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SUPPLEMENTARY INFORMATION

Allene-derived gold and platinum complexes: synthesis and first applications in catalysis.

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<u>**SUPPLEMENTARY INFORMATION**</u>

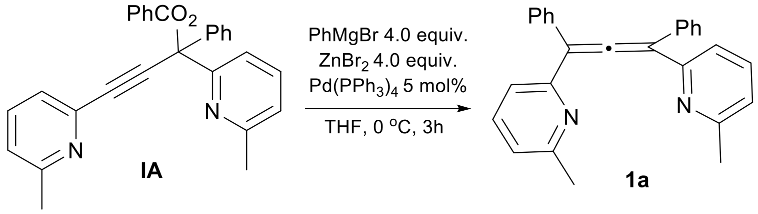
1. General information

All reagents and solvents used in described syntheses were of analytical grade and purchased from commercial suppliers; used without further purification, unless otherwise stated. Dry solvents (anhydrous $\geq$ 99.8 %) were obtained directly from commercial sources. Propargylic esters **IA-B** precursors to allenes were prepared using reported methods.[1,2] $ZnBr_2$ was dried with a heat gun under vacuum until it became visibly dry. Enynes used in catalytic screening were prepared according to reported methods.[3] For thin layer chromatography (TLC) technique, commercially available aluminium sheets pre-coated with silica gel (0.20 mm with fluorescent indicator UV254, Grace GM BH & Co) were used. Column chromatography was achieved with the use of Silica gel 60, 0.032-0.063 mm (230-450 mesh, Alfa Aesar). Ratios of the solvents used as an eluent are given in brackets. The ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AscendTM 500 or a Bruker UltrashieldTM Plus 400 spectrometers (solvent given in brackets). Chemical shifts (δ) are given in parts per million (ppm) and the values of coupling constant *J* are given in Hertz (Hz). Abbreviations for multiplicities are as follows: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, brs – signal broaden. Spectra were recorded at room temperature unless stated otherwise. High resolution mass spectra were carried out using ESI and EI techniques at the University of Sussex. ESI measurement were carried out on APEX II Bruker Daltonic Fourier transformer (FTMS) using Apollo ESI source. Electron Impact ionisation was performed using AutoSpec Fisons instrument. Microanalysis was performed with Thermo Flash 2000 Elemental Analyser configured for for %CHN, at the London Metropolitan University.

2. Experimental details

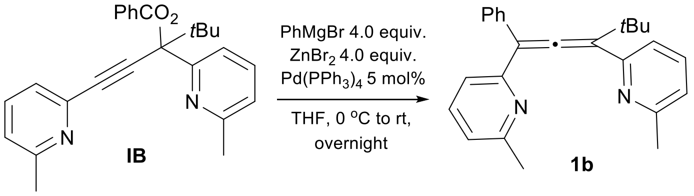
<u>2.1. Synthesis and characterisation of allenes and metal complexes</u>

Allene 1a



To a suspension of $ZnBr_2$ in anhydrous THF (0.8 M, 4.0 eq.), a phenylmagnesium bromide solution in Et_2O (4.0 eq.) was added dropwise at 0 ^{0}C under inert atmosphere. Stirring at 0 ^{0}C continued for 30 min. $Pd(PPh_3)_4$ (62 mg, 0.054 mmol, 0.05 eq.) and the propargyl benzoate **IA** (447 mg, 1.07 mmol, 1.0 eq.) in anhydrous THF (0.25 M solution of ester) were added at 0 ^{0}C. Reaction mixture was stirred at 0 ^{0}C for 3h. Water was added, aqueous layer was separated and extracted with Et_2O, combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. Column chromatography (Pet/AcOEt/NEt_3 85/14/1) yielded allene **1a** (215 mg, 54%) as a yellow oil.
The characterisation data is in agreement with previously reported.[1]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 6H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.33 (m, 4H), 7.30 – 7.26 (m, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 2.58 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 212.7, 158.4, 154.8, 136.9, 135.1, 128.7, 128.5, 127.7, 121.9, 121.5, 114.0, 24.8; **MS** (EI) ($C_{27}H_{21}N_2$) $[M-H]^+$: cacld: 373; found: 373 $[M-H]^+$

Allene 1b



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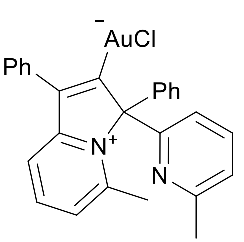
To a suspension of $ZnBr_2$ in anhydrous THF (0.8 M, 4.0 eq.), a phenylmagnesium bromide solution in Et_2O (4.0 eq.) was added dropwise at 0 ^oC under inert atmosphere. Stirring at 0 ^oC continued for 15 min, followed by 45 min at rt. $Pd(PPh_3)_4$ (145 mg, 0.125 mmol, 0.05 eq.) and the propargyl benzoate **IB** (996 mg, 2.5 mmol, 1.0 eq.) in anhydrous THF (0.25 M solution of ester) were added at 0 ^oC and stirring at this temperature continued for 15 min . Reaction mixture was brought to rt and stirred overnight. Water was added and the precipitate formed was filtered off. Aqueous layer of the filtrate was separated and extracted with Et_2O, combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. Column chromatography (Pet/AcOEt/NEt_3 93/6/1) yielded allene **1b** (264 mg, 30%) as a yellow oil.
The characterisation data is in agreement with previously reported.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.7 Hz, 1H), 7.49 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.26 – 7.21 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 2.56 (s, 6H), 1.42 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.0, 158.1, 157.3, 155.7, 155.6, 136.8, 136.3, 135.8, 128.3, 128.2, 127.1, 121.5, 121.4, 120.9, 120.9, 120.2, 112.1, 36.3, 30.3, 24.8, 24.7; **HRMS** (ESI) ($C_{25}H_{26}N_2$) $[M+Na]^+$: cacld: 377.1988 ; found: 377.1990 $[M+Na]^+$.

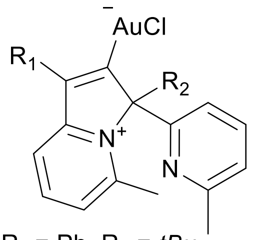
Gold(I) complex 2a



2a

To a solution of **1b** (10 mg, 0.027 mmol, 1.2 equiv.) in CH_2Cl_2 (0.8 ml) $(Me_2S)AuCl$ (6.6 mg, 0.022 mmol, 1.0 equiv.) was added. Upon addition the solution changed from colourless to bright yellow. Reaction mixture was stirred at rt for 15 min and then concentrated in *vacuo* yielding **2a** (16 mg, quant.) as a yellow solid. Crystals suitable for X-Ray crystallography were obtained by slow evaporation from the dichloromethane solution.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.45 (m, 1H), 7.99 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.28 (m, 8H), 7.10 (d, *J* = 7.6 Hz, 2H), 2.28 (s, 3H), 2.12 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.3, 159.3, 157.4, 155.9, 150.1, 144.1, 136.4, 135.6, 135.0, 134.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.1, 126.6, 122.7, 121.3, 116.5, 97.5, 24.5, 22.3; **HRMS** (ESI) ($C_{27}H_{22}N_2Au$) $[M-Cl]^+$: cacld: 571.1443 ; found: 571.1452 $[M-Cl]^+$; **Anal.** Calcd. for $C_{28.1}H_{24.2}N_2AuCl_{3.2}$ (**2a**·1.1CH_2Cl_2): C 48.28, H 3.49, N 4.01; found: C 48.21, H 3.48; N 4.10.

Gold(I) complex 2b



2b' R_1 = Ph, R_2 = *tBu*
2b'' R_1 = *t*Bu, R_2 = Ph

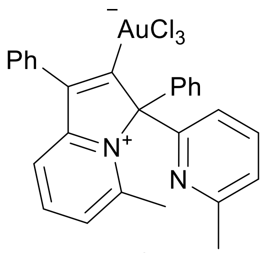
To a solution of **1b** (20 mg, 0.056 mmol, 1.0 equiv.) in CH_2Cl_2 (0.8 ml) $(Me_2S)AuCl$ (17 mg, 0.056 mmol, 1.0 equiv.) was added. Upon addition the solution changed from colourless to bright yellow. Reaction mixture was stirred at rt for 15 min and then concentrated in *vacuo* yielding **2b** (33 mg, quant.) as a yellow solid. Crystals suitable for X-Ray crystallography were obtained from dichloromethane solution containing iodopentafluorobenzene and layered with cyclohexane.

Spectral analysis of **2b'** in 1:0.85 mixture of **2b'':2b'**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H, *b''*), 8.01 (t, *J* = 8.0 Hz, 1H, *b''*), 7.90 (t, *J* = 7.8 Hz, 1H, *b'*), 7.82 (d, *J* = 8.4 Hz, 1H, *b''*), 7.75 (d, *J* = 7.1 Hz, 2H, *b'*), 7.66 (t, *J* = 7.8 Hz, 1H, b''), 7.47 – 7.31 (m, 5H, *b'*), 7.25 (m, 5H, *b''*), 7.08 – 7.00 (m, 4H, *b',b''*), 6.78 (d, *J* = 7.8 Hz, 1H, b'), 2.58 (s, 3H, *b'*), 2.25 (s, 3H, *b''*), 2.13 (s, 3H, *b'*), 2.02 (s, 3H, b''), 1.59 (s, 9H, *b''*), 1.50 (s, 9H, *b'*); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.4 (b'), 187.7 (b''), 160.1 (b''), 159.5 (b'), 157.5 (b'), 157.2 (b''), 155.8 (b'), 155.4 (b''), 155.1 (b'), 151.0 (b''), 143.6 (b'), 143.0 (b''), 141.1 (b''), 139.2 (b'), 137.4 (b'), 136.2 (b''), 135.7 (b'), 135.0 (b''), 128.9 (b'), 128.8 (b''), 128.8 (b'), 128.4 (b''), 128.1 (b'), 126.5 (b''), 123.1 (b'), 122.4 (b''), 121.9 (b'), 121.5 (b'), 120.6 (b''), 118.7 (b''), 116.2 (b'), 102.2 (b'), 96.7 (b''), 43.2 (b'), 32.7 (b''), 31.5 (b''), 30.3 (b'), 24.7 (b'), 24.5 (b''), 22.9 (b'), 22.7 (b'').

Complex **2b’’:**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.01 (dd, *J* = 8.4, 7.7 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.26 (m, 5H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), 2.03 (s, 3H), 1.60 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 160.2, 157.2, 155.4, 151.0, 142.9, 141.2, 136.2, 135.0, 128.9, 128.4, 126.6, 122.5, 120.4, 118.7, 96.7, 32.8, 31.5, 24.5, 22.7. **HRMS** (ESI) ($C_{25}H_{26}N_2Au$) [M-Cl]$^+$: cacld: 551.1756; found: 551.1766 [M-Cl]$^+$; **Anal.** Calcd. for $C_{26.6}H_{29.2}N_2AuCl_{4.2}$ (**2b**$\cdot$1.6CH_2Cl_2): C 44.30, H 4.08, N 3.89; found: C 43.94, H 3.76; N 3.85.

Gold(III) complex 3a

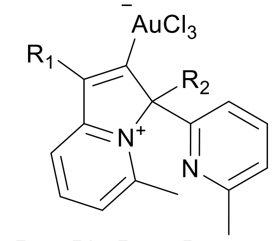


3a

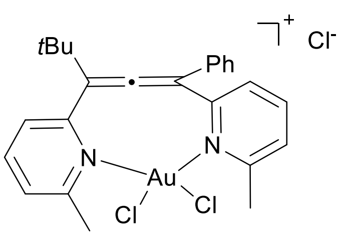
To a solution of $HAuCl_4{\cdot}xH_2O$ (18 mg, 0.053 mmol, 1.0 equiv.) in ethanol (0.8 ml) solution of **1a** (20 mg, 0.053, 1.0 equiv.) in 0.8 ml of ethanol was added. The mixture was heated at 65 °C. After 30 min yellow precipitate started to form. After 3h, yellow solid was isolated by filtration, washed with EtOH and dried under vacuum to yield **3a** (15 mg, 42%) as a yellow solid. Crystals suitable for X-Ray crystallography were obtained by slow evaporation from the dichloromethane/methanol solution.

^{1}H NMR (400 MHz, DMSO) δ 8.54 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.71 (m, 4H), 7.61 – 7.49 (m, 4H), 7.43 – 7.36 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 1H), 2.56 (s, 3H), 2.12 (s, 3H); **^{13}C NMR (101 MHz, DMSO)** δ 158.4, 158.2, 156.4, 154.7, 149.3, 146.7, 138.0, 134.0, 131.6, 131.5, 129.2, 129.10, 129.0, 128.90, 128.3, 125.9, 123.3, 120.0, 118.1, 90.9, 24.2, 21.0, peak corresponding to carbene carbon atom not detected; **HRMS** (ESI) ($C_{27}H_{22}N_2AuCl_2$) [M-Cl]$^+$: cacld: 641.0820; found: 641.0842 [M-Cl]$^+$; **Anal.** Calcd. for $C_{27}H_{22}N_2AuCl_3$: C 47.93, H 3.28, N 4.14; found: C 47.64, H 3.16; N 4.31.

Gold(III) complexes 3b and 4b



3b' R_1 = Ph, R_2 = *t*Bu
3b'' R_1 = *t*Bu, R_2 = Ph



4b

To a solution of $HAuCl_4{\cdot}xH_2O$ (15.4 mg, 0.045 mmol, 1.0 equiv.) in methanol (0.5 ml) solution of **1b** (16 mg, 0.045 mmol, 1.0 equiv.) in 0.5 ml of methanol was added. The mixture was heated at reflux. After 30 min yellow precipitate started to form. After a total of 130 min, yellow solid was isolated by filtration, washed with MeOH and dried under vacuum to yield **3b** as 0.17:1 mixture of **3b’** and **3b’’** (6 mg, 20%) as a yellow solid. The remaining filtrate was concentrated to yield **4b** (18 mg, 60%) as a yellow solid. Crystals of **3b’’** suitable for X-Ray crystallography were obtained by vapour diffusion of CH_2Cl_2/$CHCl_3$ solution with cyclohexane.

Spectral analysis of 0.5:1 mixture of **3b’**:**3b’’** isomers for ^{1}H NMR and 1:0.4 for ^{13}C NMR.

^{1}H NMR (400 MHz, DMSO) δ 8.58 – 8.51 (m, 1H, *b’’*), 8.46 (d, *J* = 8.2 Hz, 1H, b’’), 8.41 (t, *J* = 7.9 Hz, 1H, b’), 7.71 – 7.63 (m, 4H, *b’,b’’*), 7.58 (t, *J* = 7.3 Hz, 1H, *b’,b’’*), 7.54 – 7.46 (m, 1H, *b’*), 7.36 (t, *J* = 5.6 Hz, 2H, *b’,b’’*), 7.30 (dd, *J* = 7.6, 3.3 Hz, 2H, *b’,b’’*), 6.76 (d, *J* = 8.0 Hz, 1H, b’’), 6.69 (d, *J* = 7.9 Hz, 1H, b’), 2.61 (s, 3H, *b’*), 2.60 (s, 3H, b’’), 2.14 (s, 3H, *b’*), 2.03 (s, 3H, *b’’*), 1.64 (s, 9H, *b’’*), 1.54 (brs, 9H, *b’*); **^{13}C NMR (101 MHz, DMSO)** δ 158.1 *(b’’)*, 156.8 (*b’’*), 156.5 *(b’’)*, 156.3 *(b’’)*, 156.1 *(b’)*, 155.1 (*b’’*), 154.8 (*b’*), 154.2 *(b’’)*, 152.7 (*b’’*), 151.7 *(b’)*, 150.5 (*b’’*), 146.0 (*b’’*), 145.2 *(b’)*, 139.2 (*b’*), 139.0 *(b’’)*, 138.1 (*b’’*), 136.8 *(b’)*, 133.2 (*b’*), 132.3 (*b’’*), 129.3 *(b’’)*, 129.0, 128.8, 127.0 *(b’)*, 125.4 *(b’’)*, 123.3 *(b’)*, 123.1, 123.1, 122.4, 120.4 (*b’’*), 117.4 (*b’*), 97.4 *(b’)*, 89.4 *(b’’)*, 43.1 *(b’)*, 32.8 *(b’’)*, 30.0 *(b’’)*, 29.2 (*b’*), 24.2 *(b’)*, 24.1 *(b’’)*, 23.9 *(b’)*, 21.3 *(b’’)*, peak corresponding to carbene carbon atom not detected; **HRMS** (ESI) ($C_{25}H_{26}N_2AuCl_2$) [M-Cl]$^+$: Cacld: 621.1130; found: 621.1160 [M-Cl]$^+$; **Anal.** Calcd. for $C_{25}H_{26}N_2AuCl_3$: C 45.73, H 3.99, N 4.27; found: C 45.53, H 3.83; N 4.33.

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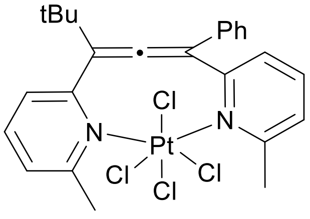
Complex **4b**:

^{1}H NMR (500 MHz, MeOD) δ 8.17 (t, *J* = 7.9 Hz, 1H), 8.11 (t, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.42 – 7.35 (m, 3H), 2.75 (s, 3H), 2.74 (s, 3H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, MeOD)** δ 208.4, 158.4, 158.1, 156.6, 153.0, 152.5, 144.0, 143.2, 134.5, 130.3, 130.0, 129.0, 126.7, 126.3, 124.5, 120.1, 111.5, 37.5, 30.1, 22.3, 22.1; **HRMS** (ESI) ($C_{25}H_{27}Cl_3N_2Au$) $[M+H]^+$: Cacld: 657.0900; found: 657.0950 $[M+H]^+$; **Anal.** Calcd. for $C_{25.5}H_{27.5}Cl_{4.5}N_2Au$ (**4b**$\cdot$0.5$CHCl_3$): C 42.73, H 3.87, N 3.91; found: C 43.01, H 3.82, N 3.93.

Platinum(IV) complex 4c

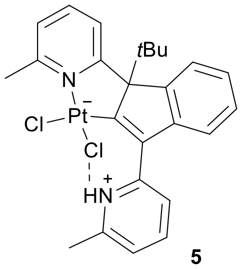


4c

To a solution of $H_2PtCl_6\cdot 6H_2O$ (29 mg, 0.056 mmol, 1.0 equiv.) in MeOH (1.2 ml) solution of **1b** (20 mg, 0.056 mmol) in MeOH (1.2 ml) was added. Upon addition a precipitate started to form instantaneously. After 40 min of stirring at rt the solid was filtered off, washed with MeOH and dried under vacuum to afford **4** (36 mg, 93%) as a pale orange solid.

^{1}H NMR (400 MHz, DMSO) δ 8.38 (t, J = 7.9 Hz, 1H), 8.18 (t, J = 7.8 Hz, 1H), 7.79 (dd, J = 12.9, 7.9 Hz, 2H), 7.70 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 7.34 (dd, J = 5.3, 3.2 Hz, 2H), 2.68 (s, 3H), 2.66 (s, 3H), 1.29 (s, 9H); **^{13}C NMR (126 MHz, DMSO, 75 °C)** δ 206.3, 156.3, 156.1, 151.3, 150.9, 141.3, 139.7, 133.7, 128.5, 127.6, 127.1, 124.0, 123.2, 122.2, 122.1, 118.3, 109.1, 35.7, 29.3, 22.2, 21.7; **HRMS** (ESI) ($C_{25}H_{27}N_2{}^{194}Pt^{35}Cl_4$) $[M+H]^+$: cacld: 692.0727; found: 692.0707 $[M+H]^+$; **Anal.** Calcd. for $C_{28.5}H_{33}N_2PtCl_{11}$ (**4**$\cdot$3.5CH_2Cl_2): C 34.80, H 3.38, N 2.85; found: C 34.90, H 3.61; N 3.13.

Platinum(II) complex 5



5

To a solution of L-ascorbic acid (76 mg, 0.43 mmol, 10.0 equiv.) in water (0.9 ml) **4** (30 mg, 0.043 mmmol, 1.0 equiv.) was added. The suspension was stirred at 25 °C for 2h 15 min until the solid was completely dissolved and formed orange solution. Water was removed in *vacuo*, the residue was taken up in CH_2Cl_2. Undissolved white residue of ascorbic acid was filtered off. Yellow filtrate was concentred to afford **5** (24 mg, 89%) as a yellow-golden solid. Crystals suitable for X-Ray crystallography were obtained by vapour diffusion of the chloroform/methanol solution with cyclohexane.

^{1}H NMR (500 MHz, DMSO, 75 °C) δ 7.82 (t, J = 7.7 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.43 – 7.34 (m, 6H), 7.32 – 7.26 (m, 2H), 7.18 (d, J = 7.7 Hz, 1H), 2.53 (s, 3H), 2.51 (s, 3H), 1.36 (s, 9H); **^{13}C NMR (126 MHz, DMSO 75 °C)** δ 156.2, 133.9, 128.4, 127.5, 127.2, 121.9, 35.6, 29.3, peaks identified with HSQC experiment: 123.5, 122.8, 22.0; **HRMS** (ESI) ($C_{25}H_{26}N_2PtCl$) $[M-Cl]^+$: cacld: 585.1434; found: 585.1452 $[M-Cl]^+$; **Anal.** Calcd. for $C_{25.5}H_{30}N_2Cl_3O_{1.5}Pt$ (**5**$\cdot$1.5$H_2O\cdot$0.5CH_2Cl_2): C 44.47, H 4.39, N 4.07; found: C 44.26, H 4.61; N 3.72.

2.2. Attempts to derivatise gold(I) complex 2b''

2.2.a. HNTf$_2$ experiment

To a solution of **2b''** (18 mg, 0.031 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (0.5 ml) HNTf$_2$ (13 mg, 0.046, 1.5 eq.) was added at rt. After few minutes a black precipitate started to form. The starting material was consumed after 3 d of stirring at rt. The reaction mixture was filtered through Celite. The filtrate was washed twice with water and aqueous washings were then extracted back with more CH_2Cl_2 three times. Combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in *vacuo* to yield 8 mg of pink solid. This residue was taken up in CH_2Cl_2 and layered with Et_2O, but no precipitation was observed. Upon slow evaporation of solvents yellow crystalline solid started to appear. Crystals of good quality for X-Ray diffraction were isolated and analysed. The sample contained crystals of Au(III) analogue of starting material **3b''** and no protodemetalation products were identified.

2.2.b. Oxidation experiments

Prolonged reactions of **2b''** with oxidation agents such as MnO_2 (4.1 eq.), Dess-Martin periodinane (1.3 eq.) and pyridine N-oxide (1.3 eq.) in CH_2I_2 resulted in isolation of unreacted starting material with the exception of Dess-Martin reaction where traces of **3b''** were also isolated.

2.2.c. Iodination

Reaction of **2b''** with I_2 (2.1 eq.) in CH_2Cl_2 resulted in complete conversion of SM within 3.5h. Two products were isolated as seen on ^{1}H NMR, but unsuccessful attempts of their separation hindered the full characterisation.

Reaction of **2b''** with NIS (1.1 eq.) in CH_2Cl_2 resulted in complete conversion of SM within 6.5h, but analysis of the reaction mixture revealed decomposition of the material.

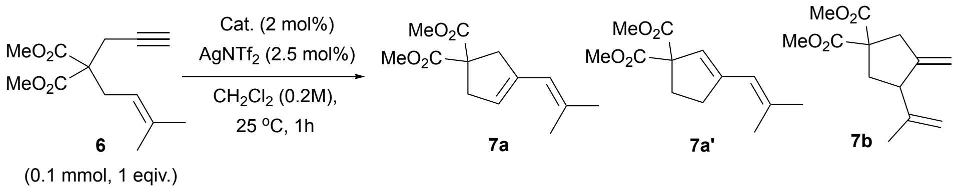
2.3. General procedure for metal-catalysed cyclisation of enynes 6, 8.

2 mol% of the catalyst and 2.5 mol% of $AgNTf_2$ were placed under N_2, 0.5 ml of CH_2Cl_2 was added. The mixture was stirred at 25 °C for 5 min. The corresponding enyne (0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 ml) was added; stirring continued for indicated amount of time. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was analysed by ^{1}H NMR to determine the ratio of isomeric products.

Tables S1 and S2 below, summarise the cycloisomerisation results with enynes **6** and **8**.

2.3.a. Results using enyne 6.

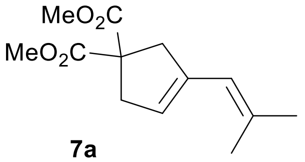
Table S1. Cycloisomerisation reaction of enyne **6**[a]



Entry	Catalyst	Conv. [%]	**7a**	**7a'**	**7b**	Y[%]
1	**2a**	>99	1.0	-	-	77
2	**2b**[b]	83	1.0	-	-	83[c]
3	**2b''**	>99	1.0	-	-	quant.[d]
4	**3a**	>99	0.6	1.0	-	79
5	**3b**[e]	>99	0.77	1.0	-	quant.
6	**5**	57	0.33	-	1.0	52

a. Catalysts (2 mol%), $AgNTf_2$ (2.5 mol%), **6** (0.1 mmol, 1 equiv.), DCM (0.2M). b. **2b** = **2b'**:**2b''** as 1:0.12 ratio. c. traces of hydroxycyclisation product d. Inseparable mixture 1(**7a**):0.09 of unidentified product. e. **3b** = **3b'**:**3b''** as 0.5:1 ratio.

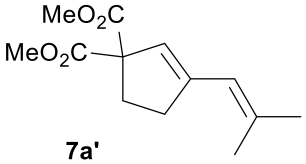
Diene 7a


7a

The characterisation data is in agreement with previously reported.[4]

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.72 (s, 1H), 5.37 (s, 1H), 3.72 (s, 6H), 3.18 (d, J = 1.7 Hz, 2H), 3.03 (s, 2H), 1.81 (s, 3H), 1.77 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.7, 138.8, 135.8, 124.5, 120.7, 59.4, 52.9, 43.4, 40.4, 27.4, 19.9.

Diene 7a'

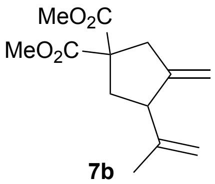

7a'

The characterisation data is in agreement with previously reported.[5]

In 1:0.6 mixture of **7a'**:**7a**.

^{1}H NMR (400 MHz, CDCl3) δ 5.80 (s, 1H), 5.59 (s, 1H), 3.72 (s, 6H), 2.65 (t, J = 6.5 Hz, 2H), 2.50 – 2.43 (m, 2H), 1.83 (s, 3H), 1.80 (s, 3H).

Diene 7b



7b

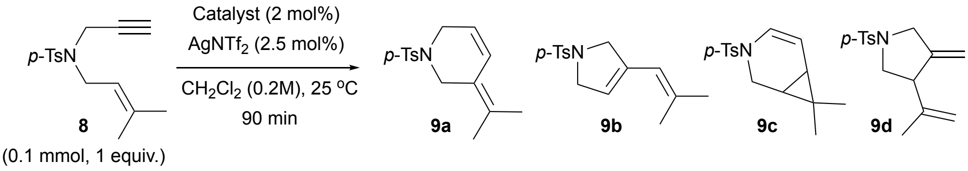
The characterisation data is in agreement with previously reported.[6]

In 1:0.33:1 mixture of **7b**:**7a**:**6**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.01 (d, *J* = 2.0 Hz, 1H), 4.83 (d, *J* = 1.1 Hz, 2H), 4.79 (dd, *J* = 4.4, 2.0 Hz, 1H), 3.73 (s, 6H), 3.31 – 3.23 (m, 1H), 3.04 (d, *J* = 1.5 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.52 (ddd, *J* = 13.0, 7.8, 1.5 Hz, 1H), 2.12 (dd, *J* = 13.0, 11.3 Hz, 1H), 1.64 (s, 3H).

2.3.b. Results with enyne 8.

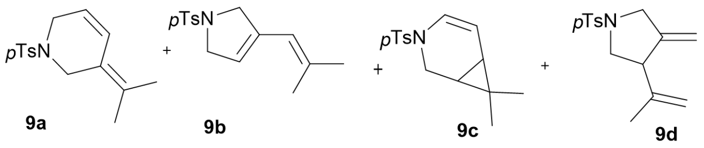
Table S2. Cycloisomerisation reaction of enyne **8**[a]



Entry	Catalyst	Conv. [%]	**9a**	**9b**	**9c**	**9d**	Y[%]
1	**2a**	>99	1.0	0.08	0.08	0.01	quant.
2	**2b**[b]	82	1.0	0.45	0.1	-	82
3	**2b’’**	>99	1.0	0.48	0.12	-	quant.
4	**3a**	77	1.0	0.55	0.11	0.06	77
5	**3b**[c]	94	1.0	0.35	0.03	0.03	80
6	**5**	48	0.14	0.07	0.4	1.0	46

a. Catalysts (2 mol%), AgNTf$_2$ (2.5 mol%), **8** (0.1 mmol, 1 equiv.), DCM (0.2M). b. **2b** = **2b’:2b’’** as 1:0.12 ratio. c. **3b** = **3b’:3b’’** as 0.5:1 ratio.

Dienes **9a**:**9b**:**9c**:**9d** 1:0.08:0.08:0.01



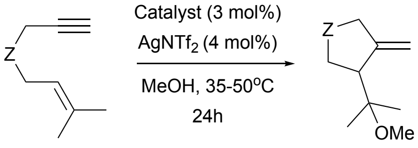
The characterisation data is in agreement with previously reported.[5,7,8]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.70 (m, 2H, *B*), 7.67 – 7.62 (m, 2H, *A*), 7.33 – 7.30 (m, 2H, *B*, *C*), 7.28 – 7.25 (m, 2H, *A*), 6.59 (d, *J* = 8.4 Hz, 1H, *C*), 6.34 (dt, *J* = 10.3, 2.1 Hz, 1H, *A*), 5.61 (s, 1H, *B*), 5.52 (dt, *J* = 10.3, 3.6 Hz, 1H, *A*), 5.38 (s, 1H, *B*), 5.06 (dd, *J* = 8.4, 4.8 Hz, 1H, *C*), 5.01 (d, *J* = 2.1 Hz, 1H, *D*), 4.87 – 4.85 (m, 1H, *D*), 4.84 – 4.82 (m, 1H, *D*), 4.80 (m, 1H, *D*), 4.23 (d, *J* = 2.7 Hz, 2H, *B*), 4.13 (s, 2H, *B*), 3.90 (s, 2H, *A*), 3.76 (s, 2H, *A*), 3.48 (dd, *J* = 12.2, 1.5 Hz, 1H, *C*), 3.36 (dd, *J* = 12.2, 6.0 Hz, 1H, *C*), 2.42 (s, 3H, *B*,*C*), 2.41 (s, 3H, *A*), 1.76 (s, 3H, *A*), 1.74 (s, 3H, *B*), 1.66 (s, 3H, *A*), 1.05 (s, 3H, *C*), 1.02 (d, *J* = 1.1 Hz, 1H, *C*), 0.97 (dd, *J* = 8.8, 4.8 Hz, 1H, *C*), 0.73 (s, 3H, *C*).

2.4. General procedure for metal-catalysed alkoxycylisation of enynes 6, 8.

3 mol% of the catalyst and 4 mol% of $AgNTf_2$ were placed under N_2, 0.5 ml of MeOH was added. The mixture was stirred at 35 °C for 5 min. The corresponding enyne (0.1 mmol, 1.0 equiv.) in MeOH (1.0 ml) was added; stirring at 35-50 °C continued for 24h. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was analysed by ^1H NMR to determine ratio of isomeric products.

Table S3. Alkoxycyclisation reaction of enynes **6** and **8**[a]



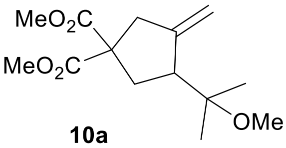
6 Z = $C(CO_2Me)_2$
8 Z = *p*-TsN

10a Z = $C(CO_2Me)_2$
11a Z = *p*-TsN

Entry	Enyne	Catalyst	Conv. [%]	Product	Y[%]
1	**6**	**2a**	>99	**10a**	quant.
2	**6**	**2b**[b]	>99	**10a**	quant.
3	**6**	**3a**	>99	**10a**	97[d]
4	**6**	**3b**[c]	91	**10a**	91
5	**6**	**5**	71	**10a**	71[e]
6	**8**	**2a**	94	**11a**	94
7	**8**	**2b**	54	**11a**	54
8	**8**	**3a**	22	**11a**	22
9	**8**	**3b**	18	**11a**	18
10	**8**	**5**	56	**11a**	56

a. Catalysts (3 mol%), $AgNTf_2$ (4 mol%), **6** or **8** (0.1 mmol, 1 equiv.), DCM (0.2M). b. **2b** = **2b’:2b’’** as 1:0.12 ratio. c. **3b** = **3b’:3b’’** as 0.5:1 ratio. d. 0.08 of **7a**. e.0.2 of hydroxycyclisation product.

10a

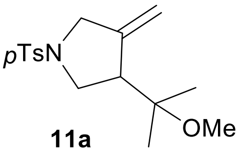


10a

The characterisation data is in agreement with previously reported.[9]

^{1}H NMR (400 MHz, CDCl3) δ 5.04 – 5.01 (m, 1H), 4.98 – 4.95 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.18 (s, 3H), 2.93 – 2.80 (m, 3H), 2.54 (ddd, J = 13.5, 8.5, 1.7 Hz, 1H), 2.00 (dd, J = 13.5, 9.3 Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.2, 172.1, 148.3, 110.7, 76.9, 58.7, 52.9, 52.8, 49.2, 49.1, 43.5, 36.1, 22.8, 22.3.

11a



11a

In 1:0.8 mixture of **11a**:**8**.
The characterisation data is in agreement with previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 2H), 3.77 (s, 2H), 3.39 (dd, *J* = 10.1, 4.4 Hz, 1H), 3.26 (m, 1H), 3.09 (s, 3H), 2.82 – 2.76 (m, 1H), 2.42 (s, 3H), 1.11 (s, 3H), 1.00 (s, 3H).

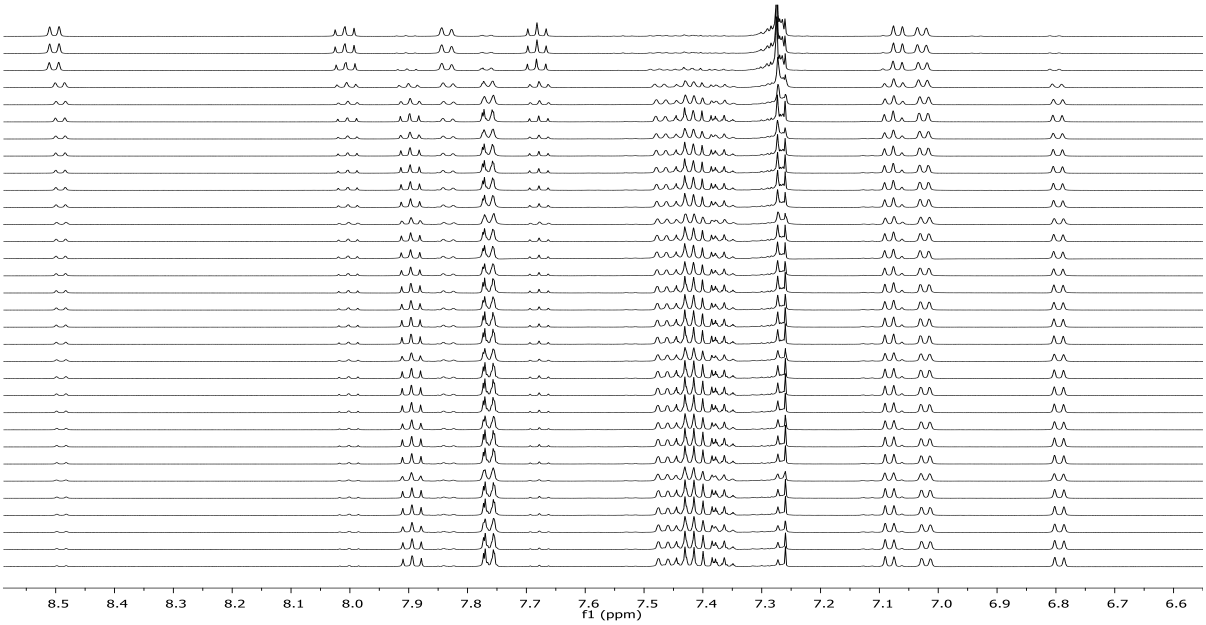
3. Isomerisation of complexes 2b' and 2b'' - Kinetic experiments

3.1. Isomerisation of 2b' and 2b''

A sample of **2b** in $CDCl_3$ of initial concentration of 0.067M and ratio 1:0.12 **2b'**/**2b''** was submitted to a series of ^{1}H NMR experiments at 10 min intervals until 2 h, then 30 min intervals until 6 h, then every hour until 10 h. Th last two points were recorded at 48 and 77 h. The ratio of both species in solution was determined by comparison of integration of signals at 6.79 ppm (**2b'**) and at 8.49 ppm (**2b''**). The corresponding concentrations of **2b'**/**2b''** are plotted vs. time till the total disappearance of the **2b'** isomer.

Fig S1. ^{1}H NMR spectra of the isomerisation reaction of **2b'** to **2b''** in $CDCl_3$ at rt. Time = 0 (bottom) to time = 4630 min (top).

a) Expansion of region from 6 to 9 ppm



b) Expansion of region from 1 to 3 ppm

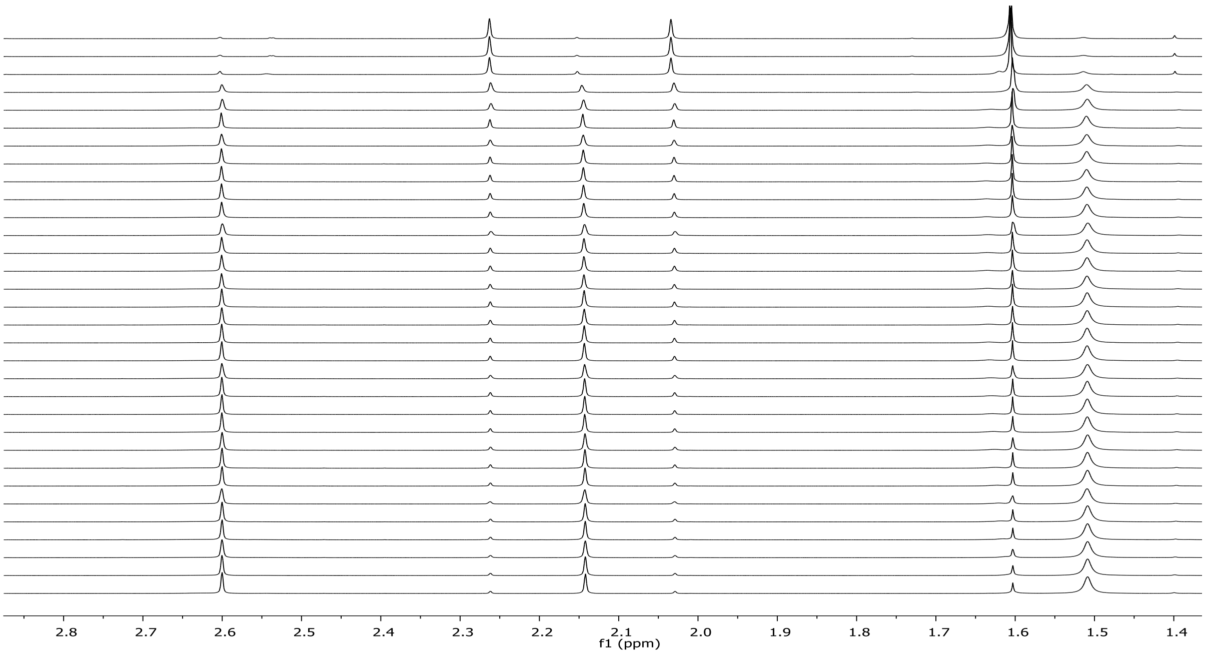


Fig S2. Graph showing [**2b'** and **2b''**] (M) versus time (min)

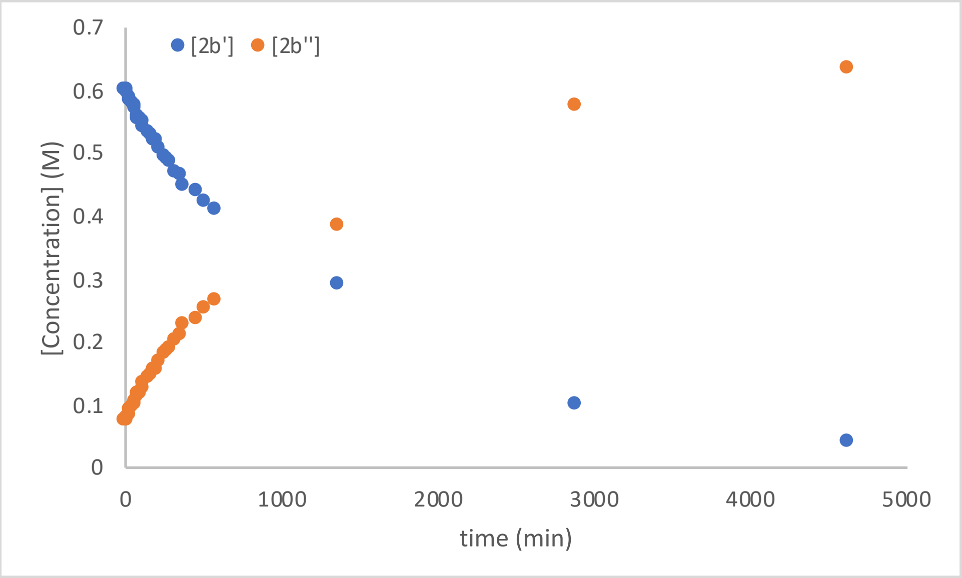
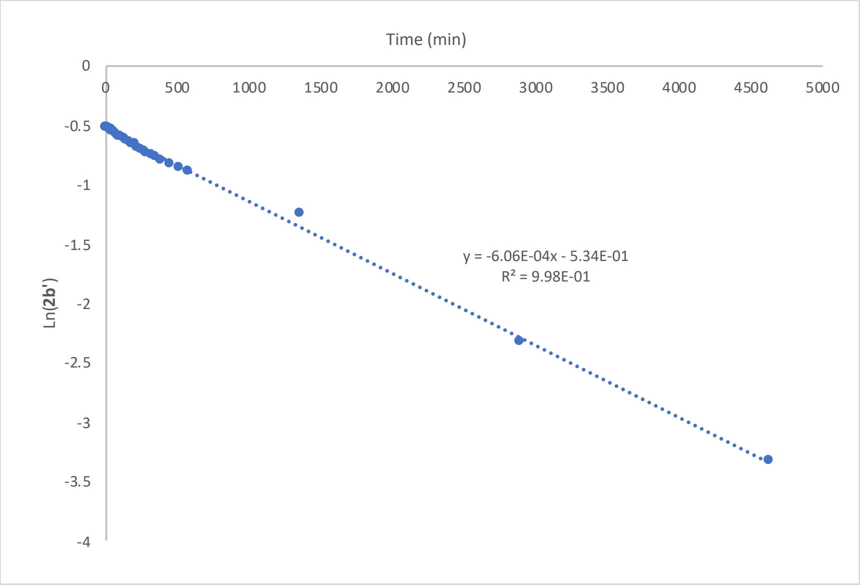


Fig. S3. First order decay of **2b'** and rate constant for the isomerisation.

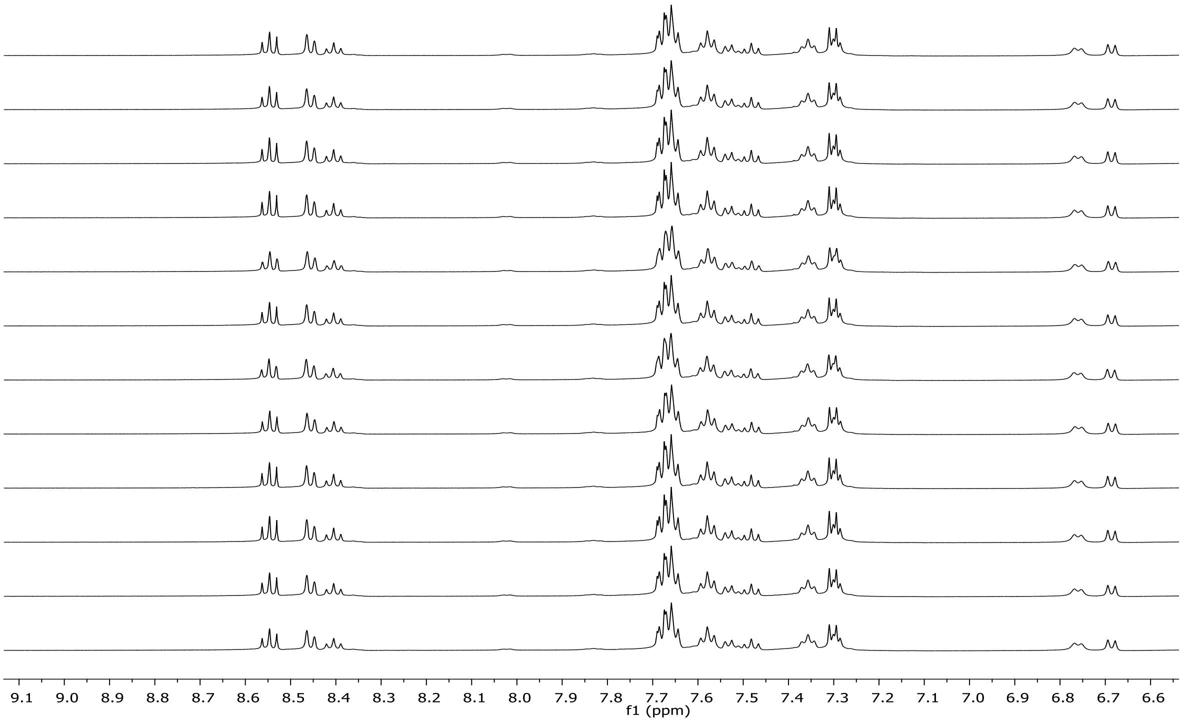


3.2. Monitoring of 3b' and 3b'' over time

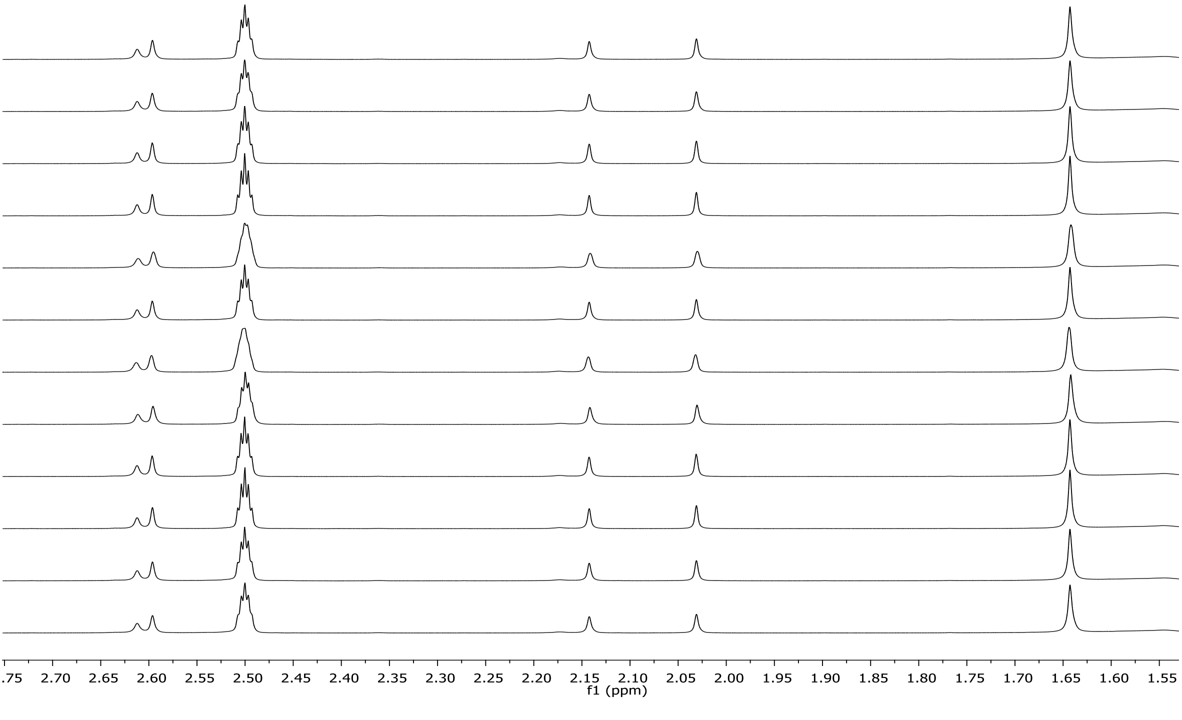
A sample of **3b** in DMSO-d$_6$ of initial ratio 0.75:1 **3b'**/**3b''** was submitted to the series of 12 ^{1}H NMR experiments with 1h interval. The ratio of both species in the solution was determined by comparison of integration of signals at 6.76 ppm (**3b''**) and at 6.69 ppm (**3b'**). Observed ratio of the two species did not change in the timescale of the experiment.

Fig S4. ^{1}H NMR spectra of the isomerisation reaction of **3b'** to **3b''** in DMSO-d$_6$ at rt over 12 h.

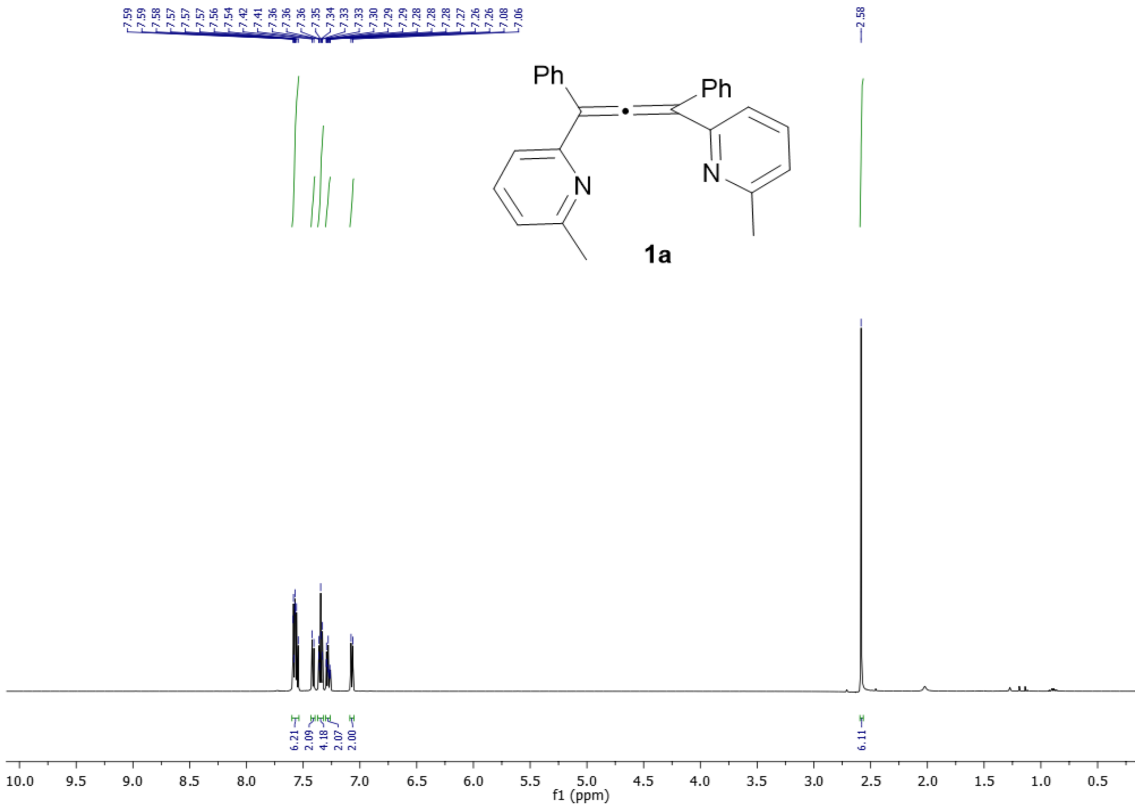
a) Expansion of region from 6 to 9 ppm

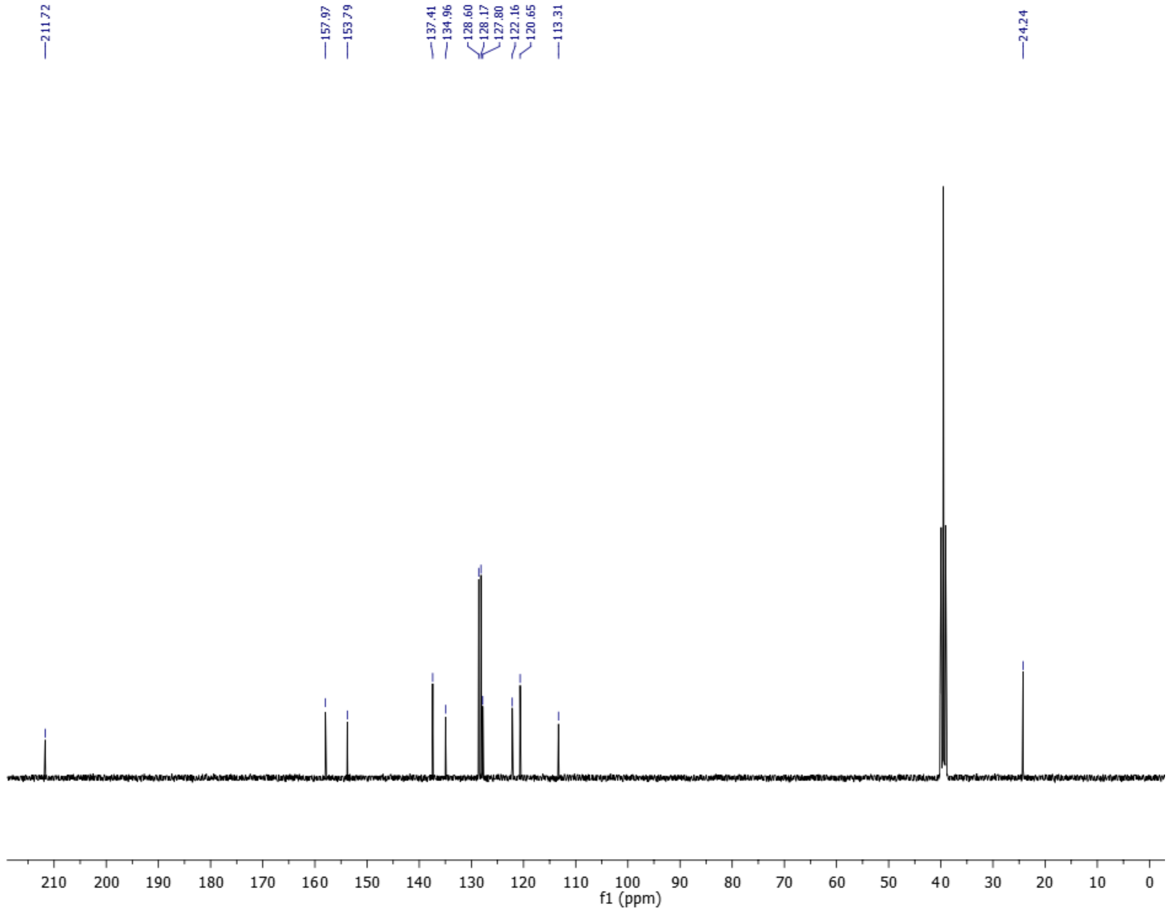


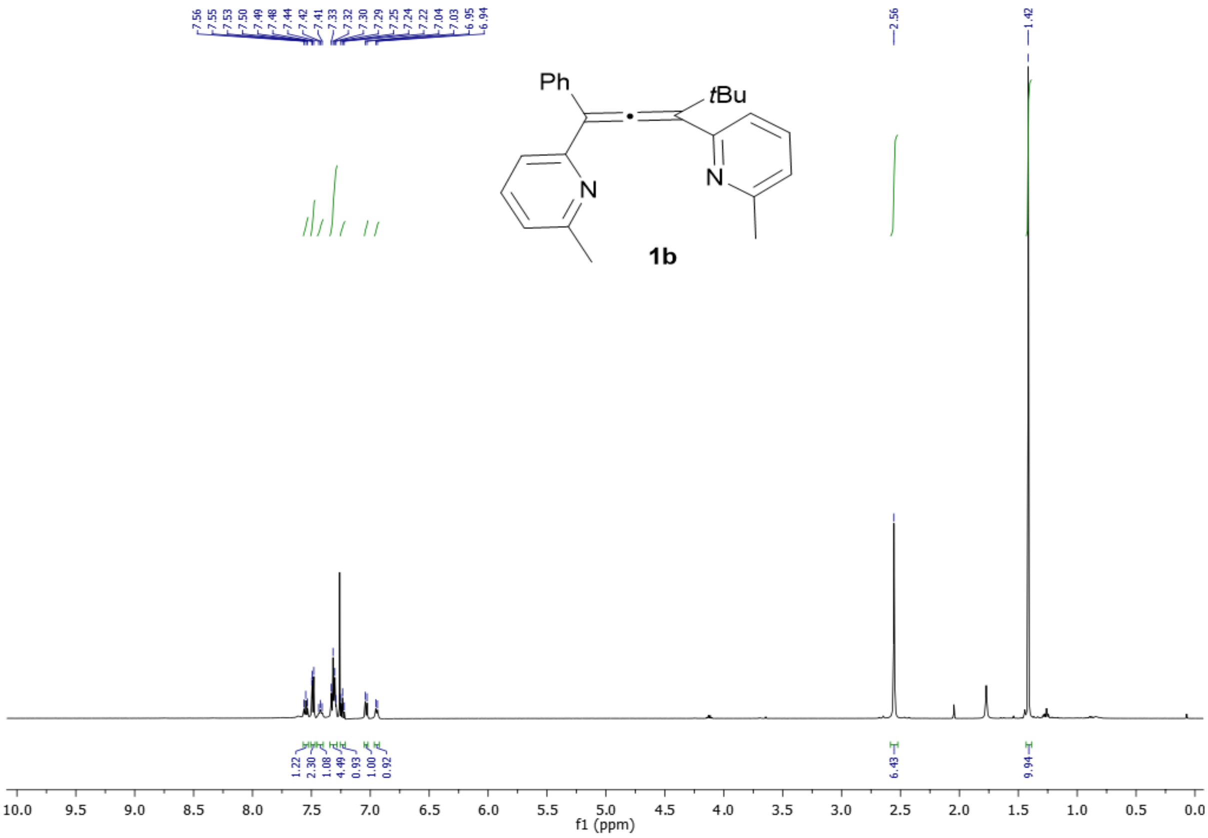
b) Expansion of region from 1 to 3 ppm



4. Spectral data


1a

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7.41
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7.29
7.25
7.24
7.22
7.04
7.03
6.95
6.94
2.56
1.42
Ph
tBu
N
N
1b
1.22
2.30
1.08
4.49
0.93
1.00
0.92
6.43
9.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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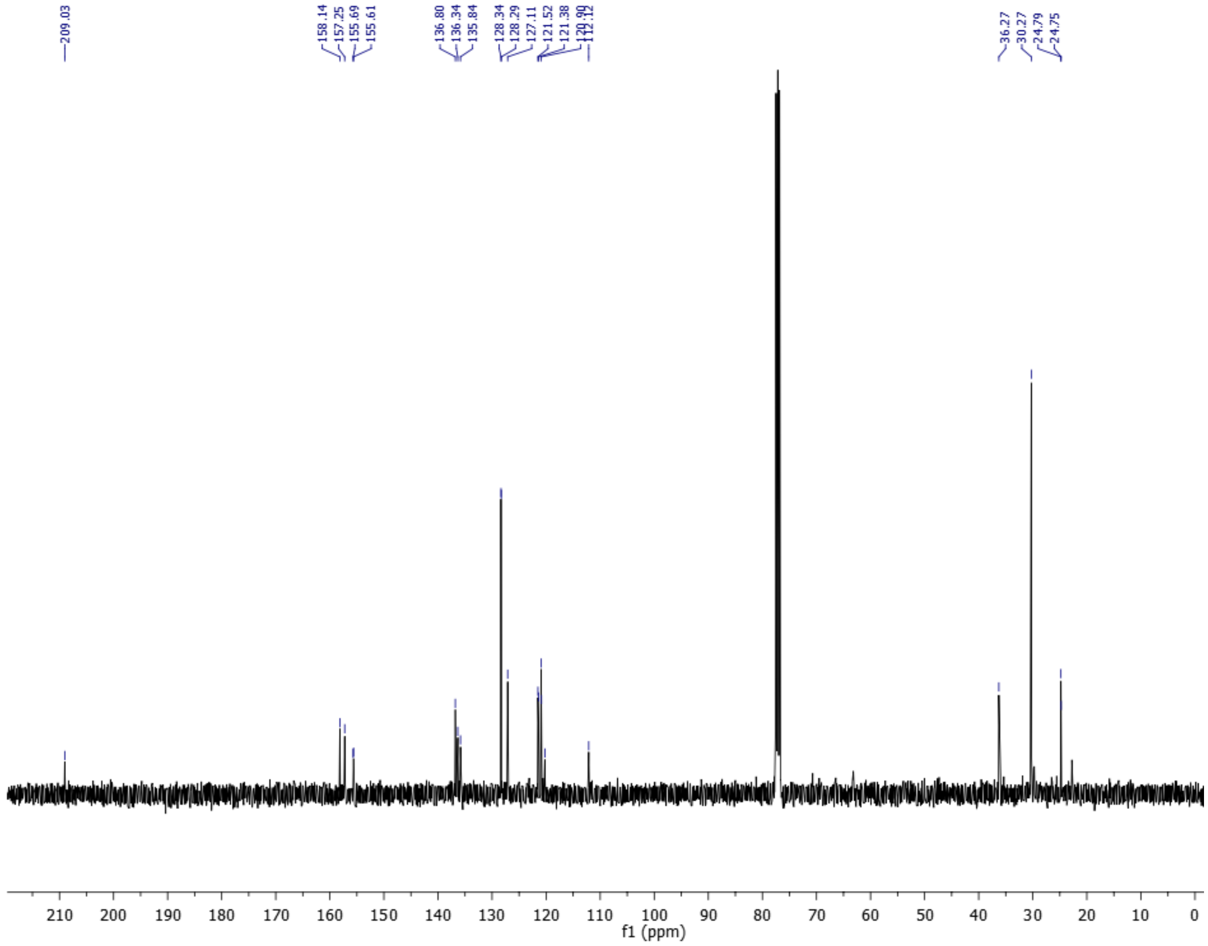
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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155.61
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136.34
135.84
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127.11
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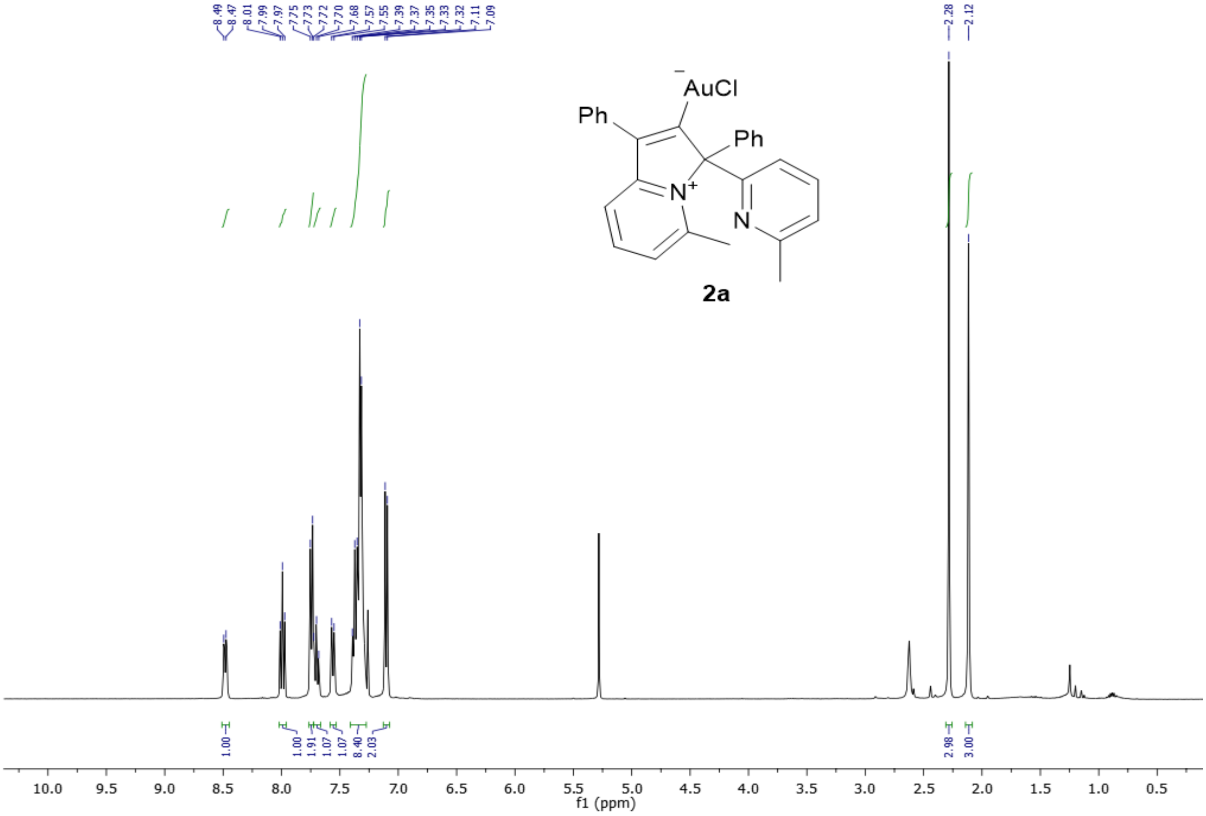
121.38
120.90
112.12
36.27
30.27
24.79
24.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.47
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7.72
7.70
7.68
7.57
7.55
7.39
7.37
7.35
7.33
7.32
7.11
7.09
2.28
2.12
AuCl
Ph
Ph
N+
N
2a
1.00
1.00
1.91
1.07
1.07
8.40
2.03
2.98
3.00
10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
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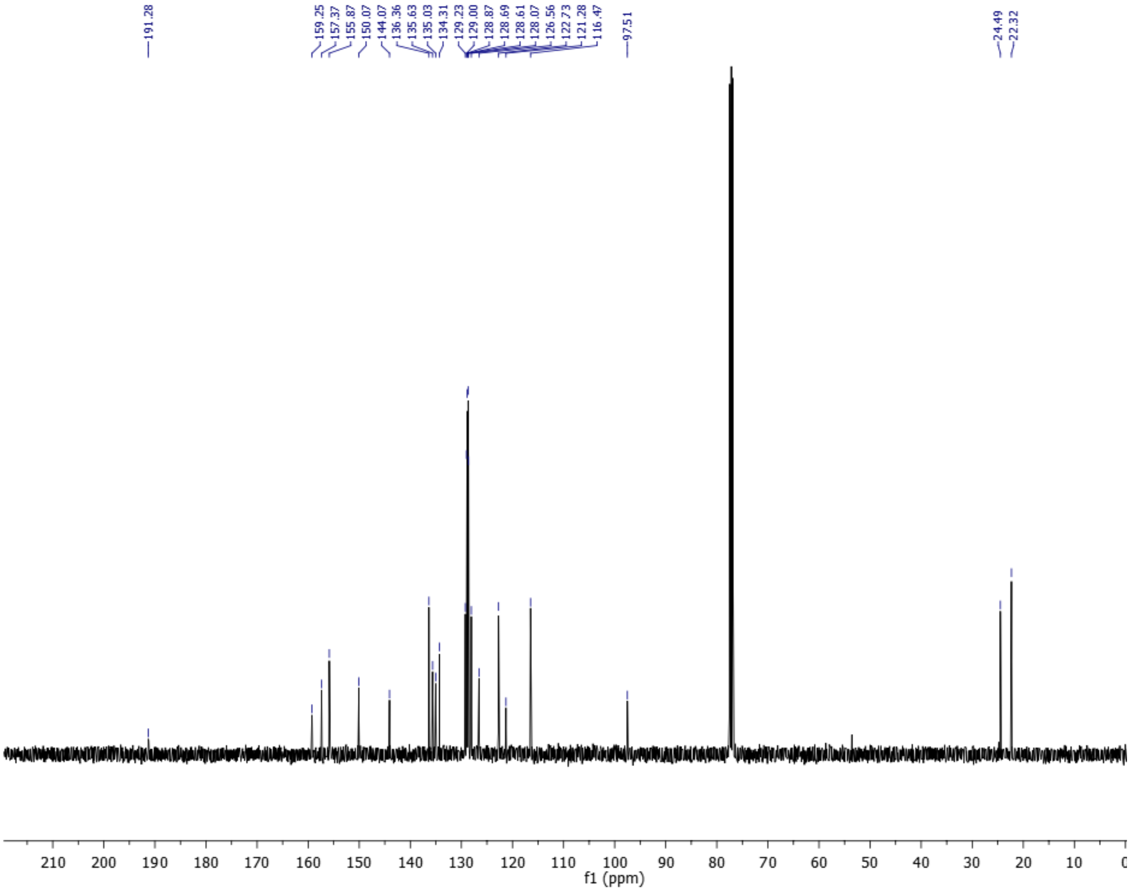
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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144.07
136.36
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128.87
128.69
128.61
128.07
126.56
122.73
121.28
116.47
97.51
24.49
22.32
210
200
190
180
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150
140
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120
110
100
90
80
70
60
50
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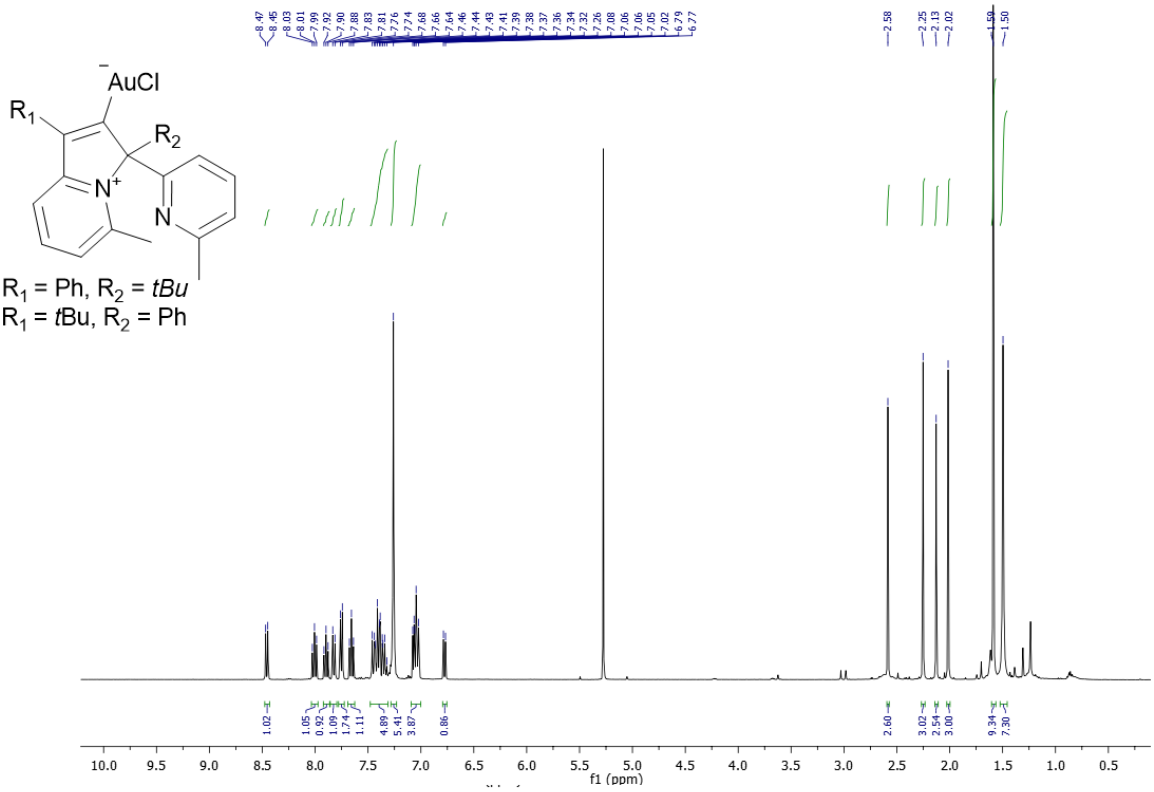
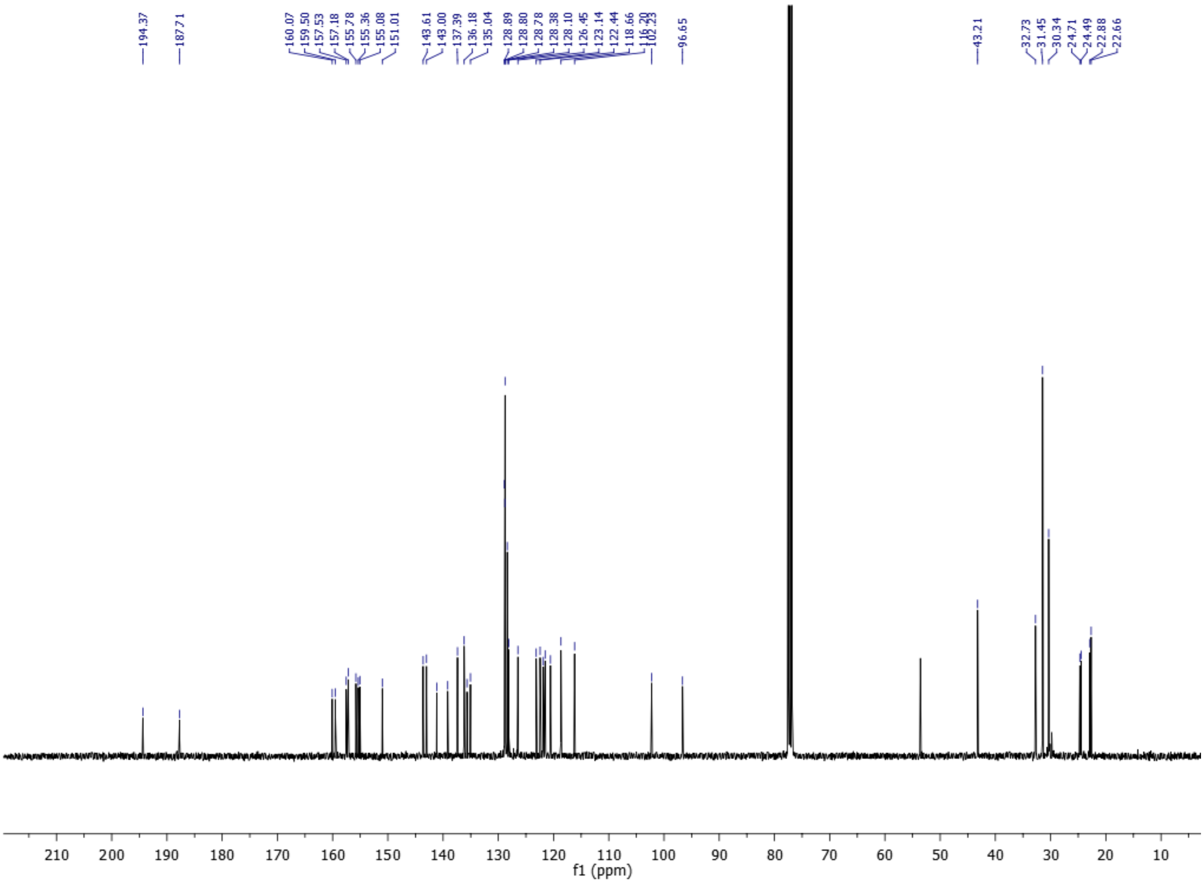
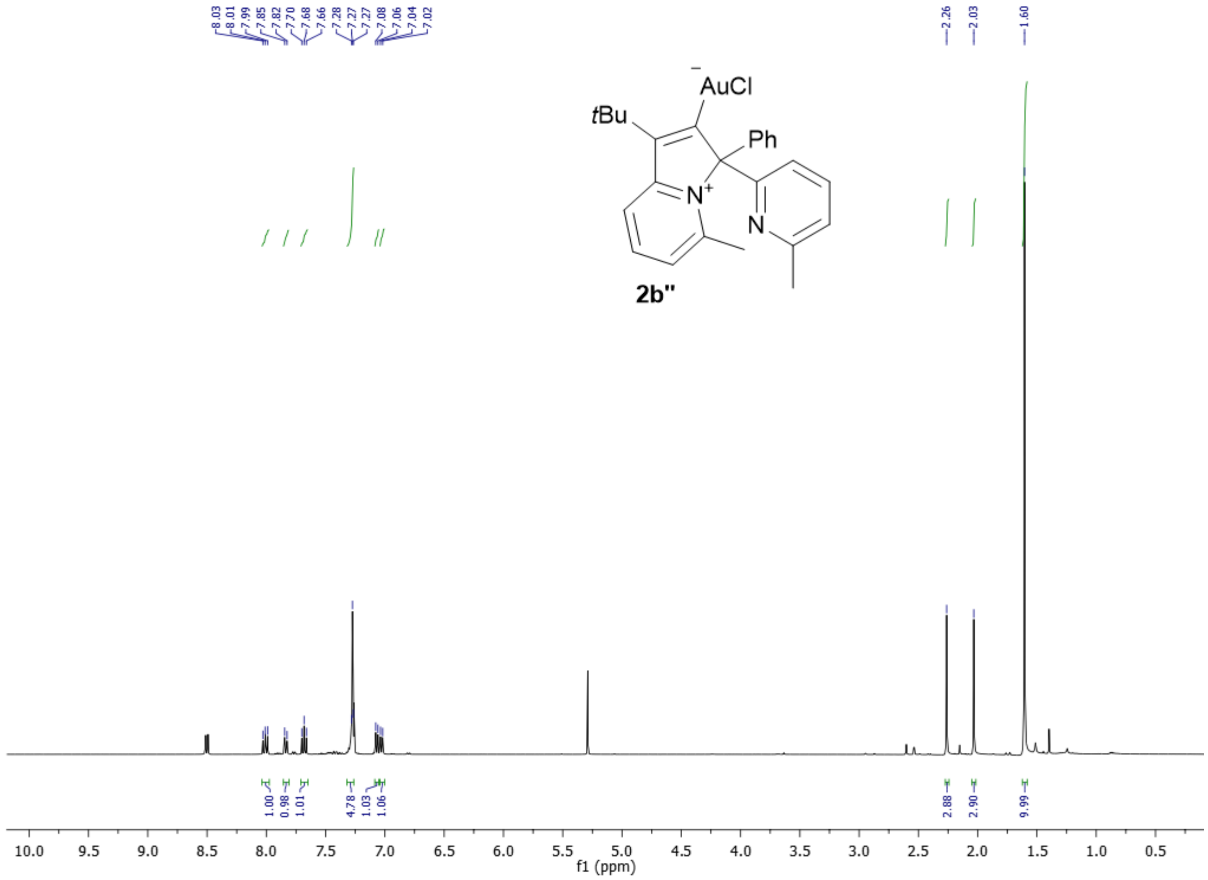
30
20
10
0
f1 (ppm)



2b' R_1 = Ph, R_2 = *tBu*
2b'' R_1 = *t*Bu, R_2 = Ph

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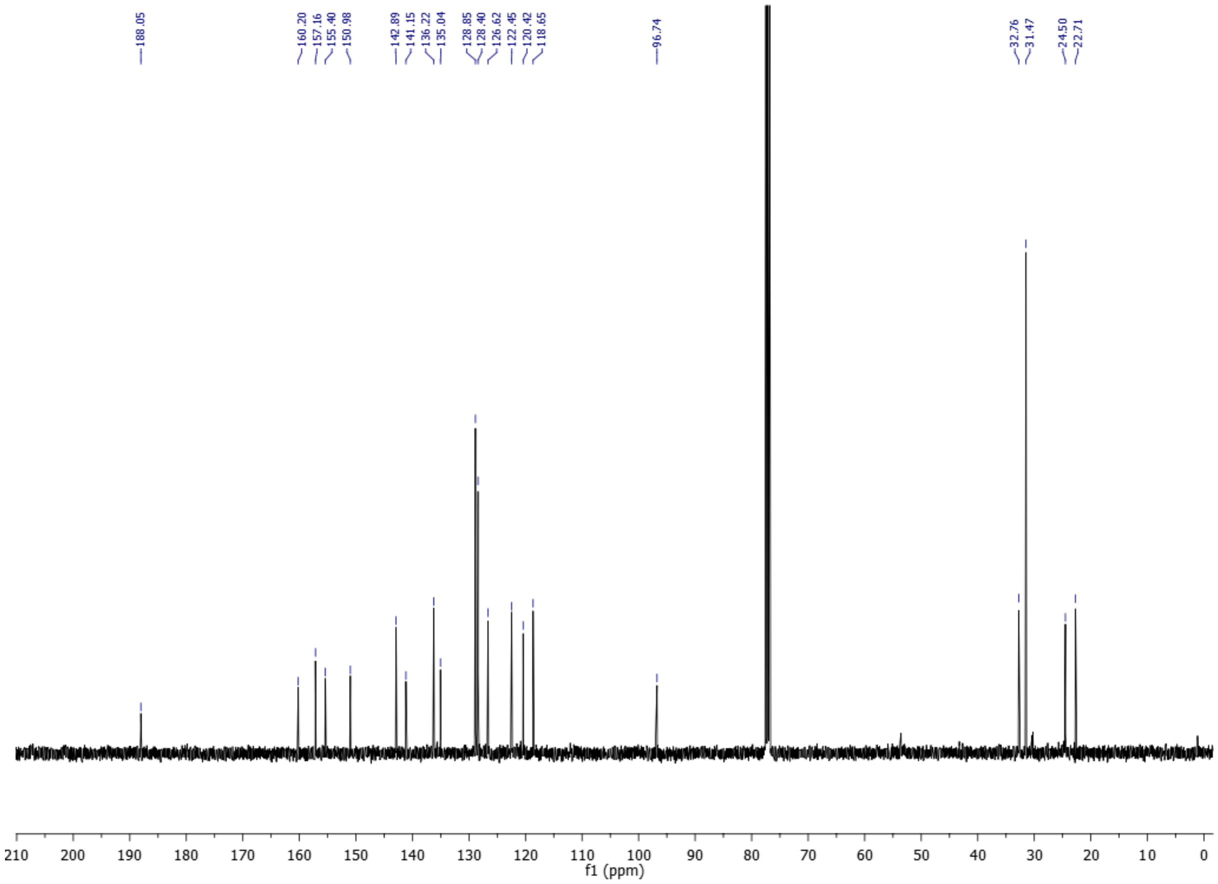
7.27
7.08
7.06
7.04
7.02
2.26
2.03
1.60
AuCl
tBu
Ph
N+
N
1.00
0.98
1.01
4.78
1.03
1.06
2.88
2.90
9.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

2b''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136.22
135.04
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120.42
118.65
96.74
32.76
31.47
24.50
22.71
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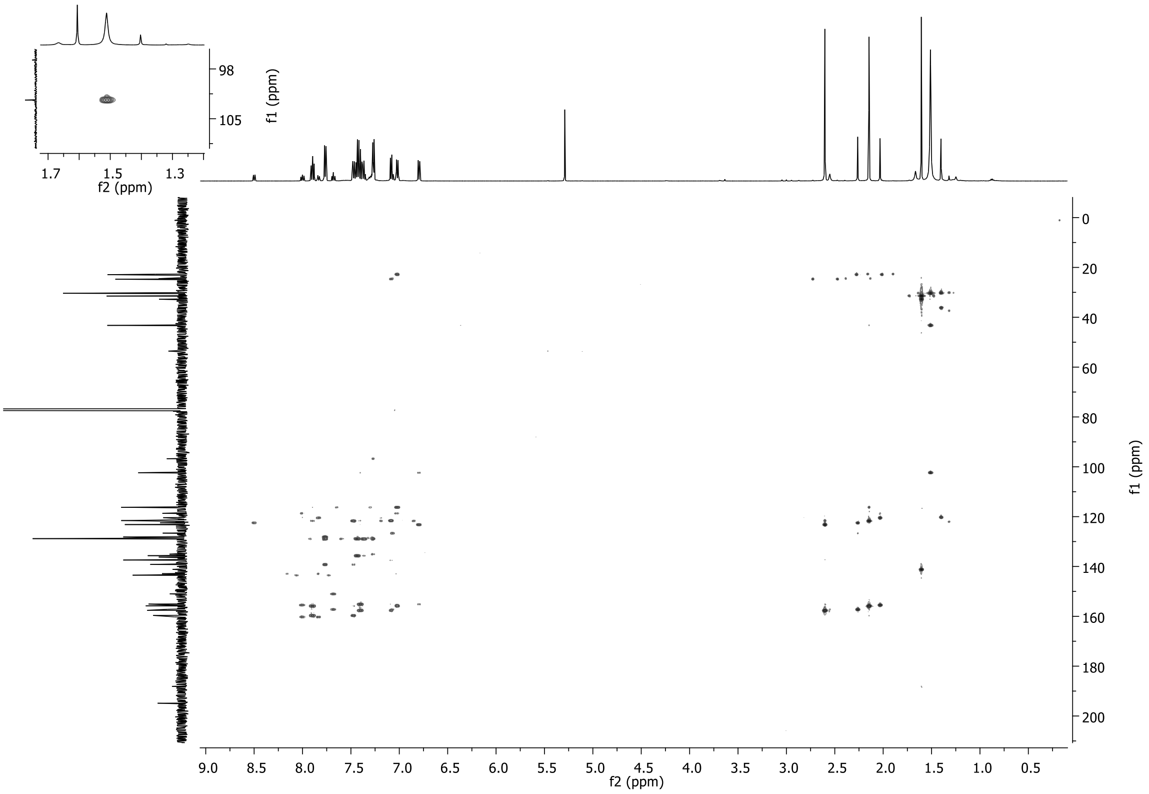
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

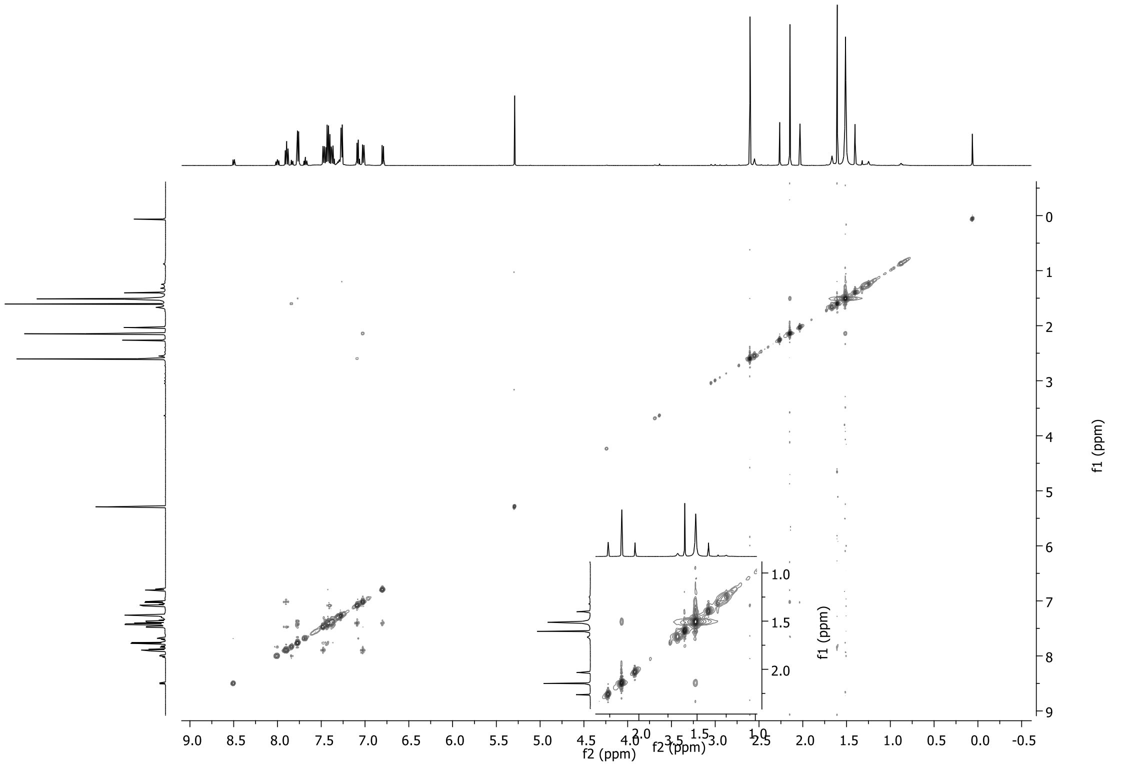
SUPPLEMENTARY INFORMATION

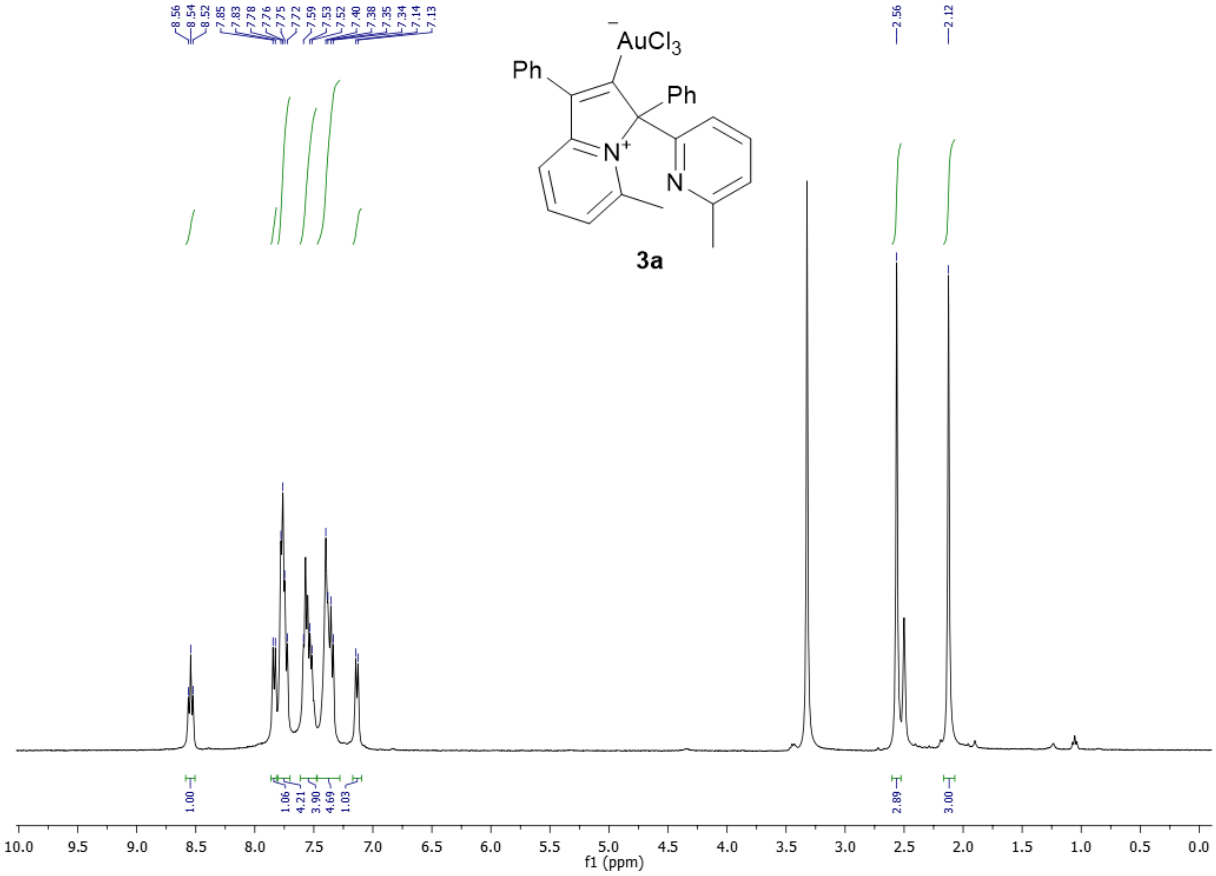
2D NMRs of 2b at 1:0.3 2b':2b'':

HMBC



NOESY

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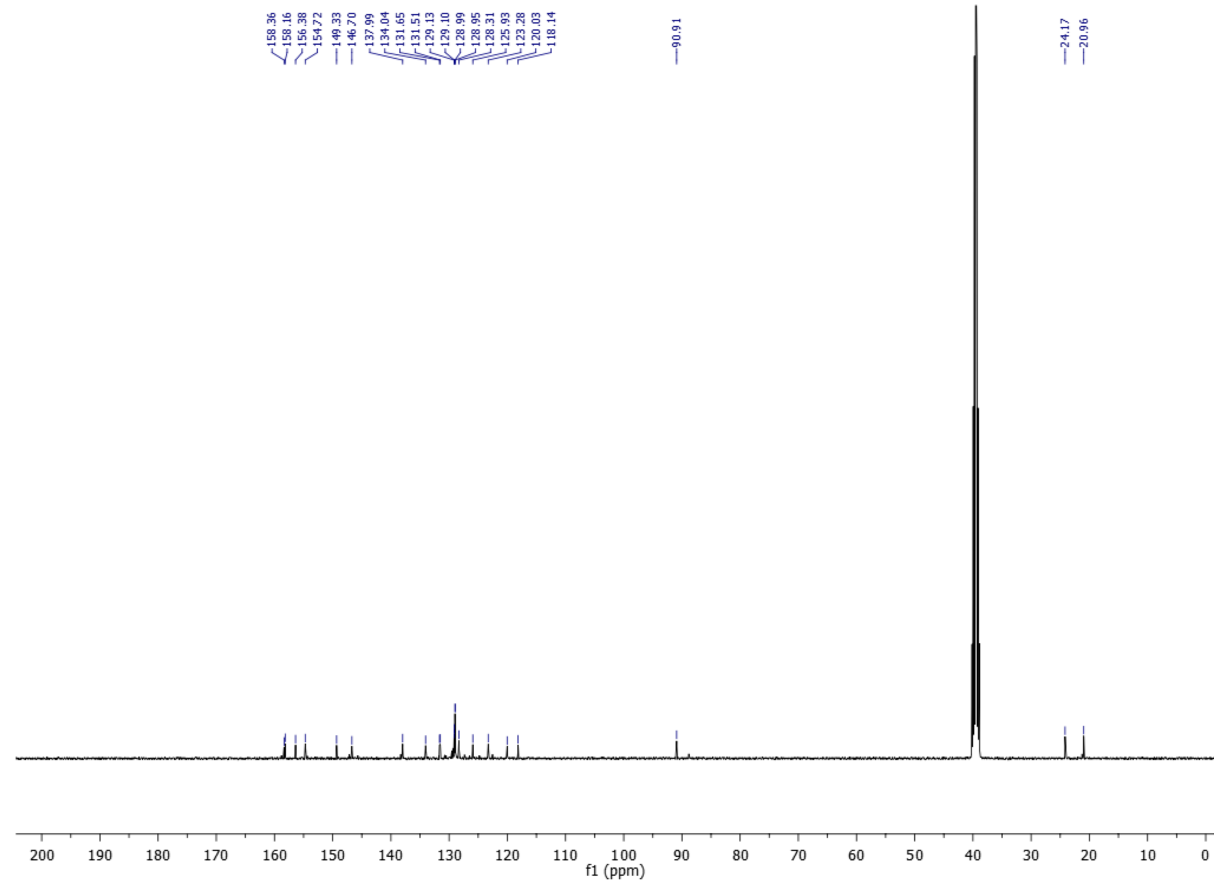
7.40
7.38
7.35
7.34
7.14
7.13
2.56
2.12
AuCl$_3$
Ph
Ph
N$^+$
N
1.00
1.06
4.21
3.90
4.69
1.03
2.89
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3a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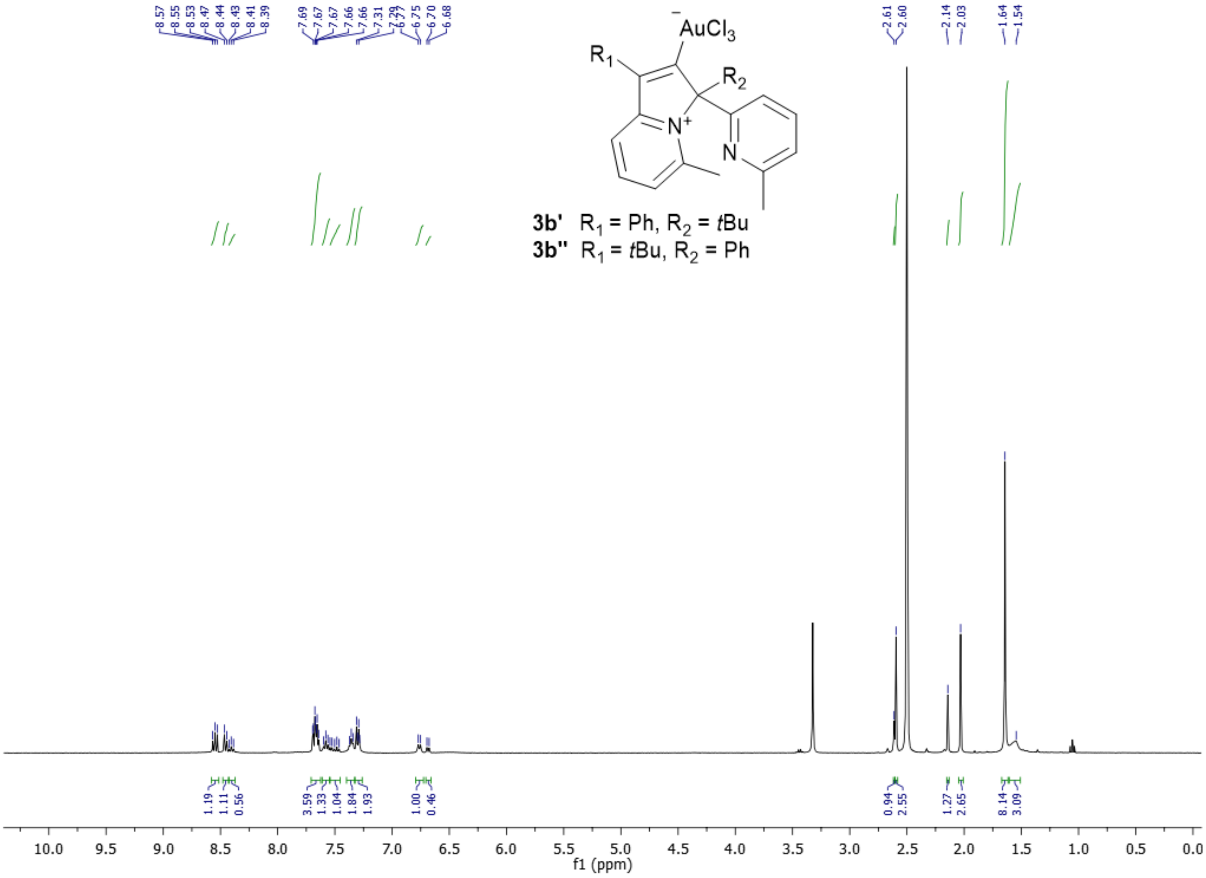
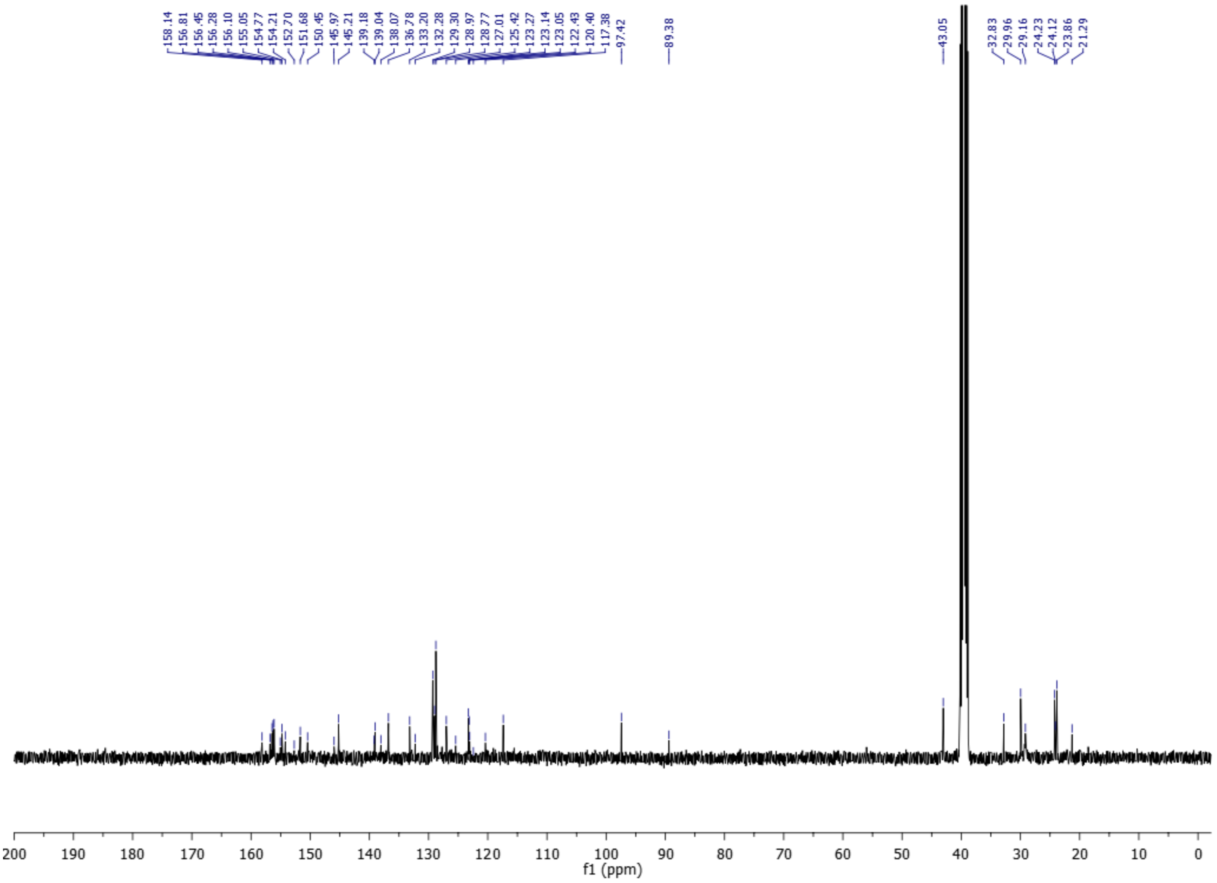
90.91
24.17
20.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

SUPPLEMENTARY INFORMATION



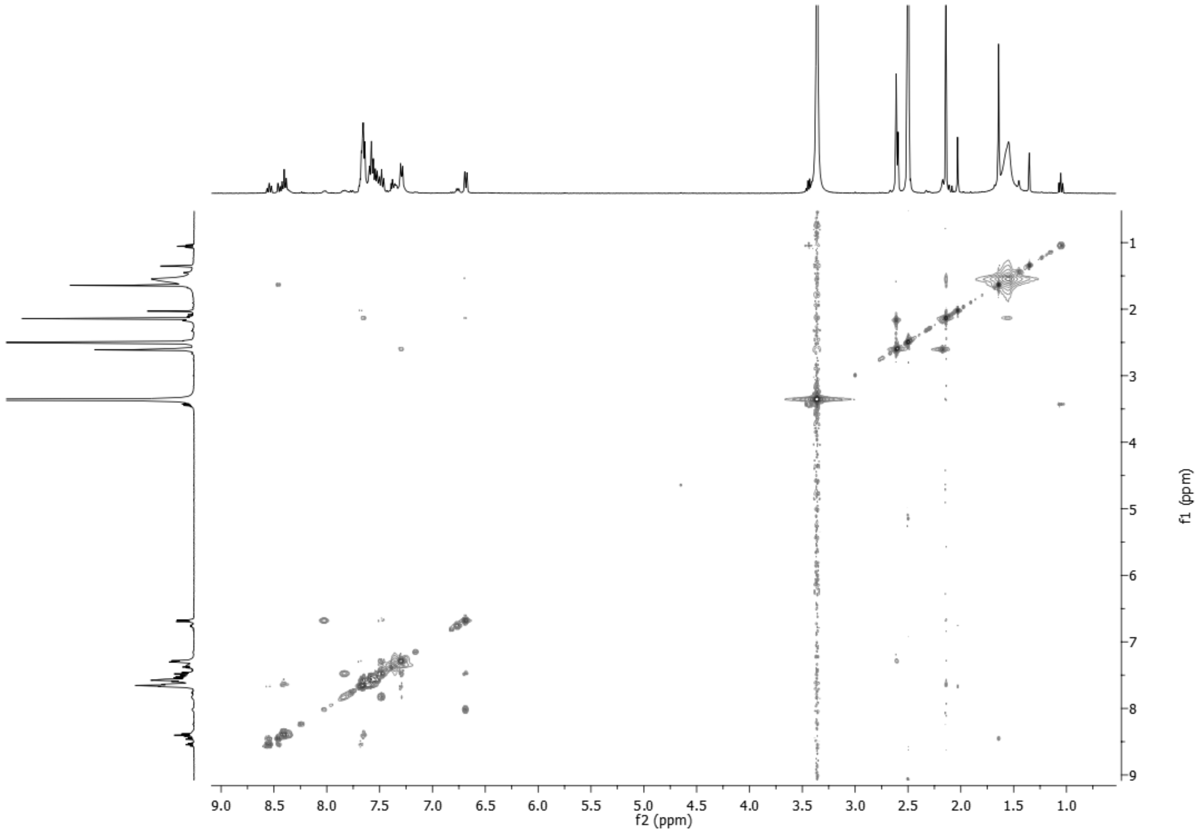
3b' R_1 = Ph, R_2 = *t*Bu
3b'' R_1 = *t*Bu, R_2 = Ph

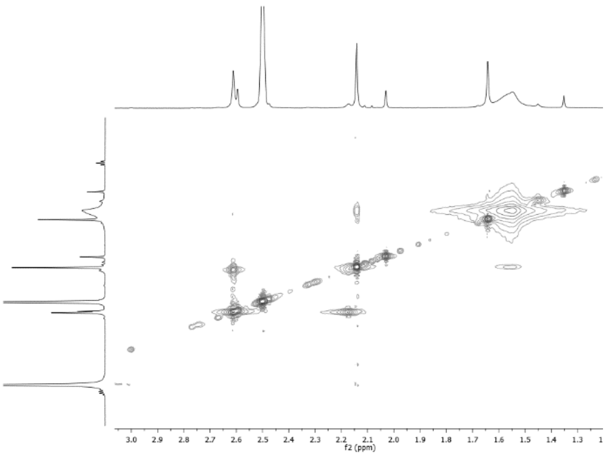


SUPPLEMENTARY INFORMATION

2D NMRs of 3b at 1:0.4 ratio of isomers:

NOESY

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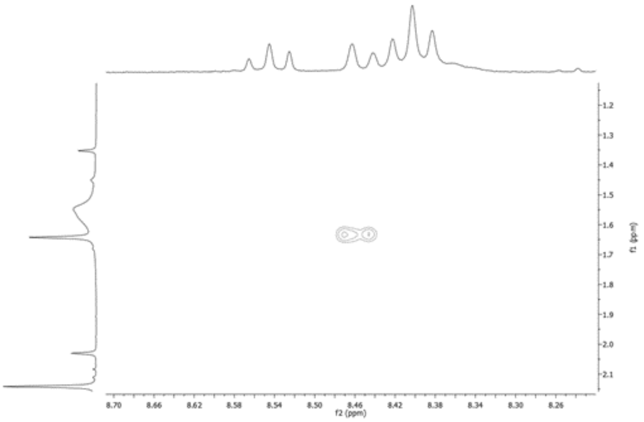
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1
f2 (ppm)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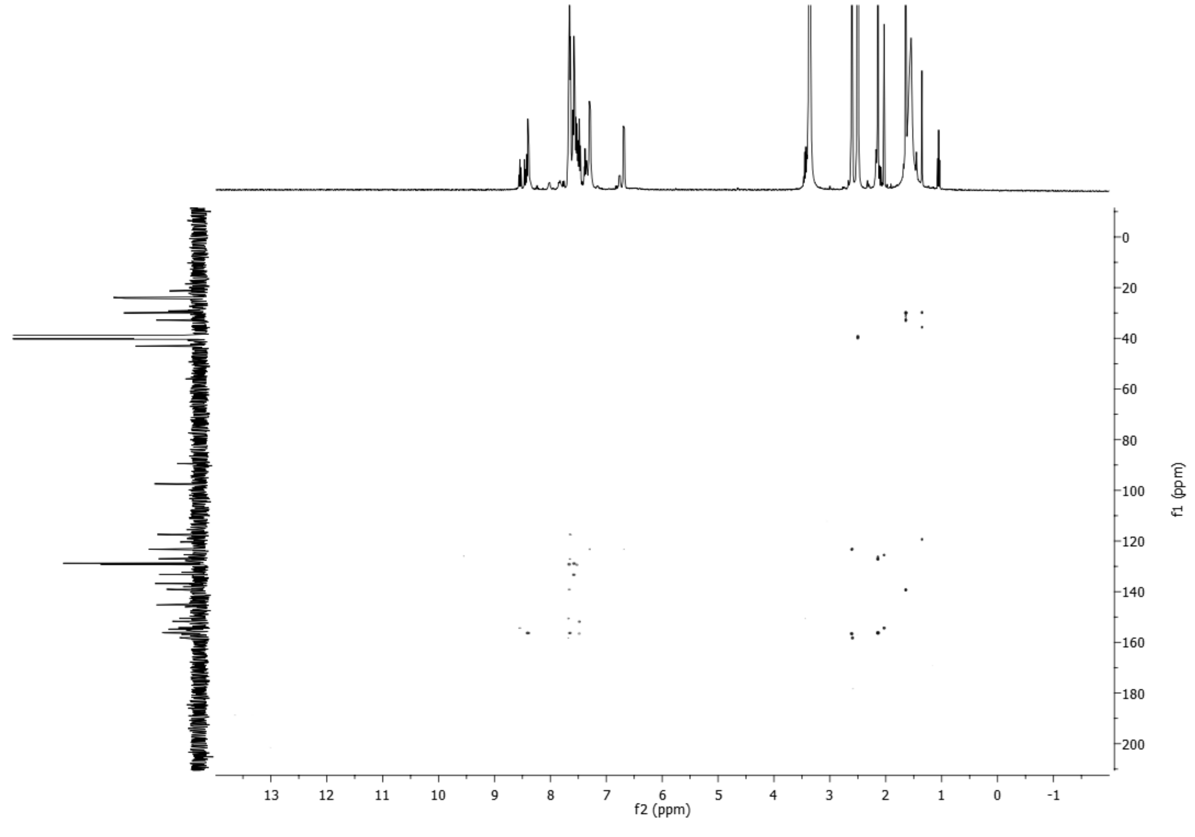
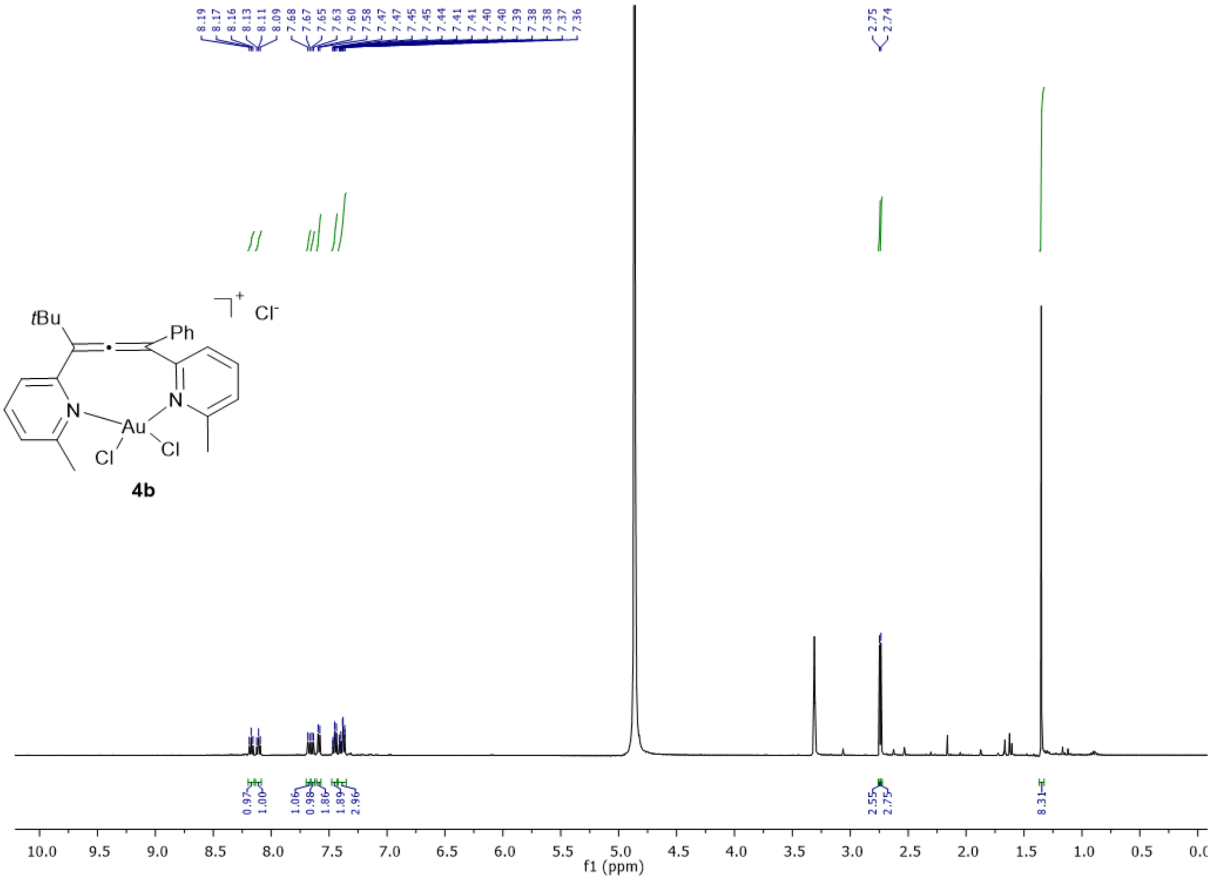
8.66
8.62
8.58
8.54
8.50
8.46
8.42
8.38
8.34
8.30
8.26
f2 (ppm)
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
f1 (ppm)

HMBC


0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f2 (ppm)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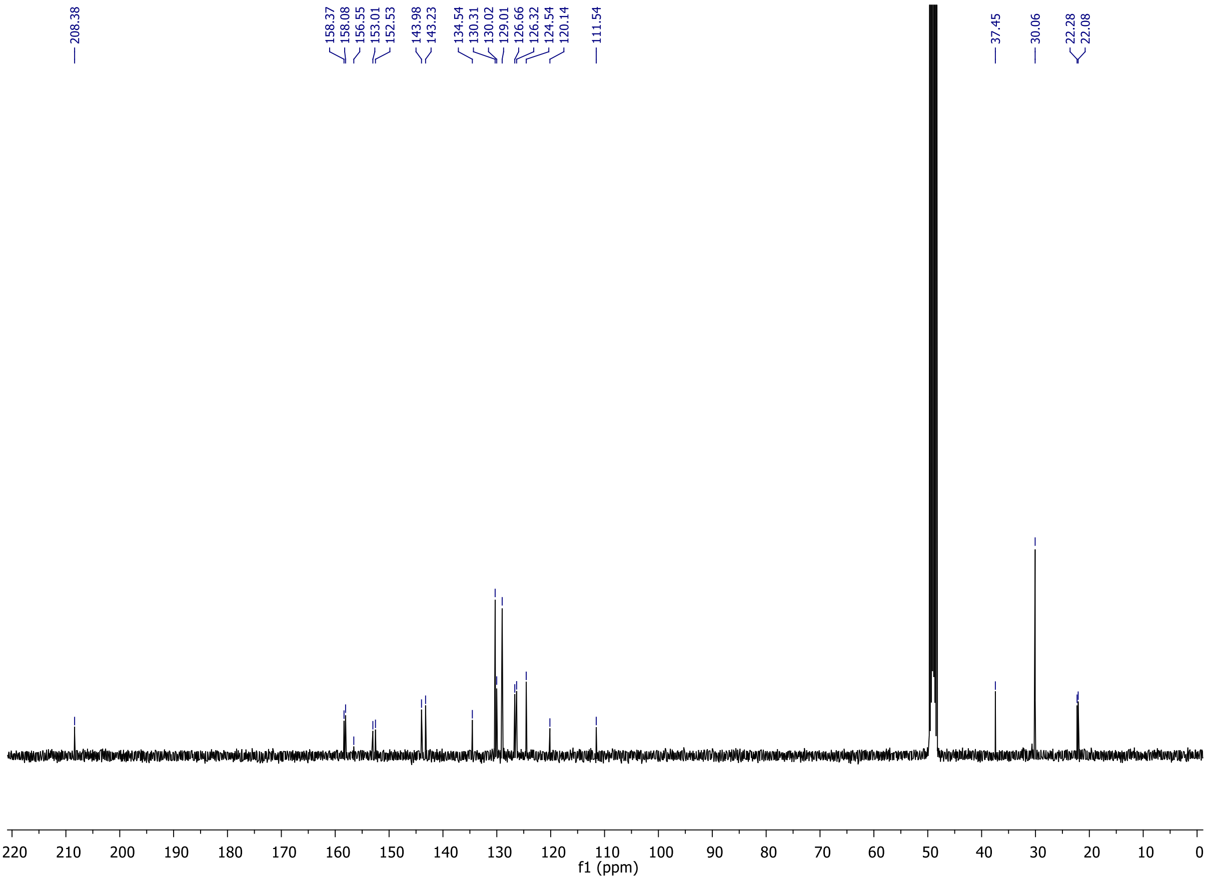
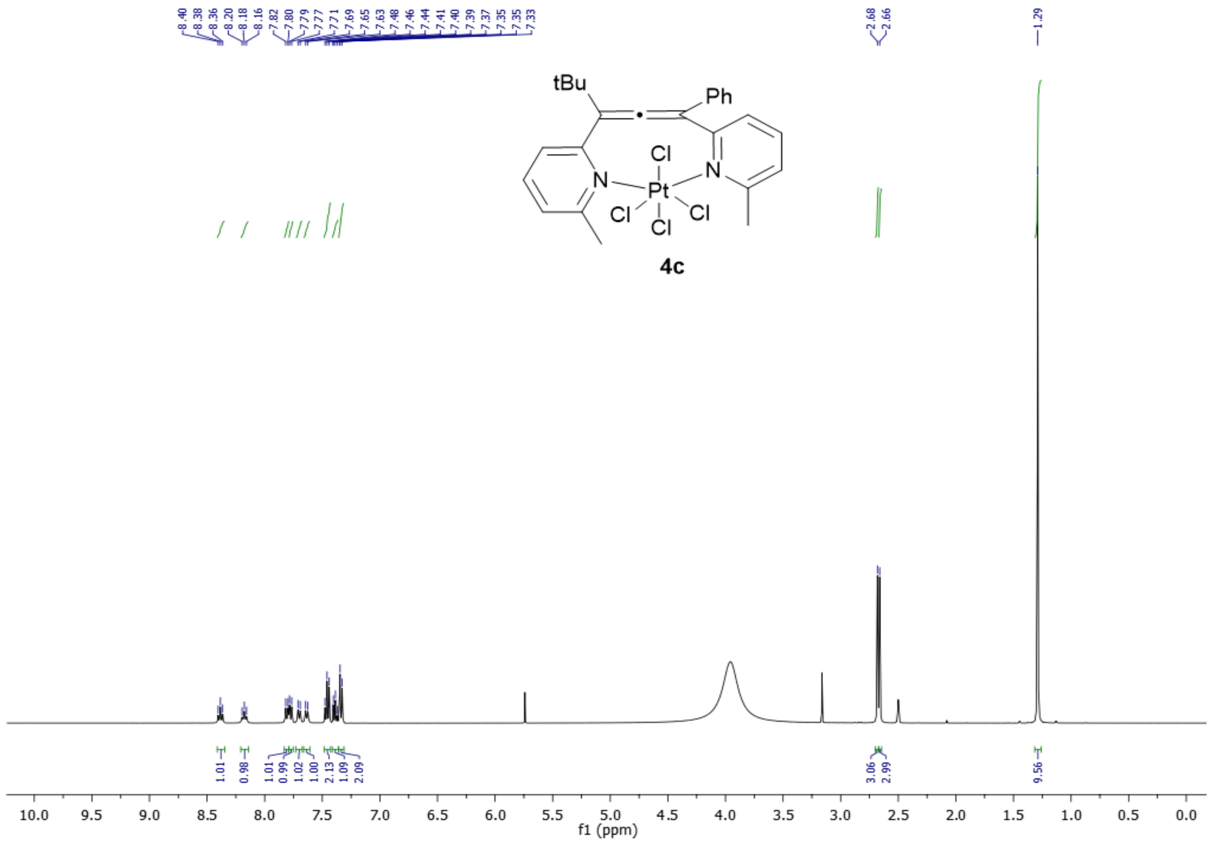
8.13
8.11
8.09
7.68
7.67
7.65
7.63
7.60
7.58
7.47
7.47
7.45
7.45
7.44
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
2.75
2.74
tBu
Ph
Cl⁻
N
N
Au
Cl
Cl
4b
0.97
1.00
1.06
0.98
1.86
1.89
2.96
2.55
2.75
8.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)


208.38
158.37
158.08
156.55
153.01
152.53
143.98
143.23
134.54
130.31
130.02
129.01
126.66
126.32
124.54
120.14
111.54
37.45
30.06
22.28
22.08
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.36
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7.80
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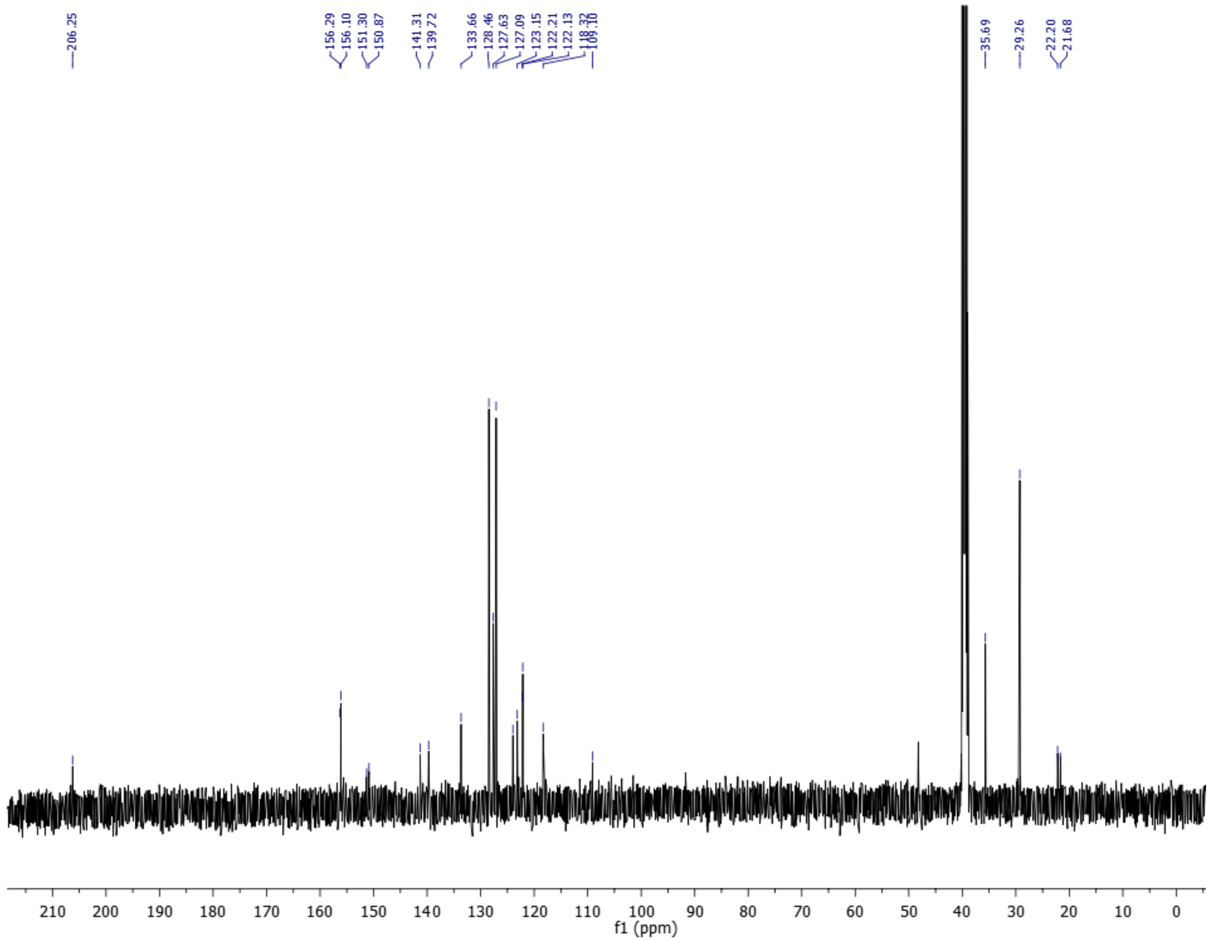
7.65
7.63
7.48
7.46
7.44
7.41
7.40
7.39
7.37
7.35
7.35
7.33
2.68
2.66
1.29
tBu
Ph
Cl
Pt
N
Cl
Cl
Cl
N
4c
1.01
0.98
1.01
0.99
1.02
1.00
2.13
1.09
2.09
3.06
2.99
9.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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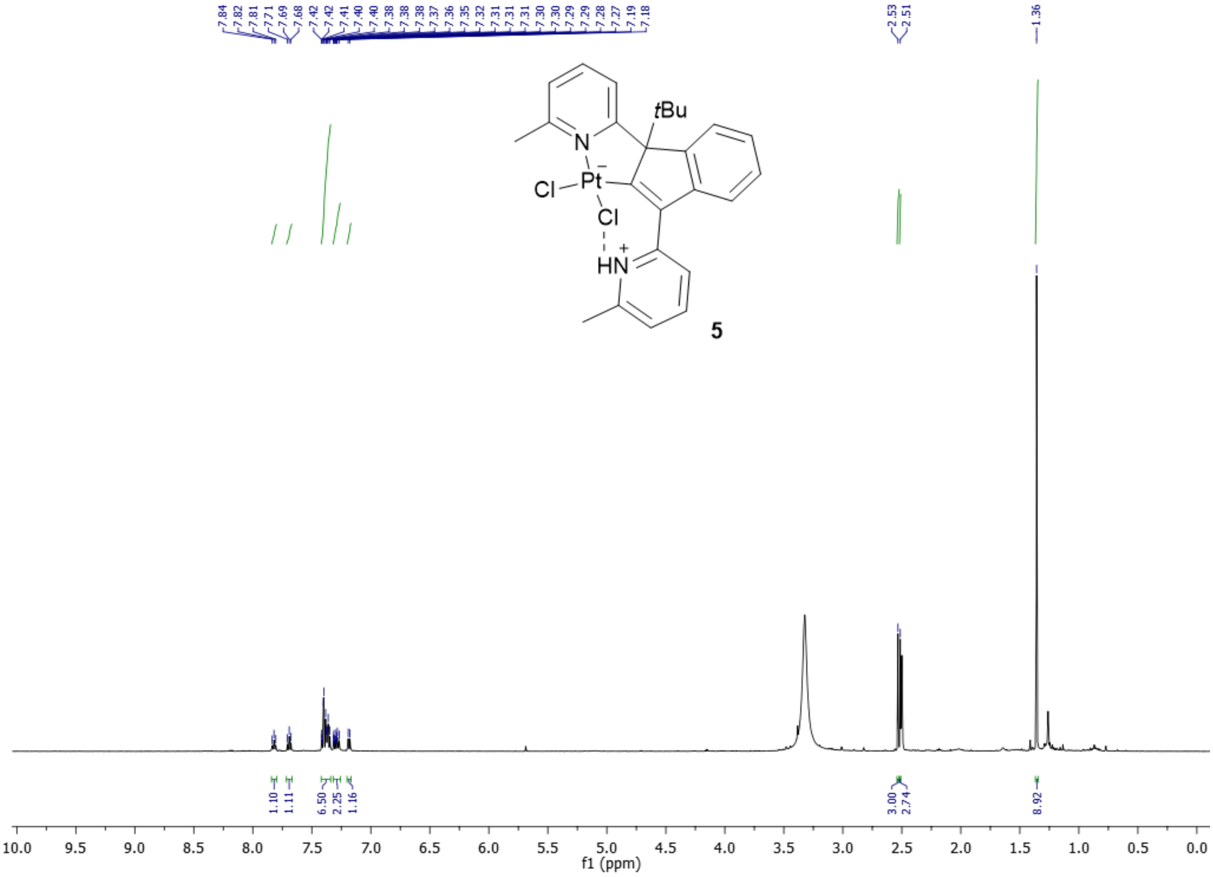
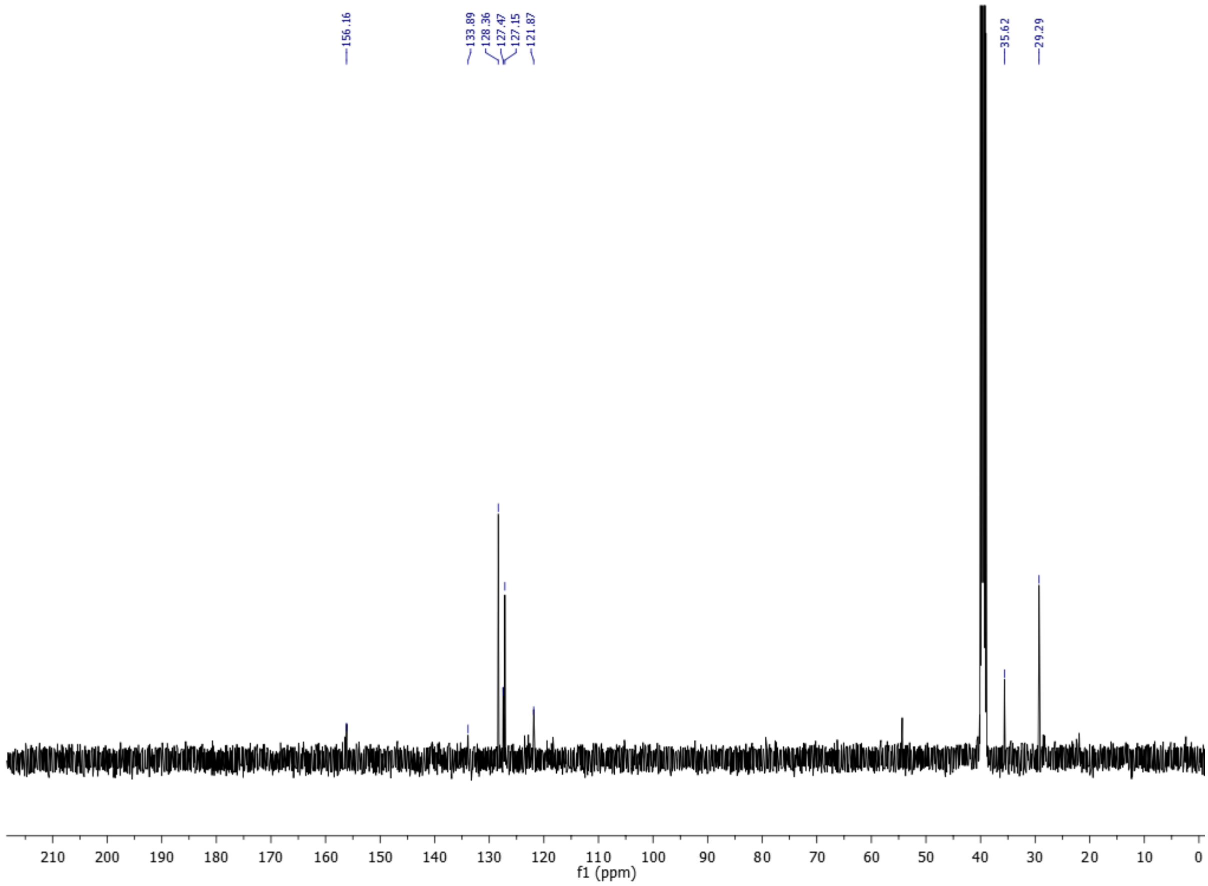
156.29
156.10
151.30
150.87
141.31
139.72
133.66
128.46
127.63
127.09
123.15
122.21
122.13
118.32
109.10
35.69
29.26
22.20
21.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.84
7.82
7.81
7.71
7.69
7.68
7.42
7.42
7.41
7.40
7.40
7.38
7.38
7.38
7.37
7.36
7.35
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.19
7.18
2.53
2.51
1.36
tBu
N
Pt
Cl
Cl
HN
5
1.10
1.11
6.50
2.25
1.16
3.00
2.74
8.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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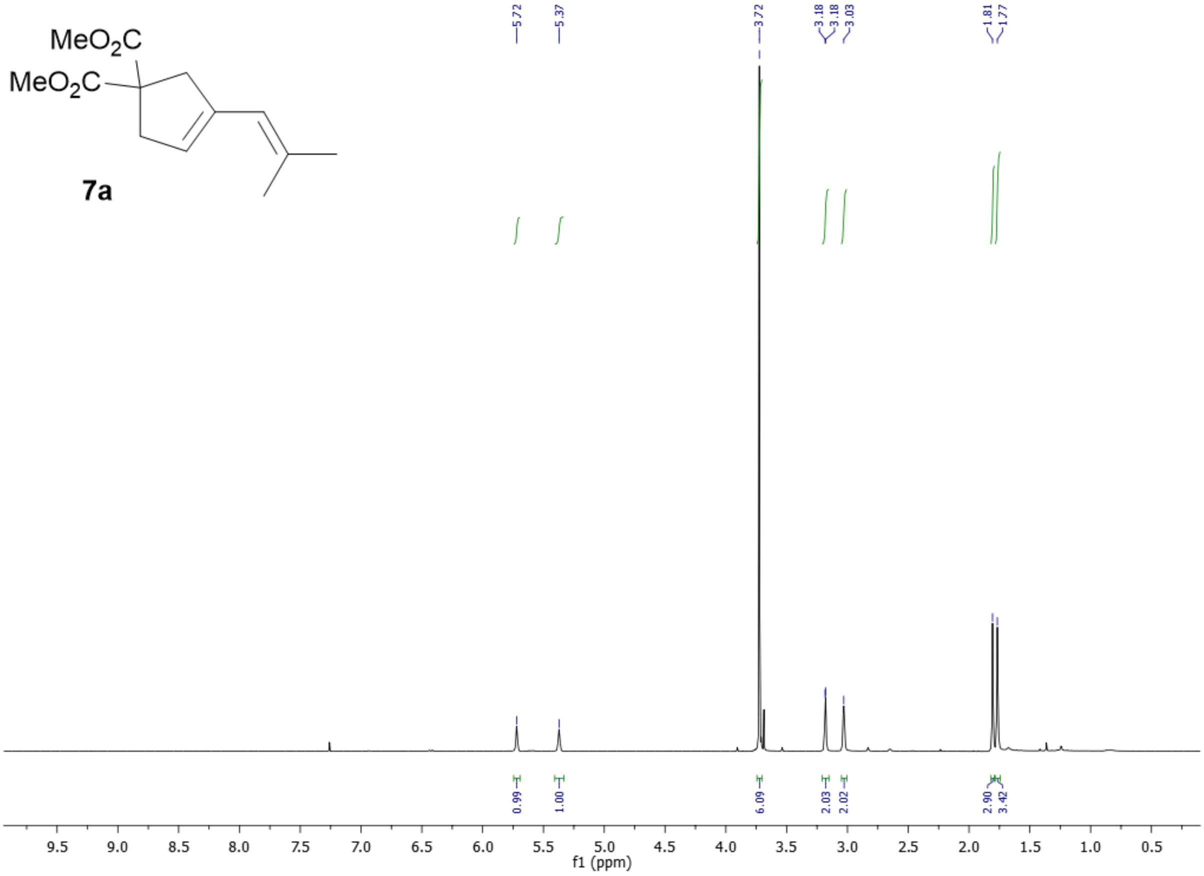
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

MeO$_2$C
MeO$_2$C

7a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5.37
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3.03
1.81
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6.09
2.03
2.02
2.90
3.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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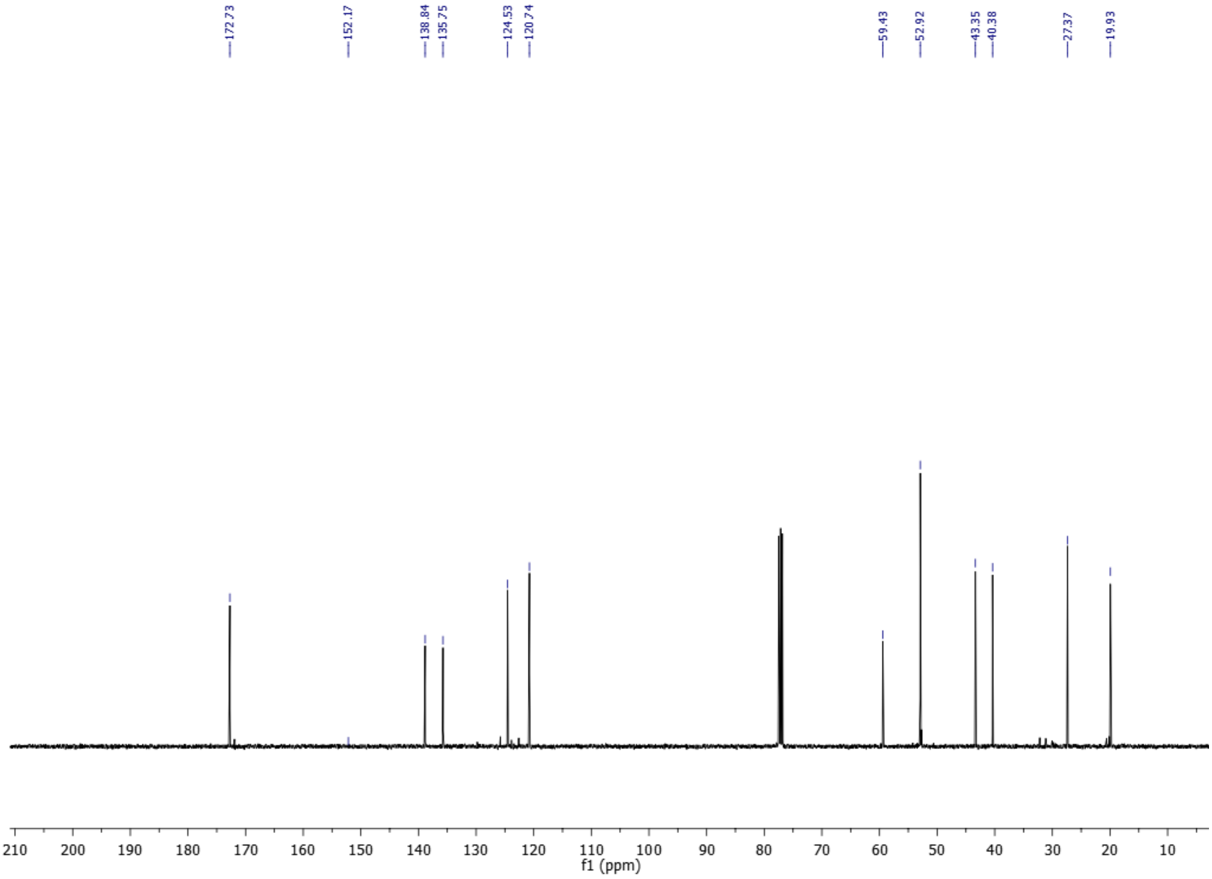
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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152.17
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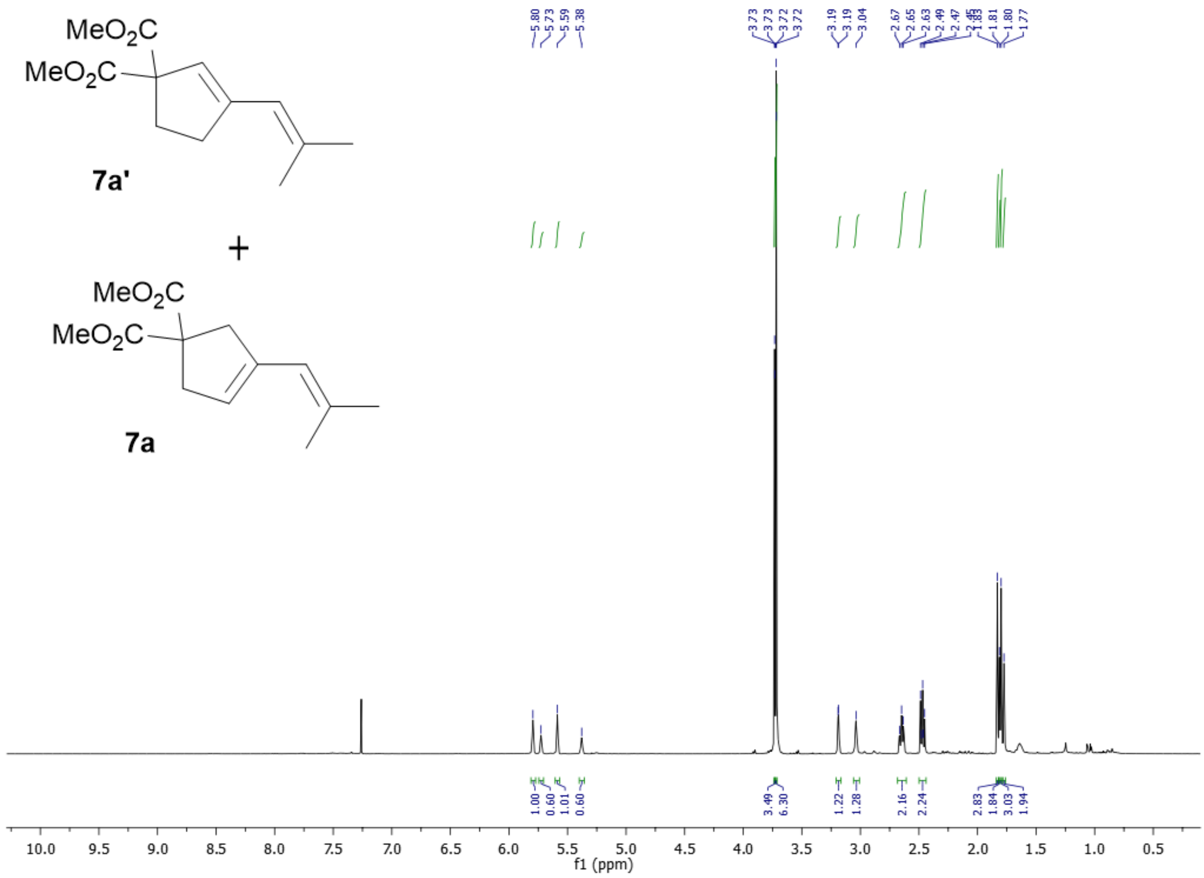
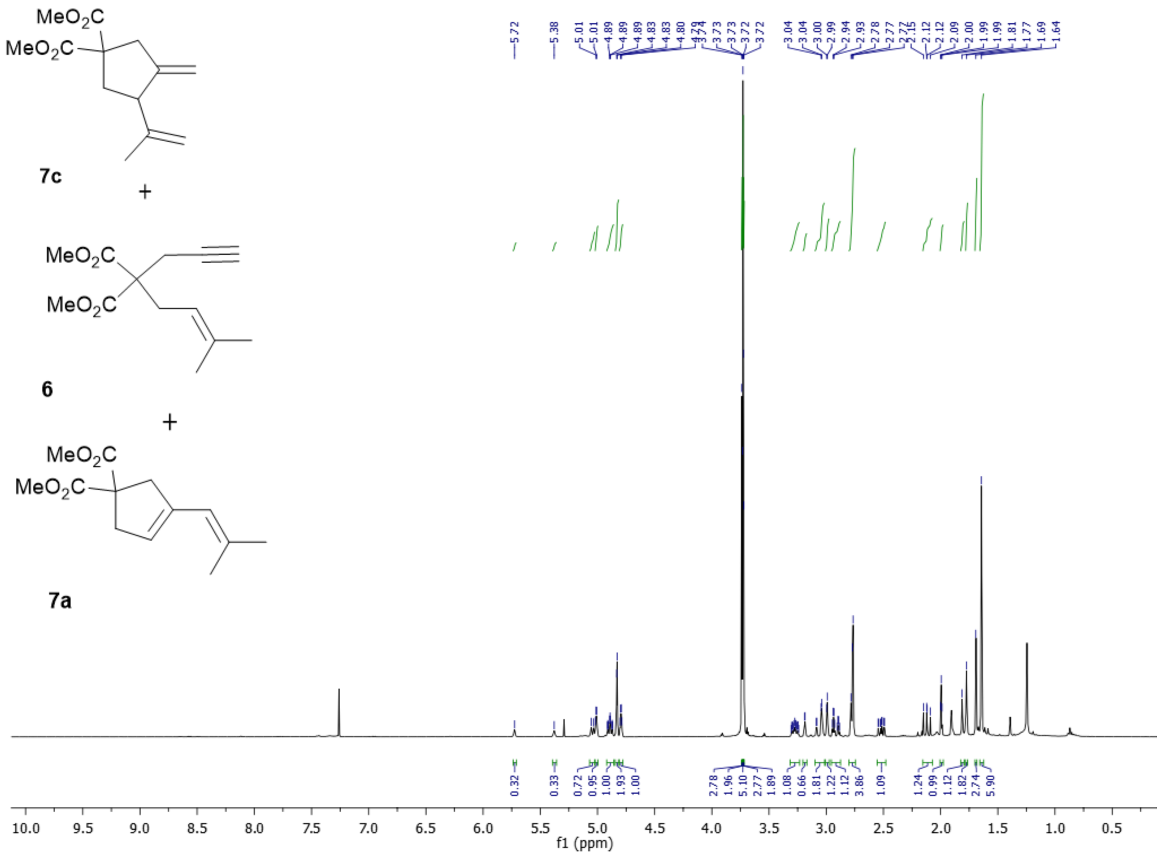
124.53
120.74
59.43
52.92
43.35
40.38
27.37
19.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

SUPPLEMENTARY INFORMATION





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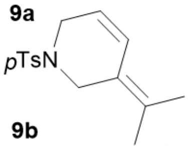

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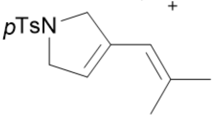

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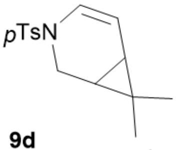
9c



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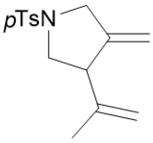
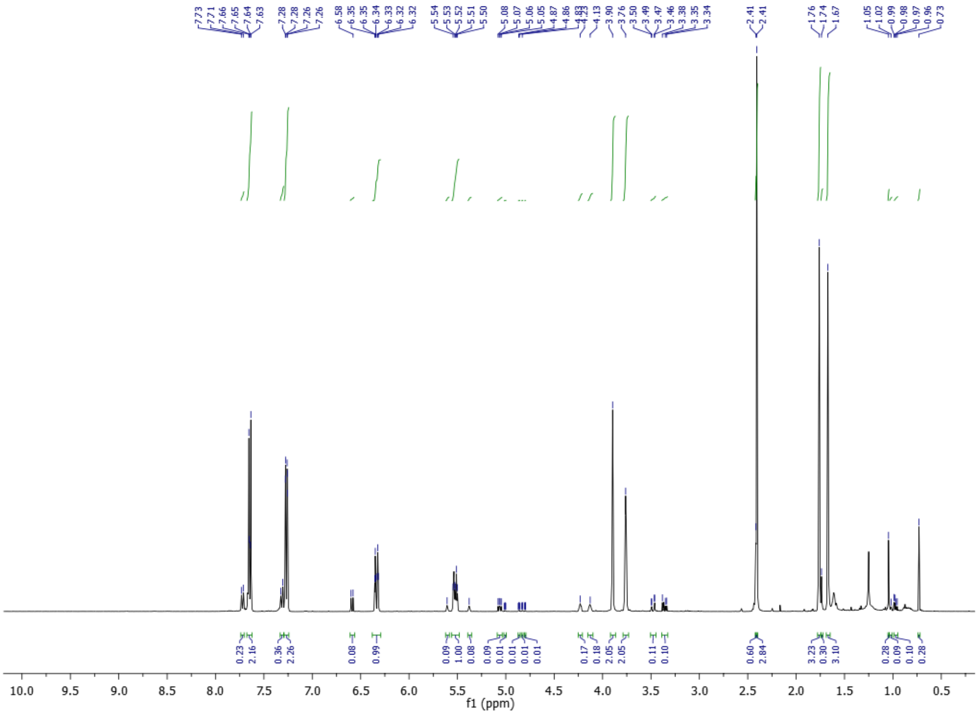


+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7.28
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7.26
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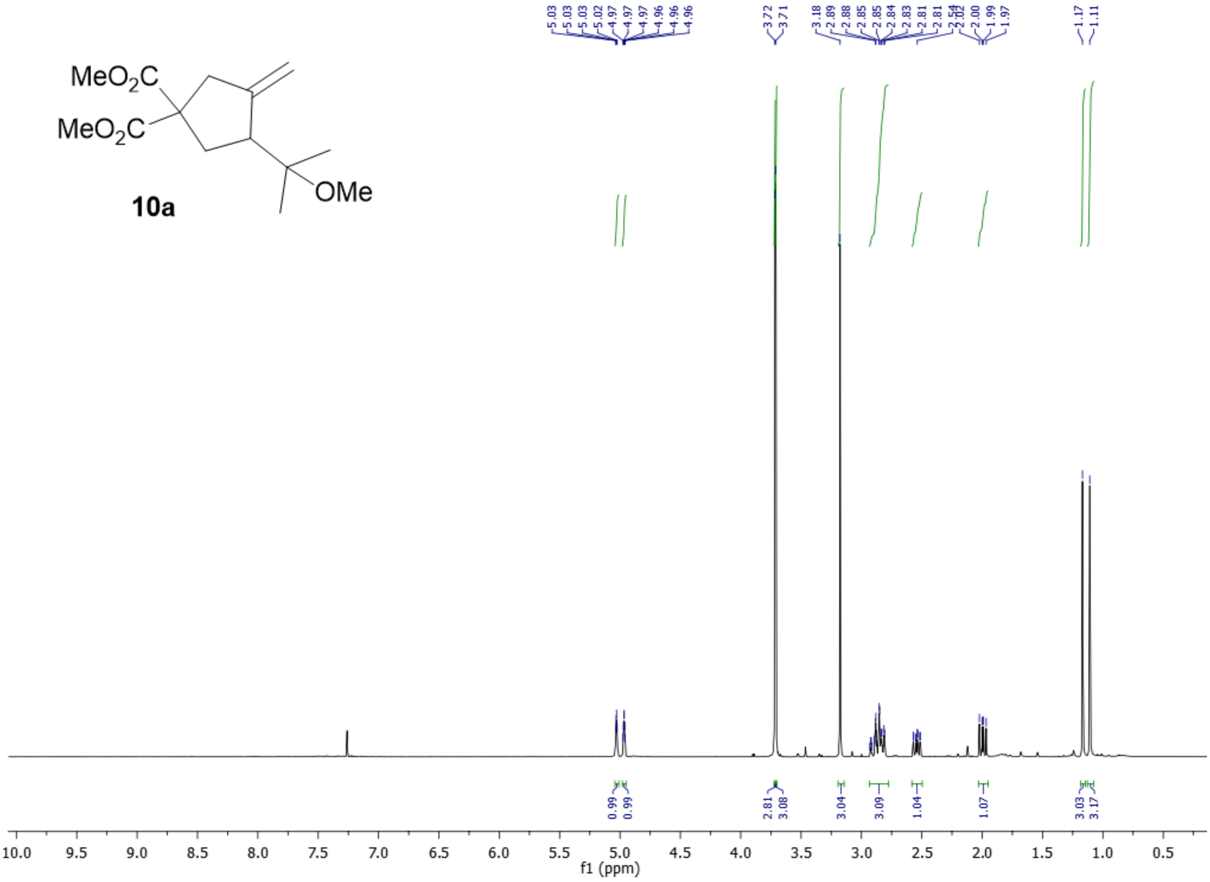
6.35
6.35
6.34
6.33
6.32
6.32
5.54
5.53
5.52
5.51
5.50
5.08
5.07
5.06
5.05
4.87
4.86
4.83
4.23
4.13
3.90
3.76
3.50
3.49
3.47
3.46
3.38
3.35
3.34
2.41
2.41
1.76
1.74
1.67
1.05
1.02
0.99
0.98
0.97
0.96
0.73
0.23
2.16
0.36
2.26
0.08
0.99
0.09
1.00
0.08
0.09
0.01
0.01
0.01
0.01
0.17
0.18
2.05
2.05
0.11
0.10
0.60
2.84
3.23
0.30
3.10
0.28
0.09
0.10
0.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

MeO$_2$C
MeO$_2$C
OMe

10a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5.03
5.03
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4.97
4.97
4.96
4.96
4.96
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3.71
3.18
2.89
2.88
2.85
2.85
2.84
2.83
2.81
2.81
2.54
2.52
2.00
1.99
1.97
1.17
1.11
0.99
0.99
2.81
3.08
3.04
3.09
1.04
1.07
3.03
3.17
10.0
9.5
9.0
8.5
8.0
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6.5
6.0
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5.0
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4.0
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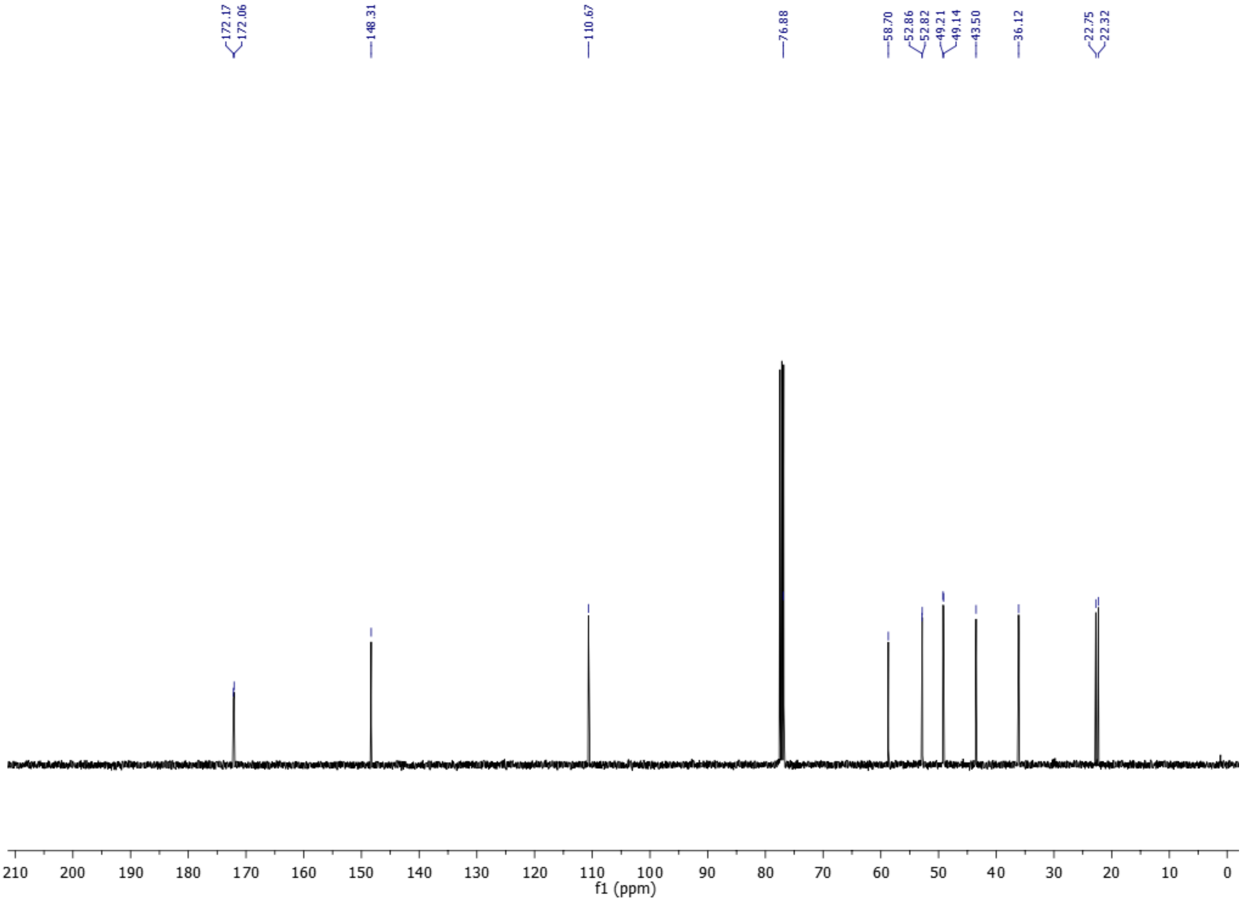
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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200
190
180
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50
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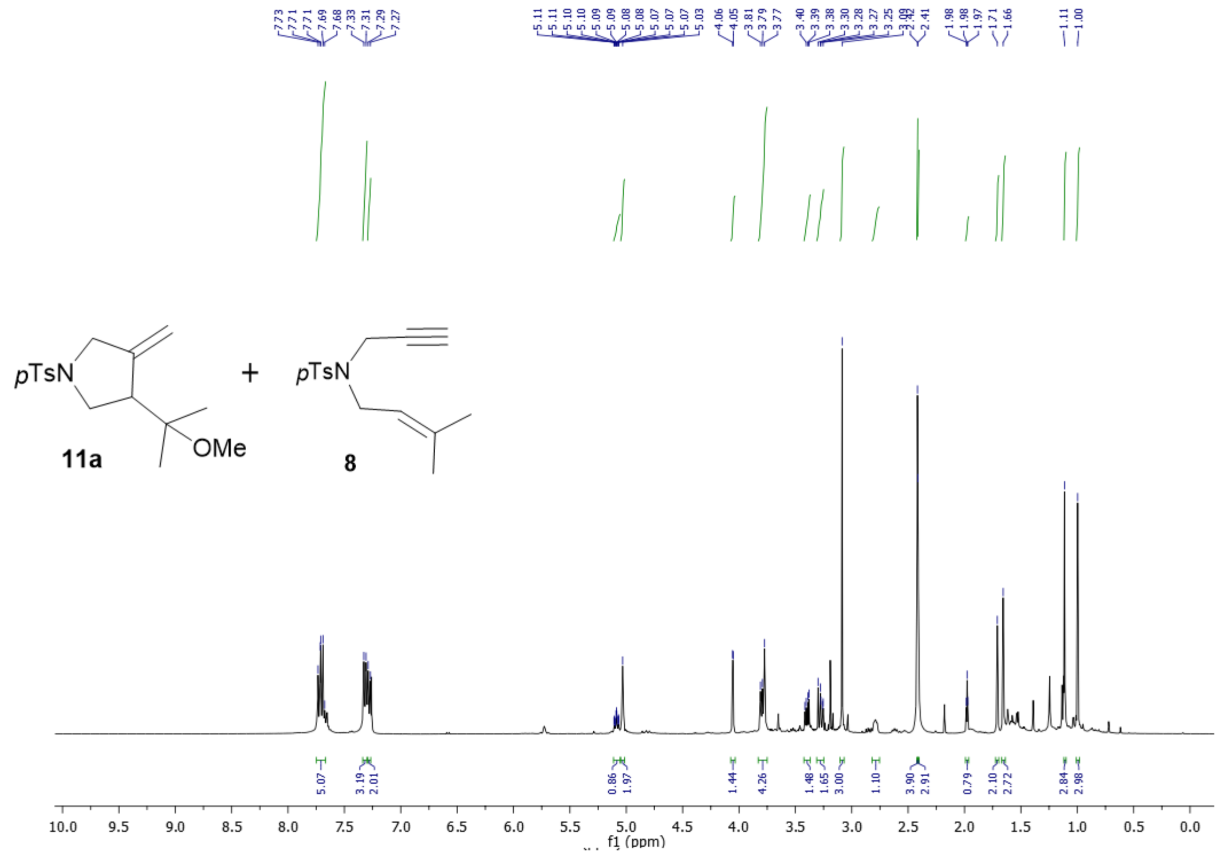
10
0
f1 (ppm)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5.09
5.09
5.08
5.08
5.07
5.07
5.07
5.03
4.06
4.05
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3.79
3.77
3.40
3.39
3.38
3.30
3.28
3.27
3.25
3.09
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2.41
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1.98
1.97
1.71
1.66
1.11
1.00
pTsN
11a
OMe
+
pTsN
8
5.07
3.19
2.01
0.86
1.97
1.44
4.26
1.48
1.65
3.00
1.10
3.90
2.91
0.79
2.10
2.72
2.84
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5. X-Ray structure determination

5.1. Crystal structure analyses

The experimental procedures for the five complexes were very similar; variations are noted below. Experimental details and results for the five complexes are listed in Table S4. Further information can be found in the file ESI_X-Ray tables.

Crystals of **2a, 3b''** and **2b''** were mounted on small loops and fixed in the cold nitrogen stream on an Rigaku Oxford Diffraction XtaLAB Synergy diffractometer, equipped with Mo-Kα radiation, HyPix detector and a mirror monochromator. Intensity data were measured by thin-slice ω-scans. For crystals of **3a** and **5**, crystals were mounted on glass fibres and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and ϕ-scans.

For each sample, data were processed using the CrysAlisPro-CCD and -RED[11] programs. The structures were determined by the intrinsic phasing routines in the SHELXT program[12] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[13] The non-hydrogen atoms were refined with anisotropic thermal parameters. For **5**, the pyridinium hydrogen atom was located in a difference map and was refined freely. All other hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms.

In the final difference map for each sample, the highest peaks were near the heavy (gold or platinum) atom.

Scattering factors for neutral atoms were taken from reference.[14] Computer programs used in this analysis have been noted above and were run through WinGX[15] on a Dell Optiplex 780 PC at the University of East Anglia.

Table S4. Summary of X-Ray data of the five complexes.

	Compound **2a**	Compound **3a**	Compound **5**	Compound **3b''**	Compound **2b''**
Elemental formula	$C_{27}H_{22}AuClN_2$	$C_{27}H_{22}AuCl_3N_2$, CH_2Cl_2	$C_{25}H_{26}Cl_2N_2Pt$, $CHCl_3$	$C_{25}H_{26}AuCl_3N_2$	$C_{25}H_{26}AuClN_2$
Formula weight	606.88	762.71	739.83	657.79	586.89
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Tetragonal
Space group	P 2_1/n (equiv. to no. 14)	P 2_1/c (no. 14)	P -1 (no. 2)	P 2_1/n (equiv. to no. 14)	P 4_1 (no. 76)
Unit cell dimensions: a = (Å)	13.6080(2)	10.7752(2)	9.3270(3)	9.46335(14)	10.03923(5)
b =	12.09078(15)	14.9805(3)	11.8674(5)	19.7083(2)	10.03923(5)
c =	14.8143(2)	17.3390(3)	12.9754(4)	14.0613(2)	21.99014(18)
α = (°)	90	90	105.467(3	90	90
β =	110.984(2)	96.371(2)	91.480(3)	108.2848(15)	90
γ =	90	90	102.873(3)	90	90
Volume (Å^3)	2275.77(6)	2781.54(9)	1343.84(9)	2490.10(6)	2216.28(2)

SUPPLEMENTARY INFORMATION

Z, Calculated density (Mg/m^3)	4, 1.771	4, 1.821	2, 1.828	4, 1.755	4, 1.759
F(000)	1176	1480	720	1280	1144
Absorption coefficient (mm^{-1})	6.598	5.790	5.737	6.245	6.772
Temperature (K)	100.01(10) K	140(1)	140(1)	100.01(10)	100.01(10)
Crystal colour, shape	colourless plate	pale yellow plate	pale yellow prism	yellow plate	yellow cuboid
Crystal size (mm)	0.07 x 0.10 x 0.16 mm	0.56 x 0.32 x 0.09	0.44 x 0.115 x 0.110	0.16 x 0.11 x 0.026	0.10 x 0.09 x 0.07
On the diffractometer:					
Theta range for data collection	2.237 to 29.995	3.594 to 29.999	3.575 to 29.999	1.842 to 30.000	2.029 to 29.990
Limiting indices	-19<=h<=19, -17<=k<=17, -20<=l<=20	-15<=h<=15, -21<=k<=21, -24<=l<=24	-13<=h<=13, -16<=k<=16, -18<=l<=18	-13<=h<=13, -27<=k<=27, -19<=l<=19	-14<=h<=14, -14<=k<=14, -30<=l<=30
Completeness to theta = 25.242 (%)	100.0	99.7	99.7	100.0	100.0
Absorption correction: Semi-empirical from equivalents					
Max. and min. transmission	1.00000 and 0.45490	1.000 and 0.236	1.000 and 0.1190	1.00000 and 0.39824	1.00000 and 0.48497
Reflections collected (not including absences)	82534	53936	26150	93429	84333
No. of unique reflections, R(int) for equivalents	6634, 0.056	8091, 0.037	7821, 0.094	7264, 0.036	6451, 0.036
No. of 'observed' reflections ($I > 2\sigma_I$)	6115	7083	7106	6792	6283
Refinement:					
Data / restraints / parameters	6634 / 0 / 282	8091 / 0 / 327	7821 / 0 / 313	7264 / 0 / 282	6451 / 1 / 264
Goodness-of-fit on F^2	1.106	1.046	1.065	1.053	1.087
Final R indices ('obsd' data)	$R_1 = 0.025$, $wR_2 = 0.056$	$R_1 = 0.023$, $wR_2 = 0.047$	R1 = 0.054, $wR_2 = 0.134$	R1 = 0.018, $wR_2 = 0.041$	R1 = 0.013, $wR_2 = 0.029$

Final R indices (all data)	$R_1 = 0.030$, $wR_2 = 0.057$	$R_1 = 0.031$, $wR_2 = 0.048$	R1 = 0.059, $wR_2 = 0.141$	R1 = 0.021, $wR_2 = 0.042$	R1 = 0.014, $wR_2 = 0.029$
Reflections weighted: 1/w = *	$\sigma^2(Fo^2)+(0.0231P)^2+4.323P$	$\sigma^2(Fo^2)+(0.0186P)^2+2.648P$	$\sigma^2(Fo^2)+(0.0835P)^2+1.455P$	$\sigma^2(Fo^2)+(0.0191P)^2+3.303P$	$\sigma^2(Fo^2)+(0.0127P)^2+1.184P$
Largest diff. peak and hole (e.Å^{-3})	1.49 and -1.11	1.42 and -0.77	7.42 and -4.37	1.27 and -0.48	0.61 and -0.44
Location of largest difference peak	near the gold atom	near the gold atom	near the Pt atom	near Cl(1)	near the Au atom

4.2. Structure of gold(I) complex 2a

The principal plane of this molecule comprises the C_8H_3N ring system, with the methyl group of C(7), the gold centre, the chloride ligand and C(11), Figure S5. The normal to the plane of the phenyl ring of C(11-16) is 53.70(11)° from that of the five-membered (pyrrole) ring, and C(10) has a tetrahedral arrangement with the phenyl ring of C(21) and the pyridyl ring of C(31) displaced out of the pyrrole ring plane. The ortho C(22)-H(22) group folds over the face of the pyrrole ring forming close contacts of 2.58 and 2.61 Å with C(9) and C(10).

The gold atom has an approximately linear arrangement of the chloride ligand and C(9) of the pyrrole ring.

The shortest intermolecular contacts appear to involve the chloride ligand, with several aromatic C-H groups forming weak hydrogen bonds; the closest H...Cl distance is 2.86 Å. A view of the molecular packing is shown in Figure S6.

The AuCl group appears to have attacked the central C atom of the C=C=C link of the starting material, and the pyridyl N(1) atom has bonded to C(10) to form the pyrrole ring.

Figure S5. View of a molecule of [ClAu(C_8H_3N-Ph-1,-C_5NH_3-Me-1,-Ph-3,-Me-7)], indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

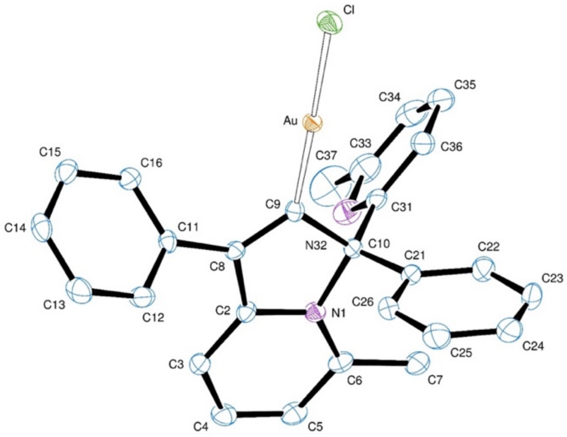
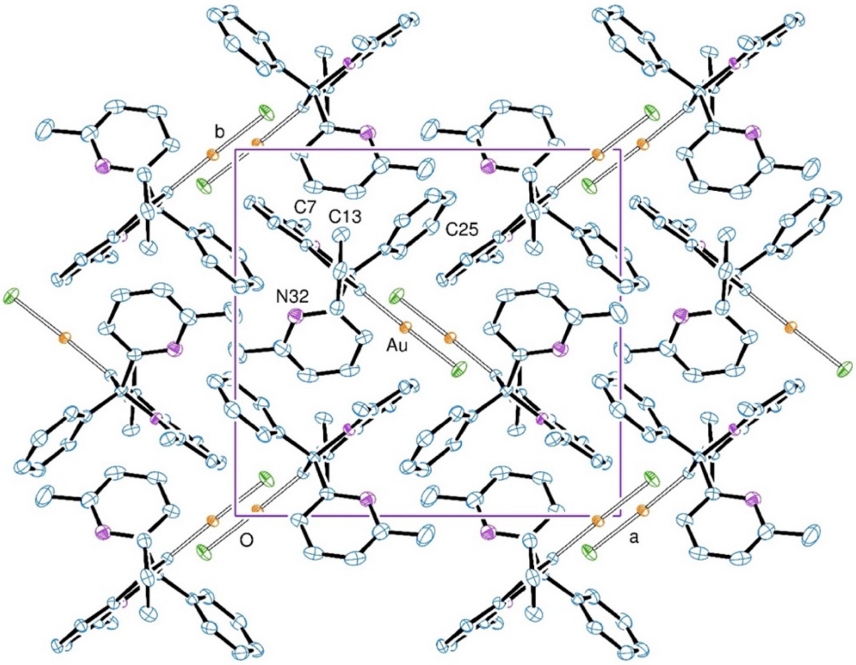


Fig. S6. View of the packing along the *c* axis.



4.3. Structure of gold(I) complex 2b''

Compound **2b''** showed chirality, i.e. all the molecules are identical, each with an asymmetric centre at C(10). There were no molecules of the inverted structure/mirror image found in the selected crystal. This crystal shows polarity: all the molecules point in the same direction, spiralling around a 4_1 symmetry axis. The absolute structure (Flack x) parameter was -0.0125(19) and the correct chirality (*S*) is shown in Figures S7 and S8.

There is no reason for this complex to be enantiomerically pure, and perhaps there were crystals in the sample which are of the opposite enantiomer – but we were not able to detected any by the simple methods available, e.g. via looking for crystals with mirror-image morphologies.

Figure S7. View of a molecule of $[ClAu(C_8H_3N\text{-}Ph\text{-}1,\text{-}C_5H_3N\text{-}Me\text{-}1,\text{-}{}^tBu\text{-}3,\text{-}Me\text{-}7)]$, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

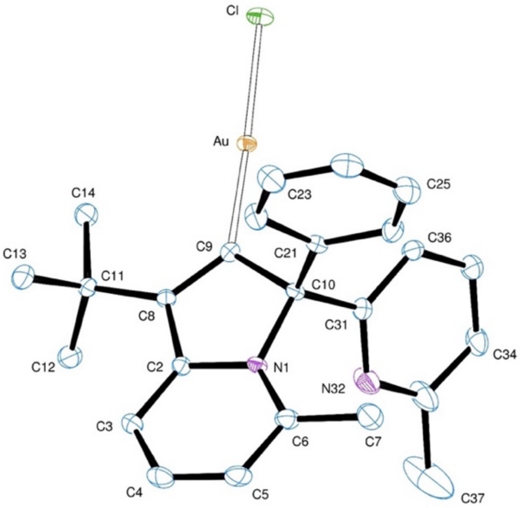
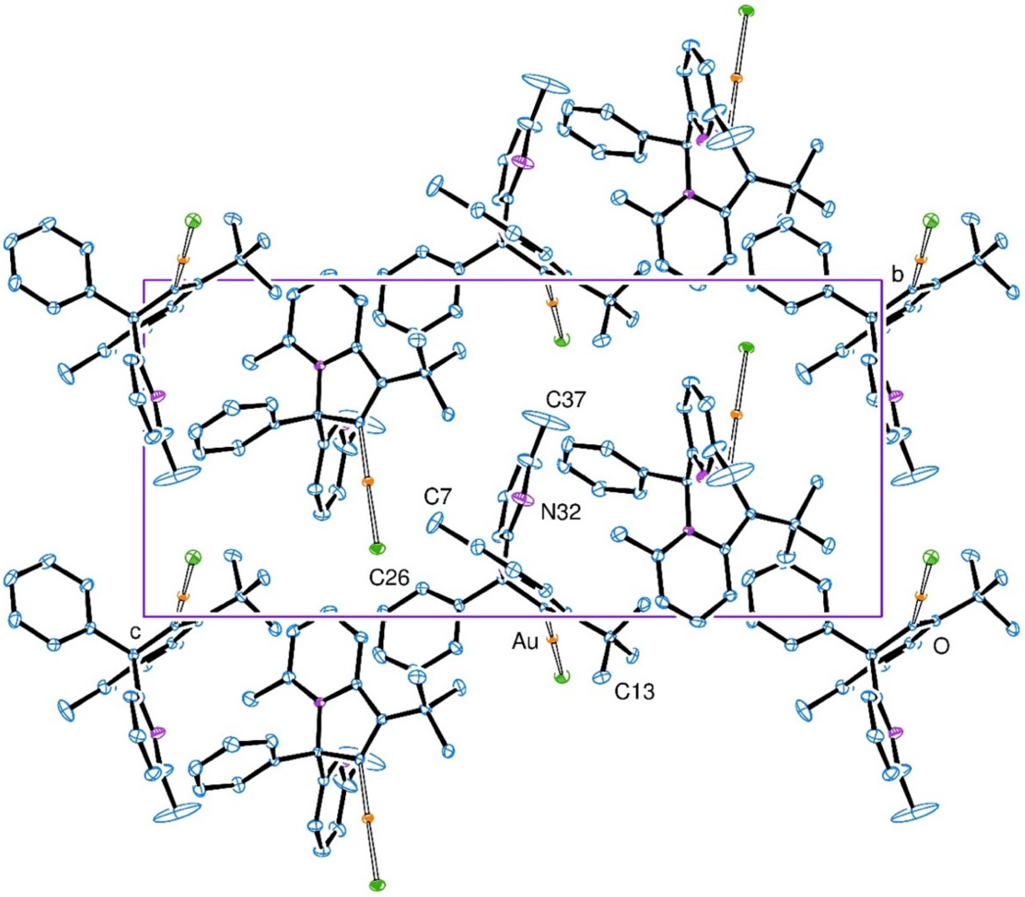


Figure S8. View of the packing along the *a* axis.



4.3. Structure of gold(III) complex 3a

The principal plane of this molecule comprises the C_8H_3N ring system, with the methyl group of C(7), the gold centre, the chloride ligand and C(11), Figure S9. The normal to the plane of the phenyl ring of C(11-16) is 53.70(11)° from that of the five-membered (pyrrole) ring, and C(10) has a tetrahedral arrangement with the phenyl ring of C(21) and the pyridyl ring of C(31) displaced out of the pyrrole ring plane. The ortho C(22)-H(22) group folds over the face of the pyrrole ring forming close contacts of 2.58 and 2.61 Å with C(9) and C(10).

The gold atom has an approximately linear arrangement of the chloride ligand and C(9) of the pyrrole ring.

The shortest intermolecular contacts appear to involve the chloride ligand, with several aromatic C-H groups forming weak hydrogen bonds; the closest H...Cl distance is 2.86 Å. A view of the molecular packing is shown in Figure S10.

The AuCl group appears to have attacked the central C atom of the C=C=C link of the starting material, and the pyridyl N(1) atom has bonded to C(10) to form the pyrrole ring.

SUPPLEMENTARY INFORMATION

Figure S9. View of a molecule of [ClAu(C_8H_3N-Ph-1,-C_5NH_3-Me-1,-Ph-3,-Me-7)], indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

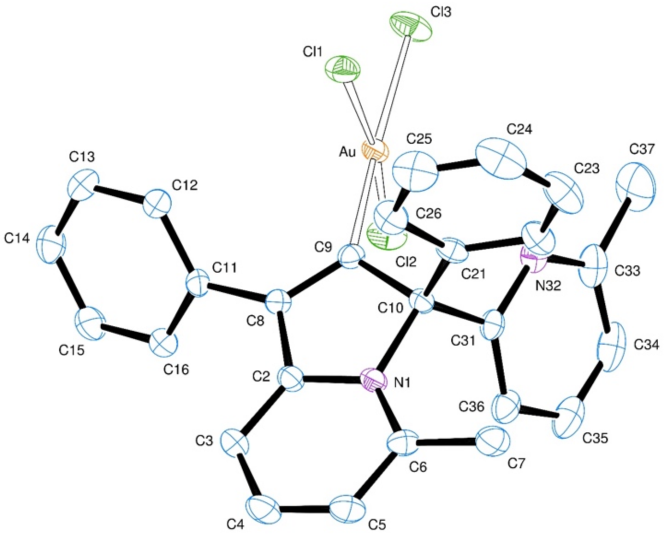
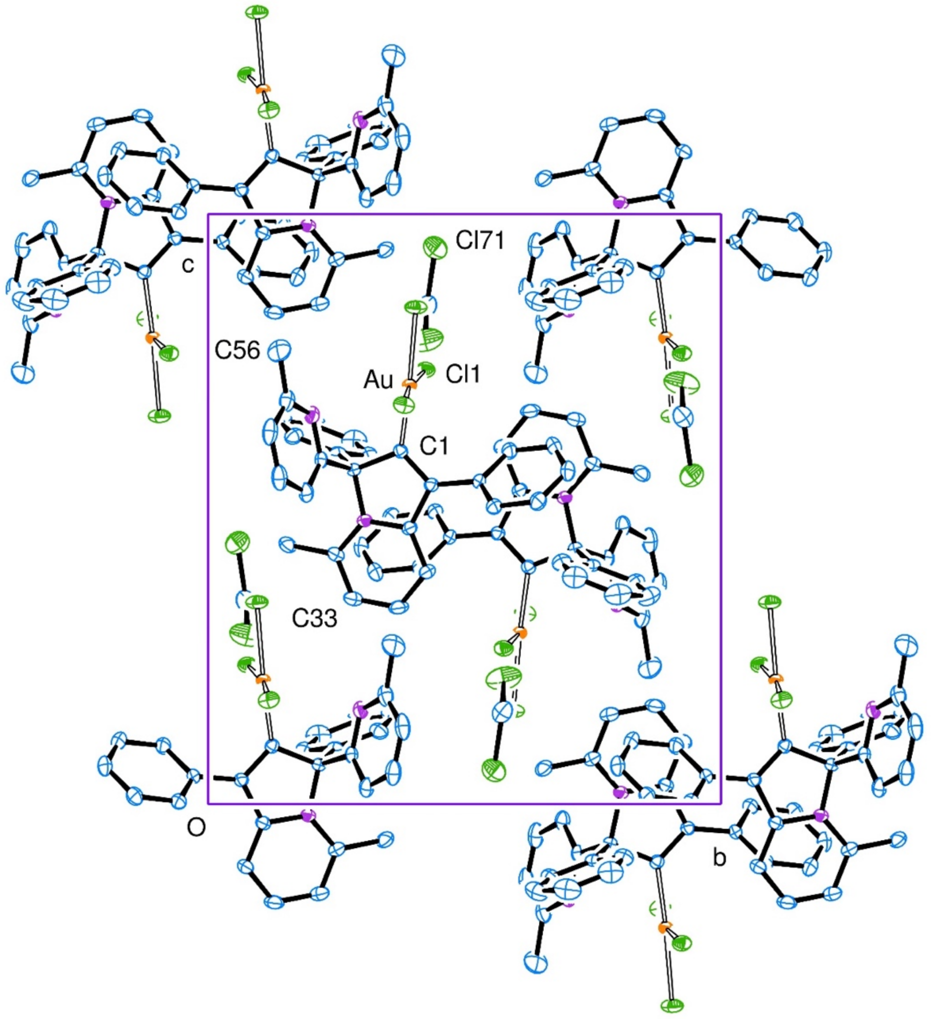


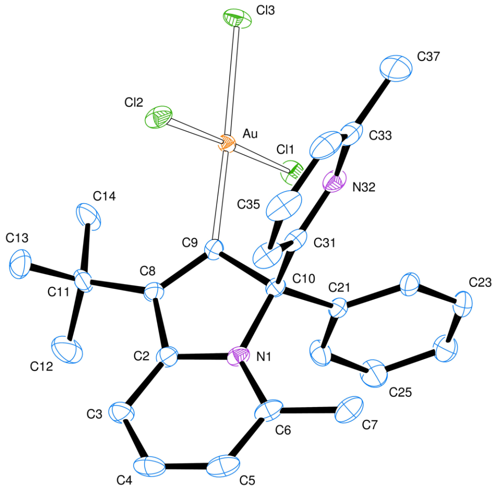
Figure S10. View of the packing along the *a* axis.



4.5. Structure of gold(III) complex 3b''

This molecule has a very similar shape to that of compound **3a**.

Figure S11. View of a molecule of [$AuCl_3(C_8H_3N\text{-Ph-1,-}C_5H_3N\text{-Me-1,-}^tBu\text{-3,-Me-7})$], indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

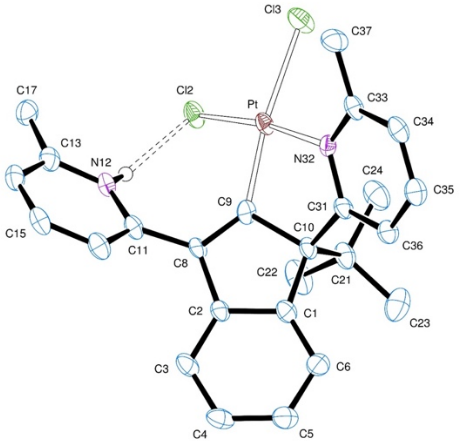


4.5. Structure of platinum(II) complex 5

The platinum atom shows an approximately square planar, fourfold configuration with the two chloride ligands and the chelating N(1)---C(9) group; the second nitrogen atom, N(22), is not bound to the Pt centre, but forms a pyridinium group which is the donor group in a good intramolecular hydrogen bond, N(22)-H(22)...Cl(1), Figure S12. The methine H atom of the solvent (chloroform) molecule is the donor in the C(41)-H(41)...Cl(2)#2 hydrogen bond.

The C(3)-C(4) bond lies over a neighbouring symmetry-related group with a π...π interaction. On the opposite side of this pyridinyl ring, one of the methyl groups of the t-butyl (intramolecular) group folds over C(2) with a short C(2)-H(34a) distance of 2.61 Å. The C(5)-H(5) bond is directed towards the centre of the C6 ring of C(11-16) of a neighbouring molecule, with the shortest H...C distance at 2.88 Å. In the pyridinium ring, a neighbouring solvent chlorine atom, Cl(43), makes a close contact with C(21) at 3.525 Å.

Figure S12. View of a molecule of the platinum complex **5**, indicating the atom numbering scheme and the hydrogen bond. Thermal ellipsoids are drawn at the 50% probability level.



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