Supporting Information

for

Synthesis, characterization and luminescence studies of gold(I)–NHC amide complexes

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Experimental part

Table of Contents

General considerations: **S3**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(phenylamino)gold Complex (2): **S3**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-2-ylamino)gold complex (3): **S3**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-3-ylamino)gold Complex (4): **S4**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-4-ylamino)gold complex (5): **S4**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-methylpyridin-2-yl)amino)gold Complex (6): **S5**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-chloropyridin-2-yl)amino)gold complex (7): **S5**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-(trifluoromethyl)pyridin-2-yl)amino)gold complex (8): **S5**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-nitropyridin-2-yl)amino)gold complex (9): **S6**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(isoquinolin-3-ylamino)gold complex (10): **S6**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-chloropyrimidin-2-yl)amino)gold complex (11): **S7**

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(diphenylamino)gold complex (12): **S7**

UV–vis and fluorescence spectra: **S8**

NMR spectra **S19**

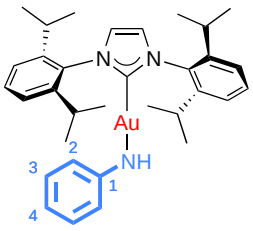
DFT Calculations **S30**

General considerations:

Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. Deuterated solvents (e.g. CD_2Cl_2) were filtered through basic alumina in order to remove traces of HCl. NMR spectra were recorded on 500, 400 and 300 MHz spectrometers at room temperature in CD_2Cl_2. Chemical shifts (δ) are reported in ppm, relative to the solvent peaks ($CDHCl_2$, 5.32 ppm for ^1H; CD_2Cl_2, 53.84 ppm for ^{13}C). Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, sept = septuplet, br = broad signal, m = multiplet), coupling constants (*J*) in Hz and integration. For the assignment of the ^1H and $^{13}C\{^1H\}$ NMR spectra COSY, HSQC and HMBC experiments were also performed. Elemental analysis was carried out by the analytical services of London Metropolitan University. UV–vis spectra were recorded in a Varian CaryWin 300Bio UV-Visible spectrophotometer at concentrations of ca. 0.13 mg/mL of complexes **2–12** in CH_2Cl_2. Fluorescence spectra (λ_{max}/excitation (nm) and λ_{max}/emission (nm)) were recorded in a Cary Eclipse Fluorimeter (settings: 5 nm excitation/emission slit, 120 nm/min scan) at concentrations of ca. 3 mg/mL of complexes **2–12** in CH_2Cl_2. CCDC 949310 (**2**), 949311 (**3**), 949312 (**7**), 949313 (**8**), 949314 (**10**), 949315 (**11**) and 949316 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(phenylamino)gold Complex (2):

[Au(IPr)(OH)] (100 mg, 166 µmol) and aniline (15.5 mg, 166 µmol) were dissolved in THF (1.5 mL). The reaction mixture was stirred at room temperature for 20 h. The solvent was then concentrated under vacuum (until ca. 0.3 mL) and the product precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **2** was obtained as a white solid in 66% yield (73 mg).



^1H NMR (300 MHz; CD_2Cl_2): δ 7.57 (t, *J* = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.36 (d, *J* = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.22 (s, 2H, C$H_{imid.}$), 6.61 (dd, *J* = 8.5, 7.1 Hz, 2H,), 6.03 (tt, *J* = 7.1, 1.1 Hz, 1H), 5.95 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.44 (bs, 1H), 2.64 (sept, *J* = 6.9 Hz, 4H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 175.51 (C_{carb}), 159.43 (C^1), 146.15 ($C_{o\text{-Ar}}$), 134.42 ($C_{N\text{-Ar}}$), 131.07 ($CH_{p\text{-Ar}}$), 130.70 (CH^3), 124.65 ($CH_{m\text{-Ar}}$), 124.48 (CH^4), 123.69 ($CH_{imid.}$), 114.86 (CH^2), 29.19 ($CH_{i\text{Pr}}$), 24.56 (CH_3), 24.13 (CH_3).

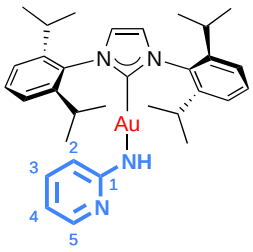
Anal. Calcd. for $C_{33}H_{42}AuN_3$ (677.67): C, 58.49; H, 6.25; N, 6.20. Found: C, 58.41; H, 6.22; N, 6.28.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-2-ylamino)gold complex (3):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 2-aminopyridine (4.9 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **3** was obtained as a white solid in 94% yield (32 mg).

^1H NMR (400 MHz; CD_2Cl_2): δ 7.50 (t, *J* = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$ + m, 1H, CH^5), 7.36 (d, *J* = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.24 (s, 2H, C$H_{imid.}$), 6.75 (t, *J* = 8.4 Hz, 1H, CH^3), 5.94 (m, 1H, CH^4), 5.59 (d, *J* = 8.5 Hz, 1H,

CH^2), 4.20 (s, 1H, N*H*), 2.62 (sept, *J* = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.34 (d, *J* = 6.9 Hz, 12H, CH_3), 1.24 (d, *J* = 6.9 Hz, 12H, CH_3).

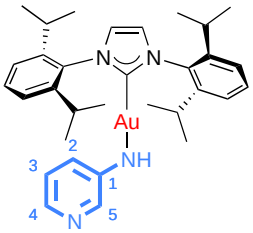


^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 179.61 (C_{carb}), 168.96 (C^1), 147.92 (CH^5), 146.41 ($C_{o\text{-Ar}}$), 135.63 (CH^3), 134.81 ($C_{\text{N-Ar}}$), 130.76 ($CH_{p\text{-Ar}}$), 124.50 ($CH_{m\text{-Ar}}$), 123.49 ($CH_{\text{imid.}}$), 109.94 (CH^2), 107.58 (CH^4), 29.19 ($CH_{i\text{Pr}}$), 24.41 (CH_3), 24.19 (CH_3).

Anal. Calcd. for $C_{32}H_{41}AuN_4$ (678.66): C, 56.63; H, 6.09; N, 8.26. Found: C, 56.55; H, 5i.98; N, 8.11.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-3-ylamino)gold Complex (4):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 3-aminopyridine (4.9 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **4** was obtained as a white solid in 85% yield (29 mg).



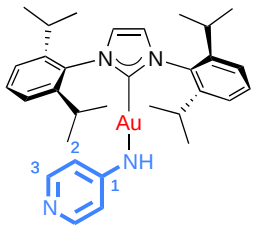
^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.57 (t, *J* = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.40 (d, *J* = 2.9 Hz, 1H, CH^5), 7.36 (d, *J* = 7.9 Hz, 4H, C$H_{m\text{-Ar}}$), 7.26 (dd, *J* = 4.5, 1.1 Hz, 1H, CH^4), 7.23 (s, 2H, C$H_{\text{imid.}}$), 6.51 (dd, *J* = 8.4, 4.5 Hz, 1H, CH^3), 6.12 (dd, *J* = 8.3, 1.6 Hz, 1H, CH^2), 3.41 (s, 1H, N*H*), 2.63 (sept, *J* = 6.8 Hz, 4H, C$H_{i\text{Pr}}$), 1.34 (d, *J* = 6.9 Hz, 12H, CH_3), 1.24 (d, *J* = 6.9 Hz, 12H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 179.85 (C_{carb}), 155.41 (C^1), 146.38 ($C_{o\text{-Ar}}$), 137.95 (CH^3), 134.81 ($C_{\text{N-Ar}}$), 132.73 (CH^4), 130.79 ($CH_{p\text{-Ar}}$), 124.50 ($CH_{m\text{-Ar}}$), 123.47 ($CH_{\text{imid.}}$), 123.21 (CH^3), 119.67 (CH^2), 29.20 ($CH_{i\text{Pr}}$), 24.42 (CH_3) 24.18 (CH_3).

Anal. Calcd. for $C_{32}H_{41}AuN_4$ (678.66): C, 56.63; H, 6.09; N, 8.26. Found: C, 56.76; H, 5.98; N, 8.16.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(pyridin-4-ylamino)gold complex (5):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 4-aminopyridine (4.9 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **9a** was obtained as a white solid in 88% yield (30 mg).



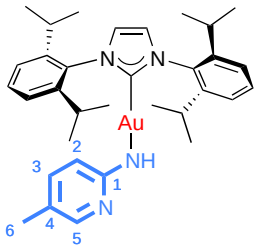
^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.58 (t, *J* = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.51 (bs, 1H, CH^3), 7.37 (d, *J* = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.26 (s, 2H, C$H_{\text{imid.}}$), 5.76 (bs, 2H, CH^2), 3.89 (bs, 1H, N*H*), 2.61 (sept, *J* = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.34 (d, *J* = 6.9 Hz, 12H, CH_3), 1.24 (d, *J* = 6.9 Hz, 12H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 179.23 (C_{carb}), 164.15 (C^1), 148.84 (CH^3), 146.41 ($C_{o\text{-Ar}}$), 134.73 ($C_{\text{N-Ar}}$), 130.85 ($CH_{p\text{-Ar}}$), 124.54 ($CH_{m\text{-Ar}}$), 123.60 ($CH_{\text{imid.}}$), 110.74 (CH^2), 29.21 ($CH_{i\text{Pr}}$), 24.43 (CH_3), 24.18 (CH_3).

Anal. Calcd. for $C_{32}H_{41}AuN_4$ (678.66): C, 56.63; H, 6.09; N, 8.26. Found: C, 56.83; H, 5.93; N, 8.34.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-methylpyridin-2-yl)amino)gold Complex (6):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 2-amino-5-methylpyridine (5.6 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **6** was obtained as a white solid in 81% yield (28 mg).



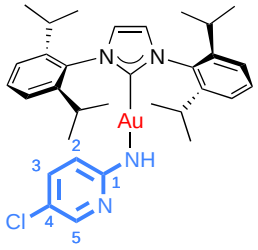
^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.57 (t, J = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.36 (d, J = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$ + 1H, CH^4), 7.24 (s, 2H, C$H_{\text{imid.}}$), 6.61 (dd, J = 8.4, 2.2 Hz, 1H, CH^3), 5.53 (d, J = 8.4 Hz, 1H, CH^2), 4.06 (bs, 1H, NH), 2.63 (sept, J = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.95 (s, 3H, C$H_3{}^6$), 1.34 (d, J = 6.9 Hz, 12H, CH_3), 1.24 (d, J = 6.9 Hz, 12H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 179.96 (C_{carb}), 167.18 (C^1), 147.22 (CH^5), 146.44 ($CH_{o\text{-Ar}}$), 136.95 (CH^3), 134.88 ($CH_{\text{N-Ar}}$), 130.74 ($CH_{p\text{-Ar}}$), 124.51 ($CH_{m\text{-Ar}}$), 123.44 ($CH_{\text{imid.}}$), 115.79 (C^4), 109.58 (CH^2), 29.21 ($CH_{i\text{Pr}}$), 24.40 (CH_3), 24.20 (CH_3), 17.33 ($CH_3{}^6$).

Anal. Calcd. for $C_{33}H_{43}AuN_4$ (692.69): C, 57.22; H, 6.26; N, 8.09. Found: C, 57.08; H, 6.13; N, 8.00.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-chloropyridin-2-yl)amino)gold complex (7):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 2-amino-5-chloropyridine (6.7 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **7** was obtained as a white solid in 87% yield (31 mg).



^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.57 (t, J = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.45 (d, J = 2.7, Hz, 1H, CH^5), 7.36 (d, J = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.24 (s, 2H, C$H_{\text{imid.}}$), 6.68 (dd, J = 9.0, 2.7 Hz, 1H, CH^3), 5.47 (d, J = 8.9 Hz, 1H, CH^2), 4.25 (s, 1H, NH), 2.61 (sept, J = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.33 (d, J = 6.9 Hz, 12H, CH_3), 1.23 (d, J = 6.9 Hz, 12H, CH_3).

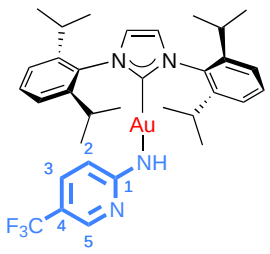
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 179.06 (C_{carb}), 167.49 (C^1), 146.43 ($CH_{o\text{-Ar}}$), 145.75 (CH^5), 135.34 (CH^3), 134.76 ($CH_{\text{N-Ar}}$), 130.80 ($CH_{p\text{-Ar}}$), 124.53 ($CH_{m\text{-Ar}}$), 123.54 ($CH_{\text{imid.}}$), 113.61 (C^4), 110.96 (CH^2), 29.20 ($CH_{i\text{Pr}}$), 24.41 (CH_3), 24.19 (CH_3).

Anal. Calcd. for $C_{32}H_{40}AuClN_4$ (713.11): C, 53.90; H, 5.65; N, 7.86. Found: C, 53.84; H, 5.53; N, 7.91.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-(trifluoromethyl)pyridin-2-yl)amino)gold complex (8):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 2-amino-5-(trifluoromethyl)pyridine (7.3 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **8** was obtained as a white solid in 72% yield (27 mg).

^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.80 (s, 1H, CH^5), 7.58 (t, J = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.37 (d, J = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.27 (s, 2H, C$H_{\text{imid.}}$), 6.90 (d, J = 8.7 Hz, 1H, CH^3), 5.52 (d, J = 8.9 Hz, 1H, CH^2), 4.67 (s, 1H, NH), 2.61 (sept, J = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.34 (d, J = 6.9 Hz, 12H, CH_3), 1.24 (d, J = 6.9 Hz, 12H, CH_3).



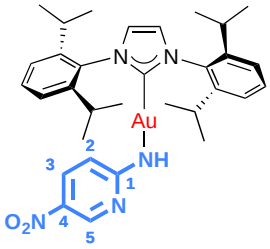
$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 178.57 (C_{carb}), 170.62 (C^1), 146.44 ($C_{o\text{-}Ar}$), 146.30 (q, $J_{C\text{-}F}$ = 3.9 Hz, CH^5), 146.15, 134.70 ($C_{N\text{-}Ar}$), 132.28 (q, $J_{C\text{-}F}$ = 2.7 Hz , CH^3), 130.88 ($CH_{p\text{-}Ar}$), 126.49 (q, $J_{C\text{-}F}$ = 258.6 Hz, CF_3), 124.57 ($CH_{m\text{-}Ar}$), 123.66 ($CH_{imid.}$), 109.5 (q, $J_{C\text{-}F}$ = 32.6 Hz, C^4), 109.20 (CH^2), 29.23 (CH_{iPr}), 24.44 (CH_3), 24.20 (CH_3).

$^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2): δ -60.85.

Anal. Calcd. for $C_{33}H_{40}AuF_3N_4$ (746.66): C, 53.08; H, 5.40; N, 7.50. Found: C, 53.02; H, 5.27; N, 7.61.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-nitropyridin-2-yl)amino)gold complex (9):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 2-amino-5-nitropyridine (7.3 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **9** was obtained as a yellow solid in 83% yield (30 mg).



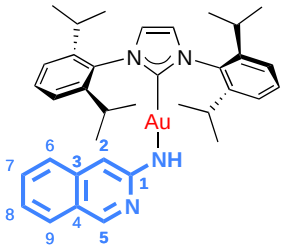
^1H NMR (400 MHz; CD_2Cl_2): δ 8.59 (d, J = 2.7 Hz, 1H, CH^5), 7.60 (t, J = 7.8 Hz, 2H, $CH_{p\text{-}Ar}$), 7.51 (dd, J = 9.5, 2.8 Hz, 1H, CH^3), 7.38 (d, J = 7.8 Hz, 4H, $CH_{m\text{-}Ar}$), 7.29 (s, 2H, $CH_{imid.}$), 5.39 (bs, 1H, NH + d, J = 9.5 Hz, 1 H, CH^2), 2.59 (sept, J = 6.9 Hz, 4H, CH_{iPr}), 1.32 (d, J = 6.9 Hz, 12H, CH_3), 1.25 (d, J = 6.9 Hz, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 177.05 (C_{carb}), 171.23 (C^1), 148.89 (CH^5), 146.41 ($C_{o\text{-}Ar}$), 134.48 ($C_{N\text{-}Ar}$), 132.07 (C^4), 131.30 (CH^3), 131.03 ($CH_{p\text{-}Ar}$), 124.64 ($CH_{m\text{-}Ar}$), 123.87 ($CH_{imid.}$), 109.32 (CH^2), 29.23 (CH_{iPr}), 24.48 (CH_3), 24.18 (CH_3).

Anal. Calcd. for $C_{32}H_{40}AuN_5O_2$ (723.66): C, 53.11; H, 5.57; N, 9.68. Found: C, 53.24; H, 5.50; N, 9.56.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(isoquinolin-3-ylamino)gold complex (10):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 3-aminoisoquinoline (7.5 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **10** was obtained as a yellow solid in 82% yield (30 mg).



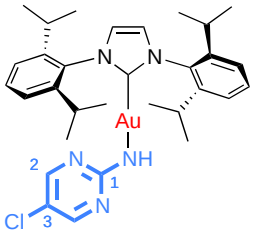
^1H NMR (400 MHz; CD_2Cl_2): δ 8.34 (s, 1H, CH^5), 7.62 (t, J = 7.8 Hz, 2H, $CH_{p\text{-}Ar}$), 7.41-7.37 (d, J = 7.8 Hz, 4H, $CH_{m\text{-}Ar}$ + m, 1H, $CH_{isoquinoline}$), 7.25 (s, 2H, $CH_{imid.}$), 7.17 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H, $CH_{isoquinoline}$), 6.95 (d, J = 8.5 Hz, 1H, $CH_{isoquinoline}$), 6.75 (ddd, J = 8.01, 6.71, 1.12 Hz, 1H, $CH_{isoquinoline}$), 5.80 (m, 1H, CH^2), 4.32 (s, 1H, NH), 2.66 (7, J = 6.9 Hz, 4H, CH_{iPr}), 1.37 (d, J = 6.9 Hz, 12H, CH_3), 1.25 (d, J = 6.9 Hz, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 179.76 (C_{carb}), 166.09 (C^1), 151.24 (CH^5), 146.45 ($C_{o\text{-}Ar}$), 140.01 (C^3), 134.90 ($C_{N\text{-}Ar}$), 130.88 ($CH_{p\text{-}Ar}$), 129.21 ($CH_{isoquinoline}$), 128.07 ($CH_{isoquinoline}$), 124.56 ($CH_{m\text{-}Ar}$), 123.75 ($CH_{isoquinoline}$), 123.52 ($CH_{imid.}$), 121.37 (C^4), 118.73 ($CH_{isoquinoline}$), 96.48 (CH^2), 29.24 (CH_{iPr}), 24.49 (CH_3), 24.18 (CH_3).

Anal. Calcd. for $C_{36}H_{43}AuN_4$ (728.72): C, 59.33; H, 5.95; N, 7.69. Found: C, 59.44; H, 6.02; N, 7.62.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)((5-chloropyrimidin-2-yl)amino)gold complex (11):

[Au(IPr)(OH)] (30 mg, 50 µmol) and 5-chloropyrimidin-2-amine (6.7 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **11** was obtained as a white solid in 87% yield (30 mg).



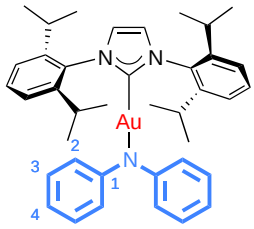
^{1}H NMR (300 MHz; CD_2Cl_2): δ 7.69-7.63 (m, 2H, CH^2), 7.54 (t, J = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.34 (d, J = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.22 (s, 2H, C$H_{\text{imid.}}$), 4.54 (s, 1H), 2.68-2.54 (sept, J = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.36 (d, J = 6.9 Hz, 12H, CH_3), 1.23 (d, J = 6.9 Hz, 12H, CH_3).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 178.55 (C_{carb}), 170.03 (C^1), 155.60 (CH^2), 146.33 ($C_{o\text{-Ar}}$), 134.85 ($C_{N\text{-Ar}}$), 130.73 ($CH_{p\text{-Ar}}$), 124.46 ($CH_{m\text{-Ar}}$), 123.57 ($CH_{\text{imid.}}$), 113.68 (C^3), 29.23 ($CH_{i\text{Pr}}$), 24.33 (CH_3), 24.20 (CH_3).

Anal. Calcd. for $C_{31}H_{39}AuClN_5$ (714.09): C, 52.14; H, 5.50; N, 9.81. Found: C, 52.26; H, 5.61; N, 9.73.

Synthesis of (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)(diphenylamino)gold complex (12):

[Au(IPr)(OH)] (30 mg, 50 µmol) and diphenylamine (8.8 mg, 52 µmol) were dissolved in THF (0.5 mL). The reaction mixture was stirred at room temperature for 20 h. The product was then precipitated by addition of pentane (3 mL), filtered, washed with more pentane (4 × 4 mL) and dried under high vacuum. Complex **12** was obtained as a yellow solid in 74% yield (28 mg).



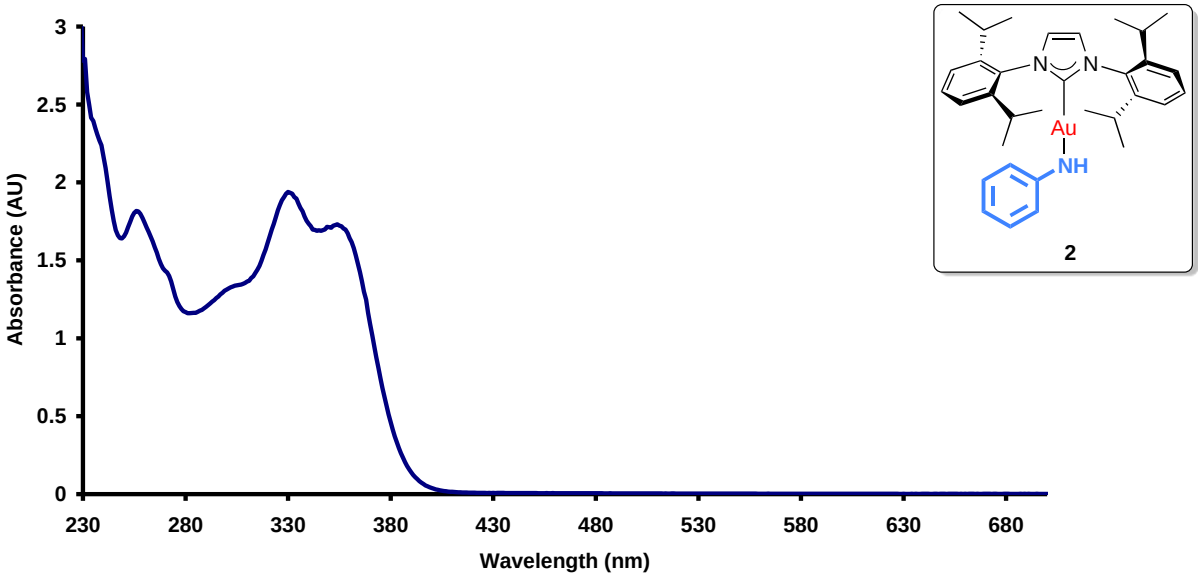
^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.60 (t, J = 7.8 Hz, 2H, C$H_{p\text{-Ar}}$), 7.37 (d, J = 7.8 Hz, 4H, C$H_{m\text{-Ar}}$), 7.27 (s, 2H, C$H_{\text{imid.}}$), 6.79-6.74 (m, 4H, CH^3), 6.65-6.62 (m, 4H, CH^2), 6.40 (tt, J = 7.1, 1.1 Hz, 2H, CH^4), 2.62 (sept, J = 6.9 Hz, 4H, C$H_{i\text{Pr}}$), 1.26 (d, J = 6.9 Hz, 12H, CH_3), 1.23 (d, J = 6.9 Hz, 12H, CH_3).

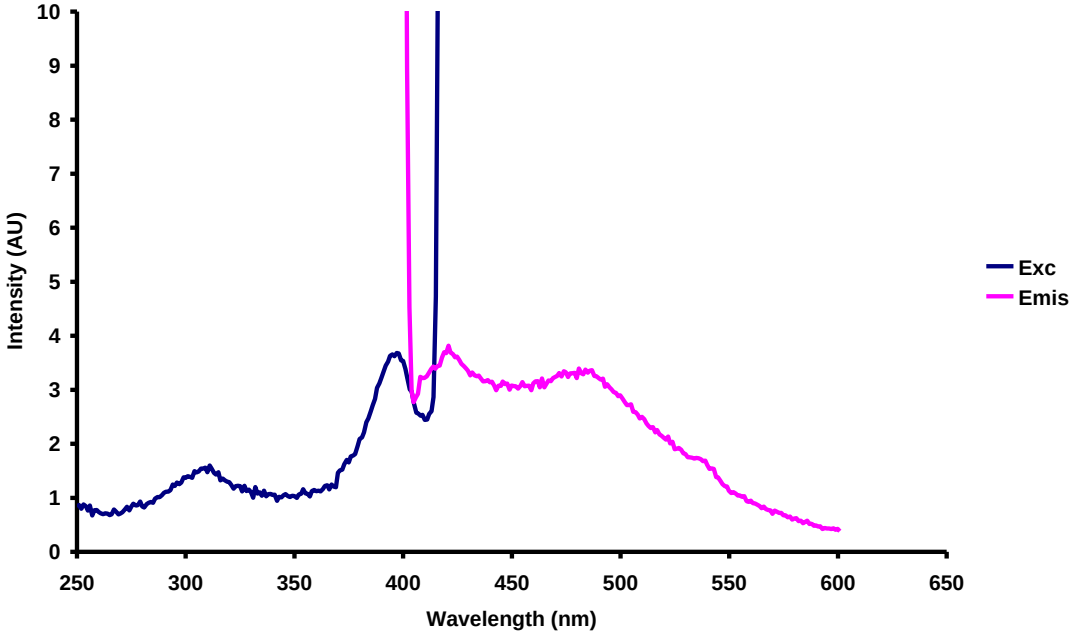
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 178.32 (C_{carb}), 154.68 (C^1), 146.41 ($C_{o\text{-Ar}}$), 134.94 ($C_{\text{N-Ar}}$), 130.72 ($CH_{p\text{-Ar}}$), 128.45 (CH^3), 124.46 ($CH_{m\text{-Ar}}$), 123.34 ($CH_{\text{imid.}}$), 119.72 (CH^2), 116.59 (CH^4), 29.22 ($CH_{i\text{Pr}}$), 24.35 (CH_3), 24.22 (CH_3).

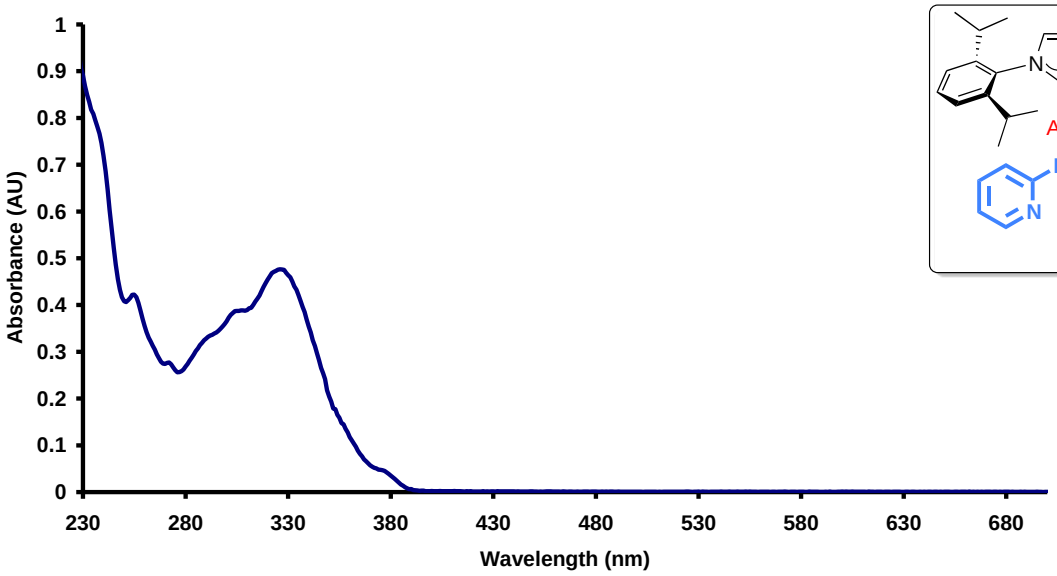
Anal. Calcd. for $C_{39}H_{46}AuN_3$ (753.77): C, 62.14; H, 6.15; N, 5.57. Found: C, 62.22; H, 6.29; N, 5.68.

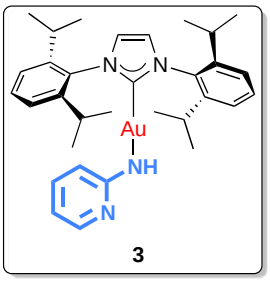
UV–vis and fluorescence spectra:

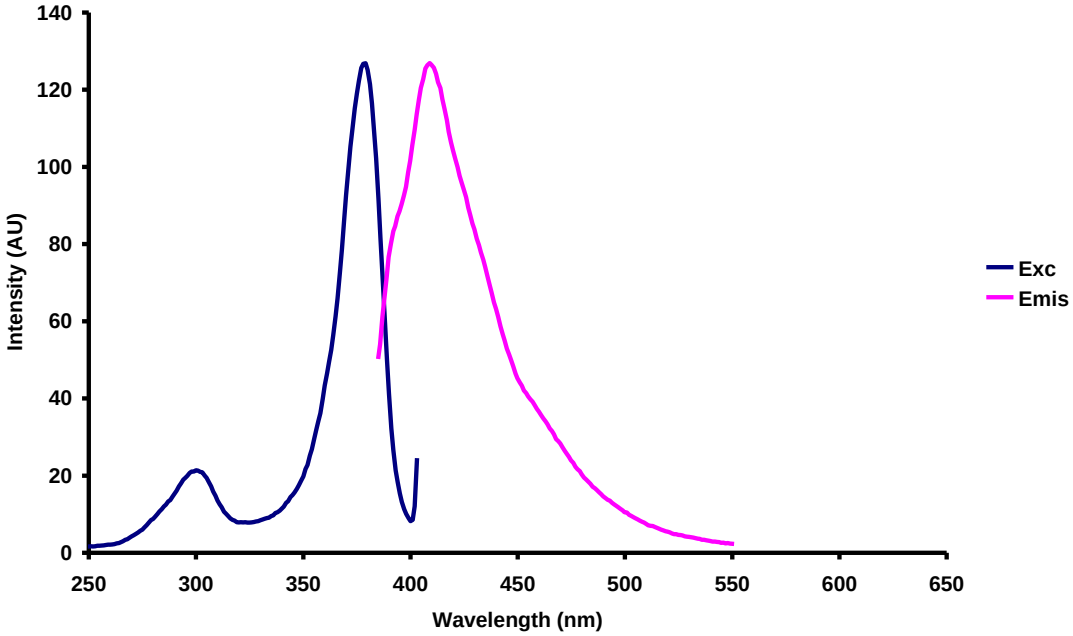
- Equipment Used:
  - **UV**: Varian CaryWin 300Bio UV–Vis spectrophotometer
  - **Fluorescence**: Cary Eclipse Fluorimeter (settings: 5 nm excitation/emission slit, 120 nm/min scan).

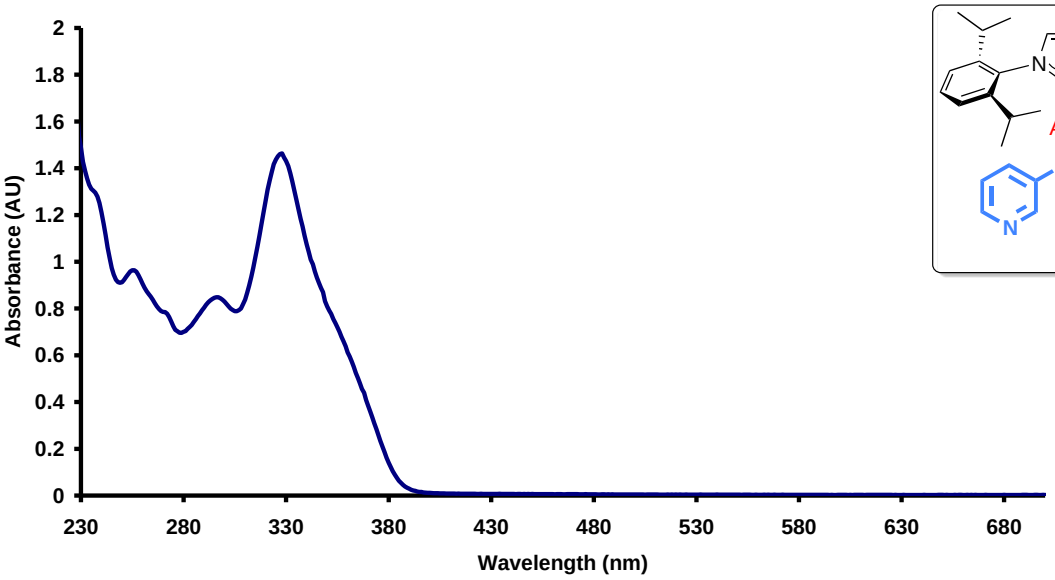


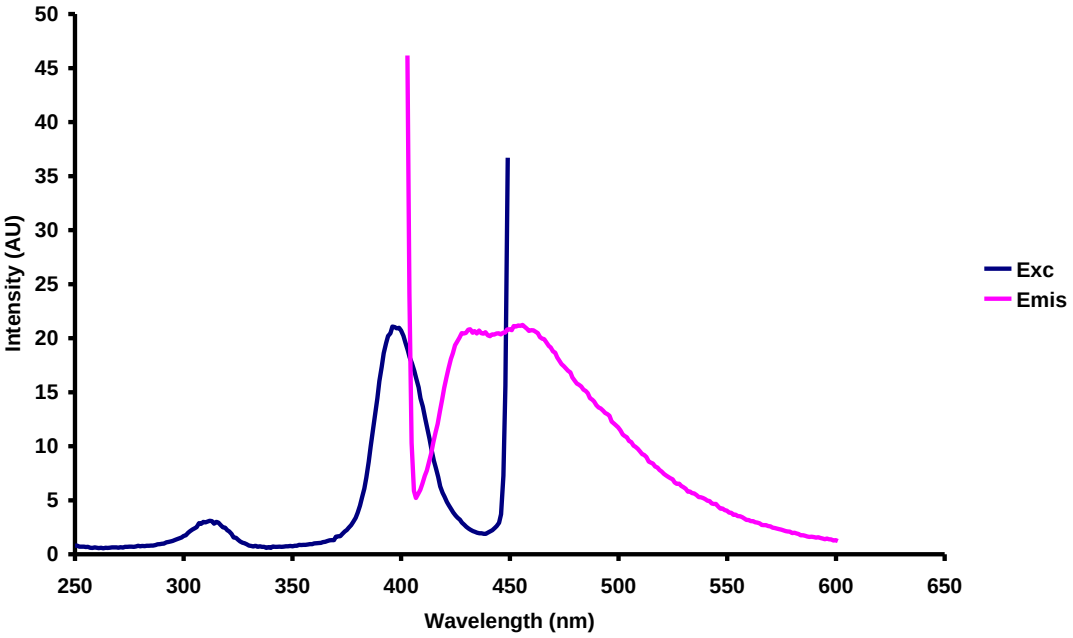


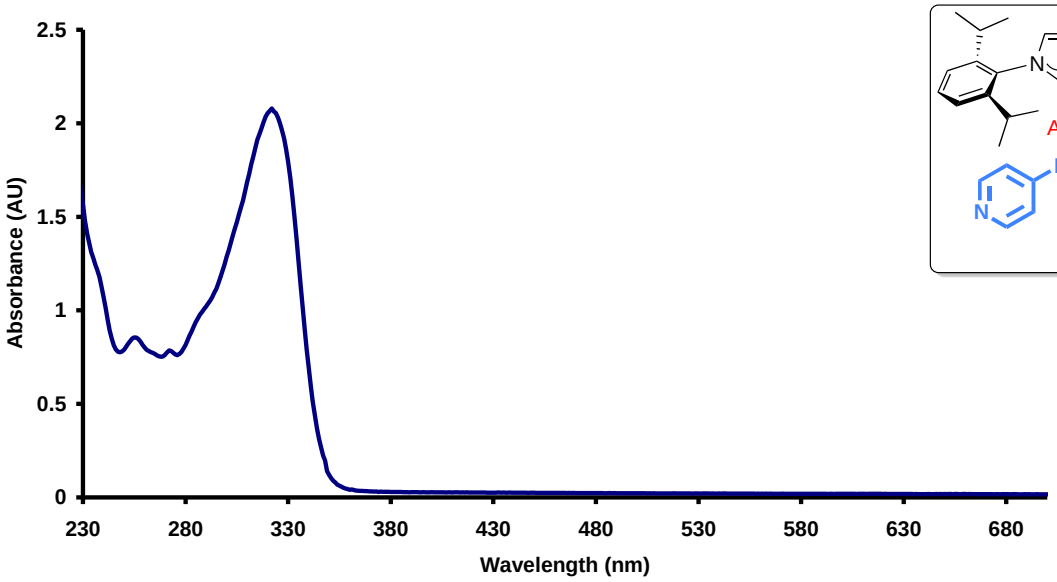

Absorbance (AU)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
230
280
330
380
430
480
530
580
630
680
Wavelength (nm)

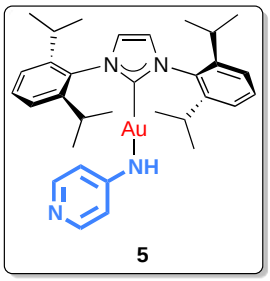

N
N
Au
NH
N
3

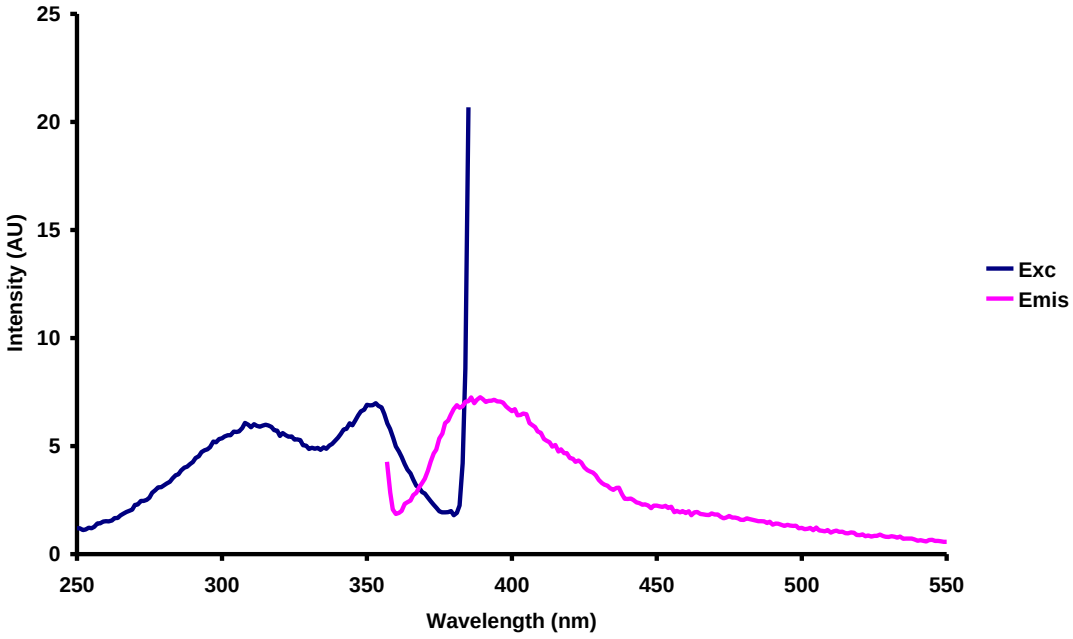

Intensity (AU)
140
120
100
80
60
40
20
0
250
300
350
400
450
500
550
600
650
Wavelength (nm)
Exc
Emis

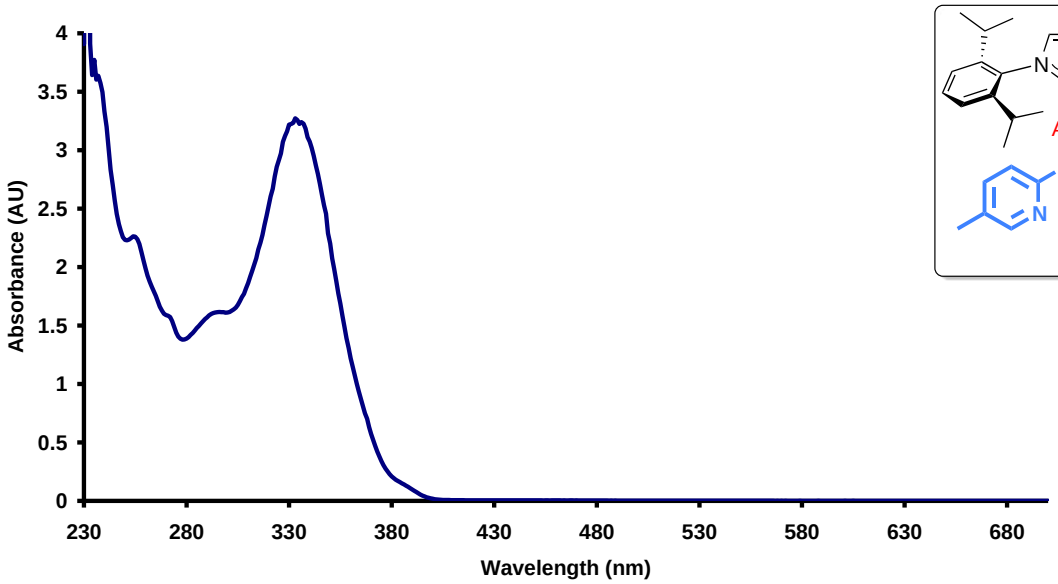

Absorbance (AU)
Wavelength (nm)
Au
NH
N
4


Intensity (AU)
Wavelength (nm)
Exc
Emis


Absorbance (AU)
2.5
2
1.5
1
0.5
0
230
280
330
380
430
480
530
580
630
680
Wavelength (nm)


N
N
Au
NH
N
5


Intensity (AU)
25
20
15
10
5
0
250
300
350
400
450
500
550
Wavelength (nm)
Exc
Emis


Absorbance (AU)
Wavelength (nm)
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0.5
1
1.5
2
2.5
3
3.5
4
230
280
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380
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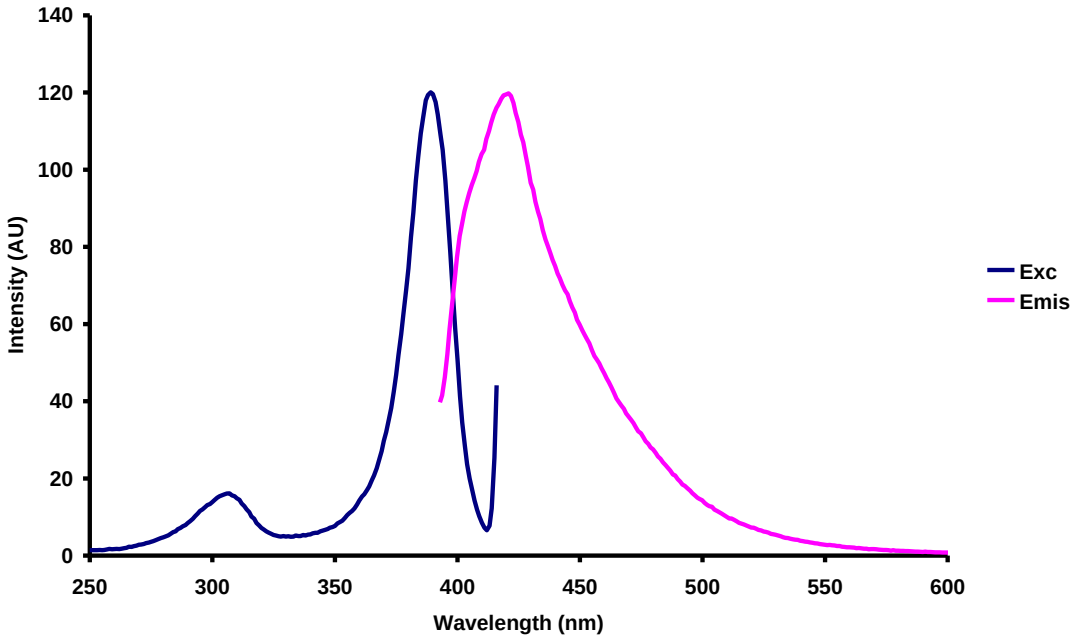
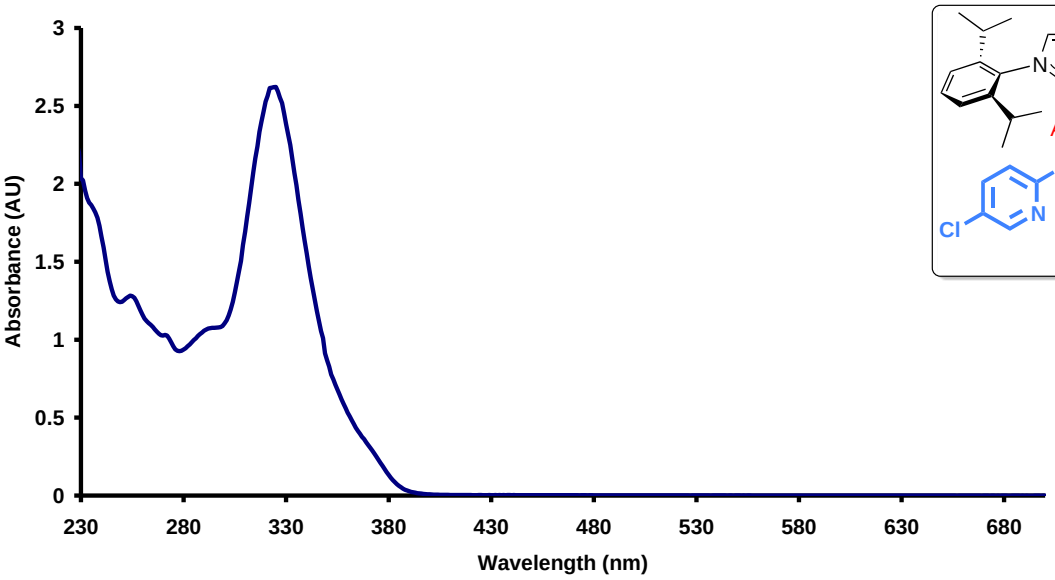
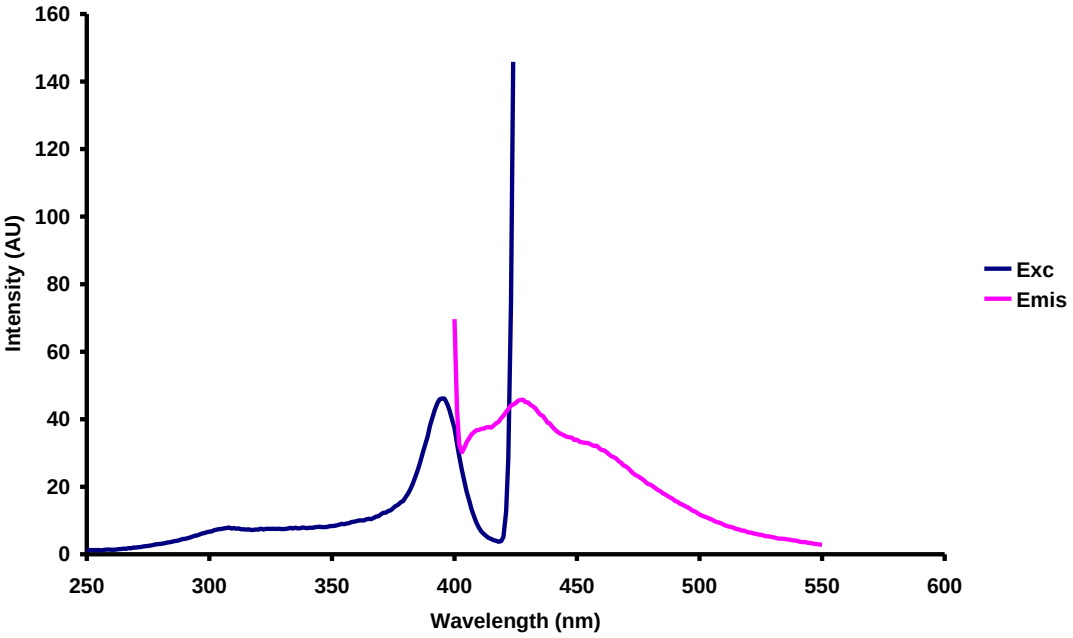
480
530
580
630
680
N
N
Au
NH
N
6


Intensity (AU)
Wavelength (nm)
0
20
40
60
80
100
120
140
250
300
350
400
450
500
550
600
Exc
Emis


Absorbance (AU)
Wavelength (nm)
3
2.5
2
1.5
1
0.5
0
230
280
330
380
430
480
530
580
630
680
N
N
Au
NH
N
Cl
7


Intensity (AU)
Wavelength (nm)
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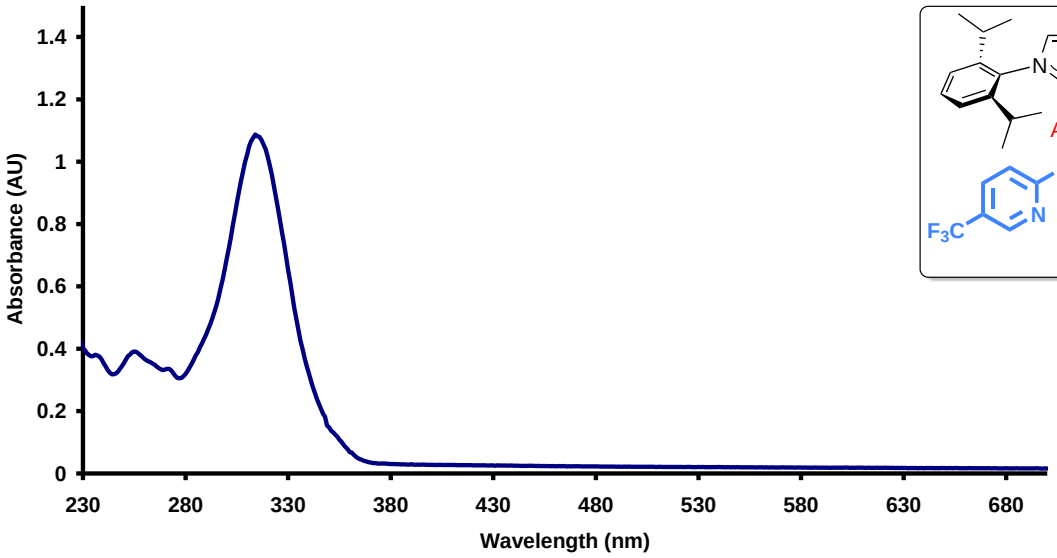
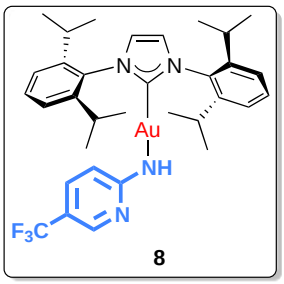
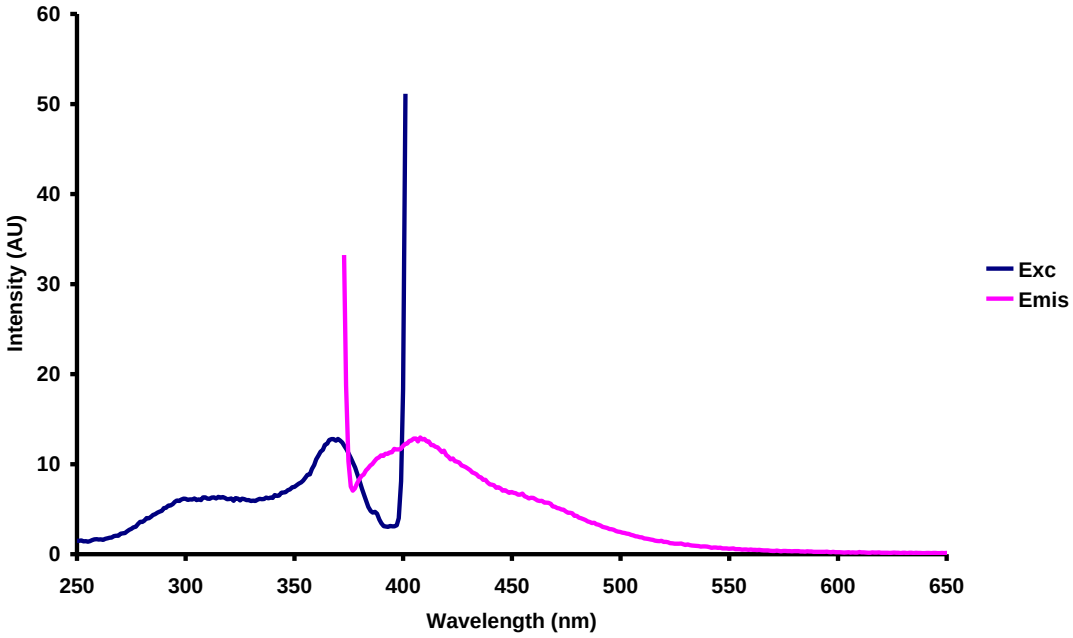
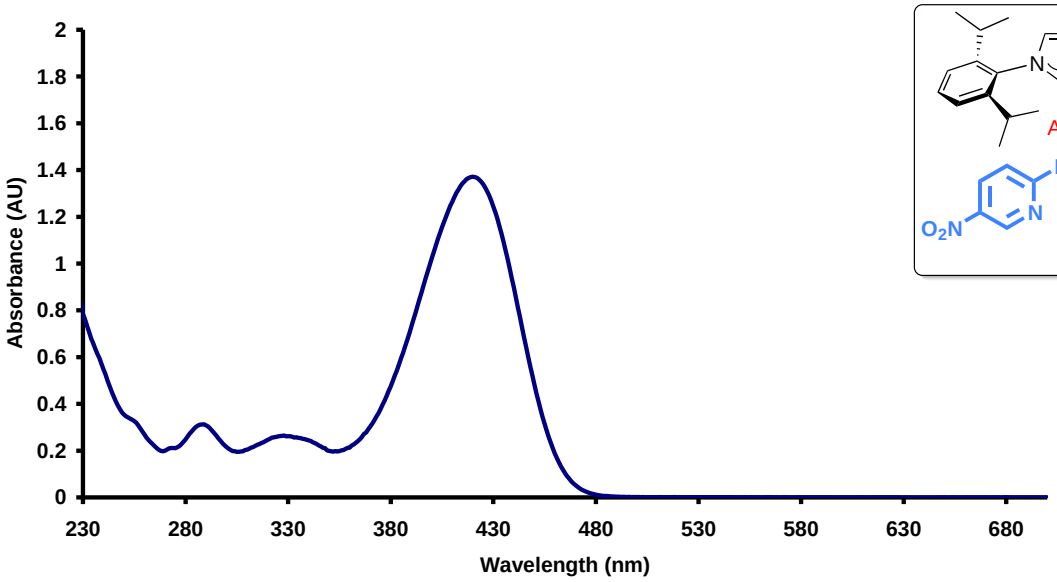
140
120
100
80
60
40
20
0
250
300
350
400
450
500
550
600
Exc
Emis


Absorbance (AU)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
230
280
330
380
430
480
530
580
630
680
Wavelength (nm)


N
N
Au
NH
N
F3C
8


Intensity (AU)
60
50
40
30
20
10
0
250
300
350
400
450
500
550
600
650
Wavelength (nm)
Exc
Emis


Absorbance (AU)
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
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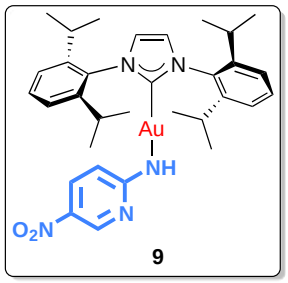
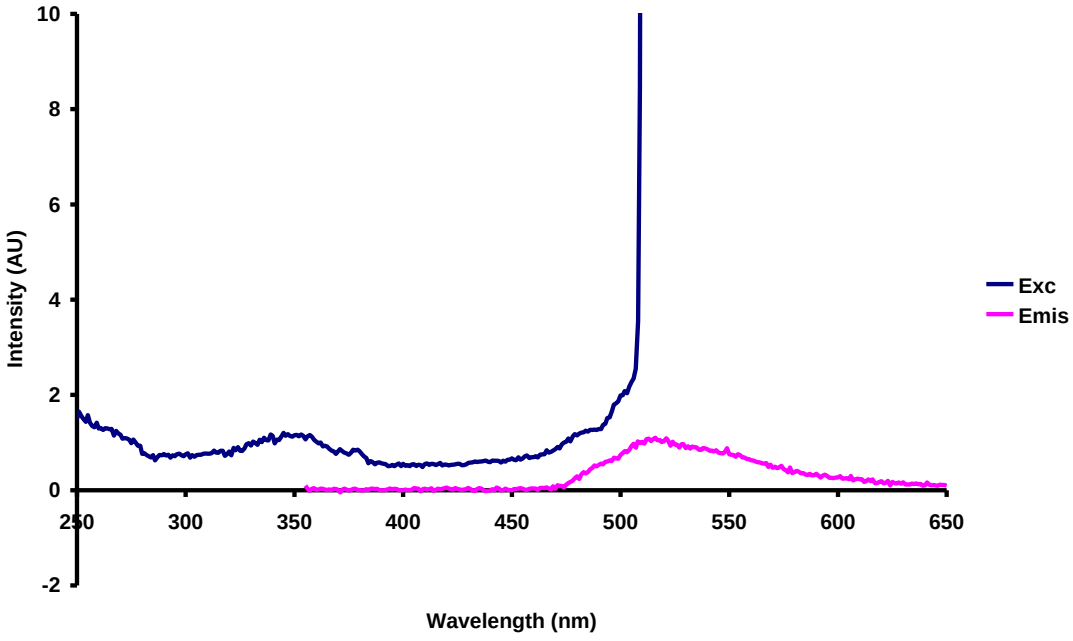
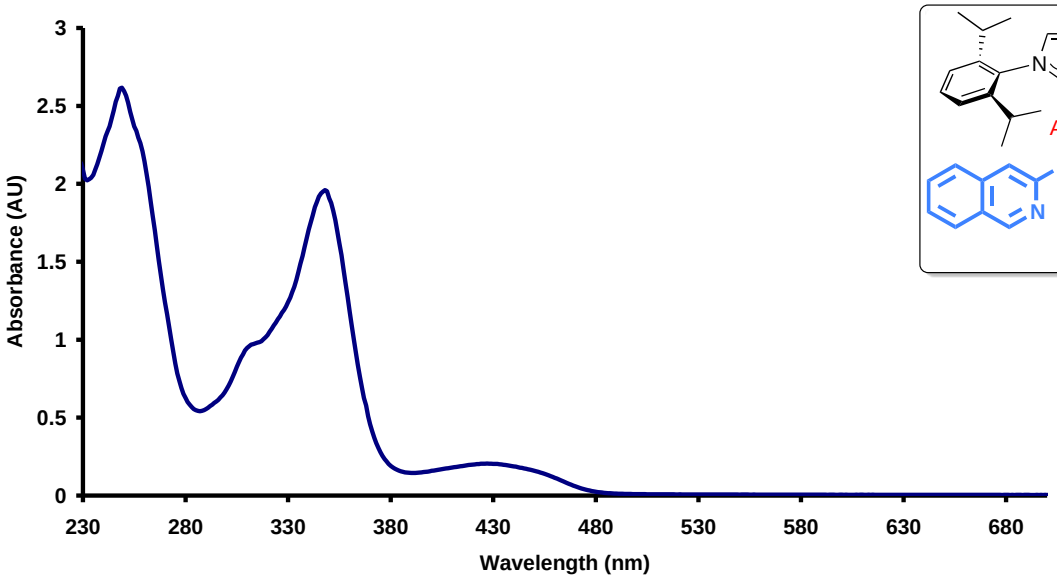
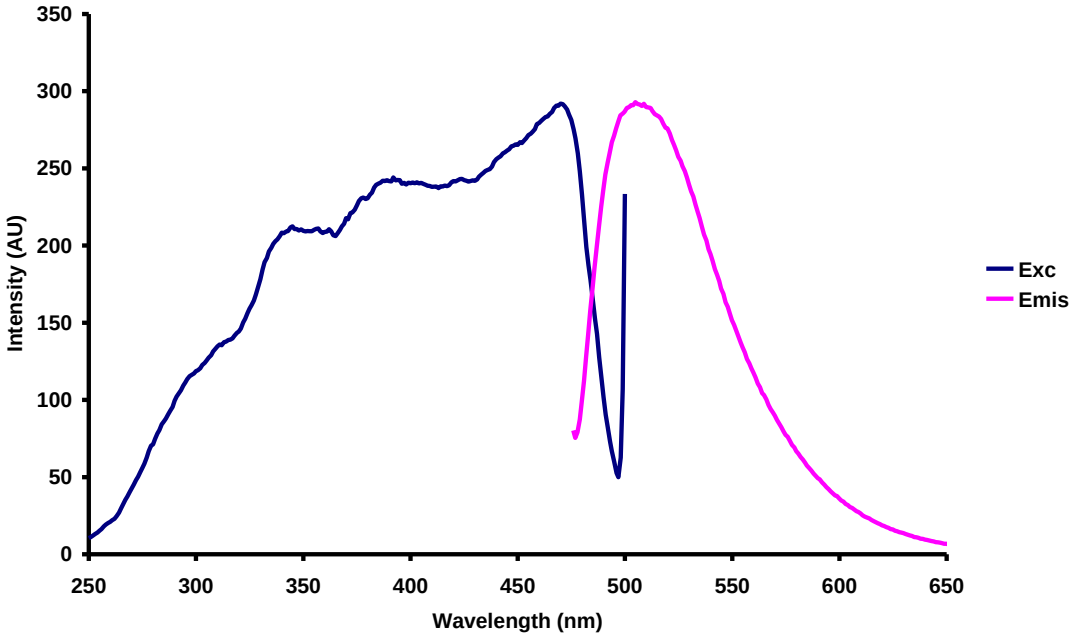
0
230
280
330
380
430
480
530
580
630
680

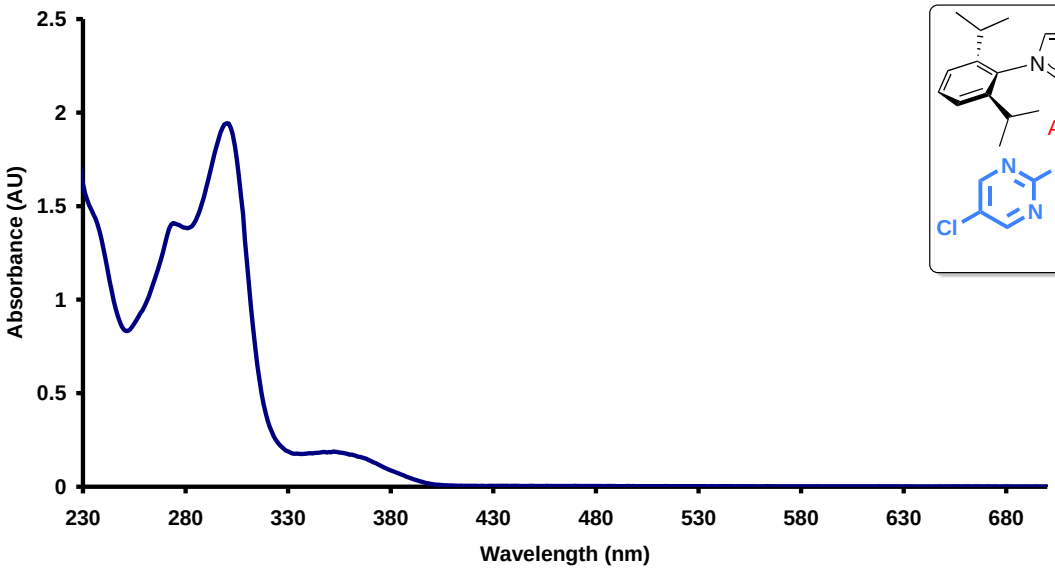

N
N
Au
NH
N
O2N

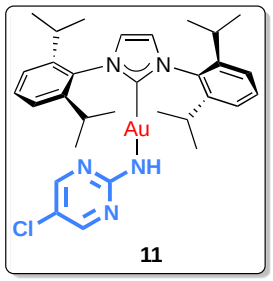
9

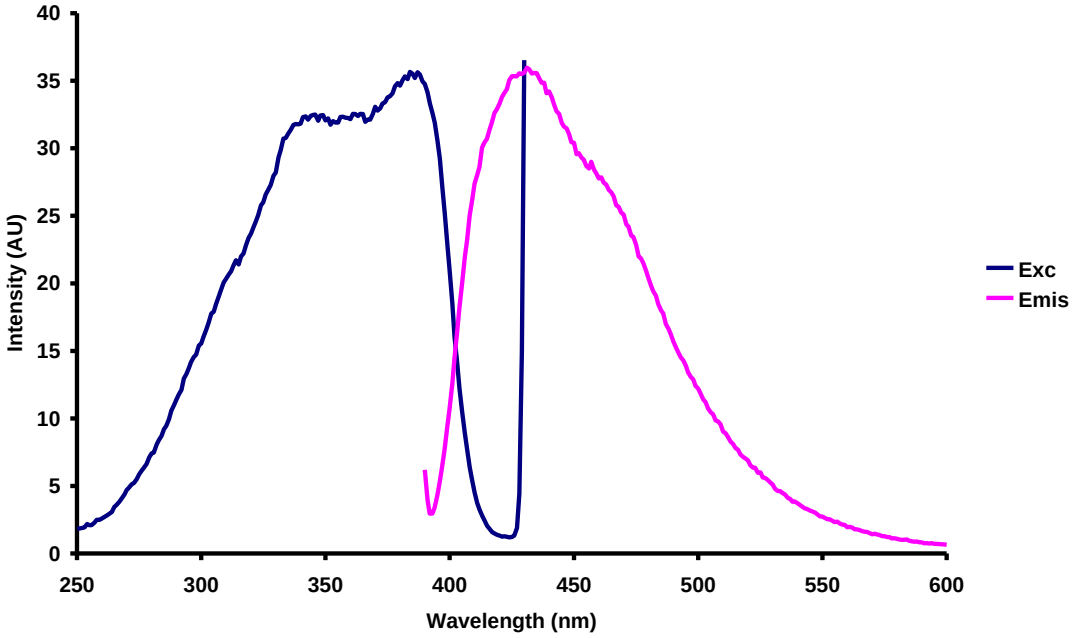

Intensity (AU)
Wavelength (nm)
Exc
Emis
10
8
6
4
2
0
-2
250
300
350
400
450
500
550
600
650

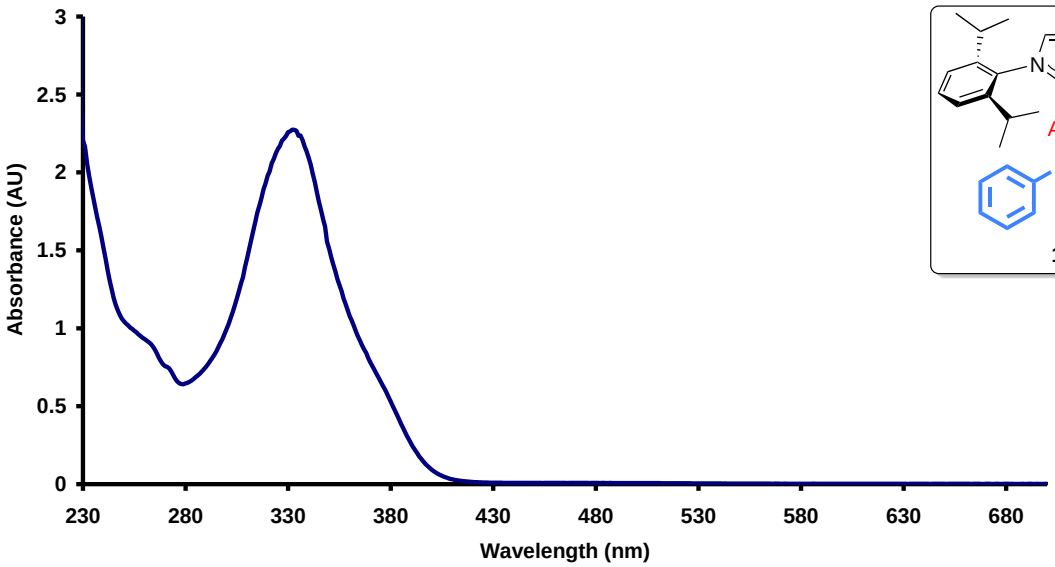

Absorbance (AU)
Wavelength (nm)
3
2.5
2
1.5
1
0.5
0
230
280
330
380
430
480
530
580
630
680
N
N
Au
NH
N
10

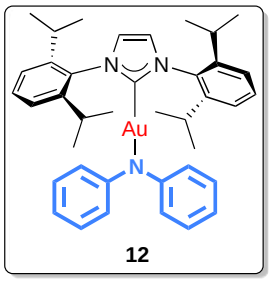

Intensity (AU)
Wavelength (nm)
350
300
250
200
150
100
50
0
250
300
350
400
450
500
550
600
650
Exc
Emis

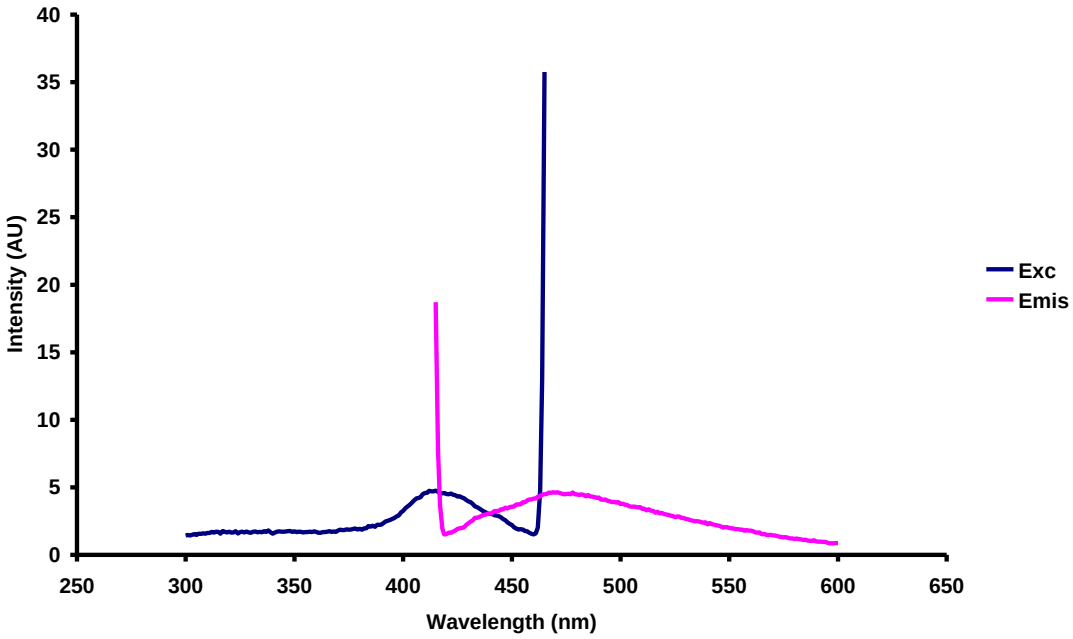

Absorbance (AU)
2.5
2
1.5
1
0.5
0
230
280
330
380
430
480
530
580
630
680
Wavelength (nm)


N
N
Au
N
NH
N
Cl
11

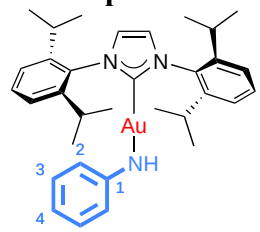

Intensity (AU)
40
35
30
25
20
15
10
5
0
250
300
350
400
450
500
550
600
Wavelength (nm)
Exc
Emis

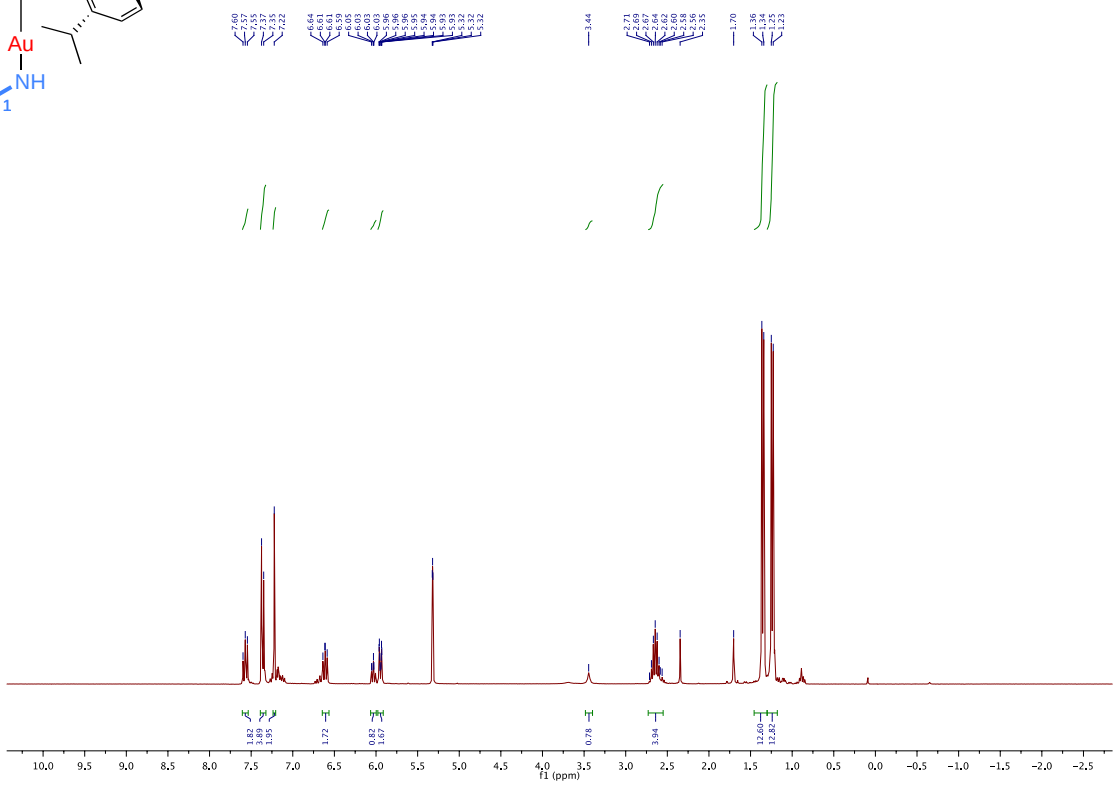

Absorbance (AU)
Wavelength (nm)
0
0.5
1
1.5
2
2.5
3
230
280
330
380
430
480
530
580
630
680

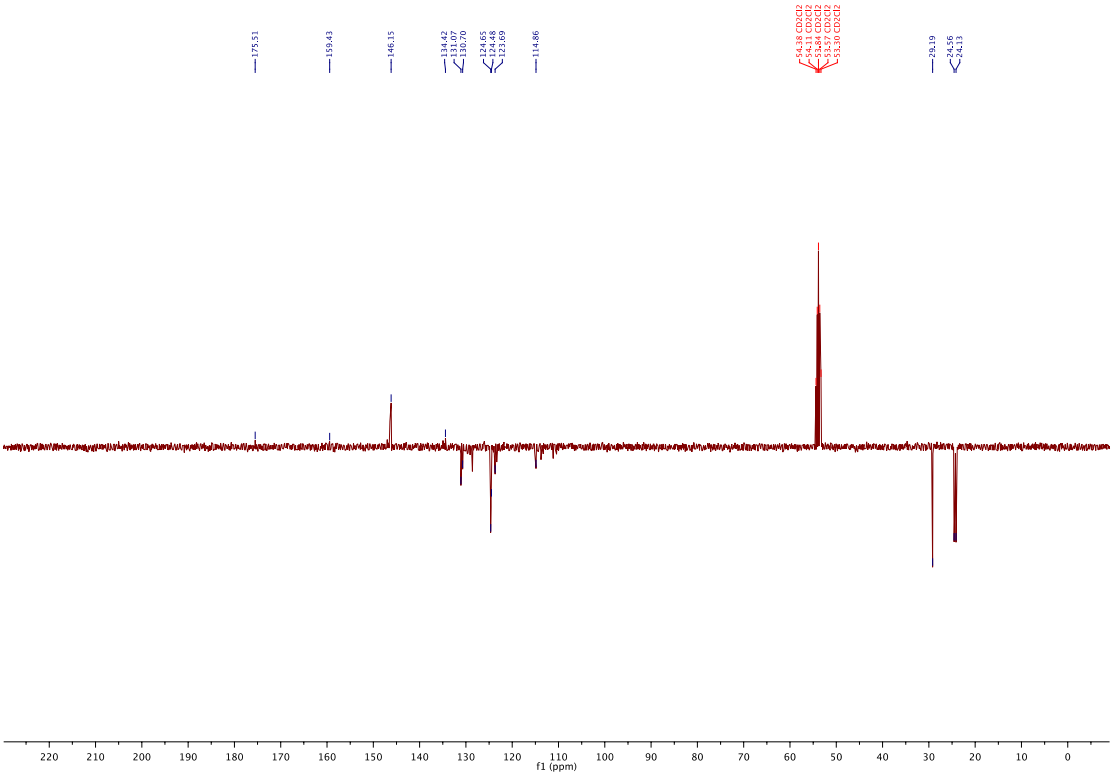

N
N
Au
N
12

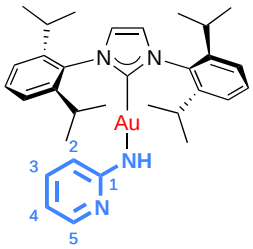

Intensity (AU)
Wavelength (nm)
Exc
Emis
0
5
10
15
20
25
30
35
40
250
300
350
400
450
500
550
600
650

NMR Spectra

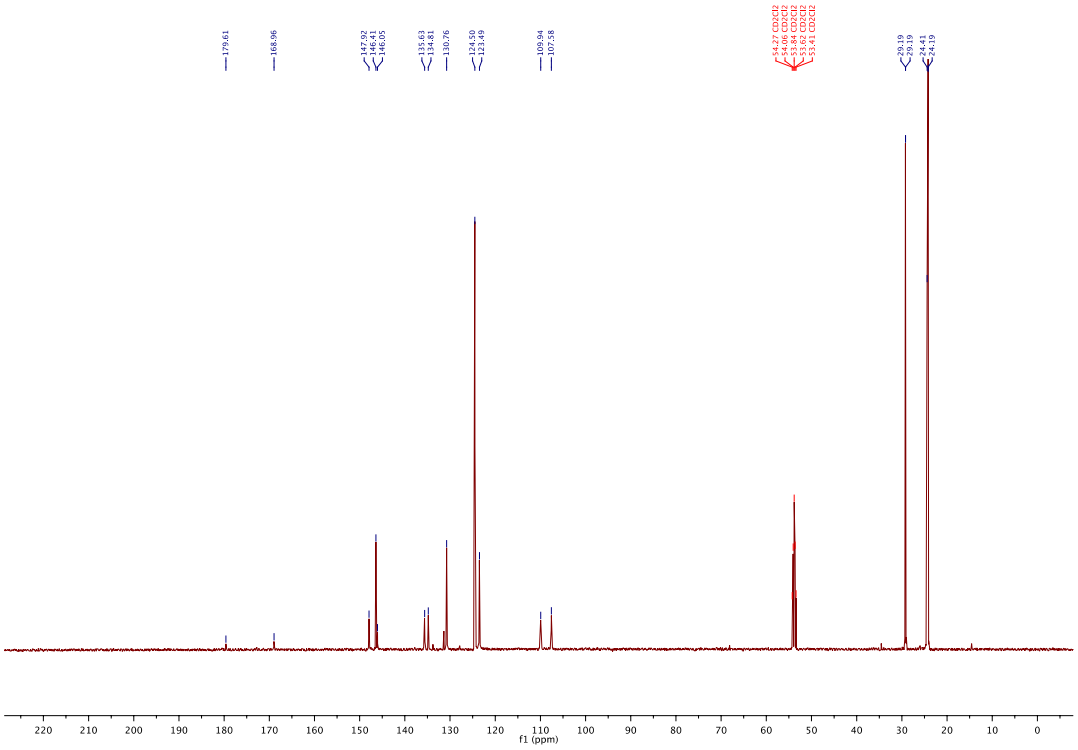


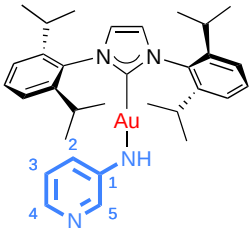




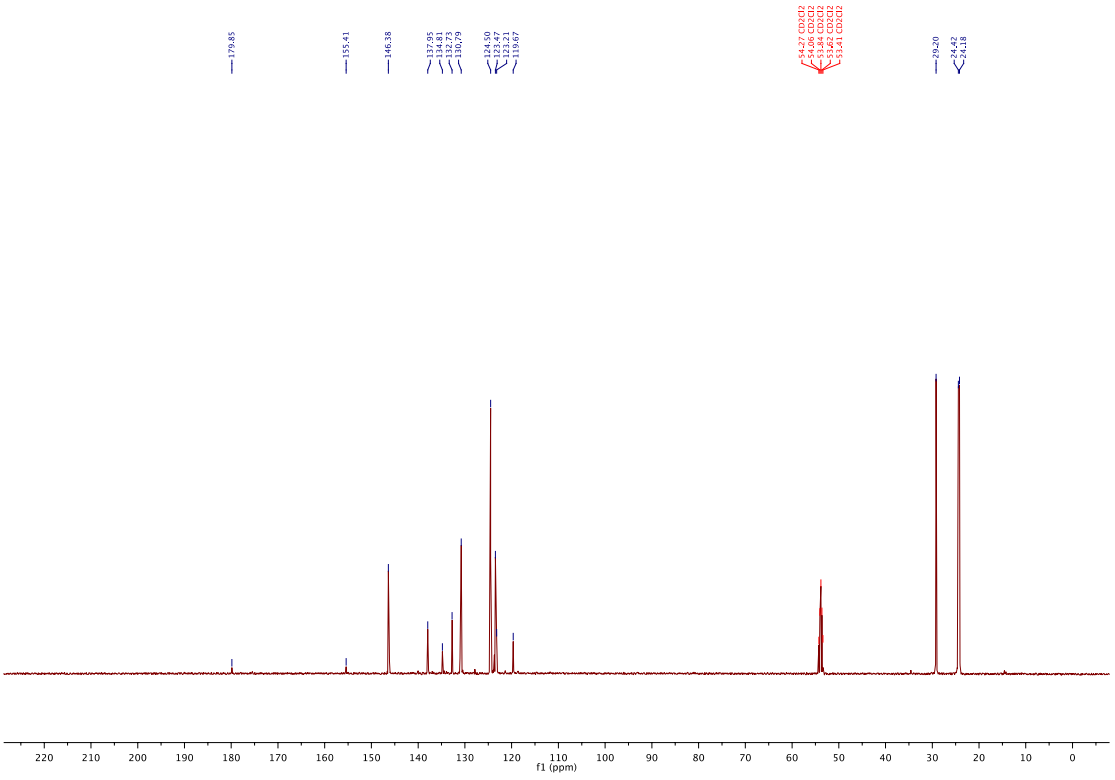

N
N
Au
NH
1
2
3
4
5
N

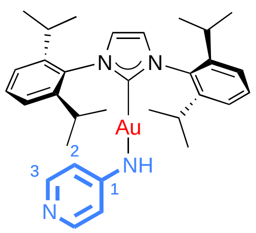
7.58
7.57
7.55
7.53
7.53
7.37
7.35
7.24
6.77
6.75
6.73
5.95
5.94
5.92
5.60
5.57
5.32
4.20
2.68
2.66
2.64
2.63
2.61
2.59
2.56
1.35
1.33
1.25
1.23
3.18
4.43
2.04
1.02
1.02
0.90
0.90
4.35
12.88
12.84
f1 (ppm)

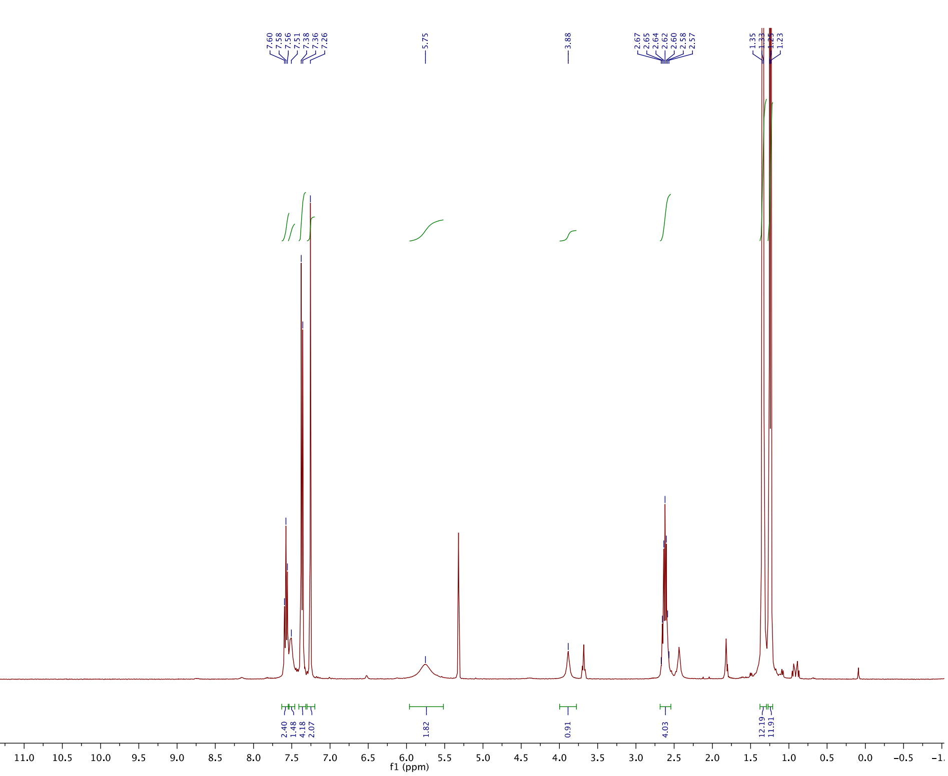

179.61
168.96
147.92
146.41
146.05
135.63
134.81
130.76
124.50
123.49
109.94
107.58
54.27 CD2Cl2
54.00 CD2Cl2
53.84 CD2Cl2
53.67 CD2Cl2
53.51 CD2Cl2
29.19
29.19
24.41
24.19
f1 (ppm)

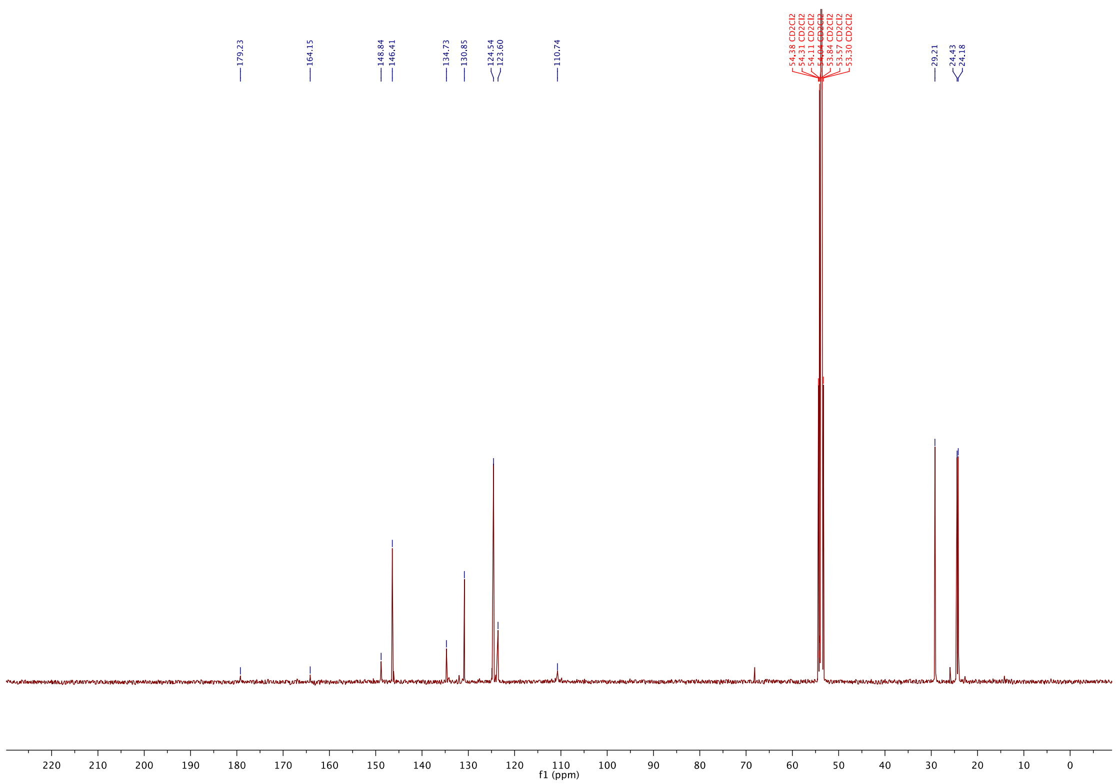

Au
NH
N
N
1
2
3
4
5

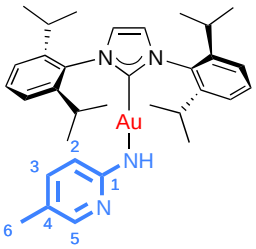
f1 (ppm)


f1 (ppm)

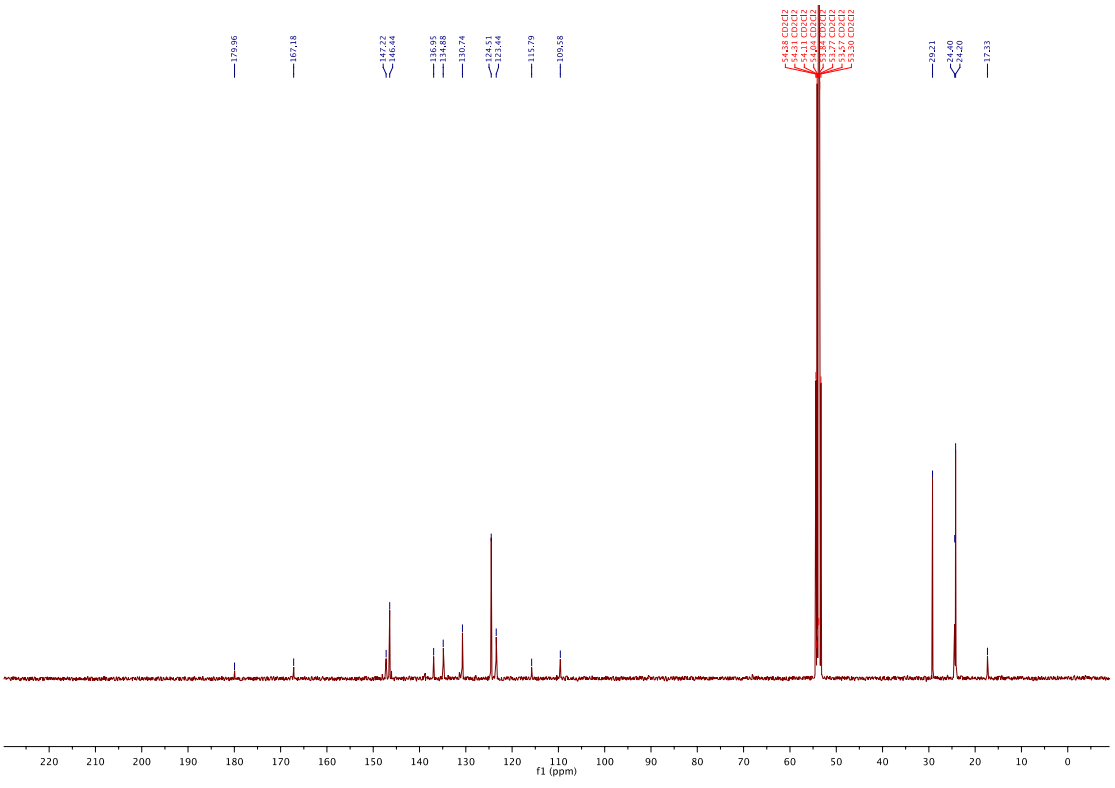

N
N
Au
NH
N
1
2
3

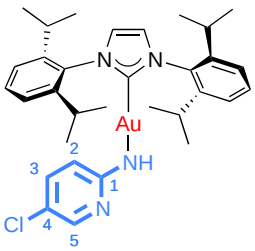

7.60
7.58
7.56
7.51
7.38
7.36
7.26
5.75
3.88
2.67
2.65
2.64
2.62
2.60
2.58
2.57
1.35
1.33
1.25
1.23
2.40
1.48
4.18
2.07
1.82
0.91
4.03
12.19
11.91
f1 (ppm)


179.23
164.15
148.84
146.41
134.73
130.85
124.54
123.60
110.74
54.38 CD2Cl2
54.11 CD2Cl2
53.84 CD2Cl2
53.57 CD2Cl2
53.30 CD2Cl2
29.21
24.43
24.18
f1 (ppm)

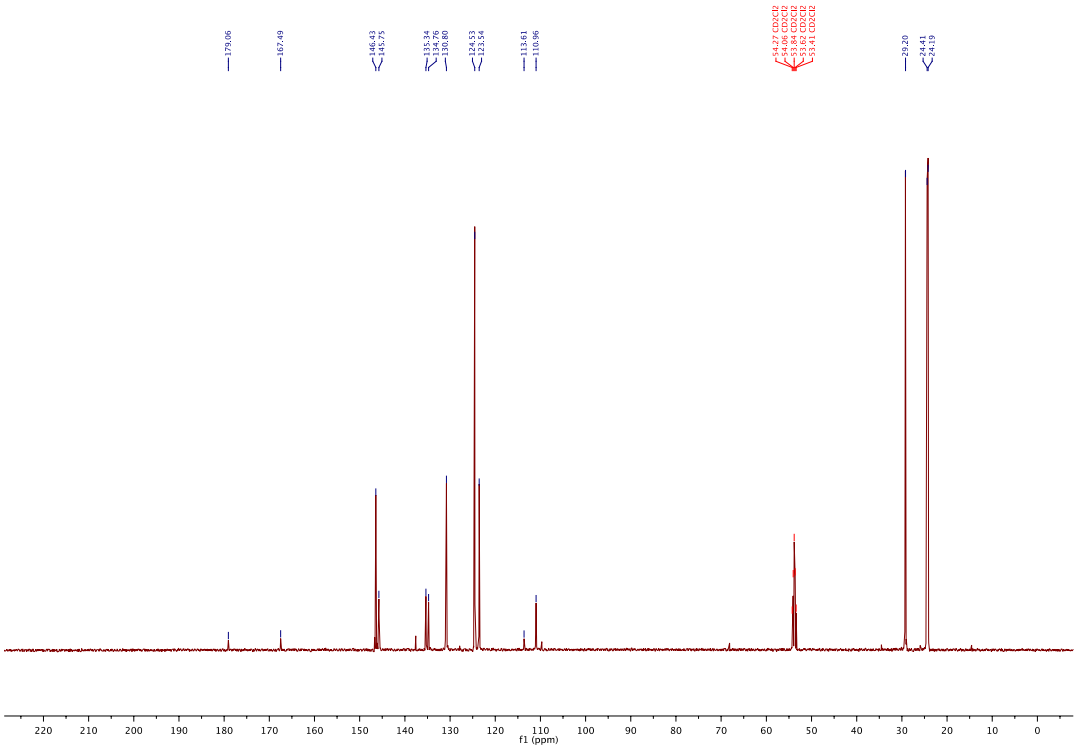

N
N
Au
NH
N
1
2
3
4
5
6

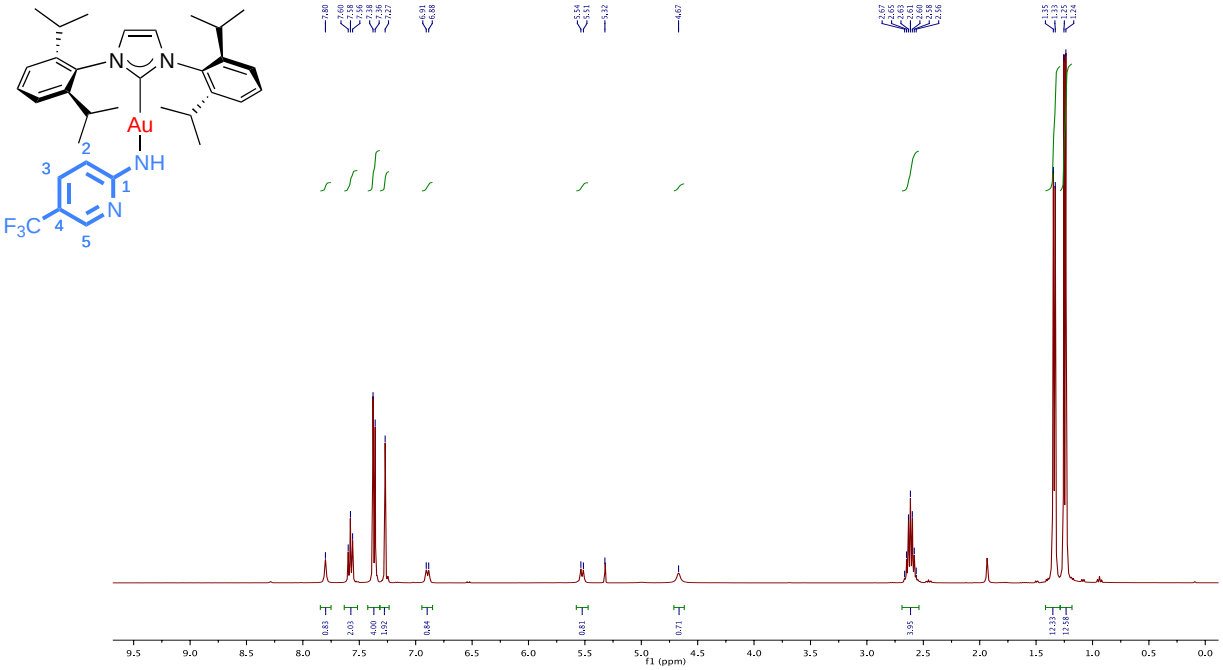
7.59
7.57
7.55
7.37
7.35
7.24
6.63
6.62
6.61
6.60
5.54
5.52
5.32
5.32
5.32
4.06
2.68
2.66
2.65
2.63
2.61
2.59
2.58
1.95
1.35
1.33
1.25
1.23
2.02
5.00
1.96
0.95
0.88
0.80
4.09
2.78
12.25
12.00
f1 (ppm)

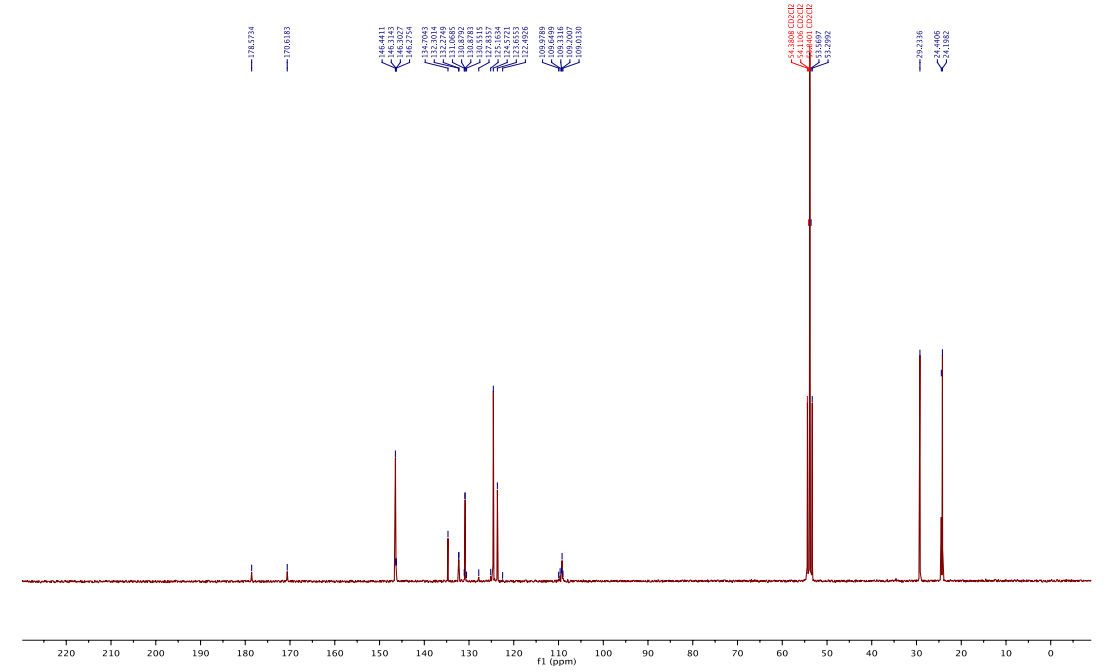

179.96
167.18
147.22
146.44
136.95
134.88
130.74
124.51
123.44
115.79
109.58
54.28 CDCl2
54.31 CDCl2
54.41 CDCl2
54.54 CDCl2
53.24 CDCl2
53.27 CDCl2
53.30 CDCl2
29.21
24.40
24.20
17.33
f1 (ppm)

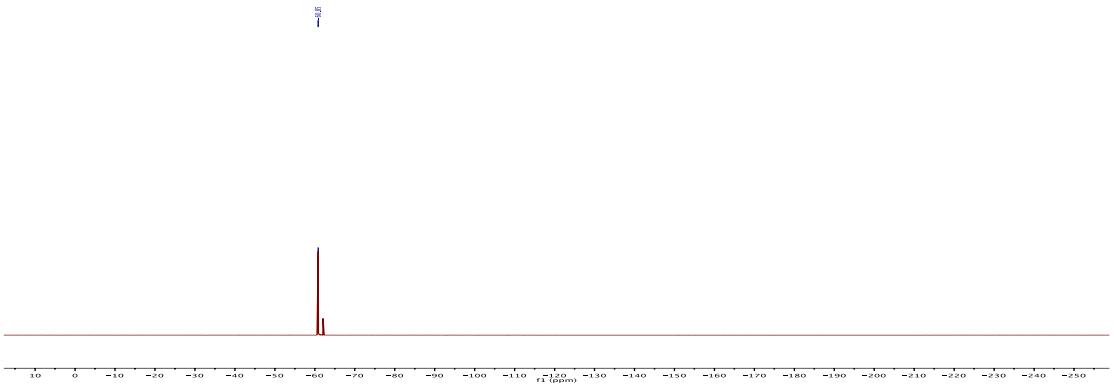

Au
NH
Cl
N
1
2
3
4
5

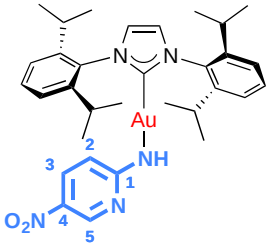
f1 (ppm)

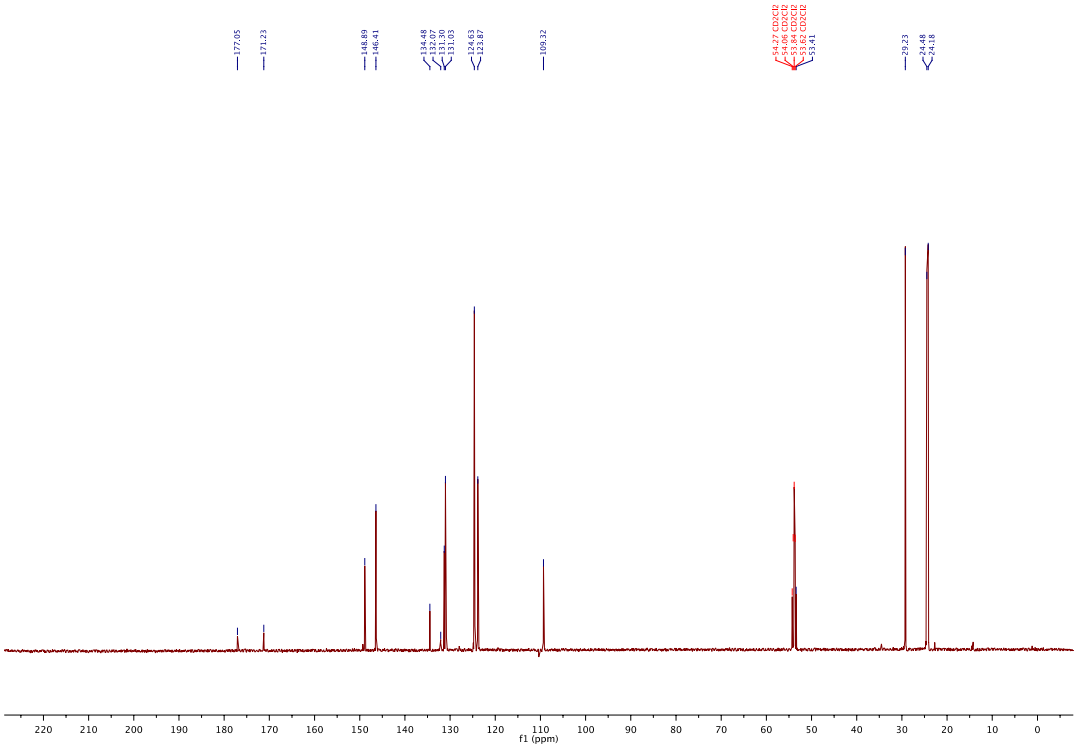

f1 (ppm)

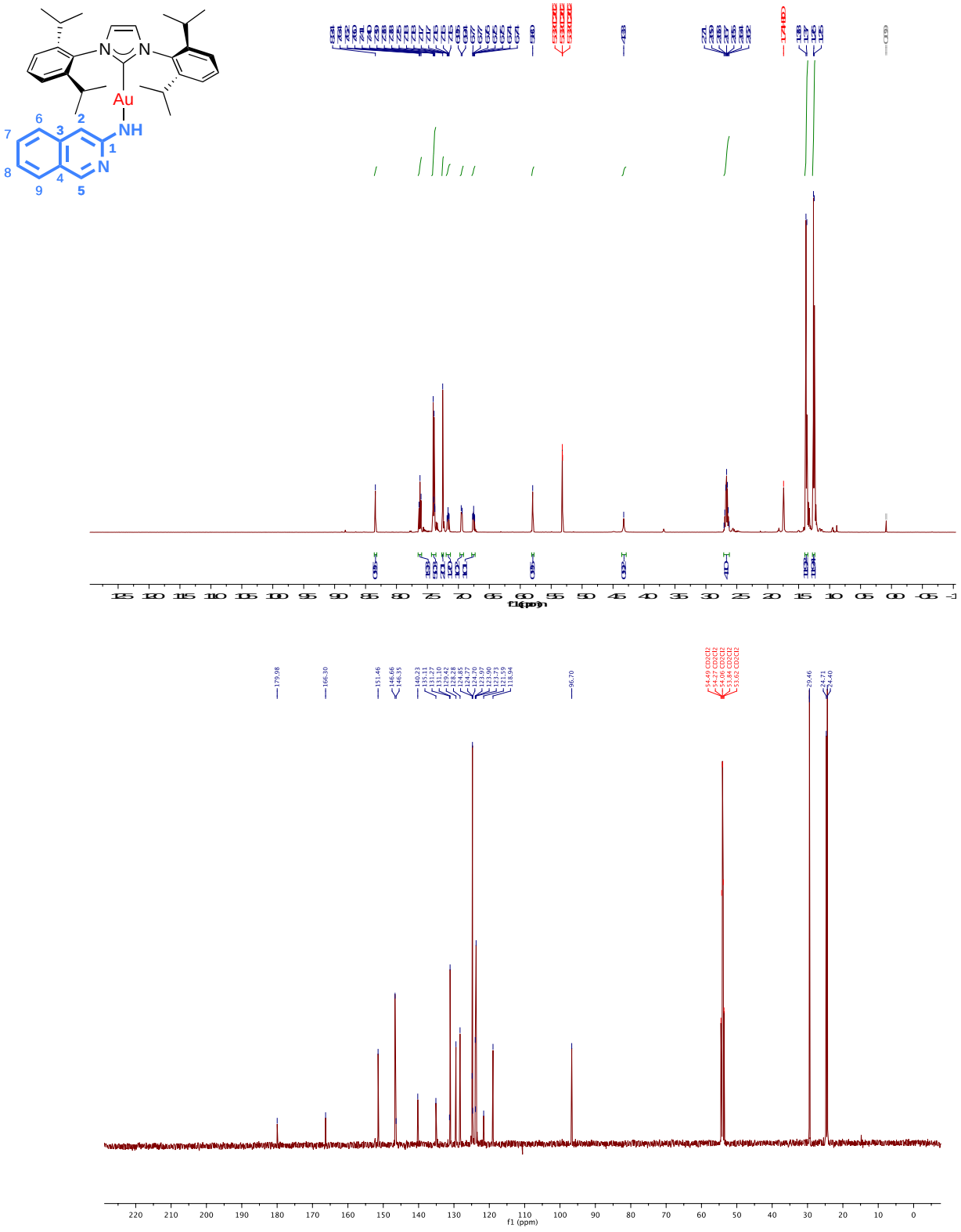

Au
NH
N
N
F3C
1
2
3
4
5
f1 (ppm)

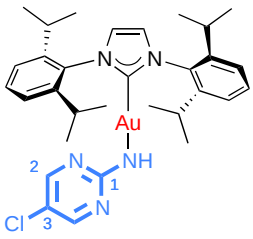

f1 (ppm)


f1 (ppm)

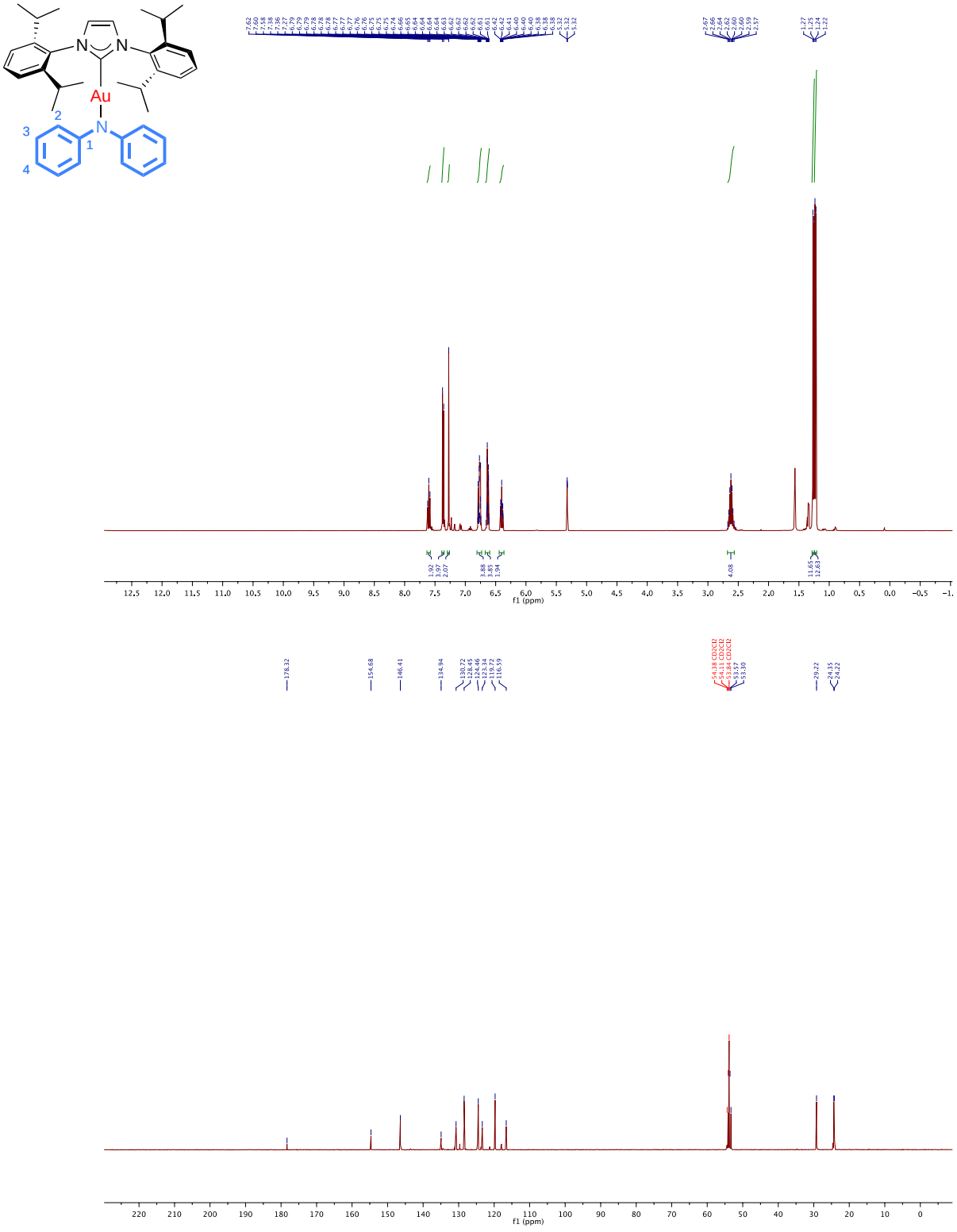

N
N
Au
NH
2
3
1
N
O_2N
4
5




Au
NH
N
N
N
1
2
3
4
5
6
7
8
9
f1 (ppm)


Au
NH
N
N
N
N
Cl
1
2
3

f1 (ppm)
f1 (ppm)


Au
N
N
N
1
2
3
4
f1 (ppm)
f1 (ppm)

DFT Calculations

Calculations were performed at the M06-L/SDD level of theory using Gaussian 09.[1] The crystal structure of **3** was used as the starting point for optimization. The structure was then optimized using tight convergence criteria and the ultrafine grid. The resulting structure was confirmed to be a minimum *via* frequency calculations (no imaginary frequencies). The co-ordinates are listed below.

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision D.02, Gaussian Inc., Wallingford, CT, 2004.

3

Au	-0.16857	-0.98801	-0.29594	C	-3.39182	1.81755	1.72913
N	2.13052	0.98404	0.32002	C	-2.00188	1.60762	1.74446
N	0.16733	1.86979	0.61737	C	-1.07330	2.94213	-1.76896
N	-1.25030	-2.64014	-0.79584	C	-1.44379	4.29862	-2.38909
C	0.78224	0.69521	0.23236	C	-1.26969	1.79922	-2.78884
C	2.34169	2.30190	0.75297	C	-1.35315	0.89277	2.91924
C	1.10538	2.85697	0.94254	C	-1.55358	1.67306	4.23149
C	3.17595	0.04263	-0.01409	C	-1.90297	-0.54236	3.03518
C	3.86150	-0.59897	1.03944	C	-2.61505	-2.59537	-0.72309
C	4.88391	-1.49870	0.69103	C	-4.50406	-1.30611	-0.20774
C	5.18843	-1.75302	-0.65120	C	-5.39340	-2.34485	-0.51622
C	4.47220	-1.11911	-1.67366	C	-4.83743	-3.56651	-0.95031
C	3.44643	-0.20502	-1.37802	C	-3.45600	-3.70079	-1.05621
C	3.44189	-0.39619	2.48939	H	3.32997	2.70634	0.87982
C	4.60263	-0.54448	3.48324	H	0.80882	3.83840	1.26556
C	2.30260	-1.38065	2.83627	H	5.43438	-2.00926	1.47409
C	2.68156	0.51843	-2.47862	H	5.97729	-2.45377	-0.90111
C	3.32666	1.89058	-2.76668	H	4.70581	-1.33947	-2.70967
C	2.55737	-0.30521	-3.76711	H	3.03848	0.61932	2.59458
C	-1.26914	2.05059	0.62633	H	4.96615	-1.57695	3.52154
C	-1.87152	2.62993	-0.51086	H	4.26815	-0.28346	4.49114
C	-3.26341	2.81585	-0.47974	H	5.44584	0.10214	3.22255
C	-4.01495	2.42621	0.63538	H	2.65944	-2.41416	2.76788

H	1.45508	-1.27512	2.14838
H	1.94405	-1.20797	3.85669
H	1.66265	0.69821	-2.11540
H	2.75012	2.43109	-3.52467
H	4.34960	1.76651	-3.13938
H	3.36684	2.51213	-1.86579
H	3.52594	-0.43519	-4.26307
H	1.89589	0.20648	-4.47241
H	2.13671	-1.29409	-3.56461
H	-3.76189	3.25186	-1.34006
H	-5.08900	2.57777	0.64101
H	-3.98634	1.48355	2.57487
H	-0.00644	2.97351	-1.51122
H	-2.48035	4.30542	-2.74244
H	-0.80436	4.50685	-3.25224
H	-1.32830	5.11517	-1.66994
H	-2.31808	1.73778	-3.10051
H	-0.99966	0.82916	-2.35342
H	-0.65394	1.96836	-3.67978
H	-0.27438	0.81927	2.73281
H	-1.06671	1.15313	5.06246
H	-2.61825	1.76485	4.47366
H	-1.13654	2.68339	4.16524
H	-2.97400	-0.53346	3.26972
H	-1.38405	-1.08696	3.83110
H	-1.77986	-1.08495	2.09111
H	-0.86078	-3.52560	-1.10092
H	-4.87632	-0.34180	0.13202
H	-6.46333	-2.20768	-0.42292
H	-5.48131	-4.40313	-1.20216
H	-3.00866	-4.63299	-1.38768
N	-3.15946	-1.39987	-0.29950