

SUPPORTING INFORMATION

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

Xinyuan Ma,^a Vladislav A. Voloshkin,^{†a} Ekaterina A. Martynova,^{†a} Marek Beliš,^a Min Peng,^a Marco Villa,^b
Nikolaos V. Tzouras,^a Wim Janssens,^a Kristof Van Hecke,^a Paola Ceroni,^b and Steven P. Nolan ^{*a}

SUPPORTING INFORMATION

Table of Contents

General Information	S3
General Procedure for Bis-imidazolium Salts	S5
General Procedure for Dinuclear Gold(I) Complexes [(L)(AuX) ₂]	S7
General Procedure for Dinuclear Gold(I) Amido Complexes [(L){Au(amido)} ₂]	S10
Photocatalytic Experiments	S15
General procedure for the [2+2] cycloaddition of indole.....	S16
General procedure for the cyclization of indole 6	S17
Absorption and PL spectroscopy	S19
Molecular Structures of Complexes	S30
NMR spectra	S33
References	S59

SUPPORTING INFORMATION

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 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 [$\text{IPr}^{\text{hexane-1,6-diyl}}\cdot 2\text{HCl}$] and the corresponding [$\text{IPr}^{\text{hexane-1,6-diyl}}(\text{AuCl})_2$] were prepared according to literature procedures.² ¹H NMR and ¹³C NMR were recorded in CDCl₃ 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™ 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 deaerated DMSO were carried out at 298 K. Degassed solutions are obtained by means of repeated pump-freeze-thaw cycles (ca. 4×10^{-6} mbar) in sealed quartz cuvettes. Emission quantum yields were measured following the method of Demas and

SUPPORTING INFORMATION

Crosby³ (standard used: $[\text{Ru}(\text{bpy})_3]^{2+}$ in air-equilibrated aqueous solution $\Phi = 0.04057$)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.

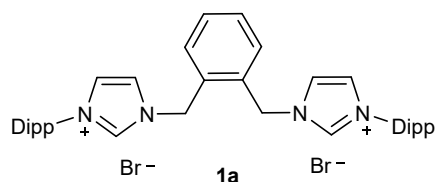
Photocatalytic experiments were performed in EvoluChem™ PhotoRedOx Box by HepatoChem, equipped with an EvoluChem™ LED. 365PF (365 nm, 18 W, 9 mW/cm) lamp was used.

SUPPORTING INFORMATION

General Procedure for Bis-imidazolium Salts

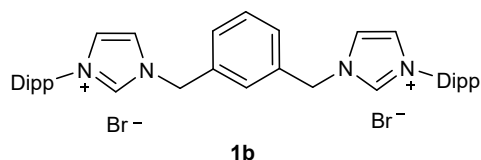
The salts were synthesized according to the modified procedure reported in the literature.² A 50 mL flask tube charged with stirring bar, imidazole (2 mmol, 2 equiv.) and aryl halide (1 mmol, 1 equiv.) was heated to 100°C in 12mL dioxane overnight. A white solid was produced in the reaction mixture over 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**



¹H NMR (300 MHz, CDCl₃) δ 10.56 (s, 2H, NCHN), 8.38 (s, 2H, CH=CH), 7.53 (t, *J* = 7.8 Hz, 2H, CH, Dipp), 7.43 – 7.37 (m, 2H, CH, *o*-xylene), 7.34 (dd, *J* = 6.6, 2.7 Hz, 2H, CH, *o*-xylene), 7.30 (d, *J* = 7.9 Hz, 4H, CH, Dipp), 7.20 (s, 2H, CH=CH), 6.53 (s, 4H, CH₂), 2.44 – 2.26 (m, 4H, CH(CH₃)₂), 1.23 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.18 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃) δ 145.5 (C(Pr), Dipp), 138.3 (NCHN), 132.8 (CH₂C, *o*-xylene), 132.1 (CH, Dipp), 130.3 (CN, Dipp), 130.0 (CH, *o*-xylene), 129.1 (CH, *o*-xylene), 124.8 (CH, Dipp), 124.7 (CH=CH), 124.4 (CH=CH), 50.4 (CH₂), 28.9 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 24.2 (CH(CH₃)₂). Analytical data obtained are in agreement with reported values.⁵

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

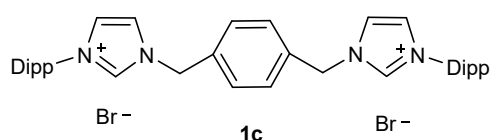


¹H NMR (400 MHz, DMSO-d₆) δ 9.83 (s, 2H, NCHN), 8.18 (d, *J* = 15.8 Hz, 4H, CH=CH), 7.74 (s, 1H, CH, *m*-xylene), 7.63 (t, *J* = 7.8 Hz, 2H, CH, Mes), 7.60 – 7.54 (m, 1H, CH, *m*-xylene), 7.49 – 7.43 (m, 6H, CH, Mes; CH, *m*-xylene), 5.63 (s, 4H, CH₂), 2.22 (dt, *J* = 13.5, 6.7 Hz, 4H, CH(CH₃)₂), 1.12 (t, *J* = 7.3 Hz, 24H, CH(CH₃)₂). ¹³C NMR (101 MHz, DMSO) δ 145.0 (C(CH₃)₂, Dipp), 138.0 (NCHN), 135.6 (CCH, *m*-xylene), 131.6 (CH, Dipp), 130.5 (CN, Dipp), 130.1 (CH, *m*-xylene), 128.7 (CH, *m*-xylene), 128.4 (CH, *m*-xylene), 125.4 (CH=CH), 124.5 (CH, Dipp), 123.6 (CH=CH), 52.2 (CH₂), 28.1

SUPPORTING INFORMATION

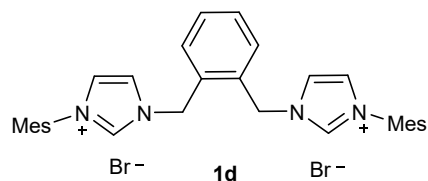
($\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)_2$), 23.8 ($\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)_2$), 23.7 ($\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)_2$). Analytical data obtained are in agreement with reported values.⁶

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



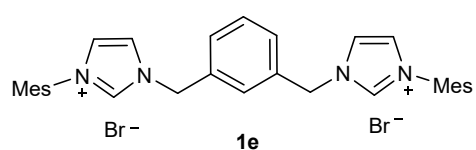
¹H NMR (300 MHz, CD₂Cl₂) δ 10.82 (s, 2H, NCHN), 8.00 (s, 2H), 7.72 (s, 4H), 7.57 (t, *J* = 7.8 Hz, 2H, CH, Dipp), 7.34 (d, *J* = 7.8 Hz, 4H, CH, Dipp), 7.21 (t, *J* = 1.6 Hz, 2H), 6.10 (s, 4H, CH₂), 2.28 (dt, *J* = 13.6, 6.8 Hz, 4H, CH(CH₃)₂), 1.21 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.15 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR (75 MHz, CD₂Cl₂) δ 146.0, 139.0, 135.6, 132.5, 130.8, 130.3, 125.3, 125.0, 123.7, 53.1(CH₂) 29.3 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 24.3 (CH(CH₃)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**



¹H NMR (300 MHz, CDCl₃) δ 10.36 (t, *J* = 1.5 Hz, 2H, NCHN), 8.15 (t, *J* = 1.7 Hz, 2H, CH=CH), 7.46 – 7.35 (m, 4H, CH, *o*-xylene), 7.18 (t, *J* = 1.8 Hz, 2H, CH=CH), 7.00 (s, 4H, CH, Mes), 6.45 (s, 4H, CH₂), 2.34 (s, 6H, CH₃, Mes), 2.12 (s, 12H, CH₃, Mes). ¹³C NMR (75 MHz, CDCl₃) 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

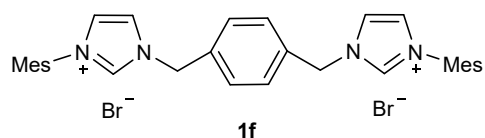
3,3'-Bis[1-mesityl-1*H*-imidazolium]-1,1-*m*-phenylenedimethylenebis(imidazolium) dibromide **1e**



¹H NMR (300 MHz, CDCl₃) δ 10.48 (s, 2H, NCHN), 8.68 (t, *J* = 1.5 Hz, 2H, CH=CH), 8.50 (s, 1H, CH, *m*-xylene), 7.70 (dd, *J* = 7.7, 1.4 Hz, 2H, CH, *m*-xylene), 7.14 – 7.05 (m, 3H, CH=CH; CH, *m*-xylene), 6.96 (s, 4H, CH, Mes), 5.91 (s, 4H, CH₂), 2.31 (s, 6H, CH₃), 2.01 (s, 12H, CH₃). ¹³C NMR (75 MHz, CDCl₃) 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 C₃₂H₃₆Br₂N₄: C, 60.39; H, 5.7; N, 8.8; found: C, 59.61; H, 5.91; N, 8.62.

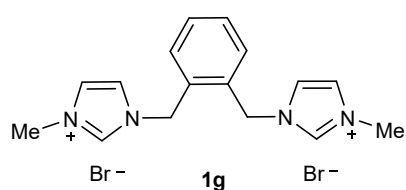
3,3'-Bis[1-mesityl-1*H*-imidazolium]-1,1-*p*-phenylenedimethylenebis(imidazolium) dibromide **1f**

SUPPORTING INFORMATION



^1H NMR (400 MHz, DMSO- d_6) δ 9.65 (t, J = 1.5 Hz, 2H, NCHN), 8.09 (t, J = 1.7 Hz, 2H, CH=CH), 7.97 (t, J = 1.8 Hz, 2H, CH=CH), 7.55 (s, 4H, CH, *p*-xylene), 7.15 (s, 4H, CH, Mes), 5.58 (s, 4H, CH₂), 2.33 (s, 6H, CH₃), 2.00 (s, 12H, CH₃). ^{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**

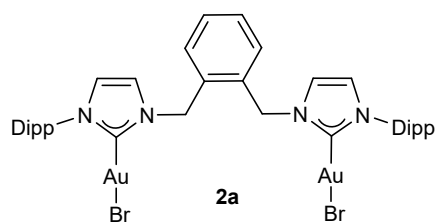


^1H NMR (300 MHz, DMSO- d_6) δ 9.25 (s, 2H, NCHN), 7.78 (dt, J = 5.6, 1.7 Hz, 4H, CH=CH), 7.48 (dd, J = 5.7, 3.4 Hz, 2H, CH, *o*-xylene), 7.33 (dd, J = 5.6, 3.5 Hz, 2H, CH, *o*-xylene), 5.67 (s, 4H, CH₂), 3.88 (s, 6H, CH₃). ^{13}C NMR (75 MHz, DMSO) δ 136.9, 132.9, 129.7, 129.6, 124.0, 122.5, 49.0, 36.0. 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.), K₂CO₃ (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*-xylene}(AuBr)₂] **2a**

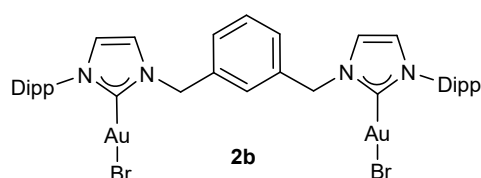


Colorless solid (506.1mg, 91%). ^1H NMR (300 MHz, CDCl₃) δ 7.51 – 7.45 (m, 2H, CH, Dipp), 7.42 (dd, J = 5.7, 3.3 Hz, 2H, CH, *o*-xylene), 7.29 – 7.25 (m, 4H, CH, Dipp), 7.24 (d, J = 1.9 Hz, 2H, CH=CH), 7.07 (d, J = 1.9 Hz, 2H, CH=CH), 7.04 (dd, J = 5.6, 3.4 Hz, 2H, CH, *o*-xylene), 5.61 (s, 4H, CH₂), 2.51 (dt,

SUPPORTING INFORMATION

$J = 13.7, 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.30 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 177.6 ($\text{N}\underline{\text{C}}\text{N}$), 145.8 ($\text{C}(\textit{i}\text{Pr})$, Dipp), 134.0 ($\text{CH}_2\underline{\text{C}}$, *o*-xylene), 133.3 ($\text{C}\underline{\text{N}}$, Dipp), 130.9, 129.6 ($\text{C}\underline{\text{H}}$, *o*-xylene), 128.3 ($\text{C}\underline{\text{H}}$, *o*-xylene), 124.8, 124.4 ($\text{C}\underline{\text{H}}$, Dipp), 121.1, 52.4 ($\text{C}\underline{\text{H}}_2$), 28.7 ($\text{CH}(\text{CH}_3)_2$), 24.6 ($\text{CH}(\text{CH}_3)_2$), 24.5 ($\text{CH}(\text{CH}_3)_2$). HRMS calculated for $\text{C}_{38}\text{H}_{46}\text{N}_4\text{Au}_2\text{Br}$ [$\text{M} - \text{Br}$] $^+$: 1031.2237; found : 1031.2241. Anal. Calcd for $\text{C}_{38}\text{H}_{46}\text{Au}_2\text{Br}_2\text{N}_4$: C, 41.02; H, 4.17; N, 5.04; found: C, 41.55; H, 3.89; N, 5.09.

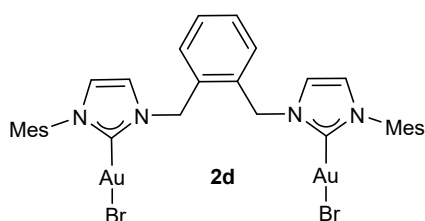
$[(\text{IPr})^{m\text{-xylene}}(\text{AuBr})_2]$ **2b**



Colorless solid (445.0mg, 80%). ^1H NMR (300 MHz, DMSO-d_6) δ 7.79 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\underline{\text{C}}\text{H}$), 7.72 (d, $J = 1.8$ Hz, 2H, $\text{C}\underline{\text{H}}=\text{CH}$), 7.57 – 7.46 (m, 3H, $\text{C}\underline{\text{H}}$, Dipp; $\text{C}\underline{\text{H}}$, *m*-xylene), 7.45 (s, 1H, $\text{C}\underline{\text{H}}$, *m*-xylene), 7.37 (d, $J = 7.7$ Hz,

4H, $\text{C}\underline{\text{H}}$, Dipp), 7.24 (d, $J = 7.7$ Hz, 2H, $\text{C}\underline{\text{H}}$, *m*-xylene), 5.53 (s, 4H, $\text{C}\underline{\text{H}}_2$), 2.35 (dt, $J = 13.6, 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.12 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, DMSO) δ 174.6 ($\text{N}\underline{\text{C}}\text{N}$), 145.3 ($\text{C}(\textit{i}\text{Pr})$), 137.3 ($\text{CH}_2\underline{\text{C}}$, *m*-xylene), 134.2 ($\text{C}\underline{\text{N}}$, Dipp), 130.3, 129.5, 126.6, 126.4, 124.7, 123.9 ($\text{C}\underline{\text{H}}$, Dipp), 122.1, 53.4 ($\text{C}\underline{\text{H}}_2$), 28.0 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$), 23.7 ($\text{CH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{38}\text{H}_{46}\text{Au}_2\text{Br}_2\text{N}_4$: C, 41.02; H, 4.17; N, 5.04; found: C, 41.04; H, 4.55; N, 5.52.

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

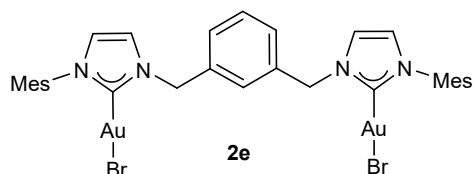


Colorless solid (426.78mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.40 (dd, $J = 5.7, 3.3$ Hz, 2H, $\text{C}\underline{\text{H}}$, *o*-xylene), 7.22 (d, $J = 2.0$ Hz, 2H, $\text{C}\underline{\text{H}}=\text{CH}$), 7.04 – 7.00 (m, 4H, $\text{C}\underline{\text{H}}$, *o*-xylene; $\text{C}\underline{\text{H}}=\text{CH}$), 6.97 (d, $J = 0.4$ Hz, 4H, $\text{C}\underline{\text{H}}$, Mes), 5.58 (s, 4H, $\text{C}\underline{\text{H}}_2$), 2.33 (s, 6H, $\text{C}\underline{\text{H}}_3$), 2.08 (s, 12H, $\text{C}\underline{\text{H}}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ

176.6 ($\text{N}\underline{\text{C}}\text{N}$), 140.0 ($\text{CH}_3\underline{\text{C}}$, Mes), 134.8 ($\text{CH}_3\underline{\text{C}}$, Mes), 134.6, 133.4, 129.7 ($\text{C}\underline{\text{H}}$, Mes), 129.6 ($\text{C}\underline{\text{H}}$, *o*-xylene), 128.3 ($\text{C}\underline{\text{H}}$, *o*-xylene), 123.6 ($\text{C}\underline{\text{H}}=\text{CH}$), 121.4 ($\text{C}\underline{\text{H}}=\text{CH}$), 52.4 ($\text{C}\underline{\text{H}}_2$), 21.3 ($\text{C}\underline{\text{H}}_3$), 18.3 ($\text{C}\underline{\text{H}}_3$). HRMS calculated for $\text{C}_{32}\text{H}_{34}\text{N}_4\text{Au}_2\text{Br}$ [$\text{M} - \text{Br}$] $^+$: 947.1298; found : 947.1294.

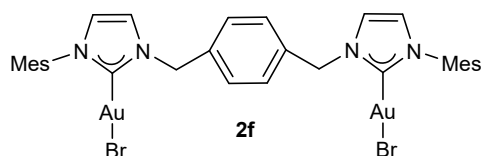
$[(\text{IMes})^{m\text{-xylene}}(\text{AuBr})_2]$ **2e**

SUPPORTING INFORMATION



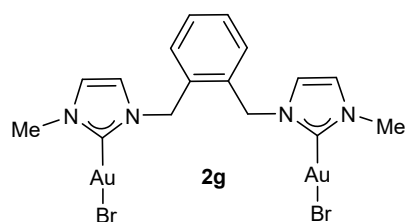
Colorless solid (390.78mg, 76%). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.49 – 7.42 (m, 2H, CH , *m*-xylene), 7.38 – 7.32 (m, 2H, CH , *m*-xylene), 7.27 (d, J = 1.9 Hz, 2H, $\text{CH}=\text{CH}$), 7.04 (s, 4H, CH , Mes), 6.97 (d, J = 2.0 Hz, 2H, $\text{CH}=\text{CH}$), 5.51 (s, 4H, CH_2), 2.37 (s, 6H, CH_3), 2.05 (s, 12H, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.4 (NCN), 140.5 (CH_3 C, Mes), 137.2 (CH_2 C, *m*-xylene), 135.5 (CH_3 C, Mes), 135.4 (CN, Mes), 130.6, 129.9 (CH, Mes), 128.3, 128.0, 123.4, 121.8, 55.2 (C H_2), 21.5 (C H_3), 18.2 (C H_3). HRMS calculated for $\text{C}_{33}\text{H}_{34}\text{N}_5\text{Au}_2$ [$\text{M}-2\text{Br}+\text{CN}^+$] $^+$: 894.2145; found : 894.2144.

[(IMes)^{*p*-xylene}(AuBr)₂] **2f**



Colorless solid (287.95mg, 56%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.82 (d, J = 1.9 Hz, 2H, $\text{CH}=\text{CH}$), 7.54 (d, J = 1.9 Hz, 2H, $\text{CH}=\text{CH}$), 7.40 (s, 4H, CH, *p*-xylene), 7.08 (s, 4H, CH, Mes), 5.49 (s, 4H, CH_2), 2.32 (s, 6H, CH_3), 1.97 (s, 12H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ 173.4 (NCN), 138.9 (CH_3 C, Mes), 136.6 (CH_2 C, *p*-xylene), 134.9, 134.5, 129.0, 127.6, 123.5, 122.4, 53.2 (C H_2), 20.6 (C H_3), 17.3 (C H_3). Anal. Calcd for $\text{C}_{32}\text{H}_{34}\text{Au}_2\text{Br}_2\text{N}_4$: C, 37.37; H, 3.33; N, 5.45; found: C, 37.48; H, 3.09; N, 5.29.

[(IMe)^{*o*-xylene}(AuBr)₂] **2g**



Colorless solid (250.13mg, 61%). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.51 (d, J = 1.9 Hz, 2H, $\text{CH}=\text{CH}$), 7.39 – 7.31 (m, 4H, CH, *o*-xylene; $\text{CH}=\text{CH}$), 7.07 (dd, J = 5.6, 3.5 Hz, 2H, $\text{CH}=\text{CH}$), 5.49 (s, 4H, CH_2), 3.82 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ 173.0 (NCN), 134.1 (CH_2 C, *o*-xylene), 128.6 (CH, *o*-xylene), 128.4 (CH, *o*-xylene), 123.4 (C $\text{H}=\text{CH}$), 121.4 123.4 (C $\text{H}=\text{CH}$), 50.7 123.4 (C H_2), 37.8 (C H_3). HRMS calculated for $\text{C}_{16}\text{H}_{18}\text{N}_4\text{Au}_2\text{Br}$ [$\text{M} - \text{Br}$] $^+$: 739.0046; found: 739.0115.

General Procedure for Dinuclear Gold(I) Amido Complexes [(L){Au(amido)}₂]

SUPPORTING INFORMATION

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), K₂CO₃ (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.

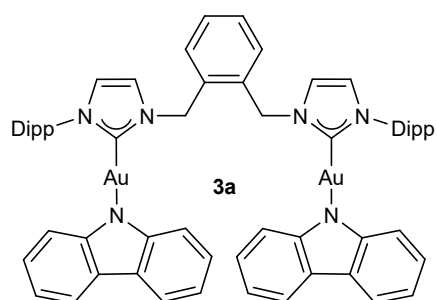
Path B (Other amines as the ligand): A 4 mL vial equipped with a screw cap and a stirring bar was charged, under air, with the corresponding [(IPr)^{o-xylene}(AuBr)₂] (0.1 mmol, 1 equiv., 111.2mg), amine (0.2 mmol, 2 equiv.), K₂CO₃ (0.6 mmol, 6 equiv., 83 mg) and EtOH (1 mL). The mixture was stirred 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-xylene}·2HCl] (0.1 mmol, 1 equiv.), 82.9 mg of K₂CO₃ (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 K₂CO₃ (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-xylene}{Au(Cbz)₂}]₂ **3a** as a colorless solid in 76% yield (97.7 mg).

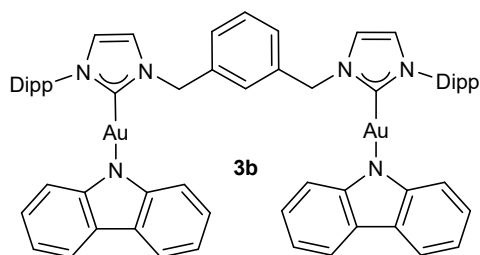
[(IPr)^{o-xylene}{Au(Cbz)₂}] **3a**

SUPPORTING INFORMATION



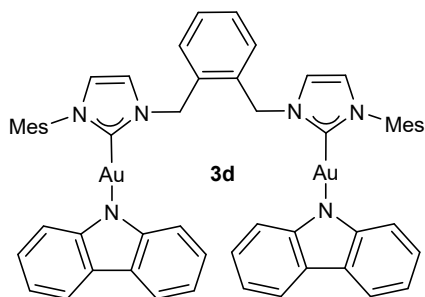
Colorless solid (106.5mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.5$ Hz, 4H, CH , Cbz), 7.57 – 7.50 (m, 4H, CH , Dipp and CH , *o*-xylene), 7.30 (d, $J = 7.8$ Hz, 4H, CH , Dipp), 7.22 (dd, $J = 5.6, 3.4$ Hz, 2H, CH , *o*-xylene), 7.11 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 4H, CH , Cbz), 7.02 (d, $J = 8.0$ Hz, 4H, CH , Cbz), 6.98 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\text{CH}$), 6.98 – 6.93 (m, 4H, CH , Cbz), 6.87 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\text{CH}$), 5.74 (s, 4H, CH_2), 2.61 – 2.47 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, CDCl_3) δ 177.8 (NCN), 149.5 (CHCN , Cbz), 146.1 ($\text{C}(\text{Pr})$), 134.3 (CH_2C , *o*-xylene), 133.9 (CN , Dipp), 130.8, 129.6 (CH , *o*-xylene), 128.6 (CH , *o*-xylene), 124.4 (CH , Dipp), 124.0 (CCH , Cbz), 123.5 (CH , Cbz), 121.3, 119.7 (CH , Cbz), 116.1 (CH , Cbz), 113.6 (CH , Cbz), 52.7 (CH_2), 28.9 (CHCH_3), 24.6 (CHCH_3), 24.3 (CHCH_3). Anal. Calcd for $\text{C}_{62}\text{H}_{62}\text{Au}_2\text{N}_6$: C, 57.95; H, 4.86; N, 6.54; found: C, 57.54; H, 4.61; N, 6.17.

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



Colorless solid (91.3mg, 71%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 7.92 (d, $J = 7.5$ Hz, 4H, CH , Cbz), 7.76 (s, 4H, $\text{CH}=\text{CH}$), 7.68 – 7.60 (m, 3H), 7.58 – 7.50 (m, 2H), 7.45 (d, $J = 7.8$ Hz, 4H, CH , Cbz), 7.41 (s, 1H, CH , *m*-xylene), 7.10 – 7.03 (m, 4H, CH , Cbz), 6.99 (d, $J = 7.9$ Hz, 4H, CH , Dipp), 6.90 – 6.79 (m, 4H, CH , Cbz), 5.69 (s, 4H, CH_2), 2.45 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, DMSO) δ 174.4 (NCN), 148.7 (CHCN , Cbz), 145.7 ($\text{C}(\text{Pr})$), 137.8, 134.7 (CN , Dipp), 130.2, 129.5, 126.6 (CCH , *m*-xylene), 124.6, 124.0, 123.5, 123.2 (CCH , Cbz), 122.5 (CH , Cbz), 119.2 (CH , Cbz), 115.8 (CH , Cbz), 113.3 (CH , Cbz), 53.5 (CH_2), 28.2 (CHCH_3), 23.9 (CHCH_3), 23.8 (CHCH_3). Anal. Calcd for $\text{C}_{62}\text{H}_{62}\text{Au}_2\text{N}_6$: C, 57.95; H, 4.86; N, 6.54; found: C, 58.02; H, 4.38; N, 5.96.

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

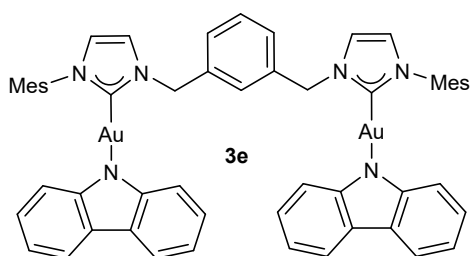


Colorless solid (99.7mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.6$ Hz, 4H, CH , Cbz), 7.54 (dd, $J = 5.7, 3.3$ Hz,

SUPPORTING INFORMATION

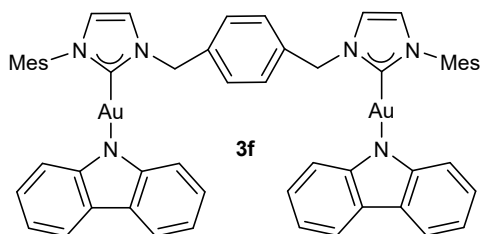
2H, $\underline{\text{CH}}$, *o*-xylene), 7.20 (dd, $J = 5.6, 3.5$ Hz, 2H, $\underline{\text{CH}}$, *o*-xylene), 7.16 – 7.11 (m, 4H, $\underline{\text{CH}}$, Cbz), 7.05 (d, $J = 8.0$ Hz, 4H, $\underline{\text{CH}}$, Cbz), 7.01 (s, 4H, $\underline{\text{CH}}$, Mes), 7.00 – 6.94 (m, 4H, $\underline{\text{CH}}$, Cbz), 6.88 (d, $J = 1.9$ Hz, 2H, $\underline{\text{CH}}=\underline{\text{CH}}$), 6.60 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\underline{\text{CH}}$), 5.63 (s, 4H, $\underline{\text{CH}}_2$), 2.37 (s, 6H, $\underline{\text{CH}}_3$), 2.09 (s, 12H, $\underline{\text{CH}}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 176.7 ($\underline{\text{NCN}}$), 149.5 ($\text{CH}\underline{\text{CN}}$, Cbz), 140.0 ($\text{CH}_3\underline{\text{C}}$, Mes), 135.0 ($\text{CH}_3\underline{\text{C}}$, Mes), 134.9 ($\underline{\text{CN}}$, Mes), 134.0 ($\underline{\text{CCH}}_2$, *o*-xylene), 129.6 ($\underline{\text{CH}}$, *o*-xylene), 129.5 ($\underline{\text{CH}}$, Mes), 128.8 ($\underline{\text{CH}}$, *o*-xylene), 124.0 ($\underline{\text{CCH}}$, Cbz), 123.6 ($\underline{\text{CH}}$, Cbz), 122.9 ($\underline{\text{CH}}=\underline{\text{CH}}$), 121.5 ($\underline{\text{CH}}=\underline{\text{CH}}$), 119.8 ($\underline{\text{CH}}$, Cbz), 116.2 ($\underline{\text{CH}}$, Cbz), 113.7 ($\underline{\text{CH}}$, Cbz), 52.5 ($\underline{\text{CH}}_2$), 21.3 ($\underline{\text{CH}}_3$), 18.2 ($\underline{\text{CH}}_3$). HRMS calculated for $\text{C}_{44}\text{H}_{42}\text{N}_5\text{Au}_2$ [$\text{M} - \text{Cbz}$] $^+$:1034.2771; found : 1034.2773.

[(IMes)*m*-xylene{Au(Cbz)}₂] **3e**



Colorless solid (109.2mg, 91%). ^1H NMR (300 MHz, DMSO-d_6) δ 7.93 (d, $J = 7.6$ Hz, 4H, $\underline{\text{CH}}$, Cbz), 7.76 (d, $J = 1.9$ Hz, 2H, $\underline{\text{CH}}=\underline{\text{CH}}$), 7.57 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\underline{\text{CH}}$), 7.51 (m, 4H, $\underline{\text{CH}}$, *m*-xylene), 7.15 (s, 4H, $\underline{\text{CH}}$, Mes), 7.10 (m, 4H, $\underline{\text{CH}}$, Cbz), 7.03 (d, $J = 7.8$ Hz, 4H, $\underline{\text{CH}}$, Cbz), 6.90 – 6.83 (m, 4H, $\underline{\text{CH}}$, Cbz), 5.67 (s, 4H, $\underline{\text{CH}}_2$), 2.39 (s, 6H, $\underline{\text{CH}}_3$), 2.06 (s, 12H, $\underline{\text{CH}}_3$). ^{13}C NMR (75 MHz, DMSO) δ 173.6 ($\underline{\text{NCN}}$), 148.7 ($\underline{\text{CN}}$, Cbz), 139.0 ($\text{CH}_3\underline{\text{C}}$, Mes), 137.9 ($\text{CH}_2\underline{\text{C}}$, *m*-xylene), 135.4 ($\underline{\text{CN}}$, Mes), 134.9 ($\text{CH}_3\underline{\text{C}}$, Mes), 129.5, 128.9 ($\underline{\text{CH}}$, Mes), 127.0 (CH , *m*-xylene), 126.1 ($\text{CH}_2\underline{\text{C}}$, *m*-xylene), 123.5, 123.2, 122.6, 119.3 ($\underline{\text{CH}}$, Cbz), 115.8 ($\underline{\text{CH}}$, Cbz), 113.4 ($\underline{\text{CH}}$, Cbz), 53.5 ($\underline{\text{CH}}_2$), 20.7 ($\underline{\text{CH}}_3$), 17.5 ($\underline{\text{CH}}_3$). HRMS calculated for $\text{C}_{44}\text{H}_{42}\text{N}_5\text{Au}_2$ [$\text{M} - \text{Cbz}$] $^+$:1034.2771; found : 1034.2767

[(IMes)*p*-xylene{Au(Cbz)}₂] **3f**

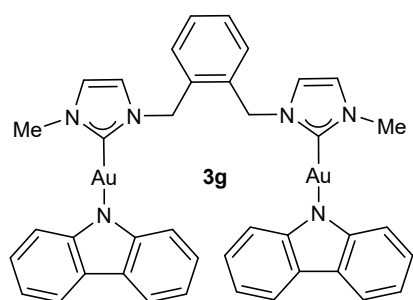


Colorless solid (81.7mg, 68%). ^1H NMR (300 MHz, DMSO-d_6) δ 7.93 (d, $J = 7.6$ Hz, 4H, $\underline{\text{CH}}$, Cbz), 7.87 (d, $J = 1.9$ Hz, 2H, $\underline{\text{CH}}=\underline{\text{CH}}$), 7.63 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\underline{\text{CH}}$), 7.60 (s, 4H, $\underline{\text{CH}}$, *p*-xylene), 7.17 (s, 4H, $\underline{\text{CH}}$, Mes), 7.06 (m, 8H, $\underline{\text{CH}}$, Cbz), 6.93 – 6.81 (m, 4H, $\underline{\text{CH}}$, Cbz), 5.66 (s, 4H, $\underline{\text{CH}}_2$), 2.39 (s, 6H, $\underline{\text{CH}}_3$), 2.06 (s, 12H, $\underline{\text{CH}}_3$). ^{13}C NMR (101 MHz, DMSO) δ 173.4 ($\underline{\text{NCN}}$),

SUPPORTING INFORMATION

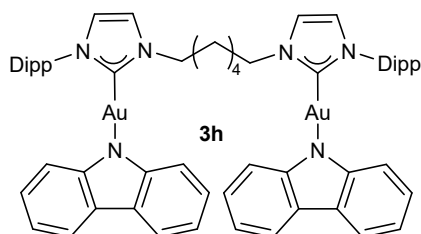
148.7 (CN, Cbz), 139.1 (CH₃C, Mes), 137.1 (CH₂C, *p*-xylene), 135.4 (CN, Mes), 134.9 (CH₃C, Mes), 128.9 (CH, Mes), 127.9 (CH, *p*-xylene), 123.5 (CH, Cbz), 123.2 (CH=CH), 122.8, 119.3 (CH, Cbz), 115.8 (CH, Cbz), 113.4 (CH, Cbz), 53.3 (CH₂), 20.7 (CH₃), 17.4 (CH₃). Anal. Calcd for C₅₆H₅₀Au₂N₆: C, 56.01; H, 4.20; N, 7.00; found: C, 55.48; H, 4.04; N, 6.62.

[(IMe)^{*o*-xylene}{Au(Cbz)}₂] **3g**



Colorless solid (71.5mg, 72%). ¹H NMR (400 MHz, DMSO-d₆) 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, CH₂), 3.61 (s, 6H, CH₃). ¹³C NMR (75 MHz, DMSO) δ 172.6 (NCN), 148.9 (CN, Cbz), 134.5 (CH₂C, *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 (CH₂), 37.4 (CH₃).

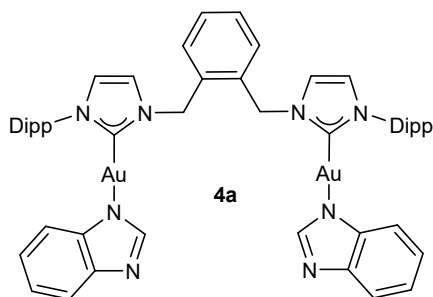
[(IPr)^{hexane-1,6-diyl}{Au(Cbz)}₂] **3h**



Colorless solid (116.4mg, 92%). ¹H NMR (400 MHz, CDCl₃) 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, CH₂), 2.48 – 2.32 (m, 4H, CH(CH₃)₂), 2.00 (t, *J* = 6.3 Hz, 4H, CH₂), 1.63 (s, 4H, CH₂), 1.28 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.12 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) 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 (CH₂), 31.1 (CH₂), 28.67 (CH(CH₃)₂), 25.1 (CH₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂). Anal. Calcd for C₆₀H₆₆Au₂N₆: C, 56.96; H, 5.26; N, 6.64; found: C, 57.61; H, 4.95; N, 6.13.

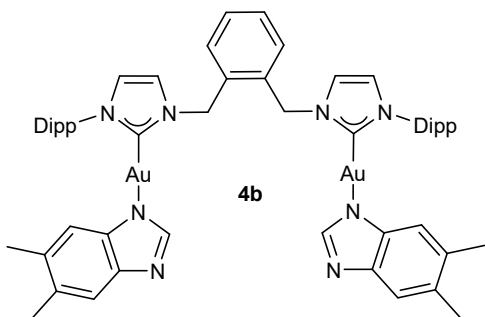
[(IPr)^{*o*-xylene}{Au(1*H*-benzimidazolato)}₂] **4a**

SUPPORTING INFORMATION



Colorless solid (96.1mg, 81%). ^1H 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, CH₂), 2.48 (dt, $J = 13.6, 6.8$ Hz, 4H, CH(CH₃)₂), 1.31 (d, $J = 6.8$ Hz, 6H, CH(CH₃)₂), 1.15 (d, $J = 6.9$ Hz, 12H, CH(CH₃)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 (CH₂C, *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 (CH₂), 28.8 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 24.4 (CH(CH₃)₂). Anal. Calcd for C₅₂H₅₆Au₂N₈: C, 52.62; H, 4.76; N, 9.44; found: C, 52.85; H, 4.11; N, 8.54.

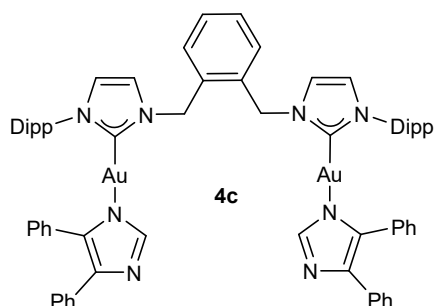
[(IPr)*o*-xylene{Au(5,6-dimethyl-1*H*-benzimidazolato)}₂]**4b**



Colorless solid (106.9mg, 86%). ^1H 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, CH₂), 2.51 (dt, $J = 13.6, 6.8$ Hz, 4H, CH(CH₃)₂), 2.28 (s, 6H, CH₃, amine), 2.20 (s, 6H, CH₃, amine), 1.32 (d, $J = 6.8$ Hz, 12H, CH(CH₃)₂), 1.15 (d, $J = 6.9$ Hz, 12H, CH(CH₃)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 (CH₂C, *o*-xylene), 131.1 (CH, Dipp), 129.7 (CH, *o*-xylene), 128.7 (CH, *o*-xylene), 128.5 (CH₃C, amine), 124.4 (CH, Dipp), 124.3, 121.4, 118.9 (CH, amine), 114.3 (CH, amine), 52.7 (CH₂), 28.9 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 20.4 (CH₃, amine), 20.4 (CH₃, amine). Anal. Calcd for C₅₆H₆₄Au₂N₈: C, 54.11; H, 5.19; N, 9.01; found: C, 53.76; H, 3.93; N, 8.86.

[(IPr)*o*-xylene{Au(4,5-diphenyl-1*H*-imidazolato)}₂]**4c**

SUPPORTING INFORMATION



Colorless solid (121.0mg, 87%). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (t, $J = 7.8$ Hz, 2H, CH , Dipp), 7.45 – 7.40 (m, 6H, CH , Ph), 7.31 (dd, $J = 8.2, 1.3$ Hz, 4H, CH , Ph), 7.25 (d, $J = 7.2$ Hz, 4H, CH , Dipp), 7.16 – 7.10 (m, 4H, CH , Ph), 7.08 (s, 2H, CH , amine), 7.06 – 7.00 (m, 4H, CH , *o*-xylene), 6.99 – 6.92 (m, 8H, CH , Ph; $\text{CH}=\text{CH}$), 6.84 (d, $J = 1.9$ Hz, 2H, $\text{CH}=\text{CH}$), 5.29 (s, 2H, CH_2), 2.38 (dt, $J = 13.7, 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.10 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, CDCl_3) δ 174.9 (NCN), 145.6 ($\text{C}(\text{Pr})$, Dipp), 143.9, 137.2, 137.1, 136.9, 134.4, 133.8 (CN , Dipp), 133.3 (CH_2C , *o*-xylene), 131.0 (CH , Dipp), 129.5, 129.4 (CH , Ph), 128.2, 128.0, 127.9 (CH , *o*-xylene), 127.4 (CH , Ph), 126.0 (CH , Dipp), 125.2 (CH , Ph), 124.7 ($\text{CH}=\text{CH}$), 124.4 (CH , Dipp), 121.2 ($\text{CH}=\text{CH}$), 52.3 (CH_2), 28.8 ($\text{CH}(\text{CH}_3)_2$), 24.5 ($\text{CH}(\text{CH}_3)_2$), 24.2 ($\text{CH}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{68}\text{H}_{68}\text{Au}_2\text{N}_8$: 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.

SUPPORTING INFORMATION

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).

¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 172.2, 152.4, 133.5, 128.3, 123.2, 119.2, 110.4,

SUPPORTING INFORMATION

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 mixture 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 Na₂SO₄, 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).

¹H NMR (300 MHz, CDCl₃) 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, CHCH₂), 4.23 – 4.00 (m, 4H, CH₂CH₃), 3.41 (s, 2H, CH₂C), 2.62 (d, *J* = 7.1 Hz, 2H, CH₂CH), 1.72 (s, 3H, CH₃C), 1.52 (s, 3H, CH₃C), 1.19 (t, *J* = 7.1 Hz, 6H, CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃) 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 (CHCH₂), 111.1 (CH^{Ar}), 110.5 (C^{Ar}), 61.3 (CH₂CH₃), 58.8 (C(CO₂Et)₂), 31.3 (CH₂CH), 27.7 (CH₂C), 26.2 (CH₃C), 18.2

SUPPORTING INFORMATION

(CH₃C), 14.1 (CH₂CH₃). **HRMS** (ESI-TOF): Calcd for C₂₁H₂₈NO₄⁺ [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**.

¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 172.0, 142.6,

SUPPORTING INFORMATION

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

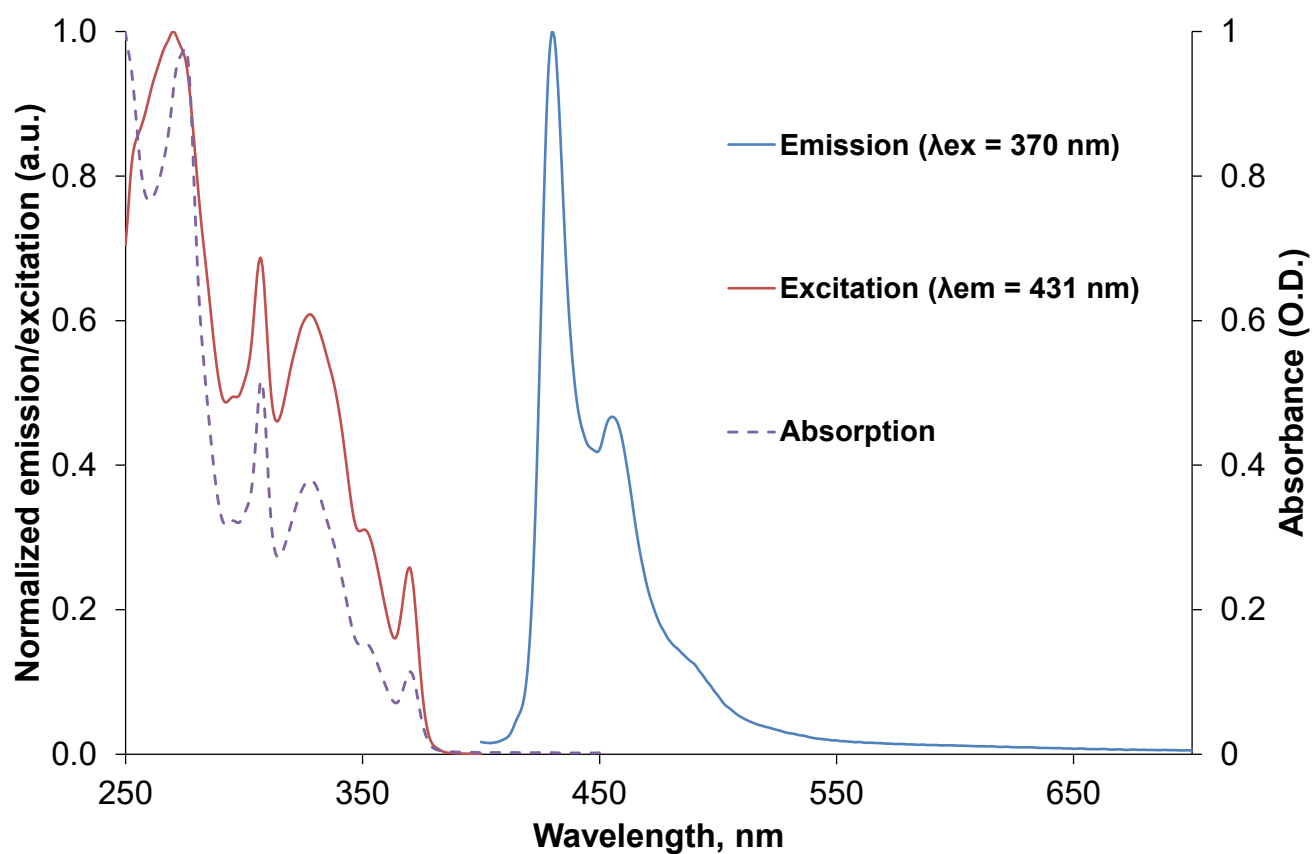


Figure S1. Absorption and emission spectra of 3a

SUPPORTING INFORMATION

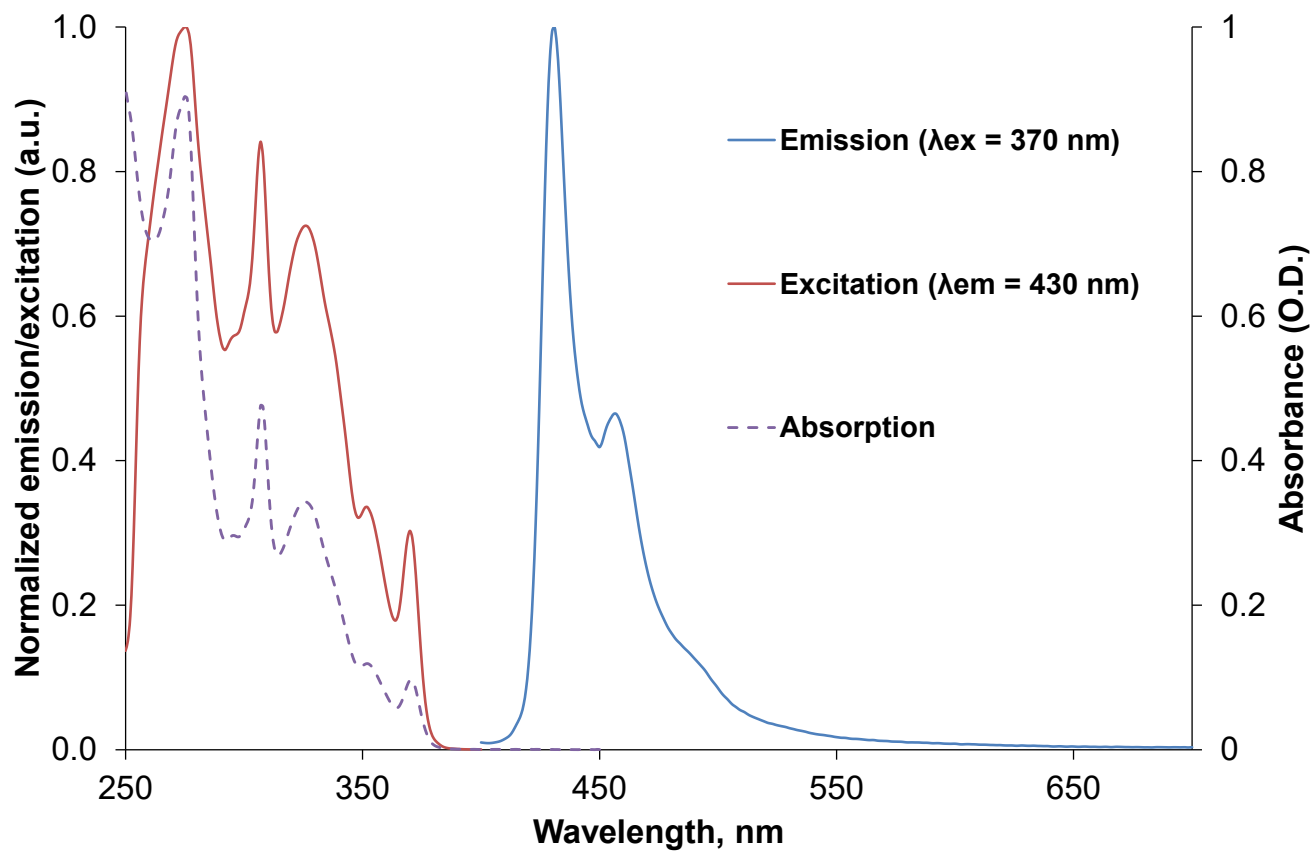


Figure S2. Absorption and emission spectra of **3b**

SUPPORTING INFORMATION

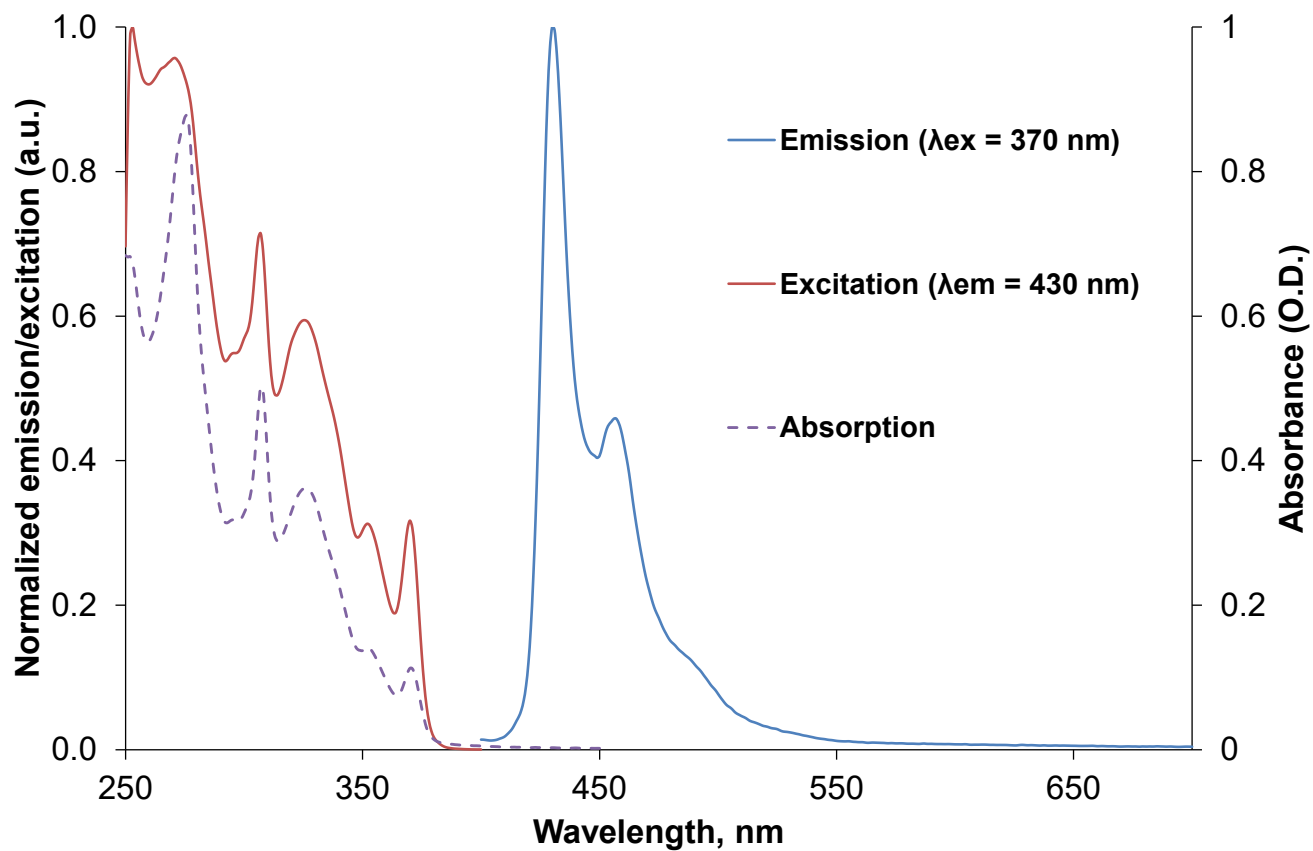


Figure S3. Absorption and emission spectra of **3d**

SUPPORTING INFORMATION

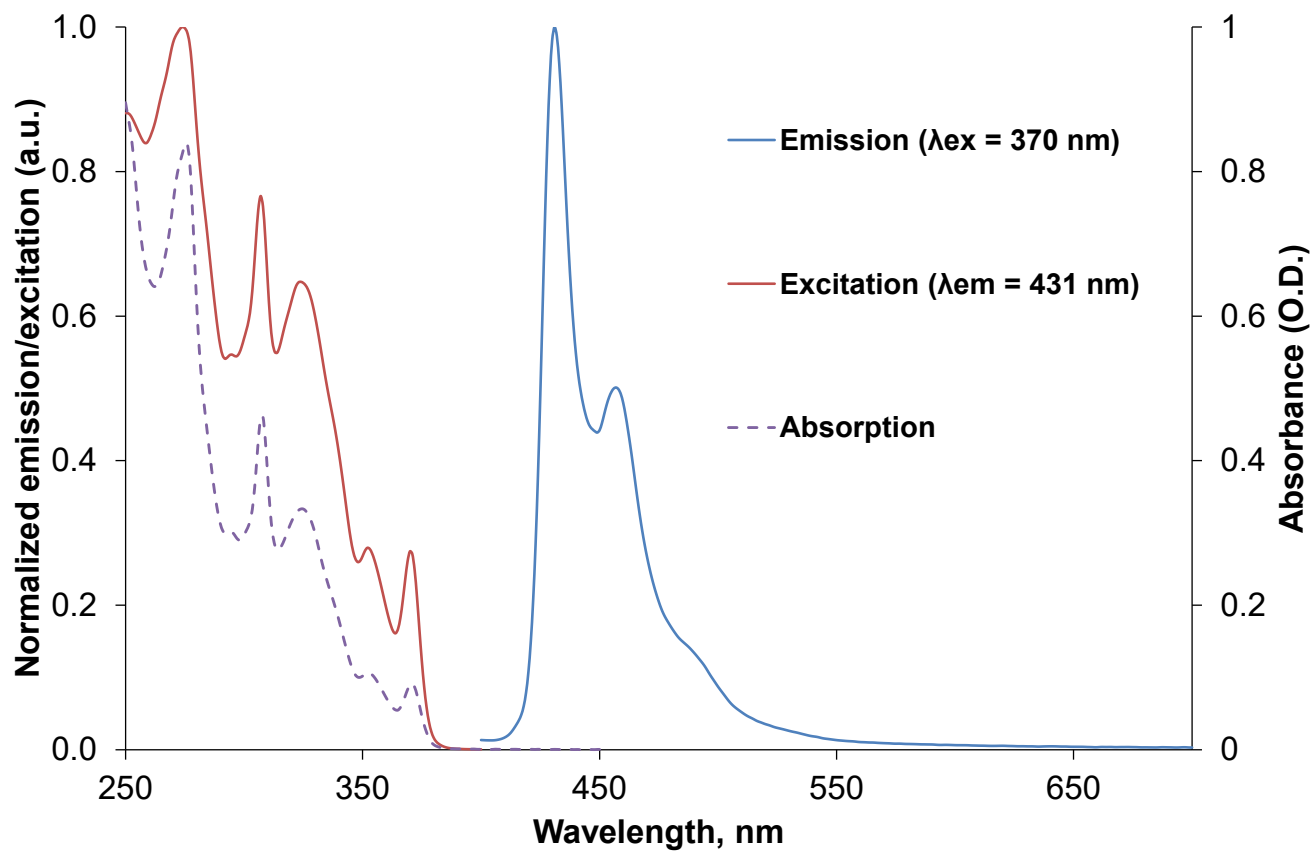


Figure S4. Absorption and emission spectra of **3e**

SUPPORTING INFORMATION

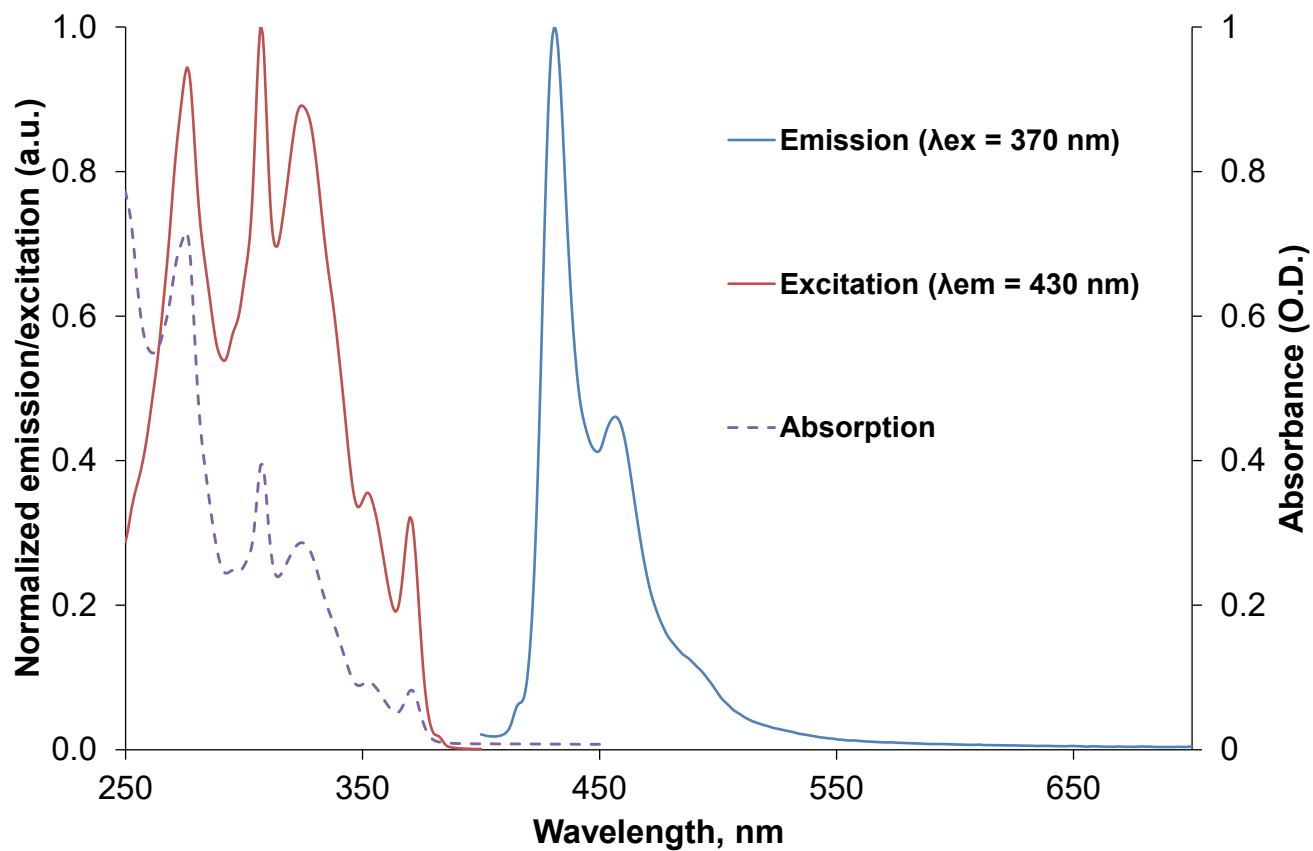


Figure S5. Absorption and emission spectra of **3f**

SUPPORTING INFORMATION

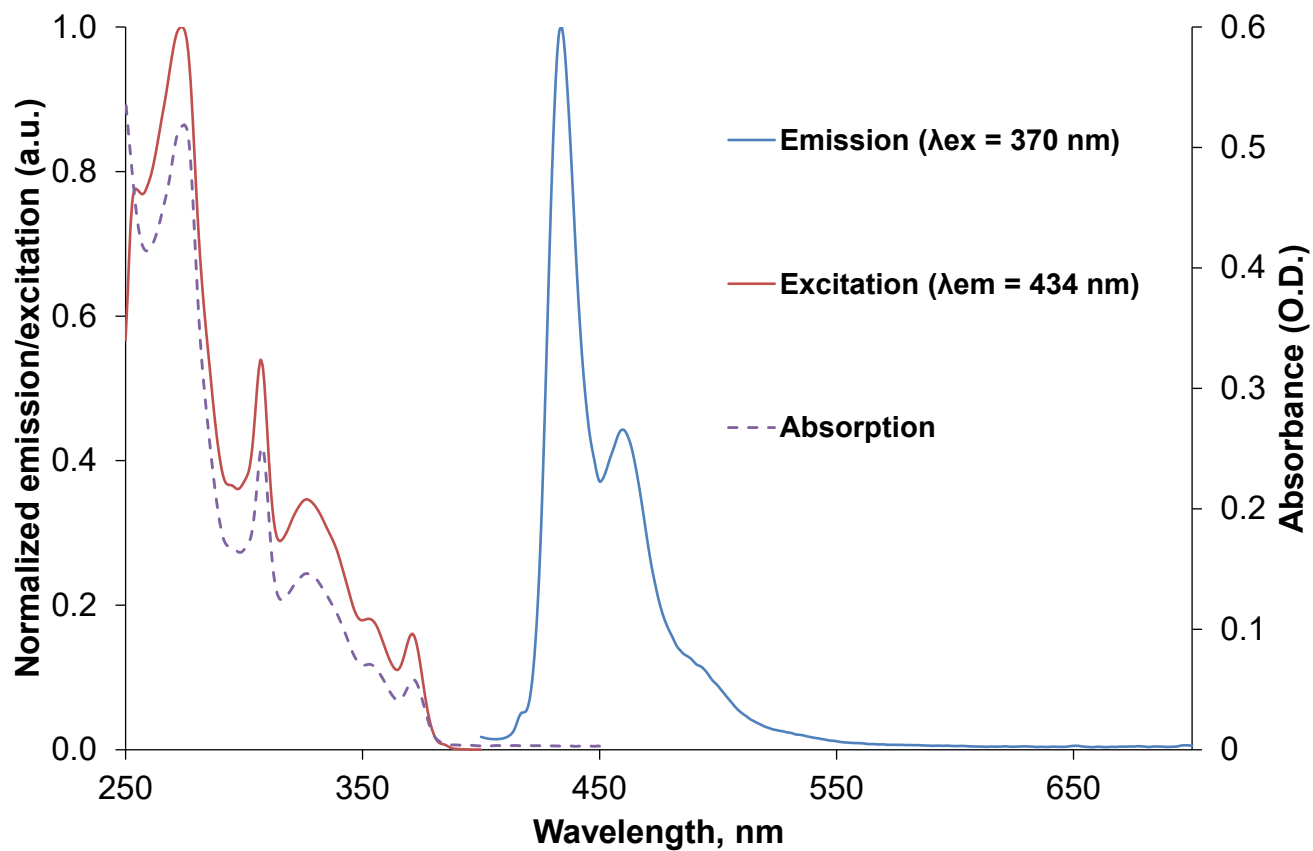


Figure S6. Absorption and emission spectra of **3g**

SUPPORTING INFORMATION

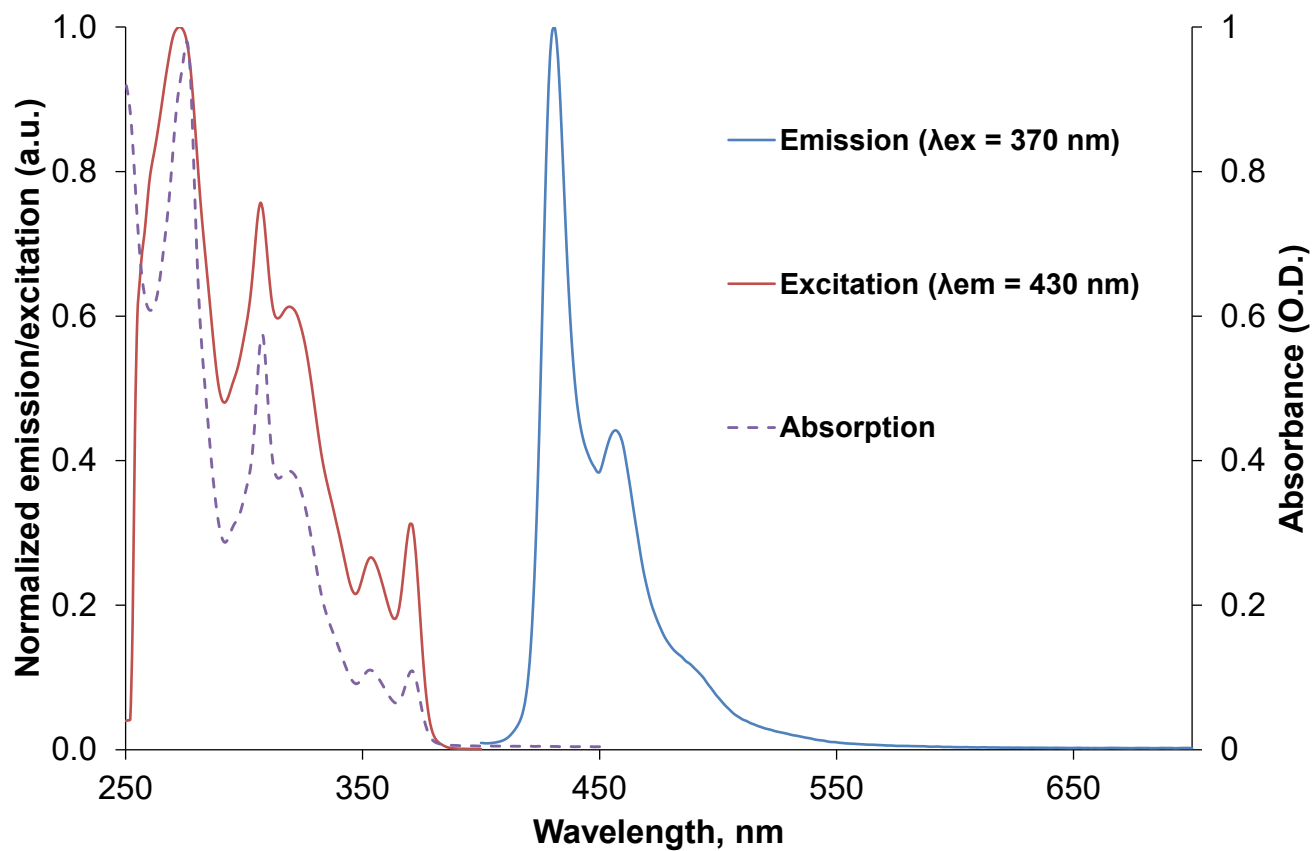


Figure S7. Absorption and emission spectra of **3h**

SUPPORTING INFORMATION

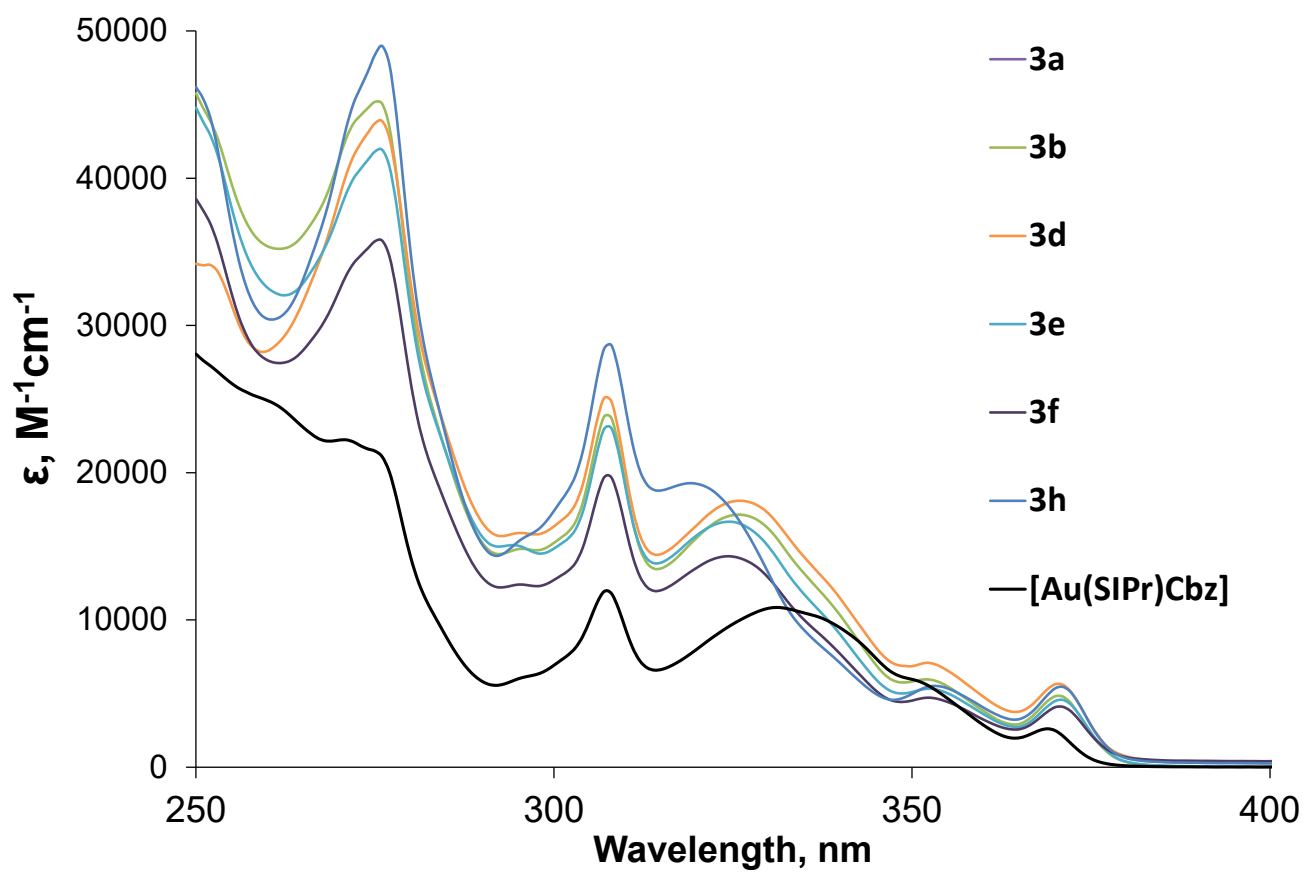


Figure S8. Absorption spectra of complexes 3a-h

SUPPORTING INFORMATION

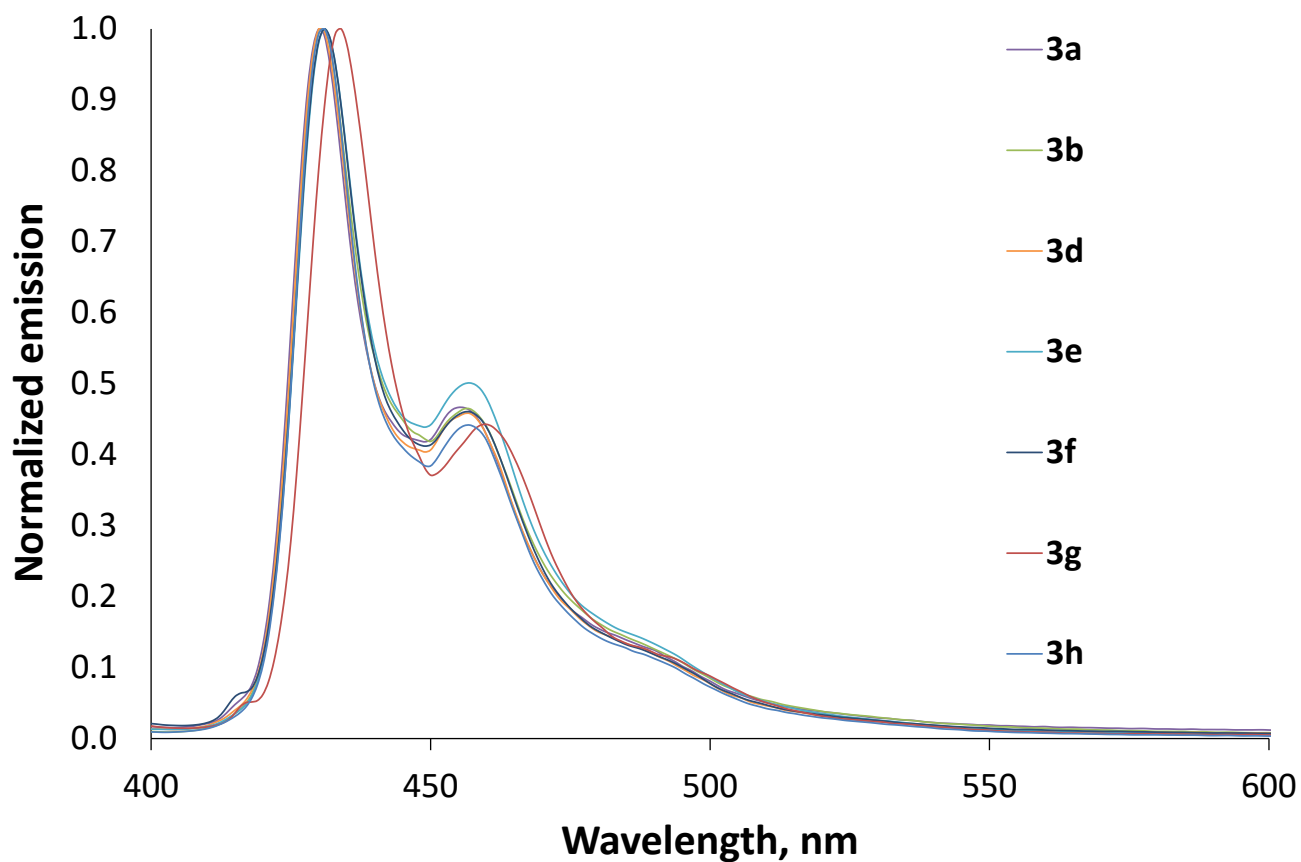


Figure S9. Emission spectra of complexes **3a-h** in THF

SUPPORTING INFORMATION

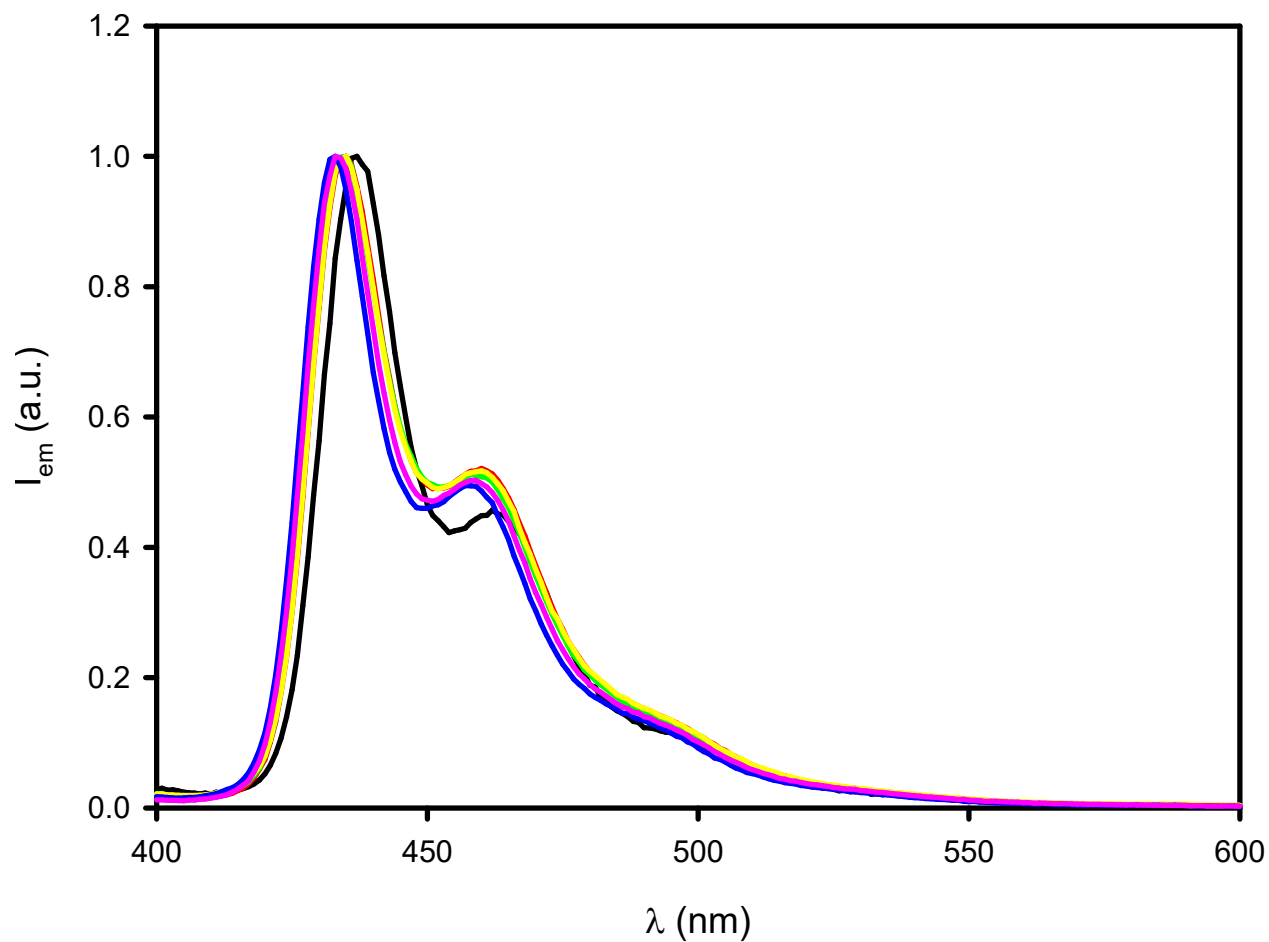


Figure S10. Emission spectra in deaerated DMSO of **3g** (black), **3f** (blue), **3e** (green), **3d** (red), **3b** (yellow), **3a** (pink) and. ($\lambda_{exc} = 370$ nm)

SUPPORTING INFORMATION

Table S3 Photophysical parameters of the complexes studied.

C	DMSO deaerated		
	λ_{em} [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 deaerated DMSO.

SUPPORTING INFORMATION

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.

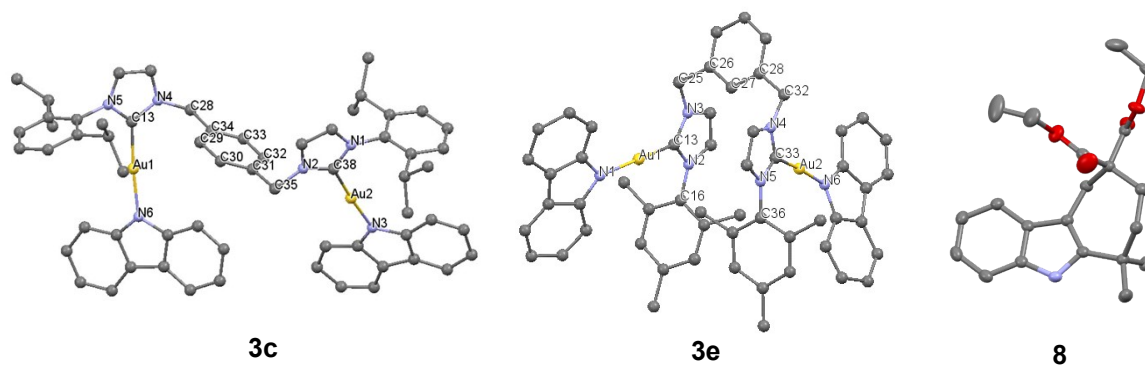


Figure S11 X-ray molecular structure of **3c**, **3e** and **8**, showing thermal displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity.

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)

SUPPORTING INFORMATION

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 ₂ N ₆ O	C ₅₆ H ₅₀ Au ₂ N 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	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	12.4705(2)	27.2565(3)	8.23200(10)
<i>b</i> /Å	14.3086(3)	17.0998(2)	15.2361(2)
<i>c</i> /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)
<i>Z</i>	2	20	4
ρ_{calc} /cm ³	1.567	1.678	1.251
μ /mm ⁻¹	9.814	6.211	0.694
<i>F</i> (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 K α (λ = 1.54184 Å)	Mo K α (λ = 0.71073 Å)	Cu K α (λ = 1.54184 Å)
2 θ range for data collection/°	5.372 to 147.72	5.026 to 57.526	8.236 to 147.91
Index ranges	-12 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -21 ≤ <i>l</i> ≤ 21	-36 ≤ <i>h</i> ≤ 32, -22 ≤ <i>k</i> ≤ 22, -69 ≤ <i>l</i> ≤ 65	-9 ≤ <i>h</i> ≤ 10, -18 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 18
Reflections collected	49365	123620	18693
Independent reflections	11431 [R _{int} = 0.0631, R _{sigma} = 0.0515]	26919 [R _{int} = 0.0723, R _{sigma} = 0.0749]	3800 [R _{int} = 0.0266, R _{sigma} = 0.0181]

SUPPORTING INFORMATION

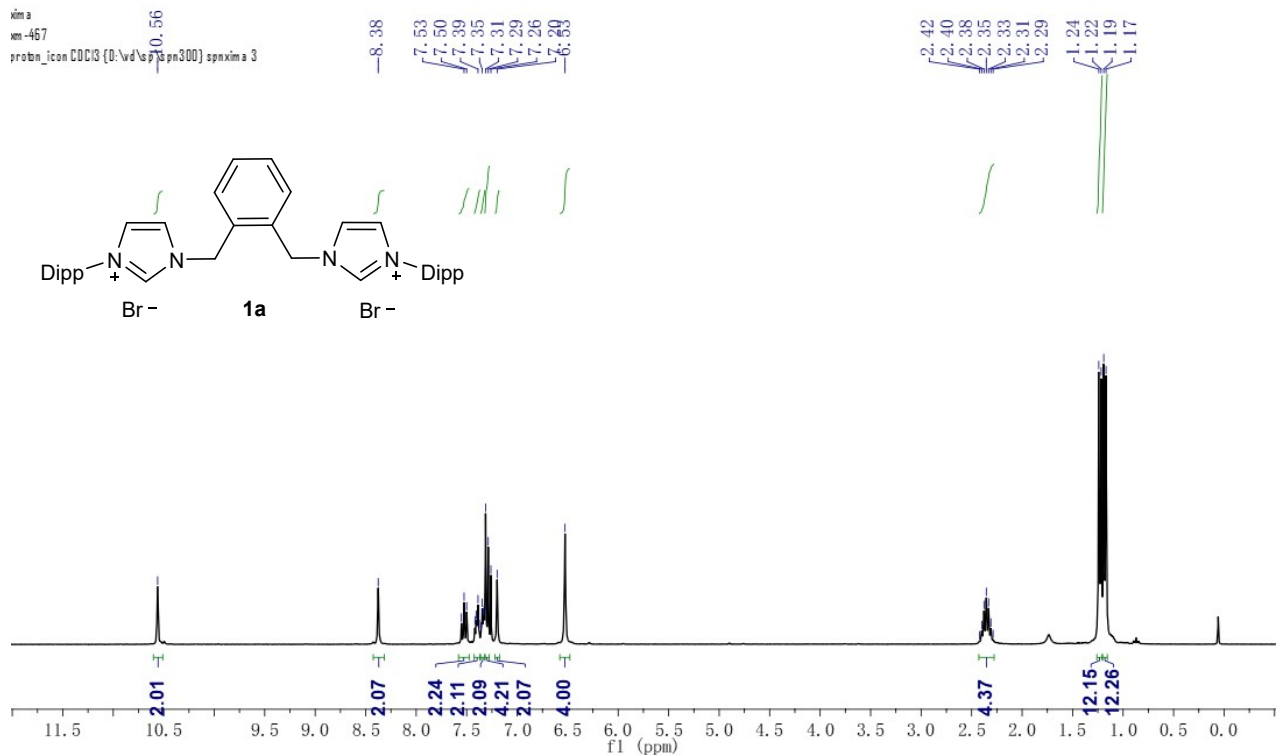
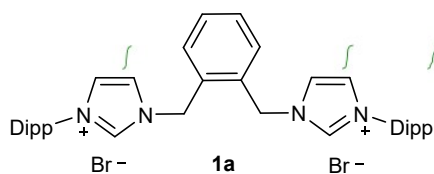
Data/restraints/parameters	11431/0/639	26919/0/1457	3800/6/254
Goodness-of-fit on F^2	1.008	1.031	1.053
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0391$, $wR_2 = 0.0823$	$R_1 = 0.0583$, $wR_2 = 0.0932$	$R_1 = 0.0457$, $wR_2 = 0.1116$
Final R indexes [all data]	$R_1 = 0.0574$, $wR_2 = 0.0892$	$R_1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

SUPPORTING INFORMATION

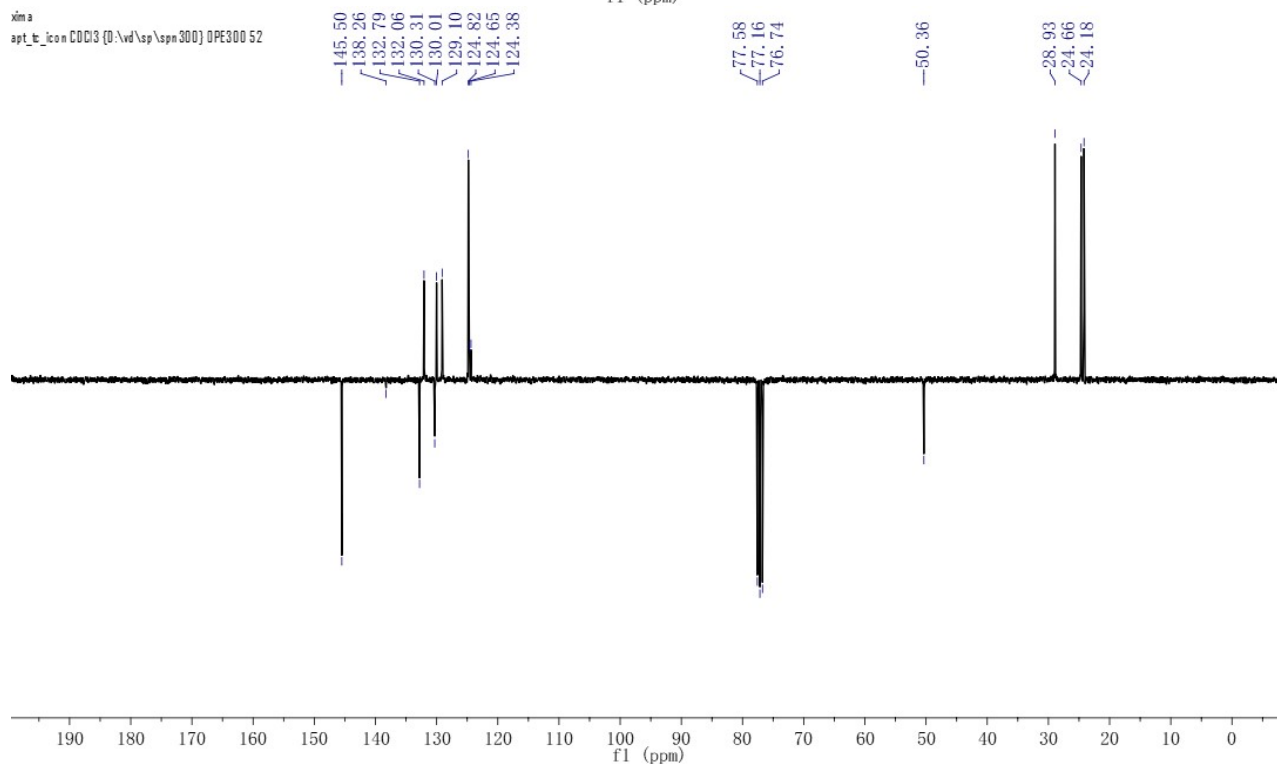
NMR spectra

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

xim a
nm-467
protn_icon CDCl3 (D:\vd\sp\spn300) spnxima 3



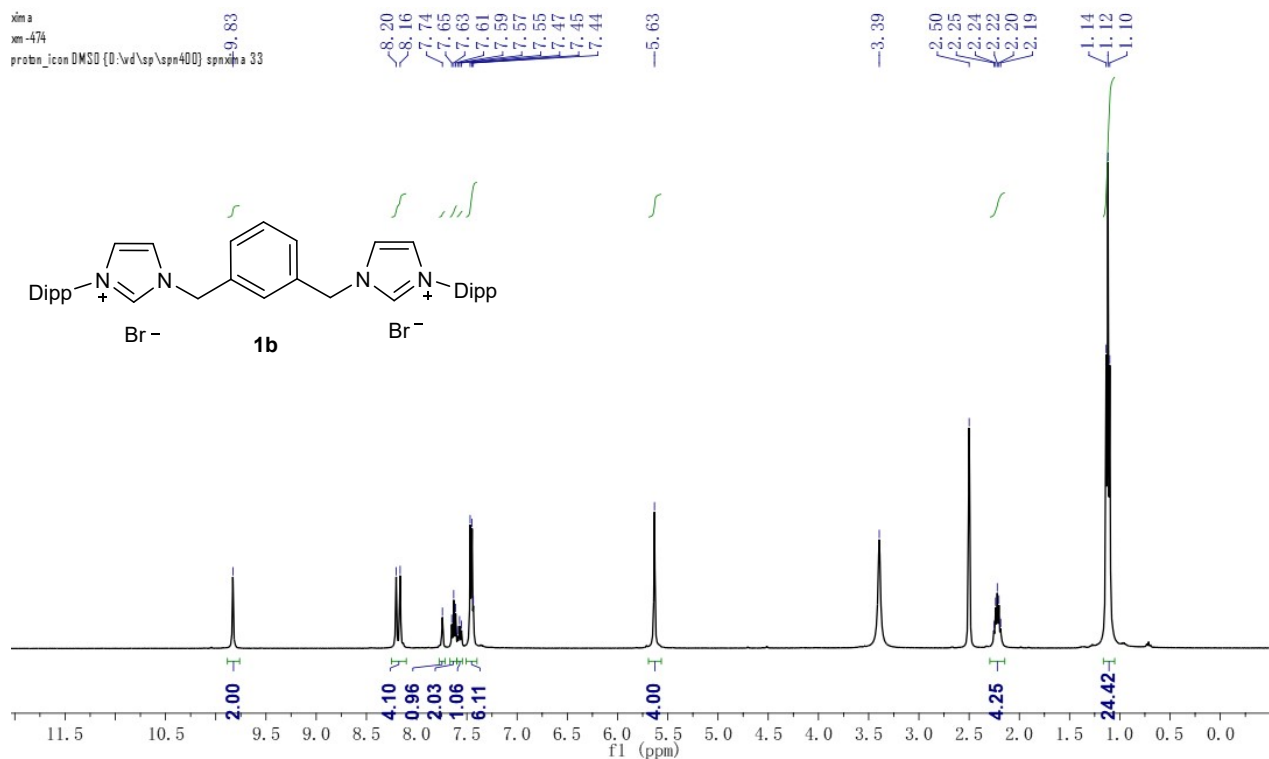
xim a
apt_t_icon CDCl3 (D:\vd\sp\spn300) DPE300 52



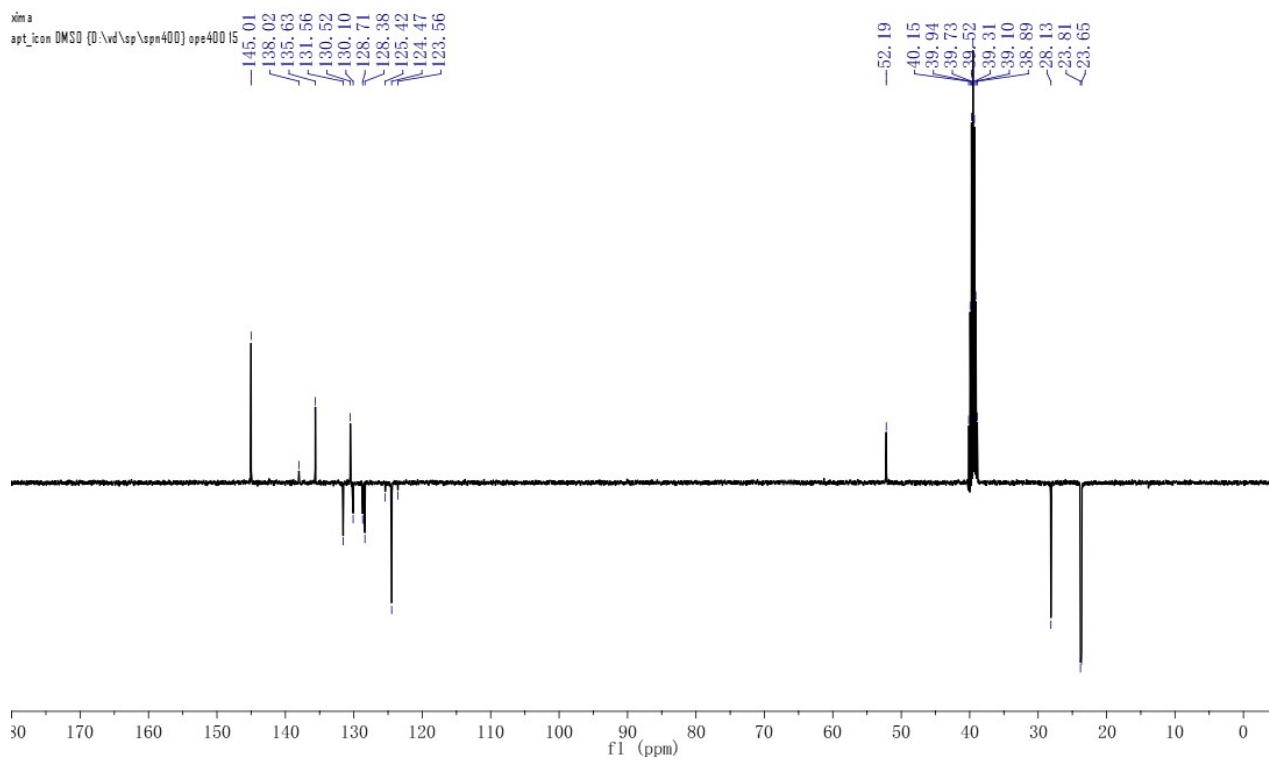
SUPPORTING INFORMATION

^1H and ^{13}C $\{^1\text{H}\}$ apt NMR of $[\text{IPr}^{m\text{-aryl}}\cdot 2\text{HBr}] \mathbf{1b}$

xima
xm-474
probin_icon DMSO (D:\vd\sp\spn400) spnxpha 33

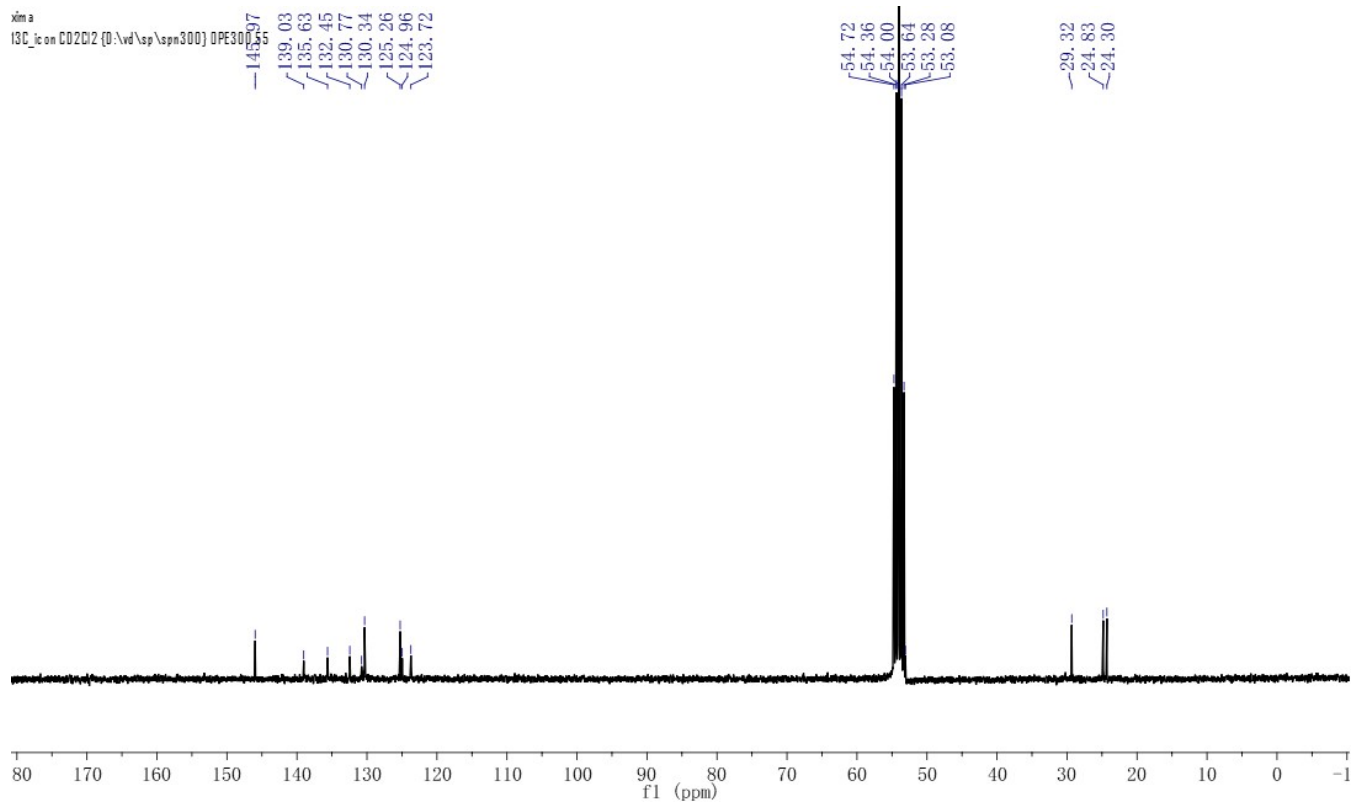
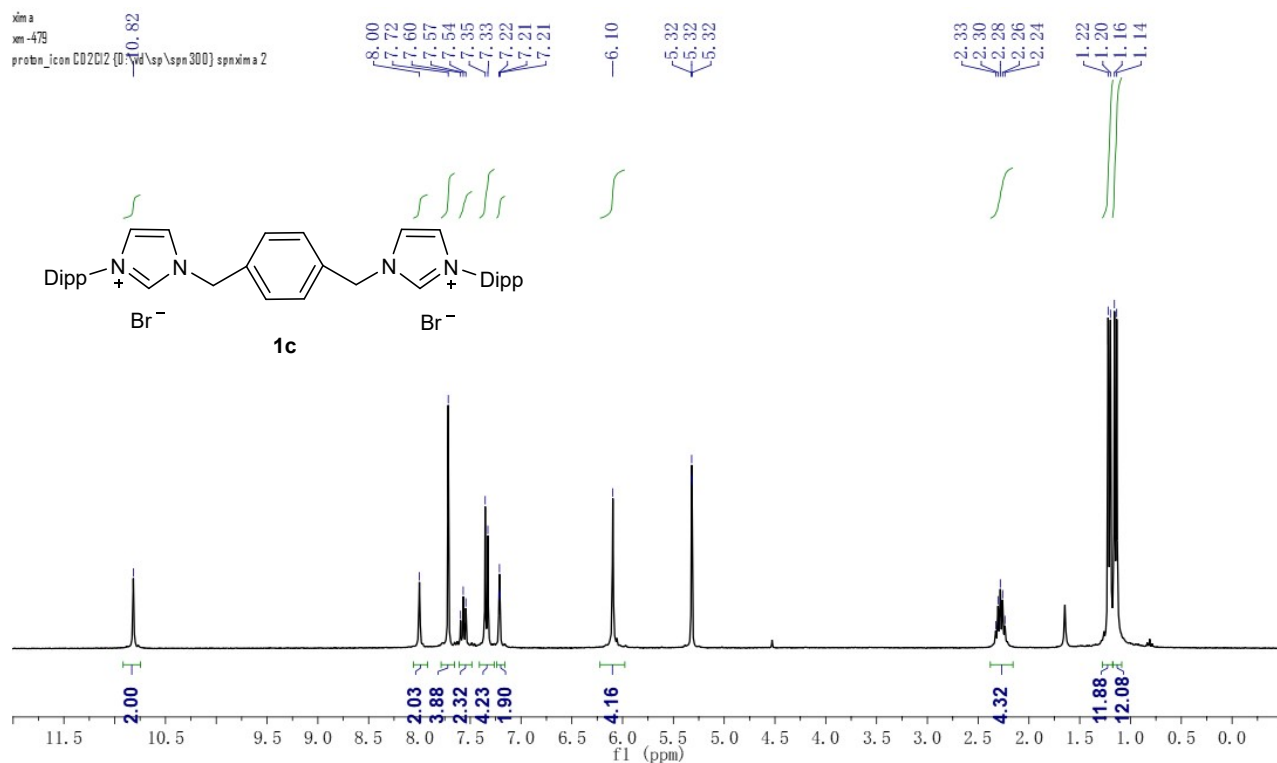


xima
apt_icon DMSO (D:\vd\sp\spn400) ope400 15



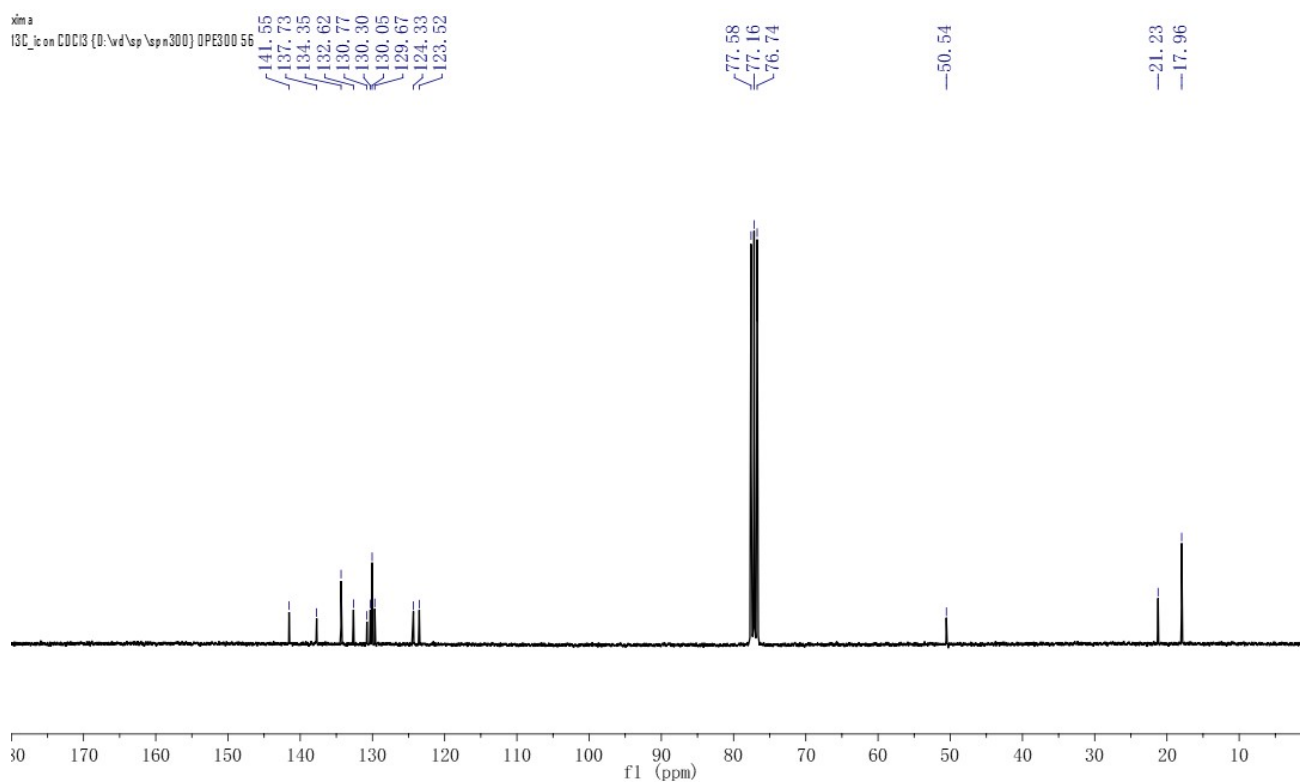
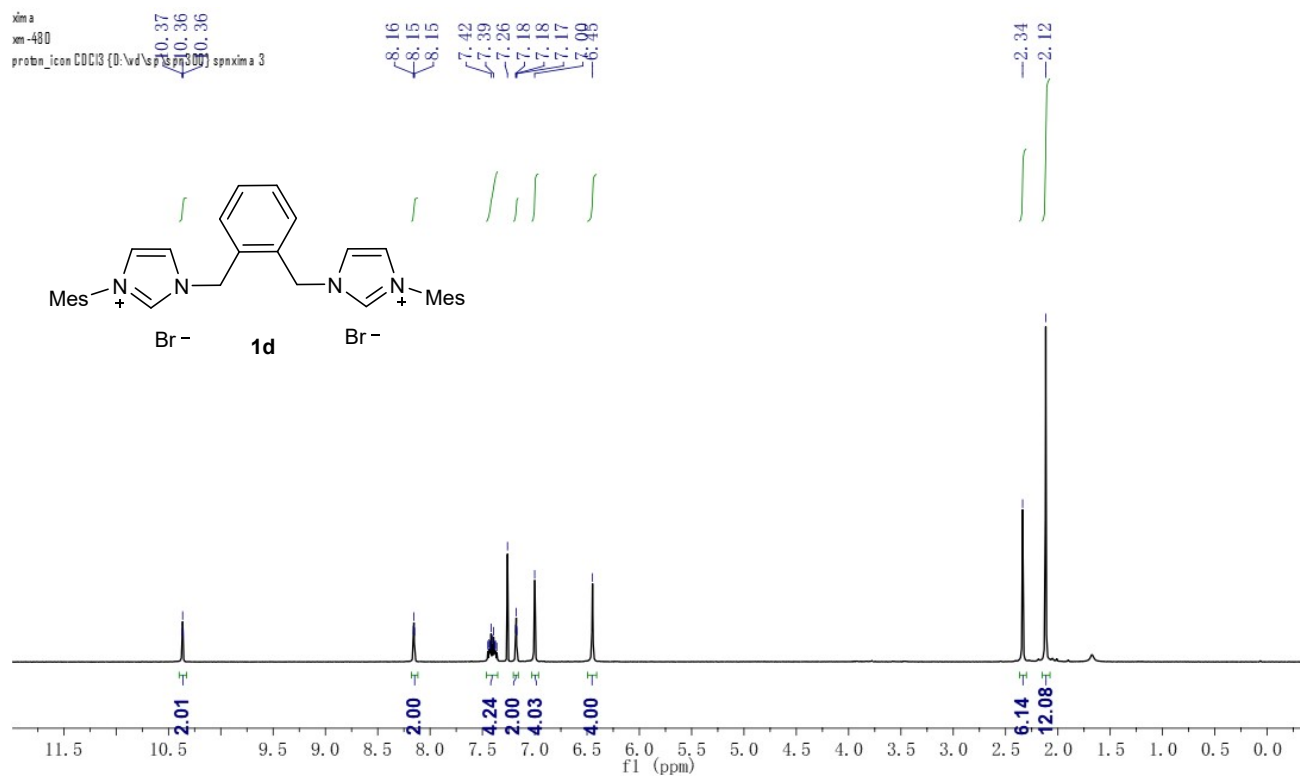
SUPPORTING INFORMATION

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



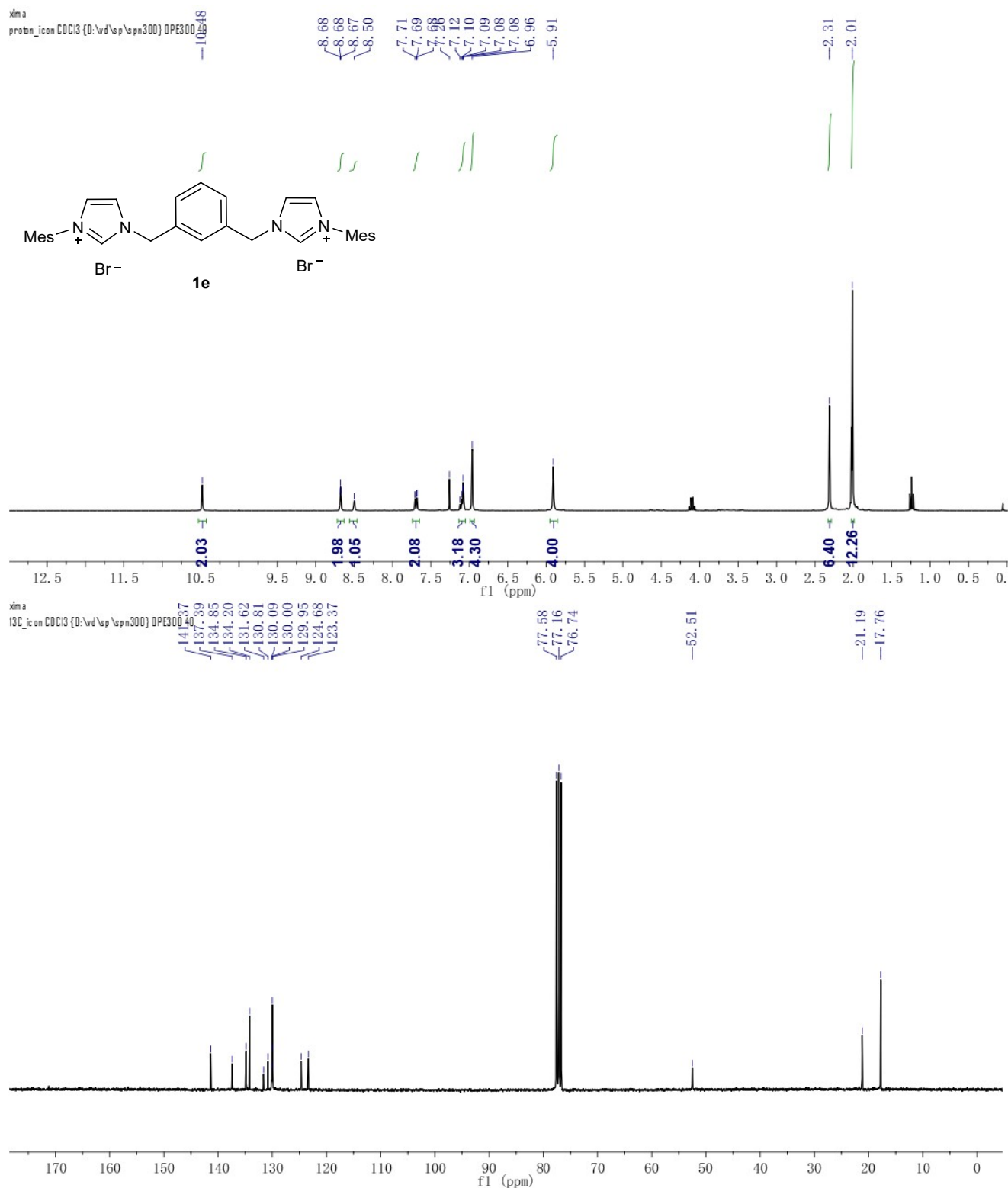
SUPPORTING INFORMATION

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



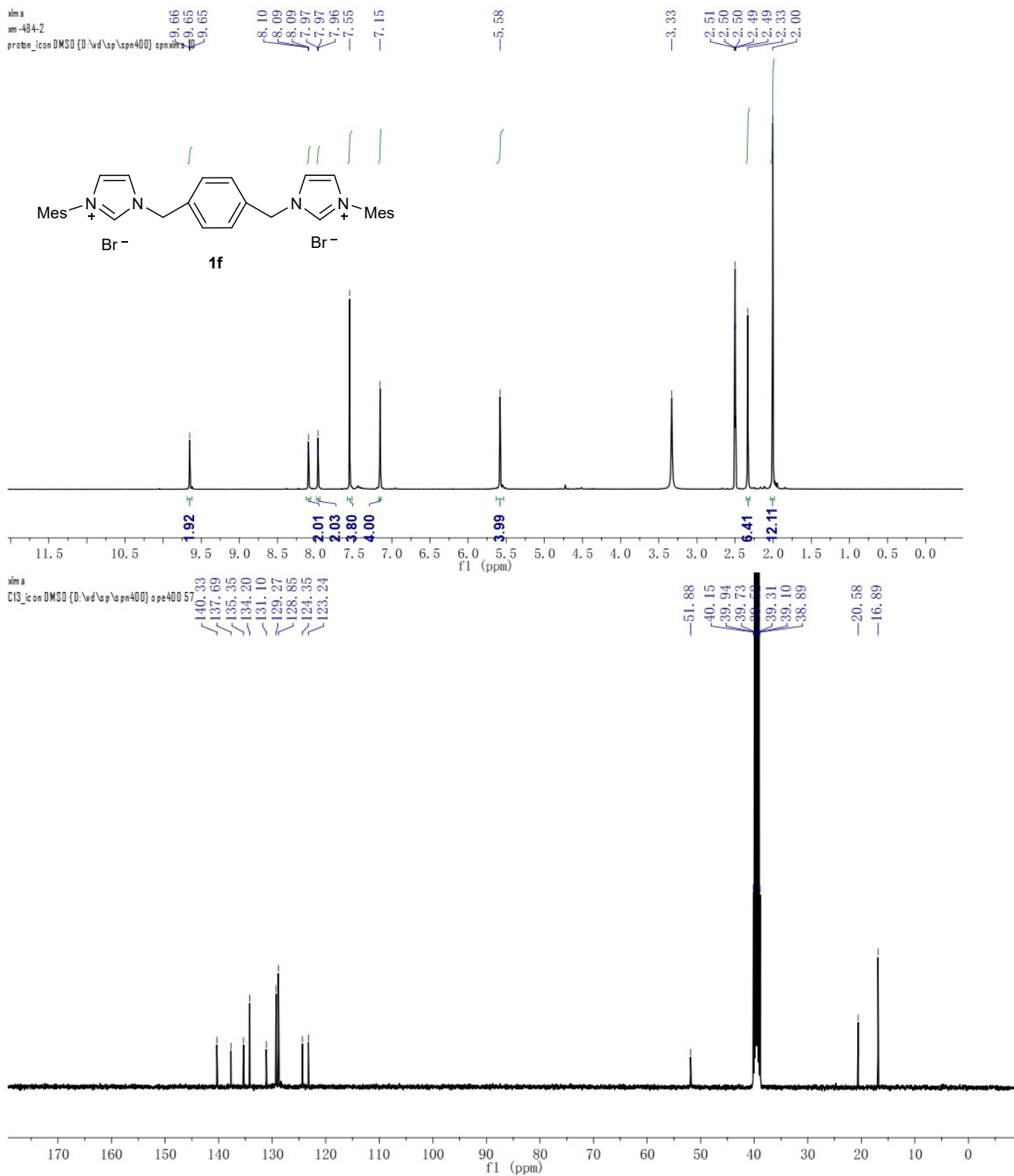
SUPPORTING INFORMATION

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



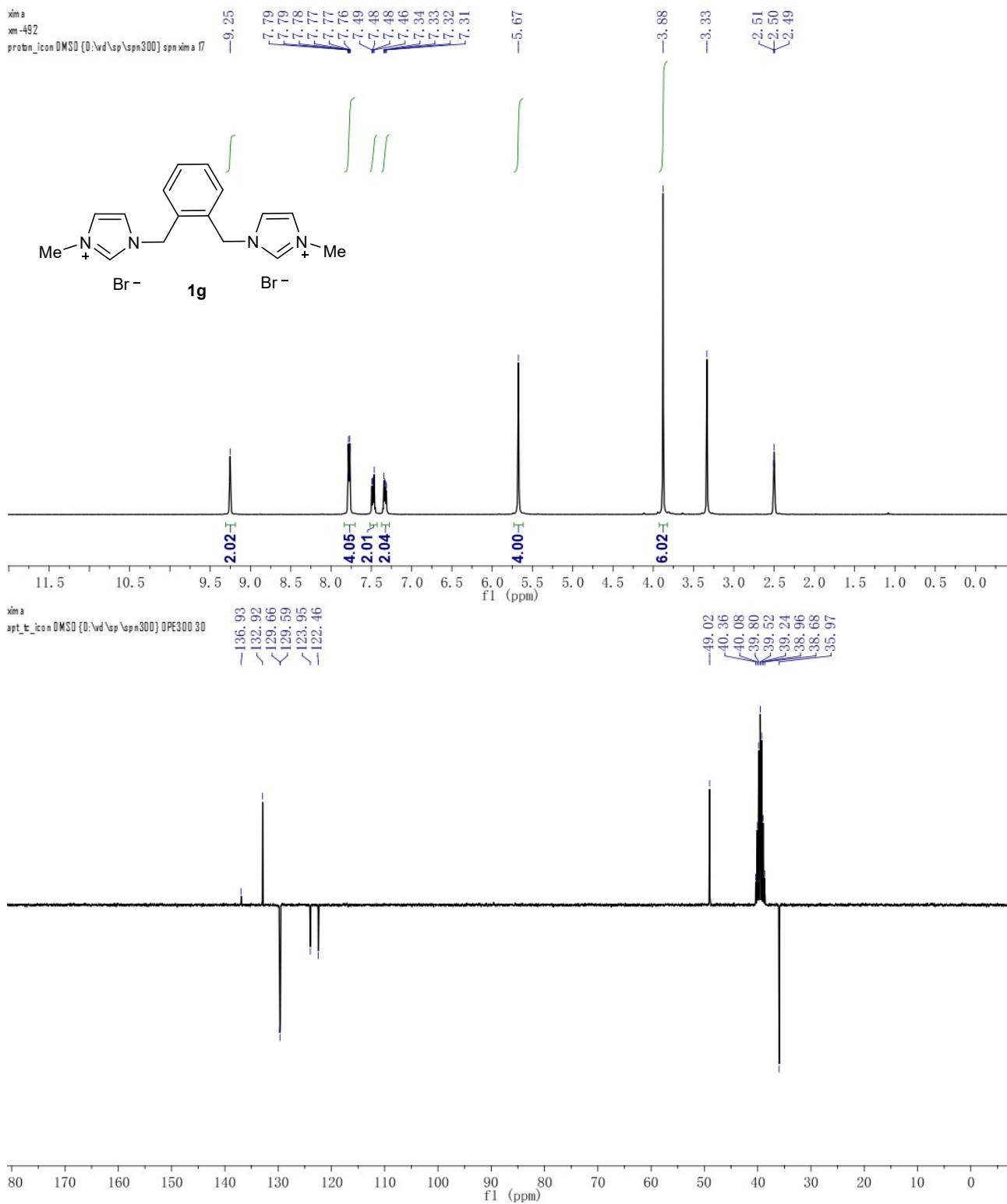
SUPPORTING INFORMATION

1H and 13C {1H} NMR of [IMes-*p*-aryl-2HBr] 1f



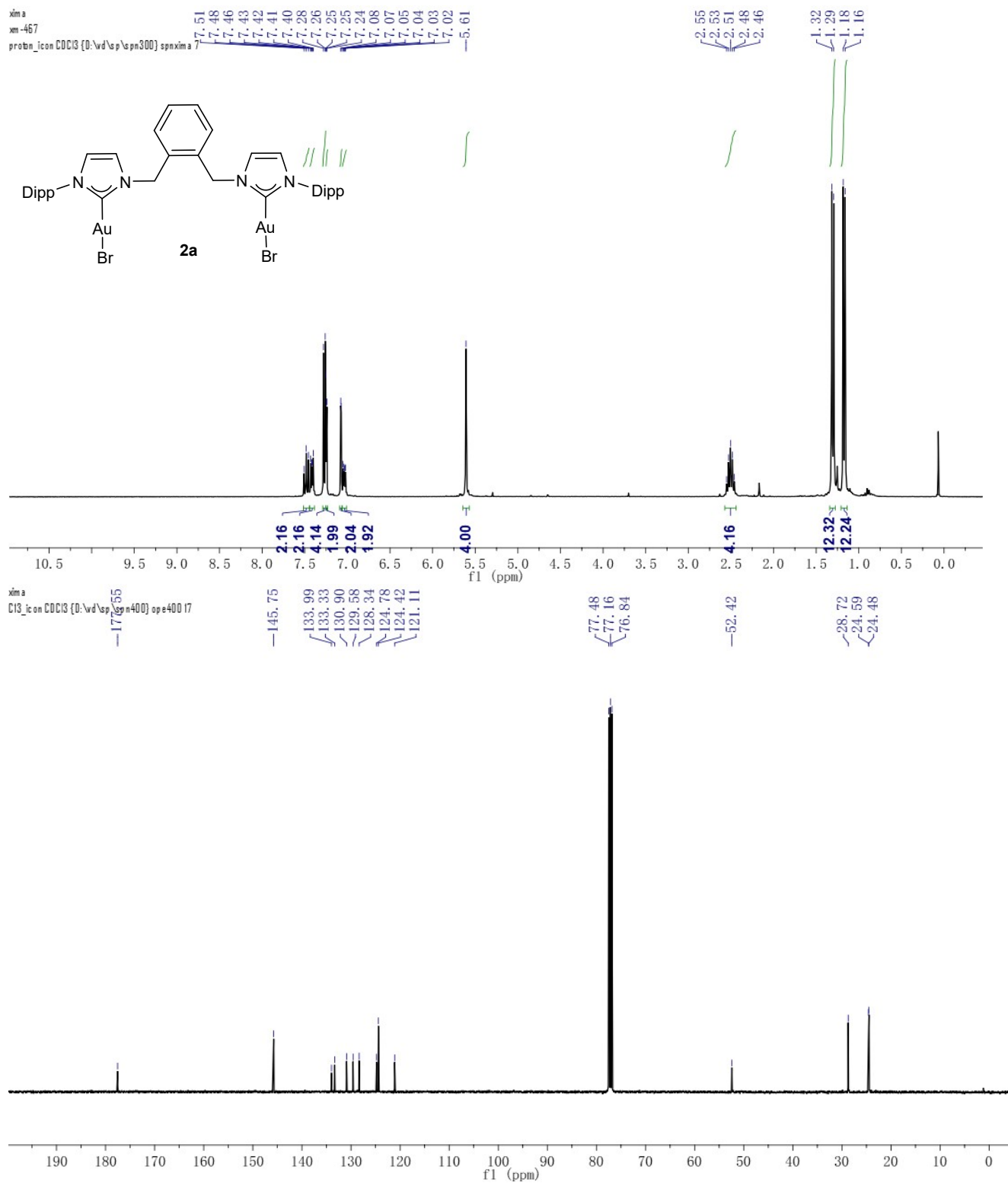
SUPPORTING INFORMATION

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



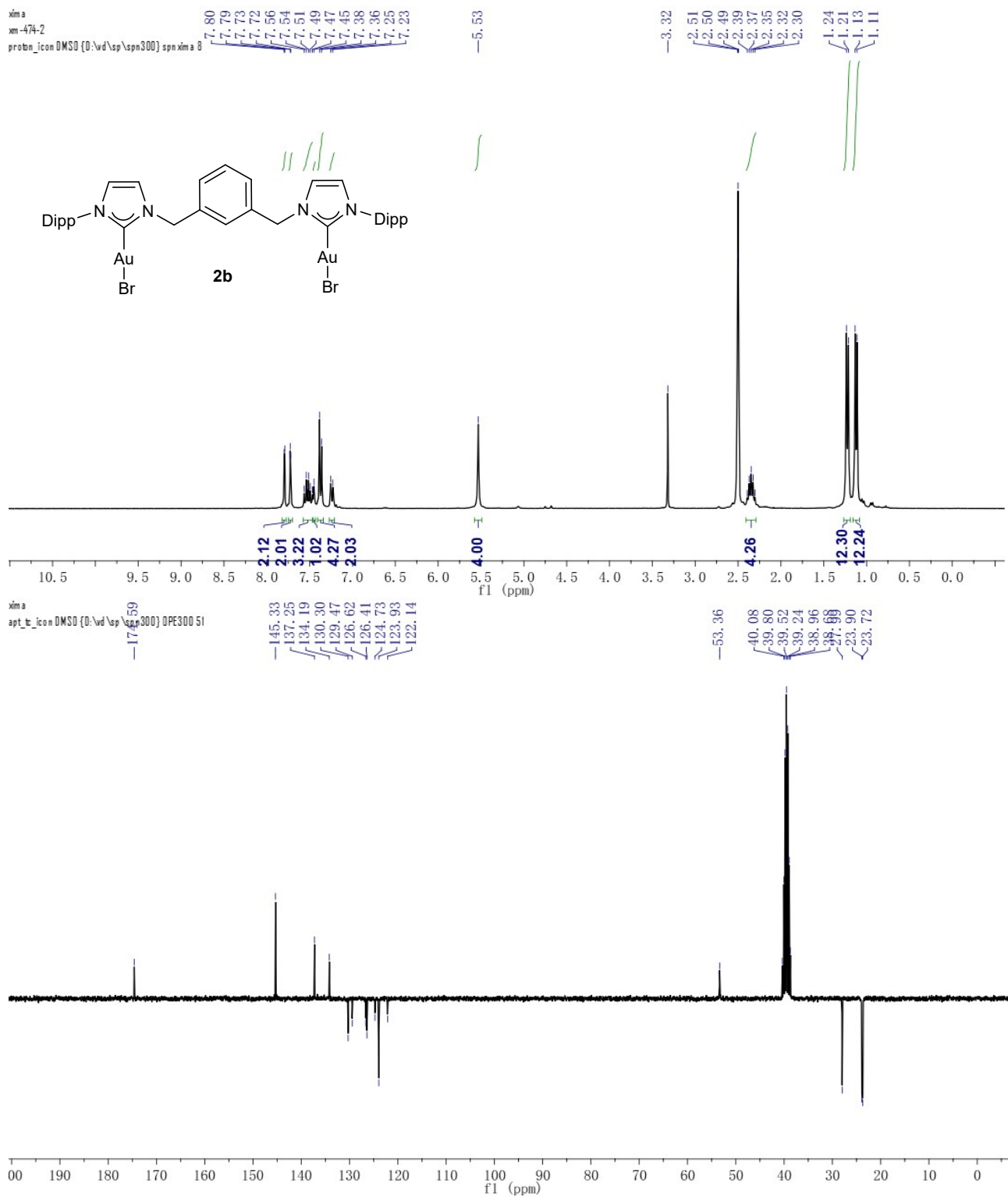
SUPPORTING INFORMATION

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



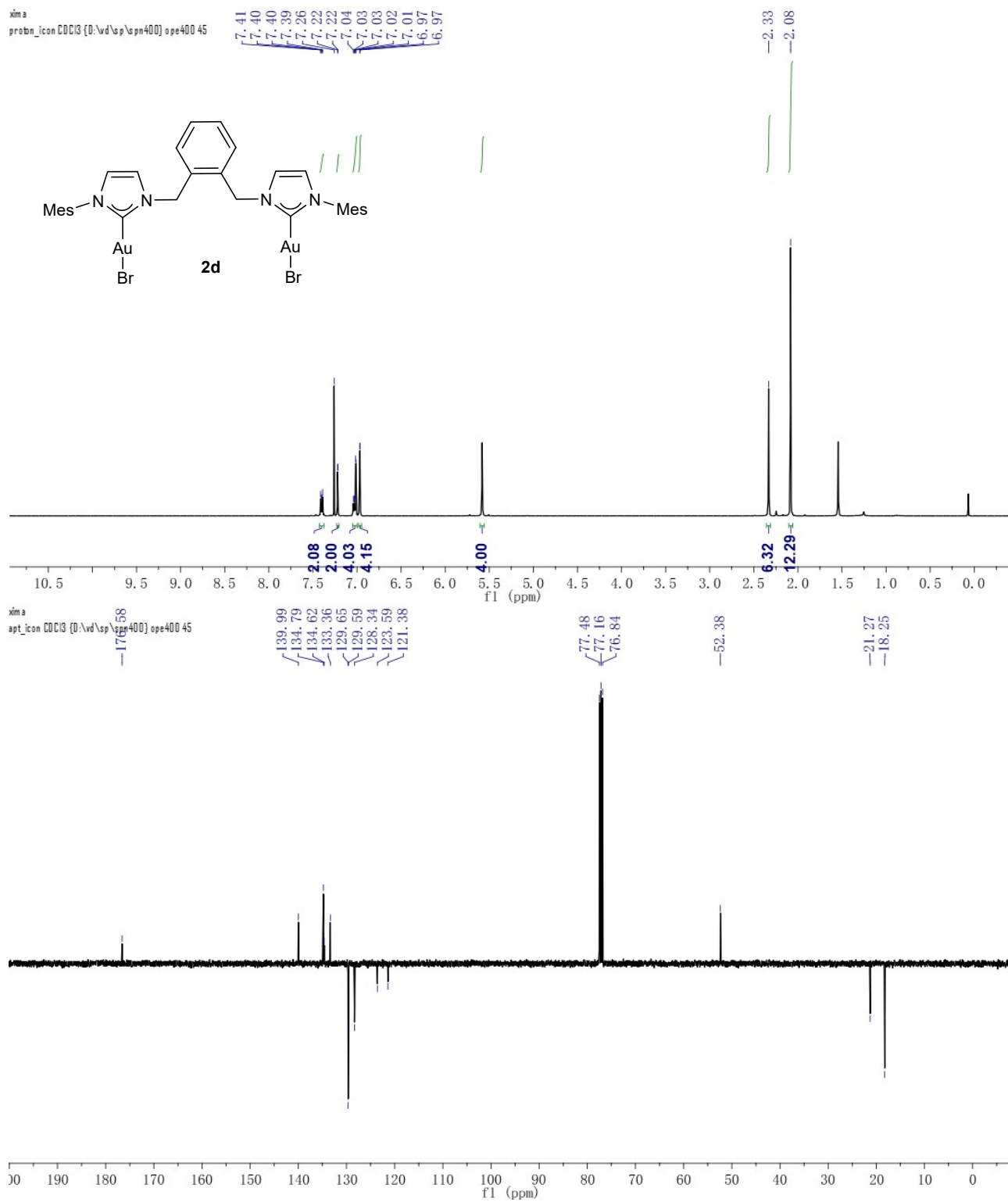
SUPPORTING INFORMATION

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



SUPPORTING INFORMATION

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



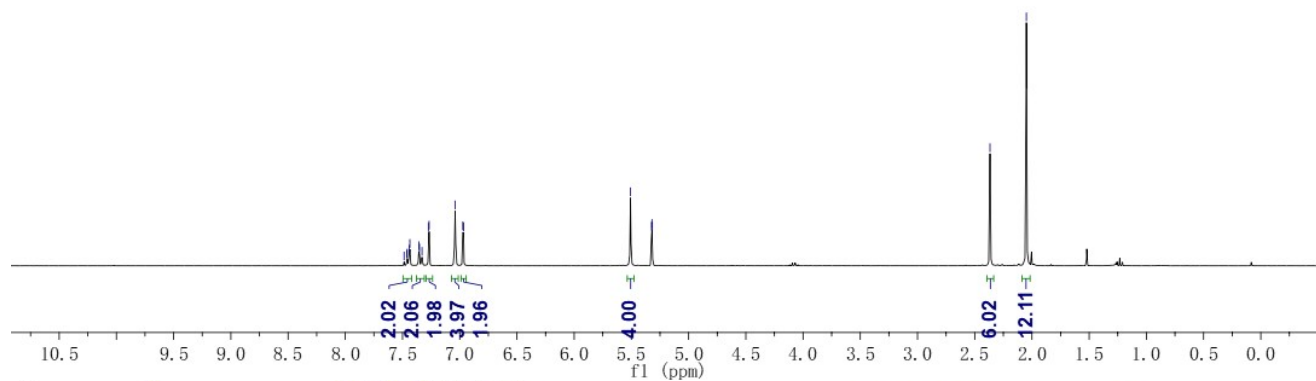
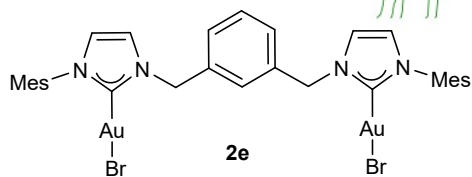
SUPPORTING INFORMATION

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

xim a
xm-486-2
probn_icon CD2D12 (0-\vd\sp\spn300) spnxima 10

7.49
7.46
7.44
7.44
7.36
7.35
7.33
7.27
7.27
7.04
6.97
5.51
5.32
5.32

-2.37
-2.05

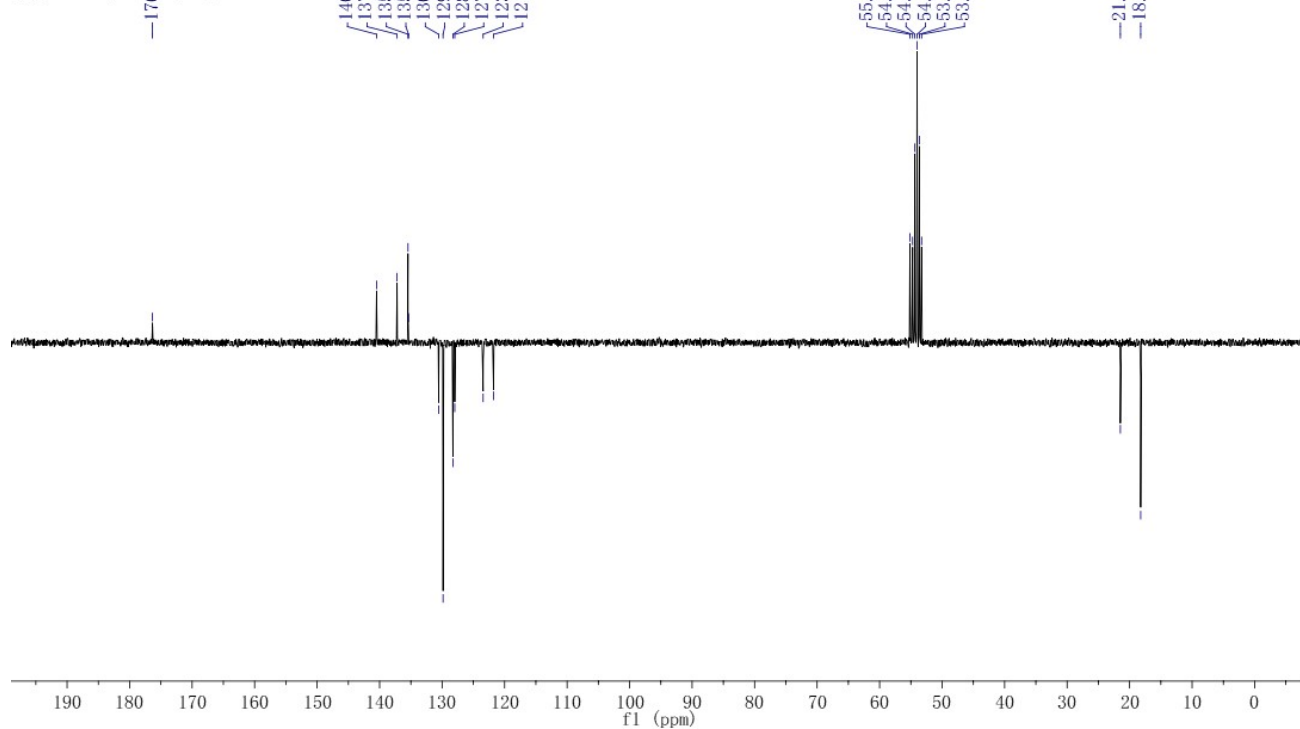


xim a
apt_t_icon CD2C12 (0-\vd\sp\spn300) DPE300 42

176.35
140.49
137.21
135.45
135.37
130.55
129.85
128.27
127.97
123.43
121.77

55.15
54.72
54.36
54.00
53.64
53.28

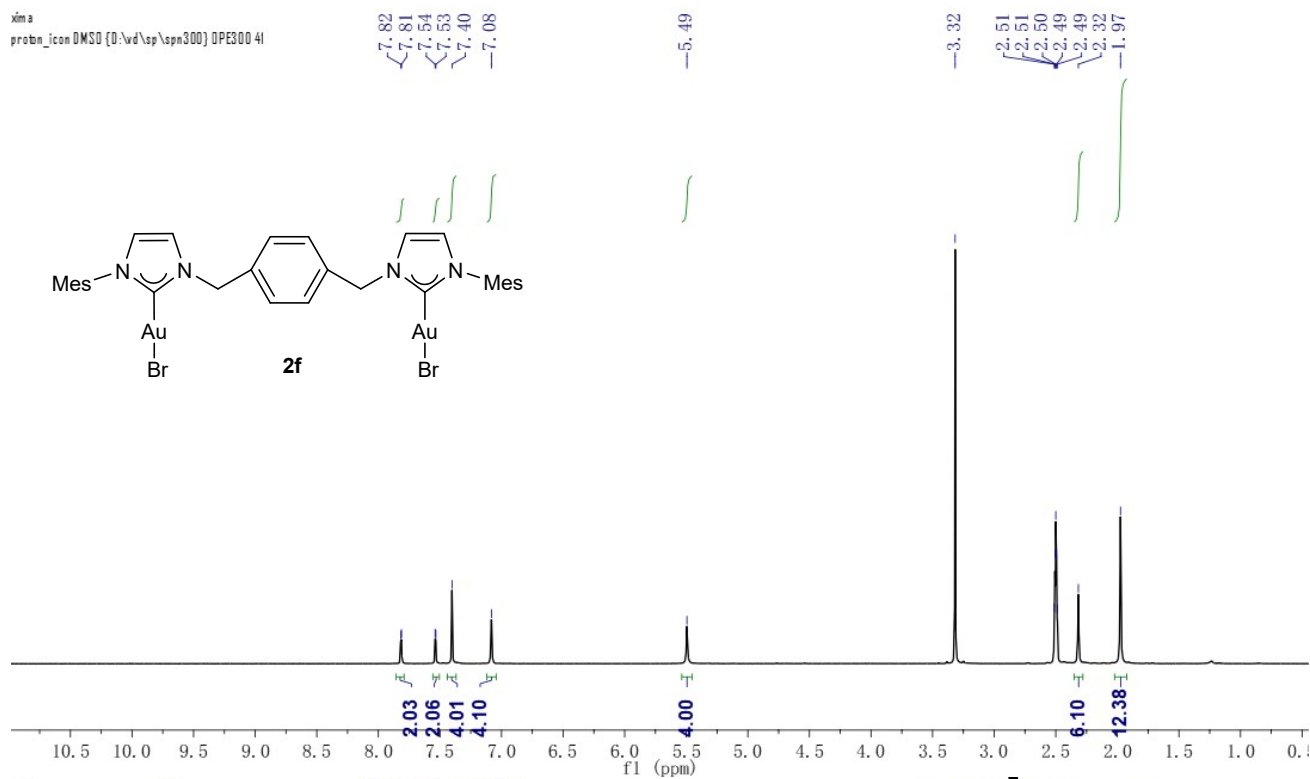
-21.48
-18.23



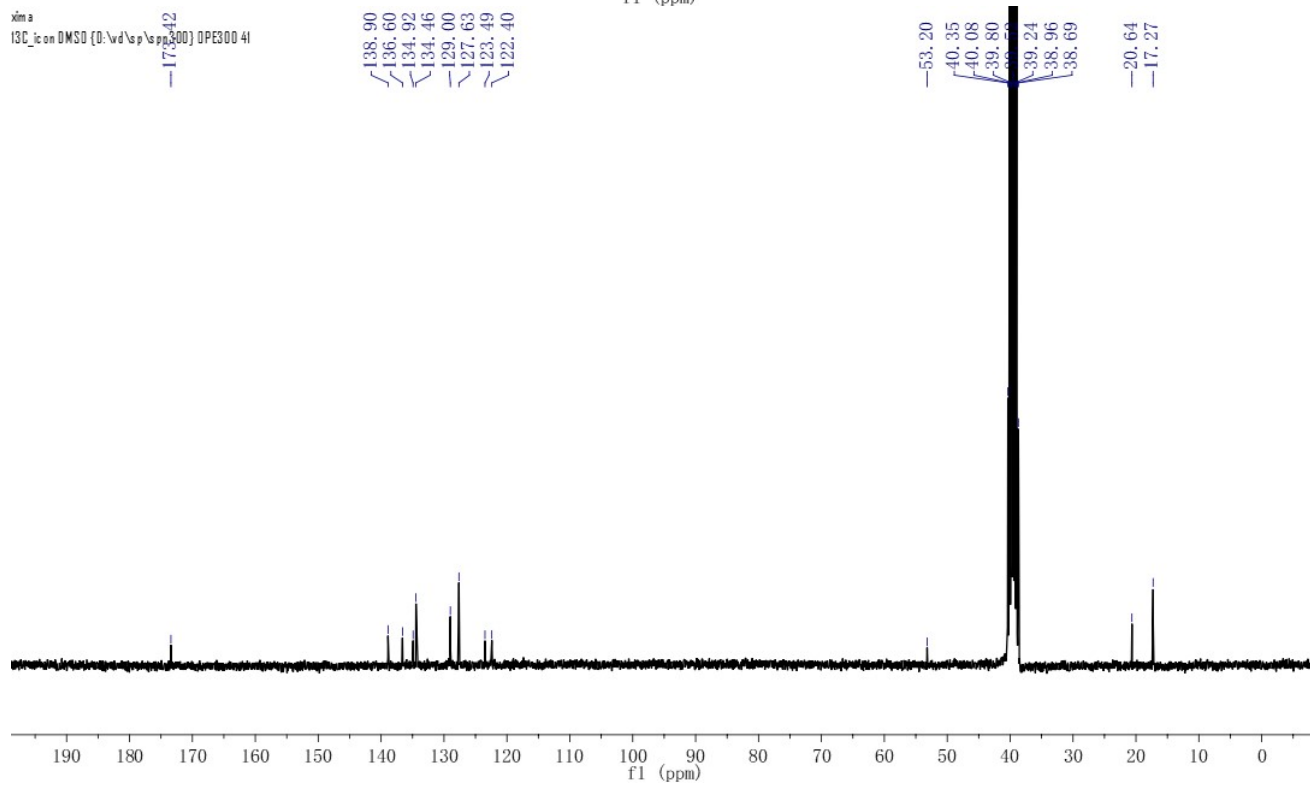
SUPPORTING INFORMATION

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

xim a
probn_1con DMSO (D:\vd\sp\spn300) DPE300 4f



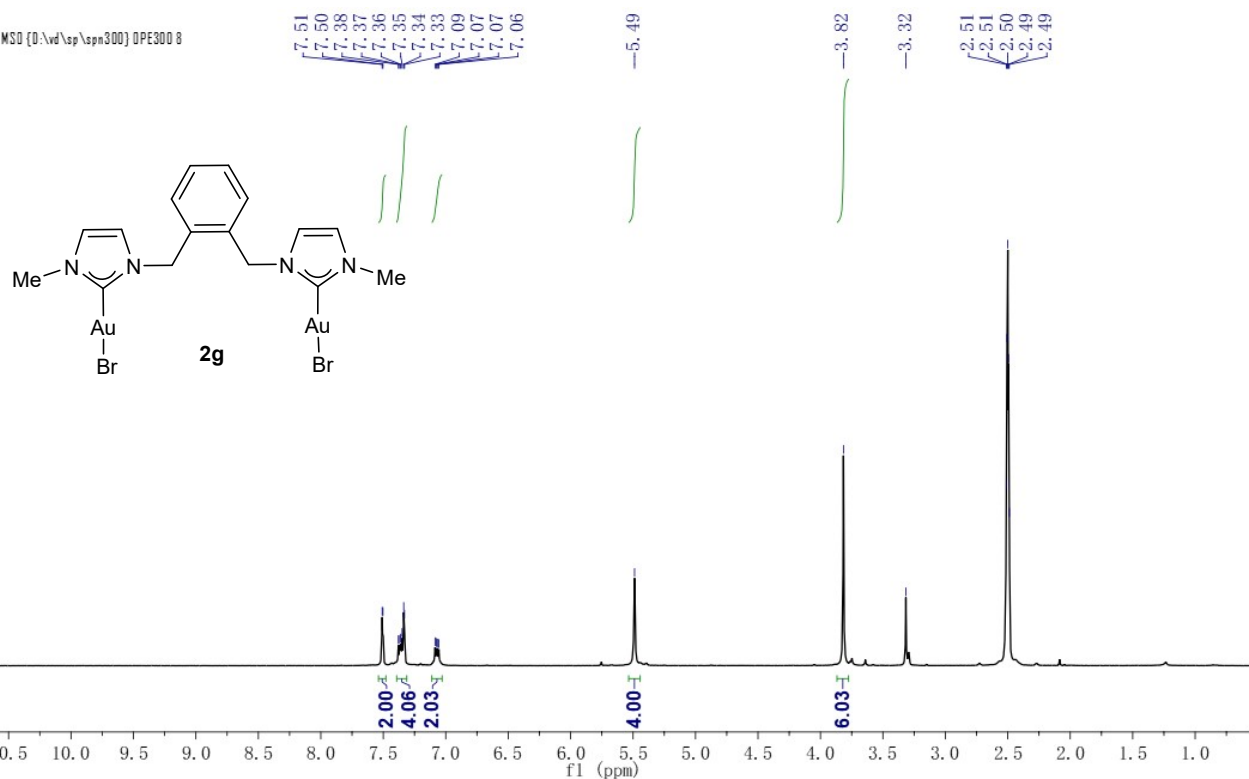
xim a
13C_1con DMSO (D:\vd\sp\spn300) DPE300 4f



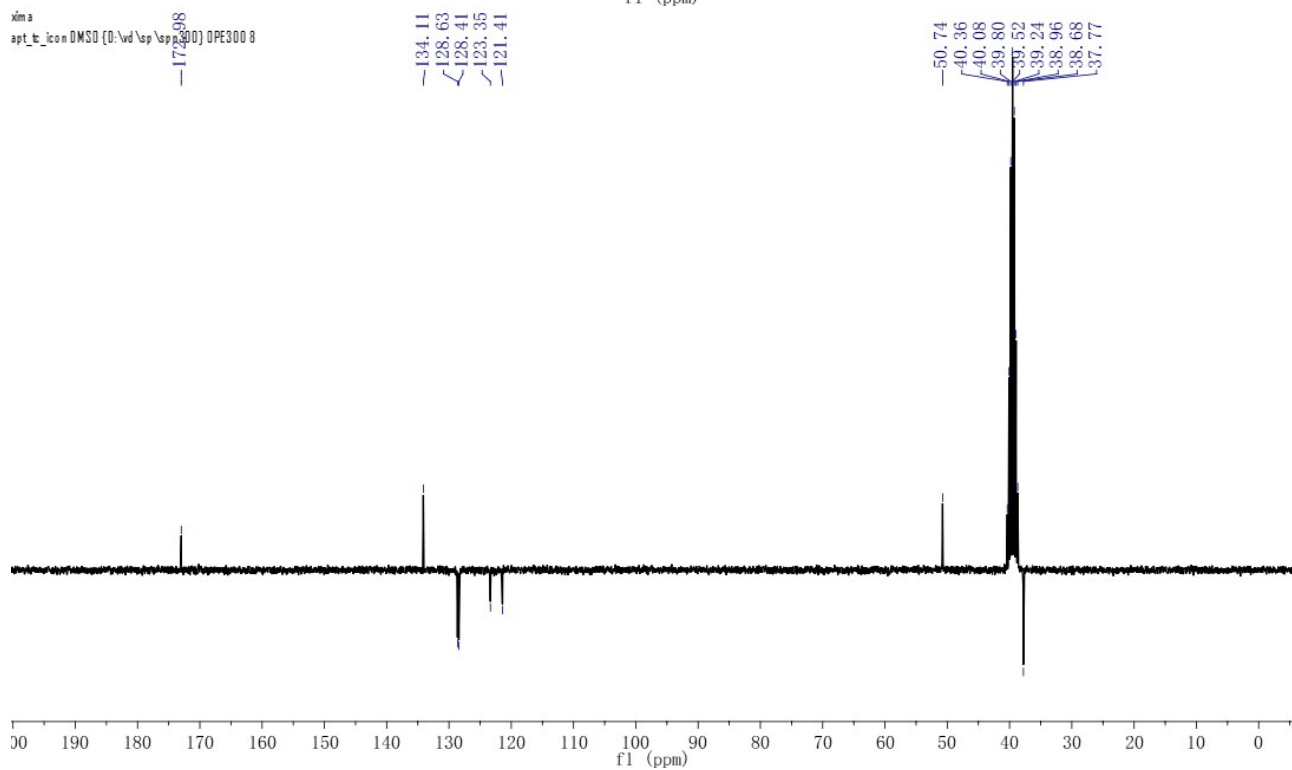
SUPPORTING INFORMATION

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

xim a
PROTON DMSO (D:\vd\asp\apn300) DPE300 8

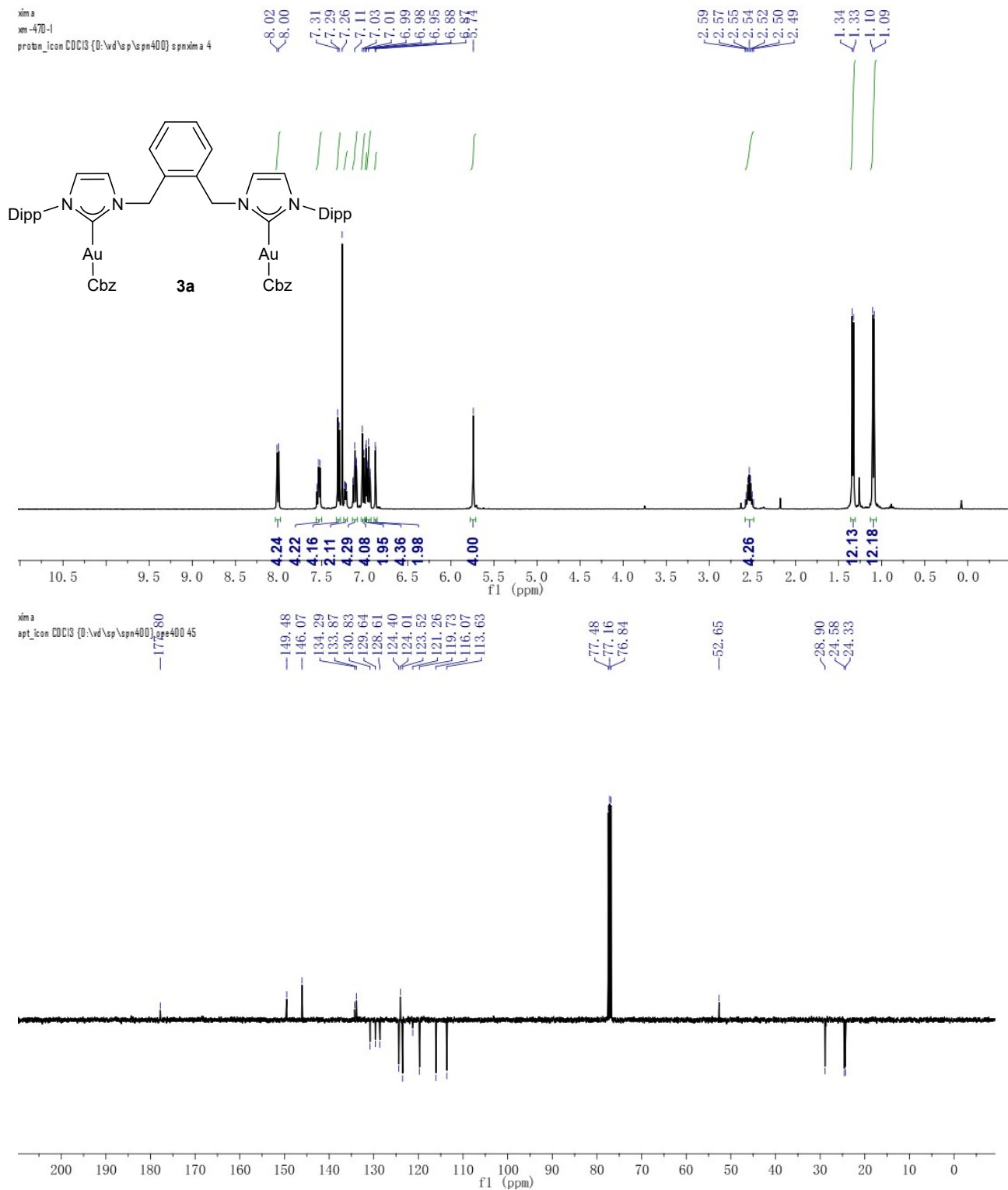


xim a
apt_t_1con DMSO (D:\vd\asp\apn300) DPE300 8



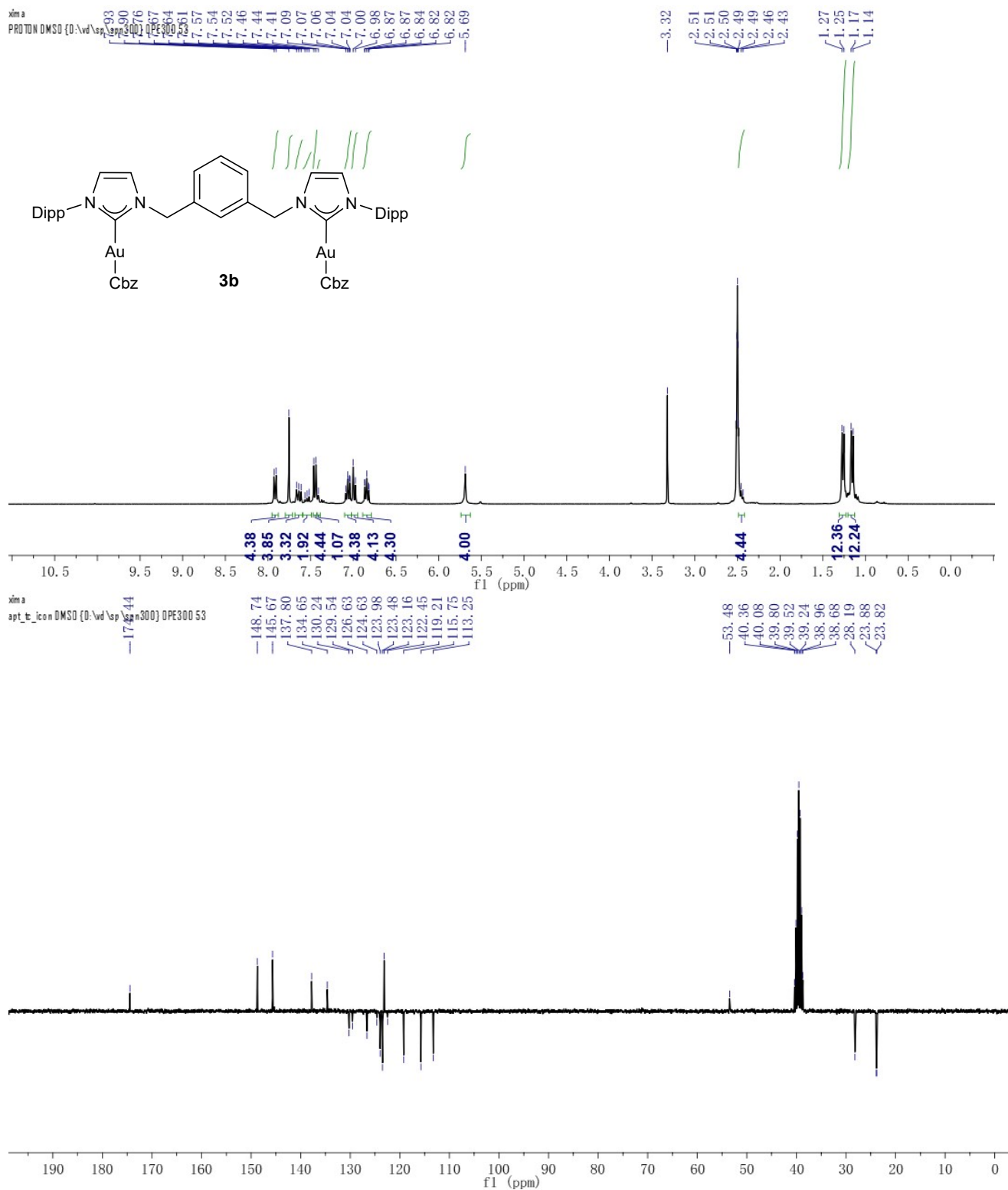
SUPPORTING INFORMATION

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



SUPPORTING INFORMATION

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



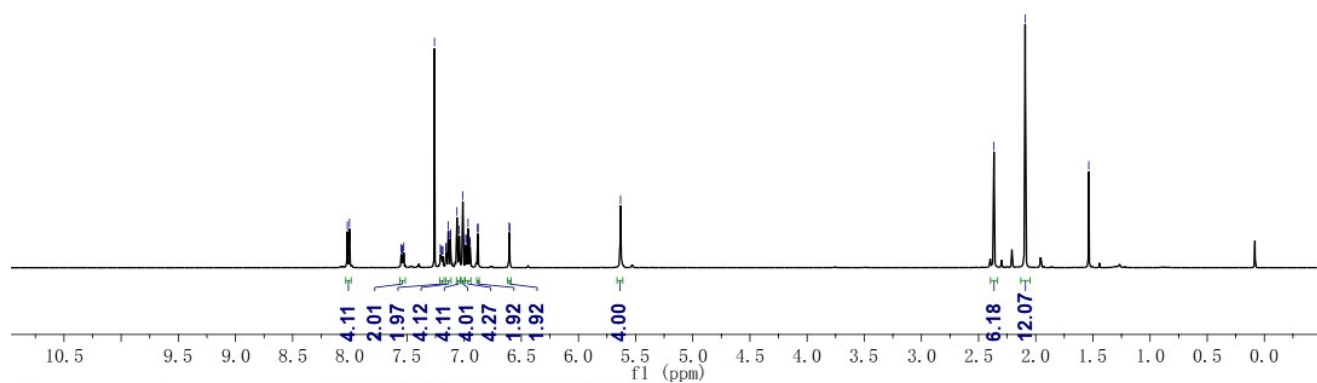
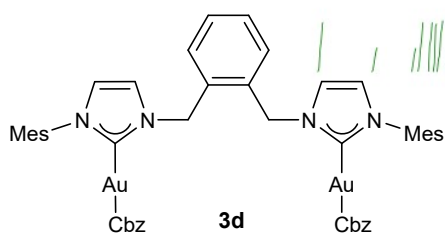
SUPPORTING INFORMATION

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

xm a
probn_icon CDCl3 [D:\vd\sp\spn400] ope400 48

8.02
8.00
7.26
7.14
7.12
7.12
7.06
7.04
7.01
6.97
6.88
6.88
6.61
6.60

-2.37
-2.09
-1.54



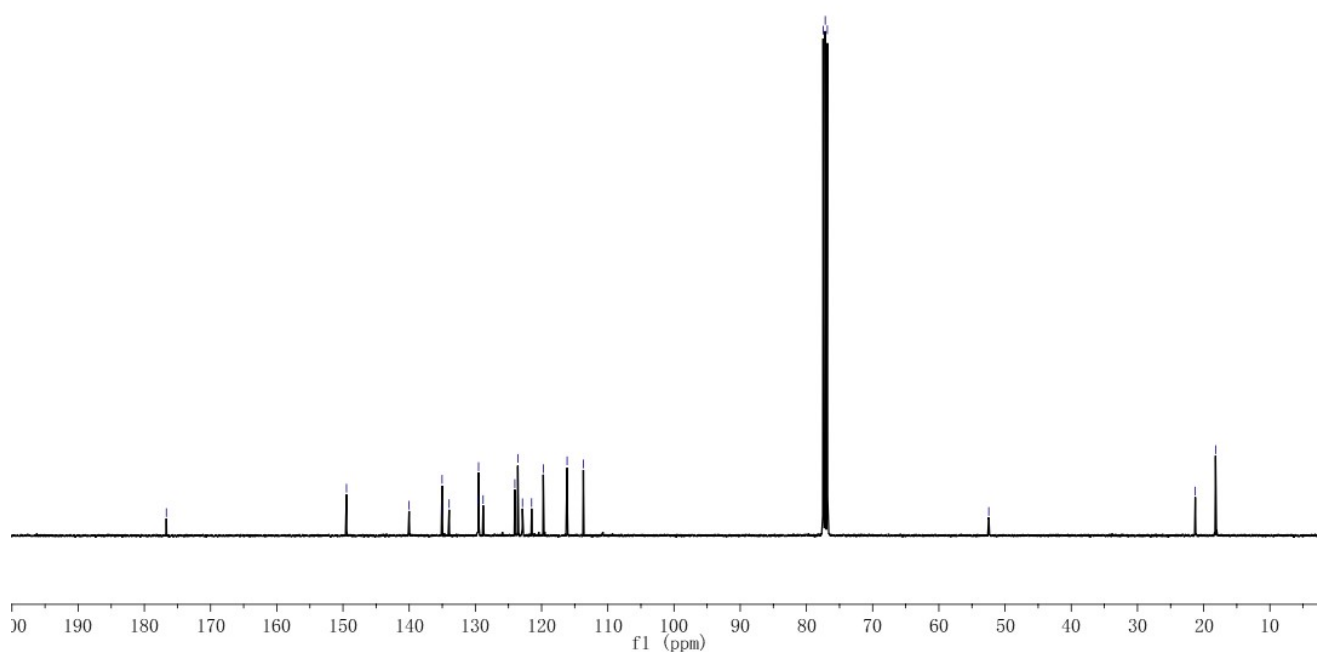
xm a
C13_icon CDCl3 [D:\vd\sp\spn400] ope400 48

149.47
140.01
135.03
134.98
133.96
129.63
129.52
128.83
124.04
123.59
122.89
121.51
119.75
116.15
113.70

77.48
77.16
76.84

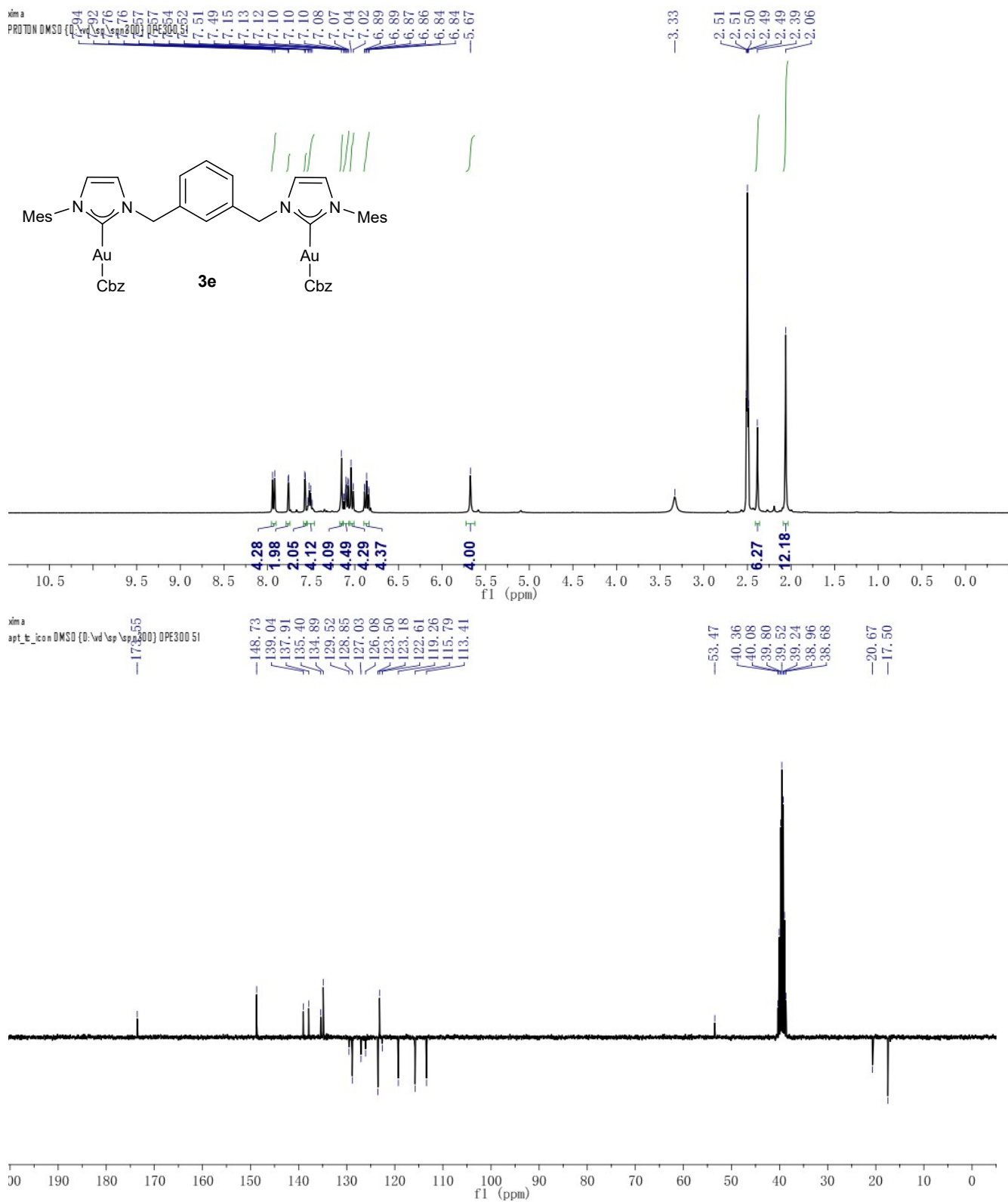
-52.46

-21.27
-18.21



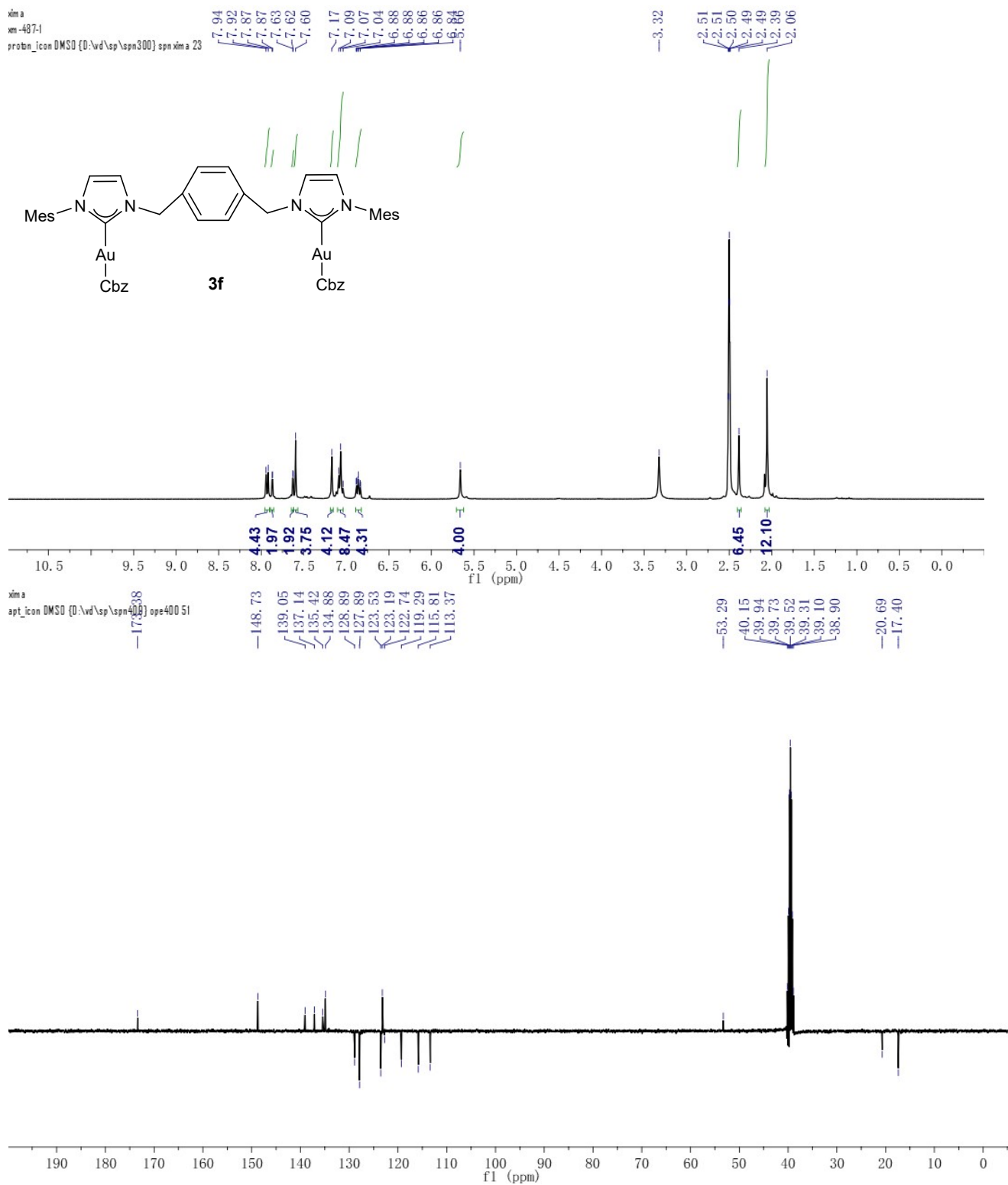
SUPPORTING INFORMATION

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



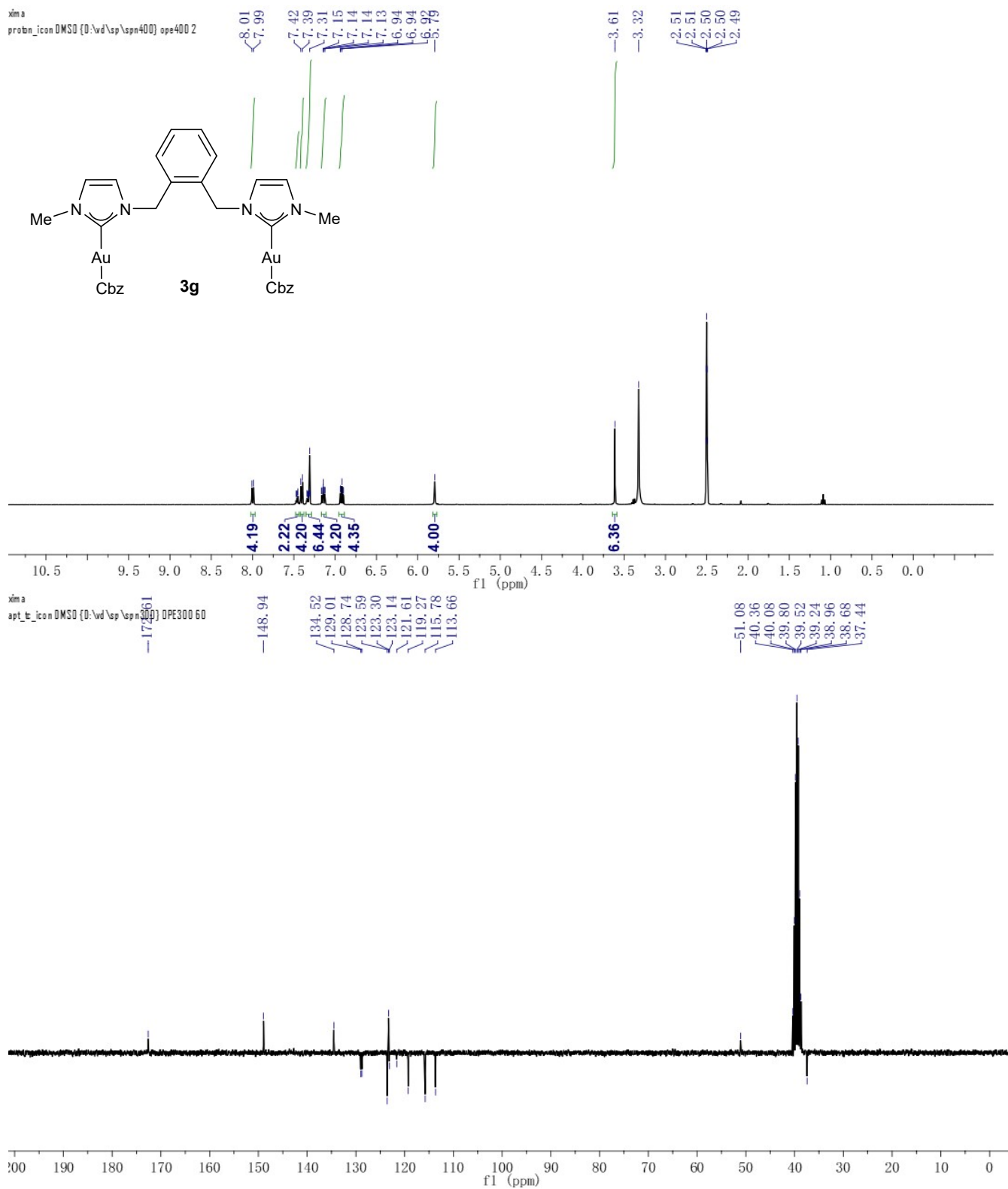
SUPPORTING INFORMATION

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



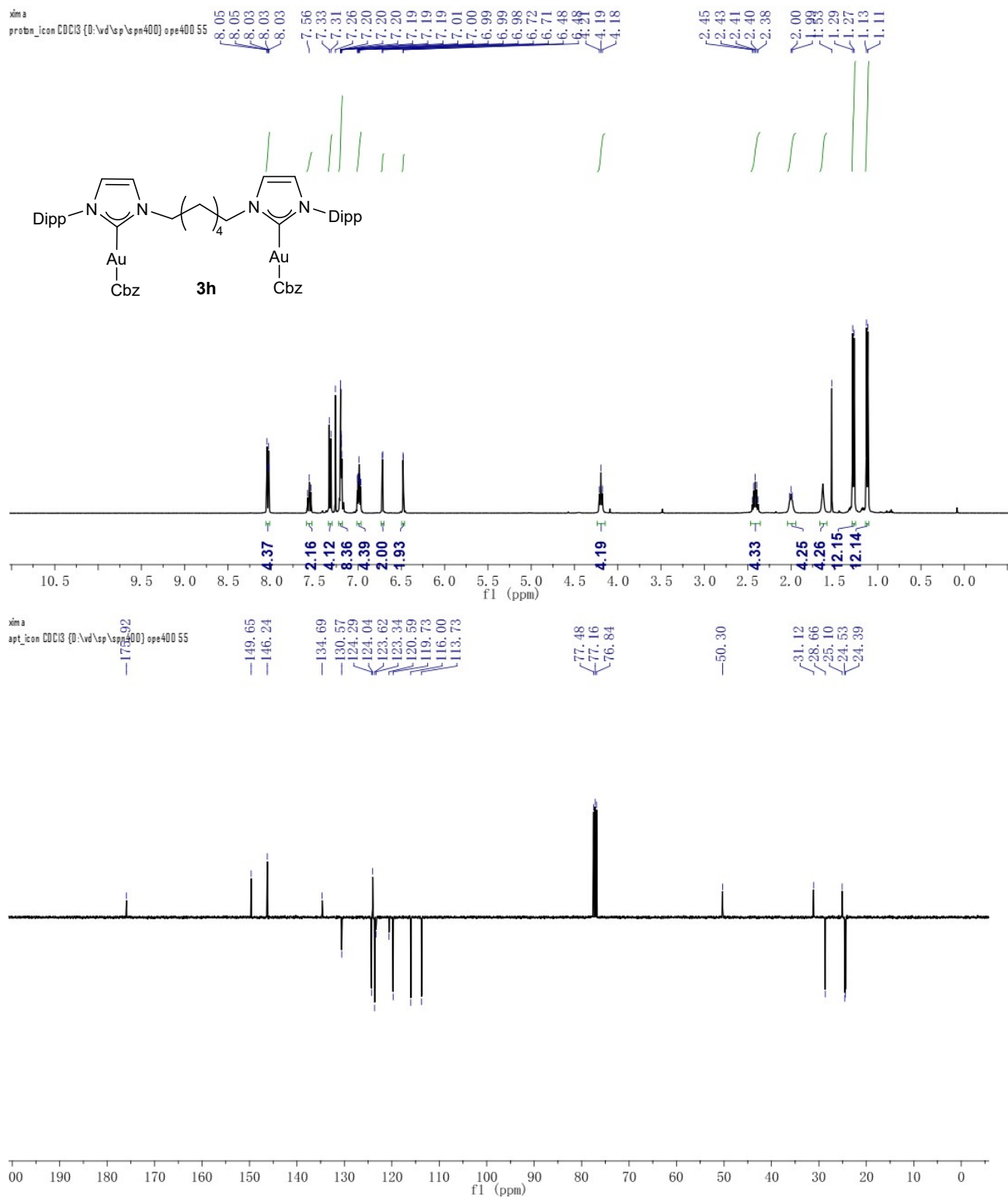
SUPPORTING INFORMATION

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



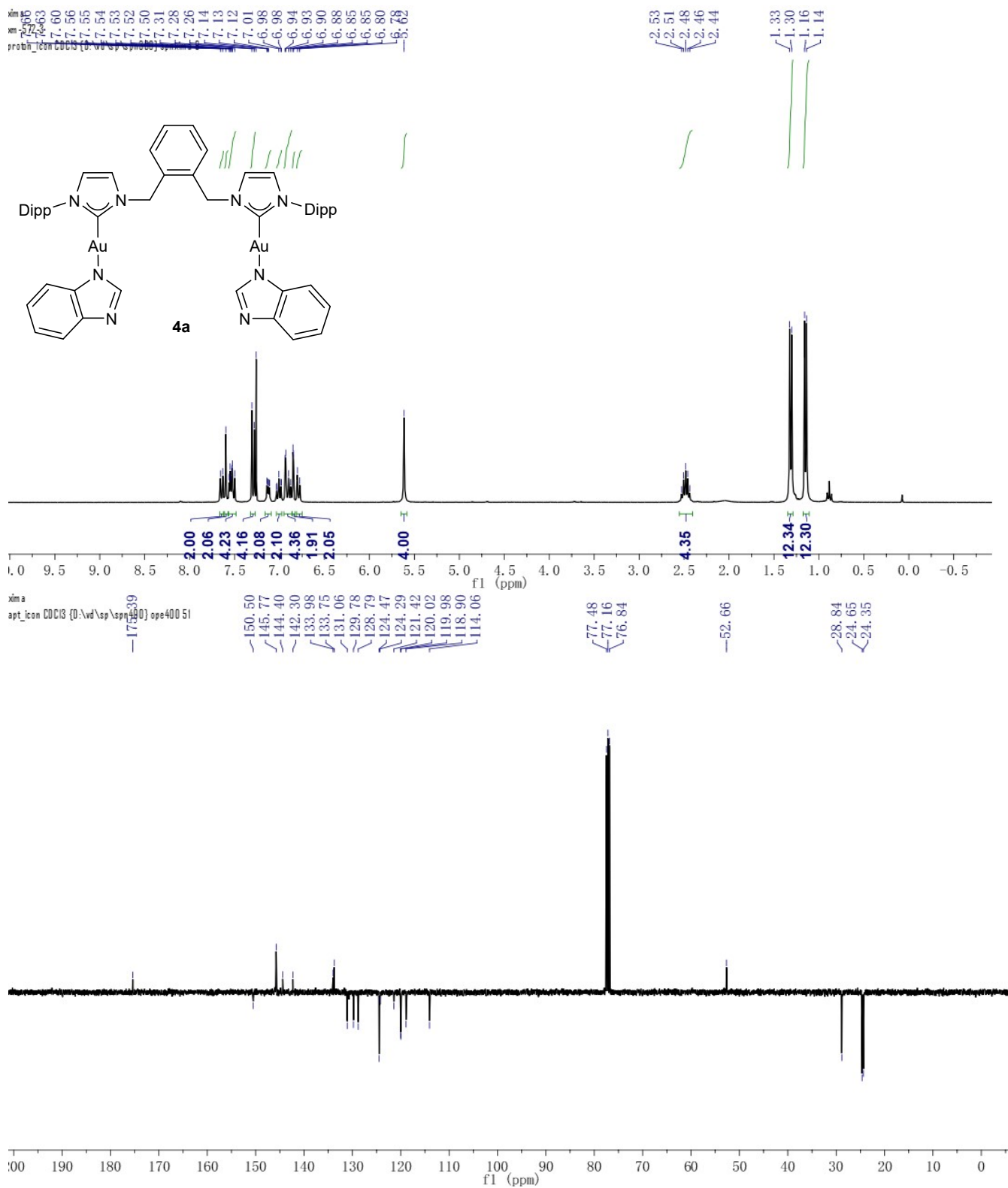
SUPPORTING INFORMATION

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



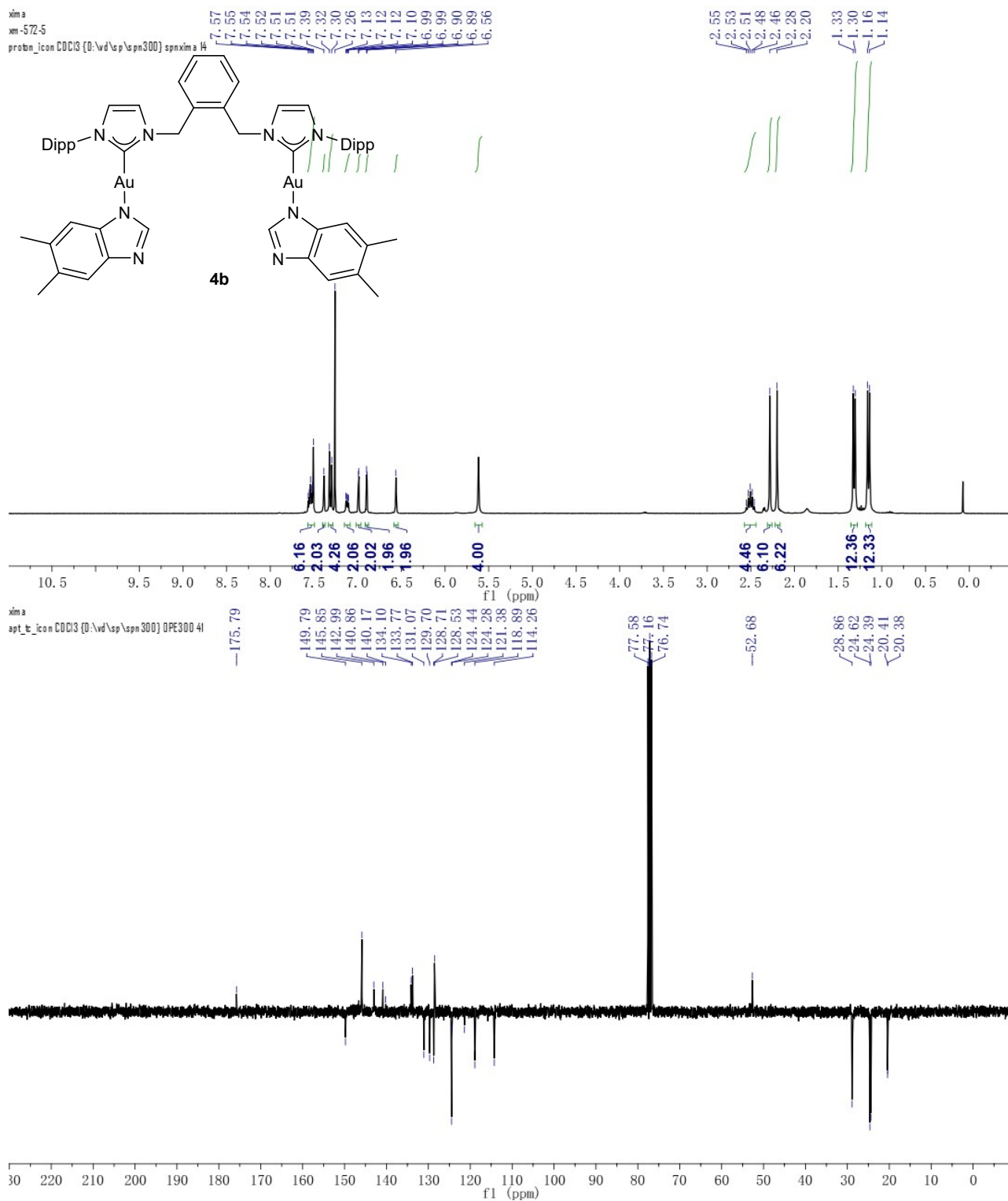
SUPPORTING INFORMATION

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



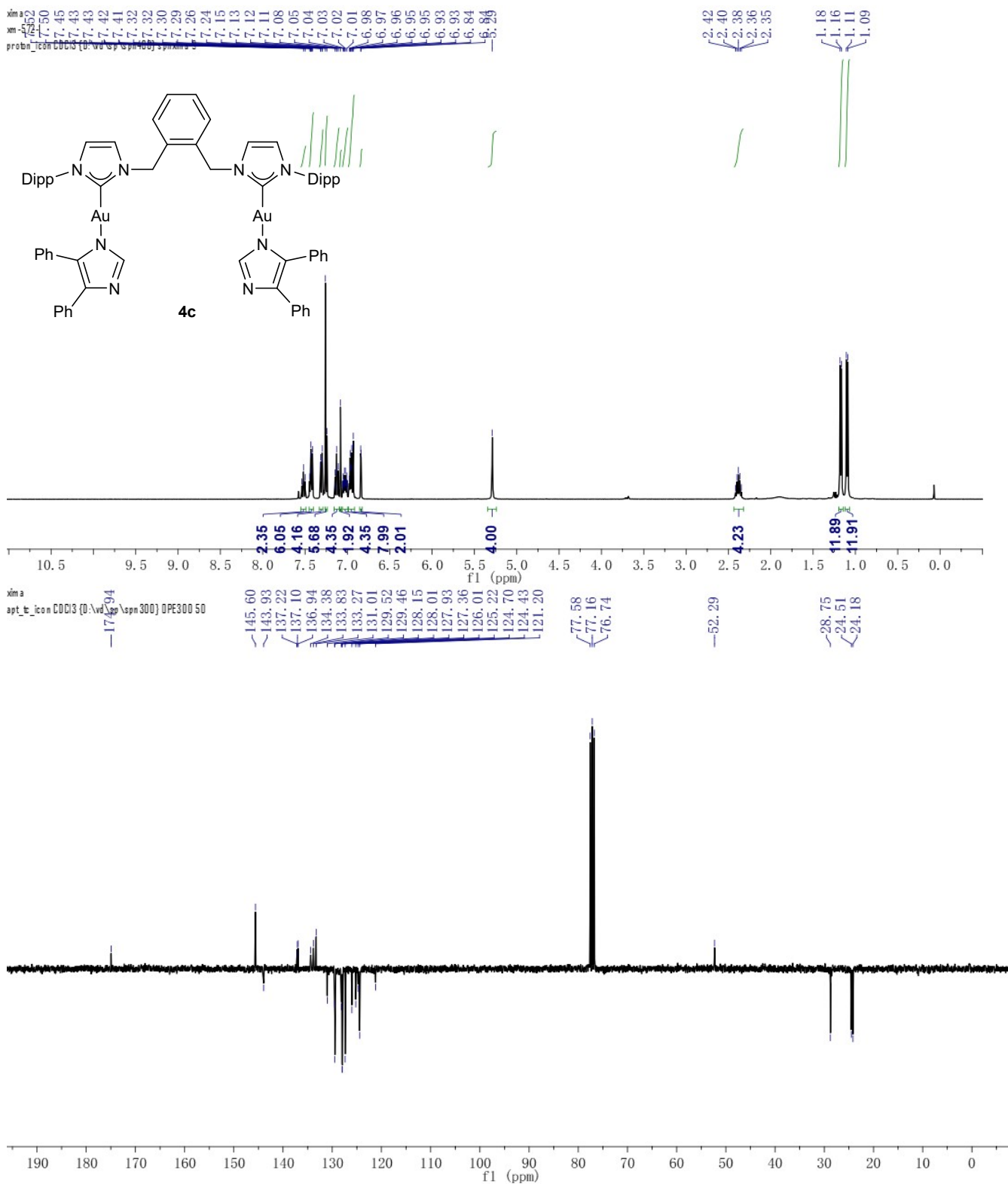
SUPPORTING INFORMATION

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



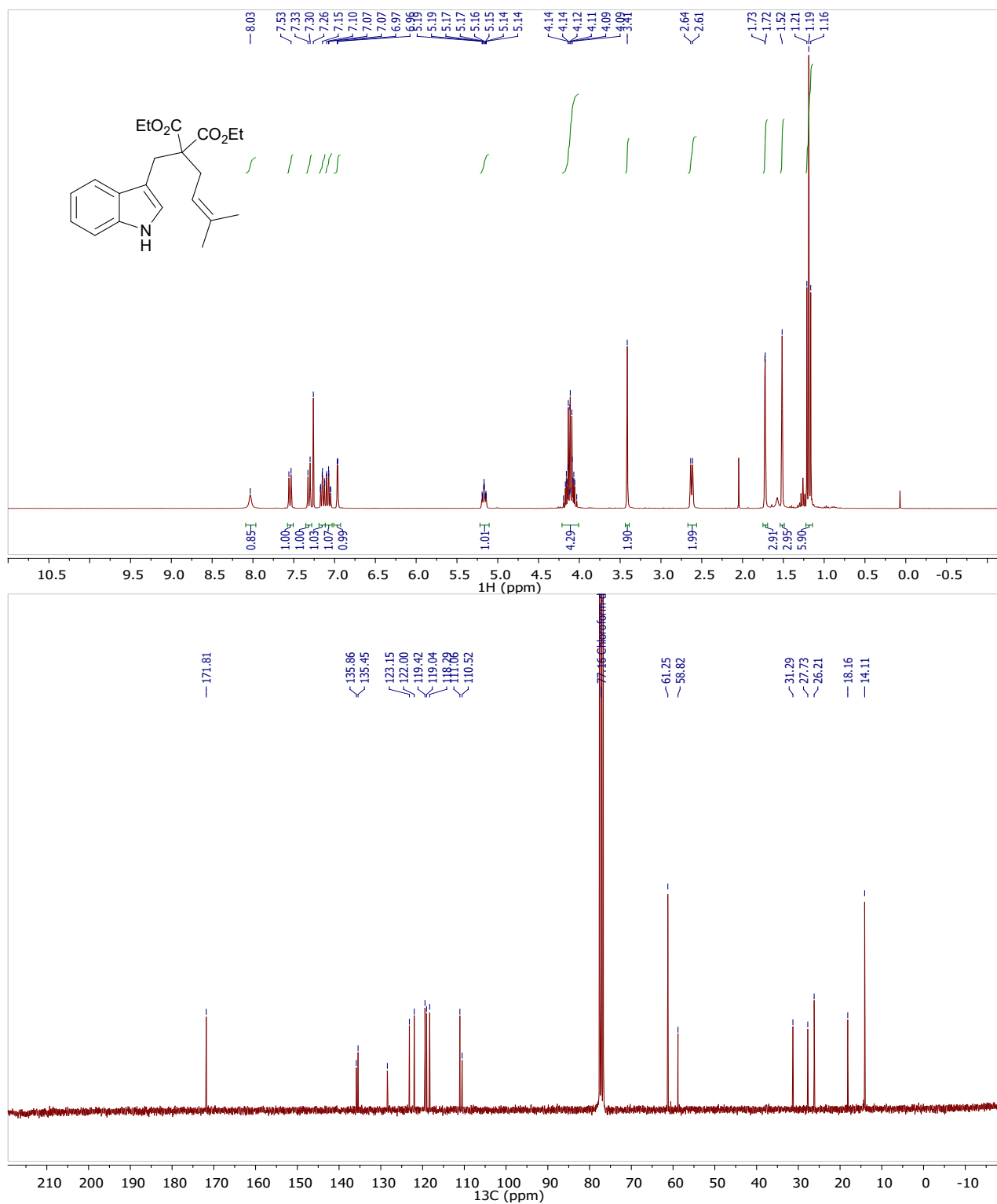
SUPPORTING INFORMATION

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



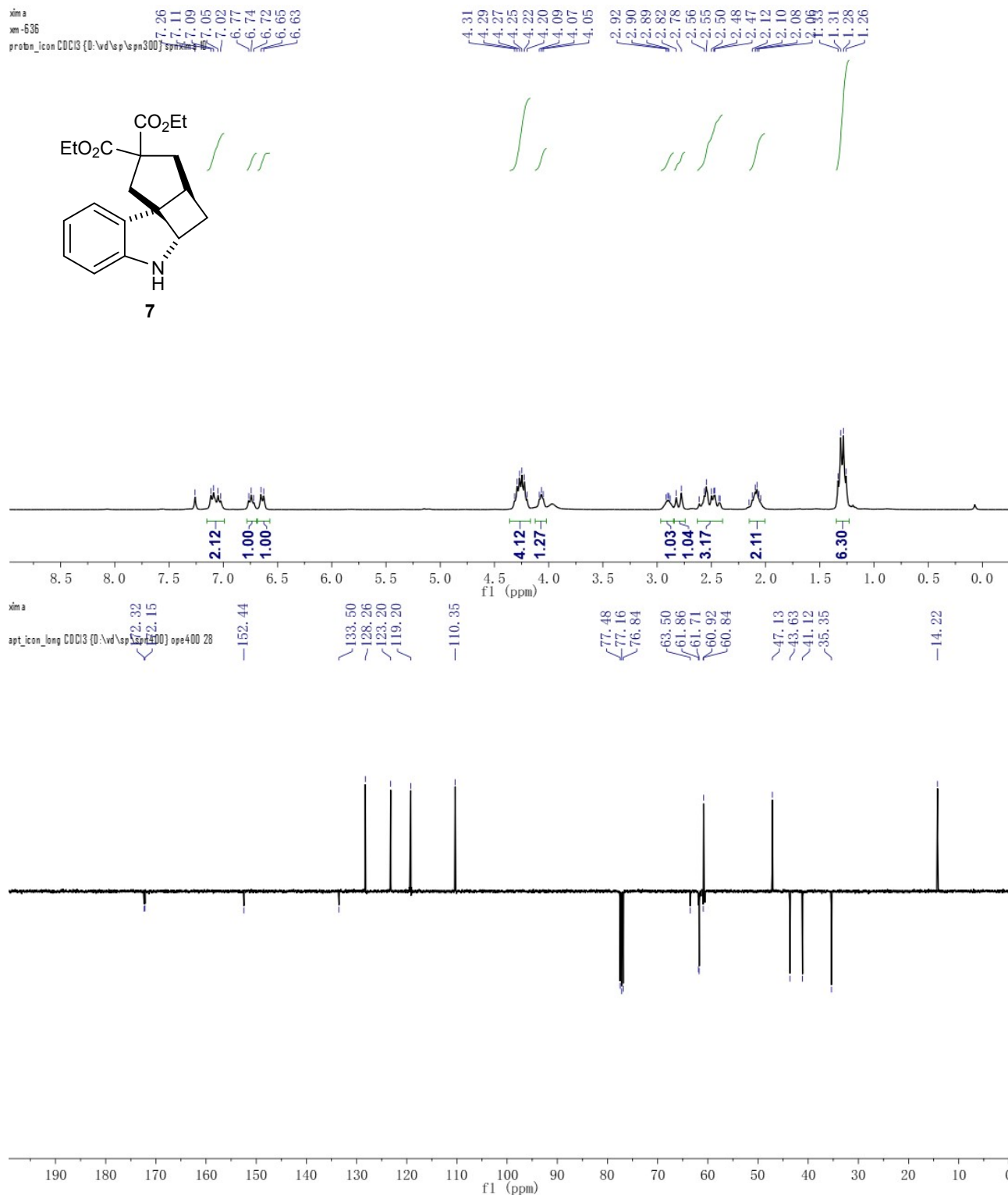
SUPPORTING INFORMATION

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



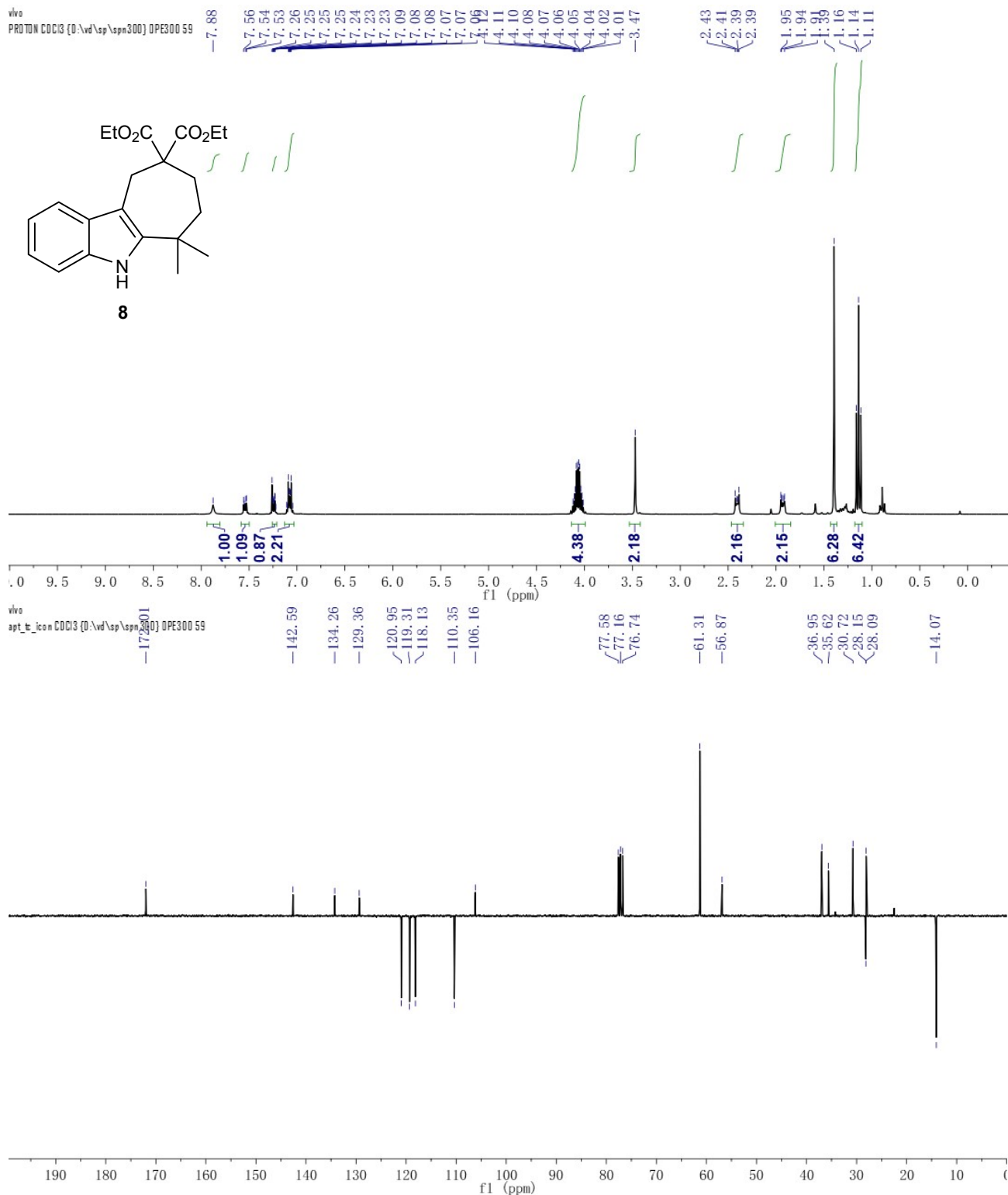
SUPPORTING INFORMATION

^1H and ^{13}C $\{^1\text{H}\}$ 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**



SUPPORTING INFORMATION

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



SUPPORTING INFORMATION

References

1. (a) Zhang, H.; Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L., *Synthesis* **2003**, 2661–2666; (b) Brill, M.; Collado, A.; Cordes, D. B.; Slawin, A. M. Z.; Vogt, M.; Grützmacher, H.; Nolan, S. P., *Organometallics* **2014**, *34*, 263–274.
2. Bayrakdar, T. A. C. A.; Nahra, F.; Davis, J. V.; Gamage, M. M.; Captain, B.; Temprado, M.; Marazzi, M.; Saab, M.; Hecke, K. V.; Ormerod, D.; Hoff, C. D. and Nolan, S. P. *Organometallics* **2020**, *39*, 2907–2916.
3. Crosby, G. A.; Demas, J. N., *Review. J. Phys. Chem.* **1971**, *75*, 991-1024.
4. Suzuki, K., Kobayashi, A., Kaneko, S., Takehira, K., Yoshihara, T., Ishida, H., Shiina, Y., Oishi, S. and Tobita, S., *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850–9860.
5. Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S. and Eastham, G. J. *Chem. Soc., Dalton Trans.* **2000**, 4499–4506.
6. Liu, J.; Zhao, Y.; Zhou, Y.; Li, L.; Zhang, T. Y. and H. Zhang. *Org. Biomol. Chem.* **2003**, *1*, 3227–3231.
7. Du, Y.; Tang, H.; Ding, H.; Shi, Y.; Cao, C. and Pang, G. *J. Chem. Res.* **2016**, *40*, 735–739.
8. Beillard, A.; Golliard, E.; Gillet, V.; Bantreil, X.; Métro, T.-X.; Martinez, J. and Lamaty, F. *Chem. Eur. J.* **2015**, *21*, 17614 – 17617.
9. Martynova, E. A.; Voloshkin, V. A.; Guillet, S. G.; Bru, F.; Beliš, M.; Hecke, K. V.; Cazin, C. S. J. and Nolan, S. P. *Chem. Sci.* **2022**, *13*, 6852–6857.