Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPORTING INFORMATION

Novel Dinuclear NHC-Gold(I)-Amido Complexes and Their Application in Energy Transfer Photocatalysis

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General Information

Except for special instructions, all manipulations were carried out under air, in scintillation vials. Solvents for photocatalytic experiments were degassed with Ar and stored over molecular sieves. Other solvents and reagents were used as received without any further purification or distillation. Syringe microfilters were purchased from CarlRoth. N-Aryl imidazoles and and N-(1-methyl)-1*H*-imidazole compounds were prepared according to literature procedures.[1] 3,3'-(hexane-1,6-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-imidazolium) chloride [$IPr^{hexane\text{-}1,6\text{-}diyl}$.2HCl] and the corresponding [$IPr^{hexane\text{-}1,6\text{-}diyl}(AuCl)_2$] were prepared according to literature procedures.[2] ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ or DMSO-d_6 at room temperature on Bruker spectrometer (300 MHz or 400 MHz). Chemical shifts (ppm) are referenced to the residual solvent peak. Coupling constants (*J*) are given in hertz. Abbreviations used in the designation of the signals: s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, td = triplet of doublets, tt = triplet of triplets, q = quadruplet, qt = quadruplet of triplets, hept = heptet.

The samples for spectroscopy were prepared in argon filled glovebox using spectroscopy grade THF as a solvent. Absorption spectra were recorded on Perkin Elmer LAMBDA^{TM} 950 spectrophotometer. Luminescence spectra were recorded in quartz cuvettes with a screw cap on FLS 920 Edinburgh Photoluminescence Spectrometer, equipped with 450W Xenon lamp as an excitation source and PMT detector. The excitation and emission spectra were collected at right angles to the excitation source and were corrected using the standard corrections supplied by the manufacturer for the spectral power of the excitation source and the sensitivity of the detector.

Photophysical analyses in deareated DMSO were carried out at 298 K. Degassed solutions are obtained by means of repeated pump-freeze-thaw cycles (ca. $4x10^{-6}$ mbar) in sealed quartz cuvettes. Emission quantum yields were measured following the method of Demas and

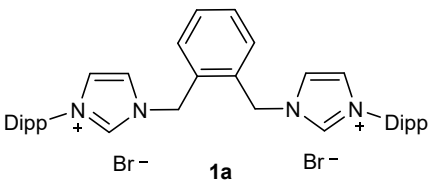
Crosby[3] (standard used: $[Ru(bpy)_3]^{2+}$ in air-equilibrated aqueous solution Φ = 0.04057)[4] Lifetimes longer 10 μs were measured by the above mentioned Edinburgh FS5 spectrofluorimeter. The estimated experimental errors are 2 nm on the band maximum, 5% luminescence lifetime and 15% for emission quantum yields.

Photocatalytic experiments were performed in EvoluChem™ PhotoRedOx Box by HepatoChem, equipped with an EvoluChemTM LED. 365PF (365 nm, 18 W, 9 mW/cm) lamp was used.

General Procedure for Bis-imidazolium Salts

The salts were synthesized according to the modified procedure reported in the literature.[2] A 50 mL flask tube charged with stirring bar, imidazole (2 mmol, 2 equiv.) and aryl halide (1 mmol, 1 equiv.) was heated to 100°C in 12mL dioxane overnight. A white solid was produced in the reaction mixture over time. The reaction mixture was cooled down to room temperature and then precipitate was filtered, washed with ethyl acetate (5 mL x 3) and dried under vacuum.

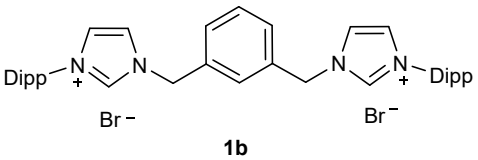
3,3-Bis[(2,6-diisopropylphenyl)-1,1-*o*-phenylenedimethylenebis(imidazolium) dibromide **1a**



1a

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 2H, NC<u>H</u>N), 8.38 (s, 2H, C<u>H</u>=CH), 7.53 (t, *J* = 7.8 Hz, 2H, C<u>H</u>, Dipp), 7.43 – 7.37 (m, 2H, C<u>H</u>, *o*-xylene), 7.34 (dd, *J* = 6.6, 2.7 Hz, 2H, C<u>H</u>, *o*-xylene), 7.30 (d, *J* = 7.9 Hz, 4H, C<u>H</u>, Dipp), 7.20 (s, 2H, CH=C<u>H</u>), 6.53 (s, 4H, C<u>H</u>$_2$), 2.44 – 2.26 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.23 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.18 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 (<u>C</u>(^{i}Pr), Dipp), 138.3 (N<u>C</u>HN), 132.8 (CH$_2$<u>C</u>, *o*-xylene), 132.1 (CH, Dipp), 130.3 (<u>C</u>N, Dipp), 130.0 (C<u>H</u>, *o*-xylene), 129.1 (C<u>H</u>, *o*-xylene), 124.8 (C<u>H</u>, Dipp), 124.7 (<u>C</u>H=CH), 124.4 (CH=<u>C</u>H), 50.4 (<u>C</u>H$_2$), 28.9 (<u>C</u>H(CH$_3$)$_2$), 24.7 (CH(<u>C</u>H$_3$)$_2$), 24.2 (CH(<u>C</u>H$_3$)$_2$). Analytical data obtained are in agreement with reported values.[5]

3,3-Bis[(2,6-diisopropylphenyl)-1,1-*m*-phenylenedimethylenebis(imidazolium) dibromide **1b**

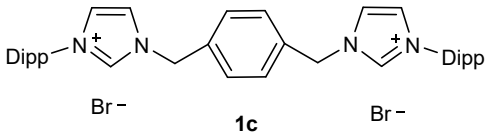


1b

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.83 (s, 2H, NC<u>H</u>N), 8.18 (d, *J* = 15.8 Hz, 4H, C<u>H</u>=CH), 7.74 (s, 1H, C<u>H</u>, *m*-xylene), 7.63 (t, *J* = 7.8 Hz, 2H, C<u>H</u>, Mes), 7.60 – 7.54 (m, 1H, C<u>H</u>, *m*-xylene), 7.49 – 7.43 (m, 6H, C<u>H</u>, Mes; CH, *m*-xylene), 5.63 (s, 4H, C<u>H</u>$_2$), 2.22 (dt, *J* = 13.5, 6.7 Hz, 4H, C<u>H</u>(CH$_3$)$_2$), 1.12 (t, *J* = 7.3 Hz, 24H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (101 MHz, DMSO) δ 145.0 (<u>C</u>(CH$_3$)$_2$, Dipp), 138.0 (N<u>C</u>HN), 135.6 (<u>C</u>CH, *m*-xylene), 131.6 (<u>C</u>H, Dipp), 130.5 (<u>C</u>N, Dipp), 130.1 (<u>C</u>H, *m*-xylene), 128.7 (<u>C</u>H, *m*-xylene), 128.4 (<u>C</u>H, *m*-xylene), 125.4 (<u>C</u>H=CH), 124.5 (<u>C</u>H, Dipp), 123.6 (CH=<u>C</u>H), 52.2 (<u>C</u>H$_2$), 28.1

(C̲H(CH$_3$)$_2$), 23.8 (CH(C̲H$_3$)$_2$), 23.7 (CH(C̲H$_3$)$_2$). Analytical data obtained are in agreement with reported values.[6]

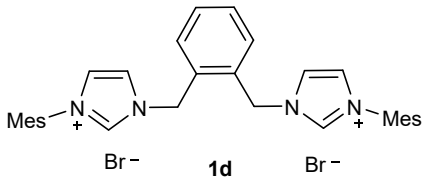
3,3-Bis[(2,6-diisopropylphenyl)-1,1-*p*-phenylenedimethylenebis(imidazolium) dibromide **1c**



1c

^{1}H NMR (300 MHz, CD_2Cl_2) δ 10.82 (s, 2H, NC̲HN), 8.00 (s, 2H), 7.72 (s, 4H), 7.57 (t, *J* = 7.8 Hz, 2H, C̲H, Dipp), 7.34 (d, *J* = 7.8 Hz, 4H, C̲H, Dipp), 7.21 (t, *J* = 1.6 Hz, 2H), 6.10 (s, 4H, C̲H$_2$), 2.28 (dt, *J* = 13.6, 6.8 Hz, 4H, C̲H(CH$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 12H, CH(C̲H$_3$)$_2$), 1.15 (d, *J* = 6.8 Hz, 12H, CH(C̲H$_3$)$_2$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 146.0, 139.0, 135.6, 132.5, 130.8, 130.3, 125.3, 125.0, 123.7, 53.1(C̲H$_2$) 29.3 (C̲H(CH$_3$)$_2$), 24.8 (CH(C̲H$_3$)$_2$), 24.3 (CH(C̲H$_3$)$_2$). Analytical data obtained are in agreement with reported values.[7]

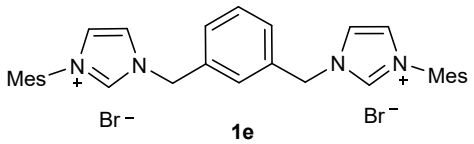
3,3'-Bis[1-mesityl-1*H*-imidazolium]-1,1-*o*-phenylenedimethylenebis(imidazolium) dibromide **1d**



1d

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.36 (t, *J* = 1.5 Hz, 2H, NC̲HN), 8.15 (t, *J* = 1.7 Hz, 2H, C̲H=CH), 7.46 – 7.35 (m, 4H, C̲H, *o*-xylene), 7.18 (t, *J* = 1.8 Hz, 2H, CH=C̲H), 7.00 (s, 4H, C̲H, Mes), 6.45 (s, 4H, C̲H$_2$), 2.34 (s, 6H, C̲H$_3$, Mes), 2.12 (s, 12H, C̲H$_3$, Mes). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 137.7, 134.4, 132.6, 130.8, 130.3, 130.1, 129.7, 124.3, 123.5, 50.5, 21.2, 18.0. Analytical data obtained are in agreement with reported values.[7]

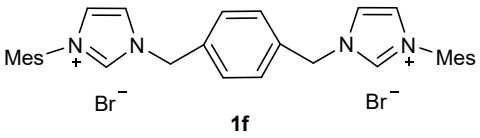
3,3'-Bis[1-mesityl-1*H*-imidazolium]-1,1-*m*-phenylenedimethylenebis(imidazolium) dibromide **1e**



1e

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.48 (s, 2H, NC̲HN), 8.68 (t, *J* = 1.5 Hz, 2H, C̲H=CH), 8.50 (s, 1H, C̲H, *m*-xylene), 7.70 (dd, *J* = 7.7, 1.4 Hz, 2H, C̲H, *m*-xylene), 7.14 – 7.05 (m, 3H, CH=C̲H; C̲H, *m*-xylene), 6.96 (s, 4H, CH, Mes), 5.91 (s, 4H, C̲H$_2$), 2.31 (s, 6H, C̲H$_3$), 2.01 (s, 12H, C̲H$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 137.4, 134.9, 134.2, 131.6, 130.8, 130.1, 130.0, 129.9, 124.7, 123.4, 52.5, 21.2, 17.8. Anal. Calcd for $C_{32}H_{36}Br_2N_4$: C, 60.39; H, 5.7; N, 8.8; found: C, 59.61; H, 5.91; N, 8.62.

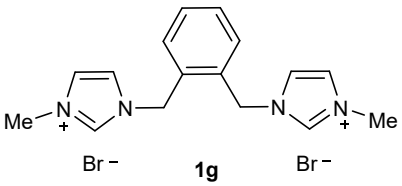
3,3'-Bis[1-mesityl-1*H*-imidazolium]-1,1-*p*-phenylenedimethylenebis(imidazolium) dibromide **1f**



1f

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (t, *J* = 1.5 Hz, 2H, NC<u>H</u>N), 8.09 (t, *J* = 1.7 Hz, 2H, C<u>H</u>=CH), 7.97 (t, *J* = 1.8 Hz, 2H, CH=C<u>H</u>), 7.55 (s, 4H, C<u>H</u>, *p*-xylene), 7.15 (s, 4H, C<u>H</u>, Mes), 5.58 (s, 4H, C<u>H</u>$_2$), 2.33 (s, 6H, C<u>H</u>$_3$), 2.00 (s, 12H, C<u>H</u>$_3$). ^{13}C NMR (101 MHz, DMSO) δ 140.3, 137.7, 135.4, 134.2, 131.1, 129.3, 128.9, 124.4, 123.2, 51.9, 20.6, 16.9. Analytical data obtained are in agreement with reported values.[7]

3,3'-Bis[1-methyl-1*H*-imidazolium]-1,1-*o*-phenylenedimethylenebis(imidazolium) dibromide **1g**



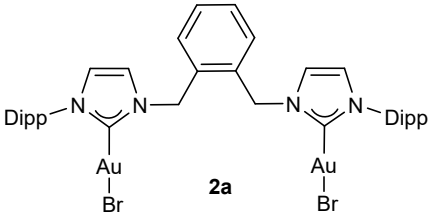
1g

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.25 (s, 2H, NC<u>H</u>N), 7.78 (dt, *J* = 5.6, 1.7 Hz, 4H, C<u>H</u>=CH), 7.48 (dd, *J* = 5.7, 3.4 Hz, 2H, C<u>H</u>, o-xylene), 7.33 (dd, *J* = 5.6, 3.5 Hz, 2H, C<u>H</u>, *o*-xylene), 5.67 (s, 4H, C<u>H</u>$_2$), 3.88 (s, 6H, C<u>H</u>$_3$). ^{13}C NMR (75 MHz, DMSO) δ 136.9, 132.9, 129.7, 129.6, 124.0, 122.5, 49.0, 36.0. Analytical data obtained are in agreement with reported values.[8]

General Procedure for Dinuclear Gold(I) Complexes [(L)(AuX)$_2$]

A vial was charged, under air, with the corresponding dinuclear NHC·2HBr (0.5 mmol, 1 equiv.), [Au(DMS)Cl] (2 equiv.), K_2CO_3 (6 equiv.) and acetone (0.2 M). The vial was closed with a screw cap, and reaction mixture was stirred at 60°C for 5-12 hours. After this time, the mixture was filtered through a pad of silica and the silica was washed with DCM or DCM/MeOH. The filtrate was then concentrated and pentane was added to precipitate the complex, affording a colorless solid after filtration. Then the compound was dried under vacuum overnight.

[(IPr)$^{o\text{-xylene}}$(AuBr)$_2$] **2a**

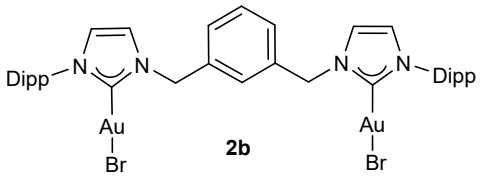


2a

Colorless solid (506.1mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H, C<u>H</u>, Dipp), 7.42 (dd, *J* = 5.7, 3.3 Hz, 2H, C<u>H</u>, *o*-xylene), 7.29 – 7.25 (m, 4H, C<u>H</u>, Dipp), 7.24 (d, *J* = 1.9 Hz, 2H, C<u>H</u>=CH), 7.07 (d, *J* = 1.9 Hz, 2H, CH=C<u>H</u>), 7.04 (dd, *J* = 5.6, 3.4 Hz, 2H, C<u>H</u>, *o*-xylene), 5.61 (s, 4H, C<u>H</u>$_2$), 2.51 (dt,

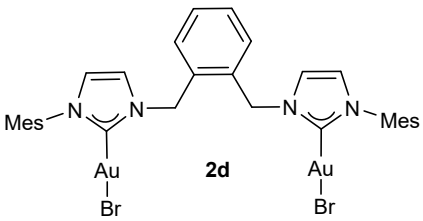
J = 13.7, 6.8 Hz, 4H, C<u>H</u>(CH$_3$)$_2$), 1.30 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.17 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.6 (N<u>C</u>N), 145.8 (<u>C</u>(*i*Pr), Dipp), 134.0 (CH$_2$<u>C</u>, *o*-xylene), 133.3 (<u>C</u>N, Dipp), 130.9, 129.6 (<u>C</u>H, *o*-xylene), 128.3 (<u>C</u>H, *o*-xylene), 124.8, 124.4 (<u>C</u>H, Dipp), 121.1, 52.4 (<u>C</u>H$_2$), 28.7 (<u>C</u>H(CH$_3$)$_2$), 24.6 (CH(<u>C</u>H$_3$)$_2$), 24.5 (CH(<u>C</u>H$_3$)$_2$). HRMS calculated for $C_{38}H_{46}N_4Au_2Br$ [M - Br$^-$]$^+$:1031.2237; found : 1031.2241. Anal. Calcd for $C_{38}H_{46}Au_2Br_2N_4$: C, 41.02; H, 4.17; N, 5.04; found: C, 41.55; H, 3.89; N, 5.09.

[(IPr)$^{m\text{-xylene}}$(AuBr)$_2$] **2b**



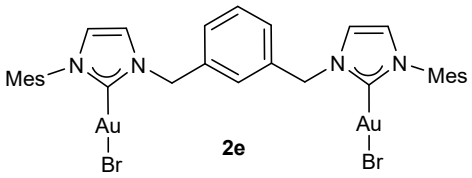
Colorless solid (445.0mg, 80%).^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.79 (d, *J* = 1.9 Hz, 2H, CH=C<u>H</u>), 7.72 (d, *J* = 1.8 Hz, 2H, C<u>H</u>=CH), 7.57 – 7.46 (m, 3H, CH, Dipp; CH, *m*-xylene), 7.45 (s, 1H, CH, *m*-xylene), 7.37 (d, *J* = 7.7 Hz, 4H, CH, Dipp), 7.24 (d, *J* = 7.7 Hz, 2H, CH, *m*-xylene), 5.53 (s, 4H, C<u>H</u>$_2$), 2.35 (dt, *J* = 13.6, 6.7 Hz, 4H, C<u>H</u>(CH$_3$)$_2$), 1.22 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.12 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (75 MHz, DMSO) δ 174.6 (N<u>C</u>N), 145.3 (<u>C</u>(*i*Pr)), 137.3 (CH$_2$<u>C</u>, *m*-xylene), 134.2 (<u>C</u>N, Dipp), 130.3, 129.5, 126.6, 126.4, 124.7, 123.9 (<u>C</u>H, Dipp), 122.1, 53.4 (<u>C</u>H$_2$), 28.0 (<u>C</u>H(CH$_3$)$_2$), 23.9 (CH(<u>C</u>H$_3$)$_2$), 23.7 (CH(<u>C</u>H$_3$)$_2$). Anal. Calcd for $C_{38}H_{46}Au_2Br_2N_4$: C, 41.02; H, 4.17; N, 5.04; found: C, 41.04; H, 4.55; N, 5.52.

[(IMes)$^{o\text{-xylene}}$(AuBr)$_2$] **2d**



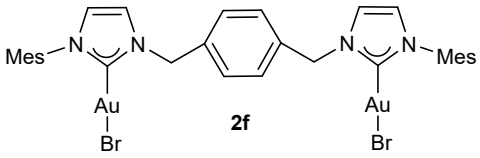
Colorless solid (426.78mg, 83%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (dd, *J* = 5.7, 3.3 Hz, 2H, C<u>H</u>, *o*-xylene), 7.22 (d, *J* = 2.0 Hz, 2H, C<u>H</u>=CH), 7.04 – 7.00 (m, 4H, C<u>H</u>, *o*-xylene; C<u>H</u>=CH), 6.97 (d, *J* = 0.4 Hz, 4H, C<u>H</u>, Mes), 5.58 (s, 4H, C<u>H</u>$_2$), 2.33 (s, 6H, C<u>H</u>$_3$), 2.08 (s, 12H, C<u>H</u>$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 176.6 (N<u>C</u>N), 140.0 (CH$_3$<u>C</u>, Mes), 134.8 (CH$_3$<u>C</u>, Mes), 134.6, 133.4, 129.7 (<u>C</u>H, Mes), 129.6(<u>C</u>H, *o*-xylene), 128.3 (<u>C</u>H, *o*-xylene), 123.6 (<u>C</u>H=CH), 121.4 (<u>C</u>H=CH), 52.4 (<u>C</u>H$_2$), 21.3 (<u>C</u>H$_3$), 18.3 (<u>C</u>H$_3$). HRMS calculated for $C_{32}H_{34}N_4Au_2Br$ [M - Br$^-$]$^+$: 947.1298; found : 947.1294.

[(IMes)$^{m\text{-xylene}}$(AuBr)$_2$] **2e**



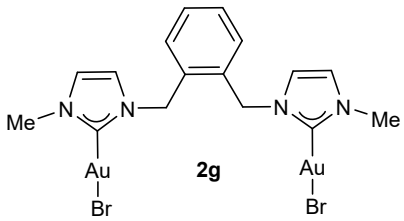
Colorless solid (390.78mg, 76%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.49 – 7.42 (m, 2H, C<u>H</u>, *m*-xylene), 7.38 – 7.32 (m, 2H, C<u>H</u>, *m*-xylene), 7.27 (d, *J* = 1.9 Hz, 2H, C<u>H</u>=CH), 7.04 (s, 4H, C<u>H</u>, Mes), 6.97 (d, *J* = 2.0 Hz, 2H, CH=C<u>H</u>), 5.51 (s, 4H, C<u>H</u>$_2$), 2.37 (s, 6H, C<u>H</u>$_3$), 2.05 (s, 12H, C<u>H</u>$_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.4 (N<u>C</u>N), 140.5 (CH$_3$<u>C</u>, Mes), 137.2 (CH$_2$<u>C</u>, *m*-xylene), 135.5 (CH$_3$<u>C</u>, Mes), 135.4 (<u>C</u>N, Mes), 130.6, 129.9 (<u>C</u>H, Mes), 128.3, 128.0, 123.4, 121.8, 55.2 (<u>C</u>H$_2$), 21.5 (<u>C</u>H$_3$), 18.2 (<u>C</u>H$_3$). HRMS calculated for $C_{33}H_{34}N_5Au_2$ [M-2Br$^-$+CN$^+$]$^+$: 894.2145; found : 894.2144.

[(IMes)$^{p\text{-xylene}}$(AuBr)$_2$] **2f**



Colorless solid (287.95mg, 56%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.82 (d, *J* = 1.9 Hz, 2H, C<u>H</u>=CH), 7.54 (d, *J* = 1.9 Hz, 2H, CH=C<u>H</u>), 7.40 (s, 4H, CH, *p*-xylene), 7.08 (s, 4H, CH, Mes), 5.49 (s, 4H, C<u>H</u>$_2$), 2.32 (s, 6H, C<u>H</u>$_3$), 1.97 (s, 12H, C<u>H</u>$_3$). ^{13}C NMR (75 MHz, DMSO) δ 173.4 (NCN), 138.9 (CH$_3$<u>C</u>, Mes), 136.6 (CH$_2$<u>C</u>, *p*-xylene), 134.9, 134.5, 129.0, 127.6, 123.5, 122.4, 53.2 (<u>C</u>H$_2$), 20.6 (<u>C</u>H$_3$), 17.3 (<u>C</u>H$_3$). Anal. Calcd for $C_{32}H_{34}Au_2Br_2N_4$: C, 37.37; H, 3.33; N, 5.45; found: C, 37.48; H, 3.09; N, 5.29.

[(IMe)$^{o\text{-xylene}}$(AuBr)$_2$] **2g**



Colorless solid (250.13mg, 61%). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.51 (d, *J* = 1.9 Hz, 2H, C<u>H</u>=CH), 7.39 – 7.31 (m, 4H, CH, *o*-xylene; C<u>H</u>=CH), 7.07 (dd, *J* = 5.6, 3.5 Hz, 2H, CH=C<u>H</u>), 5.49 (s, 4H, C<u>H</u>$_2$), 3.82 (s, 6H, C<u>H</u>$_3$). ^{13}C NMR (75 MHz, DMSO) δ 173.0 (N<u>C</u>N), 134.1 (CH$_2$<u>C</u>, *o*-xylene), 128.6 (<u>C</u>H, *o*-xylene), 128.4 (<u>C</u>H, *o*-xylene), 123.4 (<u>C</u>H=CH), 121.4 123.4 (<u>C</u>H=CH), 50.7 123.4 (<u>C</u>H$_2$), 37.8 (<u>C</u>H$_3$). HRMS calculated for $C_{16}H_{18}N_4Au_2Br$ [M - Br$^-$]$^+$: 739.0046; found: 739.0115.

General Procedure for Dinuclear Gold(I) Amido Complexes [(L){Au(amido)}$_2$]

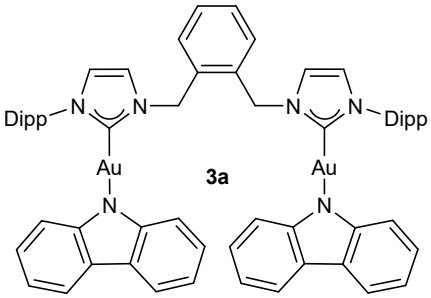
Path A (Carbazole as the ligand): A 4 mL vial equipped with a screw cap and a stirring bar was charged, under air, with the corresponding [bisNHC(AuBr)$_2$] (0.1 mmol, 1 equiv.), carbazole (0.2 mmol, 2 equiv., 33.4 mg), K_2CO_3 (0.4 mmol, 4 equiv., 55.3 mg) and acetone (1 mL). Reaction mixture was stirred at 60°C for 6-22 hours. The solvent was removed under vacuum and purification of the product was carried out by filtration through microfilter with THF (2 mL x 2) or DCM/MeOH (v:v = 10:1, 2 mL x 2). The solvent was then concentrated and pentane was added to precipitate the complex, affording a colorless solid. After filtration, the compound was dried under vacuum overnight.

Path B (Other amines as the ligand): A 4 mL vial equipped with a screw cap and a stirring bar was charged, under air, with the corresponding [(IPr)$^{o\text{-xylene}}$(AuBr)$_2$] (0.1 mmol, 1 equiv., 111.2mg), amine (0.2 mmol, 2 equiv.), K_2CO_3 (0.6 mmol, 6 equiv., 83 mg) and EtOH (1 mL). The mixture was stirred at 40°C for 12 hours. The solvent was removed under vacuum and purification of the product was carried out by filtration through an alumina plug with THF (2 mL x 2). The solvent was then concentrated and pentane was added to precipitate the complex, affording a colorless solid. Then the compound was dried under vacuum overnight.

One-pot synthesis of binuclear CMA complex

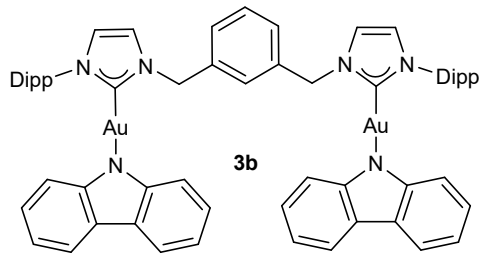
A vial was charged, under air, with 72.1 mg of [IPr$^{o\text{-xylene}}$·2HCl] (0.1 mmol, 1 equiv.), 82.9 mg of K_2CO_3 (0.6 mmol, 6 equiv.), 58.9 mg of Au(DMS)Cl (0.2 mmol, 2 equiv.), and the solids were suspended in acetone (1 mL). The reaction mixture was stirred at 60 °C for 5 hours. Then, the reaction was cooled to room temperature and 33.4 mg of carbazole (0.2 mmol, 2 equiv.), 55.3 mg of K_2CO_3 (0.4 mmol, 4 equiv.) and 1 mL of acetone were added. The reaction mixture was stirred at 60 °C for another 12h. After this time the solvent was removed under vacuum and the residue was taken up in THF (2 mL) and filtered through basic alumina which was washed using THF (1 mL x 3). The filtrate was concentrated to dryness, and the resulting solid was washed with diethyl ether and dried, affording the desired complex [(IPr)$^{o\text{-xylene}}${Au(Cbz) }$_2$] **3a** as a colorless solid in 76% yield (97.7 mg).

[(IPr)$^{o\text{-xylene}}${Au(Cbz)$_2$}] **3a**



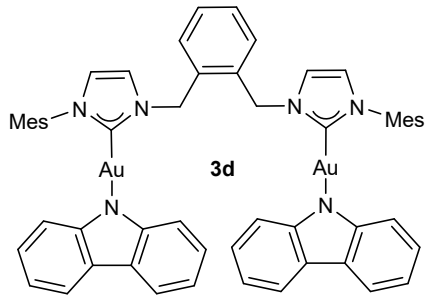
Colorless solid (106.5mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 4H, C<u>H</u>, Cbz), 7.57 – 7.50 (m, 4H, C<u>H</u>, Dipp and C<u>H</u>, *o*-xylene), 7.30 (d, *J* = 7.8 Hz, 4H, C<u>H</u>, Dipp), 7.22 (dd, *J* = 5.6, 3.4 Hz, 2H, C<u>H</u>, *o*-xylene), 7.11 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 4H, C<u>H</u>, Cbz), 7.02 (d, *J* = 8.0 Hz, 4H, C<u>H</u>, Cbz), 6.98 (d, *J* = 1.9 Hz, 2H, C<u>H</u>=CH), 6.98 – 6.93 (m, 4H, C<u>H</u>, Cbz), 6.87 (d, *J* = 1.9 Hz, 2H, CH=C<u>H</u>), 5.74 (s, 4H, C<u>H</u>$_2$), 2.61 – 2.47 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.34 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.10 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8 (N<u>C</u>N), 149.5 (CH<u>C</u>N, Cbz), 146.1 (<u>C</u>(*i*Pr)), 134.3 (CH$_2$<u>C</u>, *o*-xylene), 133.9 (<u>C</u>N, Dipp), 130.8, 129.6 (<u>C</u>H, *o*-xylene), 128.6 (<u>C</u>H, *o*-xylene), 124.4 (<u>C</u>H, Dipp), 124.0 (<u>C</u>CH, Cbz), 123.5 (<u>C</u>H, Cbz), 121.3, 119.7 (<u>C</u>H, Cbz), 116.1 (<u>C</u>H, Cbz), 113.6 (<u>C</u>H, Cbz), 52.7 (<u>C</u>H$_2$), 28.9 (<u>C</u>HCH$_3$), 24.6 (CH<u>C</u>H$_3$), 24.3 (CH<u>C</u>H$_3$). Anal. Calcd for $C_{62}H_{62}Au_2N_6$: C, 57.95; H, 4.86; N, 6.54; found: C, 57.54; H, 4.61; N, 6.17.

[(IPr)*m*-xylene{Au(Cbz)}$_2$] **3b**



Colorless solid (91.3mg, 71%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.92 (d, *J* = 7.5 Hz, 4H, C<u>H</u>, Cbz), 7.76 (s, 4H, C<u>H</u>=CH), 7.68 – 7.60 (m, 3H), 7.58 – 7.50 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 4H, C<u>H</u>, Cbz), 7.41 (s, 1H, C<u>H</u>, *m*-xylene), 7.10 – 7.03 (m, 4H, C<u>H</u>, Cbz), 6.99 (d, *J* = 7.9 Hz, 4H, C<u>H</u>, Dipp), 6.90 – 6.79 (m, 4H, C<u>H</u>, Cbz), 5.69 (s, 4H, C<u>H</u>$_2$), 2.45 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.26 (d, *J* = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.16 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (75 MHz, DMSO) δ 174.4 (N<u>C</u>N), 148.7 (CH<u>C</u>N, Cbz), 145.7 (<u>C</u>*i*Pr), 137.8, 134.7 (<u>C</u>N, Dipp), 130.2, 129.5, 126.6 (<u>C</u>CH, *m*-xylene), 124.6, 124.0, 123.5, 123.2 (<u>C</u>CH, Cbz), 122.5 (<u>C</u>H, Cbz), 119.2 (<u>C</u>H, Cbz), 115.8 (<u>C</u>H, Cbz), 113.3 (<u>C</u>H, Cbz), 53.5 (<u>C</u>H$_2$), 28.2 (<u>C</u>HCH$_3$), 23.9 (CH<u>C</u>H$_3$), 23.8 (CH<u>C</u>H$_3$). Anal. Calcd for $C_{62}H_{62}Au_2N_6$: C, 57.95; H, 4.86; N, 6.54; found: C, 58.02; H, 4.38; N, 5.96.

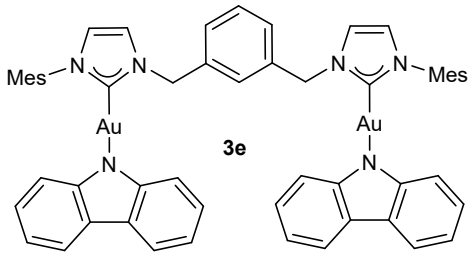
[(IMes)*o*-xylene{Au(Cbz)}$_2$] **3d**



Colorless solid (99.7mg, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 4H, C<u>H</u>, Cbz), 7.54 (dd, *J* = 5.7, 3.3 Hz,

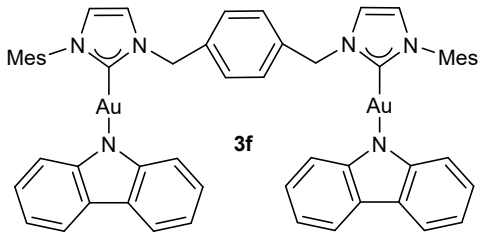
2H, CH, *o*-xylene), 7.20 (dd, *J* = 5.6, 3.5 Hz, 2H, CH, *o*-xylene), 7.16 – 7.11 (m, 4H, CH, Cbz), 7.05 (d, *J* = 8.0 Hz, 4H, CH, Cbz), 7.01 (s, 4H, CH, Mes), 7.00 – 6.94 (m, 4H, CH, Cbz), 6.88 (d, *J* = 1.9 Hz, 2H, CH=CH), 6.60 (d, *J* = 1.9 Hz, 2H, CH=CH), 5.63 (s, 4H, CH_2), 2.37 (s, 6H, CH_3), 2.09 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7 (NCN), 149.5 (CHCN, Cbz), 140.0 (CH_3C, Mes), 135.0 (CH_3C, Mes), 134.9 (CN, Mes), 134.0 (CCH_2, *o*-xylene), 129.6 (CH, *o*-xylene), 129.5 (CH, Mes), 128.8 (CH, *o*-xylene), 124.0 (CCH, Cbz), 123.6 (CH, Cbz), 122.9 (CH=CH), 121.5 (CH=CH), 119.8 (CH, Cbz), 116.2 (CH, Cbz), 113.7 (CH, Cbz), 52.5 (CH_2), 21.3 (CH_3), 18.2 (CH_3). HRMS calculated for $C_{44}H_{42}N_5Au_2$ [M -Cbz]$^+$:1034.2771; found : 1034.2773.

[(IMes)$^{m\text{-xylene}}${Au(Cbz)}$_2$] **3e**



Colorless solid (109.2mg, 91%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.93 (d, *J* = 7.6 Hz, 4H, CH, Cbz), 7.76 (d, *J* = 1.9 Hz, 2H, CH=CH), 7.57 (d, *J* = 1.9 Hz, 2H, CH=CH), 7.51 (m, 4H, CH, *m*-xylene), 7.15 (s, 4H, CH, Mes), 7.10 (m, 4H, CH, Cbz), 7.03 (d, *J* = 7.8 Hz, 4H, CH, Cbz), 6.90 – 6.83 (m, 4H, CH, Cbz), 5.67 (s, 4H, CH_2), 2.39 (s, 6H, CH_3), 2.06 (s, 12H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ 173.6 (NCN), 148.7 (CN, Cbz), 139.0 (CH_3C, Mes), 137.9 (CH_2C, *m*-xylene), 135.4 (CN, Mes), 134.9 (CH_3C, Mes), 129.5, 128.9 (CH, Mes), 127.0 (CH, *m*-xylene), 126.1 (CH_2C, *m*-xylene), 123.5, 123.2, 122.6, 119.3 (CH, Cbz), 115.8 (CH, Cbz), 113.4 (CH, Cbz), 53.5 (CH_2), 20.7 (CH_3), 17.5 (CH_3). HRMS calculated for $C_{44}H_{42}N_5Au_2$ [M -Cbz]$^+$:1034.2771; found : 1034.2767

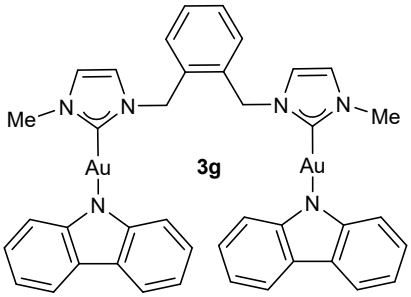
[(IMes)$^{p\text{-xylene}}${Au(Cbz)$_2$}] **3f**



Colorless solid (81.7mg, 68%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.93 (d, *J* = 7.6 Hz, 4H, CH, Cbz), 7.87 (d, *J* = 1.9 Hz, 2H, CH=CH), 7.63 (d, *J* = 1.9 Hz, 2H, CH=CH), 7.60 (s, 4H, CH, *p*-xylene), 7.17 (s, 4H, CH, Mes), 7.06 (m, 8H, CH, Cbz), 6.93 – 6.81 (m, 4H, CH, Cbz), 5.66 (s, 4H, CH_2), 2.39 (s, 6H, CH_3), 2.06 (s, 12H, CH_3). ^{13}C NMR (101 MHz, DMSO) δ 173.4 (NCN),

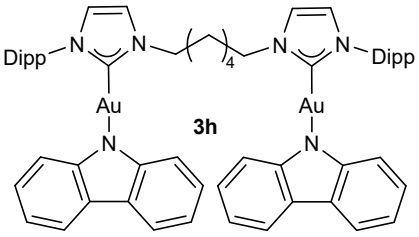
148.7 (CN, Cbz), 139.1 (CH_3C, Mes), 137.1 (CH_2C, *p*-xylene), 135.4 (CN, Mes), 134.9 (CH_3C, Mes), 128.9 (CH, Mes), 127.9 (CH, *p*-xylene), 123.5 (CH, Cbz), 123.2 (CH=CH), 122.8, 119.3 (CH, Cbz), 115.8 (CH, Cbz), 113.4 (CH, Cbz), 53.3 (CH_2), 20.7 (CH_3), 17.4 (CH_3). Anal. Calcd for $C_{56}H_{50}Au_2N_6$: C, 56.01; H, 4.20; N, 7.00; found: C, 55.48; H, 4.04; N, 6.62.

[(IMe)$^{o\text{-xylene}}${Au(Cbz)}$_2$] **3g**



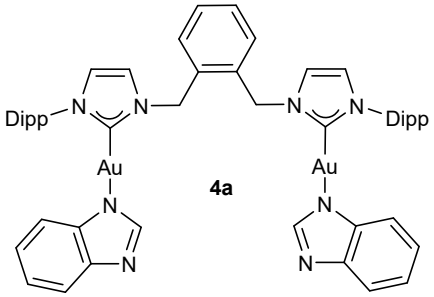
Colorless solid (71.5mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.3 Hz, 4H, CH, Cbz), 7.46 (dd, *J* = 5.7, 3.4 Hz, 2H, CH, *o*-xylene), 7.40 (d, *J* = 8.1 Hz, 4H, CH, Cbz), 7.35 – 7.29 (m, 6H, CH, *o*-xylene; CH=CH), 7.14 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 4H, CH, Cbz), 6.95 – 6.89 (m, 4H, CH, Cbz), 5.79 (s, 4H, CH_2), 3.61 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ 172.6 (NCN), 148.9 (CN, Cbz), 134.5 (CH_2C, *o*-xylene), 129.0 (CH, *o*-xylene), 128.7 (CH, *o*-xylene), 123.6 (CH, Cbz), 123.3 (CHC, Cbz), 123.1 (CH=CH), 121.5 (CH=CH), 119.3 (CH, Cbz), 115.8 (CH, Cbz), 113.7 (CH, Cbz), 51.1(CH_2), 37.4 (CH_3).

[(IPr)$^{\text{hexane-1,6-diyl}}${Au(Cbz)}$_2$] **3h**



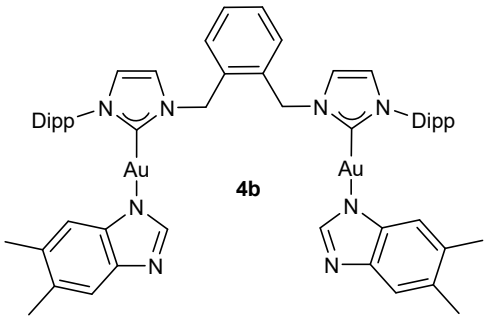
Colorless solid (116.4mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 4H, CH, Cbz), 7.56 (t, *J* = 7.8 Hz, 2H, CH, Dipp), 7.32 (d, *J* = 7.8 Hz, 4H, CH, Dipp), 7.21 – 7.17 (m, 8H, CH, Cbz), 6.99 (ddd, *J* = 7.9, 5.3, 2.7 Hz, 4H, CH, Cbz), 6.72 (d, *J* = 1.9 Hz, 2H, CH=CH), 6.48 (d, *J* = 1.9 Hz, 2H, CH=CH), 4.19 (t, *J* = 7.0 Hz, 4H, CH_2), 2.48 – 2.32 (m, 4H, $CH(CH_3)_2$), 2.00 (t, *J* = 6.3 Hz, 4H, CH_2), 1.63 (s, 4H, CH_2), 1.28 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9 (NCN), 149.7 (CN, Cbz), 146.2 (C(^{i}Pr)), 134.7 (CN, Dipp), 130.6 (CH, Dipp), 124.3 (CH, Cbz), 124.0 (CCH, Cbz), 123.6 (CH, Dipp), 123.3 (CH=CH), 120.6 (CH=CH), 119.7 (CH, Cbz), 116.0 (CH, Cbz), 113.7 (CH, Cbz), 50.3 (CH_2), 31.1 (CH_2), 28.67 ($CH(CH_3)_2$), 25.1(CH_2), 24.5 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$). Anal. Calcd for $C_{60}H_{66}Au_2N_6$: C, 56.96; H, 5.26; N, 6.64; found: C, 57.61; H, 4.95; N, 6.13.

[(IPr)$^{o\text{-xylene}}${Au(1*H*-benzimidazolato)}$_2$] **4a**



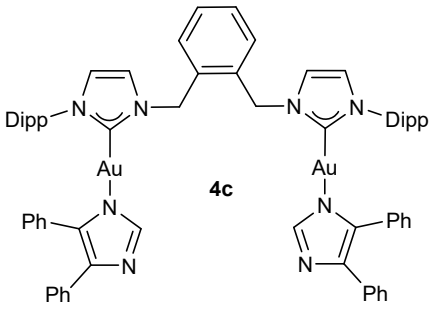
Colorless solid (96.1mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H, CH, amine), 7.60 (s, 2H, NCHN, amine), 7.56 – 7.49 (m, 4H, CH, Dipp; CH, *o*-xylene), 7.29 (d, *J* = 7.8 Hz, 4H, CH, Dipp), 7.13 (dd, *J* = 5.5, 3.5 Hz, 2H, CH, *o*-xylene), 7.05 – 6.97 (m, 2H, CH, amine), 6.91 (m, 4H, CH, amine; CH=CH), 6.85 (d, *J* = 1.9 Hz, 2H, CH=CH), 6.79 (d, *J* = 7.8 Hz, 2H, CH, amine), 5.62 (s, 4H, CH_2), 2.48 (dt, *J* = 13.6, 6.8 Hz, 4H, $CH(CH_3)_2$), 1.31 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.15 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4 (NCN), 150.5 (CH, amine), 145.8 (C(*i*Pr), Dipp), 144.4 (CN, amine), 142.3 (CN, amine), 134.0 (CN, Dipp), 133.8 (CH_2C, *o*-xylene), 131.1 (CH, Dipp), 129.8 (CH, *o*-xylene), 128.8 (CH, *o*-xylene), 124.5 (CH, Dipp), 124.4, 121.4, 120.0, 119.9, 118.9 (CH, amine), 114.1 (CH, amine), 52.7 (CH_2), 28.8 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$). Anal. Calcd for $C_{52}H_{56}Au_2N_8$: C, 52.62; H, 4.76; N, 9.44; found: C, 52.85; H, 4.11; N, 8.54.

[(IPr) $^{o\text{-xylene}}${Au(5,6-dimethyl-1*H*-benzimidazolato}$_2$)] **4b**



Colorless solid (106.9mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 6H, CH, amine; CH, Dipp; CH, *o*-xylene), 7.39 (s, 2H, CH, amine), 7.31 (d, *J* = 7.8 Hz, 4H, CH, Dipp), 7.12 (dd, J = 5.5, 3.4 Hz, 2H, CH, *o*-xylene), 6.99 (d, J = 1.9 Hz, 2H, CH=CH), 6.90 (d, *J* = 1.9 Hz, 2H, CH=CH), 6.56 (s, 2H, CH, amine), 5.62 (s, 4H, CH_2), 2.51 (dt, *J* = 13.6, 6.8 Hz, 4H, $CH(CH_3)_2$), 2.28 (s, 6H, CH_3, amine), 2.20 (s, 6H, CH_3, amine), 1.32 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.15 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8 (NCN), 149.8 (CH, amine), 145.9 (C(*i*Pr), Dipp), 143.0 (CN, amine), 140.9 (CN, amine), 140.2, 134.1 (CN, Dipp), 133.8 (CH_2C, *o*-xylene), 131.1 (CH, Dipp), 129.7 (CH, *o*-xylene), 128.7 (CH, *o*-xylene), 128.5 (CH_3C, amine), 124.4 (CH, Dipp), 124.3, 121.4, 118.9 (CH, amine), 114.3 (CH, amine), 52.7 (CH_2), 28.9 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 20.4 (CH_3, amine), 20.4 (CH_3, amine). Anal. Calcd for $C_{56}H_{64}Au_2N_8$: C, 54.11; H, 5.19; N, 9.01; found: C, 53.76; H, 3.93; N, 8.86.

[(IPr) $^{o\text{-xylene}}${Au(4,5-diphenyl-1*H*-imidazolato)}$_2$] **4c**



Colorless solid (121.0mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H, C<u>H</u>, Dipp), 7.45 – 7.40 (m, 6H, C<u>H</u>, Ph), 7.31 (dd, *J* = 8.2, 1.3 Hz, 4H, C<u>H</u>, Ph), 7.25 (d, *J* = 7.2 Hz, 4H, C<u>H</u>, Dipp), 7.16 – 7.10 (m, 4H, C<u>H</u>, Ph), 7.08 (s, 2H, C<u>H</u>, amine), 7.06 – 7.00 (m, 4H, C<u>H</u>, *o*-xylene), 6.99 – 6.92 (m, 8H, C<u>H</u>, Ph; C<u>H</u>=CH), 6.84 (d, *J* = 1.9 Hz, 2H, CH=C<u>H</u>), 5.29 (s, 2H, C<u>H</u>$_2$), 2.38 (dt, *J* = 13.7, 6.8 Hz, 4H, C<u>H</u>$(CH_3)_2$), 1.17 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3)_2$), 1.10 (d, *J* = 6.9 Hz, 12H, CH(C<u>H</u>$_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9 (N<u>C</u>N), 145.6 (<u>C</u>(^{i}Pr), Dipp), 143.9, 137.2, 137.1, 136.9, 134.4, 133.8 (<u>C</u>N, Dipp), 133.3 (CH_2<u>C</u>, *o*-xylene), 131.0 (<u>C</u>H, Dipp), 129.5, 129.4 (<u>C</u>H, Ph), 128.2, 128.0, 127.9 (<u>C</u>H, *o*-xylene), 127.4 (<u>C</u>H, Ph), 126.0 (<u>C</u>H, Dipp), 125.2 (<u>C</u>H, Ph), 124.7 (<u>C</u>H=CH), 124.4 (<u>C</u>H, Dipp), 121.2 (CH=<u>C</u>H), 52.3 (<u>C</u>H_2), 28.8 (<u>C</u>H$(CH_3)_2$), 24.5 (CH(<u>C</u>$H_3)_2$), 24.2 (CH(<u>C</u>$H_3)_2$). Anal. Calcd for $C_{68}H_{68}Au_2N_8$: C, 58.70; H, 4.93; N, 8.05; found: C, 58.65; H, 4.84; N, 7.96.

Photocatalytic Experiments

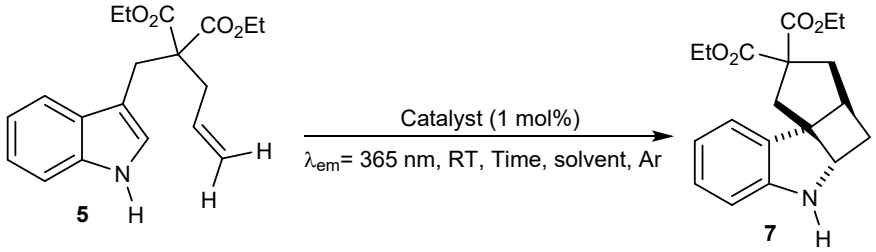
General procedure for the [2+2] cycloaddition of diallyl ether

Diallyl ether (0.16 mmol, 40 mg) was weighted and transferred in 4 mL vial equipped with stirring bar and catalyst (0.5 mol%) was added from the stock solution. Solvent (3 mL) was added in reaction mixture and the vial was closed with screw cap and was degassed by bubbling Ar for 3 minutes. The vial was placed into photoreactor for indicated time. The conversion was determined by gas chromatography using dodecane as internal standard. Each experiment was performed twice and the average conversion is reported.

General procedure for the [2+2] cycloaddition of indole

Diethyl 2-((1*H*-indol-3-yl)methyl)-2-allylmalonate (0.1 mmol, 32.9 mg) was weighted and transferred in 4 mL vial equipped with stirring bar and catalyst (1 mol%) was added from the stock solution. Solvent (2 mL) was added in reaction mixture and the vial was closed with screw cap and was degassed by bubbling Ar for 3 minutes. The vial was placed into photoreactor for indicated time. The residue was purified through silica gel column chromatography by using petroleum ether/ethyl acetate (6:1) as the eluent. Each experiment was performed twice and the average yield is reported.

Table S1 Selected optimization results of the reaction conditions for indole **5**[a]



Entry	Catalyst (mol%)	Solvent (ml)	Time (h)	Conversion (Yield)[b] (%)
1	**3a**	EtOAc	1	99 (91)
2	**3b**	EtOAc	1	99
3	**3d**	EtOAc	1	99
4	**3e**	EtOAc	1	99
5	**3f**	EtOAc	1	50

[a] Indole **5** (0.1 mol, 1 eq.), catalyst (1 mol%), solvent (2 ml) at room temperature under Ar. [b] NMR conversion (Isolated yields are in parentheses).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 19.5, 7.4 Hz, 2H), 6.74 (t, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.26 (dq, *J* = 14.1, 7.0 Hz, 4H), 4.12 – 4.03 (m, 1H), 2.90 (dd, *J* = 7.6, 3.6 Hz, 1H), 2.80 (d, *J* = 14.3 Hz, 1H), 2.66 – 2.39 (m, 3H), 2.20 – 2.00 (m, 2H), 1.30 (dd, *J* = 15.1, 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 172.2, 152.4, 133.5, 128.3, 123.2, 119.2, 110.4,

63.5, 61.9, 61.7, 60.9, 60.8, 47.1, 43.6, 41.1, 35.4, 14.2. Analytical data obtained are in agreement with reported values.[9]

General procedure for the cyclization of indole 6

Diethyl 2-((1*H*-indol-3-yl)methyl)malonate were synthesized according to previously reported procedure.[9]

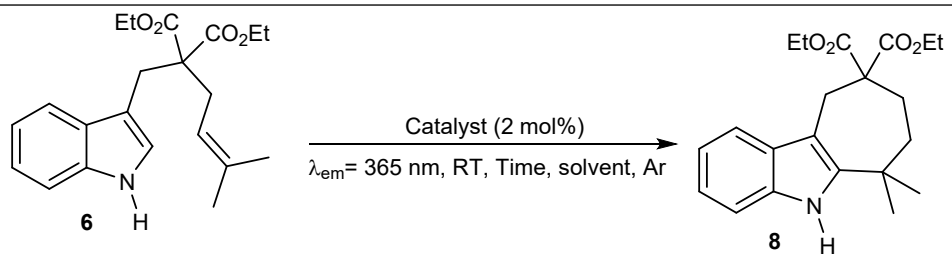
The synthetic route of diethyl 2-((1*H*-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (6): To a solution of diethyl 2-((1*H*-indol-3-yl)methyl)malonate (1.15 g, 4 mmol,1.0 equiv) in THF (10 mL) NaH (60% in oil) (191 mg, 4.8 mmol, 1.2 equiv.) was added, the reaction mixure was allowed to stir for 30 minutes at ambient temperature. After it was cooled down to 0°C in ice bath followed by the dropwise addition of 1-bromo-3-methylbut-2-ene (551 µL, 4.8 mmol, 1.2 equiv.). Then the reaction was allowed to stir at ambient temperature for 16-20 hours. After the reaction was complete (monitored by TLC), it was quenched with water (20 mL). The aqueous layer was extracted with EtOAc (30 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 5:1) to afford the desired products **6** in 63% yield (Yellow oil, 903 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (br s, 1H, NH), 7.55 (d, *J* = 7.8 Hz, 1H, CH^{Ar}), 7.34 – 7.28 (m, 1H, CH^{Ar}), 7.19 – 7.11 (m, 1H, CH^{Ar}), 7.11 – 7.03 (m, 1H, CH^{Ar}), 6.96 (d, *J* = 2.1 Hz, 1H, CH^{Ar}), 5.21 – 5.10 (m, 1H, C**H**CH_2), 4.23 – 4.00 (m, 4H, C**H**$_2CH_3$), 3.41 (s, 2H, C**H**$_2$C), 2.62 (d, *J* = 7.1 Hz, 2H, C**H**$_2$CH), 1.72 (s, 3H, C**H**$_3$C), 1.52 (s, 3H, C**H**$_3$C), 1.19 (t, *J* = 7.1 Hz, 6H, CH_2C**H**$_3$).^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8 (C=O), 135.9 (C^{Ar}), 135.5 (C^{Ar}), 128.4 (C^{Ar}), 123.2 (CH^{Ar}), 122.0 (CH^{Ar}), 119.4 (CH^{Ar}), 119.0 (CH^{Ar}), 118.3 (**C**HCH_2), 111.1 (CH^{Ar}), 110.5 (C^{Ar}), 61.3 (**C**H$_2CH_3$), 58.8 (**C**$(CO_2Et)_2$), 31.3 (**C**H$_2$CH), 27.7 (CH_2C), 26.2 (CH_3C), 18.2

(CH_3C), 14.1 ($CH_2\mathbf{C}H_3$). **HRMS** (ESI-TOF): Calcd for $C_{21}H_{28}NO_4^+$ $[M+H]^+$ 358.2013; found 358.2001.

General procedure for the cyclization of indole 6: Diethyl 2-((1*H*-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate **6** (0.2 mmol, 71.5 mg) was weighted and transferred in 20 ml flash tube equipped with stirring bar and catalyst **3a** (2 mol%) was added from the stock solution. Solvent (4 mL) was added in reaction mixture and the tube was closed with rubber cap and was degassed by bubbling Ar for 3 minutes. The tube was placed into photoreactor for indicated time. The residue was purified through silica gel column chromatography by using petroleum ether/ethyl acetate (6:1) as the eluent. Each experiment was performed twice and the average yield is reported.

Table S2 Selected optimization results of the reaction conditions for indole **6**[a]



Entry	Catalyst (mol%)	Solvent (ml)	Time (h)	Conversion (Yield)[b] (%)
1[c]	**3a**	EtOAc	1	-
2	**3a**	EtOAc	1	-
3	**3a**	EtOAc	18	74 (64)
4	**3a**	EtOAc	22	78
5	**3a**	THF	18	35

[a] Indole **6** (0.2 mol, 1 eq.), catalyst (2 mol%), solvent (4 ml) at room temperature under Ar. [b] NMR conversion (Isolated yields are in parentheses). [c] 1 mol% of **3a**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.54 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.12 – 7.03 (m, 2H), 4.16 – 3.97 (m, 4H), 3.47 (s, 2H), 2.40 (dd, *J* = 7.6, 4.1 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.39 (s, 6H), 1.14 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 142.6,

134.3, 129.4, 121.0, 119.3, 118.1, 110.4, 106.2, 61.3, 56.9, 37.0, 35.6, 30.7, 28.2, 28.1, 14.1.

HRMS calculated for $C_{21}H_{28}NO_4$ $[M+H]^+$: 358.2015; found : 358.2000

Absorption and PL spectroscopy

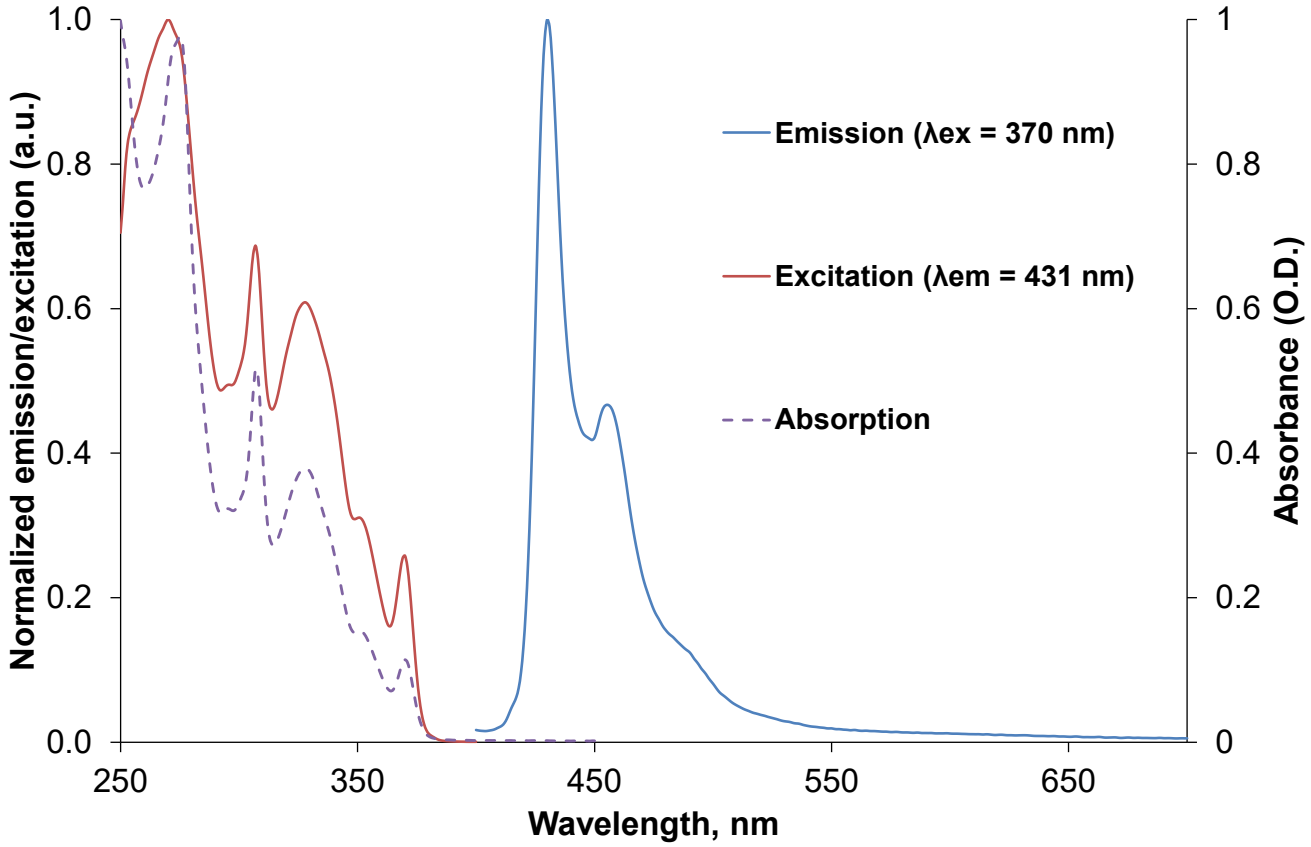


Figure S1. Absorption and emission spectra of **3a**

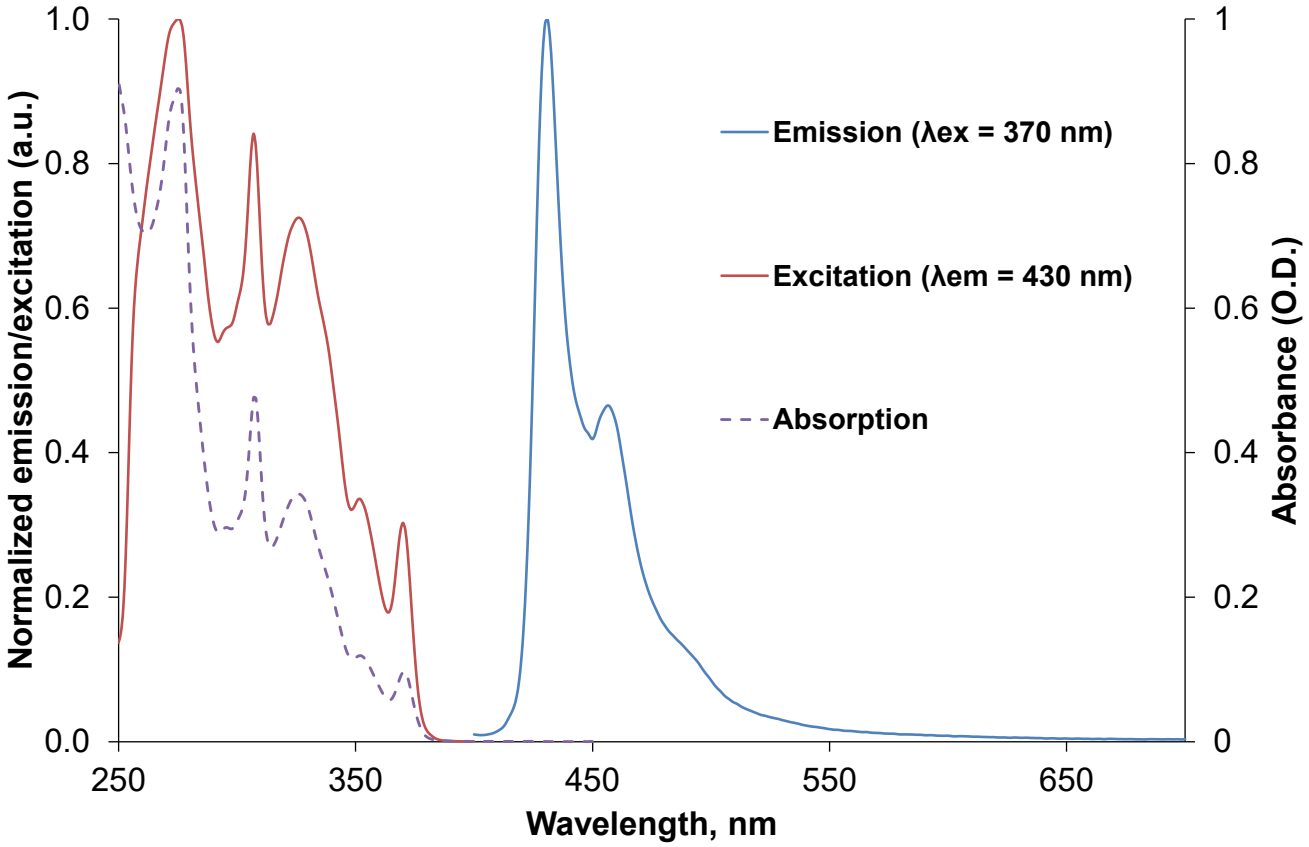


Figure S2. Absorption and emission spectra of **3b**

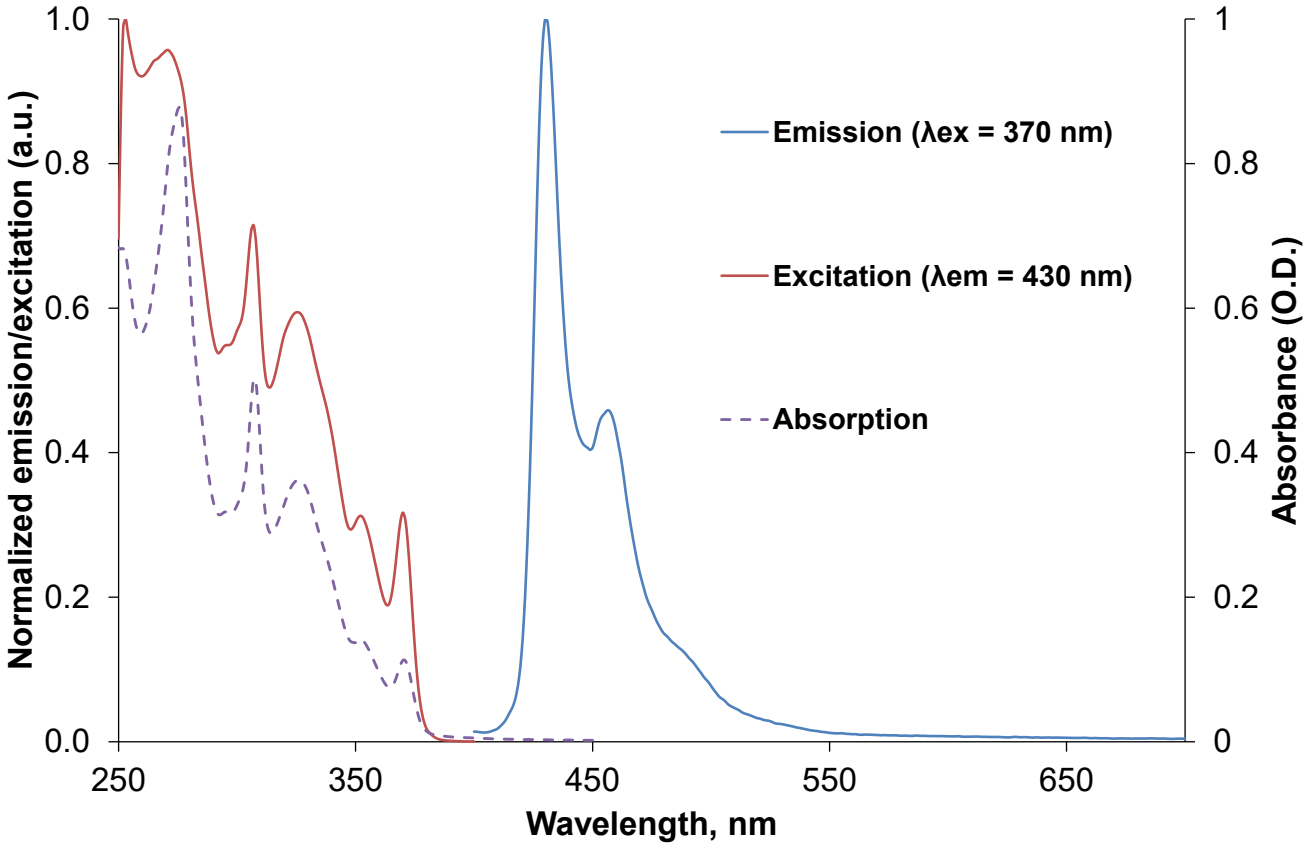


Figure S3. Absorption and emission spectra of **3d**

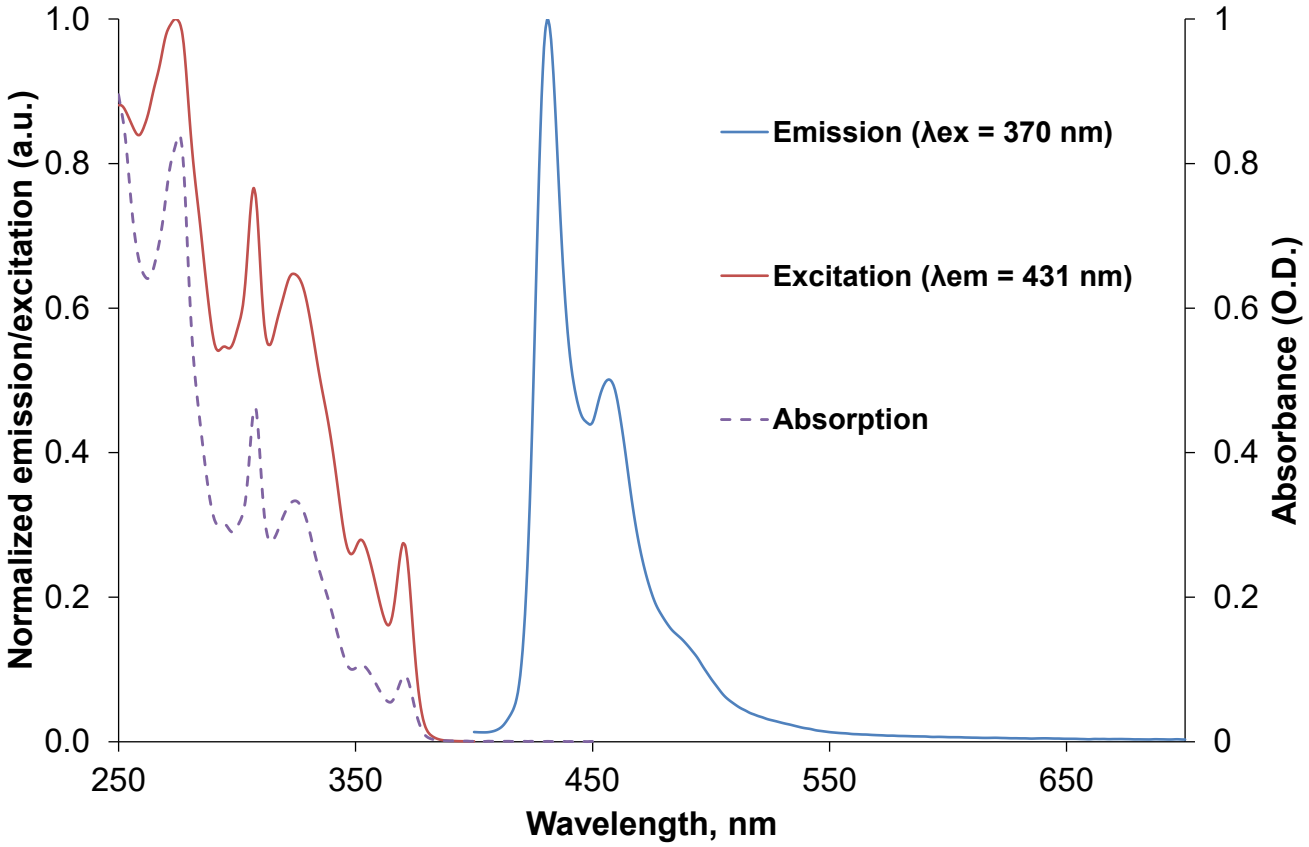


Figure S4. Absorption and emission spectra of **3e**

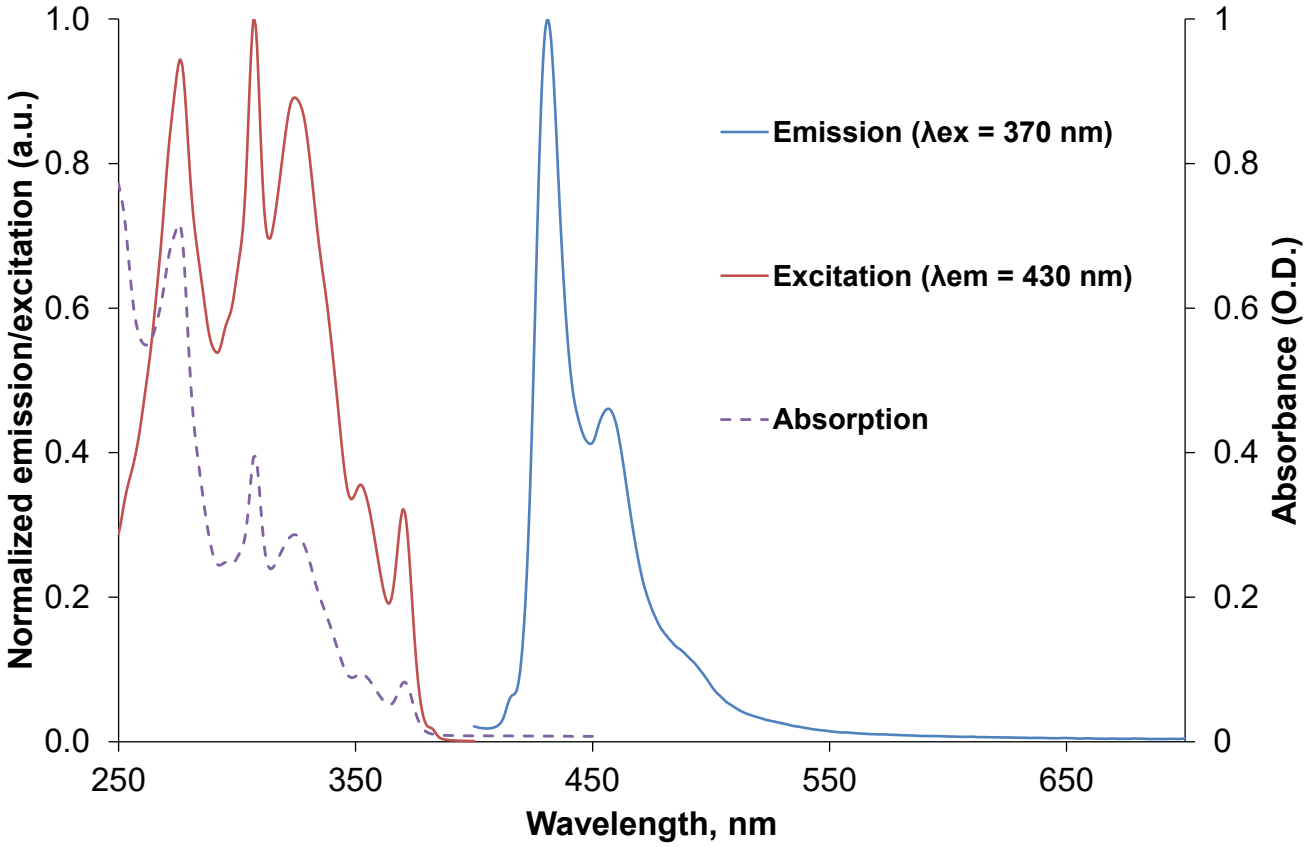


Figure S5. Absorption and emission spectra of **3f**

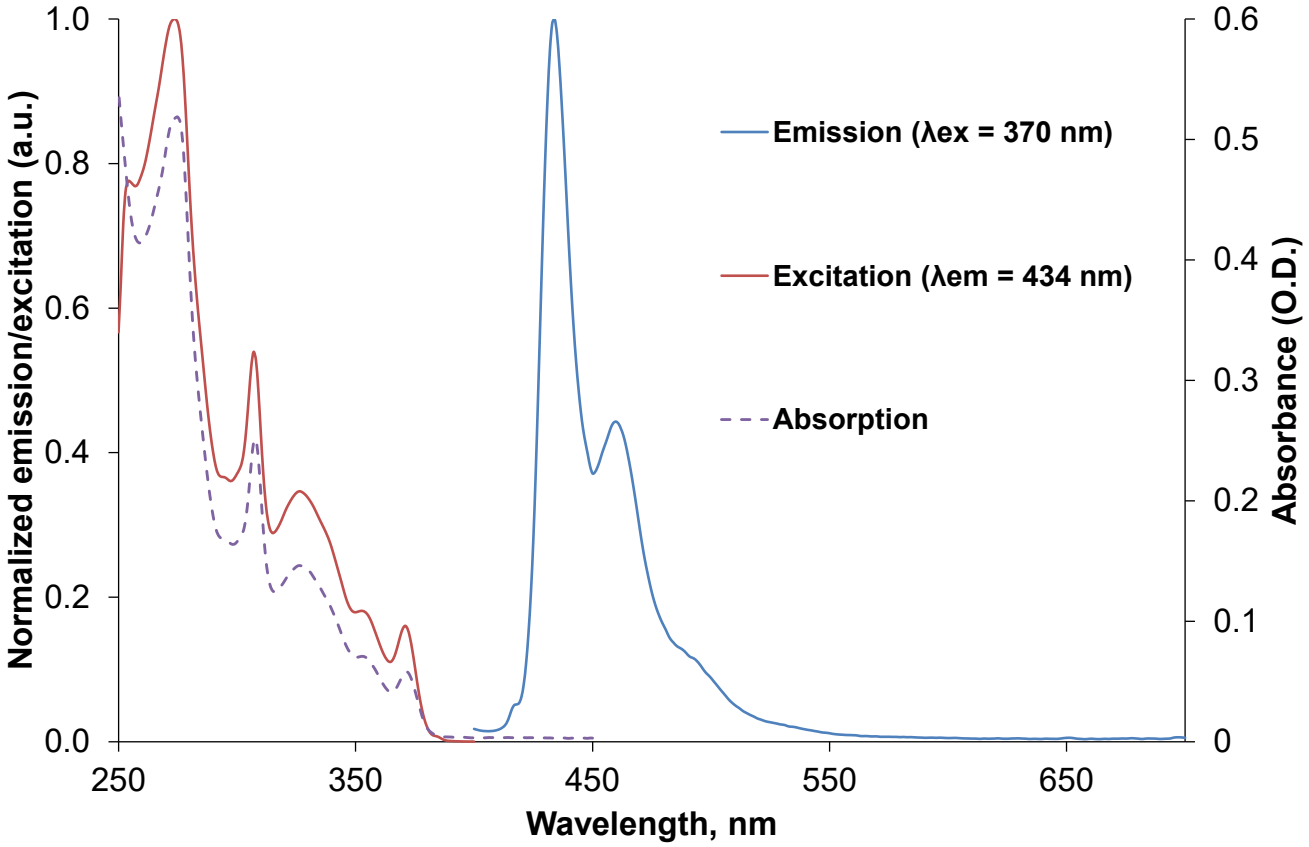


Figure S6. Absorption and emission spectra of **3g**

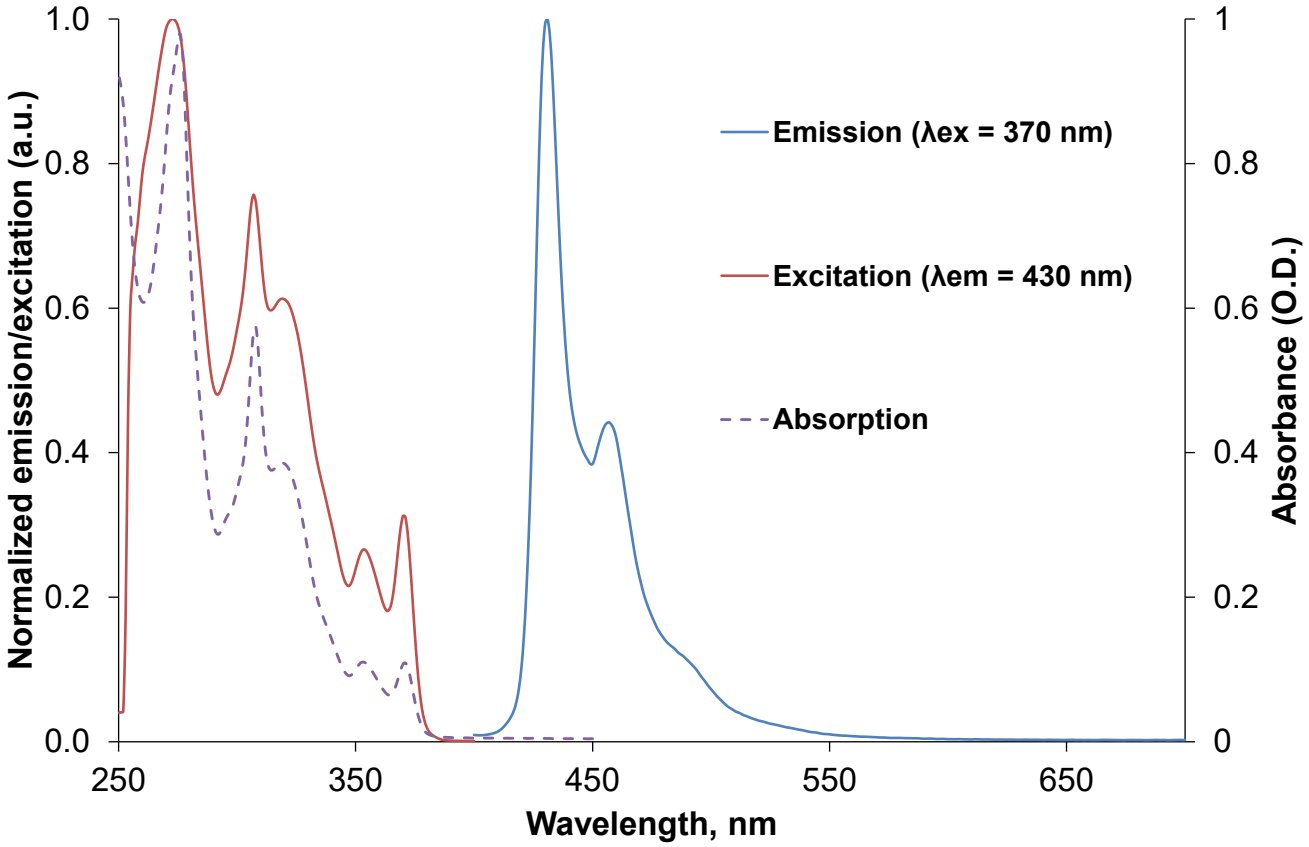


Figure S7. Absorption and emission spectra of **3h**

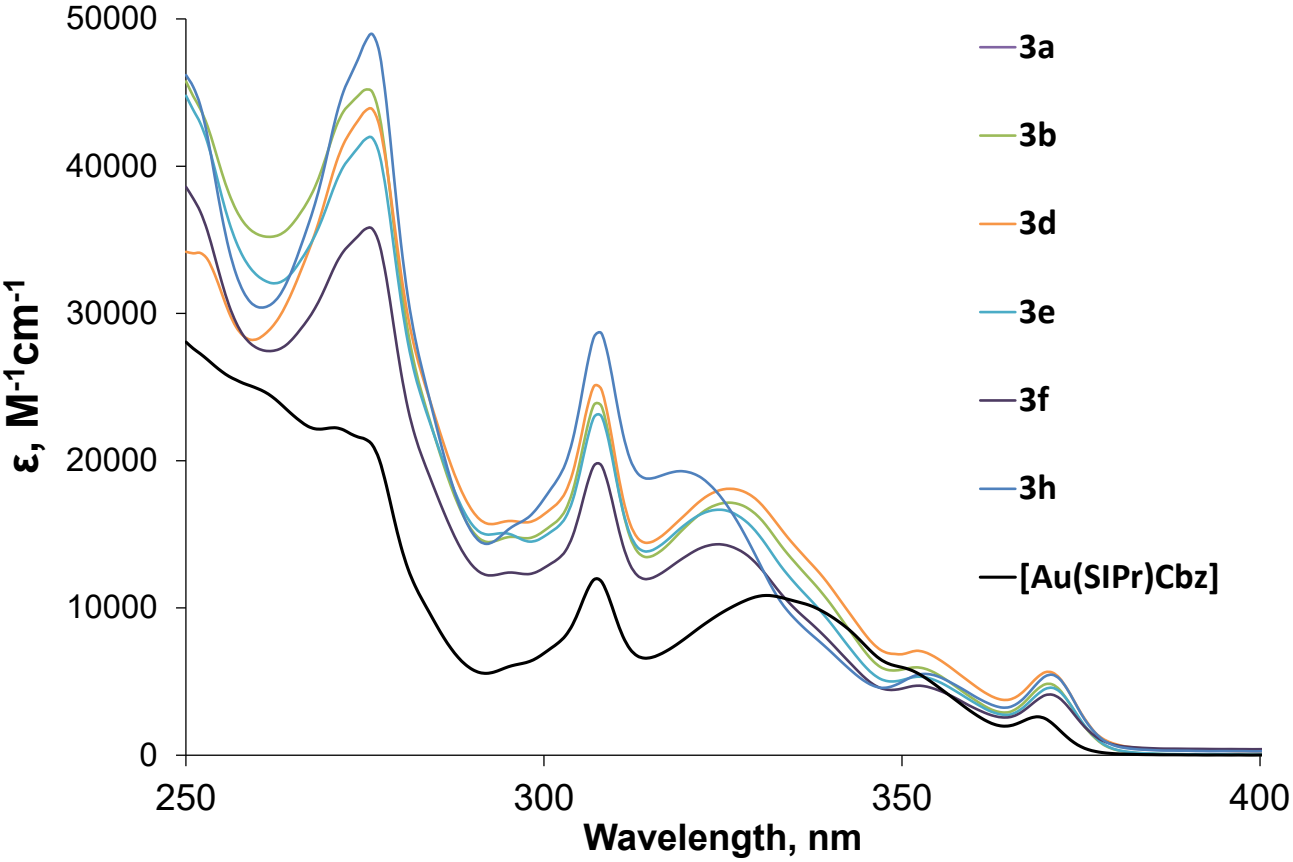


Figure S8. Absorption spectra of complexes **3a-h**

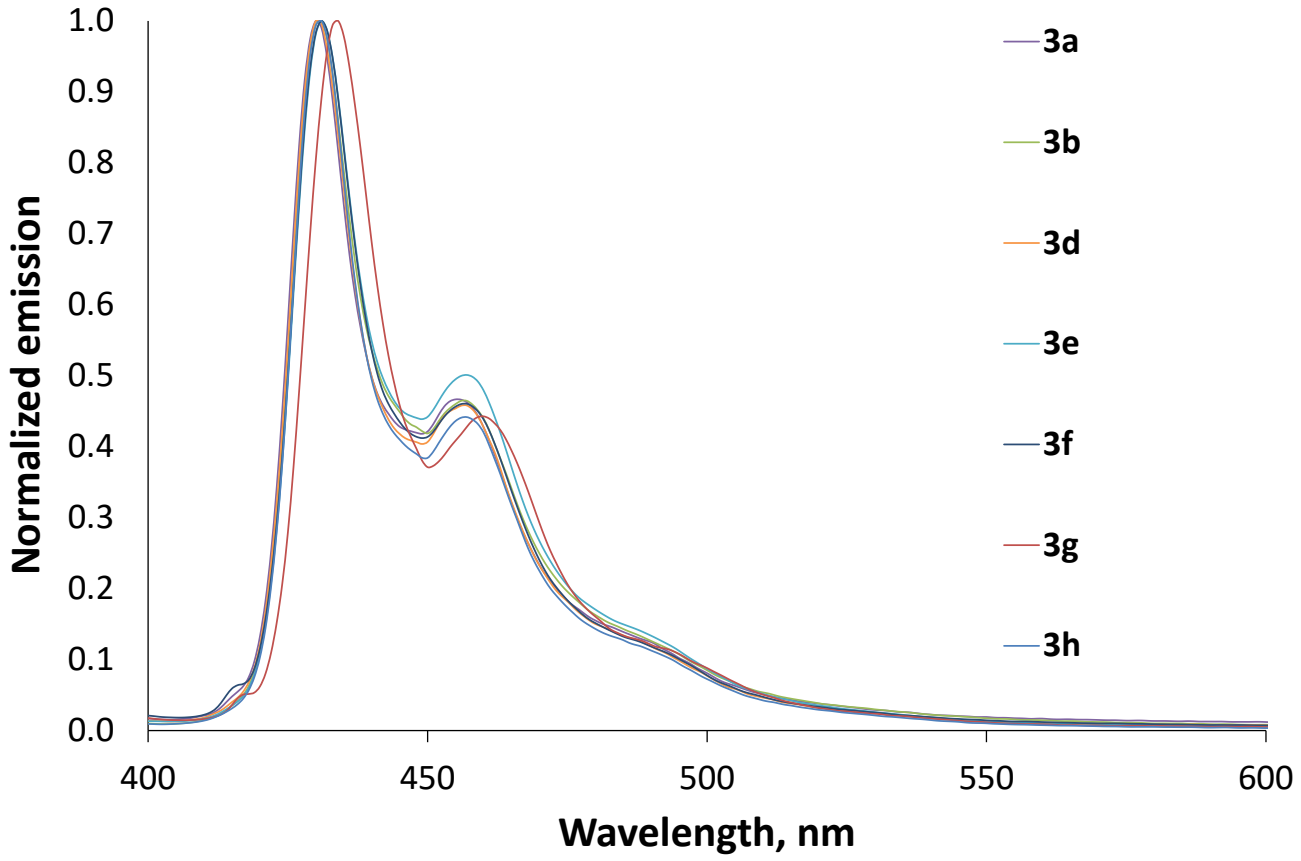


Figure S9. Emission spectra of complexes **3a-h** in THF

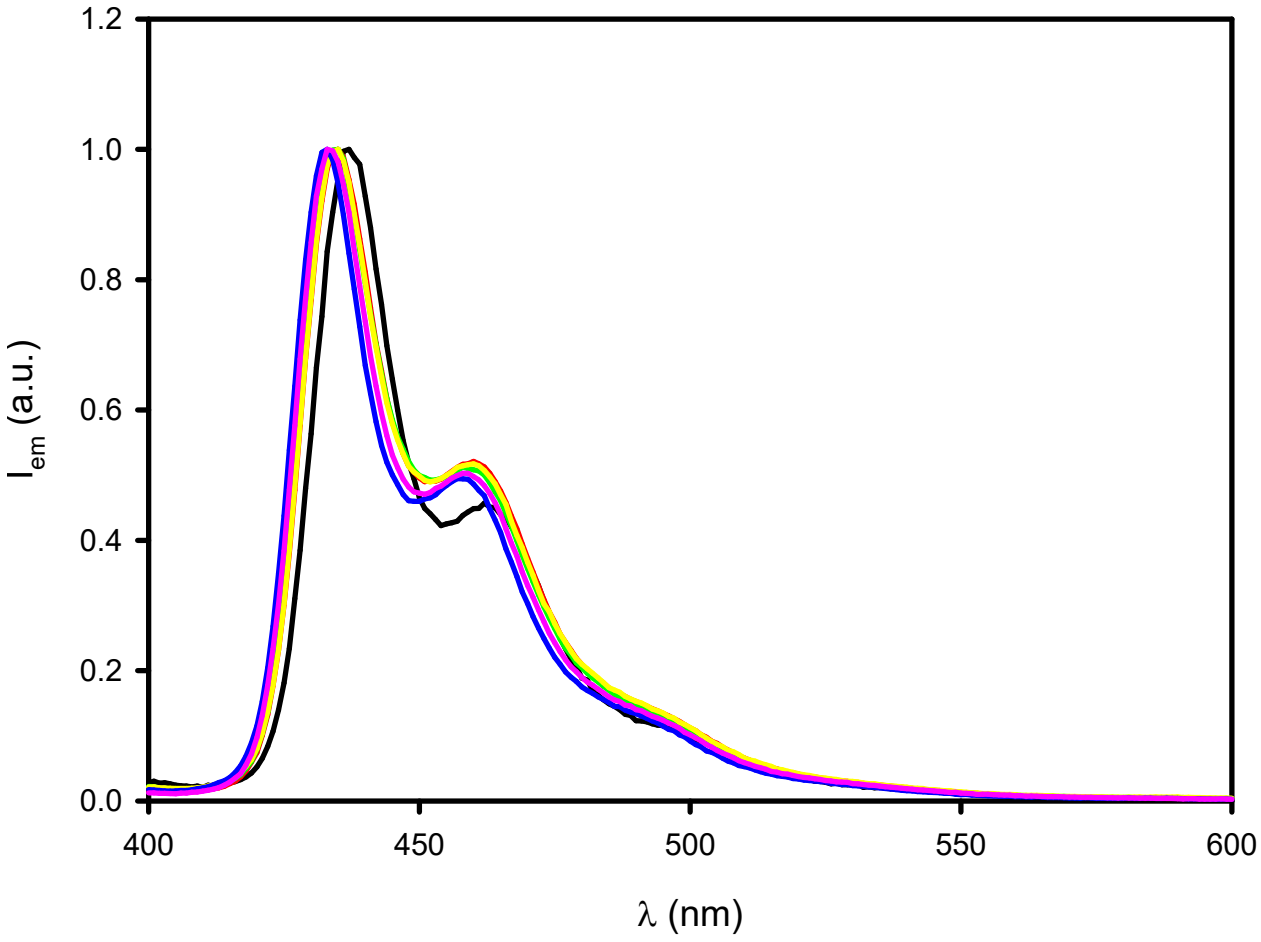


Figure S10. Emission spectra in deareated DMSO of **3g** (black), **3f** (blue), **3e** (green), **3d** (red), **3b** (yellow), **3a** (pink) and. (λ_{exc} = 370 nm)

Table S3 Photophysical parameters of the complexes studied.

	DMSO deareated		
C	**λem [nm]**	**τ [μs]**	**ϕ [%]**
3a	434	163	37
3b	435	167	45
3d	435	126	41
3e	435	224	77
3f	434	262	47
3g	437	48	16

[a] Characterization in solution was performed in deareated DMSO.

Molecular Structures of Complexes

Crystals that were of suitable quality for single crystal X-ray diffraction analysis were obtained in all cases by slow vapor diffusion of the antisolvent (hexane or pentane) into saturated solutions (THF or DCM) of the complexes at 4 °C. CCDC 2213682-2213683 (**3c** and **3e**) and CCDC 2243593 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

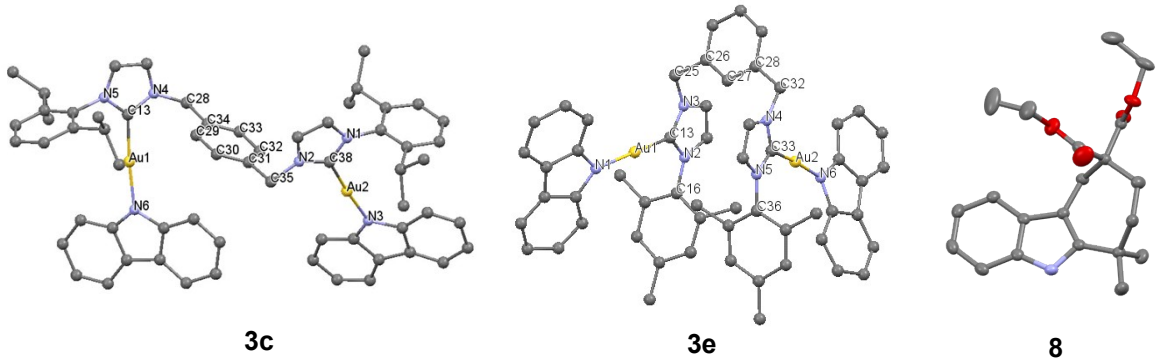


Figure S11 X-ray molecular structure of **3c**, **3e** and **8**, showing thermal displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity.

Table S4 Selected bond lengths (Å) and angles (°) for **3c** and **3e**

Complex **3c**		Complex **3e**	
C_{13}-Au_1	1.993(6)	C_{13}-Au_1	1.974(8)
C_{38}-Au_2	1.980(6)	C_{38}-Au_2	1.982(9)
Au_1-Au_2	9.0390(5)	Au_1-Au_2	6.273(1)
C_{13}-Au_1-N_6	175.7(2)	C_{13}-Au_1-N_1	174.8(3)
C_{38}-Au_2-N_3	175.4(2)	C_{33}-Au_2-N_6	174.0(3)
N_2-C_{35}-C_{31}	111.8(5)	N_3-C_{25}-C_{26}	112.2(7)

C_{34}-C_{28}-N_4 113.7(5)	C_{28}-C_{32}-N_4 115.5(7)

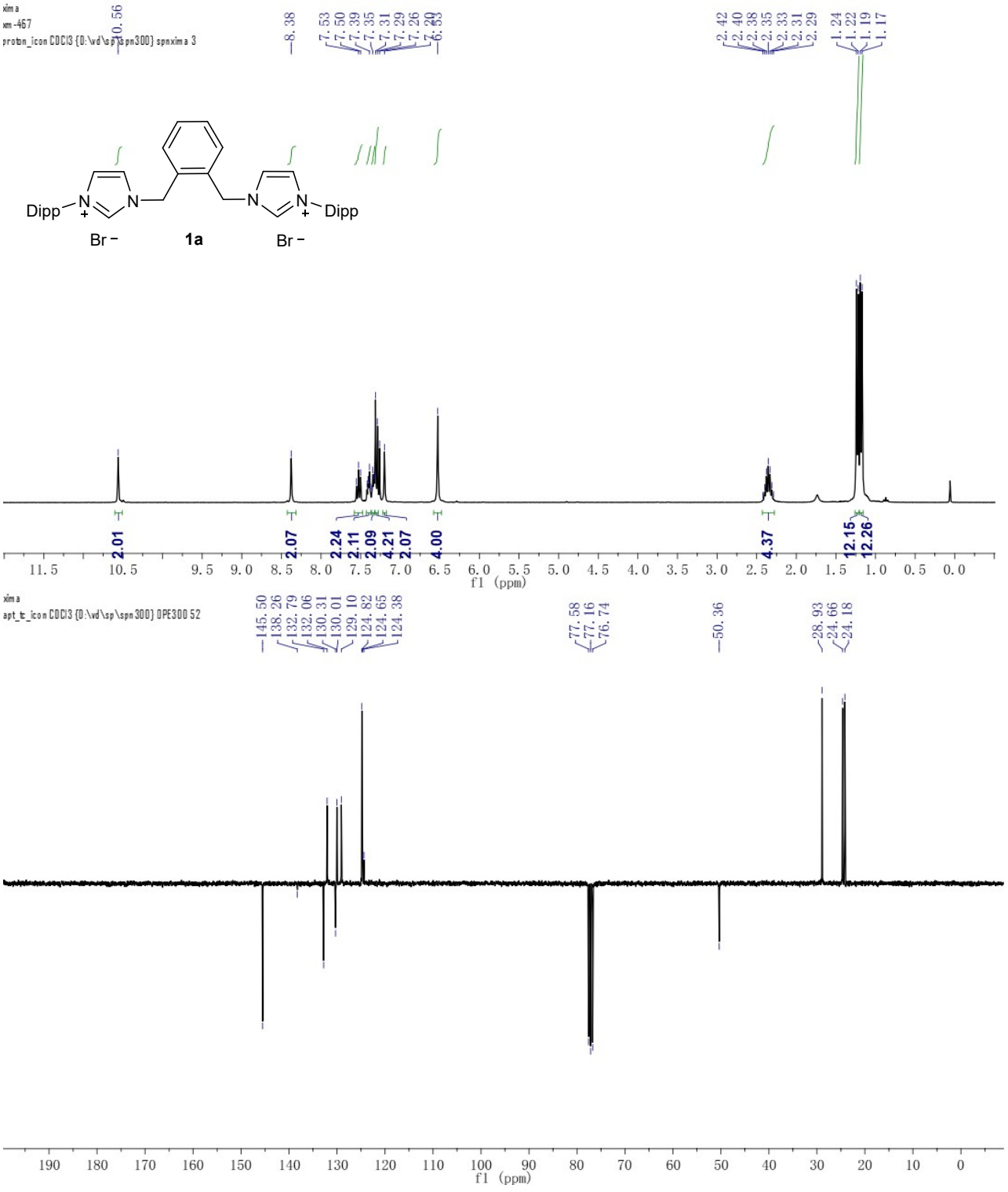
Table S5 Crystallographic data for **3c**, **3e** and **8**

	Complex **3c**·THF	Complex **3e**	Compound **8**
Empirical formula	$C_{66}H_{70}Au_2N_6O$	$C_{56}H_{50}Au_2N_6$	$C_{21}H_{27}NO_4$
Formula weight	1357.21	1200.96	235.44
Temperature/K	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	*C*2/c	$P2_1/n$
a/Å	12.4705(2)	27.2565(3)	8.23200(10)
b/Å	14.3086(3)	17.0998(2)	15.2361(2)
c/Å	17.1528(3)	52.0080(6)	15.1326(2)
α/°	103.775(2)	90	90
β/°	95.912(2)	101.3770(10)	90.3230(10)
γ/°	101.539(2)	90	90
Volume/Å^3	2875.84(10)	23763.6(5)	1897.96(4)
Z	2	20	4
ρ_{calc}g/cm^3	1.567	1.678	1.251
μ/mm^{-1}	9.814	6.211	0.694
F(000)	1348.0	11720.0	768.0
Crystal size/mm^3	0.57 × 0.08 × 0.03	0.217 × 0.114 × 0.103	0.302 × 0.227 × 0.122
Radiation	Cu Kα (λ = 1.54184 Å)	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54184 Å)
2Θ range for data collection/°	5.372 to 147.72	5.026 to 57.526	8.236 to 147.91
Index ranges	-12 ≤ h ≤ 15, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21	-36 ≤ h ≤ 32, -22 ≤ k ≤ 22, -69 ≤ l ≤ 65	-9 ≤ h ≤ 10, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	49365	123620	18693
Independent reflections	11431 [Rint = 0.0631, Rsigma = 0.0515]	26919 [Rint = 0.0723, Rsigma = 0.0749]	3800 [R Int = 0.0266, Rsigma = 0.0181]

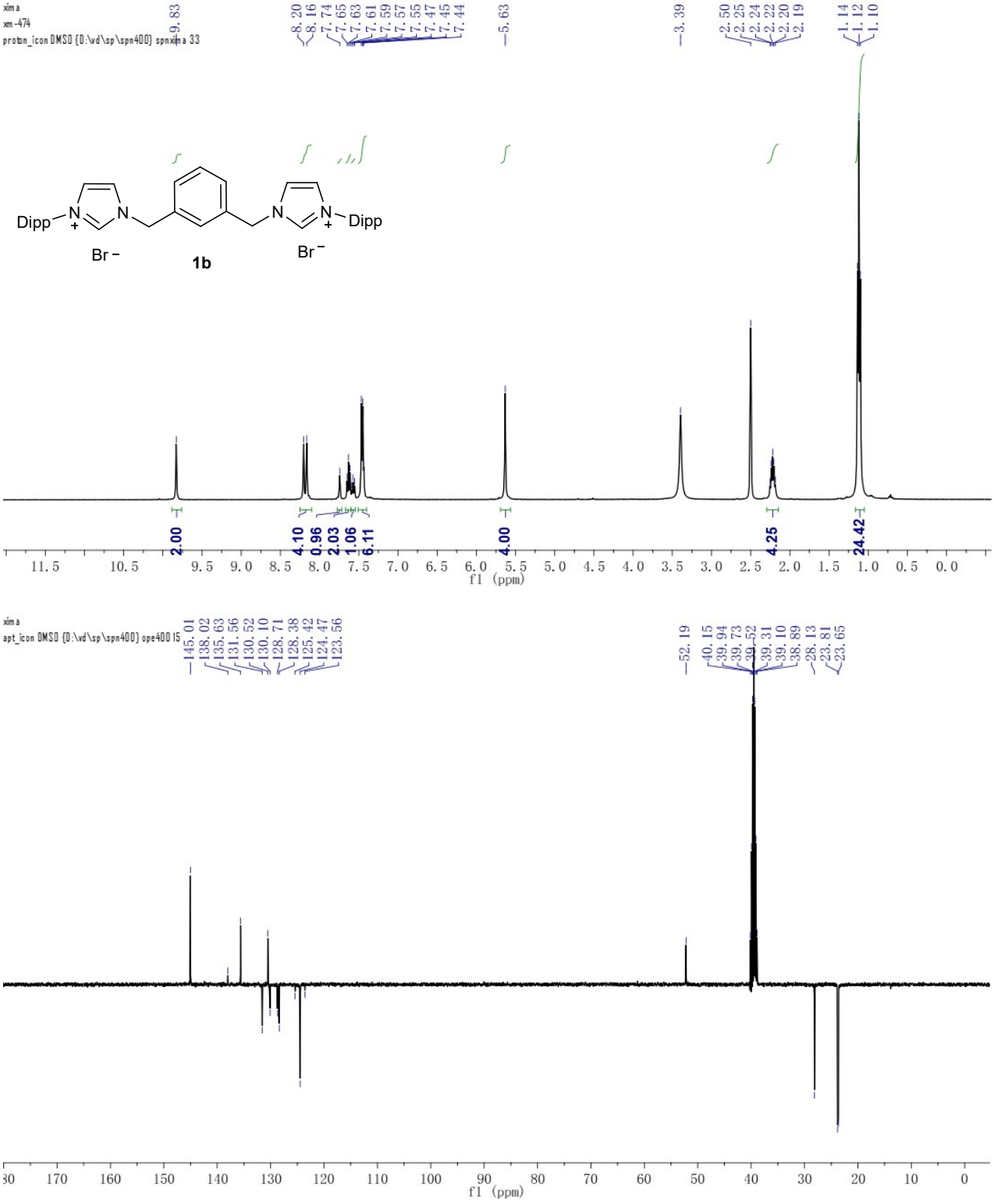
Data/restraints/parameters	11431/0/639	26919/0/1457	3800/6/254
Goodness-of-fit on F^2	1.008	1.031	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0823	R_1 = 0.0583, wR_2 = 0.0932	R_1 = 0.0457, wR_2 = 0.1116
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.0892	R_1 = 0.0842, wR_2 = 0.1014	R_1 = 0.0535, wR_2 = 0.1180
Largest diff. peak/hole / e $Å^{-3}$	2.06/-1.17	2.01/-1.37	0.49/-0.28

NMR spectra

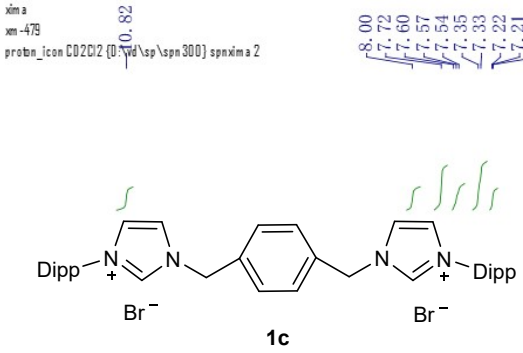
^{1}H and ^{13}C NMR of [IPr$^{o\text{-aryl}}$·2HBr)] **1a**



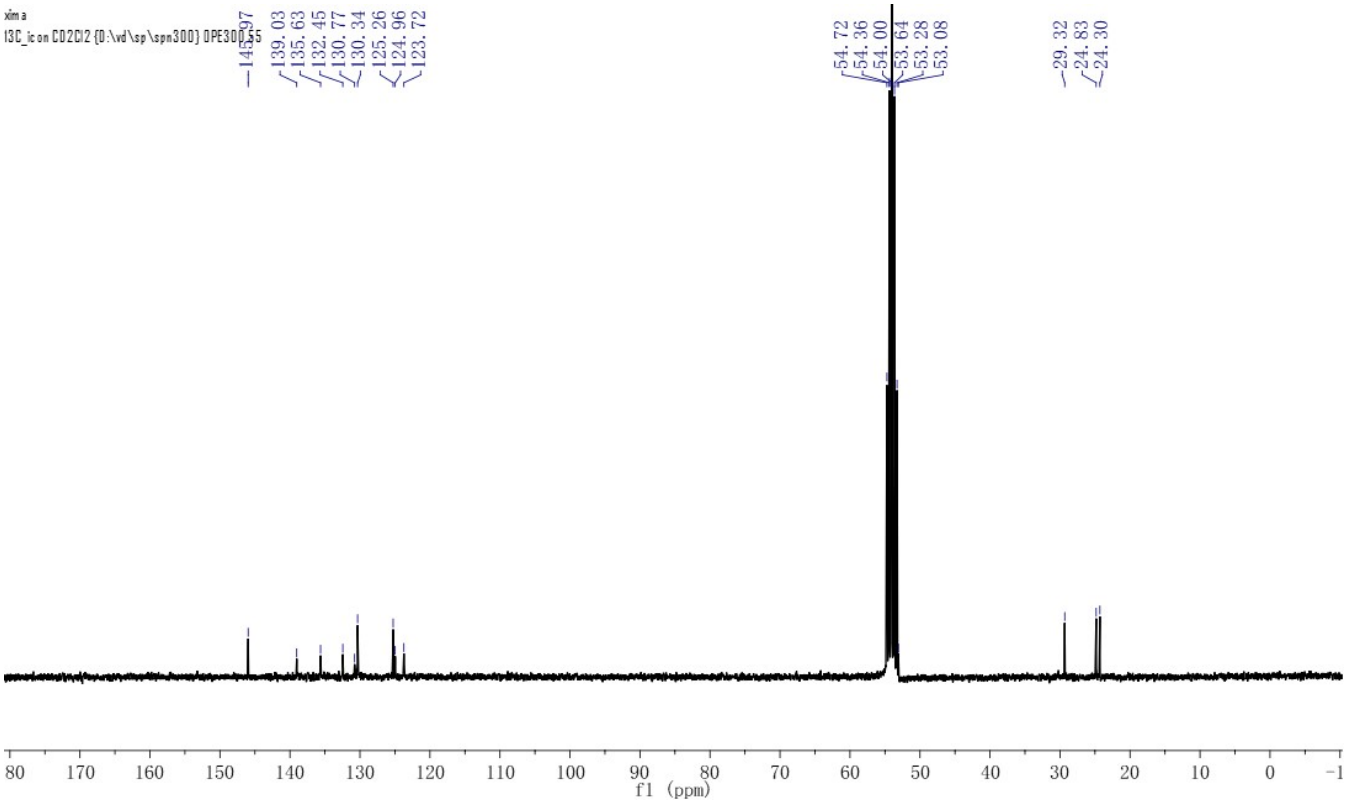
^{1}H and ^{13}C {^{1}H} apt NMR of [IPr^{m}-aryl·2HBr] **1b**



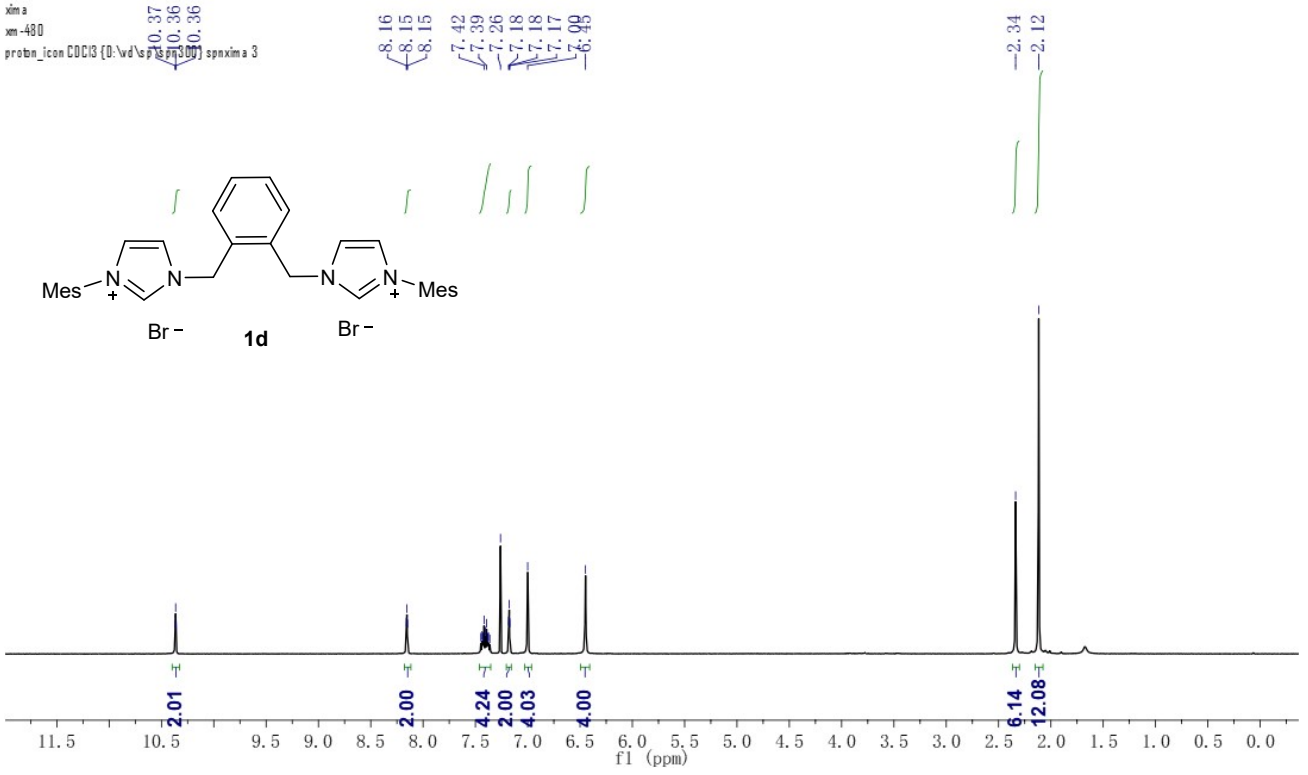
^{1}H and ^{13}C {^{1}H} apt NMR of [IPr$^{p\text{-aryl}}$·2HBr] **1c**

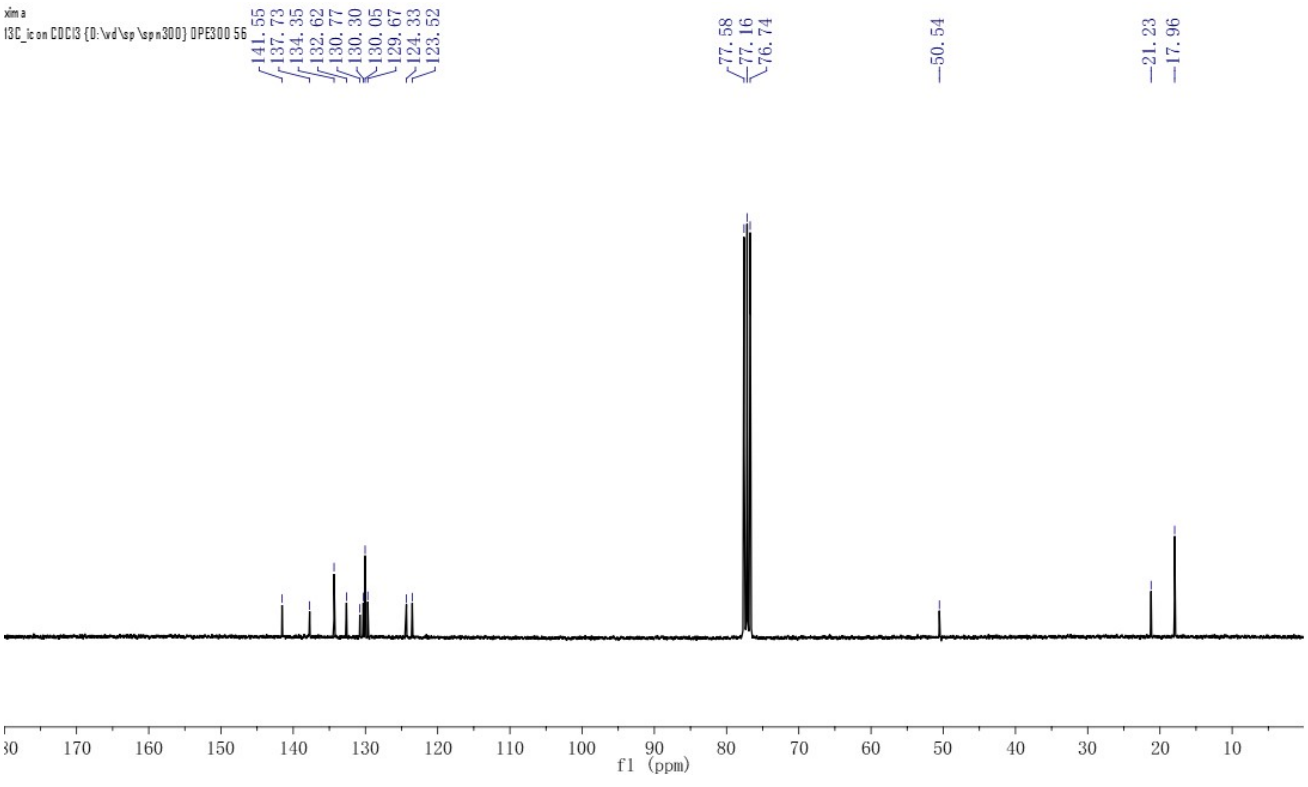


1c

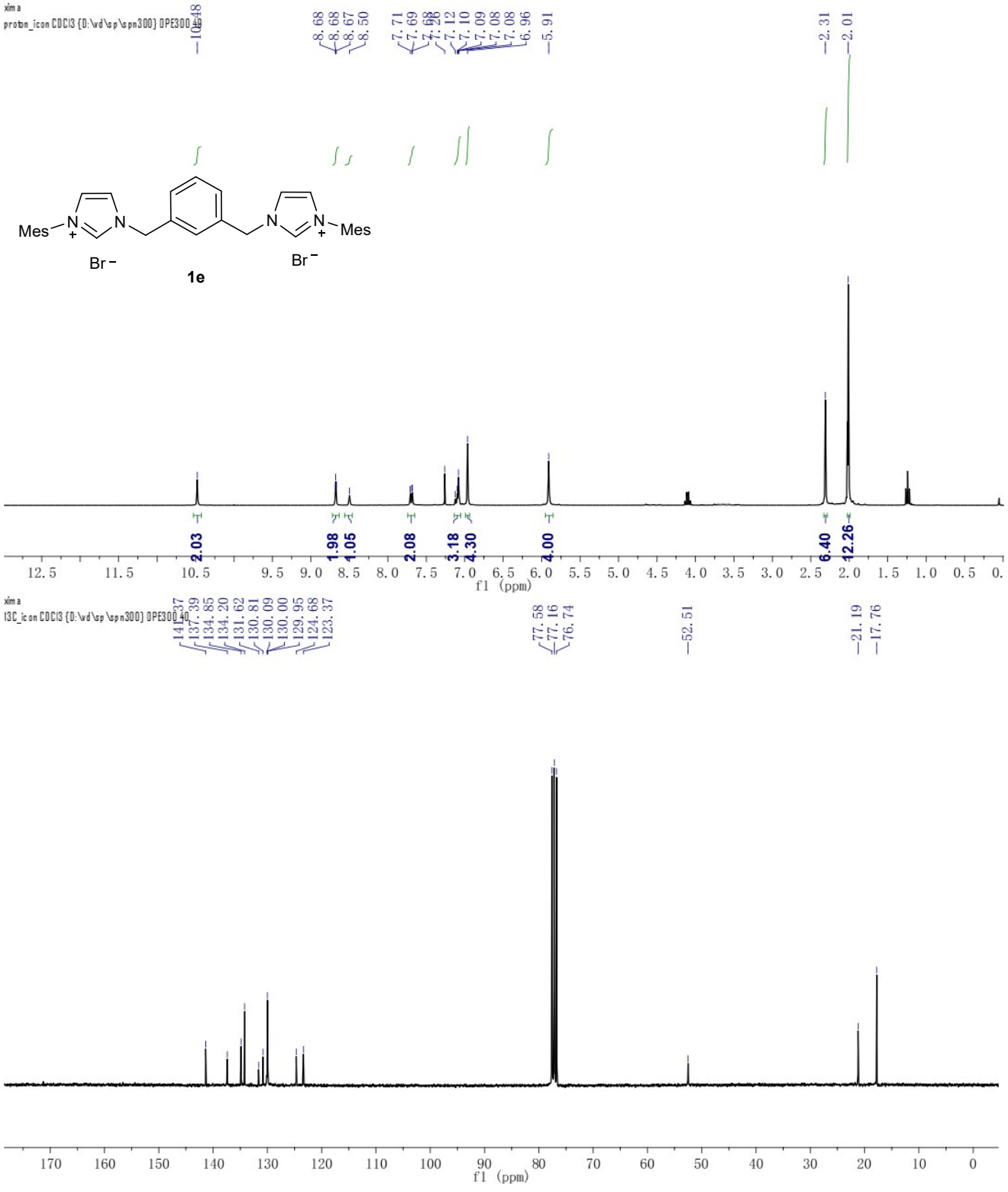


^{1}H and ^{13}C {^{1}H} NMR of [IMes$^{o\text{-aryl}}$·2HBr] **1d**

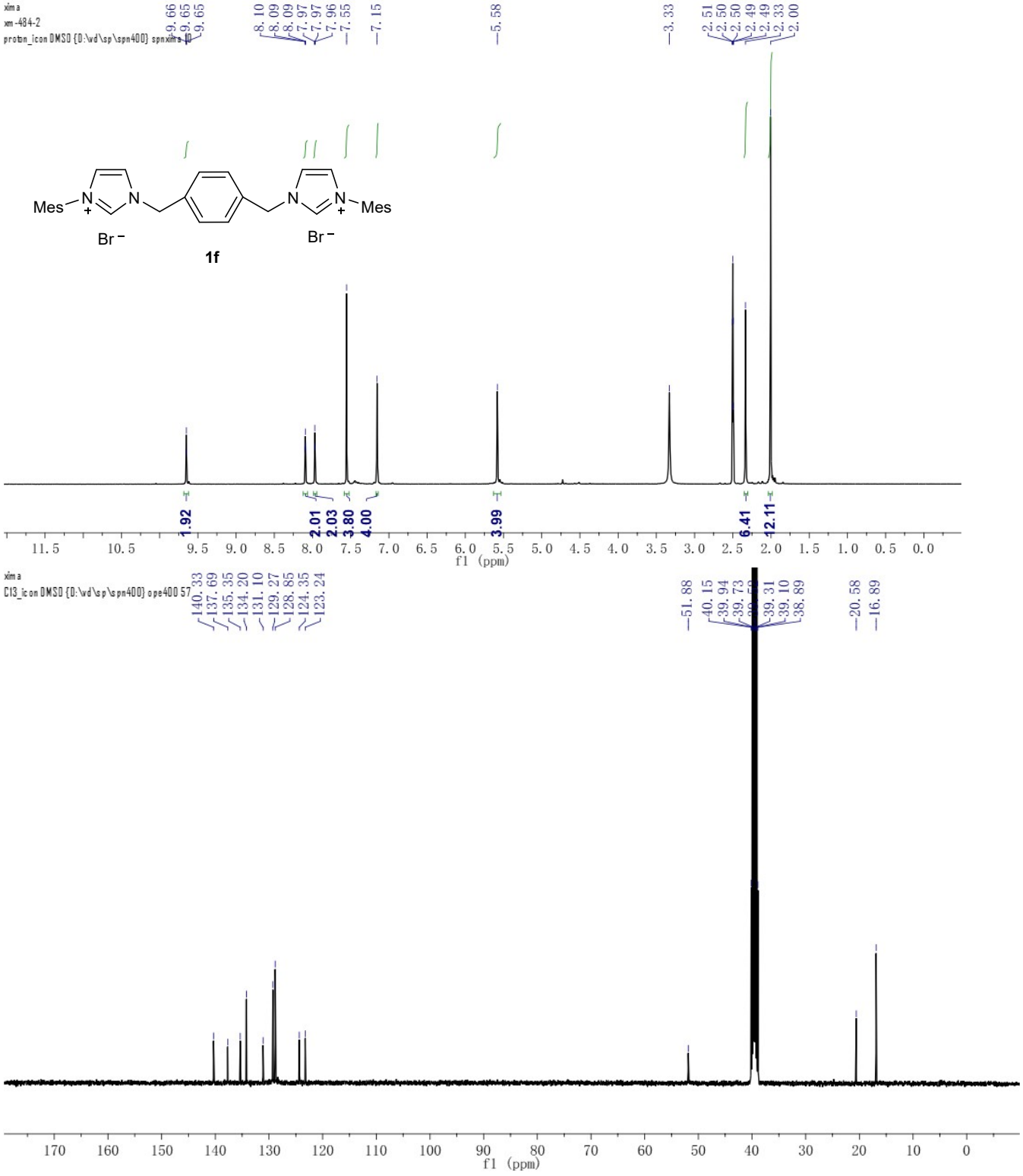




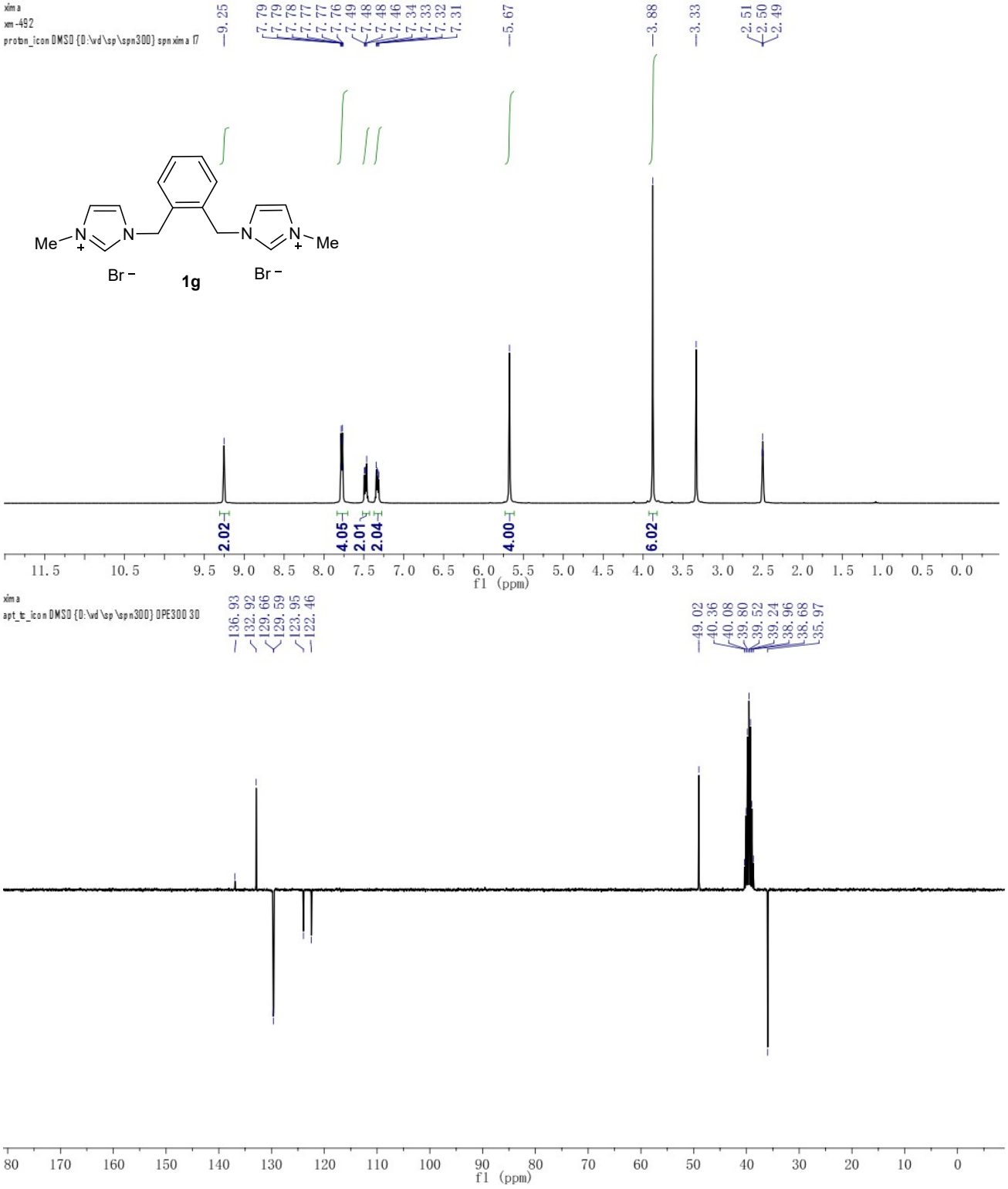
^{1}H and ^{13}C {^{1}H} NMR of [IMes$^{m\text{-aryl}}$·2HBr] **1e**



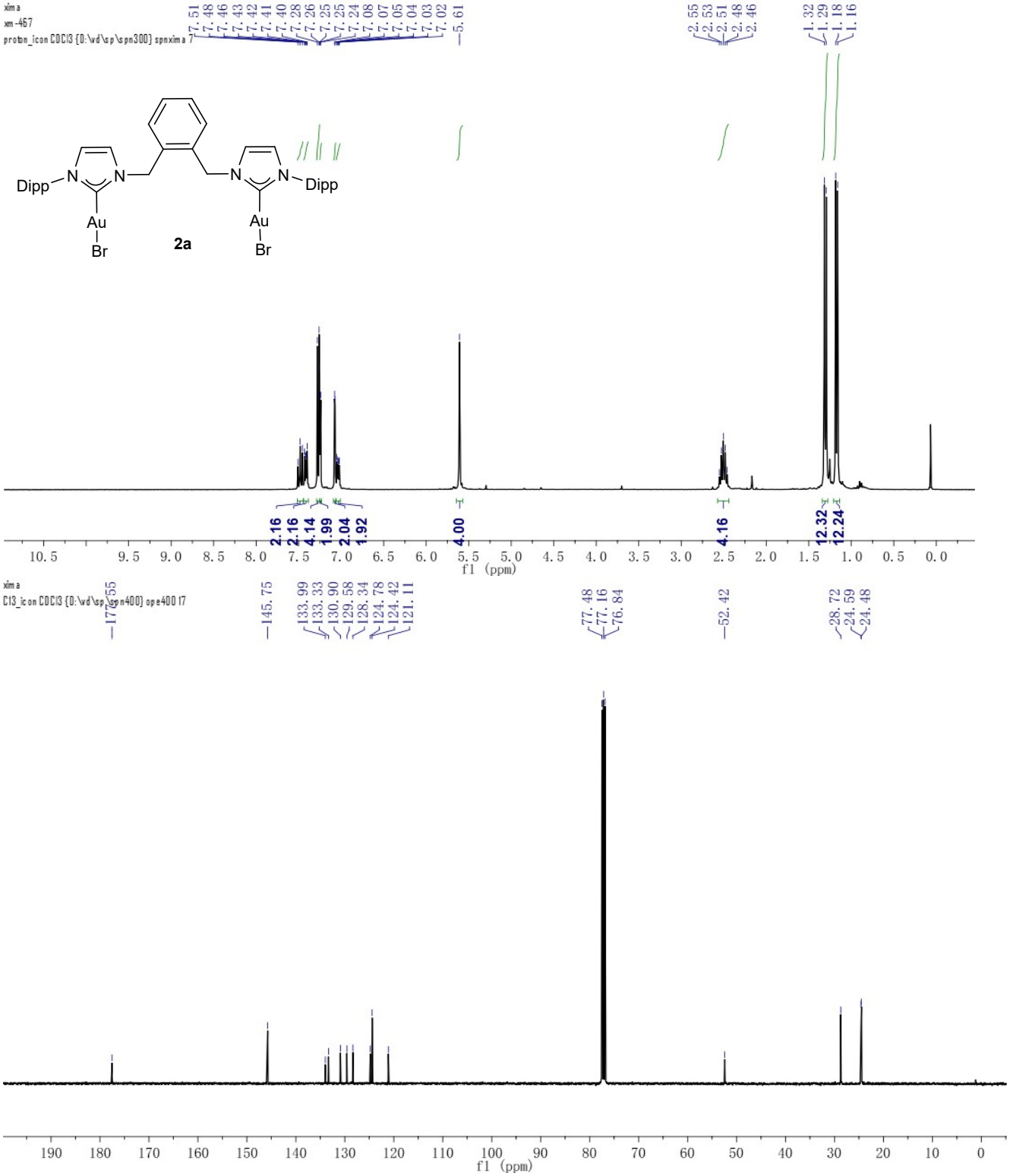
^{1}H and ^{13}C {^{1}H} NMR of [IMes$^{p\text{-aryl}}$·2HBr] **1f**



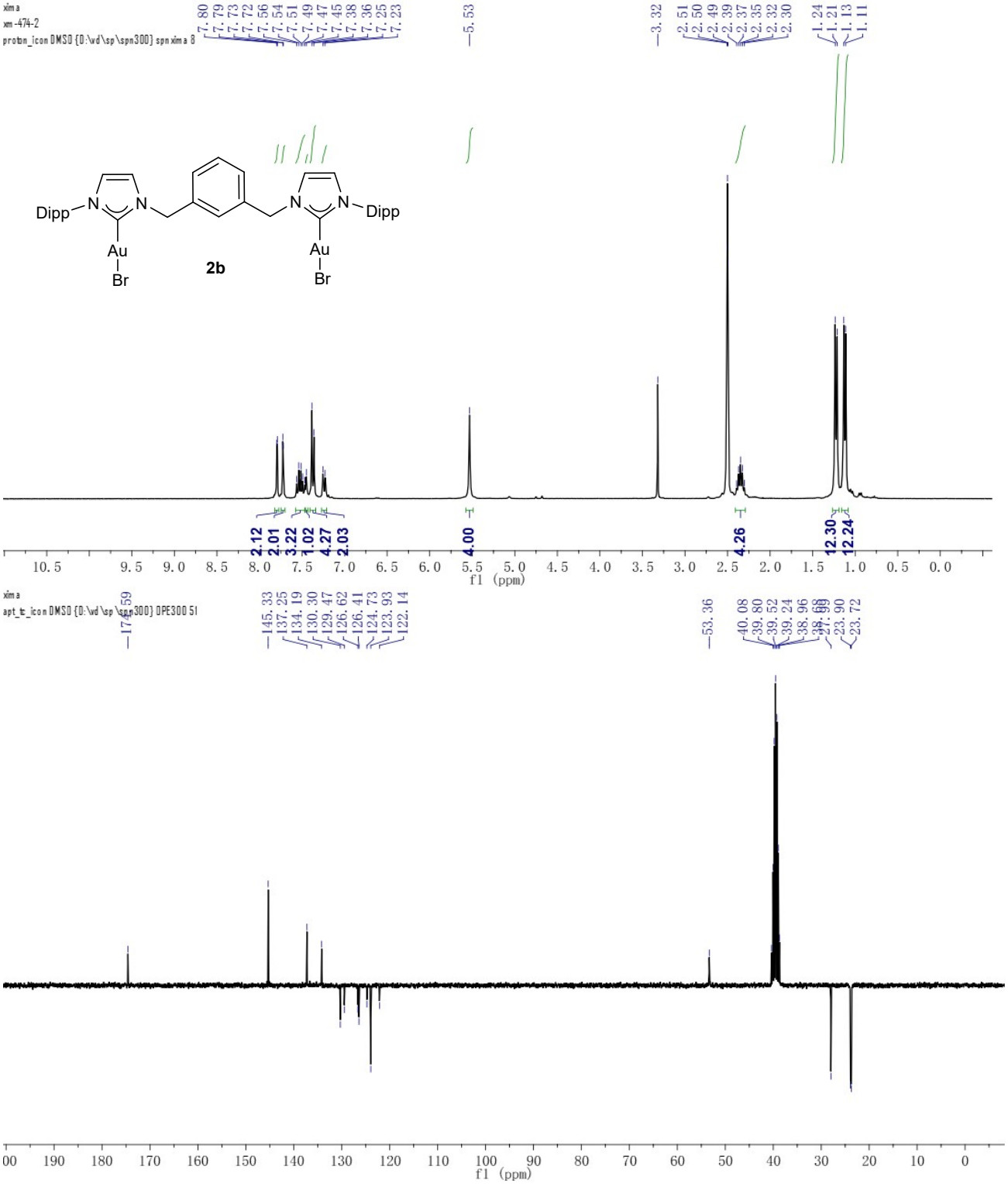
^{1}H and ^{13}C {^{1}H} apt NMR of [IMe$^{o\text{-aryl}}$·2HBr] **1g**



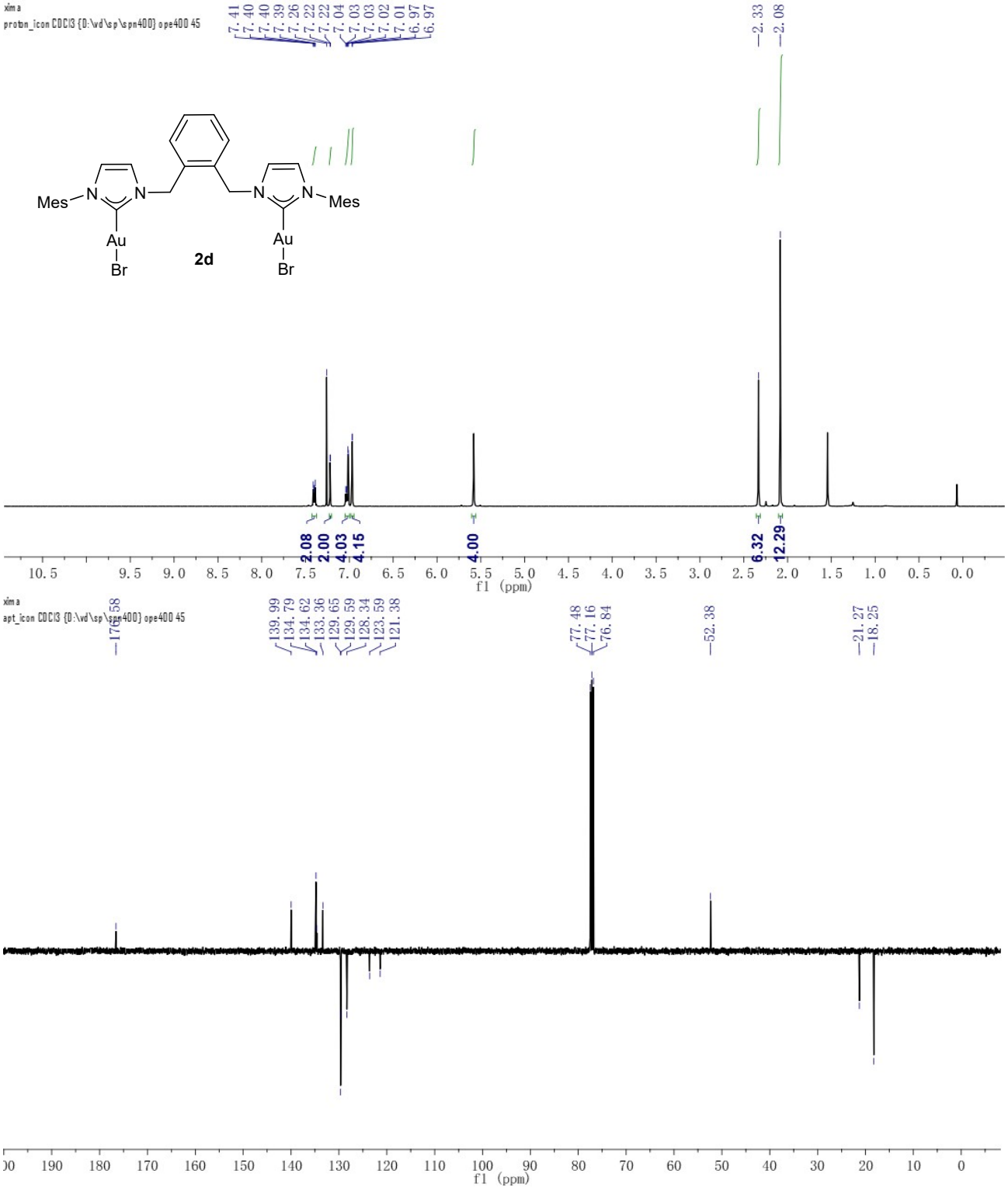
^{1}H and ^{13}C $\{^{1}H\}$ NMR of $[IPr^{o\text{-}aryl}\{AuBr\}_2]$ **2a**



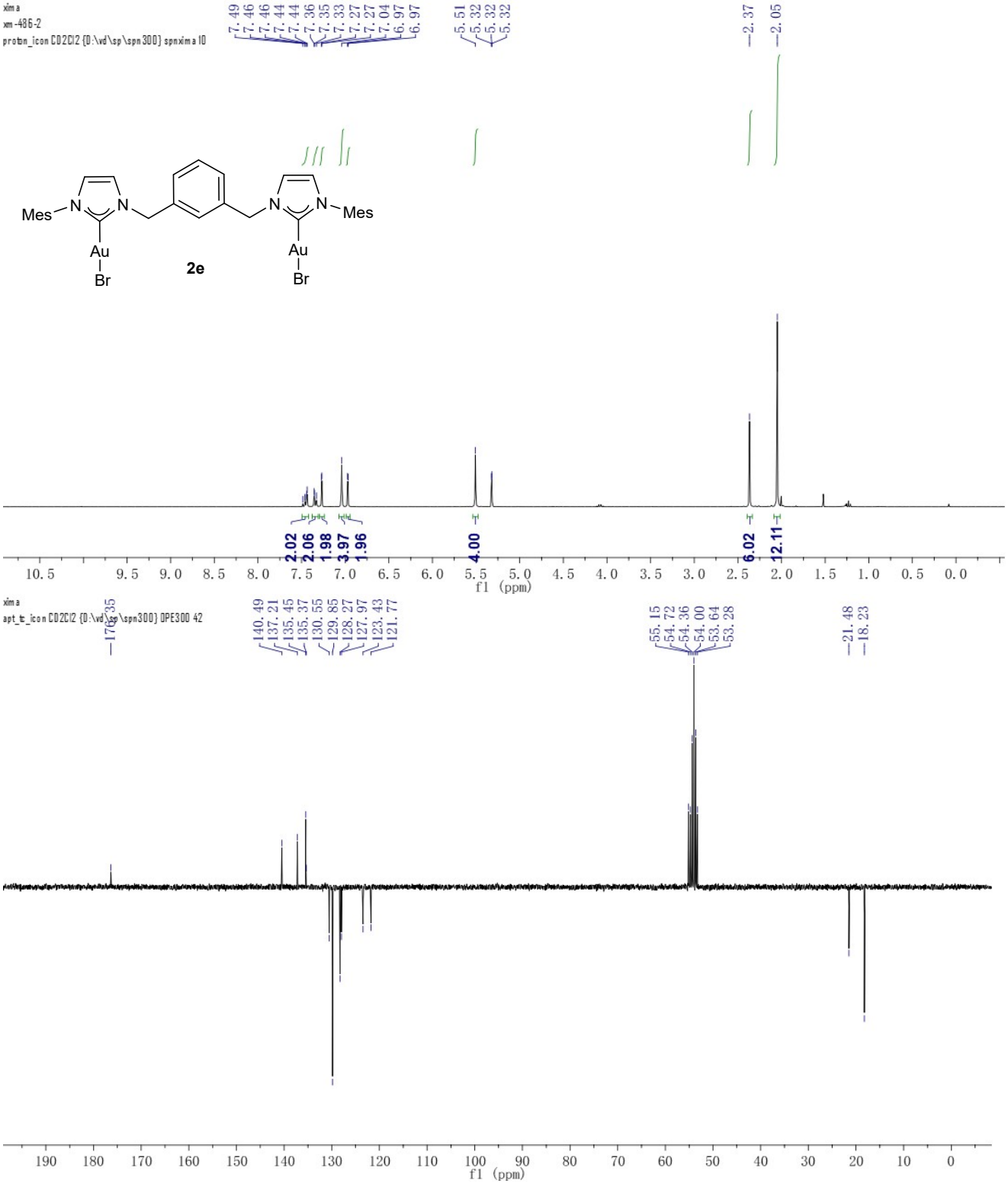
^{1}H and ^{13}C $\{^{1}H\}$ NMR of [IPr$^{m\text{-aryl}}${AuBr}$_2$] **2b**



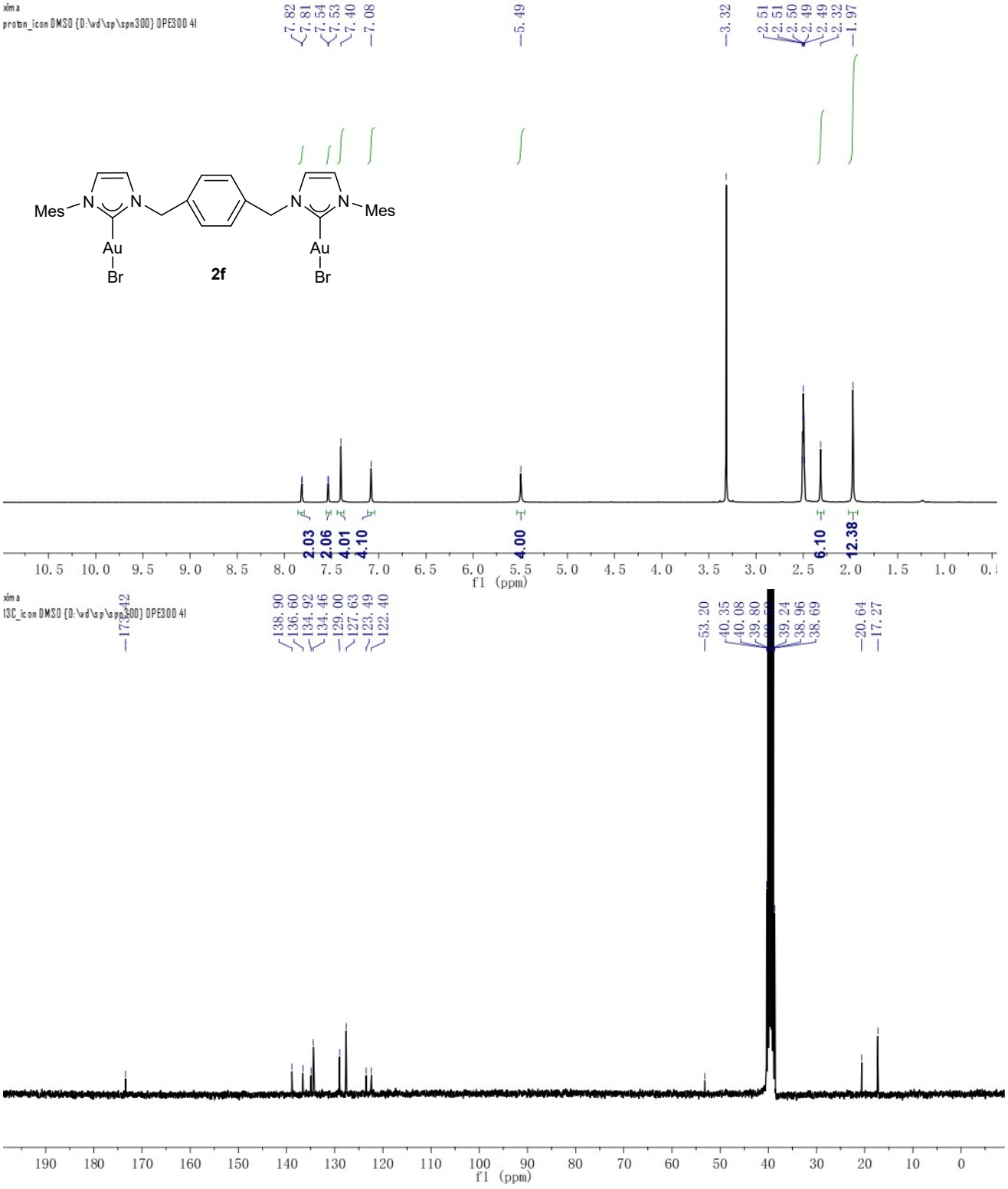
^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of [IMes$^{o\text{-aryl}}${AuBr}$_2$] **2d**



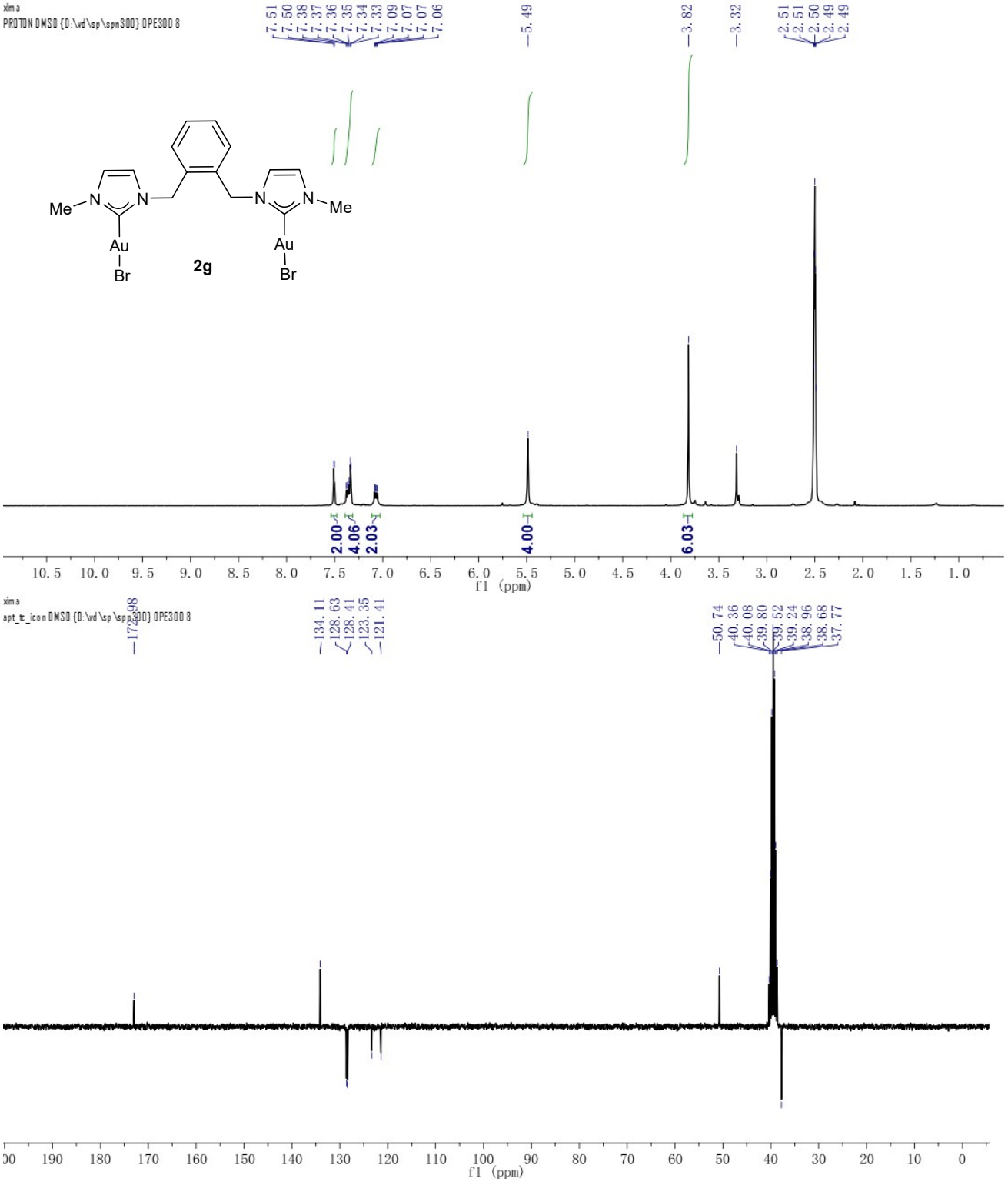
^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of [IMes$^{m\text{-aryl}}${AuBr}$_2$] **2e**



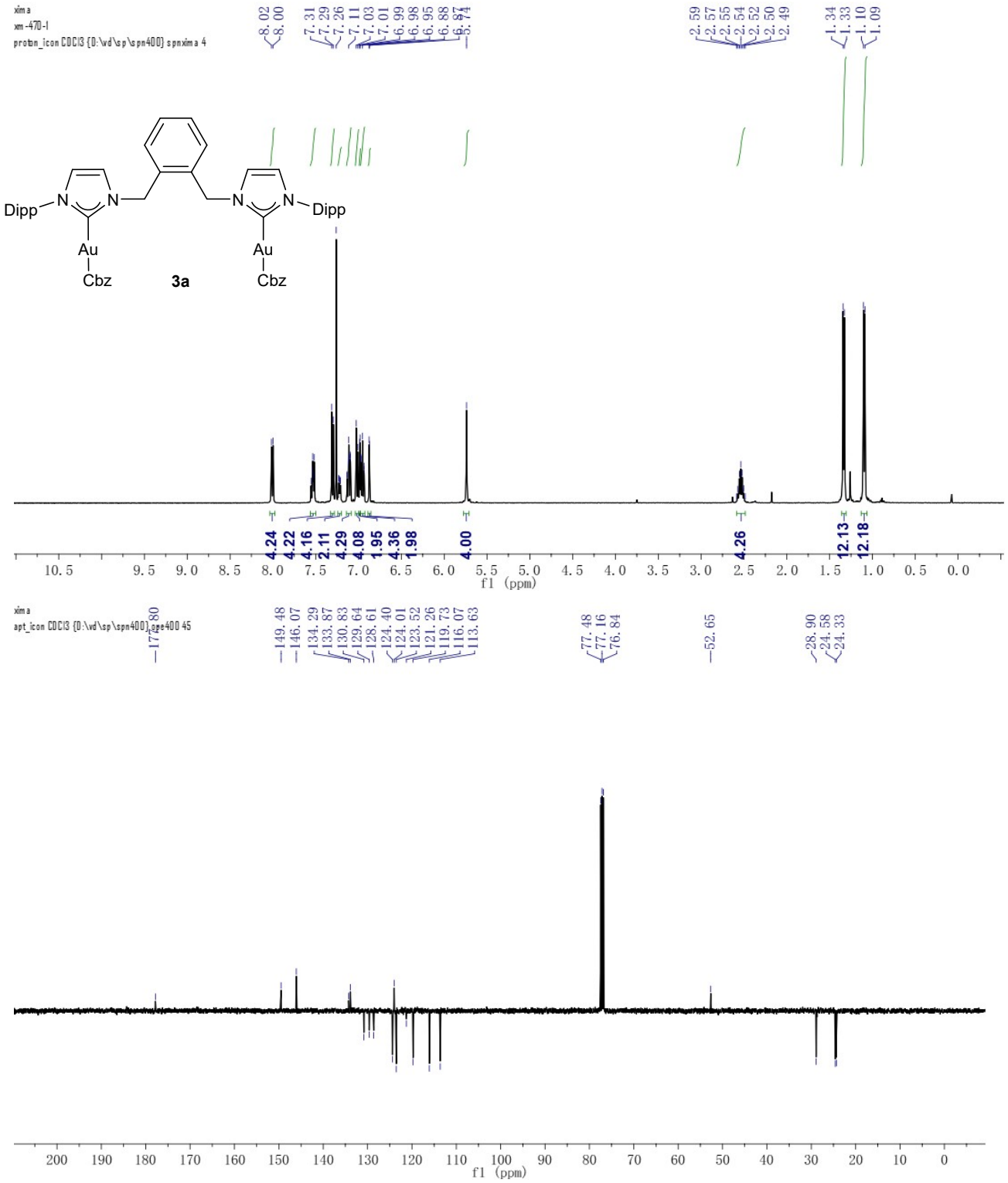
^{1}H and ^{13}C $\{^{1}H\}$ NMR of [IMes$^{p\text{-aryl}}${AuBr}$_2$] **2f**



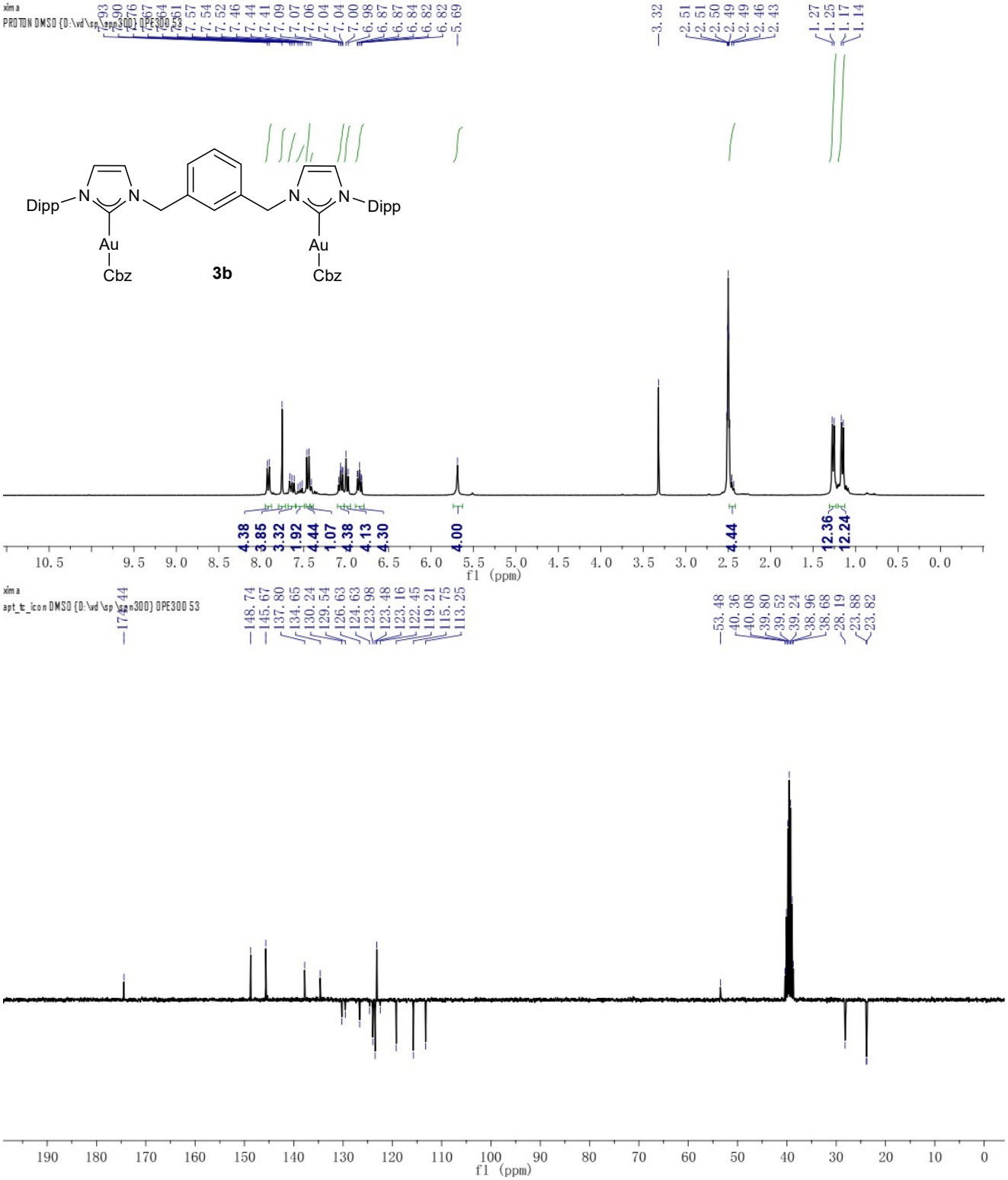
^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of [IMe$^{o\text{-aryl}}${AuBr}$_2$] **2g**



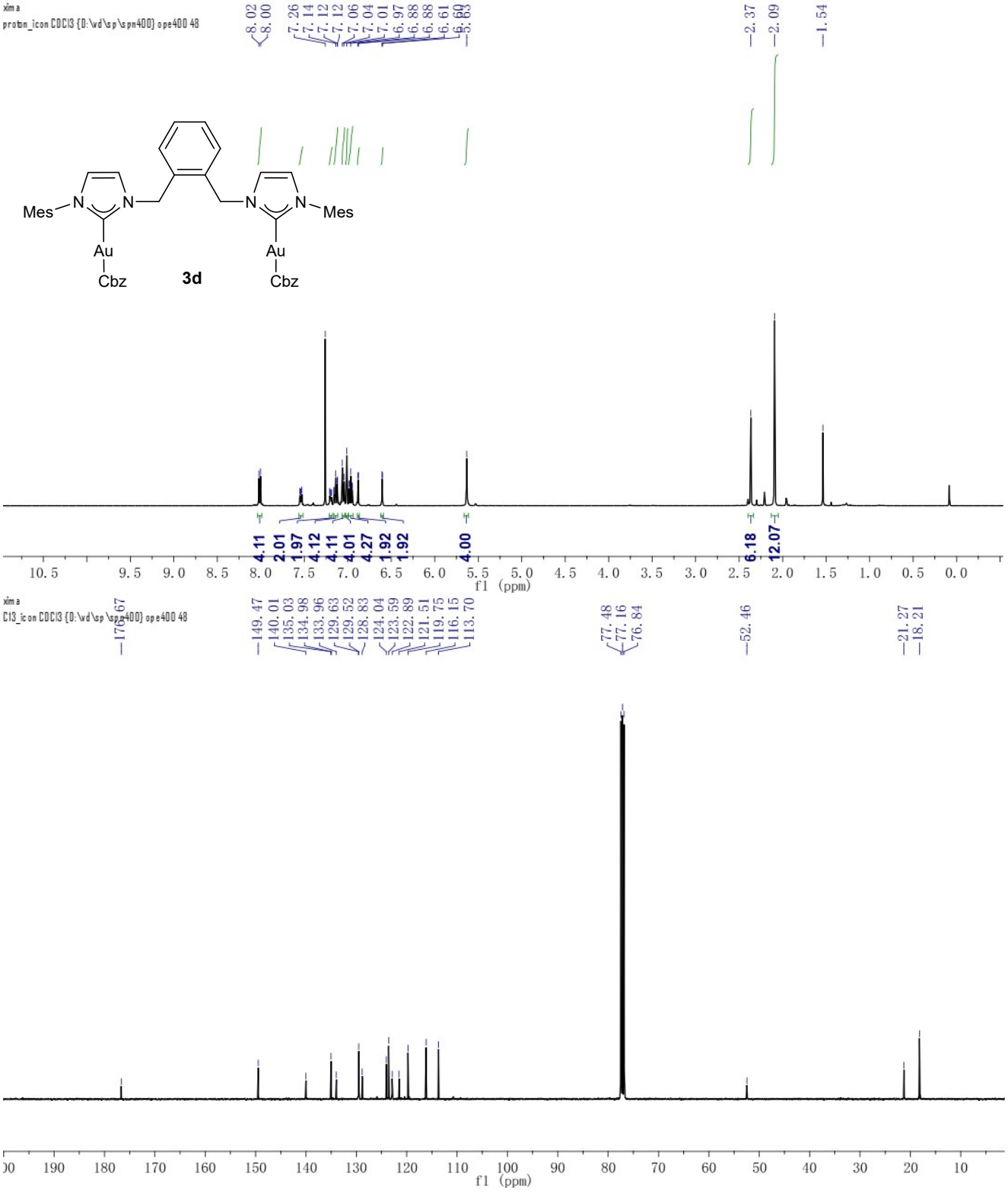
^{1}H and ^{13}C {^{1}H} apt NMR of [IPr$^{o\text{-aryl}}${Au(Cbz)}$_2$] **3a**



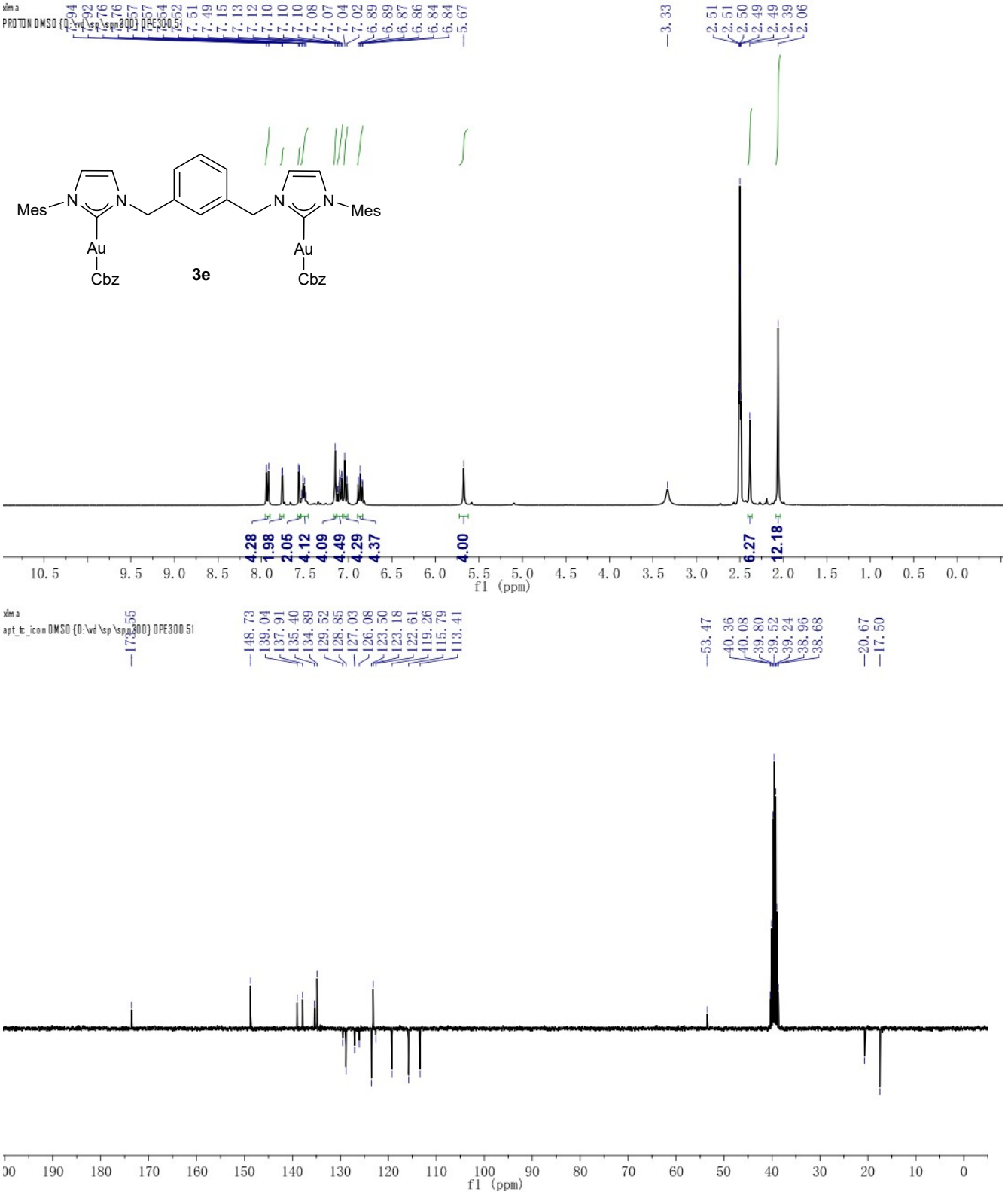
^{1}H and ^{13}C {^{1}H} apt NMR of [IPr$^{m\text{-aryl}}${Au(Cbz)}$_2$] **3b**



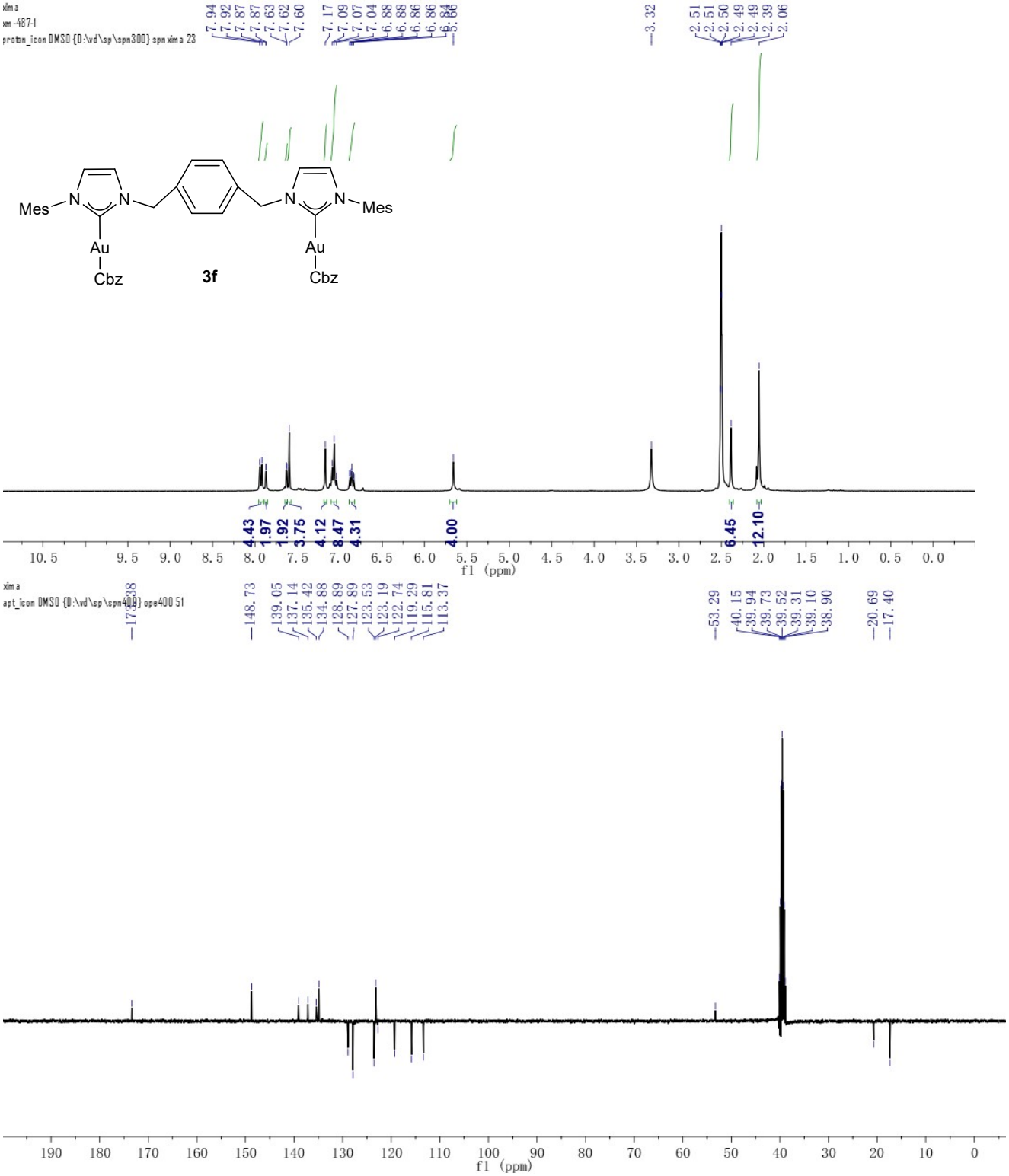
^{1}H and ^{13}C {^{1}H} NMR of [IMes$^{o\text{-aryl}}${Au(Cbz)}$_2$] **3d**



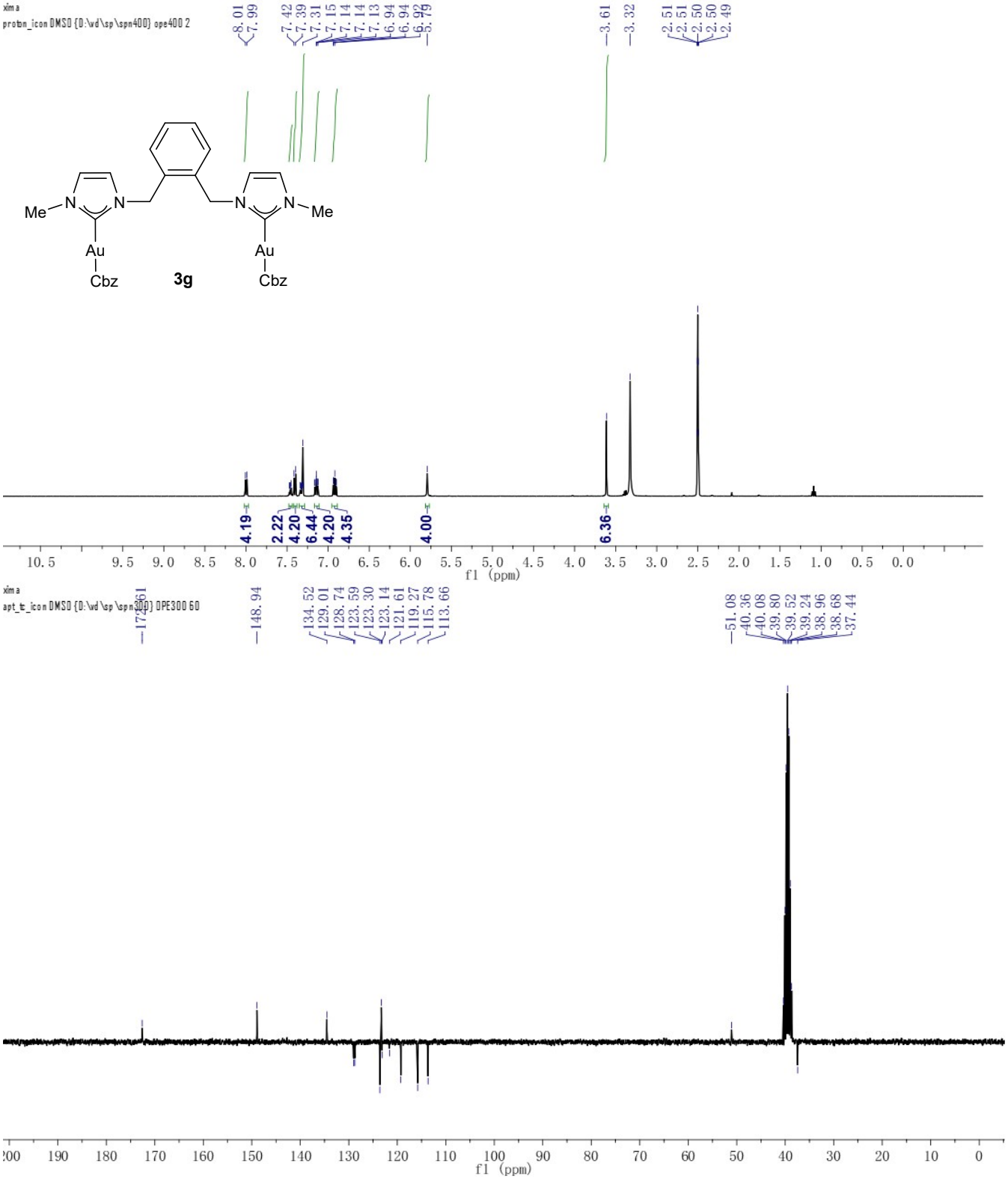
^{1}H and ^{13}C {^{1}H} apt NMR of [IMes$^{m\text{-aryl}}${Au(Cbz)}$_2$] **3e**



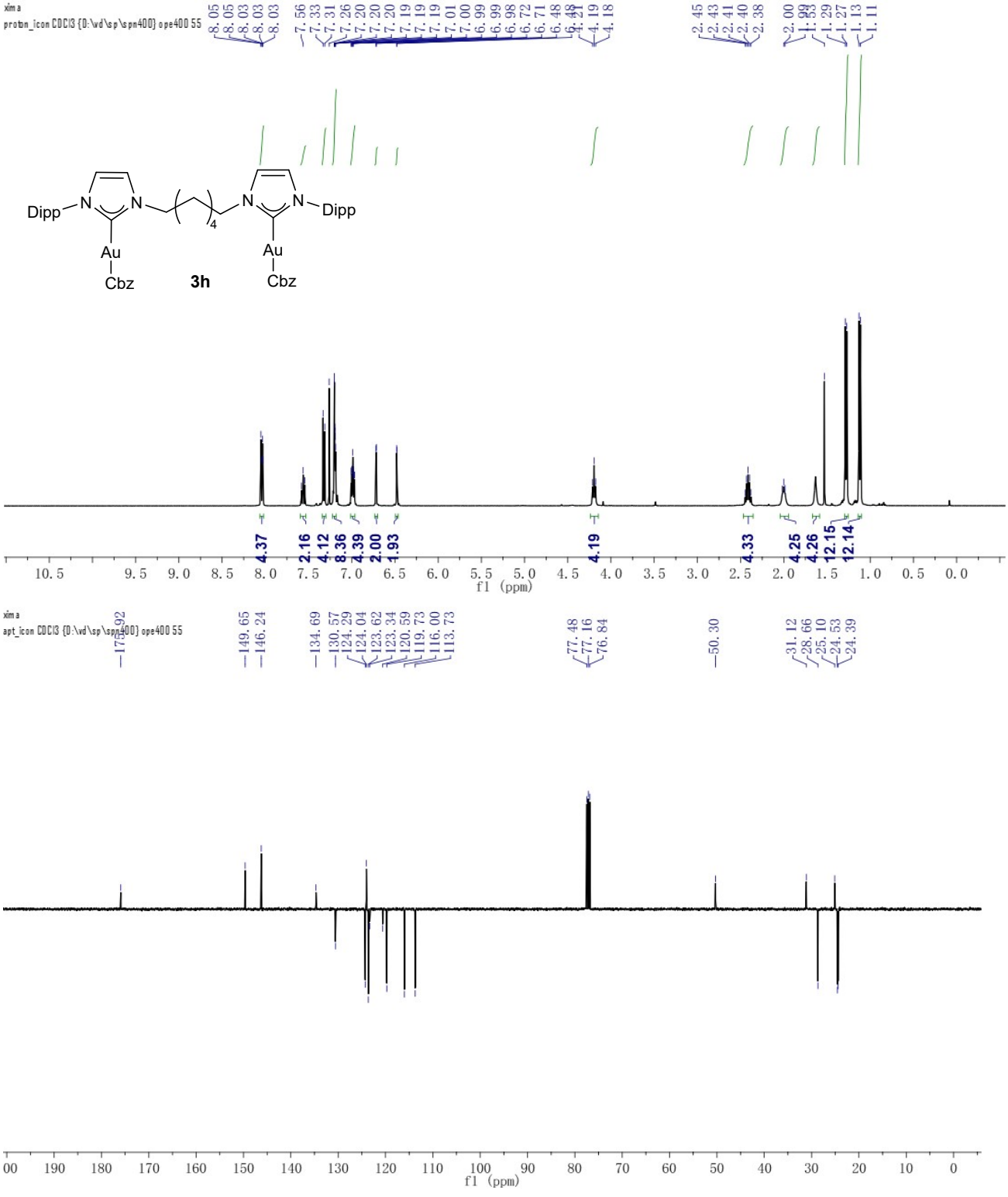
^{1}H and ^{13}C {^{1}H} apt NMR of [IMes$^{p\text{-aryl}}${Au(Cbz)}$_2$] **3f**



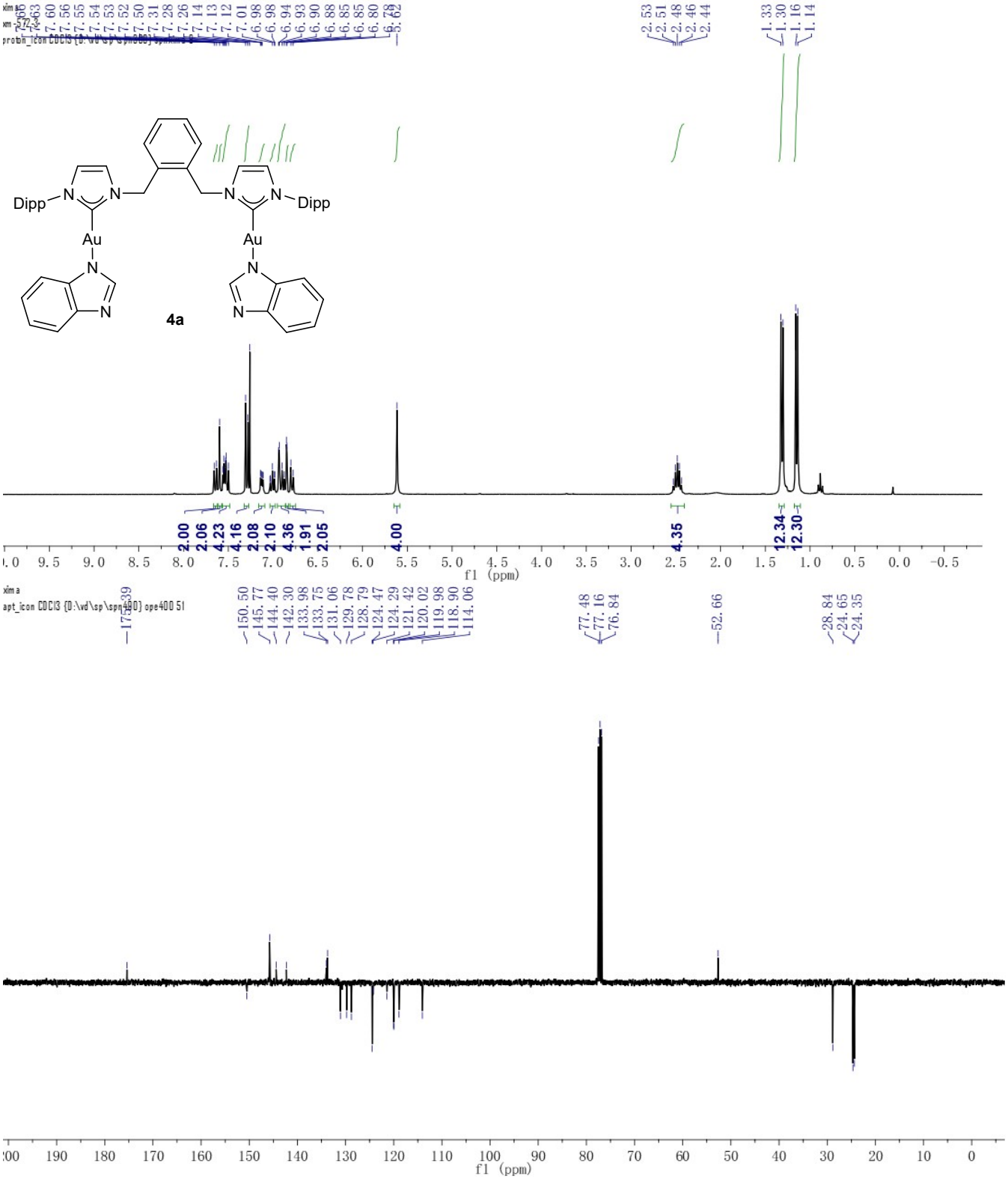
^{1}H and ^{13}C {^{1}H} apt NMR of [IMe$^{o\text{-aryl}}${Au(Cbz)}$_2$] **3g**



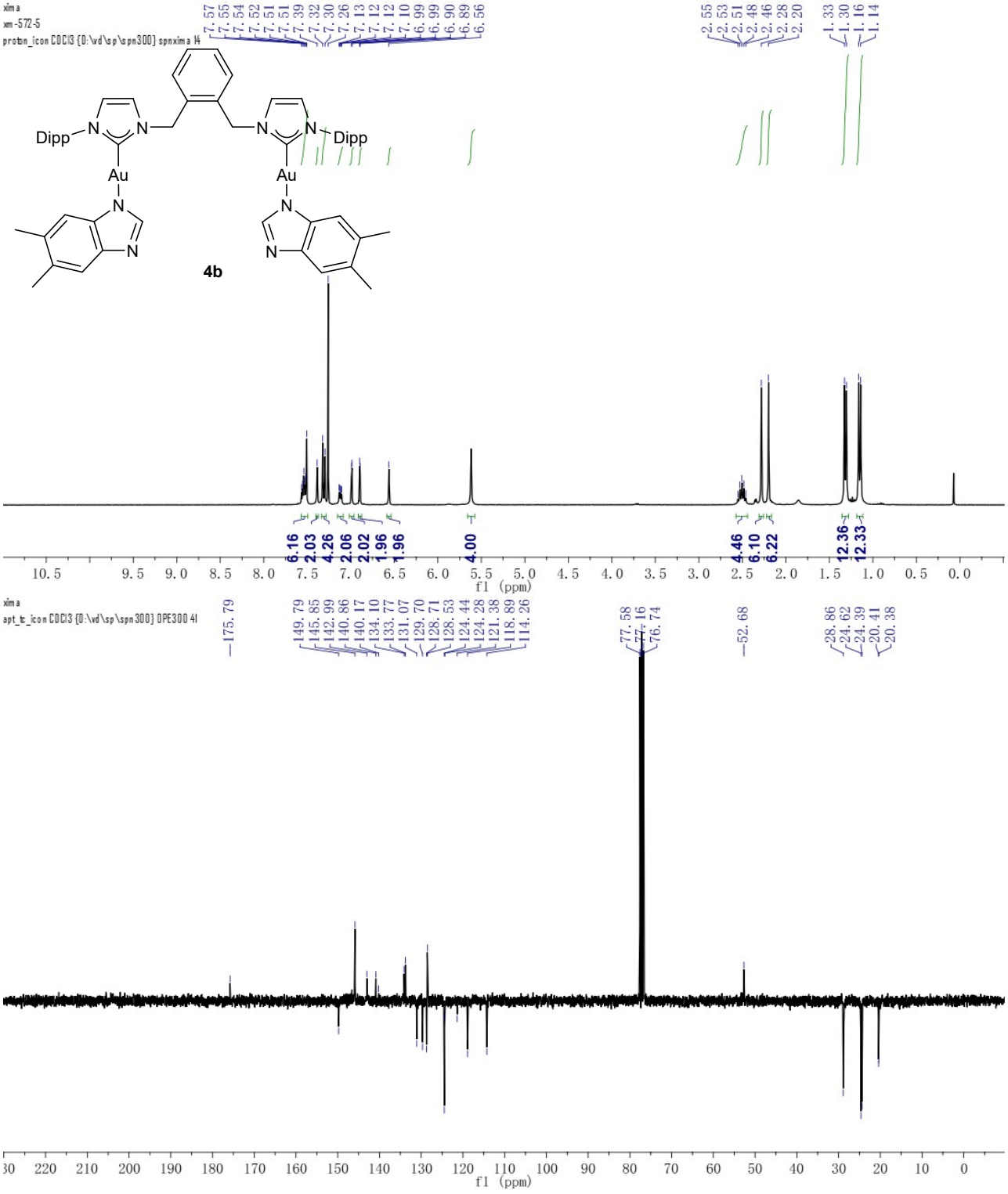
^{1}H and ^{13}C {^{1}H} apt NMR of [(IPr)$^{hexane\text{-}1,6\text{-}diyl}${Au(Cbz)}$_2$] **3h**



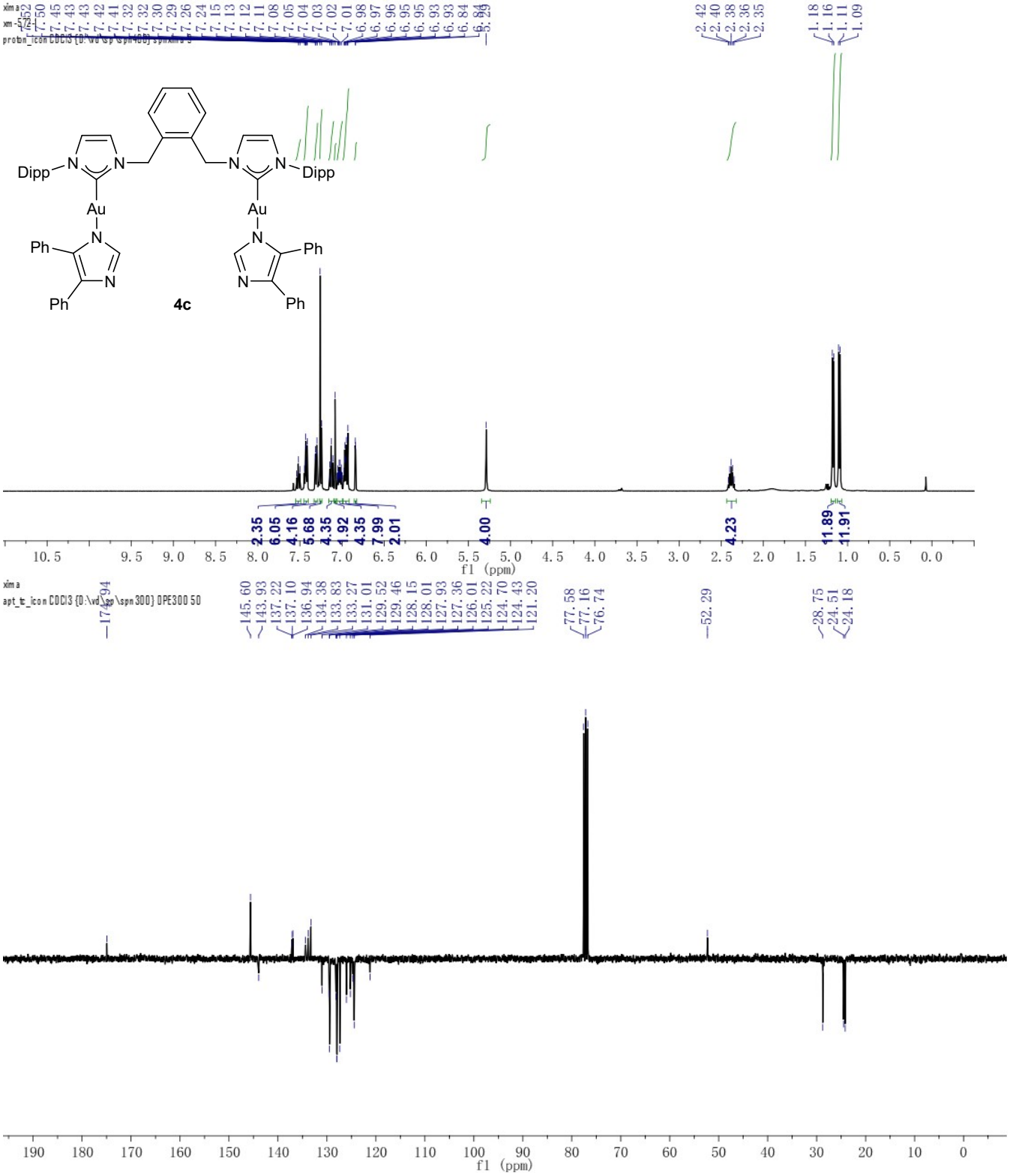
^{1}H and ^{13}C {^{1}H} apt NMR of [IPr$^{o\text{-aryl}}${Au(1H-benzimidazolato)}$_2$] **4a**



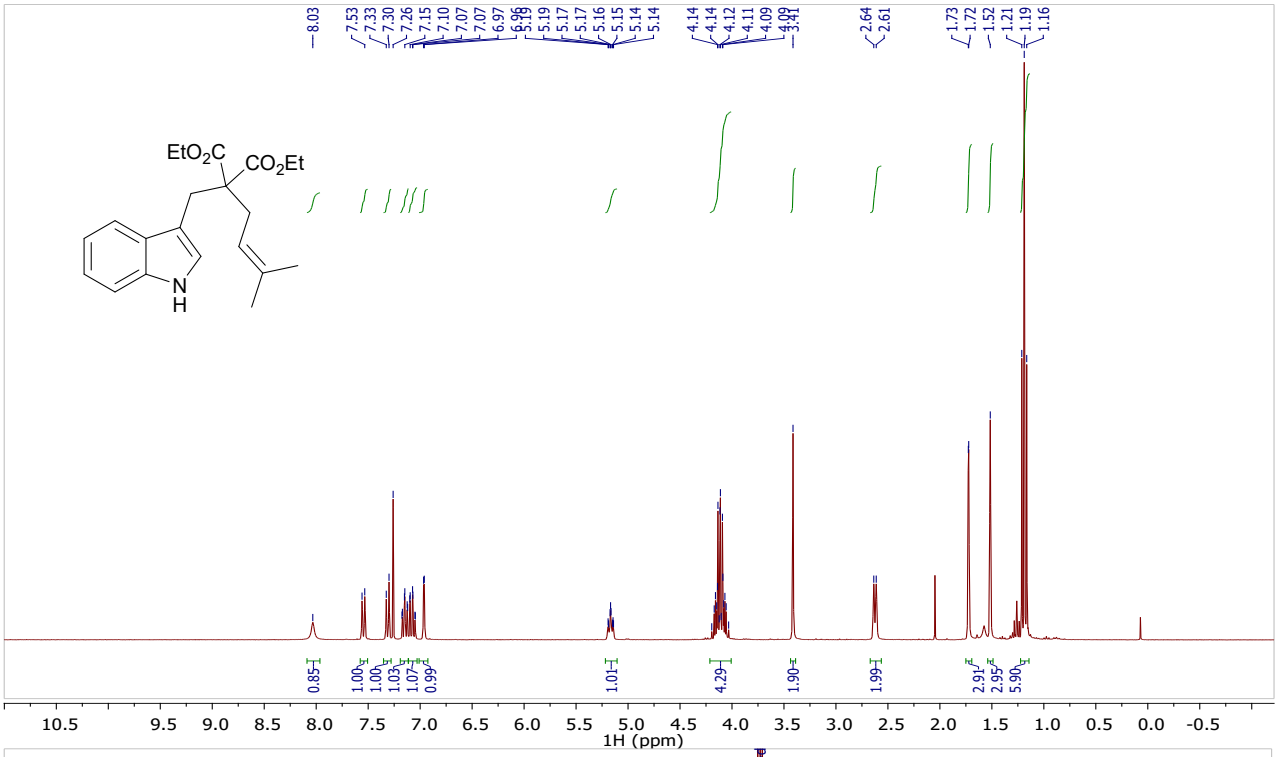
^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of [IPr$^{o\text{-aryl}}${Au(5,6-dimethyl-1H-benzimidazolato)}$_2$] **4b**

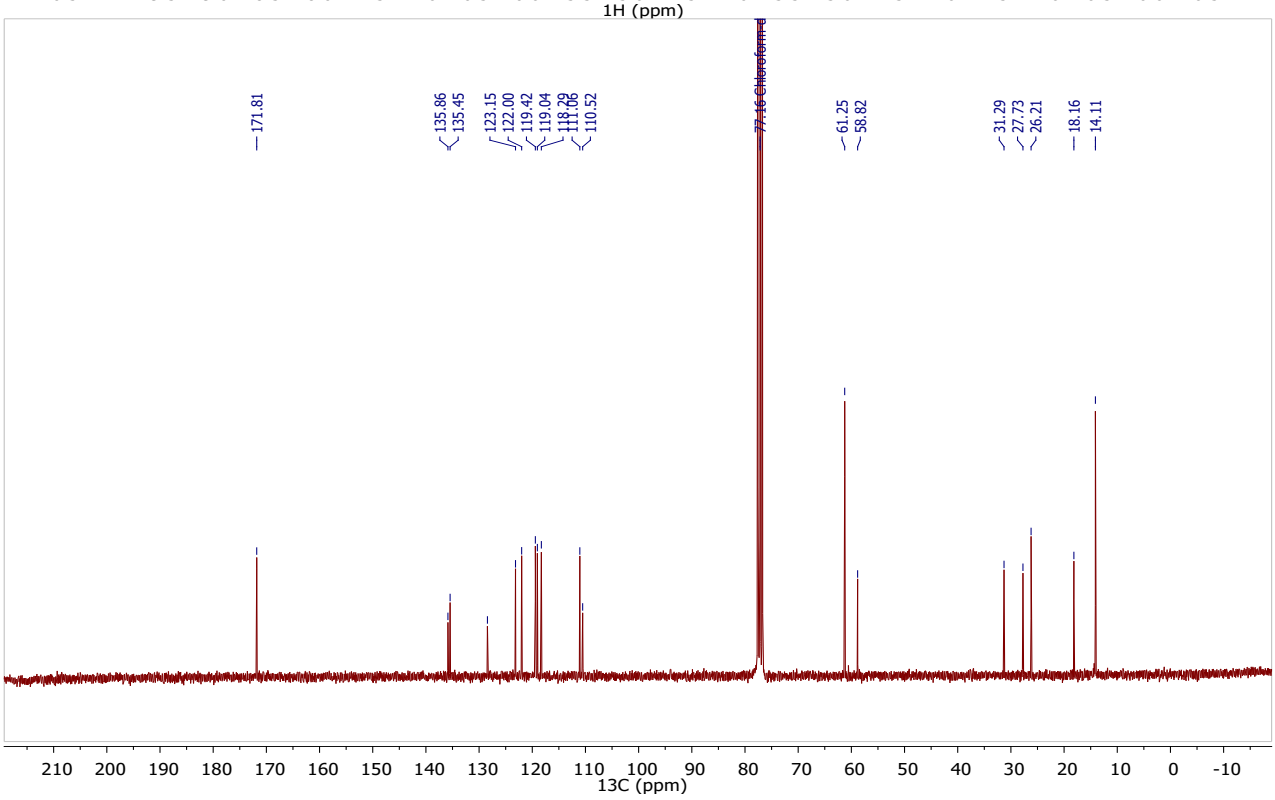


^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of $[(IPr)^{o\text{-aryl}}\{Au(4,5\text{-diphenyl-1H-imidazolato})\}_2]$ **4c**



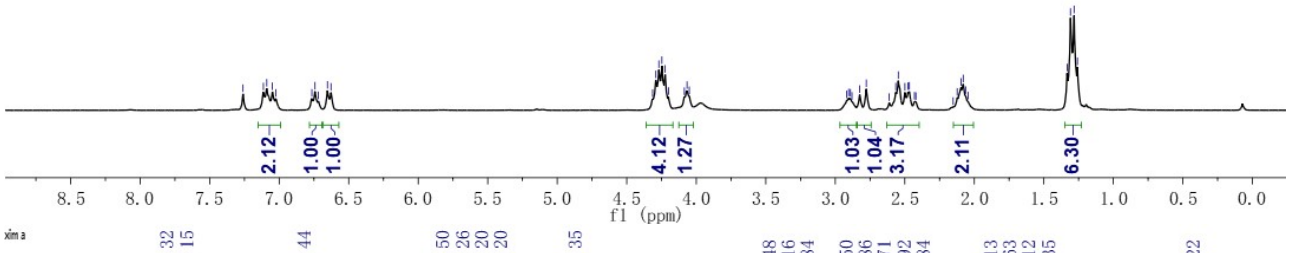
^{1}H and ^{13}C {^{1}H} NMR of Diethyl 2-((1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate **6**

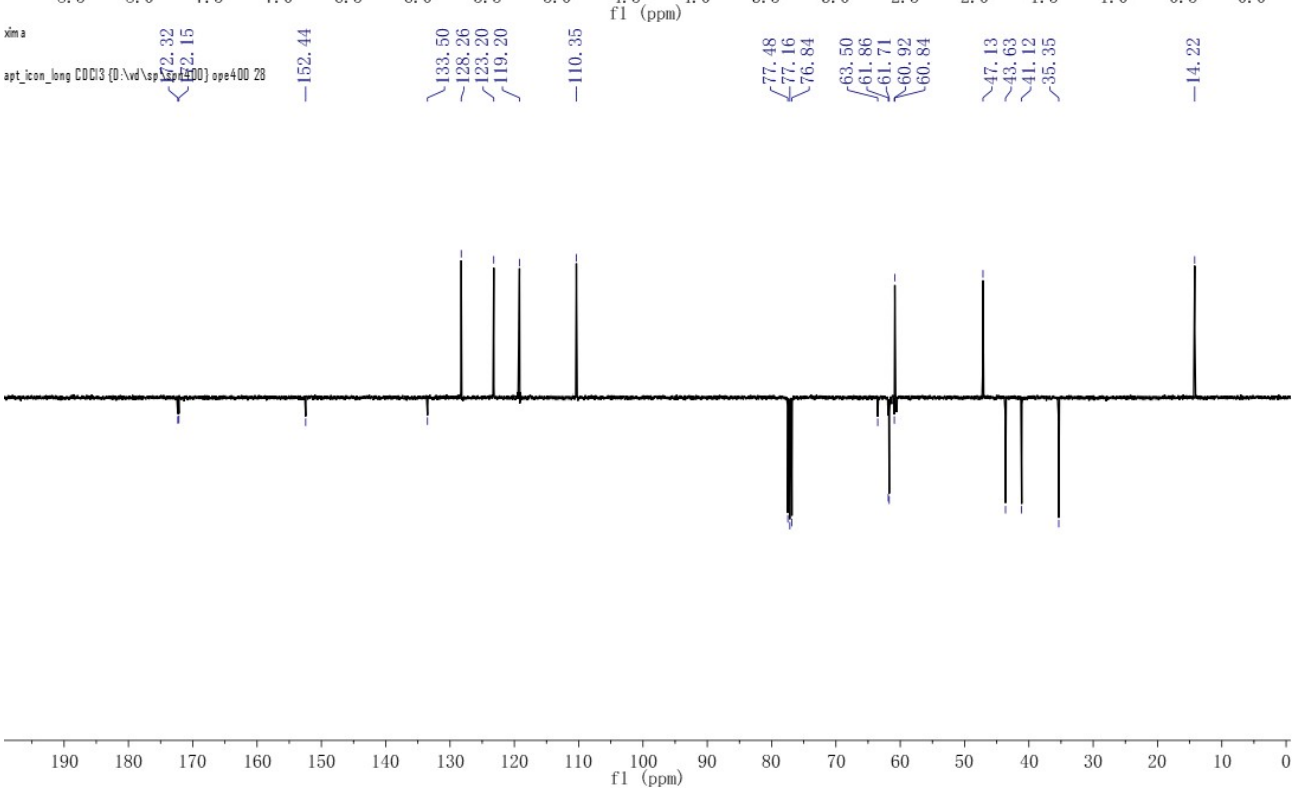




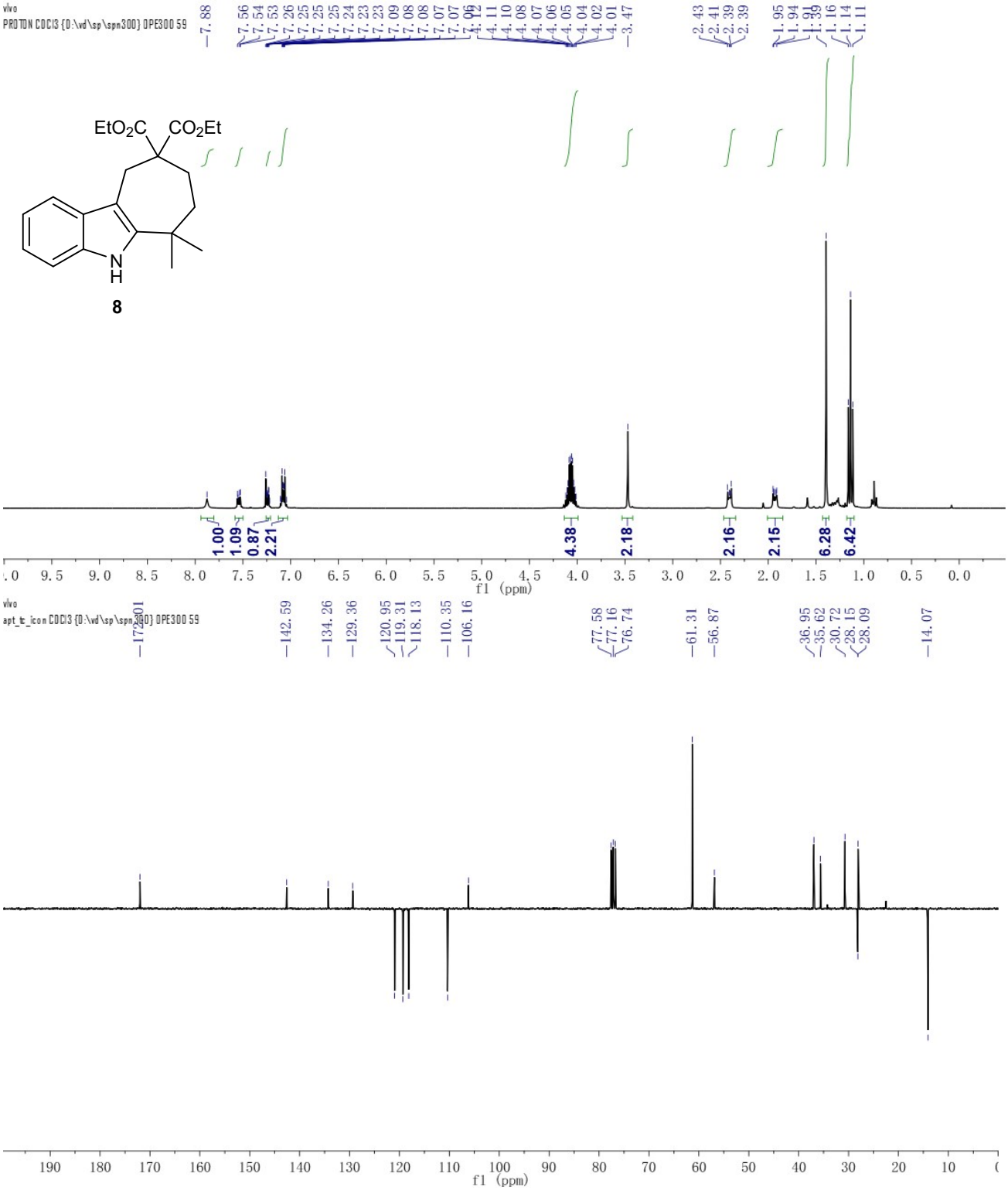
^{1}H and ^{13}C $\{^{1}H\}$ apt NMR of Diethyl (3aS*,4aS*,9bS*)-3a,4,4a,5-tetrahydro-1H-cyclopenta[2,3]cyclobuta[1,2-b]indole-2,2(3H)-dicarboxylate **7**

7





^{1}H and ^{13}C {^{1}H} apt NMR of Diethyl 6,6-dimethyl-6,7,8,10-tetrahydrocyclohepta[b]indole-9,9(5H)-dicarboxylate **8**



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