

Supporting Information for

Reversible C–F Bond Formation and the Au-Catalyzed Hydrofluorination of Alkynes

Jennifer A. Akana, Koyel X. Bhattacharyya, Peter Müller, Joseph P. Sadighi*

General Considerations: All stoichiometric reactions were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glove box under an atmosphere of purified nitrogen unless stated otherwise. Stoichiometric reactions were carried out in flame-dried glassware cooled under vacuum. Catalytic reactions were performed in 20 mL polyethylene scintillation vials sealed with polyethylene cone-lined caps. Elemental analyses were performed by Desert Analytics, Tuscon, AZ, or Atlantic Microlab, Inc., Norcross, GA. Anhydrous dichloromethane and hexanes were purchased from Aldrich in 18-L Pure-PakTM solvent delivery kegs and sparged vigorously prior to use. The solvents were further purified by passage through two packed columns of neutral alumina under Ar pressure.

Infrared spectra were recorded on an IR Nicolet Impact 410 spectrometer on KBr pellets and are reported in cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on Varian 300 MHz, Varian 500 MHz, or Bruker 400 MHz instruments with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra, recorded on a Varian 300 MHz spectrometer, are referenced with respect to an external standard of neat CFCl_3 . CD_2Cl_2 (Cambridge Isotope Laboratories) was dried over CaH_2 , degassed by three freeze-pump-thaw cycles, and vacuum-transferred prior to use. Trifluoroacetic acid (Oakwood), silver trifluoroacetate (Strem), silver tetrafluoroborate (Strem), chloro(dimethylsulfide)gold(I) (Aldrich), triethylamine trihydrofluoride (Aldrich), and potassium hydrogen sulfate (Alfa Aesar) were purchased and used as received. Fluorobenzene (Aldrich) and α,α,α -trifluorotoluene (Aldrich) were dried over activated 3 Å molecular sieves and vacuum-transferred prior to use. The alkynes 3-hexyne, 1-phenyl-1-butyne, 6-dodecyne, and diphenylacetylene were purchased from Aldrich. All other alkynes were synthesized according to literature.¹ Liquid alkynes were dried over NaBH_4 and vacuum-transferred prior to use. The following compounds were synthesized according to literature procedures: 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene² ($^{\text{Cl}}\text{IPr}$), $[(\text{Me}_2\text{N})_3\text{P}]_2\text{N}^+\text{F}^-$,³ $\text{PhNMe}_2\cdot\text{HOTf}$,⁴ $(\text{Ph}_3\text{P})\text{AuCl}$,⁵ $(\text{SIPr})\text{AuF}$,⁶ $(\text{SIPr})\text{AuOt-Bu}$,⁶ and the gold(I) chloride complexes supported by other *N*-heterocyclic carbene (NHC) ligands.⁷

Reaction of 1 with 3-hexyne: Generation of 2a. $(\text{SIPr})\text{AuF}$ (**1**) (0.0296 g, 0.0444 mmol) was dissolved in CD_2Cl_2 (0.6 mL), with fluorobenzene (0.0040 mL, 0.043 mmol) as internal standard. 3-Hexyne (0.750 mL, 6.60 mmol) was added, and after 10 minutes a new resonance was observed in the ^{19}F NMR spectrum at -95.5 ppm (t, $J = 21$ Hz). Integration of

this resonance indicates >95% conversion of the gold fluoride to the product, assigned as **2a**.

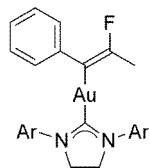
Reversion of 2a to 1. A solution of **2a** prepared as described above was transferred to a sealable Schlenk tube, and volatiles were removed under vacuum over a period of 30 min, affording a white powder. This powder was dried further for 2 h under vacuum, then taken up in dry CD₂Cl₂ under an atmosphere of N₂. Analysis by ¹H and ¹⁹F NMR indicated that complete reversion of **2a** to **1** had occurred.

In a separate experiment, an identically prepared solution was transferred to a dry sealable Schlenk tube, and concentrated to a white powder as rapidly as practical (≤5 min). The residual white powder was then dried for two hours under vacuum. A fresh aliquot of fluorobenzene (4.2 μL, 0.045 mmol) and CD₂Cl₂ (*ca.* 0.8 mL) were added to this powder under an atmosphere of N₂. A ¹⁹F NMR spectrum obtained 10 minutes later indicated the presence of **1** and **2** in a 1.2 : 1 ratio, with a total intensity 83% that of the starting (SIPr)AuF. After 2 hr, the observed ratio of **1** to **2** was 12.5 : 1.

Determination of equilibrium constant for formation of 2a. In a typical experiment, a solution of **1** (0.027 g, 0.045 mmol) in CD₂Cl₂ (0.60 mL) with fluorobenzene (5.0 μL) present as internal standard was loaded into a J. Young NMR tube. 3-Hexyne (0.020 mL, 3.9 equiv) was added; the tube was sealed, shaken thoroughly, and allowed to stand for several hours at room temperature. The equilibrium constant was then calculated based on the integration of the **1** and **2a** resonances relative to the fluorobenzene resonance in the ¹⁹F NMR spectrum, and based on the integration of 3-hexyne relative to **1** in the ¹H NMR spectrum.

Table S1. Equilibrium data for the reaction of (SIPr)AuF (**1**) with 3-hexyne.

| Initial ratios | | Observed after 3 h | | | |
|------------------|------------------|--------------------|--------------|------------|-----------------|
| 1 (equiv) | 3-hexyne (equiv) | [2a] | [1] | [3-hexyne] | K _{eq} |
| 1 | 0.49 | 0.005 | 0.068 | 0.03 | 2.4 |
| 1 | 1.2 | 0.0012 | 0.024 | 0.033 | 2.5 |
| 1 | 2.0 | 0.011 | 0.040 | 0.10 | 2.8 |
| 1 | 3.9 | 0.033 | 0.044 | 0.26 | 2.8 |
| 1 | 7.9 | 0.048 | 0.028 | 0.59 | 2.9 |



Ar = 2,6-(*i*-Pr)₂C₆H₃

(SIPr)Au[C(Ph)=CFCH₃] (2b). X-ray quality crystals of **2b** were grown at –40° C under a nitrogen atmosphere by vapor diffusion of pentane into a solution of **1** in 1:1 CH₂Cl₂/1-phenyl-1-propyne. The crystals were collected via filtration in air, transferred to the glove box, and then dissolved in CD₂Cl₂ (0.60 mL). The ¹H and ¹⁹F NMR spectra, reproduced below as

a measure of purity, were obtained within 5 minutes. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.43 (t, $J = 7.8$ Hz, *para*-CH), 7.26 (d, $J = 7.8$ Hz, *meta*-CH), 6.72–6.90 (m, 5 H), 4.04 (s, 4 H, CH_2), 3.11 (sept, $J = 6.8$ Hz, 2H, CH), 1.50 (d, $J = 16$ Hz, 1 H, CFCH_3), 1.31–1.38 (m, 24 H, $\text{CH}(\text{CH}_3)_2$). ^{19}F NMR (282 MHz, CD_2Cl_2): δ -81.4 (quart, $J = 15$ Hz).

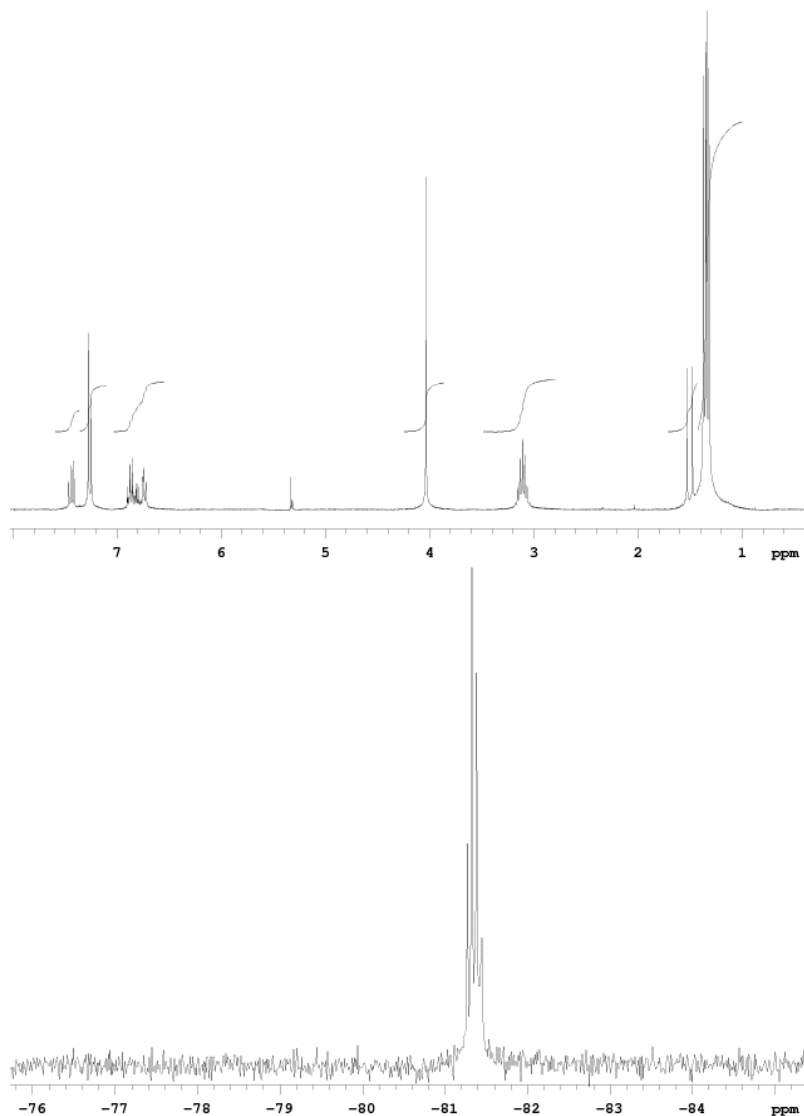
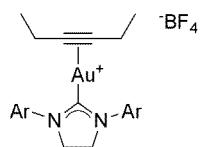


Figure S1. ^1H and ^{19}F NMR spectra of **2b** in CD_2Cl_2 .

After 25 minutes no change was observed in the spectra. However, after 110 minutes both **2b** (93%) and **1** (7%) were observed by ^1H and ^{19}F NMR. 1-Phenyl-1-propyne was observed in the ^1H NMR spectrum. The solution was allowed to sit for 13 h, when the ^1H and ^{19}F NMR spectra displayed a 32:68 ratio of **2b** : **1**, a significant amount of 1-phenyl-1-propyne, and small amounts of side products from the competing decomposition of **1** in CD_2Cl_2 .



Ar = 2,6-(*i*-Pr)₂C₆H₃

{[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I)[η²-(3-hexyne)]} tetrafluoroborate (3) Under nitrogen atmosphere, AgBF₄ (0.057 g, 0.294 mmol) was added to a solution of (SIPr)AuCl (0.181 g, 0.292 mmol) and 3-hexyne (0.050 mL, 0.438 mmol) in 3 mL CH₂Cl₂. The reaction mixture was stirred for 10 minutes, precipitates were removed by filtration through a Celite plug, and the reaction solution concentrated to 1 mL under vacuum. Hexanes (3 mL) were added, and the resulting precipitate was collected by filtration and dried under vacuum to afford the title compound (0.178 g, 0.236 mmol, 81%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.46 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.5 Hz, 4 H, *meta*-CH), 4.28 (s, 4 H, NCH₂), 3.07 (sept, *J* = 6.9 Hz, 4 H, CH), 2.08 (quart, *J* = 7 Hz, 4 H, CH₂CH₃), 1.33–1.17 (m, 24 H, CH(CH₃)₂), 0.47 (t, *J* = 7.4 Hz, 6 H, CH₂CH₃). ¹³C NMR (126 MHz, CD₂Cl₂): δ 199.2 (NCN), 147.5, 133.4, 131.2, 125.4, 87.7 (H₂CCCCCH₂), 54.8 (NCH₂), 29.5 (CH), 25.6 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 15.1 (CH₂CH₃), 13.4 (CH₂CH₃). IR: 2957, 2100, 1588, 1513, 1462, 1281, 1051, 803, 760, 447. Anal. Calcd. for C₃₃H₄₈N₂AuBF₄: C, 52.39; H, 6.40. Found: C, 52.40; H, 6.58.

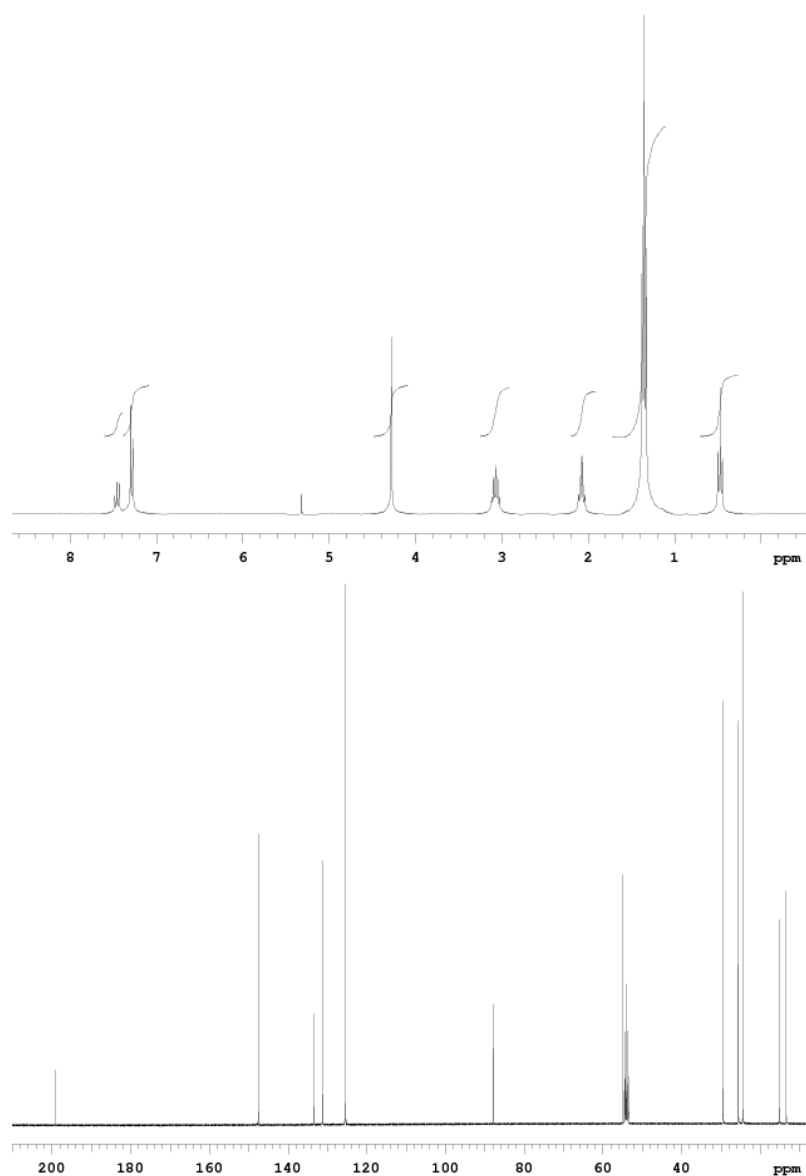
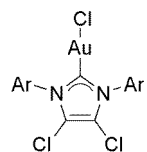


Figure S2. ^1H and ^{13}C NMR spectra of **3**.

Reaction of **3 with $[(\text{Me}_2\text{N})_3\text{P}]_2\text{N}^+\text{F}^-$** A dried glass vial was charged with a solution of **3** (0.0190 g, 0.0251 mmol) in CD_2Cl_2 (0.6 mL). $[(\text{Me}_2\text{N})_3\text{P}]_2\text{N}^+\text{F}^-$ (9 mg, 0.03 mmol) was added, and the reaction solution was transferred to a dry J. Young NMR tube. Within 10 minutes, both **1** and **2** are present in an area ratio of 12:1 as judged by ^{19}F NMR.

Reaction of **3 with $\text{Et}_3\text{N}\cdot(\text{HF})_3$** Under a nitrogen atmosphere, **3** (0.0528 g, 0.0689 mmol) was dissolved in CD_2Cl_2 (0.8 mL). The solution was transferred to a 20 mL polyethylene scintillation vial equipped with a stir bar, and the vessel was sealed with a polyethylene cone-lined cap. Under air, the vial was uncapped, $\text{Et}_3\text{N}\cdot(\text{HF})_3$ (0.0110 mL, 0.0669 mmol) was added directly to the solution; the headspace was purged with argon for 10 seconds and the vial was then resealed. The reaction mixture was stirred for 1.75 h in the dark, and was then transferred to a dry NMR tube under air. Analysis by ^1H and

^{19}F NMR indicated the presence of (*Z*)-3-fluoro-3-hexene (0.059 mmol, 64% relative to $^-\text{BF}_4$).



Ar = 2,6-(*i*-Pr) $_2$ C $_6$ H $_3$

[4,5-Dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold chloride ($^{\text{Cl}}\text{IPr}$)AuCl Under a nitrogen atmosphere, (Me $_2$ S)AuCl (0.331 g, 1.13 mmol) was added to a solution of $^{\text{Cl}}\text{IPr}$ (0.518 g, 1.12 mmol) in THF (6 mL). The reaction mixture was stirred in the dark overnight. The remaining steps were performed under air. The reaction solution was filtered through Celite and concentrated to a white solid under vacuum. This solid was dissolved in CH $_2$ Cl $_2$ (4.0 mL), and the resulting solution was filtered through silica, then concentrated under vacuum to afford the title complex as a white powder, 0.583 g (75%). ^1H NMR (500 MHz, CDCl $_3$): δ 7.57 (t, J = 8.0 Hz, 2 H, *para*-CH), 7.33 (d, J = 8.0 Hz, 4 H, *meta*-CH), 2.46 (sept, J = 6.9 Hz, 4 H, CH(CH $_3$)), 1.36 (d, J = 7.0 Hz, 12 H, CH $_3$), 1.27 (d, J = 7.0 Hz, 12 H, CH $_3$). ^{13}C NMR (126 MHz, CDCl $_3$): δ 175.3 (NCN), 146.2, 131.8, 131.3, 127.8, 119.1 (CCl), 29.4 (CH(CH $_3$) $_2$), 24.8, 23.7. IR: 3069, 2957, 2869, 1966, 1936, 1585, 1385, 1180, 1060, 803, 726, 651, 542. Anal. Calcd. for C $_{33}$ H $_{34}$ N $_2$ AuCl $_3$: C, 47.01; H, 4.97. Found: C, 46.97; H, 4.92.

Catalytic Reactions

Because Et $_3$ N•3HF corrodes glass significantly over the reaction timescales, all catalytic reactions were performed in 20 mL polyethylene scintillation vials sealed with polyethylene cone-lined caps. The reactions were set up according to the following general methods. Note: In the presence of added water or wet reagents, Au-catalyzed hydration of alkynes to ketones is a significant side reaction. Given dry starting reagents and solvents, however, reactions carried out under benchtop conditions generate only traces of ketone.

Method A: In the glovebox, a vial was charged with a stirbar, (SIPr)AuOt-Bu (0.307 g, 0.0465 mmol, 0.025 eq), PhNMe $_2$ •HOTf (0.0501 g, 0.185 mmol, 0.01 eq), and alkyne substrate (1.85 mmol). CH $_2$ Cl $_2$ (1.0 mL) was added. On the benchtop, the vial was opened, and KHSO $_4$ (0.254 g, 1.85 mmol, 1.0 eq) and Et $_3$ N•(HF) $_3$ (0.460 mL, 2.80 mmol, 1.5 eq) were added. The vial was then capped.

Method B: In the glovebox, a vial was charged with a stirbar, (NHC)AuCl (0.0444 mmol, 0.025 eq), PhNMe $_2$ •HOTf (0.0461 g, 0.170 mmol, 0.01 eq), and alkyne substrate (1.77 mmol). CH $_2$ Cl $_2$ (1.0 mL) was added, followed by AgBF $_4$ (0.010 g, 0.050 mmol, 0.028 eq). The resulting mixture was stirred for 5 minutes. On the benchtop, the vial

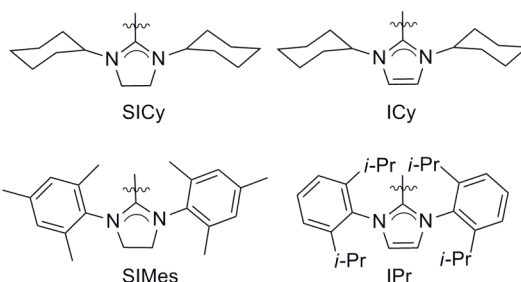
was opened, and KHSO₄ (0.240 g, 1.77 mmol, 1.0 eq) and Et₃N•(HF)₃ (0.430 mL, 2.61 mmol, 1.5 eq) were added. The vial was then capped.

In all cases, the heterogeneous reaction mixtures were protected from light and stirred at ambient temperature for the stated time. These mixtures were then quenched with saturated solutions of sodium bicarbonate, and the organics were extracted into CH₂Cl₂, dried over MgSO₄, and concentrated under vacuum. The reaction products were purified by column chromatography on silica gel using mixtures of hexanes/ethyl acetate as eluants.

Products of asymmetric alkyne hydrofluorination are reported as mixtures of regioisomers. Isolated yields for these reactions refer to the major product.

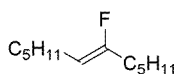
Table S2. Comparison of LAuX precatalysts for 6-dodecyne hydrofluorination.

| $n\text{-C}_5\text{H}_{11}\text{—}\equiv\text{—}n\text{-C}_5\text{H}_{11} \xrightarrow[\text{CH}_2\text{Cl}_2 (1.0 \text{ mL}), 30 \text{ hr}]{\begin{array}{l} 1.5 \text{ eq Et}_3\text{N}\cdot(\text{HF})_3 \\ 1.0 \text{ eq KHSO}_4 \\ 0.1 \text{ eq PhNMe}_2\cdot\text{HOTf} \\ 0.025 \text{ eq [Au]/AgBF}_4 \end{array}} n\text{-C}_5\text{H}_{11}\text{—}\text{C}(\text{F})=\text{CH—}n\text{-C}_5\text{H}_{11}$ | |
|--|---------|
| [Au] | % yield |
| (Ph ₃ P)AuCl | 3 |
| (ICy)AuCl | 3 |
| (SiCy)AuCl | 3 |
| (SiMes)AuCl | 15 |
| (SiPr)AuCl | 77 |
| (SiPr)AuOt-Bu ^a | 72 |
| (IPr)AuCl | 82 |
| (^{Cl} IPr)AuCl | 90 |



Comparison of LAuX precatalysts. Reactions were performed as described above using 6-dodecyne as substrate and method B. Reaction progress was assessed by an internal standard of α,α,α -trifluorotoluene after 30 h. For the reaction using the (^{Cl}IPr)AuCl / AgBF₄ precatalyst system, the complete consumption of starting alkyne was confirmed by GC-MS after workup of the reaction mixture; no remaining dodecyne was observed. In all other cases, 6-dodecyne was observed by GC-MS. (a) The reaction using (SiPr)Ot-Bu as precatalyst was set up according to method A, in the absence of AgBF₄.

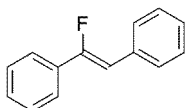
Hydrofluorination of 6-dodecyne (Table 1, Entry 1) Reactions were set up according to Method B, using (^{Cl}IPr)AuCl precatalyst. Reaction time: 30 h.



(Z)-6-fluoro-6-dodecene Yield: 0.292 g (81%). ¹H NMR spectrum⁸ is consistent with that found in the literature. ¹H NMR (500 MHz, C₆D₆): δ 4.37 (dt, J = 37, 7.4 Hz, 1 H, CH=CF), 2.13 (quart, J = 7.0 Hz, 2 H), 1.97–2.04 (m, 2 H), 1.37–1.44

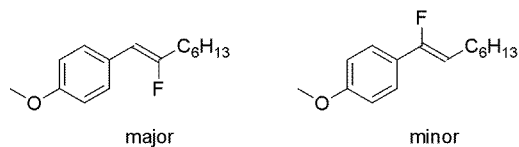
(m, 2 H), 1.14–1.33 (m, 10 H), 0.82–0.88 (m, 6 H). ^{13}C NMR (126 MHz, C_6D_6): δ 160.4 (d, J = 253 Hz, CF), 105.6 (d, J = 15 Hz, $\text{CH}=\text{CF}$), 32.7 (d, J = 28.4 Hz, CFCH_2), 32.1, 31.8, 30.1 (d, J = 1.6 Hz), 26.8 (d, J = 1.1 Hz), 24.3 (d, J = 5.2 Hz), 23.3, 23.1, 14.6, 14.5. ^{19}F NMR (282 MHz, C_6D_6): δ -107.8 (dt, J = 17, 38 Hz).

Hydrofluorination of diphenylacetylene (Table 1, Entry 2) Reactions were set up using ($^{\text{Cl}}$ IPr)AuCl precatalyst. Method B was used, except that only 0.5 mL of CH_2Cl_2 was added. This detail was essential to the complete consumption of diphenylacetylene. Reaction time: 30 h.



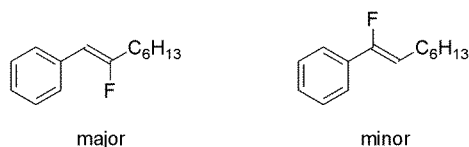
(Z)-1-Fluoro-1,2-diphenylethylene. Yield: 0.315 g (86%). NMR data are consistent with that found in the literature.⁹ ^1H NMR (300.1 MHz, CDCl_3): δ 7.64–7.78 (m, 4 H), 7.24–7.54 (m, 6 H), 6.37 (d, J = 40 Hz, $\text{CH}=\text{CF}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ 157.4 (d, J = 259 Hz, CF), 133.8 (d, J = 3.1 Hz), 133.0 (d, J = 28 Hz), 129.2, 129.0, 128.8, 128.7, 127.5 (d, J = 2.6 Hz), 124.5 (d, J = 7.4 Hz), 106.0 (d, J = 10.4 Hz, $\text{CH}=\text{CF}$). ^{19}F NMR (282 MHz, CDCl_3): δ -114.4 (d, J = 40 Hz).

Hydrofluorination of 4-(1-octynyl)anisole (Table 1, Entry 3). Reactions were set up according to Method A using (SIPr)AuOt-Bu as precatalyst. Reaction time: 30 h. Yield: 0.275 g (63%) as a 1:5 mixture of α - and β -fluorinated products.



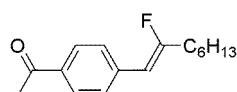
(Z)-4-(2-Fluoro-1-octenyl)anisole (major product): Yield: 0.196 g (45%). ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 9.2 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.41 (d, J = 40 Hz, 1 H, $\text{CH}=\text{CF}$), 3.81 (s, 3 H, OCF_3), 2.31 (dt, J = 7.6, 18 Hz, 2 H, CFCH_2), 1.55–1.63 (m, 2 H), 1.21–1.48 (m, 6 H), 0.91 (t, J = 7.0 Hz, 3 H, CH_3). ^{13}C NMR (126 MHz, CDCl_3): δ 161.2, 158.7 (d, J = 95 Hz, CF), 129.6 (d, J = 7.6 Hz), 126.9 (d, J = 2.3 Hz), 114.0, 105.1 (d, J = 9.2 Hz), 55.4, 33.2 (d, J = 27 Hz), 31.8, 28.8, 26.6, 22.8, 14.3. ^{19}F NMR (376 MHz, CDCl_3): δ -103.8 (m). IR: 2931, 1692, 1609, 1512, 1250, 1037, 851. Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{OF}$: C, 76.23; H, 8.96. Found: C, 76.15, 8.96. **4-(1-fluoro-octenyl)anisole (minor product)** This product was not isolated, but diagnostic resonances observed in NMR spectra of its mixtures with the major product are listed. ^1H NMR (400 MHz, CDCl_3): δ 5.26 (dt, J = 7.6, 38 Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -120.8 (d, J = 38 MHz).

Hydrofluorination of 1-phenyl-1-octyne (Table 1, Entry 4) Reactions were set up according to Method A using (SIPr)AuOt-Bu as precatalyst. Reaction time: 22 h. Yield: 0.298 g (78%) as a 1:13 mixture of α - and β -fluorinated products.



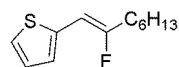
(Z)-1-Phenyl-2-fluoro-1-octene (major product): Yield: 0.275 g (72%). ^1H NMR (500 MHz, CDCl_3): δ 7.51 (d, $J = 8.5$ Hz, 2 H, *o*-CH), 7.32–7.42 (m, 2 H, *m*-CH), 7.21–7.25 (m, 2 H, *p*-CH), 5.49 (d, $J = 40$ Hz, 1 H, CH=CF), 2.35 (dt, $J = 7.5$, 18 Hz, 2 H, CFCH₂), 1.60–1.66 (m, 2 H), 1.33–1.44 (m, 6 H), 0.94 (t, $J = 7.0$ Hz, 3 H, CH₃). ^{13}C NMR (126 MHz, CDCl_3): δ 161.5 (d, $J = 266$ Hz, CF), 134.2 (d, $J = 4.2$ Hz), 128.6, 128.4 (d, $J = 12$ Hz), 126.7 (d, $J = 4.0$ Hz), 105.8 (d, $J = 17$ Hz), 33.3 (d, $J = 44$ Hz), 31.7, 28.8, 26.5, 22.8, 14.3. ^{19}F NMR (282 MHz, CDCl_3): δ –101.0 (dt, $J = 39$, 19 Hz). IR: 3059, 3026, 2924, 1691, 1495, 1449, 1151, 751, 693, 535. Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{F}$: C, 81.51; H, 9.28. Found: C, 81.75; H, 9.05. **1-phenyl-1-fluoro-1-octene (minor product):** This product was not isolated, diagnostic resonances observed in NMR spectra of its mixtures with the major product are listed. ^{19}F NMR (CDCl_3 , 282.3 MHz): δ –122.2 (d, $J = 43$ Hz).

Hydrofluorination of 4-(1-octynyl)acetophenone (Table 1, Entry 5) Reactions were set up according to Method A using (SIPr)AuOt-Bu as precatalyst. Reaction time: 18 h. Only the product of β -fluorination is observed.



(Z)-4-(2-fluoro-1-octenyl)acetophenone Yield: 0.378 g (82%). ^1H NMR (500 MHz, CDCl_3): δ 7.90 (d, $J = 7$ Hz, 2 H), 7.54 (d, $J = 8.5$ Hz, 2 H), 5.53 (d, $J = 39$ Hz, 1 H, CH=CF), 2.58 (s, 3 H, C(O)CH₃), 2.35 (dt, $J = 7.5$, 18 Hz, 2 H, CFCH₂), 1.58–1.64 (m, 2 H), 1.28–1.42 (m, 6 H), 0.90 (t, $J = 7.0$ Hz, 3 H, CH₃). ^{13}C NMR (126 MHz, CDCl_3): δ 197.8 (NCN), 163.6 (d, $J = 272$ Hz, CF), 139.0, 135.1, 128.8, 128.4, 105.3 (d, $J = 8.6$ Hz, CH=CF), 33.4 (d, $J = 26$ Hz, CFCH₂), 31.7, 28.8, 26.7 (C=O), 26.4, 22.7, 14.2. ^{19}F NMR (282 MHz, CDCl_3): δ (–96.2)–(–96.5) (m). IR: 2930, 1683, 1603, 1411, 1268, 1187, 957, 860, 597.0. Anal. Calcd. for $\text{C}_{16}\text{H}_{21}\text{FO}$: C, 77.38; H, 8.52. Found: C, 77.08; H, 8.61.

Hydrofluorination of 2-(1-octynyl)-thiophene (Table 1, Entry 6) Reactions were set up according to Method A using (SIPr)AuOt-Bu as precatalyst. Reaction time: 30 h. The product of β -fluorination was the only identifiable product.



(Z)-2-(2-fluoro-2-octenyl)-thiophene: Yield: 0.291 g (74%). ^1H NMR (500 MHz, CDCl_3): δ 7.2–7.4 (m, 1 H), 6.97–7.02 (m, 2 H), 5.81 (dt, $J = 39$, 0.5 Hz, CH=CF), 2.34 (dt, $J = 18$, 7.4 Hz, 2 H, CFCH₂), 1.54–1.17 (m, 2 H), 1.22–1.44 (m, 8 H), 0.91 (t, $J = 6.8$ Hz, 3 H, CH₃). ^{13}C NMR (126 MHz, CDCl_3): δ 160.2 (d, $J = 265$ Hz, CF), 136.4 (d, $J = 3.4$ Hz), 126.7, 125.7 (d, $J = 3.4$ Hz), 124.9 (d, $J = 9.2$ Hz), 100.6 (d, $J = 13$ Hz, HC=CF), 32.6 (d, $J = 25$ Hz, CFCH₂), 31.8, 28.8, 26.4, 22.7, 14.2. ^{19}F NMR (282 MHz, CDCl_3): δ –97.5 (dt, $J = 39$, 18 Hz). IR: 3070, 2930, 1685, 1466, 1427, 1235, 872, 841, 694, 532. Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{SF}$: C, 67.88; H, 8.07. Found: C, 68.16; H, 8.07; S, 7.81.

X-Ray Diffraction Study of (SIPr)Au[C(Ph)=CFCH₃] (2b). Crystals were grown by vapor diffusion of pentane into a solution of **2b** in CH₂Cl₂/1-phenyl-1-propyne at -40 °C. A colorless crystal was removed from the supernatant and transferred to a microscope slide coated with mineral oil. The crystal was mounted in a cryogenic loop using the oil, frozen in a nitrogen stream, and optically centered on the diffractometer. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo K α radiation (λ = 0.71073 Å), performing φ - and ω -scans. The structure was solved by direct methods using SHELXS¹⁰ and refined against F^2 on all data by full-matrix least squares with SHELXL-97¹¹. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The disordered C₉H₈F ligand was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratio between the two components of the disorder was refined freely and converged at 0.50(3). The target molecule co-crystallizes with one molecule of dichloromethane per asymmetric unit. This dichloromethane molecule is almost certainly disordered over several positions, however all attempts to parameterize this disorder failed.

Table S3. Crystal data and structure refinement for **2b**.

| | | |
|---------------------------------|---|-----------------------------|
| Identification code | 07034 | |
| Empirical formula | C ₃₇ H ₄₈ Au Cl ₂ F N ₂ | |
| Formula weight | 807.64 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | $a = 12.361(3)$ Å | $\alpha = 90^\circ$. |
| | $b = 15.078(3)$ Å | $\beta = 99.060(3)^\circ$. |
| | $c = 19.743(4)$ Å | $\gamma = 90^\circ$. |
| Volume | 3633.8(13) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.476 Mg/m ³ | |
| Absorption coefficient | 4.227 mm ⁻¹ | |
| F(000) | 1624 | |
| Crystal size | 0.25 x 0.20 x 0.15 mm ³ | |
| Theta range for data collection | 1.71 to 29.57°. | |
| Index ranges | - 17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27 | |

| | |
|-----------------------------------|---|
| Reflections collected | 68216 |
| Independent reflections | 10190 [R(int) = 0.0529] |
| Completeness to theta = 29.57° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.5697 and 0.4179 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 10190 / 330 / 468 |
| Goodness-of-fit on F ² | 1.024 |
| Final R indices [I>2sigma(I)] | R1 = 0.0256, wR2 = 0.0637 |
| R indices (all data) | R1 = 0.0319, wR2 = 0.0674 |
| Largest diff. peak and hole | 2.296 and -1.632 e.Å ⁻³ |

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | U(eq) |
|--------|-----------|----------|----------|-------|
| Au(1) | 14414(1) | 7846(1) | 5847(1) | 17(1) |
| C(31) | 13420(2) | 7392(2) | 4992(1) | 24(1) |
| C(32) | 12305(8) | 7807(11) | 4812(12) | 23(2) |
| C(33) | 11361(10) | 7335(11) | 4528(9) | 38(3) |
| C(34) | 10319(10) | 7732(14) | 4449(9) | 46(3) |
| C(35) | 10201(10) | 8596(13) | 4631(9) | 38(3) |
| C(36) | 11110(11) | 9077(10) | 4918(9) | 29(2) |
| C(37) | 12147(11) | 8681(10) | 5024(14) | 23(2) |
| C(38) | 13774(18) | 6744(19) | 4626(12) | 24(3) |
| C(39) | 14920(20) | 6390(30) | 4630(20) | 38(5) |
| F(1) | 13130(30) | 6450(30) | 4020(17) | 35(4) |
| C(32A) | 12253(8) | 7682(10) | 4861(13) | 25(2) |
| C(33A) | 11396(10) | 7100(10) | 4623(8) | 31(2) |
| C(34A) | 10320(9) | 7413(13) | 4503(7) | 39(2) |
| C(35A) | 10091(10) | 8288(14) | 4586(10) | 41(3) |
| C(36A) | 10921(12) | 8873(11) | 4817(10) | 33(2) |
| C(37A) | 12004(12) | 8576(11) | 4950(16) | 29(2) |
| C(38A) | 13835(18) | 6850(19) | 4566(12) | 24(3) |
| C(39A) | 14870(20) | 6300(30) | 4690(20) | 36(4) |
| F(1A) | 13190(30) | 6550(30) | 3964(17) | 35(4) |
| C(1) | 15345(2) | 8241(2) | 6725(1) | 17(1) |
| N(1) | 16261(2) | 7837(1) | 7023(1) | 19(1) |
| C(11) | 16748(2) | 7098(2) | 6723(1) | 20(1) |
| C(12) | 17486(2) | 7259(2) | 6269(2) | 24(1) |
| C(121) | 17788(2) | 8187(2) | 6064(2) | 28(1) |
| C(122) | 19028(3) | 8326(2) | 6211(2) | 38(1) |
| C(123) | 17328(3) | 8370(2) | 5311(2) | 38(1) |
| C(13) | 17925(3) | 6523(2) | 5979(2) | 31(1) |
| C(14) | 17644(3) | 5668(2) | 6148(2) | 32(1) |
| C(15) | 16923(3) | 5529(2) | 6602(2) | 30(1) |
| C(16) | 16457(2) | 6243(2) | 6902(2) | 24(1) |
| C(161) | 15623(3) | 6077(2) | 7373(2) | 30(1) |

| | | | | |
|--------|----------|----------|---------|--------|
| C(162) | 14564(3) | 5728(3) | 6967(2) | 53(1) |
| C(163) | 16056(3) | 5465(3) | 7970(2) | 48(1) |
| C(2) | 16739(2) | 8231(2) | 7685(1) | 23(1) |
| C(3) | 15842(2) | 8886(2) | 7812(1) | 22(1) |
| N(2) | 15112(2) | 8888(1) | 7142(1) | 18(1) |
| C(21) | 14166(2) | 9449(2) | 6994(1) | 19(1) |
| C(22) | 14315(2) | 10308(2) | 6749(1) | 22(1) |
| C(221) | 15434(2) | 10632(2) | 6631(2) | 28(1) |
| C(222) | 15567(3) | 10484(3) | 5886(2) | 44(1) |
| C(223) | 15659(4) | 11596(2) | 6842(2) | 53(1) |
| C(23) | 13385(3) | 10835(2) | 6580(2) | 29(1) |
| C(24) | 12358(3) | 10525(2) | 6652(2) | 32(1) |
| C(25) | 12232(2) | 9678(2) | 6903(2) | 29(1) |
| C(26) | 13137(2) | 9122(2) | 7083(1) | 22(1) |
| C(261) | 12983(2) | 8209(2) | 7384(2) | 26(1) |
| C(262) | 12106(3) | 7666(2) | 6934(2) | 42(1) |
| C(263) | 12722(3) | 8296(2) | 8111(2) | 37(1) |
| Cl(1) | 15513(1) | 9493(1) | 1038(1) | 112(1) |
| C(1S) | 16908(3) | 9415(3) | 1052(2) | 55(1) |
| Cl(2) | 17435(1) | 10152(1) | 514(1) | 68(1) |

Table S5. Bond lengths [Å] and angles [°] for **2b**.

| | |
|---------------|-----------|
| Au(1)–C(1) | 2.014(3) |
| Au(1)–C(31) | 2.043(3) |
| C(31)–C(38) | 1.329(9) |
| C(31)–C(38A) | 1.331(10) |
| C(31)–C(32A) | 1.490(9) |
| C(31)–C(32) | 1.504(9) |
| C(32)–C(37) | 1.406(10) |
| C(32)–C(33) | 1.406(9) |
| C(33)–C(34) | 1.406(11) |
| C(34)–C(35) | 1.366(12) |
| C(35)–C(36) | 1.382(10) |
| C(36)–C(37) | 1.400(9) |
| C(38)–F(1) | 1.400(10) |
| C(38)–C(39) | 1.511(14) |
| C(32A)–C(33A) | 1.398(10) |
| C(32A)–C(37A) | 1.400(10) |
| C(33A)–C(34A) | 1.395(10) |
| C(34A)–C(35A) | 1.365(12) |
| C(35A)–C(36A) | 1.375(11) |
| C(36A)–C(37A) | 1.396(10) |
| C(38A)–F(1A) | 1.398(10) |
| C(38A)–C(39A) | 1.504(14) |
| C(1)–N(2) | 1.337(3) |
| C(1)–N(1) | 1.338(3) |
| N(1)–C(11) | 1.437(3) |
| N(1)–C(2) | 1.471(3) |
| C(11)–C(12) | 1.398(4) |
| C(11)–C(16) | 1.399(4) |
| C(12)–C(13) | 1.395(4) |
| C(12)–C(121) | 1.520(4) |
| C(121)–C(122) | 1.529(4) |
| C(121)–C(123) | 1.530(5) |
| C(13)–C(14) | 1.389(4) |
| C(14)–C(15) | 1.376(5) |
| C(15)–C(16) | 1.397(4) |

| | |
|---------------|----------|
| C(16)–C(161) | 1.514(4) |
| C(161)–C(162) | 1.518(5) |
| C(161)–C(163) | 1.526(5) |
| C(2)–C(3) | 1.535(4) |
| C(3)–N(2) | 1.480(3) |
| N(2)–C(21) | 1.436(3) |
| C(21)–C(26) | 1.400(4) |
| C(21)–C(22) | 1.406(4) |
| C(22)–C(23) | 1.394(4) |
| C(22)–C(221) | 1.519(4) |
| C(221)–C(222) | 1.523(5) |
| C(221)–C(223) | 1.525(5) |
| C(23)–C(24) | 1.381(5) |
| C(24)–C(25) | 1.388(4) |
| C(25)–C(26) | 1.397(4) |
| C(26)–C(261) | 1.524(4) |
| C(261)–C(263) | 1.526(4) |
| C(261)–C(262) | 1.527(4) |
| Cl(1)–C(1S) | 1.725(4) |
| C(1S)–Cl(2) | 1.733(4) |

| | |
|---------------------|------------|
| C(1)–Au(1)–C(31) | 176.36(10) |
| C(38)–C(31)–C(38A) | 9(3) |
| C(38)–C(31)–C(32A) | 120.9(12) |
| C(38A)–C(31)–C(32A) | 122.0(11) |
| C(38)–C(31)–C(32) | 123.1(10) |
| C(38A)–C(31)–C(32) | 122.4(12) |
| C(32A)–C(31)–C(32) | 8.6(16) |
| C(38)–C(31)–Au(1) | 119.2(8) |
| C(38A)–C(31)–Au(1) | 119.1(9) |
| C(32A)–C(31)–Au(1) | 119.0(8) |
| C(32)–C(31)–Au(1) | 117.7(6) |
| C(37)–C(32)–C(33) | 116.6(8) |
| C(37)–C(32)–C(31) | 119.0(9) |
| C(33)–C(32)–C(31) | 123.8(9) |
| C(32)–C(33)–C(34) | 121.1(9) |
| C(35)–C(34)–C(33) | 120.8(9) |

| | |
|----------------------|------------|
| C(34)–C(35)–C(36) | 119.6(8) |
| C(35)–C(36)–C(37) | 120.2(9) |
| C(36)–C(37)–C(32) | 121.5(9) |
| C(31)–C(38)–F(1) | 120.2(14) |
| C(31)–C(38)–C(39) | 129.9(17) |
| F(1)–C(38)–C(39) | 107.8(14) |
| C(33A)–C(32A)–C(37A) | 118.4(8) |
| C(33A)–C(32A)–C(31) | 122.4(10) |
| C(37A)–C(32A)–C(31) | 119.1(10) |
| C(34A)–C(33A)–C(32A) | 119.8(9) |
| C(35A)–C(34A)–C(33A) | 121.1(9) |
| C(34A)–C(35A)–C(36A) | 120.1(8) |
| C(35A)–C(36A)–C(37A) | 120.0(9) |
| C(36A)–C(37A)–C(32A) | 120.6(9) |
| C(31)–C(38A)–F(1A) | 120.7(15) |
| C(31)–C(38A)–C(39A) | 129.1(16) |
| F(1A)–C(38A)–C(39A) | 108.6(13) |
| N(2)–C(1)–N(1) | 108.1(2) |
| N(2)–C(1)–Au(1) | 126.64(18) |
| N(1)–C(1)–Au(1) | 125.03(18) |
| C(1)–N(1)–C(11) | 123.4(2) |
| C(1)–N(1)–C(2) | 113.6(2) |
| C(11)–N(1)–C(2) | 122.9(2) |
| C(12)–C(11)–C(16) | 122.8(2) |
| C(12)–C(11)–N(1) | 119.3(2) |
| C(16)–C(11)–N(1) | 118.0(2) |
| C(13)–C(12)–C(11) | 117.4(3) |
| C(13)–C(12)–C(121) | 119.7(3) |
| C(11)–C(12)–C(121) | 122.9(2) |
| C(12)–C(121)–C(122) | 110.9(3) |
| C(12)–C(121)–C(123) | 110.8(3) |
| C(122)–C(121)–C(123) | 111.6(3) |
| C(14)–C(13)–C(12) | 120.7(3) |
| C(15)–C(14)–C(13) | 120.7(3) |
| C(14)–C(15)–C(16) | 120.7(3) |
| C(15)–C(16)–C(11) | 117.6(3) |
| C(15)–C(16)–C(161) | 119.9(3) |

| | |
|----------------------|----------|
| C(11)–C(16)–C(161) | 122.3(2) |
| C(16)–C(161)–C(162) | 110.3(3) |
| C(16)–C(161)–C(163) | 112.6(3) |
| C(162)–C(161)–C(163) | 111.5(3) |
| N(1)–C(2)–C(3) | 101.9(2) |
| N(2)–C(3)–C(2) | 102.0(2) |
| C(1)–N(2)–C(21) | 123.5(2) |
| C(1)–N(2)–C(3) | 112.9(2) |
| C(21)–N(2)–C(3) | 123.0(2) |
| C(26)–C(21)–C(22) | 122.5(2) |
| C(26)–C(21)–N(2) | 119.7(2) |
| C(22)–C(21)–N(2) | 117.8(2) |
| C(23)–C(22)–C(21) | 117.4(3) |
| C(23)–C(22)–C(221) | 121.1(3) |
| C(21)–C(22)–C(221) | 121.4(2) |
| C(22)–C(221)–C(222) | 109.9(3) |
| C(22)–C(221)–C(223) | 113.3(3) |
| C(222)–C(221)–C(223) | 111.2(3) |
| C(24)–C(23)–C(22) | 121.3(3) |
| C(23)–C(24)–C(25) | 120.3(3) |
| C(24)–C(25)–C(26) | 120.8(3) |
| C(25)–C(26)–C(21) | 117.7(2) |
| C(25)–C(26)–C(261) | 119.8(2) |
| C(21)–C(26)–C(261) | 122.5(2) |
| C(26)–C(261)–C(263) | 110.2(2) |
| C(26)–C(261)–C(262) | 112.2(3) |
| C(263)–C(261)–C(262) | 110.9(3) |
| Cl(1)–C(1S)–Cl(2) | 114.7(3) |

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Au(1) | 17(1) | 19(1) | 14(1) | −2(1) | −2(1) | 3(1) |
| C(31) | 27(1) | 25(1) | 17(1) | 1(1) | −3(1) | 1(1) |
| C(32) | 22(2) | 37(5) | 9(4) | 3(4) | 0(3) | −3(2) |
| C(33) | 35(3) | 50(5) | 25(5) | −7(5) | −9(3) | −5(3) |
| C(34) | 27(3) | 68(7) | 41(5) | −9(6) | −7(3) | −7(4) |
| C(35) | 21(3) | 68(7) | 24(4) | −6(5) | −2(3) | 2(4) |
| C(36) | 15(4) | 49(5) | 20(5) | 5(4) | 0(3) | 3(3) |
| C(37) | 17(3) | 33(4) | 18(5) | 7(3) | −1(3) | 6(3) |
| C(38) | 37(2) | 19(5) | 13(3) | 4(4) | −6(2) | 2(3) |
| C(39) | 49(4) | 30(7) | 30(10) | −4(6) | −6(4) | 17(5) |
| F(1) | 52(3) | 30(7) | 17(4) | −6(5) | −11(3) | 6(4) |
| C(32A) | 24(3) | 33(4) | 19(5) | 11(3) | 1(3) | 0(2) |
| C(33A) | 30(3) | 43(5) | 17(4) | 8(4) | −4(3) | −7(3) |
| C(34A) | 27(3) | 61(6) | 27(4) | 2(5) | −3(3) | −12(4) |
| C(35A) | 21(3) | 70(7) | 30(5) | 1(6) | −1(3) | 3(4) |
| C(36A) | 26(5) | 47(5) | 29(6) | 9(4) | 7(4) | 10(4) |
| C(37A) | 21(4) | 37(4) | 30(7) | 7(4) | 5(4) | 1(3) |
| C(38A) | 37(2) | 19(5) | 13(3) | 4(4) | −6(2) | 2(3) |
| C(39A) | 53(5) | 32(8) | 19(6) | −3(6) | −4(4) | 19(5) |
| F(1A) | 52(3) | 30(7) | 17(4) | −6(5) | −11(3) | 6(4) |
| C(1) | 16(1) | 18(1) | 17(1) | 1(1) | 2(1) | 0(1) |
| N(1) | 19(1) | 22(1) | 15(1) | −3(1) | −3(1) | 3(1) |
| C(11) | 19(1) | 22(1) | 18(1) | −1(1) | −2(1) | 7(1) |
| C(12) | 22(1) | 28(1) | 22(1) | 2(1) | 1(1) | 6(1) |
| C(121) | 28(1) | 28(1) | 31(2) | 3(1) | 10(1) | 4(1) |
| C(122) | 33(2) | 46(2) | 36(2) | −3(1) | 8(1) | −5(1) |
| C(123) | 37(2) | 40(2) | 38(2) | 13(1) | 8(1) | 4(1) |
| C(13) | 31(1) | 35(2) | 27(2) | 3(1) | 8(1) | 13(1) |
| C(14) | 40(2) | 28(1) | 29(2) | −2(1) | 3(1) | 16(1) |
| C(15) | 36(2) | 22(1) | 30(2) | 1(1) | 1(1) | 8(1) |
| C(16) | 24(1) | 23(1) | 24(1) | 1(1) | −1(1) | 4(1) |
| C(161) | 35(2) | 24(1) | 35(2) | 5(1) | 12(1) | 2(1) |

| | | | | | | |
|--------|--------|--------|--------|--------|-------|--------|
| C(162) | 41(2) | 67(3) | 49(2) | 19(2) | 6(2) | -16(2) |
| C(163) | 56(2) | 60(2) | 28(2) | 13(2) | 12(2) | 12(2) |
| C(2) | 22(1) | 26(1) | 18(1) | -4(1) | -5(1) | 2(1) |
| C(3) | 25(1) | 25(1) | 14(1) | -2(1) | -2(1) | 2(1) |
| N(2) | 19(1) | 19(1) | 15(1) | -3(1) | -1(1) | 2(1) |
| C(21) | 22(1) | 17(1) | 17(1) | -3(1) | 1(1) | 4(1) |
| C(22) | 26(1) | 21(1) | 18(1) | -2(1) | 1(1) | 2(1) |
| C(221) | 31(1) | 25(1) | 29(2) | 6(1) | 2(1) | -4(1) |
| C(222) | 45(2) | 54(2) | 36(2) | 9(2) | 15(2) | -8(2) |
| C(223) | 54(2) | 32(2) | 71(3) | -4(2) | 3(2) | -14(2) |
| C(23) | 39(2) | 21(1) | 26(2) | 4(1) | 4(1) | 9(1) |
| C(24) | 31(2) | 32(2) | 31(2) | 2(1) | 2(1) | 15(1) |
| C(25) | 22(1) | 30(1) | 34(2) | -1(1) | 6(1) | 7(1) |
| C(26) | 23(1) | 20(1) | 23(1) | -2(1) | 3(1) | 3(1) |
| C(261) | 23(1) | 21(1) | 36(2) | -1(1) | 7(1) | 0(1) |
| C(262) | 43(2) | 37(2) | 43(2) | -6(2) | 2(2) | -13(2) |
| C(263) | 45(2) | 31(2) | 36(2) | 2(1) | 10(2) | -3(1) |
| Cl(1) | 49(1) | 119(1) | 172(2) | -65(1) | 26(1) | -18(1) |
| C(1S) | 51(2) | 58(2) | 58(3) | 13(2) | 11(2) | -5(2) |
| Cl(2) | 112(1) | 57(1) | 41(1) | 2(1) | 25(1) | -11(1) |

Table S7. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2b**.

| | x | y | z | U(eq) |
|--------|-------|------|------|-------|
| H(33) | 11427 | 6738 | 4387 | 45 |
| H(34) | 9690 | 7395 | 4268 | 56 |
| H(35) | 9497 | 8865 | 4561 | 46 |
| H(36) | 11031 | 9679 | 5044 | 34 |
| H(37) | 12758 | 9010 | 5245 | 28 |
| H(39A) | 15213 | 6624 | 4234 | 57 |
| H(39B) | 14904 | 5745 | 4614 | 57 |
| H(39C) | 15391 | 6586 | 5054 | 57 |
| H(33A) | 11546 | 6495 | 4542 | 37 |
| H(34A) | 9738 | 7010 | 4361 | 47 |
| H(35A) | 9357 | 8494 | 4484 | 49 |
| H(36A) | 10758 | 9479 | 4886 | 40 |
| H(37A) | 12576 | 8984 | 5103 | 35 |
| H(39D) | 15292 | 6469 | 5137 | 53 |
| H(39E) | 15301 | 6414 | 4328 | 53 |
| H(39F) | 14674 | 5674 | 4699 | 53 |
| H(121) | 17444 | 8619 | 6350 | 34 |
| H(12A) | 19286 | 8249 | 6703 | 57 |
| H(12B) | 19204 | 8927 | 6073 | 57 |
| H(12C) | 19388 | 7892 | 5952 | 57 |
| H(12D) | 17660 | 7959 | 5018 | 57 |
| H(12E) | 17499 | 8981 | 5196 | 57 |
| H(12F) | 16532 | 8287 | 5236 | 57 |
| H(13) | 18420 | 6608 | 5662 | 37 |
| H(14) | 17954 | 5175 | 5949 | 39 |
| H(15) | 16740 | 4940 | 6713 | 35 |
| H(161) | 15455 | 6662 | 7572 | 36 |
| H(16A) | 14300 | 6141 | 6594 | 79 |
| H(16B) | 14012 | 5670 | 7270 | 79 |
| H(16C) | 14697 | 5146 | 6773 | 79 |
| H(16D) | 16200 | 4877 | 7793 | 71 |
| H(16E) | 15510 | 5415 | 8278 | 71 |

| | | | | |
|--------|-------|-------|------|----|
| H(16F) | 16736 | 5710 | 8222 | 71 |
| H(2A) | 17435 | 8541 | 7652 | 28 |
| H(2B) | 16871 | 7777 | 8051 | 28 |
| H(3A) | 15453 | 8676 | 8184 | 26 |
| H(3B) | 16148 | 9483 | 7930 | 26 |
| H(22I) | 15996 | 10260 | 6921 | 34 |
| H(22A) | 15432 | 9859 | 5766 | 67 |
| H(22B) | 16314 | 10643 | 5823 | 67 |
| H(22C) | 15042 | 10855 | 5588 | 67 |
| H(22D) | 15167 | 11985 | 6537 | 79 |
| H(22E) | 16421 | 11743 | 6809 | 79 |
| H(22F) | 15533 | 11679 | 7316 | 79 |
| H(23) | 13459 | 11420 | 6413 | 35 |
| H(24) | 11734 | 10893 | 6529 | 38 |
| H(25) | 11522 | 9473 | 6954 | 34 |
| H(26I) | 13693 | 7882 | 7411 | 32 |
| H(26A) | 11386 | 7936 | 6941 | 63 |
| H(26B) | 12107 | 7058 | 7110 | 63 |
| H(26C) | 12260 | 7657 | 6462 | 63 |
| H(26D) | 13287 | 8656 | 8387 | 55 |
| H(26E) | 12703 | 7706 | 8316 | 55 |
| H(26F) | 12007 | 8583 | 8095 | 55 |
| H(1S1) | 17084 | 8804 | 923 | 66 |
| H(1S2) | 17280 | 9517 | 1528 | 66 |

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