Supporting Information for

A New Main Group Element-rich *nido*-Octahedral Cluster System: Synthesis and Characterization of $[Et_4N][Fe_2(CO)_6E_3\{Fe(CO)_4\}_2]$

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Supporting Information

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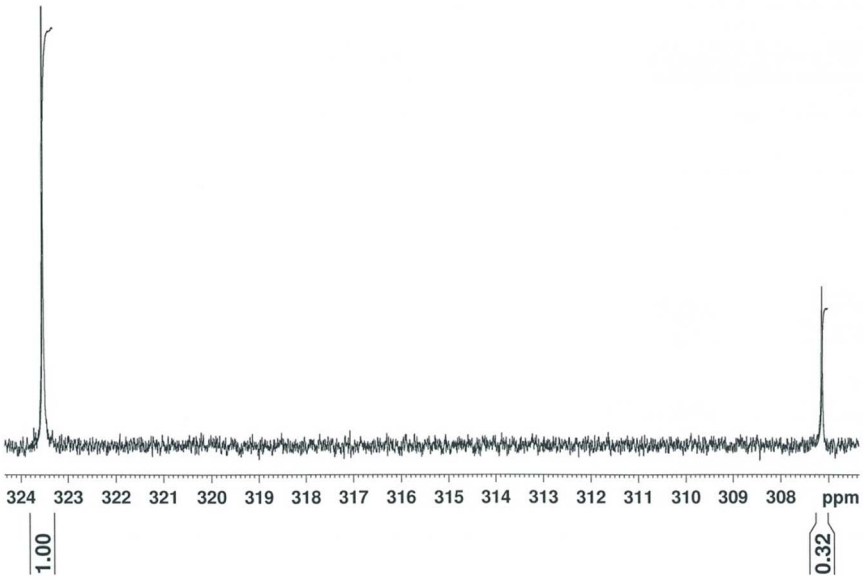
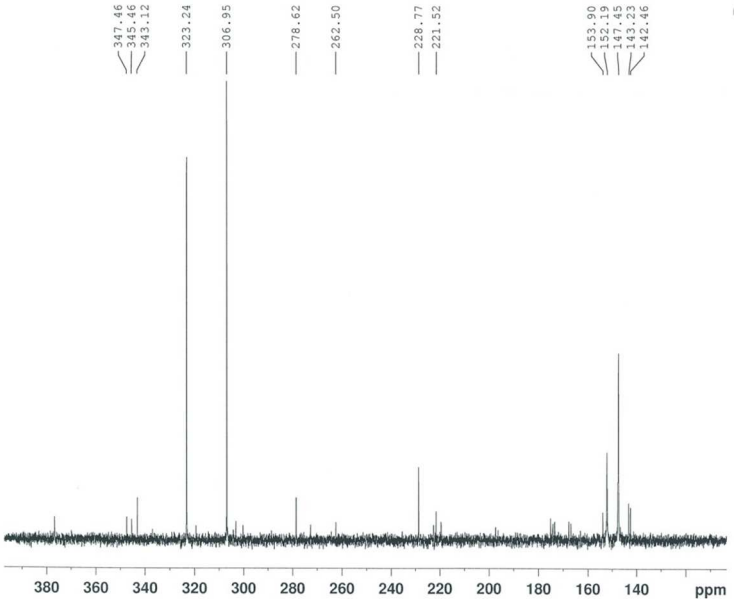
1. **Experimental ^{31}P Spectra**

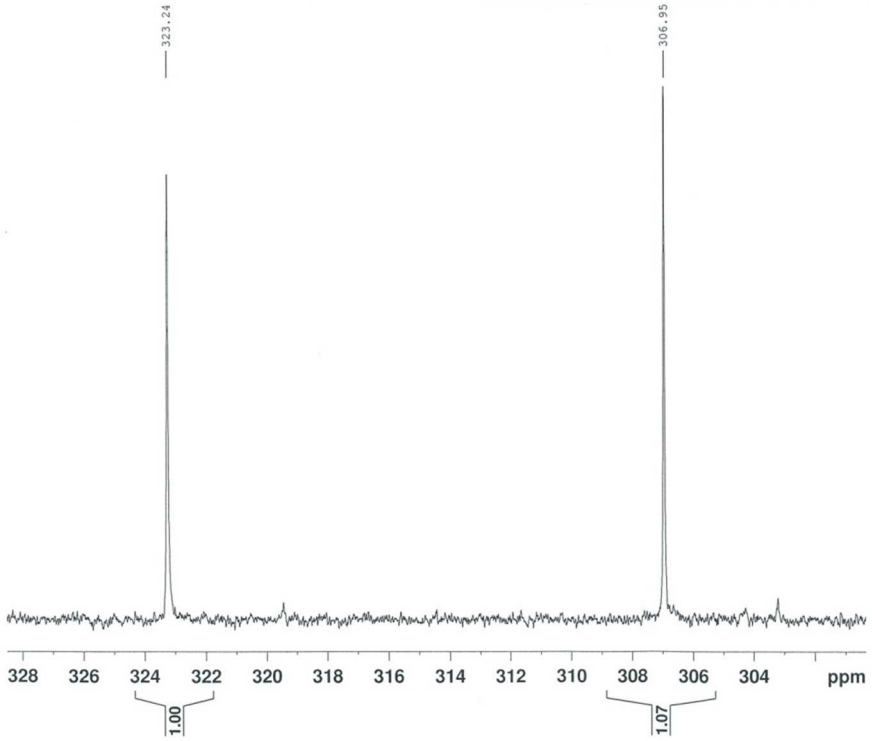
A. Crystals of $[Et_4N]$[**II**] in $CDCl_3$ SR = -70.38 Hz



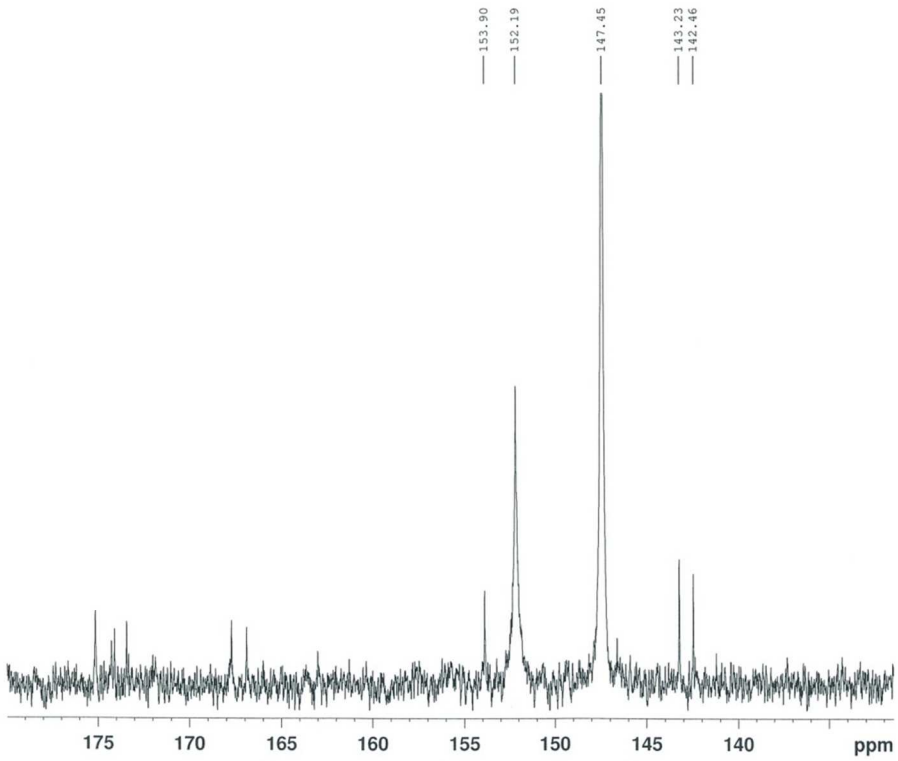
B.Crude reaction mixture (Experimental 1a), d^6-acetone, SR = -70.45 Hz



C. Crude reaction mixture (Experimental 1a) con't. C. Crude reaction mixture (1a) con't.



D. Crude reaction mixture (Experimental 1a) con't


153.90
152.19
147.45
143.23
142.46
175
170
165
160
155
150
145
140
ppm

2. DFT Calculations

A. Optimized geometries of $[Fe_2(CO)_6(\mu_3\text{-E})\}\{\mu_3\text{-EFe(CO)}_4\}_2]^+$ (E = As and/or P) noted below as As_3, P_3, As_2P and AsP_2.

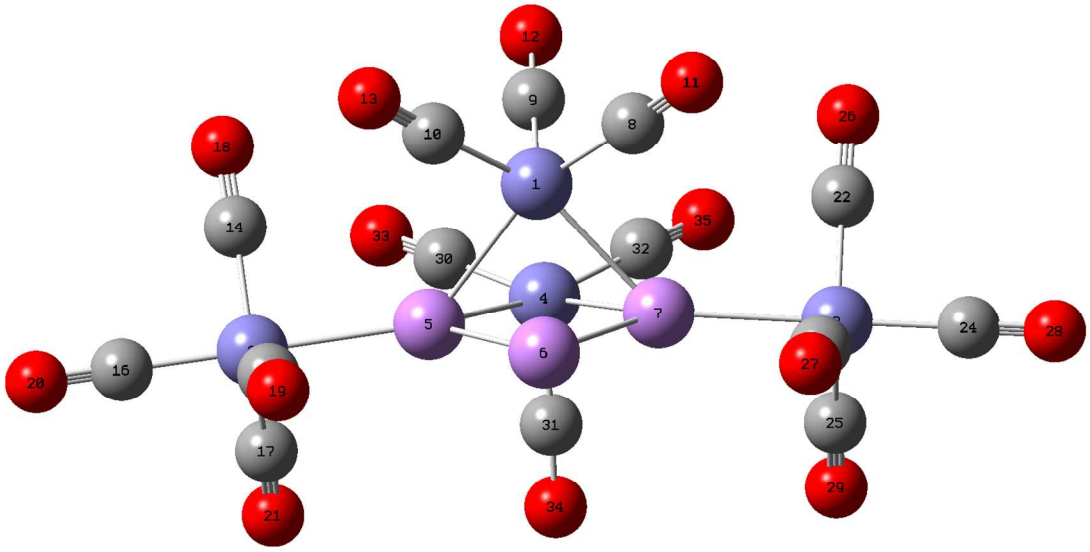


Figure 1: As_3

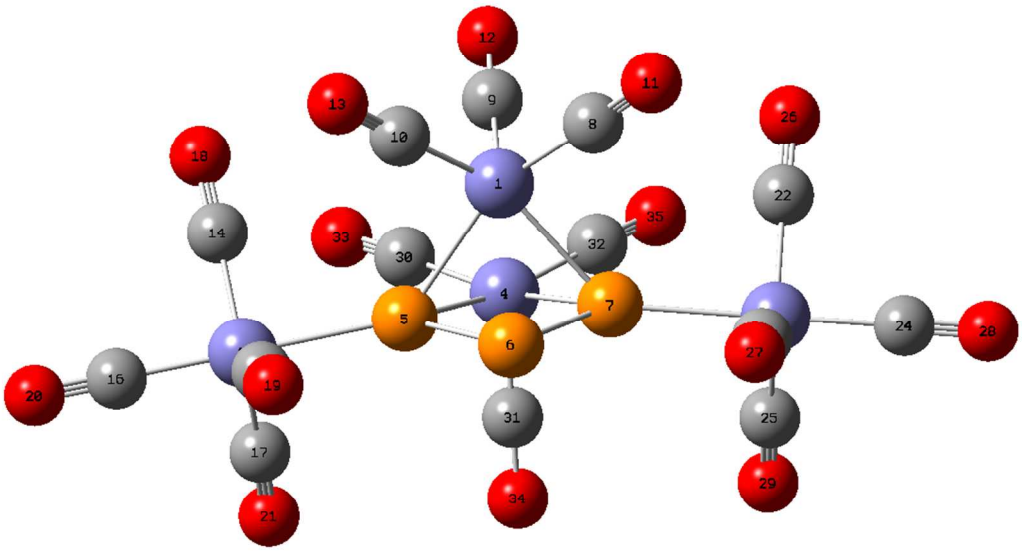


Figure 2: P_3

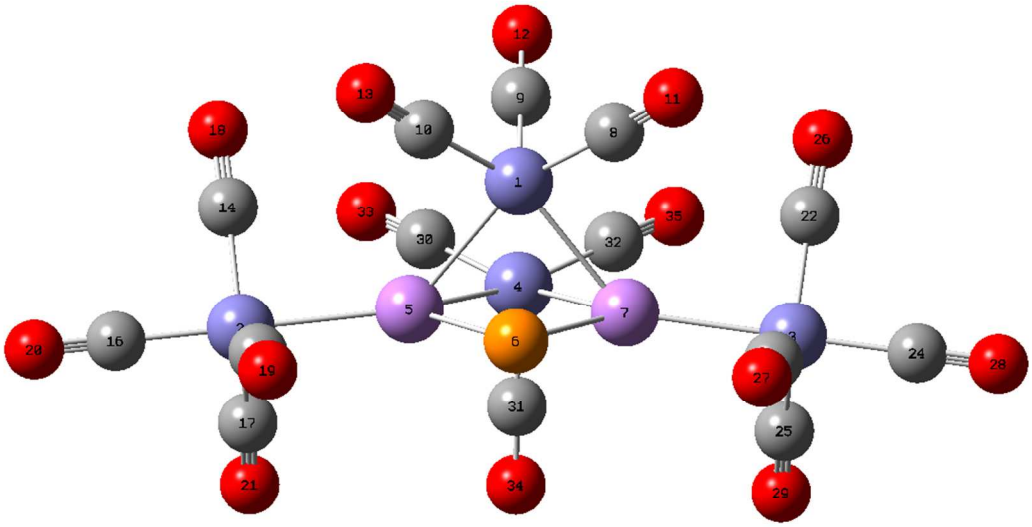


Figure 3: As_2P (isomer A)

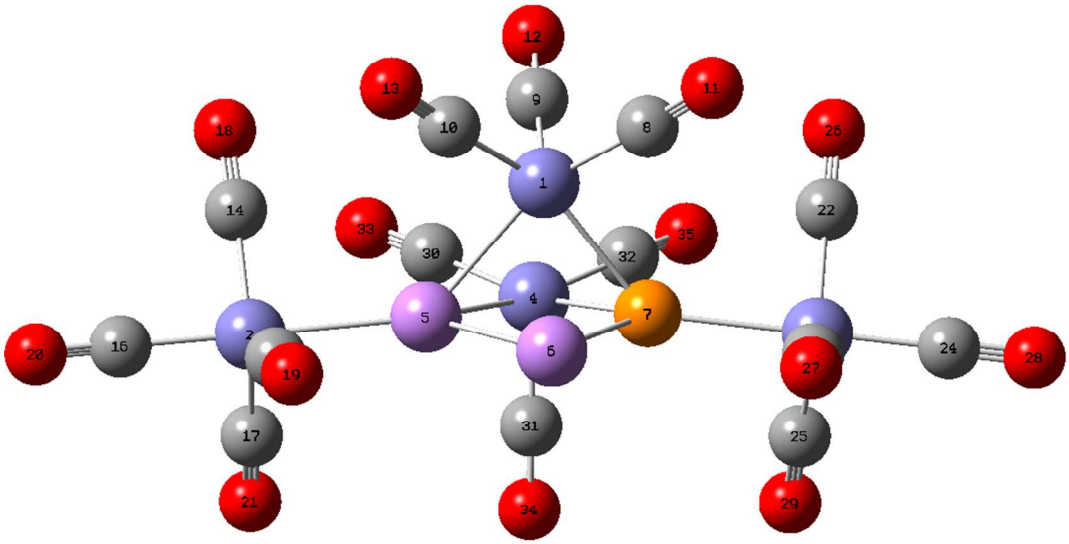


Figure 4: As_2P (isomer B)

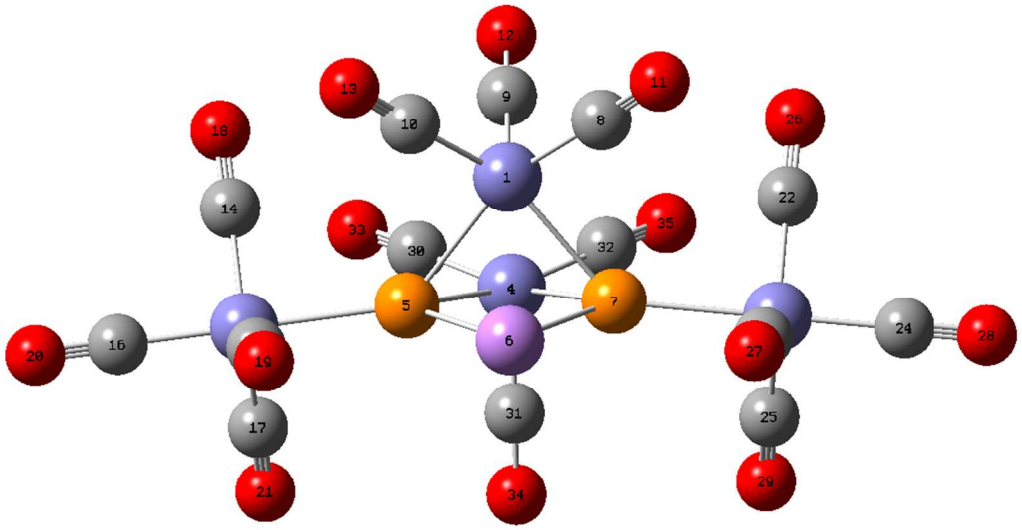


Figure 5: AsP_2 (isomer A)

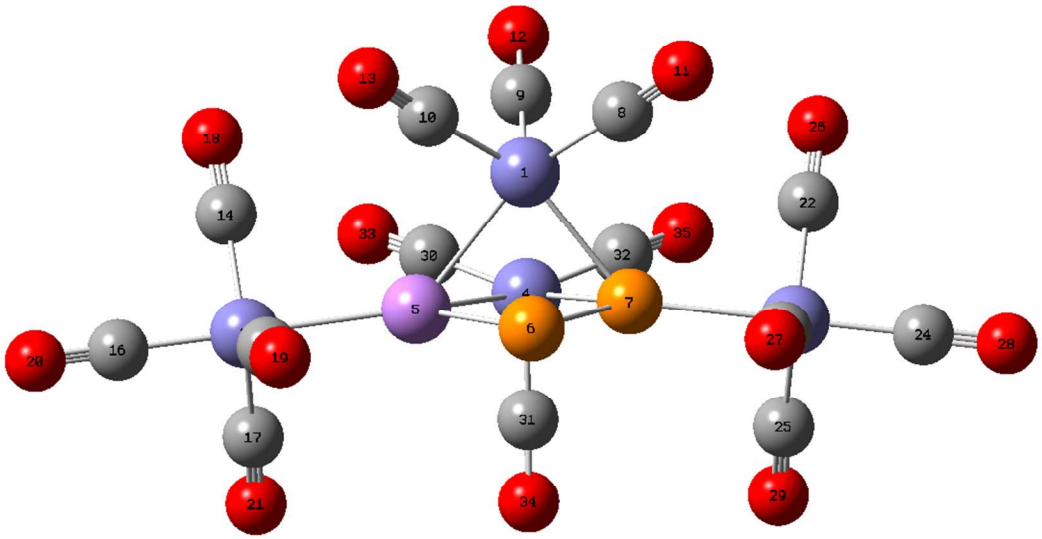


Figure 6: AsP_2 (isomer B)

B. Optimized cartesian coordinates of the computed clusters.

Cluster As_3 PBE0/Def2TZVP

C_s Symmetry

Energy = - 13346.738857 a.u.

Atom	**X**	**Y**	**Z (Angstrom)**
Fe	0.00000000	-0.93637100	1.30376000
Fe	-3.88081900	-0.12102000	-0.58666000
Fe	3.88081700	-0.12102000	-0.58666100
Fe	0.00000000	1.62139900	0.37043900
As	-1.52417900	-0.01022200	-0.31697600
As	-0.00000500	-1.60904400	-1.17804800
As	1.52417700	-0.01022700	-0.31697400
C	1.32413400	-1.98870500	1.80295000
C	0.00006000	0.10404400	2.72041700
C	-1.32417900	-1.98862400	1.80300800
O	2.14178400	-2.70381200	2.15332200
O	0.00010300	0.65090100	3.72740200
O	-2.14185400	-2.70368100	2.15342400
C	-4.03106700	0.07753100	1.17600500
C	-3.66310400	-1.72884900	-1.31703200
C	-5.62411400	-0.21155900	-0.77890600
C	-3.77485100	1.33118700	-1.61022600
O	-4.15217800	0.20269000	2.30865000
O	-3.53337300	-2.76307500	-1.79397300
O	-6.76029100	-0.27199800	-0.90340300
O	-3.73842700	2.26922700	-2.26824300
C	4.03104200	0.07745300	1.17601800
C	3.66310400	-1.72881900	-1.31710200
C	5.62411400	-0.21155100	-0.77888800
C	3.77486300	1.33122200	-1.61018000
O	4.15213300	0.20256000	2.30867000
O	3.53337500	-2.76302200	-1.79409000
O	6.76029300	-0.27198800	-0.90337100
O	3.73844700	2.26928100	-2.26817000
C	-1.30710900	2.51457000	1.20141600
C	0.00001500	2.46059200	-1.16424200
C	1.30710400	2.51457400	1.20142000
O	-2.13576800	3.11325200	1.70236000
O	0.00002700	3.02354800	-2.15680100
O	2.13575600	3.11326400	1.70236800

Cluster P_3 PBE0/Def2TZVP

C_s Symmetry

Energy = - 7663.598174 a.u.

Atom	**X**	**Y**	**Z (Angstrom)**
Fe	0.00000100	-1.34486400	0.83975300
Fe	-3.63979600	0.02445400	-0.72949300
Fe	3.63979200	0.02445400	-0.72949900
Fe	0.00000000	1.32337200	0.76926600
P	1.40298400	0.01368000	-0.36466900
P	-0.00000300	-1.05516800	-1.58061300
P	-1.40298600	0.01368000	-0.36466400
C	1.32167000	-2.51253900	0.96658900

C	0.00001600	-0.82877600	2.52166900
C	-1.32167900	-2.51252800	0.96659700
O	2.14139700	-3.30045200	1.05186800
O	0.00003100	-0.63763200	3.65137800
O	-2.14141200	-3.30043200	1.05188200
C	-3.86469300	-0.31690800	1.00032800
C	-3.41750000	-1.29765900	-1.89793900
C	-5.38099400	0.03582200	-1.00427600
C	-3.48176200	1.70996300	-1.27373600
O	-4.02506500	-0.54276600	2.11251000
O	-3.28983200	-2.14724300	-2.65591500
O	-6.51140400	0.04207700	-1.18174200
O	-3.40712500	2.79998900	-1.62043900
C	3.86470000	-0.31693100	1.00031600
C	3.41748900	-1.29765800	-1.89794500
C	5.38098700	0.03583000	-1.00429500
C	3.48175500	1.70997200	-1.27371600
O	4.02507700	-0.54280600	2.11249400
O	3.28981500	-2.14724600	-2.65591500
O	6.51139800	0.04209000	-1.18176800
O	3.40711500	2.80000400	-1.62040000
C	-1.31424700	1.92673800	1.83298000
C	-0.00000700	2.59949900	-0.42483000
C	1.31426800	1.92673600	1.83295700
O	-2.14434500	2.34725600	2.48776400
O	-0.00001000	3.43177900	-1.20440100
O	2.14438300	2.34725200	2.48772000

Cluster As_2P (isomer A) **PBE0/Def2TZVP**

C_s Symmetry

Energy= -11452.351132 a.u.

Atom	**X**	**Y**	**Z (Angstrom)**
Fe	-0.00000300	-1.27203500	1.00564200
Fe	-3.84302600	-0.05120600	-0.72030900
Fe	3.84302700	-0.05120700	-0.72030800
Fe	0.00000300	1.43974900	0.72893900
As	-1.50029400	0.01887000	-0.35647200
P	-0.00000300	-1.26242600	-1.46020600
As	1.50029400	0.01886200	-0.35647000
C	1.32325600	-2.41705900	1.22584900
C	0.00001600	-0.61995700	2.63980800
C	-1.32328000	-2.41703200	1.22588100
O	2.14008800	-3.19791200	1.38466400
O	0.00002600	-0.33629100	3.74993600
O	-2.14012100	-3.19787100	1.38471900
C	-4.04926600	-0.27270500	1.03403900
C	-3.58481600	-1.44420600	-1.79930900
C	-5.57849600	-0.10985900	-0.98268300
C	-3.73450200	1.60009600	-1.37602100
O	-4.20726200	-0.41725200	2.15979700
O	-3.43900200	-2.33869000	-2.49998700
O	-6.70955400	-0.14942800	-1.15308500
O	-3.69803100	2.66579900	-1.79682700

C	4.04926400	-0.27275300	1.03403500
C	3.58481400	-1.44417400	-1.79935100
C	5.57849700	-0.10985600	-0.98268100
C	3.73450000	1.60011200	-1.37597900
O	4.20725800	-0.41732600	2.15979000
O	3.43900100	-2.33863700	-2.50005500
O	6.70955500	-0.14942100	-1.15308200
O	3.69802500	2.66582300	-1.79675700
C	-1.31138100	2.09149500	1.75552900
C	0.00000000	2.64403200	-0.53923600
C	1.31139500	2.09148800	1.75552300
O	-2.14494800	2.53910600	2.38858700
O	-0.00000300	3.44246900	-1.35444200
O	2.14496800	2.53909300	2.38857600

Cluster As_2P (isomer B) **PBE0/Def2TZVP**

C_1 Symmetry

Energy= -11452.359381 a.u.

Atom	**X**	**Y**	**Z (Angstrom)**
Fe	0.12973000	-0.99134900	1.23742700
Fe	-3.78382200	-0.08163800	-0.55999800
Fe	3.78370900	-0.09947100	-0.62329400
Fe	0.14931100	1.56966200	0.40657400
As	-1.42423600	0.00585700	-0.31724000
As	0.11734800	-1.52075500	-1.26276100
P	1.53386600	-0.03236100	-0.30977600
C	1.44960800	-2.07215000	1.68222500
C	0.15102800	-0.00905000	2.69494500
C	-1.19562100	-2.06314300	1.70849400
O	2.26900500	-2.80293600	1.99138300
O	0.16802300	0.49669700	3.72299100
O	-2.01272400	-2.79115600	2.03176300
C	-3.91125500	0.04170500	1.21153800
C	-3.57741100	-1.65528000	-1.36497100
C	-5.52936400	-0.16242200	-0.73426400
C	-3.68822300	1.41634400	-1.51698600
O	-4.01748800	0.11904200	2.34988000
O	-3.45365400	-2.66687100	-1.88957200
O	-6.66704500	-0.21679800	-0.84718900
O	-3.65919400	2.38363400	-2.13136700
C	3.97308800	0.04414300	1.13800700
C	3.59298200	-1.69146400	-1.38892700
C	5.53008100	-0.13847000	-0.85908500
C	3.62075000	1.37052500	-1.60960200
O	4.11019200	0.13047300	2.27271200
O	3.47802800	-2.71648400	-1.88935500
O	6.66401900	-0.16429700	-1.01102900
O	3.53985200	2.32310100	-2.24239500
C	-1.12465400	2.46516600	1.29966300
C	0.12761100	2.44868000	-1.10486300
C	1.48866400	2.42960800	1.21982500
O	-1.93402200	3.05689000	1.83862800
O	0.11322200	3.02950700	-2.08656100
O	2.32972200	3.01977500	1.70914400

Cluster AsP_2 (isomer A) **PBE0/Def2TZVP**
C_s Symmetry
Energy= -9557.980112 a.u.

Atom	X	Y	Z (Angstrom)
Fe	0.00000100	-1.04354600	1.17115400
Fe	-3.68325700	-0.05872200	-0.59681200
Fe	3.68325600	-0.05872100	-0.59681000
Fe	0.00000000	1.52082400	0.43941900
P	-1.43129200	-0.01789800	-0.31229900
As	-0.00000100	-1.43564100	-1.33980800
P	1.43129100	-0.01789600	-0.31230000
C	1.32192800	-2.14112400	1.58731300
C	-0.00000200	-0.11960300	2.66663400
C	-1.32192200	-2.14113000	1.58731600
O	2.14166000	-2.88221500	1.86897800
O	-0.00000400	0.34557900	3.71371000
O	-2.14165100	-2.88222000	1.86898500
C	-3.84830400	0.01695200	1.17134300
C	-3.50106400	-1.61638600	-1.43207000
C	-5.43251500	-0.08930300	-0.81176100
C	-3.53118700	1.45365100	-1.51923900
O	-3.96884500	0.06004700	2.31033200
O	-3.38761800	-2.61871700	-1.97680900
O	-6.56824800	-0.11032000	-0.95032100
O	-3.45774500	2.43326800	-2.11002300
C	3.84830800	0.01696900	1.17134300
C	3.50106200	-1.61639300	-1.43205700
C	5.43251400	-0.08930600	-0.81176800
C	3.53118200	1.45364800	-1.51924500
O	3.96885200	0.06007100	2.31033000
O	3.38761300	-2.61872900	-1.97678700
O	6.56824600	-0.11032700	-0.95033400
O	3.45773800	2.43326300	-2.11003200
C	-1.30847600	2.38202200	1.31535200
C	-0.00000300	2.43808200	-1.04841300
C	1.30847700	2.38202400	1.31534600
O	-2.13195000	2.96397300	1.84254500
O	-0.00000300	3.03444500	-2.02043400
O	2.13195600	2.96397600	1.84253300

Cluster AsP_2 (isomer B) **PBE0/Def2TZVP**
C_1 Symmetry
Energy = -9557.974539 a.u.

Atom	X	Y	Z (Angstrom)
Fe	0.13380700	-1.31118000	0.92027900
Fe	-3.74274100	-0.00748200	-0.68557000
Fe	3.74347100	-0.01899200	-0.76537300
Fe	0.16184800	1.37881700	0.75309600
As	-1.39587500	0.03975200	-0.35019100
P	0.11970200	-1.15237400	-1.52583900

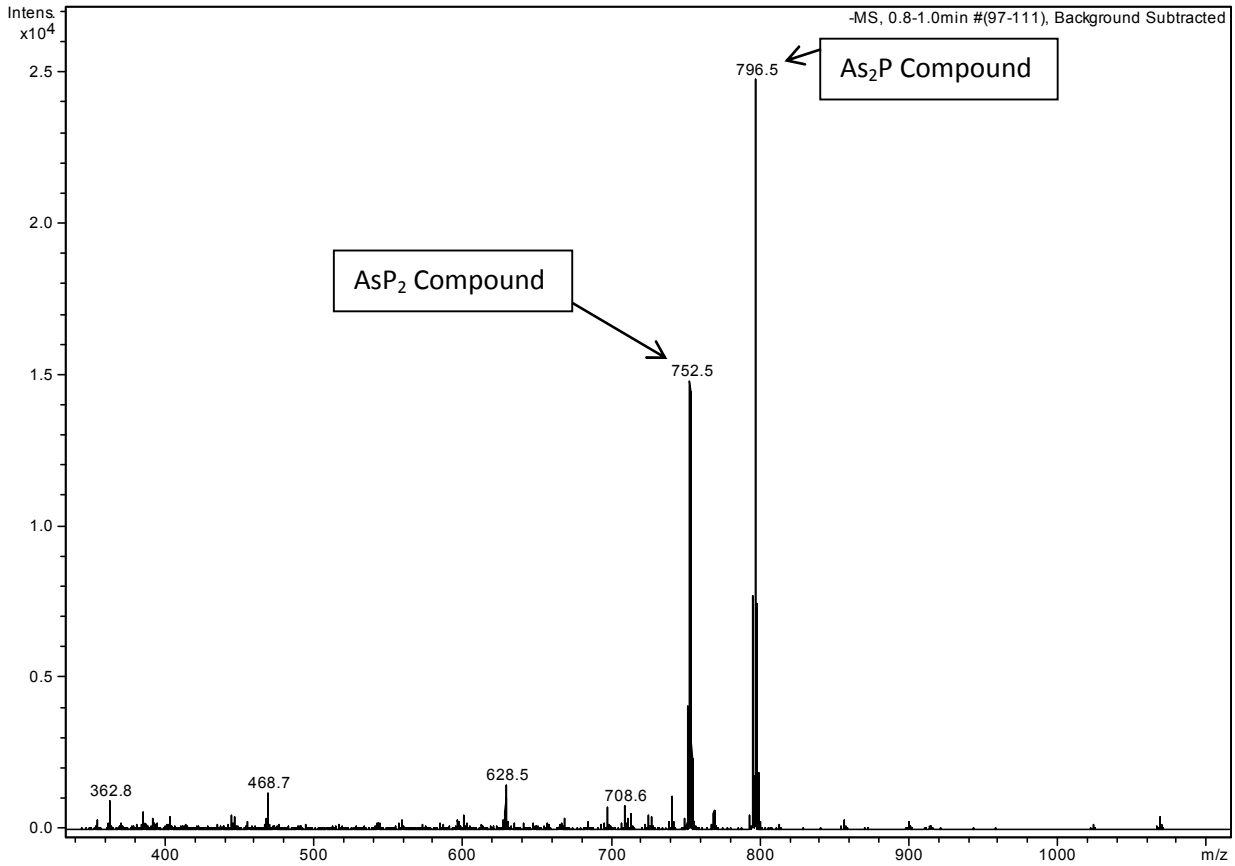
P	1.51021600	-0.00413100	-0.36656000
C	1.45721000	-2.46558200	1.08160900
C	0.15075400	-0.73056000	2.58099900
C	-1.18674900	-2.47314500	1.10093100
O	2.27772000	-3.24905600	1.19737900
O	0.16422000	-0.49583900	3.70241300
O	-2.00175000	-3.26178900	1.22553300
C	-3.92662000	-0.31150500	1.05920200
C	-3.49628600	-1.34611300	-1.83413500
C	-5.48111900	-0.05585100	-0.92916900
C	-3.64363300	1.67484400	-1.26020300
O	-4.07009600	-0.50876900	2.17881500
O	-3.35588600	-2.20517900	-2.57884200
O	-6.61410900	-0.08896900	-1.08753400
O	-3.61401500	2.75992500	-1.62828300
C	3.99455800	-0.28815100	0.97331800
C	3.51112800	-1.39379600	-1.86949900
C	5.48077900	-0.01527200	-1.06380500
C	3.57441000	1.63817400	-1.38646300
O	4.17293100	-0.46827800	2.09117000
O	3.38213100	-2.27762500	-2.58696000
O	6.60876400	-0.01331400	-1.25637200
O	3.49195900	2.71050400	-1.78351700
C	-1.10864800	2.01776100	1.84950800
C	0.13645000	2.62136600	-0.47663600
C	1.51338800	1.99410500	1.74850400
O	-1.91827700	2.44937300	2.52320500
O	0.11886000	3.43864400	-1.27225300
O	2.36446700	2.43135800	2.36450800

3. ESI Mass Spectra.

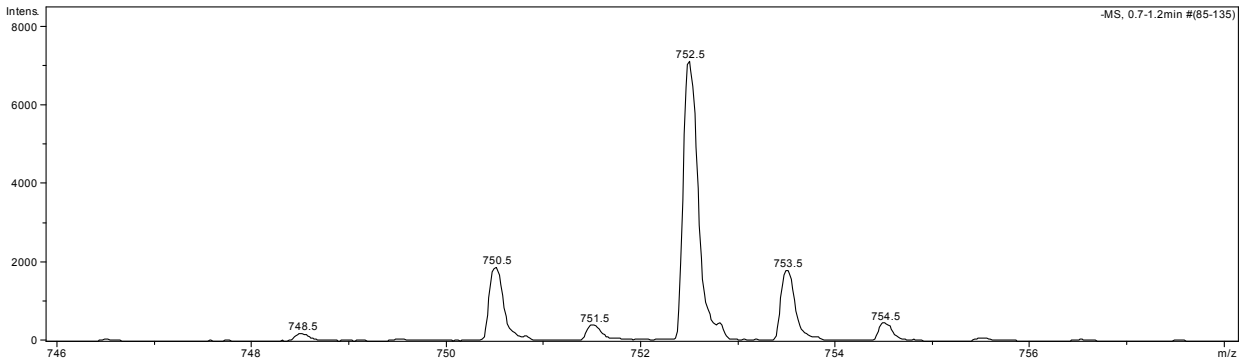
Mass spectra were collected for the crude reaction mixture for the three reactions listed in the experimental as well as for crystals of $[Et_4N]$[**II**] in negative-ion mode.

A. $[Et_4N]$[II] Crystalline product of Reaction 1a (*Experimental*):

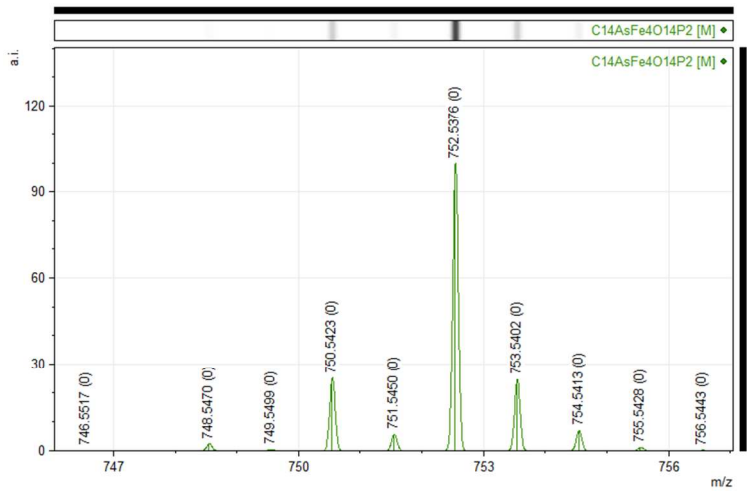
1. Wide view:



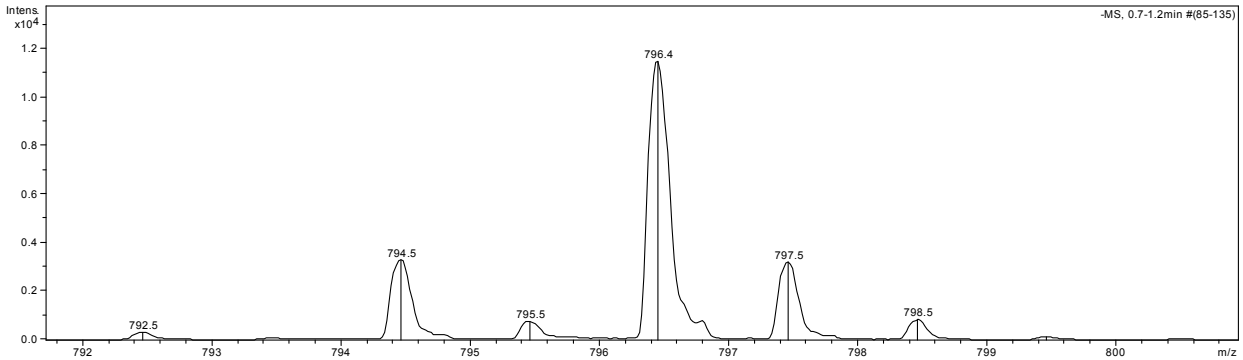
2. $[Fe_2(CO)_6AsP_2\{Fe(CO)_4\}_2]^-$



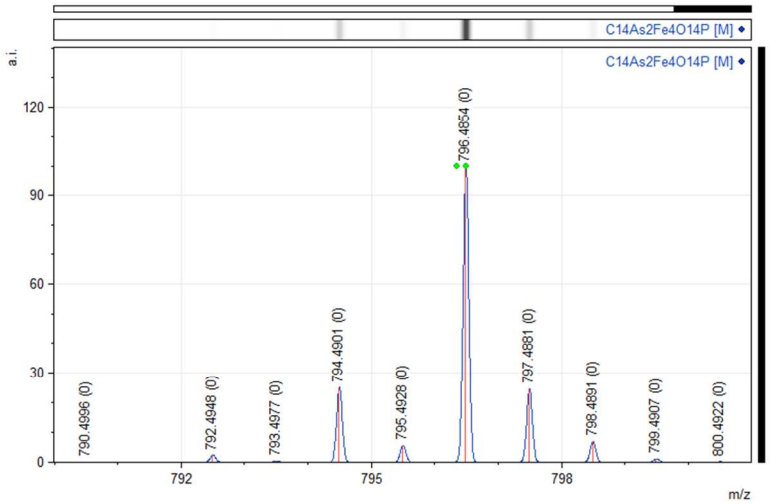
Calculated Spectrum:



3. $[Fe_2(CO)_6AsP_2\{Fe(CO)_4\}_2]^-$

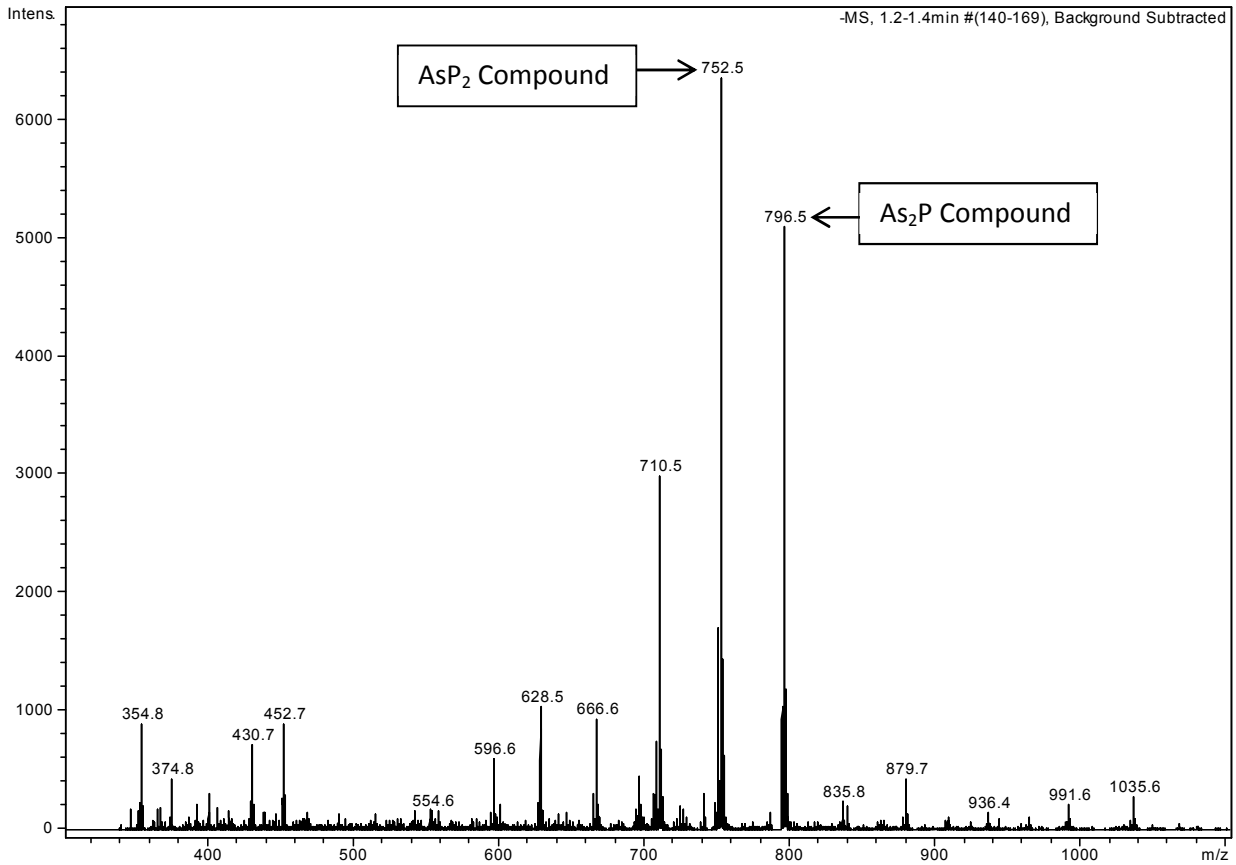


Calculated Spectrum

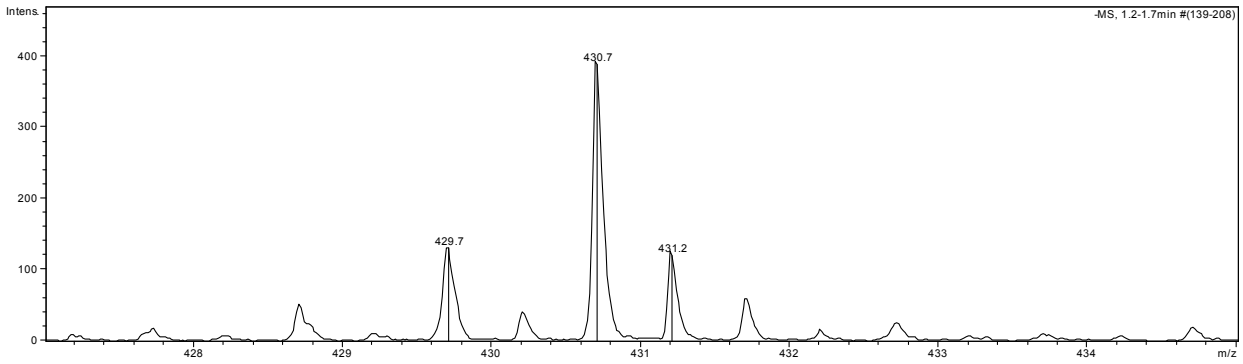


B. Crude Reaction Mixture (1a).

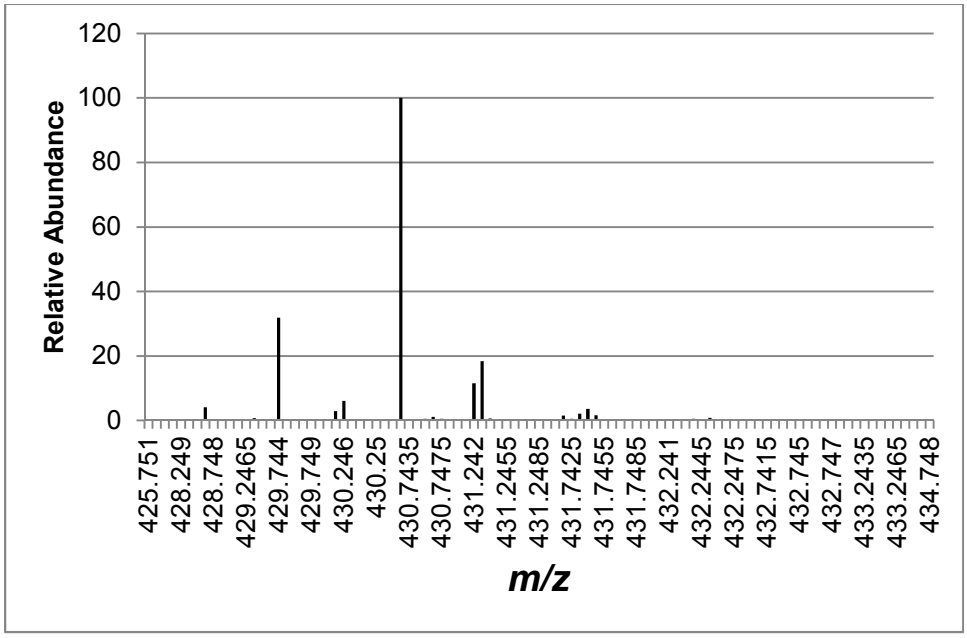
1. Wide View



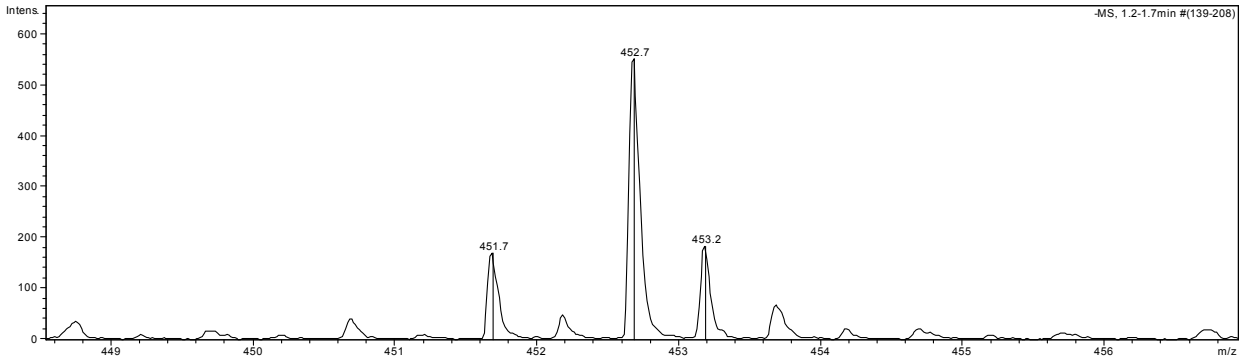
2. $[\{Fe_3(CO)_{9}\}(\mu_3\text{-}AsFe(CO)_4)(\mu_3\text{-}PFe(CO)_4)]^{2-}$



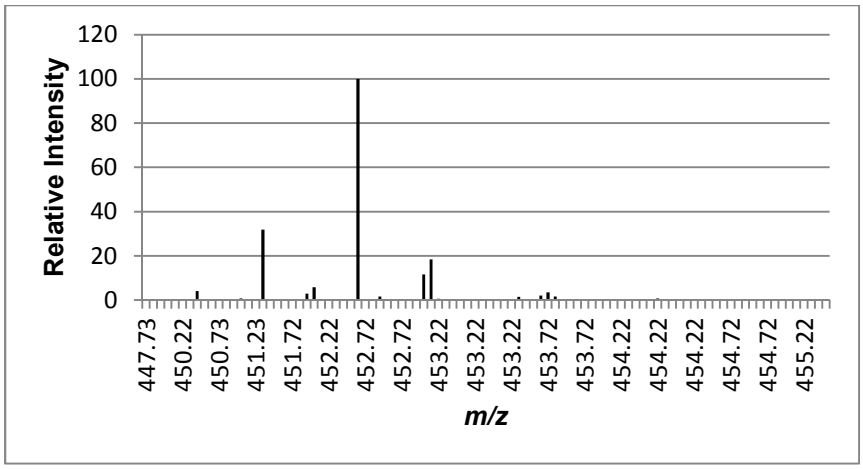
Calculated Spectrum:



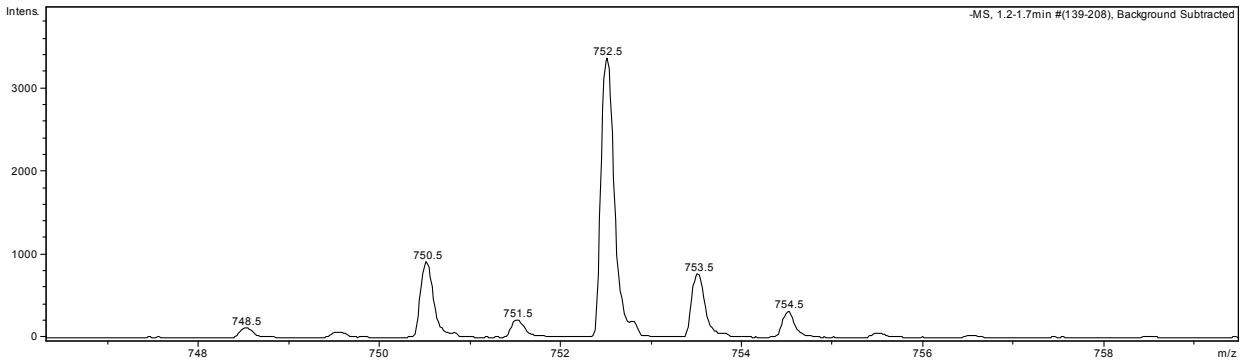
3. $[Fe_3(CO)_9\{\mu_3\text{-}AsFe(CO)_4\}_2]^{2-}$



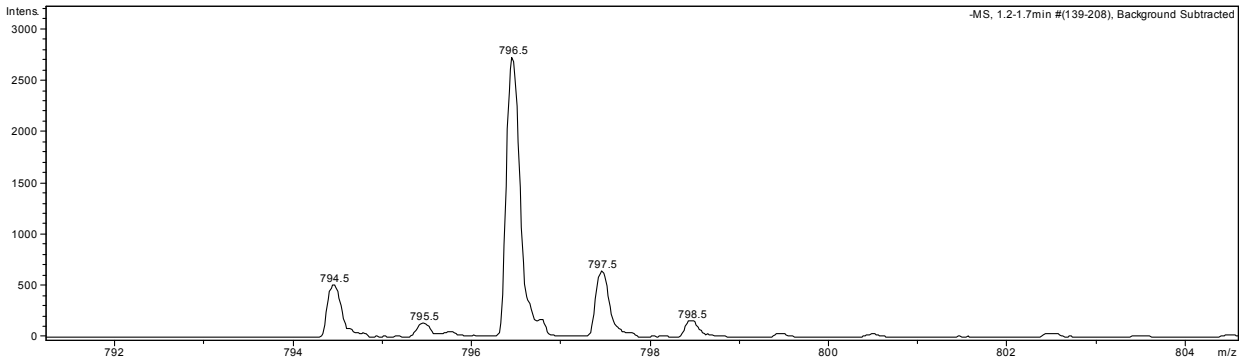
Calculated Spectrum:



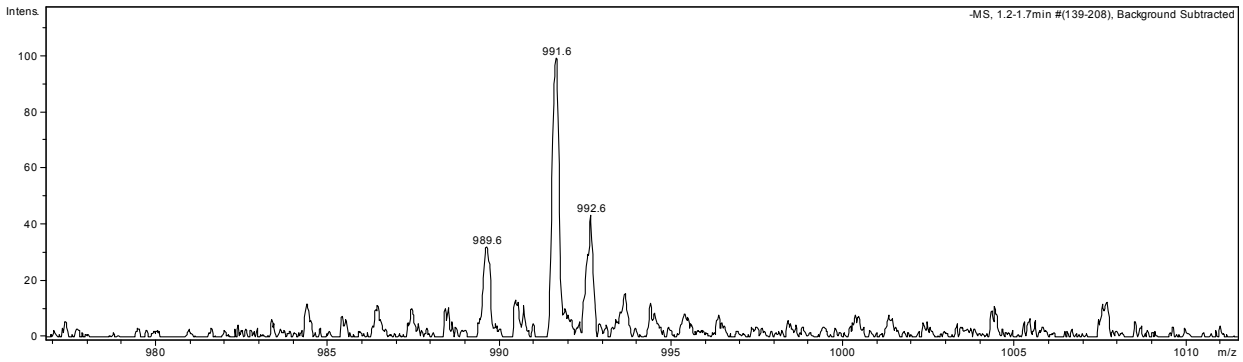
4. $[Fe_2(CO)_6AsP_2\{Fe(CO)_4\}_2]^-$



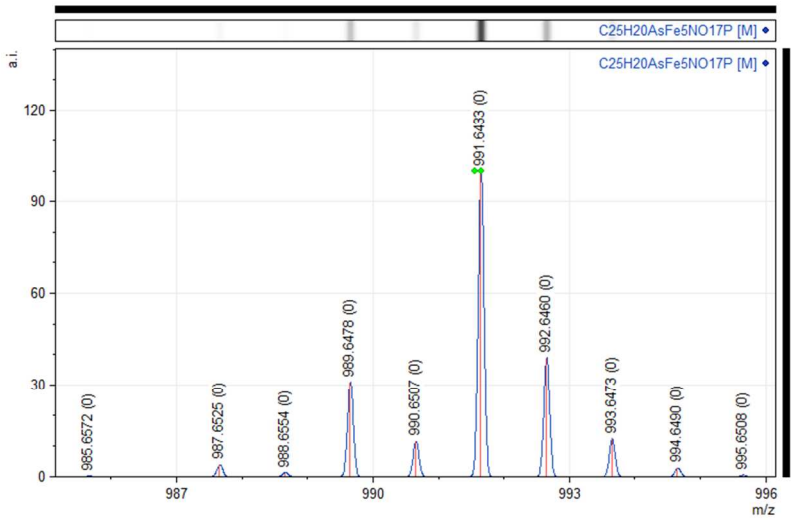
5. $[Fe_2(CO)_6As_2P\{Fe(CO)_4\}_2]^-$



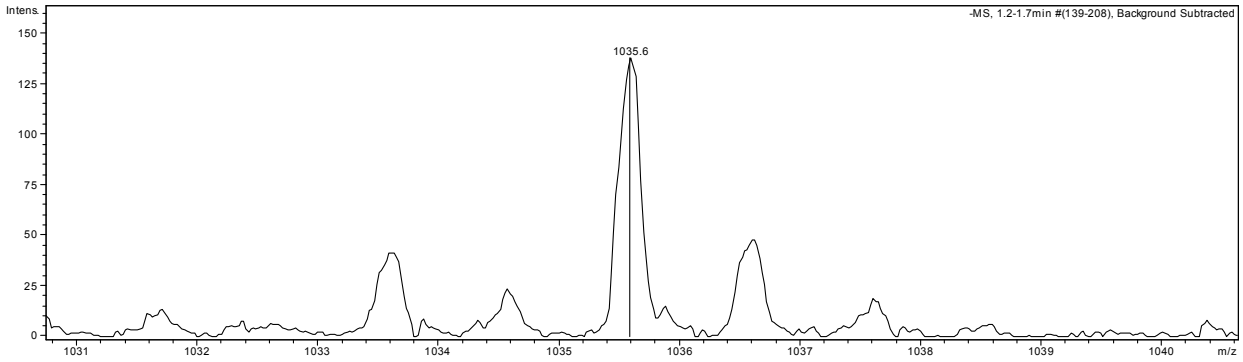
6. $[Et_4N][Fe_3(CO)_9\{\mu_3\text{-}AsFe(CO)_4\}\{\mu_3\text{-}PFe(CO)_4\}]^{1-}$



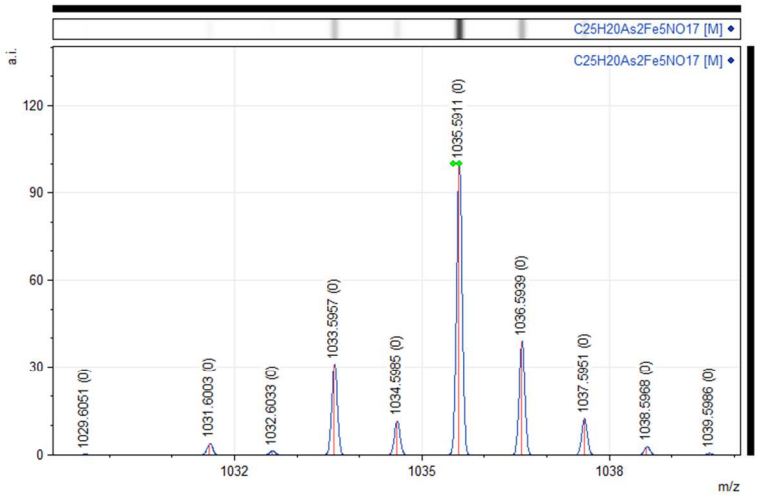
Calculated Spectrum:



7. $[Et_4N][Fe_3(CO)_9\{\mu_3\text{-}AsFe(CO)_4\}_2]^-$

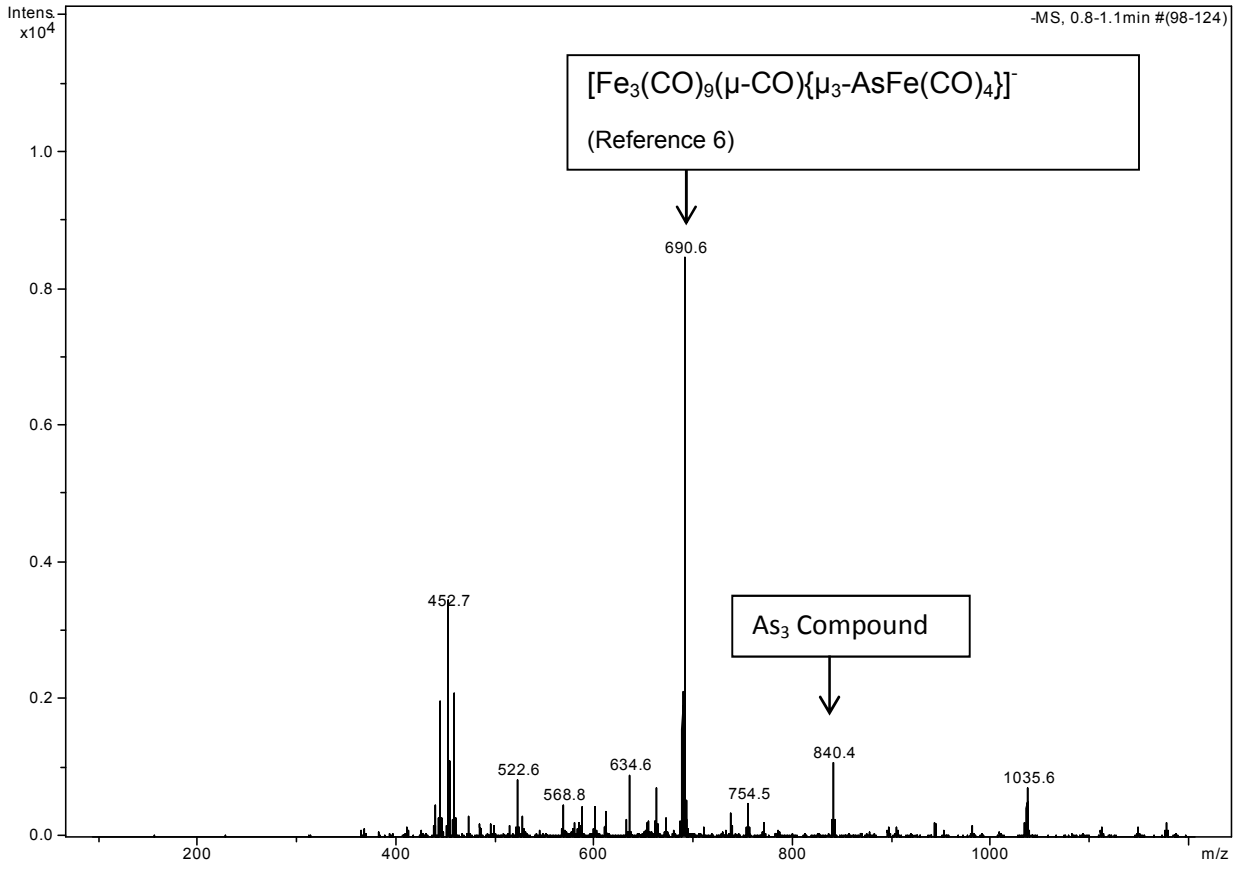


Calculated Spectrum:

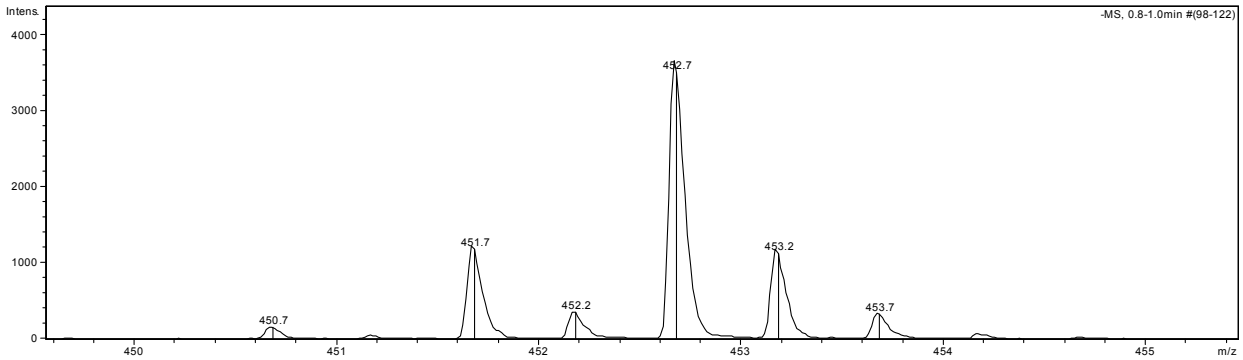

C25H20As2Fe5NO17 [M] ◆
C25H20As2Fe5NO17 [M] ◆
a.i.
120
90
60
30
0
1029.6051 (0)
1031.6003 (0)
1032.6033 (0)
1033.5957 (0)
1034.5985 (0)
1035.5911 (0)
1036.5939 (0)
1037.5951 (0)
1038.5968 (0)
1039.5986 (0)
1032
1035
1038
m/z

C. Crude Reaction Mixture (1b)

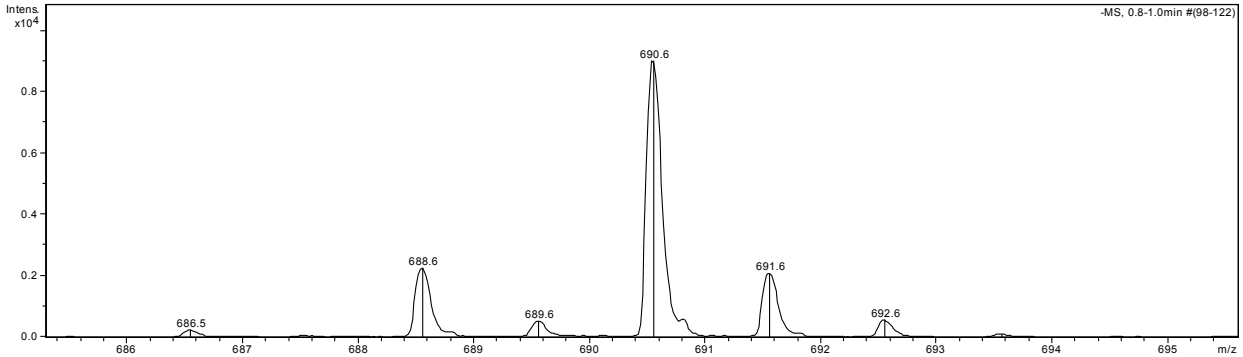
1. Wide View



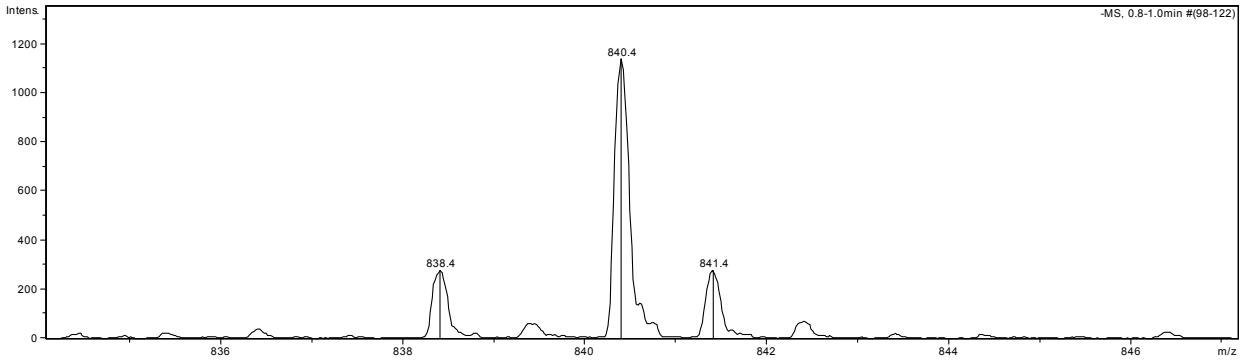
2. $[Fe_3(CO)_{9\}}\{\mu_3\text{-}AsFe(CO)_4\}_2]^{2-}$



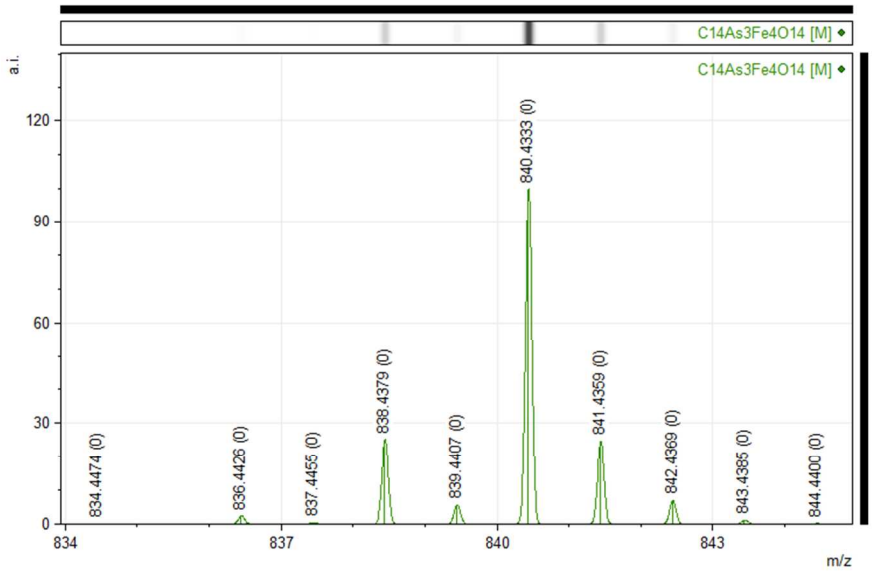
3. $[Fe_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}AsFe(CO)_4\}]^-$ (Reference 6)



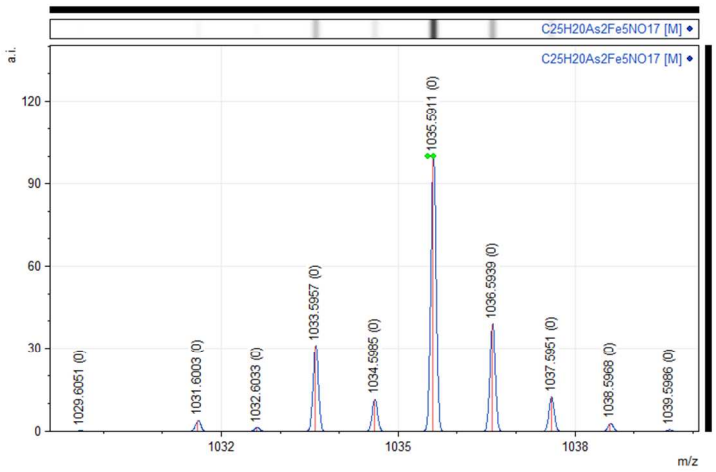
4. $[Fe_2(CO)_6As_3\{Fe(CO)_4\}_2]^-$ (As_3 Fe_4E_3 Species)

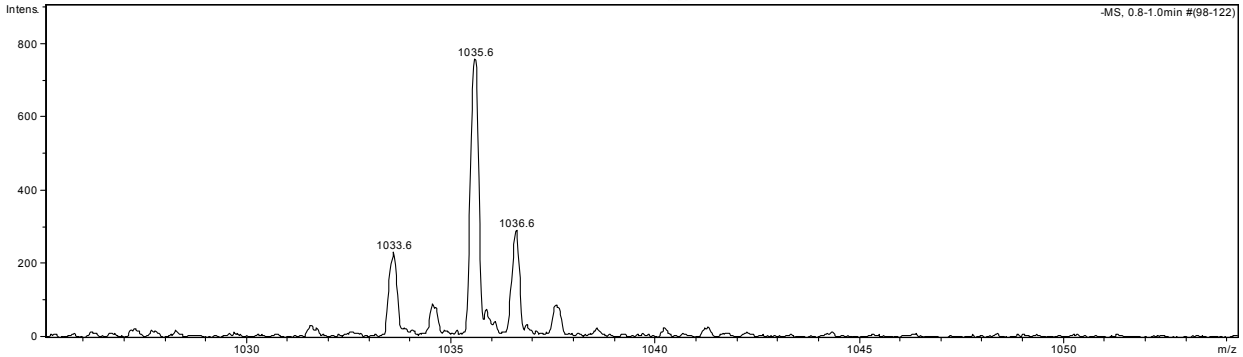


Calculated Spectrum:



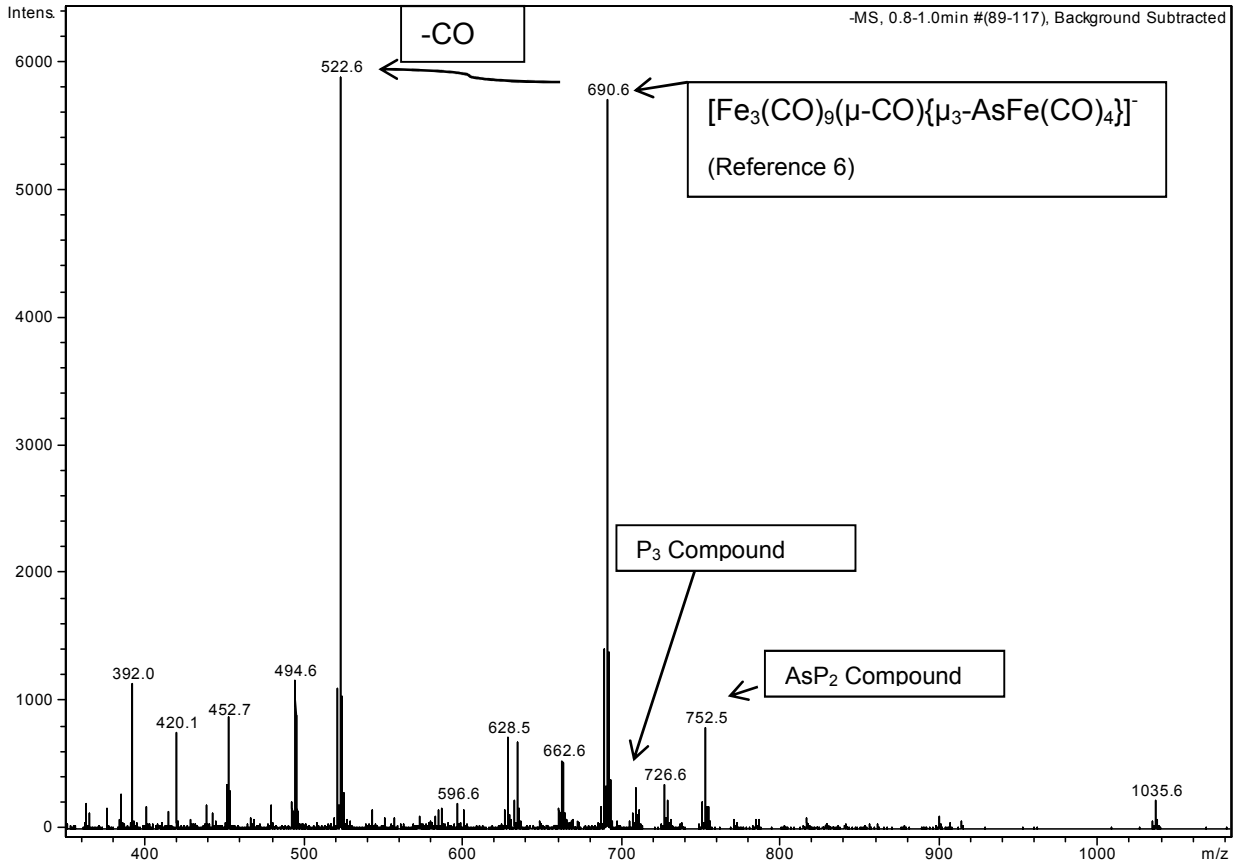
5. $[Et_4N][Fe_3(CO)_9\{\mu_3\text{-}AsFe(CO)_4\}_2]^-$


C25H20As2Fe5NO17 [M] ◆
C25H20As2Fe5NO17 [M] ◆
a.i.
120
90
60
30
0
1029.6051 (0)
1031.6003 (0)
1032.6033 (0)
1033.5957 (0)
1034.5985 (0)
1035.5911 (0)
1036.5939 (0)
1037.5951 (0)
1038.5968 (0)
1039.5986 (0)
1032
1035
1038
m/z

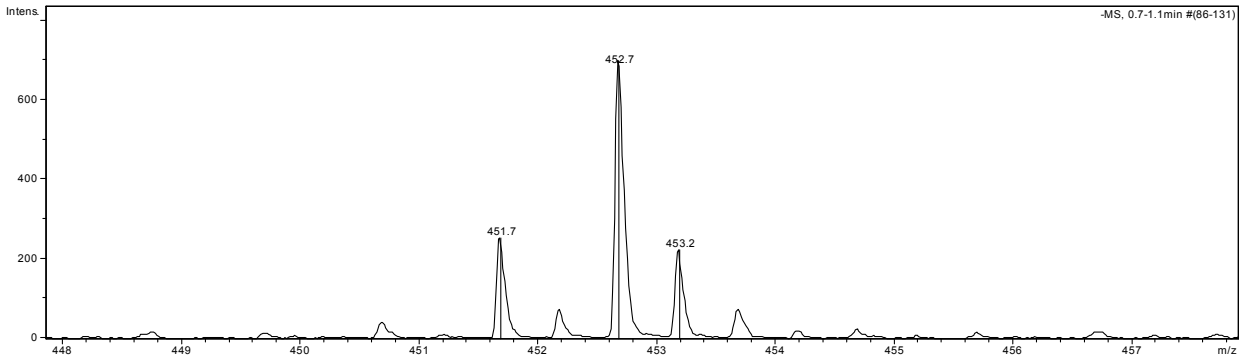

Intens.
-MS, 0.8-1.0min #(98-122)
800
600
400
200
0
1035.6
1036.6
1033.6
1030
1035
1040
1045
1050
m/z

D. Crude Reaction Mixture (1c):

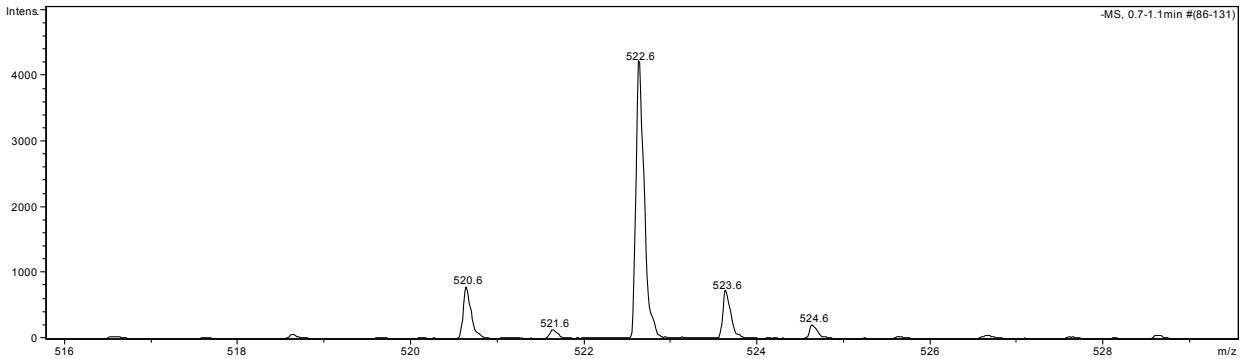
1. Wide View



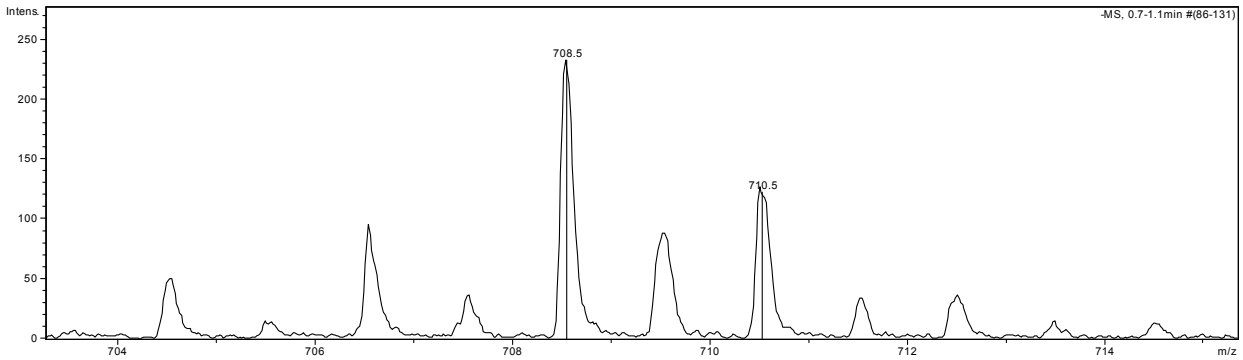
2. $[\{Fe_3(CO)_9\}(\mu_3\text{-}AsFe(CO)_4)_2]^{2-}$



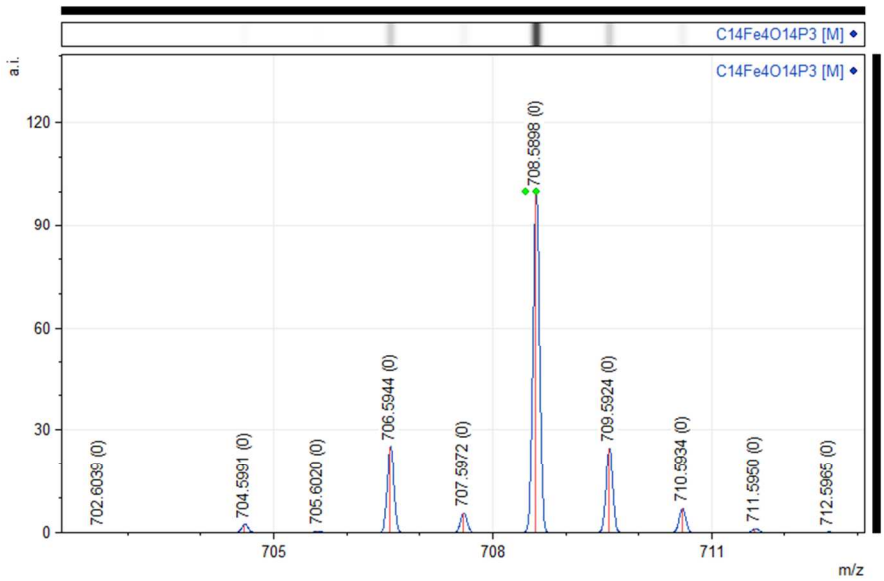
3. $[Fe_3(CO)_{10}As]^-$ (Ref. 6)



4. $[Fe_2(CO)_6P_3\{Fe(CO)_4\}_2]^-$

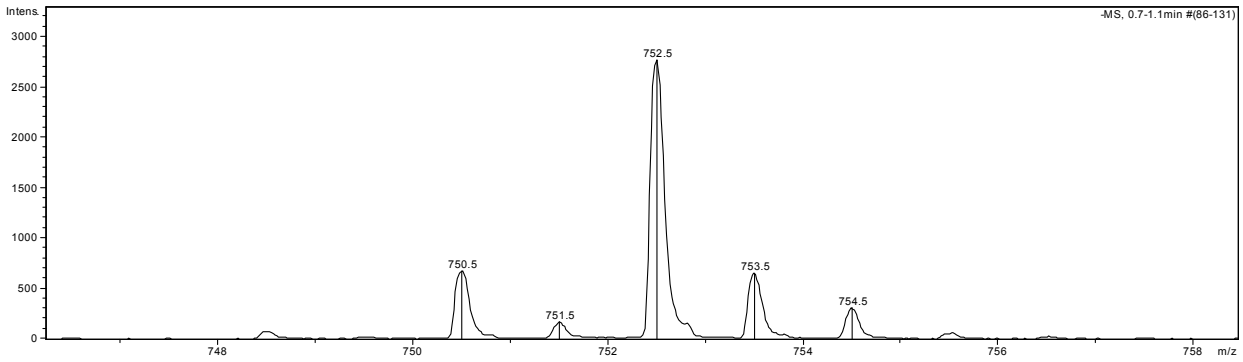
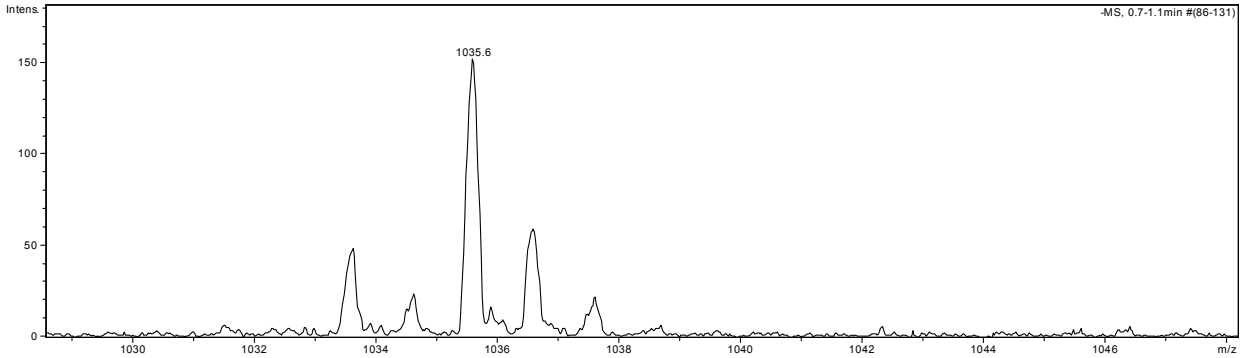


Calculated Spectrum



Overlaps with unidentified peak at 710.5 *m/z*.

5. $[Fe_2(CO)_6AsP_2\{Fe(CO)_4\}_2]^-$



6. $[Et_4N][\{Fe_3(CO)_9\}(\mu_3\text{-}AsFe(CO)_4)_2]^-$