Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Bimetallic Gold(I) Complexes of Photoswitchable Phosphines: Synthesis and Uses in Cooperative Catalysis

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I. General information

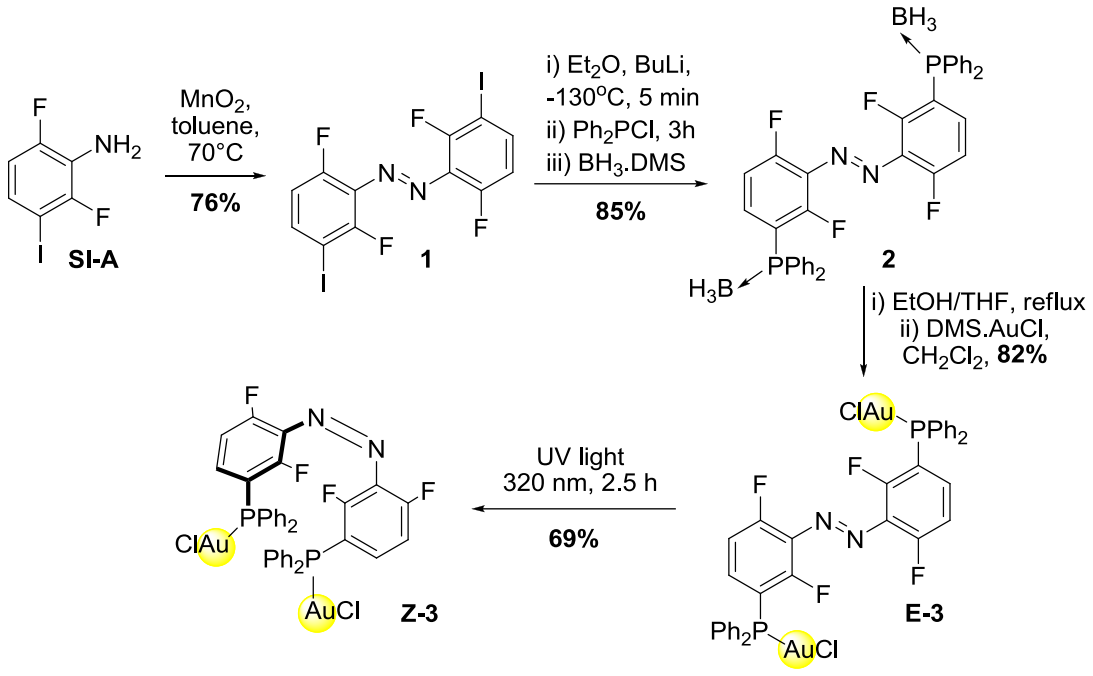
All reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2). All reagents and solvents were of commercial quality and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel. The developed chromatograms were visualized by UV absorbance and by immersion in phosphomolybdic acid or $KMnO_4$ solutions, followed by heating. Flash column chromatography was performed using 40-63 mesh silica gel. Purifications have been performed on a automated flash chromatography system (SiO_2), unless otherwise stated. NMR spectra (^1H, ^{13}C, ^{31}P) were recorded on either AV 500 or AV 300 spectrometers. NMR spectra were recorded at room temperature. Chemical shifts are reported in parts per million relative to an internal standard of residual chloroform (δ = 7.27 ppm for ^1H NMR and 77.00 ppm for ^{13}C NMR). *J* couplings are reported in Hz. The ^{13}C NMR spectra were assigned by standard methods using HSQC or DEPT experiments.

Substrates **4**[1] and **7**[2] have been synthesized according to the reported procedures.

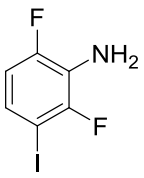
[1] Kojima, M.; Mikami, K. *Synlett* **2012**, 57.
[2] Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.

II. Experimental Procedures

A. Synthesis of complexes *E*-3 and *Z*-3:



II.1. 2,6-difluoro-3-iodoaniline (SI-A).



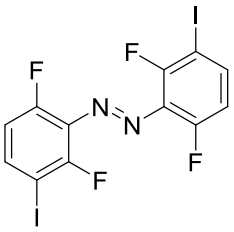
To a solution of 2,6-difluoroacetanilide[3] (210 mg, 1.23 mmol) in *conc.* H_2SO_4 (12.3 mL) was added *N*-iodosuccinimide (277 mg, 1.23 mmol) portion-wise at room temperature. The resulting mixture was stirred over night at room temperature then poured into crushed ice (200 g). The aqueous layer was extracted with EtOAc (3x30 mL), washed with H_2O (100 mL), washed with *sat. aq.* $NaHCO_3$ (100 mL), dried ($MgSO_4$), filtered, evaporated to give the title compound (351 mg, 96%) as white solid. Mp 62–64°C; R_f 0.42 (40% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) 7.60 (1H, dt, J_1 9, J_2 6, CH_{Ar}), 7.28 (1H, br. s. N*H*), 6.78 (1H, td, J_1 9, J_2 1, CH_{Ar}), 2.20 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 160.0 (*C*=O), 158.6 (*C*q), 158.4 (*C*q), 143.8 (*C*q), 136.4 (*C*H$_{Ar}$), 113.4 (d, *J* 21, *C*H$_{Ar}$), 77.2 (*C*I), 23.0 (*C*H$_3$); ^{19}F NMR (282 MHz) -96.1 (s), -116.6 (s); HRMS (ESI) calcd. for $C_8H_7F_2INO$ $[M+H]^+$: 297.9540, found: 297.9515.

To a solution of *N*-(2,6-difluoro-3-iodophenyl)acetamide (351 mg, 1.18 mmol) in MeOH (1.5 mL) was added *conc.* HCl (1 mL). The reaction mixture was stirred at 60 °C for 12 h then allowed to reach room temperature, diluted with H_2O (50 mL), neutralized with solid $NaHCO_3$, extracted with EtOAc (3x50 mL), dried, evaporated and purified by chromatography to give the compound **SI-A** (290 mg, 96%) as white solid.

R_f 0.50 (20% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) 7.03 (1H, ddd, J_1 9, J_2 7, J_3 6, CH_{Ar}), 6.65 (1H, ddd, J_1 10, J_2 9, J_3 2, CH_{Ar}), 3.83 (2H, br.s. NH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 153.1 (dd, J_1 7, J_2 93, *C*qF), 150.0 (dd, J_1 6, J_2 90, *C*qF), 132.3 (*C*q), 125.1 (d, *J* 8, *C*HAr), 112.5 (d, *J* 19, *C*HAr), 74.6 (d, *J* 20, *C*qI); ^{19}F NMR (282 MHz) -111.6 (s), -132.1 (s); HRMS (ESI) calcd. for $C_6H_5F_2IN$ $[M+H]^+$: 255.9435, found: 255.9435.

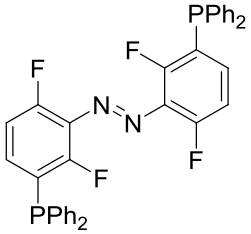
[3] Finger, G. S.; Reed, F. H.; Finnerty, J. L. *J Am. Chem. Soc.* **1951**, *73*, 153-155.

II.2. (*E*)-1,2-bis(2,6-difluoro-3-iodophenyl)diazene (1).



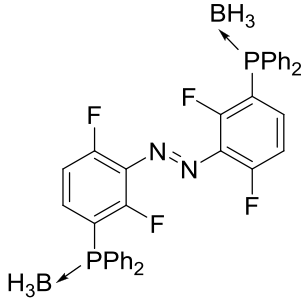
To a solution of aniline **SI-A** (1.61 g, 6.3 mmol) in toluene (120 mL) was added MnO_2 (13.75 g, 158 mmol). The reaction mixture was stirred at 70°C for 48 h then allowed to reach room temperature, filtered through a pad of silica, evaporated and purified by chromatography to give the title compound (1.21 g, 76%, >95/5 : *E*/*Z*) as orange red solid; R_f 0.46 (20% EtOAc/hexane). Mp 124–126°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.85-7.78 (2H, m, C*H*$_{Ar}$), 7.00-6.90 (2H, m, C*H*$_{Ar}$); *Z* isomer: 7.62 (2H, m, C*H*$_{Ar}$), 6.73 (2H, m, C*H*$_{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$) 156.0 (d, *J* 264, *C*qF), 154.0 (dd, J_1 4, J_2 262, *C*qF), 140.1 (d, *J* 7, *C*HAr), 131.7 (t, *J* 12, *C*qN), 114.4 (d, *J* 20, *C*HAr), 76.6 (dd, J_1 5, J_2 25, *C*qI); ^{19}F NMR (282 MHz) 140.3 (dd, J_1 10, J_2 3), 114.5 (dd, J_1 4, J_2 21); HRMS (ESI) calcd. for $C_{12}H_5F_4I_2N_2$ $[M+H]^+$: 506.8478, found: 506.8491.

II.3. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene.

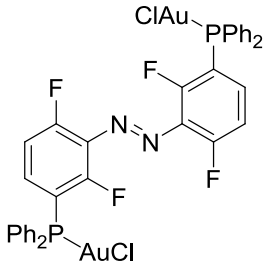


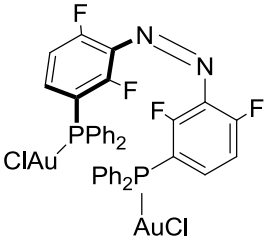
A stirred solution of diazene **1** (30 mg, 0.06 mmol) in Et_2O (3 mL) was cooled to -130°C (pentane/liquid N_2) and *n*-BuLi (74 µL, 0.119 mmol, 1.6 M in Hexanes) was added rapidly. To the resulting dark red reaction mixture was added after 5 min, a solution of distilled Ph_2PCl (24 µL, 0.132 mmol) in Et_2O (1 mL). After 10 min the cooling bath was removed and the reaction mixture was stirred at room temperature for 3 h; quenched with H_2O (3 drops), dried ($MgSO_4$), evaporated and purified by chromatography to give the desired product (31 mg, 80%, 95/5 : *E*/*Z*) as orange solid. Mp 168–170°C; R_f 0.20 (5% EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) 7.45-7.31 (20H, m, C*H*$_{Ar}$), 6.99 (2H, t, *J* 9, C*H*$_{Ar}$), 6.92-6.83 (2H, m, C*H*$_{Ar}$); [Discernable data for *Z* isomer: 7.19-7.14 (2H, m, C*H*$_{Ar}$), 7.10-7.04 (2H, m, C*H*$_{Ar}$)]; ^{13}C NMR (75 MHz, $CDCl_3$): 157.0 (ddd, J_1 5, J_2 16, J_3 261, *C*qF), 155.7 (dd, J_1 4, J_2 264, *C*qF), 136.0-135.7 (m, *C*H$_{Ar}$), 134.7 (d, *J* 11, *C*qP), 133.8 (d, *J* 21, *C*H$_{Ar}$), 131.8-131.4 (m, *C*qP), 129.3 (s, *C*H$_{Ar}$), 128.8 (d, *J* 7, *C*H$_{Ar}$), 122.8-122.2 (m, N-*C*$_q$), 113.0-112.5 (m, *C*H$_{Ar}$); ^{31}P NMR (121.5 MHz): -18.9 (d, *J* 59); ^{19}F NMR (282 MHz): -110.5 (d, *J* 59), -120.0 (s); [Discernable data for *Z* isomer: -110.8 (d, *J* 58), -120.3 (s).]; HRMS (ESI) calcd. for $C_{36}H_{25}F_4N_2P_2$ $[M+H]^+$: 623.1429, found: 623.1444.

II.4. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6- difluorophenyl)diazene (2).

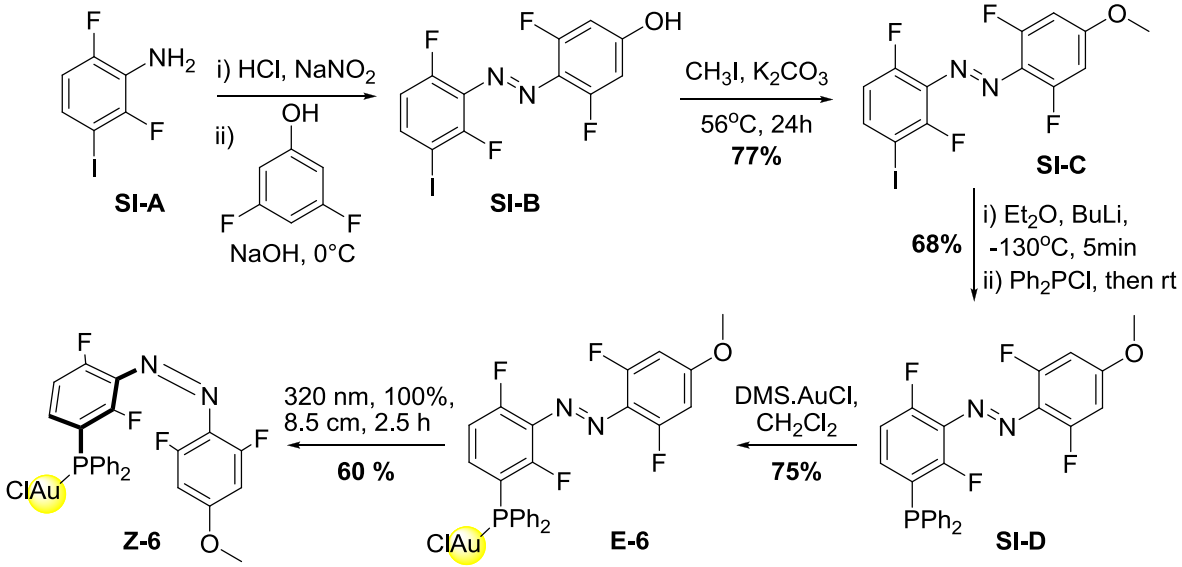


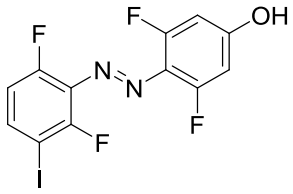
A stirred solution of diazene **1** (30 mg, 0.06 mmol) in Et_2O (3 mL) was cooled to -130°C (pentane/liquid N_2) and *n*-BuLi (74 µL, 0.119 mmol, 1.6 M in Hexanes) was added rapidly. To the resulting dark red reaction mixture was added after 5 min, a solution of distilled Ph_2PCl (24 µL, 0.132 mmol) in Et_2O (1 mL). After 10 min the cooling bath was removed and the reaction mixture was stirred at room temperature for 3 h; then re-cooled to 0 °C and $BH_3.Me_2S$ (75 µL, 0.15 mmol, 2M in THF) was added and stirred at room temperature for 3 h. The excess borane was quenched with H_2O (3 drops), dried ($MgSO_4$), evaporated and purified by chromatography to give the desired complex (33 mg, 85%) as orange solid. R_f 0.26 (20% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) 7.88-7.78 (2H, m, C*H*$_{Ar}$), 7.70-7.64 (6H, m, C*H*$_{Ar}$), 7.57-7.30 (14H, m, C*H*$_{Ar}$), 7.17 (2H, t, *J* 9, C*H*$_{Ar}$), 2.10-0.30 (6H, br. s. B*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 157.7 (dd, J_1 5, J_2 267, *C*qF), 157.1 (dd, *J* 267, *C*qF), 138.1-137.7 (m, *C*qP), 136.9-136.6 (m, *C*qP), 132.8 (d, *J* 10, *C*H$_{Ar}$), 132.5-132.1 (m, *C*H$_{Ar}$), 131.7 (d, *J* 2, *C*H$_{Ar}$), 129.0 (d, *J* 11, *C*H$_{Ar}$), 127.7-126.4 (m, *C*qN), 113.6 (m, *C*H$_{Ar}$); ^{31}P NMR (121.5 MHz) 18.9 (m); ^{19}F NMR (282 MHz) -103.9 (dd, J_1 7, J_2 4), -114.2 (d, *J* 7); HRMS (ESI) calcd. for $C_{36}H_{30}B_2F_4N_2NaP_2$ $[M+Na]^+$: 673.1904, found: 673.1915.

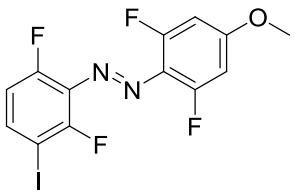
II.5. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (*E*-3). 
To a stirred solution of phosphine-borane **2** (30 mg, 0.046 mmol) in THF (5 mL) was added EtOH (10 mL). The resulting solution was degassed and refluxed for 3 h under argon in dark. The reaction was monitored by ^{31}P NMR. After complete deprotection, the solvents and $(EtO)_3B$ were removed under high vacuum at 40°C. The crude diphosphine was dissolved in CH_2Cl_2 (5 mL) and AuCl.Me_2S (28 mg, 0.094 mmol, 2.05 equiv.) was added under argon, stirred at rt for 1 h, then solvent was removed and purified by chromatography to give desired gold complex (41 mg, 82%) as orange solid. Mp >250°C; R_f 0.37 (70% CH_2Cl_2/hexane); ^1H NMR (500 MHz, $CDCl_3$) 7.66-7.58 (10H, m, C*H*$_{Ar}$), 7.56-7.46 (10H, m, C*H*$_{Ar}$), 7.32-7.25 (2H, m, C*H*$_{Ar}$), 7.14 (2H, t, *J* 9, C*H*$_{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$) 157.7 (d, *J* 269, *C*qF), 156.9 (d, *J* 265, *C*qF), 137.5-137.2 (m, *C*H$_{Ar}$), 136.6-136.4 (m, *C*qP), 134.0 (d, *J* 15, *C*H$_{Ar}$), 132.8-132.5 (m, *C*H$_{Ar}$), 132.6 (s, *C*H$_{Ar}$), 129.6 (d, *J* 12, *C*H$_{Ar}$), 126.6 (d, *J* 66, *Cq*N), 113.9-113.5 (m, *C*H$_{Ar}$). One *C*qP is missing; ^{31}P NMR (121.5 MHz): 25.6 (d, *J* 20); ^{19}F NMR (282 MHz) -103.9 (dd, J_1 7, J_2 21), -112.5 (d, *J* 7); HRMS (ESI) calcd. for $C_{36}H_{24}Au_2ClF_4N_2P_2$ $[M\text{-}Cl]^+$: 1051.0371, found: 1051.0452.

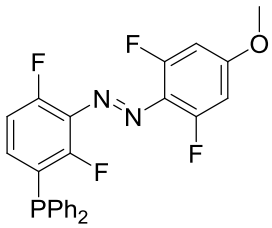
II.6. (*Z*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (*Z*-3). 
An orange solution of *E*-gold complex *E*-**3** (50 mg, 0.046 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature and irradiated with UV light (*Semrock*® optical filter: 320/40, intensity: 100%, distance: 8.5 cm, time: 2.5 h). The resulting yellow solution was evaporated in the dark at 30 °C and purified by chromatography in dark to give desired *Z*-**3** (34 mg, 69%) as yellow solid; R_f 0.49 (50% EtOAc/hexane) and recovered *E*-**3** (11 mg, 22%) as light orange solid. R_f 0.40 (50% EtOAc/hexane); ^1H NMR (500 MHz, $CDCl_3$) 7.69-7.44 (20H, m, C*H*$_{Ar}$), 7.15-7.05 (4H, m, C*H*$_{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$) 156.9 (d, *J* 262, *C*qF), 149.6 (d, *J* 254, *C*qF), 137.5-137.3 (m, *C*qP), 136.4 (m, *C*H$_{Ar}$), 134.0 (d, *J* 14, *C*H$_{Ar}$), 132.8 (d, *J* 2, *C*H$_{Ar}$), 129.6 (d, *J* 13, *C*H$_{Ar}$), 126.1 (d, *J* 64, *C*qN), 114.0-113.6 (m, *C*H$_{Ar}$). One *C*qP is missing; ^{31}P NMR (121.5 MHz): 24.8 (s); ^{19}F NMR (282 MHz) -103.5 (s), -111.5 (s).

B. Synthesis of complexes *E*-6 and *Z*-6:

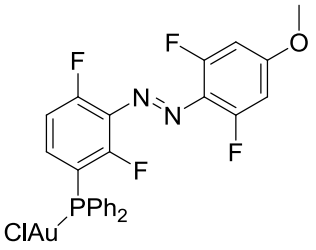


II.7. (*E*)-4-((2,6-difluoro-3-iodophenyl)diazenyl)-3,5-difluorophenol (SI-B).  Finely powdered 2,6-difluoro-3-iodoaniline **SI-A** (255 mg, 1 mmol) was added to 3 mL of HCl (27%) at 0°C. A solution of $NaNO_2$ (83 mg, 1.2 mmol) in H_2O (3 mL) was added dropwise and the temperature was kept below 5°C. The precipitate was dissolved by dropwise addition of HCl (37%, 2 mL) and the resulting solution was stirred for 30 min at 0 °C. Excess $NaNO_2$ was quenched by addition of NH_2SO_3H (25 mg, 0.25 mmol). Meanwhile, in another flask, 3,5-difluorophenol (195 mg, 1.5 mmol) was dissolved in aqueous NaOH (prepared from 400 mg/5 mL of H_2O). This solution was cooled to 0°C and a freshly prepared solution of the precooled (0°C) diazonium salt was added dropwise. During addition the pH was controlled to remain strongly alkaline. The reaction mixture was stirred for 1 h at room temperature. The pH was adjusted to 4 by addition of 2N CH_3COOH. The precipitate was filtered, washed with water and dried under high vacuum to yield the desired azo compound **SI-B** as an orange red solid (324 mg; MS-EI: *m/z* 397 $[M+H]^+$). The crude azo compound was used in next step without further purification. *Caution!* Solid diazonium salts are heat and shock sensitive towards explosion.

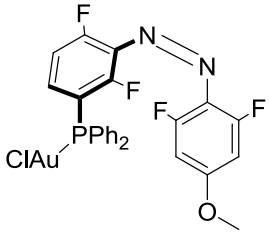
II.8. (*E*)-1-(2,6-difluoro-3-iodophenyl)-2-(2,6-difluoro-4-methoxyphenyl)diazene (SI-C).  A solution of crude (*E*)-4-((2,6-difluoro-3-iodophenyl)diazenyl)-3,5-difluorophenol **SI-B** (324 mg, 0.82 mmol), methyl iodide (190 mg, 1.34 mmol), K_2CO_3 (592 mg, 4.28 mmol), 18-crown-6 (55 mg, 0.21 mmol) in dry acetone (25 mL) was refluxed under argon for 24 h. After removal of solvent by evaporation, the residue was purified by chromatography to give the desired product **SI-C** (258 mg, 77%, >95/5 : *E*/*Z*) as orange solid. R_f 0.52 (40% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) 7.75-7.66 (1H, m, *p*-C*H*$_{Ar}$), 6.90 (1H, ddd, J_1 10, J_2 9, J_3 2, *m*-C*H*$_{Ar}$), 6.63-6.57 (2H, dd, J_1 14, J_2 3, C*H*$_{Ar}$), 3.88 (3H, s, OC*H*$_3$); [Discernable data for *Z* isomer: 7.85 (1H, dd, J_1 9, J_2 6, *p*-C*H*$_{Ar}$), 7.02 (1H, dd, J_1 10, J_2 9, *m*-C*H*$_{Ar}$), 6.50 (2H, dd, J_1 14, J_2 3, C*H*$_{Ar}$), 3.84 (3H, s, OC*H*$_3$)]; ^{13}C NMR (75 MHz, $CDCl_3$) 163.1 (t, *J* 14, *C*qOCH$_3$), 157.6 (dd, J_1 9, J_2 262, *C*qF), 156.6 (dd, J_1 3, J_2 135, *C*qF), 153.2 (dd, J_1 4, J_2 132, *C*qF), 138.6 (dd, J_1 9, J_2 3, *C*H$_{Ar}$), 132.3 (t, *J* 12, *C*qN), 125.8 (t, *J* 9, *C*qN), 114.2 (dd, J_1 4, J_2 21, *C*HAr), 98.8 (dd, J_1 3 , J_2 24, *C*H$_{Ar}$), 76.2 (dd, J_1 4, J_2 26, *C*qI), 56.2 (s, O*C*H$_3$); ^{19}F NMR (282 MHz) -100.2 (s), -116.4 (d, *J* 11), -121.6 (s); HRMS (ESI) calcd. for $C_{13}H_8F_4IN_2O$ $[M+H]^+$: 410.9617, found: 410.9609.

II.9. (*E*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (**SI-D**).  A stirred solution of **SI-C** (220 mg, 0.54 mmol) in anhydrous Et_2O (27 mL) was cooled to -130°C (pentane/liquid N_2) and *n*-BuLi (370 µL, 0.59 mmol, 1.6 M in Hexanes) was added rapidly. To the resulting dark red reaction mixture was added after 5 min, a solution of freshly distilled Ph_2PCl (116 µL, 0.65 mmol) in Et_2O (5 mL). After 10 min the cooling bath was removed and the reaction mixture was stirred at room temperature for 3 h, evaporated and purified by chromatography to give the desired phosphine (171 mg, 68%, 95/5 : *E*/*Z*) as orange solid. R_f 0.30 (10% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41-7.32 (10H, m, C*H*$_{Ar}$), 7.00-6.93 (1H, m, *p*-C*H*$_{Ar}$), 6.86-6.77 (1H, m, *m*-C*H*$_{Ar}$), 6.69 (2H, dd, J_1 3, J_2 14, C*H*$_{Ar}$), 3.88 (3H, s, OC*H*$_3$), [Discernable data for *Z* isomer: 7.19 (1H, td, J_1 8, J_2 2, *p*-C*H*$_{Ar}$), 6.37 (1H, dd, J_1 2, J_2 11, C*H*$_{Ar}$), 3.80 (3H, s, OC*H*$_3$)]; ^{13}C NMR (75 MHz, $CDCl_3$) 162.8 (t, *J* 17, *C*qOCH$_3$), 158.5 (dd, J_1 8, J_2 262, *C*qF), 158.6 (m, *C*qP), 155.7 (dd, J_1 5, J_2 262, *C*qF), 134.8 (d, *J* 11, *C*H$_{Ar}$), 134.7-134.5 (m, *C*H$_{Ar}$), 133.8 (d, *J* 21, *C*H$_{Ar}$), 132.5-132.4 (m, *C*qP), 131.8 (t, *J* 8, *C*qN), 129.3 (s, *C*H$_{Ar}$), 128.8 (d, *J* 7, *C*H$_{Ar}$), 122.1 (t, *J* 20, *C*qN), 112.8 (dd, J_1 3, J_2 20, *C*H$_{Ar}$), 98.9 (dd, J_1 3, J_2 24, *C*H$_{Ar}$), 56.2 (O*C*H$_3$);

^{31}P NMR (121.5 MHz) : -19.0 (d, *J* 62); ^{19}F NMR (282 MHz): -111.6 (d, *J* 59), -116.8 (d, *J* 12), -121.0 (s); HRMS (ESI) calcd. for $C_{25}H_{18}F_4N_2OP$ $[M+H]^+$: 469.1093, found: 469.1086.



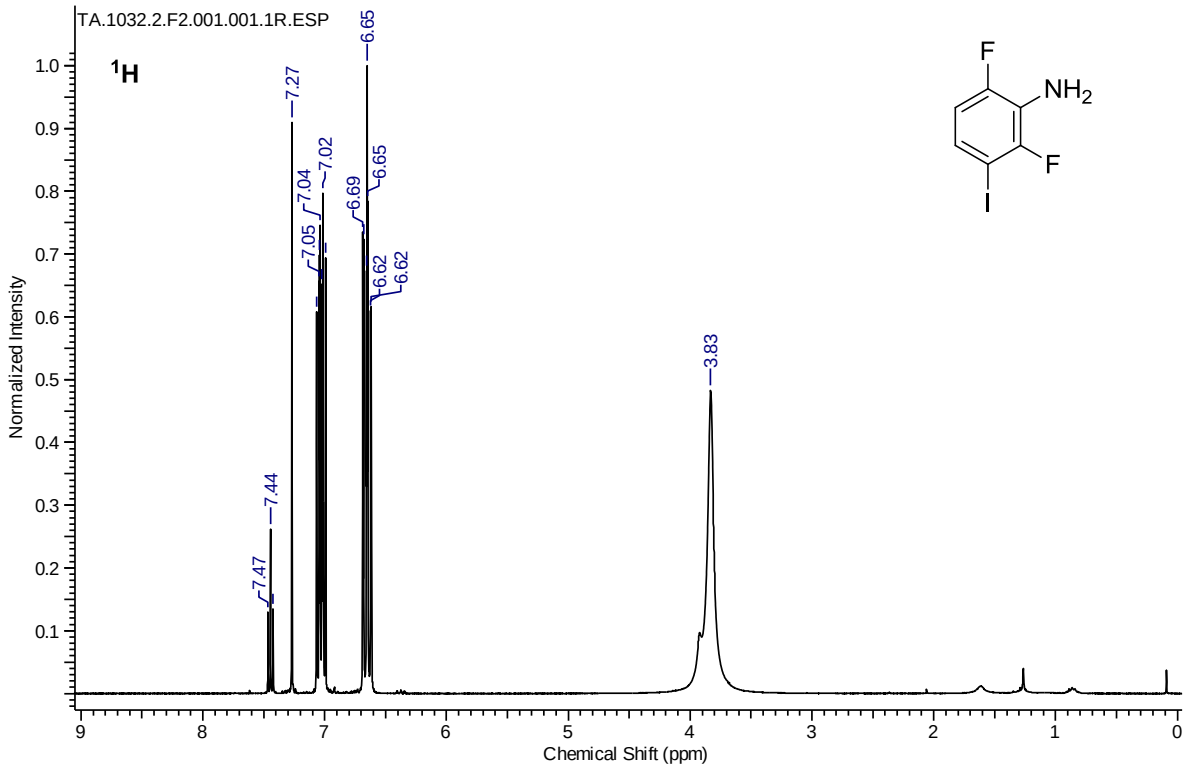
II.10. (*E*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)- 2,6-difluorophenyl) diazene (*E*-6). To a stirred solution of phosphine **SI-D** in CH_2Cl_2 (5 mL) and AuCl.Me_2S (28 mg, 0.094 mmol, 2.05 equiv.) was added at 0 °C under argon. The resulting solution stirred at rt for 1 h, then solvent was removed and purified by chromatography to give desired gold complex (47 mg, 75%, >95/5 : *E*/*Z*) as orange-red solid. Mp 90-92°C; R_f 0.54 (50% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): 7.69-7.45 (10H, m, C*H*$_{Ar}$), 7.32-7.19 (1H, m, C*H*$_{Ar}$), 7.12 (1H, t, *J* 8, C*H*$_{Ar}$), 6.59 (2H, dd, J_1 3, J_2 14, C*H*$_{Ar}$), 3.89 (3H, s, OC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): 163.5 (t, *J* 15, *C*qOCH$_3$), 160.0 (dd, J_1 14, J_2 230, *C*qF), 157.7 (dd, J_1 7, J_2 264, *C*qF), 158.7-158.5 (m, *C*qP), 152.7 (dd, J_1 8, J_2 253, *C*qF), 135.7 (td, J_1 11, J_2 5, *C*H$_{Ar}$), 134.0 (d, *J* 15, *C*H$_{Ar}$), 132.4 (s, *C*H$_{Ar}$), 129.5 (d, *J* 13, *C*H$_{Ar}$), 127.4 (s, *C*qN), 126.5 (s, *C*qN), 113.8-113.3 (m, *C*H$_{Ar}$), 99.2-98.5 (m, *C*H$_{Ar}$), 56.3 (s, O*C*H$_3$); ^{31}P NMR (121.5 MHz): 26.4 (s); ^{19}F NMR (282 MHz): -105.7 (m), -114.4 (d, *J* 7), -115.7 (d, *J* 11); HRMS (ESI) calcd. for $C_{27}H_{20}AuF_4N_3OP$ $[M\text{-}Cl+CH_3CN]^+$: 706.0946, found: 706.0938.

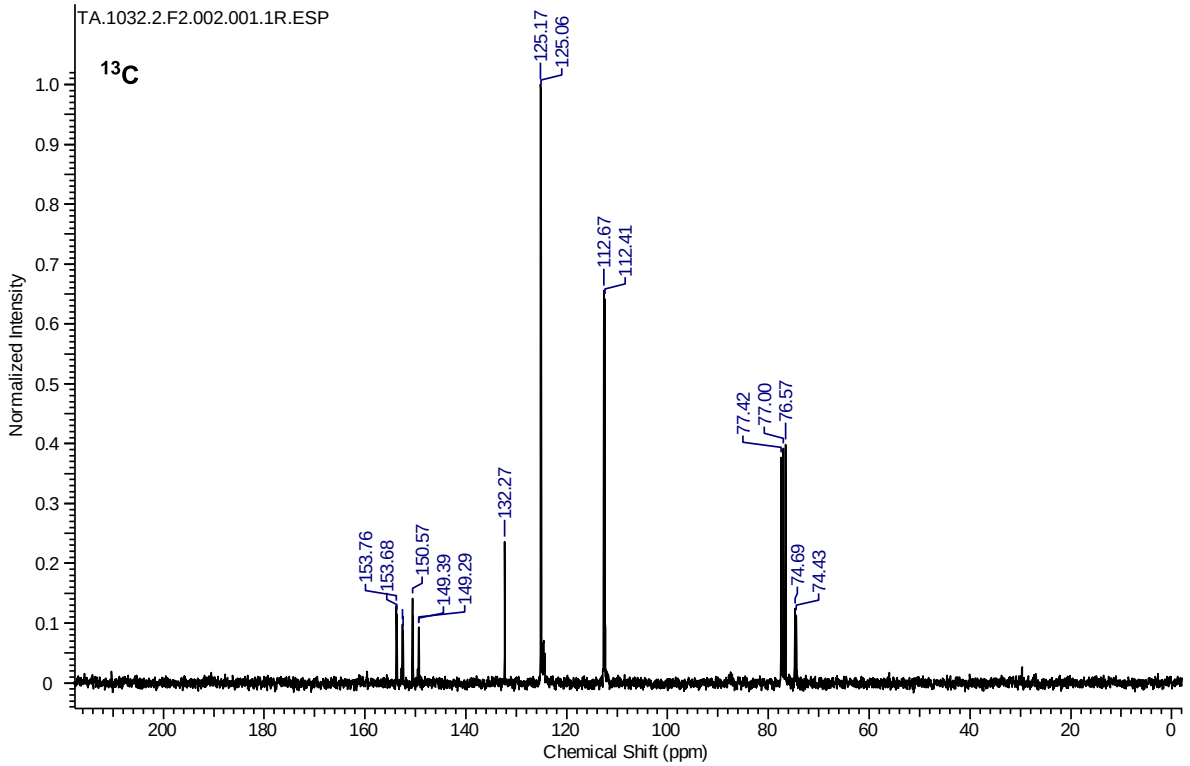


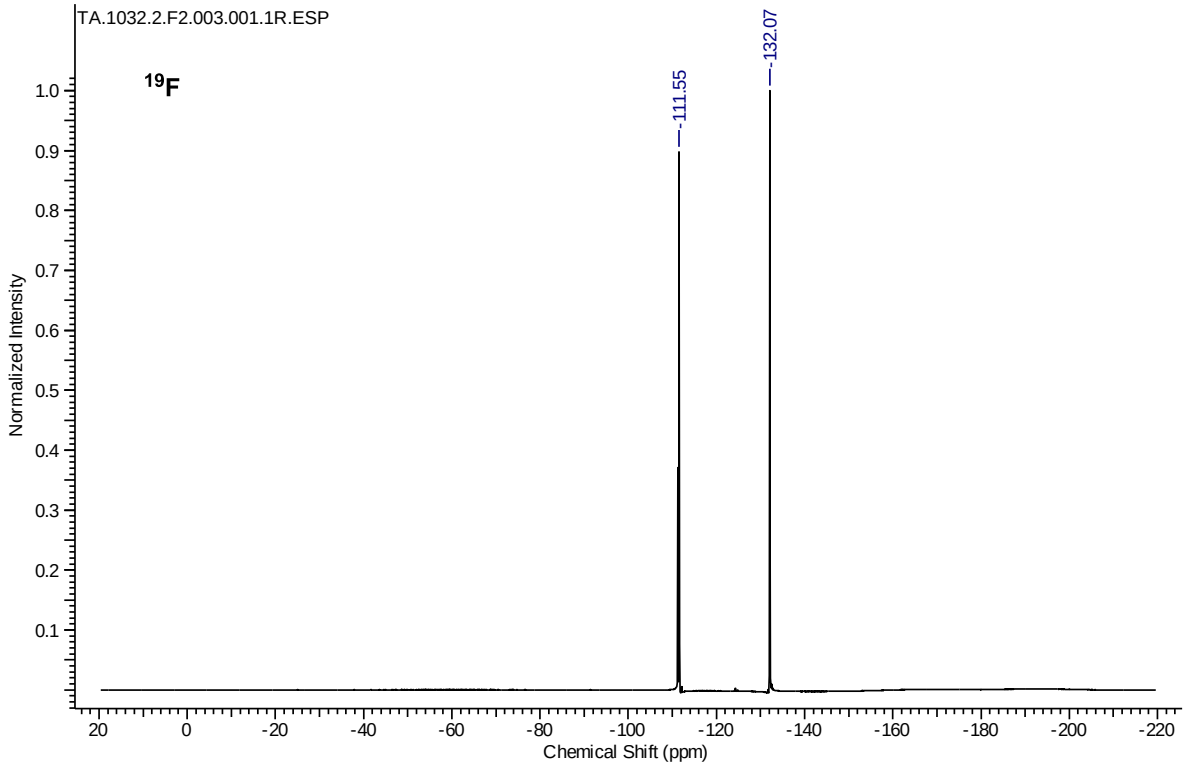
II.11. (*Z*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)-2,6-difluorophenyl) diazene (*Z*-6). An orange solution of *E*-**6** (25 mg, 0.035 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature and irradiated with UV light (*Semrock*® optical filter: 320/40, intensity: 100%, distance: 8.5 cm, time: 2 h). The resulting solution yellow solution was evaporated in the dark at 30°C and purified by HPLC to give *Z*-**6** (15 mg, 60%, >95/5 : *Z*/*E*) as yellow solid and recovered *E*-**6** (9 mg, 35%) as light orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) 7.58-7.53 (2H, m, C*H*$_{Ar}$), 7.51-7.44 (8H, m, C*H*$_{Ar}$), 7.23 (1H, dt, J_1 14, J_2 7, C*H*$_{Ar}$), 7.04 (1H, t, *J* 9, C*H*$_{Ar}$), 6.40 (2H, d, *J* 10, C*H*$_{Ar}$), 3.85 (3H, s, C*H*$_3$O); ^{13}C NMR (75 MHz, $CDCl_3$) 161.8-161.5 (m, *C*qP), 156.9 (dd, J_1 262, J_2 7, *C*qF), 152.8 (dd, J_1 253, J_2 8, *C*qF), 150.8 (d, *J* 263, *C*qF), 135.6-135.3 (m, *C*H$_{Ar}$), 133.8 (d, *J* 14, *C*H$_{Ar}$), 132.4 (d, *J* 2, *C*H$_{Ar}$), 129.4 (d, *J* 13, *C*H$_{Ar}$), 127.0 (*C*qN), 126.2 (*C*qN), 113.3 (dd, J_1 17, J_2 12, *C*H$_{Ar}$), 98.7 (dd, J_1 24, J_2 3, *C*H$_{Ar}$), 56.2 (s, *C*H$_3$O). One *C*qP is missing; ^{31}P NMR (121.5 MHz) 27.0 (s); ^{19}F NMR (282 MHz): -103.3 (s), -111.5 (s), -117.0 (s).

III. NMR Spectra (^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR)

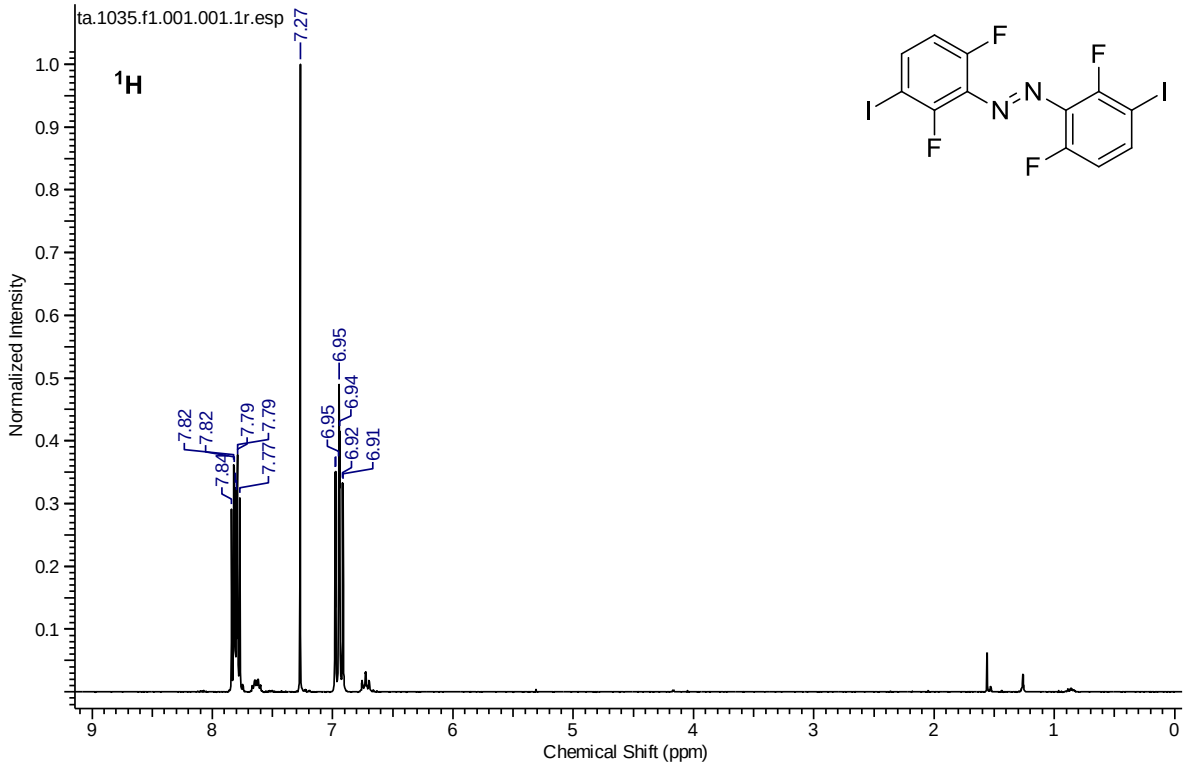
III.1. (SI-A).

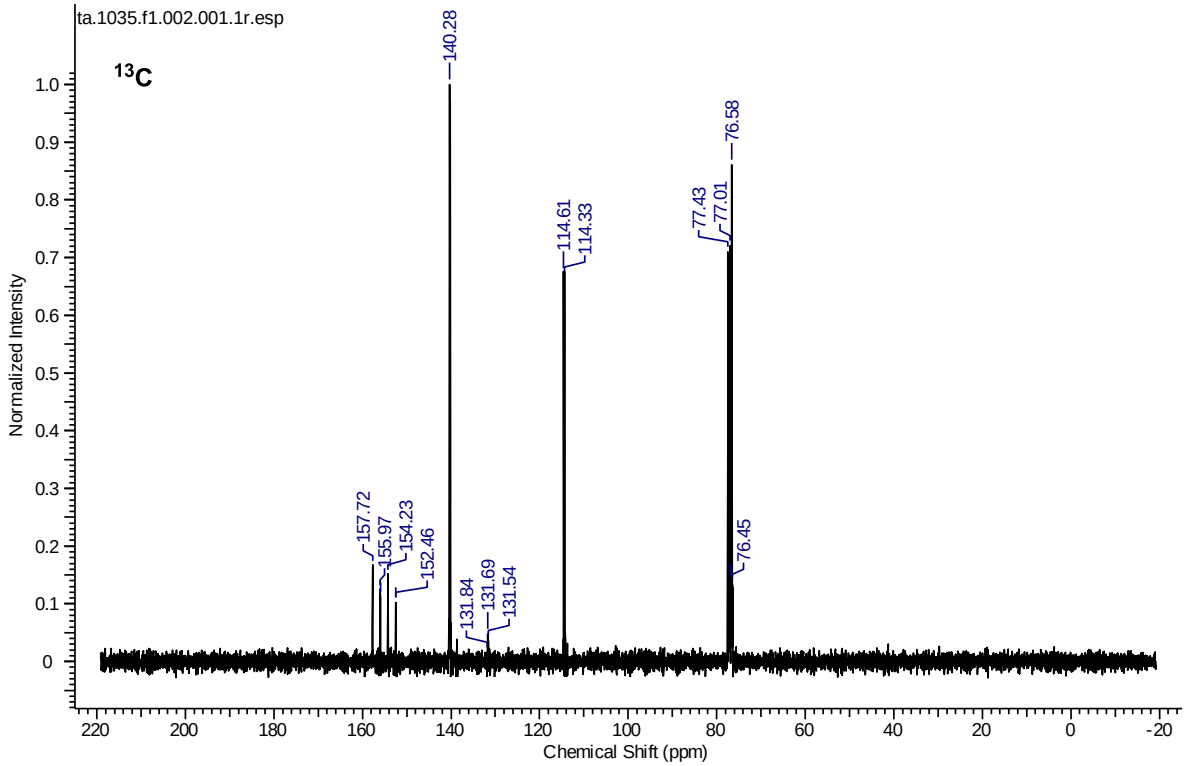


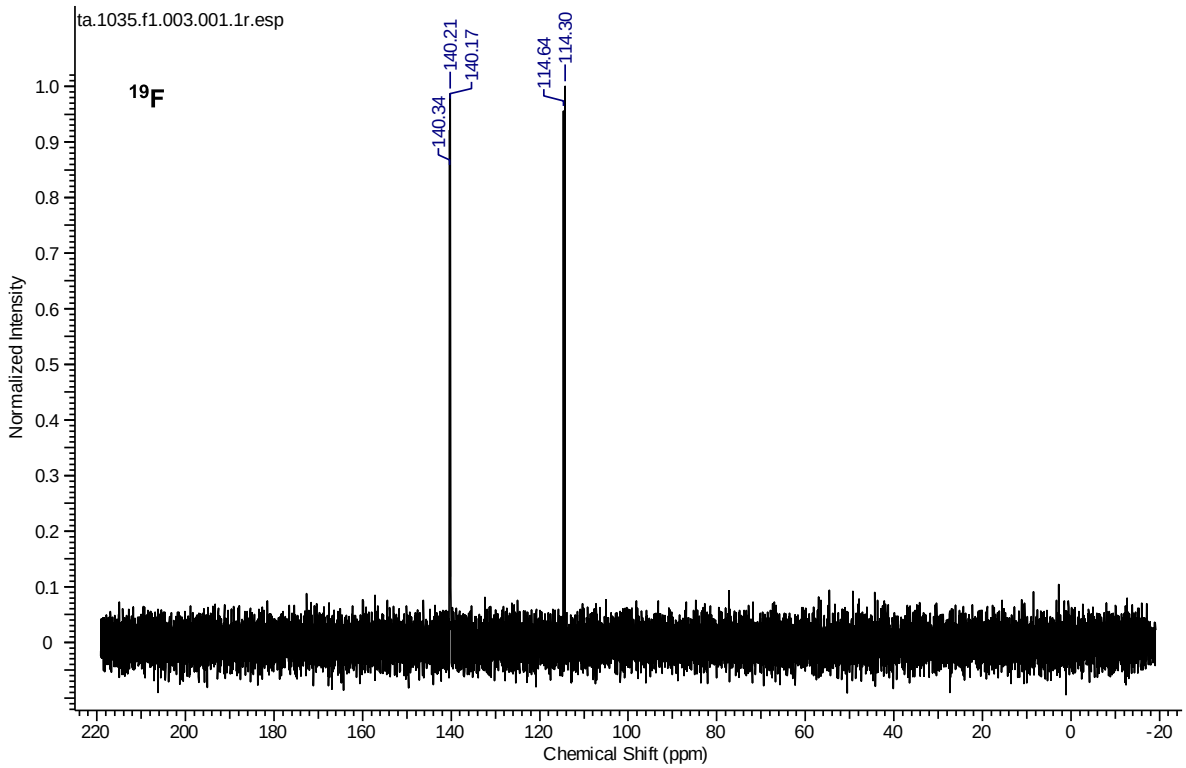




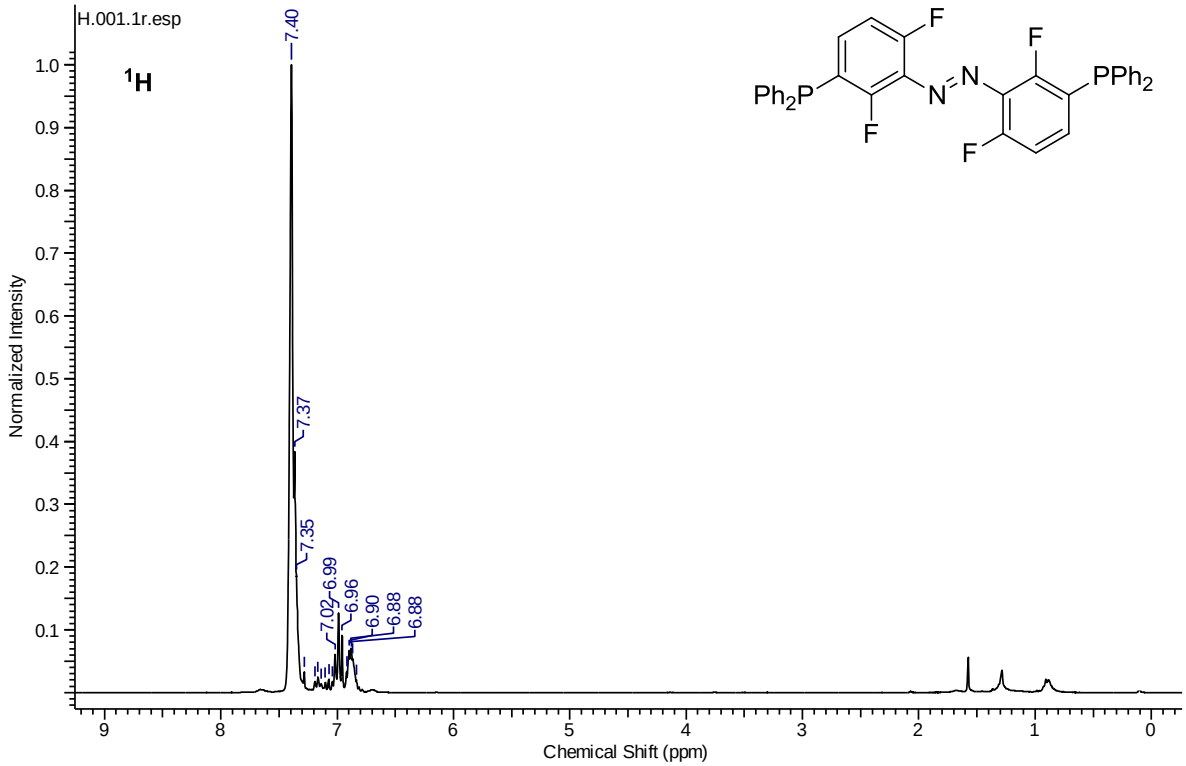
III.2. (*E*)-1,2-bis(2,6-difluoro-3-iodophenyl)diazene (1).

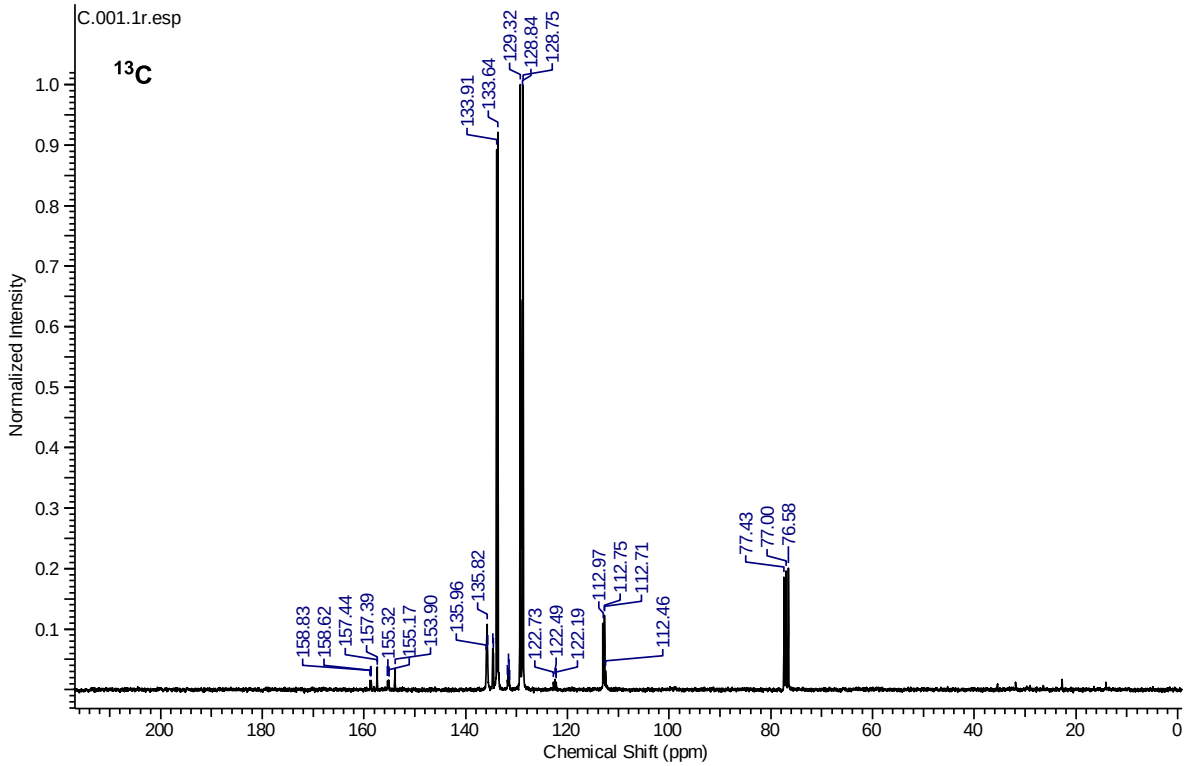


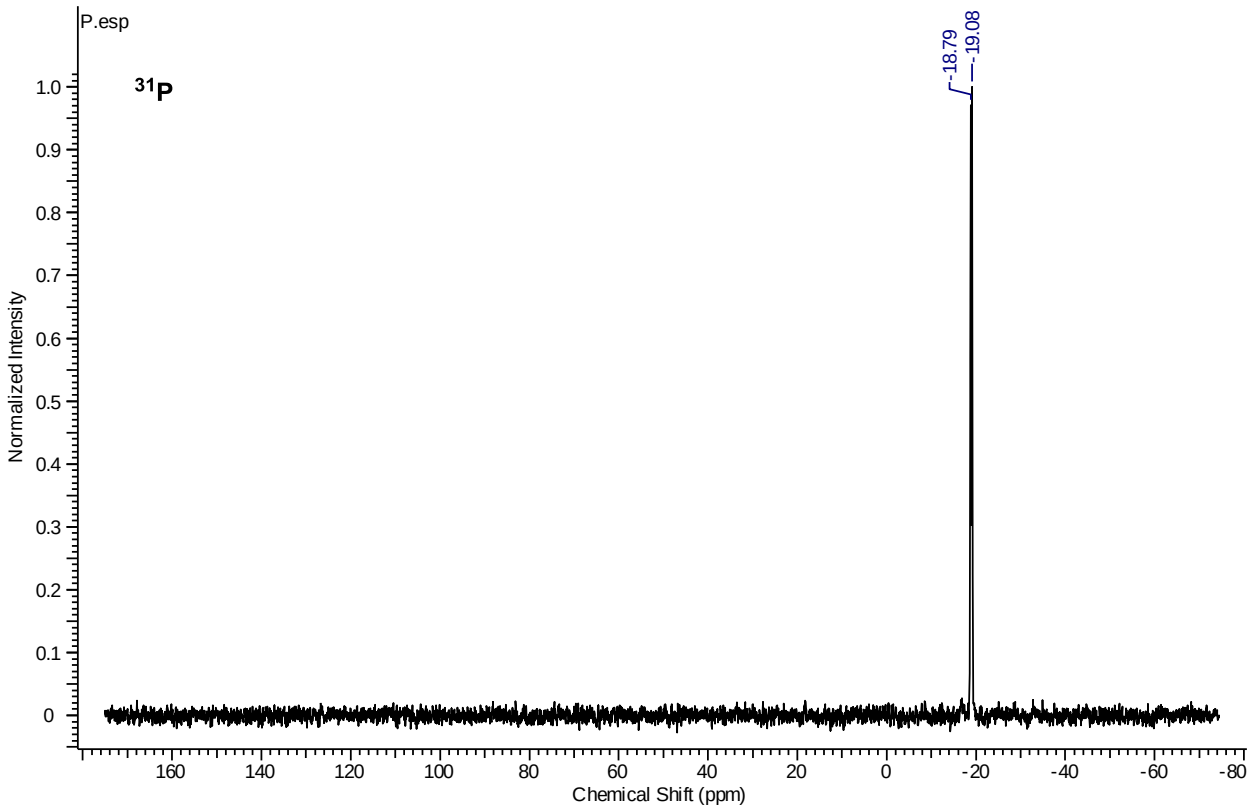

ta.1035.f1.002.001.1r.esp
13C
140.28
76.58
77.43
77.01
114.61
114.33
157.72
155.97
154.23
152.46
131.84
131.69
131.54
76.45
Normalized Intensity
Chemical Shift (ppm)

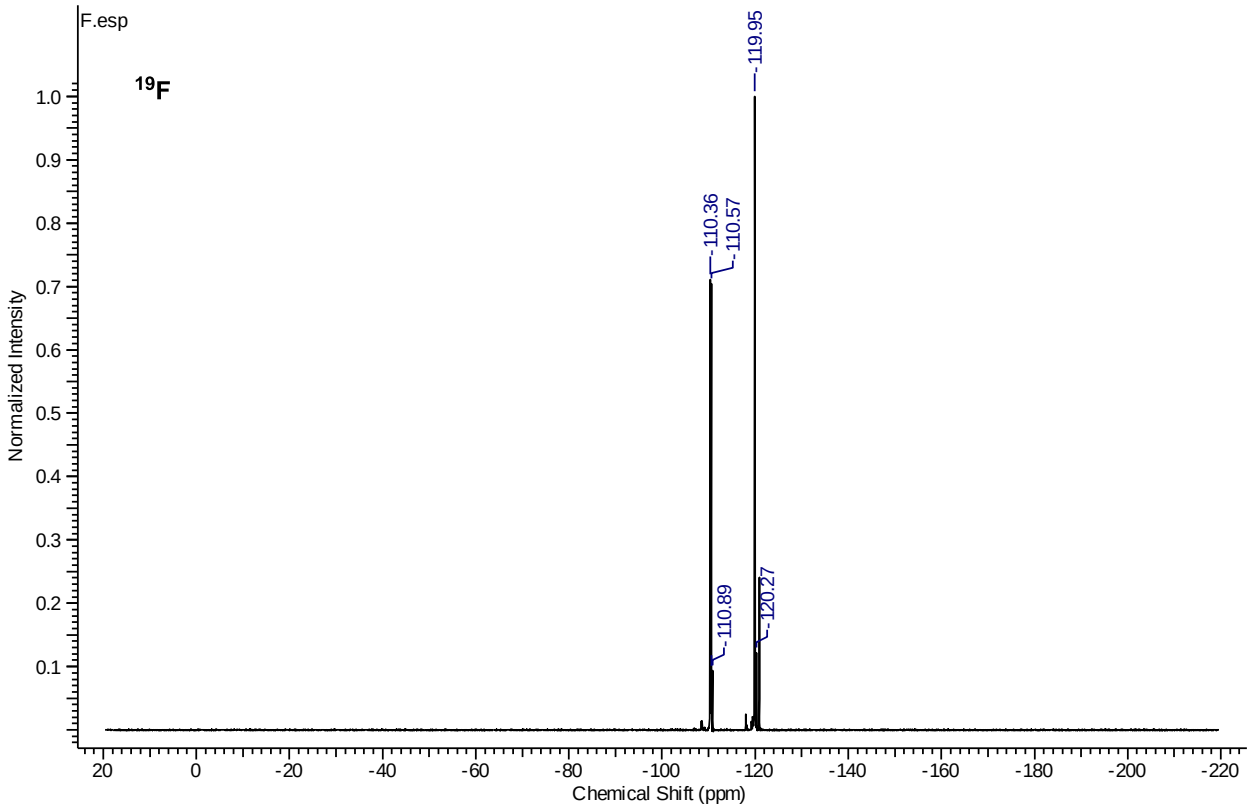

ta.1035.f1.003.001.1r.esp
19F
140.21
140.17
140.34
114.64
114.30
Normalized Intensity
Chemical Shift (ppm)

III.3. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene.

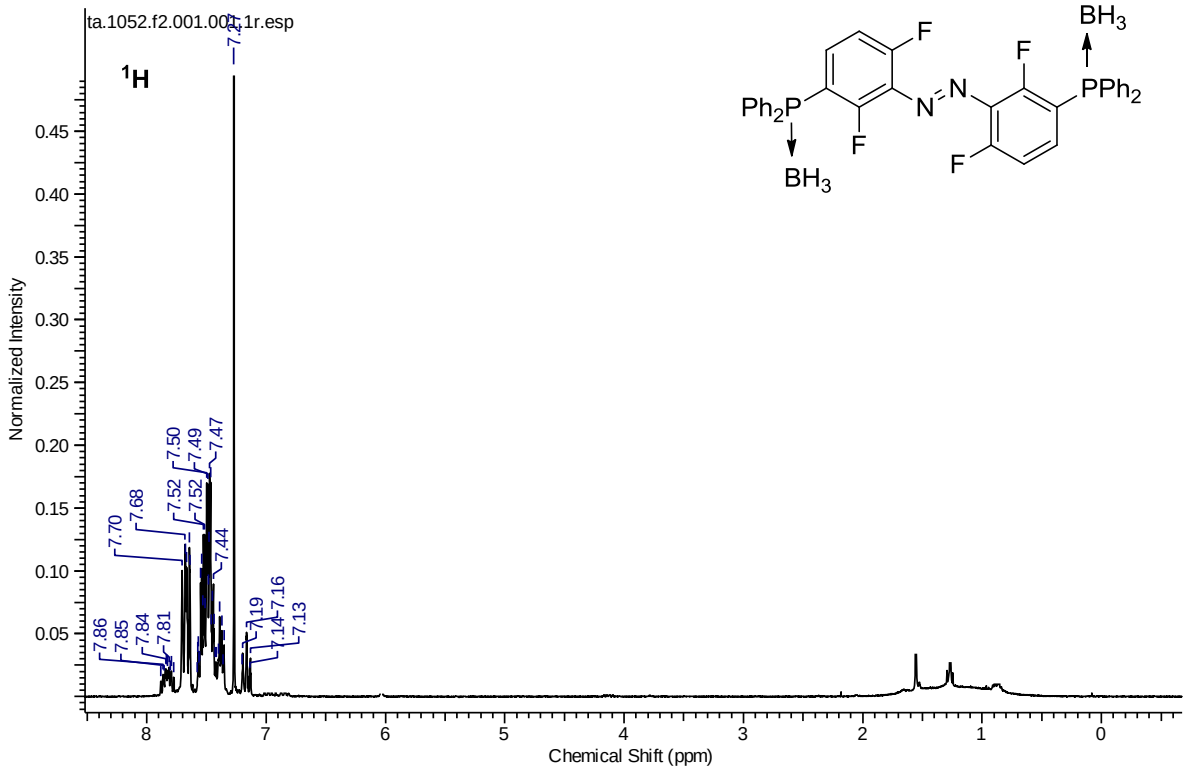


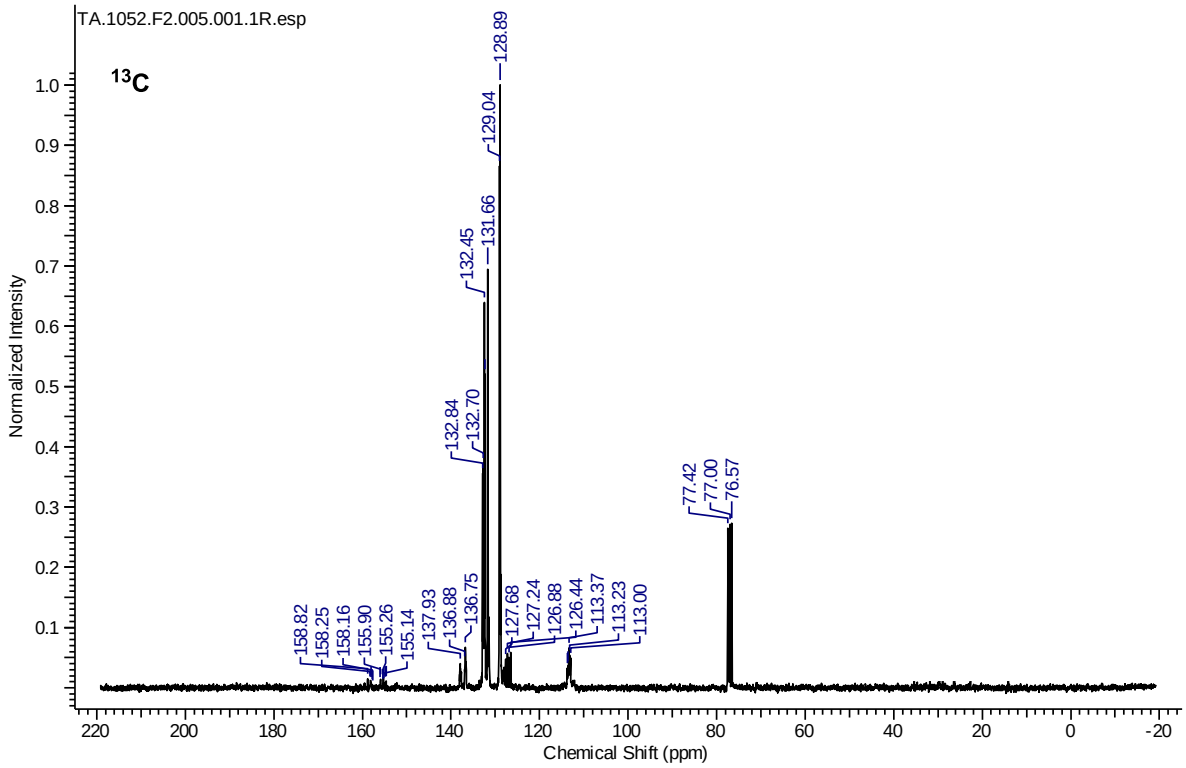


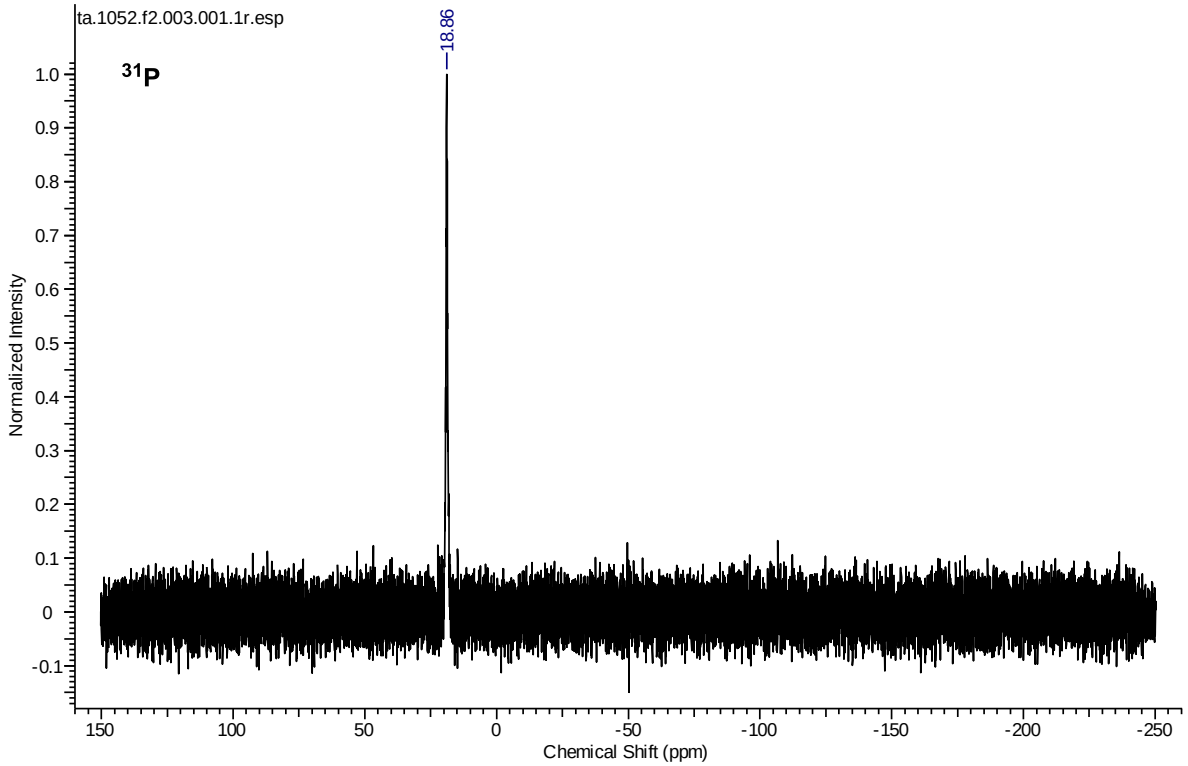

P.esp
31P
-18.79
-19.08
Normalized Intensity
Chemical Shift (ppm)

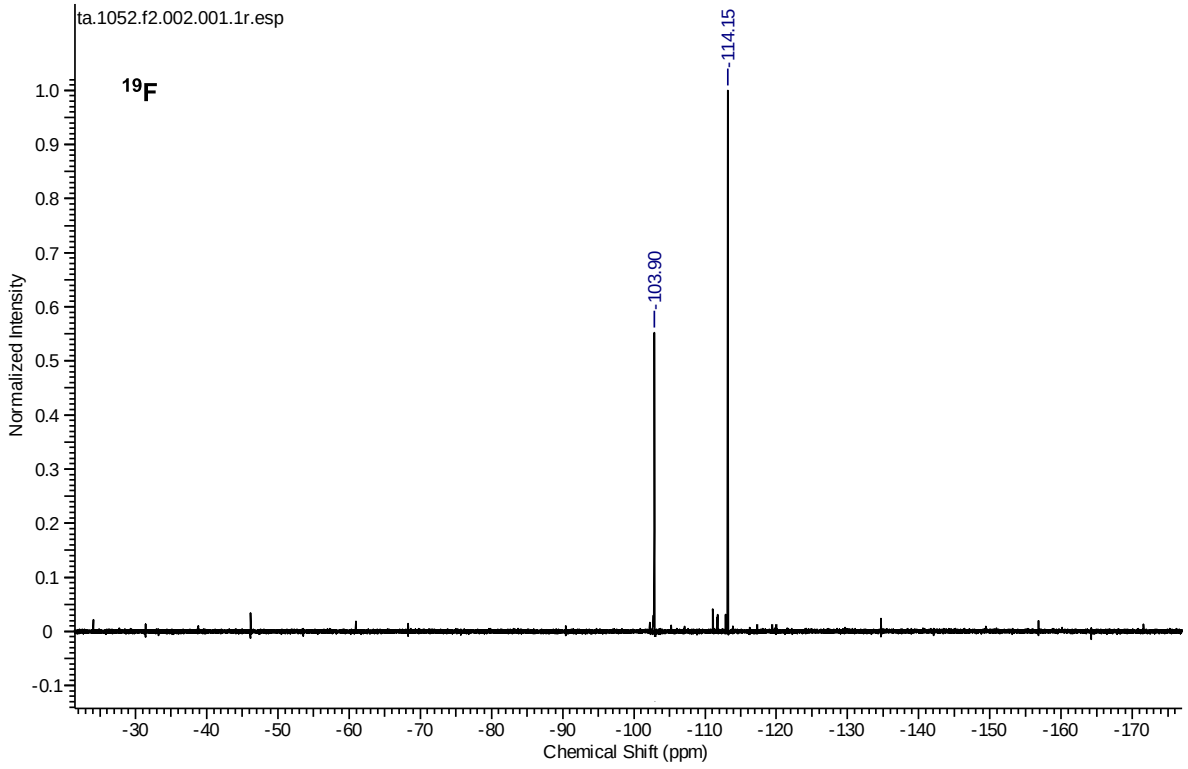

F.esp
19F
-119.95
-110.36
-110.57
-110.89
-120.27
Normalized Intensity
Chemical Shift (ppm)

III.4. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (2).

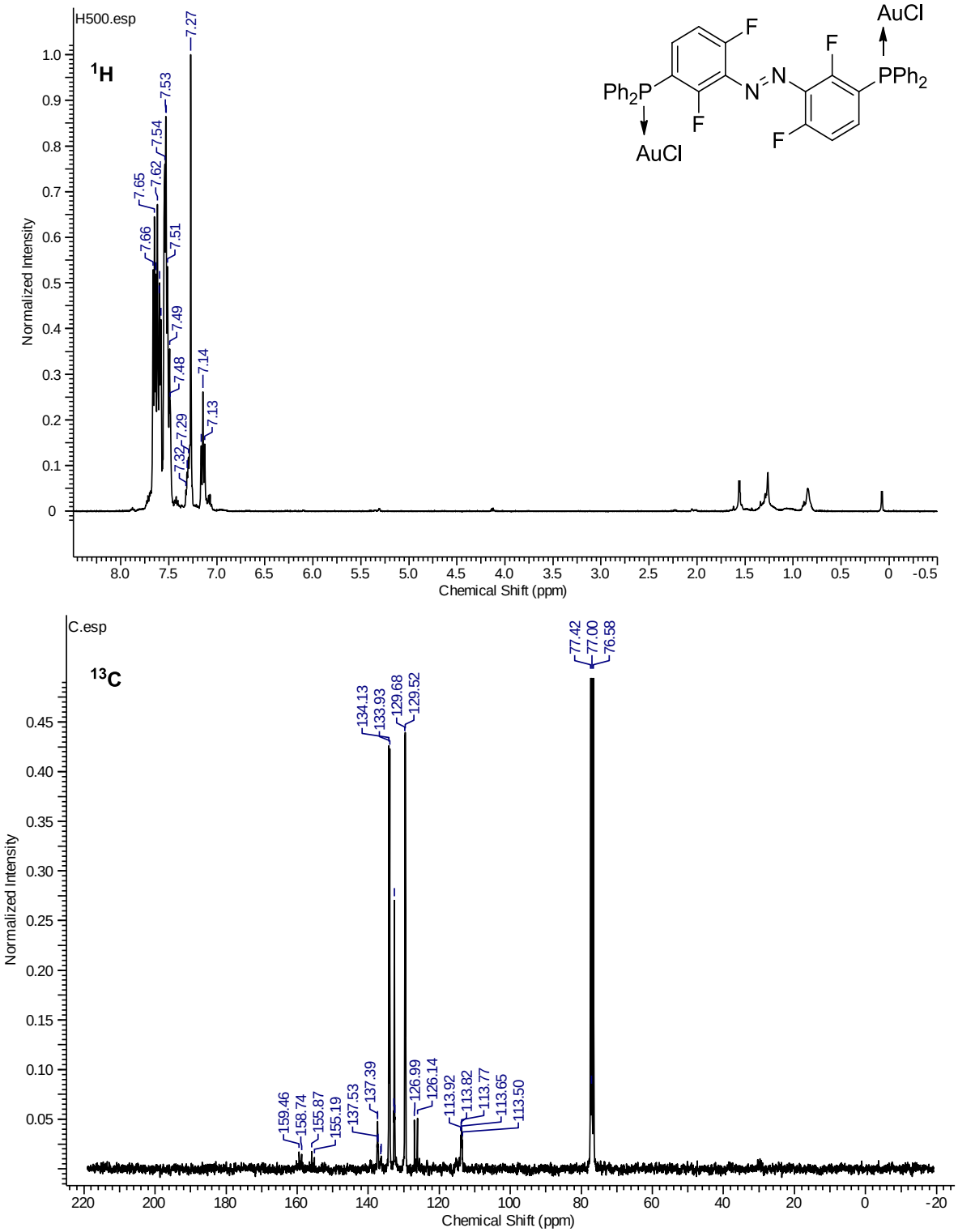


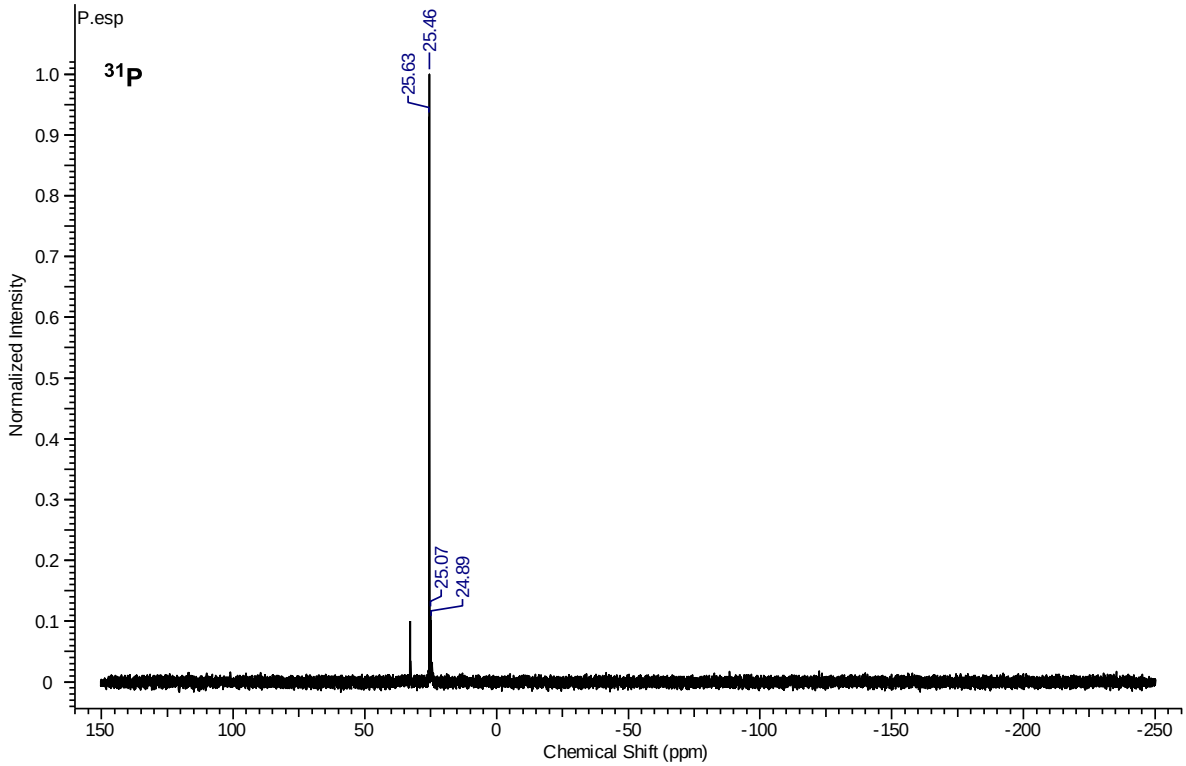


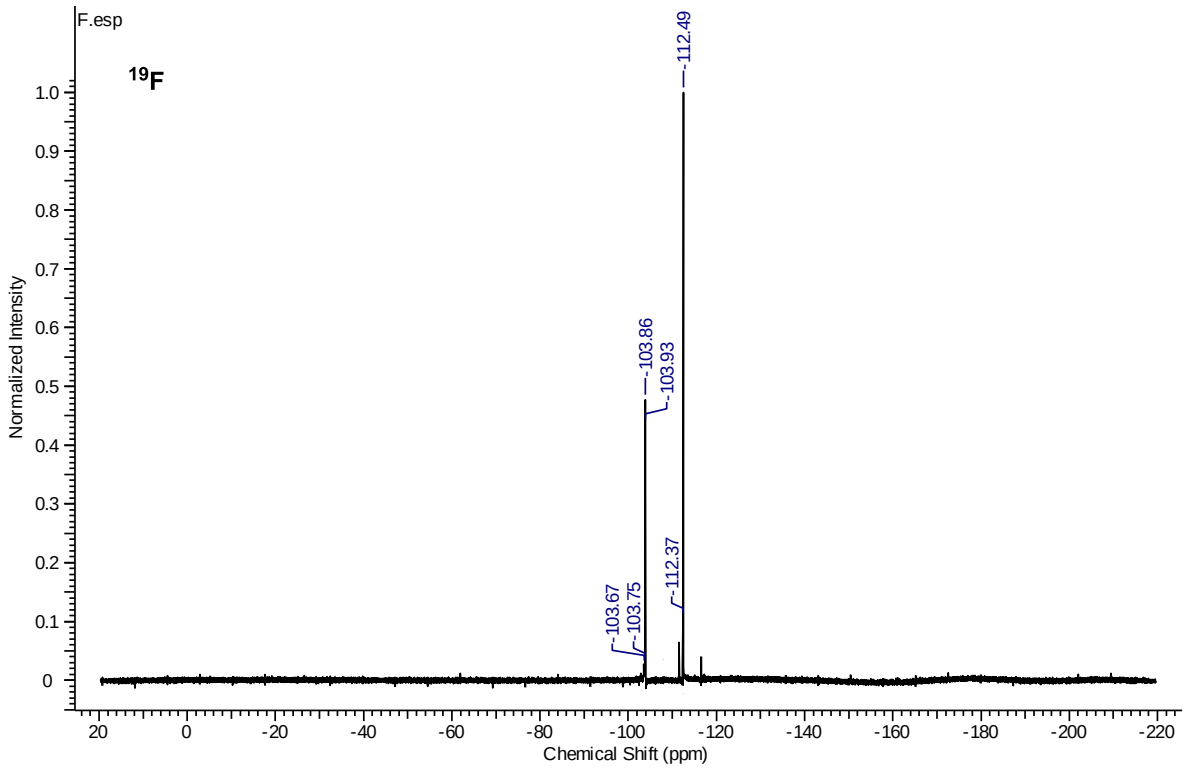

ta.1052.f2.003.001.1r.esp
31P
18.86
Normalized Intensity
Chemical Shift (ppm)


ta.1052.f2.002.001.1r.esp
19F
-114.15
-103.90
Normalized Intensity
Chemical Shift (ppm)

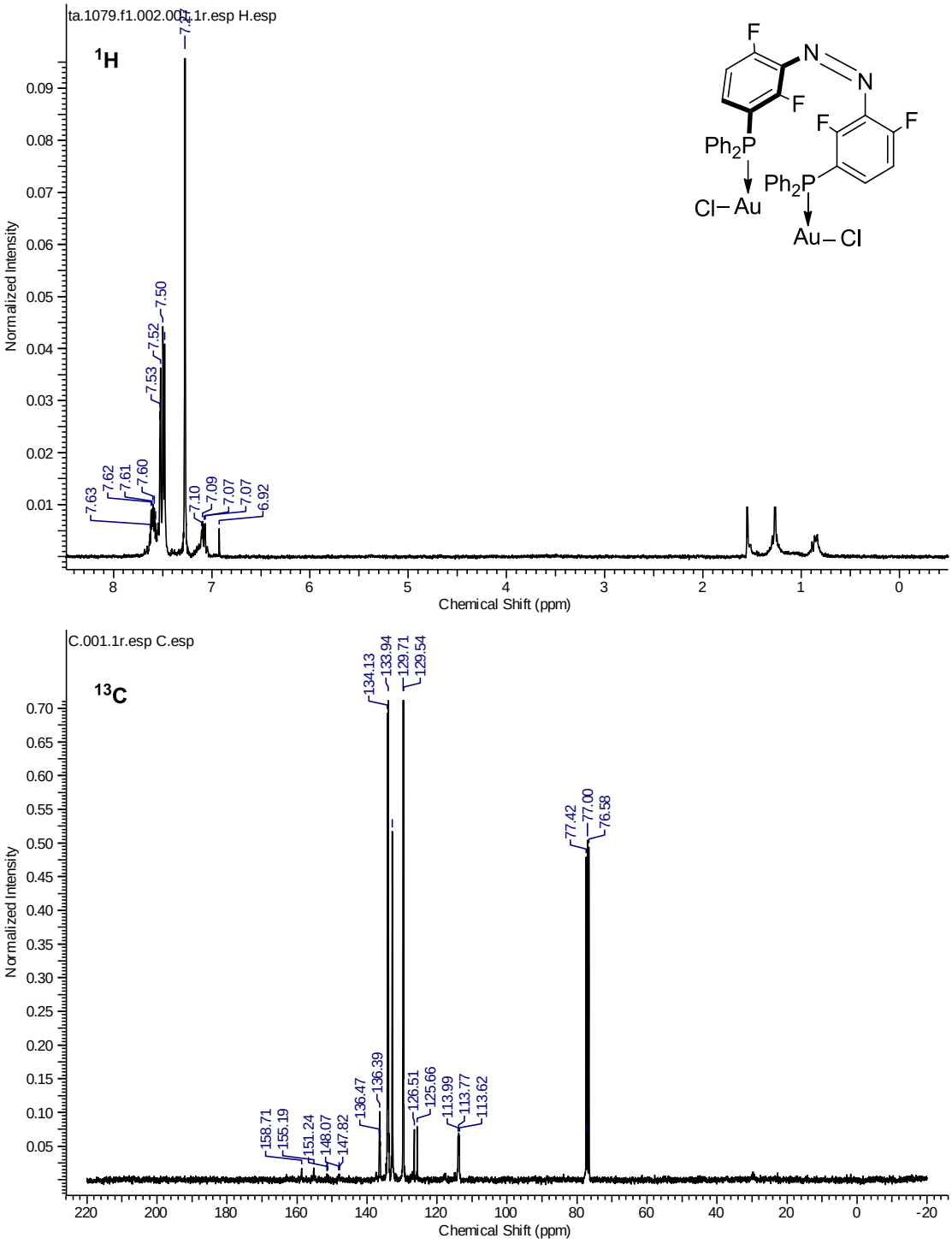
III.5. (*E*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (*E*-3).

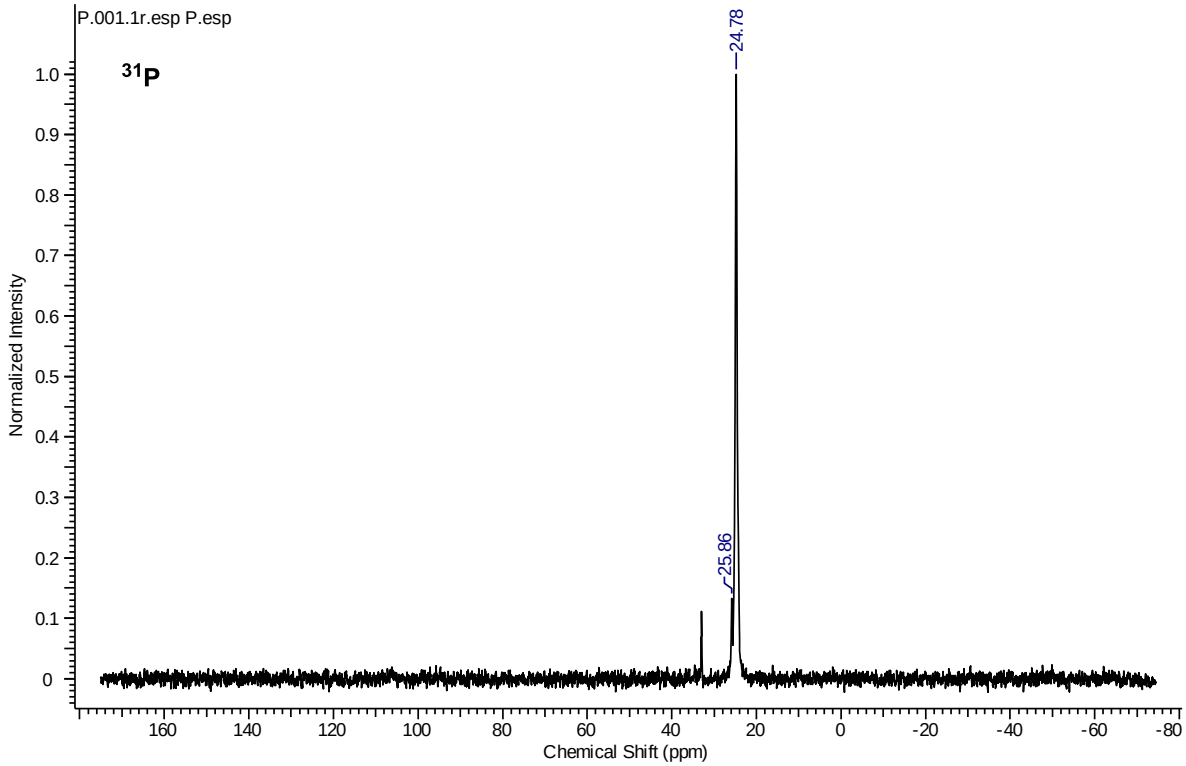


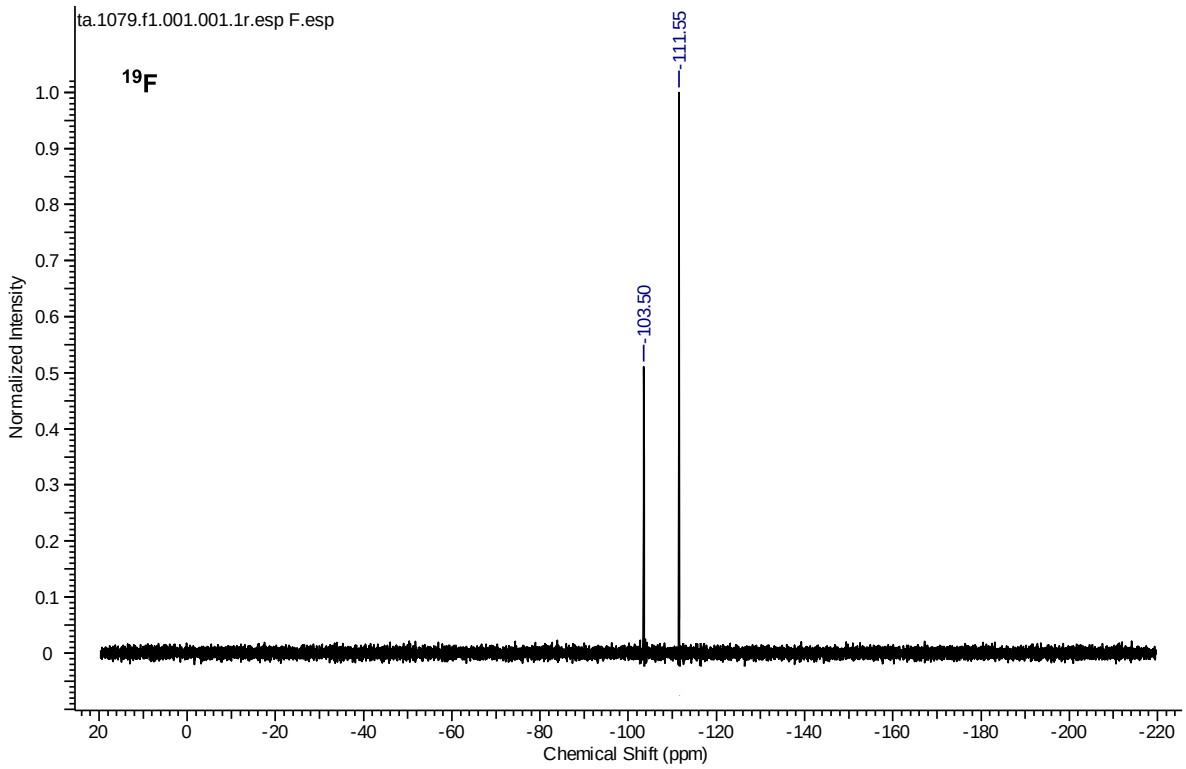

P.esp
31P
25.63
25.46
25.07
24.89
Normalized Intensity
Chemical Shift (ppm)


F.esp
19F
-112.49
-103.86
-103.93
-112.37
-103.67
-103.75
Normalized Intensity
Chemical Shift (ppm)

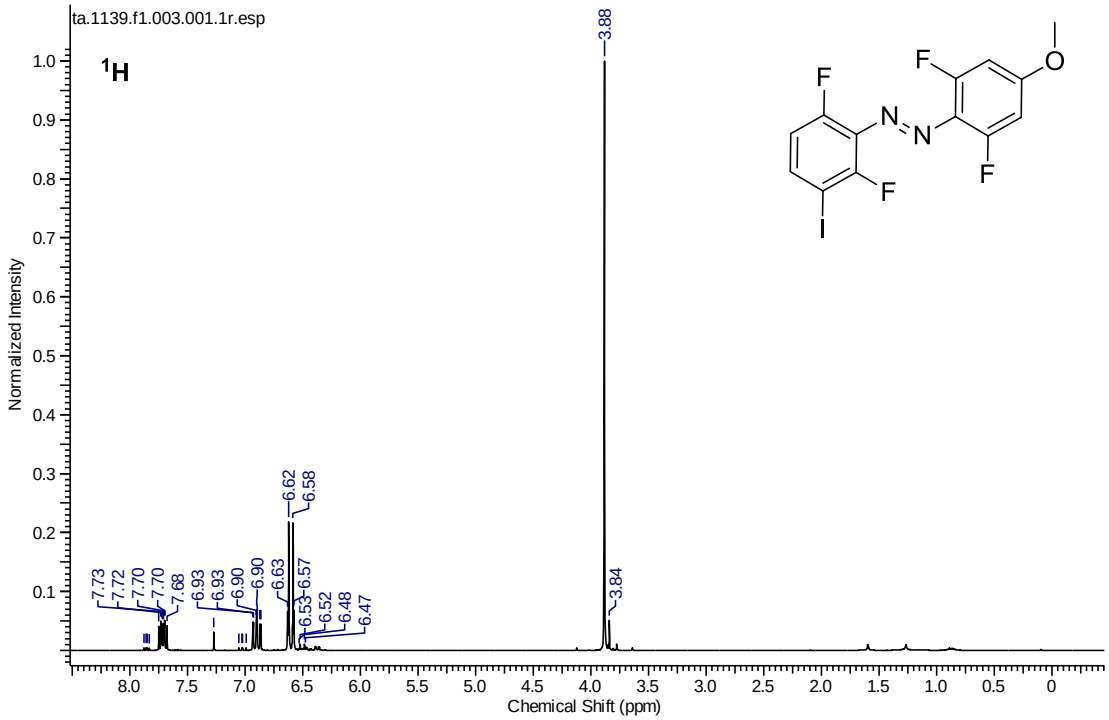
III.6. (*Z*)-1,2-bis(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (*Z*-3).

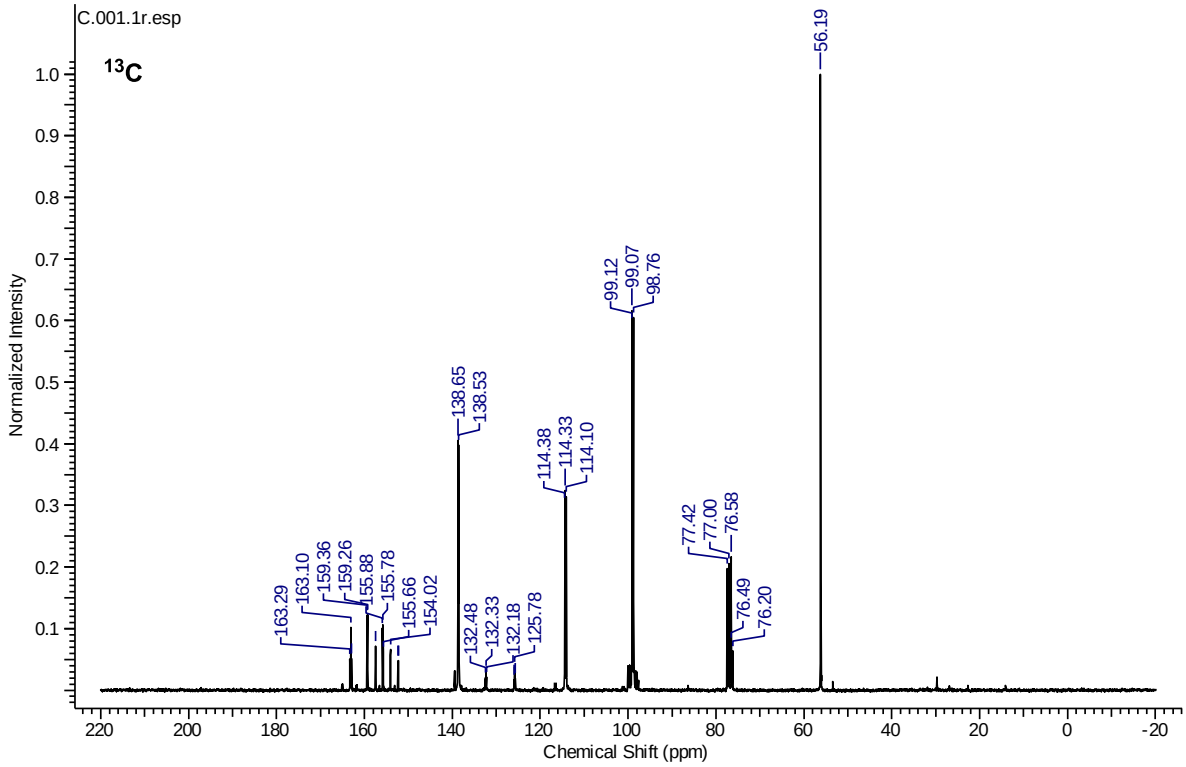


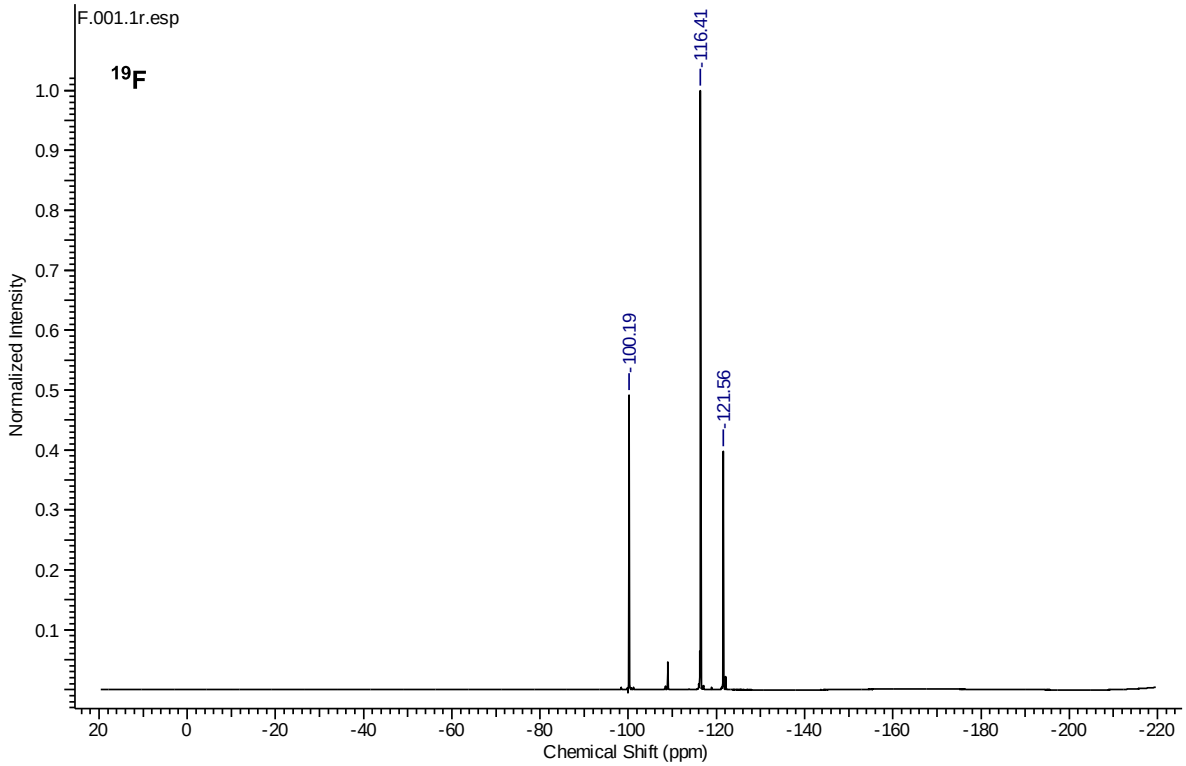

P.001.1r.esp P.esp
31P
24.78
25.86
Normalized Intensity
Chemical Shift (ppm)


ta.1079.f1.001.001.1r.esp F.esp
19F
-111.55
-103.50
Normalized Intensity
Chemical Shift (ppm)

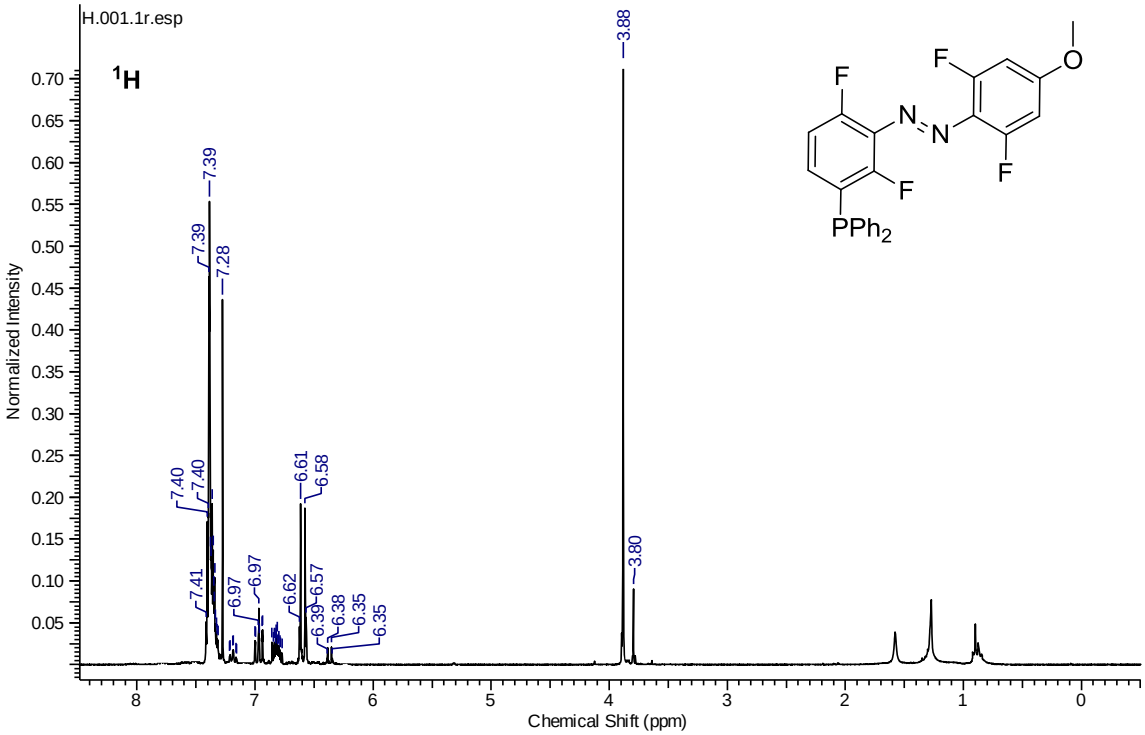
III.7. (*E*)-1-(2,6-difluoro-3-iodophenyl)-2-(2,6-difluoro-4-methoxyphenyl)diazene (SI-C).

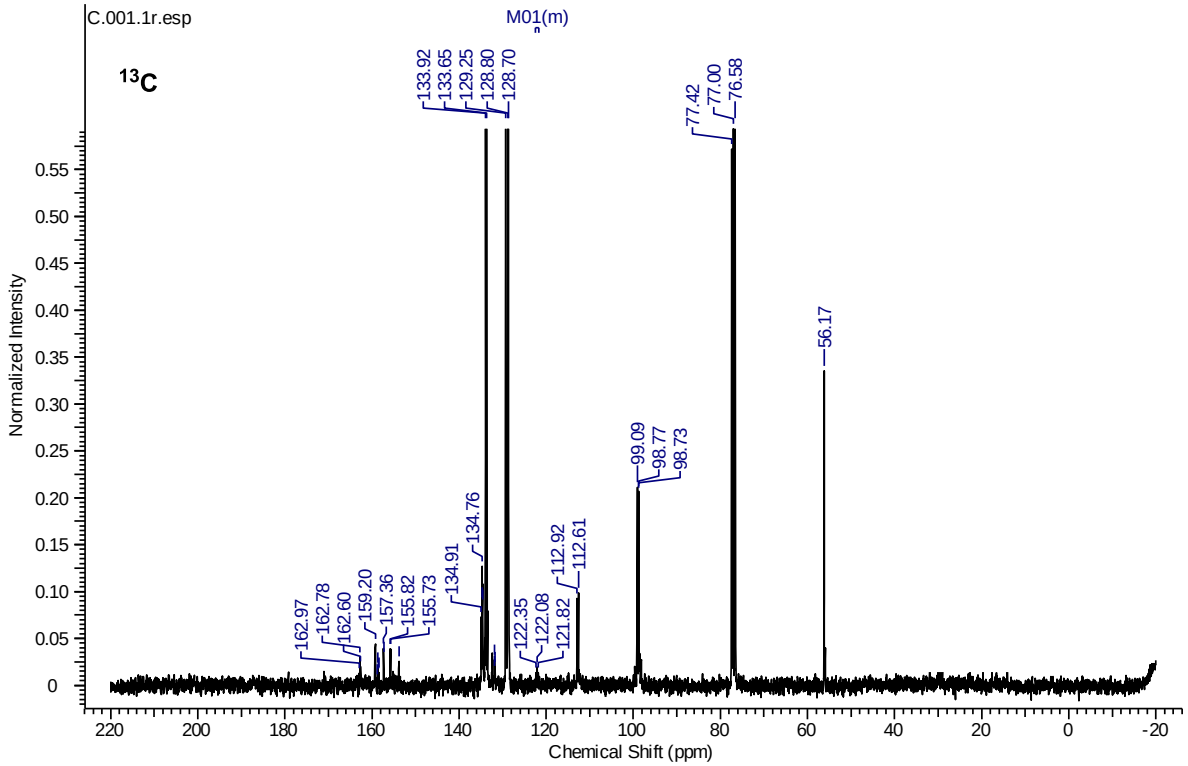


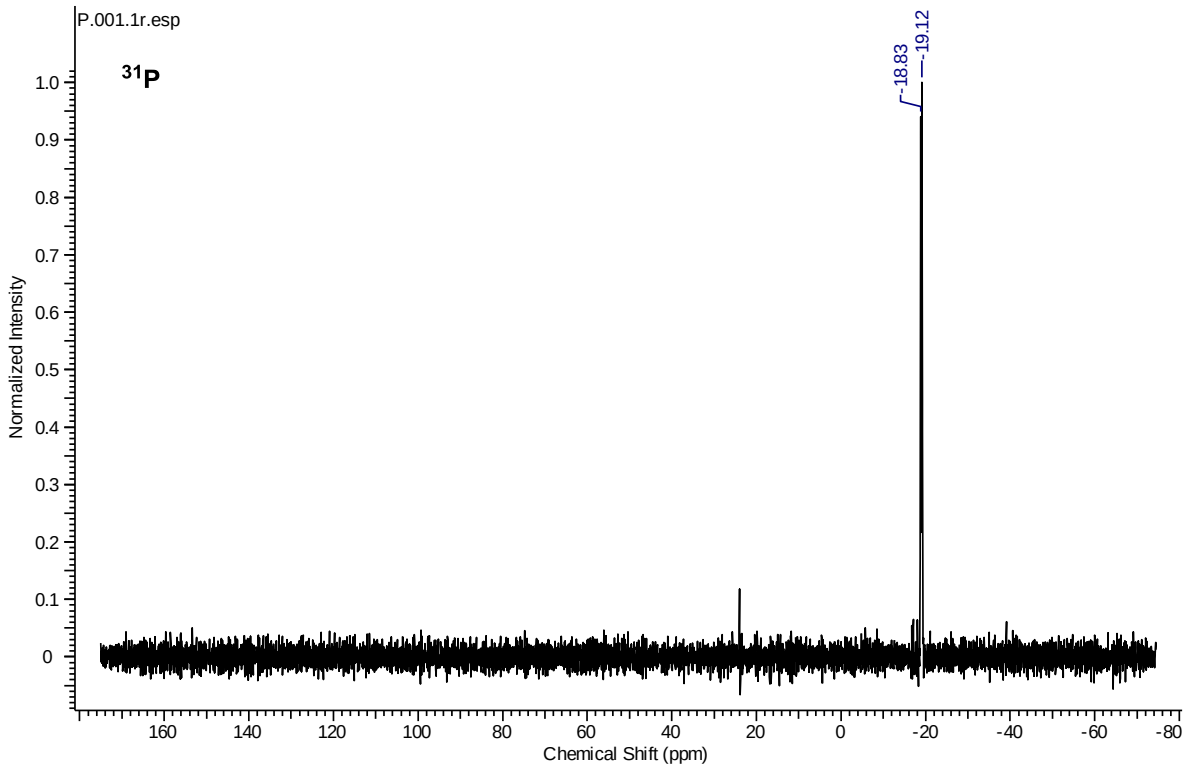


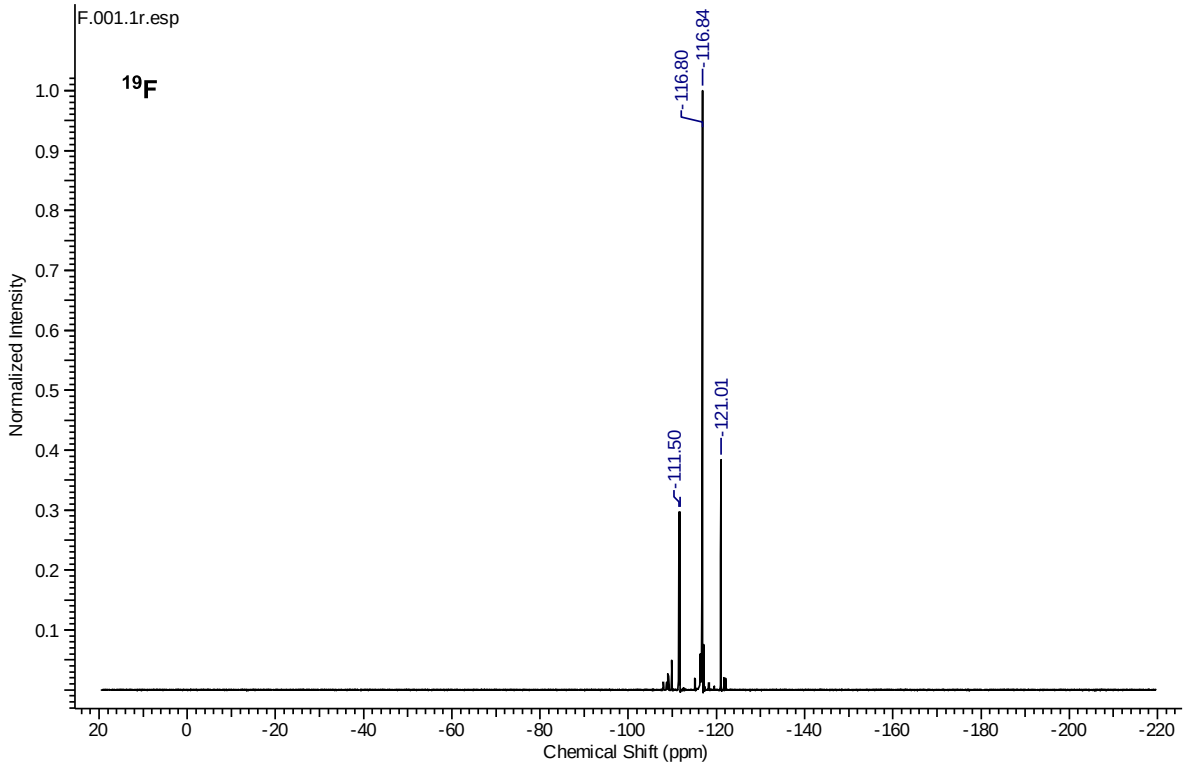


III.8.(*E*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)-2,6-difluorophenyl)diazene (SI-D).

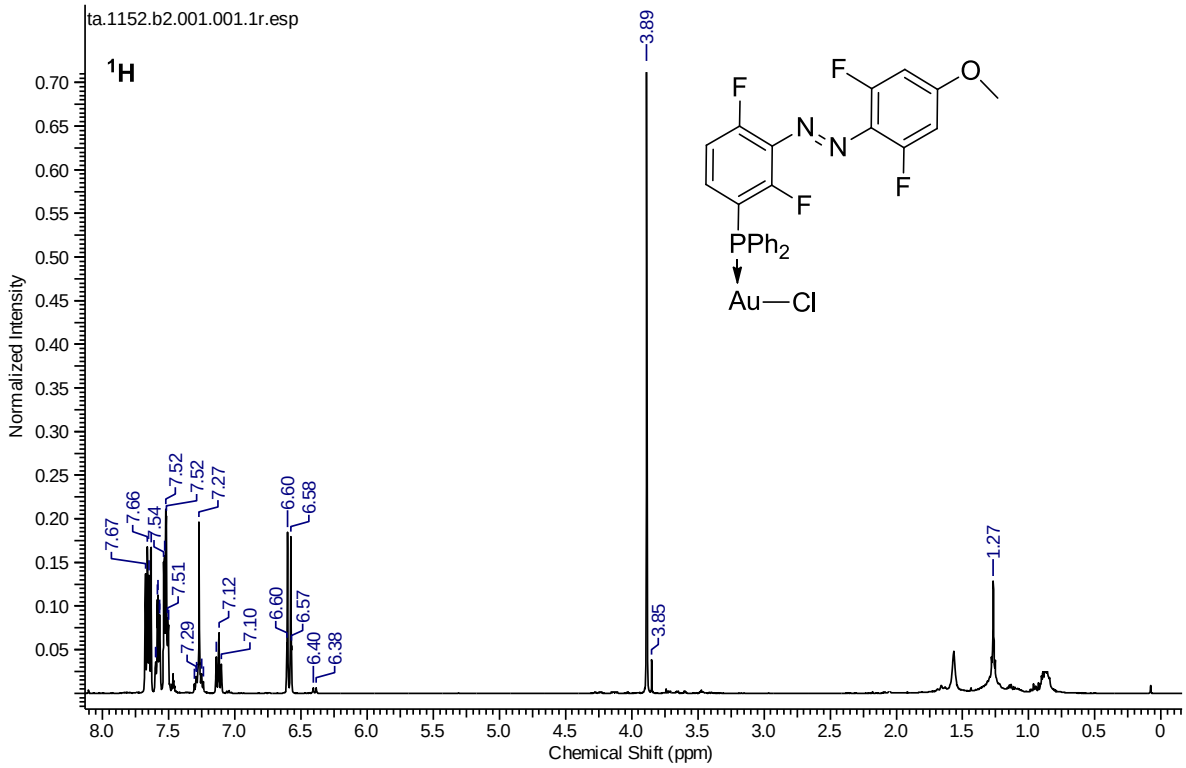


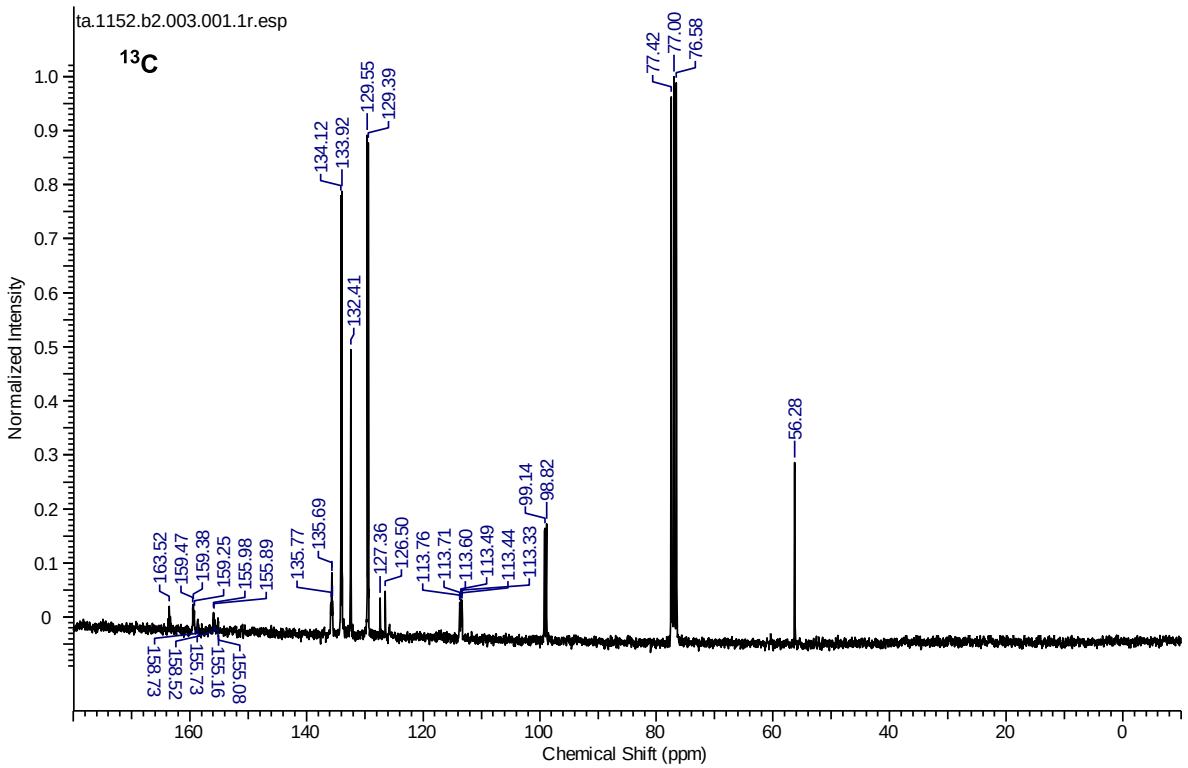

C.001.1r.esp
M01(m)
^{13}C
133.92
133.65
129.25
128.80
128.70
77.42
77.00
76.58
56.17
99.09
98.77
98.73
134.76
134.91
112.92
112.61
162.97
162.78
162.60
159.20
157.36
155.82
155.73
122.35
122.08
121.82
Normalized Intensity
Chemical Shift (ppm)

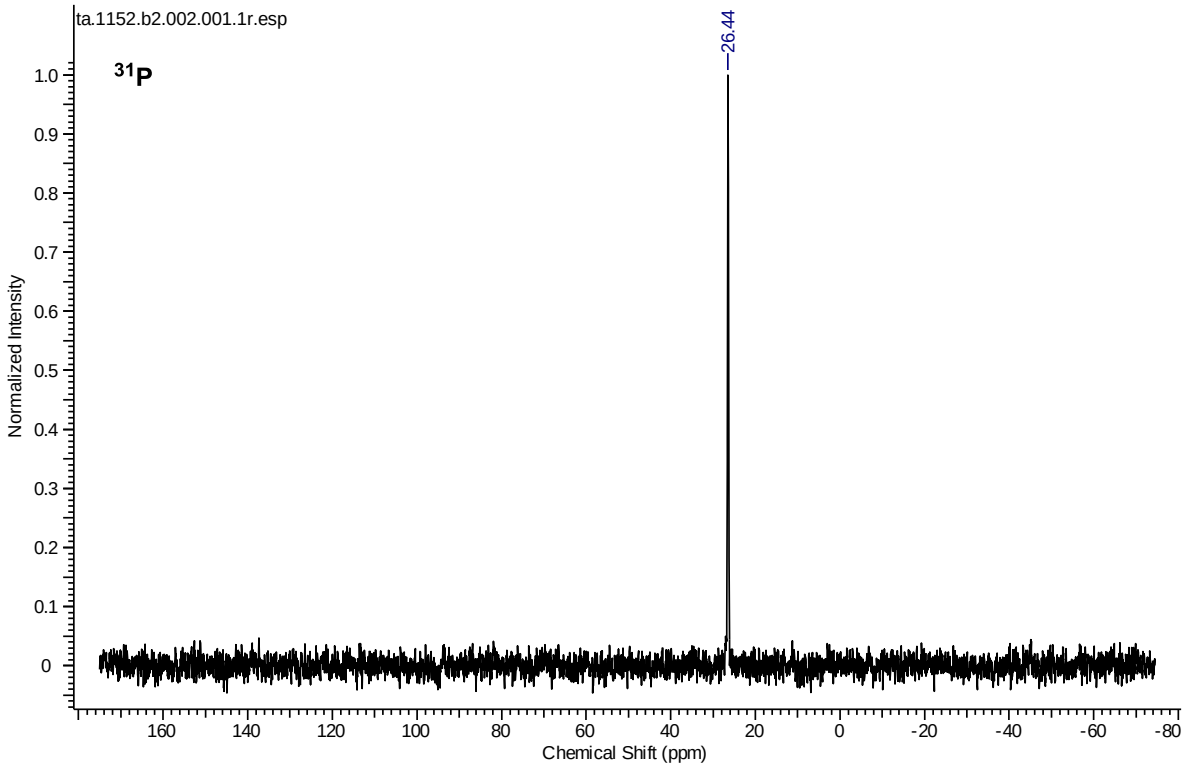

P.001.1r.esp
^{31}P
18.83
19.12
Normalized Intensity
Chemical Shift (ppm)

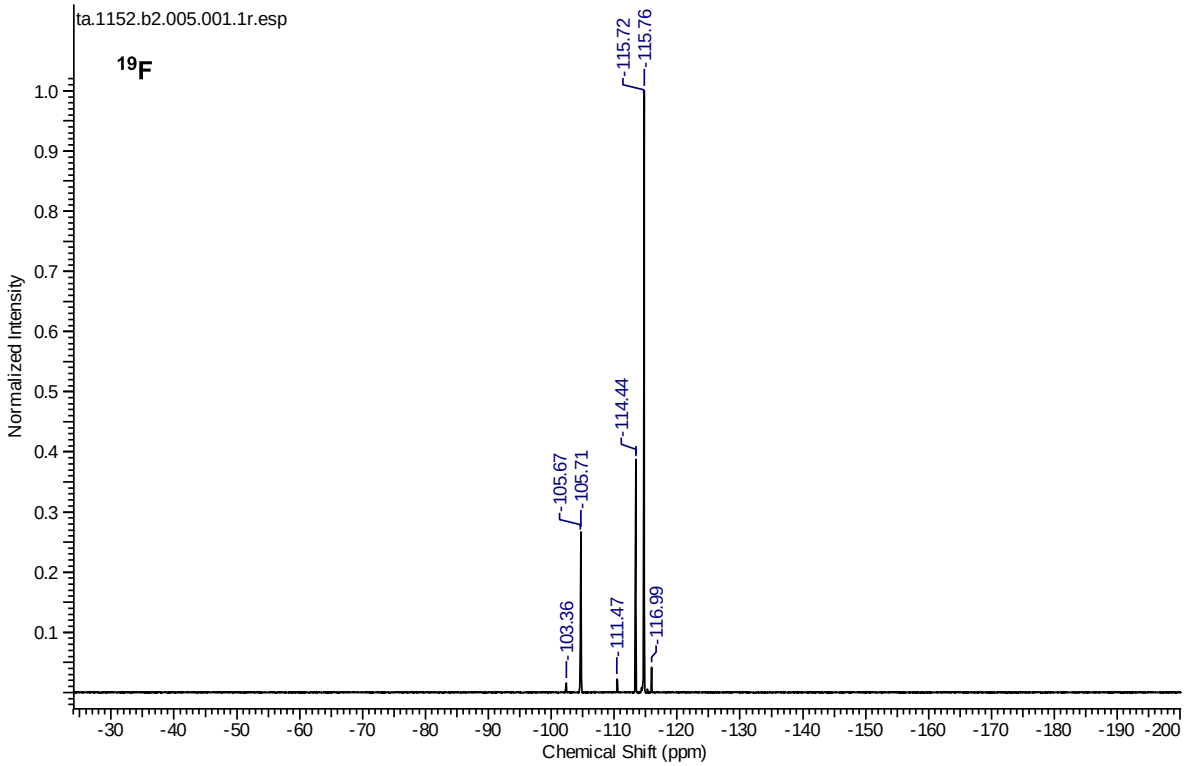


III.9. (*E*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)-2,6-difluorophenyl) diazene (*E*-6).

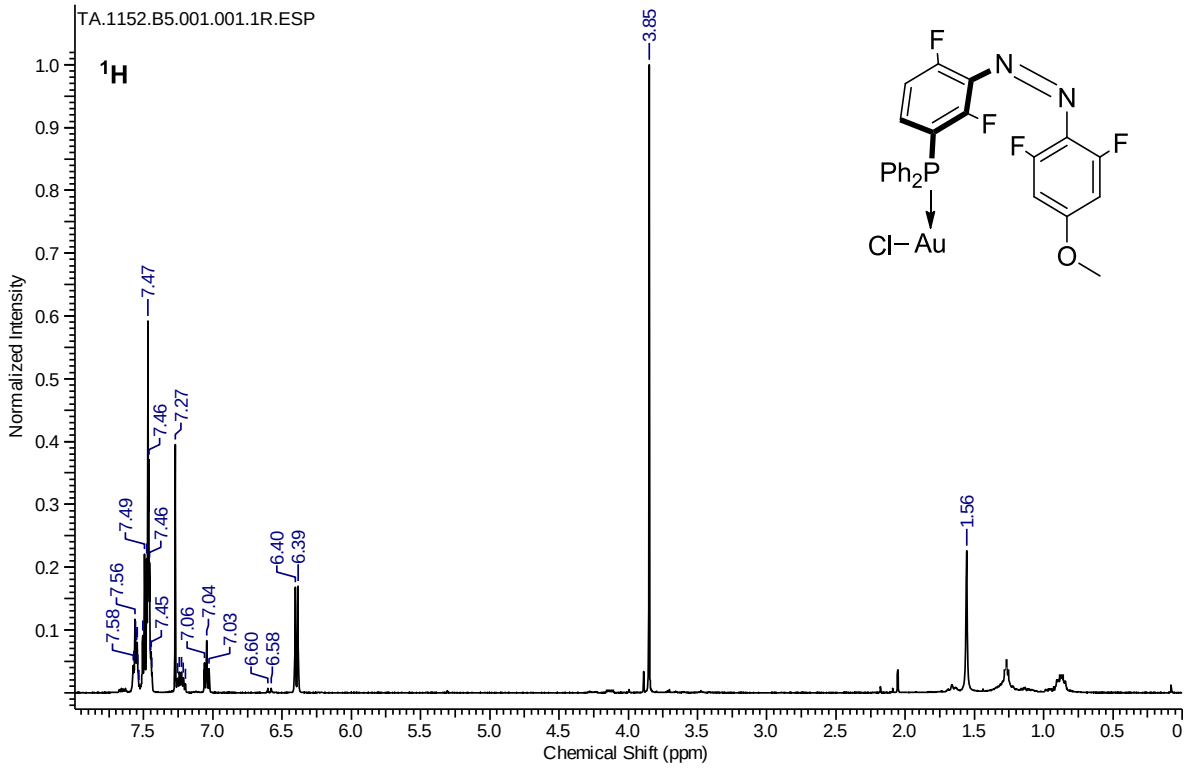


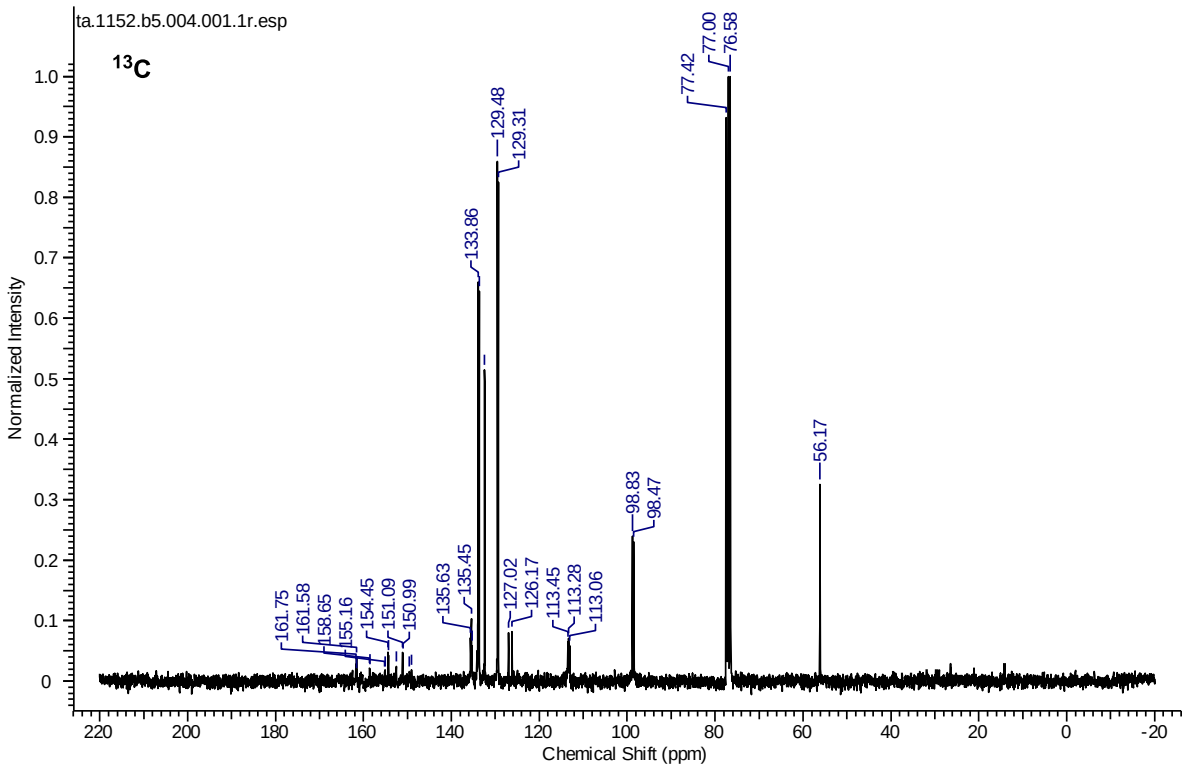

ta.1152.b2.003.001.1r.esp
13C
Normalized Intensity
Chemical Shift (ppm)
77.42
77.00
76.58
129.55
129.39
134.12
133.92
132.41
56.28
99.14
98.82
163.52
159.47
159.38
159.25
155.98
155.89
135.77
135.69
127.36
126.50
113.76
113.71
113.60
113.49
113.44
113.33
158.73
158.52
156.73
156.16
156.08

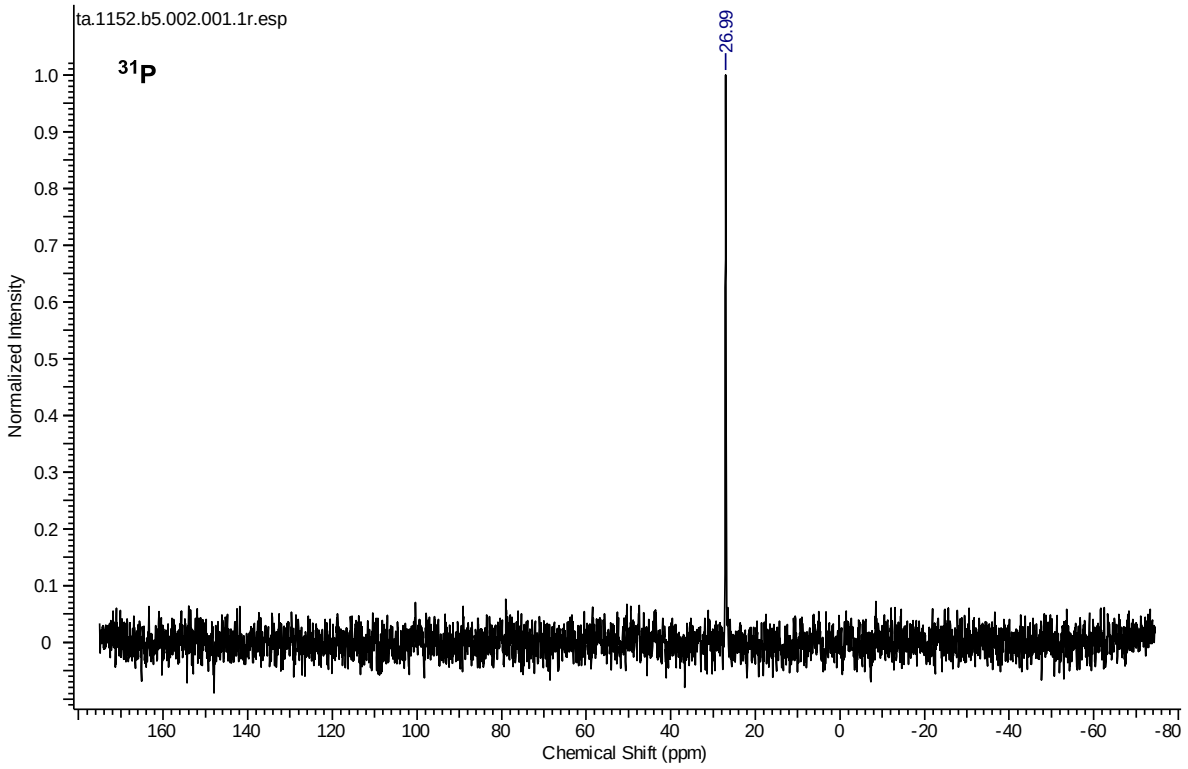

ta.1152.b2.002.001.1r.esp
31P
Normalized Intensity
Chemical Shift (ppm)
26.44

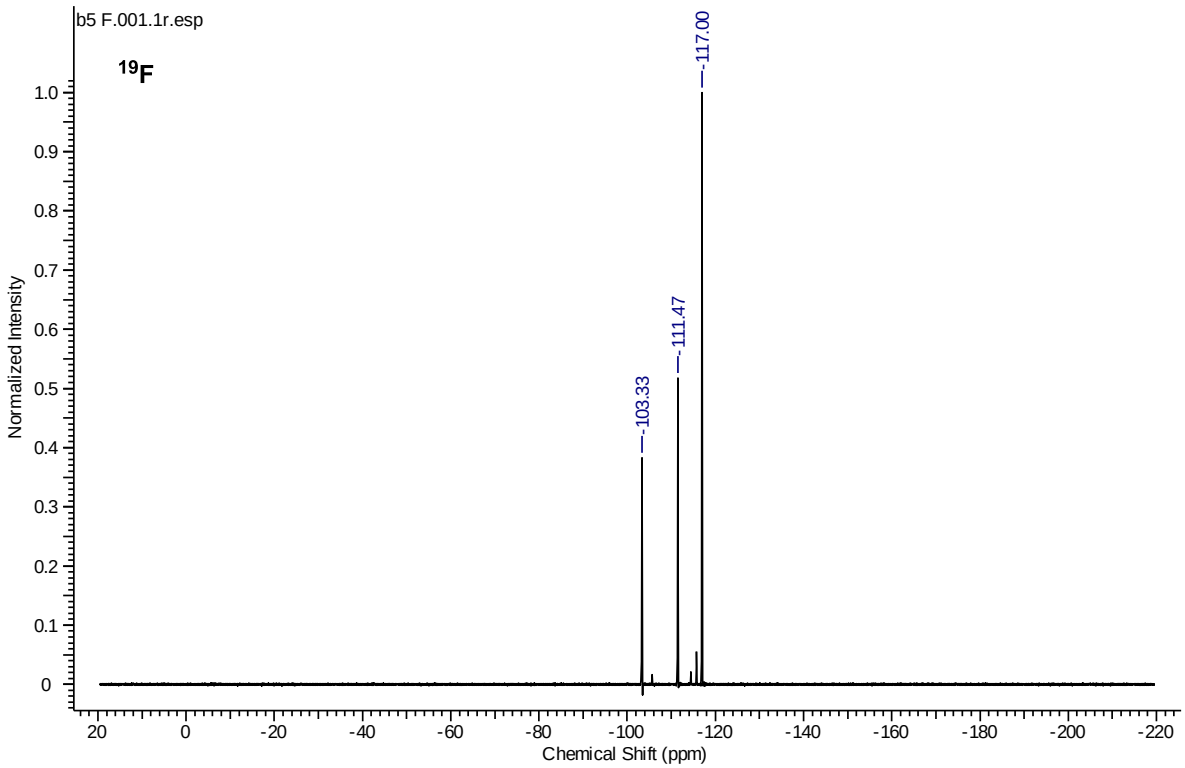


III.10. (*Z*)-1-(2,6-difluoro-4-methoxyphenyl)-2-(3-(diphenylphosphino)-2,6-difluorophenyl) diazene (*Z*-6).




ta.1152.b5.004.001.1r.esp
13C
Normalized Intensity
Chemical Shift (ppm)
161.75
161.58
158.65
155.16
154.45
151.09
150.99
135.63
135.45
133.86
129.48
129.31
127.02
126.17
113.45
113.28
113.06
98.83
98.47
77.42
77.00
76.58
56.17

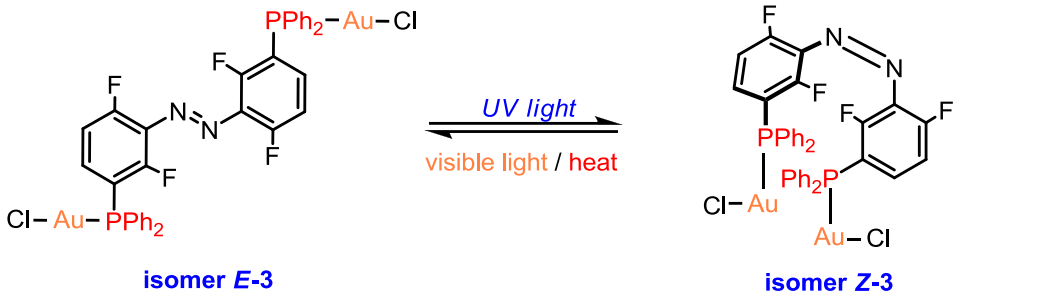

ta.1152.b5.002.001.1r.esp
31P
Normalized Intensity
Chemical Shift (ppm)
26.99


b5 F.001.1r.esp
19F
-117.00
-111.47
-103.33
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

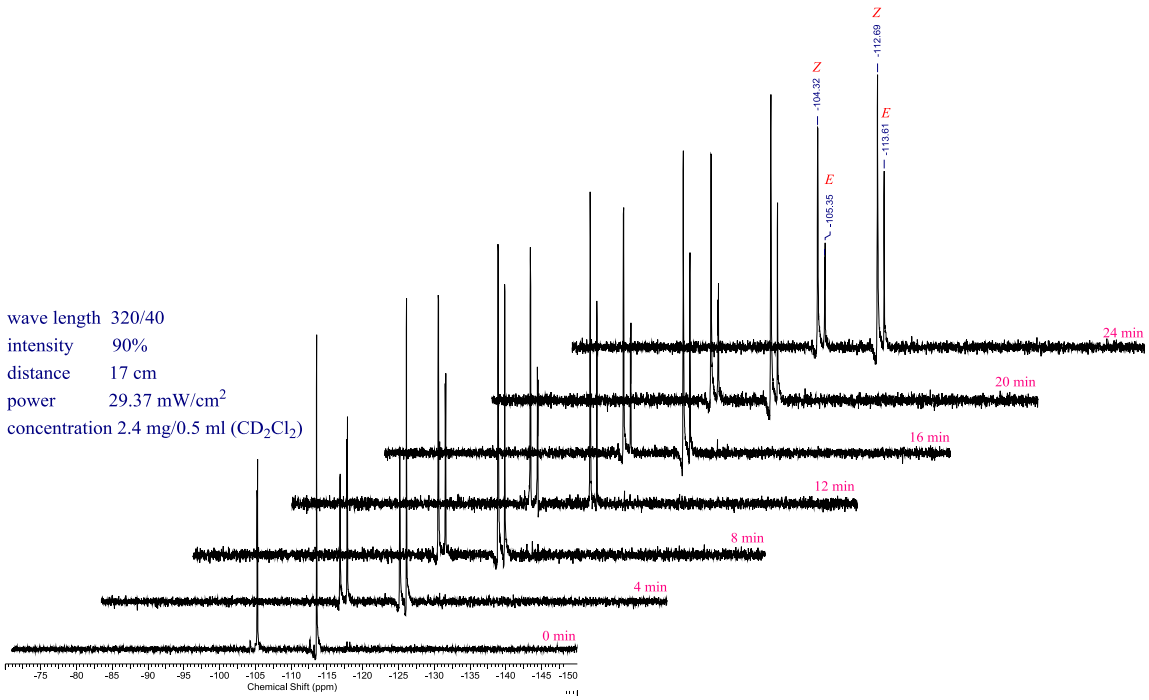
IV. Photochromic Behaviour of complexes 3 and 6.

Complexes *E*-3 and *Z*-3: study of isomeric transition by ^{19}F NMR.

A solution of ***E*-3** (2.4 mg) in CD_2Cl_2 (0.5 mL) was placed in NMR tube and irradiated with UV light (320/40 nm). The rate of isomerization was monitored by ^{19}F NMR. The photo-stationary state (PPS) was reached after 16 minutes of irradiation. At PPS the isomeric ratio obtained was *E:Z* = 27:73.

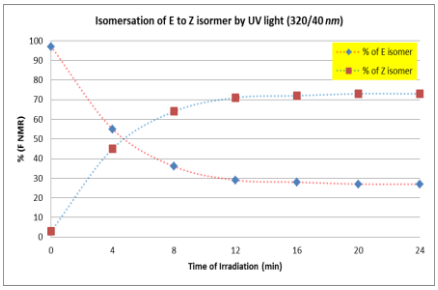


isomer *E*-3 isomer *Z*-3



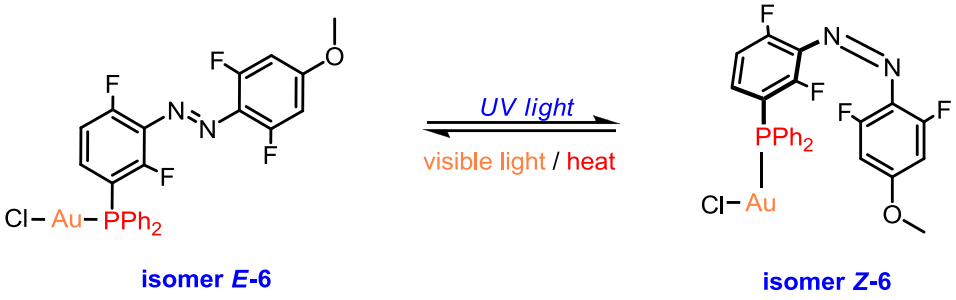
Changes in ^{19}F NMR spectrum upon photo-isomerization in [d_2]-dichloromethane.

Time of irradiation	% *E* isomer	% *Z* isomer
0 min	97	3
4 min	55	45
8 min	36	64
12 min	29	71
16 min	28	72
20 min	27	73
24 min	27	73

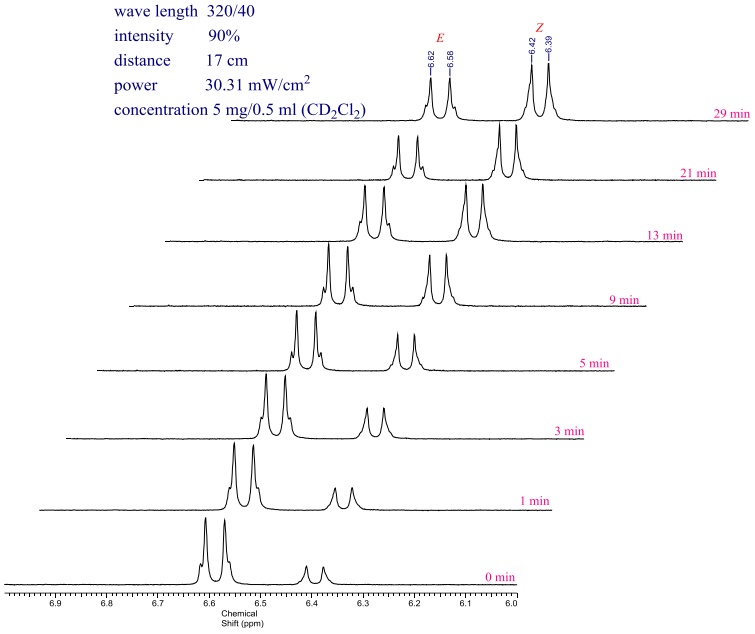


Complexes *E*-6 and *Z*-6: study of isomeric Transition by ^{1}H NMR:

A solution of *E*-**6** (5 mg) in CD_2Cl_2 (0.5 mL) was placed in NMR tube and irradiated with UV light (320/40 nm). The rate of isomerization was monitored by ^{1}H NMR. The photo-stationary state (PPS) was reached after 29 minutes of irradiation. At PPS the isomeric ration obtained was *E*:*Z* = 42:58.

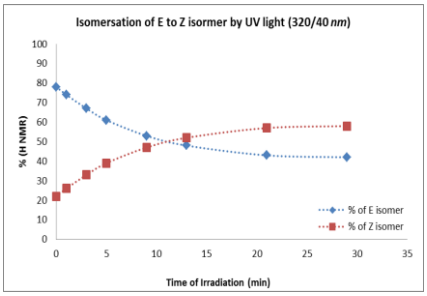


isomer *E*-6 **isomer *Z*-6**



Changes in ^{1}H NMR spectrum upon photo-isomerization in [d_2]-dichloromethane.

Time of irradiation	% of *E* isomer	% of *Z* isomer
0	78	22
1	74	26
3	67	33
5	61	39
9	53	47
13	48	52
21	43	57
29	42	58



Spectroscopic Measurements:

Acetonitrile was purchased from Aldrich (spectrometric grade), UV/Vis absorption spectra were recorded on a Cary5000 spectrophotometer from Agilent Technologies using a Peltier cuvette holder to monitor the temperature. Photo-isomerizations were induced by a continuous irradiation Hg/Xe lamp (Hamamatsu, LC6 Lightningcure, 200 W) equipped with narrow band interference filters of appropriate wavelengths (Semrock FF01-320/40 for λ_{irr} = 320 nm; FF01-406/15-25 for λ_{irr} = 406 nm). The irradiation power was measured using a photodiode from Ophir (PD300-UV).

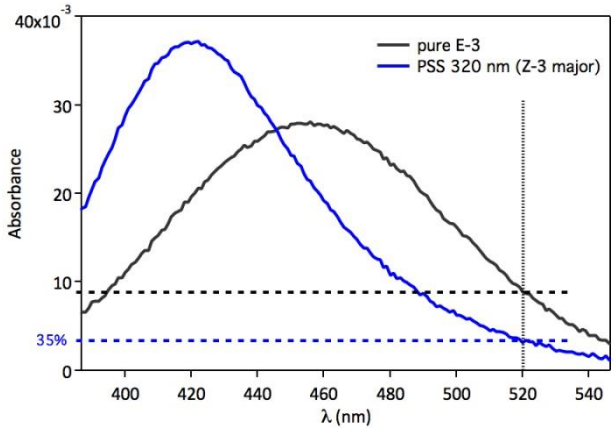


Figure SI1. Magnification of the absorption spectrum of *E*-**3** and PSS 320 nm (*Z*-**3** major) in MeCN at 25 °C allowing determination of a ratio *Z*-**3**:*E*-**3** ≈ 65:35 in PSS 320 nm.

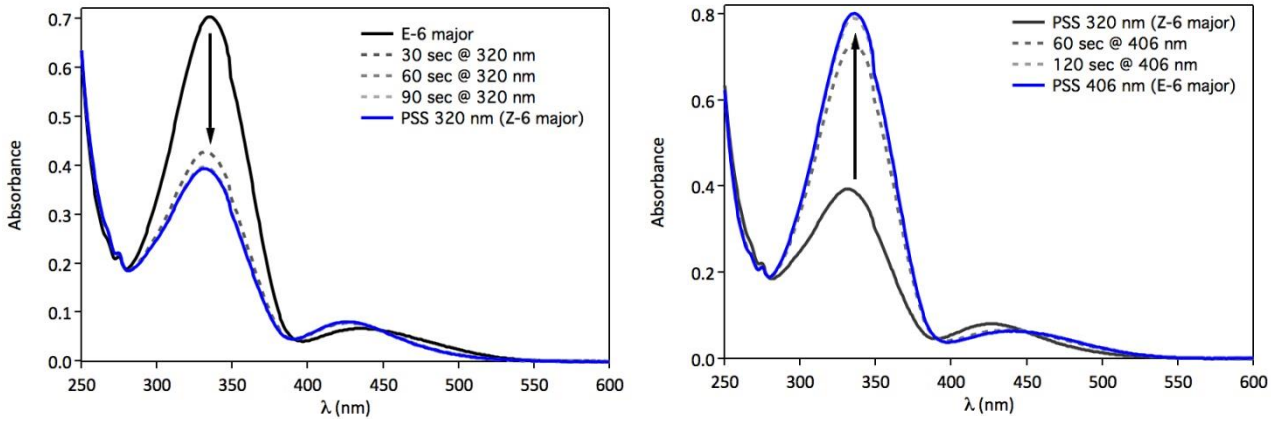


Figure SI2. Left: Absorption spectrum of *E*-**6** (major) in MeCN at 25 °C and its stepwise evolution upon irradiation pulses at 320 nm (4 mW.cm^{-2}). Right: Evolution of absorption spectrum of the previous solution at PSS 320 nm (*Z*-**6** major) in MeCN at 25 °C and its stepwise evolution upon irradiation pulses at 406 nm (10 mW.cm^{-2}).

General method for the determination of the half-lives of the complexes 3 and 6.

A solution of complex *E*-**3** or *E*-**6** (C ~ 20 µM) in MeCN at 25°C was irradiated at 320 nm (4 mW.cm^{-2}) for 6 min. Then, the sample was placed in a thermostated cuvette holder at 60°C, and *Z*→*E* thermal back-isomerization was monitored by recording absorption at an appropriate wavelength (310 nm and 335 nm for **3** and **6**, respectively).

Absorption was plotted versus time and fitted with an exponential curve corresponding to a first order kinetics reaction.

$$A(t) = A_\infty + (A_0 - A_\infty)e^{-kt}$$

where *A(t)* is the absorption at time *t*

A_0 the absorption after irradiation

A_∞ the absorbance after full thermal relaxation in the dark, corresponding to the absorption before irradiation (*E*-isomer)

k the kinetic constant in min^{-1}

The half-life $t_{1/2}$ in minutes of the (*Z*) isomer was calculated with the following equation:

$$t_{\frac{1}{2}} = \frac{ln2}{k}$$

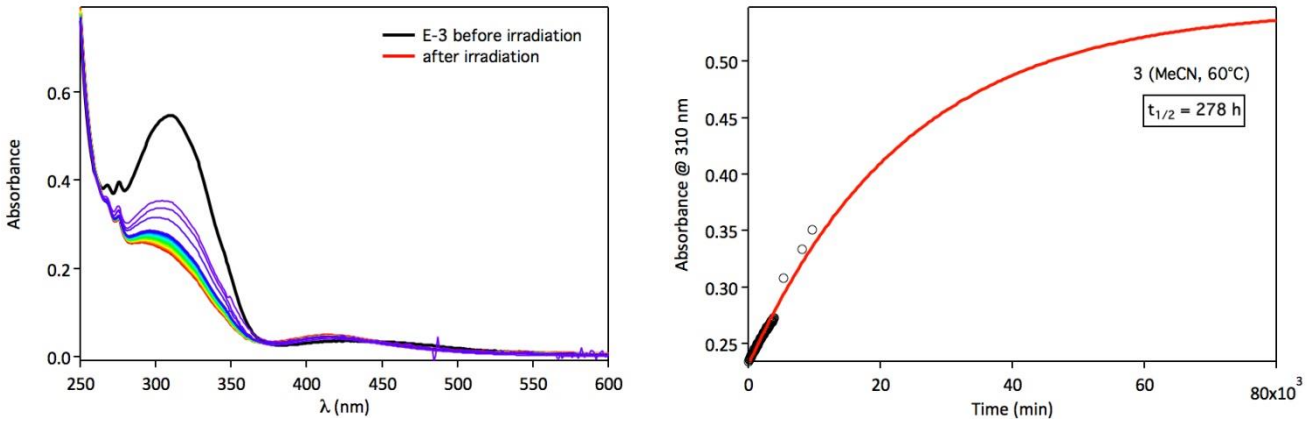


Figure SI3. Left: Absorption spectra of *E*-**3** in MeCN at 25°C before (black line) and after irradiation (red line) at 320 nm (6 min at 4 mW.cm^{-2}), and its evolution in the dark at 60°C (red to violet lines). Right: Evolution of absorption at 310 nm as a function of time in the dark at 60°C.

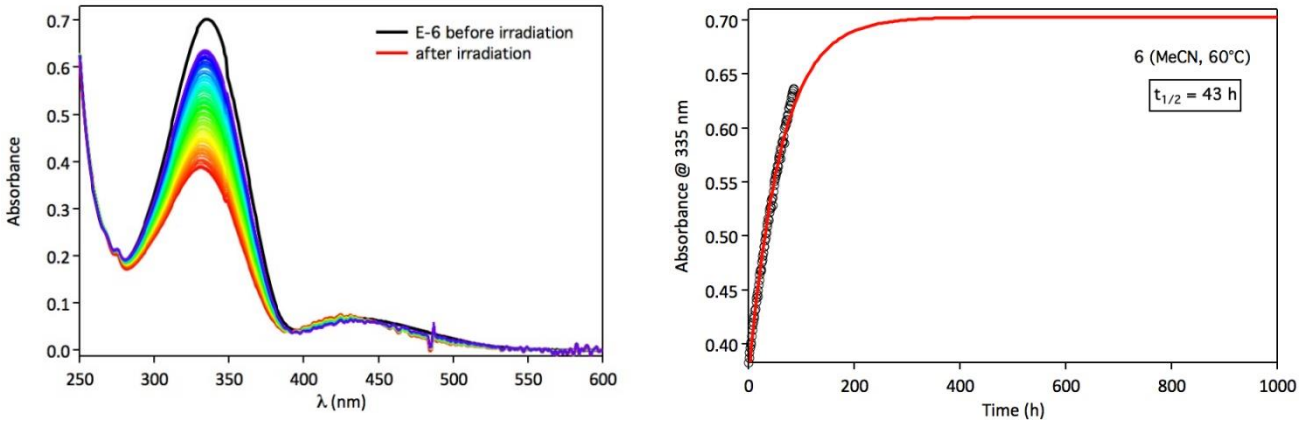
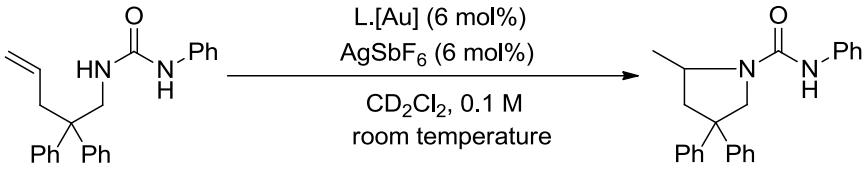


Figure SI4. Left: Absorption spectra of *E*-**6** in MeCN at 25°C before (black line) and after irradiation (red line) at 320 nm (6 min at 4 mW.cm^{-2}), and its evolution upon resting in the dark at 60°C (red to violet lines). Right: Evolution of absorption at 335 nm as a function of time in the dark at 60°C.

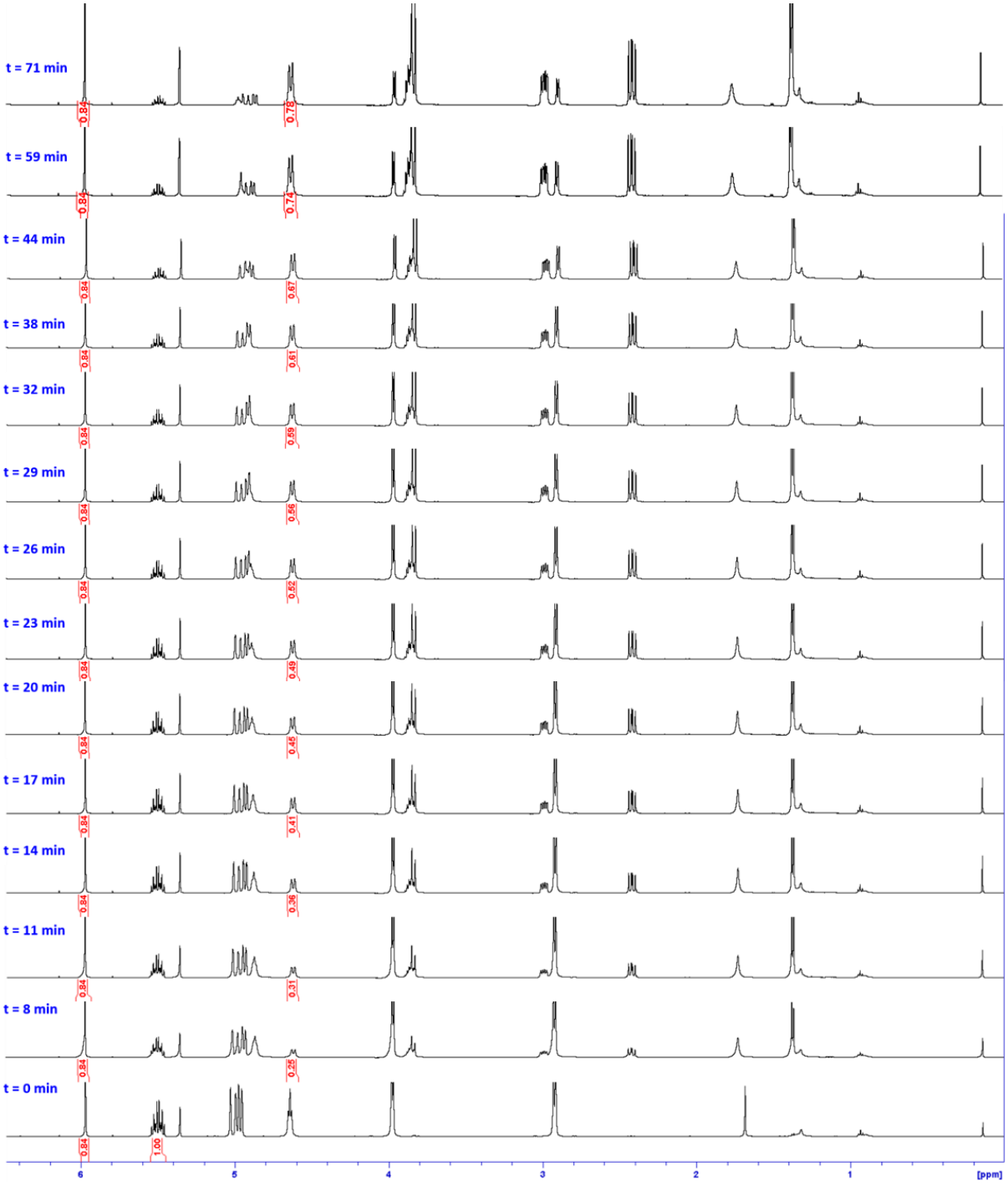
V. Intramolecular hydroamination of *N*-alkenyl ureas 4.

We have investigated the comparative rate of reaction for the hydroamination of *N*-alkenyl urea **4** with complexes *E*-**3**, *Z*-**3,** *E*-**6,** *Z*-**6** and Ph_3PAuCl. A careful weighed sample of *N*-alkenyl urea (0.15 mmol), gold complex and internal standard were dissolved in CD_2Cl_2 (1.5 ml). 0.5 ml of the solution was taken out and ^1H NMR was recorded before initiating the reaction. In order to initiate the reaction, the silver salt (6 mol% of $AgSbF_6$ with respect to the remaining 0.1 mmol of substrate) was weighed in 1 mL screw capped vial and then the 1 ml solution remained was transferred to this 1 mL screw capped vial and time was noted (t = 0). The reaction mixture was quickly mixed (2-3 min) and 0.5 ml of the reaction mixture transferred back to an NMR tube with a syringe and the reaction was monitored by automatic recording of ^1H NMR spectra at regular time intervals.

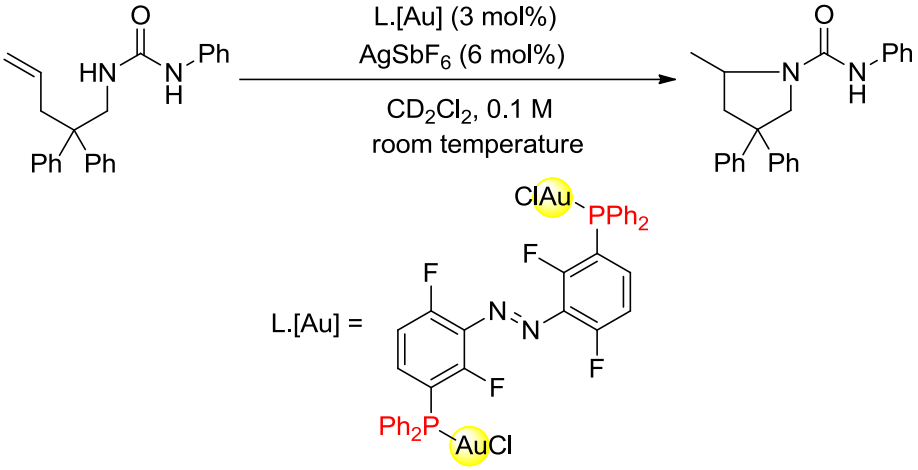
^{1}H NMR monitoring of the reaction with PPh_3-Au-Cl

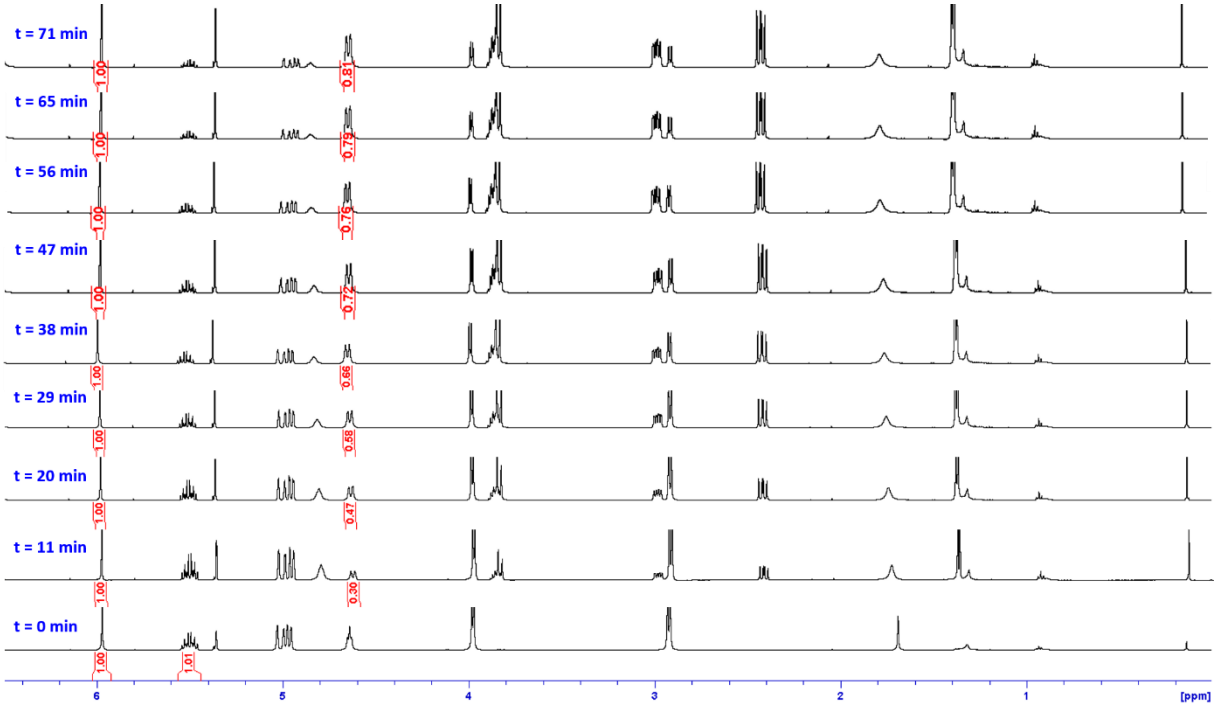


L.[Au] = PPh_3-Au-Cl

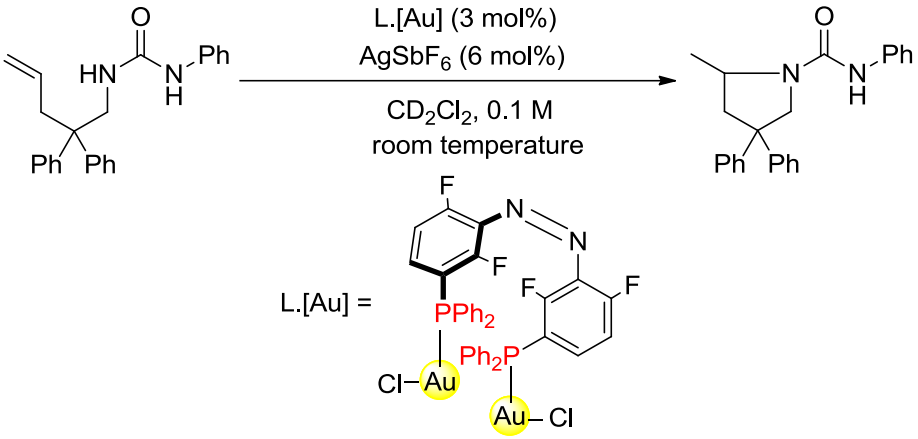


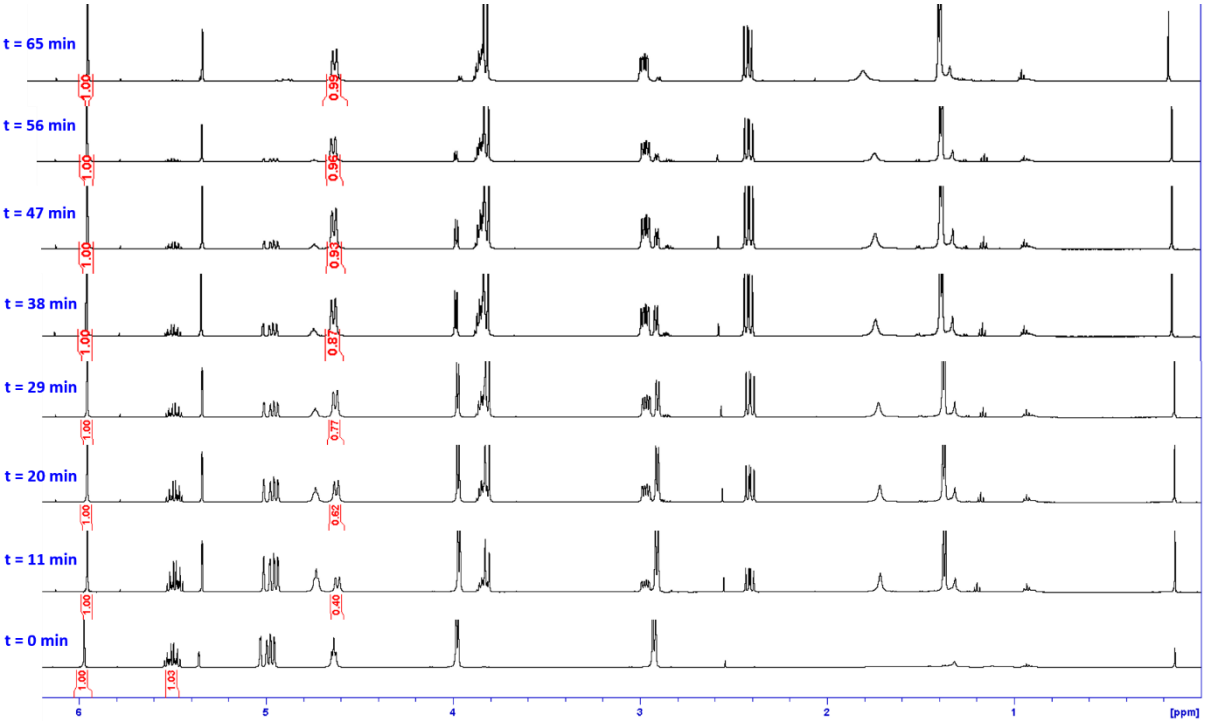
^{1}H NMR monitoring of the reaction with *E*-3



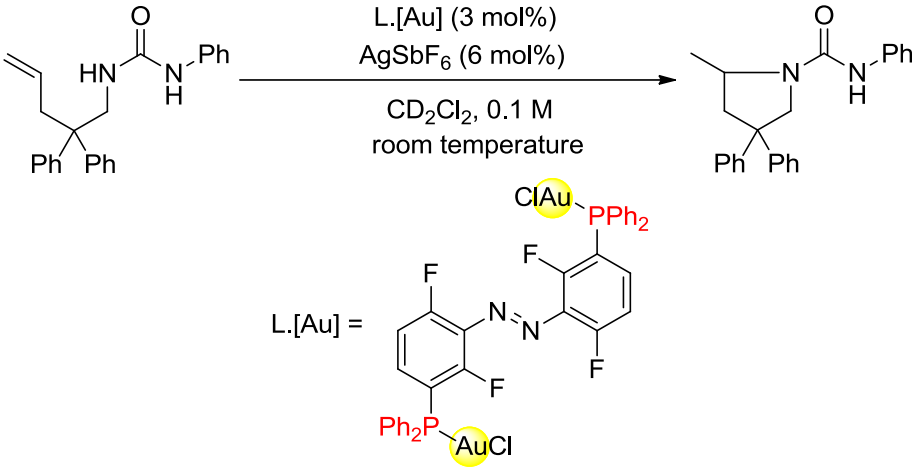


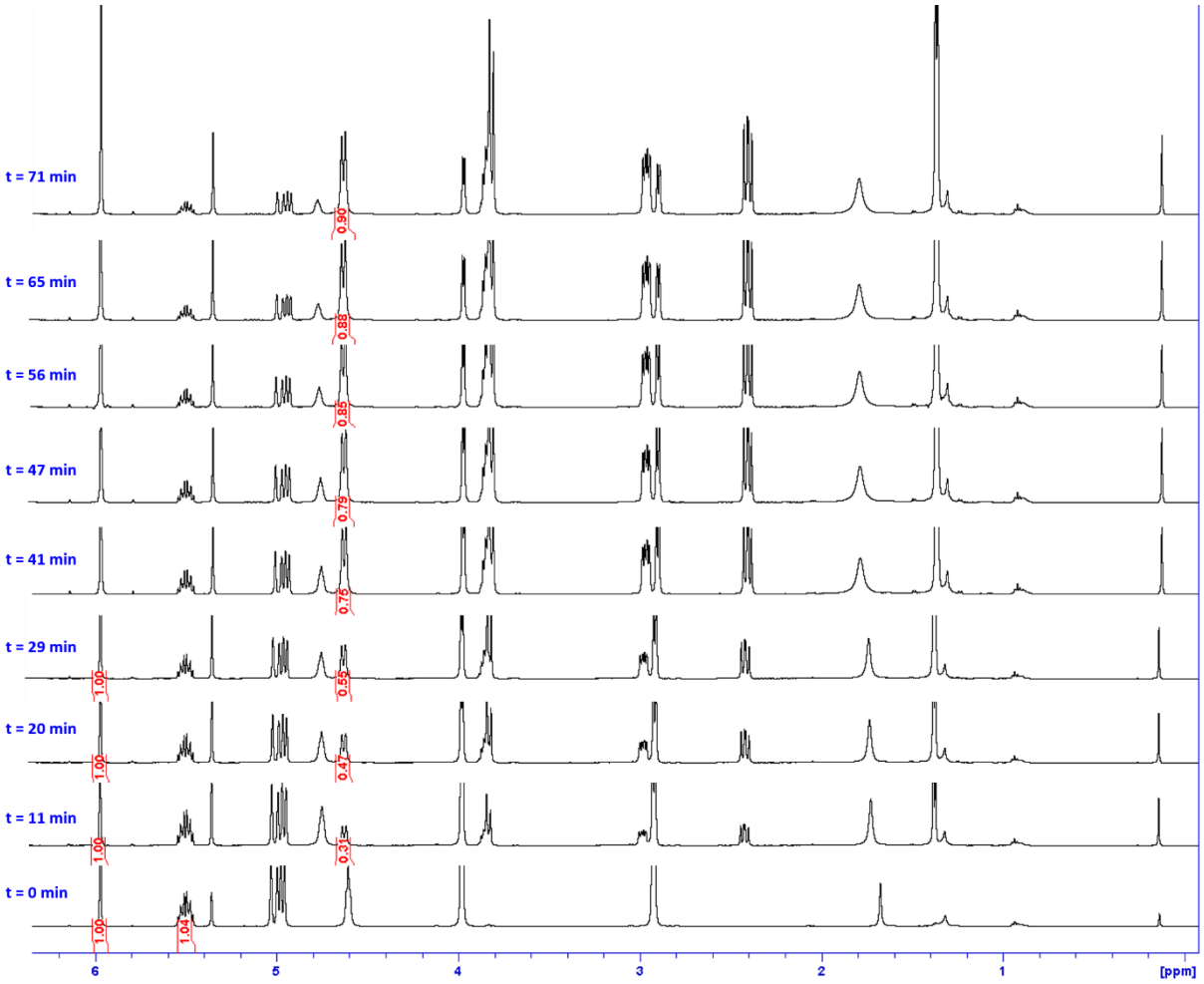
^{1}H NMR monitoring of the reaction with *Z-3*



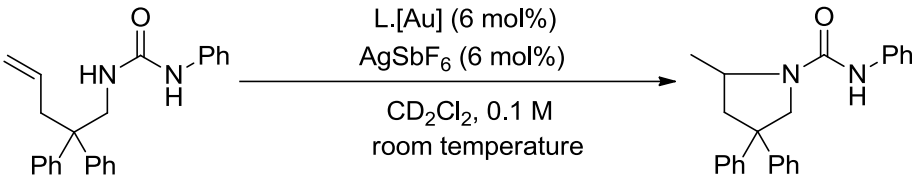


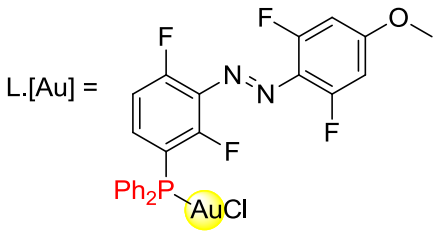
^{1}H NMR monitoring of the reaction with *E-3:* irradiation at 320 nm after 30 min reaction.

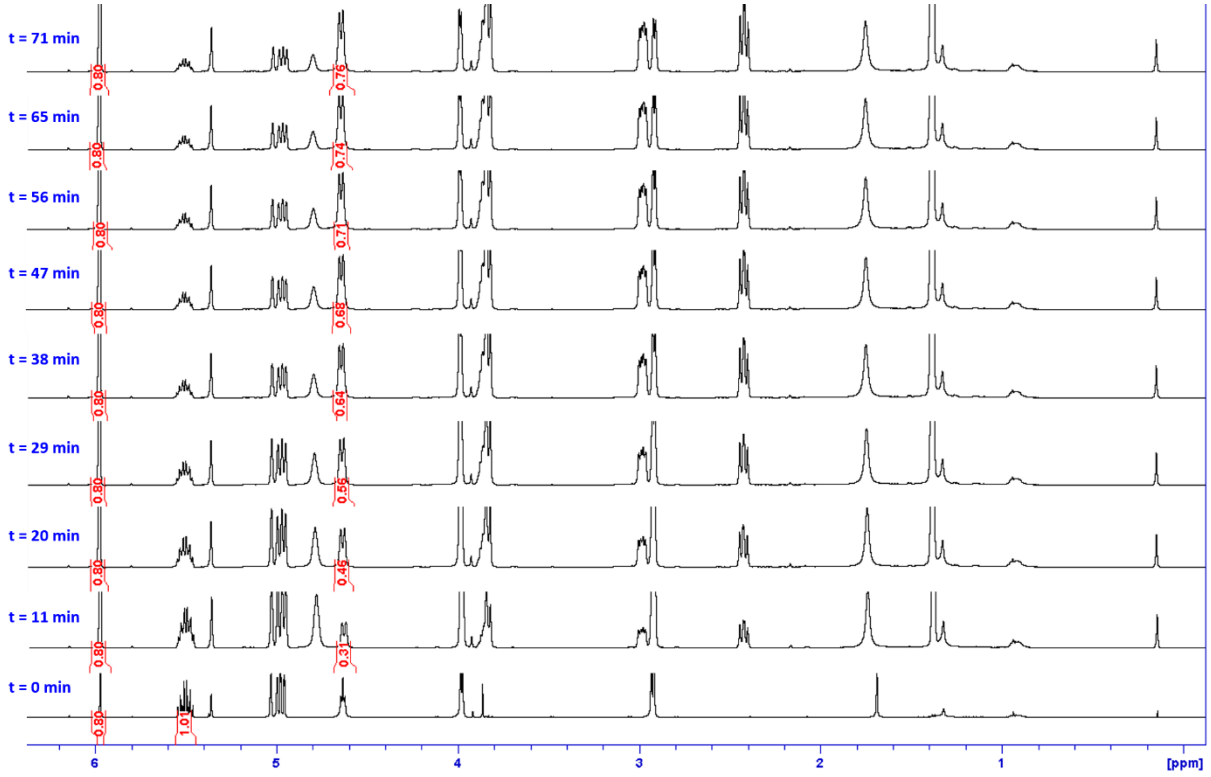




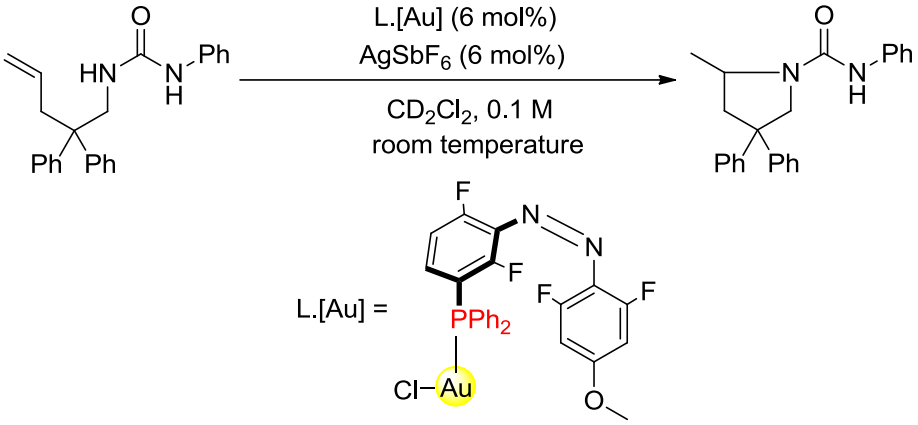
^{1}H NMR monitoring of the reaction with *E-6*

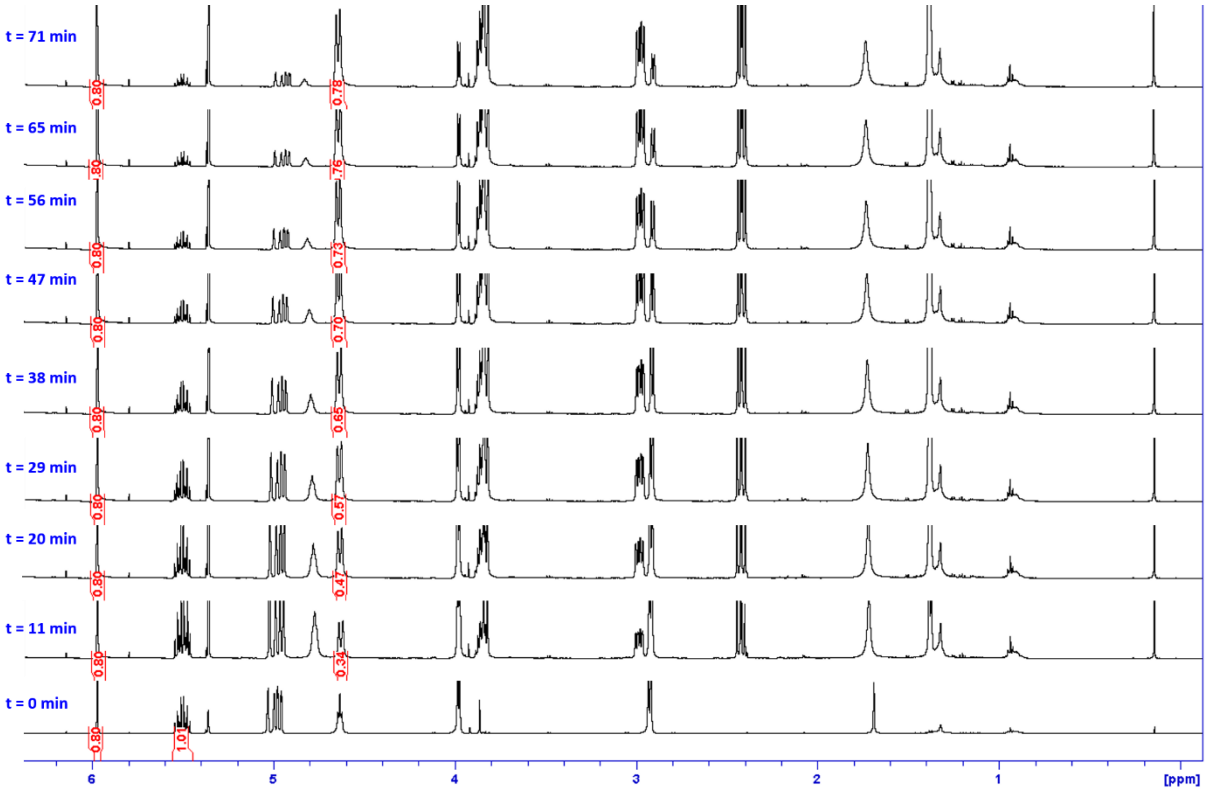






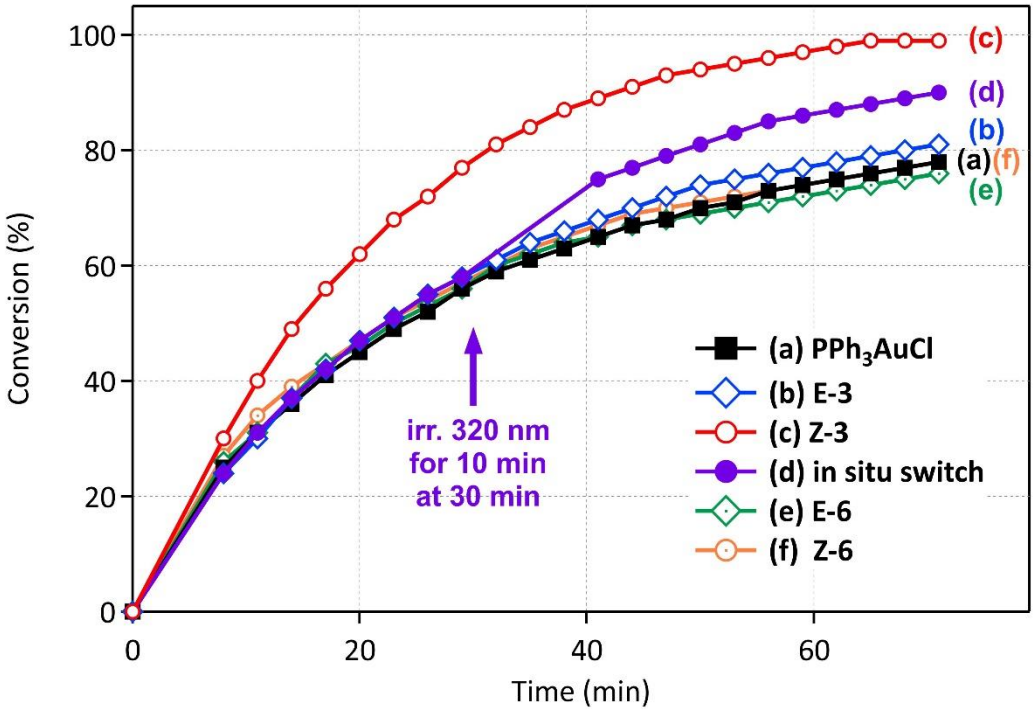
^{1}H NMR monitoring of the reaction with *Z*-6





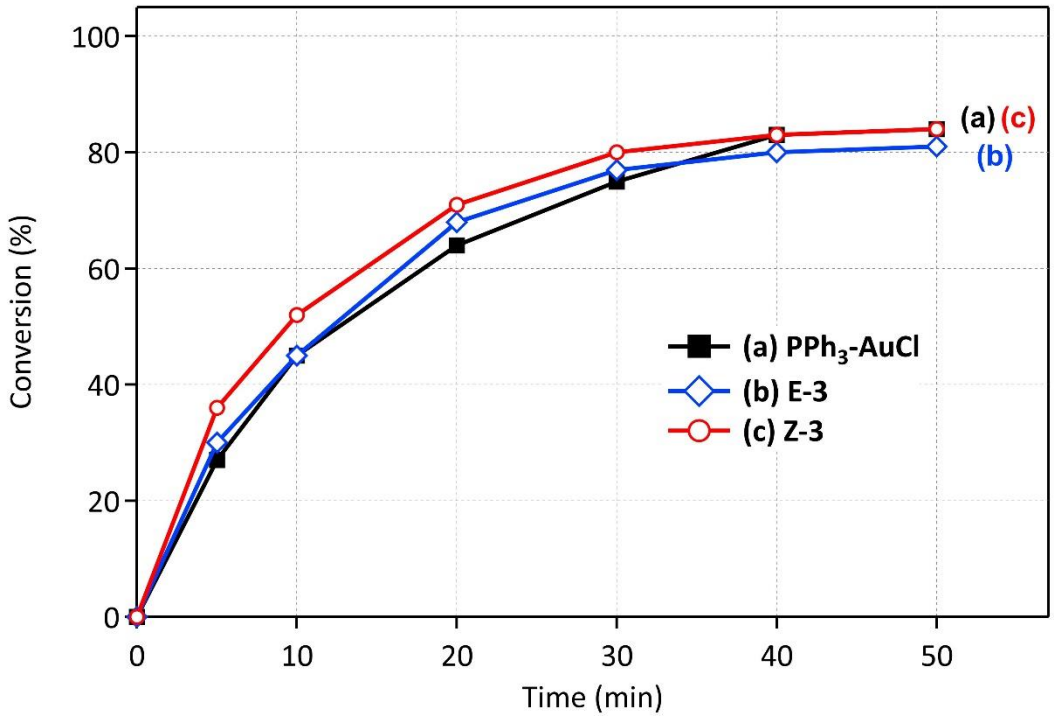
Reaction profiles for the intramolecular Hydroamination of *N*-Alkenyl Ureas:

The conversion rate for the hydroamination reactions with complexes *E*-**3**, *Z*-**3,** *E*-**6,** *Z*-**6** and Ph_3PAuCl are plotted against time.



VI. Intramolecular [4+2] cycloadditions of 7:

A careful weighed sample of dimethyl 2-(3-methylbut-2-enyl)-2-(3-phenylprop-2-ynyl)malonate, gold complex and internal standard was dissolved in CD_2Cl_2 and proton NMR was taken. In order to initiate the reaction, the silver salt ($AgSbF_6$) was weighed in a 1 mL screw capped vial and then the solution from NMR tube was transferred to this 1 mL screw capped vial and time was noted. The reaction mixture was quickly mixed and transferred back to the NMR tube with a syringe. NMR spectra were recorded at the given time intervals.
The NMR conversion rates are plotted against the time.



VII. X-Ray crystal structure determination

Single crystals suitable for X-ray diffraction were obtained by recrystallization from $CHCl_3$-CH_2Cl_2-heptane mixture. X-ray crystallographic data were collected on a Rigaku XtaLabPro diffractometer equipped with a microfocus source (MicroMax003_Mo) and multilayer confocal mirrors (Mo Kα radiation, λ = 0.71075 Å) using ω-scans. Data were indexed, integrated and scaled using *d*TREK* from the *CrystalClear*[4] software suite (*E*-**3**) or *CrysalisPRO*[5] (*Z*-**3**, *E*-**6** and *Z*-**6**). They were also corrected for polarization, Lorentz and absorption effects (*REQAB* (*E*-**3**) or *CrysalisPRO* (*Z*-**3**, *E*-**6** and *Z*-**6**)). For each complex, the structure was solved by direct methods with SHELXT[3], and refined with SHELXL-2014/7[6]. The model was refined using full-matrix least-squares, all non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms have been added geometrically and treated as riding on their parent atoms (U_H = 1.2 U_C).

For *E*-**3**, data quality was not so good despite suitable redundancy (ca. 4). This may be due to poor crystals quality and/or twin crystals. Attempts to detwin data using CrysalisPRO were unsuccessful and lead to high Rint, so a TWIN refinement was done (scales: 0.9454(12), 0.0546(12)). Restraints were applied along the entire connectivity set, using RIGU command (with standard deviation values), leading to more reasonable anisotropic displacement parameters. $CHCl_3$ and DCM molecules were refined with free occupancy factors using FVAR variables ($CHCl_3$ occupancy factors: 0.77(2) and 0.64(2), DCM occupancy factor: 0.44(4)).

For Z-**3**, Restraints were applied on $CHCl_3$ molecule, using RIGU command (with standard deviation values), leading to more reasonable anisotropic displacement parameters. $CHCl_3$ molecule was refined over two positions using PART command and its occupancy factor fixed at 0.4 for each position.

For *E*-**6**, Phenyl rings (C1-C6, C7-C12, C26-C31 and C32-37) were refined as rigid bodies (AFIX 66, C–C distance of 1.39 Å and bond angles of 120°). Due to a disorder on N=N bond, we refined N atoms over two positions with restraints (DFIX for C-N and N=N bond length, distances determined from Mogul database (Cambridge Structural Database)) and using EADP command to equate their anisotropic displacement parameters.

Molecular graphics were computed with Ortep-3[7]. CCDC 1484587-1484590 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[4] Rigaku, CrystalClear-SM Expert 2.1 b43. (2015).

[5] Rigaku Oxford Diffraction, CrysAlisPro Software system, version 38.41, Rigaku Corporation, Oxford, UK. (2015).

[6] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. Found. Adv.* **2015**, *71*, 3–8.

[7] Farrugia, L. J. *ORTEP* -3 for Windows - a version of *ORTEP* -III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **1997**, *30*, 565–565.

Crystal Data for *E*-**3 :**

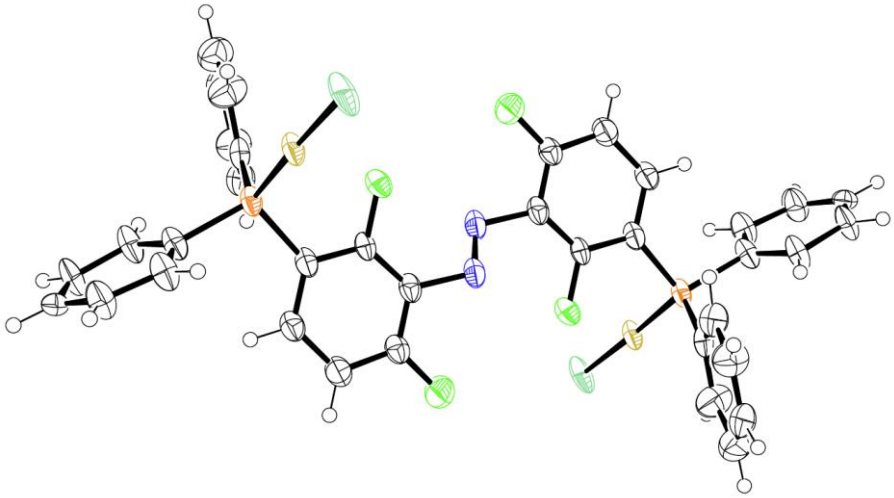


Figure SI5 : Ortep view of the complex (Color scheme: C, gray; N, blue; F, green; Au, brown; Cl, pale green; P, orange)

$C_{37.85}H_{26.29}Au_2Cl_{7.115}F_4N_2P_2$ (*M* =1293.03 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.051(3) Å, *b* = 15.816(4) Å, *c* = 16.857(5) Å, *α* = 109.459(3)°, *β* = 103.933(5)°, *γ* = 104.747(5)°, *V* = 2509.4(12) Å^3, *Z* = 2, *T* = 130.0 K, μ(MoKα) = 6.325 mm^{-1}, *Dcalc* = 1.713 g/cm^3, 46126 reflections measured (7.232° ≤ 2Θ ≤ 50.702°), 9151 unique (R_{int} = 0.1024, R_{sigma} = 0.0966) which were used in all calculations. The final R_1 was 0.1038 (I > 2σ(I)) and wR_2 was 0.2689 (all data).

Table 1 Crystal data and structure refinement for *E*-3	
CCDC number	1484589
Empirical formula	$C_{37.85}H_{26.29}Au_2Cl_{7.12}F_4N_2P_2$
Formula weight	1293.03
Temperature/K	130.0
Crystal system	triclinic
Space group	P-1
a/Å	11.051(3)
b/Å	15.816(4)
c/Å	16.857(5)
α/°	109.459(3)
β/°	103.933(5)
γ/°	104.747(5)
Volume/Å^3	2509.4(12)
Z	2
ρ_{calc}g/cm^3	1.713
μ/mm^{-1}	6.325
F(000)	1224.5
Crystal size/mm^3	0.2 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	7.232 to 50.702
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	46126
Independent reflections	9151 [R_{int} = 0.1024, R_{sigma} = 0.0966]
Data/restraints/parameters	9151/423/533
Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.1038, wR_2 = 0.2582
Final R indexes [all data]	R_1 = 0.1239, wR_2 = 0.2689
Largest diff. peak/hole / e Å^{-3}	5.21/-2.74

Table 2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for *E*-3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	0.473(2)	0.2100(18)	0.7931(16)	0.038(4)
C2	0.495(3)	0.297(2)	0.860(2)	0.061(7)
C3	0.562(3)	0.388(2)	0.860(2)	0.061(6)
C4	0.596(2)	0.380(2)	0.7851(19)	0.050(5)
C5	0.571(3)	0.294(2)	0.717(2)	0.059(6)
C6	0.517(2)	0.211(2)	0.7215(17)	0.046(5)
C7	0.655(2)	0.099(2)	0.8426(18)	0.047(6)
C8	0.531(2)	0.0584(19)	0.8432(16)	0.039(4)
C9	0.500(3)	-0.010(2)	0.8787(18)	0.049(6)
C10	0.611(3)	-0.031(2)	0.915(2)	0.053(6)
C11	0.733(2)	0.0010(16)	0.9162(15)	0.036(4)
C12	0.755(2)	0.066(2)	0.8767(19)	0.050(6)
C13	0.302(2)	0.0092(17)	0.6857(15)	0.035(4)
C14	0.1972(18)	0.0204(15)	0.6336(13)	0.026(3)
C15	0.114(2)	-0.0462(17)	0.5487(14)	0.032(4)
C16	0.133(2)	-0.1310(17)	0.5162(14)	0.033(4)
C17	0.239(2)	-0.1490(19)	0.5636(16)	0.043(5)
C18	0.325(2)	-0.0753(17)	0.6485(15)	0.037(4)
C19	0.748(2)	-0.0912(16)	0.6345(15)	0.035(4)
C20	0.639(2)	-0.0768(16)	0.5801(15)	0.033(4)
C21	0.645(2)	0.0127(17)	0.5838(16)	0.037(4)
C22	0.761(2)	0.0896(17)	0.6430(16)	0.036(4)
C23	0.873(2)	0.0826(18)	0.6970(17)	0.042(5)
C24	0.859(3)	-0.0100(19)	0.6938(19)	0.051(6)
C25	0.701(2)	-0.2913(17)	0.5207(16)	0.037(4)
C26	0.748(2)	-0.253(2)	0.4678(18)	0.046(5)
C27	0.738(3)	-0.318(2)	0.3826(19)	0.053(5)
C28	0.684(3)	-0.410(2)	0.360(2)	0.058(6)
C29	0.633(4)	-0.447(2)	0.416(2)	0.070(8)
C30	0.643(3)	-0.3866(19)	0.496(2)	0.052(5)
C31	0.871(2)	-0.1937(17)	0.7124(16)	0.036(4)
C32	0.880(2)	-0.184(2)	0.7997(18)	0.050(6)
C33	0.999(2)	-0.171(2)	0.8618(19)	0.051(6)
C34	1.112(3)	-0.165(2)	0.8351(19)	0.056(7)
C35	1.106(2)	-0.1817(19)	0.7509(17)	0.042(5)
C36	0.983(2)	-0.195(2)	0.6860(18)	0.046(6)
C37	0.146(6)	-0.457(4)	0.437(5)	0.087(10)
C38	0.411(4)	-0.340(3)	0.871(3)	0.066(7)
Au1	0.25512(8)	0.10393(7)	0.87630(6)	0.0366(3)
Au2	0.53296(9)	-0.25386(7)	0.66724(7)	0.0428(3)
Cl1	0.1039(6)	0.1063(6)	0.9471(5)	0.0548(17)
Cl2	0.3330(7)	-0.3002(6)	0.6871(6)	0.062(2)
Cl3	0.2851(18)	-0.4199(13)	0.4250(11)	0.101(6)
Cl4	0.0614(15)	-0.5810(11)	0.3885(15)	0.107(7)
Cl5	0.033(2)	-0.4039(15)	0.4169(18)	0.145(10)
Cl7	0.5784(13)	-0.3214(12)	0.8871(9)	0.099(5)
Cl8	0.3841(11)	-0.2454(9)	0.9453(7)	0.073(4)
Cl6	0.3521(16)	-0.4432(9)	0.8884(9)	0.092(4)
F1	0.1736(12)	0.1032(9)	0.6727(8)	0.036(3)
F2	0.0511(15)	-0.2017(11)	0.4358(9)	0.050(3)
F3	0.7651(15)	0.1782(10)	0.6512(10)	0.051(3)
F4	0.5301(13)	-0.1533(10)	0.5256(9)	0.044(3)
N1	-0.0094(18)	-0.0425(14)	0.4956(13)	0.036(4)
N2	0.5388(18)	0.0337(13)	0.5386(12)	0.034(4)
P1	0.3956(5)	0.0990(5)	0.8013(4)	0.0320(12)
P2	0.7154(6)	-0.2086(4)	0.6338(4)	0.0337(12)
Cl9	0.917(3)	0.321(3)	0.879(3)	0.154(18)

Cl10	1.166(3)	0.325(3)	0.846(4)	0.170(19)
C39	1.086(4)	0.336(6)	0.925(3)	0.13(2)

Table 3 Anisotropic Displacement Parameters for *E*-3

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.022(8)	0.051(6)	0.039(8)	0.021(5)	0.004(6)	0.014(6)
C2	0.064(16)	0.052(7)	0.057(10)	0.016(6)	0.026(10)	0.011(7)
C3	0.055(15)	0.053(9)	0.065(11)	0.018(7)	0.021(10)	0.011(8)
C4	0.029(11)	0.048(9)	0.064(10)	0.020(7)	0.015(9)	0.005(8)
C5	0.061(15)	0.056(8)	0.062(11)	0.028(7)	0.026(10)	0.018(8)
C6	0.040(11)	0.053(9)	0.045(9)	0.023(7)	0.014(8)	0.013(8)
C7	0.033(7)	0.075(13)	0.057(14)	0.041(12)	0.023(7)	0.034(8)
C8	0.034(6)	0.059(10)	0.042(10)	0.028(9)	0.018(6)	0.029(6)
C9	0.041(8)	0.068(12)	0.055(14)	0.038(12)	0.019(8)	0.030(8)
C10	0.044(8)	0.064(14)	0.066(15)	0.039(13)	0.017(8)	0.029(8)
C11	0.039(8)	0.031(9)	0.031(10)	0.004(8)	0.008(7)	0.019(7)
C12	0.032(8)	0.069(13)	0.070(15)	0.042(13)	0.020(8)	0.033(8)
C13	0.027(7)	0.047(7)	0.035(5)	0.019(5)	0.010(5)	0.019(5)
C14	0.018(6)	0.041(6)	0.030(5)	0.021(5)	0.016(4)	0.013(5)
C15	0.024(7)	0.047(7)	0.031(6)	0.018(5)	0.013(5)	0.016(5)
C16	0.030(7)	0.047(7)	0.031(6)	0.019(5)	0.016(5)	0.019(6)
C17	0.039(8)	0.052(9)	0.040(7)	0.017(6)	0.012(6)	0.024(7)
C18	0.032(8)	0.051(7)	0.035(7)	0.019(6)	0.014(6)	0.022(6)
C19	0.035(6)	0.042(6)	0.040(8)	0.024(5)	0.021(5)	0.019(5)
C20	0.034(6)	0.041(6)	0.038(8)	0.022(5)	0.020(6)	0.020(5)
C21	0.034(6)	0.041(6)	0.048(9)	0.025(5)	0.020(6)	0.021(5)
C22	0.034(7)	0.044(6)	0.044(8)	0.025(6)	0.022(6)	0.018(5)
C23	0.034(8)	0.046(8)	0.054(10)	0.028(7)	0.017(7)	0.016(6)
C24	0.045(8)	0.048(7)	0.057(11)	0.025(6)	0.008(8)	0.017(6)
C25	0.018(8)	0.048(7)	0.049(6)	0.019(5)	0.013(6)	0.020(6)
C26	0.039(11)	0.056(9)	0.055(8)	0.025(7)	0.023(8)	0.029(8)
C27	0.044(13)	0.059(9)	0.060(9)	0.020(7)	0.027(9)	0.025(9)
C28	0.054(14)	0.055(9)	0.065(10)	0.018(8)	0.026(10)	0.025(9)
C29	0.08(2)	0.048(9)	0.073(10)	0.016(7)	0.040(11)	0.019(9)
C30	0.050(12)	0.047(7)	0.063(9)	0.021(6)	0.025(9)	0.024(7)
C31	0.029(6)	0.043(11)	0.046(7)	0.022(7)	0.017(5)	0.021(6)
C32	0.029(8)	0.082(19)	0.049(7)	0.031(9)	0.019(6)	0.028(9)
C33	0.032(8)	0.080(18)	0.051(8)	0.033(10)	0.019(6)	0.027(9)
C34	0.032(8)	0.10(2)	0.052(9)	0.039(10)	0.020(7)	0.034(10)
C35	0.032(8)	0.063(15)	0.053(8)	0.033(9)	0.021(6)	0.030(8)
C36	0.033(7)	0.074(16)	0.052(9)	0.035(9)	0.023(6)	0.035(8)
C37	0.093(13)	0.063(13)	0.11(2)	0.055(13)	0.019(12)	0.020(9)
C38	0.067(12)	0.070(11)	0.067(14)	0.029(9)	0.027(10)	0.032(9)
Au1	0.0247(4)	0.0584(6)	0.0340(5)	0.0210(4)	0.0127(4)	0.0224(4)
Au2	0.0339(5)	0.0513(6)	0.0704(7)	0.0403(5)	0.0312(5)	0.0262(4)
Cl1	0.037(3)	0.098(5)	0.063(4)	0.047(4)	0.036(3)	0.044(4)
Cl2	0.044(3)	0.073(5)	0.108(6)	0.057(5)	0.051(4)	0.034(3)
Cl3	0.094(10)	0.096(11)	0.081(10)	0.041(9)	0.010(8)	-0.001(7)
Cl4	0.066(9)	0.062(8)	0.175(18)	0.051(9)	0.015(9)	0.021(6)
Cl5	0.123(13)	0.090(12)	0.18(2)	0.043(12)	-0.007(12)	0.050(10)
Cl7	0.076(7)	0.150(12)	0.088(9)	0.055(9)	0.038(6)	0.055(7)
Cl8	0.071(7)	0.084(7)	0.062(6)	0.026(5)	0.016(5)	0.040(6)
Cl6	0.129(11)	0.072(7)	0.085(8)	0.036(6)	0.044(8)	0.040(7)
F1	0.034(6)	0.046(6)	0.039(6)	0.021(5)	0.019(5)	0.022(5)
F2	0.050(7)	0.058(7)	0.035(5)	0.013(5)	0.008(5)	0.022(6)
F3	0.051(8)	0.043(6)	0.063(9)	0.027(6)	0.020(7)	0.019(5)
F4	0.037(6)	0.043(6)	0.054(7)	0.021(5)	0.014(5)	0.020(5)
N1	0.025(7)	0.047(10)	0.036(8)	0.018(8)	0.007(6)	0.016(7)

N2	0.034(7)	0.046(10)	0.042(9)	0.028(8)	0.025(6)	0.024(7)
P1	0.022(2)	0.049(3)	0.031(3)	0.020(2)	0.012(2)	0.017(2)
P2	0.028(3)	0.040(3)	0.044(3)	0.022(3)	0.017(2)	0.019(2)
Cl9	0.14(2)	0.19(4)	0.15(3)	0.08(3)	0.05(2)	0.06(2)
Cl10	0.16(3)	0.12(3)	0.26(4)	0.10(3)	0.09(3)	0.04(2)
C39	0.12(3)	0.06(4)	0.22(4)	0.09(3)	0.05(2)	0.03(3)

Table 4 Bond Lengths for *E*-3

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	**C2**	1.37(4)	**C22**	**C23**	1.40(3)
C1	**C6**	1.41(3)	**C22**	**F3**	1.35(3)
C1	**P1**	1.81(2)	**C23**	**C24**	1.42(3)
C2	**C3**	1.44(4)	**C25**	**C26**	1.36(3)
C3	**C4**	1.38(4)	**C25**	**C30**	1.35(4)
C4	**C5**	1.35(4)	**C25**	**P2**	1.86(2)
C5	**C6**	1.33(4)	**C26**	**C27**	1.42(4)
C7	**C8**	1.37(3)	**C27**	**C28**	1.30(4)
C7	**C12**	1.41(3)	**C28**	**C29**	1.41(4)
C8	**C9**	1.40(3)	**C29**	**C30**	1.32(4)
C8	**P1**	1.85(2)	**C31**	**C32**	1.41(3)
C9	**C10**	1.42(3)	**C31**	**C36**	1.41(3)
C10	**C11**	1.30(4)	**C31**	**P2**	1.81(2)
C11	**C12**	1.41(3)	**C32**	**C33**	1.38(3)
C13	**C14**	1.37(3)	**C33**	**C34**	1.41(3)
C13	**C18**	1.39(3)	**C34**	**C35**	1.34(4)
C13	**P1**	1.82(2)	**C35**	**C36**	1.44(3)
C14	**C15**	1.37(3)	**C37**	**Cl3**	1.58(7)
C14	**F1**	1.38(2)	**C37**	**Cl4**	1.73(6)
C15	**C16**	1.36(3)	**C37**	**Cl5**	1.71(6)
C15	**N1**	1.47(3)	**C38**	**Cl7**	1.73(4)
C16	**C17**	1.40(3)	**C38**	**Cl8**	1.75(4)
C16	**F2**	1.34(3)	**C38**	**Cl6**	1.74(4)
C17	**C18**	1.41(3)	**Au1**	**Cl1**	2.276(6)
C19	**C20**	1.44(3)	**Au1**	**P1**	2.226(5)
C19	**C24**	1.38(4)	**Au2**	**Cl2**	2.287(6)
C19	**P2**	1.79(2)	**Au2**	**P2**	2.231(6)
C20	**C21**	1.38(3)	**N1**	**N1**[1]	1.26(4)
C20	**F4**	1.32(3)	**N2**	**N2**[2]	1.28(4)
C21	**C22**	1.38(3)	**Cl9**	**C39**	1.7603
C21	**N2**	1.42(3)	**Cl10**	**C39**	1.7599

[1]-X,-Y,1-Z; [2]1-X,-Y,1-Z

Table 5 Bond Angles for *E*-3

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	**C1**	**C6**	118(2)	**C22**	**C23**	**C24**	116(2)
C2	**C1**	**P1**	120(2)	**C19**	**C24**	**C23**	122(2)
C6	**C1**	**P1**	122.4(19)	**C26**	**C25**	**P2**	118.8(19)
C1	**C2**	**C3**	123(3)	**C30**	**C25**	**C26**	124(3)
C4	**C3**	**C2**	113(3)	**C30**	**C25**	**P2**	118(2)
C5	**C4**	**C3**	124(3)	**C25**	**C26**	**C27**	117(3)
C6	**C5**	**C4**	121(3)	**C28**	**C27**	**C26**	118(3)
C5	**C6**	**C1**	120(3)	**C27**	**C28**	**C29**	123(3)
C8	**C7**	**C12**	117(2)	**C30**	**C29**	**C28**	119(3)
C7	**C8**	**C9**	124(2)	**C29**	**C30**	**C25**	119(3)
C7	**C8**	**P1**	119.2(18)	**C32**	**C31**	**C36**	120(2)
C9	**C8**	**P1**	117.0(17)	**C32**	**C31**	**P2**	119.7(17)

C8	**C9**	**C10**	113(2)	**C36**	**C31**	**P2**	120.7(18)
C11	**C10**	**C9**	128(3)	**C33**	**C32**	**C31**	121(2)
C10	**C11**	**C12**	115(2)	**C32**	**C33**	**C34**	118(2)
C11	**C12**	**C7**	122(2)	**C35**	**C34**	**C33**	124(2)
C14	**C13**	**C18**	117(2)	**C34**	**C35**	**C36**	119(2)
C14	**C13**	**P1**	119.3(17)	**C31**	**C36**	**C35**	119(2)
C18	**C13**	**P1**	123.6(16)	**Cl3**	**C37**	**Cl4**	117(4)
C13	**C14**	**F1**	116.1(18)	**Cl3**	**C37**	**Cl5**	119(3)
C15	**C14**	**C13**	124(2)	**Cl5**	**C37**	**Cl4**	108(3)
C15	**C14**	**F1**	119.7(17)	**Cl7**	**C38**	**Cl8**	114(2)
C14	**C15**	**N1**	125.5(19)	**Cl7**	**C38**	**Cl6**	105(2)
C16	**C15**	**C14**	117.8(19)	**Cl6**	**C38**	**Cl8**	109(2)
C16	**C15**	**N1**	115.7(19)	**P1**	**Au1**	**Cl1**	177.5(2)
C15	**C16**	**C17**	122(2)	**P2**	**Au2**	**Cl2**	173.7(3)
F2	**C16**	**C15**	121.3(19)	**N1**[1]	**N1**	**C15**	110(2)
F2	**C16**	**C17**	116(2)	**N2**[2]	**N2**	**C21**	114(2)
C16	**C17**	**C18**	117(2)	**C1**	**P1**	**C8**	107.5(11)
C13	**C18**	**C17**	122(2)	**C1**	**P1**	**C13**	105.7(11)
C20	**C19**	**P2**	117.1(17)	**C1**	**P1**	**Au1**	115.6(8)
C24	**C19**	**C20**	117(2)	**C8**	**P1**	**Au1**	114.3(8)
C24	**C19**	**P2**	124.9(18)	**C13**	**P1**	**C8**	104.4(11)
C21	**C20**	**C19**	123(2)	**C13**	**P1**	**Au1**	108.5(7)
F4	**C20**	**C19**	117.5(19)	**C19**	**P2**	**C25**	106.9(11)
F4	**C20**	**C21**	120.0(19)	**C19**	**P2**	**C31**	102.6(11)
C20	**C21**	**N2**	126(2)	**C19**	**P2**	**Au2**	110.6(7)
C22	**C21**	**C20**	117(2)	**C25**	**P2**	**Au2**	113.1(7)
C22	**C21**	**N2**	117(2)	**C31**	**P2**	**C25**	106.5(10)
C21	**C22**	**C23**	125(2)	**C31**	**P2**	**Au2**	116.2(8)
F3	**C22**	**C21**	117.6(19)	**Cl10**	**C39**	**Cl9**	112.9
F3	**C22**	**C23**	118(2)				

[1]-X,-Y,1-Z; [2]1-X,-Y,1-Z

Table 6 Atomic Occupancy for *E*-3

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C37	0.64(2)	**C38**	0.77(2)	**C39**	0.44(4)
H37	0.64(2)	**H38**	0.77(2)	**H39A**	0.44(4)
Cl3	0.64(2)	**Cl6**	0.77(2)	**H39B**	0.44(4)
Cl4	0.64(2)	**Cl7**	0.77(2)	**Cl9**	0.44(4)
Cl5	0.64(2)	**Cl8**	0.77(2)	**Cl10**	0.44(4)

Crystal Data for *Z*-**3** :

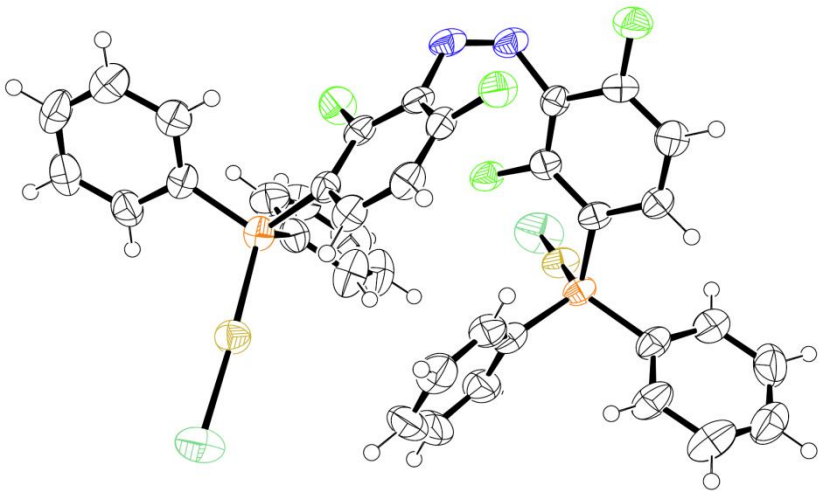


Figure SI6 : Ortep view of the complex (Color scheme: C, gray; N, blue; F, green; Au, brown; Cl, pale green; P, orange)

$C_{36.75}H_{24.75}Au_2Cl_{4.25}F_4N_2P_2$ (*M* =1182.85 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 18.4530(16) Å, *b* = 18.5065(19) Å, *c* = 11.1568(13) Å, *β* = 97.085(10)°, *V* = 3781.0(7) Å^3, *Z* = 4, *T* = 250 K, μ(MoKα) = 8.198 mm^{-1}, *Dcalc* = 2.078 g/cm^3, 55840 reflections measured (6.978° ≤ 2Θ ≤ 59.556°), 9695 unique (R_{int} = 0.0781, R_{sigma} = 0.0596) which were used in all calculations. The final R_1 was 0.0403 (I > 2σ(I)) and wR_2 was 0.1115 (all data).

Table 1 Crystal data and structure refinement for *Z*-3	
CCDC number	1484590
Empirical formula	$C_{36.8}H_{24.8}Au_2Cl_{4.4}F_4N_2P_2$
Formula weight	1182.85
Temperature/K	250
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.4530(16)
b/Å	18.5065(19)
c/Å	11.1568(13)
α/°	90
β/°	97.085(10)
γ/°	90
Volume/Å^3	3781.0(7)
Z	4
ρ_{calc}g/cm^3	2.078
μ/mm^{-1}	8.198
F(000)	2234.0
Crystal size/mm^3	0.24 × 0.16 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.978 to 59.556
Index ranges	-25 ≤ h ≤ 25, -24 ≤ k ≤ 25, -15 ≤ l ≤ 15
Reflections collected	55840
Independent reflections	9695 [R_{int} = 0.0781, R_{sigma} = 0.0596]
Data/restraints/parameters	9695/36/493
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0991
Final R indexes [all data]	R_1 = 0.0727, wR_2 = 0.1115
Largest diff. peak/hole / e Å^{-3}	1.25/-0.97

Table 2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for *Z*-3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Au1	0.59832(2)	0.60511(2)	0.51272(2)	0.05450(9)
Au2	0.97394(2)	0.38836(2)	0.66358(2)	0.05508(9)
C1	0.5510(3)	0.5387(3)	0.7651(4)	0.0483(12)
C2	0.5449(3)	0.6070(3)	0.8148(6)	0.0608(15)
C3	0.4915(4)	0.6222(4)	0.8859(6)	0.0709(17)
C4	0.4418(4)	0.5687(4)	0.9057(5)	0.0703(18)
C5	0.4464(3)	0.5011(4)	0.8576(5)	0.0643(16)
C6	0.5022(3)	0.4850(4)	0.7881(5)	0.0573(14)
C7	0.7072(3)	0.5320(3)	0.7557(5)	0.0537(13)
C8	0.7688(3)	0.5266(4)	0.6955(6)	0.0733(18)
C9	0.8374(3)	0.5273(4)	0.7597(7)	0.081(2)
C10	0.8458(4)	0.5326(4)	0.8834(7)	0.0723(18)
C11	0.7863(4)	0.5380(4)	0.9426(6)	0.0718(17)
C12	0.7164(3)	0.5371(3)	0.8770(5)	0.0626(15)
C13	0.6133(3)	0.4337(3)	0.6102(4)	0.0460(11)
C14	0.5891(3)	0.4185(3)	0.4889(5)	0.0502(12)
C15	0.5903(3)	0.3503(3)	0.4435(5)	0.0510(13)
C16	0.6178(3)	0.2951(3)	0.5186(5)	0.0458(11)
C17	0.6437(3)	0.3070(3)	0.6382(4)	0.0459(11)
C18	0.6381(3)	0.3760(3)	0.6819(4)	0.0463(12)
C19	0.8457(3)	0.4457(3)	0.4410(5)	0.0503(12)
C20	0.8751(3)	0.5149(3)	0.4554(6)	0.0686(17)
C21	0.8334(4)	0.5741(4)	0.4126(8)	0.087(2)
C22	0.7635(4)	0.5640(4)	0.3565(8)	0.088(2)
C23	0.7343(4)	0.4951(4)	0.3405(6)	0.0707(17)
C24	0.7757(3)	0.4367(3)	0.3855(5)	0.0545(13)
C25	0.9554(3)	0.3549(3)	0.3599(5)	0.0531(13)
C26	1.0126(3)	0.3083(4)	0.3723(6)	0.0671(16)
C27	1.0492(4)	0.2942(4)	0.2704(8)	0.085(2)
C28	1.0290(4)	0.3283(4)	0.1650(6)	0.0757(19)
C29	0.9733(4)	0.3757(5)	0.1532(6)	0.081(2)
C30	0.9346(4)	0.3902(4)	0.2505(5)	0.0653(17)
C31	0.8485(3)	0.2909(3)	0.4949(4)	0.0443(11)
C32	0.8025(3)	0.2858(3)	0.5836(4)	0.0455(11)
C33	0.7628(3)	0.2245(3)	0.6033(4)	0.0453(11)
C34	0.7726(3)	0.1649(3)	0.5293(5)	0.0487(12)
C35	0.8162(3)	0.1670(3)	0.4394(4)	0.0514(13)
C36	0.8539(3)	0.2300(3)	0.4225(5)	0.0504(12)
Cl1	0.57157(10)	0.68576(9)	0.35919(16)	0.0770(5)
Cl2	1.03851(13)	0.40628(12)	0.84780(15)	0.0911(6)
F1	0.6582(2)	0.38673(18)	0.7997(3)	0.0629(8)
F2	0.61820(18)	0.22678(17)	0.4764(3)	0.0567(7)
F3	0.79638(17)	0.34324(16)	0.6558(3)	0.0540(7)
F4	0.7364(2)	0.10434(16)	0.5506(3)	0.0622(8)
N1	0.6699(3)	0.2504(3)	0.7220(4)	0.0526(11)
N2	0.7228(3)	0.2125(2)	0.7040(4)	0.0500(10)
P1	0.61864(7)	0.52669(8)	0.66464(12)	0.0484(3)
P2	0.90543(7)	0.37095(8)	0.48767(11)	0.0461(3)
Cl8	0.1948(3)	0.2908(5)	0.9662(7)	0.129(3)
C38	0.2719(3)	0.2554(3)	0.9061(6)	0.114(6)

Cl6	0.2489(5)	0.2287(4)	0.7536(7)	0.121(3)
Cl7	0.3454(3)	0.3178(6)	0.9216(9)	0.103(4)
Cl5	0.3278(5)	0.3333(5)	0.9070(9)	0.095(3)
Cl4	0.2156(7)	0.2700(6)	1.0377(10)	0.220(7)
Cl3	0.2546(5)	0.1994(4)	0.8205(10)	0.167(5)
C37	0.2867(5)	0.2521(4)	0.9489(7)	0.157(8)

Table 3 Anisotropic Displacement Parameters for *Z*-3

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Au1	0.05442(14)	0.05611(15)	0.05254(14)	0.00253(9)	0.00496(10)	-0.00033(9)
Au2	0.05944(14)	0.06476(16)	0.03929(12)	0.00068(9)	-0.00087(9)	-0.01185(10)
C1	0.046(3)	0.059(3)	0.040(3)	-0.001(2)	0.005(2)	0.004(2)
C2	0.058(3)	0.065(4)	0.059(4)	-0.005(3)	0.007(3)	0.010(3)
C3	0.073(4)	0.075(4)	0.064(4)	-0.008(3)	0.007(3)	0.020(4)
C4	0.061(4)	0.099(5)	0.052(3)	0.002(3)	0.012(3)	0.024(4)
C5	0.052(3)	0.087(5)	0.053(3)	0.015(3)	0.003(3)	0.006(3)
C6	0.052(3)	0.070(4)	0.049(3)	-0.004(3)	0.002(2)	0.002(3)
C7	0.052(3)	0.052(3)	0.055(3)	-0.005(3)	0.000(2)	-0.001(2)
C8	0.059(4)	0.098(5)	0.061(4)	-0.017(4)	-0.002(3)	0.003(4)
C9	0.051(3)	0.094(5)	0.097(5)	-0.032(4)	0.004(3)	0.001(3)
C10	0.060(4)	0.062(4)	0.087(5)	-0.010(3)	-0.021(3)	-0.008(3)
C11	0.075(4)	0.078(5)	0.057(4)	0.002(3)	-0.010(3)	-0.011(4)
C12	0.060(3)	0.068(4)	0.059(3)	0.001(3)	0.004(3)	-0.009(3)
C13	0.040(3)	0.054(3)	0.044(3)	-0.001(2)	0.007(2)	0.000(2)
C14	0.046(3)	0.063(3)	0.041(3)	0.001(2)	0.002(2)	0.004(2)
C15	0.042(3)	0.072(4)	0.037(3)	-0.006(3)	-0.001(2)	-0.001(2)
C16	0.044(3)	0.051(3)	0.043(3)	-0.005(2)	0.011(2)	-0.008(2)
C17	0.047(3)	0.055(3)	0.037(2)	0.003(2)	0.012(2)	0.000(2)
C18	0.046(3)	0.060(3)	0.032(2)	0.000(2)	0.006(2)	-0.004(2)
C19	0.050(3)	0.059(3)	0.043(3)	0.003(2)	0.011(2)	-0.008(3)
C20	0.054(3)	0.059(4)	0.095(5)	0.010(3)	0.015(3)	-0.007(3)
C21	0.075(5)	0.061(4)	0.129(7)	0.014(4)	0.031(5)	-0.007(4)
C22	0.081(5)	0.083(5)	0.103(6)	0.035(5)	0.027(4)	0.020(4)
C23	0.067(4)	0.081(5)	0.063(4)	0.020(3)	0.002(3)	0.012(3)
C24	0.060(3)	0.055(3)	0.049(3)	-0.003(3)	0.007(2)	-0.001(3)
C25	0.047(3)	0.067(4)	0.047(3)	-0.004(3)	0.010(2)	-0.013(3)
C26	0.063(4)	0.069(4)	0.072(4)	0.007(3)	0.020(3)	0.001(3)
C27	0.072(4)	0.070(4)	0.120(7)	-0.013(4)	0.041(4)	0.001(4)
C28	0.084(5)	0.085(5)	0.064(4)	-0.010(4)	0.031(4)	-0.022(4)
C29	0.083(5)	0.113(6)	0.050(4)	0.004(4)	0.019(3)	-0.014(4)
C30	0.065(4)	0.091(5)	0.040(3)	0.005(3)	0.009(3)	-0.003(3)
C31	0.045(3)	0.051(3)	0.036(2)	0.001(2)	0.000(2)	-0.006(2)
C32	0.053(3)	0.049(3)	0.034(2)	0.003(2)	0.003(2)	0.001(2)
C33	0.051(3)	0.050(3)	0.035(2)	0.002(2)	0.006(2)	0.000(2)
C34	0.052(3)	0.049(3)	0.044(3)	0.002(2)	0.003(2)	-0.004(2)
C35	0.056(3)	0.053(3)	0.044(3)	-0.007(2)	0.004(2)	0.002(2)
C36	0.050(3)	0.061(3)	0.040(3)	-0.001(2)	0.006(2)	0.000(3)
Cl1	0.0938(12)	0.0665(10)	0.069(1)	0.0152(8)	0.0039(9)	-0.0052(9)
Cl2	0.1186(15)	0.0989(14)	0.0474(9)	-0.0014(8)	-0.0229(9)	-0.0193(11)
F1	0.078(2)	0.066(2)	0.0427(17)	-0.0033(14)	0.0004(15)	0.0028(16)
F2	0.0700(19)	0.0546(18)	0.0461(16)	-0.0064(14)	0.0098(14)	-0.0036(15)
F3	0.0681(19)	0.0532(18)	0.0428(15)	-0.0060(13)	0.0151(14)	-0.0103(15)

F4	0.073(2)	0.0494(18)	0.067(2)	0.0001(15)	0.0171(17)	-0.0069(15)
N1	0.070(3)	0.055(3)	0.036(2)	0.0009(19)	0.015(2)	-0.010(2)
N2	0.060(3)	0.049(2)	0.043(2)	0.0035(19)	0.013(2)	-0.001(2)
P1	0.0460(7)	0.0533(8)	0.0450(7)	-0.0031(6)	0.0021(5)	0.0018(6)
P2	0.0467(7)	0.0549(7)	0.0371(6)	0.0014(5)	0.0060(5)	-0.0050(6)
Cl8	0.079(3)	0.160(7)	0.152(6)	-0.075(6)	0.026(4)	-0.021(4)
C38	0.088(9)	0.117(13)	0.141(11)	-0.019(9)	0.034(8)	-0.011(8)
Cl6	0.130(6)	0.095(5)	0.147(6)	-0.034(4)	0.051(5)	-0.031(4)
Cl7	0.082(5)	0.099(5)	0.123(6)	0.033(4)	-0.003(4)	-0.003(4)
Cl5	0.093(4)	0.105(6)	0.088(4)	-0.012(5)	0.005(4)	0.000(5)
Cl4	0.224(13)	0.179(10)	0.268(14)	0.067(9)	0.067(11)	-0.022(9)
Cl3	0.142(7)	0.126(7)	0.208(9)	-0.092(7)	-0.079(7)	0.046(5)
C37	0.183(16)	0.130(13)	0.151(13)	-0.022(9)	-0.015(10)	-0.067(11)

Table 4 Bond Lengths for *Z*-3

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	**Cl1**	2.2797(16)	**C19**	**P2**	1.805(6)
Au1	**P1**	2.2278(14)	**C20**	**C21**	1.389(10)
Au2	**Cl2**	2.2693(16)	**C21**	**C22**	1.376(11)
Au2	**P2**	2.2230(13)	**C22**	**C23**	1.386(11)
C1	**C2**	1.390(8)	**C23**	**C24**	1.382(9)
C1	**C6**	1.385(8)	**C25**	**C26**	1.358(9)
C1	**P1**	1.792(5)	**C25**	**C30**	1.395(8)
C2	**C3**	1.368(9)	**C25**	**P2**	1.815(5)
C3	**C4**	1.386(10)	**C26**	**C27**	1.416(10)
C4	**C5**	1.369(10)	**C27**	**C28**	1.346(11)
C5	**C6**	1.395(8)	**C28**	**C29**	1.345(11)
C7	**C8**	1.394(8)	**C29**	**C30**	1.397(9)
C7	**C12**	1.346(8)	**C31**	**C32**	1.384(7)
C7	**P1**	1.817(5)	**C31**	**C36**	1.397(7)
C8	**C9**	1.375(9)	**C31**	**P2**	1.824(5)
C9	**C10**	1.374(10)	**C32**	**C33**	1.383(7)
C10	**C11**	1.353(10)	**C32**	**F3**	1.346(6)
C11	**C12**	1.404(8)	**C33**	**C34**	1.402(7)
C13	**C14**	1.401(7)	**C33**	**N2**	1.435(6)
C13	**C18**	1.378(7)	**C34**	**C35**	1.361(7)
C13	**P1**	1.823(5)	**C34**	**F4**	1.341(6)
C14	**C15**	1.361(8)	**C35**	**C36**	1.383(8)
C15	**C16**	1.378(8)	**N1**	**N2**	1.238(6)
C16	**C17**	1.378(7)	**Cl8**	**C38**	1.7710
C16	**F2**	1.350(6)	**C38**	**Cl6**	1.7724
C17	**C18**	1.376(7)	**C38**	**Cl7**	1.7743
C17	**N1**	1.447(7)	**Cl5**	**C37**	1.7717
C18	**F1**	1.337(6)	**Cl4**	**C37**	1.7695
C19	**C20**	1.392(8)	**Cl3**	**C37**	1.7748
C19	**C24**	1.372(8)			

Table 5 Bond Angles for *Z*-3

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	**Au1**	**Cl1**	177.12(6)	**C26**	**C25**	**P2**	119.2(5)
P2	**Au2**	**Cl2**	177.04(7)	**C30**	**C25**	**P2**	119.9(5)
C2	**C1**	**P1**	117.3(4)	**C25**	**C26**	**C27**	118.5(7)

C6	**C1**	**C2**	119.5(5)	**C28**	**C27**	**C26**	120.4(7)
C6	**C1**	**P1**	123.1(4)	**C29**	**C28**	**C27**	121.2(7)
C3	**C2**	**C1**	121.2(6)	**C28**	**C29**	**C30**	120.4(7)
C2	**C3**	**C4**	118.9(6)	**C25**	**C30**	**C29**	118.6(7)
C5	**C4**	**C3**	121.0(6)	**C32**	**C31**	**C36**	117.0(5)
C4	**C5**	**C6**	119.9(6)	**C32**	**C31**	**P2**	119.6(4)
C1	**C6**	**C5**	119.4(6)	**C36**	**C31**	**P2**	123.1(4)
C8	**C7**	**P1**	117.3(4)	**C33**	**C32**	**C31**	123.5(5)
C12	**C7**	**C8**	118.7(5)	**F3**	**C32**	**C31**	118.6(4)
C12	**C7**	**P1**	124.0(5)	**F3**	**C32**	**C33**	117.9(4)
C9	**C8**	**C7**	120.2(6)	**C32**	**C33**	**C34**	116.3(4)
C10	**C9**	**C8**	120.4(7)	**C32**	**C33**	**N2**	125.7(4)
C11	**C10**	**C9**	119.9(6)	**C34**	**C33**	**N2**	117.1(5)
C10	**C11**	**C12**	119.6(6)	**C35**	**C34**	**C33**	122.8(5)
C7	**C12**	**C11**	121.3(6)	**F4**	**C34**	**C33**	116.7(5)
C14	**C13**	**P1**	120.7(4)	**F4**	**C34**	**C35**	120.5(5)
C18	**C13**	**C14**	116.6(5)	**C34**	**C35**	**C36**	118.6(5)
C18	**C13**	**P1**	122.5(4)	**C35**	**C36**	**C31**	121.8(5)
C15	**C14**	**C13**	121.9(5)	**N2**	**N1**	**C17**	120.8(4)
C14	**C15**	**C16**	118.9(5)	**N1**	**N2**	**C33**	122.1(4)
C15	**C16**	**C17**	121.9(5)	**C1**	**P1**	**Au1**	109.30(18)
F2	**C16**	**C15**	120.0(4)	**C1**	**P1**	**C7**	107.0(3)
F2	**C16**	**C17**	118.1(5)	**C1**	**P1**	**C13**	108.2(2)
C16	**C17**	**N1**	124.0(5)	**C7**	**P1**	**Au1**	116.5(2)
C18	**C17**	**C16**	117.3(5)	**C7**	**P1**	**C13**	104.2(2)
C18	**C17**	**N1**	118.5(4)	**C13**	**P1**	**Au1**	111.34(17)
C17	**C18**	**C13**	123.2(5)	**C19**	**P2**	**Au2**	113.85(18)
F1	**C18**	**C13**	119.2(5)	**C19**	**P2**	**C25**	104.5(3)
F1	**C18**	**C17**	117.5(5)	**C19**	**P2**	**C31**	107.5(2)
C20	**C19**	**P2**	117.1(4)	**C25**	**P2**	**Au2**	115.38(18)
C24	**C19**	**C20**	119.7(5)	**C25**	**P2**	**C31**	104.6(2)
C24	**C19**	**P2**	123.0(4)	**C31**	**P2**	**Au2**	110.28(16)
C21	**C20**	**C19**	119.7(6)	**Cl8**	**C38**	**Cl6**	111.0
C22	**C21**	**C20**	119.8(7)	**Cl8**	**C38**	**Cl7**	111.2
C21	**C22**	**C23**	120.8(7)	**Cl6**	**C38**	**Cl7**	111.4
C24	**C23**	**C22**	119.0(6)	**Cl5**	**C37**	**Cl3**	111.4
C19	**C24**	**C23**	121.1(6)	**Cl4**	**C37**	**Cl5**	111.1
C26	**C25**	**C30**	120.8(6)	**Cl4**	**C37**	**Cl3**	111.0

Table 6 Atomic Occupancy for *Z*-3

Atom	***Occupancy***	**Atom**	***Occupancy***
C38	0.4	**C37**	0.4
H38	0.4	**H1**	0.4
Cl6	0.4	**Cl3**	0.4
Cl7	0.4	**Cl4**	0.4
Cl8	0.4	**Cl5**	0.4

Crystal Data for *E*-**6** :

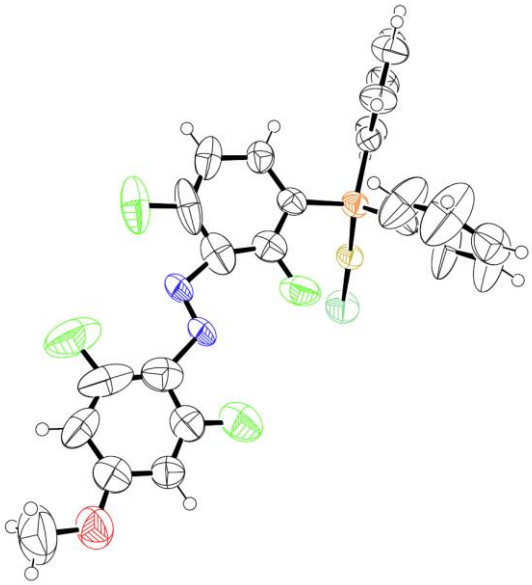


Figure SI7 : Ortep view of the complex (Color scheme: C, gray; N, blue; F, green; Au, brown; Cl, pale green; P, orange)

$C_{25}H_{17}AuClF_4N_2OP$ (M =700.79 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 19.942(2) Å, b = 10.9697(7) Å, c = 24.135(2) Å, β = 112.700(11)°, V = 4870.6(8) Å^3, Z = 8, T = 250 K, μ(MoKα) = 6.268 mm^{-1}, *Dcalc* = 1.911 g/cm^3, 44413 reflections measured (6.666° ≤ 2Θ ≤ 52.738°), 9919 unique (R_{int} = 0.0720, R_{sigma} = 0.0726) which were used in all calculations. The final R_1 was 0.0486 (I > 2σ(I)) and wR_2 was 0.1371 (all data).

Table 1 Crystal data and structure refinement for *E*-6	
CCDC number	1484587
Empirical formula	$C_{25}H_{17}AuClF_4N_2OP$
Formula weight	700.79
Temperature/K	250
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	19.942(2)
b/Å	10.9697(7)
c/Å	24.135(2)
α/°	90
β/°	112.700(11)
γ/°	90
Volume/Å^3	4870.6(8)
Z	8
ρ_{calc}g/cm^3	1.911
μ/mm^{-1}	6.268
F(000)	2688.0
Crystal size/mm^3	0.23 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.666 to 52.738
Index ranges	-24 ≤ h ≤ 24, -13 ≤ k ≤ 12, -30 ≤ l ≤ 30
Reflections collected	44413
Independent reflections	9919 [R_{int} = 0.0720, R_{sigma} = 0.0726]
Data/restraints/parameters	9919/10/585
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0486, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.1371
Largest diff. peak/hole / e Å^{-3}	1.02/-1.23

Table 2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for *E*-6

Atom	*x*	*y*	*z*	U(eq)
Au1	0.06879(2)	0.24009(3)	0.79035(2)	0.05406(13)
Cl1	0.00203(18)	0.0658(2)	0.76163(13)	0.0892(9)
P1	0.13434(13)	0.4093(2)	0.82145(10)	0.0512(5)
F1	0.2504(3)	0.2352(5)	0.8858(3)	0.0913(19)
F2	0.2840(4)	0.3388(7)	1.0845(3)	0.122(3)
F3	0.4044(6)	0.0679(8)	1.1394(5)	0.162(4)
F4	0.3851(4)	-0.0226(6)	0.9457(3)	0.108(2)
O1	0.5454(5)	-0.2437(8)	1.1018(4)	0.103(3)
N1	0.3179(8)	0.1983(15)	1.0266(7)	0.062(2)
N2	0.3378(10)	0.1269(16)	0.9967(11)	0.062(2)
N3	0.3241(10)	0.1742(16)	0.9888(11)	0.062(2)
N4	0.3482(8)	0.1293(13)	1.0415(7)	0.062(2)
C1	0.1960(3)	0.4411(6)	0.7857(3)	0.056(2)
C6	0.1785(4)	0.3946(8)	0.7282(3)	0.129(6)
C5	0.2215(5)	0.4225(10)	0.6964(3)	0.142(6)
C4	0.2821(5)	0.4970(9)	0.7220(4)	0.099(4)
C3	0.2996(4)	0.5435(9)	0.7795(5)	0.170(9)
C2	0.2566(4)	0.5155(8)	0.8113(3)	0.132(6)
C7	0.0778(3)	0.5445(4)	0.8099(3)	0.050(2)
C8	0.0028(3)	0.5303(4)	0.7876(3)	0.064(2)
C9	-0.0420(2)	0.6320(6)	0.7769(3)	0.076(3)
C10	-0.0117(4)	0.7481(5)	0.7885(3)	0.073(3)
C11	0.0634(4)	0.7623(4)	0.8108(3)	0.082(3)
C12	0.1081(3)	0.6605(5)	0.8215(3)	0.072(3)
C13	0.1877(5)	0.4016(7)	0.9023(4)	0.053(2)
C14	0.2372(5)	0.3091(9)	0.9257(5)	0.066(3)
C15	0.2731(6)	0.2777(10)	0.9853(6)	0.085(3)
C16	0.2544(7)	0.3549(15)	1.0233(5)	0.103(5)
C17	0.2055(6)	0.4534(12)	1.0046(5)	0.083(3)
C18	0.1734(5)	0.4746(9)	0.9436(4)	0.062(2)
C19	0.3900(6)	0.0354(10)	1.0379(7)	0.088(3)
C20	0.4150(6)	-0.0420(10)	1.0061(5)	0.078(3)
C21	0.4632(5)	-0.1321(9)	1.0247(5)	0.068(3)
C22	0.4947(6)	-0.1512(10)	1.0860(6)	0.081(3)
C23	0.4733(7)	-0.0837(13)	1.1242(6)	0.096(4)
C24	0.4225(9)	0.0049(13)	1.0998(9)	0.115(5)
C25	0.5892(10)	-0.2614(18)	1.1649(7)	0.171(8)
Au2	0.44221(2)	0.37654(3)	0.39042(2)	0.04605(12)
Cl2	0.50957(12)	0.20410(19)	0.39845(10)	0.0604(6)
P2	0.37402(11)	0.53786(19)	0.39002(9)	0.0456(5)
F5	0.2716(3)	0.3488(5)	0.3941(3)	0.0811(16)
F6	0.2857(3)	0.4130(6)	0.5902(3)	0.100(2)
F7	0.1591(4)	0.1380(6)	0.5642(3)	0.122(3)
F8	0.1235(5)	0.1326(7)	0.3602(4)	0.132(3)
O2	0.0135(4)	-0.1623(6)	0.4409(3)	0.0797(19)
N5	0.2350(8)	0.2833(13)	0.5035(6)	0.059(2)
N6	0.1904(9)	0.2427(15)	0.4542(7)	0.059(2)
N7	0.2205(10)	0.2736(15)	0.4630(7)	0.059(2)
N8	0.1965(8)	0.2379(12)	0.4985(6)	0.059(2)
C26	0.4247(2)	0.6798(4)	0.4108(2)	0.0442(18)
C31	0.4994(3)	0.6735(4)	0.4427(2)	0.052(2)
C30	0.5397(2)	0.7799(5)	0.4613(2)	0.060(2)
C29	0.5054(3)	0.8926(4)	0.4481(3)	0.058(2)
C28	0.4306(3)	0.8989(3)	0.4163(3)	0.068(3)
C27	0.3903(2)	0.7925(5)	0.3977(3)	0.059(2)
C32	0.2985(3)	0.5684(5)	0.3200(2)	0.052(2)
C33	0.2351(3)	0.6240(6)	0.3184(2)	0.066(3)

C34	0.1812(3)	0.6566(6)	0.2637(3)	0.084(3)
C35	0.1907(3)	0.6338(7)	0.2105(2)	0.096(4)
C36	0.2540(4)	0.5782(7)	0.2121(2)	0.094(4)
C37	0.3079(3)	0.5456(6)	0.2668(3)	0.070(3)
C38	0.3386(4)	0.5138(7)	0.4496(4)	0.0472(19)
C39	0.3629(4)	0.5788(8)	0.5018(4)	0.051(2)
C40	0.3455(5)	0.5448(8)	0.5496(4)	0.059(2)
C41	0.3023(5)	0.4481(9)	0.5433(4)	0.064(3)
C42	0.2721(5)	0.3791(8)	0.4912(5)	0.066(3)
C43	0.2932(5)	0.4160(8)	0.4455(4)	0.057(2)
C44	0.1471(6)	0.1433(10)	0.4643(7)	0.097(4)
C45	0.1297(6)	0.0859(11)	0.5093(6)	0.084(3)
C46	0.0877(6)	-0.0129(11)	0.5021(5)	0.079(3)
C47	0.0565(5)	-0.0641(9)	0.4464(5)	0.071(3)
C48	0.0687(6)	-0.0125(9)	0.3977(5)	0.080(3)
C49	0.1134(6)	0.0878(10)	0.4087(7)	0.090(4)
C50	-0.0207(7)	-0.2157(10)	0.3834(6)	0.101(4)

Table 3 Anisotropic Displacement Parameters for *E*-6

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Au1	0.0651(3)	0.0421(2)	0.0558(2)	0.00004(15)	0.02437(19)	-0.00493(16)
Cl1	0.121(2)	0.0546(15)	0.0912(19)	-0.0083(13)	0.0394(18)	-0.0293(16)
P1	0.0565(14)	0.0433(12)	0.0543(13)	0.0015(10)	0.0219(11)	-0.0039(11)
F1	0.087(4)	0.068(4)	0.100(5)	0.000(3)	0.016(4)	0.023(3)
F2	0.113(5)	0.167(7)	0.057(4)	0.028(4)	0.001(4)	-0.053(5)
F3	0.197(9)	0.140(7)	0.207(9)	-0.041(7)	0.142(8)	0.011(7)
F4	0.094(5)	0.096(5)	0.116(6)	0.014(4)	0.020(4)	0.013(4)
O1	0.089(6)	0.128(7)	0.086(6)	0.018(5)	0.027(5)	0.021(5)
N1	0.060(6)	0.063(8)	0.054(6)	0.019(7)	0.012(6)	0.027(5)
N2	0.060(6)	0.063(8)	0.054(6)	0.019(7)	0.012(6)	0.027(5)
N3	0.060(6)	0.063(8)	0.054(6)	0.019(7)	0.012(6)	0.027(5)
N4	0.060(6)	0.063(8)	0.054(6)	0.019(7)	0.012(6)	0.027(5)
C1	0.062(6)	0.045(5)	0.058(5)	0.010(4)	0.018(5)	-0.003(4)
C6	0.126(11)	0.219(16)	0.059(7)	-0.030(8)	0.053(8)	-0.086(11)
C5	0.115(11)	0.257(19)	0.066(8)	-0.011(10)	0.048(8)	-0.045(13)
C4	0.087(9)	0.098(9)	0.129(11)	0.024(8)	0.063(8)	-0.004(7)
C3	0.144(14)	0.24(2)	0.166(16)	-0.101(15)	0.102(13)	-0.119(15)
C2	0.098(10)	0.190(15)	0.136(12)	-0.080(11)	0.079(9)	-0.067(10)
C7	0.063(6)	0.042(5)	0.052(5)	0.002(4)	0.030(4)	-0.001(4)
C8	0.062(6)	0.052(6)	0.075(6)	0.004(5)	0.024(5)	0.002(5)
C9	0.066(7)	0.076(8)	0.084(7)	0.015(6)	0.026(6)	0.014(6)
C10	0.094(8)	0.058(7)	0.070(7)	0.017(5)	0.037(6)	0.018(6)
C11	0.092(9)	0.053(6)	0.098(8)	0.002(5)	0.032(7)	0.007(6)
C12	0.065(6)	0.052(6)	0.098(8)	-0.003(5)	0.032(6)	-0.006(5)
C13	0.053(5)	0.040(5)	0.060(5)	-0.001(4)	0.017(4)	-0.011(4)
C14	0.057(6)	0.055(6)	0.076(7)	-0.004(5)	0.015(5)	-0.012(5)
C15	0.070(7)	0.082(8)	0.077(8)	0.013(7)	0.000(7)	-0.025(6)
C16	0.083(9)	0.136(12)	0.060(8)	0.044(8)	-0.007(7)	-0.062(9)
C17	0.086(8)	0.112(9)	0.047(6)	-0.004(6)	0.023(6)	-0.031(7)
C18	0.065(6)	0.064(6)	0.055(6)	0.002(5)	0.023(5)	-0.008(5)
C19	0.082(8)	0.071(8)	0.120(11)	0.001(8)	0.050(8)	-0.001(6)
C20	0.077(7)	0.072(7)	0.076(8)	0.003(6)	0.019(6)	-0.005(6)
C21	0.064(6)	0.071(7)	0.071(7)	0.002(5)	0.027(6)	0.006(5)
C22	0.076(7)	0.072(7)	0.093(9)	0.001(6)	0.029(7)	-0.008(6)
C23	0.118(10)	0.105(9)	0.085(8)	-0.029(7)	0.063(8)	-0.020(9)
C24	0.117(11)	0.078(9)	0.195(17)	-0.051(11)	0.109(13)	-0.027(8)
C25	0.159(16)	0.24(2)	0.091(12)	0.038(12)	0.022(12)	0.038(14)
Au2	0.0482(2)	0.0369(2)	0.0509(2)	-0.00624(14)	0.01665(16)	0.00190(14)

Cl2	0.0695(14)	0.0414(12)	0.0739(15)	-0.0043(10)	0.0316(12)	0.0113(11)
P2	0.0461(12)	0.0403(12)	0.0476(12)	-0.0027(9)	0.0150(10)	0.0045(9)
F5	0.083(4)	0.064(3)	0.104(4)	-0.024(3)	0.045(3)	-0.029(3)
F6	0.097(5)	0.124(5)	0.102(5)	0.038(4)	0.065(4)	0.018(4)
F7	0.117(6)	0.105(5)	0.100(5)	-0.025(4)	-0.006(4)	-0.007(4)
F8	0.160(8)	0.106(6)	0.155(7)	-0.013(5)	0.088(6)	-0.056(5)
O2	0.085(5)	0.074(5)	0.077(5)	0.004(4)	0.028(4)	-0.024(4)
N5	0.074(8)	0.051(6)	0.059(5)	-0.001(5)	0.033(7)	-0.021(5)
N6	0.074(8)	0.051(6)	0.059(5)	-0.001(5)	0.033(7)	-0.021(5)
N7	0.074(8)	0.051(6)	0.059(5)	-0.001(5)	0.033(7)	-0.021(5)
N8	0.074(8)	0.051(6)	0.059(5)	-0.001(5)	0.033(7)	-0.021(5)
C26	0.050(5)	0.038(5)	0.040(4)	-0.001(4)	0.014(4)	0.002(4)
C31	0.053(5)	0.038(5)	0.057(5)	0.006(4)	0.012(4)	-0.001(4)
C30	0.055(5)	0.052(5)	0.065(6)	-0.003(5)	0.013(5)	0.000(5)
C29	0.066(6)	0.046(5)	0.065(6)	-0.008(4)	0.030(5)	-0.020(5)
C28	0.072(7)	0.036(5)	0.092(7)	-0.002(5)	0.027(6)	0.005(5)
C27	0.046(5)	0.042(5)	0.079(6)	0.007(5)	0.014(5)	0.006(4)
C32	0.043(5)	0.048(5)	0.055(5)	-0.004(4)	0.006(4)	0.004(4)
C33	0.053(6)	0.060(6)	0.072(7)	-0.008(5)	0.011(5)	-0.002(5)
C34	0.050(6)	0.079(7)	0.085(8)	0.004(6)	-0.016(6)	0.008(5)
C35	0.081(9)	0.115(10)	0.051(7)	0.012(6)	-0.019(6)	-0.001(7)
C36	0.078(8)	0.141(11)	0.051(6)	0.012(7)	0.012(6)	0.019(8)
C37	0.065(6)	0.091(7)	0.049(6)	0.001(5)	0.016(5)	0.009(5)
C38	0.047(5)	0.040(5)	0.055(5)	-0.007(4)	0.020(4)	0.007(4)
C39	0.046(5)	0.053(5)	0.054(5)	-0.002(4)	0.018(4)	0.004(4)
C40	0.061(6)	0.060(6)	0.060(6)	0.001(4)	0.026(5)	0.010(5)
C41	0.065(6)	0.074(7)	0.071(7)	0.029(6)	0.045(6)	0.023(5)
C42	0.058(6)	0.055(6)	0.092(8)	0.019(6)	0.036(6)	0.008(5)
C43	0.055(5)	0.040(5)	0.069(6)	-0.010(4)	0.017(5)	0.002(4)
C44	0.054(7)	0.067(8)	0.141(12)	-0.033(8)	0.006(7)	0.006(6)
C45	0.073(8)	0.068(8)	0.083(8)	-0.019(7)	-0.002(7)	0.007(6)
C46	0.063(6)	0.085(8)	0.078(8)	-0.011(6)	0.015(6)	-0.010(6)
C47	0.061(6)	0.064(7)	0.088(8)	0.001(6)	0.028(6)	-0.007(5)
C48	0.069(7)	0.064(7)	0.098(8)	-0.008(6)	0.022(6)	-0.007(6)
C49	0.088(8)	0.051(6)	0.145(12)	0.002(7)	0.062(9)	-0.008(6)
C50	0.115(10)	0.068(7)	0.106(10)	0.007(7)	0.026(8)	-0.023(7)

Table 4 Bond Lengths for *E*-6

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	**Cl1**	2.280(3)	**Au2**	**Cl2**	2.285(2)
Au1	**P1**	2.227(2)	**Au2**	**P2**	2.230(2)
P1	**C1**	1.788(5)	**P2**	**C26**	1.818(4)
P1	**C7**	1.818(5)	**P2**	**C32**	1.810(5)
P1	**C13**	1.829(9)	**P2**	**C38**	1.850(8)
F1	**C14**	1.360(11)	**F5**	**C43**	1.362(10)
F2	**C16**	1.374(12)	**F6**	**C41**	1.352(9)
F3	**C24**	1.339(14)	**F7**	**C45**	1.351(12)
F4	**C20**	1.361(12)	**F8**	**C49**	1.354(14)
O1	**C22**	1.379(13)	**O2**	**C47**	1.351(11)
O1	**C25**	1.447(16)	**O2**	**C50**	1.415(13)
N1	**N2**	1.23(3)	**N5**	**N6**	1.260(16)
N1	**C15**	1.365(14)	**N5**	**C42**	1.382(13)
N2	**C19**	1.509(14)	**N6**	**C44**	1.468(15)
N3	**N4**	1.27(3)	**N7**	**N8**	1.198(15)
N3	**C15**	1.505(15)	**N7**	**C42**	1.523(14)
N4	**C19**	1.348(14)	**N8**	**C44**	1.450(14)
C1	**C6**	1.3900	**C26**	**C31**	1.3900
C1	**C2**	1.3900	**C26**	**C27**	1.3900

C6	**C5**	1.3900	**C31**	**C30**	1.3900
C5	**C4**	1.3900	**C30**	**C29**	1.3900
C4	**C3**	1.3900	**C29**	**C28**	1.3900
C3	**C2**	1.3900	**C28**	**C27**	1.3900
C7	**C8**	1.3900	**C32**	**C33**	1.3900
C7	**C12**	1.3900	**C32**	**C37**	1.3900
C8	**C9**	1.3900	**C33**	**C34**	1.3900
C9	**C10**	1.3900	**C34**	**C35**	1.3900
C10	**C11**	1.3900	**C35**	**C36**	1.3900
C11	**C12**	1.3900	**C36**	**C37**	1.3900
C13	**C14**	1.376(13)	**C38**	**C39**	1.364(11)
C13	**C18**	1.392(12)	**C38**	**C43**	1.382(12)
C14	**C15**	1.381(14)	**C39**	**C40**	1.377(11)
C15	**C16**	1.402(18)	**C40**	**C41**	1.339(13)
C16	**C17**	1.408(18)	**C41**	**C42**	1.391(13)
C17	**C18**	1.378(13)	**C42**	**C43**	1.384(13)
C19	**C20**	1.362(15)	**C44**	**C45**	1.410(17)
C19	**C24**	1.42(2)	**C44**	**C49**	1.388(17)
C20	**C21**	1.330(14)	**C45**	**C46**	1.340(16)
C21	**C22**	1.383(15)	**C46**	**C47**	1.366(14)
C22	**C23**	1.372(15)	**C47**	**C48**	1.408(14)
C23	**C24**	1.363(19)	**C48**	**C49**	1.377(14)

Table 5 Bond Angles for *E*-6

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P1	**Au1**	**Cl1**	178.15(9)	**P2**	**Au2**	**Cl2**	174.41(8)
C1	**P1**	**Au1**	115.1(2)	**C26**	**P2**	**Au2**	113.94(19)
C1	**P1**	**C7**	105.5(3)	**C26**	**P2**	**C38**	104.2(3)
C1	**P1**	**C13**	107.4(4)	**C32**	**P2**	**Au2**	115.9(2)
C7	**P1**	**Au1**	112.3(2)	**C32**	**P2**	**C26**	105.8(3)
C7	**P1**	**C13**	105.8(4)	**C32**	**P2**	**C38**	108.8(3)
C13	**P1**	**Au1**	110.2(3)	**C38**	**P2**	**Au2**	107.4(2)
C22	**O1**	**C25**	118.0(11)	**C47**	**O2**	**C50**	118.3(8)
N2	**N1**	**C15**	104.3(15)	**N6**	**N5**	**C42**	107.9(13)
N1	**N2**	**C19**	109.5(18)	**N5**	**N6**	**C44**	110.6(13)
N4	**N3**	**C15**	109.5(17)	**N8**	**N7**	**C42**	108.4(13)
N3	**N4**	**C19**	103.7(15)	**N7**	**N8**	**C44**	101.4(13)
C6	**C1**	**P1**	117.1(4)	**C31**	**C26**	**P2**	118.2(3)
C6	**C1**	**C2**	120.0	**C31**	**C26**	**C27**	120.0
C2	**C1**	**P1**	122.8(4)	**C27**	**C26**	**P2**	121.7(3)
C1	**C6**	**C5**	120.0	**C30**	**C31**	**C26**	120.0
C6	**C5**	**C4**	120.0	**C31**	**C30**	**C29**	120.0
C3	**C4**	**C5**	120.0	**C28**	**C29**	**C30**	120.0
C4	**C3**	**C2**	120.0	**C29**	**C28**	**C27**	120.0
C3	**C2**	**C1**	120.0	**C28**	**C27**	**C26**	120.0
C8	**C7**	**P1**	118.6(3)	**C33**	**C32**	**P2**	121.8(3)
C8	**C7**	**C12**	120.0	**C33**	**C32**	**C37**	120.0
C12	**C7**	**P1**	121.4(3)	**C37**	**C32**	**P2**	117.9(3)
C9	**C8**	**C7**	120.0	**C32**	**C33**	**C34**	120.0
C8	**C9**	**C10**	120.0	**C35**	**C34**	**C33**	120.0
C11	**C10**	**C9**	120.0	**C34**	**C35**	**C36**	120.0
C12	**C11**	**C10**	120.0	**C35**	**C36**	**C37**	120.0
C11	**C12**	**C7**	120.0	**C36**	**C37**	**C32**	120.0
C14	**C13**	**P1**	120.1(7)	**C39**	**C38**	**P2**	122.5(6)
C14	**C13**	**C18**	116.3(9)	**C39**	**C38**	**C43**	117.5(8)
C18	**C13**	**P1**	122.8(7)	**C43**	**C38**	**P2**	119.4(6)
F1	**C14**	**C13**	116.9(9)	**C38**	**C39**	**C40**	121.1(8)
F1	**C14**	**C15**	115.2(10)	**C41**	**C40**	**C39**	118.7(9)

C13	**C14**	**C15**	127.8(10)	**F6**	**C41**	**C42**	116.3(9)
N1	**C15**	**C14**	148.2(14)	**C40**	**C41**	**F6**	119.1(10)
N1	**C15**	**C16**	99.9(13)	**C40**	**C41**	**C42**	124.6(8)
C14	**C15**	**N3**	108.3(13)	**N5**	**C42**	**C41**	107.4(10)
C14	**C15**	**C16**	111.7(10)	**N5**	**C42**	**C43**	138.3(11)
C16	**C15**	**N3**	139.9(14)	**C41**	**C42**	**N7**	143.1(10)
F2	**C16**	**C15**	120.9(14)	**C43**	**C42**	**N7**	103.1(10)
F2	**C16**	**C17**	113.7(15)	**C43**	**C42**	**C41**	113.8(8)
C15	**C16**	**C17**	125.4(10)	**F5**	**C43**	**C38**	117.0(8)
C18	**C17**	**C16**	116.8(11)	**F5**	**C43**	**C42**	118.7(8)
C17	**C18**	**C13**	121.9(10)	**C38**	**C43**	**C42**	124.2(8)
N4	**C19**	**C20**	151.9(14)	**C45**	**C44**	**N6**	142.6(12)
N4	**C19**	**C24**	98.9(13)	**C45**	**C44**	**N8**	101.3(12)
C20	**C19**	**N2**	110.7(14)	**C49**	**C44**	**N6**	105.2(13)
C20	**C19**	**C24**	109.2(10)	**C49**	**C44**	**N8**	146.5(14)
C24	**C19**	**N2**	140.2(15)	**C49**	**C44**	**C45**	112.2(10)
F4	**C20**	**C19**	113.7(11)	**F7**	**C45**	**C44**	115.1(12)
C21	**C20**	**F4**	116.0(11)	**C46**	**C45**	**F7**	118.7(13)
C21	**C20**	**C19**	130.3(11)	**C46**	**C45**	**C44**	126.2(11)
C20	**C21**	**C22**	116.4(10)	**C45**	**C46**	**C47**	118.9(11)
O1	**C22**	**C21**	112.9(10)	**O2**	**C47**	**C46**	117.1(10)
C23	**C22**	**O1**	126.6(12)	**O2**	**C47**	**C48**	123.1(10)
C23	**C22**	**C21**	120.5(12)	**C46**	**C47**	**C48**	119.8(10)
C24	**C23**	**C22**	117.7(13)	**C49**	**C48**	**C47**	117.9(11)
F3	**C24**	**C19**	119.4(15)	**F8**	**C49**	**C44**	119.9(11)
F3	**C24**	**C23**	114.8(17)	**F8**	**C49**	**C48**	115.1(12)
C23	**C24**	**C19**	125.8(11)	**C48**	**C49**	**C44**	124.9(12)

Crystal Data for *Z*-**6**:

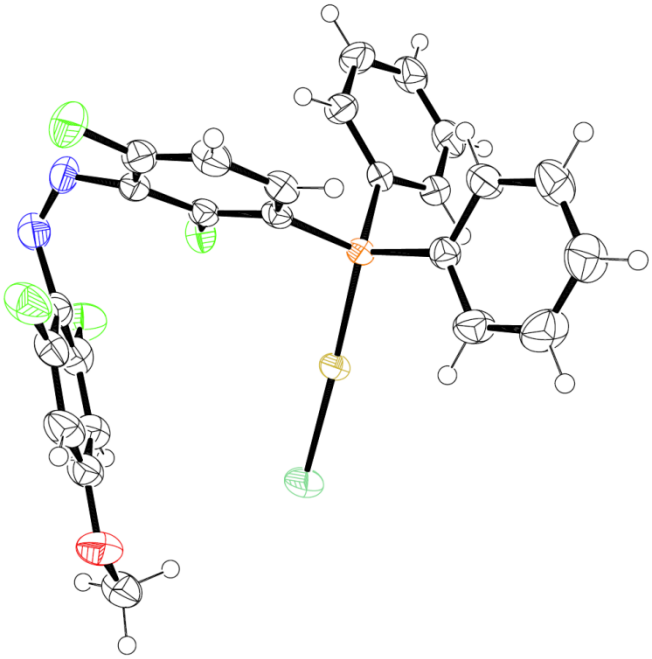


Figure SI8: Ortep view of the complex (Color scheme: C, gray; N, blue; F, green; Au, brown; Cl, pale green; P, orange)

$C_{25}H_{17}AuClF_4N_2OP$ (*M* =700.79 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 16.0034(5) Å, *b* = 8.3754(2) Å, *c* = 19.2521(5) Å, *β* = 111.188(3)°, *V* = 2406.02(13) Å^3, *Z* = 4, *T* = 200 K, μ(MoKα) = 6.345 mm^{-1}, *Dcalc* = 1.935 g/cm^3, 25630 reflections measured (7.496° ≤ 2Θ ≤ 60.118°), 6263 unique (R_{int} = 0.0393, R_{sigma} = 0.0405) which were used in all calculations. The final R_1 was 0.0258 (I > 2σ(I)) and wR_2 was 0.0598 (all data).

Table 1 Crystal data and structure refinement for *Z*-6	
CCDC number	1484588
Empirical formula	$C_{25}H_{17}AuClF_4N_2OP$
Formula weight	700.79
Temperature/K	200
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.0034(5)
b/Å	8.3754(2)
c/Å	19.2521(5)
α/°	90
β/°	111.188(3)
γ/°	90
Volume/Å^3	2406.02(13)
Z	4
ρ_{calc}g/cm^3	1.935
μ/mm^{-1}	6.345
F(000)	1344.0
Crystal size/mm^3	0.28 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71075)
2Θ range for data collection/°	7.496 to 60.118
Index ranges	$-21 \le h \le 20$, $-10 \le k \le 11$, $-27 \le l \le 25$
Reflections collected	25630
Independent reflections	6263 [R_{int} = 0.0393, R_{sigma} = 0.0405]
Data/restraints/parameters	6263/0/317
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0566
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0598
Largest diff. peak/hole / e Å^{-3}	1.41/-0.84

Table 2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters Z-6

Atom	*x*	*y*	*z*	U(eq)
Au1	0.14051(2)	0.42917(2)	0.53278(2)	0.02940(5)
C1	0.1642(2)	0.0942(3)	0.44570(15)	0.0295(6)
C2	0.1205(3)	0.0246(4)	0.48879(19)	0.0431(8)
C3	0.0904(3)	-0.1313(5)	0.4760(2)	0.0571(10)
C4	0.1025(3)	-0.2179(4)	0.4198(2)	0.0547(9)
C5	0.1468(3)	-0.1519(4)	0.3773(2)	0.0506(9)
C6	0.1777(2)	0.0030(4)	0.38979(17)	0.0394(7)
C7	0.18573(18)	0.3828(3)	0.37181(14)	0.0255(5)
C8	0.0985(2)	0.4145(3)	0.32438(17)	0.0335(6)
C9	0.0830(2)	0.4822(4)	0.25529(17)	0.0416(7)
C10	0.1535(2)	0.5189(4)	0.23358(17)	0.0434(8)
C11	0.2397(2)	0.4880(5)	0.27956(17)	0.0492(9)
C12	0.2565(2)	0.4169(4)	0.34913(17)	0.0380(7)
C13	0.32360(18)	0.2845(3)	0.50970(13)	0.0269(6)
C14	0.3709(2)	0.1412(4)	0.52255(15)	0.0321(6)
C15	0.4633(2)	0.1375(4)	0.55902(16)	0.0370(7)
C16	0.5075(2)	0.2780(4)	0.58126(15)	0.0372(7)
C17	0.4641(2)	0.4246(3)	0.57288(16)	0.0315(6)
C18	0.3723(2)	0.4236(3)	0.53534(15)	0.0283(6)
C19	0.4448(2)	0.6366(4)	0.67290(16)	0.0356(7)
C20	0.4632(2)	0.5138(4)	0.72552(16)	0.0397(7)
C21	0.4172(3)	0.4937(4)	0.77219(17)	0.0449(8)
C22	0.3475(2)	0.5982(4)	0.76686(17)	0.0404(8)
C23	0.3264(2)	0.7217(4)	0.71539(17)	0.0405(7)
C24	0.3767(2)	0.7385(4)	0.67184(17)	0.0405(7)
C25	0.2298(3)	0.6686(5)	0.8091(2)	0.0514(9)
Cl1	0.08525(6)	0.55569(10)	0.61219(5)	0.0494(2)
F1	0.32914(12)	0.56428(18)	0.52115(10)	0.0358(4)
F2	0.59769(12)	0.2788(3)	0.61422(11)	0.0520(5)
F3	0.53214(15)	0.4156(2)	0.73122(11)	0.0546(6)
F4	0.35809(16)	0.8603(3)	0.62255(12)	0.0613(6)
N1	0.51491(18)	0.5723(3)	0.58927(15)	0.0397(6)
N2	0.50042(19)	0.6731(3)	0.63133(15)	0.0433(7)
O1	0.30316(19)	0.5680(3)	0.81350(14)	0.0515(6)
P1	0.20218(5)	0.29764(9)	0.46283(3)	0.02505(14)

Table 3 Anisotropic Displacement Parameters for *Z*-6.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	0.03056(7)	0.03458(7)	0.02486(6)	-0.00283(4)	0.01218(5)	0.00008(5)
C1	0.0299(15)	0.0301(15)	0.0272(13)	0.0003(11)	0.0090(12)	-0.0002(12)
C2	0.056(2)	0.0377(17)	0.0447(18)	0.0012(15)	0.0291(17)	-0.0026(16)
C3	0.075(3)	0.0372(18)	0.072(3)	0.0076(19)	0.043(2)	-0.008(2)
C4	0.070(3)	0.0311(16)	0.064(2)	-0.0028(17)	0.026(2)	-0.0054(18)
C5	0.067(2)	0.0330(17)	0.0491(19)	-0.0087(16)	0.0176(18)	-0.0022(18)
C6	0.0475(19)	0.0395(17)	0.0330(15)	-0.0048(14)	0.0166(14)	-0.0030(16)
C7	0.0271(14)	0.0251(13)	0.0222(12)	-0.0022(11)	0.0062(11)	-0.0009(11)
C8	0.0313(15)	0.0378(17)	0.0319(14)	-0.0024(12)	0.0122(12)	-0.0020(13)
C9	0.0409(18)	0.0457(18)	0.0279(15)	0.0009(14)	0.0001(13)	0.0060(16)
C10	0.054(2)	0.0476(19)	0.0240(14)	0.0047(14)	0.0081(14)	-0.0049(17)
C11	0.0421(19)	0.078(3)	0.0300(15)	0.0047(17)	0.0162(14)	-0.0143(19)
C12	0.0288(15)	0.060(2)	0.0238(13)	0.0046(13)	0.0076(12)	-0.0021(14)
C13	0.0294(14)	0.0337(14)	0.0170(11)	0.0014(11)	0.0078(10)	0.0026(12)
C14	0.0377(16)	0.0348(15)	0.0233(13)	-0.0003(12)	0.0102(12)	0.0014(14)
C15	0.0387(17)	0.0412(17)	0.0279(14)	0.0026(14)	0.0080(12)	0.0115(15)

C16	0.0287(14)	0.0561(19)	0.0246(13)	0.0023(14)	0.0070(12)	0.0025(15)
C17	0.0295(15)	0.0429(17)	0.0229(13)	-0.0007(12)	0.0105(11)	-0.0035(13)
C18	0.0289(14)	0.0356(16)	0.0204(12)	0.0007(11)	0.0090(11)	0.0011(12)
C19	0.0411(17)	0.0338(16)	0.0287(14)	-0.0061(13)	0.0090(13)	-0.0108(14)
C20	0.0425(18)	0.0439(18)	0.0275(15)	-0.0044(14)	0.0065(13)	0.0003(16)
C21	0.061(2)	0.0439(18)	0.0282(15)	0.0047(15)	0.0143(15)	-0.0014(18)
C22	0.051(2)	0.0411(18)	0.0306(15)	-0.0013(13)	0.0158(14)	-0.0069(15)
C23	0.0499(19)	0.0343(16)	0.0395(16)	-0.0009(14)	0.0188(15)	-0.0012(15)
C24	0.052(2)	0.0275(16)	0.0397(16)	0.0025(13)	0.0133(15)	-0.0081(14)
C25	0.061(2)	0.056(2)	0.0422(18)	-0.0103(16)	0.0237(17)	-0.0037(19)
Cl1	0.0498(5)	0.0634(6)	0.0442(4)	-0.0156(4)	0.0280(4)	-0.0007(4)
F1	0.0353(9)	0.0303(9)	0.0358(9)	-0.0013(7)	0.0059(7)	-0.0009(7)
F2	0.0256(9)	0.0691(13)	0.0540(11)	0.0015(10)	0.0055(8)	0.0054(9)
F3	0.0551(13)	0.0692(15)	0.0344(10)	0.0044(9)	0.0101(9)	0.0192(10)
F4	0.0866(17)	0.0414(11)	0.0702(14)	0.0199(11)	0.0454(13)	0.0084(12)
N1	0.0295(13)	0.0497(17)	0.0373(14)	-0.0018(12)	0.0088(11)	-0.0118(12)
N2	0.0426(15)	0.0495(17)	0.0359(13)	-0.0040(13)	0.0118(12)	-0.0116(13)
O1	0.0655(17)	0.0552(16)	0.0425(13)	0.0058(11)	0.0299(13)	0.0017(12)
P1	0.0261(3)	0.0288(3)	0.0203(3)	-0.0008(3)	0.0084(3)	-0.0013(3)

Table 4 Bond Lengths for *Z*-6

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	**Cl1**	2.2845(8)	**C14**	**C15**	1.389(4)
Au1	**P1**	2.2276(7)	**C15**	**C16**	1.361(5)
C1	**C2**	1.392(4)	**C16**	**C17**	1.391(4)
C1	**C6**	1.399(4)	**C16**	**F2**	1.350(3)
C1	**P1**	1.799(3)	**C17**	**C18**	1.383(4)
C2	**C3**	1.382(5)	**C17**	**N1**	1.451(4)
C3	**C4**	1.371(6)	**C18**	**F1**	1.343(3)
C4	**C5**	1.379(5)	**C19**	**C20**	1.398(5)
C5	**C6**	1.378(5)	**C19**	**C24**	1.380(5)
C7	**C8**	1.390(4)	**C19**	**N2**	1.428(4)
C7	**C12**	1.382(4)	**C20**	**C21**	1.363(5)
C7	**P1**	1.821(3)	**C20**	**F3**	1.348(4)
C8	**C9**	1.383(4)	**C21**	**C22**	1.391(5)
C9	**C10**	1.373(5)	**C22**	**C23**	1.387(4)
C10	**C11**	1.367(5)	**C22**	**O1**	1.355(4)
C11	**C12**	1.400(4)	**C23**	**C24**	1.363(5)
C13	**C14**	1.393(4)	**C24**	**F4**	1.351(4)
C13	**C18**	1.389(4)	**C25**	**O1**	1.423(4)
C13	**P1**	1.826(3)	**N1**	**N2**	1.248(4)

Table 5 Bond Angles for *Z*-6

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	**Au1**	**Cl1**	175.70(3)	**C18**	**C17**	**N1**	121.6(3)
C2	**C1**	**C6**	118.7(3)	**C17**	**C18**	**C13**	123.0(3)
C2	**C1**	**P1**	119.8(2)	**F1**	**C18**	**C13**	118.8(3)
C6	**C1**	**P1**	121.5(2)	**F1**	**C18**	**C17**	118.2(2)
C3	**C2**	**C1**	120.4(3)	**C20**	**C19**	**N2**	123.6(3)
C4	**C3**	**C2**	120.1(3)	**C24**	**C19**	**C20**	115.1(3)
C3	**C4**	**C5**	120.4(3)	**C24**	**C19**	**N2**	120.5(3)
C6	**C5**	**C4**	120.1(3)	**C21**	**C20**	**C19**	123.1(3)
C5	**C6**	**C1**	120.2(3)	**F3**	**C20**	**C19**	117.4(3)
C8	**C7**	**P1**	118.0(2)	**F3**	**C20**	**C21**	119.5(3)
C12	**C7**	**C8**	119.7(3)	**C20**	**C21**	**C22**	118.9(3)

C12	**C7**	**P1**	122.3(2)	**C23**	**C22**	**C21**	120.2(3)
C9	**C8**	**C7**	119.9(3)	**O1**	**C22**	**C21**	115.6(3)
C10	**C9**	**C8**	120.2(3)	**O1**	**C22**	**C23**	124.2(3)
C11	**C10**	**C9**	120.5(3)	**C24**	**C23**	**C22**	118.1(3)
C10	**C11**	**C12**	120.0(3)	**C23**	**C24**	**C19**	124.5(3)
C7	**C12**	**C11**	119.6(3)	**F4**	**C24**	**C19**	116.7(3)
C14	**C13**	**P1**	123.6(2)	**F4**	**C24**	**C23**	118.8(3)
C18	**C13**	**C14**	117.4(3)	**N2**	**N1**	**C17**	119.8(3)
C18	**C13**	**P1**	119.1(2)	**N1**	**N2**	**C19**	121.2(3)
C15	**C14**	**C13**	121.3(3)	**C22**	**O1**	**C25**	118.0(3)
C16	**C15**	**C14**	118.6(3)	**C1**	**P1**	**Au1**	112.66(10)
C15	**C16**	**C17**	123.0(3)	**C1**	**P1**	**C7**	105.84(13)
F2	**C16**	**C15**	119.9(3)	**C1**	**P1**	**C13**	105.19(13)
F2	**C16**	**C17**	117.0(3)	**C7**	**P1**	**Au1**	116.52(9)
C16	**C17**	**N1**	120.7(3)	**C7**	**P1**	**C13**	104.90(12)
C18	**C17**	**C16**	116.5(3)	**C13**	**P1**	**Au1**	110.84(8)