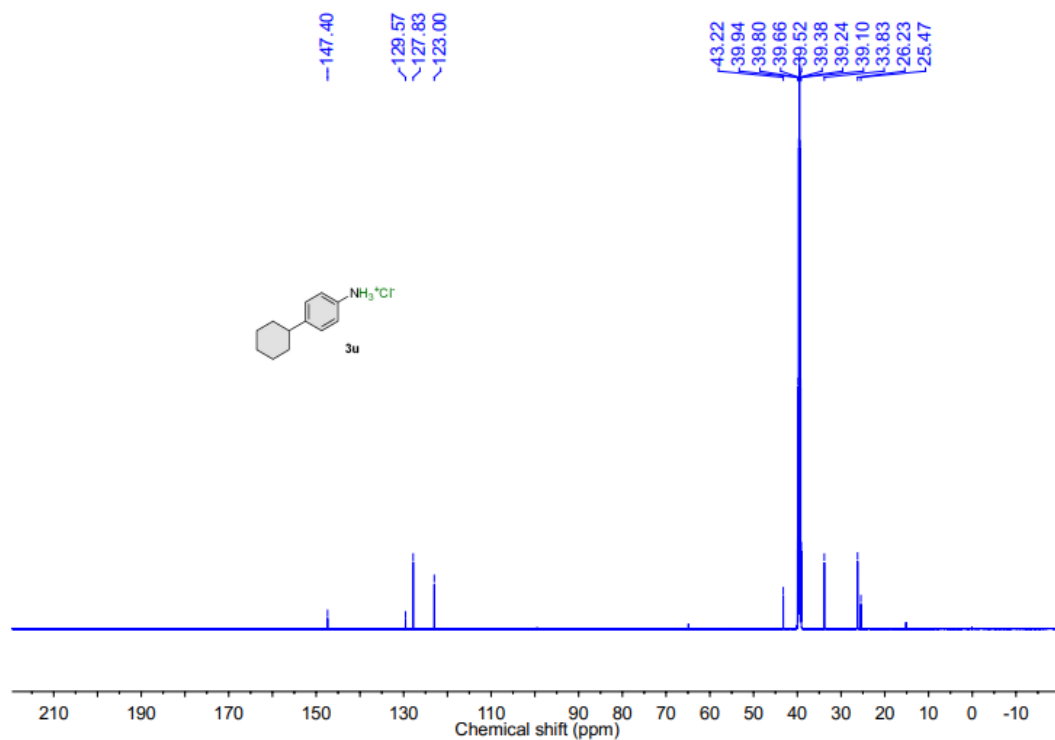
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3t**·HCl



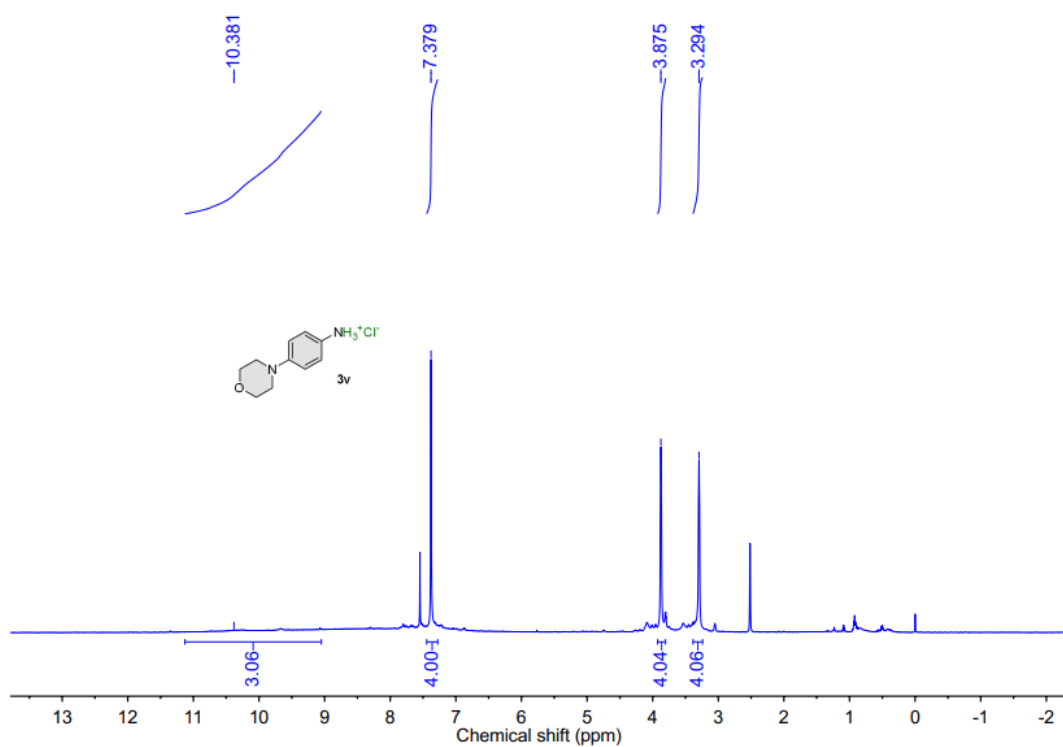
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3t**·HCl



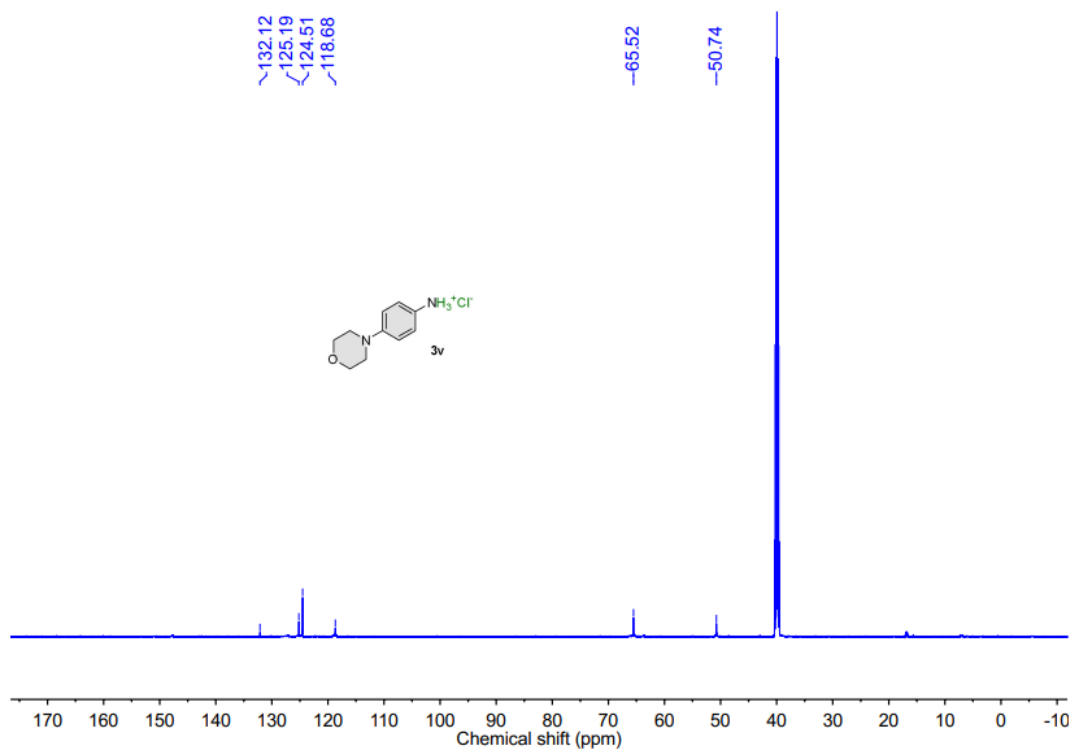
^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3u**·HCl



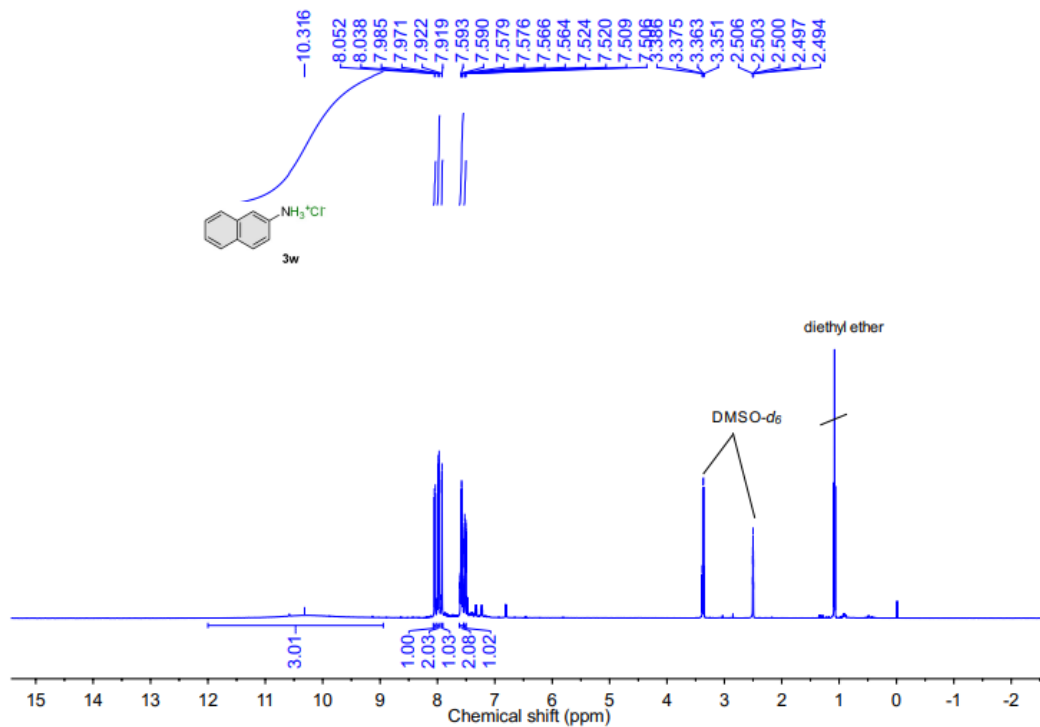
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3u**·HCl



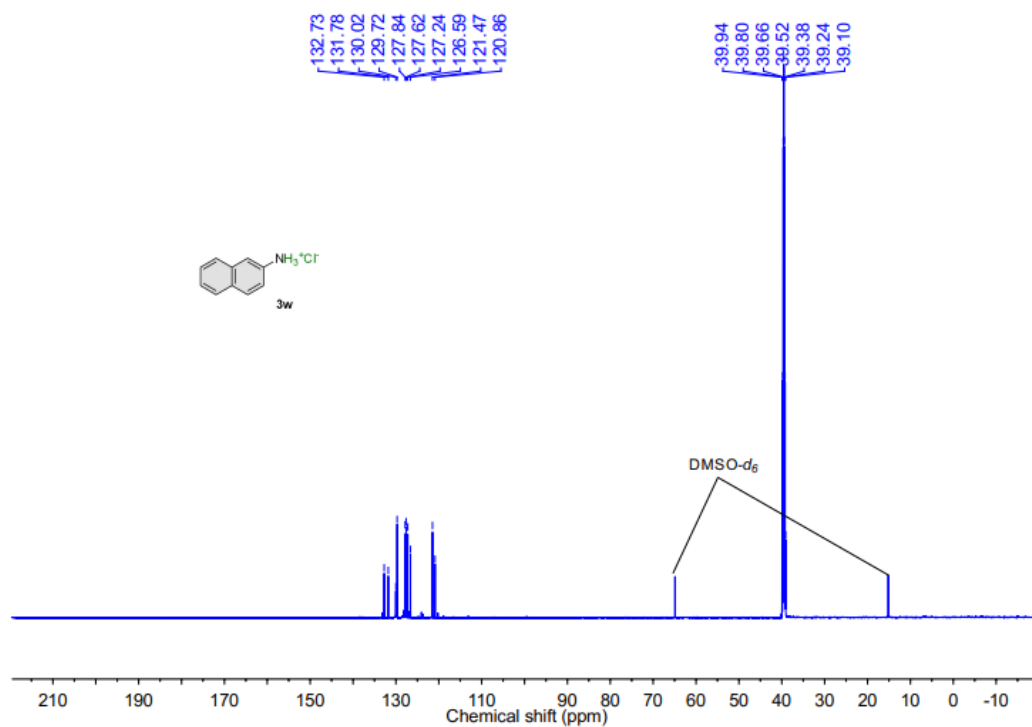
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3v**·HCl



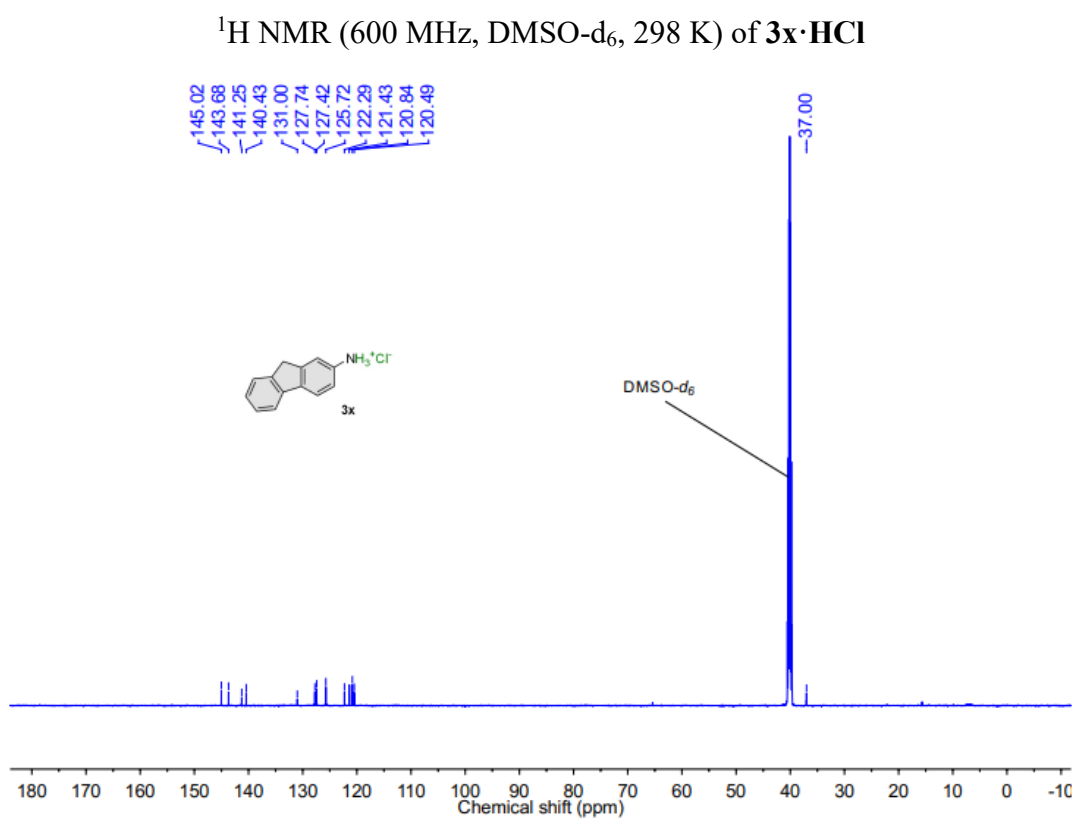
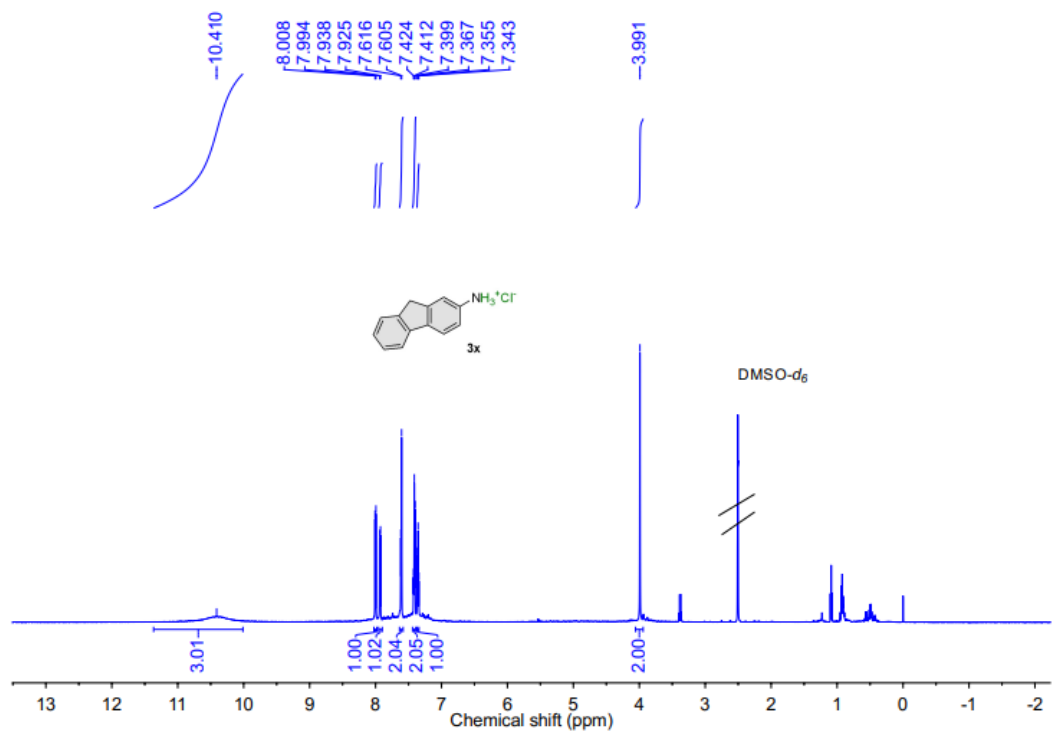
¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3v**·HCl

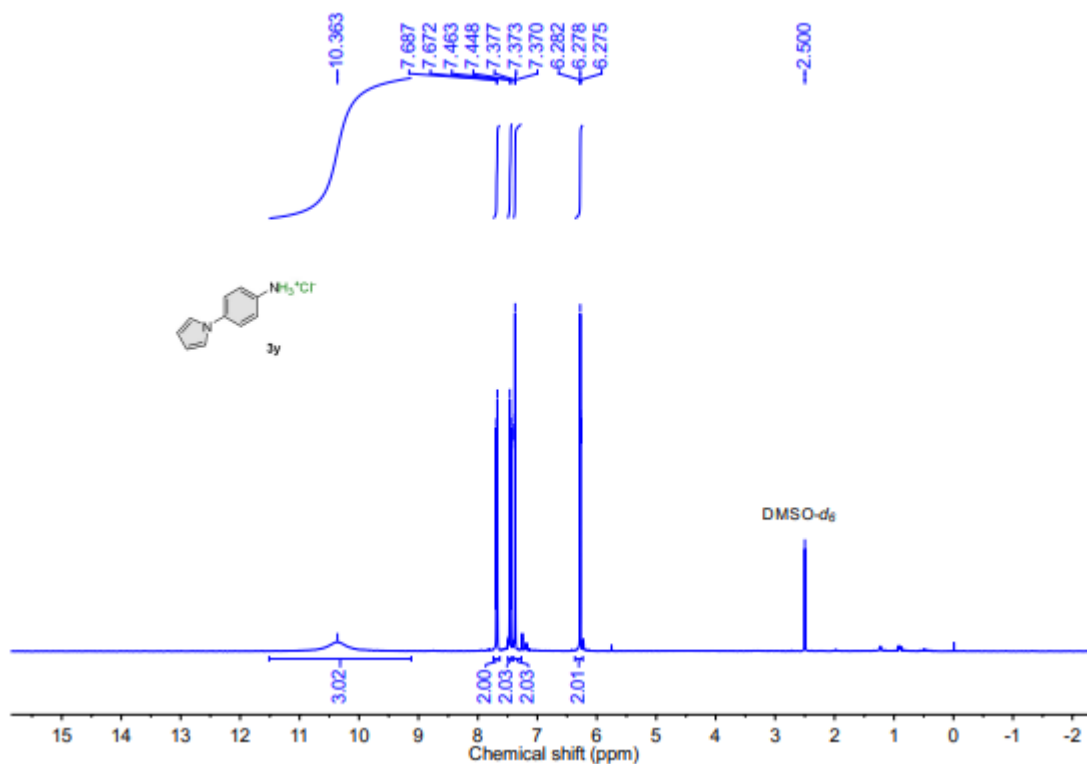


¹H NMR (600 MHz, DMSO-*d*₆, 298 K) of **3w·HCl**

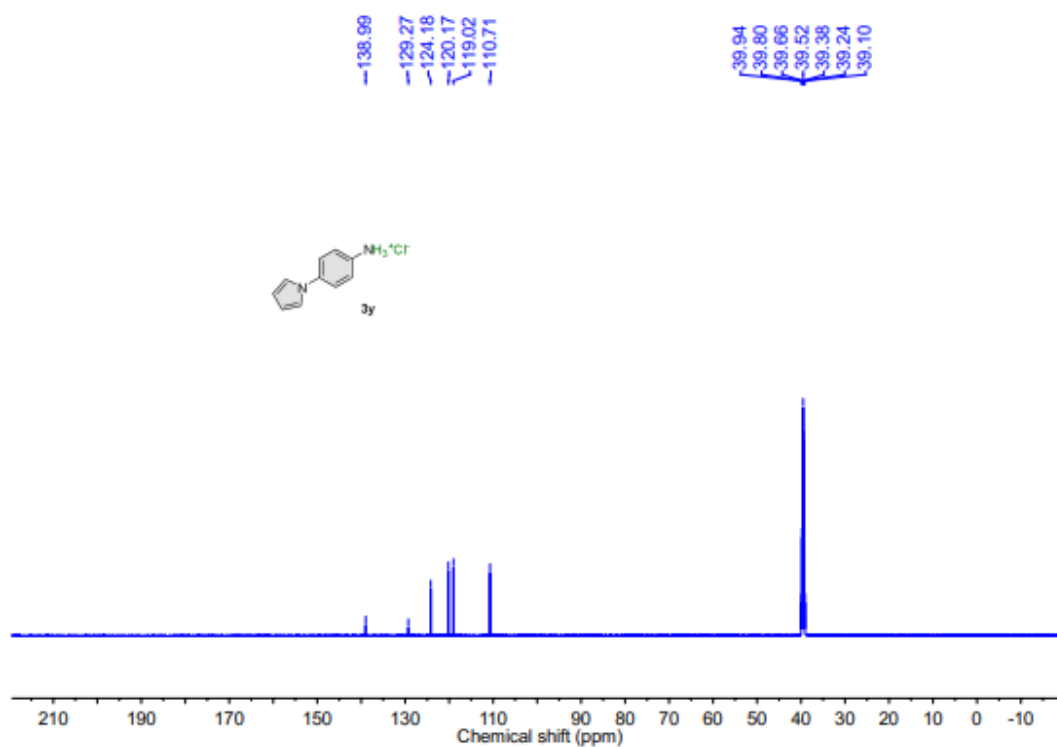


¹³C {¹H} NMR (151 MHz, DMSO-*d*₆, 298 K) of **3w·HCl**

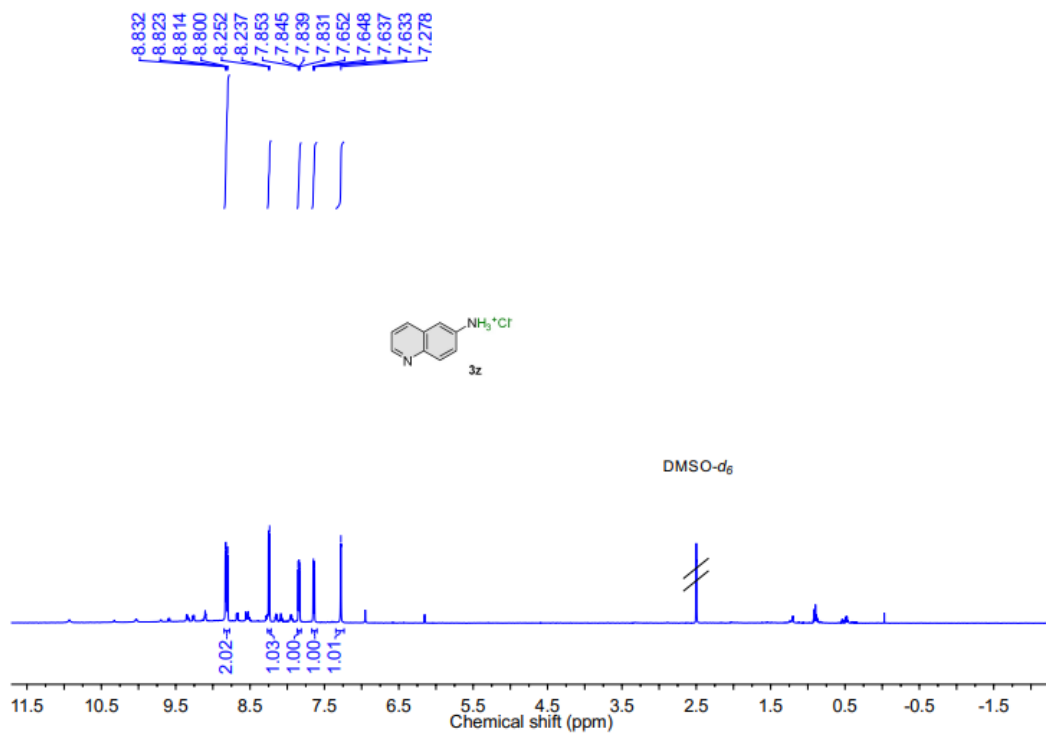




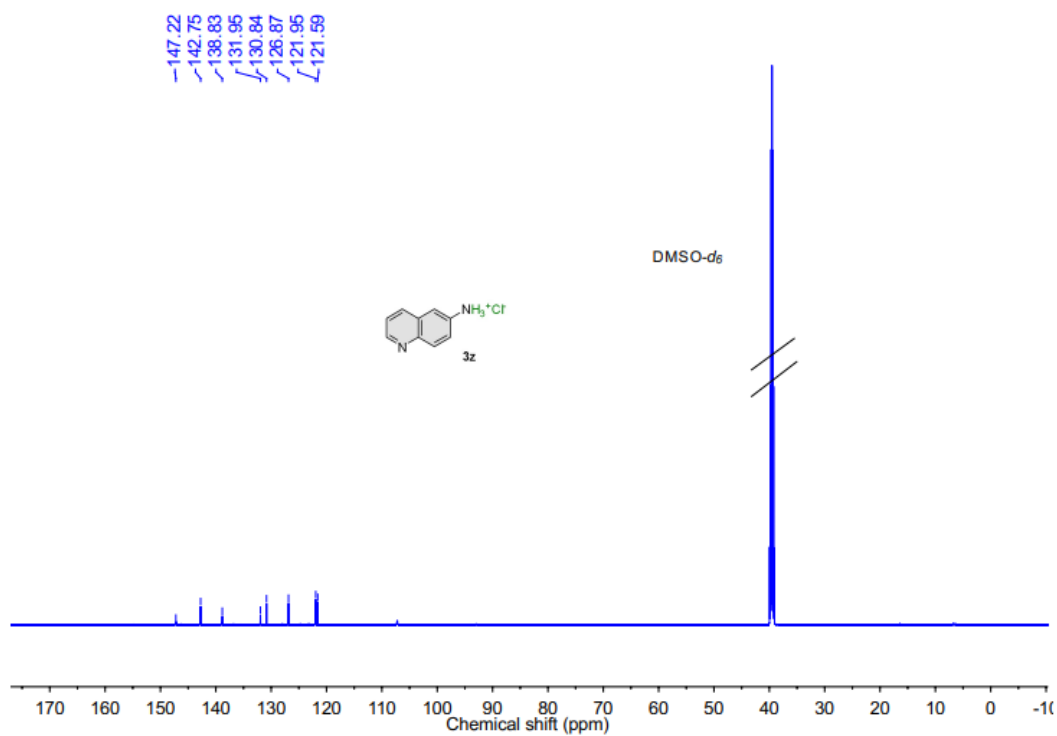
¹H NMR (600 MHz, DMSO-d₆, 298 K) of **3y·HCl**



¹³C{¹H} NMR (151 MHz, DMSO-d₆, 298 K) of **3y·HCl**



^1H NMR (600 MHz, DMSO- d_6 , 298 K) of **3z**·HCl

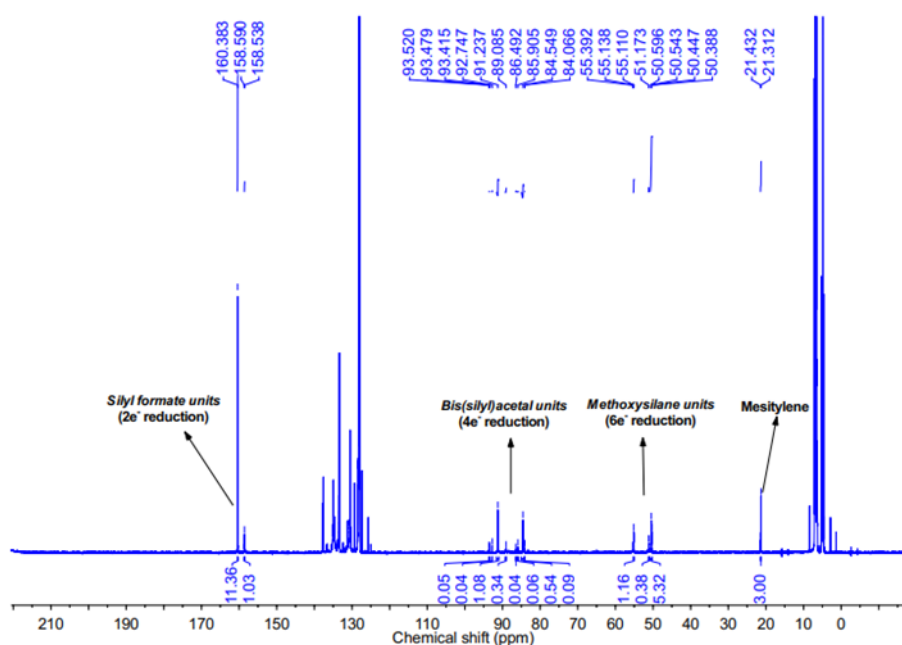


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO- d_6 , 298 K) of **3z**·HCl

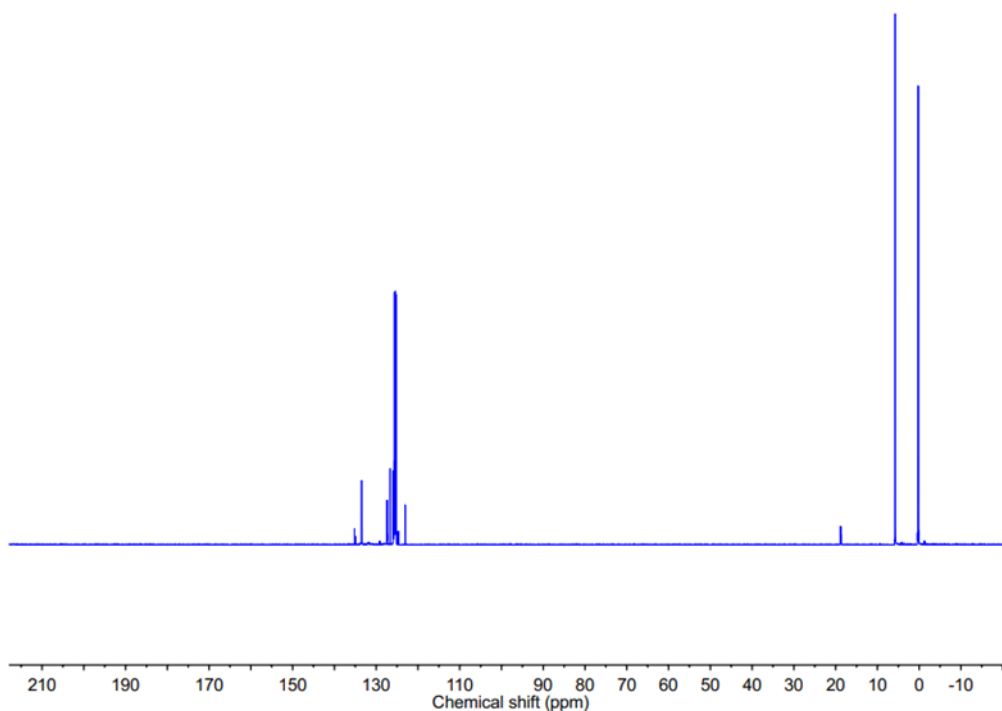
11. Hydrosilylation of CO_2

In the glove box of argon atmosphere, add the catalyst of Co(dppbsa), NaBAR^F₄, internal standard mesitylene, phenylsilane, triethylsilane, and benzene-d₆ to the inner lining of the 30 mL high pressure resistant reactor with magnetic particles in order, and then put them into the reactor for sealing, remove them from the glove box, and finally fill the reactor with 3 MPa CO₂ gas. Put them on the matching metal module for heating, set the speed and temperature parameters. After a certain time of reaction, cool the reactor to room temperature, slowly open the gas valve to relieve pressure. The mixture was filtered through a syringe filter and analyze the filtrate with ¹³C NMR.

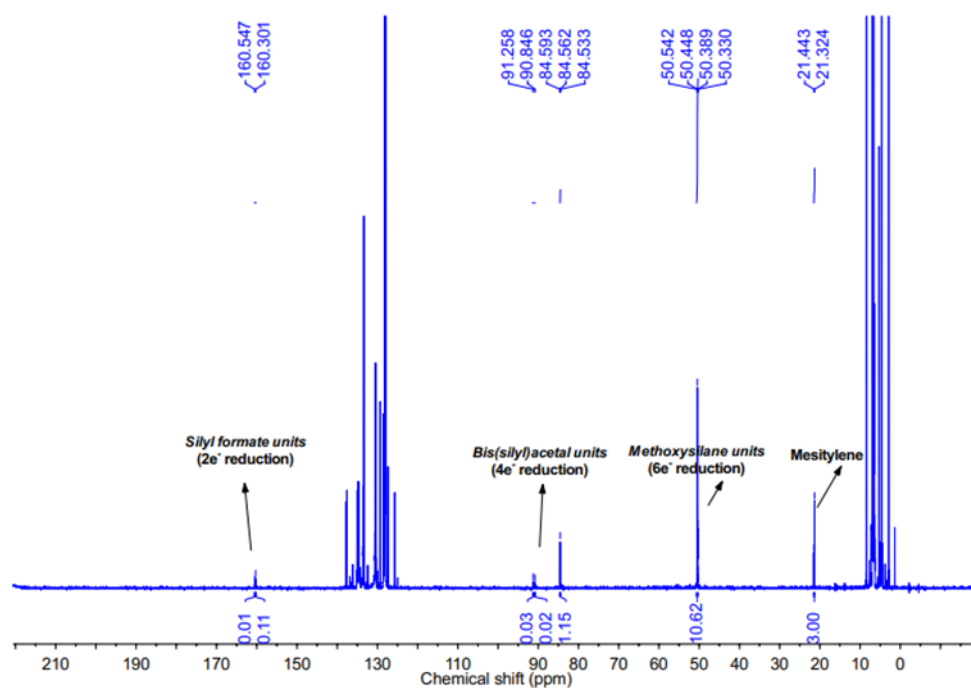
$$TON = \frac{\frac{\text{The NMR integration of silylated products}}{\text{The NMR integration of mesitylene}} \times n(\text{Mesitylene})}{3 \times n(\text{Co(dppbsa)})}$$



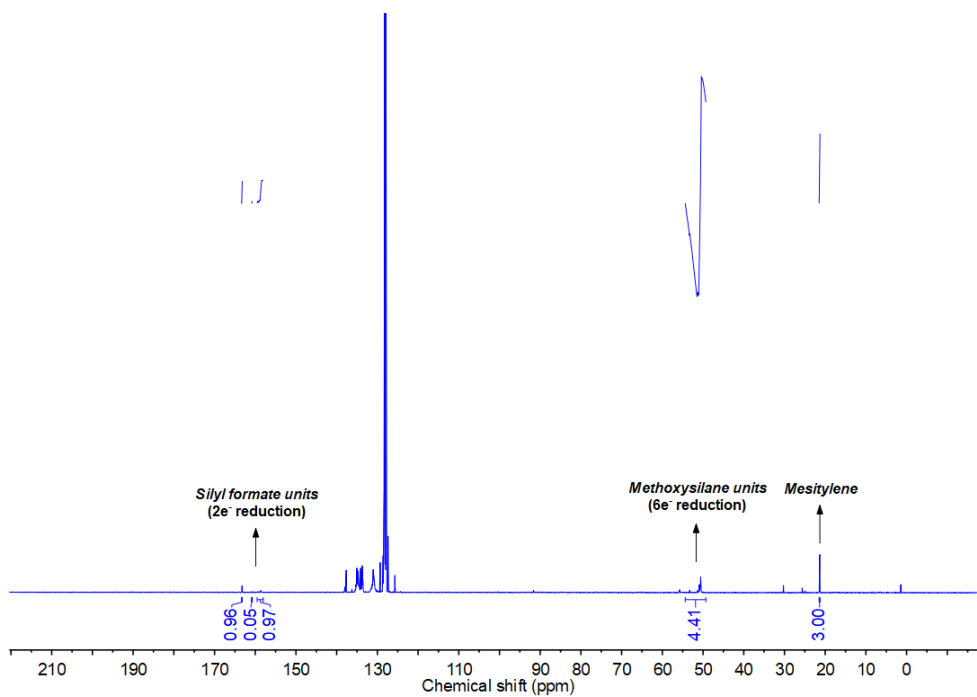
¹³C{¹H} NMR (151 MHz, C₆D₆, 298 K) of a CO₂ hydrosilylation experiment (Co(dppbsa) (5 mol%), NaBAR^F₄ (5 mol%), CO₂ (3 MPa), PhSiH₃ (1.2 mmol), Et₃SiH (3.0 mmol), 150 °C, 4 h, C₆D₆; Figure 2A).



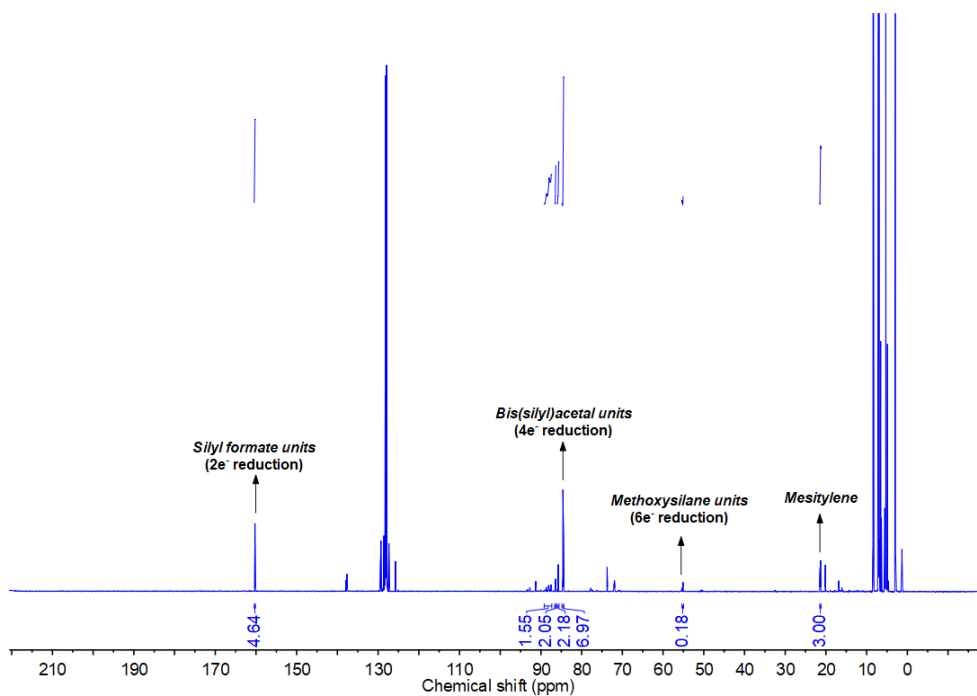
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment (Co(dppbsa) (5 mol%), CO_2 (3 MPa), PhSiH_3 (1.2 mmol), Et_3SiH (3.0 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2B).



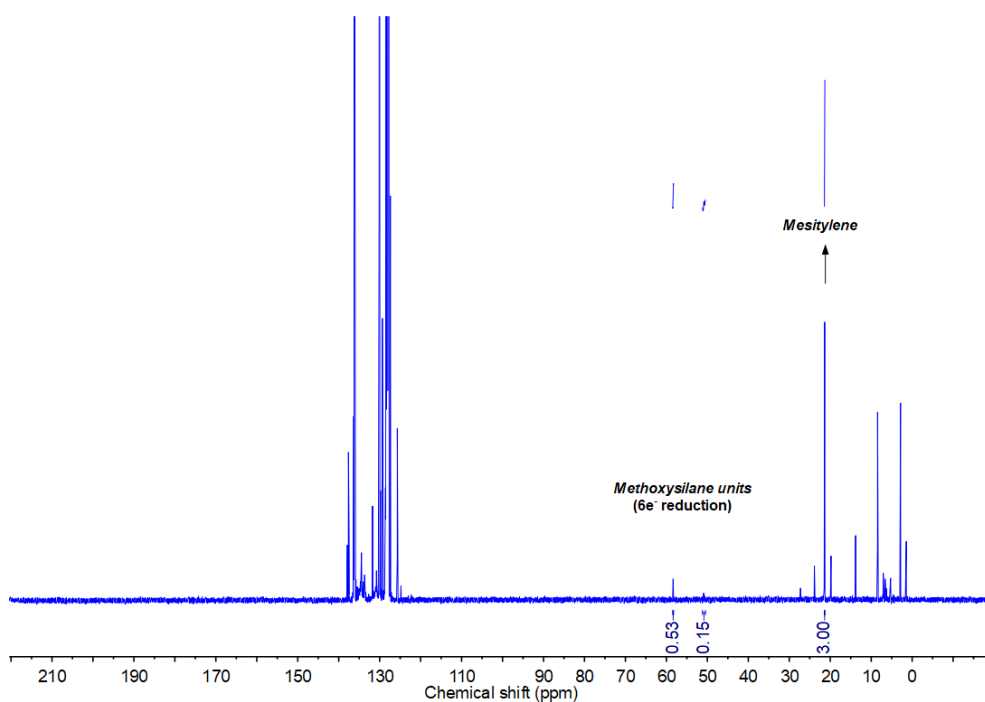
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment ($\text{NaBAR}^{\text{F}_4}$ (5 mol%), CO_2 (3 MPa), PhSiH_3 (1.2 mmol), Et_3SiH (3.0 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2C).



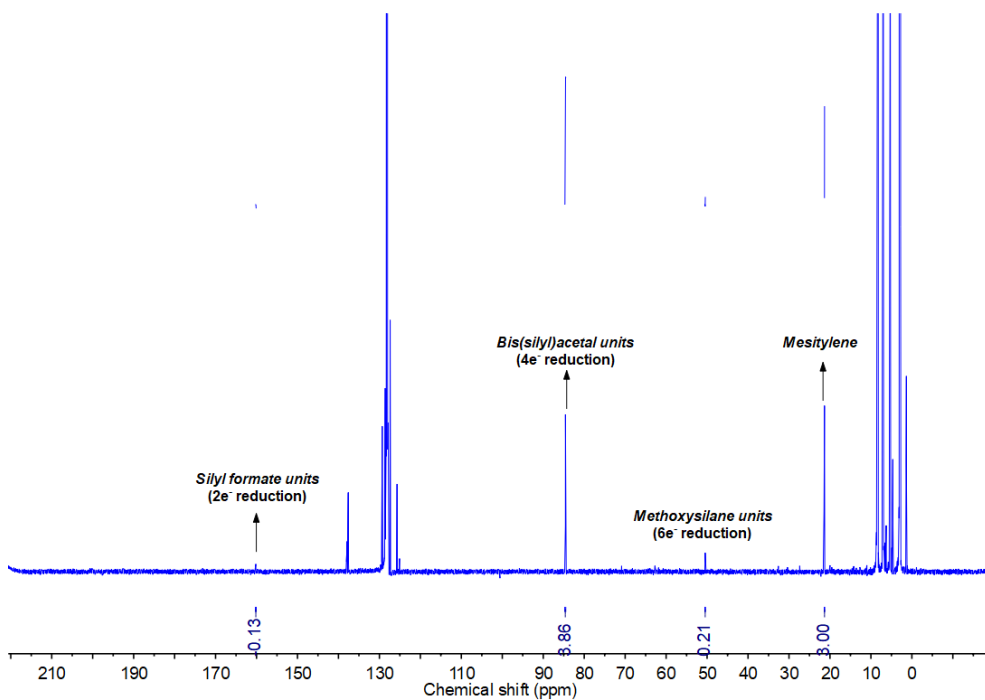
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment (Co(dppbsa) (5 mol%), NaBAR^F₄ (5 mol%), CO_2 (3 MPa), PhSiH₃ (2.2 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2D).



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment (NaBAR^F₄ (5 mol%), CO_2 (3 MPa), Et₃SiH (6.6 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2E).



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment (CO_2 (3 MPa), $\text{NaBAR}^{\text{F}}_4$ (5 mol%), PhSiH_3 (2.2 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2F).



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 298 K) of a CO_2 hydrosilylation experiment (CO_2 (3 MPa), $\text{NaBAR}^{\text{F}}_4$ (5 mol%), Et_3SiH (6.6 mmol), 150 °C, 4 h, C_6D_6 ; Figure 2G).

12. References

- 1 (a) L. Piche, J. C. Daigle, G. Rehse and J. P. Claverie, *Chem. Eur. J.*, **2012**, 18, 3277-3285; (b) S. Ito, K. Munakata, A. Nakamura and K. Nozaki, *J. Am. Chem. Soc.*, **2009**, 131, 14606-14607.