Synthesis of *N*-Substituted Pyrroles Catalyzed by Low-cost and Commercially Available Aluminas

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SUPPORTING INFORMATION

Content:

1. Copies of NMR spectra for compounds 3

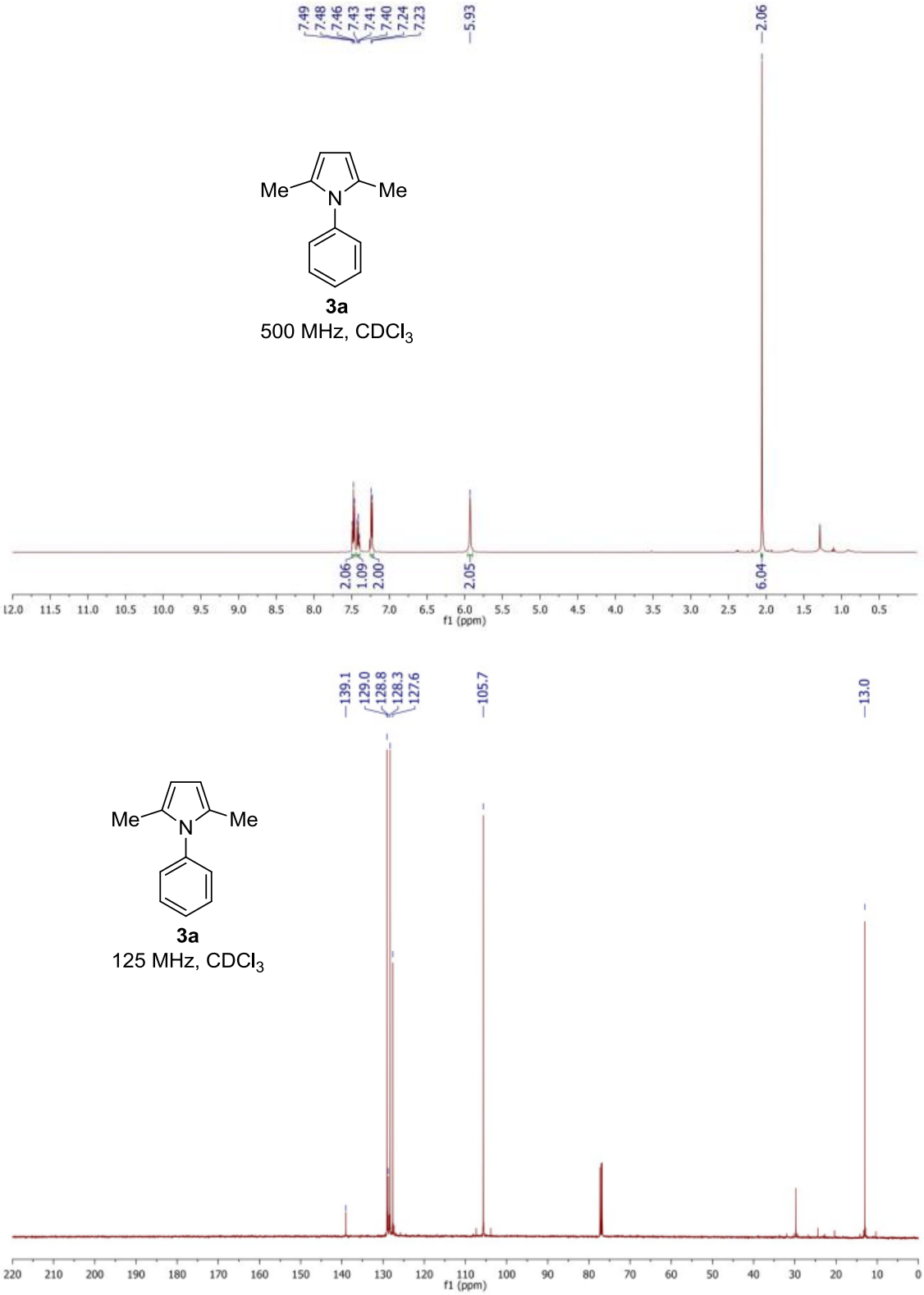
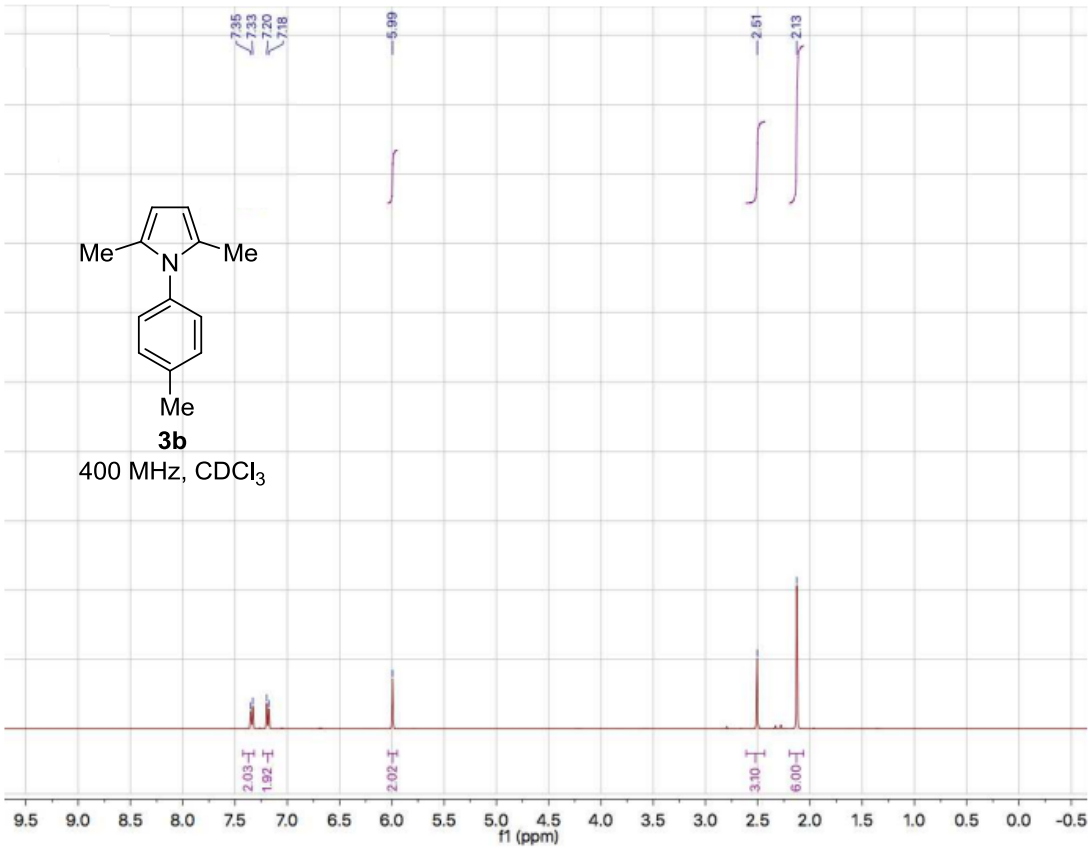


Figure S1: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2,5-dimethyl-1-phenyl-1*H*-pyrrole **3a**. [1]



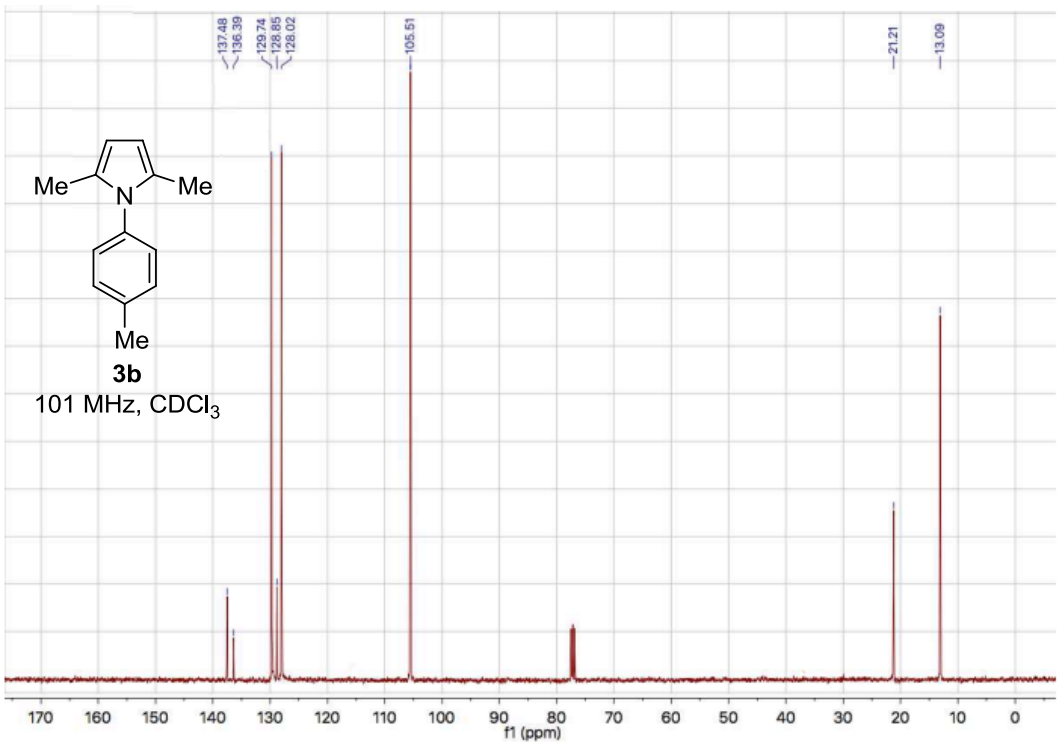
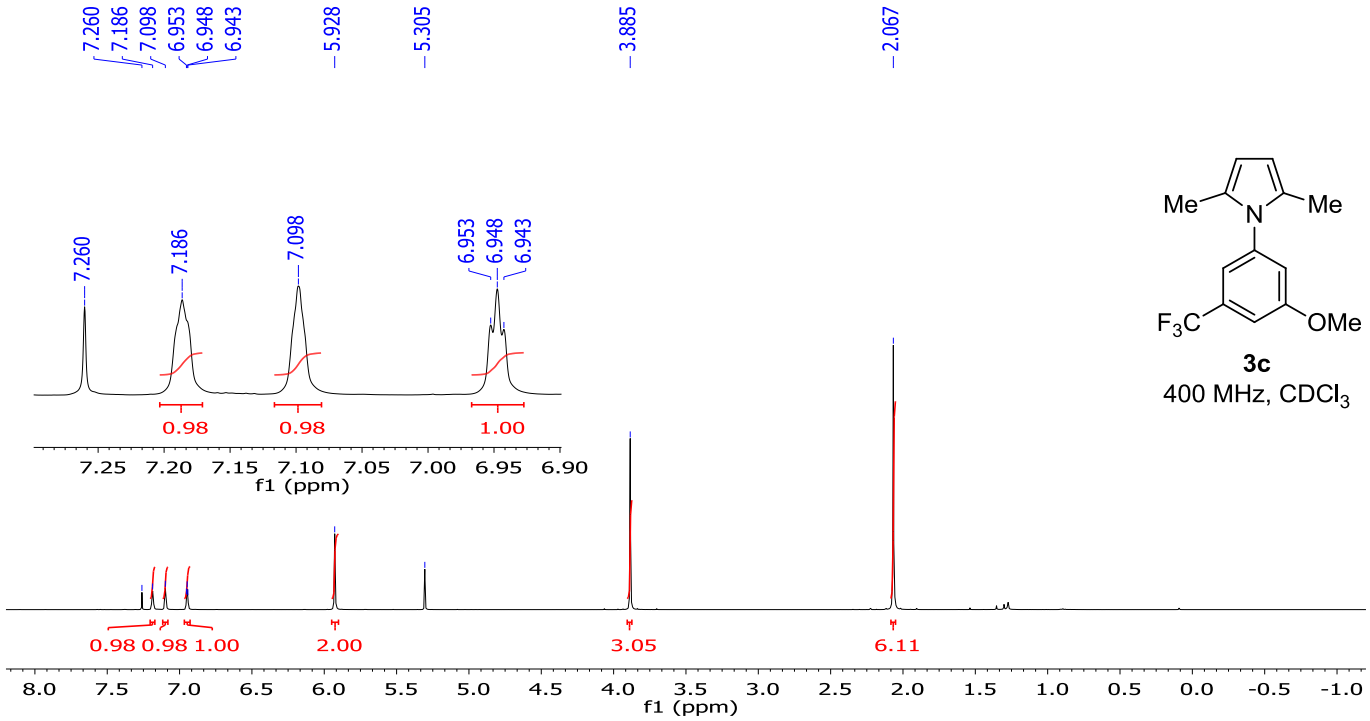
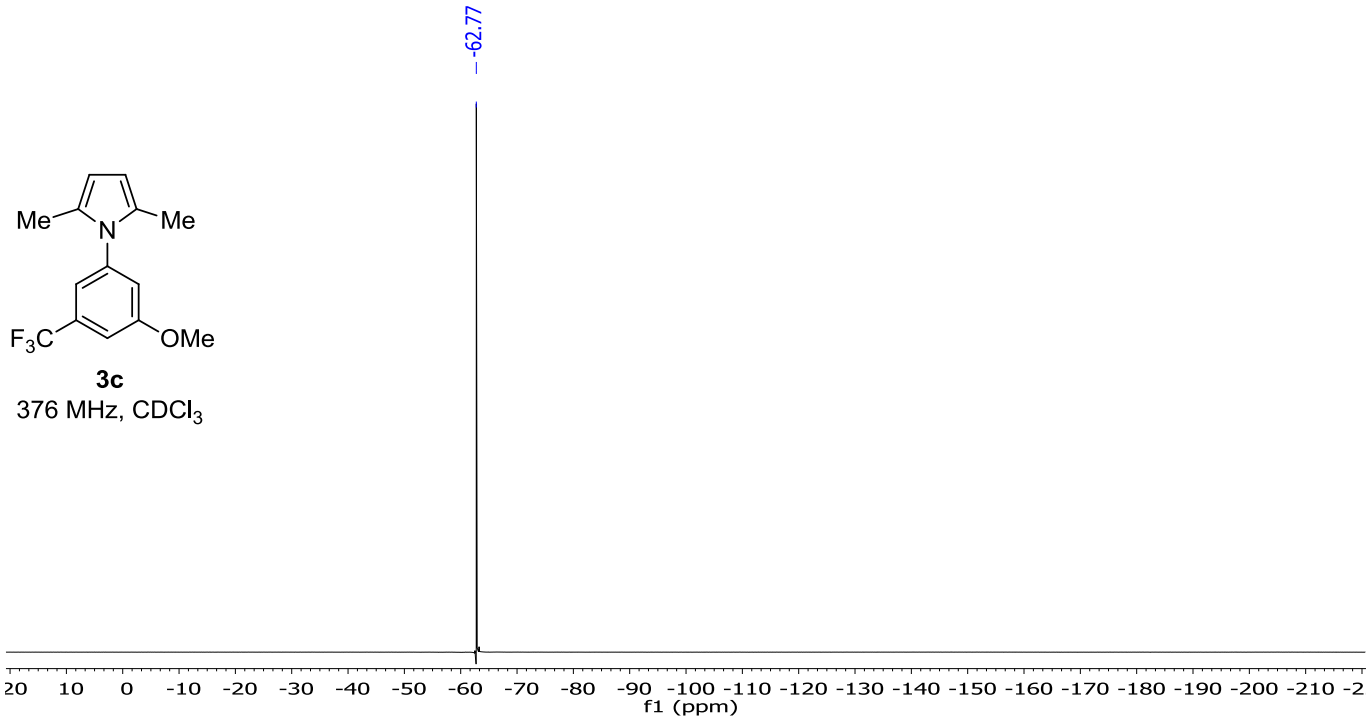


Figure S2: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2,5-dimethyl-1-(*p*-tolyl)-1*H*-pyrrole **3b**. [2]


7.260
7.186
7.098
6.953
6.948
6.943
5.928
5.305
3.885
2.067
0.98
0.98
1.00
0.98 0.98 1.00
2.00
3.05
6.11
f1 (ppm)
Me
Me
N
F3C
OMe
3c
400 MHz, CDCl3


-62.77
f1 (ppm)
Me
Me
N
F3C
OMe
3c
376 MHz, CDCl3

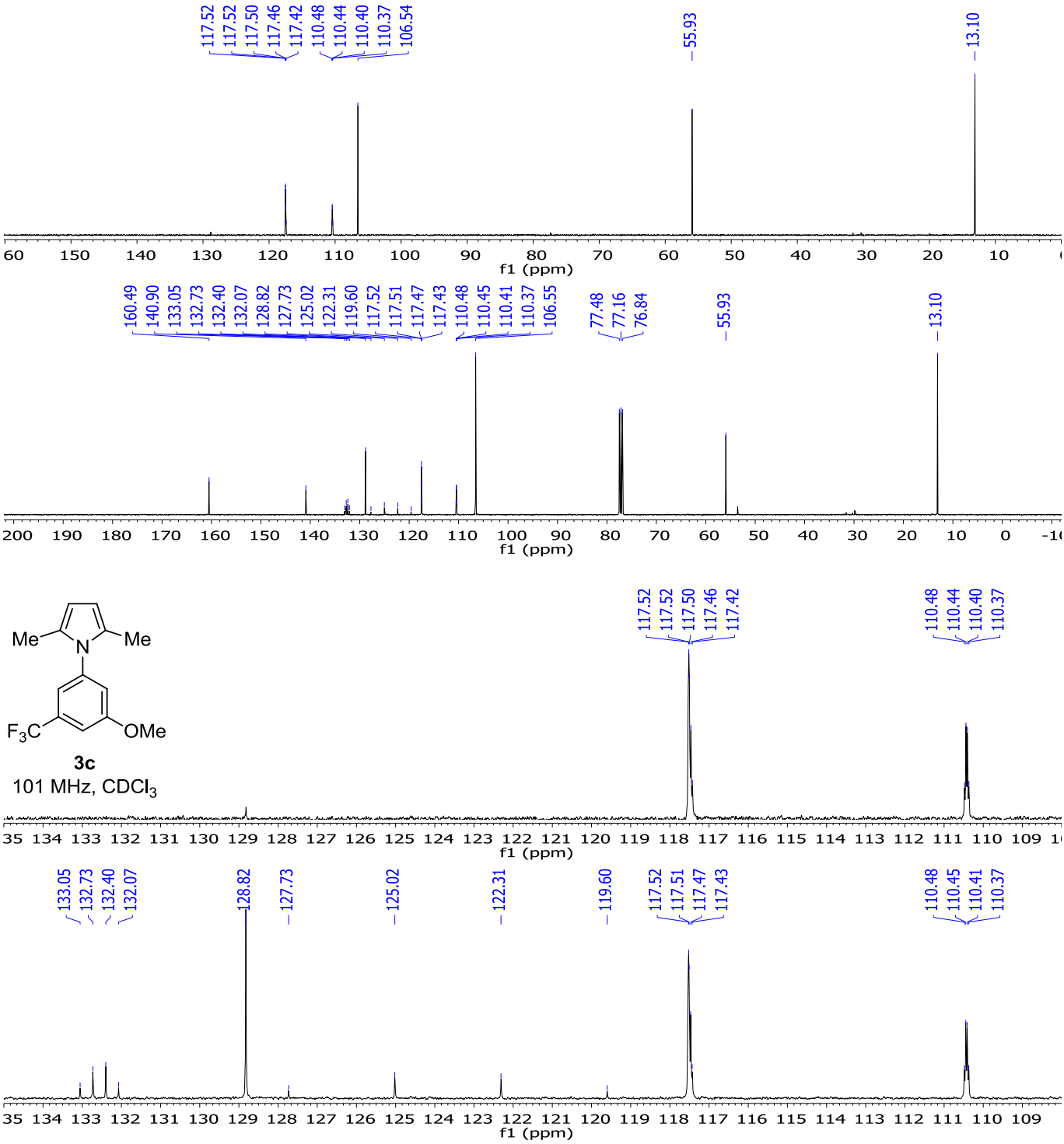


Figure S3: ^{1}H, $^{19}F\{^{1}H\}$, $^{13}C\{^{1}H\}$, and DEPT-135 spectra for 1-(3-methoxy-5-(trifluoromethyl)phenyl)-2,5-dimethyl-1*H*-pyrrole **3c**

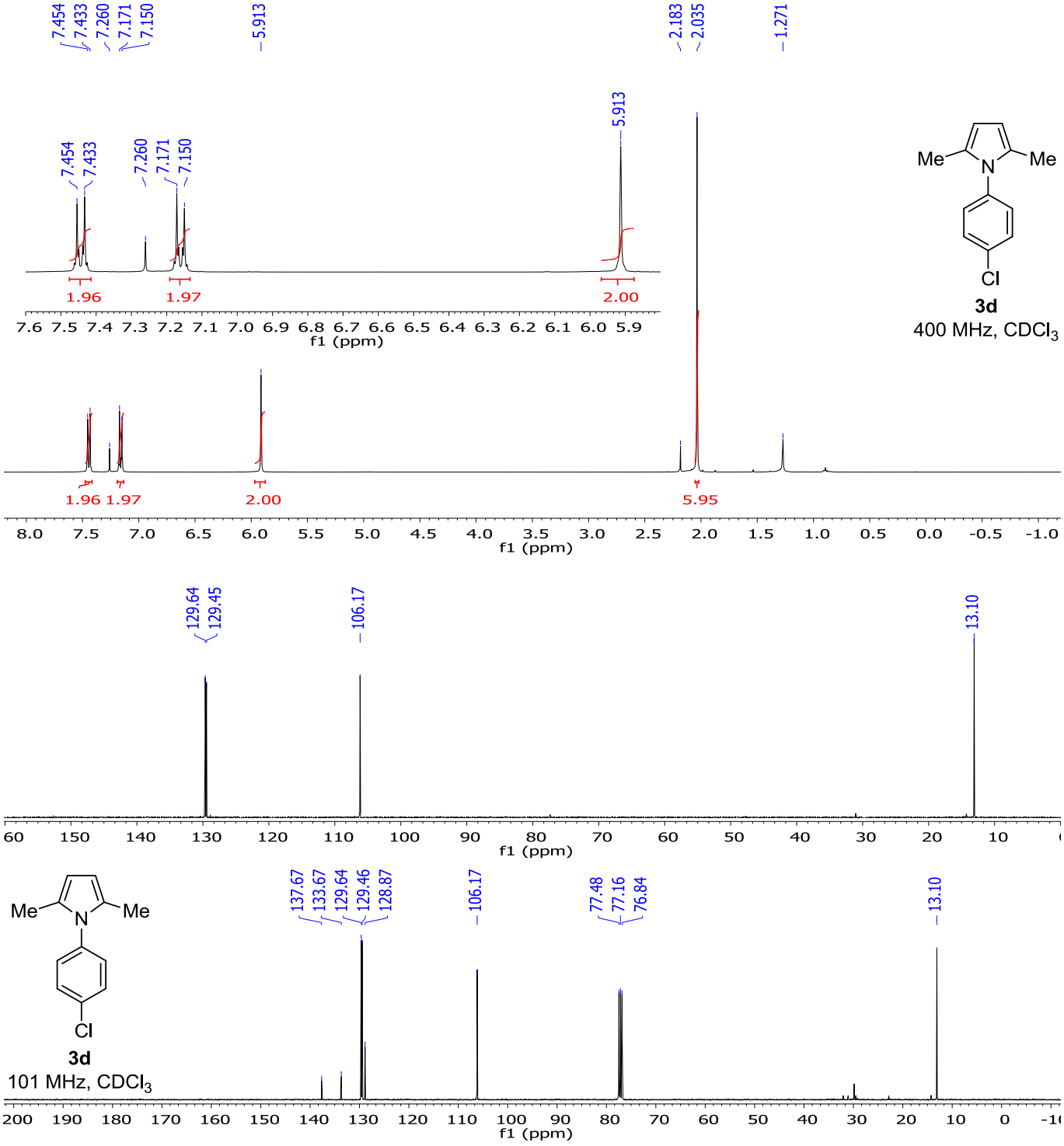


Figure S4: ^{1}H, ^{13}C{^{1}H}, and DEPT-135 spectra for 1-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole **3d**. [3]

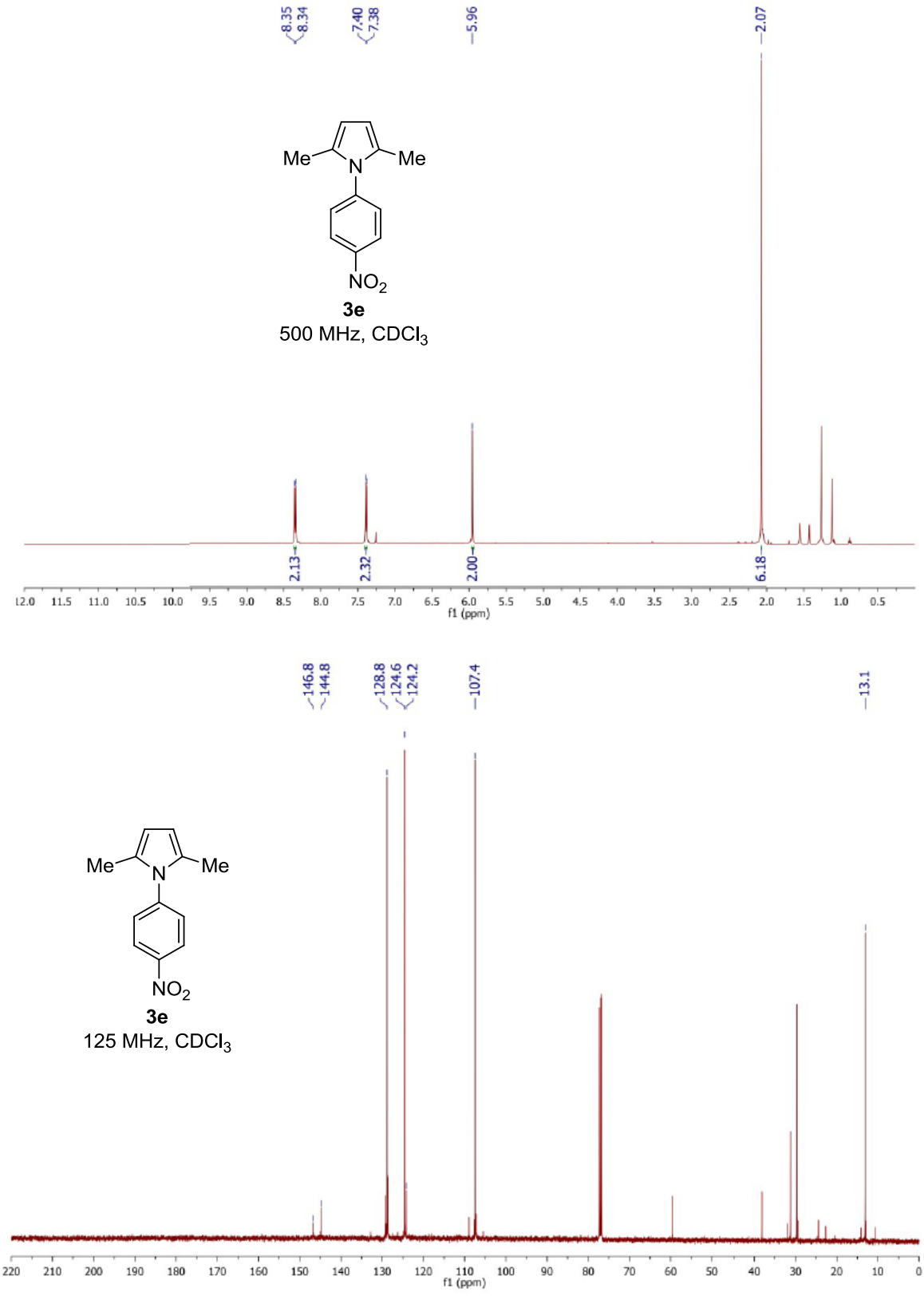


Figure S5: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2,5-dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole **3e**. [1]

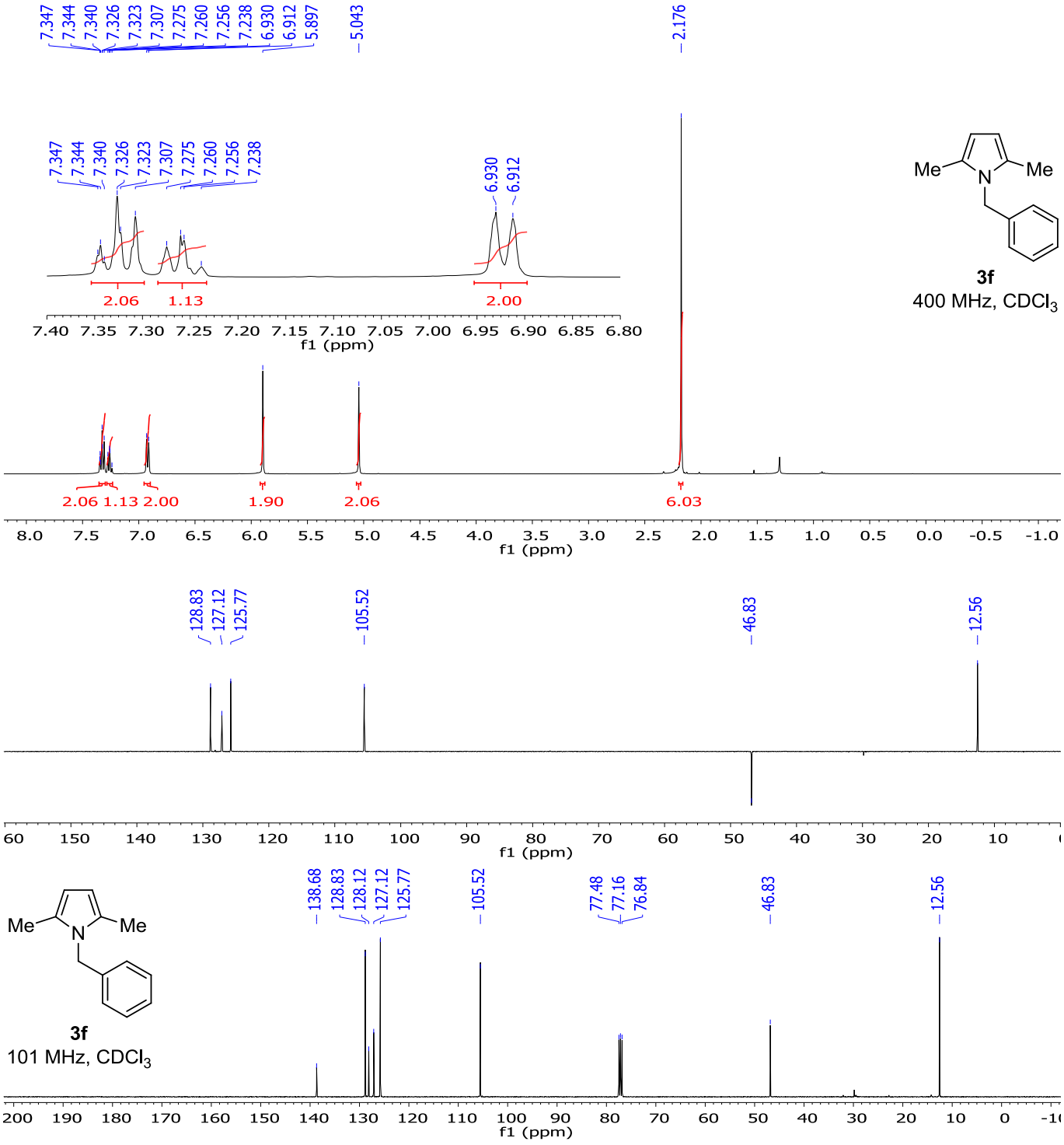


Figure S6: ^{1}H, ^{13}C{^{1}H}, and DEPT-135 spectra for 1-benzyl-2,5-dimethyl-1*H*-pyrrole **3f**. [3]

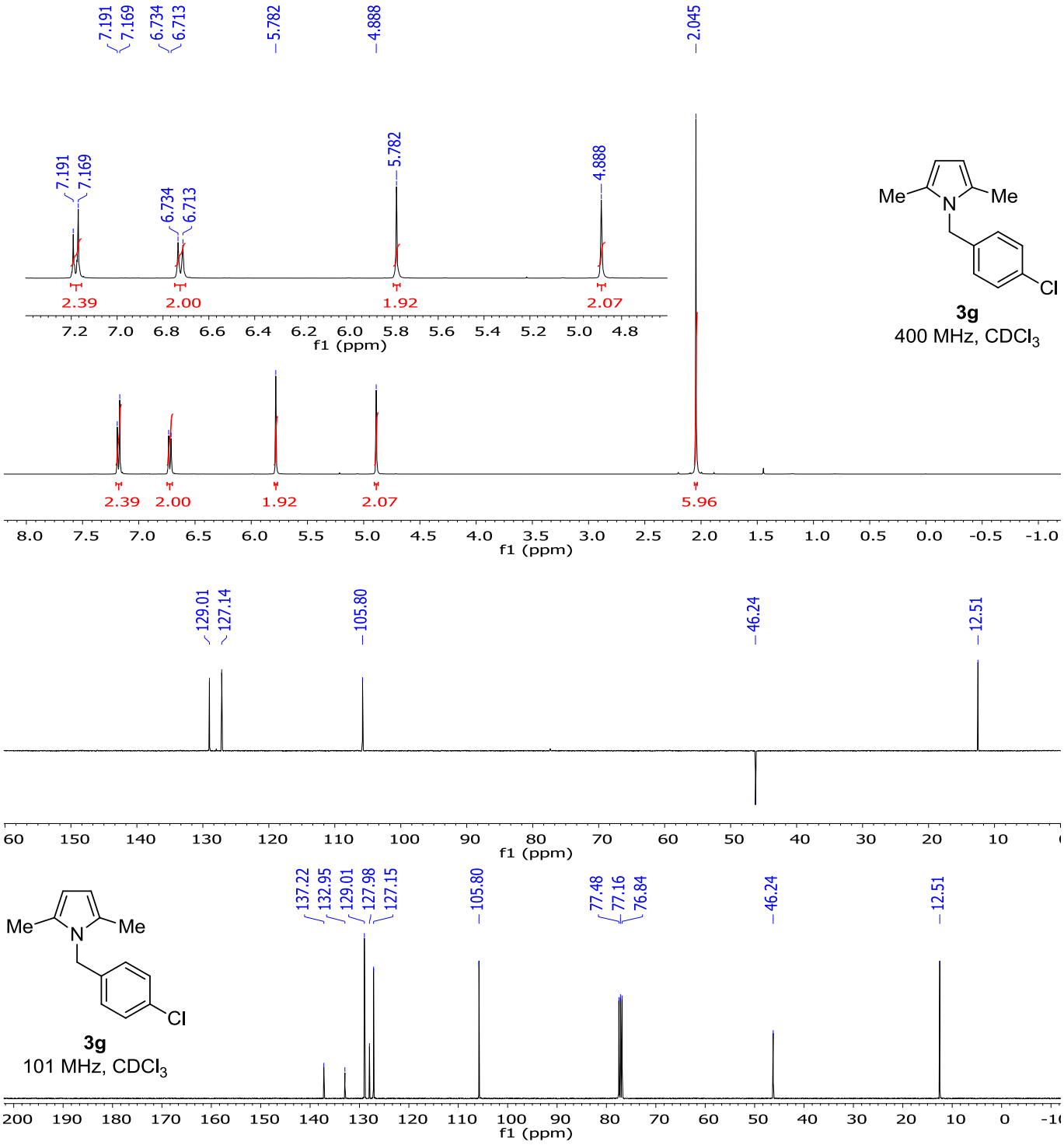
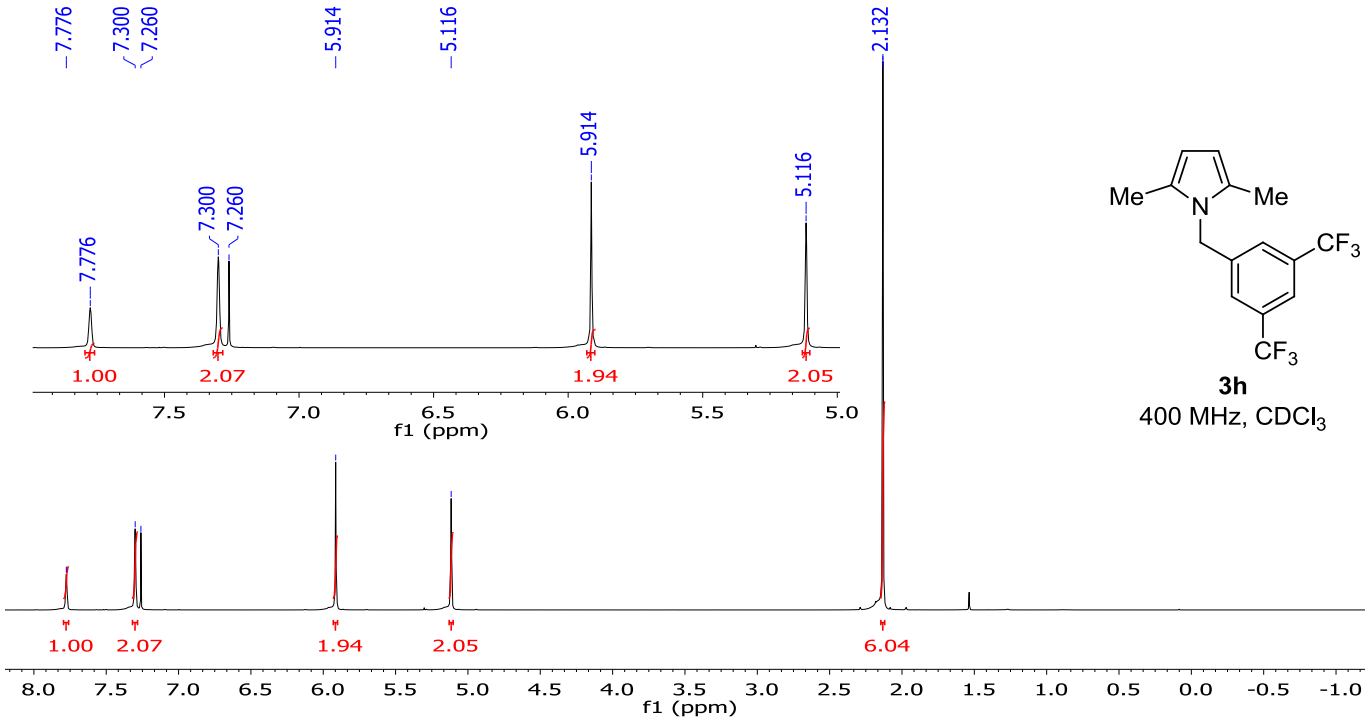
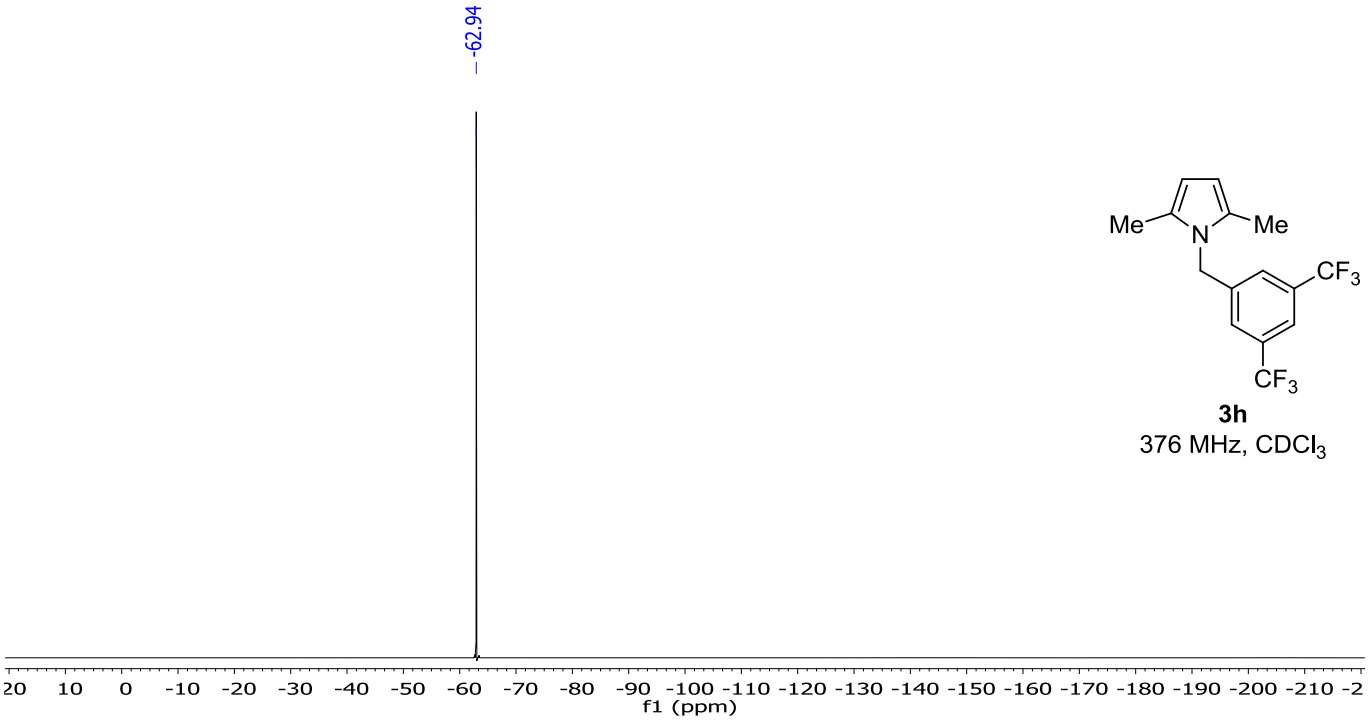


Figure S7: ^{1}H, $^{13}C\{^{1}H\}$, and DEPT-135 spectra for 1-(4-chlorobenzyl)-2,5-dimethyl-1*H*-pyrrole **3g**. [4]



3h
400 MHz, $CDCl_3$



3h
376 MHz, $CDCl_3$

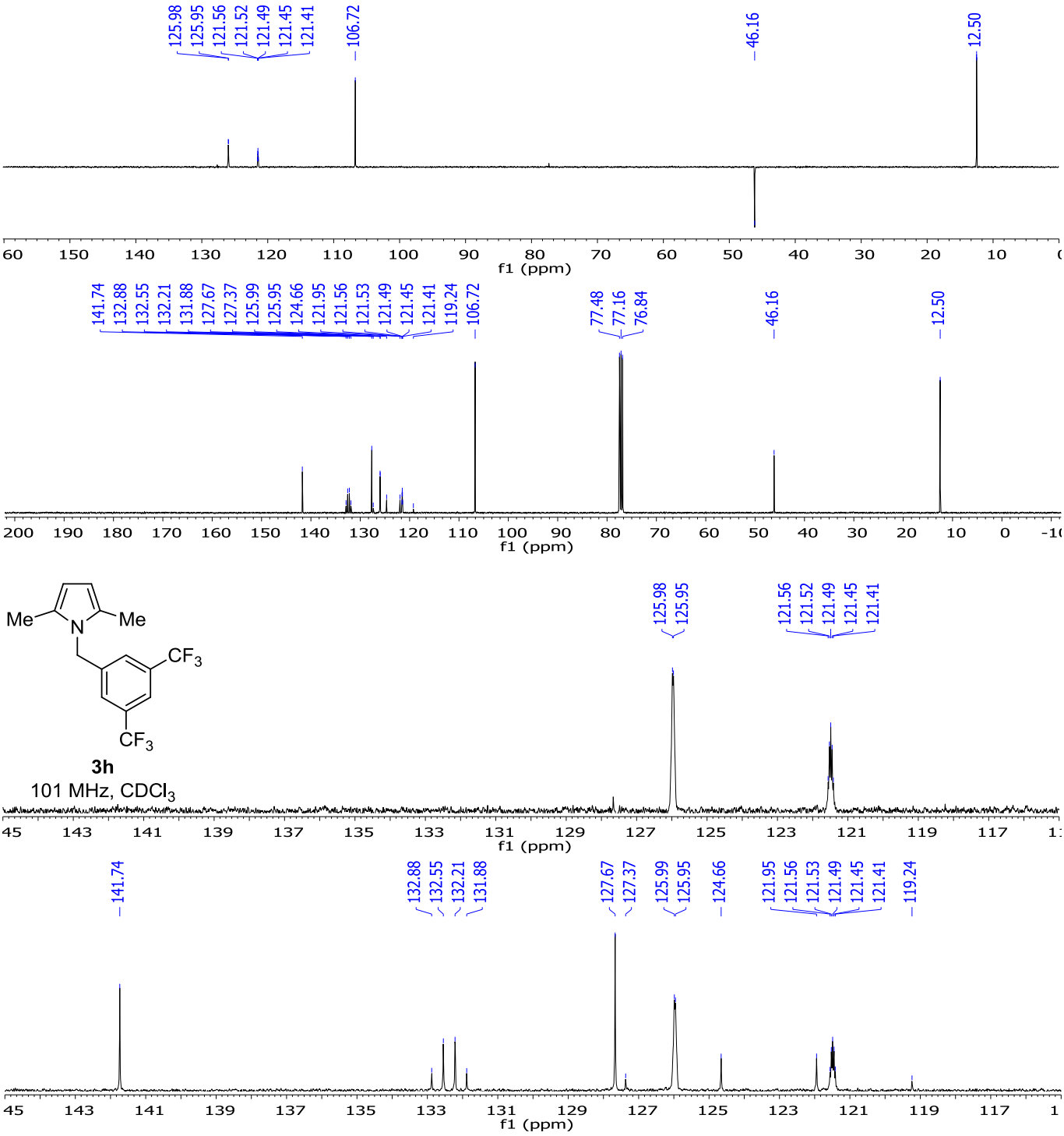
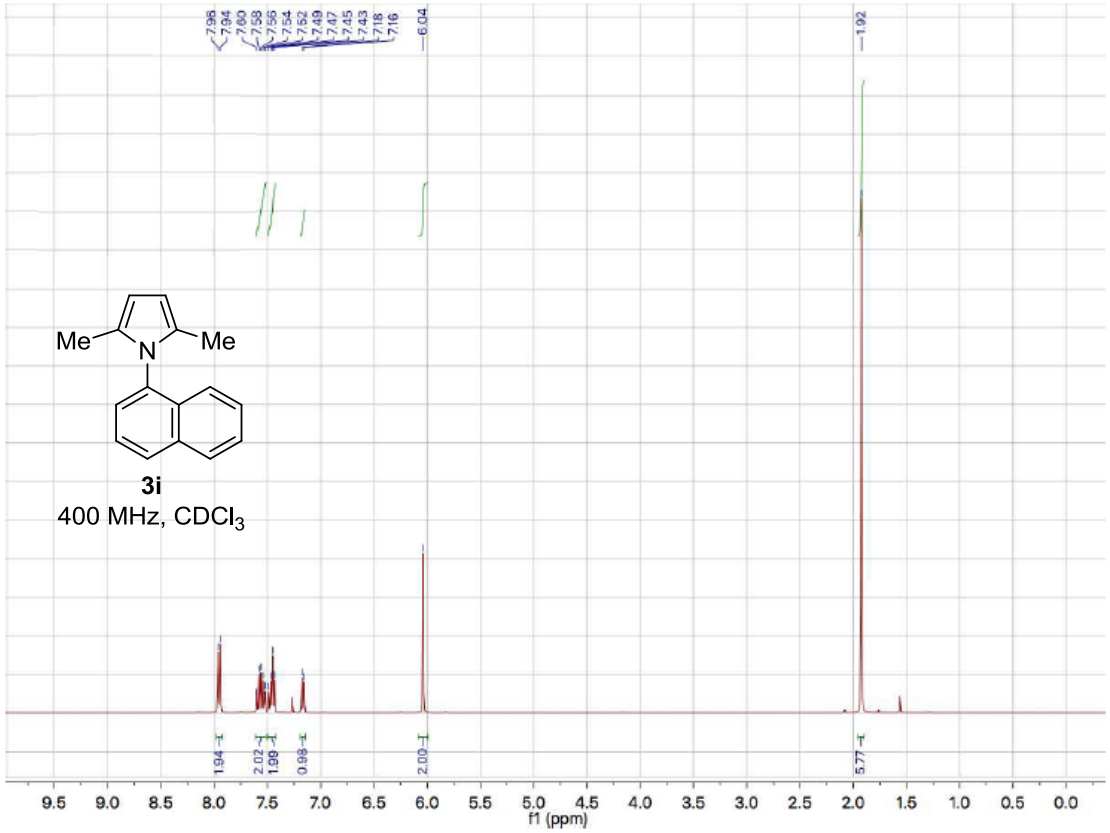


Figure S8: ^{1}H, ^{19}F{^{1}H}, ^{13}C{^{1}H}, and DEPT-135 spectra for 1-(3,5-*bis*(trifluoromethyl)benzyl)-2,5-dimethyl-1*H*-pyrrole **3h**.



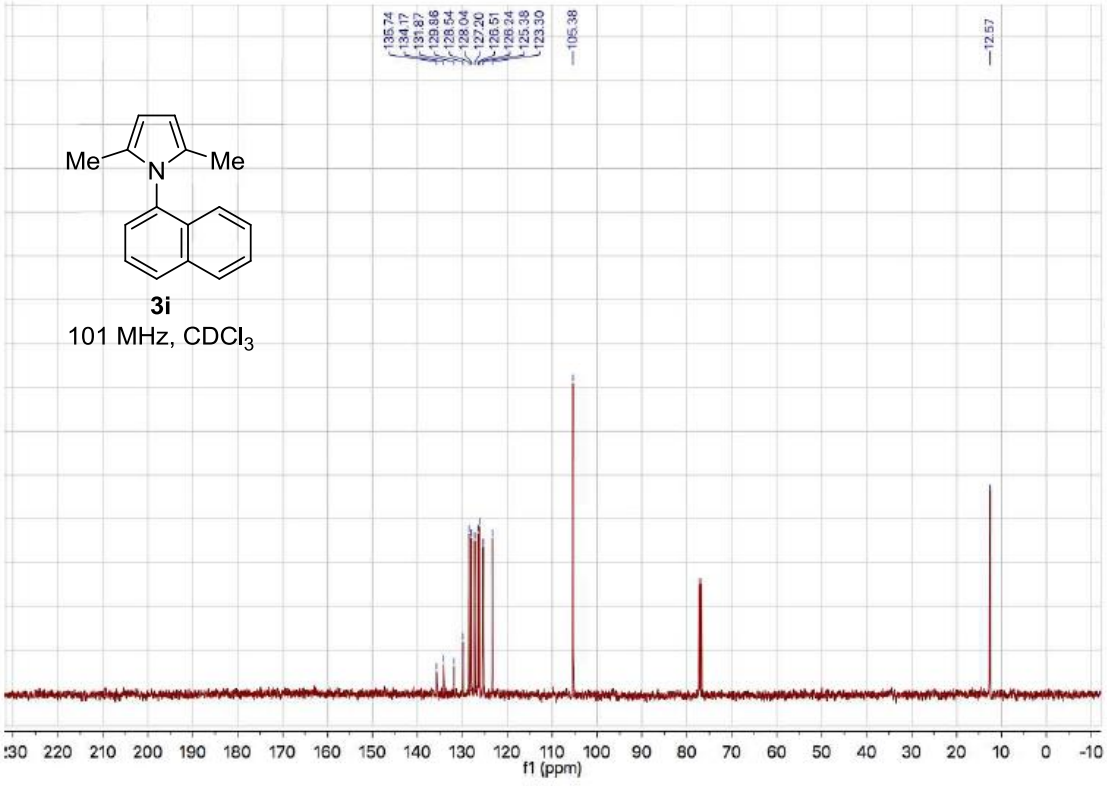


Figure S9: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2,5-dimethyl-1-(naphthalen-1-yl)-1*H*-pyrrole **3i**. [3]

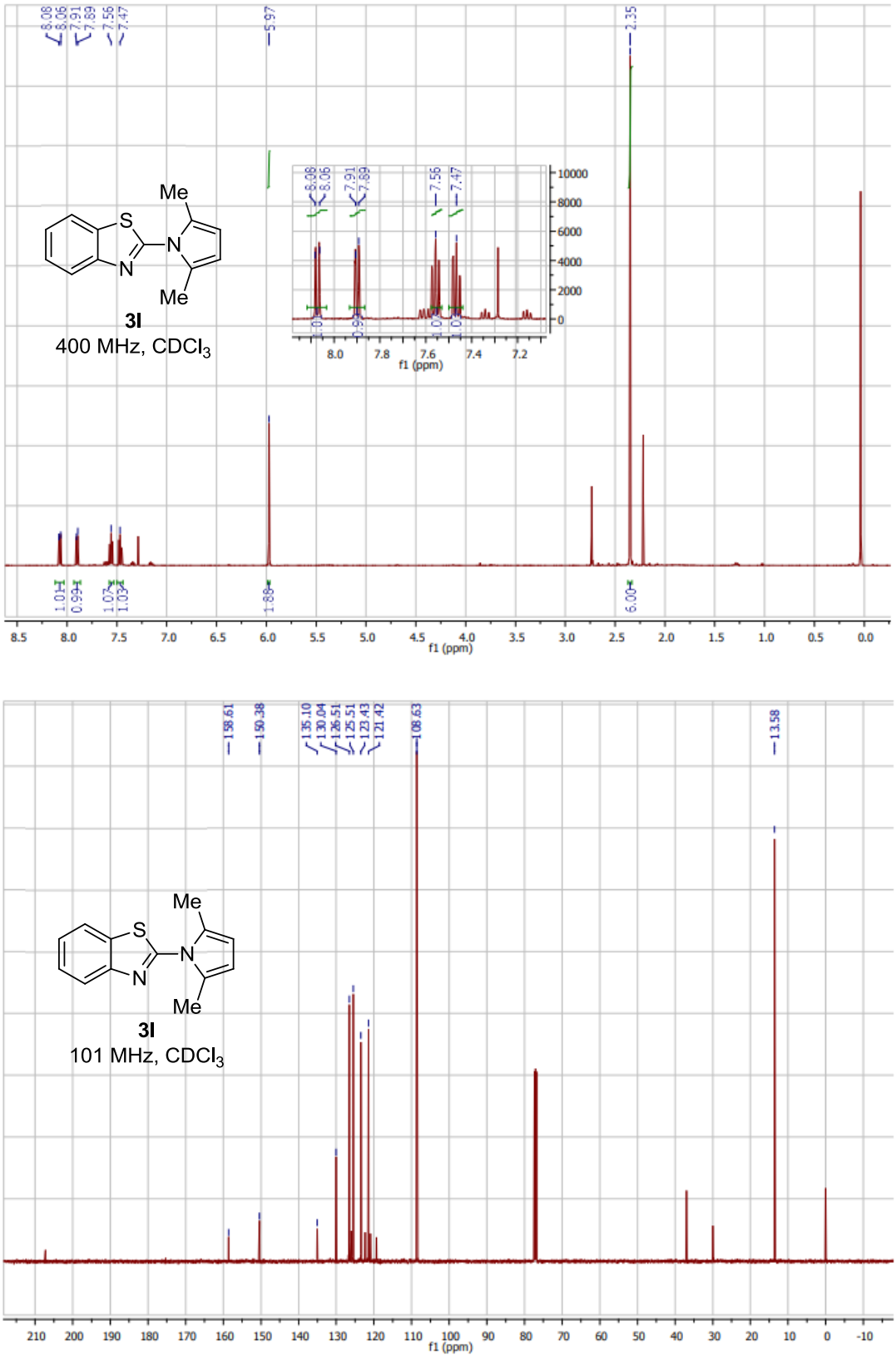


Figure S10: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzo[*d*]thiazole **3l**. [5]

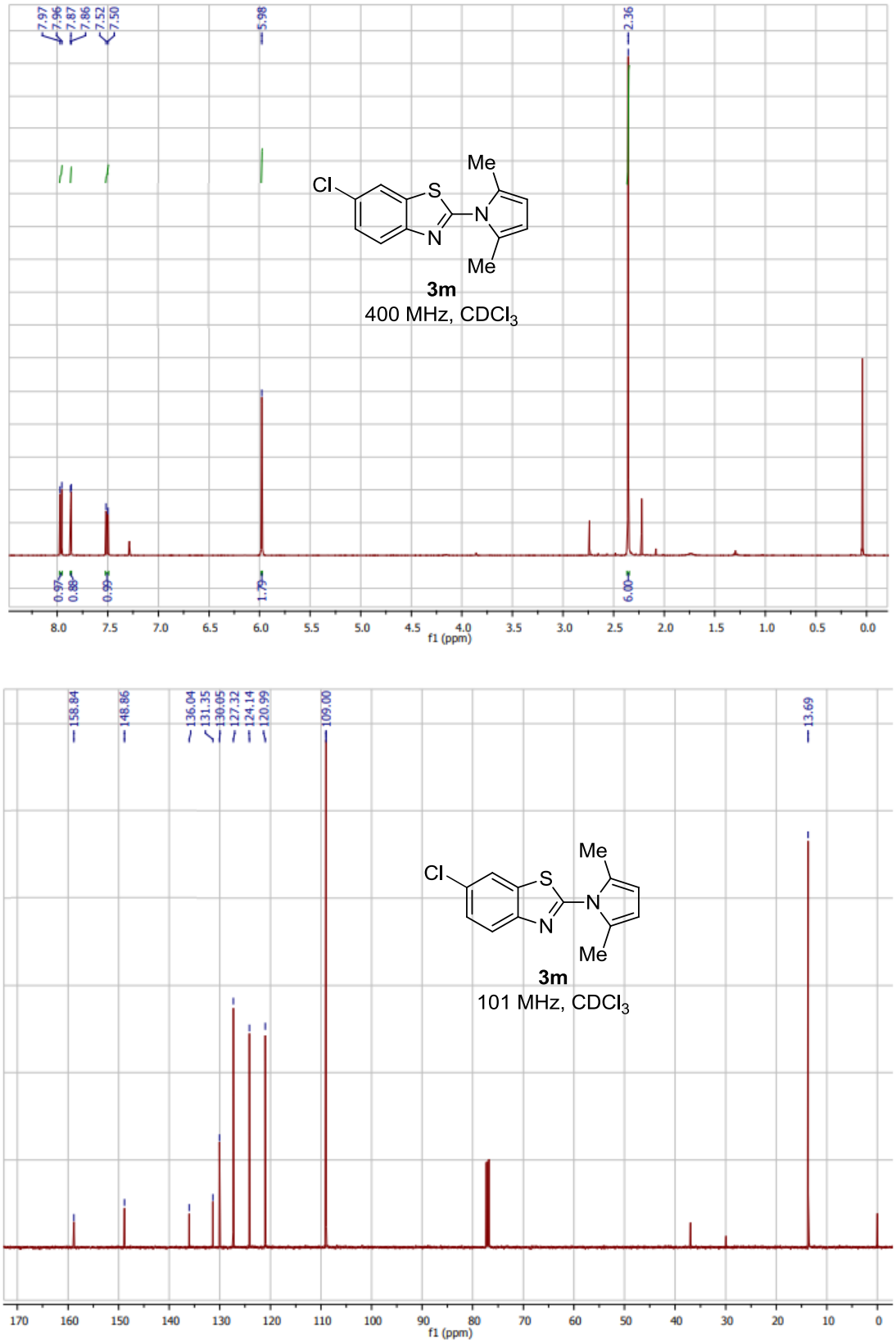


Figure S11: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 6-chloro-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzo[*d*]thiazole **3m**. [5]

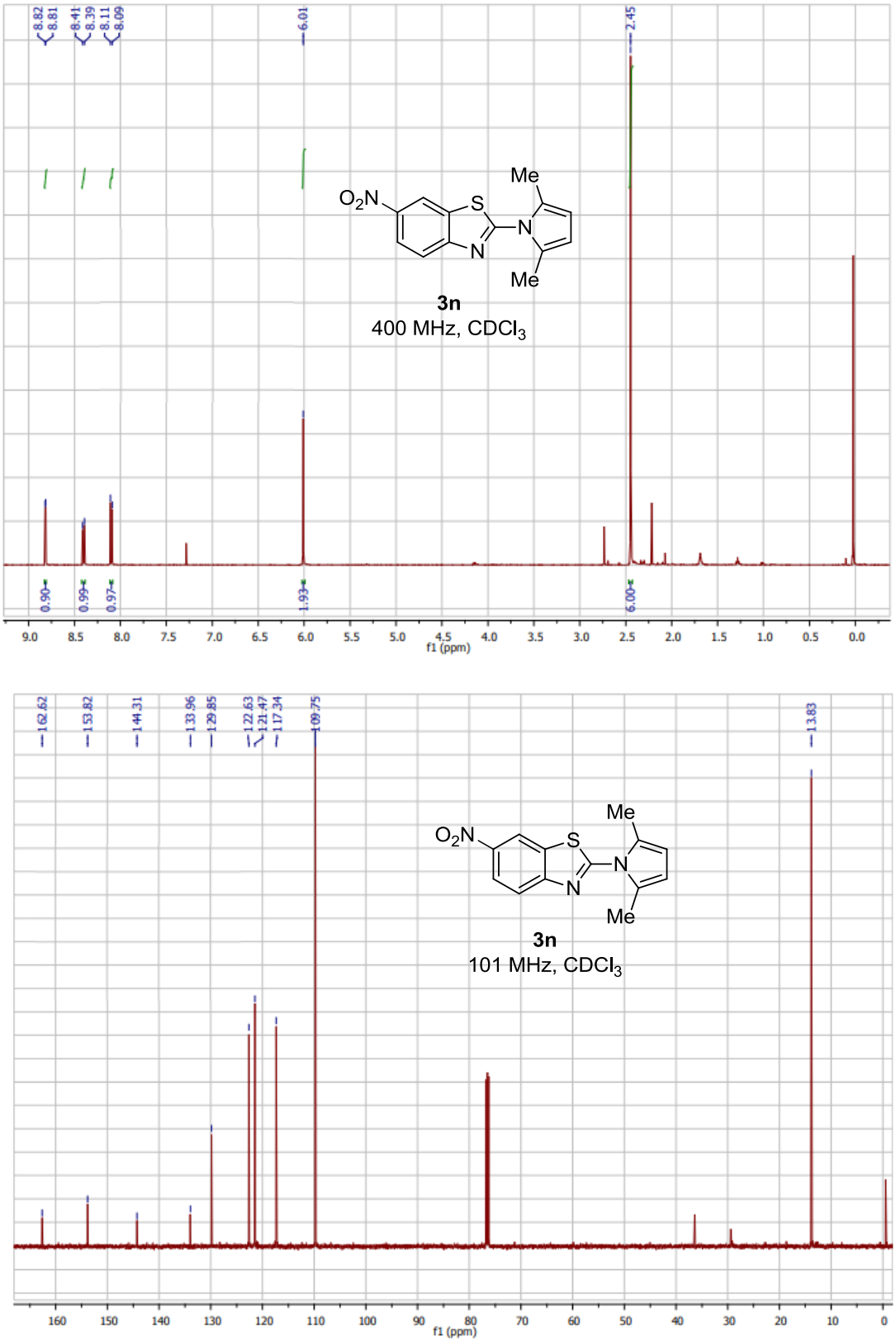


Figure S12: ^{1}H and $^{13}C\{^{1}H\}$ spectra for 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-6-nitrobenzo[*d*]thiazole **3n**. [5]

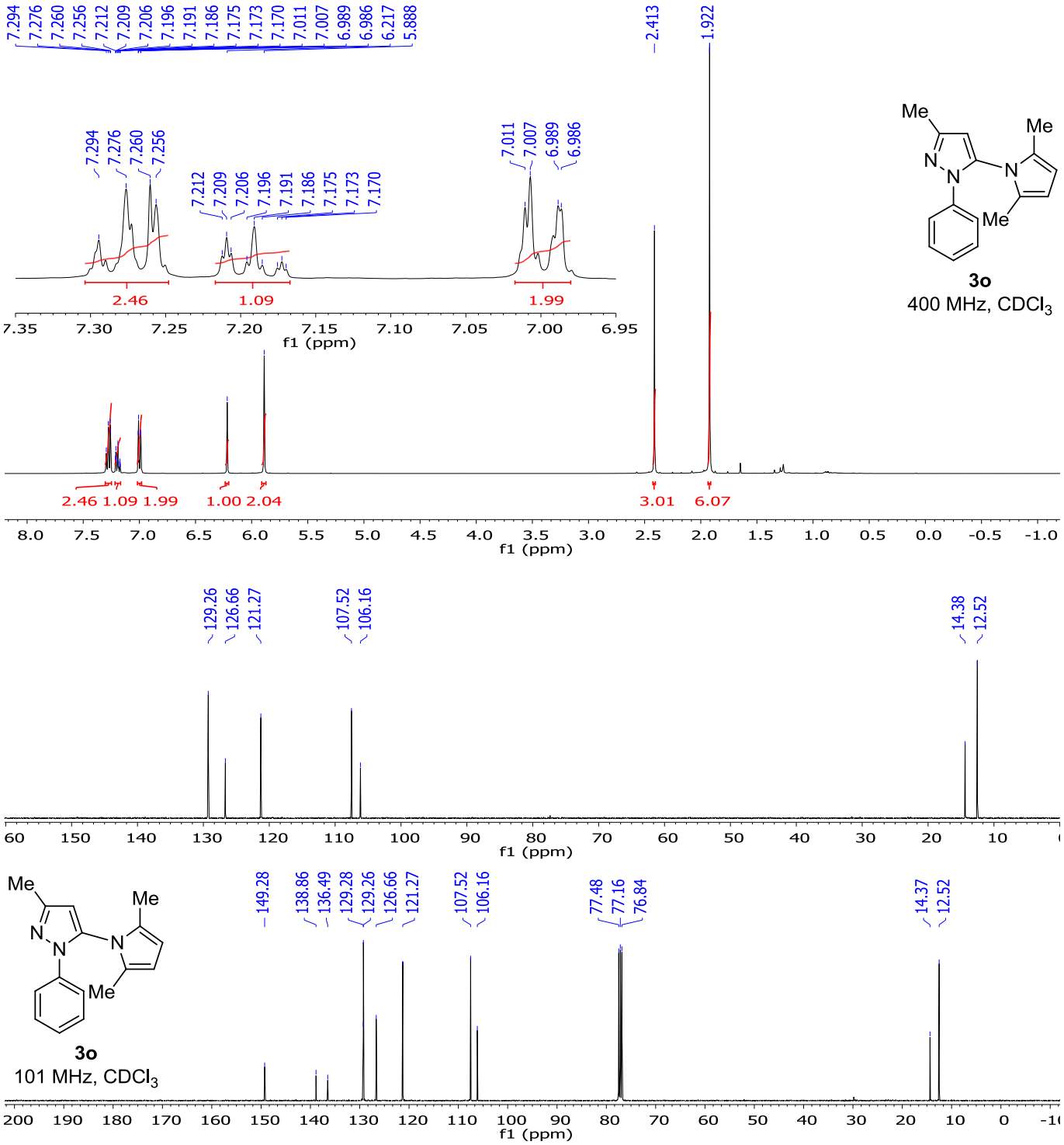
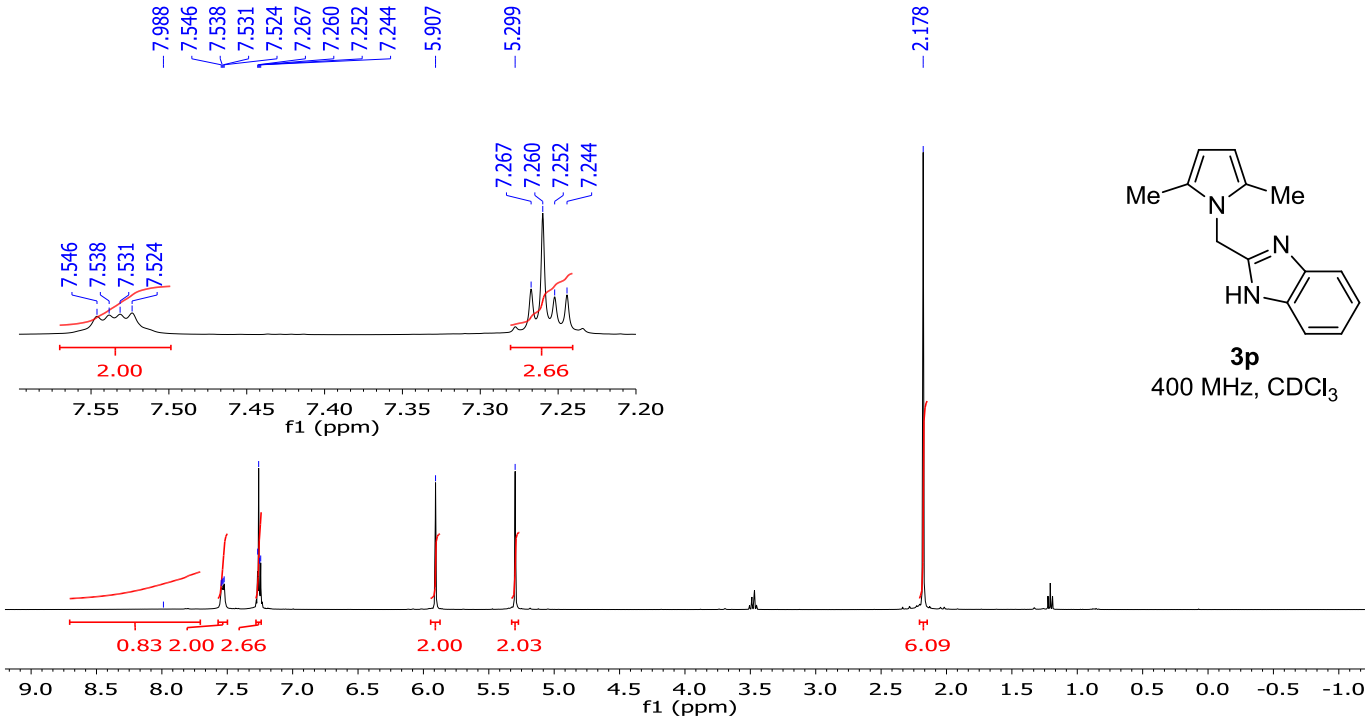
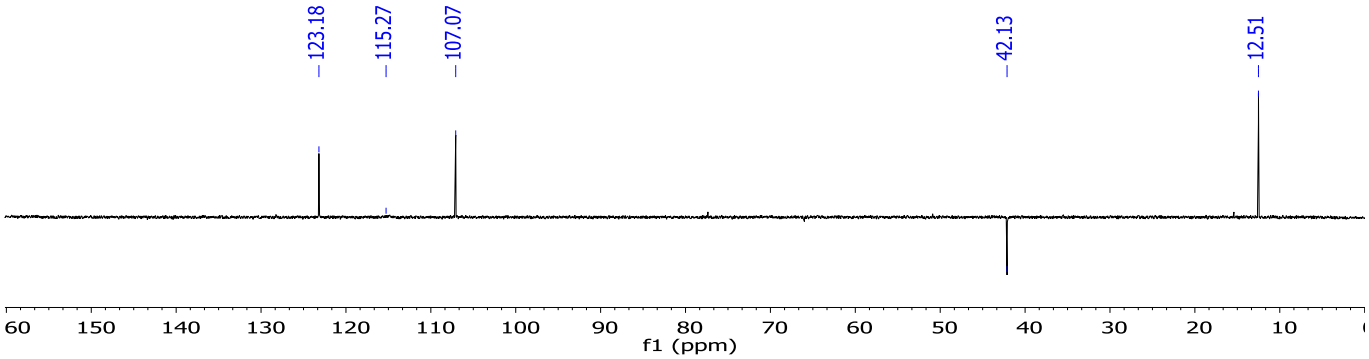
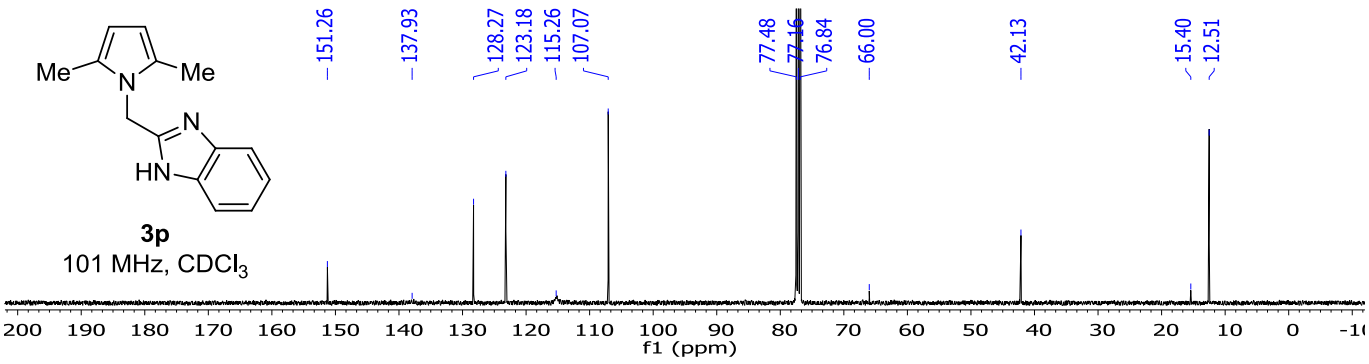


Figure S13: ^{1}H, ^{13}C{^{1}H}, and DEPT-135 spectra for 5-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-methyl-1-phenyl-1*H*-pyrazole **3o**.


7.988
7.546
7.538
7.531
7.524
7.267
7.260
7.252
7.244
5.907
5.299
2.178
2.00
2.66
0.83 2.00 2.66
2.00
2.03
6.09
f1 (ppm)
Me
N
Me
N
HN
3p
400 MHz, CDCl3


123.18
115.27
107.07
42.13
12.51
f1 (ppm)


151.26
137.93
128.27
123.18
115.26
107.07
77.48
77.16
76.84
66.00
42.13
15.40
12.51
f1 (ppm)
Me
N
Me
N
HN
3p
101 MHz, CDCl3

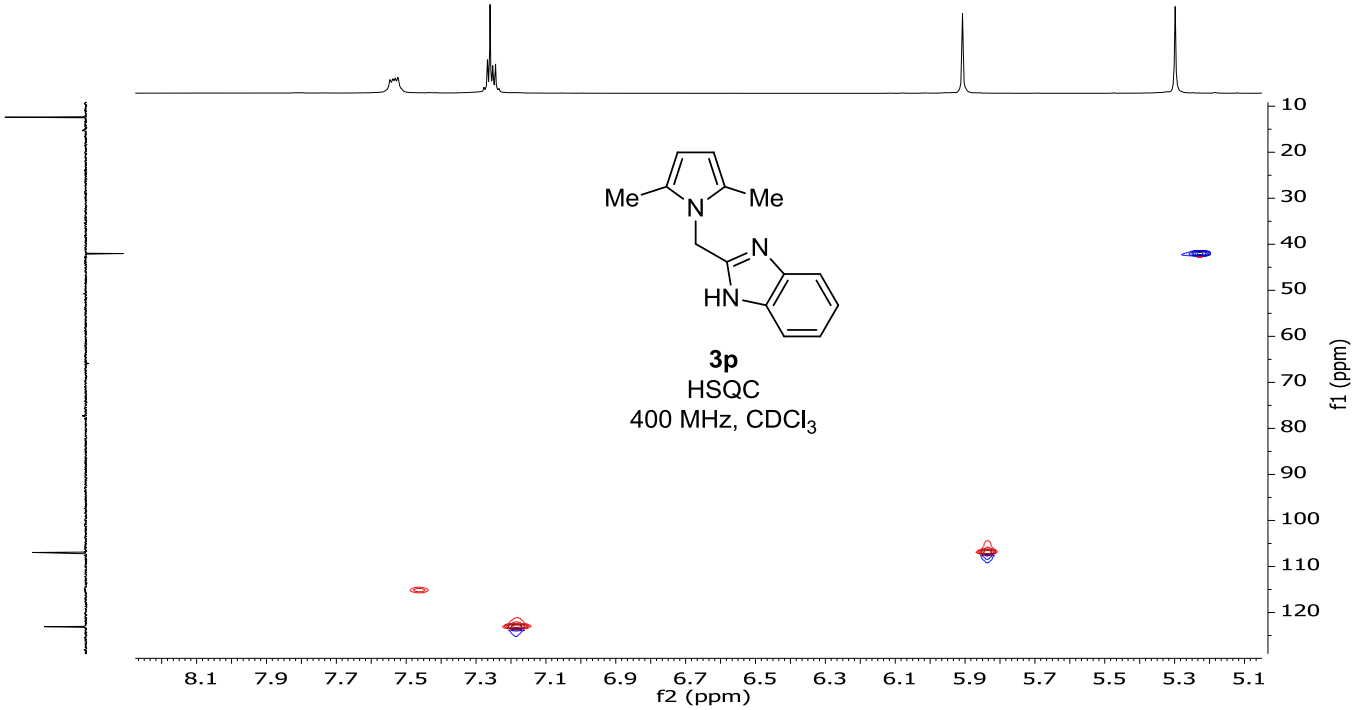


Figure S14: ^{1}H, ^{13}C{^{1}H}, DEPT-135, and HSQC spectra for 2-((2,5-dimethyl-1*H*-pyrrol-1-yl)methyl)-1*H*-benzo[*d*]imidazole **3p**.

2. Copies of HRMS spectra for compounds 3

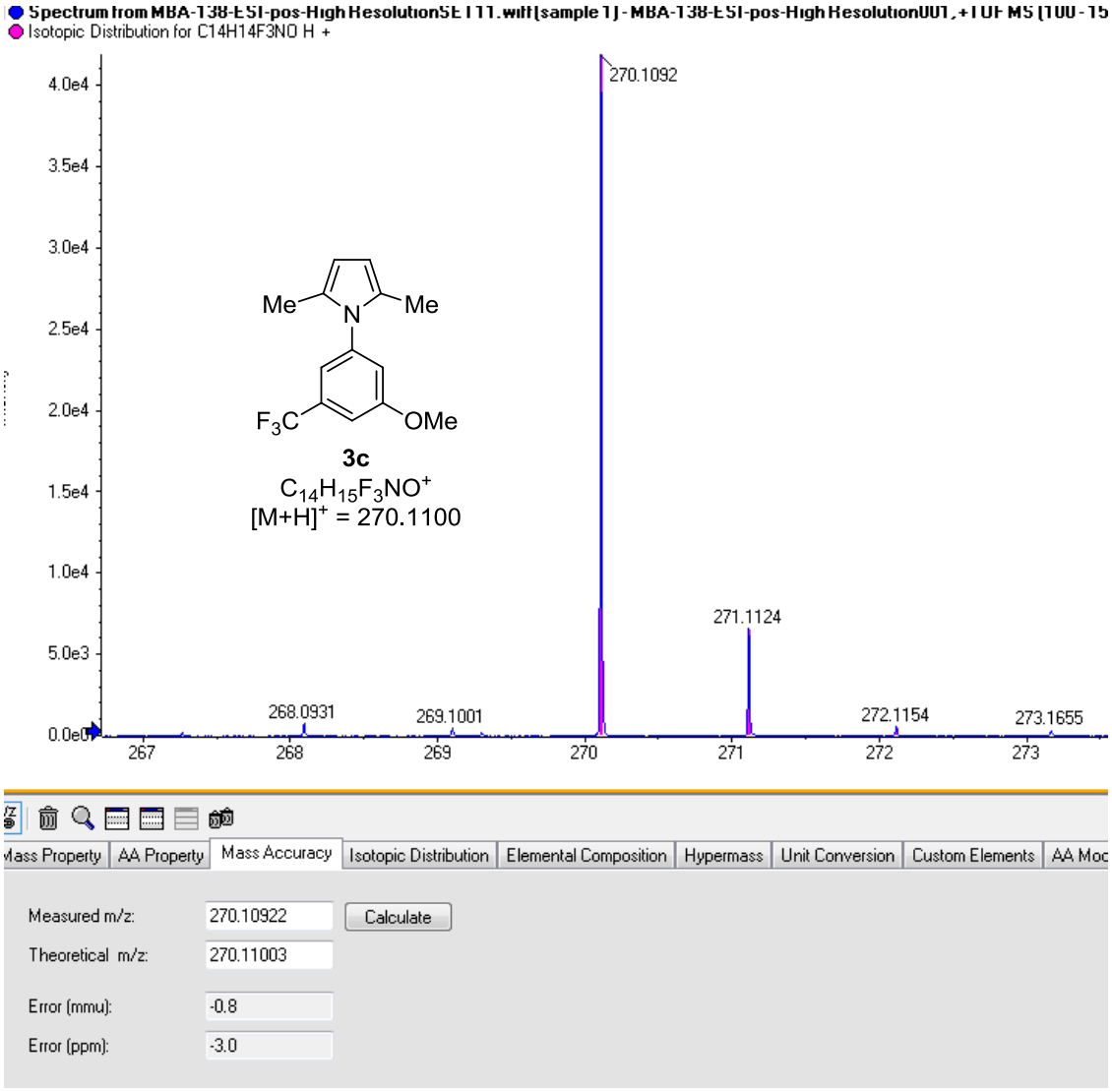


Figure S15: HRMS spectrum for 1-(3-methoxy-5-(trifluoromethyl)phenyl)-2,5-dimethyl-1*H*-pyrrole **3c.**

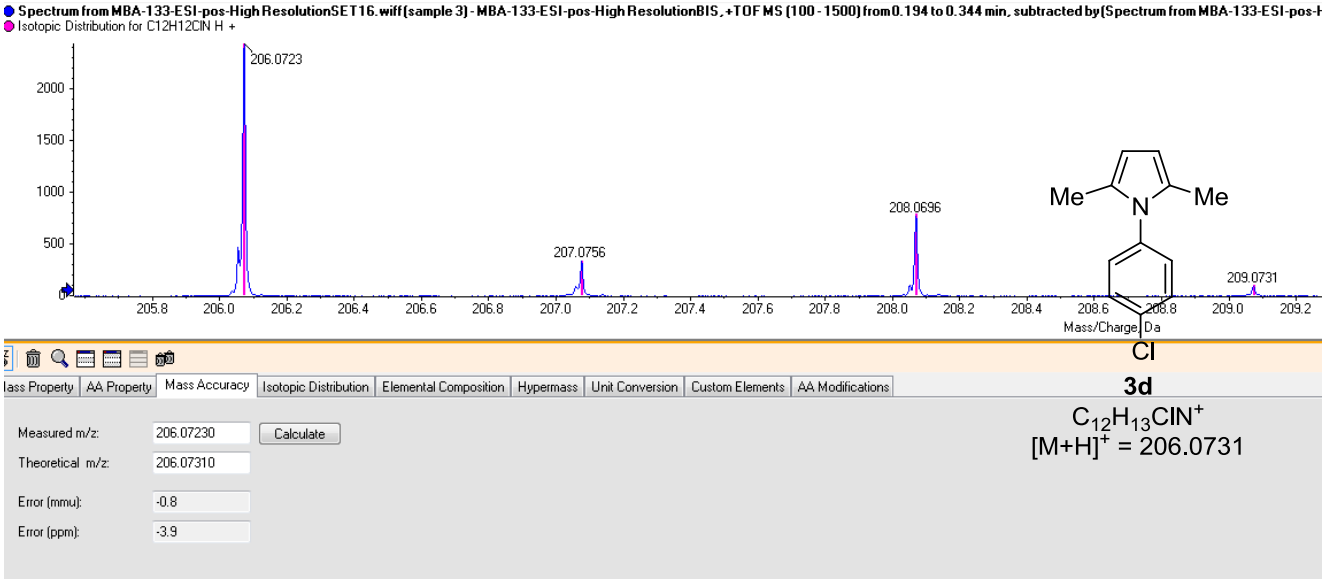


Figure S16: HRMS spectrum for 1-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole **3d**.

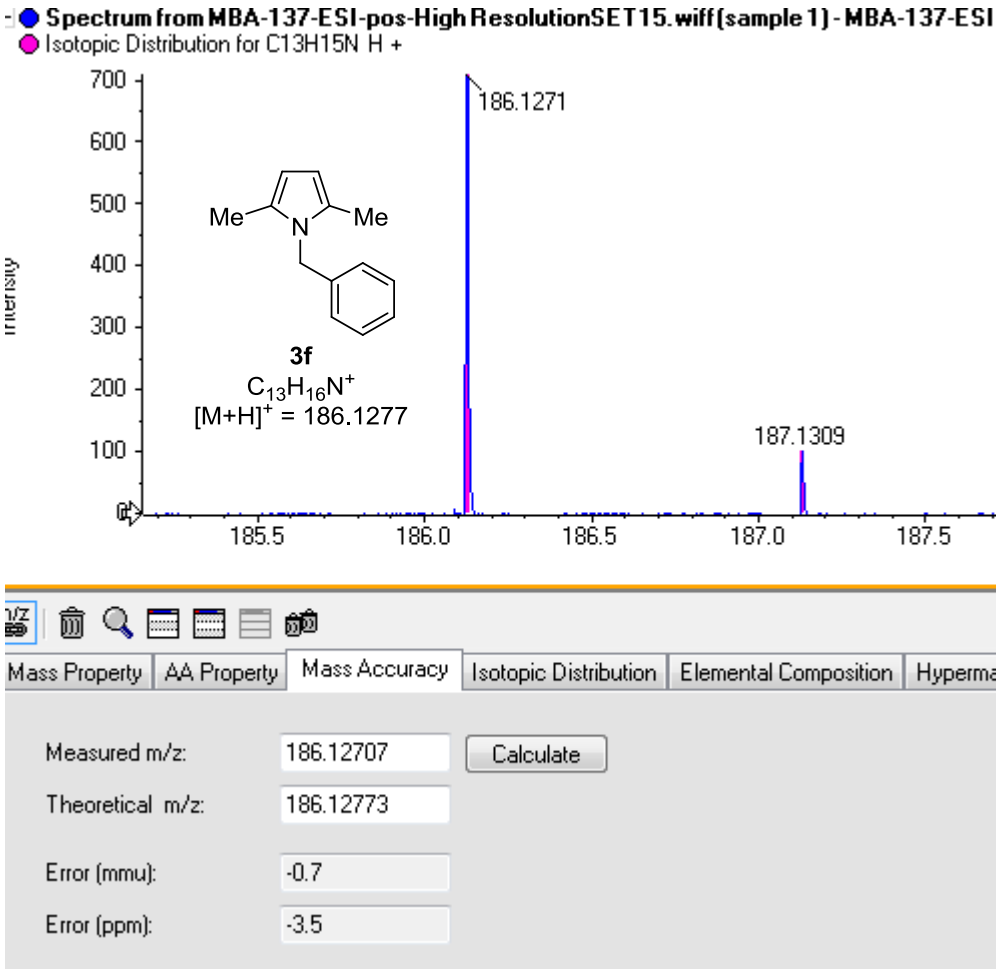


Figure S17: HRMS spectrum for 1-benzyl-2,5-dimethyl-1*H*-pyrrole **3f**.

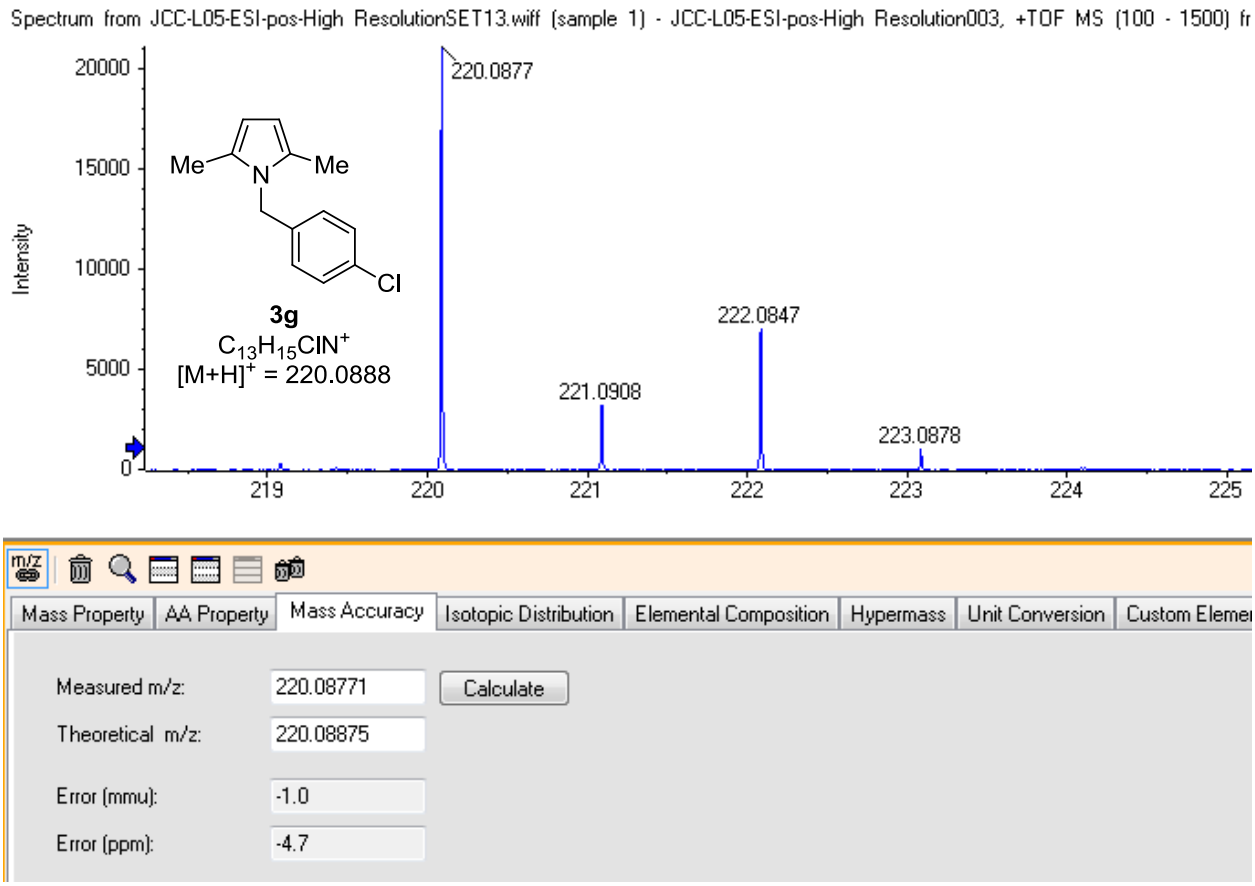


Figure S18: HRMS spectrum for 1-(4-chlorobenzyl)-2,5-dimethyl-1*H*-pyrrole **3g**.

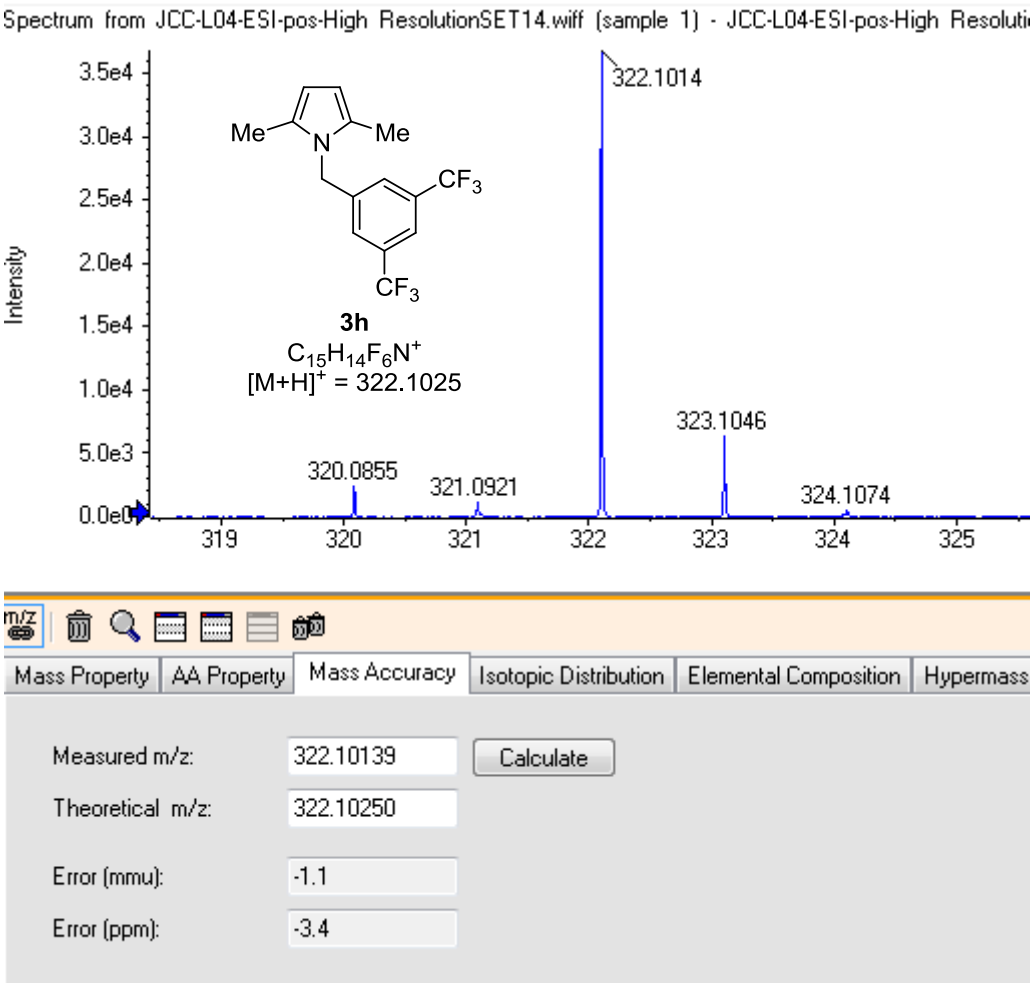


Figure S19: HRMS spectrum for 1-(3,5-*bis*(trifluoromethyl)benzyl)-2,5-dimethyl-1*H*-pyrrole **3h**.

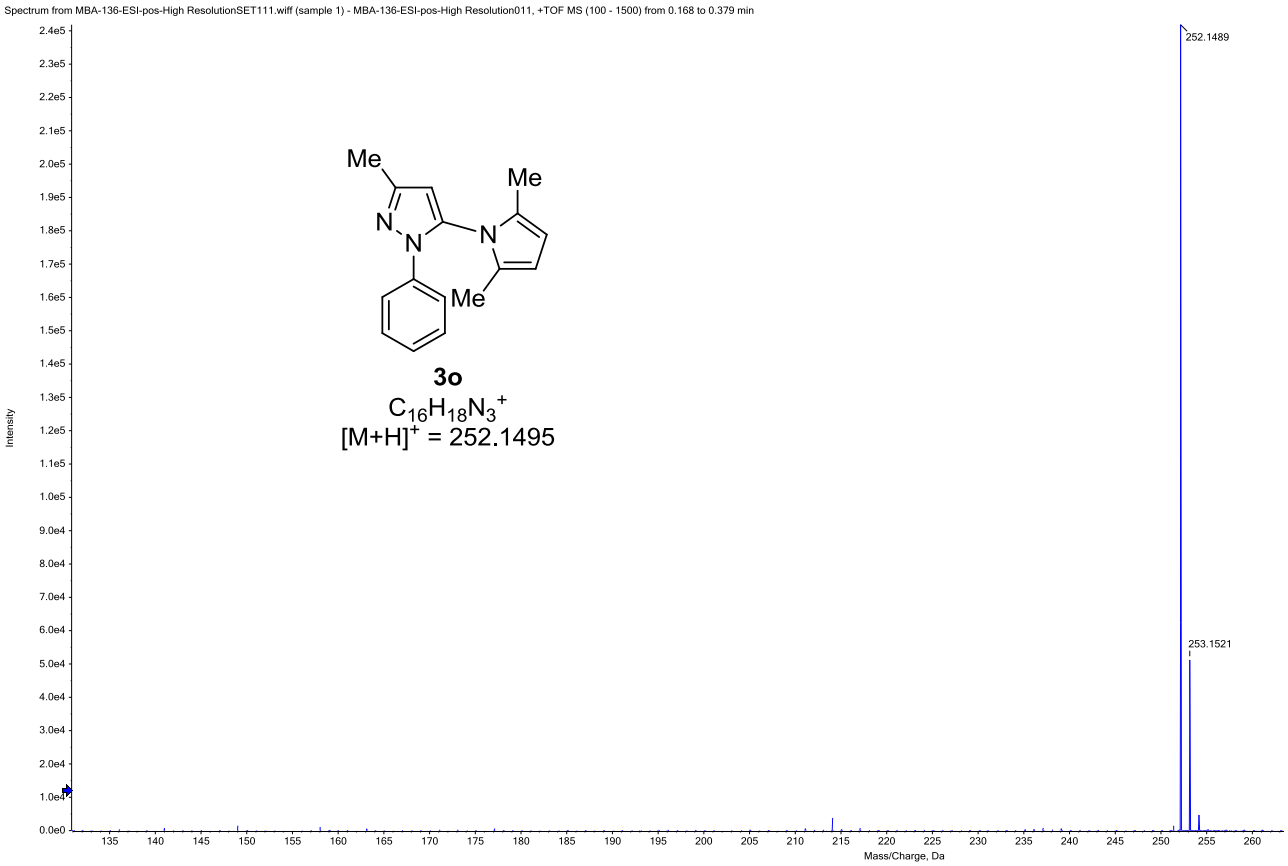


Figure S20: HRMS spectrum for 5-(2,5-dimethyl-1*H*-pyrrol-1-yl)-3-methyl-1-phenyl-1*H*-pyrazole **3o**.

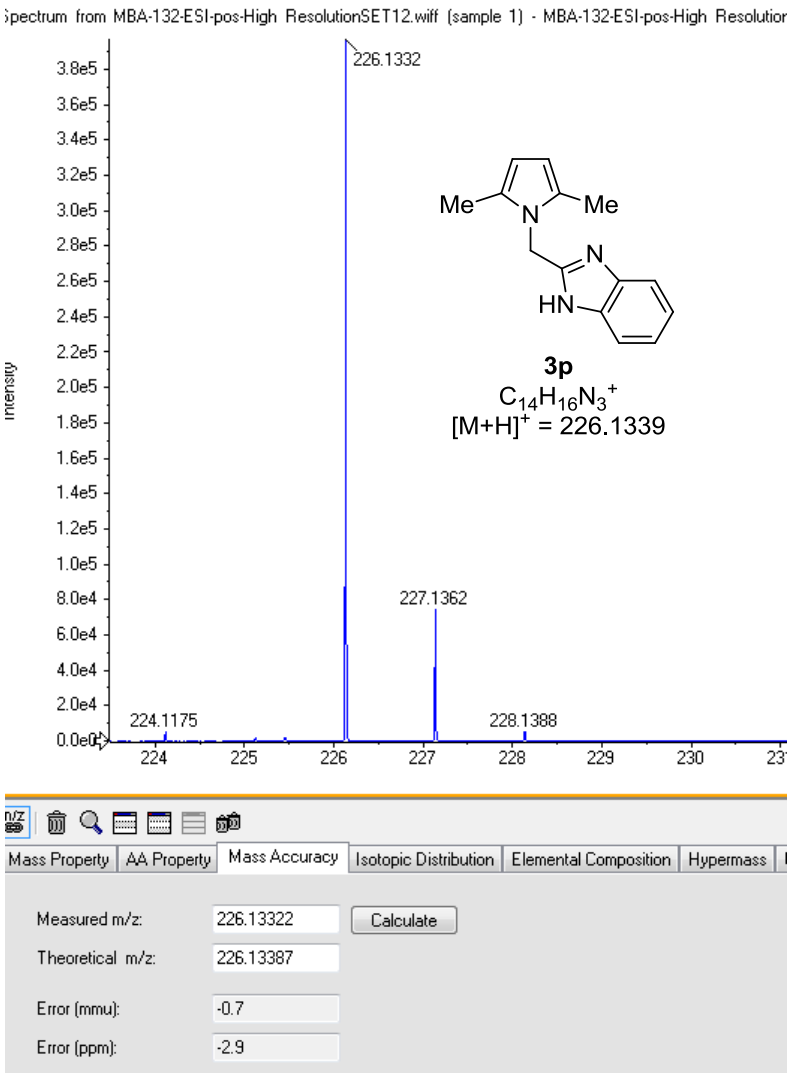


Figure S21: HRMS spectrum for 2-((2,5-dimethyl-1*H*-pyrrol-1-yl)methyl)-1*H*-benzo[*d*]imidazole **3p**.

3. Crystal data, data collection, and structure refinement details for compound 3g

Table S1: Experimental data for X-ray diffraction analysis for compound **3g**.

Crystal data	**Compound 3g**
CCDC[a] code	2239500
Formula	$C_{13}H_{14}ClN$
M_r	219.70
T [K]	200(2)
λ [Å]	0.71073
crystal system	Monoclinic
space group	*C*2
a [Å]; α [º]	19.000(1)
b [Å]; β [º]	6.100(1); 135.17(1)
c [Å]; γ [º]	14.256(1)
V [Å^3]	1164.8(1)
Z	4
ρ_{calcd} [g cm^{-3}]	1.253
$\mu_{MoK\alpha}$ [mm^{-1}]	0.294
F(000)	464
crystal size [mm^3]	0.56×0.38×0.21
θ range (deg)	2.03 to 27.48
index ranges	−24 to 24, −7 to 7, −18 to 18
Reflections collected	29796
Unique data	2676 [R_{int} = 0.039]
obsd data [I>2σ(I)]	2532
Goodness-of-fit on F^2	1.131
final R^a indices [I>2σ(I)]	$R1$ = 0.030, w$R2$ = 0.089
R^b indices (all data)	$R1$ = 0.035, w$R2$ = 0.101
largest diff. peak/hole [e Å^{-3}]	0.246/−0.245

[a] Cambridge Crystallographic Data Centre. [b] $R1 = \Sigma||F_0|-|F_c|| / [\Sigma|F_0|]$, $wR2 = \{[\Sigma w(F_0^2-F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

4. X-Ray powder difraction data for compound 3g

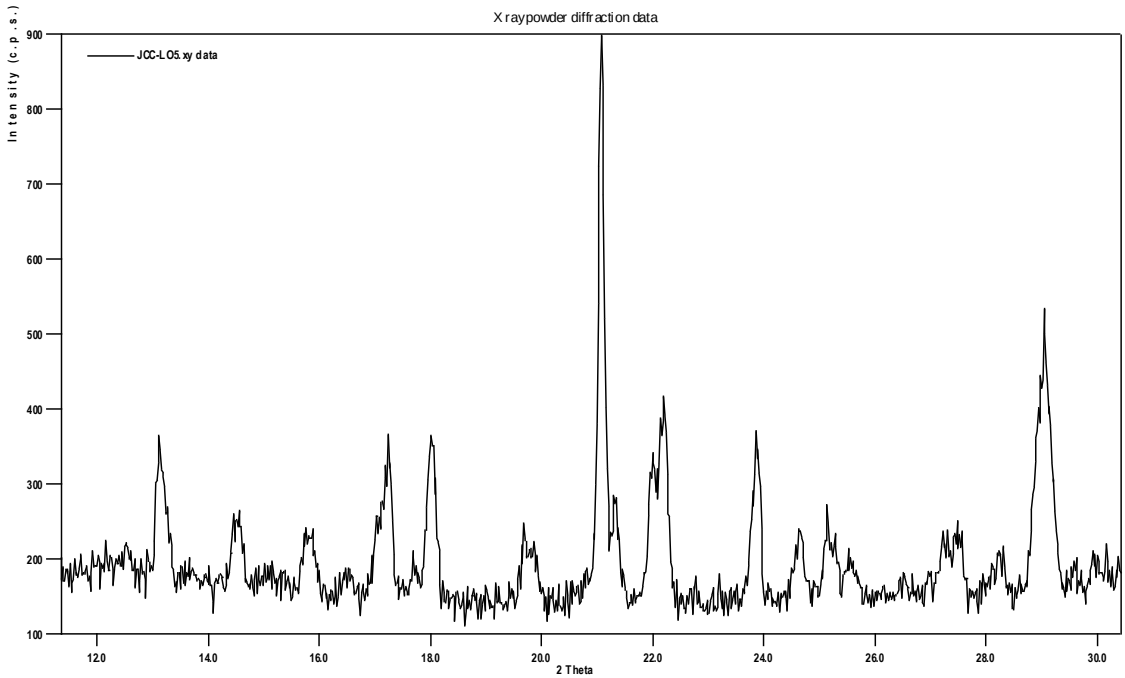


Figure S22: X-Ray powder difraction data for compound **3g**.

5. Surface area, pore volume, and pore size of aluminas

Table S2: Surface area, pore volume, and pore size of CATAPAL 200.

micromeritics®

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Sample: 4PORTI
Operator: Ing. Edgardo Soto/Lic. Fetsis
Submitter: Omar Portilla
File: C:\2020\DATA\4PORTI.SMP

Started: 25/10/2016 5:28:46p.m.
Completed: 26/10/2016 3:46:51a.m.
Report Time: 26/10/2016 3:46:52a.m.
Sample Mass: 0.1926 g
Cold Free Space: 47.6600 cm³
Low Pressure Dose: None

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Thermal Correction: No
Warm Free Space: 16.1098 cm³ Measured
Equilibration Interval: 10 s
Automatic Degas: Yes

Summary Report

Surface Area

Single point surface area at P/Po = 0.200241514: 46.1978 m²/g

BET Surface Area: 46.9425 m²/g

Langmuir Surface Area: 536.3472 m²/g

t-Plot Micropore Area: 7.2455 m²/g

t-Plot External Surface Area: 39.6970 m²/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 50.243 m²/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 87.3445 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 1339.820 Å width at P/Po = 0.985474056: 0.443699 cm³/g

t-Plot micropore volume: 0.003199 cm³/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.463089 cm³/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.465721 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 378.0782 Å

BJH Adsorption average pore width (4V/A): 368.682 Å

BJH Desorption average pore width (4V/A): 213.280 Å

Freundlich

Qm·C: 1.1841 ± 0.1882 cm³/g STP

m: 1.7332 ± 0.1970

Temkin

q·alpha/Qm: 0.027726 ± 0.007606 kJ/mol·(cm³/g STP)

A: 0.0324 ± 0.0582 mmHg

BET Surface Area Report

BET Surface Area: 46.9425 ± 0.0634 m²/g
Slope: 0.092341 ± 0.000125 g/cm³ STP
Y-Intercept: 0.000393 ± 0.000013 g/cm³ STP
C: 235.769893
Qm: 10.7835 cm³/g STP
Correlation Coefficient: 0.9999873
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.009774073	7.9929	0.001235
0.015758448	8.8682	0.001805
0.022187218	9.3707	0.002421
0.029681599	9.7638	0.003133
0.040172001	10.1587	0.004120
0.050069385	10.4464	0.005046
0.055158248	10.5732	0.005521
0.060349078	10.7077	0.005998
0.070326726	10.9371	0.006917
0.080405117	11.1517	0.007841
0.100240473	11.5223	0.009669
0.120317474	11.8900	0.011503
0.140358624	12.2334	0.013347
0.160404302	12.5795	0.015187
0.180344468	12.9197	0.017030
0.200241514	13.2695	0.018869

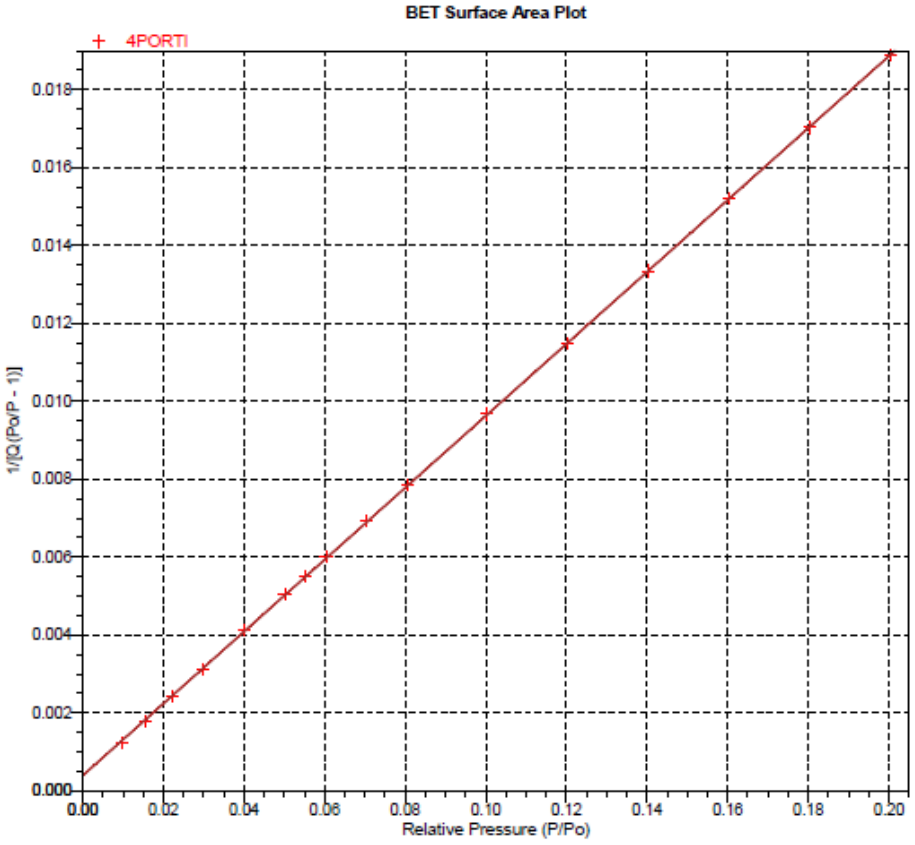

Table S3: Surface area, pore volume, and pore size of CATAPAL C-1.

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Sample: 2PORTI
Operator: Ing. Edgardo Soto/Lic. Fetsis
Submitter: Omar Portilla
File: C:\2020\DATA\2PORTI.SMP

Started: 21/10/2016 9:37:19a.m.
Completed: 21/10/2016 5:06:48p.m.
Report Time: 21/10/2016 5:06:51p.m.
Sample Mass: 0.1568 g
Cold Free Space: 48.3692 cm³
Low Pressure Dose: None

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Thermal Correction: No
Warm Free Space: 16.3928 cm³ Measured
Equilibration Interval: 10 s
Automatic Degas: Yes

Summary Report

Surface Area

Single point surface area at P/Po = 0.200525222: 234.9990 m²/g

BET Surface Area: 239.0706 m²/g

Langmuir Surface Area: 1416.8247 m²/g

t-Plot Micropore Area: 33.3750 m²/g

t-Plot External Surface Area: 205.6956 m²/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 227.509 m²/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 277.4043 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 1860.680 Å width at P/Po = 0.989596767: 0.374051 cm³/g

t-Plot micropore volume: 0.014613 cm³/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.356414 cm³/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.381550 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 62.5842 Å

BJH Adsorption average pore width (4V/A): 62.664 Å

BJH Desorption average pore width (4V/A): 55.017 Å

Freundlich

Qm·C: 9.9220 ± 0.6958 cm³/g STP

m: 2.2265 ± 0.1432

Temkin

q·alpha/Qm: 0.012587 ± 0.001192 kJ/mol·(cm³/g STP)

A: 0.0652 ± 0.0384 mmHg

BET Surface Area Report

BET Surface Area: 239.0706 ± 0.4532 m²/g
Slope: 0.018124 ± 0.000034 g/cm³ ST
Y-Intercept: 0.000085 ± 0.000004 g/cm³ ST
C: 214.979066
Qm: 54.9184 cm³/g STP
Correlation Coefficient: 0.9999749
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.009685705	40.1011	0.000244
0.014719229	44.0100	0.000339
0.019621575	46.2323	0.000433
0.032905282	49.8231	0.000683
0.043144985	51.6938	0.000872
0.049427555	52.6496	0.000988
0.055154497	53.4529	0.001092
0.059759451	54.0397	0.001176
0.070231696	55.3012	0.001366
0.080256312	56.4072	0.001547
0.100093476	58.4295	0.001904
0.120277457	60.3433	0.002266
0.140270583	62.1646	0.002625
0.160312254	63.9505	0.002985
0.180435288	65.7216	0.003350
0.200525222	67.5232	0.003715

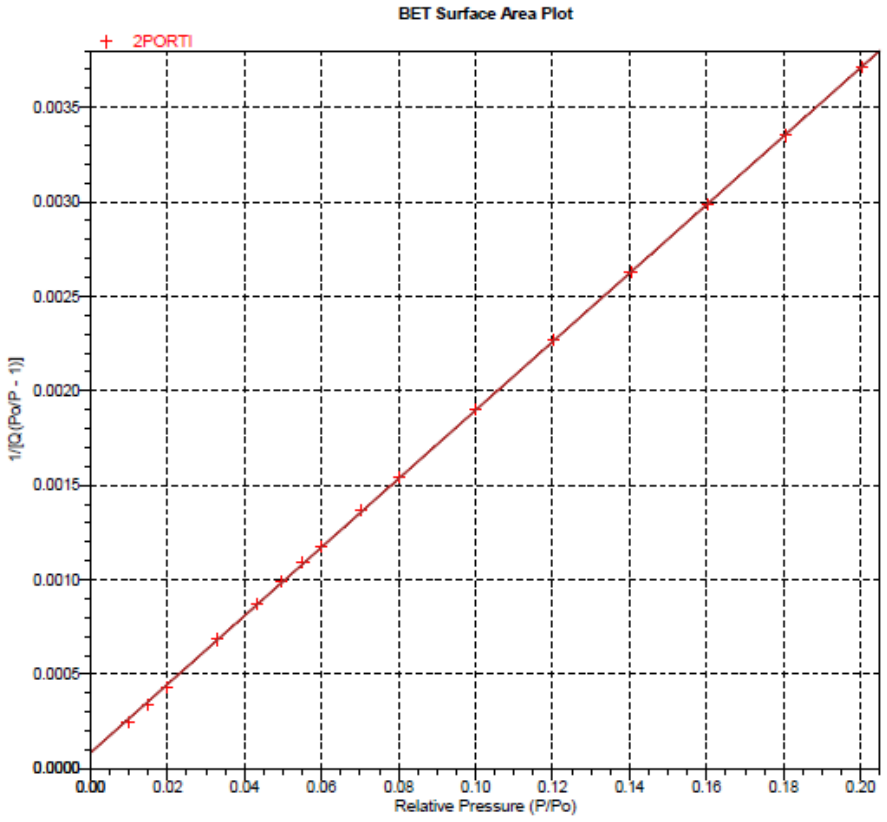

Table S4: Surface area, pore volume, and pore size of CATALOX SBA-90.

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Sample: 1PORTI
Operator: Ing. Edgardo Soto/Lic. Fetsis
Submitter: Omar Portilla
File: C:\2020\DATA\1PORTI.SMP

Started: 24/10/2016 9:49:52a.m.
Completed: 24/10/2016 6:32:14p.m.
Report Time: 24/10/2016 6:31:09p.m.
Sample Mass: 0.1855 g
Cold Free Space: 48.9476 cm³
Low Pressure Dose: None

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Thermal Correction: No
Warm Free Space: 16.4755 cm³ Measured
Equilibration Interval: 10 s
Automatic Degas: Yes

Summary Report

Surface Area

Single point surface area at P/Po = 0.200200904: 104.2507 m²/g

BET Surface Area: 106.6336 m²/g

Langmuir Surface Area: 1556.2280 m²/g

t-Plot Micropore Area: 10.8103 m²/g

t-Plot External Surface Area: 95.8234 m²/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 101.186 m²/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 134.4968 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 1616.757 Å width at P/Po = 0.988001590: 0.389821 cm³/g

t-Plot micropore volume: 0.004434 cm³/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.384812 cm³/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.392077 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 146.2283 Å

BJH Adsorption average pore width (4V/A): 152.120 Å

BJH Desorption average pore width (4V/A): 116.606 Å

Freundlich

Qm·C: 2.4121 ± 0.3463 cm³/g STP

m: 1.6779 ± 0.1668

Temkin

q·alpha/Qm: 0.014000 ± 0.002266 kJ/mol·(cm³/g STP)

A: 0.0350 ± 0.0369 mmHg

BET Surface Area Report

BET Surface Area: 106.6336 ± 0.4010 m²/g
Slope: 0.040569 ± 0.000153 g/cm³ STP
Y-Intercept: 0.000255 ± 0.000016 g/cm³ STP
C: 159.889310
Qm: 24.4955 cm³/g STP
Correlation Coefficient: 0.9999008
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.010001076	17.4902	0.000578
0.015103394	18.7257	0.000819
0.021234551	19.7979	0.001096
0.030056956	20.9216	0.001481
0.039918060	21.8993	0.001899
0.050146727	22.7156	0.002324
0.054816488	23.0719	0.002514
0.060181446	23.4507	0.002731
0.070200667	24.0455	0.003140
0.080241782	24.6371	0.003541
0.099949319	25.6458	0.004330
0.119988042	26.5994	0.005126
0.140167470	27.4759	0.005933
0.160008250	28.3171	0.006727
0.180179458	29.1444	0.007541
0.200200904	29.9426	0.008360

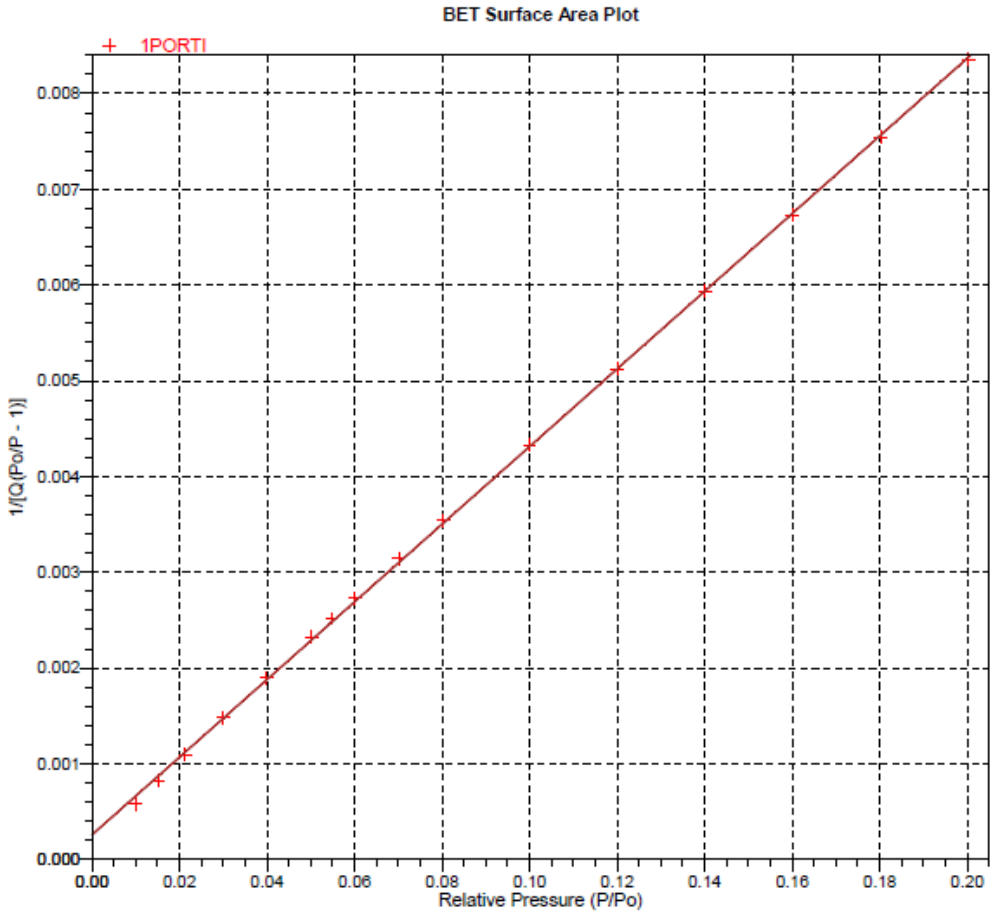

Table S5: Surface area, pore volume, and pore size of CATALOX SBA-200.

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Sample: 3PORTI
Operator: Ing. Edgardo Soto/Lic. Fetsis
Submitter: Omar Portilla
File: C:\2020\DATA\3PORTI.SMP

Started: 25/10/2016 8:40:08a.m.
Completed: 25/10/2016 5:19:01p.m.
Report Time: 25/10/2016 5:19:04p.m.
Sample Mass: 0.1845 g
Cold Free Space: 49.5223 cm³
Low Pressure Dose: None

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Thermal Correction: No
Warm Free Space: 16.5324 cm³ Measured
Equilibration Interval: 10 s
Automatic Degas: Yes

Summary Report

Surface Area

Single point surface area at P/Po = 0.200199284: 194.9608 m²/g

BET Surface Area: 199.2839 m²/g

Langmuir Surface Area: 1977.1800 m²/g

t-Plot Micropore Area: 5.1076 m²/g

t-Plot External Surface Area: 194.1763 m²/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 220.924 m²/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 264.5917 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 1856.500 Å width at P/Po = 0.989573005: 0.417257 cm³/g

t-Plot micropore volume: 0.001792 cm³/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.412826 cm³/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.421420 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 83.7513 Å

BJH Adsorption average pore width (4V/A): 74.745 Å

BJH Desorption average pore width (4V/A): 63.709 Å

Freundlich

Qm·C: 5.5407 ± 0.5153 cm³/g STP

m: 1.8375 ± 0.1296

Temkin

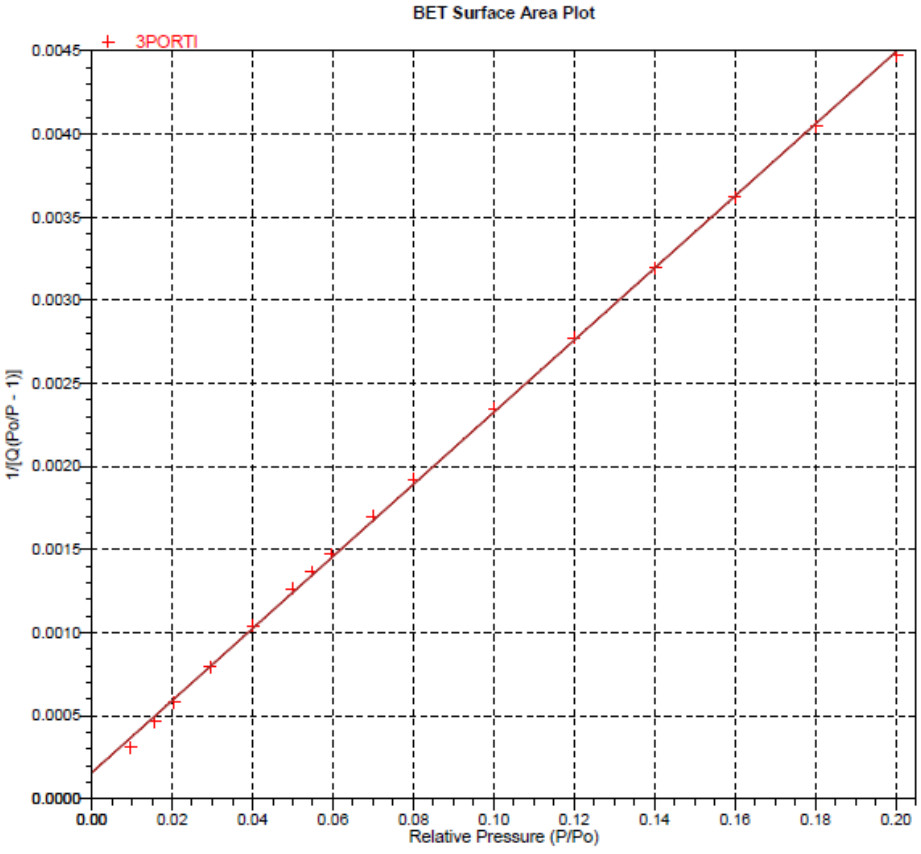
q·alpha/Qm: 0.010634 ± 0.001132 kJ/mol·(cm³/g STP)

A: 0.0458 ± 0.0311 mmHg

BET Surface Area Report

BET Surface Area: 199.2839 ± 1.0643 m²/g
Slope: 0.021688 ± 0.000116 g/cm³ STP
Y-Intercept: 0.000156 ± 0.000012 g/cm³ STP
C: 139.889767
Qm: 45.7787 cm³/g STP
Correlation Coefficient: 0.9997996
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.009760075	31.9705	0.000308
0.015750683	34.5900	0.000463
0.020465298	36.0562	0.000579
0.029480266	38.2287	0.000795
0.040097118	40.1986	0.001039
0.049958053	41.6878	0.001261
0.054740960	42.3514	0.001367
0.059538748	42.9717	0.001473
0.069862587	44.2213	0.001699
0.080155705	45.3424	0.001922
0.100046957	47.3666	0.002347
0.119998995	49.2180	0.002771
0.140090729	50.9875	0.003195
0.160037764	52.6723	0.003617
0.180183680	54.3369	0.004045
0.200199284	55.9960	0.004470



6. References

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