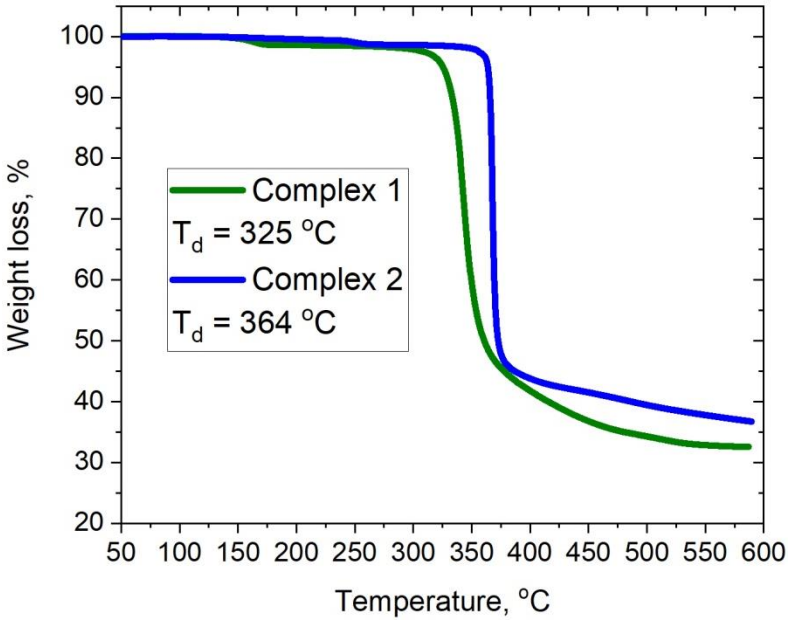
Supplementary Information for

Highly Efficient Blue Organic Light-Emitting Diodes Based on Carbene-Metal-Amides

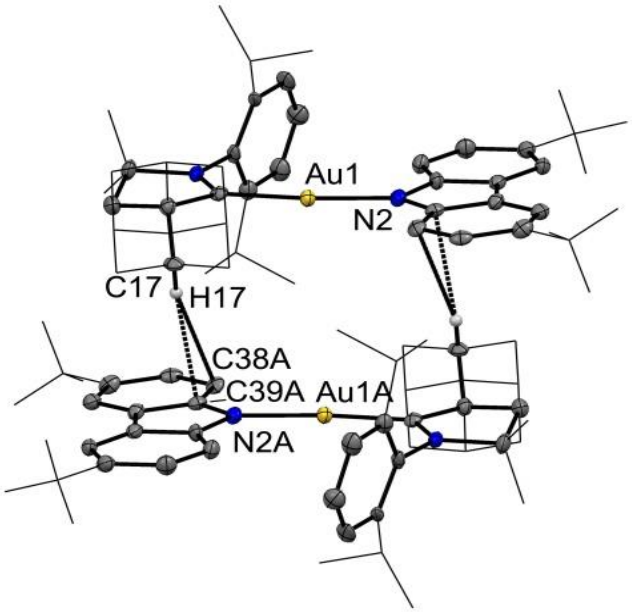
Conaghan et al.

Supplementary Figures



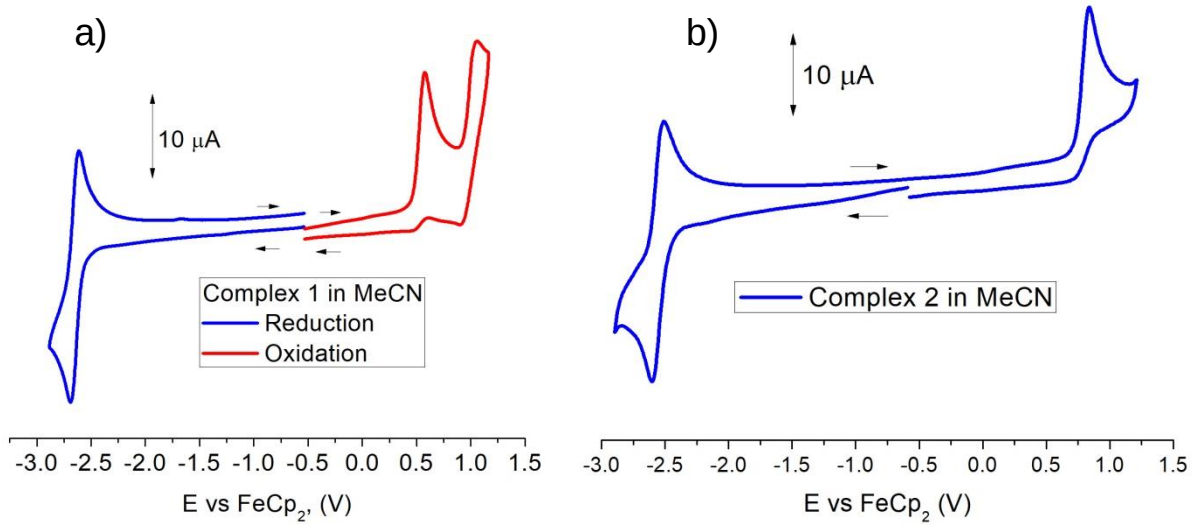
Supplementary Figure 1. TGA curves for gold complexes 1 and 2.

Thermal gravimetric analysis (TGA) for complexes **1** and **2** with a decomposition temperature (T_d).



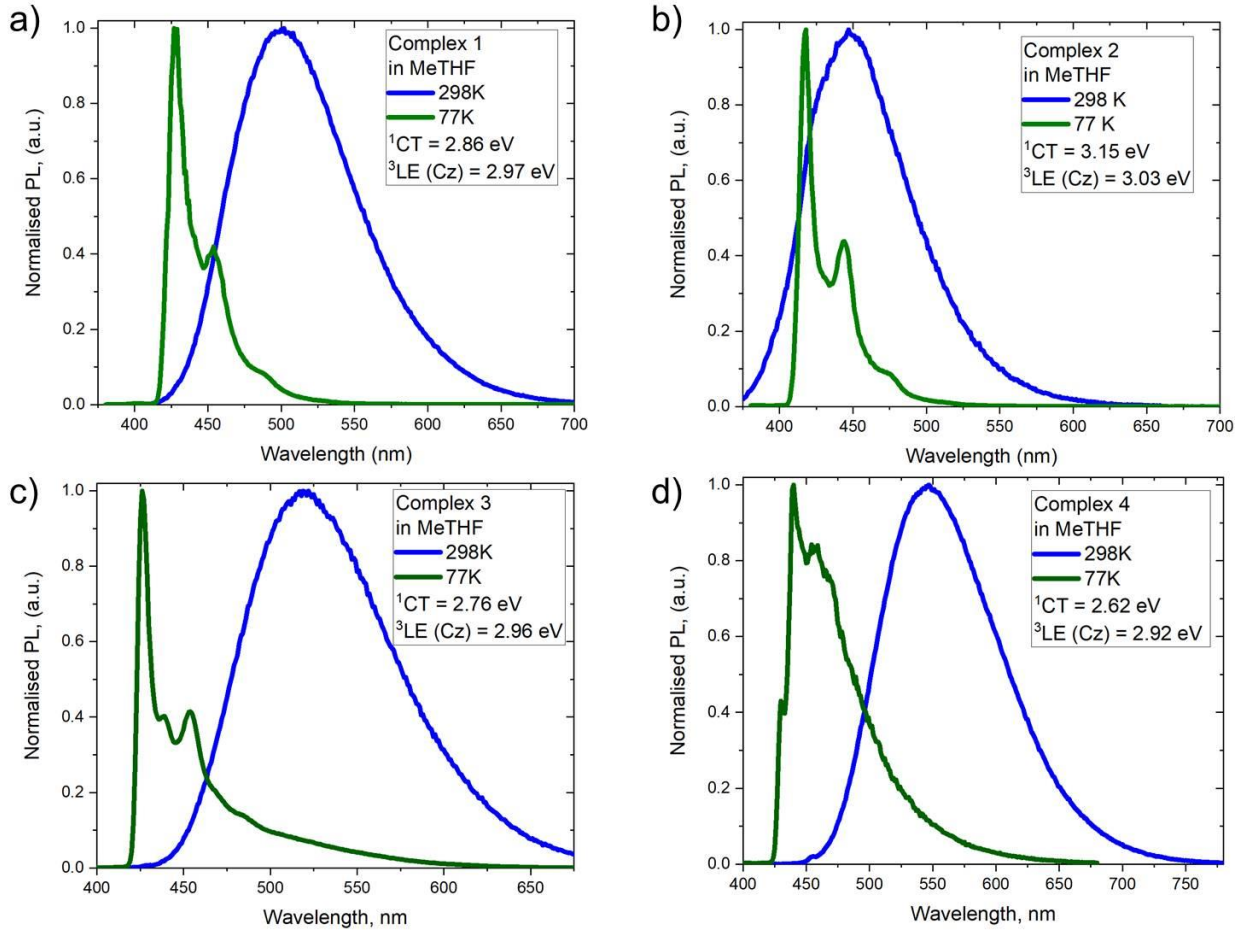
Supplementary Figure 2. Intermolecular interactions for complex 2.

The scheme for the intermolecular C–H···π interaction for complex **2**. Ellipsoids are shown at 50 % probability.



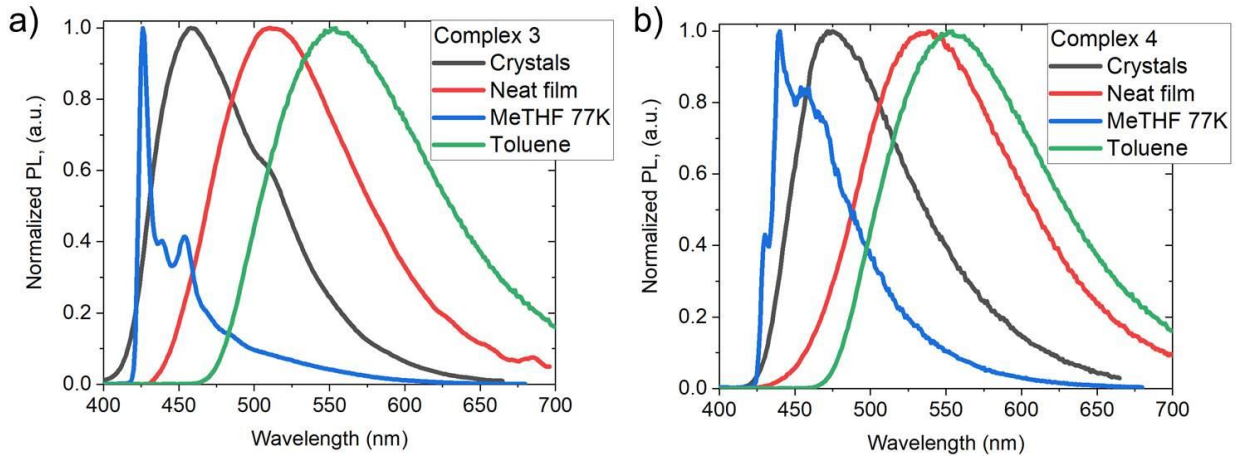
Supplementary Figure 3. Cyclic voltammetry for complexes 1 and 2.

(a) reduction (blue) and oxidation (red) cyclic voltammetry scans for gold complex **1**. (b) Full range cyclic voltammogram for gold complex **2**. Recorded using a glassy carbon electrode in MeCN solution (1.4 mM) with $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte (0.13 M), scan rate 0.1 Vs^{-1}.



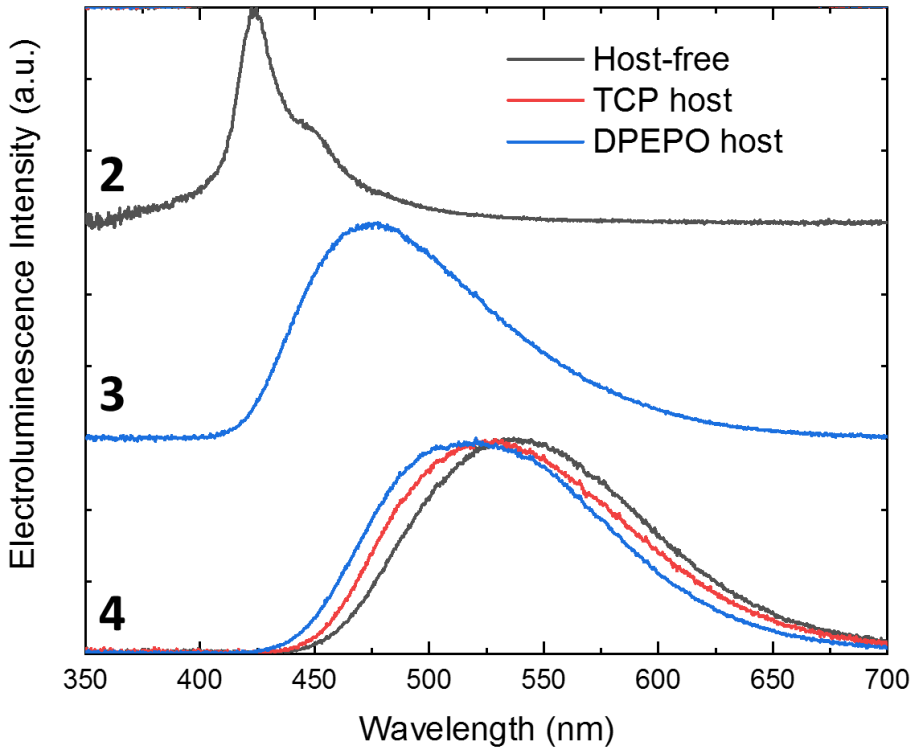
Supplementary Figure 4. Photoluminescence spectra for complex 1–4.

Emission spectra for complexes **CMA1** (a), **CMA4** (b), **1** (c) and **2** (d) in MeTHF solutions at 77 and 298K (excitation at 360 nm, under nitrogen).



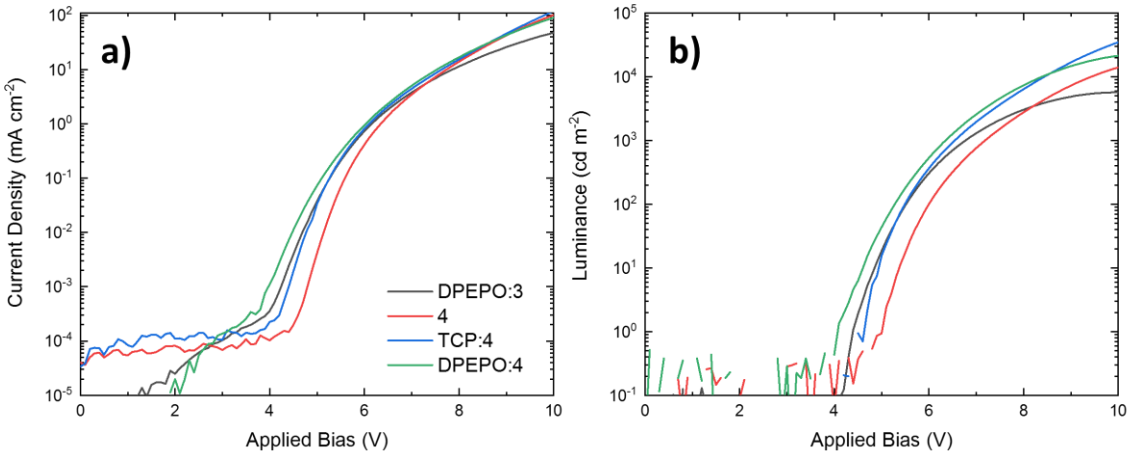
Supplementary Figure 5. Photoluminescence spectra for complex 1–4.

PL spectra of (a) **3** and (b) **4** at 298K as crystals, in neat film, in frozen MeTHF solution and in liquid toluene solution (excitation at 365 nm).



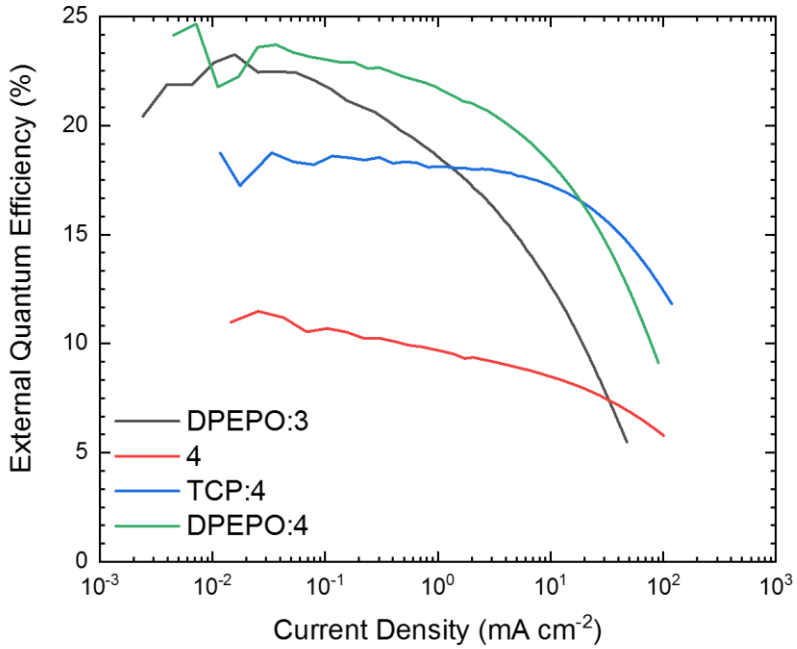
Supplementary Figure 6. Electroluminescence spectra.

Normalised electroluminescence spectra for devices incorporating **2**, **3** and **4** in host-free and host-guest structures.



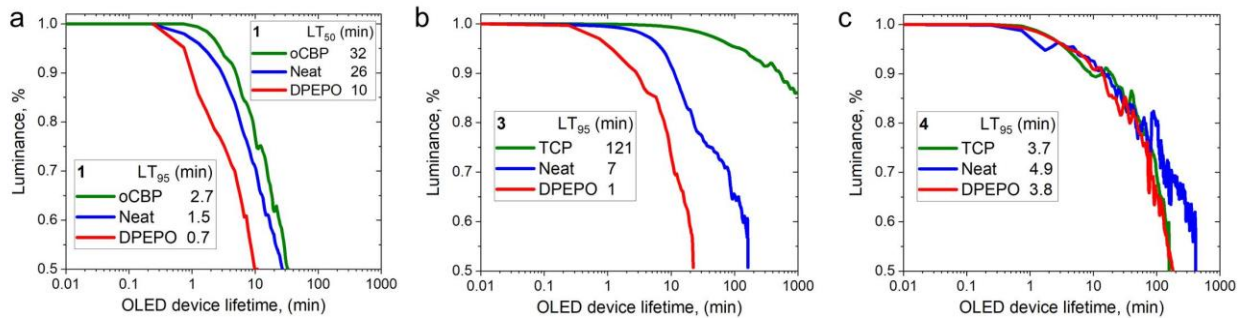
Supplementary Figure 7. Current density-voltage-luminance (J-V-L) curves.

a Current density-voltage. **b** luminance-voltage characteristics for OLEDs based on complexes **3** and **4**



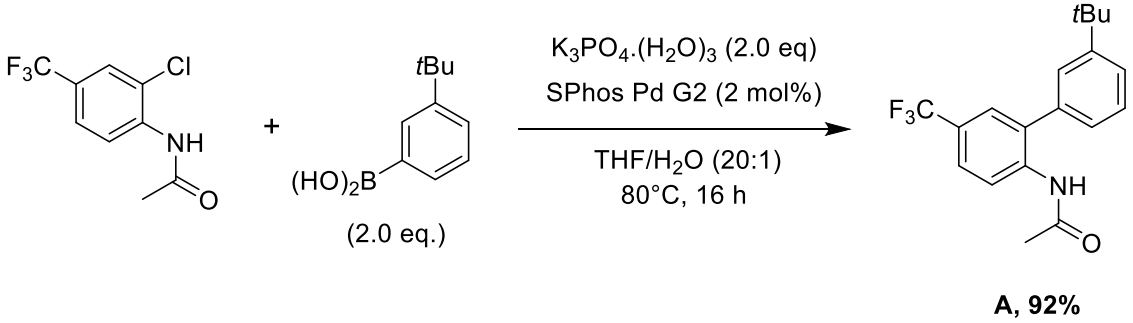
Supplementary Figure 8. External electroluminescence quantum efficiency.

External Quantum efficiency as a function of current density for OLEDs based on **3** and **4**.



Supplementary Figure 9. OLED device lifetime curves.

OLED device operating lifetime curves (initial luminance 100 cd/m^2) at constant current under vacuum for complexes **1** (a), **3** (b) and **4** (c).

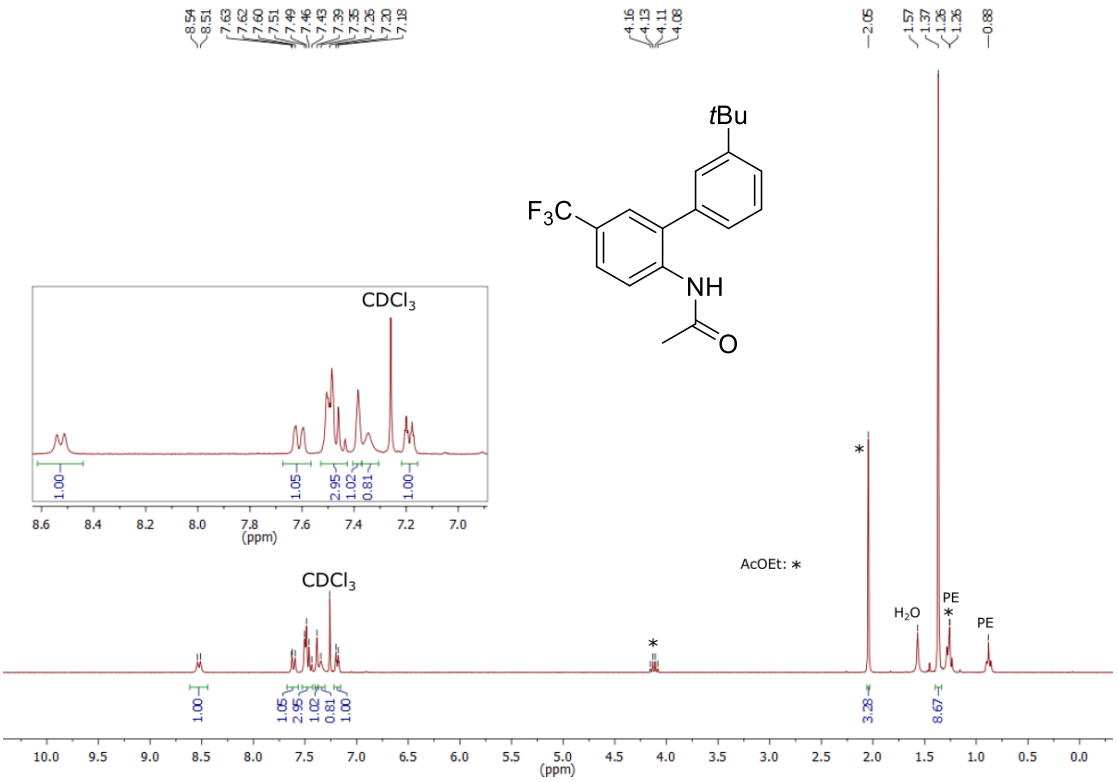


A, 92%

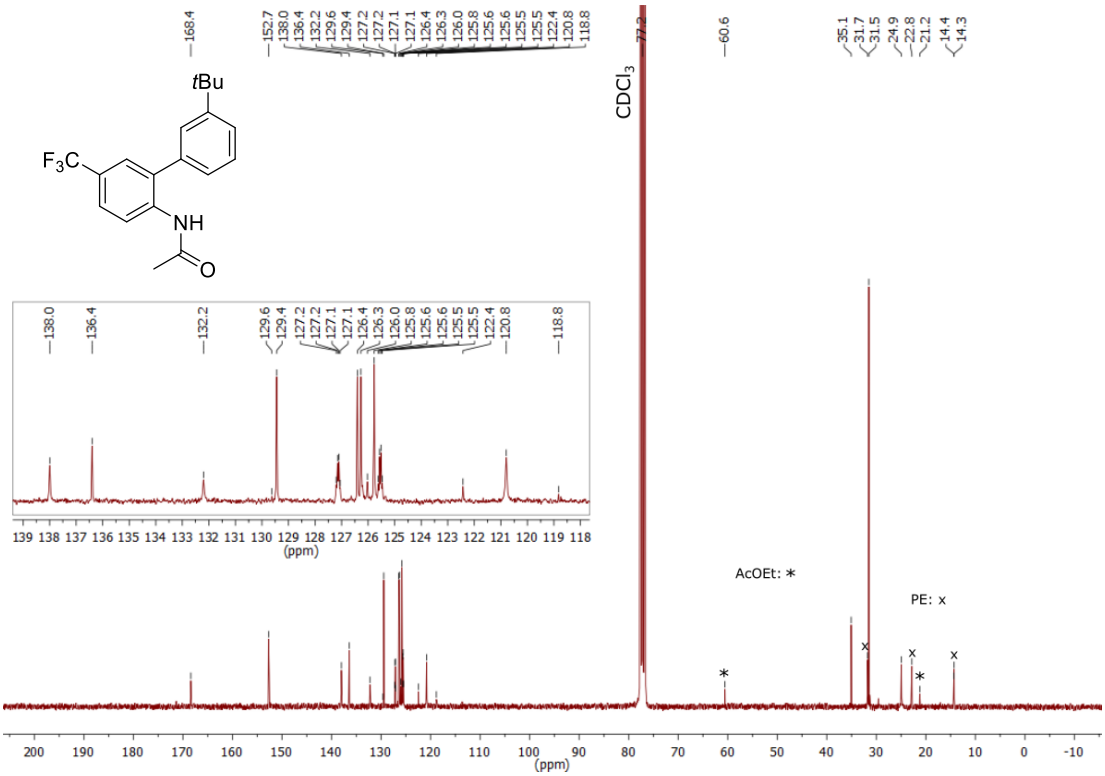
Supplementary Figure 10. Synthesis of compound A.

Synthetic scheme to obtain *N*-(3'-(*tert*-butyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acetamide (**A**).

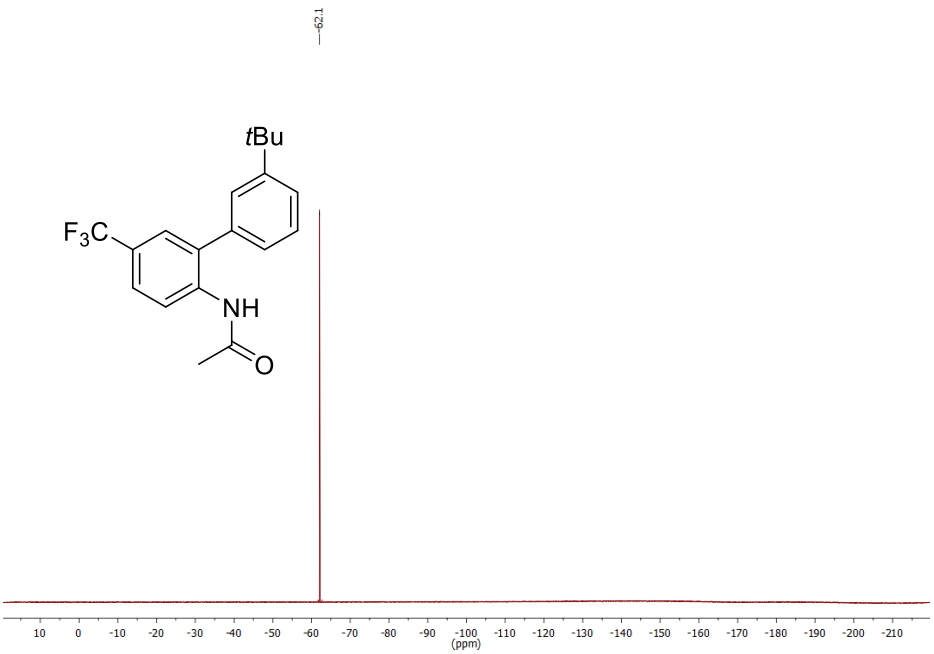
a


tBu
F3C
NH
O
CDCl3
AcOEt: *
H2O
PE
(ppm)

b

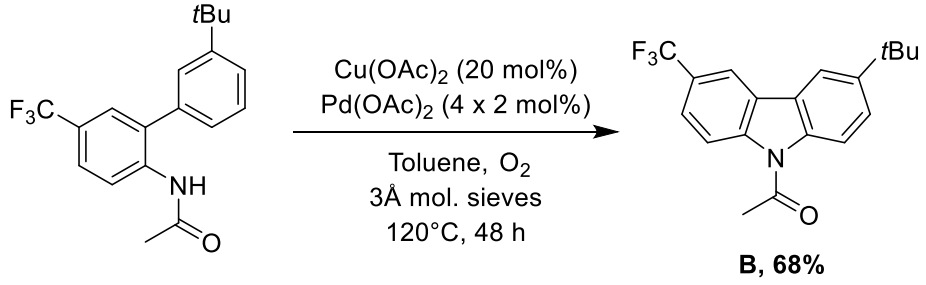

tBu
F3C
NH
O
CDCl3
AcOEt: *
PE: x
(ppm)

c



Supplementary Figure 11. NMR spectra for *N*-(3'-(*tert*-butyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acetamide.

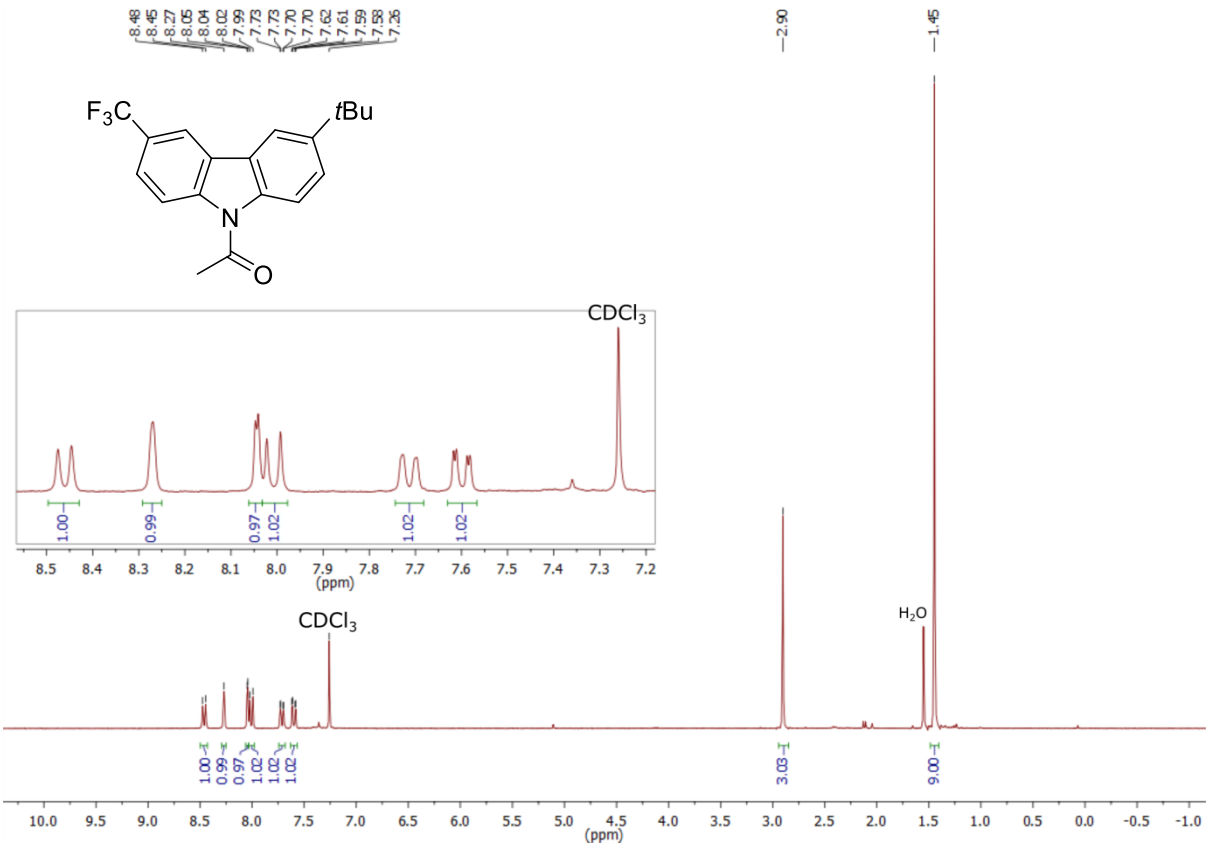
(a) ^{1}H NMR (300 MHz, $CDCl_3$); (b) ^{13}C NMR (75 MHz, $CDCl_3$); (c) ^{19}F NMR (282 MHz, $CDCl_3$).



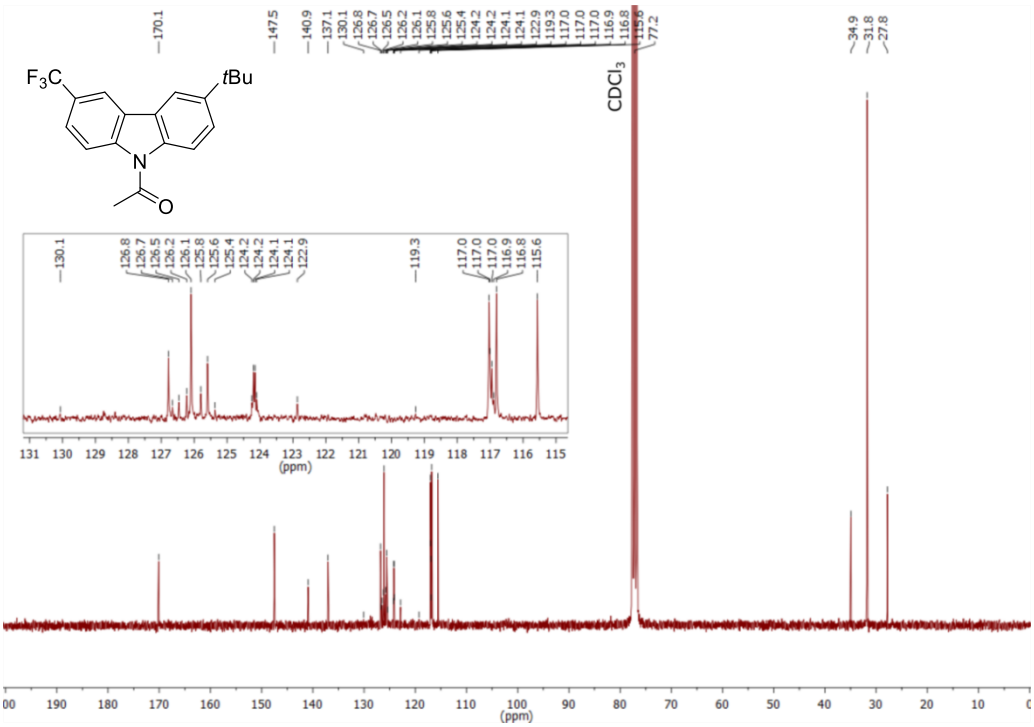
Supplementary Figure 12. Synthesis of compound B.

Synthetic scheme to obtain 6-(*tert*-butyl)-3-(trifluoromethyl)-9-acetylcarbazole (**B**).

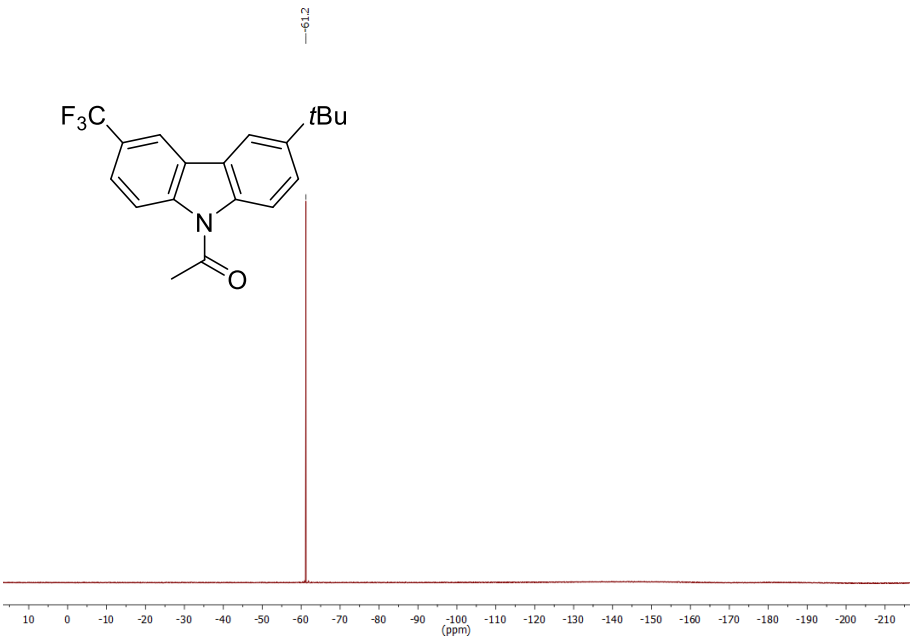
a


8.48
8.45
8.27
8.05
8.04
8.02
7.99
7.73
7.73
7.70
7.70
7.62
7.61
7.59
7.58
7.26
2.90
1.45
F3C
tBu
N
O
CDCl3
1.00
0.99
0.97
1.02
1.02
1.02
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
(ppm)
CDCl3
H2O
1.00
0.99
0.97
1.02
1.02
1.02
3.03
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
(ppm)

b

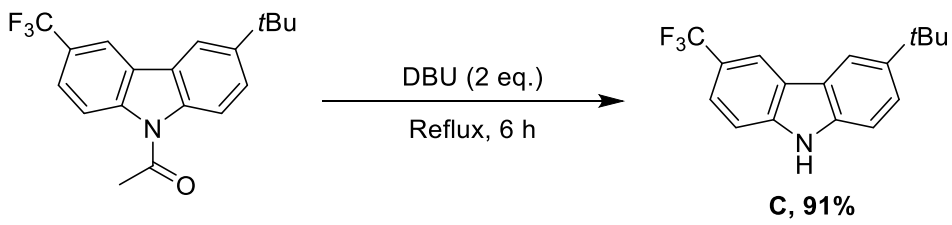


c



Supplementary Figure 13. NMR spectra for 6-(*tert*-butyl)-3-(trifluoromethyl)-9-acetylcarbazole.

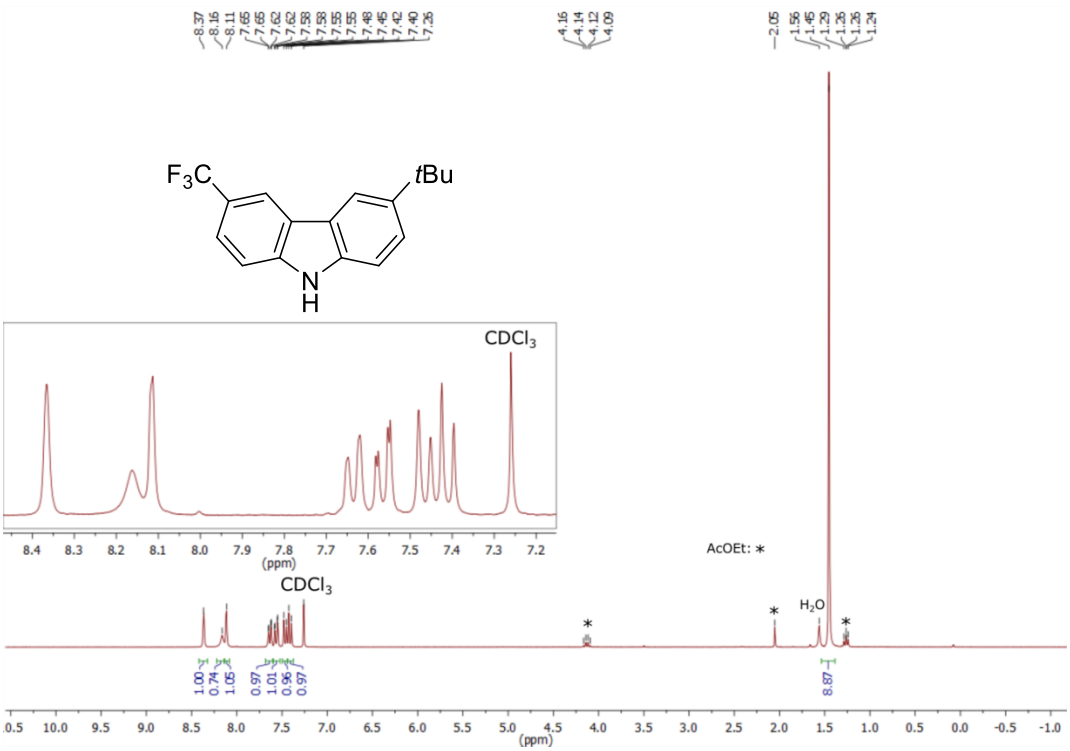
(a) ^{1}H NMR (300 MHz, $CDCl_3$); (b) ^{13}C NMR (75 MHz, $CDCl_3$); (c) ^{19}F NMR (282 MHz, $CDCl_3$).



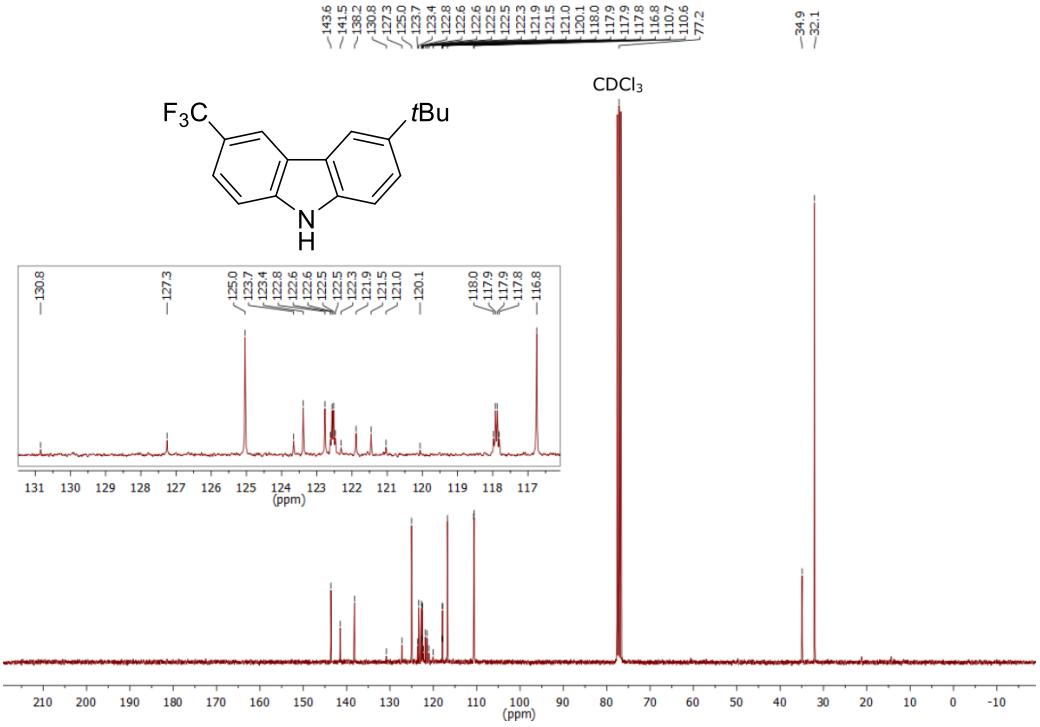
Supplementary Figure 14. Synthesis of compound C.

Synthetic scheme to obtain 6-(*tert*-butyl)-3-(trifluoromethyl)-9H-carbazole (C).

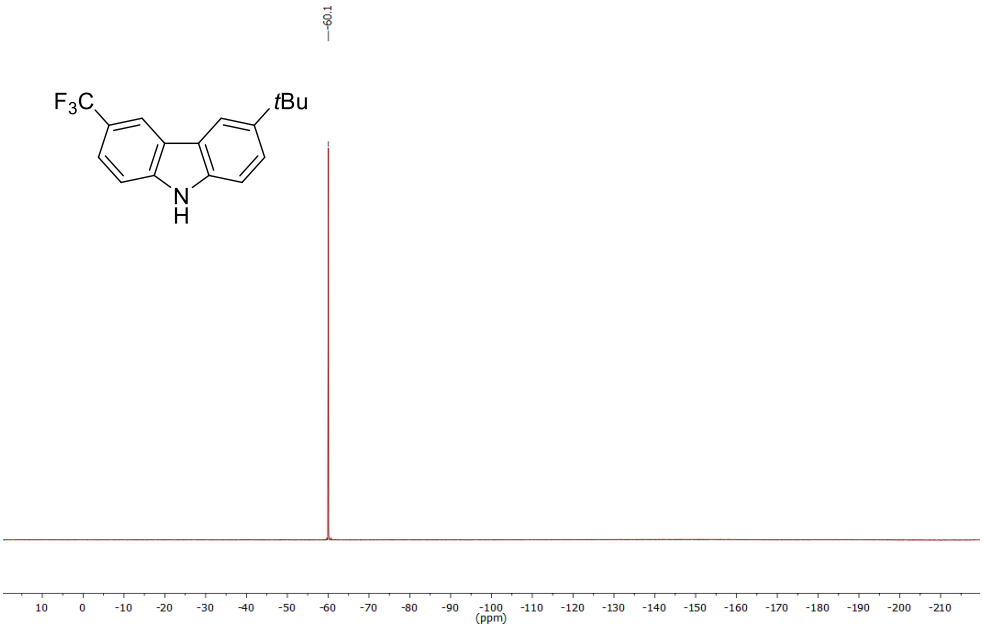
a



b



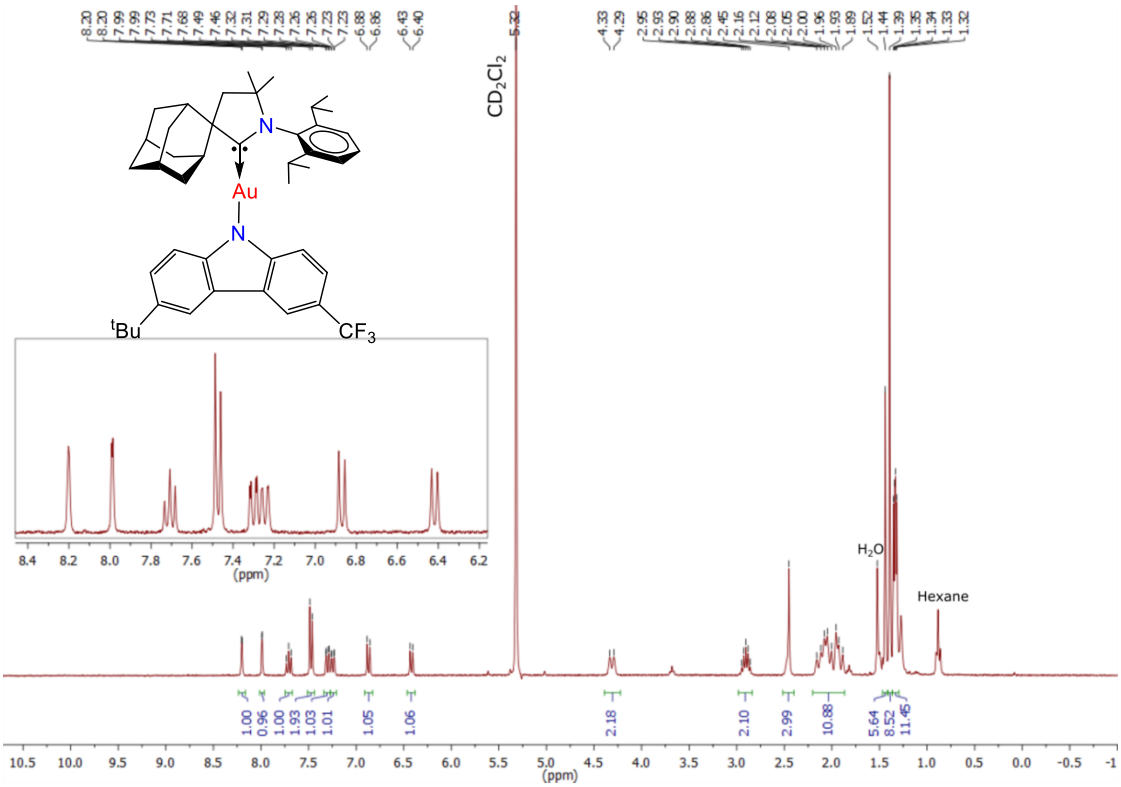
c



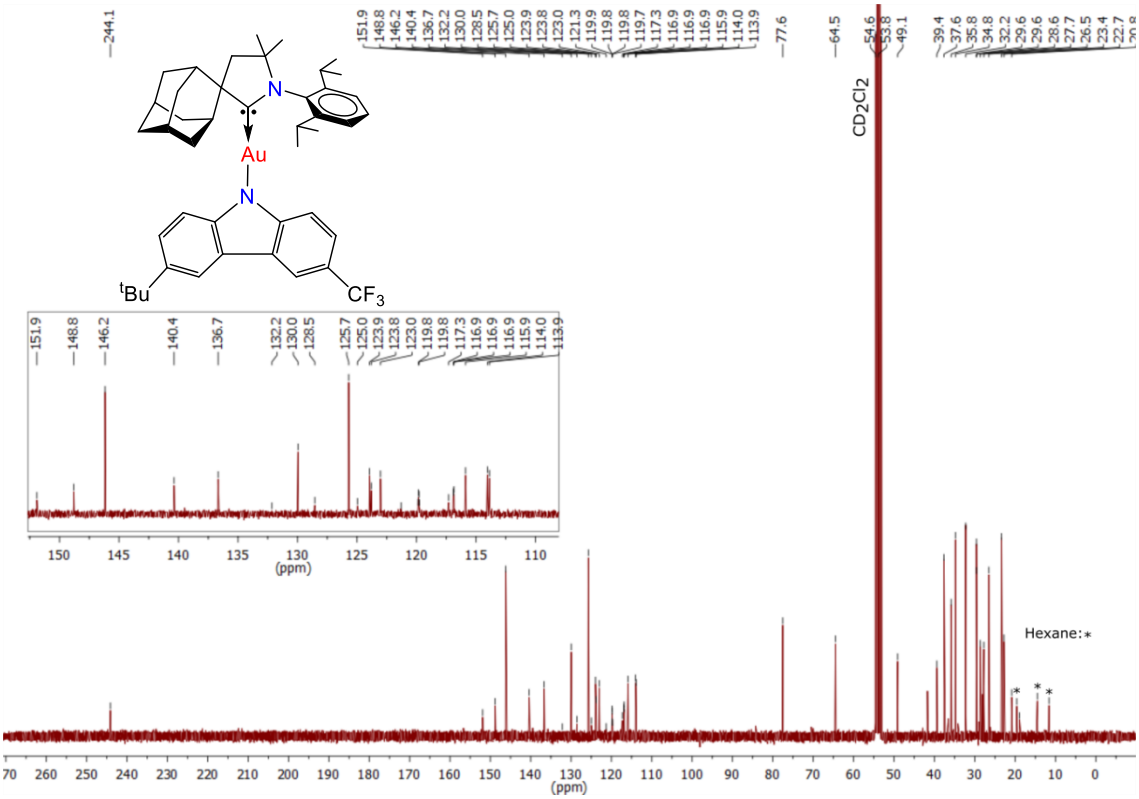
Supplementary Figure 15. NMR spectra for 6-(*tert*-butyl)-3-(trifluoromethyl)-9-acetylcarbazole.

(a) ^{1}H NMR (300 MHz, $CDCl_3$); (b) ^{13}C NMR (75 MHz, $CDCl_3$); (c) ^{19}F NMR (282 MHz, $CDCl_3$).

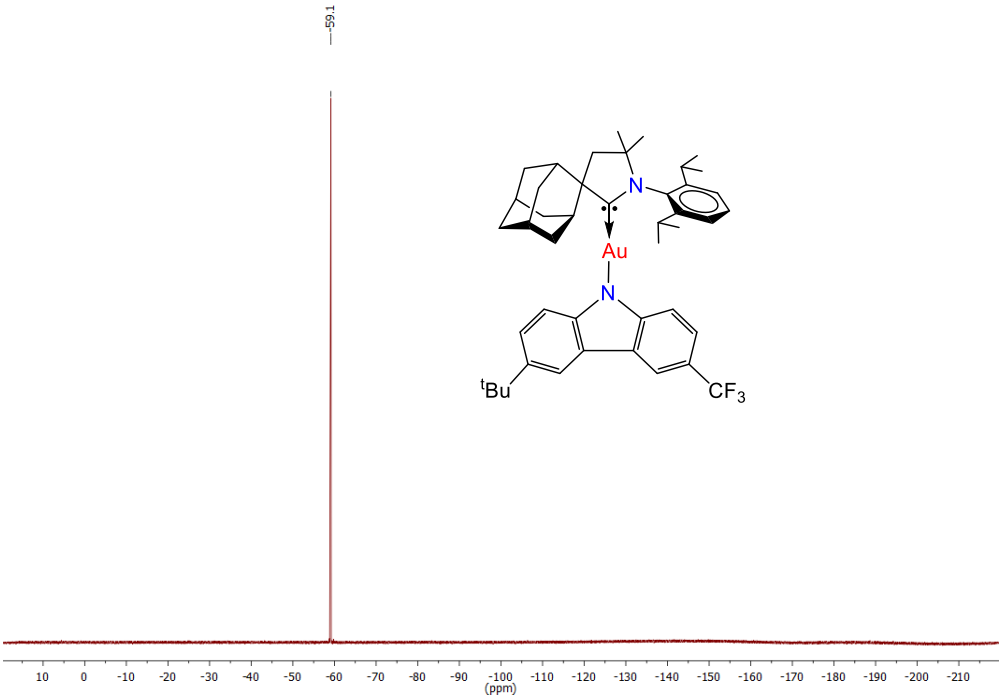
a


CD2Cl2
H2O
Hexane
tBu
CF3
Au
N
(ppm)

b


CD2Cl2
Hexane:*
tBu
CF3
Au
N
(ppm)

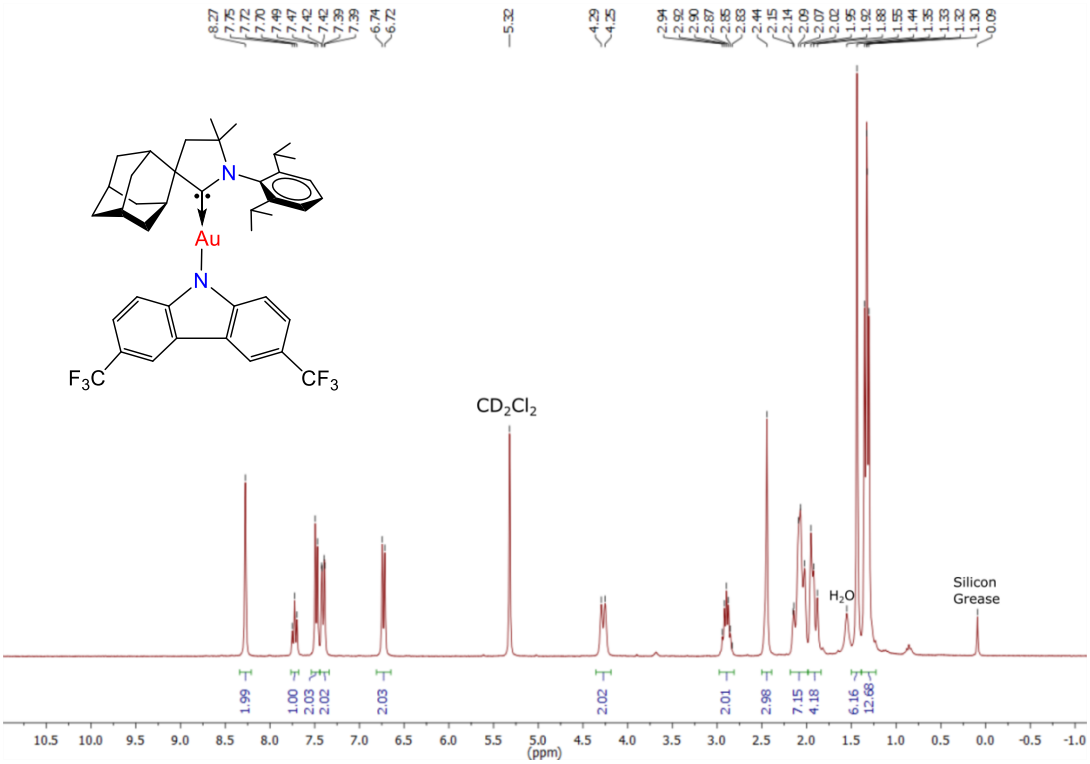
c



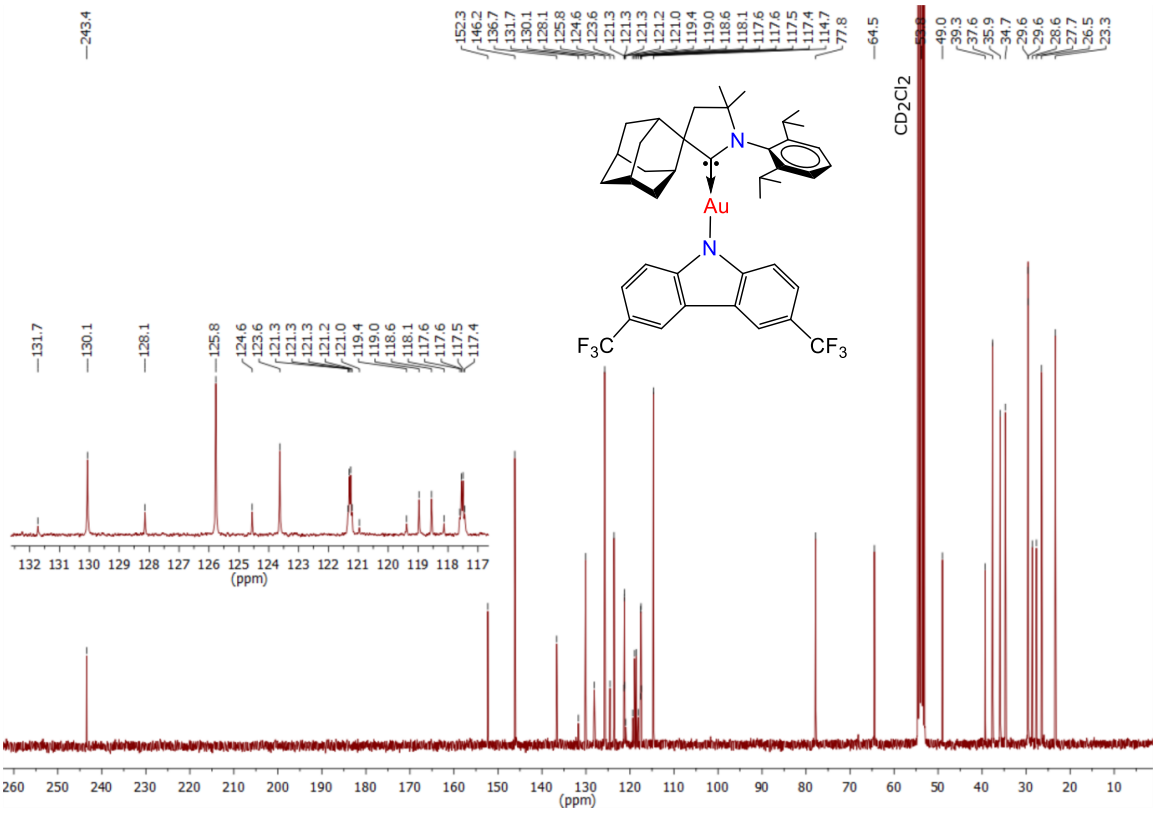
Supplementary Figure 16. NMR spectra for complex 1.

(a) ^{1}H NMR (300 MHz, $CDCl_3$); (b) ^{13}C NMR (75 MHz, $CDCl_3$); (c) ^{19}F NMR (282 MHz, $CDCl_3$).

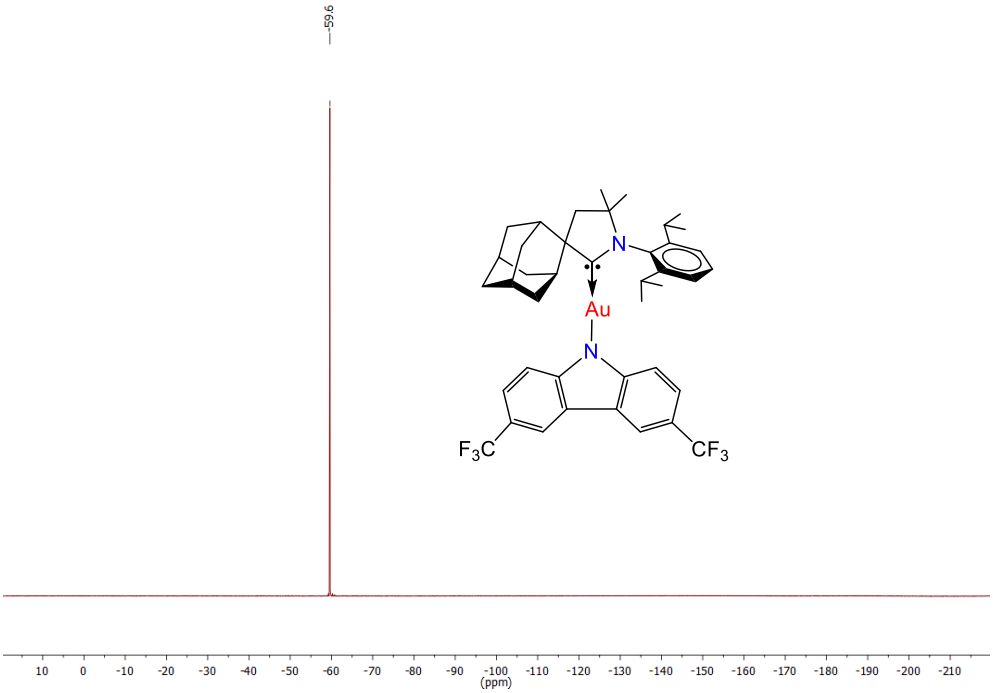
a


Au
N
F3C
CF3
CD2Cl2
H2O
Silicon
Grease
(ppm)

b


Au
N
F3C
CF3
CD2Cl2
(ppm)

c



Supplementary Figure 17. NMR spectra for complex 2.

(a) ^{1}H NMR (300 MHz, $CDCl_3$); (b) ^{13}C NMR (75 MHz, $CDCl_3$); (c) ^{19}F NMR (282 MHz, $CDCl_3$).

Supplementary Methods

Synthesis of *N*-(3'-(*tert*-butyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acetamide: *N*-(2-chloro-4-(trifluoromethyl)phenyl)acetamide (1 eq., 5.05 mmol, 1.20 g), 3-(*tert*-butyl)phenylboronic acid (2.0 eq., 10.1 mmol, 1.80 g,) and potassium phosphate trihydrate (2.0 eq., 10.1 mmol, 2.33 g) were mixed in THF/H_2O 20:1 (10 mL) and purged with argon. SPhos Pd G2 (1 mol%, 0.051 mmol, 37 mg) was added and the mixture was heated at 80°C for 16 h. Reaction was cooled to r.t., Et_2O (30 mL) was added and the mixture was filtered through Celite®. The filtrate was diluted with AcOEt (100 mL), washed with water and brine, and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by silica column chromatography (PE/AcOEt) to afford the product as an off-white solid (92%, 1.55 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.7 Hz, 1H), 7.61 (pseudo dd, *J* = 8.7, 2.2 Hz, 1H), 7.52 – 7.42 (m, 3 x 1H overlapped), 7.40 – 7.37 (m, 1H), 7.37 – 7.32 (bs, NH), 7.19 (pseudo dt, *J* = 6.6, 1.9 Hz, 1H), 2.05 (s, 3H, Ac), 1.37 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4 (s,

C=O), 152.7 (s, C–*t*Bu), 138.0 (s, C_q), 136.4 (s, C_q), 132.2 (s, C_q)), 129.5 (s, CH), 127.1 (q, *J* = 3.6 Hz, CH–C–CF_3), 126.4 (s, CH), 126.3 (s, CH), 125.8 (s, CH), 125.5 (q, *J* = 3.7 Hz, CH–C–CF_3), 124.2 (q, *J* = 271.8 Hz, CF_3), 120.8 (s, CH), 35.1 (s, $C(CH_3)_3$), 31.5 (s, $C(CH_3)_3$), 25.0 (s, CH_3 Ac), (C_{ipso}–CF_3 was not observed due to overlap with aromatic signals). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.1 ppm. Anal. Calcd. for $C_{19}H_{20}F_3NO$ 335.37): C, 68.05; H, 6.01; N, 4.18. Found: C, 68.17; H, 6.18; N, 4.31. See Supplementary Figs. 10 and 11.

Synthesis of 6-(*tert*-butyl)-3-(trifluoromethyl)-9-acetylcarbazole: In an oven-dried Schlenk tube, under argon, *N*-(3'-(*tert*-butyl)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acetamide (1 eq., 4.47 mmol, 1.50 g), $Cu(OAc)_2$ (20 mol%, 0.89 mmol, 162 mg), $Pd(OAc)_2$ (2 mol%, 0.089 mmol, 20 mg) and 3 Å molecular sieves were mixed in toluene (20 mL). The flask was purged by oxygen and heated at 120°C. The $Pd(OAc)_2$ was added every 8 h (4 × 20 mg). The reaction was monitored by ^{19}F NMR indicating full completion after 48 h. The mixture was cooled to r.t., diluted with AcOEt (60 mL) and filtered through Celite®. The filtrate was diluted with AcOEt (100 mL) washed with water and brine and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by silica column chromatography (PE/AcOEt) to afford the product as an off-white solid (68%, 1.01 g).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.8 Hz, 1H, CH^1), 8.27 (pseudo s, 1H, CH^4), 8.04 (d, *J* = 2.1 Hz, 1H, CH^5), 8.01 (d, *J* = 8.9 Hz, 1H, CH^8), 7.71 (pseudo dd, *J* = 8.8, 1.9 Hz, 1H, CH^2), 7.60 (dd, *J* = 8.9, 2.1 Hz, 1H, CH^7), 2.90 (s, 3H, Ac), 1.45 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 (s, C=O), 147.5 (C–*t*Bu), 140.9 (s, C_q), 137.1 (s, C_q), 126.8 (s, C_q), 126.1 (s, CH^7), 126.0 (q, *J* = 32.6 Hz, C–CF_3), 125.6 (s, C_q), 124.7 (q, *J* = 271.7 Hz, CF_3), 124.2 (q, *J* = 3.6 Hz, CH^2), 117.0 (s, CH^1 overlapped with CH^4), 116.9 (q, *J* = 3.9 Hz, CH^4 overlapped with CH^1), 116.8 (s, CH^5), 115.6 (s, CH^8), 34.9 (s, $C(CH_3)_3$, 31.8 ($C(CH_3)_3$, 27.8 (s, CH_3 Ac). ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.2. Anal. Calcd. for $C_{19}H_{18}F_3NO$ (333.35): C, 68.46; H, 5.44; N, 4.20. Found: C, 68.13; H, 5.68; N, 3.97. See Supplementary Figs. 12 and 13.

Synthesis of 6-(*tert*-butyl)-3-(trifluoromethyl)-9H-carbazole. DBU (2 eq., 6.06 mmol, 904 µL) was added to 6-(*tert*-butyl)-3-(trifluoromethyl)-9-acetylcarbazole (1 eq., 3.03 mmol, 1.01 g) in MeOH (30 mL), and the mixture was refluxed for 6 h. The reaction was cooled to r.t. and volatiles were evaporated. AcOEt (120 mL) was added, washed with water and brine, and dried

over $MgSO_4$. The residue was purified by silica column chromatography (PE/AcOEt) to afford the product as a white solid (91%, 800 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1H, CH^4), 8.16 (bs, 1H, NH), 8.12 (pseudo s, 1H, CH^5), 7.64 (pseudo dd, J = 8.5, 1.7 Hz, 1H, CH^2), 7.56 (dd, J = 8.6, 1.9 Hz, 1H, CH^8), 7.47 (d, J = 8.5 Hz, 1H, CH^1), 7.41 (d, J = 8.6 Hz, 1H, CH^7), 1.45 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (s, C–*t*Bu), 141.5 (s, C_q), 138.2 (s, C_q), 125.5 (q, J = 271.2 Hz, CF_3), 125.0 (s, CH^7), 123.4 (s, C_q), 122.8 (s, C_q), 122.5 (q, J = 3.7 Hz, CH^2), 121.7 (q, J = 32.1 Hz, C–CF_3), 117.9 (q, J = 4.1 Hz, CH^4), 116.8 (s, CH^5), 110.7 (s, CH^1), 110.6 (s, CH^8), 34.9 (s, C(CH_3)$_3$), 32.1 (s, C(CH_3)$_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.1. Anal. Calcd. for $C_{17}H_{16}F_3N$ (291.32): C, 70.09; H, 5.54; N, 4.81. Found: C, 69.82; H, 5.72; N, 4.63. See Supplementary Figs. 14 and 15.

X-Ray Crystallography.

Crystals of **1** and **2** suitable for X-ray diffraction study were obtained by layering a toluene solution with hexanes. Complex **1** and **2** crystallizes with two independent molecules in the unit cell and molecules of toluene. The CF_3-group was disordered over two half-populated positions for the complex **1** (independent molecule A). For the final refinement, the contribution of severely disordered toluene molecules in the crystals of **1** was removed from the diffraction data with PLATON/SQUEEZE.[1,2] Crystals were mounted in oil on glass fiber and fixed on the diffractometer in a cold nitrogen stream. Data were collected using an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) at 140 K. Data were processed using the CrystAlisPro-CCD and –RED software.[3] The structure was solved by direct methods and refined by the full-matrix least-squares against F^2 in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in a "riding" model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where U(C_i) and U(C_{ii}) are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software.[4]

The principal crystallographic data and refinement parameters:

Complex **1**, CCDC number 1916996, $C_{51}H_{62}AuF_3N_2$, Monoclinic, space group $P2_1/n$, a = 23.0603(9) Å, b = 15.7169(5) Å, c = 26.0909(9) Å, β = 103.114(4)°, V = 9209.7(6) Å^3, Z = 8, d_{calc} = 1.380 g cm^{-3}, μ = 3.242 mm^{-1}, colorless/block, crystal size 0.25 × 0.21 × 0.09 mm, F(000)

= 3904, T_{min}/T_{max} 0.73420/1.00000, R_1 = 0.0341 (from 18085 unique reflections with $I>2\sigma(I)$; R_{int} = 0.0449, R_{sigma} = 0.0392) and wR_2 = 0.0852 (from all 73935 unique reflections), *GOF* = 1.096, $\Delta\rho_{min}/\Delta\rho_{max}$ = 1.65/–1.28.

Complex **2**, CCDC number 1916995, $C_{41}H_{45}AuF_6N_2$, Triclinic, space group *P-1*, *a* = 13.2995(6) Å, *b* = 14.8662(6) Å, *c* = 26.4244(10) Å, α = 74.133(4)°, β = 77.531(3)°, γ = 71.883(4)°, *V* = 4727.0(4) $Å^3$, *Z* = 4, d_{calc} = 1.232 g cm^{-3}, μ = 3.160 mm^{-1}, colorless/block, crystal size 0.16 × 0.11 × 0.07 mm, *F*(000) = 1752, T_{min}/T_{max} 0.70618/1.00000, R_1 = 0.0396 (from 18562 unique reflections with $I>2\sigma(I)$; R_{int} = 0.0548, R_{sigma} = 0.0852) and wR_2 = 0.0754 (from all 41002 unique reflections), *GOF* = 1.022, $\Delta\rho_{min}/\Delta\rho_{max}$ = 1.15/–1.28.

Supplementary References

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