Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Boosting Catalyst Activity in Cis-Selective Semi-Reduction of Internal Alkynes by Tailoring the Assembly of All-Metal Aromatic Tri-Palladium Complexes

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1. General remarks

$Pd(dba)_2$, disulfides and phosphines and reagents used for catalytic reactions were purchased from commercial sources and used as received.

3-(Diphenylphosphino)benzenesulfonic acid sodium salt was kept under vacuum for at least 30 minutes prior to use to remove water traces.

Solvents were degassed by bubbling N_2 for at least 40 minutes prior to use.

For both the synthesis of complexes and catalytic reactions the use of dry solvents is not required.

Comparable results were observed using either dry solvents or wet ones.

Reactions and filtrations were carried out under N_2 using standard Schlenk technique.

^{1}H-NMR spectra were recorded in $CDCl_3$, acetone-d_6 or methanol-d_4 at 298 K on Bruker 300 and 400 AVANCE spectrometers fitted with a BBFO probe-head at 300 and 400 MHz respectively, using the solvent as internal standard (7.26 ppm for $CDCl_3$, 2.05 ppm for acetone-d_6 and 3.34 ppm for methanol-d_4). Reported assignements were based on COSY, NOESY and ROESY correlation experiments.

^{31}P NMR spectra were recorded in $CDCl_3$, acetone-d_6 or methanol-d_4 at 298 K on a Bruker 400 AVANCE spectrometer fitted with a BBFO probe-head at 162 MHz.

^{19}F NMR spectra were recorded in $CDCl_3$ at 298 K on a Bruker 400 AVANCE spectrometer fitted with a BBFO probe-head at 376 MHz.

The terms m, s, d, t, q represent multiplet, singlet, doublet, triplet, quadruplet respectively, and the term br means a broad signal.

Exact masses of complexes A-D were recorded on a LTQ ORBITRAP XL Thermo Mass Spectrometer (electrospray source). Complex E did not afford any Pd-containing ion within the orbitrap analyser. Mass analysis on complex E was performed on an Infusion Water Acquity Ultra Performance LC HO6UPS-823M instrument (elecrtospray source, quadrupole analyser).

Spectroscopic data of complexes of general formula $[Pd_3]X$ presented in the article (I, II and III) correspond to literature references (described in refs 3-5 of the manuscript).

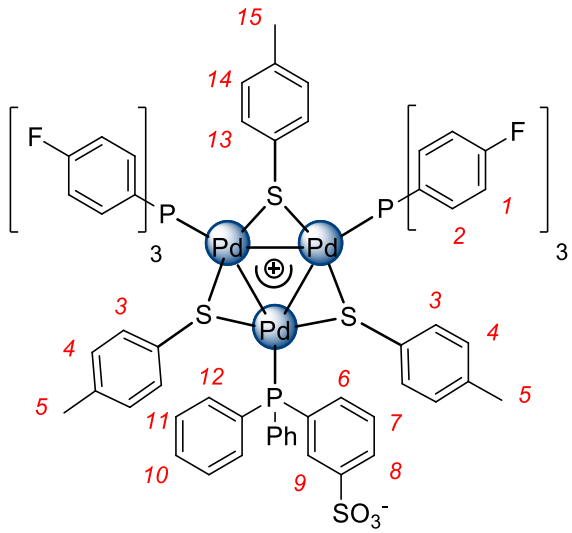
2. Experimental procedures

Synthesis of zwitterionic triangular tripalladium complexes A-E

$Pd(dba)_2$ (1 eq., 0.2 mmol, 115 mg) was added to a 50 ml schlenk and the vessel underwent at least three vacuum/N_2 cycles. 20 mL of freshly degassed $CHCl_3$ were immediately syringed under N_2. 3-(Diphenylphosphino)benzenesulfonic acid sodium salt (0.33 eq., 0.066 mmol, 24 mg), the desired phosphine (0.66 eq., 0.132 mmol) and the disulfide (0.5 eq., 0.1 mmol) were then added under N_2 and the solution rapidly turn deep red. The resulting mixture was kept under magnetic stirring at room temperature for 3 hours and then filtered through a celite pad under N_2 to remove traces of black metals. The solvent was removed under vacuum and the resulting solid was purified by $CHCl_3$/hexane washings (1/60 v/v, 3 x 30 mL). Evaporation of volatiles afforded pure clusters as orange/red solids. Zwitterionic clusters were characterized by TLC, HRMS, ^{1}H, ^{31}P and ^{19}F NMR spectroscopy. Owing to their reduced symmetry compared to previously described Pd_3^+ complexes, acquisition of ^{13}C NMR spectra proved extremely difficult.

3. Spectroscopic data of complexes A-E

Complex A



Isolated as a red powder. Yield = 71%

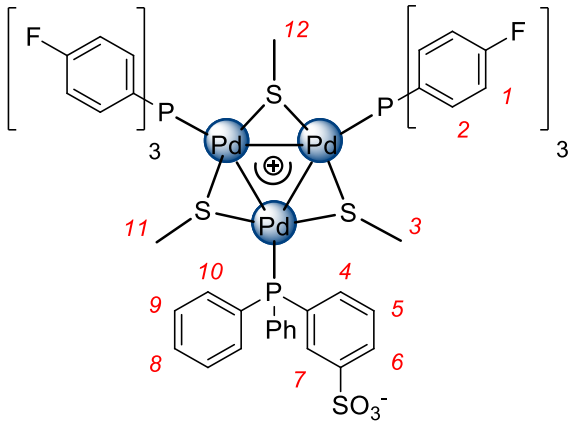
HRMS calculated for $C_{75}H_{60}F_6O_3P_3Pd_3S_4^+$ [M+H$^+$]: 1662.9680, found: 1662.9676.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 14.37 Hz, 1H, H_9), 8.16 (d, J = 7.58 Hz, 1H, H_8), 7.11 (m, 12H, H_1), 7.00 (m, 10H, $H_{10\text{-}12}$), 6.88 (t, J = 8.56 Hz, 12H, H_2), 6.74 (m, 2H, H_6, H_7), 6.52 (d, J = 7.87 Hz, 2H, H_{14}), 6.44 (d, J = 8.02 Hz, 4H, H_4), 6.16 (d, J = 8.03 Hz, 2H, H_{13}), 6.12 (d, J = 7.99 Hz, 4H, H_3), 2.17 (s, 3H, H_{15}), 2.14 (s, 6H, H_5).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.45 (t, J = 106.9 Hz, P($C_{18}H_{14}SO_3^-$)), 13.27 (2 overlapping d, J = 108.5 Hz, 2P(C_6H_4F)$_3$).

^{19}F NMR (376 MHz, $CDCl_3$): δ -108.39

Complex B



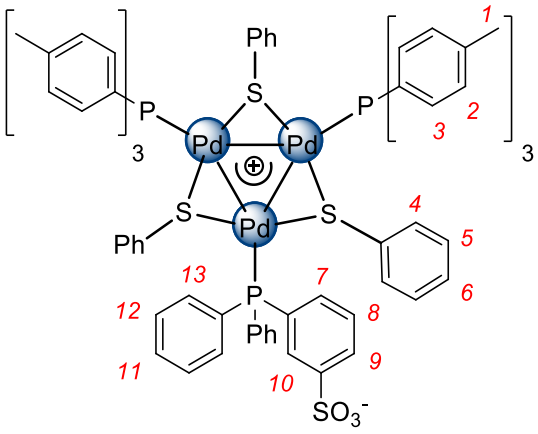
Isolated as an orange powder. Yield = 55%

HRMS calculated for $C_{57}H_{48}F_6O_3P_3Pd_3S_4$ [M+H$^+$]: 1432.8734, found: 1432.8742.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 7.33 Hz, 1H, H_6), 8.15 (d, J = 14.72 Hz, 1H, H_7), 7.49 (m, 24H, H_1, H_4, H_5, $H_{8\text{-}10}$), 7.17 (t, J = 8.56 Hz, 12H, H_2), 1.18 (s, 3H, H_3), 1.15 (s, 3H, H_{11}), 1.07 (s, 3H, H_{12}).

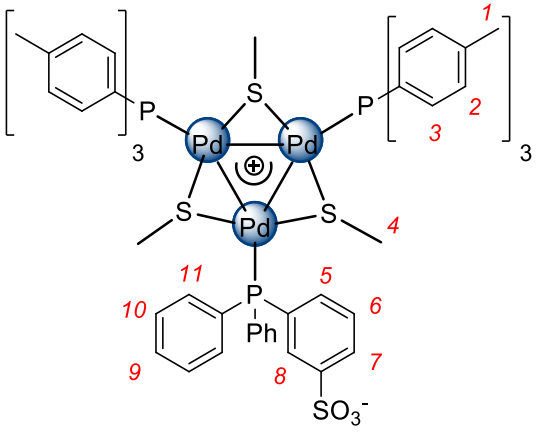
^{31}P NMR (162 MHz, $CDCl_3$): δ 19.35 (dd, J = 97.2, 110.8 Hz, P($C_{18}H_{14}SO_3^-$)), 14.41 (2 overlapping d, J = 100.4, 106.0 Hz, 2P(C_6H_4F)$_3$).
^{19}F NMR (376 MHz, $CDCl_3$): δ -106.72

Complex C



Isolated as a red powder. Yield = 59%
HRMS calculated for $C_{78}H_{72}O_3P_3Pd_3S_4$ [M+H$^+$]: 1597.0716, found: 1597.0702.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (m, 1H, H_{10}), 7.18 (m, 47H, $H_{2\text{-}9}$, $H_{11\text{-}13}$), 6.60 (m, 3H, H_5, H_6), 6.24 (m, 2H, H_4), 2.32 (m, 18H, H_1).
^{31}P NMR (162 MHz, $CDCl_3$): δ 16.47 (t, J = 82.6 Hz, P($C_{18}H_{14}SO_3^-$)), 14.85 (2 overlapping d, J = 79.4 Hz, 2P(C_7H_7)$_3$).

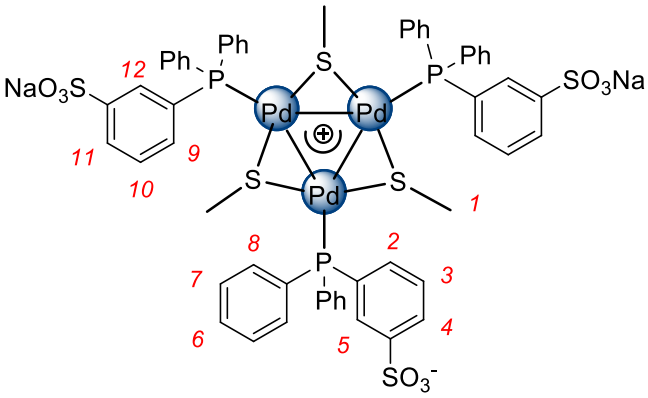
Complex D



Isolated as an orange powder. Yield = 76%
HRMS calculated for $C_{63}H_{66}O_3P_3Pd_3S_4$ [M+H$^+$]: 1409.0240, found: 1409.0236.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, J = 7.94 Hz, 1H, H_7), 8.07 (d, J = 12.80 Hz, 1H, H_8), 7.61 (m, 4H, H_{11}), 7.37 (m, 18H, H_3, H_9, H_{10}), 7.18 (d, J = 7.70 Hz, 12H, H_2), 7.07 (d, J = 7.25 Hz, 1H, H_5), 6.92 (d, J = 8.07 Hz, 1H, H_6), 2.37 (s, 18H, H_1), 1.05 (m, 9H, H_4).

^{31}P NMR (162 MHz, $CDCl_3$): δ 17.67 (dd, J = 124.9, 83.7 Hz, P($C_{18}H_{14}SO_3^-$)), 15.81 (2 overlapping d, J = 124.7, 84.2 Hz, 2P(C_7H_7)$_3$).

Complex E



Isolated as a brown powder. Yield = 72%

For complex E we were unable to obtain the exact mass with ESI$^+$-ORBITRAP, we thus performed a low resolution analysis by LC-ESI$^+$ MS (quadrupole analyser).

MS calculated for $C_{57}H_{51}Na_3O_9P_3Pd_3S_6$ [M+Na$^+$]: 1552.79, found: 1552.83.

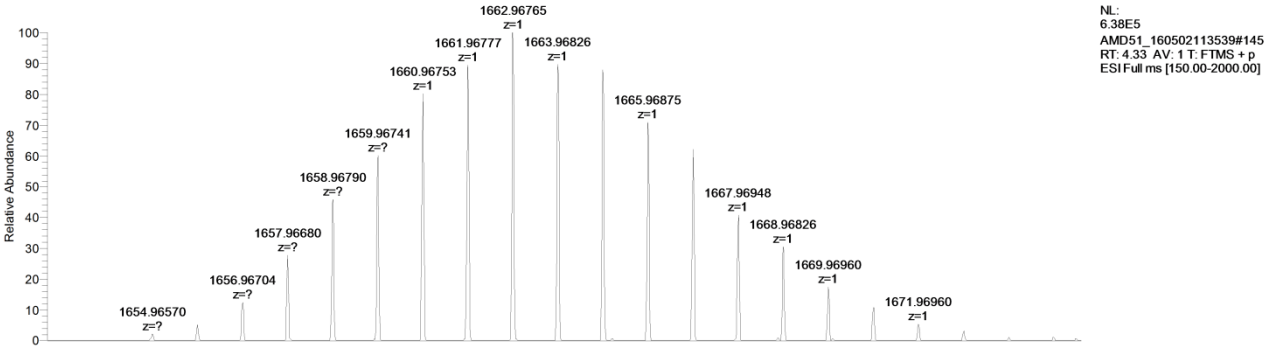
^{1}H NMR (300 MHz, methanol-d_4): δ 8.11 (2 overlapping d, J = 10.21, 6 Hz, 5H, H_5, H_{11}, H_{12}), 7.98 (d, J = 7.12 Hz, 3H, H_2, H_9), 7.84 (m, 4H, H_3, H_{10}), 7.63 (m, 30H, $H_{6\text{-}8}$), 1.32 (m, 4H, H_1, overlapping with m, 8H, CH_2 hexane), 1.08 (m, 4H, H_1), 0.93 (t, 6H, CH_3 hexane).

^{31}P NMR (162 MHz, methanol-d_4): δ 31.50 (s, 2P, P($C_{18}H_{14}SO_3Na$)), 17.39 (s, 1P, P($C_{18}H_{14}SO_3^-$))

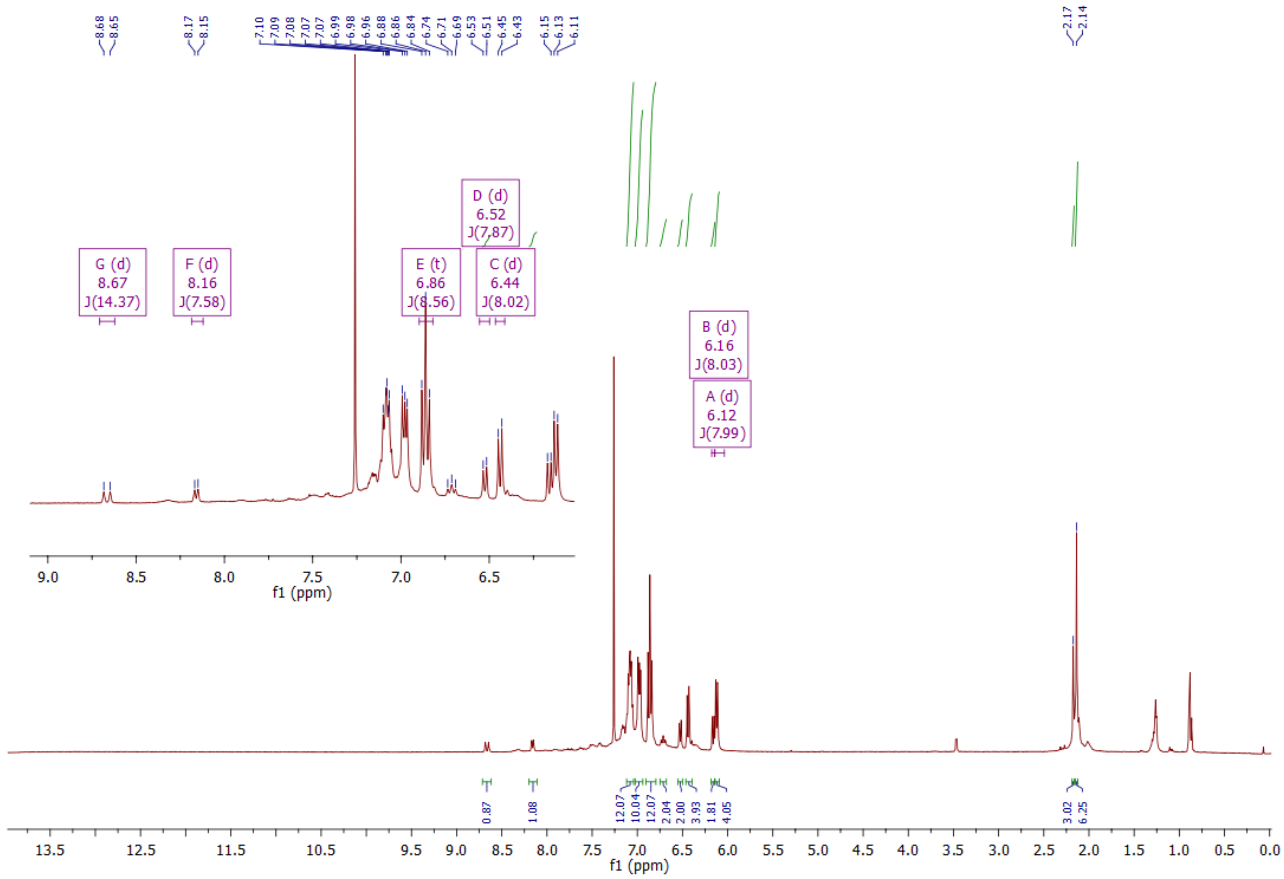
4. Copies of HRMS and NMR spectra

4.1 Spectra of complex A

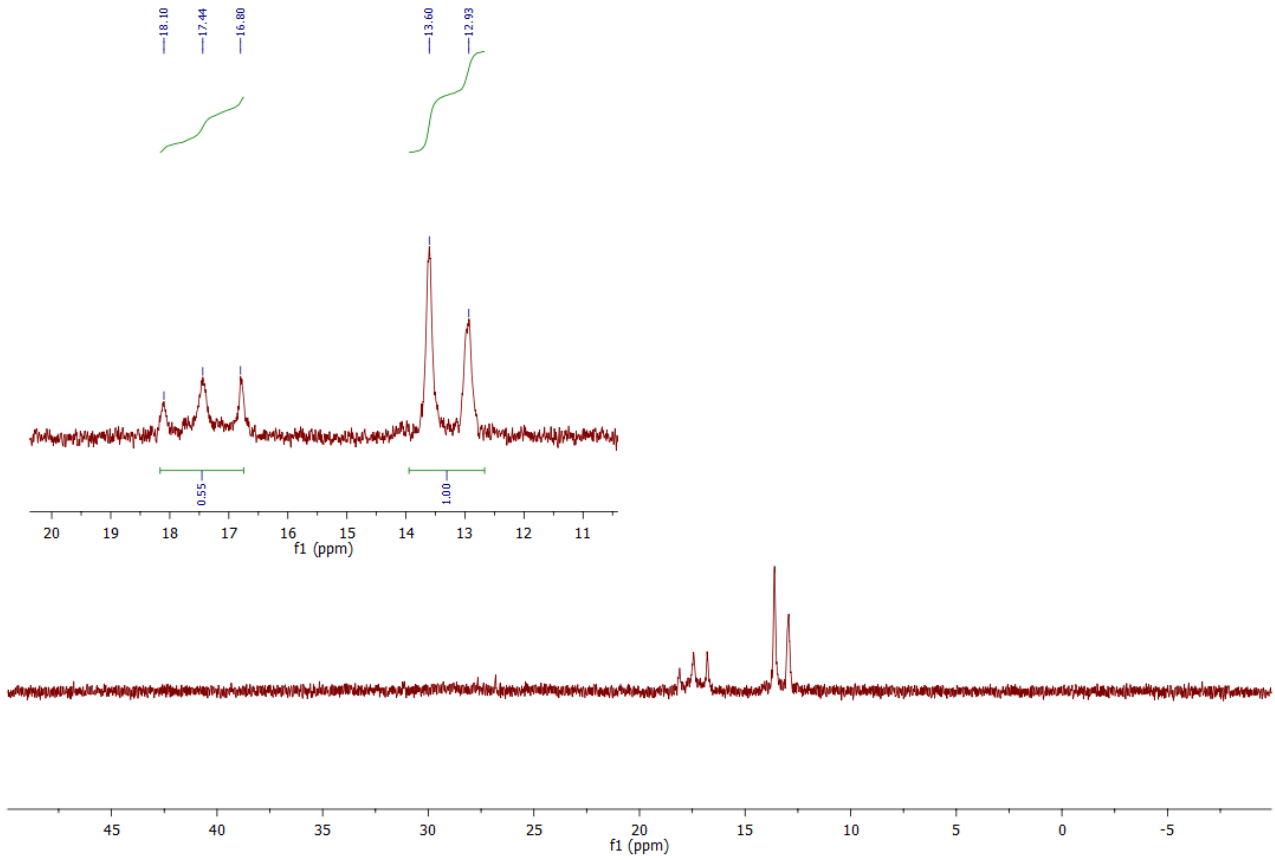
HRMS of complex A



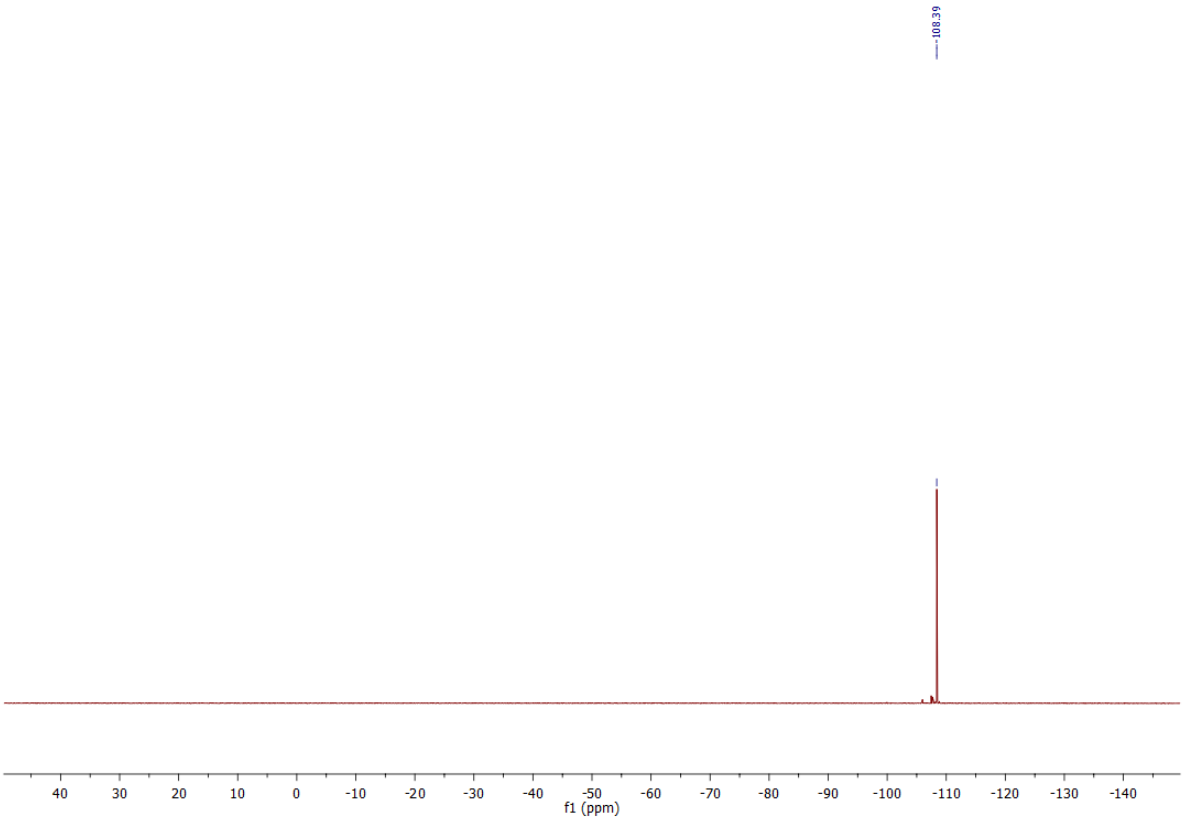
^{1}H NMR of complex A



^{31}P NMR of complex A

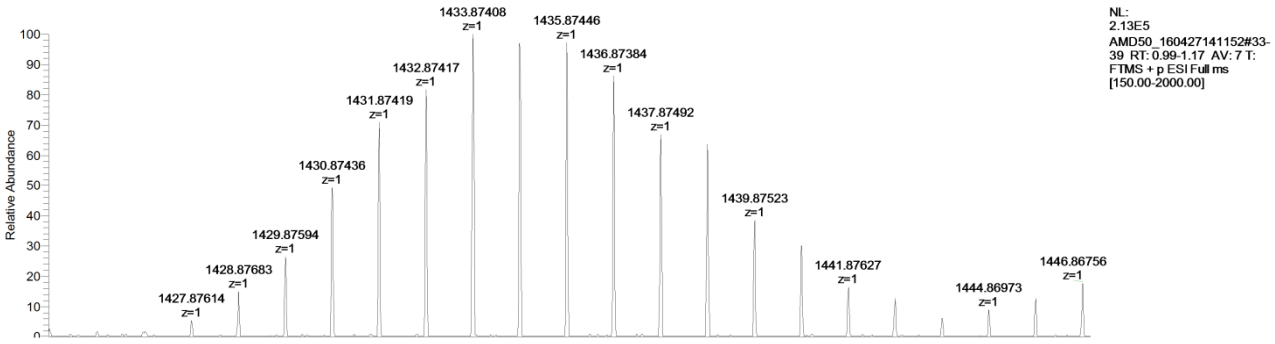


^{19}F NMR of complex A

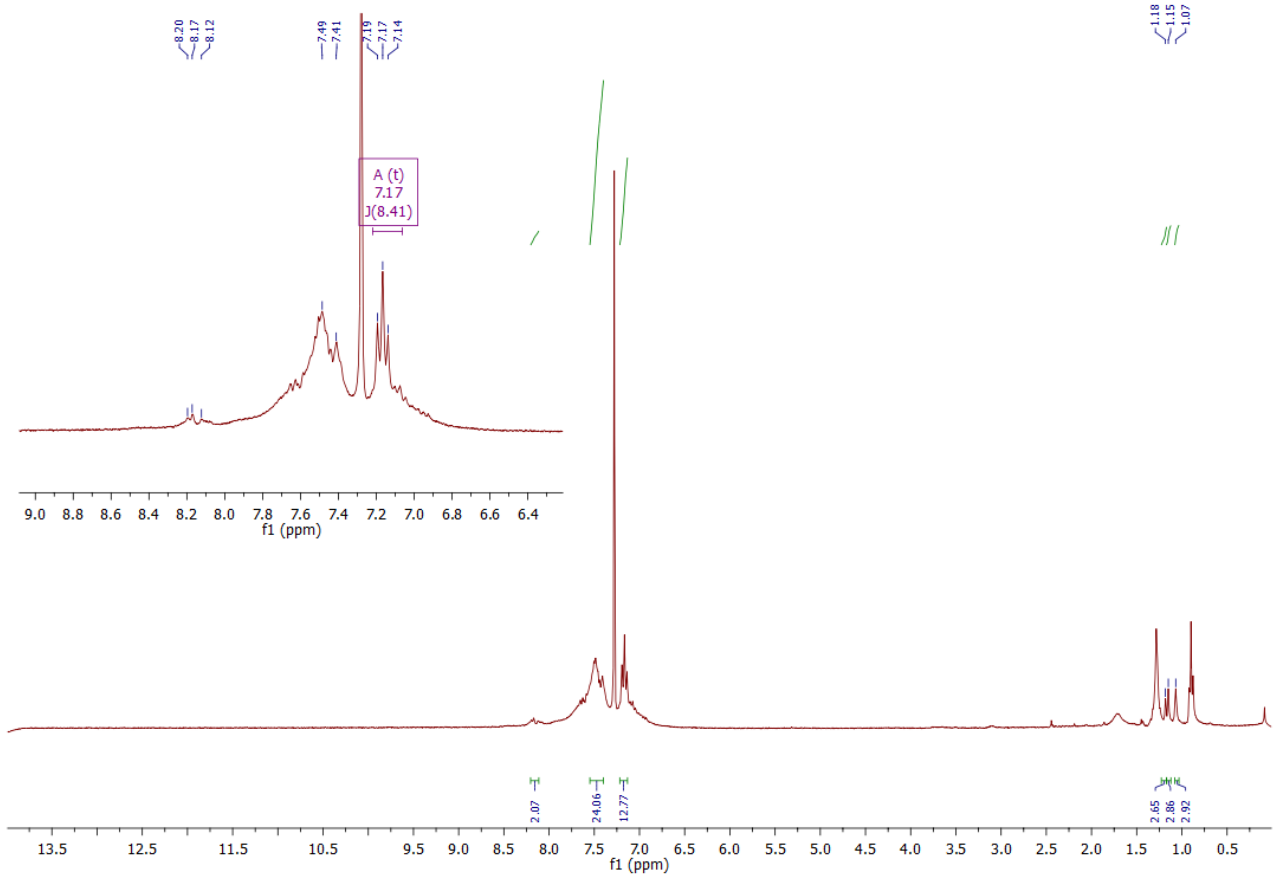


4.2 Spectra of complex B

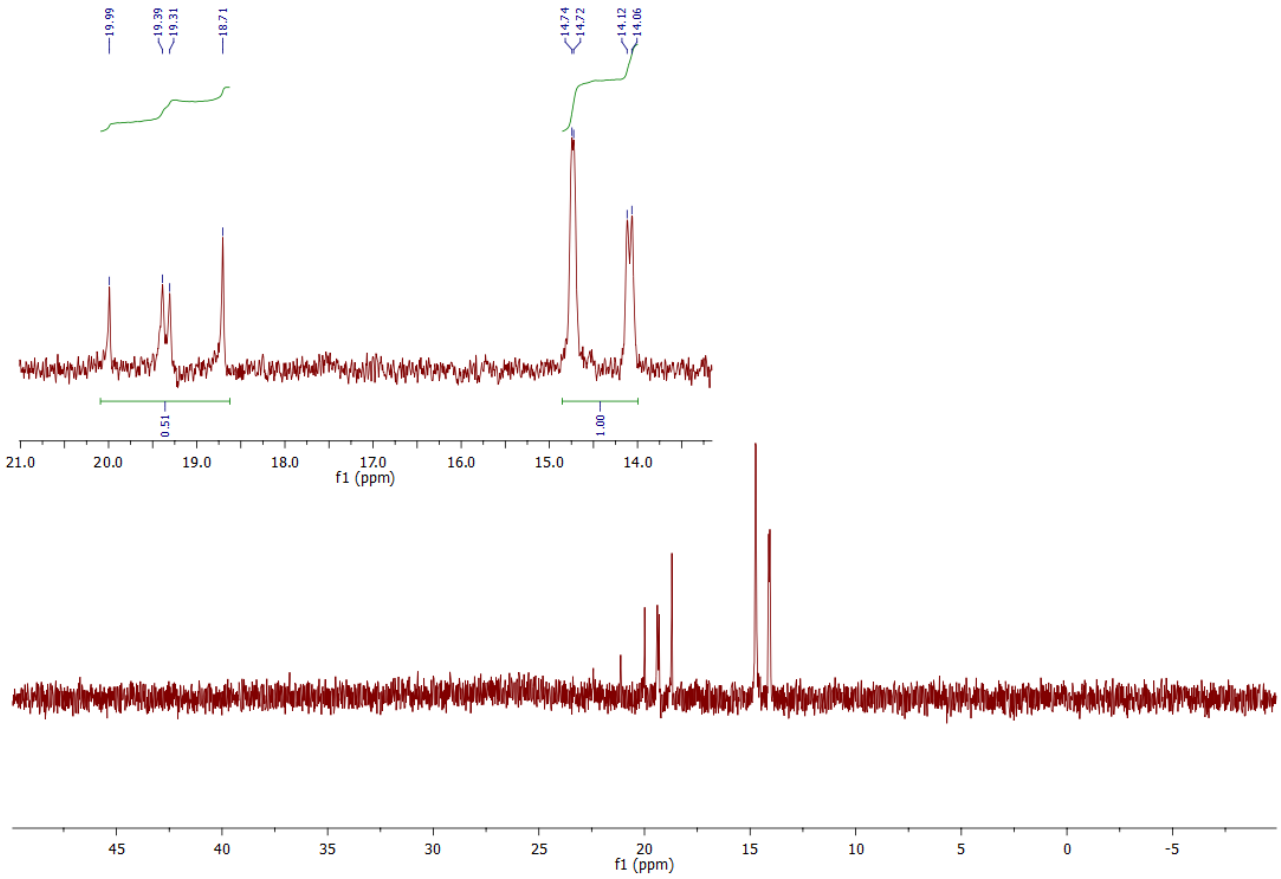
HRMS of complex B



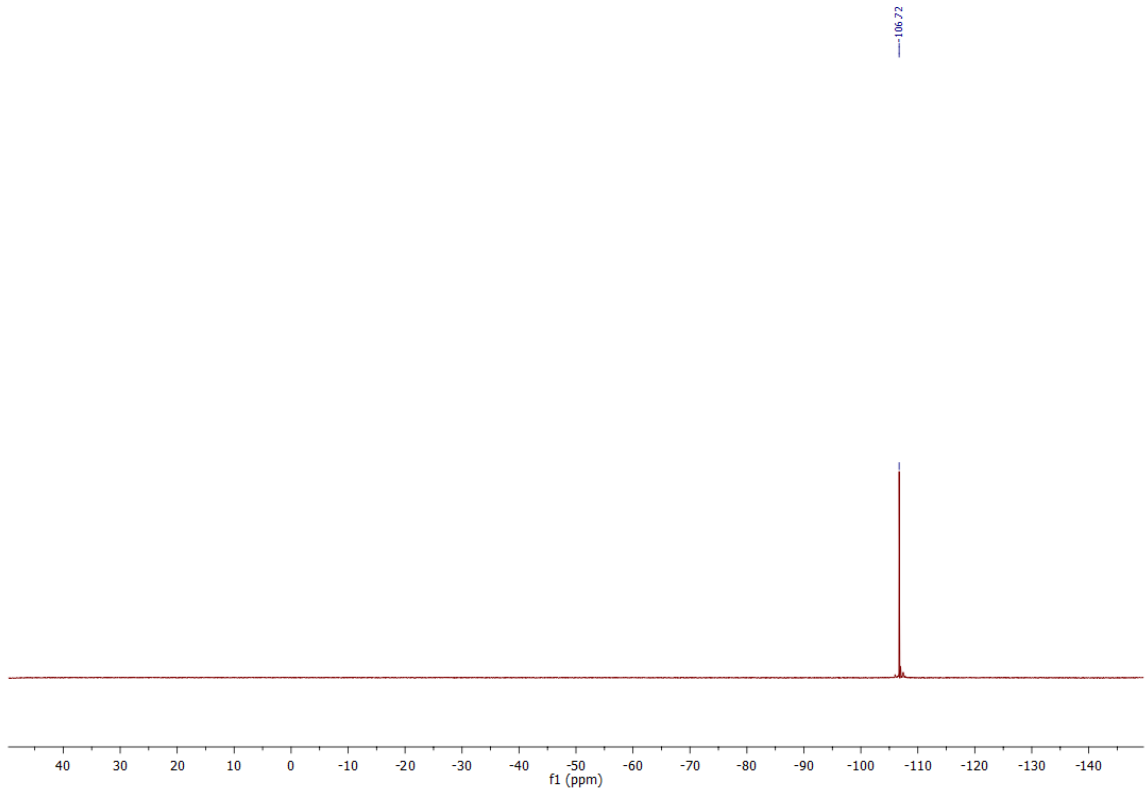
^{1}H NMR of complex B



^{31}P NMR of complex B

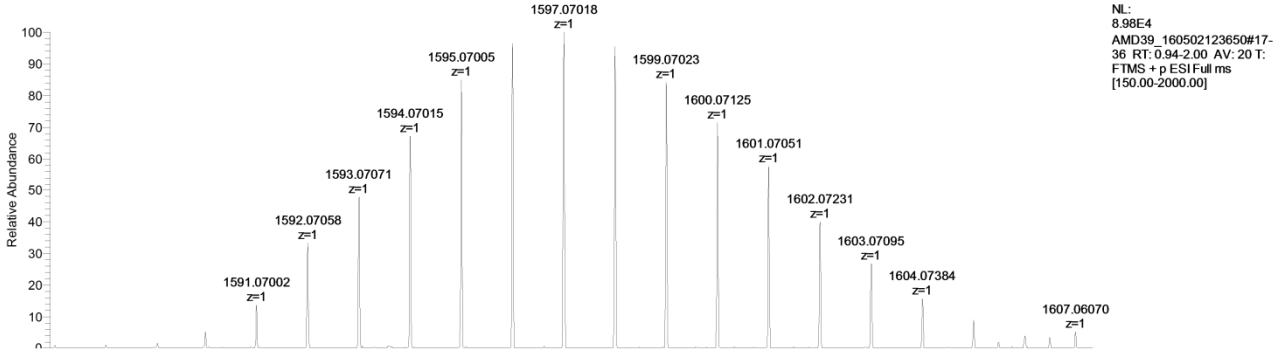


^{19}F NMR of complex B

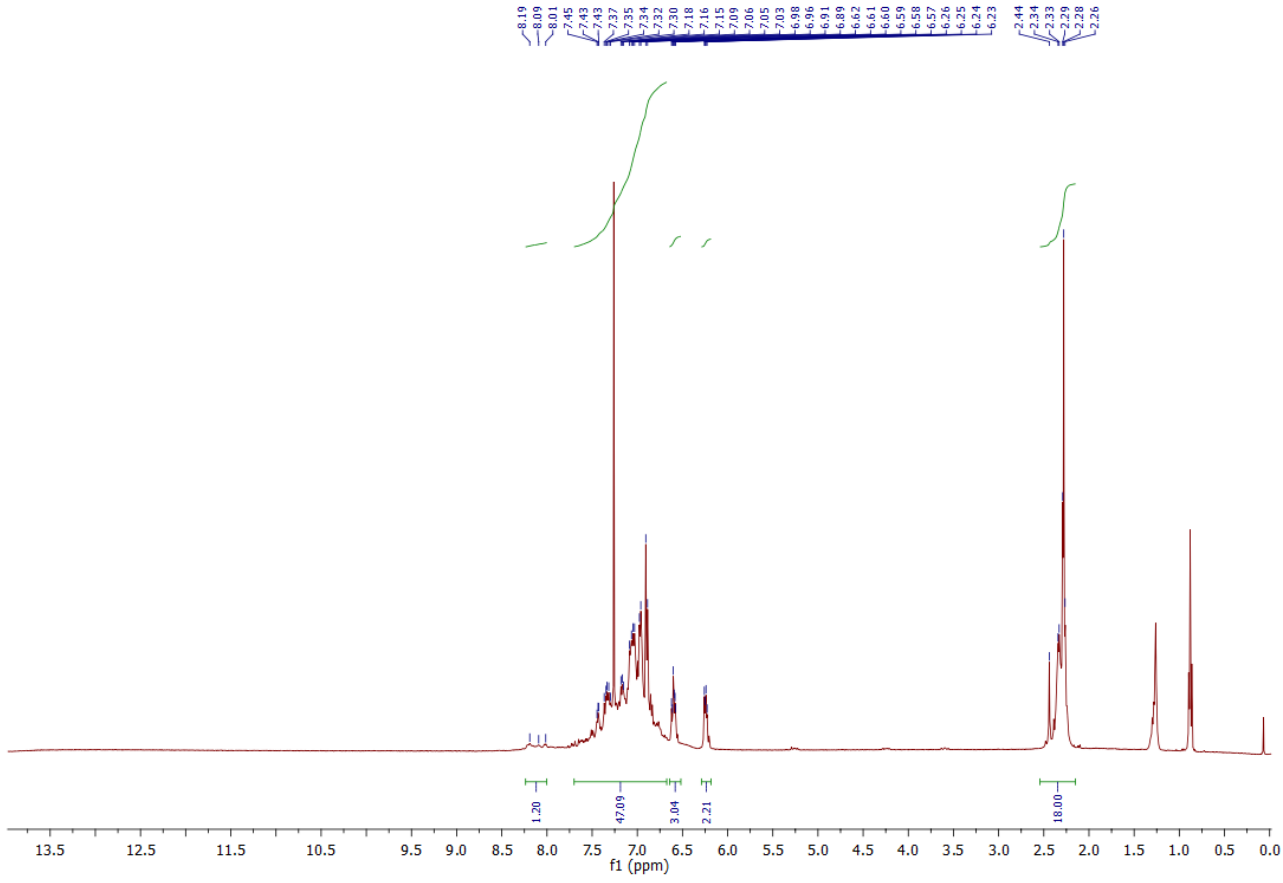


4.3 Spectra of complex C

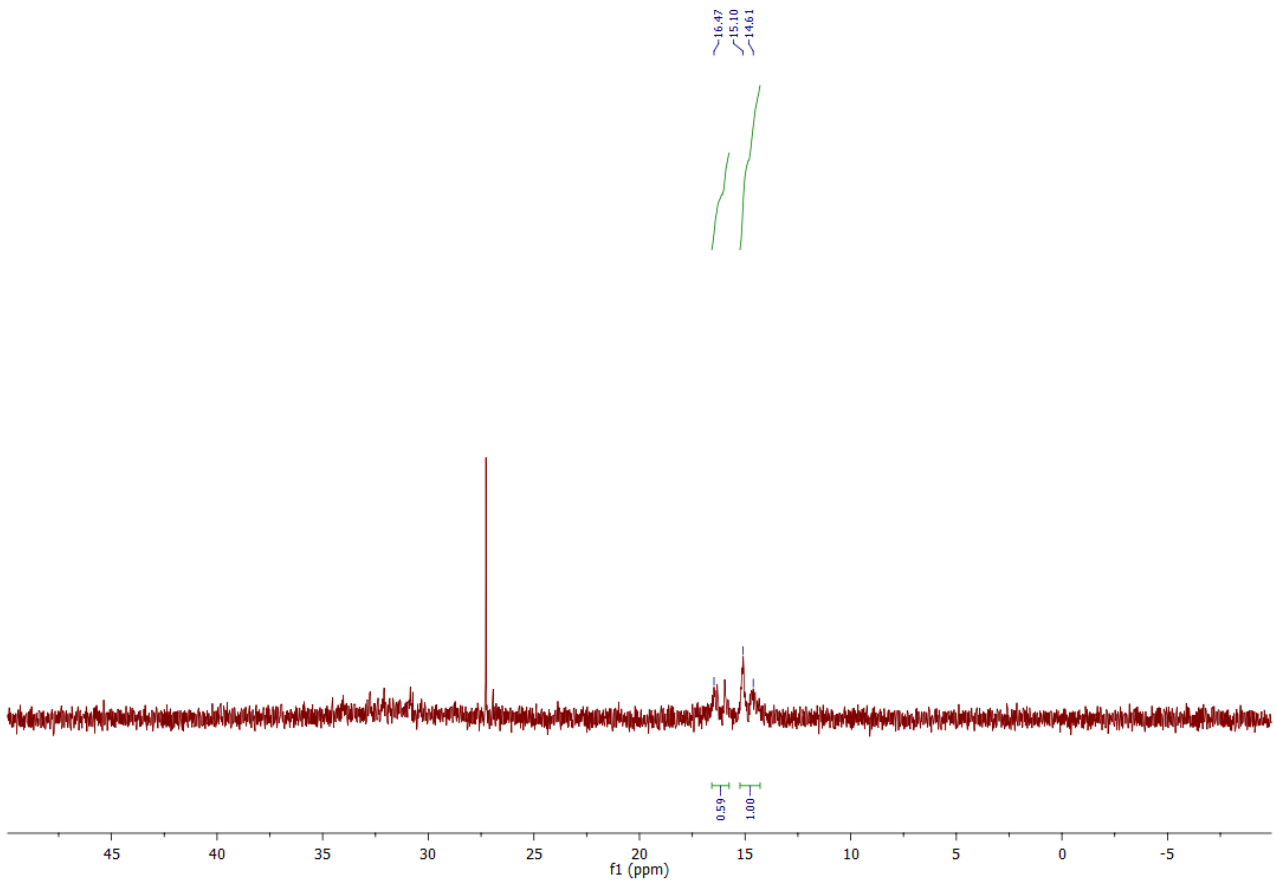
HRMS of complex C



^{1}H NMR of complex C



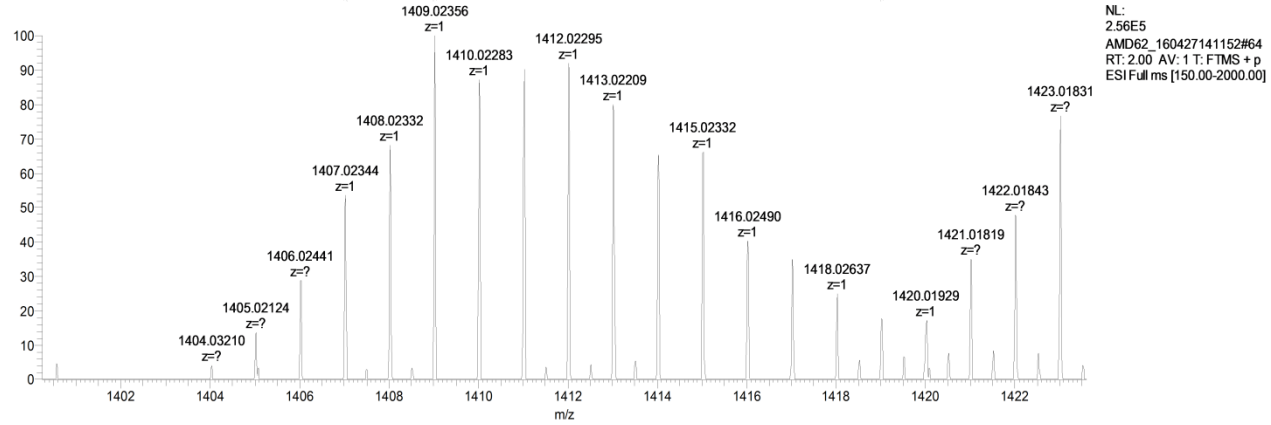
^{31}P NMR of complex C



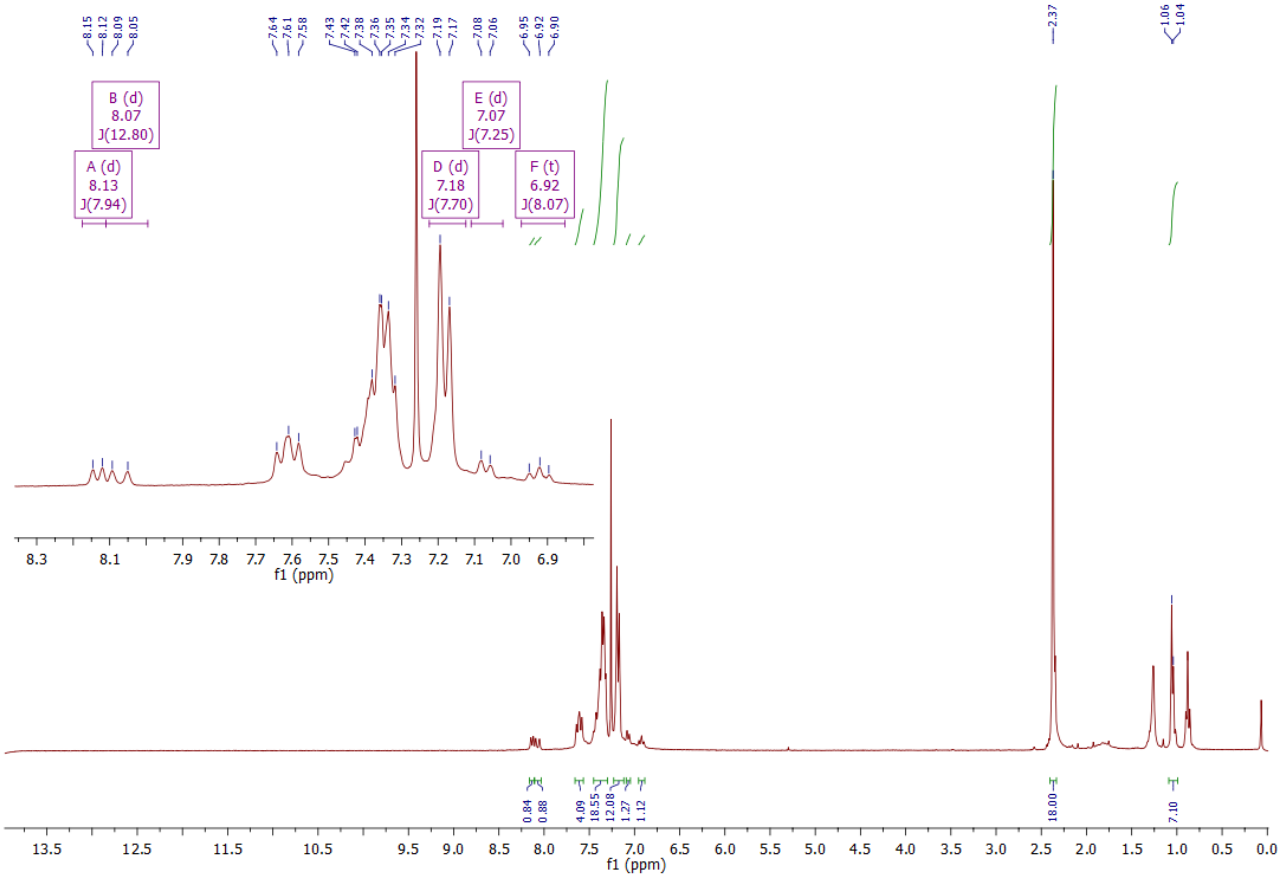
The resonance at 27 ppm is due to traces of oxidised phosphine.

4.4 Spectra of complex D

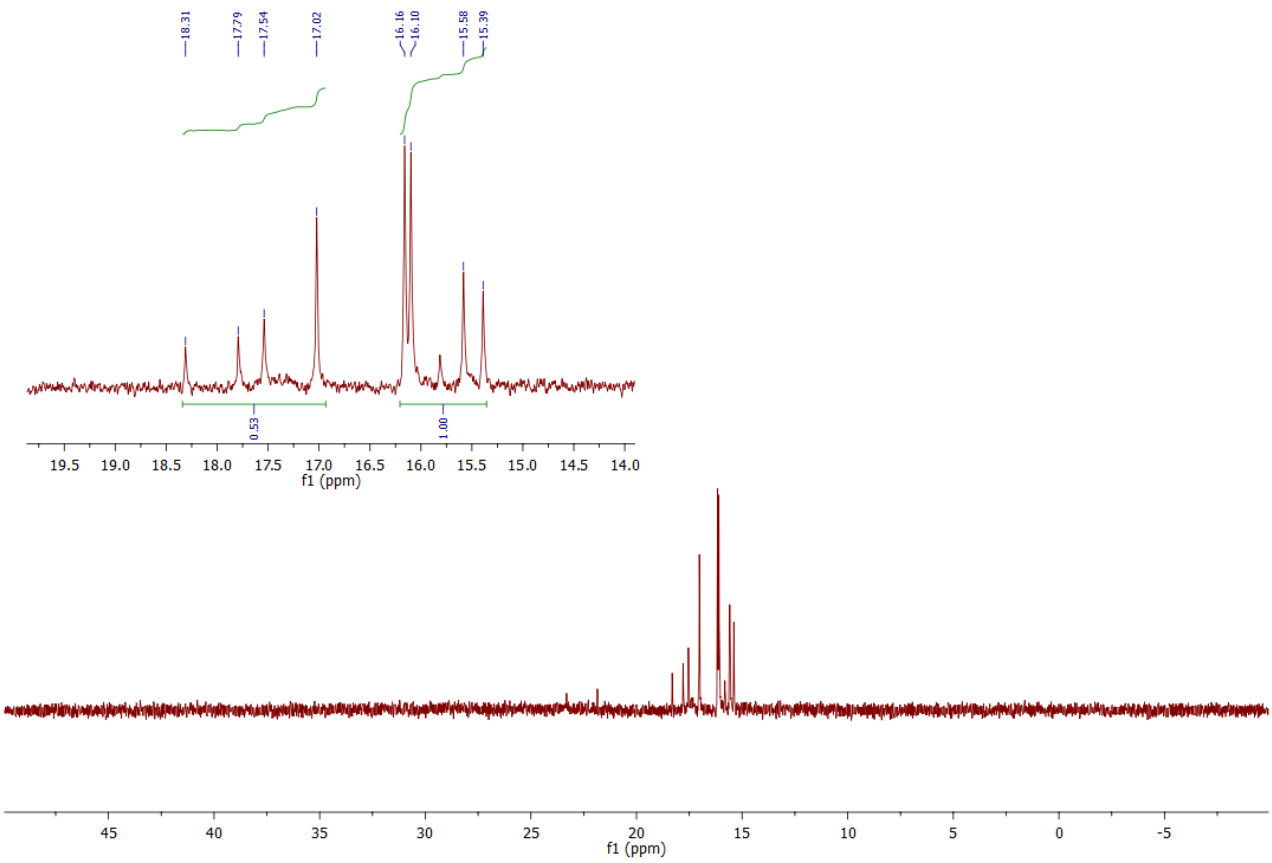
HRMS of complex D



^{1}H NMR of complex D

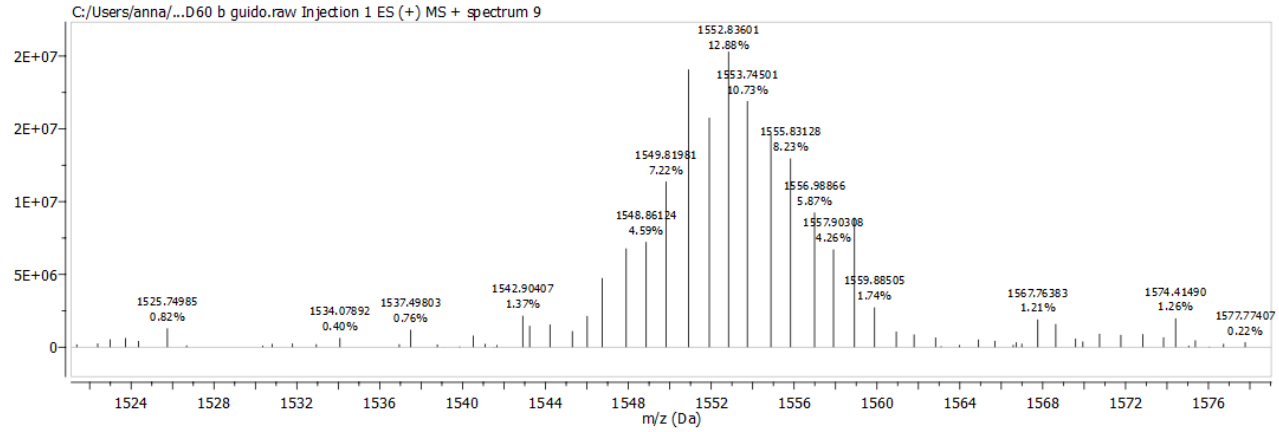


^{31}P NMR of complex D

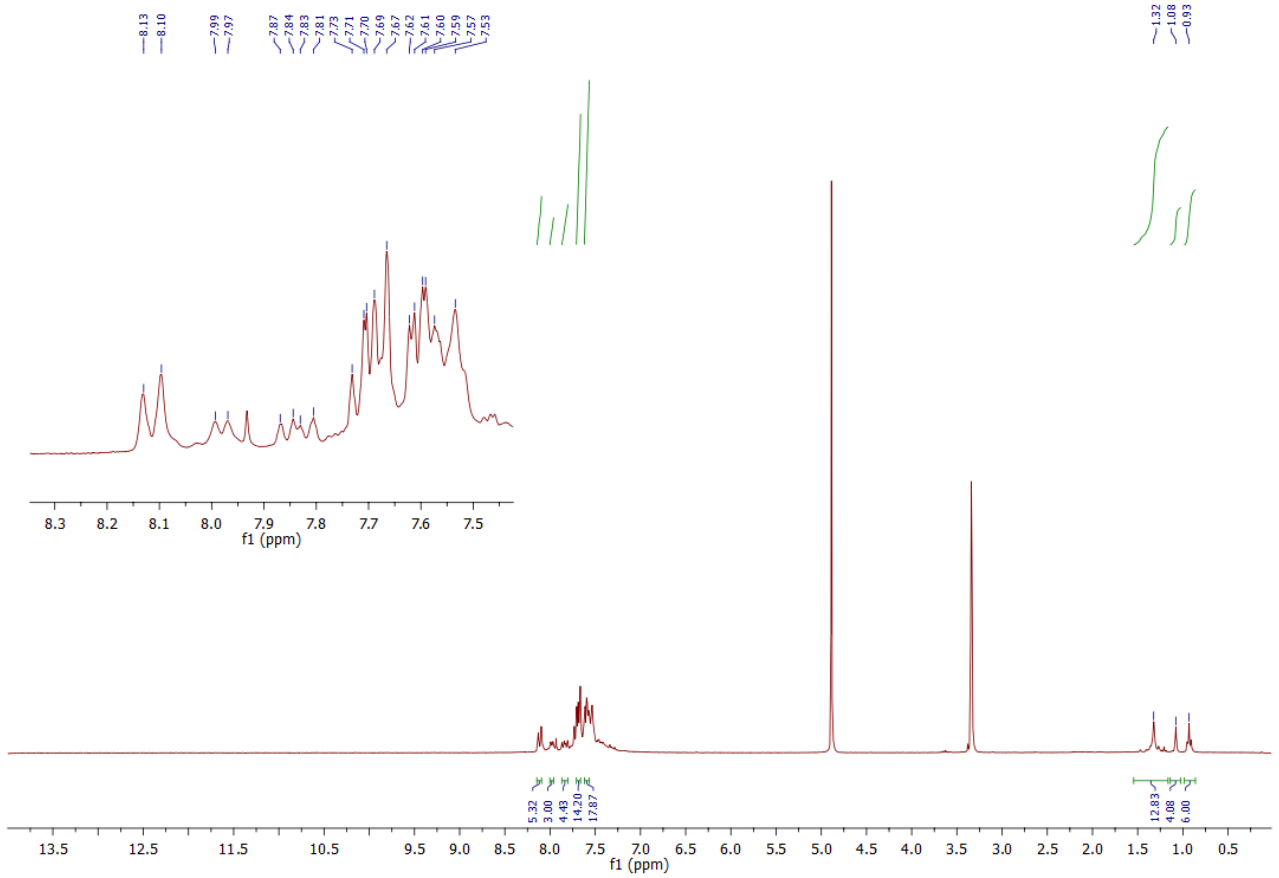


4.5 Spectra of complex E

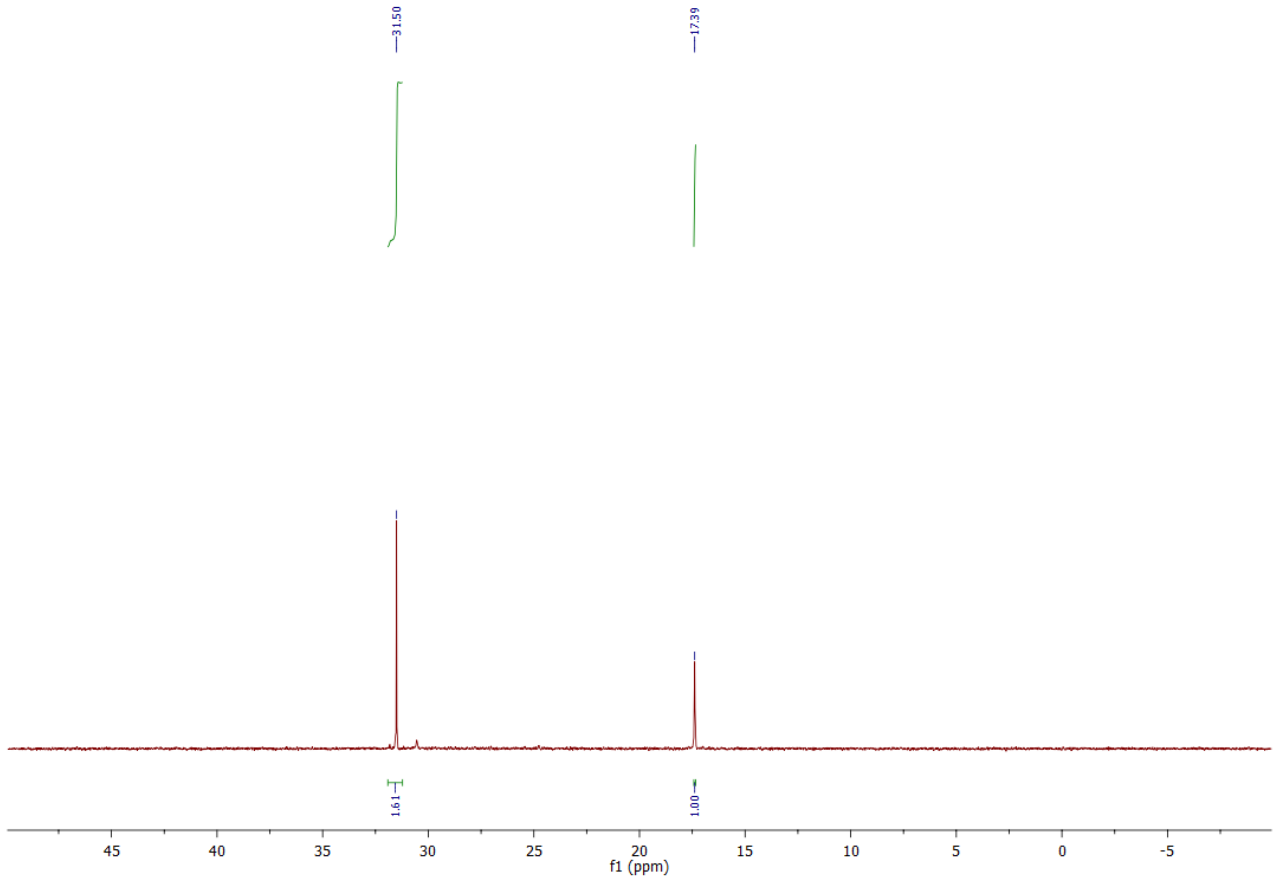
MS of complex E



^{1}H NMR of complex E

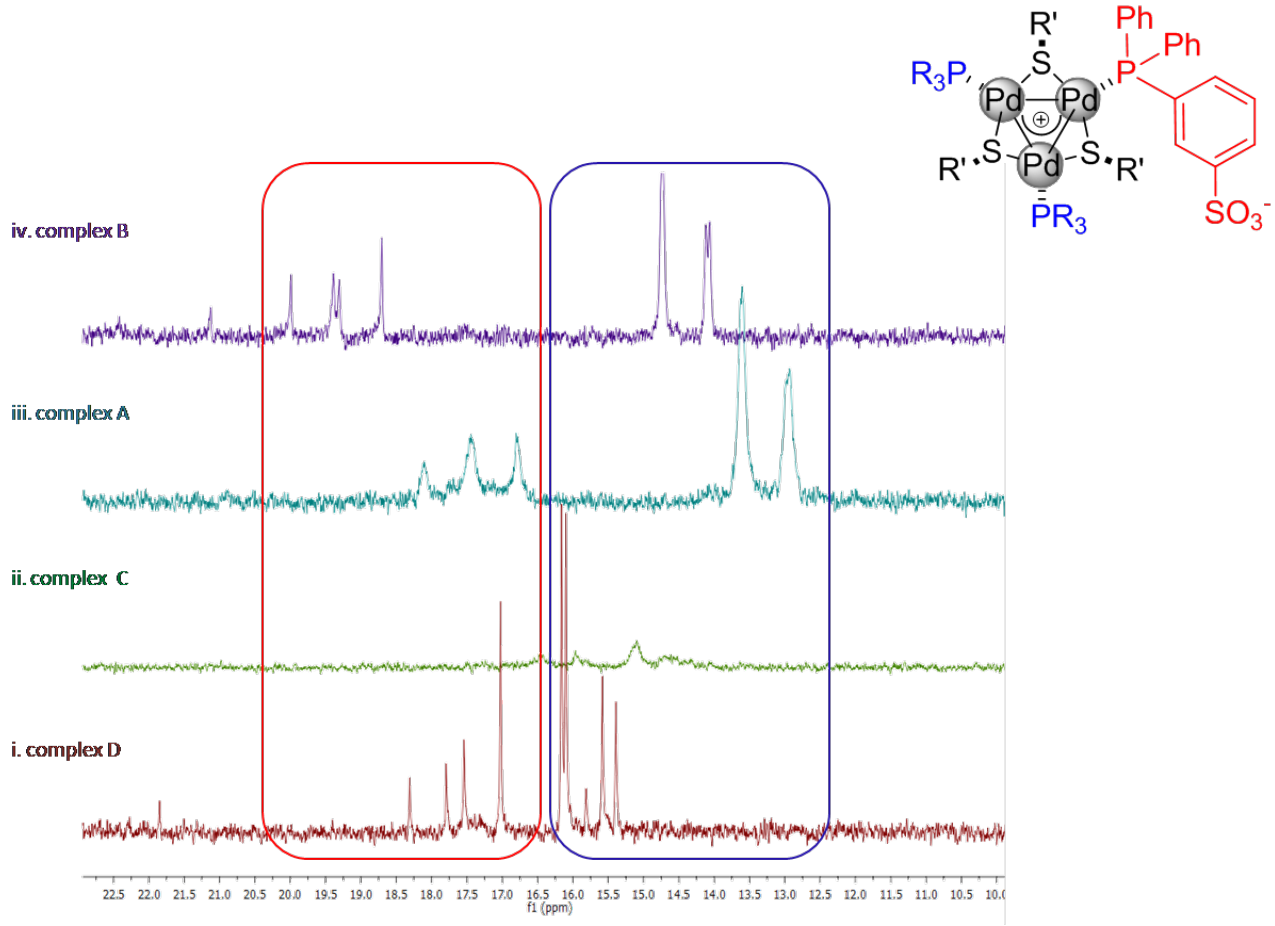


^{31}P NMR of complex E



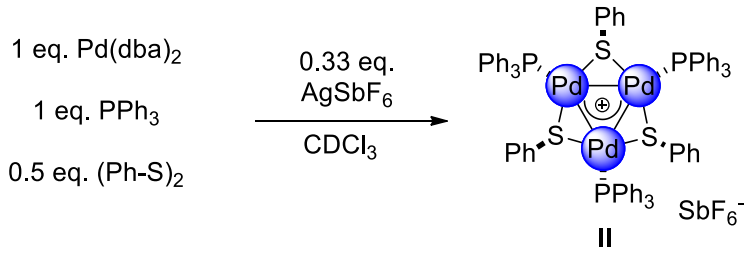
4.6 Comparison of ^{31}P NMR spectra of complexes A-D

Complexes A-D show the same pattern of ^{31}P resonances. A broad triplet and 2 overlapping broad doublets corresponding to the anionic and neutral phosphines respectively were observed in a 1:2 ratio for each of them.



5. NMR samples from the synthesis of $[Pd]_3^+$ complex II in $CDCl_3$

5.1 Experimental procedure

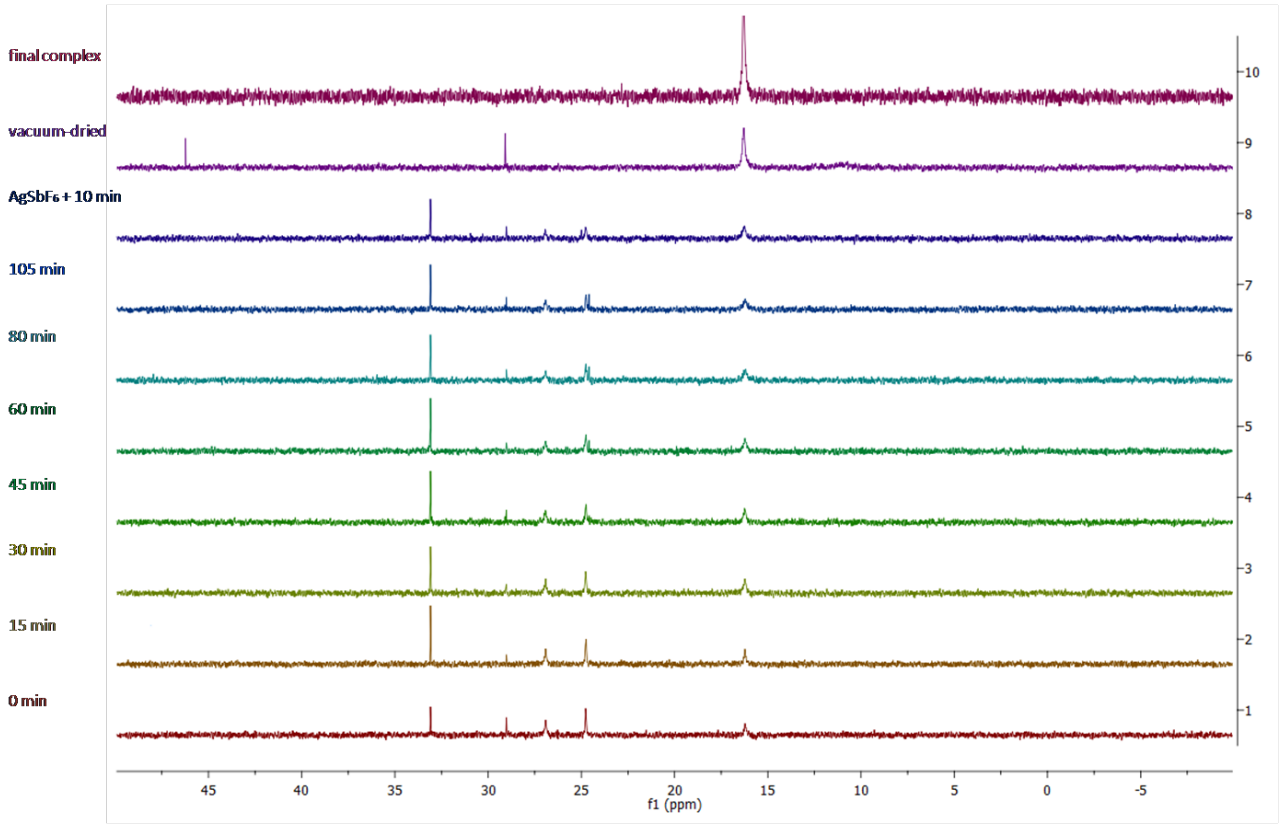


$Pd(dba)_2$ (1 eq., 0.2 mmol, 115 mg) was added to a 50 ml schlenk and the vessel underwent at least three vacuum/N_2 cycles. 20 ml of freshly degassed $CDCl_3$ were immediately syringed under N_2. Triphenylphosphine (1 eq., 0.2 mmol, 52.4 mg) and diphenyldisulfide (0.5 eq., 0.1 mmol, 21.8 mg) were then added under N_2 and the solution rapidly turned deep red. The resulting mixture was kept under magnetic stirring at room temperature for 2 hours, then $AgSbF_6$ (0.33 eq.) was added under N_2 and stirring was mantained for 1 hour. The mixture was then filtered through a celite pad under N_2 to remove traces of black metals. The solvent was removed under vacuum and the resulting solid was purified by $CDCl_3$/hexane washings (1/60 v/v, 3x30 ml). Evaporation of volatiles afforded pure cluster II as a red powder (86% yield, spectroscopic data corresponds to the literature, see refs 3-5 in the main article).

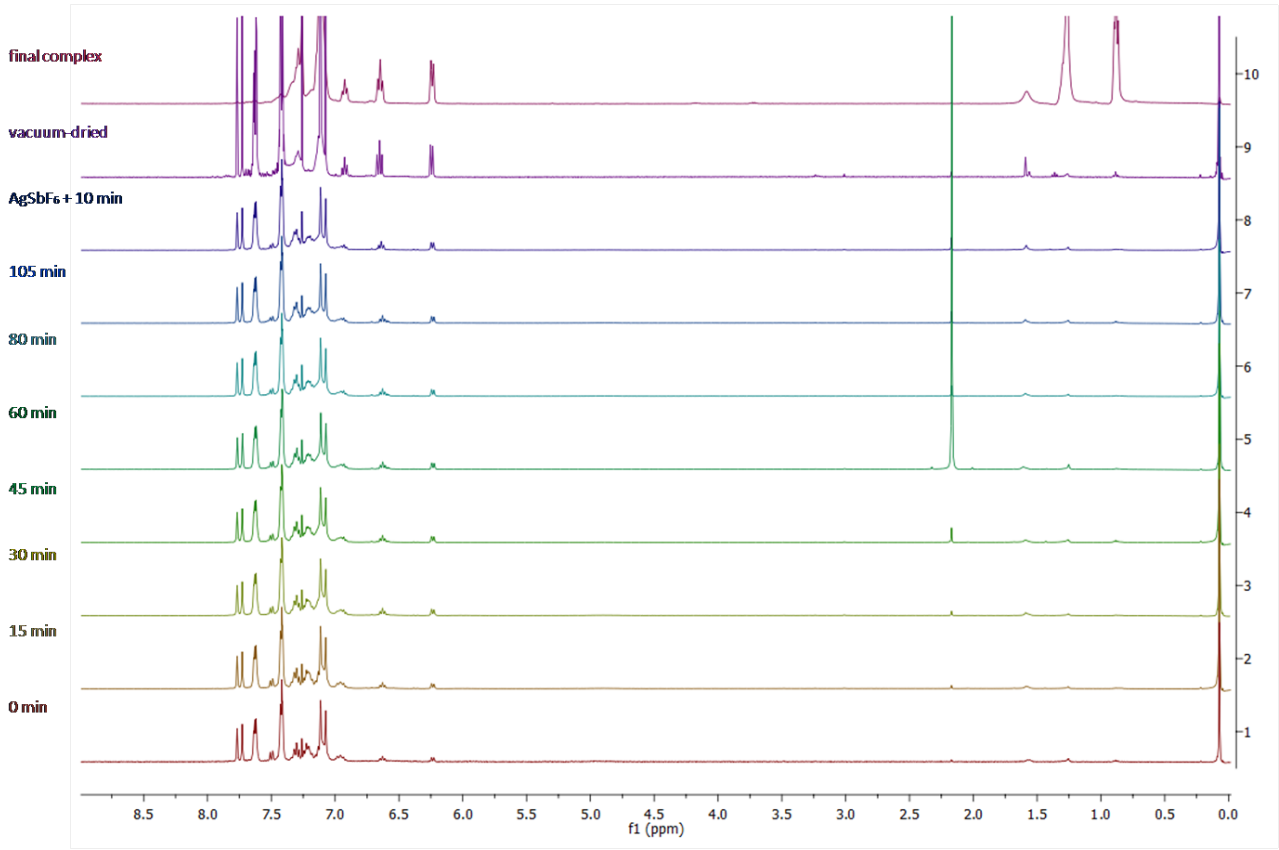
0.5 ml samples were taken at regular intervals to collect ^1H and ^{31}P NMR spectra, showed hereafter.
Diagnostic resonances of II, the broad singlet at 15 ppm for 31P and signals of thiolate fragments in the 6-7 ppm regions for 1H are clearly visible since the beginning of the experiment.

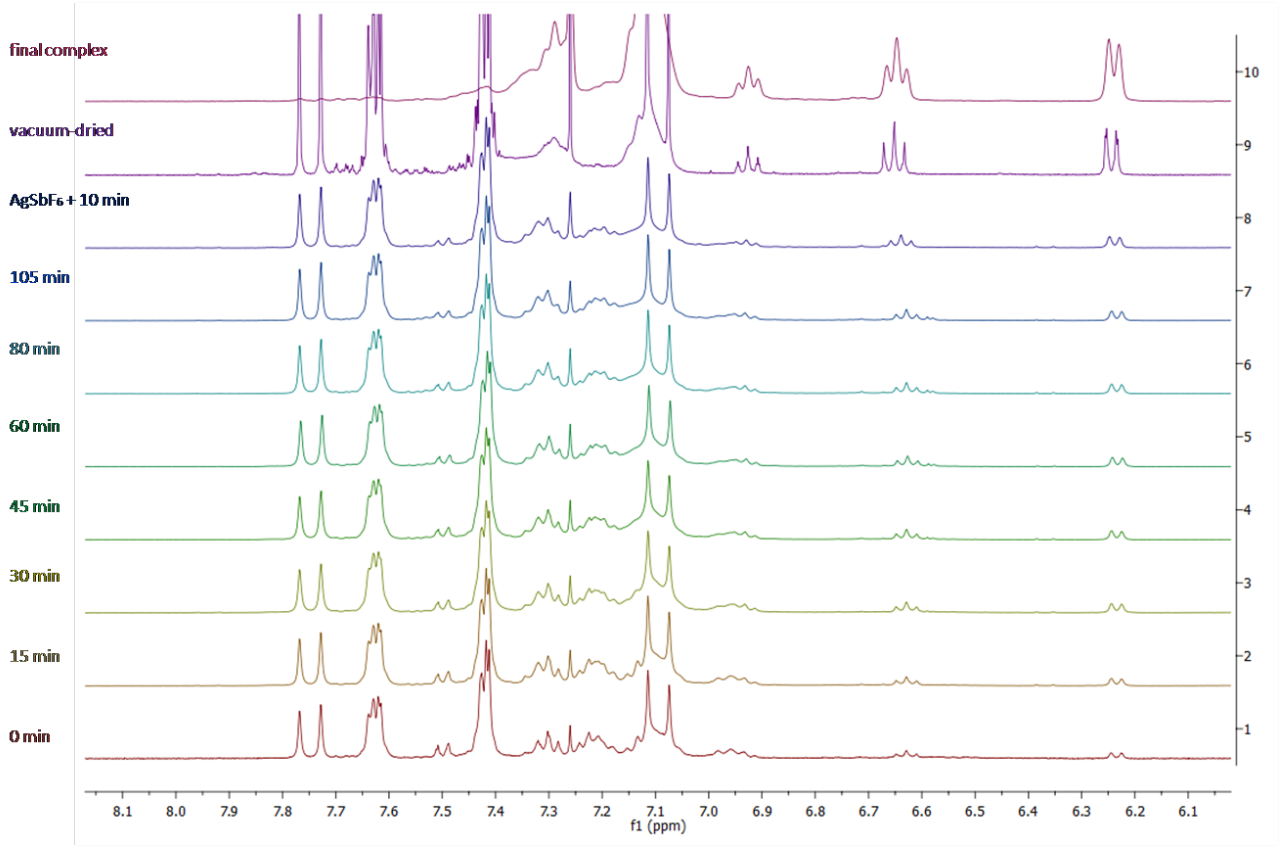
5.2 Copies of NMR spectra

^{31}P NMR spectra of crude samples of II



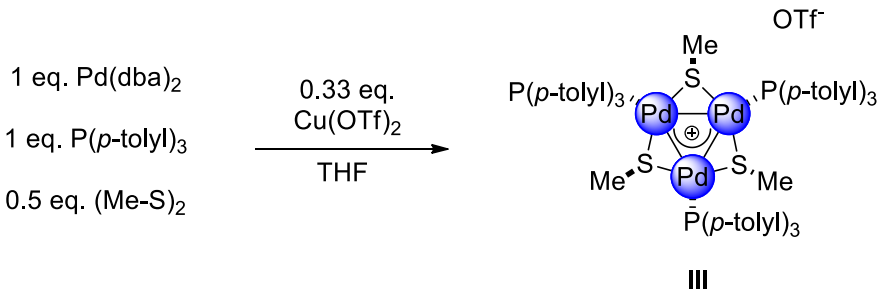
^{1}H NMR spectra of crude samples of II





6. NMR samples from the synthesis of $[Pd]_3^+$ complex III in THF

6.1 Experimental procedure



III

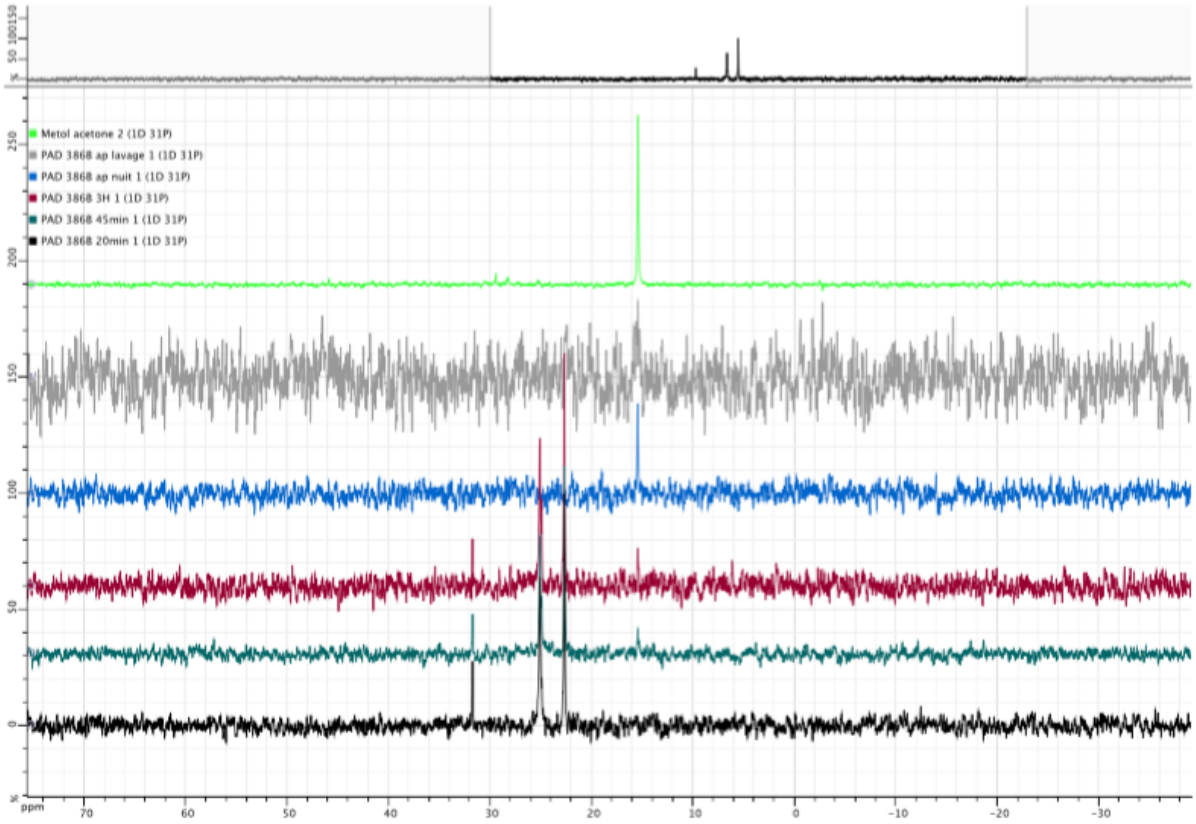
$Pd(dba)_2$ (1 eq., 0.2 mmol, 115 mg) was added to a 50 ml schlenk and the vessel underwent at least three vacuum/N_2 cycles. 20 ml of freshly degassed THF were immediately syringed under N_2. Tri(p-tolyl)phosphine (1 eq., 0.2 mmol, 60.9 mg) and dimethyldisulfide (0.5 eq., 0.1 mmol, 9 µL) were then added under N_2 to obtain a brown solution. The resulting mixture was kept under magnetic stirring at room temperature for 2 hours, then $Cu(OTf)_2$ (0.33 eq., 0.067 mmol, 24.23 mg) was added under N_2 and stirring was maintained for 24 hours. The solution slowly turned red.

The mixture was then filtered through a celite pad under N_2 to remove traces of black metals. The solvent was removed under vacuum and the resulting solid was purified by THF/hexane washings (2/60 v/v, 3x30 ml). Evaporation of volatiles afforded cluster III as a red powder (71% yield, spectroscopic data corresponds to the literature, see ref 3 in the main article).

0.5 ml samples were taken at regular intervals to collect ^{1}H and ^{31}P NMR spectra. They were dried and immediately dissolved in acetone-d6 to ensure the absence of any possible chloride source.

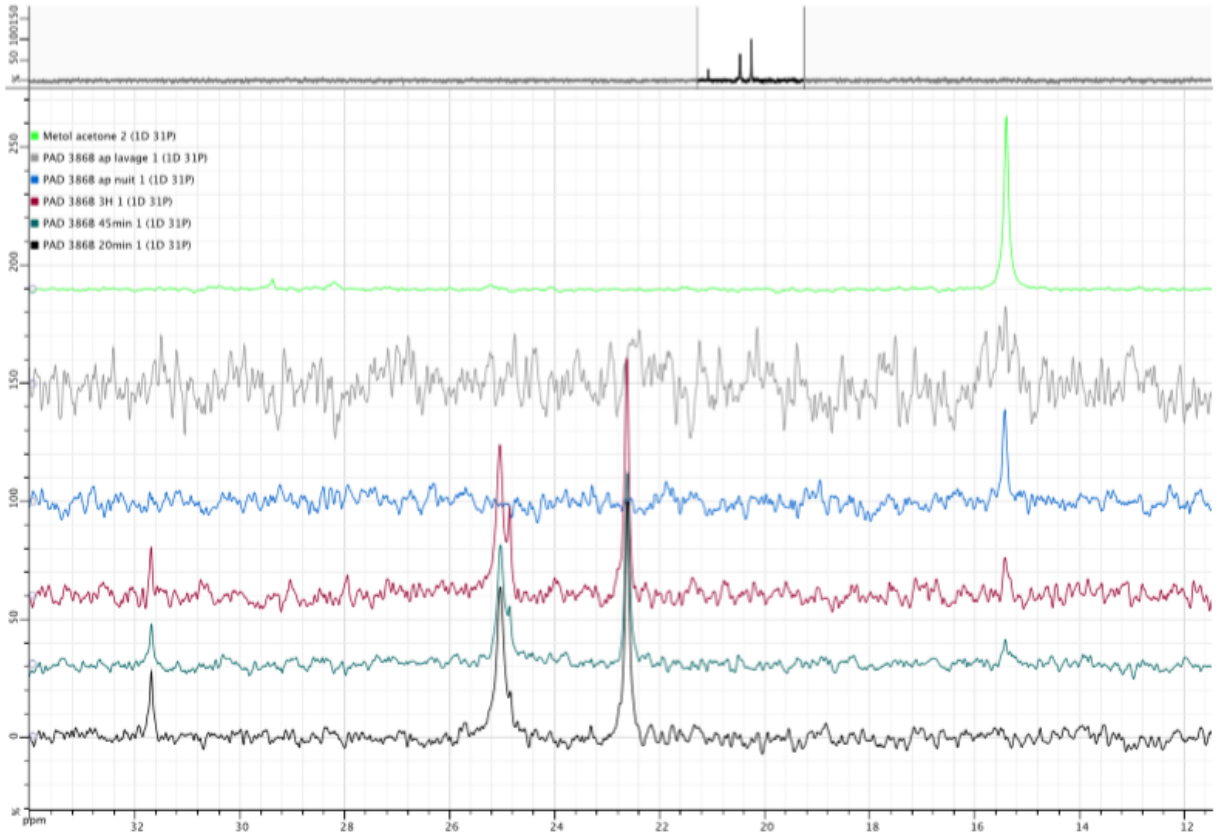
6.2 Copies of NMR spectra

^{31}P NMR spectra of crude samples of III



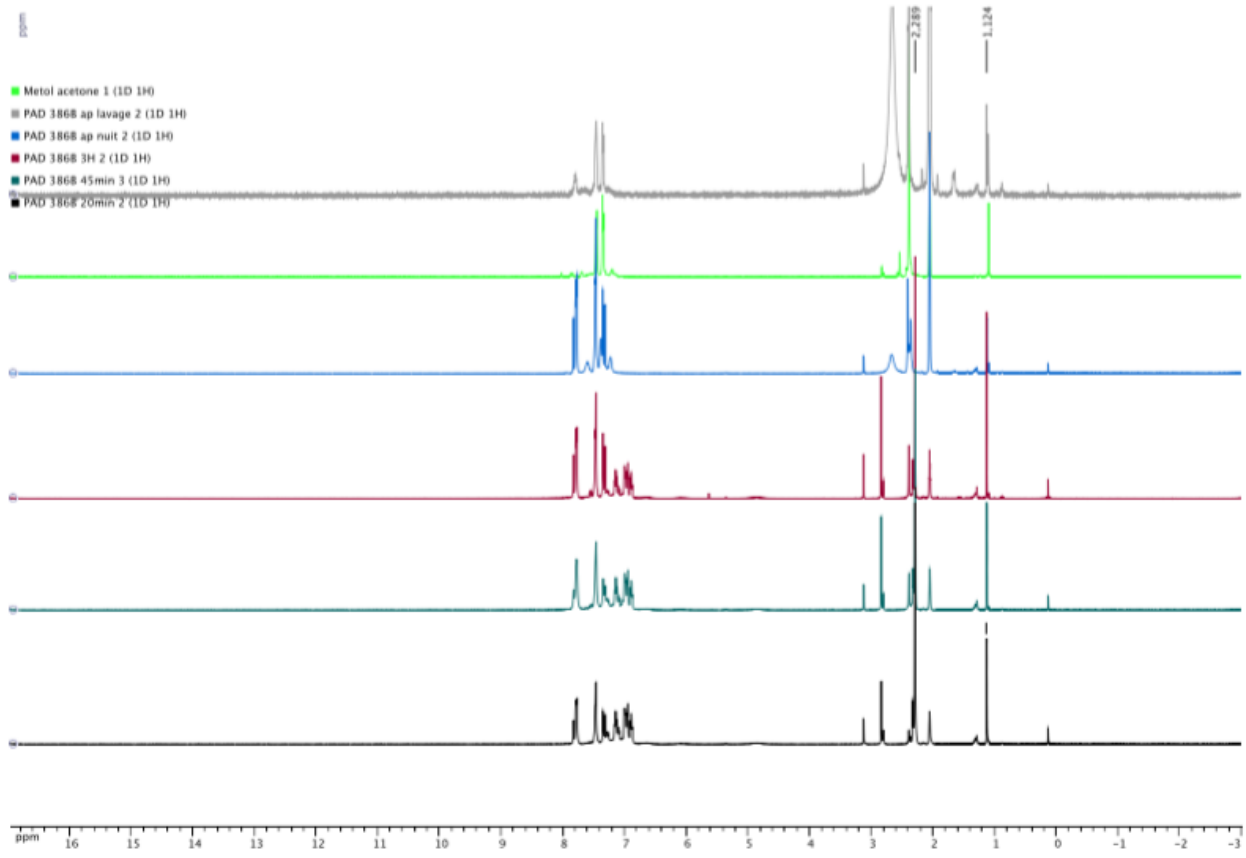
From bottom to top: two hours stirring without any oxidant, then 20 minutes after addition of Cu(II) (black line), 45 minutes after (dark green), 3 hours after (red), overnight (blu, showing a single peak at 15 ppm), after 24 hours (grey), purified complex III (pale green).

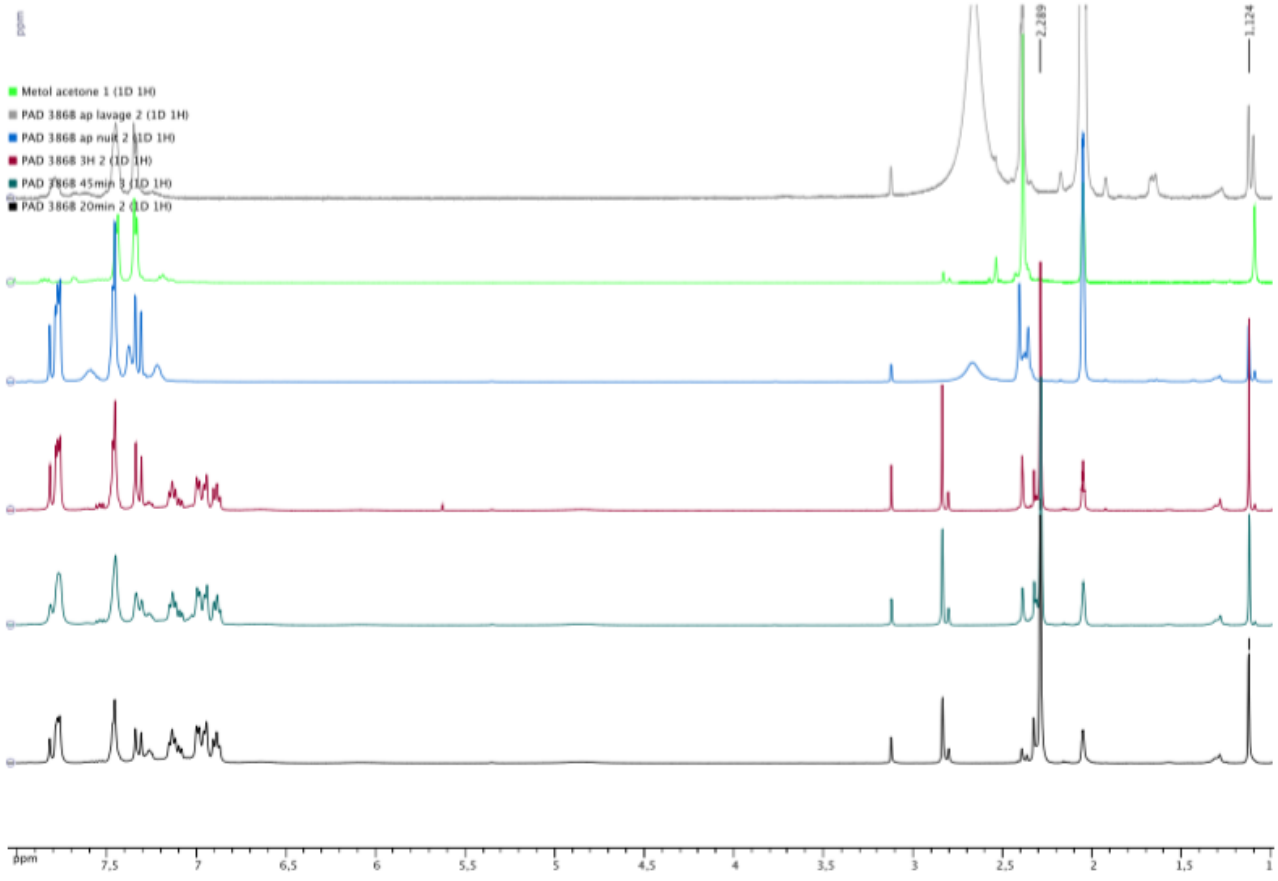
As mentioned in the main article, the diagnostic resonance at 15 ppm of the three equivalent phosphines of III appears just upon addition of the (weak) Cu(II) oxidant (compare black line and every other one).



Zoom of the key 31P region presented in the previous page. Note peaks at 15 ppm corresponding to III.

The 1H spectra follows (full spactra and zoom). Note diagnostic resonance of Me groups of phosphines (at 2.38 ppm) and of thiolates (1.09 ppm). They evenly correlate with phosphorous NMR.

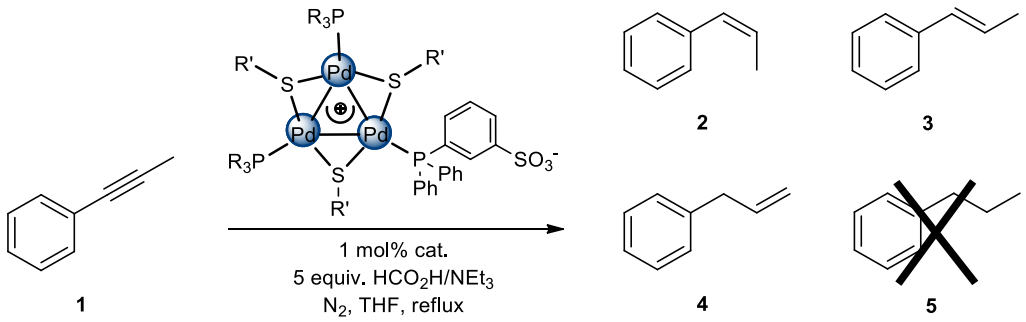

ppm
2.289
1.124
Metol acetone 1 (1D 1H)
PAD 3868 ap lavage 2 (1D 1H)
PAD 3868 ap nuit 2 (1D 1H)
PAD 3868 3H 2 (1D 1H)
PAD 3868 45min 3 (1D 1H)
PAD 3868 20min 2 (1D 1H)
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


ppm
2.289
1.124
Metol acetone 1 (1D 1H)
PAD 3868 ap lavage 2 (1D 1H)
PAD 3868 ap nuit 2 (1D 1H)
PAD 3868 3H 2 (1D 1H)
PAD 3868 45min 3 (1D 1H)
PAD 3868 20min 2 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1

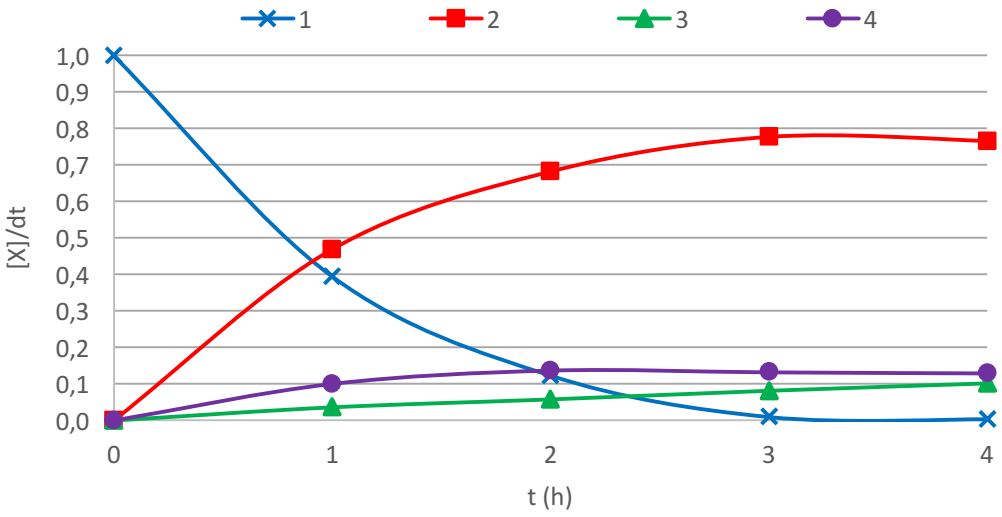
7. Catalytic semihydrogenations

7.1 Experimental procedure for the catalytic semi-reduction of phenylpropyne

The zwitterionic complex D (5.0 mg, 0.0035 mmol, 1 mol%, see table 2 entry 4) and freshly degassed THF (3.5 mL) are added under N_2 to a Schlenk-tipe flask. Phenylpropyne (44 µL, 0.35 mmol, 1 equiv., 0.1 M), triethylamine (244 µL, 1.75 mmol, 5 equiv.), formic acid (66 µL, 1.75 mmol, 5 equiv.) and *p*-xylene (43 µL, 0.35 mmol, 1 equiv.) were sequentially added via syringes. The mixture was heated to reflux and the conversion was followed analysing samples *via* GC using *p*-xylene as internal standard (100 µL of crude mixture diluted with 900 µL of methanol).



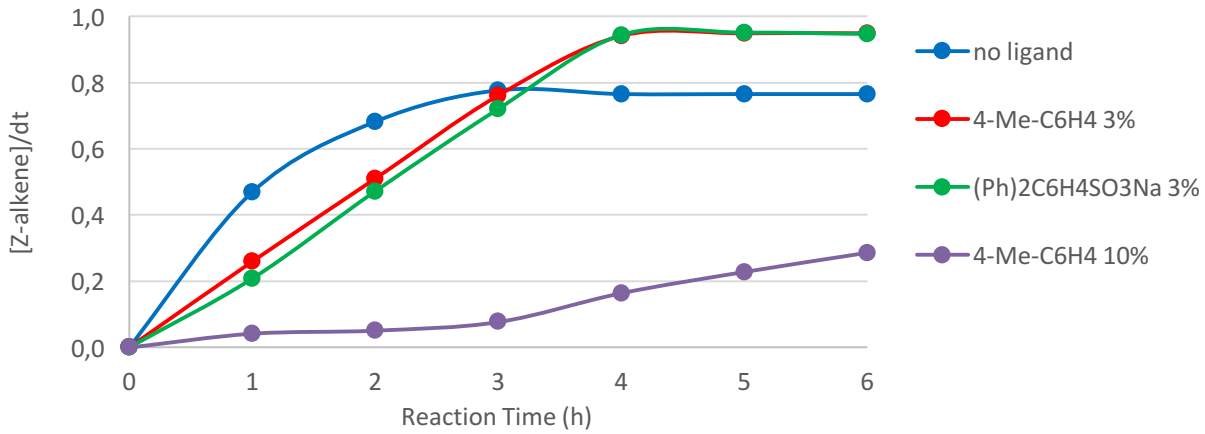
Plot of conversion through time in the reduction of 1 to 2/3/4



Under optimized conditions, the best Pd_3 catalyst (complex D) allows complete conversion in 3 hours with a selectivity towards 2/3/4 of 77, 10 and 13% respectively. It is worth noting that 3 and 4 forms since the beginning of the reaction in this case.

7.2 Ligand addition

The semi-reduction of 1-phenylpropine was performed following conditions presented above, with the addition of a ligand (see table 3 of the manuscript).



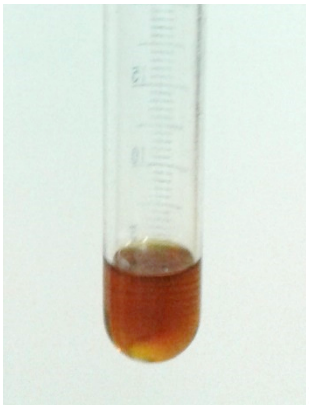
In the presence of 3 mol% of ligand (red and green curves), the reaction is slightly slower, requiring 4 hours to attain full conversion.

The reaction did not show any induction time, and the slope of the curve remains remarkably straight. These results are consistent with the presence of a homogeneous catalysts.

Barely no traces of isomerisation products 3 and 4 were observed, even prolonging heating for two hours upon full conversion of 1.

A similar outcome is observed with 10 mol% of phosphine (purple curve, 24 hours to attain full conversion were required in this case).

7.3 Screenshots from crude mixtures


1a


1b

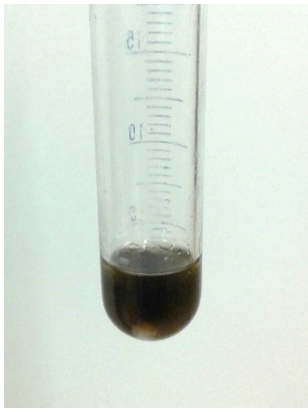
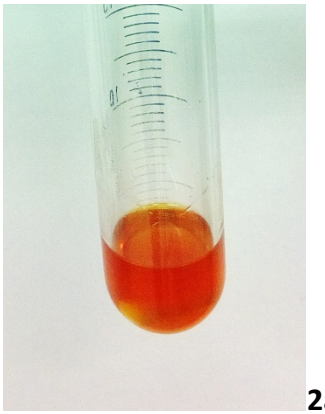
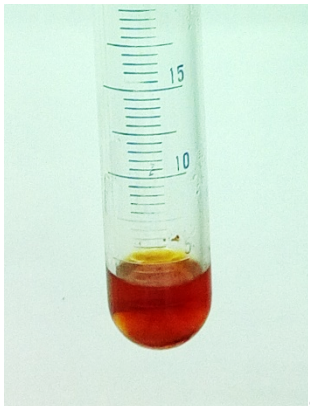

1c

***Figure 1*:** crude mixture in absence of extra ligand using catalyst D at time 0 (1a), after warming for 2 h (1b, >80% conv. Of phenylpropyne from GC) and 30' after complete conversion of the alkyne (1c).

Reactions with first generation catalysts had always the same aspect. This correlates with LC-HRMS analyses on samples from crude mixtures that showed the diagnostic isotopic pattern of the [Pd3]+ complexes slowly fading away during alkyne conversion, see ref 5 for details.


2a


2b


2c

***Figure 2*:** crude mixture upon addition of 3 mol% tri(*p*-tolyl)phosphyne as ligand (corresponding to Table 3 entry 1 and to the red curve of the graph in the previous page) at time 0 (2a), after warming for 4 h (2b, full conversion of reagent) and after warming for two more hours upon complete conversion alkyne (2c).

7.4 Reduction of the catalyst loading

The reaction of semi-reduction of 1-phenylpropine was performed reducing the catalyst loading (see table 4).

The $[Pd_3]^+$catalyst (complex D, 5.0 mg, 0.0035 mmol) is added under N_2 to a Schlenk-tipe flask. Phenylpropyne (1 equiv.), triethylamine (5 equiv.), formic acid (5 equiv.) and *p*-xylene (1 equiv.) were sequentially added via syringes and their amount (mmol) was calculated in order to change the [propyne]/[cat] ratio from 100 up to 2000.

The volume of THF was further reduced for each experiment in order to keep constant the catalyst concentration. For these reasons, entry 4-6 become formal solvent-free experiments, thus minimising production of wastes.

Remarkably, no noticeable isomerization to alkenes 3 and 4 occurred in these cases.

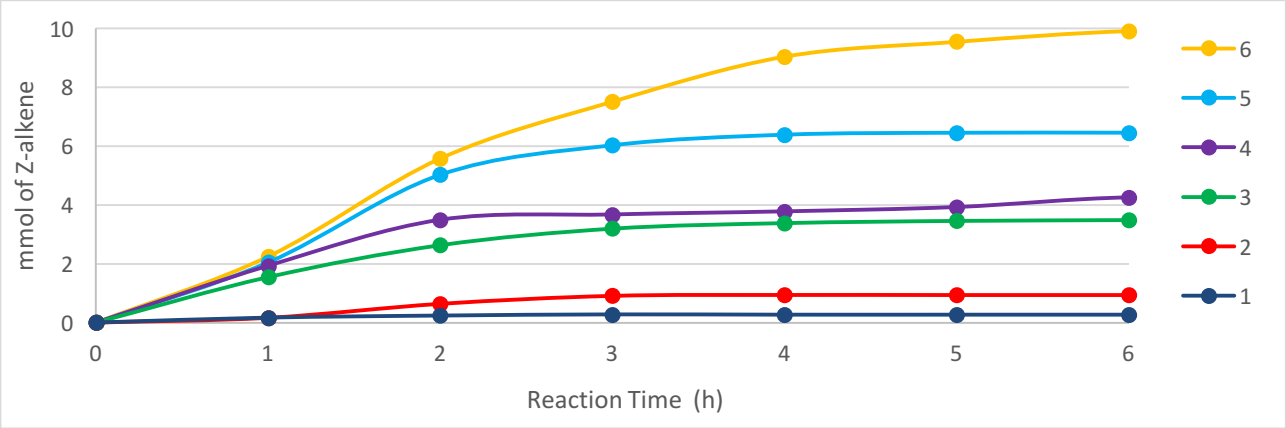
In the last case, the GC standard, p-xylene, had to be removed too. This allowed to attain a very low catalyst loading. Values of selectivity and conversion obtained from GC and GC-MS for this last experiment were calculated without an internal standard. They were validated with the direct isolation of pure product 2 in almost quantitative return (see next section).

Entry	mmol cat	mmol alkyne	ml THF	[cat]	[alkyne]	[alkyne]/[cat]
1	0.0035	0.35	3.5	0.001	0.1	100
2	0.0035	1.05	3	0.001	0.3	300
3	0.0035	3.5	0.5	0.001	1.0	1000
4	0.0035	7	-	0.0005	1.0	2000
5[a]	0.0035	7	-	0.0005	1.0	2000
6[a, b]	0.0035	10.5	-	0.0003	1.0	3000

a: reaction conducted in presence of tri(*p*-tolyl)phosphine as ligand (3 equiv. compared to cat D).

b: reaction conducted in absence of *p*-xylene.

Plot of alkene production/time reducing catalyst loadings for entries of Table 4.



Reducing the catalyst loading improved the Z-alkene selectivity up to 98% and complete alkyne conversion was obtained within a few hours in each case.

From the comparison of the curves showing the absolute amount of moles of product obtained during time by using different [cat]/[alkyne] ratios, it is possible to observe an increased apparent rate throughout the series.

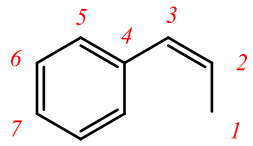
The linear part of the slope of each curve has been used to calculate the TOF (mmol of 2/ mmol of cat * hour) of each reaction presented in Table 4, assuming that the amount of complex corresponds to the amount of active species. This likely correspond to an underestimation of the actual TOF.

7.5 Gram-scale reaction

Complex D, 5.0 mg, 0.0035 mmol, 0.03% mol) and tri(p-tolyl)phosphine (3.2 mg, 0.0105 mmol, 0.09% mol) are added under N_2 to a Schlenk-tipe flask. Phenylpropyne (1.3 mL, 1.20 g, 10.5 mmol, 1 equiv.), triethylamine (7.3 mL, 52.5 mmol, 5 equiv.) and formic acid (2.0 mL, 52.5 mmol, 5 equiv.) were sequentially added via syringes. All reagents were used without any preliminary purification.

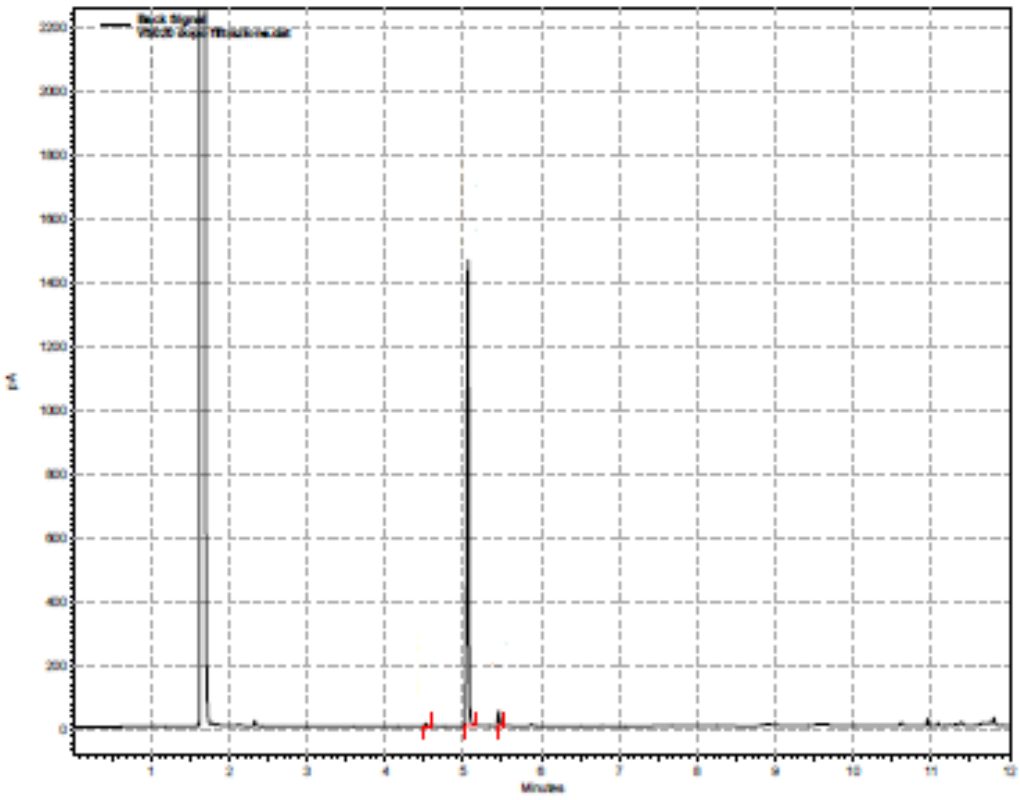
The mixture was heated to 70 °C until full conversion of 1 (6 h). The crude mixture was poured and adsorbed over a short pad of silica (2 cm) and washed with 5 mL of pentane, recovering 1.15 g of 2 (96% yield) within a few minutes. The purity of 2 was verified by NMR and GC, spectra copied hereafter. For sake of comparison, the proton spectrum obtained with the first generation catalyst is also presented. It clearly highlights that undesired isomerisation of the double bond is completely prevent with the improved catalytic systems.

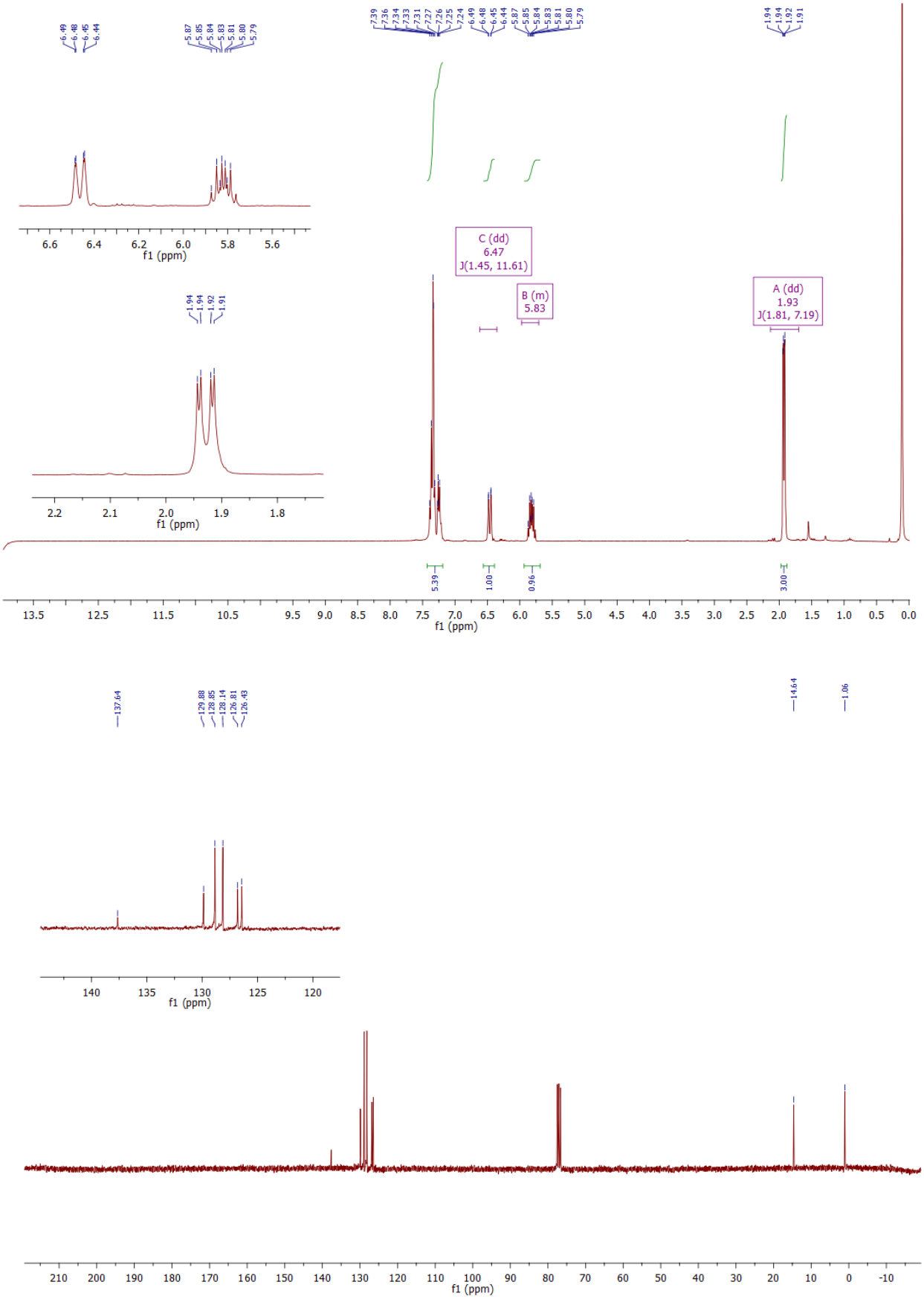
Spectroscopic data of 2



^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.39-7.24 (m, 5H, $H_{5\text{-}7}$), 6.47 (dd, 1H, *J* = 1.45, 11.61 Hz, H_3), 5.83 (m, 1H, H_2), 1.93 (dd, 3H, *J* = 1.81, 7.19 Hz, H_1).

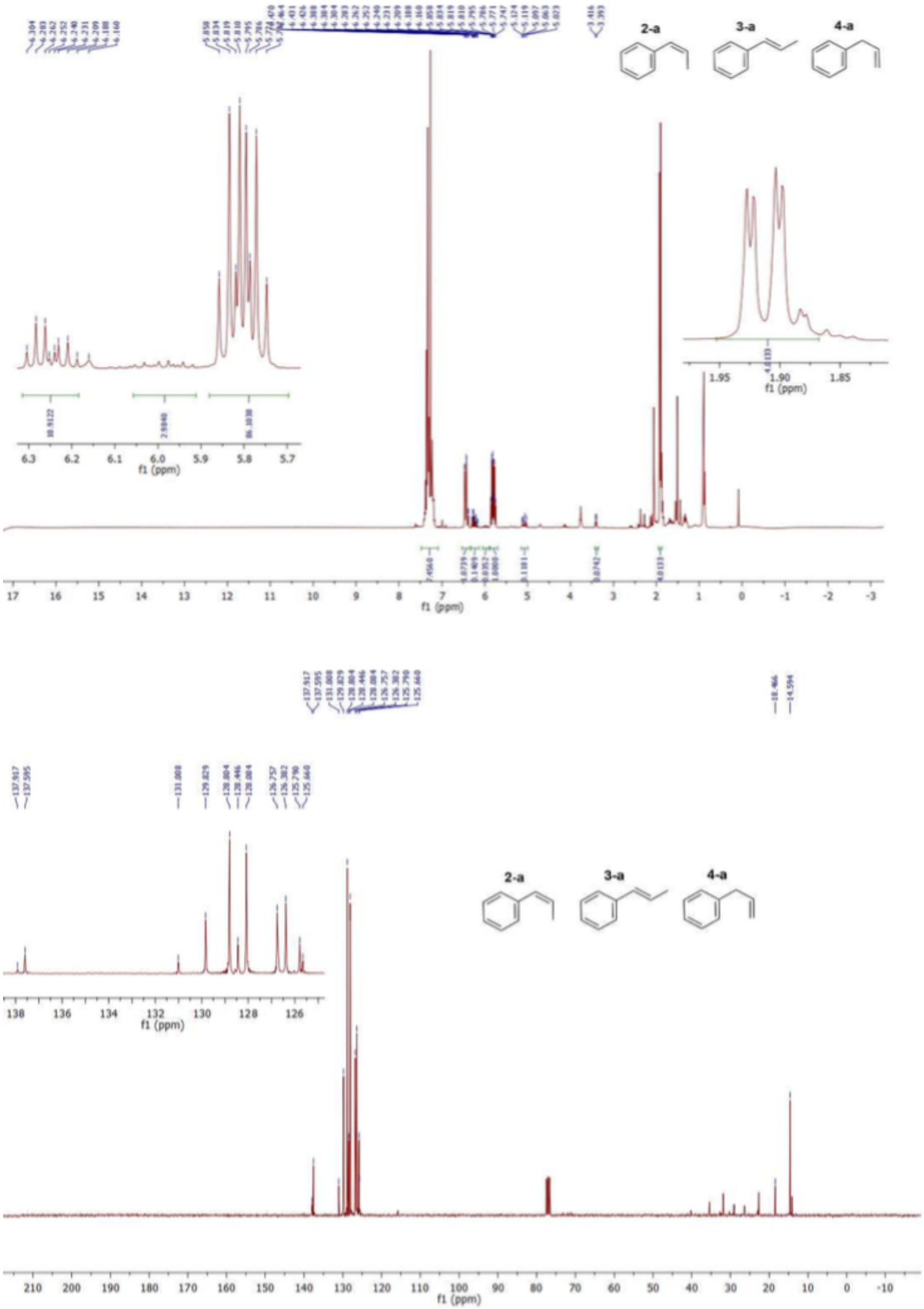
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 137.64 (C_4), 129.88 (C_3), 128.85 (C_5), 128.14 (C_6), 126.81 (C_2), 126.43 (C_7), 14.64 (C_1), 1.06 (silicon grease).





^{1}H & ^{13}C of product **2** from the reaction of Table 4, entry 6; no resonance from **3** and **4** could be observed.

^{1}H & ^{13}C of product **2** from the reaction with 1 mol% of complex **I** (1st gen catalyst). Resonanaces from **3** and **4** were clearly visible in this case (2-4 could not be separeted by silica gel chromatography, see ref 5).



8. DFT modelling on cation I and zwitterion complex D

As mentioned in the main article, we hypothesised that the superior reactivity of zwitterionic complexes compared to their previously described peers might be due to a trans-like effect exerted by their anionic phosphine that could labilise the neutral phosphine at the opposite edge of the tripalladium kernel. An indirect confirmation of this effect has been observed by DFT analysis using Gaussian09.

The X-ray structure of complex **I** (CCDC 1017253) has been used as starting point. It present three identical Pd-P distances (2.2612(11) Å). Full optimisation without any constraint of its Pd_3^+ cation has been carried out at the M06/lacvp(d), M06/Def2-svp and M11/lacvp(d) level. These models proved accurate to describe the delocalised metal-metal bonding of these complexes (see refs 3 and 4 of the main article). In all cases, optimised structures remained very similar to that observed at the solid state. In particular, the best correlation has been found with the M11 functional. In all the three calculated structures, the cation of **I** present three degenerate Pd-P distances. With the three level of theory describe above, these distances were 2.3480, 2.3381 and 2.2979 Å respectively.

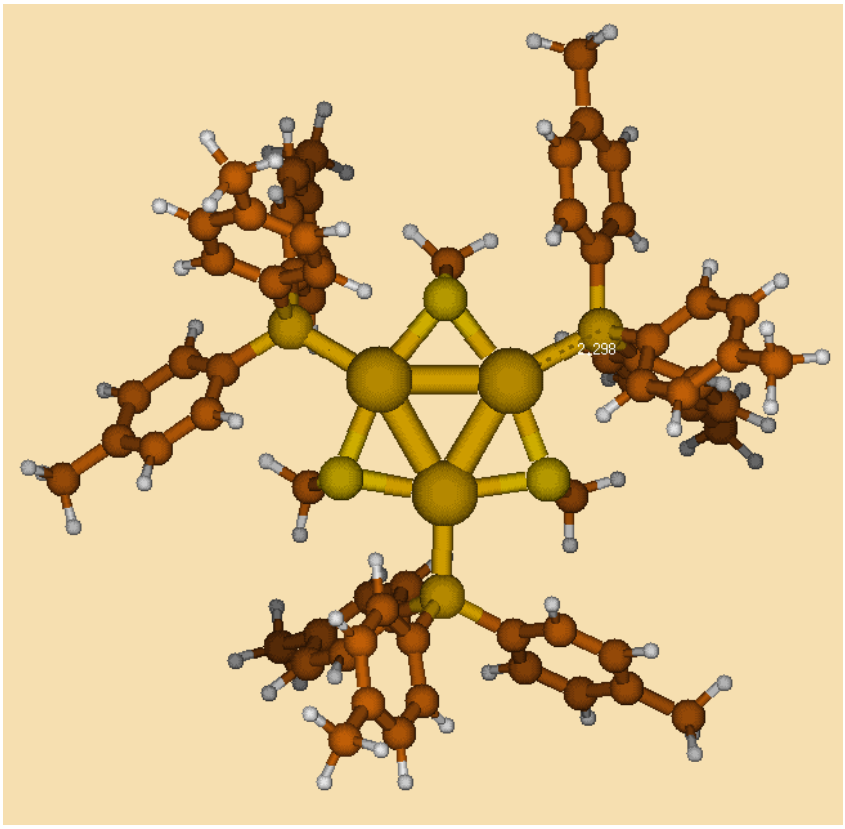
We then modelled zwitterionic complex **D** at the same level. The Pd-P distance of the sulfonated phosphine becomes (slightly) shorter in all the three cases. It is 2.3423, 2.3311 and 2.2901 Å at the M06/lacvp(d), M06/Def2-svp and M11/lacvp(d) level respectively.

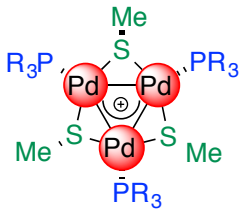
This is consistent with a relatively stronger Pd-P($Ph_2C_6H_4SO_3^-$) bond.

On the contrary, the Pd-P bond opposite to the sulfonate group moved inversely, and the corresponding distance is invariably (slightly) longer than those observed with cation **I**. Values in the three cases were 2.3518, 2.3399 and 2.3021 Å respectively.

This is consistent with a relatively weaker Pd-P(C_7H_8)$_3$ bond and supports the possible explanation of the increased activity of **D** compared to **I** presented in the main article.

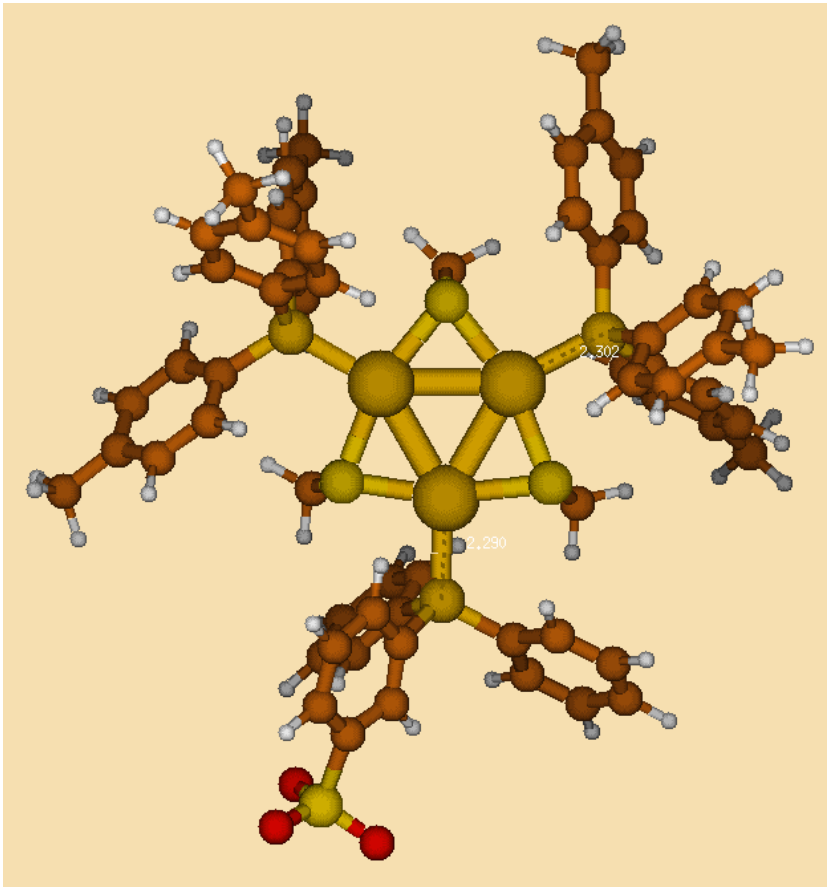
Calculated structures highlighting these Pd-P distances at the M11/lacvp(d) level follows. This section eventually present XYZ coordinates and energies for all the six modelled complexes in AU.

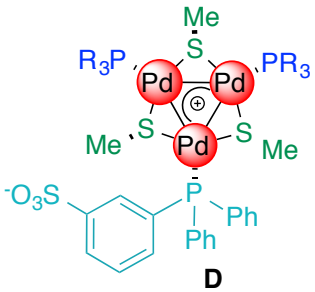




I

Cation **I**, optimised at the M11/lacvp(d) level (Pd-P is 2.2979 A).





D

Zwitterion **D**, optimised at the M11/lacvp(d) level (Pd-P are 2.2901 and 2.3021 A respectively).

Cation I, M06/lacvp(d)

147

scf done: -5155.160557

Pd	17.210267	5.696539	17.166378
S	16.838067	3.938890	18.673989
P	15.449163	5.315091	15.660934
C	14.144079	6.582154	15.672681
C	12.907129	6.335815	15.060081
H	12.717812	5.372433	14.584474
C	11.925341	7.313658	15.053953
H	10.967055	7.115425	14.572495
C	12.139608	8.555579	15.664472
C	13.371919	8.791272	16.272968
H	13.554165	9.752451	16.753810
C	14.366410	7.818658	16.280586
H	15.324281	8.019294	16.760758
C	11.057071	9.590896	15.673601
H	10.227021	9.289058	16.327090
H	10.634302	9.738131	14.671298
H	11.425286	10.558750	16.032537
C	16.100868	5.261624	13.960867
C	15.639293	6.106133	12.948859
H	14.832454	6.810235	13.149945
C	16.211163	6.055706	11.681638
H	15.845547	6.723791	10.901199
C	17.240812	5.160161	11.385980
C	17.703926	4.324607	12.407643
H	18.517011	3.628457	12.200154
C	17.153175	4.381495	13.680162
H	17.547786	3.739884	14.471916
C	17.820403	5.085208	10.006328
H	17.200412	4.456175	9.352319
H	18.827733	4.652294	10.013279
H	17.877887	6.075379	9.537828
C	14.532437	3.750062	15.874234
C	13.846384	3.558153	17.082203
H	13.850809	4.342764	17.840045
C	13.167246	2.375277	17.322063
H	12.639096	2.238079	18.266241
C	13.151254	1.345325	16.372785
C	13.827504	1.546915	15.171457
H	13.817881	0.761818	14.415124
C	14.509562	2.735240	14.917599
H	15.019338	2.865833	13.963821
C	12.415086	0.070745	16.651794
H	11.335305	0.247819	16.748550
H	12.747518	-0.383291	17.594765
H	12.560965	-0.665932	15.853451
C	17.333213	2.439009	17.749546
H	16.523679	2.190095	17.050778
H	17.457366	1.615164	18.461938
H	18.268768	2.595139	17.203112
Pd	19.576092	7.284709	17.944071
S	18.068492	7.656889	16.186411
P	21.081484	9.045868	17.562664
C	21.069714	10.350930	18.829752
C	21.682295	11.587891	18.583427
H	22.157899	11.777226	17.620047

C	21.688413	12.569670	19.561281
H	22.169858	13.527964	19.363057
C	21.077896	12.355383	20.803199
C	20.469415	11.123062	21.038877
H	19.988573	10.940801	22.000054
C	20.461809	10.128580	20.066253
H	19.981641	9.170705	20.266879
C	21.068748	13.437910	21.838524
H	20.415232	14.267945	21.536699
H	22.071040	13.860707	21.985754
H	20.709829	13.069679	22.806378
C	22.781570	8.394225	17.509121
C	23.793565	8.855736	18.353677
H	23.592452	9.662471	19.057890
C	25.060810	8.283923	18.303165
H	25.841238	8.649478	18.971295
C	25.356507	7.254414	17.407472
C	24.334857	6.791373	16.571859
H	24.542376	5.978394	15.875594
C	23.062314	7.342057	16.628837
H	22.270569	6.947504	15.987178
C	26.736187	6.674906	17.332411
H	27.390042	7.294808	16.703129
H	26.729241	5.667482	16.899716
H	27.204859	6.617678	18.322515
C	20.868153	9.962617	15.997661
C	19.660188	10.648689	15.805790
H	18.902366	10.644267	16.590419
C	19.420313	11.327841	14.622925
H	18.476145	11.856016	14.485756
C	20.369566	11.343819	13.592949
C	21.570885	10.667542	13.794500
H	22.327197	10.677151	13.009382
C	21.824762	9.985475	14.982816
H	22.778532	9.475677	15.113388
C	20.090532	12.079993	12.318377
H	19.993701	13.159764	12.495471
H	19.147590	11.747507	11.864319
H	20.888895	11.934178	11.581711
C	18.992927	7.161716	14.686532
H	19.691801	7.971180	14.437689
H	18.280548	7.037692	13.862656
H	19.539241	6.226085	14.842625
Pd	18.798421	4.918856	19.532220
S	20.556081	6.426454	19.904400
P	19.179833	3.413462	21.293377
C	17.912792	3.425295	22.598485
C	18.159140	2.812736	23.835453
H	19.122508	2.337100	24.024766
C	17.181321	2.806681	24.817267
H	17.379560	2.325253	25.775566
C	15.939419	3.417242	24.603011
C	15.703719	4.025701	23.370683
H	14.742555	4.506578	23.188446
C	16.676307	4.033242	22.376165
H	16.475663	4.513390	21.418283
C	14.904133	3.426457	25.685576
H	15.206017	4.079975	26.515588
H	14.756873	2.424179	26.108395
H	13.936282	3.785411	25.317372
C	19.233293	1.713363	20.641757
C	18.388772	0.701383	21.103370

H	17.684632	0.902523	21.910162
C	18.439225	-0.565876	20.531587
H	17.771125	-1.346292	20.897224
C	19.334817	-0.861602	19.501998
C	20.170394	0.160030	19.038856
H	20.866585	-0.047514	18.225820
C	20.113477	1.432586	19.589517
H	20.755112	2.224315	19.194892
C	19.409801	-2.241295	18.922509
H	20.038909	-2.895224	19.542509
H	19.842645	-2.234406	17.915149
H	18.419648	-2.709848	18.865133
C	20.744880	3.626743	22.210064
C	20.936854	4.834722	22.896078
H	20.152277	5.592597	22.891649
C	22.119762	5.074550	23.575174
H	22.257013	6.018736	24.103297
C	23.149675	4.125231	23.591158
C	22.948021	2.923896	22.914937
H	23.733093	2.167536	22.924546
C	21.759666	2.670070	22.232920
H	21.629021	1.716293	21.723154
C	24.424289	4.404210	24.327280
H	24.247247	4.501011	25.407063
H	24.878355	5.347150	23.994803
H	25.160928	3.605831	24.181409
C	22.055968	5.502042	19.409221
H	22.304830	4.803176	20.218686
H	22.879832	6.214433	19.285188
H	21.899877	4.955719	18.473594

Zero-point correction= 1.195257 (Hartree/Particle)
Thermal correction to Energy= 1.278410
Thermal correction to Enthalpy= 1.279355
Thermal correction to Gibbs Free Energy= 1.066824
Sum of electronic and zero-point Energies= -5153.965300
Sum of electronic and thermal Energies= -5153.882147
Sum of electronic and thermal Enthalpies= -5153.881202
Sum of electronic and thermal Free Energies= -5154.093733

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	802.215	307.906	447.308

Cation I, M06/Def2-svp

147
scf done: -5156.276324

Pd	17.225364	5.690166	17.172009
S	16.852792	3.935735	18.671567
P	15.467316	5.317434	15.676328
C	14.157397	6.586491	15.684123
C	12.919851	6.335083	15.071646
H	12.731477	5.366771	14.593751
C	11.933004	7.310432	15.063741
H	10.972376	7.105270	14.578587
C	12.140436	8.557620	15.671813
C	13.375250	8.797114	16.279656
H	13.556993	9.764424	16.759591
C	14.374674	7.826771	16.289411

H	15.335658	8.036920	16.770642
C	11.054531	9.585686	15.680173
H	10.234948	9.288864	16.356382
H	10.609169	9.709022	14.680025
H	11.422116	10.566158	16.016289
C	16.111593	5.260884	13.968953
C	15.652237	6.105581	12.955667
H	14.847485	6.820479	13.155594
C	16.220691	6.047170	11.683672
H	15.853807	6.718163	10.899793
C	17.245913	5.145781	11.385218
C	17.707656	4.309557	12.412566
H	18.520273	3.604789	12.205153
C	17.160448	4.372905	13.686857
H	17.556004	3.727698	14.482347
C	17.827495	5.056594	10.010021
H	17.433265	4.178050	9.471134
H	18.922756	4.945818	10.038770
H	17.586592	5.944228	9.406795
C	14.540256	3.752672	15.884191
C	13.838383	3.569845	17.085367
H	13.831610	4.364154	17.840589
C	13.151647	2.388679	17.325395
H	12.609466	2.260788	18.268567
C	13.140956	1.350095	16.382343
C	13.835544	1.544280	15.186484
H	13.835506	0.750605	14.431932
C	14.525412	2.729853	14.933165
H	15.050961	2.849928	13.980658
C	12.383750	0.087943	16.647982
H	11.298832	0.242507	16.518960
H	12.532356	-0.262495	17.681595
H	12.683050	-0.719748	15.963953
C	17.342314	2.443026	17.740816
H	16.526069	2.195737	17.042432
H	17.469341	1.611827	18.451392
H	18.280274	2.598754	17.187685
Pd	19.570551	7.269704	17.937641
S	18.070911	7.642326	16.183299
P	21.066252	9.027723	17.564913
C	21.058514	10.337629	18.833974
C	21.671002	11.575173	18.582587
H	22.148872	11.763567	17.614267
C	21.678939	12.561989	19.557967
H	22.164095	13.522620	19.352824
C	21.070899	12.354523	20.805165
C	20.463050	11.119707	21.044640
H	19.983141	10.937941	22.011958
C	20.453258	10.120315	20.074265
H	19.972020	9.159326	20.284389
C	21.062584	13.440394	21.833267
H	20.386416	14.260019	21.536469
H	22.062753	13.885704	21.956621
H	20.726449	13.072793	22.813725
C	22.773618	8.383424	17.508324
C	23.786921	8.842780	18.352994
H	23.587022	9.647571	19.067858
C	25.058905	8.274290	18.294593
H	25.842802	8.641178	18.965562
C	25.357318	7.249023	17.393249
C	24.329951	6.787281	16.557042
H	24.537342	5.974632	15.852302

C	23.055677	7.334523	16.620377
H	22.260170	6.938959	15.975198
C	26.732465	6.667318	17.304102
H	27.271098	7.060783	16.425061
H	26.703611	5.571966	17.194226
H	27.335974	6.908889	18.191360
C	20.858341	9.954787	16.000155
C	19.657116	10.656590	15.817369
H	18.901912	10.663302	16.611698
C	19.417007	11.343320	14.636218
H	18.473796	11.885442	14.508362
C	20.360026	11.354081	13.597605
C	21.555931	10.659563	13.791744
H	22.310459	10.659654	12.998046
C	21.809329	9.969693	14.977300
H	22.761871	9.444204	15.097343
C	20.094300	12.111287	12.335471
H	20.223298	13.196208	12.490038
H	19.060674	11.962653	11.985085
H	20.778299	11.812016	11.527744
C	19.001579	7.152783	14.690547
H	19.700000	7.968988	14.443244
H	18.290962	7.025801	13.859369
H	19.554669	6.214792	14.846233
Pd	18.804941	4.924467	19.517136
S	20.559299	6.424077	19.889756
P	19.177658	3.428718	21.275114
C	17.908580	3.436430	22.585005
C	18.159981	2.823930	23.822541
H	19.128314	2.346085	24.010934
C	17.184598	2.815946	24.809354
H	17.389753	2.330782	25.769978
C	15.937382	3.423952	24.601894
C	15.697896	4.031818	23.367089
H	14.730567	4.511706	23.185328
C	16.668273	4.041652	22.367698
H	16.458135	4.522903	21.406721
C	14.909273	3.432206	25.687758
H	15.206072	4.108311	26.507435
H	14.785903	2.432006	26.132996
H	13.928821	3.768376	25.320173
C	19.234258	1.721363	20.630795
C	18.389660	0.708020	21.090199
H	17.674826	0.907886	21.895023
C	18.448090	-0.563959	20.521706
H	17.777177	-1.347888	20.888630
C	19.349393	-0.862331	19.496387
C	20.185519	0.165077	19.034594
H	20.890218	-0.042276	18.221902
C	20.122153	1.439348	19.581843
H	20.767269	2.234886	19.186239
C	19.438582	-2.237483	18.914702
H	20.317573	-2.776121	19.308274
H	19.548577	-2.208648	17.819362
H	18.551292	-2.840979	19.156192
C	20.742404	3.636641	22.202198
C	20.925178	4.837840	22.904046
H	20.130845	5.593037	22.910779
C	22.106321	5.077929	23.590800
H	22.234164	6.021120	24.132959
C	23.144938	4.134914	23.601539
C	22.950809	2.939032	22.906977

H	23.744509	2.184506	22.907053
C	21.765262	2.685655	22.217085
H	21.645233	1.733126	21.691564
C	24.407060	4.400612	24.358774
H	24.252482	4.271559	25.443686
H	24.757441	5.434248	24.210196
H	25.214795	3.716634	24.059478
C	22.052042	5.493394	19.400227
H	22.299265	4.794910	20.216411
H	22.883247	6.203990	19.273354
H	21.896391	4.940381	18.462185

Zero-point correction= 1.185838 (Hartree/Particle)
Thermal correction to Energy= 1.269689
Thermal correction to Enthalpy= 1.270633
Thermal correction to Gibbs Free Energy= 1.054432
Sum of electronic and zero-point Energies= -5155.090486
Sum of electronic and thermal Energies= -5155.006635
Sum of electronic and thermal Enthalpies= -5155.005691
Sum of electronic and thermal Free Energies= -5155.221892

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	796.742	309.489	455.034

Cation I, M11/lacvp(d)

147
scf done: -5154.941534

Pd	17.152933	5.768357	17.269145
S	16.797878	4.026125	18.751709
P	15.462612	5.350566	15.769656
C	14.131792	6.587350	15.693853
C	12.935945	6.291884	15.025208
H	12.798123	5.310636	14.563898
C	11.926721	7.241989	14.952373
H	10.998376	7.006526	14.427704
C	12.076927	8.499926	15.550267
C	13.269986	8.782259	16.217049
H	13.401622	9.757273	16.690344
C	14.291910	7.838111	16.292407
H	15.219503	8.072815	16.817703
C	10.957651	9.510803	15.494173
H	10.174974	9.260135	16.225603
H	10.487425	9.528119	14.501639
H	11.318842	10.521557	15.722954
C	16.189637	5.263653	14.102403
C	15.766245	6.062087	13.040377
H	14.927766	6.748647	13.171224
C	16.427003	5.995307	11.813653
H	16.095388	6.630837	10.989903
C	17.504494	5.129458	11.617427
C	17.919795	4.330209	12.690094
H	18.766814	3.653579	12.556990
C	17.279965	4.402186	13.920188
H	17.633019	3.793404	14.759725
C	18.193448	5.038429	10.277413
H	17.769720	4.216832	9.680779
H	19.267859	4.842949	10.392948
H	18.070887	5.964669	9.701304

C	14.563275	3.771432	15.963331
C	13.861245	3.564963	17.159271
H	13.857767	4.341760	17.928012
C	13.185967	2.373263	17.377191
H	12.645179	2.222497	18.313913
C	13.190275	1.354483	16.414827
C	13.883131	1.572296	15.224806
H	13.891547	0.793574	14.459343
C	14.562177	2.769383	14.992799
H	15.089987	2.914899	14.049045
C	12.445686	0.065340	16.664173
H	11.359574	0.238229	16.668631
H	12.713938	-0.363338	17.639904
H	12.665236	-0.680276	15.889524
C	17.286180	2.529923	17.819981
H	16.493087	2.315277	17.089556
H	17.367450	1.687122	18.517972
H	18.245100	2.676691	17.309602
Pd	19.473329	7.342088	18.015855
S	17.990777	7.697136	16.273614
P	20.972831	9.032400	17.598085
C	21.048668	10.363178	18.834909
C	21.717354	11.559013	18.539489
H	22.178682	11.696850	17.558251
C	21.790210	12.568204	19.489627
H	22.314912	13.496540	19.254200
C	21.192296	12.417977	20.747551
C	20.525476	11.224929	21.029841
H	20.052169	11.093275	22.004847
C	20.450099	10.203037	20.085661
H	19.924778	9.275449	20.320331
C	21.248417	13.537219	21.758465
H	20.517024	14.319935	21.507808
H	22.240971	14.007404	21.775812
H	21.019606	13.176006	22.769204
C	22.640069	8.305349	17.511147
C	23.702104	8.728703	18.309589
H	23.571278	9.567182	18.996152
C	24.928809	8.067910	18.242808
H	25.752568	8.399499	18.878341
C	25.125004	6.990414	17.376959
C	24.052325	6.575143	16.577710
H	24.185404	5.728118	15.901083
C	22.822251	7.215012	16.649682
H	21.982704	6.861979	16.040903
C	26.464999	6.301420	17.285934
H	27.061669	6.725164	16.464371
H	26.349432	5.227021	17.090404
H	27.041087	6.423922	18.212194
C	20.779145	9.931786	16.018978
C	19.583207	10.633832	15.812548
H	18.814476	10.637288	16.589355
C	19.365275	11.309152	14.620873
H	18.428554	11.849950	14.470138
C	20.327627	11.304875	13.602081
C	21.517647	10.612007	13.819856
H	22.283101	10.603618	13.041125
C	21.749665	9.932919	15.016916
H	22.693422	9.405106	15.162404
C	20.078267	12.049514	12.312969
H	20.073817	13.135619	12.485900
H	19.102528	11.781284	11.884294

H	20.852904	11.829987	11.567333
C	18.922502	7.208845	14.777406
H	19.652922	8.001944	14.562759
H	18.224506	7.127575	13.934609
H	19.432888	6.249928	14.924166
Pd	18.726653	5.021663	19.589556
S	20.468863	6.504249	19.944636
P	19.144412	3.522190	21.279899
C	17.907579	3.446370	22.610670
C	18.203001	2.777721	23.806525
H	19.184246	2.316415	23.944385
C	17.252855	2.704875	24.815711
H	17.488284	2.180202	25.744062
C	15.994922	3.302763	24.665458
C	15.712631	3.969547	23.472389
H	14.737618	4.442832	23.340714
C	16.656818	4.044913	22.450503
H	16.422147	4.570206	21.522899
C	14.984002	3.246662	25.784695
H	15.234592	3.978152	26.567342
H	14.966734	2.254153	26.254976
H	13.973247	3.475356	25.423452
C	19.231376	1.854933	20.552887
C	18.432945	0.792900	20.976265
H	17.746374	0.923738	21.814736
C	18.499746	-0.433823	20.315506
H	17.864223	-1.257581	20.647113
C	19.365605	-0.630037	19.238021
C	20.164845	0.442641	18.822729
H	20.841483	0.309546	17.975714
C	20.092852	1.672731	19.462563
H	20.701627	2.512276	19.109515
C	19.456650	-1.970045	18.549057
H	20.278301	-2.566646	18.972728
H	19.652055	-1.854495	17.474633
H	18.530443	-2.546194	18.671674
C	20.723505	3.715921	22.179299
C	20.929922	4.911906	22.881269
H	20.153111	5.680635	22.884665
C	22.121592	5.129894	23.556579
H	22.272316	6.066652	24.097315
C	23.140391	4.167550	23.552369
C	22.922630	2.977483	22.859576
H	23.701368	2.212037	22.851237
C	21.725575	2.745411	22.180494
H	21.580100	1.801622	21.652737
C	24.429497	4.416964	24.297000
H	24.256581	4.421351	25.383109
H	24.858099	5.392746	24.028810
H	25.175183	3.642389	24.077428
C	21.965089	5.572562	19.456326
H	22.179712	4.842089	20.249380
H	22.807888	6.270564	19.375132
H	21.818359	5.062245	18.497367

Zero-point correction= 1.200147 (Hartree/Particle)
Thermal correction to Energy= 1.284301
Thermal correction to Enthalpy= 1.285245
Thermal correction to Gibbs Free Energy= 1.058358
Sum of electronic and zero-point Energies= -5153.741387
Sum of electronic and thermal Energies= -5153.657233
Sum of electronic and thermal Enthalpies= -5153.656289

Sum of electronic and thermal Free Energies= -5153.883176

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	805.911	305.764	477.525

Zwitterion D, M06/lacvp(d)

141
scf done: -5660.524699

C	17.218101	5.765139	17.148701
C	16.988613	4.698590	18.018197
C	15.939651	3.811804	17.736818
C	15.150914	3.990887	16.612472
C	15.383576	5.051227	15.728019
C	16.423970	5.931646	16.015773
P	18.011487	4.360315	19.496282
C	19.205915	5.736189	19.549855
C	19.172812	6.734167	20.526318
C	20.150662	7.723069	20.550516
C	21.175324	7.752638	19.602601
C	21.204609	6.748083	18.630644
C	20.243002	5.747512	18.609031
C	22.207105	8.839368	19.624905
C	14.525227	5.226652	14.512266
Pd	19.139688	2.297168	19.534531
S	18.159232	1.258415	17.667945
C	18.881649	2.140572	16.235616
Pd	21.174129	0.561852	20.760182
S	21.348500	-1.487757	19.638799
C	22.868370	-1.435763	18.621356
S	20.413395	2.644099	21.497204
C	21.755083	3.812292	21.075993
P	22.876860	0.182936	22.323363
C	23.262675	1.579412	23.435991
C	22.267349	1.988419	24.331860
C	22.492689	3.057777	25.186474
C	23.712746	3.731573	25.155329
C	24.708067	3.323414	24.275942
C	24.487532	2.249099	23.416992
H	23.889800	4.568216	25.828908
Pd	19.740528	-0.348770	18.358531
P	19.400963	-1.945721	16.668274
C	20.523523	-3.385356	16.637885
C	20.576288	-4.188857	17.785783
C	21.429045	-5.279033	17.839833
C	22.256841	-5.601882	16.757461
C	22.189997	-4.806107	15.615422
C	21.332987	-3.709691	15.549115
C	23.190104	-6.770745	16.841312
C	22.606360	-1.229421	23.409593
C	23.604418	-1.543674	24.333691
C	23.559529	-2.752228	25.014009
C	22.456968	-3.587260	24.869840
C	21.414173	-3.232367	24.015905
C	21.499045	-2.072197	23.253530
H	22.448286	-4.520171	25.431931
C	24.426095	-0.121953	21.403800
C	25.281626	-1.196467	21.667747

C	26.437566	-1.360956	20.905763
C	26.748300	-0.464015	19.890008
C	25.900033	0.610135	19.625401
C	24.741703	0.774619	20.373085
H	27.655906	-0.597941	19.303585
C	17.744120	-2.704995	16.625717
C	17.517590	-3.882323	15.899952
C	16.245428	-4.429211	15.834354
C	15.167423	-3.828751	16.494510
C	15.401712	-2.659956	17.217381
C	16.674015	-2.101119	17.287333
C	13.803586	-4.446848	16.437321
C	19.611881	-1.142157	15.043286
C	18.605044	-1.108011	14.076919
C	18.804014	-0.426102	12.879886
C	20.007556	0.226045	12.609061
C	21.009267	0.193718	13.584440
C	20.813406	-0.468680	14.787543
C	20.229219	0.923675	11.301199
C	16.858377	4.640412	20.878801
C	15.889297	5.651763	20.820716
C	15.039697	5.866480	21.894770
C	15.123209	5.079645	23.049799
C	16.087517	4.074049	23.098370
C	16.946326	3.851520	22.026676
C	14.183502	5.312543	24.193363
H	24.463147	-0.888960	24.497773
S	25.068976	-3.276153	25.862253
H	20.544298	-3.880557	23.915849
H	20.718766	-1.817860	22.535775
H	25.078940	-1.905153	22.471433
H	27.098899	-2.195462	21.129639
H	26.139069	1.315660	18.830935
H	24.064248	1.604813	20.156601
H	21.313228	1.460317	24.359901
H	21.716234	3.364600	25.884778
H	25.669977	3.832902	24.262928
H	25.279738	1.924774	22.743766
H	22.539899	3.709247	21.836283
H	21.356995	4.832872	21.109163
H	22.166256	3.608952	20.081851
H	18.344465	-4.369907	15.381692
H	16.078884	-5.344473	15.264895
H	14.574179	-2.180616	17.740927
H	16.839426	-1.186697	17.856787
H	13.759454	-5.364043	17.040853
H	13.532329	-4.726933	15.411111
H	13.034862	-3.764408	16.818233
H	17.656135	-1.612474	14.257749
H	18.006614	-0.403283	12.136225
H	21.953332	0.706788	13.397803
H	21.601655	-0.460795	15.543421
H	20.640868	0.234340	10.550445
H	20.939758	1.753255	11.400937
H	19.292959	1.323475	10.892786
H	19.958648	-3.942969	18.650729
H	21.466431	-5.889399	18.742538
H	22.819340	-5.048998	14.758736
H	21.298266	-3.108674	14.641079
H	22.655451	-7.689403	17.116754
H	23.959801	-6.610671	17.608493
H	23.700865	-6.950072	15.888018

H	22.769450	-2.184607	17.825366
H	23.721826	-1.702228	19.255988
H	23.031080	-0.442853	18.191075
H	15.806758	6.274554	19.928782
H	14.290132	6.657184	21.841390
H	16.164311	3.449824	23.988591
H	17.693131	3.059674	22.081538
H	13.154893	5.034181	23.925351
H	14.161249	6.371140	24.483836
H	14.466074	4.726019	25.075136
H	18.384852	6.736214	21.278732
H	20.117635	8.491622	21.323551
H	22.005212	6.745663	17.890450
H	20.301046	4.955088	17.858617
H	21.815572	9.767534	19.185277
H	23.101556	8.560171	19.055468
H	22.517624	9.077436	20.649972
H	15.751314	2.967123	18.400739
H	14.339978	3.291681	16.405176
H	16.616565	6.768313	15.343463
H	18.019281	6.475559	17.350178
H	13.479165	5.419980	14.786891
H	14.527171	4.323791	13.886853
H	14.866464	6.064769	13.893348
H	18.370922	3.108632	16.138801
H	18.700345	1.547771	15.331033
H	19.958087	2.294956	16.361924
O	24.669071	-4.475388	26.613107
O	25.947127	-3.523972	24.697930
O	25.448657	-2.105291	26.668430

Zero-point correction= 1.114263 (Hartree/Particle)
Thermal correction to Energy= 1.195480
Thermal correction to Enthalpy= 1.196424
Thermal correction to Gibbs Free Energy= 0.985125
Sum of electronic and zero-point Energies= -5659.410435
Sum of electronic and thermal Energies= -5659.329219
Sum of electronic and thermal Enthalpies= -5659.328275
Sum of electronic and thermal Free Energies= -5659.539573

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	750.175	301.875	444.715

Zwitterion D, M06/Def2-svp

141
scf done: -5661.436312

C	17.205897	5.752081	17.125675
C	16.979529	4.697505	18.012564
C	15.917875	3.816091	17.755936
C	15.114381	3.987787	16.639068
C	15.342787	5.035579	15.734551
C	16.396459	5.911497	16.000002
P	18.017257	4.359250	19.485112
C	19.193825	5.755788	19.546342
C	19.163772	6.733384	20.545360
C	20.129628	7.736551	20.574833
C	21.141416	7.802262	19.611536
C	21.168979	6.813358	18.619413

C	20.219753	5.798735	18.591903
C	22.153035	8.904500	19.635879
C	14.469701	5.201015	14.530954
Pd	19.154400	2.314416	19.507515
S	18.176747	1.284392	17.642646
C	18.908826	2.169133	16.222461
Pd	21.161100	0.591101	20.740389
S	21.318976	-1.466127	19.649688
C	22.844740	-1.467946	18.648194
S	20.424927	2.681317	21.459743
C	21.774165	3.829486	21.026835
P	22.841963	0.193330	22.305888
C	23.239126	1.585190	23.426966
C	22.249993	1.985383	24.335604
C	22.478198	3.053630	25.194025
C	23.696015	3.734575	25.155254
C	24.686069	3.333380	24.263971
C	24.462413	2.260891	23.400424
H	23.876447	4.572689	25.834334
Pd	19.744019	-0.314200	18.356448
P	19.396897	-1.915360	16.687836
C	20.494856	-3.378791	16.704019
C	20.433437	-4.207062	17.835417
C	21.278658	-5.299381	17.954346
C	22.217187	-5.602355	16.956055
C	22.261716	-4.781674	15.827619
C	21.412120	-3.682194	15.695976
C	23.133762	-6.773809	17.110278
C	22.558688	-1.220413	23.394094
C	23.581708	-1.544152	24.287270
C	23.609733	-2.804632	24.869938
C	22.536620	-3.674621	24.705515
C	21.450553	-3.299439	23.912928
C	21.477575	-2.094727	23.213691
H	22.597152	-4.655934	25.187461
C	24.408022	-0.134149	21.409718
C	25.272368	-1.196762	21.704253
C	26.444978	-1.357915	20.963885
C	26.763910	-0.474226	19.937285
C	25.905268	0.586107	19.640857
C	24.731577	0.750032	20.368144
H	27.687740	-0.605853	19.366143
C	17.727527	-2.656234	16.628350
C	17.496664	-3.833406	15.900826
C	16.220237	-4.374151	15.829200
C	15.138954	-3.768469	16.485051
C	15.379703	-2.599267	17.209946
C	16.656631	-2.046500	17.285993
C	13.775063	-4.379949	16.423432
C	19.643989	-1.141843	15.049693
C	18.657060	-1.118369	14.059991
C	18.883799	-0.452427	12.856994
C	20.095437	0.196680	12.600953
C	21.075614	0.175560	13.601826
C	20.852377	-0.471405	14.810909
C	20.346015	0.874266	11.290491
C	16.860470	4.628510	20.873632
C	15.879622	5.630417	20.814164
C	15.028991	5.841457	21.890509
C	15.121671	5.061219	23.052456
C	16.098405	4.064153	23.100359
C	16.958173	3.845071	22.026068

C	14.184814	5.291726	24.195591
H	24.431529	-0.874092	24.468853
S	25.220188	-3.355878	25.503937
H	20.597624	-3.974878	23.793968
H	20.673325	-1.837116	22.516599
H	25.090594	-1.911958	22.515345
H	27.110143	-2.186080	21.225193
H	26.150352	1.285496	18.835926
H	24.048252	1.575195	20.125788
H	21.295402	1.447817	24.372564
H	21.703129	3.354515	25.904316
H	25.649833	3.850002	24.244291
H	25.254000	1.944044	22.714414
H	22.556296	3.737396	21.797812
H	21.382632	4.858051	21.037730
H	22.194213	3.606164	20.034783
H	18.325979	-4.328902	15.382843
H	16.052224	-5.291657	15.254364
H	14.549475	-2.111677	17.731904
H	16.822718	-1.128282	17.858927
H	13.724142	-5.295115	17.037685
H	13.510679	-4.673399	15.394861
H	13.002431	-3.690434	16.794240
H	17.697503	-1.619290	14.225600
H	18.097599	-0.438569	12.094307
H	22.028339	0.688447	13.430764
H	21.626788	-0.450104	15.587991
H	20.756030	0.165057	10.550643
H	21.074429	1.693450	11.388374
H	19.419597	1.285621	10.861034
H	19.718429	-3.987677	18.636653
H	21.225013	-5.930542	18.847875
H	22.979912	-5.004586	15.031293
H	21.473104	-3.061488	14.796518
H	22.567691	-7.718298	17.170247
H	23.721548	-6.699945	18.039853
H	23.837722	-6.855022	16.269287
H	22.739642	-2.238076	17.867547
H	23.689617	-1.737127	19.301409
H	23.036616	-0.485159	18.193692
H	15.787366	6.253998	19.917458
H	14.269445	6.629194	21.833982
H	16.186073	3.441818	23.996920
H	17.716865	3.058223	22.087011
H	13.153160	5.006843	23.927972
H	14.154732	6.355756	24.481041
H	14.471399	4.707728	25.082365
H	18.386805	6.708848	21.315984
H	20.096914	8.490269	21.369047
H	21.961893	6.835104	17.864205
H	20.280282	5.018640	17.821688
H	21.751216	9.821423	19.170998
H	23.065576	8.633627	19.083988
H	22.439235	9.168356	20.665832
H	15.725349	2.981807	18.440181
H	14.289686	3.290792	16.453785
H	16.587262	6.742843	15.312838
H	18.017510	6.463828	17.308138
H	13.419264	5.373046	14.819625
H	14.478584	4.295899	13.901278
H	14.789129	6.049127	13.907545
H	18.376165	3.128237	16.105985

H	18.761683	1.564311	15.313544
H	19.984147	2.349829	16.368390
O	24.950524	-4.645193	26.156158
O	25.957831	-3.446623	24.217550
O	25.669148	-2.260154	26.376309

Zero-point correction= 1.106835 (Hartree/Particle)
Thermal correction to Energy= 1.189258
Thermal correction to Enthalpy= 1.190202
Thermal correction to Gibbs Free Energy= 0.975903
Sum of electronic and zero-point Energies= -5660.329476
Sum of electronic and thermal Energies= -5660.247054
Sum of electronic and thermal Enthalpies= -5660.246109
Sum of electronic and thermal Free Energies= -5660.460409

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	746.271	305.004	451.031

Zwitterion D, M11/lacvp(d)

141
scf done: -5660.301885

C	17.518883	5.845519	17.066556
C	17.168655	4.762812	17.872649
C	16.092855	3.949280	17.487867
C	15.396876	4.214542	16.317605
C	15.751915	5.291245	15.493881
C	16.816118	6.099689	15.887663
P	18.060004	4.326243	19.411696
C	19.276451	5.667660	19.626369
C	19.213494	6.581413	20.677657
C	20.221776	7.531423	20.838467
C	21.298337	7.600487	19.953284
C	21.353331	6.677813	18.900567
C	20.365093	5.715266	18.744617
C	22.373403	8.648410	20.110879
C	14.991192	5.558399	14.217406
Pd	19.115456	2.282324	19.500866
S	18.156915	1.247190	17.659841
C	18.931552	2.079843	16.226219
Pd	21.068658	0.579837	20.793905
S	21.267272	-1.448648	19.696615
C	22.752157	-1.385800	18.630990
S	20.312796	2.652135	21.476379
C	21.688316	3.804546	21.123321
P	22.761883	0.217866	22.292780
C	23.147860	1.589359	23.438353
C	22.128112	2.046552	24.281907
C	22.367582	3.096179	25.160014
C	23.626699	3.696639	25.202720
C	24.646020	3.236262	24.375641
C	24.411141	2.181625	23.492861
H	23.814591	4.520303	25.892895
Pd	19.671829	-0.345343	18.429395
P	19.333289	-1.954723	16.824300
C	20.468348	-3.385795	16.806832
C	20.516895	-4.184286	17.958764
C	21.403680	-5.247546	18.036943
C	22.267978	-5.545269	16.974713

C	22.199832	-4.758049	15.826240
C	21.308633	-3.687650	15.735106
C	23.246473	-6.688621	17.089186
C	22.618271	-1.252606	23.324096
C	23.716809	-1.576591	24.118762
C	23.812789	-2.847171	24.666839
C	22.755154	-3.740228	24.556512
C	21.602103	-3.371434	23.859407
C	21.546760	-2.146038	23.199875
H	22.875255	-4.729673	25.001233
C	24.283991	0.022004	21.294371
C	25.214345	-1.010970	21.451320
C	26.309748	-1.082385	20.586741
C	26.484557	-0.138271	19.579738
C	25.564632	0.901357	19.431918
C	24.468443	0.976388	20.282208
H	27.343641	-0.205924	18.910482
C	17.682444	-2.722229	16.842376
C	17.434079	-3.891563	16.110714
C	16.170343	-4.465516	16.123354
C	15.129427	-3.898968	16.870367
C	15.387788	-2.737438	17.598458
C	16.651849	-2.150646	17.589665
C	13.769410	-4.553540	16.899914
C	19.521597	-1.189771	15.179005
C	18.508708	-1.182768	14.221999
C	18.692470	-0.503523	13.016647
C	19.884268	0.165334	12.738124
C	20.897710	0.150358	13.705850
C	20.717528	-0.506764	14.914835
C	20.091283	0.885053	11.426962
C	16.799213	4.582560	20.701856
C	15.899494	5.653239	20.618068
C	14.955876	5.849276	21.617066
C	14.878354	4.982027	22.714357
C	15.776822	3.916846	22.786911
C	16.730723	3.713171	21.791693
C	13.827327	5.188247	23.778011
H	24.557756	-0.887500	24.251608
S	25.461180	-3.346125	25.230607
H	20.762797	-4.064615	23.782088
H	20.691330	-1.884924	22.573437
H	25.131262	-1.767751	22.235786
H	27.029813	-1.889275	20.726460
H	25.699413	1.648624	18.648283
H	23.732090	1.777706	20.158596
H	21.140654	1.580496	24.240180
H	21.569872	3.447001	25.815729
H	25.636670	3.690175	24.420490
H	25.217089	1.815458	22.854870
H	22.502753	3.576281	21.825077
H	21.347012	4.832876	21.294488
H	22.036785	3.700206	20.089270
H	18.240431	-4.352900	15.534635
H	15.983915	-5.376923	15.550940
H	14.589001	-2.286461	18.190715
H	16.841735	-1.244929	18.168743
H	13.800067	-5.483087	17.487297
H	13.433480	-4.815298	15.886899
H	13.017657	-3.894295	17.352461
H	17.567761	-1.700467	14.416858
H	17.890208	-0.497813	12.275677

H	21.835313	0.674629	13.507715
H	21.507529	-0.488549	15.673477
H	20.852316	0.375491	10.817901
H	20.437459	1.915214	11.591300
H	19.163247	0.925061	10.842387
H	19.869851	-3.953716	18.808592
H	21.442403	-5.851640	18.945727
H	22.859129	-4.980687	14.984671
H	21.276192	-3.089161	14.823355
H	22.723888	-7.632869	17.298295
H	23.952067	-6.515181	17.914232
H	23.825756	-6.815074	16.165598
H	22.633948	-2.148071	17.848155
H	23.633739	-1.628068	19.237989
H	22.878147	-0.392493	18.185419
H	15.943286	6.333695	19.763613
H	14.260047	6.688335	21.547791
H	15.730332	3.231848	23.635832
H	17.429096	2.876732	21.860915
H	12.851805	4.810885	23.436685
H	13.704700	6.254254	24.013297
H	14.085991	4.658300	24.703621
H	18.384068	6.544748	21.385755
H	20.169053	8.234344	21.672477
H	22.195931	6.707559	18.206112
H	20.439075	4.978516	17.937285
H	22.204472	9.484395	19.415652
H	23.367358	8.234075	19.894228
H	22.386086	9.057510	21.129256
H	15.808923	3.096429	18.109076
H	14.562806	3.570959	16.029201
H	17.102985	6.949775	15.265021
H	18.338980	6.504302	17.354639
H	13.921795	5.710635	14.422099
H	15.074994	4.707804	13.525484
H	15.370463	6.451873	13.705145
H	18.513215	3.094099	16.157643
H	18.680002	1.524340	15.313793
H	20.020842	2.127147	16.339167
O	25.272743	-4.720404	25.729899
O	26.210382	-3.234475	23.952089
O	25.833431	-2.330770	26.232448

Zero-point correction= 1.121984 (Hartree/Particle)
Thermal correction to Energy= 1.201523
Thermal correction to Enthalpy= 1.202468
Thermal correction to Gibbs Free Energy= 0.994227
Sum of electronic and zero-point Energies= -5659.179901
Sum of electronic and thermal Energies= -5659.100362
Sum of electronic and thermal Enthalpies= -5659.099418
Sum of electronic and thermal Free Energies= -5659.307658

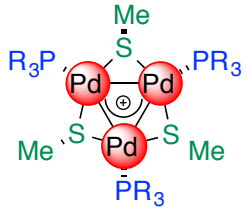
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	753.967	294.707	438.279

9. Analyses on complex D during catalytic reactions

Using 1st generation catalyst **I**, we previously reported ESI-MS analyses (see reference 5 in the main article, MS spectra in the supporting info) on samples collected at regular intervals from the semi-reduction of phenylpropyne 1. The diagnostic isotopic pattern of the Pd_3^+ cation was visible from the beginning of the experiment till complete consumption of 1 (upon 10 hours at reflux). Its concentration slowly faded away through time, and this was consistent with the concomitant formation of visible black metal particles.

We tried the same approach using zwitterionic complex **D**. To this end, we performed both the reaction of Table 3, entry 1 (1 mol% of **D**) and that of Table 4, entry 6 (0.03 mol% of **D**). The concentration of D is the same in both cases (0.001 M). In both cases, despite the absence of any visible traces of Pd black, we did not detect by ESI-MS neither the protonated cation of D or any other species showing an isotopic distribution compatible with the presence of Pd atoms in the ion. This outcome was observed with all samples (from time 0, before warming, up to complete conversion of the alkyne, 4 and 6 hours later respectively).

We then noticed that ESI-MS analyses of salt **I** and zwitterion **D** provided very different ion currents. Preparing samples at the same concentration of both pure complexes, the intensity of the most abundant isotopic signal of **I** is almost two order of magnitude compared to that observed with **D**. This is likely the result of the zwitterionic nature of D, which requires to be ionised to be analysed by MS in contrast to the cation of I.

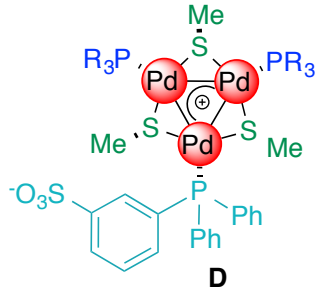


I

Pd_3^+ **I** = 1373 m/z

Total ion current of a 0.1 mg/mL sample: $3*10^9$

Ion current of the most abundant isotope (1373.5): $4*10^7$



$PR_3 = P(C_7H_8)_3$

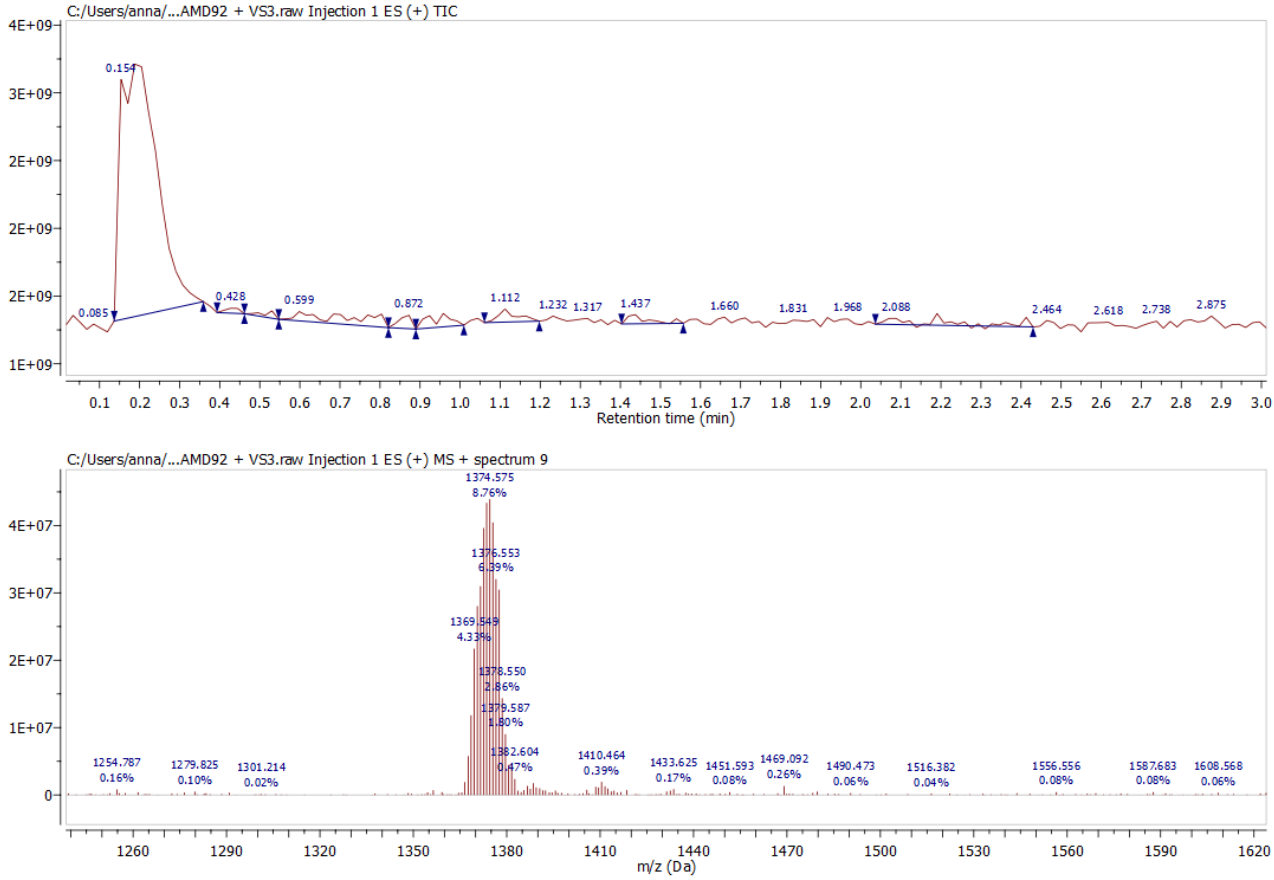
D

[**D** + H^+] = 1412 m/z

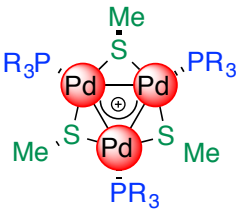
Total ion current of a 0.1 mg/mL sample: $1*10^9$

Ion current of the most abundant isotope (1412.5): $2*10^6$

We confirmed this outcome analysing a 1:1 mixture of I and D. As expected from samples of pure clusters, mixing a sample of **I** (0.1 mg/mL) with a sample of **D** (0.1 mg/mL) leads to a TIC value of $4 \cdot 10^9$ which can be almost totally referred to the cation of **I**. The protonated zwitterionic complex is barely visible (m/z = 1412).

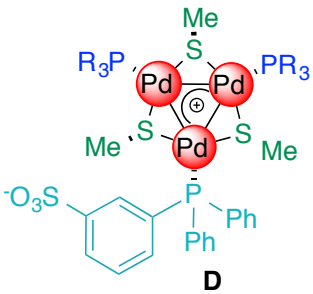


For this reason, we turned to an alternative strategy to monitor the fate of complex **D** during the catalytic semi-reduction of 1. Reasoning that the complex is the sole species in solution that shows significant absorption in the visible region, we monitored reaction samples by UV-Vis. We collect the absorption spectra of D in THF (Figure 1, pink line). It shows a broad and almost flat band between 340 and 380 nm, followed by a smaller one with a saddle around 450 nm. For sake of comparison, the absorption spectrum of I is presented too (red curve). No significant difference was observed adding extra p-tolylphosphine (blue line). These features paralleled those observed with previously reported complexes (see references 3 and 4).



I

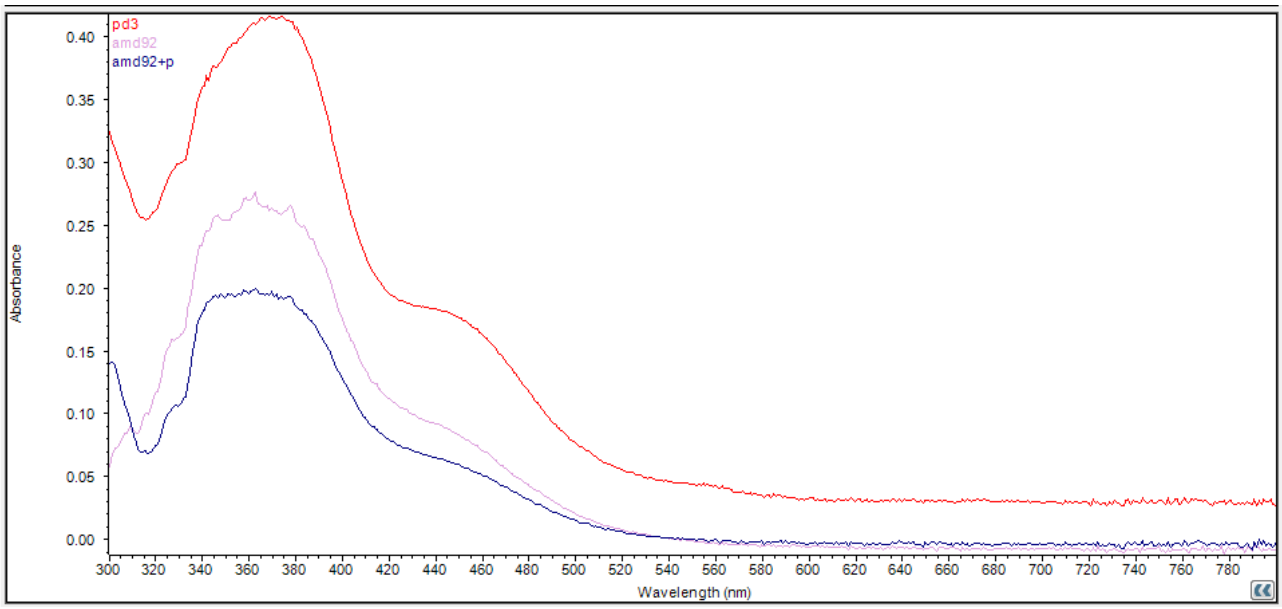
Red curve



D

$PR_3 = P(C_7H_8)_3$

Pink curve



$Pd_3^+ SbF_6^-$ complex I: c = 2.1 · 10^{-5} M; λ_{max} = 369 nm; ε_{max} = 1.98 · 10^4 M^{-1} cm^{-1}

Complex D : c = 2.4 · 10^{-5} M; λ_{max} = 363 nm; ε_{max} = 1.15 · 10^4 M^{-1} cm^{-1}

Complex D + P(tolyl)$_3$: c = 1.4 · 10^{-5} M; λ_{max} = 363 nm; ε_{max} = 1.42 · 10^4 M^{-1} cm^{-1}

	λ_1 (nm)	A_1	ε_1 (M^{-1} cm^{-1})
I	344	0.374293	$1.78 \cdot 10^4$
D	345	0.254896	$1.06 \cdot 10^4$
D + P(tolyl)$_3$	345	0.192824	$1.38 \cdot 10^4$

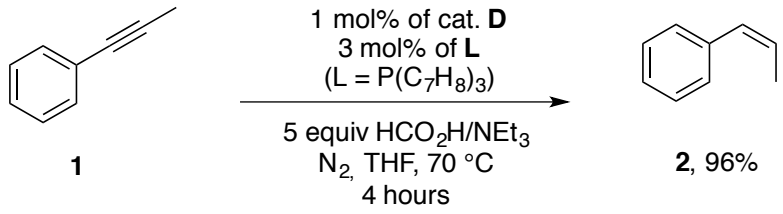
	λ_2 (nm)	A_2	ε_2 (M^{-1} cm^{-1})
I	374	0.416	$1.98 \cdot 10^4$
D	377	0.263277	$1.10 \cdot 10^4$
D + P(tolyl)$_3$	372	0.194571	$1.40 \cdot 10^4$

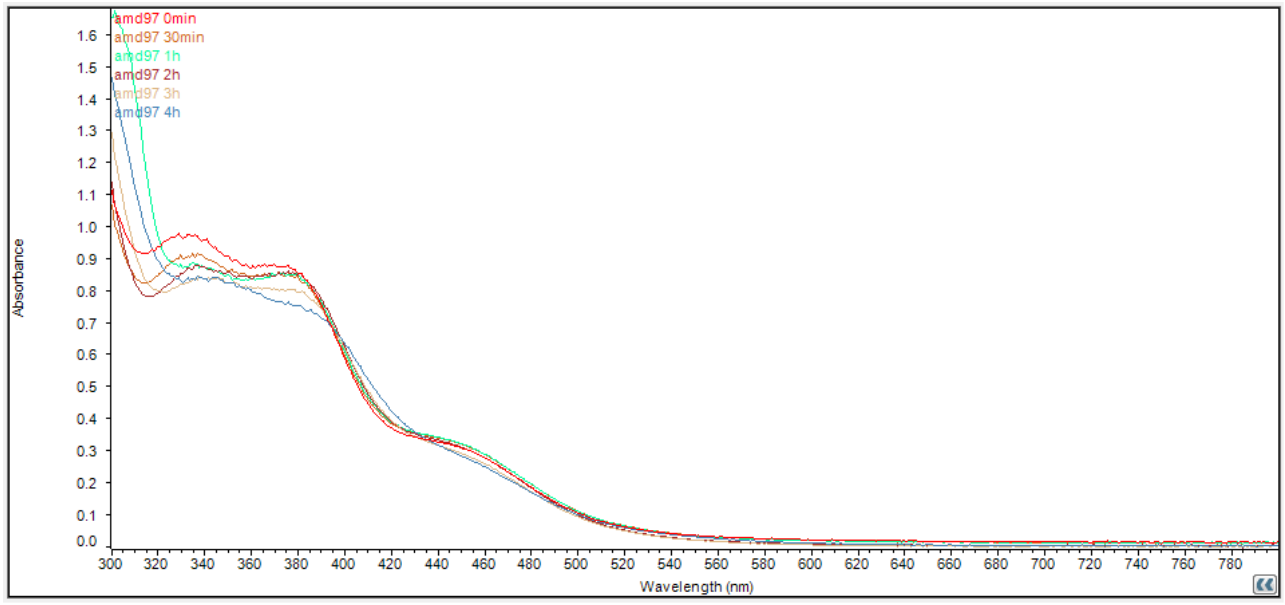
	λ_3 (nm)	A_3	ε_3 (M^{-1} cm^{-1})
I	445	0.180532	$8.60 \cdot 10^3$
D	443	0.089838	$3.74 \cdot 10^3$
D + P(tolyl)$_3$	441	0.06372	$4.55 \cdot 10^3$

The table shows the calculated apparent ε values corresponding to the absorption band in the near UV (plateau between 340 and 380 nm for D) and that in the visible region, around 445 nm.

We then repeated the experiment presented in Table 3, entry 1 and collected samples at regular intervals to analyse their UV-Vis absorption. Spectra are stacked in Figure 2. Small changes occurred during the experiment, both in respect to the position of bands and in their relative intensity, which is just slightly lower upon four hours at reflux.

These results confirm the relative stability of complex **D** during the semi-reduction of phenylpropyne. In particular, apparent ε values barely shift only throughout the experiment. Small changes compared to analyses on pure complexes are likely due to the presence of substrate and triethylammonium formate in this case.



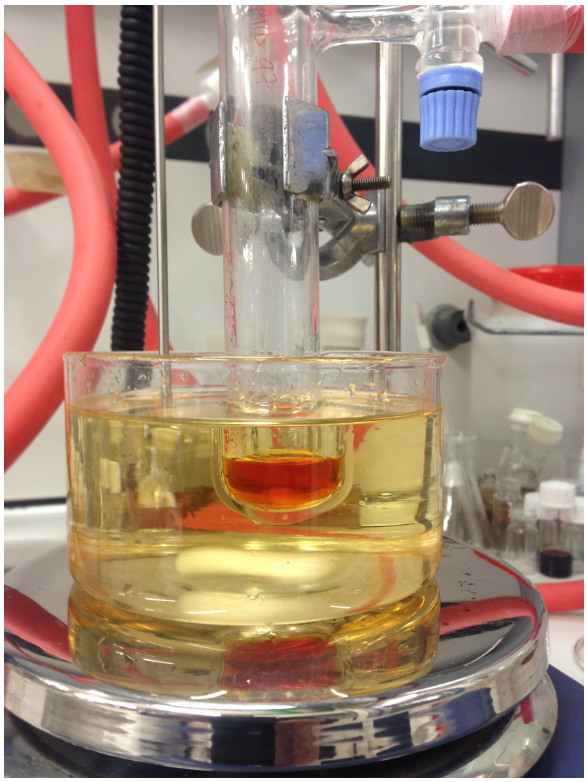


$c = 2.16 \cdot 10^{-5}$ M

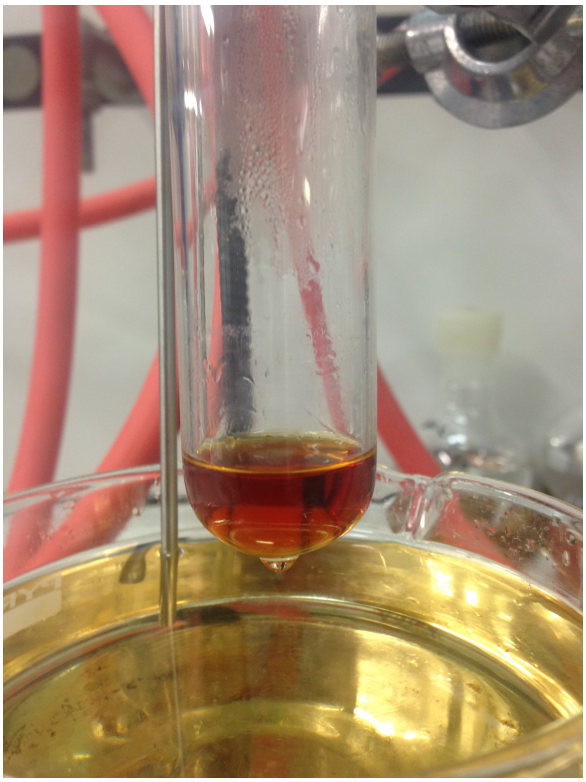
	λ_1 (nm)	A_1	ε_1 (M^{-1} cm^{-1})
0 min	329	0.975181	$4.51 \cdot 10^4$
30 min	337	0.915504	$4.24 \cdot 10^4$
1h	335	0.884850	$4.10 \cdot 10^4$
2h	337	0.877049	$4.06 \cdot 10^4$
3h	337	0.840745	$3.90 \cdot 10^4$
4h	338	0.839245	$3.88 \cdot 10^4$

	λ_2 (nm)	A_2	ε_2 (M^{-1} cm^{-1})
0 min	370	0.879497	$4.07 \cdot 10^4$
30 min	366	0.850369	$3.94 \cdot 10^4$
1h	380	0.850248	$3.94 \cdot 10^4$
2h	381	0.853171	$3.95 \cdot 10^4$
3h	382	0.794607	$3.68 \cdot 10^4$
4h	382	0.839245	$3.46 \cdot 10^4$

	λ_3 (nm)	A_3	ε_3 (M^{-1} cm^{-1})
0 min	446	0.313733	$1.45 \cdot 10^3$
30 min	445	0.327832	$1.52 \cdot 10^3$
1h	457	0.297407	$1.38 \cdot 10^3$
2h	454	0.296036	$1.37 \cdot 10^3$
3h	463	0.244791	$1.13 \cdot 10^3$
4h	459	0.248811	$1.15 \cdot 10^3$



After 30 min warming (orange curve)



Upon full conversion of alkyne (4 h, blue curve)