A stiboranyl-platinum triflate complex as an electrophilic catalyst

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SUPPORTING INFORMATION

General experimental considerations. *cis*–$PtCl_2(Et_2S)_2$[1] was prepared according to the reported procedures. Solvents were dried by passing through an alumina column (n–pentane and CH_2Cl_2) or by reflux under N over Na/K (Et_2O and THF). All other solvents were used as received. Commercially available chemicals were purchased and used as provided (Commercial sources: Aldrich for $SbCl_3$ and Bu_4NF; Matrix Scientific for AgOTf). Ambient temperature NMR spectra were recorded on a Varian Unity Inova 500 FT NMR (499.42 MHz for ^1H, 125.62 MHz for ^{13}C, 469.89 MHz for ^{19}F, 202.16 MHz for ^{31}P). ^1H and ^{13}C NMR chemical shifts are given in ppm and are referenced against SiMe4 using residual solvent signals used as secondary standards. ^{19}F NMR chemical shifts are given in ppm and are referenced against $CFCl_3$ using BF_3–Et_2O as an external secondary standard with δ -153.0 ppm. Elemental analyses (EA) were performed at Atlantic Microlab (Norcross, GA).

General procedure for the catalysis assays. Catalytic reactions were carried out at ambient temperature under air in $CDCl_3$. The enyne cyclization reaction were carried out as previously described for the evaluation of **C** with a catalyst loading of 5 mol% in 1 mL of $CDCl_3$.[2] Reactions involving alkynes and heteroaryls were carried out by first mixing the alkyne (0.67 mmol) with the heteroaryl (2 mmol) in $CDCl_3$ and subsequently adding the catalyst (5 mol%). The reaction mixture was stirred and monitored by ^1H NMR. The conversion was determined by ^1H NMR. The ^1H NMR spectra of compounds **6**[3], **7**[4], and **8**[5] have been reported. Some representative spectra are included in this supporting information (Figures S14-S16).

Computational Details. Density functional theory (DFT) structural optimizations were performed on the solid state structures of complexes **1**, **2**, **3**, **4** using Gaussian 09 suite of programs with effective core potentials on all heavy atoms (functional: BP86; mixed basis set: Sb/Pt: cc–pVTZ–PP; P/S/Cl: 6–31g(d'); H/C/O: 6–31g, F: 6–31+g(d'). Frequency calculations were used to confirm convergence of the calculations. The optimized structures (available as xyz files submitted as supporting electronic information), which are in excellent agreement with the solid-state structures, were subjected to a Natural Bond Orbital (NBO6) analysis. The resulting NBOs and Natural Localized Molecular Orbitals (NLMOs)[6-7] were visualized and plotted using the Avogadro program (version 1.2.0).[8]

Crystallographic Measurements. The crystallographic measurements were performed at 110(2) K using a Bruker APEX–II CCD area detector diffractometer (Mo-K_α radiation, λ = 0.71069 Å). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Semi–empirical absorption corrections were applied. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed location of the remaining non–hydrogen atoms. Complex **2** crystallizes with two interstitial molecules of *o*-$C_6H_4F_2$ per molecule of the complex. Some of these interstitial solvent molecules were subjected to geometrical and displacement parameter constraints in order to aid the refinement.

Synthesis of 2: Complex **1** (208 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (2 mL) and treated with AgOTf (169 mg, 0.66 mmol) under an N_2 atmosphere. The reaction mixture was allowed to stir for 16 h during which time a colorless precipitate of AgCl formed. The solution was filtered over Celite and treated with hexane (2 mL), leading to the precipitation of the product as a white solid. The product was separated from the solution by decantation and dried in vacuo to afford **2** (220 mg, 78% yield). ^{1}H NMR (399.43 MHz; $CDCl_3$): δ 8.72 (d, 2H, *o*-P(Sb)C_6H_4, $^3J_{H–H}$ = 8.0 Hz), 7.90 (t, 2H, $^3J_{H–H}$ = 7.6 Hz), 7.76 - 7.61 (m, 12H), 7.59 -7.45 (m, 12H). ^{13}C{^{1}H} NMR (125.62 MHz; $CDCl_3$): δ 135.28 (s), 134.82 (brs), 134.49 (s), 134.12 (t, J_{C-P} = 6.9 Hz), 133.87 (brs), 132.82 (s), 129.62 (t, J_{C-P} = 5.8 Hz), 126.34 (t, J_{C-P} = 29.5 Hz). ^{31}P{1H} NMR (161.74 MHz; $CDCl_3$): δ 49.41 (s, $^1J_{Pt–P}$ = 2450 Hz). ^{19}F{^{1}H} NMR (469.89 MHz; CD_2Cl_2): δ -80.4 (brs), -80.85 (s).

Alternative Synthesis of 2: Complex **1** (46.7 mg/ 0.049 mmol) was dissolved in 1 mL of *o*-$C_6H_4F_2$. To this solution, AgOTf (49 mg/ 0.191 mmol) was added and the solution was stirred overnight. The reaction mixture was then filtered over Celite and the product was isolated by vapor diffusion of pentane (2 mL) into *o*-$C_6H_4F_2$ to yield colorless crystals of **2-**2(*o*-$C_6H_4F_2$**)** (50.7 mg, 68.3% yield) suitable for X-ray diffraction. Elemental analysis calcd (%) for $C_{39}H_{28}F_9O_9P_2PtS_3Sb$•0.3 (*o*-$C_6H_4F_2$): C: 37.10, H: 2.23; found: C 37.13, H 2.20. These EA results are consistent with partial loss of the interstitial *o*-$C_6H_4F_2$ molecules observed in the crystal structure of this compound. Integration of the ^{1}H NMR spectrum also shows the presence of 0.3 molecules of *o*-$C_6H_4F_2$ per molecule of the complex.

Synthesis of 3: A solution of $PtCl_2(Et_2S)_2$ (50.3 mg, 0.13 mmol) in CH_2Cl_2 was added to a solution of (*o*-(^{i}Pr$_2$P)C_6H_4)$_2$SbCl[9] (70.4 mg, 0.13 mmol) in CH_2Cl_2 under N_2. The solution was brought to reflux for 16 h. The resulting yellow reaction mixture was concentrated to 2 mL in vacuo, and the product was precipitated by addition of Et_2O. The product was filtered and washed with pentane to afford **3** (86 mg, 83% yield) as a yellow solid. Single crystals of **3** suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a solution of the compound in CH_2Cl_2. ^{1}H NMR (499.43 MHz; $CDCl_3$): δ 8.26 (d, 2H, *o*-P(Sb)C_6H_4, $^3J_{H–H}$ = 7.6 Hz), 7.75 (m, 4H), 7.52 (t, 2H, *m*-P(Sb)C_6H_4, $^3J_{H–H}$ = 6.9 Hz), 3.22 (m, 4H, C*H*CH_3), 1.43 (t, 6H, *J* = 7.5 Hz), 1.41 (t, 6H, *J* = 8.0 Hz), 1.25 (t, 6H, *J* = 7.5 Hz), 1.24 (t, 6H, *J* = 7.5 Hz). ^{13}C{^{1}H} NMR (125.62 MHz; $CDCl_3$): δ 167.88 (t, J_{C-P} = 15.6 Hz), 134.41 (s), 131.89 (t, J_{C-P} = 3.1 Hz), 131.64 (t, J_{C-P} = 7.0 Hz), 129.88 (t, J_{C-P} = 3.5 Hz), 125.48 (t, J_{C-P} = 25.0 Hz), 27.98 (t, J_{C-P} = 14.6 Hz, *C*$(CH_3)_2$), 19.19 (s, *C*H_3), 19.09 (s, *C*H_3). ^{31}P{1H} NMR (161.74 MHz; $CDCl_3$): δ 72.63 (s, $^1J_{Pt–P}$ = 2473 Hz). Elemental analysis calcd (%) for $C_{24}H_{36}Cl_3P_2PtSb$: C, 35.60; H, 4.48. Found: C, 35.38; H, 4.39.

Synthesis of 4: Complex **3** (80 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (2 mL) and treated with AgOTf (77 mg, 0.30 mmol) under an N_2 atmosphere. The reaction mixture was allowed to stir for 16 h during which time a colorless precipitate of AgCl formed. The solution was filtered over Celite and treated with hexane (2 mL), leading to the precipitation of the product as a pale yellow solid. The product was separated from the solution by decantation and dried in vacuo to afford **4** (84 mg, 73% yield). ^{1}H NMR (399.43 MHz; $CDCl_3$): δ 8.74 (d, 2H, *o*-P(Sb)C_6H_4, $^3J_{H–H}$ = 7.9 Hz), 8.01-7.88 (m, 4H), 7.85 (t, 2H, *m*-P(Sb)C_6H_4, $^3J_{H–H}$ = 7.4 Hz), 3.44 (m, 4H, C*H*CH_3), 1.36 (t, 6H, *J* = 7.3 Hz), 1.32 (t, 6H, *J* = 8.3 Hz), 1,26 (t, 6H, *J* = 7.5 Hz), 1.24 (t, 6H, *J* = 7.3 Hz). ^{13}C{^{1}H} NMR (125.62 MHz; $CDCl_3$): 152.04 (t, J_{C-P} = 11.6 Hz), 135.14 (t, J_{C-P} = 5.5 Hz), 134.64 (s), 133.47 (s), 133.19 (t, J_{C-P} = 3.5 Hz), 131.39 (t, J_{C-P} = 23.9 Hz), 27.95 (t, J_{C-P} = 13.9 Hz, *C*$(CH_3)_2$), 18.69 (s, *C*H_3), 18.58 (s, *C*H_3). ^{31}P{1H} NMR (161.74 MHz; $CDCl_3$): δ 73.94 (s, $^1J_{Pt–P}$ = 2383 Hz). ^{19}F{^{1}H} NMR (469.89 MHz; CD_2Cl_2): δ -79.2 (s, 3F), -81.5 (s, 9F). Elemental analysis calcd (%) for $C_{27}H_{36}F_9O_9P_2PtS_3Sb$: C, 28.19; H, 3.15. Found: C, 28.19; H, 2.99.

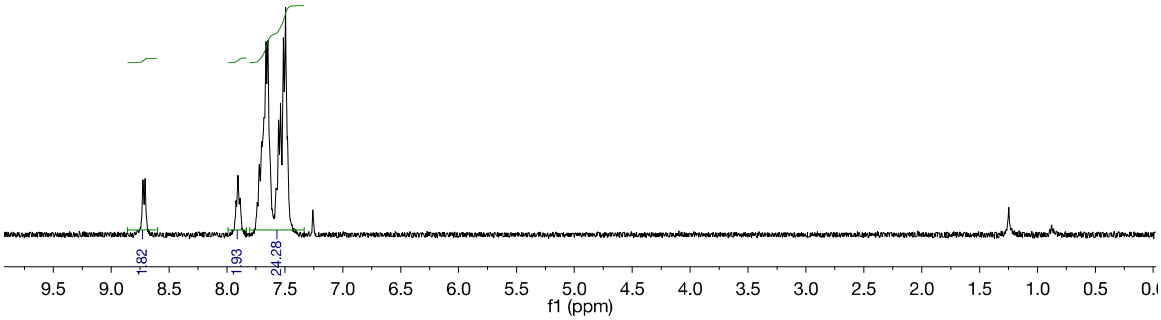

Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$

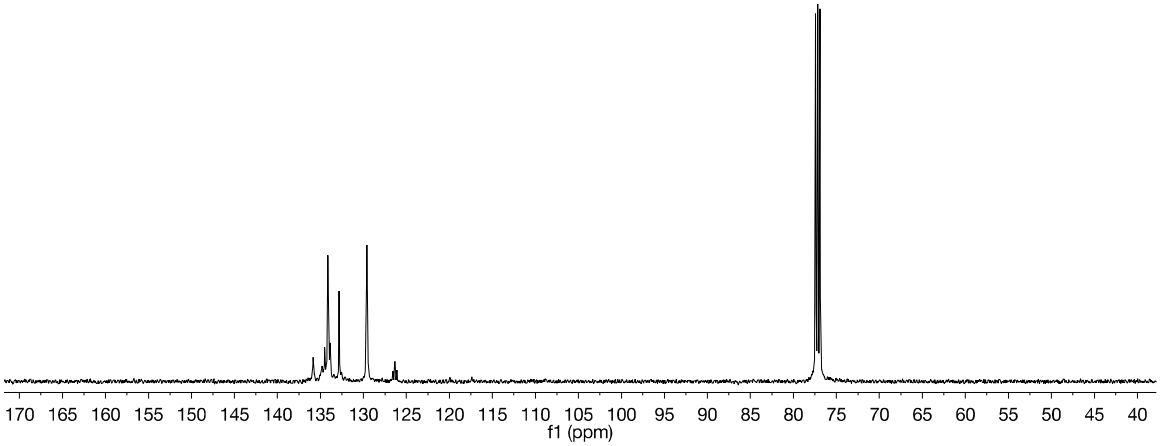

Figure S2. ^{13}C NMR spectrum of **2** in $CDCl_3$

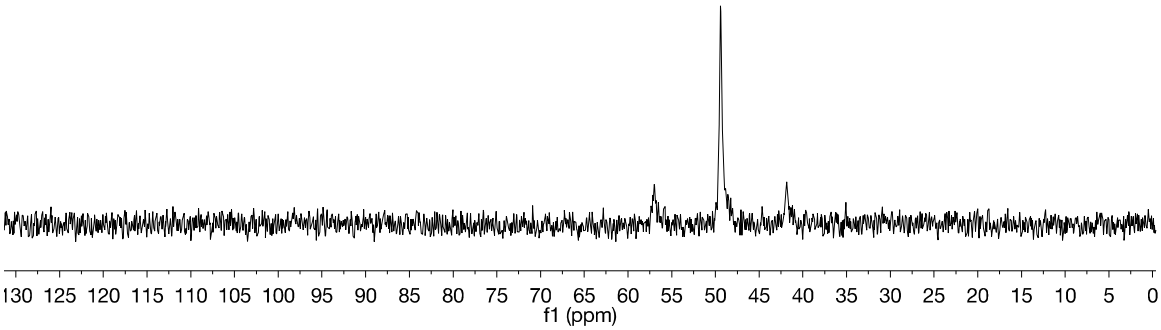

Figure S3. ^{31}P NMR spectrum of **2** in $CDCl_3$

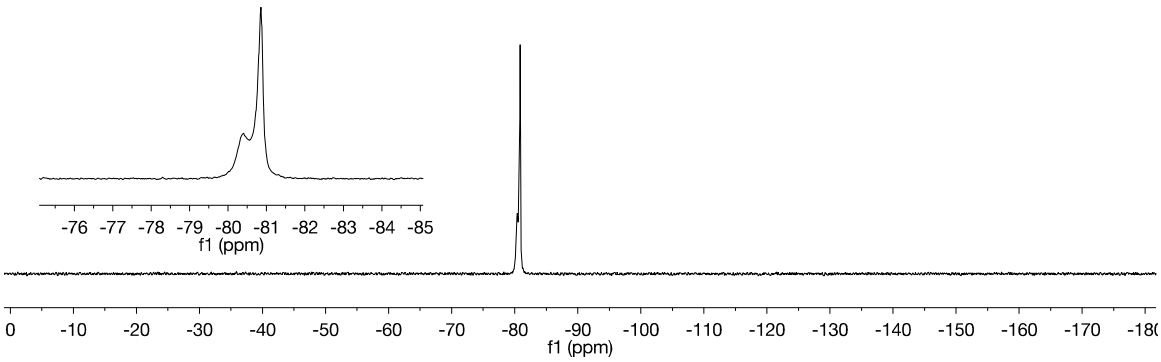

Figure S4. ^{19}F NMR spectrum of **2** in $CDCl_3$.

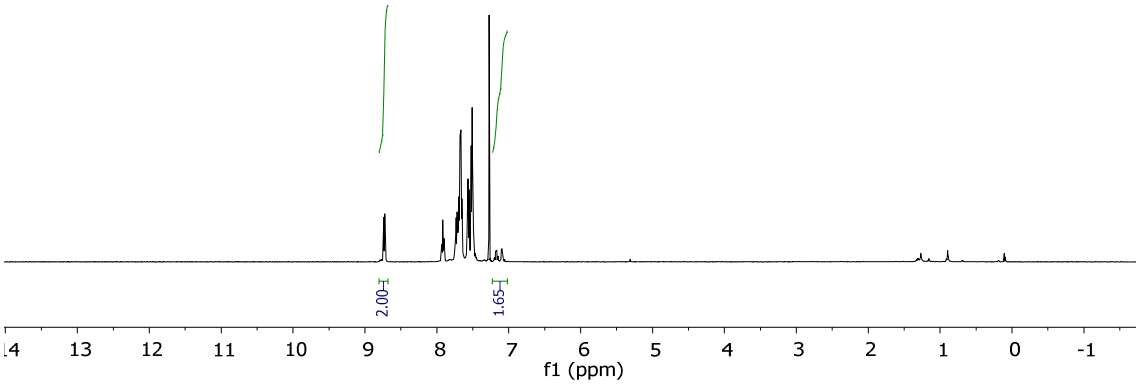

Figure S5. ^{1}H NMR spectrum of **2** in $CDCl_3$ (crystallized from *o*-$C_6H_4F_2$).

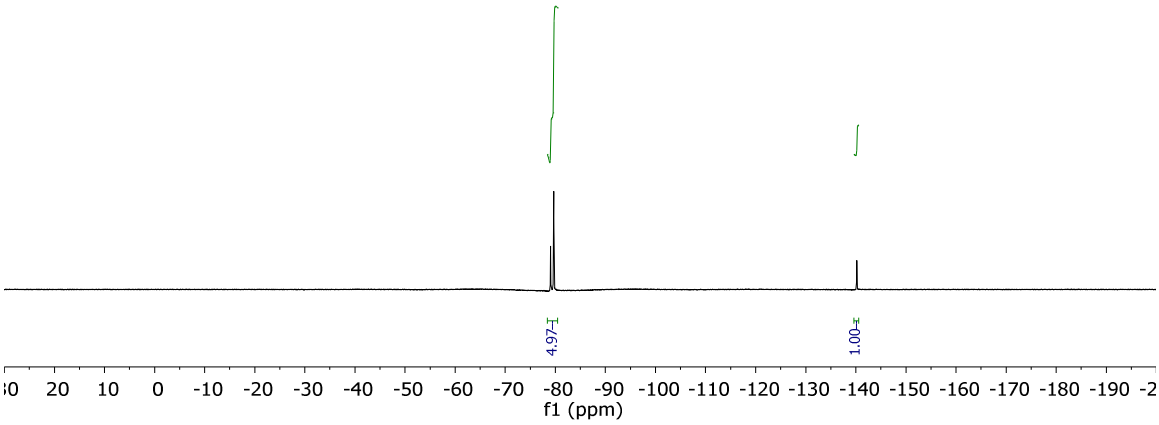

Figure S6. ^{19}F NMR spectrum of of **2** in $CDCl_3$ (crystallized from *o*-$C_6H_4F_2$).

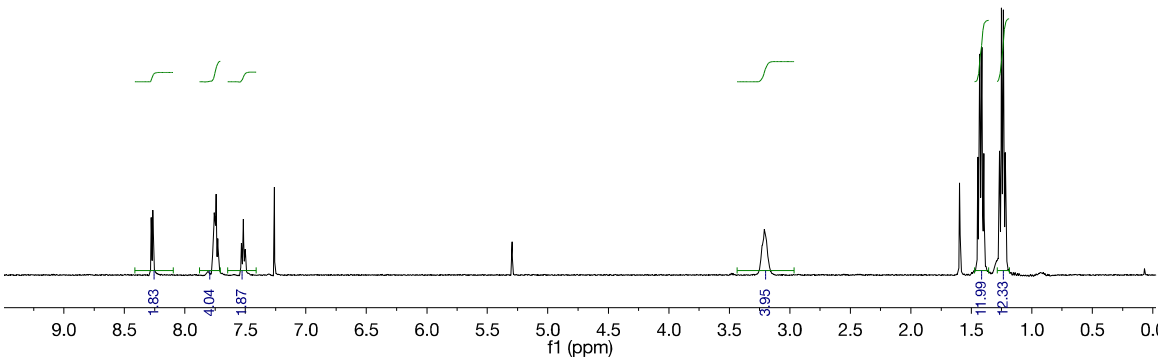

Figure S7. ^{1}H NMR spectrum of **3** in $CDCl_3$

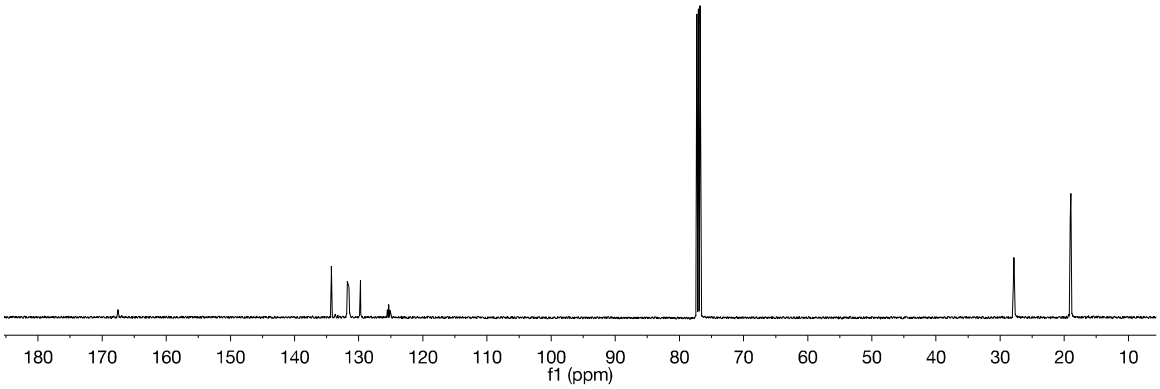

Figure S8. ^{13}C NMR spectrum of **3** in $CDCl_3$

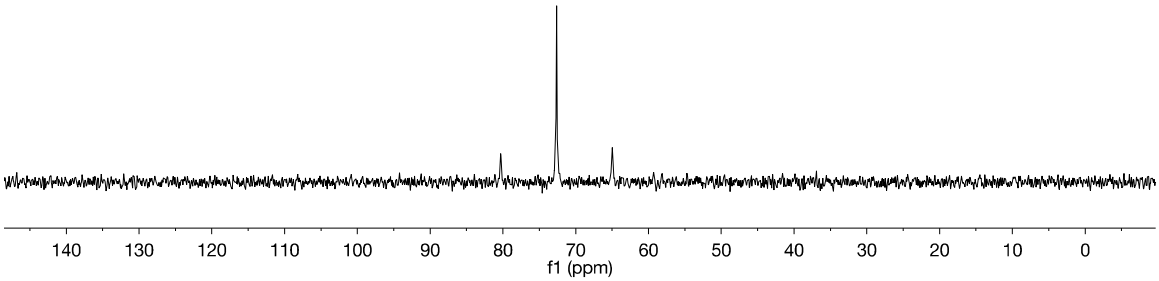

Figure S9. ^{31}P NMR spectrum of **3** in $CDCl_3$

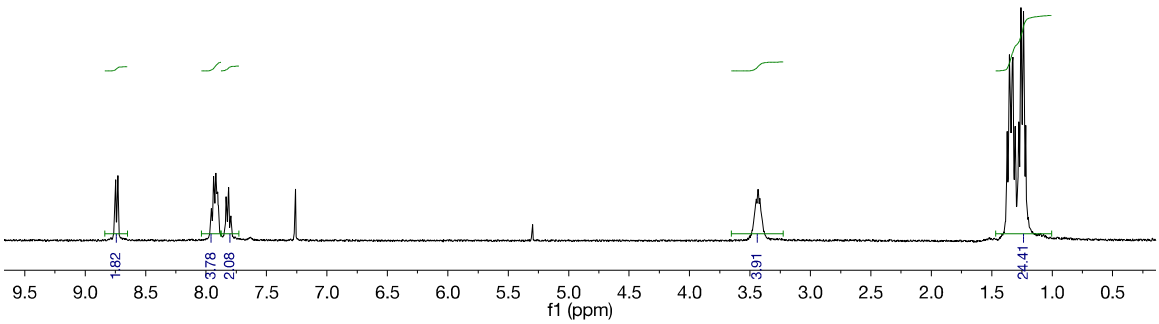

Figure S10. ^{1}H NMR spectrum of **4** in $CDCl_3$

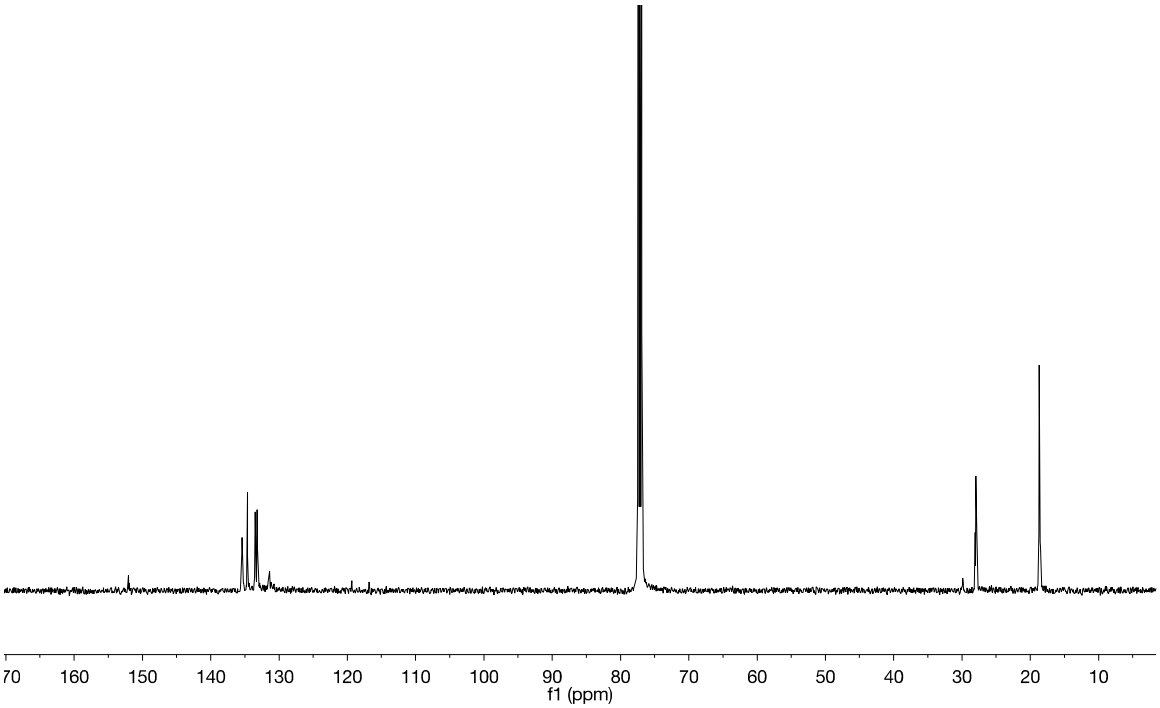

Figure S11. ^{13}C NMR spectrum of **4** in $CDCl_3$. The $CDCl_3$ solvent residue peak has been truncated.

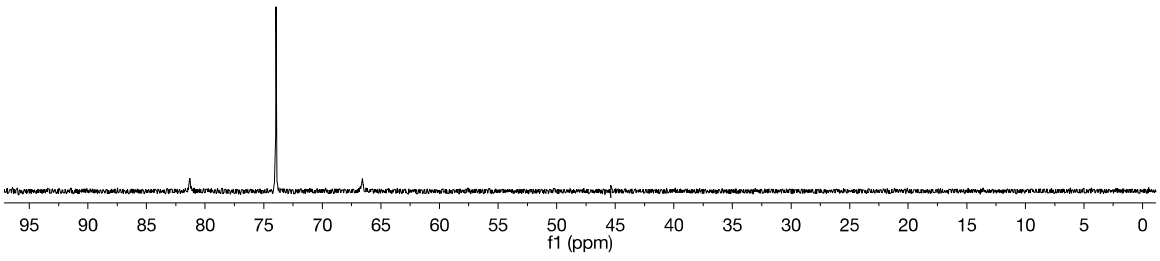

Figure S12. ^{31}P NMR spectrum of **4** in $CDCl_3$

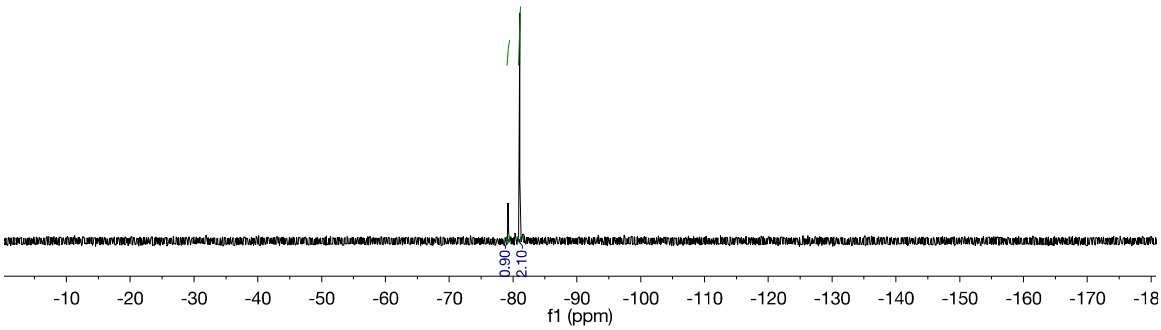

Figure S13. ^{19}F NMR spectrum of **4** in $CDCl_3$.

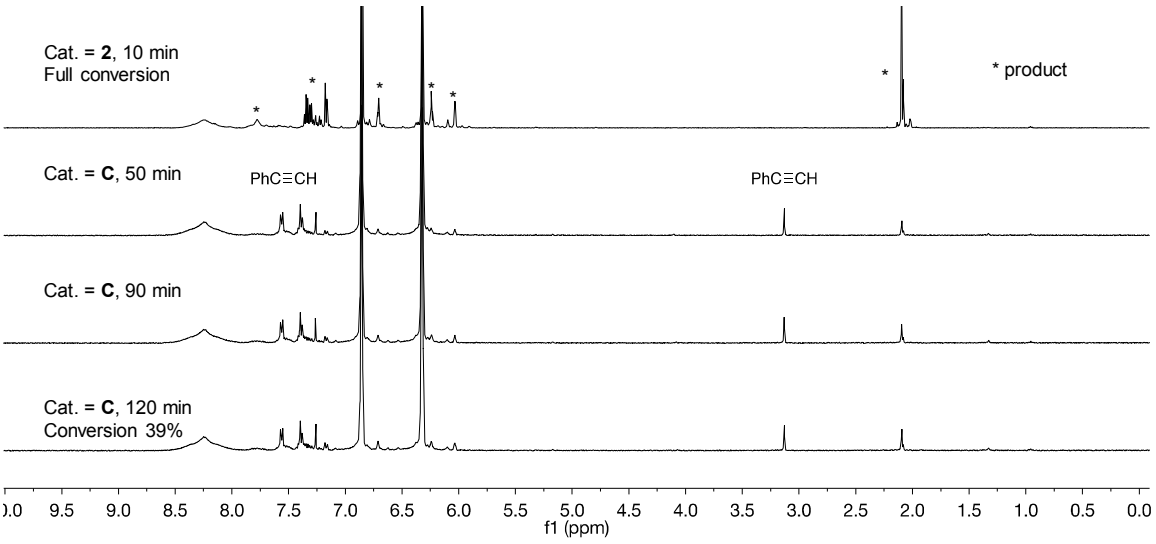

Figure S14. In situ ^1H NMR monitoring of the reaction between phenylacetylene and pyrrole, with **2** and **C** as catalysts (5 mol% loading).

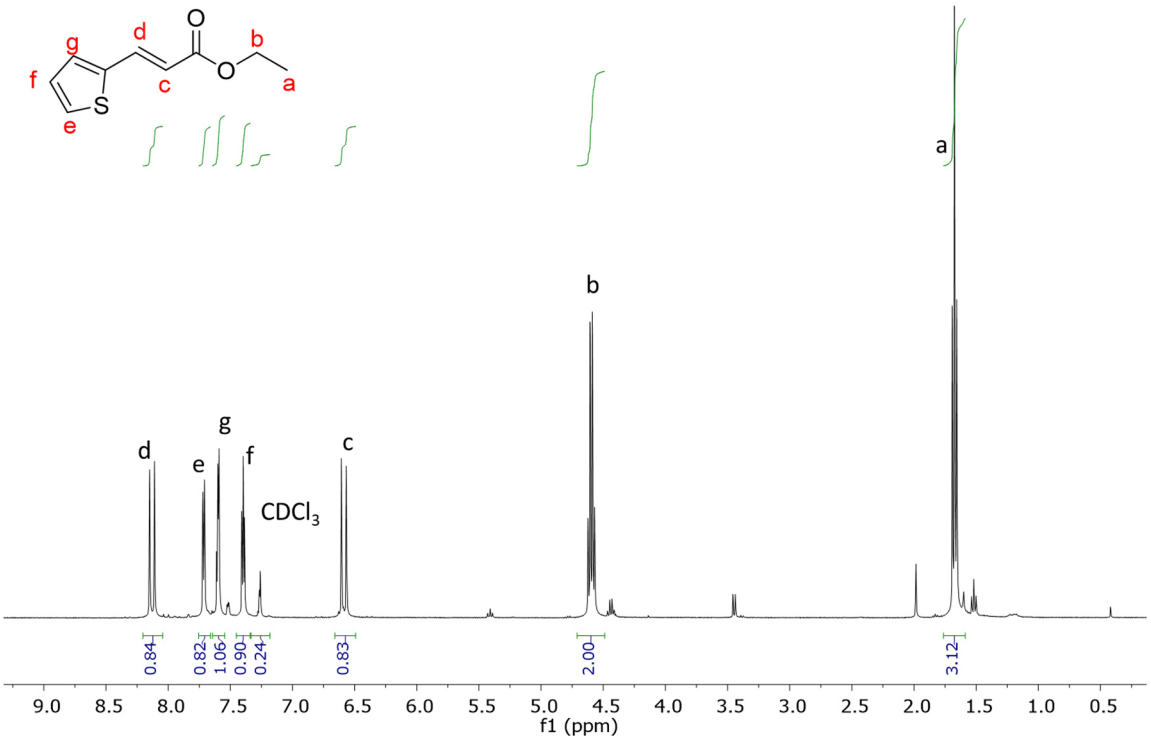

Figure S15. ^{1}H NMR spectrum of isolated **7** following the reaction of thiophene and ethyl propiolate catalyzed by **2**.

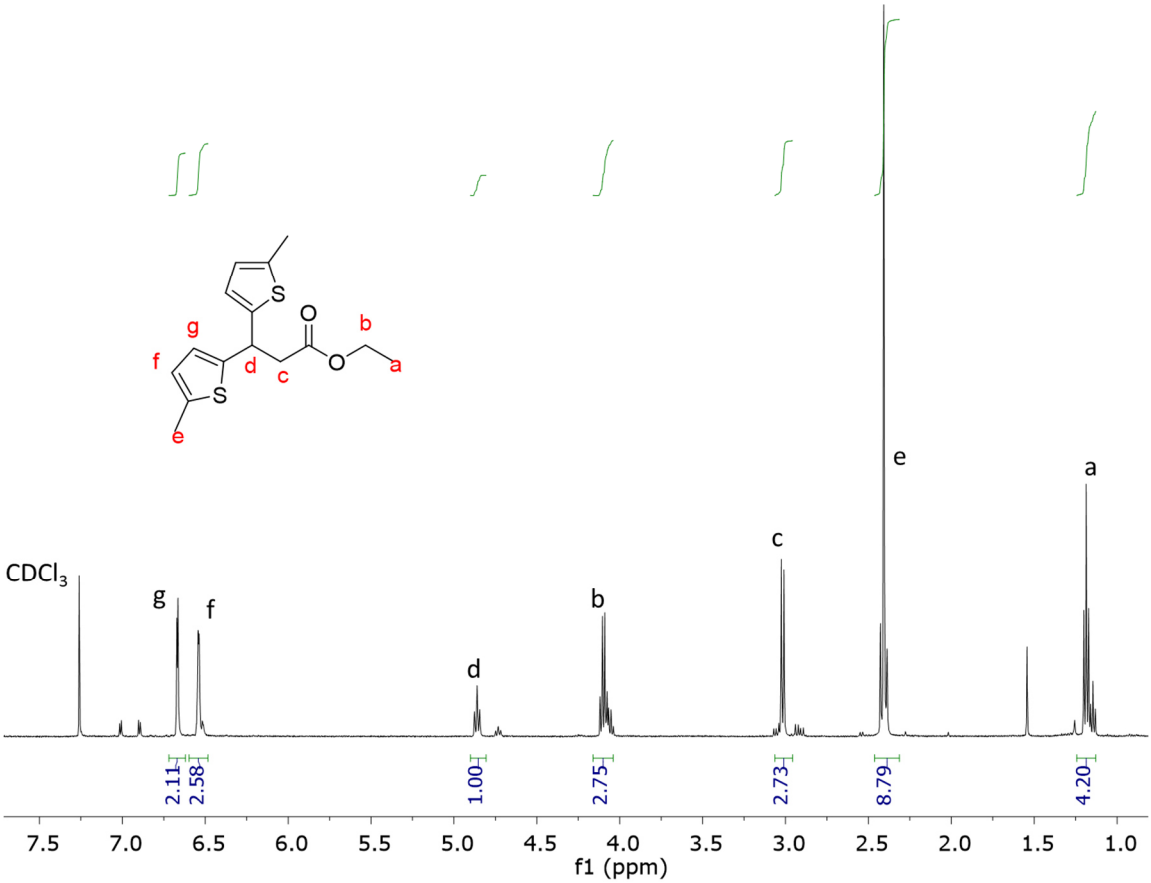

Figure S16. ^{1}H NMR spectrum of isolated **8** following the reaction of thiophene and ethyl propiolate catalyzed by **2**.

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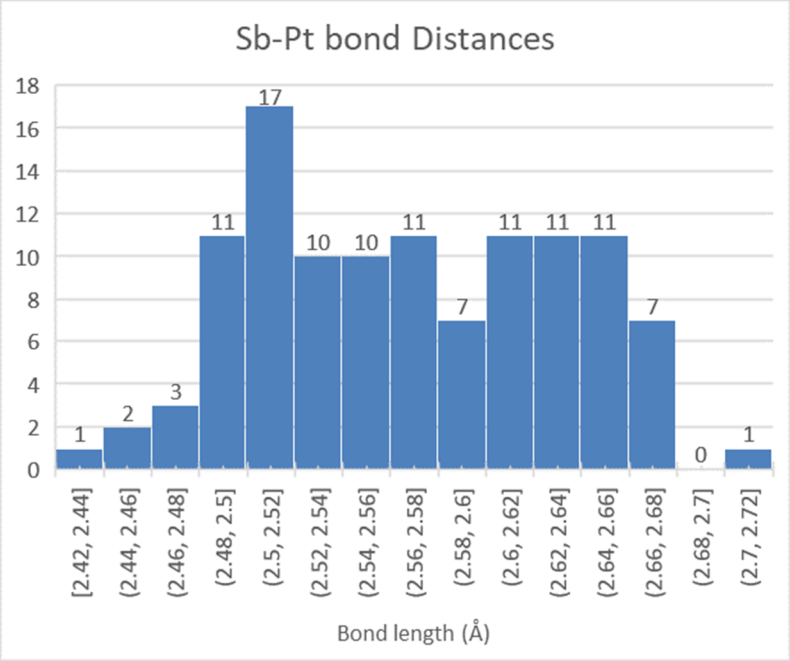

Figure S17. Reported Sb-Pt bond distances from the Cambridge Crystal Database.

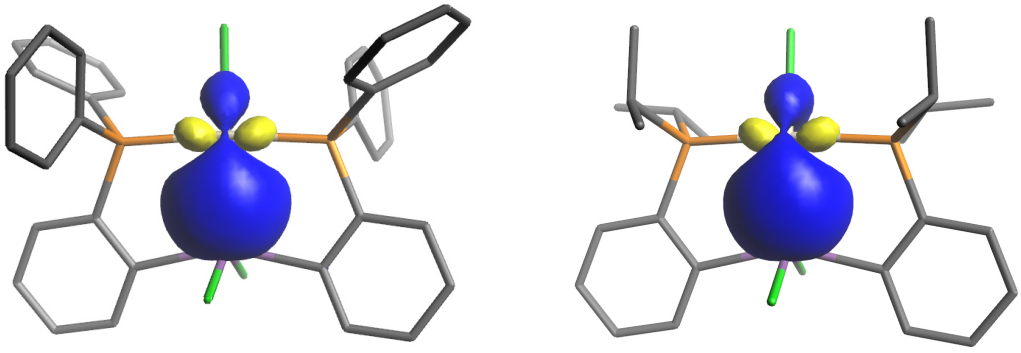

Figure S18. NLMO plot (isosurface value: 0.04) of the major Sb–Pt bonding interaction in **1** (left) and **3** (right).

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