Electronic Supplementary Material (ESI) for ChemComm.

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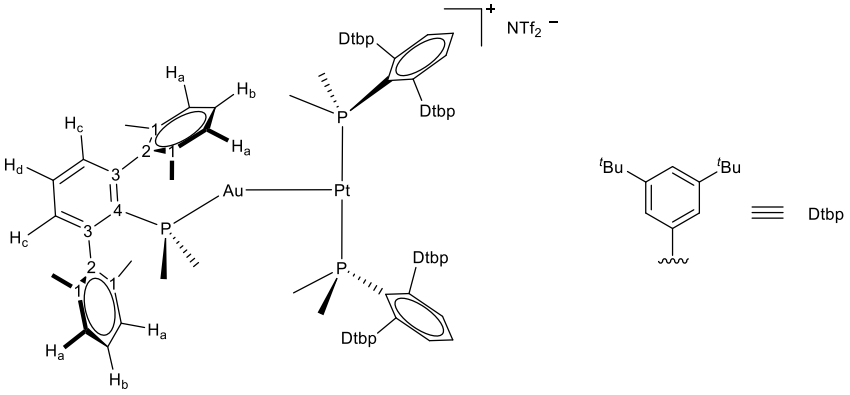
1. General considerations

All preparations and manipulations were performed by using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. Toluene (C_7H_8) and *n*-pentane (C_5H_{12}) were distilled under nitrogen over sodium, while CH_2Cl_2 was distilled under nitrogen over CaH_2. Toluene-d_8 and THF-d_8 were dried over sodium and distilled under argon and CD_2Cl_2 were dried over CaH_2 and distilled under argon. [AuCl(THT)] (THT = tetrahydrothiophene),[1] phosphine ligands PMe_2Ar^{Xyl2},[2] PMe_2Ar^{Dipp2},[3] $PCyp_2Ar^{Xyl2}$,[2] and compounds **2a-c**[4,5] and **2**[6] were prepared as previously described. All other reagents were used as received from commercial suppliers. Solution NMR spectra were recorded with Bruker AMX-300, DRX-400, and DRX-500 spectrometers. Spectra were referenced to external $SiMe_4$ (d: 0 ppm) by using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments), while ^{31}P was referenced to H_3PO_4. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. The ^{1}H and ^{13}C resonance signals were attributed by means of 2D HSQC and HMBC experiments. Infrared spectra were recorded with a Bruker Vector 22 spectrometer and sampling preparation was made in Nujol. For elemental analyses a LECO TruSpec CHN elementary analyzer was utilized.

2. Synthesis and characterization of new compounds

[(PMe$_2$Ar^{Xyl2})Au-Pt(PMe$_2$Ar^{Dtbp2})$_2$]NTf$_2$ (Compound 3a)



In a *J. Young* Schlenk, a mixture of compounds **1a** (100 mg, 0.121 mmol) and **2** (149 mg, 0.121 mmol) was stirred in dichloromethane (10 mL) at room temperature for 10 min. Addition of pentane (20 mL) caused precipitation of an orange solid which was washed with pentane affording compound **3a** (208 mg, 84 %).

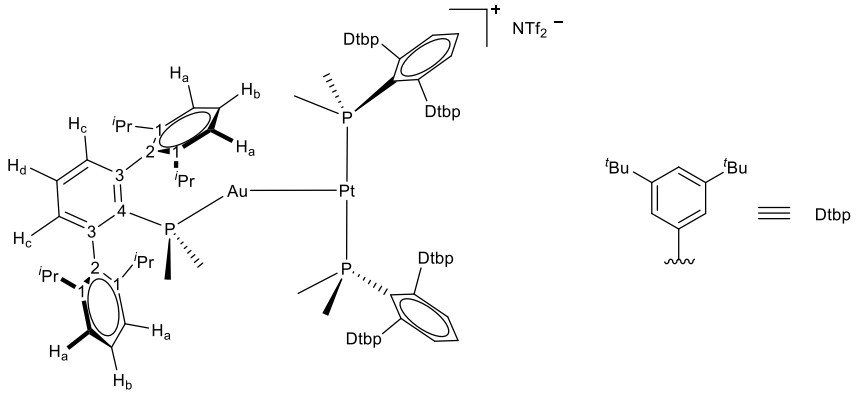
Anal. Calcd. for $C_{98}H_{129}AuF_6NO_4P_3PtS_2$: C, 57.5; H, 6.4; N, 0.7; S, 3.1. **Found**: C, 57.4; H, 6.4; N, 0.9; S, 3.5.

^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C) δ: 13.5 ($^1J_{PPt}$ = 3077 Hz, Pt-PMe$_2$Ar^{Dtbp2}), -23.2 ($^2J_{PPt}$ = 2060 Hz, Au-P).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ: 7.57 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 1.8 Hz, H$_d$), 7.49 (br, 2H, *p*-C$_6$H$_3$), 7.36 (br, 4H, *p*-Dtbp), 7.24 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H$_b$), 7.13 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-C$_6$H$_3$), 7.03 (s, 8H, *o*-Dtbp), 6.96 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 3.3 Hz, H$_c$), 6.95 (d, 4H, $^3J_{HH}$ = 7.6 Hz, H$_a$), 1.86 (s, 12H, Me$_{Xyl}$), 1.32, (s, 72H, ^{t}Bu), 1.11 (br t, 12H, P*Me*$_2$Ar^{Dtbp2}), 0.58 (d, 6H, $^2J_{HP}$ = 10 Hz, P*Me*$_2$).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C) δ: 151.3 (*m*-Dtbp), 150.7 (br t, *o*-C$_6$H$_3$), 145.3 (d, $^2J_{CP}$ = 10 Hz, C$_3$), 142.8 (*ipso*-Dtbp), 140.9 (d, $^3J_{CP}$ = 4 Hz, C$_2$), 136.5 (C$_1$), 132.6 (*m*-C$_6$H$_3$), 132.2 (CH$_d$), 131.6 (d, $^3J_{CP}$ = 8 Hz, CH$_c$), 130.1 (*p*-Dtbp), 128.8 (CH$_b$), 128.4 (d, $^1J_{CP}$ = 54 Hz, C$_4$), 128.2 (CH$_a$), 124.5 (*o*-Dtbp), 123.4 (*p*-C$_6$H$_3$), 118.8 (q, $^1J_{CF}$ = 321 Hz, CF$_3$), 35.3 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 21.9 (Me$_{Xyl}$), 21.9 (t, $^1J_{CP}$ = 28 Hz, P*Me*$_2$Ar^{Dtbp2}), 17.5 (d, $^1J_{CP}$ = 36 Hz, P*Me*$_2$).

[(PMe$_2$Ar^{Dipp2})Au-Pt(PMe$_2$Ar^{Dtbp2})$_2$]NTf$_2$ (Compound 3b)



In a *J. Young* Schlenk, a mixture of compounds **1b** (100 mg, 0.106 mmol) and **2** (131 mg, 0.106 mmol) was stirred in dichloromethane (10 mL) at room temperature for 10 min. An orange powder was obtained after addition of pentane (20 mL) producing a precipitation of compound **3b** (181 mg, 79 %).

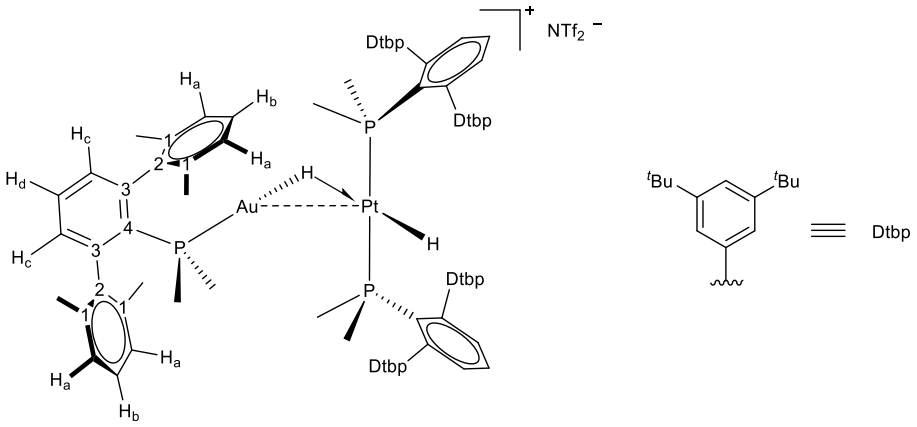
Anal. Calcd. for $C_{106}H_{147}AuF_6NO_4P_3PtS_2$: C, 58.9; H, 6.8; N, 0.7; S, 3.0. **Found**: C, 59.1; H, 6.7; N, 0.7; S, 2.8.

^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C) δ: 11.5 ($^1J_{PPt}$ = 3054 Hz, Pt-PMe$_2$Ar^{Dtbp2}), -25.4 (Au-P).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ: 7.50 (br t, 1H, $^3J_{HH}$ = 7.6 Hz, H_d), 7.47 (br, 2H, *p*-C_6H_3), 7.36 (br, 4H, *p*-Dtbp), 7.32 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H_c), 7.24 (br t, 2H, H_b), 7.16 (br, 1H, H_c), 7.11 (d, 4H, $^3J_{HH}$ = 7.6 Hz, H_a), 7.06 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3), 7.03 (s, 8H, *o*-Dtbp), 2.44 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr(CH)), 1.34 (br, 3H, P*Me*$_2$), 1.31, (br, 72H, ^{t}Bu), 1.20 (d, 6H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr(CH_3)), 1.11 (br t, 6H, P*Me*$_2$Ar^{Dtbp2}), 1.04 (d, 3H, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr(CH_3)), 0.96 (d, 6H, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr(CH_3)), 0.77 (d, 3H, $^2J_{HP}$ = 10 Hz, P*Me*$_2$).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C) δ: 151.1 (*m*-Dtbp), 150.7 (bt, *o*-C_6H_3), 146.8 (d, $^2J_{CP}$ = 10 Hz, C_3), 142.7 (*ipso*-Dtbp), 138.6 (d, $^3J_{CP}$ = 4 Hz, C_2), 133.3 (C_1), 132.8 (*m*-C_6H_3), 129.7 (CH_d), 130.0 (d, $^1J_{CP}$ = 36 Hz, C_4), 129.9 (d, $^3J_{CP}$ = 7.6 Hz, CH_c), 128.7 (*p*-Dtbp), 124.9 (*o*-Dtbp), 123.9 (CH_b), 123.7 (CH_a), 123.3 (*p*-C_6H_3), 118.8 (q, $^1J_{CF}$ = 321 Hz, CF_3), 35.2 (*C*(CH_3)$_3$), 31.8 (C(*C*H_3)$_3$), 31.7 (^{i}Pr(*C*H)), 25.5 (^{i}Pr(*C*H_3)), 24.0 (^{i}Pr(*C*H_3)), 23.1 (t, $^1J_{CP}$ = 22 Hz, P*Me*$_2$Ar^{Dtbp2}), 18.2 (d, $^1J_{CP}$ = 36 Hz, P*Me*$_2$).

[(PMe2Ar^{Xyl2})Au(μ-H)Pt(H)(PMe$_2$Ar^{Dtbp2})$_2$]NTf$_2$ (Compound 4a)



A mixture of compounds **1a** (100 mg, 0.121 mmol) and **2** (149 mg, 0.121 mmol) was dissolved in toluene (10 mL) inside the glovebox, placed in an ampoule and stirred at room temperature for 1 hour under H_2 atmosphere (1 bar). The solution remained undisturbed at room temperature overnight to yield compound **4a** as white crystals (128 mg, 52 %).

Anal. Calcd. for $C_{98}H_{131}AuF_6NO_4P_3PtS_2$: C, 57.4; H, 6.4; N, 0.7; S, 3.1. **Found**: C, 57.6; H, 6.5; N, 0.5; S, 3.0.

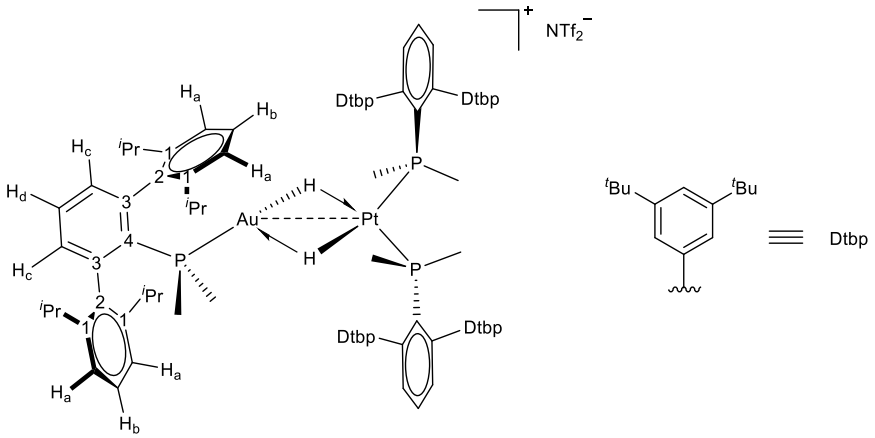
^{31}P{^{1}H} NMR (160 MHz, C_6D_8, 0 °C) δ: 13.6 ($^2J_{PPt}$ = 197 Hz, Au-P), -9.6 ($^1J_{PPt}$ = 2401 Hz, PMe$_2$Ar^{Dtbp2}).

^{1}H NMR (400 MHz, C_6D_8, 0 °C) δ: 7.95, 7.67, 7.59 (br, 8H, *o*-Dtbp), 7.37, 7.32 (br, 4H, *p*-Dtbp), 7.25 (br, 2H, H_b/*p*-C_6H_3), 7.18 (br, 4H, H_a/*m*-C_6H_3), 7.13 (br, 4H, H_a/*m*-C_6H_3), 6.92 (br t, 2H, H_b/*p*-C_6H_3), 7.02 (br, 1H, H_d), 6.61 (br, 2H, H_c), 2.21, 2.18, 2.16 (br s, 12H, Me_{Xyl}), 1.47, 1.25, 1.19 (br s, 72H, ^{t}Bu), 1.33, 1.22 (s, 12H, P*Me*$_2$Ar^{Dtbp2}), 1.12, 0.92 (d, $^2J_{HP}$ = 10 Hz, 6H, P*Me*$_2$), -1.15 (m, 1H, $^2J_{HP}$ = 100 Hz, $^1J_{HPt}$ = 585 Hz, Au(μ-H)Pt), -6.93 (m, 1H, $^1J_{HPt}$ = 1223 Hz, Pt-H).

^{13}C{^{1}H} NMR (100 MHz, C_6D_8, 0 °C) δ: 150.9 (*m*-Dtbp), 148.1 (*o*-C_6H_3), 145.7 (d, $^2J_{CP}$ = 8 Hz, C_3), 143.1 (*ipso*-Dtbp), 141.2 (C_2), 136.6 (C_1), 132.8 (CH_b/*p*-C_6H_3), 131.0 (d, $^3J_{CP}$ = 7.6 Hz, CH_c), 129.5 (CH_d), 128.6 (CH_a/*m*-C_6H_3), 128.4 (CH_a/*m*-C_6H_3, CH_b/*p*-C_6H_3), 125.6, 125.3 (*p*-Dtbp), 123.7, 122.7 (*o*-Dtbp), 35.1 (*C*$(CH_3)_3$), 31.8 (C(*C*$H_3)_3$), 29.1, 24.2 (br t, P*Me*$_2$Ar^{Dtbp2}), 22.4, 21.0 (Me_{Xyl}), 16.4 (d, $^1J_{CP}$ = 35 Hz, P*Me*$_2$).

IR (Nujol): ν(Pt/Au-H) 2064 cm^{-1}.

[(PMe$_2$Ar^{Dipp2})Au(μ-H)$_2$Pt(PMe$_2$Ar^{Dtbp2})$_2$]NTf$_2$ (Compound 5b)



A mixture of compounds **1a** (100 mg, 0.107 mmol) and **2** (131 mg, 0.107 mmol) was dissolved in toluene (10 mL) inside the glovebox, placed in a *J. Young* Schlenk and stirred at room temperature for 1 hour under H_2 atmosphere (1 bar). Addition of pentane (20 mL) caused precipitation of a white solid which was washed with pentane affording compound **5b** (162 mg, 70 %).

Anal. Calcd. for $C_{106}H_{147}AuF_6NO_4P_3PtS_2$: C, 58.9; H, 6.9; N, 0.7; S, 3.0. **Found**: C, 59.2; H, 7.1; N, 0.5; S, 2.7.

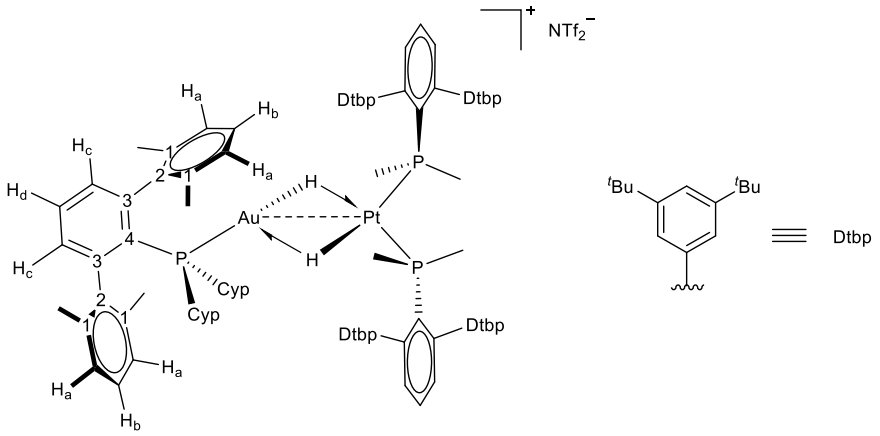
^{31}P{^{1}H} NMR (160 MHz, C_6D_8, 0 °C) δ: 23.0 (t, $^2J_{PPt}$ = 326 Hz, $^3J_{PP}$ = 28 Hz, Au-P), -4.5 (d, $^1J_{PPt}$ = 2956 Hz, $^3J_{PP}$ = 29 Hz, PMe$_2$Ar^{Dtbp2}).

^{1}H NMR (400 MHz, C_6D_8, 0 °C) δ: 7.47 (br, 2H, *p*-C_6H_3), 7.28 (br t, 2H, H_b), 7.18 (br, 2H, *p*-Dtbp/*o*-Dtbp), 7.13 (br, 4H, *m*-C_6H_3), 7.09 (br, 3H, H_d, *p*-Dtbp/*o*-Dtbp), 7.06 (br d, $^3J_{HH}$ = 7.8 Hz, 4H, H_a), 7.04 (br, 2H, H_c), 7.01 (br, 2H, *p*-Dtbp/*o*-Dtbp), 6.97 (br, 6H, *o*-Dtbp), 2.65 (m, 4H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr(CH)), 1.30, (br, 78H, ^{t}Bu, P*Me*$_2$Ar^{Dtbp2}), 1.19 (d, 18H, ^{i}Pr(CH$_3$), P*Me*$_2$), 1.01 (d, 6H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr(CH$_3$)), 0.93, 0.90 (d, 6H, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr(CH$_3$)), -4.03 (m, 2H, $^2J_{HP}$ = 57 Hz, $^1J_{HPt}$ = 581 Hz, Au(μ-H)Pt).

^{13}C{^{1}H} NMR (100 MHz, C_6D_8, 0 °C) δ: 150.6 (*m*-Dtbp), 146.7 (C_1), 144.3 (d, $^2J_{CP}$ = 11 Hz, C_3), 143.1 (*ipso*-Dtbp), 138.4 (C_2), 133.1 (d, $^3J_{CP}$ = 7.7 Hz, CH_c), 130.1 (CH_b), 132.2 (*p*-Dtbp/*o*-Dtbp), 129.2 (CH_d, *o*-Dtbp), 125.2 (*p*-Dtbp/*o*-Dtbp), 123.7 (CH_a), 122.6 (*p*-C_6H_3), 35.1 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 31.4 (^{i}Pr(*C*H)), 26.0, 25.6, 23.7 (^{i}Pr(*C*H$_3$)), 22.9 (P*Me*$_2$Ar^{Dtbp2}), 18.1 (d, $^1J_{CP}$ = 35 Hz, P*Me*$_2$).

IR (Nujol): ν(Pt/Au-H) 2144 cm^{-1}.

[(PCyp$_2$Ar^{Xyl2})Au(μ-H)$_2$Pt(PMe$_2$Ar^{Dtbp2})$_2$]NTf$_2$ (Compound 5c)



A mixture of compounds **1c** (100 mg, 0.107 mmol) and **2** (131 mg, 0.107 mmol) was dissolved in toluene (10 mL) inside the glovebox, placed in a *J. Young* Schlenk and stirred at room temperature for 1 hour under H_2 atmosphere (1 bar). The solution remained undisturbed at room temperature overnight to yield compound **5c** as white crystals (134 mg, 58 %).

Anal. Calcd. for $C_{106}H_{143}AuF_6NO_4P_3PtS_2$: C, 59.0; H, 6.7; N, 0.7; S, 3.0. **Found**: C, 59.3; H, 6.9; N, 0.5; S, 2.7.

^{31}P{^{1}H} NMR (160 MHz, THF-d_8, 0 °C) δ: 60.7 (t, $^2J_{PPt}$ = 638 Hz, $^3J_{PP}$ = 26 Hz, Au-P), -2.5 (d, $^1J_{PPt}$ = 3001 Hz, $^3J_{PP}$ = 26 Hz, PMe$_2$Ar^{Dtbp2}).

^{1}H NMR (400 MHz, THF-d_8, 0 °C) δ: 7.68 (br t, 1H, $^3J_{HH}$ = 7.6 Hz, H_d), 7.59 (br, 2H, *o*-Dtbp), 7.37 (br, 4H, *m*-C_6H_3), 7.26 (br, 6H *o*-Dtbp), 7.24 (br, 4H, H_a), 7.16 (br, 2H, H_c), 7.06 (br, *p*-C_6H_3), 7.00, 6.97 (br, 4H, *p*-Dtbp), 6.89 (br, 2H, H_b), 2.41, 2.14 (br s, 2H, PCH), 2.05 (br s, 12H, Me$_{Xyl}$), 2.00 (br, 6H, P*Me*$_2$Ar^{Dtbp2}), 1.82-0.89 (m, 16H, CH_2), 1.46, 1.37, 1.24, 1.20 (br s, 72H, ^{t}Bu), 0.03 (br, 6H, P*Me*$_2$Ar^{Dtbp2}), -4.28 (m, 2H, $^2J_{HP}$ = 51 Hz, $^1J_{HPt}$ = 564 Hz, Au(μ-H)Pt).

^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 0 °C) δ: 152.4, 151.4, 151.0, 150.0 (*m*-Dtbp), 148.8 (C_3), 147.4 (*ipso*-Dtbp), 144.5 (C_1), 143.4 (C_2), 129.9 (*m*-C_6H_3), 128.3 (*p*-C_6H_3), 133.2 (CH_b, CH_c), 132.7 (CH_d), 131.6 (CH_a), 126.2 (*p*-C_6H_3), 124.6 (*m*-C_6H_3), 124.6 (*p*-Dtbp), 123.9, 122.7 (*o*-Dtbp), 119.5 (q, $^1J_{CF}$ = 321 Hz, CF_3), 40.7, 39.2 ($^1J_{CP}$ = 32 Hz, PCH), 36.5, 33.2 (CH_2), 35.7, 35.6, 35.5 ($C(CH_3)_3$), 32.2, 31.9, 31.8 ($C(CH_3)_3$), 31.5, 26.7 (CH_2), 23.1 (t, $^1J_{CP}$ = 14 Hz, P*Me*$_2$Ar^{Dtbp2}), 22.0 (Me$_{Xyl}$), 20.1 (t, $^1J_{CP}$ = 18 Hz, P*Me*$_2$Ar^{Dtbp2}).

IR (Nujol): ν(Pt/Au-H) 2141 cm^{-1}.

3. NMR spectra of compounds

Figure S1. $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 25 ºC) for compound **3a**

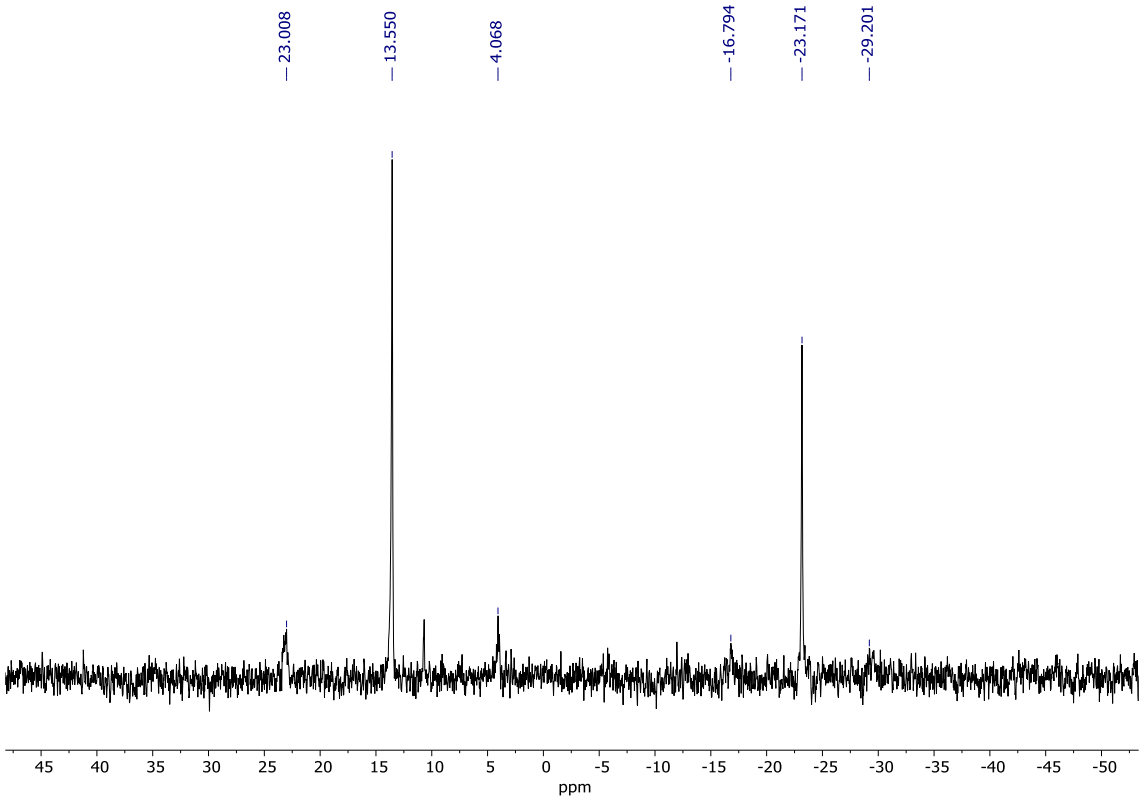


Figure S2. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) for compound **3a**

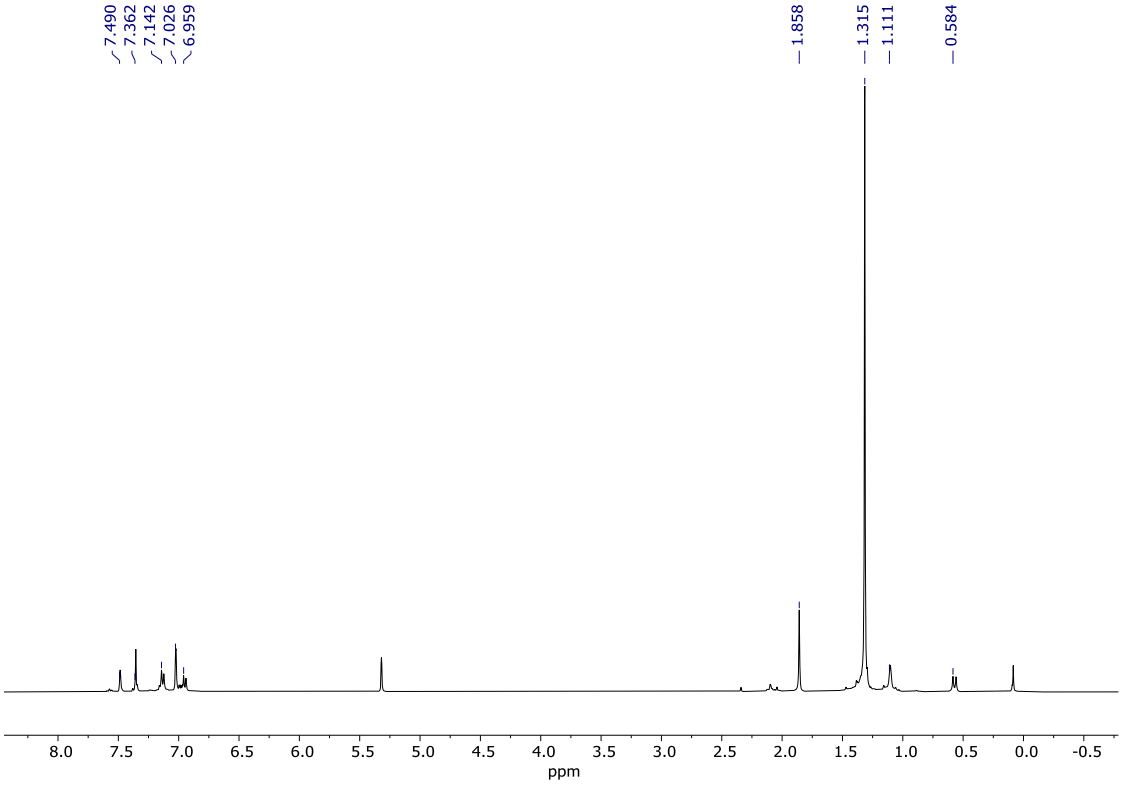


Figure S3. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 25 ºC) for compound **3a**

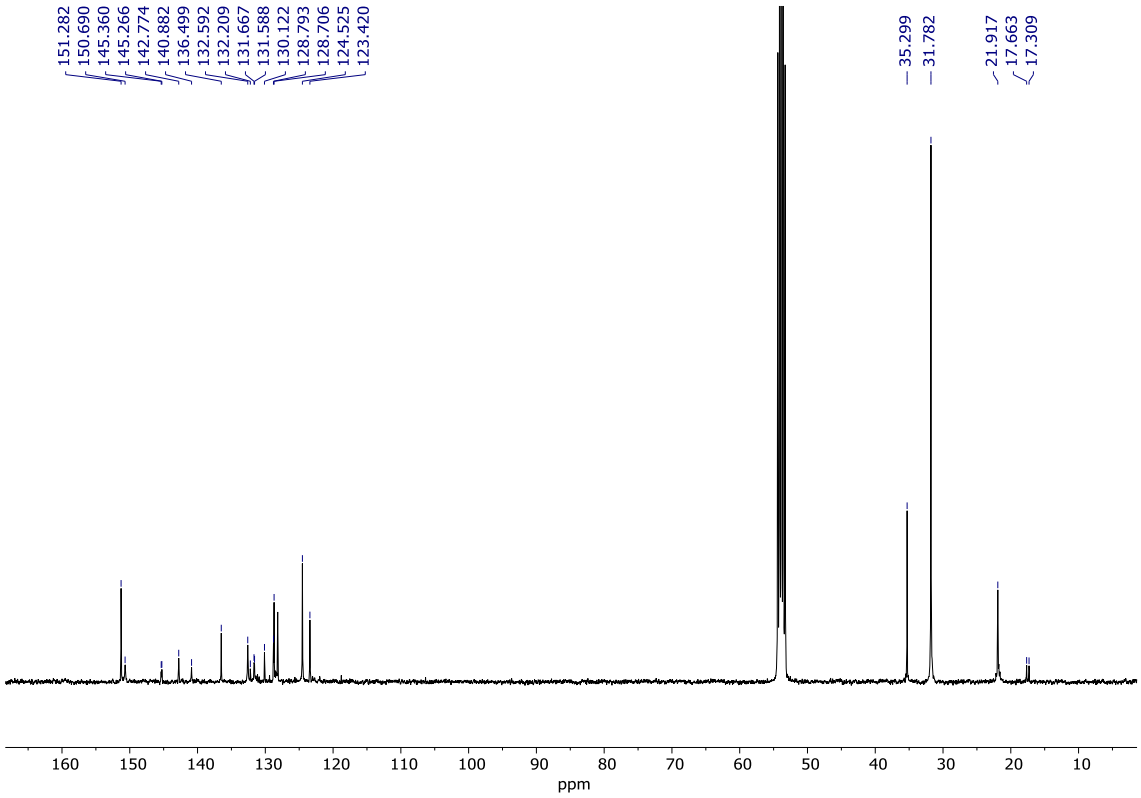


Figure S4. $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 25 ºC) for compound **3b**

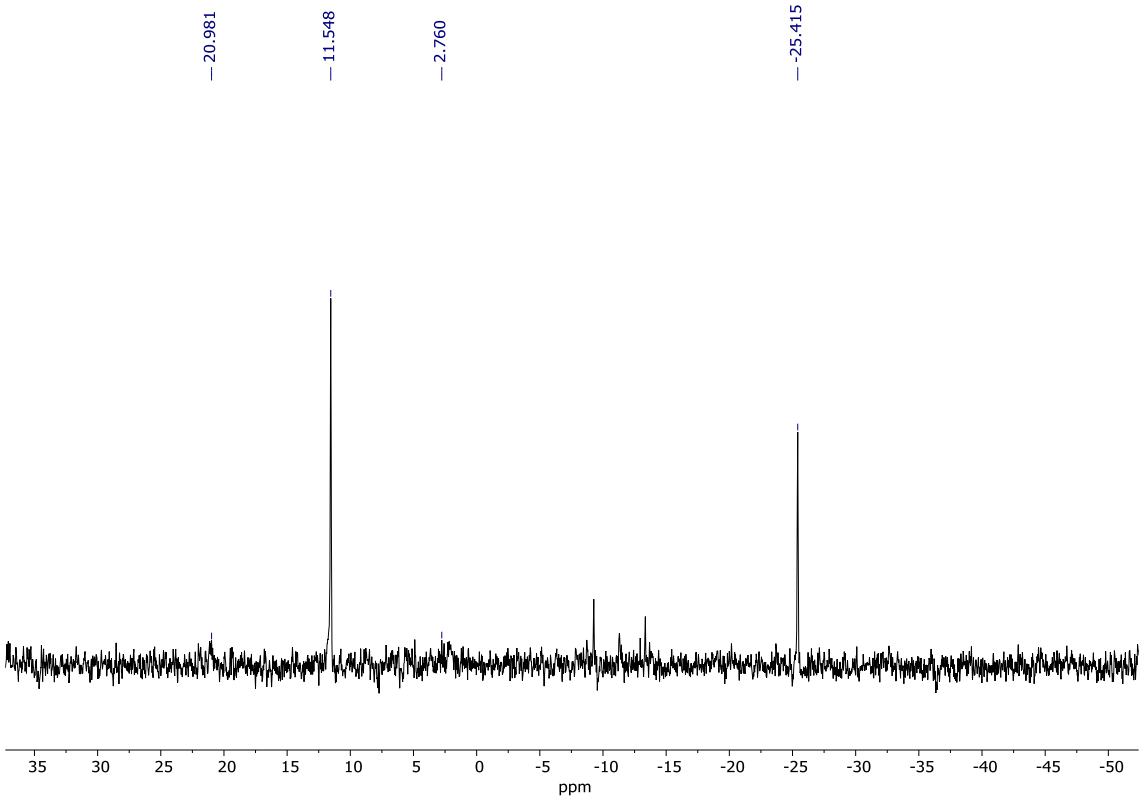


Figure S5. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) for compound **3b**

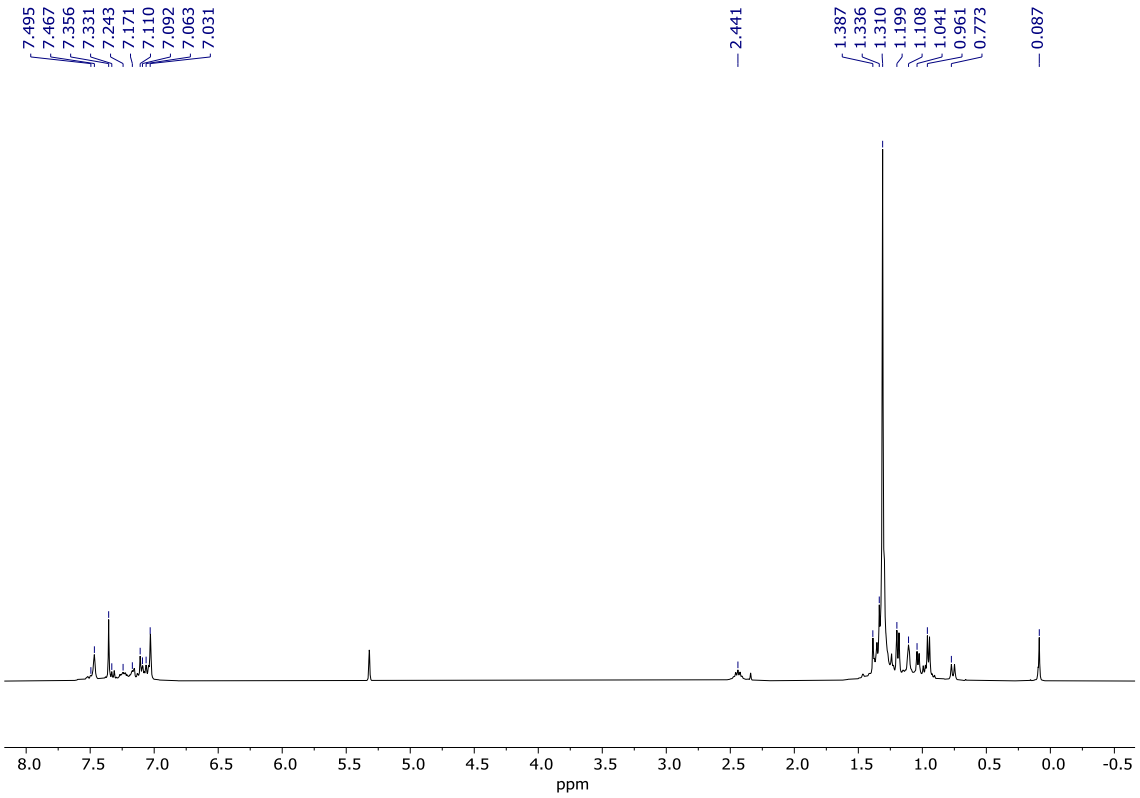


Figure S6. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 25 ºC) for compound **3b**

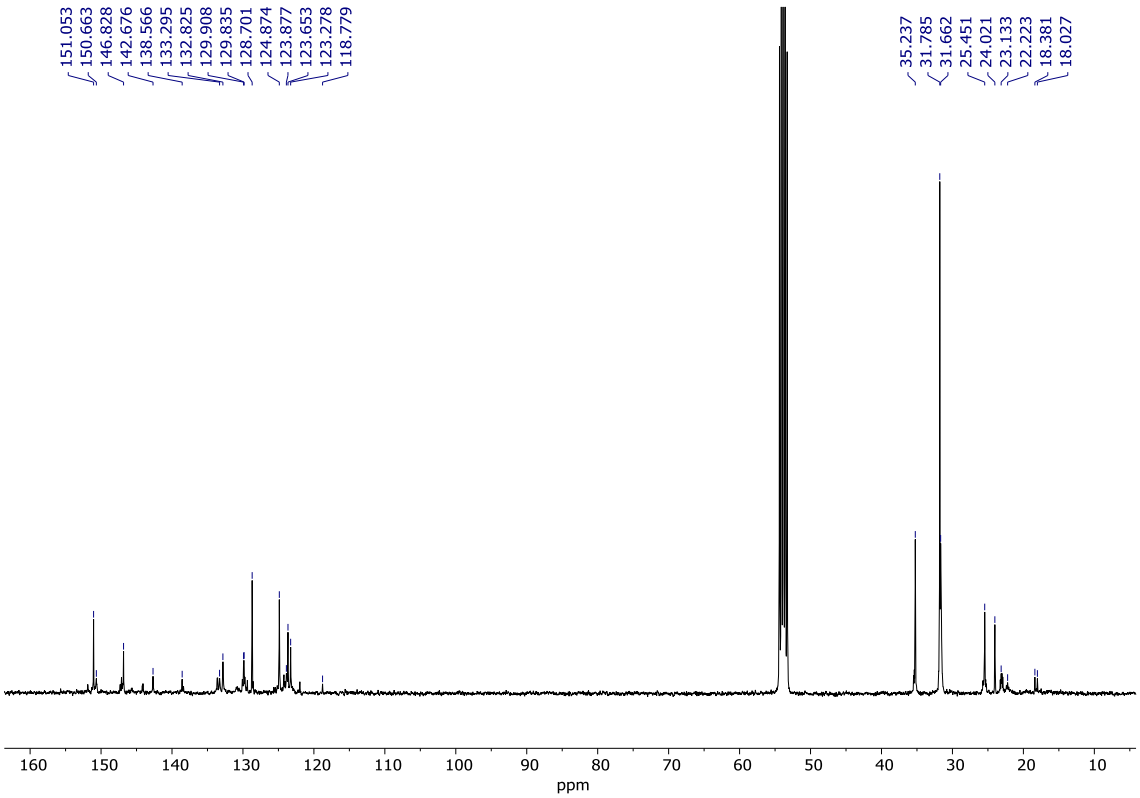


Figure S7. $^{31}P\{^{1}H\}$ NMR (160 MHz, tol-d_8, 0 ºC) for compound **4a**

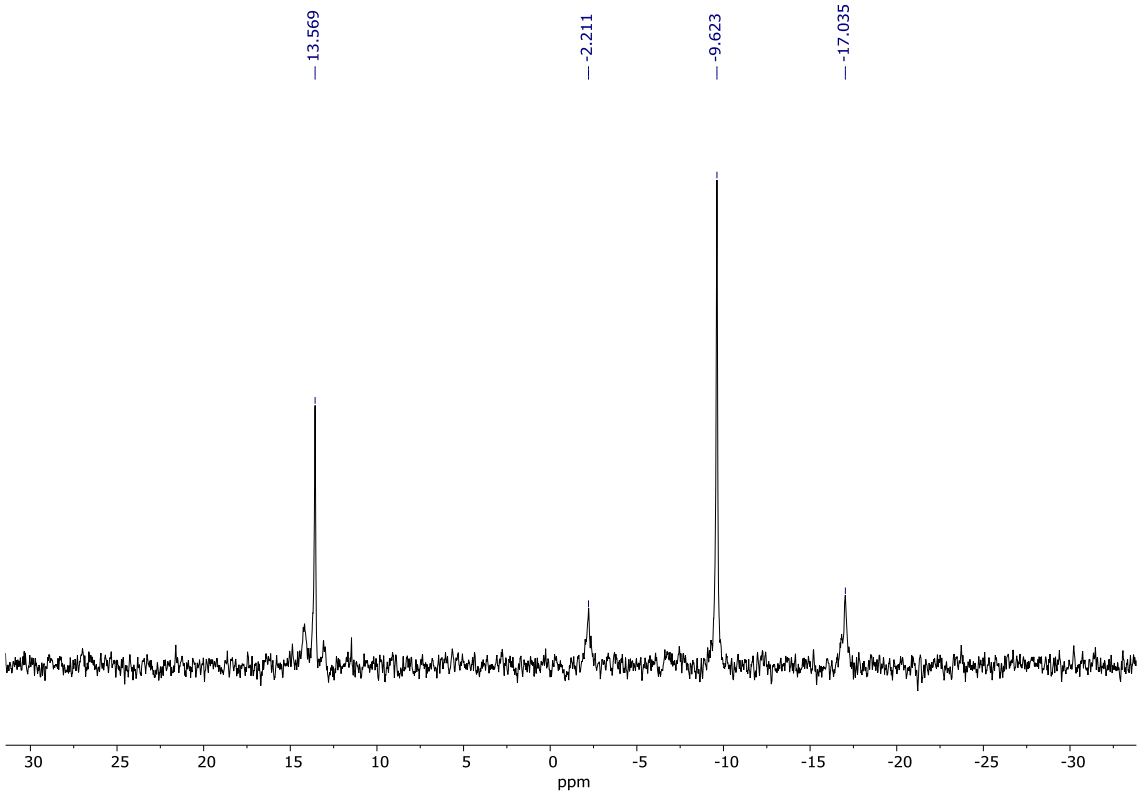
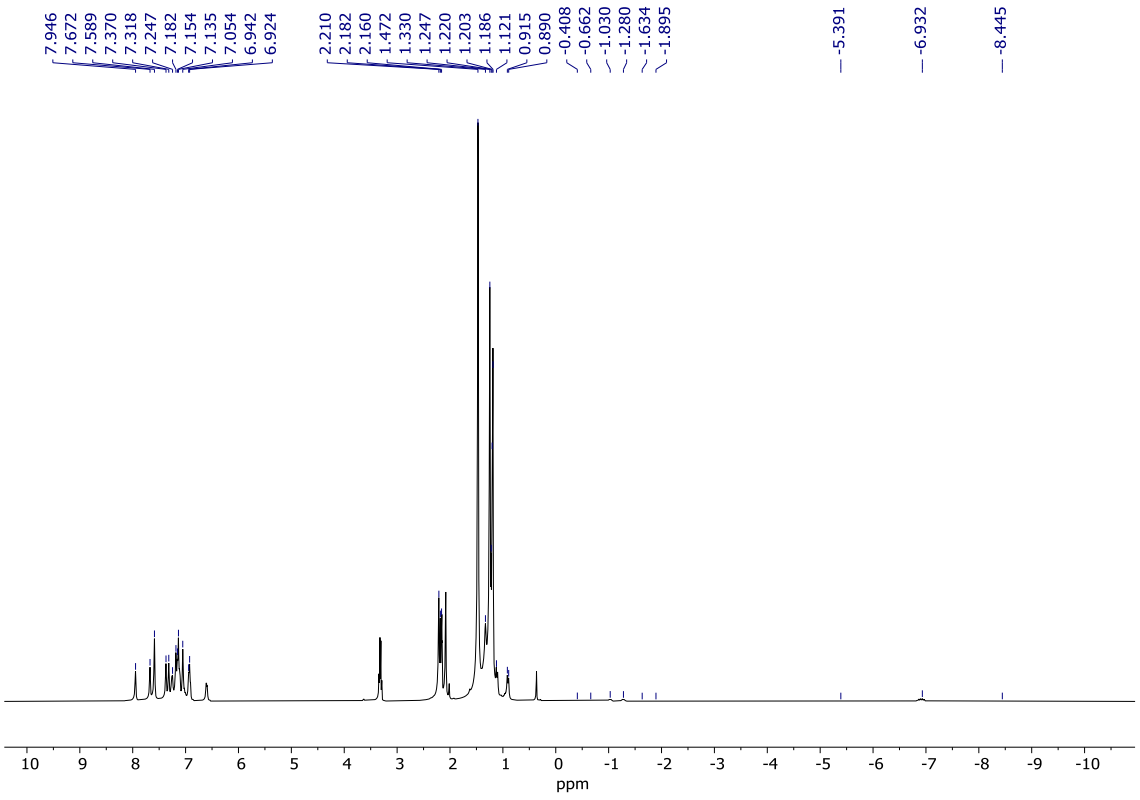


Figure S8. ^{1}H NMR (400 MHz, tol-d_8, 0 ºC) for compound **4a**



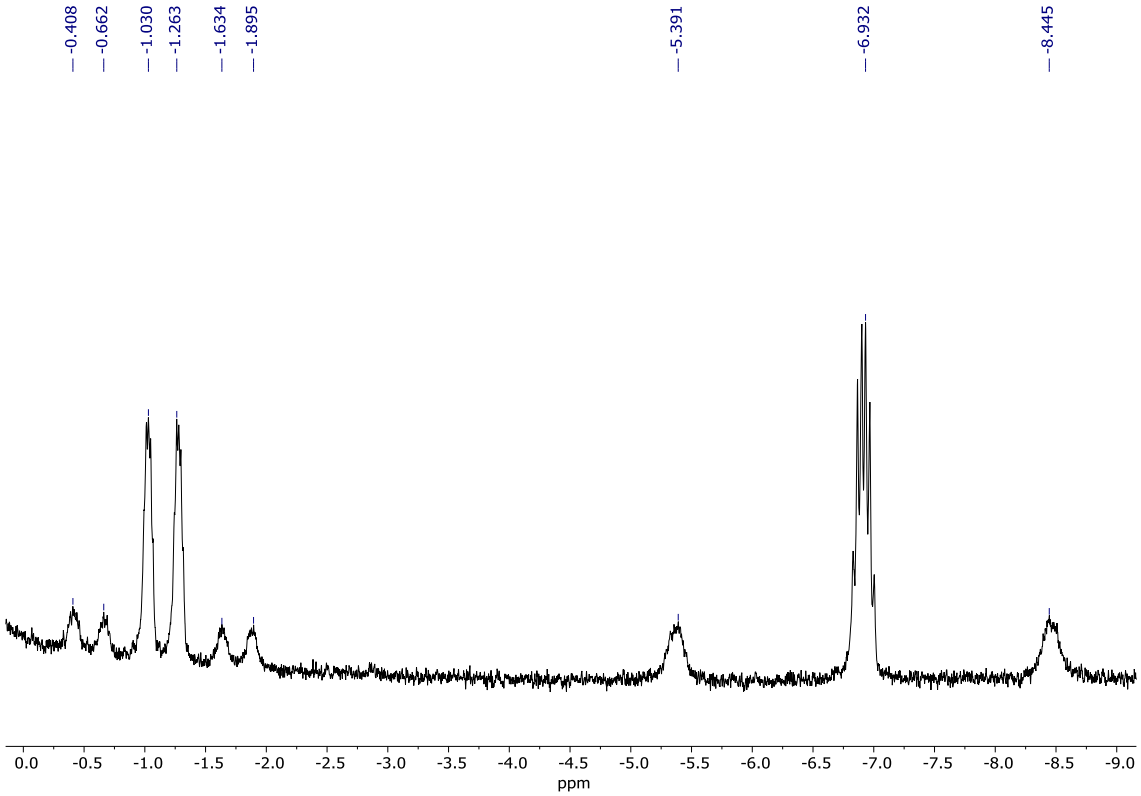


Figure S9. $^{13}C\{^{1}H\}$ NMR (100 MHz, tol-d_8, 0 ºC) for compound **4a**

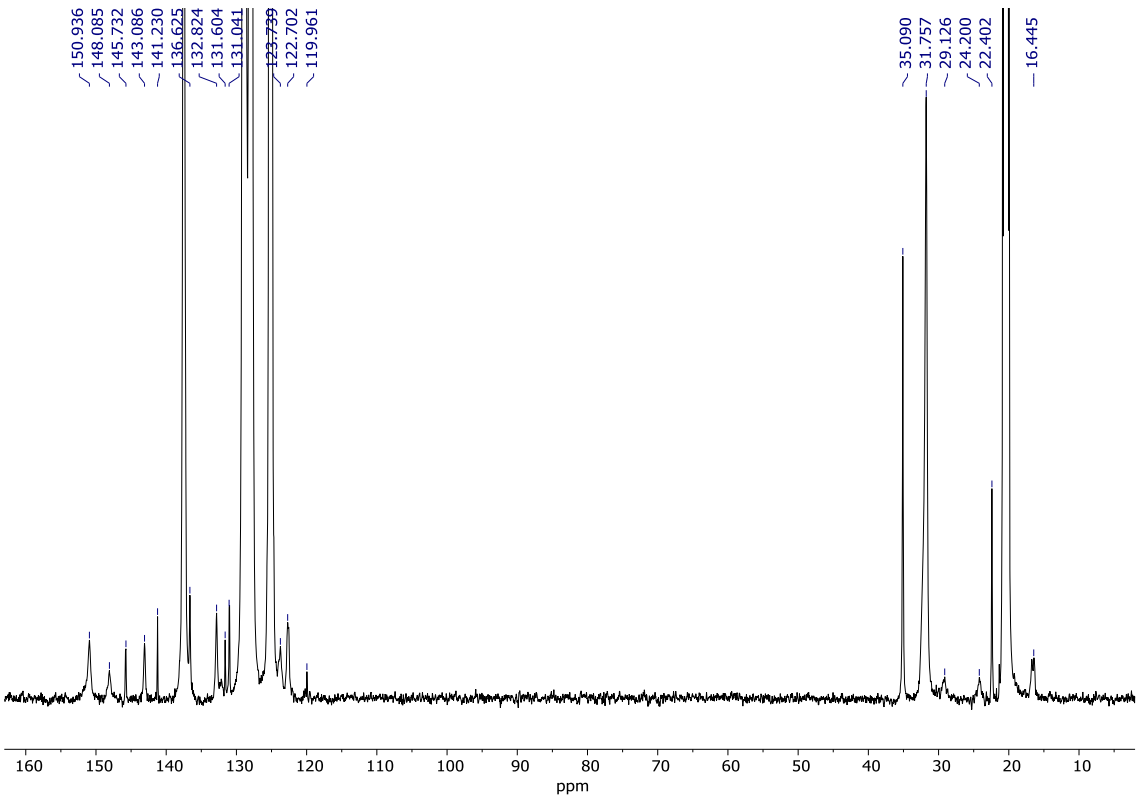


Figure S10. $^{31}P\{^{1}H\}$ NMR (160 MHz, tol-d_8, 0 ºC) for compound **5b**

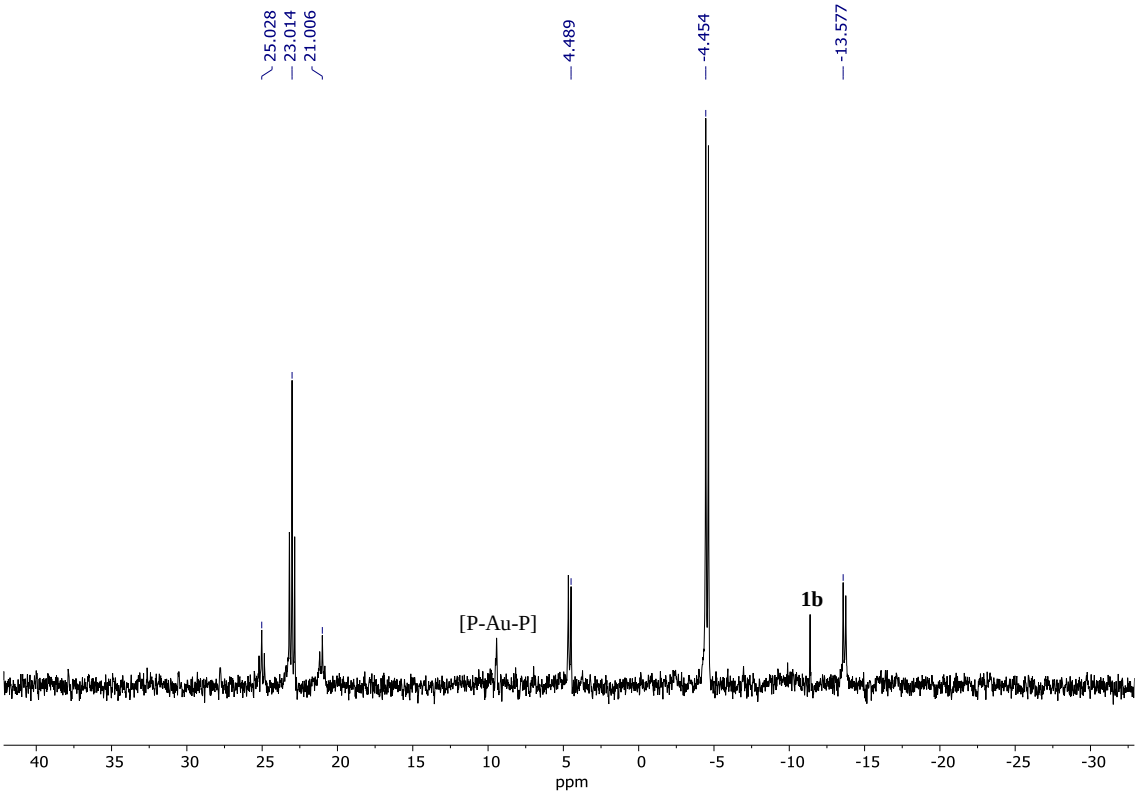
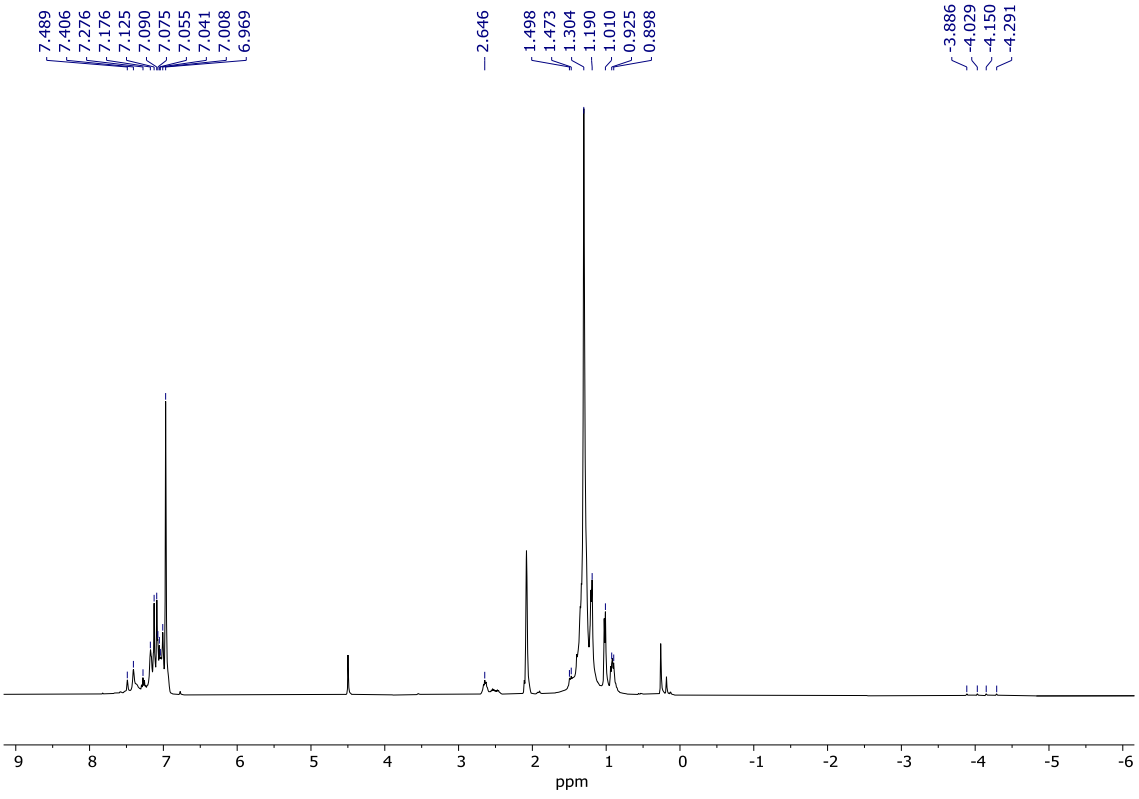


Figure S11. ^{1}H NMR (400 MHz, tol-d_8, 0 ºC) for compound **5b**



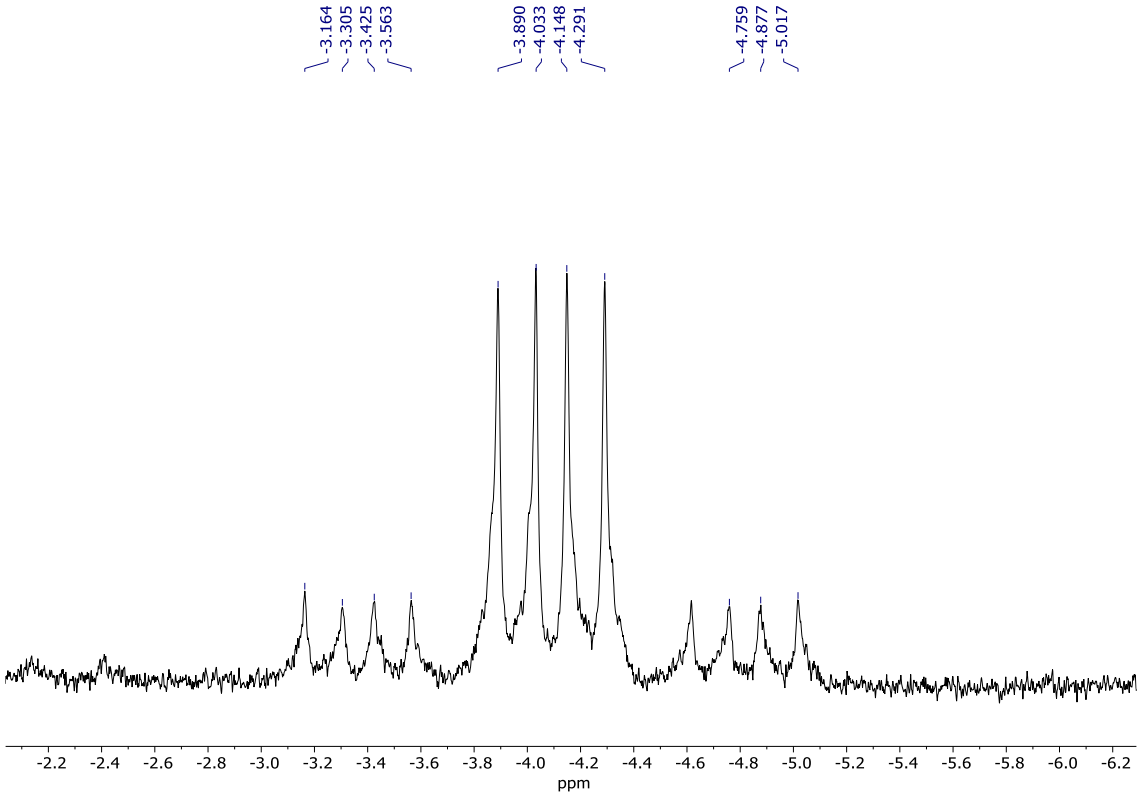


Figure S12. ^{13}C {^{1}H} NMR (100 MHz, tol-d_8, 0 ºC) for compound **5b**

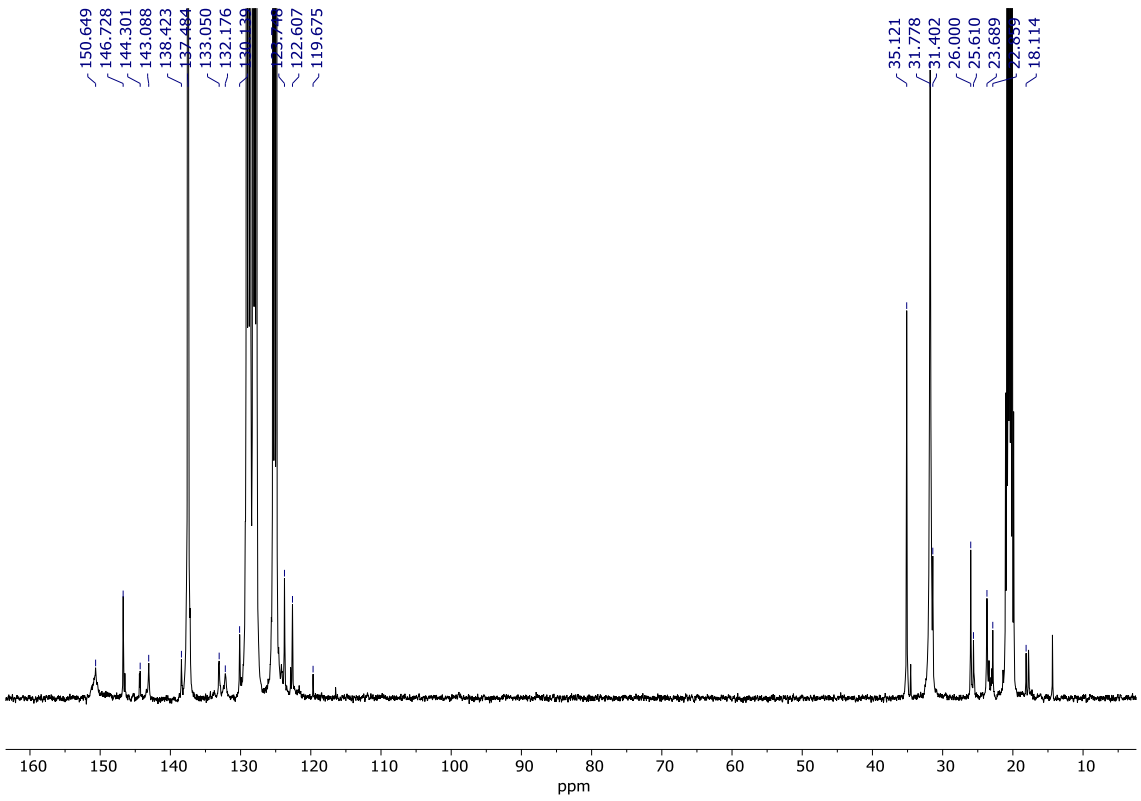


Figure S13. $^{31}P\{^{1}H\}$ NMR (160 MHz, THF-d_8, 0 ºC) for compound **5c**

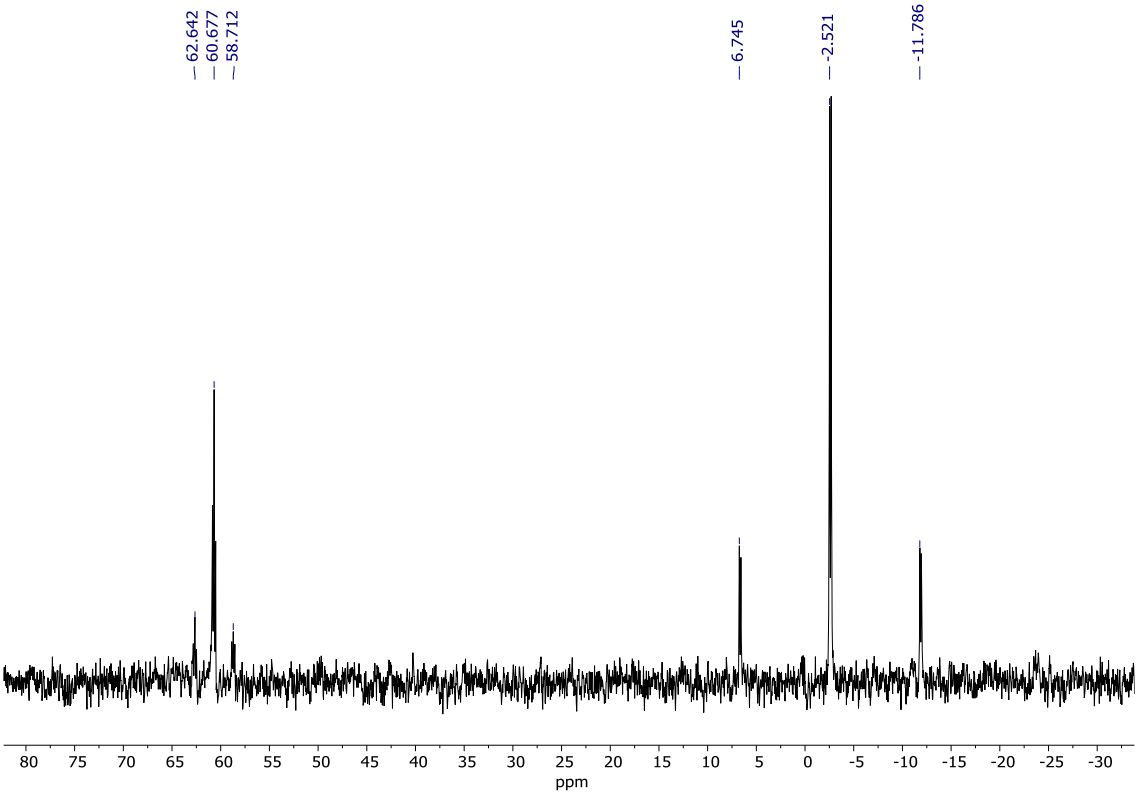
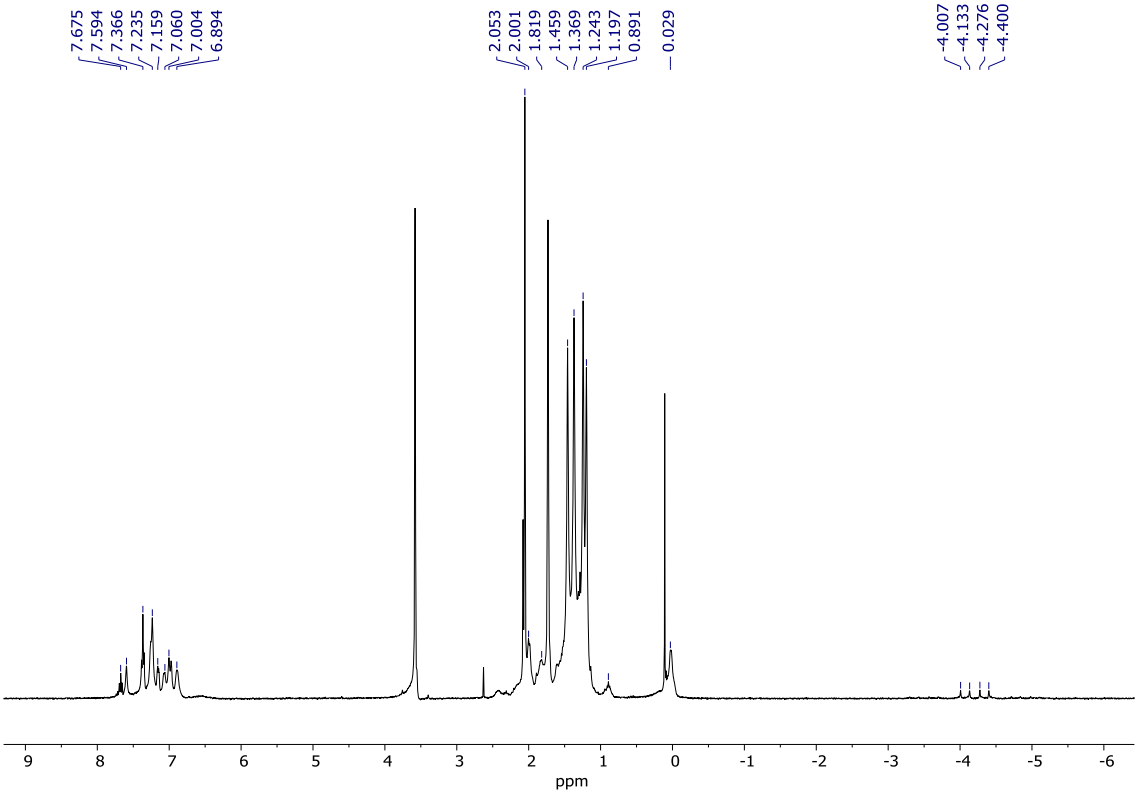


Figure S14. ^{1}H NMR (400 MHz, THF-d_8, 0 ºC) for compound **5c**



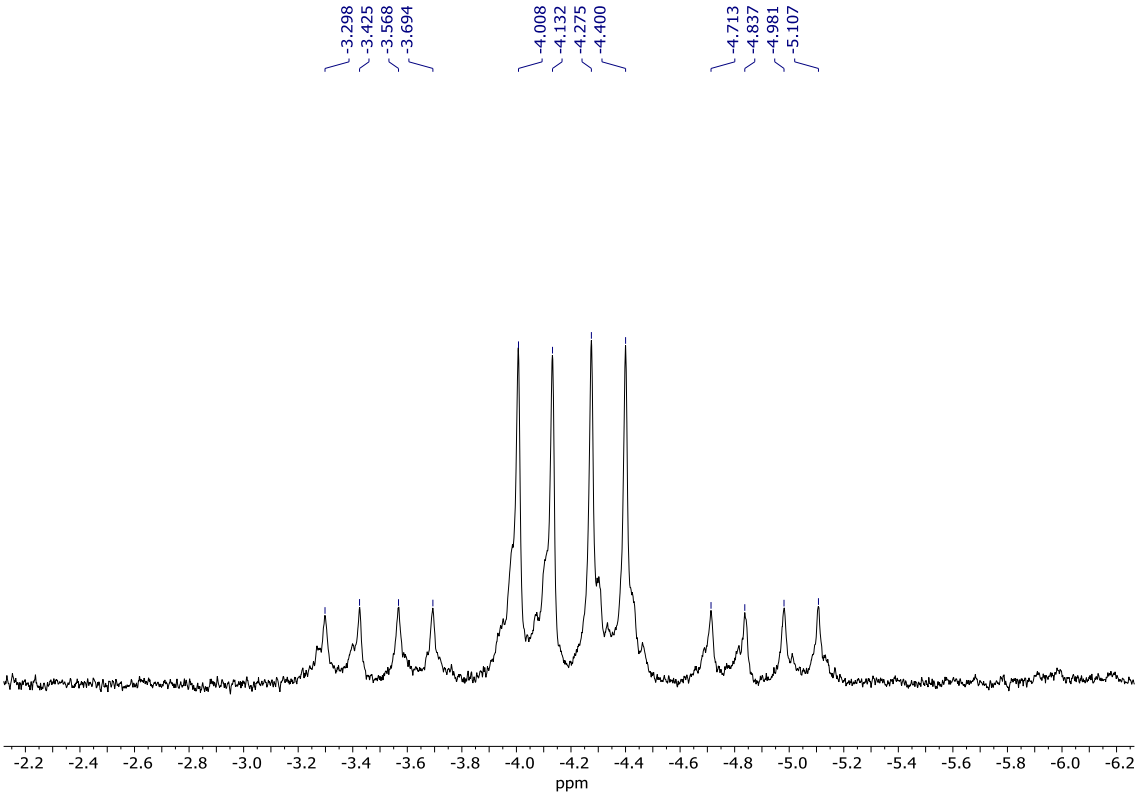


Figure S15. Simulated hydridic region of the ^{1}H NMR spectrum of compound **5c** using *gnmr* software.[7]

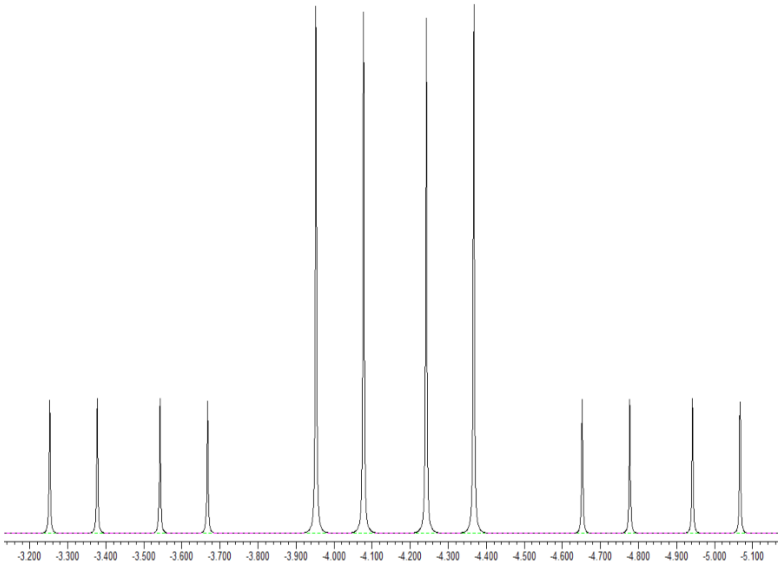


Figure S15. $^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8, 0 ºC) for compound **5c**

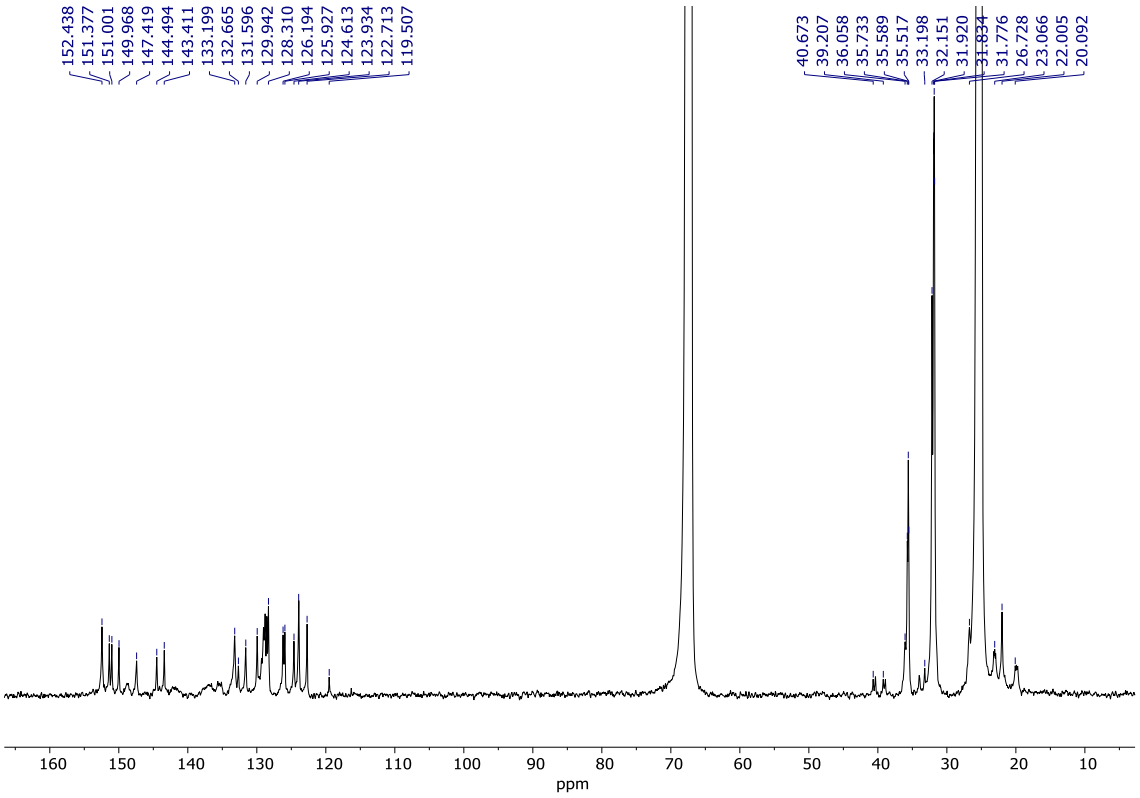
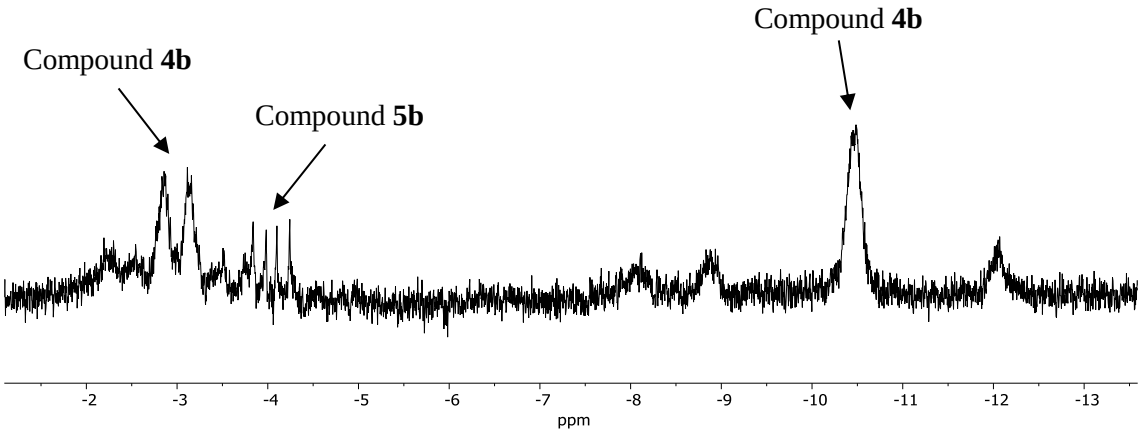


Figure S16. ^{1}H NMR (400 MHz, THF-d_8, 0 ºC) in the hydride region for the isomerization process of **5b** to **4b** promoted by THF as solvent.



4. Variable temperature experiments

4.1. Activation parameters for the process involving THF in compound 4a

The activation parameters of this process were estimated by using an iterative method where three different regions are considered:

- Slow exchange $T < T_c$ where $k << \delta\nu$ with formula: $\mathbf{k = \pi(w\text{-}w_0)}$
- At coalescence $T = T_c$ where $k \approx \delta\nu$ with formula: $\mathbf{k = \pi(\delta\nu)(2)^{-1/2}}$
- Fast exchange $T > T_c$ where $k >> \delta\nu$ with formula: $\mathbf{k = \pi(\delta\nu)2\ (w\text{-}w_f)^{-1}(2)^{-1/2}}$

with $\delta\nu$ (chemical shift difference at low temperature), w (width of peak), w_0 (width of peak at low temperature) and w_f (width of the peak at high temperature).

These constants were measured in the temperature range 353-333 K, and then, it was plotted *k*/T vs 1/T to obtain the activation parameters through the Eyring equation (Equation 1).

$$ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\#}}{R}\ \frac{1}{T} + \left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R} \qquad Eq.1$$

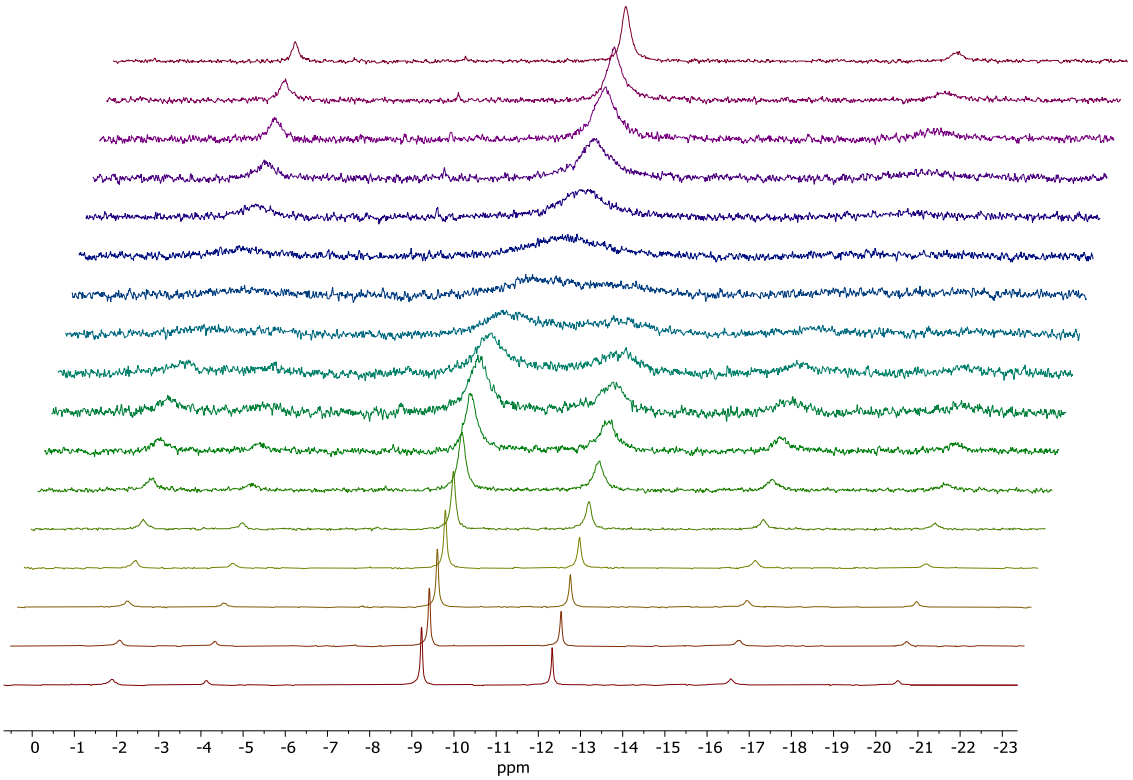


Figure S17. Variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of compound **4a** in THF-d_8 (from 253 K, bottom, to 333 K, top, with 5 K increments).

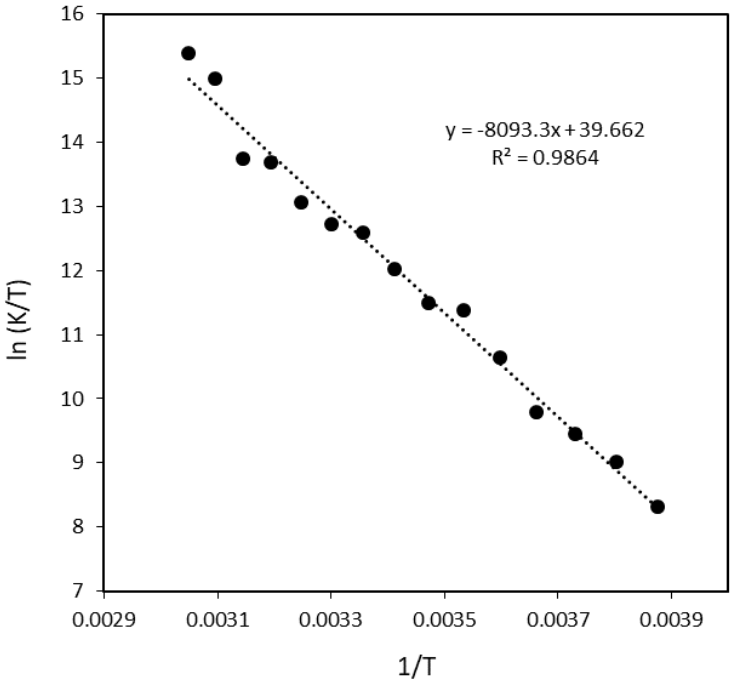
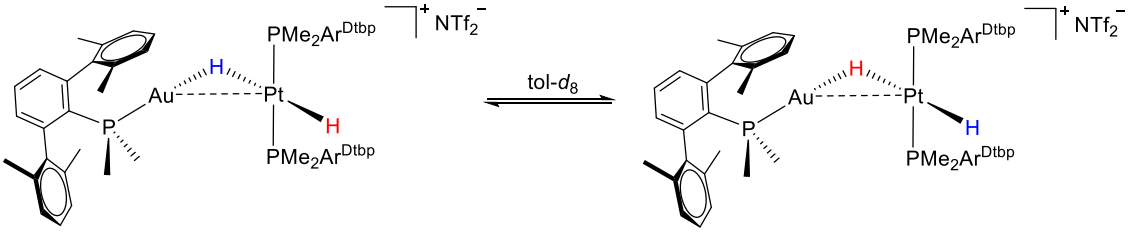


Figure S18. Eyring plot for the exchange process over the temperature range 253-333 K.

4.1. Activation parameters for the process involving hydride exchange in compound 4a

EXSY experiments were carried out to determine the activation parameters for the process involving hydride exchange in compound **4a** (Scheme S1).



Scheme S1. Hydride exchange process in compound **4a**.

Essays were recorded in toluene-d_8 at constant temperature. For each experiment, two ^{1}H 2D NOESY spectra were acquired sequentially, one with the desired mixing time (τ_m = 800 ms) and a second reference spectrum at τ_m = 5 ms. The rate constant *k* for each process was calculated from the integral value of hydrogens that are well-resolved in each of the two exchanging sites using the EXSYCalc program (Mestrelab Research).[8] These constants were measured in the temperature range 303-328 K, and then, it was plotted *k*/T vs 1/T to obtain the activation parameters through the Eyring equation.

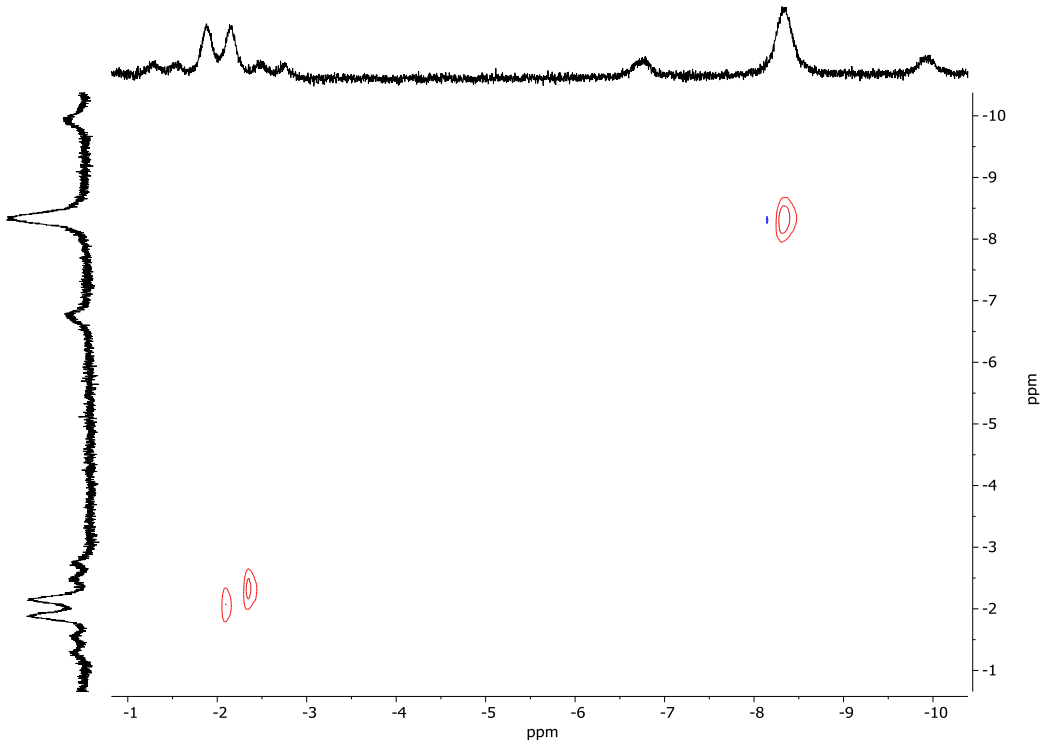


Figure S19. Representative example of NOESY spectrum for the exchange process at 328 K and τ_m = 5 ms (400 MHz, toluene-d_8).

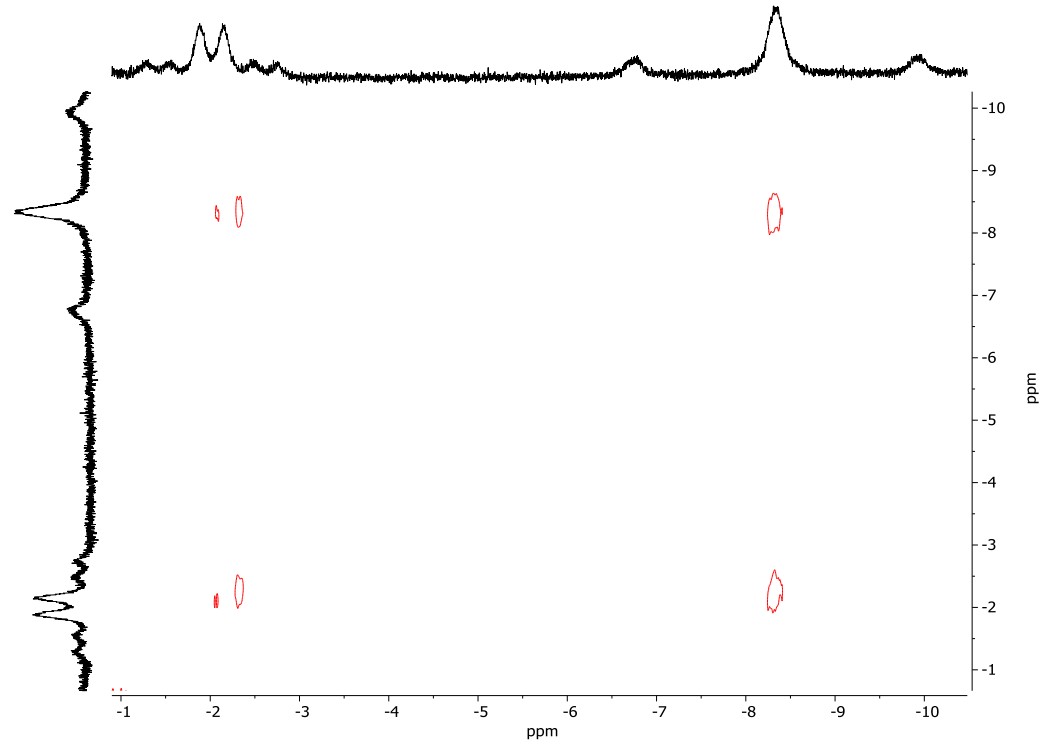


Figure S20. Representative example of NOESY spectrum for the exchange process at 328 K and τ_m = 800 ms (400 MHz, toluene-d_8).

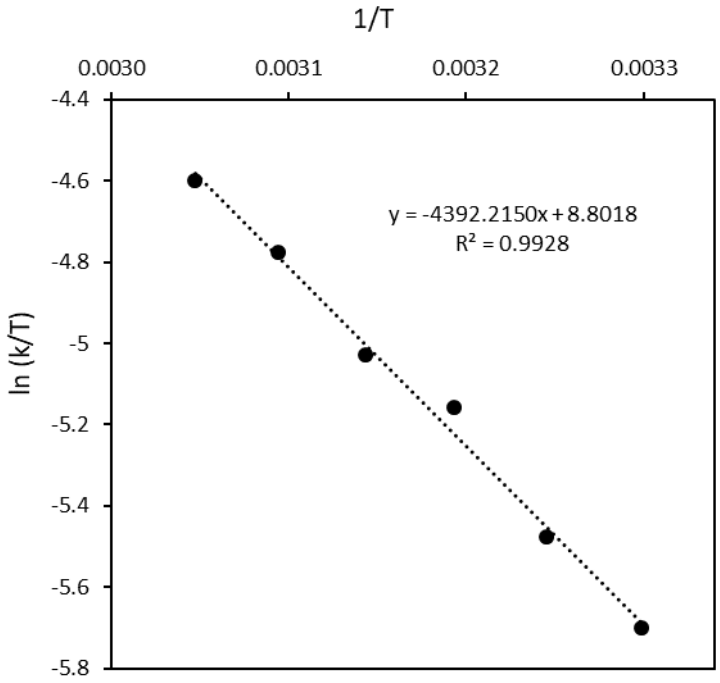


Figure S21. Eyring plot for the exchange process over the temperature range 303-328 K.

5. Kinetic isotopic effect (KIE) experiments

Kinetic studies were carried out to determine the kinetic isotopic effect (KIE) of dihydrogen activation by the bimetallic pairs **1a**:**2** and **1b**:**2**. Experiments were performed at 0 ºC in toluene-d_8 or THF-d_8, and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 0 ºC by means of the disappearance of the corresponding adduct and using triphenylphosphine oxide as internal standard.

In a representative example, a mixture of compounds **1a** (7.4 mg, 0.006 mmol) and **2** (5 mg, 0.006 mmol) was placed in a *J. Young* NMR tube and dissolved in toluene-d_8 (0.3 mL) at room temperature. The resulting solution was frozen and the inert gas was removed under high vacuum. H_2 or D_2 (2 bar) was subsequently added, the solution was shaken and the tube was finally placed into the NMR equipment at 0 ºC.

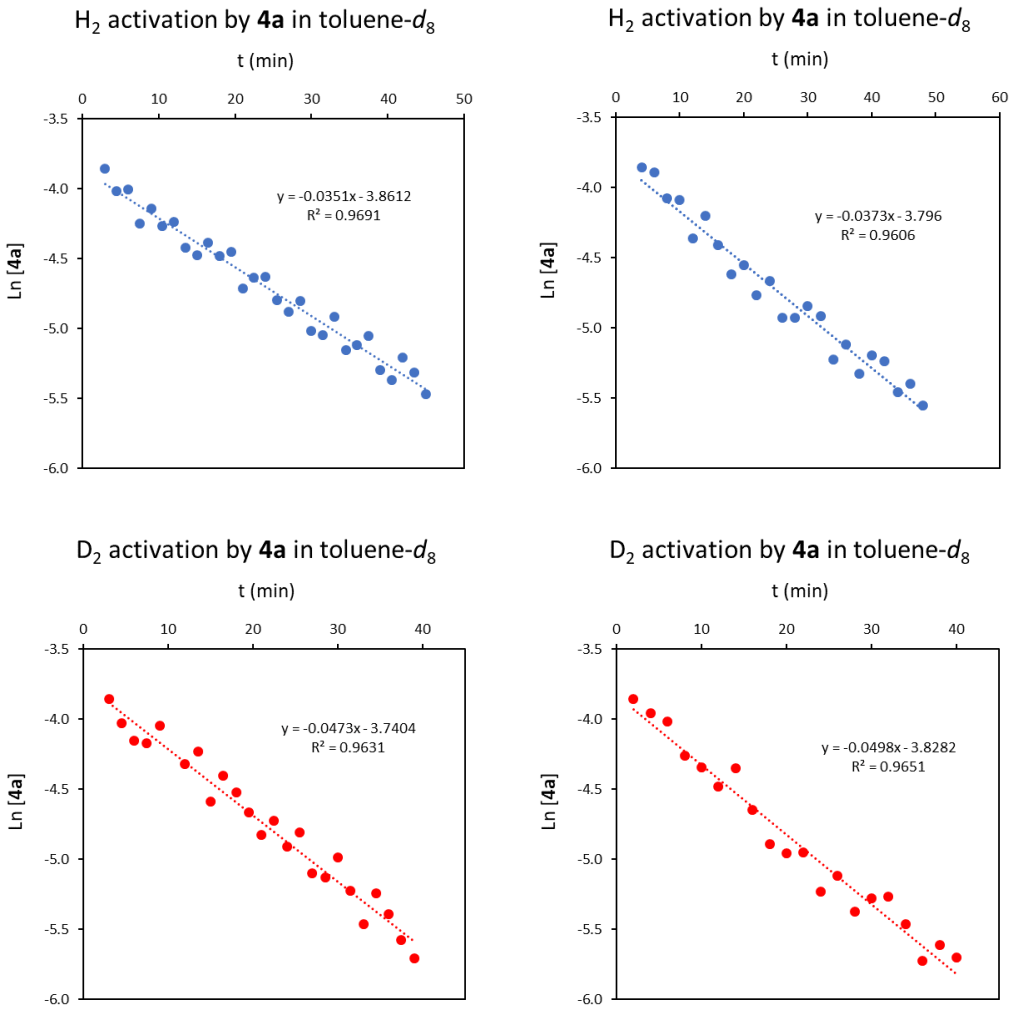


Figure S22. Kinetic profiles for the activation of H_2 and D_2 by the presynthesized adduct **4a** in toluene-d_8 (k_H/k_D = 0.74 ± 0.04).

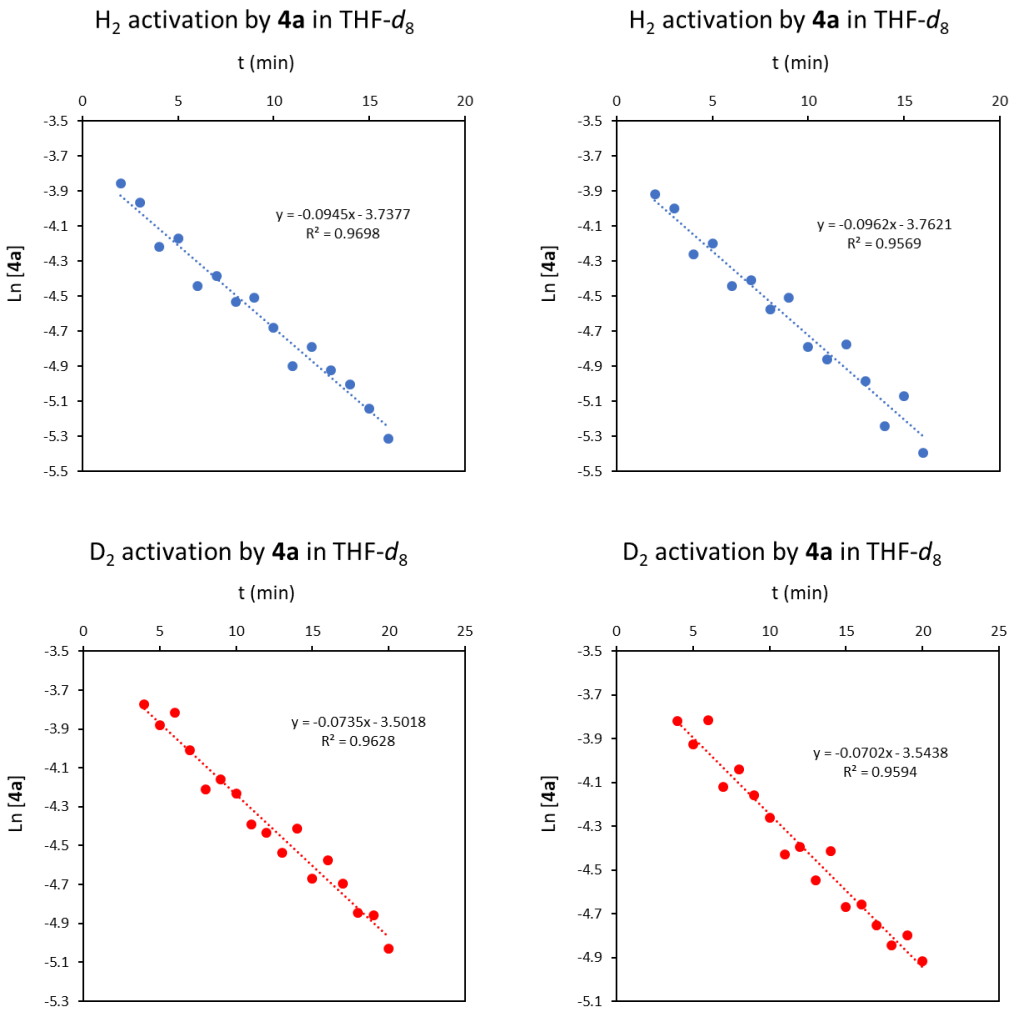


Figure S23. Kinetic profiles for the activation of H_2 and D_2 by the presynthesized adduct **4a** in THF-d_8 (k_H/k_D = 1.33 ± 0.05).

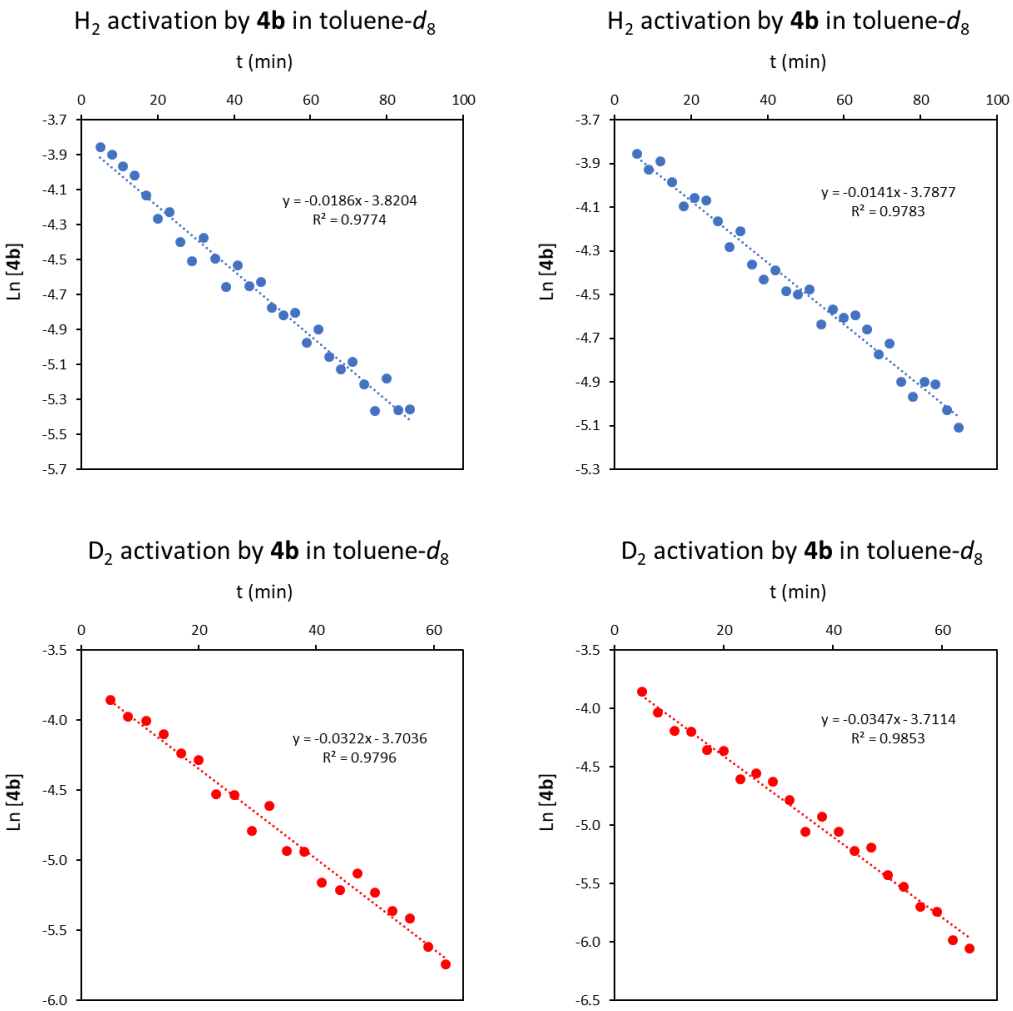


Figure S24. Kinetic profiles for the activation of H_2 and D_2 by the presynthesized adduct **4b** in toluene-d_8 (k_H/k_D = 0.49 ± 0.09).

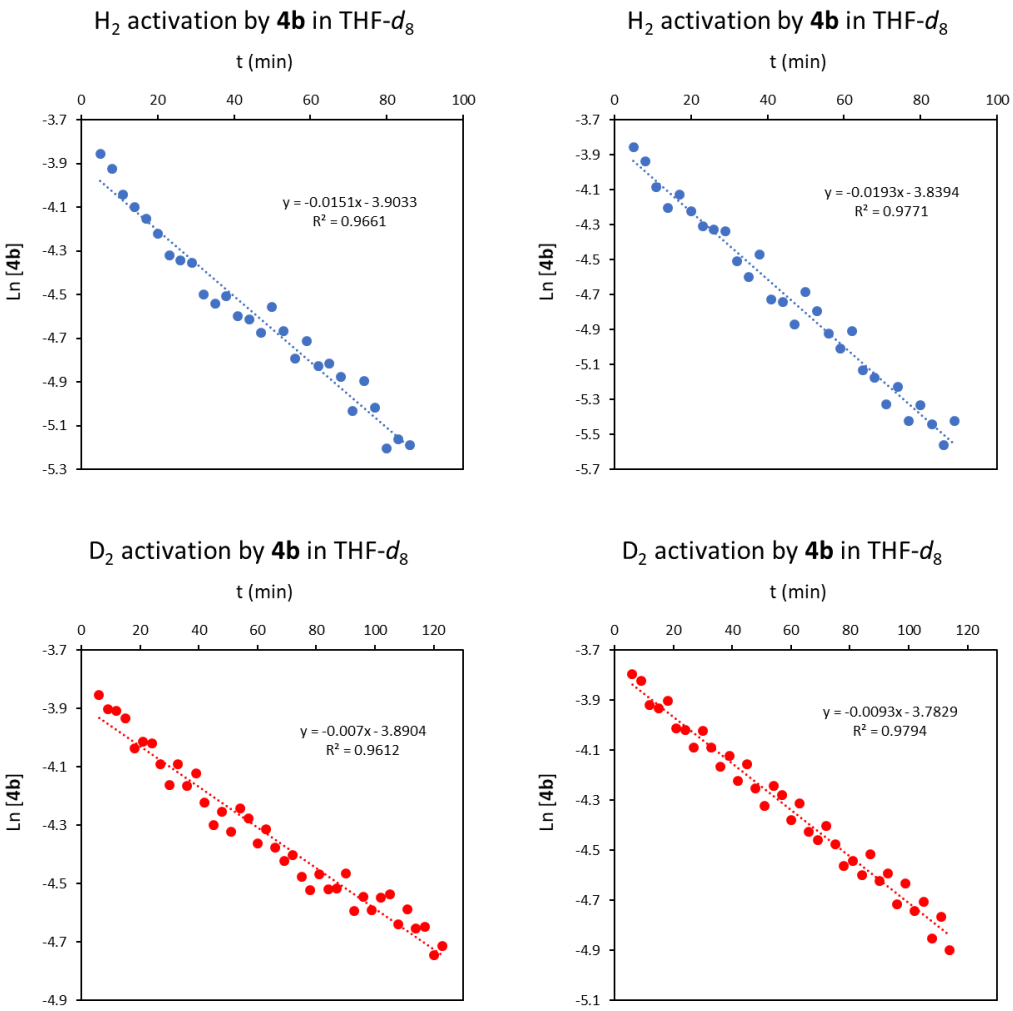


Figure S25. Kinetic profiles for the activation of H_2 and D_2 by the presynthesized adduct **4b** in THF-d_8 (k_H/k_D = 2.11 ± 0.55).

6. Crystal structure determinations

Low-temperature diffraction data were collected either on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IμS 3.0 microfocus X-ray source. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1). The structures were solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Metal hydrides could not be reliable located on the Fourier electron density map. The two reported structures contain in their unit cells disordered solvent or anion molecules that could not be modelled and were treated as a diffuse contribution to the overall scattering without specific atom positions. In particular, structure **4a** contains 22 toluene molecules per unit cell, while structure **5c** contains half a triflimidate anion and half benzene molecule per unit cell. Similarity restraints have been applied on bond lengths and angles (SADI) for the disordered triflimide anion, and on displacement parameters (SIMU, DELU, RIGU) for some tert-butyl groups. There are some problems associated to structure **4a**, as detailed in the corresponding CIF file, and as such Figures S26-S28 are appended to better understand some deficiencies of the final model which so far do not affect considerably to the overall notable quality of the structural model, in both cases in perfect agreement with all other spectroscopic parameters and experimental data.

Table S1. Crystal data and structure refinement for compounds **4a** and **5c**

	Compound **4a**	Compound **5c**
Formula	$C_{98}H_{128}AuF_6NO_4P_3PtS_2 \cdot 5.5[C_7H_8]$	$C_{110}H_{147}AuF_6NO_2P_3PtS_2$
Fw	2553.83	2178.36
Crystal size (mm)	0.17 × 0.05 × 0.05	0.19 × 0.18 × 0.04
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a (Å)	13. 9936 (7)	13.5057 (6)
b (Å)	44.882 (2)	15.9591 (7)
c (Å)	21.8761 (12)	26.6862 (9)
α (º)	90	83.099 (1)
β (º)	102.909 (2)	86.733 (1)
γ (º)	90	71.238 (2)
V (Å^3)	13392.2 (12)	5405.8 (4)
T (K)	193	193
Z	4	2
ρ_{calc} (g·cm^{-3})	1.267	1.314
μ, mm^{-1} (MoKα)	2.26	2.79
F(000)	5272	2192
Absorption corrections	Multi-scan, 0.359-0.491	Multi-scan, 0.623-0.746
θ range (º)	1.8 – 25.3	1.9 – 28.3
Nº reflections measd	141684	283643
R_{int}	0.047	0.044
Nº reflections unique	24233	26722
Nº parameters/restraints	1064 / 134	1041 / 18
R_1 ($I > 2\sigma(I)$)[a]	0.097	0.029
R_1 (all data)	0.102	0.041
wR_2 ($I > 2\sigma(I)$)	0.291	0.067
wR_2 (all data)	0.295	0.074
Diff. Fourier. peaks min/max, eÅ^{-3}	4.05 / -2.93	1.28 / -1.04
CCDC number	2175895	2175896

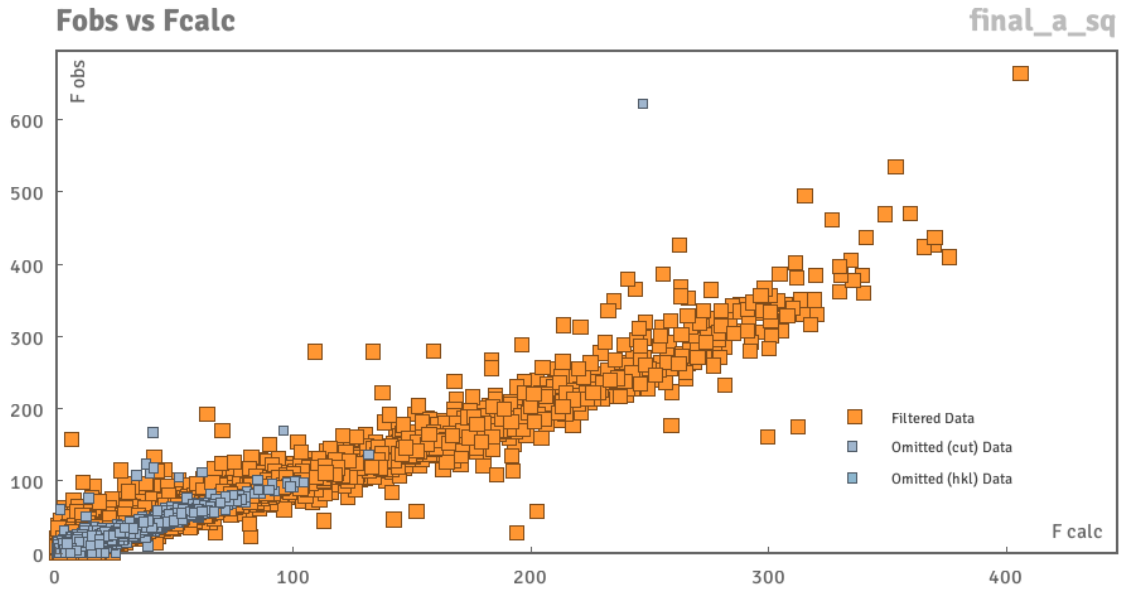


Figure S26. F_{obs}–F_{calc} plot for structure **4a**.[10]

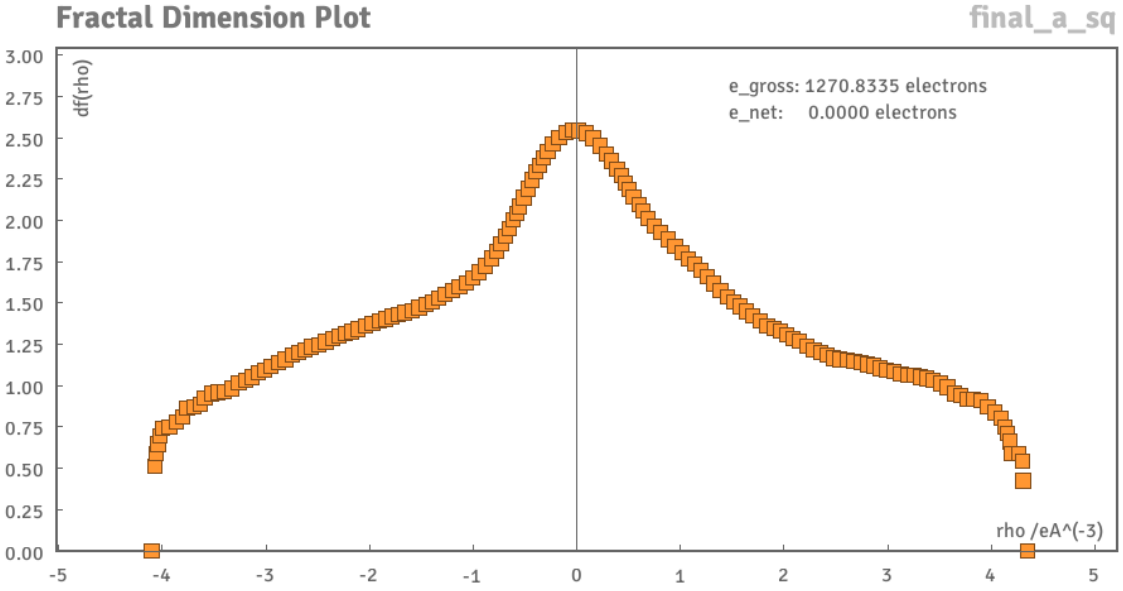


Figure S27. Fractal dimension plot for structure **4a**.[10]

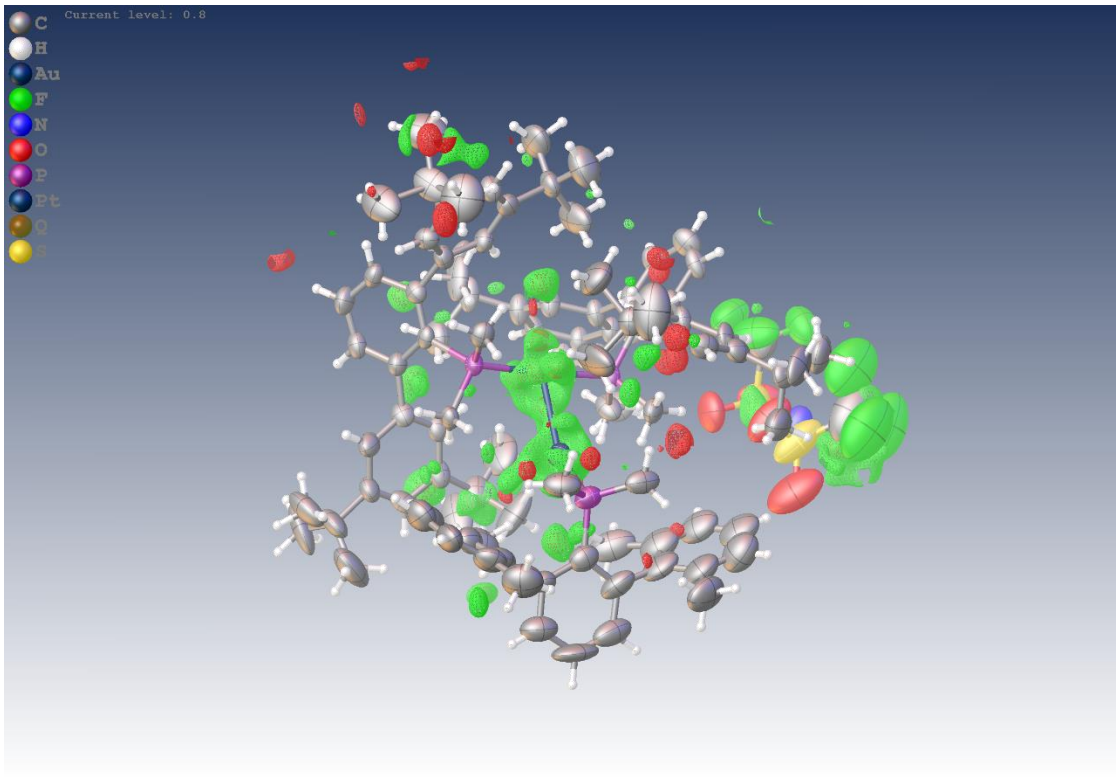


Figure S28. ORTEP diagram of structure **4a** (50% ellipsoid probability) with overlay electron-density map showing positive (green) and negative (red) residual density.[10]

7. References

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