Supporting Information

Formation of the silver-flavin coordination polymers and their morphological studies

M. S. S. Vinod Mouli and Ashutosh Kumar Mishra*

Department of Chemistry, IIT Hyderabad, 502285, India

Table of contents

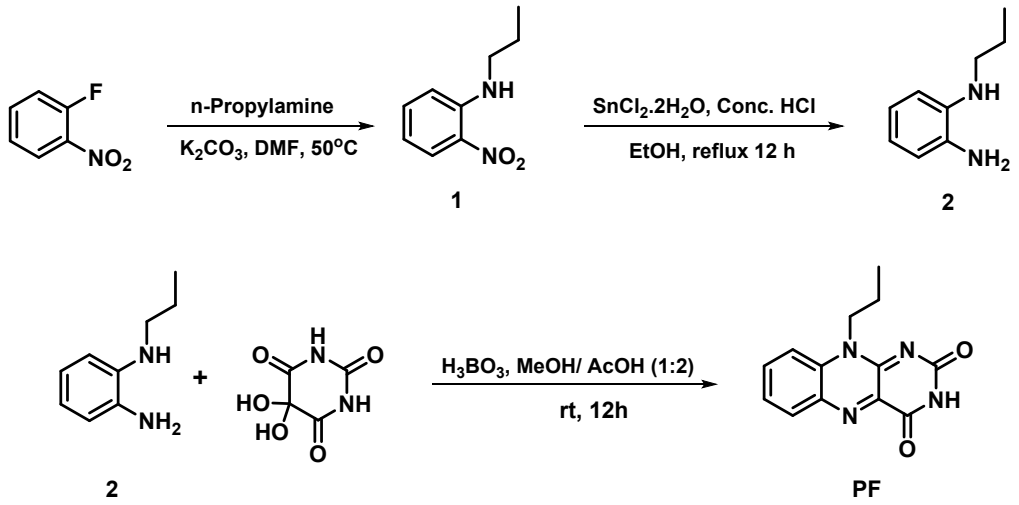
1. Materials and Physical Measurements…….....…2
2. Synthetic Procedure…….….3
3. Photophysical studies…….…….7
4. IR Spectra…….…….…….9
5. SC-XRD analysis of **1** and **2**…….…….…….….10
6. References…….…..…….19
7. List of NMR spectra…….…….20
8. List of HRMS spectra..…….…….33

1. Materials and Physical Measurements.

All chemicals and reagents are purchased from commercial sources SRL and Avra, and were used without purification. Nuclear magnetic resonance spectra were collected using a Bruker AVANCE III-400 spectrometer using TMS as reference. ^{13}C NMR spectra were collected at 100 MHz, and 1 H NMR spectra were collected at 400 MHz. Resonances are reported in parts per million (ppm) and coupling constants, J, are reported in hertz (Hz). High resolution mass spectra were obtained by the Electron Spray Ionization method (ESI) using Agilent QTOF 6538. For diffraction measurements, crystal with suitable dimensions was mounted on a nylon Loop with a layer of paraben oil covered. X-ray diffraction measurements were recorded using Agilent Supernova Xcalibur Eos CCD detector with graphite-monochromatic Cu-Kα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S1. The structures were solved by direct methods and refined on F2 by full-matrix least-squares methods using SHELXS[1] and SHELXL-97.[2] Optical images were taken using Leica DM 2700M at 20x and 50x magnification. AFM images were recorded at 25 ^{o}C by tapping mode at a scan rate of 0.5Hz using Park NX 10 AFM. TEM images were recorded using Transmission electron microscopy (JEOL JEM 2100FX TEM, Japan) at the accelerating voltage of 200kV. UV-Visible spectral measurements were obtained from JASCO Spectrophotometer V730 and Fluorescence measurements were taken from JASCO Spectrofluorometer FP-8300.

2. Synthetic Procedure

10-Propyl Flavin (**PF**) is synthesized by a slight modification of the previously reported procedure.[3,4]



Scheme S1. Synthetic route for preparing **PF**

N-Propyl-2-nitroaniline (1). To 1-Fluoro-2-nitrobenzene (2g, 14.18 mmol) added DMF (3 mL) followed by the addition of n-Propylamine amine (4.2 mmol) and anhydrous Potassium Carbonate (5.3 mmol). The contents were stirred at 50 °C until all the starting material is consumed monitored by TLC. After completion of the reaction, solvent extraction is done with chloroform (100 × 4 mL) and brine (150 × 2 mL) and dried over Na_2SO_4, filtered and concentrated using reduced pressure. Silica gel column chromatography using Hexane/Ethyl acetate was done to give nitroaniline as an orange oil with 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 1H, *J* = 8.6 Hz), 8.07 (s, 1H), 7.42 (ddd, 1H, *J* = 7.9, 1.4, 0.7 Hz), 6.84 (d, 1H, *J* = 8.7 Hz), 6.61 (t, 1H, *J* = 7.76 Hz), 3.27 (dd, 2H, *J* = 12.4, 6.9 Hz), 1.76 (d, 2H, *J* = 7.2 Hz), 1.05 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.66, 136.18, 131.7, 126.86, 115.03, 113.8, 44.76, 22.25, 11.57.

N^1-propylbenzene-1,2-diamine (2). 11.22 mmol of nitroaniline (**1**) was dissolved in ethanol (50 mL) added Conc. HCl (10 mL) followed by addition of $SnCl_2.2H_2O$ (15.2g, 67.34 mmol). Refluxed reaction mixture for 12hrs under nitrogen. After the completion reaction mixture was concentrated to remove ethanol and pH was adjusted to 8 with 5M NaOH until white solid is obtained which was filtered through celite and the filtrate was extracted with $CHCl_3$ (150 × 2 mL) from water (100 mL).

Dried the organic portion with Na_2SO_4 and concentrated under reduced pressure to give diamine **2** as a brown oil which was used for the next reaction without any further purification.

10-Propyl Flavin (PF). Alloxan monohydrate (1.79g, 11.22 mmol) and boric acid (0.69g, 11.22 mmol) were dissolved in methanol (5 mL). Diamine **2** in acetic acid (10 mL) was added dropwise to the reaction mixture for 1 hour. Continued stirring at room temperature under nitrogen for 12 h. To yellow precipitate obtained was added diethyl ether (5 mL) followed by stirring for 30 minutes. Filtered under suction and yellow solid was washed with diethyl ether (10 mL) followed with water (10 mL). Dried the yellow solid and silica gel column chromatography was done using $CHCl_3$ and MeOH to give pure flavin with a yield of 58%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.4 (s, 1H), 8.14 (dd, 1H, J = 8.1, 1.3 Hz), 8.0 (d, 1H, J = 8 Hz), 7.94 (ddd, 1H, J = 8.6, 7, 1.4 Hz), 7.73-7.54 (m, 1H), 4.55 (t, 2H, J = 7.8 Hz), 1.84-1.67 (m, 2H), 1.04 (t, 3H, J = 7.4Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.73, 155.69, 150.38, 138.68, 134.90, 134.83, 132.40, 131.78, 125.92, 116.39, 45.53, 19.81, 10.96. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}N_4O_2$: 257.1033 Found 257.1034.

Crystallization of PF with Ag(I). To 3mg of PF, 2ml acetic acid is added and heated it to 80 ^{o}C. Silver nitrate (for PF-$AgNO_3$) or Silver tetrafluoroborate (for PF-$AgBF_4$) in methanol (5 equivalents) was added dropwise. The solution was filtered and left for slow evaporation for one week to give orangish colored crystals which were used for diffraction measurements.

For NMR titration experiments, to **PF** dissolved in DMSO-d_6 gradually added $AgNO_3$ salt dissolved in MeOH-d_4. Five-minute incubation was done before recording NMR after addition of $AgNO_3$. Because of precipitation of complex beyond addition of 1eq. of Ag(I) we have recorded ^{13}C NMR for **PF** containing 1eq. of $AgNO_3$ or $AgBF_4$.

PF + 0.37 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 1H), 8.15 (dd, 1H, J = 8.1, 1.3 Hz), 8.01 (d, 1H, J = 8.1 Hz), 7.95 (ddd, 1H, J = 8.6, 7, 1.4 Hz), 7.67-7.63 (m, 1H), 4.55 (t, 2H, J = 7.8 Hz), 1.81-1.71 (m, 2H), 1.04 (t, 3H, J = 7.4Hz).

PF + 1 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 1H), 8.18 (dd, 1H, J = 8.1, 1.3 Hz), 8.02 (d, 1H, J = 8.1 Hz), 7.96 (ddd, 1H, J = 8.6, 7, 1.4 Hz), 7.68-7.64 (m, 1H), 4.56 (t, 2H, J = 7.8 Hz), 1.81-1.71 (m, 2H), 1.04 (t, 3H, J = 7.4Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.86, 155.61, 150.41, 138.49, 135.06, 134.63, 132.57, 131.82, 126.00, 116.46, 45.60, 19.83, 10.96.

PF + 1.6 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.5 (s, 1H), 8.19 (dd, 1H, *J* = 8.1, 1.3 Hz), 8.03 (d, 1H, *J* = 8.1 Hz), 7.96 (ddd, 1H, *J* = 8.6, 7, 1.4 Hz), 7.69-7.65 (m, 1H), 4.56 (t, 2H, *J* = 7.8 Hz), 1.81-1.71 (m, 2H), 1.04 (t, 3H, *J* = 7.4Hz).

PF + 2.22 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (s, 1H), 8.2 (dd, 1H, *J* = 8.2, 1.3 Hz), 8.03 (d, 1H, *J* = 8.2 Hz), 7.97 (ddd, 1H, *J* = 8.6, 7.1, 1.4 Hz), 7.69-7.65 (m, 1H), 4.56 (t, 2H, *J* = 7.8 Hz), 1.81-1.71 (m, 2H), 1.04 (t, 3H, *J* = 7.4Hz).

PF + 2.83 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.54 (s, 1H), 8.21 (dd, 1H, *J* = 8.2, 1.3 Hz), 8.04 (d, 1H, *J* = 8.2 Hz), 7.97 (ddd, 1H, *J* = 8.6, 7.1, 1.4 Hz), 7.69-7.65 (m, 1H), 4.56 (t, 2H, *J* = 7.8 Hz), 1.81-1.71 (m, 2H), 1.04 (t, 3H, *J* = 7.4Hz).

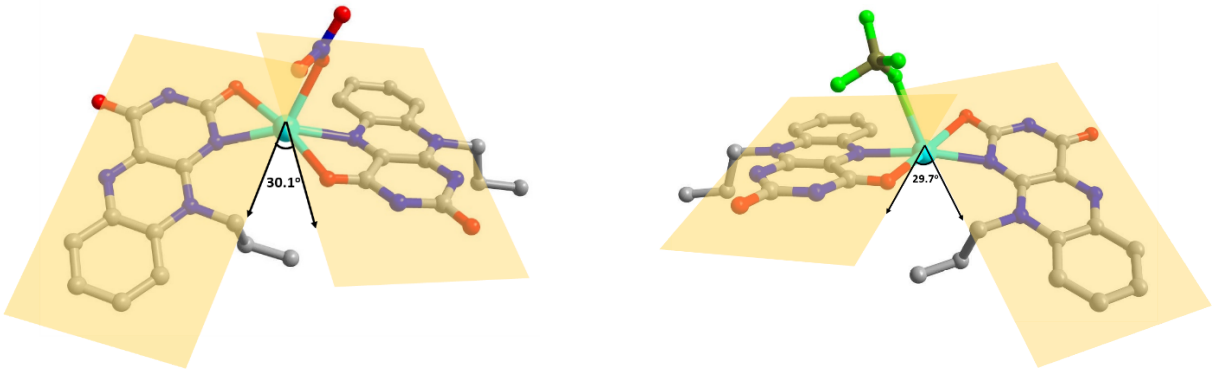
PF + 3.48 eq. $AgNO_3$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 8.22 (dd, 1H, *J* = 8.2, 1.3 Hz), 8.04 (d, 1H, *J* = 8.2 Hz), 7.97 (ddd, 1H, *J* = 8.6, 7.1, 1.4 Hz), 7.7-7.66 (m, 1H), 4.59-4.55 (m, 2H), 1.81-1.72 (m, 2H), 1.04 (t, 3H, *J* = 7.4Hz).

PF-$AgNO_3$: HRMS (ESI) *m*/*z*: [PF-$^{107}Ag^+$] calcd 363.0006 Found 362.9994. [PF-$^{109}Ag^+$] calcd 365.0002 Found 364.9992. [PF_2-$^{107}Ag_2^{2+}$] calcd 364.0004 Found 364.0019. [PF_2-$^{109}Ag_2^{2+}$] calcd 366.0004 Found 366.0018. [PF_2-$^{107}Ag^+$] calcd 619.0966 Found 619.0936. [PF_2-$^{107}Ag^+$] calcd 621.0963 Found 621.0934.

PF + 1 eq. $AgBF_4$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (s, 1H), 8.19 (dd, 1H, *J* = 8.1, 1.2 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 7.98-7.92 (m, 1H), 7.68-7.64 (m, 1H), 4.56 (t, 2H, *J* = 7.8 Hz), 1.81-1.72 (m, 2H), 1.04 (t, 3H, *J* = 7.4Hz). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.87, 155.59, 150.41, 138.45, 135.09, 134.59, 132.60, 131.83, 126.02, 116.45, 45.62, 19.83, 10.95.

PF-$AgBF_4$: HRMS (ESI) *m*/*z*: [PF-$^{107}Ag^+$] calcd 363.0006 Found 362.9990. [PF-$^{109}Ag^+$] calcd 365.0002 Found 364.9992. [PF_2-$^{107}Ag_2^{2+}$] calcd 364.0004 Found 364.0020. [PF_2-$^{109}Ag_2^{2+}$] calcd 366.0004 Found 366.0016. [PF_2-$^{107}Ag^+$] calcd 619.0966 Found 619.0925. [PF_2-$^{107}Ag^+$] calcd 621.0963 Found 621.0941.

Sample Preparation for Assembly on the surface. To 0.1 mM solution of PFL in acetic acid added 17µl Ag(I) salt ($AgNO_3$ or $AgBF_4$) of methanolic solution (29.4 mM). This mixture is then incubated for 24hrs. Then 5-10µl of the mixture is taken and drop-casted on the respective surface – glass slide (for optical microscopic observation), freshly cleaved HOPG (Highly oriented pyrolytic graphite) surface (for Atomic force microscopy), and carbon coated copper grid (for TEM imaging). The substrate is then left for 2-3hrs for solvent evaporation and then kept in vacuum desiccator and dried for 12hrs. The surfaces were then used for recording morphological features with corresponding technique.



(a) **(b)**

Figure S1. Angle between the planes of adjacent flavin rings (a) 30.1^{O} in **1** (b) 29.7^{O} in **2**

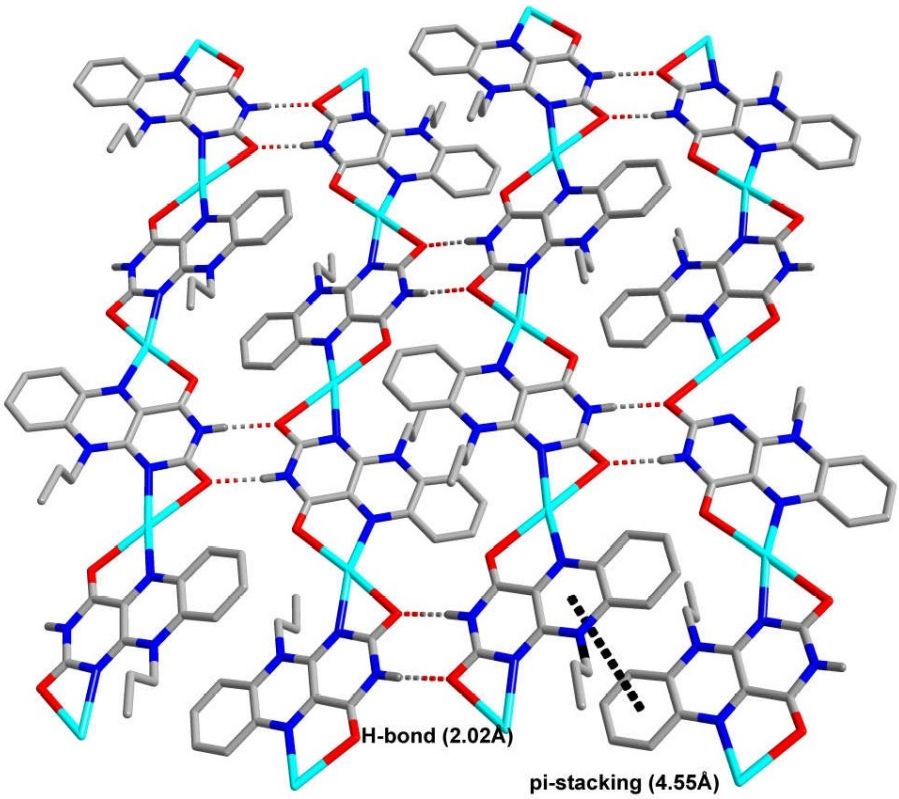


Figure S2. Lattice formation in **2** stabilized by H-bonding and π-π stacking between strands

3. Photophysical Studies

The UV-Vis absorption studies of **PF** were done in Acetic acid as solvent having concentration of 32 μM. The spectra for Flavins without the addition of Ag(I) (as depicted in Figure S3) consists of three peaks observed between 250-500 nm range which is characteristic for isoalloxazine ring.[5] These peaks arise due to π-π^* transitions with lowest energy band centered at 432 nm. Absorption studies of CPs **1** and **2** were done by adding 100 equivalents of Ag(I) salt dissolved in methanol to Flavin in Acetic acid. The solution was incubated for 3 days and recorded UV-Vis spectra. The spectra for CPs **1** and **2** were observed to be similar to parent flavin **PF** with slight bathochromic shift of low energy band which can be ascribed to formation of Flavin-Ag(I) complexation through primary chelation site.[6]

PF, **1** and **2** upon excitation at 432nm in Acetic acid showed a single peak with maximum at 525 nm (Figure S4). Addition of Silver(I) resulted in quenching of emission intensity for all the cases. This can be explained based on Metal to Ligand Charge Transfer (MLCT) phenomena.[7]

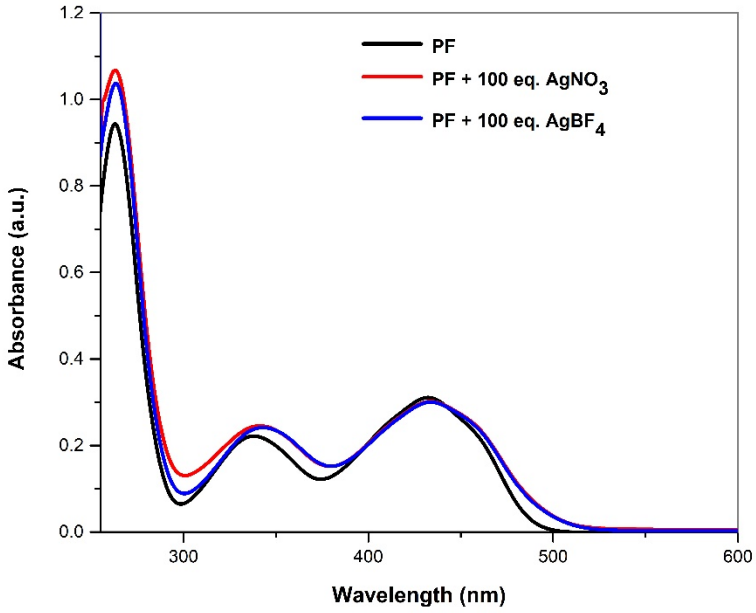


Figure S3. UV-Vis absorption spectra of PF-Ag(I) complexes

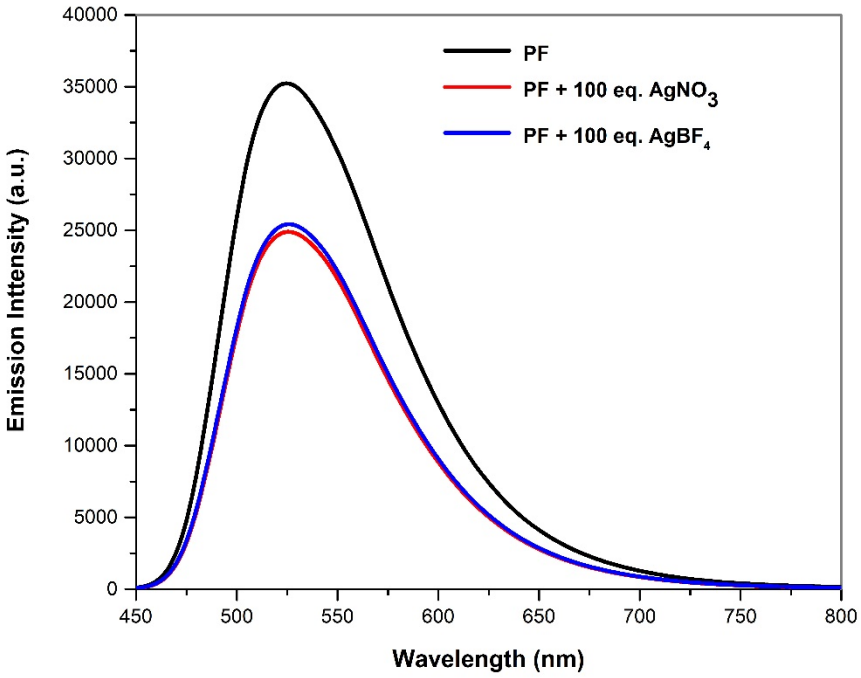


Figure S4. Emission spectra of PF-Ag(I) complexes (Excitation wavelength at 432 nm)

4. IR Spectra

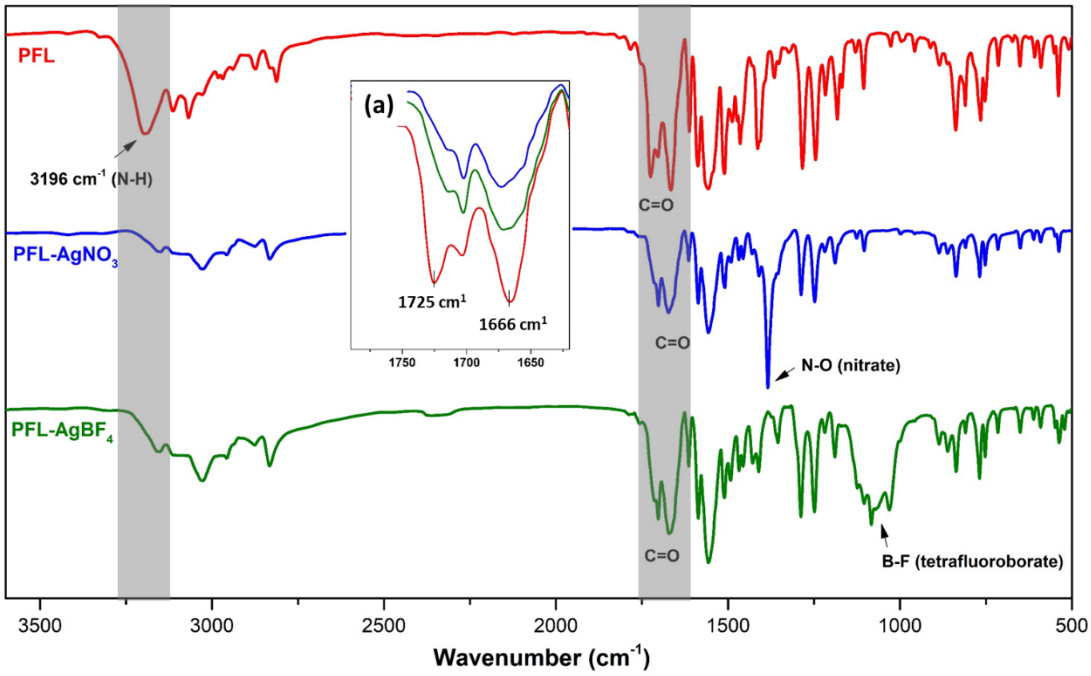


Figure S5. IR spectra of **PF**, **1** and **2**. Inset (a) represents the change in C=O stretching frequency upon Ag(I) coordination

5. SC-XRD analysis

Crystallographic data has been deposited in the Cambridge Crystallographic Data Centre and assigned the deposition number CCDC: 2120628 for **1** and 2120629 for **2**. Crystallographic data and structure refinement parameters are summarized in Table S1.

Table S1. Crystallographic and Refinement Data of **1** and **2**

Compound Reference	**1**	**2**
empirical formula	$C_{13}H_{12}N_5O_5Ag$	$C_{13}H_{12}N_4O_2AgBF_4$
formula weight	426.15	450.95
crystal colour	Orangish	Orangish
crystal system	Monoclinic	Monoclinic
space group	P 2_1/n	P 2_1/n
a/Å	8.2976(4)	8.9525(4)
b/Å	14.3385(5)	14.4114(4)
c/Å	12.5030(4)	11.948(3)
α/deg	90	90
β/deg	92.169	93.496
γ/deg	90	90
volume/Å^3	1486.48(9)	1538.64(9)
D_{calcd} (g/cm^3)	1.904	1.947
temp/K	293	293
Z	4	4
μ (mm^{-1})	11.238	1.371
F(000)	848	888
Reflections measured	4757	6392
Reflections observed	2490	3538
Rint	0.0242	0.0237
No. of param	218	227
final R1 values (all data)	0.0441	0.0506
final wR(F2) values(all data)	0.1242	0.1359
GOF	1.038	1.045

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: PF-AgNO3

```
Bond precision:   C-C = 0.0075 A          Wavelength=1.54184

Cell:             a=8.2976(4)     b=14.3385(5)        c=12.5030(4)
                  alpha=90        beta=92.169(4)      gamma=90
Temperature:      298 K

                 Calculated                Reported
Volume           1486.48(10)               1486.48(9)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C13 H12 Ag N5 O5          C13 H12 Ag N5 O5
Sum formula      C13 H12 Ag N5 O5          C13 H12 Ag N5 O5
Mr               426.15                    426.15
Dx,g cm-3        1.904                     1.904
Z                4                         4
Mu (mm-1)        11.238                    11.238
F000             848.0                     848.0
F000'            851.11
h,k,lmax         10,17,15                  10,17,15
Nref             2809                      2490
Tmin,Tmax        0.468,0.570               0.591,1.000
Tmin'            0.388

Correction method= # Reported T Limits: Tmin=0.591 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.886           Theta(max)= 69.931

R(reflections)= 0.0441( 2101)                    wR2(reflections)=
                                                 0.1242( 2490)
S = 1.038                  Npar= 218
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.901 Why?

Author response

This alert arises due to single collection of data and when we processed the data later, we observed reduced completeness.

Alert level B

PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of N11 Check

Author response

This alert is due to large anisotropic displacement of O5, O6 and O7 attached to N11 in nitrate anion.

Alert level C

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O5 Check
PLAT410_ALERT_2_C Short Intra H...H Contact H2 ..H11B . 1.97 Ang.
x,y,z = 1_555 Check

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 1 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT432_ALERT_2_G Short Inter X...Y Contact O6 ..C2 2.73 Ang.
1/2+x,3/2-y,1/2+z = 4_676 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 1.9 Low

1 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

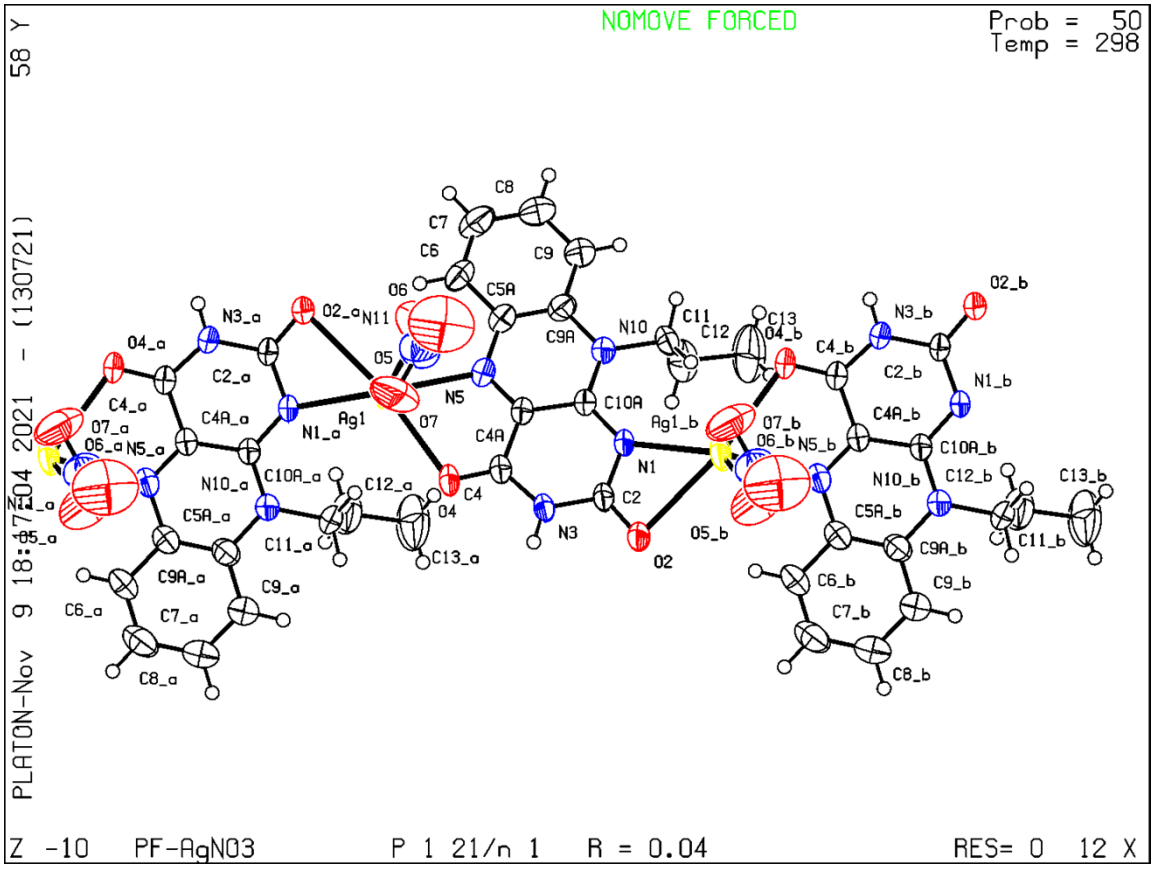
Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT029_PF-AgNO3
;
PROBLEM: _diffrn_measured_fraction_theta_full value Low .      0.901 Why?
RESPONSE: ...
;
_vrf_PLAT242_PF-AgNO3
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of        N11 Check
RESPONSE: ...
;
_vrf_PLAT241_PF-AgNO3
;
PROBLEM: High   'MainMol' Ueq as Compared to Neighbors of         O5 Check
RESPONSE: ...
;
_vrf_PLAT410_PF-AgNO3
;
PROBLEM: Short Intra H...H Contact  H2       ..H11B     .       1.97 Ang.
RESPONSE: ...
;
# end Validation Reply Form
```

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock PF-AgNO3 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: PF-AgBF4

```
Bond precision:   C-C = 0.0076 A           Wavelength=0.71073

Cell:              a=8.9525(18)      b=14.411(3)        c=11.948(2)
                   alpha=90          beta=93.50(3)      gamma=90
Temperature:       298 K

                 Calculated                 Reported
Volume           1538.6(5)                  1538.6(5)
Space group      P 21/n                     P 1 21/n 1
Hall group       -P 2yn                     -P 2yn
Moiety formula   C13 H12 Ag N4 O2, B F4     C13 H12 Ag N4 O2, B F4
Sum formula      C13 H12 Ag B F4 N4 O2      C13 H12 Ag B F4 N4 O2
Mr               450.95                     450.95
Dx,g cm-3        1.947                      1.947
Z                4                          4
Mu (mm-1)        1.371                      1.371
F000             888.0                      888.0
F000'            884.90
h,k,lmax         11,18,15                   11,18,15
Nref             3530                       3411
Tmin,Tmax        0.398,0.504                0.898,1.000
Tmin'            0.368

Correction method= # Reported T Limits: Tmin=0.898 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.966            Theta(max)= 27.484

R(reflections)= 0.0506( 2505)                wR2(reflections)=
                                             0.1359( 3411)
S = 1.048                  Npar= 227
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        3.8 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.4 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including        F1      0.135 Check
```

Alert level G

```
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT063_ALERT_4_G Crystal Size Possibly too Large for Beam Size ..       0.70 mm
PLAT244_ALERT_4_G Low    'Solvent' Ueq as Compared to Neighbors of         B1 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F1       ..C2              2.96 Ang.
                                       1/2+x,1/2-y,1/2+z  =      4_666 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3       ..C4A             2.83 Ang.
                                                x,y,z  =      1_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3       ..C4              2.92 Ang.
                                                x,y,z  =      1_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F4       ..C4A             2.93 Ang.
                                       1/2+x,1/2-y,1/2+z  =      4_666 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        1.8 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT220_PF-AgBF4
;
PROBLEM: NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        3.8 Ratio
RESPONSE: ...
;
_vrf_PLAT250_PF-AgBF4
;
PROBLEM: Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.4 Note
RESPONSE: ...
;
```

```
_vrf_PLAT260_PF-AgBF4
;
PROBLEM: Large Average Ueq of Residue Including        F1      0.135 Check
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

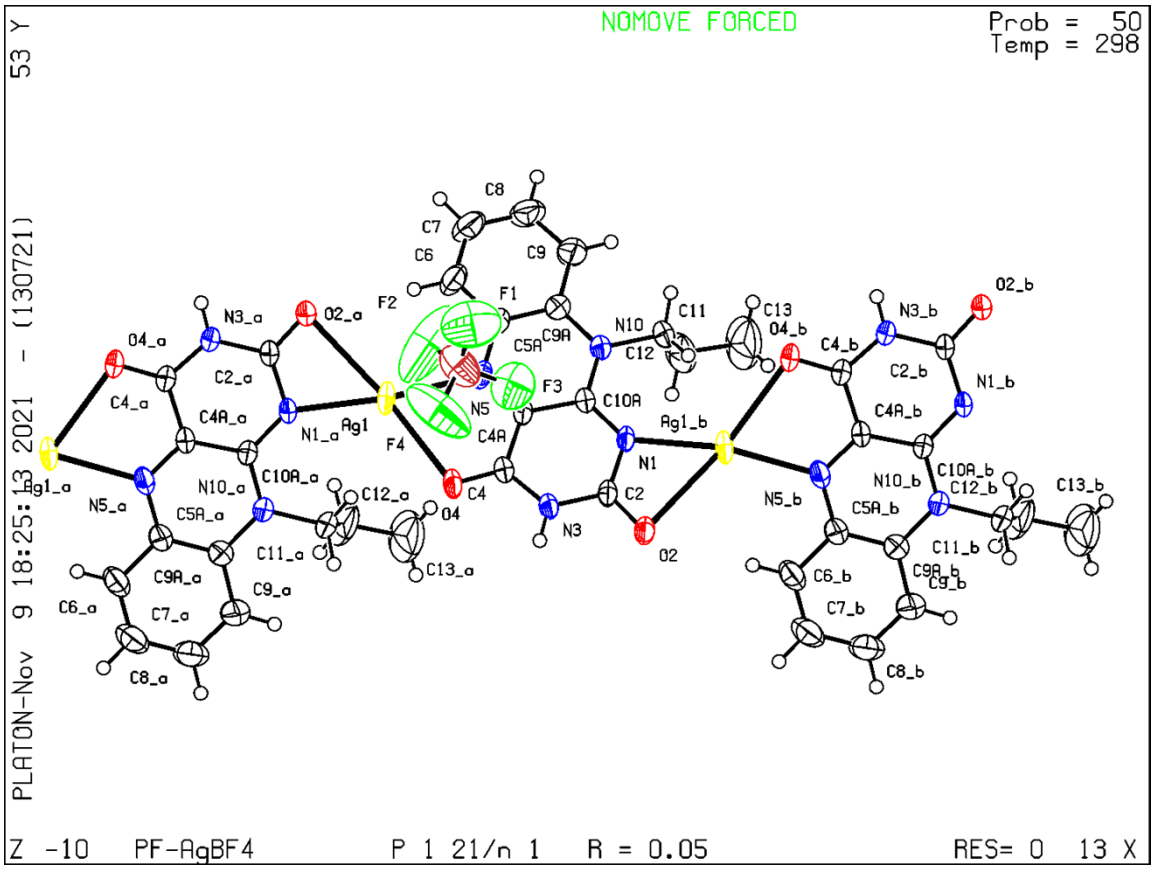
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock PF-AgBF4 - ellipsoid plot



6. References

(1) Sheldrick, G. M. Acta Cryst. Sect. A **1990**, *46*, 467.

(2) Sheldrick, G. M. SHELXL 97, Universita¨t Go¨ttingen, Go¨ttingen, Germany, **1997**.

(3) Kanhed, A. M.; Sinha, A.; Machhi, J.; Tripathi, A.; Parikh, Z. S.; Pillai, P. P.; Giridhar, R.; Yadav, M. R. Bioorg. Chem. **2015**, *61*, 7.

(4) Henwood, A. F.; Antón-García, D.; Morin, M.; Rota Martir, D.; Cordes, D. B.; Casey, C.; Slawin, A. M. Z.; Lebl, T.; Bühl, M.; Zysman-Colman, E. Dalt. Trans. **2019**, *48*, 9639.

(5) (a) Kobayashi, A.; Ohbayashi, K.; Aoki, R.; Chang, H.-C.; Kato, M. *Dalt. Trans.* **2011**, *40*, 3484. (b) Salzmann, S.; Martinez-Junza, V.; Zorn, B.; Braslavsky, S. E.; Mansurova, M.; Marian, C. M.; Gärtner, W. *J. Phys. Chem. A* **2009**, *113*, 9365. (c) Salzmann, S.; Tatchen, J.; Marian, C. M. *J. Photochem. Photobiol. A Chem.* **2008**, *198*, 221. (d) Weigel, A.; Dobryakov, A. L.; Veiga, M.; Pérez Lustres, J. L. J. Phys. Chem. A **2008**, *112*, 12054. (e) Insińska-Rak, M.; Sikorska, E.; Bourdelande, J. L.; Khmelinskii, I. V.; Prukała, W.; Dobek, K.; Karolczak, J.; Machado, I. F.; Ferreira, L. F. V.; Komasa, A.; Worrall, D. R.; Sikorski, M. *J. Mol. Struct.* **2006**, *783*, 184.

(6) Clarke, M. J.; Dowling, M. G.; Garafalo, A. R.; Brennan, T. F. *J. Biol. Chem.* **1980**, 255, 3472.

(7) Li, Y.; Lu, S. H.; Zhao, R. D.; Lu, Z. X.; Liu, X. L.; Qin, Y.; Yang, S. X.; Zheng, L. Y.; Cao, Q. E. *Polym. Chem*. **2019**, *10*, 2653.

7. List of NMR Spectra

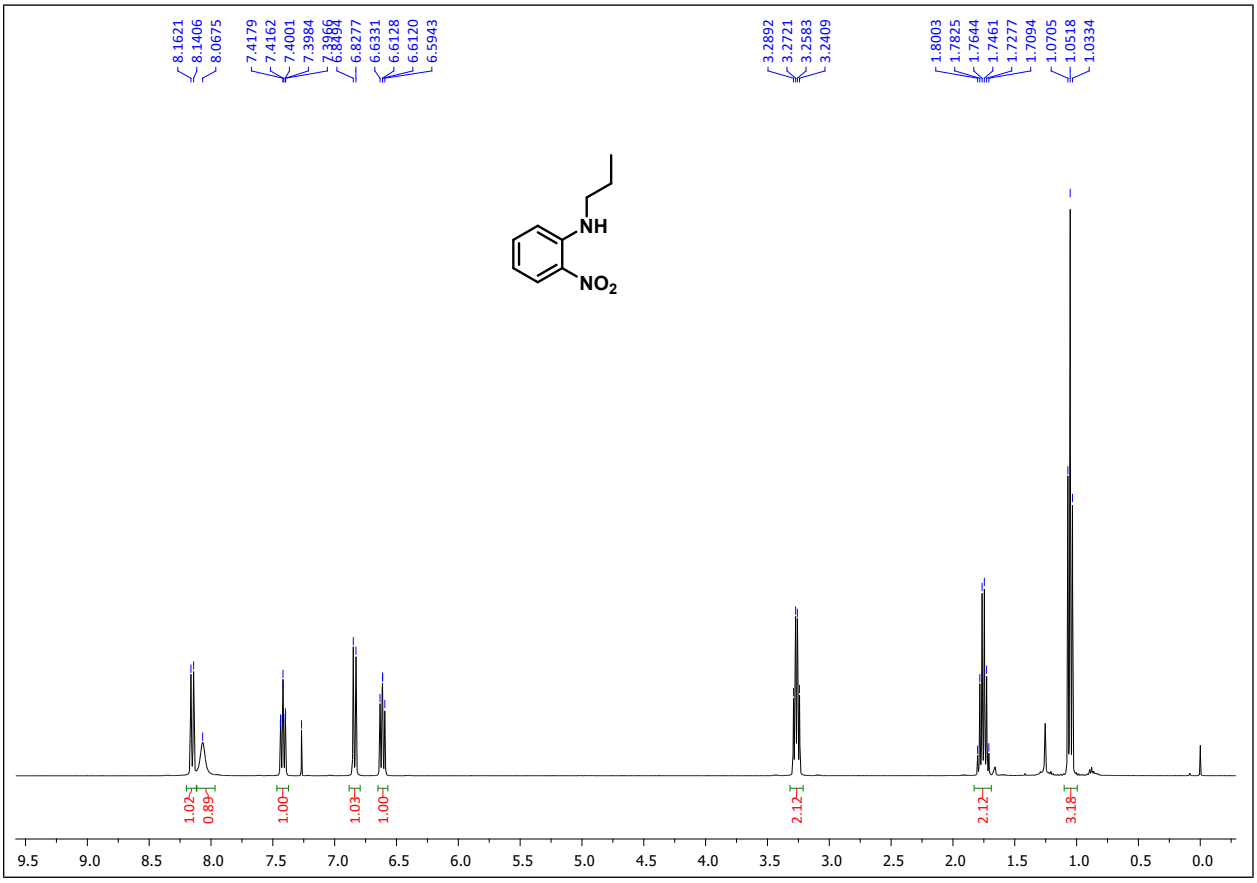


Figure S6. ^{1}H NMR of **N-Propyl-2-nitroaniline** in $CDCl_3$

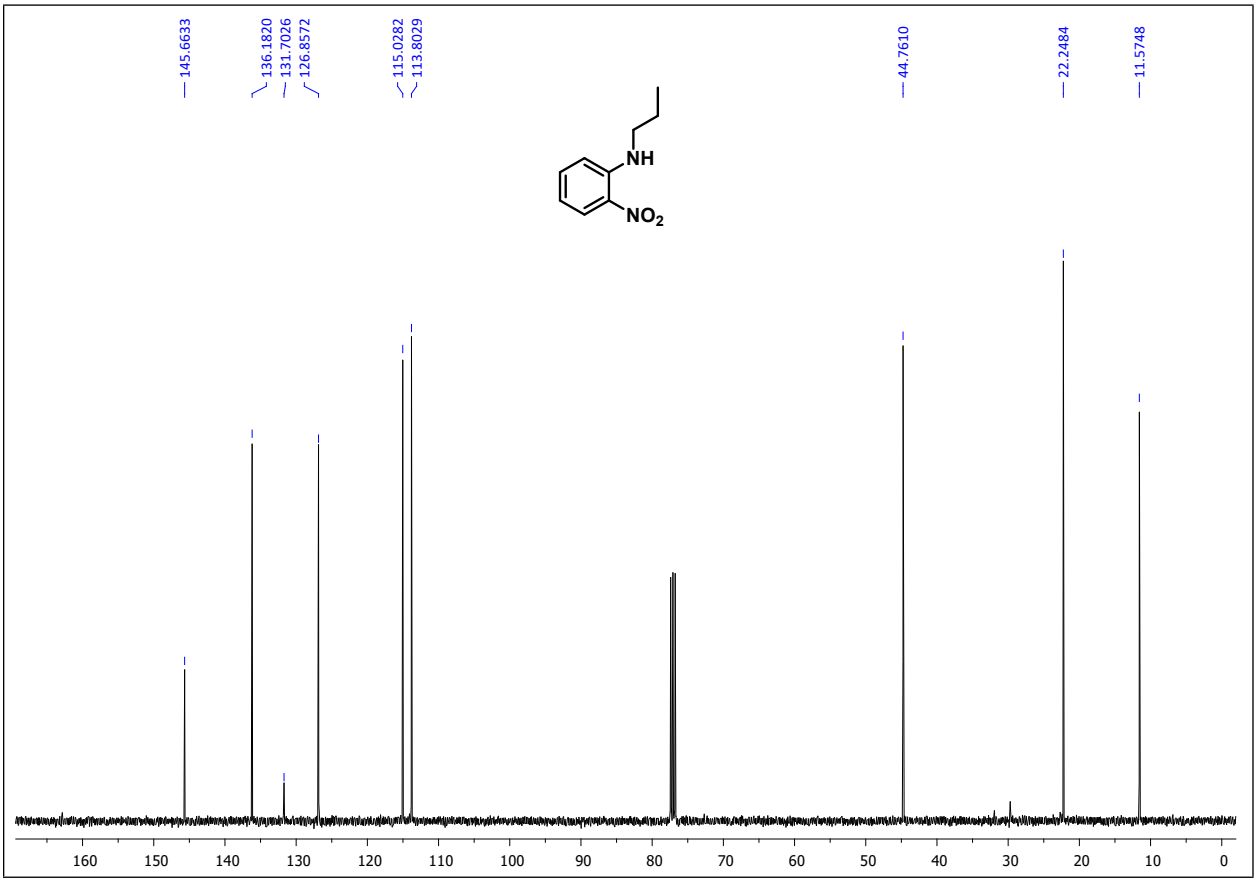


Figure S7. ^{13}C NMR of **N-Propyl-2-nitroaniline** in $CDCl_3$

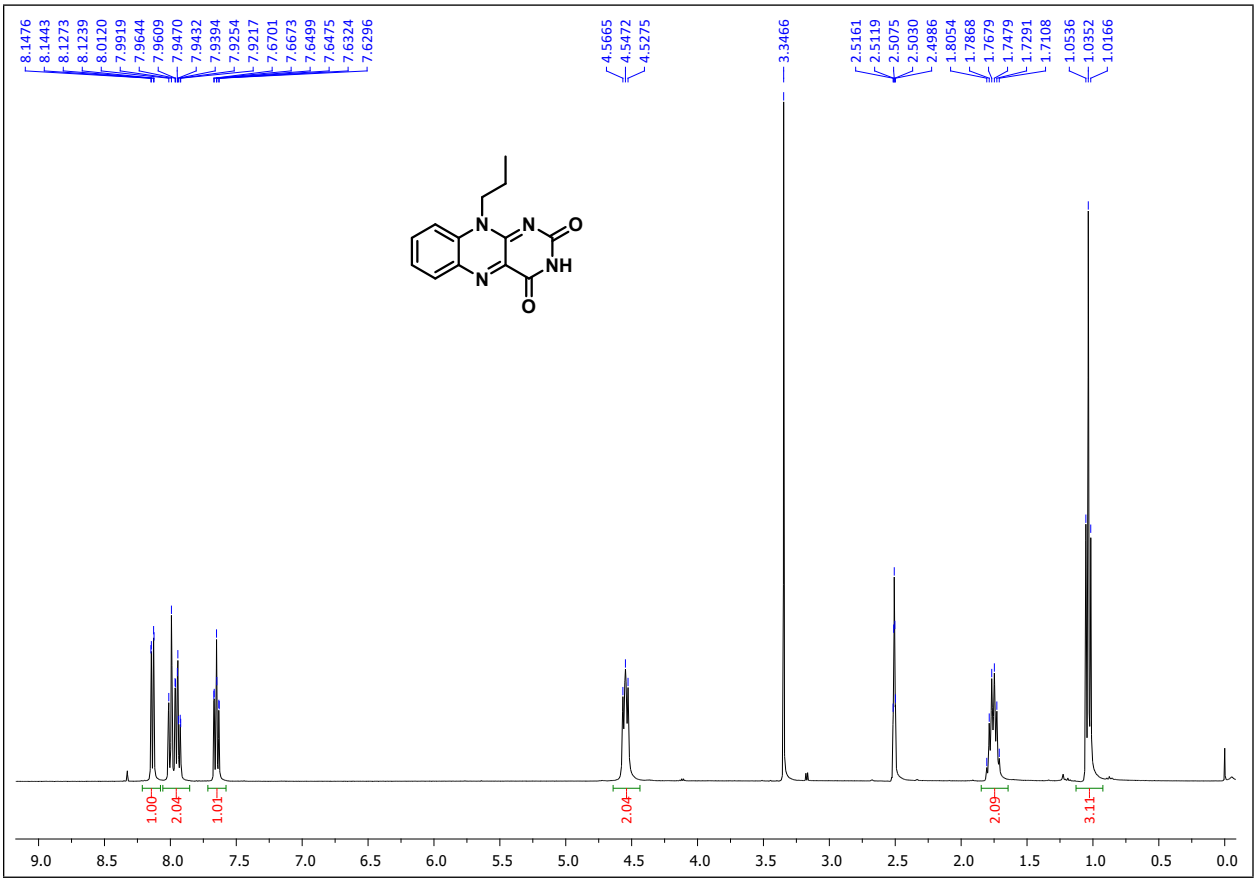


Figure S8. ^{1}H NMR of **PF** in DMSO-d_6

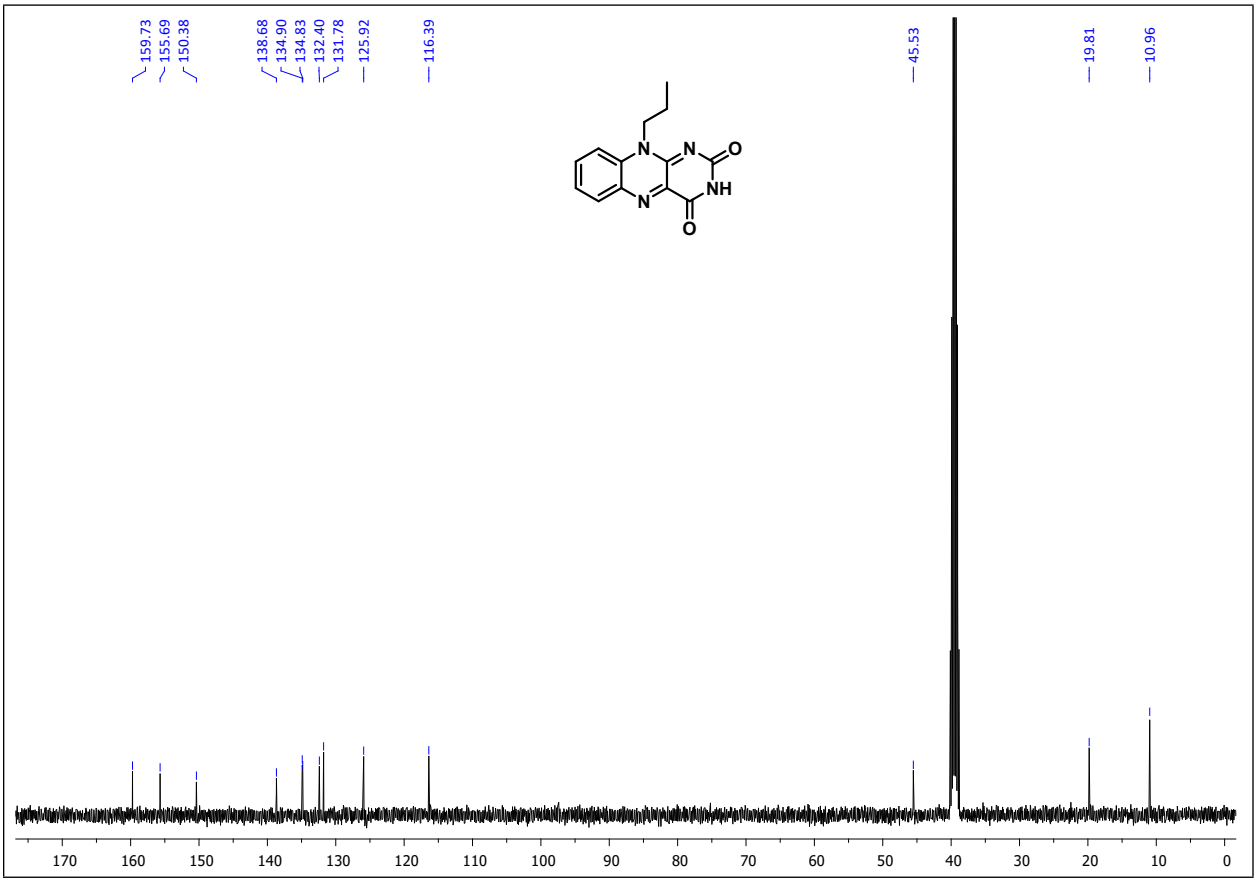


Figure S9. ^{13}C NMR of **PF** in DMSO-d_6

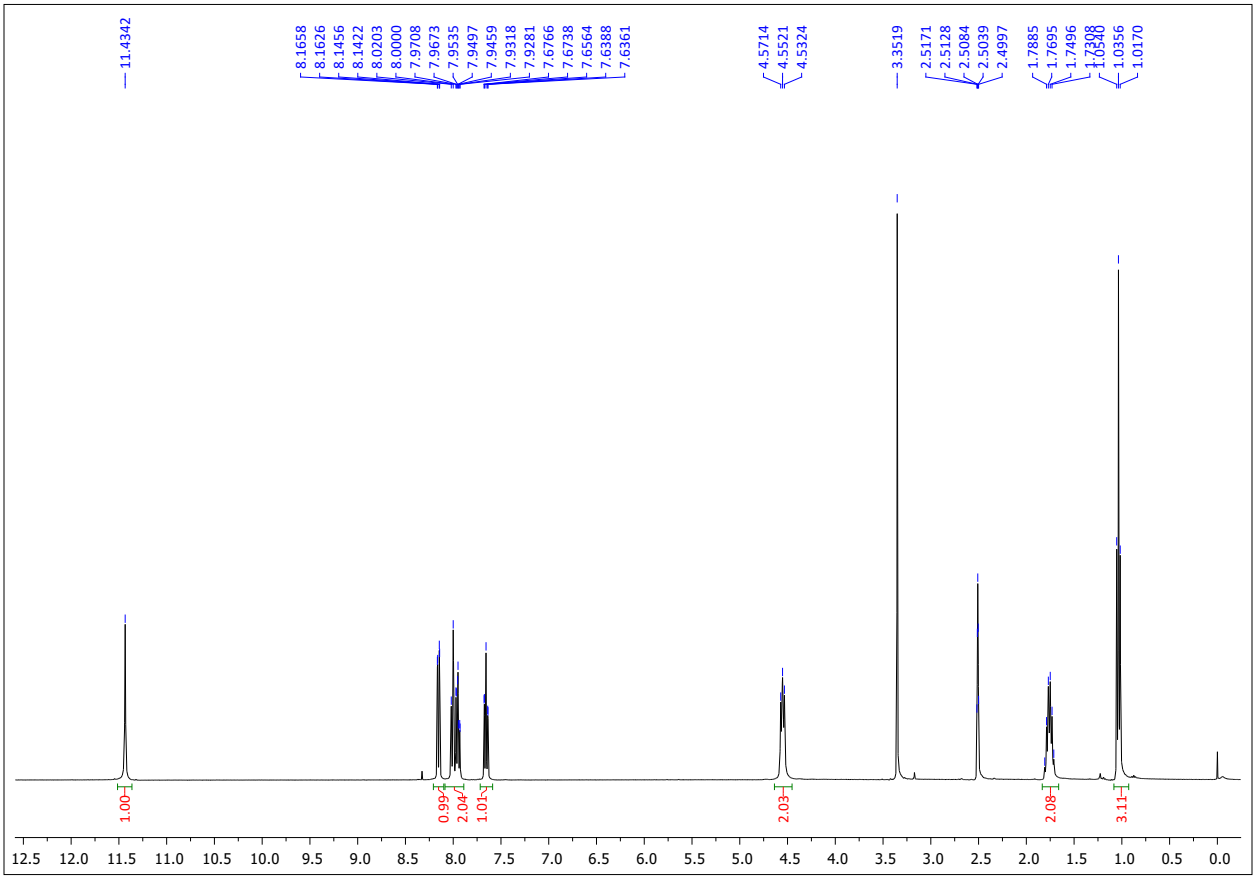


Figure S10. ^{1}H NMR of **PF + 0.37 eq $AgNO_3$** in DMSO-d_6

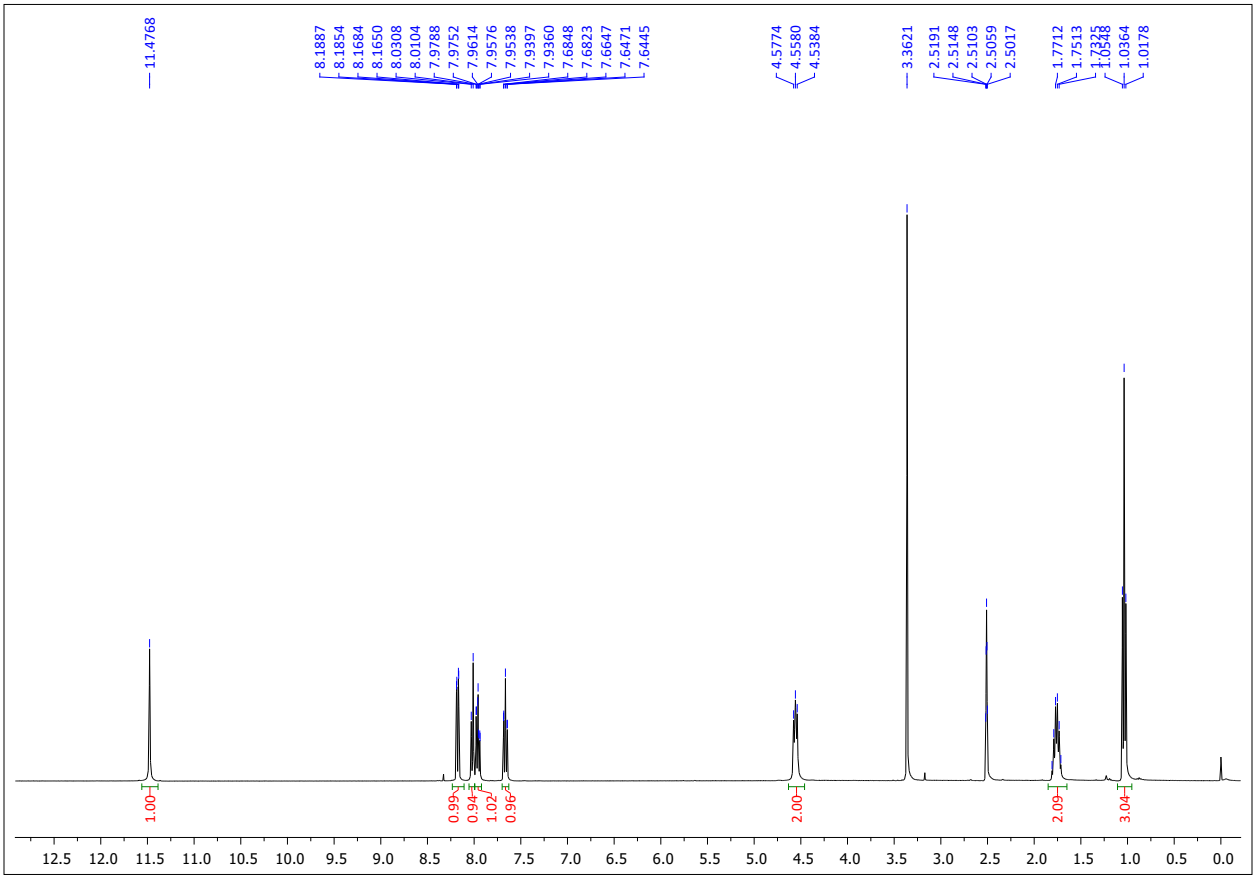


Figure S11. ^{1}H NMR of **PF + 1 eq $AgNO_3$** in DMSO-d_6

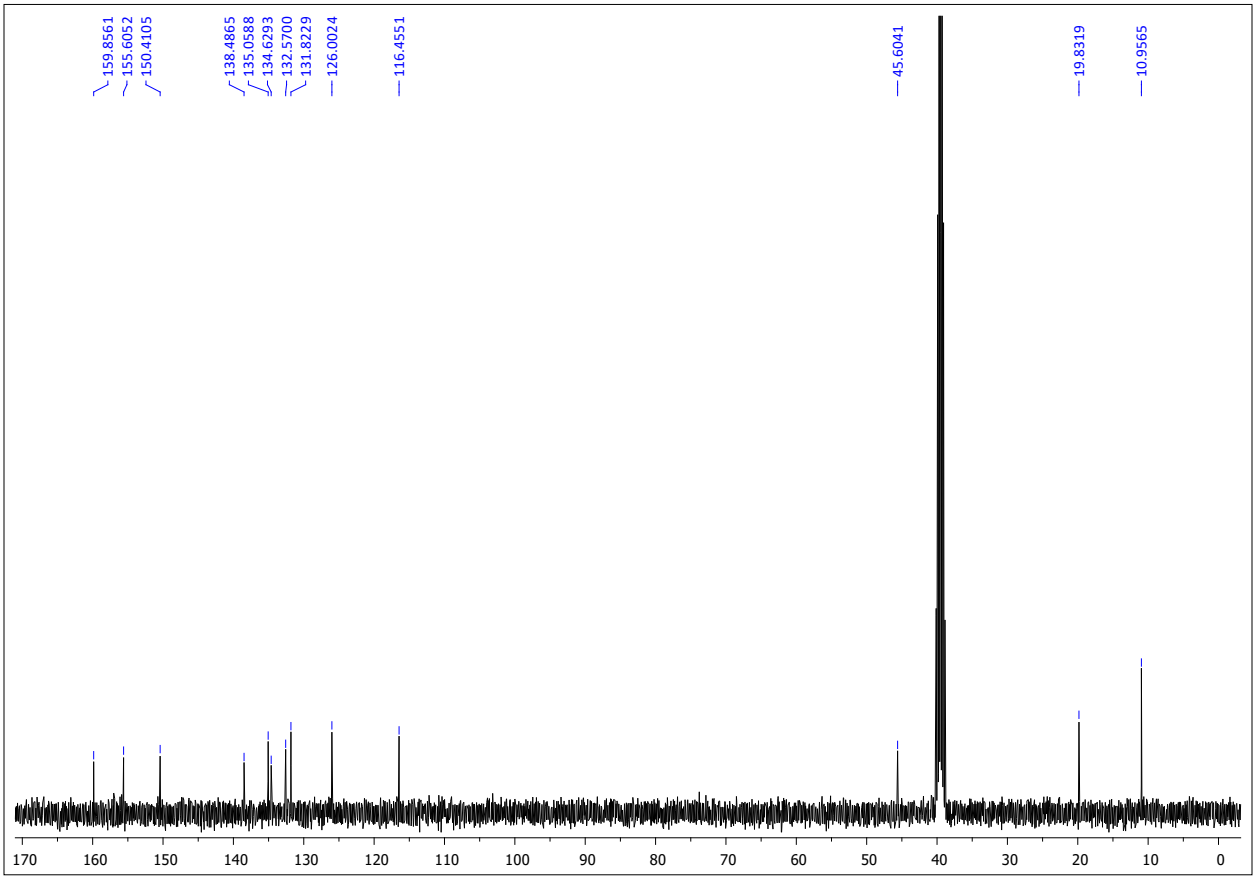


Figure S12. ^{13}C NMR of **PF + 1 eq $AgNO_3$** in DMSO-d_6

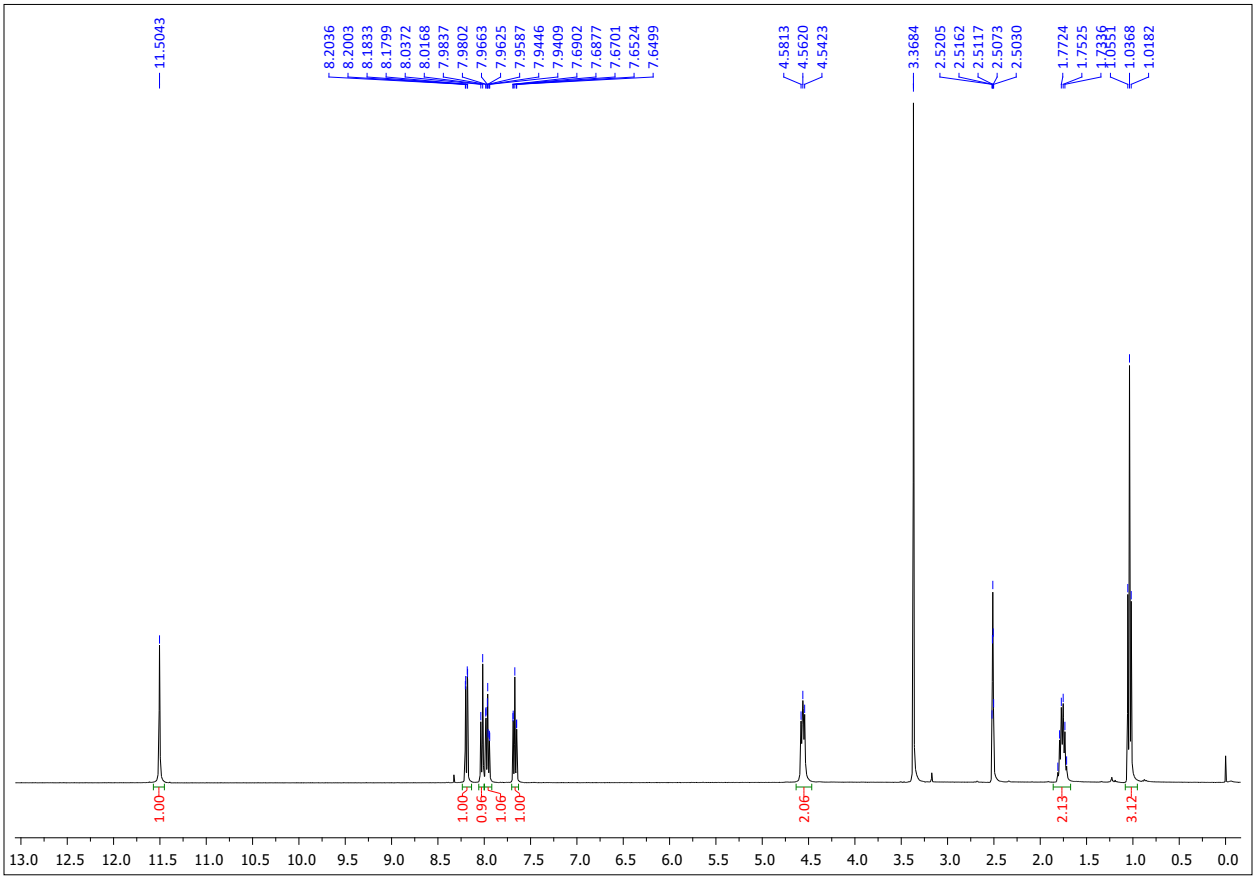


Figure S13. ^{1}H NMR of **PF + 1.6 eq $AgNO_3$** in DMSO-d_6

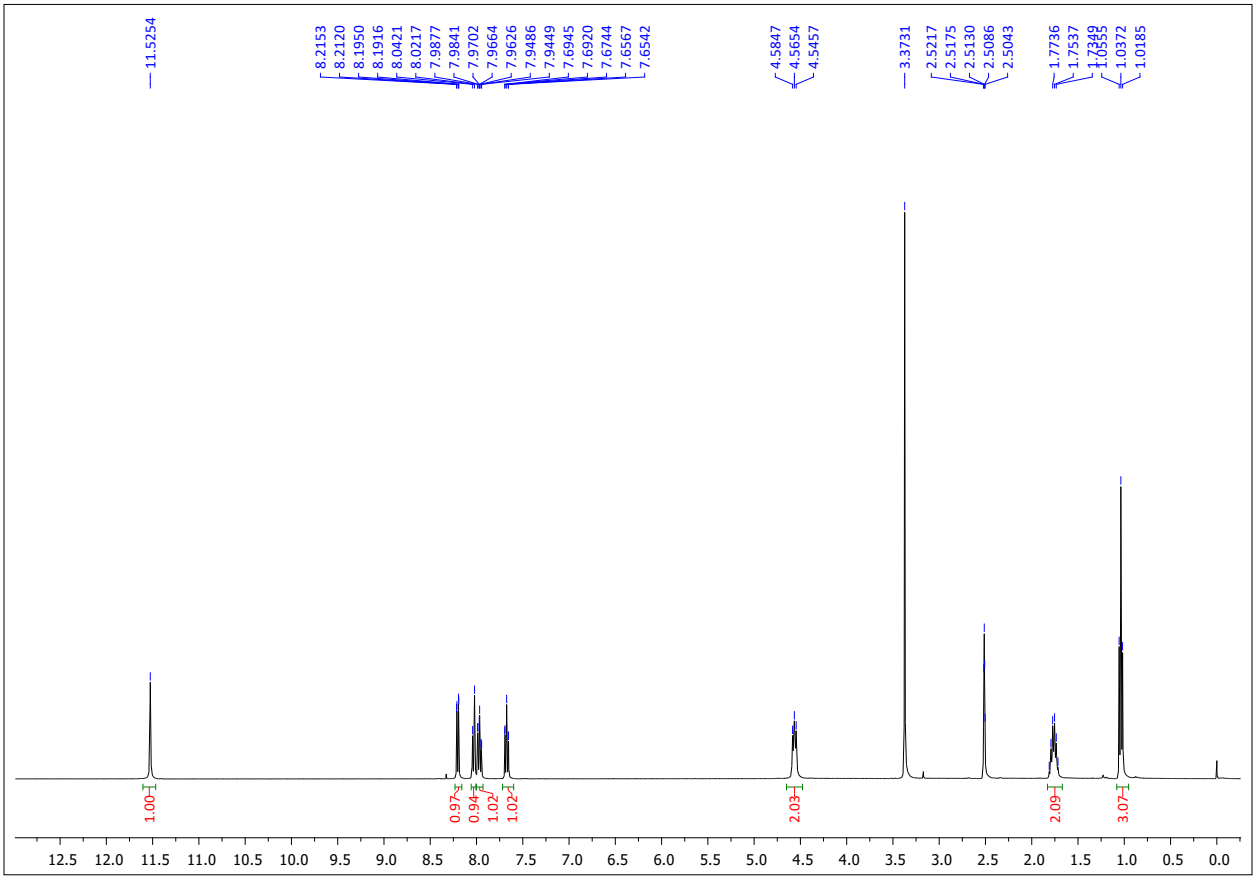


Figure S14. ^{1}H NMR of **PF + 2.22 eq $AgNO_3$** in DMSO-d_6

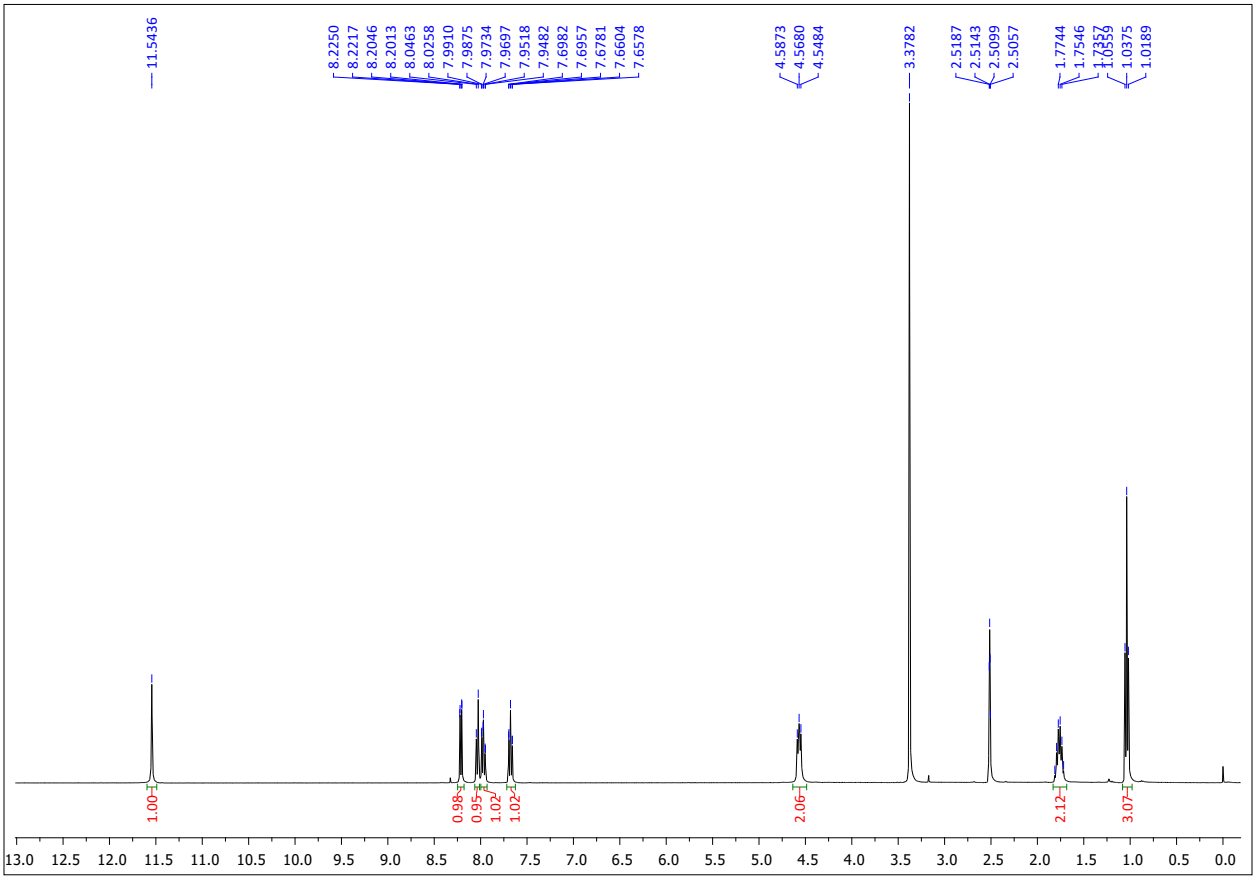


Figure S15. ^{1}H NMR of **PF + 2.83 eq $AgNO_3$** in DMSO-d_6

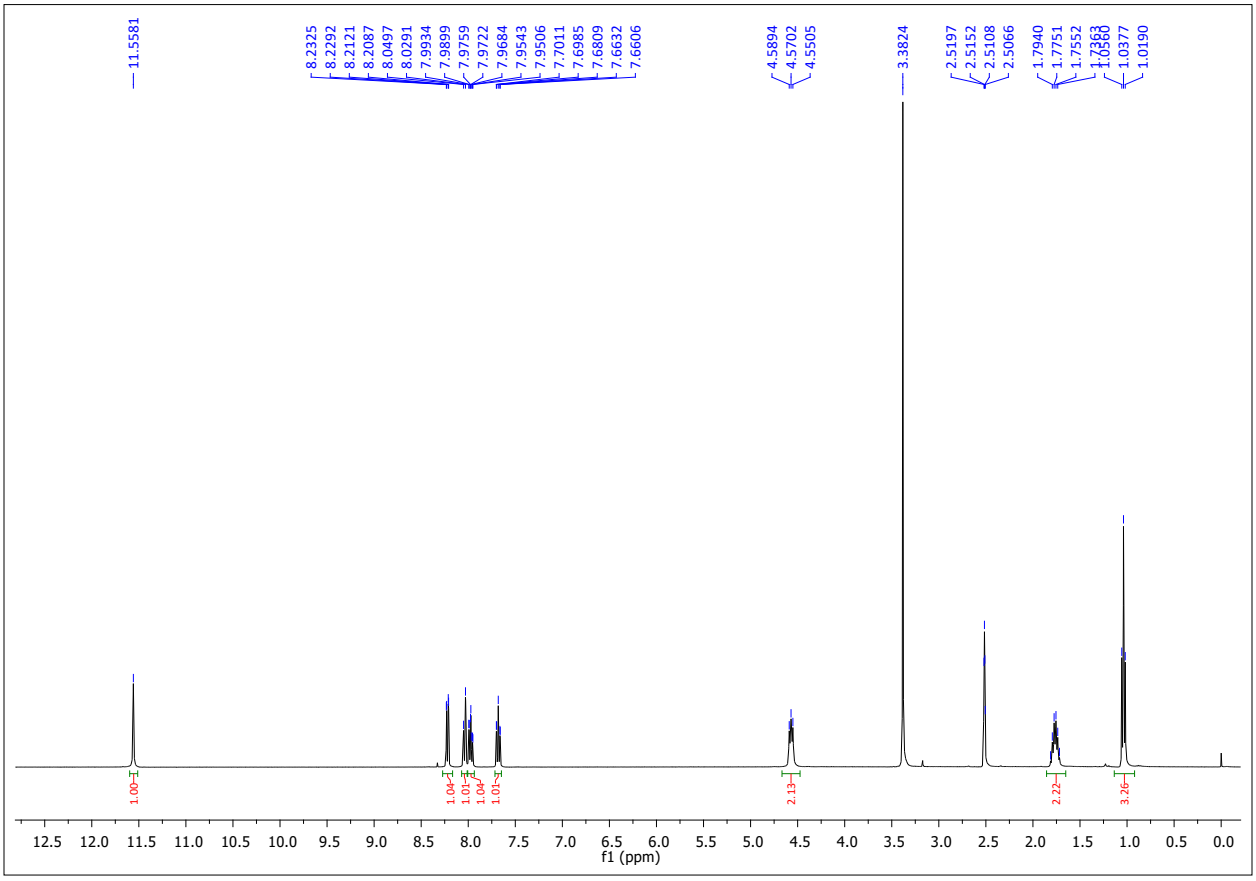


Figure S16. ^{1}H NMR of **PF + 3.48 eq $AgNO_3$** in DMSO-d_6

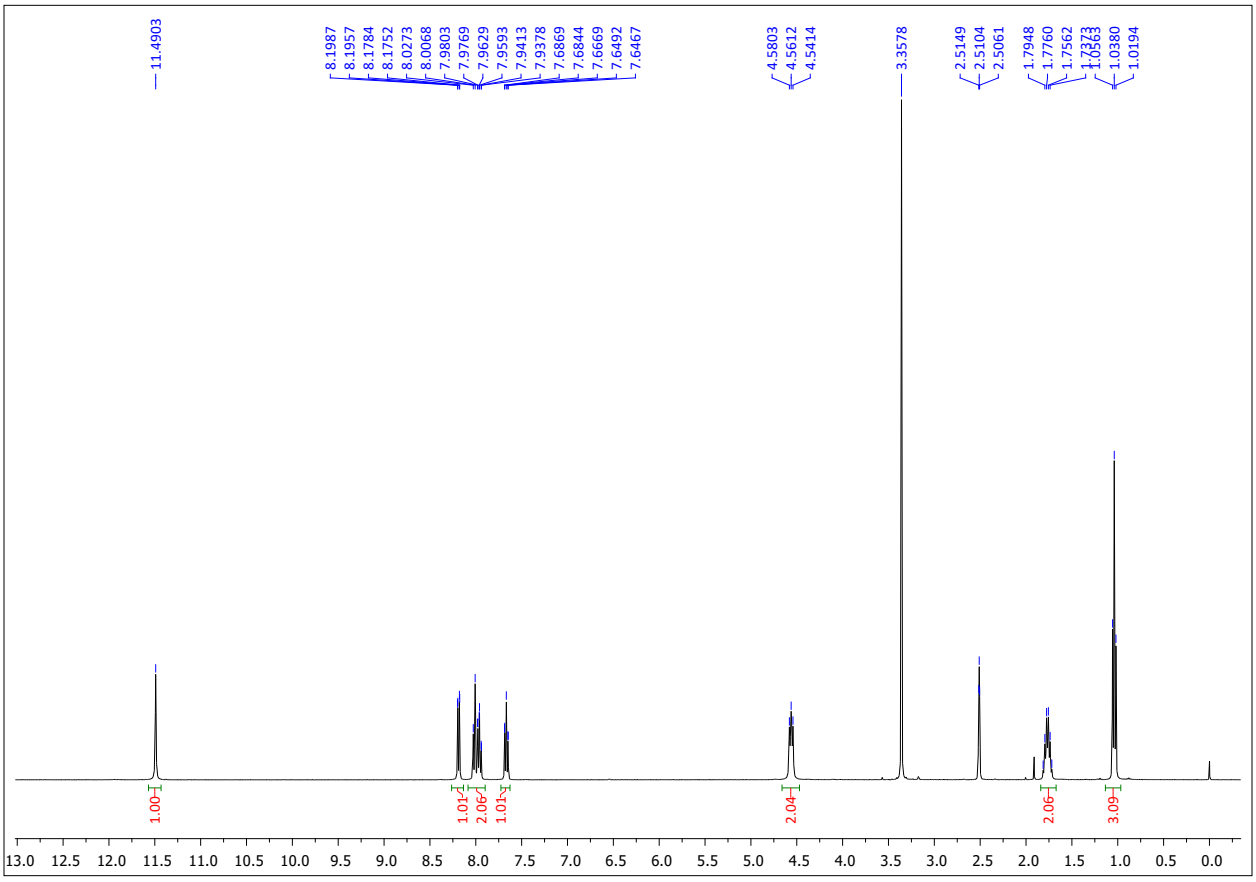


Figure S17. ^{1}H NMR of **PF + 1 eq $AgBF_4$** in DMSO-d_6

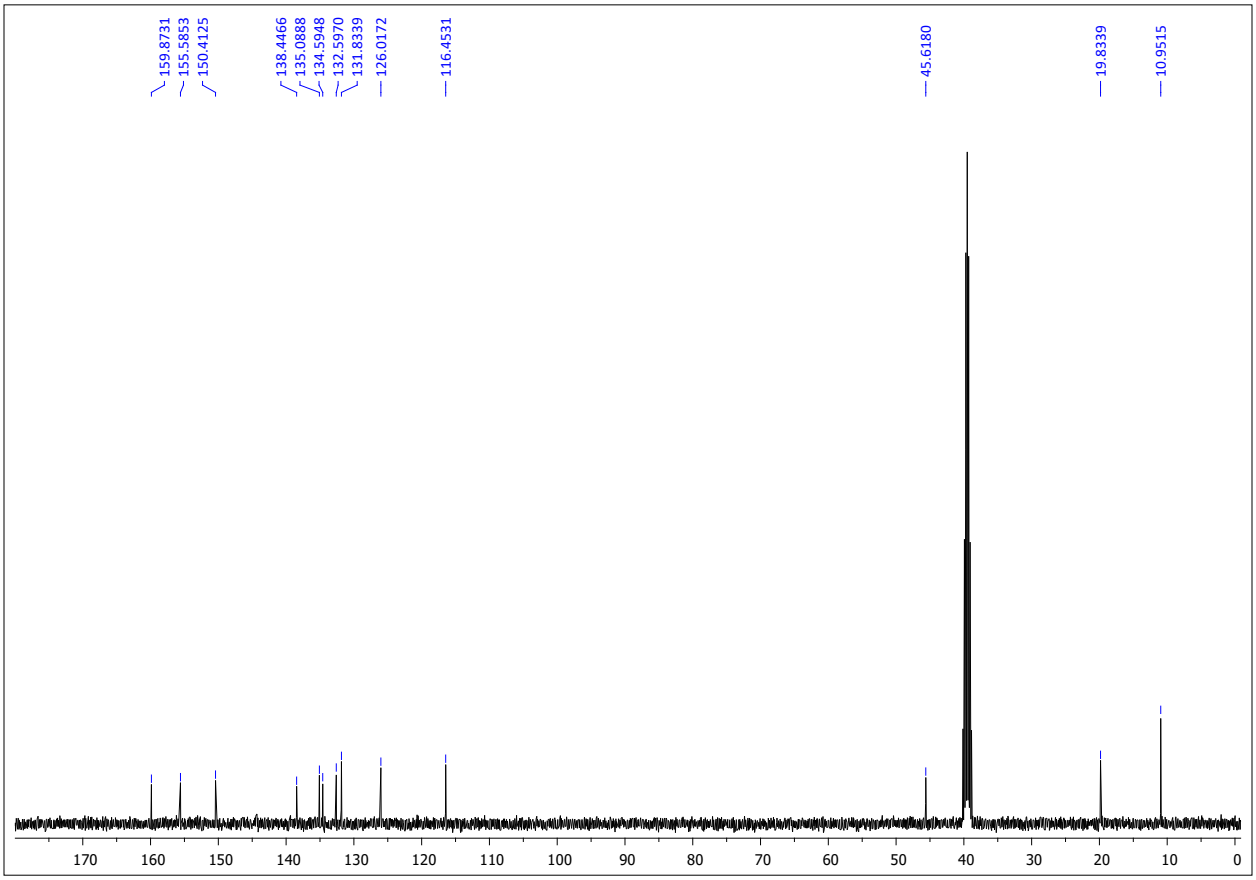


Figure S18. ^{13}C NMR of **PF + 1 eq $AgBF_4$** in DMSO-d_6

8. List of NMR Spectra

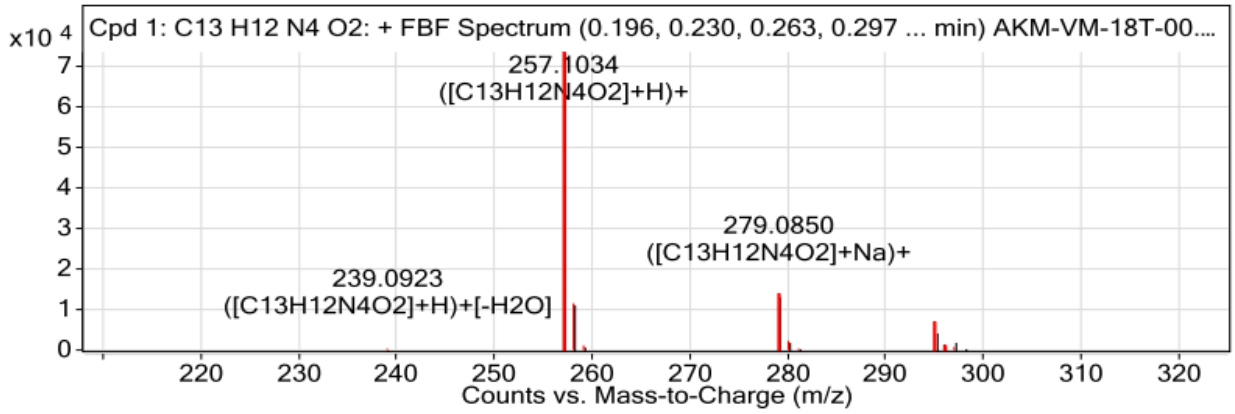


Figure S19. HRMS of **PF**

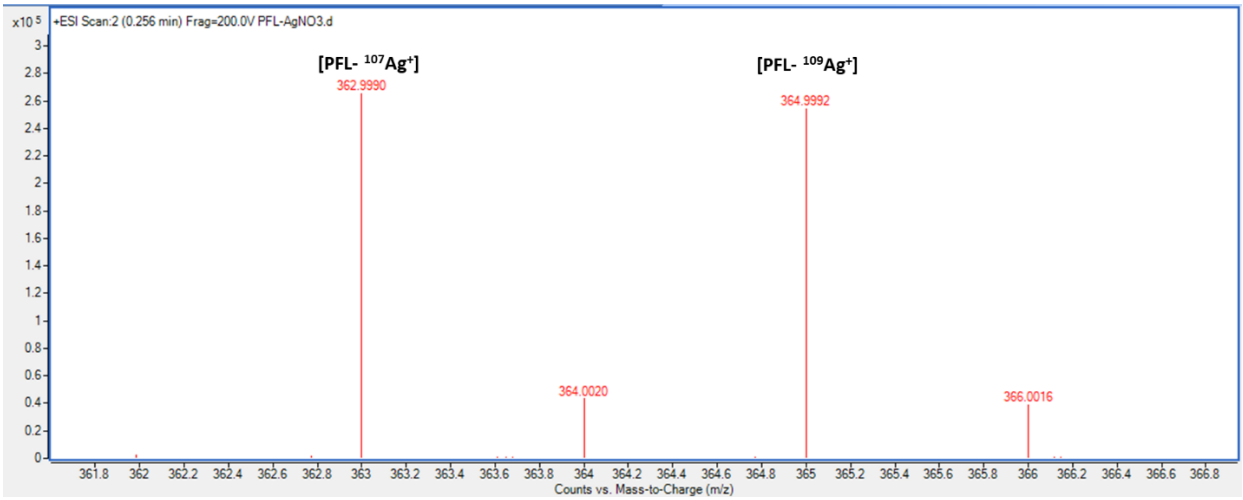


Figure S20. HRMS of **PFAg**$^{+}$ fragment of **1**

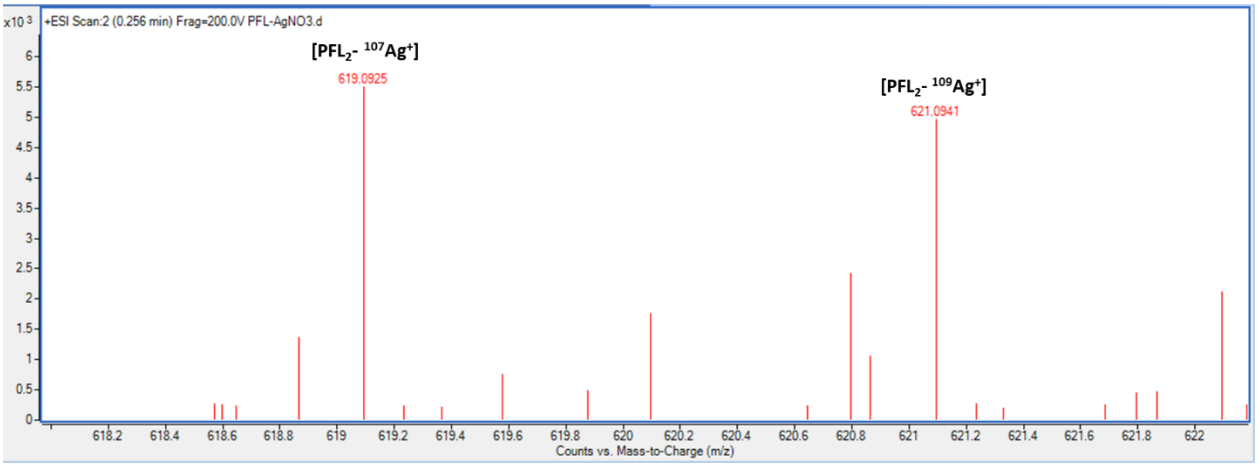


Figure S21. HRMS of $\mathbf{PF_2Ag^+}$ fragment of **1**

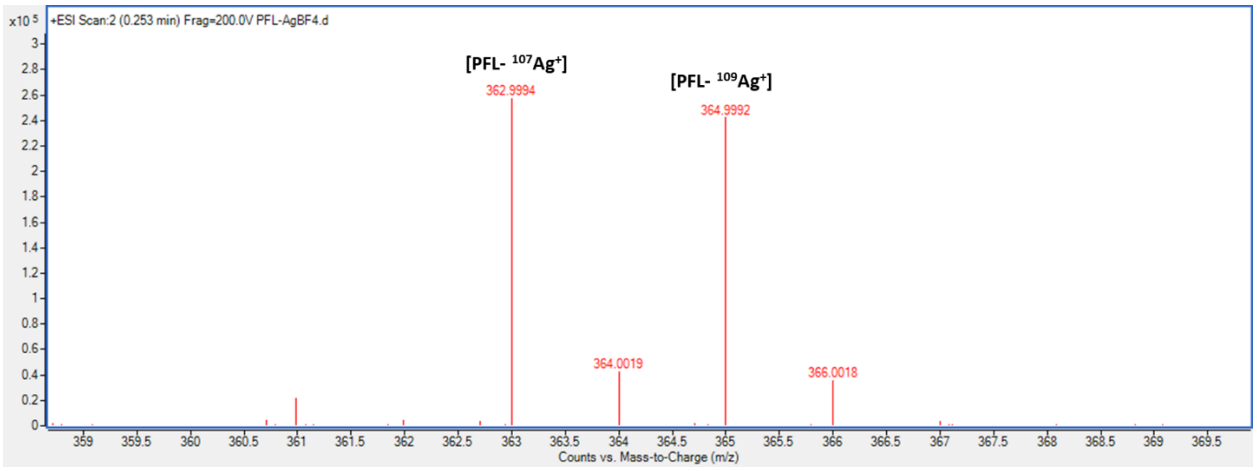


Figure S22. HRMS of $\mathbf{PFAg^+}$ fragment of **2**

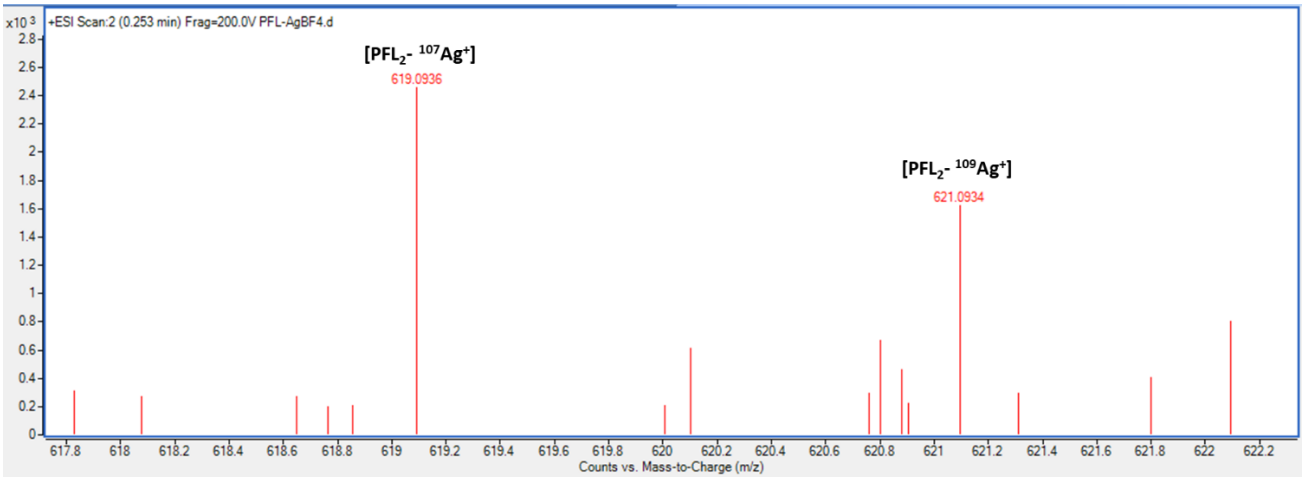


Figure S23. HRMS of $\mathbf{PF_2Ag^+}$ fragment of **2**