

SUPPORTING INFORMATION

Characterization of palladium species in the after γ -irradiation of a TBP-alkane- $\text{Pd}(\text{NO}_3)_2$ system

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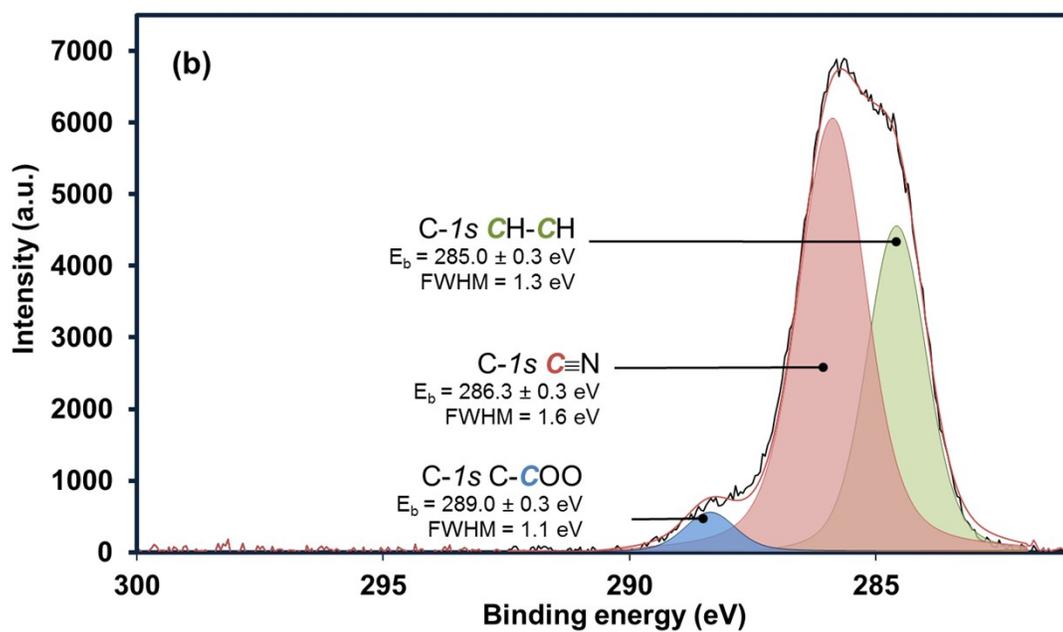
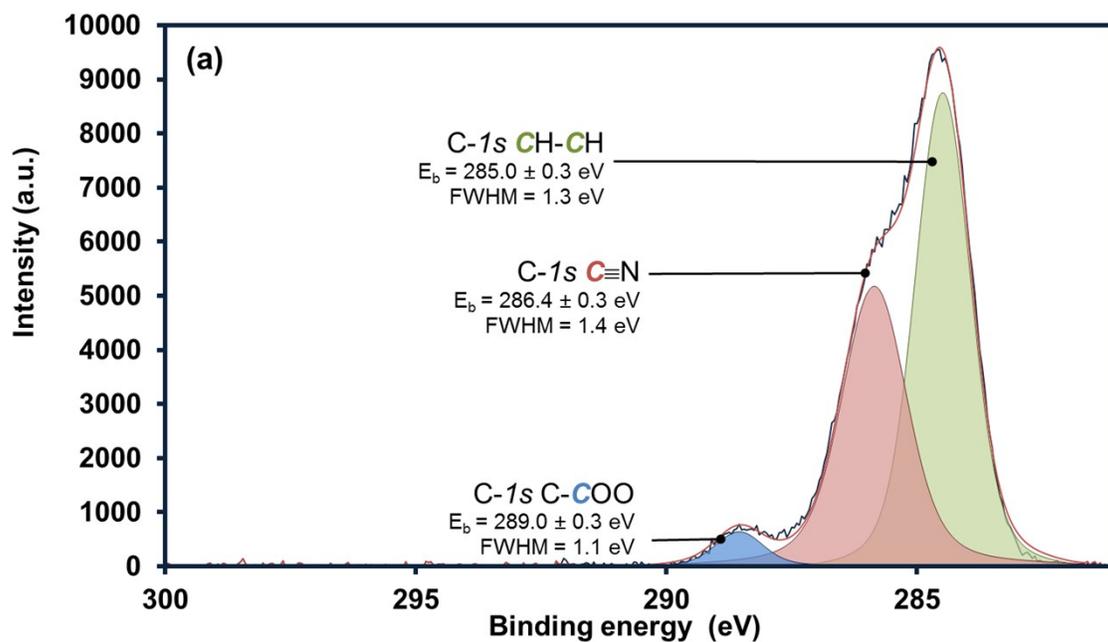


Figure S1: XPS core level spectra C-1s for (a) $\Phi_{s,1}$ and (b) $\Phi_{s,2}$.

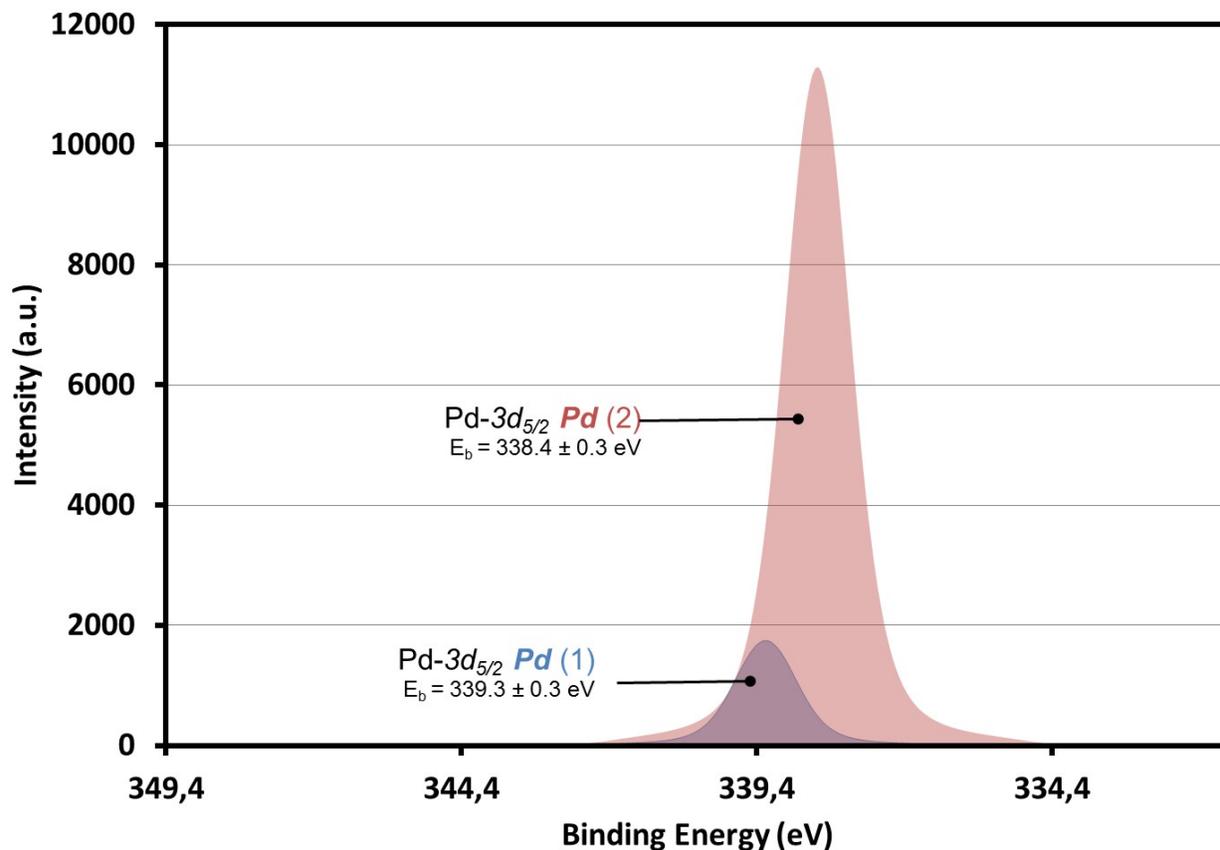


Figure S2: XPS core level spectra Pd3d_{5/2} for $\Phi_{S,3}$ obtained after a partial dissolution of $\Phi_{S,1}$ in 1 mol.L⁻¹NH₃ (solid/liquid ratio= 9; dissolution time=15 minutes).

XPS spectra shows Pd-CN contribution disappears after $\Phi_{S,1}$ dissolution in 1 mol.L⁻¹ NH₃ at a solid:liquid ratio of 9 during 15 minutes. In this case, two peaks are observed for $\Phi_{S,3}$ (Figure S2) with a lower binding energy value for the main contribution of Pd (338.4 instead of 338.7 eV). Furthermore, the area of the peak attributed to Pd linked to -C≡N at 339.3 eV is relatively small and close to the detection limit.

^{31}P NMR spectra decoupled of ^1H spectrum was done on $\Phi_{S,2}$. This experiment allows determining the number of different phosphorous compounds present in the precipitate. For $\Phi_{S,2}$, the value is 2 (Figure S1 (b)). The ^{31}P spectra coupled with ^1H (Figure S3 (a)) gives information on the number of $-\text{CH}_2$ two bonds far from the phosphorous atoms. The peak observed at -0.8 ppm is a septuplet and -1.2 ppm is a quintuplet (Figure S3 (a)). Based on the literature⁷⁰, these two peaks are assigned respectively to TBP and HDBP molecules. This is consistent with the ^1H integration rates showing the TBP is the main compound while the HDBP (the degradation product) is growing. The 2D $^{31}\text{P} - ^1\text{H}$ spectrum based on the CIGARAD pulse sequence (for ^{31}P 2 to 4 bounds far from ^1H nuclei) allows attributing the ^1H observed to the butyl chain of TBP or HDBP (Figure S2).

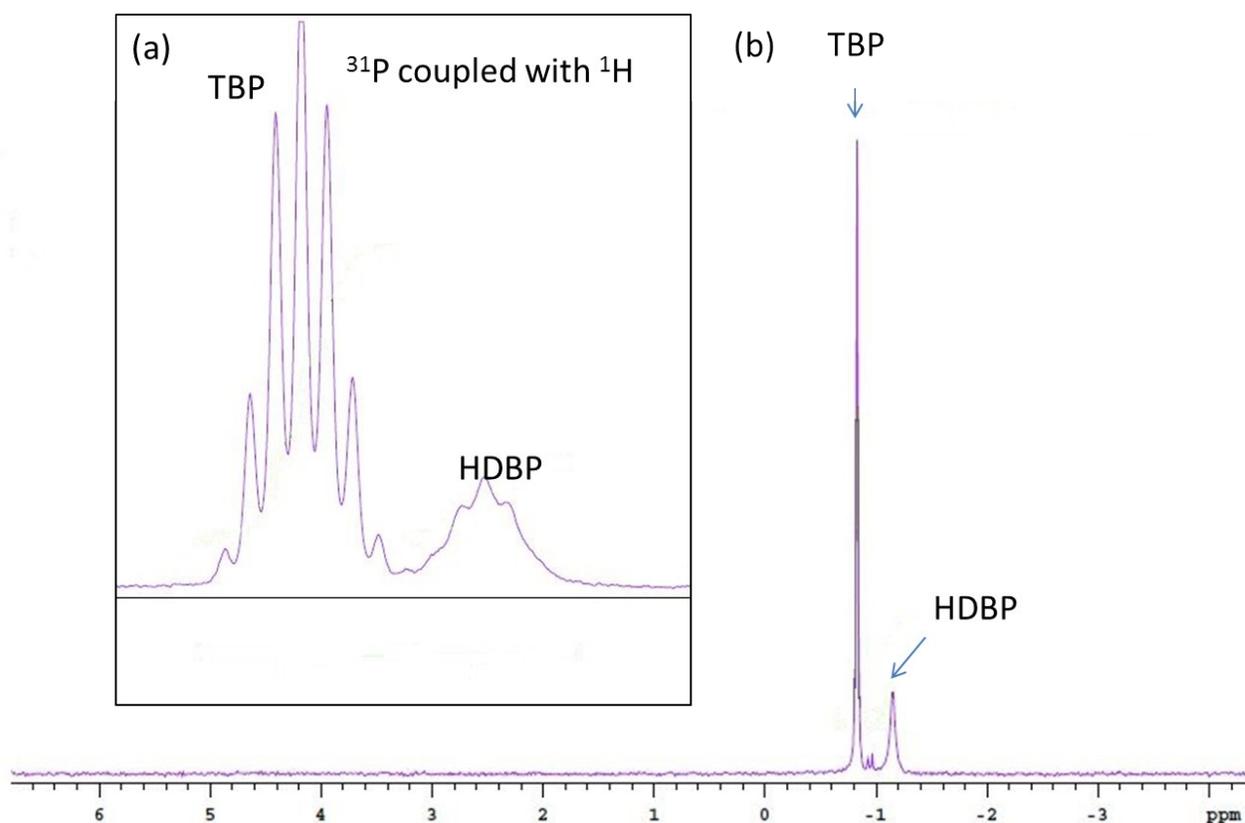


Figure S3: 1D NMR spectrum (a) ^{31}P coupled with ^1H and (b) of ^{31}P decoupled of ^1H for $\Phi_{S,2}$ partially dissolved in DMSO-D6 with $m(\Phi_{S,2}) = 9.8$ mg in $650\mu\text{L}$ of DMSO-D6) ($S/L = 15.07$ g of precipitate /L of solvent).

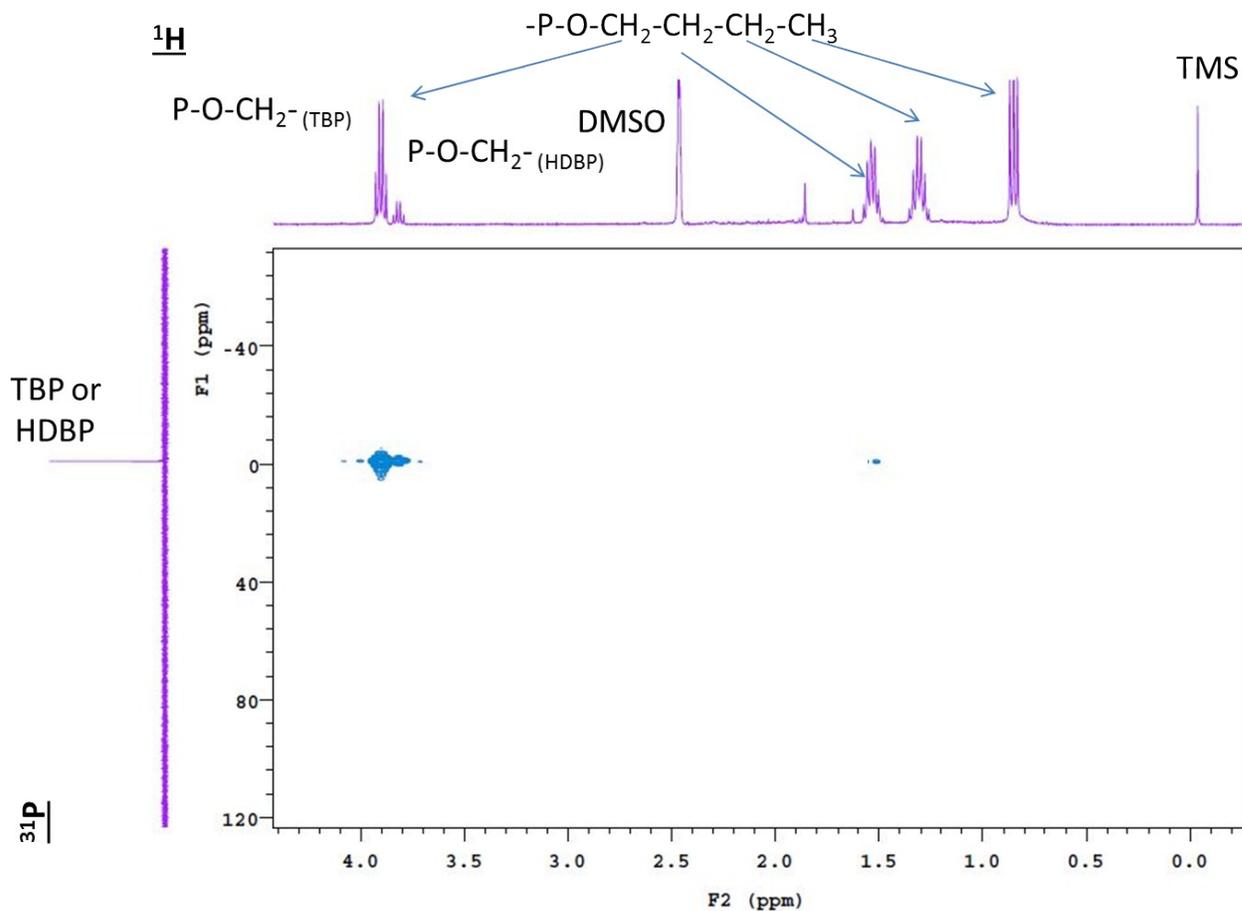


Figure S4: 2D ^{31}P - ^1H NMR spectrum of $\Phi_{\text{S},2}$ partially dissolved in DMSO-D6 ($m_{\Phi_{\text{S},2}} = 9.8$ mg of $\Phi_{\text{S},2}$ in 650 μL of DMSO-D6 at S/L = 15.07 g of precipitate /L of solvent).

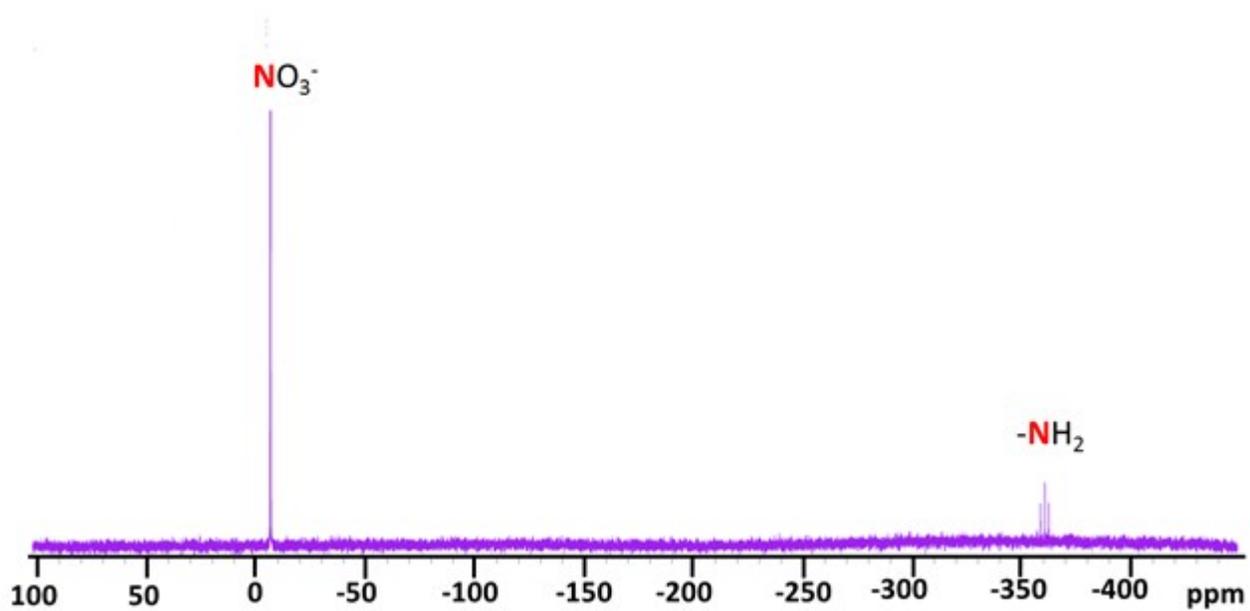


Figure S5: ^{15}N NMR spectrum of an aqueous phase of $3 \text{ mol.L}^{-1} \text{HNO}_3$ containing palladium(II) nitrate (5 g.L^{-1} of Pd) and $\text{Na}^{15}\text{NO}_3$ (66 g/L) (98 % atomic of ^{15}N) in contact with 30%_{vol.} TBP diluted in TPH after γ -irradiation at 500 kGy (dose rate= 5 kGy/h).

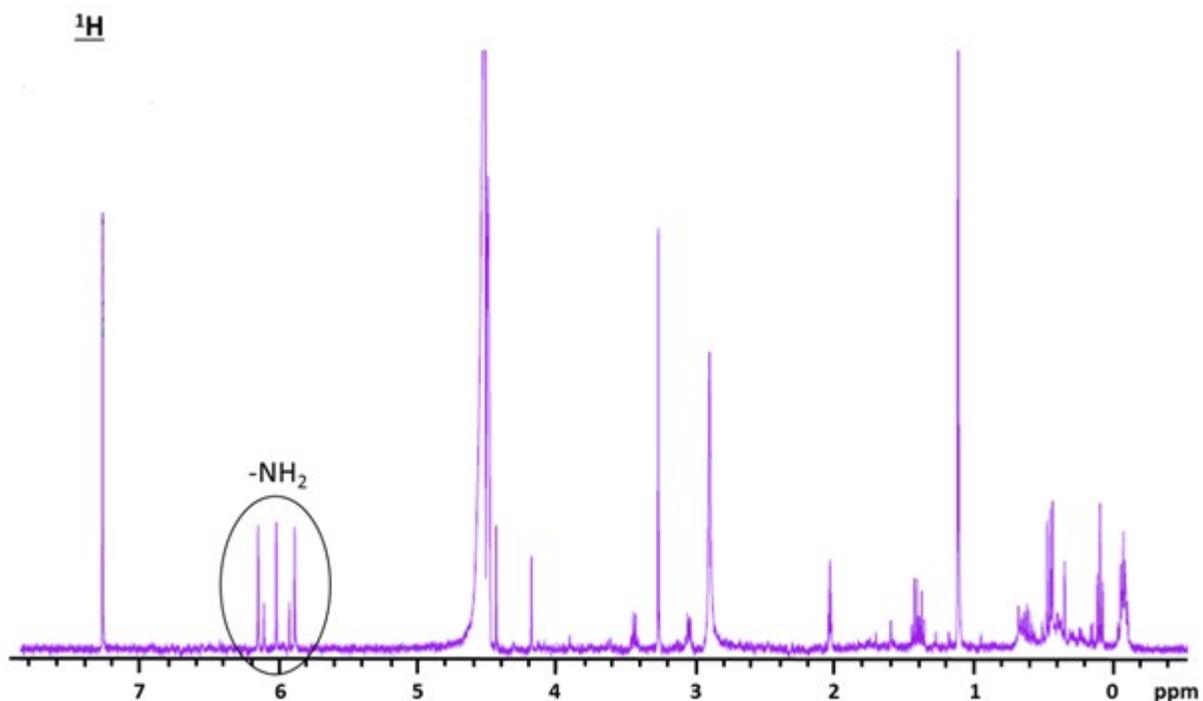


Figure S6: ^1H NMR spectrum of an aqueous phase of $3 \text{ mol}\cdot\text{L}^{-1} \text{H}^{14}\text{NO}_3$ in the presence of palladium(II) nitrate ($\text{Pd } 5 \text{ g}\cdot\text{L}^{-1}$) and $\text{Na}^{15}\text{NO}_3$ (66 g/L) (98 % atomic of ^{15}N) in contact with 30%_{vol.} TBP diluted in TPH after γ -irradiation at 500 kGy .

A mixture of ^{14}N and ^{15}N is present in the aqueous nitric acid (H^{14}NO_3) solution containing palladium(II) nitrate and sodium nitrite ($\text{Na}^{15}\text{NO}_3$). A triplet attributed to ^{14}N is observed around 6 ppm and a doublet attributed to ^{15}N is observed in the same region. The presence of proton in the region can be characteristic of amine ($-\text{NH}_2$).

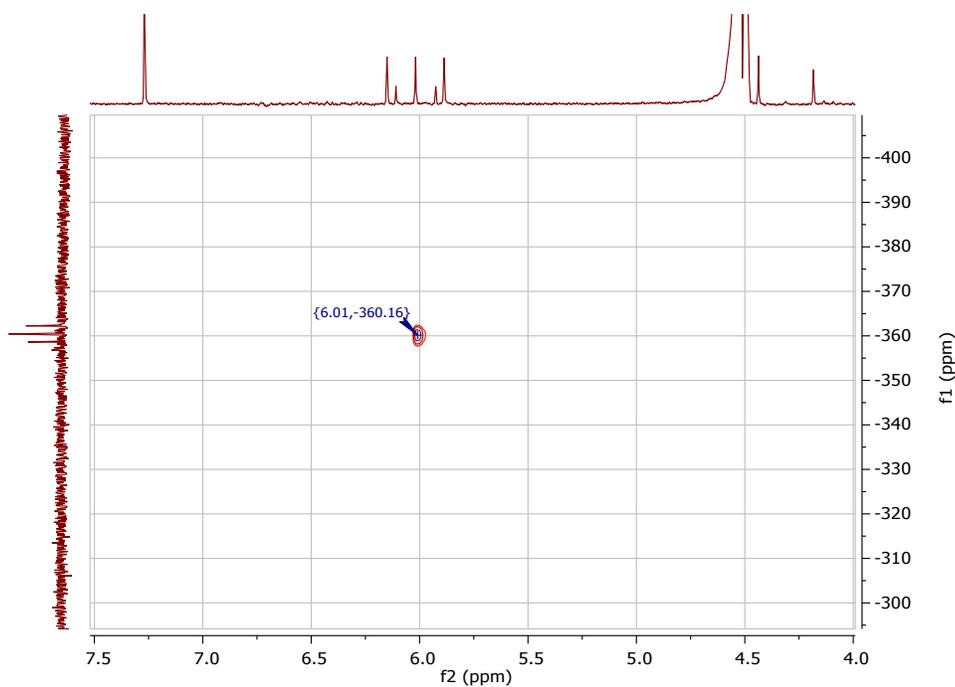


Figure S7: gHSQCAD ^{15}N - ^1H spectra of the an aqueous phase containing H^{14}NO_3 enriched with ^{15}N ($\text{Na}^{15}\text{NO}_3 - 66 \text{ g/L}$) in the presence of palladium(II) nitrate (5 g.L^{-1} of Pd) in DMSO- D_6 . ^{15}N reference scale is CH_3NO_2 and ^1H reference scale is TMS.

A mixture of ^{14}N and ^{15}N is present in the aqueous nitric acid (H^{14}NO_3) solution containing palladium(II) nitrate and sodium nitrate ($\text{Na}^{15}\text{NO}_3$). Consequently, the triplet is assigned to ^{14}N - ^1H coupling around 6 ppm while the doublet is assigned to ^{15}N - ^1H coupling. The observed ^{15}N chemical shift at about 360 ppm is consistent with an amine ($-\text{NH}_2$) group (Figure S7).