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Supporting Information

Towards new coordination modes of 1,2,3-triazolylidene: controlled by the nature of the 1st metalation in a heteroditopic bis-NHC ligand

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Table of contents

General experimental procedures

All manipulations were performed under an argon/N_2 atmosphere using either standard Schleck line or glovebox techniques. All glassware was oven-dried at 130 °C overnight prior to use. The solvents used were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were carried out on Bruker 400 and 500 MHz FT-NMR spectrometers. ESI-MS was recorded using an Agilent 6545A Q-TOF Mass spectrometer. The chemical shifts in the ^1H NMR spectra were referenced to the residual proton signals of the deuterated solvents ($CDCl_3$, ^1H 7.26 ppm and $^{13}C\{^1H\}$ 77.16 ppm; DMSO-d_6, ^1H 2.50 ppm and $^{13}C\{^1H\}$ 39.5 ppm) and reported relative to tetramethylsilane (TMS). The coupling constants are expressed in hertz. The metal precursors $[Ir/Rh(Cp^*)Cl_2]_2$,[1a] $[Pd(CH_3CN)_2Cl_2]$,[1b] and $[Au(SMe_2)Cl]$[1c] were prepared according to the reported procedures. All other chemicals were purchased from the commercial sources and used as received without further purification.

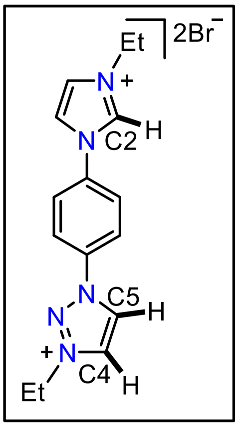
Synthesis of aryl azides

The substituted aryl azides were synthesized either following or modifying the reported procedure.[2] All spectroscopic values of the synthesized aryl azides are in good agreement with the reported values. ***Caution!*** *Organic azides are toxic and explosive. Therefore, these materials must be handled with appropriate safety measures.*

Synthesis of compounds 1-phenyl triazole (A) and 4-bromophenyl triazole (B): Compounds **A** and **B** were synthesized following a modified reported procedure[2] and the spectroscopic data of isolated compounds are in good agreement with the reported values.

Synthesis of compound C: Compound **C** was synthesized following the Ullmann coupling of compound **B** with imidazole. To a 50 mL Schlenk tube, compound **B** (1.0 g, 4.46 mmol), imidazole (334 mg, 4.91 mmol), K_2CO_3 (679 mg, 4.91 mmol) and CuO (36 mg, 0.45 mmol) were added under an inert condition. Dry DMSO (6 mL) was then added and stirred for 48 h at 150 °C. After the reaction, the product was extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and solvent was evaporated to get a white precipitate in good yield (0.845 g, 4 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.61 (d, J = 9.3 Hz, 3H), 7.30 (d, J = 8.9 Hz, 2H), 6.98 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.8, 136.2, 134.9, 122.8, 122.3, 121.8 ppm. HRMS (ESI): $C_{11}H_9N_3$ m/z calcd. for $[M+H]^+$: 212.0936; found: 212.0935.

Synthesis of [L1-H]Br: To a 25 mL Schlenk flask containing a magnetic stirring bar, 1 g (6.89 mmol) of compound **A** and 5 mL dry DMF were added. To that, ethyl bromide (2.6 mL, 34.45 mmol) was added and heated to 90 °C for 24 h. After cooling the reaction mixture, all volatiles were removed in high vacuum. The resulting residue was washed with diethyl ether (3 x 10 mL) to yield a hygroscopic brown powder in good yield (1.4 g, 5.51 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H, $\text{Tz}_{\text{C5-}H}$), 10.05 (s, 1H, $\text{Tz}_{\text{C4-}H}$), 8.12 (d, J = 8.1 Hz, 2H), 7.61-7.65 (m, 3H), 5.04 (q, J = 7.4 Hz, 2H), 1.80 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.9, 133.1, 132.0, 130.6, 129.9, 121.6, 50.5, 15.2 ppm. HRMS (ESI): $C_{10}H_{12}N_3Br_2$ *m/z* calcd. for $[M+Na]^+$: 356.9275; found: 356.9273.



Synthesis of [L2-H$_2$]Br$_2$: To a 25 mL Schlenk flask containing a magnetic stirring bar, 1 g (4.73 mmol) of compound **C** and dry DMF (5 mL) were added. To that, ethyl bromide (3.5 mL, 47.3 mmol) was added and heated to 90 °C for 24 h. After cooling the reaction mixture, all the volatiles were removed in high vacuum. The resulting residue was washed with diethyl ether (3 x 10 mL) to provide a hygroscopic brown powder in excellent yield (1.9 g, 4.43 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.20 (s, 1H, $\text{Im}_{\text{C2-}H}$), 9.79 (s, 1H, $\text{Tz}_{\text{C5-}H}$), 9.37 (s, 1H, $\text{Tz}_{\text{C4-}H}$), 8.53 (s, 1H), 8.38 (d, J = 7.3 Hz, 2H), 8.27 (d, J = 7.3 Hz, 2H), 8.18 (s, 1H), 4.83 (q, J = 7.3 Hz, 2H), 4.35 (q, J = 7.3 Hz, 2H), 1.64 (t, J = 7.3 Hz, 3H), 1.54 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 136.7, 135.8, 135.1, 131.5, 129.6, 123.5, 123.4, 123.3, 121.0, 49.4, 44.9, 14.8, 14.1 ppm. HRMS (ESI): $C_{15}H_{19}N_5Br_2$ *m/z* calcd. for $[M+Na]^+$: 451.9885 found: 451.9876.

Synthesis of complex 1: To a 25 mL Schlenk tube equipped with a magnetic stirring bar, [**L1**-H]Br (50 mg, 0.20 mmol), $[Pd(CH_3CN)_2Cl_2]$ (52 mg, 0.20 mmol), Cs_2CO_3 (78 mg, 0.24 mmol), and KBr (71 mg, 0.60 mmol) were added. After drying in vacuo for 30 minutes, acetonitrile (5 mL) and pyridine (1 mL) were added. The resulting solution was stirred at 70 °C for 24 h. After the reaction, the resultant mixture was cooled and all the volatiles were removed in high vacuum. The residue was extracted with dichloromethane and filtered through a pad of celite. The obtained clear brown solution was concentrated and precipitated with n-hexane. The precipitate was then collected and dried to yield a pale brown solid. The analytically pure compound was obtained after recrystallization of the crude product *via* slow diffusion of n-hexane into a saturated dichloromethane solution of the compound. Yield: 62 mg (0.12 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J = 8.1 Hz, 2H), 8.37 (d, J = 7.4 Hz, 2H), 7.71 (s, 1H), 7.63–7.57 (m, 3H), 7.30–7.26 (m, 2H), 4.47 (q, J = 7.4 Hz, 2H), 1.70 (t, J = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 152.8, 152.3, 139.5, 138.6, 137.8, 131.3, 131.1, 130.3, 129.2, 129.2, 125.4, 125.3, 124.6, 48.2, 14.3 ppm. ESI-MS: $C_{15}H_{16}N_6PdBr_2$ *m/z* calcd. for $[M-Br+CH_3OH+H_2O]^+$: 489.00 found: 489.0639.

Synthesis of complex 2: To a 25 mL Schlenk tube equipped with a magnetic stirring bar, [**L1**-H]Br (50 mg, 0.20 mmol), $[Au(SMe_2)Cl]$ (65 mg, 0.22 mmol), Cs_2CO_3 (78 mg, 0.24 mmol), and acetonitrile (6 mL) were added and stirred at 70 °C for 24 h. After that, the reaction mixture was cooled and filtered through celite to get a colourless solution. The solution was then concentrated and the compound was precipitated by the addition of diethyl ether. The obtained precipitate was dried in high vacuum to get a stable white powder. Single crystals suitable for X-ray crystallographic analysis were grown *via* slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. Yield: 72 mg (0.16 mmol, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07–8.03 (m, 2H), 7.76 (s, 1H), 7.55–7.54 (m, 3H), 4.58 (q, J = 7.4 Hz, 2H), 1.71 (t, J = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.9, 139.1, 133.7, 133.4, 130.6, 129.7, 124.1, 124.0, 48.3, 14.8 ppm. ESI-MS: $C_{10}H_{11}N_3AuBr$, *m/z* calcd. for $[M-Br]^+$: 370.0618; found: 370.0619; calcd. for $[M-Br+CH_3CN]^+$: 411.0884; found 411.0884.

Synthesis of complex 3: To a 25 mL Schlenk tube equipped with a magnetic stirring bar, [**L2**-H_2]Br_2 (50 mg, 0.12 mmol), $[Pd(CH_3CN)_2Cl_2]$ (31 mg, 0.12 mmol), Cs_2CO_3 (47 mg, 0.14 mmol), and KBr (71 mg, 0.6 mmol) were added under inert condition. A solvent mixture of acetonitrile: pyridine (5:1 mL) was then added to that and stirred at room temperature for 15 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was then extracted with dichloromethane and filtered through celite pad to obtain a clear yellow solution which was concentrated. Addition of diethyl ether to this solution induced the precipitation of a compound which was washed with diethyl ether and dried in vacuum to obtain a pale-yellow air stable powder. Single crystals suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. Yield: 54 mg (0.08 mmol, 67%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.92 (s, 1H), 8.88 (d, J = 5.5 Hz, 2H), 8.41 (q, J = 8.6 Hz, 4H), 7.72 (t, J = 7.6 Hz, 1H), 7.34 (s, 1H), 7.33–7.26 (m, 2H), 7.20 (s, 1H), 5.04 (q, J = 7.3 Hz, 2H), 4.75 (q, J = 7.3 Hz, 2H), 1.81 (t, J = 7.3 Hz, 3H), 1.70 (t, J = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 152.7, 150.2, 150.0, 142.6, 138.1, 136.1, 134.5, 133.0, 130.0, 128.0, 124.8, 123.9, 123.2, 122.7, 122.5, 50.6, 47.1, 15.6, 15.0 ppm. ESI-MS: $C_{20}H_{23}N_6PdBr_3$ *m/z* calcd. for $[M-Br-py]^+$: 533.8952; found: 533.8794.

Synthesis of complex 4a/a': To a 25 mL Schlenk tube equipped with a magnetic stirring bar, [**L2**-H_2]Br_2 (50 mg, 0.12 mmol), [Ir(Cp*)Cl_2]$_2$ (48 mg, 0.06 mmol), K_2CO_3 (50 mg, 0.36 mmol), NaOAc (30 mg, 0.36 mmol) and KBr (71 mg, 0.6 mmol for **4a**)/KI (100 mg, 0.6 mmol for **4a'**) were added. Acetonitrile (6 mL) was then added and stirred at 75 ℃ for 24 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The residue obtained was extracted with dichloromethane and filtered through a celite pad to obtain a clear yellow solution. Concentration followed by the addition of diethyl ether resulted in the precipitation of a compound. The precipitate was then washed with diethyl ether and dried in vacuum to obtain a bright yellow air stable powder. Single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. Yield: for **4a** (71 mg, 0.094 mmol, 78%) and for **4a'** (77 mg, 0.096 mmol, 80%). For **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H, $Tz_{C4\text{-}H}$), 9.05 (s, 1H, $Tz_{C5\text{-}H}$), 8.05 (s, 1H), 7.57 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.17 (s, 1H), 5.03 (q, J = 8.0 Hz, 2H), 4.45-4.36 (m, 1H), 4.28-4.20 (m, 1H), 1.83 (s, 15H), 1.78 (d, J = 7.4 Hz, 3H), 1.56 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8, 150.0, 145.7, 132.7, 131.3, 128.7, 128.1, 120.4, 116.0, 111.4, 92.0, 50.2, 45.3, 16.8, 15.1, 10.0 ppm. ESI-MS: $C_{25}H_{32}N_5IrBr_2$ m/z calcd. for $[M\text{-}Br]^+$: 674.1455; found: 674.1472. For **4a'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H, $Tz_{C4\text{-}H}$), 9.08 (s, 1H, $Tz_{C5\text{-}H}$), 8.00 (s, 1H), 7.58 (s, 1H), 7.46 (s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.16 (s, 1H), 4.96 (q, J = 7.4 Hz, 2H), 4.35-4.26 (m, 1H), 4.24-4.16 (m,1H), 1.90 (s, 15H), 1.76 (t, J = 7.3 Hz, 3H), 1.55 (t, J = 7.3 Hz, 3H) ppm. ESI-MS: $C_{25}H_{32}N_5IrI_2$ m/z calcd. for $[M\text{-}I]^+$: 722.1333; found: 722.1321.

Synthesis of complex 4b: To a 25 mL Schlenk tube equipped with magnetic stirring bar, [**L2**-H_2]Br_2 (50 mg, 0.12 mmol), [Rh(Cp*)Cl_2]$_2$ (37 mg, 0.06 mmol), Cs_2CO_3 (59 mg, 0.18 mmol), NaOAc (15 mg, 0.18 mmol) and KBr (71 mg, 0.6 mmol) were added under inert condition. Acetonitrile (6 mL) was then added to that and stirred at 75 °C for 24 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The residue obtained was extracted with dichloromethane and filtered through a celite pad to obtain a clear yellow solution. Concentration followed by the addition of diethyl ether resulted in the precipitation of a compound. The precipitate was washed with diethyl ether and dried in vacuum to obtain a bright yellow air stable powder. Yield: 65 mg (0.098 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H, $Tz_{C4\text{-}H}$), 9.09 (s, 1H, $Tz_{C5\text{-}H}$), 8.12 (d, J = 2.6 Hz, 1H), 7.66 (d, J = 2.3 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 4.99 (q, 2H), 4.47-4.38 (m, 1H), 4.32-4.23 (m, 1H), 1.80 (d, J = 7.3 Hz, 3H), 1.77 (s, 15H), 1.58 (t, J = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 183.2 (d, $^1J_{Rh\text{-}C_{NHC}}$ = 55 Hz), 162.4 (d, $^1J_{Rh\text{-}C_{Ar}}$ = 38 Hz), 149.2, 132.5, 130.8, 129.8, 128.4, 121.5, 116.8, 116.7, 111.9, 98.5, 98.4, 50.2, 45.6, 16.5, 15.0, 10.2, 8.8 ppm. ESI-MS: $C_{25}H_{32}N_5RhBr_2$ *m/z* calcd. for $[M\text{-}Br]^+$: 584.0896; found: 584.0893.

Synthesis of complex 5: To a 25 mL Schlenk tube equipped with magnetic stirring bar, compound **3** (50 mg, 0.07 mmol), $[Pd(CH_3CN)_2Cl_2]$ (18 mg, 0.07 mmol), Cs_2CO_3 (27 mg, 0.08 mmol), and KBr (42 mg, 0.35 mmol) were added. A solvent mixture of dry acetonitrile: pyridine (5:1 mL) was added and stirred at 75 °C for 24 h. The reaction mixture was then cooled and volatiles were removed in vacuo. The residue obtained was extracted with dichloromethane and filtered through a celite pad to obtain a clear orange colored solution. Concentration followed by addition of diethyl ether resulted in the precipitation of a compound. The precipitate was washed with diethyl ether and dried under vacuum to get an orange air stable powder. Single crystals suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. Yield: 57 mg (0.06 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 5.1 Hz, 2H), 8.84 (d, J = 5.3 Hz, 2H), 8.60 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 7.74 (s, 1H), 7.61 (q, J = 8.0 Hz, 2H), 7.32 (s, 1H), 7.23–7.17 (m, 5H), 4.77 (d, J = 14.6 Hz, 2H), 4.50 (q, J = 7.4 Hz, 2H), 1.72 (t, J = 7.4 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 152.8, 152.8, 152.3, 152.2, 150.6, 141.2, 140.4, 139.6, 137.7, 137.6, 131.5, 127.5, 126.6, 124.6, 123.4, 121.9, 48.3, 46.9, 15.7, 14.3 ppm. ESI-MS: $C_{25}H_{27}N_7Pd_2Br_4$, *m/z* calcd. for $[M\text{-}2py\text{-}Br]^+$: 719.7047, found: 719.7049; calcd. for $[M\text{-}2py\text{-}Br+CH_3CN]^+$: 760.7354, found: 760.7320.

Synthesis of complex 6: To a 25 mL Schlenk tube equipped with magnetic stirring bar, compound **3** (50 mg, 0.07 mmol) and Ag_2O (9.7 mg, 0.042 mmol) were added. Dry dichloromethane (5 mL) was then added to it and stirred for 12 h under the exclusion of light. After the specified time, the reaction mixture was filtered through a small pad of celite and $[Au(SMe_2)Cl]$ (21 mg, 0.07 mmol) was added to the collected filtrate and stirred for further 12 h under exclusion of light. The solution was then filtered through a celite pad and concentrated to ~1 mL. Addition of diethyl ether (3 mL) resulted in the formation of precipitate which was further washed with diethyl ether (3 x 3 mL). All the volatiles were dried in high vacuum which provided a pale-yellow air and moisture stable powder. Suitable single crystals were grown for X-ray crystallographic analysis *via* slow diffusion of diethyl ether into a saturated solution of the compound in DCM. Yield: 34 mg (0.041 mmol, 58%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.88

(d, *J* = 4.9 Hz, 2H), 8.36 (t, *J* = 7.3 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H), 7.74 (2H), 7.35 (t, *J* = 6.7 Hz, 2H), 7.30 (s, 1H), 7.18 (s, 1H), 4.77 (q, *J* = 7.0, 2H), 4.58 (q, *J* = 7.0 Hz, 2H), 1.75–1.68 (m, 6H) ppm. ESI-MS: M = $C_{20}H_{22}N_6PdAuBr_2Cl$, *m/z* calcd. For $[M\text{-}Cl\text{-}py]^+$: 729.8540, found: 729.8502; calcd. For $[M\text{-}Cl\text{-}py+CH_3CN]^+$: 770.8806, found: 770.8759; calcd. For $[M\text{-}Cl\text{-}py+2CH_3CN]^+$: 811.9072, found: 811.9022.

Synthesis of complex 7: To a 25 mL Schlenk tube equipped with magnetic stirring bar, compound **4a** (50 mg, 0.07 mmol), $[Pd(CH_3CN)_2Cl_2]$ (18 mg, 0.07 mmol), Cs_2CO_3 (27 mg, 0.08 mmol), and KBr (42 mg, 0.35 mmol) were added. A solvent mixture of acetonitrile: pyridine (5:1 mL) was then added and stirred at 75 ℃ for 24 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was extracted with dichloromethane and filtered through a celite pad to obtain a clear orange solution which was further concentrated to ~1 mL. Addition of diethyl ether (3 mL) resulted in the formation of precipitate which was washed with diethyl ether and dried in vacuum to obtain an orange air stable powder. Single crystals suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. Yield: 46 mg (0.045 mmol, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, *J* = 5.0 Hz, 2H), 8.03 (s, 1H), 7.93 (s, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.40 (s, 1H), 7.36–7.33 (m, 2H), 7.25 (s, 2H), 7.09 (s, 1H), 5.07 (q, *J* = 7.4 Hz, 2H), 4.45–4.38 (m, 1H), 4.27-4.19 (m, 1H), 1.88 (t, *J* = 7.3 Hz, 3H), 1.85 (s, 15H), 1.55 (d, *J* = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.7, 152.9, 148.7, 144.8, 137.8, 136.3, 132.4, 129.2, 128.6, 124.6, 119.9, 115.4, 115.2, 110.8, 91.8, 51.1, 45.3, 16.8, 15.5, 10.0 ppm. ESI-MS: $C_{30}H_{36}N_6IrPdBr_3$, *m/z* calcd. for $[M\text{-}Br\text{-}py+2CH_3CN]^+$: 942.0123, found: 942.0142; calcd. for $[M\text{-}Br\text{-}py+CH_3CN]^+$: 900.9857 found: 900.9872.

Synthesis of complex 8: To a 25 mL Schlenk tube equipped with a magnetic stirring bar, compound **4a** (50 mg, 0.07 mmol) and Ag_2O (9.7 mg, 0.042 mmol) were added. Dry dichloromethane (5 mL) was then added to it and stirred for 12 h under the exclusion of light. After the specified time, the reaction mixture was filtered through a small pad of celite and $[Au(SMe_2)Cl]$ (21 mg, 0.07 mmol) was added to the collected filtrate and stirred for further 12 h under the exclusion of light. The solution was then filtered through a celite pad and concentrated to ~1 mL. Addition of diethyl ether (3 mL) resulted in the formation of a pale-yellow precipitate in decent yield. Analytically pure sample was obtained after the crystallization *via* slow diffusion of diethyl ether into saturated solution of the compound in DCM. The compound exists as a dimer in solution as indicated by the integration in ^{1}H NMR as well as two sets of signals in the $^{13}C\{^1H\}$ NMR spectra[3] however, the single crystal analysis of the complex shows a monomeric structure. Yield: 39 mg (0.043 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.98 (s, 1H), 7.90 (d, J = 4.3 Hz, 2H), 7.43 (s, 2H), 7.28 (d, J = 4.1 Hz, 4H), 7.11 (s, 2H), 4.73–4.64 (m, 4H), 4.47 (d, J = 13.3 Hz, 1H), 4.43–4.39 (m, 1H), 4.28–4.22 (m, 2H), 1.84 (s, 15H), 1.82 (s, 15H), 1.72 (t, J = 7.2 Hz, 6H), 1.56 (t, J = 7.3 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.3, 165.7, 156.7, 149.2, 149.0, 146.0, 145.2, 132.2, 132.0, 131.3, 128.9, 128.4, 120.3, 120.1, 115.6, 115.6, 115.5, 115.4, 111.1, 111.0, 91.9, 91.7, 51.1, 45.3, 17.1, 16.8, 16.0, 15.4, 10.0, 9.8 ppm. ESI-MS: $C_{25}H_{31}N_5IrAuBrCl$ m/z calcd. for $[M\text{-}Br+CH_3CN]^+$: 867.1821, found: 867.1790; calcd. for $[M\text{-}Cl+CH_3CN]^+$: 911.1308, found: 911.1284; calcd. for $[M\text{-}Br]^+$: 826.1555, found: 826.1530.

Synthesis of complex 9: To a 25 mL Schlenk tube equipped with magnetic stirring bar, compound **4b** (50 mg, 0.075 mmol), $[Pd(CH_3CN)_2Cl_2]$ (19.5 mg, 0.075 mmol), Cs_2CO_3 (29 mg, 0.09 mmol), and KBr (45 mg, 0.375 mmol) were added. A solvent mixture of acetonitrile: pyridine (5:1 mL) was then added and stirred at 80 ℃ for 24 h. After that, the reaction mixture was cooled and volatiles were removed in vacuo. The obtained residue was extracted with dichloromethane and filtered through a celite pad to obtain a clear orange solution which was further concentrated to ~1 mL. Addition of diethyl ether (3 mL) resulted in the formation of a precipitate which was washed with diethyl ether and dried in vacuum to obtain a yellow air stable powder. Analytically pure sample was obtained by column chromatography of the crude product using DCM: methanol as eluent. Yield: 46 mg (0.05 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, J = 4.9 Hz, 2H), 8.09 (d, J = 2.4 Hz, 1H), 7.93 (s, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 7.36–7.33 (m, 2H), 7.27 (1H), 7.18 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 5.08 (q, 2H), 4.46-4.39 (m, 1H), 4.30-4.23 (m, 1H), 1.88 (t, J = 7.3 Hz, 3H), 1.78 (s, 15H), 1.57 (t, J = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 183.3 (d, $^1J_{Rh\text{-}C_{NHC}}$ = 55 Hz), 161.7 (d, $^1J_{Rh\text{-}C_{Ar}}$ = 36 Hz), 152.9, 148.0, 137.8, 136.5, 131.9, 129.9, 129.2, 124.6, 120.7, 116.0, 115.8, 111.2, 98.3, 98.2, 51.1, 45.5, 16.6, 15.5, 10.2 ppm. $C_{30}H_{36}N_6RhPdBr_3$, m/z calcd. for $[M\text{-}Br\text{-}py+2CH_3CN]^+$: 851.9560, found: 851.9538; calcd. for $[M\text{-}Br\text{-}py+CH_3CN]^+$: 810.9294, found: 810.9277; calcd. for $[M\text{-}Br\text{-}py]^+$: 769.9027 found: 769.9012.

NMR spectra of the isolated compounds

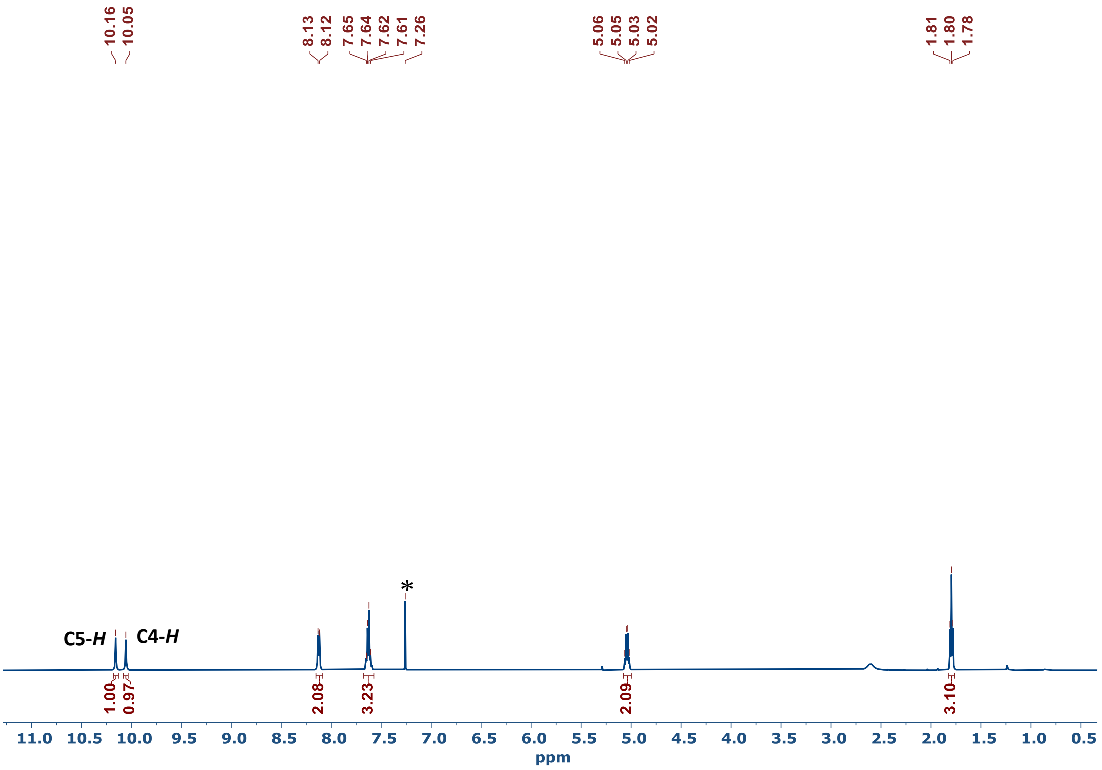


Figure S1. ^{1}H NMR spectrum of [**L1**-H]Br in $CDCl_3$ (*).

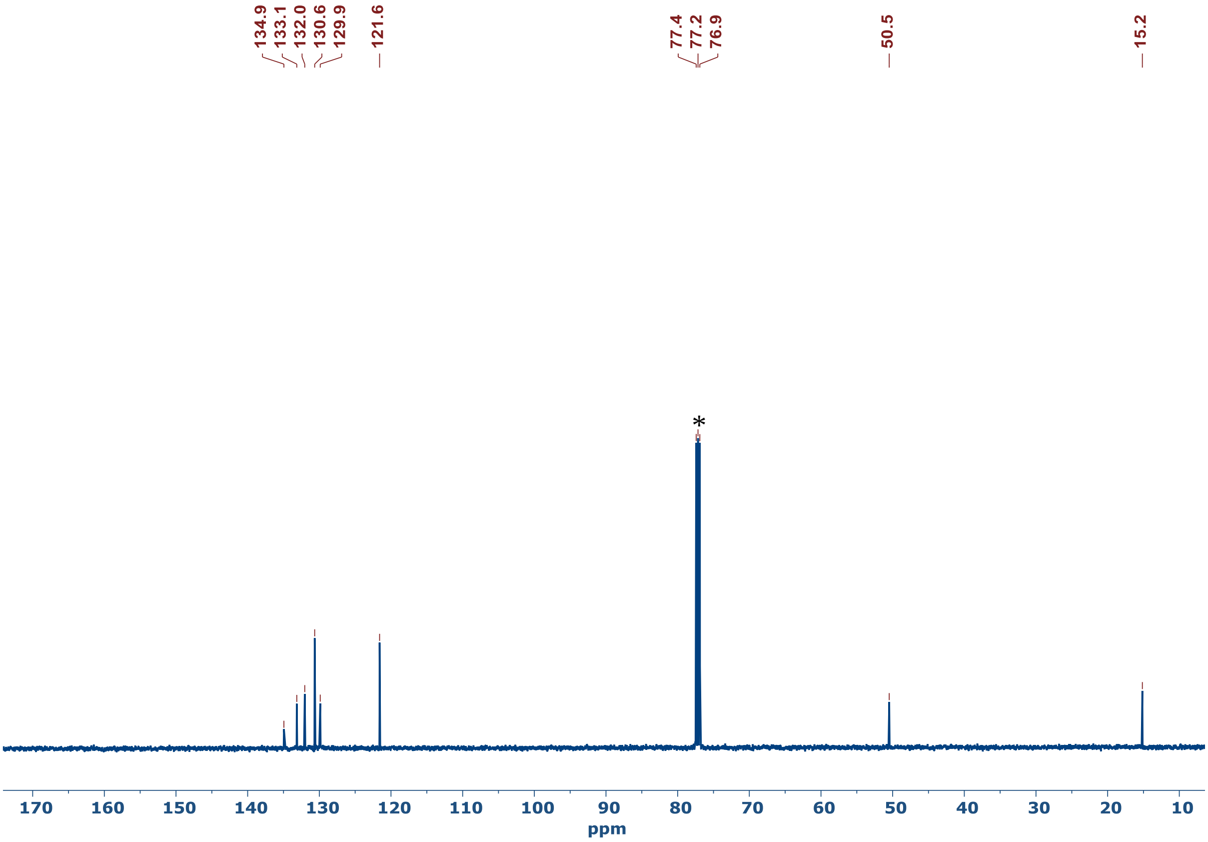


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of [**L1**-H]Br in $CDCl_3$ (*).

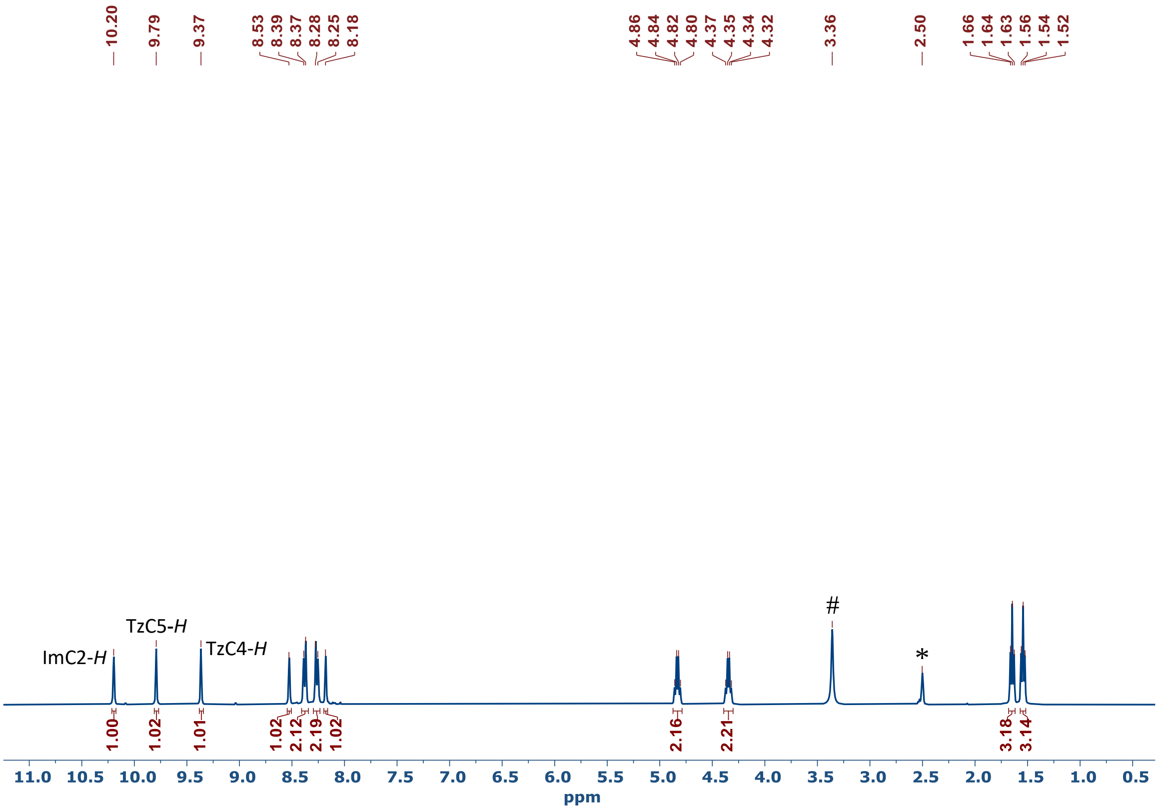


Figure S3. ^{1}H NMR spectrum of [**L2**-H_2]Br_2 in DMSO-d_6 (*). # represents the solvent impurity of water in DMSO-d_6.

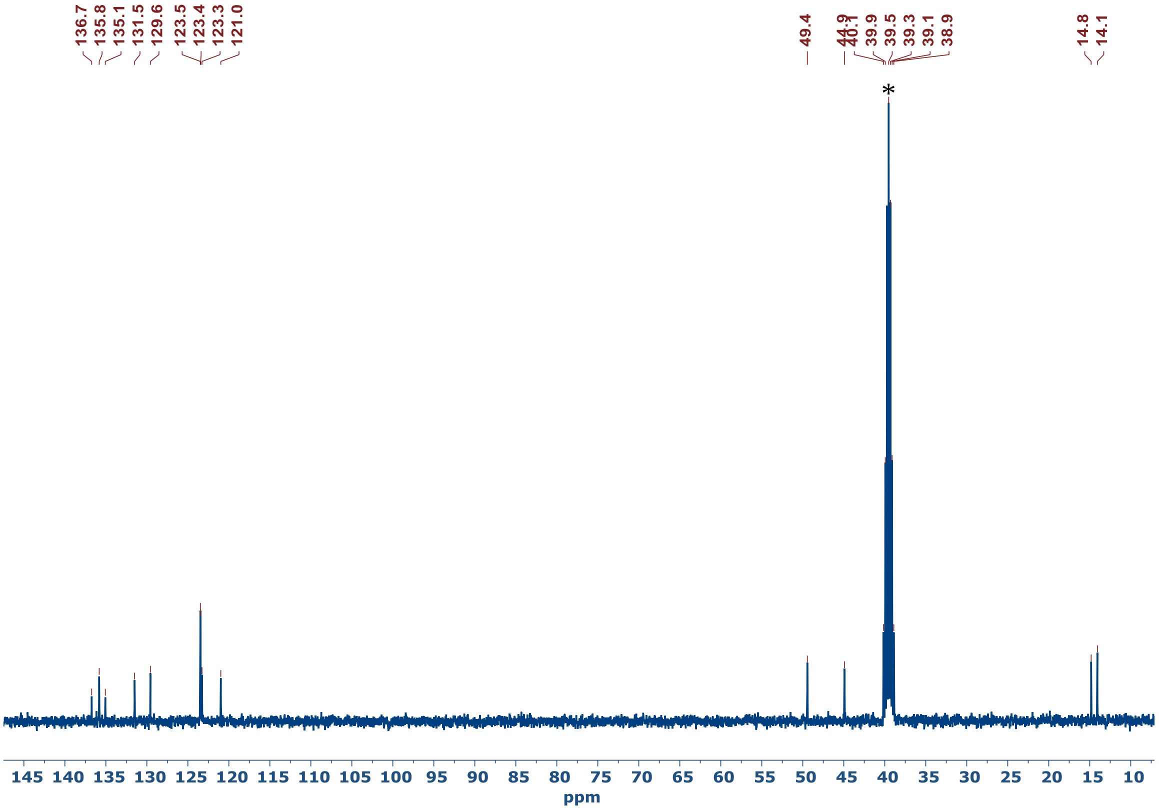


Figure S4. ^{13}C{^{1}H} NMR spectrum of [**L2**-H_2]Br_2 in DMSO-d_6 (*).

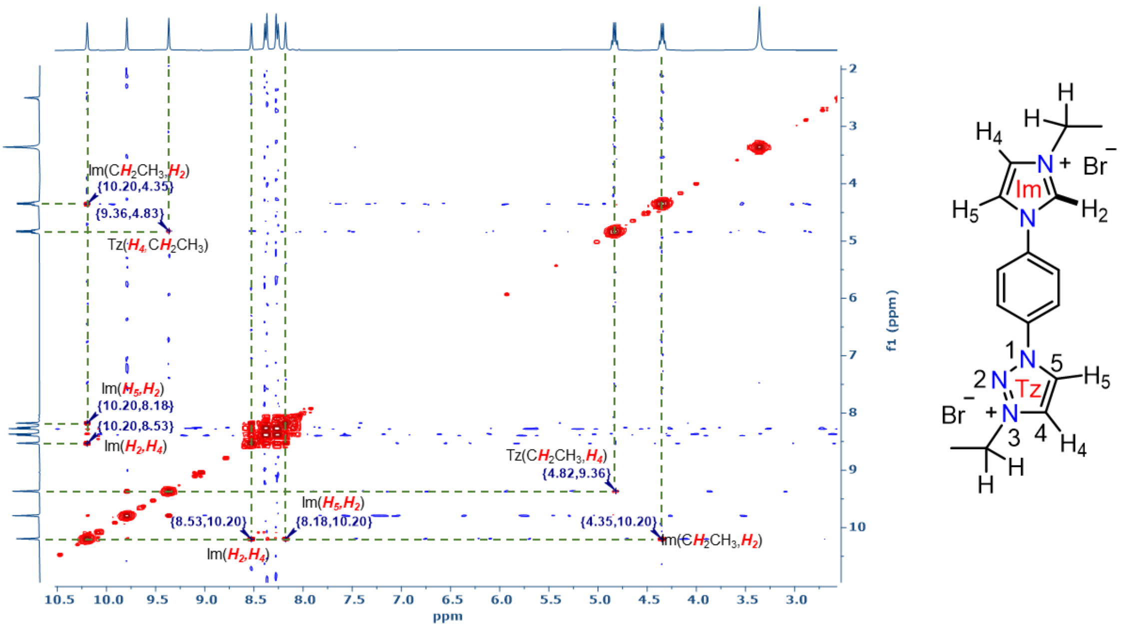


Figure S5. Selected portion of ^{1}H-^{1}H COSY spectrum of [**L2**-H$_2$]Br$_2$ in DMSO-d_6.

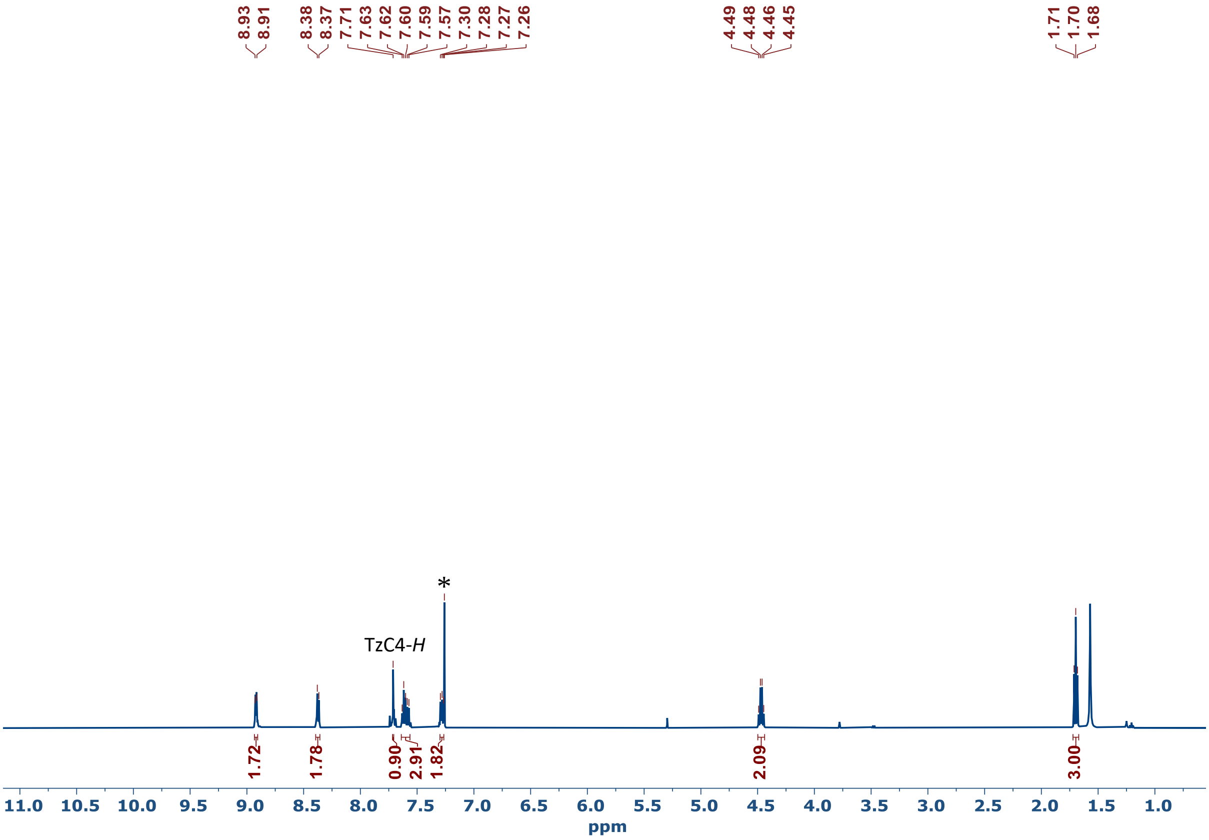


Figure S6. ^{1}H NMR spectrum of complex **1** in CDCl$_3$ (*).

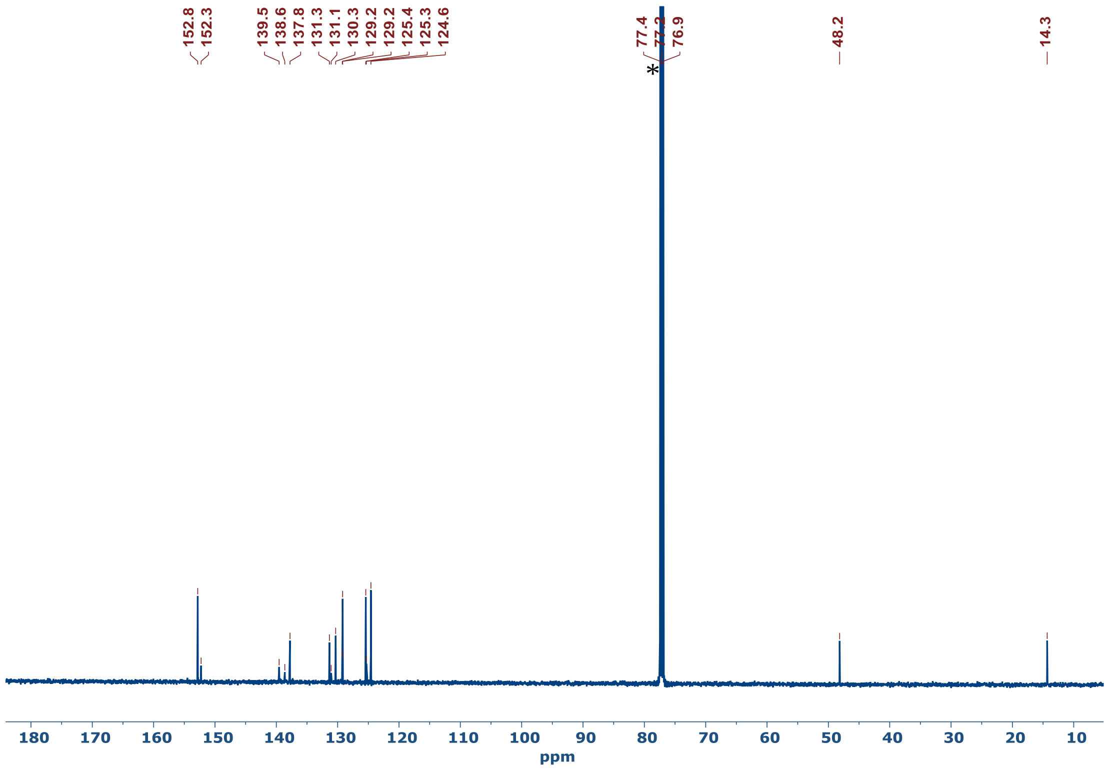


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$ (*).

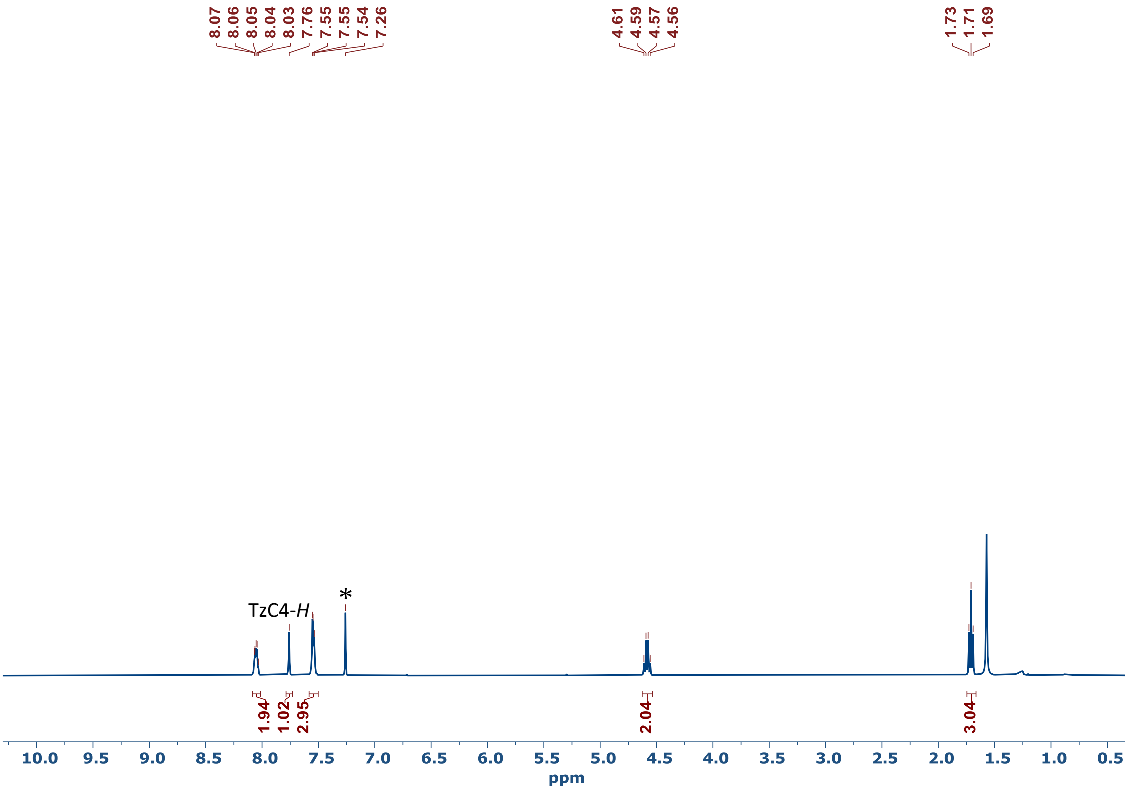


Figure S8. ^{1}H NMR spectrum of complex **2** in $CDCl_3$ (*).

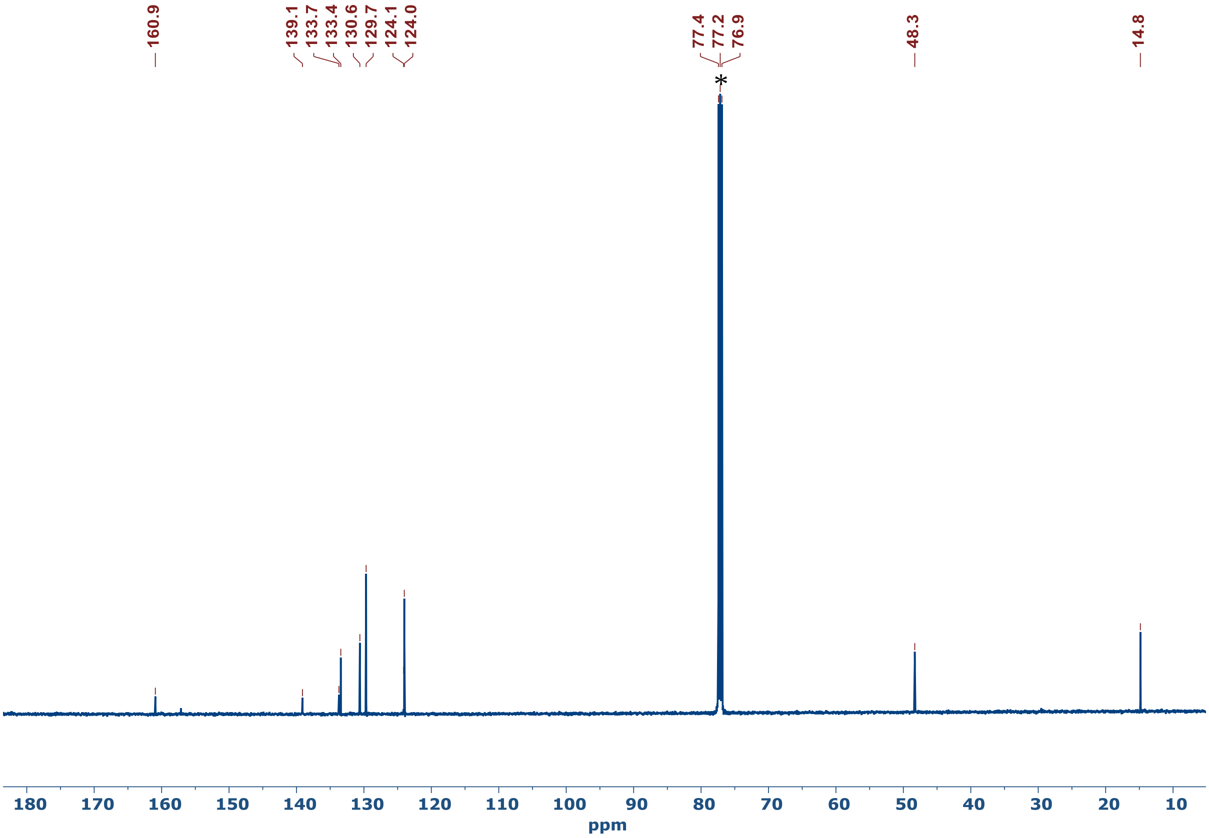


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$ (*).

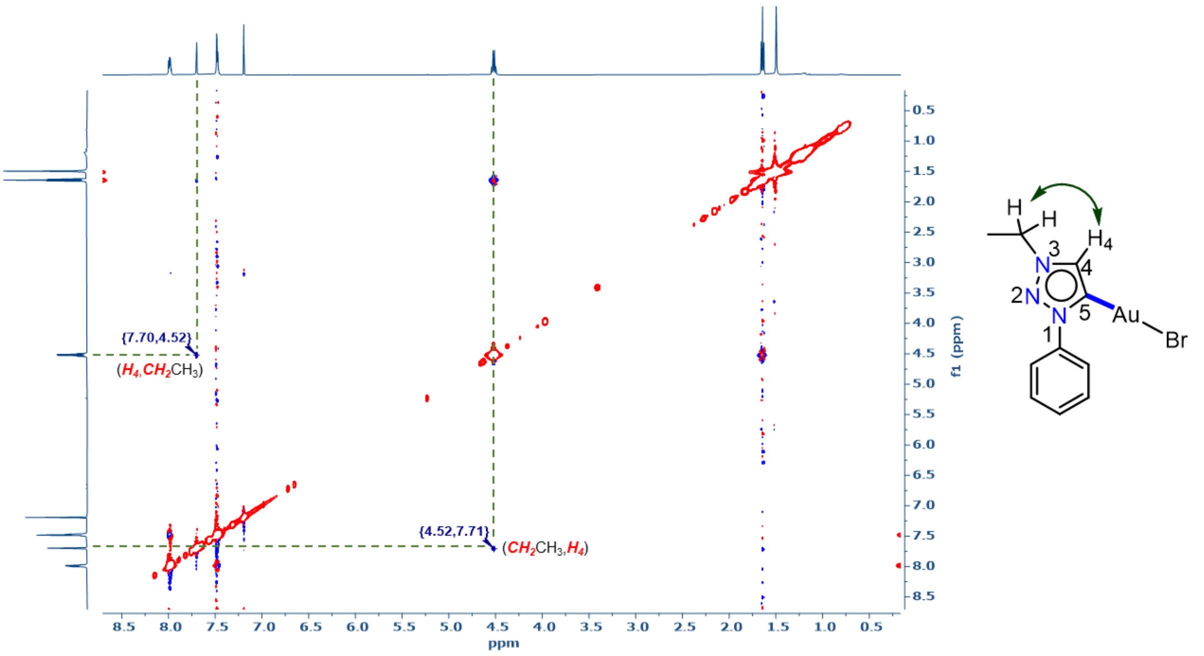


Figure S10. ^{1}H-^{1}H NOESY NMR spectrum of complex **2** in $CDCl_3$.

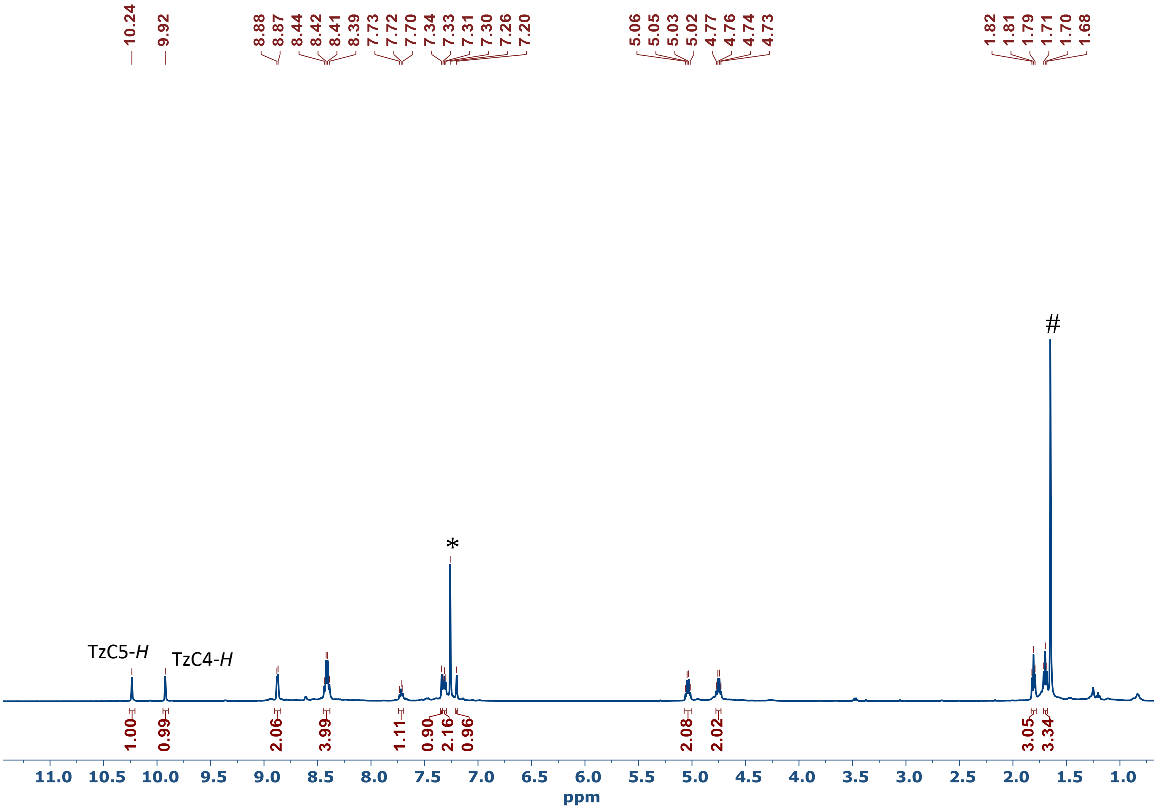


Figure S11. ^{1}H NMR spectrum of complex **3** in $CDCl_3$ (*). # represents the solvent impurity of water in $CDCl_3$.

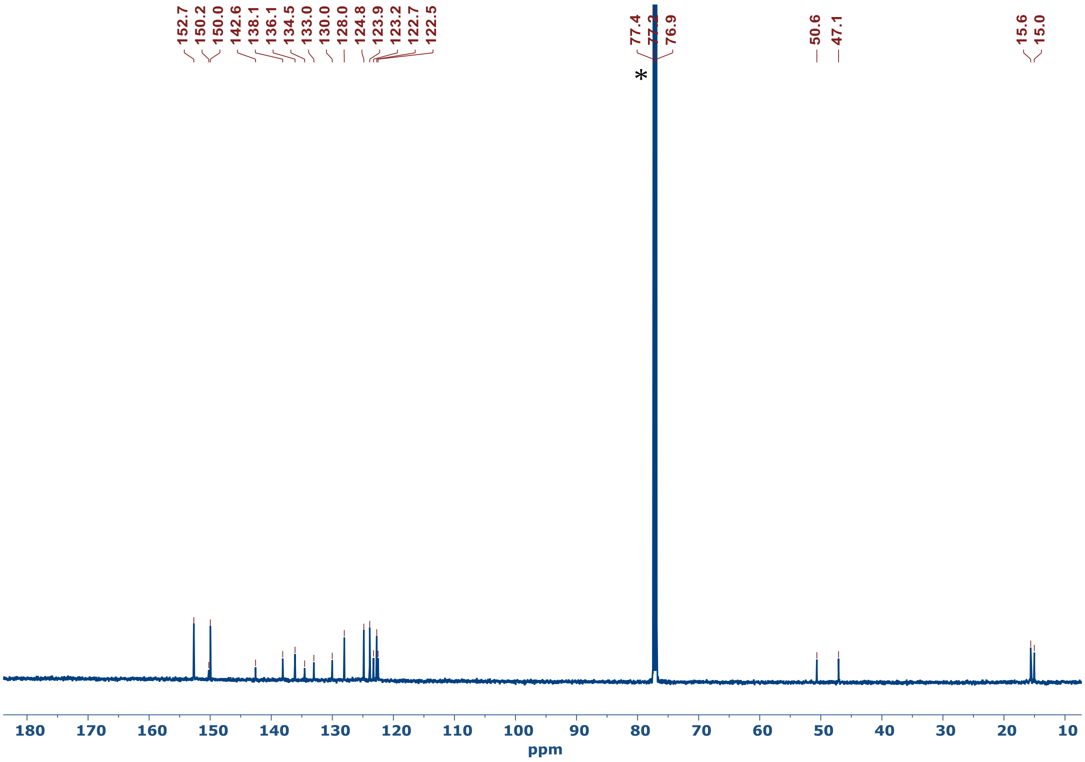


Figure S12. $^{13}C\{^1H\}$ NMR spectrum of complex **3** in $CDCl_3$ (*).

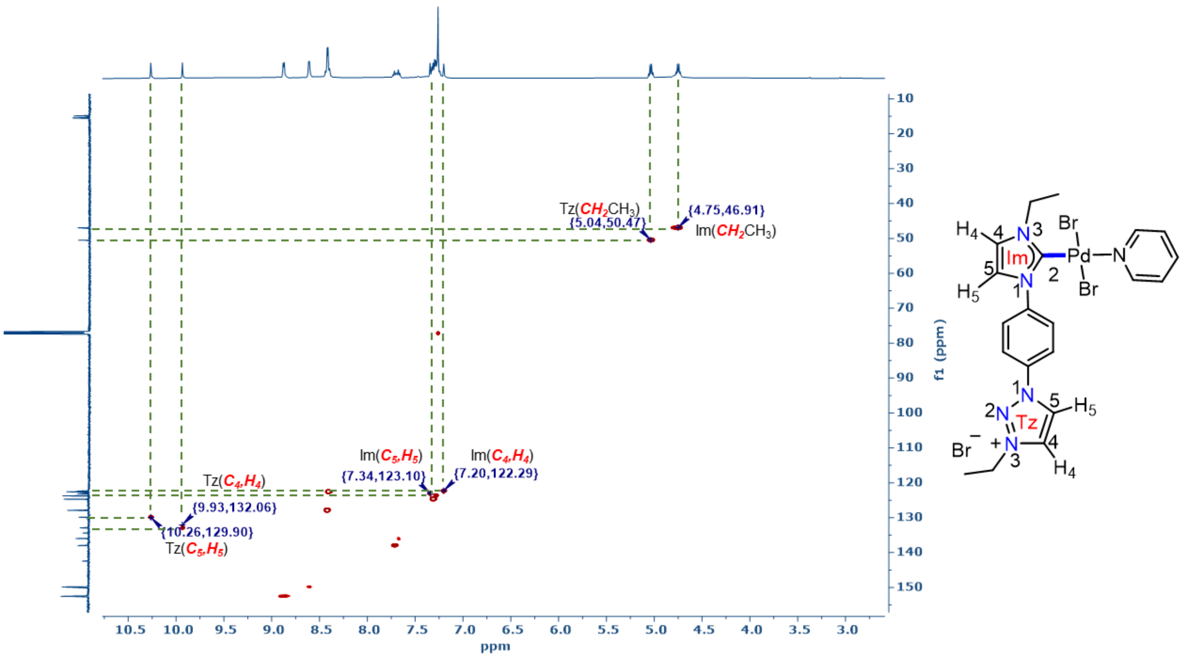


Figure S13. Selected portion of ^{1}H-^{13}C{^{1}H} HSQC NMR spectrum of complex **3** in $CDCl_3$.

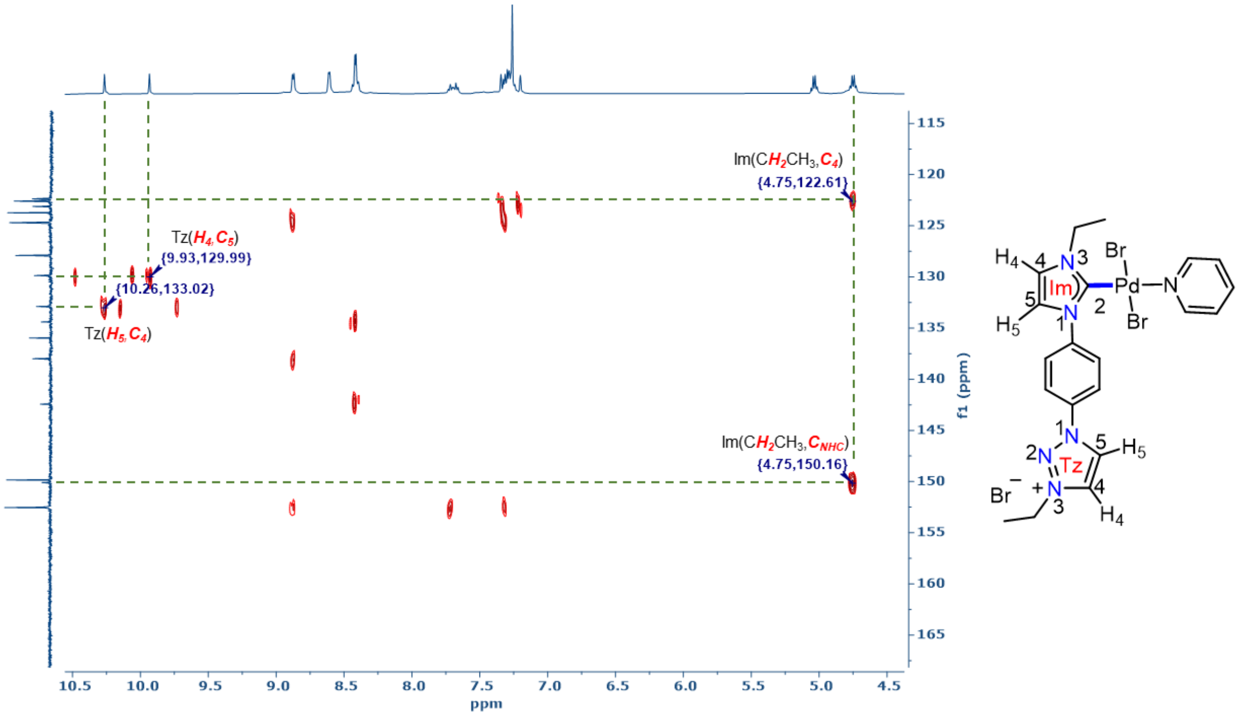


Figure S14. Selected region of ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum of complex **3** in $CDCl_3$.

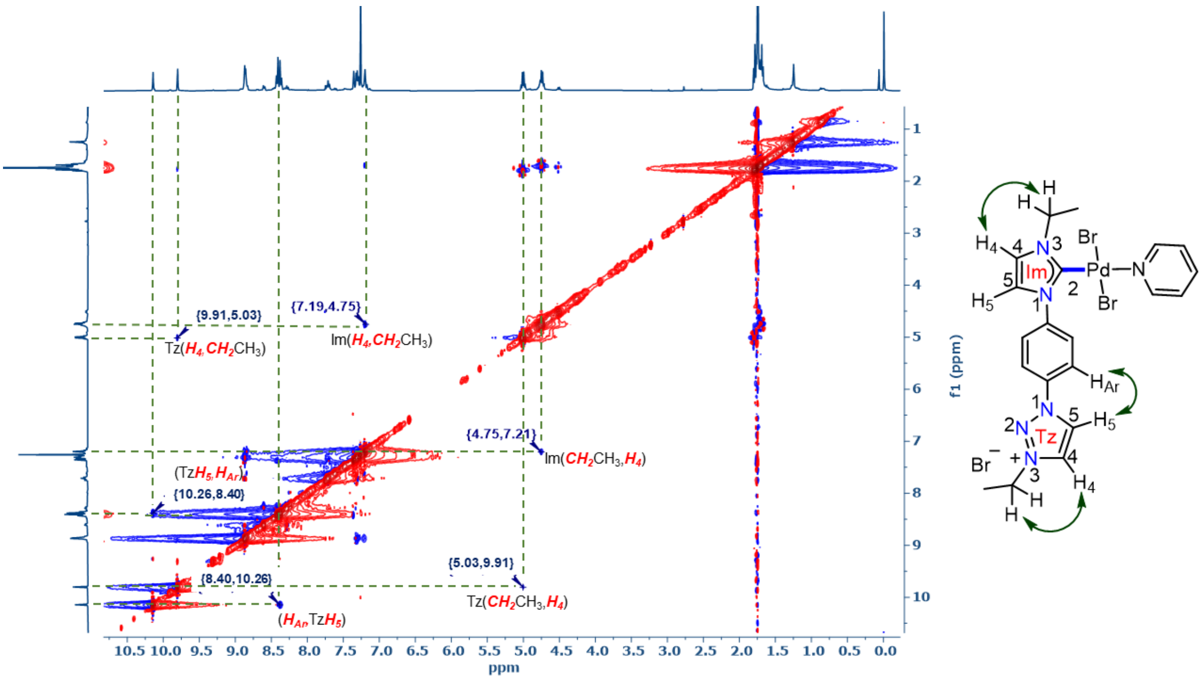


Figure S15. ^{1}H-^{1}H NOESY NMR spectrum of complex **3** in $CDCl_3$.

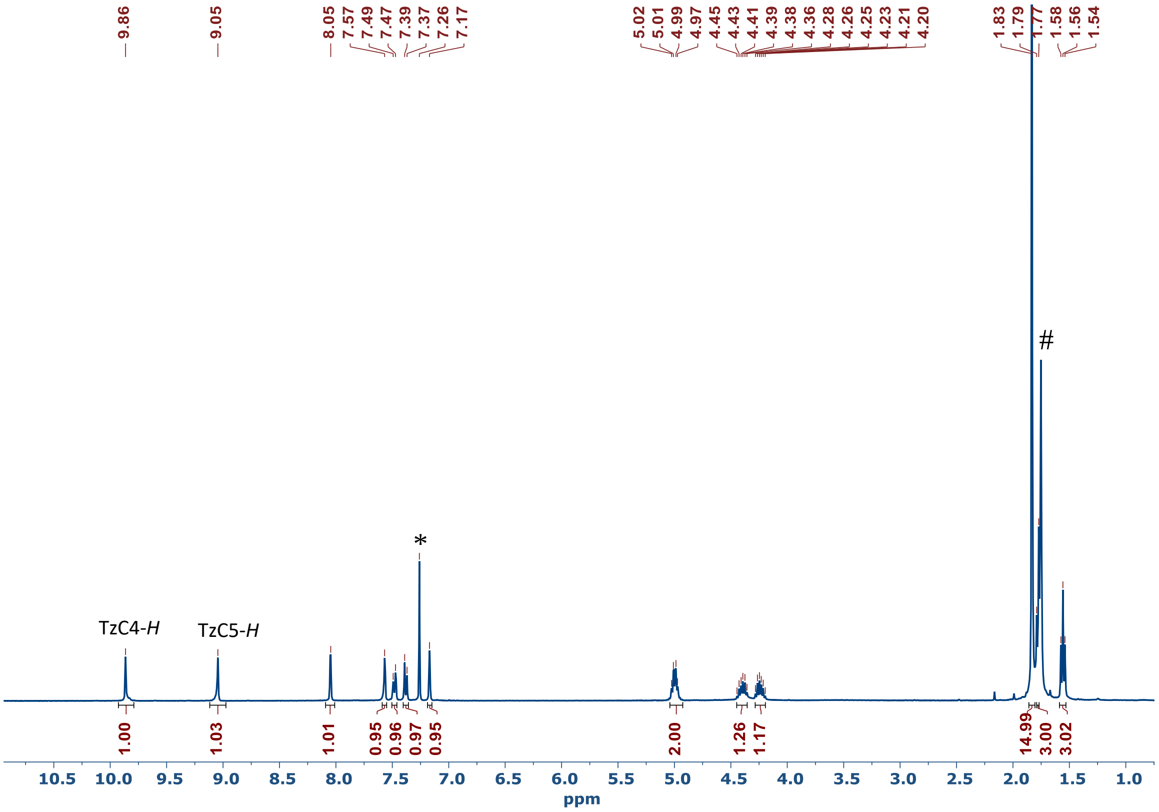


Figure S16. ^{1}H NMR spectrum of complex **4a** in $CDCl_3$ (*). # represents the solvent impurity of water in $CDCl_3$.

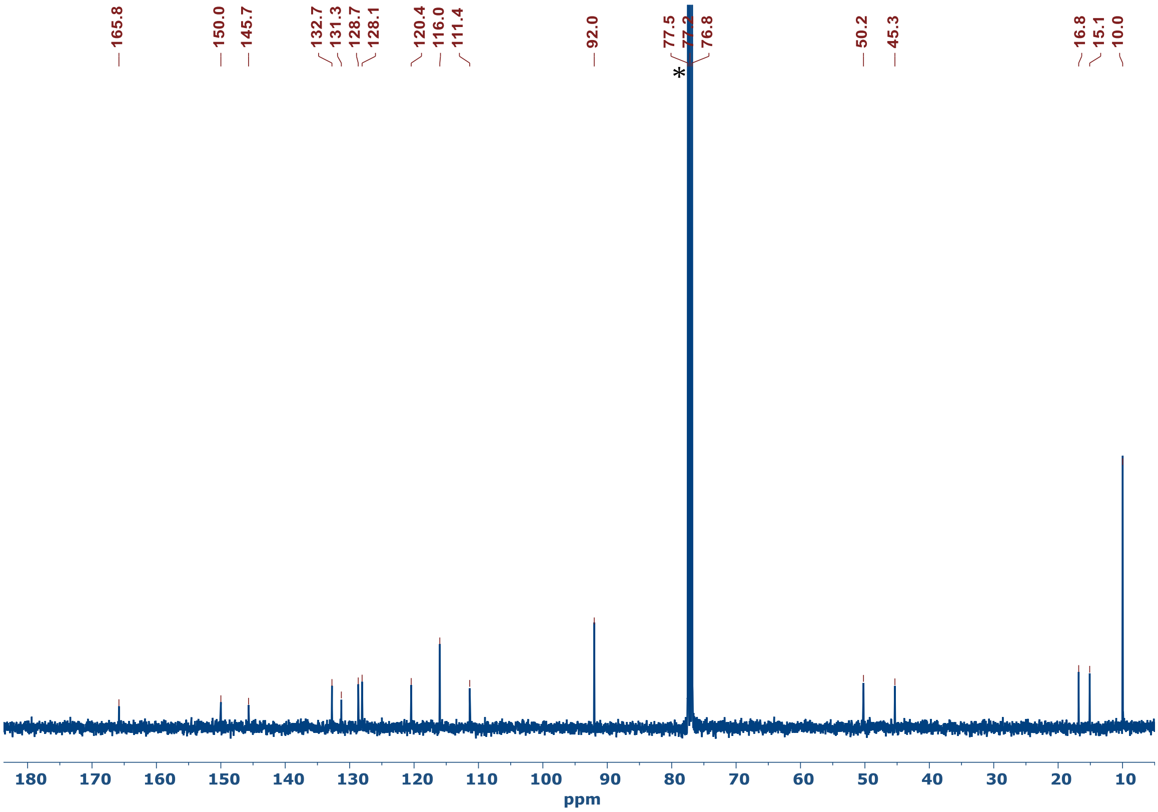


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of complex **4a** in $CDCl_3$ (*).

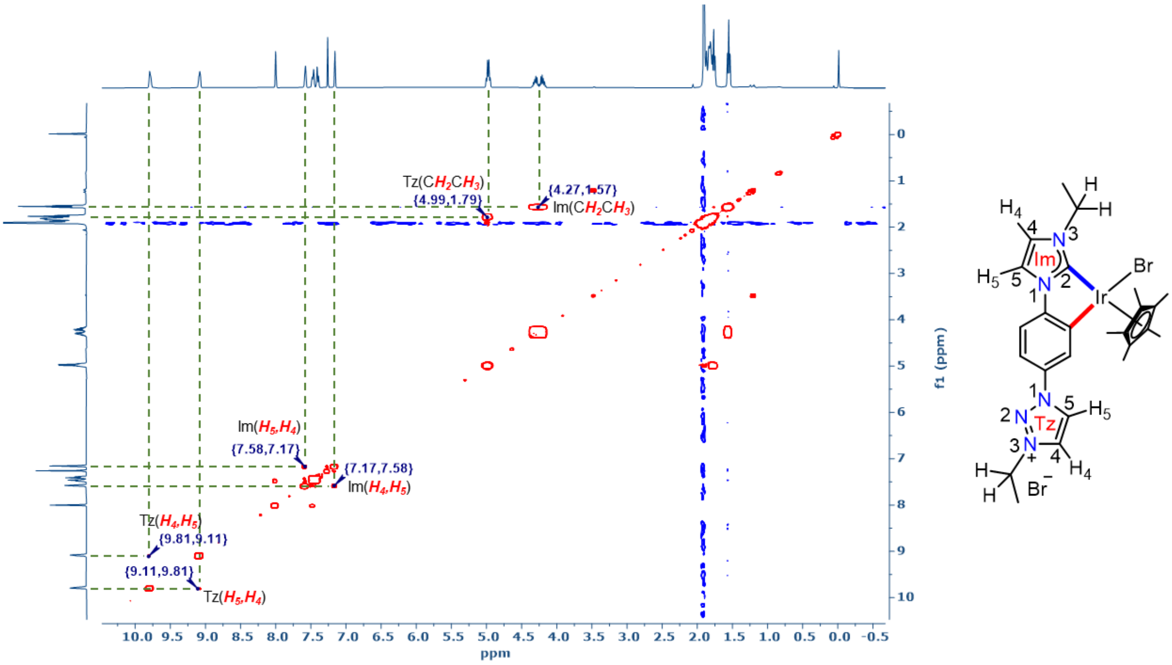


Figure S18. ^{1}H-^{1}H COSY NMR spectrum of complex **4a** in $CDCl_3$.

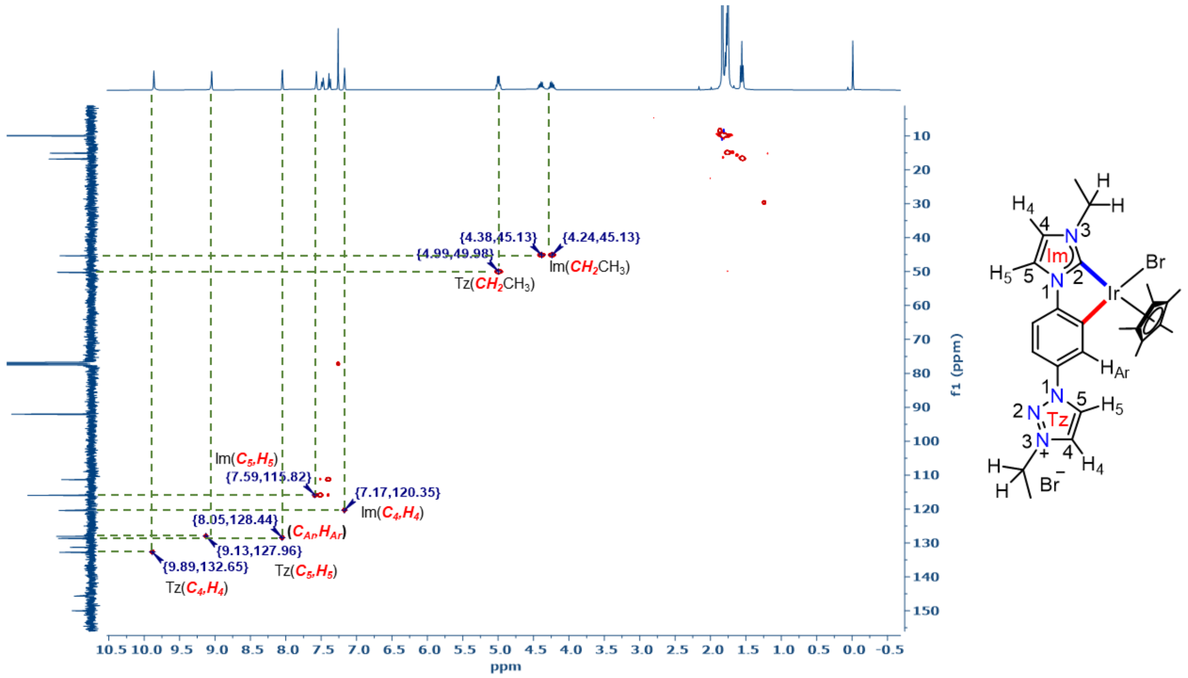


Figure S19. ^{1}H-^{13}C{^{1}H} HSQC NMR spectrum of complex **4a** in CDCl$_3$.

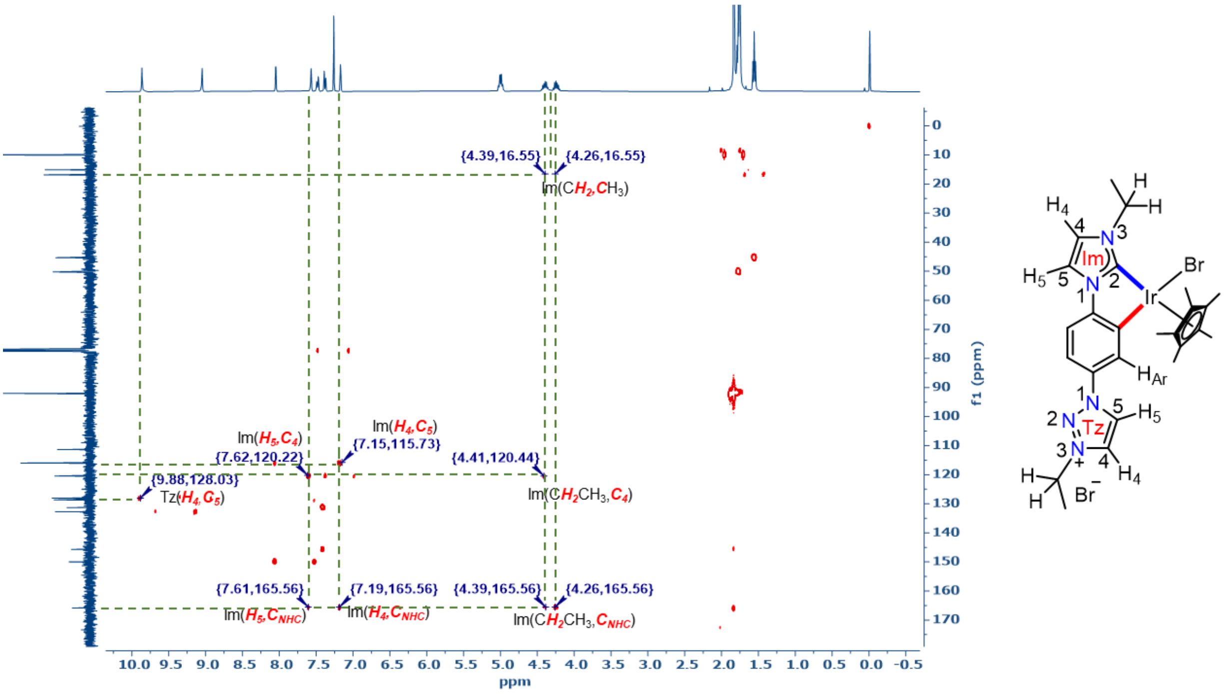


Figure S20. ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum of complex **4a** in CDCl$_3$.

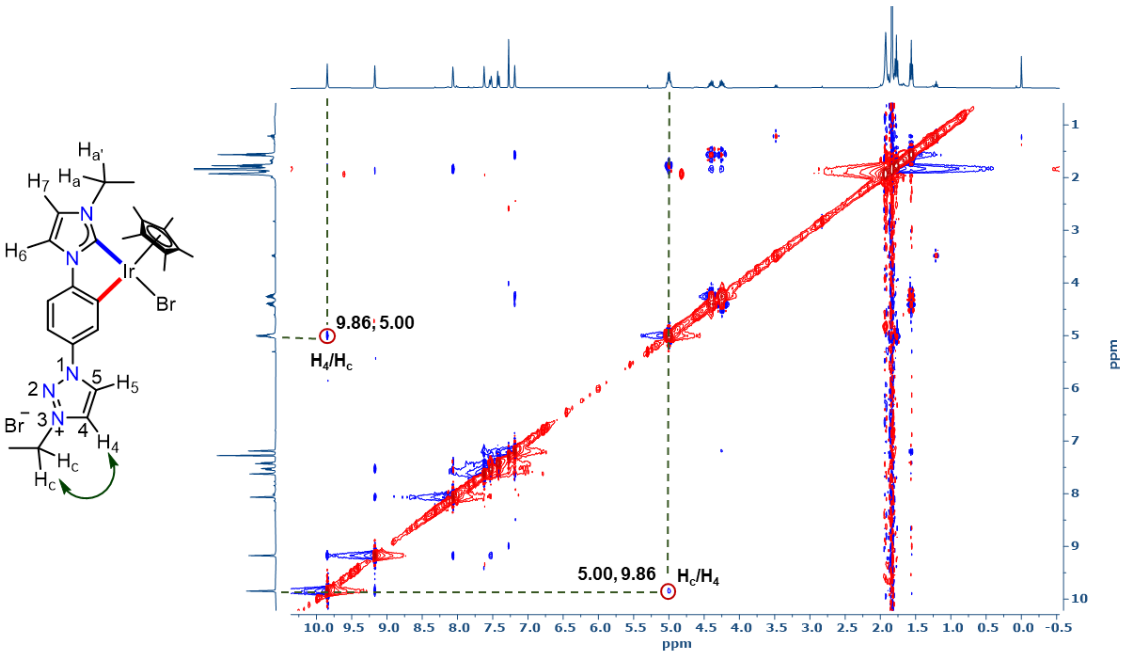


Figure S21. ^{1}H-^{1}H NOESY NMR spectrum of complex **4a** in CDCl$_3$.

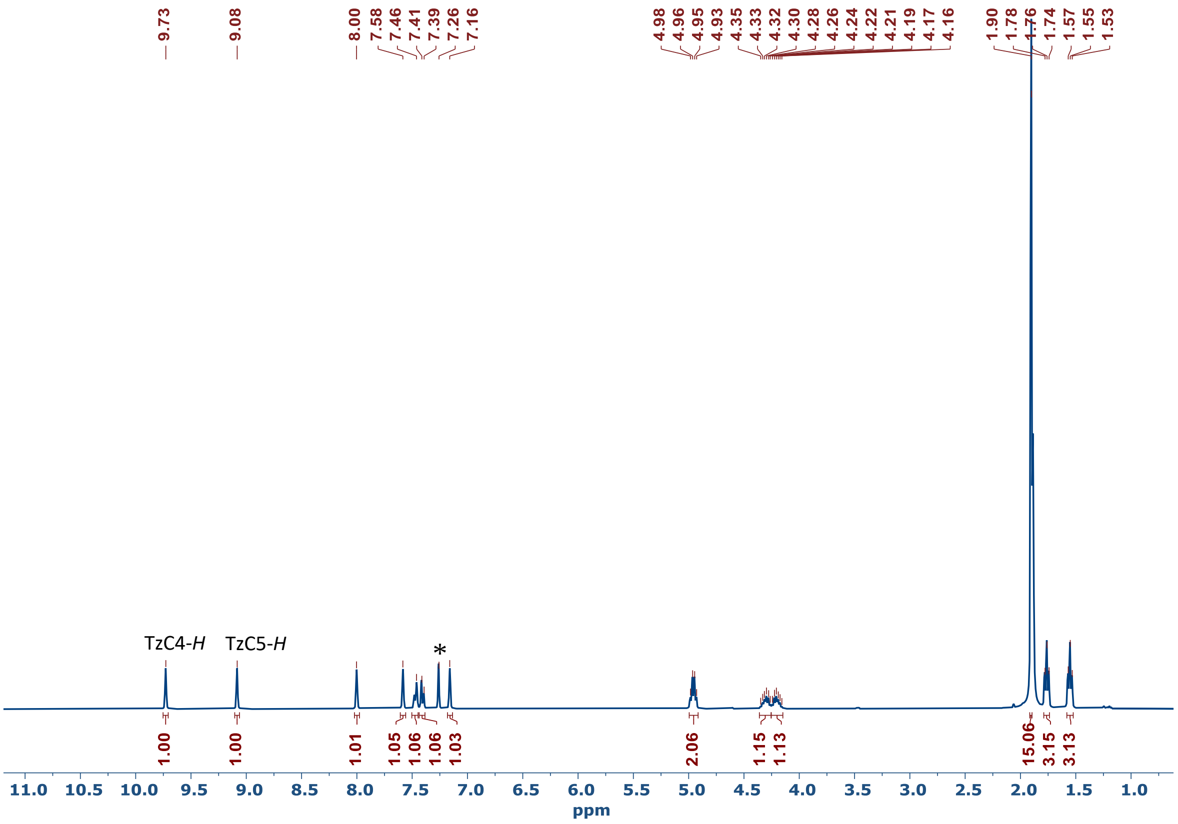


Figure S22. ^{1}H NMR spectrum of complex **4a’** in CDCl$_3$ (*).

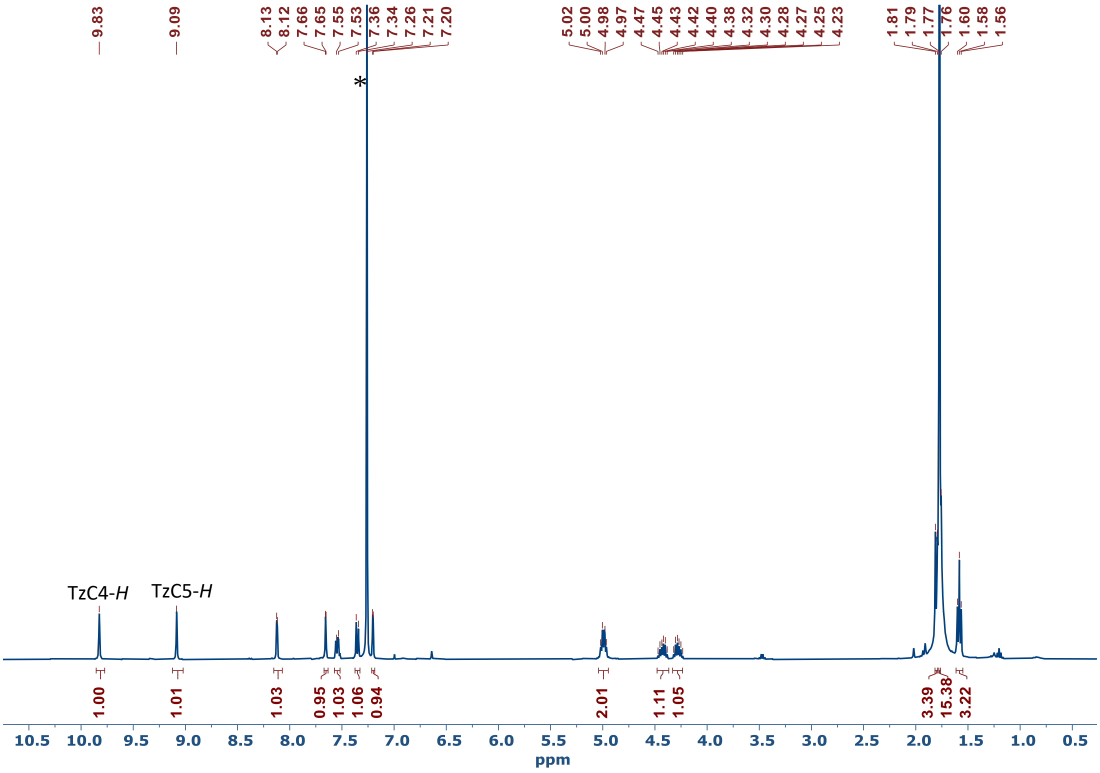


Figure S23. ^{1}H NMR spectrum of complex **4b** in CDCl$_3$ (*).

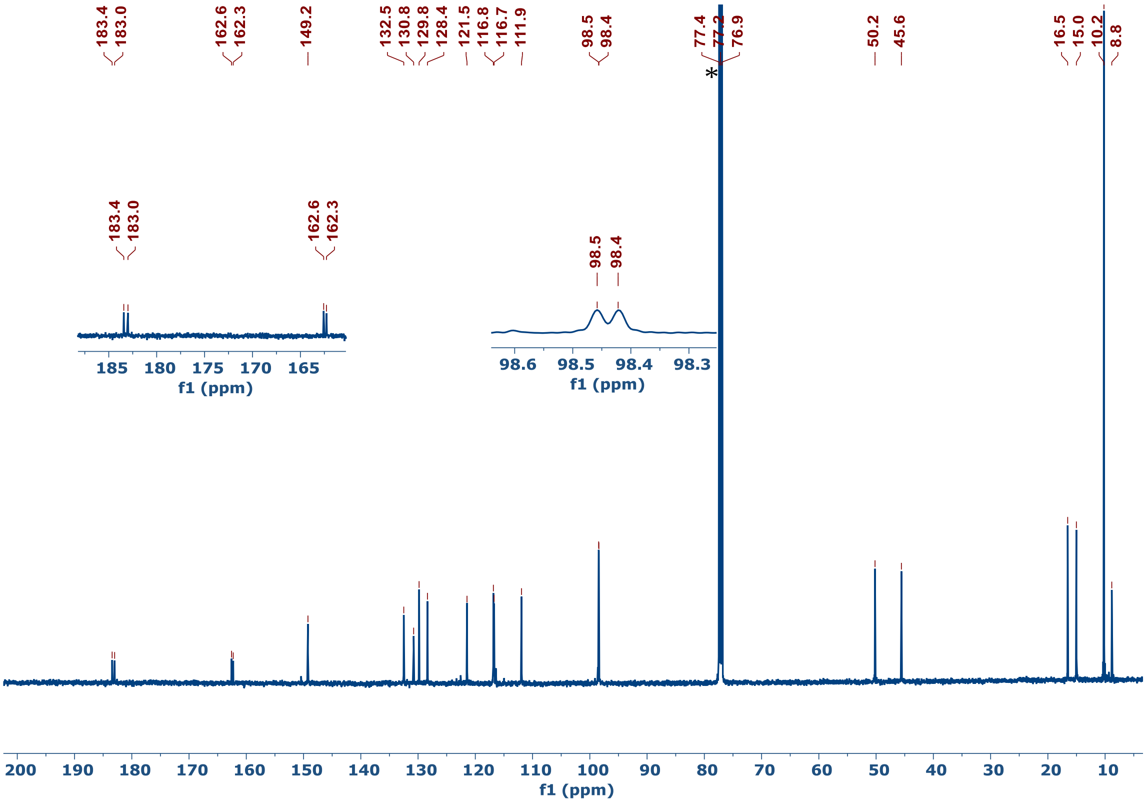


Figure S24. ^{13}C{^{1}H} NMR spectrum of complex **4b** in CDCl$_3$ (*).

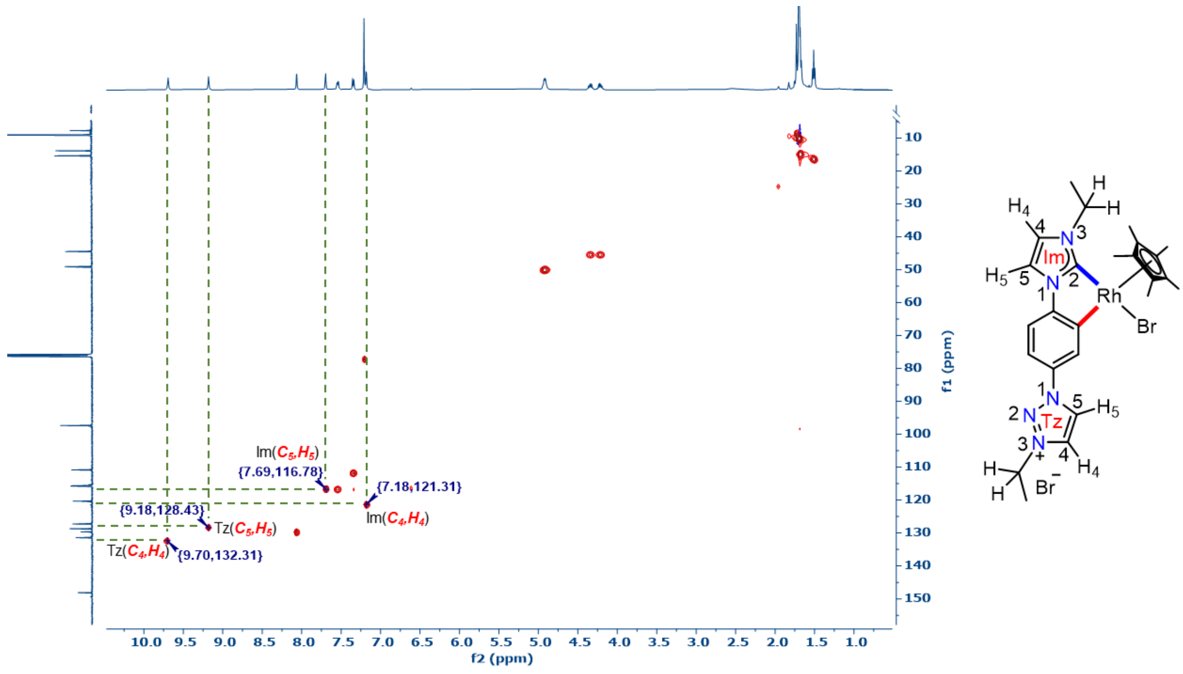


Figure S25. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR spectrum of complex **4b** in $CDCl_3$.

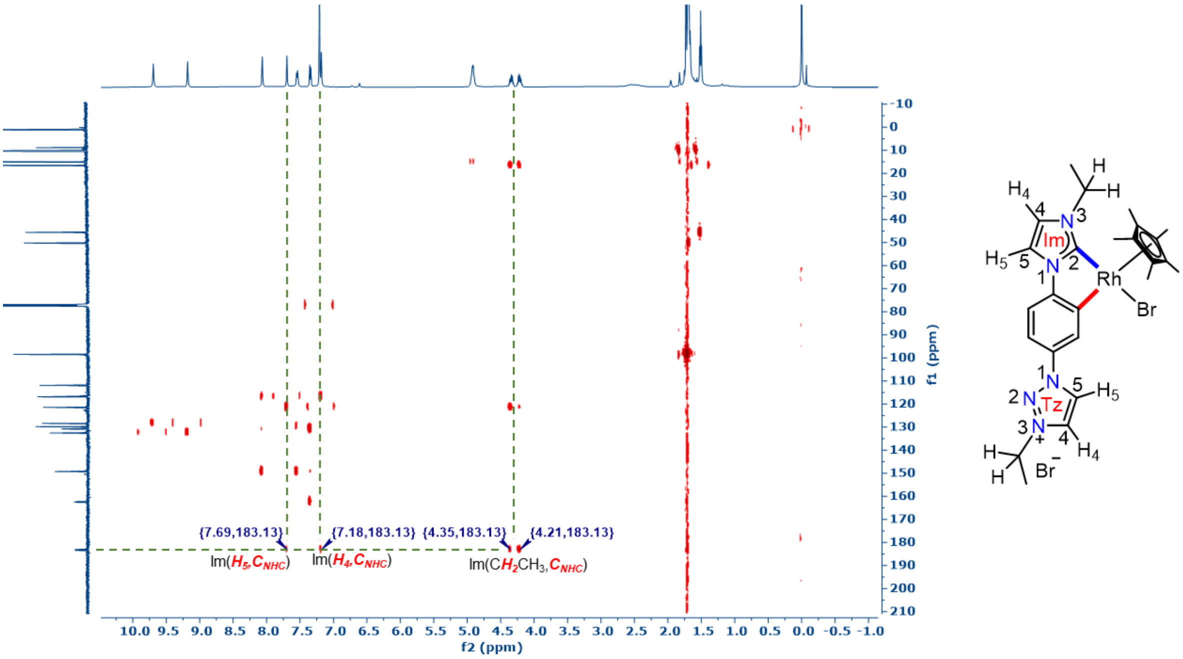


Figure S26. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR spectrum of complex **4b** in $CDCl_3$.

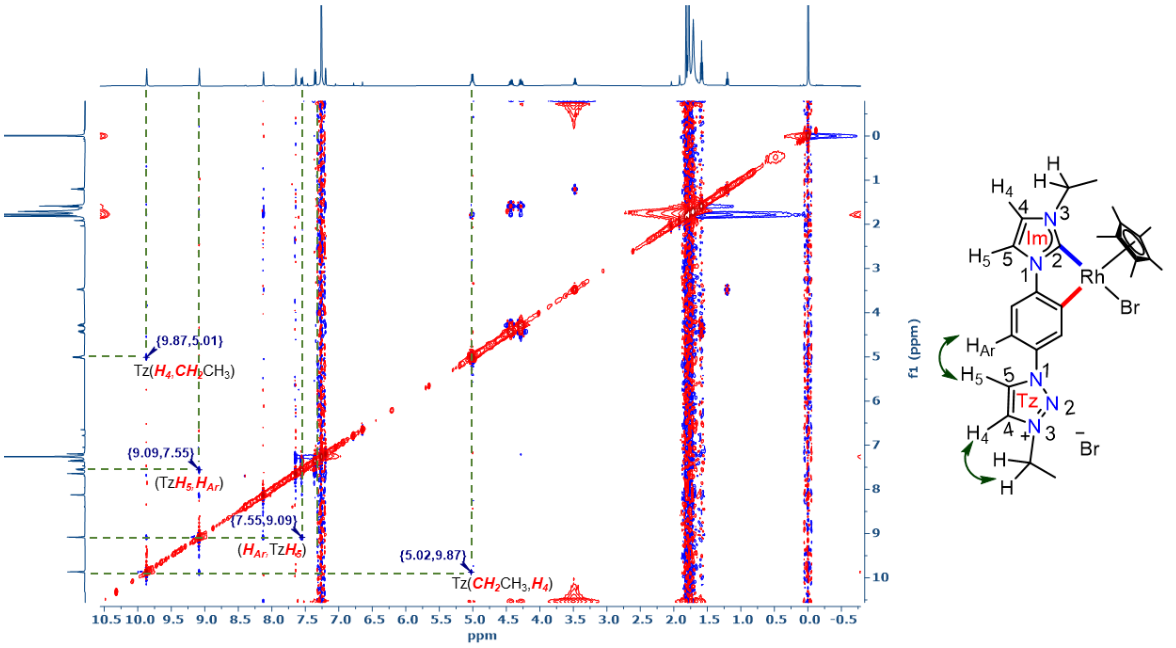


Figure S27. ^{1}H-^{1}H NOESY NMR spectrum of complex **4b** in CDCl$_3$.

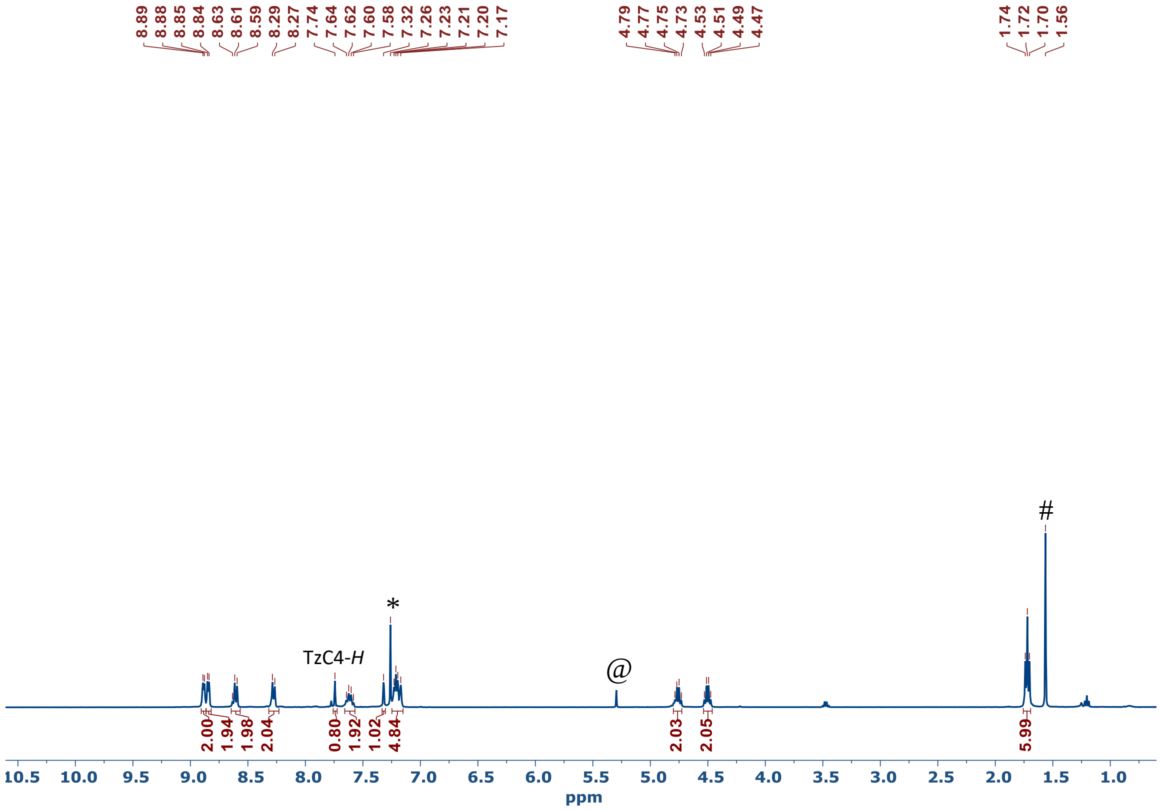


Figure S28. ^{1}H NMR spectrum of complex **5** in CDCl$_3$ (*). # and @ represent the solvent impurities of water and DCM in CDCl$_3$.

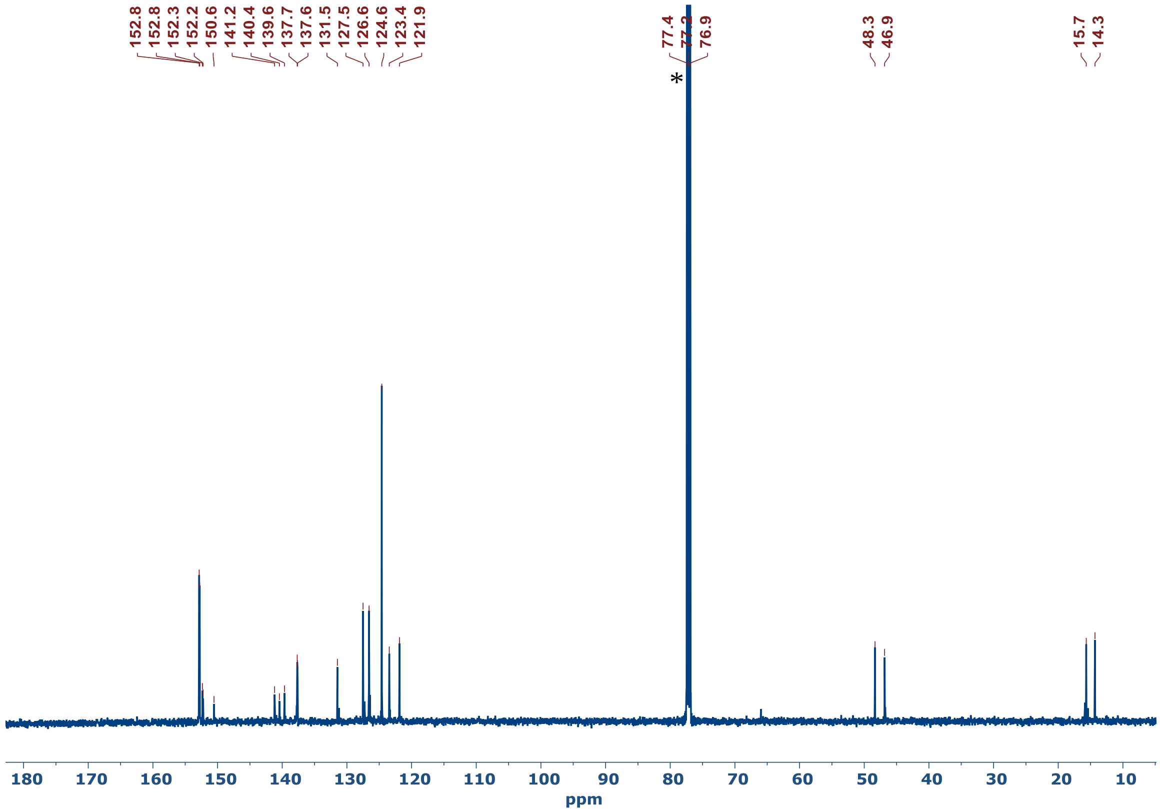


Figure S29. $^{13}C\{^1H\}$ NMR spectrum of complex **5** in $CDCl_3$ (*).

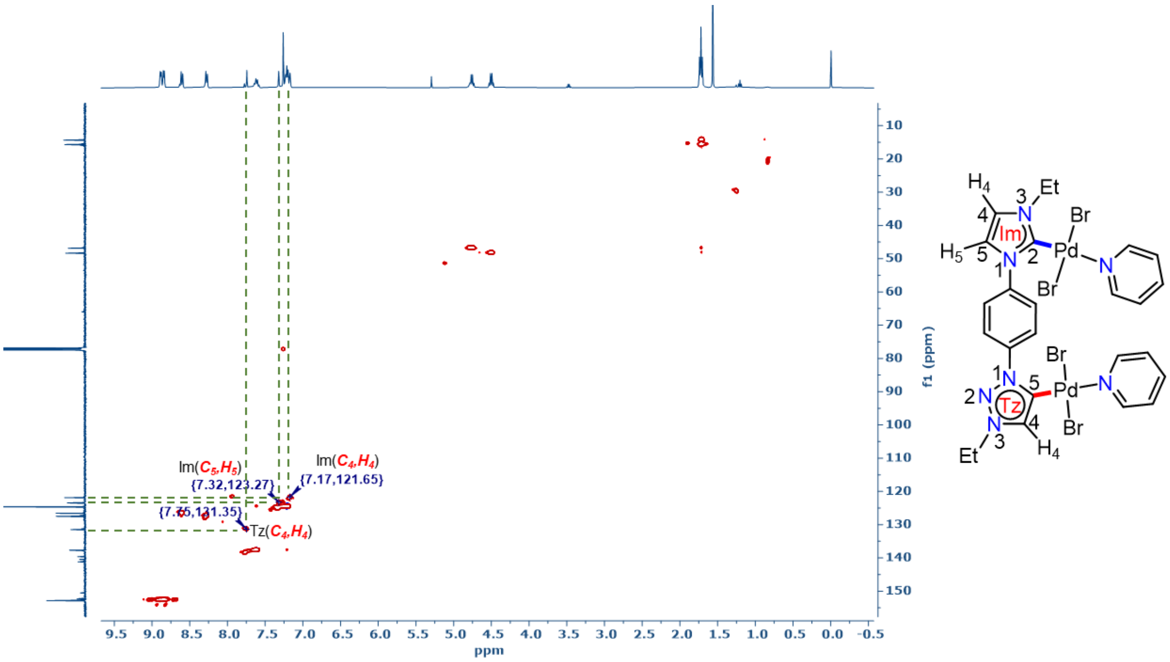


Figure S30. ^1H-$^{13}C\{^1H\}$ HSQC NMR spectrum of complex **5** in $CDCl_3$.

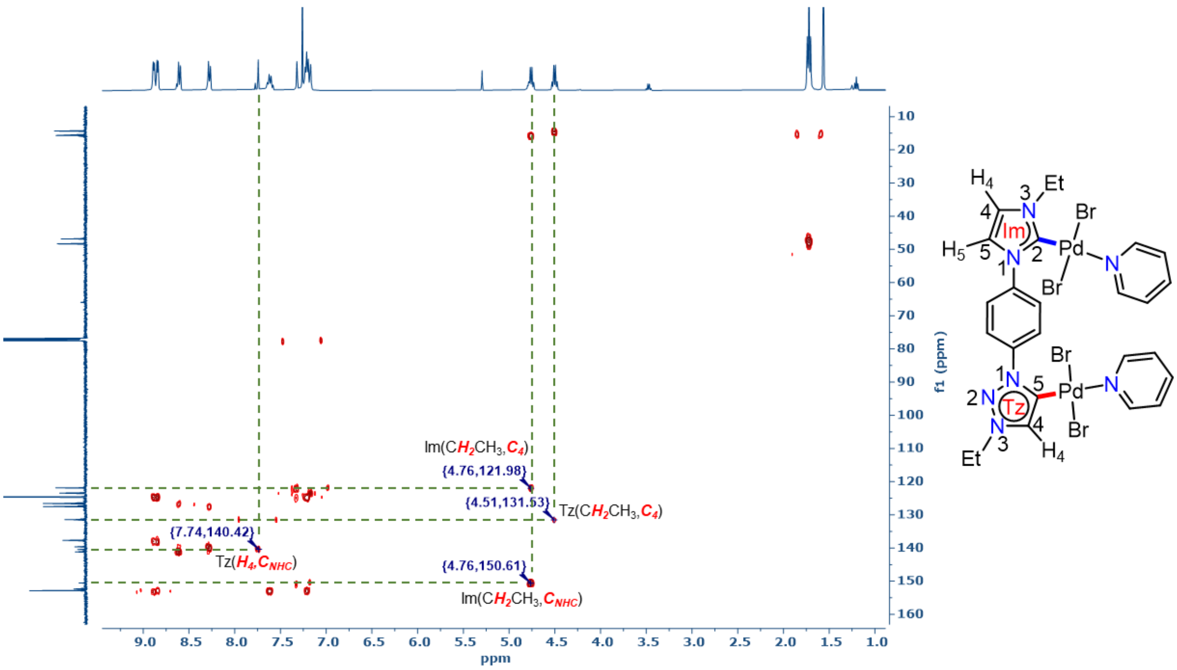


Figure S31. ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum of complex **5** in CDCl$_3$.

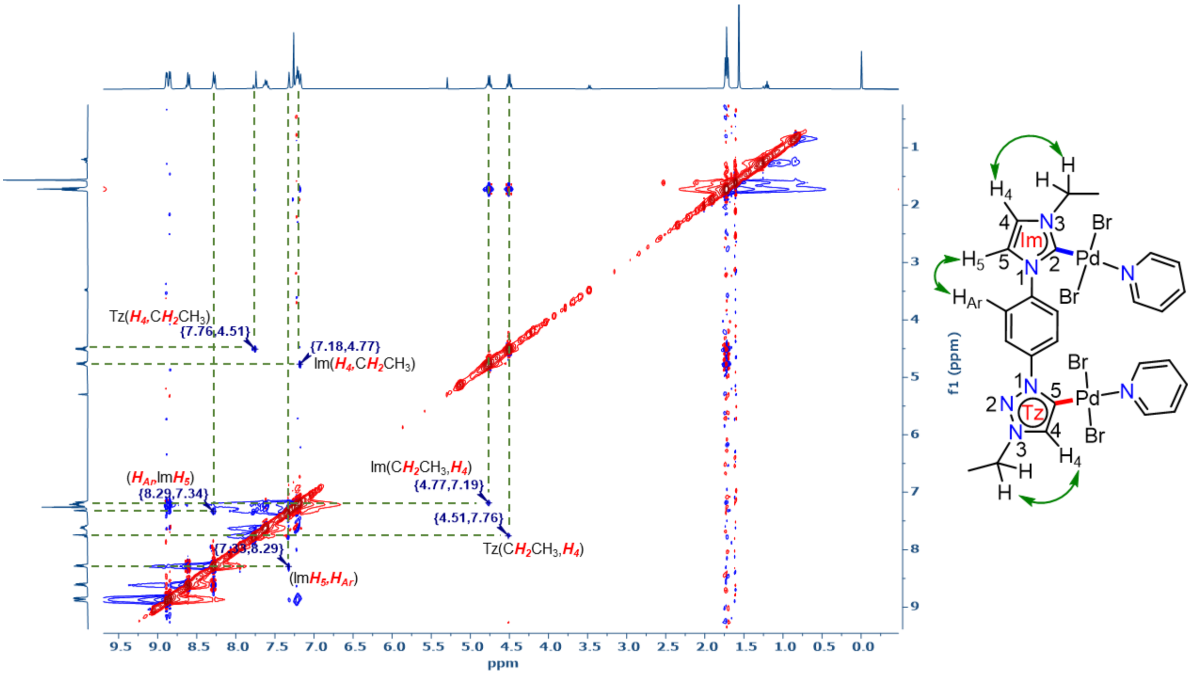


Figure S32. ^{1}H-^{1}H NOESY NMR spectrum of complex **5** in CDCl$_3$.

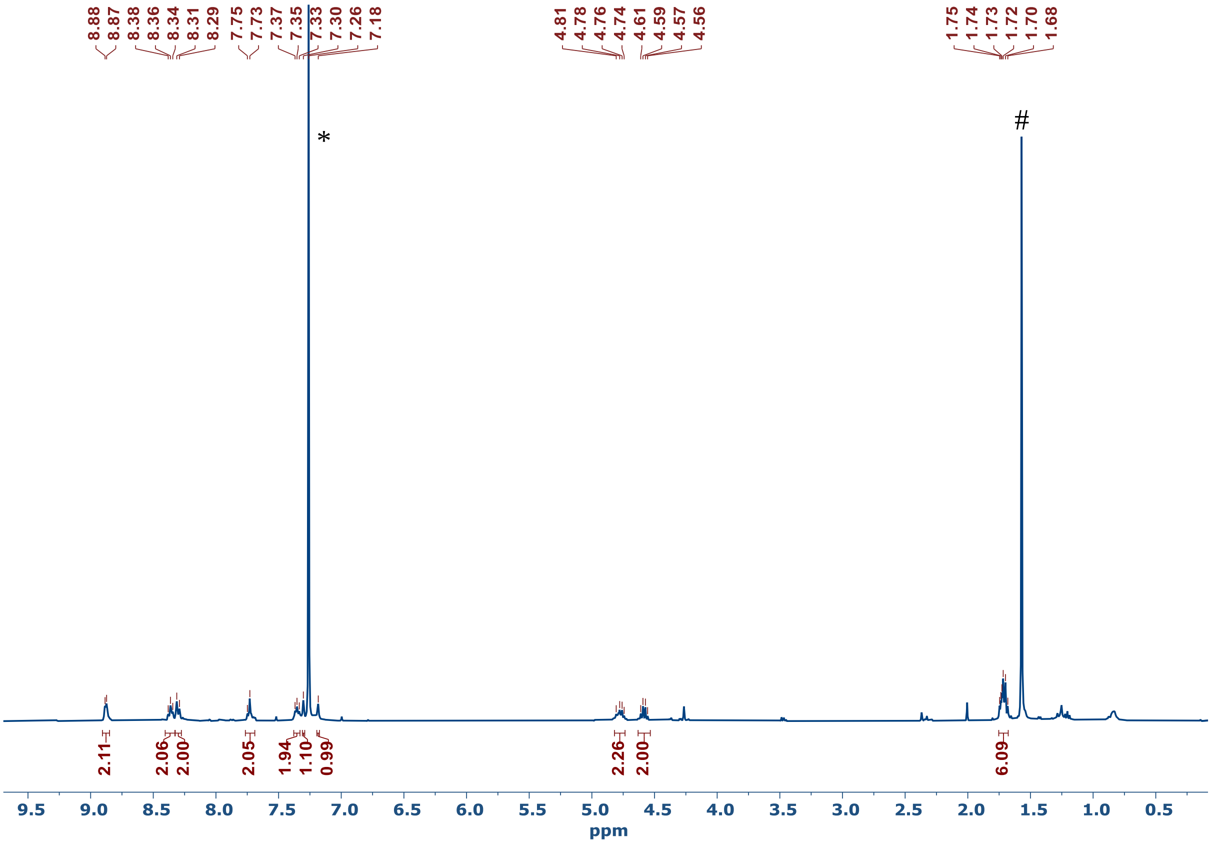


Figure S33. ^{1}H NMR spectrum of complex **6** in $CDCl_3$ (*). # represents the solvent impurity water in $CDCl_3$.

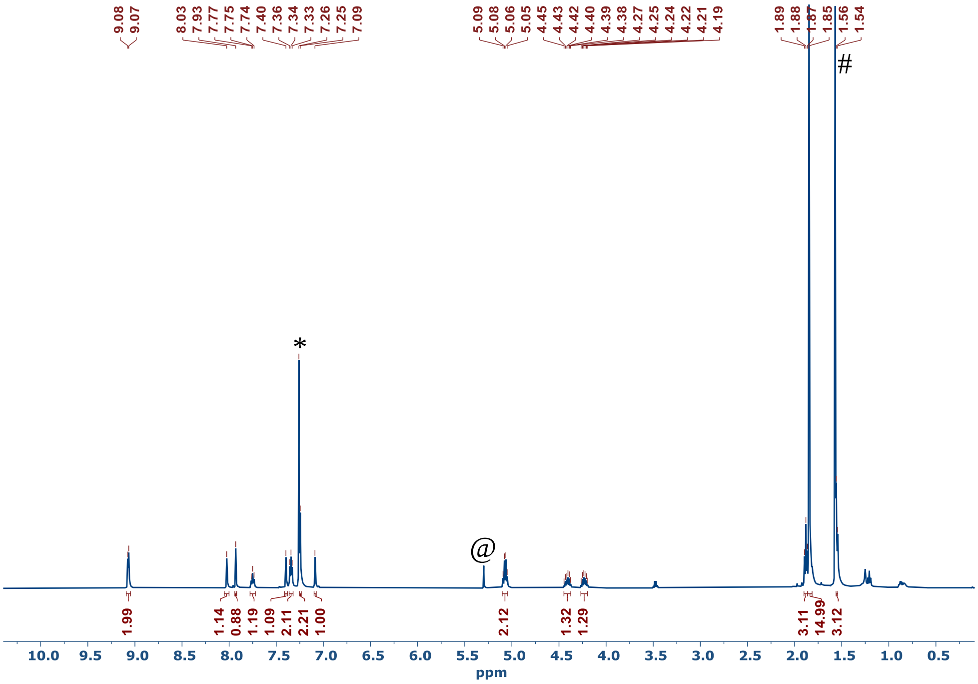


Figure S34. ^{1}H NMR spectrum of complex **7** in $CDCl_3$ (*). # represents the solvent impurity of water in $CDCl_3$. @ represents DCM.

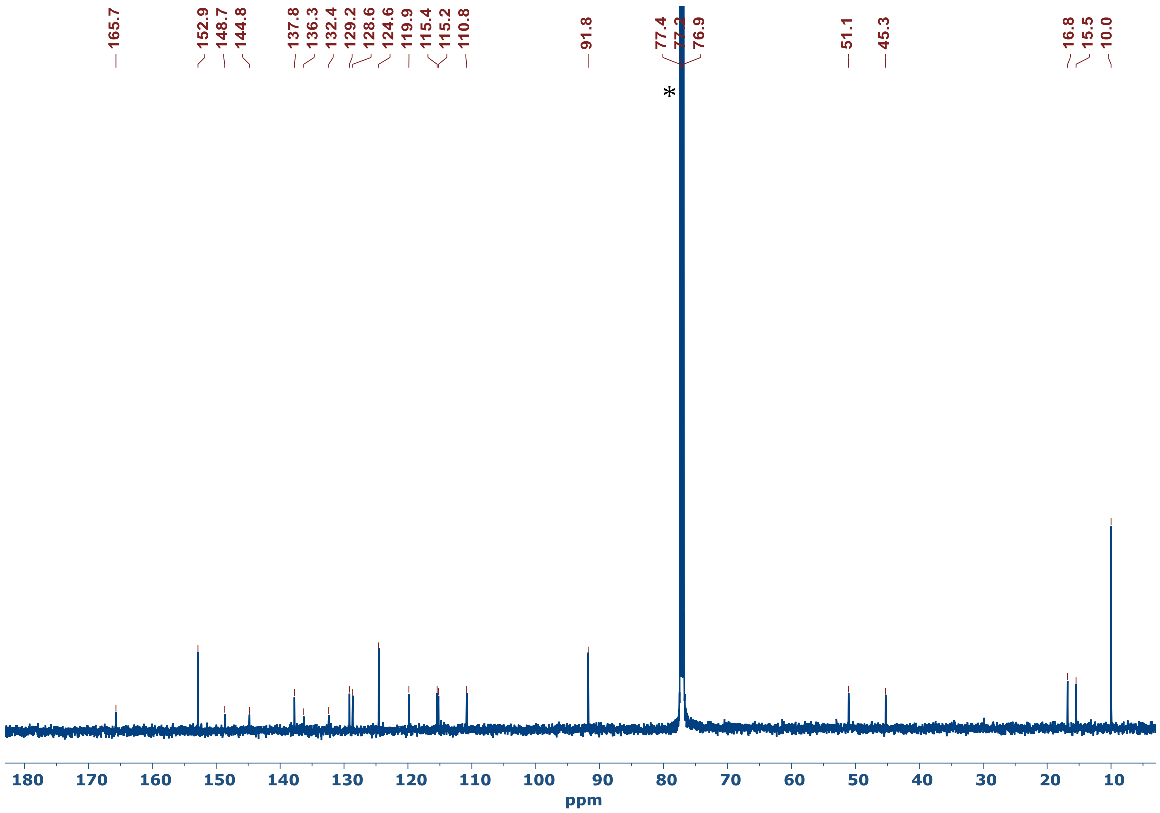


Figure S35. $^{13}C\{^1H\}$ NMR spectrum of complex **7** in $CDCl_3$ (*).

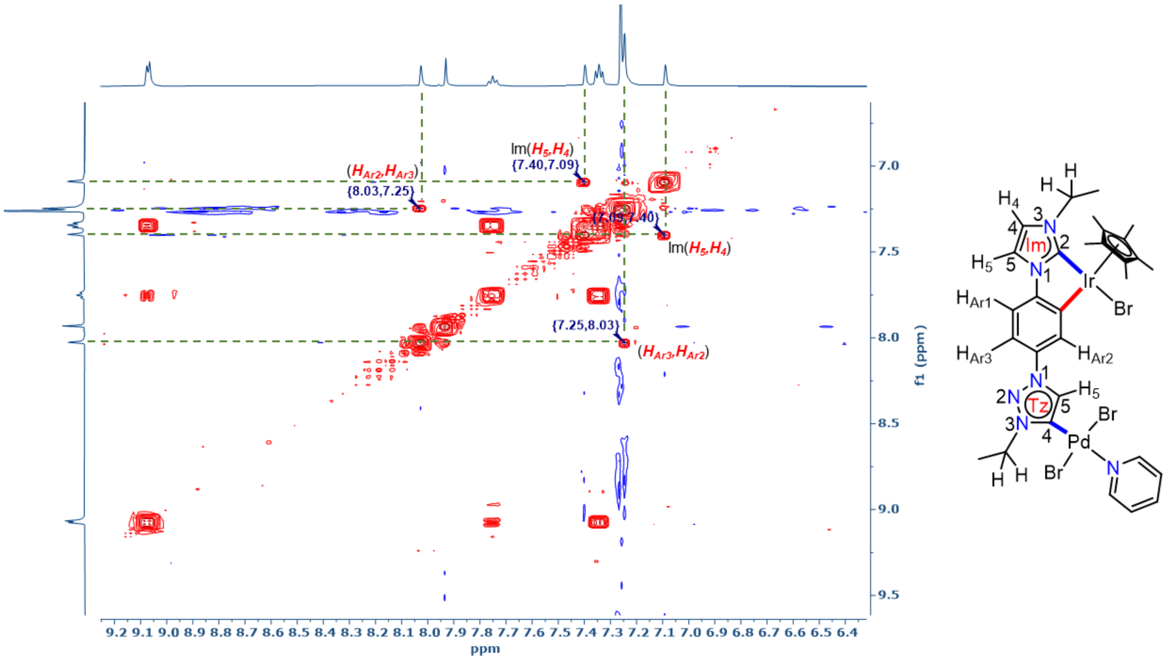


Figure S36. Selected portion of the ^1H-^1H COSY NMR spectrum of complex **7** in $CDCl_3$.

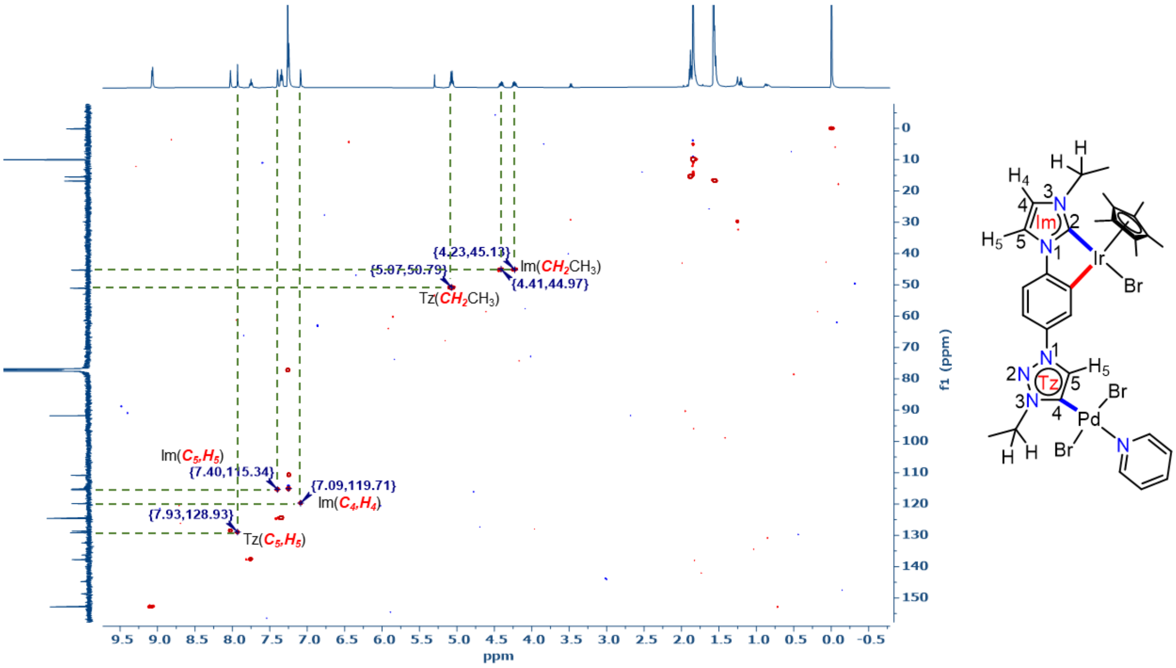


Figure S37. ^{1}H-^{13}C{^{1}H} HSQC NMR spectrum of complex **7** in CDCl$_3$.

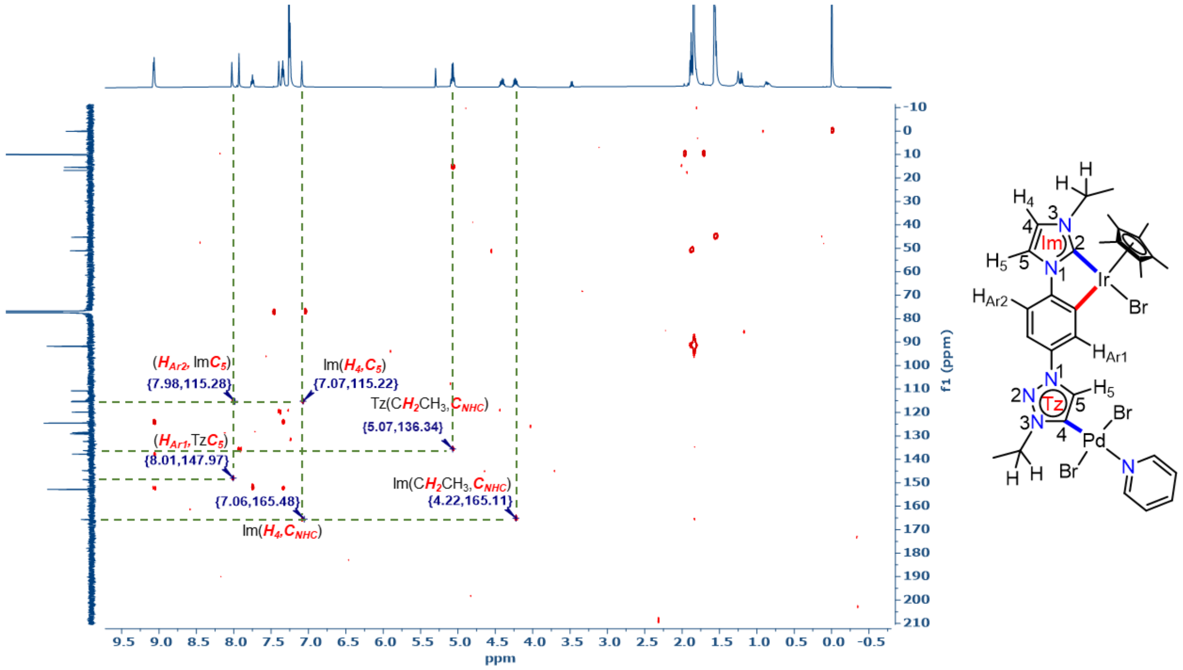


Figure S38. ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum of complex **7** in CDCl$_3$.

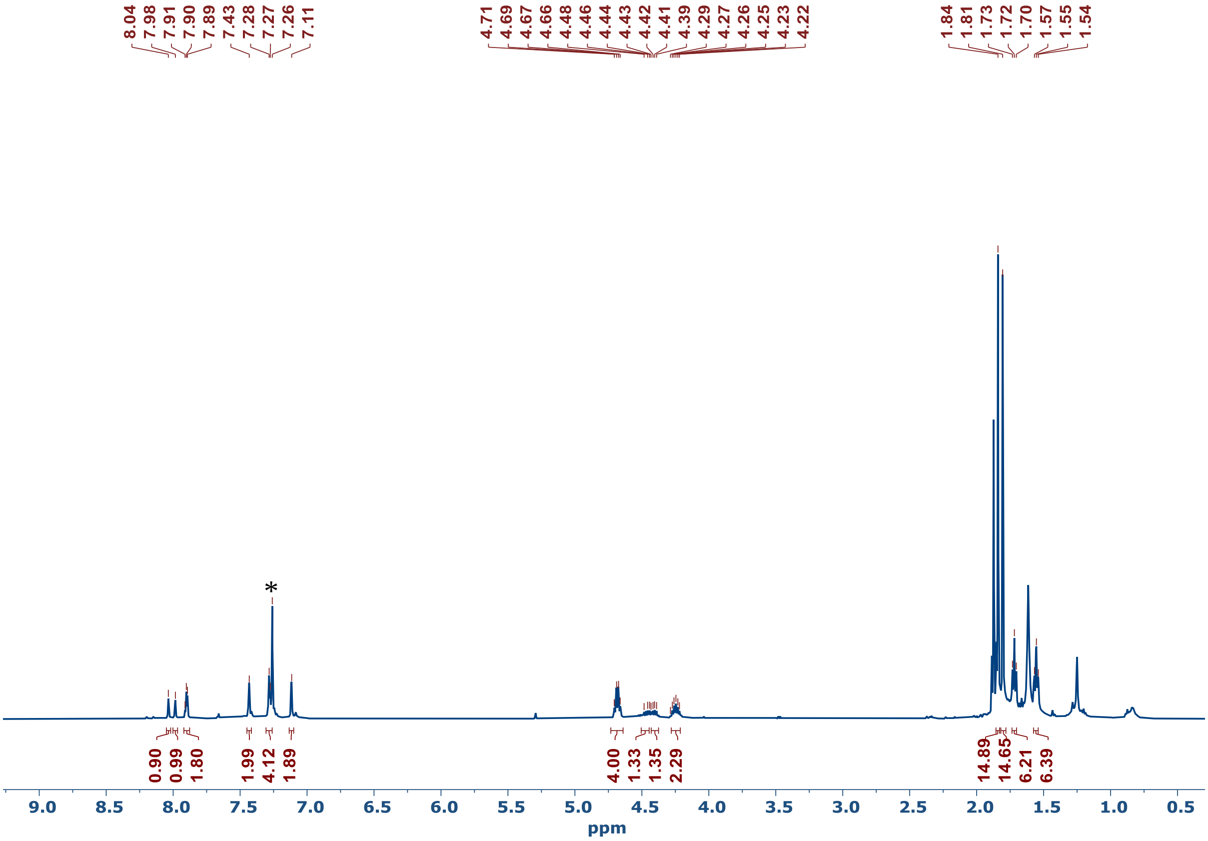


Figure S39. ^{1}H NMR spectrum of complex **8** in $CDCl_3$ (*).

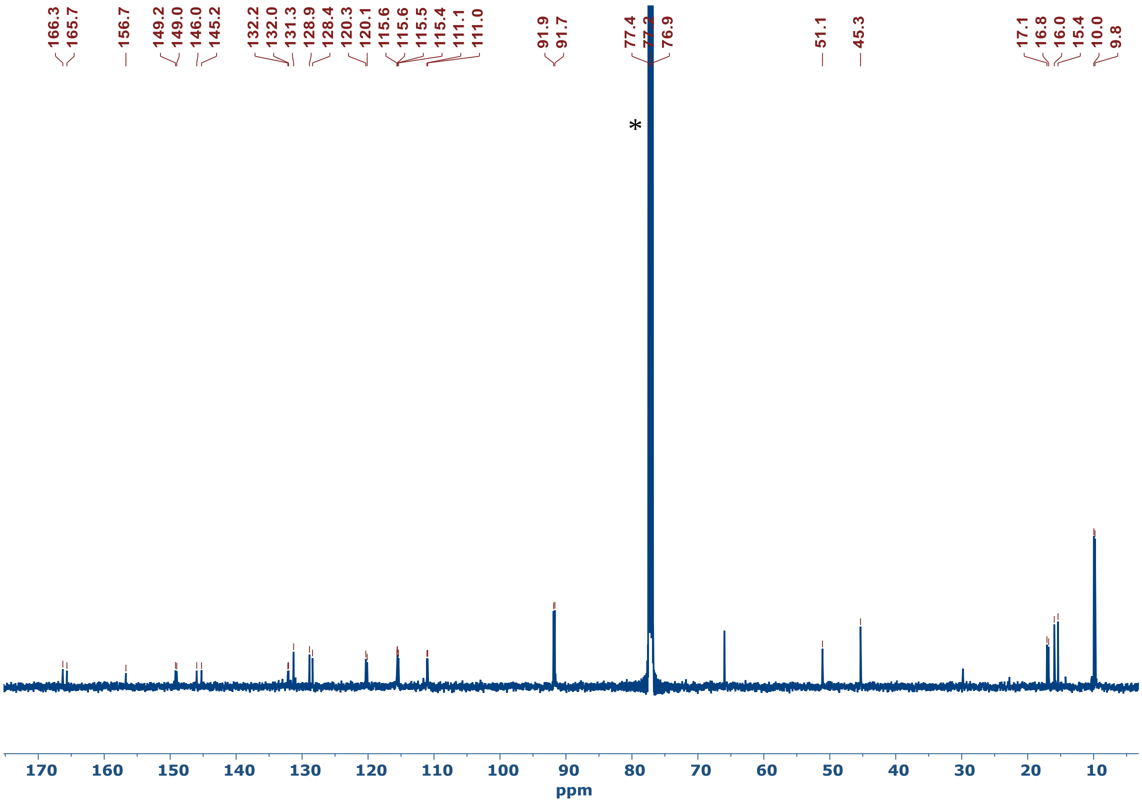


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of complex **8** in $CDCl_3$ (*).

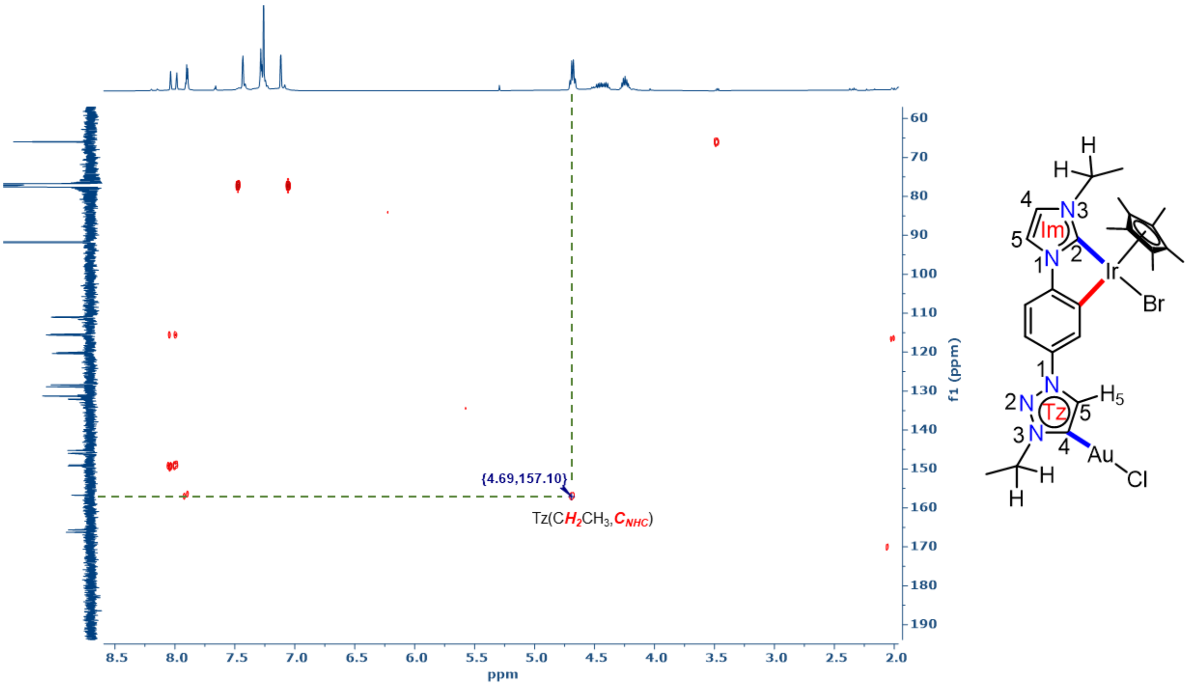


Figure S41. Selected portion of the ^{1}H -^{13}C{^{1}H} HMBC spectrum of complex **8** in CDCl$_3$.

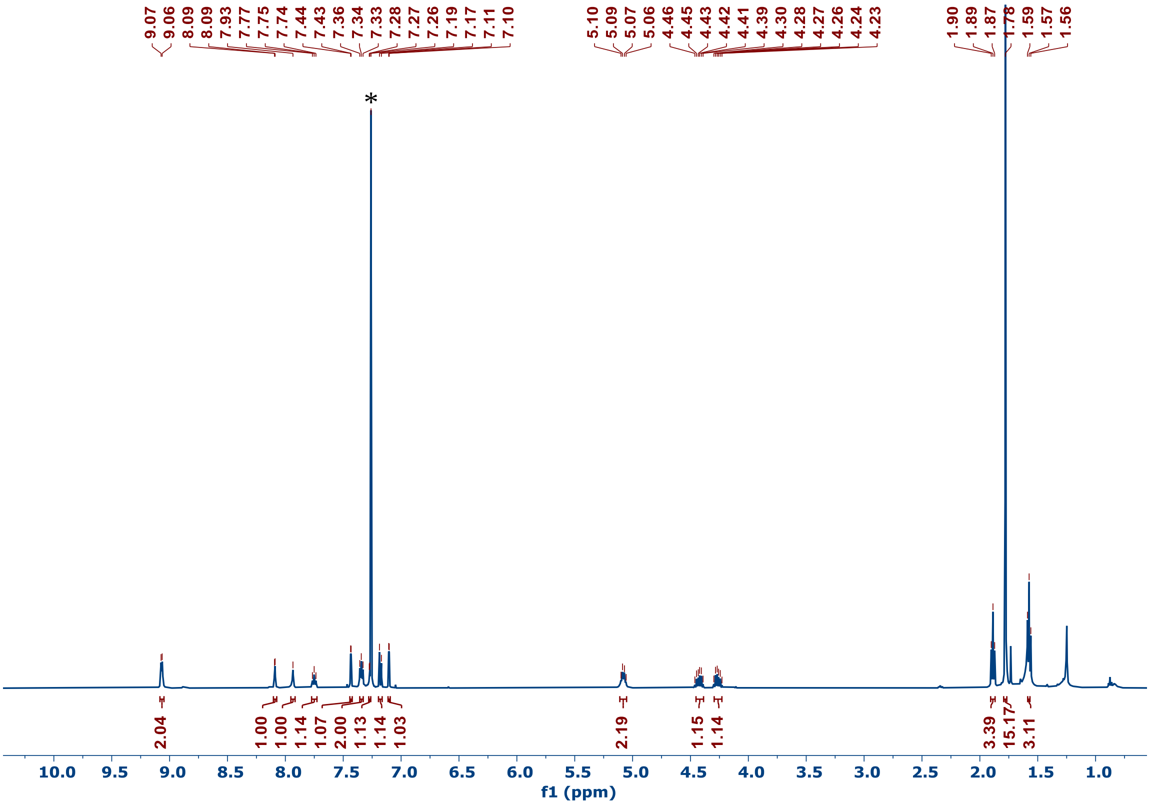


Figure S42. ^{1}H NMR spectrum of complex **9** in CDCl$_3$ (*).

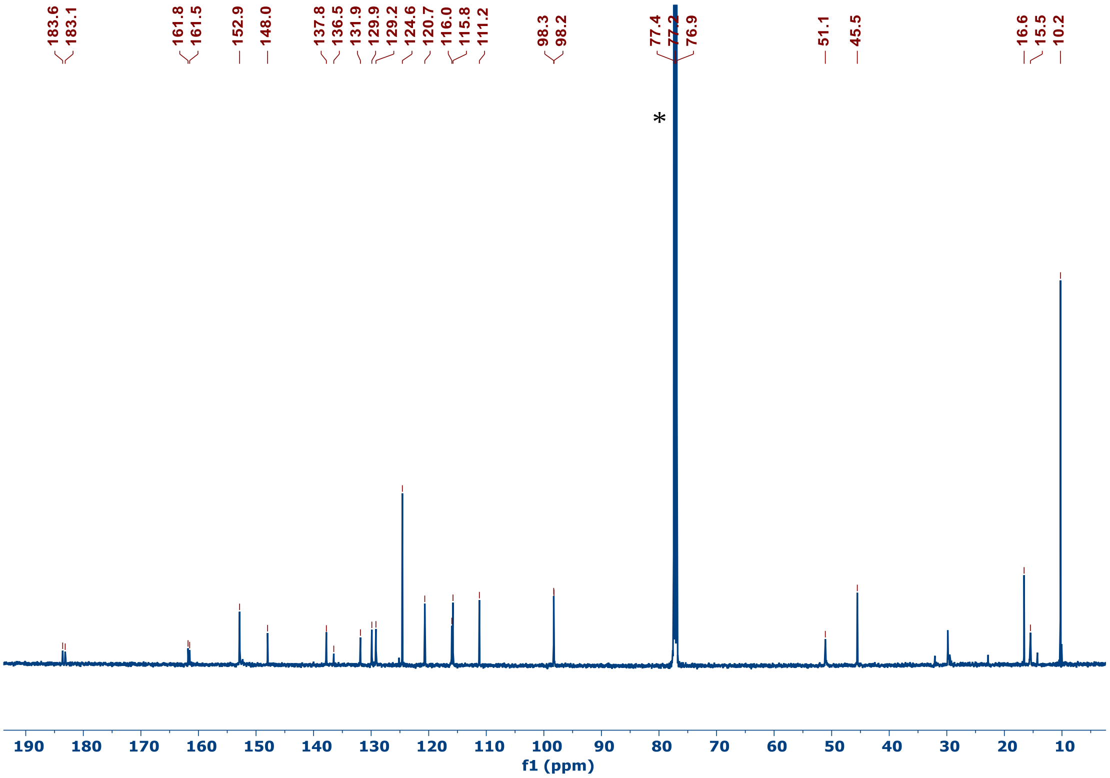


Figure S43. $^{13}C\{^{1}H\}$NMR spectrum of complex **9** in $CDCl_3$ (*).

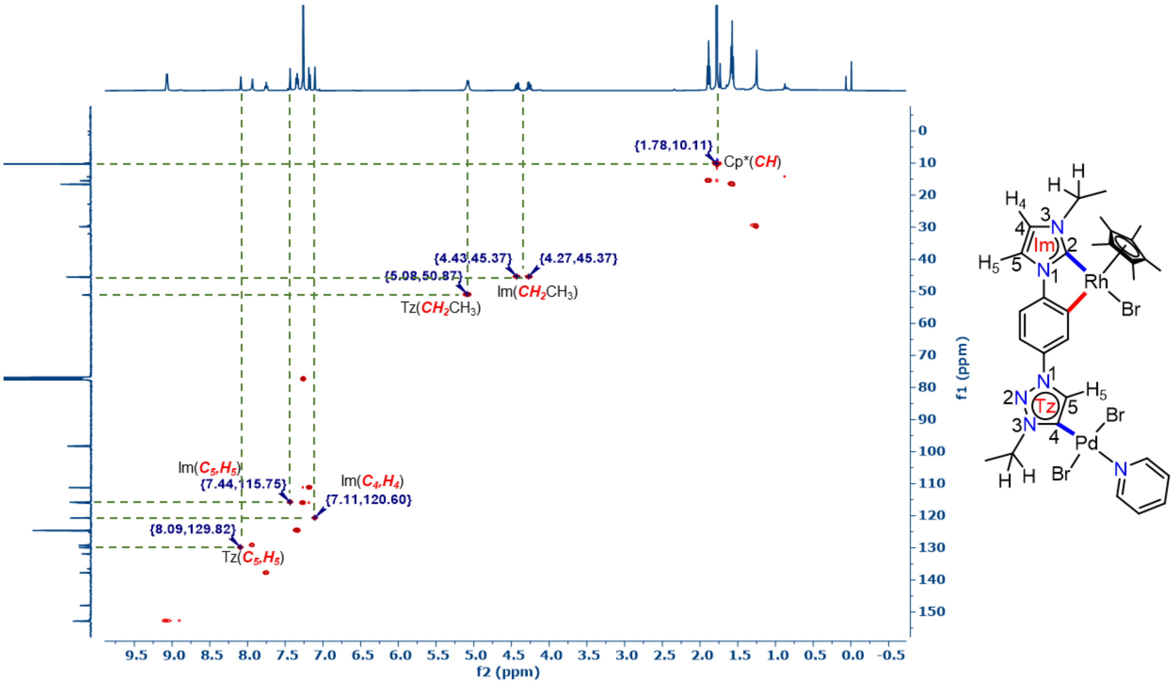


Figure S44. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR spectrum of complex **9** in $CDCl_3$.

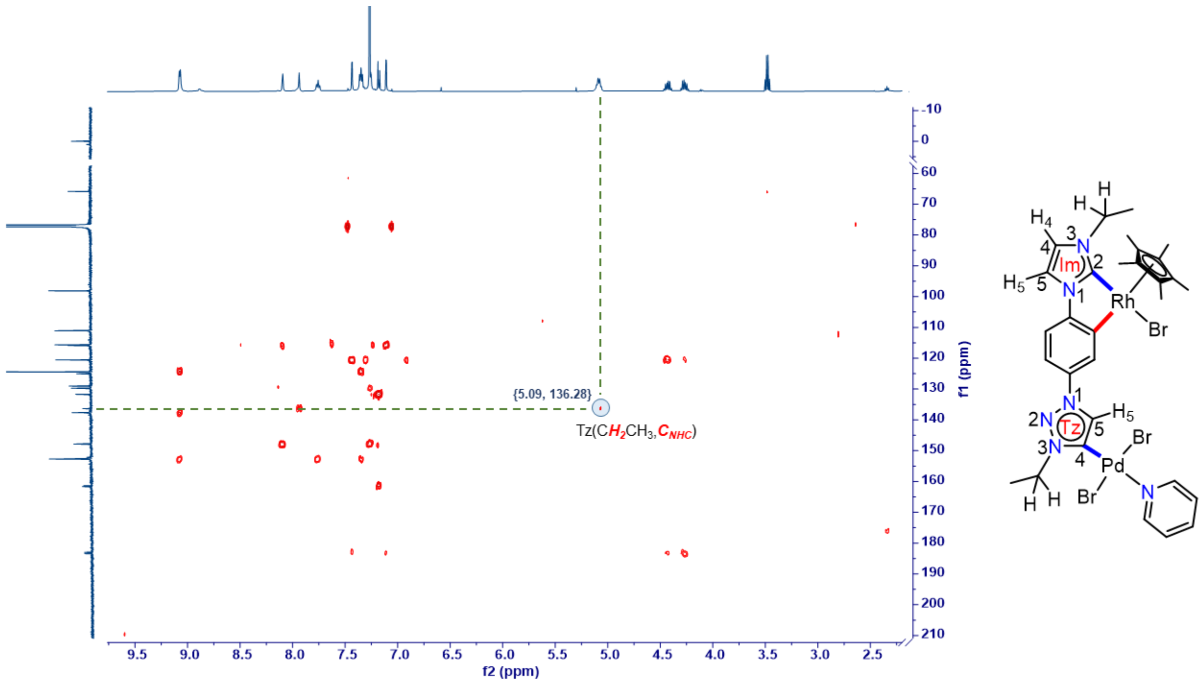


Figure S45. Selected portion of the ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum of complex **9** in $CDCl_3$.

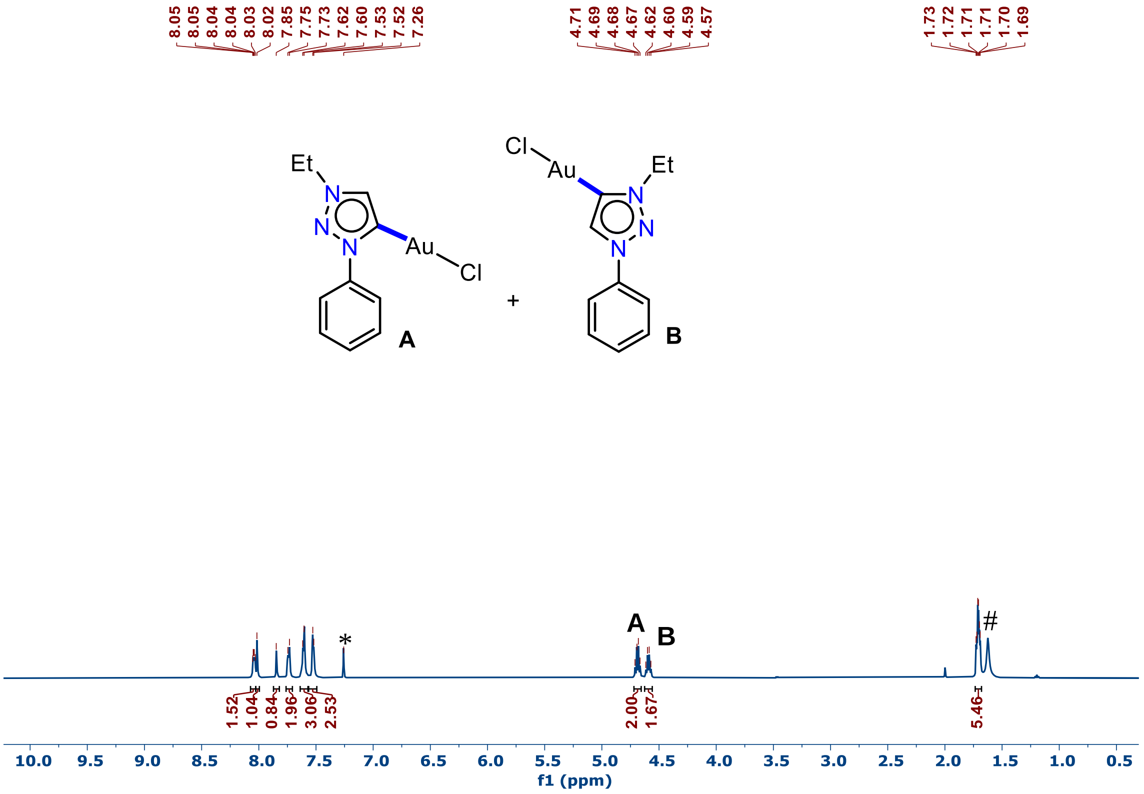


Figure S46. ^{1}H NMR spectrum of the gold complex of [**L1**-H]Br in $CDCl_3$ (*) formed *via* Ag_2O transmetalation pathway.

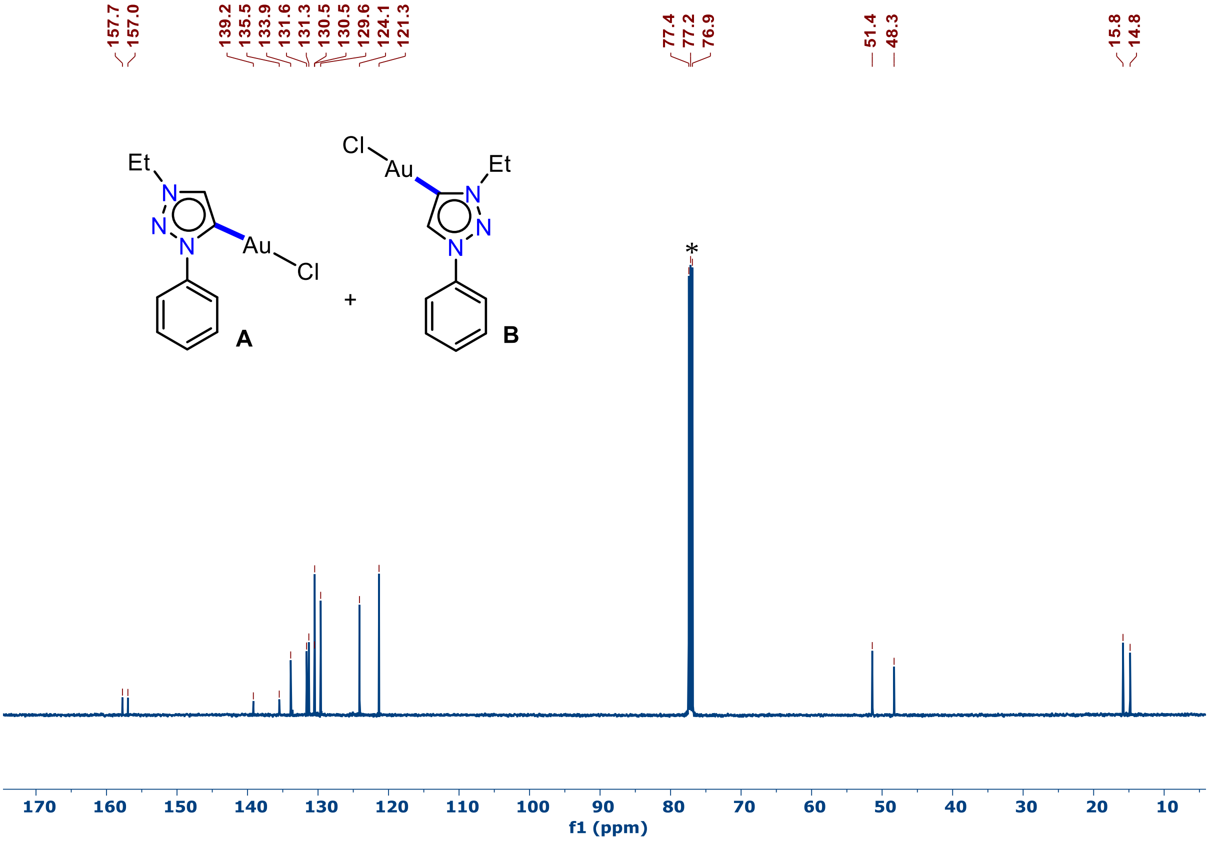


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of the gold complex of [**L1**-H]Br in $CDCl_3$ (*) formed *via* Ag_2O transmetalation pathway.

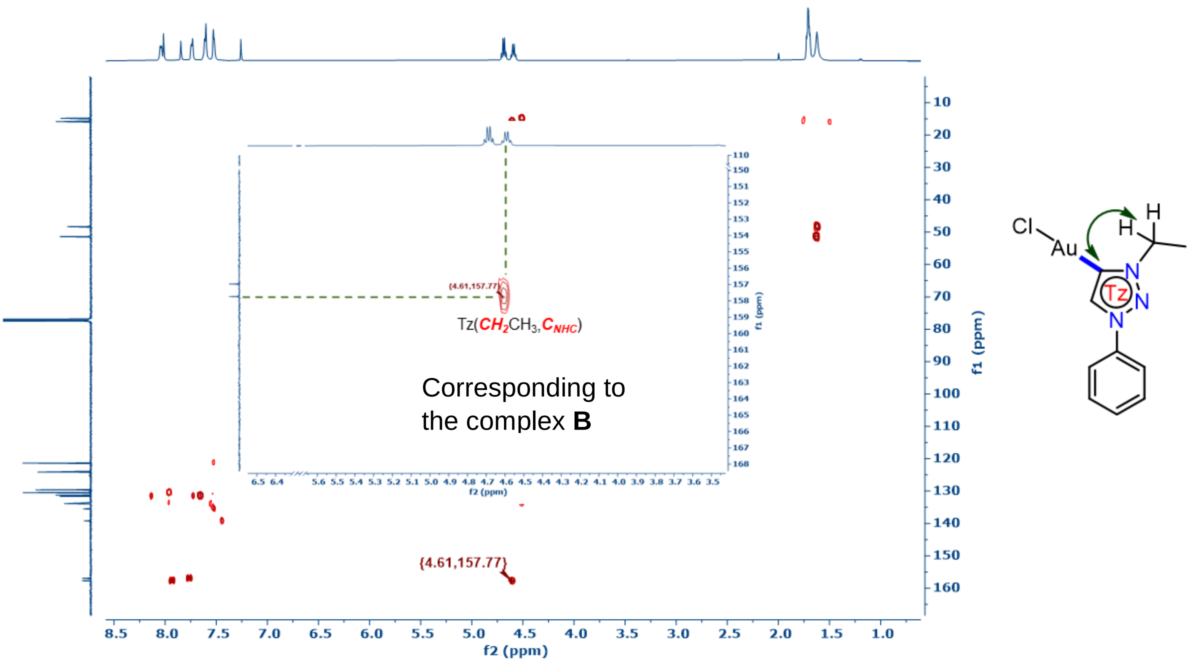


Figure S48. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR spectrum of the gold complex of [**L1**-H]Br in $CDCl_3$ formed *via* Ag_2O transmetalation pathway.

ESI-MS Spectra

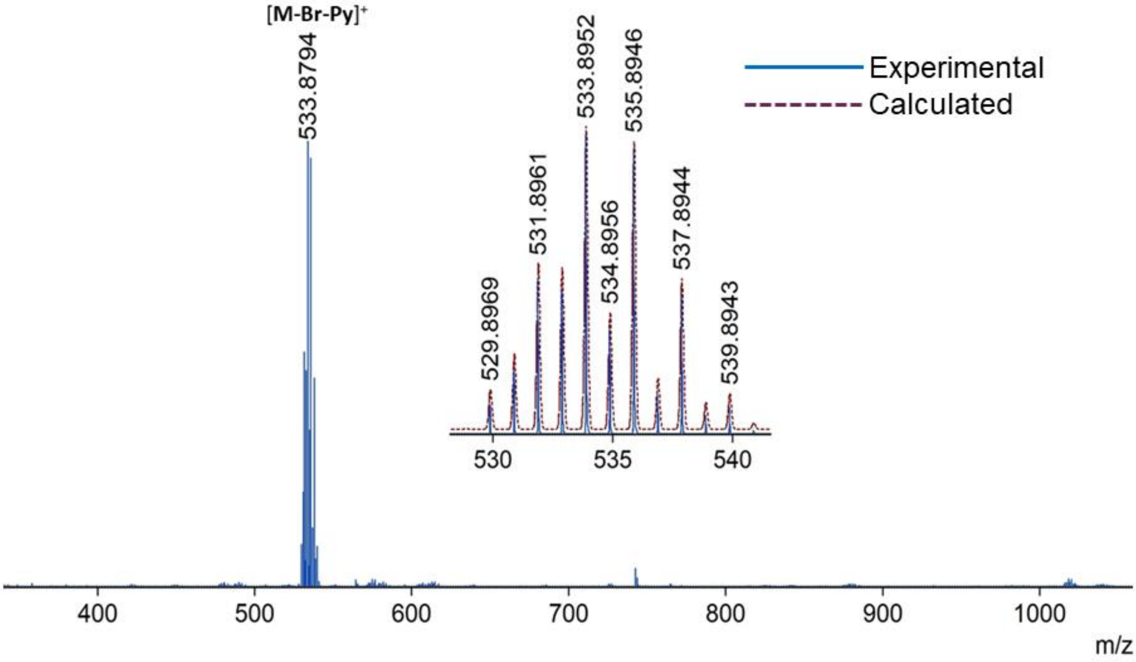


Figure S49. Mass spectrum of the complex **3**, [M-Br-Py]$^+$, M = $C_{20}H_{23}N_6PdBr_3$.

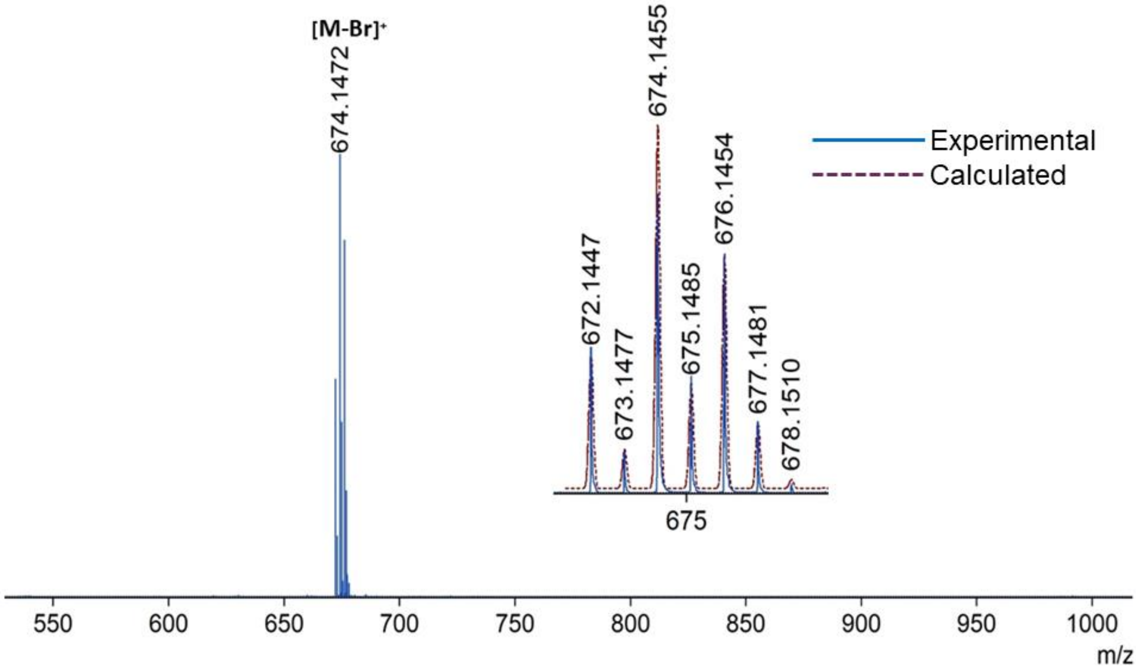


Figure S50. Mass spectrum of the complex **4a**, [M-Br]$^+$, M = $C_{25}H_{32}N_5IrBr_2$.

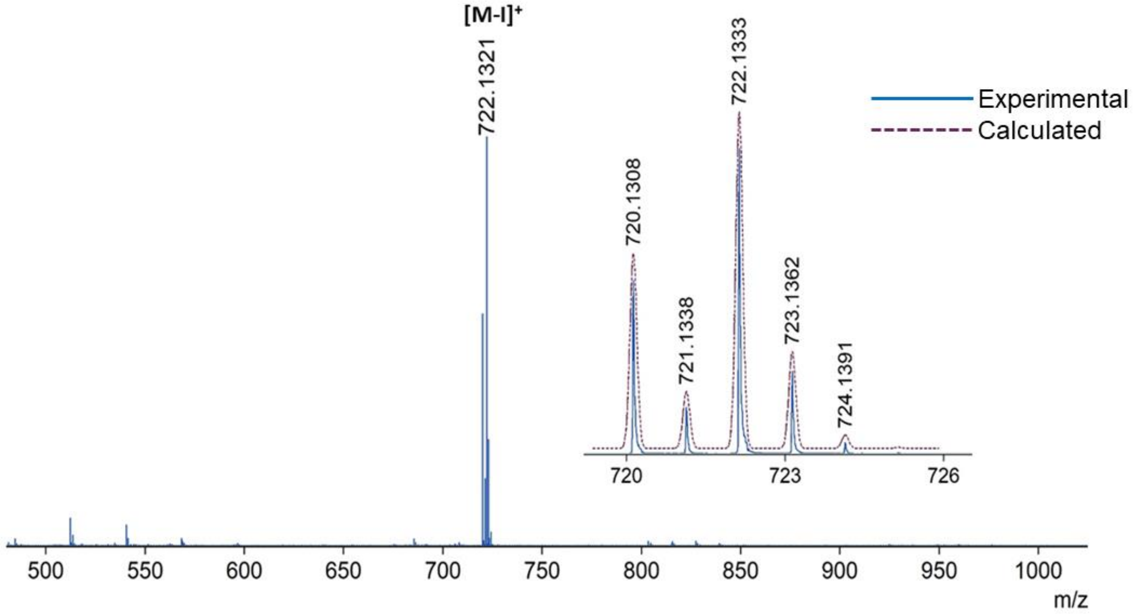


Figure S51. Mass spectrum of the complex **4a'**, $[M\text{-}I]^+$, M = $C_{25}H_{32}N_5IrI_2$.

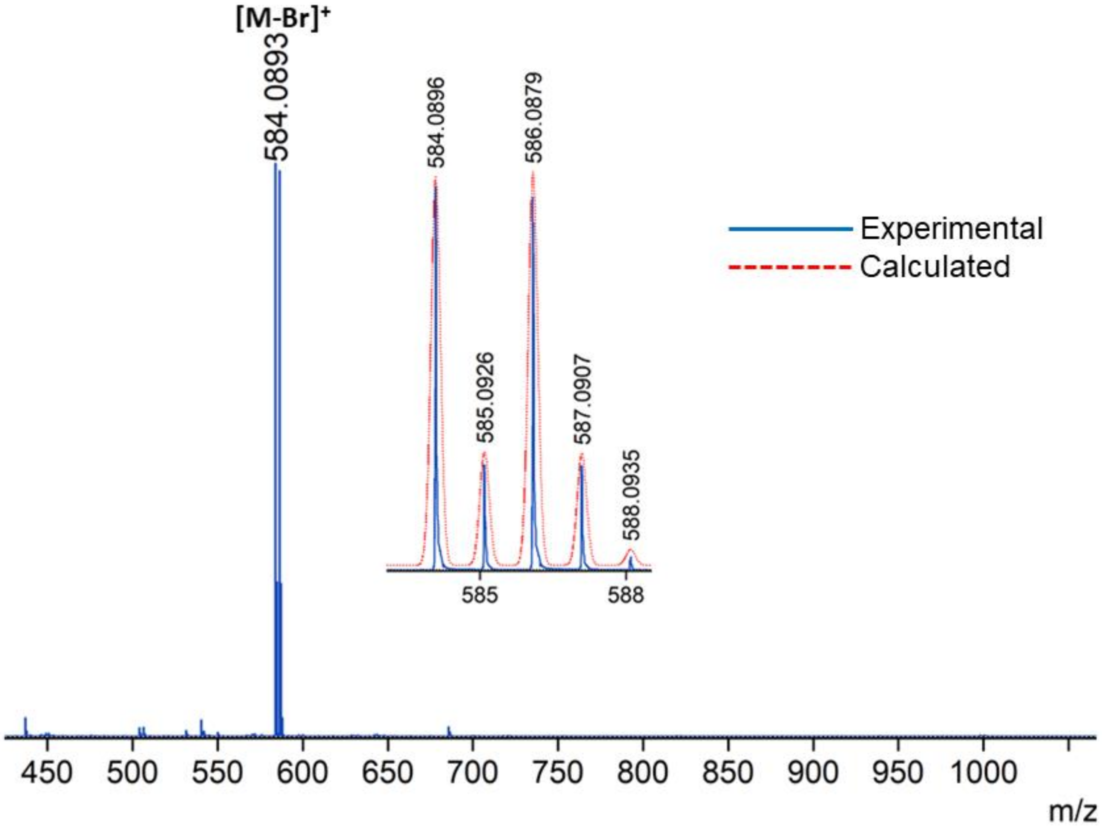


Figure S52. Mass spectrum of the complex **4b**, $[M\text{-}Br]^+$, M = $C_{25}H_{32}N_5RhBr_2$.

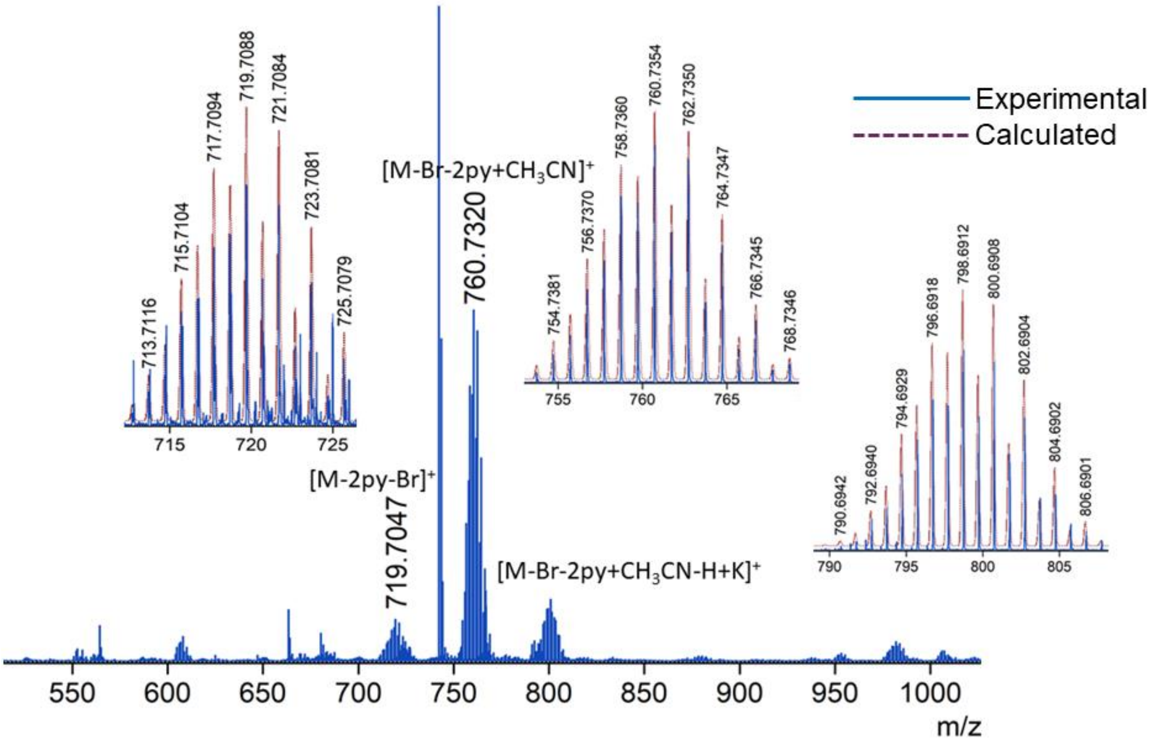


Figure S53. Mass spectrum of the complex **5**, M = $C_{25}H_{27}N_7Pd_2Br_4$.

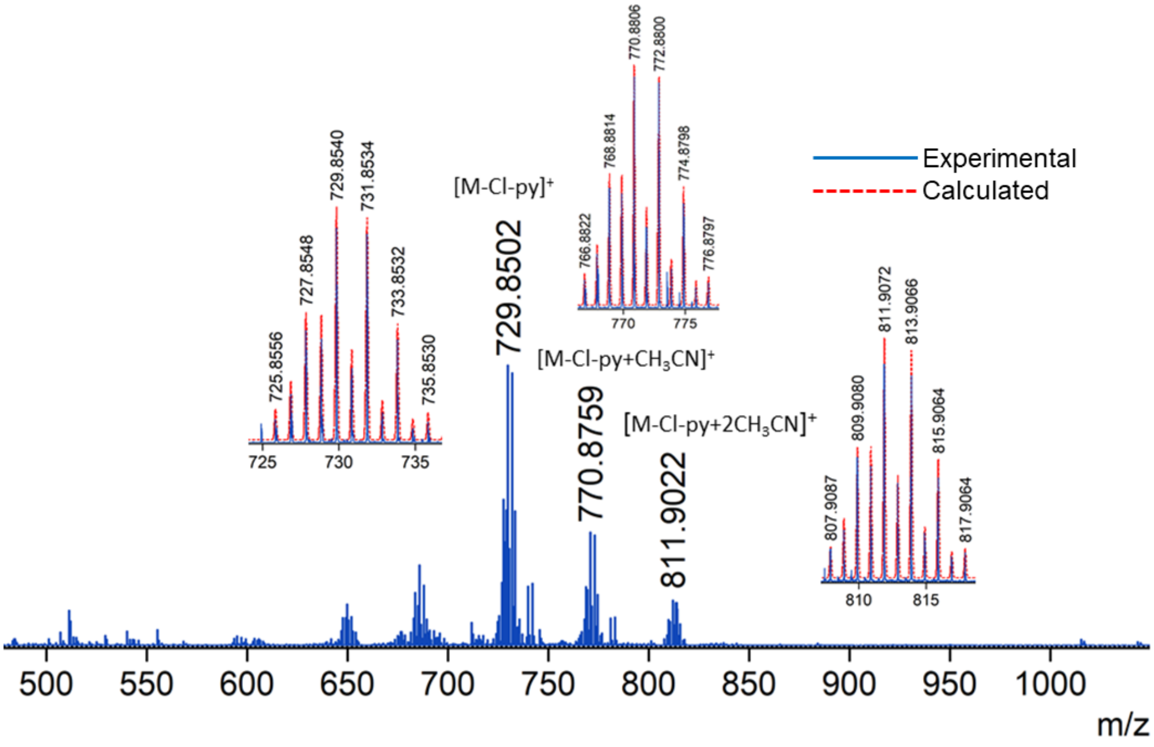


Figure S54. Mass spectrum of the complex **6**, M = $C_{20}H_{22}N_6PdAuBr_2Cl$.

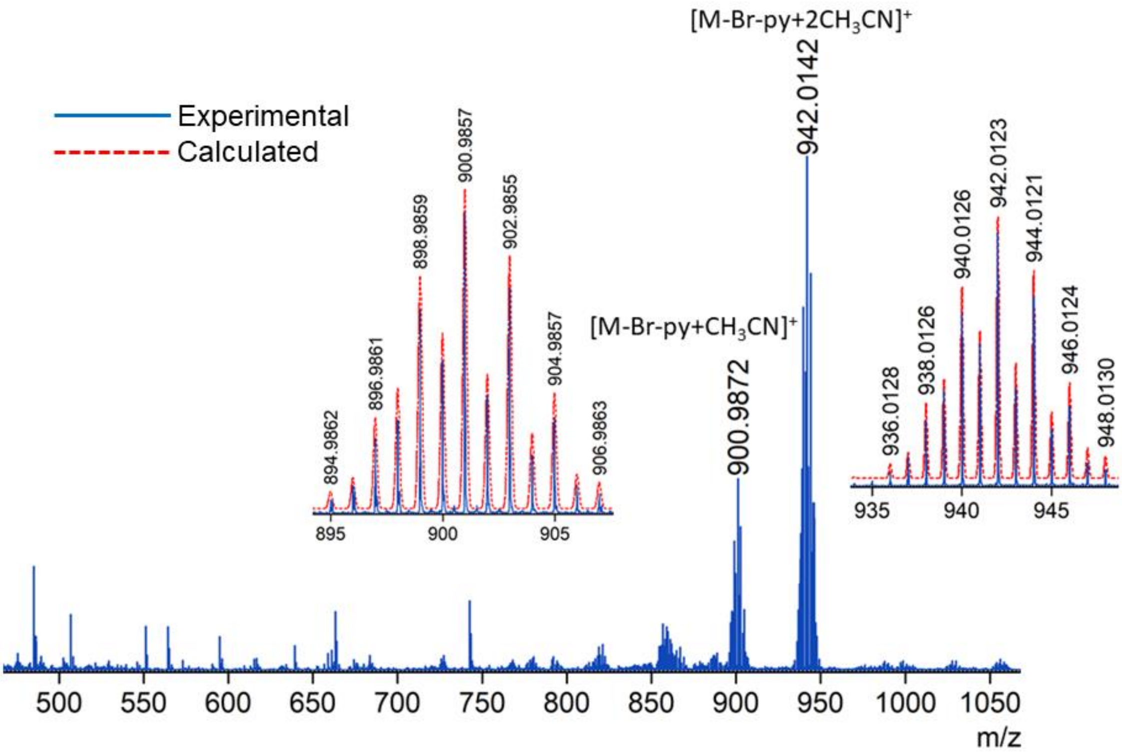


Figure S55. Mass spectrum of the complex **7**, M = $C_{30}H_{36}N_6IrPdBr_3$.

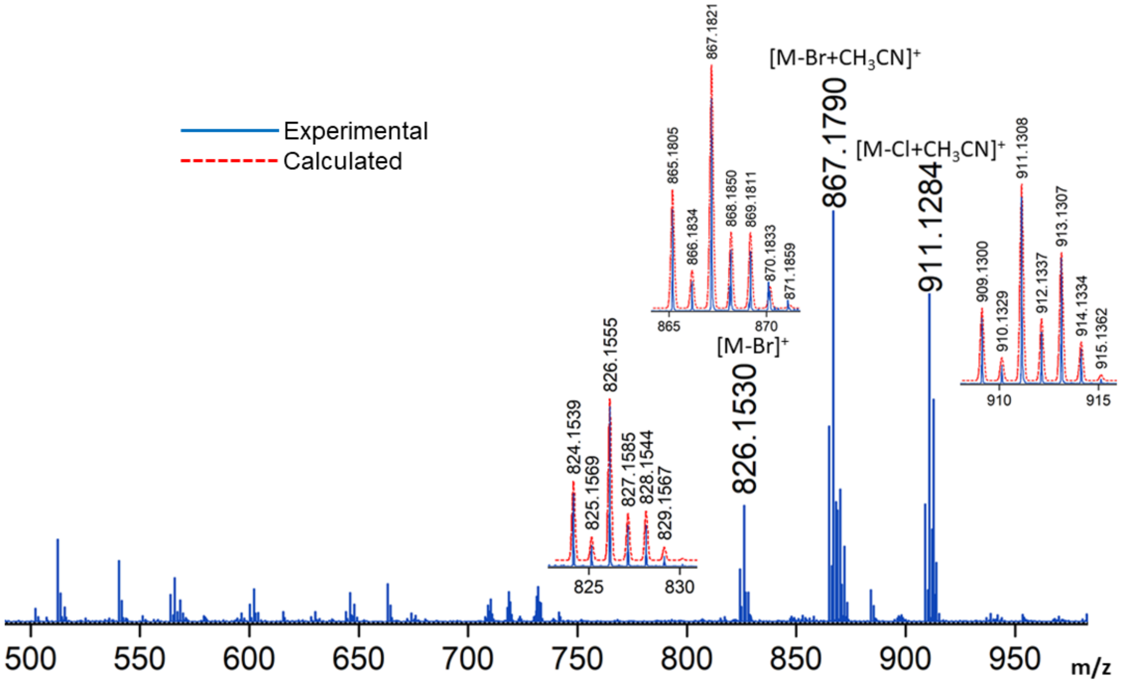


Figure S56. Mass spectrum of the complex **8**, M = $C_{25}H_{31}N_5IrAuBrCl$.

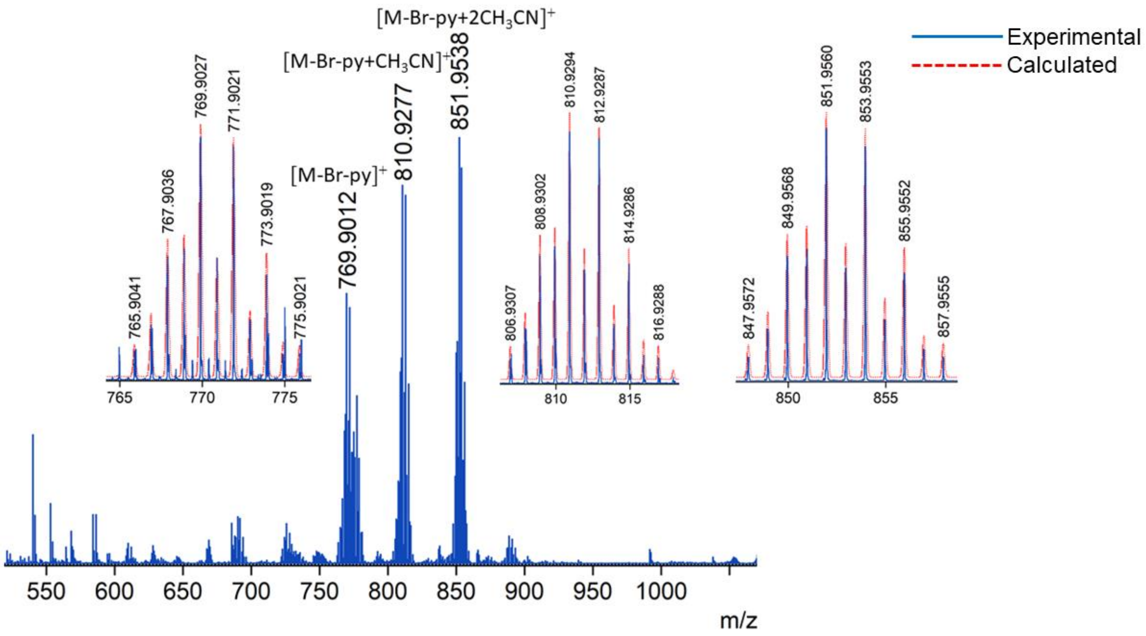


Figure S57. Mass spectrum of the complex **9**, M = $C_{25}H_{36}N_6RhPdBr_3$.

Single crystal X-ray Crystallography: X-ray data were collected on a Bruker AXS Kappa APEX-II CCD diffractometer or a Bruker APEX-II or Bruker-D8 venture instrument equipped with a PHOTON 100 CMOS area detector. Compounds **1**, **2**, **3**, **5**, **6**, **7**, and **8** were measured by using MoKα radiation (λ = 0.71073 Å) and CuKα radiation (λ = 1.54178 Å) was used for the compound **4a'**.[4a] Crystals were either frozen in paratone oil inside a cryo-loop under a cold stream of N_2 or placed inside a cryo-loop using paratone oil and after mounting on the goniometer head, it was optically centered. The APEX3 and APEX3-SAINT/Bruker SAINT programme were used for the data collection and unit cell determination, respectively. Processing of the raw frame data was performed using SAINT/XPREP or Bruker SAINT.[4b-c] The structures were solved by SHELXT-2014/4 or SHELXS-97 methods[4d] and refined against F^2 using all reflections with SHELXL-2014/7 or SHELXL-2018/3 (WinGX) program.[4e-f] Non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in calculated positions. The graphical representations were performed using the program Mercury.[4g]

Crystallographic Data

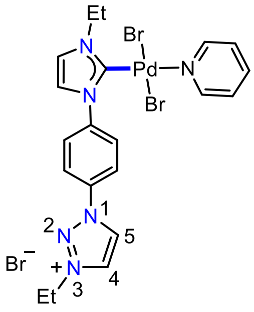
Compound	**[L2-H_2]Br_2**	**1**	**2**
CCDC No	2176104	2176099	2176097
Empirical formula	$C_{15}H_{21}Br_2N_5O$	$C_{15}H_{16}Br_2N_4Pd$	$C_{10}H_{11}AuBrN_3$
Formula weight	447.19	518.54	450.09
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/n	P21/c	P-1
a (Å)	7.7483(3)	17.7060(18)	6.0635(2)
b (Å)	23.2239(11)	6.2505(7)	9.6309(4)
c (Å)	10.3010(5)	15.8120(14)	11.0320(5)
α (°)	90	90	101.765(2)
β (°)	102.9736(17)	98.771(3)	104.967(2)
γ (°)	90	90	97.601(2)
V (Å^3)	1806.30(14)	1729.5(3)	597.54(4)
Z	4	4	2
D calc (Mg/m^3)	1.644	1.991	2.502
F (000)	896	1000	412
μ (mm^{-1})	4.499	5.694	15.624
θ Range (°)	2.63 to 26.13	3.461 to 30.516	2.57 to 26.32
Crystal size (mm^3)	0.250 x 0.220 x 0.160	0.180 x 0.070 x 0.068	0.150 x 0.120 x 0.100
No. of total reflns collected	10998	59679	7349
No. of unique reflns [I > 2σ(I)]	2468	5270	2102
Data/restraints/ parameters	2468/2/218	5270 / 0 / 200	2102/0/129
Goodness-of-fit on F^2	1.112	1.033	1.079
Final R indices [I > 2σ(I)]	R1 = 0.0390, wR2 = 0.0714	R1 = 0.0311, wR2 = 0.0670	R1 = 0.0340, wR2 = 0.0922
R indices (all data)	R1 = 0.0528, wR2 = 0.0752	R1 = 0.0478, wR2 = 0.0757	R = 0.0373, wR2 = 0.0947

Compound	**3**	**4a’**	**5**
CCDC No	2176098	2176101	2176100
Empirical formula	$C_{20}H_{23}Br_3N_6Pd$	$C_{50}H_{66}I_4Ir_2N_{10}O$	$C_{25}H_{27}Br_4N_7Pd_2$
Formula weight	693.57	1715.12	957.97
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P21/n
a (Å)	19.5000(9)	10.1579(3)	13.8366(3)
b (Å)	11.2281(5)	12.7784(3)	12.6469(3)
c (Å)	23.8483(10)	22.2614(5)	17.6415(4)
α (°)	90	95.693(2)	90
β (°)	96.656(2)	98.9580(10)	103.8322(9)
γ (°)	90	94.414(2)	90
V ($Å^3$)	5186.3(4)	2827.66(13)	2997.56(12)
Z	8	2	4
D calc (Mg/m^3)	1.777	2.014	2.123
F (000)	2688	1620	1832
μ (mm^{-1})	5.356	26.465	6.560
θ Range (°)	1.719 to 24.946	3.491 to 66.957	1.688 to 24.993
Crystal size (mm)	0.200 x 0.150 x 0.100	0.150 x 0.150 x 0.100	0.250 x 0.220 x 0.160
No. of total reflns collected	15547	70001	23937
No. of unique reflns [I > 2σ(I)]	4548	10047	5266
Data/restraints/ parameters	4548 / 63 / 293	10047 / 110 / 629	5266 / 0 / 345
Goodness-of-fit on F^2	1.010	1.032	1.055
Final R indices [I > 2σ(I)]	R1 = 0.0399, wR2 = 0.0830	R1 = 0.0581, wR2 = 0.1310	R1 = 0.0332, wR2 = 0.0782
R indices (all data)	R1 = 0.0696, wR2 = 0.0923	R1 = 0.0888, wR2 = 0.1456	R1 = 0.0457, wR2 = 0.0831

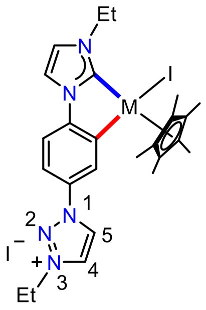
Compound	**6**	**7**	**8**
CCDC No	2176102	2176105	2176103
Empirical formula	$C_{20}H_{22}AuBr_{2.59}Cl_{0.41}N_6Pd$	$C_{30}H_{36}Br_3IrN_6Pd$	$C_{25}H_{30}AuBrClIrN_5$
Formula weight	871.30	1018.98	906.07
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	P21/c
a (Å)	8.2856(4)	25.915(2)	9.6523(9)
b (Å)	12.0023(6)	20.090(2)	25.471(3)
c (Å)	12.6741(6)	15.4825(16)	11.1422(12)
α (°)	83.517(2)	90	90
β (°)	83.226(2)	115.662(5)	104.835(5)
γ (°)	88.824(2)	90	90
V (Å^3)	1243.56(10)	7265.5(13)	2648.0(5)
Z	2	8	4
D calc (Mg/m^3)	2.327	1.863	2.270
F (000)	813	3888	1692
μ (mm^{-1})	10.840	7.481	12.188
θ Range (°)	2.800 to 24.998	3.165 to 25.000	2.053 to 22.151
Crystal size (mm)	0.150 x 0.120 x 0.100	0.200 x 0.150 x 0.100	0.100 x 0.080 x 0.050
No. of total reflns collected	51560	52952	13474
No. of unique reflns [I > 2σ(I)]	4327	6379	3309
Data/restraints/ parameters	4327 / 0 / 290	6379 / 462 / 450	3309 / 18 / 314
Goodness-of-fit on F^2	1.057	1.211	1.030
Final R indices [I > 2σ(I)]	R1 = 0.0310, wR2 = 0.0881	R1 = 0.0571, wR2 = 0.1172	R1 = 0.0492, wR2 = 0.1179
R indices (all data)	R1 = 0.0344, wR2 = 0.0920	R1 = 0.0974, wR2 = 0.1504	R1 = 0.0743, wR2 = 0.1317

Analysis of steric properties

The %V_{bur} at the C4 and C5 positions of the triazolium moiety in the complexes **3** and **4a’** was calculated using the SambVca 2.0 tool.[5a] The bond radii were scaled by 1.17 and the sphere radii of 3.5 Å and 5 Å were chosen. A mesh spacing of 0.10 Å for numerical integration was applied. Hydrogens were neglected during the calculations. The steric map[5b] obtained for each case is also given along with the %V_{bur} values.[5c]

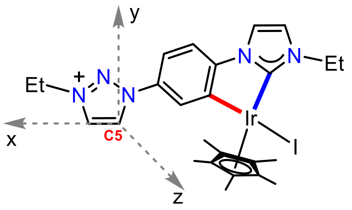


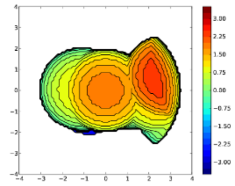
Complex 3



Complex 4a'

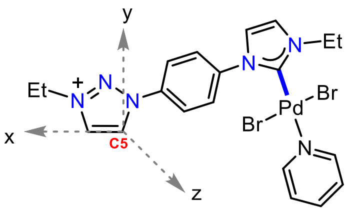
1) **<u>At C5 position of complex 4a’</u> (r = 3.5 Å)**

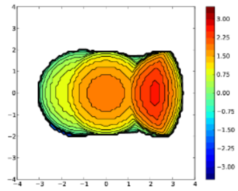




%V Free		%V Buried		% V Tot/V Ex	
49.6		**50.4**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	26.3	18.5	44.9	58.7	41.3
NW	25.3	19.6	44.9	56.4	43.6
NE	17.6	27.3	44.9	39.2	60.8
SE	19.8	25.1	44.9	44.1	55.9

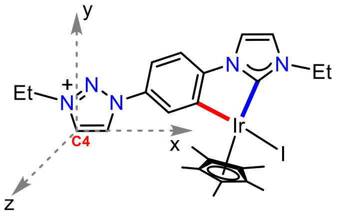
2) **<u>At C5 position of complex 3</u> (r = 3.5 Å)**

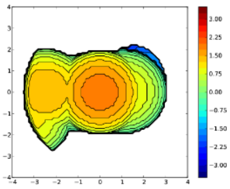




%V Free		%V Buried		% V Tot/V Ex	
49.9		**50.1**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	25.6	19.2	44.9	57.2	42.8
NW	25.5	19.3	44.9	56.9	43.1
NE	19.4	25.4	44.9	43.3	56.7
SE	18.9	25.9	44.9	42.2	57.8

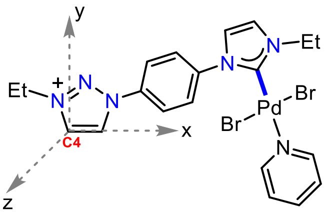
3) **<u>At C4 position of complex 4a’</u> (r = 3.5 Å)**

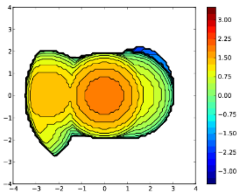




%V Free		%V Buried		% V Tot/V Ex	
51.9		**48.1**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	20.2	24.7	44.9	45.0	55.0
NW	21.6	23.2	44.9	48.2	51.8
NE	25.3	19.6	44.9	56.3	43.7
SE	26.1	18.7	44.9	58.2	41.8

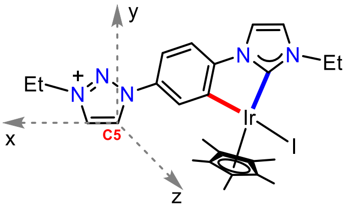
4) **At C4 position of complex 3** (r = 3.5 Å)

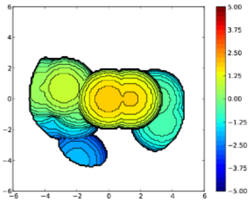




%V Free		**%V Buried**		% V Tot/V Ex	
51.2		**48.8**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	17.7	27.1	44.9	39.6	60.4
NW	23.4	21.5	44.9	52.2	47.8
NE	24.7	20.1	44.9	55.1	44.9
SE	26.0	18.8	44.9	58.0	42.0

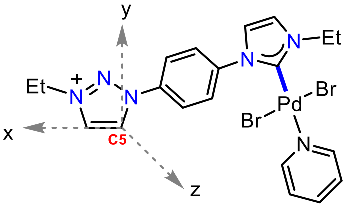
5) **At C5 position of complex 4a’** (r = 5.0 Å)

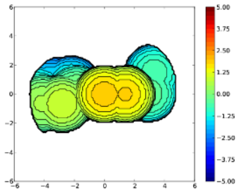




%V Free		**%V Buried**		% V Tot/V Ex	
69.8		**30.2**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	87.8	43.0	130.8	67.1	32.9
NW	89.3	41.6	130.8	68.2	31.8
NE	98.3	32.5	130.8	75.2	24.8
SE	89.6	41.2	130.8	68.5	31.5

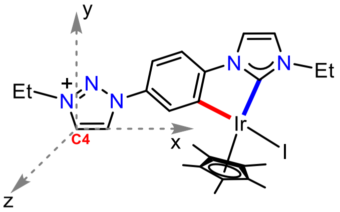
6) **At C5 position of complex 3** (r = 5.0 Å)

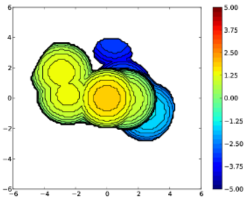




%V Free		**%V Buried**		% V Tot/V Ex	
70.6		**29.4**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	89.6	41.3	130.8	68.5	31.5
NW	92.1	38.7	130.8	70.4	29.6
NE	89.6	41.2	130.8	68.5	31.5
SE	98.4	32.4	130.8	75.2	24.8

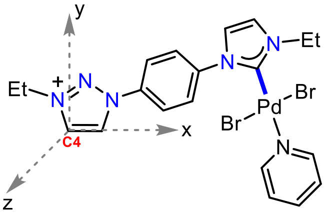
7) **At C4 position of complex 4a’** (r = 5.0 Å)

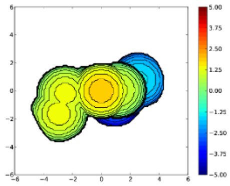




%V Free		**%V Buried**		% V Tot/V Ex	
72.7		**27.3**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	104.7	26.1	130.8	80.0	20.0
NW	81.2	49.6	130.8	62.1	37.9
NE	99.8	31.0	130.8	76.3	23.7
SE	94.7	36.1	130.8	72.4	27.6

8) **At C4 position of Complex 3** (r = 5.0 Å)





%V Free		**%V Buried**		% V Tot/V Ex	
73.0		**27.0**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	82.2	48.6	130.8	62.8	37.2
NW	104.1	26.7	130.8	79.6	20.4
NE	95.3	35.5	130.8	72.9	27.1
SE	100.4	30.4	130.8	76.8	23.2

Computational data

All the calculations were performed using the Gaussian 16, Revision B.01 program.[6] All structures were optimized with B3LYP[7] functional. Metals (Ir and Pd) were treated with SDD (Stuttgart-Dresden)[8] basis set with an effective core potential, while the other atoms were treated using 6-31G**,[9] a double-ζ Pople type basis set. Further, the solvent (chloroform) effect was incorporated by using CPCM solvent model, scrf= (cpcm, solvent=chloroform).

Optimized ground state energy for **5** = -11893.535557 Hartree

5' = -11893.534442 Hartree

7 = -9439.647239 Hartree

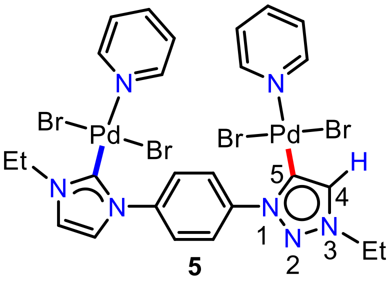
7' = -9439.645026 Hartree

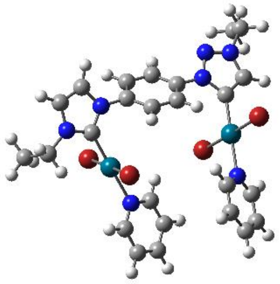
The difference in ground state energies of **5** and **5'** = 0.001115 Hartree = 0.7 Kcalmol^{-1}

The difference in ground state energies of **7** and **7'** = 0.002213 Hartree = 1.4 Kcalmol^{-1}

Cartesian coordinates of all the optimized geometries:

1. Complex 5





35	4.004957000	0.596015000	-2.469277000
35	2.241872000	0.545273000	2.206199000
35	-3.050556000	1.135474000	-2.227682000
35	-3.231507000	-0.927967000	2.318754000
6	5.908985000	-4.414231000	2.205072000
1	6.207247000	-3.492268000	2.711165000
1	6.672812000	-5.173148000	2.394637000
1	4.963281000	-4.760358000	2.629954000
6	5.782056000	-4.202331000	0.697809000

1	6.717902000	-3.852009000	0.258397000
1	5.479872000	-5.116635000	0.185516000
6	4.897611000	-1.839894000	0.329063000
1	5.844779000	-1.355694000	0.502890000
6	3.651285000	-1.305255000	0.040072000
6	1.459488000	-2.516329000	-0.335065000
6	0.884515000	-1.656319000	-1.271822000
1	1.503801000	-0.961366000	-1.826638000
6	-0.490174000	-1.710309000	-1.489784000
1	-0.960782000	-1.040672000	-2.200546000
6	-1.267138000	-2.627267000	-0.778927000
6	-0.681068000	-3.512766000	0.128061000
1	-1.297376000	-4.216060000	0.677149000
6	0.691604000	-3.454754000	0.357474000
1	1.157240000	-4.112030000	1.081829000
6	-3.542280000	-1.637698000	-0.733088000
6	-4.685361000	-3.412134000	-1.527374000
1	-5.554664000	-3.958924000	-1.855834000
6	-3.380444000	-3.772553000	-1.471952000
1	-2.878575000	-4.684162000	-1.752234000
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1	-6.615957000	-1.537087000	-1.830916000
1	-5.758443000	-0.294642000	-0.913312000
6	-6.794522000	-1.748301000	0.328882000
1	-7.066192000	-2.808209000	0.312777000
1	-7.716440000	-1.162194000	0.389695000
1	-6.195106000	-1.553812000	1.222404000
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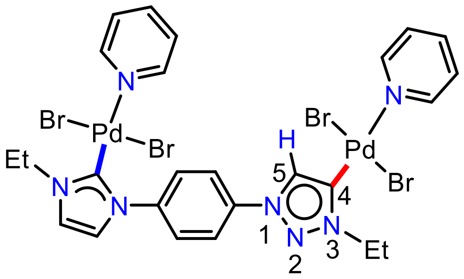

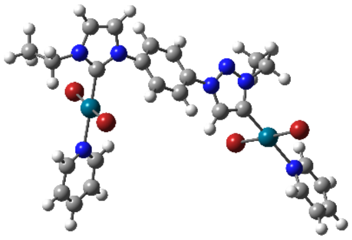

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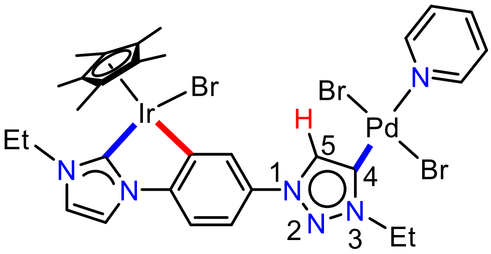
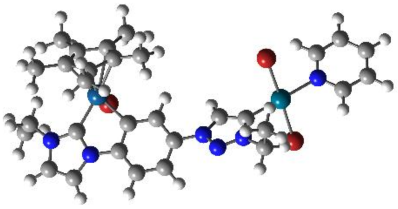
3. Complex 7





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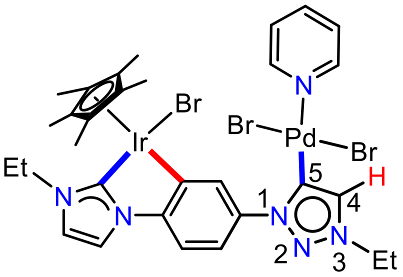
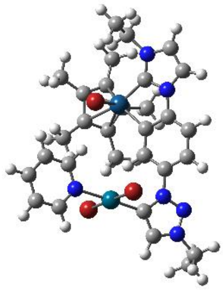
4. Complex 7’





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[6] *Gaussian 16, Revision B.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam,

M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

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