Supporting Information for Publication of RSC Advances

Highly Selective Separation of Individual Platinum Group Metals (Pd, Pt, Rh) from Acidic Chloride Media using Phosphonium-based Ionic Liquid in Aromatic Diluent

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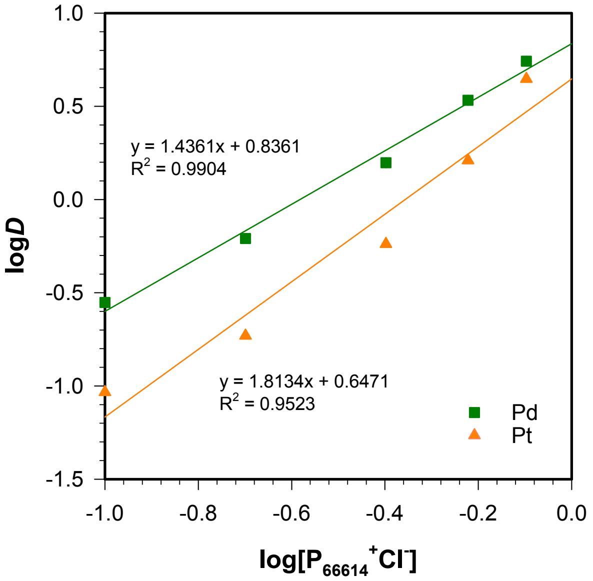
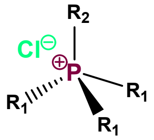


Fig. S1 Plot of log*D* vs. log[$P_{66614}^{+}Cl^{-}$]

Organic phase: 0.1–0.8 g L^{-1} [P_{66614}]$^{+}Cl^{-}$; Aqueous phase: 100 mg L^{-1} Pt(IV), 55 mg L^{-1} Pd(II), 25 mg L^{-1} Rh(III), 0.1 mol L^{-1} HCl; O/A =1; t = 10 min; T = 298 K.

Nuclear magnetic resonance spectroscopy:

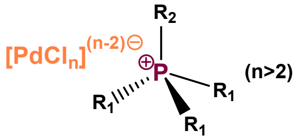
^1H, ^{13}C and ^{31}P NMR spectra of neat compounds were recorded on a Bruker ARX-500 spectrometer. The ionic liquid phases fully loaded with PGMs were concentrated to dryness under reduced pressure in a rotary evaporator at 70 °C. The residues were diluted in CDCl3 before NMR analysis. Chemical shifts are reported in ppm downfield from the external references $(CH_3)_4Si$ (^1H and ^{13}C NMR) and H_3PO_4 (^{31}P NMR).



(1)

$R_1 = -\overset{a}{C}H_2-(\overset{b}{C}H_2)_2-(\overset{c}{C}H_2)_2-\overset{d}{C}H_3$

$R_2 = -\overset{a}{C}H_2-(\overset{b}{C}H_2)_2-(\overset{c}{C}H_2)_{10}-\overset{d}{C}H_3$



(2)

$R_1 = -\overset{a}{C}H_2-(\overset{b}{C}H_2)_2-(\overset{c}{C}H_2)_2-\overset{d}{C}H_3$

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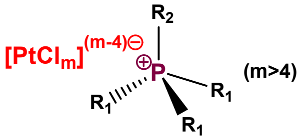


(3)

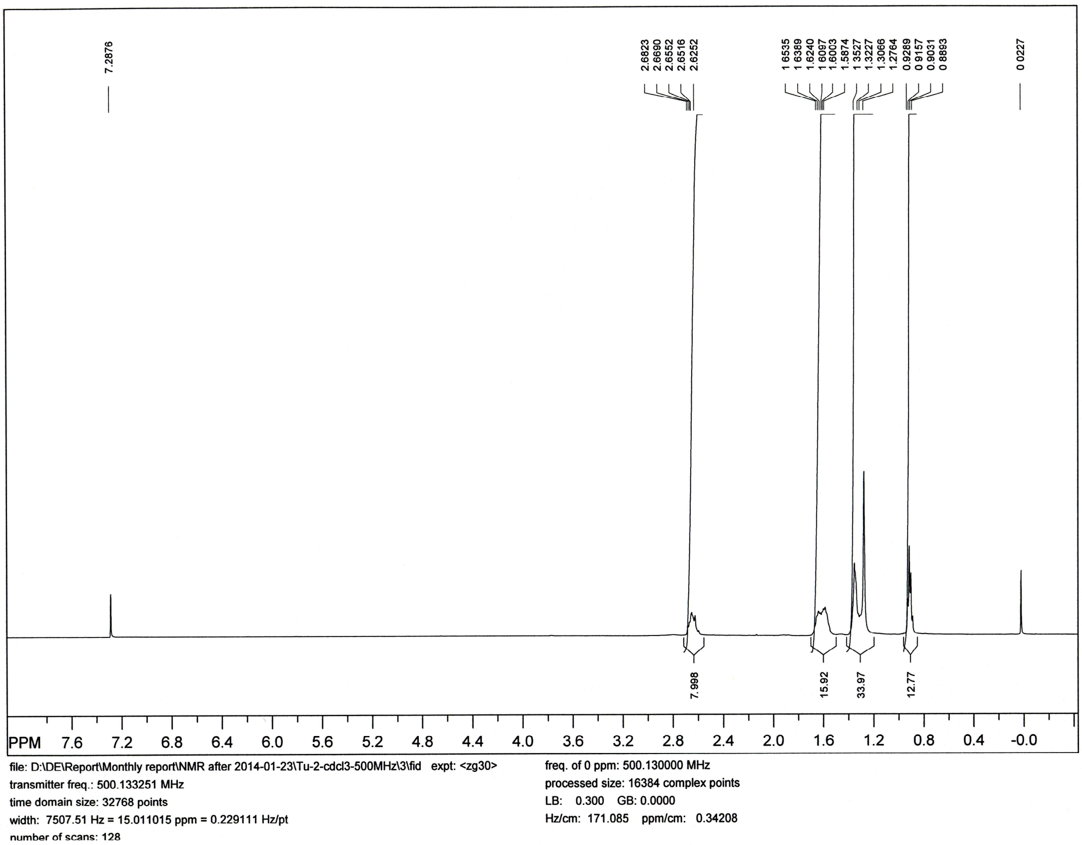
$R_1 = -\overset{a}{C}H_2-(\overset{b}{C}H_2)_2-(\overset{c}{C}H_2)_2-\overset{d}{C}H_3$

$R_2 = -\overset{a}{C}H_2-(\overset{b}{C}H_2)_2-(\overset{c}{C}H_2)_{10}-\overset{d}{C}H_3$

(1): δH(500 MHz; $CDCl_3$; $(CH_3)_4Si$) 2.6823–2.5965 (8 H_a, m, 4×CH_2) 1.6535–1.5867 (16 H_b, m, 8×CH_2), 1.3527–1.2759 (32 H_c, m, 16×CH_2), and 0.9157 (12 H_d, t, ^3J 6.6, 4×CH_3). δC(125 MHz; $CDCl_3$; $(CH_3)_4Si$) 31.75, 30.94, 30.71, 30.60, 30.39, 30.27, 29.51, 29.48, 29.45, 29.35, 29.18, 29.16, 28.83, 22.52, 22.20, 21.78, 21.74, 19.33, 18.96, 13.96, 13.81, 13.79. δP(202 MHz; $CDCl_3$; H_3PO_4) 32.69 (1 P, s, $–(CH_2)_4P^+$).

(2): δH(500 MHz; $CDCl_3$; $(CH_3)_4Si$) 2.5253–2.4676 (8 H_a, m, 4×CH_2), 1.5616–1.5268 (16 H_b, m, 8×CH_2), 1.3480–1.2777 (32 H_c, m, 16×CH_2), and 0.9204 (12 H_d, t, ^3J 6.9, 4×CH_3). δC(125 MHz; $CDCl_3$; $(CH_3)_4Si$) 31.78, 31.08, 30.69, 30.56, 30.37, 30.25, 29.56, 29.54, 29.53, 29.52, 29.49, 29.47, 29.22, 28.95, 22.54, 22.25, 21.96, 21.92, 19.62, 19.24, 13.98, 13.88. δP(202 MHz; $CDCl_3$; H_3PO_4) 32.39 (1 P, s, $[–(CH_2)_4P]^+[PdCl_n]^{(n–2)–}$).

(3): δH(500 MHz; $CDCl_3$; $(CH_3)_4Si$) 2.4171–2.3623 (8 H_a, m, 4×CH_2), 1.5624 (16 H_b, br s, 8×CH_2), 1.3234–1.2749 (32 H_c, m, 16×CH_2), and 0.9075 (12 H_d, t, ^3J 7.0, 4×CH_3). δC(125 MHz; $CDCl_3$; $(CH_3)_4Si$) 31.81, 31.11, 30.67, 30.56, 30.34, 30.22, 29.55, 29.53, 29.52, 29.50, 29.25, 29.01, 22.57, 22.27, 21.91, 21.88, 19.55, 19.51, 19.17, 19.13, 14.00, 13.90. δP(202 MHz; $CDCl_3$; H_3PO_4) 32.48 (1 P, s, $[–(CH_2)_4P]^+[PtCl_m]^{(m–4)–}$).



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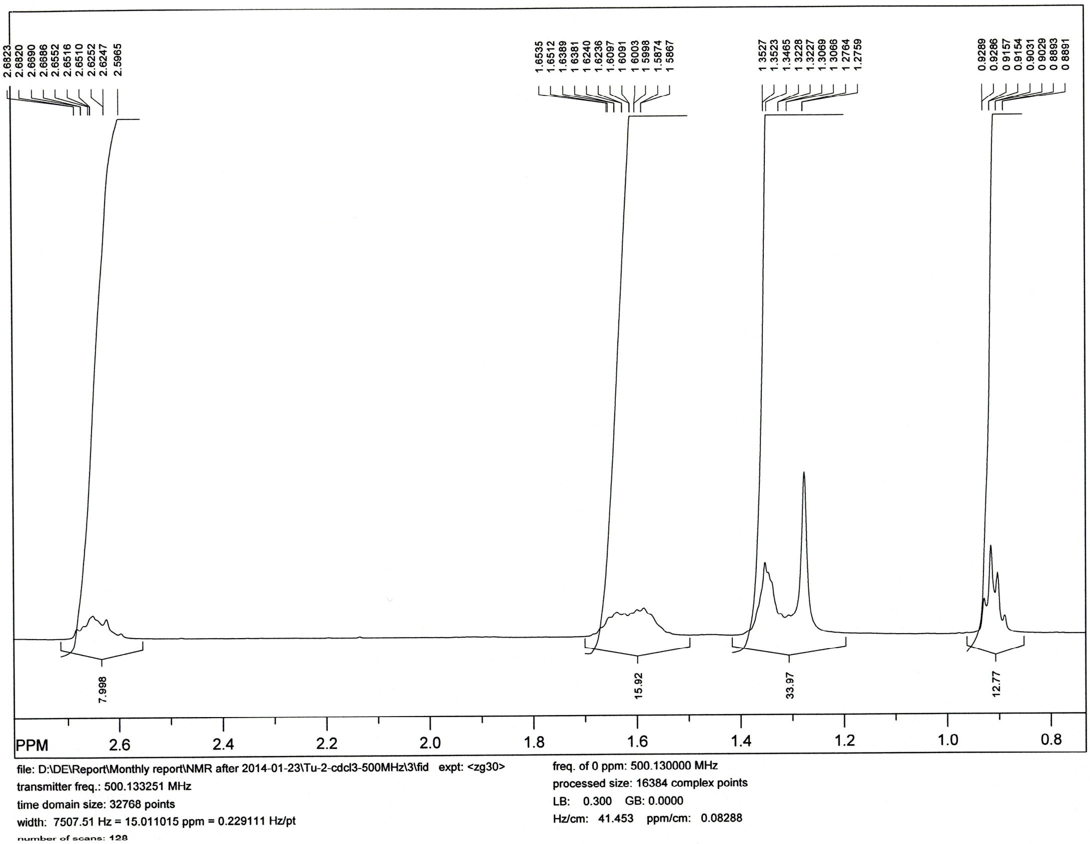

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Fig. S2 ^{1}H NMR spectra of neat $[P_{66614}]^{+}Cl^{-}$ before PGMs extraction

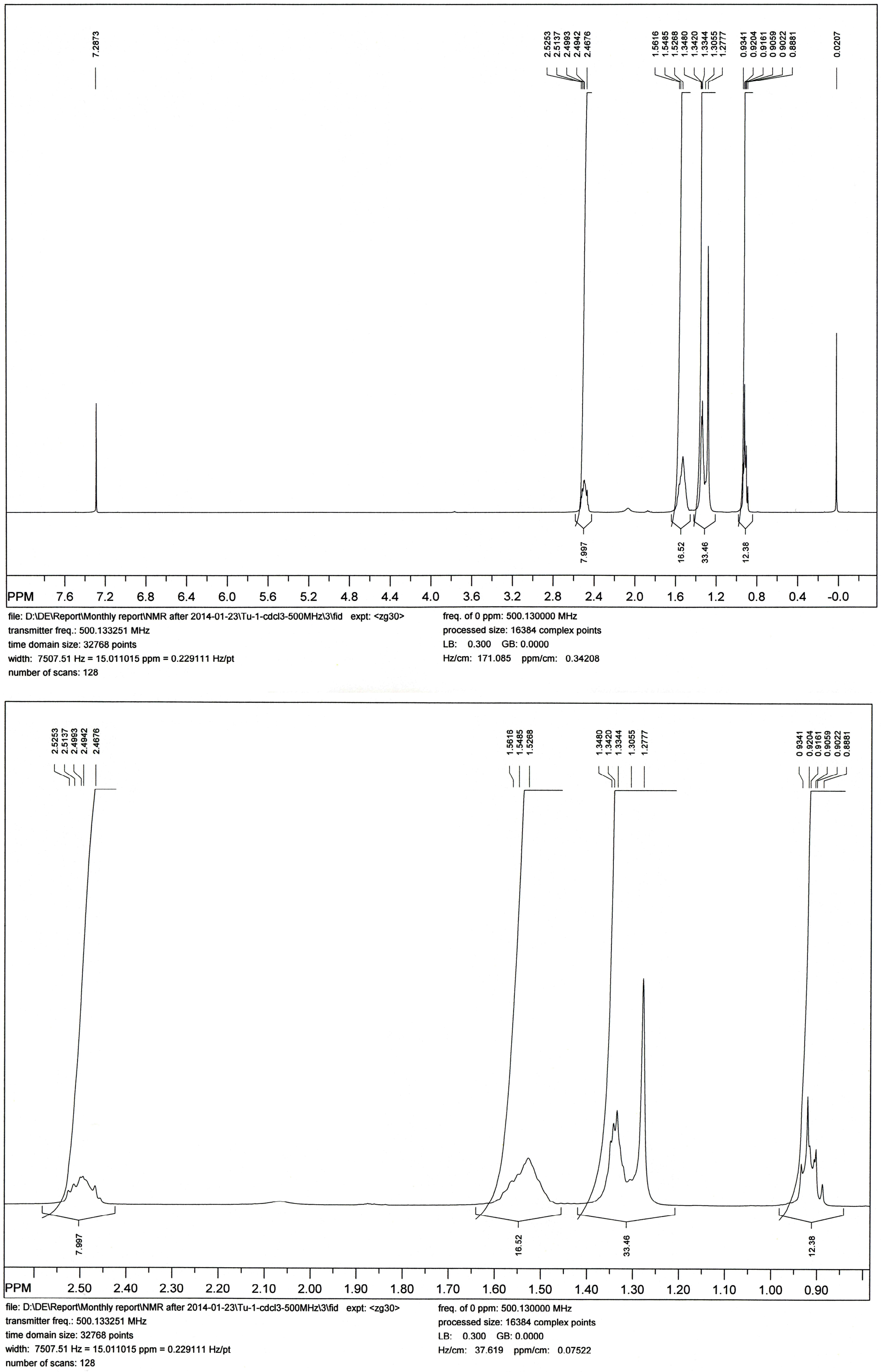
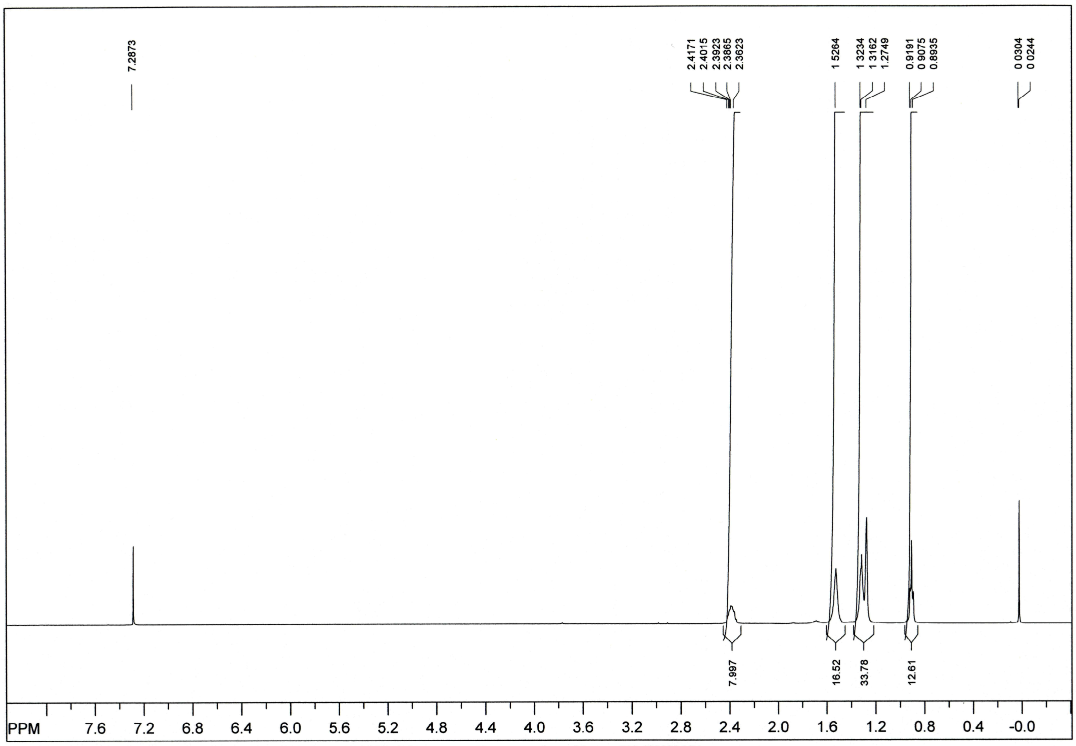


Fig. S3 ^{1}H NMR spectra of loaded $[P_{66614}]^+Cl^-$ after Pd(II) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 55 mg L^{-1} Pd(II), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.



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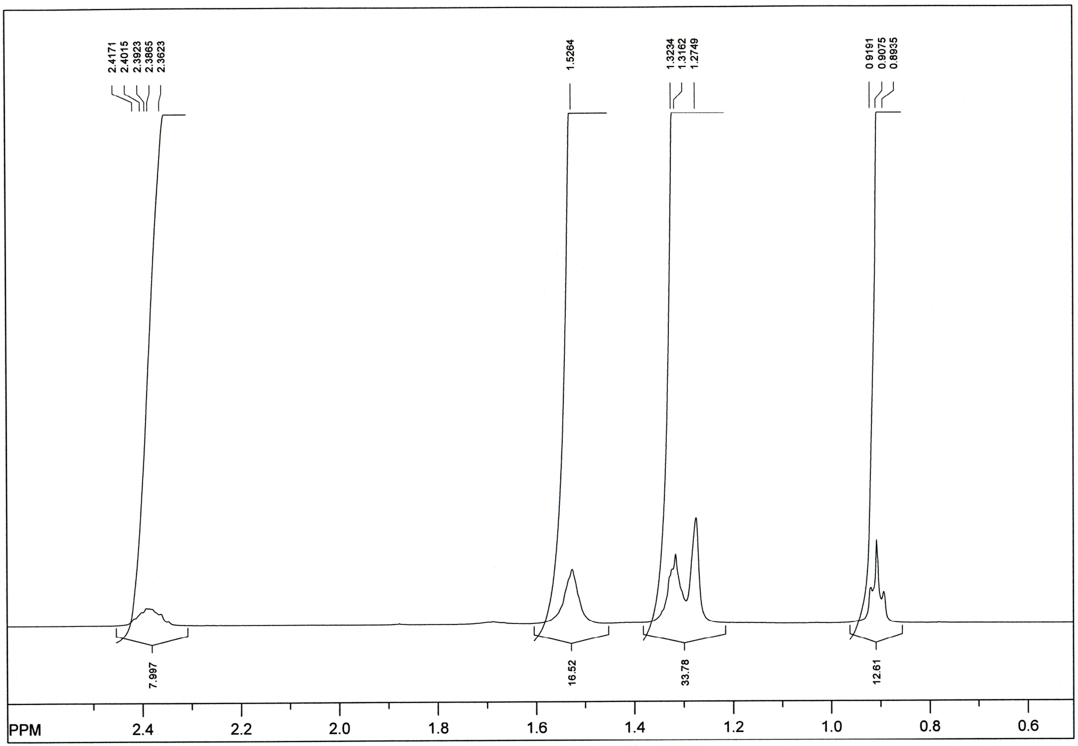

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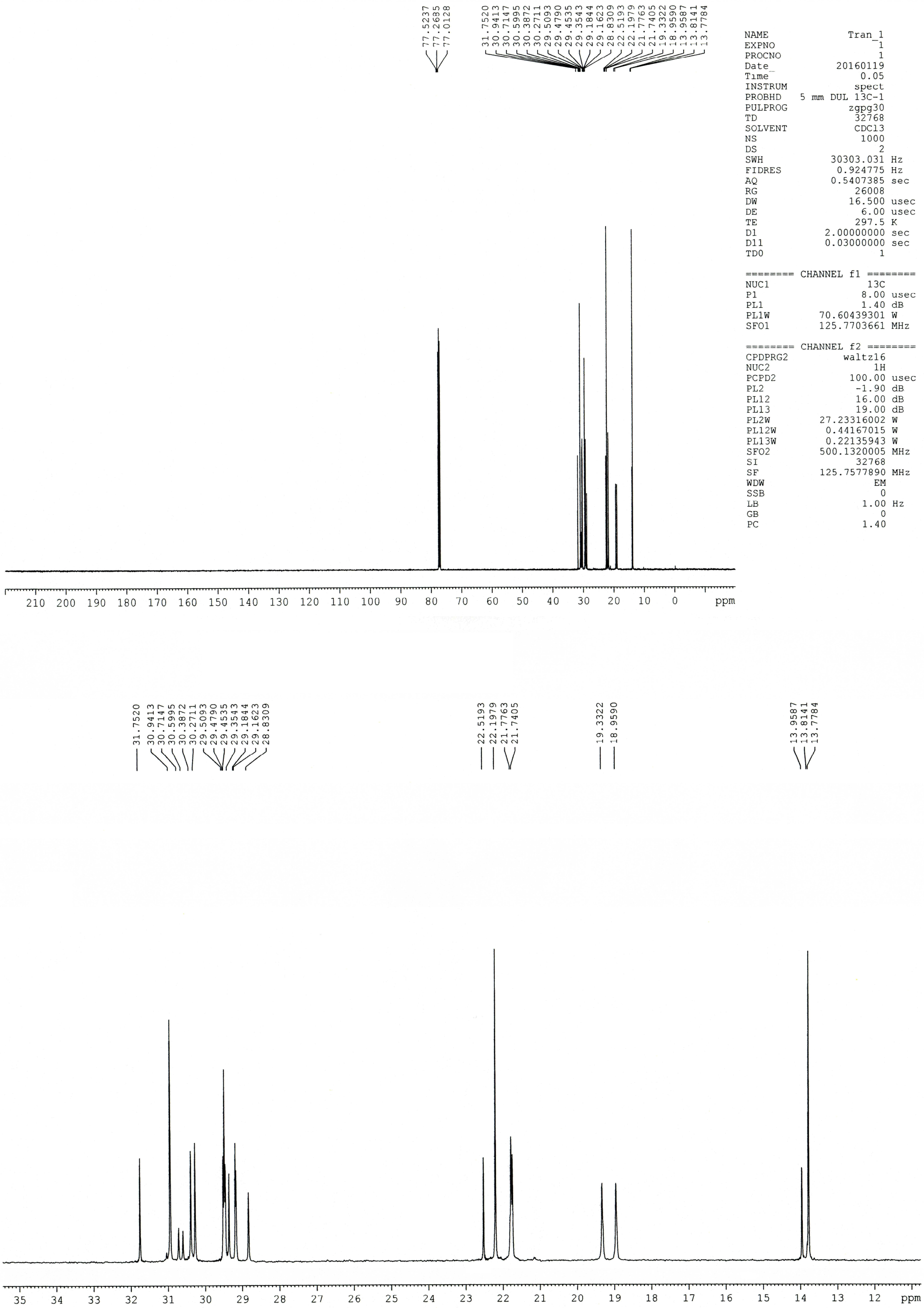
Fig. S4 ^{1}H NMR spectra of loaded $[P_{66614}]^+Cl^-$ after Pt(IV) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 100 mg L^{-1} Pt(IV), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.



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PL12                 16.00 dB
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Fig. S5 ^{13}C NMR spectra of neat $[P_{66614}]^+Cl^-$ before PGMs extraction

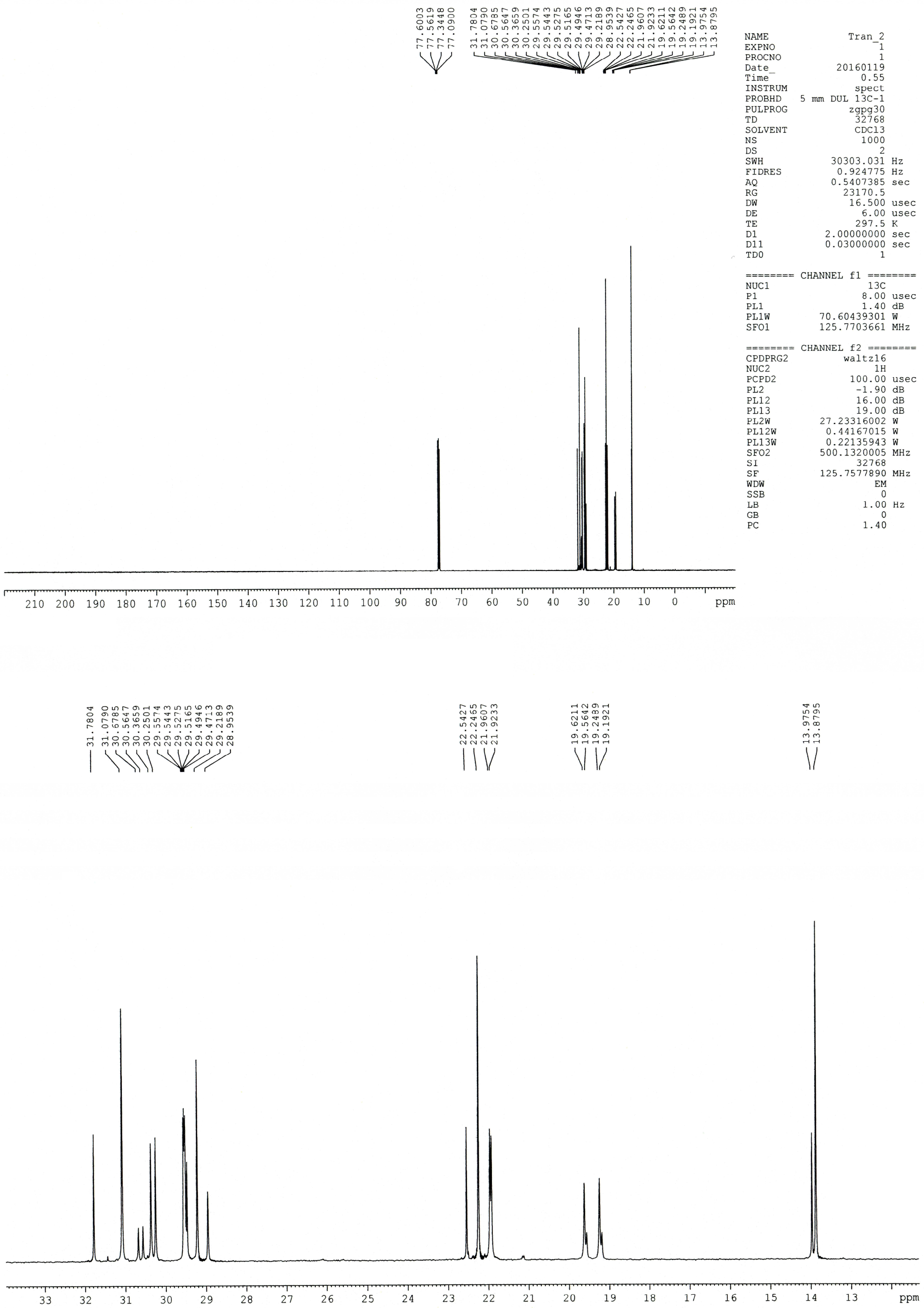
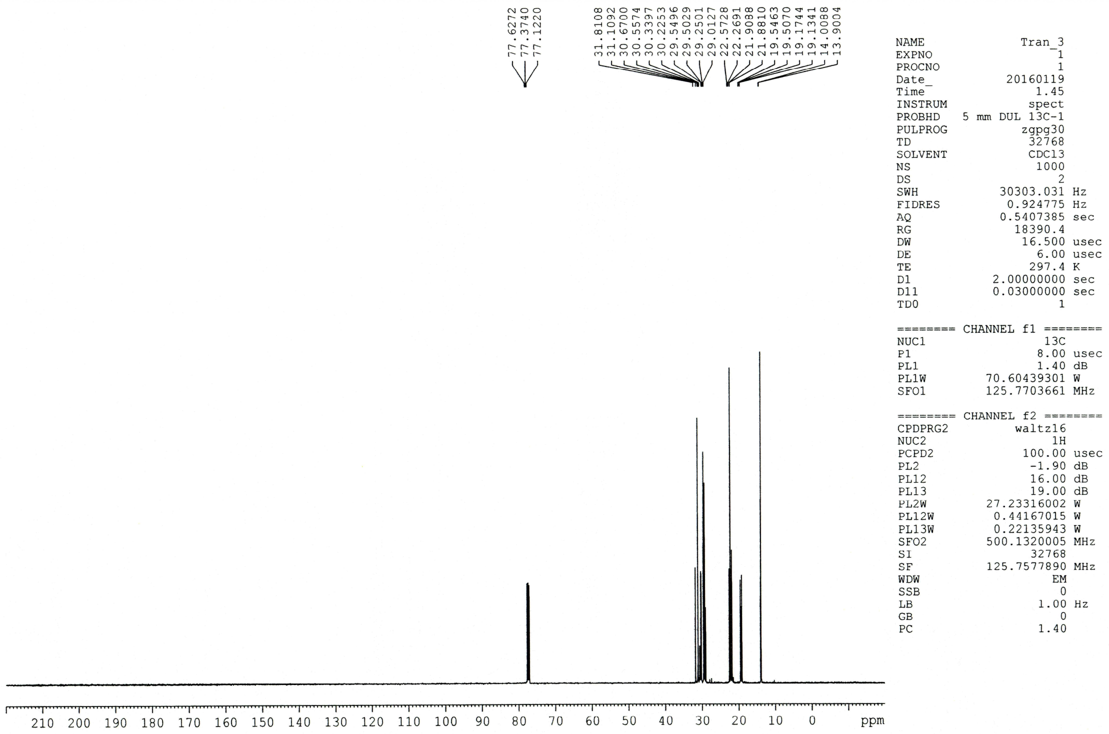


Fig. S6 ^{13}C NMR spectra of loaded $[P_{66614}]^{+}Cl^{-}$ after Pd(II) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^{+}Cl^{-}$; Aqueous phase: 55 mg L^{-1} Pd(II), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.



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SFO1        125.7703661 MHz

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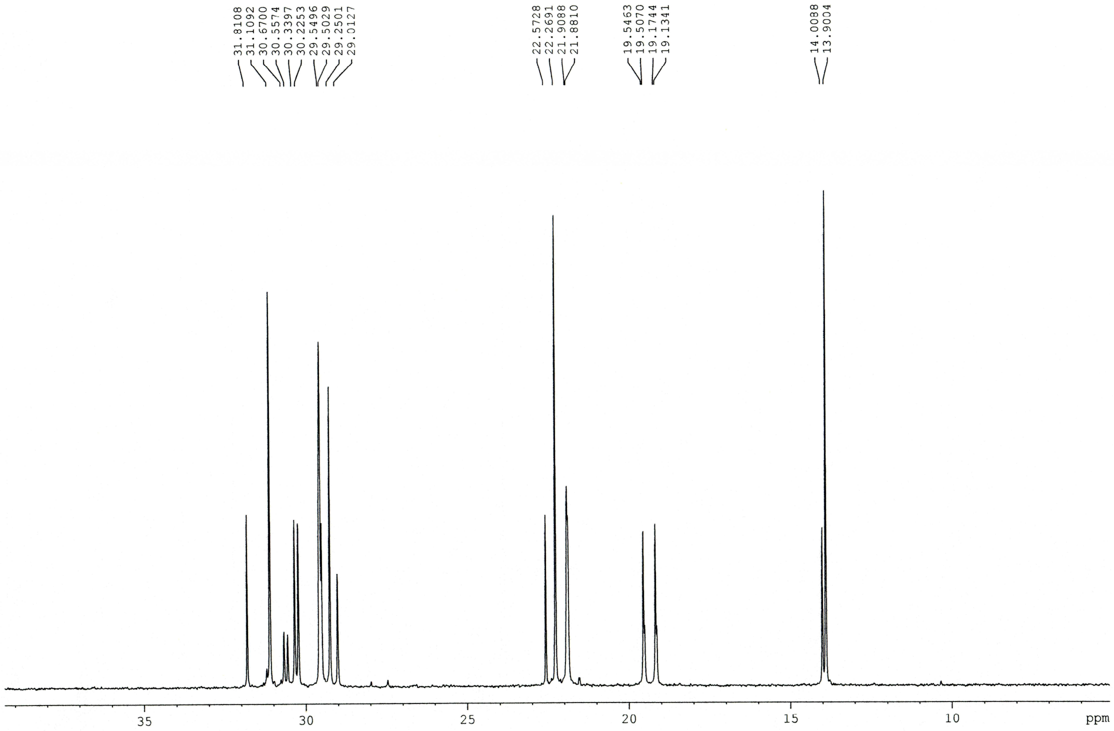
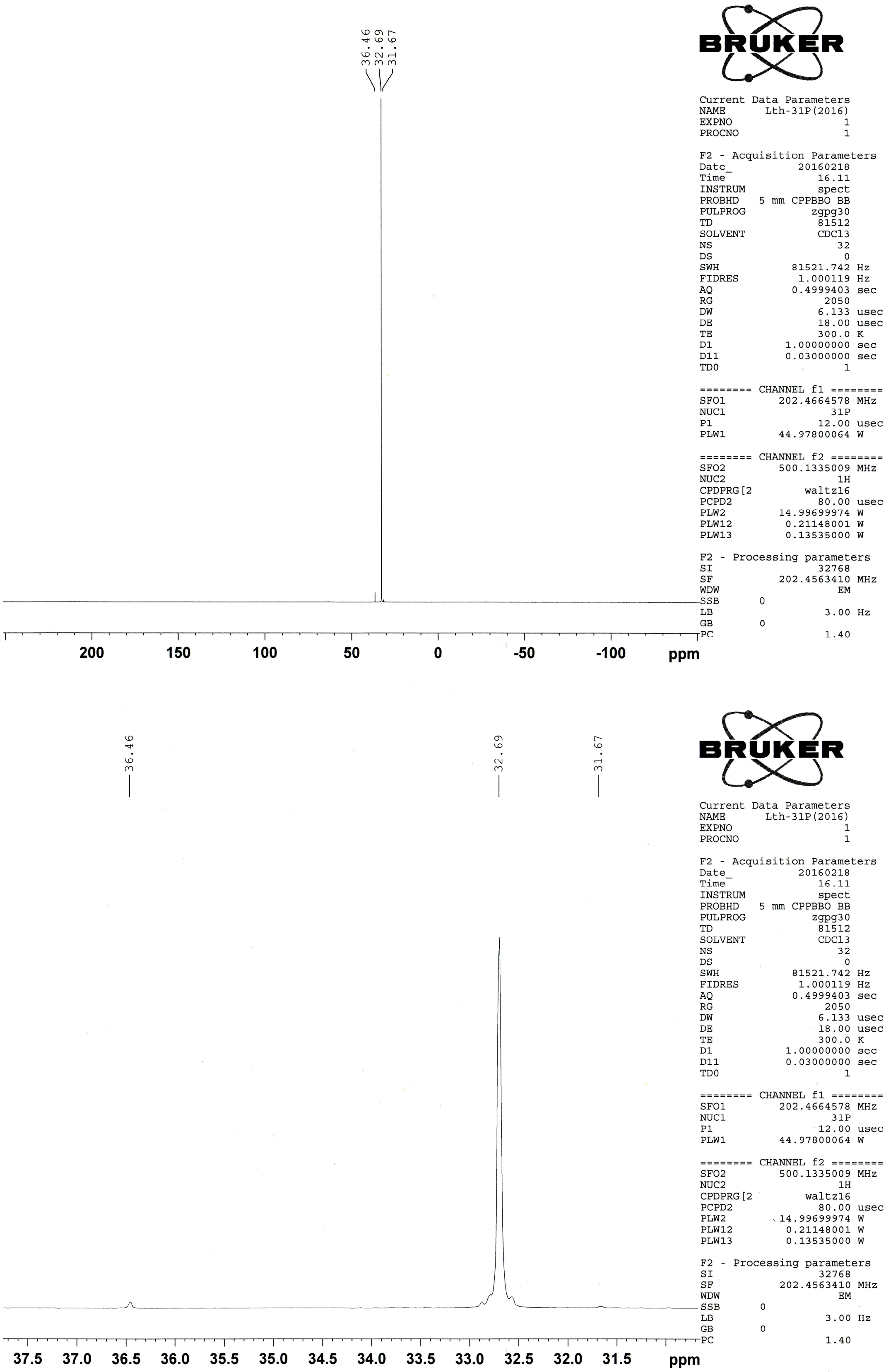


Fig. S7 ^{13}C NMR spectra of loaded $[P_{66614}]^+Cl^-$ after Pt(IV) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 100 mg L^{-1} Pt(IV), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.



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NS                   32
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NUC1                31P
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PCPD2             80.00 usec
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PLW12        0.21148001 W
PLW13        0.13535000 W

F2 - Processing parameters
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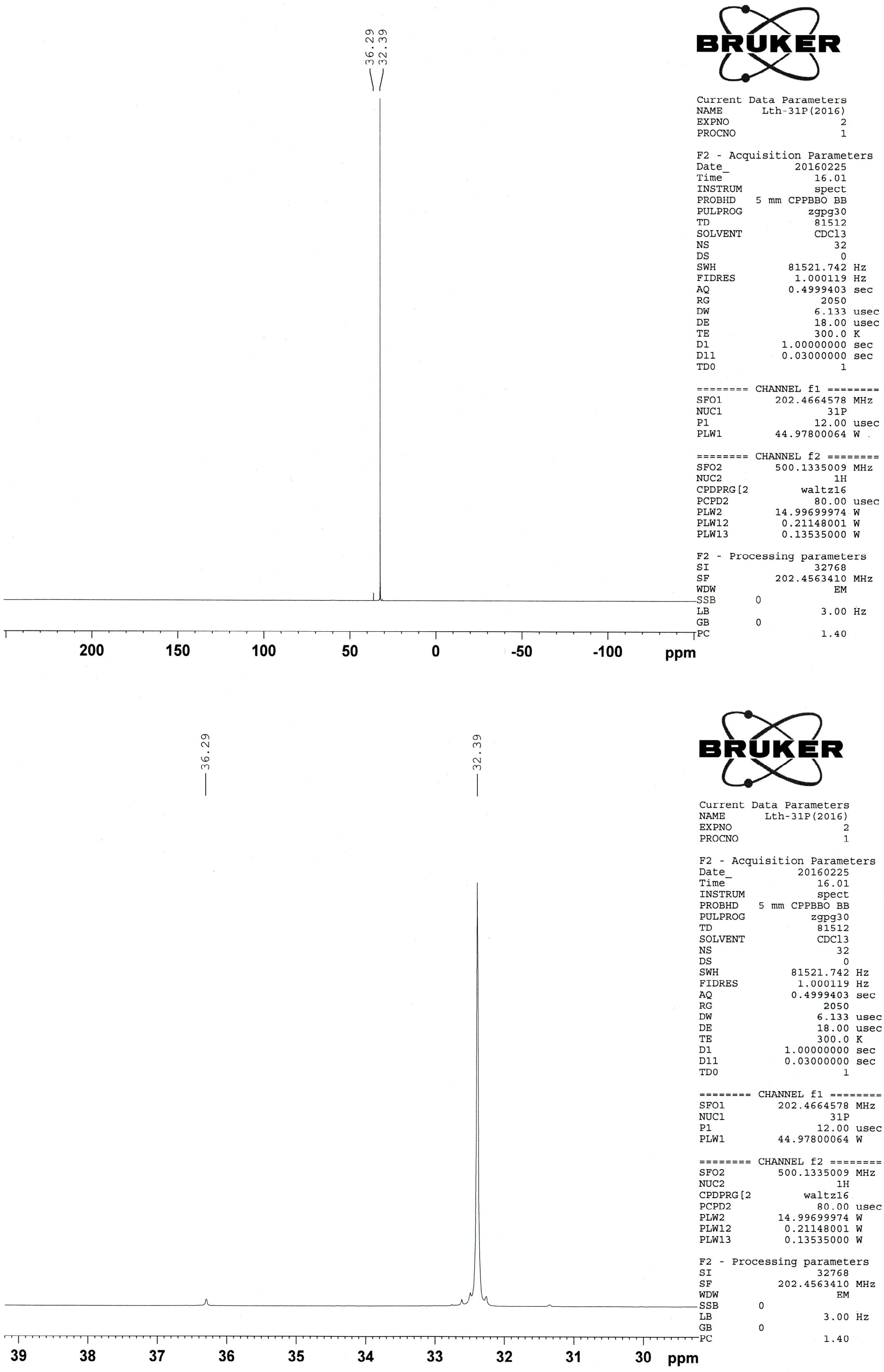
Fig. S8 ^{31}P NMR spectra of neat $[P_{66614}]^+Cl^-$ before PGMs extraction



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TE                 300.0 K
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NUC1                 31P
P1                 12.00 usec
PLW1         44.97800064 W

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NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
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PLW12         0.21148001 W
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F2 - Processing parameters
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WDW                   EM
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P1                 12.00 usec
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PLW2         14.99699974 W
PLW12         0.21148001 W
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PC                  1.40
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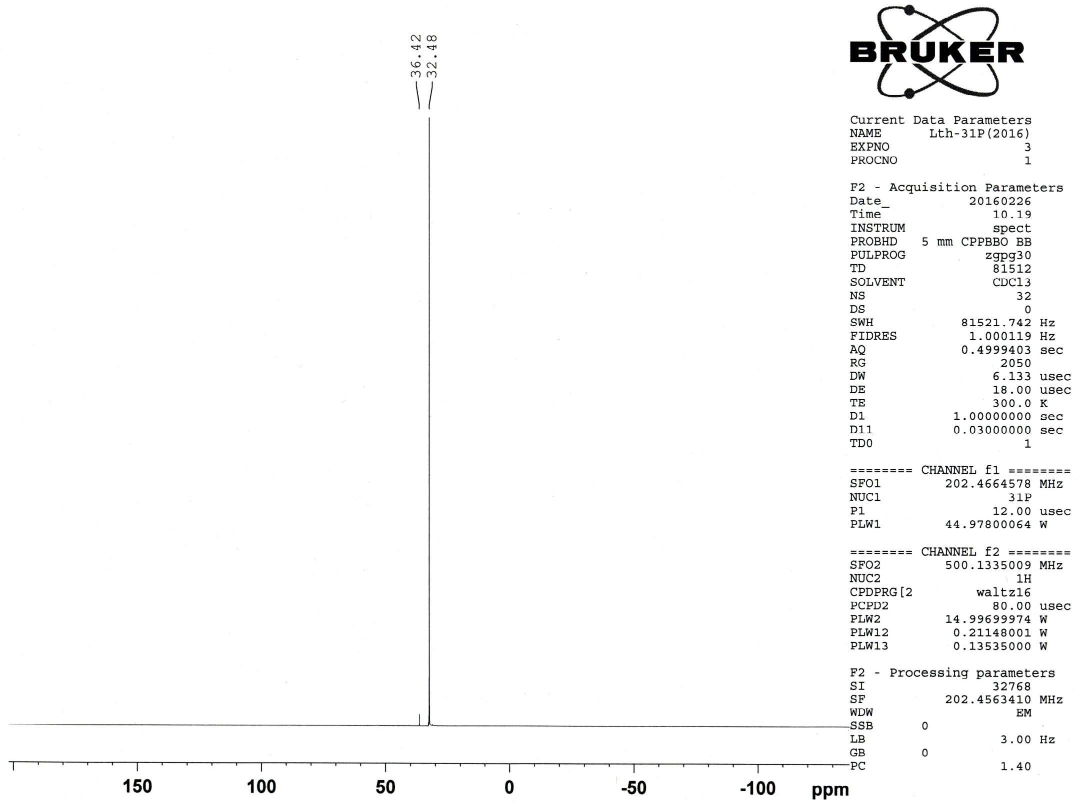
Fig. S9 ^{31}P NMR spectra of loaded $[P_{66614}]^+Cl^-$ after Pd(II) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 55 mg L^{-1} Pd(II), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.



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D11          0.03000000 sec
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NUC1                31P
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NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        14.99699974 W
PLW12        0.21148001 W
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Fig. S10 ^{31}P NMR spectra of loaded $[P_{66614}]^+Cl^-$ after Pt(IV) extraction

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 100 mg L^{-1} Pt(IV), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.

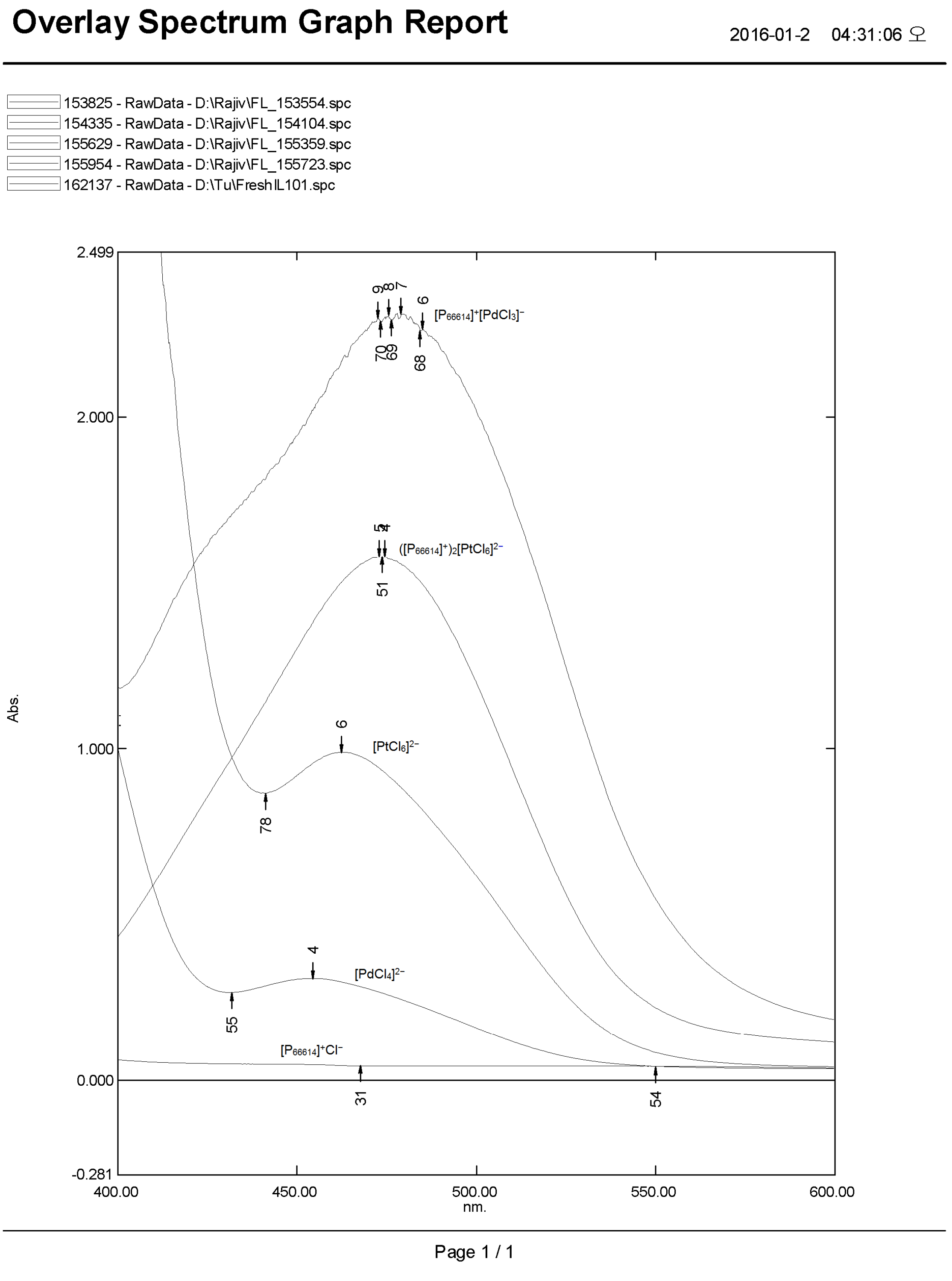

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Fig. S11 UV-vis spectra of PGMs species in aqueous and organic phase

Organic phase: 0.6 g L^{-1} (i.e., 1.16 mmol L^{-1}) $[P_{66614}]^+Cl^-$; Aqueous phase: 100 mg L^{-1} Pt(IV) or 55 mg L^{-1} Pd(II), 0.1 mol L^{-1} HCl; O/A =1; three co-current stages; t = 10 min; T = 298 K.