Supporting Information

Synthesis and Fluorescence Spectroscopy of Tris(pyrenyl) Pnictogen Compounds

Kira Behm, Jeremy B. Essner, Charles L. Barnes, Gary A. Baker, and Justin R. Walensky

Department of Chemistry, University of Missouri, Columbia, MO 65211

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Table S1. Calculated solution concentrations and excitation/emission wavelengths monitored.

Compound	Concentration (μM)	Excitation Wavelengths (nm)	Emission Wavelengths (nm)
Py	12.5	325, 333	373, 379, 384, 393, 410
$P(Py)_3$	10.5	325, 333, 350, 375	381, 400, 422, 450, 500
$OP(Py)_3$	11.2	Same as above	Same as above
$SP(Py)_3$	10.2	325, 333, 350	381, 400, 434, 450, 500
$As(Py)_3$	11.0	325, 333, 350, 375	380, 399, 422, 450, 500
$OAs(Py)_3$	11.0	Same as above	379, 399, 419, 487, 525
$Sb(Py)_3$	10.9	325, 333, 350	385, 406, 434, 450
$Bi(Py)_3$	10.9	325, 333, 350, 375, 400	385, 406, 430, 450, 500

Table S2. Extinction coefficients at the indicated wavelengths.

Compound	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	ε ($M^{-1}cm^{-1}$)
Py	320	22948	335	38949
$P(Py)_3$	348	57684	364	67767
$OP(Py)_3$	347	74806	363	101857
$SP(Py)_3$	353	64560	367	71591
$As(Py)_3$	344	57214	361	73108
$OAs(Py)_3$	344	45495	360	64822
$Sb(Py)_3$	342	77078	360	117110
$Bi(Py)_3$	338	84570	356	132628

Table S3. Reference fluorophore used to determine quantum yield (Φ) values.

Fluorophore	Excitation Wavelength (nm)	Solvent	*n* [a]	Φ (%)	Ref.
Quinine sulfate	350	0.1 M H_2SO_4	1.343	57.7	[1]

[a] refractive index.

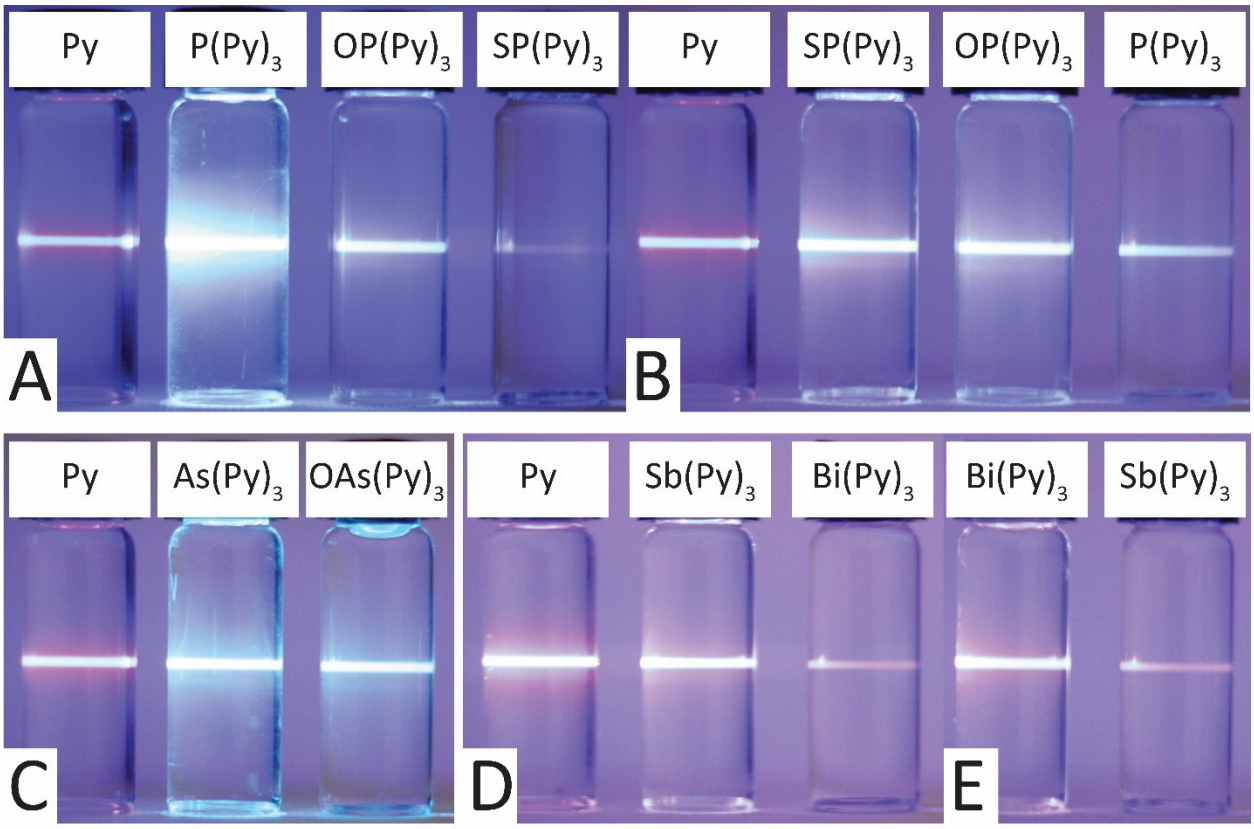


Figure S1. (A–E) Images of pyrene (Py; 12.5 μM) and the indicated compounds (~11 μM) showing their fluorescence emission under UV excitation (325 nm) using a He-Cd laser (illumination occurs from the left side). Panels A and B are of the same three compounds with the 2nd and 4th vials reversed to better show the fluorescence of $SP(Py)_3$. The same is the case for panels D and E to better illustrate the fluorescence of $Sb(Py)_3$.

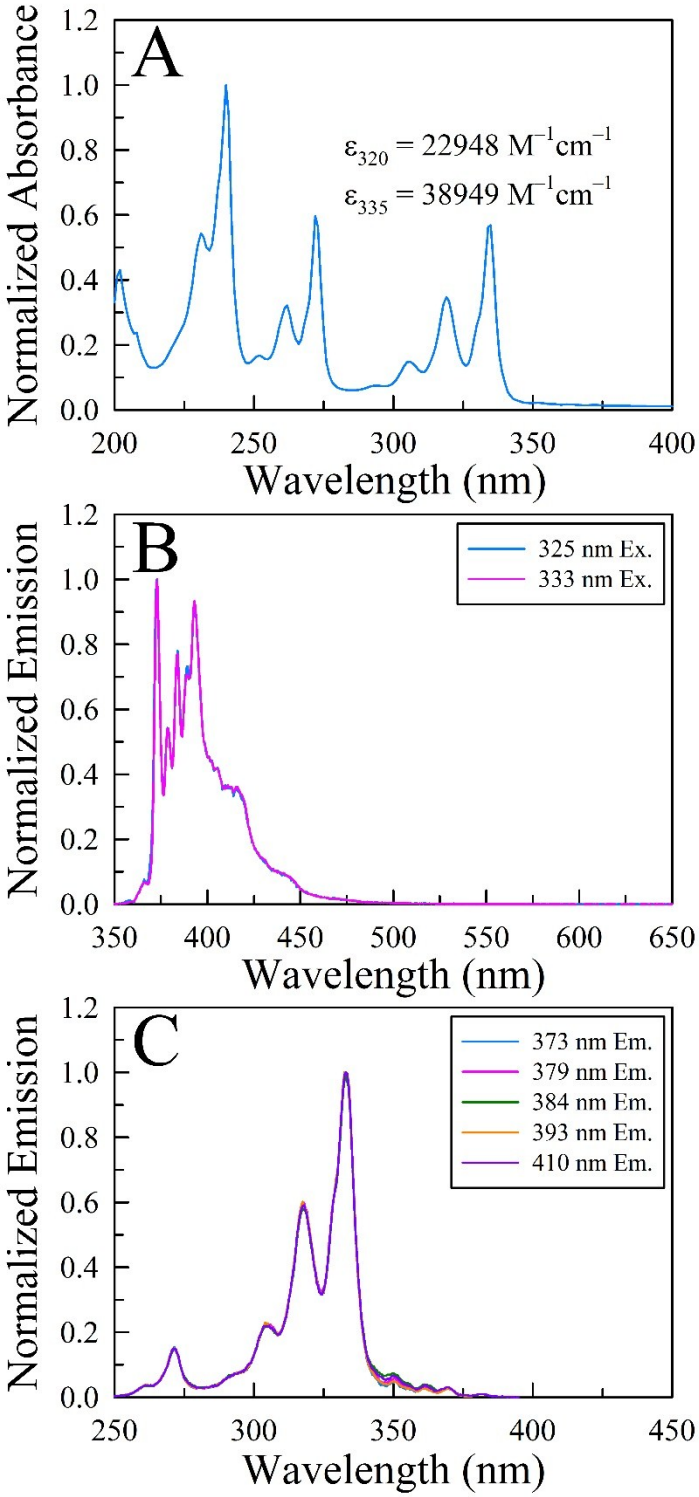


Figure S2. Normalized (A) absorbance and steady-state (B) emission and (C) excitation spectra of pyrene (12.5 μM) dissolved in methanol, monitored at the wavelengths indicated within the legends of (B) and (C). The emission and excitation spectra were normalized to the highest energy emission peak.

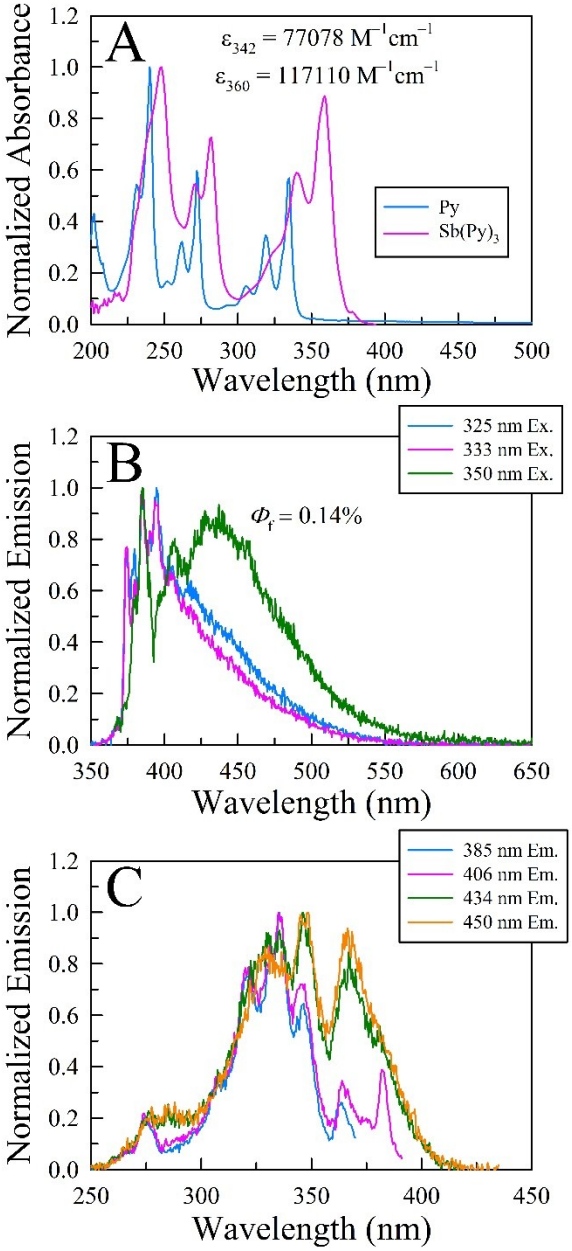


Figure S3. Normalized (A) absorbance and steady-state (B) emission and (C) excitation spectra of $Sb(Py)_3$ (10.9 μM) dissolved in DCM. The absorbance of free pyrene (12.5 μM in MeOH) is also provided in panel A as a benchmark. The emission and excitation spectra were monitored at the wavelengths indicated within the legends of (B) and (C), normalizing to the highest energy emission peak. The quantum yield, calculated at 350 nm excitation, was found to be 0.14%.

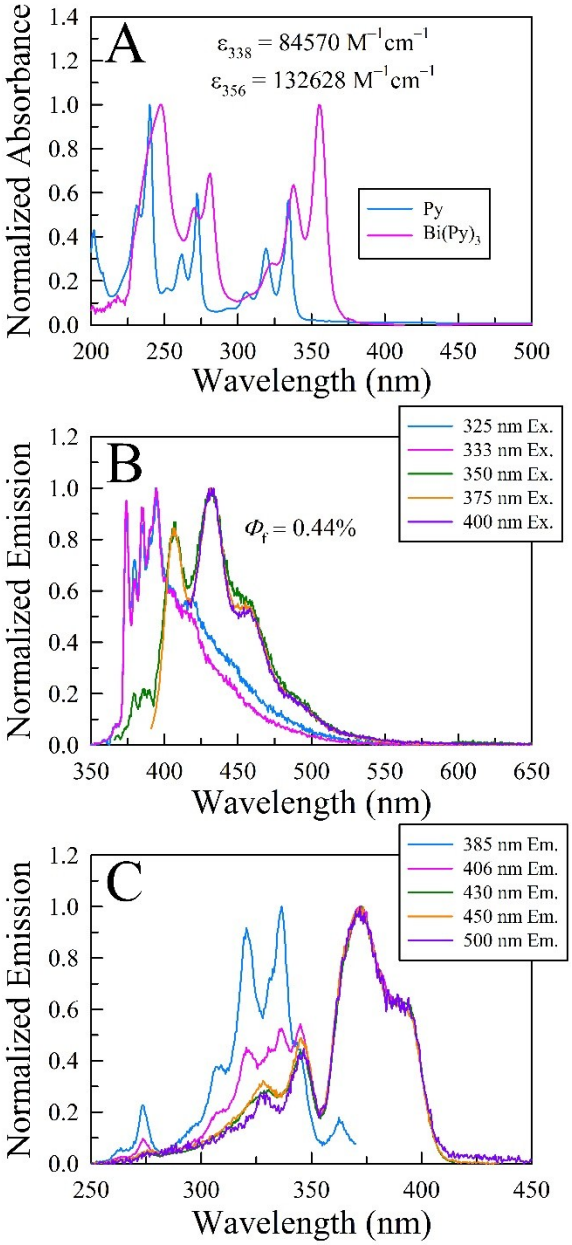


Figure S4. Normalized (A) absorbance and steady-state (B) emission and (C) excitation spectra of $Bi(Py)_3$ (10.9 µM) dissolved in DCM. The absorbance of free pyrene (12.5 µM in MeOH) is also provided in panel A as a benchmark. The emission and excitation spectra were monitored at the wavelengths indicated within the legends of (B) and (C), normalizing to the highest energy emission peak. The quantum yield, calculated at 350 nm excitation, was found to be 0.44%.

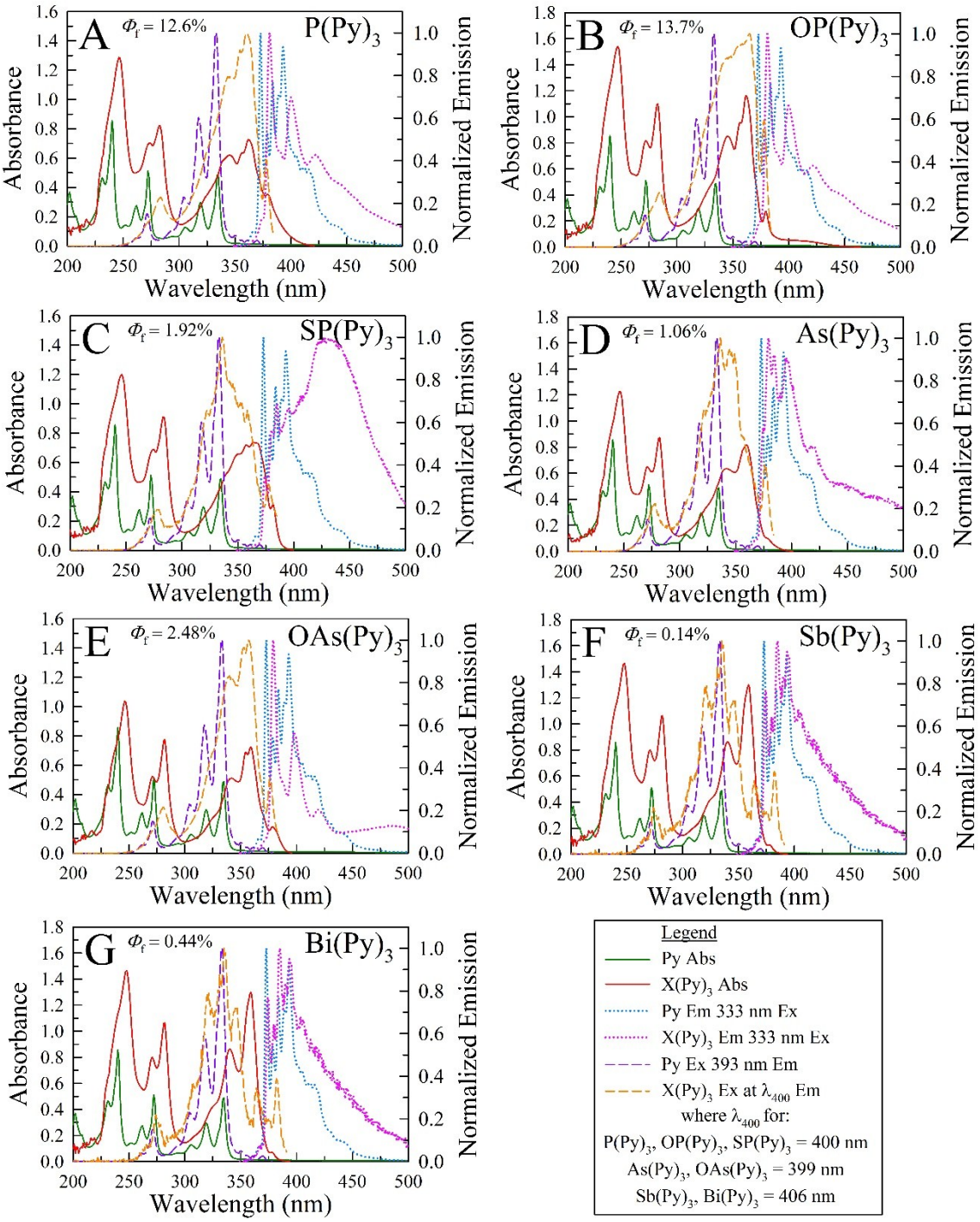
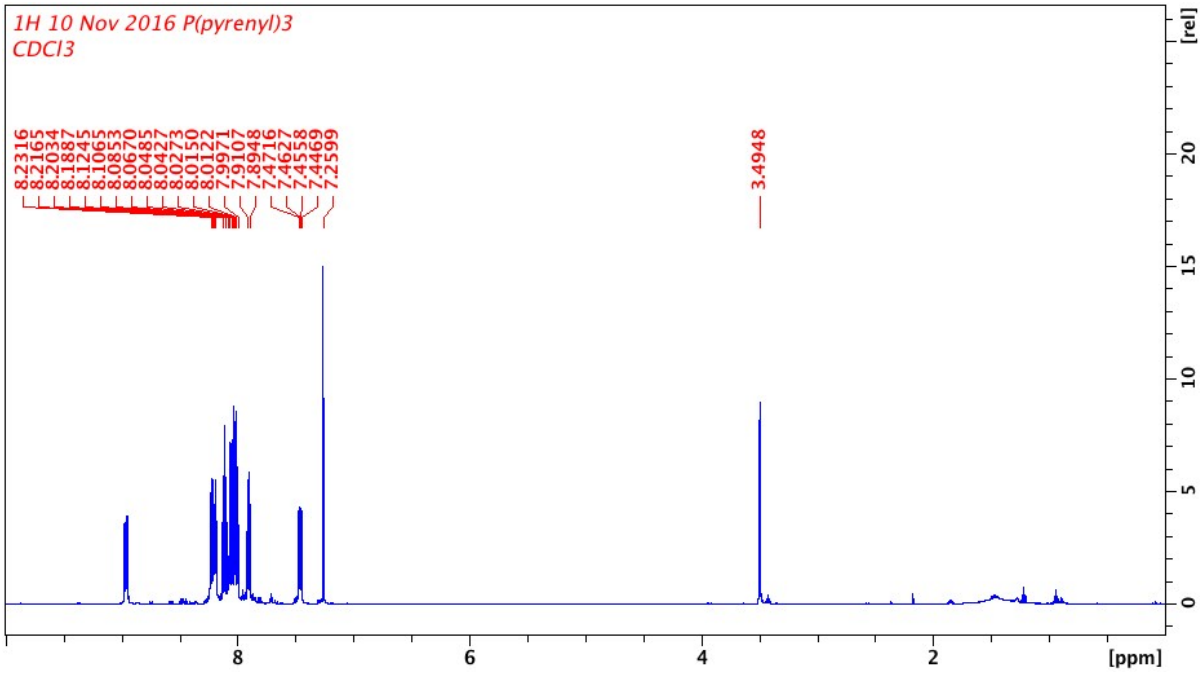


Figure S5. Absorbance (left y-axis) and normalized steady-state emission and excitation (right y-axis) spectra of (A) $P(Py)_3$, (B) $OP(Py)_3$, (C) $SP(Py)_3$, (D) $As(Py)_3$, (E) $OAs(Py)_3$, (F) $Sb(Py)_3$, and (G) $Bi(Py)_3$ compared to the spectra of pyrene. All emission spectra were monitored under 333 nm excitation while the excitation spectra were monitored at the emission band nearest to 400 nm (the exact wavelengths monitored are indicated within the legends). All fluorescence spectra were normalized to the highest energy emission peak. The quantum yields of each compound are indicated within their respective panel.

$P(C_{16}H_9)_3$, 1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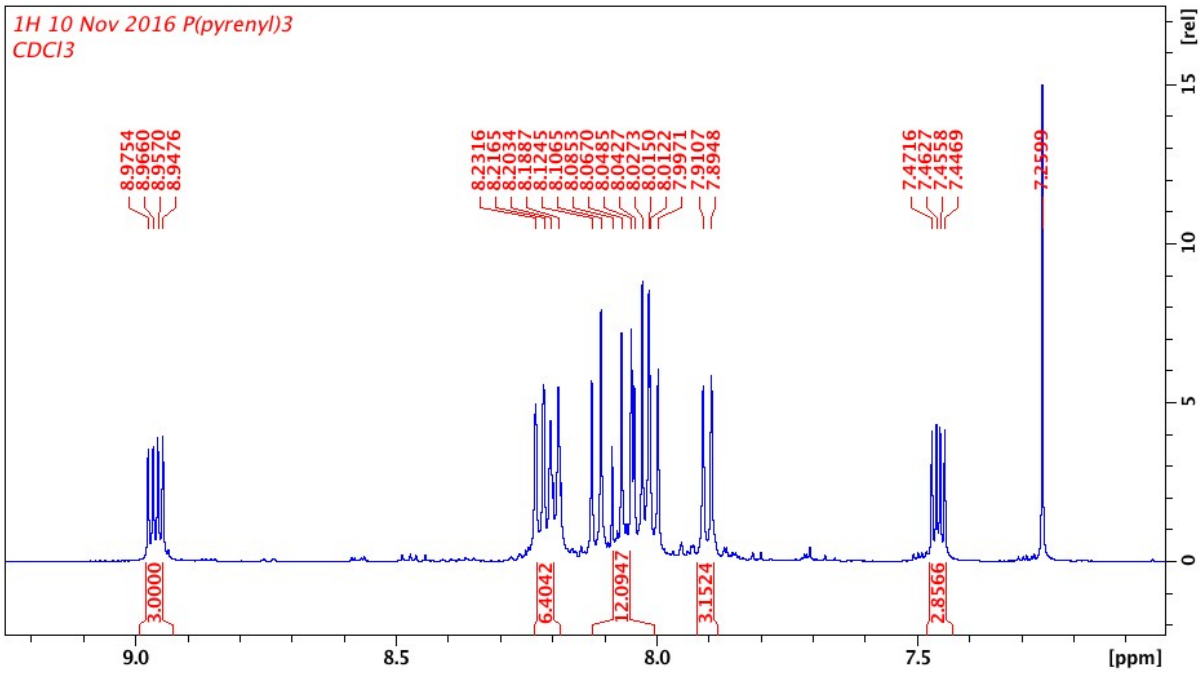
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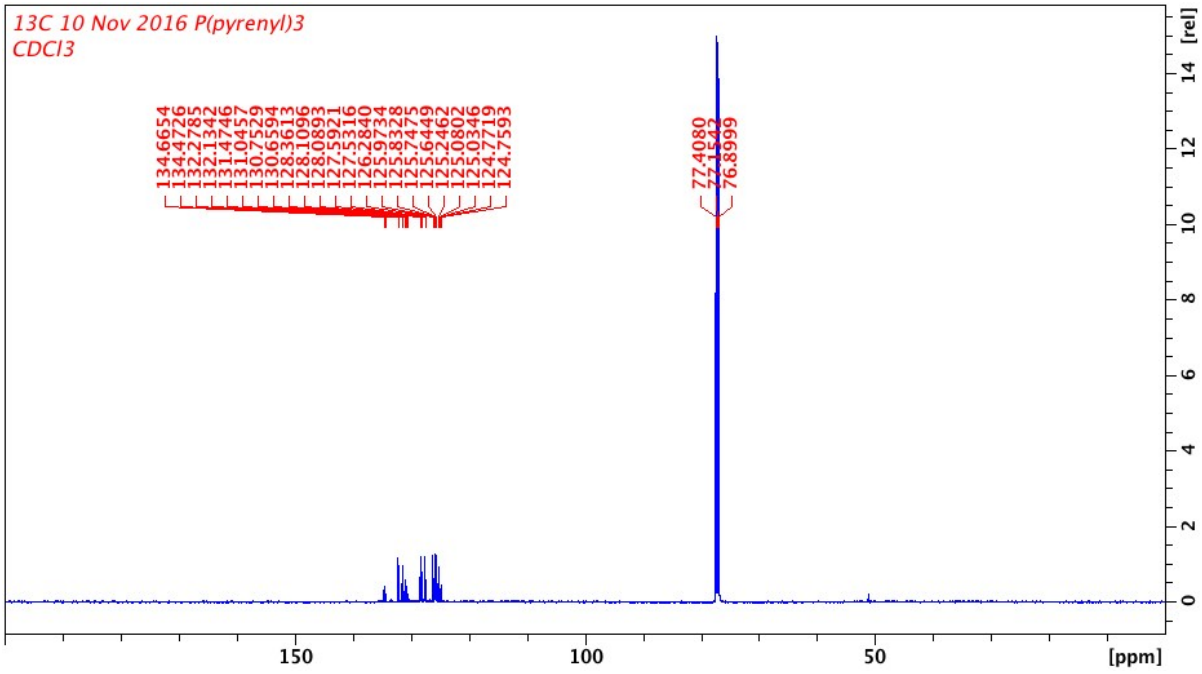
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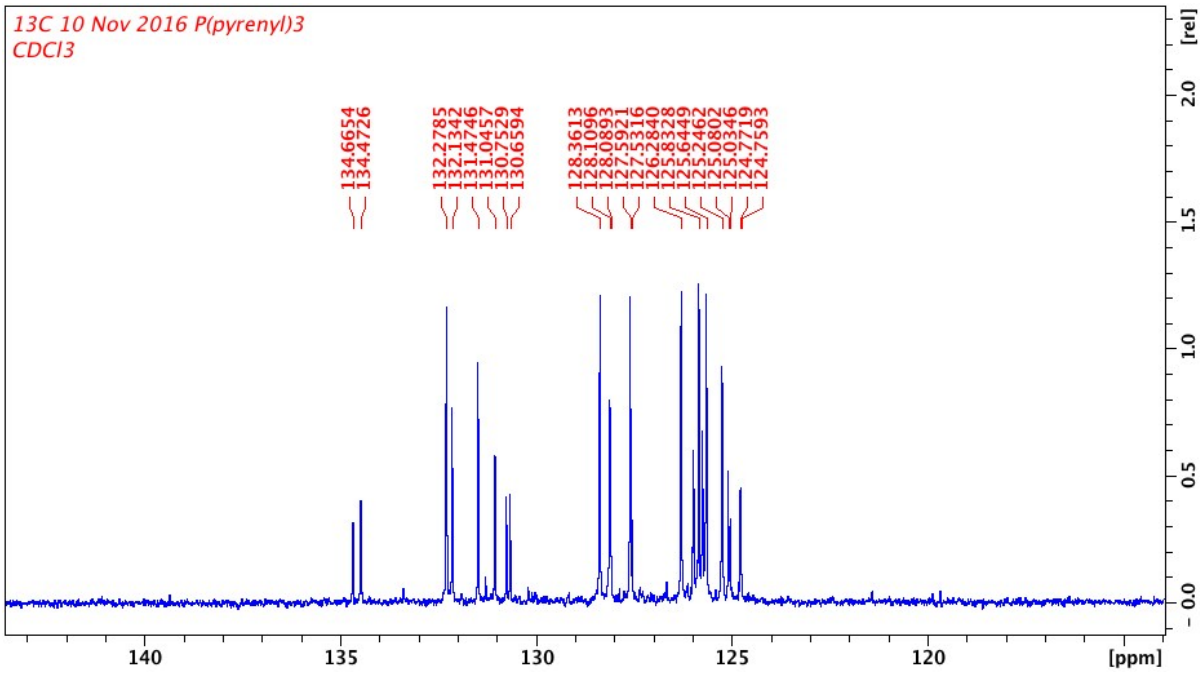
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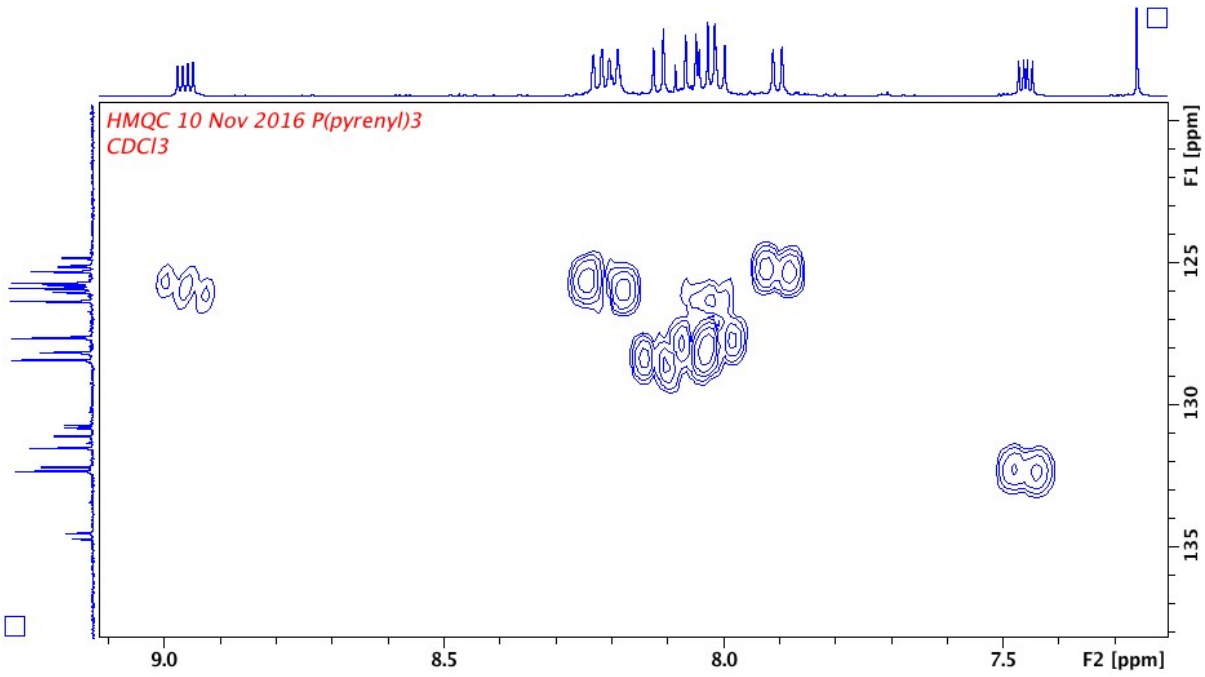
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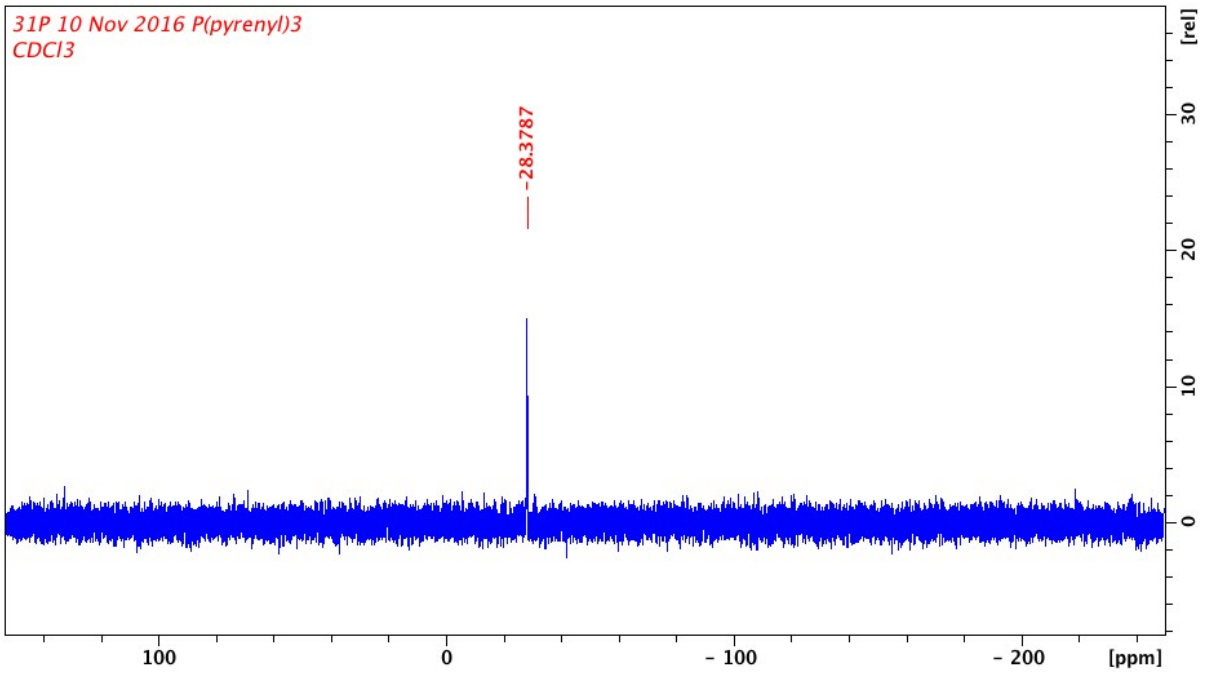
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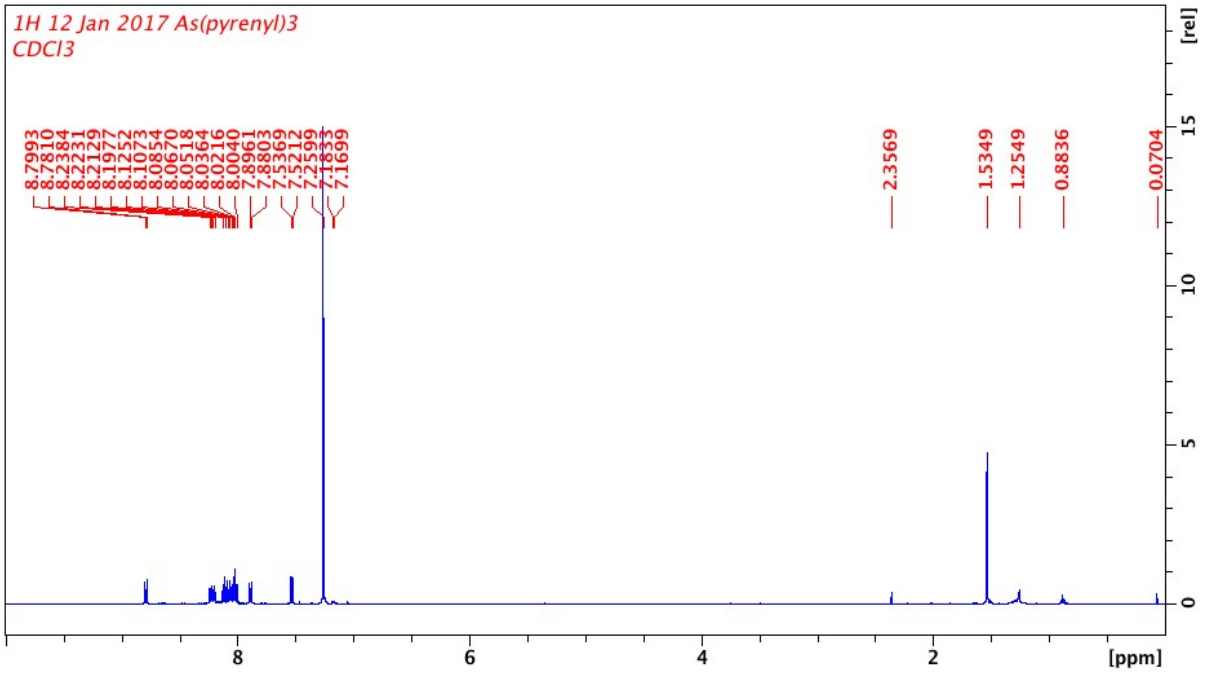
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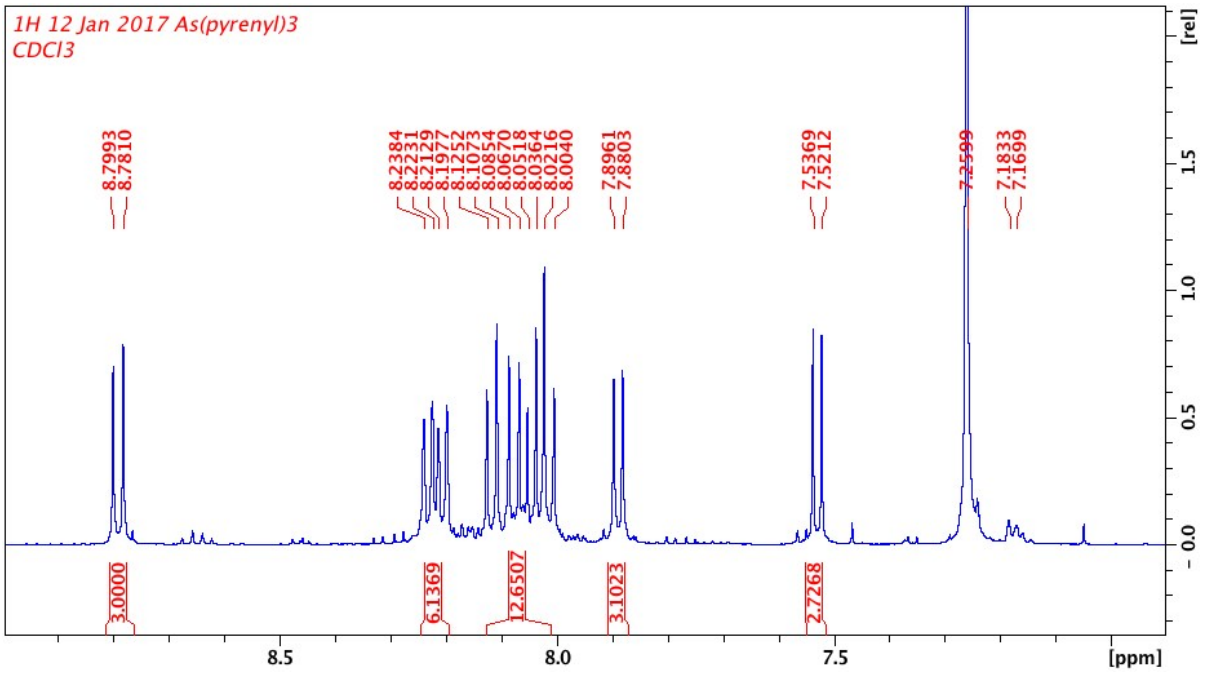
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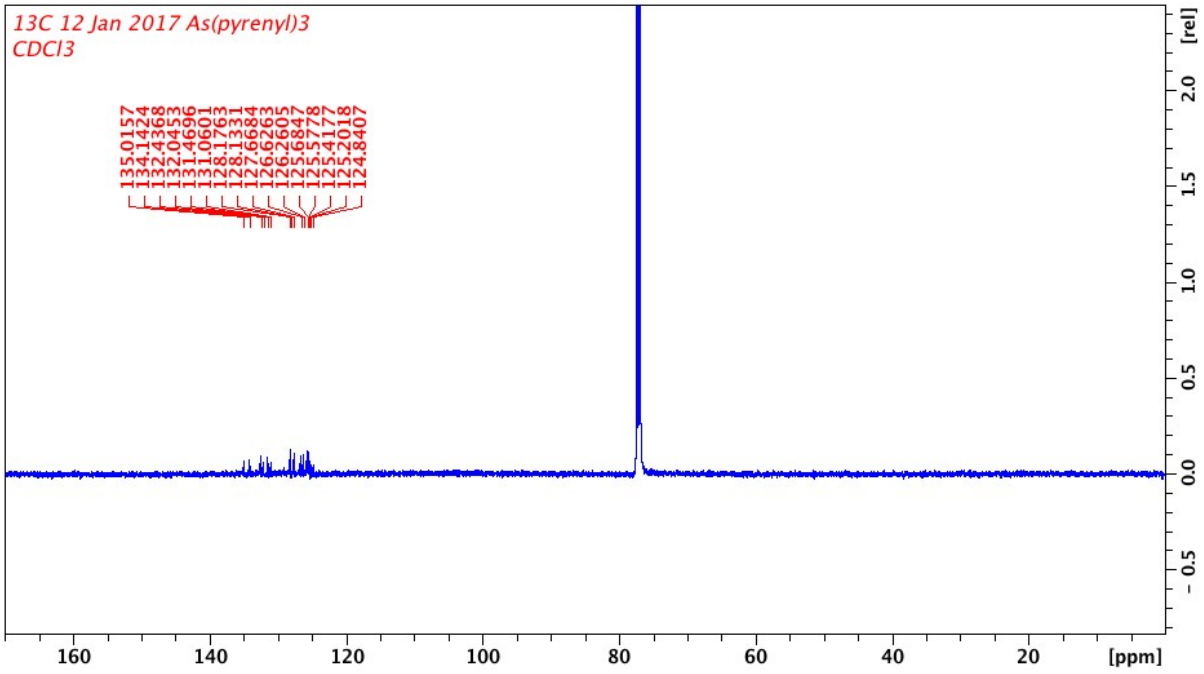
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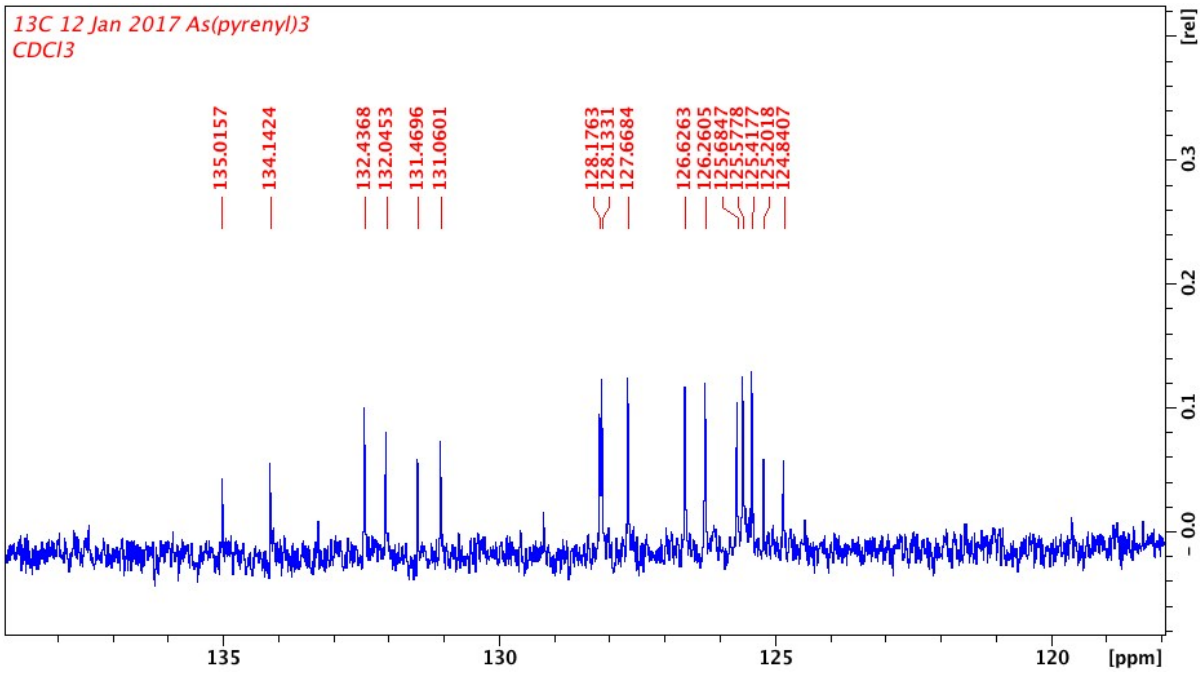
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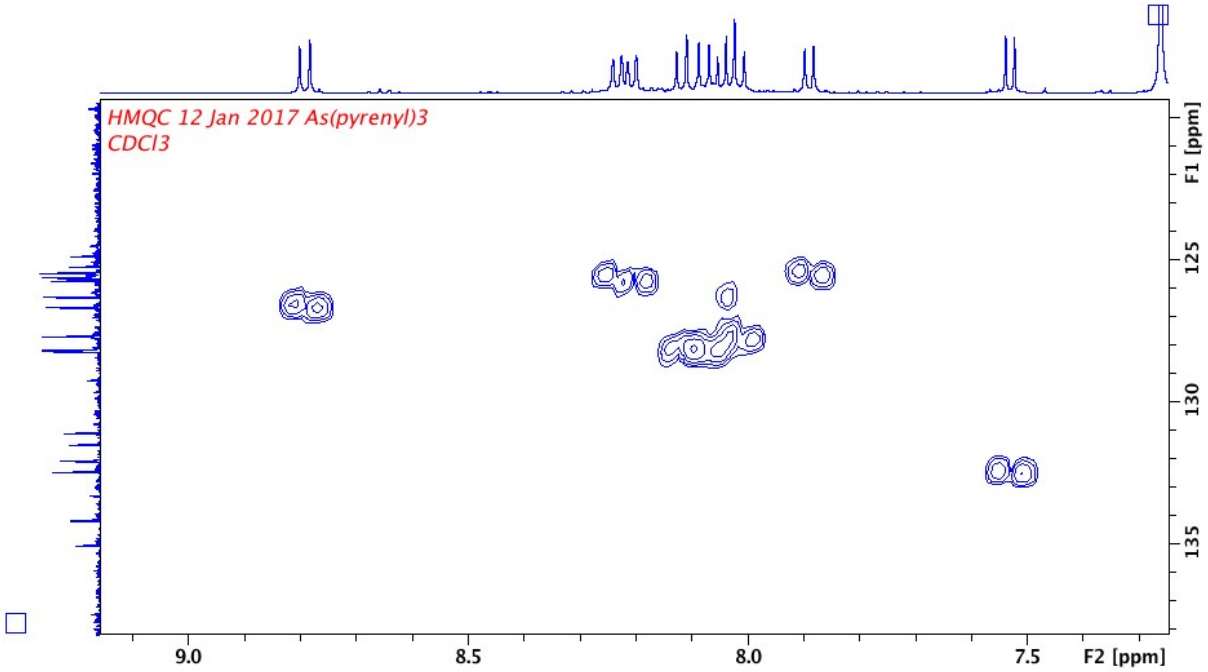
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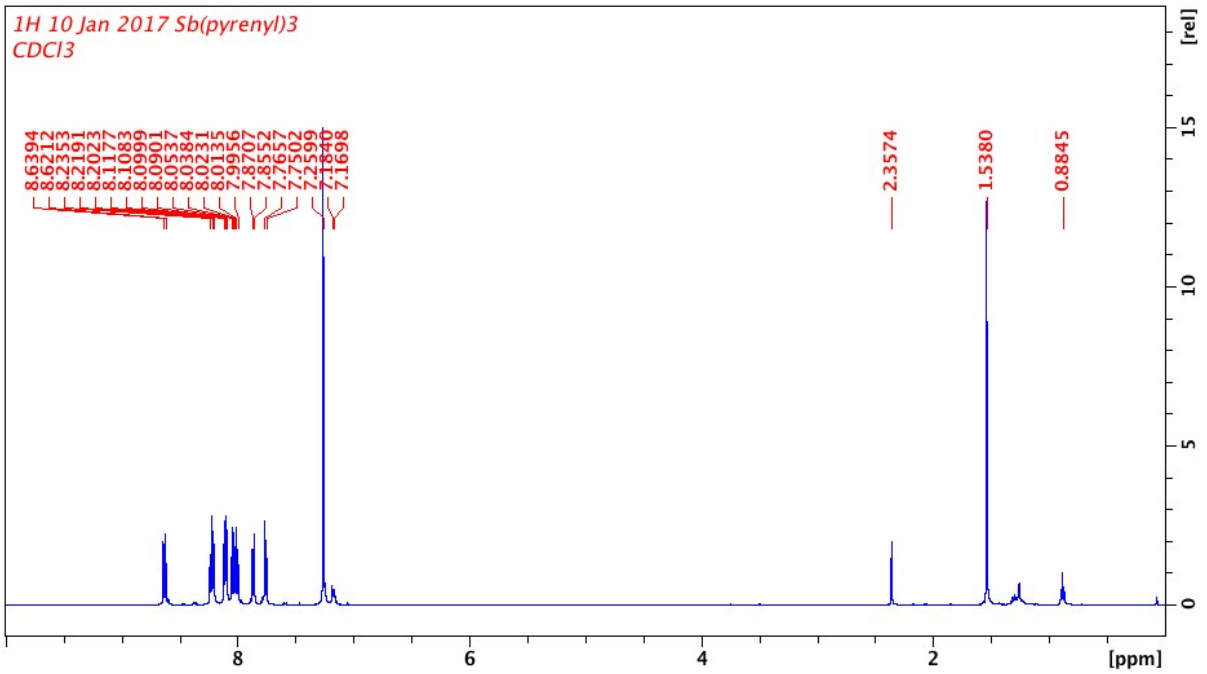
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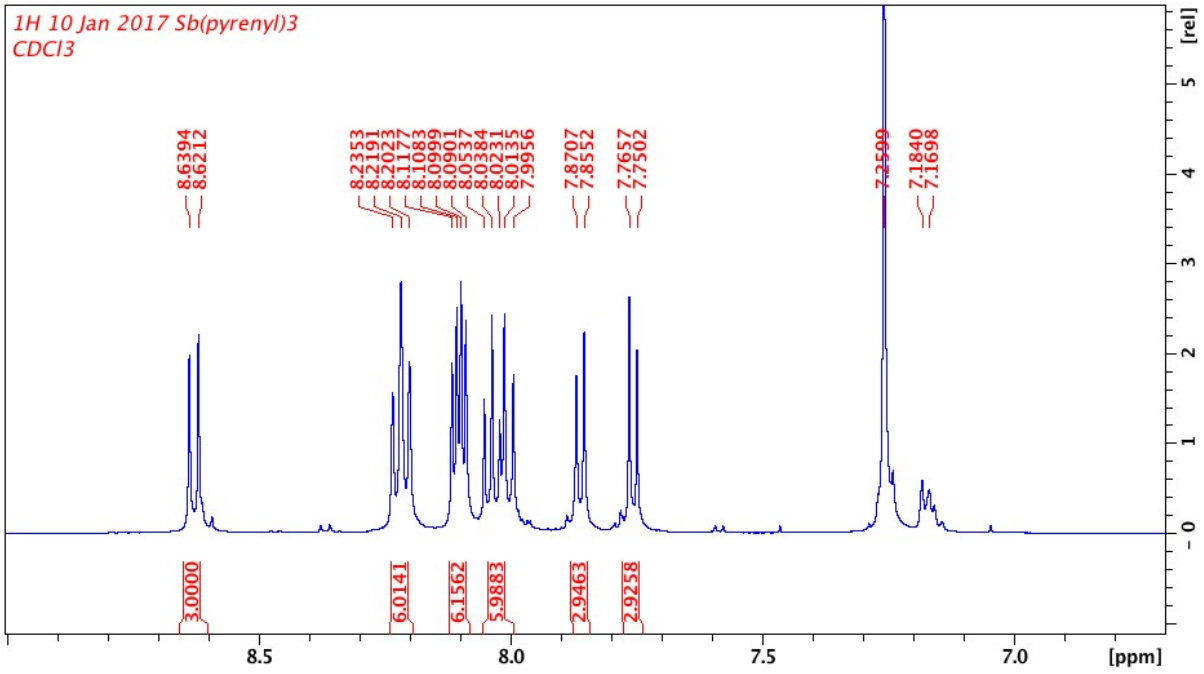
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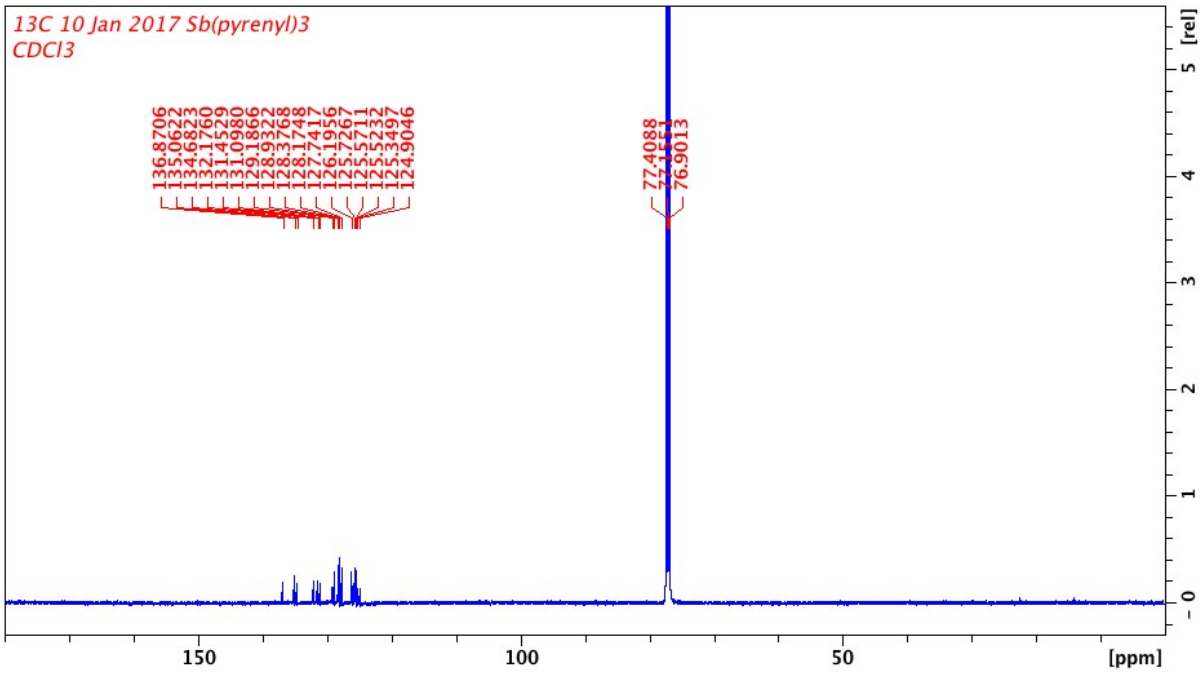
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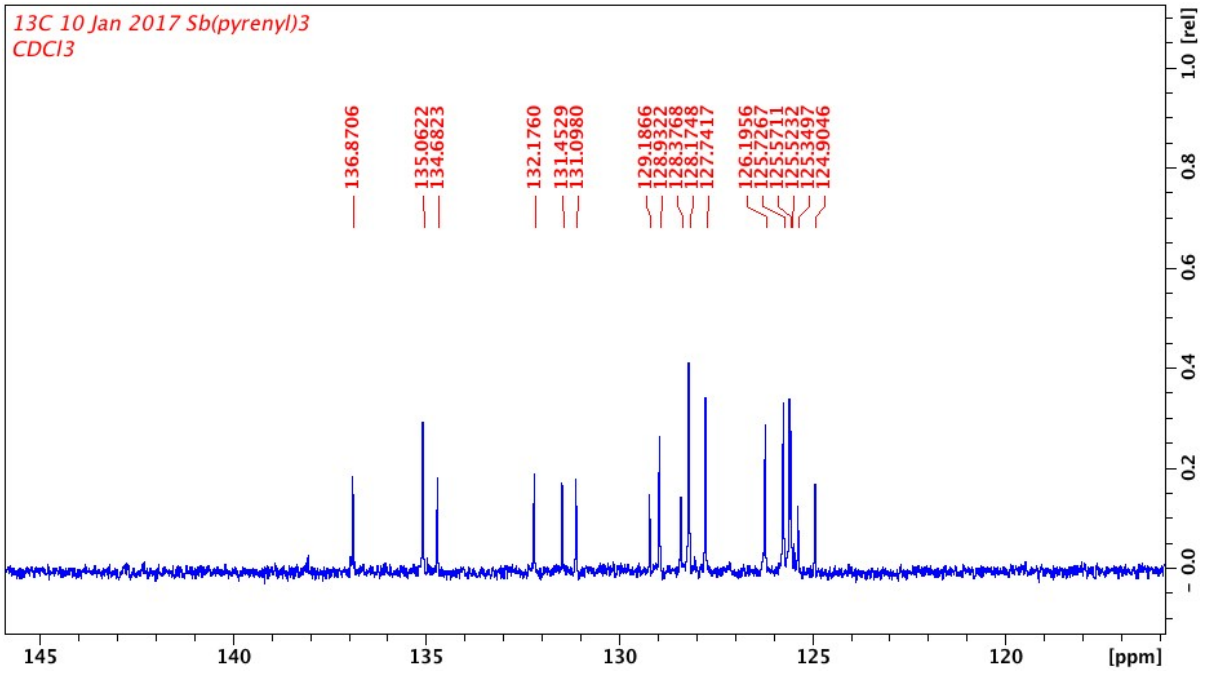
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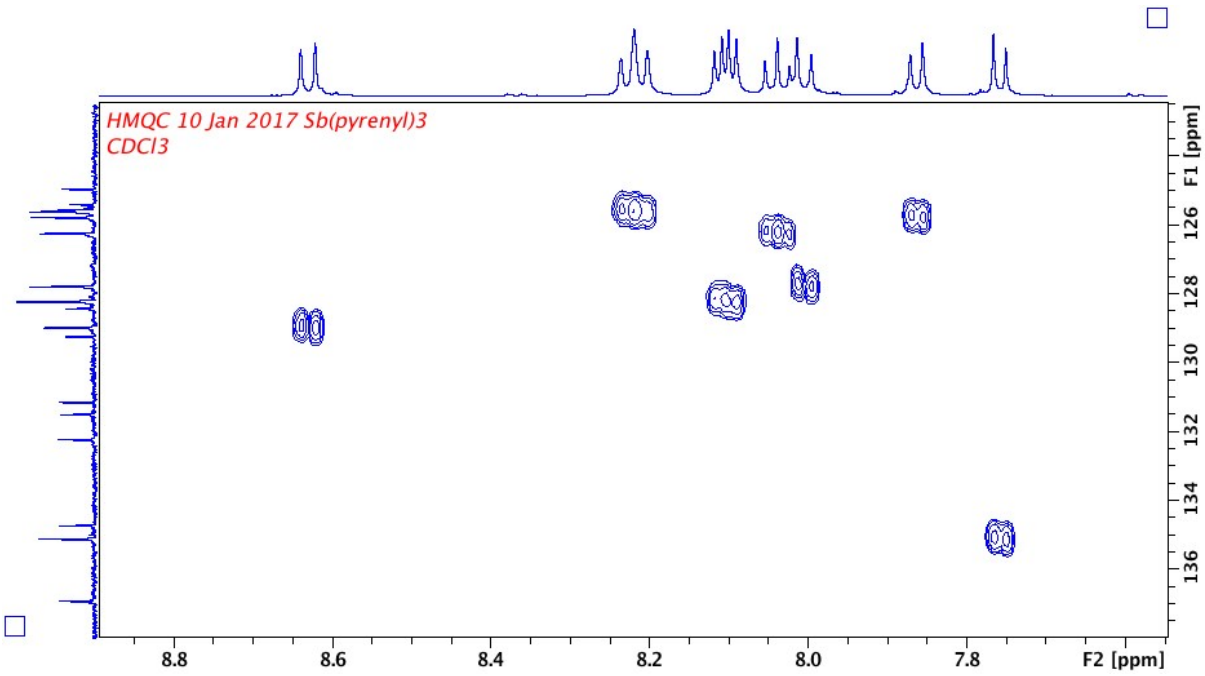
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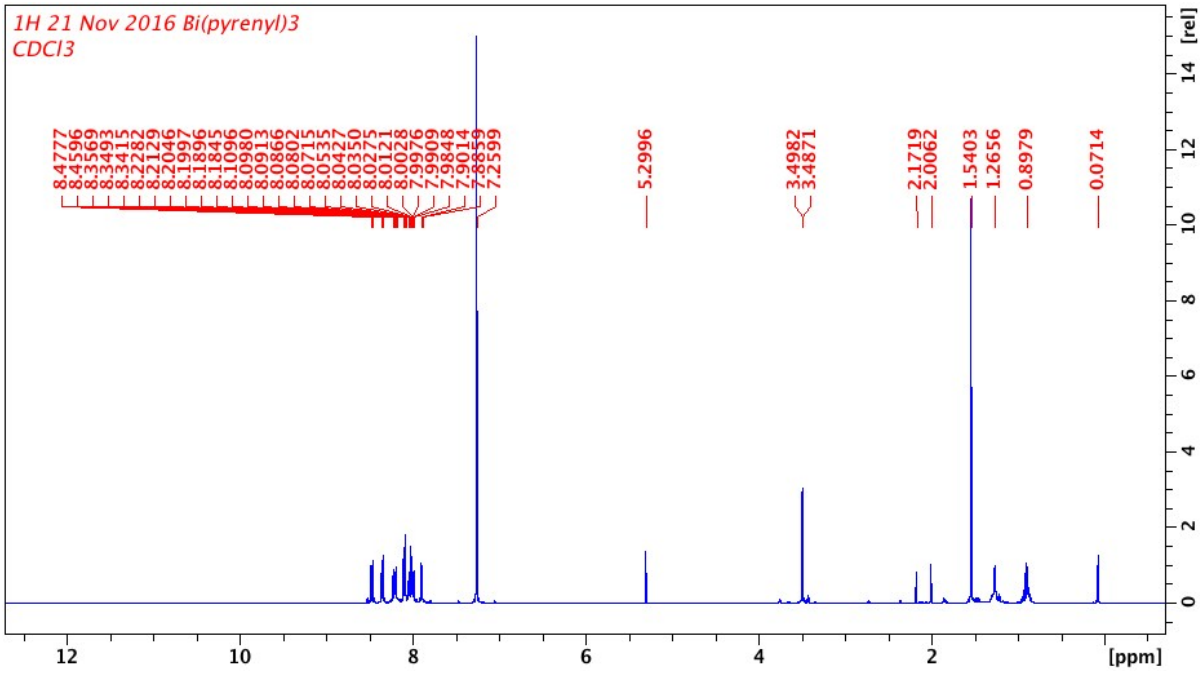
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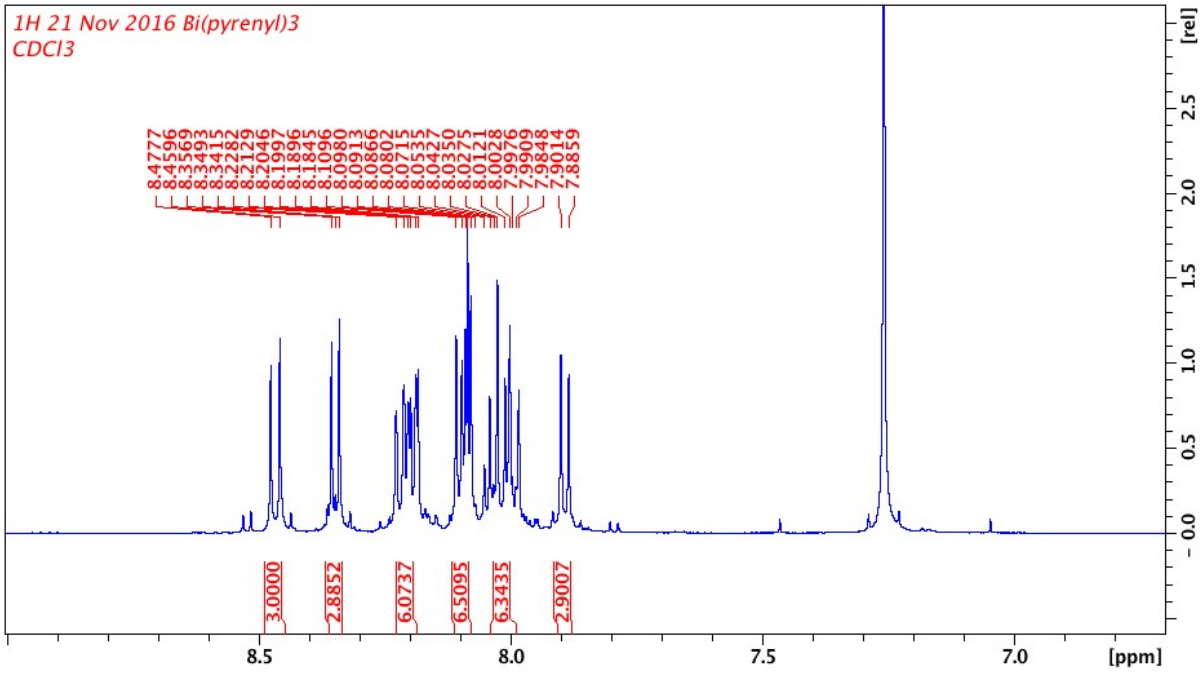
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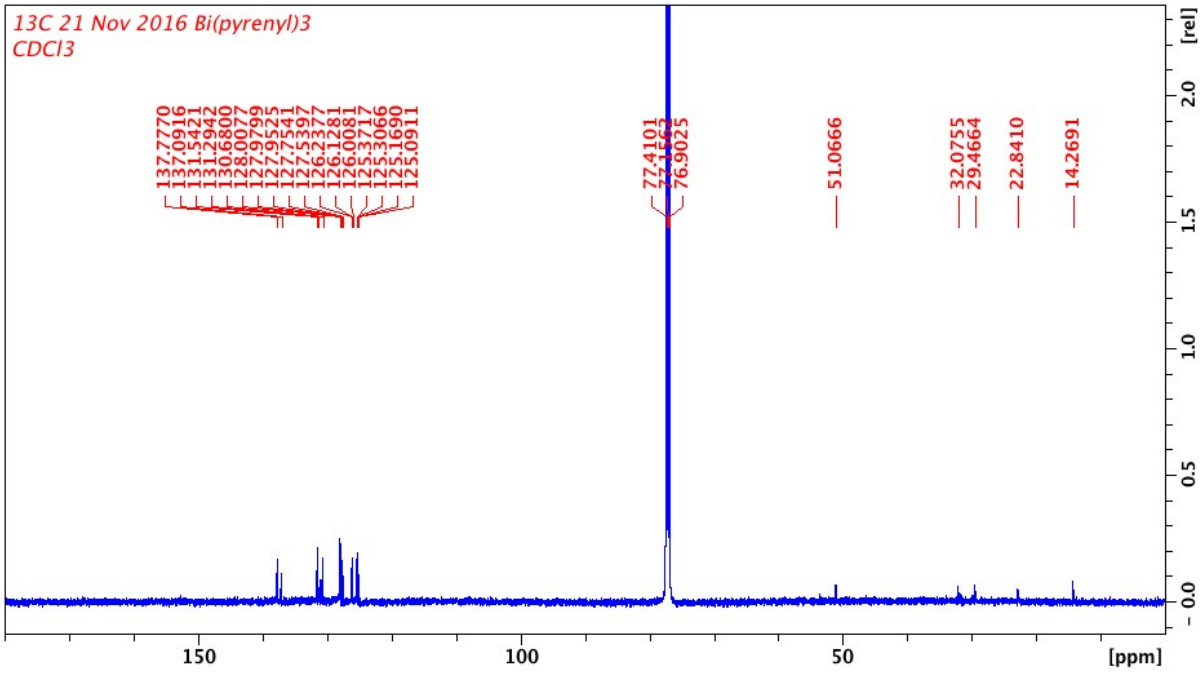
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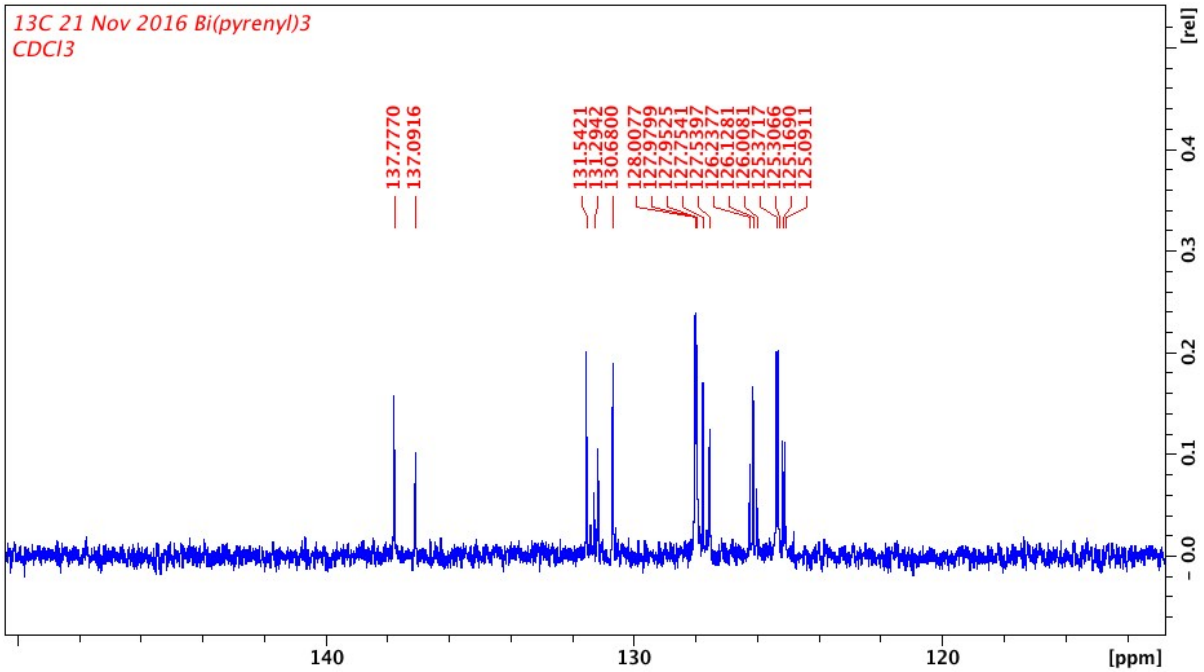
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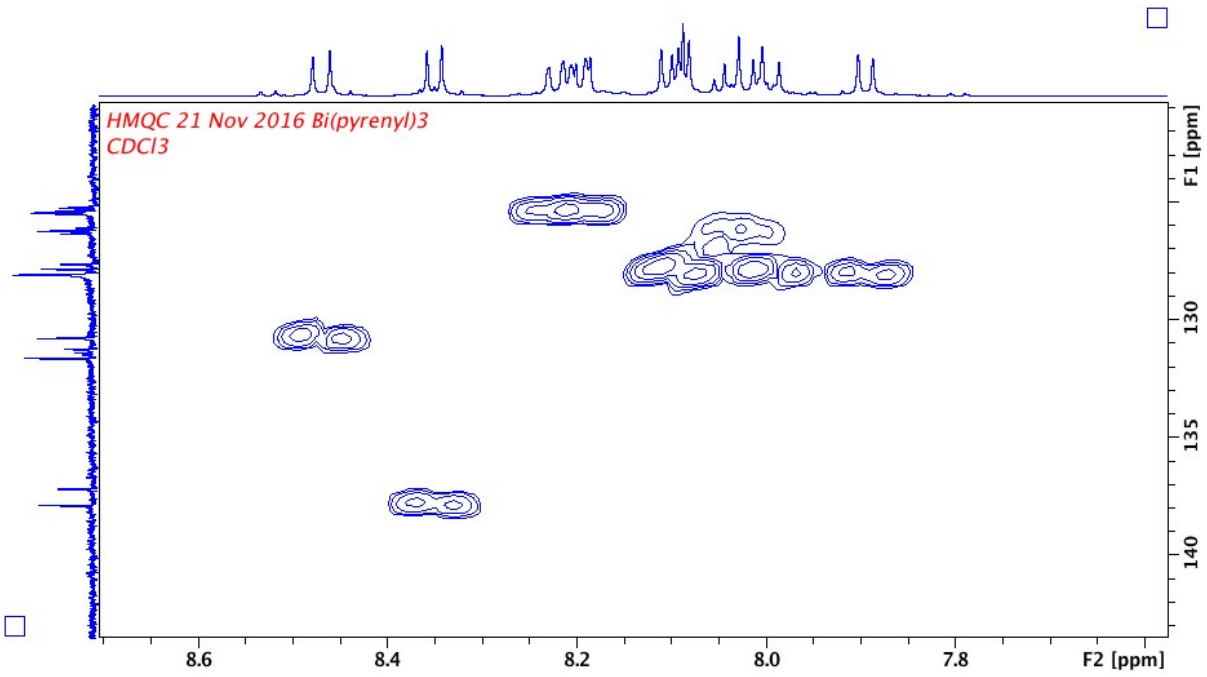
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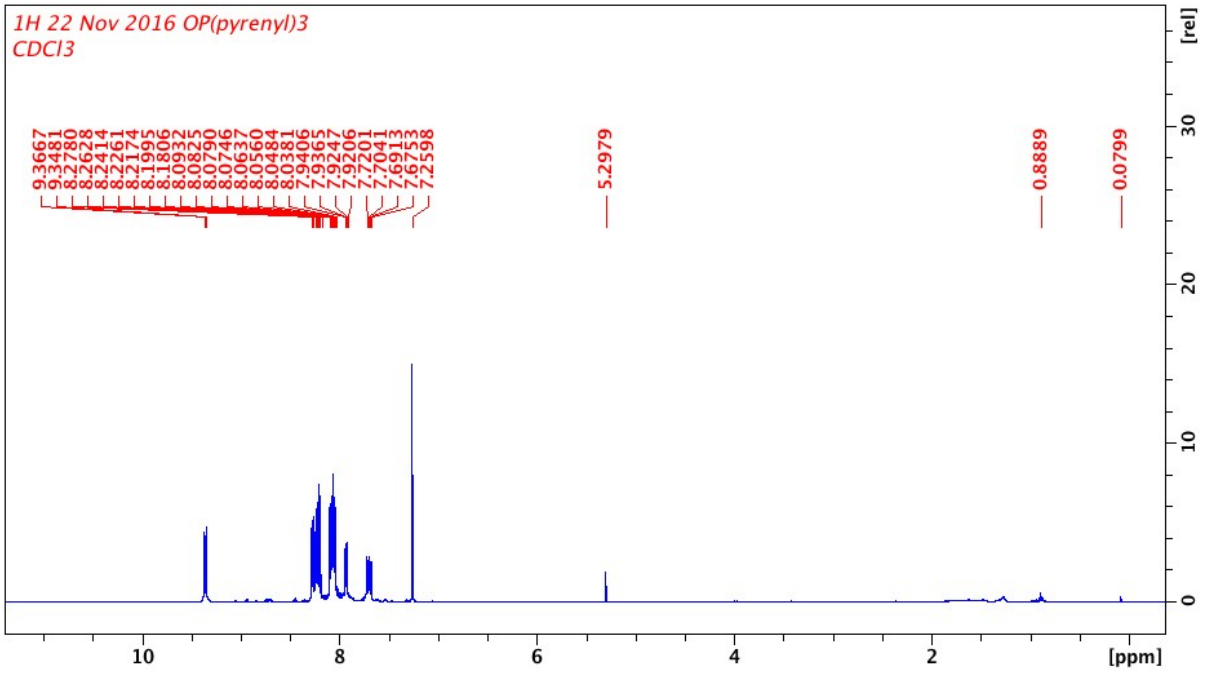
F2 [ppm]

$OP(C_{16}H_9)_3$, 5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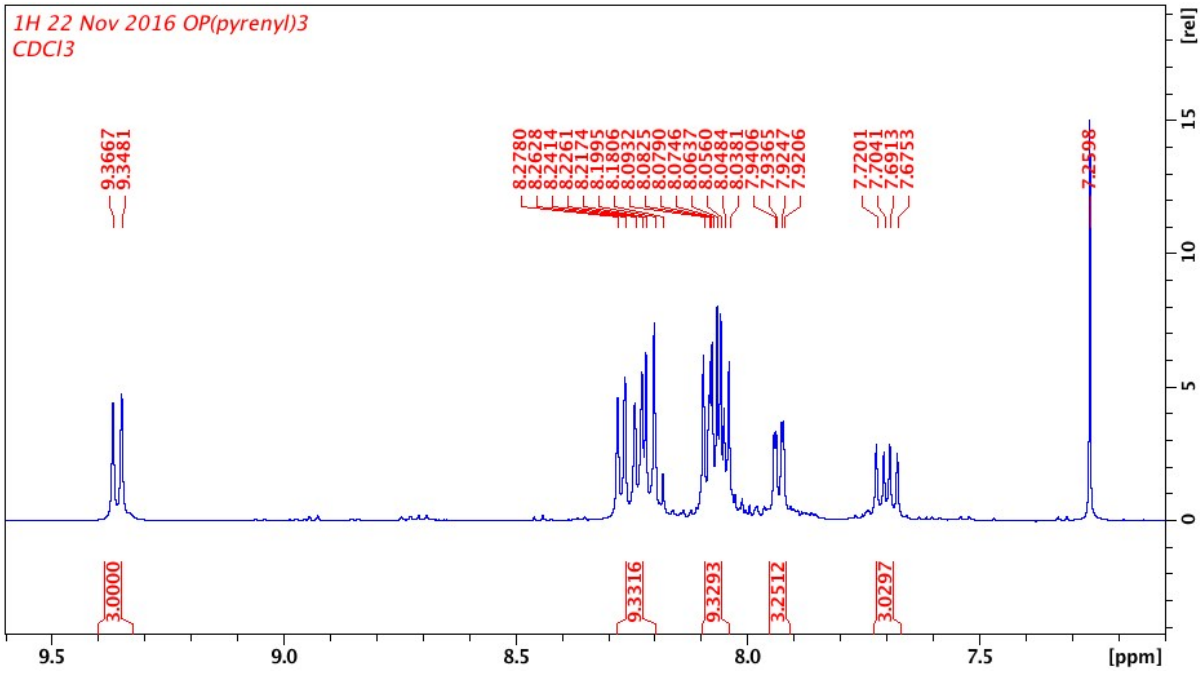
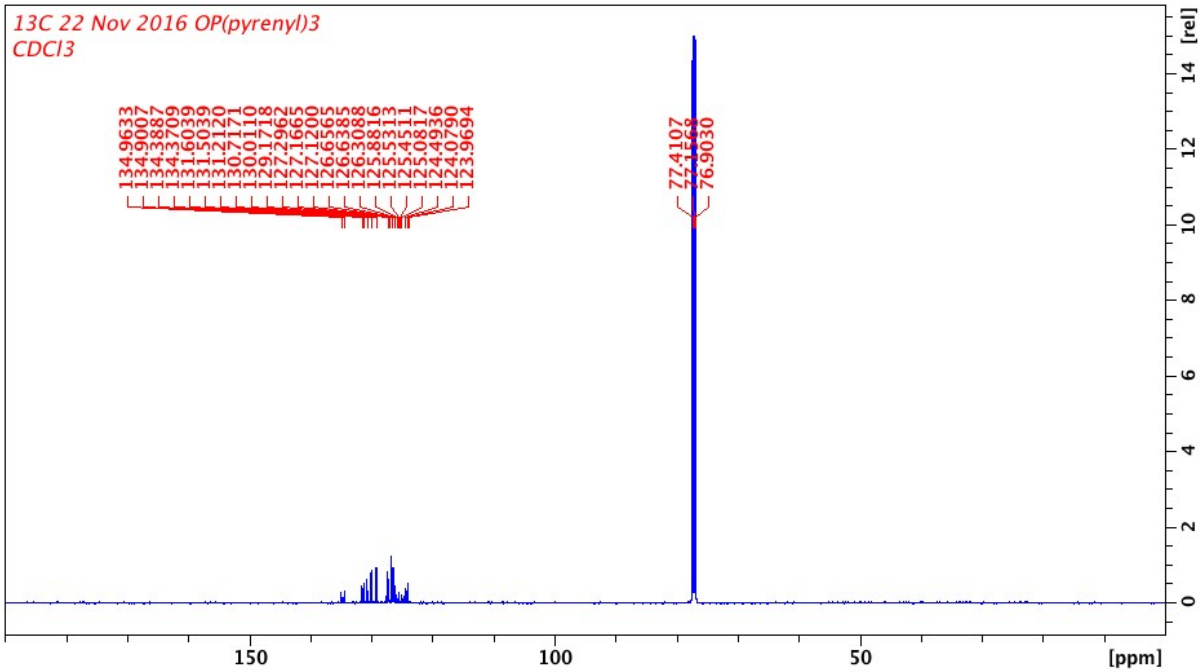
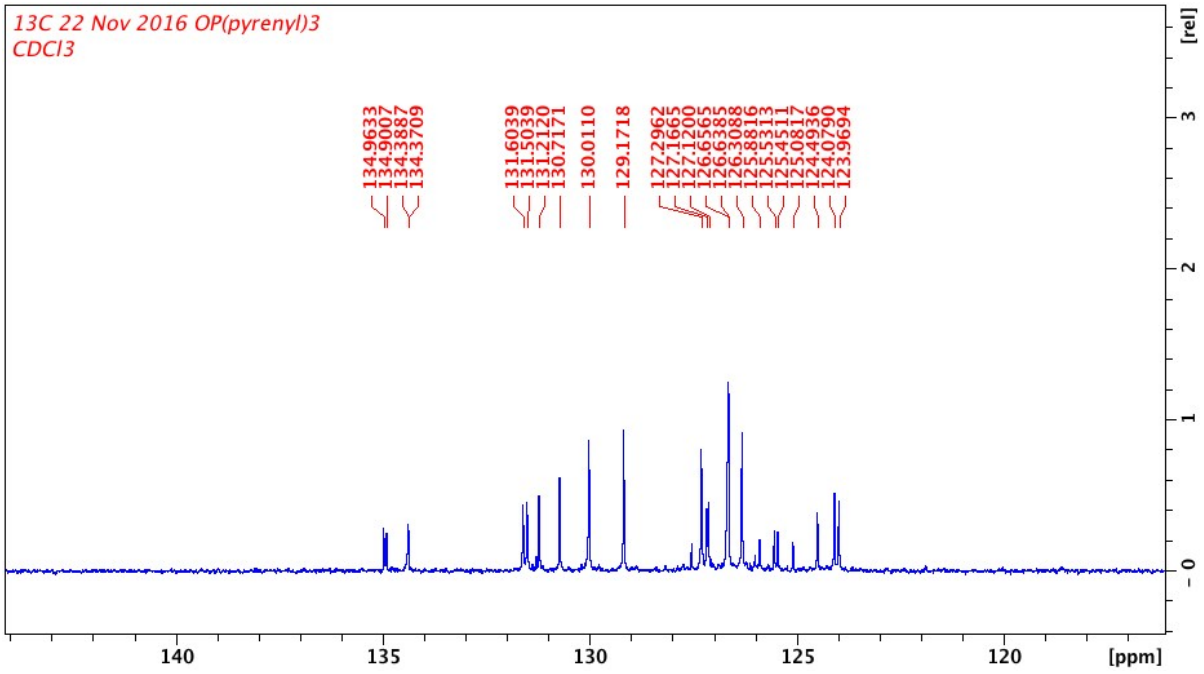
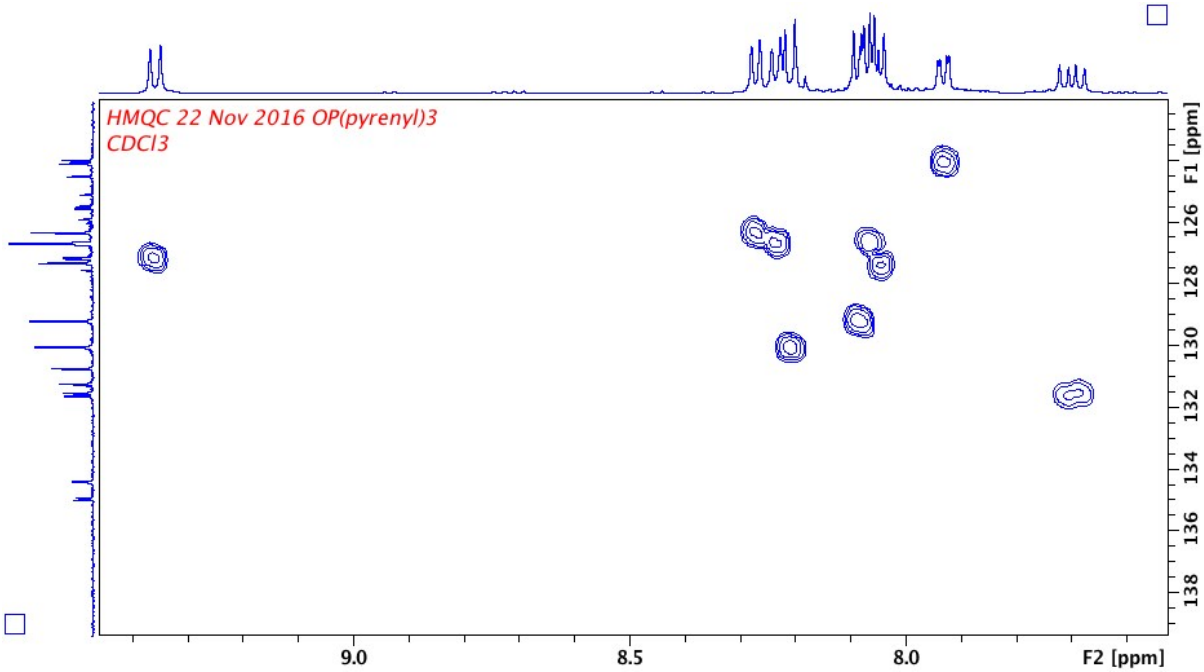
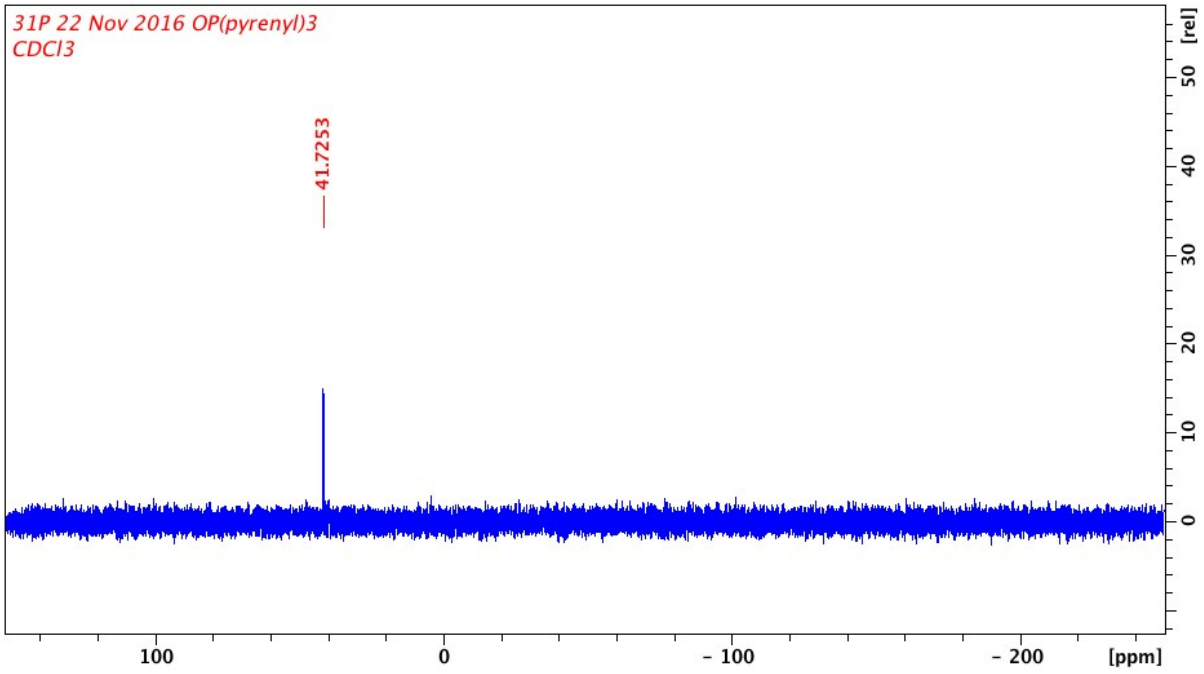
8.2174
8.1995
8.1806
8.0932
8.0825
8.0790
8.0746
8.0637
8.0560
8.0484
8.0381
7.9406
7.9365
7.9247
7.9206
7.7201
7.7041
7.6913
7.6753
7.2598
5.2979
0.8889
0.0799
[rel]
30
20
10
0
10
8
6
4
2
[ppm]


1H 22 Nov 2016 OP(pyrenyl)3
CDCl3
9.3667
9.3481
8.2780
8.2628
8.2414
8.2261
8.2174
8.1995
8.1806
8.0932
8.0825
8.0790
8.0746
8.0637
8.0560
8.0484
8.0381
7.9406
7.9365
7.9247
7.9206
7.7201
7.7041
7.6913
7.6753
7.2598
3.0000
9.3316
9.3293
3.2512
3.0297
9.5
9.0
8.5
8.0
7.5
[ppm]
[rel]

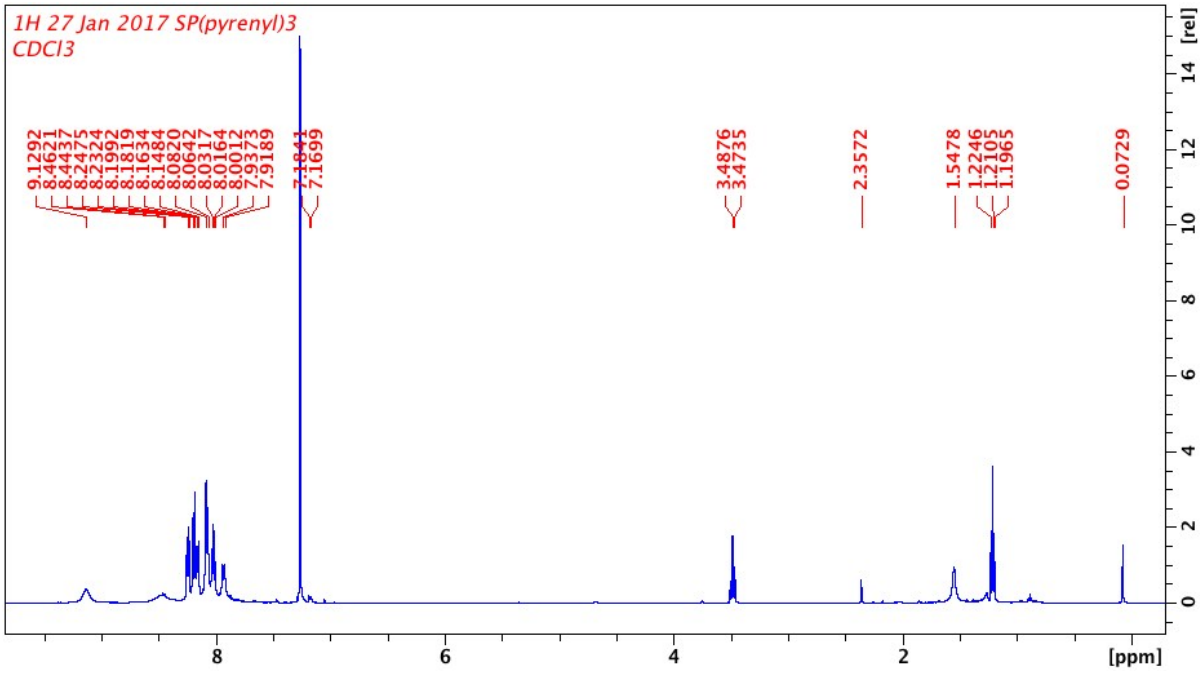

13C 22 Nov 2016 OP(pyrenyl)3
CDCl3
134.9633
134.9007
134.3887
134.3709
131.6039
131.5039
131.2120
130.7171
130.0110
129.1718
127.2962
127.1665
127.1200
126.6565
126.6385
126.3088
125.8816
125.5313
125.4511
125.0817
124.4936
124.0790
123.9694
77.4107
77.1568
76.9030
150
100
50
[ppm]
[rel]

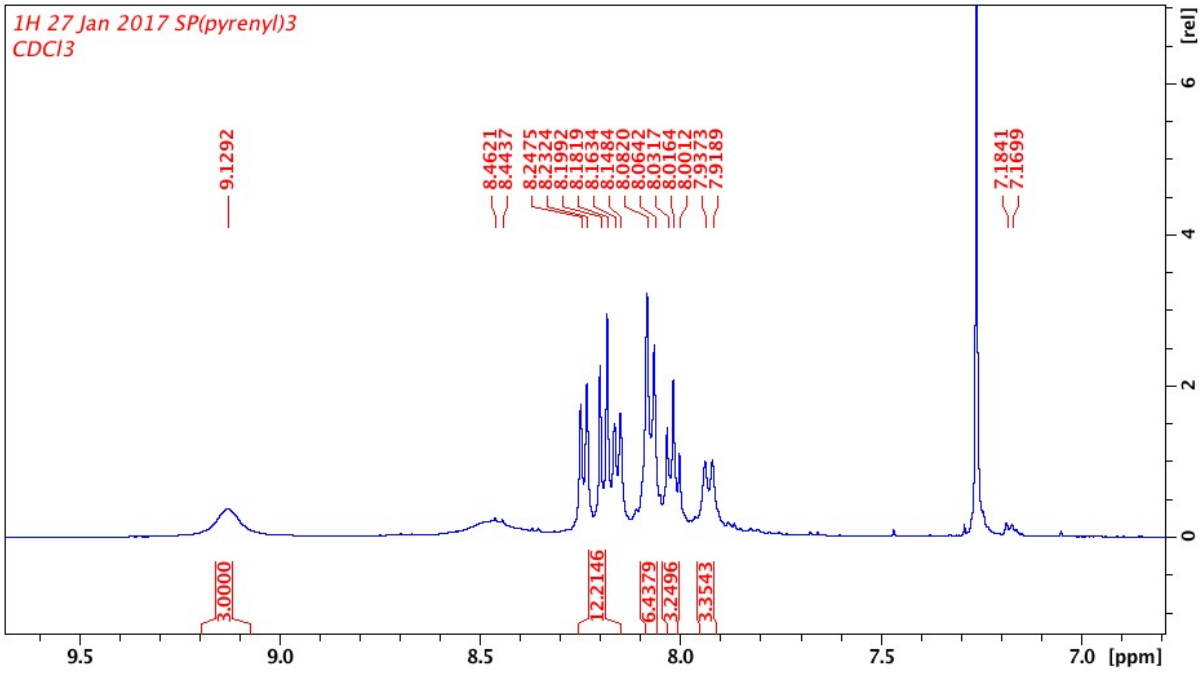

13C 22 Nov 2016 OP(pyrenyl)3
CDCl3
134.9633
134.9007
134.3887
134.3709
131.6039
131.5039
131.2120
130.7171
130.0110
129.1718
127.2962
127.1665
127.1200
126.6565
126.6385
126.3088
125.8816
125.5313
125.4511
125.0817
124.4936
124.0790
123.9694
[rel]
3
2
1
0
140
135
130
125
120
[ppm]

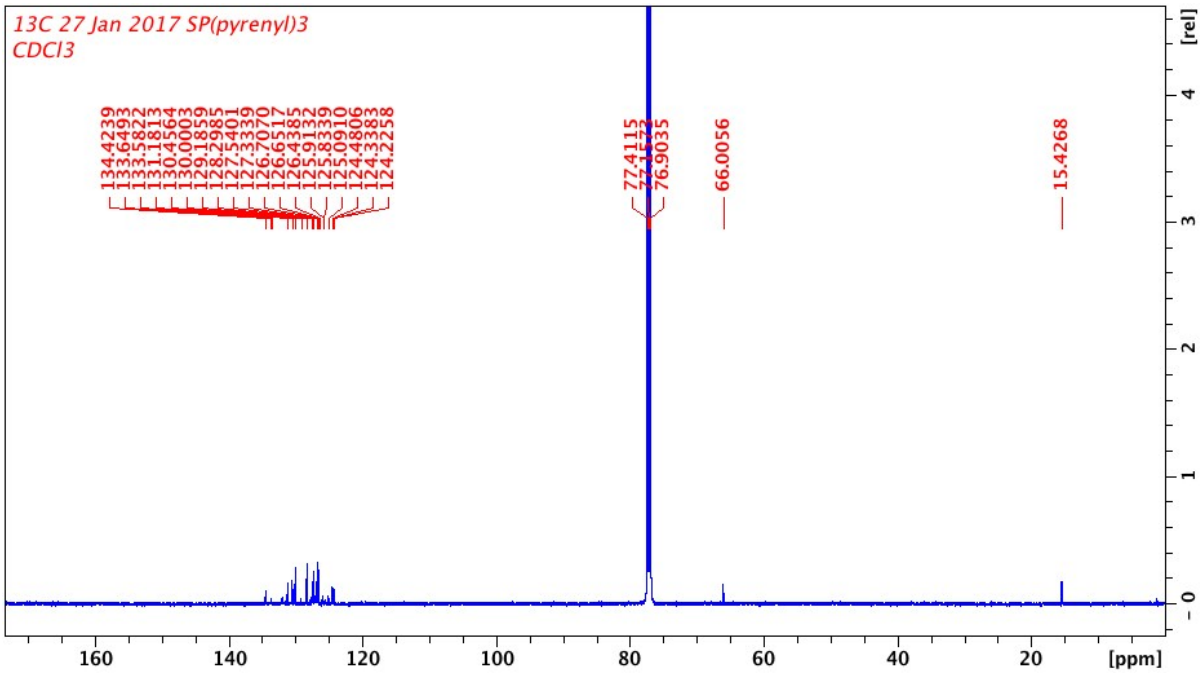

HMQC 22 Nov 2016 OP(pyrenyl)3
CDCl3
F1 [ppm]
126
128
130
132
134
136
138
9.0
8.5
8.0
F2 [ppm]

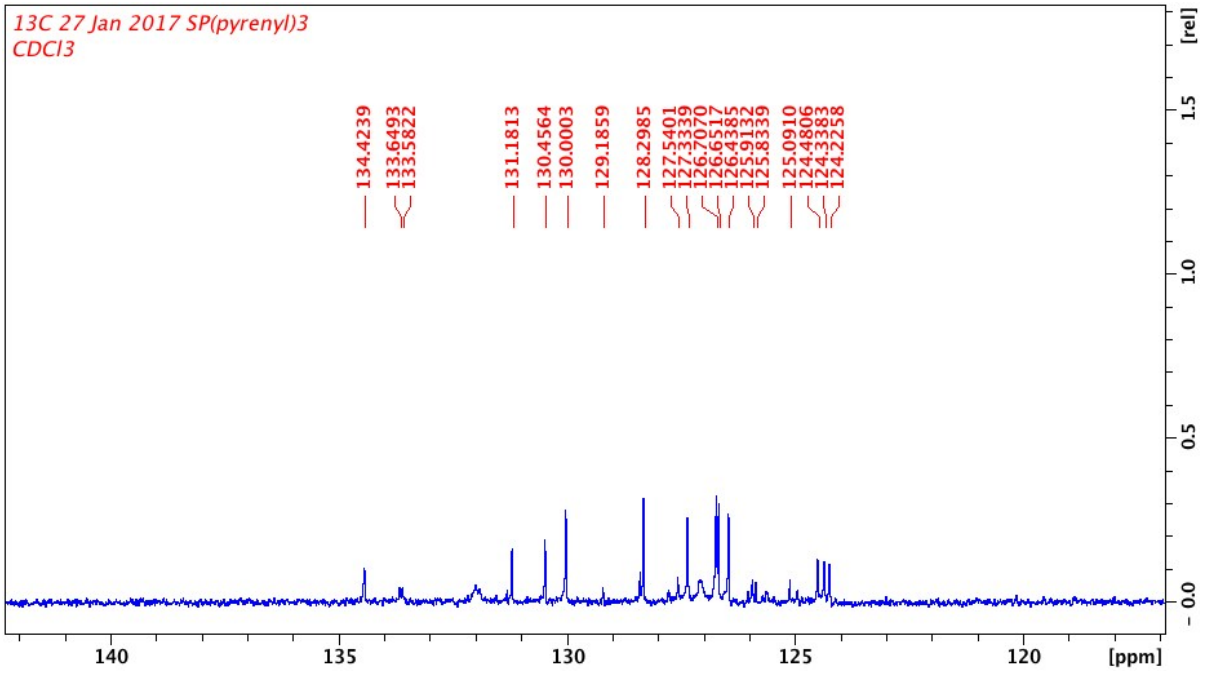

31P 22 Nov 2016 OP(pyrenyl)3
CDCl3
41.7253
100
0
- 100
- 200
[ppm]
[rel]

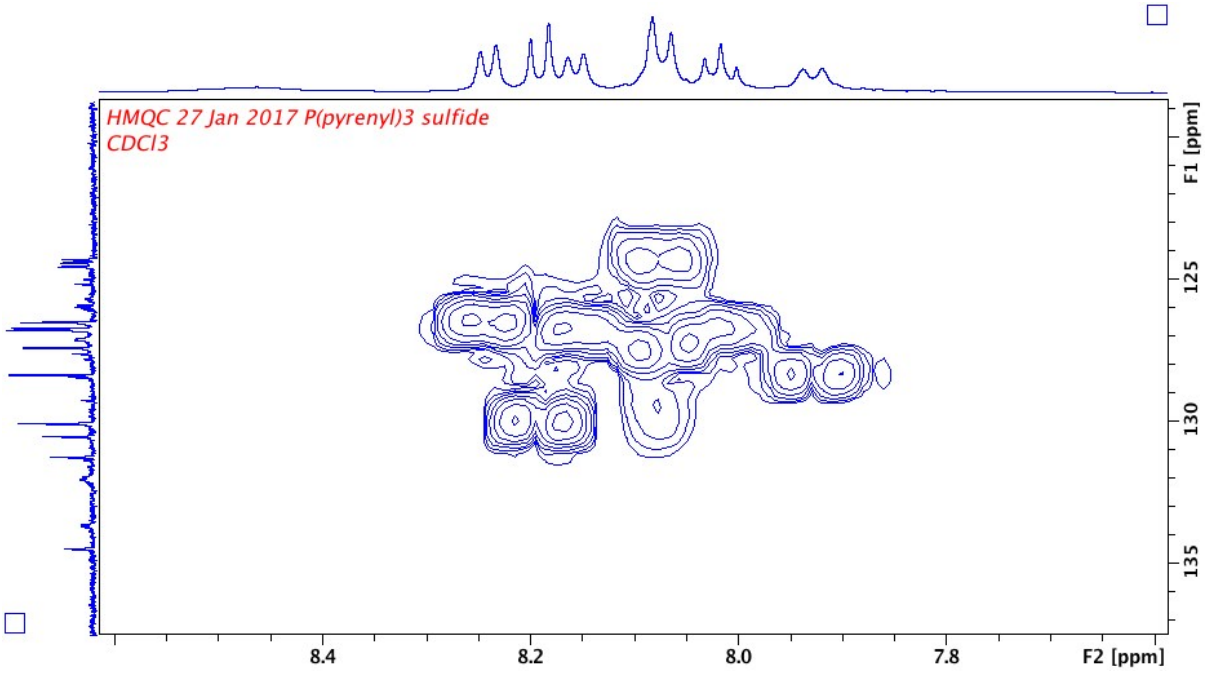
$SP(C_{16}H_9)_3$, 6

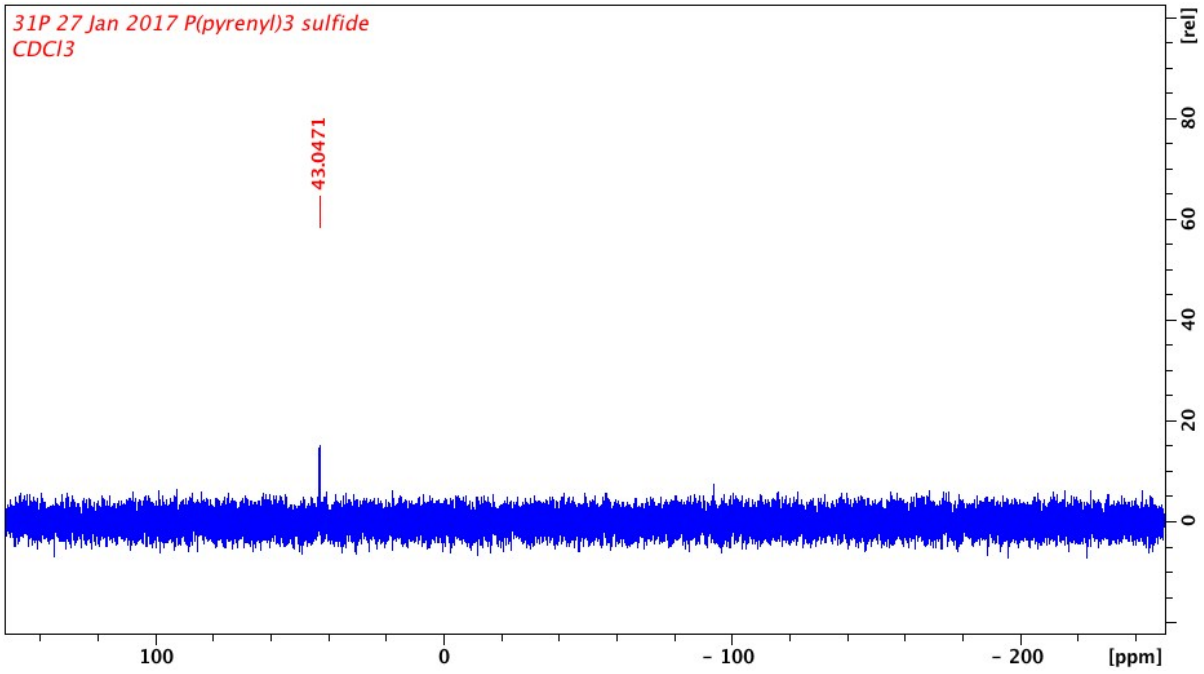

1H 27 Jan 2017 SP(pyrenyl)3
CDCl3
9.1292
8.4621
8.4437
8.2475
8.2324
8.1992
8.1819
8.1634
8.1484
8.0820
8.0642
8.0317
8.0164
8.0012
7.9373
7.9189
7.1841
7.1699
3.4876
3.4735
2.3572
1.5478
1.2246
1.2105
1.1965
0.0729
8
6
4
2
[ppm]
[rel]


1H 27 Jan 2017 SP(pyrenyl)3
CDCl3
9.1292
8.4621
8.4437
8.2475
8.2324
8.1992
8.1819
8.1634
8.1484
8.0820
8.0642
8.0317
8.0164
8.0012
7.9373
7.9189
7.1841
7.1699
3.0000
12.2146
6.4379
3.2496
3.3543
[rel]
[ppm]

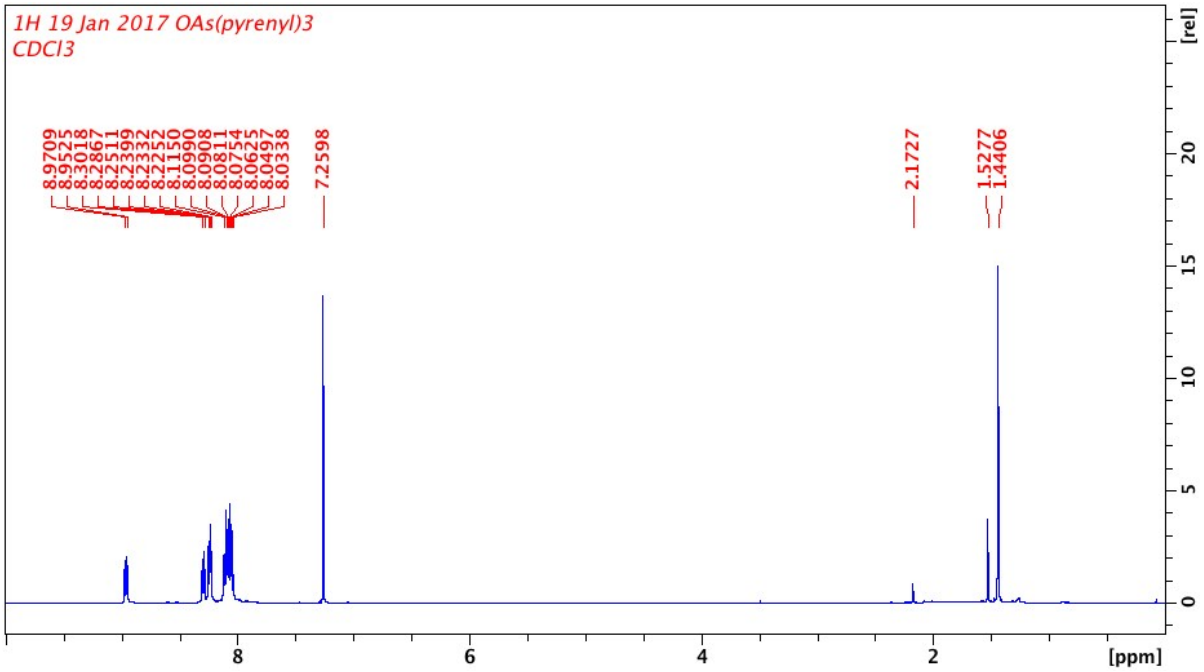

13C 27 Jan 2017 SP(pyrenyl)3
CDCl3
134.4239
133.6493
133.5822
131.1813
130.4564
130.0003
129.1859
128.2985
127.5401
127.3339
126.7070
126.6517
126.4385
125.9132
125.8339
125.0910
124.4806
124.3383
124.2258
77.4115
77.1572
76.9035
66.0056
15.4268
[rel]
[ppm]

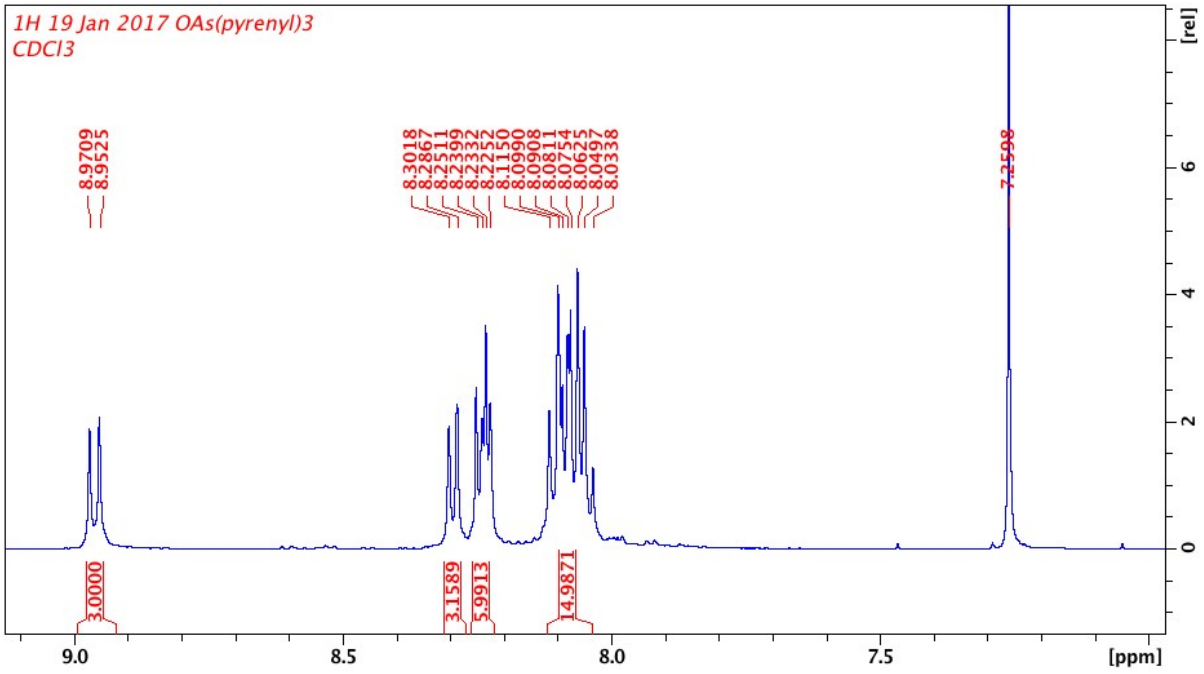

13C 27 Jan 2017 SP(pyrenyl)3
CDCl3
134.4239
133.6493
133.5822
131.1813
130.4564
130.0003
129.1859
128.2985
127.5401
127.3339
126.7070
126.6517
126.4385
125.9132
125.8339
125.0910
124.4806
124.3383
124.2258
[rel]
1.5
1.0
0.5
0.0
140
135
130
125
120
[ppm]

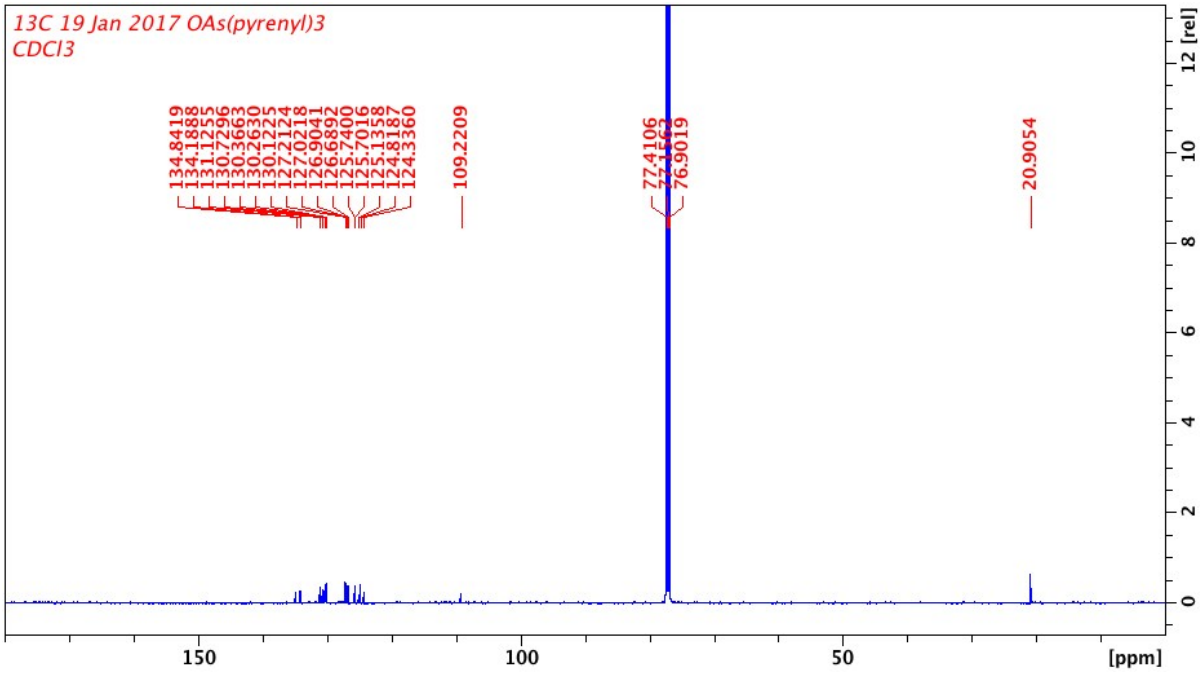

HMQC 27 Jan 2017 P(pyrenyl)3 sulfide
CDCl3
F1 [ppm]
125
130
135
8.4
8.2
8.0
7.8
F2 [ppm]

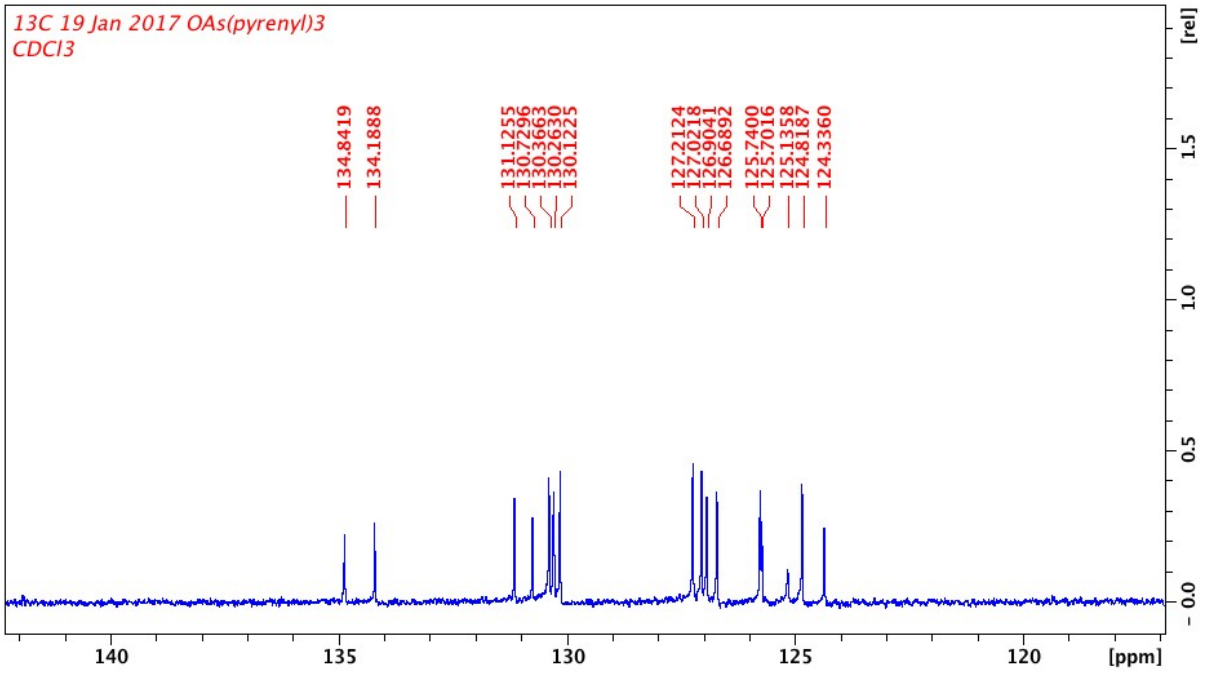

31P 27 Jan 2017 P(pyrenyl)3 sulfide
CDCl3
43.0471
[rel]
80
60
40
20
0
100
0
- 100
- 200
[ppm]

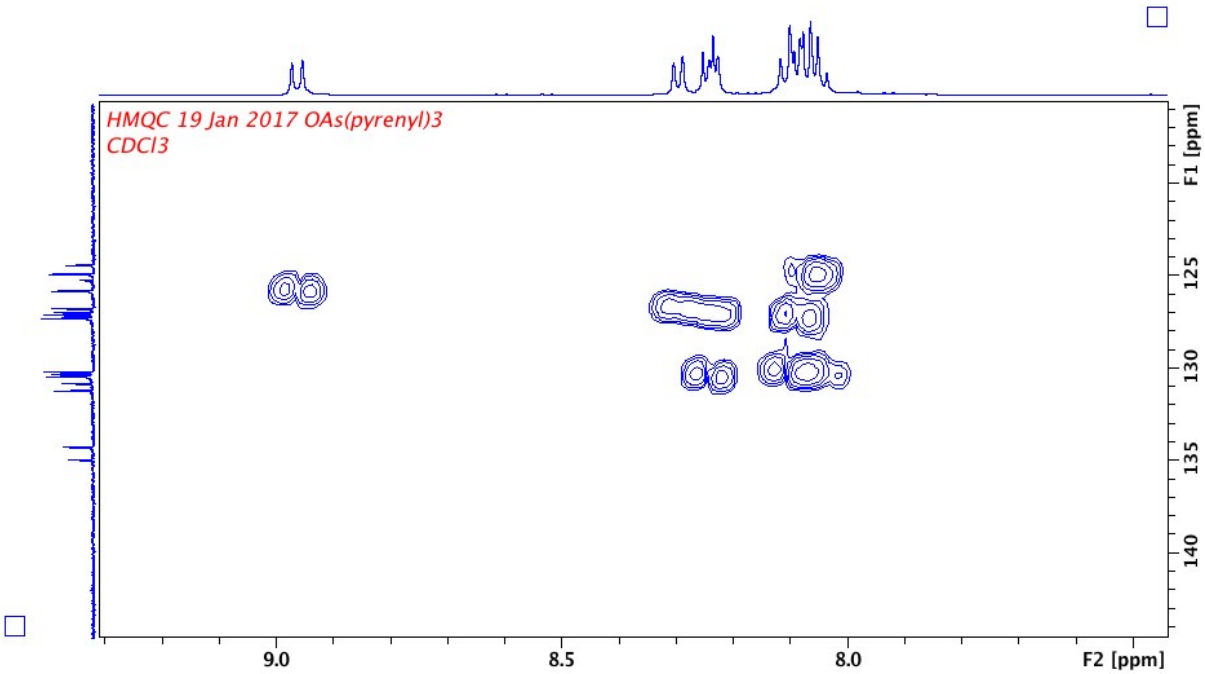
$OAs(C_{16}H_9)_3$, 7


1H 19 Jan 2017 OAs(pyrenyl)3
CDCl3
8.9709
8.9525
8.3018
8.2867
8.2511
8.2399
8.2332
8.2252
8.1150
8.0990
8.0908
8.0811
8.0754
8.0625
8.0497
8.0338
7.2598
2.1727
1.5277
1.4406
[rel]
20
15
10
5
0
8
6
4
2
[ppm]


1H 19 Jan 2017 OAs(pyrenyl)3
CDCl3
8.9709
8.9525
8.3018
8.2867
8.2511
8.2399
8.2332
8.2252
8.1150
8.0990
8.0908
8.0811
8.0754
8.0625
8.0497
8.0338
7.2598
3.0000
3.1589
5.9913
14.9871
9.0
8.5
8.0
7.5
[ppm]
[rel]


13C 19 Jan 2017 OAs(pyrenyl)3
CDCl3
134.8419
134.1888
131.1255
130.7296
130.3663
130.2630
130.1225
127.2124
127.0218
126.9041
126.6892
125.7400
125.7016
125.1358
124.8187
124.3360
109.2209
77.4106
77.1581
76.9019
20.9054
150
100
50
[ppm]
12 [rel]





References

1. Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*. Springer: 2007.