Transmetalation reactions triggered by electron transfer between organo-copper complexes

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S1. General methods and reagent availability

All the manipulations were performed under N\textsubscript{2} atmosphere, using standard Schlenk techniques. Solvents were dried using a solvent purification system SPS-MD5 or distilled from appropriate drying agents under nitrogen according to literature\textsuperscript{1} and storing them over 3 Å zeolites for a week. Prior to its use, solvents were degassed by three freeze-pump-thaw cycles. NMR spectra were recorded on Bruker AV 400 or Varian Inova 500-MR instruments equipped with variable-temperature probes. All glassware was flame dried or dried overnight at 110 °C and allowed to cool under vacuum. Chemical shifts are reported in ppm from tetramethylsilane (\textsuperscript{1}H and \textsuperscript{13}C), CCl\textsubscript{3}F (\textsuperscript{19}F), with positive shifts downfield, at 298 K unless otherwise stated. The temperature for the NMR probe was calibrated with a methanol standard.\textsuperscript{2} For the \textsuperscript{19}F NMR spectra registered in non-deuterated solvents, an internal coaxial tube containing acetone-d6 was used to maintain the lock \textsuperscript{2}H signal.

Compounds [Cu(C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3})(tht)]\textsubscript{4},\textsuperscript{3} C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3}I,\textsuperscript{4} C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3}H,\textsuperscript{5} C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3}-C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3},\textsuperscript{5} [Cu(bipy)](C\textsubscript{6}F\textsubscript{3})\textsubscript{3},\textsuperscript{6} [Cu(bipy)]\textsubscript{2},\textsuperscript{7} and [Cu(bipy)]\textsubscript{2}BF\textsubscript{4}\textsuperscript{8} were prepared according to reported procedures. The rest of reactants were available from commercial sources and used as received without further purification.

Numbering of the complexes:

\begin{align*}
[Cu(bipy)](C\textsubscript{6}F\textsubscript{3}) \quad (1) \quad [Cu(C\textsubscript{6}F\textsubscript{3})\textsubscript{2}]^\pi \quad (2) \quad [Cu(bipy)]\textsubscript{2}^\pi \quad (3) \\
[Cu(bipy)](C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3}) \quad (4) \quad [Cu(bipy)](C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3})(C\textsubscript{6}F\textsubscript{3})I \quad (5) \quad [Cu(bipy)]\textsubscript{2}I \quad (6) \\
[Cu(bipy)](C\textsubscript{6}F\textsubscript{3})\textsubscript{2}I \quad (7) \quad [Cu(bipy)](C\textsubscript{6}Cl\textsubscript{2}F\textsubscript{3})(C\textsubscript{6}F\textsubscript{3})\textsubscript{2} \quad (8)
\end{align*}

S2. Synthetic procedures

\textit{Synthesis of (NBu\textsubscript{4})[Cu(C\textsubscript{6}F\textsubscript{3})\textsubscript{2}]}

C\textsubscript{6}F\textsubscript{5}Br (555 μL, 4.45 mmol) was charged in a 100 mL Schlenk flask protected from the light. Et\textsubscript{2}O (17 mL) was added and the solution was cooled to -60 °C in a isopropanol bath cooled using a cryostator. Then, a solution of BuLi 1.6M in hexanes (2.72 mL, 4.35 mmol) was added and the mixture was stirred for 45 min. Freshly prepared (NBu\textsubscript{4})[CuCl\textsubscript{2}] (800 mg, 2.12 mmol) was then added and the mixture was stirred during 4 h. After that, the bath was allowed to warm during another hour, at that moment the mixture is a light yellowish suspension. Solvents were removed under vacuum and the solid residue was stirred with 18 mL of CH\textsubscript{3}Cl\textsubscript{2}, then, solids were separated by filtering through Celite using a Schlenk frit and rinsed with
another 2 mL. The filtrates were collected in another 100 mL Schlenk flask and then, vacuum eliminated up to 13 mL. Hexane (24 mL) was slowly added on top of them forming a layer and the flask was put under N₂ pressure and stored at -32 ºC for 24 h. After that time, colourless crystals of (NBu₄)[Cu(C₆F₅)₂] had precipitated, the yellowish liquors were quickly removed at -32 ºC using a syringe. The precipitate was washed with cold Et₂O (3 mL) and vacuum dried. Yield 923 mg, 68%. Calcd. for C₂₈H₃₆CuF₁₀N: C, 52.54; H, 5.67; N 2.19; Found: C, 52.52; H, 5.59; N, 2.16.

1H NMR (500 MHz, CDCl₃): δ 3.00 (m, 2H), 1.49 (m, 2H), 1.32 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). 19F NMR (470 MHz, CDCl₃): δ -111.21 (m, 2Fortho), -161.06 (t, J = 19.8 Hz, 1Fpara), -162.87 (m, 2Fmeta). 13C{¹H} NMR (126 MHz, CDCl₃): δ 149.3 (dm, J = 219.5 Hz, Cortho), 137.8 (dm, J = 243.1 Hz, Cpara), 136.1 (dm, J = 253.1 Hz, Cmeta), 128.3 (tm, J = 76.7 Hz, Cipso) 58.8, 23.7, 19.5, 13.3.

The compound obtained contained crystals suitable for X-ray diffraction that allowed the obtention of the solid state structure of compound (NBu₄)[Cu(C₆F₅)₂] (See S10)

**Synthesis of [Cu(bipy)](C₆Cl₂F₃)**

[Cu(C₆Cl₂F₃)(tht)]₄ (130 mg, 0.10 mmol) and 2,2’-bipyridine (64 mg, 0.41 mmol) were charged in a 100 mL Schlenk flask. CH₂Cl₂ (8 mL) was added and the mixture was stirred for 15 min conforming an orange suspension. Then, hexane (12 ml) was added and the mixture was stirred for another 5 min. The orange precipitate was separated from the solution using a Schlenk frit, washed there with hexane (3 mL) and vacuum dried. Yield 138 mg, 82%. Calcd. for C₁₆H₈Cl₂CuF₃N₂: C, 45.79; H, 1.92; N 6.67; Found: C, 45.53; H, 1.90; N, 6.45.

1H NMR (500 MHz, THF-d8): δ 8.96 (br s, 1H), 8.41 (d, J = 8.1 Hz 1H), 8.13 (dt, J₁ = 7.8, J₂ = 1.1 Hz, 1H), 7.69 (m, 1H). 19F NMR (470 MHz, THF-d8): δ -84.23 (s, 2Fortho), -122.35 (s, 1Fpara). 13C{¹H} NMR (126 MHz, THF-d8): δ 150.1, 138.9, 126.2, 121.3. Due to the low solubility and the instability of this compound, carbon atoms not linked to a hydrogen atom could not be detected.

**Synthesis of (NBu₄)[CuCl₂]**

This compound was synthesized by a method adapted from the bibliography.⁹ CuCl (300 mg, 3.03 mmol) and (NBu₄)Cl (842 mg, 3.03 mmol) were charged in a 100 mL Schlenk flask. CH₂Cl₂ (10 mL) was added and the mixture was stirred for 15 min conforming a light yellowish suspension. Solids were filtered off using a filtering paper plugged cannula and the filtrate was collected in another 50 mL Schlenk flask, where solvent was vacuum removed up to 2 mL. Then, Et₂O (4 ml) was slowly added on top of the filtrate
forming a layer, the flask was closed under N₂ pressure and stored at -32 °C for 6h. After that time, colorless crystals of (NBu₄)[CuCl₂] had precipitated, the yellowish liquors were quickly removed at -32 °C using a syringe. The precipitate was washed with cold Et₂O (2x3 mL) and vacuum dried. Yield 920 mg, 79%. Calcd. for C₁₆H₃₆Cl₂CuN: C, 50.99; H, 9.63; N 3.72; Found: C, 50.82; H, 9.57; N, 3.69.

¹H NMR (500 MHz, CDCl₃): δ 3.24 (m, 2H), 1.66 (m, 2H), 1.45 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 59.1, 24.1, 19.8, 13.7.
S3. Calculation of the ionization equilibrium constant at 298 K through Van’t Hoff plot

$$2 \left[ \text{Cu(bipy})(C_6F_5) \right] \rightleftharpoons [\text{Cu(bipy)}]_2^+ + [\text{Cu(C}_6\text{F}_5)_2]^+$$

\[ K_{eq} = \frac{[\text{Cu(C}_6\text{F}_5)_2]^+] \cdot [\text{Cu(bipy)}]_2^+}{[\text{Cu(bipy})(C}_6\text{F}_5)]^2} \]

**Scheme S1:** Ionization equilibrium of complex 1 and its equilibrium constant.

A solution $5.94 \cdot 10^{-2}$ M of 1 was prepared by adding 1 (5.05 mg, 0.0131 mmol) and THF (2.20 mL) inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor, a flame sealed coaxial capillary containing acetone-d$_6$ was added to keep the lock signal. After that, the tube was transferred to the NMR spectrometer previously set to 170 K. $^{19}$F NMR spectra were recorded at 170, 176, 182, 185, 193 and 198 by raising the temperature of the spectrometer. Integration of the broad signals corresponding to the -ortho fluorine nuclei of the compounds lead to relative ratios of neutral and ionic compounds used to calculate $K_{ion}$ at each temperature through van’t Hoff’s equation (eq. S1). Signals belonging to neutral and ionic complexes were told apart by comparison with the signals of compound (NBu$_4$)[Cu(C$_6$F$_5$)$_2$] at that temperature.

$$\ln(K_{eq}) = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{eq. S1}$$

| Rate at 170°C | Rate at 176 K | Rate at 182 K | Rate at 185 K | Rate at 193 K | Rate at 198 K | Calcd. Rate at 298 K | $K_{ion}$ at 298 K |
|---------------|---------------|---------------|---------------|---------------|---------------|-----------------------|---------------------|
| 1 : 0.32      | 1 : 0.31      | 1 : 0.27      | 1 : 0.24      | 1 : 0.20      | 1 : 0.19      | 1 : 0.030             | 8.73 $\cdot 10^{-4}$ |

**Figure S1:** van’t Hoff plot for the ionic disproportion equilibrium of [Cu(bipy)(C$_6$F$_5$)].
DFT calculations give a ΔG of 4.4 kcal mol\(^{-1}\) for the ionization equilibrium in THF at 25ºC, that corresponds to a \(K_{\text{eq}}\) of \(5.8 \times 10^{-4}\), in very good agreement with the experimental measurement.
S4. Experiments of pentafluorophenylation of non-perhalogenated aryl halides

The reaction of complex 1 with an excess of iodobenzene in THF at 50 °C was monitored by $^{19}$F NMR. The main product of this reaction is the coupling product C$_6$F$_5$-Ph. Also, significant amounts of the hydrolysis product C$_6$F$_5$H and trace amounts of the homocoupling product C$_6$F$_5$-C$_6$F$_5$ (~2% conversion) attributed to the reaction of compound 1 with O$_2$ (see below) could be detected. Non-linear fitting of the concentration/time data by non-linear least squares (NLLS) using the software COPASI$^{10}$ for the products C$_6$F$_5$-Ph and C$_6$F$_5$H lead to the obtainment of the kinetic constant for aryl heterocoupling, $k_{ph-I} = 2.14 \cdot 10^{-4}$ s$^{-1}$·M$^{-1}$.

![Figure S2](image_url)

**Figure S2:** Experimental (dots) and best least square fitted (continuous line) concentration vs time plot of the formed species in the reaction of 1 ($2.4 \cdot 10^{-2}$M) with PhI ($4.3 \cdot 10^{-1}$M) in THF at 50 °C. •1; •C$_6$F$_5$-Ph; •C$_6$F$_5$H; •C$_6$F$_5$-C$_6$F$_5$.

To study the effect of the electronic properties of the aryl iodides in the oxidative addition reaction to compound 1, several competitive experiments containing para-substituted aryl iodides along with iodobenzene were carried out.
Scheme S2: Competitive reactions between complex 1, iodobenzene and aryl iodides 9a-9g in THF at 50 ºC.

Yields for the pentafluorophenylation reaction of each aryl iodide were derived from $^{19}$F NMR spectra performed after the heating time, taking into account the amount of each aryl iodide added and the loss of reagent 1 due to the hydrolysis reaction with water traces. Relative reaction rates for each aryl iodide respect to the one of iodobenzene could be calculated and plotted against the Hammett parameters. (Figure 1 in main text)

Kinetic independent constants for each aryl iodide were calculated by comparison with the measured value for iodobenzene.

Table S1: Values of coupling constants for the reaction of aryl iodides 9a-9g with complex 1 in THF at 50 ºC.

| Ar-I   | 9a    | 9b    | 9c    | 9d    | 9e    | 9f    | 9g    |
|--------|-------|-------|-------|-------|-------|-------|-------|
| $k / s^{-1} \cdot M^{-1}$ | 2.23·$10^{-4}$ | 1.36·$10^{-3}$ | 1.32·$10^{-3}$ | 4.04·$10^{-4}$ | 2.10·$10^{-4}$ | 1.59·$10^{-4}$ | 1.50·$10^{-4}$ |

It has been reported that pentafluorophenyalted Cu(I) complexes react with residual $O_2$ traces present in the media to yield the homocoupling product C$_6$F$_5$-C$_6$F$_5$. However, the formation of C$_6$F$_5$-C$_6$F$_5$ could also be attributed to some other reactivity derived from the interaction of complex 1 with the aryl halides. To rule out this possibility for the non-perhalogenated aryl halides, compound 1 was let react in the absence of aryl iodides and in the same conditions as in the competitive experiments.
Figure S3: Comparison of $^{19}$F NMR spectra in the orto- fluorine region of the standard reaction without aryl halides and the competitive reaction of iodobenzene and 9a with complex 1 after 12 h at 50 °C in THF.

This reaction yielded a much higher amount of the coupling product C$_6$F$_5$-C$_6$F$_5$ than that observed in the competitive experiments. These results imply that, in absence of aryl iodides, complex 1 reacts with both H$_2$O and O$_2$ impurities present in the medium being the latter reaction much slower. Once the water has been consumed, the remaining concentration of complex 1 is still high compared to the one in competitive experiments and O$_2$ can keep reacting with 1 to yield compound C$_6$F$_5$-C$_6$F$_5$. 
Experimental procedure for monitorization and competitive experiments

Monitoring of the reaction of compound 1 with PhI

Complex 1 (35.74 mg, 0.092 mmol) was added inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d6 to keep the lock signal. The tube was cooled to -75 °C in an isopropanol bath and 4,4’-difluorobiphenyl (0.60 mg, 0.003 mmol), PhI (62 µL, 0.555 mmol) and THF (1.28 mL) were added. The tube was closed inside the adaptor and then, taken out of the cool bath, manually shaken until total dissolution of solids and transferred to the NMR probe, which had been preheated to the monitoring temperature (50 °C).

Recording started after about 2 min required for the setup of the experiment, time zero for the measurements is taken at that moment. 19F NMR spectra parameters are 64 scans, relaxation delay of 1 s, pulse angle of 30º, spectral width of 48076.9 Hz, and size of 32768 points. Spectra were collected every 300 s.

Preparation of the stock solution for competitive experiments

Compound 1 (369 mg, 0.955 mmol) was added into a Schlenk flask and successive cycles of vacuum/N2 were applied, then, 11 mg (0.059 mmol) of 4,4’-difluorobiphenyl and 13.32 mL of THF were added. Manual stirring of the mixture lead to a clear red solution

Competitive experiments of aryl iodides 9a - 9e

A weighted amount of the aryl halide (0.105 mmol) and a volume of iodobenzene (35.5 µL, 0.317 mmol) were placed inside a screwed cap NMR tube with the aid of a Schlenk NMR tube adaptor. Then, 1.47 mL of a freshly prepared stock solution containing 1 (0.072 M) and 4,4’-difluorobiphenyl (0.0044 M) in THF were added. Finally, a flame sealed coaxial capillary containing acetone-d6 was added and the tube was closed and manually shaken until dissolution of solids. The tubes were heated at 50 °C in an oil bath for 12 h. In the case of aryl iodide 9b, instead of a weighted amount of the compound, a volume of the compound was added using a 25 µL microsyringe.

Competitive experiments of aryl iodides 9f and 9g

A weighted amount of the aryl halide (0.317 mmol) and a volume of iodobenzene (11,8
µL, 0.105 mmol) were placed inside a screwed cap NMR tube with the aid of a Schlenk NMR tube adaptor, then, 1.47 mL of a freshly prepared stock solution containing 1 (0.072 M) and 4,4′-difluorobiphenyl (0.0044 M) in THF were added. Finally, a flame sealed coaxial capillary containing acetone-d$_6$ was added and the tube was closed and manually shaken until dissolution of solids. The tubes were heated at 50 ºC for 12h in an oil bath.
S5. $^{19}$F NMR monitoring of the reaction between compound 1 and C$_6$Cl$_2$F$_3$I

Monitoring of the reactions of compound 1 with C$_6$Cl$_2$F$_3$I

Weighted amounts of complex 1 were added inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d$_6$ to keep the lock signal. The tube was cooled to -75 °C in an isopropanol bath and a weighted amount of 4,4’difluorobiphenyl, THF and a weighted amount of C$_6$Cl$_2$F$_3$I were added. The tube was closed inside the adaptor and then, taken out of the cool bath, manually shaken until total dissolution of solids and transferred to the NMR probe, which had been preheated to the monitoring temperature (25 °C).

Table S2: Amounts of reagents used in the monitoring experiments of the reaction of compound 1 and C$_6$Cl$_2$F$_3$I

| Exp. | Compound 1  | C$_6$Cl$_2$F$_3$I | 4,4’-difluorobiphenyl | THF   |
|------|-------------|--------------------|-----------------------|-------|
| 1    | 15.34 mg    | 13.01 mg           | 0.88 mg               | 0.56 mL |
|      | 7.1·10$^{-2}$ M | 7.1·10$^{-2}$ M   | 1.3·10$^{-4}$ M       |       |
| 2    | 23.25 mg    | 13.08 mg           | 0.96 mg               | 0.56 mL |
|      | 1.07·10$^{-1}$ M | 7.1·10$^{-2}$ M   | 9.0·10$^{-3}$ M       |       |
| 3    | 5.15 mg     | 13.78 mg           | 0.96 mg               | 0.59 mL |
|      | 2.4·10$^{-2}$ M | 7.1·10$^{-2}$ M   | 8.6·10$^{-3}$ M       |       |

Recording started after about 2 min required for the setup of the experiment, time zero for the measurements is taken at that moment. $^{19}$F NMR spectra parameters are 64 scans, relaxation delay of 1 s, pulse angle of 30°, spectral width of 48076.9 Hz, and size of 32768 points. Spectra were collected every 300 s.

Values of concentration vs time were obtained by integration of $^{19}$F NMR signals relative to the internal standard, 4,4’difluorobiphenyl. These values had to be corrected to compensate the different relaxation times of nuclei in different substances by applying a correction factor. Correction factors were obtained by measuring the integral of $^{19}$F NMR experiments performed in the exact same conditions of the monitoring of samples containing mixtures of 4,4’difluorobiphenyl as internal standard and accurately weighted amounts of (NBu$_4$)[Cu(C$_6$F$_5$)$_2$], C$_6$Cl$_2$F$_3$I, C$_6$F$_5$I, C$_6$Cl$_2$F$_3$H, C$_6$F$_5$H, C$_6$Cl$_2$F$_3$C$_6$Cl$_2$F$_3$, C$_6$F$_5$C$_6$F$_5$, [Cu(bipy)(C$_6$F$_5$)$_3$] and [Cu(bipy)(C$_6$Cl$_2$F$_3$)]. The correction factor for the product C$_6$Cl$_2$F$_3$· C$_6$F$_5$ was estimated as the average of the homocoupling products.
S6. Control experiments

To test the capability of species \([\text{Cu}((\text{C}_6\text{F}_5)_2])^-\) to undergo oxidative addition reaction with aryl iodides, the reaction of compound \((\text{NBu}_4)[\text{Cu}((\text{C}_6\text{F}_5)_2)]\) \(2\) with PhI was monitored in the same conditions as in the reaction of compound \(1\) (See S4). After 6.7 h, coupling product \(\text{C}_6\text{F}_5\text{-Ph}\) was formed only in trace amounts >1%.

Also, the potential of species \([\text{Cu}((\text{bipy})\text{I})]\) and \([\text{Cu}((\text{bipy})_2]^{+}\) to undergo oxidative addition reaction with aryl iodides was evaluated by letting the complexes \([\text{Cu}((\text{bipy})\text{I})]\) and \([\text{Cu}((\text{bipy})_2]^{+}\text{BF}_4\) react with \(\text{C}_6\text{F}_5\text{I}\) in the same reaction conditions as in the monitoring experiments of the reaction between \(1\) and \(\text{C}_6\text{Cl}_2\text{F}_3\text{I}\) (See S5) for 4 h. No coupling products containing the moiety \(\text{C}_6\text{F}_5\) were detected.

To assess that the behavior of the system does not depend on the electronic properties of the complexes containing similar yet different aryl moieties, complex \([\text{Cu}((\text{bipy})(\text{C}_6\text{Cl}_2\text{F}_3))]\) \(4\) was synthesized and its reaction with \(\text{C}_6\text{F}_5\text{I}\) in THF at 25 °C was monitored by \(^{19}\text{F}\) NMR. Initial concentration of the reactants for this experiment differ from the used in the monitoring of the reaction of \(1\) and \(\text{C}_6\text{Cl}_2\text{F}_3\text{I}\) due to solubility problems (See S5). Again, the formation of the homocoupling product \(\text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{Cl}_2\text{F}_3\) containing the group that initially forms the organometallic reactant, shows a much higher rate of formation at the beginning of the reaction course than \(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5\).

![Graph](Figure S4: Concentration vs time plot of the formed species in the reaction of \(4\) (5.8·10^{-3} \text{ M}) with \(\text{C}_6\text{F}_5\text{I} (1.2\cdot10^{-2} \text{ M})\) in THF at 25 °C.

- 1; - \(\text{C}_6\text{Cl}_2\text{F}_3\text{I}\); - \(\text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{F}_5\); - \(\text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{Cl}_2\text{F}_3\); - \(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5\); - \(\text{C}_6\text{Cl}_2\text{F}_3\text{H}\); - \(\text{C}_6\text{F}_5\text{H}\). Data belonging to species \(4\) and \(\text{C}_6\text{F}_5\text{I}\) were omitted for clarity.)
**Experimental procedures for control experiments**

**Monitoring of the reaction of compound 4 with C₆F₅I**

Complex 4 (2.35 mg, 0.006 mmol) was added inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d₆ to keep the lock signal. The tube was cooled to -75 °C in an isopropanol bath and a weighted amount of 4,4’-difluorobiphenyl (0.45 mg, 0.002 mmol), THF (0.96 mL) and C₆F₅I (1.5 µL, 0.011 mmol) were added. The tube was closed inside the adaptor and then, taken out of the cool bath, manually shaken until total dissolution of solids and transferred to the NMR probe, which had been preheated to the monitoring temperature (25 °C). The ^{19}F NMR recording started after about 2 min used for the setup of the experiment, time zero for the measurements is taken at that moment.

**Monitoring of the reaction of Compound 2 with PhI**

Complex 2 (25.60 mg, 0.040 mmol) was added inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d₆ to keep the lock signal. The tube was cooled to -75 °C in an isopropanol bath and a weighted amount of 4,4’-difluorobiphenyl (2.50 mg, 0.013 mmol), THF (0.54 mL) and PhI (27 µL, 0.241 mmol) were added. The tube was closed inside the adaptor and then, taken out of the cool bath, manually shaken until total dissolution of solids and transferred to the NMR probe, which had been preheated to the monitoring temperature (50 °C). The ^{19}F NMR recording started after about 2 min used for the setup of the experiment. After 6.6 h the conversion of complex 2 in C₆F₅-Ph was lower than 2%.

**Reaction of [Cu(bipy)] and [Cu(bipy)]²BF₄ with C₆F₅I**

Compounds [Cu(bipy)] (50 mg, 0.142 mmol) or [Cu(bipy)]²BF₄ (65 mg, 0.142 mmol) were added inside a 5 mL Schlenk flask along with a magnetic stir bar. Three vacuum/N₂ cycles were performed, then, C₆F₅I (18.9 µL, 0.142 mmol) and THF (2.00 mL) were added under nitrogen countercurrent. The flask was closed under nitrogen pressure and the red suspension was stirred for 4 h at room temperature. After that, the suspension was decanted and an aliquot of 0.5 mL was transferred inside an NMR with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d₆ to keep the lock signal. The tube was closed inside the adaptor and transferred to the spectrometer to acquire a ^{19}F NMR spectrum.
S7. Kinetic data analysis

S7-1. Determination of the kinetic order of reaction of compound 1 in oxidative addition reactions with perhaloaryl iodides

Monitoring of the reactions of compound 1 with C$_6$F$_5$I

Weighted amounts of complex 1 were added inside a screw cap NMR tube with the aid of a Schlenk NMR tube adaptor along with a flame sealed coaxial capillary containing acetone-d$_6$ to keep the lock deuterium signal. The tube was cooled to -75 °C in an isopropanol bath and a weighted amount of 4,4'-difluorobiphenyl, THF and a volume of C$_6$F$_5$I taken with a microsyringe. The tube was closed inside the adaptor and then, taken out of the cool bath, manually shaken until total dissolution of solids and transferred to the NMR probe, which had been preheated to the monitoring temperature (25 °C).

Table S3: Amounts of reagents used in the monitoring experiments of the reaction of compound 1 and C$_6$F$_5$I

| Exp. | Compound 1 | C$_6$F$_5$I | 4,4'-difluorobiphenyl | THF |
|------|------------|-------------|----------------------|-----|
| 1    | 23.13 mg   | 39.9 µL     | 0.77 mg              | 0.84 mL |
|      | 7.1·10$^{-2}$ M | 3.6·10$^{-1}$ M | 4.8·10$^{-3}$ M |     |
| 2    | 27.44 mg   | 66.4 µL     | 1.42 mg              | 1.40 mL |
|      | 5.1·10$^{-2}$ M | 3.6·10$^{-1}$ M | 5.3·10$^{-3}$ M |     |
| 3    | 12.88 mg   | 61.7 µL     | 1.23 mg              | 1.30 mL |
|      | 2.5·10$^{-2}$ M | 3.6·10$^{-1}$ M | 5.0·10$^{-3}$ M |     |
| 4    | 6.60 mg    | 47.8 µL     | 2.25 mg              | 1.01 mL |
|      | 1.7·10$^{-2}$ M | 3.6·10$^{-1}$ M | 1.2·10$^{-2}$ M |     |
| 5    | 6.60 mg    | 70.3 µL     | 0.95 mg              | 1.34 mL |
|      | 1.3·10$^{-2}$ M | 3.6·10$^{-1}$ M | 3.7·10$^{-3}$ M |     |

Recording started after about 2 min used for the setup of the experiment, time zero for the measurements is taken at that moment. $^{19}$F NMR spectra parameters are 64 scans, relaxation delay of 1 s, pulse angle of 30°, spectral width of 48076 Hz, and size of 32768 points. Spectra were collected every 300 s.

Order of reaction for compound 1 in the reaction of 1 and C$_6$F$_5$I was determined by initial rates method, measuring the linear rates for the formation of C$_6$F$_5$-C$_6$F$_5$ up to 33% of total conversion.
| Exp. | $[1]_0 / \text{M}$ | $[\text{C}_6\text{F}_5\text{I}]_0 / \text{M}$ | $r_0 / \text{s} \cdot \text{M}^{-1}$ |
|------|-----------------|-----------------|-----------------|
| 1    | $7.1 \cdot 10^{-2}$ | $3.6 \cdot 10^{-1}$ | $4.5 \cdot 10^{-5}$ |
| 2    | $5.1 \cdot 10^{-2}$ | $3.6 \cdot 10^{-1}$ | $3.5 \cdot 10^{-5}$ |
| 3    | $2.6 \cdot 10^{-2}$ | $3.6 \cdot 10^{-1}$ | $2.0 \cdot 10^{-5}$ |
| 4    | $1.7 \cdot 10^{-2}$ | $3.6 \cdot 10^{-1}$ | $9.6 \cdot 10^{-5}$ |
| 5    | $1.3 \cdot 10^{-2}$ | $3.6 \cdot 10^{-1}$ | $8.1 \cdot 10^{-5}$ |

**Figure S5:** Experimental values of initial reaction rates and initial concentrations of compound 1 and plot of $\text{Ln}(r_0)$ versus $\text{Ln}(C_0)$. The slope of the straight line is the kinetic order of the reaction on complex 1.
Complex 1 reacts with $C_6Cl_2F_3I$ in THF at 25 °C producing the cross-coupling product $C_6Cl_2F_3C_6F_5$, the homocoupling biaryls $C_6F_5C_6F_5$ and $C_6Cl_2F_3C_6Cl_2F_3$ and residual amounts of the hydrolysis products $C_6F_5H$ and $C_6Cl_2F_3H$ (Scheme S3).

\[
[Cu(bipy)]PF + RF \rightarrow [Cu(bipy)(RF)] + Pf \quad \text{exchange}
\]
\[
RF-RF + [Cu(bipy)]I + Pf-Pf + RF-Pf \quad \text{coupling}
\]
\[
PfH + RFH \quad \text{protonolysis}
\]

\[Pf = C_6F_5\]
\[RF = C_6Cl_2F_3\]

**Scheme S3**: Detected products in the reaction of 1 and $C_6Cl_2F_3I$ in THF at 25 °C.

We have hypothesized two possible routes for the formation of the homocoupling products, in both of them the equilibrium of formation of the cuprate and the hydrolysis reactions have been taken into account. The model I includes consecutive oxidative-addition / reductive elimination equilibria leading to the aryl exchange process (Scheme S4). In this mechanism the formation of $C_6F_5I$ and the complex $[Cu(bipy)](C_6Cl_2F_3)$ (4) are merely the consequence of the reversibility of the oxidative addition step. The accumulation in solution of $C_6F_5I$ enables the formation of the homocoupling product $C_6F_5C_6F_5$ by reacting with the abundant complex 1 and the accumulation of $[Cu(bipy)](C_6Cl_2F_3)$ (4) accounts for the formation of the homocoupling product $C_6Cl_2F_3C_6Cl_2F_3$ by reacting with the aryl halide $C_6Cl_2F_3I$ which is used in large excess.
The second mechanism (model II) assumes as possible transmetalation reactions involving copper(I) and copper(II) complexes. Scheme S5 shows two possible pathways for the formation of \( \text{C}_6\text{F}_5\text{-C}_6\text{F}_5 \). In pathway “a” the transmetalation produces the exchange of aryls between Cu(I) and Cu(III) producing the observed Cu(I) complex 4 and [Cu(bipy)(C\(_6\text{F}_5\))\(_2\)] (7), from which \( \text{C}_6\text{F}_5\text{-C}_6\text{F}_5 \) would be formed. Pathway “b” proposes the transmetalation of the aryl by the iodine atom, forming the triarylic intermediate [Cu(bipy)(C\(_6\text{Cl}_2\text{F}_3\))\(_2\)] (8) and [Cu(bipy)]I (6). From 8 the homocoupling or the cross-coupling product could be formed. For simplicity Scheme S5 does not show the pathways for the formation of \( \text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{Cl}_2\text{F}_3 \), but, since the concentration of 5 is small, it requires a double oxidative addition process. For this study we have assumed that the polifluorated groups (C\(_6\text{Cl}_2\text{F}_3\)) and (C\(_6\text{F}_5\)) behave as electronically equivalent groups, in agreement with the control experiment described above (See S6).\(^{13}\)
**Scheme S5:** Diagram of some of the reactions considered for model II explaining the formation of C₆F₅-C₆F₅

Figure 1 in the main text shows the experimental concentration time plot of the formation of C₆Cl₂F₃-C₆Cl₂F₃ and C₆F₅-C₆F₅ and the best fitting for both models. In both models the fitting of the formation of C₆Cl₂F₃-C₆Cl₂F₃ is quite good although model II fits better at long reaction times. That is the expected result because in both models C₆Cl₂F₃-C₆Cl₂F₃ requires the accumulation of 4 to take place. However, the models and the fitting differ substantially about the formation of C₆F₅-C₆F₅ (in blue in figure 1 main text). In this case the experimental results do not support the requirement of the accumulation of C₆F₅I which is implicit on model I. On the contrary, the experimental line and the fitting indicates that C₆F₅-C₆F₅ is formed independently of [C₆F₅I], and at high rate since the beginning of the reaction.

The kinetic models were fit to the final concentration / time data by non-linear least squares (NLLS) using the software COPASI.¹⁰
**Used models in the non-linear fit with program COPASI**

In all the models rate constants $k_{\text{ion}}$ and $k_{\text{neutro}}$ were forced to be related based on the measured value of $K_{\text{ion}}$.

\[
K_{\text{ion}} = \frac{k_{\text{ion}}}{k_{\text{neutro}}} = 8.73 \cdot 10^{-4} \quad ; \quad k_{\text{ion}} = 8.73 \cdot 10^{-4} \cdot k_{\text{neutro}}
\]

Also, values for the initial $\text{H}_2\text{O}$ concentration and hydrolysis kinetic constants $k_1$ and $k_2$ were fitted by the program without restrictions.

**Table S4**: Model I containing ionic disproportionation equilibrium, an aryl methatesis mechanism, aryl coupling reactions and hydrolysis reactions.

| Reaction |
|-------------------|
| $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] + \text{C}_6\text{Cl}_2\text{F}_3\text{I} \xrightarrow{k_{\text{met}}} \text{[Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] \rightarrow \text{C}_6\text{F}_5\text{I}$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] + [\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] \xrightarrow{k_{\text{ion}}} \text{[Cu(C}_6\text{Cl}_2\text{F}_3)(\text{C}_6\text{F}_5)]^+ + [\text{Cu(bipy)}]_2^+$ |
| 2 $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] \xrightarrow{k_{\text{ion}}} \text{[Cu(C}_6\text{Cl}_2\text{F}_3]_2^+ + [\text{Cu(bipy)}]_2^+$ |
| 2 $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] \xrightarrow{k_{\text{ion}}} \text{[Cu(C}_6\text{F}_5]_2^+ + [\text{Cu(bipy)}]_2^+$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] + \text{C}_6\text{Cl}_2\text{F}_3\text{I} \xrightarrow{k_{\text{coup1}}} [\text{Cu(bipy)}]_2^+ + \text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{F}_5$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] + \text{C}_6\text{F}_5\text{I} \xrightarrow{k_{\text{coup2}}} [\text{Cu(bipy)}]_2^+ + \text{C}_6\text{F}_5\text{-C}_6\text{F}_5$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] + \text{C}_6\text{Cl}_2\text{F}_3\text{I} \xrightarrow{k_{\text{coup3}}} [\text{Cu(bipy)}]_2^+ + \text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{Cl}_2\text{F}_3$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] + \text{C}_6\text{F}_5\text{I} \xrightarrow{k_{\text{coup4}}} [\text{Cu(bipy)}]_2^+ + \text{C}_6\text{Cl}_2\text{F}_3\text{-C}_6\text{F}_5$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)] + \text{H}_2\text{O} \xrightarrow{k_2} [\text{Cu(bipy)}\text{OH}] + \text{C}_6\text{Cl}_2\text{F}_3\text{H}$ |
| $[\text{Cu(bipy)}(\text{C}_6\text{F}_5)] + \text{H}_2\text{O} \xrightarrow{k_1} [\text{Cu(bipy)}\text{OH}] + \text{C}_6\text{F}_5\text{H}$ |

No restrictions were applied to the kinetic constants for the coupling reactions (Table S4 $k_{\text{coup 1-4}}$) involving $\text{C}_6\text{F}_5$ or $\text{C}_6\text{Cl}_2\text{F}_3$ groups in order to get the best fitting. When restrictions due to the similar behavior of $\text{C}_6\text{F}_5$ and $\text{C}_6\text{Cl}_2\text{F}_3$ groups were imposed ($k_{\text{met}} = k_{\text{met-1}}$; $k_{\text{coup1}} = k_{\text{coup2}} = k_{\text{coup3}} = k_{\text{coup4}}$ ) no fitting minimum could be reached.
Table S5: Model II pathway (a). Best fit reaction model containing ionic disproportionation equilibrium, reversible oxidative addition reactions leading to Cu(III) intermediates, a Cu(I)/Cu(III) transmetalation mechanism, biaryl reductive elimination reactions and hydrolysis reactions.

Reaction

\[
\begin{align*}
[Cu(bpy)](C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bpy)](C_6F_5)_2] \quad \xrightarrow{k_{trans}} \quad [Cu(bpy)](C_6F_5)_2] + [Cu(bpy)](C_6Cl_2F_3)] \\
[Cu(bpy)](C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bpy)](C_6Cl_2F_3)] \quad \xrightarrow{k_{trans}} \quad [Cu(bpy)](C_6Cl_2F_3)_2] + [Cu(bpy)](C_6F_5)] \\
[Cu(bpy)](C_6Cl_2F_3)] & \quad + \quad C_6F_5] \quad \xrightarrow{k_{ad-ox}} \quad [Cu(bpy)](C_6Cl_2F_3)(C_6F_5)] \\
[Cu(bpy)](C_6F_5)] & \quad + \quad C_6Cl_2F_3] \quad \xrightarrow{k_{ad-ox}} \quad [Cu(bpy)](C_6Cl_2F_3)(C_6F_5)] \\
[Cu(bpy)](C_6Cl_2F_3)] & \quad + \quad C_6Cl_2F_3] \quad \xrightarrow{k_{ad-ox}} \quad [Cu(bpy)](C_6Cl_2F_3)_2] \\
[Cu(bpy)](C_6F_5)] & \quad + \quad C_6F_5] \quad \xrightarrow{k_{ad-ox}} \quad [Cu(bpy)](C_6F_5)_2] \\
[Cu(bpy)](C_6F_5)] & \quad + \quad [Cu(bpy)](C_6Cl_2F_3)] \quad \xrightarrow{k_{non}} \quad \frac{k_{non}}{k_{neu}} [Cu(C_6Cl_2F_3)(C_6F_5)] + [Cu(bpy)]_2]^* \\
2 \quad [Cu(bpy)](C_6Cl_2F_3)] & \quad \xrightarrow{k_{non}} \quad [Cu(C_6Cl_2F_3)_2]^* + [Cu(bpy)]_2]^* \\
2 \quad [Cu(bpy)](C_6F_5)] & \quad \xrightarrow{k_{non}} \quad [Cu(C_6F_5)_2]^* + [Cu(bpy)]_2]^* \\
[Cu(bpy)](C_6Cl_2F_3)(C_6F_5)] \quad k_{atm} \quad [Cu(bpy)]] + C_6Cl_2F_3-C_6F_5 \\
[Cu(bpy)](C_6F_5)_2] \quad k_{el} \quad [Cu(bpy)]] + C_6F_5-C_6F_5 \\
[Cu(bpy)](C_6Cl_2F_3)_2)] \quad k_{atm} \quad [Cu(bpy)]] + C_6Cl_2F_3-C_6Cl_2F_3 \\
[Cu(bpy)](C_6Cl_2F_3)] + H_2O \quad k_2 \quad [Cu(bpy)OH] + C_6Cl_2F_3H \\
[Cu(bpy)](C_6F_5)] + H_2O \quad k_1 \quad [Cu(bpy)OH] + C_6F_5H
\end{align*}
\]
Table S6: Model II pathway (b). Alternative reaction model proposed containing ionic disproportionation equilibrium, reversible oxidative addition reactions leading to Cu(III) halogenated intermediates, a Cu(I)/Cu(III) transmetalation mechanism leading to triaryllic Cu(III) species, biaryl reductive elimination reactions and hydrolysis reactions.

Reaction

\[
\begin{align*}
[Cu(bipy)(C_6Cl_2F_3)(C_6F_5)] & \quad + \quad [Cu(bipy)(C_6Cl_2F_3)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)_2(C_6F_5)] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6Cl_2F_3)(C_6F_5)] & \quad + \quad [Cu(bipy)(C_6F_5)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6Cl_2F_3)_2] & \quad + \quad [Cu(bipy)(C_6Cl_2F_3)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6Cl_2F_3)_2] & \quad + \quad [Cu(bipy)(C_6F_5)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6F_5)_2] & \quad + \quad [Cu(bipy)(C_6Cl_2F_3)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6F_5)_2] & \quad + \quad [Cu(bipy)(C_6F_5)] \quad \xrightleftharpoons[k_{trans}]{k_{retro}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] & \quad + \quad [Cu(bipy)] \\
[Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad C_6F_5 \quad \xrightleftharpoons[k_{k,2}]{k_{ad,ox}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)] \\
[Cu(bipy)(C_6F_5)] & \quad + \quad C_6Cl_2F_3 \quad \xrightleftharpoons[k_{k,2}]{k_{ad,ox}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)] \\
[Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad C_6Cl_2F_3 \quad \xrightleftharpoons[k_{k,2}]{k_{ad,ox}} \quad [Cu(bipy)(C_6Cl_2F_3)_2] \\
[Cu(bipy)(C_6F_5)] & \quad + \quad C_6F_5 \quad \xrightleftharpoons[k_{k,2}]{k_{ad,ox}} \quad [Cu(bipy)(C_6F_5)_2] \\
[Cu(bipy)(C_6F_5)] & \quad + \quad [Cu(bipy)(C_6Cl_2F_3)] \quad \xrightleftharpoons[k_{k,2}]{k_{ad,ox}} \quad [Cu(bipy)(C_6Cl_2F_3)(C_6F_5)] & \quad + \quad [Cu(bipy)] \\
2 \quad [Cu(bipy)(C_6Cl_2F_3)] \quad \xrightleftharpoons[k_{k,2}]{k_{retro}} \quad [Cu(C_6Cl_2F_3)_2]^+ & \quad + \quad [Cu(bipy)]^+ \\
2 \quad [Cu(bipy)(C_6F_5)] \quad \xrightleftharpoons[k_{k,2}]{k_{retro}} \quad [Cu(C_6F_5)_2]^+ & \quad + \quad [Cu(bipy)]^+ \\
[Cu(bipy)(C_6Cl_2F_3)_2(C_6F_5)] \quad k_{lim} \quad [Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad C_6Cl_2F_3-C_6F_5 \\
[Cu(bipy)(C_6Cl_2F_3)_2(C_6F_5)] \quad 2k_{lim} \quad [Cu(bipy)(C_6F_5)] & \quad + \quad C_6Cl_2F_3-C_6Cl_2F_3 \\
[Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] \quad k_{lim} \quad [Cu(bipy)(C_6F_5)] & \quad + \quad C_6Cl_2F_3-C_6F_5 \\
[Cu(bipy)(C_6Cl_2F_3)(C_6F_5)_2] \quad 2k_{lim} \quad [Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad C_6F_5-C_6F_5 \\
[Cu(bipy)(C_6Cl_2F_3)_3] \quad 3k_{lim} \quad [Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad C_6Cl_2F_3-C_6Cl_2F_3 \\
[Cu(bipy)(C_6F_5)_3] \quad 3k_{lim} \quad [Cu(bipy)(C_6F_5)] & \quad + \quad C_6F_5-C_6F_5 \\
[Cu(bipy)(C_6Cl_2F_3)] & \quad + \quad H_2O \quad k_2 \quad [Cu(bipy)OH] & \quad + \quad C_6Cl_2F_3^+ \\
[Cu(bipy)(C_6F_5)] & \quad + \quad H_2O \quad k_1 \quad [Cu(bipy)OH] & \quad + \quad C_6F_5^+ 
\end{align*}
\]
For the non-linear fitting using both pathways of model II, different complexes bearing groups (C₆F₅) and (C₆Cl₂F₃) were considered similar in terms of reactivity,¹³ and therefore, reactions involving them are computed with the same kinetic constants:

- $k_{\text{elim}}$ for the reductive elimination irreversible reactions from Cu(III) species.
- $k_{\text{ad-ox}}$ and $k_{\text{x-I}}$ for the oxidative addition equilibria between aryl iodides and Cu(I) arylated complexes.
- $k_{\text{trans}}$ and $k_{\text{retro}}$ for the transmetalation equilibria between Cu(I) and Cu(III) complexes.

For model II Pathway b, in the reductive elimination reactions, constant $k_{\text{elim}}$ is multiplied for a number representing the statistical probability for that reductive elimination to take place from the starting Cu(III) complex.

Even applying these restrictions, the fitting of model II pathway a is more appropriate than that obtained using model I (see below graphics of the models).
Data fitting using model I

- Exp. 1. Compound 1 / C₆Cl₂F₃I  1 : 1

| Value / s⁻¹; M⁻¹·s⁻¹ | kₘₑᵗ | kₘₑᵗ⁻¹ | kₙₑₜ | kₙₑₜ | kₙₑₜ | kₙₑₜ |
|----------------------|------|--------|-------|-------|-------|-------|
| 1.1·10⁻³            | 0    | 1.9·10⁻³ | 9.7·10⁻⁴ | 2.2·10⁻³ | 0     |
| Std. deviation       | 2.4·10⁻⁵ | 5.0·10⁻³ | 8.6·10⁻⁵ | 2.1·10⁻⁴ | 4.0·10⁻⁴ | 4.8·10⁻³ |

Figure S6: Experimental (dots) and least square fit using model I (continuous line) concentration vs time plot of the formed species in the reaction of 1 (7.1·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products.

• 1; • C₆Cl₂F₃I; • C₆Cl₂F₃-C₆F₅; • C₆Cl₂F₃-C₆Cl₂F₃; • C₆F₅-C₆F₅; • 4; • C₆F₅I; • C₆Cl₂F₃H; • C₆F₃H.
- Exp. 2. Compound 1 / C₆Cl₂F₃I  1.5 : 1

![Figure S7](imageurl)

Table: Value of reaction rate constants for the reaction of 1 (1.07·10⁻¹ M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 ºC.

| Value / s⁻¹, M⁻¹·s⁻¹ | kₙₑᵣₙ | kₙₑᵣₙ₋₁ | kₙₑᵣₙ₋₂ | kₙₑᵣₙ₋₃ | kₙₑᵣₙ₋₄ |
|----------------------|--------|--------|--------|--------|--------|
|                      | 1.3·10⁻³ | 4.6·10⁻⁸ | 1.9·10⁻³ | 5.2·10⁻³ | 2.4·10⁻³ | 2.3·10⁻⁷ |
| Std. deviation        | 1.6·10⁻⁵ | 1.0·10⁻³ | 4.6·10⁻⁵ | 6.3·10⁻⁵ | 3.1·10⁻⁵ | 9.5·10⁻⁴ |

**Figure S7:** Experimental (dots) and least square fit using model I (continuous line) concentration vs time plot of the formed species in the reaction of 1 (1.07·10⁻¹ M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 ºC. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products.

• 1; • C₆Cl₂F₃I; • C₆Cl₂F₃-C₆F₅; • C₆Cl₂F₃-C₆Cl₂F₃; • C₆F₅-C₆F₅; • 4; • C₆F₅I; • C₆Cl₂F₃H; • C₆F₅H.
- Compound 1 / C₆Cl₂F₃I 0.33 : 1

Figure S8: Experimental (dots) and least square fit using model I (continuous line) concentration vs time plot of the formed species in the reaction of 1 (2.4·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products.

| Value / s⁻¹·M⁻¹·s⁻¹ | kₘₑₜ | kₘₑₜ⁻¹ | kₖₑₜ¹ | kₖₑₜ² | kₖₑₜ³ | kₖₑₜ⁴ |
|----------------------|-------|---------|--------|--------|--------|--------|
|                      | 8.0·10⁻⁴ | 4.5·10⁻⁵ | 2.1·10⁻³ | 5.5·10⁻² | 2.5·10⁻³ | 0      |
| Std. deviation       | 1.5·10⁻⁵ | 2.0·10⁻² | 7.6·10⁻⁵ | 1.5·10⁻³ | 4.6·10⁻⁵ | 2.2·10⁻² |

Inconsistencies of the model I:
The best fitting leads to rate constants values that are very different for analogous reactions with C₆F₅ and C₆Cl₂F₃, contrarily to the experimental observations.¹³ Note also the very poor fitting of the points due to [C₆F₅-C₆F₃] in all the graphics.
**Best data fitting using model II pathway a**

- Exp. 1. Compound 1 / C₆Cl₂F₃I 1 : 1

![Graphs showing concentration vs time plots](image)

|   | k_{trans} | k_{retro} | k_{ad-ox} | k_{e-i} | k_{elim} |
|---|-----------|-----------|-----------|---------|----------|
| Value / s⁻¹; M⁻¹s⁻¹ | 1.7       | 3.6       | 3.4·10⁻³  | 4.3·10⁻² | 1.7·10⁻¹ |
| Std. deviation | 6.0       | 1.2·10⁻²  | 2.5·10⁻⁵  | 3.0·10⁻¹ | 6.0·10⁻¹ |

**Figure S9:** Experimental (dots) and least square fit using model II pathway a (continuous line) concentration vs time plot of the formed species in the reaction of 1 (7.1·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 ºC. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. • 1; • C₆Cl₂F₃I; • C₆Cl₂F₃-C₆F₅; • C₆Cl₂F₃-C₆Cl₂F₃; • C₆F₅-C₆F₅; • 4; • C₆F₅I; • C₆Cl₂F₃H; • C₆F₅H.
Exp. 2. Compound 1 / C₆Cl₂F₃I 1.5 : 1

Figure S10: Experimental (dots) and least square fit using model II pathway a (continuous line) concentration vs time plot of the formed species in the reaction of 1 (1.07·10⁻¹ M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 ºC. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. • 1; • C₆Cl₂F₃I; • C₆Cl₂F₃-C₆F₅; • C₆Cl₂F₃-C₆Cl₂F₅; • C₆F₅-C₆F₅; • 4; • C₆F₅I; • C₆Cl₂F₃H; • C₆F₅H.
- Compound 1 / C₆Cl₂F₃I 0.33 : 1

![Graph showing concentration vs time plot of the formed species in the reaction of 1 (2.4·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. •1; •C₆Cl₂F₃I; •C₆Cl₂F₃-C₆F₃; •C₆Cl₂F₃-C₆Cl₂F₃; •C₆F₅-C₆F₃; •4; •C₆F₅I; •C₆Cl₂F₃H; •C₆F₅H.]

| Value / s⁻¹; M⁻¹.s⁻¹ | k_{trans} | k_{retro} | k_{ad-ox} | k_{k,i} | k_{elim} |
|----------------------|-----------|-----------|-----------|---------|----------|
|                      | 1.2       | 2.1       | 2.9·10⁻³  | 3.2·10⁻³| 4.4·10⁻² |
| Std. deviation        | 1.7       | 1.2       | 2.8·10⁻⁵  | 1.3     | 6.3·10⁻² |

**Figure S11:** Experimental (dots) and least square fit using model II pathway a (continuous line) concentration vs time plot of the formed species in the reaction of 1 (2.4·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. •1; •C₆Cl₂F₃I; •C₆Cl₂F₃-C₆F₃; •C₆Cl₂F₃-C₆Cl₂F₃; •C₆F₅-C₆F₃; •4; •C₆F₅I; •C₆Cl₂F₃H; •C₆F₅H.
Data fitting using model II pathway b

- Exp. 1. Compound 1 / C₆Cl₂F₃I  1 : 1

Figure S12: Experimental (dots) and least square fit using model II pathway b (continuous line) concentration vs time plot of the formed species in the reaction of 1 (7.1·10⁻² M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. •1; •C₆Cl₂F₃I; •C₆Cl₂F₃-C₆F₅; •C₆Cl₂F₃-C₆Cl₂F₃; •C₆F₅-C₆F₅; •4; •C₆F₃I; •C₆Cl₂F₃H; •C₆F₃H.

| Value / s⁻¹; M⁻¹·s⁻¹ | k_{trans} | k_{retro} | k_{ad-ox} | k_{x-i} | k_{elim} |
|----------------------|-----------|-----------|-----------|---------|----------|
| 4.7·10⁻¹             | 4.2·10⁻⁶  | 3.7·10⁻³  | 5.9·10⁻³  | 1.4·10¹⁵|          |
Exp. 2. Compound **1** / C₆Cl₂F₃I 1.5 : 1

**Figure S13:** Experimental (dots) and least square fit using model II pathway b (continuous line) concentration vs time plot of the formed species in the reaction of **1** (1.07·10⁻¹ M) with C₆Cl₂F₃I (7.1·10⁻² M) in THF at 25 °C. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products. • **1**; • C₆Cl₂F₃I; • C₆Cl₂F₃-C₆F₅; • C₆Cl₂F₃-C₆Cl₂F₅; • C₆F₅-C₆F₅; •C₆F₅I; • C₆Cl₂F₃H; • C₆F₃H.

| Value / s⁻¹; M⁻¹·s⁻¹ | kₜrans | kₜretro | kₐd-ox | kₐ-i | kₐ elim |
|-----------------------|--------|---------|--------|------|--------|
| 3.4·10⁻⁴              | 2.0·10⁻⁹ | 3.4·10⁻³ | 1.4·10⁻¹⁵ | 2.8·10⁴ |
**Compound 1 / C₆Cl₂F₃I 0.33 : 1**

**Figure S14:** Experimental (dots) and least square fit using model II pathway b (continuous line) concentration vs time plot of the formed species in the reaction of 1 (2.4 · 10⁻² M) with C₆Cl₂F₃I (7.1 · 10⁻² M) in THF at 25 ºC. Both graphics represent the same experiment, in the lower one, the concentration vs time lines of the reagents have been omitted to show more clearly the fitting of the products.

- • 1;
- • C₆Cl₂F₃I;
- • C₆Cl₂F₃-C₆F₅;
- • C₆Cl₂F₃-C₆Cl₂F₅;
- • C₆F₅-C₆F₅;
- • 4;
- • C₆F₅I; • C₆Cl₂F₃H; • C₆F₃H.

**Inconsistencies of the model II pathway b:**
Using this model, the correlation matrix could not be calculated. Also note that kinetic constant values between different experiments differ significatively.
S8. NMR spectra

**Spectrum S1:** $^1$H NMR of (NBu$_4$)[Cu(C$_6$F$_5$)$_2$].

**Spectrum S2:** $^{19}$F NMR of (NBu$_4$)[Cu(C$_6$F$_5$)$_2$].
Spectrum S3: $^{13}\text{C} \{^1\text{H}\}$ NMR of (NBu$_4$)[Cu(C$_6$F$_5$)$_2$].

Spectrum S4: $^1\text{H}$ NMR of (NBu$_4$)[CuCl$_2$].
Spectrum S5: $^{13}$C($^1$H) NMR of (NBu$_4$)[CuCl$_2$].

Spectrum S6: $^1$H NMR of [Cu(bipy)(C$_6$Cl$_2$F$_3$)].
Spectrum S7: $^{19}$F NMR of $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)]$.

Spectrum S8: $^{13}$C {$^1$H} NMR of $[\text{Cu(bipy)}(\text{C}_6\text{Cl}_2\text{F}_3)]$. 
S9. Concentration/time data from fitted kinetic experiments

Reactions of compound 1 and aryl iodide C₆Cl₂F₃I

- Compound 1 / C₆Cl₂F₃I  1 : 1

Table S7: Concentration vs time data fed to program COPASI to obtain kinetic parameters of the reaction of 1 (7.1·10⁻²M) with C₆Cl₂F₃I (7.1·10⁻²M) in THF at 25 °C.

| Time / s | [4] / 10⁻² M | [1] / 10⁻² M | [C₆Cl₂F₃-] / 10⁻² M | [C₆Cl₂F₃-] / 10⁻² M | [C₆Cl₂F₃-] / 10⁻² M | [C₆Cl₂F₃-] / 10⁻² M | [C₆Cl₂F₃I] / 10⁻² M | [C₆Cl₂F₃I] / 10⁻² M | [C₆Cl₂F₃I] / 10⁻² M |
|----------|--------------|--------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 0        | 0.130        | 6.674        | 0.200                | 0.098                | 0.027                | 7.006                | 0.049                | 0.031                | 0.016                |
| 300      | 0.273        | 6.170        | 0.407                | 0.195                | 0.028                | 6.562                | 0.110                | 0.040                | 0.034                |
| 600      | 0.441        | 5.784        | 0.619                | 0.306                | 0.042                | 6.275                | 0.173                | 0.049                | 0.050                |
| 900      | 0.546        | 5.208        | 0.777                | 0.388                | 0.057                | 5.819                | 0.223                | 0.059                | 0.071                |
| 1200     | 0.629        | 4.787        | 0.940                | 0.464                | 0.076                | 5.520                | 0.265                | 0.074                | 0.087                |
| 1500     | 0.695        | 4.465        | 1.089                | 0.528                | 0.102                | 5.294                | 0.306                | 0.087                | 0.102                |
| 1800     | 0.734        | 4.163        | 1.215                | 0.579                | 0.123                | 5.044                | 0.333                | 0.100                | 0.118                |
| 2100     | 0.767        | 3.913        | 1.345                | 0.622                | 0.146                | 4.846                | 0.360                | 0.115                | 0.138                |
| 2400     | 0.785        | 3.659        | 1.453                | 0.656                | 0.169                | 4.627                | 0.381                | 0.132                | 0.156                |
| 2700     | 0.806        | 3.480        | 1.574                | 0.685                | 0.194                | 4.475                | 0.400                | 0.150                | 0.174                |
| 3000     | 0.813        | 3.289        | 1.654                | 0.721                | 0.216                | 4.313                | 0.417                | 0.164                | 0.193                |
| 3300     | 0.831        | 3.132        | 1.747                | 0.759                | 0.239                | 4.196                | 0.431                | 0.176                | 0.203                |
| 3600     | 0.816        | 2.936        | 1.822                | 0.773                | 0.258                | 4.010                | 0.439                | 0.190                | 0.219                |
| 3900     | 0.826        | 2.805        | 1.898                | 0.797                | 0.280                | 3.899                | 0.450                | 0.207                | 0.238                |
| 4200     | 0.818        | 2.685        | 1.979                | 0.818                | 0.305                | 3.793                | 0.462                | 0.219                | 0.258                |
| 4500     | 0.808        | 2.536        | 2.033                | 0.828                | 0.323                | 3.643                | 0.462                | 0.236                | 0.272                |
| 4800     | 0.801        | 2.440        | 2.102                | 0.841                | 0.343                | 3.549                | 0.469                | 0.256                | 0.294                |
| 5100     | 0.779        | 2.294        | 2.137                | 0.840                | 0.356                | 3.407                | 0.469                | 0.269                | 0.308                |
| 5400     | 0.784        | 2.247        | 2.224                | 0.877                | 0.383                | 3.379                | 0.482                | 0.282                | 0.323                |
| 5700     | 0.762        | 2.113        | 2.248                | 0.888                | 0.395                | 3.265                | 0.482                | 0.292                | 0.335                |
| 6000     | 0.759        | 2.045        | 2.297                | 0.900                | 0.412                | 3.188                | 0.483                | 0.307                | 0.355                |
| 6300     | 0.738        | 1.947        | 2.339                | 0.913                | 0.428                | 3.107                | 0.487                | 0.320                | 0.369                |
| 6600     | 0.726        | 1.892        | 2.404                | 0.923                | 0.449                | 3.058                | 0.491                | 0.342                | 0.389                |
| 6900     | 0.718        | 1.793        | 2.408                | 0.927                | 0.457                | 2.953                | 0.483                | 0.346                | 0.398                |
| 7200     | 0.709        | 1.737        | 2.450                | 0.939                | 0.471                | 2.900                | 0.487                | 0.362                | 0.415                |
| 7500     | 0.700        | 1.696        | 2.521                | 0.962                | 0.494                | 2.876                | 0.498                | 0.383                | 0.434                |
| 7800     | 0.687        | 1.604        | 2.518                | 0.950                | 0.500                | 2.769                | 0.488                | 0.394                | 0.447                |
| 8100     | 0.661        | 1.542        | 2.535                | 0.958                | 0.511                | 2.696                | 0.484                | 0.402                | 0.457                |
| 8400     | 0.657        | 1.491        | 2.609                | 0.975                | 0.529                | 2.684                | 0.488                | 0.417                | 0.474                |
| 8700     | 0.645        | 1.436        | 2.611                | 0.970                | 0.537                | 2.614                | 0.490                | 0.431                | 0.482                |
### Compound 1 / C₆Cl₂F₃I  1.5 : 1

**Table S8:** Concentration vs time data fed to program COPASI to obtain kinetic parameters of the reaction of 1 (1.07 \( \times \) 10⁻¹M) with C₆Cl₂F₃I (7.1 \( \times \) 10⁻²M) in THF at 25 °C.

| Time / s | [4] / 10⁻² | [1] / 10⁻² | [Cl₆Cl₂F₃] / 10⁻² M | [Cl₆Cl₂F₃] / 10⁻² M | [Cl₆Cl₂F₃] / 10⁻² M | [Cl₆Cl₂F₃] / 10⁻² M | [Cl₆Cl₂F₃] / 10⁻² M |
|----------|-------------|-------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 0        | 0.132       | 9.935       | 0.140                | 0.122                | 0.021                | 5.987                | 0.070                |
| 300      | 0.380       | 9.471       | 0.403                | 0.255                | 0.023                | 5.513                | 0.185                |
| 600      | 0.611       | 8.894       | 0.647                | 0.392                | 0.034                | 5.030                | 0.289                |
| 900      | 0.813       | 8.306       | 0.862                | 0.519                | 0.054                | 4.590                | 0.373                |
| 1200     | 0.956       | 7.746       | 1.059                | 0.630                | 0.076                | 4.207                | 0.437                |
| 1500     | 1.050       | 7.330       | 1.233                | 0.722                | 0.100                | 3.877                | 0.486                |
| 1800     | 1.150       | 6.944       | 1.387                | 0.799                | 0.126                | 3.593                | 0.522                |
| 2100     | 1.209       | 6.620       | 1.527                | 0.864                | 0.152                | 3.351                | 0.552                |
| 2400     | 1.247       | 6.331       | 1.658                | 0.926                | 0.174                | 3.141                | 0.574                |
| 2700     | 1.296       | 6.070       | 1.785                | 0.990                | 0.200                | 2.921                | 0.589                |
| 3000     | 1.329       | 5.831       | 1.893                | 1.038                | 0.222                | 2.746                | 0.598                |
| 3300     | 1.347       | 5.572       | 1.975                | 1.077                | 0.243                | 2.565                | 0.603                |
| 3600     | 1.353       | 5.382       | 2.075                | 1.115                | 0.265                | 2.434                | 0.609                |
| 3900     | 1.363       | 5.170       | 2.145                | 1.150                | 0.283                | 2.292                | 0.608                |
| 4200     | 1.363       | 4.978       | 2.215                | 1.195                | 0.302                | 2.164                | 0.610                |
| 4500     | 1.355       | 4.787       | 2.243                | 1.229                | 0.320                | 2.041                | 0.609                |
| 4800     | 1.349       | 4.626       | 2.313                | 1.261                | 0.337                | 1.922                | 0.604                |
| 5100     | 1.357       | 4.528       | 2.401                | 1.303                | 0.357                | 1.848                | 0.608                |
| 5400     | 1.347       | 4.400       | 2.464                | 1.329                | 0.371                | 1.749                | 0.603                |
| 5700     | 1.345       | 4.305       | 2.532                | 1.349                | 0.388                | 1.664                | 0.594                |
| 6000     | 1.335       | 4.178       | 2.566                | 1.364                | 0.401                | 1.590                | 0.583                |
| 6300     | 1.343       | 4.082       | 2.632                | 1.390                | 0.415                | 1.504                | 0.575                |
| 6600     | 1.308       | 3.997       | 2.665                | 1.403                | 0.427                | 1.426                | 0.563                |
| 6900     | 1.298       | 3.955       | 2.724                | 1.428                | 0.443                | 1.378                | 0.559                |
| 7200     | 1.285       | 3.852       | 2.768                | 1.443                | 0.452                | 1.319                | 0.546                |
| 7500     | 1.295       | 3.783       | 2.807                | 1.463                | 0.464                | 1.263                | 0.541                |
| 7800     | 1.283       | 3.713       | 2.838                | 1.479                | 0.474                | 1.203                | 0.527                |
| 8100     | 1.265       | 3.691       | 2.902                | 1.504                | 0.490                | 1.159                | 0.523                |
| 8400     | 1.244       | 3.589       | 2.915                | 1.505                | 0.495                | 1.105                | 0.509                |
| 8700     | 1.255       | 3.546       | 2.952                | 1.521                | 0.506                | 1.071                | 0.502                |
| 9000     | 1.237       | 3.436       | 2.948                | 1.540                | 0.514                | 1.023                | 0.490                |
| 9300     | 1.212       | 3.372       | 2.968                | 1.568                | 0.523                | 0.986                | 0.481                |
| 9600     | 1.214       | 3.322       | 3.008                | 1.570                | 0.528                | 0.949                | 0.471                |
| 9900     | 1.197       | 3.290       | 3.028                | 1.575                | 0.539                | 0.911                | 0.461                |
| 10200    | 1.179       | 3.240       | 3.062                | 1.584                | 0.547                | 0.876                | 0.449                |
| 10500    | 1.175       | 3.211       | 3.101                | 1.603                | 0.554                | 0.842                | 0.444                |
| 10800    | 1.162       | 3.116       | 3.059                | 1.608                | 0.557                | 0.813                | 0.433                |
| 11100    | 1.164       | 3.063       | 3.072                | 1.636                | 0.563                | 0.783                | 0.422                |
| 11400    | 1.145       | 3.041       | 3.112                | 1.635                | 0.572                | 0.757                | 0.415                |
| 11700    | 1.134       | 3.012       | 3.154                | 1.646                | 0.579                | 0.730                | 0.408                |
| 12000    | 1.119       | 2.965       | 3.160                | 1.659                | 0.584                | 0.704                | 0.398                |
| Time / s | [4] / 10^{-2} M | [1] / 10^{-2} M | [C_6Cl_2F_3I] / 10^{-2} M | [C_6F_5Cl] / 10^{-2} M | [C_6F_5Cl] / 10^{-3} M | [C_6Cl_2F_3I] / 10^{-5} M | [C_6F_3I] / 10^{-4} M | [C_6Cl_2F_3H] / 10^{-3} M | [C_6F_3H] / 10^{-3} M |
|---------|----------------|----------------|----------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0       | 0.020          | 2.359          | 0.058                | 0.020          | 7.486          | 0.004          | 0.005          | 0.010          |
| 300     | 0.056          | 2.230          | 0.152                | 0.050          | 7.383          | 0.013          | 0.004          | 0.010          |
| 600     | 0.097          | 2.086          | 0.239                | 0.084          | 7.265          | 0.020          | 0.004          | 0.009          |
| 900     | 0.134          | 1.944          | 0.325                | 0.118          | 7.167          | 0.028          | 0.005          | 0.014          |
| 1200    | 0.170          | 1.784          | 0.401                | 0.153          | 7.011          | 0.033          | 0.006          | 0.014          |
| 1500    | 0.201          | 1.644          | 0.474                | 0.184          | 6.895          | 0.040          | 0.007          | 0.016          |
| 1800    | 0.221          | 1.519          | 0.541                | 0.210          | 6.781          | 0.046          | 0.007          | 0.019          |
| 2100    | 0.234          | 1.399          | 0.599                | 0.229          | 6.669          | 0.051          | 0.008          | 0.017          |
| 2400    | 0.245          | 1.293          | 0.656                | 0.247          | 6.596          | 0.053          | 0.009          | 0.018          |
| 2700    | 0.249          | 1.188          | 0.708                | 0.261          | 6.520          | 0.059          | 0.010          | 0.018          |
| 3000    | 0.252          | 1.099          | 0.763                | 0.274          | 6.446          | 0.063          | 0.011          | 0.022          |
| 3300    | 0.257          | 1.032          | 0.803                | 0.284          | 6.389          | 0.066          | 0.013          | 0.023          |
| 3600    | 0.253          | 0.932          | 0.840                | 0.295          | 6.329          | 0.067          | 0.014          | 0.030          |
| 3900    | 0.244          | 0.864          | 0.872                | 0.302          | 6.240          | 0.072          | 0.015          | 0.029          |
| 4200    | 0.246          | 0.794          | 0.906                | 0.311          | 6.179          | 0.073          | 0.016          | 0.030          |
| 4500    | 0.240          | 0.748          | 0.938                | 0.316          | 6.118          | 0.075          | 0.018          | 0.031          |
| 4800    | 0.233          | 0.691          | 0.975                | 0.324          | 6.099          | 0.078          | 0.020          | 0.035          |
| 5100    | 0.231          | 0.647          | 1.001                | 0.328          | 6.048          | 0.080          | 0.023          | 0.034          |
| 5400    | 0.221          | 0.603          | 1.024                | 0.335          | 6.008          | 0.082          | 0.024          | 0.038          |
| 5700    | 0.225          | 0.570          | 1.042                | 0.339          | 5.960          | 0.084          | 0.026          | 0.037          |
| 6000    | 0.218          | 0.514          | 1.064                | 0.343          | 5.915          | 0.085          | 0.027          | 0.038          |
| 6300    | 0.207          | 0.483          | 1.089                | 0.348          | 5.891          | 0.086          | 0.029          | 0.034          |
| 6600    | 0.205          | 0.445          | 1.111                | 0.351          | 5.850          | 0.088          | 0.033          | 0.037          |
| 6900    | 0.200          | 0.425          | 1.144                | 0.355          | 5.842          | 0.090          | 0.036          | 0.044          |
| 7200    | 0.188          | 0.401          | 1.148                | 0.356          | 5.878          | 0.091          | 0.037          | 0.042          |
| 7500    | 0.184          | 0.376          | 1.159                | 0.361          | 5.764          | 0.093          | 0.038          | 0.042          |
| 7800    | 0.179          | 0.356          | 1.182                | 0.366          | 5.744          | 0.094          | 0.040          | 0.048          |
| 8100    | 0.171          | 0.330          | 1.194                | 0.368          | 5.706          | 0.097          | 0.042          | 0.051          |
| 8400    | 0.168          | 0.302          | 1.207                | 0.368          | 5.686          | 0.095          | 0.045          | 0.050          |
| 8700    | 0.160          | 0.295          | 1.227                | 0.370          | 5.668          | 0.098          | 0.049          | 0.053          |
| 9000    | 0.154          | 0.271          | 1.237                | 0.374          | 5.638          | 0.098          | 0.050          | 0.057          |
| 9300    | 0.146          | 0.251          | 1.245                | 0.376          | 5.638          | 0.101          | 0.051          | 0.055          |

**Compound 1 / C_6Cl_2F_3I 0.33 : 1**

**Table S9:** Concentration vs time data fed to program COPASI to obtain kinetic parameters of the reaction of 1 (2.4·10^{-3}M) with C_6Cl_2F_3I (7.1·10^{-3}M) in THF at 25 °C.
Table S10: Concentration vs time data used as input in program COPASI to obtain kinetic parameters of the reaction of 1 (2.4·10^{-2}M) with PhI (4.3·10^{-1}M) in THF at 50 ºC.

| Time / s | [1] / 10^{-2} M | [C_{6}F_{5}-C_{6}H_{5}] / 10^{-2} M | [C_{6}F_{5}H] / 10^{-2} M |
|----------|-----------------|----------------------------------|------------------------|
| 86       | 7.145           | 0.019                            | 0.042                  |
| 404      | 7.037           | 0.210                            | 0.019                  |
| 712      | 6.620           | 0.395                            | 0.106                  |
| 1030     | 6.497           | 0.518                            | 0.128                  |
| 1346     | 6.236           | 0.726                            | 0.208                  |
| 1656     | 6.008           | 0.865                            | 0.233                  |
| 1968     | 5.790           | 1.115                            | 0.273                  |
| 2282     | 5.750           | 1.130                            | 0.284                  |
| 2590     | 5.488           | 1.297                            | 0.305                  |
| 2897     | 5.291           | 1.425                            | 0.356                  |
| 3206     | 5.078           | 1.720                            | 0.364                  |
| 3513     | 4.969           | 1.794                            | 0.377                  |
| 3820     | 4.699           | 1.987                            | 0.409                  |
| 4128     | 4.619           | 2.002                            | 0.457                  |
| 4435     | 4.593           | 2.161                            | 0.419                  |
| 4745     | 4.434           | 2.226                            | 0.484                  |
| 5061     | 4.363           | 2.402                            | 0.454                  |
| 5372     | 4.155           | 2.477                            | 0.488                  |
| 5679     | 4.010           | 2.608                            | 0.508                  |
| 5987     | 3.832           | 2.784                            | 0.532                  |
| 6300     | 3.894           | 2.871                            | 0.489                  |
| 6608     | 3.692           | 3.026                            | 0.505                  |
| 6919     | 3.535           | 3.015                            | 0.562                  |
|     |      |      |      |
|-----|------|------|------|
| 7237| 3.428| 3.104| 0.621|
| 7548| 3.331| 3.281| 0.586|
| 7855| 3.185| 3.360| 0.606|
| 8163| 3.146| 3.369| 0.603|
| 8480| 3.029| 3.540| 0.544|
| 8788| 2.919| 3.658| 0.616|
| 9101| 2.880| 3.565| 0.617|
| 9418| 2.790| 3.701| 0.644|
| 9728| 2.658| 3.842| 0.633|
|10035| 2.529| 3.895| 0.671|
|10348| 2.445| 4.055| 0.678|
|10672| 2.346| 4.086| 0.682|
|10980| 2.338| 4.110| 0.644|
|11294| 2.186| 4.209| 0.744|
|11610| 2.181| 4.269| 0.680|
|11926| 2.080| 4.329| 0.686|
|12239| 2.059| 4.393| 0.658|
|12560| 1.990| 4.359| 0.729|
|12872| 1.917| 4.584| 0.702|
|13181| 1.852| 4.560| 0.716|
|13489| 1.759| 4.603| 0.698|
|13797| 1.711| 4.564| 0.773|
|14105| 1.708| 4.624| 0.762|
|14421| 1.652| 4.658| 0.733|
|14735| 1.502| 4.787| 0.818|
|15043| 1.558| 4.876| 0.751|
|15357| 1.443| 4.945| 0.804|
|15665| 1.388| 4.855| 0.790|
|15979| 1.408| 5.050| 0.808|
|16296| 1.356| 5.026| 0.776|
|16604| 1.308| 5.052| 0.777|
|16920| 1.244| 5.036| 0.804|
|17237| 1.286| 5.098| 0.730|
|17550| 1.104| 5.171| 0.834|
|17865| 1.093| 5.286| 0.777|
|18177| 1.100| 5.211| 0.771|
|18493| 1.033| 5.113| 0.820|
|18800| 0.985| 5.136| 0.867|
For the compound C_{28}H_{36}CuF_{10}N, (NBu_{4})[Cu(C_{6}F_{5})_{2}] \textbf{2}, suitable single crystals were obtained by layering hexane in a CH_{2}Cl_{2} solution of the compound at -32 °C under nitrogen, the crystal was submerged in immersion oil, attached to a loop and transferred to the diffractometer.

Diffraction data for the crystal were recorded in an Oxford Diffraction Super Nova diffractometer with an Atlas CCD area detector. The crystal was kept at 210 K during data collection. Data collection was performed with Mo-Kα radiation (λ = 0.71073 Å). Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package.\textsuperscript{14} The structure was solved using the programs Olex2.\textsuperscript{15} The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Table S11. CCDC 2072143 contains the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

**Figure S15:** Molecular structure obtained from X-ray diffraction of complex \textbf{2} showing 50% probability ellipsoids. Hydrogen atoms have been set in ideal positions. Blue: Nitrogen; Green: Fluorine; Brown: Copper; Grey: Carbon; White: Hydrogen.
### Table S11: Crystal data and structure refinement for C$_{28}$H$_{36}$NF$_{10}$Cu

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | CuPf2NBu4 Gabriel A                        |
| Empirical formula                             | C$_{28}$H$_{36}$NF$_{10}$Cu                |
| Formula weight                                | 640.12                                     |
| Temperature/K                                 | 210.00(14)                                 |
| Crystal system                                | monoclinic                                 |
| Space group                                   | P2$_{1}$/n                                  |
| a/Å                                          | 9.3714(2)                                  |
| b/Å                                          | 16.6405(3)                                 |
| c/Å                                          | 18.7821(4)                                 |
| α/°                                          | 90                                         |
| β/°                                          | 90.341(2)                                  |
| γ/°                                          | 90                                         |
| Volume/Å$^3$                                  | 2928.92(10)                                |
| Z                                            | 4                                          |
| $\rho_{\text{calc}}$/g/cm$^3$                 | 1.452                                      |
| $\mu$/mm$^{-1}$                               | 0.827                                      |
| F(000)                                        | 1320.0                                     |
| Crystal size/mm$^3$                           | 0.937 × 0.619 × 0.414                      |
| Radiation                                     | Mo Kα ($\lambda = 0.71073$)               |
| 2Θ range for data collection/°                | 6.542 to 60.376                            |
| Index ranges                                  | -12 ≤ h ≤ 12, -21 ≤ k ≤ 22, -26 ≤ l ≤ 23   |
| Reflections collected                         | 50296                                      |
| Independent reflections                       | 7755 [R$_{\text{int}} = 0.0394$, R$_{\text{sigma}} = 0.0312$] |
| Data/restraints/parameters                    | 7755/0/365                                 |
| Goodness-of-fit on F$^2$                      | 1.016                                      |
| Final R indexes [I>=2σ(I)]                    | R$_1 = 0.0457$, wR$_2 = 0.1084$            |
| Final R indexes [all data]                    | R$_1 = 0.0749$, wR$_2 = 0.1261$            |
| Largest diff. peak/hole/e Å$^{-3}$            | 1.01/-0.55                                 |
S11. Computational Details

Theoretical calculations were performed at DFT level of theory using Gaussian16 software. The structures of all the intermediates and transition states were optimized in tetrahydrofuran solvent (THF, \( \varepsilon = 7.4257 \)) with the SMD continuum model using the B3LYP functional combined with the Grimme’s D3 correction for dispersion. Additional calibration calculations employing a set of functionals were carried out for certain structures (see section S16 in the Supporting Information). Basis set BS1 was used for the optimizations. BS1 includes the 6-31G(d,p) basis set for the main group elements, excluding iodine, and the scalar relativistic Stuttgart-Dresden SDD pseudopotential and its associated double-\( \zeta \) basis set, complemented with a set polarization functions, for the copper (\( f \) polarization functions) and iodine (\( d \) polarization functions) atoms. Frequency calculations were carried out for all the optimized geometries in order to characterize the stationary points as either minima or transition states.

Gibbs energies in tetrahydrofuran were calculated at 298.15 K adding to the potential energies in tetrahydrofuran, obtained with single point calculations using an extended basis set (BS2) at the BS1 optimized geometries, the thermal and entropic corrections obtained with BS1. BS2 consists in the def2-TZVP basis set for the main group elements, and the quadruple-\( \zeta \) def2-QZVP basis set for Cu. A correction of 1.9 kcal mol\(^{-1}\) was applied to all Gibbs values to change the standard state from the gas phase (1 atm) to solution (1 M) at 298.15 K. In this way, all the energy values in the energy profiles are Gibbs energies in THF solution calculated using the formula:

\[
G = E(\text{BS2}) + G(\text{BS1}) - E(\text{BS1}) + \Delta G_{1\text{atm}\to1\text{M}}
\]

where \( \Delta G_{1\text{atm}\to1\text{M}} = 1.9 \) kcal mol\(^{-1}\) is the Gibbs energy change for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution phase standard state.

To locate the minimum energy crossing points (MECP) between singlet and triplet potential energy surfaces, the program developed by the group of Harvey was employed. To confirm that the MECP connects the two intermediates located in the two energy surfaces, the MECP structure was optimized in the different spin states involved in the crossing. The Gibbs energies in solution of the MECP was estimated by adding to the calculated potential energy of the MECP thermal and entropic corrections calculated with the option freq = projected of the Gaussian 09 program. 3D-structures were generated using CYLview.
S12. Optimized structures of all the intermediates and transition states in the reaction of [Cu(bipy)Pf] (1) with Rf-I (Gibbs energy profile in Figure 2 of the main text)

**Heterocoupling pathway**

*Figure S16.* Optimized structures of all the intermediates and transition states in the pathway for the formation of the heterocoupling product, Rf-Pf. In red, relative Gibbs energies in THF, in kcal mol\(^{-1}\).
Homocoupling pathway
**Figure S17.** Optimized structures of all the intermediates and transition states in the pathway for the formation of the homocoupling product, \( \text{Pf-Pf} \). In red, relative Gibbs energies in THF, in kcal mol\(^{-1}\).
S13. Spin-density plots

Figure S18. Spin density plots of intermediate T1 (left) and transmetalation transition state (right). In blue Mulliken atomic spin populations

Table S12: Atomic charges\(^a\) at the copper centers of intermediates I0, S1 and T1.

| Intermediate | Cu oxidation state | Spin state | Atomic charge  |
|--------------|--------------------|------------|----------------|
| I0           | Cu(I)              | singlet    | 0.340          |
| S1           | Cu(III) Cu(I)      | singlet    | 0.632 0.349    |
| T1           | Cu(II) Cu(II)      | triplet    | 0.617 (0.566)\(^b\) 0.642 (0.532)\(^b\) |

\(^a\) Computed with the CM5 model.\(^{29}\)

\(^b\) Mulliken spin populations.
S14. Gibbs energy profile for the reaction of [Cu(bipy)Pf] (1) with $p$-substituted phenyl iodides ($p$-$X$-Ar-I; $X = $ H, OMe, Br, NO2)

Figure S19. DFT-computed (B3LYP-D3/BS2 in THF) pathway for the formation of the heterocoupling product $p$-$X$-Ar-Pf in the reaction of 1 with $p$-substituted phenyl iodides. Relative Gibbs energies are given in kcal mol$^{-1}$.

Table S13: Atomic charges$^a$ at ipso-carbon of para-substituted aryl iodides in the intermediates preceding oxidative addition.

| substituent | Atomic charge |
|-------------|---------------|
| OMe         | -0.038        |
| H           | -0.022        |
| Br          | -0.019        |
| NO$_2$      | -0.003        |

$^a$Computed with the CM5 model.$^{29}$
S15. Optimized structures of all the intermediates and transition states in the reaction of [Cu(bipy)Pf] (1) with Ph-I (Gibbs energy profile in Figure S19)

Figure S20. Optimized structures of all the intermediates and transition states in the pathway for the formation of the heterocoupling product, Ph-Pf. In red, relative Gibbs energies in THF, in kcal mol$^{-1}$. 
S16. DFT benchmark study of the relative stabilities of Cu$^I$-Cu$^{III}$ (S1) and Cu$^{II}$-Cu$^{II}$ (T1) species

**Table S14.** Relative energies in THF of S1 (Cu(III)-Cu(I), singlet) and T1 (Cu(II)-Cu(II), triplet) intermediates with respect to $1 + RF-I$ and T1-S1 energy difference ($\Delta E(T1-S1)$), calculated with different functionals. Energies in kcal mol$^{-1}$. All single-point calculations are done using BS2 on B3LYP-D3/BS1 singlet and triplet optimized geometries in THF.

| Method          | %HF exchange | S1/singlet | T1/triplet | $\Delta E(T1-S1)$ |
|-----------------|--------------|------------|------------|-------------------|
| PBE-D3/BS2      | 0            | -21,3      | -23,1      | -1,8              |
| M11-L/BS2       | 0            | -14,6      | -30,3      | -15,7             |
| TPSSh-D3/BS2    | 10           | -22,9      | -32,0      | -9,1              |
| B3LYP-D3/BS2    | 20           | -19,0      | -29,6      | -10,5             |
| PBE0-D3/BS2     | 25           | -15,6      | -29,2      | -13,7             |
| M06/BS2         | 27           | -2,3       | -6,1       | -3,8              |
| M06-D3/BS2      | 27           | -13,6      | -16,9      | -3,3              |
| MN15/BS2        | 44           | -6,5       | -9,8       | -3,3              |
| M06-2X-D3/BS2   | 54           | -3,3       | -38,2      | -38,2             |
| CAM-B3LYP-D3/BS2| 19(SR)65(LR)$^a$ | -13,0     | -27,1      | -14,1             |
| wB97XD/BS2      | 22(SR)/100(LR)$^a$ | -9,7       | -25,2      | -15,5             |
| M11/BS2         | 42.8(SR)/100(LR)$^a$ | -5,3       | -28,1      | -22,7             |

$^a$ SR=short range, LR=long range
S17. Cartesian coordinates and absolute E and G energies in THF of the optimized structures

Reaction between [Cu(bipy)Pf] and Rf-I (Gibbs energy profile in Figure 2 of the main text)

1 [Cu(bipy)Pf]

| Property                      | Value          |
|-------------------------------|----------------|
| Charge                        | 0              |
| Spin State                    | Singlet       |
| Electronic Energy, BS1 (a.u.) | -1420.627334  |
| Thermal and entropic correction, BS1 (a.u.) | 0.155681 |
| Electronic Energy, BS2 (a.u.) | -2864.399240  |
| Gibbs Energy, BS2 (a.u.)      | -2864.243559  |
| Number of Imaginary Frequencies | 0             |

Molecular Geometry in Cartesian Coordinates

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -4.400490 | -1.514032 | -0.049028 |
| C    | 3.234283  | -0.742748 | -0.007870 |
| C    | 1.915118  | -2.657293 | 0.007582  |
| C    | -3.030299 | -3.492355 | -0.028083 |
| C    | -4.293791 | -2.903964 | -0.058083 |
| H    | -5.377165 | -1.046101 | -0.077693 |
| C    | -0.904505 | -3.053126 | 0.029115  |
| H    | -2.904347 | -4.569485 | -0.033586 |
| C    | 5.189208  | -3.516976 | -0.089410 |
| C    | 3.231945  | 0.746954  | 0.007676  |
| C    | -4.395686 | 1.522010  | 0.048720  |
| C    | -1.906482 | 2.657001  | -0.007548 |
| C    | -4.284327 | 2.916090  | 0.057946  |
| H    | 5.373941  | 1.057401  | 0.029115  |
| C    | -0.894534 | 3.049409  | -0.028937 |

Rf-I

| Property                      | Value          |
|-------------------------------|----------------|
| Charge                        | 0              |
| Spin State                    | Singlet       |
| Electronic Energy, BS1 (a.u.) | -1459.932205  |
| Thermal and entropic correction, BS1 (a.u.) | 0.007392 |
| Electronic Energy, BS2 (a.u.) | -1746.619319  |
| Gibbs Energy, BS2 (a.u.)      | -1746.619272  |
| Number of Imaginary Frequencies | 0             |

Molecular Geometry in Cartesian Coordinates

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.190474 | 1.197664  | -0.000009 |
| C    | 1.587109  | -2.143434 | -0.00010  |
| C    | -2.724207 | 0.000004  | -0.00005  |
| C    | -1.587096 | -1.214351 | -0.00009  |
| C    | -0.190480 | -1.197667 | -0.00013  |
| C    | 0.523998  | 0.000007  | -0.00007  |

IO

| Property                      | Value          |
|-------------------------------|----------------|
| Charge                        | 0              |
| Spin State                    | Singlet       |
| Electronic Energy, BS1 (a.u.) | -2880.589496  |
| Thermal and entropic correction, BS1 (a.u.) | 0.184712 |
| Electronic Energy, BS2 (a.u.) | -4610.039706  |
| Gibbs Energy, BS2 (a.u.)      | -4610.854994  |
| Number of Imaginary Frequencies | 0             |

Molecular Geometry in Cartesian Coordinates

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| Cl   | 2.457410  | 2.716660  | -0.00000  |
| Cl   | 2.457410  | 2.716660  | -0.00000  |
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| Cu      | 0.061147 | -0.797375| 1.148603 |
| F       | -2.266934| -2.836598| 0.429119 |
| F       | -1.912168| 1.634504 | 2.044519 |
| F       | -0.042184| -0.020844| 0.495309 |
| C       | 2.861418  | -0.907284| 1.612398 |
| N       | 1.270242  | -2.371866| 0.579609 |
| C       | 2.574210  | -2.053446| 0.708970 |
| C       | 3.567959  | -2.735562| -0.000665|
| H       | 4.609574  | -2.450375| 0.086655 |
| C       | 4.145849  | -0.592420| 2.066520 |
| H       | 4.991772  | -1.217597| 1.806451 |
| C       | -1.966214 | -0.619441| 1.266789 |
| N       | 1.792103  | -0.154101| 1.958862 |
| C       | -3.967822 | 0.808792 | 1.296204 |
| C       | -2.785735 | -1.608897| 0.737683 |
| C       | -2.617218 | 0.577564 | 1.539585 |
| C       | 1.846394  | -4.107951| -0.970064|
| H       | 1.514718  | -4.908766| -1.622169|
| C       | 3.224468  | 1.318290 | 3.198965 |
| H       | 3.322236  | 2.206516 | 3.813237 |
| C       | -4.736297 | -0.215796| 0.751510 |
| C       | 0.917102  | -3.372055| -0.235386|

**TS_OA**

| Charge | 0 |
| Spin State | Singlet |
| Electronic Energy, BS1 (a.u.) | -2880.556950 |
| Thermal and entropic correction, BS1 (a.u.) | 0.185326 |
| Electronic Energy, BS2 (a.u.) | -4611.006402 |
| Gibbs Energy, BS2 (a.u.) | -4610.821076 |
| Number of Imaginary Frequencies | 1 |
| Imaginary Frequencies (cm⁻¹) | -134.1i |

**Molecular Geometry in Cartesian Coordinates**

| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| Cu      | -0.910718| 0.192393 | -0.052244|
| F       | 1.062543 | 0.672760 | -2.520909|
| F       | 0.088771 | -2.894239| 0.416132 |
| F       | 4.560886 | -1.624071| -0.356982|
| C       | -3.511431| -0.097017| 1.490565 |
| N       | -2.695271| 1.357703 | -0.246855|
| C       | -3.763703| 0.967851 | 0.480013 |
| N       | -5.020907| 1.550811 | 0.277514 |
| H       | -5.883721| 1.222390 | 0.844199 |
| C       | -4.457780| -0.468539| 2.453751 |
| H       | -5.427963| 0.011162 | 2.496398 |
| C       | 0.508243 | -1.076432| -1.035746|
| N       | -2.292469| -0.675620| 1.447486 |
| C       | 2.330849 | -2.289722| 0.045450 |
| C       | 1.470466 | -0.314158| -1.710094|
| C       | 0.974310 | -2.101473| -0.208862|
| C       | -4.043998| 2.960400 | -1.409393|
| H       | -4.107910| 3.742416 | -2.158159|
| C       | -2.868321| -2.043470| 3.331628 |

| H    | -0.147133 | -3.570783 | -0.299948 |
| C    | -0.413155 | -1.441652 | 0.469008  |
| C    | 1.972915  | 0.931061  | 2.727780  |
| C    | 1.077569  | 1.498217  | 2.959520  |
| C    | 3.194859  | -3.776608 | -0.849842 |
| H    | 3.950154  | -3.418431 | -1.414197|
| C    | 4.327973  | 0.533123  | 2.866935  |
| C    | 3.193134  | 0.791014  | 3.226365  |
| C    | 0.098347  | 2.187172  | -0.998760 |
| C    | 1.058131  | 1.227975  | -1.322176|
| C    | 0.624733  | 0.009882  | -1.846550|
| C    | -0.730852 | -0.258043 | -2.046579|
| C    | -1.664189 | 0.724616  | -1.715762|
| C    | -1.263533 | 1.957225  | -1.200573|
| C    | 0.478220  | 3.360410  | -0.485191|
| C    | -2.962910 | 0.476146  | -1.883103|
| C    | 1.517372  | -0.933959 | -2.161276|
| I    | 3.108511  | 1.631174  | -1.054324|
| C    | -4.884707 | -2.432760 | -0.063787|
| C    | -4.540829 | 2.001574  | 1.554229  |
| Cl    | -1.255229 | -1.786174 | -2.676239|
| Cl    | -2.437235 | 3.173222  | -0.81139  |

| Imaginary Frequencies (cm⁻¹) | -134.1i |

| | | |
| | | |

| | | |
| | | |
|     | F    | Molecular Geometry in Cartesian Coordinates | Cl |     |     |
|-----|------|--------------------------------------------|----|-----|-----|
| C   | 1.057008 | -0.489215 | 2.300883 | Cl  | 2.865689 | -3.515288 | 1.155622 |
| I   | -1.527415 | -1.447913 | -2.129508 | F   | 2.527922 | 4.290290 | 0.098433 |
| Cl  | 3.990760 | 0.579400 | -2.241104 | F   | 3.326257 | 0.737496 | 3.123814 |

**I1**

- **Charge**: 0
- **Spin State**: Singlet
- **Electronic Energy, BS1 (a.u.)**: -2880.585650
- **Thermal and entropic correction, BS1 (a.u.)**: 0.189974
- **Gibbs Energy, BS1 (a.u.)**: -4611.027897
- **Number of Imaginary Frequencies**: 0

### Molecular Geometry in Cartesian Coordinates

|     |     |     | C    |     |     |
|-----|-----|-----|------|-----|-----|
| Cu  | -0.483020 | -0.542997 | 0.322862 | H   | -1.659401 | -0.576323 | -2.919920 |
| F   | 1.645270 | 0.419884 | -2.296218 | C   | 3.609754 | 0.135504 | -1.031517 |
| F   | 1.321993 | -1.264659 | 2.096987 | C   | -1.644540 | -0.837964 | 2.959424 |
| F   | 5.535201 | -0.161732 | 0.303211 | H   | -0.607386 | -1.034135 | 3.201154 |
| C   | -3.207612 | -0.502725 | 1.290374 | H   | -4.939213 | -0.467559 | -2.087177 |
| N   | -2.393083 | -0.498910 | -0.994355 | H   | -5.940862 | -0.456903 | -2.503711 |
| C   | -3.465824 | -0.472323 | -0.172777 | C   | -3.911543 | -0.394508 | 3.588869 |
| C   | -4.760365 | -0.459782 | -0.707913 | H   | -4.684243 | -0.246858 | 4.337389 |
| H   | -5.621880 | -0.464708 | -0.052222 | C   | -0.589970 | 2.209991 | -1.201786 |
| C   | -4.223793 | -0.302212 | 2.234844 | C   | -0.359111 | 1.386471 | -0.107706 |
| H   | -5.236819 | -0.072271 | 1.928396 | C   | -0.114334 | 2.002858 | 1.112549 |
| C   | 1.410073 | -0.399907 | -0.098202 | C   | -0.145441 | 3.387885 | 1.259301 |
| N   | -1.937297 | -0.751102 | 1.658303 | C   | -0.404338 | 4.189395 | 0.151691 |
| C   | 3.434737 | -0.700988 | 1.238062 | C   | -0.625163 | 3.598080 | -1.088090 |
| C   | 2.220068 | 0.052538 | -1.136122 | F   | -0.801213 | 1.692778 | -2.430276 |
| C   | 2.048165 | -0.771845 | 1.079186 | F   | -0.436162 | 5.522235 | 0.277655 |
| C   | -3.820281 | -0.507072 | -2.917752 | F   | 0.194515 | 1.279280 | 2.207067 |
| H   | -3.909139 | -0.529438 | -3.997864 | I   | -0.231782 | -3.088207 | -0.898774 |
| C   | -2.599314 | -0.677598 | 3.963465 | Cl  | 4.192444 | -1.189067 | 2.725970 |
| H   | -2.312656 | -0.764665 | 5.006040 | Cl  | 4.580507 | 0.702650 | -2.358765 |
| C   | 4.207815 | -0.239585 | 0.172288 | F   | 0.084452 | 3.954443 | 2.453729 |
| C   | -2.563704 | -0.529058 | -2.327135 | F   | -0.871553 | 4.366312 | -2.160260 |

**TS_RE_Het**

- **Charge**: 0
- **Spin State**: Singlet
- **Electronic Energy, BS1 (a.u.)**: -2880.580332
- **Thermal and entropic correction, BS1 (a.u.)**: 0.188553
- **Gibbs Energy, BS1 (a.u.)**: -4611.020303
- **Number of Imaginary Frequencies**: 1

### Molecular Geometry in Cartesian Coordinates

|     |     |     | Cu  |     |     |
|-----|-----|-----|-----|-----|-----|
| F   | -0.375963 | -0.672818 | -0.186477 | C   | -4.630036 | -1.123121 | -0.844102 |
| F   | 1.665113 | 0.681713 | -2.364217 | H   | -5.520623 | -1.116487 | -0.228396 |
| F   | 1.377495 | -0.587621 | 2.181128 | C   | -4.236369 | -0.422263 | 2.054903 |
| F   | 5.548318 | 0.386297 | 0.261762 | H   | -5.254078 | -0.353017 | 1.690641 |
| C   | -3.170898 | -0.665678 | 1.178715 | C   | 1.411153 | 0.131709 | -0.079328 |
| N   | -2.255351 | -0.938734 | -1.038273 | N   | -1.896301 | -0.717417 | 1.614990 |
| C   | -3.368854 | -0.902355 | -0.276458 | C   | 3.456805 | -0.056782 | 1.261574 |
### Molecular Geometry in Cartesian Coordinates

| Atom | X | Y | Z |
|------|---|---|---|
| C    | 2.224288 | 0.452306 | -1.169849 |
| C    | 2.072001 | -0.137706 | 1.126058 |
| C    | -3.570906 | -1.427473 | -2.980137 |
| H    | -3.601182 | -1.637034 | -4.043460 |
| C    | -2.654905 | -0.345874 | 3.861350 |
| H    | -2.403624 | -0.236364 | 4.910782 |
| C    | 4.228225 | 0.296943 | 0.150547 |
| C    | -2.351977 | -1.206234 | -2.349285 |
| H    | -1.416307 | -1.243975 | -2.893935 |
| C    | 3.613338 | 0.540972 | -1.079392 |
| C    | -1.649713 | -0.569968 | 2.921523 |
| H    | -0.610563 | -0.627091 | 3.218318 |
| C    | -4.731049 | -1.380086 | -2.208190 |
| H    | -5.703406 | -1.554201 | -2.668209 |
| C    | -3.971093 | -0.259368 | 3.412682 |

### P1

| Charge | Spin State | Electronic Energy, BS1 (a.u.) | Thermal and entropic correction, BS1 (a.u.) | Electronic Energy, BS2 (a.u.) |
|--------|------------|--------------------------------|-----------------------------------------------|-------------------------------|
| 0      | Singlet    | -2880.669175                  | 0.189147                                      | -4611.109654                 |

### Number of Imaginary Frequencies

0
### Molecular Geometry in Cartesian Coordinates

|     |  X     |  Y     |  Z     |
|-----|--------|--------|--------|
| F   | 1.177573 | 1.919905 | -1.389996 |
| F   | 1.177706 | 1.919979 | 1.390082 |
| F   | 5.242984 | 0.000038 | -0.000030 |
| C   | 1.093067 | -0.000085 | -0.000036 |
| C   | 3.211002 | -0.984788 | 0.694842 |
| C   | 1.820655 | 0.972202 | -0.694002 |
| C   | 1.820711 | -0.972312 | 0.693970 |
| C   | 3.907765 | 0.000038 | -0.000029 |
| C   | 3.210944 | 0.984754 | -0.694877 |
| C   | -1.114204 | 1.135696 | 0.362837 |
| C   | -0.384389 | -0.000071 | 0.000014 |

### S1

|     |  X     |  Y     |  Z     |
|-----|--------|--------|--------|
| Cu  | 0.579587 | -0.000836 | 0.000123 |
| C   | -2.256743 | 0.745976 | -0.000849 |
| N   | -1.040194 | -1.332338 | -0.039584 |
| C   | -2.257280 | -0.745008 | 0.000834 |
| C   | -3.427017 | -1.511311 | 0.045252 |
| H   | -4.400933 | -1.039393 | 0.088122 |
| C   | -3.425912 | 1.513129 | -0.045678 |
| H   | -4.400171 | 1.041951 | -0.088932 |
| N   | -1.039257 | 1.332411 | 0.040013 |
| C   | -2.071006 | -3.497619 | -0.005939 |
| H   | -1.951322 | -4.575400 | -0.011729 |

### S57
H  1.647166  5.125054  1.189326  C  2.057452 -1.699899  3.359093
C  -0.759352  5.462096  0.041776  C  1.181784 -1.797487  4.438555
H  -0.146588  6.041932  0.721030  C  0.016249 -2.545781  4.277613
C  -2.277382 -0.281214 -0.964888  H  -1.137907 -3.741863  2.910295
N  -1.309434  3.350423 -0.960703  H  2.975621 -1.123299  3.417284
C  -4.131667 -0.844456 -2.454707  H  1.404477 -1.287690  5.369767
C  -2.513151 -1.474555 -0.295999  H  -0.704503 -2.626687  5.085033
C  -3.107987  0.010501 -2.039152  C  0.525548 -3.636228  0.675977
C  2.649082  1.925255  1.649182  C  -0.425715 -4.619609  0.390534
C  3.435325  1.315913  2.077430  C  1.203475 -3.583839 -1.548920
C  -2.593322  5.305695 -1.500683  C  -0.559617 -5.074177 -0.919815
H  -3.414741  5.741228 -2.059446  H  -1.054265 -5.024591  1.173432
C  -4.339387 -2.029601 -1.748910  C  0.262929 -4.544444 -1.913467
C  1.600041  1.320222  0.968731  H  1.872663 -3.135037 -2.274763
H  1.559825  0.245979  0.838916  H  -1.300352 -5.830319 -1.159340
C  -3.533551 -2.357150 -0.659847  H  0.185135 -4.864443 -2.946685
C  -2.310524  3.945152 -1.617651  N  1.824580 -2.297724  2.183576
H  -2.911592  3.303713 -2.249813  N  1.334759 -3.145556 -0.288384
C  2.660599  3.314815  1.744083  Cu  2.866871 -1.906814  0.315237
H  3.469191  3.828393  2.254519  C  4.377216 -0.830384 -0.183393
C  -1.806336  6.072872 -0.644039  C  4.672148 -0.531767 -1.514002
H  -2.002896  7.131776 -0.507141  C  5.168688 -0.159879  0.733132
C  -1.548837  0.595007  2.346677  C  5.650371 0.375261 -1.912180
C  -2.029157  1.118607  1.154145  C  6.158036 0.761369  0.405431
C  -3.279707  1.718680  1.180726  C  6.400884 1.029174 -0.938568
C  -4.010306  1.846335  2.360804  F  4.963727 -0.351647  2.080114
C  -3.494735  1.331583  3.547009  F  3.975134 -1.134443 -2.522850
C  -2.256652  0.695737  3.540679  F  5.883940 0.637567 -3.214411
F  -0.362816  -0.047203  2.391049  F  7.352048 1.911689 -1.293578
F  -4.189904  1.442317  4.686744  F  6.875103 1.400143  1.353200
F  -3.857410  2.170649  0.048616  Cl  -3.842041 -3.811214  0.244828
I  0.588410  0.225837 -2.425962  Cl  -5.132508 -0.449853 -3.821794
C  -0.224921 -3.178672  3.059846  F  -1.759224 0.181465  4.678010
C  0.707944 -3.038560  2.026777  F  -5.213410 2.441770  2.360572

MECP1

| Charge | 0 |
| Spin State | Singlet-Triplet |
| Electronic Energy, BS1 (a.u.) | -4301.234563 |
| Thermal and entropic correction, BS1 (a.u.) | 0.365662 |
| Electronic Energy, BS2 (a.u.) | -7475.438113 |
| Gibbs Energy, BS2 (a.u.) | -7475.072451 |
| Number of Imaginary Frequencies | 0 |

Molecular Geometry in Cartesian Coordinates

| Cu | -0.801774 | 0.948974 | -0.476715 |
| F | -2.085214 | -1.409709 | 1.208385 |
| F | -2.190105 | 0.301995 | -3.200580 |
| F | -5.040642 | -3.237291 | -1.970069 |
| Cu | -0.378526 | 3.989906 | -1.136508 |
| N | 0.661765 | 2.255042 | 0.196365 |
| C | 0.692084 | 3.544180 | -0.207537 |

S58
| Charge | Spin State | Electronic Energy, BS1 (a.u.) | Thermal and entropic correction, BS1 (a.u.) | Electronic Energy, BS2 (a.u.) | Gibbs Energy, BS2 (a.u.) | Number of Imaginary Frequencies |
|--------|-----------|-----------------------------|---------------------------------|-------------------------------|--------------------------|-------------------------------|
|        |           |                             |                                 |                               |                          |                                |
| 0      | Triplet   | -4301.263912                | 0.367782                        | -7475.464925                  | -7475.097143             |                                |

**Molecular Geometry in Cartesian Coordinates**

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Cu      | 1.692199 | -1.641897 | 0.436868 |
| F       | 3.322530 | 1.051654 | 1.466811 |
| F       | 2.258094 | -1.193740 | -2.570841 |
| F       | 4.320643 | 3.028028 | -2.675223 |
| C       | 1.470513 | -4.324828 | -0.782874 |
| N       | 0.052270 | -2.924286 | 0.536885 |
| C       | 0.142512 | -4.070783 | -0.170991 |
| C       | -0.960061 | -4.918460 | -0.305049 |
| H       | -0.887593 | -5.835050 | -0.877327 |
| C       | 1.814933 | -5.507553 | -1.443589 |

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| H       | -1.439624 | -3.173292 | 3.538725 |
| H       | 2.590405 | -0.395811 | 3.419347 |
| H       | 1.133940 | -0.303783 | 5.448060 |
| H       | -0.948716 | -1.717632 | 5.482067 |
| C       | 0.112153 | -3.397759 | 1.245739 |
| C       | -0.895130 | -4.360881 | 1.147728 |
| C       | 0.804786 | -3.852890 | -0.935301 |
| C       | -1.047581 | -5.071115 | -0.040267 |
| H       | -1.560281 | -4.549617 | 1.979931 |
| C       | -0.182915 | -4.817859 | -1.104599 |
| C       | 1.502627 | -3.605237 | -1.726798 |
| C       | -1.836353 | -5.810463 | -0.131727 |
| C       | -0.267888 | -5.348814 | -2.046182 |
| N       | 1.427566 | -1.775260 | 2.432341 |
| C       | 0.946521 | -3.163581 | 0.208305 |
| Cu      | 2.428821 | -1.827250 | 0.447263 |
| C       | 4.155932 | -0.966460 | 0.150993 |
| C       | 4.750306 | -1.085497 | -1.101964 |
| C       | 4.811646 | -1.009598 | 1.012279 |
| C       | 5.880412 | -0.378050 | -1.499476 |
| C       | 5.937595 | 0.643371 | 0.674200 |
| C       | 6.475719 | 0.503654 | -0.600342 |
| F       | 4.348876 | 0.089496 | 2.287120 |
| F       | 4.216980 | -1.928304 | -2.033554 |
| F       | 6.404264 | -0.528861 | -2.731200 |
| F       | 7.564057 | 1.203993 | -0.958495 |
| F       | 6.504772 | 1.491213 | 1.554234 |
| Cl      | -4.210717 | -3.414736 | 0.854143 |
| Cl      | -4.252322 | -1.504784 | -4.235193 |
| H       | -2.243356 | 1.350814 | 4.610365 |
| F       | -5.439786 | 2.885103 | 1.468407 |

**T1**
|     |   |   |
|-----|---|---|
| C   | 3.834380 | 1.993490 | -1.974739 |
| C   | -1.106420 | -2.578321 | 1.108097 |
| H   | -1.111998 | -1.633564 | 1.632416 |
| C   | 3.825767 | 2.042390 | -0.583057 |
| C   | 3.595624 | -3.447178 | -1.148170 |
| H   | 4.251416 | -2.593989 | -1.008652 |
| H   | -2.167314 | -4.559742 | 0.294961 |
| H   | -0.034911 | -5.204042 | 0.192941 |
| C   | 3.102136 | -5.642390 | -1.960645 |
| H   | 3.87544 | -6.555084 | -2.474327 |
| C   | 0.673092 | 0.063436 | 2.713468 |
| C   | 1.526072 | -0.944313 | 2.309978 |
| C   | 2.354983 | -1.455464 | 3.291956 |
| C   | 2.358639 | -1.000979 | 4.608289 |
| C   | 1.480734 | 0.018662 | 4.967729 |
| C   | 0.622720 | 0.558266 | 4.012905 |
| F   | -0.175335 | 0.631917 | 1.804191 |
| F   | 1.456088 | 0.475903 | 6.232491 |
| F   | 3.242759 | -2.447172 | 2.982181 |
| I   | -1.300971 | -0.748794 | -2.279721 |
| C   | -0.255826 | 4.340564 | 1.915908 |
| C   | -0.657102 | 3.584191 | 0.812621 |
| C   | -2.485294 | 2.750229 | 1.986347 |
| C   | -2.159829 | 3.493485 | 3.116958 |
| C   | -1.016115 | 4.288418 | 3.082350 |
| H   | 0.640266 | 4.947758 | 1.873458 |
| H   | -3.347007 | 2.095369 | 1.963504 |
| H   | -2.778316 | 3.427484 | 4.004652 |

**TS_Transmet**

|          |     |   |
|----------|-----|---|
| Charge   | 0   |   |
| Spin State | Triplet |   |
| Electronic Energy, BS1 (a.u.) | -4301.239642 |   |
| Thermal and entropic correction, BS1 (a.u.) | 0.365627 |   |
| Electronic Energy, BS2 (a.u.) | -7475.440563 |   |
| Gibbs Energy, BS2 (a.u.) | -7475.074936 |   |
| Number of Imaginary Frequencies | 1 |   |
| Imaginary Frequencies (cm⁻¹) | -49.0i |   |

**Molecular Geometry in Cartesian Coordinates**

|     |     |     |     |
|-----|-----|-----|-----|
| Cu  | -1.465339 | 0.424358 | -0.496765 |
| F   | -2.339262 | -1.214421 | 2.051454 |
| F   | -3.679864 | -0.670250 | -2.445154 |
| F   | -5.983479 | -3.684184 | 0.357314 |
| C   | -2.652272 | 3.171280 | -0.256945 |
| N   | -1.686247 | 1.985797 | -2.108326 |
| C   | -2.179737 | 3.160298 | -1.667240 |
| C   | -2.240358 | 4.282135 | -2.502696 |
| H   | -2.629794 | 5.227392 | -2.145608 |
| C   | -3.203503 | 4.303185 | 0.356342 |
| H   | -3.289839 | 5.237838 | -0.183425 |
| C   | -2.937074 | -0.894334 | -0.213461 |
### T2

| Element | Atomic Number | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|---------------|--------------|--------------|--------------|
| Cu      | 29            | -2.984188    | 1.924579     | 1.684941     |
| H       | 1             | -2.864582    | 0.963018     | 2.165330     |
| C       | 6             | -1.792207    | 4.170829     | -3.817066    |
| H       | 1             | -1.830442    | 5.031020     | -4.478831    |
| C       | 6             | -3.646238    | 4.221826     | 1.673693     |
| H       | 1             | -4.070506    | 5.095149     | 2.159040     |
| C       | 6             | 1.004804     | 2.429854     | -0.560773    |
| H       | 1             | 0.445461     | 1.477708     | 0.287063     |
| C       | 6             | 0.241159     | 1.922164     | 1.590631     |
| C       | 6             | 0.546687     | 3.195812     | 0.045029     |
| Cu      | 29            | 1.104079     | 4.106056     | 1.148036     |
| C       | 6             | 1.334014     | 3.725236     | -0.171113    |
| F       | 9             | -0.288206    | 1.076061     | 2.515124     |
| I       | 53            | 0.016245     | -1.463476    | -1.932757    |
| F       | 9             | 0.309492     | 0.401137     | 4.080510     |
| F       | 9             | 2.523906     | -0.165900    | 2.936159     |
| C       | 6             | 3.605169     | 1.397057     | 1.581898     |
| F       | 9             | 4.215908     | 2.004713     | 2.673947     |
| C       | 6             | 3.947471     | 1.497420     | 3.946304     |
| F       | 9             | 2.876812     | 0.004884     | 3.947471     |
| Cl      | 35            | 3.768800     | 1.742726     | 0.566958     |
| H       | 1             | 4.875459     | 2.852884     | 2.525883     |
| H       | 1             | 4.392687     | 1.949872     | 4.826933     |
| C       | 6             | 1.603483     | -1.334272    | 2.977199     |

### Molecular Geometry in Cartesian Coordinates

| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| Cu      | -2.029171    | 0.389943     | -0.990410    |
| F       | -1.633869    | -1.465577    | 1.626659     |
| F       | -3.579565    | -1.615078    | -2.669238    |
| F       | -3.845871    | -5.370460    | 0.174630     |
| C       | -3.681573    | 2.638510     | -0.084827    |
| N       | -2.158541    | 2.262261     | -1.900139    |
| C       | -3.067378    | 3.102921     | -1.350861    |
| C       | -3.358625    | 4.335999     | -1.938033    |
| H       | -0.901461    | 5.000044     | -1.497926    |
| C       | -4.512312    | 3.433422     | 0.709115     |
| H       | -4.771787    | 4.440154     | 0.407383     |
| C       | -2.576636    | -1.464901    | -0.537612    |
| N       | -3.341323    | 1.387147     | 0.299429     |
| C       | -3.719078    | -3.509005    | -1.279718    |
| C       | -2.315380    | -2.122034    | 0.652083     |

### Electronic Energy, BS1 (a.u.)

| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| Cu      | 1.399704     | -2.101584    | 4.129578     |
| F       | 0.142837     | -2.669417    | 1.769947     |
| C       | 0.522755     | -3.183956    | 4.074297     |
| H       | 1.920807     | -1.873529    | 5.051448     |
| C       | -0.120833    | -3.477974    | 2.874329     |
| H       | -0.328542    | -2.849369    | 0.809186     |
| C       | 0.351242     | -3.790021    | 4.958493     |
| H       | -0.812568    | -4.308729    | 2.788112     |
| C       | 2.777746     | 0.351813     | 1.715803     |
| Cu      | 0.975935     | -1.627177    | 1.820714     |
| C       | 1.636834     | -0.380986    | 0.081188     |
| C       | 3.253997     | -1.222882    | -0.737049    |
| C       | 3.570388     | -2.567486    | -0.630842    |
| C       | 4.164818     | -0.447776    | -1.434350    |
| C       | 4.718087     | -3.129185    | -1.186514    |
| C       | 5.327814     | -0.952394    | -2.010420    |
| C       | 5.603866     | -2.310856    | -1.882095    |
| C       | 3.938338     | 0.891645     | -1.591671    |
| C       | 2.739988     | -3.418858    | 0.030900     |
| C       | 4.987120     | -4.443599    | -1.062545    |
| C       | 6.719062     | -2.829325    | -2.425351    |
| C       | 6.183678     | -0.159086    | -2.683676    |
| Cl      | -4.354774    | -3.232019    | 2.788290     |
| Cl      | -5.927800    | -2.578188    | -2.382309    |
| F       | 0.325163     | 3.567795     | 3.320538     |
| F       | 1.870656     | 4.608648     | -1.033832    |

### Charge

0

### Spin State

Triplet

### Electronic Energy, BS2 (a.u.)

\[-4301.257248\]

### Gibbs Energy, BS2 (a.u.)

\[-7475.089510\]

### Number of Imaginary Frequencies

0

### Electronic Energy, BS1 (a.u.)

\[-4301.257248\]

### Electronic Energy, BS2 (a.u.)

\[-7475.089510\]

### Gibbs Energy, BS2 (a.u.)

\[-7475.089510\]
| Element | X (Å) | Y (Å) | Z (Å) |
|---------|------|------|------|
| C       | 0.142729 | 2.635129 | 0.440139 |
| C       | 0.450987 | 1.439487 | 1.075179 |
| C       | -0.187599 | 1.249102 | 2.293852 |
| C       | -1.085664 | 2.159280 | 2.847629 |
| C       | -1.353058 | 3.344855 | 2.170970 |
| C       | -0.734556 | 3.588369 | 0.949922 |
| F       | 0.713338 | 2.931899 | -0.763831 |
| F       | -2.228056 | 4.231994 | 2.676552 |
| F       | 0.053615 | 0.134637 | 3.031583 |
| I       | 0.182581 | -0.529384 | -2.274488 |
| C       | 3.808398 | -0.512054 | 4.164271 |
| C       | 3.109546 | -0.585710 | 2.951515 |
| C       | 3.732863 | 1.598112 | 2.430768 |
| C       | 4.444980 | 1.741969 | 3.617632 |
| C       | 4.478157 | 0.661378 | 4.498825 |
| H       | 3.829707 | -1.356024 | 4.842368 |
| H       | 3.678465 | 2.394162 | 1.696603 |
| H       | 4.956411 | 2.672812 | 3.837155 |
| H       | 5.020394 | 0.728348 | 5.436887 |
| C       | 2.368613 | -1.802649 | 2.514791 |
| C       | 2.367564 | -2.993411 | 3.253595 |
| C       | 1.017258 | -2.755810 | 0.891534 |
| C       | 1.658056 | -4.090253 | 2.768965 |

**TS_t-c**

| Charge | Spin State | Electronic Energy, BS1 (a.u.) | Thermal and entropic correction, BS1 (a.u.) | Electronic Energy, BS2 (a.u.) | Gibbs Energy, BS2 (a.u.) | Number of Imaginary Frequencies | Imaginary Frequencies (cm⁻¹) |
|--------|------------|-------------------------------|---------------------------------------------|-----------------------------|--------------------------|-------------------------------|--------------------------|
| 0      | Triplet    | -4301.249067                 | 0.366608                                   | -7475.449347                | -7475.082739             | 1                             | -153.41                  |

**Molecular Geometry in Cartesian Coordinates**

| Element | X (Å) | Y (Å) | Z (Å) |
|---------|------|------|------|
| Cu      | 2.020940 | -0.577444 | -0.886140 |
| F       | 1.175806 | 1.595301 | 1.362260 |
| F       | 3.897374 | 1.217718 | -2.473225 |
| F       | 3.617436 | 5.325707 | -0.170235 |
| C       | 3.501717 | -2.646787 | 0.585317 |
| N       | 2.198755 | -2.582000 | -1.428755 |
| C       | 3.023784 | -3.317847 | -0.645623 |
| C       | 3.347170 | -4.636463 | -0.972585 |
| H       | 4.012622 | -5.214195 | -0.343660 |
| C       | 2.438189 | -3.292419 | 1.581876 |
| H       | 4.529075 | -4.329287 | 1.472349 |
| C       | 2.499851 | 1.328018 | -0.575212 |
| N       | 3.125116 | -1.359291 | 0.723104 |
| C       | 3.771464 | 3.282074 | -1.352978 |
| C       | 2.025236 | 2.130911 | 0.448258 |
| C       | 3.380427 | 1.944274 | -1.450410 |
| C       | 1.939653 | -4.450218 | -2.908126 |
C 1.017413 -3.221009 2.673055
C 0.459743 -3.471661 1.423897
F -0.798202 -2.778487 -0.418702
F 1.787597 -4.148733 3.269114
F -0.166258 0.138076 3.287862
I 0.138739 0.169607 -2.727439
C -3.858588 2.403375 3.667549
C -3.206490 1.959557 2.510544
C -3.852517 -0.235674 2.943051
C -4.531424 0.132807 4.101220
C -4.525233 1.478471 4.467827
H -3.815318 -1.263808 2.599835
H -5.042771 -0.616708 4.695199
H -5.032925 1.807747 5.368904
C -2.472037 2.866640 1.585422
C -2.516136 4.261301 1.699625
C -1.071154 3.021128 -0.261212
Cl -1.800013 5.040094 0.793724
H -3.104696 4.736552 2.474785
C -1.058355 4.411947 -0.204832

T3
Charge 0
Spin State Triplet
Electronic Energy, BS1 (a.u.) -4301.261225
Thermal and entropic correction, BS1 (a.u.) 0.367660
Electronic Energy, BS2 (a.u.) -7475.461640
Gibbs Energy, BS2 (a.u.) -7475.093980
Number of Imaginary Frequencies 0

Molecular Geometry in Cartesian Coordinates

Cu 2.299381 -0.522202 -0.608824
F 0.908096 1.530745 1.457291
F 4.193250 1.490303 -1.935314
F 2.977069 5.551675 0.129125
C 3.333234 -2.554109 1.250446
N 2.618905 -2.527950 -1.045345
C 3.113158 -3.273411 -0.025892
C 3.360686 -4.638888 -0.182190
H 3.732646 -5.231616 0.643379
C 3.796229 -3.174149 2.414976
H 0.438817 -4.228684 2.422959
C 2.526329 1.422441 -0.265201
N 3.021952 -1.239161 1.237762
C 3.607374 3.528903 -0.924696
C 1.794458 2.168029 0.645842
C 3.431191 2.146782 -1.025454
C 2.626844 -4.464661 -2.460323
H 2.419015 -4.887409 -3.436757
H 3.597062 -1.068088 3.554903
H 3.674080 -0.447015 4.440063

I 0.813271 0.077504 -2.853241

S63
| C     | -3.976414 | 2.978346 | 3.094174 | N     | -2.671261 | 1.116911 | 2.334778 |
|-------|------------|---------|---------|-------|-----------|---------|---------|
| C     | -3.071386  | 2.396547 | 2.197479| N     | -1.825947 | 2.357521 | 0.135253 |
| C     | -3.142033  | 0.383333 | 3.348111| Cu    | -1.707120 | 0.314410 | 0.459839 |
| C     | -4.040312  | 0.888804 | 4.286810| C     | -3.189192 | -0.346522 | -0.731378 |
| C     | -4.463602  | 2.210724 | 4.150483| C     | -3.419258 | 0.055226 | -2.037054 |
| H     | -4.311444  | 4.001078 | 2.967415| C     | -4.063159 | -1.302986 | -0.238465 |
| H     | -2.779352  | -0.637392 | 3.401132| C     | -4.440453 | -0.464647 | -2.830181 |
| H     | -4.396751  | 0.259921 | 5.095530| C     | -5.101711 | -1.854915 | -0.983568 |
| H     | -5.169320  | 2.641129 | 4.854222| C     | -5.288089 | -1.429863 | -2.295816 |
| C     | -2.484539  | 3.120139 | 1.039336| F     | -3.925795 | -1.765622 | 1.037023 |
| C     | -2.560668  | 4.507225 | 0.884946| F     | -2.633114 | 1.000658 | -2.620004 |
| C     | -1.218147  | 2.939005 | -0.908904| F     | -4.623143 | -0.048141 | -4.098332 |
| C     | -1.933281  | 5.109519 | -0.203693| F     | -6.284587 | -1.942949 | -3.038421 |
| H     | -3.075787  | 5.115432 | 1.618072| F     | -5.926672 | -2.784757 | -0.461758 |
| C     | -1.240742  | 4.315427 | -1.114609| Cl    | 0.976236 | 4.423652 | 1.989960  |
| H     | -0.704437  | 2.271107 | -1.589221| Cl    | 4.759601 | 4.383169 | -1.917862 |
| H     | -1.975499  | 6.187071 | -0.327604| F     | 0.862518 | -2.809724 | 3.906917  |
| H     | -0.724367  | 4.741725 | -1.967394| F     | 0.073075 | -4.708805 | -0.350896 |

**MECP2**

Charge 0

Spin State

Electronic Energy, BS1 (a.u.) -4301.242122

Thermal and entropic correction, BS1 (a.u.) 0.365919

Electronic Energy, BS2 (a.u.) -7475.439586

Gibbs Energy, BS2 (a.u.) -7475.073667

Number of Imaginary Frequencies 0

**Molecular Geometry in Cartesian Coordinates**

| Cu    | -0.682714 | 0.993611 | -2.125406 |
|-------|-----------|---------|-----------|
| F     | -4.209155 | 2.067598 | 0.832621  |
| F     | -1.805583 | 5.496595 | -1.328336 |
| H     | -3.787619 | -2.616350 | -2.174333 |
| C     | -3.703144 | -2.187986 | 0.194462  |
| C     | -4.071979 | -3.050074 | -0.783016 |
| C     | -4.660967 | -4.278745 | -0.467883 |
| H     | -9.446769 | -4.970936 | -1.250259 |
| C     | -1.40073 | -3.357350 | -3.307524 |
| C     | -4.683568 | -4.290195 | -3.218036 |
| C     | -2.467366 | 1.427783 | -0.632847 |
| N     | -3.122179 | -1.448337 | -2.285145 |
| C     | -3.038015 | 3.793018 | -0.241055 |
| C     | -1.489381 | 1.894140 | -1.499388 |
| C     | -3.228111 | 2.424374 | -0.031661 |
| C     | -4.469801 | -3.725463 | 1.864098  |
| H     | -4.599231 | -3.949229 | 2.916701  |
| C     | -3.075077 | -1.678570 | -4.665418 |
| C     | -2.765808 | -1.278736 | -5.625113 |
| C     | -2.030435 | 4.192186 | -1.120524 |
| C     | -3.895537 | -2.516755 | 1.481760  |
| H     | -3.569057 | -1.783201 | 2.211887  |
**S2**

| Number of Imaginary Frequencies | Electronic Energy, BS1 (a.u.) | Spin State | Charge |
|--------------------------------|--------------------------------|------------|--------|
|                                |                                |            | 0      |

**Molecular Geometry in Cartesian Coordinates**

|            | Cu     | F       | H       | C       |
|------------|--------|---------|---------|---------|
| Number      | -1.026695 | -0.294699 | 2.129190 | -6.446412 |
| X           | -1.229805 | 0.970231 | 1.321197|
| Y           | 1.918907  | 1.520417 | 5.966374|
| Z           | -4.237457 | 1.072572 | 0.369178|
| Number      | -0.343036 | 0.234827 | 2.021105|
| X           | -0.639199 | 0.527699 | 0.614896|
| Y           | -0.514476 | 1.580478 | 1.651797|
| Z           | -0.824673 | 1.528111 | 0.990677|
| Number      | -0.504247 | 1.552016 | 0.094826|
| X           | 1.297688  | 3.285049 | 1.366900|
| Y           | 1.200847  | 2.535805 | -2.846484|
| Z           | -1.427344 | 1.113430 | 0.163222|
| Number      | -0.486142 | 2.049442 | 1.635152|
| X           | -1.226966 | 0.295100 | 2.049442|
| Y           | 1.427344  | 1.113430 | 0.163222|
| Z           | -0.504247 | 1.552016 | 0.094826|
| Number      | 1.285404  | -4.257992 | 1.366900|
| X           | 1.854634  | -1.61787 | 1.783257|
| Y           | 0.652960  | 1.322258 | -2.044565|
| Z           | -0.554604 | -0.561726 | 0.503274|
| Number      | 0.631274  | 1.538747 | -2.082431|
| X           | 1.429800  | -1.448712 | 2.077141|
| Y           | 0.340561  | 1.119851 | -1.764749|
| Z           | -3.724205 | -0.952246 | 0.503274|
| Number      | 0.305392  | 1.538747 | -2.082431|
| X           | -6.69571 | 0.021579 | -0.165296|
| Y           | 2.429452  | 0.021579 | -1.785711|
| Z           | 1.620108  | -0.038291 | 0.503274|
| Number      | 0.631614  | 1.538747 | -2.082431|

**S65**
Molecular Geometry in Cartesian Coordinates

TS_RE_Homo

Charge

Spin State

Electronic Energy, BS1 (a.u.)

Thermal and entropic correction, BS1 (a.u.)

Electronic Energy, BS2 (a.u.)

Gibbs Energy, BS2 (a.u.)

Number of Imaginary Frequencies

Imaginary Frequencies (cm⁻¹)

-220.3

S66
S3
Charge
0
Spin State
Singlet
Electronic Energy, BS1 (a.u.)
-4301.314552
Thermal and entropic correction, BS1 (a.u.)
0.368868
Electronic Energy, BS2 (a.u.)
-7475.502919
Gibbs Energy, BS2 (a.u.)
-7475.134051
Number of Imaginary Frequencies
0

Molecular Geometry in Cartesian Coordinates

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Cu   | -1.099501 | 0.670748 | -1.686114 |
| F    | -0.165458 | -2.310238 | -1.774765 |
| C    | 1.532708  | 2.015682  | -2.658082 |
| F    | 4.256432  | -1.769342 | -3.317943 |
| C    | -4.088449 | 0.406853  | -1.921068 |
| N    | -2.485489 | 1.992157  | -1.059476 |
| C    | -3.796777 | 1.675377  | -1.196349 |
| C    | -4.794730 | 2.491326  | -0.655696 |
| H    | -5.838593 | 2.214415  | -0.732720 |
| C    | -5.371643 | 0.035458  | -2.340444 |
| H    | -6.223979 | 0.683811  | -2.178259 |
| C    | 0.588660  | -0.101423 | -2.184426 |
| N    | -3.022720 | -0.389240 | -2.139847 |
| C    | 2.890734  | 0.144769  | -3.042273 |
| H    | 0.830593  | -1.469338 | -2.182479 |
| C    | 1.660977  | 0.665220  | -2.632140 |
| C    | -3.085834 | 3.992925  | 0.122212 |
| H    | -2.755393 | 4.894487  | 0.625885 |
| C    | -4.435629 | -2.012428 | -3.193905 |
| H    | -4.529758 | -2.978112 | -3.678529 |
| C    | 3.074911  | -1.237544 | -2.973238 |
| C    | -2.143702 | 3.125582  | -0.425165 |
| H    | -1.082445 | 3.334012  | -0.350828 |
| C    | 2.040367  | -2.067918 | -2.544190 |
| H    | -3.188949 | -1.561557 | -2.761258 |
| H    | -2.290092 | -2.156398 | -2.891854 |
| C    | -4.439910 | 3.661816  | 0.010476 |
| H    | -5.200161 | 4.301730  | 0.437135 |
| C    | -5.542009 | -1.191414 | -2.980618 |
| Cu   | -6.530926 | -1.501607 | -3.303671 |
| Cl   | -2.321948 | -0.262832 | 1.716631 |
| F    | -2.102089 | -1.092094 | 1.563772 |

Energy, BS2 (a.u.)
3.095294

N -3.119130 0.669572 -1.393369  F -3.005240 -1.742950 1.129895
N -0.570823 1.376569 -1.326900  F -1.231727 -2.886971 -3.144751
Cu -1.454488 -0.400857 -1.039003  F -2.948908 -4.932400 -3.283638
C -1.992142 -2.259727 -0.975508  F -4.656099 -5.451997 -1.214221
C -2.049029 -3.091061 -2.101632  F -4.655452 -3.831235 0.982219
C -2.896504 -2.545147 0.060964  Cl -4.263986 1.580548 2.005037
C -2.933452 -4.160371 -2.190951  Cl -1.132813 5.882578 0.883708
C -3.787272 -3.611180 -0.012516  F 1.880242 -3.317610 2.001856
C -3.801926 -4.429782 -1.137536  F 3.076181 -2.177490 -2.418684
### Molecular Geometry in Cartesian Coordinates

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Cu      | -2.08766 | 0.478826 | 0.913546 |
| F       | -1.492400 | 1.649181 | -1.904861 |
| F       | -0.587446 | 2.466935 | 2.669944 |
| F       | 0.589452 | 5.662111 | -0.588145 |
| C       | 1.148912 | 0.224636 | 0.568583 |
| N       | -3.281259 | -0.839392 | 1.983735 |
| C       | -4.585725 | -1.048566 | 1.675231 |
| C       | -5.341797 | -2.003802 | 2.362497 |
| H       | -6.374478 | -2.184510 | 2.091218 |
| C       | -6.519024 | -0.155104 | 0.285411 |
| H       | -7.243568 | -0.697805 | 0.880907 |
| C       | -1.091801 | 1.959205 | 0.411463 |
| N       | -4.247548 | 0.466129 | -0.155693 |
| Cu      | -0.025779 | 4.087760 | 1.069225 |
| C       | -1.006729 | 2.426322 | -0.893522 |
| C       | -0.572988 | 2.834853 | 1.359577 |
| C       | -3.420075 | -2.500780 | 3.714528 |
| H       | -2.922264 | -3.042466 | 4.511106 |
| C       | -6.006954 | 1.353478 | -1.519409 |
| C       | -6.300759 | 1.981122 | -2.353908 |
| C       | 0.037285 | 4.483699 | -0.267228 |
| C       | -2.724312 | -1.542101 | 2.985861 |
| C       | -1.687118 | -1.316800 | 3.198448 |
| C       | -0.459541 | 3.654365 | -1.271915 |
| C       | -4.662852 | 1.233671 | -1.165838 |
| H       | -3.881224 | 1.748951 | -1.719291 |
| C       | -4.753995 | -2.738722 | 3.388337 |
| H       | -5.31638 | -3.486145 | 3.923062 |
| H       | -6.947581 | 0.643633 | -0.773702 |
| H       | -8.005509 | 0.710871 | -1.009077 |
| H       | -1.914198 | -2.617312 | -0.668890 |
| H       | -0.736035 | -2.069906 | -1.191455 |
| C       | -0.858707 | -1.253891 | -2.316707 |
| C       | -2.090137 | -0.968428 | -2.892192 |
| C       | -3.241598 | -1.525882 | -2.349732 |

### TS_I

| Charge         | 0 |
|----------------|---|
| Spin State     | Singlet |
| Electronic Energy, BS1 (a.u.) | -4301.316900 |
| Thermal and entropic correction, BS1 (a.u.) | 0.370831 |
| Electronic Energy, BS2 (a.u.) | -7475.506390 |
| Gibbs Energy, BS2 (a.u.) | -7475.135559 |
| Number of Imaginary Frequencies | 1 |
| Imaginary Frequencies (cm⁻¹) | -35.2i |

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S68
F  3.368485  -4.595987  -1.672671  F  -2.175508  -0.139394  -3.936891
Cl -0.411829  4.172076  -2.938790  F  -4.267929  -2.863696  -0.695132
Cl  0.565107  5.159512  2.317198  I  4.879300  -1.144506  -0.589235

P2
Charge
Spin State
Electronic Energy, BS1 (a.u.)
-4301.326982
Electronic Energy, BS2 (a.u.)
-7475.526096
Gibbs Energy, BS2 (a.u.)
-7475.157514
Number of Imaginary Frequencies
0

Molecular Geometry in Cartesian Coordinates
Cu  -2.830598  0.946750  0.312862  F  1.755984  0.237474  1.935935
F  -0.789227  -0.711410  1.957019  I  0.534163  1.702182  -2.351795
F  -4.836534  -1.330435  -0.406165  C  0.522577  -4.730586  -0.633067
F  -2.774202  -4.984735  1.746592  C  0.111542  -3.422513  -0.909021
C  -2.564024  3.724049  1.512366  C  1.932194  -2.575363  0.260486
N  -2.843870  2.691238  -0.653221  C  2.411565  -3.847178  0.559264
C  -2.679973  3.847725  0.304021  C  1.688811  -4.945419  0.093359
C  -2.643951  5.079366  -0.627255  H  -0.047734  -5.575014  -1.00695
H  -2.516215  5.988378  -0.068581  H  2.435253  -1.688278  0.612841
C  -2.088565  4.756717  2.329844  H  3.324445  -3.957709  1.134741
H  -1.769416  5.701338  1.956565  H  2.022183  -5.957501  0.306123
C  -2.814786  -0.917252  0.754301  C  -1.108783  -3.109045  -1.703143
N  -2.926765  2.531102  0.209294  C  -2.087487  -4.058148  -2.019624
C  -3.841816  -3.159193  0.679713  C  -2.295912  -1.443877  -2.799713
C  -1.813509  -1.495494  1.524207  C  -3.198483  -3.658544  -2.760774
C  -3.813328  -1.799118  0.360641  H  -2.006071  -5.082166  -1.675620
C  -2.991745  3.927929  -2.707205  C  -3.311892  -2.327398  -3.160327
H  -3.120673  3.909593  -3.783457  H  2.325359  -0.392963  -3.074114
C  -2.377388  3.302277  4.224473  H  -3.972688  -4.377341  -3.007357
H  -2.318106  3.092599  5.287248  H  -4.166093  -1.977243  -3.729559
C  -2.795400  -3.677126  1.442487  N  0.824520  -2.358640  -0.463782
C  -2.999425  2.736524  -1.986420  N  -1.228482  -1.826097  -2.093613
H  -3.119166  1.779357  -2.480155  Cu  0.326348  -0.543994  -1.243314
C  -1.765371  -2.845630  1.881185  C  4.120710  0.334877  0.436021
C  -2.833505  2.326702  3.338364  C  4.395832  -0.189204  -0.831383
H  -3.131212  1.341218  3.687961  C  4.585480  -0.384720  1.542457
C  -2.798978  5.118956  -2.011465  C  5.075769  -1.390696  -0.996496
H  -2.777631  6.069661  -2.530566  C  5.255877  -1.594423  1.398460
C  -1.997285  4.538639  3.702713  C  5.500588  -2.098101  0.124049
H  -1.624310  5.322967  4.354394  F  4.347430  0.066660  2.781525
C  3.481614  2.723331  -0.048451  F  3.937851  0.430757  -1.926380
C  3.241993  1.510311  0.598653  F  5.279435  -1.890973  -2.220882
C  2.059636  1.399777  1.335914  F  6.114893  -3.275347  -0.018413
C  1.151346  2.444208  1.431578  F  5.644693  -2.290971  2.473770
C  1.413896  3.638985  0.770250  Cl  -0.465837  -3.503773  2.845470
C  2.585037  3.782218  0.033529  Cl  -5.128817  -4.211675  0.140122
F  4.583106  2.875304  -0.797260  F  0.006068  2.280735  2.104743
F  0.522648  4.635596  0.802388  F  2.816735  4.919498  -0.633990
4 [Cu(bipy)Rf]

Charge
Spin State
Electronic Energy, BS1 (a.u.)
Thermal and entropic correction, BS1 (a.u.)
Electronic Energy, BS2 (a.u.)
Gibbs Energy, BS2 (a.u.)
Number of Imaginary Frequencies

Molecular Geometry in Cartesian Coordinates

Reaction between [Cu(bipy)Pf] and p-substituted Ar-I (p-X-Ar-I; X = H, OMe, Br, NO2)

PhH-I

Charge
Spin State

S70
### Electronic Energy, BS1 (a.u.)
-243.080884

### Thermal and entropic correction, BS1 (a.u.)
0.058391

### Electronic Energy, BS2 (a.u.)
-529.548381

### Gibbs Energy, BS2 (a.u.)
-529.489990

### Number of Imaginary Frequencies
0

#### Molecular Geometry in Cartesian Coordinates

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| C     | -1.260003 | -1.218455 | -0.000000 | I     | 1.564232 | 0.000000 | -0.000001 |
| C     | -2.657986 | -1.208516 | 0.000000 | H     | -4.443947 | 0.000000 | 0.000002  |
| C     | -3.357904 | 0.000000  | 0.000002 | H     | -3.195490 | 2.152567 | 0.000003  |
| C     | -2.657986 | 1.208516  | 0.000002 | H     | -0.718026 | 2.157733 | 0.000002  |
| C     | -1.260003 | 1.218455  | 0.000001 | H     | -3.195490 | -2.152567| -0.000000 |
| C     | -0.578337 | 0.000000  | 0.000000 | H     | -0.718026 | -2.157733| -0.000001 |

#### PhBr-I

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| Charge| 0     |       |       |       |       |
| Spin State| Singlet |       |       |       |       |
| Electronic Energy, BS1 (a.u.)| -2813.886115 |       |       |       |       |
| Thermal and entropic correction, BS1 (a.u.)| 0.045134 |       |       |       |       |
| Electronic Energy, BS2 (a.u.)| -3103.131816 |       |       |       |       |
| Gibbs Energy, BS2 (a.u.)| -3103.086682 |       |       |       |       |
| Number of Imaginary Frequencies| 0 |       |       |       |       |

#### Molecular Geometry in Cartesian Coordinates

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| C     | -0.141984 | 1.215807 | -0.000001 | I     | -2.964340 | 0.000000 | -0.000001 |
| C     | 1.254617  | 1.215390 | 0.000001  | H     | 1.795759  | -2.154856| 0.000002  |
| C     | 1.936978  | 0.000000 | 0.000001  | H     | -0.677390 | -2.158576| 0.000001  |
| C     | 1.254617  | -1.215390| 0.000001  | H     | 1.795759  | 2.154856 | -0.000001 |
| C     | -0.141984 | -1.215807| 0.000001  | H     | -0.677390 | 2.158576 | -0.000002 |
| C     | -0.828175 | 0.000000 | 0.000000  | Br    | 3.853396  | 0.000000 | 0.000002  |

#### PhOMe-I

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| Charge| 0     |       |       |       |       |
| Spin State| Singlet |       |       |       |       |
| Electronic Energy, BS1 (a.u.)| -357.609848 |       |       |       |       |
| Thermal and entropic correction, BS1 (a.u.)| 0.087665 |       |       |       |       |
| Electronic Energy, BS2 (a.u.)| -644.123883 |       |       |       |       |
| Gibbs Energy, BS2 (a.u.)| -644.036218 |       |       |       |       |
| Number of Imaginary Frequencies| 0 |       |       |       |       |

#### Molecular Geometry in Cartesian Coordinates

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| C     | -0.190523 | 0.073919 | -0.000258 | H     | 2.285924 | 2.401801 | 0.000154 |
| C     | 1.797813  | 1.432281 | -0.000160 | H     | 0.120780 | -2.062848| -0.000629 |
| C     | 0.585328  | -1.082768| -0.000541 | H     | 2.568286 | -1.896345| -0.000852 |
| C     | 0.410558  | 1.337231 | -0.000090 | O     | 3.936516 | 0.483826 | 0.000374  |
| C     | 2.593599  | 0.274873 | -0.000398 | C     | 4.797949 | -0.654382| 0.000973  |
| C     | 1.981004  | -0.985846| -0.000646 | H     | 4.650257 | -1.271280| 0.896281  |
| I     | -2.325434 | -0.077759| 0.000129  | H     | 4.651871 | -1.272161| -0.894021 |
| H     | -0.191228 | 2.239476 | 0.000260  | H     | 5.815644 | -0.259895| 0.001711  |

#### PhNO2-I

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| Charge| 0     |       |       |       |       |
| Spin State| Singlet |       |       |       |       |
| Electronic Energy, BS1 (a.u.)| -447.582194 |       |       |       |       |
| Thermal and entropic correction, BS1 (a.u.)| 0.056779 |       |       |       |       |
### IO-PhH

**Charge**

0

**Spin State**

Singlet

| Property                                    | Value                      |
|---------------------------------------------|----------------------------|
| Electronic Energy, BS1 (a.u.)                | -1663.729967               |
| Thermal and entropic correction, BS1 (a.u.) | 0.235098                   |
| Electronic Energy, BS2 (a.u.)                | -3393.963093               |
| Gibbs Energy, BS2 (a.u.)                     | -3393.727995               |
| Number of Imaginary Frequencies              | 0                          |

**Molecular Geometry in Cartesian Coordinates**

| Atom | C      | I     | H     |
|------|--------|-------|-------|
| C    | -0.49294 | 0.750494 | 1.294748 |
| C    | 2.300531 | 2.019484 | -0.125539 |
| N    | 1.887738 | 0.536722 | 1.731958 |
| C    | 2.818372 | 1.189188 | 0.994691 |
| C    | 4.182351 | 1.189188 | 1.271550 |
| H    | 4.912763 | 2.063082 | -1.227790 |
| C    | 3.086992 | 2.377220 | -1.227790 |
| H    | 4.121763 | 2.063082 | -1.295562 |
| C    | 0.470709 | -1.462509 | -1.539804 |
| N    | 1.006643 | 2.362700 | -0.039950 |
| C    | -0.985970 | 0.203378 | -2.572741 |
| C    | -0.694366 | -2.298082 | -1.347644 |
| C    | 0.279739 | -0.212658 | -2.148752 |
| C    | 6.29061 | -0.447588 | 3.060481 |
| H    | 3.901914 | -1.105536 | 3.878040 |
| C    | 1.161045 | 3.481487 | -2.156261 |
| H    | 0.670950 | 4.056339 | -2.934913 |
| C    | -2.096637 | -0.618754 | -2.393068 |
| C    | 2.288572 | -0.260115 | 2.736588 |
| H    | 1.498560 | -0.765135 | 3.213132 |
| C    | -1.950540 | -1.865759 | -1.781740 |
| C    | 0.447853 | 3.074245 | -1.028479 |

### IO-PhBr

**Charge**

0

**Spin State**

Singlet

| Property                                    | Value                      |
|---------------------------------------------|----------------------------|
| Electronic Energy, BS1 (a.u.)                | -4234.537814               |
| Thermal and entropic correction, BS1 (a.u.) | 0.222859                   |
| Electronic Energy, BS2 (a.u.)                | -5967.548221               |
| Gibbs Energy, BS2 (a.u.)                     | -5967.325262               |
### Molecular Geometry in Cartesian Coordinates

|          | X   | Y   | Z   |
|----------|-----|-----|-----|
| Cu       | -0.702691 | -0.954838 | 1.405600 |
| C       | -2.671366 | -1.959340 | -0.661872 |
| N       | -2.691528 | -0.772522 | 1.438626 |
| C       | -3.431537 | -1.298783 | 0.432904 |
| C       | -4.826008 | -1.199136 | 0.432572 |
| H       | -5.406421 | -1.650864 | -0.363037 |
| C       | -3.195090 | -2.132007 | -1.949356 |
| H       | -4.194600 | -1.791845 | -2.194438 |
| C       | -0.532098 | 1.674561 | -1.102589 |
| N       | -1.415823 | -2.334935 | -0.350538 |
| C       | 1.003731 | 0.105239 | -2.097081 |
| C       | 0.530406 | 2.442001 | -0.622485 |
| C       | -0.307704 | 0.508342 | -1.836032 |
| C       | -4.694794 | 0.016233 | 2.501762 |
| H       | -5.148537 | 0.545483 | 3.332283 |
| C       | -1.096820 | -3.117940 | -2.595561 |
| H       | -0.441360 | -3.578013 | -3.327474 |
| C       | 2.062780 | 0.875278 | -1.621898 |
| C       | -3.312252 | -0.132513 | 2.443755 |
| H       | -2.665874 | 0.277202 | 3.212161 |
| C       | 1.840923 | 2.038648 | -0.886342 |
| C       | -0.651097 | -2.899615 | -1.291579 |

### IO-PhOMe

|          | X   | Y   | Z   |
|----------|-----|-----|-----|
| Cu       | -0.560124 | 0.428518 | -1.406089 |
| C       | -3.026354 | 1.814846 | -0.417832 |
| N       | -2.500280 | 0.236919 | -1.559594 |
| C       | -3.467086 | 0.502611 | -0.969862 |
| C       | -4.779425 | 0.028598 | -0.873479 |
| H       | -5.550827 | 0.619529 | -0.395352 |
| C       | -3.891100 | 2.723215 | 0.204399 |
| H       | -4.949937 | 2.514699 | 0.300076 |
| C       | 0.068253 | -0.805727 | 1.884783 |
| N       | -1.708710 | 2.075321 | -0.539465 |
| C       | 1.222306 | 1.299738 | 2.069537 |
| C       | 1.285086 | -1.480967 | 1.825066 |
| C       | 0.029957 | 0.587126 | 2.007814 |
| C       | -0.687587 | -1.981205 | -1.999479 |
| H       | -4.285963 | -2.963204 | -2.414657 |
| C       | -2.007098 | 4.175099 | 0.575994 |
| H       | -1.564482 | 5.089941 | 0.954990 |

### Number of Imaginary Frequencies

|          |       |
|----------|-------|
| IO-PhOMe | 0     |

### Molecular Geometry in Cartesian Coordinates

|          | X   | Y   | Z   |
|----------|-----|-----|-----|
| Cu       | 2.456311 | 0.632447 | 2.012924 |
| C       | 2.804304 | -1.443376 | -2.059277 |
| N       | 1.980264 | -1.988254 | -2.507581 |
| C       | 2.483535 | -0.763527 | 1.895040 |
| C       | -1.213084 | 3.221507 | -0.059332 |
| H       | -0.143844 | 3.357829 | -0.184799 |
| C       | -5.090574 | -1.226849 | -1.392608 |
| H       | -6.104353 | -1.608335 | -1.320876 |
| C       | -3.370868 | 3.915006 | 0.706790 |
| N       | -4.026338 | 4.630205 | 1.194084 |
| C       | 1.854640 | -1.164949 | -1.675061 |
| C       | 1.327593 | 0.110899 | -1.520730 |
| C       | 2.271075 | 1.094889 | -1.257317 |
| C       | 3.636062 | 0.856202 | -1.135940 |
| H       | 4.103915 | -0.444955 | -1.285202 |
| C       | 3.207104 | -1.472689 | -1.558638 |
| H       | 1.022523 | -2.222712 | -1.919218 |
**IO-PhNO₂**

**Charge**

0

**Spin State**

Singlet

**Electronic Energy, BS1 (a.u.)**

-1868.235707

**Thermal and entropic correction, BS1 (a.u.)**

0.234105

**Electronic Energy, BS2 (a.u.)**

-3598.561736

**Gibbs Energy, BS2 (a.u.)**

-3598.327631

**Number of Imaginary Frequencies**

0

**Molecular Geometry in Cartesian Coordinates**

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 0.279495 | -0.598093 | 1.296616 |
| C    | -0.209360 | -2.200821 | 0.314017 |
| C    | -1.654621 | -0.375765 | 1.821207 |
| C    | -2.575297 | -1.250505 | 1.350853 |
| C    | -3.895686 | -1.230169 | 1.809673 |
| C    | -4.613303 | -1.956048 | 1.446061 |
| C    | -2.954887 | -2.847891 | -0.579940 |
| C    | -4.025685 | -2.686153 | -0.536372 |
| C    | -1.535810 | 1.284945  | -1.390423 |
| C    | -0.756949 | -2.355569 | 0.248369 |
| C    | 0.127178  | -0.180091 | -2.328446 |
| C    | -0.556643 | 2.219621  | -1.039008 |
| C    | -1.207961 | 0.092617  | -2.042494 |
| C    | -3.329036 | 0.635780  | 3.217354 |
| C    | -3.582455 | 1.399564  | 3.940510 |
| C    | -1.023029 | -3.842197 | -1.614626 |
| C    | -0.558104 | -4.478373 | -2.360236 |
| C    | 1.098375  | 0.752540  | -1.970656 |
| C    | -2.028855 | 0.545283  | 2.724649 |
| H    | -1.250896 | 1.225694  | 3.053502 |
| C    | 0.777192  | 1.953357  | -1.339147 |
| C    | -0.236599 | -3.155348 | -0.688938 |
| H    | 0.846461  | -3.227944 | -0.696416 |

**TS_OA-PhH**

**Charge**

0

**Spin State**

Singlet

**Electronic Energy, BS1 (a.u.)**

-1663.693335

**Thermal and entropic correction, BS1 (a.u.)**

0.235349

**Electronic Energy, BS2 (a.u.)**

-3393.927444

**Gibbs Energy, BS2 (a.u.)**

-3393.692095

**Number of Imaginary Frequencies**

1

**Imaginary Frequencies (cm⁻¹)**

-176.0i

**Molecular Geometry in Cartesian Coordinates**

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 5.414642 | -0.712110 | -1.113993 |
| F    | 1.874658 | 2.390049  | -1.063596 |
| I    | -1.762812 | -1.904066 | 1.774213 |
| F    | 3.663151  | -2.737120 | -1.681334 |
| F    | 4.508399  | 1.838656  | -0.828085 |
| H    | -0.914626 | 1.116482  | 2.042828 |
| H    | 1.215182  | 2.381853  | 2.148955 |

**Molecular Geometry in Cartesian Coordinates**
TS_OA-PhBr

Charge
Spin State
Electronic Energy, BS1 (a.u.)
Thermal and entropic correction, BS1 (a.u.)
Electronic Energy, BS2 (a.u.)
Gibbs Energy, BS2 (a.u.)
Number of Imaginary Frequencies
Imaginary Frequencies (cm\(^{-1}\))

Molecular Geometry in Cartesian Coordinates

| Atomic Symbol | X       | Y       | Z       |
|---------------|---------|---------|---------|
| Cu            | -0.901488 | -0.038058 | -0.168436 |
| C             | -3.345844 | -0.131209 | 1.714178 |
| N             | -2.859973 | 0.812745 | -0.446519 |
| C             | -3.814894 | 0.525092 | 0.461841 |
| C             | -5.156078 | 0.851072 | 0.222970 |
| C             | -5.927506 | 0.593807 | 0.938529 |
| C             | -4.162305 | -0.273489 | 2.843965 |
| H             | -5.185305 | 0.082273 | 2.840684 |
| C             | 0.633331 | -1.399082 | -0.684412 |
| N             | -2.062186 | -0.547747 | 1.720039 |
| C             | 2.387671 | -2.211375 | 0.760927 |
| C             | 1.583529 | -0.898891 | -1.586989 |
| C             | 1.028923 | -2.111426 | 0.452738 |
| C             | -4.496025 | 1.822226 | -1.876797 |
| H             | -4.717626 | 2.339520 | -2.803992 |
| C             | -2.305753 | -1.274960 | 3.950013 |
| H             | -1.850947 | -1.723630 | 4.871529 |
| C             | 3.326763 | -1.650140 | -0.102216 |
I  -1.413031  -2.174529  -1.688395  H  2.700386  -2.730517  1.660438
F  1.876682  4.118760  -2.046673  H  1.268942  -0.376695  -2.482685
F  2.801132  2.863328  2.425006  Br  5.191833  -1.788211  0.315351
H  0.290975  -2.560586  1.105353  H  3.676183  -0.586242  -1.953419

**TS_OA-PhOMe**

| Charge | 0 |
| Spin State | Singlet |
| Electronic Energy, BS1 (a.u.) | 1778.221513 |
| Thermal and entropic correction, BS1 (a.u.) | 0.265004 |
| Electronic Energy, BS2 (a.u.) | 3508.499541 |
| Gibbs Energy, BS2 (a.u.) | 3508.234537 |
| Number of Imaginary Frequencies | 1 |
| Imaginary Frequencies (cm⁻¹) | -124.3i |

**Molecular Geometry in Cartesian Coordinates**

| C  | Cu | 0.698750 | -0.067286 | -0.190165 |
| C  | 3.242296 | -0.187915 | 1.570519 |
| N  | -2.397763 | 1.350722 | -0.084702 |
| C  | -3.438708 | 1.008267 | 0.703996 |
| C  | -4.616792 | 1.766598 | 0.704462 |
| H  | -5.452488 | 1.496253 | 1.338233 |
| C  | -4.224457 | -0.656364 | 2.453928 |
| H  | -5.192906 | -0.175568 | 2.520329 |
| C  | 0.675491 | -1.214023 | -1.023125 |
| N  | -2.039922 | -0.790999 | 1.478101 |
| C  | 2.246486 | -2.652418 | 0.087761 |
| C  | 1.710006 | -0.586279 | -1.719628 |
| C  | 0.926350 | -2.312772 | -0.197568 |
| C  | -3.623191 | 3.233152 | -0.921129 |
| H  | -3.649609 | 4.100477 | -1.571571 |
| C  | -2.687508 | -2.357107 | 3.177259 |
| H  | -2.421229 | -3.207062 | 3.796315 |
| C  | 3.304368 | -1.927076 | -0.480330 |
| C  | -2.484868 | 2.433433 | -0.867954 |
| H  | -1.603054 | 2.657432 | -1.453731 |
| C  | 3.030173 | -0.923635 | -1.425991 |
| C  | -1.768220 | -1.833676 | 2.269513 |
| H  | -0.772525 | -2.252821 | 2.172816 |
| C  | -4.709332 | 2.885571 | -0.119140 |

**TS_OA-PhNO₂**

| Charge | 0 |
| Spin State | Singlet |
| Electronic Energy, BS1 (a.u.) | -1868.198873 |
| Thermal and entropic correction, BS1 (a.u.) | 0.233430 |
| Electronic Energy, BS2 (a.u.) | -3598.527820 |
| Gibbs Energy, BS2 (a.u.) | -3598.294390 |
| Number of Imaginary Frequencies | 1 |
| Imaginary Frequencies (cm⁻¹) | -138.3i |

**Molecular Geometry in Cartesian Coordinates**

| C  | Cu | -0.715094 | -0.026084 | -0.171626 |
| C  | 3.203937 | 0.168496 | 1.603091 |

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### P1-PhH

| Atomic Number | X       | Y       | Z       |
|---------------|---------|---------|---------|
| N             | -2.524247 | 1.057342 | -0.529130 |
| C             | -3.530320 | 0.920615 | 0.359313  |
| C             | -4.788438 | 1.482909 | 0.109616  |
| H             | -5.600312 | 1.366666 | 0.816874  |
| C             | -4.106534 | 0.033833 | 2.665747  |
| H             | -5.102011 | 0.456768 | 2.608738  |
| C             | 0.653509  | -1.558085 | -0.658577 |
| N             | -1.961429 | -0.355647 | 1.669036  |
| C             | 2.315855  | -2.487845 | 0.824695  |
| C             | 1.657397  | -1.176294 | -1.574977 |
| C             | 0.981868  | -2.277043 | 0.505172  |
| C             | -3.938815 | 2.346849  | -1.969106 |
| H             | -4.053786 | 2.903687  | -2.892600 |
| C             | -2.415011 | -1.162418 | 3.883727  |
| H             | -2.057469 | -1.685347 | 4.764111  |
| C             | 3.308484  | -2.036492 | -0.050974 |
| C             | -2.717719 | 1.756213  | -1.654814 |
| H             | -1.855581 | 1.841633  | -2.307634 |
| C             | 2.985371  | -1.395932 | -1.257099 |
| C             | -1.577800 | -0.988343 | 2.783543  |
| H             | -0.558127 | -1.357268 | 2.790137  |
| C             | -4.992798 | 2.198093  | -1.068179 |

#### Molecular Geometry in Cartesian Coordinates

| Atomic Number | X       | Y       | Z       |
|---------------|---------|---------|---------|
| Cu            | -0.269236 | -1.307231 | -0.827172 |
| C             | 1.475788  | 0.804999 | -1.819065 |
| N             | 1.836940  | -1.306377 | -0.719392 |
| C             | 2.412482  | -0.200878 | -1.240522 |
| C             | 3.799225  | -0.020106 | -1.195100 |
| H             | 4.259993  | 0.867384  | -1.610384 |
| C             | 1.900890  | 2.034351  | -2.332172 |
| H             | 2.949727  | 2.302955  | -2.331941 |
| C             | -1.817868 | 2.038576  | 0.972879  |
| N             | 0.162432  | 0.477911  | -1.788866 |
| C             | -3.367539 | 3.881089  | 0.655471  |
| C             | -2.776302 | 1.161122  | 0.437056  |
| C             | -2.127382 | 3.404214  | 1.079545  |
| C             | 3.988204  | -2.138115 | -0.068638 |
| H             | 4.569260  | -2.920314 | 0.407257  |
| C             | -0.391406 | 2.573873  | -2.816044 |
| H             | -1.160420 | 3.238379  | -3.193888 |
| C             | -4.314066 | 3.003865  | 0.119950  |
| C             | 2.601785  | -2.248299 | -0.152528 |

**Charge** 0  
**Spin State** Singlet  
**Electronic Energy, BS1 (a.u.)** -1663.810820  
**Thermal and entropic correction, BS1 (a.u.)** 0.240302  
**Electronic Energy, BS2 (a.u.)** -3394.036215  
**Gibbs Energy, BS2 (a.u.)** -3393.795913  
**Number of Imaginary Frequencies** 0
P1-PhBr
Charge 0
Spin State Singlet
Electronic Energy, BS1 (a.u.) -4234.615756
Thermal and entropic correction, BS1 (a.u.) 0.227872
Electronic Energy, BS2 (a.u.) -5967.618666
Gibbs Energy, BS2 (a.u.) -5967.390794
Number of Imaginary Frequencies 0

Molecular Geometry in Cartesian Coordinates

Cu 0.074851 -1.743636 0.562686
C -1.696228 -0.002782 2.125476
N -1.940007 -1.651645 0.386129
C -2.573459 -0.808895 1.236072
C -3.968331 -0.733677 1.279150
H -4.558604 -0.065620 1.977871
C -2.102323 1.203918 2.705381
H -2.544272 0.1066 0.331180
C -4.740971 0.952676 -0.404485

P1-PhOMe
Charge 0
Spin State Singlet
Electronic Energy, BS1 (a.u.) -1778.339131
Thermal and entropic correction, BS1 (a.u.) 0.268487
Electronic Energy, BS2 (a.u.) -3508.613478
Gibbs Energy, BS2 (a.u.) -3508.344991
Number of Imaginary Frequencies 0

Molecular Geometry in Cartesian Coordinates

Cu -1.381949 -0.733665 -1.010819
C -0.050406 1.718600 -1.845270
N 0.623526 -0.577886 -1.594147
H 0.955494 0.643655 -2.068877
Molecular Geometry in Cartesian Coordinates

|   |        |        |        |
|---|--------|--------|--------|
| C | 2.183050 | 0.865734 | -2.701788 |
| H | 2.430945 | 1.842085 | -3.099735 |
| C | 0.247747 | 3.078651 | -1.976375 |
| H | 1.245109 | 3.402044 | -2.247979 |
| C | 0.448618 | 0.864436 | 1.830325 |
| N | -1.277376 | 1.304210 | -1.458919 |
| C | -1.065139 | 2.745730 | 2.133892 |
| C | -0.658081 | 0.004579 | 1.909741 |
| C | 0.217806 | 2.248508 | 1.959772 |
| C | 2.747725 | -1.437406 | -2.302325 |
| H | 3.428903 | -2.279385 | -2.358655 |
| C | -2.012641 | 3.583082 | -1.328444 |
| H | -2.813127 | 4.281226 | -1.109985 |
| C | -2.165623 | 1.873960 | 2.181787 |
| C | 1.497007 | -1.588310 | -1.707437 |
| H | 1.172973 | -2.540777 | -1.300337 |
| C | -1.952390 | 0.493112 | 2.086637 |
| C | -2.229339 | 2.212321 | -1.206266 |
| H | -3.188777 | 1.815769 | -0.890827 |
| C | 3.088738 | -0.186640 | -2.816378 |
| H | 4.049628 | -0.027842 | -3.294915 |
| C | -0.747648 | 4.019107 | -1.718695 |

P1-PhNO₂

Charge
Spin State
Electronic Energy, BS1 (a.u.)
Thermal and entropic correction, BS1 (a.u.)
Electronic Energy, BS2 (a.u.)
Gibbs Energy, BS2 (a.u.)
Number of Imaginary Frequencies

|   |        |        |
|---|--------|--------|
| Cu | 0.527783 | -1.595804 | 0.550360 |
| C | -1.421205 | -0.070428 | 2.126107 |
| N | -1.476752 | -1.757801 | 0.404954 |
| C | -2.199457 | -0.997239 | 1.261832 |
| C | -3.591278 | -1.105026 | 1.330702 |
| H | -4.151612 | -0.501534 | 2.035300 |
| C | -1.970000 | 1.089353 | 2.684494 |
| H | -2.985255 | 1.389550 | 2.451003 |
| C | 0.482117 | 1.621039 | -1.106760 |
| N | -0.129327 | -0.410150 | 2.318984 |
| C | 2.416978 | 2.056597 | 0.297720 |
| C | 1.332098 | 1.469909 | -2.216969 |
| C | 1.042957 | 1.931049 | 0.145234 |
| C | -3.494770 | -2.796562 | -0.374413 |
| H | -3.962668 | -3.511514 | -1.041548 |
| C | 0.152958 | 1.499405 | 3.742863 |
| H | 0.805553 | 2.084833 | 4.381511 |
| C | 3.233343 | 1.880308 | -0.817320 |
| C | -2.11028 | -2.638329 | -0.386593 |

Electronic Energy, BS1 (a.u.)
-1668.311544

Gibbs Energy, BS2 (a.u.)
-3598.389751
|   | 0.121132 | 2.580591 | 0.237773 | H   | 3.370312 | 1.469256 | -2.924254 |
|---|----------|----------|----------|-----|----------|----------|------------|
| H | 0.405255 | 2.054136 | 1.008252 | N   | 4.687518 | 1.969363 | -0.654784 |
| H | 2.853335 | 2.267080 | 1.265485 | O   | 5.393655 | 1.802958 | -1.651758 |
| H | 0.918548 | 1.243877 | -3.191942| O   | 5.130672 | 2.203803 |  0.472036 |

**PhH-Pf**

- Charge: 0
- Spin State: Singlet
- Electronic Energy, BS1 (a.u.): -959.457152
- Thermal and entropic correction, BS1 (a.u.): 0.100056
- Electronic Energy, BS2 (a.u.): -959.872007
- Gibbs Energy, BS2 (a.u.): -959.771951
- Number of Imaginary Frequencies: 0

### Molecular Geometry in Cartesian Coordinates

|   |     |     |     | C   | 1.652555 | 0.000107 | 0.000004 | C   | -1.965679 | -1.194547 | -0.125273 |
|---|-----|-----|-----|-----|----------|----------|----------|-----|----------|----------|----------|
| H |     |     |     | F   | 0.049482 | -2.364534 | -0.268509|     |          |          |          |
| H |     |     |     | F   | -4.004660 | -0.000064 | -0.000236|     |          |          |          |
| H |     |     |     | F   | -2.632448 | -2.350081 | -0.255730|     |          |          |          |
| H |     |     |     | F   | -2.632636 | 2.349963 | 0.256010 |     |          |          |          |
| C |     |     |     | H   | 1.828671 | 1.711319 | -1.305260|     |          |          |          |
| C |     |     |     | H   | 4.298097 | 1.711218 | -1.304587|     |          |          |          |
| C |     |     |     | H   | 5.548975 | -0.000012 | -0.000103|     |          |          |          |
| C |     |     |     | H   | 1.828608 | -1.711189 | 1.305206 |     |          |          |          |
| C |     |     |     | H   | 4.298143 | -1.711189 | 1.304452 |     |          |          |          |
S18. References

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