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SUPPORTING INFORMATION

Suzuki-Miyaura Coupling of Arylboronic Acids to Gold(III)

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Experimental Information.

General Information. All experimental procedures involving air- or moisture-sensitive substances were performed under argon using Schlenk line techniques or in a nitrogen-filled MBraun drybox. The toluene used for the arylation reactions was degassed by purging with argon for 45 min and then dried with a MBraun solvent purification system comprising column containing activated alumina. Other anhydrous solvents were purchased from Sigma-Aldrich. TLC plates were visualized by ultraviolet light and cerium molybdate staining solution. Analytical thin layer chromatography was carried out using glass bedded Whatman silica gel UV254, 0.25 mm plates. Column chromatography was performed using activated basic alumina, ~150 mesh, 58 Å (Aldrich).

Instruments. ^{1}H NMR experiments were performed on a Varian-400 FT NMR spectrometer operating at 399.7 MHz. ^{1}H chemical shifts are reported in parts per million (δ) with integration and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublets of doublets and m = multiplet), measured from tetramethylsilane (0 ppm) and are referenced to residual solvent in $CDCl_3$ (7.26 ppm), C_6D_6 (7.15) or CD_2Cl_2 (5.32 ppm). $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian INOVA AS-600 spectrometer operating at 150.0 MHz. ^{13}C NMR chemical shifts are reported in parts per million (δ), measured from tetramethylsilane (0 ppm) and are referenced to solvent residuals in $CDCl_3$ (77.00 ppm). ^{19}F NMR spectra were recorded on a Varian INOVA AS-400 spectrometer operating at 376.1 MHz. ^{19}F NMR chemical shifts are reported in parts per million (δ) and measured from $CFCl_3$ (0.00 ppm) or C_6H_5F (–113.15 ppm) as reference. Solvents were degassed by bubbling argon for 20 min prior to use for UV/Vis and luminescence measurements. UV/Vis and luminescence data were recorded using a Cary 5G UV/Vis/NIR spectrometer and a Cary Eclipse spectrometer, respectively. Elemental analyses were carried out by Robertson Microlit Laboratories, Ledgewood, NJ. ***Caution:*** Safety precautions, including use of a blast shield, are recommended for reactions run under pressure.

Materials. All reagents were purchased from commercial sources and used without further purification. $HAuCl_4 \cdot H_2O$ was purchased from Strem Chemicals; 2-(*p*-tolyl)pyridine was purchased from Sigma-Aldrich; all boronic acids were purchased from Sigma-Aldrich, Acros Organics, Oakwood Chemicals and Frontier Scientific. Pd-catalysts and phosphine ligands were purchased from Strem Chemicals and Sigma-Aldrich and were used as received. K_2CO_3 was purchased from Sigma-Aldrich and K_3PO_4 from Strem Chemicals.

Synthesis of [(tpy)AuCl$_2$] (tpy = 2-(*p*-tolyl)pyridine), 1:

(tpy)AuCl$_2$ was synthesized with a slight modification of literature procedure.[11] A high-pressure flask was used in place of microwave heating. Into a high-pressure reaction flask, equipped with a stir bar, was added $HAuCl_4 \cdot H_2O$ (1.015 g, 2.990 mmol) followed by 10 mL deionized water. To this was added a solution of 2-(*p*-tolyl)pyridine (tpy) (0.57 mL, 3.330 mmol) in 2 mL acetonitrile. A yellow precipitate formed immediately. The reaction mixture was warmed at 60 °C for 30 min. After cooling, the yellow precipitate was collected by filtration and was washed thoroughly with water. The crude product was again loaded back into the high-pressure reaction flask followed by 10 mL of 1:1 (v/v) acetonitrile and water. After securely closing the cap of the vessel, the reaction mixture was heated at 180 °C for 12 h. After cooling down to room temperature, the precipitate was collected as off-white solid by filtration. The precipitate was washed with methanol and diethyl ether. Drying under vacuum yielded analytically pure product. Yield: 0.88 g (68%). ^1H NMR is reported elsewhere;[1] analysis (calcd., found for $C_{12}H_{10}AuCl_2N$): C (33.05, 33.34), H (2.31, 2.59), N (3.21, 3.47).

Synthesis of [(Fppy)AuCl$_2$] (Fppy = 2-(4-fluorophenyl)pyridine), 1a:

(Fppy)AuCl$_2$ was synthesized following the procedure described above. A high-pressure flask was used in place of microwave heating. Into a high-pressure reaction flask, equipped with a stir bar, was added HAuCl$_4$·H$_2$O (974 mg, 2.866 mmol) followed by 10 mL deionized water. To this was added a solution of 2-(4-fluorophenyl)pyridine (Fppy) (546 mg, 3.153 mmol) in 2 mL acetonitrile. A yellow precipitate formed immediately. The reaction mixture was warmed at 60 °C for 30 min. After cooling, the yellow precipitate was collected by filtration and was washed thoroughly with water. The crude product was again loaded back into the high-pressure reaction flask followed by 10 mL of 1:1 (v/v) acetonitrile and water. After securely closing the cap of the vessel, the reaction mixture was heated at 180 °C for 12 h. After cooling down to room temperature, the precipitate was collected as off-white solid by filtration. The precipitate was washed with methanol and diethyl ether. Drying under vacuum yielded analytically pure product. Yield: 656 mg (52%); ^{1}H NMR (400 MHz, DMSO): δ 9.47 (d, *J* = 5.9 Hz, 1H), 8.40-8.38 (m, 2H), 8.15 (t, *J* = 5.9, 1H), 7.76 (t, *J* = 5.3 Hz, 1H), 7.57 (dd, *J* = 5.3, 1.8 Hz, 1H), 7.42 (td, *J* = 8.0, 2.1 Hz, 1H); ^{19}F NMR (376.1 MHz, DMSO): δ –103.8 (m, 1F); analysis (calcd., found for $C_{11}H_7AuCl_2FN$): C (30.02, 30.21), H (1.60, 1.94), N (3.18, 3.34).

3a. [(tpy)Au(*p*-C$_6$H$_5$F)$_2$]: Please see manuscript.

3b. [(tpy)Au(2,4-difluorophenyl)$_2$]:

Pd(OAc)$_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added P^{t}Bu$_3$·HBF$_4$ (9.9 mg, 0.034 mmol) and K$_2$CO$_3$ (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)AuCl$_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture, followed by 2,4-difluorophenylboronic acid (90.5 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. Upon completion, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 76 mg (56%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.70$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.13–8.06 (m, 1H), 8.00–7.93 (m, 2H), 7.69 (d, *J* = 8.25 Hz, 1H), 7.49–7.32 (m, 2H), 7.22–7.18 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.86–6.71 (m, 4H), 6.68–6.65 (m, 1H), 2.21 (s, 3H); ^{19}F NMR (376.1 MHz, CD_2Cl_2): δ –93.52 (s, 1F), –95.97 (s, 1F), –117.51 (s, 1F), –118.55 (s, 1F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 270 (sh, 42000), 330 (14000); emission (methylene chloride): λ_{ex}, nm (Int.) 468 (149), 495 (172); analysis (calcd., found for $C_{24}H_{16}AuF_4N$): C (48.75, 48.94), H (2.73, 2.80), N (2.37, 2.61).

3c. [(tpy)Au(4-(trifluoromethyl)phenyl)$_2$]:

$Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (15 mL) inside a 100-mL argon-filled Schlenk flask. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)$AuCl_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture, followed by 4-(trifluoromethyl)phenylboronic acid (109 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear solution. Removal of solvent under reduced pressure rendered an off-white solid which was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 112 mg (75%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.65$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (d, *J* = 5.5 Hz, 1H), 7.98–7.96 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.22–7.18 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.72 (s, 1H), 2.21 (s, 3H); ^{19}F NMR (376.1 MHz, CD_2Cl_2): δ –63.01 (s, 3F), –63.05 (s, 3F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 272 (sh, 22000), 329 (8000); emission (methylene chloride): λ_{ex}, nm (Int.) 466 (182), 495 (210); analysis (calcd., found for $C_{26}H_{18}AuF_6N$): C (47.65, 47.71), H (2.77, 2.85), N (2.14, 2.27).

3d. [(tpy)Au(3-nitrophenyl)$_2$]

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 12 mL dry toluene under argon. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)$AuCl_2$ (100 mg, 0.229 mmol), followed by 3-nitrophenylboronic acid (95.7 mg, 0.573 mmol) and 12 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 20 mL methylene chloride and passed through a plug of Celite. The volume of the solvent was reduced and finally purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:3, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 103 mg (74%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.40; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.35 (dd, *J* = 2.5, 0.9 Hz, 1H), 8.29 (dd, *J* = 1.3, 1.0 Hz, 1H), 7.99–7.98 (m, 3H), 7.92 (t, *J* = 8.5 Hz, 2H), 7.86 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.81 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.21–7.18

(m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 2.19 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 272 (31000), 324 (13000); emission (methylene chloride): λ_{ex}, nm (Int.) 486 (73); analysis (calcd., found for $C_{24}H_{18}AuN_3O_4$): C (47.30, 47.55), H (2.98, 3.11), N (6.90, 7.29).

3e. [(tpy)Au(3-ethoxycarbonylphenyl)$_2$]:

$Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)$AuCl_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture followed by 3-ethoxycarbonylphenylboronic acid (111 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 117 mg (77%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.41$; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.18 (t, *J* = 1.2 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.01 (dt, *J* = 5.4, 1.1 Hz, 1H), 7.96 (d, *J* = 1.3 Hz, 1H), 7.95 (t, *J* = 1.2 Hz, 1H), 7.74–7.70 (m, 4H), 7.66 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.16 (q, *J* = 4.4 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.71 (s, 1H), 4.32 (q, *J* = 3.9 Hz, 2H), 4.29 (q, *J* = 3.2 Hz, 2H), 2.19 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 273 (22000), 330 (10000); emission (methylene chloride): λ_{ex}, nm (Int.) 466 (136), 495 (162); analysis (calcd., found for $C_{30}H_{28}AuNO_4$): C (54.31, 54.59), H (4.25, 4.33), N (2.11, 2.38).

3f. [(tpy)Au(4-acetylphenyl)$_2$]

$Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (15 mL) inside a 100-mL argon-filled Schlenk flask. To this was added $P^tBu_3·HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)$AuCl_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture followed by 4-acetylphenylboronic acid (94 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. After completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 20 mL of methylene chloride and filtered through Celite to obtain a clear solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:9, v/v). The desired product was eluted using hexanes/diethyl ether (1:9, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 78 mg (57%); TLC (hexanes:diethyl ether, 10:90 v/v): $R_f = 0.55$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.02 (br s, 1H), 7.98–7.96 (m, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.73 (t, J = 6.4 Hz, 3H), 7.64 (d, J = 6.4 Hz, 2H), 7.59 (d, J = 6.4 Hz, 2H), 7.18 (t, J = 5 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.74 (s, 1H), 2.53 (s, 3H), 2.52 (s, 3H), 2.20 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 329 (8000); emission (methylene chloride): λ_{ex}, nm (Int.) 465 (141), 494 (167); analysis (calcd., found for $C_{28}H_{24}AuNO_2$): C (55.73, 55.84), H (4.01, 4.29), N (2.32, 2.53).

3g. [(tpy)Au(phenyl)$_2$]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL of dry toluene under argon. To this was added $P^tBu_3·HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)AuCl$_2$ (100 mg, 0.229 mmol) followed by phenylboronic acid (70 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 8 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and finally purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 78 mg (66%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.42$; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.09 (dt, *J* = 5.6, 1.3 Hz, 1H), 7.94–7.92 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.48 (d, 7.7 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.41 Hz, 2H), 7.18–713 (m, 3H), 7.05 (q, *J* = 6.9 Hz, 3H), 6.81 (s, 1H), 2.21 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 328 (17000); emission (methylene chloride): λ_{ex}, nm (Int.) 464 (82), 493 (97); analysis (calcd., found for $C_{24}H_{20}AuN$): C (55.50, 55.73), H (3.88, 4.19), N (2.70, 2.92).

3h. [(tpy)Au(2-naphthyl)$_2$]:

Pd(OAc)$_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added P^{t}Bu$_3$·HBF$_4$ (9.9 mg, 0.034 mmol) and K$_2$CO$_3$ (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)AuCl$_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture followed by 2-naphthylboronic acid (98.6 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid which was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 103 mg (73%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.64$; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.11 (d, J = 5.7 Hz, 1H), 8.00–7.91 (m, 4H), 7.75–7.67 (m, 8H), 7.61 (d, J = 8.4 Hz, 1H), 7.40–7.31 (m, 4H), 712–7.07 (m, 2H), 6.85 (s, 1H), 2.14 (s, 3H); analysis (calcd., found for $C_{32}H_{24}AuN$): C (62.04, 62.18), H (3.90, 4.15), N (2.26, 2.35); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 273 (sh, 70000), 323 (22000); emission (methylene chloride): λ_{ex}, nm (Int.) 369 (771).

3i. [(tpy)Au(2-anthracenyl)$_2$]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 15 mL dry toluene under argon. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)$AuCl_2$ (100 mg, 0.229 mmol), followed by 2-anthraceneboronic acid (127 mg, 0.573 mmol) and 15 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 24 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced. The product was purified on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a yellow solid, which was dried under vacuum for 6 h. Yield: 69 mg (42%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.53; ^1H NMR (400 MHz, C_6D_6): δ 8.44 (s, 1H), 8.31 (s, 1H), 8.26 (s, 1H), 8.19–8.18 (m, 2H), 8.11 (s, 1H), 8.09 (d, J = 5.6 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 4.5 Hz, 2H), 7.85–

7.72 (m, 2H), 7.52 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.35 (s, 2H), 7.23–7.20 (m, 3H), 7.10–7.05 (m, 2H), 6.98–6.95 (m, 2H), 6.74 (t, *J* = 8.4 Hz, 1H), 5.95 (t, *J* = 6.8 Hz, 1H), 1.94 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 298 (64000), 315 (52000), 367 (19000), 387 (15000); emission (methylene chloride): λ_{ex}, nm (Int.) 433 (457), 459 (527); analysis (calcd., found for $C_{40}H_{28}AuN$): C (66.76, 66.91), H (3.92, 4.18), N (1.95, 2.30).

3j. [(tpy)Au(benzo[b]thien-2-yl)$_2$]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL of dry toluene under argon. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added $(tpy)AuCl_2$ (0.100 g, 0.229 mmol) followed by benzo[b]thien-2-ylboronic acid (102 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and finally purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted with hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 98 mg (68%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.44; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.36 (d, *J* = 5.8 Hz, 1H), 8.01–7.94 (m, 2H), 7.78–7.70 (m, 5H), 7.29 (s, 1H), 7.26–7.19 (m, 4H), 7.15 (t, *J* = 8.0 Hz, 3H), 7.04 (s, 1H), 2.21 (s, 3H). UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 333 (22000); emission (methylene chloride): λ_{ex}, nm (Int.) 378 (405), 462 (48); analysis (calcd., found for $C_{28}H_{20}AuNS_2$): C (53.25, 53.41), H (3.19, 3.30), N (2.22, 2.37).

3k. [(tpy)Au(*m*-tolyl)$_2$]:

In a 100-mL Schlenk flask, Pd(OAc)$_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL of dry toluene under argon. To this was added P^{t}Bu$_3$·HBF$_4$ (9.9 mg, 0.034 mmol) and K$_2$CO$_3$ (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)AuCl$_2$ (100 mg, 0.229 mmol) followed by *m*-tolylboronic acid (78 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and finally purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 90 mg (72%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.78$; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.06 (dt, *J* = 5.4, 1.3 Hz, 1H), 7.93 (d, *J* = 1.3 Hz, 1H), 7.93–7.92 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.32–7.26 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.18–7.02 (m, 4H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.82 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 330 (18000); emission (methylene chloride): λ_{ex}, nm (Int.) 464 (95), 491 (112); analysis (calcd., found for $C_{26}H_{24}AuN.CH_2Cl_2$): C (51.28, 51.39), H (4.14, 4.35), N (2.21, 2.46).

3l. [(tpy)Au(*o*-tolyl)$_2$]:

Pd(OAc)$_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added P^{t}Bu$_3$·HBF$_4$ (9.9 mg, 0.034 mmol) and K$_2$CO$_3$ (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)AuCl$_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture, followed by *o*-tolylboronic acid (78 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed with three successive freeze-pump-thaw cycles and stirred at room temperature for 24 h. After completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 76 mg (61%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.75$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.94 (m, 3H), 7.71 (dd, *J* = 7.91, 1.9 Hz, 1H), 7.51 (d, *J* = 5.9 Hz, 1H), 7.43–7.27 (m, 1H), 7.15–6.90 (m, 8H), 6.63 (d, *J* = 5.9 Hz, 1H), 2.50 (s, 3H), 2.40 (s, 3H), 2.17 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 329 (17000); emission (methylene chloride): λ_{ex}, nm (Int.) 463 (96), 491 (109); analysis (calcd., found for $C_{26}H_{24}AuN$): C (57.04, 57.26), H (4.42, 4.38), N (2.56, 2.80).

3m. [(tpy)Au(4-methoxyphenyl)$_2$]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL dry toluene under argon. To this was added $P^tBu_3\cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)$AuCl_2$ (100 mg, 0.229 mmol) followed by 4-methoxyphenylboronic acid (87.1 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced. The crude product was purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 99 mg (75%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.65$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.11 (dt, *J* = 5.3, 1.4 Hz, 1H), 7.92 (d, *J* = 1.1 Hz, 1H), 7.91 (m, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.17–7.14 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 2.21 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 328 (19000); emission (methylene chloride): λ_{ex}, nm (Int.) 493 (133); analysis (calcd., found for $C_{26}H_{24}AuNO_2$): C (53.89, 54.18), H (4.17, 4.24), N (2.42, 2.71).

3n. [(tpy)Au(4-isopropoxyphenyl)$_2$]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL dry toluene under argon. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)$AuCl_2$ (100 mg, 0.229 mmol) followed by 4-isopropoxyphenylboronic acid (0.103 g, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced. The crude product purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 97 mg (67%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.70$; ^{1}H NMR (400 MHz, C_6D_6): δ 8.13 (dd, *J* = 5.5, 1.2 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.95 (dd, J = 7.9, 1.2 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.75 (td, J = 7.4, 1.2 Hz, 1H), 6.04 (td, J = 7.1, 1.2 Hz, 1H), 4.25 (sep, J = 5.8 Hz, 1H), 4.19 (sep, J = 5.8 Hz, 1H), 2.06 (s, 3H), 1.14 (d, J = 5.8 Hz, 6H), 1.11 (d, J = 5.8 Hz, 6H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 328 (29000); emission (methylene chloride): λ_{ex}, nm (Int.) 492 (112); analysis (calcd., found for $C_{30}H_{32}AuNO_2.CH_2Cl_2$): C (51.68, 51.80), H (4.76, 4.93), N (1.94, 2.29).

3o. [(tpy)Au(4-(benzyloxy)phenyl)$_2$]:

$Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) followed by K_2CO_3 (128 mg, 0.917 mmol). The resultant yellow reaction mixture was stirred for 5 min under argon. (tpy)$AuCl_2$ (100 mg, 0.229 mmol) was added to the stirred reaction mixture followed by 4-(benzyloxy)phenylboronic acid (130.7 mg, 0.573 mmol) and 2-propanol (10 mL). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 10 h. Progress of the reaction was monitored by TLC. Upon completion, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:1, v/v). The desired product was eluted using hexanes/diethyl ether (1:1, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 130 mg (78%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.68; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.12 (d, J = 4.9 Hz, 1H), 7.93–7.91 (m, 2H), 7.70 (d, J = 7.7 Hz, 1H), 7.50–7.30 (m, 14H), 7.18–7.15 (m, 1H), 7.07 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.02 (s, 2H), 5.01 (s, 2H), 2.22 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1})

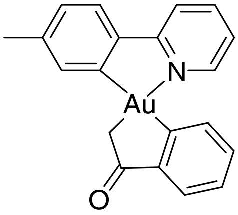
328 (16000); emission (methylene chloride): λ_{ex}, nm (Int.) 467 (88), 493 (105); analysis (calcd., found for $C_{38}H_{32}AuNO_2$): C (62.38, 62.39), H (4.41, 4.78), N (1.91, 2.22).

4a. [(tpy)Au(Cl)(4-fluorophenyl)]:

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL of dry toluene under argon. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added $(tpy)AuCl_2$ (100 mg, 0.229 mmol) followed by 4-fluorophenylboronic acid (80.2 mg, 0.573 mmol). The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 12 h at room temperature. Progress of the reaction was monitored by TLC. After 12 h, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced. The crude product was purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted as the second fraction using hexanes/diethyl ether (1:3, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 73 mg (65%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.30$; ^1H NMR (400 MHz, $CDCl_3$): δ 9.44 (d, $J = 5.8$ Hz, 1H), 8.02 (t, $J = 7.5$ Hz, 1H), 7.91 (t, $J = 7.8$ Hz, 1H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.55–7.45 (m, 4H), 7.12 (d, $J = 7.7$ Hz, 1H), 7.02 (t, $J = 8.8$ Hz, 1H), 6.65 (s, 1H), 2.22 (s, 3H); analysis (calcd., found for $C_{18}H_{14}AuClFN$): C (43.61, 43.53), H (2.85, 2.76), N (2.83, 3.19).

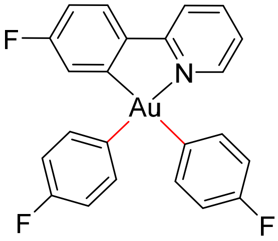
4b. [(tpy)Au(Cl)(1-naphthyl)]:

$Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in dry toluene (10 mL) inside a 100-mL argon-filled Schlenk flask. To this was added $P^tBu_3 \cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a light yellow reaction mixture, which was stirred for 5 min at room temperature under argon. (tpy)AuCl_2 (100 mg, 0.229 mmol) was added to the stirred reaction mixture followed by 1-naphthylboronic acid (98.6 mg, 0.573 mmol). The reaction mixture was degassed by three successive freeze-pump-thaw cycles and stirred at room temperature for 12 h. After the time period, the solvent was evaporated under reduced pressure. The resultant mixture was suspended in 10 mL methylene chloride and filtered through Celite to obtain a clear yellow solution. Removal of solvent under reduced pressure rendered an off-white solid that was chromatographed on a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product was eluted as second fraction using hexanes/diethyl ether (1:3, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 49 mg (41%); TLC (hexanes:diethyl ether, 40:60 v/v): $R_f = 0.25$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.45 (d, *J* = 5.1 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.08 (td, *J* = 7.4, 1.8 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.07 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.66–7.63 (m, 2H), 7.55 (t, *J* = 6.1 Hz, 1H), 7.45–7.37 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.28 (s, 1H), 1.98 (s, 3H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 283 (63000), 326 (22000); emission (methylene chloride): λ_{ex}, nm (Int.) 485 (147); analysis (calcd., found for $C_{22}H_{17}AuClN$): C (50.06, 50.37), H (3.25, 3.55), N (2.65, 2.90).



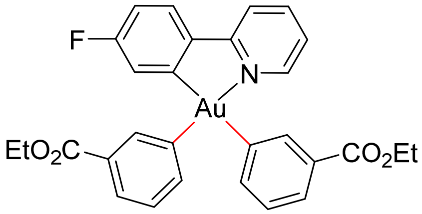
4c.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (2.6 mg, 0.011 mmol) was dissolved in 10 mL of dry toluene under argon. To this was added $P^tBu_3\cdot HBF_4$ (9.9 mg, 0.034 mmol) and K_2CO_3 (128 mg, 0.917 mmol) resulting in a pale yellow solution, which was stirred for 5 min at room temperature under argon. To this flask was added (tpy)AuCl_2 (100 mg, 0.229 mmol) followed by 2-acetylphenylboronic acid (94 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 24 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and finally purified by a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:9, v/v). The desired product was eluted using hexanes/diethyl ether (1:9, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 88 mg (80%); TLC (hexanes:diethyl ether, 10:90 v/v): $R_f = 0.75$; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.14 (d, *J* = 6.5 Hz, 1H), 8.07–8.00 (m, 3H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.59 (td, *J* = 7.7, 1.6 Hz, 1H), 7.55 (s, 1H), 7.49 (t, *J* = 6.4 Hz, 1H), 7.33 (td, *J* = 7.5, 0.9 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 3.57 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 209.3, 168.6, 167.1, 166.2, 148.9, 145.2, 143.7, 141.6, 140.6, 135.3, 132.5, 131.9, 127.6, 127.2, 126.8, 125.1, 122.9, 120.5, 45.3, 22.1; IR (KBr): 1666.4 cm^{-1}; UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 302 (10000), 321 (11000); emission (methylene chloride): λ_{ex}, nm (Int.) 492 (74); analysis (calcd., found for $C_{20}H_{16}AuNO$): C (49.70, 49.85), H (3.34, 3.48), N (2.90, 3.13).



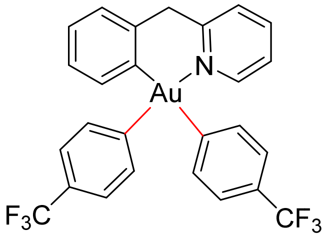
5a.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (1.3 mg, 0.005 mmol) was dissolved in 8 mL dry toluene under argon. To this was added $[HP(t\text{-Bu})_3]BF_4$ (4.9 mg, 0.017 mmol) and K_2CO_3 (63 mg, 0.454 mmol). A pale yellow solution resulted, which was stirred for 5 min at room temperature under argon. To this flask was added (Fppy)$AuCl_2$ (50 mg, 0.114 mmol) followed by 4-fluorophenylboronic acid (40.0 mg, 0.284 mmol) and 8 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and the mixture was passed through a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 46 mg (73%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.54; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 5.6 Hz, 1H), 7.38–7.29 (m, 6H), 7.13–7.06 (m, 2H), 6.91 (t, *J* = 8.8 Hz, 3H), 6.83 (q, *J* = 2.8 Hz, 2H), 6.12 (t, *J* = 6 Hz, 1H). ^{19}F NMR (376.1 MHz, $CDCl_3$): δ –107.6 (m, 1F), –118.3 (m, 1F), –118.6 (m, 1F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 328 (3500); emission (methylene chloride): λ_{ex}, nm (Int.) 485 (40); analysis (calcd., found for $C_{23}H_{15}AuF_3N$): C (49.39, 49.62), H (2.70, 3.07), N (2.50, 2.24).



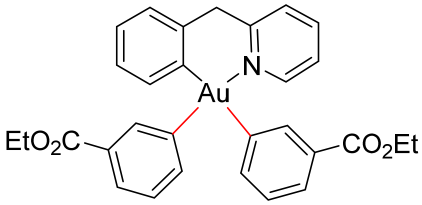
5b.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (1.3 mg, 0.005 mmol) was dissolved in 7 mL dry toluene under argon. To this flask was added $[HP(t\text{-}Bu)_3]BF_4$ (4.9 mg, 0.017 mmol) and K_2CO_3 (63 mg, 0.454 mmol). A pale yellow solution resulted, which was stirred for 5 min at room temperature under argon. To this flask was added $(Fppy)AuCl_2$ (50 mg, 0.114 mmol) followed by 3-ethoxycarbonylphenylboronic acid (55.1 mg, 0.284 mmol) and 7 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and the mixture was passed through a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 50 mg (66%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 5.6 Hz, 1H), 7.66 (t, *J* = 5.6 Hz, 2H), 7.26–7.21 (m, 3H), 7.07 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.85–6.80 (m, 2H), 6.05 (t, J = 6.4 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 1.12 (t, J = 8.0 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H); ^{19}F NMR (376.1 MHz, $CDCl_3$): δ –107.5 (m, 1F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 331 (2500); emission (methylene chloride): λ_{ex}, nm (Int.) 484 (16); analysis (calcd., found for $C_{29}H_{25}AuFNO_4$): C (52.18, 52.03), H (3.78, 4.12), N (2.10, 2.33).



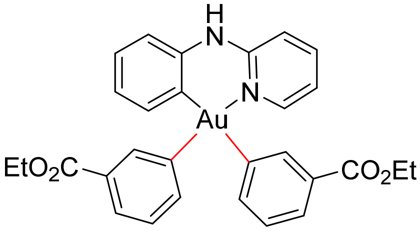
6a.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (1.3 mg, 0.006 mmol) was dissolved in 6 mL dry toluene under argon. To this flask was added $[HP(t\text{-}Bu)_3]BF_4$ (5.0 mg, 0.017 mmol) and K_2CO_3 (63.5 mg, 0.460 mmol). A pale yellow solution resulted, which was stirred for 5 min at room temperature under argon. To the same flask was added (bnp)$AuCl_2$ (50 mg, 0.115 mmol) followed by 4-(trifluoromethyl)phenylboronic acid (54.5 mg, 0.287 mmol) and 6 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 17 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, contents were filtered through Celite plug and volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and the mixture was passed through a short basic alumina column using variant polarity between hexanes and hexanes/diethyl ether (1:3, v/v). The desired product eluted using hexanes/diethyl ether (1:2, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 45.2 mg (60%); TLC (hexanes:diethyl ether, 40:60 v/v): R_f = 0.65; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 4.8, 1H), 7.78 (td, J = 10, 1H), 7.58 (d, J = 7.2, 1H), 7.49 (d, J = 8.4, 2H), 7.42 (d, J = 8.0, 2H), 7.31 (d, J = 8.0 2H), 7.25 (d, J = 8.0, 2H), 7.21 (d, J = 6.4, 1H), 7.10 (m, 2H), 6.95 (m, 2H), 4.30 (s, 2H); ^{19}F NMR (376.1 MHz, $CDCl_3$): δ –62.54 (s, 3F), –62.60 (s, 3F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 272 (6500); emission (methylene chloride): λ_{ex}, nm (Int.) 488 (31); analysis (calcd., found for $C_{26}H_{18}AuF_6N$): C (47.65, 48.02), H (2.77, 2.83), N (2.14, 2.10).



6b.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (0.8 mg, 0.003 mmol) was dissolved in 10 mL dry toluene under argon. To this flask was added $[HP(t\text{-}Bu)_3]BF_4$ (3.1 mg, 0.010 mmol) and K_2CO_3 (38.4 mg, 0.278 mmol). A pale yellow solution resulted, which was stirred for 5 min at room temperature under argon. To the flask was added (bnp)$AuCl_2$ (30.3 mg, 0.070 mmol) followed by 3-ethoxycabonylboronic acid (25.4 mg, 0.198 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 17 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, contents were filtered through Celite plug and volatiles were removed under reduced pressure. The resulting product was suspended in 5 mL methylene chloride, reduced in volume and crude product was precipitated by addition of pentane. The product was purified by preparative TLC using hexanes/diethyl ether (1:1, v/v). The product was recovered from the TLC plate with methanol. Removal of solvent rendered a white solid. Yield: 35.3 mg (77 %); TLC (hexanes:diethyl ether, 30:70 v/v): $R_f = 0.36$, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 5.6 Hz, 1H), 8.12 (s, 1H), 8.04 (s, 1H), 7.81 (td, *J* = 7.6 Hz, 1 H), 7.64 (m, 5 H), 7.18 (m, 5H), 6.99 (td, *J* = 6.4, 2H), 4.39 (s, 2H), 4.31 (m, 4 H), 1.34 (m, 6H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 245 (27000), 271 (sh, 13000), 284 (sh, 11000); emission (methylene chloride): λ_{ex}, nm (Int.) 551 (62), 584 (45); analysis (calcd., found for $C_{30}H_{28}AuNO_4\cdot CH_2Cl_2\cdot H_2O$): C (48.58, 48.80), H (4.21, 3.89), N (1.83, 1.77).



7a.

In a 100-mL Schlenk flask, $Pd(OAc)_2$ (1.3 mg, 0.005 mmol) was dissolved in 10 mL dry toluene under argon. To this was added $[HP(t\text{-}Bu)_3]BF_4$ (4.9 mg, 0.017 mmol) and K_2CO_3 (63 mg, 0.454 mmol). A pale yellow solution resulted, which was stirred for 5 min at room temperature under argon. To the flask was added (anp)$AuCl_2$ (50 mg, 0.114 mmol) followed by 3-ethoxycarbonylphenylboronic acid (55.1 mg, 0.284 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed by three successive freeze-pump-thaw cycles. Finally the reaction mixture was sealed and stirred for 10 h at room temperature. Progress of the reaction was monitored by TLC. Upon completion, volatiles were removed under reduced pressure. The resulting crude product was suspended in 10 mL methylene chloride and passed through a plug of Celite. The volume of solvent was reduced and the mixture was passed through a short basic alumina column using variant polarity between hexanes and diethyl ether/methanol (19:1, v/v). The desired product eluted using diethyl ether/methanol (19:1, v/v). Removal of solvent rendered a white solid, which was dried under vacuum for 6 h. Yield: 42 mg (55%); TLC (hexanes:diethyl ether, 10:90 v/v): $R_f = 0.40$; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.04 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.66 (t, 7.8 Hz, 2H), 7.59–7.54 (m, 2H), 7.21–7.11 (m, 3H), 7.08–6.95 (m, 4H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.47 (t, *J* = 6.8 Hz, 1H), 4.30 (q, *J* = 4.0 Hz, 4H), 1.37–1.33 (m, 6H); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 293 (3000), 336 (2500); emission (methylene chloride): λ_{ex}, nm (Int.) 466 (12); analysis (calcd., found for $C_{29}H_{27}AuN_2O_4$): C (52.42, 52.61), H (4.10, 3.77), N (4.22, 3.91).

Synthesis of [(bnp)$AuCl_2$] (bnp = 2-benzylpyridine), 6. Into a high-pressure reaction flask, equipped with a stir bar, was added $HAuCl_4{\cdot}H_2O$ (0.5224 g, 1.5374 mmol) followed by 150 mL deionized water and 5 mL acetonitrile. To this was added 2-benzylpyridine (bnp) (0.25 mL, 1.5571 mmol). A yellow precipitate formed immediately. High pressure flask was sealed and the reaction mixture was heated at 130 °C for 15 h. After this time period a white precipitate had formed. After cooling to room temperature, the precipitate was collected by filtration as off-white solid. The precipitate was washed with water. Drying under vacuum for 6 h at 45 °C yielded analytically pure product. Yield: 0.5346 g (80%); characterization was previously reported.[2]

Synthesis of [(anp)AuCl$_2$] (anp = 2-anilinopyridine), 7.

Synthesis reported previously.[3]

X-ray Crystallography. Crystallographic data for **3a**, **3c**, **3d**, **3j**, **3l**, **3n**, **4a**, **4b**, **4c** and the p-fluoro derivative of **1** were collected on either a Bruker AXS SMART APEXII CCD diffractometer or a Bruker AXS Quest diffractometer using monochromatic Mo Kα radiation with omega and/or phi scan techniques. The unit cells were retrieved using the APEX2 Crystallographic Suite. Structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXL2013 and SHELXLE. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (CH$_3$) or 1.2 (all others) times that of the adjacent carbon atom.

Complex **3c**: The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180 degree rotation around the real a-axis. The two components were initially integrated using Saint giving the twin matrix 0.99994 0.01611 -0.03295, 0.69290 -0.98912 -0.02860, 0.32732 0.02563 -1.01045. Integration proofed problematic due to excessive multiple overlap of reflections, resulting in large numbers of rejected reflections. Attempts were made to adjust integration parameters to avoid excessive rejections (through adjustements to integration queue size, blending of profiles, integration box slicing and twin overlap parameters), which led to less but still substantial numbers of rejected reflections. With no complete dataset obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, with only the major domain integrated, and converted into an hklf 5 type format hkl file after integration using the "Make HKLF5 File" routine as implemented in WinGX. The twin law matrix was used as obtained from SAINT, see above. The Overlap R1 and R2 values used were 0.32, i.e. reflections with a discriminator function less or equal to overlap radius of 0.32 were counted overlapped, all others as single. The discriminator fucntion used was the "delta function on index non-integrality". No reflections were omitted. The structure was solved using direct methods with the hklf 4 type file and was refined using the hklf 5 type file, resulting in a BASF value of 0.199(4). A refinement using the incomplete data obtained through SAINT and TWINABS gave similar refinement statistics, but with higher overall R values (around 8-9% for R1) and with less well defined ADPs (two atoms NPD or close to NPD). No Rint value is obtainable for the hklf 5 type file using the WinGX routine. The value from TWINABS is given instead, which is for all reflections available and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2009)).

Complex **3j**: The compound exhibits two different types of disorder. Thiophene rings are disordered by 180 degree rotations around the Au-C bond. In addition, whole molecule disorder is observed due to 180 rotation of the tpy ligand which, due to the steric demand if the methyl group, induces a shift of the whole molecule. The disorder of the tpy ligand and of the the two thiophene moieties are independent of each other, thus leading to eight different combinations of disordered moieties. Due to their low prevalence, the minor flip disordered thiophene moieties associated with the minor rotated tpy ligand were omitted from the refinement. All chemically equivalent disordered organic moieties were restrained to have similar geometries (SAME restraint of Shelxl). The gold bonded carbon atoms of equivalent flip disordered thiophene units were constrained to have identical positions and ADPs. The Au-C and Au-N distances of the flip disordered tpy ligand were restrained to be similar to that of the major moiety complex. All disordered atoms were subjected to a rigid bond restraint (RIGU in Shelxl). Overlapping atoms C22B and S2 were restrained to have similar ADPs (SIMU in Shelxl). Overlapping atoms C15 and C15C, C16 and C16C, C5 and C6C, and C4 and C7C were constrained to have identical ADPs.

Complex **3l**: The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180 degree rotation around the reciprocal c-axis. The two components were initially integrated using Saint and corrected for absorption using twinabs. The exact twin matrix identified by the integration program was found to be -0.99994 -0.00155 0.00043, 0.00707 -0.99999 -0.00013, 0.25079 0.00006 0.99995. Integration proofed problematic due to excessive multiple overlap of reflections, resulting in large numbers of rejected reflections. Attempts were made to adjust integration parameters to avoid excessive rejections (through adjustments to integration queue size, blending of profiles, integration box slicing and twin overlap parameters), which led to less but still substantial numbers of rejected reflections. With no complete data set obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, with only the major domain integrated, and converted into an hklf 5 type format hkl file after integration using the "Make HKLF5 File" routine as implemented in WinGX. The twin law matrix was used as obtained from SAINT, see above. The Overlap R1 and R2 values used were 0.41, i.e. reflections with a discriminator function less or equal to overlap radius of 0.41 were counted overlapped, all others as single. The discriminator function used was the "delta function on index non-integrality". No reflections were omitted. The structure was solved using direct methods with the hklf 4 type file and was refined using the hklf 5 type file, resulting in a BASF value of 0.150(2). A refinement using the incomplete data obtained through SAINT and TWINABS gave similar refinement statistics, but with higher overall R values and with less well defined ADPs (several atoms NPD or close to NPD). No Rint value is obtainable for the hklf 5 type file using the WinGX routine. The value from a refinement with the uncorrected hklf 4 type file is given instead.

Complex **4c**: The structure is partially racemically twinned (Flack parameter 0.224(16)) and emulates a higher symmetry centrosymmetric structure with a mirror plane bisecting the main molecule of the structure. For the C and N atoms directly located on the pseudo mirror plane, large correlation of position and ADP results, leading to deformed or non-positive definite ADPs. The thermal parameters of the affected atoms were restrained to be close to isotropic (ISOR 0.003 restraint of Shelxl for atoms N1, C1, C2, C6, C11, C10 and C20). A partially occupied methylene chloride molecule is disordered within channels parallel to the c-axis. Packing of the solvate molecules in the channels is incommensurate with the lattice dimensions, and molecules show large ADPs that stretch along the channel direction if unrestrained. For refinement, the methylene chloride position was split into two partially occupied molecules translated from each other by 1.1 and 2.4 Å along the channel. C-Cl distances were restrained to be similar (SADI), atoms were subjected to a rigid bond restraint (RIGU), and to be approximately isotropic (ISOR 0.01). Subject to these conditions occupancy ratios refined to 0.367(16) and 0.250(16), with a total occupancy for the site of 0.617(16).

Calculations. Spin-restricted density-functional theory calculations were executed within the program Gaussian09.[4] Geometry optimizations proceeded without imposition of symmetry. The parameter-free exchange and correlation functionals of Perdew, Burke, and Ernzerhof, were used.[5] Basis sets were the TZVP basis of Godbout, Andzelm, and co-workers for nonmetal atoms.[6] For gold, the SDD effective core potential and basis set were employed;[7] scalar relativistic effects are included implicitly. Frequency calculations returned all real harmonic vibrational frequencies. All calculations include continuum CH_2Cl_2 solvation using the integral equation formalism of the polarizable continuum model (IEFPCM).[8–11] Relative energies are calculated from sums of electronic and thermal free energies.

Figure S1. Crystal structure of dichloro(2-(4-fluorophenyl)pyridine)gold(III) (**1a**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

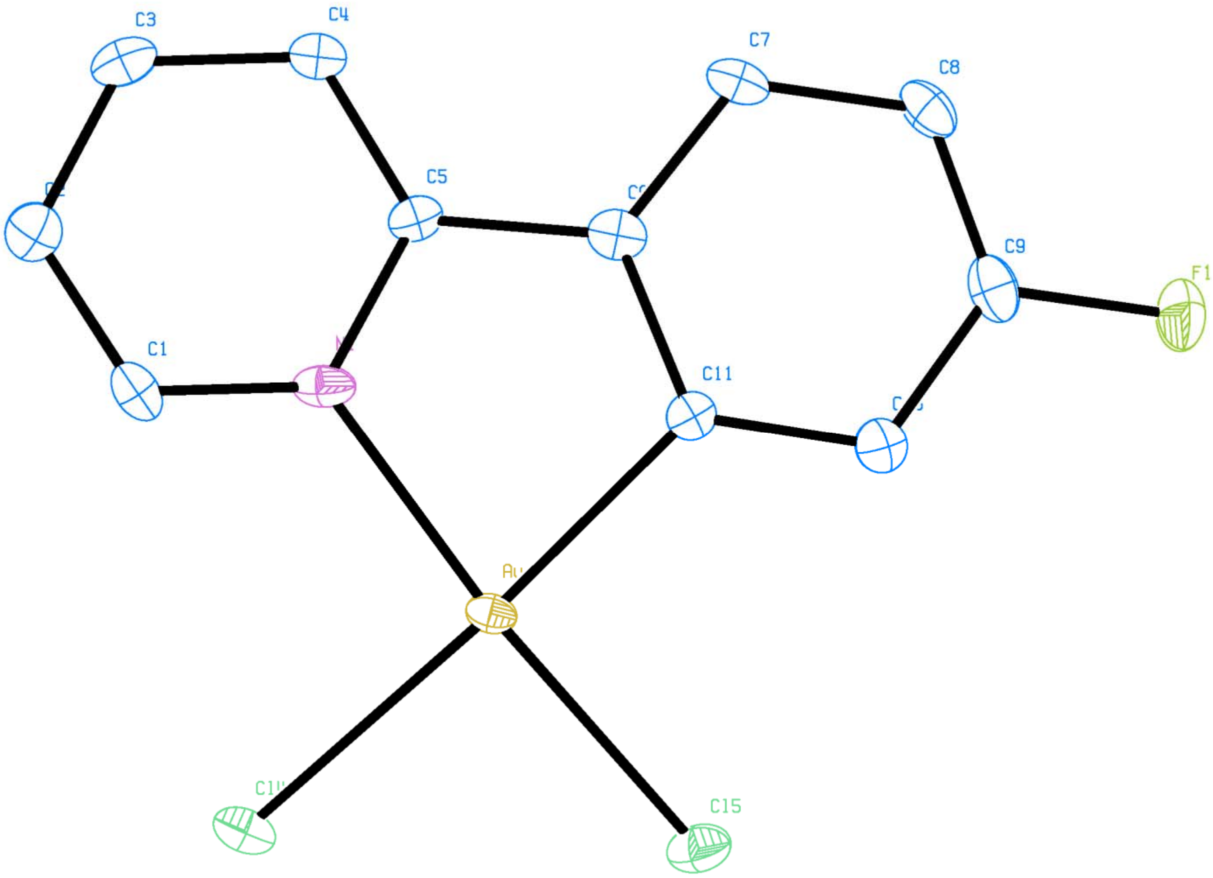


Figure S2. Crystal structure of **3a** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

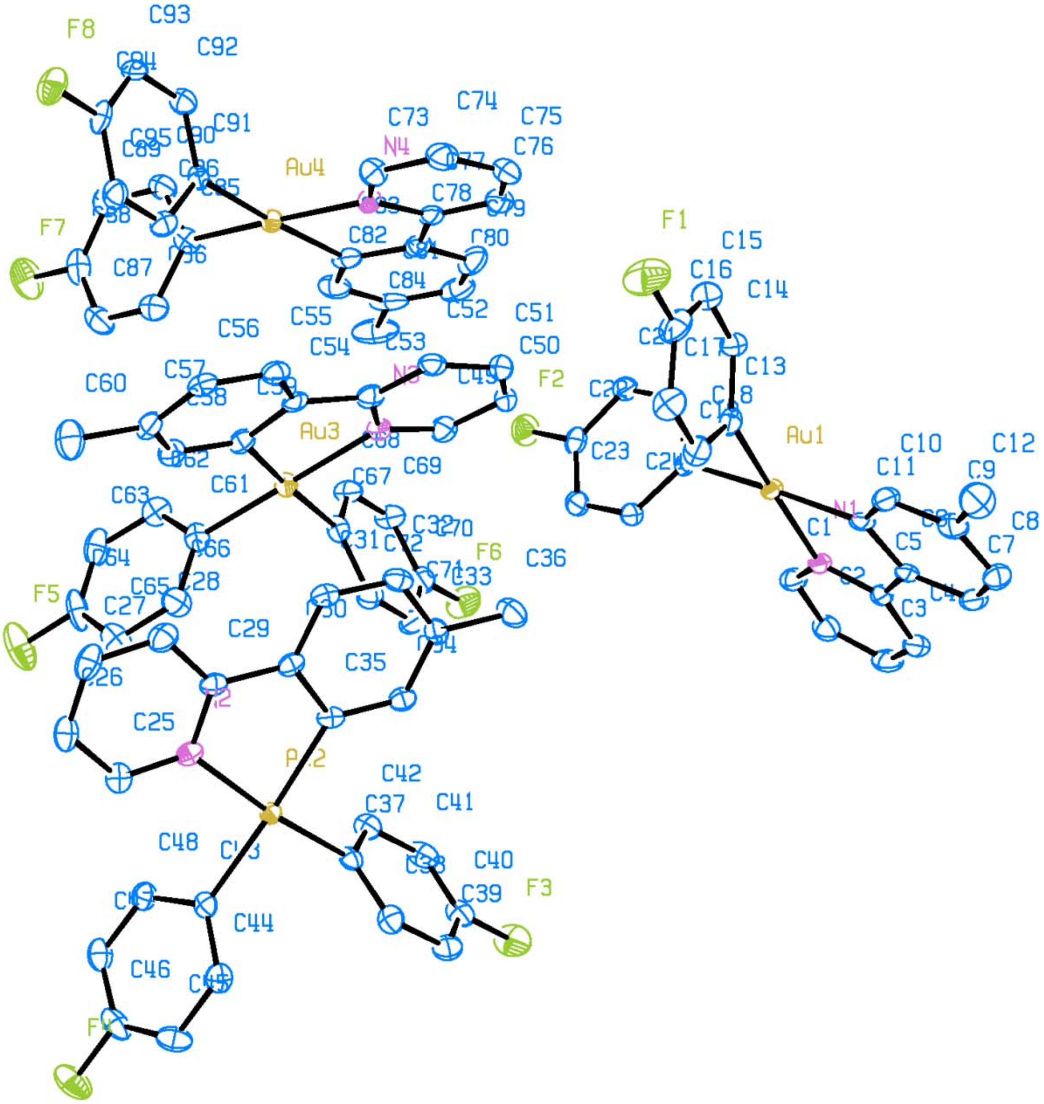


Figure S3. Crystal structure of **3c** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

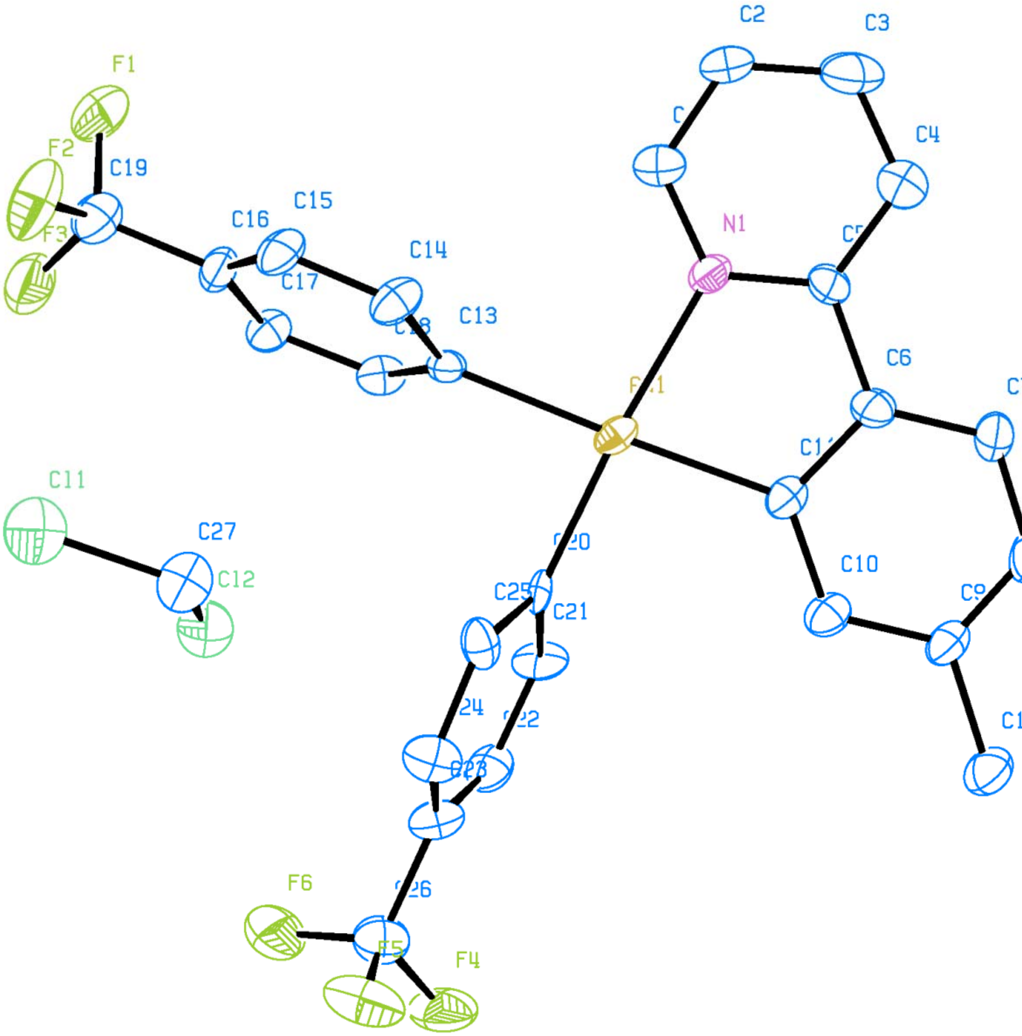


Figure S4. Crystal structure of **3d** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

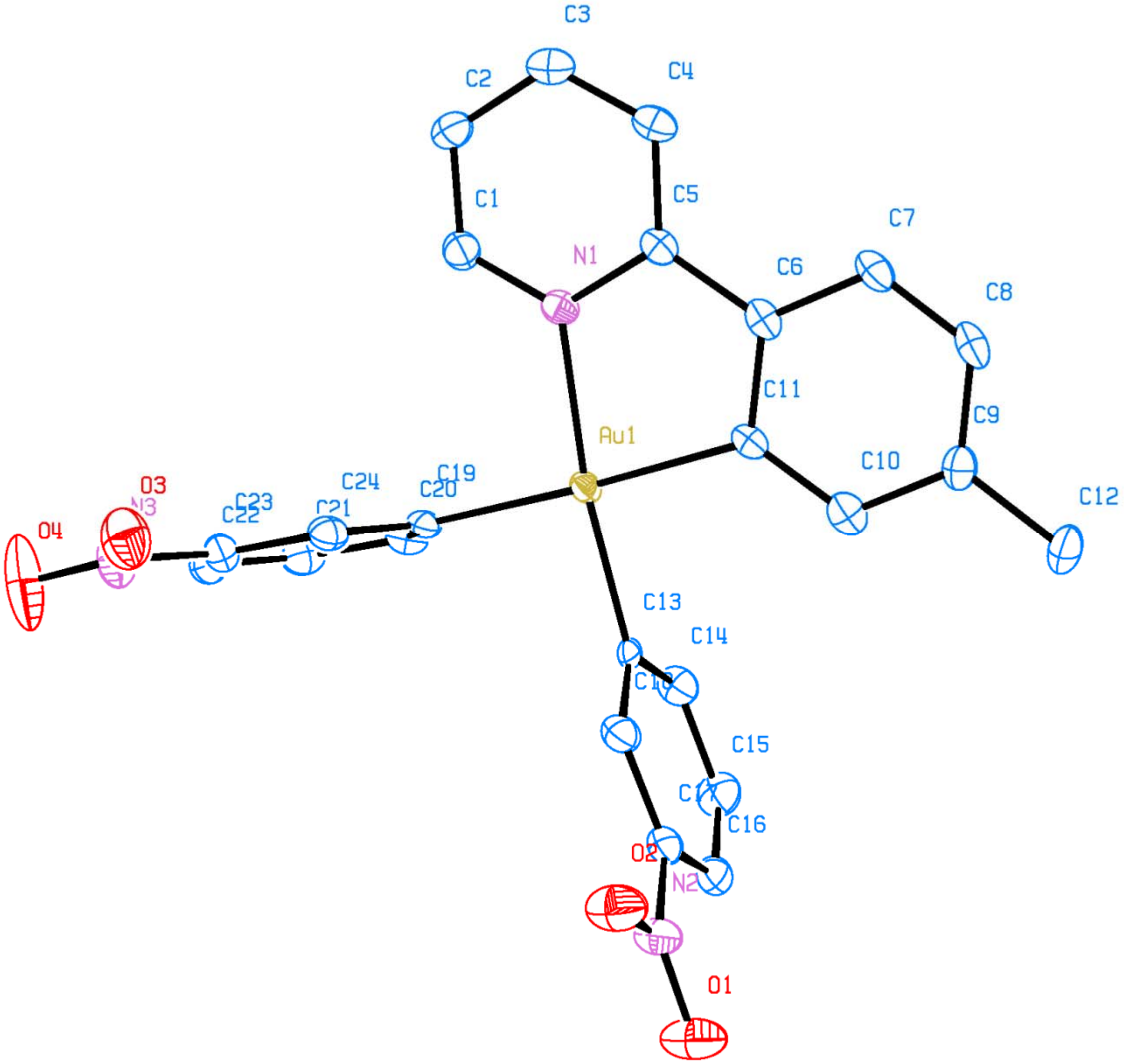
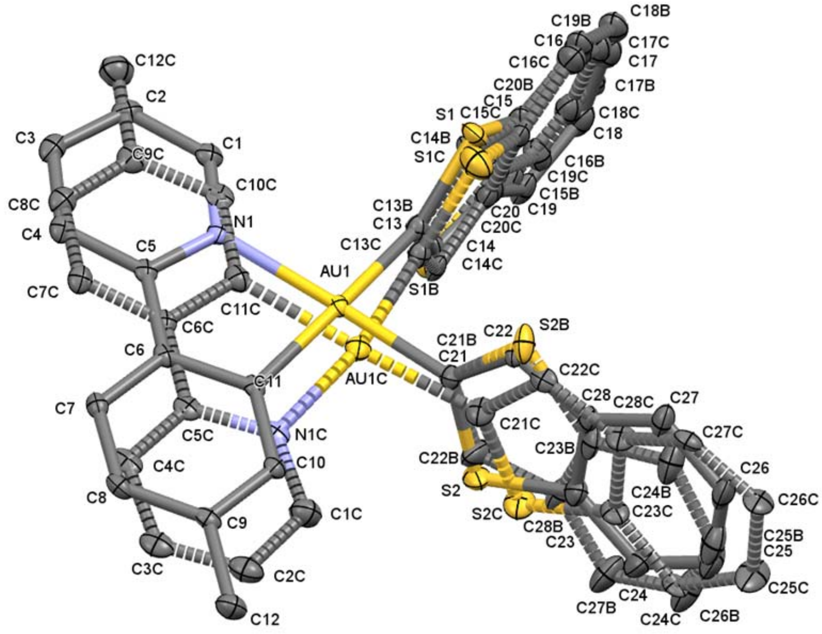


Figure S5. Crystal structure of **3j** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. This structure is disordered. (a) Thermal ellipsoid depiction showing both domains.



(b) Thermal ellipsoid depiction showing only major domain.

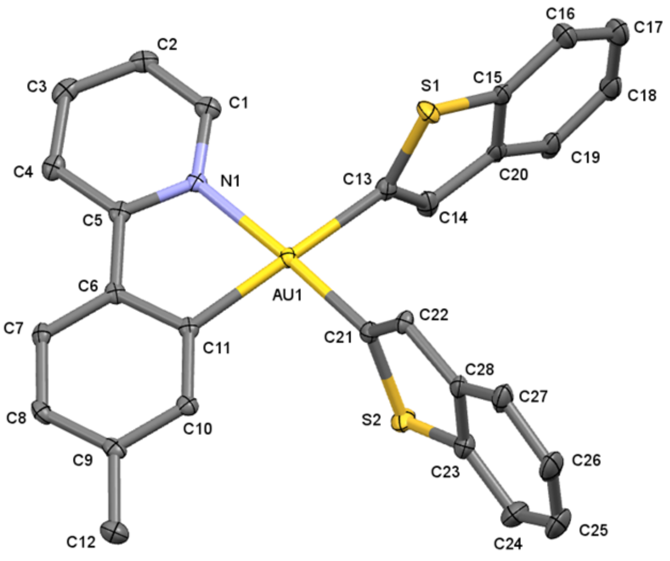


Figure S6. Crystal structure of **3l** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

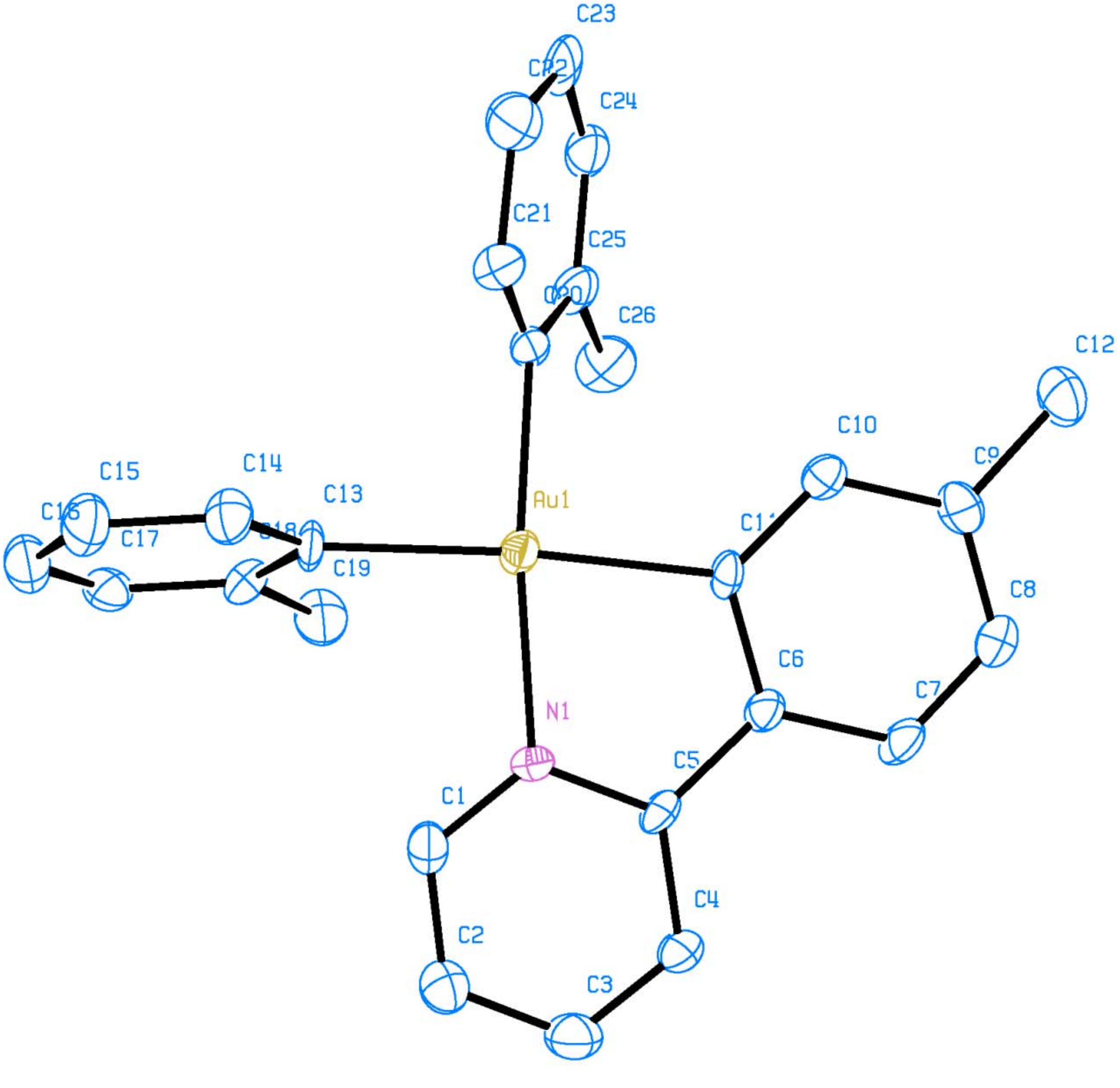


Figure S7. Crystal structure of **3n** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

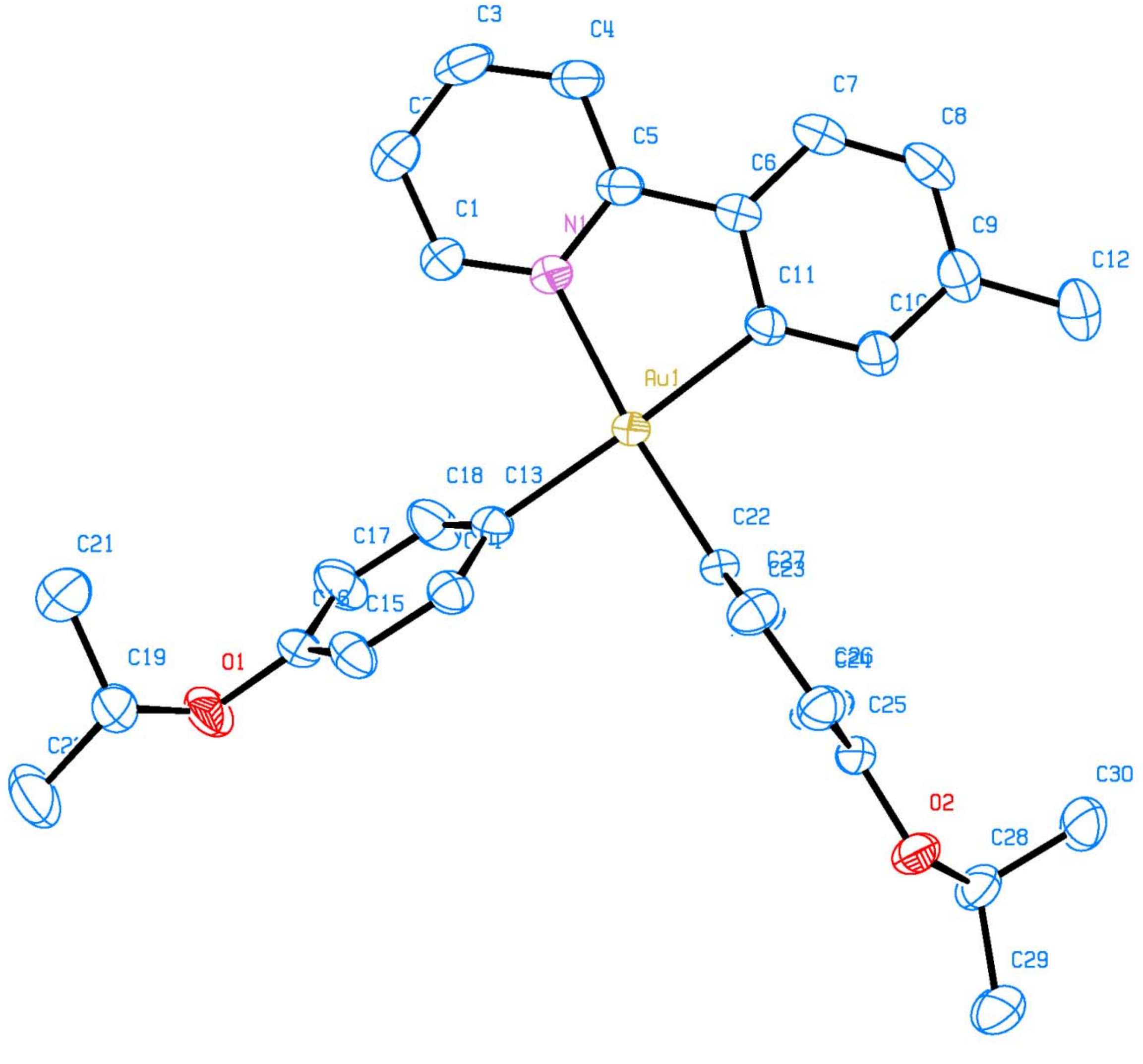


Figure S8. Crystal structure of **4a** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

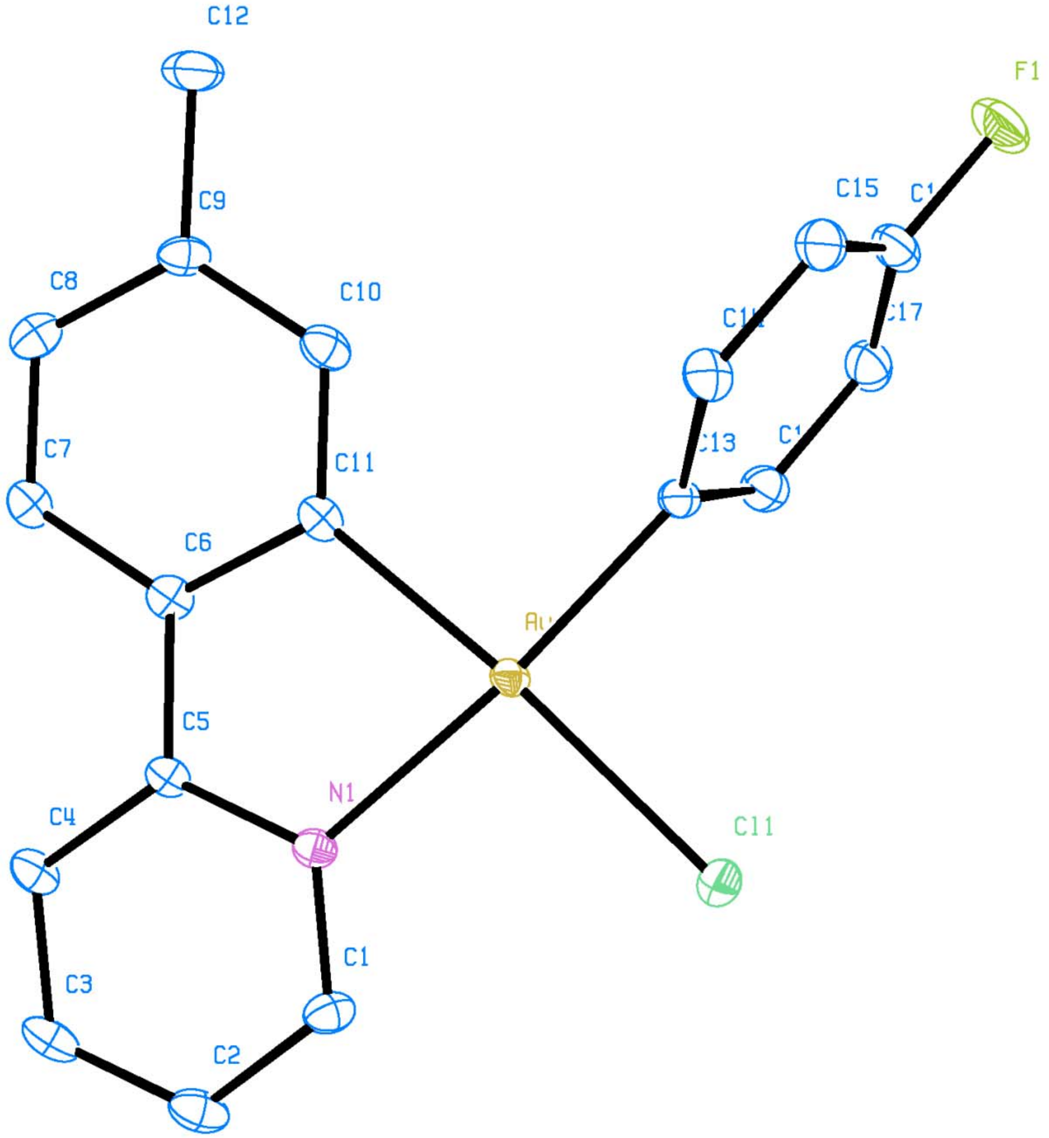


Figure S9. Crystal structure of **4b** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

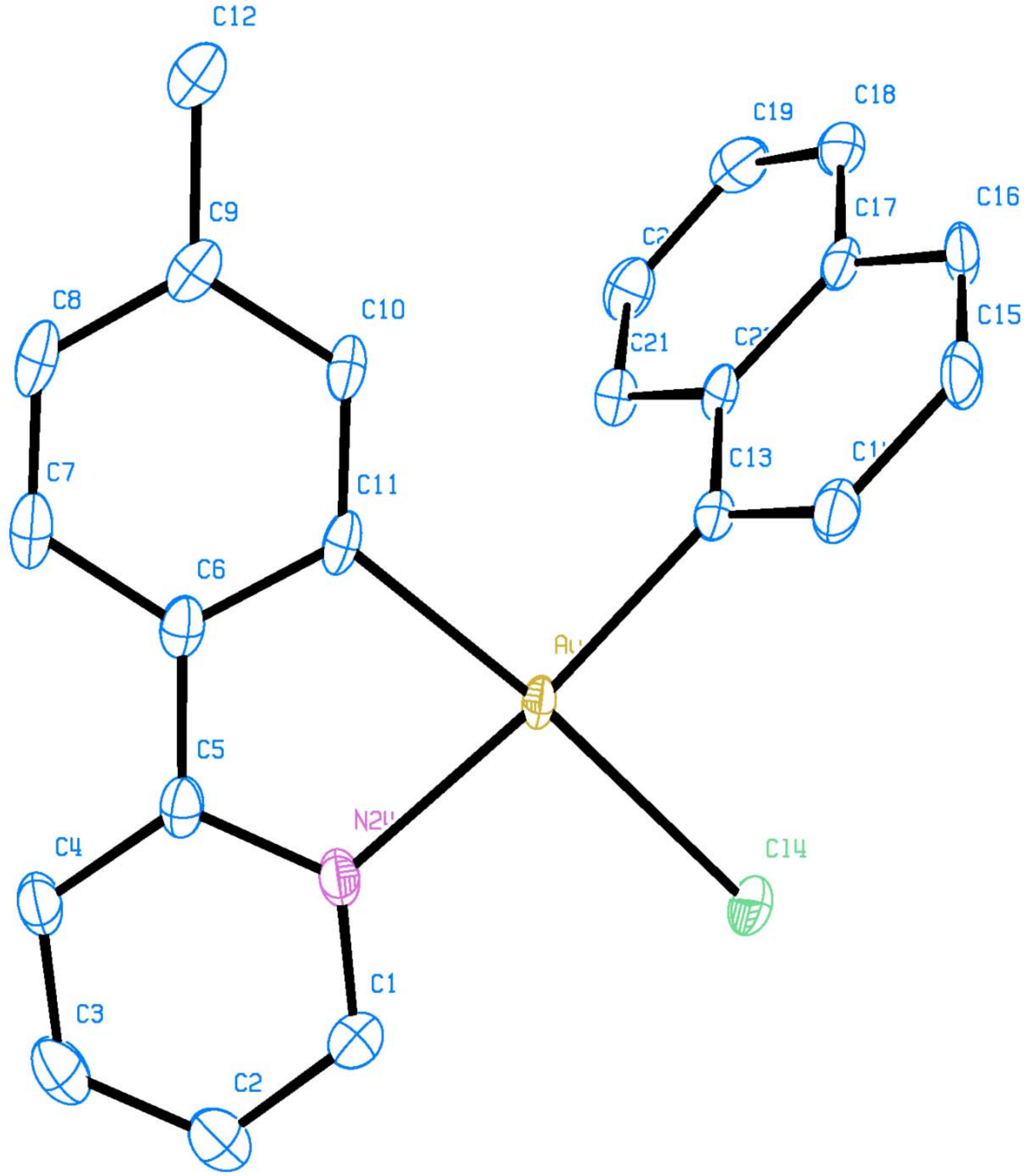


Figure S10. Crystal structure of **4c** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

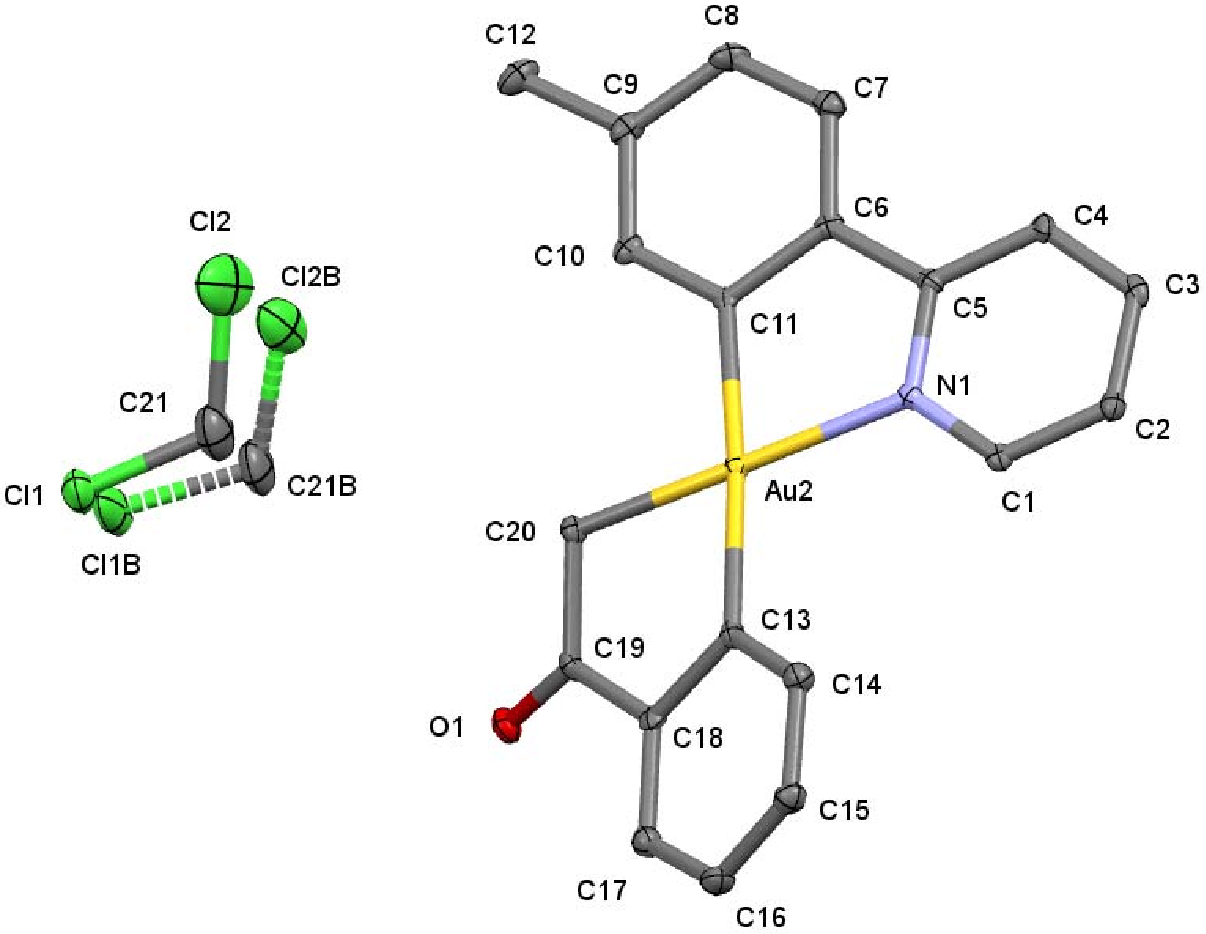


Table S1. Relative sums of electronic and thermal free energies of 1-naphthyl complexes **4b** (observed) and **4b′**. The calculation includes continuum CH_2Cl_2 solvation (IEFPCM).

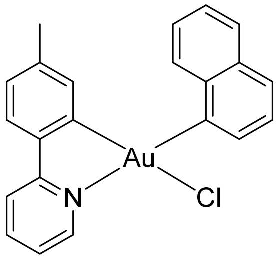
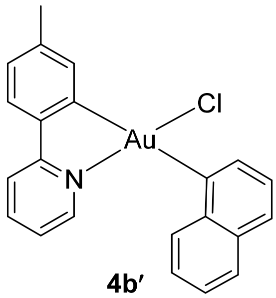
		
	4b (observed)	**4b′**
E_{relative} (kcal mol^{-1})	0	+17.0

Table S2. Relative sums of electronic and thermal free energies of enolate complexes. The calculation includes continuum CH_2Cl_2 solvation (IEFPCM).

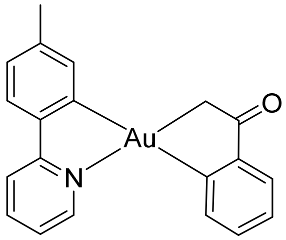
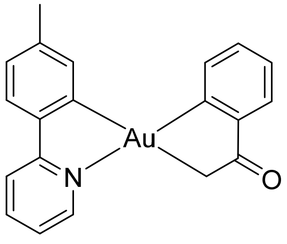
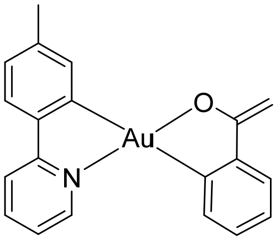
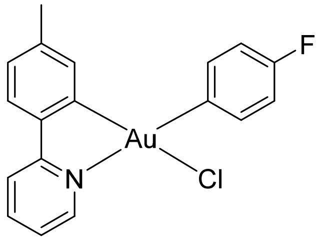
			
	4c (observed)	**4c′**	**4c″**
E_{relative} (kcal mol^{-1})	0	+0.5	+25.1

Table S3. Optimized Cartesian coordinates (Å) of **4a**.



4a (observed)

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 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         79           0        0.136538   -0.697606    0.000375
      2          6           0        0.475347    1.297227   -0.001341
      3          6           0        1.843928    1.625976   -0.002481
      4          6           0        2.215569    2.970014   -0.009667
      5          6           0        1.255989    3.966977   -0.013361
      6          6           0       -0.100963    3.652424   -0.007256
      7          6           0       -0.472625    2.305099   -0.005196
      8          6           0        2.814012    0.530667   -0.001049
      9          6           0        4.198015    0.677732   -0.001000
     10          6           0        5.004554   -0.445927    0.001291
     11          6           0        4.425111   -1.707069    0.003496
     12          6           0        3.046765   -1.794033    0.003382
     13          7           0        2.275863   -0.707309    0.001258
     14          1           0        3.262798    3.250249   -0.016098
     15          1           0        1.566595    5.006466   -0.022893
     16          1           0       -1.526748    2.055587   -0.008325
     17          1           0        4.640119    1.664628   -0.002584
     18          1           0        6.082868   -0.337345    0.001381
     19          1           0        5.023092   -2.608759    0.005295
     20          1           0        2.521963   -2.742440    0.004985
     21          6           0       -1.143122    4.728273    0.022227
     22          1           0       -2.055942    4.411383   -0.485277
     23          1           0       -1.412249    4.974569    1.054481
     24          1           0       -0.782682    5.644152   -0.449336
     25         17           0       -0.083948   -3.094340    0.002716
     26          6           0       -1.870354   -0.487187   -0.000858
     27          6           0       -2.570051   -0.426025    1.199572
     28          6           0       -2.568530   -0.425993   -1.202188
     29          6           0       -3.955115   -0.299137    1.206335
     30          6           0       -3.953590   -0.299085   -1.210690
     31          6           0       -4.618582   -0.236982   -0.002590
     32          1           0       -2.045799   -0.475186    2.147031
     33          1           0       -2.043089   -0.475121   -2.148989
     34          1           0       -4.511698   -0.250654    2.134957
     35          1           0       -4.509006   -0.250680   -2.140015
     36          9           0       -5.962091   -0.110973   -0.003441
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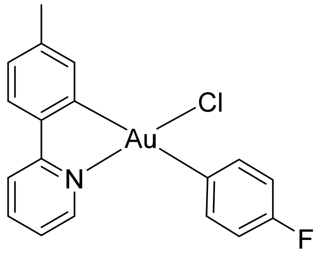
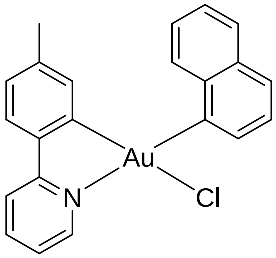
Table S4. Optimized Cartesian coordinates (Å) of **4a′**.



4a′

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	79	0	-0.175106	-0.713239	0.000003
2	7	0	-0.557543	1.307322	0.000000
3	6	0	-1.868916	1.646995	0.000001
4	6	0	-2.206611	2.996962	0.000002
5	6	0	-1.220911	3.961206	-0.000002
6	6	0	0.124720	3.596717	-0.000006
7	6	0	0.401248	2.241156	-0.000004
8	6	0	-2.813882	0.533614	0.000002
9	6	0	-4.199439	0.705670	0.000001
10	6	0	-5.029517	-0.403537	0.000000
11	6	0	-4.480523	-1.680671	0.000001
12	6	0	-3.099126	-1.851933	0.000002
13	6	0	-2.252449	-0.754217	0.000003
14	1	0	-3.248679	3.286711	0.000004
15	1	0	-1.496411	5.010485	-0.000002
16	1	0	1.418415	1.873011	-0.000005
17	1	0	-4.639487	1.696651	-0.000001
18	1	0	-6.105553	-0.271892	-0.000001
19	1	0	-5.132262	-2.548247	0.000001
20	1	0	-2.681102	-2.853140	0.000003
21	6	0	1.225389	4.608433	-0.000014
22	1	0	2.204798	4.129515	0.000029
23	1	0	1.160691	5.251990	-0.880827
24	1	0	1.160645	5.252057	0.880746
25	17	0	0.081381	-3.009815	-0.000015
26	6	0	1.903644	-0.527237	0.000002
27	6	0	2.617619	-0.457023	-1.195624
28	6	0	2.617617	-0.457007	1.195629
29	6	0	4.001437	-0.306697	-1.208196
30	6	0	4.001434	-0.306682	1.208202
31	6	0	4.665016	-0.233932	0.000003
32	1	0	2.099344	-0.519592	-2.147580
33	1	0	2.099340	-0.519561	2.147586
34	1	0	4.557942	-0.251785	-2.136924
35	1	0	4.557938	-0.251756	2.136930
36	9	0	6.008513	-0.088205	0.000002

Table S5. Optimized Cartesian coordinates (Å) of **4b**.

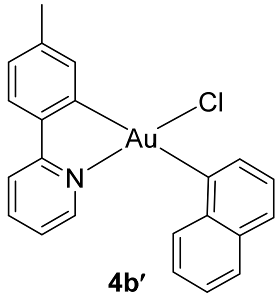


4b (observed)

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         79           0       -0.346245   -0.679304   -0.245709
      2          6           0       -0.715094    1.307476   -0.148956
      3          6           0       -2.066114    1.607608    0.108769
      4          6           0       -2.454010    2.943032    0.209020
      5          6           0       -1.526921    3.959397    0.057465
      6          6           0       -0.188639    3.673095   -0.200348
      7          6           0        0.200211    2.333760   -0.297626
      8          6           0       -3.000836    0.493079    0.266584
      9          6           0       -4.364499    0.613195    0.518309
     10          6           0       -5.139099   -0.525776    0.643587
     11          6           0       -4.548643   -1.775307    0.516596
     12          6           0       -3.191403   -1.835369    0.267683
     13          7           0       -2.451022   -0.733963    0.149169
     14          1           0       -3.487234    3.200772    0.411772
     15          1           0       -1.848011    4.992088    0.143248
     16          1           0        1.241389    2.105332   -0.492270
     17          1           0       -4.816316    1.591060    0.614871
     18          1           0       -6.201488   -0.438156    0.839120
     19          1           0       -5.121989   -2.688366    0.607405
     20          1           0       -2.660047   -2.773441    0.155290
     21          6           0        0.814083    4.769441   -0.392947
     22          1           0        1.785063    4.496753    0.025083
     23          1           0        0.964298    4.971346   -1.458366
     24          1           0        0.482593    5.697992    0.074633
     25          6           0        1.617307   -0.426549   -0.666555
     26          6           0        2.582929   -0.315571    0.369026
     27          6           0        2.006446   -0.389766   -1.980992
     28          6           0        2.250488   -0.338634    1.745046
     29          6           0        3.957966   -0.164282    0.010384
     30          6           0        3.366114   -0.241814   -2.327800
     31          6           0        3.213164   -0.224288    2.712020
     32          6           0        4.928136   -0.052089    1.034478
     33          6           0        4.320816   -0.131645   -1.355309
     34          6           0        4.568421   -0.080464    2.354537
     35          1           0        1.272477   -0.476151   -2.774599
     36          1           0        1.209087   -0.451245    2.027521
     37          1           0        3.645463   -0.217826   -3.375701
     38          1           0        2.933099   -0.246172    3.759412
```

39	1	0	5.969963	0.059000	0.750551
40	1	0	5.367886	-0.017877	-1.616883
41	1	0	5.323280	0.006966	3.128159
42	17	0	-0.078465	-3.070619	-0.300601

Table S6. Optimized Cartesian coordinates (Å) of **4b′**.

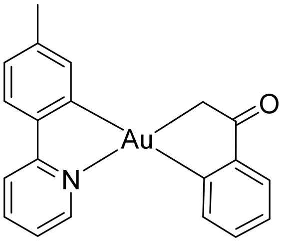


4b′

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	-0.204526	-0.421057	-0.267448
2	7	0	-0.477896	1.613175	-0.156498
3	6	0	-1.756222	2.015670	0.063532
4	6	0	-2.026570	3.378559	0.158446
5	6	0	-1.005999	4.299958	0.032799
6	6	0	0.290951	3.857170	-0.189023
7	6	0	0.515705	2.500439	-0.278363
8	6	0	-2.740848	0.948227	0.184397
9	6	0	-4.101753	1.173616	0.398595
10	6	0	-4.970939	0.101917	0.499510
11	6	0	-4.507661	-1.210482	0.393561
12	6	0	-3.143269	-1.420857	0.174634
13	6	0	-2.254638	-0.365026	0.070620
14	1	0	-3.041452	3.709008	0.332343
15	1	0	-1.219927	5.359600	0.108086
16	1	0	1.120478	4.543747	-0.291964
17	1	0	1.500702	2.090138	-0.453612
18	1	0	-4.496421	2.180268	0.482935
19	1	0	-6.028244	0.285072	0.661183
20	1	0	-2.775550	-2.438767	0.083541
21	6	0	-5.447766	-2.368632	0.535174
22	1	0	-5.523220	-2.677330	1.583009
23	1	0	-6.453410	-2.109874	0.198278
24	1	0	-5.101219	-3.232892	-0.034233
25	6	0	1.847863	-0.325827	-0.672394
26	6	0	2.830970	-0.301055	0.357191
27	6	0	2.258668	-0.273264	-1.983340
28	6	0	2.495396	-0.358808	1.732922
29	6	0	4.214683	-0.207181	0.010563
30	6	0	3.624762	-0.182919	-2.328509
31	6	0	3.458182	-0.325196	2.706747
32	6	0	5.185888	-0.176823	1.039442

```
     33          6           0        4.583027   -0.150093   -1.353216
     34          6           0        4.820123   -0.232863    2.357399
     35          1           0        1.527315   -0.302910   -2.786241
     36          1           0        1.449618   -0.439273    2.011606
     37          1           0        3.908851   -0.142566   -3.375123
     38          1           0        3.173844   -0.374259    3.752219
     39          1           0        6.233514   -0.108004    0.762575
     40          1           0        5.635365   -0.081656   -1.610622
     41          1           0        5.575501   -0.209171    3.135237
     42         17           0       -0.059192   -2.725828   -0.341143
 ---------------------------------------------------------------------
```

Table S7. Optimized Cartesian coordinates (Å) of **4c**.



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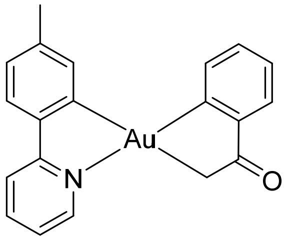
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         79           0        0.259267   -0.192866   -0.040062
      2          6           0       -1.759642   -0.665652   -0.020375
      3          6           0       -2.604457    0.460460   -0.037549
      4          6           0       -3.987980    0.299598   -0.131566
      5          6           0       -4.540819   -0.966727   -0.201536
      6          6           0       -3.728734   -2.099830   -0.176746
      7          6           0       -2.345478   -1.922446   -0.094784
      8          6           0       -1.969606    1.774886    0.072457
      9          6           0       -2.658647    2.981947    0.184473
     10          6           0       -1.962555    4.162237    0.358185
     11          6           0       -0.577379    4.129520    0.436520
     12          6           0        0.052888    2.908365    0.308971
     13          7           0       -0.617125    1.771752    0.110396
     14          1           0       -4.648641    1.159121   -0.158619
     15          1           0       -5.617643   -1.077916   -0.278342
     16          1           0       -1.722483   -2.812082   -0.094112
     17          1           0       -3.739403    2.991153    0.149120
     18          1           0       -2.497804    5.100420    0.447632
     19          1           0        0.008206    5.025446    0.594770
     20          1           0        1.128575    2.824205    0.375025
     21          6           0       -4.325647   -3.474007   -0.215194
     22          1           0       -3.638857   -4.193575   -0.664814
     23          1           0       -4.550173   -3.825912    0.797100
     24          1           0       -5.260553   -3.487645   -0.778916
     25          8           0        2.852324   -3.124447    1.023951
     26          6           0        0.942132   -2.117439    0.001501
     27          6           0        2.374512   -2.152349    0.467994
     28          6           0        3.113063   -0.919032    0.140504
```

```
    29          6           0        2.311751    0.173055   -0.218324
    30          6           0        4.505146   -0.862187    0.131310
    31          6           0        2.968548    1.321994   -0.659911
    32          6           0        5.131977    0.298785   -0.286438
    33          6           0        4.358368    1.381121   -0.698631
    34          1           0        5.077218   -1.732794    0.436064
    35          1           0        6.214196    0.361689   -0.311962
    36          1           0        2.412992    2.184777   -1.012215
    37          1           0        4.845391    2.281751   -1.059201
    38          1           0        0.317498   -2.757857    0.623877
    39          1           0        0.905986   -2.484807   -1.030040
---------------------------------------------------------------------
```

Table S8. Optimized Cartesian coordinates (Å) of **4c′**.

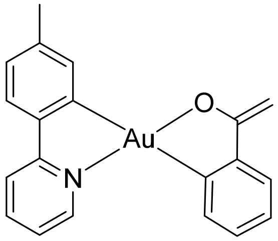


4c′

```
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
     1         79           0        0.238251   -0.481828   -0.089576
     2          7           0       -1.677690   -1.418421   -0.048125
     3          6           0       -2.722875   -0.560832   -0.067073
     4          6           0       -4.020891   -1.062316   -0.154104
     5          6           0       -4.231607   -2.425946   -0.216457
     6          6           0       -3.142365   -3.286352   -0.196048
     7          6           0       -1.879698   -2.736593   -0.114057
     8          6           0       -2.373862    0.857118    0.024730
     9          6           0       -3.342264    1.854241    0.154328
    10          6           0       -2.968528    3.176326    0.313754
    11          6           0       -1.621436    3.529568    0.365281
    12          6           0       -0.664153    2.520070    0.233301
    13          6           0       -1.004086    1.188596    0.037287
    14          1           0       -4.861652   -0.382608   -0.175699
    15          1           0       -5.240197   -2.816758   -0.284490
    16          1           0       -3.261121   -4.360666   -0.243387
    17          1           0       -0.996075   -3.359691   -0.100365
    18          1           0       -4.398224    1.607562    0.148975
    19          1           0       -3.731431    3.940967    0.418732
    20          1           0        0.379819    2.804947    0.305102
    21          6           0       -1.207341    4.959325    0.540373
    22          1           0       -1.933188    5.514997    1.137324
    23          1           0       -0.231376    5.033339    1.023715
    24          1           0       -1.130668    5.461430   -0.429694
    25          8           0        3.355430   -2.457592    1.428861
```

```
     26          6           0        1.462571   -2.213674   -0.034868
     27          6           0        2.727392   -1.789875    0.623029
     28          6           0        3.121413   -0.426739    0.191076
     29          6           0        2.068089    0.363960   -0.279509
     30          6           0        4.433922    0.033364    0.185204
     31          6           0        2.362306    1.602692   -0.838182
     32          6           0        4.713643    1.279215   -0.352719
     33          6           0        3.680382    2.047674   -0.880979
     34          1           0        5.221579   -0.598294    0.582936
     35          1           0        5.733053    1.647646   -0.381050
     36          1           0        1.582071    2.224344   -1.258998
     37          1           0        3.901935    3.009281   -1.332384
     38          1           0        1.035347   -3.091521    0.453018
     39          1           0        1.665017   -2.439810   -1.087482
 ---------------------------------------------------------------------
```

Table S9. Optimized Cartesian coordinates (Å) of **4c″**.



4c″

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         79           0        0.253213   -0.109078    0.032733
      2          6           0       -1.732106   -0.664142    0.008118
      3          6           0       -2.612511    0.420319   -0.105610
      4          6           0       -3.982467    0.194484   -0.247295
      5          6           0       -4.464144   -1.102799   -0.269171
      6          6           0       -3.602456   -2.195549   -0.146533
      7          6           0       -2.231981   -1.953593   -0.016559
      8          6           0       -1.998863    1.736943   -0.020598
      9          6           0       -2.686942    2.947075    0.005330
     10          6           0       -2.003027    4.131622    0.191639
     11          6           0       -0.627065    4.100129    0.372909
     12          6           0        0.013638    2.881082    0.322156
     13          7           0       -0.643944    1.738738    0.101852
     14          1           0       -4.680203    1.019003   -0.347791
     15          1           0       -5.529408   -1.274197   -0.384894
     16          1           0       -1.545437   -2.791873    0.062629
     17          1           0       -3.762834    2.947299   -0.105223
     18          1           0       -2.540283    5.072349    0.214458
     19          1           0       -0.051934    4.998607    0.551799
     20          1           0        1.079357    2.798703    0.470012
     21          6           0       -4.138933   -3.594563   -0.133066
     22          1           0       -3.411178   -4.302631   -0.533516
     23          1           0       -4.370304   -3.908240    0.890184
     24          1           0       -5.059275   -3.674669   -0.714707
```

```
     25          8           0        0.889450   -1.992007    0.087009
     26          6           0        2.217832   -2.163367    0.246019
     27          6           0        3.024055   -0.947438    0.043017
     28          6           0        2.304969    0.253150   -0.121269
     29          6           0        4.417357   -0.955845   -0.038435
     30          6           0        3.023229    1.405014   -0.430017
     31          6           0        5.110552    0.212238   -0.306609
     32          6           0        4.411062    1.394101   -0.518759
     33          1           0        4.964151   -1.883782    0.090175
     34          1           0        6.193058    0.198009   -0.371792
     35          1           0        2.516835    2.341422   -0.638748
     36          1           0        4.944409    2.307134   -0.762231
     37          6           0        2.699629   -3.380681    0.542264
     38          1           0        3.761189   -3.552593    0.652176
     39          1           0        2.029054   -4.221542    0.667335
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REFERENCES

[1] A. P. Shaw, M. Tilset, R. H. Heyn, and S. Jakobsen, *J. Coord. Chem.,* **2011**, *64,* 38–47.

[2] C. Structure, H. C, M. A. Cinellu, A. Zucca, S. Stoccoro, and G. M. A, *J. Chem. Soc., Dalton Trans.*, **1995**, 2865–2872.

[3] W. Henderson, B. K. Nicholson, S. J. Faville, D. Fan, and J. D. Ranford, *J. Organomet. Chem.*, **2001**, *631*, 41–46.

[4] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[5] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[6] A. Schäfer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.*, **1994**, *100*, 5829–5835.

[7] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866–872.

[8] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.

[9] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093.

[10] E. Cancès, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032–3041.

[11] B. Mennucci, E. Cancès, J. Tomasi, *J. Phys. Chem. B* **1997**, *101*, 10506–10517.