A Systematic Study of the Effects of Complex Structure on Aryl Iodide Oxidative Addition at Bipyridyl-Ligated Gold(I) Centers

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1. Materials and methods

Materials
All starting materials were obtained from commercial supplied and, except where otherwise state, used as purchased. Anhydrous solvents (CH₂Cl₂, MeCN, hexane and Et₂O) were dried using an Anhydrous Engineering Grubbs-type system (alumina)[1] and stored over 4 Å molecular sieves. Mesitylene and TMEDA were distilled over CaH₂. DMF, MeOH and acetone were used as purchased. CD₂Cl₂ was distilled over calcium hydride for NMR spectroscopy. CDCl₃ was used directly as purchased.

Methods
For all reactions performed, unless stated otherwise, inert conditions were employed using standard Schlenk line and/or glove box techniques under an atmosphere of dinitrogen or argon using oven-dried glassware. Room temperature (rt) typically fluctuated between 18 – 25 °C depending on the season and time of day. In instances where reactions were monitored, they were followed by NMR spectroscopy or analytical thin-layer chromatography (TLC). Merck TLC silica gel 60 F254 plates were used for TLC and were visualised using UV light and/or with a potassium permanganate solution and exposure to heat. Normal phase flash chromatography was carried out using 60 Å silica with solvent systems specified below.
**Instrumentation**

$^1$H NMR spectra were measured at 300 MHz on a Jeol ECS 300, at 400 MHz on a Bruker Avance 400, Varian 400-MR, Jeol ECZ400 or Jeol ECS400 and at 500 MHz on a Bruker Avance III HD Cryo. Corresponding $^{13}$C frequencies are 75.4 MHz, 101 MHz and 126 MHz. Corresponding $^{19}$F frequencies are 282 MHz, 376 MHz and 470 MHz. NMR samples were analysed as solutions with solvents specified below and, unless otherwise stated, at 298 K. $^1$H and $^{13}$C{ $^1$H}. NMR spectra were referenced to residual solvent peaks (CDCl$_3$ $^\delta$H 7.26 and $^\delta$C 77.2; CD$_2$Cl$_2$ $^\delta$H 5.32 and $^\delta$C 53.8). Chemical shifts ($^1$H and $^{13}$C) are reported in parts per million (ppm) relative to tetramethylsilane standard. $^{19}$F spectra were measured against CF$_3$Cl as an external standard. Other internal standards are specified below. Coupling constants ($J$) are reported to the nearest 0.1 Hz and were calculated using MestReNova 11.0. Coupling constants that did not match as a result of digitisation are reported as rounded averages. Multiplicities are defined as followed: s singlet; d doublet; t triplet; q quartet; m multiplet and combinations thereof. Characterisation of novel compounds was supported by 2D NMR experiments.

Mass spectra were recorded on a Bruker microTOF II spectrometer or a Waters Synapt G2S spectrometer by the University of Bristol mass spectrometry service.

Infra-red (IR) spectra were recorded on a Pekin-Elmer Spectrum Two FTIR spectrometer with an attenuated total reflectance (ATR) attachment.

Raman spectra were recorded on a Renishaw 2000 laser Raman spectrometer using a 785 nm excitation wavelength. Spectra were collected at room temperature in air with the sample as a fine powder.
2. Experimental

2.1. Aryl iodide substrate synthesis

1-Iodo-4-vinylbenzene (3g)

Following a modified literature procedure,\textsuperscript{[2]} methyltriphenylphosphonium iodide (3.50 g, 8.62 mmol) was suspended in THF (40 mL) and cooled to \(-78^\circ C\). \(n\)-Butyllithium (4.1 mL of a 2.5 M solution in hexane) was added dropwise and the reaction mixture was stirred for 30 minutes. 4-Iodobenzaldehyde (2.00 g, 8.62 mmol) was added, the reaction mixture was stirred for a further 30 minutes then warmed to room temperature. After heating to 55 °C for four hours and cooling to room temperature, sat. aq. \(\text{NH}_4\text{Cl}\) (30 mL) was added followed by ethyl acetate (40 mL). The organic portion was separated and the aqueous phase was washed with ethyl acetate (3 \(\times\) 40 mL). The organic extracts were combined, dried (MgSO\(_4\)), filtered and evaporated \textit{in vacuo}. The crude material was purified by normal phase flash chromatography (hexane) to give 3g (1.00 g, 50%) as a colorless solid; \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.65 (d, \(J = 8.4\) Hz, 2H, \(C_{Ar}-H\)), 7.15 (d, \(J = 8.4\) Hz, 2H, \(C_{Ar}-H\)), 6.64 (dd, \(J = 17.6, 10.9\) Hz, 1H, \(CH=CH_2\)), 5.76 (d, \(J = 17.6\) Hz, 1H, \(CH=CH_2\)), 5.28 (d, \(J = 10.9\) Hz, 1H, \(CH=CH_2\)); \(^{13}\text{C}\{(^1\text{H}) NMR (101 MHz, CDCl}_3\) \(\delta\) 137.7 (\(C_{Ar}\)), 137.2 (\(C_{Ar}\)), 136.0 (\(C_{Ar}\)), 128.1 (\(C_{Ar}\)), 114.9 (C=CH\(_2\)), 93.3 (C=CH\(_2\)). The spectroscopic properties of this compound were consistent with literature data.\textsuperscript{[3]}

2.2. 2,2'-Bipyridyl ligand synthesis

Many of the ligands used in this study were available from commercial suppliers (2,2'-bipyridine (1a), 4,4'-di(tert-butyl)-2,2'-bipyridyl (1b), 4,4'-dibromo-2,2'-bipyridyl (1c), 4,4'-dinitro-2,2'-bipyridyl (1h), 4,4'-dimethoxy-2,2'-bipyridyl (1i) and 6,6'-dimethyl-2,2'-bipyridyl (1j). Others ligands (1d-g and 1k) were synthesised \textit{via} halopyridine homocoupling reactions or further derivitization of commercially available 2,2'-bipyridyls which are outlined below.
5,5'-Difluoro-2,2'-bipyridyl (1d)

Following a modified literature procedure,[4] 2-bromo-5-fluoropyridine (3.50 g, 19.9 mmol), indium powder (1.14 g, 10.0 mmol), lithium chloride (1.27 g, 30.0 mmol) and palladium(II) acetate (112 mg, 0.50 mmol) were suspended in DMF (40 mL) which was deoxygenated by sparging with dinitrogen for 10 minutes. The reaction mixture was heated at 100 °C for two hours, after which sat. aq. NaHCO₃ (50 mL), water (100 mL) and ethyl acetate (50 mL) were added sequentially. The organic portion was separated and the aqueous phase was washed with ethyl acetate (3 × 50 mL). The organic extracts were combined, dried (MgSO₄), filtered and evaporated in vacuo. The crude material was purified by normal phase flash chromatography (5% ethyl acetate in hexane) to give 1d (1.52 g, 80%) as a colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, J = 2.9 Hz, 2H, C₂Ar-H), 8.38 (dd, J = 8.8, 4.4 Hz, 2H, Ar-H), 7.51 (app. td, J = 8.4, 2.9 Hz, 2H, C₂Ar-H); ¹³C¹H NMR (101 MHz, CDCl₃) δ 159.9 (d, J = 260 Hz, C₂Ar), 151.7 (d, J = 4.1 Hz, C₂Ar), 137.4 (d, J = 24 Hz, C₂Ar), 123.8 (d, J = 18 Hz, C₂Ar), 122.2 (d, J = 5.4 Hz, C₂Ar). The spectroscopic properties of this compound were consistent with literature data.[5]

Dimethyl [2,2'-bipyridyl]-4,4'-dicarboxylate (1e)

Following a modified literature procedure,[6] 2,2'-dipyridyl-4,4'-dicarboxylic acid (1.00 g, 4.09 mmol) was suspended in methanol (30 mL) and approx. 10 drops of conc. H₂SO₄ were added. After heating at 80 °C for 34 hours, the reaction mixture was cooled to room temperature and added to water (75 mL). To the resultant slurry, 25% w/v aq. NaOH (75 mL) was added followed by chloroform (75 mL). The organic portion was separated and the aqueous phase was washed with chloroform (3 × 75 mL). The organic extracts were combined, dried (MgSO₄), filtered and evaporated in vacuo to give 1e (638 mg, 58%) as a colourless solid; ¹H NMR (400 MHz, CDCl₃) δ 8.97 (dd, J = 1.6, 0.9 Hz, 2H, C₂Ar-H), 8.87 (dd, J = 5.0, 0.9 Hz, 2H, C₂Ar-H), 7.91 (dd, J = 5.0, 1.6 Hz, 2H, C₂Ar-H), 4.00 (s, 6H, CH₃); ¹³C¹H NMR (101 MHz, CDCl₃) δ
The spectroscopic properties of this compound were consistent with literature data.\[6\]

4,4′-Bis(trifluoromethyl)-2,2′-bipyridyl (1f)

Following a modified literature procedure,\[4\] 3-bromo-4-(trifluoromethyl)pyridine (1.20 mL, 8.89 mmol), palladium(II) acetate (50.0 mg, 0.222 mmol), indium powder (511 mg, 4.45 mmol) and lithium chloride (564 mg, 13.3 mmol) were suspended in DMF (18 mL) which was deoxygenated by sparging with dinitrogen for 10 minutes. After three hours of heating at 100 °C, sat. aq. NaHCO₃ (20 mL), water (20 mL) and ethyl acetate (20 mL) were added. The organic portion was separated and the aqueous phase was washed with ethyl acetate (3 × 30 mL). The organic extracts were combined, dried (MgSO₄), filtered and evaporated in vacuo. The crude material was purified by normal phase flash chromatography (5% to 10% ethyl acetate in hexane) to give 1f (688 mg, 53%) as a colorless solid; \(^1\)H NMR (400 MHz, CDCl₃) δ 8.89 (d, J = 5.0 Hz, 2H, C₆H₄-H), 8.75 – 8.72 (m, 2H, C₆H₄-H), 7.59 (ddd, J = 5.0, 1.7, 0.8 Hz, 2H, C₆H₄-H); \(^{13}\)C\(^{1}\)H NMR (126 MHz, CDCl₃) δ 156.2 (C₆H₄), 150.4 (C₆H₄), 139.8 (q, J = 34 Hz, C₆H₄), 122.9 (q, J = 273 Hz, CF₃), 120.1 (C₆H₄), 117.4 (C₆H₄); \(^{19}\)F NMR (377 MHz, CDCl₃) δ -64.83. The spectroscopic properties of this compound were consistent with literature data.\[7\]

[2,2′-Bipyridyl]-4,4′-dicarbonitrile (1g)

Following a modified literature procedure,\[8\] 4,4′-dibromobipyridyl (1.90 g, 6.12 mmol), sodium cyanide (600 mg, 12.2 mmol), palladium(II) acetate (69.0 mg, 0.306 mmol), 1,5-bis(diphenylphosphino)-pentane (539 mg, 1.22 mmol) and TMEDA (1.40 mL, 9.18 mmol) were suspended in mesitylene and deoxygenated by sparging with dinitrogen for 10 minutes. The reaction was then heated at 170 °C for 17 hours after which was allowed to cool to room temperature and deoxygenated water (30 mL) was added. The resultant slurry was filtered and
the collected solid was washed with pentane, air-dried and purified by normal phase flash chromatography (30% to 50% ethyl acetate in hexane) to give \( 1g \) (584 mg, 45%) as a colorless solid; \(^{1}H\) NMR \((400\text{ MHz, CDCl}_3\) \(\delta \) 8.88 (dd, \( J = 5.0, 0.9 \text{ Hz}, 2H, C_{Ar}-H\)), 8.72 (dd, \( J = 1.6, 0.9 \text{ Hz}, 2H, C_{Ar}-H\)), 7.60 (dd, \( J = 5.0, 1.6 \text{ Hz}, 2H, C_{Ar}-H\)); \(^{13}C\left({^{1}H}\right)\) NMR \((101\text{ MHz, CDCl}_3\) \(\delta \) 155.6 \((C\equiv N\)), 150.5 \((C_{Ar}\)), 126.0 \((C_{Ar}\)), 123.3 \((C_{Ar}\)), 122.0 \((C_{Ar}\)), 116.5 \((C_{Ar}\)). The spectroscopic properties of this compound were consistent with literature data.\[^{[8]}\]

6-Methyl-2,2'-bipyridyl \((1k)\)

Following a modified literature procedure,\[^{[9]}\] 2,2'-bipyridine \((8.00\text{ g, 51.2 mmol})\) was dissolved in diethyl ether \((170\text{ mL})\) and cooled to \(0\text{ °C}\). Methyl lithium \((32\text{ mL\ of a 1.63 M solution in diethyl ether})\) was added dropwise over 30 minutes. Once addition was complete, the reaction mixture was stirred at room temperature for one hour. After heating at \(50\text{ °C}\) for a further four hours, water \((120\text{ mL})\) was added once the reaction was at room temperature. The organic portion was separated and the aqueous phase was washed with diethyl ether \((3 \times 100\text{ mL})\). The organic extracts were combined, dried \((\text{Na}_2\text{SO}_4)\), filtered and evaporated \(\text{in vacuo}\) to give an orange oil. This was dissolved in a sat. solution of potassium permanganate in acetone \((200\text{ mL})\) and stirred for 16 hours. The reaction mixture was filtered and the filtrate was evaporated \(\text{in vacuo}\). The crude material was purified by normal phase flash chromatography \((10\% \text{ to } 20\% \text{ ethyl acetate in hexane})\) to give \(1k\) \((3.23\text{ g, 37%})\) as a colorless solid; \(^{1}H\) NMR \((400\text{ MHz, CDCl}_3\) \(\delta \) 8.67 (ddt, \( J = 4.8, 1.7, 0.8 \text{ Hz}, 1H, C_{Ar}-H\)), 8.40 (dq, \( J = 8.0, 1.0 \text{ Hz}, 1H, C_{Ar}-H\)), 8.16 (d, \( J = 8.0 \text{ Hz}, 1H, C_{Ar}-H\)), 7.79 (td, \( J = 7.7, 1.8 \text{ Hz}, 1H, C_{Ar}-H\)), 7.69 (t, \( J = 7.7 \text{ Hz}, 1H, C_{Ar}-H\)), 7.31 – 7.23 (m, 1H, C_{Ar}-H)), 7.16 (d, \( J = 7.7 \text{ Hz}, 1H, C_{Ar}-H\)), 2.63 (s, 3H, CH\(_3\)); \(^{13}C\left({^{1}H}\right)\) NMR \((101\text{ Hz, CDCl}_3\) \(\delta \) 158.1 \((C_{Ar}\)), 156.7 \((C_{Ar}\)), 155.7 \((C_{Ar}\)), 149.3 \((C_{Ar}\)), 137.2 \((C_{Ar}\)), 136.9 \((C_{Ar}\)), 123.6 \((C_{Ar}\)), 123.4 \((C_{Ar}\)), 121.3 \((C_{Ar}\)), 118.2 \((C_{Ar}\)), 24.8 \((CH_{3}\)). The spectroscopic properties of this compound were consistent with literature data.\[^{[9]}\]

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2.3. 2,2'-Bipyridyl Au(I) ethylene complex synthesis

2.3.1. General Procedure A – Crystallization of complex

Following a modified literature procedure,[5] in a glovebox, a J. Young’s tube was charged with gold(I) chloride (1.0 eq.) and silver(I) triflimide (1.0 eq.) in the absence of light. Outside the glove box, the tube was placed under an atmosphere of ethylene (1 bar) and dichloromethane was added to give a 0.02 M solution. After three hours stirring at room temperature, the reaction mixture was filtered through a pad of Celite into a flask containing the 2,2'-bipyridyl ligand (1 eq.) whilst maintaining darkness. After stirring for one hour, the solution was evaporated in vacuo to approx. 2 mL and filtered through a pad of Celite. The filtrate was layered with diethyl ether and stored for 24 hours at −18 °C to give the desired Au(I) complex.

2.2.2. General Procedure B – Precipitation of complex

Complexes were prepared in a manner identical to that given in General Procedure A, however the Au(I) complexes were precipitated by adding an excess of diethyl ether to the dichloromethane solution. The mother liquor was removed and the complex was washed thrice with diethyl ether and dried in vacuo.

\[
[(\kappa^2-2,2'-\text{Bipy})-(\eta^2-\text{ethylene})\text{gold(I)}][\text{NTf}_2] \ (2a\cdot\text{NTf}_2)
\]

Following General Procedure A on a 0.861 mmol scale with bipyridyl ligand 1a gave 2a•NTf\textsubscript{2} (136 mg, 24%) as pale yellow needles; ν\textsubscript{Raman (neat)} / cm\textsuperscript{-1} 1493 (C=C); \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 8.86 – 8.81 (m, 2H, C2-H), 8.48 (app. dt, \(J = 7.8, 1.4 \text{ Hz}, 2\text{H}, C5-H\)), 8.31 (app. td, \(J = 7.8, 1.4, 2\text{H}, C4-H\)), 7.85 (ddd, \(J = 7.8, 5.2, 1.4 \text{ Hz}, 2\text{H}\)), 3.83 (s, 4H, C1-H\textsubscript{2}); \textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 152.5 (C6), 152.4 (C2), 142.4 (C4), 128.5 (C3), 124.4 (C5), 120.4 (q, \(J = 322 \text{ Hz}, \text{ anion CF}_3\)), 62.3 (C1); HRMS (ESI\textsuperscript{+}) calcd. 381.0666 for [M–NTf\textsubscript{2}]\textsuperscript{+}.
[C_{12}H_{12}AuN_2]^+}, found 381.0645. The spectroscopic properties of this compound were consistent with literature data.[3]

$$[(\kappa^2-4,4'-\text{Di(tert-butyl)-bipy})-(\eta^2\text{-ethylene})\text{gold(I)}][\text{NTf}_2] \ (2b\cdot\text{NTf}_2)$$

Following General Procedure A on a 0.430 mmol scale with bipyridyl ligand 1b gave 2b•NTf₂ (72 mg, 22%) as a colorless crystalline solid; vRaman (neat) / cm⁻¹: 1486 (C=C); ¹H NMR (400 MHz, CD₂Cl₂) δ 8.73 (dd, J = 5.7, 0.7 Hz, 2H, C2-H), 8.28 (dd, J = 1.9, 0.7 Hz, 2H, C7-H), 7.80 (dd, J = 5.7, 1.9 Hz, 2H, C3-H), 3.77 (s, 4H, C1-H₂); ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 167.3 (C₈), 152.8 (C₄), 152.1 (C₂), 125.6 (C₃), 120.6 (C₇), 61.4 (C₁), 36.6 (C₅), 30.6 (C₆); HRMS (ESI⁺) calcd. 493.1918 for [M–NTf₂]^+ [C_{20}H_{28}AuN₂]^+, found 493.1919.

$$[(\kappa^2-4,4'-\text{Dibromo-bipy})-(\eta^2\text{-ethylene})\text{gold(I)}][\text{NTf}_2] \ (2c\cdot\text{NTf}_2)$$

Following General Procedure A on a 0.430 mmol scale with bipyridyl ligand 1c gave 2c•NTf₂ (134 mg, 38%) as a colorless crystalline solid; vRaman (neat) / cm⁻¹: 1547 (C=C); ¹H NMR (500 MHz, CD₂Cl₂) δ 8.76 – 8.64 (m, 2H, C2-H), 8.60 – 8.48 (m, 2H, C5-H), 8.04 (dd, J = 5.6, 1.8 Hz, 2H, C3-H), 3.90 (s, 4H, C1-H₂); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 152.3 (C₂), 151.8 (C₆), 139.0 (C₄), 131.7 (C₃), 127.3 (C₅), 119.8 (q, J = 322 Hz, anion CF₃), 63.6 (C₁); HRMS (ESI⁺) calcd. 538.8856 for [M–NTf₂]^+ [C_{12}H_{10}Au_{79}Br₂N₂]^+, found 538.8873. Crystals suitable for single-crystal X-ray diffraction were obtained by layering a dichloromethane solution of 2c•NTf₂ with diethyl ether followed by storage at –18 °C (X-ray data are given in Section 3).

With carbon NMR spectra acquired on lower field instruments (101 MHz), the carbon signal corresponding to the NTf₂⁻ anion was not observed.
Following General Procedure A on a 0.861 mmol scale with bipyridyl ligand 1d gave 2d•NTf₂ (360 mg, 60%) as colorless needles; \( \nu_{\text{Raman}} \) (neat) / cm\(^{-1} \) 1585 (C=C); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 8.71 (d, \( J = 2.7 \) Hz, 2H, C2-H), 8.58 (dd, \( J = 9.1, 4.2 \) Hz, 2H, C5-H), 8.11 – 8.03 (m, 2H, C4-H), 3.93 (s, 4H, C1-H\(_2\)); \(^{13}\)C{\(^1\)H} NMR (126 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 161.1 (d, \( J = 260 \) Hz, C3), 147.8 (d, \( J = 3.1 \) Hz, C6), 140.6 (d, \( J = 320 \) Hz, C2), 129.0 (d, \( J = 18.6 \) Hz, C4), 125.7 (d, \( J = 7.4 \) Hz, C5), 119.8 (q, \( J = 320 \) Hz, anion C\(_{\text{F}}\)), 63.8 (C1); \(^{19}\)F NMR (377 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) -77.53 (anion C\(_{\text{F}}\)), -115.71 – -116.72 (C3-F); HRMS (ESI\(^+\)) calcd. 417.0472 for \([\text{C}_{12}\text{H}_{10}\text{AuF}_2\text{N}_2]^+\) [M–NTf\(_2\)]\(^+\), found 417.0478. The spectroscopic properties of this compound were consistent with literature data.\(^5\)

Following General Procedure A on a 0.430 mmol scale with bipyridyl ligand 1e gave 2e•NTf₂ (89 mg, 27%) as light yellow needles; \( \nu_{\text{max}} \) (ATR, neat) / cm\(^{-1} \) 1732 (C=O); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.04 (dd, \( J = 5.4, 0.7 \) Hz, 2H, C2-H), 9.02 (dd, \( J = 1.6, 0.7 \) Hz, C7-H), 8.39 (dd, \( J = 5.4, 1.6 \) Hz, 2H, C3-H), 4.09 (s, 6H, C6-H\(_3\)), 3.69 (s, 4H, C1-H\(_2\)); \(^{13}\)C{\(^1\)H} NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 163.8 (C5), 153.6 (C2), 152.9 (C4), 143.0 (C8), 128.2 (C3), 123.8 (C7), 64.4 (C1), 54.3 (C6); HRMS (ESI\(^+\)) calcd. 497.0776 for \([\text{M–NTf}_2]^+\) [M–NTf\(_2\)]\(^+\), found 497.0779. Crystals suitable for single-crystal X-ray diffraction were obtained by layering a dichloromethane solution of 2e•NTf₂ with diethyl ether followed by storage at –18 °C (X-ray data are given in Section 3).
Following General Procedure A on a 0.274 mmol scale with bipyridyl ligand 1f gave 2f•NTf₂ (72 mg, 33%) as a colorless crystalline solid; \( \text{\textit{IR}} \) (neat) / cm\(^{-1}\) 1573 (C=C); \(^1\text{H} \) NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.13 (d, \( J = 5.4 \) Hz, 2H, C2-H), 8.65 (s, 2H, C6-H), 8.15 (d, \( J = 5.4 \) Hz, 2H, C3-H), 4.05 (s, 4H, C1-H\(_2\)); \(^{13}\text{C} \)\{\(^1\text{H}\)\} NMR (126 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 154.2 (C2), 152.8 (C7), 143.6 (q, \( J = 35.8 \) Hz, C4), 125.3 (q, \( J = 3.4 \) Hz, C3), 122.4 (q, \( J = 274 \) Hz, C5), 120.7 (q, \( J = 3.4 \) Hz, C6), 120.1 (q, \( J = 321 \) Hz, anion CF\(_3\)), 65.7 (C1); \(^{19}\text{F} \) NMR (377 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) -65.31 (C5\(_{\text{F3}}\)), -79.47 (anion CF\(_3\)); HRMS (ESI\(^{+}\)) calcd. 517.0414 for [M−NTf₂]+ [C\(_{14}\)H\(_{10}\)AuN\(_4\)F\(_6\)]\(^+\), found 517.0396. Crystals suitable for single-crystal X-ray diffraction were obtained by layering a dichloromethane solution of 2f•NTf₂ with diethyl ether followed by storage at −18 °C (X-ray data are given in Section 3).

Following General Procedure B on a 0.430 mmol scale with bipyridyl ligand 1g gave 2g•NTf₂ (97 mg, 32%) as a colorless solid; \(^1\text{H} \) NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 9.07 (d, \( J = 5.7 \) Hz, 2H, C2-H), 8.66 (s, 2H, C6-H), 8.14 (d, \( J = 5.7 \) Hz, 2H, C3-H), 4.03 (s, 4H, C1-H\(_2\)); \(^{13}\text{C} \)\{\(^1\text{H}\)\} NMR (101 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) 153.1 (C2), 151.5 (C4), 130.4 (C3), 126.3 (C6), 125.8 (C7), 114.4 (C5), 65.7 (C1); HRMS (ESI\(^{+}\)) calcd. 431.0571 for [M−NTf₂]+ [C\(_{14}\)H\(_{10}\)AuN\(_4\)]\(^+\), found 431.0567.
[($\kappa^2$-$4,4'$-Dinitro-bipy)-($\eta^2$-ethylene)gold(I)] [NTf$_2$] (2h•NTf$_2$)

Following General Procedure A on a 0.861 mmol scale with bipyridyl ligand 1h gave 2h•NTf$_2$ (98 mg, 30%) as a colorless crystalline solid; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.22 (d, $J = 5.6$ Hz, 2H, C$_2$-H), 9.19 (d, $J = 2.1$ Hz, 2H, C$_5$-H), 8.59 (d, $J = 4.4$ Hz, 2H, C$_3$-H), 4.08 (s, 4H, C$_1$-H$_2$); $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$) δ 156.5 (C$_4$), 155.4 (C$_2$), 154.1 (C$_6$), 122.3 (C$_3$), 118.4 (C$_5$), 66.6 (C$_1$). Due to the instability of the complex, analysis by HRMS was not possible.

[($\kappa^2$-$4,4'$-Dimethoxy-bipy)-($\eta^2$-ethylene)gold(I)] [NTf$_2$] (2i•NTf$_2$)

Following General Procedure A on a 0.215 mmol scale with bipyridyl ligand 1i gave 2i (44 mg, 31%) as colorless needles; v$_{\text{Raman (neat)}}$ / cm$^{-1}$ 1462 (C=C); $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 8.62 (d, $J = 6.2$ Hz, 2H, C$_2$-H), 7.77 (d, $J = 2.5$ Hz, 2H, C$_6$-H), 7.25 (dd, $J = 6.2$, 2.5 Hz, 2H, C$_3$-H), 4.08 (s, 6H, C$_5$-H$_3$), 3.69 (s, 4H, C$_1$-H$_2$); $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$) δ 169.6 (C$_4$), 154.4 (C$_7$), 153.4 (C$_2$), 120.3 (q, $J = 321.6$ Hz, anion CF$_3$), 113.1 (C$_3$), 110.6 (C$_6$), 60.3 (C$_1$), 57.4 (C$_5$); HRMS (ESI$^+$) calcd. 441.0877 for [M–NTf$_2$]$^+$ [C$_{14}$H$_{16}$AuN$_2$O$_2$]$^+$, found 441.0875. Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of 2i•NTf$_2$ with diethyl ether followed by storage at −18 °C (X-ray data are given in Section 3).
[(κ²-6,6'-Dimethyl-bipy)-(η²-ethylene)gold(I)] [NTf₂] (2j•NTf₂)

Following General Procedure A on a 0.215 mmol scale with bipyridyl ligand 1j gave 2j•NTf₂ (40 mg, 26%) as colorless needles; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.26 (d, J = 8.0 Hz, 2H, C4-H), 8.16 (t, J = 7.8 Hz, 2H, C6-H), 7.72 (ddd, J = 7.8, 1.2, 0.6 Hz, 2H, C5-H), 3.79 (s, 4H, C1-H₂), 2.92 (s, 6H, C3-H₃); ¹³C{¹H} NMR (101 MHz, CD₂Cl₂) δ 160.5 (C₂), 142.3 (C₄), 128.5 (C₆), 121.8 (C₄), 101.0 (C₅), 61.2 (C₁), 28.8 (C₃); HRMS (ESI⁺) calcd. 409.0979 for [M−NTf₂]⁺ [C₁₄H₁₆AuN₂]⁺, found 409.0966.

[(κ²-6-Methyl-bipy)-(η²-ethylene)gold(I)] [NTf₂] (2k•NTf₂)

Following General Procedure A on a 0.430 mmol scale with bipyridyl ligand 1k gave 2k•NTf₂ (86 mg, 30%) as a colorless solid; ¹H NMR (500 MHz, CD₂Cl₂) δ 8.82 (ddd, J = 5.2, 1.7, 0.8 Hz, 1H, C₂-H), 8.45 (dt, J = 8.3, 1.0 Hz, 1H, C₅-H), 8.33 – 8.25 (m, 2H, C₄-H and C₁₀-H), 8.18 (t, J = 7.9 Hz, 1H, C₈-H), 7.83 (ddd, J = 7.7, 5.2, 1.2 Hz, C₃-H), 7.74 (dd, J = 7.9, 1.0 Hz, 1H, C₉-H), 3.81 (s, 4H, C₁-H₂), 2.92 (s, 3H, C₁₂-H₃); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 160.5 (C₁₁), 153.3 (C₆), 152.4 (C₂), 152.2 (C₇), 142.3 (C₈), 142.3 (C₄), 128.6 (C₉), 128.3 (C₃), 124.5 (C₅), 121.6 (C₁₀), 120.6 (q, J = 322 Hz, anion CF₃), 61.6 (C₁), 28.9 (C₁₂); HRMS (ESI⁺) calcd. 395.0823 for [M−NTf₂]⁺ [C₁₃H₁₄AuN₂]⁺, found 395.0808.

[(κ²-5,5'-Difluoro-bipy)-(η²-ethylene)gold(I)] [SbF₆] (2d•SbF₆)

Following General Procedure B on a 0.430 mmol scale with bipyridyl ligand 1d and AgSbF₆ gave 2d•SbF₆ (114 mg, 41%) as a colorless solid; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.71 (d, J
= 2.5 Hz, 2H, C2-H), 8.52 (dd, J = 9.0, 4.2 Hz, 2H, C5-H), 8.10 – 8.03 (m, 2H, C4-H), 3.94 (s, 4H, C1-H2); \(^{13}\)C\(^{1}\)H NMR (126 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 161.5 (d, J = 262.5 Hz, C3), 148.1 (d, J = 3.3 Hz, C6), 141.1 (d, J = 30.3 Hz, C2), 129.4 (d, J = 18.4 Hz, C4), 125.9 (d, J = 7.4 Hz, C5), 64.3 (C1); \(^{19}\)F NMR (377 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) -118.00 – -118.06 (m, C3-F); HRMS (ESI\(^{+}\)) calcd. 417.0478 for [M–SbF\(_6\)]\(^{+}\) [C\(_{12}\)H\(_{10}\)AuF\(_2\)N\(_2\)]\(^{+}\), found 417.0480.

\[ ([\kappa^2,5',5'\text{-Difluoro-bipy})-(\eta^2\text{-ethylene})\text{gold(I)}] \text{ [BF}_4\text{]} (2d•BF\(_4\)) \]

Following General Procedure B on a 0.220 mmol scale with bipyridyl ligand 1d and AgBF\(_4\) gave 2d•BF\(_4\) (58 mg, 54%) as a colorless solid; \(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\) 8.83 (d, J = 2.4 Hz, 2H, C2-H), 8.52 (dd, J = 8.8, 4.6 Hz, 2H, C5-H), 8.09 (ddd, J = 8.8, 7.6, 2.4 Hz, 2H, C4-H), 3.87 (s, 4H, C1-H2); \(^{13}\)C\(^{1}\)H NMR (126 MHz, CD\(_3\)CN) \(\delta\) 162.0 (d, J = 258 Hz, C3), 148.9 (C6), 141.8 (d, J = 30.4 Hz, C2), 129.6 (d, J = 19.4 Hz, C4), 126.5 (d, J = 4.9 Hz, C5), 64.3 (C1); \(^{19}\)F NMR (377 MHz, CD\(_3\)CN) \(\delta\) -118.22 (C4-F), -152.41 (BF\(_4\)), 152.35 (BF\(_4\)); HRMS (ESI\(^{+}\)) calcd. 417.0478 for [M–BF\(_4\)]\(^{+}\) [C\(_{12}\)H\(_{10}\)AuF\(_2\)N\(_2\)]\(^{+}\), found 417.0478.

2.4. **Bona fide oxidative addition complex synthesis**

To verify the presence of the oxidative addition complexes in solution for the kinetic studies, *bona fide* samples were synthesised according to the General Procedure below. Literature spectroscopic data was used for complexes 4a•NTf\(_2\), 4d•NTf\(_2\), 5b•NTf\(_2\) and 5f•NTf\(_2\).[5]

2.4.1. **General Procedure C – Oxidative addition complex synthesis**

Following a modified literature procedure,[5] gold(I) complex (1.0 eq.) was dissolved in dichloromethane (to give a 0.01 M solution) and the aryl iodide (20 eq.) was added. In the cases where the aryl iodides were solids, they were added at the same time as the gold(I) complex.
The reaction mixture was subjected to three freeze-pump-thaw cycles and heated to 50 °C under static vacuum. After one hour, the reaction mixture was again subjected to three freeze-pump-thaw cycles and returned to heat under static vacuum. This process was continued until the reaction was complete by $^{19}$F NMR spectroscopy (typically ~2 h). The reaction mixture was filtered (using a Millipore Millex-HV 0.45 μm PVDF membrane syringe filter) and evaporated in vacuo to a minimum volume (approx. 0.5 mL). Hexane was added to precipitate the gold(III) oxidative addition complexes which were subsequently washed with hexane and dried under vacuum.

$^{[( \kappa^2-4,4'-\text{Di(tert-butyl)-bipy})\text{Au}(4-\text{FC}_6\text{H}_4)\text{I}][\text{NTf}_2]}$ (4b•NTf$_2$)

Following General Procedure C on a 25.9 μmol scale with Au(I) complex 2b•NTf$_2$ and 4-fluoriodobenzene (3a) gave 4b•NTf$_2$ (8 mg, 32%) as light brown solid; $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 9.59 (d, $J = 6.0$ Hz, 1H, C5-H or C18-H), 8.35 (d, $J = 2.0$ Hz, 1H, C10-H or C13-H), 8.29 (d, $J = 2.1$ Hz, 1H, C10-H or C13-H), 7.90 (dd, $J = 6.0$, 2.1 Hz, 1H, C6-H or C17-H), 7.70 (dd, $J = 6.0$, 2.1 Hz, 1H, C5-H or C18-H), 7.45 (d, $J = 6.0$ Hz, 1H, C6-H or C17-H), 7.31 – 7.25 (m, 2H, C3-H), 7.21 – 7.09 (m, 2H, C2-H), 1.51 (s, 9H, C9-H$_3$ or C16-H$_3$), 1.46 (s, 9H, C9-H$_3$ or C16-H$_3$); $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 170.3 (C7 or C14), 169.2 (C7 or C14), 163.8 (d, $J = 248$ Hz, C1), 155.6 (C11 or C12), 154.2 (C11 or C12), 151.0 (C5 or C18), 146.6 (C6 or C17), 134.9 (d, $J = 7.2$ Hz, C3), 127.4 (C6 or C17), 126.3 (C5 or C9), 122.4 (C10 or C13), 120.1 (q, $J = 320$ Hz, anion CF$_3$), 119.1 (C4), 118.3 (d, $J = 21.5$ Hz, C2), 37.1 (C8 or C15), 37.0 (C8 or C15), 30.4 (C9 or C16), 30.3 (C9 or C16); $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$) $\delta$ -79.37 (anion CF$_3$), -114.61 – -114.78 (m, C1-F).
Following General Procedure C on a 26.9 μmol scale with Au(I) complex 2c•NTf₂ and 4-fluoriodobenzene (3a) gave 4c•NTf₂ (24 mg, 87%) as a yellow solid; ¹H NMR (500 MHz, CD₂Cl₂) δ 9.48 (d, J = 6.1 Hz, 1H, C5-H or C14-H), 8.62 (d, J = 2.0 Hz, 1H, C8-H or C11-H), 8.57 (d, J = 2.0 Hz, 1H, C6-H or C13-H), 7.93 (dd, J = 6.1, 2.0 Hz, 1H, C5-H or C14-H), 7.34 (d, J = 6.1 Hz, 1H, C8-H or C11-H), 7.30 – 7.24 (m, 2H, C3-H), 7.17 (t, J = 8.6 Hz, 2H, C2-H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 164.0 (d, J = 248 Hz, C₁), 155.2 (C₉ or C₁₀), 153.9 (C₉ or C₁₀), 151.6 (C₅ or C₁₄), 147.2 (C₅ or C₁₄), 142.5 (C₇ or C₁₂), 141.3 (C₇ or C₁₄), 135.0 (d, J = 7.3 Hz, C₃), 133.8 (C₆ or C₁₃), 132.7 (C₆ or C₁₃), 129.6 (C₈ and C₁₁), 120.3 (q, J = 321 Hz, anion CF₃), 118.6 (C₄), 118.5 (d, J = 21.7 Hz, C₂); ¹⁹F NMR (377 MHz, CD₂Cl₂) δ -79.17 (anion CF₃), -114.02 (C₁-F); HRMS (ESI⁺) calcd. 730.7905 for [M–NTf₂]⁺ [C₁₆H₁₀N₂²⁹Br₂AuIF]⁺, found 730.7916.

Following General Procedure C on a 14.1 μmol scale with Au(I) complex 2e•NTf₂ and 4-fluoriodobenzene (3a) to give 4e•NTf₂ (11 mg, 80%) as a yellow solid; νmax (ATR, neat) / cm⁻¹ 3088, 2958, 1732 (C=O), 1483, 1347, 1179, 1132, 1051, 824, 762, 614; ¹H NMR (500 MHz, CD₂Cl₂) δ 9.85 (dd, J = 5.7, 0.7 Hz, 1H, C5-H or C14-H), 9.07 (d, J = 1.5 Hz, 1H, C10-H or C13-H), 9.01 (d, J = 1.7 Hz, 1H, C10-H or C13-H), 8.46 (dd, J = 5.7, 1.7 Hz, 1H, C6-H or C17-H), 8.26 (dd, J = 5.7, 1.7 Hz, 1H, C5-H or C18-H), 7.71 (dd, J = 5.7, 0.7 Hz, 1H, C6-H or C17-H), 7.36 – 7.26 (m, 2H, C3-H), 7.20 – 7.10 (m, 2H, C2-H), 4.12 (s, 3H, C₉-H₃ or C₁₆-
H3, 4.08 (s, 3H, C9-H3 or C16-H3); 13C{1H} NMR (126 MHz, CD2Cl2) δ 164.0 (d, J = 248 Hz, C1), 163.2 (C8 or C15), 162.9 (C8 or C15), 156.2 (C7 or C14), 154.9 (C7 or C14), 152.6 (C5 or C18), 148.2 (C6 or C17), 144.5 (C11 or C12), 143.8 (C11 or C12), 139.6 (d, J = 7.7 Hz, C3), 135.0 (d, J = 7.3 Hz, C4), 129.7 (C6 or C17), 128.7 (C5 or C18), 125.5 (C10 or C13), 125.4 (C10 or C13), 120.1 (q, J = 322 Hz, anion C3F), 118 (d, J = 21.5 Hz, C2); 19F NMR (377 MHz, CD2Cl2) δ -79.29 (anion C3F), -114.15 (tt, J = 8.8, 5.3 Hz, C1-F); HRMS (ESI+) calcd. 690.9804 for [M–NTf2]+ [C20H16AuF3N4O4]+, found 690.9830.

[(κ2-4,4′-Bis(trifluoromethyl)-bipy)Au(4-FC6H4)I][NTf2] (4f•NTf2)

Following General Procedure C on a 46.2 μmol scale with Au(I) complex 2f•NTf2 and 4-fluoroiodobenzene (3a) gave 4f•NTf2 (33 mg, 78%) as a yellow solid; 1H NMR (500 MHz, CD2Cl2) δ 9.91 (d, J = 5.9 Hz, 1H, C5-H or C16-H), 8.74 (s, 1H, C9-H or C12-H), 8.68 (s, 1H, C9-H or C12-H), 8.21 (dd, J = 5.9, 1.8 Hz, 1H, C6-H or C15-H), 8.02 (dd, J = 5.9, 1.8 Hz, 1H, C6-H or C15-H), 7.77 (d, J = 5.9 Hz, 1H, C5-H or C16-H), 7.32 – 7.26 (m, 2H, C3-H), 7.16 (t, J = 8.9 Hz, 2H, C2-H); 13C{1H} NMR (126 MHz, CD2Cl2) δ 164.1 (d, J = 249 Hz, C1), 156.2 (C10 or C11), 155.0 (C10 or C11), 153.1 (C5 or C16), 148.8 (C5 or C16), 145.1 (q, J = 36.6 Hz, C7 or C13), 144.5 (q, J = 36.6 Hz, C7 or C13), 135.0 (d, J = 7.3 Hz, C3), 126.8 (q, J = 3.2 Hz, C6 or C15), 125.9 (q, J = 3.1 Hz, C6 or C15), 122.8 (q, J = 3.6 Hz, C9 or C12), 122.6 (q, J = 3.4 Hz, C9 or C12), 118.7 (d, J = 21.7 Hz, C2), 116.4 (C4); 19F NMR (377 MHz, CD2Cl2) δ -65.34 (C8-F3 or C14-F3), -65.44 (C8-F3 or C14-F3), -79.20 (anion CF3), -113.70 (C1-F); HRMS (ESI+) calcd. 710.9442 for [M–NTf2]+ [C18H16N2F5IAu]+, found 710.9422.
Following General Procedure C on a 27.2 µmol scale with Au(I) complex 2d•NTf₂ and 4-iodoanisole (3c) gave 5d•NTf₂ (13 mg, 51%)b as a dark yellow solid; ¹H NMR (500 MHz, CD₂Cl₂) δ 9.52 (app. t, J = 2.3 Hz, 1H, C7-H or C16-H), 8.76 – 8.65 (m, 2H, C10-H and C11-H), 8.25 – 8.16 (m, 2H, C9-H or C14-F), -113.61 (ddt, J = 6.7, 4.4, 2.2 Hz, C7-F or C14-F); HRMS (ESI⁺) calcd. 622.9706 for [M–NTf₂⁺] [C₁₇H₁₃AuF₂IN₂O]⁺, found 622.9700.

b Contains Au(I) ethylene complex 2d•NTf₂
1H, C7-H or C16-H), 7.19 – 7.11 (m, 2H, C4-H), 1.39 (s, 9H, C1-H3); 13C\textsuperscript{1}H NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 163.2 (d, J = 181 Hz, C8 or C15), 161.1 (d, J = 181 Hz, C8 or C15), 153.4 (C3), 151.4 (d, J = 4.2 Hz, C11 or C12), 150.0 (d, J = 4.1 Hz, C11 or C12), 140.4 (d, J = 32.7 Hz, C7 or C16), 136.6 (d, J = 34.3 Hz, C7 or C16), 133.0 (C4), 132.0 (d, J = 19.0 Hz, C9 or C14), 130.9 (d, J = 19.0 Hz, C9 or C14), 129.3 (C5), 128.3 (d, J = 7.1 Hz, C10 or C13), 128.2 (d, J = 6.3 Hz, C10 or C13), 122.9 (C6), 120.3 (q, J = 322 Hz, anion CF\textsubscript{3}), 35.0 (C2), 31.7 (C1); 19F NMR (377 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ -80.3 (anion CF\textsubscript{3}), -113.9 (ddt, J = 6.8, 4.6, 2.5 Hz, C8-F or C15-F), -114.8 (ddt, J = 6.5, 4.3, 2.1 Hz, C8-F or C15-F), HRMS (ESI\textsuperscript{+}) calcd. 649.0226 for [M–NTf\textsubscript{2}]\textsuperscript{+} [C\textsubscript{20}H\textsubscript{19}N\textsubscript{2}F\textsubscript{2}AuI]\textsuperscript{+}, found 649.2030.

![Chemical structure of the complex](image)

Following General Procedure C on a 18.6 μmol scale with Au(I) complex 2d•NTf\textsubscript{2} and 4-iodotoluene (3e) gave 5e•NTf\textsubscript{2} (16 mg, 97%) as a yellow solid; \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 9.52 (dd, J = 2.7, 1.8 Hz, 1H, C6-H or C15-H), 8.73 (dd, J = 9.1, 4.5 Hz, 1H, C9-H or C12-H), 8.69 (dd, J = 9.1, 4.5 Hz, 1H, C9-H or C12-H), 8.24 – 8.17 (m, 2H, C8-H or C13-H), 7.40 (app. t, J = 2.4 Hz, 1H, C6-H or C15-H), 7.21 – 7.16 (m, 2H, C4-H), 7.13 – 7.07 (m, 2H, C3-H), 2.48 (s, 3H, C1-H3); 13C\textsuperscript{1}H NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 163.2 (d, J = 176.0 Hz, C7 or C14), 161.1 (d, J = 175.7 Hz, C7 or C14), 151.4 (d, J = 4.2 Hz, C10 or C11), 150.0 (d, J = 4.3 Hz, C10 or C11), 140.4 (d, J = 32.9 Hz, C6 or C15), 140.4 (C2), 136.5 (d, J = 34.1 Hz, C6 or C15), 133.3 (C3), 132.8 (C4), 132.1 (d, J = 19.0 Hz, C8 or C13), 130.9 (d, J = 19.1 Hz, C8 or C13), 128.4 (d, J = 6.9 Hz, C9 or C12), 128.2 (d, J = 7.1 Hz, C9 or C12), 122.5 (C5), 120.3 (q, J = 320 Hz, anion CF\textsubscript{3}), 20.3 (C1); 19F NMR (377 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ -77.43 (anion CF\textsubscript{3}), -110.82 (ddt, J = 6.6, 4.5, 2.2 Hz, C6-F or C14-F), -111.74 (ddt, J = 6.8, 4.6, 2.2 Hz, C6-F or C14-F); HRMS (ESI\textsuperscript{+}) calcd. 606.9757 for [M–NTf\textsubscript{2}]\textsuperscript{+} [C\textsubscript{17}H\textsubscript{13}AuF\textsubscript{2}I]\textsuperscript{+}, found 606.9767.
[(κ²-5,5'-Difluoro-bipy)Au(4-Br-C₆H₄)I][NTf₂] (5f•NTf₂)

Following General Procedure C on a 33.0 μmol scale with Au(I) complex 2d•NTf₂ and 1-bromo-4-iodobenzene (3f) gave 5f•NTf₂ (19 mg, 62%) as a yellow solid; ¹H NMR (500 MHz, CD₂Cl₂) δ 9.56 (app. t, J = 2.3 Hz, 1H, C5-H or C14-H), 8.69 (dd, J = 9.1, 4.6 Hz, 1H, C8-H or C11-H), 8.65 (dd, J = 9.1, 4.6 Hz, 1H, C8-H or C11-H), 8.25 – 8.16 (m, 2H, C7-H and C12-H), 7.54 – 7.49 (m, 2H, C2-H), 7.45 (app. t, J = 2.4 Hz, 1H, C5-H or C14-H), 7.19 – 7.14 (m, 2H, C3-H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 163.2 (d, J = 176 Hz, C6 or C13), 161.1 (d, J = 177 Hz, C6 or C13), 151.6 (d, J = 4.5 Hz, C9 or C10), 150.22 (d, J = 4.1 Hz, C9 or C10), 140.7 (d, J = 33.2 Hz, C5 or C14), 136.4 (d, J = 33.9 Hz, C5 or C14), 135.4 (C3), 134.5 (C2), 132.1 (d, J = 19.0 Hz, C7 or C12), 131.0 (d, J = 19.1 Hz, C7 or C12), 128.4 (d, J = 7.1 Hz, C8 or C11), 128.3 (d, J = 7.1 Hz, C8 or C11), 124.5 (C1), 123.1 (C4), 120.4 (q, J = 32 Hz, anion CF₃); ¹⁹F NMR (377 MHz, CD₂Cl₂) δ -79.19 (anion CF₃), -112.23 – -112.33 (m, C6-F or C13-F), -113.29 – -113.37 (m, C6-F or C13-F); HRMS (ESI⁺) calcd. 670.8706 for [M–NTf₂]⁺ [C₁₆H₁₀N₂F₂⁷⁹BrIAu]⁺, found 670.8726.

[(κ²-5,5'-Difluoro-bipy)Au(4-formyl-C₆H₄)I][NTf₂] (5g•NTf₂)

Following General Procedure C on a 27.2 μmol scale with Au(I) complex 2d•NTf₂ and 4-iodobenzaldehyde (3g) gave 5g•NTf₂ (16 mg, 18.2 mmol 67%) as a yellow solid; ¹H NMR (500 MHz, CD₂Cl₂) δ 10.08 (s, 1H, C1-H), 9.58 (app. t, J = 2.4 Hz, 1H, C6-H or C15-H), 8.67 (m, 2H, C9-H and C10-H), 8.58 (d, J = 2.9 Hz, 1H, C6-H or C15-H), 8.21 (m, 2H, C8-H and C13-H), 7.84 (d, J = 8.5 Hz, 2H, C3-H), 7.54 (d, J = 8.5 H, 2H, C4-H); ¹³C{¹H} NMR (126 MHz) calcd. 670.8706 for [M–NTf₂]⁺ [C₁₆H₁₀N₂F₂⁷⁹BrIAu]⁺, found 670.8726.

Contains traces of aryl iodide substrate
MHz, CD$_2$Cl$_2$) $\delta$ 191.5 (C1), 163.2 (d, $J = 180$ Hz, C7 or C14), 161.1 (d, $J = 180$ Hz, C7 or C14), 151.7 (d, $J = 4.0$ Hz, C10 or C11), 150.2 (d, $J = 3.8$ Hz, C10 or C11), 140.8 (d, $J = 33.2$ Hz, C6 or C15), 137.6 (C2), 136.4 (d, $J = 33.5$ Hz, C6 or C15), 135.0 (C4), 132.8 (C5), 132.1 (d, $J = 18.8$ Hz, C8 or C13), 131.8 (C3), 131.0 (d, $J = 18.9$ Hz, C8 or C13), 128.4 (d, $J = 7.2$ Hz, C9 or C12), 128.3 (d, $J = 7.5$ Hz, C9 or C12), 120.3 (q, $J = 321$ Hz, anion CF$_3$); $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$) $\delta$ -80.18 (anion CF$_3$), -113.39 (C7-F or C14-F), -114.30 (C7-F or C14-F); HRMS (ESI+) calcd. 620.9550 for [M–NTf$_2$]$^+$ [C$_{17}$H$_{11}$N$_2$OF$_2$Au]$^+$, found 620.9541.
3. Crystallographic information

X-ray diffraction experiments on 2c•NTf₂, 2e•NTf₂, 2f•NTf₂ and 2i•NTf₂ (Figures S1 to S4) were carried out at 100(2) K on a Bruker APEX II diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Intensities were integrated in SAINT[10] and absorption corrections based on equivalent reflections were applied using SADABS.[11] The structures were solved using Superflip[12] (2c•NTf₂, 2e•NTf₂ and 2i•NTf₂) or ShelXT[13] (2f•NTf₂) and refined by full matrix least squares against $F^2$ in ShelXL[14] using Olex2.[15] All of the non-hydrogen atoms were refined anisotropically, while all of the hydrogen atoms were located geometrically and refined using a riding model. Crystal structure and refinement data are given in Tables S1 and S2. Crystallographic data for compounds 2c•NTf₂, 2e•NTf₂, 2f•NTf₂ and 2i•NTf₂ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC deposition numbers: 2056126 (2c•NTf₂); 2056141 (2e•NTf₂); 2058337 (2f•NTf₂); 2056142 (2i•NTf₂). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. Fax: (+44) 1223 336033. Email: deposit@ccdc.cam.ac.uk.
Figure S1: Thermal ellipsoid plot of complex 2e\textbullet{}NTf\textsubscript{2} determined by single-crystal X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au1-N1 2.166(4), Au1-N2 2.175(5), N1-Au1-N2 75.06(17), Au1-C1 2.071(6), Au1-C2 2.099(6), Au1-C1=C2(centroid) 1.964, C1-C2 1.397(10).

Figure S2: Thermal ellipsoid plot of the grown structure of complex 2e\textbullet{}NTf\textsubscript{2} determined by single-crystal X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au1-N1 2.1793(17), N1-Au1-N1 74.581, Au1-C1 2.092(2), Au1-C1=C1(centroid) 1.970, C1-C1 1.408(5).
Table S1: Crystal data and structure refinement for 2c•NTf₂ and 2e•NTf₂

| Identification code | 2c•NTf₂ | 2e•NTf₂ |
|---------------------|---------|---------|
| Empirical formula   | C₁₄H₁₀AuBr₂F₆N₃O₄S₂ | C₁₈H₁₆AuF₆N₃O₈S₂ |
| Formula weight      | 819.16  | 777.42  |
| Temperature/K       | 100(2)  | 100(2)  |
| Crystal system      | orthorhombic | monoclinic |
| Space group         | Pnna    | C2/c    |
| a/Å                 | 19.9969(4) | 15.7300(3) |
| b/Å                 | 22.6201(4) | 13.8004(3) |
| c/Å                 | 9.7743(2)  | 12.6977(2) |
| α/°                 | 90       | 90      |
| β/°                 | 90       | 117.4250(10) |
| γ/°                 | 90       | 90      |
| Volume/Å³           | 4421.23(15) | 2446.64(8) |
| Z                   | 8        | 4       |
| ρcalc/g/cm³         | 2.461    | 2.111   |
| μ/mm⁻¹              | 10.536   | 6.279   |
| F(000)              | 3056.0   | 1496.0  |
| Crystal size/mm³    | 0.536 × 0.247 × 0.189 | 0.641 × 0.467 × 0.244 |
| Radiation           | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 3.062 to 55.79 | 4.15 to 57.394 |
| Index ranges        | -26 ≤ h ≤ 26, | -20 ≤ h ≤ 21, |-29 ≤ k ≤ 29, | -18 ≤ k ≤ 17, |-12 ≤ l ≤ 12, | -15 ≤ l ≤ 17 |
| Reflections collected | 57350 | 12290 |
| Rint / Rσ          | 0.0598 / 0.0291 | 0.0303 / 0.0249 |
| Data/restraints/parameters | 5286/286/425 | 3159/108/233 |
| Goodness-of-fit on F² | 1.113 | 1.062 |
| Final R indexes [I>2σ (I)] | R₁ = 0.0379, wR₁ = 0.0735 | R₁ = 0.0178, wR₁ = 0.0435 |
| Final R indexes [all data] | R₁ = 0.0532, wR₁ = 0.0781 | R₁ = 0.0191, wR₁ = 0.0441 |
| Largest diff. peak/hole / e Å⁻³ | 1.54/-1.46 | 1.37/-0.90 |
**Figure S3:** Thermal ellipsoid plot of complex 2f•NTf₂ determined by single-crystal X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au1-N1 2.177(7), Au1-N2 2.168(6), N1-Au1-N2 74.8(2), Au1-C1 2.087(8), Au1-C2 2.098(8), Au1-C1=C2(centroid) 1.970, C1-C2 1.413(14).

![Thermal ellipsoid plot of complex 2f•NTf₂](image)

**Figure S4:** Thermal ellipsoid plot of complex 2i•NTf₂ determined by single-crystal X-ray diffraction. Thermal ellipsoids are shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au1-N1 2.177(3), Au1-N2 2.158(3), N1-Au1-N2 75.242, Au1-C1 2.095(3), Au1-C2 2.075(3), Au1-C1=C2(centroid) 1.963, C1-C2 1.408(5).

![Thermal ellipsoid plot of complex 2i•NTf₂](image)
Table S2: Crystal data and structure refinement for 2f•NTf₂ and 2i•NTf₂:

| Identification code | 2f•NTf₂ | 2i•NTf₂ |
|---------------------|---------|---------|
| **Empirical formula** | C_{16}H_{10}AuF_{12}N_{3}O_{4}S_{2} | C_{16}H_{16}AuF_{6}N_{3}O_{6}S_{2} |
| **Formula weight** | 797.36 | 721.40 |
| **Temperature/K** | 100(2) | 100(2) |
| **Crystal system** | monoclinic | triclinic |
| **Space group** | P2₁/c | P-1 |
| **a/Å** | 28.4787(5) | 7.22700(10) |
| **b/Å** | 8.3437(2) | 15.8266(3) |
| **c/Å** | 21.3689(4) | 19.6496(3) |
| **α/°** | 90 | 98.4070(10) |
| **β/°** | 111.5147(10) | 99.3110(10) |
| **γ/°** | 90 | 95.6050(10) |
| **Volume/Å³** | 4723.84(17) | 2177.04(6) |
| **Z** | 8 | 4 |
| **ρ calc/g/cm³** | 2.242 | 2.201 |
| **μ/mm⁻¹** | 6.530 | 7.041 |
| **F(000)** | 3024.0 | 1384.0 |
| **Crystal size/mm³** | 0.56 × 0.436 × 0.072 | 0.38 × 0.3 × 0.2 |
| **Radiation** | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| **2θ range for data collection/°** | 1.538 to 52.744 | 3.092 to 55.128 |
| **Index ranges** | -35 ≤ h ≤ 35 | -9 ≤ h ≤ 9 |
| | -10 ≤ k ≤ 10 | -20 ≤ k ≤ 20 |
| | -26 ≤ l ≤ 26 | -25 ≤ l ≤ 25 |
| **Reflections collected** | 73238 | 38712 |
| **R int / R sigma** | 0.0447 / 0.0258 | 0.0406 / 0.0370 |
| **Data/restraints/parameters** | 9670/66/713 | 10062/30/710 |
| **Goodness-of-fit on F²** | 1.268 | 1.027 |
| **Final R indexes [I>=2σ (I)]** | R₁ = 0.0446, wR₂ = 0.0989 | R₁ = 0.0237, wR₂ = 0.0480 |
| **Final R indexes [all data]** | R₁ = 0.0503, wR₂ = 0.1007 | R₁ = 0.0327, wR₂ = 0.0506 |
| **Largest diff. peak/hole / e Å⁻³** | 1.95/-1.69 | 1.00/-0.88 |
4. Mechanistic studies

4.1. Linear free energy relationships

4.1.1. General considerations

Stock solutions were prepared by weighing reagents directly into J. Young’s tubes, which were subsequently placed under an atmosphere of dinitrogen. The necessary amount of solvent (CH₂Cl₂) was measured using 0.1 mL or gas-tight μL-syringes. In instances where reagents were liquids, the volume required was measured using a gas-tight μL syringe. All Au(I) complex stock solutions were freshly prepared as above for immediate use. Amounts of stock solution required were measured using a gas-tight μL syringe where volumes were ≤ 0.1 mL. Volumes above this were measured using a 0.1 mL syringe. Arrays of ¹⁹F NMR spectra were collected at 50 ± 0.1 °C at 470 MHz on a Varian VNMR 500 MHz spectrometer and were implemented using the standard Varian software. A stock solution of trifluorotoluene was used as an internal standard. Each acquisition had 8 scans per spectrum and a 15 s delay between the end of one spectrum and the start of the next. NMR array data was processed using MestReNova 11.0. Spectrometer probe temperature was periodically calibrated using the ethylene glycol/methanol-thermometer methods.[16]

4.1.2. Representative experiment

Au(I) complex (7.6 μmol), trifluorotoluene (7.6 μmol) and aryl iodide (0.153 mmol) were added as stock solutions in dichloromethane at −78 °C into a J. Young’s NMR tube under an atmosphere of dinitrogen. Once the tube had been sealed, and the contents mixed by shaking, it was manually loaded into the NMR spectrometer which had been pre-heated, pre-tuned and pre-shimmed on a dummy sample. The kinetics experiment was started immediately without tuning or shimming. The time between removing the NMR tube from the cold bath and the middle of the first acquisition (i.e., 4th scan, typically <90 s) and the time between collected arrays (typically <30 s) were measured using a stopwatch.
4.1.3. Kinetic data

In all NMR kinetics experiments, initial rates (i.e., before the system reaches equilibrium) were used to determine the rate of oxidative addition as shown by a representative example in Figure S5. Initial rates are quoted in Table S3 for the ligands and aryl iodides with errors given as 95% confidence intervals.

**Figure S5**: Representative determination of initial rate from raw $^{19}$F NMR spectroscopic concentration data. Example is for the oxidative addition of parent bipy complex 2a$^{\bullet}$NTf$_2$ and 4-fluoriodobenzene (3a).

![Graph showing oxidative addition rate over time](image)

**Table S3**: Initial oxidative addition rates for ligand and aryl iodide with different substituents

| Ligand substituent effects | Aryl iodide substituent effects |
|----------------------------|---------------------------------|
| Substituent               | $\sigma^{[17]}$ | Initial rate / $\times 10^{-6}$ M s$^{-1}$ | Substituent | $\sigma^{[17]}$ | Initial rate / $\times 10^{-6}$ M s$^{-1}$ |
| H                         | 0                | 0.66 ± 0.2 | H               | 0                | 8.6 ± 1.9 |
| $p$-$^3$Bu                | −0.2             | 0.43 ± 0.08 | $p$-OMe        | −0.27            | 17 ± 0.6  |
| $p$-Br                    | 0.23             | 1.0 ± 0.2  | $p$-$^3$Bu      | −0.20            | 7.7 ± 2.4  |
| $m$-F                     | 0.34             | 1.1 ± 0.3  | $p$-Me         | −0.17            | 12 ± 5.2  |
| $p$-COOMe                 | 0.45             | 1.4 ± 0.5  | $p$-F          | 0.06             | 1.8 ± 0.2  |
| $p$-CF$_3$                | 0.54             | 1.9 ± 0.3  | $p$-Br         | 0.23             | 0.99 ± 0.09 |
|                           |                   |           | $p$-CHO        | 0.42             | 0.63 ± 0.06 |
|                           |                   |           | $p$-CF$_3$     | 0.54             | 0.26 ± 0.02 |
|                           |                   |           | $p$-CH=CH$_2$  | −0.04            | 0.76 ± 0.8  |
4.2. \textit{van’t Hoff} analysis

Using a similar \textsuperscript{19}F NMR method outlined above, equilibrium constants \((K)\) were approximated\textsuperscript{d} according to Equation 1 based on the concentration of Au(III) oxidative addition complex \(4\text{d} \bullet \text{NTf}_2\) and starting Au(I) ethylene complex \(2\text{d} \bullet \text{NTf}_2\) (from the reaction with 4-fluoriodobenzene \(3\text{a}\)).

\[
K \approx \frac{[\text{Au(III) product}]}{[\text{Au(I) starting complex}]} \quad (I)
\]

Equilibrium constants at the specified temperatures are given in Table S4 and added to the \textit{van’t Hoff} plot given in Figure S6.

\begin{table}[h]
\centering
\begin{tabular}{c|cccccc}
\textbf{T} / °C & 25 & 35 & 40 & 45 & 55 & 65 \\
\hline
\textbf{\(K\)} & 0.08 & 0.18 & 0.23 & 0.46 & 0.84 & 1.98 \\
\end{tabular}
\caption{Equilibrium constants at different temperatures}
\end{table}

\textbf{Figure S6:} \textit{van’t Hoff} plot for the oxidative addition of 4-fluoriodobenzene \(3\text{a}\) to Au(I) complex \(2\text{d} \bullet \text{NTf}_2\)

\textsuperscript{d} Due to the nature of the reaction which follows \(\text{bipyAu-C}_2\text{H}_4 + \text{ArI} \rightleftharpoons \text{bipyAu-ArI} + \text{C}_2\text{H}_4\), where ethylene is lost in the forward reaction and the determination of its concentration is non-trivial, the reaction equation may be simplified to \(\text{bipyAu-C}_2\text{H}_4 \rightleftharpoons \text{bipyAu-ArI}\) for the equilibrium constant approximation. Also, given the reaction is under pseudo-first-order conditions (20 eq.), the concentration of ArI is assumed to be constant.
The enthalpy of reaction ($\Delta H$) may be approximated by extracting the gradient of the above by rearrangement of the van’t Hoff equation (Equation 2) which gives $\Delta_{\text{rxn}}H \approx 16 \text{ kcal mol}^{-1}$. Where $K$ is the equilibrium constant, $\Delta H$ is the enthalpy of reaction, $R = 1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$ is the gas constant, $T$ is the temperature, $\Delta S$ is the entropy of reaction.

$$lnK = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$  \hspace{1cm} (2)

4.3. Aryl iodide kinetic isotope effect

Absolute initial oxidative addition rates with both iodobenzene (3b) and iodobenzene-$d_5$ (3j) were measured in a manner similar to above and the kinetic isotope effect was calculated according to Equation 3.

$$\frac{k_D}{k_H} = \frac{8.6 \times 10^{-6} \text{ M s}^{-1}}{8.3 \times 10^{-6} \text{ M s}^{-1}} = 1.04$$  \hspace{1cm} (3)

**Figure S7:** $^{19}$F NMR spectroscopic raw data for oxidative addition of iodobenzene (3b) and iodobenzene-$d_5$ (3j) with bipy complex 2d•NTf₂. Dashed lines are data fitted to a 6th order polynomial arbitrary function.
4.4. **Counterion and solvent kinetic data**

For these experiments related to changing of the Au(I) complex counterion and solvent, initial rates were measured in a manner identical to those described above. In all cases with Au(I) complexes $\text{2d•NTf}_2$, $\text{2d•SbF}_6$ and $\text{2d•BF}_4$, 4-fluoriodobenzene (3a) was used as the substrate. Initial rate data is given in Table S5. Errors are given as 95% confidence intervals.

**Table S5**: Initial rates for counterion and solvent switching experiments

| Solvent  | Counterion | Initial rate / $\times 10^{-6}$ M s$^{-1}$ |
|----------|------------|------------------------------------------|
| CH$_2$Cl$_2$ | NTf$_2^-$   | 1.1 $\pm$ 0.3                           |
| CH$_2$Cl$_2$ | SbF$_6^-$   | 1.1 $\pm$ 0.4                           |
| MeCN     | NTf$_2^-$   | 1.5 $\pm$ 0.2                           |
| MeCN     | BF$_4^-$    | 1.3 $\pm$ 0.1                           |
5. Computational details

5.1. General considerations

All calculations were performed using Gaussian 09, Revision D.01.\textsuperscript{[18]} The ωB97-XD functional\textsuperscript{[19]} with an ultrafine integration grid was used throughout with Ahlrichs’ def2-TZVP basis set on Pd, Pt and Au; def2-SVP on C, N, I and def2-SV on all other atoms.\textsuperscript{[20]} The 60-electron def2 pseudopotentials were used for Pt and Au; 28-electron def2 pseudopotentials were used for Pd and I.\textsuperscript{[21]} Solvation (dichloromethane) was modelled using the SMD model.\textsuperscript{[22]} The nature of all stationary points was confirmed by analysis of the harmonic vibrational frequencies. Energies and Cartesian coordinates relating to \textit{p}-OMe vs \textit{p}-CF\textsubscript{3} aryl iodide electronic effects on oxidative addition to \textit{[bipyAu(C\textsubscript{2}H\textsubscript{4})]}\textsuperscript{+} can be found in reference 5.
5.2.  Palladium and platinum comparison

5.2.1  Full potential energy surface comparison for palladium oxidative addition

**Figure S8:** Calculated potential energy surfaces for $p$-OMe, $p$-Bu, $p$-H, $p$-CHO and $p$-CF$_3$ substiututed aryl iodides. See Section 5.1 for computational details.
### 5.2.2. Energies and Cartesian coordinates (Å) for stationary points

| (bipy)Pd(C₂H₄) | C   | 4.40770 | 1.38860 | -0.37330 |
|                | C   | 4.43730 | 2.62540 | -1.01140 |
|                | C   | 2.06190 | 2.49140 | -1.21510 |
|                | N   | 2.03300 | 1.30520 | -0.60420 |
|                | H   | 5.33830 | 0.94260 | -0.02080 |
|                | H   | 5.38910 | 3.14110 | -1.16420 |
|                | H   | 3.21650 | 4.15930 | -1.95080 |
|                | H   | 1.09670 | 2.89670 | -1.53150 |
|                | C   | 3.18090 | 0.21420 | 0.06820 |
|                | H   | 3.53450 | -3.49410 | 0.05470 |
|                | C   | 1.25460 | -4.58020 | -0.01000 |
|                | H   | 1.52870 | 0.74720 | -0.00230 |
|                | C   | 3.70490 | 1.50220 | -0.03460 |
|                | H   | 3.62230 | 2.89170 | -0.03020 |
|                | H   | 3.68330 | 1.02200 | -0.06820 |
|                | C   | 2.94470 | 1.34920 | -0.04430 |
|                | H   | 3.53380 | 3.49470 | -0.05470 |
|                | H   | 0.76230 | 3.09860 | 0.05210 |
|                | H   | -1.25370 | 4.58040 | 0.01000 |
|                | N   | 0.32300 | -1.34070 | -0.02460 |
|                | N   | 0.32270 | 1.34070 | -0.02460 |
|                | Pd  | 4.44420 | -0.00010 | 0.00000 |
|                | C   | 3.37850 | 0.71380 | 0.01940 |
|                | C   | 3.37850 | -0.71420 | -0.01940 |
|                | H   | 3.65060 | -1.28170 | 0.88490 |
|                | H   | 3.65170 | -1.23240 | -0.95240 |
|                | H   | 3.65180 | 1.23190 | 0.95240 |
|                | H   | 3.65070 | 1.28130 | -0.88490 |

### (bipy)Pd(4-OMe-C₆H₄) transition state

| SCF = -1266.41521 au | ZPE = -1266.18292 au |
|-----------------------|-----------------------|
| Pd    | -0.20980 | -0.72050 | -0.06390 |
| I     | -3.46180 | -0.88490 | 0.06970 |
| C     | 2.35880 | -4.27730 | 0.23360 |
| C     | 2.87670 | -0.09580 | -0.21840 |
| C     | 3.67640 | 0.65160 | 0.63880 |
| C     | 3.74410 | 2.03580 | 0.45870 |
| C     | 3.02900 | 2.61520 | -0.58610 |
| C     | 2.26180 | 1.77620 | -1.39250 |
| N     | 2.18770 | 0.46300 | -1.21780 |
| H     | 4.19560 | 0.16230 | 1.47900 |
| H     | 3.03770 | 3.69100 | -0.76950 |
| H     | 1.68160 | 2.16880 | -2.24650 |
| C     | 2.73590 | -1.58030 | -0.05130 |
| C     | 3.84620 | -2.40760 | 0.10890 |
| C     | 3.65210 | -3.77770 | 0.25440 |
| C     | 1.30440 | -3.39000 | 0.08240 |
| N     | 1.48530 | -2.07350 | -0.05200 |
| H     | 4.84850 | -1.97490 | 0.11060 |

### (bipy)Pd(4-OMe-C₆H₄) η² intermediate

| SCF = -1266.42942 au | ZPE = -1266.14394 au |
|-----------------------|-----------------------|
| C     | 3.24240 | 3.19130 | -1.44560 |
| C     | 3.06440 | -0.58520 | 0.84780 |
| C     | 4.17790 | -1.33930 | 0.86950 |
| C     | 3.98380 | -2.56500 | 1.50070 |
| C     | 2.68570 | -3.00900 | 1.73460 |
| C     | 1.63080 | -2.20350 | 1.31520 |
| N     | 1.81730 | -1.03060 | 0.70930 |
| H     | 5.19220 | -0.98830 | 0.67650 |
| H     | 4.84460 | -3.16690 | 1.80410 |
| H     | 2.48590 | -3.96250 | 2.22870 |
| H     | 0.59140 | -2.51100 | 1.46590 |
| C     | 3.18090 | 0.74500 | -0.18550 |

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| Atom | X  | Y  | Z   |
|------|----|----|-----|
| H    | 2.15420 | -5.35590 | 0.31410 |
| H    | 0.26670  | -3.75210  | 0.05810  |
| C    | -1.79280  | 0.56000   | -0.03160  |
| C    | -1.73830  | 1.38940   | -1.19370  |
| C    | -1.15200  | 0.97930   | 1.15720   |
| C    | -1.04100  | 2.57740   | -1.14350  |
| C    | -0.45040  | 2.21810   | 1.17650   |
| C    | -0.39390  | 3.06300   | 0.04090   |
| H    | -1.35880  | 0.49750   | 2.11770   |
| H    | -0.97430  | 3.21180   | -2.02800  |
| H    | -2.25100  | 1.10100   | -2.12040  |
| H    | 4.50740   | -4.44190  | 0.39060   |
| H    | 4.34730   | 2.64710   | 1.13720   |
| O    | 0.23480   | 4.20340   | -0.05110  |
| H    | -0.00380  | 2.54300   | 2.11140   |
| C    | 0.79120   | 4.77400   | 1.09900   |
| H    | 1.18870   | 5.74960   | 0.81230   |
| H    | 0.02900   | 4.95000   | 1.88760   |
| H    | 1.62080   | 4.15970   | 1.48700   |

(bipy)Pd(4-OMe-C₆H₄) product

SCF = −1266.48953 au
ZPE = −1266.20189 au

Pd  -0.37690  -0.22420  0.02090
I   0.01370  -2.83480  0.05070
C  -1.47130  4.53090  0.07610
C  -0.13320  4.15630  0.10690
C   0.17690  2.80170  0.07900
N  -0.75990  1.84930  0.02420
C  -2.06520  2.19820  -0.01110
C  -2.44660  3.54030  0.01410
H   0.67020  4.89440  0.15290
H   1.21430  2.46280  0.10280
H  -3.49920  3.82210  -0.01140
C  -5.28810  0.20590  -0.20250
C  -4.75000  -1.07610  -0.18800
C  -3.36700  -1.21120  -0.11960
N  -2.54460  -0.16200  -0.06650
C  -3.05240  1.08590  -0.07750
C  -4.42990  1.30800  -0.14680
C  -5.38260  -1.96530  -0.22910
H  -2.89270  -2.19660  -0.10650
H  -4.84220  2.30970  -0.15740
C   4.35620  0.61310  0.18230
C   3.60500  0.52360  1.36330
C   2.24680  0.21860  1.31550
C   1.58910  0.00400  0.09250
C   2.35320  0.08440  -1.07500
C   3.72140  0.38850  -1.04390
H   1.69250  0.15380  2.25830
H   1.88720  -0.09010  -2.05100
H   4.27480  0.44120  -1.98450
H  -1.76060  5.58460  0.09850
H  -6.36870  0.36050  -0.25660
O   5.66860  0.91350  0.32400
H   4.11090  0.69130  2.31890
C   6.47900  0.96940  -0.82050
H   7.49660  1.20380  -0.47290
H   6.49950  0.00220  -1.35760
H   6.15140  1.76280  -1.51930

4'-Bu-C₆H₄I

SCF = −686.26061 au
ZPE = −686.05718 au

C   -0.07260  0.81980  0.00000
C  -1.19610  -0.09000  0.00000
C   -1.02820  -1.39140  0.00000
C   0.24420  -1.98640  0.00000
C   1.35040  -1.12800  0.00000
C   1.20290  0.26190  0.00000
I  -0.31250  2.91540  0.00000
H  -2.20380  0.41460  0.00000
H  -1.92610  -2.01630  0.00000
C   0.37240  -3.51660  0.00000
H   2.36590  -1.52830  0.00000
H   2.09250  0.89760  0.00000
C   1.83650  -3.97640  0.00000
C  -0.31250  -4.08260  1.25830
C  -0.31250  -4.08260  -1.25830
H   1.87760  -5.07980  0.00000
H   2.37910  -3.62510  -0.89500
H   2.37910  -3.62510  0.89500
H  -0.22270  -5.18380  1.28070
H   0.15490  -3.68300  2.17610
H  -1.38780  -3.83590  1.28960
H  -0.22270  -5.18380  -1.28070
H  -1.38780  -3.83590  -1.28960
H   0.15490  -3.68300  -2.17610

(bipy)Pd(4'-Bu-C₆H₄I) η² intermediate

SCF = −1309.11871 au
ZPE = −1308.75376 au

C   2.35920  3.81630  -1.73620
C   3.30720  0.42980  0.64380
C   4.55350  0.19230  1.23110
C   4.73740  -0.95850  1.99270
C   3.67520  -1.84410  2.14950
\[
\begin{array}{cccc}
C & 2.46700 & -1.53720 & 1.53000 \\
N & 2.29150 & -0.43440 & 0.80120 \\
H & 5.38190 & 0.88890 & 1.09790 \\
H & 5.70640 & -1.15860 & 2.45790 \\
H & 3.77380 & -2.75920 & 2.73750 \\
H & 1.60290 & -2.20280 & 1.61830 \\
C & 3.02260 & 1.64230 & -0.18380 \\
C & 3.95470 & 2.66940 & -0.35900 \\
C & 3.61780 & 3.76810 & -1.14460 \\
C & 1.48620 & 2.75630 & -1.51080 \\
N & 1.80910 & 1.70240 & \\
H & 3.61780 & 4.15820 & 0.38680 \\
H & 3.95470 & 1.64230 & 0.86380 \\
Pd & 0.39650 & 0.04600 & -0.30110 \\
C & -3.06080 & 1.04850 & 0.43110 \\
C & -2.46500 & 0.93930 & -0.80240 \\
C & -2.75700 & 0.03680 & 1.40510 \\
H & -2.70680 & 1.64290 & -1.60330 \\
H & -3.21430 & 0.09010 & 2.39800 \\
C & -1.52810 & -0.10760 & -1.12740 \\
C & -1.91910 & -1.01440 & 1.14130 \\
H & -1.75150 & -1.78180 & 1.90360 \\
C & -1.24890 & -1.12270 & -0.13180 \\
I & -0.84060 & -3.16510 & -0.78190 \\
H & -1.40170 & -0.33030 & -2.19430 \\
C & -4.24970 & 3.16170 & -0.34910 \\
C & -4.02780 & 2.17930 & 0.80820 \\
C & -5.39360 & 1.58770 & 1.20430 \\
C & -3.44670 & 2.96450 & 2.00020 \\
H & -4.94200 & 3.96230 & -0.03310 \\
H & -3.30800 & 3.64330 & -0.66630 \\
H & -4.69640 & 2.66630 & -1.22910 \\
H & -6.09670 & 2.39190 & 1.48940 \\
H & -5.83980 & 1.02790 & 0.36270 \\
H & -5.31270 & 0.89810 & 2.06240 \\
H & -4.11870 & 3.79610 & 2.28200 \\
H & -3.31670 & 2.32580 & 2.89110 \\
H & -2.46060 & 3.39380 & 1.74590
\end{array}
\]

**SCF = -1309.10388 au**

**ZPE = -1308.73959 au**

**Pd**

| Element | SCF | ZPE |
|---------|-----|-----|
| Pd      | 0.81140 | -0.24240 |
| I       | 0.63700 | -2.87580 |
| C       | 1.50270 | 4.58760 |
| C       | 0.20020 | 4.10260 |
| C       | 0.00560 | 2.72650 |

**SCF = -1309.17812 au**

**ZPE = -1308.81103 au**

**Pd**

| Element | SCF | ZPE |
|---------|-----|-----|
| Pd      | 0.81140 | -0.24240 |
| I       | 0.63700 | -2.87580 |
| C       | 1.50270 | 4.58760 |
| C       | 0.20020 | 4.10260 |
| C       | 0.00560 | 2.72650 |

**ZPE = -1308.81103 au**

**Pd**

| Element | SCF | ZPE |
|---------|-----|-----|
| Pd      | 0.81140 | -0.24240 |
| I       | 0.63700 | -2.87580 |
| C       | 1.50270 | 4.58760 |
| C       | 0.20020 | 4.10260 |
| C       | 0.00560 | 2.72650 |
|   | 1.02000 | 1.85550 | 0.00330 |
|---|---------|---------|---------|
| C | 2.29180 | 2.31200 | -0.00620 |
| C | 2.55860 | 3.68140 | -0.02980 |
| H | -0.66300 | 4.77120 | -0.02100 |
| H | -0.99990 | 2.30160 | 0.00890 |
| H | 3.58500 | 4.04730 | -0.04540 |
| C | 5.67510 | 0.59630 | 0.04970 |
| C | 5.24610 | -0.72610 | 0.03220 |
| C | 3.87770 | -0.97630 | 0.00900 |
| N | 2.96990 | 0.00110 | -0.00040 |
| C | 3.37150 | 1.28700 | 0.01100 |
| C | 4.72770 | 1.61660 | 0.03950 |
| H | 5.95250 | -1.55890 | 0.03830 |
| H | 3.48660 | -1.99750 | -0.00210 |
| C | 5.05500 | 2.65640 | 0.05700 |
| C | -3.99470 | 0.23430 | 0.04300 |
| C | -3.27270 | 0.15890 | -1.15980 |
| C | -1.89290 | -0.04650 | -1.17870 |
| C | -1.16500 | -0.17730 | 0.01310 |
| C | -1.87870 | -0.12100 | 1.21460 |
| C | -3.26350 | 0.08450 | 1.22770 |
| H | -1.38120 | -0.09660 | -2.14620 |
| H | -1.35730 | -0.23270 | 2.17160 |
| H | -3.76510 | 0.12480 | 2.19760 |
| H | 1.70290 | 5.66190 | -0.05350 |
| H | 6.74050 | 0.83970 | 0.07170 |
| H | -3.79470 | 0.26060 | -2.11700 |
| C | -6.11510 | 0.54480 | 1.42420 |
| C | -5.51370 | 0.46580 | 0.01450 |
| C | -5.81810 | 1.78920 | -0.71250 |
| C | -6.19300 | -0.69480 | -0.73670 |
| H | -7.20340 | 0.72060 | 1.35610 |
| H | -5.96540 | -0.39160 | 1.98960 |
| H | -5.68130 | 1.37450 | 2.00990 |
| H | -6.90760 | 1.97420 | -0.73740 |
| H | -5.34040 | 2.64290 | -0.19860 |
| H | -5.45830 | 1.77740 | -1.75600 |
| H | -7.28840 | -0.54830 | -0.76570 |
| H | -5.83860 | -0.77120 | -1.77940 |
| H | -5.99040 | -1.65990 | -0.23900 |

|   | 1.20710 | 2.64360 | 0.00000 |
|---|---------|---------|---------|
| C | 2.16340 | 0.70570 | 0.00000 |
| H | 0.00000 | -1.55310 | 0.00000 |
| H | -2.16340 | 0.70560 | 0.00000 |
| H | -2.15760 | 3.18480 | 0.00000 |
| H | -0.00010 | 4.43730 | 0.00000 |
| H | 2.15750 | 3.18490 | 0.00000 |

**SCF =** -1152.02988 au
**ZPE =** -1152.01852 au

**SCF =** -1152.01852 au

**ZPE =** -1151.76652 au
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Pd      | 0.15450 | -0.67880 | 0.08880 |
| I       | -2.62840 | 1.29910 | -1.07590 |
| C       | 4.04060 | -2.48520 | -1.10710 |
| C       | 2.51320 | 1.17350 | 0.40290 |
| C       | 3.27970 | 2.28920 | 0.74400 |
| C       | 2.64470 | 3.42410 | 1.24230 |
| C       | 1.26120 | 3.41860 | 1.38700 |
| C       | 0.56480 | 2.26870 | 1.02760 |
| N       | 1.17570 | 1.18300 | 0.55260 |
| H       | 4.36450 | 2.28070 | 0.63250 |
| H       | 0.72070 | 4.28610 | 1.77140 |
| H       | -0.52450 | 2.21450 | 1.11130 |
| C       | 3.10610 | -0.08500 | -0.13580 |
| C       | 4.46210 | -0.21690 | -0.44140 |
| C       | 4.93280 | -1.43150 | -0.93310 |
| C       | 2.70330 | -2.27520 | -0.78560 |
| N       | 2.25280 | -1.10940 | -0.31710 |
| H       | 5.15170 | 0.61710 | -0.30780 |
| H       | 4.36640 | -3.45560 | -1.48740 |
| C       | 1.96040 | -3.06840 | -0.90600 |
| C       | -1.73030 | -0.74750 | 0.43850 |
| C       | -2.35890 | -0.67740 | 1.70210 |
| C       | -1.67470 | -1.96280 | -0.29540 |
| C       | -2.85020 | -1.84630 | 2.25620 |
| C       | -2.20400 | -3.13520 | 0.30690 |
| C       | -2.77350 | -3.07750 | 1.56470 |
| H       | -1.46940 | -1.97570 | -1.37240 |
| H       | -3.28800 | -1.81830 | 3.25920 |
| H       | -2.40910 | 0.26920 | 2.24710 |
| H       | 5.99150 | -1.54890 | -1.17870 |
| H       | 3.23240 | 4.30490 | 1.51400 |
| H       | -2.20850 | -0.07180 | -0.26010 |
| H       | -3.19100 | -3.97530 | 2.02170 |

**SCF** = -1152.08997 au

**ZPE** = -1151.3543 au

**SCF** = -642.37694 au

**ZPE** = -642.27646 au

**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -642.37694 au

**ZPE** = -642.27646 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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**SCF** = -1265.24141 au

**ZPE** = -1265.97926 au

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(bipy)Pd(4-CHO-C₆H₄I) product

| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | 3.65190 | 2.03520 | -1.22160 |
| C    | 3.21800 | 2.82280 | -2.28420 |
| C    | 1.89140 | 2.73270 | -2.69570 |
| C    | 1.05360 | 1.85370 | -2.01460 |
| N    | 1.46970 | 1.09830 | -1.00110 |
| H    | 4.68630 | 2.10920 | -0.88480 |
| H    | 1.50570 | 3.33210 | -3.52360 |
| H    | -0.00100 | 1.75430 | -2.29130 |
| C    | 3.13930 | 0.29610 | 0.55130 |
| C    | 4.46840 | 0.16920 | 0.96890 |
| C    | 4.77130 | -0.65230 | 2.05010 |
| C    | 2.44490 | -1.16000 | 2.21370 |
| N    | 2.15300 | -0.37280 | 1.17360 |
| H    | 5.27200 | 0.69690 | 0.45410 |
| H    | 3.92640 | -1.98500 | 3.54640 |
| H    | 1.60160 | -1.67550 | 2.68180 |
| C    | -1.79600 | -0.26330 | -0.17310 |
| C    | -2.31130 | 0.72820 | -1.06010 |
| C    | -2.17970 | -0.25320 | 1.20510 |
| C    | -3.05530 | 1.76830 | -0.54660 |
| C    | -2.91680 | 0.83160 | 1.69280 |
| C    | -3.35240 | 1.84650 | 0.83670 |
| H    | -2.01030 | -1.12100 | 1.84780 |
| H    | -3.41650 | 2.55680 | -1.21670 |
| H    | -2.08900 | 0.67360 | -2.12900 |
| H    | 5.80670 | -0.76010 | 2.38370 |
| H    | 3.91430 | 3.50390 | -2.78100 |
| H    | -3.19400 | 0.87480 | 2.75080 |
| C    | -4.14100 | 2.97240 | 1.35450 |
| O    | -4.45870 | 3.13250 | 2.51440 |
| H    | -4.44940 | 3.72000 | 0.58020 |

(bipy)Pd(4-CHO-C₆H₄I) transition state

| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | 3.53200 | 2.87810 | -1.49460 |
| C    | 2.92000 | -0.81400 | 0.51220 |
| C    | 3.93940 | -1.63900 | 0.99570 |
| C    | 3.60500 | -2.82700 | 1.64000 |
| C    | 2.26280 | -3.16450 | 1.78580 |
| C    | 1.30680 | -2.29100 | 1.27600 |
| N    | 1.62830 | -1.15300 | 0.65960 |
| H    | 4.98860 | -1.36750 | 0.87700 |
| H    | 4.39190 | -3.48210 | 2.02300 |
| H    | 1.95370 | -4.08620 | 2.28370 |
| H    | 0.23860 | -2.51250 | 1.35980 |
| C    | 3.19020 | 0.47780 | -0.19050 |
| C    | 4.48260 | 0.96940 | -0.39340 |
| C    | 4.65370 | 2.18310 | -1.05350 |

SCF = -1265.22715 au
ZPE = -1264.96579 au
(bipy)Pd(4-CF₃-C₆H₄I) transition state

SCF = -1488.72187 au
ZPE = -1488.46522 au

Pd  0.97210  -0.39810  -0.08370
I   0.87340  -3.38560  0.02030
C   4.87700  1.64660  0.27770
C   0.82520  2.78980  -0.21680
C   0.26200  3.83050  0.52700
C   -1.09200 4.11660  0.35310
C   -1.82020 3.36510  -0.56130
C   -1.16900 2.35140  -1.26210
N   0.11880  2.06570  -1.09470
H   0.86360  4.38360  1.25730
H   -2.88710 3.55810  -0.72220
H   -1.71230 1.74890  -1.99080
C   2.25870  2.41860  -0.04600
C   3.25200  3.39600  0.06500
C   4.57890  3.00600  0.22750
C   3.80800  0.73590  0.16320
N   2.55330  1.10690  0.01120
H   2.98720  4.45470  0.01770
H   5.90070  1.28830  0.40230
H   4.01880  -0.34050  0.19970
C   -0.52100 -1.75550  -0.00110
C   -1.39550 -1.63730  -1.12420
C   -0.81790 -1.11090  1.22240
C   -2.54810 -0.88210  -1.02830
C   -2.04350 -0.33460  1.28270
C   -2.87410 -0.21940  0.17900
H   -0.34180 -1.33800  2.14510
H   -3.20190 -0.78340  -1.90870
H   -1.15360 -2.13010  -2.07230
H   5.31700  3.75560  0.31390
H   -1.56660 4.91070  0.94130
H   -2.30830 0.15690  2.21810
F   -4.12660 1.49280  1.22260
C   -4.14980 0.55700  0.26710
F   -4.46230 1.18650  -0.89070
F   -5.19510 -0.20850  0.51340

(bipy)Pd(4-CF₃-C₆H₄I) product

SCF = -1488.79551 au
ZPE = -1488.53587 au

Pd  0.78910  -0.23290  0.00460
(bipy)Pt(4-OMe-C₆H₄) η² intermediate

SCF = -1257.89203 au
ZPE = -1257.605976 au

(bipy)Pt(C₆H₆)

SCF = -692.84247 au
ZPE = 692.62636 au

\[
\begin{align*}
\text{C} & : 2.95620 & 1.51070 & 0.02750 \\
\text{C} & : 2.85650 & 2.89870 & 0.02280 \\
\text{H} & : 3.93830 & 1.03740 & 0.05530 \\
\text{C} & : 0.47860 & 2.65510 & -0.02210 \\
\text{C} & : 1.59410 & 3.48470 & -0.00500 \\
\text{H} & : 3.76000 & 3.51370 & 0.04150 \\
\text{C} & : -1.32090 & 0.01720 \\
\text{N} & : 0.57350 & 1.32090 & -0.01720 \\
\text{Pt} & : -1.16470 & -0.00000 & 0.00000 \\
\text{C} & : -3.07830 & 0.72910 & -0.01440 \\
\text{C} & : -3.07830 & -0.72910 & 0.01440 \\
\text{H} & : -3.40280 & -1.27560 & -0.88770 \\
\text{H} & : -3.40350 & -1.24010 & 0.93680 \\
\text{H} & : -3.40270 & 1.27560 & 0.88770 \\
\text{C} & : 0.20990 & 0.17640 & -0.14790 \\
\text{H} & : 3.25720 & 4.04050 & 0.01740 \\
\text{H} & : 5.43440 & 2.97870 & 0.01740 \\
\text{C} & : 2.48900 & 2.89870 & 0.01740 \\
\text{H} & : 3.48470 & 1.03740 & 0.01740 \\
\text{C} & : 0.47860 & 2.65510 & -0.02210 \\
\text{C} & : 1.59410 & 3.48470 & -0.00500 \\
\text{H} & : 3.76000 & 3.51370 & 0.04150 \\
\text{H} & : -1.32090 & 0.01720 \\
\text{N} & : 0.57350 & 1.32090 & -0.01720 \\
\text{Pt} & : -1.16470 & -0.00000 & 0.00000 \\
\text{C} & : -3.07830 & 0.72910 & -0.01440 \\
\text{C} & : -3.07830 & -0.72910 & 0.01440 \\
\text{H} & : -3.40280 & -1.27560 & -0.88770 \\
\text{H} & : -3.40350 & -1.24010 & 0.93680 \\
\text{H} & : -3.40270 & 1.27560 & 0.88770 \\
\end{align*}
\]
\begin{verbatim}
H  -2.38020  -1.11430   2.04690
C   -1.71900  -0.34130   0.08430
I   -2.30270  -2.23580  -0.90190
H   -1.74020   0.78310  -1.83060
O   -3.28470   3.24790   1.65270
C   -3.32410   4.44800   0.93120
H   -2.30950   4.78580   0.64340
H   -3.94240   4.35640   0.01730
H   -3.77690   5.20150   1.59380

(bipy)Pt(4-OMe-C₆H₄I) product

SCF = -1257.96689 au
ZPE = -1257.67885 au

Pt  -0.33910  -0.17030   0.02300
I   0.07230  -2.76970   0.03730
C   -1.51070   4.52930   0.03070
C   -0.16830   4.17100   0.07260
C   0.16360   2.82300   0.06370
N   -0.76260   1.85510   0.01790
C   -2.07520   2.18900  -0.02600
C   -2.47200   3.52530  -0.02140
H   0.62620   4.91890   0.11210
H   1.20440   2.49870   0.09570
H   -3.52880   3.78980  -0.05610
C   -5.25070   0.12700  -0.17960
C   -4.67940  -1.14060  -0.16380
C   -3.29430  -1.24460  -0.10540
N   -2.49580  -0.17420  -0.06380
C   -3.03770   1.06160  -0.07800
C   -4.41920   1.24240  -0.13630
H   -5.28900  -2.04590  -0.19560
H   -2.79820  -2.21830  -0.09060
H   -4.85320   2.24210  -0.14680
C   -2.69960  -1.41980   0.05420
C   -3.84400  -2.21230  -0.02900
C   -3.71580  -3.59150  -0.16620
C   -1.34260  -3.28880  -0.13920
N   -1.46130  -1.95620  -0.01160
H   -4.82800  -1.74170   0.02880
H   -2.27850  -5.21560  -0.32000
H   -0.32330  -3.67790  -0.18830
C   1.66880   0.73420   0.05400
C   1.67450   1.53170   1.23370
C   1.19930   1.29500  -1.15870
C   1.15010   2.80490   1.19980
C   0.65100   2.59470  -1.17130
C   0.60700   3.33710   0.00400
H   1.35320   0.78280  -2.11180
H   1.11090   3.41800   2.10430
H   2.06460   1.12240   2.16930
H   -4.60290  -4.22770  -0.22590
H   -4.17240   2.82780  -1.21090
O   0.07740   4.57110   0.10770
H   0.27700   2.99660  -2.11460
C   -0.49580   5.16370  -1.03200
H   -0.90360   6.13230  -0.70650
H   0.25940   5.33900  -1.82090
\end{verbatim}
5.3. Ligand electronic effect

5.3.1 Full potential energy surface comparison

Figure S9: Calculated potential energy surfaces for $p$-OMe, $p$-Bu, $p$-H, $p$-COOMe and $p$-CF$_3$ substituted 2,2'-bipyridyl ligands. See Section 5.1 for computational details.
5.3.2. Energies and Cartesian coordinates (Å) for stationary points

\((\text{OMe-bipy})\text{Au(C}_6\text{H}_4)\)^+  

\[
\begin{array}{ccc}
\text{Au} & 1.90020 & 0.000100 \quad 0.00000 \\
\text{C} & -2.17110 & 2.897100 \quad 0.00570 \\
\text{C} & -0.89910 & 3.488100 \quad 0.07520 \\
\text{N} & 0.12620 & 1.331100 \quad 0.06440 \\
\text{C} & -1.08130 & 0.748500 \quad 0.01210 \\
\text{H} & -0.79850 & 4.574500 \quad 0.10250 \\
\text{H} & 1.21600 & 3.093800 \quad 0.14330 \\
\text{H} & -3.23230 & 1.001800 \quad -0.08200 \\
\text{C} & -2.17070 & -2.897200 \quad -0.00550 \\
\text{C} & -0.89860 & -3.488100 \quad -0.07470 \\
\text{N} & 0.12640 & -1.330800 \quad -0.06370 \\
\text{C} & -1.08130 & -0.748500 \quad -0.01160 \\
\text{C} & -2.25520 & -1.496600 \quad 0.02320 \\
\text{H} & -0.79790 & -4.574400 \quad -0.10200 \\
\text{H} & 1.21640 & -3.093500 \quad -0.14230 \\
\text{H} & -3.22310 & -1.002000 \quad 0.08190 \\
\text{O} & -3.21290 & 3.714400 \quad -0.03090 \\
\text{O} & -3.21250 & 3.714700 \quad 0.03060 \\
\text{C} & -4.52560 & -3.190500 \quad 0.12470 \\
\text{H} & -5.19760 & -4.059400 \quad 0.14930 \\
\text{H} & -4.65300 & -2.605200 \quad 1.05190 \\
\text{H} & -4.76820 & -2.568000 \quad -0.75380 \\
\text{C} & -4.52590 & 3.189900 \quad -0.12540 \\
\text{H} & -5.19810 & 4.058700 \quad -0.15000 \\
\text{H} & -4.65300 & 2.604800 \quad -1.05260 \\
\text{H} & -4.76860 & 2.567300 \quad 0.75300 \\
\text{C} & 3.88720 & -0.705200 \quad -0.03610 \\
\text{C} & 3.88750 & 0.705000 \quad 0.03540 \\
\text{H} & 4.09440 & -1.301100 \quad 0.86250 \\
\text{H} & 4.09560 & 1.208100 \quad 0.98890 \\
\text{H} & 4.09480 & 1.300700 \quad -0.86330 \\
\text{H} & 4.09490 & -1.208200 \quad -0.98970 \\
\end{array}
\]

\((\text{OMe-bipy})\text{Au(4-OMe-C}_6\text{H}_4\text{I})\)\(^\eta^2\) intermediate

\[
\begin{array}{ccc}
\text{SCF} = -1502.93851 \text{ au} \\
\text{ZPE} = -1502.58517 \text{ au} \\
\text{Au} & -0.51190 & -0.21850 \quad -0.15650 \\
\text{C} & 3.81100 & -2.61770 \quad -0.92800 \\
\text{C} & 2.59240 & -3.26360 \quad -1.19230 \\
\end{array}
\]

\((\text{OMe-bipy})\text{Au(4-OMe-C}_6\text{H}_4\text{I})^+\) transition state

\[
\begin{array}{ccc}
\text{SCF} = -1502.92272 \text{ au} \\
\text{ZPE} = -1502.57038 \text{ au} \\
\end{array}
\]
\[
\begin{array}{cccc}
\text{C} & 3.46740 & -2.93840 & -0.19430 \\
\text{C} & 2.23600 & 1.13020 & -0.00220 \\
\text{C} & 3.11140 & 2.20750 & 0.02840 \\
\text{C} & 2.59580 & 3.51350 & 0.09250 \\
\text{C} & 1.20580 & 3.68390 & 0.12440 \\
\text{C} & 0.41420 & 2.54170 & 0.08580 \\
\text{N} & 0.90890 & 1.31050 & 0.02340 \\
\text{H} & 4.19480 & 2.09240 & 0.00360 \\
\text{H} & 0.73520 & 4.66590 & 0.17770 \\
\text{H} & -0.67700 & 2.62650 & 0.10910 \\
\text{C} & 2.70840 & -0.29400 & -0.06610 \\
\text{C} & 4.06590 & -0.60980 & -0.05630 \\
\text{C} & 4.46350 & -1.95250 & -0.11570 \\
\text{C} & 2.14810 & -2.54060 & -0.19500 \\
\text{N} & 1.76890 & -1.25280 & -0.12900 \\
\text{H} & 4.81300 & 0.17930 & 0.00110 \\
\text{H} & 3.73730 & -3.99450 & -0.24590 \\
\text{H} & 1.34750 & -3.28300 & -0.24770 \\
\text{Au} & -0.37110 & -0.77090 & -0.02780 \\
\text{C} & -2.47880 & -0.30050 & 0.09310 \\
\text{C} & -2.83360 & 0.34920 & -1.10520 \\
\text{C} & -2.72000 & 0.34680 & 1.32850 \\
\text{C} & -3.34100 & 1.64580 & -1.01890 \\
\text{C} & -3.22590 & 1.63390 & 1.34460 \\
\text{C} & -3.53720 & 2.29970 & 0.14380 \\
\text{H} & -2.50190 & -0.16220 & 2.27090 \\
\text{H} & -3.58630 & 2.13090 & -2.20820 \\
\text{H} & -3.39690 & 2.15260 & 2.29120 \\
\text{I} & -2.49200 & -2.56850 & 0.09000 \\
\text{H} & -2.71110 & -0.15830 & -2.06560 \\
\text{O} & -4.00980 & 3.54460 & 0.26700 \\
\text{C} & -4.35540 & 4.27700 & -0.88890 \\
\text{H} & -3.48060 & 4.42640 & -1.54770 \\
\text{H} & -5.16440 & 3.78000 & -1.45370 \\
\text{H} & -4.71160 & 5.25580 & -0.53670 \\
\text{O} & 3.48560 & 4.50000 & 0.11850 \\
\text{O} & 5.72270 & -2.36450 & -0.10250 \\
\text{C} & 6.77530 & -1.42180 & 0.00380 \\
\text{H} & 7.70550 & -2.00690 & 0.01120 \\
\text{H} & 6.78440 & -0.73530 & -0.86060 \\
\text{H} & 6.69820 & -0.84740 & 0.94330 \\
\text{C} & 3.03960 & 5.84180 & 0.19840 \\
\text{H} & 3.94560 & 6.46360 & 0.20280 \\
\text{H} & 2.41900 & 6.10780 & -0.67530 \\
\text{H} & 2.47280 & 6.01680 & 1.12970 \\
\end{array}
\]

\[\text{(OMe-bipy)Au(4-OMe-C}_6\text{H}_4\text{I)}^+ \text{ product} \]

\[
\begin{align*}
\text{SCF} & = -1502.96092 \text{ au} \\
\text{ZPE} & = -1502.66405 \text{ au} \\
\end{align*}
\]

\[\text{(Bu-bipy)Au(C}_2\text{H}_4)^+ \]

\[
\begin{align*}
\text{SCF} & = -1023.26070 \text{ au} \\
\text{ZPE} & = -1023.81873 \text{ au} \\
\end{align*}
\]
|   |   |   |   |
|---|---|---|---|
| Au | -2.38880 | 0.00040 | -0.00000 |
| C  | 1.70890  | 2.90010  | 0.01280  |
| C  | 0.43270  | 3.47890  | 0.04690  |
| C  | -0.69190 | 2.66960  | 0.05490  |
| N  | -0.61480 | 1.33550  | 0.03520  |
| C  | 0.59000  | 0.74680  | 0.00830  |
| C  | 1.76170  | 1.50290  | -0.00650 |
| H  | 0.29640  | 4.56200  | 0.06400  |
| H  | -1.69550 | 3.10140  | 0.07720  |
| H  | 2.72390  | 0.99620  | -0.03830 |
| C  | 1.70810  | -2.90050 | -0.01270 |
| C  | 0.43170  | -3.47890 | -0.04690 |
| C  | -0.69270 | -2.66930 | -0.05500 |
| N  | -0.61520 | -1.33520 | -0.03520 |
| C  | 0.58980  | -0.74690 | -0.00820 |
| C  | 1.76130  | -1.50330 | 0.00660  |
| H  | 0.29510  | -4.56200 | -0.06400 |
| H  | -1.69640 | -3.10090 | -0.07730 |
| H  | 2.72360  | -0.99690 | 0.03830  |
| C  | 2.95980  | 3.77940  | -0.01450 |
| C  | 4.25150  | 2.95230  | 0.00910  |
| C  | 2.93380  | 4.62150  | -1.30440 |
| C  | 2.94550  | 4.71030  | 1.21300  |
| C  | 2.95870  | -3.78030 | 0.01450  |
| C  | 4.25070  | -2.95360 | -0.00940 |
| C  | 2.93260  | -4.62220 | 1.30450  |
| C  | 2.94390  | -4.71130 | -1.12180 |
| C  | -4.37730 | -0.70520 | -0.02000 |
| C  | -4.37740 | 0.70580  | 0.02010  |
| H  | -4.58380 | -1.22930 | -0.96240 |
| H  | -4.58370 | 1.28190  | -0.89160 |
| H  | -4.58380 | 1.23000  | 0.96250  |
| H  | -4.58350 | -1.28120 | 0.89170  |
| H  | 5.12090  | 3.63160  | -0.00340 |
| H  | 4.32830  | 2.33240  | 0.91970  |
| H  | 4.33700  | 2.29240  | -0.87180 |
| H  | 3.82730  | 5.26920  | -1.34700 |
| H  | 2.93630  | 3.97600  | -2.20060 |
| H  | 2.04380  | 5.27250  | -1.35340 |
| H  | 3.85510  | 5.33620  | 1.21720  |
| H  | 2.07500  | 5.38820  | 1.20890  |
| H  | 2.92610  | 4.12990  | 2.15250  |
| H  | 5.11980  | -3.63330 | 0.00280  |
| H  | 4.32750  | -2.33360 | -0.91980 |
| H  | 4.33670  | -2.29400 | 0.87160  |
| H  | 3.82580  | -5.27030 | 1.34700  |
| H  | 2.93560  | -3.97660 | 2.20060  |
| H  | 2.04240  | -5.27280 | 1.35370  |
| H  | 3.85330  | -5.33750 | -1.21720 |
| H  | 2.07310  | -5.38890 | -1.20850 |
| H  | 2.92450  | -4.13100 | -2.15250 |

(Bu-bipy)\text{Au(4-OMe-C}_4\text{H}_4\text{I})^+ \eta^2\text{ intermediate}

\[ \text{SCF} = -1588.31076 \text{ au} \]
\[ \text{ZPE} = -1587.79792 \text{ au} \]
|          | SCF | ZPE  |
|----------|-----|------|
| H        | -4.15580 | 2.13750  | -1.94180 |
| H        | -3.83570 | 2.08930  | 2.36990  |
| I        | -3.05460 | -2.60870 | 0.07760  |
| H        | -3.30510 | -0.15870 | -2.04190 |
| O        | -4.50120 | 3.51700  | 0.38730  |
| C        | -4.87340 | 4.27150  | -0.74590 |
| H        | -4.01490 | 4.42970  | -1.42400 |
| H        | -5.69840 | 3.78770  | -1.29900 |
| H        | -5.21640 | 5.24490  | -0.36700 |
| C        | 3.12650  | 4.57080  | 0.08860  |
| C        | 5.40130  | -2.47620 | 0.00670  |
| C        | 3.93230  | 4.45620  | 1.39640  |
| C        | 2.41690  | 5.93050  | 0.07170  |
| C        | 4.08060  | 4.49890  | -1.11830 |
| C        | 5.98850  | -1.90440 | 1.31140  |
| C        | 6.12550  | -1.85850 | -1.20380 |
| C        | 5.62370  | -3.99350 | -0.00700 |
| C        | 4.64630  | 5.29540  | 1.47120  |
| C        | 3.26690  | 4.49470  | 2.27690  |
| C        | 4.51260  | 3.51890  | 1.44670  |
| C        | 3.16890  | 6.73660  | 0.12240  |
| C        | 1.83270  | 6.07890  | -0.85310 |
| C        | 1.74090  | 6.05330  | 0.93580  |
| C        | 4.79950  | 5.33630  | -1.07970 |
| C        | 4.66240  | 3.56150  | -1.13270 |
| C        | 3.52340  | 4.57020  | -2.06930 |
| C        | 7.05810  | -2.16790 | 1.38670  |
| C        | 5.91240  | -0.80420 | 1.35340  |
| C        | 5.47120  | -2.31880 | 2.19470  |
| C        | 7.19800  | -2.11940 | -1.17120 |
| C        | 5.71010  | -2.23970 | -2.15340 |
| C        | 6.05060  | -0.75750 | -1.21280 |
| C        | 6.70530  | -4.20590 | 0.04440  |
| C        | 5.14680  | -4.48700 | 0.85760  |
| C        | 5.23800  | -4.45880 | -0.93070 |
| Au       | 0.73840  | -0.72530 | -0.02920 |
| I        | 1.76520  | -3.10360 | 0.03500  |
| C        | -1.44320 | 3.67010  | -0.02450 |
| C        | -0.04940 | 3.58730  | -0.05060 |
| C        | 0.57170  | 2.34630  | -0.06730 |
| N        | -0.12020 | 1.20510  | -0.06590 |
| C        | -1.47280 | 1.23990  | -0.05710 |
| C        | -2.14350 | 2.45370  | -0.03510 |
| C        | 0.58250  | 4.47520  | -0.05230 |
| H        | 1.66040  | 2.26380  | -0.07770 |

(Bu-bipy)Au(4-OMe-C₆H₄I)+ transition state

SCF = -1588.29445 au
ZPE = -1587.78312 au

(Bu-bipy)Au(4-OMe-C₆H₄I)+ product

SCF = -1588.332567 au
ZPE = -1587.818458 au

Au  0.73840  -0.72530  -0.02920
I   1.76520  -3.10360  0.03500
C  -1.44320  3.67010  -0.02450
C  -0.04940  3.58730  -0.05060
C   0.57170  2.34630  -0.06730
N  -0.12020  1.20510  -0.06590
C  -1.47280  1.23990  -0.05710
C  -2.14350  2.45370  -0.03510
C   0.58250  4.47520  -0.05230
C   1.66040  2.26380  -0.07770
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | -3.23340 | 2.45580 | -0.02130 |
| C    | -4.16830 | -1.44790 | -0.05440 |
| C    | -3.31450 | -2.55770 | -0.11030 |
| C    | -1.94180 | -2.37670 | -0.13350 |
| N    | -1.38320 | -1.16270 | -0.10860 |
| C    | -2.17130 | -0.07220 | -0.07190 |
| C    | -3.55770 | -0.18910 | -0.04590 |
| H    | -3.70330 | -3.57770 | -0.12840 |
| H    | -1.25740 | -3.22830 | -0.16640 |
| C    | -4.16410 | 0.71350  | -0.01510 |
| C    | 5.13290  | 1.20340  | 0.25490  |
| C    | 4.41170  | 0.89390  | 1.41960  |
| C    | 3.17510  | 0.26410  | 1.33980  |
| C    | 2.63580  | -0.05460 | 0.08890  |
| C    | 3.35220  | 0.23060  | -1.06980 |
| C    | 4.59730  | 0.86440  | -0.99400 |
| H    | 4.84440  | 1.15420  | 2.38930  |
| H    | 2.63570  | 0.03040  | 2.26220  |
| H    | 2.95500  | -0.03120 | -2.05480 |
| H    | 5.13570  | 1.07930  | -1.91910 |
| O    | 6.31720  | 1.81580  | 0.43490  |
| C    | 7.09260  | 2.16200  | -0.68790 |
| H    | 7.99750  | 2.65220  | -0.29940 |
| H    | 7.38990  | 1.26910  | -1.26820 |
| H    | 6.55790  | 2.86910  | -1.34910 |
| C    | -2.20440 | 4.99390  | 0.02790  |
| C    | -5.68390 | -1.63540 | 0.01030  |
| C    | -3.01190 | 5.03940  | 1.33930  |
| C    | -1.25710 | 6.19910  | -0.01170 |
| C    | -3.16170 | 5.07490  | -1.17640 |
| C    | -6.43330 | -0.29830 | 0.05850  |
| C    | -6.14540 | -2.41760 | -1.23330 |
| C    | -6.01840 | -2.43650 | 1.28350  |
| H    | -3.56950 | 5.99030  | 1.40000  |
| H    | -3.74470 | 4.21640  | 1.40130  |
| H    | -2.34720 | 4.97570  | 2.21870  |
| H    | -1.84850 | 7.12990  | 0.02480  |
| H    | -0.56800 | 6.21120  | 0.85060  |
| H    | -0.65840 | 6.22190  | -0.93910 |
| H    | -3.69290 | 6.04240  | -1.16190 |
| H    | -2.60850 | 5.00290  | -2.12940 |
| H    | -3.92500 | 4.27820  | -1.15850 |
| H    | -7.51890 | -0.49060 | 0.10060  |
| H    | -6.16790 | 0.29240  | 0.95250  |
| H    | -6.24100 | 0.31490  | -0.83880 |
| H    | -7.23870 | -2.56620 | -1.19470 |
| H    | -5.90760 | -1.86750 | -2.16080 |
| H    | -5.67480 | -3.41370 | -1.29390 |
| H    | -7.11110 | -2.57380 | 1.36070  |
| H    | -5.55440 | -3.43760 | 1.27550  |

(ZPE = -164.03966 au)

(3COOMe-bipy)Au(C2H4)*

SCF = -1164.34380 au
ZPE = -1164.03966 au

Au -2.47690 0.00020 -0.00000
C 1.59160 -2.89300 0.00070
C 0.33490 -3.49140 0.03660
C -0.78610 -2.67070 0.04920
N -0.69050 -1.33990 0.03380
C 0.51330 -0.74610 0.00430
C 1.68450 -1.50180 -0.01940
H 0.23050 -4.57760 0.05310
H -1.79390 -3.09160 0.07280
H 2.66480 -1.02840 -0.05710
C 1.59190 2.89290 -0.00060
C 0.33530 3.49140 -0.03620
C -0.78590 2.67080 -0.04860
N -0.69040 1.34000 -0.03320
C 0.51330 0.74610 -0.00390
C 1.68460 1.50170 0.01960
H 0.23100 4.57760 -0.05260
H -1.79360 3.09190 -0.07190
H 2.66480 1.02820 0.05710
C -4.47030 0.70420 -0.02030
C -4.46990 -0.70470 0.01950
H -4.67120 1.28090 0.89210
H -4.67070 -1.22990 0.96250
H -4.67010 -1.28150 -0.89290
H -4.67100 1.22920 -0.96340
C 2.81020 -3.77440 -0.01240
C 2.81060 3.77410 0.01230
O 2.75210 -4.97720 -0.00920
O 3.93300 -3.07470 -0.02360
C 5.15670 -3.80690 -0.02930
H 5.95620 -3.05410 -0.03200
H 5.23160 -4.43790 0.87070
H 5.22450 -4.43670 -0.93060
O 2.75260 4.97690 0.00920
O 3.93330 3.07430 0.02330
C 5.15700 3.80640 0.02890
C 5.95650 3.05360 0.03100
H 5.23170 4.43780 -0.87090
H 5.22520 4.43590 0.93040

S48
(COOMe-bipy)Au(4-OMe-C₈H₄I)⁺ η¹ intermediate

SCF = -1729.39428 au
ZPE = -1729.02076 au

Au  -1.06250  -0.29280  -0.14440
C   3.26130  -2.75460  -0.57890
C   2.05870  -3.42470  -0.78730
C   0.87550  -2.70930  -0.65640
N   0.86020  -1.41060  -0.34610
C   2.00990  -0.74780  -0.14390
C   3.23790  -1.40010  -0.25130
H   2.04350  -4.48490  -1.04560
H  -0.09330  -3.19200  -0.80540
H   4.17600  -0.87180  -0.08700
C   2.81750  2.86050   0.72310
C   1.51970  3.36030   0.80110
C   0.46410  2.48620   0.56770
N   0.66020  1.20180   0.27540
C   1.89980  0.70400   0.19550
C   3.01390  1.51430   0.41670
H   1.33580  4.40950   1.03920
H  -0.57310  2.82900   0.61590
H   4.02750  1.12060   0.35730
C   3.96710  3.79630   0.97480
O   3.82160  4.95310   1.27660
C  -3.12420  0.31530  -0.05500
C  -3.13460  1.07790  -0.38700
C  -3.47900  0.69780  1.28770
C  -3.49770  2.04720   0.60060
H  -3.15930  1.39320  -1.43490
I  -3.37570  1.78620  -1.58740
C  -3.79290  0.25380   2.21680
C  -3.80900  1.64330   1.88330
O  -4.15860  2.45900   2.88530
C  -4.22250  3.84770   2.64940
H  -3.32920  2.44750   2.34030
H  -4.97780  4.09030   1.88010
H  -4.51690  4.30990   3.60260
H  -3.50590  1.75660   1.55640
H  -4.05580  0.03230   3.23840
H  -3.54370  0.09410   0.29710
O   5.13960  3.20080   0.82460
C   6.30340  3.99460   1.04310
H   7.15880  3.32850   0.86940
H   6.33020  4.83900   0.33600
H   6.32140  4.37600   2.07650
C   4.54840  3.51890  -0.72120
O   4.59250  4.68350  -1.02510
O   5.60710  1.59100   0.47680

(COOMe-bipy)Au(4-OMe-C₈H₄I)⁺ transition state

SCF = -1729.37883 au
ZPE = -1729.00575 au

Au  -0.99070  -0.79140  -0.05210
I  -3.20230  -2.43410   0.06110
C   2.68170  -3.26100  -0.16730
C   1.75270   0.89050  -0.03620
C   2.70670   1.91070  -0.01730
C   2.27180   3.23540   0.02480
C   0.90530   3.50700   0.04510
C   0.02410   2.43070   0.01900
N   0.44820   1.17160  -0.01940
H   3.77500   1.70070  -0.03600
H   0.53960   4.53480   0.08000
H  -1.05960   2.58250   0.03160
C   2.12190  -0.56090  -0.07680
C   3.44990  -0.98810  -0.04270
C   3.73240  -2.35180  -0.08270
C   1.38580  -2.76430  -0.19190
N   1.12060  -1.45500  -0.14310
H   4.27220  -0.27720   0.01990
H   2.86830  -4.33550  -0.20440
H   0.52710  -3.43810  -0.24810
C  -3.04610  -0.15570   0.10510
C  -3.39160   0.53750  -1.07080
C  -3.22190   0.47460   1.35930
C  -3.83470   1.85600  -1.00680
C  -3.66190   1.78510   1.41530
C  -3.97190   2.49110   0.23740
H  -3.00800  -0.06510   2.28540
H  -4.07900   2.37280  -1.93640
H  -3.78460   2.28960   2.37680
H  -3.31410   0.04730  -2.04470
O  -4.38740   3.75130   0.39880
C  -4.73200   4.52250  -0.73220
H  -3.86620   4.65780  -1.40560
H  -5.56870   4.06570  -1.29070
H  -5.04750   5.50380  -0.34980
C   3.23600   4.38820   0.05310
O   2.88830   5.53850   0.13650
O   4.49590   3.98870  -0.02420
C   5.14040  -2.87640  -0.02940
C   5.50290   4.99700   0.00330
|       |       |       | Au    | -2.60200 | 4.71630 | 0.01180 |
|-------|-------|-------|-------|----------|---------|---------|
|       |       |       | C     | -5.38640 | -2.29090 | -0.06140 |
|       |       |       | O     | -2.09960 | 5.81020 | 0.01250 |
|       |       |       | O     | -5.77770 | -3.42900 | -0.08130 |
|       |       |       | O     | -3.90210 | 4.48020 | 0.01560 |
|       |       |       | C     | -4.76650 | 5.61580 | 0.02000 |
|       |       |       | O     | -6.16580 | -1.22360 | -0.03490 |
|       |       |       | C     | -7.57480 | -1.44620 | -0.02480 |
|       |       |       | H     | -8.03600 | -0.45040 | 0.00670 |
|       |       |       | H     | -7.88530 | -1.98160 | -0.93600 |
|       |       |       | H     | -7.86550 | -2.02780 | 0.86440 |
|       |       |       | H     | -5.78890 | 5.21590 | 0.02550 |
|       |       |       | H     | -4.59130 | 6.22680 | 0.91950 |
|       |       |       | H     | -4.60050 | 6.22650 | -0.88140 |

**(COOMe-bipy)Au(4-OMe-C₆H₄)⁺**

SCF = -1729.41273 au  
ZPE = -1729.03724 au

|       |       |       | Au    | 2.36470 | -0.00050 | 0.00000 |
|-------|-------|-------|-------|---------|----------|---------|
|       |       |       | C     | -1.70390 | 2.88750 | -0.00910 |
|       |       |       | C     | -0.45070 | 3.49260 | 0.02530 |
|       |       |       | C     | 0.66870 | 2.67050 | 0.04030 |
|       |       |       | N     | 0.57260 | 1.33960 | 0.02940 |
|       |       |       | C     | -0.62920 | 0.74620 | 0.00130 |
|       |       |       | C     | -1.80210 | 1.50120 | -0.02550 |
|       |       |       | C     | -0.33340 | 4.57810 | 0.03850 |
|       |       |       | H     | 1.67610 | 3.09220 | 0.06230 |
|       |       |       | H     | -2.78100 | 1.02500 | -0.06300 |
|       |       |       | N     | -1.70460 | -2.88700 | 0.00910 |
|       |       |       | C     | -0.45170 | -3.49250 | -0.02550 |
|       |       |       | C     | 0.66800 | -2.67070 | -0.04060 |
|       |       |       | N     | 0.57220 | -1.33970 | -0.02960 |
|       |       |       | C     | -0.62940 | -0.74600 | -0.00140 |
|       |       |       | C     | -1.80250 | -1.50070 | 0.02550 |
|       |       |       | C     | -0.33460 | -4.57800 | -0.03880 |
|       |       |       | C     | 1.67520 | -3.09260 | -0.06270 |
|       |       |       | H     | -2.78120 | -1.02420 | 0.06310 |
|       |       |       | N     | -1.70460 | -2.88700 | 0.00910 |
|       |       |       | C     | -0.45170 | -3.49250 | -0.02550 |
|       |       |       | C     | 0.66800 | -2.67070 | -0.04060 |
|       |       |       | N     | 0.57220 | -1.33970 | -0.02960 |
|       |       |       | C     | -0.62940 | -0.74600 | -0.00140 |
|       |       |       | C     | -1.80250 | -1.50070 | 0.02550 |
|       |       |       | N     | -0.33460 | -4.57800 | -0.03880 |
|       |       |       | C     | 1.67520 | -3.09260 | -0.06270 |
|       |       |       | H     | -2.78120 | -1.02420 | 0.06310 |

**(CF₃-bipy)Au(C₂H₄)⁺**

SCF = -1382.46738 au  
ZPE = -1382.24049 au
|     |       |       |       |       |
|-----|-------|-------|-------|-------|
| H   | 4.55760 | 1.27900 | -0.89610 | H   | -3.99790 | -0.00590 | 3.22240 |
| H   | 4.55920 | -1.23160 | -0.95970 | H   | -3.45750 | -3.14650 | 0.30120 |

**SCF** = -1947.51823 au  
**ZPE** = -1947.22142 au

**Intermediate**

|     |       |       |       |       |
|-----|-------|-------|-------|-------|
| Au  | -0.99480 | -0.32030 | -0.15110 |
| C   | 3.38210 | -2.68440 | -0.51260 |
| C   | 2.20020 | -3.38690 | -0.72790 |
| C   | 1.00310 | -2.69150 | -0.62250 |
| N   | 0.95850 | -1.38960 | -0.32860 |
| C   | 2.09070 | -0.70170 | -0.12160 |
| C   | 3.33410 | -1.32990 | -0.20670 |
| H   | 2.19600 | -4.45130 | -0.97090 |
| H   | 0.04670 | -3.19610 | -0.77760 |
| H   | 4.25800 | -0.77760 | -0.03970 |
| C   | 2.81570 | 2.92490 | 0.71280 |
| C   | 1.51140 | 3.41060 | 0.75780 |
| C   | 0.47720 | 2.51330 | 0.51950 |
| N   | 0.70180 | 1.22870 | 0.24970 |
| C   | 1.94880 | 0.75190 | 0.19910 |
| C   | 3.04650 | 1.58330 | 0.43210 |
| H   | 1.29410 | 4.45880 | 0.97370 |
| H   | -0.56630 | 2.83870 | 0.54390 |
| H   | 4.06700 | 1.20410 | 0.39950 |
| C   | 4.70800 | -3.40210 | -0.64640 |
| F   | 5.72460 | -2.66410 | -0.20390 |
| F   | 4.70620 | -4.54560 | 0.03990 |
| F   | 4.95250 | -3.70360 | -1.92400 |
| C   | 3.96630 | 3.87190 | 0.97890 |
| F   | 5.15040 | 3.27620 | 0.84650 |
| F   | 3.93660 | 4.06700 | 0.13650 |
| F   | 3.89750 | 4.36510 | 2.21750 |
| C   | -3.06460 | 0.26320 | -0.07160 |
| C   | -3.06410 | -1.13180 | -0.39390 |
| C   | -3.42280 | 0.65160 | 1.26820 |
| C   | -3.42050 | -2.09740 | 0.59810 |
| H   | -3.07840 | -1.45440 | -1.43970 |
| I   | -3.31960 | 1.72250 | -1.61490 |
| C   | -3.73150 | -0.29660 | 2.20300 |
| C   | -3.73780 | -1.68770 | 1.87820 |
| O   | -4.08330 | -2.49990 | 2.88390 |
| C   | -4.13770 | -3.89070 | 2.65640 |
| H   | -3.15100 | -4.28580 | 2.35240 |
| H   | -4.88930 | -4.14270 | 1.88650 |
| H   | -4.43170 | -4.34870 | 3.61160 |
| H   | -3.45770 | 1.71190 | 1.53030 |

**SCF** = -1947.50295 au  
**ZPE** = -1947.20706 au

**Transition State**

|     |       |       |       |       |
|-----|-------|-------|-------|-------|
| C   | -3.01220 | -2.99870 | 0.13070 |
| C   | -1.72880 | 1.05980 | 0.02840 |
| C   | -2.58640 | 2.15980 | -0.00010 |
| C   | -2.02840 | 3.43770 | -0.02340 |
| C   | -0.64780 | 3.59310 | -0.01590 |
| C   | 0.13120 | 2.43800 | 0.01340 |
| N   | -0.40440 | 1.22460 | 0.03430 |
| H   | -3.67090 | 2.04490 | -0.00420 |
| H   | -0.17640 | 4.57670 | -0.03290 |
| H   | 1.22420 | 2.49250 | 0.01920 |
| C   | -2.22130 | -0.35400 | 0.05810 |
| C   | -3.57920 | -0.66460 | 0.02180 |
| C   | -3.97310 | -2.00010 | 0.05340 |
| C   | -1.67700 | -2.61120 | 0.15880 |
| N   | -1.29950 | -1.33190 | 0.11870 |
| H   | -4.33470 | 0.12000 | -0.03430 |
| H   | -3.27420 | -4.05720 | 0.16120 |
| H   | -0.88220 | -3.35960 | 0.21040 |
| Au  | 0.86610 | -0.86150 | 0.03870 |
| C   | 2.95950 | -0.37930 | -0.09740 |
| C   | 3.35390 | 0.27390 | 1.08530 |
| C   | 3.20990 | 0.23540 | -1.34640 |
| C   | 3.91880 | 1.54560 | 1.03290 |
| C   | 3.77260 | 1.49850 | -1.39130 |
| C   | 4.13040 | 2.16930 | -0.20650 |
| H   | 2.95940 | -0.27950 | -2.27750 |
| H   | 4.19820 | 2.03420 | 1.96790 |
| H   | 3.95520 | 1.99200 | -2.34910 |
| I   | 2.93470 | -2.67100 | -0.05970 |
| H   | 3.22020 | -0.21080 | 2.05580 |
| C   | 4.66180 | 3.38650 | -0.35660 |
| O   | 5.05350 | 4.12300 | 0.78230 |
| C   | 4.19510 | 4.32040 | 1.44990 |
| H   | 5.84870 | 3.60130 | 1.34450 |
| H   | 5.44570 | 5.07950 | 0.40830 |
| C   | -2.95490 | 4.63340 | -0.07300 |
| C   | -5.45140 | -2.32690 | 0.01420 |
| F   | -3.64350 | 4.65530 | -1.21790 |
| F   | -2.29430 | 5.78520 | 0.02110 |
| F   | -3.84500 | 4.59340 | 0.92210 |
| F   | -6.04260 | -1.73690 | -1.02740 |
(CF₃-bipy)Au(4-OMe-C₆H₄I)⁺ product

SCF = -1947.53507 au
ZPE = -1947.23713 au

|       |       |       |
|-------|-------|-------|
| Au    | 0.72190 | -0.72270 | 0.01440 |
| I     | 1.76420 | -3.08720 | 0.03010 |
| C     | -1.44900 | 3.65020 | 0.02650 |
| C     | -0.06330 | 3.60250 | 0.05020 |
| C     | 0.55000 | 2.35440 | 0.04310 |
| N     | -0.15460 | 1.22290 | 0.01620 |
| C     | -1.50500 | 1.25160 | -0.00620 |
| C     | -2.18200 | 2.46490 | -0.00210 |
| H     | 0.55020 | 4.50390 | 0.07430 |
| H     | 1.63780 | 2.26230 | 0.06130 |
| H     | -3.27200 | 2.49580 | -0.02030 |
| C     | -4.15830 | -1.44190 | -0.07430 |
| C     | -3.33840 | -2.56550 | -0.09500 |
| C     | -1.96300 | -2.37250 | -0.08060 |
| N     | -1.42220 | -1.15340 | -0.04980 |
| C     | -2.20410 | -0.05900 | -0.03390 |
| C     | -3.59180 | -0.17210 | -0.04410 |
| H     | -3.74590 | -3.57810 | -0.12050 |
| H     | -1.27020 | -3.21780 | -0.09320 |
| H     | -4.22740 | 0.71260 | -0.03080 |
| C     | 5.11650 | 1.20560 | 0.18460 |
| C     | 4.43560 | 0.88130 | 1.36970 |
| C     | 3.20050 | 0.24500 | 1.32590 |
| C     | 2.62420 | -0.05950 | 0.08870 |
| C     | 3.29860 | 0.23740 | -1.09180 |
| C     | 4.54210 | 0.87640 | -1.04990 |
| H     | 4.89990 | 1.13290 | 2.32690 |
| H     | 2.69320 | -0.00340 | 2.26230 |
| H     | 2.87050 | -0.01880 | -2.06510 |
| H     | 5.04930 | 1.10210 | -1.99000 |
| O     | 6.30220 | 1.82150 | 0.33130 |
| C     | 7.04720 | 2.16880 | -0.81230 |
| H     | 7.96230 | 2.65780 | -0.44750 |
| H     | 7.32750 | 1.27590 | -1.40100 |
| H     | 6.49530 | 2.87700 | -1.45790 |
| C     | -2.19890 | 4.96740 | 0.02650 |
| C     | -5.66370 | -1.61880 | -0.06290 |
| F     | -3.05040 | 5.02440 | 1.05180 |
| F     | -1.37960 | 6.01000 | 0.11640 |
| F     | -2.91080 | 5.10030 | -1.09370 |
| F     | -6.30350 | -0.46380 | -0.23350 |
| F     | -6.05310 | -2.44780 | -1.03060 |
| F     | -6.06560 | -2.13890 | 1.09810 |
5.3.3. *Comparison with experimental rate data*

The oxidative addition barriers ($\Delta G^\ddagger$) may be calculated from the observed rates ($k_{obs}$) given in Table 1 using the Eyring equation (Equation 4) which is rearranged to give Equation 5. $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$ is the Boltzmann constant, $T$ is the temperature in K, $h = 6.626 \times 10^{-34}$ J s is Planck’s constant and $R = 8.314$ J K$^{-1}$ mol$^{-1}$ is the gas constant. Free energies were then converted to kcal mol$^{-1}$.

$$k_{obs} = \frac{k_B T}{h} \exp \left( -\frac{\Delta G^\ddagger}{RT} \right)$$  \hspace{1cm} (4)

$$\Delta G^\ddagger = -RT \ln \left( k_{obs} \left( \frac{k}{k_B T} \right) \right)$$  \hspace{1cm} (5)

**Table S6**: Comparison of Gibbs free energies of experimental and calculated oxidative addition barriers.

| Ligand subsituent | $k_{obs}$ / s$^{-1}$ | $\Delta G^\ddagger$ / kcal mol$^{-1}$ |
|-------------------|----------------------|-------------------------------------|
| **Experimental oxidative addition barriers**  |                       |                                     |
| H                 | $6.6 \times 10^{-7}$ | 28.1                                |
| EDG ($p$-Bu)      | $4.3 \times 10^{-7}$ | 28.4                                |
| EWG ($p$-CF$_3$)  | $1.9 \times 10^{-6}$ | 27.4                                |
| **Calculated oxidative addition barriers**  |                       |                                     |
| H                 | -                    | 27.1                                |
| EDG ($p$-Bu)      | -                    | 28.7                                |
| EWG ($p$-CF$_3$)  | -                    | 26.7                                |

The calculated Gibbs free energy for the oxidative addition barriers show good agreement compared to the experimentally obtained values. Differences in the Gibbs free energy for the representative examples of electron-donating groups (EDG) and electron-withdrawing groups (EWG) are small for both experimental and calculated sets. The small differences observed in the experimental data (also consistent with the small value of $\rho$ in the Hammett study) show that the computational model is a reasonable depiction of differences in barriers between EDGs and EWGs. Further studies are currently in progress to further explain the stark differences in rate of oxidative addition with different ligand substituents (*i.e.*, with $p$-substituted complex 2i•NTf$_2$).
5.4. Oxidative addition with 4-vinylidobenzene

5.4.1. Calculated potential energy surface

The calculated potential energy surface given in Figure S10 below broadly follows the same profile as the previously calculated examples.\textsuperscript{[5]} There is a clear preference for the formation of the vinyl-\(\pi\)-bound intermediate given in gray vs the \(\eta^2-\pi\)-bound intermediate (\(\Delta E = 17.5\) kcal mol\(^{-1}\)). This additional equilibrium in solution between competing \(\pi\)-bound species would lead to a slower oxidative addition. The geometry of the calculated vinyl-\(\pi\)-bound intermediate in Figure S10 inset (B) is consistent with related structures that have been isolated in the literature.\textsuperscript{[23]}

Figure S10: Calculated potential energy surface for the oxidative addition of 4-vinylidobenzene (3i). See Section 5.1 for computational details. Inset (A) transition state geometry and inset (B) geometry of vinyl-\(\pi\)-bound intermediate with selected bond lengths given in Å.
### 5.4.2. Energies and Cartesian coordinates (Å) for stationary points

**C₅H₅-C₆H₆I**  
SCF = -606.48590 au  
ZPE = -606.36173 au

|         |          |          |          |          |          |          |
|---------|----------|----------|----------|----------|----------|----------|
| C       | 0.00000  | -0.16810 | 0.00000  |          |          |          |
| C       | -1.38980 | -0.05230 | 0.00000  |          |          |          |
| C       | -1.97000 | 1.21560  | 0.00000  |          |          |          |
| C       | -1.18880 | 2.38120  | 0.00000  |          |          |          |
| C       | 0.20840  | 2.23510  | 0.00000  |          |          |          |
| C       | 0.80230  | 0.97630  | 0.00000  |          |          |          |
| I       | 0.89720  | -2.07500 | 0.00000  |          |          |          |
| H       | -2.02620 | -0.94090 | 0.00000  |          |          |          |
| H       | -3.06150 | 1.29920  | 0.00000  |          |          |          |
| C       | -1.86540 | 3.69470  | 0.00000  |          |          |          |
| H       | 0.85760  | 3.11500  | 0.00000  |          |          |          |
| H       | 1.89230  | 0.89330  | 0.00000  |          |          |          |
| C       | -1.28840 | 4.90260  | 0.00000  |          |          |          |
| H       | -1.90270 | 5.81030  | 0.00000  |          |          |          |
| H       | -0.20110 | 5.04620  | 0.00000  |          |          |          |
| H       | -2.96180 | 3.64300  | 0.00000  |          |          |          |

**Au(bipy)(C₅H₅-C₆H₆I)**⁺ η²-arene bound  
SCF = -1237.03689 au  
ZPE = -1236.75016 au

|         |          |          |          |          |          |          |
|---------|----------|----------|----------|----------|----------|----------|
| C       | 3.47850  | 2.79140  | -0.57880 |          |          |          |
| C       | 2.95600  | -0.85170 | 0.54310  |          |          |          |
| C       | 3.99030  | -1.66210 | 1.01420  |          |          |          |
| C       | 3.67440  | -2.83100 | 1.70260  |          |          |          |
| C       | 2.33850  | -3.16490 | 1.90430  |          |          |          |
| C       | 1.36470  | -2.30840 | 1.40180  |          |          |          |
| N       | 1.67450  | -1.19100 | 0.74310  |          |          |          |
| H       | 5.03500  | -1.39590 | 0.85390  |          |          |          |
| H       | 4.47350  | -3.47560 | 2.07780  |          |          |          |
| H       | 2.04830  | -4.07100 | 2.44000  |          |          |          |
| H       | 0.29980  | -2.52430 | 1.52820  |          |          |          |
| C       | 3.19670  | 0.42240  | -0.20070 |          |          |          |
| C       | 4.47600  | 0.92580  | -0.44030 |          |          |          |
| C       | 4.61620  | 2.12320  | -1.13710 |          |          |          |
| C       | 2.23730  | 2.22910  | -1.30370 |          |          |          |
| H       | 2.10910  | 1.08000  | -0.63530 |          |          |          |
| H       | 5.36370  | 0.39830  | -0.09030 |          |          |          |
| H       | 5.61270  | 2.52870  | -1.33020 |          |          |          |
| H       | 3.54250  | 3.73320  | -2.12750 |          |          |          |
| H       | 1.31260  | 2.71410  | -1.62710 |          |          |          |
| Au      | 0.10530  | 0.19620  | -0.16000 |          |          |          |
| N       | -1.87480 | 1.34780  | -0.58380 |          |          |          |
| H       | -4.08600 | 3.63380  | 0.52700  |          |          |          |
| H       | -2.51630 | 5.14690  | -0.65120 |          |          |          |
| H       | -0.49410 | 4.16580  | -1.79940 |          |          |          |
| H       | -0.16210 | 1.68680  | -1.70170 |          |          |          |
| Au      | -1.57700 | -0.85710 | -0.47470 |          |          |          |
| C       | 0.10120  | -1.83940 | -1.34500 |          |          |          |
| C       | -0.73420 | -2.77490 | -0.68830 |          |          |          |

**Au(bipy)(C₂H₃-C₆H₆I)⁺ η²-vinyl bound**  
SCF = -1237.06726 au  
ZPE = -1236.77810 au

|         |          |          |          |          |          |          |
|---------|----------|----------|----------|----------|----------|----------|
| C       | -3.84010 | 0.85770  | 0.71520  |          |          |          |
| C       | -5.00050 | 1.21690  | 1.40100  |          |          |          |
| C       | -5.76310 | 0.22410  | 2.01130  |          |          |          |
| C       | -5.35280 | -1.10240 | 1.92270  |          |          |          |
| C       | -4.18570 | -1.38500 | 1.22220  |          |          |          |
| N       | -3.45770 | -0.42870 | 0.64010  |          |          |          |
| H       | -5.31640 | 2.25810  | 1.46680  |          |          |          |
| H       | -6.67370 | 0.49130  | 2.55360  |          |          |          |
| H       | -5.92090 | -1.91120 | 2.38660  |          |          |          |
| H       | -3.81780 | -2.40940 | 1.12280  |          |          |          |
| C       | -2.95630 | 1.84850  | 0.03260  |          |          |          |
| C       | -3.21120 | 3.22000  | 0.02490  |          |          |          |
| C       | -2.32840 | 4.07040  | -0.63670 |          |          |          |
| C       | -1.02360 | 2.15850  | -1.22170 |          |          |          |
| N       | -1.87480 | 1.34780  | -0.58380 |          |          |          |
| H       | -4.08600 | 3.63380  | 0.52700  |          |          |          |
| H       | -2.51630 | 5.14690  | -0.65120 |          |          |          |
| H       | -0.49410 | 4.16580  | -1.79940 |          |          |          |
| H       | -0.16210 | 1.68680  | -1.70170 |          |          |          |
| Au      | -1.57700 | -0.85710 | -0.47470 |          |          |          |
| C       | 0.10120  | -1.83940 | -1.34500 |          |          |          |
| C       | -0.73420 | -2.77490 | -0.68830 |          |          |          |
### Au(bipy)(C₂H₃-C₆H₄I)⁺ transition state

| I    | Au(bipy)(C₂H₃-C₆H₄I)⁺ product |
|------|--------------------------------|
| SCF  | SCF = -1237.02171 au          |
| ZPE  | ZPE = -1236.73554 au          |
| Au   | Au                      |
| C    | C                        |
| H    | H                        |
| N    | N                        |
| I    | I                        |
| ZPE  | Au(bipy)(C₂H₃-C₆H₄I)⁺ product |
| SCF  | SCF = -1237.05941 au        |
| ZPE  | ZPE = -1236.82305 au        |
| Au   | Au                      |
| C    | C                        |
| H    | H                        |
| N    | N                        |
| I    | I                        |

**I**

-2.41170  -2.08210  -0.86230

**H**

-1.84010  0.87970  -1.88460

**C**

-2.74100  3.74840  1.68880

**H**

-2.07150  3.12810  -0.91640

**C**

-2.33910  4.93180  1.21010

**H**

-2.58540  5.85930  1.73950

**H**

-1.75010  5.02820  0.28940

**H**

-3.29940  3.72450  2.63320

**Au(bipy)(C₂H₃-C₆H₄I)⁺ product**

| Au   | SCF = -1237.05941 au |
|------|---------------------|
| C    | ZPE = -1236.82305 au |

**Au**

-0.30930  -0.20960  0.00760

**I**

0.11090  -2.76370  0.04000

**C**

-1.34560  4.55630  0.10520

**C**

-0.01140  4.16720  0.12040

**C**

0.28470  2.81140  0.07880

**N**

-0.67550  1.88230  0.02450

**C**

-1.98030  2.23790  0.00420

**C**

-2.33940  3.58250  0.04460

**H**

0.80060  4.89540  0.16440

**H**

1.31680  2.45620  0.09020

**H**

-3.37870  3.87950  0.03160

**C**

-5.20760  0.25650  -0.17810

**C**

-4.67600  -1.02790  -0.17330

**C**

-3.29500  -1.17280  -0.11410

**N**

-2.47590  -0.11980  -0.06010

**C**

-2.97360  1.13440  -0.06180

**C**

-4.37460  1.35130  -0.12190

**H**

-5.31260  -1.91370  -0.21550

**H**

-2.82370  -2.15910  -0.10960

**H**

-4.75610  2.36160  -0.12480

**C**

4.43330  0.60370  0.13680

**C**

3.70030  0.43040  1.32030

**C**

2.34210  0.11060  1.29590

**C**

1.69630  -0.03120  0.06860

**C**

2.40840  0.10990  -1.12520

**C**

3.76390  0.42880  -1.08580

**H**

4.20270  0.54820  2.28570

**H**

1.80100  -0.01880  2.23730

**H**

1.91600  -0.02300  -2.09250

**H**

4.30300  0.53610  -2.03120

**H**

-1.61970  5.61340  0.13910

**H**

-6.28770  0.41470  -0.22560

**C**

5.86600  0.95390  0.22870

**C**

6.69470  1.23280  -0.78450

**H**

7.74450  1.48030  -0.58990

**H**

6.37540  1.22950  -1.83370

**H**

6.26320  0.98590  1.25110

**S56**
5.5. Additional aryl iodides

5.5.1. Full potential energy surface comparison

**Figure S11:** Calculated potential energy surfaces for p-OMe, p-t-Bu, p-H, p-CHO and p-CF$_3$ substituted aryl iodides. See Section 5.1 for computational details.
### 5.5.2. Energies and Cartesian coordinates (Å) for stationary points

|          | (bipy)Au(4-′Bu-C₆H₄I)⁺ η² intermediate |          | (bipy)Au(4-′Bu-C₆H₄I)⁺ transition state |
|----------|----------------------------------------|----------|----------------------------------------|
| SCF      | -1316.81251 au                         | SCF      | -1316.79777 au                         |
| ZPE      | -1316.44589 au                         | ZPE      | -1316.43213 au                         |
| Au       | -0.32980  0.01490  -0.27250             | Au       | 0.80130   -0.43210  -0.00540           |
| C        | -3.82630  3.42930  -1.37260             | C        | 5.19700   0.06640  0.36980             |
| C        | -2.57460  3.51590  -1.97440             | C        | 1.80820   2.59910  -0.09170            |
| C        | -1.62210  2.55640  -1.65070             | C        | 1.85020   3.99530  -0.04470            |
| N        | -1.87180  1.56850  -0.78770             | C        | 0.66580   4.70970  -0.21200            |
| C        | -3.07240  1.47280  -0.19380             | C        | -0.52590  4.02060  -0.42020            |
| C        | -4.07980  2.39790  -0.47190             | C        | -0.48210  2.62950  -0.44420            |
| H        | -2.33240  4.30960  -2.68410             | N        | 0.65310   1.95430  -0.28270            |
| H        | -0.62350  2.57770  -2.09510             | H        | 2.78390   4.53210  0.12660             |
| H        | -5.05880  2.32400  0.00210              | H        | -1.47360  4.54530  -0.55940            |
| C        | -4.52290  -0.94920  2.35000             | H        | -1.38650  2.03220  -0.60900            |
| C        | -3.42850  -1.79640  2.49520             | C        | 3.02850   1.74570  0.06660             |
| C        | -2.28250  -1.52040  1.75700             | C        | 4.31610   2.28450  0.10260             |
| N        | -2.20850  -0.48200  0.92340             | C        | 5.40950   1.43670  0.25590             |
| C        | -3.25480  0.34120  0.76670              | C        | 3.88980   -0.40070  0.31730             |
| C        | -4.43870  0.13220  1.47630              | C        | 2.84320   0.41820  0.16870             |
| H        | -3.45300  -2.65550  3.16870             | N        | 4.47670   3.35810  0.00410             |
| H        | -1.39250  -2.15170  1.83330             | H        | 6.02340   -0.63640  0.49280             |
| H        | -5.29170  0.80070  1.36070              | H        | 3.66790   -1.46850  0.39530             |
| C        | 1.48370   -1.15400  -0.13670            | Au       | 0.80130   -0.43210  -0.00540           |
| C        | 1.70750   -0.11070  -1.09410            | C        | -1.20500  -1.29050  -0.01460           |
| C        | 2.06220   -1.01010  1.16640             | C        | -1.87450  -0.89250  -1.18990           |
| C        | 2.50240   1.01660   -0.72020            | C        | -1.76070  -0.97810  1.23790             |
| H        | 1.54960   -0.29510  -2.16180            | C        | -3.03310  -0.13490  -1.09100           |
| I        | 1.01690   -3.13150  -0.79470            | C        | -2.92290  -0.20820  1.30440             |
| C        | 2.79130   0.11070   1.48420             | C        | -3.58180  0.23480  0.15160             |
| C        | 3.03690   1.15540   0.54430             | H        | -1.28940  -1.32830  2.15970             |
| H        | 1.93160   -1.80580  1.90390             | H        | -3.51840  0.17740  -0.21980             |
| H        | 3.20550   0.17390  2.49170              | H        | -3.31040  0.03380  2.29530             |
| H        | 2.69510   1.76420  -1.49430             | I        | 0.16370   -3.10140  -0.13730           |
| H        | -5.44340  -1.12560  2.91240             | H        | -1.48220  -1.16780  -2.17200           |
| H        | -4.60670  4.16010  -1.59890             | H        | 0.67930   5.80230  -0.17800            |
| C        | 3.88200   2.39070   0.88970             | H        | 6.42110   1.84960  0.28300             |
| C        | 4.35610   2.38130   2.34900             | C        | -4.84610  1.10140  0.19500             |
| C        | 5.12220   2.42510  -0.02270             | C        | -5.29970  1.39380  1.63110             |
| C        | 3.03720   3.65810   0.66140             | C        | -4.55230  2.44350  -0.50340            |
| C        | 3.03720   3.65810   0.66140             | C        | -5.98850  0.37500  -0.53910            |
| H        | 4.94770   3.29120   2.54990             | H        | -6.20840  2.02040  1.61140             |
| H        | 3.51010   2.37240   3.05870             | H        | -5.54700  0.46960  2.18180             |
| H        | 5.00200   1.51320   2.56760             | H        | -4.53090  1.94320  2.20230             |
| H        | 5.74720   3.30470   0.21490             | H        | -5.45120  3.08550  -0.48840            |
| H        | 5.73950   1.52000   0.11720             | H        | -3.74020  2.98750  0.01170             |
| H        | 4.84740   2.48820  -1.08980             | H        | -4.25860  2.30680  -1.55860            |
\[
\begin{align*}
\text{SCF} &= -1316.83458 \text{ au} \\
\text{ZPE} &= -1316.46621 \text{ au}
\end{align*}
\]

\[
\begin{align*}
\text{(bipyAu}(4\text{-Bu-C}_6\text{H}_5\text{I})^+ \text{ product)}
\end{align*}
\]

\[
\begin{align*}
\text{Au} &: -0.73080 & -0.22850 & -0.00120 \\
I &: -0.50140 & -2.81050 & -0.02110 \\
C &: -1.39170 & 4.60650 & -0.03020 \\
C &: -0.99230 & 4.11340 & -0.01090 \\
C &: 0.09480 & 2.73780 & 0.00430 \\
N &: -0.93620 & 1.88630 & 0.00560 \\
C &: -2.20870 & 2.34340 & -0.00440 \\
C &: -2.45940 & 3.71260 & -0.02780 \\
H &: 0.77530 & 4.77580 & -0.00990 \\
H &: 1.09550 & 2.30160 & 0.01500 \\
H &: -3.48220 & 4.08780 & -0.04560 \\
C &: -5.58700 & 0.62260 & 0.04880 \\
C &: -5.15850 & -0.69960 & 0.02440 \\
C &: -3.79200 & -0.95220 & 0.00100 \\
N &: -2.89190 & 0.03360 & -0.00380 \\
C &: -3.28890 & 1.32280 & 0.01180 \\
C &: -4.64300 & 1.64750 & 0.04360 \\
H &: -5.86470 & -1.53210 & 0.02600 \\
H &: -3.39920 & -1.97220 & -0.01360 \\
H &: -4.97170 & 2.68650 & 0.06690 \\
C &: 4.07010 & 0.24920 & 0.04140 \\
C &: 3.34820 & 0.07740 & 1.22850 \\
C &: 1.96800 & -0.14920 & 1.22220 \\
C &: 1.28390 & -0.19720 & 0.01130 \\
C &: 1.97820 & -0.05310 & -1.19090 \\
C &: 3.35330 & 0.17340 & -1.16440 \\
H &: 3.85120 & 0.11610 & 2.19670 \\
H &: 1.44330 & -0.28060 & 2.17270 \\
H &: 1.46000 & -0.10680 & -2.15260 \\
H &: 3.87340 & 0.29120 & -2.11950 \\
H &: -1.58210 & 5.68230 & -0.04700 \\
H &: -6.65250 & 0.86400 & 0.07230 \\
C &: 5.58400 & 0.50610 & 0.01400 \\
C &: 6.18260 & 0.59440 & 1.42390 \\
C &: 6.27910 & -0.64430 & -0.73830 \\
C &: 5.86140 & 1.83510 & -0.71350 \\
H &: 7.26700 & 0.79010 & 1.35430 \\
H &: 5.73440 & 1.41550 & 2.01050 \\
H &: 6.05150 & -0.34590 & 1.98710 \\
H &: 7.37110 & -0.47810 & -0.76660 \\
H &: 6.09370 & -1.61230 & -0.23960 \\
H &: 5.92640 & -0.72600 & -1.78120 \\
H &: 6.94690 & 2.04070 & -0.73190 \\
H &: 5.50840 & 1.81450 & -1.75900 \\
H &: 5.36450 & 2.67900 & -0.20200
\end{align*}
\]

\[
\begin{align*}
\text{(bipyAu}(4\text{-Bu-C}_6\text{H}_5\text{I})^+ \eta^2 \text{ intermediate)}
\end{align*}
\]

\[
\begin{align*}
\text{SCF} &= -1159.72260 \text{ au} \\
\text{ZPE} &= -1159.46892 \text{ au}
\end{align*}
\]

\[
\begin{align*}
\text{C} &: -3.82560 & -2.58720 & -1.10080 \\
C &: -2.64720 & 1.26250 & 0.25880 \\
C &: -3.50880 & 2.33880 & 0.47880 \\
C &: -2.98320 & 3.54510 & 0.93570 \\
C &: -1.61410 & 3.65180 & 1.16060 \\
C &: -0.82010 & 2.53660 & 0.91610 \\
N &: -1.33010 & 1.38400 & 0.47990 \\
H &: -4.58080 & 2.25290 & 0.30070 \\
H &: -3.64570 & 4.39600 & 1.11370 \\
H &: -1.16140 & 4.57850 & 1.51890 \\
H &: 0.26180 & 2.56570 & 1.07420 \\
C &: -3.11720 & -0.07190 & -0.22510 \\
C &: -4.45880 & -0.35160 & -0.48970 \\
C &: -4.81440 & -1.62310 & -0.93210 \\
C &: -2.51060 & -2.23580 & -0.81880 \\
N &: -2.17540 & -1.01440 & -0.39540 \\
H &: -5.23050 & 0.40630 & -0.35480 \\
H &: -5.86190 & -1.85460 & -1.14150 \\
H &: -4.06060 & -3.59690 & -1.44360 \\
H &: -1.69610 & -2.95590 & -0.93280 \\
\text{Au} &: -0.05390 & -0.45200 & 0.05770 \\
C &: 2.05370 & -2.66630 & 2.03830 \\
C &: 1.71640 & -2.84300 & 0.72050 \\
C &: 2.41560 & -1.37930 & 2.52090 \\
H &: 2.69150 & -1.25560 & 3.57180 \\
C &: 1.71000 & -1.73300 & -0.18890 \\
C &: 2.45210 & -0.29190 & 1.68380 \\
H &: 2.77020 & 0.68550 & 2.05460 \\
C &: 2.09270 & -0.43720 & 0.29890 \\
I &: 2.85260 & 1.02870 & -1.06110 \\
H &: 1.72990 & -1.94800 & -1.26260 \\
H &: 1.47890 & -3.83610 & 0.32970 \\
H &: 2.06780 & -3.52010 & 2.72100
\end{align*}
\]

\[
\begin{align*}
\text{(bipyAu}(\text{C}(\text{H})(\text{I})^+ \text{ transition state)}
\end{align*}
\]

\[
\begin{align*}
\text{SCF} &= -1159.70656 \text{ au} \\
\text{ZPE} &= -1159.45341 \text{ au}
\end{align*}
\]

\[
\begin{align*}
\text{C} &: 3.08970 & -3.31730 & 0.47290
\end{align*}
\]
|        | C   | H   | N   | Au  | SCF   |
|--------|-----|-----|-----|-----|-------|
| C      | 2.8768 | 0.89010 | -0.13490 | -2.31120 | -2.13060 | -0.00880 |
| C      | 3.98490 | 1.74140 | -0.16790 | -1.94750 | -0.84600 | -0.00860 |
| C      | 3.78220 | 3.10470 | -0.37010 | -2.87970 | 0.12920 | 0.00640 |
| C      | 2.48660 | 3.58550 | -0.53620 | -4.23550 | -0.18750 | 0.02690 |
| C      | 1.43770 | 2.67140 | -0.48890 | -3.90400 | -3.57730 | 0.00700 |
| N      | 1.63930 | 1.37080 | -0.29460 | -1.50330 | -2.86710 | -0.02190 |
| H      | 4.99810 | 1.36180 | -0.03280 | -4.99490 | 0.59430 | 0.04050 |
| H      | 2.28550 | 4.64680 | -0.69750 | 4.19210 | 2.37370 | 0.02760 |
| H      | 0.39730 | 2.99000 | -0.61190 | 3.56930 | 2.03230 | 1.22870 |
| C      | 2.99900 | -0.58770 | 0.07800 | 2.41830 | 1.23980 | 1.22630 |
| C      | 4.23610 | -1.22810 | 0.17820 | 1.89170 | 0.80380 | 0.00910 |
| C      | 4.28100 | -2.60460 | 0.37910 | 2.51510 | 1.12620 | -1.19750 |
| C      | 1.89590 | -2.61610 | 0.35970 | 3.66610 | 1.91830 | -1.18210 |
| N      | 1.85900 | -1.29310 | 0.17000 | 1.94020 | 0.97450 | 2.17360 |
| H      | 5.16640 | -0.66610 | 0.09660 | 2.11470 | 0.76970 | -2.15060 |
| H      | 3.07630 | -4.39750 | 0.63070 | 4.15550 | 2.17480 | -2.12650 |
| H      | 0.93250 | -3.12900 | 0.42290 | 3.29720 | 4.79400 | -0.01920 |
| Au     | -0.10320 | -0.25640 | -0.00510 | -5.68270 | -1.78670 | 0.04450 |
| C      | -2.07660 | 0.69020 | 0.15970 | 5.09490 | 2.99120 | 0.03470 |
| C      | -2.22490 | 1.65030 | -0.86290 | 3.98120 | 2.37990 | 2.18090 |
| C      | -2.17010 | 1.07180 | 1.51370 |         |         |         |
| C      | -2.40690 | 2.98660 | -0.52010 |         |         |         |
| C      | -2.34270 | 2.41940 | 1.83130 |         |         |         |
| C      | -2.46370 | 3.37440 | 0.82220 |         |         |         |
| H      | -2.11600 | 0.32310 | 2.30800 |         |         |         |
| I      | -2.55760 | -1.45850 | -0.33820 |         |         |         |
| H      | 5.24480 | -3.11380 | 0.45940 |         |         |         |
| H      | 4.63720 | 3.78540 | -0.39550 |         |         |         |
| H      | -2.39940 | 2.71650 | 2.88220 |         |         |         |
| H      | -2.19360 | 1.34860 | -1.91290 |         |         |         |
| H      | -2.61370 | 4.42630 | 1.08060 |         |         |         |
| H      | -2.50810 | 3.73260 | -1.31350 |         |         |         |

(bipy)Au(4-CHO-C₆H₅I)+ η² intermediate
SCF = -1272.92653 au
ZPE = -1272.66316 au

|        | Au  | C   | H   | N   | SCF   |
|--------|-----|-----|-----|-----|-------|
| Au     | 0.09760 | -0.11370 | -0.00710 | -0.11430 | 0.20680 | -0.14550 |
| C      | 1.43700 | -2.33280 | 0.00600 | -4.62070 | 2.11190 | -1.17070 |
| C      | -2.64780 | 3.91530 | -0.02070 | -3.48440 | 2.79230 | -1.59710 |
| C      | -1.62480 | 4.05300 | -0.04160 | -2.24070 | 2.24570 | -1.30180 |
| C      | -0.48400 | 2.90500 | -0.04040 | -2.11000 | 1.10060 | -0.62730 |
| N      | -1.02710 | 1.68300 | -0.02000 | -3.19610 | 0.43260 | -0.20490 |
| C      | -2.37050 | 1.52500 | -0.00440 | -4.47740 | 0.91920 | -0.46610 |
| C      | -3.20540 | 2.63930 | -0.00280 | -3.55120 | 3.73130 | -2.15020 |
| H      | -0.78320 | 5.03220 | -0.05790 | -1.31700 | 2.74030 | -1.61320 |
| H      | 0.60620 | 2.96050 | -0.05580 | -5.36370 | 0.38300 | -0.12640 |
| H      | -4.28880 | 2.52240 | 0.01230 | -3.66100 | -2.80160 | 1.73300 |
| C      | -4.62160 | -1.52620 | 0.02840 | -2.32410 | -3.13450 | 1.92880 |
| C      | -3.64630 | -2.51650 | 0.00820 | -1.35290 | -2.28440 | 1.41170 |
| N      |       |       |       | -1.66630 | -1.17260 | 0.74400 |
| C      |       |       |       | -2.94990 | -0.83400 | 0.54880 |
| C      |       |       |       | -3.98060 | -1.63950 | 1.03500 |
| H      |       |       |       | -2.03070 | -4.03550 | 2.47140 |
| H      |       |       |       | -0.28770 | -2.50070 | 1.53310 |
| H      |       |       |       | -5.02620 | -1.37420 | 0.87840 |
| C      |       |       |       | 2.00080 | -0.18520 | 0.03250 |
| C      |       |       |       | 1.82320 | 0.99390 | -0.77350 |
| C      |       |       |       | 2.41850 | -0.03950 | 1.40280 |
| C      |       |       |       | 2.07740 | 2.27240 | -0.18570 |
| H      |       |       |       | 1.80710 | 0.92360 | -1.86610 |
|    | 2.39790 | -2.05710 | -0.91050 |
|----|---------|----------|----------|
| I  | 2.62580 | 1.20910  | 1.92770  |
| C  | 2.45970 | 2.37930  | 1.13260  |
| H  | 2.58520 | -0.93270 | 2.09030  |
| H  | 2.94370 | 1.31170  | 2.97000  |
| H  | 1.99640 | 3.17130  | -0.80280 |
| H  | -4.45810| -3.44150 | 2.12020  |
| H  | -5.61870| 2.50430  | -1.38160 |
| C  | 2.72110 | 3.71740  | 1.72300  |
| O  | 2.57390 | 4.75980  | 1.13170  |
| H  | 3.07210 | 3.70470  | 2.78290  |

(bipy)Au(4-CHO-C\(_6\)H\(_4\))\(^+\) transition state

SCF = -1272.91084 au
ZPE = -1272.64828 au

| Au  | -0.28710 | -0.45200 | 0.03730  |
|-----|----------|----------|----------|
| I   | 1.27200  | -2.64600 | -0.49730 |
| C   | -4.52900 | -1.55150 | 0.86760  |
| C   | -2.35160 | 1.93810  | -0.22180 |
| C   | -2.92280 | 3.19730  | -0.42280 |
| C   | -2.10170 | 4.26300  | -0.78450 |
| C   | -0.73470 | 4.05070  | -0.93610 |
| C   | -0.24380 | 2.76720  | -0.71650 |
| N   | -1.03470 | 1.75420  | -0.37240 |
| H   | -3.99370 | 3.36180  | -0.30210 |
| H   | -0.05640 | 4.85810  | -1.21970 |
| H   | 0.82160  | 2.53910  | -0.82280 |
| C   | -3.15820 | 0.73550  | 0.16000  |
| C   | -4.54490 | 0.78530  | 0.31500  |
| C   | -5.23560 | -0.36890 | 0.67220  |
| C   | -3.15100 | -1.52880 | 0.69190  |
| N   | -2.49280 | -0.41660 | 0.34990  |
| N   | -5.09390 | 1.71350  | 0.15700  |
| H   | -5.02960 | -2.48050 | 1.14790  |
| H   | -2.54940 | -2.43150 | 0.82790  |
| C   | 1.90420  | -0.56390 | 0.04810  |
| C   | 2.23870  | -0.33260 | 1.39890  |
| C   | 2.43680  | 0.25760  | -0.97290 |
| C   | 3.03280  | 0.76530  | 1.72210  |
| C   | 3.23130  | 1.33780  | -0.62650 |
| C   | 3.52780  | 1.60430  | 0.72030  |
| H   | 2.21300  | 0.04840  | -2.02160 |
| H   | 3.27760  | 0.96200  | 2.77070  |
| H   | 3.63390  | 1.99470  | -1.40230 |

(bipy)Au(4'-Bu-C\(_6\)H\(_4\))\(^+\) product

SCF = -1272.95017 au
ZPE = -1272.68496 au

| Au  | -0.29900 | -0.20250 | 0.02410  |
|-----|----------|----------|----------|
| I   | 0.19410  | -2.74580 | -0.02540 |
| C   | -1.45510 | 4.53270  | -0.00860 |
| C   | -0.11180 | 4.17860  | 0.03920  |
| C   | 0.21870  | 2.83040  | 0.05670  |
| N   | -0.71730 | 1.87550  | -0.03100 |
| C   | -2.03080 | 2.19670  | -0.01410 |
| C   | -2.42380 | 3.53230  | -0.03540 |
| H   | 0.68130  | 4.92840  | 0.06070  |
| H   | 1.25980  | 2.50390  | 0.09140  |
| H   | -3.47910 | 3.80230  | -0.07330 |
| C   | -5.20600 | 0.12770  | -0.09290 |
| C   | -4.64090 | -1.14190 | -0.06450 |
| C   | -3.25580 | -1.25000 | -0.02610 |
| N   | -2.46370 | -0.17520 | -0.01410 |
| C   | -2.99430 | 1.06570  | -0.03770 |
| C   | -4.37390 | 1.24510  | -0.07880 |
| H   | -5.25440 | -2.04480 | -0.07300 |
| H   | -2.75930 | -2.22350 | -0.00620 |
| H   | -4.80770 | 2.24440  | -0.09940 |
| C   | 4.40500  | 0.67120  | 0.16000  |
| C   | 3.69550  | 0.46980  | 1.34790  |
| C   | 2.34100  | 0.13910  | 1.31200  |
| C   | 1.70260  | 0.01880  | 0.07590  |
| C   | 2.40550  | 0.19740  | -1.12600 |
| C   | 3.75610  | 0.52950  | -1.07330 |
| H   | 4.20590  | 0.57190  | 2.31130  |
| H   | 1.79510  | -0.01920 | 2.24580  |
| H   | 1.90710  | 0.08360  | -2.08690 |
| H   | 4.32280  | 0.68080  | -1.99630 |
| H   | -1.75550 | 5.85300  | -0.02640 |
| H   | -6.29050 | 0.25680  | -0.12610 |
| C   | 5.84320  | 1.03090  | 0.21380  |
| O   | 6.53140  | 1.23760  | -0.75690 |
| H   | 6.26950  | 1.10640  | 1.24380  |
6. Selected spectra

2b•NTf₂: $^1$H NMR (400 MHz, CD$_2$Cl$_2$)

[Chemical shift diagram for $^1$H NMR]

2b•NTf₂: $^{13}$C{${}^1$H} NMR (101 MHz, CD$_2$Cl$_2$)

[Chemical shift diagram for $^{13}$C{${}^1$H} NMR]
2b•NTf₂: Raman (neat)

![Raman Spectrum](image)

2c•NTf₂: ¹H NMR (500 MHz, CD₂Cl₂)

![NMR Spectrum](image)
2c•NTf₂: $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$)

2c•NTf₂: Raman (neat)
2e•NTf₂: $^1$H NMR (400 MHz, CD$_2$Cl$_2$)

2e•NTf₂: $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$)
$2e\textbullet\text{NTf}_2$: FTIR (ATR, neat)

$2e\textbullet\text{NTf}_2$: Raman (neat)
$^{2f \cdot \text{NTf}_2}$: $^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{2f \cdot \text{NTf}_2}$: $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$)
$2f\text{•NTf}_2$: $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$)

$2f\text{•NTf}_2$: Raman (neat)
2g•NTf$_2$: $^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$)
2h•NTf₂: ¹H NMR (400 MHz, CD₂Cl₂)

2h•NTf₂: ¹³C{¹H} NMR (101 MHz, CD₂Cl₂)
$2i\cdot$NTf$_2$: $^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$2i\cdot$NTf$_2$: $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$)
2j•NTf$_2$: Raman (neat)

![Raman spectrum of 2j•NTf$_2$](image)

2j•NTf$_2$: $^1$H NMR (400 MHz, CD$_2$Cl$_2$)

![$^1$H NMR spectrum of 2j•NTf$_2$](image)
$2j \cdot \text{NTf}_2$: $^{13}\text{C}^\text{[H]} \text{NMR} (101 \text{ MHz, CD}_2\text{Cl}_2)$

$2k \cdot \text{NTf}_2$: $^1\text{H} \text{NMR} (500 \text{ MHz, CD}_2\text{Cl}_2)$
2k•NTf₂: $^{13}\text{C}^{1}\text{H}$ NMR (126 MHz, CD₂Cl₂)

2d•SbF₆: $^1\text{H}$ NMR (400 MHz, CD₂Cl₂)

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$2d\cdot SbF_6$: $^{13}C\{^1H\}$ NMR (126 MHz, CD$_2$Cl$_2$)

$2d\cdot SbF_6$: $^{19}F$ NMR (377 MHz, CD$_2$Cl$_2$)
**2d•BF₄**: $^1$H NMR (500 MHz, CD₃CN)

**2d•BF₄**: $^{13}$C($^1$H)
NMR (126 MHz, CD₃CN)
2d•BF₄: $^{19}$F NMR (377 MHz, CD₃CN)

4b•NTf₂: $^1$H NMR (500 MHz, CD₂Cl₂)
4b·NTf₂: $^{13}$C{¹H} NMR (126 MHz, CD$_2$Cl$_2$)

4b·NTf₂: $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$)
**4c•NTf₂: **\(^1^H\) NMR (400 MHz, CD\(_2\)Cl\(_2\))

**13C\(^1^H\) NMR (126 MHz, CD\(_2\)Cl\(_2\))**
4c⋅NTf₂: $^{19}$F NMR (377 MHz, CD₂Cl₂)

4c⋅NTf₂: $^1$H NMR (500 MHz, CD₂Cl₂)
**$4e \cdot N\text{TF}_2$: $^{13}C\{^1H\}$ NMR (126 MHz, CD$_2$Cl$_2$)**

**$4e \cdot N\text{TF}_2$: $^{19}F$ NMR (377 MHz, CD$_2$Cl$_2$)**
**4e·NTf₂: FTIR (ATR, neat)**

**4f·NTf₂: ¹H NMR (500 MHz, CD₂Cl₂)**
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD$_2$Cl$_2$)

$^{19}\text{F}$ NMR (377 MHz, CD$_2$Cl$_2$)
$5c\cdot\text{NTf}_2$: $^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$13$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$)
5c•NTf₂: $^1$H NMR (377 MHz, CD$_2$Cl$_2$)

5d•NTf₂: $^1$H NMR (500 MHz, CD$_2$Cl$_2$)
**5d•NTf₂: **$^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$)

**5d•NTf₂: **$^{19}$F NMR (377 MHz, CD$_2$Cl$_2$)
5e•NTf₂: $^1$H NMR (500 MHz, CD$_2$Cl$_2$)

5e•NTf₂: $^{13}$C{H} NMR (126 MHz, CD$_2$Cl$_2$)
5e·NTf₂: ¹⁹F NMR (377 MHz, CD₂Cl₂)

5g·NTf₂: ¹H NMR (500 MHz, CD₂Cl₂)
5g\(\text{NTf}_2\): \(^{13}\text{C}^1\text{H}\) NMR (126 MHz, CD\(_2\)Cl\(_2\))

5g\(\text{NTf}_2\): \(^{19}\text{F}\) NMR (377 MHz, CD\(_2\)Cl\(_2\))
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