Supporting Information

Experimental:

General Considerations.

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun Labmaster inert atmosphere dry-box containing an atmosphere of purified nitrogen. THF-d_8, CD_2Cl_2 and C_6D_6 were purchased from Sigma Aldrich. CD_2Cl_2 was dried over CaH_2 and distilled, THF-d_8 and C_6D_6 were distilled over potassium. All glassware was stored in a 170°C oven for several hours and was degassed prior to use. Solvents were distilled over the appropriate drying agent. Anhydrous grade MeCN was obtained from Sigma-Aldrich and used without distillation but stored over 3 Å molecular sieves. Solvents were additionally tested using a ketyl test to guarantee oxygen and moisture free conditions. TMSOTf (99%) were distilled before use. $P(Pyr)_3$ [1] was synthesized following literature procedures.

NMR tubes fitted with J-Young valves were charged and sealed inside the glovebox. ^1H NMR spectra were recorded on Bruker spectrometers operating at 300, 360 MHz, ^{13}C NMR at 76 MHz MHz. ^{31}P NMR at 121.6 MHz. All ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the ^1H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard.

Infrared spectra were obtained on a Perkin Elmer Frontier instrument equipped with a diamond ATR module. Elemental analyses were carried out by Canadian Microanalytical Ltd. in Delta, British Columbia, Canada. All quantum chemical calculations were carried out using Gaussian 09. [1]

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a Bruker X8 APEX2 equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data was collected to determine the crystal system. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) on OLEX2 completed by Fourier synthesis and refined by full-matrix least-squares procedures.

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[1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Synthesis of $[AsCl(P(Pyr)_3)][OTf]_2 \bullet 0.5$ DCM: To a solution of $AsCl_3$ (207 µL, 2.5 mmol) in 10 mL of DCM, tripyridylphosphine (800 mg, 3 mmol) was added at room temperature. To this mixture TMSOTf (1405 µL, 7.5 mmol) was added over a time period of 5 minutes which resulted in the precipitation of a colourless solid. The mixture was stirred for 16 hours and the solid was isolated by filtration and was washed with 4 mL of DCM and 2 mL of diethyl ether to isolate 1.62 g (91 %) of a colourless solid of the composition $C_{17}H_{12}AsClF_6N_3O_6PS_2 \bullet 0.5\ CH_2Cl_2$.

EA [calc. for $C_{17}H_{12}AsClF_6N_3O_6PS_2 \bullet 0.5\ CH_2Cl_2$ (MW = 716.2 g/mol)]: C, 29.35; H, 1.83; N, 5.87

EA [found.]: C, 29.25; H, 2.00; N 6.02

Mp. 153°C (dec.)

^{1}H NMR (300 MHz, MeCN-d3): δ = 9.61 (d, *J* = 5.7 Hz, 3H), 8.58 (t, *J* = 8.6 Hz, 3H), 8.47 (t, *J* = 7.7 Hz, 3H), 8.08 (t, *J* = 6.8 Hz, 3H).

^{19}F NMR (283 MHz, MeCN-d3): δ = - 79.28

^{31}P NMR (121.6 MHz, MeCN-d3): δ = - 46.1 (lb = 32.07 Hz)

^{13}C NMR (76 MHz, CD_3CN): δ = 152.5 (s), 151.1 (d, $J_{P,C}$ = 24.4 Hz, 1C), 147.0 (d, $J_{P,C}$ = 14.3 Hz, 1C), 137.2 (d, $J_{P,C}$ = 47.4 Hz, 1C), 129.89 (s)

Synthesis of $[As(PPyr_3)][OTf]_3 \bullet$ MeCN: To a solution of **$[AsCl(PPyr_3)][OTf]_2$** (400 mg, 0.56 mmol) in 3 mL of acetonitrile, one equivalent of TMS(OTf) (116 µL, 0.6 mmol) was added by means of a micro pipette. The reaction mixture was stirred for 2 hours (which can yield a light blue colour of the reaction mixture) after that the solution was layered with 5 mL of diethyl ether and placed in the freezer for 16 hours. The white crystalline solid was isolated by filtration and was washed with 2 mL of diethyl ether. The mother liquor was placed in the freezer again to isolate a total of 470 mg (98 %) of the composition $C_{20}H_{15}AsF_9N_4O_9PS_3 \bullet 0.8\ C_2H_3N_1$.

EA [calc. for $C_{20}H_{15}AsF_9N_4O_9PS_3 \bullet 0.8\ C_2H_3N_1$ MW = 861.3 g/mol]: C, 28.70; H, 1.77; N, 6.49

EA [found.]: C 28.70; H 1.74; N 6.63

Mp. 188 °C (dec.)

^{1}H NMR (300 MHz, MeCN-d3): δ = 9.67 (*pseudo*-d, *J* = 6.2 Hz, 3H), 8.75 (m, 3H), 8.64 (tdd, *J* = 7.7, 2.2 and 1.5 Hz, 3H), 8.23 (dddd, *J* = 7.7, 6.2, 1.5, 1.0 Hz, 3H).

^{19}F NMR (283 MHz, MeCN-d3): δ = - 75.84

^{31}P NMR (121.6 MHz, MeCN-d3): δ = - 62.8

^{13}C NMR (76 MHz, CD_3CN) : δ = 153.8 (s), 149.43 (d, $J_{P,C}$ = 13.2 Hz, 1C), 148.80 (d, $J_{P,C}$ = 29.5 Hz, 1C), 138.30 (d, $J_{P,C}$ = 44.4 Hz, 1C) 130.4 (s).

$[PPyr_3SbF][OTf]_2$: Trispyridylphosphine (133 mg, 0.5 mmol) was dissolved in 4 mL of DCM and was added to a solution of $[SbF(OTf)_2]$ (220 mg, 1 mmol) in acetonitrile. The reaction mixture was stirred for 2 hours, layered with diethyl ether and placed in the freezer to isolate an off white solid 520 mg (74 %) of the composition $C_{17}H_{12}F_7N_3O_6PS_2Sb$

EA [calc. for $C_{17}H_{12}F_7N_3O_6PS_2Sb$ MW = 704.14 g/mol]: C, 29.00; H, 1.72; N, 5.97

EA [found.]: C, 29.87; H, 1.94; N, 5.80

Mp. 154°C (dec.)

^{1}H NMR (300 MHz, MeCN-d3): δ = 9.28 (d, *J* = 5.2 Hz, 1H), 8.54 (dd, *J* = 8.2, 10.2 Hz, 1H), 8.35 (t, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 12.9 Hz, 1H).

^{19}F NMR (283 MHz, MeCN-d3): δ = -79.2 (s, OTf), –68.7 (s, SbF, lb = 273 Hz)

^{31}P NMR (121.6 MHz, MeCN-d3): δ = - 36.1 (s)

^{13}C NMR (76 MHz, CD_3CN): δ = 151.22 (d, *J* = 22.2 Hz), 150.8 (s), 144.20 (d, *J* = 15.0 Hz), 136.20 (d, *J* = 52.2 Hz), 128.7 (s).

[PPyr$_3$Sb][OTf]$_3$: Trispyridylphosphine (265 mg, 1 mmol) was dissolved in 4 mL of DCM and was added to a solution of [$SbF(OTf)_2$] (439 mg, 1 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred while one equivalent of TMSOTf (94 µL, 0.5 mmol) was added. The reaction mixture was layered with diethylether and was left unstirred at room temperature for 16 hours to isolate 510 mg of a colourless crystalline solid. The mother liquor was placed in the freezer to isolate another 160 mg of the product. Combined yield 670 mg (78 %) of the composition $C_{18}H_{12}F_9N_3O_9PSbS_3 \bullet 0.8C_2H_3N_1$.

EA [calc. for $C_{18}H_{12}F_9N_3O_9PSbS_3 \bullet 0.8C_2H_3N_1$ MW = 854.73 g/mol]: C, 25.92; H, 1.45; N, 5.04

EA [found.]: C, 29.87; H, 1.94; N, 5.80

Mp. 265°C (dec.)

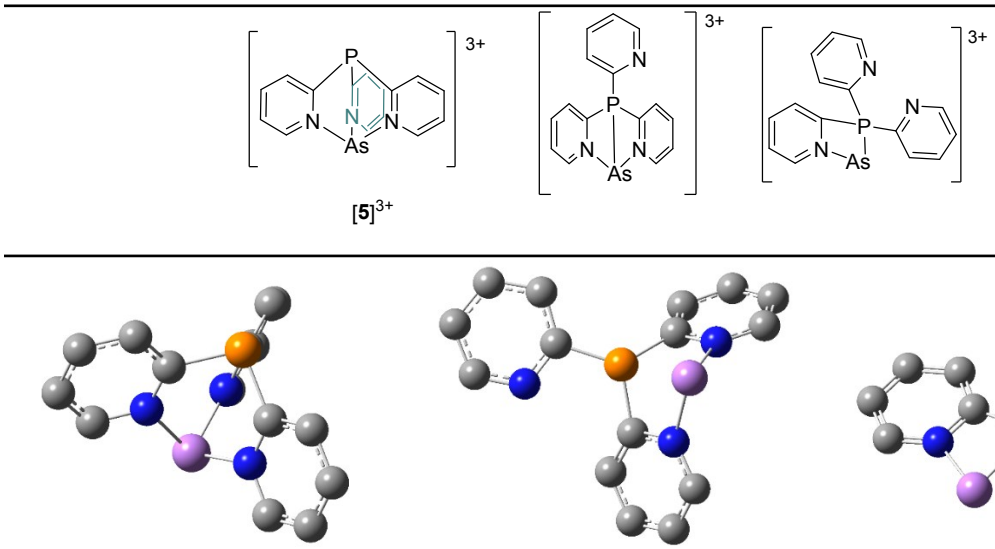
^{1}H NMR (300 MHz, MeCN-d3): δ = 9.35 (dd, *J* = 1.0, 5.8 Hz, 1H), 8.65 (dddd, *J* = 11.1, 7.9, 0.8, 0.6 Hz, 1H), 8.45 (tt, *J* = 7.8, 1.8 Hz, 1H), 8.10 (dddd, *J* = 7.6, 6.1, 1.25, 0.9 Hz, 1H).

^{19}F NMR (283 MHz, MeCN-d3): δ = -79.13 (s, OTf)

^{31}P NMR (121.6 MHz, MeCN-d3): δ = -42.7 (s)

^{13}C NMR (76 MHz, CD_3CN): δ = 151.3 (s), 149.6 (d, *J* = 25.0 Hz), 145. 0 (d, *J* = 14.9 Hz), 136.2 (d, *J* = 50.9 Hz), 128.6 (s).

Once formed, $[\mathbf{5}_{\mathbf{AsP}}][OTf]_3$ is a rather inert complex, to highlight the dissociation of one or two pyridine ligands calculation using DFT on the PBEPBE/6-311+G(d,p) level of theory have been performed. The η^2 coordinated $P(Pyr)_3$ complex is 157 kJ/mol higher in energy and is stabilized by a significant donation of the phosphine to the arsenic centre, indicated by the As – P distance of 2.4644 Å ($^{cov}\Sigma_{P,As}$ = 2.31 Å, $^{vdW}\Sigma_{P,As}$ = 3.65 Å).[2] Even though this does not overcome the increased energy from the third pyridine donation. This effect is even more pronounced in the case where only one pyridine is bound, which results in a shorter As – P distance (2.3686 Å), this structure has been found to be 266 kJ/mol higher in energy than the isolated complex $[\mathbf{5}_{\mathbf{AsP}}]^{3+}$ and is therefore very unlikely to been observed. The rather large energy differences support the fact, that $[\mathbf{5}_{\mathbf{AsP}}]^{3+}$ is an inert complex and a dissociation of the ligand is not very likely under normal conditions, which allows to study the reactivity of the cationic arsenic centre and it's lone pair.

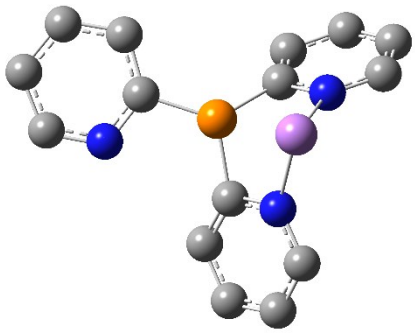


Energy difference compared to the global minimum $[\mathbf{5}_{\mathbf{AsP}}]^{3+}$	+ 157 kJ/mol	+ 266 kJ/mol

Scheme 1: η^3, η^2 and η^1-coordination of $P(Pyr)_3$ at arsenic trications.and the difference compared to the sum of electronic and thermal Free Energies of $[\mathbf{5}_{\mathbf{AsP}}]^{3+}$

Optimizations

INT1



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C	1.73642631	-3.21247984	1.74103897
C	2.89438535	-2.99877049	0.98247078
C	2.90781362	-2.00919040	-0.00758699
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N	1.28427381	1.61676899	-0.25368143
C	2.07517969	2.70803037	-0.09228300
C	1.70520077	3.67895592	0.84414902
C	0.52840506	3.51977133	1.58788481
C	0.12763533	1.43999256	0.47703929
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C	-4.23124825	0.82925326	0.10753113
C	-4.99834361	-0.33303126	-0.14204463
C	-4.35435793	-1.55244310	-0.39061358
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H	3.77765689	-1.81126370	-0.63972740
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H	2.96693520	2.79230374	-0.71897028
H	2.33918507	4.56084065	0.96855106
H	0.22796377	4.28837081	2.30601786
H	-4.70886211	1.79343873	0.30167300
H	-6.08947851	-0.26600008	-0.15283998
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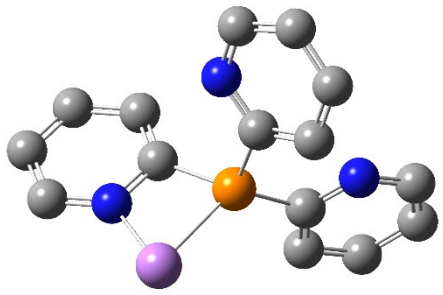
INT2



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Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies=
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Sum of electronic and thermal Free Energies=
-3317.715364

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N	2.68894469	-0.68398461	-0.23653259
C	1.40084709	-2.71621677	-0.09736497
C	2.55980849	-3.44062369	-0.41077669
C	3.76531913	-2.76796879	-0.63356872
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As	-1.48468038	-0.32093134	1.94423338
C	-1.72457431	-0.40655050	-2.11221373
N	-2.38787085	-0.37434479	0.20594719
C	-3.70688413	-0.46550846	-0.10244256
C	-4.07770929	-0.53788253	-1.44852004
C	-3.09493302	-0.51649075	-2.45010923
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C	0.75863053	1.58043109	0.11044427
N	0.08190828	2.31785417	-0.75298188
C	0.51824753	3.53516918	-1.08292559
C	1.71597836	4.04465849	-0.50964061
C	2.39114174	3.29175863	0.45379856
C	1.90759107	2.02476820	0.81721539
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H	2.51760873	-4.53235787	-0.47411916

H	4.69066135	-3.30949943	-0.84997843
H	4.73385743	-0.79350689	-0.62710427
H	-0.95264739	-0.37921507	-2.88478577
H	-4.42622657	-0.48942057	0.72083306
H	-5.13850588	-0.61875388	-1.70075282
H	-3.38745867	-0.58058722	-3.50238951
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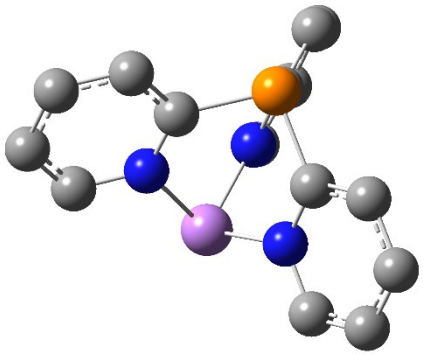
Optimized Product



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Sum of electronic and thermal Enthalpies=
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H	-0.24071678	-2.80331860	2.68917429
H	-2.30719416	1.60985212	2.68939429
H	4.50595718	2.10980944	-1.08001293
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H	-4.09507969	2.85779031	1.44776427
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$[PPyr3Bi]^{3+}$

Bi	0.00163343	0.00007171	-1.40407787
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C	3.05722046	-0.00724798	-0.67071622
C	-2.11737026	-3.63406762	0.10926151
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C	-2.03606255	3.53566541	1.50289598
C	4.20849158	-0.00990267	0.11180866
C	-2.05213831	-3.52665034	1.50229167
C	4.08190204	-0.00967471	1.50468756
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H	-2.61014948	-4.47754602	-0.38041105
H	2.68137650	-0.00642625	3.16801529
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H	-2.58824919	4.49040370	-0.37958223
H	-1.33606726	2.32381042	3.16706647
H	-2.47977999	4.30538025	2.14066375
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[PPyr3Sb]$^{3+}$

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N	0.30443326	-1.74579209	-0.33586704
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H	2.32320177	1.94313706	-2.03236188
H	0.52231068	-2.98071436	-2.03534698
H	-4.82118596	1.76581408	-0.69390526
H	0.46257210	-2.67527167	2.90766271
H	-2.54848151	0.93096309	2.90996506
H	3.94234021	3.28869742	-0.69352163
H	2.08552584	1.73486021	2.91041901
H	3.82440624	3.18420742	1.83104102
H	0.88204377	-5.05647176	-0.69840149
H	-4.67398607	1.70952577	1.83057961
H	0.85144947	-4.90429729	1.82628283

[PPyr3P]$^{3+}$

P	0.00092129	-0.00017929	-1.53685040
P	-0.00049813	0.00147317	1.71780180
N	-0.32371248	-1.52981030	-0.62944259
N	1.48823095	0.48391319	-0.62985754
N	-1.16294118	1.04578020	-0.63035797
C	1.52310890	0.49609290	0.75121545
C	-0.56183611	-2.65381942	-1.38629875
C	-0.33300547	-1.56476249	0.75142989
C	-1.19055001	1.07092725	0.75001124
C	-2.01713114	1.81364463	-1.38768736
C	2.58136146	0.83728502	-1.38663734

C	-0.82173836	-3.86900690	-0.76545011	H	2.46798802	0.79907928	-2.47403501
C	2.69673784	0.87683130	1.39280314	H	-1.00872225	-4.75099513	-1.38320655
C	-0.59186033	-2.77109849	1.39276462	H	2.73512254	0.88894035	2.48537202
C	-2.94100368	2.64512659	-0.76736601	H	-0.60251135	-2.80936431	2.48534397
C	-2.10803030	1.89628603	1.39123965	H	-3.61138829	3.24778240	-1.38532935
C	-2.99107261	2.69093021	0.63164200	H	-2.13795870	1.92250620	2.48383137
C	3.76370451	1.22070278	-0.76555577	H	-3.71156964	3.34045321	1.13792328
C	-0.83816912	-3.93365695	0.63351758	H	4.62159399	1.49772960	-1.38337549
C	3.82707592	1.24279756	0.63350583	H	-1.04058228	-4.88209532	1.14020272
H	-0.53640267	-2.53703786	-2.47366463	H	4.74956497	1.54160008	1.14043363
H	-1.92807164	1.73313129	-2.47496470				

Summary of Natural Population Analysis and Wiberg bond index matrices:

[PPyr$_3$As]$^{3+}$

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
As	1	1.51279	27.99687	3.46902	0.02132	31.48721
P	2	0.92362	9.99824	4.04437	0.03376	14.07638
N	3	-0.59131	1.99922	5.56789	0.02420	7.59131
N	4	-0.59138	1.99922	5.56796	0.02421	7.59138
N	5	-0.59129	1.99922	5.56786	0.02421	7.59129
C	6	-0.06006	1.99900	4.02194	0.03912	6.06006
C	7	0.09517	1.99916	3.88428	0.02139	5.90483
C	8	-0.06000	1.99900	4.02188	0.03912	6.06000
C	9	-0.06018	1.99900	4.02207	0.03911	6.06018
C	10	0.09514	1.99916	3.88431	0.02138	5.90486
C	11	0.09514	1.99916	3.88431	0.02138	5.90486
C	12	-0.16875	1.99916	4.15442	0.01518	6.16875
C	13	-0.17645	1.99902	4.15937	0.01807	6.17645
C	14	-0.17648	1.99902	4.15940	0.01807	6.17648
C	15	-0.16873	1.99916	4.15439	0.01518	6.16873
C	16	-0.17642	1.99902	4.15934	0.01806	6.17642
C	17	-0.04857	1.99916	4.03345	0.01596	6.04857
C	18	-0.16876	1.99916	4.15443	0.01518	6.16876
C	19	-0.04857	1.99916	4.03346	0.01596	6.04857
C	20	-0.04858	1.99916	4.03346	0.01596	6.04858
H	21	0.26254	0.00000	0.73614	0.00131	0.73746
H	22	0.26255	0.00000	0.73614	0.00131	0.73745
H	23	0.26256	0.00000	0.73613	0.00131	0.73744
H	24	0.29825	0.00000	0.70071	0.00104	0.70175
H	25	0.28808	0.00000	0.71067	0.00125	0.71192
H	26	0.28807	0.00000	0.71068	0.00125	0.71193
H	27	0.29826	0.00000	0.70070	0.00104	0.70174
H	28	0.28807	0.00000	0.71068	0.00125	0.71193
H	29	0.28902	0.00000	0.70999	0.00099	0.71098
H	30	0.29826	0.00000	0.70070	0.00104	0.70174
H	31	0.28900	0.00000	0.71001	0.00099	0.71100
H	32	0.28901	0.00000	0.71000	0.00099	0.71099
* Total *		3.00000	73.97923	93.55017	0.47059	168.00000

Atom	1	2	3	4	5	6	7	8	9
1. As	0.0000	0.0128	0.6825	0.6826	0.6826	0.0134	0.0122	0.0134	0.0134
2. P	0.0128	0.0000	0.0199	0.0199	0.0199	0.9032	0.0166	0.9031	0.9033
3. N	0.6825	0.0199	0.0000	0.0111	0.0111	0.0071	1.2445	1.2007	0.0071
4. N	0.6826	0.0199	0.0111	0.0000	0.0111	1.2007	0.0044	0.0071	0.0071
5. N	0.6826	0.0199	0.0111	0.0111	0.0000	0.0071	0.0044	0.0071	1.2008
6. C	0.0134	0.9032	0.0071	1.2007	0.0071	0.0000	0.0035	0.0174	0.0174
7. C	0.0122	0.0166	1.2445	0.0044	0.0044	0.0035	0.0000	0.0906	0.0035
8. C	0.0134	0.9031	1.2007	0.0071	0.0071	0.0174	0.0906	0.0000	0.0174
9. C	0.0134	0.9033	0.0071	0.0071	1.2008	0.0174	0.0035	0.0174	0.0000
10. C	0.0122	0.0166	0.0044	0.0044	1.2445	0.0035	0.0008	0.0035	0.0906
11. C	0.0122	0.0166	0.0044	1.2444	0.0044	0.0906	0.0009	0.0035	0.0035
12. C	0.0169	0.0013	0.0162	0.0011	0.0011	0.0029	1.4571	0.0805	0.0029
13. C	0.0228	0.0120	0.0018	0.0236	0.0018	1.4779	0.0012	0.0105	0.0105
14. C	0.0228	0.0120	0.0236	0.0018	0.0018	0.0105	0.0679	1.4779	0.0105
15. C	0.0168	0.0013	0.0011	0.0011	0.0162	0.0029	0.0003	0.0029	0.0805
16. C	0.0228	0.0120	0.0018	0.0018	0.0236	0.0105	0.0012	0.0105	1.4779
17. C	0.0040	0.0120	0.0025	0.0025	0.0882	0.0018	0.0007	0.0018	0.0357
18. C	0.0168	0.0013	0.0011	0.0162	0.0011	0.0805	0.0003	0.0029	0.0029
19. C	0.0040	0.0120	0.0882	0.0025	0.0025	0.0018	0.0509	0.0357	0.0018
20. C	0.0040	0.0120	0.0025	0.0882	0.0025	0.0357	0.0007	0.0018	0.0018

[PPyr$_3$P]$^{3+}$

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
P	1	1.41742	9.99863	3.54449	0.03946	13.58258
P	2	0.93596	9.99825	4.03225	0.03354	14.06404
N	3	-0.60177	1.99923	5.57711	0.02544	7.60177
N	4	-0.60173	1.99923	5.57706	0.02544	7.60173
N	5	-0.60180	1.99923	5.57714	0.02544	7.60180
C	6	-0.05225	1.99901	4.01374	0.03949	6.05225
C	7	0.10796	1.99918	3.87144	0.02142	5.89204
C	8	-0.05242	1.99901	4.01392	0.03949	6.05242
C	9	-0.05243	1.99901	4.01394	0.03948	6.05243
C	10	0.10794	1.99918	3.87147	0.02142	5.89206
C	11	0.10793	1.99917	3.87147	0.02142	5.89207
C	12	-0.17219	1.99916	4.15769	0.01534	6.17219
C	13	-0.17757	1.99901	4.16005	0.01851	6.17757
C	14	-0.17746	1.99901	4.15994	0.01851	6.17746
C	15	-0.17218	1.99916	4.15768	0.01534	6.17218
C	16	-0.17745	1.99901	4.15993	0.01851	6.17745
C	17	-0.03872	1.99916	4.02354	0.01602	6.03872
C	18	-0.17221	1.99916	4.15771	0.01534	6.17221
C	19	-0.03873	1.99916	4.02355	0.01602	6.03873
C	20	-0.03873	1.99916	4.02355	0.01602	6.03873
H	21	0.26930	0.00000	0.72935	0.00135	0.73070
H	22	0.26930	0.00000	0.72934	0.00135	0.73070
H	23	0.26932	0.00000	0.72933	0.00135	0.73068
H	24	0.30021	0.00000	0.69873	0.00106	0.69979
H	25	0.29041	0.00000	0.70834	0.00126	0.70959
H	26	0.29040	0.00000	0.70834	0.00126	0.70960
H	27	0.30022	0.00000	0.69872	0.00106	0.69978
H	28	0.29041	0.00000	0.70833	0.00126	0.70959
H	29	0.29024	0.00000	0.70879	0.00097	0.70976
H	30	0.30021	0.00000	0.69873	0.00106	0.69979
H	31	0.29022	0.00000	0.70881	0.00097	0.70978
H	32	0.29021	0.00000	0.70882	0.00097	0.70979
* Total *		3.00000	55.98111	93.52332	0.49557	150.00000

	Atom	1	2	3	4	5	6	7	8	9
1.	P	0.0000	0.0104	0.7305	0.7305	0.7305	0.0164	0.0130	0.0164	0.0164
2.	P	0.0104	0.0000	0.0191	0.0191	0.0191	0.9003	0.0163	0.9005	0.9005
3.	N	0.7305	0.0191	0.0000	0.0160	0.0160	0.0076	1.2178	1.1730	0.0076
4.	N	0.7305	0.0191	0.0160	0.0000	0.0160	1.1730	0.0056	0.0076	0.0076
5.	N	0.7305	0.0191	0.0160	0.0160	0.0000	0.0076	0.0056	0.0076	1.1730
6.	C	0.0164	0.9003	0.0076	1.1730	0.0076	0.0000	0.0038	0.0185	0.0185
7.	C	0.0130	0.0163	1.2178	0.0056	0.0056	0.0038	0.0000	0.0947	0.0038
8.	C	0.0164	0.9005	1.1730	0.0076	0.0076	0.0185	0.0947	0.0000	0.0185
9.	C	0.0164	0.9005	0.0076	0.0076	1.1730	0.0185	0.0038	0.0185	0.0000
10.	C	0.0130	0.0163	0.0056	0.0056	1.2178	0.0038	0.0011	0.0038	0.0947
11.	C	0.0130	0.0163	0.0056	1.2179	0.0056	0.0947	0.0011	0.0038	0.0038
12.	C	0.0139	0.0012	0.0160	0.0012	0.0012	0.0028	1.4647	0.0779	0.0029
13.	C	0.0209	0.0115	0.0020	0.0231	0.0020	1.4917	0.0014	0.0108	0.0108
14.	C	0.0209	0.0115	0.0231	0.0020	0.0020	0.0108	0.0644	1.4916	0.0108
15.	C	0.0139	0.0012	0.0012	0.0012	0.0160	0.0029	0.0003	0.0028	0.0779
16.	C	0.0209	0.0115	0.0020	0.0020	0.0231	0.0108	0.0014	0.0108	1.4915
17.	C	0.0042	0.0122	0.0028	0.0028	0.0857	0.0020	0.0010	0.0020	0.0385
18.	C	0.0139	0.0012	0.0012	0.0160	0.0012	0.0779	0.0003	0.0028	0.0028
19.	C	0.0042	0.0122	0.0857	0.0028	0.0028	0.0020	0.0558	0.0385	0.0020
20.	C	0.0042	0.0122	0.0028	0.0858	0.0028	0.0385	0.0010	0.0020	0.0020

[PPyr$_3$Sb]$^{3+}$

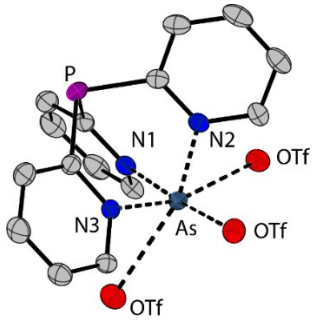
Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Sb	1	1.90136	46.00000	3.09644	0.00219	49.09864
P	2	0.89989	9.99820	4.06749	0.03442	14.10011
N	3	-0.66344	1.99925	5.63767	0.02652	7.66344
N	4	-0.66322	1.99925	5.63744	0.02652	7.66322
N	5	-0.66347	1.99925	5.63770	0.02652	7.66347
C	6	-0.07091	1.99899	4.03080	0.04112	6.07091
C	7	0.08559	1.99916	3.89295	0.02230	5.91441
C	8	-0.07111	1.99899	4.03103	0.04109	6.07111
C	9	-0.07090	1.99899	4.03081	0.04110	6.07090
C	10	0.08551	1.99916	3.89303	0.02231	5.91449
C	11	0.08556	1.99916	3.89297	0.02231	5.91444
C	12	-0.16879	1.99915	4.15484	0.01479	6.16879
C	13	-0.17855	1.99902	4.16217	0.01736	6.17855
C	14	-0.17844	1.99902	4.16207	0.01736	6.17844
C	15	-0.16879	1.99915	4.15484	0.01479	6.16879
C	16	-0.17849	1.99902	4.16212	0.01736	6.17849
C	17	-0.05600	1.99915	4.04122	0.01563	6.05600
C	18	-0.16882	1.99915	4.15487	0.01479	6.16882
C	19	-0.05599	1.99915	4.04121	0.01563	6.05599
C	20	-0.05605	1.99915	4.04127	0.01563	6.05605
H	21	0.25191	0.00000	0.74673	0.00137	0.74809
H	22	0.25193	0.00000	0.74670	0.00137	0.74807
H	23	0.25193	0.00000	0.74671	0.00137	0.74807
H	24	0.29515	0.00000	0.70378	0.00107	0.70485
H	25	0.28452	0.00000	0.71417	0.00132	0.71548
H	26	0.28453	0.00000	0.71415	0.00132	0.71547
H	27	0.29514	0.00000	0.70379	0.00107	0.70486
H	28	0.28454	0.00000	0.71415	0.00132	0.71546
H	29	0.28676	0.00000	0.71223	0.00101	0.71324
H	30	0.29514	0.00000	0.70379	0.00107	0.70486
H	31	0.28676	0.00000	0.71223	0.00101	0.71324
H	32	0.28676	0.00000	0.71223	0.00101	0.71324
* Total *		3.00000	91.98237	93.55359	0.46404	186.00000

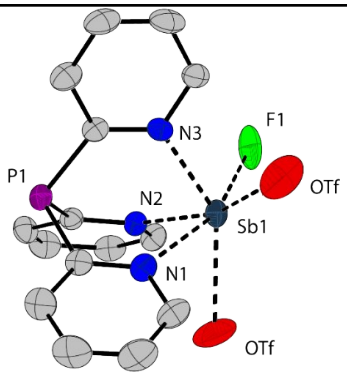
	Atom	1	2	3	4	5	6	7	8	9
1.	Sb	0.0000	0.0107	0.5337	0.5336	0.5336	0.0121	0.0114	0.0121	0.0121
2.	P	0.0107	0.0000	0.0222	0.0222	0.0222	0.9092	0.0171	0.9096	0.9094
3.	N	0.5337	0.0222	0.0000	0.0064	0.0064	0.0069	1.2695	1.2235	0.0069
4.	N	0.5336	0.0222	0.0064	0.0000	0.0064	1.2237	0.0033	0.0069	0.0069
5.	N	0.5336	0.0222	0.0064	0.0064	0.0000	0.0069	0.0033	0.0069	1.2236
6.	C	0.0121	0.9092	0.0069	1.2237	0.0069	0.0000	0.0033	0.0164	0.0164
7.	C	0.0114	0.0171	1.2695	0.0033	0.0033	0.0033	0.0000	0.0849	0.0033
8.	C	0.0121	0.9096	1.2235	0.0069	0.0069	0.0164	0.0849	0.0000	0.0163
9.	C	0.0121	0.9094	0.0069	0.0069	1.2236	0.0164	0.0033	0.0163	0.0000
10.	C	0.0114	0.0171	0.0033	0.0033	1.2695	0.0033	0.0007	0.0033	0.0849
11.	C	0.0114	0.0171	0.0033	1.2696	0.0033	0.0849	0.0007	0.0033	0.0033
12.	C	0.0178	0.0014	0.0163	0.0010	0.0010	0.0029	1.4521	0.0833	0.0029
13.	C	0.0234	0.0129	0.0016	0.0253	0.0016	1.4689	0.0011	0.0102	0.0102
14.	C	0.0234	0.0129	0.0253	0.0016	0.0016	0.0103	0.0706	1.4689	0.0102
15.	C	0.0178	0.0014	0.0010	0.0010	0.0163	0.0029	0.0003	0.0029	0.0833
16.	C	0.0234	0.0129	0.0016	0.0016	0.0253	0.0102	0.0011	0.0102	1.4689
17.	C	0.0039	0.0120	0.0020	0.0021	0.0903	0.0018	0.0006	0.0018	0.0343
18.	C	0.0178	0.0014	0.0010	0.0163	0.0010	0.0833	0.0003	0.0029	0.0029
19.	C	0.0039	0.0120	0.0903	0.0021	0.0020	0.0018	0.0474	0.0343	0.0018
20.	C	0.0039	0.0120	0.0020	0.0903	0.0020	0.0343	0.0006	0.0018	0.0018

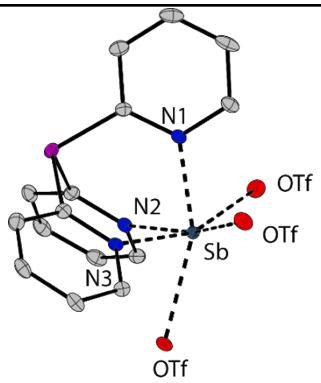
[PPyr$_3$Bi]$^{3+}$

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Bi	1	1.93430	78.00000	3.06361	0.00209	81.06570
P	2	0.88980	9.99819	4.07728	0.03473	14.11020
N	3	-0.64528	1.99923	5.62050	0.02555	7.64528
N	4	-0.64505	1.99923	5.62029	0.02553	7.64505
N	5	-0.64526	1.99923	5.62047	0.02555	7.64526
C	6	-0.07456	1.99898	4.03501	0.04057	6.07456
C	7	0.07874	1.99916	3.89995	0.02215	5.92126
C	8	-0.07442	1.99898	4.03485	0.04059	6.07442
C	9	-0.07444	1.99898	4.03488	0.04059	6.07444
C	10	0.07875	1.99916	3.89994	0.02215	5.92125
C	11	0.07879	1.99916	3.89990	0.02215	5.92121
C	12	-0.16866	1.99915	4.15480	0.01471	6.16866
C	13	-0.17897	1.99902	4.16282	0.01713	6.17897
C	14	-0.17901	1.99902	4.16285	0.01714	6.17901
C	15	-0.16866	1.99915	4.15480	0.01471	6.16866
C	16	-0.17901	1.99902	4.16285	0.01714	6.17901
C	17	-0.06153	1.99915	4.04674	0.01565	6.06153
C	18	-0.16863	1.99915	4.15476	0.01471	6.16863
C	19	-0.06152	1.99915	4.04673	0.01564	6.06152
C	20	-0.06150	1.99915	4.04671	0.01565	6.06150
H	21	0.24673	0.00000	0.75188	0.00140	0.75327
H	22	0.24673	0.00000	0.75187	0.00140	0.75327
H	23	0.24679	0.00000	0.75182	0.00139	0.75321
H	24	0.29337	0.00000	0.70556	0.00107	0.70663
H	25	0.28296	0.00000	0.71574	0.00130	0.71704
H	26	0.28297	0.00000	0.71573	0.00130	0.71703
H	27	0.29337	0.00000	0.70556	0.00107	0.70663
H	28	0.28297	0.00000	0.71573	0.00130	0.71703
H	29	0.28562	0.00000	0.71336	0.00102	0.71438
H	30	0.29338	0.00000	0.70555	0.00107	0.70662
H	31	0.28562	0.00000	0.71336	0.00102	0.71438
H	32	0.28563	0.00000	0.71335	0.00102	0.71437
* Total *		3.00000	123.98227	93.55924	0.45848	218.00000

Atom	1	2	3	4	5	6	7	8	9
1. Bi	0.0000	0.0116	0.5150	0.5152	0.5149	0.0114	0.0110	0.0115	0.0115
2. P	0.0116	0.0000	0.0229	0.0229	0.0229	0.9107	0.0173	0.9105	0.9106
3. N	0.5150	0.0229	0.0000	0.0051	0.0051	0.0067	1.2830	1.2371	0.0067
4. N	0.5152	0.0229	0.0051	0.0000	0.0051	1.2370	0.0030	0.0067	0.0067
5. N	0.5149	0.0229	0.0051	0.0051	0.0000	0.0067	0.0030	0.0067	1.2371
6. C	0.0114	0.9107	0.0067	1.2370	0.0067	0.0000	0.0032	0.0159	0.0159
7. C	0.0110	0.0173	1.2830	0.0030	0.0030	0.0032	0.0000	0.0816	0.0032
8. C	0.0115	0.9105	1.2371	0.0067	0.0067	0.0159	0.0816	0.0000	0.0160
9. C	0.0115	0.9106	0.0067	0.0067	1.2371	0.0159	0.0032	0.0160	0.0000
10. C	0.0110	0.0173	0.0030	0.0030	1.2830	0.0032	0.0006	0.0032	0.0815
11. C	0.0110	0.0173	0.0030	1.2831	0.0030	0.0815	0.0006	0.0032	0.0032
12. C	0.0191	0.0015	0.0165	0.0009	0.0009	0.0029	1.4485	0.0847	0.0029
13. C	0.0236	0.0133	0.0015	0.0254	0.0015	1.4628	0.0010	0.0101	0.0101
14. C	0.0236	0.0133	0.0254	0.0015	0.0015	0.0101	0.0728	1.4628	0.0101
15. C	0.0191	0.0015	0.0009	0.0009	0.0165	0.0029	0.0003	0.0030	0.0847
16. C	0.0236	0.0133	0.0015	0.0015	0.0254	0.0101	0.0011	0.0101	1.4628
17. C	0.0037	0.0120	0.0019	0.0019	0.0918	0.0017	0.0005	0.0017	0.0330
18. C	0.0192	0.0015	0.0009	0.0165	0.0009	0.0846	0.0003	0.0030	0.0030
19. C	0.0037	0.0120	0.0918	0.0019	0.0019	0.0017	0.0447	0.0330	0.0017
20. C	0.0037	0.0120	0.0019	0.0918	0.0019	0.0330	0.0005	0.0017	0.0017



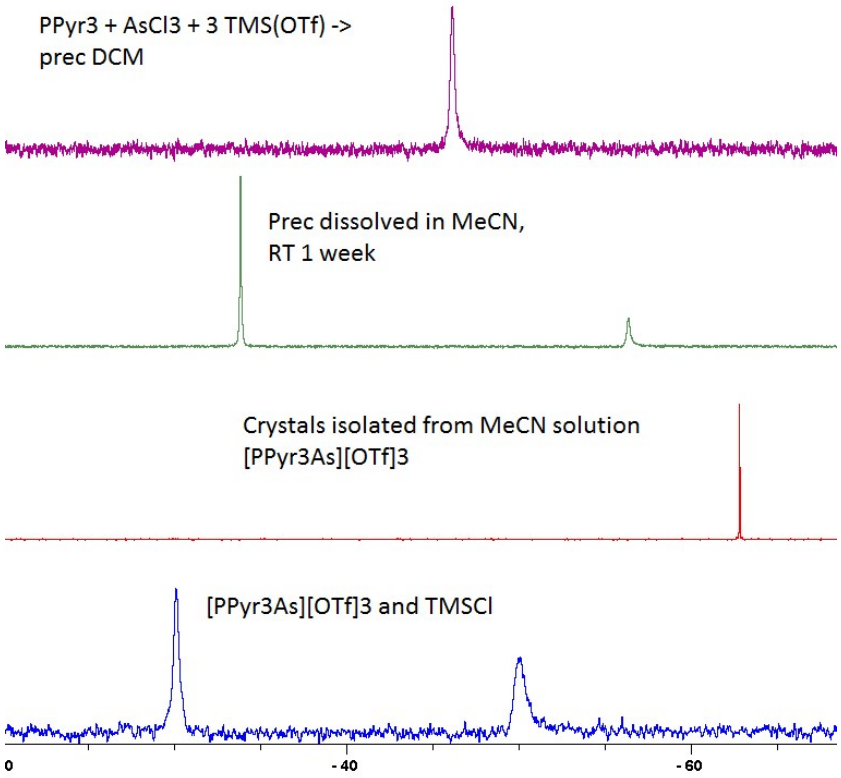




Identification code	[**1**$_{As}$][OTf]$_3$ • MeCN	[**2**$_{SbF}$](OTf)$_2$ • (MeCN)$_2$	[**1**$_{Sb}$](OTf)$_3$ • (MeCN)$_{0.5}$
Empirical formula	$C_{40}H_{30}As_2F_{18}N_8O_{18}P_2S_6$	$C_{21}H_{18}F_7N_5O_6PS_2Sb$	$C_{19}H_{13.5}F_9N_{3.5}O_9PS_3Sb$
Formula weight	1656.86	786.24	854.73
Temperature/K	173.15	173.05	100.01(10)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	Cc
a/Å	12.0563(6)	14.1583(3)	21.6061(2)
b/Å	12.0768(6)	15.6137(3)	12.18356(10)
c/Å	12.0815(6)	13.3459(3)	21.5114(2)
α/°	87.1950(10)	90	90
β/°	62.1340(10)	95.5100(10)	91.2212(9)
γ/°	73.9630(10)	90	90
Volume/Å^3	1487.92(13)	2936.66(11)	5661.34(9)
Z	1	4	8
ρ_{calc}g/cm^3	1.849	1.778	2.006
μ/mm^{-1}	1.519	10.133	1.368
F(000)	824	1552.0	3353.0
Crystal size/mm^3	0.376 × 0.274 × 0.144	0.257 × 0.252 × 0.044	0.24 × 0.22 × 0.22
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.524 to 56.564	6.272 to 148.062	5.682 to 58.26
Index ranges	-13 ≤ h ≤ 16, -15 ≤ k ≤ 16, 0 ≤ l ≤ 16	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -16 ≤ l ≤ 16	-29 ≤ h ≤ 29, -16 ≤ k ≤ 16, -29 ≤ l ≤ 29
Reflections collected	7323	93719	58737
Independent reflections	7323 [R_{int} = 0.0301, R_{sigma} = N/A]	5958 [R_{int} = 0.1225, R_{sigma} = 0.0380]	15038 [R_{int} = 0.0198, R_{sigma} = 0.0187]
Data/restraints/parameters	7323/0/426	5958/0/390	15038/2/824
Goodness-of-fit on F^2	1.084	1.053	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0763	R_1 = 0.0455, wR_2 = 0.1260	R_1 = 0.0165, wR_2 = 0.0391
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0784	R_1 = 0.0511, wR_2 = 0.1307	R_1 = 0.0168, wR_2 = 0.0392
Largest diff. peak/hole / e Å^{-3}	0.48/-0.32	1.71/-1.66	0.34/-0.32
Flack Parameter			0.002(3)

NMR Spectra

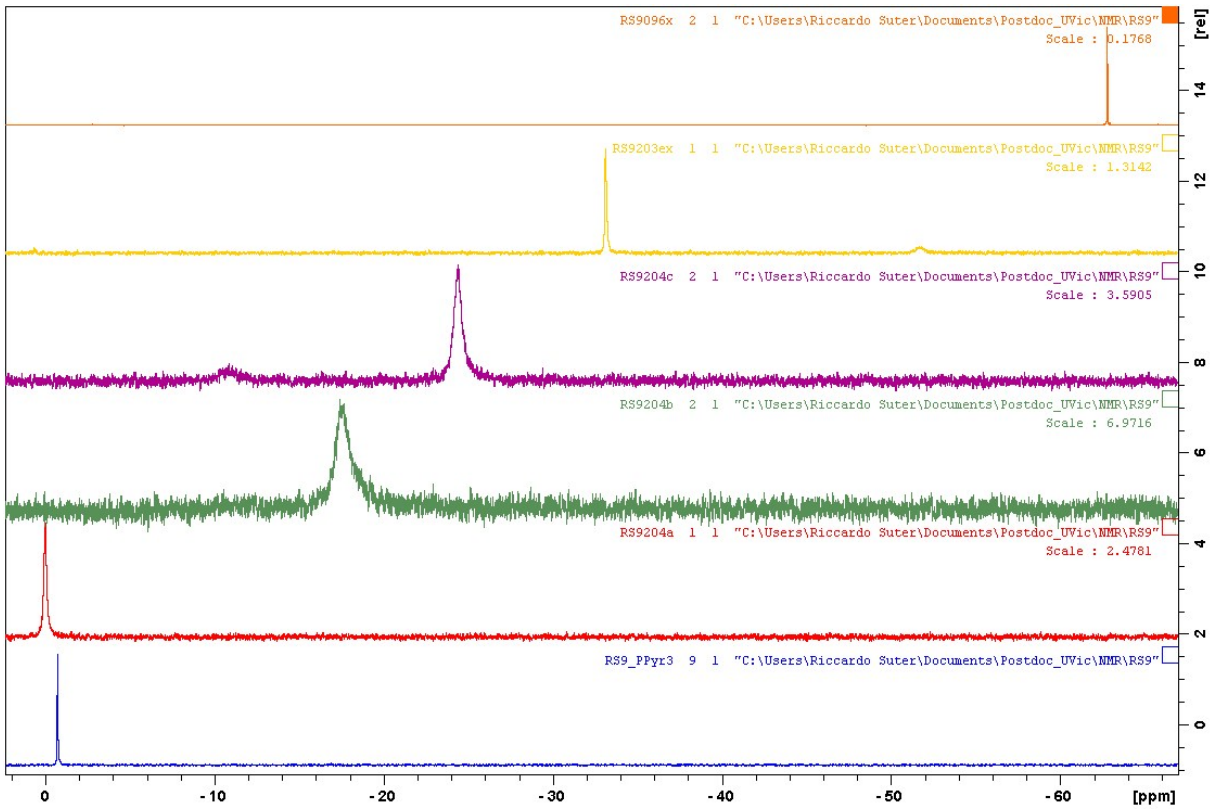
Reactions described in **Scheme 1**



Scheme 2: ^{31}P-NMR spectra for the reactions described in Scheme 1.

Reaction of $AsCl_3$ + x TMSOTf in MeCN

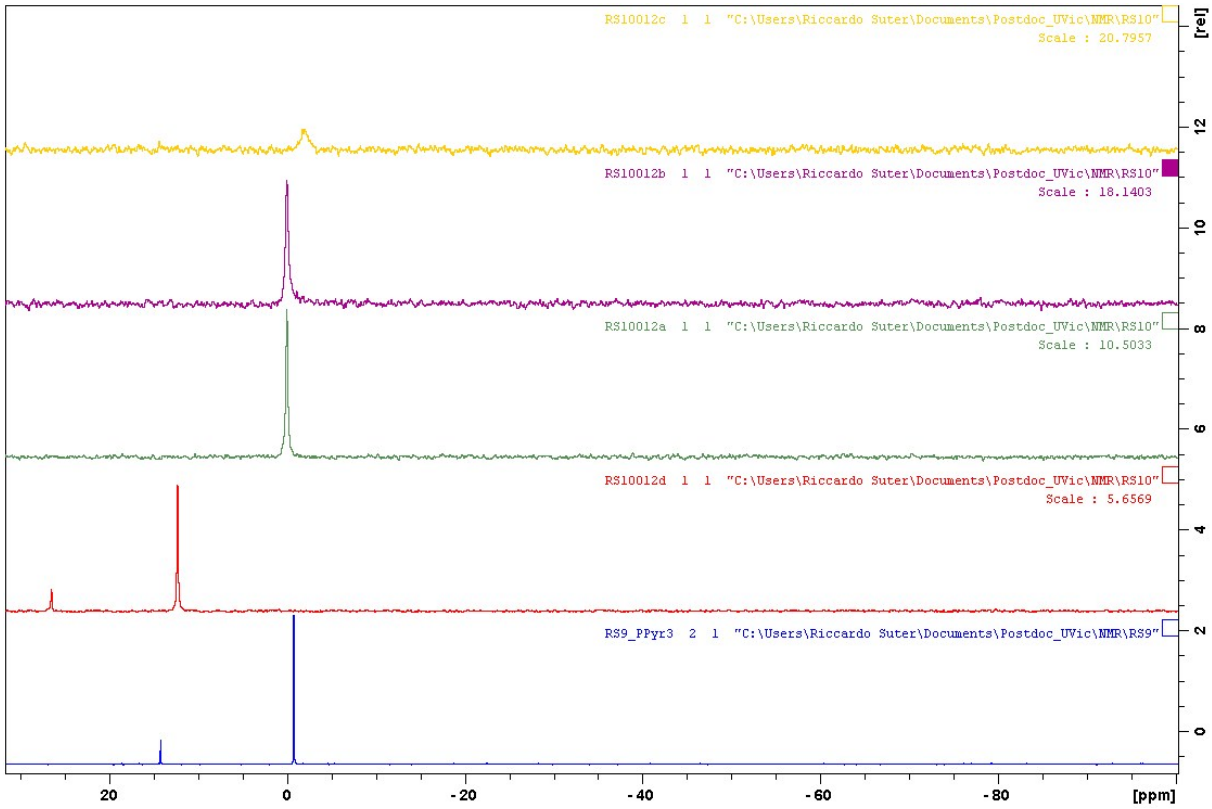
$AsCl_3$ + x TMSOTf reactions
from top to bottom
isolated $[PPyr_3As][OTf]_3$ dissolved in MeCN
excess TMSOTf
3 equivalent of TMSOTf
2 equivalent of TMSOTf
1 equivalent of TMSOTf
free ligand



Scheme 3: NMR spectra of the reaction of $AsCl_3$ and TMSOTf in MeCN

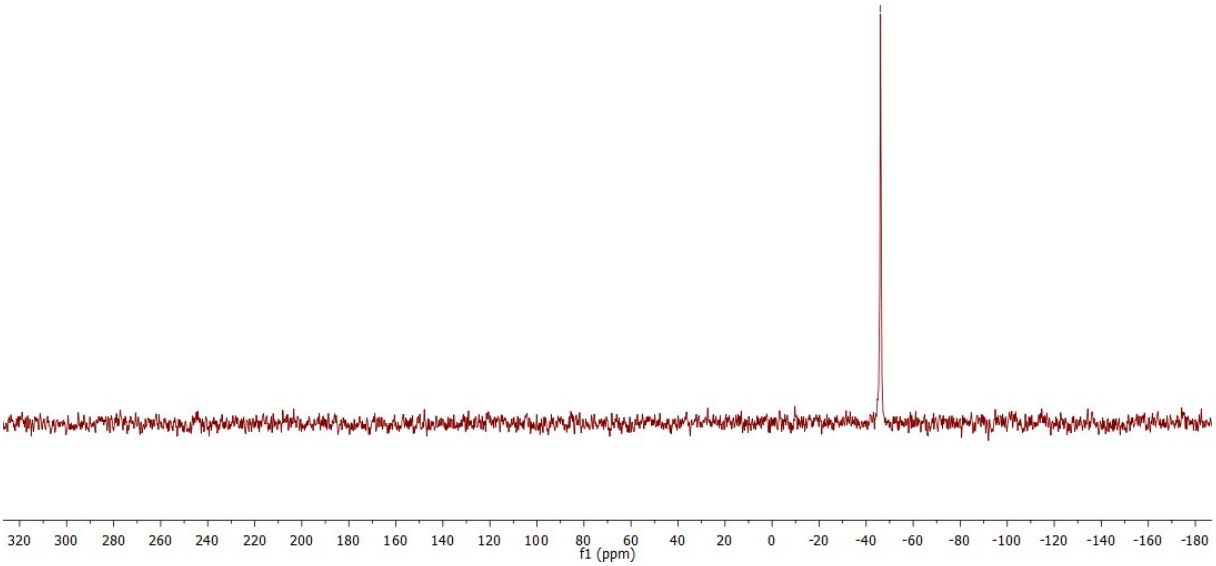
Reaction of $AsCl_3$ + x TMSOTf in DCM

$AsCl_3$ + x TMSOTf reactions
from top to bottom
3 equivalent of TMSOTf
2 equivalent of TMSOTf
1 equivalent of TMSOTf
only $AsCl_3$ and $PPyr_3$
free ligand

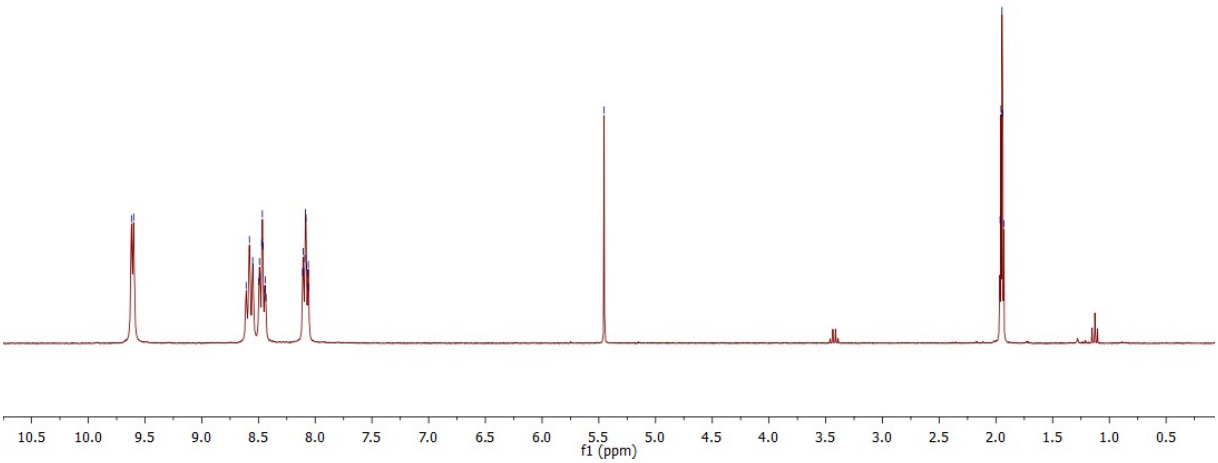


Scheme 4: NMR spectra of the reaction of $AsCl_3$ and TMSOTf in DCM

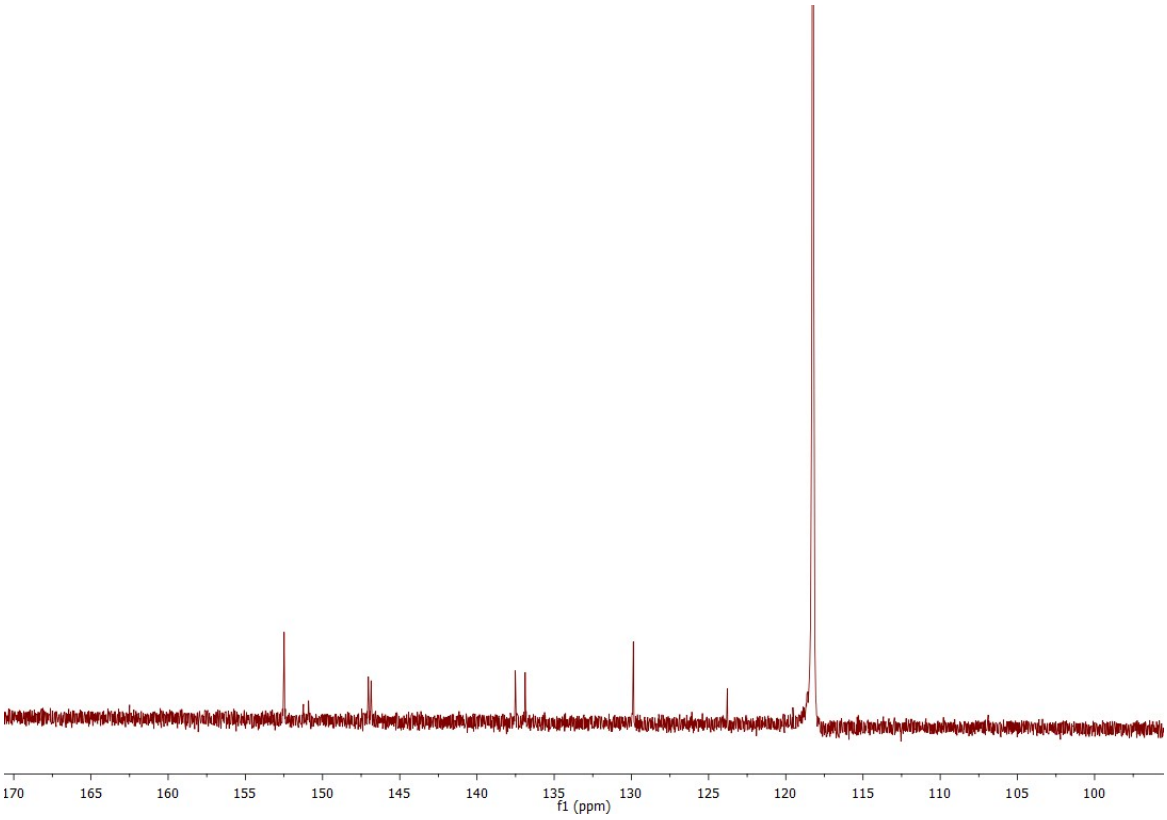
NMR Spectra for $[2_{AsCl}][OTf]_2$ $[AsCl(PPyr_3)][OTf]_2$:



Scheme 5: ^{31}P-NMR spectrum

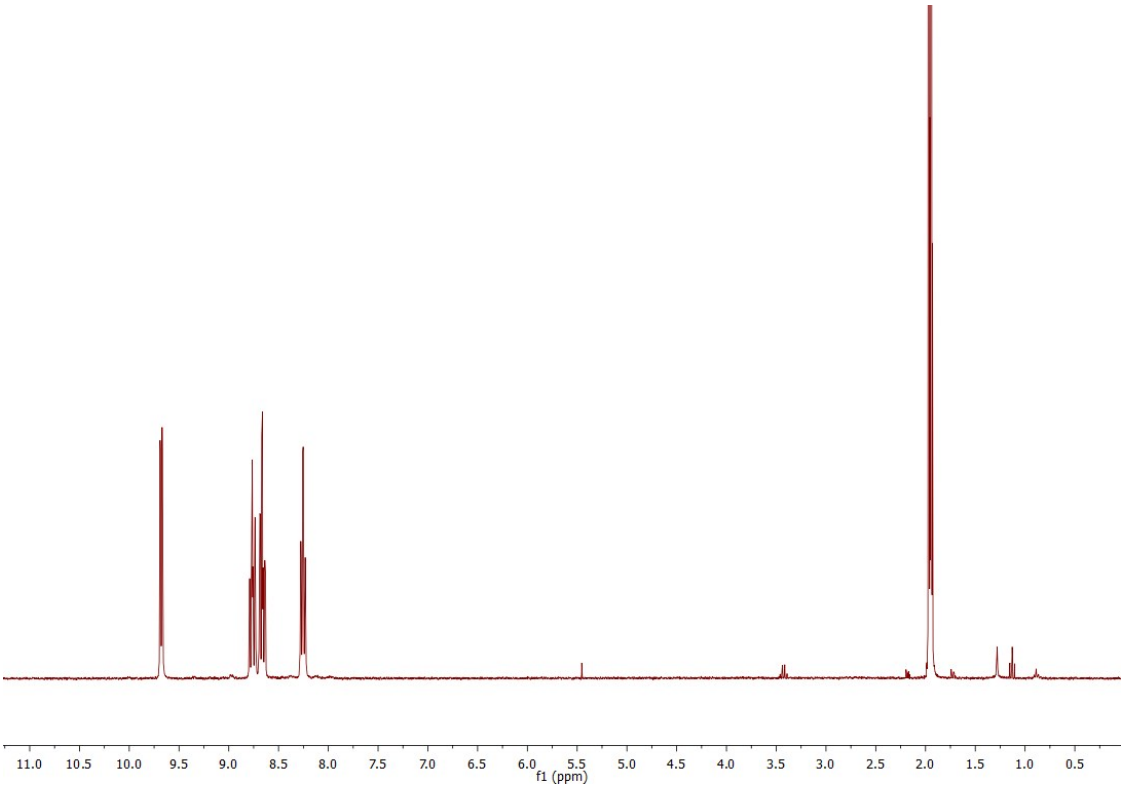


Scheme 6: ^{1}H-NMR spectrum

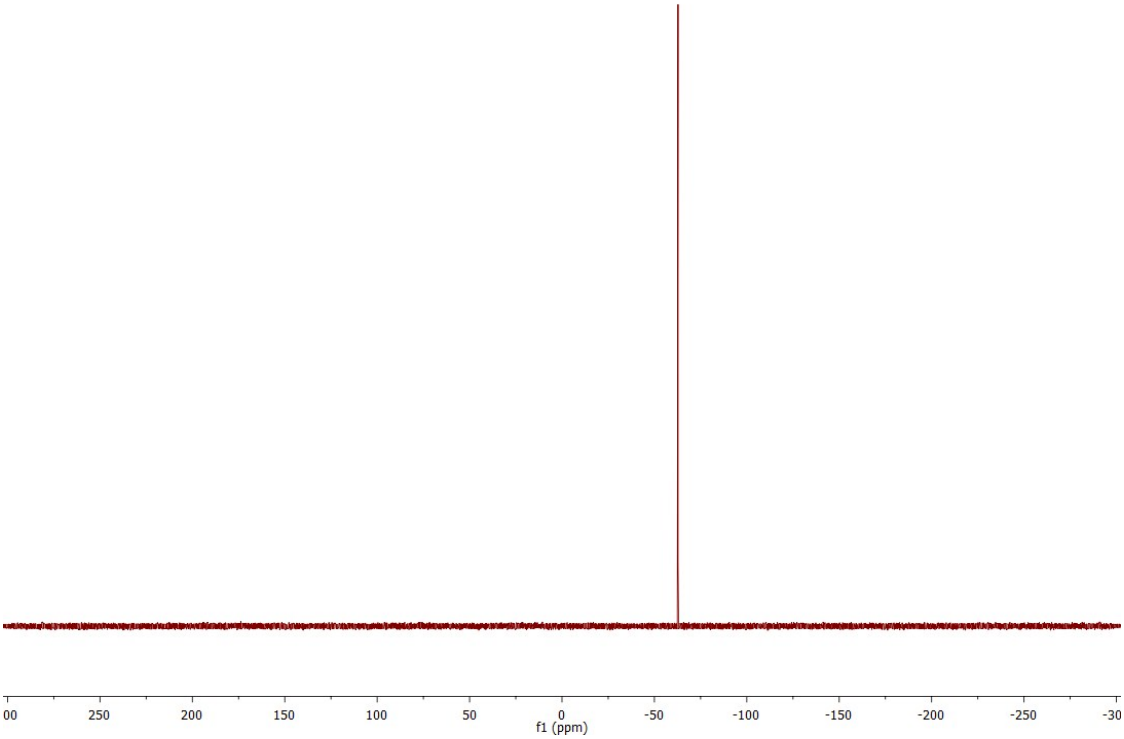


Scheme 7: ^{13}C-NMR spectrum

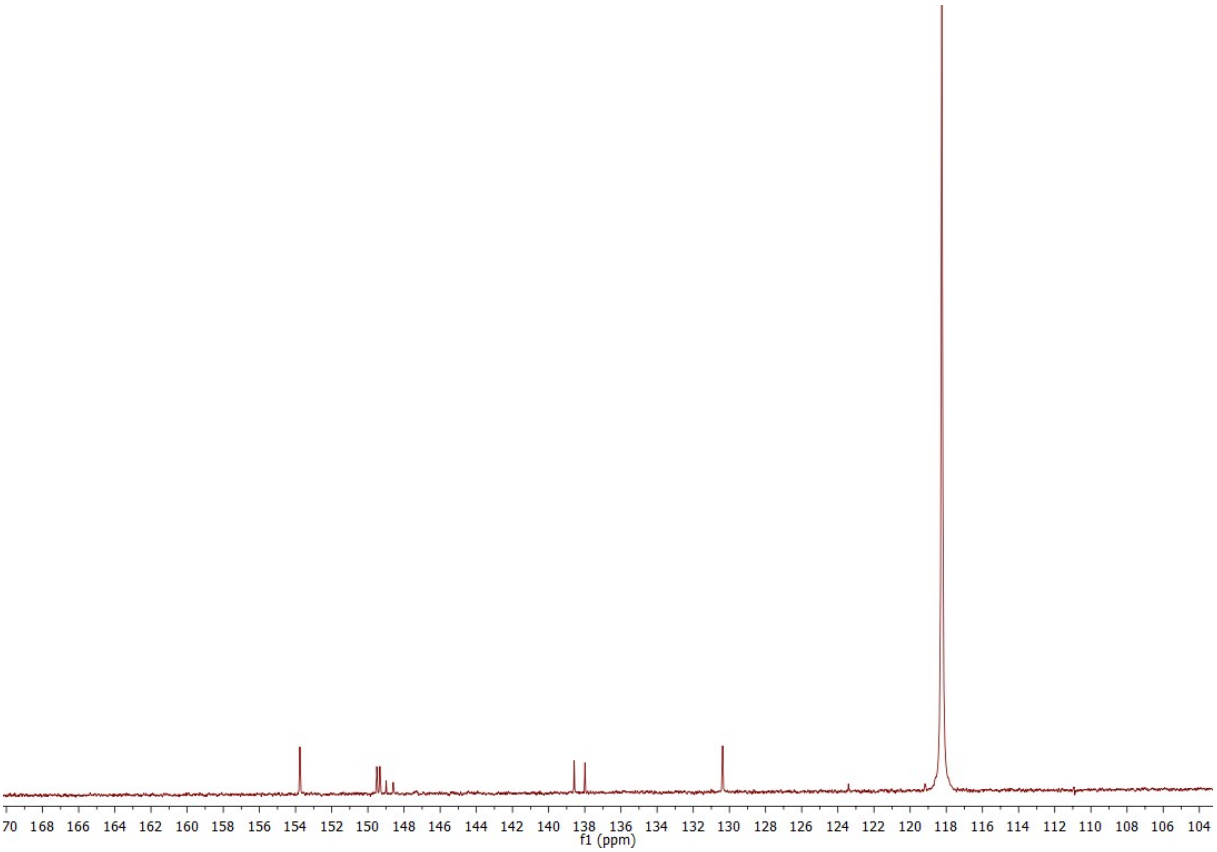
NMR Spectra for [1As][OTf]3 [As(PPyr3)][OTf]3 • MeCN:



Scheme 8: ^{1}H-NMR spectrum

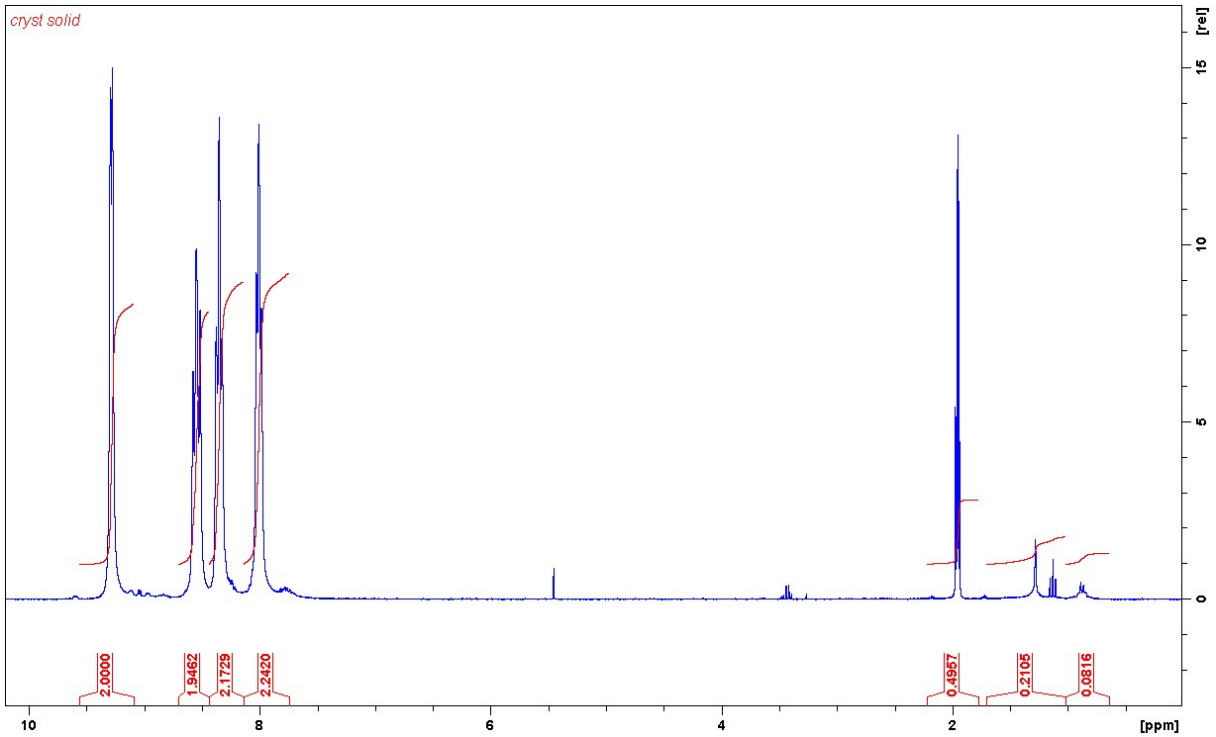


Scheme 9: ^{31}P-NMR spectrum

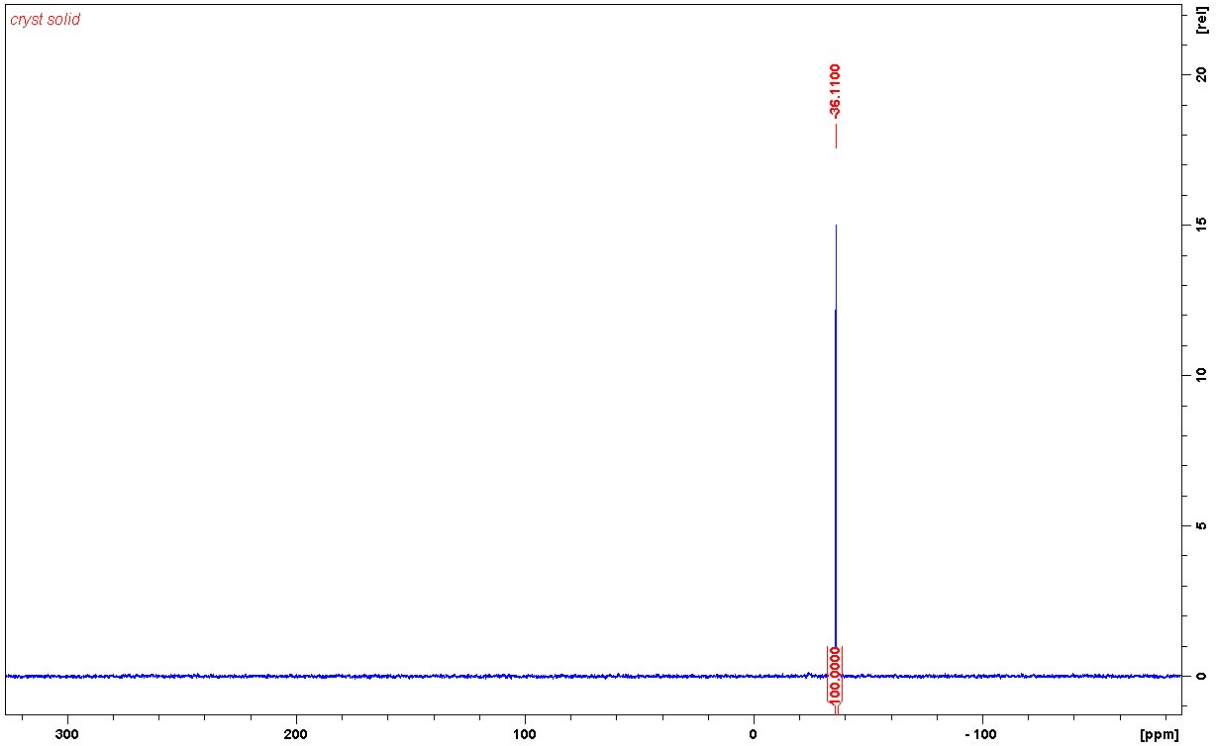


Scheme 10: ^{13}C-NMR spectrum

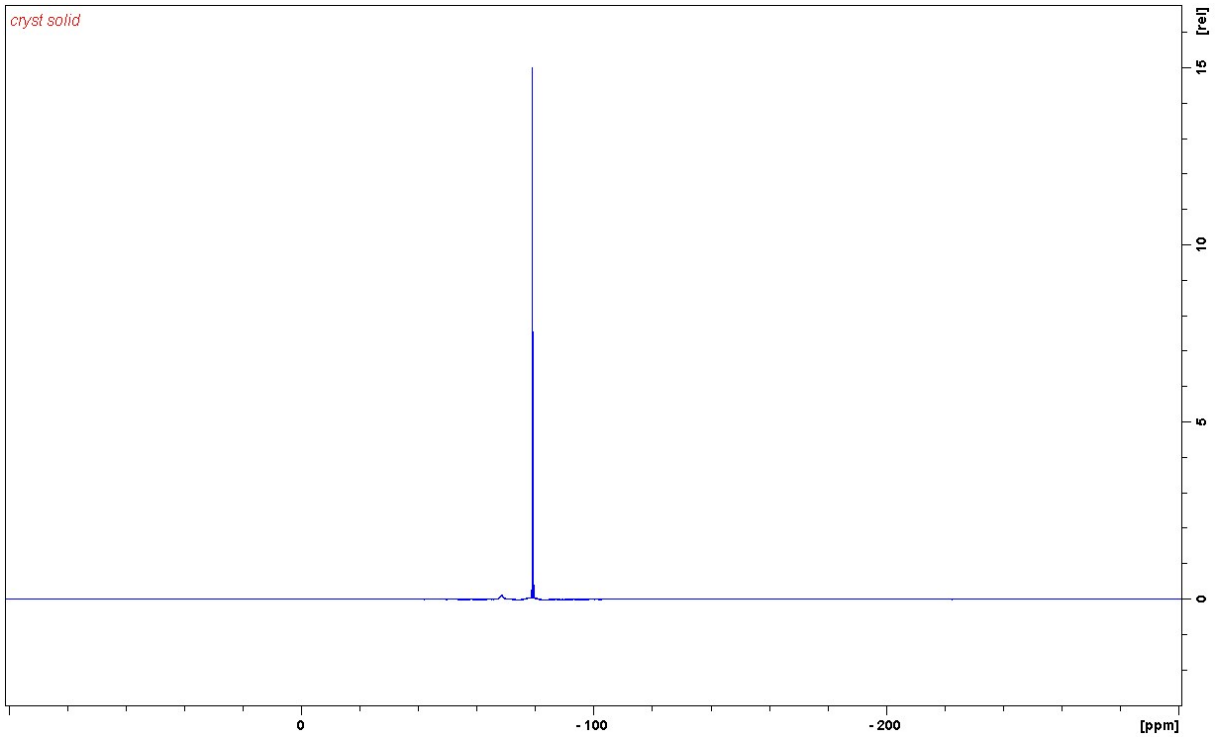
NMR Spectra for [2SbF][OTf]2 [SbF(PPyr3)][OTf]2:



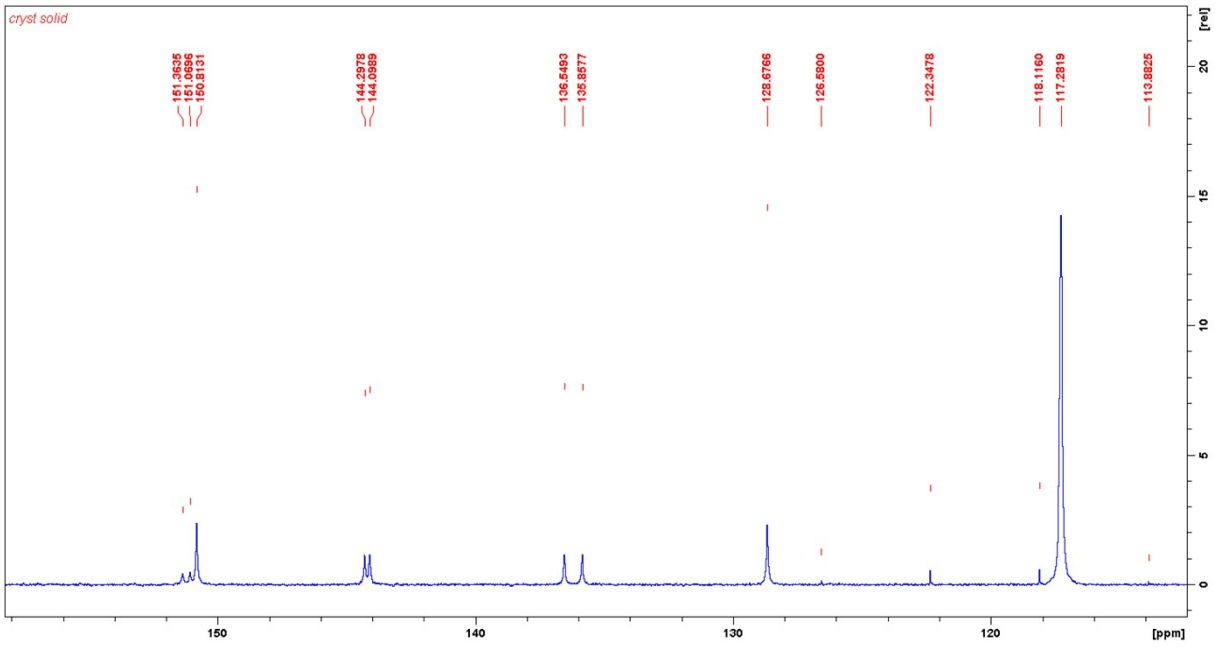
Scheme 11: ^{1}H-NMR spectrum



Scheme 12: ^{13}C-NMR spectrum

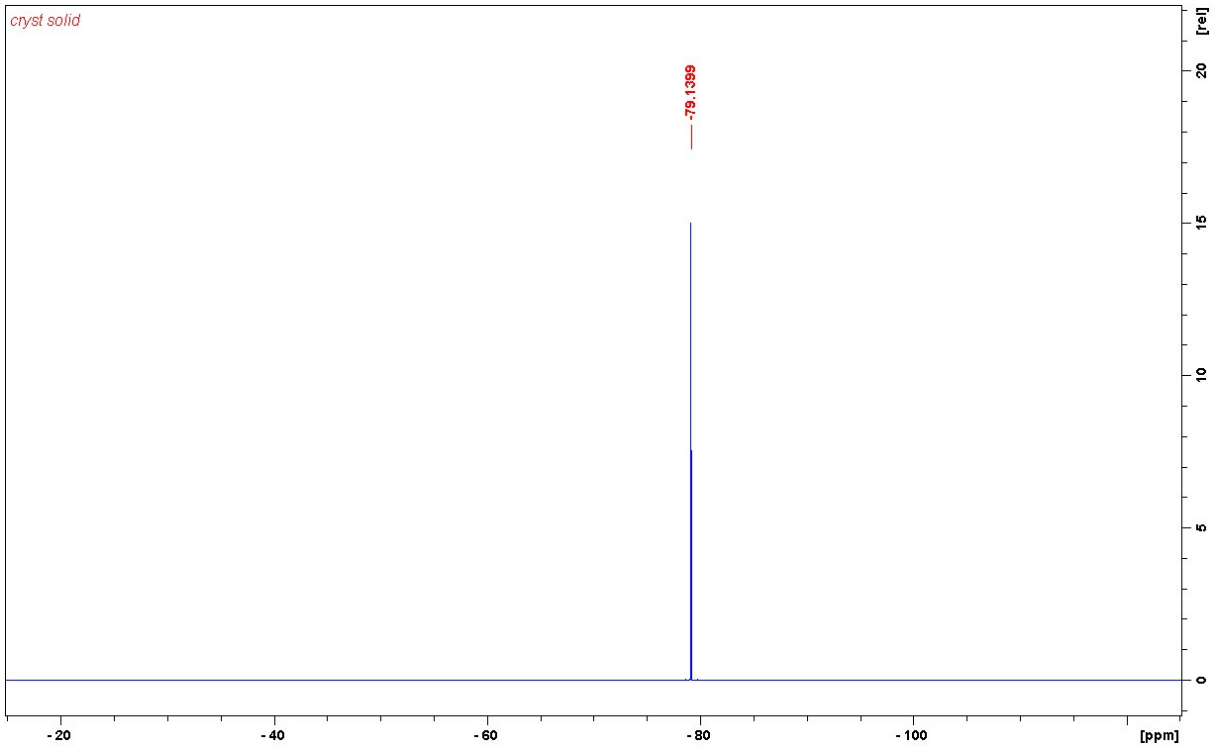


Scheme 13: ^{19}F-NMR spectrum

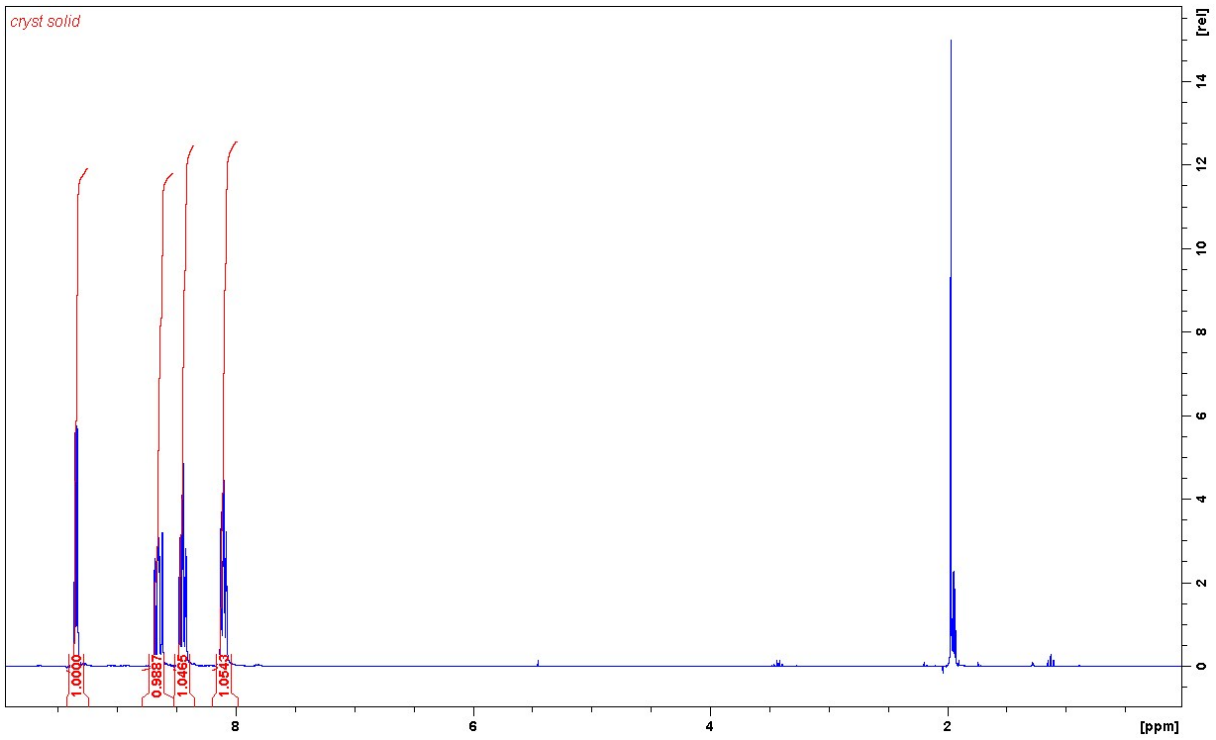


Scheme 14: ^{13}C-NMR spectrum

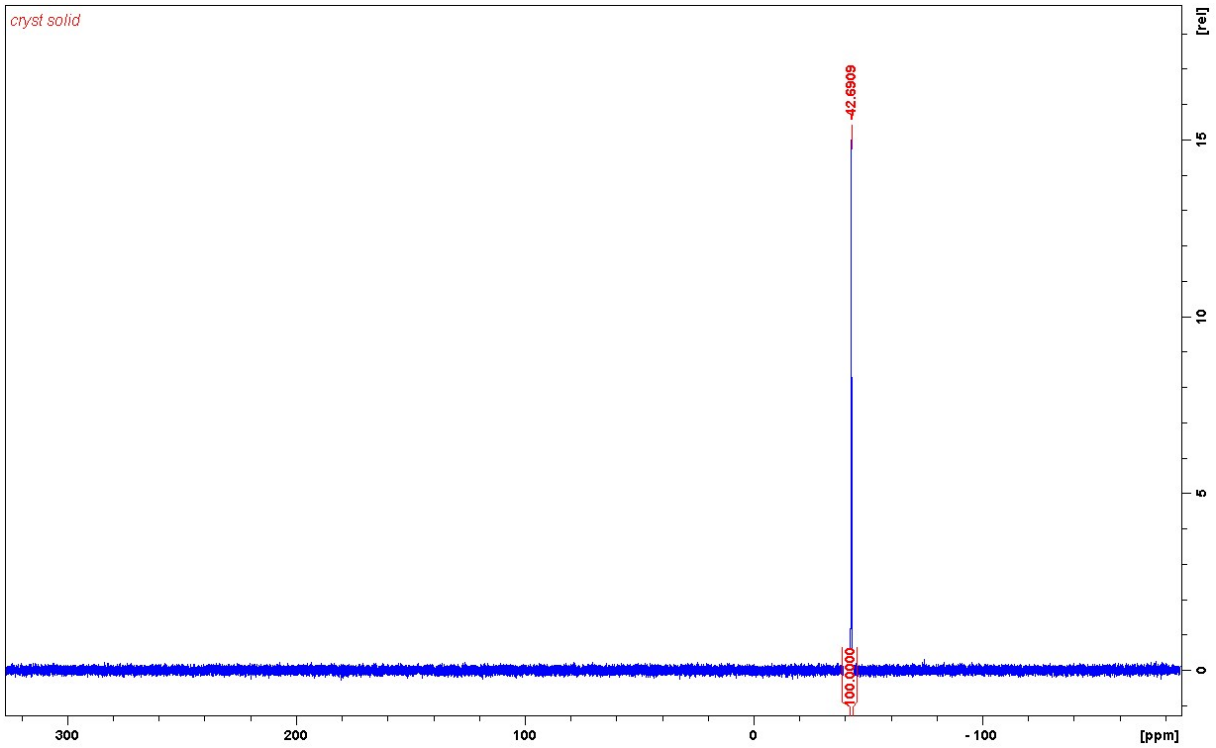
NMR Spectra for [1Sb][OTf]3 [Sb(PPyr3)][OTf]3:



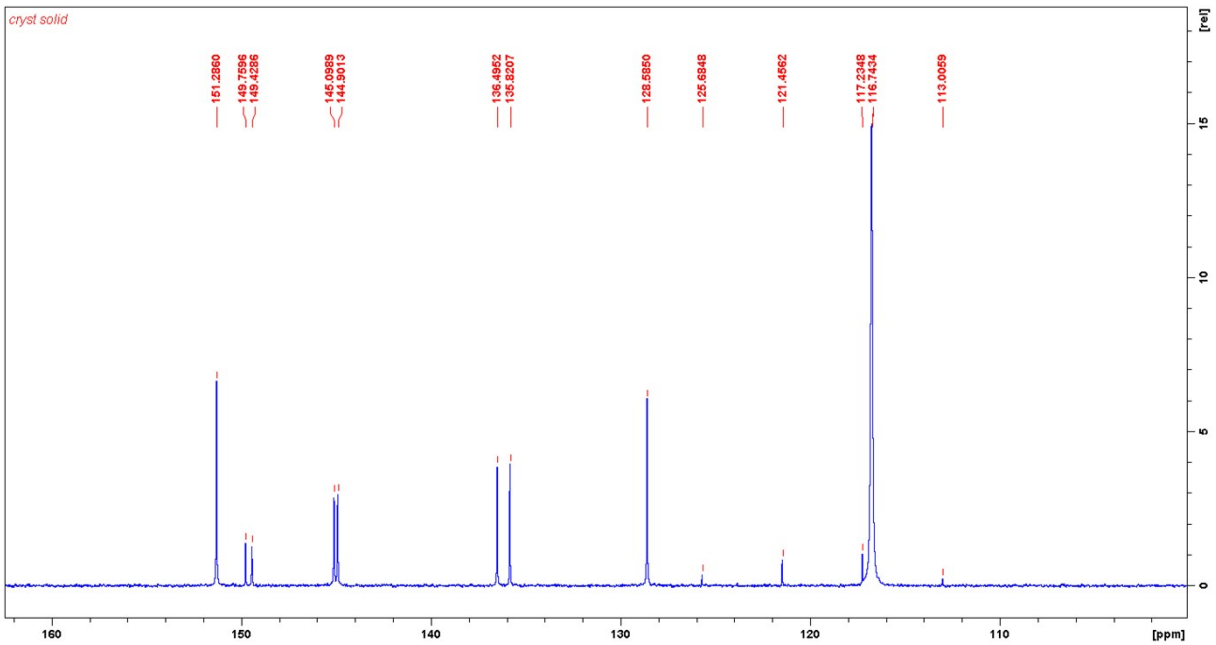
Scheme 15: ^{19}F-NMR spectrum



Scheme 16: ^{1}H-NMR spectrum



Scheme 17: ^{31}P-NMR spectrum



Scheme 18: ^{13}C-NMR spectrum

References

[1] a) B. A. Trofimov, A. V. Artem'ev, S. F. Malysheva, N. K. Gusarova, N. A. Belogorlova, A. O. Korocheva, Y. V. Gatilov, V. I. Mamatyuk, *Tetrahedron Lett.* **2012**, *53*, 2424-2427; b) Gneu, M. J. Leitl, L. H. Finger, N. Rau, H. Yersin, J. Sundermeyer, *Dalton Trans.* **2015**, *44*, 8506-8520.

[2] a) P. Pyykkö, M. Atsumi, *Chem. - Eur. J.* **2009**, *15*, 186-197; b) M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806-5812.