Supplementary Information

for

Carbon Supported Hybrid Catalysts for Controlled Product Selectivity in the Hydrosilylation of Alkynes

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Content:

1. Syntheses

General

Experiments were conducted under Ar atmosphere unless stated otherwise. Starting materials and solvents were purchased from Sigma-Aldrich, AK Scientific, Honeywell and Merck. Solvents were purified using an LC Technology Solution Inc. solvent purification system, and further dried by storage over 4 Å molecular sieves. NMR spectra were recorded on Bruker AV

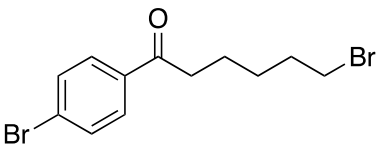
NEO 300, -AVIIIHD 300 MHz, -AVIIIHD 400 MHz, AV 400MHz, and AVIIIHD 500 MHz spectrometers. NMR spectra were referenced to residual solvent signals.[1] Mass spectra were acquired on a Q Exactive Plus hybrid quadrupole-Orbitrap mass spectrometer (ThermoFisher Scientific) equipped with a Vanquish UHPLC, a Bruker amaZon SL mass spectrometer, a Bruker Solarix 2xR 7T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer and on an Agilent 7820A GC coupled to an Agilent 5977B MSD instrument. Microanalyses were obtained from the Macquarie University Chemical Analyses Facility. The reported value is the average of two individual measurements. IR spectra were recorded at a Thermo Scientific Nicolet iS5 spectrometer equipped with an iD5 ATR accessory and on a Shimadzu IRSpirit spectrometer equipped with QATR-S single-reflection ATR accessory.

Syntheses of Ligands

Propargylpyrazole: Pyrazole (3.0 g, 44.1 mmol) and propargylbromide (10.5 mL, 80 wt% in toluene) were dissolved in acetone (60 mL). An excess of K_2CO_3 (5 eq., 30.5 g, 220.3 mmol) was added and the suspension was refluxed for 16 h. The mixture was allowed to cool down to room temperature and was filtered through a glass frit. The acetone was removed using rotary evaporator and the crude product was dried under vacuum. Subsequently, it was filtered through a plug of celite using ethyl acetate as solvent. Solvent evaporation and drying under high vacuum afforded the product as a dark oil (4.10 g, 38.7 mmol, 88 %). ^{1}H and ^{13}C NMR spectroscopic data was in agreement with the literature.[2]

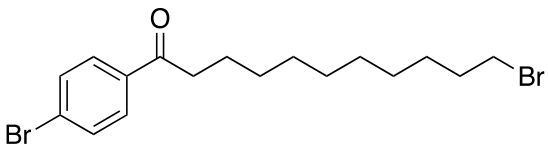
(4-Bromophenyl)tri-*n*-butylstannane (2): 1,4-Dibromobenzene (3.5 g, 14.8 mmol) was dissolved in THF (140 mL) in a Schlenk flask and cooled to - 78 °C. *n*-Butyllithium (9.7 mL, 15.6 mmol, 1.05 eq.) was added slowly over 30 min under stirring using a syringe pump. Stirring was continued for another 30 min before tri-*n*-butyltin chloride (5.32 g, 16.3 mmol)

were added over 15 min using a syringe pump. The cooling bath was removed and the mixture was allowed to warm up to room temperature. Water (150 mL) was added and the mixture was transferred into a separatory funnel. The mixture was extracted with hexane (3 × 200 mL). The combined organic layers were dried over $MgSO_4$ and solvent evaporation afforded a colourless oil, which was either subject to column chromatography on silica using hexane eluent giving a major product fraction as first fraction, and another fraction containing minor impurities as second fraction, which was re-chromatographed. The obtained clean product fractions were combined and the solvent was evaporated using a rotary evaporator. This was followed by drying under vacuum, affording 5.25 g (11.8 mmol, 79 %) of a colorless oil. ^{1}H and ^{13}C NMR spectroscopic data was in agreement with the literature.[3]



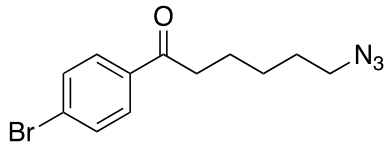
3a: A Schlenk flask was charged with 6-bromohexanoic acid (1.1 g, 5.6 mmol) and dichloromethane (30 mL). Oxalyldichloride (1.4 mL, 16.8 mmol) was added while stirring at room temperature, followed two drops of DMF. The mixture was stirred for 45 min after which the gas evolution had ceased. The solvents and the excess of oxalyldichloride were removed under vacuum and the colorless oily solids were dried and subsequently re-dissolved in 50 mL dichloromethane, followed by addition of aluminum(III) chloride (0.75 g, 5.6 mmol). The mixture was stirred for 15 min at room temperature. A second Schlenk flask was charged with **2** (2.5 g, 5.6 mmol) and dichloromethane (50 mL) and cooled to -78 °C. The acid chloride / aluminum(III) chloride mixture was taken up with a syringe and added slowly over 1 h under stirring to the solution of **2** using a syringe pump. After completed addition, the cooling bath was removed and the mixture was allowed to warm up to room temperature, at which point water (100 mL) was added and the work-up was conducted on air. Phases were separated and the aqueous layer was extracted twice with dichloromethane (100 mL). The combined organic

extracts were dried over $MgSO_4$ and concentrated to dryness using a rotary evaporator. The crude mixture was flash-filtered through a short column (12 cm × 3 cm), filled with silica/KF (1:1 /vol) in the upper half and silica in the lower half with pure silica, using dichloromethane as eluent, which removed efficiently the tin by-products.[4, 5] Solvent evaporation gave a colorless oil, which crystallized upon standing. Re-crystallization from pentane at -20 °C afforded colorless needles, which was repeated twice to yield the title compound as white crystalline solid (859 mg, 2.6 mmol, 46 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.61 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 3.43 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 2H, C*H*$_2$Br), 2.92 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, COC*H*$_2$), 1.92 (m, 2H), 1.77 (m, 2H), 1.54 (m, overlaps with H_2O signal, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.0, 135.8, 132.0, 129.7, 128.3, 38.4, 33.7, 32.7, 27.9, 23.3 ppm. MS (APCI) m/z: 385 $[M + H]^+$ (100%). HRMS (APCI): m/z [M + H] calcd for $C_{12}H_{15}Br_2O$: 334.94637; found: 334.94636.

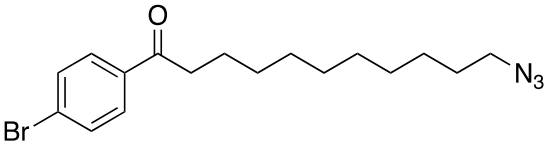


3b: The title compound was prepared analogously to compound **3a**. 11-bromoundecanoic acid (1.55 g, 5.8 mmol) and **2** (2.6 g, 5.8 mmol) gave a colorless oil, which crystallized upon standing. Re-crystallization from pentane (250 mL) at 6 °C gave the product as white solid. The solids were collected using a Büchner funnel, washed with little pentane and dried under high vacuum, affording the product as white microcrystalline powder (1250 mg, 3.1 mmol, 53 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.82 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.60 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 3.41 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, C*H*$_2$Br), 2.92 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 2H, COC*H*$_2$), 1.85 (m, 2H), 1.72 (m, 2H), 1.44-1.29 (brd, 12H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 199.5, 135.9, 132.0, 131.71, 131.66, 130.0, 129.7, 128.7, 128.1, 38.7, 34.2, 32.9, 29.51, 29.47, 29.45, 29.4,

28.8, 28.3, 24.3 ppm. MS (APCI) m/z: 405 $[M + H]^+$ (100%), HRMS (APCI) m/z: calcd for $C_{17}H_{25}Br_2O$: 405.02462; found: 405.02474.

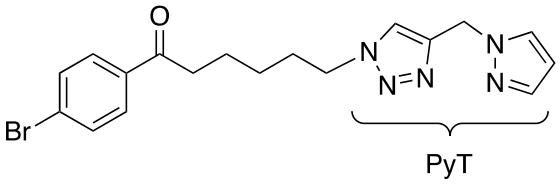


4a: Compound **3a** (600 mg, 1.8 mmol) was dissolved DMF (20 mL). Sodium azide (175 mg, 2.7 mmol) was added and the mixture was heated to 120 °C under stirring for 3h. The mixture was allowed to cool down to room temperature, diluted with ethyl acetate (120 mL) and extracted with water (3 × 150 mL). The organic layer was collected, dried over $MgSO_4$ and solvents were evaporated using a rotary evaporator, which was followed by drying under high vacuum. The product was obtained as pale yellow oil (0.526 mg, 1.8 mmol, 99 %). The reactive azide was only characterized by ^{1}H and ^{13}C NMR spectroscopy and immediately used in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dm, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, Ar-*H*), 7.59 (dm, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, Ar-*H*), 3.28 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H, CH_2N$_3$), 2.94 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, COCH_2), 1.75 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 1.45 (m, 2H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.0, 135.7, 132.0, 129.6, 128.2, 51.3, 38.3, 28.9, 26.5, 23.7 ppm.



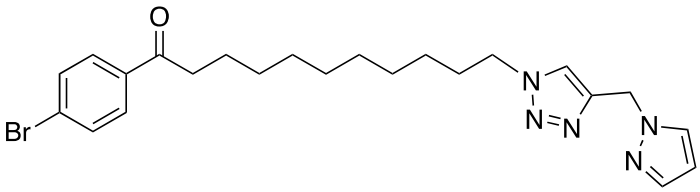
4b: The title compound was prepared analogously to compound **4a**. Compound **3b** (1.05 g, 2.6 mmol) and sodium azide (255 mg, 3.9 mmol) in DMF (40 mL) gave the product as pale yellow oil (0.949 mg, 2.6 mmol, 99%), which crystallized upon standing. The reactive azide was only characterized by ^{1}H and ^{13}C NMR spectroscopy and immediately used in the next step. ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 7.81 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.59 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 3.25 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, CH_2N$_3$), 2.91 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, 2H), 1.71 (m, 2H), 1.58 (m, 2H), 1.34 - 1.29 (brd, 14 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ= 199.6,

135.9, 132.0, 129.7, 128.1, 77.5, 77.2, 76.8, 51.6, 38.7, 29.51, 29.45, 29.4, 29.2, 28.9, 26.8, 24.3 ppm.



5a: A round bottom flask was charged with compound **4a** (500 mg, 1.7 mmol), *tert.*-butanol (20 mL) and water (40 mL). Propargylpyrazole (223 mg, 2.1 mmol), coppersulfate · 5 H_2O (34 mg, 0.1 mmol) and sodium ascorbate (27 mg, 0.1 mmol) were added while stirring. The mixture was stirred for 16 h at 50 °C. After the reaction was completed, water (100 mL) was added, which led to the formation of a precipitate. Work-up was carried out by extraction with ethyl acetate (3 × 80 mL). The combined organic layers were dried over $MgSO_4$, concentrated to dryness and dried under high vacuum to afford a light brown oil which crystallized upon standing. Yield: 656 mg (1.6 mmol, 97%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.80 (dm, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, Ar-*H*), 7.61 (dm, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, Ar-*H*), 7.57 (brm, 2H, PyT), 7.52 (brm, 1H, PyT), 6.31 (brm, 1H, PyT), 5.39 (s, 2H, N_3CHC-CH_2), 4.33 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2PyT), 2.92 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, COCH_2), 1.92 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 1.37 (m, 2H, CH_2) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 198.9, 144.5 (brd[1]), 140.3 (brd[1]), 136.1, 132.2, 129.8, 128.2, 123.5 (brd[1]), 106.9 (brd[1]), 50.5, 47.6, 38.4, 30.4, 26.4, 23.5 ppm. MS (ESI) m/z: 402 $[M + H]^+$ (100%). HRMS (ESI) m/z: calcd for $C_{18}H_{20}BrN_5O$: 402.0930; found: 402.0914.

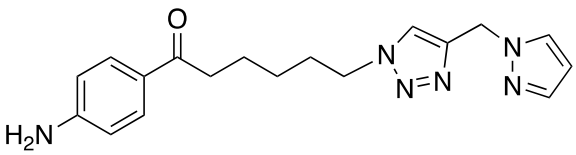
[1] These signals consistently appeared broadened, thus resulting in loss of intensity.



5b: A round bottom flask was charged with compound **4b** (850 mg, 2.6 mmol), *tert.*-butanol (70 mL) and water (80 mL). While stirring, propargylpyrazole (365 mg, 3.4 mmol), copper sulfate · 5 H_2O

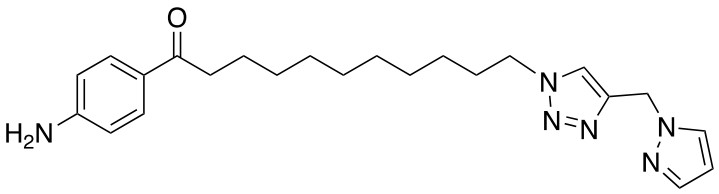
(57 mg, 0.2 mmol) and sodium ascorbate (45 mg, 0.2 mmol) of were added. The mixture was stirred for 16 h, after which a thick off-white precipitation formed. The mixture was diluted with water (100 mL) and the solids were collected using a Büchner funnel and washed with several portions of water. Drying under high vacuum afforded 1.103 g of an off-white solid. Extraction of the remaining solution of the reaction mixture and washings 3 × with 100 mL ethyl acetate, drying the combined organic phases over $MgSO_4$, solvent evaporation and drying under high vacuum gave another 110 mg of the title compound. Combined yield: 1.213 g (0.25 mmol, 90 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.82 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.61 (dm, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.52 (m, 1H, PyT), 7.49 (m, 1H, PyT), 7.47 (m, 1H, PyT), 6.25 (t, $^3J_{H\text{-}H}$ = 2.0 Hz, 1H, PyT), 5.40 (s, 2H, $N_3CHC\text{-}CH_2$), 4.29 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, CH_2PyT), 2.92 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, $COCH_2$), 1.86 (m, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.36-1.28 (brd, 12H, CH_2) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 199.6, 143.9 (brd[1]), 139.9 (brd[1]), 136.4, 132.2, 129.9, 128.1, 122.8 (brd[1]), 106.3 (brd[1]), 50.8, 47.8, 38.9, 30.6, 29.8, 29.76, 29.69, 29.6, 29.3, 26.8, 24.5 ppm. MS (ESI) m/z: 472 $[M + H]^+$ (100%). HRMS (ESI) m/z: calcd for $C_{23}H_{31}BrN_5O$: 472.17120; found: 472.1701.

[1] These signals consistently appeared broadened, thus resulting in loss of intensity.

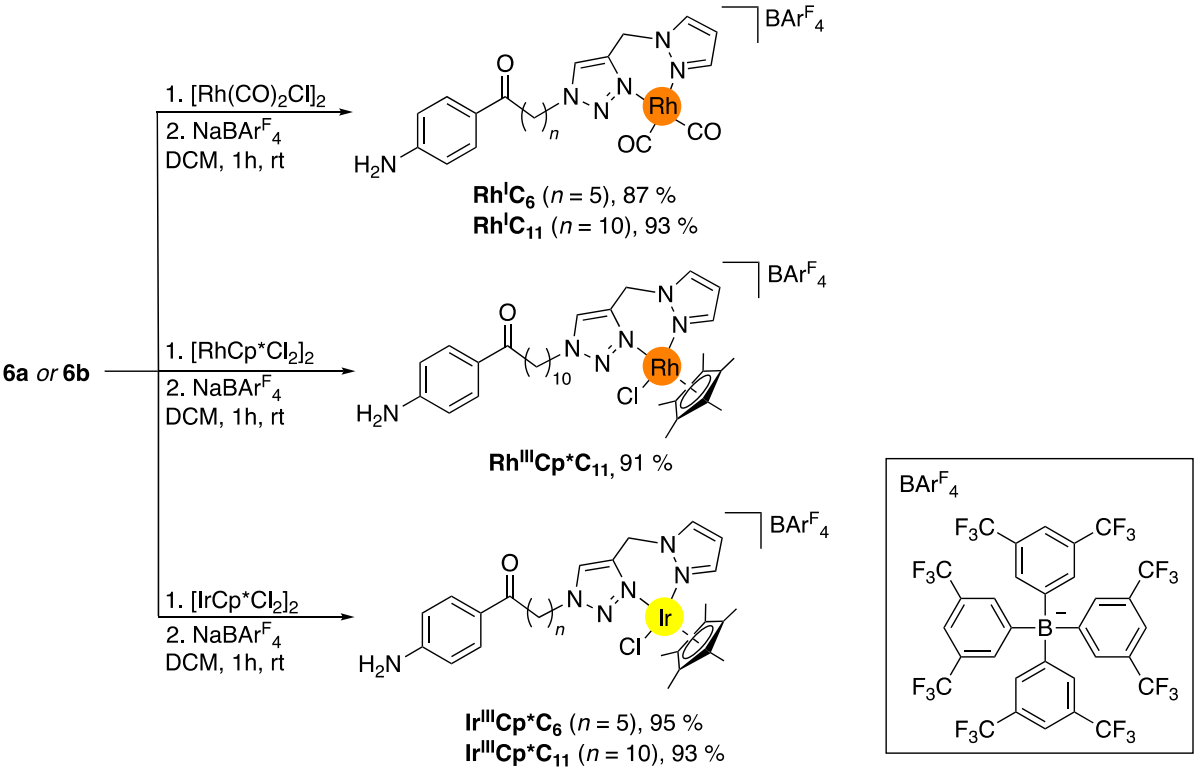


6a: Aryl bromide **5a** (180 mg, 0.45 mmol) was dissolved in ethanol/water (7:3; 9 mL). Copper iodide (85 mg, 0.45 mmol), sodium azide (117 mg, 1.80 mmol) and sodium ascorbate (89 mg, 0.45 mmol) were added and the mixture was refluxed for 24 h. After cooling down to room temperature, water was added (80 mL) and the mixture was extracted with ethyl acetate (3 × 80 mL). The combined organic extracts were dried over magnesium sulfate, the solvents were removed using a rotary evaporator and the crude solids were dried under vacuum. The crude mixture was re-dissolved in little

dichloromethane (~ 2 mL) and applied on a short column prefilled with silica and wetted with ethyl acetate. Flash chromatography using ethyl acetate as eluent afforded a pure fraction, which was concentrated to dryness using a rotary evaporator, followed by drying under high vacuum. The product crystallized upon standing, giving an off-white crystalline solid (113 mg, 0.33 mmol, 74 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.75 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.52 (m, 2H, PyT), 7.47 (m, 1H, PyT), 6.64 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 6.25 (t, $^{3}J_{H\text{-}H}$ = 2.1 Hz, 1H, PyT), 5.40 (s, 2H, N_3CHC-C*H*$_2$), 4.31 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, PyTC*H*$_2$), 3.41 (brd, 2H, N*H*$_2$), 2.84 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, COC*H*$_2$), 1.90 (m, 2H, C*H*$_2$), 1.70 (m, 2H, C*H*$_2$), 1.36 (m, 2H, C*H*$_2$) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 198.1, 151.8, 143.7, 139.8, 130.6, 129.6, 127.7, 122.9, 113.9, 106.1, 50.6, 47.7, 37.8, 30.5, 26.5, 24.1 ppm. MS (ESI) m/z: 339 $[M + H]^+$ (100%). HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_6O$: 339.1933; 339.1920.

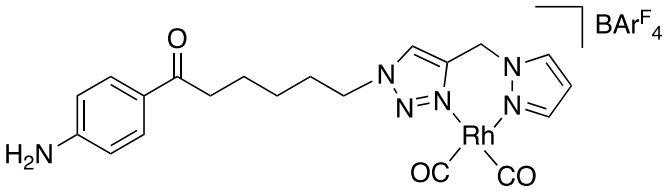


6b: The compound was prepared analogously to compound **6a**. Aryl bromide **5b** (200 mg, 0.42 mmol), copper iodide (81 mg, 0.2 mmol), sodium azide (110 mg, 1.7 mmol) and sodium ascorbate (84 mg, 0.42 mmol) in EtOH/H_2O (7:3; 9 mL) gave the title compound as off-white crystalline solid (120 mg, 0.28 mmol, 67 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.77 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.52 (m, 1H, PyT), 7.51 (m, 1H, PyT), 7.47 (m, 1H, PyT), 6.64 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 6.25 (t, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, PyT), 5.40 (s, 2H, N_3CHC-C*H*$_2$), 4.30 (concealed s, 2H, N*H*$_2$), 4.27 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 2H, C*H*$_2$PyT), 2.83 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, COC*H*$_2$), 1.86 (m, 2H, C*H*$_2$), 1.66 (m, 2H, C*H*$_2$), 1.35-1.27 (brd, 12H, C*H*$_2$) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 198.8, 151.7, 143.7, 139.8, 130.7, 129.6, 127.8, 122.8, 113.9, 106.1, 50.8, 47.7, 38.2, 30.5, 29.8, 29.73, 29.68, 29.65, 29.3, 26.8, 25.1 ppm. MS (ESI) m/z: 409 $[M + H]^+$ (100%), HRMS (ESI) m/z: calcd for $C_{23}H_{33}N_6O$: 409.27160; found: 409.2701.



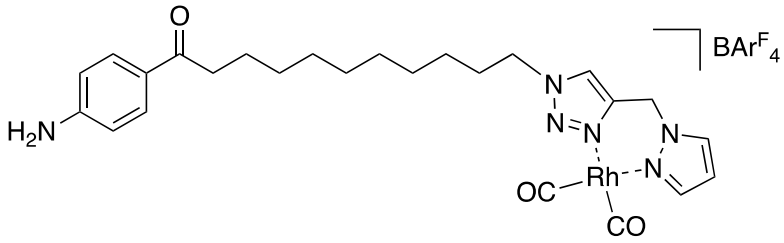
Syntheses of Metal Complexes

Scheme S1. Syntheses of complexes $\mathbf{Rh^{I}C_6}$, $\mathbf{Rh^{I}C_{11}}$, $\mathbf{Rh^{III}Cp^{*}C_{11}}$, $\mathbf{Ir^{III}Cp^{*}C_6}$, $\mathbf{Ir^{III}Cp^{*}C_{11}}$ from the ligands **6a**/**b** and metal precursors.



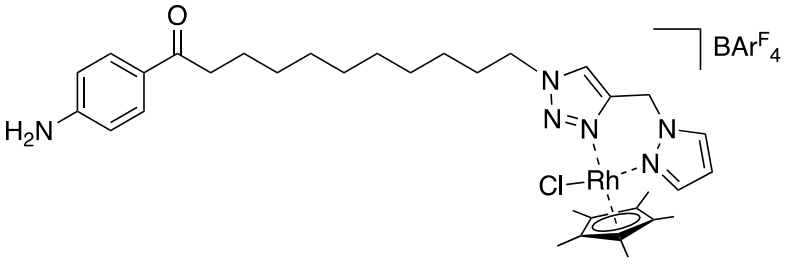
$\mathbf{Rh^{I}C_6}$: A Schlenk flask was charged with ligand **6a** (50 mg, 0.15 mmol) of and dichloromethane (6 mL). Di-μ-chloro-tetracarbonyldirhodium(I) (39 mg, 0.07 mmol) was added and the solution was stirred for 30 min at room temperature after which sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBAr^{F}_4$) (131 mg, 0.15 mmol) was added and the mixture was stirred for another 30 min. After the addition of $NaBAr^{F}_4$, the solution turned cloudy. The crude mixture was filtered through a plug of celite (4 × 3 cm) using dichloromethane as eluent and concentrated to a volume of about 2 mL using rotary evaporator. Pentane (4 mL) was added to precipitate the product as red-brown oil. The slightly turbid solution was allowed to stand for 20 min, and the

now colorless liquids were removed and discarded. The oil was re-dissolved in dichloromethane (1 mL) and the procedure was repeated, followed by drying under high vacuum, which afforded 174 mg (0.12 mmol, 87 %) of a red-brown solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.02 (m, 1H, PyT), 7.82 (m, 1H, PyT), 7.77-7.72 (brd, 11H, PyT/Ar-*H*/BAr^F_4), , 7.57 (m, 4H, BAr^F_4), 6.65 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 6.53 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, PyT), 5.43 (s, 2H, N_3CHC-C*H*$_2$), 4.53 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 2H, C*H*$_2$PyT), 4.22 (brd, 2H, N*H*$_2$), 2.90 (t, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 2H, COC*H*$_2$), 2.00 (m, 2H, C*H*$_2$), 1.76 (m, 2H, C*H*$_2$), 1.39 (m, 2H, C*H*$_2$) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 198.1, 182.9 (d, $^{1}J_{C\text{-}Rh}$ = 68.8 Hz), 182.0 (d,$^{1}J_{C\text{-}Rh}$ = 70.2 Hz), 162.2 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz, ipso-*C*, BAr^F_4), 151.9, 147.1 (d, $^{2}J_{C\text{-}Rh}$ ≈ 2.1 Hz), 139.7, 135.2 (brd, m-*C*H, BAr^F_4), 135.1, 130.7, 129.3 (qq, $^{2}J_{C\text{-}F}$ = 31.5 Hz, $^{3}J_{C\text{-}B}$ = 2.9 Hz, *C*-CF_3, BAr^F_4), 128.3, 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz, *C*F_3, BAr^F_4), 123.9, 117.9 (m, p-*C*H, BAr^F_4), 114.0, 108.90 (d, $^{3}J_{C\text{-}Rh}$ ≈ 1.3 Hz), 52.9, 45.9, 37.3, 29.9, 26.0, 23.3 ppm. MS (ESI) m/z: 497 $[M]^+$ (100%). HRMS (ESI) m/z: calcd for $C_{20}H_{22}N_6O_3Rh$: 497.08084; found: 497.08047. Elemental analysis: calcd (%) for $C_{52}H_{34}BF_{24}N_6O_3Rh$: C (45.91); H (2.52); N (6.18); found: C (45.66); H (2.15); N (6.16). IR (ATR): 2107 (m), 2048 (m), 1661 (w), 1662 (w), 1598 (w), 1572 (w), 1522 (w), 1465 (w), 1439 (w), 1421 (w), 1353 (m), 1273 (s), 1114 (s), 1001 (w), 973 (w), 933 (w), 886 (m), 893 (m), 790 (w), 762 (w), 745 (w), 712 (m), 682 (m), 669 (m), 638 (w), 622 (w), 609 (w), 602 (w), 577 (w), 566 (w), 556 (w).



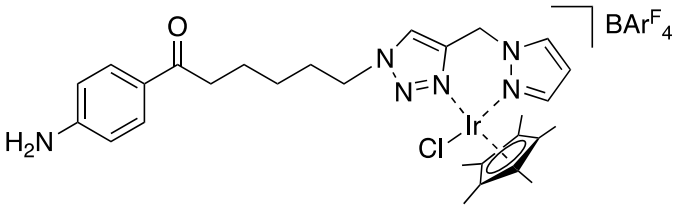
Rh^{I}C$_{11}$: A Schlenk flask was charged with ligand **6b** (135 mg, 0.32 mmol) and dichloromethane (15 mL). Reaction with di-μ-chloro-tetracarbonyldirhodium(I) (62 mg, 0.16 mmol) and $NaBAr^F_4$ (283 mg, 0.32 mmol), followed by work-up analogously to the above described preparation of **RhC$_6$**

gave 425 mg (0.29 mmol, 93 %) of a red-brown solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.86 (m, 1H, PyT), 7.84 (m, 1H, PyT), 7.77 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.75 (m, 1H, PyT), 7.72 (m, 8H, BAr^{F}_4), 7.55 (m, 4H, BAr^{F}_4), 6.65 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 6.53 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, PyT), 5.45 (s, 2H, $N_3CHC\text{-}CH_2$), 4.47 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, CH_2PyT), 4.19 (brd, 2H, NH_2), 2.84 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, $COCH_2$), 1.95 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.33-1.28 (brd, 12H, CH_2) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 199.3, 182.7 (d, $^{1}J_{C\text{-}Rh} \approx$ 70.6 Hz), 182.0 (d, $^{1}J_{C\text{-}Rh} \approx$ 70.9 Hz), 162.2 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz, ipso-*C*, BAr^{F}_4), 151.8, 147.1 (d, $^{2}J_{C\text{-}Rh} \approx$ 2.1 Hz), 139.9, 135.3 (brd, m-*C*H, BAr^{F}_4), 135.2, 130.8, 129.3 (qq, $^{2}J_{C\text{-}F}$ = 31.5 Hz, $^{3}J_{C\text{-}B}$ = 2.9 Hz, *C*-CF_3, BAr^{F}_4), 127.8, 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz, *C*F_3, BAr^{F}_4), 124.0, 118.0 (m, p-*C*H, BAr^{F}_4), 114.0, 108.9 (d, $^{3}J_{C\text{-}Rh} \approx$ 1.3 Hz), 53.4, 45.8, 38.3, 30.0, 29.71, 29.68, 29.5, 29.4, 29.0, 26.4, 25.2 ppm. MS (ESI) m/z: 567 $[M]^+$ (100%). HRMS (ESI) m/z: calcd for $C_{25}H_{32}N_6O_3Rh$: 567.15909; found: 567.15857. Elemental analysis: calcd (%) for $C_{57}H_{44}BF_{24}N_6O_3Rh$: C (47.85); H (3.10); N (5.87); found: C (48.19); H (2.72); N (6.12). IR (ATR): 2934 (w), 2860 (w), 2107 (m), 2048 (m), 1784 (w), 1660 (w), 1622 (w), 1598 (w), 1522 (w), 1465 (w), 1439 (w), 1421 (w), 1553 (s), 1272 (s), 1158 (m), 1113 (s), 1094 (s), 1001 (w), 945 (w), 933 (w), 886 (m), 838 (m), 796 (w), 761 (w), 745 (w), 712 (m), 681 (m), 669 (m), 638 (w), 621 (w), 609 (w), 602 (w), 586 (w), 577 (w), 566 (w), 556 (w).



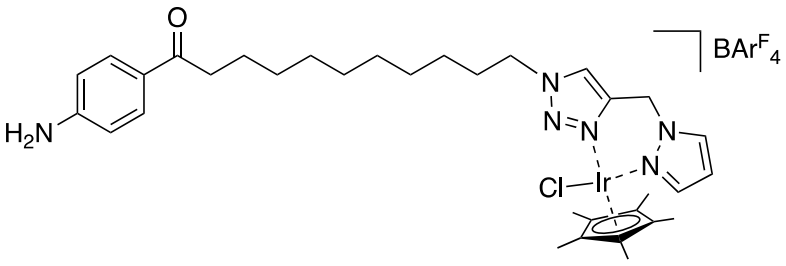
$Rh^{III}Cp^*C_{11}$: A Schlenk flask was charged with ligand **6b** (50 mg, 0.12 mmol) and dichloromethane (6 mL). Pentamethylcyclopentadienylrhodium(III)chloride dimer (38 mg, 0.06 mmol) was added and the mixture was stirred for 30 min at room temperature. This was followed by addition of $NaBAr^{F}_4$ (108 mg, 0.12 mmol). Stirring was continued for another 30 min before work-up was

carried out analogously to the above described procedure, giving the title compound (172 mg, 0.11 mmol, 91 %) as orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.80 (m, 2H, PyT), 7.76 (dm, $^{3}J_{H\text{-}H}$ = 8.7 Hz, 2H, Ar-*H*), 7.72 (brm, 9H, BAr^{F}_{4}/PyT), 7.56 (m, 4H, BArF), 6.65 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, Ar-*H*), 6.56 (t, $^{3}J_{H\text{-}H}$ = 2.5 Hz, 1H, PyT), 5.57 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, N_3CHC-C*H*$_2$), 5.07 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, N_3CHC-C*H*$_2$), 4.49 (m, 2H, C*H*$_2$PyT), 4.17 (brd, 2H, N*H*$_2$), 2.84 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, COC*H*$_2$), 1.96 (m, 2H, C*H*$_2$), 1.68 (s, 15H, Cp*, C*H*$_3$), 1.66 (m, 2H, C*H*$_2$) 1.33-1.26 (brm, 12H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 198.9, 162.2 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz, ipso-*C*, BAr^{F}_{4}), 151.7, 145.4, 139.6, 135.2 (brd, m-*C*H, BAr^{F}_{4}), 134.7, 130.7, 129.3 (qq, $^{2}J_{C\text{-}F}$ = 31.5 Hz, $^{3}J_{C\text{-}B}$ = 2.9 Hz, *C*-CF_3, BAr^{F}_{4}), 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz, *C*F_3, BAr^{F}_{4}), 124.1, 117.9 (m, p-*C*H, BAr^{F}_{4}), 114.0, 109.1, 97.5 (d, $^{1}J_{C\text{-}Rh}$ = 8.3 Hz), 45.4, 38.2, 30.2, 29.70, 29.66, 29.5, 29.0, 26.5, 25.0, 9.4 ppm. MS (ESI) m/z: 681 $[M]^{+}$ (100%), 323 (94 %). HRMS (ESI) m/z: calcd for $C_{33}H_{47}ClN_6ORh$: 681.25494, found: 681.25440. Elemental analysis: calcd (%) for $C_{65}H_{59}BCl\,F_{24}N_6ORh$: C (50.52), H (3.85), N (5.44); found: C (50.79), H (3.79), N (5.33). IR (ATR): 3341 (w), 2932 (w), 2859 (w), 2361 (w), 2340 (w), 1659 (w), 1623 (w), 1597 (w), 1569 (w), 1519 (w), 1487 (w), 1463 (w), 1438 (w), 1417 (w), 1353 (m), 1323 (w), 1273 (s), 1159 (m), 1116 (s), 1072 (m), 1023 (w), 993 (w), 945 (w), 932 (w), 866 (m), 839 (m), 792 (w), 758 (w), 745 (w), 712 (m), 682 (m), 669 (m), 640 (w), 621 (w), 603 (w), 580 (w), 569 (w).



Ir^{III}Cp*C$_6$: A Schlenk flask was charged with ligand **6a** (79 mg, 0.23 mmol) and dichloromethane (10 mL). Pentamethylcyclopentadienyliridium(III)chloride dimer (93 mg, 0.12 mmol) was added and the mixture was stirred for 30 min at room temperature. This was followed by addition of $NaBAr^{F}_{4}$ (207 mg, 0.23 mmol). Stirring was continued for another 30 min before work-up was carried out analogously to the above described procedure for the rhodium complexes, giving

the title compound as light yellow solid (350 mg, 0.22 mmol, 95 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.93 (m, 1H, PyT), 7.78-7.73 (brm, 11H, BAr^F_4/PyT/Ar-*H*) 7.69 (m, 1H, PyT), 7.59 (m, 4H, BAr^F_4), 6.65 (dm, $^{3}J_{H\text{-}H}$ = 8.8 Hz, 2H, Ar-*H*), 6.55 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, PyT-*H*), 5.54 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, $N_3CHC\text{-}CH_2$), 4.93 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, $N_3CHC\text{-}CH_2$), 4.46 (m, 2H, CH_2PyT), 4.22 (brd, 2H, NH_2), 2.89 (apparent t, $^{3}J_{H\text{-}H} \approx$ 7 Hz, 2H, COC*H*), 2.00 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 1.62 (s, 15H, Cp*, CH_3), 1.39 (m, 2H, CH_2) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 198.0, 162.2 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz, ipso-*C*, BAr^F_4), 152.0, 145.4, 138.7, 135.2 (brd, BAr^F_4), 134.3, 130.7, 129.3 (qq, $^{2}J_{C\text{-}F}$ = 31.5 Hz, $^{3}J_{C\text{-}B}$ = 2.8 Hz, *C*-CF_3, BAr^F_4), 127.6, 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz, *C*F_3, BAr^F_4), 124.4, 117.9 (m, p-*C*H, BAr^F_4), 114.0, 109.4, 89.4, 52.8, 45.7, 37.4, 30.1, 26.1, 23.4, 9.2 ppm. MS (ESI) m/z: 701 $[M]^+$ (100%), 333 (65 %). HRMS (ESI) m/z: calcd for $C_{28}H_{37}ClIrN_6O$: 701.23467, found: 701.23244. Elemental analysis: calcd (%) for $C_{60}H_{49}Cl\ BF_{24}IrN_6O$: C (46.06), H (3.16), N (5.37); found: C (45.80), H (2.99), N (5.37). IR (ATR): 3351 (w), 2341 (w), 2113 (w), 1829 (w), 1661 (w), 1622 (w), 1598 (w), 1570 (w), 1456 (w), 1436 (w), 1419 (w), 1354 (m), 1323 (w), 1274 (s), 1158 (m), 1116 (s), 1030 (w), 997 (w), 946 (w), 930 (w), 886 (m), 839 (m), 974 (w), 757 (w), 745 (w), 712 (m), 682 (m), 669 (m), 639 (w), 622 (w), 602 (w), 587 (w), 577 (w), 566 (w), 556 (w).



$Ir^{III}Cp^*C_{11}$: A Schlenk flask was charged with ligand **6b** (84 mg, 0.21 mmol) and dichloromethane (10 mL). Pentamethylcyclopentadienyliridium(III)chloride dimer (82 mg, 0.10 mmol) was added and the mixture was stirred for 30 min at room temperature. This was followed by addition of $NaBAr^F_4$ (182 mg, 0.21 mmol). Stirring was continued for another 30 min before work-up was carried out analogously to the above described procedure, giving the title compound (311 mg,

0.19 mmol, 93 %) of as light yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.82 (m, 1H, PyT), 7.79 - 7.74 (brm, 11H, BAr^F_4/PyT/Ar-*H*), 7.68 (m, 2H, PyT), 7.59 (m, 2H, BAr^F_4), 6.65 (dm, $^{3}J_{H\text{-}H}$ = 8.8 Hz, 2H, Ar-*H*), 6.54 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, PyT), 5.56 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, $N_3CHC\text{-}CH_2$), 4.93 (d, $^{2}J_{H\text{-}H}$ = 15.7 Hz, $N_3CHC\text{-}CH_2$), 4.51 (m, 2H, CH_2PyT), 4.21 (brd, 2H, NH_2), 2.86 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, $COCH_2$), 1.95 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.63 (s, 15H, Cp*, CH_3), 1.34-1.30 (m, 12H, CH_2) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ =199.1 (C^4), 162.2 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz, ipso-*C*, BAr^F_4), 151.8, 145.4, 138.8, 135.2 (brd, m-*C*H, BAr^F_4), 134.3, 130.7, 129.3 (qq, $^{2}J_{C\text{-}F}$ = 31.5 Hz, $^{3}J_{C\text{-}B}$ = 2.9 Hz, *C*-CF_3, BAr^F_4), 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz, *C*F_3, BAr^F_4), 127.8, 124.0, 118.0, 117.9, 117.9 (m, p-*C*H, BAr^F_4), 114.0, 109.4, 89.5, 53.2, 45.7, 38.3, 30.2, 29.70, 29.66, 29.5, 29.0, 26.5, 25.1, 9.1 ppm. MS (ESI) m/z: 771 $[M]^+$ (100%), 386 (90 %). HRMS (ESI) m/z: calcd for $C_{33}H_{47}ClIrN_6O$: 771.31293, found: 771.31174. Elemental analysis: calcd (%) for $C_{65}H_{59}BClF_{24}IrN_6O$: C (47.76), H (3.64), N (5.14); found: C (47.55), H (3.74), N (5.03). IR (ATR): 3351 (w), 2933 (w), 2860 (w), 2340 (w), 2340 (w), 2113 (w), 1660 (w), 1622 (w), 1598 (w), 1570 (w), 1520 (w), 1457 (w), 1436 (w), 1419 (w), 1354 (m), 1273 (s), 1157 (m), 1117 (s), 1030 (w), 997 (w), 944 (w), 933 (w), 866 (m), 839 (m), 794 (w), 757 (w), 745 (w), 712 (m), 682 (m), 669 (m), 639 (w), 622 (w), 602 (w), 587 (w), 577 (w), 566 (w), 555 (w).

2. X-ray Single Crystal Diffraction

Crystals suitable for X-ray single crystal diffraction were obtained by crystallization from pentane (**3a**), and slow diffusion of pentane into a solution in dichloromethane (**6a** and **6b**). Crystals were selected using a microscope and mounted on the diffractometer. Details from the data collection, structure solution and refinement are reported in Table S1. Molecular graphics: OLEX2.[6]

Table S1. Crystal data and structure refinement for compound **3a, 6a** and **6b**.

Identification code	**3a**	**6a**	**6b**
CCDC-number	1961819	1961820	1961821
Empirical formula	$C_{12}H_{14}Br_2O$	$C_{18}H_{22}N_6O$	$C_{23}H_{32}N_6O$
Formula weight	334.05	338.41	408.54
Temperature/K	149.97	149.95	99.57
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	15.7970(11)	14.6540(14)	5.4266(5)
b/Å	10.6695(7)	7.0476(7)	52.494(5)
c/Å	7.5330(5)	17.0806(19)	8.0320(8)
α/°	90	90	90
β/°	91.679(3)	91.653(4)	107.835(3)
γ/°	90	90	90
Volume/Å^3	1269.11(15)	1763.3(3)	2178.1(4)
Z	4	4	4
ρ_{calc}g/cm^3	1.748	1.275	1.246
μ/mm^{-1}	6.360	0.084	0.080
F(000)	656.0	720.0	880.0
Crystal size/mm^3	0.334 × 0.218 × 0.02	0.19 × 0.154 × 0.03	0.303 × 0.274 × 0.088
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.608 to 55.448	4.772 to 55.236	4.656 to 55.02
Index ranges	$-20 \le h \le 20$ $-13 \le k \le 13$ $-9 \le l \le 9$	$-19 \le h \le 19$ $-9 \le k \le 9$ $-22 \le l \le 22$	$-7 \le h \le 7$ $-68 \le k \le 68$ $-10 \le l \le 10$
Reflections collected	40852	52028	110638
Independent reflections	2947 [R_{int} = 0.0769, R_{sigma} = 0.0344]	4072 [R_{int} = 0.1027, R_{sigma} = 0.0425]	4987 [R_{int} = 0.2120, R_{sigma} = 0.0524]
Data/restraints/ parameters	2947/0/136	4072/0/234	4987/0/279
Goodness-of-fit on F^2	1.021	1.053	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0338 wR_2 = 0.0772	R_1 = 0.0462 wR_2 = 0.0985	R_1 = 0.0425 wR_2 = 0.1063
Final R indexes [all data]	R_1 = 0.0495 wR_2 = 0.0855	R_1 = 0.0903 wR_2 = 0.1202	R_1 = 0.0511 wR_2 = 0.1091
Largest diff. peak/hole / e Å^{-3}	1.03/-1.19	0.16/-0.23	0.27/-0.32

The molecular structure of dibromide **3a** is shown in Figure S1.

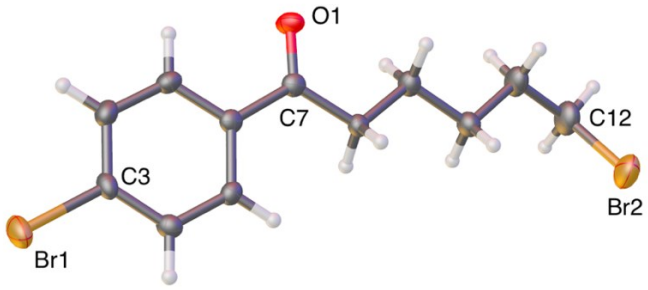


Figure S1. Molecular structure as determined by X-ray single crystal diffraction for 1-bromo-4-(6-bromoundecanoyl)benzene (**3a**).

The packing of the molecules in the crystal of **6a** shows hydrogen bonds between amine H and O (2.0 Å) and in-between H and N of the pyrazole-triazole (PyT) groups (Figure S2). The packing of compound **6b** is featuring a network of weak H-bonds involving PyT groups and amines with molecules aligned pair wise head to tail (Figure S3). Overall, the packing regarding **6b** is alkyl dominated with the long alkyl chains aligned straight, and the PyT head-group pointing along the imaginary axis through the alkyl chain. Regarding **6a**, PyT head-groups are also arranged pair-wise, however head-to-head.

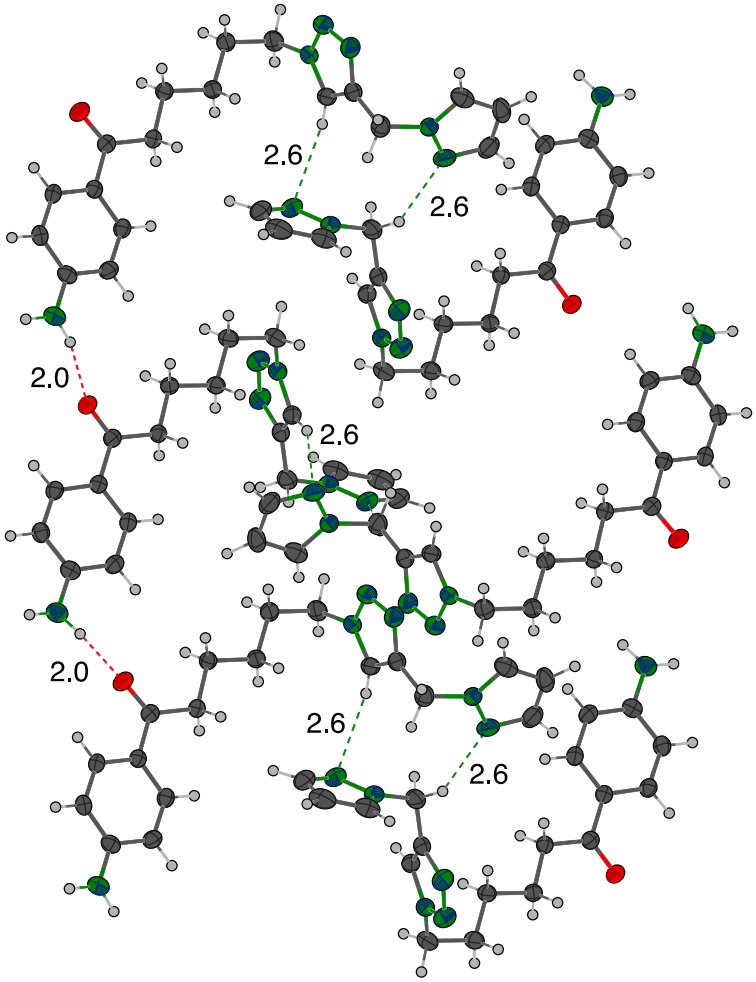


Figure S2. Crystal packing for compound **6a**. View along crystallographic b-axis. The lengths of selected hydrogen bonds are reported in Å.

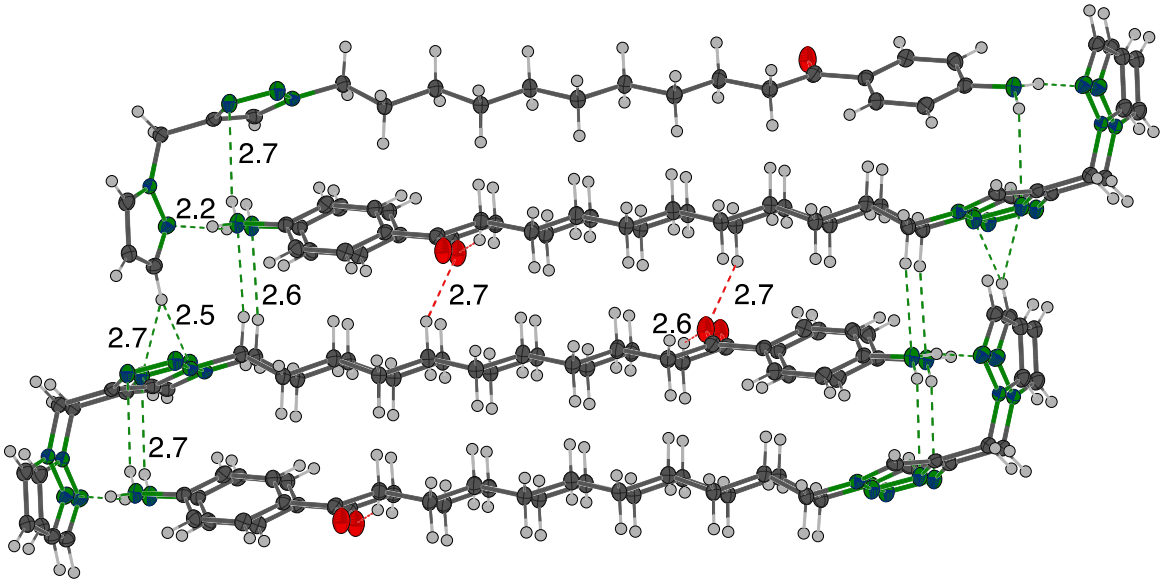


Figure S3. Crystal packing for compound **6b**. View along crystallographic a-axis. The lengths of selected hydrogen bonds are reported in Å.

3. Surface Immobilization and Characterization

Optimized Procedure for Catalyst Immobilization on Carbon Black

A Schlenk flask was charged with the Rh- or Ir-based metal complex (0.035 mmol) and degassed nitromethane (10 mL). The solution was cooled to 0 °C before degassed hydrochloric acid (0.1 M, 0.5 mL) was added slowly under stirring, followed by sodium nitrite (4.8 mg, 0.07 mmol). Stirring was continued for another 10 min. Carbon black (50 mg) was added and the mixture was stirred for 16 h at room temperature. Subsequently, the black mixture was transferred into glass centrifuge tubes and centrifuged for 20 min at 4000 rpm. The liquids were removed and discarded, and the remaining black solids were treated with washing and centrifugation steps: 8 mL methanol, 8 mL deionized water (MilliQ, 18 Ω), and finally 8 mL methanol. After each washing step, the samples were centrifuged for 20 min at 4000 rpm and the liquids were removed and discarded. The obtained black solids were allowed to dry overnight at room temperature on air and finally dried under vacuum (~ 2.0×10^{-1} mbar), affording the hybrid catalysts as black powders. The isolated yields of the hybrid catalysts based on the Rh^{I} precursors were slightly higher compared to those of the Rh^{III}/Ir^{III} precursors (Table S2).

Table S2. Isolated yields of hybrid catalysts.

Entry	Precursor	m [mg]	n [mol]	CB [mg]	Hybrid catalyst	Yield [mg]
1[a]	**$Rh^{I}C_{11}$**	50	0.035	50	**$Rh^{III}C_{11}CB$**	49
2	**$Rh^{I}C_{11}$**	100	0.070	100	**$Rh^{III}C_{11}CB$**	106
3[a]	**$Rh^{I}C_{6}$**	48	0.035	50	**$Rh^{III}C_{6}CB$**	43
4	**$Rh^{I}C_{6}$**	96	0.070	100	**$Rh^{III}C_{6}CB$**	111
5[a]	**$Rh^{I}C_{0}$**	44	0.035	50	**$Rh^{III}C_{0}CB$**	51
6	**$Rh^{I}C_{0}$**	88	0.070	100	**$Rh^{III}C_{0}CB$**	116
7[a]	**$Rh^{III}Cp^{*}C_{11}$**	27	0.017	25	**$Rh^{III}Cp^{*}C_{11}CB$**	20
8	**$Rh^{III}Cp^{*}C_{11}$**	108	0.070	100	**$Rh^{III}Cp^{*}C_{11}CB$**	81
9[a]	**$Ir^{III}Cp^{*}C_{11}$**	57	0.035	50	**$Ir^{III}Cp^{*}C_{11}CB$**	36
10[a]	**$Ir^{III}Cp^{*}C_{6}$**	55	0.035	50	**$Ir^{III}Cp^{*}C_{6}CB$**	36
11[a]	**$Ir^{III}Cp^{*}C_{0}$**	51	0.035	50	**$Ir^{III}Cp^{*}C_{0}CB$**	34

[a] These batches were used for characterization

3.1 Characterization by Energy Dispersive X-ray Spectroscopy (EDX)

Scanning electron microscope (SEM) images and EDX spectra were acquired using a Zeiss EVO MA15 Scanning electron microscope equipped with Oxford Instruments Aztec Synergy EDS/EBSD). The hybrid catalyst (~ 1-2 mg), in form of a black powder, was placed onto a round and flat sample holder equipped with a double sided adhesive tape. The sample was pressed onto the tape using a spatula and non-attached powder was carefully removed using a gentle stream of air. Sample holders were mounted on a revolving holder disc, which was placed in the chamber and evacuated. Calibration was carried out using a copper standard and the sample to detector distance was 12 mm using an energy of 12.5 keV.

Initially, the sample was screened by SEM and flat areas were identified. For determination of elemental compositions, typically five to six areas were selected and scanned. This was followed by EDX area mapping. Analyses were performed with the Oxford Instruments AZtec software package. Data deconvolution and background removal was performed with AZtec TruMap. Determined metal concentrations by EDX and XPS are reported in Table S3.

Obtained EDX spectra are shown for **$Rh^{III}C_{11}CB$** and **$Ir^{III}Cp^*C_{11}CB$** in Figure S4 and S9, respectively. EDX maps of all samples are shown in Figures S5-S11, and determined elemental compositions are reported in Tables S4-S10.

Table S3. Determined metal concentrations by EDX and XPS.

Hybrid catalyst	at% Rh	wt% Rh	at% Ir	wt% Ir	at% Rh	at% Ir
	EDX		EDX		XPS	
$Rh^{III}C_{11}CB$	0.49	3.93	-	-	0.96	-
$Rh^{III}C_6CB$	0.52	4.14	-	-	0.97	-
$Rh^{III}C_0CB$	0.82	6.37	-	-	1.22	-
$Rh^{III}Cp^*C_{11}CB$	0.25	2.00	-	-	0.63	-
$Ir^{III}Cp^*C_{11}CB$	-	-	0.13	2.08	-	0.24
$Ir^{III}Cp^*C_6CB$	-	-	0.11	1.68	-	0.28
$Ir^{III}Cp^*C_0CB$	-	-	0.08	1.20	-	0.22

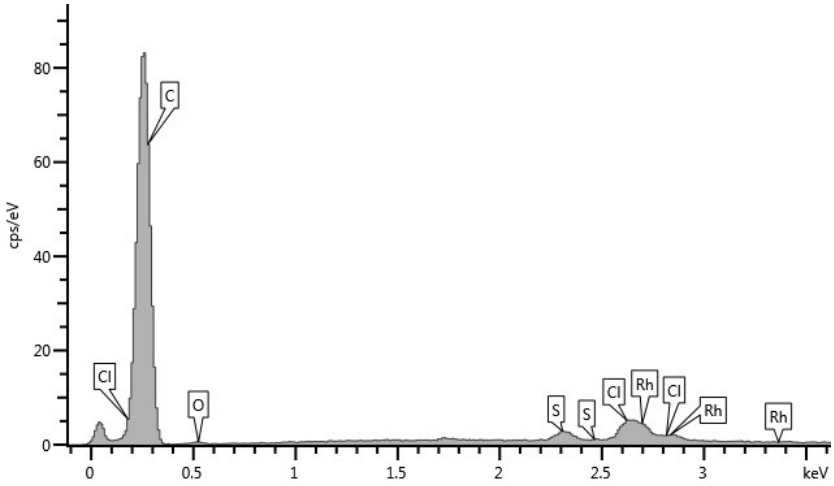


Figure S4. EDX spectrum of **$Rh^{III}C_{11}CB$**.

Table S4. Determined elemental composition of **$Rh^{III}C_{11}CB$** in wt% by EDX.

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	**Area 6**	**Average**
C	88.54	89.07	87.99	88.84	89.71	89.03	88.86
O	3.96	3.55	4.42	4.03	3.55	3.99	3.92
S	0.95	1.06	1.06	0.92	0.98	1.02	1
Cl	2.35	2.35	2.42	2.27	2.22	2.17	2.3
Rh	4.21	3.96	4.11	3.94	3.54	3.79	3.93
Total	100	100	100	100	100	100	100

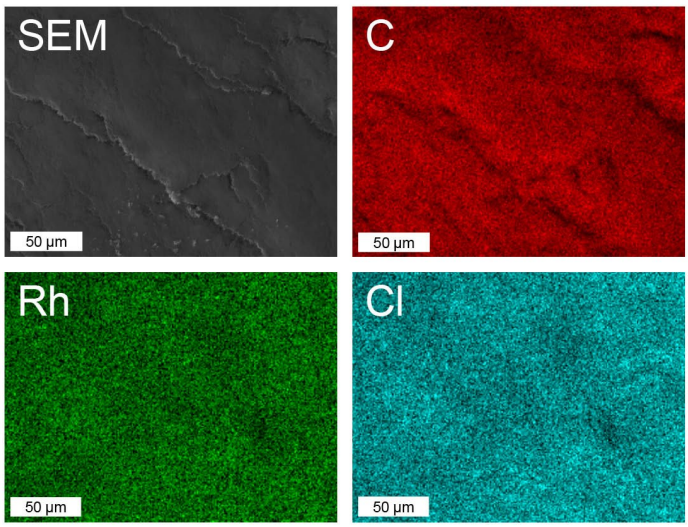


Figure S5. (a) SEM image of **$Rh^{III}C_6CB$** and EDX maps for carbon (C), rhodium (Rh) and chlorine (Cl).

Table S5. Determined elemental composition of **$Rh^{III}C_6CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Average
C	86.38	86.12	85.91	85.97	86.21	86.12
O	6.46	6.54	6.54	6.78	6.12	6.49
S	1	1.03	1.05	0.99	1.05	1.02
Cl	2.15	2.24	2.29	2.15	2.26	2.22
Rh	4.01	4.07	4.22	4.12	4.27	4.14
Total	100	100	100	100	100	100

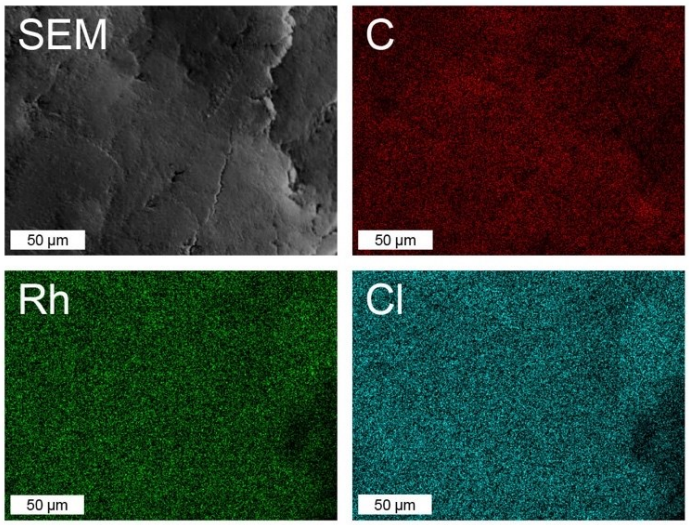


Figure S6. (a) SEM image of **$Rh^{III}C_0CB$** and EDX maps for carbon (C), rhodium (Rh) and chlorine (Cl).

Table S6. Determined elemental composition of **$Rh^{III}C_0CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average
C	85.87	85.67	85.34	86.58	85.73	85.75	85.82
O	3.99	2.97	3.85	2.14	3.3	3.14	3.23
S	0.89	1.05	1.04	1.09	0.97	0.98	1.00
Cl	3.41	3.69	3.39	3.79	3.44	3.71	3.57
Rh	5.84	6.63	6.38	6.39	6.56	6.41	6.37
Total	100	100	100	100	100	100	100

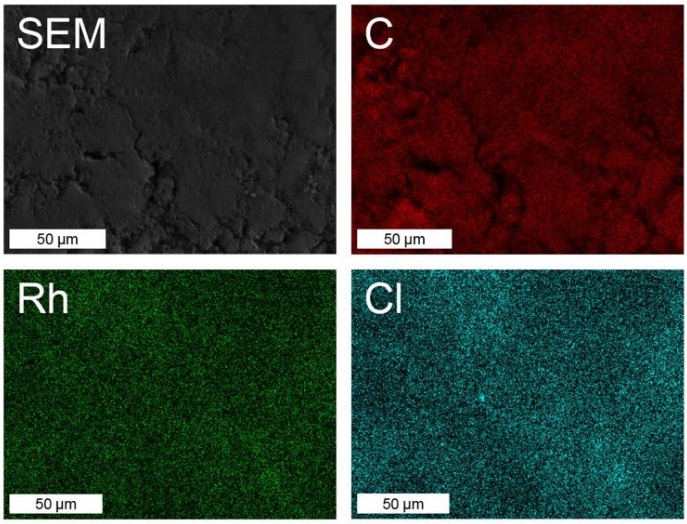


Figure S7. (a) SEM image of **$Rh^{III}Cp^*C_{11}CB$** and EDX maps for carbon (C), rhodium (Rh) and chlorine (Cl).

Table S7. Determined elemental composition of **$Rh^{III}Cp^*C_{11}CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6
C	88.41	87.68	87.93	87.75	87.86	87.93
O	7.57	7.74	7.84	7.44	8.29	7.78
S	1.20	1.21	1.18	1.18	1.03	1.16
Cl	1.05	1.26	1.02	1.39	0.99	1.14
Rh	1.77	2.11	2.02	2.24	1.84	2.00
Total	100	100	100	100	100	100

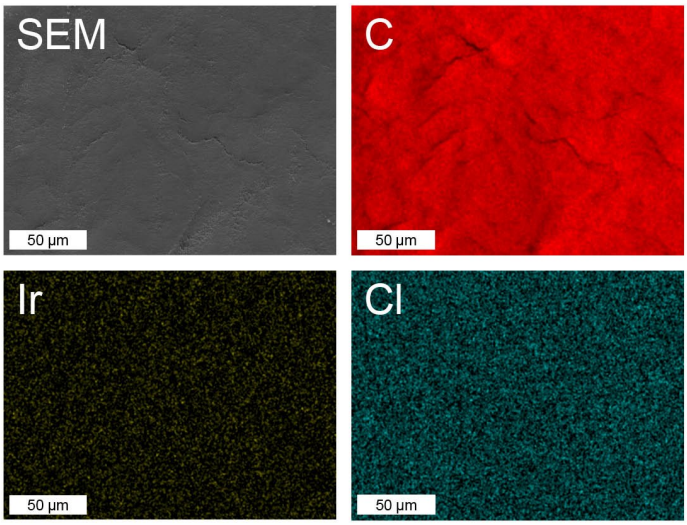


Figure S8. SEM image of **$Ir^{III}Cp^*C_{11}CB$** and EDX maps for carbon (C), iridium (Ir) and chlorine (Cl).

Table S8. Determined elemental composition of **$Ir^{III}Cp^*C_{11}CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Average
C	95.22	94.9	95.42	94.83	94.82	95.04
O	1.59	1.39	1.19	1.33	1.6	1.42
S	0.76	0.72	0.83	0.66	0.68	0.73
Cl	0.74	0.76	0.71	0.73	0.71	0.73
Ir	1.70	2.24	1.85	2.44	2.18	2.08
Total	100	100	100	100	100	100

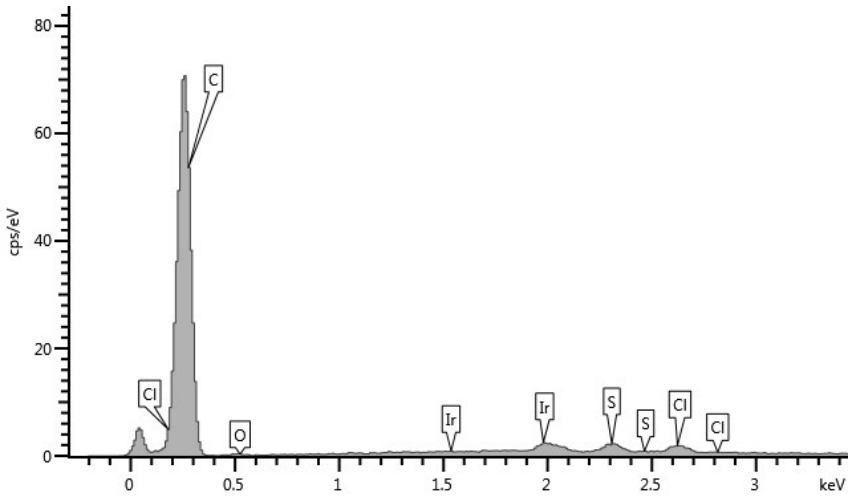


Figure S9. EDX spectrum of **$Ir^{III}Cp^*C_{11}CB$**.

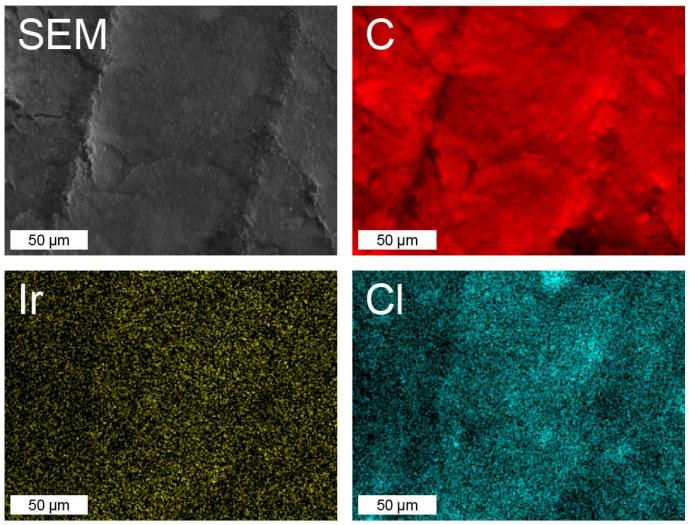


Figure S10. SEM image of **$Ir^{III}Cp^*C_6CB$** and EDX maps for carbon (C), iridium (Ir) and chlorine (Cl).

Table S9. Determined elemental composition of **$Ir^{III}Cp^*C_6CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Average
C	93.81	93.81	93.64	93.87	93.55	93.74
O	3.20	3.20	3.19	3.02	3.67	3.26
S	0.65	0.65	0.68	0.68	0.64	0.66
Cl	0.67	0.67	0.68	0.71	0.59	0.66
Ir	1.67	1.67	1.8	1.71	1.55	1.68
Total	100	100	100	100	100	100

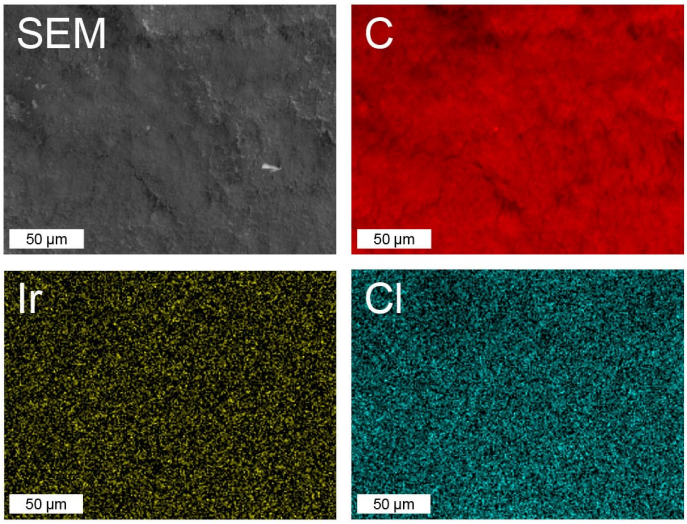


Figure S11. SEM image of **$Ir^{III}Cp^*C_0CB$** and EDX maps for carbon (C), iridium (Ir) and chlorine (Cl).

Table S10. Determined elemental composition of **$Ir^{III}Cp^*C_0CB$** in wt% by EDX.

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Average
C	94.75	94.21	94.45	94.71	94.52	94.53
O	2.91	3.50	3.38	2.99	3.23	3.20
S	0.64	0.64	0.63	0.7	0.63	0.65
Cl	0.44	0.44	0.39	0.44	0.42	0.43
Ir	1.27	1.21	1.16	1.16	1.2	1.20
Total	100	100	100	100	100	100

Control Sample

We prepared a blank CB control sample by applying the same procedure as described above for the catalyst immobilization on CB, but under absence of a metal complex. EDX analysis revealed presence of only trace amounts of Cl (Table S11), which suggests that the bulk of the Cl found in the Rh^{I} hybrid catalysts is either bound to the ligand or attached to the metal center as counterion.

Table S11. Determined elemental composition of a control sample of CB in wt% by EDX.

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	Average
C	97.2	97.16	97.34	97.14	97.24	97.22
O	2.51	2.51	2.34	2.55	2.45	2.47
S	0.27	0.29	0.28	0.27	0.27	0.28
Cl	0.02	0.03	0.03	0.03	0.04	0.03
Total	100	100	100	100	100	100

3.2 Characterization by X-ray Photoelectron Spectroscopy (XPS)

Characterization by X-ray photoelectron spectroscopy was performed on an ESCALab Xi (Thermo Scientific) spectrometer with a monochromatic Al Kα source. The pressure in the analysis chamber during measurements was < 10^{-8} mbar. The pass energy and step size for narrow scans were 20 eV and 0.1 eV, respectively. The take-off angle was normal to the sample surface. Spectral analysis was performed using Avantage 4.73 software and curve fitting was carried out with a mixture of Gaussian-Lorentzian functions. Peaks were calibrated to the carbon black C–C at 284.5 eV.

XPS survey and narrow band scans are shown in Figures S12-S18 and determined elemental compositions are reported in Tables S12-S18. Narrow band scans were conducted for the elements O, N, C, Rh or Ir and for a number of measurements also including for Cl and F. We note that inclusion of Cl and F in the elemental composition has only a subtle effect on the

overall metal concentration, it varied from 0.01 to 0.05 at% for the analyzed samples. For the sake of consistency, all metal concentration are reported without inclusion of Cl and F.

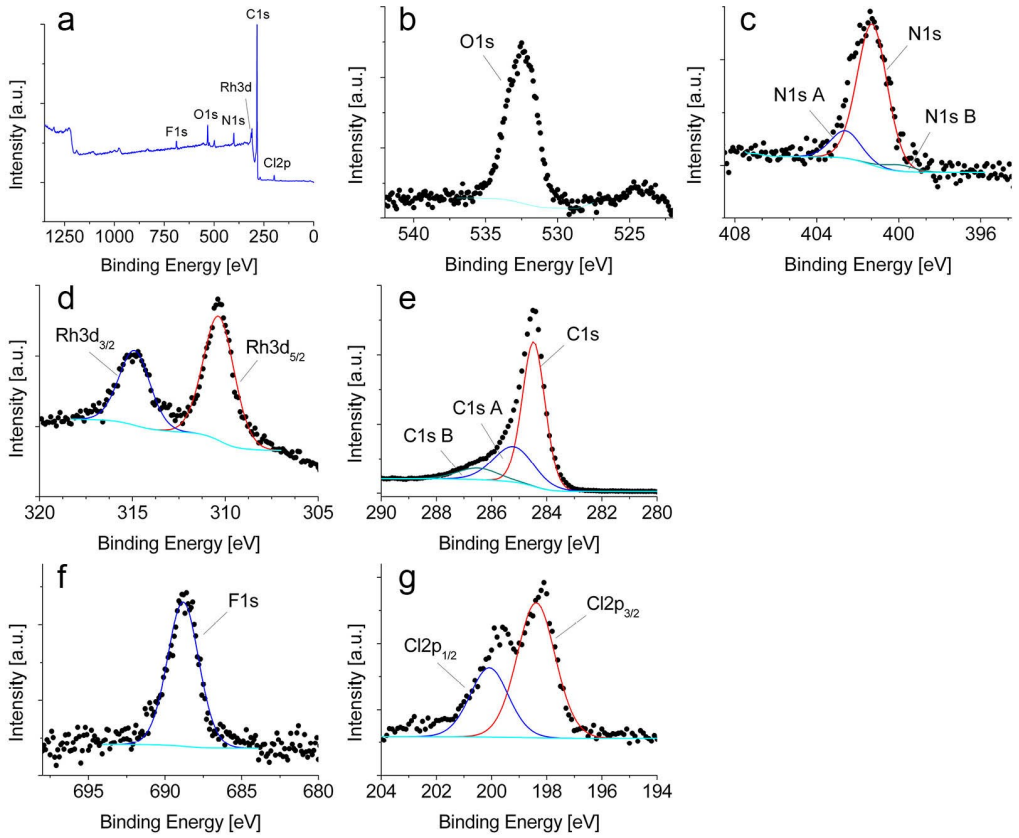


Figure S12. X-ray photoelectron spectra of the hybrid catalyst **$Rh^{III}C_{11}CB$** optimized (Loading 4). (a) Survey scan, narrow scans of the (b) O1s signal, (b) N1s signals, (d) $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals, (e) C1s signals as well as the signals originating from the counterions, (f) F1s signal, (g) Cl $2p_{1/2}$/$2p_{3/2}$ signals.

Table S12. Determined elemental composition of **$Rh^{III}C_{11}CB$** in at% by XPS.

Element	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*	**Atomic %** *including F, Cl*
C1s	284.47	0.97	21917.55	55.95	54.33
C1s A	285.20	1.73	9708.56	24.79	24.07
C1s B	286.50	1.73	3161.21	8.07	7.84
O1s	532.40	2.54	5978.17	5.46	5.30
N1s	401.30	1.73	2497.24	3.85	3.74
N1s A	402.60	1.73	486.88	0.75	0.73
N1s B	400.00	1.73	111.94	0.17	0.17
$Rh3d_{5/2}$	310.35	1.97	3754.37	0.96	0.93
$Rh3d_{3/2}$	314.89	1.97	2260.26	0	0
F1s	688.82	2.42	2510.55	0	1.69
Cl2p3	198.38	1.64	905.45	0	1.22
Cl2p1	200.08	1.64	464.72	0	0

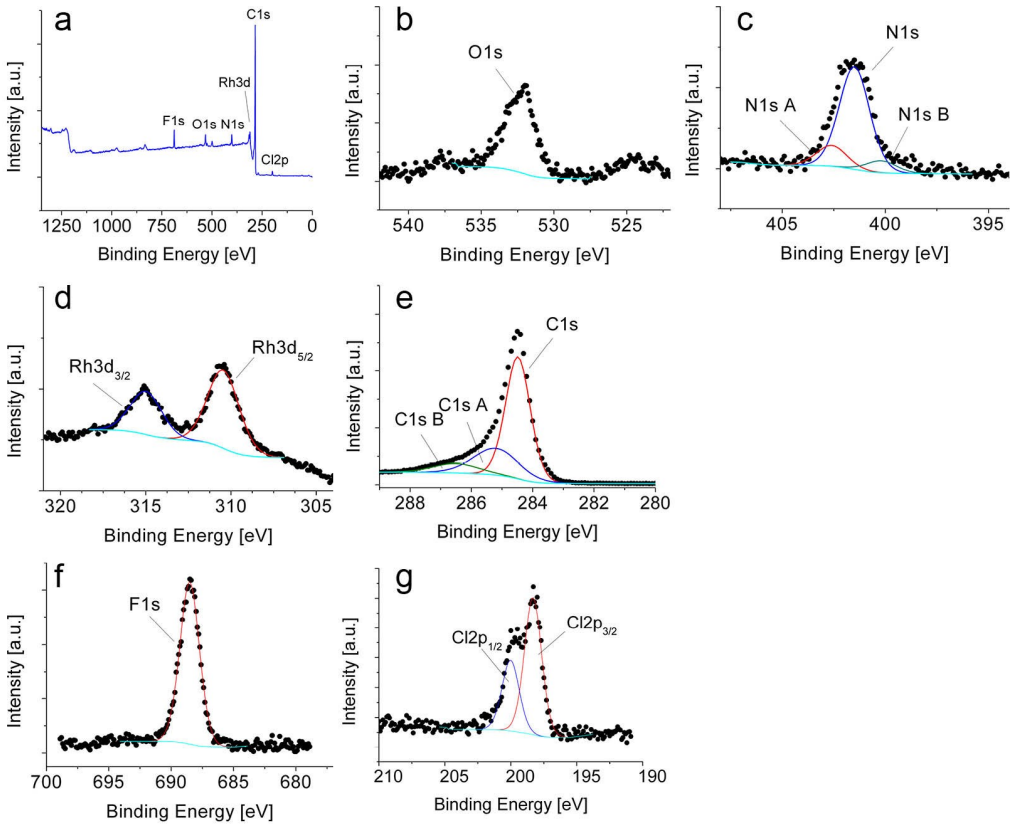


Figure S13. X-ray photoelectron spectra of the hybrid catalyst **$Rh^{III}C_6CB$**. (a) Survey scan, narrow scans of the (b) O1s signal, (b) N1s signals, (d) $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals, (e) C1s signals as well as the signals originating from the counterions, (f) F1s signal, (g) Cl $2p_{1/2}$/$2p_{3/2}$ signals.

Table S13. Determined elemental composition of **$Rh^{III}C_6CB$** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*	**Atomic %** *including F, Cl*
C1s	284.48	0.95	21940.43	58.55	55.53
C1s A	285.20	1.73	8793.80	23.47	22.26
C1s B	286.50	1.73	3092.25	8.25	7.83
O1s	532.21	2.30	3893.77	3.71	3.52
N1s	401.50	1.73	2373.69	3.82	3.63
N1s A	402.60	1.73	482.54	0.78	0.74
N1s B	400.20	1.73	275.37	0.44	0.42
$Rh3d_{5/2}$	310.45	2.18	3639.73	0.97	0.92
$Rh3d_{3/2}$	314.99	2.18	2020.63	0	0
F1s	688.82	2.42	2510.55	0	4.11
$Cl2p_{3/2}$	198.38	1.64	905.45	0	1.06
$Cl2p_{1/2}$	200.08	1.64	464.72	0	0

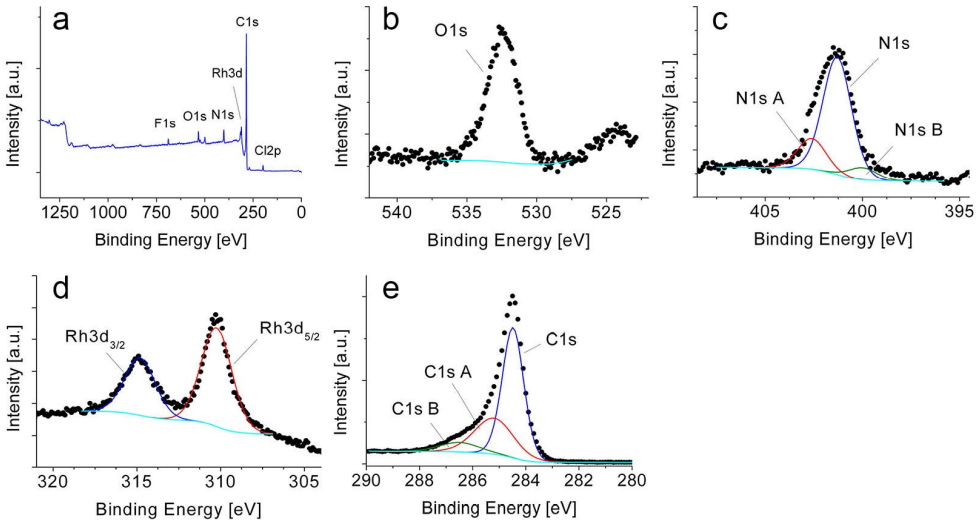


Figure S14. X-ray photoelectron spectra of the hybrid catalyst **$Rh^{III}C_0CB$** (Loading 4). (a) Survey scan, narrow scans of the (b) O1s signal, (c) N1s signals, (d) $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals, and (e) C1s signal.

Table S14. Determined elemental composition of **$Rh^{III}C_0CB$** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*
C1s	284.48	0.96	32264.29	54.54
C1s A	285.20	1.73	16096.87	27.21
C1s B	286.50	1.73	4246.83	7.18
O1s	532.43	2.51	5650.62	3.41
N1s	401.30	1.73	4627.76	4.72
N1s A	402.60	1.73	1210.41	1.24
N1s B	400.00	1.73	476.04	0.49
$Rh3d_{5/2}$	310.24	2.15	7204.84	1.22
$Rh3d_{3/2}$	314.81	2.15	4180.44	

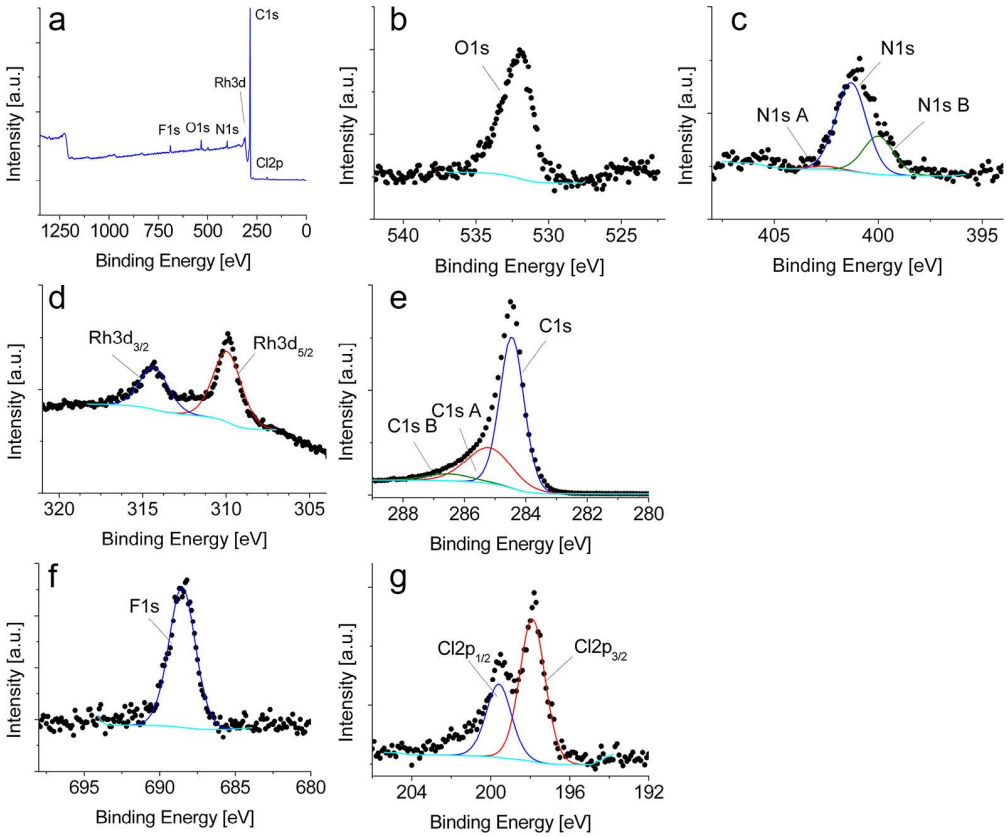


Figure S15. X-ray photoelectron spectra of the hybrid catalyst **Rh^{III}Cp*C$_{11}$CB**. (a) Survey scan, narrow scans of the (b) O1s signal, (b) N1s signals, (d) Rh3d$_{3/2}$/Rh3d$_{5/2}$ signals, (e) C1s signals as well as (f) F1s signal and (g) Cl 2p$_{1/2}$/2p$_{3/2}$ signals.

Table S15. Determined elemental composition of **Rh^{III}Cp*C$_{11}$CB** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*	**Atomic %** *including F, Cl*
C1s	284.45	0.92	28983.96	61.18	59.81
C1s A	285.20	1.73	12815.33	27.05	26.45
C1s B	286.50	1.73	2470.49	5.22	5.10
O1s	532.03	2.44	4000.37	3.02	2.95
N1s	401.30	1.73	1562.33	1.99	1.95
N1s A	402.60	1.73	53.18	0.07	0.07
N1s B	400.00	1.73	669.23	0.85	0.83
Rh3d$_{5/2}$	309.93	2.02	2966.93	0.63	0.61
Rh3d$_{3/2}$	314.32	2.02	1793.74	0	0
F1s	688.51	2.06	3005.94	0	1.68
Cl2p$_{3/2}$	197.89	1.51	494.82	0	0.56
Cl2p$_{1/2}$	199.59	1.51	253.97	0	0

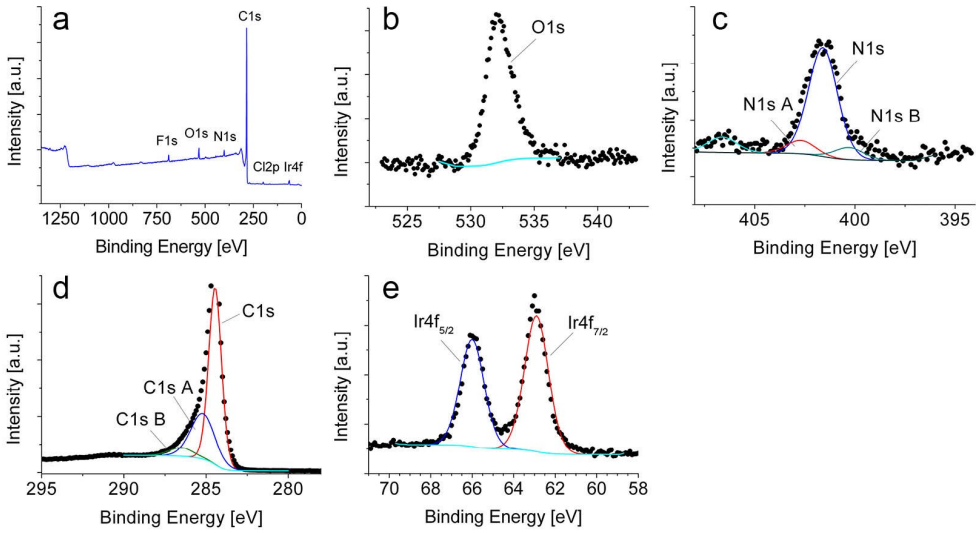


Figure S16. X-ray photoelectron spectra of the hybrid catalyst **$Ir^{III}Cp^*C_{11}CB$**. (a) Survey scan, (b) O1s signal, (c) N1s signal, (d) C1s signal and (e) $Ir4f_{5/2}$/$Ir4f_{7/2}$ signals.

Table S16. Determined elemental composition of **$Ir^{III}Cp^*C_{11}CB$** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*
C1s	284.45	0.92	62624.64	59.51
C1s A	285.20	1.73	30486.37	28.97
C1s B	286.50	1.73	5722.30	5.44
O1s	532.12	2.30	8879.90	3.02
N1s	401.40	1.70	3561.49	2.04
N1s A	402.50	1.70	434.50	0.25
N1s B	400.10	1.70	393.68	0.23
N1s C	406.43	1.73	508.65	0.29
$Ir4f_{7/2}$	62.91	1.36	2024.78	0.24
$Ir4f_{5/2}$	66.01	1.36	1592.76	

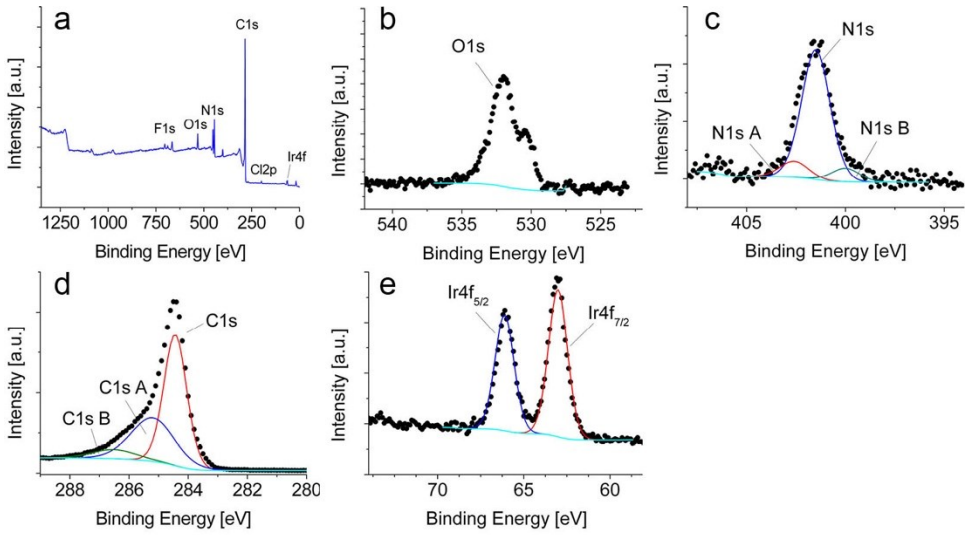


Figure S17. X-ray photoelectron spectra of the hybrid catalyst **$Ir^{III}Cp^*C_6CB$**. (a) Survey scan, (b) O1s signal, (c) N1s signal, (d) C1s signal and (e) $Ir4f_{5/2}$/$Ir4f_{7/2}$ signals.

Table S17. Determined elemental composition of **$Ir^{III}Cp^*C_6CB$** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*
C1s	284.44	0.91	48255.82	52.12
C1s A	285.20	1.73	30374	32.81
C1s B	286.50	1.73	6330.84	6.84
O1s	532.03	1.98	11979.28	4.63
N1s	401.50	1.69	4144.49	2.70
N1s A	402.60	1.69	513.4	0.33
N1s B	400.00	1.69	433.05	0.28
$Ir4f_{7/2}$	63.02	1.30	2046.81	0.28
$Ir4f_{5/2}$	66.12	1.30	1610.09	

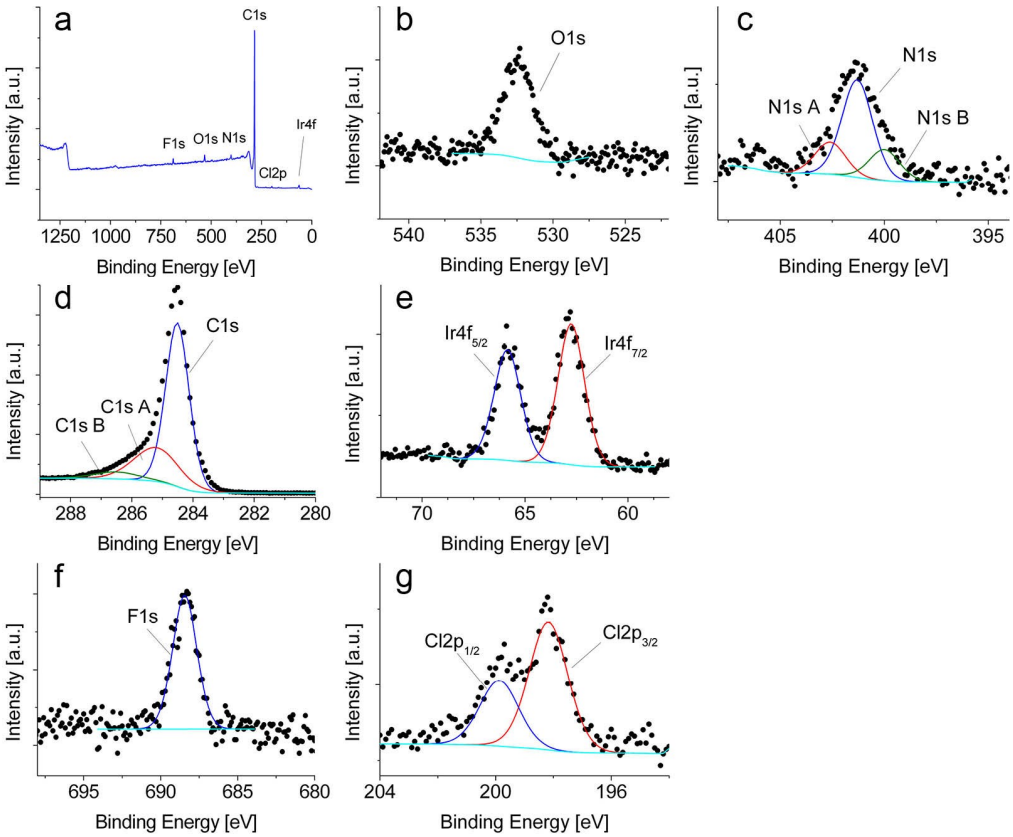


Figure S18. X-ray photoelectron spectra of the hybrid catalyst **Ir^{III}Cp*C$_0$CB**. (a) Survey scan, narrow scans of the (b) O1s signal, (b) N1s signals, (d) C1s signal, (e) Ir4f$_{5/2}$/Ir4f$_{7/2}$ signals and (f) F1s signal and (g) Cl 2p$_{1/2}$/2p$_{3/2}$ signals.

Table S18. Determined elemental composition of **Ir^{III}Cp*C$_0$CB** in at% by XPS.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F,Cl*	**Atomic %** *including F, Cl*
C1s	284.51	0.90	26844.16	64.55	63.52
C1s A	285.20	1.73	10609.55	25.51	25.10
C1s B	286.50	1.73	2159.06	5.19	5.11
O1s	532.41	2.36	2646.25	2.27	2.24
N1s	401.30	1.73	942.41	1.37	1.35
N1s A	402.60	1.73	308.46	0.45	0.44
N1s B	400.00	1.73	298.74	0.43	0.43
Ir4f$_{7/2}$	62.76	1.52	711.56	0.22	0.21
Ir4f$_{5/2}$	65.86	1.52	559.73	0	0
F1s	688.44	1.86	1775.74	0	1.14
Cl2p$_{3/2}$	198.17	1.58	361.26	0	0.47
Cl2p$_{1/2}$	199.87	1.58	185.41	0	0

3.2. Optimization of Grafting Conditions

Optimization of Grafting for **$Rh^{I}C_{11}$** *on CB*

To optimize the catalyst loading on CB, the amount of catalyst used in the grafting process was varied from 0.7 - 14.0 µmoles per mg CB. The obtained hybrid catalysts of the series with varying metal concentration (Loadings 1, 2, 3 and 5) were analyzed by EDX (Figure S19) and XPS (Figure S20). Data of loading 4, the optimized loading, is shown in Figure 3 (EDX) and Figures S12 (XPS). The determined elemental compositions are summarized in Tables S20 (EDX) and S21 (XPS); and for the loading 4 in Tables S4 (EDX) and S12 (XPS). All samples show an even distribution of Rh along the surface (EDX, Figures S19, S12). The Rh concentration increases with increasing amount of catalyst used. In the regime of lower loading a doubling of the amount of catalyst gives nearly twice as much metal on the surface (Loading 1 and 2). The surface bound amount becomes less proportional when increasing the amount further and reaches saturation (Loading 5) as doubling the amount from sample 4 to 5 gives only a slightly higher Rh reading using EDX and no increase using XPS.

Overall, the metal loading obtained by XPS are slightly higher than those obtained by EDX. This is likely due to differences in both elemental detection and data evaluation. While for instance the N1s signals are well resolved in XPS, N is not detectable by EDX in the analyzed Rh^{I} samples. Likewise, sulfur as impurity in the CB gives a distinct signal in EDX (Figure S5) but not in XPS. In addition, we note that all samples contain Cl, which is expressed in both EDX and XPS. We included Cl in the EDX data evaluation, but not in the XPS. As noted above, we tested inclusion of Cl and F for several samples and note that this results only in subtle differences for the Rh concentration.

Table S19. Summary of determined metal concentrations by EDX and XPS for **$Rh^{I}C_{11}$** on CB.

Loading	µmoles/mg[1]	wt % Rh (EDX)	at% Rh (EDX)	at% Rh (XPS)
1	0.07	1.13 ± 0.11	0.15 ± 0.03	0.27
2	0.14	2.02 ± 0.16	0.25 ± 0.02	0.53
3	0.28	2.89 ± 0.15	0.36 ± 0.02	0.69
4	0.70	3.93 ± 0.22	0.49 ± 0.03	0.96
5	1.40	5.32 ± 0.45	0.68 ± 0.06	0.94

[1] Moles of catalyst per mg of carbon black applied in the grafting process.

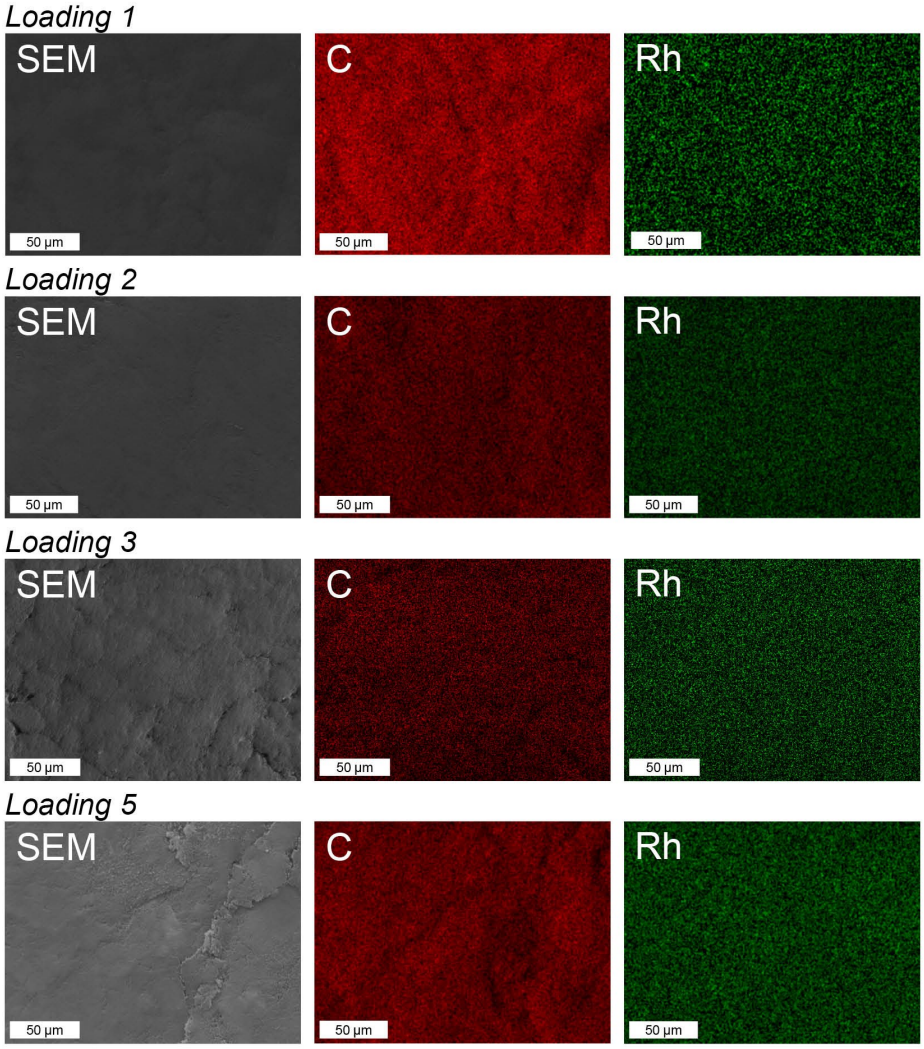


Figure S19. (a) SEM images and EDX maps for carbon (C) and rhodium (Rh) for the **$Rh^{III}C_{11}$CB** samples 1, 2, 3 and 5 with varying catalyst loadings. Data of Loading 4 (optimized conditions) is shown in the main manuscript, Figure 2.

Table S20. Determined elemental compositions of the optimization series for **$Rh^{III}C_{11}CB$** in wt% by EDX. The determined values for Loading 4 are reported on page S20.

Loading 1

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	**Average**
C	92.78	92.84	92.97	94.55	93.33	93.29
O	3.64	3.72	3.53	1.31	3.43	3.13
S	1.12	1.1	1.08	0.96	1.06	1.06
Cl	1.24	1.25	1.13	2.16	1.13	1.38
Rh	1.21	1.09	1.29	1.01	1.04	1.13
Total	100	100	100	100	100	100

Loading 2

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	**Average**
C	92.07	92.07	92.52	92.53	92.11	92.26
O	3.56	3.29	3.13	2.84	3.98	3.36
S	1.09	1.06	1.07	1.04	0.97	1.05
Cl	1.38	1.38	1.21	1.43	1.16	1.31
Rh	1.90	2.19	2.07	2.15	1.77	2.02
Total	100	100	100	100	100	100

Loading 3

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	**Average**
C	89.59	88.72	89.02	89.01	88.39	88.95
O	4.73	5.10	4.79	4.62	5.09	4.87
S	1.07	1.06	1.11	1.05	1.14	1.09
Cl	2.00	2.26	2.15	2.33	2.29	2.21
Rh	2.60	2.86	2.92	2.99	3.09	2.89
Total	100	100	100	100	100	100

Loading 5

Element	**Area 1**	**Area 2**	**Area 3**	**Area 4**	**Area 5**	**Area 6**	**Average**
C	86.49	86.91	87.78	88.25	86.83	87.38	87.27
O	3.21	2.62	2.81	3.59	4.03	3.92	3.36
S	1.13	1.08	0.96	0.87	0.93	0.95	0.99
Cl	3.47	3.43	3.27	2.63	2.75	2.83	3.06
Rh	5.71	5.96	5.18	4.66	5.46	4.92	5.32
Total	100	100	100	100	100	100	100

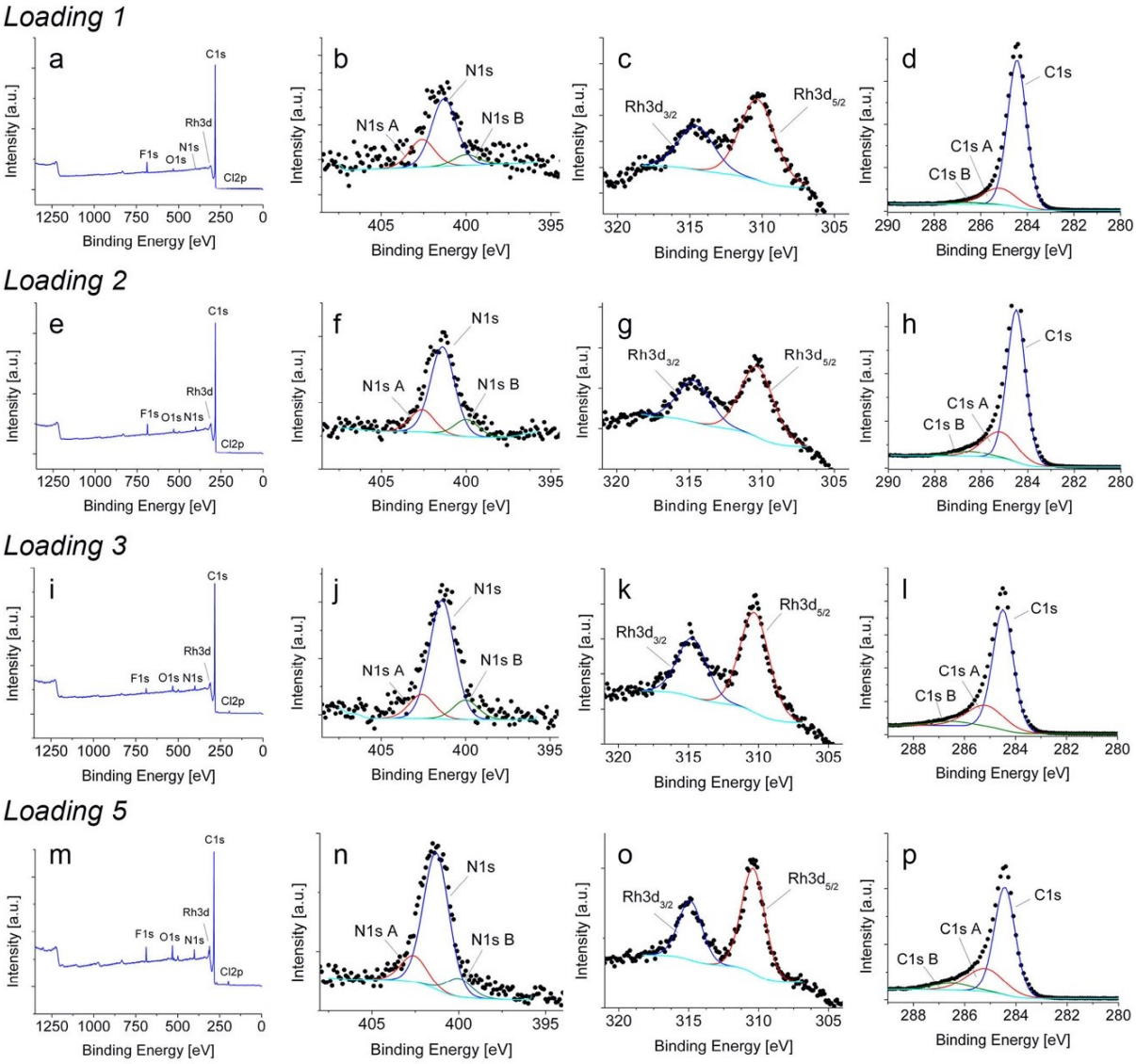


Figure S20. X-ray photoelectron spectra of the hybrid catalyst $\mathbf{Rh^{III}C_{11}CB}$ with different catalyst loadings (Loadings 1, 2, 3, and 5). Survey scans (a, e, i, m), N1s signals (b, f, j, n), $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals (c, g, k, o), and (e) C1s signals (d, h, l, p). The spectra of loading 4 is shown on p S26.

Table S21. Determined elemental composition of the optimization series for **$Rh^{III}C_{11}$CB** on CB in at% by XPS. The determined values for Loading 4 are reported on p 26.

Loading 1

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.44	0.96	70590.51	79.96
C1s A	285.20	1.73	14245.06	16.14
C1s B	286.50	1.73	1418.26	1.61
O1s	532.14	2.23	3070.51	1.24
N1s	401.30	1.73	726.98	0.50
N1s A	402.60	1.73	295.89	0.20
N1s B	400.00	1.73	114.61	0.08
$Rh3d_{5/2}$	310.31	2.87	2414.98	0.27
$Rh3d_{3/2}$	314.55	2.87	1313.82	

Loading 2

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.50	0.94	65731.38	69.19
C1s A	285.20	1.73	21063.82	22.17
C1s B	286.50	1.73	4145.68	4.36
O1s	532.22	2.52	4105.75	1.55
N1s	401.40	1.67	2384.37	1.52
N1s A	402.60	1.67	601.37	0.38
N1s B	400.00	1.67	463.55	0.29
$Rh3d_{5/2}$	310.32	2.68	5040.46	0.53
$Rh3d_{3/2}$	314.65	2.68	2979.34	

Loading 3

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.49	0.96	37373.22	67.48
C1s A	285.20	1.73	12379.17	22.35
C1s B	286.50	1.73	2382.39	4.30
O1s	532.17	2.57	3445.08	2.22
N1s	401.40	1.73	1981.32	2.16
N1s A	402.60	1.73	400.52	0.44
N1s B	400.00	1.73	323.43	0.35
$Rh3d_{5/2}$	310.27	2.48	3840.58	0.69
$Rh3d_{3/2}$	314.72	2.48	2259.90	

Loading 5

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.43	0.96	20085.07	58.80
C1s A	285.20	1.73	7837.23	22.95
C1s B	286.50	1.73	2365.94	6.93
O1s	532.23	2.51	5065.69	5.30
N1s	401.30	1.73	2170.43	3.84
N1s A	402.60	1.73	416.49	0.74
N1s B	400.00	1.73	289.10	0.51
$Rh3d_{5/2}$	310.39	1.96	3195.20	0.94
$Rh3d_{3/2}$	314.88	1.96	1811.01	0

Optimization of Grafting for ***$Rh^{I}C_{0}$*** *on CB*

The optimization was carried out analogously to the above described optimization for **$Rh^{I}C_{11}$**.

The obtained hybrid catalysts of the series with varying metal concentration (Loadings 1,2,3 and 5) were analyzed by EDX (Figure S21) and XPS (Figure S22). Data of loading 4, the optimized loading, is shown in Figure S6 (EDX) and Figures S14 (XPS). The determined elemental compositions are summarized in Tables S23 (EDX) and S24 (XPS); and for the loading 4 in Tables S6 (EDX) and S14 (XPS). The observed trend is in line with the above described while the obtained overall Rh loadings are slightly higher for the **$Rh^{III}C_{0}$CB** derivatives compared to the **$Rh^{III}C_{11}$CB** derivatives, which is likely due to the size of the molecule. The smaller molecule may bind at sites, which are less accessible to the larger analogues, explaining the observed differences.

Table S22. Summary of determined metal concentrations for **$Rh^{III}C_{0}$CB** on CB:

Sample	µmoles/mg[1]	wt % Rh (EDX)	at % Rh (EDX)	at% Rh (XPS)
1	0.07	1.32 ± 0.25	0.16 ± 0.03	0.45
2	0.14	1.91 ± 0.32	0.23 ± 0.04	0.62
3	0.28	2.58 ± 0.30	0.32 ± 0.03	0.70
4	0.70	6.37 ± 0.28	0.82 ± 0.04	1.22
5	1.40	8.79 ± 1.13	1.17 ± 0.04	1.25

[1] Moles of catalyst per mg of carbon black applied in the grafting process.

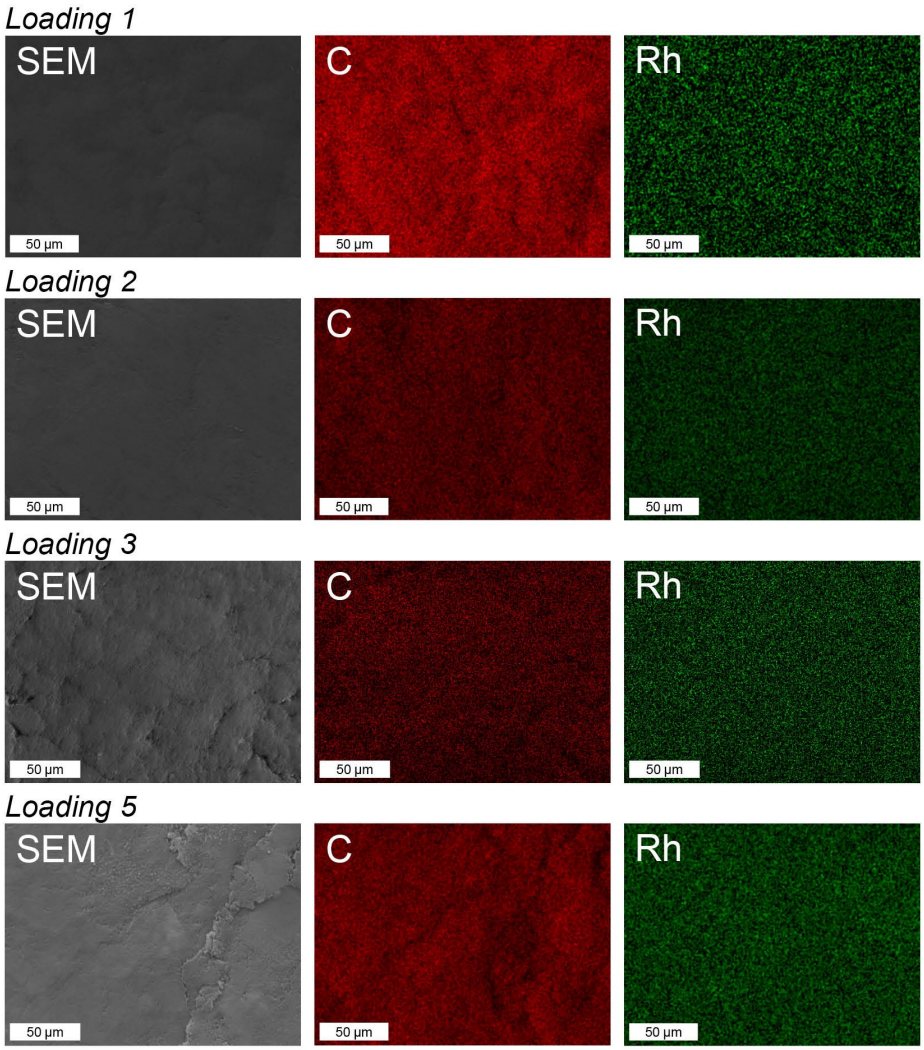


Figure S21. (a) SEM images and EDX maps for carbon (C) and rhodium (Rh) for the **$Rh^{III}C_0CB$** samples 1, 2, 3 and 5 with varying catalyst loadings. Data of loading 4 (optimized conditions) is shown in Figure S6.

Table S23. Determined elemental compositions of the optimization series for **$Rh^{III}C_0CB$** in wt% by EDX. The determined values for Loading 4 are reported on p S21.

Loading 1

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average
C	93.73	92.74	92.96	92.84	94.61	92.91	93.30
O	3.27	3.79	3.61	3.78	2.62	3.22	3.38
S	1.03	1.04	1.14	1.03	1.10	1.17	1.09
Cl	0.78	1.05	0.89	0.90	0.78	1.09	0.92
Rh	1.19	1.38	1.39	1.44	0.89	1.60	1.32
Total	100	100	100	100	100	100	100

Loading 2

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average
C	91.71	91.93	91.76	92.54	92.2	92.71	92.14
O	3.35	3.93	4.28	3.05	3.33	2.82	3.46
S	1.08	1.11	1.16	1.11	1.09	1.14	1.12
Cl	1.44	1.38	1.30	1.38	1.42	1.36	1.38
Rh	2.42	1.65	1.50	1.93	1.96	1.97	1.91
Total	100	100	100	100	100	100	100

Loading 3

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average
C	89.92	90.84	90.66	92.5	91.31	91.86	91.18
O	4.94	3.34	3.70	2.11	3.63	3.05	3.46
S	0.89	0.96	1.02	0.88	0.93	0.95	0.94
Cl	1.88	1.90	1.77	1.77	1.88	1.81	1.84
Rh	2.38	2.95	2.85	2.73	2.25	2.33	2.58
Total	100	100	100	100	100	100	100

Loading 5

Element	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average
C	80.63	83.85	82.23	85.19	83.5	79.15	82.43
O	3.11	3.54	3.16	2.73	2.63	4.56	3.29
S	0.87	0.79	0.96	0.86	0.94	0.89	0.89
Cl	5.34	4.09	4.89	3.75	4.35	5.24	4.61
Rh	10.05	7.73	8.77	7.47	8.57	10.15	8.79
Total	100	100	100	100	100	100	100

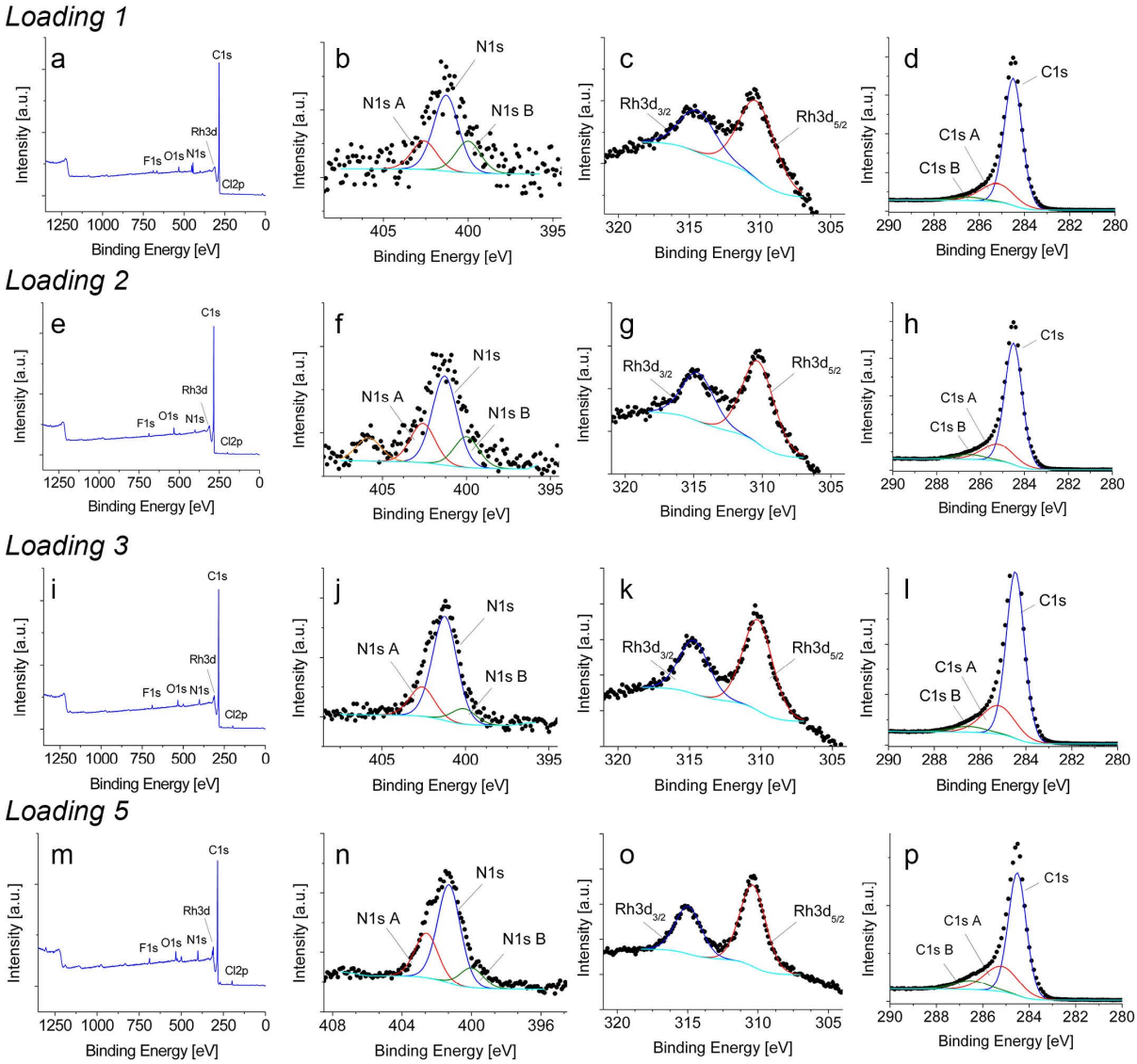


Figure S22. X-ray photoelectron spectra of the hybrid catalyst **$Rh^{III}C_0CB$** with different catalyst loadings (Loadings 1, 2, 3, and 5). Survey scans (a, e, i, m), N1s signals (b, f, j, n), $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals (c, g, k, o), and (e) C1s signals (d, h, l. p). The spectra of loading 4 is shown on p S14.

Table S24. Determined elemental composition of of the optimization series for **$Rh^{III}C_0CB$** on CB in at% by XPS. The determined values for Loading 4 are reported on p S14.

Loading 1

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.50	0.93	66769.23	73.33
C1s A	285.20	1.73	17666.29	19.40
C1s B	286.50	1.61	3068.72	3.37
O1s	532.35	2.37	5610.24	2.20
N1s	401.30	1.73	1054.13	0.70
N1s A	402.60	1.73	393.11	0.26
N1s B	400.00	1.73	437.05	0.29
$Rh3d_{5/2}$	310.21	3.01	4056.33	0.45
$Rh3d_{3/2}$	314.41	3.01	2184.51	

Loading 2

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.50	0.93	66181.53	71.30
C1s A	285.20	1.73	16641.32	17.93
C1s B	286.50	1.61	4471.69	4.82
O1s	532.59	2.34	7210.08	2.78
N1s	401.30	1.73	1926.69	1.25
N1s A	402.60	1.73	844.82	0.55
N1s B	400.00	1.73	662.98	0.43
N1s C	405.82	1.73	500.92	0.33
$Rh3d_{5/2}$	310.29	2.76	5736.71	0.62
$Rh3d_{3/2}$	314.69	2.76	3393.44	

Loading 3

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.46	0.93	66680.44	68.39
C1s A	285.20	1.73	21080.56	21.62
C1s B	286.50	1.73	4239.97	4.35
O1s	532.51	2.43	5496.64	2.02
N1s	401.24	1.73	3294.51	2.04
N1s A	402.60	1.73	927.89	0.57
N1s B	400.10	1.73	488.82	0.30
$Rh3d_{5/2}$	310.21	2.46	6816.78	0.70
$Rh3d_{3/2}$	314.68	2.46	4029.66	

Loading 5

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*
C1s	284.45	0.91	25326.36	57.95
C1s A	285.20	1.73	9938.73	22.74
C1s B	286.50	1.73	3459.75	7.92
O1s	532.47	2.41	4639.02	3.79
N1s	401.30	1.56	2785.79	3.85
N1s A	402.60	1.56	1260.48	1.74
N1s B	400.00	1.56	551.44	0.76
$Rh3d_{5/2}$	310.18	2.17	5460.04	1.25
$Rh3d_{3/2}$	314.71	2.17	3182.5	0

3.4 Characterization by X-ray Absorption Spectroscopy (XAS)

XAS measurements were performed at the Australian Synchrotron. XANES and EXAFS data was recorded of the Rh and Ir precursors and the Rh and Ir hybrid catalysts the XAS Beamline in transmission mode, at the Rh K-edge (~ 23.2 keV) and the Ir L3 edge (~ 11.2 keV). Samples were measured using Hutch B under ambient temperature and pressure.

Sample preparation

The Rh or Ir complex (~ 70 mg) was ground to a fine powder and mixed with cellulose (~ 5 mg) as binding agent. The mixture was pressed into a 7 mm pellet using a handheld mechanical press. The hybrid catalyst samples were treated analogously or pressed into pellets under absence of the binding agent using a hydraulic press applying a force of 3t. The pellets were mounted on 7 mm sample holders with Kapton tape, and the sample holders were mounted on a revolving holder plate on the XAS spectrometer and subsequently measured.

Measurements and data analysis

We conducted radiation hardness tests for a number of samples. The Rh samples were measured twice for each sample and the reported data is the average of two individual measurements. The Ir samples were measured once. Recorded spectra were aligned to an internal reference standard of Rh or Ir foil. Data processing was performed with the Demeter software package using Athena.[7]

Radial distributions

To compare experimental radial distributions originating in the combined scattering paths attributed to molecular structure to predicted ones, we modelled individual and combined scattering paths of the relevant functional groups and structure elements of the catalyst by employing Feff calculations using Artemis.[7] As reasonable approximation, we used the known

molecular structures obtained from X-ray single crystal diffraction[8, 9] for the three different cationic fragments of the precursor head groups in this study, i.e. $[Rh(CO)_2(PyTPh)]^+$, $[RhCp^*Cl(PyTPh)]^+$, $[IrCp^*Cl(PyTPh)]^+$, to calculate expected scattering paths with weighted contributions. Figure S23 shows experimental (Exp.) and calculated (Calc.) radial distributions for the selected scattering paths.

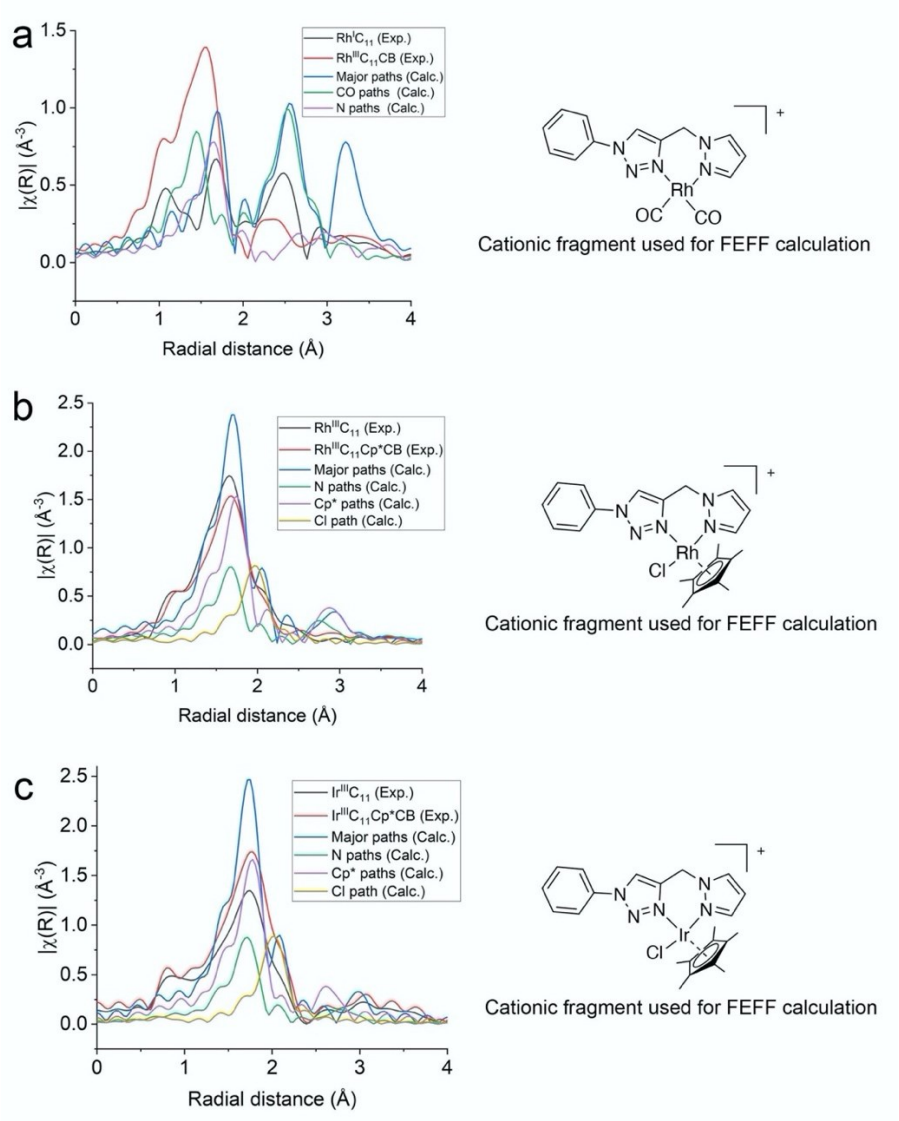


Figure S23. Comparison of experimental radial distributions for compounds before and after immobilization vs calculated scattering paths for the depicted cationic fragments. (a) **Rh^{I}C$_{11}$** and **Rh^{III}C$_{11}$CB** vs calculated combined major scattering paths and scattering paths attributed to CO ligands and N atoms of PyT ligands. (b) **Rh^{III}C$_{11}$** and **Rh^{III}C$_{11}$Cp*CB** vs calculated combined major scattering paths and scattering paths attributed to N atoms of PyT ligands, Cp* ligands and Cl atoms. (c) **Ir^{III}C$_{11}$** and **Ir^{III}C$_{11}$Cp*CB** vs calculated combined major scattering paths and scattering paths attributed to N atoms of PyT ligands, Cp* ligands and Cl atoms.

Curve Fitting

We conducted fitting of the experimental data versus data obtained from FEFF calculations involving the X-ray crystallography data of the matching cationic fragments mentioned above, using the Artemis software. For the set of $Ir^{III}Cp^*C_n$ complexes and the CB immobilised hybrid catalysts $Ir^{III}Cp^*C_nCB$, as well as **$Rh^{III}Cp^*C_{11}$** and **$Rh^{III}Cp^*C_{11}CB$**, obtained fits match the experiment which further supports that the immobilised catalysts do not undergo structural changes during immobilisation on the head-group. Starting guess values for the refinement for selected scattering paths were: $\sigma^2 = 0.003$; Amplitude factor = 1, delr = 0 and $E_0 = 0$. We implemented in certain circumstance restraints of σ^2 to obtain reasonable fits. The calculated bond distance for the first coordination shell, i.e. the two binding N atoms, five C atoms of the Cp* ring and, the Cl atoms are reported below. N denotes the coordination number for each atom in the relevant scattering path. Fourier transformed EXAFS data (k^2 weighted) are shown in Figures S24-27.

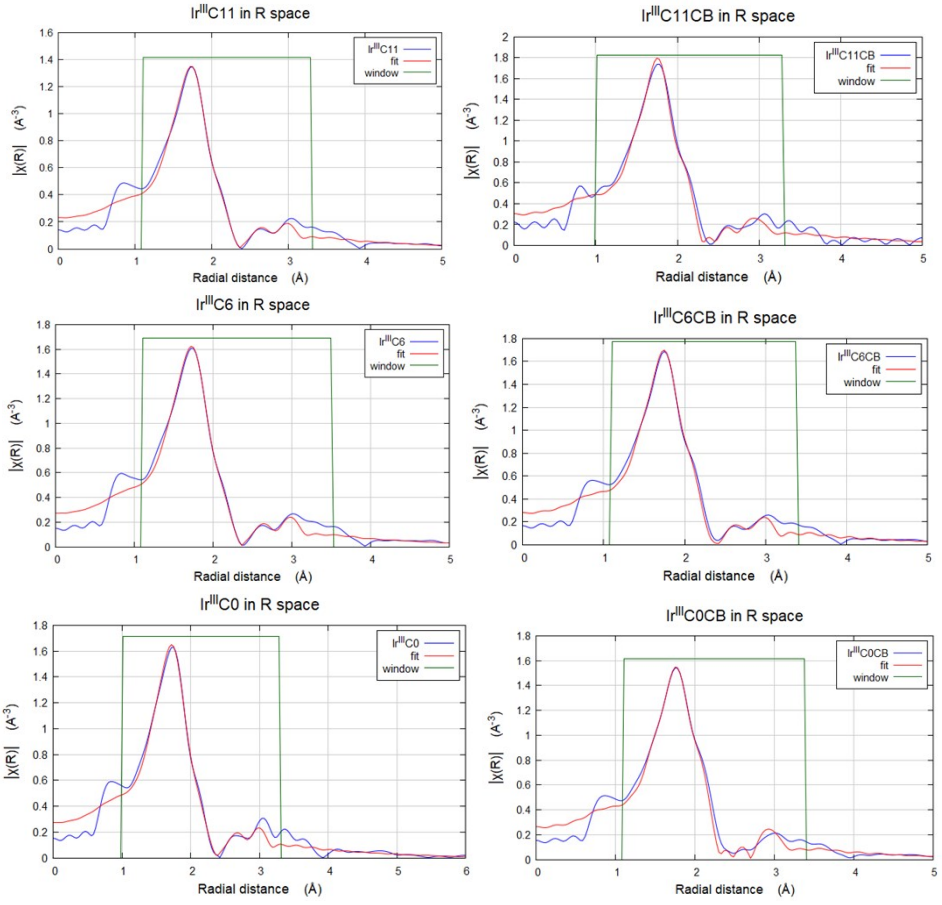


Figure S24. Fourier transformed EXAFS data (k^2 weighted) for $Ir^{III}Cp^*C_n$ and $Ir^{III}Cp^*C_nCB$ (n = 11, 6, 0) showing the experimental data and obtained fit, and the applied fitting window.

Table S25. Summary of refined parameters for the first coordination shell from the fit for $Ir^{III}Cp^*C_n$ and $Ir^{III}Cp^*C_nCB$ (n = 11, 6, 0) involving the major scattering paths.

Compound	Bond	N	Bond length [Å]	σ^2	E_0 [eV]	R-factor
$Ir^{III}Cp^*C_{11}$	Ir-N (PyT, 2N)	2	2.094	0.005(2)	9.03 +/- 1.07	0.005
	Ir-C (Cp*, 5C)	5	2.166	0.006(1)		
	Ir-Cl	1	2.400	0.007(2)		
$Ir^{III}Cp^*C_{11}CB$	Ir-N (PyT, 2N)	2	2.091	0.005(3)	12.00 +/- 0.84	0.013
	Ir-C (Cp*, 5C)	5	2.163	0.003(1)		
	Ir-Cl	1	2.396	0.003(1)		
$Ir^{III}Cp^*C_6$	Ir-N (PyT, 2N)	2	2.101	0.005(3)	8.53 +/- 1.64	0.007
	Ir-C (Cp*, 5C)	5	2.174	0.007(2)		
	Ir-Cl	1	2.408	0.008(3)		
$Ir^{III}Cp^*C_6CB$	Ir-N (PyT, 2N)	2	2.091	0.006(3)	9.05 +/- 0.89	0.007
	Ir-C (Cp*, 5C)	5	2.163	0.004(1)		
	Ir-Cl	1	2.396	0.004(1)		
$Ir^{III}Cp^*C_0$	Ir-N (PyT, 2N)	2	2.097	0.006(3)	7.75 +/- 1.36	0.007
	Ir-C (Cp*, 5C)	5	2.169	0.007(2)		
	Ir-Cl	1	2.403	0.008(3)		
$Ir^{III}Cp^*C_0CB$	Ir-N (PyT, 2N)	2	2.091	0.009(6)	9.27 +/- 1.04	0.011
	Ir-C (Cp*, 5C)	5	2.163	0.004(1)		
	Ir-Cl	1	2.396	0.003(1)		

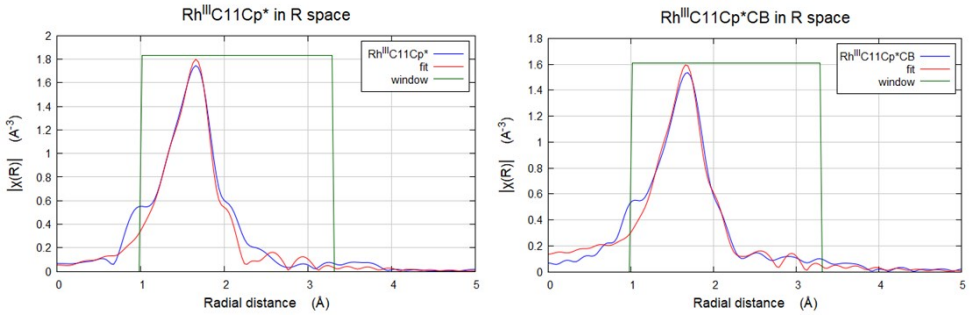


Figure S25. Fourier transformed EXAFS data (k^2 weighted) for **$RhCp^*C_{11}$** and **$RhCp^*C_{11}CB$** showing the experimental data and obtained fit, and the applied fitting window.

Table S26. Summary of refined parameters for the first coordination shell from the fit for **$Rh^{III}Cp^*C_{11}$** and **$Rh^{III}Cp^*C_{11}CB$** involving the major scattering paths.

Compound	Bond	N	Bond length [Å]	σ^2	E_0 [eV]	R-factor
$Rh^{III}Cp^*C_{11}$	Rh-N (PyT, 2N)	2	2.093	0.004[a]	-9.14 +/- 1.69	0.020
	Rh -C (Cp*, 5C)	5	2.153	0.003(1)		
	Rh-Cl	1	2.377	0.003(2)		
$Rh^{III}Cp^*C_{11}CB$	Rh-N (PyT, 2N)	2	2.094	0.003[a]	-0.33 +/- 1.26	0.018
	Rh-C (Cp*, 5C)	5	2.154	0.003(1)		
	Rh-Cl	1	2.378	0.002(1)		

[a] These were set to the reported value for the refinement

Regarding the series of homogeneous Rh^{I} complexes, $Rh^{I}C_{n}$, all fits contained significant portions of misfit in the range of ~ 1-1.3 Å, which is attributed to a distinct peak at ~ 1.1 Å for all samples which appears below the first coordination shell. It is very unlikely that this low-R value represents a real bond distance as it is significantly below the first coordination shell. Thus, we constrained the fitting window to exclude this non-physical interatomic distance, which resulted in a more reasonable result at higher radial distance albeit still high R-values.

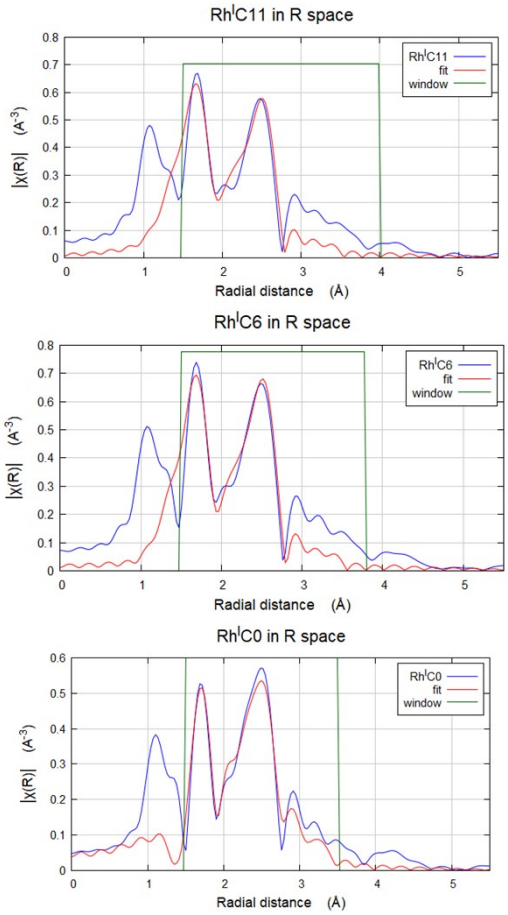


Figure S26. Fourier transformed EXAFS data (k^2 weighted) for $Rh^{I}C_n$ (n = 11, 6, 0) showing the experimental data and obtained fit, and the applied fitting window.

Table S27. Summary of refined parameters for the first coordination shell from the fit for $Rh^{I}C_n$ (n = 11, 6, 0) involving the major scattering paths.

Compound	Bond	N	Bond length [Å]	σ^2	E_0 [eV]	R-factor
$Rh^{I}C_{11}$	Rh-N (PyT, 2N) Rh-C (CO, 2C)	2 2	2.097 1.888	0.045(38) 0.001(3)	-0.50 +/- 2.63	0.097
$Rh^{I}C_{6}$	Rh-N (PyT, 2N) Rh-C (CO, 2C)	2 2	2.099 1.890	0.039(31) 0.003(2)	0.87 +/- 24.75	0.081
$Rh^{I}C_{0}$	Rh-N (PyT, 2N) Rh-C (CO, 2C)	2 2	2.089 1.880	0.009(7) 0.002(1)	-3.38 +/- 2.82	0.056

Lastly, we consider the hybrid catalysts $Rh^{III}C_nCB$. Based on our experimental results of the control experiments, CO ligands are absent in the hybrid catalysts. The samples are composed of two PyT-ligands and two co-ligands (Cl, NO_2, NO_3 or OH) coordinated to one Rh. We have conducted a first shell fitting for the samples, using only the first shell N scattering path with a set amplitude factor of 1.2 for **$Rh^{III}C_{11}CB$** and 1.4 for **$Rh^{III}C_6CB$** and **$Rh^{III}C_0CB$**, and the

following guess starting values: $\sigma^2 = 0.003$, $E_0 = 0$, delr = 0 in order to calculate the coordination number. This model ignores the co-ligands X_1/X_2 and only focuses on the first shell possibly explaining the high R factors, while the obtained coordination numbers are 6, as expected.

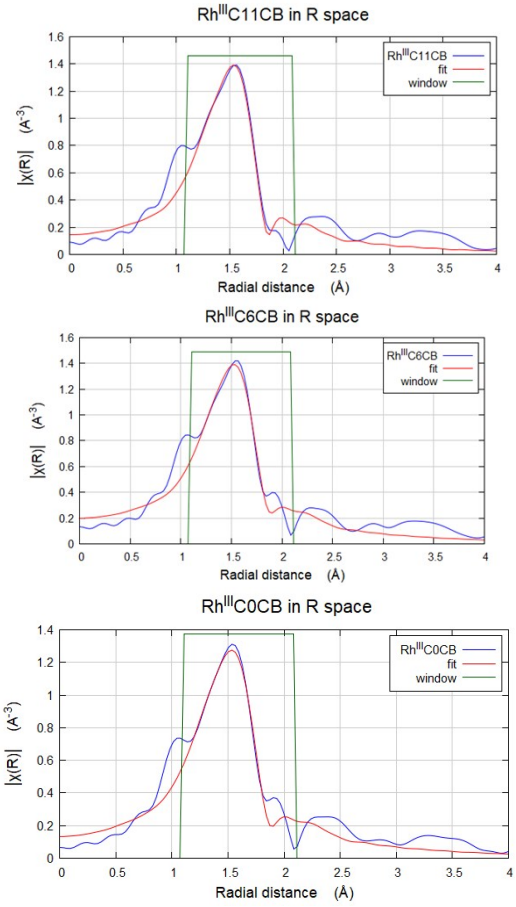


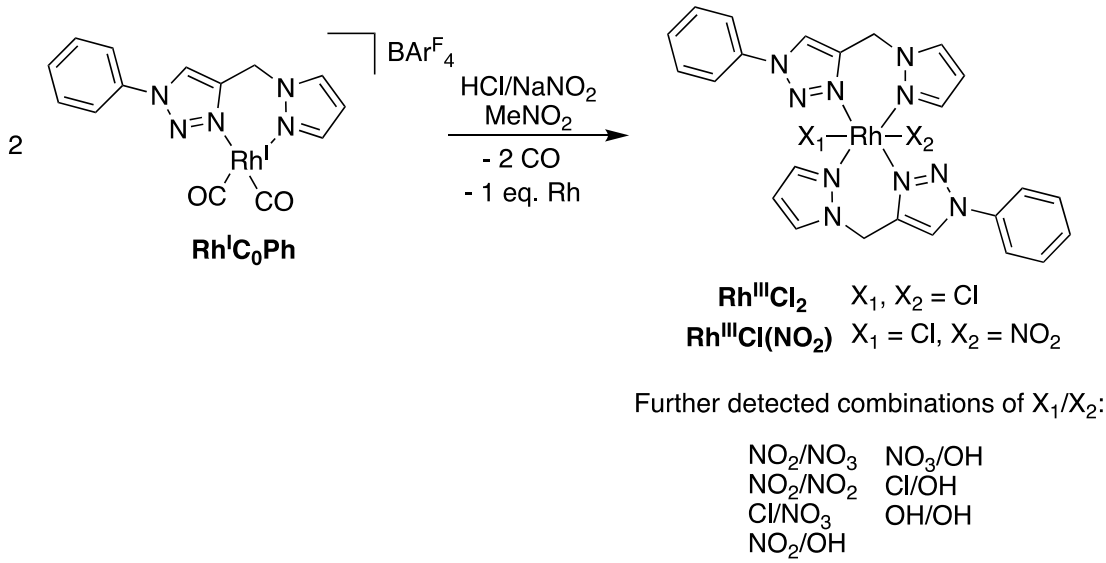
Figure S27. Fourier transformed EXAFS data (k^2 weighted) for $Rh^{III}C_nCB$ (n = 11, 6, 0) showing the experimental data and obtained fit, and the applied fitting window.

Table S28. Summary of refined parameters for the first coordination shell from the fit for $Rh^{III}C_nCB$ (n = 11, 6, 0) involving the major scattering paths.

Compound	Bond	Coordination Number	Bond length [Å]	σ^2	E_0 [eV]	S_0^2	R-factor
$Rh^{III}C_{11}CB$	Rh-N (PyT, 2N)	6.30 +/- 0.81	2.035	0.006(2)	-2.93 +/- 2.04	1.2	0.023
$Rh^{III}C_6CB$	Rh-N (PyT, 2N)	6.31+/-0.97	2.040	0.008(2)	-1.00 +/- 2.25	1.4	0.040
$Rh^{III}C_0CB$	Rh-N (PyT, 2N)	5.8 +/- 0.91	2.093	0.007(2)	-2.70 +/- 2.35	1.4	0.041

4. Control Experiments

Rh^{I}C$_0$, **Rh^{I}C$_{11}$** and **Rh^{I}C$_0$Ph**, prepared analogously to the Rh^{I}C*n* according to the literature[8], were treated with HCl/$NaNO_2$ in $MeNO_2$ under absence of CB. The reaction is shown for **RhC$_0$Ph** in Scheme S2.



Scheme S2. Treatment of the **Rh^{I}C$_0$Ph** compound with HCl/$NaNO_2$ in $MeNO_2$ under absence of CB.

Exemplary procedure for **Rh^{I}C$_0$Ph**: The title compound (20 mg, 0.16 mmol) was dissolved in nitromethane (4 mL) in a Schlenk flask and cooled to 0 °C. HCl (0.2 mL) was added dropwise, which was followed by addition of $NaNO_2$ (2.2 mg, 0.32 mmol, 2 eq.). The mixture was stirred at room temperature for 16 h. The organic layer phase for separated using a pipette and the solvent was evaporated to dryness using a rotary evaporator, which was followed by drying under vacuum. The obtained light brown solids were taken up in DCM and filtered through celite. Solvent evaporation and drying under vacuum gave the Rh^{III} based material (21 mg) as light brown solid.

Both **Rh^{I}C$_0$** and **Rh^{I}C$_{11}$** were treated analogously. The obtained products are poorly soluble in DCM. Thus, the no filtration through celite was carried out.

IR spectra showed absence of the CO vibrational bands for all three examples (Figures 24-26). For **$Rh^{I}C_0Ph$**, we stopped the reaction as well at time points of 1.5 h and 4 h and note that some starting material is still present at these time points, and that the ^{1}H NMR spectra gain complexity over time (Figure S24) while the IR spectra did not show major changes apart from low intensity CO vibrations at 1.5 h and 4 h due to remaining **$Rh^{I}C_0Ph$**, which is absent after 16 h reaction time (Figure S25).

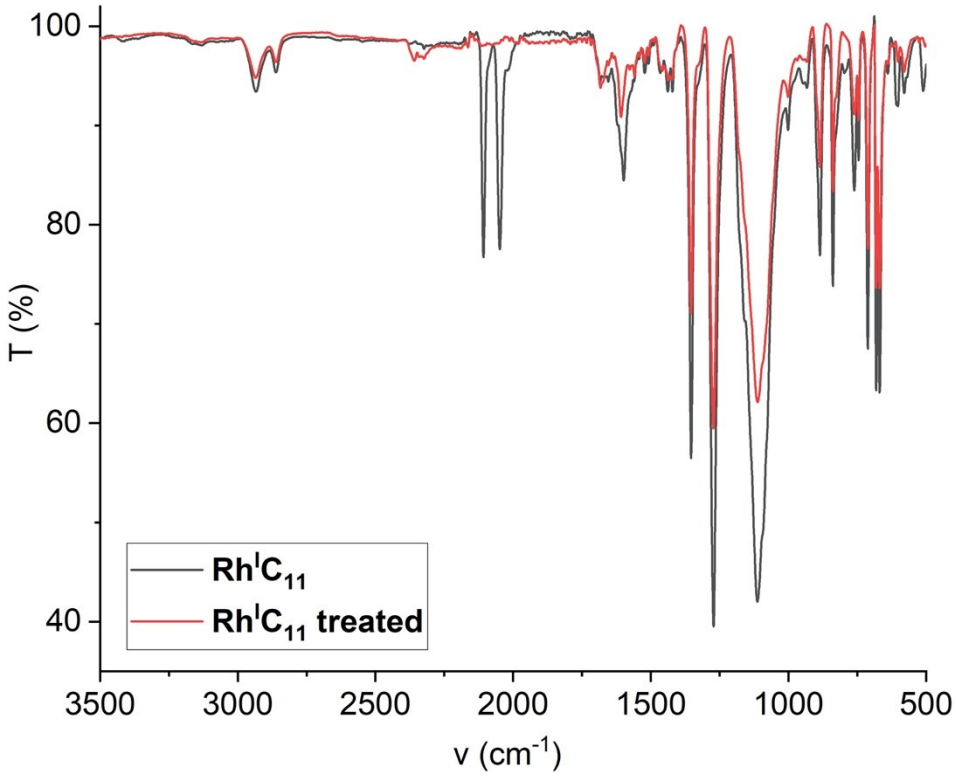


Figure S28. IR spectrum of **$Rh^{I}C_{11}$** before and after treatment with $HCl/NaNO_2$ in $MeNO_2$.

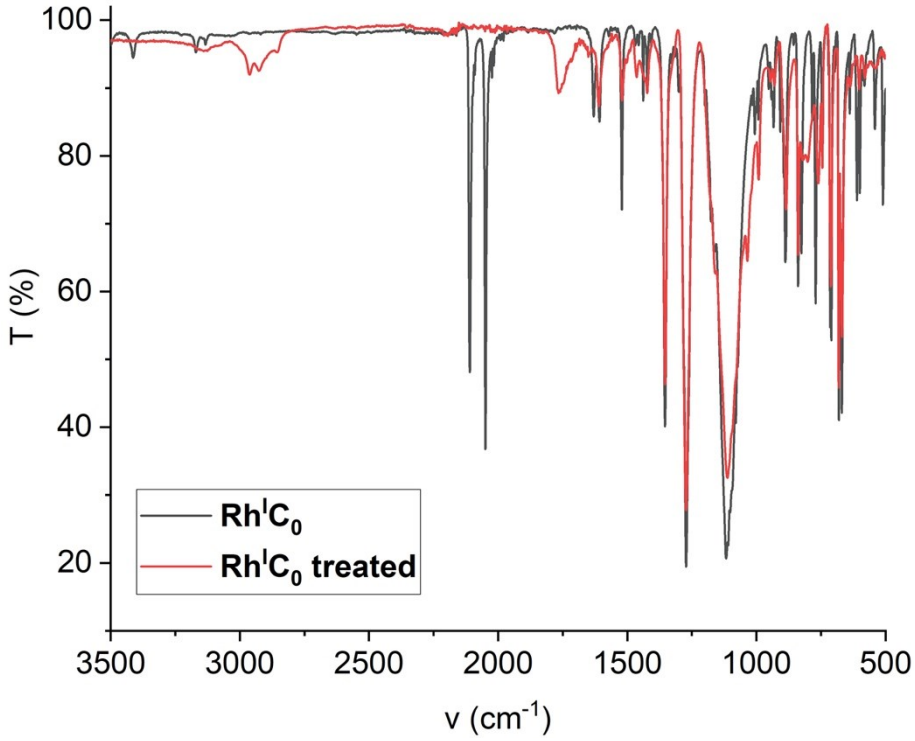


Figure S29. IR spectrum of **$Rh^{I}C_0$** before and after treatment with $HCl/NaNO_2$ in $MeNO_2$.

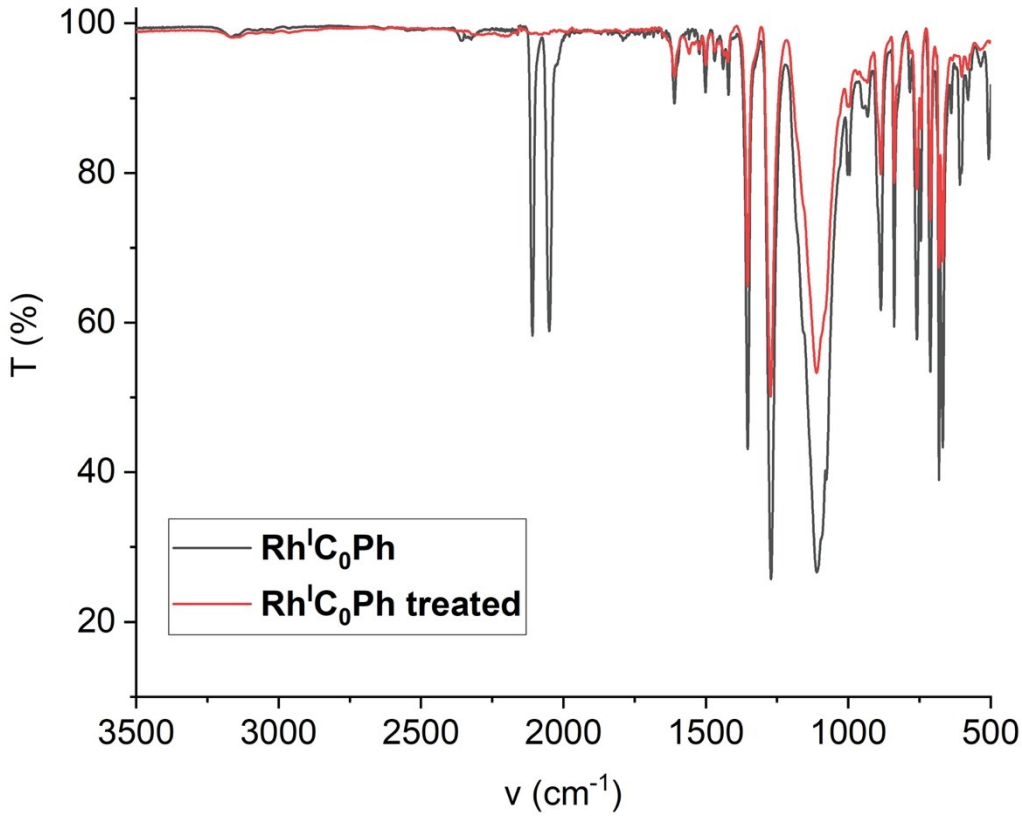


Figure S30. IR spectrum of **$Rh^{I}C_0Ph$** before and after treatment with $HCl/NaNO_2$ in $MeNO_2$.

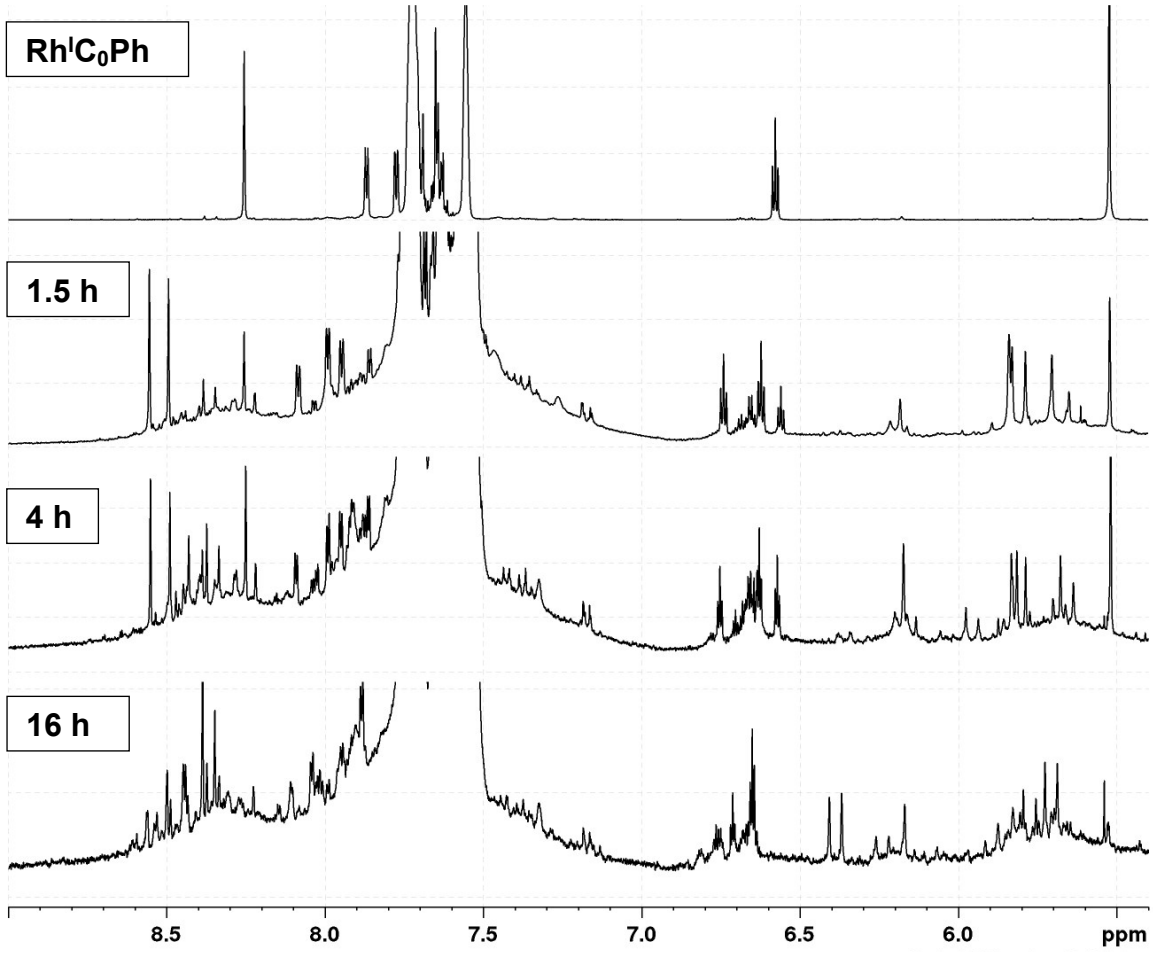


Figure S31. Selected ranges of ^{1}H NMR spectra of the parent **Rh^{I}C$_0$Ph** and after treatment with HCl/$NaNO_2$ after 1.5 h, 4 h and 16 h.

Analysis by MS/HRMS (ESI^+) of the material obtained from treatment of **Rh^{I}C$_0$Ph** showed a number of fragments, all bearing two PyT-ligands per Rh atom, i.e. $Rh(PyT)_2$ as described in the main manuscript. The spectra are shown in Figures S28-S36.

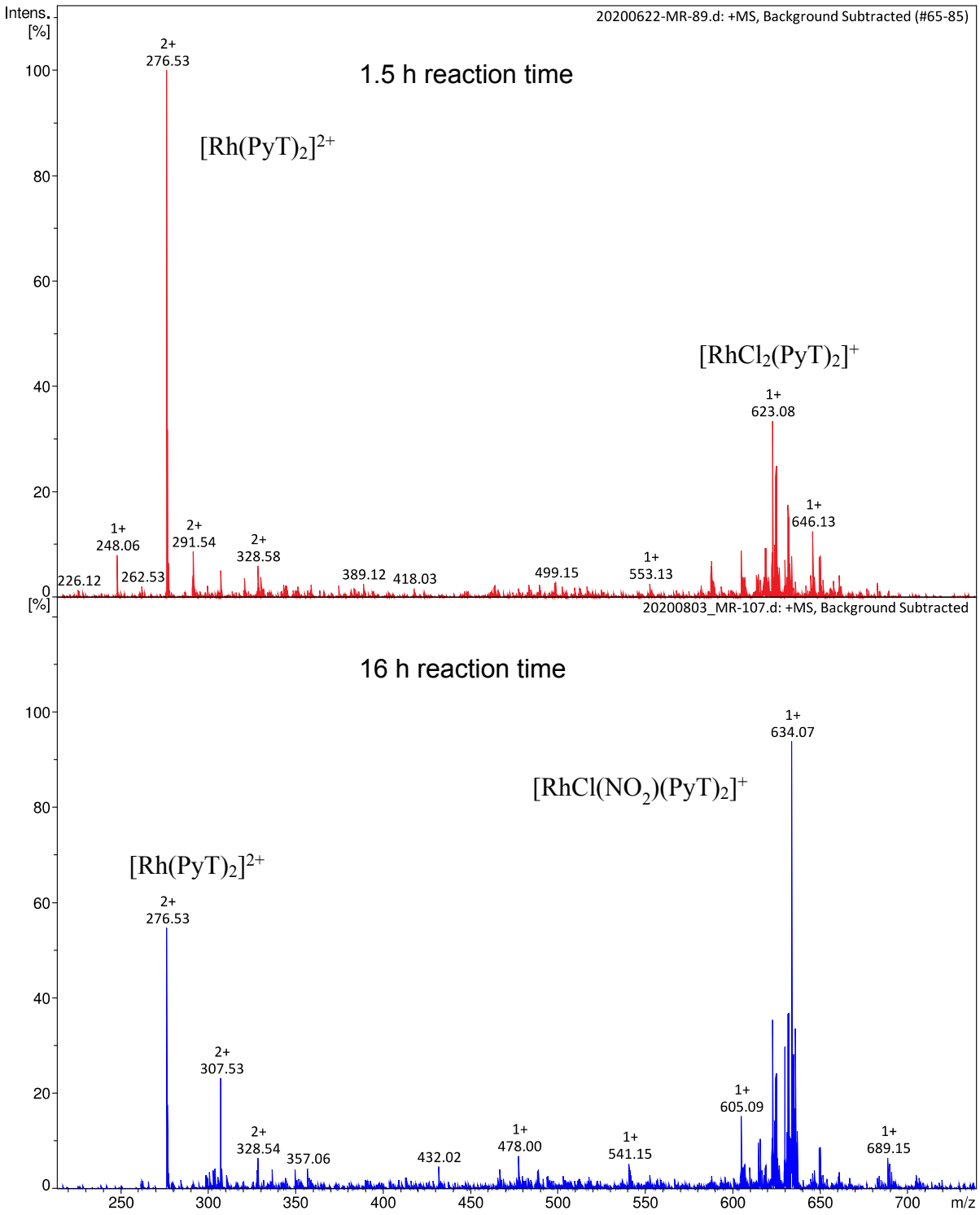


Figure S32. ESI$^+$ mass spectra of the material obtained from treatment of **Rh^{I}C$_0$Ph** with HCl/NaNO$_2$ after work-up at 1.5 h and 16 h.

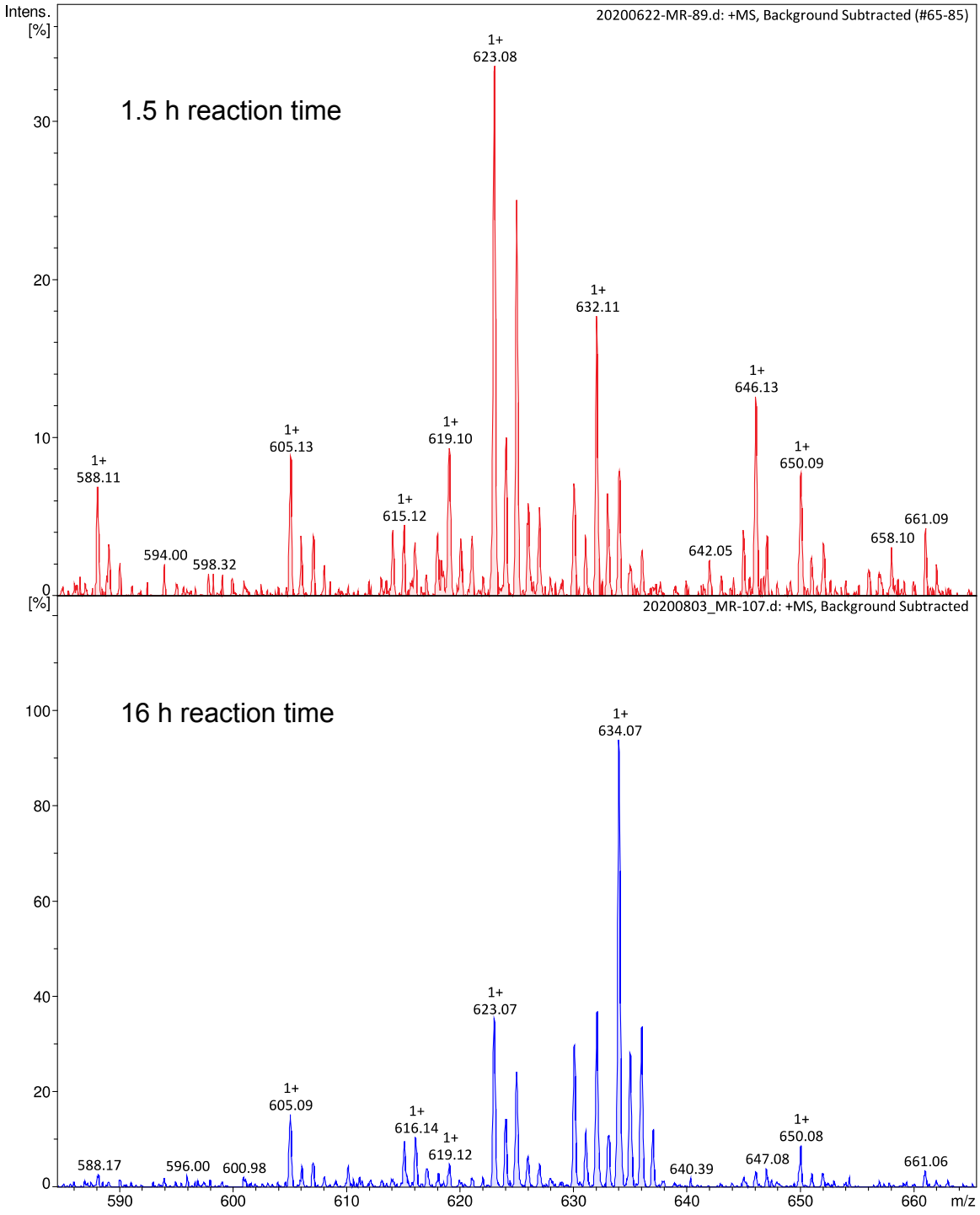


Figure S33. ESI$^+$ mass spectra in range of ~ 580-670 Da of the material obtained from treatment of **Rh^{I}C$_0$Ph** with HCl/$NaNO_2$ after work-up at 1.5 h and 16 h.

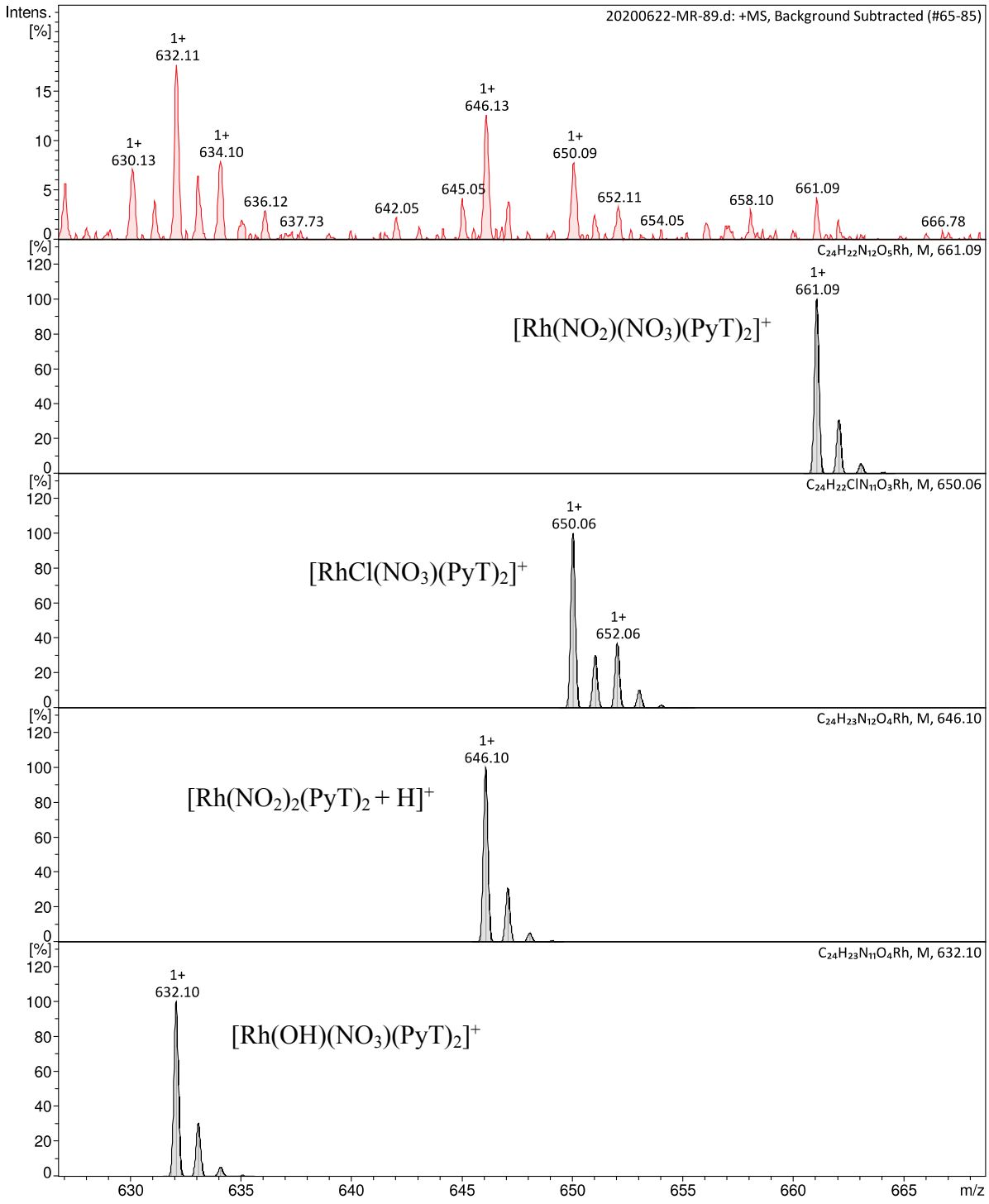


Figure S34. Experimental and simulated mass patterns for the materials obtained from treatment of **$Rh^{I}C_0Ph$** with $HCl/NaNO_2$ after work-up at 1.5 h.

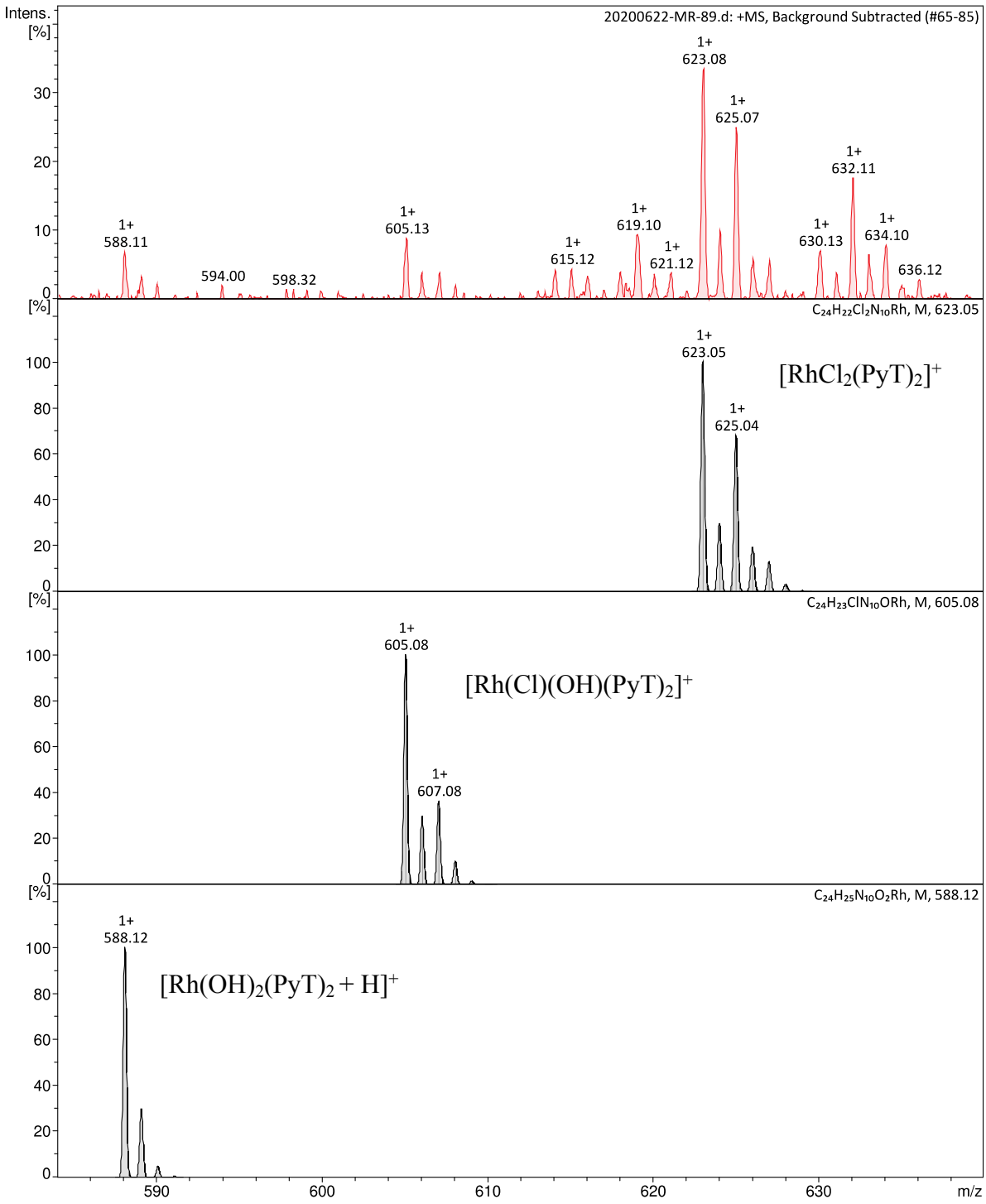


Figure S35. Experimental and simulated mass patterns for the materials obtained from treatment of **Rh^{I}C$_0$Ph** with HCl/$NaNO_2$ after work-up at 1.5 h.

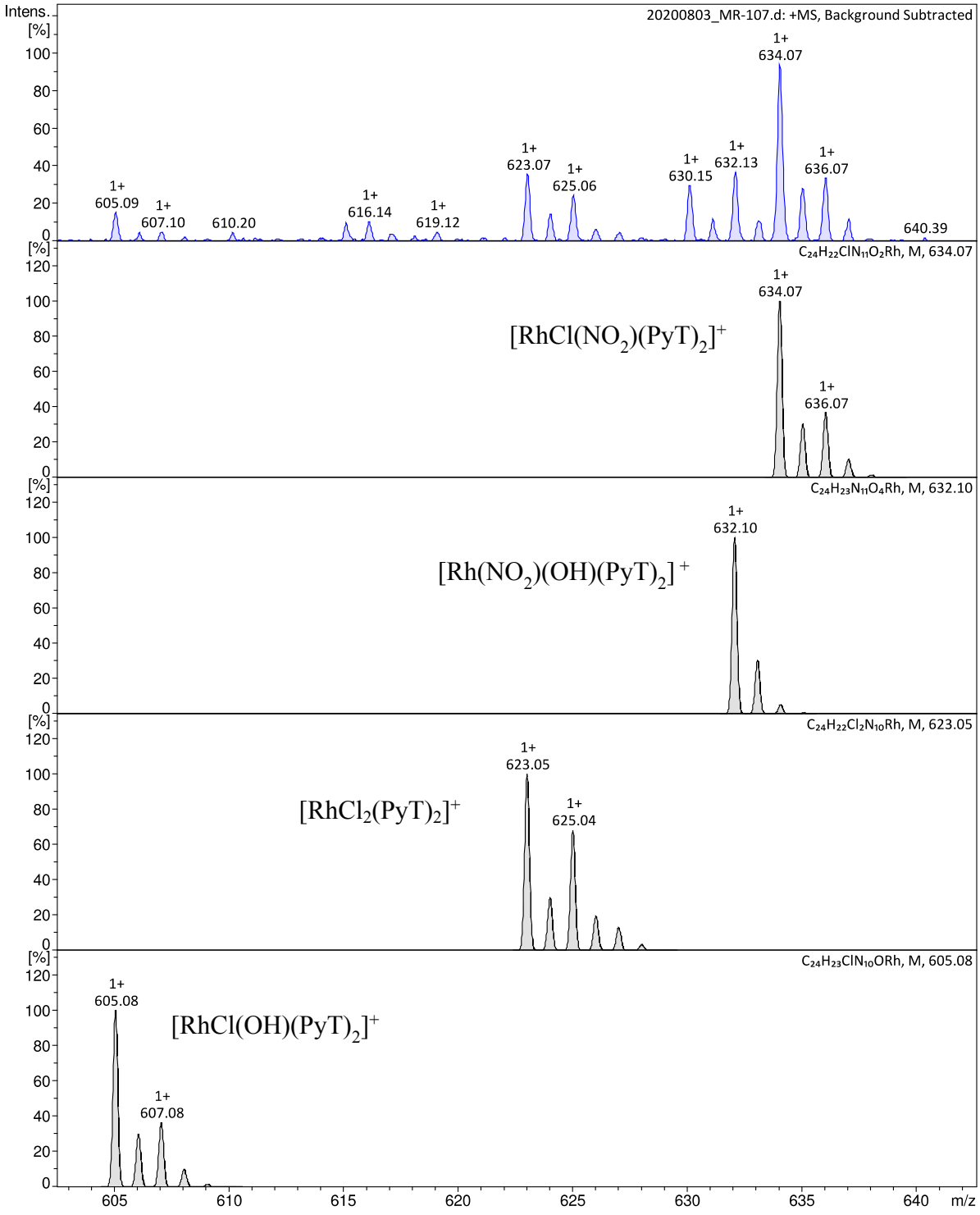


Figure S36. Experimental and simulated mass patterns for the materials obtained from treatment of **Rh^{I}C$_0$Ph** with HCl/NaNO$_2$ after work-up at 16 h.

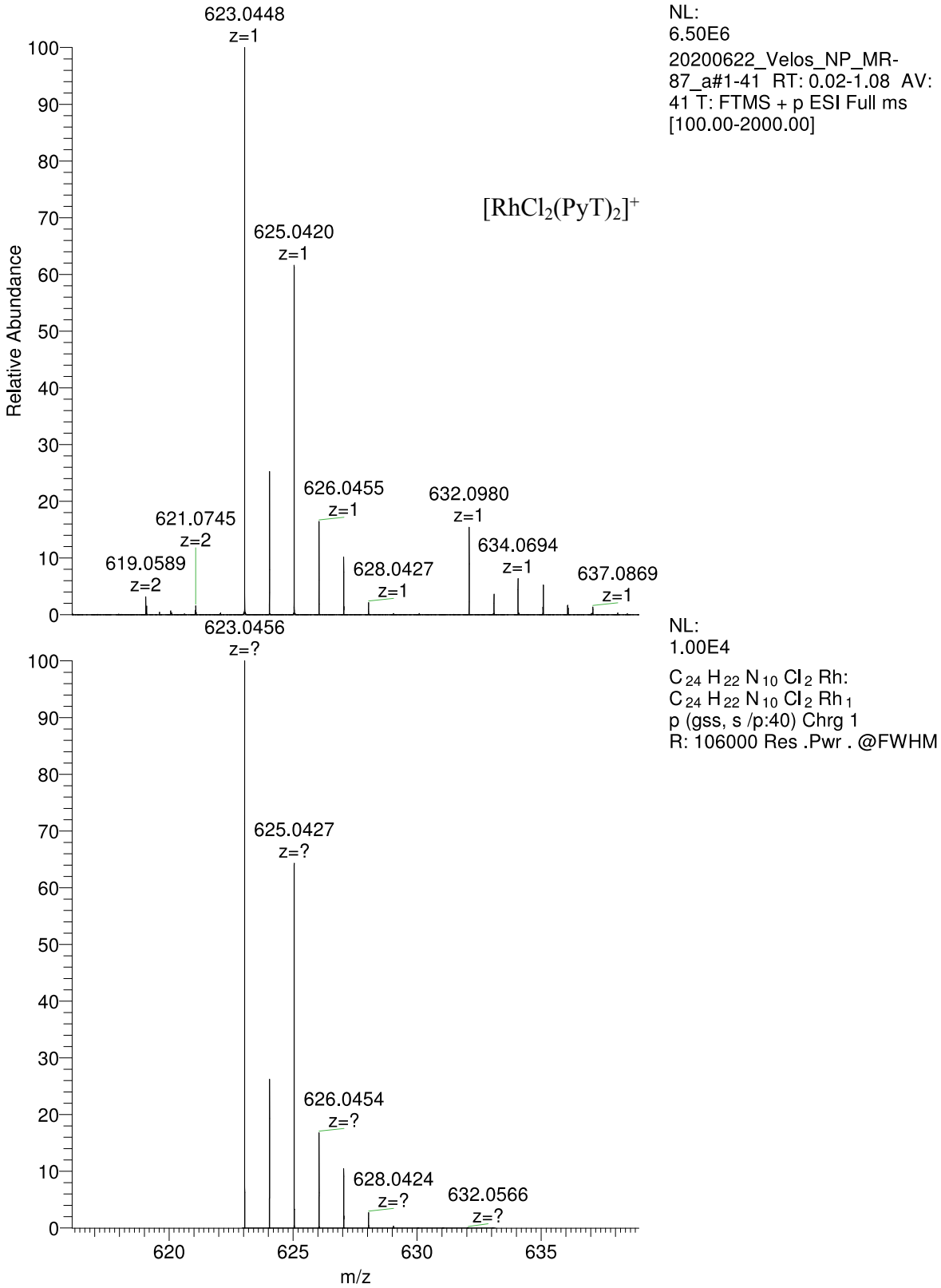


Figure S37. Experimental (top) and calculated (bottom) high resolution mass spectrum of the peak assigned to $[(PhPyT)_2RhCl_2]^+$.

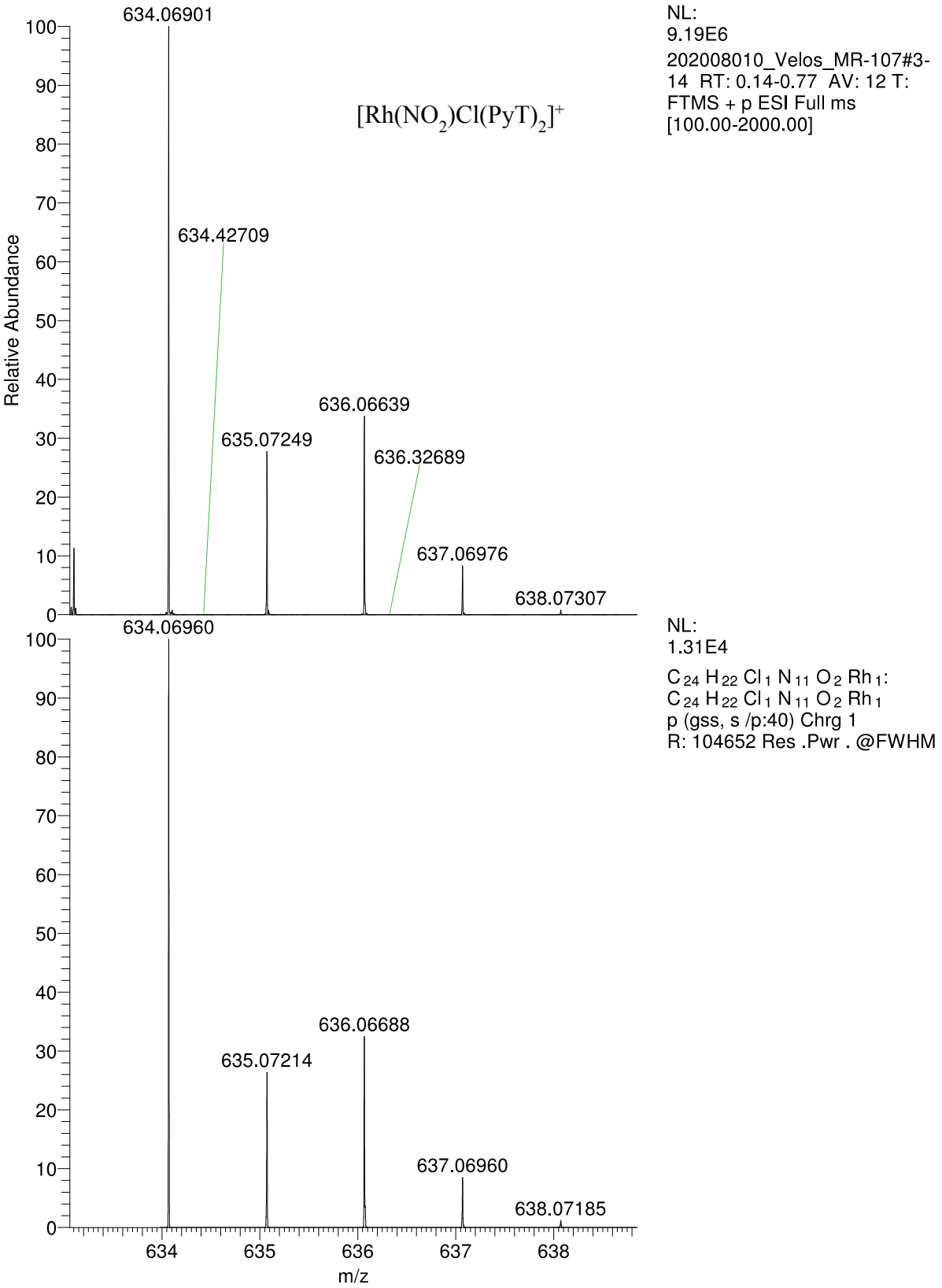


Figure S38. Experimental (top) and calculated (bottom) high resolution mass spectrum of the peak assigned to $[Rh(NO_2)Cl(PyT)_2]^+$.

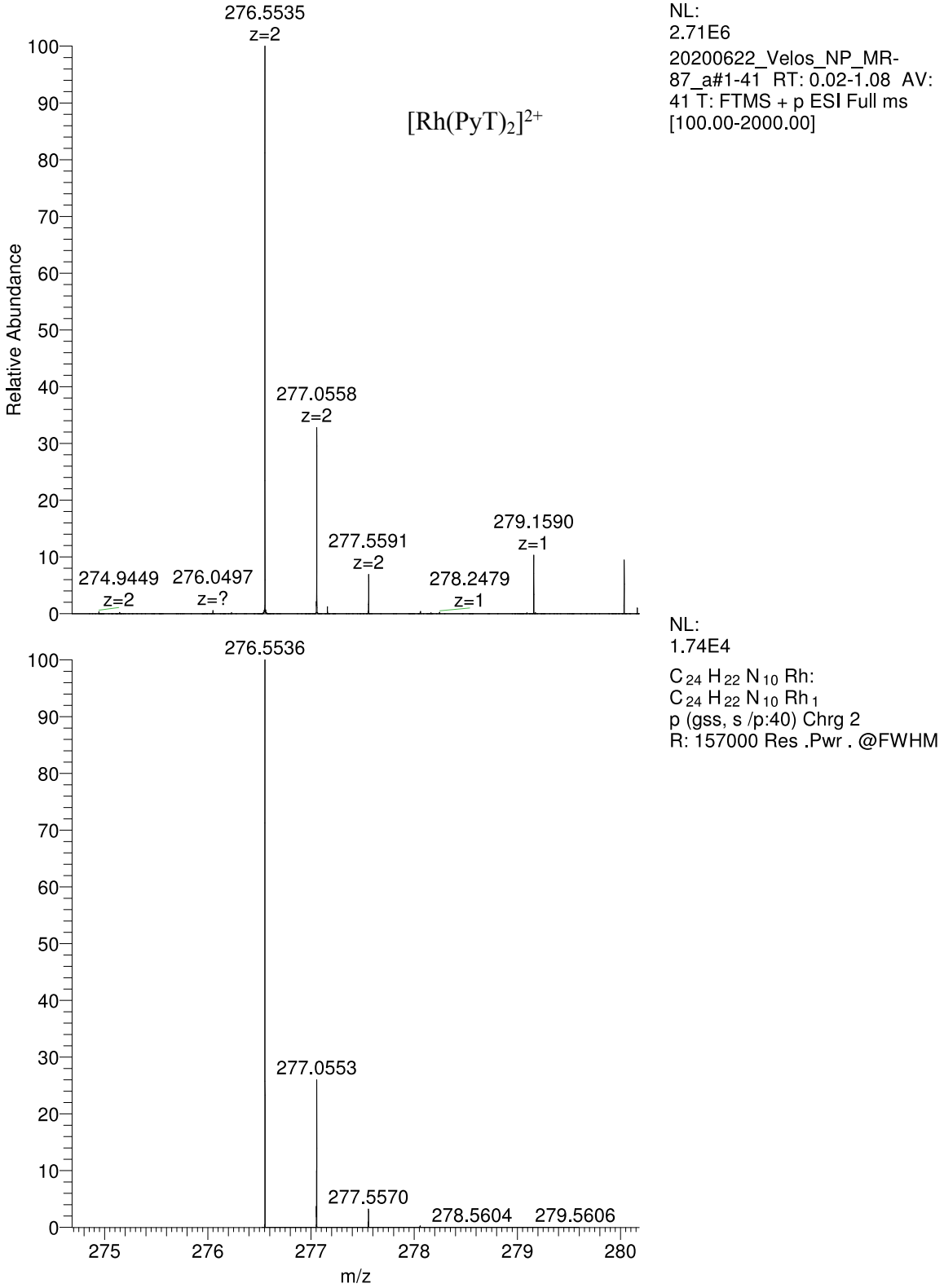


Figure S39. Experimental (top) and calculated (bottom) high resolution mass spectrum of the peak assigned to $[Rh(PyT)_2]^{2+}$.

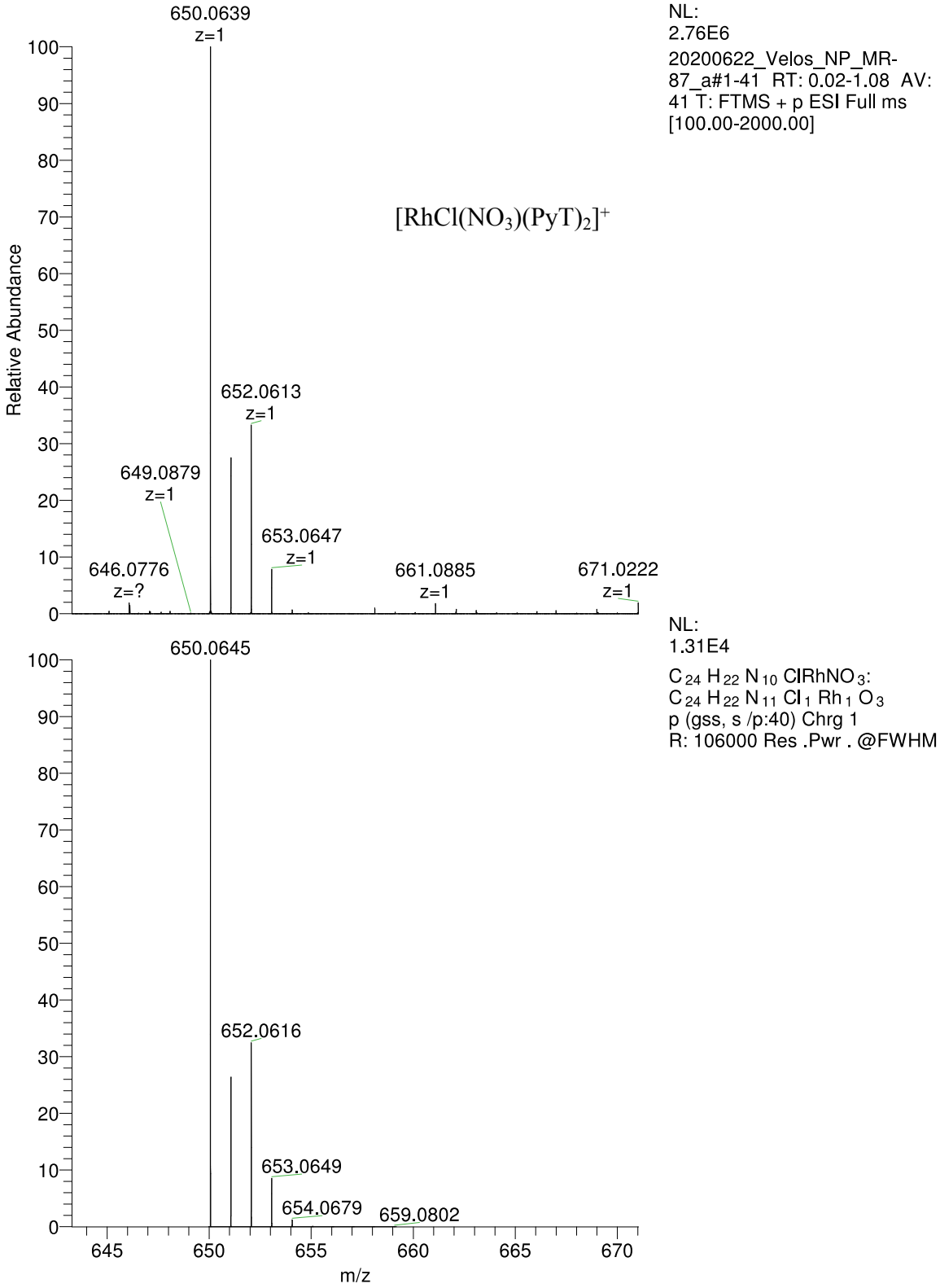


Figure S40. Experimental (top) and calculated (bottom) high resolution mass spectrum of the peak assigned to $[Rh(NO_3)Cl(PyT)_2]^+$.

5. Thermogravimetric Analyses

To test thermal stability of the hybrid catalysts, we conducted thermogravimetric measurements. Figure 37 shows weight loss as function of temperature for the hybrid catalysts. Experiments were conducted on a TA Instruments Discovery Thermogravimetric analyzer. Approximately 0.5 mg of the hybrid catalyst was placed into a flame cleaned Pt pan and placed into the analyser. Weight loss was monitored while ramping up the temperature from room temperature to 700 °C with a heating rate of 20°C/min. The obtained TGA traces for the hybdirc catalysts and a control sample of CB are shown in Figure S37. Up to ~ 300 °C the curves are essentially featureless with the **$Rh^{III}C_0CB$** sample showing a slightly higher weight loss than all other examples. At ~ 380 °C, all catalysts exhibit a first process, which is followed for all $M^{III}Cp^*C_nCB$ examples by another at ~ 490 °C while the $Rh^{III}C_nCB$ hybrid catalysts exhibit a more gradual weight decrease.

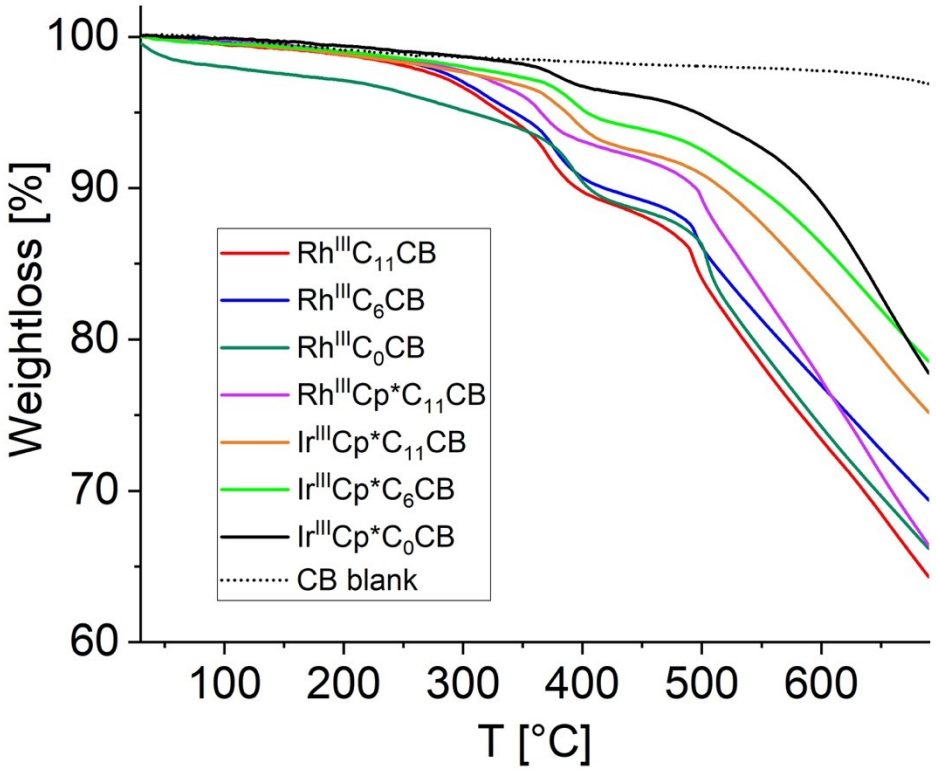
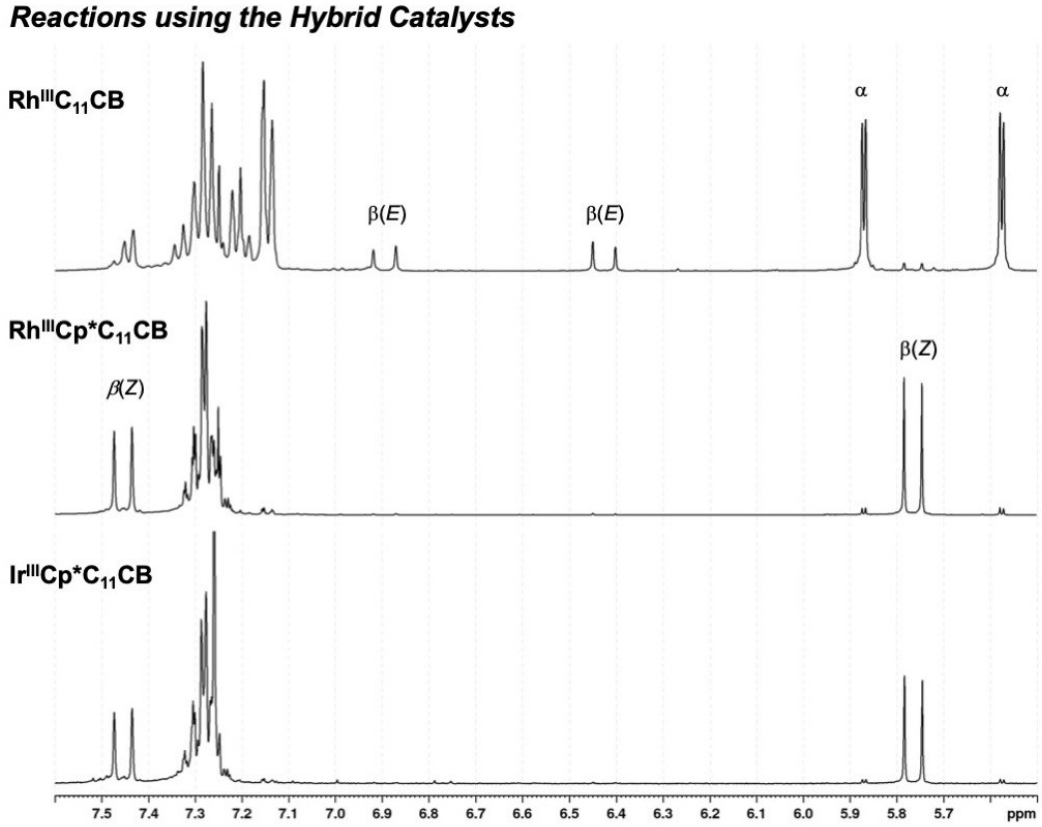


Figure S41. Thermogravimetric analysis of the hybrid catalysts and a control sample of CB treated under grafting conditions.

6. Catalysis Experiments

6.1 Hydrosilylation of Phenylacetylene

A flame dried 4 mL Schlenk tube, equipped with a PTFE stopcock and magnetic stirring bar, was charged with the hybrid catalyst and THF (1 mL). Phenylacetylene (9 mg, 0.09 mmol) and triethylsilane (18 mg, 0.16 mmol) were added. The mixture was heated while stirring for the specified amount of time using an oil bath. The headspace was fully submerged in the oil. After the reaction was completed, the mixture was allowed to cool down to room temperature and transferred into a V-shaped centrifuge vial and centrifuged at 4000 rpm for 20 min. The solution was removed and concentrated to dryness using rotary evaporator and briefly dried under high vacuum. The product mixture was re-dissolved in chloroform-*d*, filtered through a



PTFE-syringe filter (45 μm) and analyzed by ^{1}H NMR spectroscopy.

Figure S42. Selected ranges of the ^{1}H NMR spectra of the reaction mixtures from hydrosilylation of phenylacetylene using the hybrid catalysts **Rh^{III}C$_{11}$CB**, **Rh^{III}Cp*C$_{11}$CB** and **Ir^{III}Cp*C$_{11}$CB.**
The products were identified by comparison of the vinylic ^{1}H NMR resonances of the β(*E*)-, β(*Z*)- and α-isomers to the literature.[10] Conversions were calculated by integration of combined vinylic proton resonances of all isomers and comparison to the proton signal of unreacted terminal alkyne.

Table S29. Summary of the hydrosilylation reactions of phenylacetylene using the different Rh- and Ir-catalysts.

No.	Catalyst	Metal [mol%][a]	Loading [wt%][b]	Et_3SiH [eq.]	Solvent	T [°C]	Time [min]	Conversion [%]	Ratio β(*E*) : β(*Z*) : α
Heterogeneous reactions									
1	**Rh^{III}C$_{11}$CB**	1.1	3.9	4.8	THF	75	15	97	16 : 4 : 80
2	**Rh^{III}C$_{11}$CB**	1.3	3.9	4.8	THF	70	15	97	13 : 3 : 84
3	**Rh^{III}C$_{11}$CB**	2.0	3.9	3.5	THF	60	60	100	12 : 4 : 84
4	**Rh^{III}C$_{11}$CB**	1.3	3.9	4.8	THF	60	60	100	15 : 6 : 80
5	**Rh^{III}C$_{11}$CB**	1.3	3.9	1.8	THF	50	60	99	11 : 7 : 82
6	**Rh^{III}C$_{11}$CB**	1.1	3.9	1.8	DCM	40	30	24	13 : 19 : 68
7	**Rh^{III}C$_{11}$CB**	1.1	3.9	1.8	DCM	40	120	95	6 : 15 : 79
8	**Rh^{III}C$_{11}$CB**	1.0	3.9	1.8	THF	60	60	96	11 : 4 : 85
9	**Rh^{III}C$_6$CB**	1.0	4.1	1.8	THF	60	60	95	11 : 4 : 85
10	**Rh^{III}C$_0$CB**	1.0	6.4	1.8	THF	60	60	56	10 : 8 : 82
11	**Rh^{III}C$_6$CB**	1.4	4.1	1.8	THF	60	60	85	11 : 5 : 84
12	**Rh^{III}C$_0$CB**	2.1	6.4	1.8	THF	60	60	95	10 : 7 : 83
13	**Ir^{III}Cp*C$_{11}$CB**	0.4	2.1	4.8	THF	70	60	60	8 : 72 : 20
14	**Ir^{III}Cp*C$_{11}$CB**	0.5	2.1	1.8	THF	60	60	98	2 : 95 : 3
15	**Ir^{III}Cp*C$_6$CB**	0.5	1.9	1.8	THF	60	60	60	2 : 95 : 3
16	**Ir^{III}Cp*C$_0$CB**	0.5	1.3	1.8	THF	60	60	85	2 : 95 : 3
17	**Ir^{III}Cp*C$_6$CB**	0.3	1.9	1.8	THF	70	60	98	2 : 94 : 4
18	**Ir^{III}Cp*C$_0$CB**	0.2	1.3	1.8	THF	70	60	97	3 : 94 : 3
19	**Rh^{III}Cp*C$_{11}$CB**	0.7	2.0	1.8	THF	70	60	99	1 : 94 : 4
Control									
20[c]	-	1.0	-	-	THF	70	180	0	-

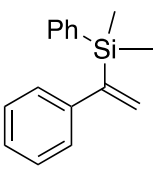
Reaction conditions: 1 mL solvent in sealed Schlenk tube under Ar on a 0.1 mmol scale.
[a] Calculated molar amount of metal used in the reaction.
[b] Determined by EDX.
[c] Control experiment under absence of catalyst. CB (3 mg) treated under the applied grafting conditions was added to the reaction.

Preparative Reaction on a ~ 0.1 g Scale

A glass ampule equipped with PTFE stop cock and magnetic stirring bar was filled with **$Rh^{III}C_{11}CB$** hybrid catalyst (23 mg, ~ 1 mol%) and THF (10 mL). Phenylacetylene (90 mg, 0.9 mmol) and triethylsilane (183 mg, 15.8 mmol) were added, the ampule was sealed and placed into an oil bath with the sealed volume fully submerged up to the stop cock and heated to 60 °C for 1h. After that, the mixture was cooled, transferred into two 5 ml glass centrifuge tubes, and centrifuged for 20 min at 4000 rpm. The solution was taken up with a syringe and filtered through a PTFE syringe filter (45 µm) into a round bottom flask and concentrated using a rotary evaporator. The remaining hybrid catalyst was washed once with pentane (8 mL) and centrifuged for 5 min at 4000 rpm. The pentane was also filtered through the syringe filter, combined with the content of the round bottom flask, concentrated again using a rotary evaporator and dried under high vacuum (~ 5.0×10^{-1} mbar). Subsequently, the mixture was flash-filtered through a silica column (10 cm × 1 cm) eluting with pentane, giving after solvent evaporation and drying under vacuum the isomeric product mixture (176 mg, 0.8 mmol, 92 %). It contained mostly the α-isomer (88 %), minor amounts of the β(*Z*)-isomer (10 %), and small amounts of the β(*E*)-isomer (2 %), as determined by ^{1}H NMR spectroscopy (Fig. S111-114).

Reaction with Phenyldimethylsilane

Furthermore, we tested compatibility of **$Rh^{III}C_{11}CB$** for the hydrosilylation of phenylacetylene with phenyldimethylsilane. Under the same applied conditions using 1.8 eq. of dimethylphenylsilane, the reaction affords dimethyl(phenyl)(1-phenylvinyl)silane accompanied by the *E* isomer (ratio 84/16) with a conversion of 94%.



Dimethyl(phenyl)(1-phenylvinyl)silane: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 2H), 7.39-7.36 (m, 3H), 7.28-7.19 (m, 3H), 7.15-7.12 (m, 2H), 6.01

(d, ^2J = 2.9 Hz, 1H), 5.70 (d, ^2J = 2.9 Hz, 1H), 0.44 (s, 6H, Si(CH_3)$_2$). The data is in agreement with the literature.[11]

Recyclability

To test recyclability, the **Rh^{III}C$_{11}$CB** hybrid catalyst was recycled in several consecutive runs. Reactions were conducted using custom built glass centrifuge tubes equipped with PTFE taps (Figure S43) in a similar fashion as described above, but at 70 °C for 1 h, and using a catalyst loading of ~ 2 mol %.

Figure S43. Custom built centrifuge tube with PTFE tap.

After each run, the reaction mixture was centrifuged for 20 min at 4000 rpm, the solution was removed with a syringe equipped with a PTFE-syringe filter, concentrated to dryness and briefly dried under vacuum, followed by analysis with ^{1}H NMR spectroscopy. The remaining black solids were washed with pentane (1 mL), centrifuged at 4000 rpm for 1 min and the clear solution was discarded. This was repeated once before the catalyst was dried under high-vacuum and the vial was refilled with Ar. This was followed by addition of THF (1 mL), phenylacetylene and triethylsilane and the reaction was repeated.

A sample of hybrid catalyst was analyzed by XPS after five runs. The corresponding XP spectra are shown in Figure S44, and the determined elemental composition is reported in Table S30.

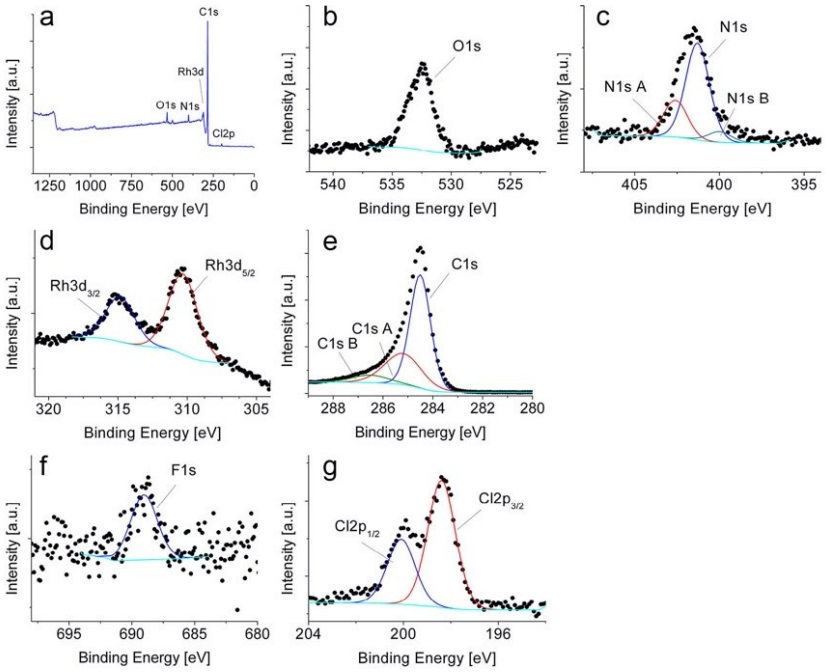


Figure S44. X-ray photoelectron spectra of the hybrid catalyst **$Rh^{III}C_{11}CB$** recovered after five subsequent reaction runs. (a) Survey scan, narrow scans of the (b) O1s signal, (b) N1s signals, (d) C1s signal, (e) $Rh3d_{3/2}$/$Rh3d_{5/2}$ signals and (f) F1s signal and (g) Cl $2p_{1/2}$/$2p_{3/2}$ signals.

Table S30. Determined elemental composition of **$Rh^{III}C_{11}CB$**, recovered after five subsequent runs, in at% by XPS. a) Calculated elemental composition with inclusion of F and Cl, b) Calculated elemental composition under absence of F and Cl.

Signal	**Binding Energy [eV]**	**FWHM [eV]**	**Area [CPS × eV]**	**Atomic %** *excluding F, Cl*	**Atomic %** *including F, Cl*
C1s	284.50	0.97	25546.79	56.48	55.84
C1s A	285.20	1.73	12526.38	27.70	27.38
C1s B	286.50	1.73	2992.59	6.62	6.54
O1s	532.44	2.35	5316.71	4.20	4.15
N1s	401.30	1.65	2088.59	2.79	2.76
N1s A	402.60	1.65	793.92	1.06	1.05
N1s B	400.00	1.65	226.44	0.30	0.30
$Rh3d_{5/2}$	310.30	2.45	3876.51	0.86	0.85
$Rh3d_{3/2}$	314.83	2.45	2172.66	0	0
F1s	689.04	2.51	643.47	-	0.38
$Cl2p_{3/2}$	198.39	1.38	631.47	-	0.75
$Cl2p_{1/2}$	200.09	1.38	324.10	-	0

The determined elemental composition indicates that only minor metal leaching has occurred. The Rh content was 0.86 at% (0.85 at%) for the recycled, compared to 0.96 at% (0.92%) for a freshly prepared sample. Furthermore, the change of the N/Rh ratio was only subtle, from 4.97

at% to 4.84 at%. This in turn suggests that small amounts of physisorbed material dissolve and are subsequently removed from the reaction mixture during the runs. Furthermore, the F signal decreased for the recycled sample which underwent five consecutive runs, from 1.69 at% to 0.38 at%, while Cl decreased from 1.22 at% to 0.75 at%. This may indicate also removal of some of the remaining counterions, $BAr^F_4^-$ and Cl^-. The weakly coordinating $BAr^F_4^-$ is more readily removed compared to the stronger coordinating Cl^-.

Test for Heterogeneity

We tested catalytic activity of a reaction solution by hot filtering a suspension of **$Rh^{III}C_{11}CB$** and adding further substrate. The experiment was conducted as described in the following: A centrifuge tube with Schlenk tap was charged with **$Rh^{III}C_{11}CB$** (2.3 mg, ~ 1.0 mol%), THF (1 mL), phenylacetylene (9 mg, 0.09 mmol) and triethylsilane (18 mg, 0.16 mmol) and sealed. The mixture was heated under stirring to 60 °C for 1 h in an oil bath, centrifuged at 4000 rpm for 20 min and the solution was taken up with a syringe and discarded. The black solids were washed twice with pentane (1 mL) followed by centrifugation for 1 min at 4000 rpm. The pentane washings were discarded, and the catalyst was dried under vacuum. THF (1 mL) was added and the suspension was stirred for 15 min at 60 °C, after which the tube was placed into a pre-heated metal centrifuge bucket (60 °C), briefly centrifuged at 4000 rpm and placed back into the hot oil bath. The suspension was quickly drawn up with a pre-heated syringe (60 °C), flushed with Ar and equipped with two pre-heated PTFE filters (0.45 μm) with a small of pad celite / cotton wool in-between the two filters. The obtained filtrate was a clear solution, which was was transferred into an oven dried Schlenk tube under Ar. Phenylacetylene (9 mg, 0.09 mmol) and triethylsilane (18 mg, 0.16 mmol) were added. The tube was sealed and heated under stirring for one hour. Analysis by ^{1}H NMR spectroscopy showed no reaction had occurred as only starting material was detected.

Homogeneous Reactions

An oven dried 4 mL Schlenk tube was charged with **Rh^{I}C$_{n}$** (n = 0, 6 or 11; 0.9 µmol, 1 %), THF (1 mL), phenylacetylene (9 mg, 0.09 mmol) and triethylsilane (18 mg, 0.16 mmol) and heated to 60 °C for 1 h. The mixture was allowed to cool down to room temperature and the solvent was removed under reduced pressure, which was followed by drying under high vacuum and analysis by ^{1}H NMR spectroscopy (Figure S45).

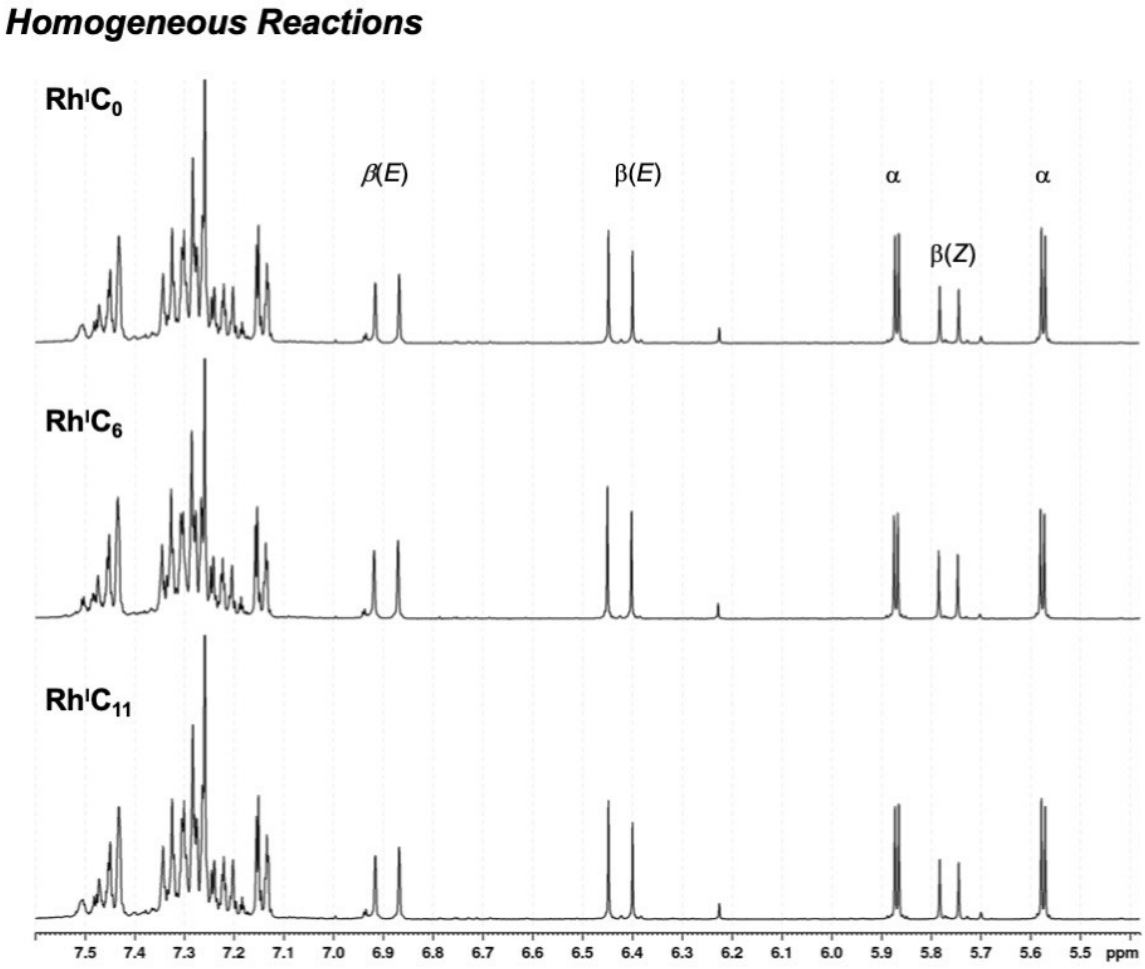


Figure S45. Selected ranges of the ^{1}H NMR spectra of the crude reaction mixtures using the catalysts **Rh^{I}C$_{0}$**, **Rh^{I}C$_{6}$** and **Rh^{I}C$_{11}$**. The vinylic protons of each of the three different isomers give rise to two doublets. The d of the *β*(*Z*)-isomer at 7.45 ppm is buried under aromatic resonances.

The control reactions were performed analogously to the above described procedure using the catalysts **Rh^{I}C$_{0}$Ph** and **Rh^{III}C$_{0}$Ph** without NH_2-groups and **Rh^{III}Cl$_{2}$** and **Rh^{III}C$_{11}$Cl$_{2}$**,

which were prepared as described in section 5. For the latter two, a composition of $[(PhPyT)_2RhCl_2]BAr^F{}_4$ and $[(PhCO(CH_2)_{10}PyT)_2RhCl_2]BAr^F{}_4$ was used as approximation for calculation of the catalyst amount applied. ^{1}H NMR spectra of the reaction mixtures are shown in the Figure S46.

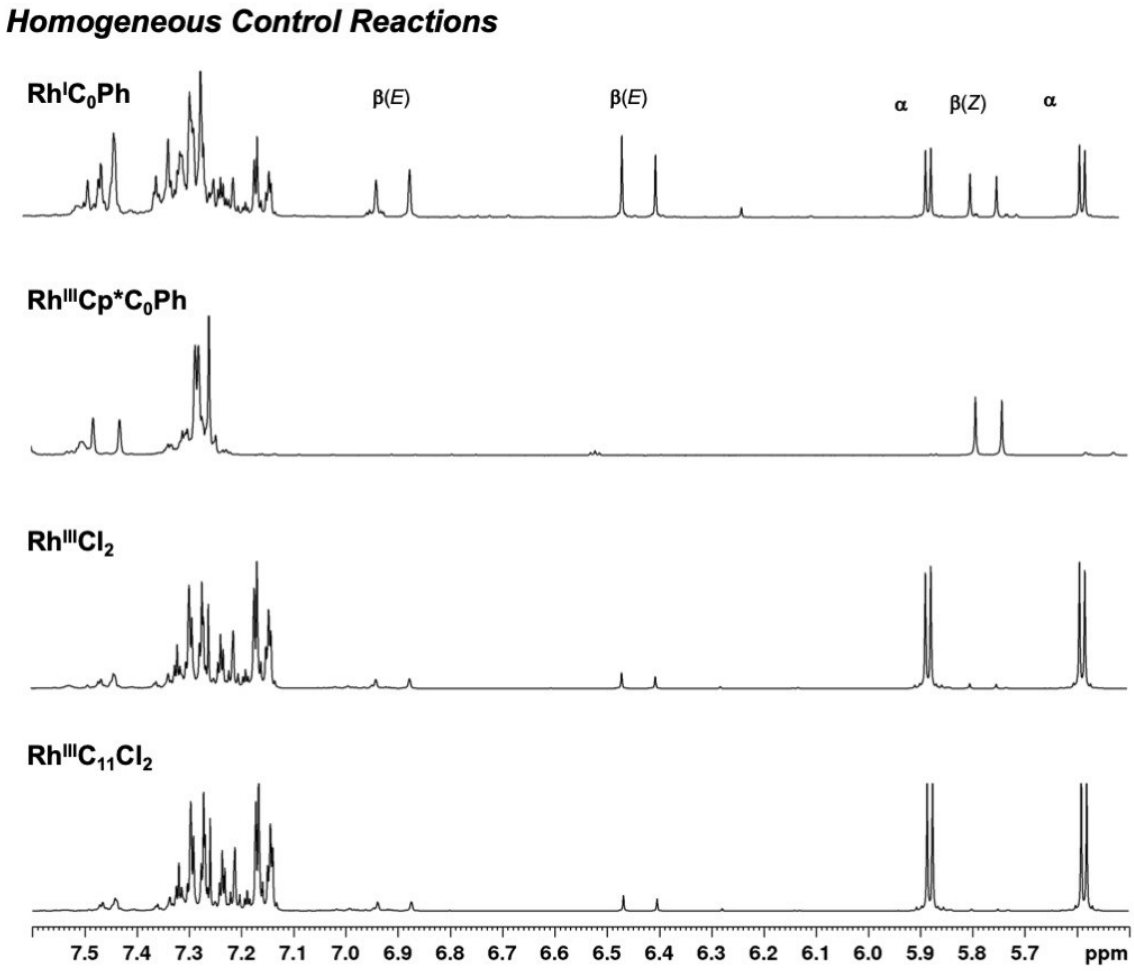
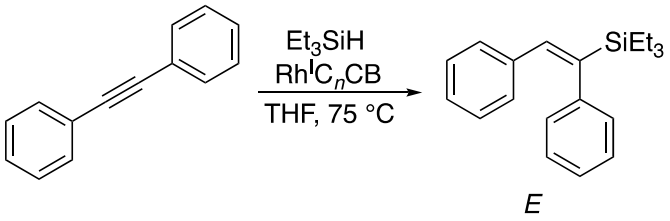


Figure S46. Selected ranges of the ^{1}H NMR spectra of the reaction mixtures from hydrosilylation of phenylacetylene using the control Rh catalysts **Rh^{I}C$_0$Ph** and **Rh^{III}Cp*C$_0$Ph** as well as the materials **Rh^{III}Cl$_2$** and **Rh^{III}C$_{11}$Cl$_2$** obtained from treatment of the **Rh^{I}C$_0$Ph** and **Rh^{I}C$_{11}$** with $NaNO_2$/HCl under absence of CB.

6.2 Hydrosilylation of Diphenylacetylene

We tested the series of catalysts for the hydrosilylation of diphenylacetylene (Scheme S2). This reaction affords for all Rh^{I} catalysts the *Z*-isomer with the Rh^{I} catalysts not being active towards this reaction under the applied reaction conditions as only traces of the product formed over the same period of time, which led to near quantitative conversion for the Rh^{I} derivatives (Table S31).



Scheme S3. Hydrosilylation of diphenylacetylene.

Table S31. Summary of the hydrosilylation reactions of diphenylacetylene using the Rh and Ir based catalysts.

Entry	Catalyst	mol[%] cat.	T [°C]	t [min]	Conversion [%]
1	**$Rh^{III}C_{11}CB$**	1.0	75	15	80
2	**$Rh^{III}C_{11}CB$**	1.0	75	30	99
3	**$Rh^{III}C_{11}CB$**[1]	1.0	75	60	100 (100[2])
4	**$Rh^{III}C_{6}CB$**	1.0	75	15	27
5	**$Rh^{III}C_{6}CB$**	1.0	75	30	96
6	**$Rh^{III}C_{0}CB$**	1.0	75	15	12
7	**$Rh^{III}C_{0}CB$**	1.0	75	30	25
8	**$Rh^{III}Cp^{*}C_{11}CB$**	1.0	75	30	Traces (< 1)
9	**$Ir^{III}Cp^{*}C_{11}CB$**	0.5	75	30	Traces (< 1)
10	**$Ir^{III}Cp^{*}C_{6}CB$**	0.5	75	30	Traces (< 1)
11	**$Ir^{III}Cp^{*}C_{0}CB$**	0.5	75	30	Traces (< 1)

Reaction were conducted on a 15 mg scale in 1 mL THF using the specified amount of catalyst and 1.8 eq. of Et_3SiH. [1] This reaction was conducted a preparative 60 mg scale. [2] Isolated yield.

Preparative scale reaction:

(*E*)-(1,2-Diphenylvinyl)triethylsilane: A Schlenk tube was charged with diphenylacetylene (60 mg, 0.32 mmol), THF (4 mL), triethylsilane (72 mg, 0.60 mmol) and **$Rh^{III}C_{11}CB$** (8.8 mg, ~ 1.0 mol %). The tube was sealed with PTFE stopcock and the mixture was heated under

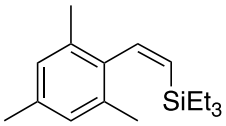
stirring for 1 h to 75 °C using an oil bath. After cooling down to room temperature, the mixture was transferred to glass centrifuge tubes as centrifuged for 20 min at 4000 rpm. The solution was removed and the remaining catalyst was washed with pentane (4 mL) and centrifuged again for 2 min. This was repeated one more time and the pentane from washings was combined with the reaction solution, filtered through a PTFE syringe filter and concentrated to dryness using a rotary evaporator. This was followed by drying under vacuum, affording the product as colorless oil (99 mg, 0.32 mmol; > 99%).

6.3 Scope: Hydrosilylation of Terminal Alkynes

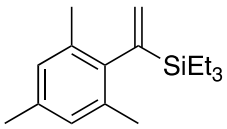
Typical procedure for the hydrosilylation reactions: An oven dried Schlenk tube equipped with magnetic stirring bar and PTFE stopcock was charged with hybrid catalyst (~1.0 mol %), THF (1 mL), 0.009 mmol of the terminal alkyne and 18 mg (0.16 mmol) of triethylsilane. The mixture was heated to 75 °C for 1 h or 4 h while stirring using an oil bath with the head space fully submerged in the oil. After the specified time, the Schlenk tube was allowed to cool down to room temperature and the black suspension was transferred to a glass centrifuge tube and centrifuged for 20 min at 4000 rpm. The clear solution was transferred to a round bottom flask and the solvent was evaporated using a rotary evaporator. The product was briefly dried under vacuum. The product composition was analyzed by ^{1}H NMR spectroscopy. Vinylic proton resonances of formed isomeric products were integrated to each other and to unreacted terminal alkyne, allowing determination of isomeric ratios and conversions.

For preparative runs, the remaining black solids from the centrifugation were washed with pentane (2 mL) and centrifuged again for 5 min at 4000 rpm. The pentane was combined with the extract obtained from the first centrifugation and concentrated to dryness. This was followed by flash chromatography on silica using hexane as eluent. All silanes were obtained as colorless oils after solvent evaporation and drying under vacuum. Most reactions afforded

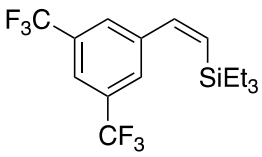
isomeric mixtures of the silanes, which did not separate on the column. We characterized these as isomeric mixtures. Reported ^{1}H- and ^{13}C NMR chemical shifts are assigned to the major components of the isomeric mixture.



(*Z*)-triethyl(2,4,6-trimethylstyryl)silane (7b): 2-Ethynyl-1,3,5-trimethylbenzene (13 mg, 0.09 mmol) afforded the title compound as mixture with **7c** (9 mg, 0.03 mmol, 38 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, $^{3}J_{H\text{-}H}$ = 15.4 Hz, 1H), 6.80 (2H), 5.97 (d, $^{3}J_{H\text{-}H}$ = 15.4 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 6H), 0.81 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.33 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 137.5, 136.0, 135.2, 131.7, 127.8, 21.1, 20.6, 7.6, 3.7 ppm. MS (APCI) m/z: $[M + H]^+$ 261 (32%), 249 (18%), $[M\text{-}Et + H]^+$ 231 (100%).

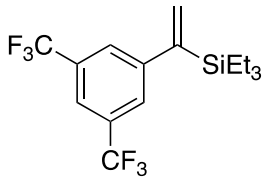


Triethyl(1-mesitylvinyl)silane (7c): 2-Ethynyl-1,3,5-trimethylbenzene (26 mg, 0.18 mmol) afforded the title compound as mixture with **7a/b** (27 mg, 0.10 mmol, 57 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (m, 2H), 5.78 (d, $^{2}J_{H\text{-}H}$ = 3.4 Hz, 1H), 5.67 (d, $^{2}J_{H\text{-}H}$ = 3.4 Hz, 1H), 2.27 (s, CH_3, 3H), (s, CH_3, 6H), 0.93 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.63 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 141.8, 134.7, 134.1, 129.5, 128.1, 21.0, 7.4, 4.4 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{29}Si_1$: 261.20330; found: 261.20318.

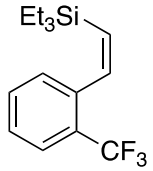


(*Z*)-(3,5-bis(trifluoromethyl)styryl)triethylsilane (8b): 1-Ethynyl-3,5-bis(trifluoromethyl)benzene (21 mg, 0.09 mmol) afforded the title compound as mixture with **8c** (7 mg, 0.02 mmol, 22 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 1H), 7.73 (m, 2H), 7.46 (d, $^{3}J_{H\text{-}H}$ = 15.3 Hz, 1H), 6.03 (d, $^{3}J_{H\text{-}H}$ = 15.3 Hz, 1H), 0.87 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.54 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0

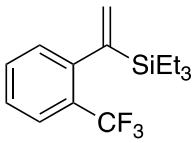
Hz, Si(CH_2CH$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3, 142.4, 134.6, 131.5 (q, $^2J_{C\text{-}F}$ = 33 Hz), 128.1 (m), 123.5, (q, $^1J_{C\text{-}F}$ = 273 Hz), 121.1 (m), 7.4, 4.7 ppm. MS (GC/EI) m/z: [M - Et]$^+$ 325 (60%), [M – Et – C_2H_4]$^+$ 297 (100%), [M – 2 Et – C_2H_3]$^+$ 269 (42%), 230 (64%).



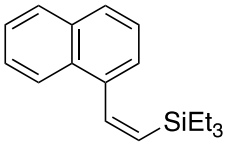
(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)triethylsilane (8c): 1-Ethynyl-3,5-bis(trifluoromethyl)benzene (40 mg, 0.17 mmol) afforded the title compound as mixture with **8a** (49 mg, 0.14 mmol, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (m, 1H), 7.56 (m, 2H), 5.94 (d, $^2J_{H\text{-}H}$ = 2.5 Hz, 1H), 5.74 (d, $^2J_{H\text{-}H}$ = 2.5 Hz, 1H), 0.93 (apparent t, $^3J_{H\text{-}H}$ ≈ 8.0 Hz, 9H, Si(CH$_2$CH_3)$_3$, 0.67 (apparent q, $^3J_{H\text{-}H}$ ≈ 8.0 Hz, 6H, Si(CH_2CH$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 147.8, 131.62, 131.59 (q, $J_{C\text{-}F}$ = 33 Hz), 126.9 (m), 123.60, (q, $^2J_{C\text{-}F}$ = 273 Hz), 120.1 (m), 7.3, 3.4 ppm. MS (GC/EI) m/z: [M - Et]$^+$ 325 (58%), [M – Et – C_2H_4]$^+$ 297 (100%), [M – 2 Et – C_2H_3]$^+$ 269 (42%), 230 (64%).



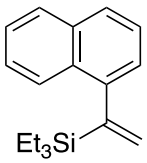
(*Z*)-Triethyl(2-(trifluoromethyl)styryl)silane (9b): 1-Ethynyl-2-(trifluoromethyl)benzene (15 mg, 0.09 mmol) afforded the title compound as mixture with **9c** (22 mg, 0.08 mmol, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68-7.31 (m, 5H), 5.94 ($^2J_{H\text{-}H}$ = 15.2 Hz, 1H), 0.83 (apparent t, $^3J_{H\text{-}H}$ ≈ 8.0 Hz, 9H, Si(CH$_2$CH_3)$_3$, 0.42 (apparent q, $^3J_{H\text{-}H}$ ≈ 8.0 Hz, 6H, Si(CH_2CH$_3$)$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3, 139.8 (m), 132.8, 131.3 (m), 130.6, 128.1 (q, $^2J_{C\text{-}F}$ = 30 Hz), 127.5, 125.6 (q, $^3J_{C\text{-}F}$ = 5 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 274 Hz), 7.4, 4.6 ppm. MS (GC/EI) m/z: [M - Et]$^+$ 257 (4%), [M – $SiEt_3$ – HF]$^+$ 151 (22%), 143 (35%), [M – $SiEt_3$ – 2F]$^+$ 133 (50%), [M – C_2SiEt_3 – F]$^+$ 128 (100%), [M – $SiEt_3$ – 3F]$^+$ 115 (22%).



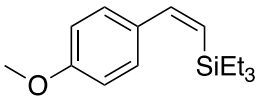
Triethyl(1-(2-(trifluoromethyl)phenyl)vinyl)silane (9c): 1-Ethynyl-2-(trifluoromethyl)benzene (30 mg, 0.21 mmol) afforded the title compound as mixture with **9a/b** (51 mg, 0.18 mmol, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (m, 2H), 7.42 (m, 2H), 7.28 (m, 2H), 7.02 (m, 2H), 5.76 (m, 1H), 5.59 (dm, $^{2}J_{H\text{-}H}$ = 2.9 Hz, 1H), 0.90 (apparent t, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.61 (apparent q, 6H, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 144.8 (m), 140.8 (m), 130.9, 129.9 (m), 129.3, 127.2 (q, $^{2}J_{C\text{-}F}$ = 29 Hz), 126.3 (q, $^{3}J_{C\text{-}F}$ = 5 Hz), 125.8, ~ 124.5, (q, $^{1}J_{C\text{-}F}$ = 273 Hz), 7.2, 3.5 ppm. MS (APCI) m/z: $[M\text{-}Et + H]^+$ 257 (100%), 285 (45%).



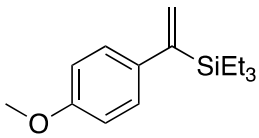
(*Z*)-Triethyl(2-(naphthalen-1-yl)vinyl)silane (10b): 2-Ethynylnaphthalene (13 mg, 0.09 mmol) afforded the title compound as mixture with **10c** (20 mg, 0.07 mmol, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0-7.3 (m, 7H), 7.91 (d, 1H, ^{3}J = 15.2 Hz, 1H), 6.06 (d, ^{3}J = 15.2 Hz, 1H), 0.79 (apparent t, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.38 (apparent q, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.2, 138.5, 133.3, 131.9, 131.8, 128.4, 128.0, 125.9, 125.9, 125.6, 125.3, 125.2, 29.9, 7.5, 4.7 ppm. MS (APCI) m/z $[M + H]^+$ 269 (100%).



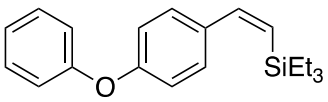
Triethyl(1-(naphthalen-1-yl)vinyl)silane (10c): 2-Ethynyl-naphthalene (26 mg, 0.17 mmol) afforded the title compound as mixture with **10a/b** (31 mg, 0.01 mmol, 68 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (m, 1H), 7.84 (m, 1H), 7.72 (m, 1H), 7.50-7.39 (m, 3H), 7.09 (m, 1H), 5.95 (d, $^{2}J_{H\text{-}H}$ = 3.5 Hz, 1H), 5.88 (d, $^{2}J_{H\text{-}H}$ = 3.5 Hz, 1H), 0.93 (apparent t, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.63 (apparent q, $^{3}J_{H\text{-}H}$ ≈ 8.0 Hz, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1, 143.5, 133.9, 131.5, 130.5, 128.3, 126.4, 126.1, 125.7, 125.3, 125.3, 123.8, 7.4, 3.4 ppm. The data is in agreement with the literature.[12]



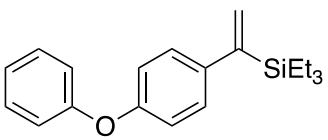
(*Z*)-triethyl(4-methoxystyryl)silane (11b): 1-Ethynyl-4-methoxybenzene (12 mg, 0.09 mmol) afforded the title compound as mixture with **11c**. We analyzed the product mixture by ^{1}H NMR spectroscopy without isolating the compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, $^{3}J_{H\text{-}H}$ = 15.2 Hz, 1H), 7.23 (m, 2H), 6.85 (m, 2H), 3.82 (s, 3H, OCH_3), 0.89 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, Si(CH_2CH_3)$_3$, 0.58 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). The data is in agreement with the literature.[13]



Triethyl(1-(4-methoxyphenyl)vinyl)silane (11c): 1-Ethynyl-4-methoxybenzene (23 mg, 0.17 mmol) afforded the title compound as mixture with **11c** (38 mg, 0.15 mmol, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 (dm, $^{3}J_{H\text{-}H}$ = 8.8 Hz, 2H), 6.86 (dm, $^{3}J_{H\text{-}H}$ = 8.8 Hz, 2H), 5.88 (d, $^{3}J_{H\text{-}H}$ = 3.1 Hz, 1H), 5.54 (d, $^{3}J_{H\text{-}H}$ = 3.1 Hz, 1H), 3.81 (s, 3H), 0.95 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, Si(CH_2CH_3)$_3$, 0.70 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 6H, Si(CH_2CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 149.5, 137.9, 127.9, 127.7, 113.5, 55.2, 7.3, 3.4 ppm. MS (APCI) m/z $[M + H]^+$ 249 (100%).

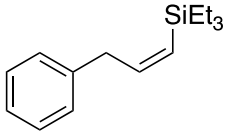


(*Z*)-Triethyl(4-phenoxystyryl)silane (12b): 1-Ethynyl-4-phenoxybenzene (18 mg, 0.09 mmol) afforded the title compound as mixture with **12c** (26 mg, 0.08 mmol, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, 1H, $^{3}J_{H\text{-}H}$ = 15.0 Hz, 1H), 5.73 (d, $^{3}J_{H\text{-}H}$ = 15.0 Hz, 1H), 0.89 (apparent t, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 9H, Si(CH_2CH_3)$_3$, 0.58 (apparent q, $^{3}J_{H\text{-}H} \approx$ 8.0 Hz, 6H, Si(CH_2CH_3)$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 156.7, 147.0, 135.9, 129.9, 129.4, 129.0, 123.4, 119.0, 118.5, 7.6, 4.9 ppm. MS (APCI) m/z $[M + H]^+$ 310 (100%).

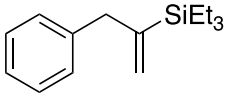


Triethyl(1-(4-phenoxyphenyl)vinyl)silane (12c): 1-Ethynyl-4-phenoxybenzene (36 mg, 0.19 mmol) afforded the title compound as mixture with **12a/b** (48 mg, 0.15 mmol, 83 %).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (m,

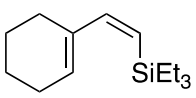
2H), 7.14 (m, 3H), 7.04 (m, 2H), 6.96 (m, 2H), 5.91 (d, $^{2}_{H\text{-}H}$ = 3.1 Hz, 1H), 5.59 (d, $^{2}J_{H\text{-}H}$ = 3.1 Hz, 1H), 0.93 (apparent t, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 9H, $Si(CH_2C\mathit{H}_3)_3$, 0.70 (apparent q, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 6H, $Si(C\mathit{H}_2CH_3)_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 155.8, 149.7, 140.7, 129.9, 128.7, 128.1, 123.2, 118.9, 118.7, 7.5, 3.5 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{27}O_1Si_1$: 311.18257; found: 311.18238.



(*Z*)-Triethyl(3-phenylprop-1-en-1-yl)silane (13b): Prop-2-yn-1-ylbenzene (10 mg, 0.09 mmol) afforded the title compound as mixture with **13c**. We analyzed the product mixture by ^{1}H NMR spectroscopy without isolating the compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.19 (m, 5H, Ph-*H*), 6.51 (dt, $^{3}J_{H\text{-}H}$ = 14.0 Hz, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 1H), 5.57 (dt, ^{3}J = 14.1 Hz, ^{4}J = 1.5 Hz, 1H), 3.49 (m, 2H, $PhC\mathit{H}_2$), 1.00 (apparent t, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 9H, $Si(CH_2C\mathit{H}_3)_3$, 0.69 (apparent q, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 6H, $Si(C\mathit{H}_2CH_3)_3$). The data is in agreement with the literature.[14]

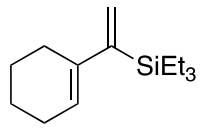


Triethyl(3-phenylprop-1-en-2-yl)silane (13c): Prop-2-yn-1-ylbenzene (20 mg, 0.17 mmol) afforded the title compound as mixture with **13a/b** (26 mg, 0.1 mmol, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 – 7.15 (m, 5H, Ph-*H*), 5.51 (m, 1H), 5.41 (m, 1H), 3.43 (m, 2H, $PhC\mathit{H}_2$), 0.89 (apparent t, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 9H, $Si(CH_2C\mathit{H}_3)_3$, 0.54 (apparent q, $^{3}J_{H\text{-}H} \approx 8.0$ Hz, 6H, $Si(C\mathit{H}_2CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 140.2, 129.5, 128.2, 127.4, 126.0, 43.2, 7.4, 3.0 ppm. The data is in agreement with the literature.[15]

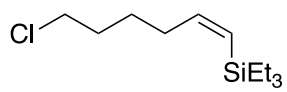


(*Z*)-(2-(Cyclohex-1-en-1-yl)vinyl)triethylsilane (14b): 1-Ethynylcyclohex-1-ene (9 mg, 0.09 mmol) afforded the title compound as mixture with **14c** (14 mg, 0.06 mmol, 74 %). We analyzed the product mixture by ^{1}H NMR spectroscopy without

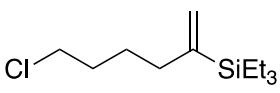
isolating the compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, $^3J_{H\text{-}H}$ = 14.8 Hz, 1H), 5.65 (m, 1H), 5.32 (d, $^3J_{H\text{-}H}$ = 14.8 Hz, 1H), 2.07 (m, 4H), 1.6 (m, 4H), 0.93 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.59 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). The data is in agreement with the literature.[16]



(1-(Cyclohex-1-en-1-yl)vinyl)triethylsilane (14c): 1-Ethynylcyclohex-1-ene (20 mg, 0.19 mmol) afforded the title compound as mixture with **14a/b** (35 mg, 0.15 mmol, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.71 (d, $^2J_{H\text{-}H}$ = 2.9 Hz, 1H), 5.60 (m, 1H), 5.27 (d, $^2J_{H\text{-}H}$ = 2.9 Hz, 1H), 2.14 (m, 4H), 1.6 (m, 4H), 0.93 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.64 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). The data is in agreement with the literature.[17]

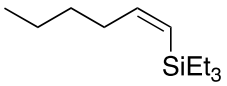


(*Z*)-(6-Chlorohex-1-en-1-yl)triethylsilane (15b): 6-Chlorohex-1-yne (10 mg, 0.09 mmol) afforded the title compound isometrically pure. We analyzed the product mixture by ^{1}H NMR spectroscopy without isolating the compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.35 (dt, $^3J_{H\text{-}H}$ = 14.1 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz 1H), 5.44 (dt, $^3J_{H\text{-}H}$ = 14.1 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz 1H), 3.54 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 2H, CH_2Cl), 2.14 (m, 2H), 1.80 (m, 2H), 1.53 (m, 2H), 0.95 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.61 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). The data is in agreement with the literature.[13]

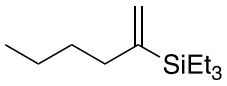


(6-Chlorohex-1-en-2-yl)triethylsilane (15c): 6-Chlorohex-1-yne (20 mg, 0.17 mmol) afforded the title compound as mixture with **15a/b** (39 mg, 0.17 mmol, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94 (m, 1H), 5.32 (m, 1H), 3.55 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H), 2.11 (m, 2H), 1.79 (m, 2H), 1.56 (m, 2H), 0.92 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.60 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$) ppm. ^{13}C NMR (75

MHz, $CDCl_3$): δ = 148.5, 125.6, 45.1, 35.5, 32.6, 26.2, 7.5, 3.1 ppm. MS (GC/EI) m/z: $[M - Et]^+$ 203 (5%), $[M - Et - C_2H_4]^+$ 175 (10%), $[M - 2\,Et - C_2H_3]^+$ 147 (9%), $[M - SiEt_2 - C_2H_2]^+$ 121 (100%), $[C_4H_{10}Cl]^+$ 92 (48%).



(Z)-Triethyl(hex-1-en-1-yl)silane (16b): Hex-1-yne (7 mg, 0.09 mmol) afforded the title compound title compound isometrically pure. We analyzed the product mixture by ^{1}H NMR spectroscopy without isolating the compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.34 (dt, $^3J_{H\text{-}H}$ = 14.1 Hz, ^3J = 7.3 Hz 1H), 5.44 (dt, $^3J_{H\text{-}H}$ = 14.1 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz 1H), 2.10 (m, 2H), 1.80 (m, 2H), 1.35 (m, 4H), 0.94 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.93 (m, 3H, overlapping), 0.61 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). The data is in agreement with the literature.[13]



Triethyl(hex-1-en-2-yl)silane (16c): Hex-1-yne (14 mg, 0.17 mmol) afforded the title compound as mixture with **16a/b** (32 mg, 0.16 mmol, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.63 (m, 1H), 5.28 (m, 1H), 2.08 (m, 2H), 1.35 (m, 4H), 0.92 (apparent t, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 9H, $Si(CH_2CH_3)_3$, 0.91 (m, 3H, overlapping), 0.60 (apparent q, $^3J_{H\text{-}H} \approx$ 8.0 Hz, 6H, $Si(CH_2CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 125.1, 36.2, 31.3, 22.8, 14.2, 7.5, 3.1 ppm. MS (GC/EI) m/z: $[M - Et]^+$ 169 (97%), $[M - Et - C_2H_4]^+$ 141 (100%), $[M - 2\,Et - C_2H_3]^+$ 113 (29%).

7. Computational details

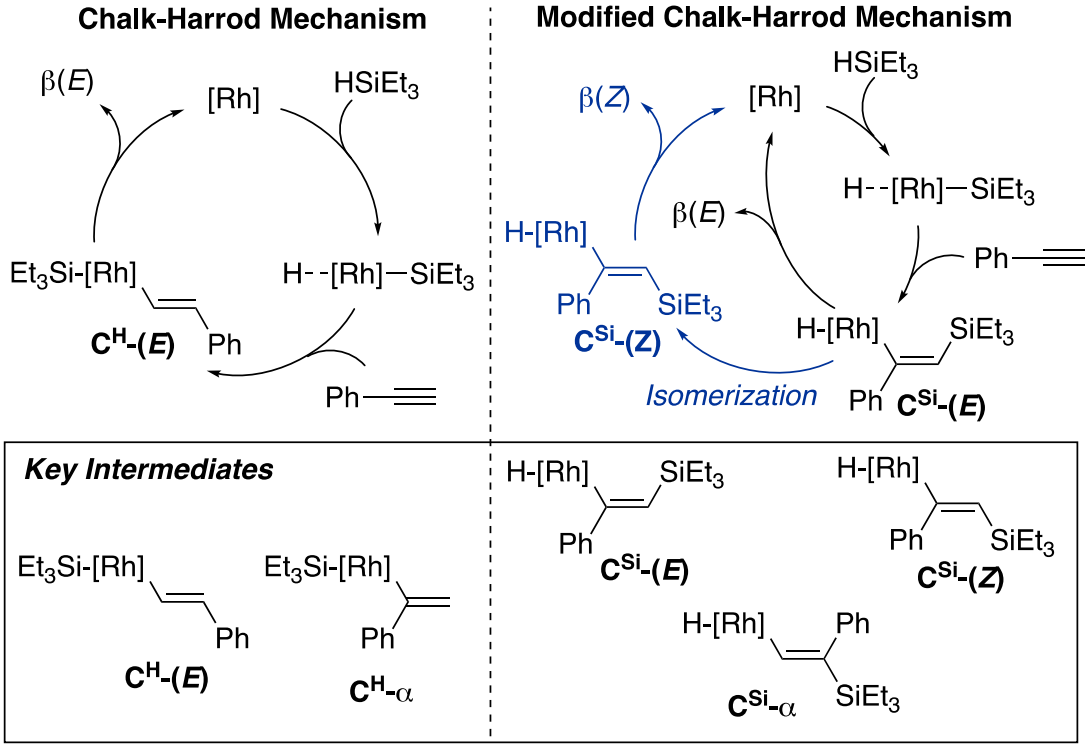
All calculations were performed using the Gaussian 16 software[18] on the Australian National Computational Infrastructure, with access provided through the Macquarie University Partner Scheme (project ID gy32). All images of the calculated structures were generated using CYLView.[19] The frequency calculations and structure optimizations were performed at 25 °C using ωB97XD with the 6-31G(d) basis set for C, O, H, Cl and N, and the SDD ECP for Rh and Si. Single point energy calculations were performed using the M06L method, and the def2TZVP basis set. The CPCM solvation model was used to incorporate the solvent effects of tetrahydrofuran. Frequency calculations were performed to confirm whether the calculated structure is a local minimum or a transition state. For transition state structures, intrinsic reaction coordinate (IRC) calculations were performed to confirm whether the located transition state connects the correct minima.

Table S32. Summary of data obtained from the DFT calculations.[a]

$Rh^{I}(CO)_2$	**Gibbs free energy (kcal mol^{-1})**	
H-Rh-Si intermediate (+ free phenylacetylene)	18.0	
	Intermediate	*Reductive Elimination*
C^{Si}-(*E*)	17.0	35.3
C^{Si}-(*Z*)	14.0	26.8
C^{Si}-α	11.4	23.0
C^{H}-(*E*)	4.5	14.6
C^{H}-α	7.2	30.2
$Rh^{III}ClCp^*$		
Rh-H-Si intermediate (+ free phenylacetylene)	13.5	
	Intermediate	*Reductive Elimination*
C^{Si}-(*E*), two N coordinated	61.0 *(C-Cl bond formed)*	
C^{Si}-(*E*), one N coordinated	65.6	72.5
C^{Si}-(*Z*) two N coordinated	50.2	
C^{Si}-(*Z*) one N coordinated	43.8	45.4
C^{Si}-α two N coordinated	52.8	
C^{Si}-α one N coordinated	44.4	42.2
$Rh^{III}Cl_2$		
Rh-H-Si intermediate (+ free	-7.0	

phenylacetylene)		
	Intermediate	*Reductive Elimination*
C^{Si}-α	6.8	18.8
β(*E*) product (+ free catalyst)	-20.9	
β(*Z*) product (+ free catalyst)	-25.0	
α product (+ free catalyst)	-21.5	

[a] All energies are relative to the sum of the energies of the free catalyst, phenylacetylene and triethylsilane.



Scheme S4. Chalk-Harrod and modified Chalk-Harrod mechanism for the hydrosilylation of phenylacetylene using the Rh catalysts.

The most commonly reported mechanism for Rh catalyzed hydrosilylation is a modified Chalk-Harrod mechanism, which involves 4 keys steps: 1) oxidative addition of the silane to Rh; 2) silyl insertion into the alkyne to give the C^{Si}-(*E*) intermediate; 3)

potential isomerization of C^{Si}-(*E*) to C^{Si}-(*Z*); and 4) reductive elimination to generate the product(s) (Scheme 3).[20-22] This mechanism is consistent with the commonly observed β(*E*) selectivity for cationic Rh catalysts and the products observed here on application of the homogeneous controls. The **$Rh^{I}C_0Ph$** catalyst gave a mixture of β(*E*), β(*Z*) and a products in our experimental analyses, in analogy to the series $Rh^{I}C_n$ (*n* = 0, 6, 11). If a step-wise Chalk-Harrod type mechanism is operative, the reaction should proceed via a H-Rh-Si intermediate (Scheme 3) - this species was readily located (18.0 kcal mol^{-1}) confirming that a Chalk-Harrod type mechanism is feasible. Alkyne insertion to H-Rh-Si could either occur at the Rh-H bond (Chalk Harrod) or at the Rh-Si bond (modified Chalk-Harrod), followed by potential isomerisation, resulting in five possible intermediates. All five intermediates were located, with subsequent reductive elimination from each intermediate feasible (see SI). The C^{Si}-(*E*) intermediate was the least stable (17.0 kcal mol^{-1}), with the corresponding reductive elimination transition state highest in energy (35.3 kcal mol^{-1}), suggesting that isomerisation to the thermodynamically favored C^{Si}-(*Z*) intermediate (14.0 kcal mol^{-1}) is likely. Reductive elimination from C^{Si}-(*Z*) proceeds *via* a lower energy transition state (26.8 kcal mol^{-1}), accounting for the experimental formation of β(*Z*). While it is unclear whether C^{Si}-α or C^{H}-α form directly in the insertion step, or result from isomerisation, the experimental observation of the α-product indicates that a pathway involving C^{Si}-α or C^{H}-α formation is likely.

Cartesian Coordinates

1. Different isomers of $RhCl_2PyT_2$

C	2.40146100	-1.76701300	0.86061400
C	3.75348700	-1.81869300	0.64606900
H	4.50969600	-2.53277700	0.93034200
N	2.95418500	0.04792000	-0.23185500
N	1.96895200	-0.60318800	0.30732600
N	4.04139100	-0.67579500	-0.02309500
C	5.31669100	-0.21192200	-0.47799800
C	5.65122100	1.12514200	-0.29291100
C	6.18454000	-1.11243200	-1.08530800
C	6.89379400	1.56643500	-0.73339400
H	4.95322000	1.79851500	0.19278300
C	7.42938800	-0.65811500	-1.50824900
H	5.88593200	-2.14340800	-1.24815300
C	7.78270900	0.67771200	-1.33467300
H	7.17149800	2.60610300	-0.59640800
H	8.11678600	-1.34782200	-1.98610600
H	8.75284000	1.02797800	-1.67113900
C	1.47609000	-2.69698100	1.57476600
H	1.97838600	-3.64328300	1.77982300
H	1.15055600	-2.24882700	2.51695600
N	0.30901800	-2.99811200	0.76208900
C	-0.15544700	-4.21622900	0.41838400
C	-1.25198500	-4.03369100	-0.39590700
H	0.32573000	-5.11250700	0.78111100
C	-1.38696900	-2.64747100	-0.51231700
H	-1.86177700	-4.79490500	-0.85588600
H	-2.09347200	-2.06321800	-1.07913300
N	-0.44824300	-2.02926000	0.20380000
Rh	-0.00000600	-0.00006600	0.27001100
Cl	-0.00007300	0.00007700	-2.06820800
Cl	0.00001000	-0.00017400	2.66466600
N	-1.96897000	0.60309300	0.30742200
C	-2.40141600	1.76694900	0.86071200
C	-3.75344300	1.81868600	0.64618100
H	-4.50964100	2.53279300	0.93043200
N	0.44824300	2.02917300	0.20397400
C	0.15557600	4.21612800	0.41884200
C	1.25211400	4.03363100	-0.39546900
H	-0.32558500	5.11238200	0.78164900
H	1.86195700	4.79486800	-0.85534300
C	-1.47604000	2.69684200	1.57496600
H	-1.15059200	2.24859500	2.51714400
H	-1.97831900	3.64314700	1.78006300
N	-2.95422300	-0.04795900	-0.23178400
N	-4.04139100	0.67580400	-0.02299200
C	-5.31671100	0.21204100	-0.47794800
C	-6.18417200	1.11248500	-1.08591100
C	-5.65164400	-1.12483200	-0.29224800
C	-7.42905200	0.65829300	-1.50888900
H	-5.88522400	2.14329000	-1.24922100
C	-6.89424400	-1.56601400	-0.73277900
H	-4.95392800	-1.79815400	0.19392800
C	-7.78278100	-0.67735200	-1.33470100
H	-8.11616300	1.34793800	-1.98724900
H	-7.17225500	-2.60553800	-0.59532200
H	-8.75294000	-1.02751300	-1.67119600
N	-0.30894600	2.99799200	0.76240400
C	1.38700600	2.64742100	-0.51206900
H	2.09345400	2.06319200	-1.07898100

Thermal correction to Gibbs Free Energy= 0.394575
E(RM06L) = -2506.64671226

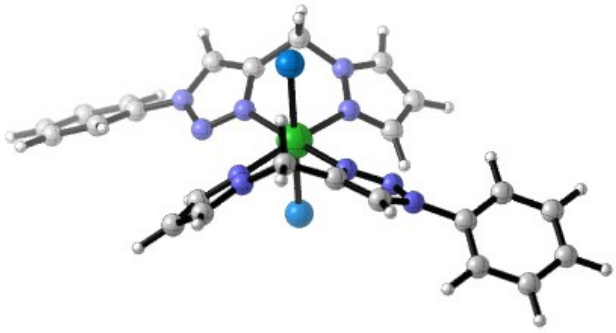


Figure S47. Calculated structure of isomer 1.

C	2.78315600	1.29229100	0.45096400
C	4.08960900	0.88185100	0.47565200
H	5.01033900	1.39653500	0.69845000
N	2.80736400	-0.81462500	-0.15348100
N	2.04922100	0.21809000	0.05173700
N	4.04579800	-0.41961500	0.09284800
C	5.13340300	-1.33691800	-0.07445700
C	5.04317300	-2.30833700	-1.06582500
C	6.24291100	-1.23230500	0.75735300
C	6.10359400	-3.19298800	-1.22508600
H	4.15717600	-2.37232100	-1.68769500
C	7.30036500	-2.11716900	0.57493200
H	6.27531000	-0.49552900	1.55401600
C	7.23194400	-3.09529600	-0.41380400
H	6.04642200	-3.95929500	-1.99066500
H	8.17092500	-2.04969100	1.21857500
H	8.05657400	-3.78758100	-0.54731600
C	2.14529600	2.61434700	0.73725100
H	2.88158800	3.30949200	1.14292600
H	1.73806600	3.04598700	-0.18251800
N	1.07365400	2.49965000	1.71585200
C	0.93106600	3.16442900	2.88267800
C	-0.22898900	2.71614300	3.47879200
H	1.65820500	3.89896000	3.19639500
C	-0.73466500	1.75177900	2.59956800
H	-0.64038000	3.02661300	4.42623400
H	-1.59626600	1.10745400	2.69346200
N	0.05275700	1.63915900	1.53168300
Rh	-0.00000500	0.18441600	-0.00000600
Cl	-0.01925300	-1.40915000	-1.68108100
N	-2.04921600	0.21809200	-0.05174400
C	-2.78315700	1.29229500	-0.45095400
C	-4.08961000	0.88184900	-0.47564500
H	-5.01034200	1.39653100	-0.69843300
N	-0.05276800	1.63917200	-1.53167300
C	-0.93106200	3.16446800	-2.88264700
C	0.22897700	2.71616200	-3.47877800
H	-1.65818700	3.89902000	-3.19634700
H	0.64036300	3.02663500	-4.42622100
C	-2.14530300	2.61435600	-0.73722900
H	-1.73807100	3.04598600	0.18254300
H	-2.88159500	3.30950300	-1.14289800
N	-2.80735400	-0.81463200	0.15346100
N	-4.04579100	-0.41962000	-0.09285500
C	-5.13339300	-1.33692500	0.07445400
C	-6.24290900	-1.23231000	-0.75734500
C	-5.04315300	-2.30834900	1.06581800
C	-7.30036000	-2.11717700	-0.57491800
H	-6.27531500	-0.49553100	-1.55400500
C	-6.10357000	-3.19300200	1.22508400
H	-4.15714900	-2.37233400	1.68767900
C	-7.23192800	-3.09530800	0.41381300
H	-8.17092500	-2.04969700	-1.21855300
H	-6.04639000	-3.95931300	1.99065900
H	-8.05655600	-3.78759500	0.54733000
N	-1.07365700	2.49967300	-1.71583100
C	0.73464600	1.75178300	-2.59956600
H	1.59623000	1.10743900	-2.69347700
Cl	0.01924600	-1.40916900	1.68105300

Thermal correction to Gibbs Free Energy= 0.393204
E(RM06L) = -2506.64070055

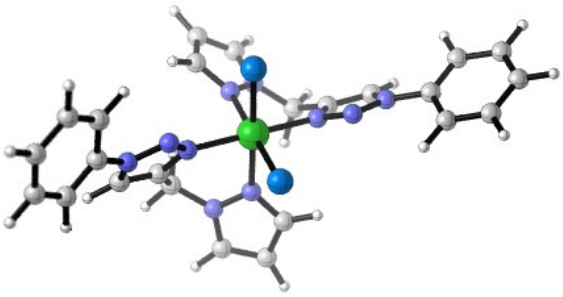


Figure S48. Calculated structure of isomer 2.

C	0.39970100	2.71640000	0.78849200
C	-0.79109900	3.39380100	0.79267100
H	-1.05543800	4.39459000	1.09411700
N	-1.11155400	1.37461100	-0.05827700
N	0.14055300	1.49040900	0.25622200
N	-1.68702200	2.51838200	0.26963600
C	-3.09216800	2.67724000	0.05101100
C	-3.67179600	2.04590700	-1.04608000
C	-3.84094200	3.43339400	0.94589800
C	-5.04181200	2.18119500	-1.24267000
H	-3.05802200	1.46511100	-1.72603800
C	-5.20770800	3.57131600	0.72491100
H	-3.37594900	3.88795700	1.81514700
C	-5.80832700	2.94519100	-0.36433500
H	-5.50670400	1.69897700	-2.09629300
H	-5.80371700	4.15917800	1.41477000
H	-6.87512100	3.05427200	-0.52967700
C	1.76838900	3.10020100	1.25239500
H	1.80993700	4.16938800	1.46403400
H	2.02905400	2.54210400	2.15393700
N	2.75449400	2.83050700	0.21529200
C	3.56710500	3.73109700	-0.37422800
C	4.17765000	3.11350000	-1.44304900
H	3.64551000	4.73741900	0.00988400
C	3.65397100	1.81889100	-1.44857900
H	4.88714600	3.54025700	-2.13385500
H	3.79466500	1.03568800	-2.17463400
N	2.81071600	1.64414600	-0.43119100
Rh	1.54663900	0.01790900	-0.00795300
Cl	1.10454300	-0.11430700	-2.29960500
Cl	1.99866900	0.08483700	2.34349600
N	2.98956600	-1.49252600	-0.19470200
C	3.93557600	-3.48501800	0.06246900
H	4.03184200	-4.48201000	0.46613800
N	0.22482500	-1.50902200	0.30533700
C	0.50872000	-2.71323500	0.86497500
C	-0.65637100	-3.43377900	0.84278700
H	-0.90805200	-4.41644700	1.20751400
C	1.86881500	-3.02308600	1.39072500
H	2.05408900	-2.45789800	2.30778200
H	1.95762700	-4.08990200	1.60015300
N	-1.01374500	-1.45076000	-0.07344100
N	-1.56103500	-2.60445100	0.26138300
C	-2.95623200	-2.80899200	0.01603400
C	-3.42564700	-4.08809400	-0.25804700
C	-3.80481600	-1.70627300	0.05545400
C	-4.78735100	-4.26656100	-0.48194200
H	-2.74414000	-4.93052900	-0.32240100
C	-5.15942200	-1.90006700	-0.18488400
H	-3.40534200	-0.71993100	0.26399000
C	-5.65312700	-3.17664900	-0.44667600
H	-5.16710400	-5.25943000	-0.69791300
H	-5.82978800	-1.04706500	-0.15883800
H	-6.71294900	-3.32250300	-0.62739500
N	2.90176600	-2.69543200	0.41770400
C	4.08478100	-1.54493300	-0.94966000
C	4.72340600	-2.77950400	-0.81868800
H	4.36488500	-0.70724100	-1.56169200
H	5.62648700	-3.10956000	-1.30662500

Thermal correction to Gibbs Free Energy= 0.394262
E(RM06L) = -2506.64141586

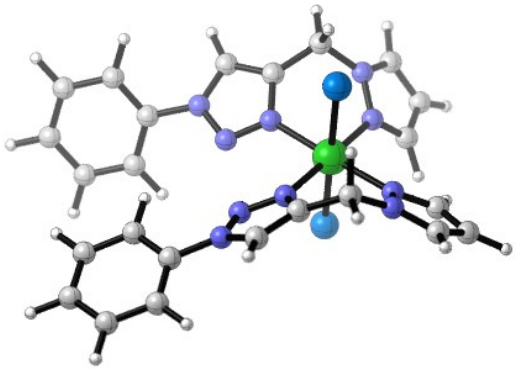


Figure S49. Calculated structure of isomer 3.

C	-4.65758600	-1.51875100	-1.58548900
H	-5.66703200	-1.15705900	-1.45487800
N	-2.49731400	-1.69836300	-1.11126800
C	-3.75370400	-0.20692000	0.36576800
H	-4.77574900	0.17280100	0.40050300
H	-3.57367600	-0.78464800	1.27913400
C	-2.94284300	2.28745500	0.34455700
H	-3.81373900	2.91917800	0.41867500
N	-1.45240800	0.70080500	0.13472000
Rh	-0.63679000	-1.14863000	-0.38194100
Cl	0.22167700	-3.22822700	-0.97018700
N	1.20886200	-0.63910400	0.32859900
C	1.48794800	-0.41814100	1.64083800
C	2.84040500	-0.22074600	1.72135000
H	3.49388300	0.01672500	2.54517800
N	-1.04490900	-1.95837300	1.51758200
C	-0.72729600	-2.40219000	3.66724800
C	-1.57171000	-3.37452800	3.17391100
H	-0.32299200	-2.24135200	4.65586200
H	-1.99702500	-4.20695400	3.71191100
C	0.41125800	-0.37682700	2.67687300
H	-0.22127800	0.50412100	2.52775600
H	0.84954700	-0.31313500	3.67377200
N	2.28653000	-0.60693500	-0.39091500
N	3.27962800	-0.34530500	0.44331700
C	4.61571400	-0.21849500	-0.05578200
C	5.67904500	-0.62669000	0.74202600
C	4.80825600	0.30789000	-1.32873900
C	6.97382000	-0.48435000	0.25442700
H	5.50538100	-1.07580600	1.71498900
C	6.10830000	0.42982100	-1.80578400
H	3.95556200	0.60327100	-1.92996800
C	7.18901500	0.04255500	-1.01637100
H	7.81277100	-0.80182400	0.86444000
H	6.27497100	0.83334100	-2.79880700
H	8.20055700	0.14428800	-1.39530000
N	-0.42605700	-1.56741700	2.64921300
C	-1.73055800	-3.05909200	1.81959600
H	-2.26677800	-3.57966600	1.03978200
Cl	-0.19137300	-0.23454100	-2.46940600
C	-2.78254800	0.92729100	0.28162500
N	-0.78827800	1.81813200	0.11602500
N	-1.68543800	2.78544900	0.24393800
C	-1.27411300	4.15623600	0.20998300
C	-0.30586100	4.53866200	-0.71258000
C	-1.86053900	5.06220500	1.08701600
C	0.08322700	5.87308200	-0.74814100
H	0.11957300	3.80515000	-1.38924800
C	-1.46903300	6.39574500	1.02863000
H	-2.59571800	4.73250700	1.81505000
C	-0.49826600	6.79967600	0.11510400
H	0.83487200	6.19063200	-1.46291000
H	-1.91670600	7.11584700	1.70519700
H	-0.19435000	7.84045900	0.07544900
N	-3.66014400	-1.09502600	-0.77800000
C	-4.11767300	-2.41533700	-2.48072600
C	-2.75915300	-2.48792000	-2.15053700
H	-4.62888900	-2.93900300	-3.27281600
H	-1.95272900	-3.04433000	-2.60465000

Thermal correction to Gibbs Free Energy= 0.393126
E(RM06L) = -2506.64200104

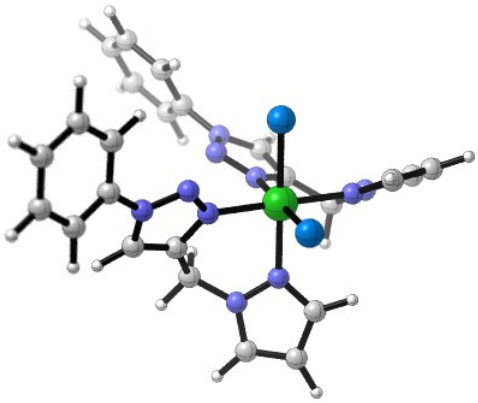


Figure S50. Calculated structure of isomer 4.

C	-0.74750400	0.82726100	4.08346500
H	-0.64515100	0.20875500	4.96306500
N	-0.63081100	1.29587500	1.91887500
C	0.05722000	-0.97215100	2.51954600
H	0.21902600	-1.51322100	3.45290600
H	-0.74267600	-1.47918600	1.96859800
C	2.52309400	-1.58502100	1.87049200
H	2.92470400	-2.20869900	2.65322900
N	1.39567100	-0.25668500	0.54972600
Rh	-0.00016500	1.16662800	-0.04367700
Cl	-1.58957100	2.74761700	-0.68347800
N	0.63017900	1.14718500	-2.01011500
C	0.74825500	0.51450400	-4.13244000
H	0.64712500	-0.16948200	-4.96229500
N	-1.39528300	-0.29882500	-0.52809900
C	-2.52091400	-1.72464900	-1.74472000
H	-2.92142800	-2.40611000	-2.47830700
C	-0.05428900	-1.16121000	-2.43572600
H	0.74547300	-1.62333400	-1.84647900
H	-0.21409500	-1.77245200	-3.32510100
Cl	1.58816600	2.79198200	0.47473000
C	-1.31166000	-1.08911500	-1.62836700
N	-2.55756900	-0.41347500	0.04265900
N	-3.24626400	-1.27718600	-0.68961400
C	-4.60192600	-1.58654800	-0.34860200
C	-5.43238000	-0.55694800	0.08179300
C	-5.04922100	-2.89795900	-0.46765800
C	-6.75037700	-0.86089300	0.40375800
H	-5.05091600	0.45609000	0.15200400
C	-6.37442900	-3.18167000	-0.15440800
H	-4.37339100	-3.68822900	-0.78065600
C	-7.22219500	-2.16642000	0.28221300
H	-7.41303000	-0.07040200	0.73944400
H	-6.73980500	-4.19928100	-0.24216400
H	-8.25412400	-2.39351700	0.52853600
N	0.39003100	0.14462800	-2.88266900
C	1.11599700	2.16384900	-2.71625400
C	1.21690000	1.80725000	-4.06655500
H	1.34773700	3.09110400	-2.21442900
H	1.57308700	2.41776000	-4.88095900
N	2.55752100	-0.41388300	-0.01168400
N	3.24716100	-1.21917600	0.78352800
C	1.31346100	-0.96071400	1.70734700
C	4.60232700	-1.55421000	0.46564000
C	5.43320800	-0.56089500	-0.04210100
C	5.04854000	-2.85329000	0.68328700
C	6.75072300	-0.88961400	-0.34100800
H	5.05255400	0.44426900	-0.18853100
C	6.37327800	-3.16112100	0.39155000
H	4.37222700	-3.61699400	1.05558700
C	7.22155300	-2.18257900	-0.12126200
H	7.41379800	-0.12740200	-0.73603900
H	6.73784200	-4.16951300	0.55580600
H	8.25310500	-2.42857100	-0.35042000
N	-0.38872400	0.36348900	2.86559600
C	-1.11862900	2.36263400	2.54522200
C	-1.21870500	2.11023700	3.91890000
H	-1.35206200	3.24839100	1.97402000
H	-1.57605100	2.78058800	4.68429700

Thermal correction to Gibbs Free Energy = 0.392701
E(RM06L) = -2506.64295929

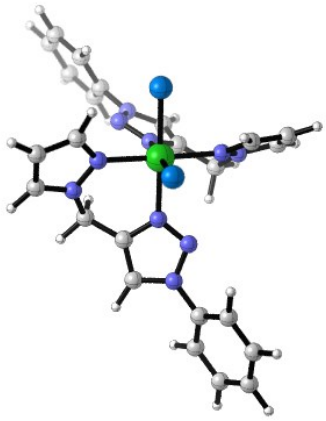


Figure S51. Calculated structure of isomer 5.

2. Reactants and Products

Phenylacetylene

C	2.20667200	0.00001000	-0.00003300
C	1.50913800	1.20556000	-0.00001600
C	0.11970600	1.20948400	0.00001600
C	-0.58768800	-0.00002300	0.00003300
C	0.11972300	-1.20949400	0.00001600
C	1.50917400	-1.20553900	-0.00001500
H	3.29252500	0.00003400	-0.00005800
H	2.04958000	2.14729700	-0.00002800
H	-0.42952800	2.14546700	0.00003200
H	-0.42946400	-2.14550500	0.00003100
H	2.04961400	-2.14727600	-0.00002800
C	-2.02175700	-0.00000900	0.00008400
C	-3.22798600	0.00001100	0.00003200
H	-4.29462300	-0.00002600	-0.00064600

Thermal correction to Gibbs Free Energy= 0.080603
E(RM06L) = -308.462724253

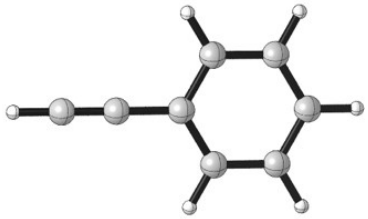


Figure S52. Calculated structure of phenylacetylene.

Triethylsilane

Si	0.00008000	0.00004200	0.27961800
H	0.00025100	0.00037700	1.78763300
C	1.72842500	0.54786200	-0.31881200
H	1.70787700	0.62937600	-1.41393700
H	1.92333500	1.56076700	0.05611500
C	-0.38954600	-1.77091400	-0.31814700
H	0.38968200	-2.44608400	0.05798200
H	-0.30763200	-1.79455600	-1.41319000
C	-1.33870000	1.22270300	-0.31860300
H	-2.31320800	0.88501400	0.05666100
H	-1.39925800	1.16400400	-1.41371300
C	2.85973400	-0.39291300	0.11431700
H	2.90425000	-0.48591500	1.20563100
H	2.72222700	-1.39959900	-0.29648600
H	3.83534000	-0.02915200	-0.22685600
C	-1.77043100	-2.27973700	0.11402000
H	-2.57293700	-1.65731600	-0.29787000
H	-1.94319800	-3.30670000	-0.22661400
H	-1.87421600	-2.27112600	1.20523400
C	-1.08962400	2.67288500	0.11431500
H	-0.14870800	3.05683200	-0.29599500
H	-1.89211400	3.33603200	-0.22742900
H	-1.03195000	2.75814500	1.20564500

Thermal correction to Gibbs Free Energy= 0.171568
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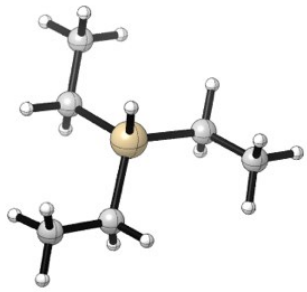

Figure S53. Calculated structure of triethylsilane.

β(*E*)-Vinylsilane

Si	2.02325500	0.21999500	-0.19492000
C	3.03370300	-0.15584600	1.38902000
H	4.08740800	-0.26679900	1.09927500
H	2.99366600	0.72088200	2.04779800
C	2.74622700	-0.76151400	-1.66838300
H	3.75252300	-0.37367600	-1.87792200
H	2.13992600	-0.53217300	-2.55440300
C	2.10495400	2.08341100	-0.60924300
H	1.50154100	2.26528800	-1.50890400
H	3.13854700	2.31827600	-0.89686900
C	2.57504700	-1.39335100	2.17240900
H	1.55560700	-1.26281200	2.55175500
H	2.57994700	-2.29624700	1.55114400
H	3.22577200	-1.58307200	3.03339300
C	2.80889000	-2.27910200	-1.45912500
H	1.81894700	-2.69345400	-1.23482800
H	3.18536700	-2.79196100	-2.35135000

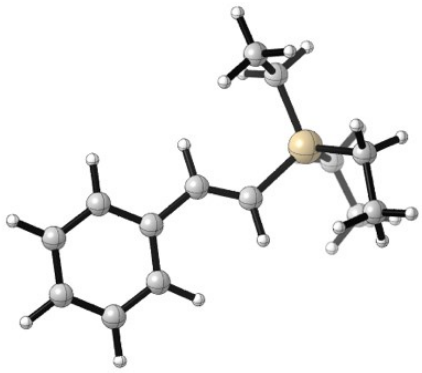

Figure S54. Calculated structure of the β(*E*)-vinylsilane.

H	3.47332000	-2.53937500	-0.62724700
C	1.65680700	3.01791300	0.52129400
H	2.30338600	2.91785000	1.40016200
H	1.68934300	4.06771600	0.20889400
H	0.63371100	2.79695800	0.84511900
C	0.22383200	-0.30054000	0.06850000
H	0.04110200	-1.27756900	0.51994600
C	-0.83545100	0.44446900	-0.27774500
H	-0.66394800	1.43239600	-0.70975000
C	-2.26302100	0.09923700	-0.13097700
C	-2.70520600	-1.19106800	0.18997900
C	-3.22407600	1.09934700	-0.32192700
C	-4.05990900	-1.46468500	0.32861400
H	-1.98419900	-1.99265900	0.32043200
C	-4.58145500	0.82883700	-0.18235200
H	-2.89882800	2.10505700	-0.57800100
C	-5.00446700	-0.45570200	0.14550000
H	-4.38230900	-2.47212600	0.57540400
H	-5.30854200	1.62176300	-0.33128700
H	-6.06310400	-0.67263800	0.25273000

Thermal correction to Gibbs Free Energy= 0.278641
E(RM06L) = -836.372149089

β(*Z*)-Vinylsilane

Si	-1.40191300	-0.21396400	-0.28265200
C	-3.09441100	-1.09482900	-0.13316300
H	-3.42267500	-1.37931300	-1.14196800
H	-2.94368900	-2.03682400	0.41075300
C	-1.65263800	1.52282900	-1.05426300
H	-2.44973300	1.44609200	-1.80628000
H	-0.74186100	1.78336000	-1.60887400
C	-0.26927200	-1.26610700	-1.40429100
H	0.66041500	-0.71741400	-1.59328000
H	-0.77177700	-1.36616500	-2.37654400
C	-4.19049000	-0.26885000	0.55063700
H	-3.88840100	0.05535500	1.55397100
H	-4.42580900	0.63249600	-0.02673200
H	-5.11867200	-0.84160500	0.65766900
C	-1.98645500	2.63494300	-0.05238200
H	-1.19969500	2.73832800	0.70401700
H	-2.10136900	3.60361100	-0.55191700
H	-2.91825700	2.42708200	0.48485800
C	0.05248300	-2.65289500	-0.83660900
H	-0.85742400	-3.24245100	-0.67294100
H	0.69765400	-3.22165800	-1.51550700
H	0.57178700	-2.57088200	0.12443600
C	-0.72279600	-0.11989900	1.49416300
H	-1.45860200	-0.25529200	2.28962800
C	0.55398000	-0.03040600	1.88989700
H	0.79441200	-0.12862400	2.95057000
C	1.71594900	0.16682700	0.99206000
C	2.79795100	-0.71986200	1.03088500
C	1.75475700	1.23112400	0.08574300
C	3.86750700	-0.57358800	0.15426100
H	2.78604800	-1.54387800	1.73995600
C	2.82766600	1.38387100	-0.78776200
H	0.93973300	1.94857800	0.07759400
C	3.88311100	0.47655600	-0.76186400
H	4.69100300	-1.28107300	0.18480800
H	2.84024000	2.21575400	-1.48601600
H	4.71940600	0.59173500	-1.44494700

Thermal correction to Gibbs Free Energy= 0.281897
E(RM06L) = -836.368811139

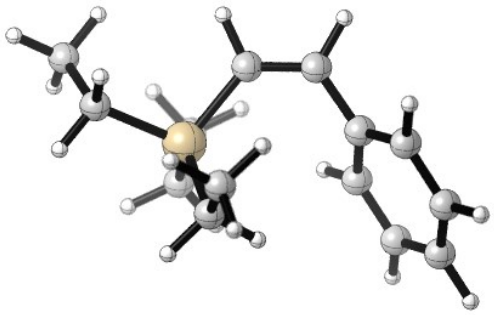

Figure S55. Calculated structure of the β(*Z*)-vinylsilane.

α-Vinylsilane

Si	-1.40622100	-0.02111400	0.17399400
C	-1.06184800	-0.57123400	-1.62089400
H	-0.46509100	0.20664000	-2.11433300
H	-0.42726000	-1.46550700	-1.61459900
C	-2.18618600	-1.45001700	1.17338300
H	-3.12249100	-1.73918900	0.67710400
H	-2.47462100	-1.05610300	2.15682000
C	-2.62624700	1.44729700	0.15019100
H	-2.82934900	1.75889400	1.18313200
H	-3.58567800	1.09030500	-0.24732600
C	-2.34086700	-0.84475100	-2.42145400
H	-2.94796800	-1.62886500	-1.95329100
H	-2.96638600	0.05246200	-2.49712300
H	-2.11190400	-1.17252900	-3.44145300
C	-1.28644600	-2.67714300	1.35069900
H	-0.37371700	-2.41922900	1.90011100
H	-1.79401600	-3.47163600	1.90895600
H	-0.98691600	-3.09799200	0.38290000
C	-2.12705400	2.64223600	-0.66955600
H	-1.96331300	2.36519500	-1.71777800
H	-2.84517700	3.46964200	-0.65526400
H	-1.17569000	3.01765800	-0.27611400
C	0.21648100	0.57190600	1.00271200
C	0.14799600	1.31941900	2.11204400
H	-0.80233700	1.59930100	2.56279600
C	1.54003000	0.25990200	0.40091000
C	1.88712600	-1.04705500	0.03697500
C	2.47499500	1.27857600	0.17867200
C	3.13365600	-1.33010200	-0.51090100
H	1.17956600	-1.85467600	0.20280900
C	3.72060200	0.99865800	-0.37492100
H	2.20903600	2.30127700	0.43131300
C	4.05572600	-0.30755900	-0.72053700
H	3.38521500	-2.35321500	-0.77513700
H	4.42884200	1.80522300	-0.54207700
H	5.02640200	-0.52693000	-1.15524300
H	1.04217200	1.67406600	2.62394300

Thermal correction to Gibbs Free Energy= 0.280634
E(RM06L) = -836.368446189

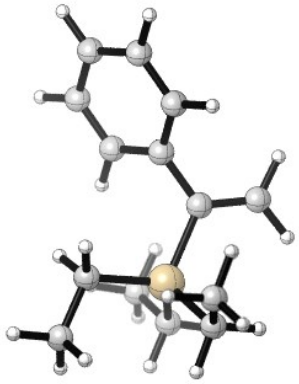

Figure S56. Calculated structure of the α-vinylsilane.

3. $Rh(CO)_2$ based compounds

Catalyst

C	-0.31534300	1.24738300	0.85745900
C	-1.65452700	1.53502900	0.81933800
H	-2.23248100	2.37474900	1.17121700
N	-1.31945400	-0.46540500	-0.07321500
N	-0.16649600	0.01469800	0.30571600
N	-2.22384000	0.44830900	0.23996000
C	-3.61343100	0.22154400	-0.03180100
C	-4.14700300	-1.04223400	0.19585300
C	-4.38436500	1.27580400	-0.50989700
C	-5.49685600	-1.24819900	-0.06557500
H	-3.51923500	-1.84256600	0.57150400
C	-5.73572900	1.05572600	-0.75379900
H	-3.93723900	2.24403100	-0.71349000
C	-6.29029900	-0.20276800	-0.53342700
H	-5.93008500	-2.22772000	0.10540700
H	-6.35081500	1.86636400	-1.12915900
H	-7.34389800	-0.37036500	-0.73017800
C	0.86642200	1.98894400	1.39648800
H	0.57866600	2.98968600	1.72086200
H	1.28623800	1.45844500	2.25828800
N	1.90662900	2.13561600	0.38968000
C	2.49459700	3.26862900	-0.04524200
C	3.46311200	2.91484300	-0.96157100
H	2.18952300	4.23352400	0.33259400
C	3.40089500	1.52088700	-1.02466200
H	4.12241900	3.57170000	-1.50651200
H	3.98169200	0.83736400	-1.62657100
N	2.45827800	1.05270200	-0.20063200
Rh	1.69077000	-0.91253500	-0.00016600
C	0.91725400	-2.62320300	0.13635100
C	3.40534700	-1.66226100	-0.20107800
O	0.42178100	-3.64525500	0.21898300
O	4.45625700	-2.08891200	-0.31244100

Thermal correction to Gibbs Free Energy= 0.194631
E(RM06L) = -1075.11385799

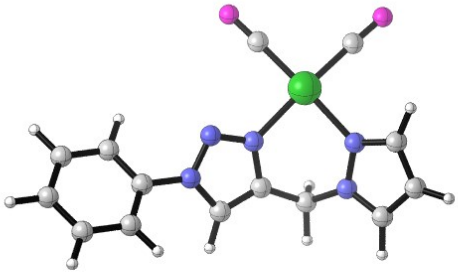

Figure S57. Calculated structure of **$Rh^{I}C_0Ph$**.

H-Rh-Si intermediate

C	-0.65535700	2.06206300	0.92779400
C	-2.02205200	2.18730600	0.93604700
H	-2.68371400	2.94665400	1.32176700
N	-1.47069800	0.26142500	-0.00642400
N	-0.37400000	0.86462700	0.35086700
N	-2.47462900	1.05164700	0.35262500
C	-3.82907200	0.65173600	0.11498300
C	-4.17929500	-0.68118500	0.30265300
C	-4.75341200	1.60592900	-0.29632300
C	-5.49605200	-1.06161100	0.07048400
H	-3.43537800	-1.40056200	0.62681500
C	-6.06984500	1.21153700	-0.51126200
H	-4.45009100	2.63376100	-0.47052800
C	-6.44041800	-0.11862900	-0.32996800
H	-5.78561600	-2.09736400	0.21193600
H	-6.80188500	1.94399100	-0.83393700
H	-7.46735300	-0.42191400	-0.50419300
C	0.42543700	2.95700300	1.44788100
H	-0.00784400	3.87268700	1.85310600
H	0.96867700	2.46065800	2.25978000
N	1.37924400	3.34408600	0.42035100
C	1.75752200	4.59314800	0.06565500
C	2.76518500	4.47136700	-0.86604200
H	1.29207200	5.46361700	0.50455400
C	2.94409200	3.08944500	-1.01638200
H	3.29702700	5.26642400	-1.36457000
H	3.63376000	2.55117800	-1.65062000

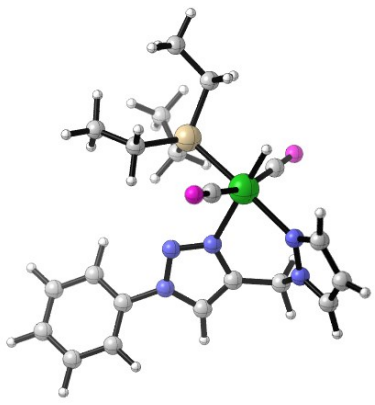

Figure S58. Calculated structure of the H-Rh-Si intermediate.

N	2.10605600	2.41421100	-0.23276100
Rh	1.63915700	0.19516400	-0.17266000
C	1.28113700	0.08909300	-2.06766100
O	1.14519300	0.04764900	-3.19553000
Si	1.03724700	-2.21084400	-0.05496800
C	0.00171900	-2.43221900	1.54968300
H	0.32589000	-1.71786000	2.31574000
H	-1.03334500	-2.15901500	1.30906600
C	2.65664100	-3.22551200	-0.00842200
H	3.36817700	-2.75666500	-0.69907000
H	3.09986300	-3.12255700	0.99149900
C	-0.04959200	-2.67204400	-1.56330400
H	-0.72152200	-1.83275500	-1.77920100
H	0.59572200	-2.79519300	-2.44275600
C	0.05126500	-3.84986900	2.13781200
H	-0.56782700	-3.91836000	3.03841600
H	-0.31460800	-4.59926100	1.42880900
H	1.07220600	-4.12966000	2.41840600
C	-0.89659700	-3.93653600	-1.35614100
H	-1.59932500	-3.81197200	-0.52478000
H	-1.48465100	-4.15588100	-2.25320500
H	-0.28164400	-4.81623000	-1.14262200
C	2.50724700	-4.71074200	-0.36796600
H	2.12731300	-4.83618400	-1.38763400
H	3.47535900	-5.21887500	-0.31427100
H	1.82430400	-5.23253800	0.30973500
C	2.35088400	-0.10694000	1.58652200
O	2.84703800	-0.29640900	2.59385400
H	3.07463300	-0.24862800	-0.59844600

Thermal correction to Gibbs Free Energy= 0.391147
E(RM06L) = -1602.95322855

C^{Si}-(E) intermediate

C	-2.34985000	-1.70823400	0.96676600
C	-3.70357500	-1.48672200	0.98808500
H	-4.50630700	-1.90747800	1.57260200
N	-2.77684500	-0.23347500	-0.58778900
N	-1.83594200	-0.92564500	-0.01476500
N	-3.91431100	-0.57350300	0.00928300
C	-5.15724600	0.00414300	-0.40701800
C	-5.39276800	0.19168300	-1.76471700
C	-6.09356700	0.35688900	0.55916300
C	-6.60435200	0.74855100	-2.15837500
H	-4.64295800	-0.09495400	-2.49355400
C	-7.30611800	0.90010400	0.14788800
H	-5.87373400	0.23425700	1.61531900
C	-7.56089300	1.09675100	-1.20710300
H	-6.80319000	0.90238400	-3.21355800
H	-8.04547100	1.18176100	0.88989900
H	-8.50613500	1.52575100	-1.52248300
C	-1.46684300	-2.61852300	1.75759800
H	-2.04322900	-3.13459700	2.52660800
H	-1.02758600	-3.38333900	1.10738700
N	-0.39304900	-1.90553900	2.43309500
C	-0.08242900	-1.95317400	3.74680400
C	1.05672800	-1.20206500	3.93585700
H	-0.68813100	-2.51909900	4.43948200
C	1.38416200	-0.72280100	2.66366200
H	1.57689200	-1.01973300	4.86284800
H	2.19539600	-0.08427300	2.34774400
N	0.50923900	-1.15721600	1.75722700
Rh	0.33451800	-0.58460100	-0.30280800
C	0.24015600	0.23149600	-1.98914300
C	0.61891000	-2.56173600	-1.02879000
O	0.18063200	0.73537100	-3.00719700
O	0.71001700	-3.60681800	-1.45633100
H	0.12031100	0.84773200	0.23526700
C	2.34633700	-0.12296500	-0.34329900
C	3.17040000	-1.29649700	-0.75233500
C	3.58682400	-1.42156200	-2.08340400
C	3.50846700	-2.30517600	0.15901100
C	4.30934500	-2.53669700	-2.49697800
H	3.34314800	-0.63461700	-2.79268800

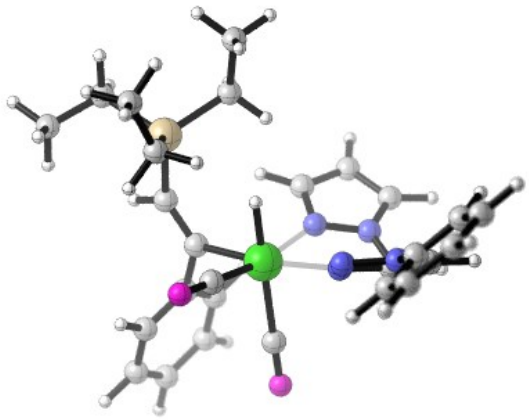

Figure S59. Calculated structure of the C^{Si}-(*E*) intermediate.

C	4.23677300	-3.41631200	-0.25502500
H	3.20006800	-2.21700500	1.19701700
C	4.63123300	-3.53974900	-1.58533700
H	4.62684500	-2.61951200	-3.53184900
H	4.50044500	-4.18641700	0.46364800
H	5.19553600	-4.40880200	-1.90807200
C	2.90169700	1.05857700	-0.05003100
H	3.99708800	1.04699900	-0.08564500
Si	2.18950500	2.77253000	0.40074600
C	3.69864800	3.93409300	0.46714600
H	3.36136700	4.93365600	0.76982900
H	4.36859600	3.58997000	1.26633000
C	1.35735400	2.71107200	2.12490500
H	0.61200800	1.90533300	2.14366600
H	2.12851700	2.43060700	2.85594000
C	4.46925400	4.02569900	-0.85687000
H	5.32032000	4.70938100	-0.77509400
H	4.86183400	3.04970100	-1.16478400
H	3.83146900	4.39025700	-1.67034600
C	0.69484100	4.02593300	2.55603800
H	0.32080600	3.96295200	3.58356200
H	1.39570900	4.86689500	2.51365200
H	-0.15593900	4.27101000	1.91115900
C	0.97051600	3.40568700	-0.93653100
H	1.32117300	3.05184600	-1.91434500
H	-0.01546300	2.94880100	-0.78000300
C	0.82299000	4.93399600	-0.97857000
H	1.77791800	5.42255800	-1.19788000
H	0.11343700	5.23648900	-1.75587000
H	0.46207700	5.33755900	-0.02739100

Thermal correction to Gibbs Free Energy= 0.495328
E(RM06L) = -1911.43812412

C^{Si}-(Z) intermediate

C	-3.10057800	-1.52347700	0.23425000
C	-4.44459900	-1.32628000	0.42557900
H	-5.24810400	-1.98415800	0.71660300
N	-3.51049200	0.56850500	-0.24567200
N	-2.58188300	-0.33972700	-0.17981500
N	-4.64531800	-0.02298400	0.11314800
C	-5.87641800	0.70908100	0.12859300
C	-6.13747400	1.61184700	-0.89648400
C	-6.77651800	0.49202800	1.16656800
C	-7.33770100	2.31324700	-0.87484500
H	-5.41546200	1.75790600	-1.69206200
C	-7.97863500	1.19159700	1.16606000
H	-6.53588900	-0.19117000	1.97536700
C	-8.25852200	2.10079200	0.14892100
H	-7.55594000	3.02210100	-1.66638100
H	-8.68971700	1.03435700	1.96994300
H	-9.19519200	2.64814100	0.15607000
C	-2.23373800	-2.73482400	0.36794700
H	-2.81090700	-3.57602600	0.75422900
H	-1.83593700	-3.03038000	-0.60912100
N	-1.12077200	-2.52143100	1.28049300
C	-0.80821800	-3.24280600	2.37877100
C	0.34580900	-2.71227500	2.91315000
H	-1.42265000	-4.07527700	2.68920600
C	0.67692900	-1.64885000	2.06723700
H	0.87356900	-3.04229300	3.79393500
H	1.50117400	-0.95199900	2.11392900
N	-0.20920100	-1.54431700	1.07632400
Rh	-0.40028100	0.04060700	-0.36059000
C	-0.45657700	1.68093300	-1.27111700
C	-0.28098300	-1.19354200	-2.06200800
O	-0.48091000	2.69772600	-1.78065000
O	-0.28043000	-1.80879700	-3.01361500
H	-0.50368700	0.95591200	0.89004800
C	1.64193800	0.34450200	-0.26445100
C	2.40506400	-0.47257200	-1.24602600
C	2.94082100	0.13861500	-2.38568300
C	2.59511800	-1.84878400	-1.06522200
C	3.66071800	-0.60567600	-3.31639900

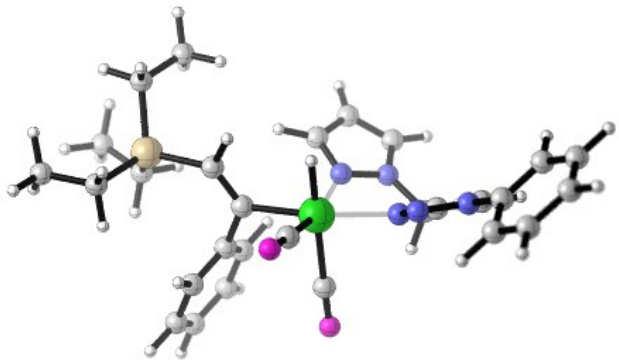

Figure S60. Calculated structure of the C^{Si}-(*Z*) intermediate.

H	2.79591100	1.20558700	-2.53243200
C	3.31946100	-2.59004400	-1.99203600
H	2.19083200	-2.33371800	-0.18088200
C	3.85271900	-1.97112900	-3.12122000
H	4.07577000	-0.11693700	-4.19237700
H	3.47585700	-3.65218700	-1.83004200
H	4.41796100	-2.55058100	-3.84411700
C	2.22619600	1.18439100	0.59669900
H	1.58666500	1.79520200	1.23537600
Si	4.10469800	1.42657600	0.88310800
C	4.24012400	1.99156000	2.70128700
H	5.29775900	2.15171700	2.94500000
H	3.75556900	2.97077000	2.80846900
C	4.73169900	2.79130200	-0.29461900
H	4.54945000	2.46699000	-1.32698700
H	4.10672400	3.68097000	-0.14032200
C	3.62589500	0.99253400	3.69017200
H	3.75335400	1.31989900	4.72730300
H	2.54836900	0.87318700	3.51703200
H	4.08828800	0.00184200	3.59893700
C	6.21187800	3.15641400	-0.12113100
H	6.48869500	3.99731000	-0.76562000
H	6.44067500	3.44478100	0.91099800
H	6.86269400	2.31569100	-0.38369100
C	5.06594500	-0.21328300	0.66618200
H	4.43364000	-1.03771700	1.02067700
H	5.21672700	-0.39863400	-0.40452700
C	6.41196500	-0.24952800	1.40343800
H	6.28136700	-0.14113700	2.48594700
H	6.92910600	-1.19884000	1.22810500
H	7.08066600	0.55289200	1.07551400

Thermal correction to Gibbs Free Energy= 0.494467
E(RM06L) = -1911.44193550

C^{Si}-α intermediate

C	-3.14757600	-1.64932600	-0.71201500
C	-4.47359200	-1.34612700	-0.53413700
H	-5.37795600	-1.92121100	-0.65469400
N	-3.25029700	0.45841300	-0.13549600
N	-2.44719200	-0.51134700	-0.46452800
N	-4.48170200	-0.03755500	-0.18226900
C	-5.61205600	0.79171800	0.11191300
C	-5.62033900	2.10620300	-0.34208500
C	-6.66950100	0.25624200	0.83985700
C	-6.72462100	2.90081900	-0.05539000
H	-4.78027800	2.49362900	-0.90761900
C	-7.77246500	1.06048500	1.10629900
H	-6.62591500	-0.76184100	1.21463800
C	-7.80001300	2.37980000	0.66102200
H	-6.74650000	3.92863200	-0.40143700
H	-8.60406200	0.65741000	1.67423700
H	-8.66038300	3.00471100	0.87600700
C	-2.46497100	-2.91206600	-1.13681400
H	-3.19526200	-3.71361000	-1.25728700
H	-1.96882700	-2.76907900	-2.10318200
N	-1.47515400	-3.36682800	-0.17247000
C	-1.41018400	-4.56355100	0.45269500
C	-0.26276100	-4.57070800	1.21599800
H	-2.17242500	-5.31403500	0.30224300
C	0.32178900	-3.31804500	0.98985100
H	0.10055100	-5.36684900	1.84651100
H	1.23129700	-2.90045600	1.39890600
N	-0.41357700	-2.59801800	0.14410600
Rh	-0.25039700	-0.42401900	-0.38701800
C	-0.22764600	0.17386500	1.46960300
C	0.06310200	-0.56906900	-2.28313600
O	-0.18832000	0.55319200	2.53725800
O	0.30031800	-0.57383500	-3.39454400
H	-0.15809400	1.09056200	-0.69414900
C	1.80024800	-0.49512600	-0.26280900
C	2.67730700	0.49984700	-0.12419400
Si	4.55269800	0.11487000	0.06364400
C	5.04473800	0.57204800	1.84929100

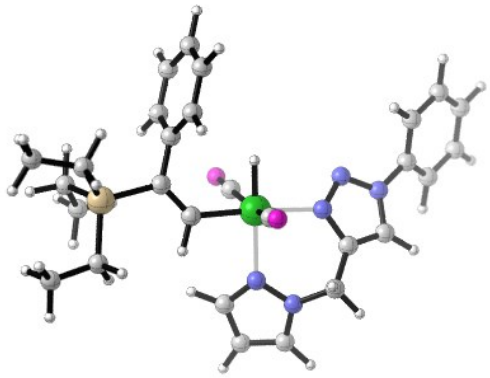

Figure S61. Calculated structure of the C^{Si}-α intermediate.

H	6.12472700	0.41271700	1.96204700
H	4.88575800	1.64836400	1.99259100
C	5.51350900	1.17180500	-1.20041700
H	5.48813900	0.65957300	-2.17135000
H	4.96992600	2.11489400	-1.34089900
C	4.28800900	-0.22615300	2.91660100
H	4.56559100	0.08991200	3.92750700
H	3.20168500	-0.10240000	2.81670900
H	4.50301800	-1.29839600	2.83778300
C	6.96476800	1.47630100	-0.80199700
H	7.46770300	2.06639400	-1.57504400
H	7.00761900	2.04977700	0.13020300
H	7.55075400	0.56300500	-0.65237600
C	4.82830700	-1.75397300	-0.21370700
H	4.23672300	-2.31314100	0.52439600
H	4.43170700	-2.03144200	-1.19947600
C	6.30067500	-2.17499500	-0.11170500
H	6.73270800	-1.89863100	0.85691200
H	6.41348100	-3.25824000	-0.22512300
H	6.90495000	-1.69955700	-0.89149200
C	2.28479900	1.93383600	-0.08209800
C	2.02135800	2.63101800	-1.26708100
C	2.18583900	2.61415000	1.13581300
C	1.64411900	3.97037400	-1.23284200
H	2.12099900	2.11567100	-2.21906300
C	1.80242800	3.95284800	1.16995900
H	2.40589800	2.08980200	2.06213300
C	1.52862300	4.63381000	-0.01319900
H	1.44619800	4.49821600	-2.16094500
H	1.72454500	4.46561200	2.12393200
H	1.23743000	5.67910300	0.01388300
H	2.14447300	-1.53014100	-0.32048600

Thermal correction to Gibbs Free Energy= 0.492320
E(RM06L) = -1911.44390772

C^{H}-(E) intermediate

C	-2.36689000	1.94375300	0.82324500
C	-3.70219400	1.84906200	0.52161900
H	-4.53940200	2.50534100	0.69945900
N	-2.67180500	0.00627800	-0.14351400
N	-1.78627800	0.78567700	0.40771900
N	-3.83637200	0.63729000	-0.06861200
C	-5.02851800	0.01213800	-0.55695400
C	-5.21491800	-1.34681700	-0.32625100
C	-5.96417000	0.78011000	-1.24139500
C	-6.37606400	-1.94741000	-0.79931400
H	-4.46672200	-1.91510400	0.21580500
C	-7.12666500	0.16650200	-1.69631200
H	-5.78121100	1.83206100	-1.43827800
C	-7.33170700	-1.19356100	-1.47755000
H	-6.53748500	-3.00639600	-0.62860500
H	-7.86554600	0.75131100	-2.23351700
H	-8.23787700	-1.66809000	-1.83903200
C	-1.58696900	3.03071700	1.49528100
H	-2.24338700	3.87042800	1.72898000
H	-1.16511400	2.66974300	2.43986100
N	-0.50610500	3.53818200	0.66647400
C	-0.25398300	4.81815500	0.30807200
C	0.93791800	4.82468700	-0.38367800
H	-0.92957900	5.61744800	0.57626700
C	1.35243600	3.48491300	-0.39404200
H	1.43752800	5.67568300	-0.81938700
H	2.23338900	3.03318900	-0.82928700
N	0.47601500	2.71635400	0.24763900
Rh	0.39345400	0.42888200	0.34155400
C	0.25495100	0.29457100	-1.58972000
C	0.55758100	0.28318300	2.25619100
O	0.13013500	0.28240600	-2.71909100
O	0.63817300	0.22903700	3.39032300
C	2.41974000	0.34350900	0.20422300
C	3.17374500	-0.00631600	-0.84692900
H	2.71074200	-0.42765100	-1.73947700
Si	0.50076000	-2.06185500	0.47743300

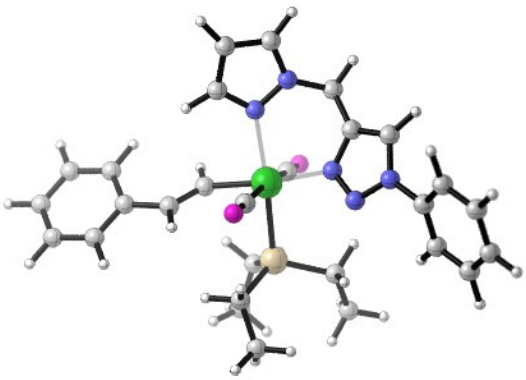

Figure S62. Calculated structure of the C^{H}-(*E*) intermediate.

C	1.80659500	-2.55514200	1.79362800
H	1.35685000	-2.44478500	2.78940200
H	2.63642200	-1.84128800	1.74408700
C	0.94763600	-2.83203900	-1.22019600
H	2.03289600	-2.74469400	-1.35466700
H	0.48967900	-2.25629100	-2.03145600
C	-1.24167900	-2.63232400	1.04673300
H	-1.90295700	-2.63673700	0.17177900
H	-1.65626700	-1.87894000	1.72866100
C	-1.25869700	-4.00299200	1.73957100
H	-2.27596000	-4.27162700	2.04458500
H	-0.89263000	-4.79871000	1.08358000
H	-0.63624400	-4.00451800	2.64068900
C	2.36783000	-3.97594300	1.64237000
H	3.10772400	-4.17942300	2.42313300
H	1.58663000	-4.73868000	1.72325900
H	2.86730300	-4.10644500	0.67662700
C	0.51491100	-4.29835500	-1.37185200
H	-0.57295600	-4.40164200	-1.29687600
H	0.81493100	-4.68581600	-2.35091900
H	0.96565000	-4.94314300	-0.61186100
H	2.93376400	0.69461600	1.10105100
C	4.64768500	0.06601700	-0.91348200
C	5.31933600	-0.73716300	-1.84271400
C	5.40369400	0.90600900	-0.08577400
C	6.70740000	-0.72320500	-1.92711800
H	4.74610700	-1.38597100	-2.50116400
C	6.79054300	0.92103900	-0.16937000
H	4.90561900	1.56739000	0.61822600
C	7.44778300	0.10426000	-1.08764900
H	7.21064900	-1.35741500	-2.65033900
H	7.36167400	1.57978800	0.47774000
H	8.53106500	0.12049600	-1.15389900

Thermal correction to Gibbs Free Energy= 0.497867
E(RM06L) = -1911.46047864

C^H-α intermediate

C	1.73760800	2.00125500	-0.89387300
C	3.10596800	2.02893300	-0.99117100
H	3.79532000	2.75783000	-1.38703300
N	2.47566400	0.10355000	-0.10024500
N	1.40428100	0.79677000	-0.35623600
N	3.50982300	0.83614500	-0.49188300
C	4.84051200	0.31906000	-0.38138700
C	5.06062900	-1.02601200	-0.65951400
C	5.87093500	1.17313000	-0.00394000
C	6.35490500	-1.52244900	-0.55439100
H	4.23406700	-1.66397400	-0.95363700
C	7.16219000	0.66326400	0.08336200
H	5.66970400	2.21142900	0.24151600
C	7.40383300	-0.68085200	-0.18964700
H	6.54434900	-2.56911000	-0.76719400
H	7.97658600	1.31626900	0.37816100
H	8.41206300	-1.07440900	-0.11501200
C	0.70172300	3.01701100	-1.26126900
H	1.17777700	3.90935100	-1.67066200
H	0.02777500	2.62028400	-2.02812400
N	-0.08855500	3.42834500	-0.11258900
C	-0.27492200	4.67420000	0.37954000
C	-1.14683900	4.57015000	1.44224200
H	0.21518900	5.52942500	-0.06265100
C	-1.44559000	3.20294000	1.52640900
H	-1.51602700	5.36825300	2.06702300
H	-2.09689400	2.67405200	2.20873900
N	-0.80419300	2.52140100	0.58013900
Rh	-0.65321500	0.24589800	0.30559400
C	0.08652300	0.07508400	2.09112600
C	-1.23380300	0.08453800	-1.53461100
O	0.59699500	0.03727700	3.10612500
O	-1.45527400	-0.00251300	-2.64780500
C	-2.56870500	0.00201700	1.00966300
C	-3.69864900	0.29230500	0.07947600
C	-4.74775900	-0.63233100	-0.02926200

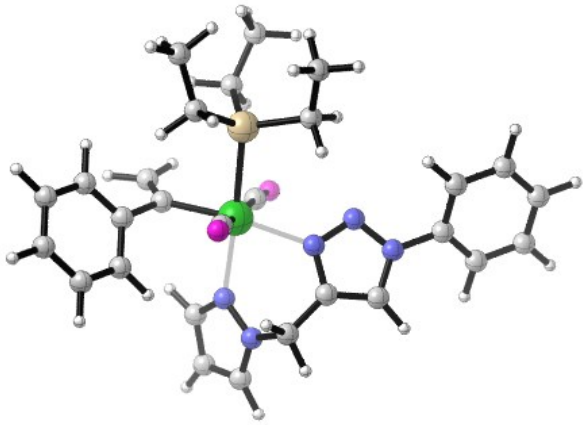

Figure S63. Calculated structure of the C^H-α intermediate.

C	-3.76834900	1.46327300	-0.68814300
C	-5.82172800	-0.40035800	-0.88228600
H	-4.70807700	-1.54708400	0.55565400
C	-4.84601300	1.69887700	-1.53568400
H	-2.98288500	2.20797300	-0.60477900
C	-5.87387400	0.76556200	-1.64099900
H	-6.61789900	-1.13470300	-0.95543300
H	-4.88579700	2.61839900	-2.11192500
H	-6.71102600	0.94730600	-2.30734100
C	-2.85778100	-0.33879300	2.27390000
H	-3.89055200	-0.33985500	2.61962200
H	-2.11976800	-0.64107300	3.00981400
Si	-0.59787400	-2.25075900	0.13467000
C	-2.01724700	-2.84646100	-1.00923300
H	-1.67328000	-2.76221300	-2.04867700
H	-2.87168800	-2.16808900	-0.91878600
C	-0.75671800	-3.05511200	1.86854700
H	-1.81983200	-3.05835900	2.13684500
H	-0.25963100	-2.43550400	2.62239800
C	1.07889900	-2.69392200	-0.68589100
H	1.87293000	-2.60560600	0.06530200
H	1.30422500	-1.93579200	-1.44641600
C	1.10805100	-4.08378900	-1.33974700
H	2.08392300	-4.27539100	-1.79938900
H	0.92500000	-4.88371700	-0.61627100
H	0.35367200	-4.17183700	-2.12879700
C	-2.49184400	-4.28177200	-0.74489700
H	-3.31124200	-4.54452300	-1.42187400
H	-1.69210100	-5.01351200	-0.89884900
H	-2.86024000	-4.40102800	0.27979900
C	-0.18258200	-4.47639100	1.96123700
H	0.89250500	-4.48716000	1.75205900
H	-0.32523500	-4.88019800	2.96889500
H	-0.66713900	-5.16395400	1.26172500

Thermal correction to Gibbs Free Energy= 0.500394
E(RM06L) = -1911.45875492

Reductive elimination from C^{Si}-(E)

C	-0.99387000	-2.87626000	-0.08973200
C	-2.30408100	-2.90552800	0.31950000
H	-2.87287200	-3.61444800	0.89936300
N	-1.94800400	-1.09953900	-0.91250100
N	-0.83193300	-1.76202400	-0.84242100
N	-2.84953500	-1.78545200	-0.21579900
C	-4.17194800	-1.25967200	-0.06406700
C	-4.68684500	-0.43943300	-1.06312000
C	-4.88371100	-1.53277400	1.09922300
C	-5.94631200	0.12068300	-0.88217400
H	-4.10787200	-0.23820700	-1.95687600
C	-6.14905500	-0.97790200	1.25701400
H	-4.45137700	-2.13774000	1.88973700
C	-6.67902100	-0.14917900	0.27162100
H	-6.35667000	0.76640200	-1.65115400
H	-6.71226200	-1.18156100	2.16139500
H	-7.66239100	0.28926300	0.40429900
C	0.18446000	-3.75338400	0.16487000
H	-0.11337100	-4.68442800	0.64863600
H	0.67164500	-4.00553100	-0.78313700
N	1.16186200	-3.11447100	1.04047600
C	1.70459700	-3.64148800	2.15829000
C	2.65546900	-2.76011600	2.62233400
H	1.37876700	-4.60156100	2.53111500
C	2.63460100	-1.70078500	1.71064300
H	3.27952300	-2.86492000	3.49560000
H	3.22489600	-0.79686800	1.69647700
N	1.73082300	-1.91766100	0.75409700
Rh	1.15086500	-0.63585200	-0.87726900
C	0.69823300	0.54821000	-2.25497000
C	2.36436500	-1.71258800	-2.09444700
O	0.46747800	1.23133600	-3.13622500
O	3.11810600	-2.33528000	-2.67574900
H	0.59380400	0.25214100	0.29378900
C	1.87071200	1.21848300	0.02834800

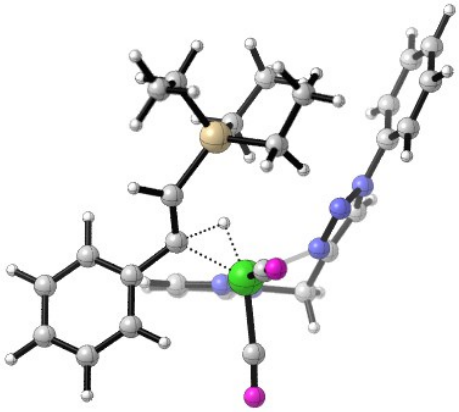

Figure S64. Calculated structure of the reductive elimination intermediate from C^{Si}-(*E*).

C	3.34443600	1.20242100	0.24057000
C	4.25314900	0.84705600	-0.76309300
C	3.84808600	1.59884700	1.48793000
C	5.62243400	0.88836800	-0.52989300
H	3.88535400	0.55954400	-1.74324800
C	5.21966100	1.62507000	1.72695500
H	3.15227300	1.87588200	2.27521800
C	6.11063400	1.26770200	0.71945600
H	6.31164700	0.62597000	-1.32648400
H	5.59015900	1.92806900	2.70137000
H	7.17999700	1.28821700	0.90335400
C	1.14394100	2.31535200	0.31604200
H	1.75060800	3.18195600	0.59885500
Si	-0.74364200	2.59028000	0.53104700
C	-0.90909100	4.33917600	1.26403600
H	-1.95932900	4.51061500	1.53288700
H	-0.34825800	4.38048600	2.20695700
C	-1.36143400	1.28942300	1.79957400
H	-1.12241300	0.27970900	1.43846900
H	-0.77291600	1.42649700	2.71669700
C	-0.42908700	5.44705000	0.31661300
H	-0.53891400	6.43563000	0.77351700
H	0.62769700	5.32489700	0.05170800
H	-1.00028000	5.45098000	-0.61880000
C	-2.85870700	1.36978100	2.12354600
H	-3.13088800	0.66464700	2.91709800
H	-3.14610200	2.37064300	2.46368000
H	-3.47087300	1.12914400	1.24846300
C	-1.72546700	2.49209000	-1.10702700
H	-1.13866700	2.98182500	-1.89357700
H	-1.82531300	1.43920000	-1.39720600
C	-3.11864000	3.13646000	-1.04487500
H	-3.06258300	4.19526800	-0.77056900
H	-3.61502400	3.07842200	-2.01984700
H	-3.76817000	2.64248400	-0.31553200

Thermal correction to Gibbs Free Energy= 0.494627
E(RM06L) = -1911.40821001

Reductive elimination from C^{Si}-(Z)

C	-3.27992200	-1.36411200	-0.61507500
C	-4.60891600	-1.08141900	-0.42831000
H	-5.50899000	-1.65664900	-0.57640300
N	-3.39833300	0.71097000	0.05917600
N	-2.58795200	-0.23922600	-0.30699700
N	-4.62709400	0.21023600	-0.01749900
C	-5.76446500	1.01683500	0.30946300
C	-5.78472100	2.34856000	-0.09084000
C	-6.81785300	0.44334600	1.01381500
C	-6.89617000	3.12129800	0.22620700
H	-4.94794100	2.76637100	-0.63932200
C	-7.92838100	1.22624000	1.31097500
H	-6.76497200	-0.58844800	1.34753800
C	-7.96755800	2.56214700	0.91949400
H	-6.92678900	4.16207900	-0.07790500
H	-8.75677800	0.79301400	1.86114700
H	-8.83366900	3.17017000	1.15855200
C	-2.55152100	-2.58782000	-1.06564400
H	-3.24063100	-3.42244200	-1.20055500
H	-2.05455500	-2.40822200	-2.02416400
N	-1.56090900	-3.00143200	-0.08498700
C	-1.55964500	-4.15323300	0.61912900
C	-0.51486300	-4.09722800	1.51308400
H	-2.29469600	-4.92068900	0.42539300
C	0.07475200	-2.84986400	1.29308800
H	-0.21531800	-4.84960700	2.22511500
H	0.93103400	-2.41143600	1.77934400
N	-0.55476100	-2.18657400	0.32220900
Rh	-0.37041100	-0.13987700	-0.35857100
C	-0.49964200	1.69840100	-0.66412400
C	-0.13925300	-0.59572000	-2.40799600
O	-0.66708400	2.81030700	-0.84990300
O	0.28929400	-0.61964200	-3.46165300
H	0.40761400	0.20993100	1.01744000

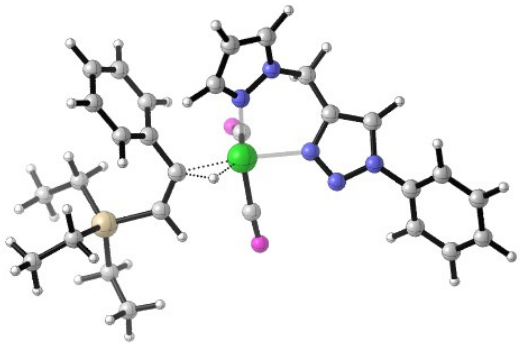

Figure S65. Calculated structure of the reductive elimination intermediate from C^{Si}-(*Z*).

C	1.69633700	0.11725600	0.17411900
C	2.49125400	-1.13535200	0.29204000
C	2.62160700	-2.04759900	-0.75790900
C	3.15911000	-1.39394700	1.49536400
C	3.41174300	-3.18242100	-0.61609300
H	2.12075400	-1.85808100	-1.70183900
C	3.94404700	-2.53465200	1.64290300
H	3.05383600	-0.69260700	2.31841800
C	4.07231000	-3.43163500	0.58580600
H	3.51865100	-3.87209200	-1.44761800
H	4.45723400	-2.71901000	2.58165800
H	4.68712700	-4.31935500	0.69514200
C	2.30336100	1.31653300	0.23898600
H	1.67869900	2.20781500	0.28998500
Si	4.18336600	1.69940800	0.16946200
C	4.28985600	3.45458100	-0.57385300
H	5.35068600	3.69628400	-0.71825400
H	3.84833600	3.44354000	-1.57919500
C	5.09188200	0.44638500	-0.95159600
H	5.26824200	-0.47546600	-0.38377100
H	4.41794300	0.16790200	-1.77207100
C	3.63066500	4.54368400	0.28158700
H	3.74481100	5.53155700	-0.17649000
H	2.55535900	4.37024800	0.41047700
H	4.07534300	4.59170200	1.28213100
C	6.41405500	0.96809900	-1.53144300
H	6.89548200	0.20536600	-2.15244200
H	6.25703500	1.85218200	-2.15860300
H	7.12473800	1.24515100	-0.74562600
C	4.89414700	1.73472100	1.94474700
H	4.18036300	2.25955300	2.59323500
H	4.94904100	0.70543200	2.31944000
C	6.27495200	2.39589300	2.05130000
H	6.26017700	3.42687200	1.68065900
H	6.61757200	2.42563600	3.09091900
H	7.02828900	1.84903700	1.47467900

Thermal correction to Gibbs Free Energy= 0.490605
E(RM06L) = -1911.41768484

Reductive elimination from C^{Si}-α

C	3.10986100	1.78283100	0.02875400
C	4.43343800	1.43777900	0.13130300
H	5.31114800	1.99339200	0.42120400
N	3.28552700	-0.30207900	-0.61541500
N	2.45374900	0.68583200	-0.43849400
N	4.48728300	0.14737400	-0.27721900
C	5.63642900	-0.70212400	-0.37338200
C	5.75183900	-1.56152800	-1.46061100
C	6.60543100	-0.63858800	0.62243500
C	6.87461100	-2.37715900	-1.54617900
H	4.97905300	-1.58647700	-2.22075900
C	7.72883600	-1.45140500	0.51473200
H	6.47721600	0.01440300	1.48030900
C	7.86313000	-2.31940300	-0.56603600
H	6.97966900	-3.05361500	-2.38762300
H	8.49229400	-1.41396200	1.28435700
H	8.73894800	-2.95504200	-0.64300500
C	2.41936000	3.08539600	0.29270300
H	3.13027000	3.80626600	0.69990900
H	2.02464900	3.50152500	-0.64094100
N	1.32719100	2.95732000	1.23949500
C	1.12665800	3.63131100	2.39560700
C	-0.09597900	3.23388300	2.89240000
H	1.85467800	4.33784600	2.76696800
C	-0.57536900	2.30645800	1.95464200
H	-0.57336600	3.56773600	3.80034200
H	-1.49700200	1.74188200	1.94791900
N	0.28827800	2.15069800	0.95592600
Rh	0.26097300	0.43691300	-0.66743800
C	0.47339300	-0.94163700	0.72158100
C	0.36089600	1.49572200	-2.26915600
O	0.84585200	-1.67367900	1.50542200
O	0.48671400	2.09280300	-3.23022400
H	-0.63207700	-0.60392100	-1.51935900
C	-1.78771200	0.18878800	-0.99506000
C	-2.68953600	-0.54955800	-0.32673100
Si	-4.57719800	-0.27484300	-0.61955500
C	-5.37408800	0.20908200	1.04336500
H	-6.46080000	0.25050400	0.89568500
H	-5.20367300	-0.59812400	1.76678100
C	-5.28775400	-1.92934500	-1.25097100
H	-5.05717800	-2.01713000	-2.32077800
H	-4.74626200	-2.74564700	-0.75570400
C	-4.88015700	1.54726200	1.60223300
H	-5.33642600	1.77176700	2.57187600
H	-3.79111300	1.54887400	1.73917900
H	-5.11861700	2.37516700	0.92510300
C	-6.79505300	-2.10710200	-1.01893400
H	-7.14200400	-3.06359300	-1.42298300
H	-7.03666000	-2.09404000	0.04927100
H	-7.38160600	-1.31631300	-1.49850300
C	-4.79973200	1.14466600	-1.87332400
H	-4.26568400	2.02954800	-1.50083800
H	-4.31706200	0.86860300	-2.82023600
C	-6.26910400	1.50636800	-2.13264600
H	-6.78822200	1.77577900	-1.20576100
H	-6.35111500	2.35846200	-2.81499900
H	-6.81243300	0.67086000	-2.58602300
C	-2.32441600	-1.64761200	0.60059700
C	-1.91184700	-2.88746500	0.09464200
C	-2.42917000	-1.48282200	1.98733100
C	-1.58219300	-3.92750900	0.95814000
H	-1.85388900	-3.02971300	-0.98135200
C	-2.09507700	-2.52289500	2.84876000
H	-2.76988500	-0.53236300	2.38931300
C	-1.66617200	-3.74554000	2.33660200
H	-1.26060600	-4.88204100	0.55334300
H	-2.17193800	-2.37957800	3.92215100
H	-1.40854200	-4.55710500	3.00948800
H	-2.15263700	0.90864800	-1.72427700

Thermal correction to Gibbs Free Energy= 0.490476
E(RM06L) = -1911.42368487

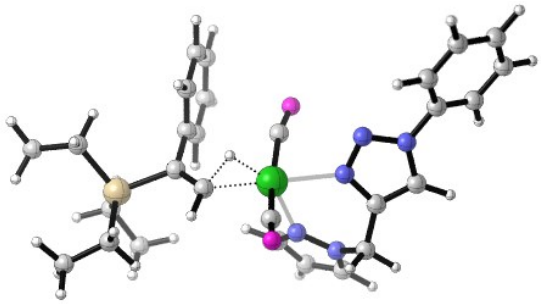

Figure S66. Calculated structure of the reductive elimination intermediate from C^{Si}-α.

Reductive elimination from C^H-(E)

C	-2.38272900	-2.09048800	-0.73791000
C	-3.74951300	-1.97889600	-0.68362400
H	-4.54379700	-2.67411500	-0.90504900
N	-2.84774400	-0.03769500	-0.12662500
N	-1.87989900	-0.87307500	-0.39382000
N	-3.98230300	-0.69932600	-0.30615100
C	-5.24192300	-0.04940500	-0.10380700
C	-5.39808400	1.26641200	-0.52641500
C	-6.27412700	-0.75447500	0.50602600
C	-6.62656600	1.88678200	-0.32928800
H	-4.57449600	1.78770000	-1.00146700
C	-7.50100100	-0.12383400	0.68369200
H	-6.11939300	-1.76960200	0.85856100
C	-7.67707800	1.19378200	0.26856100
H	-6.76456200	2.91282300	-0.65318700
H	-8.31478200	-0.66078500	1.15914100
H	-8.63458500	1.68276300	0.41376400
C	-1.53095700	-3.26201600	-1.13330100
H	-2.15505400	-4.15484700	-1.21613000
H	-1.06874000	-3.08616100	-2.10860500
N	-0.45856900	-3.52479300	-0.19963500
C	-0.46470100	-4.31339200	0.90249600
C	0.76687100	-4.16764900	1.50366800
H	-1.31972900	-4.92330100	1.15656800
C	1.45263000	-3.25067100	0.68566600
H	1.12467000	-4.66756400	2.39059600
H	2.45517600	-2.85755000	0.78858000
N	0.70326600	-2.86007600	-0.34326000
Rh	0.15835800	-0.22841700	-0.09516500
C	-0.20676700	-0.22264100	1.80893700
C	0.30719800	0.00092600	-2.00619900
O	-0.46413500	-0.22238300	2.91824200
O	0.30314100	0.09103600	-3.14257200
C	2.13249500	0.25895100	0.33939800
C	3.11438600	-0.00392900	-0.56368000
Si	1.27605900	2.25422500	0.19071100
C	1.66247500	2.88250800	-1.57460100
H	0.71865200	2.92952500	-2.13273600
H	2.29622200	2.16368900	-2.10428700
C	2.55142300	2.85021700	1.49683100
H	3.55286000	2.69815300	1.07431800
H	2.48843100	2.17504500	2.36085200
C	-0.45608500	2.90280100	0.73494300
H	-0.52925100	2.80773100	1.82692400
H	-1.24412900	2.26774000	0.31925400
C	-0.71415200	4.35916100	0.31671200
H	-1.69527200	4.68832700	0.67510000
H	0.03003000	5.05138900	0.72095000
H	-0.71036000	4.46679700	-0.77354100
C	2.34813700	4.25690800	-1.60382800
H	2.55164000	4.56198100	-2.63511600
H	1.72482300	5.03291400	-1.14881900
H	3.30346100	4.23860800	-1.06889200
C	2.38845900	4.29173700	1.99382300
H	1.42355200	4.43771700	2.49032100
H	3.16982700	4.53178300	2.72235200
H	2.46317700	5.02086500	1.18148900
H	2.41407600	0.13027000	1.38387700
H	2.90965500	0.14608200	-1.62345700
C	4.47015900	-0.47404300	-0.28794700
C	4.92610000	-0.78619700	1.00376000
C	5.35311900	-0.62579500	-1.36769800
C	6.22528600	-1.22933800	1.20306900
H	4.26572000	-0.68198600	1.85942900
C	6.65368600	-1.07130900	-1.16757200
H	5.01278300	-0.38995300	-2.37296100
C	7.09199800	-1.37308600	0.11890900
H	6.56686000	-1.46518000	2.20587500
H	7.32445000	-1.18246500	-2.01325500
H	8.10738400	-1.72138500	0.27938400

Thermal correction to Gibbs Free Energy= 0.494426
E(RM06L) = -1911.44090421

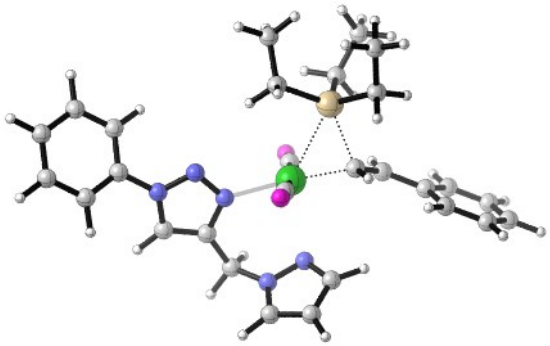

Figure S67. Calculated structure of the reductive elimination intermediate from C^H-(*E*).

Reductive elimination from C^H-α

C	-2.27279900	-1.91691200	-0.63973200
C	-3.60235500	-1.62037300	-0.80764600
H	-4.44692900	-2.22139200	-1.10568500
N	-2.52452300	0.22616200	-0.24053300
N	-1.65949700	-0.75100700	-0.29824400
N	-3.70229200	-0.29368100	-0.55375800
C	-4.87229800	0.53143600	-0.59491100
C	-4.77693200	1.81041300	-1.13265500
C	-6.07030500	0.02688200	-0.10035600
C	-5.91955400	2.60145100	-1.17242200
H	-3.82872000	2.17247400	-1.51418700
C	-7.20703200	0.82623000	-0.15969200
H	-6.11390300	-0.96249400	0.34457700
C	-7.13213500	2.11063200	-0.69283200
H	-5.86248100	3.60139900	-1.58896300
H	-8.14836200	0.44709300	0.22327600
H	-8.02073600	2.73174600	-0.73253900
C	-1.54629700	-3.21879600	-0.79828600
H	-2.26973400	-4.01730100	-0.98665600
H	-0.86048200	-3.17973100	-1.64818700
N	-0.73665900	-3.54709800	0.35486600
C	-1.14953300	-3.86405000	1.60817300
C	-0.01366600	-4.03884300	2.36704000
H	-2.19835200	-3.95460000	1.85261500
C	1.04720300	-3.80091900	1.47016800
H	0.04128100	-4.31924400	3.40784200
H	2.11223000	-3.84165100	1.65243100
N	0.60445800	-3.49923500	0.25520400
Rh	0.36759500	-0.33780800	0.17969800
C	-0.15856300	-0.46203800	2.04062600
C	0.65602800	-0.19399900	-1.74492900
O	-0.55527600	-0.52843700	3.10549600
O	0.68588000	-0.14013800	-2.88038300
C	2.48703600	-0.11623400	0.58761400
C	3.40977000	-0.49014500	-0.54167400
C	3.25211700	-1.72665200	-1.18188400
C	4.46632800	0.33789100	-0.93389700
C	4.11904600	-2.11049800	-2.20105500
H	2.44668000	-2.38991900	-0.87497600
C	5.32923100	-0.04632000	-1.95626000
H	4.62228200	1.29291000	-0.44182900
C	5.15584000	-1.26984400	-2.59649600
H	3.98460000	-3.07418600	-2.68292000
H	6.14165100	0.61201400	-2.24777300
H	5.82953600	-1.56920800	-3.39300100
C	2.82747300	-0.58997300	1.80846000
H	3.71621600	-1.20522600	1.94402000
H	2.27173000	-0.36329400	2.71428500
Si	1.79668400	1.96693400	0.63309800
C	2.02680200	2.59008800	-1.15944200
H	1.02586800	2.71947900	-1.59154300
H	2.52764400	1.82173200	-1.75621200
C	3.18286100	2.53277400	1.84031100
H	4.15700200	2.29024600	1.40039900
H	3.09670700	1.89265500	2.72744400
C	0.14414400	2.66283300	1.35016600
H	0.17220800	2.57301800	2.44427900
H	-0.71467500	2.07949600	1.00589100
C	-0.08222500	4.12945200	0.94413700
H	-1.00246900	4.50741600	1.40137700
H	0.73335200	4.78711100	1.25627200
H	-0.19035400	4.22700800	-0.14134200
C	2.81757200	3.90006600	-1.27624700
H	2.93155900	4.18602600	-2.32651000
H	2.31784000	4.72682700	-0.76155300
H	3.82220100	3.80054900	-0.85043600
C	3.15421700	3.99939000	2.28461000
H	2.24118200	4.23217600	2.84175700
H	4.00027500	4.20728600	2.94774800
H	3.22270500	4.69280200	1.44133500

Thermal correction to Gibbs Free Energy= 0.496989
E(RM06L) = -1911.41872491

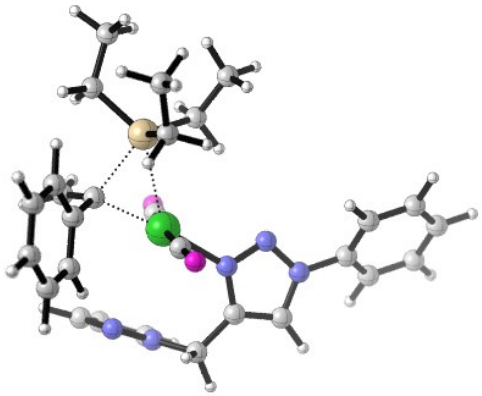

Figure S68. Calculated structure of the reductive elimination from C^H-α intermediate.

RhClCp* based compounds

Catalyst

C	1.05422800	1.80356800	-0.63736100
C	2.42138900	1.90158600	-0.58197400
H	3.10548200	2.70392300	-0.80856600
N	1.81444600	-0.14930500	-0.01462200
N	0.73941100	0.53103100	-0.28628900
N	2.84040200	0.67199300	-0.19938000
C	4.18114300	0.21234800	-0.00316200
C	4.54404100	-1.03642300	-0.49662600
C	5.08380000	1.02926600	0.66913800
C	5.84963300	-1.47432200	-0.30469200
H	3.81936100	-1.64243300	-1.02948700
C	6.38997500	0.58272100	0.84096000
H	4.76889100	1.98808900	1.06951500
C	6.77166100	-0.66650600	0.35779300
H	6.14959900	-2.44482600	-0.68537900
H	7.10543900	1.20863800	1.36345100
H	7.79061300	-1.01169000	0.49786400
C	0.01777700	2.78346900	-1.07486700
H	0.45046500	3.78277800	-1.14173900
H	-0.36864200	2.48852800	-2.05527900
N	-1.10157300	2.86457000	-0.14660500
C	-1.70498200	3.99445300	0.27995600
C	-2.82794600	3.62915600	0.98934300
H	-1.29617300	4.96508200	0.04080900
C	-2.83559900	2.23210500	0.93545400
H	-3.54012900	4.27793000	1.47414300
H	-3.54475000	1.54024000	1.35979200
N	-1.79187300	1.77404200	0.24533700
Rh	-1.23168600	-0.27380000	-0.15568000
C	-2.94654600	-1.45251000	0.40807300
C	-2.14170700	-2.22889000	-0.49515900
C	-2.15534300	-1.21276300	1.59961200
C	-0.83530400	-2.37196200	0.07423500
C	-0.85982400	-1.76150700	1.39151400
C	-4.38708300	-1.10999500	0.18498400
H	-5.01057200	-2.00430300	0.29385600
H	-4.74652200	-0.36817000	0.90149500
H	-4.53782200	-0.70692400	-0.81983300
C	-2.60115300	-2.79512200	-1.79585400
H	-3.00554900	-3.79858900	-1.61429700
H	-3.38108600	-2.18030400	-2.24737000
H	-1.78241200	-2.87346800	-2.51251500
C	-2.60841000	-0.56613200	2.87237700
H	-2.55741100	-1.29545700	3.68793200
H	-1.97543800	0.28386600	3.14300800
H	-3.64201100	-0.22077700	2.80921000
C	0.25279700	-1.78032700	2.38834900
H	0.24573500	-2.73569900	2.92612100
H	1.22370100	-1.67059700	1.90063600
H	0.14301200	-0.97735200	3.12131300
C	0.30902600	-3.12731100	-0.52251400
H	0.23814600	-4.18804400	-0.25585500
H	0.30519200	-3.04597500	-1.61195000
H	1.26270000	-2.74161600	-0.15664400
Cl	-1.47818300	0.21367300	-2.48889300

Thermal correction to Gibbs Free Energy= 0.396597
E(RM06L) = -1698.81492915

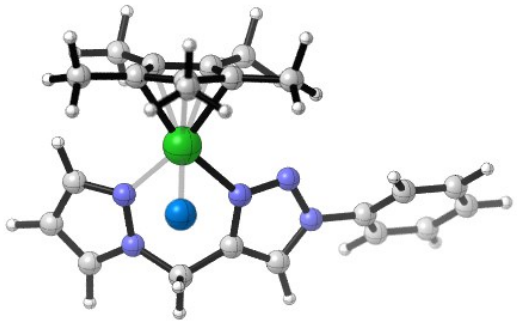

Figure S69. Calculated structure of **$Rh^{III}C_0Ph$**.

Rh-H-Si intermediate

C	2.61045200	0.21129200	0.15508400
C	3.81317800	0.85237400	0.32249100
H	4.08571900	1.80641400	0.74578800
N	4.12620000	-1.13925300	-0.60292100
N	2.85304400	-1.00204300	-0.40961700
N	4.72552700	-0.02154200	-0.16452200
C	6.14419300	0.12394200	-0.24110800
C	6.94910900	-0.99460800	-0.04866700
C	6.68910900	1.37710100	-0.50356700
C	8.32963200	-0.84623100	-0.11992300
H	6.49550100	-1.95905100	0.14887400
C	8.07246600	1.51285500	-0.55662700
H	6.04591100	2.23196700	-0.68852900
C	8.89272800	0.40397400	-0.36638500
H	8.96711400	-1.71192200	0.02597400
H	8.50704300	2.48567300	-0.76114800
H	9.97112600	0.51316700	-0.41474900
C	1.22319400	0.64136900	0.48979000
H	1.19084100	1.71059500	0.72350600
H	0.55906700	0.46241700	-0.35739100
N	0.67719700	-0.10908900	1.61769900
C	1.28147700	-0.33492800	2.80295300
C	0.35538900	-0.91008000	3.64657900
H	2.31795100	-0.07031100	2.95136500
C	-0.81706300	-0.99048400	2.88729800
H	0.50379800	-1.22537800	4.66739000
H	-1.79664900	-1.36163200	3.15109400
N	-0.61526500	-0.50010300	1.66378000
Rh	-1.96070400	-0.74244100	0.02313100
H	-1.67682100	0.96211900	-0.42290000
Cl	-3.73142400	-0.19666300	1.52488200
C	-1.04309500	-1.67157100	-1.72805500
C	-1.03484300	-2.59885300	-0.64127900
C	-2.43037800	-1.33613300	-2.00848000
C	-2.39880700	-2.81382200	-0.21784700
C	-3.26221000	-2.06186500	-1.10950200
C	-2.86412500	-3.74140900	0.85695500
H	-2.06844300	-3.94760900	1.57616800
H	-3.71278700	-3.31431900	1.39682900
H	-3.17805500	-4.69466100	0.41609700
C	0.17158700	-3.23143900	-0.02818800
H	0.30896300	-4.23015600	-0.45919500
H	1.07784800	-2.64960200	-0.21406800
H	0.05101500	-3.34652800	1.05220000
C	0.13612100	-1.26596500	-2.55362500
H	0.22251500	-1.94042200	-3.41389800
H	0.02533500	-0.25173900	-2.94432600
H	1.06991500	-1.32543800	-1.98903400
C	-2.89834700	-0.43417600	-3.10549100
H	-3.84105800	0.05203300	-2.84507200
H	-2.16221100	0.34194600	-3.32537400
H	-3.05777700	-1.01857200	-4.01908800
C	-4.75437000	-2.08446400	-1.09259100
H	-5.10607300	-2.93939900	-1.68216400
H	-5.13619400	-2.17871600	-0.07465000
H	-5.17480900	-1.17355200	-1.52301800
Si	-2.11865000	2.44788600	-0.13804800
C	-1.90030300	2.81415300	1.70899300
H	-2.79049700	2.45931900	2.23755400
H	-1.06987100	2.20816000	2.09329600
C	-3.87199700	2.61998800	-0.83118300
H	-3.83648800	2.47370200	-1.91857600
H	-4.48231600	1.81129900	-0.41397300
C	-0.83804500	3.38819100	-1.18955400
H	-1.14961100	4.44145700	-1.21119800
H	0.13137000	3.38068200	-0.67521600
C	-0.68175000	2.86125000	-2.61830100
H	-1.63483100	2.87102500	-3.15909600
H	0.02708200	3.46474600	-3.19356800
H	-0.30902300	1.83000900	-2.61574900
C	-1.64668100	4.30277700	1.99360800
H	-1.54078200	4.47479500	3.06910700
H	-0.73140000	4.66179800	1.50940100

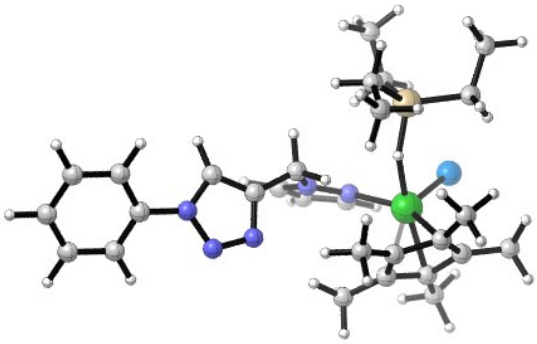

Figure S70. Calculated structure of the Rh-H-Si intermediate.

H	-2.47278000	4.93093600	1.64335600
C	-4.50224600	3.98250400	-0.50240600
H	-5.49859300	4.06454400	-0.94696900
H	-4.61409400	4.11608800	0.57877800
H	-3.90311600	4.81659500	-0.88581100

Thermal correction to Gibbs Free Energy= 0.587028
E(RM06L) = -2226.65529716

C^{Si}-(E) intermediate, two N coordinated

C	-2.62347500	-1.17088600	1.56970000
C	-3.97083200	-0.92342900	1.61661100
H	-4.72347300	-1.09373100	2.36990400
N	-3.14079800	-0.18536000	-0.30038100
N	-2.16310000	-0.70858400	0.37815800
N	-4.24146600	-0.31898000	0.43508800
C	-5.49949200	0.16304300	-0.04539800
C	-5.54325000	1.37843500	-0.72043700
C	-6.64471600	-0.59339200	0.18008200
C	-6.77104200	1.84176200	-1.17949000
H	-4.63274600	1.94644400	-0.87620600
C	-7.86759200	-0.10934700	-0.27302500
H	-6.58235100	-1.55491200	0.68051300
C	-7.93131100	1.10431900	-0.95278100
H	-6.82118200	2.78787400	-1.70793600
H	-8.76847900	-0.68970800	-0.10461900
H	-8.88668500	1.47522700	-1.30878900
C	-1.65743500	-1.66551300	2.59189400
H	-2.17119400	-2.03477700	3.48030400
H	-1.04224600	-2.47474500	2.18893200
N	-0.79447000	-0.56922400	3.01058600
C	-0.67615800	-0.03545300	4.24466700
C	0.17144100	1.04628900	4.15118500
H	-1.19719500	-0.46700100	5.08677800
C	0.52621300	1.10783100	2.79984300
H	0.49643900	1.69763700	4.94698800
H	1.19801100	1.78190100	2.29373800
N	-0.06453400	0.13130600	2.11091600
Rh	0.07636100	-0.41164100	0.06343500
H	-0.25444900	0.99675200	-0.32160800
C	2.01158500	0.18202100	0.25423700
C	2.93852900	-0.87594200	0.77386600
C	4.26204400	-0.95875200	0.31243100
C	2.55102700	-1.78305600	1.76928000
C	5.14582200	-1.91122400	0.80383400
H	4.60506000	-0.26203600	-0.44415400
C	3.43272400	-2.73906300	2.26618000
H	1.55071100	-1.73657200	2.18456700
C	4.73352500	-2.81476900	1.78052400
H	6.16180100	-1.94771000	0.42175300
H	3.10054400	-3.42271300	3.04191500
H	5.42155200	-3.56104400	2.16501800
C	2.48610900	1.43377100	0.11015700
H	3.54381100	1.53370500	0.38610300
Si	1.84508500	3.18054800	-0.27531500
C	2.33401800	4.25414900	1.23647400
H	2.21732800	5.30554100	0.94385200
H	1.60126600	4.09492700	2.04001300
C	-0.04079200	3.41879200	-0.50835300
H	-0.41414100	2.79734200	-1.33024400
H	-0.55445000	3.07258800	0.39911600
C	3.75272300	4.02578500	1.77113600
H	4.00029600	4.74101000	2.56245100
H	3.86794700	3.01928100	2.18905700
H	4.50477300	4.13855000	0.98096300
C	-0.41626800	4.88308500	-0.78342600
H	-1.50208300	5.00381100	-0.86228800
H	-0.06937800	5.54824200	0.01463300
H	0.02156500	5.23571900	-1.72343200
C	2.80054900	3.81095000	-1.81825900
H	3.71898000	3.21765400	-1.91886800
H	2.20467300	3.59240100	-2.71507200
C	3.15972600	5.30282500	-1.79812400

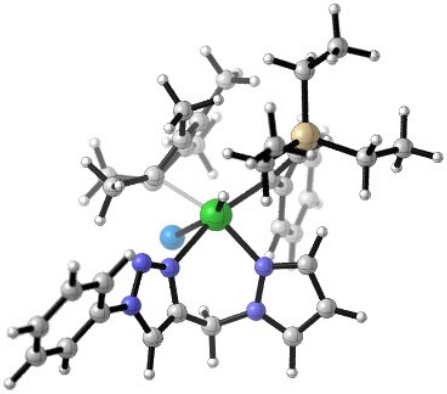

Figure S71. Calculated structure of the C^{Si}-(*E*) intermediate, two N coordinated.

H	3.82309500	5.54168000	-0.96008600
H	3.67416000	5.59670400	-2.71904900
H	2.27125000	5.93587200	-1.70047600
Cl	0.26015700	-3.36625400	-0.03124300
C	0.58199100	-2.78706100	-1.75658500
C	-0.12593700	-1.44122700	-1.94649000
C	2.05182200	-2.48013800	-1.95467800
C	0.85680300	-0.53217400	-2.30618200
C	2.18142600	-1.19937900	-2.34701000
C	0.63757500	0.77185200	-2.99841600
H	-0.38197600	1.14082100	-2.87924700
H	1.33633600	1.52781900	-2.63348700
H	0.83417400	0.63613600	-4.06991700
C	-1.53274600	-1.41678300	-2.48161200
H	-1.52546500	-1.74571100	-3.52843800
H	-2.19051400	-2.08479400	-1.92207600
H	-1.96746900	-0.41840100	-2.44381200
C	0.09065300	-3.87838900	-2.70057900
H	0.26916100	-3.56223700	-3.73381800
H	0.63599100	-4.80864500	-2.52447400
H	-0.97601600	-4.07179200	-2.56724300
C	3.10831700	-3.50594300	-1.72574700
H	4.09715100	-3.12663000	-1.98847100
H	3.13426400	-3.78633000	-0.66538200
H	2.92537600	-4.41661100	-2.30738300
C	3.39669600	-0.48062600	-2.83696500
H	3.29230400	-0.23721900	-3.90138800
H	3.53168400	0.46321700	-2.29840100
H	4.30060600	-1.08134900	-2.72108500

Thermal correction to Gibbs Free Energy= 0.703207
E(RM06L) = -2535.07488222

C^{Si}-(E) intermediate, one N coordinated

C	-1.83057900	-2.24258400	1.99890700
C	-2.56116900	-1.18043200	1.52181800
H	-2.47915900	-0.11430900	1.65487800
N	-3.36054700	-3.09209800	0.72906200
N	-2.35438200	-3.38873000	1.49123000
N	-3.49893600	-1.75556800	0.73302200
C	-4.45622300	-1.11095100	-0.10428100
C	-4.84776000	-1.73429100	-1.28643800
C	-4.96096800	0.13464600	0.25885200
C	-5.75934500	-1.09047000	-2.11643100
H	-4.45113300	-2.71175700	-1.53623500
C	-5.86290400	0.77096700	-0.58771800
H	-4.67490100	0.59676000	1.19854900
C	-6.26245200	0.16253400	-1.77481200
H	-6.07557000	-1.57288600	-3.03545100
H	-6.26626600	1.73870800	-0.30763500
H	-6.97214000	0.66004400	-2.42744000
C	-0.65226400	-2.27034400	2.92307900
H	-0.91046000	-2.75753800	3.86659600
H	0.17424500	-2.83540200	2.48089500
N	-0.20491700	-0.92790000	3.25188900
C	-0.24980300	-0.32860800	4.45910700
C	0.21853300	0.95922700	4.30888800
H	-0.60630500	-0.86419800	5.32679000
C	0.52938400	1.07018100	2.95163500
H	0.32820400	1.71220800	5.07318700
H	0.93819700	1.90372200	2.40191300
N	0.26979300	-0.07468400	2.31271400
Rh	0.42608400	-0.58055400	0.27591700
H	-0.69891400	0.37171200	-0.00348200
C	1.68487500	0.95975400	0.09222600
C	3.10185600	0.54775200	0.31899200
C	4.12312400	1.06542700	-0.49264000
C	3.47005300	-0.30625900	1.36712700
C	5.45285300	0.72597800	-0.28007100
H	3.86977700	1.74851200	-1.29550400
C	4.80227800	-0.64974100	1.58007100
H	2.71538700	-0.69769000	2.04087100
C	5.79894200	-0.14232500	0.75339100
H	6.22240300	1.14270000	-0.92286500

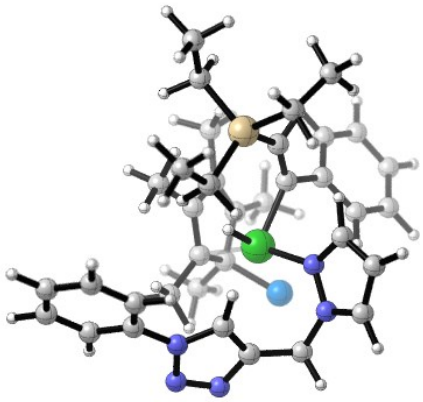

Figure S72. Calculated structure of the C^{Si}-(*E*) intermediate, one N coordinated.

H	5.05985100	-1.31030100	2.40218800
H	6.83750900	-0.41034200	0.91914500
C	1.34673000	2.23840500	-0.12076900
H	2.21750000	2.90596800	-0.12649400
Si	-0.21733000	3.31867200	-0.22649100
C	-0.02573900	4.60098600	1.18200000
H	-0.77728900	5.38421200	1.01988200
H	-0.30107400	4.12208300	2.13195500
C	-1.91493500	2.47249900	0.04742400
H	-2.08473800	1.66517900	-0.67518600
H	-1.90562100	2.00969300	1.04430900
C	1.36247000	5.24110800	1.30250300
H	1.36776900	6.03888800	2.05204900
H	2.12048100	4.50765800	1.60013300
H	1.68899900	5.68204600	0.35310800
C	-3.07690900	3.47249200	-0.04656000
H	-4.03395300	2.98173800	0.15846600
H	-2.96646200	4.29483200	0.66807500
H	-3.14447900	3.90742200	-1.04920000
C	-0.17959900	4.21165000	-1.92396900
H	0.85093100	4.19287600	-2.30212500
H	-0.77209600	3.62606000	-2.64024200
C	-0.68825900	5.65981500	-1.90462000
H	-0.07192200	6.29073900	-1.25562200
H	-0.66485200	6.09743500	-2.90784100
H	-1.71882800	5.72665000	-1.54009700
Cl	1.94367600	-3.00867200	0.16997100
C	1.55730600	-2.60698000	-1.59475800
C	0.27532700	-1.77946000	-1.58647500
C	2.60146700	-1.67540700	-2.17649200
C	0.56136600	-0.58051300	-2.21178700
C	1.99622400	-0.54692800	-2.59341700
C	-0.41506500	0.39623900	-2.78000900
H	-1.43182200	0.22943400	-2.41993300
H	-0.11827000	1.42146100	-2.54342900
H	-0.41466000	0.30109200	-3.87301700
C	-1.06785700	-2.44697900	-1.49577600
H	-1.25859300	-3.02295400	-2.41014900
H	-1.12068000	-3.14601900	-0.65680000
H	-1.87582600	-1.71903200	-1.39458200
C	1.43430800	-3.91821700	-2.35877000
H	1.17856700	-3.69734800	-3.40078100
H	2.38095700	-4.46363700	-2.34175000
H	0.65840600	-4.55588500	-1.92827600
C	4.04433900	-2.04366400	-2.22414200
H	4.63413900	-1.28692300	-2.74409800
H	4.44139900	-2.13161300	-1.20507300
H	4.20254100	-3.00454200	-2.72665500
C	2.56299900	0.60016200	-3.36588300
H	2.15494800	0.61581300	-4.38382100
H	2.29730900	1.55346700	-2.89632200
H	3.65011800	0.54303600	-3.44440200

Thermal correction to Gibbs Free Energy= 0.701686
E(RM06L) = -2535.06609306

C^{Si}-(Z) intermediate, two N coordinated

C	-2.69598500	-0.29768400	1.91776000
C	-3.97003000	0.19189000	2.06138400
H	-4.59403900	0.37989300	2.92068100
N	-3.39844600	0.20350000	-0.07736500
N	-2.39500300	-0.26647800	0.59413700
N	-4.36137400	0.48267400	0.79739100
C	-5.59647000	1.04145500	0.34502200
C	-5.56177600	2.02479000	-0.63907900
C	-6.79201300	0.59073300	0.89440400
C	-6.76432100	2.56460800	-1.08160500
H	-4.60900000	2.36269000	-1.03294000
C	-7.98547700	1.15130600	0.45065000
H	-6.79404400	-0.19640200	1.64241200
C	-7.97236700	2.13349900	-0.53675400
H	-6.75496800	3.33487600	-1.84552300
H	-8.92607200	0.81083700	0.87041600
H	-8.90612800	2.56491500	-0.88195300
C	-1.65949400	-0.71433100	2.90941400
H	-2.07488200	-0.77602600	3.91628100
H	-1.24971200	-1.69476800	2.64522000
N	-0.57561400	0.25319800	2.94179400
C	-0.19258400	1.04576100	3.96740300
C	0.76856000	1.90853600	3.48874900
H	-0.63267100	0.93545200	4.94772400
C	0.90520700	1.58193500	2.13420000
H	1.29781200	2.67120700	4.03769900
H	1.54723600	2.00393700	1.37676900
N	0.08871000	0.58198200	1.81334800
Rh	-0.14931400	-0.36564900	-0.09424500
H	0.09636000	-1.65046000	0.75305000
C	1.90285500	-0.28621000	-0.18760200
C	2.68749100	-1.31351600	0.55528700
C	3.75115800	-1.94750100	-0.10178900
C	2.45562200	-1.65412700	1.89546800
C	4.56645900	-2.86512300	0.55269800
H	3.93559800	-1.71444200	-1.14606900
C	3.27123900	-2.56822900	2.55461900
H	1.65298400	-1.17318100	2.44343700
C	4.33144500	-3.17827400	1.88780100
H	5.38463700	-3.33588400	0.01598700
H	3.08462700	-2.79705800	3.59983800
H	4.96682700	-3.89023800	2.40493000
C	2.49999200	0.73865500	-0.80752400
Cl	-0.59588800	1.89319500	-0.91282400
C	-1.59003000	-2.74007000	-1.02648600
C	-2.50294200	-2.07299900	-1.81019600
C	-0.20417700	-2.19096400	-1.25613800
C	-1.79890100	-1.00099400	-2.42499200
C	-0.36034000	-1.08067900	-2.12978300
C	-2.38475600	0.07071600	-3.23215900
H	-2.18797800	1.00926200	-2.67877500
H	-1.84787700	0.17671100	-4.18258500
H	-3.45347700	-0.05073600	-3.40850000
C	-3.97827600	-2.30629100	-1.91987900
H	-4.24552000	-2.62201700	-2.93411400
H	-4.31257900	-3.09017500	-1.23610700
H	-4.53830300	-1.39465300	-1.69213500
C	-1.84390900	-3.84581100	-0.07210400
H	-1.60674000	-4.80427900	-0.55427000
H	-1.18827200	-3.76026600	0.79970400
H	-2.88492700	-3.88572500	0.25552500
C	0.92261000	-3.18472700	-1.32142600
H	1.84600100	-2.71643300	-1.65587200
H	1.11979700	-3.66021600	-0.35766700
H	0.65566700	-3.96321900	-2.04813300
C	0.62085800	-0.57638200	-3.15513200
H	0.42702800	-1.05413000	-4.12398700
H	0.53055900	0.50698500	-3.27301100
H	1.64711200	-0.79272000	-2.86193100
H	1.85870600	1.42138800	-1.36423700
Si	4.30489400	1.36543200	-0.68001600
C	4.14296600	3.20939100	-1.17137400
H	3.18456000	3.57162600	-0.77376700

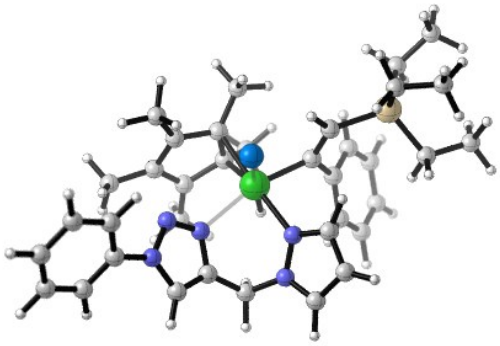

Figure S73. Calculated structure of the C^{Si}-(*Z*) intermediate, two N coordinated.

H	4.04775800	3.26971600	-2.26419800
C	5.26970000	4.13303400	-0.69227100
H	5.09077800	5.16805800	-1.00294300
H	5.35029700	4.12828400	0.40073700
H	6.24320200	3.83361600	-1.09423600
C	4.93744800	1.22782800	1.12260900
H	4.57114600	0.29437200	1.56392000
H	4.47876700	2.04070000	1.70284100
C	6.46450200	1.28754600	1.26061600
H	6.76992800	1.21402400	2.30997800
H	6.94167300	0.46117500	0.72171300
H	6.87586300	2.22154100	0.86293100
C	5.47385800	0.45055400	-1.89556700
H	4.87563500	0.10489900	-2.74984800
H	5.84909600	-0.45378100	-1.40004400
C	6.65733700	1.28292800	-2.40546800
H	6.31785800	2.17835000	-2.93724600
H	7.30281800	1.61115300	-1.58380300
H	7.27692600	0.70336600	-3.09835900

Thermal correction to Gibbs Free Energy= 0.697948
E(RM06L) = -2535.08686280

C^{Si}-(Z) intermediate, one N coordinated

C	3.18044400	1.60139400	1.48078000
C	3.36970100	0.26324500	1.23792300
H	2.69162700	-0.57661000	1.19196700
N	5.28861200	1.37102600	1.07277700
N	4.37348500	2.23935700	1.37255700
N	4.69680200	0.16507600	0.98859200
C	5.44531700	-0.99698500	0.63534700
C	6.65783100	-0.84337800	-0.03228700
C	4.93927700	-2.25953400	0.93449400
C	7.37017600	-1.97856300	-0.40317200
H	7.03370100	0.15062900	-0.24454600
C	5.65812700	-3.38496400	0.54459500
H	4.00419000	-2.37429100	1.47304000
C	6.87239600	-3.24878300	-0.12272300
H	8.31890200	-1.86589500	-0.91761200
H	5.26884200	-4.37086800	0.77649100
H	7.43214000	-4.13011000	-0.41801600
C	1.92344700	2.36825900	1.74655900
H	2.12628800	3.19607200	2.42932500
H	1.50495000	2.79832800	0.83026200
N	0.90100800	1.53753400	2.34716700
C	0.63115800	1.41448900	3.66263300
C	-0.23038800	0.34974400	3.82052700
H	1.08434400	2.08295800	4.38001200
C	-0.42376700	-0.14909700	2.53107000
H	-0.66028500	-0.01825700	4.73857900
H	-1.03567800	-0.96980000	2.19208000
N	0.27272300	0.56761000	1.64406000
Rh	0.13519400	0.31632700	-0.46475700
H	-0.33197900	1.79047000	-0.31181200
C	-1.92166200	0.11283500	-0.19493500
C	-2.68544200	1.37731500	-0.02118300
C	-3.76098200	1.63670700	-0.88249000
C	-2.40121700	2.32075800	0.97903500
C	-4.53187000	2.78804400	-0.74650000
H	-3.99825000	0.91896200	-1.66000300
C	-3.17284500	3.46898700	1.11657100
H	-1.59376900	2.14234600	1.68031400
C	-4.23993700	3.71026700	0.25315200
H	-5.36254500	2.96038700	-1.42394200
H	-2.94693700	4.17409900	1.91063900
H	-4.84036700	4.60744800	0.36340500
C	-2.46424200	-1.10230200	-0.25284800
Cl	0.68301200	-1.95972300	0.13385700
C	0.48042600	1.83940500	-2.03867200
C	1.89789800	1.44175800	-1.85976500
C	-0.23525200	0.70471900	-2.58881600
C	1.99101700	0.09113900	-2.11592700
C	0.64351700	-0.39649800	-2.50949700

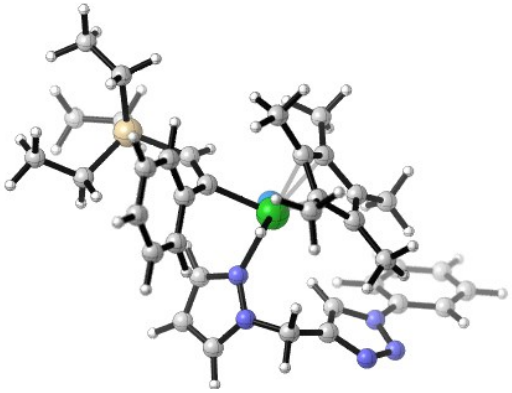

Figure S74. Calculated structure of the C^{Si}-(*Z*) intermediate, one N coordinated.

C	3.19038500	-0.78836900	-2.07441700
H	3.03224100	-1.60729300	-1.36241500
H	3.36301900	-1.23864500	-3.05856100
H	4.08984100	-0.24355700	-1.78390000
C	3.01015200	2.40820200	-1.61869200
H	3.23208100	2.93188400	-2.55715300
H	2.76142100	3.17321200	-0.88026600
H	3.92295200	1.91198900	-1.28721500
C	0.02145100	3.26305500	-2.14041200
H	0.25360700	3.63198700	-3.14669900
H	-1.05569000	3.35277500	-1.97937200
H	0.53537700	3.90510000	-1.42115500
C	-1.55802900	0.73704200	-3.28104000
H	-2.11989800	-0.18383700	-3.11269600
H	-2.16797100	1.57622300	-2.94537800
H	-1.38741500	0.84728500	-4.35864800
C	0.36072000	-1.75603400	-3.05168500
H	0.52740300	-1.73957300	-4.13658900
H	1.01029100	-2.50902600	-2.60528900
H	-0.67687600	-2.04540600	-2.86982700
H	-1.80664900	-1.94617600	-0.45743500
Si	-4.25686200	-1.63531100	0.19603500
C	-4.04594900	-3.48405500	0.63709300
H	-3.08341700	-3.59199000	1.15589000
H	-3.94431000	-4.05428900	-0.29638200
C	-5.15732300	-4.09049200	1.50347600
H	-4.95671300	-5.14545300	1.71746100
H	-5.24033100	-3.57099300	2.46467000
H	-6.13473900	-4.03525000	1.01325300
C	-4.88335200	-0.65041100	1.71006800
H	-4.54637300	0.38943400	1.63241500
H	-4.39746500	-1.06301500	2.60471000
C	-6.40836600	-0.67598300	1.88413300
H	-6.71235400	-0.10943400	2.77049400
H	-6.91309900	-0.22913300	1.02015200
H	-6.79098600	-1.69565900	1.99885100
C	-5.42604200	-1.42173000	-1.30844000
H	-4.82978100	-1.51112700	-2.22707600
H	-5.82040900	-0.39765600	-1.29773000
C	-6.59280600	-2.41733100	-1.35824200
H	-6.23542800	-3.45151900	-1.40557100
H	-7.23506700	-2.32891200	-0.47566000
H	-7.21950300	-2.24421900	-2.23938900

Thermal correction to Gibbs Free Energy= 0.699540
E(RM06L) = -2535.09861785

C^{Si}-α intermediate, two N coordinated

C	-1.50670700	1.44590500	-1.31013400
C	-2.72615300	1.90677900	-1.73847800
H	-3.02374900	2.56034600	-2.54318000
N	-3.00786500	0.51814300	-0.04001500
N	-1.73334800	0.60189800	-0.26908600
N	-3.62040200	1.30582200	-0.91768700
C	-5.04627400	1.39712500	-0.92040200
C	-5.78829300	0.22768800	-0.78536400
C	-5.65191700	2.64117800	-1.05703100
C	-7.17584900	0.31614700	-0.78194200
H	-5.28027600	-0.72740300	-0.70408300
C	-7.04154000	2.71147600	-1.06595300
H	-5.05012400	3.54143000	-1.13694800
C	-7.80175700	1.55311300	-0.92508400
H	-7.76939400	-0.58659100	-0.68260900
H	-7.52853700	3.67497300	-1.17250500
H	-8.88502100	1.61400700	-0.92925200
C	-0.12610500	1.66177200	-1.83748500
H	-0.12279300	2.44005300	-2.60219800
H	0.55146600	1.96859200	-1.03695800
N	0.39759500	0.45445300	-2.45246400
C	0.86839100	0.30596300	-3.71049400
C	1.21299500	-1.01699100	-3.87363600
H	0.91607800	1.14814800	-4.38520100
C	0.91224900	-1.61909500	-2.64668600
H	1.63005400	-1.48524300	-4.75075200
H	1.02895600	-2.64503200	-2.33354500
N	0.41804700	-0.72384900	-1.79767300
Rh	-0.21193100	-1.12807000	0.21272500
H	0.81925000	-2.23274600	0.28299500
C	1.35677700	0.15796300	0.58244500
C	2.64325200	0.09782600	0.22275800
Cl	-1.73777100	-2.58257200	-0.99855600
C	-0.96686900	0.06032400	2.80934000
C	-2.31674500	-0.23241500	2.68636900
C	-0.13198700	-1.10778300	2.39983400
C	-2.40348600	-1.52191900	2.13163400
C	-1.04283300	-2.09758000	1.96115700
C	-3.62006300	-2.25133700	1.76033100
H	-3.54737500	-2.46904600	0.68010500
H	-3.63839900	-3.23105400	2.25431900
H	-4.53749300	-1.70641200	1.98241800
C	-3.44065400	0.71197600	2.98573500
H	-3.61529800	0.78772600	4.06503800
H	-3.21638200	1.71551100	2.61078600
H	-4.37057100	0.39337600	2.51173600
C	-0.42391100	1.36093700	3.26108200
H	0.60330900	1.28405900	3.62197600
H	-0.42939800	2.06056200	2.41051600
H	-1.05429200	1.80450000	4.03761800
C	1.15038700	-1.38391100	3.13721900
H	1.58984600	-2.32769600	2.81209700
H	1.89239000	-0.59742100	2.98330300
H	0.94057600	-1.46330800	4.21167500
C	-0.84805100	-3.58767600	2.05396800
H	-1.17421500	-3.94404500	3.03983900
H	-1.42211600	-4.10343200	1.28135000
H	0.20098400	-3.85893300	1.92354100
Si	3.74640400	1.65302600	0.50079400
C	5.57280300	1.10022500	0.48962200
H	5.87881400	0.92588400	-0.54942600
H	5.62180300	0.11575600	0.97325300
C	6.55706000	2.05862400	1.17240900
H	7.57941300	1.67057200	1.11818000
H	6.55718500	3.04872800	0.70388200
H	6.31449200	2.19329800	2.23237500
C	3.36378000	2.87912300	-0.92757400
H	2.45545100	3.43846000	-0.65845600
H	3.10457200	2.29493300	-1.82152300
C	4.49334100	3.86030400	-1.26557800
H	4.21428800	4.52299800	-2.09188200
H	4.74909200	4.49254300	-0.40896700
H	5.40301200	3.32723800	-1.56258500

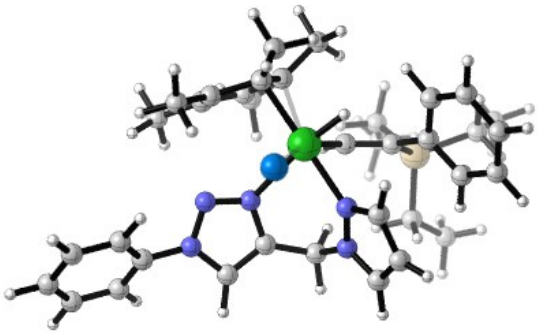

Figure S75. Calculated structure of the C^{Si}-α intermediate, two N coordinated.

C	3.28254400	2.46140900	2.17301700
H	3.72377300	1.85914500	2.97871900
H	2.19510500	2.39072600	2.30484600
C	3.70272700	3.93003700	2.32243700
H	4.78459100	4.05711700	2.21824800
H	3.22361100	4.55954800	1.56399500
H	3.41966600	4.32505700	3.30399200
C	3.28739800	-1.05662300	-0.45640100
C	3.88400800	-0.88938700	-1.71151400
C	3.34817300	-2.32075600	0.13921600
C	4.47967600	-1.95920000	-2.37063600
H	3.85643400	0.08524000	-2.19213400
C	3.94468800	-3.39456000	-0.51630000
H	2.93878900	-2.45689700	1.13462400
C	4.50587400	-3.21942000	-1.77843100
H	4.92464600	-1.80790000	-3.34957500
H	3.98082500	-4.36702800	-0.03433300
H	4.97391800	-4.05488700	-2.28938500
H	1.00261500	1.07032300	1.06757400

Thermal correction to Gibbs Free Energy= 0.700306
E(RM06L) = -2535.08505259

C^{Si}-α intermediate, one N coordinated

C	2.36191500	-2.45676100	-0.41447900
C	3.01141400	-1.32126000	-0.83372700
H	2.66167500	-0.37180900	-1.21109500
N	4.46691400	-2.83708200	-0.11163100
N	3.28459100	-3.35474900	0.01455300
N	4.31918700	-1.60184800	-0.62555600
C	5.44505600	-0.74975500	-0.82909900
C	6.60877000	-0.98140800	-0.09999800
C	5.35088300	0.31376700	-1.72325700
C	7.69329500	-0.12887600	-0.27554700
H	6.65813700	-1.82196200	0.58232600
C	6.44012700	1.16525800	-1.87674200
H	4.44929400	0.47556400	-2.30520800
C	7.61140100	0.94704500	-1.15621800
H	8.60563500	-0.30736300	0.28411400
H	6.37295300	1.99450500	-2.57331600
H	8.46032900	1.61032200	-1.28531900
C	0.89804600	-2.73827600	-0.28018900
H	0.70489000	-3.80424200	-0.41631100
H	0.52692900	-2.46084700	0.71256300
N	0.11792200	-2.01008400	-1.25773100
C	-0.31193500	-2.46756300	-2.45113800
C	-0.72294800	-1.38208200	-3.19533500
H	-0.27028500	-3.52176000	-2.68269700
C	-0.48054300	-0.27591500	-2.37715400
H	-1.13348300	-1.38629800	-4.19270700
H	-0.67206600	0.77000200	-2.55957800
N	0.04090300	-0.66193800	-1.21060100
Rh	0.20820300	0.65684400	0.49536700
H	-0.84723200	1.65193800	-0.00780200
C	-1.75418700	-0.09819300	0.56403400
C	-2.88442900	0.33216200	0.00908000
Cl	1.35742000	1.98903200	-1.11682700
C	0.28175500	-0.10404600	2.63660500
C	1.67817600	-0.23278600	2.29928100
C	-0.08860100	1.28996600	2.55835000
C	2.13451300	1.02110300	1.87388100
C	1.02619500	1.98088900	2.00459200
C	3.51572400	1.39356100	1.45901200
H	3.50753400	1.86056400	0.46782000
H	3.93054900	2.12264400	2.16456800
H	4.18128500	0.52930500	1.42773800
C	2.50515400	-1.44678900	2.57258000
H	2.76336000	-1.45280100	3.63920300
H	1.97628300	-2.37941200	2.36725100
H	3.43743300	-1.45678200	2.00754900
C	-0.53090700	-1.17299400	3.28856300
H	-1.58467500	-0.89764600	3.36044600
H	-0.45482300	-2.13044900	2.76287500
H	-0.15591000	-1.33482100	4.30640500

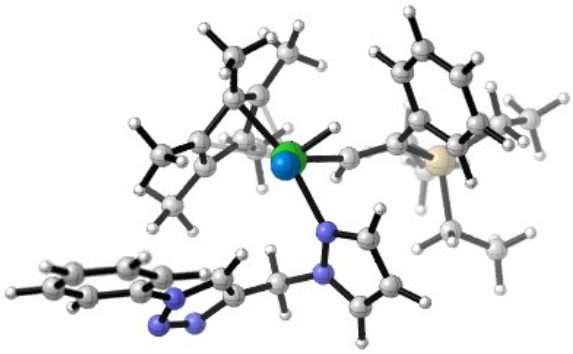

Figure S76. Calculated structure of the C^{Si}-α intermediate, one N coordinated.

C	-1.33358800	1.89046800	3.12896900
H	-1.44539000	2.93279400	2.82485800
H	-2.22689500	1.34036700	2.82257600
H	-1.27162500	1.86734800	4.22302300
C	1.16096500	3.46092700	1.84600400
H	1.49230200	3.89571500	2.79675900
H	1.88954800	3.70887300	1.07301300
H	0.20987000	3.92030600	1.56772200
Si	-4.40327300	-0.86478300	0.08085300
C	-5.95770900	0.12437100	-0.40706800
H	-5.95709400	0.26273100	-1.49569400
H	-5.86443700	1.13301900	0.01623500
C	-7.28509700	-0.50231300	0.04170600
H	-8.13314700	0.10912300	-0.28252100
H	-7.42556200	-1.50571500	-0.37437700
H	-7.33912900	-0.58492900	1.13281200
C	-4.01748900	-2.26959000	-1.16004700
H	-3.30094900	-2.95295300	-0.68180800
H	-3.47948300	-1.83201100	-2.01125000
C	-5.23890100	-3.04787100	-1.66553000
H	-4.94507400	-3.83343700	-2.36965900
H	-5.78502200	-3.52785100	-0.84687900
H	-5.94065100	-2.38638300	-2.18525200
C	-4.53782000	-1.54825100	1.86185800
H	-4.99420300	-0.77326200	2.49201900
H	-3.52465700	-1.69939400	2.25811400
C	-5.32238200	-2.86137700	1.99046700
H	-6.34866100	-2.76034300	1.62364500
H	-4.84601800	-3.66591000	1.41924100
H	-5.37805400	-3.18648900	3.03449700
C	-3.00578800	1.59223300	-0.76131600
C	-3.31343000	1.55447700	-2.12775700
C	-2.80469300	2.83862400	-0.15515800
C	-3.37432800	2.72599000	-2.87306500
H	-3.48906100	0.59610900	-2.60997100
C	-2.87189500	4.01362200	-0.90166700
H	-2.62469400	2.88549000	0.91388600
C	-3.14759700	3.95949400	-2.26322500
H	-3.60378600	2.67868000	-3.93310300
H	-2.71856800	4.97142200	-0.41406500
H	-3.19947300	4.87299300	-2.84653200
H	-1.70869500	-1.06670800	1.05961500

Thermal correction to Gibbs Free Energy= 0.699677
E(RM06L) = -2535.09787152

Reductive elimination from C^{Si}-(E)

C	-2.74011700	-1.90503100	0.80035000
C	-3.54419100	-1.18939700	-0.05149600
H	-3.34171100	-0.57025600	-0.91012900
N	-4.77348800	-2.26304700	1.45338300
N	-3.53476300	-2.54746900	1.69964000
N	-4.79714000	-1.43983800	0.38942400
C	-6.02911300	-0.94226100	-0.12659500
C	-7.14130000	-1.77720700	-0.15495800
C	-6.09294800	0.36918000	-0.58862700
C	-8.33713800	-1.28315500	-0.66445300
H	-7.06292000	-2.79117400	0.22040800
C	-7.29096500	0.84509400	-1.11065300
H	-5.22591900	1.01910500	-0.51453800
C	-8.41278400	0.02094900	-1.14884600
H	-9.21170800	-1.92480100	-0.68890300
H	-7.35000700	1.86642000	-1.47240200
H	-9.34812600	0.39705400	-1.55014400
C	-1.25473400	-2.00010200	0.87726700
H	-0.95045600	-3.02913200	1.08770900
H	-0.79142100	-1.68331100	-0.06008400
N	-0.71231200	-1.12373200	1.92132400
C	-1.21170100	-0.93400000	3.15888000
C	-0.43433300	0.02027500	3.78378400
H	-2.08535500	-1.48230400	3.48149100
C	0.53290700	0.36904800	2.83908800
H	-0.55713300	0.41596900	4.77947900
H	1.32973800	1.09449600	2.90600900
N	0.36242400	-0.33014000	1.71332000
Rh	1.60881900	-0.48053600	0.03892900
H	0.99360500	0.62493600	-0.86271000
C	1.67419300	1.59909000	0.10289800
C	3.06190200	1.97833600	0.50872700
C	3.65332800	3.12131600	-0.04833500
C	3.77562000	1.27525300	1.49151600
C	4.90849700	3.55361800	0.36965800
H	3.11766300	3.67417000	-0.81498500
C	5.02664600	1.71217200	1.91501100
H	3.34906600	0.38300100	1.94141900
C	5.59781100	2.85273400	1.35640700
H	5.34614300	4.44201100	-0.07485400
H	5.55445800	1.16003400	2.68642900
H	6.57380200	3.19307000	1.68711100
C	0.69798000	2.52209000	0.06809900
H	1.00291800	3.51190800	0.42012100
Si	-1.11614900	2.42978400	-0.50321300
C	-2.24269200	1.97362600	0.96516700
H	-3.28712900	1.99578500	0.62445400
H	-2.04626100	0.93960300	1.26646800
C	-1.29541600	1.15923300	-1.92908400
H	-0.43339300	1.27373800	-2.60142900
H	-1.21609900	0.14423500	-1.51730500
C	-2.06999200	2.90728600	2.16931300
H	-2.72118600	2.61018100	2.99764900
H	-1.03805700	2.88791900	2.53729100
H	-2.31060100	3.94548400	1.91384000
C	-2.58400900	1.30297500	-2.75081000
H	-2.67868000	0.50264800	-3.49265800
H	-3.48318100	1.27936700	-2.12292400
H	-2.60081400	2.25487100	-3.29061900
C	-1.56052500	4.18379800	-1.11492100
H	-1.05543100	4.90876500	-0.46301500
H	-1.12611800	4.33033600	-2.11272700
C	-3.06326600	4.49632400	-1.14494500
H	-3.50739100	4.41957300	-0.14629200
H	-3.24515800	5.51340000	-1.50648800
H	-3.61231200	3.81304300	-1.80162000
Cl	2.12789300	-2.88962300	0.56827900
C	3.07109700	-2.68293800	-1.06109800
C	2.32853800	-1.52952700	-1.74361400
C	4.43215700	-2.12838700	-0.72020300
C	3.20013000	-0.44990400	-1.75604900
C	4.50275300	-0.85234100	-1.14223800
C	3.10597400	0.73599900	-2.66807900

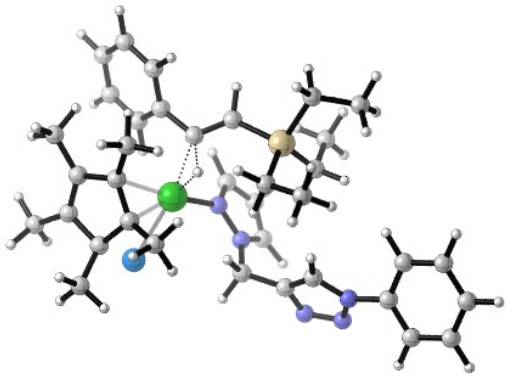

Figure S77. Calculated structure of the reductive elimination intermediate from C^{Si}-(*E*).

H	2.07987000	0.93758200	-2.98242300
H	3.50880000	1.63641900	-2.20066100
H	3.70421200	0.53390400	-3.56555900
C	1.18134000	-1.80070600	-2.67691600
H	1.53897200	-2.32248200	-3.57404600
H	0.42202000	-2.43294500	-2.20533200
H	0.69749300	-0.87527100	-2.99407200
C	3.06529800	-4.01203500	-1.78304200
H	3.59718600	-3.88821800	-2.73314900
H	3.58368200	-4.77479400	-1.19642300
H	2.04976600	-4.35672700	-1.99117800
C	5.46010500	-2.95866600	-0.02571800
H	6.32410000	-2.36039200	0.27043900
H	5.04531100	-3.42088000	0.87821100
H	5.82232800	-3.76904700	-0.66976200
C	5.68106900	0.06509600	-1.12675100
H	6.10977300	0.14624300	-2.13334000
H	5.39836400	1.07202300	-0.81041700
H	6.46659800	-0.29228600	-0.45792500

Thermal correction to Gibbs Free Energy= 0.698879
E(RM06L) = -2535.05228471

Reductive elimination from C^{Si}-(Z)

C	3.35052500	1.73045100	1.30947600
C	3.43211300	0.36568500	1.18136800
H	2.68892000	-0.41830600	1.19524300
N	5.43490000	1.29861400	0.94514200
N	4.59156100	2.25953200	1.16248500
N	4.74741900	0.14107100	0.95318200
C	5.39626900	-1.10171500	0.68632600
C	6.63270300	-1.09508400	0.04524000
C	4.77097700	-2.29535200	1.03897700
C	7.24782500	-2.30843000	-0.24302200
H	7.10112100	-0.15219300	-0.21122000
C	5.39448200	-3.50034700	0.73186700
H	3.81499400	-2.29698200	1.55235500
C	6.63132400	-3.51129500	0.09272400
H	8.21421400	-2.30984900	-0.73655000
H	4.91174500	-4.43276000	1.00567900
H	7.11578800	-4.45434300	-0.13811000
C	2.15172900	2.61265900	1.46255200
H	2.40861800	3.50260400	2.04090800
H	1.76881500	2.94920300	0.49415500
N	1.06887600	1.93281600	2.14089100
C	0.81220900	1.95545000	3.46458200
C	-0.09925800	0.95727900	3.73564300
H	1.30919200	2.66739900	4.10726100
C	-0.33098800	0.34227200	2.50334600
H	-0.53554200	0.70476300	4.68906400
H	-0.98390600	-0.47991900	2.25542800
N	0.38589900	0.93194700	1.54169000
Rh	0.17828300	0.39429100	-0.53378500
H	-0.90944300	1.46353000	-0.36354400
C	-2.01373300	0.22480600	-0.18423500
C	-2.90025000	1.41071200	-0.01033200
C	-4.00724200	1.55884700	-0.85710900
C	-2.67304500	2.38601900	0.97245000
C	-4.88565800	2.62654200	-0.70110800
H	-4.17720400	0.82535100	-1.63793100
C	-3.55326400	3.45097700	1.12709000
H	-1.82410300	2.29503200	1.64252100
C	-4.66394400	3.57354700	0.29435000
H	-5.74233600	2.71809900	-1.36149100
H	-3.37606700	4.18406700	1.90778000
H	-5.34961400	4.40532800	0.41917500
C	-2.44058700	-1.03555000	-0.22535200
Cl	0.66410900	-1.81651800	0.35592500
C	0.62702100	1.83353900	-2.12986600
C	1.95522100	1.28027600	-1.95015500
C	-0.23552000	0.77479200	-2.62623400
C	1.87196600	-0.10739900	-2.12446500
C	0.49387500	-0.43783200	-2.52015100
C	2.97734800	-1.10329900	-2.05715600

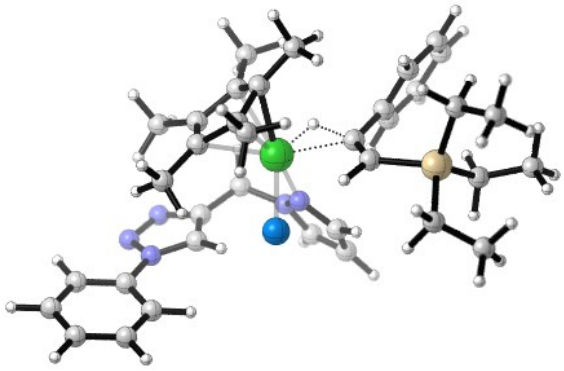

Figure S78. Calculated structure of the reductive elimination intermediate from C^{Si}-(*Z*).

H	2.72639200	-1.90422700	-1.35355800
H	3.12463800	-1.55838400	-3.04355300
H	3.91962500	-0.65110700	-1.74407100
C	3.20539300	2.08534400	-1.81174500
H	3.50530000	2.41148800	-2.81595400
H	3.07556600	2.98681500	-1.21127400
H	4.03121200	1.51238400	-1.39019000
C	0.30059700	3.29420400	-2.16520900
H	0.54842700	3.70134500	-3.15275600
H	-0.76078300	3.47416400	-1.97865700
H	0.87535500	3.85427100	-1.42368800
C	-1.58023700	0.95966700	-3.24851600
H	-2.19386800	0.06260300	-3.14906400
H	-2.12511500	1.79583800	-2.80562800
H	-1.44455900	1.16911800	-4.31609800
C	0.03855500	-1.78812000	-2.96415800
H	0.30098100	-1.92792000	-4.01988200
H	0.51591600	-2.57387600	-2.37605100
H	-1.04396200	-1.89485300	-2.86496400
H	-1.72150500	-1.82644800	-0.42641300
Si	-4.17644300	-1.71970400	0.26320800
C	-3.77637700	-3.53145600	0.72167800
H	-2.80138800	-3.53671100	1.22803900
H	-3.63141900	-4.10050000	-0.20684400
C	-4.81229800	-4.23234200	1.61013400
H	-4.50557300	-5.25923900	1.83410900
H	-4.93403600	-3.71084600	2.56602100
H	-5.79627800	-4.28039800	1.13237600
C	-4.86863400	-0.77688800	1.77435800
H	-4.63413500	0.28930400	1.68111400
H	-4.33373200	-1.13177600	2.66561400
C	-6.38200100	-0.94650100	1.97029100
H	-6.72575200	-0.40328300	2.85659600
H	-6.93901800	-0.55749500	1.11050300
H	-6.66388600	-1.99686700	2.09905400
C	-5.37467200	-1.63876000	-1.23060300
H	-4.78238900	-1.67843900	-2.15528100
H	-5.86935500	-0.65930300	-1.22555300
C	-6.43553600	-2.74740900	-1.25606400
H	-5.97639800	-3.74093800	-1.29507600
H	-7.07525700	-2.71280300	-0.36799200
H	-7.08449600	-2.64892900	-2.13246700

Thermal correction to Gibbs Free Energy= 0.697073
E(RM06L) = -2535.09357752

Reductive elimination from C^{Si}-α

C	2.53859100	-2.43306800	-0.66219900
C	3.08487800	-1.21044800	-0.96828000
H	2.65028600	-0.25776700	-1.23239500
N	4.67474100	-2.67265600	-0.44765500
N	3.54065500	-3.29486800	-0.35387200
N	4.41637100	-1.40513400	-0.81995100
C	5.46757700	-0.45006900	-0.95816800
C	6.68750100	-0.69125600	-0.33105900
C	5.24740600	0.71618800	-1.68703300
C	7.69968800	0.25581000	-0.44150700
H	6.83529100	-1.61063000	0.22317300
C	6.26622800	1.65906300	-1.77662400
H	4.30216000	0.89185600	-2.19016400
C	7.49223200	1.43261100	-1.15693100
H	8.65476100	0.07091200	0.03923300
H	6.09996900	2.56854500	-2.34461100
H	8.28553900	2.16860400	-1.23609200
C	1.10521500	-2.84307000	-0.53059500
H	0.98797000	-3.89664300	-0.79230100
H	0.74423200	-2.71689500	0.49500200
N	0.24356400	-2.06461900	-1.39342800
C	-0.17284100	-2.40531600	-2.63037300
C	-0.67819300	-1.27273800	-3.23163200
H	-0.05722400	-3.41763000	-2.98900300
C	-0.50329300	-0.25966600	-2.28577400
H	-1.10729900	-1.18693000	-4.21744000
H	-0.77274300	0.78387400	-2.34046200

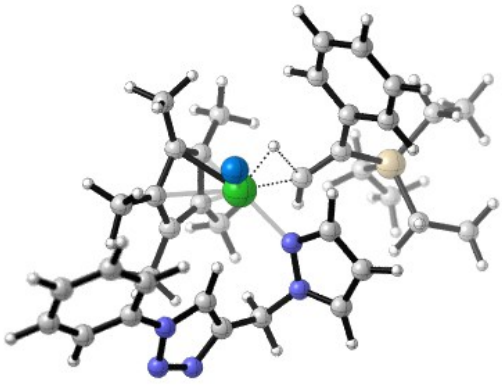

Figure S79. Calculated structure of the reductive elimination intermediate from C^{Si}-α.

N	0.06580200	-0.74184300	-1.17862400
Rh	0.21686700	0.43504600	0.64737700
H	-0.95288300	1.38895200	0.30033800
C	-1.84662000	-0.10430600	0.53996500
C	-2.93885500	0.41284300	-0.01864300
Cl	1.22759800	1.99844700	-0.85198600
C	0.29052400	-0.58232800	2.64617100
C	1.69033400	-0.60721600	2.29489700
C	-0.12017700	0.79607200	2.76462600
C	2.09747400	0.71184500	2.02967500
C	0.96460300	1.60070000	2.30155600
C	3.46143000	1.18277600	1.65380200
H	3.42144700	1.80082800	0.75059300
H	3.87623300	1.79707900	2.46123200
H	4.14477700	0.35184600	1.47119100
C	2.57890600	-1.80076500	2.42208900
H	2.88397100	-1.87695300	3.47377200
H	2.08036600	-2.73759600	2.16784800
H	3.48494400	-1.72124900	1.82179300
C	-0.49352400	-1.76200300	3.12470100
H	-1.55852400	-1.53396100	3.20717300
H	-0.37629000	-2.62806700	2.46598000
H	-0.14133500	-2.05861900	4.11966800
C	-1.39193300	1.27848600	3.38626400
H	-1.56176800	2.33579300	3.17501600
H	-2.26024200	0.71482800	3.03700000
H	-1.31947700	1.16231200	4.47372900
C	1.03792900	3.09340500	2.31989100
H	1.37491900	3.42846300	3.30808400
H	1.73723100	3.45850500	1.56628600
H	0.06421300	3.54392200	2.11498400
Si	-4.51204100	-0.71123400	-0.07647300
C	-6.00816800	0.38403100	-0.51607700
H	-5.97921600	0.60291400	-1.59096900
H	-5.87926600	1.35266100	-0.01579700
C	-7.37087500	-0.21418700	-0.13961400
H	-8.18431000	0.45830400	-0.42969500
H	-7.54689700	-1.17520500	-0.63473900
H	-7.45080100	-0.37796400	0.94070500
C	-4.15287400	-2.02703200	-1.41753700
H	-3.46980800	-2.77165700	-0.98430900
H	-3.58313100	-1.54380100	-2.22232300
C	-5.39123200	-2.71706400	-2.00370800
H	-5.11087200	-3.45627200	-2.76137200
H	-5.97096200	-3.23821800	-1.23482000
H	-6.05789800	-1.99191700	-2.48317800
C	-4.72044500	-1.51953400	1.64461600
H	-5.17232900	-0.77804200	2.31686700
H	-3.72559000	-1.73268800	2.05927200
C	-5.54970200	-2.81118900	1.65166700
H	-6.56054900	-2.64740000	1.26506000
H	-5.08231900	-3.58642000	1.03440400
H	-5.64779400	-3.21118600	2.66613100
C	-2.96423100	1.74143700	-0.67279100
C	-3.26632400	1.86035400	-2.03559000
C	-2.66164600	2.90036300	0.05250000
C	-3.22300600	3.09948200	-2.66283000
H	-3.51910100	0.97123200	-2.60801900
C	-2.62366900	4.14321300	-0.57625500
H	-2.48657800	2.82820600	1.12243100
C	-2.89567400	4.24384300	-1.93574100
H	-3.44808800	3.17535300	-3.72205400
H	-2.39092500	5.03282100	0.00064900
H	-2.86581100	5.21053000	-2.42769900
H	-1.85921200	-1.09176900	0.99618700

Thermal correction to Gibbs Free Energy= 0.695658
E(RM06L) = -2535.09736703

$RhCl_2$ based compounds

Catalyst

C	0.15296000	1.24321100	-0.68126200
C	1.48157600	1.58121400	-0.66559700
H	2.00682500	2.47468300	-0.96409500
N	1.28381000	-0.50439600	0.06375800
N	0.10932000	-0.03572400	-0.23239200
N	2.12448100	0.47495500	-0.21016600
C	3.53623500	0.29466100	-0.01598100
C	4.12034700	-0.90234600	-0.41449600
C	4.26722000	1.32840300	0.55925800
C	5.48862600	-1.06103600	-0.22704000
H	3.51999800	-1.68642500	-0.86284500
C	5.63676100	1.15588000	0.72746500
H	3.77876200	2.23777300	0.89596000
C	6.24467300	-0.03505100	0.33657800
H	5.96462300	-1.98717900	-0.52998200
H	6.22457800	1.94815400	1.17791000
H	7.31249600	-0.16593600	0.47572800
C	-1.08678600	1.93569200	-1.14934600
H	-0.91444900	3.00764400	-1.24912900
H	-1.39437200	1.52963000	-2.11895200
N	-2.17860600	1.76154000	-0.19759600
C	-3.05101000	2.68733800	0.25096200
C	-3.98175200	2.05360100	1.04864700
H	-2.94854200	3.72359000	-0.03613500
C	-3.61142700	0.70874100	1.05189400
H	-4.81096600	2.50229200	1.57233600
H	-4.03821800	-0.13336900	1.57658000
N	-2.53362300	0.54873300	0.27861400
Rh	-1.50615600	-1.08839300	-0.02769400
Cl	-1.29188100	-1.51313300	2.19879300
Cl	-1.86964500	-1.20044200	-2.28897900

Thermal correction to Gibbs Free Energy= 0.181984
E(RM06L) = -1768.76458763

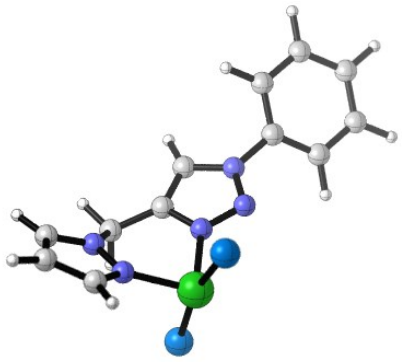

Figure S80. Calculated structure of $\mathbf{Rh^{III}Cl_2}$.

Rh-H-Si intermediate

C	1.22969300	-0.16270900	1.47600800
C	2.54954400	0.12891000	1.70357400
H	3.13407200	0.22602300	2.60455500
N	2.18806700	0.05316400	-0.48310700
N	1.07151400	-0.19924900	0.13109600
N	3.08882400	0.25733900	0.46473100
C	4.45206700	0.53623200	0.11849600
C	5.02846500	-0.15654400	-0.94067000
C	5.15305900	1.48422900	0.85601100
C	6.35272700	0.11631600	-1.26467300
H	4.45251500	-0.89183000	-1.49207700
C	6.48070300	1.73454500	0.52610200
H	4.66916500	2.03581300	1.65646200
C	7.07824800	1.05355100	-0.53194500
H	6.81984100	-0.41310700	-2.08802700
H	7.04256700	2.47210900	1.08889900
H	8.11266500	1.25636400	-0.78847300
C	0.05327100	-0.36501800	2.37313800
H	0.37222200	-0.49309100	3.40805200
H	-0.60709400	0.50855700	2.32750100
N	-0.71022300	-1.55048300	2.01168300
C	-1.15541400	-2.52894100	2.82850300
C	-1.93353400	-3.38969300	2.08437300
H	-0.89118700	-2.53242400	3.87585100
C	-1.92710900	-2.86868200	0.78895800
H	-2.43265000	-4.28291400	2.42505000
H	-2.38154700	-3.22990500	-0.12128400
N	-1.20195000	-1.74769000	0.76556300
Rh	-0.67222300	-0.73535500	-0.83283200
H	-1.38828600	0.69571100	-0.17246900
Cl	-2.56618700	-1.17226800	-2.05504600

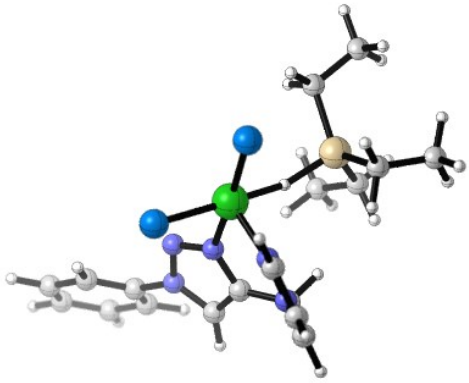

Figure S81. Calculated structure of the Rh-H-Si intermediate.

Si	-2.59950300	1.71893500	0.00391200
C	-4.03193000	0.70291600	0.70540200
H	-4.50732800	0.15787300	-0.11658600
H	-3.62094300	-0.06132200	1.37864400
C	-2.83199800	2.51708100	-1.69112300
H	-1.89871700	3.01737900	-1.97779900
H	-3.00584100	1.72456500	-2.42680900
C	-1.81489900	2.88313000	1.28566400
H	-2.47137000	3.76063800	1.36544400
H	-1.84646500	2.41188000	2.27710200
C	-0.39063900	3.33177100	0.93716300
H	-0.35850700	3.84907300	-0.02731400
H	0.00197500	4.02019500	1.69162000
H	0.29658000	2.47894700	0.87105800
C	-5.05559300	1.56983700	1.45808100
H	-5.86805800	0.94864200	1.84595300
H	-4.60188300	2.09036600	2.30872700
H	-5.50650700	2.32593800	0.80712100
C	-3.99807900	3.52095600	-1.70143500
H	-4.07742200	3.99647600	-2.68306700
H	-4.95402700	3.02638100	-1.50033500
H	-3.86510100	4.31818400	-0.96129800
Cl	0.42143900	-2.51770500	-1.73632700

Thermal correction to Gibbs Free Energy= 0.373837
E(RM06L) = -2296.63908594

C^{Si}-α intermediate

C	-3.08075900	-1.59926100	-0.55171300
C	-4.38550400	-1.27324700	-0.28673700
H	-5.30188500	-1.84072800	-0.31773200
N	-3.11844900	0.53053700	-0.05093900
N	-2.35344500	-0.46212600	-0.39751100
N	-4.35459000	0.04905800	0.01248600
C	-5.45170000	0.90368500	0.34963900
C	-5.48747100	2.19281300	-0.17096000
C	-6.45483400	0.41868500	1.18225100
C	-6.56143000	3.01290200	0.15622700
H	-4.69130200	2.53934100	-0.82027500
C	-7.52948500	1.24681200	1.48877200
H	-6.38938000	-0.57988100	1.60340400
C	-7.58261200	2.54145300	0.97848200
H	-6.60368200	4.02104400	-0.24208800
H	-8.31861400	0.88178500	2.13745200
H	-8.42063000	3.18530900	1.22404400
C	-2.43089900	-2.88079200	-0.96790600
H	-3.14479200	-3.70450100	-0.92822200
H	-2.04596900	-2.79186600	-1.98749300
N	-1.32594200	-3.22134300	-0.08058800
C	-1.19140300	-4.32942900	0.67688200
C	-0.02870100	-4.19792900	1.40648700
H	-1.92349100	-5.12248500	0.63600700
C	0.48237600	-2.95234400	1.02823300
H	0.38760200	-4.89969900	2.11178200
H	1.36942700	-2.44683300	1.37782800
N	-0.30194700	-2.36891500	0.12202300
Rh	-0.19952500	-0.30646000	-0.74079300
C	1.51845000	0.30555700	-1.07610500
C	2.13676600	0.92765300	0.06428000
Si	3.78974100	-0.22288700	0.39103200
C	4.12952000	-0.40581100	2.25433800
H	5.17088600	-0.75674400	2.29767100
H	4.14932600	0.59469300	2.70192200
C	5.16247400	0.79326000	-0.44597700
H	4.79634400	1.15461800	-1.41570400
H	5.34874500	1.69125100	0.15414400
C	3.24848600	-1.33994100	3.09046400
H	3.61674000	-1.38861900	4.11981100
H	2.21055000	-0.99856300	3.13039500
H	3.25691500	-2.36234400	2.69849800
C	6.46404400	0.00304500	-0.64415600
H	7.23690300	0.64286600	-1.08029800
H	6.85768200	-0.38337400	0.30286500
H	6.32196500	-0.84644100	-1.32050500

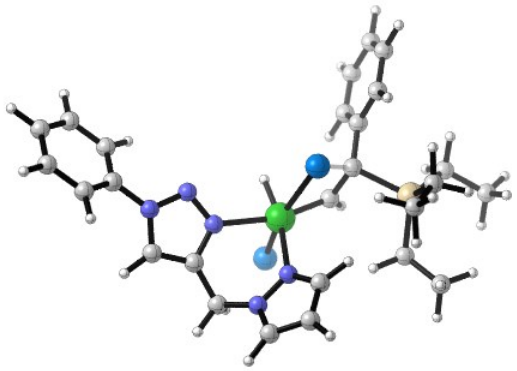

Figure S82. Calculated structure of the C^{Si}-α intermediate.

C	3.55606000	-1.87519300	-0.53823700
H	2.51353800	-2.20848800	-0.52220800
H	3.77807100	-1.67528100	-1.59548300
C	4.46845800	-3.00508500	-0.03556700
H	4.21952700	-3.30356600	0.98752300
H	4.36426200	-3.88953200	-0.67103400
H	5.52433800	-2.71667100	-0.04521000
C	2.49848100	2.38828700	0.01278100
C	2.36222100	3.11011900	-1.17570400
C	3.00102000	3.02801200	1.15066900
C	2.75078000	4.44610900	-1.23015200
H	1.95130700	2.64193000	-2.06530500
C	3.37367100	4.36424600	1.09583900
H	3.08391600	2.48583400	2.08823400
C	3.25793700	5.07440800	-0.09821000
H	2.64428700	4.99619200	-2.15937300
H	3.75646100	4.85226400	1.98622500
H	3.55413400	6.11738300	-0.14115200
H	2.03574800	0.31488200	-2.03902100
Cl	-0.43584400	-0.98047600	-2.92887700
Cl	0.78263800	0.65702200	1.36484300
H	-0.45721600	1.12748500	-1.27872200

Thermal correction to Gibbs Free Energy= 0.484258
E(RM06L) = -2605.10654682

Reductive elimination from C^{Si}-α

C	1.06630900	0.00461300	1.73797600
C	2.26633100	-0.54408800	1.29721300
H	2.64666400	-1.55362700	1.25970700
N	2.37564900	1.67055100	1.29393100
N	1.18509800	1.36077000	1.70863400
N	3.04328000	0.54334000	1.05280800
C	4.39711400	0.57237000	0.59281500
C	5.24372500	1.56520900	1.07530000
C	4.82749200	-0.39141900	-0.31250900
C	6.56123700	1.58686000	0.63327100
H	4.87407100	2.30241800	1.77902500
C	6.15243500	-0.36151200	-0.73376800
H	4.13607400	-1.12678800	-0.71165800
C	7.01741100	0.62363800	-0.26427700
H	7.23415300	2.35545200	0.99844000
H	6.50147800	-1.10265900	-1.44481300
H	8.04842400	0.64420500	-0.60193300
C	-0.14580000	-0.59580000	2.38709900
H	0.03586200	-0.75430200	3.45377300
H	-0.97522000	0.11099100	2.28717600
N	-0.51486900	-1.87861600	1.82217700
C	-1.02547300	-2.95976600	2.44413400
C	-1.30971000	-3.90293200	1.47713200
H	-1.14139100	-2.97884800	3.51789700
C	-0.93469300	-3.30723700	0.26990800
H	-1.71244900	-4.89221000	1.62563600
H	-0.94800400	-3.70558500	-0.73273900
N	-0.47441500	-2.07635200	0.48805900
Rh	0.53572200	-0.72594300	-0.73796000
H	-0.31177500	-1.03776800	-2.02534200
C	-0.97746500	0.41303900	-1.41825000
C	-2.13808500	0.35728700	-0.76433200
Si	-2.70698400	2.21205100	-0.23428300
C	-4.57142200	2.18532800	-0.63194300
H	-4.73410200	1.58814400	-1.53756800
H	-5.08779100	1.65319600	0.17658000
C	-1.74705400	3.48760000	-1.26166700
H	-1.79008800	3.22234400	-2.32619700
H	-2.32324300	4.41955700	-1.18093800
C	-5.17293100	3.58615000	-0.82139600
H	-6.25073700	3.51565200	-0.99590700
H	-5.02318100	4.22293700	0.05656800
H	-4.73300400	4.09753700	-1.68334700
C	-0.30026500	3.74910100	-0.81544000
H	0.15081700	4.53176900	-1.43215000
H	-0.25696000	4.08229400	0.22629600
H	0.34056800	2.86507300	-0.89632000

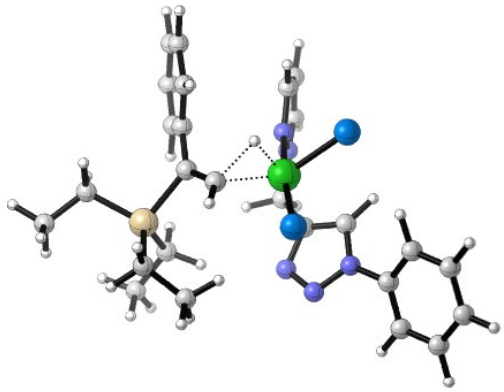

Figure S83. Calculated structure of the reductive elimination intermediate from C^{Si}-α.

C	-2.28812300	2.43641300	1.60693400
H	-2.76215400	1.66045100	2.22028300
H	-1.20183900	2.32696000	1.72211000
C	-2.72841800	3.81880300	2.11878600
H	-2.29464300	4.62866000	1.52241500
H	-3.81727800	3.93023400	2.09730900
H	-2.40175700	3.96490100	3.15249300
C	-2.99175900	-0.78531700	-0.48285600
C	-3.17997300	-1.75288800	-1.48582900
C	-3.67534000	-0.91731400	0.73521000
C	-4.02941100	-2.82832500	-1.26862800
H	-2.67728200	-1.64227400	-2.44249000
C	-4.49096200	-2.01693300	0.96160600
H	-3.55168100	-0.16950300	1.51116100
C	-4.67539500	-2.96820400	-0.04121500
H	-4.18560500	-3.55974900	-2.05468100
H	-5.00037200	-2.12387500	1.91350200
H	-5.33305200	-3.81418100	0.13070800
H	-0.60092500	1.15335100	-2.11819100
Cl	1.88046200	0.70106800	-1.96400200
Cl	1.80982500	-2.51177100	-1.43303100

Thermal correction to Gibbs Free Energy= 0.483481
E(RM06L) = -2605.08667647

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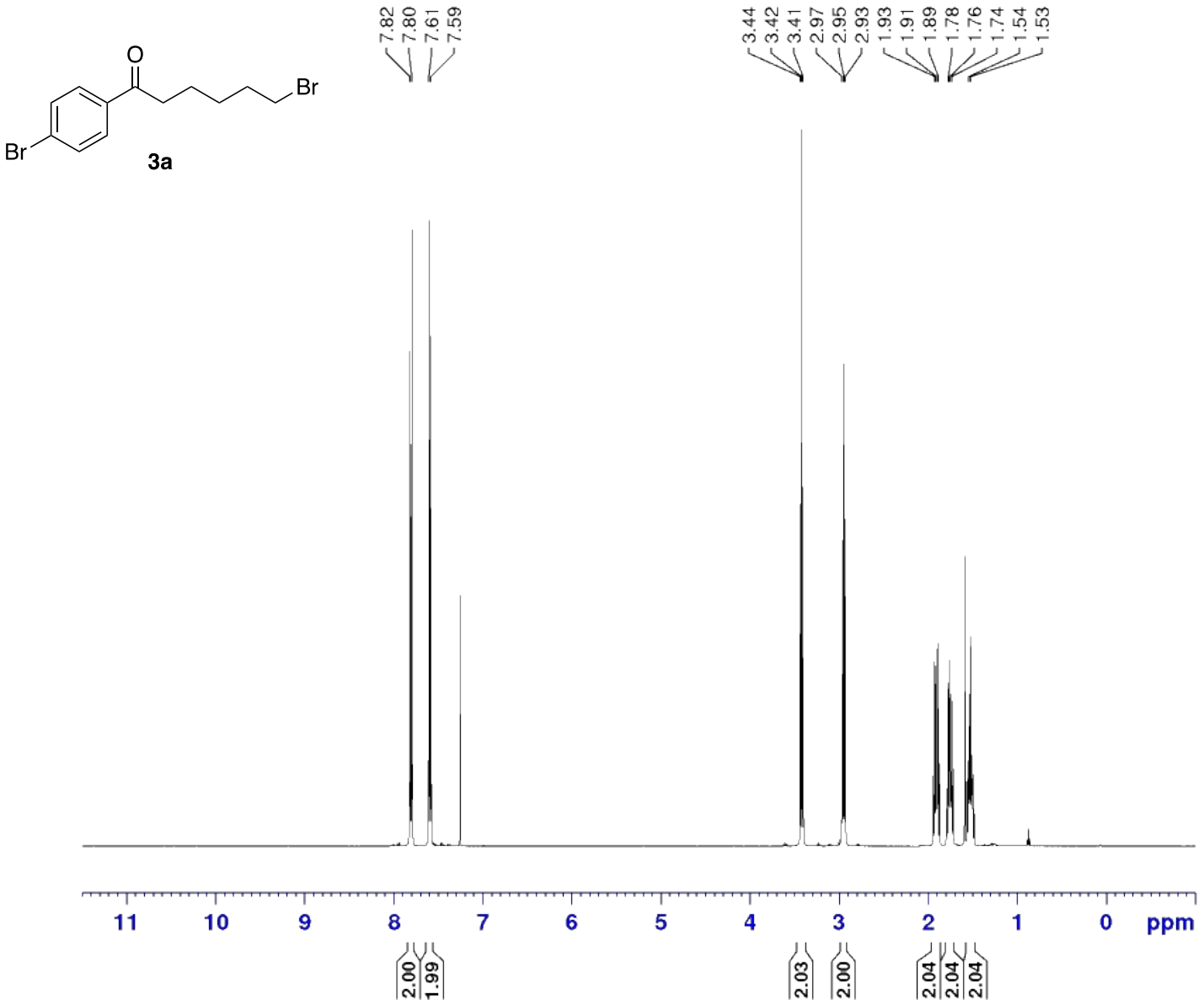


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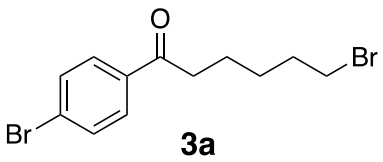
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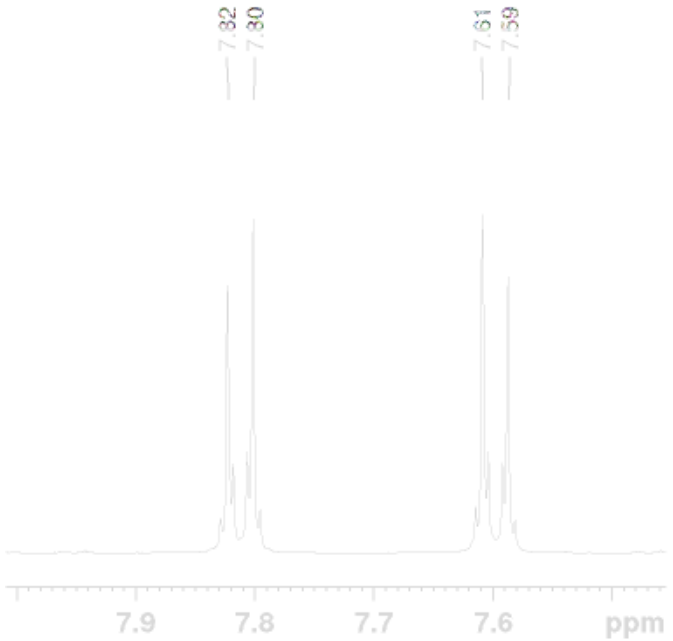
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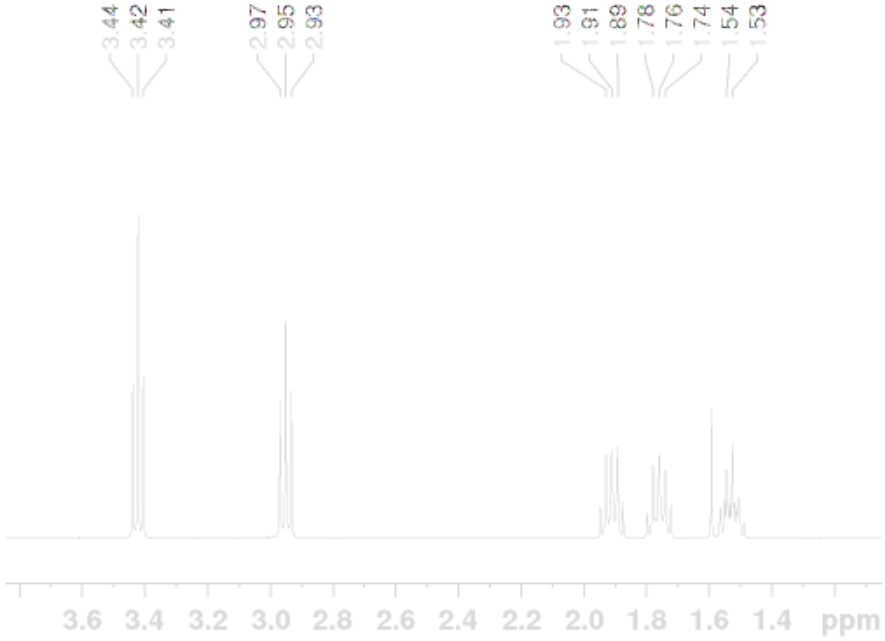
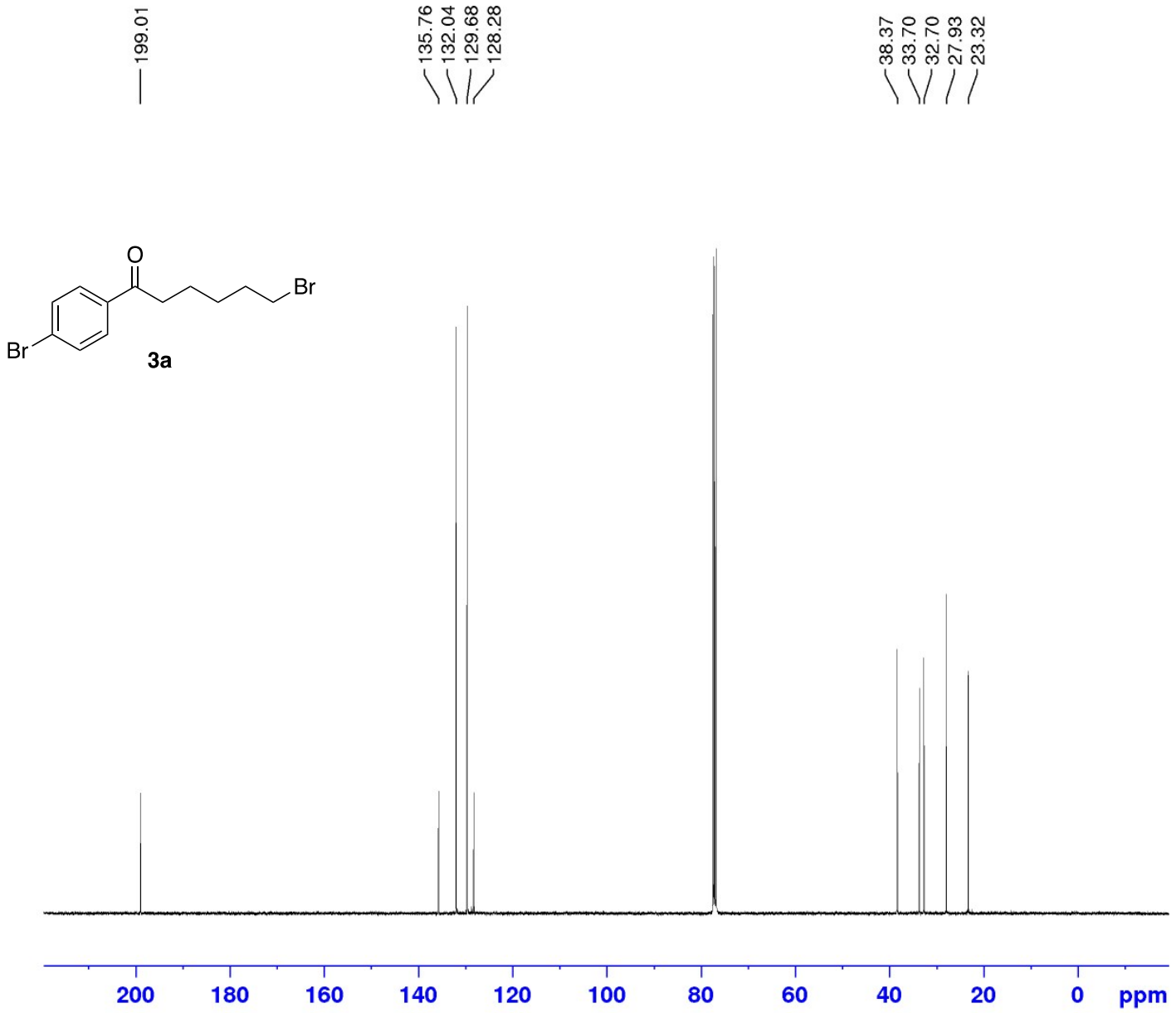
7.8
7.7
7.6
ppm

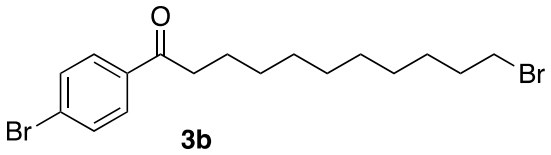

3.44
3.42
3.41
2.97
2.95
2.93
1.93
1.91
1.89
1.78
1.76
1.74
1.54
1.53
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm




```
Current Data Parameters
NAME                  MR-204
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190726
Time                 23.13 h
INSTRUM              spect
PROBHD    Z116098_0573 (
PULPROG              zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    3000
DS                       4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  198.41
DW                  20.800 usec
DE                   6.50 usec
TE                  298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           100.6278593 MHz
NUC1                   13C
P1                  10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

F2 - Processing parameters
SI                   32768
SF             100.6177859 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

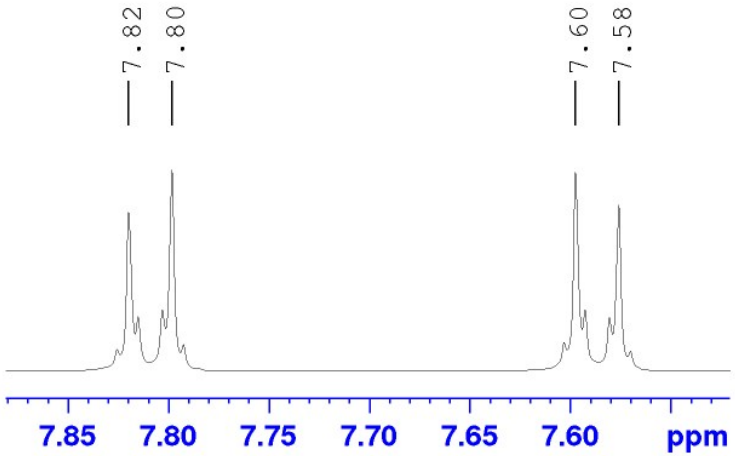


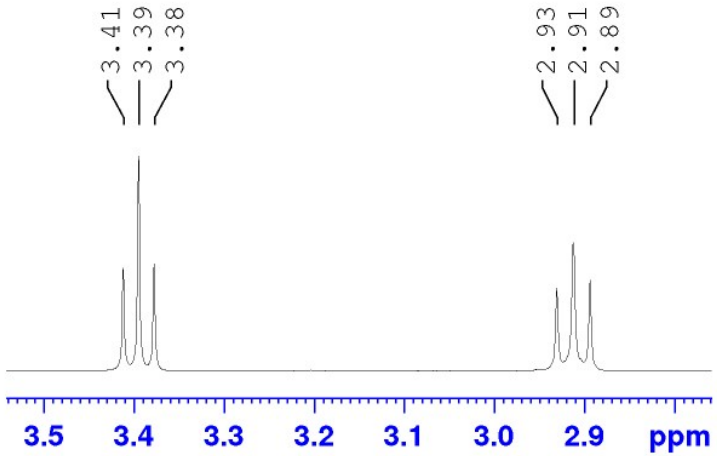
3b

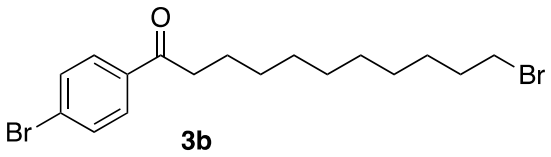
7.82
7.80
7.60
7.58

3.41
3.39
3.38
2.93
2.91
2.89
1.86
1.84
1.82
1.73
1.71
1.69
1.41
1.39
1.35
1.33
1.29

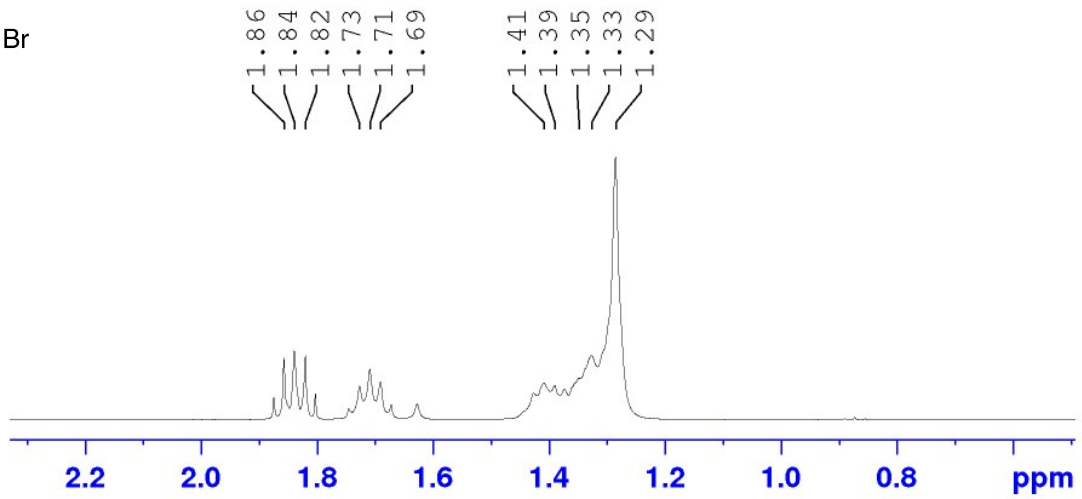
Current Data Parameters
NAME MR-212

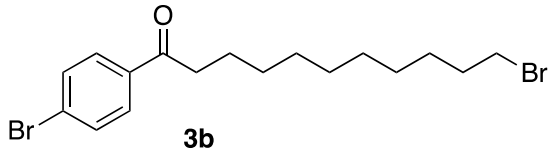

7.82
7.80
7.60
7.58
7.85
7.80
7.75
7.70
7.65
7.60
ppm


3.41
3.39
3.38
2.93
2.91
2.89
3.5
3.4
3.3
3.2
3.1
3.0
2.9
ppm


O
Br
Br

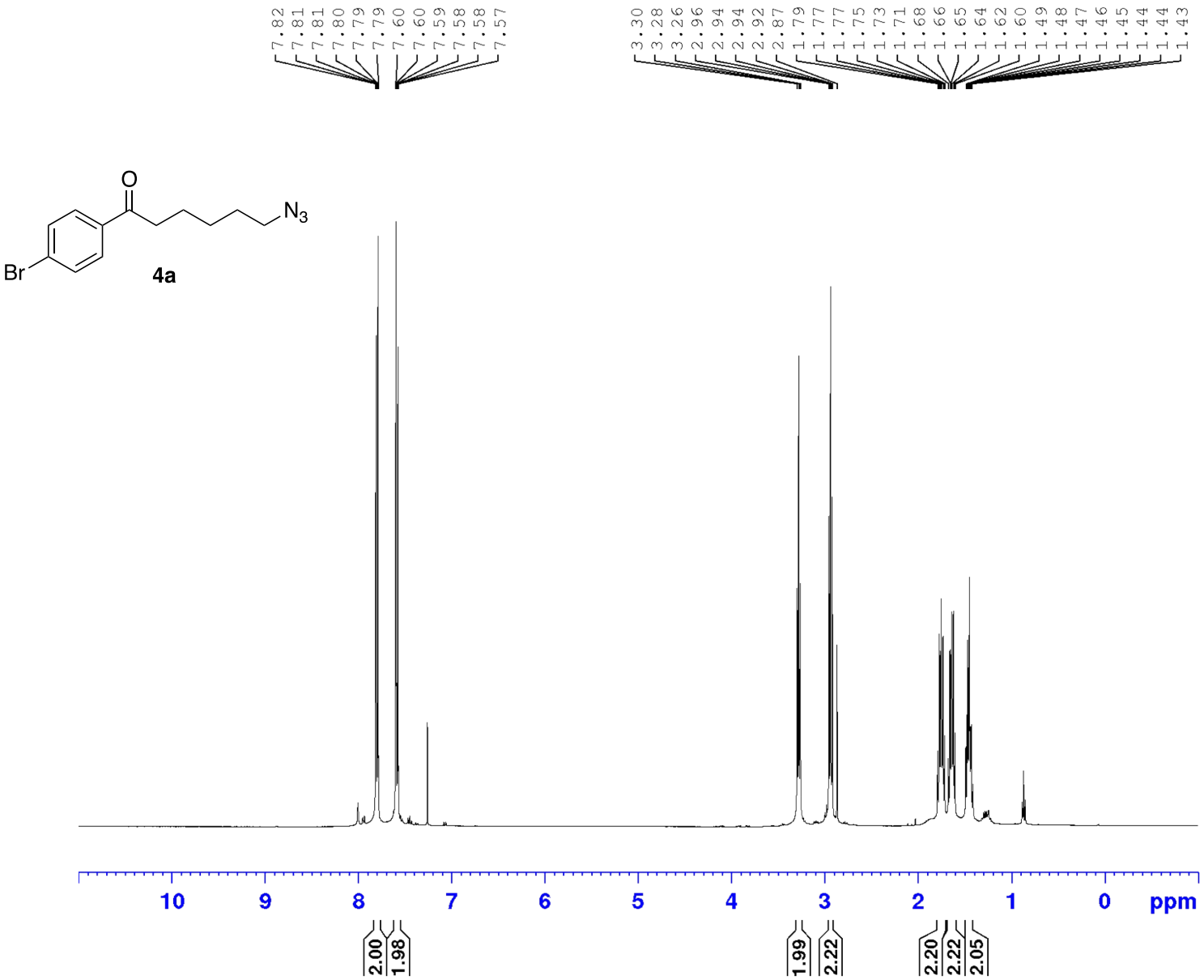
3b


1.86
1.84
1.82
1.73
1.71
1.69
1.41
1.39
1.35
1.33
1.29
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm


O
Br
Br

3b

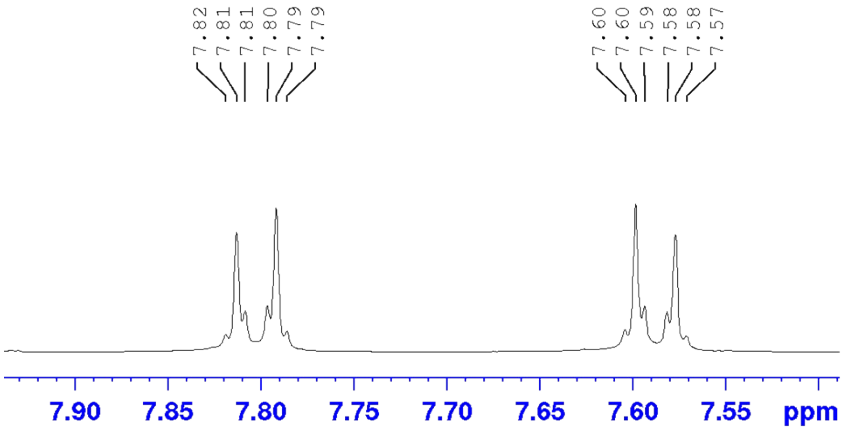
7.55
7.88
7.97
7.71
7.66
7.97
7.71
7.66
7.10
67
16
92
51
47
45
38
34
26
34
Current Data Parameters

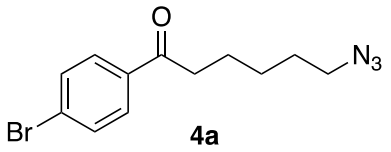



```
Current Data Parameters
NAME                  MR-94
EXPNO                     1
PROCNO                    1

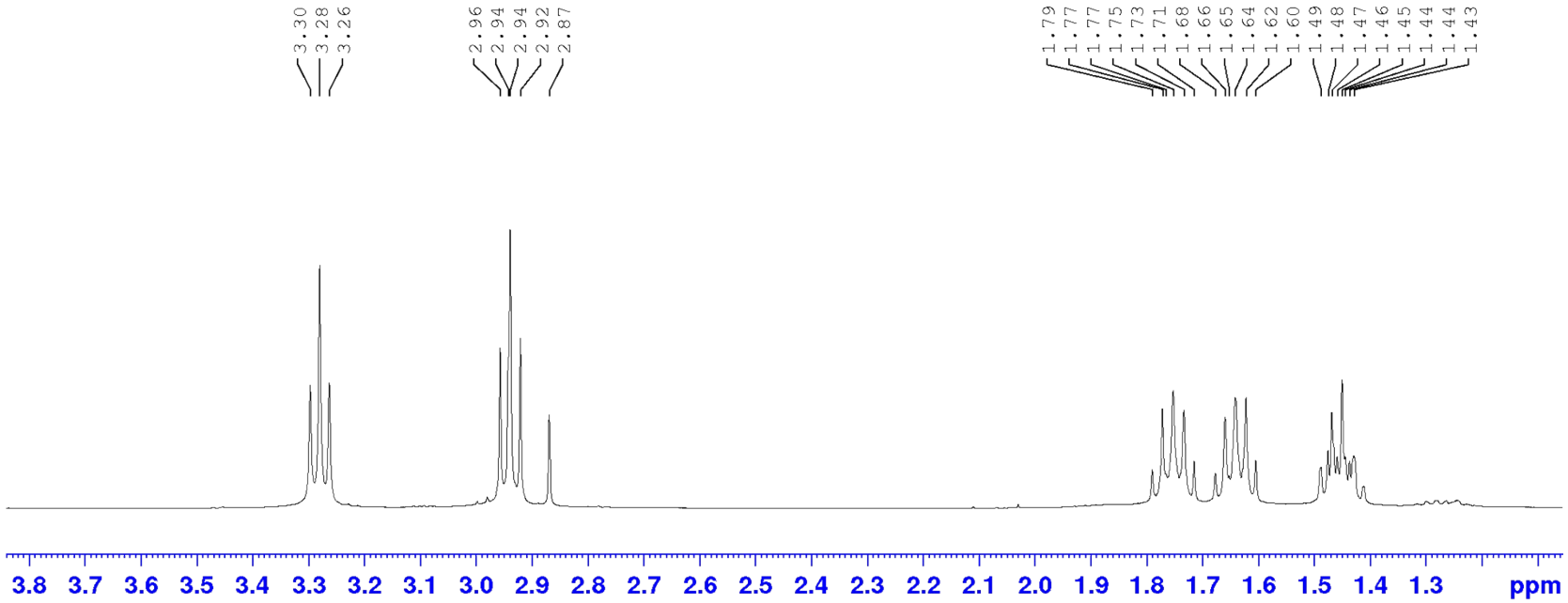
F2 - Acquisition Parameters
Date_              20190226
Time                 15.55 h
INSTRUM              spect
PROBHD    Z116098_0573 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                    55.9
DW                  62.400 usec
DE                  12.00 usec
TE                  298.0 K
D1               2.50000000 sec
TD0                      1
SFO1           400.1524709 MHz
NUC1                    1H
P1                  10.00 usec
PLW1           15.75399971 W

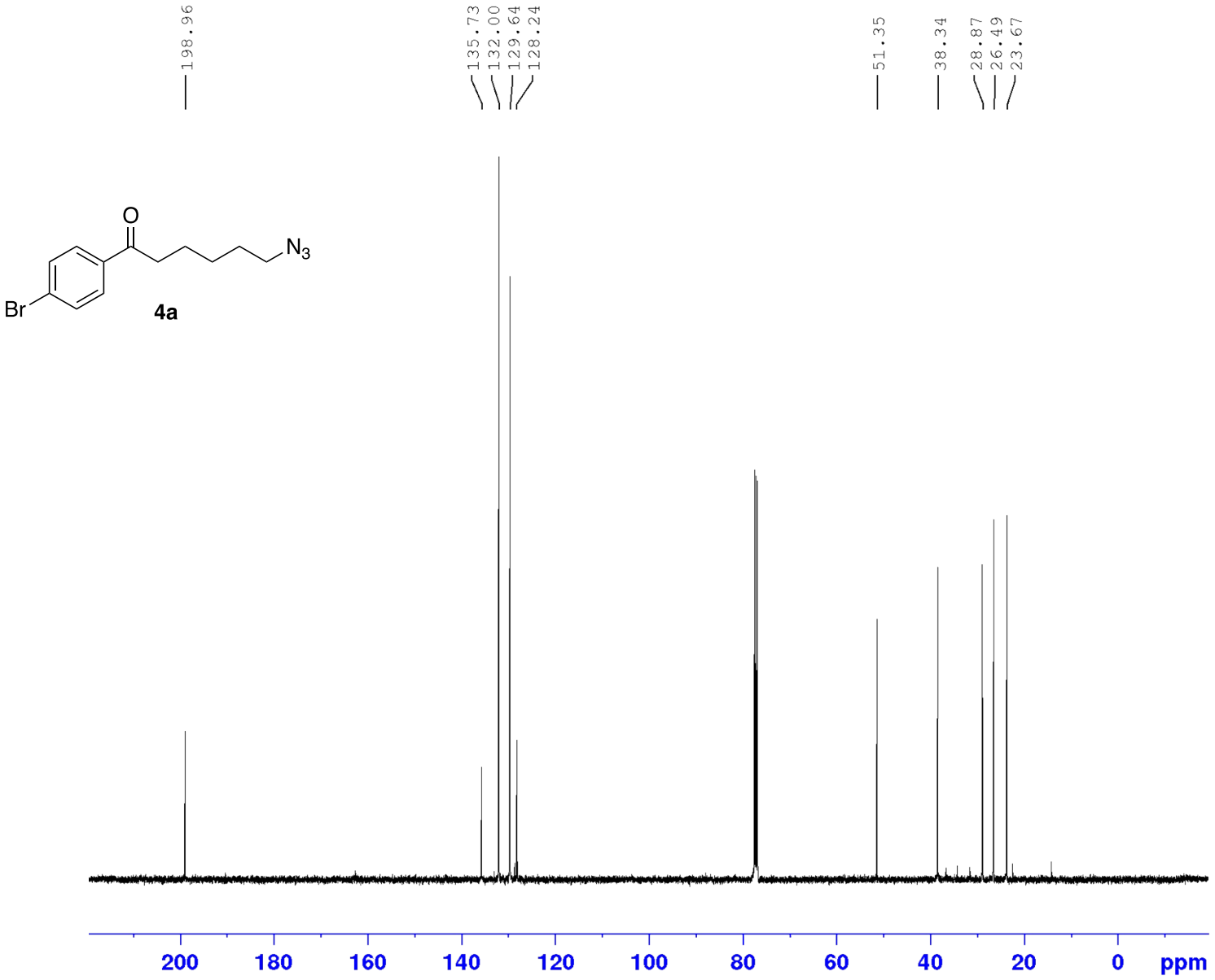
F2 - Processing parameters
SI                   65536
SF             400.1500098 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```


7.82
7.81
7.81
7.80
7.79
7.79
7.60
7.60
7.59
7.58
7.58
7.57
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
ppm


O
N3
Br

4a

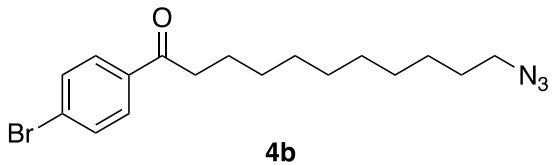

3.30
3.28
3.26
2.96
2.94
2.94
2.92
2.87
1.79
1.77
1.77
1.75
1.73
1.71
1.68
1.66
1.65
1.64
1.62
1.60
1.49
1.48
1.47
1.46
1.45
1.44
1.44
1.43
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
ppm




```
Current Data Parameters
NAME                  MR-94
EXPNO                     2
PROCNO                    1

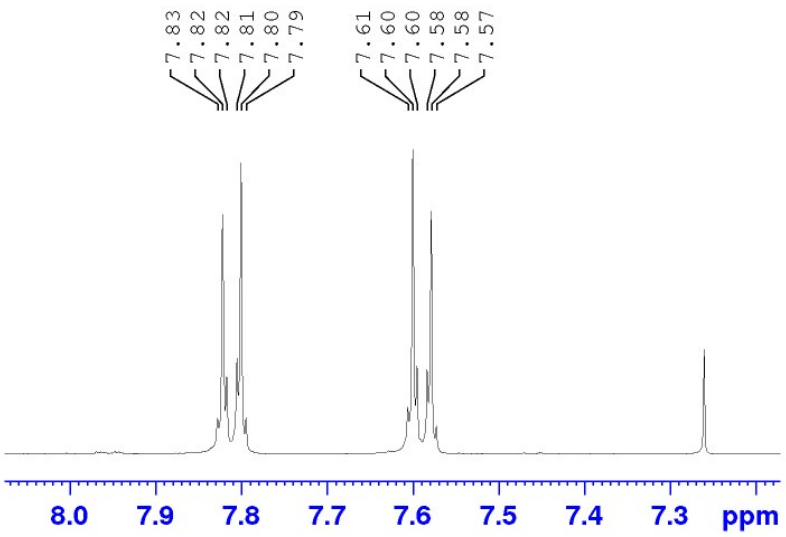
F2 - Acquisition Parameters
Date_              20190226
Time                 16.17 h
INSTRUM              spect
PROBHD    Z116098_0573 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    350
DS                      4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                 198.41
DW                 20.800 usec
DE                  6.50 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1           100.6278593 MHz
NUC1                  13C
P1                 10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2              90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

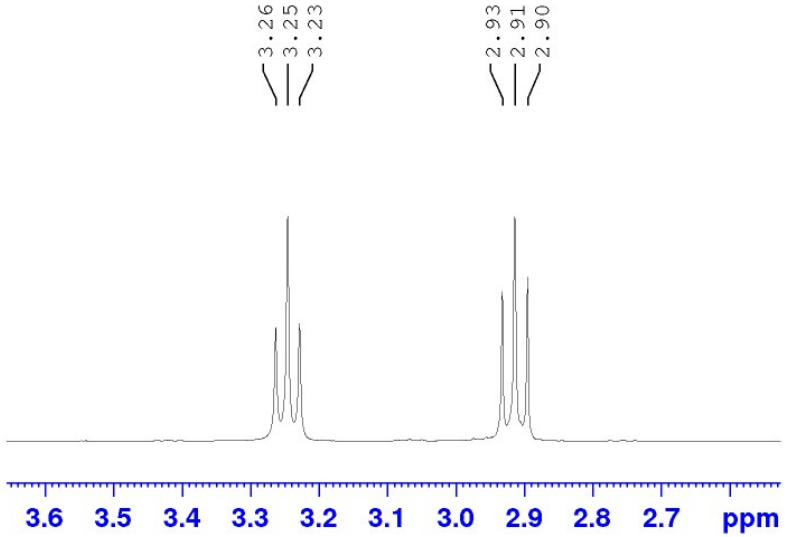
F2 - Processing parameters
SI                    32768
SF             100.6177887 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

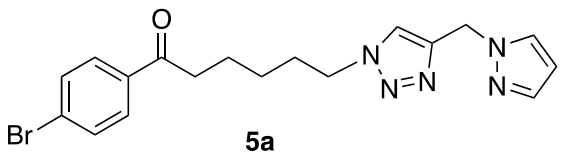

O
Br
N3

4b

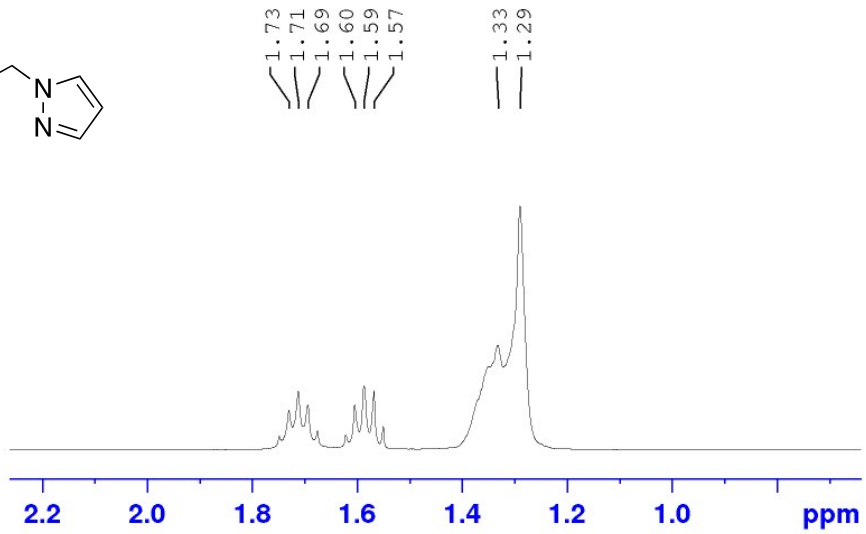
7.82
7.80
7.60
7.58
7.41
7.39
7.38
7.93
7.91
7.89
7.86
7.84
7.82
7.73
7.71
7.69
7.41
7.39
7.35
7.33
7.29
Current Data Parameters

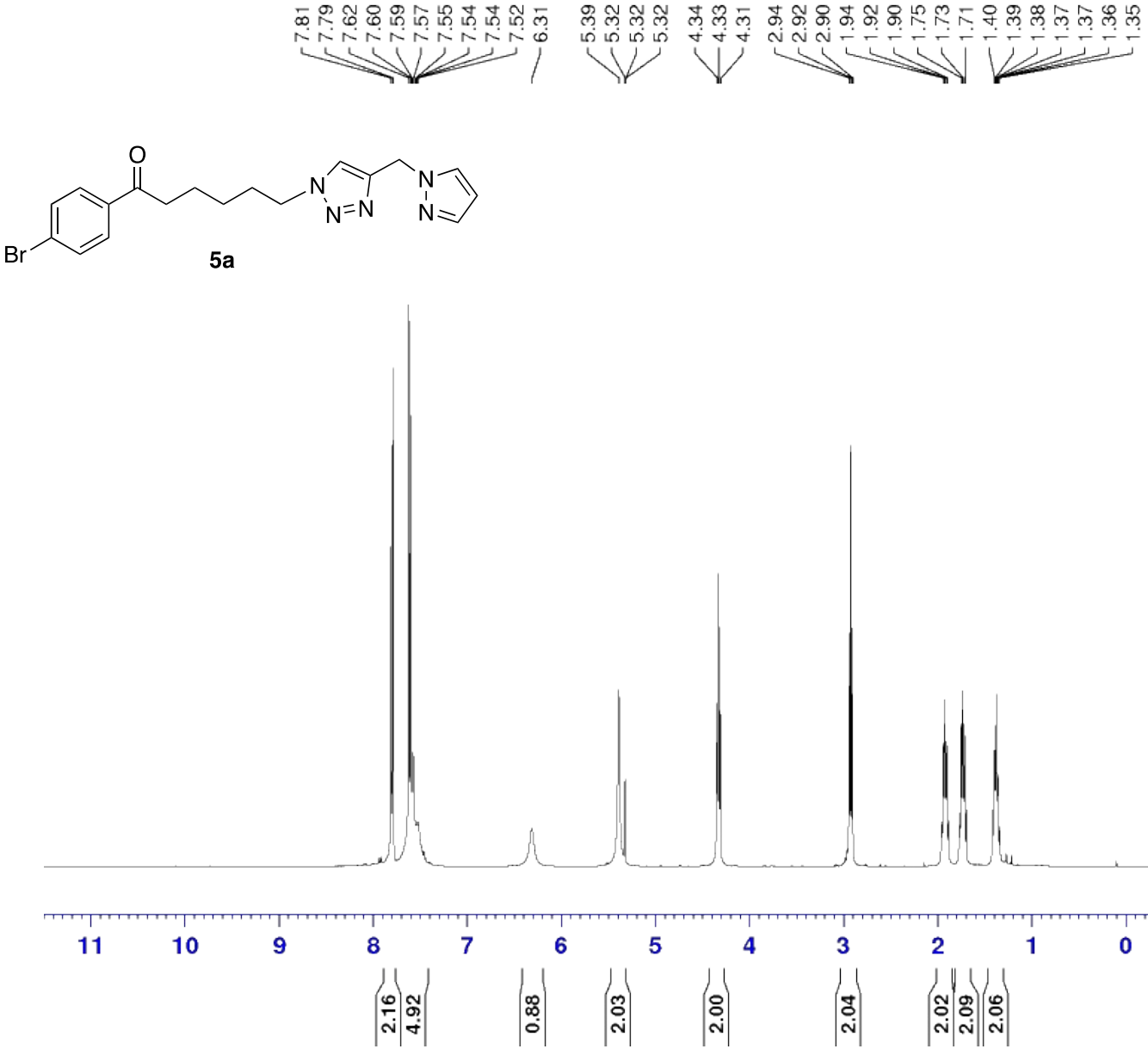

7.83
7.82
7.82
7.81
7.80
7.79
7.61
7.60
7.60
7.58
7.58
7.57
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm


3.26
3.25
3.23
2.93
2.91
2.90
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
ppm


O
N
N
N
N
Br

5a

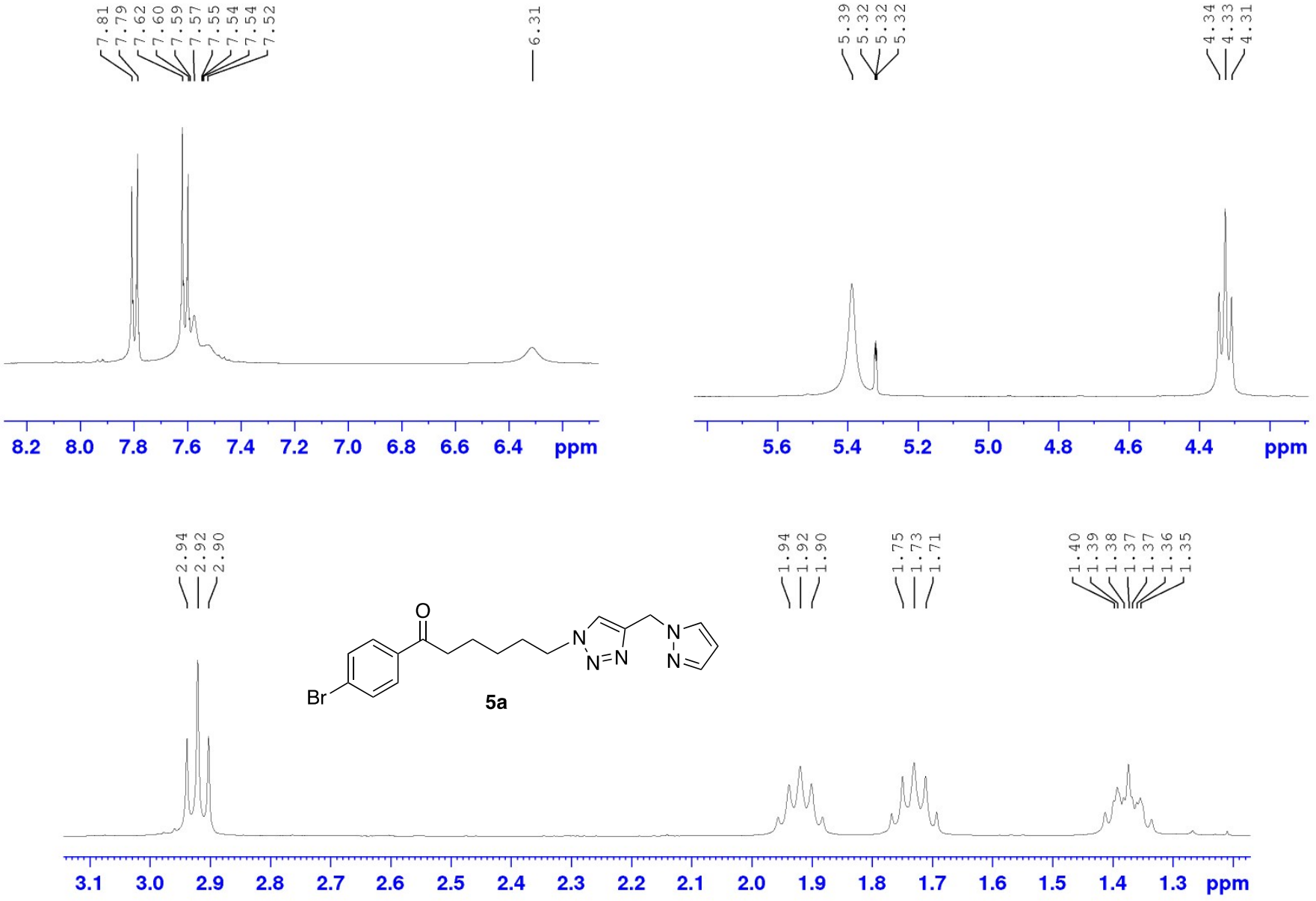

1.73
1.71
1.69
1.60
1.59
1.57
1.33
1.29
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm



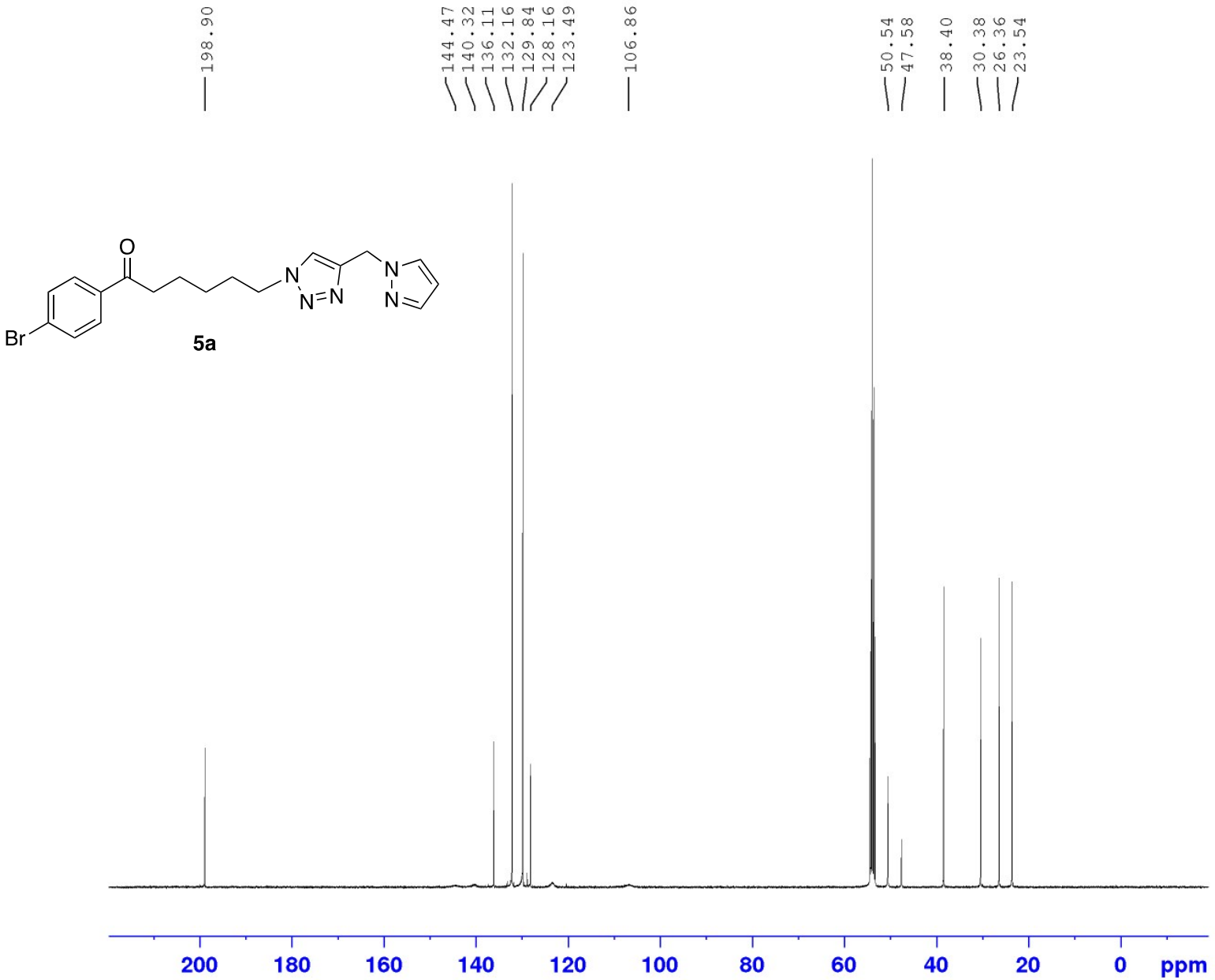

```
Current Data Parameters
NAME                  MR-95_2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20190808
Time                    9.09 h
INSTRUM                 spect
PROBHD    Z116098_0573 (
PULPROG                 zg30
TD                     65536
SOLVENT             CD2Cl2
NS                         16
DS                          2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                     31.83
DW                     62.400 usec
DE                     12.00 usec
TE                     298.0 K
D1                 2.50000000 sec
TD0                         1
SFO1            400.1524709 MHz
NUC1                       1H
P1                     10.00 usec
PLW1            15.75399971 W

F2 - Processing parameters
SI                     65536
SF              400.1500154 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```


7.81
7.79
7.62
7.60
7.59
7.57
7.55
7.54
7.54
7.52
6.31
5.39
5.32
5.32
5.32
4.34
4.33
4.31
2.94
2.92
2.90
1.94
1.92
1.90
1.75
1.73
1.71
1.40
1.39
1.38
1.37
1.37
1.36
1.35
O
Br
N
N
N
N
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
5.6 5.4 5.2 5.0 4.8 4.6 4.4 ppm
3.1 3.0 2.9 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 ppm

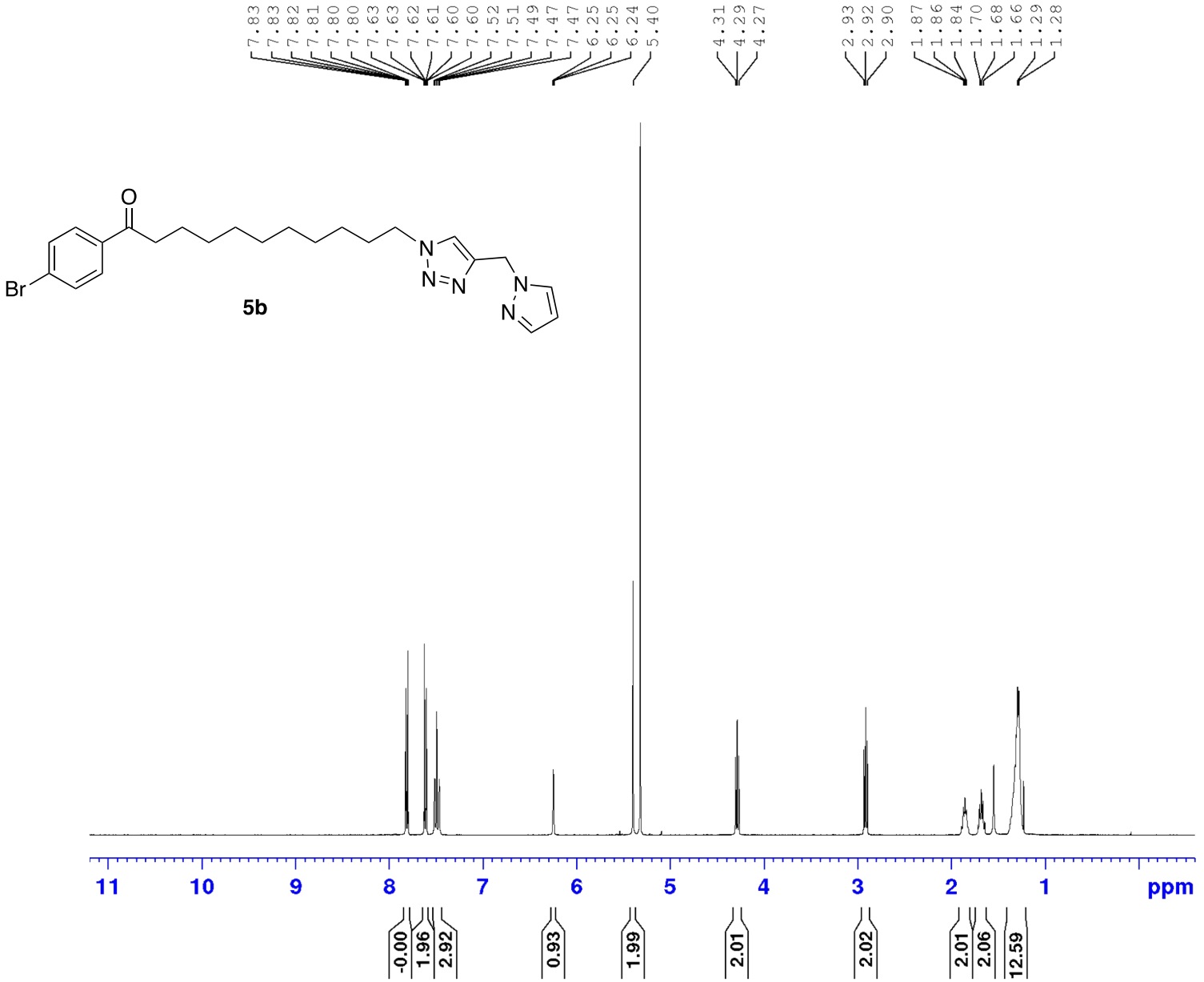
5a




```
Current Data Parameters
NAME                  MR-95_2
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20190812
Time                    2.04 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG                zgpg30
TD                      65536
SOLVENT                CD2Cl2
NS                        4000
DS                           4
SWH                24038.461 Hz
FIDRES              0.733596 Hz
AQ                  1.3631488 sec
RG                     198.41
DW                     20.800 usec
DE                      6.50 usec
TE                     298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                          1
SFO1             100.6278593 MHz
NUC1                      13C
P1                     10.00 usec
PLW1             80.53199768 W
SFO2             400.1516006 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                  90.00 usec
PLW2             15.75399971 W
PLW12             0.19449000 W
PLW13             0.09782900 W

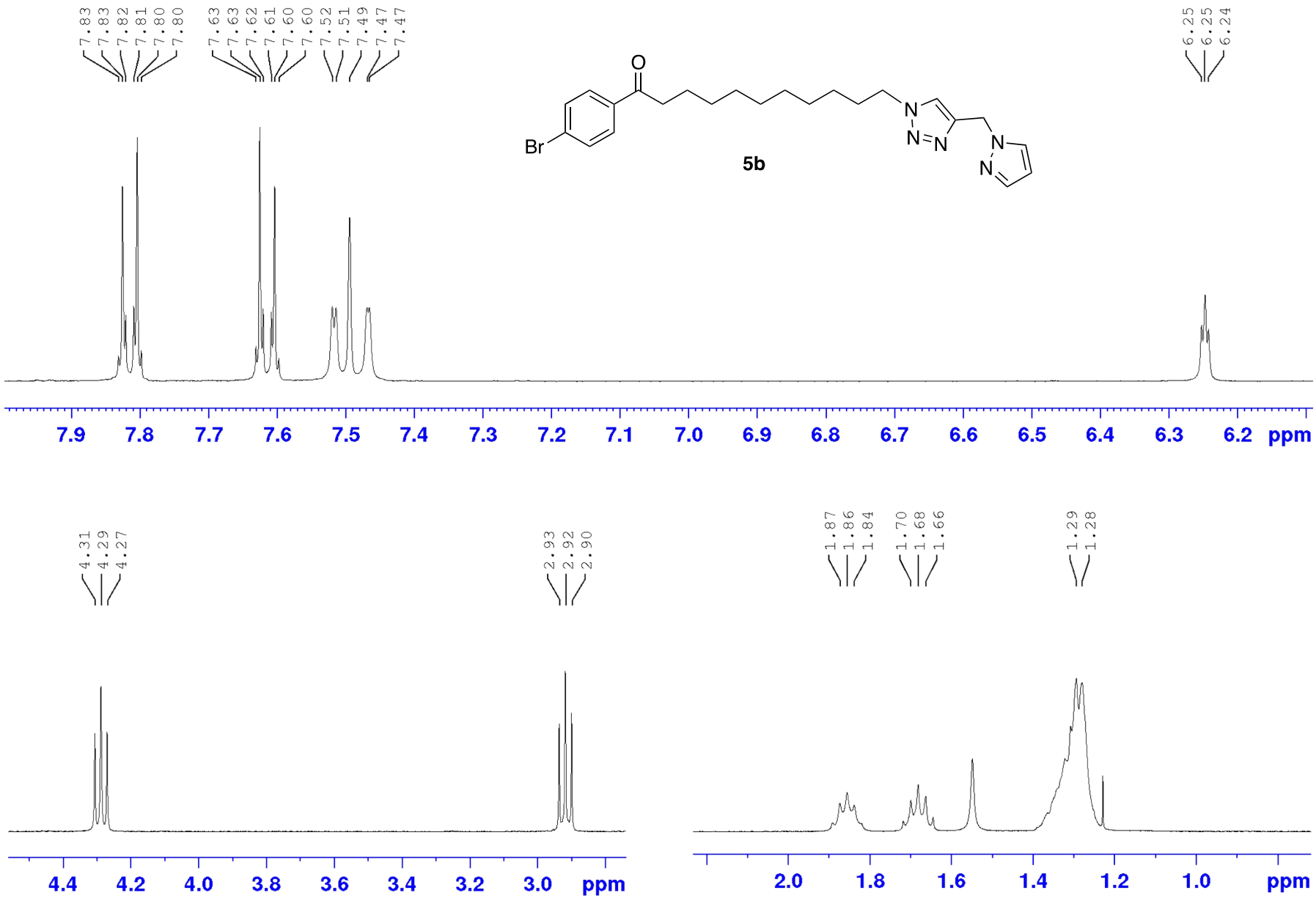
F2 - Processing parameters
SI                        32768
SF               100.6177654 MHz
WDW                         EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

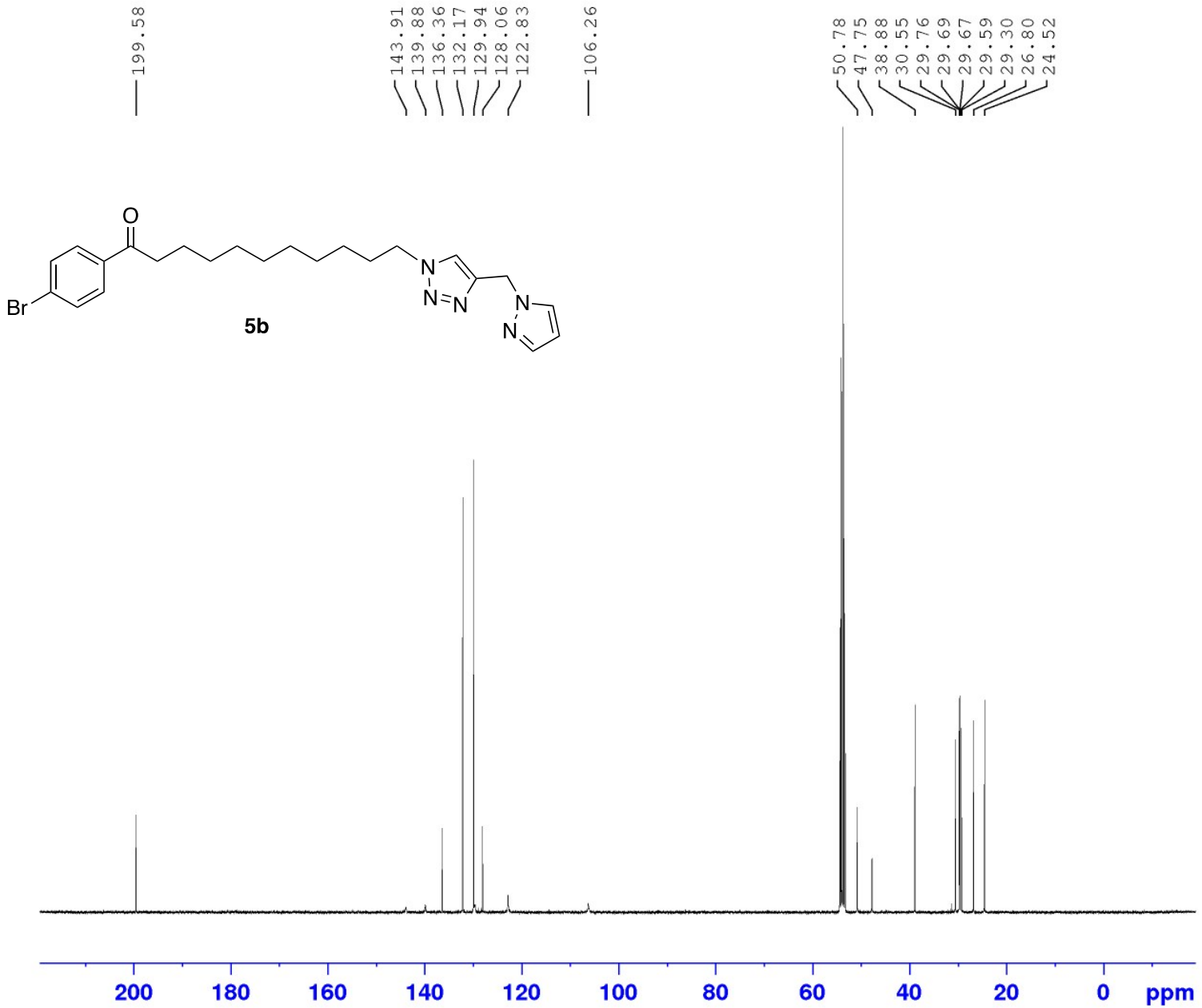



```
Current Data Parameters
NAME                  MR-80
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190125
Time                  9.06 h
INSTRUM               spect
PROBHD    Z116098_0573 (
PULPROG                zg30
TD                    65536
SOLVENT            CD2Cl2
NS                        16
DS                         2
SWH               8012.820 Hz
FIDRES           0.244532 Hz
AQ              4.0894465 sec
RG                   198.41
DW                  62.400 usec
DE                  12.00 usec
TE                  298.0 K
D1             2.50000000 sec
TD0                       1
SFO1          400.1524709 MHz
NUC1                   1H
P1                  10.00 usec
PLW1          15.75399971 W

F2 - Processing parameters
SI                    65536
SF            400.1500155 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                    1.00
```

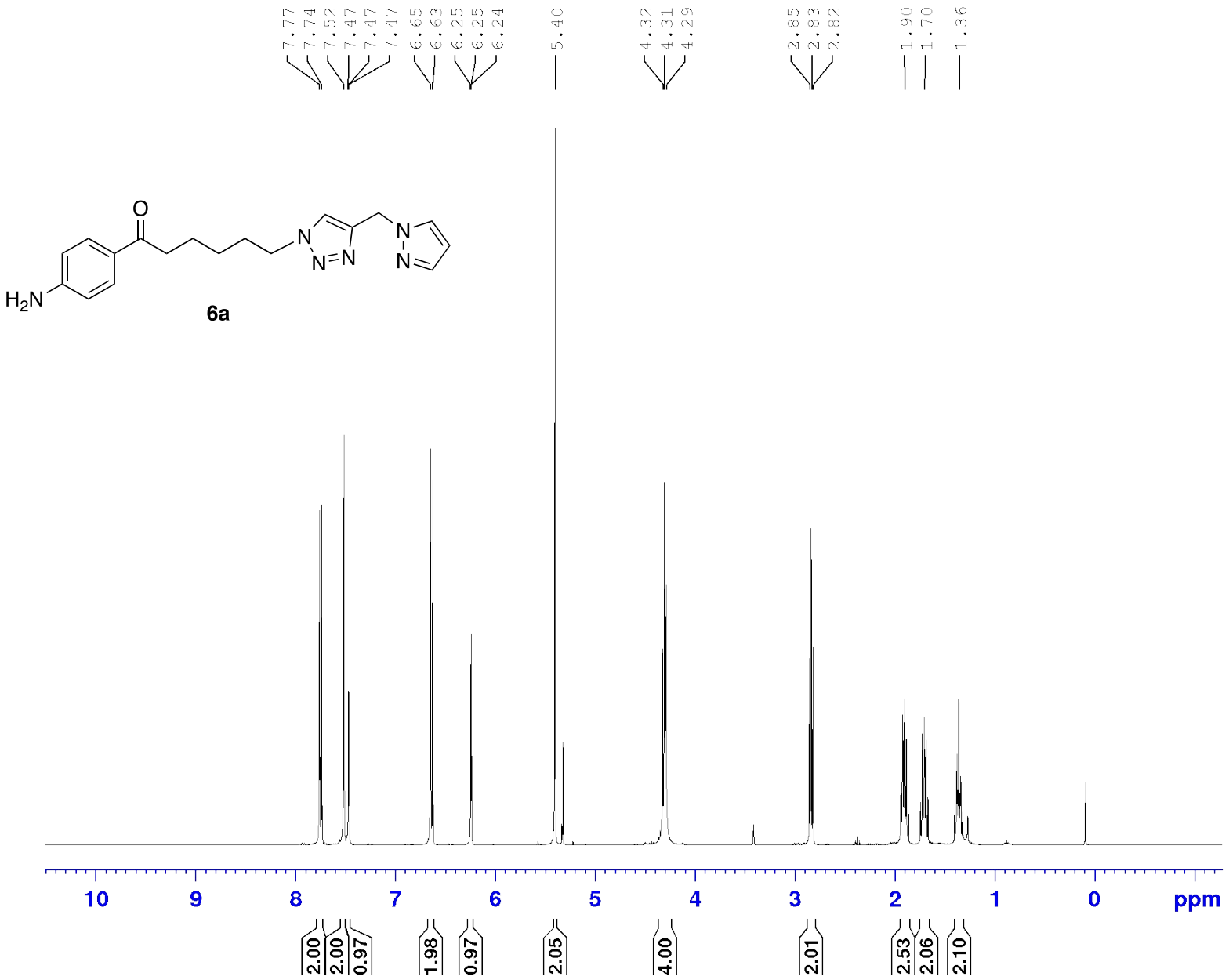

7.83
7.83
7.82
7.81
7.80
7.80
7.63
7.63
7.62
7.61
7.60
7.60
7.52
7.51
7.49
7.47
7.47
6.25
6.25
6.24
O
Br
N
N
N
N
N
5b
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
ppm
4.31
4.29
4.27
2.93
2.92
2.90
1.87
1.86
1.84
1.70
1.68
1.66
1.29
1.28
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm
2.0
1.8
1.6
1.4
1.2
1.0
ppm




```
Current Data Parameters
NAME                  MR-80
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190315
Time                 22.59 h
INSTRUM              spect
PROBHD    Z116098_0573 (
PULPROG             zgpg30
TD                   65536
SOLVENT             CD2Cl2
NS                    3000
DS                       4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                  198.41
DW                  20.800 usec
DE                   6.50 usec
TE                  298.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1           100.6278593 MHz
NUC1                   13C
P1                  10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2               90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

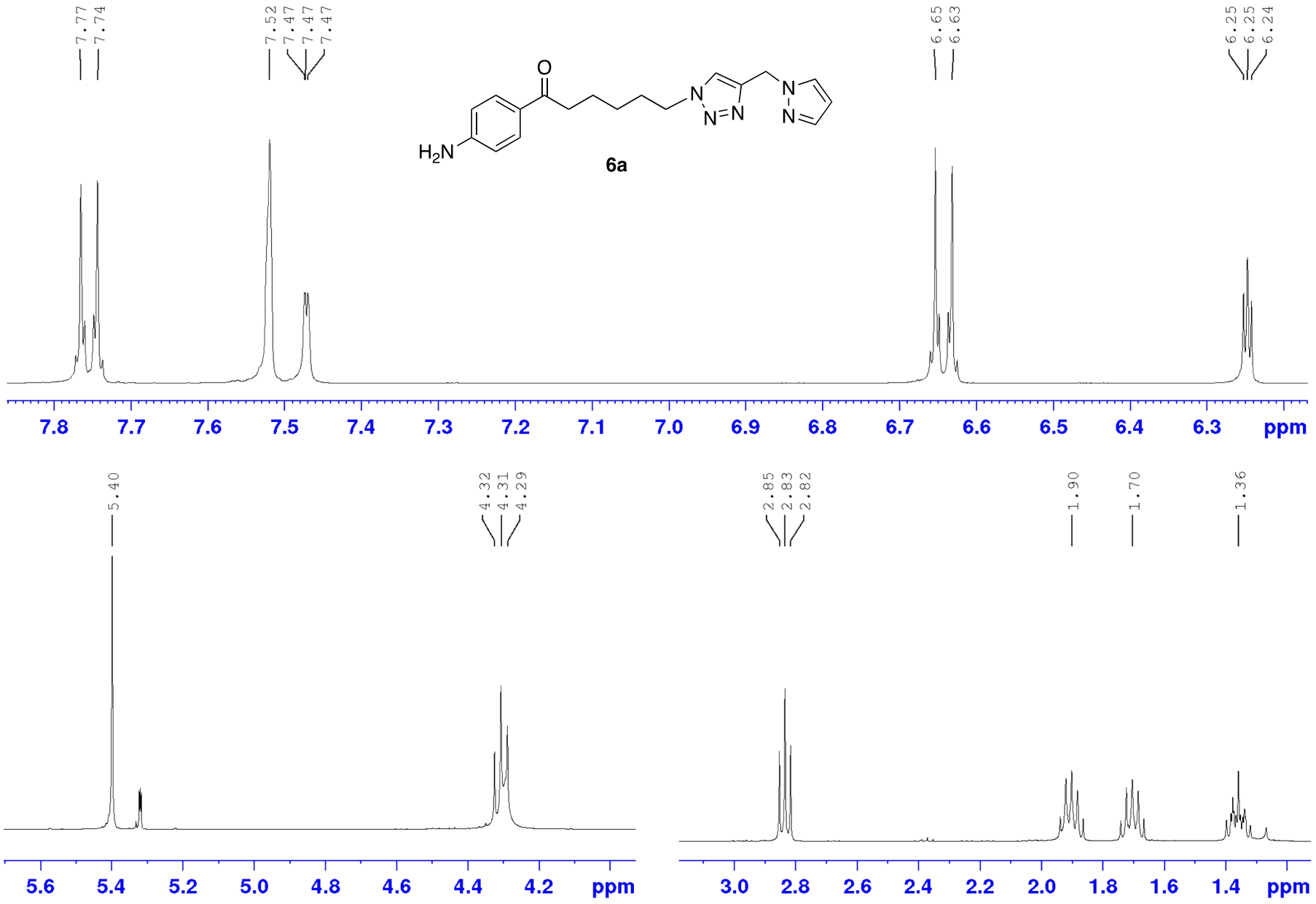
F2 - Processing parameters
SI                    32768
SF             100.6177582 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

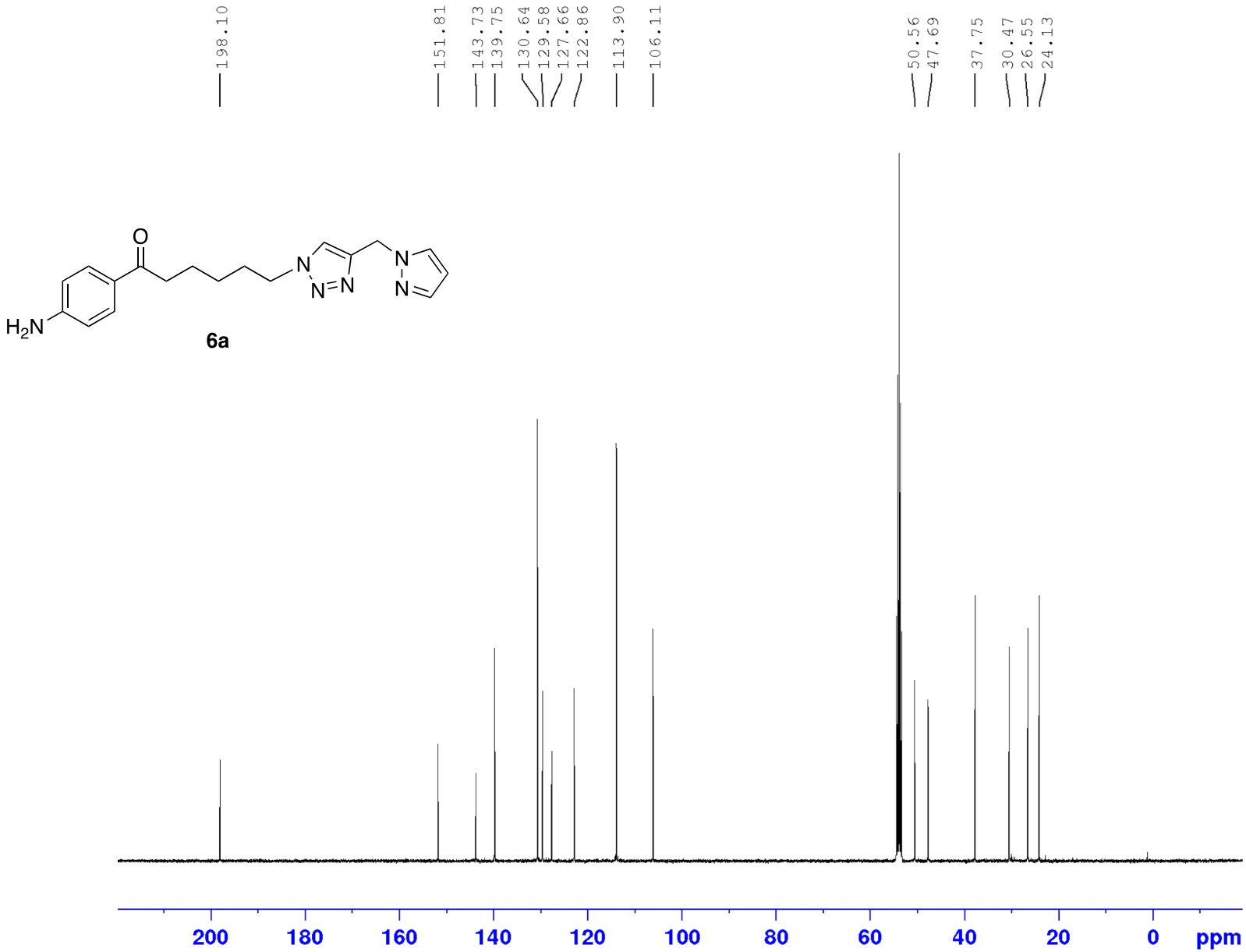



```
Current Data Parameters
NAME                  MR-132
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190409
Time                 11.46 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG                zg30
TD                    65536
SOLVENT            CD2Cl2
NS                        16
DS                         2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                    63.59
DW                   62.400 usec
DE                   12.00 usec
TE                   298.0 K
D1              2.50000000 sec
TD0                        1
SFO1           400.1524709 MHz
NUC1                      1H
P1                   10.00 usec
PLW1           15.75399971 W

F2 - Processing parameters
SI                    65536
SF              400.1500154 MHz
WDW                       EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```


7.77
7.74
7.52
7.47
7.47
7.47
6.65
6.63
6.25
6.25
6.24
O
N
N
N
N
H_2N
6a
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 ppm
5.40
4.32
4.31
4.29
2.85
2.83
2.82
1.90
1.70
1.36
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 ppm
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm

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Current Data Parameters
NAME                  MR-132
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190409
Time                 23.00 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG              zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                     3000
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   198.41
DW                   20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1
SFO1           100.6278593 MHz
NUC1                    13C
P1                   10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

F2 - Processing parameters
SI                    32768
SF             100.6177608 MHz
WDW                     EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
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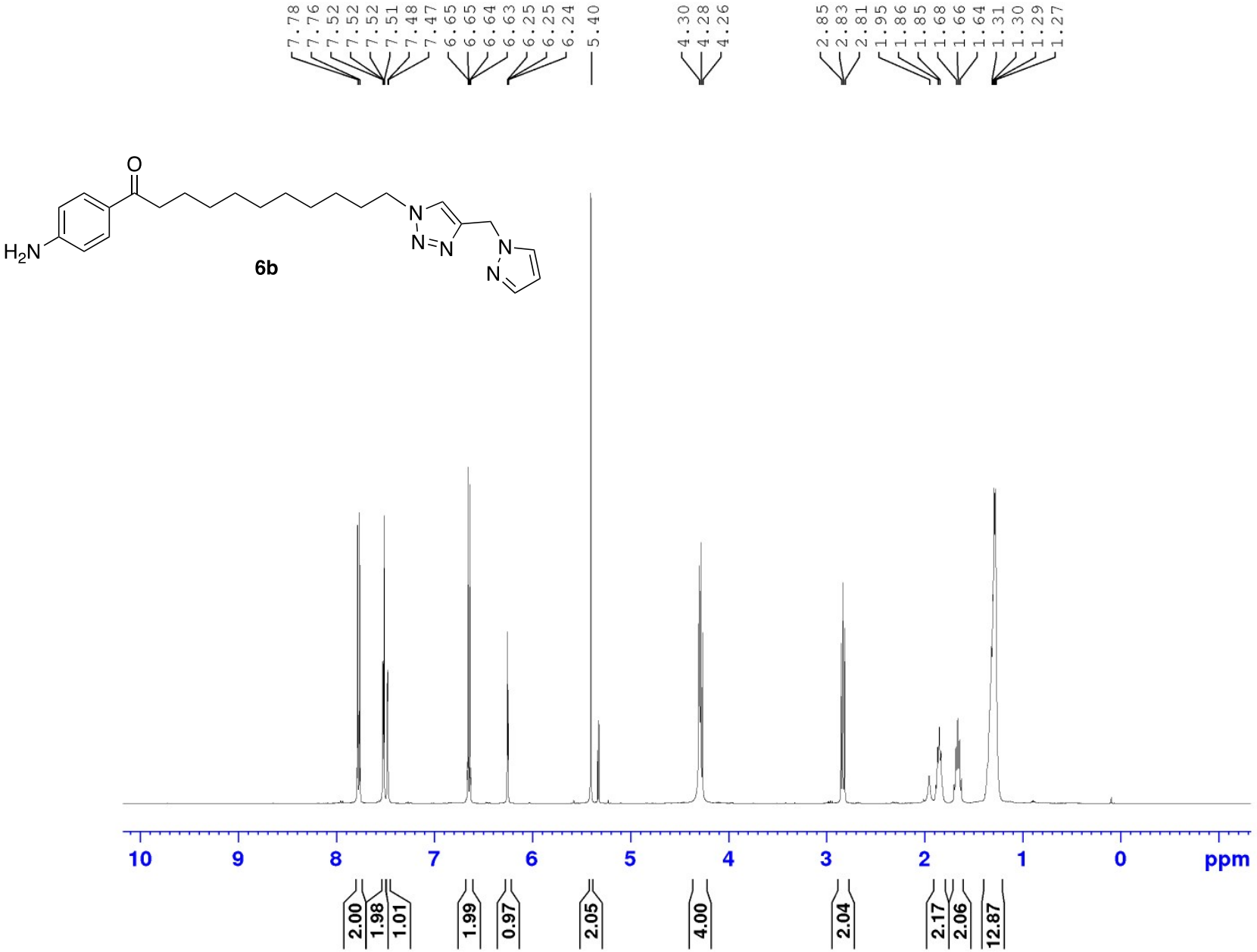


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Current Data Parameters
NAME                  MR-129
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190403
Time                 18.20 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG                zg30
TD                    65536
SOLVENT             CD2Cl2
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                     31.83
DW                    62.400 usec
DE                    12.00 usec
TE                    298.0 K
D1              2.50000000 sec
TD0                        1
SFO1           400.1524709 MHz
NUC1                      1H
P1                    10.00 usec
PLW1           15.75399971 W

F2 - Processing parameters
SI                    65536
SF             400.1500154 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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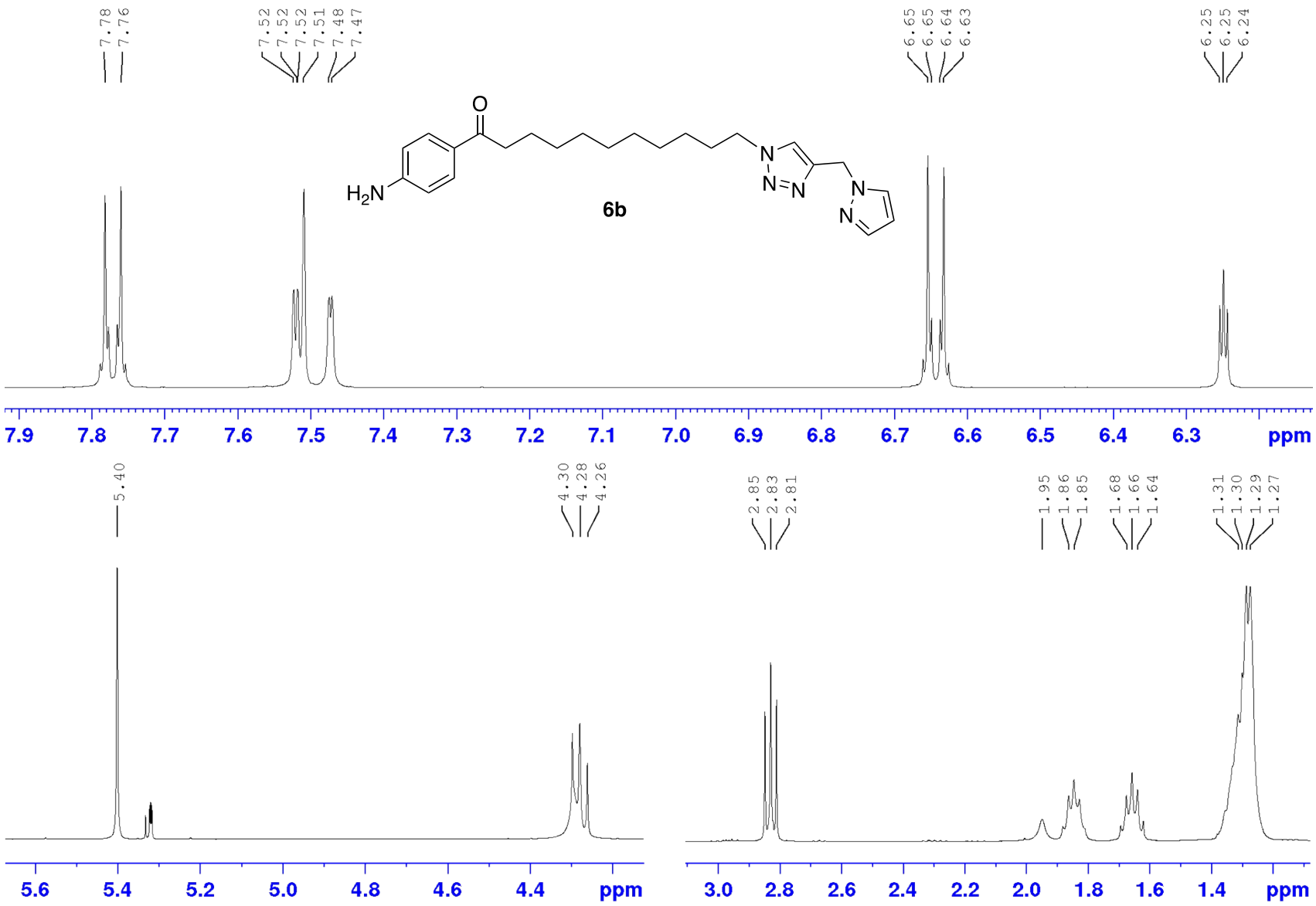
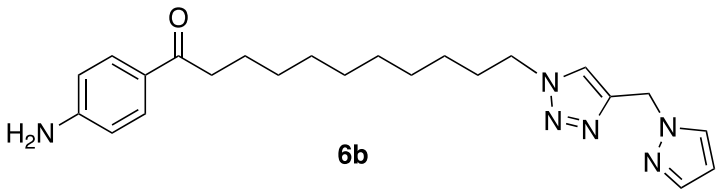

7.78
7.76
7.52
7.52
7.52
7.51
7.48
7.47
6.65
6.65
6.64
6.63
6.25
6.25
6.24
O
H2N
N
N=N
N
N
6b
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
ppm
5.40
4.30
4.28
4.26
2.85
2.83
2.81
1.95
1.86
1.85
1.68
1.66
1.64
1.31
1.30
1.29
1.27
5.6
5.4
5.2
5.0
4.8
4.6
4.4
ppm
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm

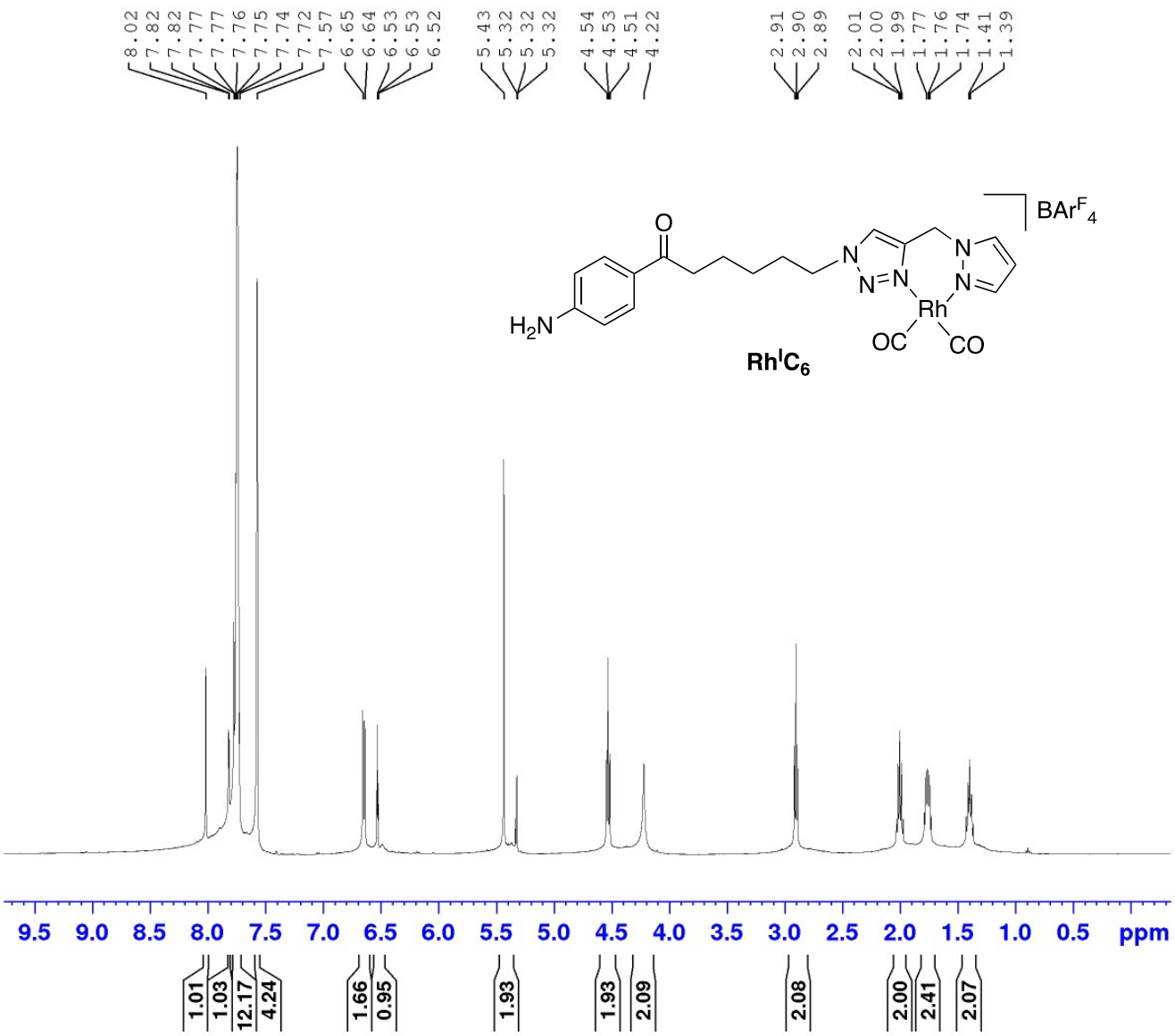


6b

198.79
151.72
143.73
139.77
130.68
129.58
127.83
122.77
113.90
106.12

150.76
147.70
143.23
140.54
139.76
139.73
139.68
139.65
139.27
136.78
135.12

Current Data Parameters
NAME MR-129
EXPNO 3

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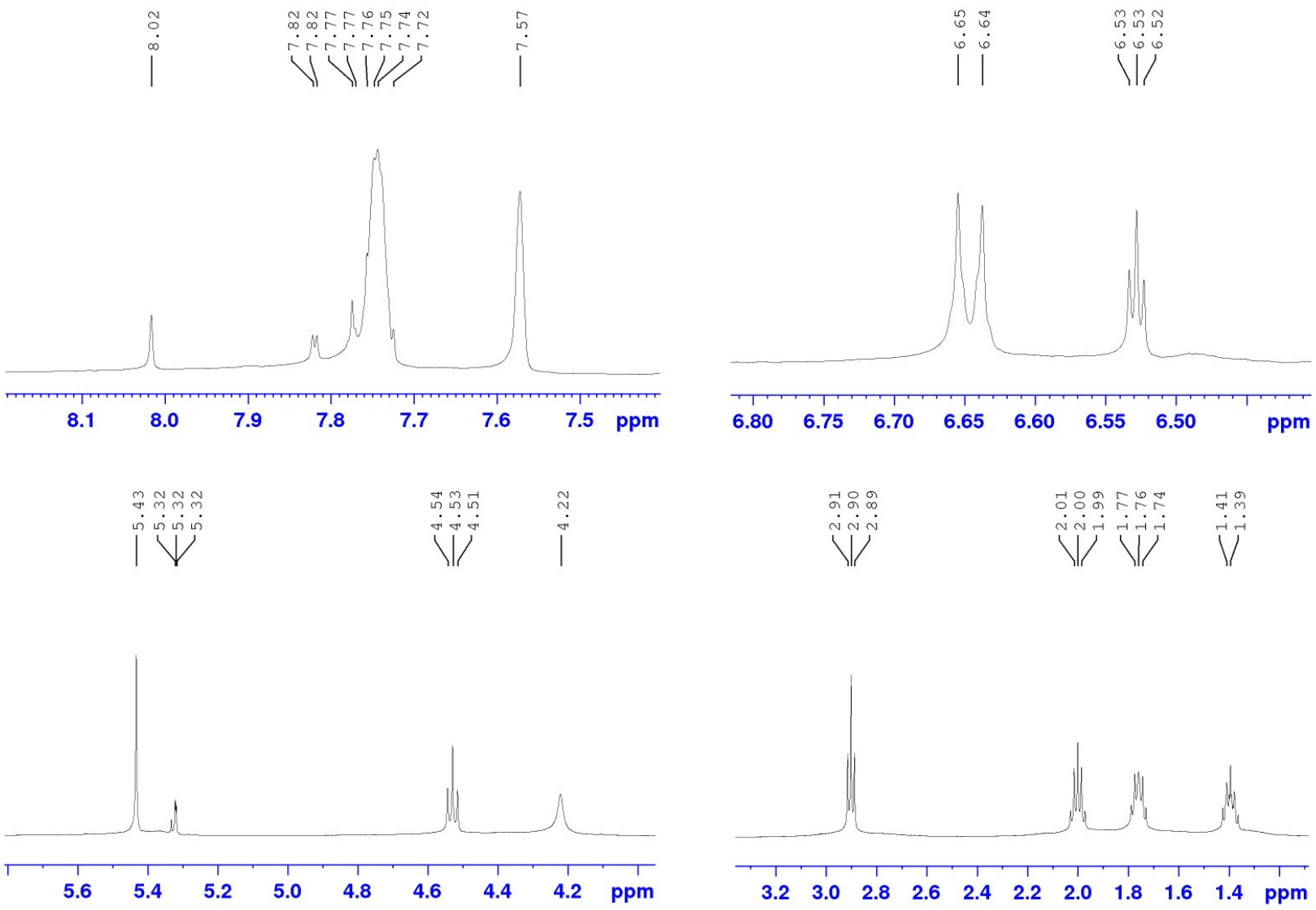
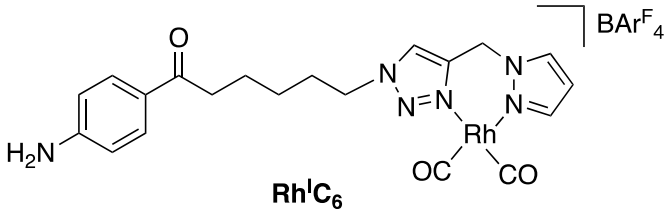
Current Data Parameters
NAME                  MR-314
EXPNO                      6
PROCNO                     1

F2 - Acquisition Parameters
Date_              20191204
Time                 16.27 h
INSTRUM                spect
PROBHD    Z119470_0266 (
PULPROG                   zg
TD                     65536
SOLVENT              CD2Cl2
NS                         8
DS                         0
SWH              10000.000 Hz
FIDRES               0.305176 Hz
AQ                3.2767999 sec
RG                      37.71
DW                    50.000 usec
DE                     6.50 usec
TE                    298.0 K
D1               5.00000000 sec
TD0                        1
SFO1           500.1622533 MHz
NUC1                      1H
P1                    11.10 usec
PLW1           25.00000000 W

F2 - Processing parameters
SI                    131072
SF             500.1600193 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

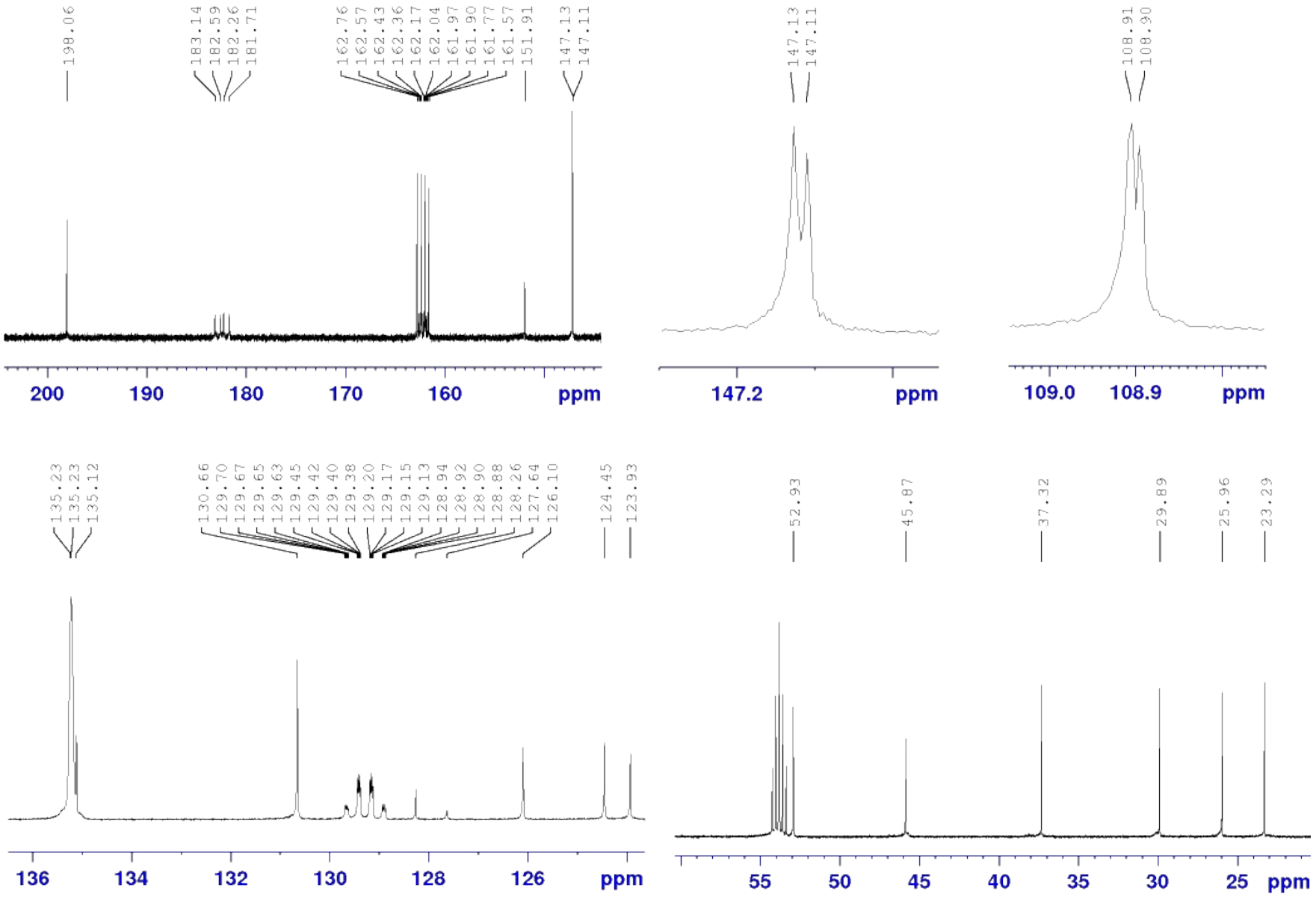

8.02
7.82
7.82
7.77
7.77
7.76
7.75
7.74
7.72
7.57
8.1 8.0 7.9 7.8 7.7 7.6 7.5 ppm
6.65
6.64
6.53
6.53
6.52
6.80 6.75 6.70 6.65 6.60 6.55 6.50 ppm
5.43
5.32
5.32
5.32
4.54
4.53
4.51
4.22
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 ppm
2.91
2.90
2.89
2.01
2.00
1.99
1.77
1.76
1.74
1.41
1.39
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm

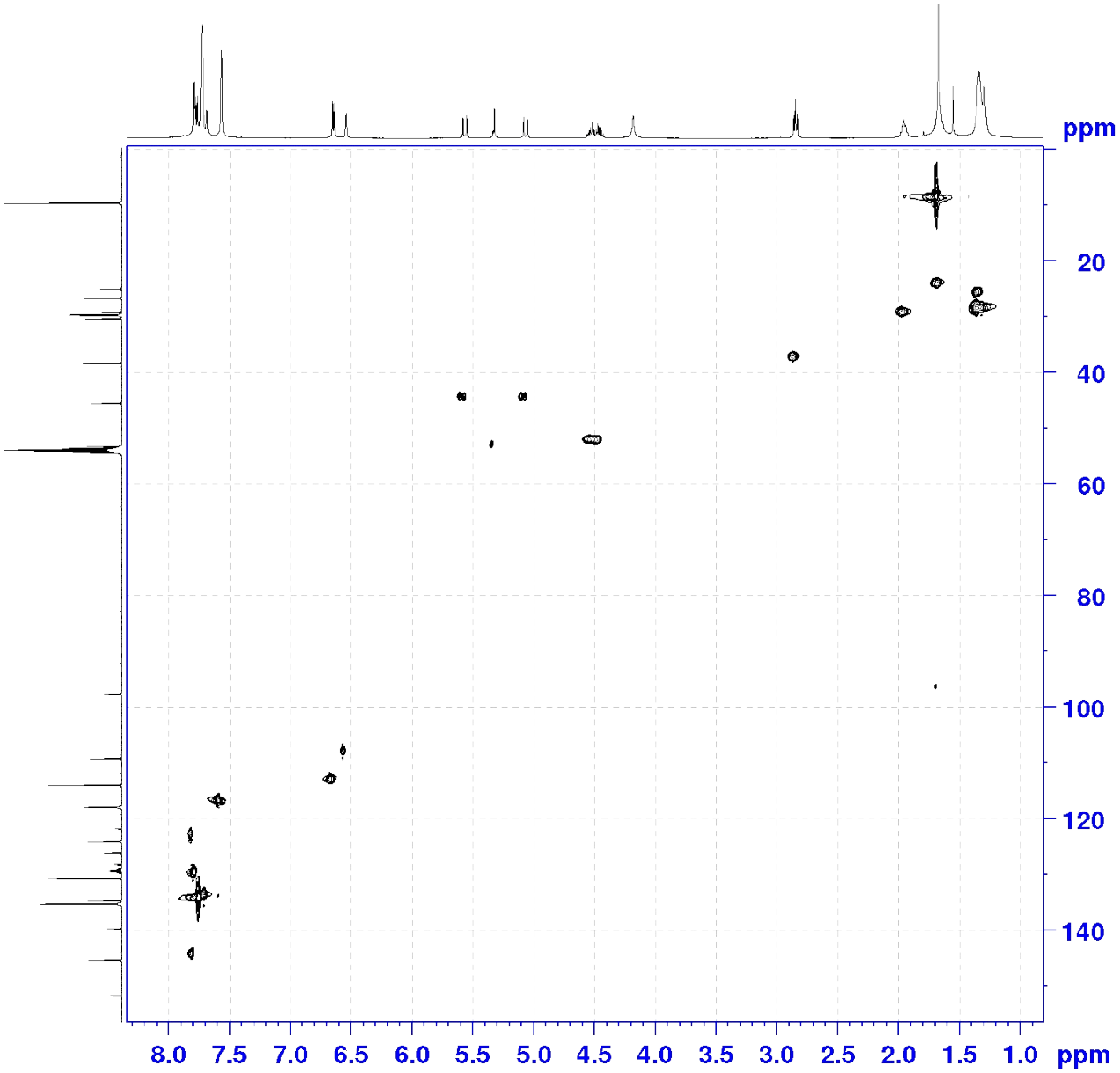


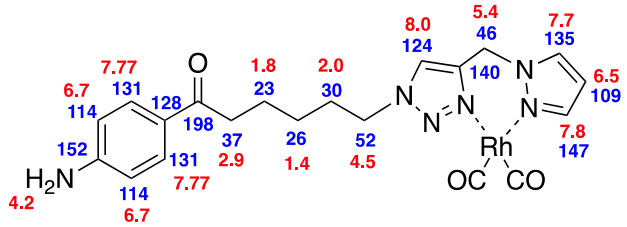
Rh^IC_6

8.06
3.14
2.59
2.27
1.71
2.76
2.43
2.37
2.04
1.97
1.57
1.92
7.13
7.11
9.69
5.23
5.12
0.66
9.67
9.65
9.44
9.42
9.40
9.38
9.19
9.17
9.15
8.94
8.92
8.90
8.26
7.64
6.10
4.45
3.93
1.76
7.95
7.92
7.89
4.01
8.91
.93
.87
.32
.89
.97
.29

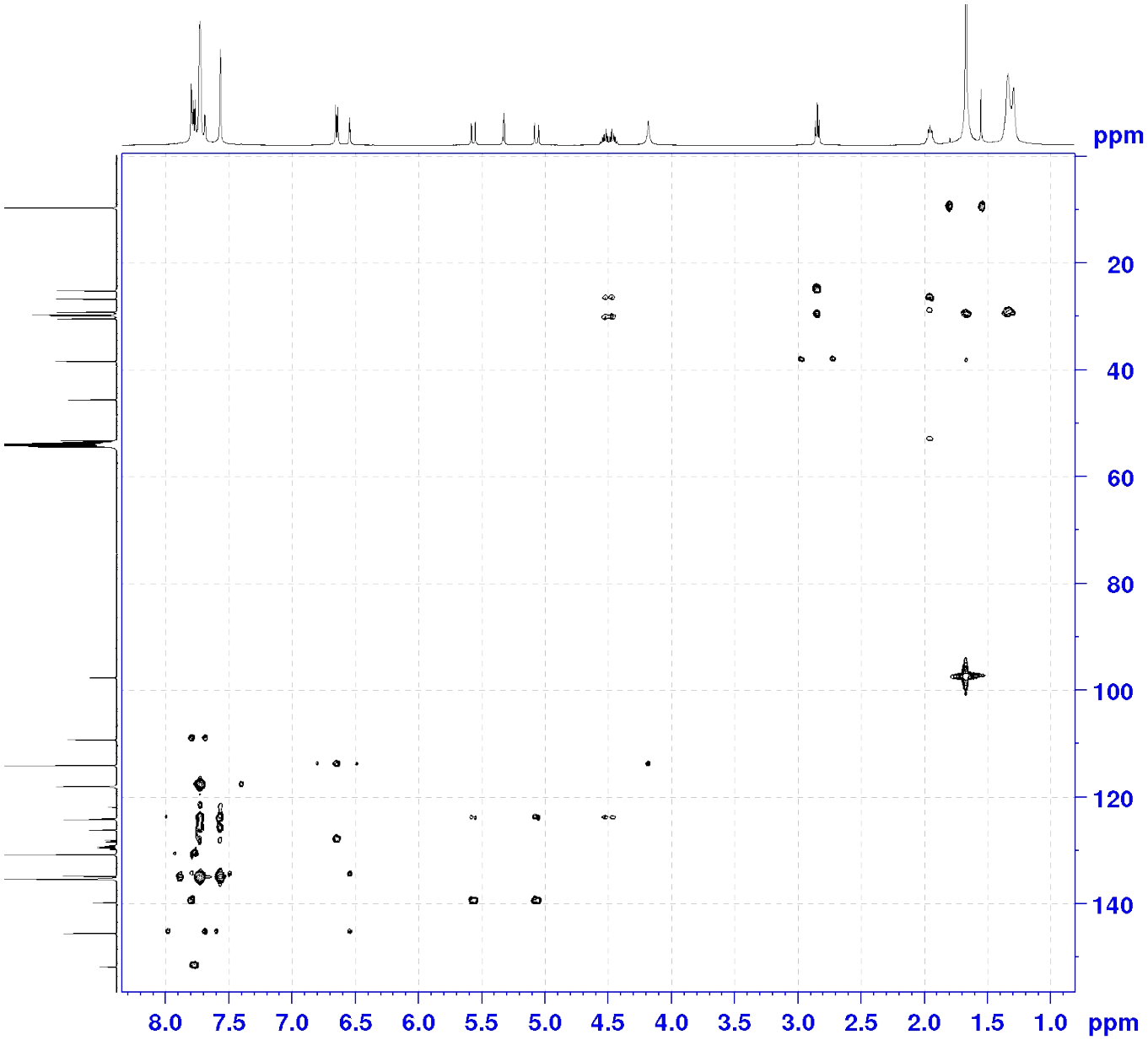
Current Data Parameters
NAME MR-314


198.06
183.14
182.59
182.26
181.71
162.76
162.57
162.43
162.36
162.17
162.04
161.97
161.90
161.77
161.57
151.91
147.13
147.11
200
190
180
170
160
ppm
147.13
147.11
147.2
ppm
108.91
108.90
109.0
108.9
ppm
135.23
135.23
135.12
130.66
129.70
129.67
129.65
129.63
129.45
129.42
129.40
129.38
129.20
129.17
129.15
129.13
128.94
128.92
128.90
128.88
128.26
127.64
126.10
124.45
123.93
136
134
132
130
128
126
ppm
52.93
45.87
37.32
29.89
25.96
23.29
55
50
45
40
35
30
25
ppm

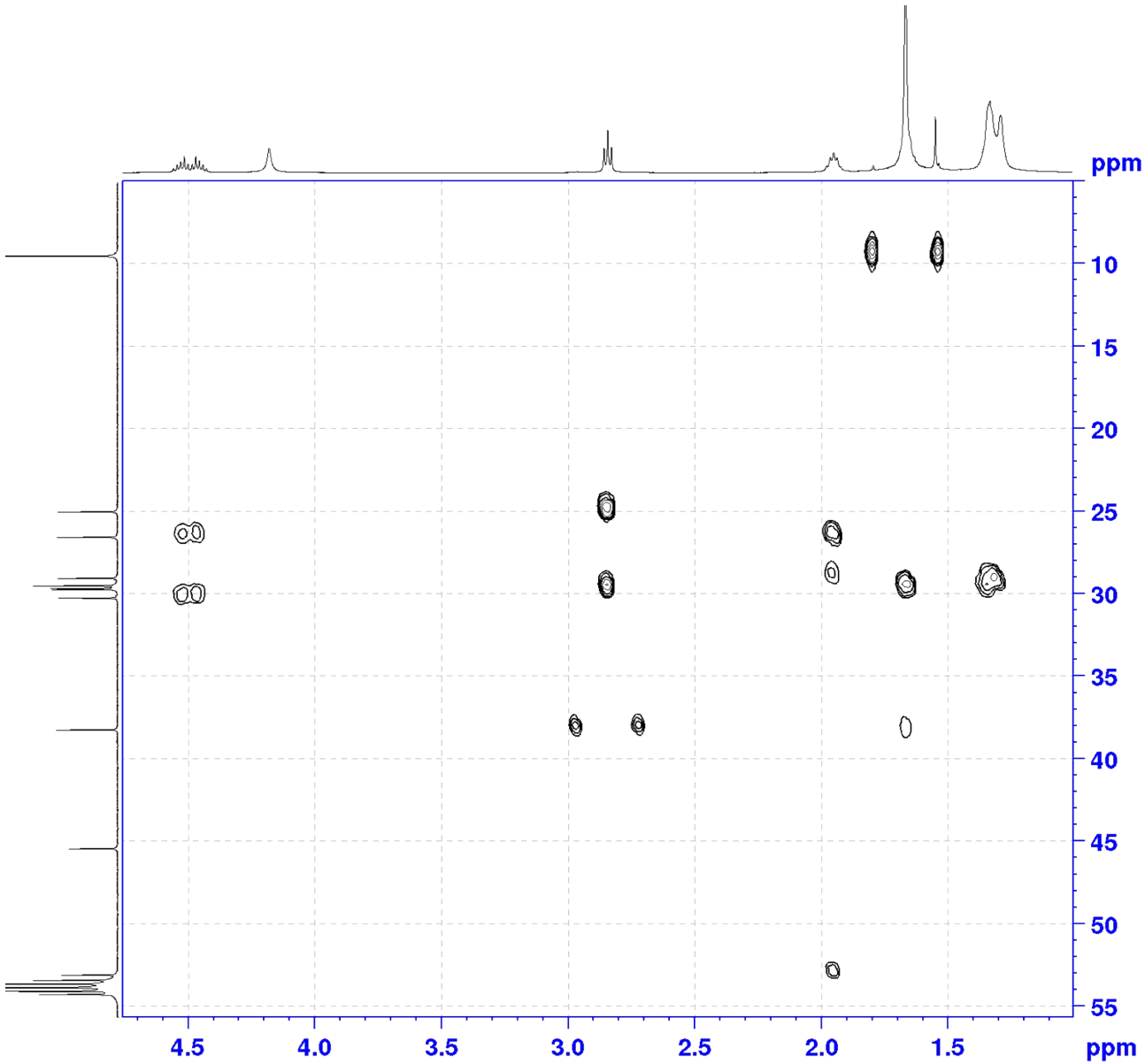




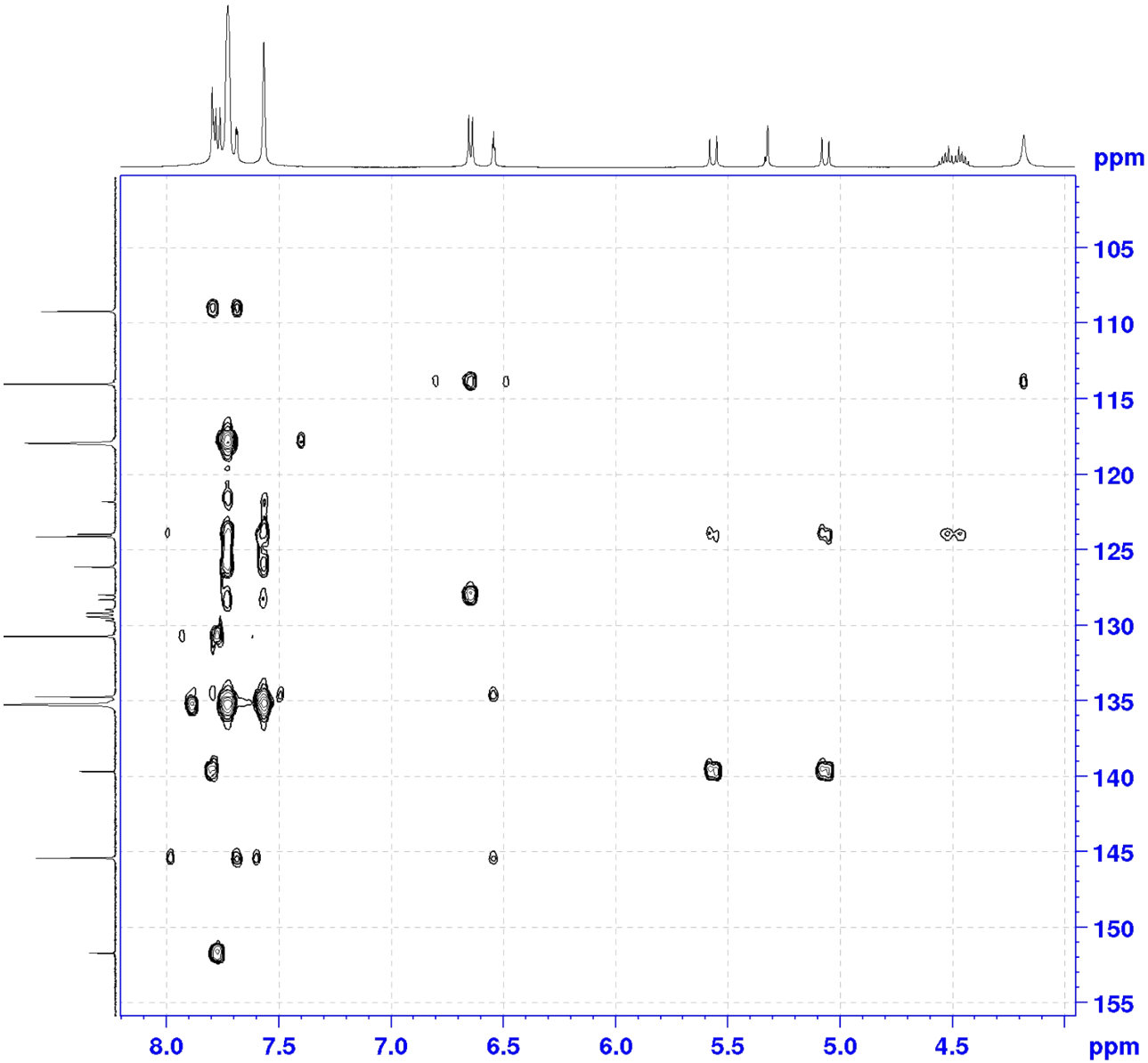
2D HSQC NMR spectrum of compound **Rh^{I}C$_6$** in CD_2Cl_2 and assignment of ^{1}H (red) and ^{13}C (blue) NMR resonances.



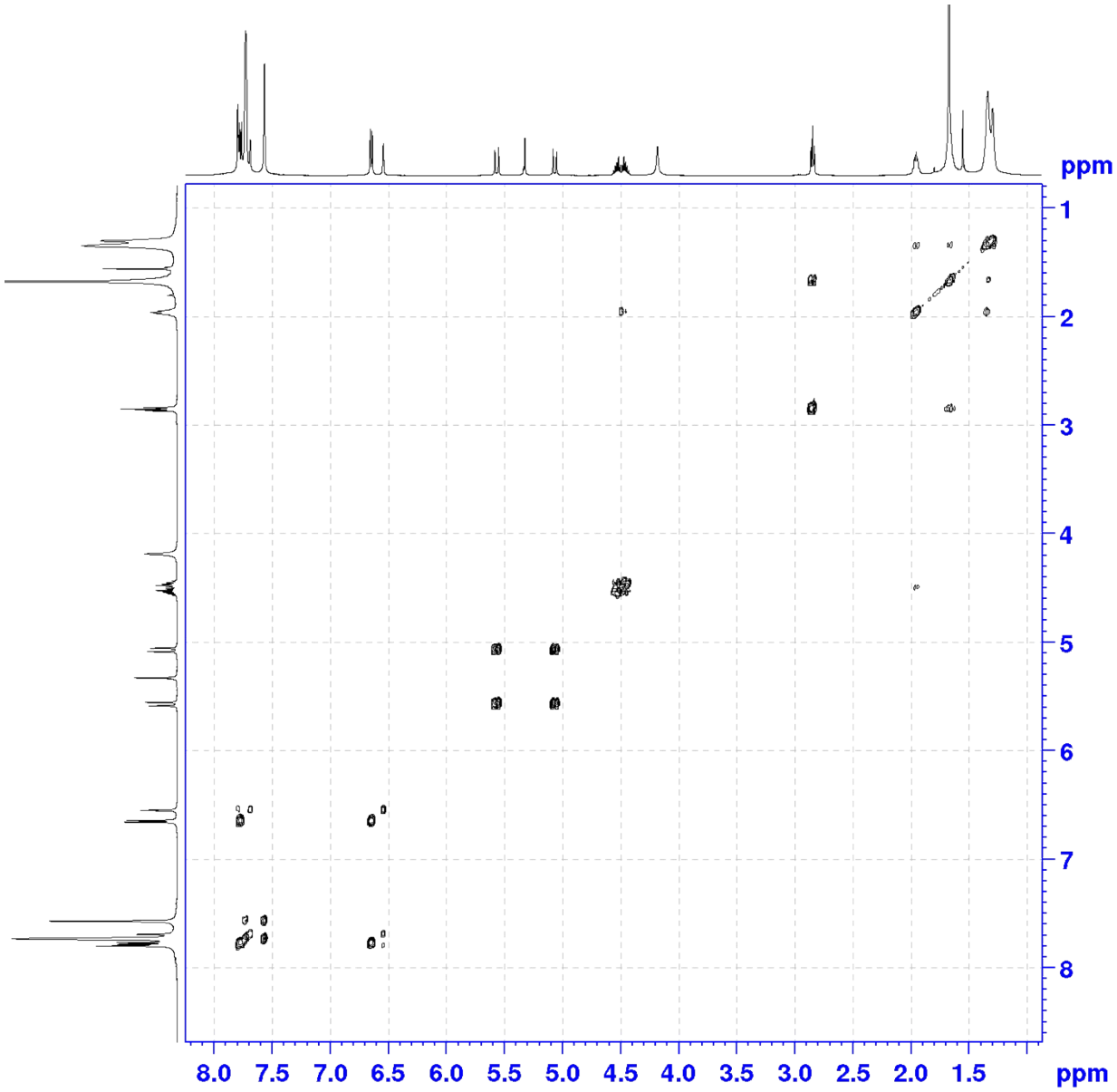
2D HMBC NMR spectrum of compound **$Rh^{I}C_6$** in CD_2Cl_2.



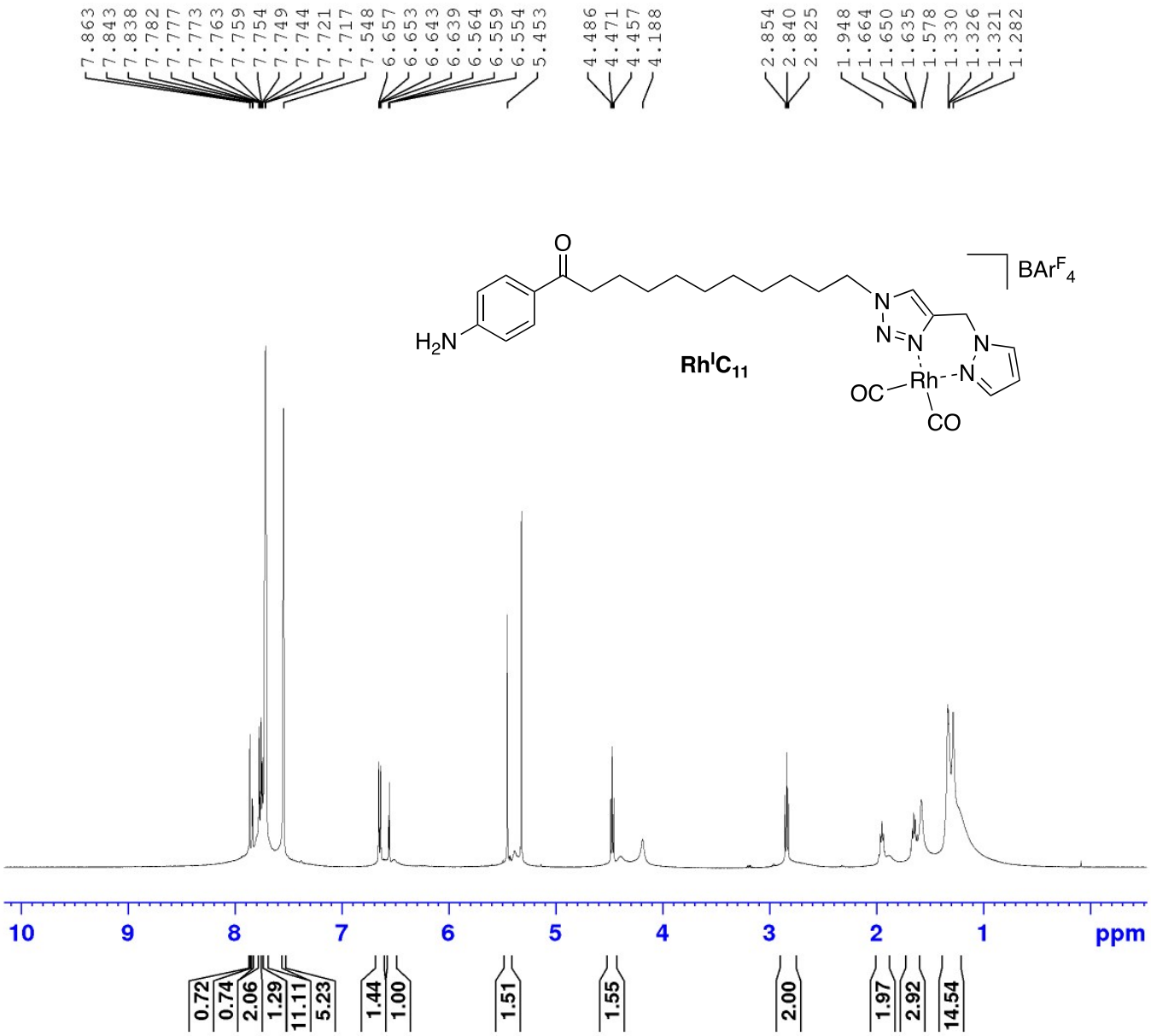
Selected range of the 2D HMBC NMR spectrum of compound **$Rh^{I}C_6$** in CD_2Cl_2.



Selected range of the 2D HMBC NMR spectrum of compound **$Rh^{I}C_6$** in CD_2Cl_2.



2D COSY NMR spectrum of compound **Rh^{I}C$_6$** in CD_2Cl_2.

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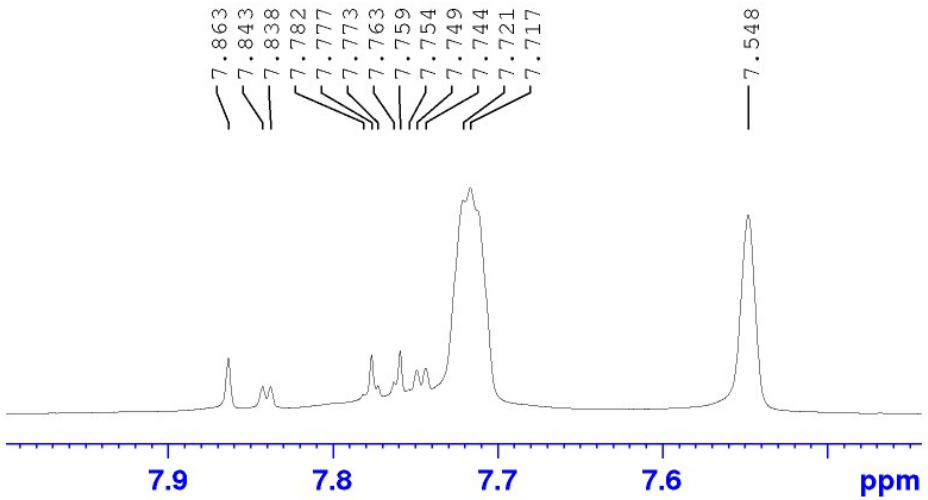
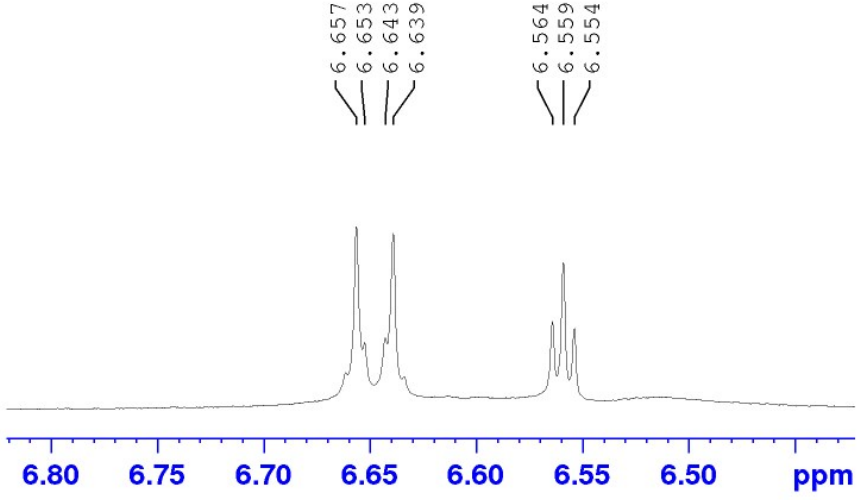
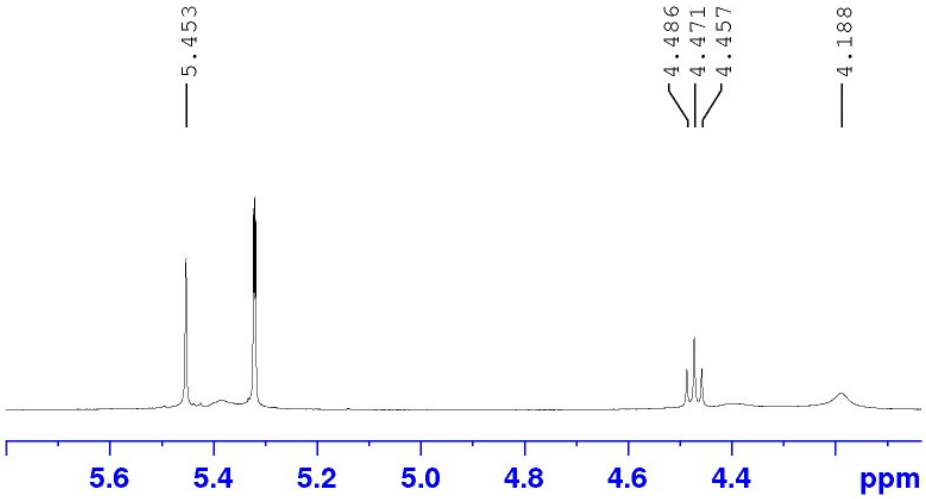
Current Data Parameters
NAME                  MR-104
EXPNO                      7
PROCNO                     1

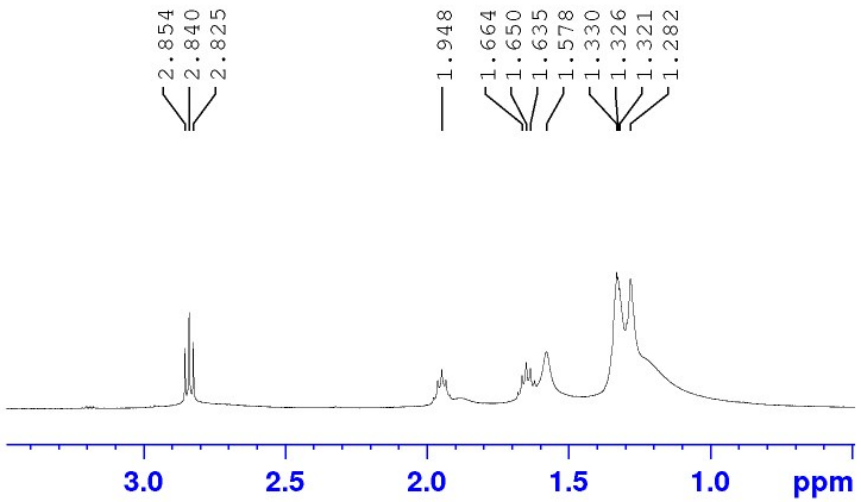
F2 - Acquisition Parameters
Date_              20200116
Time                 15.52 h
INSTRUM              spect
PROBHD    Z119470_0266 (
PULPROG                  zg
TD                    65536
SOLVENT              CD2Cl2
NS                         8
DS                         0
SWH              10000.000 Hz
FIDRES               0.305176 Hz
AQ                3.2767999 sec
RG                    65.43
DW                   50.000 usec
DE                    6.50 usec
TE                   298.0 K
D1             5.00000000 sec
TD0                        1
SFO1           500.1622533 MHz
NUC1                    1H
P1                   11.10 usec
PLW1          25.00000000 W

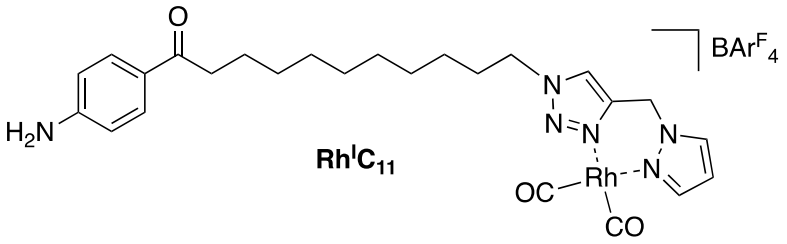
F2 - Processing parameters
SI                    131072
SF             500.1600194 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```


7.863
7.843
7.838
7.782
7.777
7.773
7.763
7.759
7.754
7.749
7.744
7.721
7.717
7.548
7.9
7.8
7.7
7.6
ppm


6.657
6.653
6.643
6.639
6.564
6.559
6.554
6.80
6.75
6.70
6.65
6.60
6.55
6.50
ppm


5.453
4.486
4.471
4.457
4.188
5.6
5.4
5.2
5.0
4.8
4.6
4.4
ppm

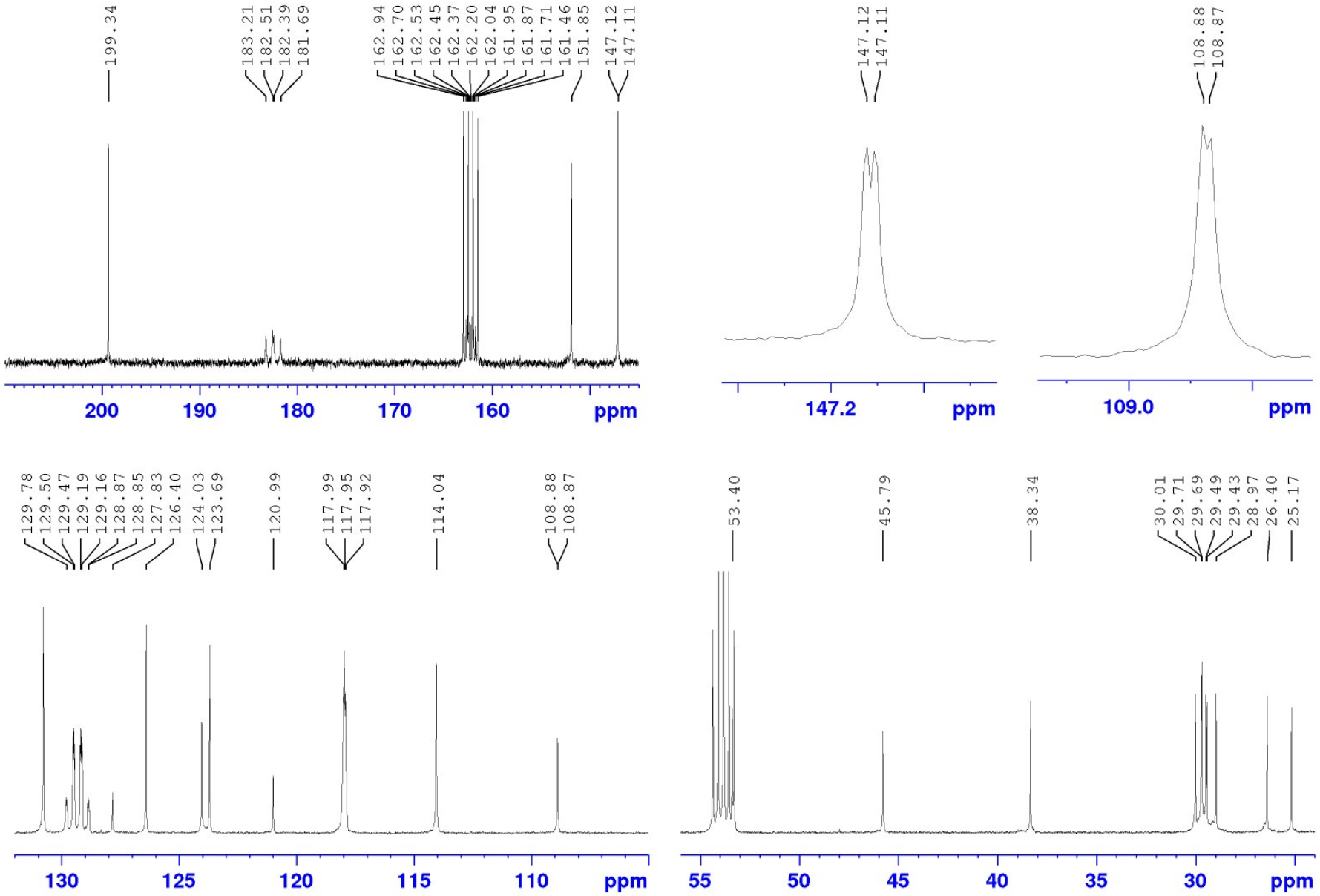

2.854
2.840
2.825
1.948
1.664
1.650
1.635
1.578
1.330
1.326
1.321
1.282
3.0
2.5
2.0
1.5
1.0
ppm

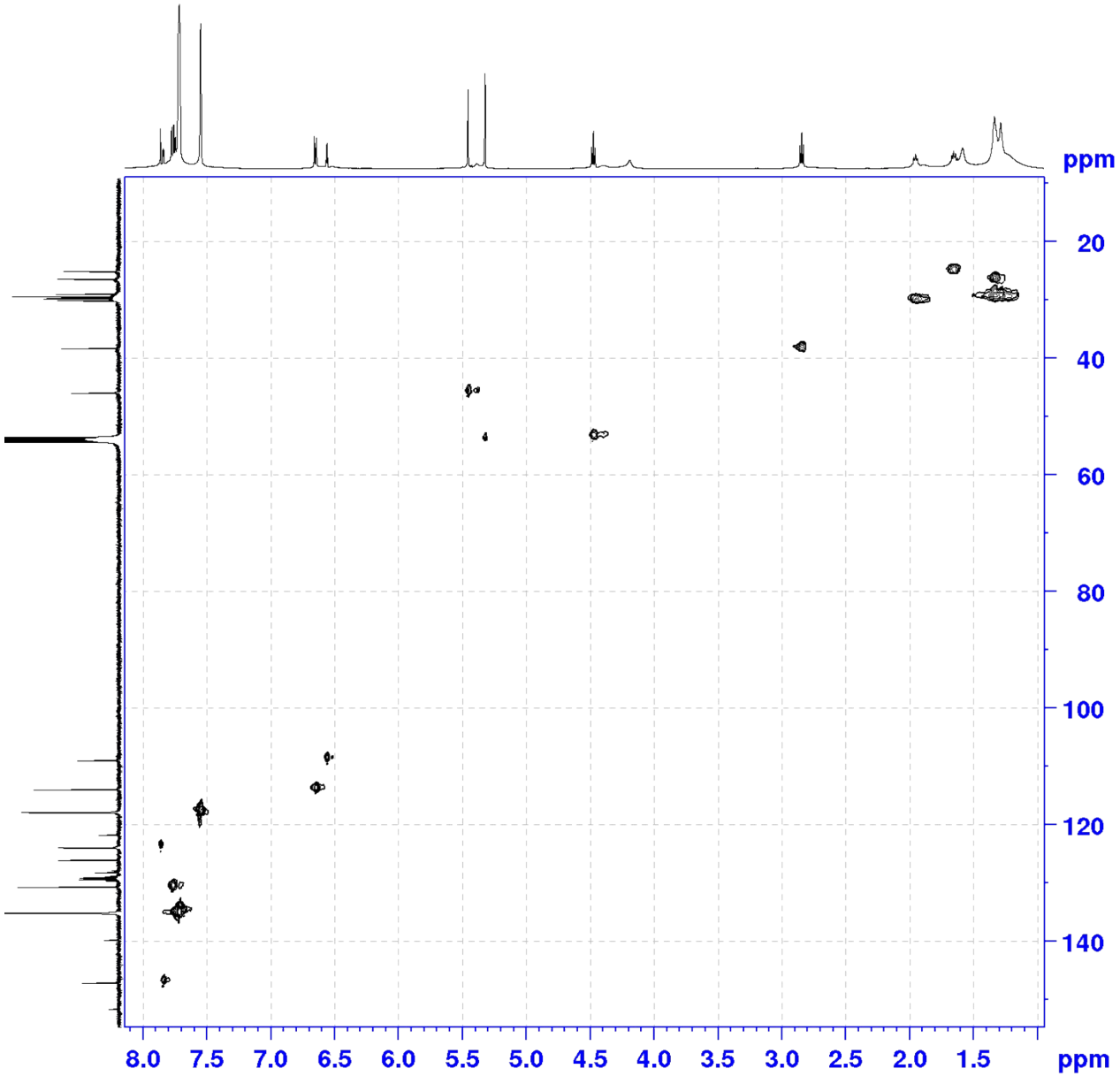


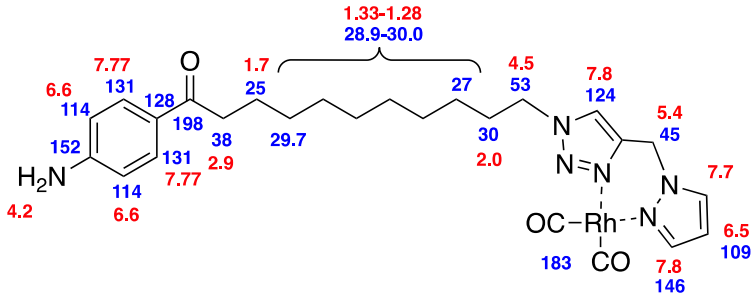
Rh^IC_{11}

1.69
2.94
2.70
2.53
2.45
2.37
2.20
2.04
1.95
1.87
1.71
1.46
1.85
7.12
7.11
9.88
5.26
5.16
0.77
9.81
9.78
9.50
9.47
9.19
9.16
8.87
8.85
7.83
6.40
4.03
3.69
0.99
7.99
7.95
7.92
4.04
8.88
8.87
.40
.79
.34
.01
.71
.69
.49
.43
.97
.40
.17

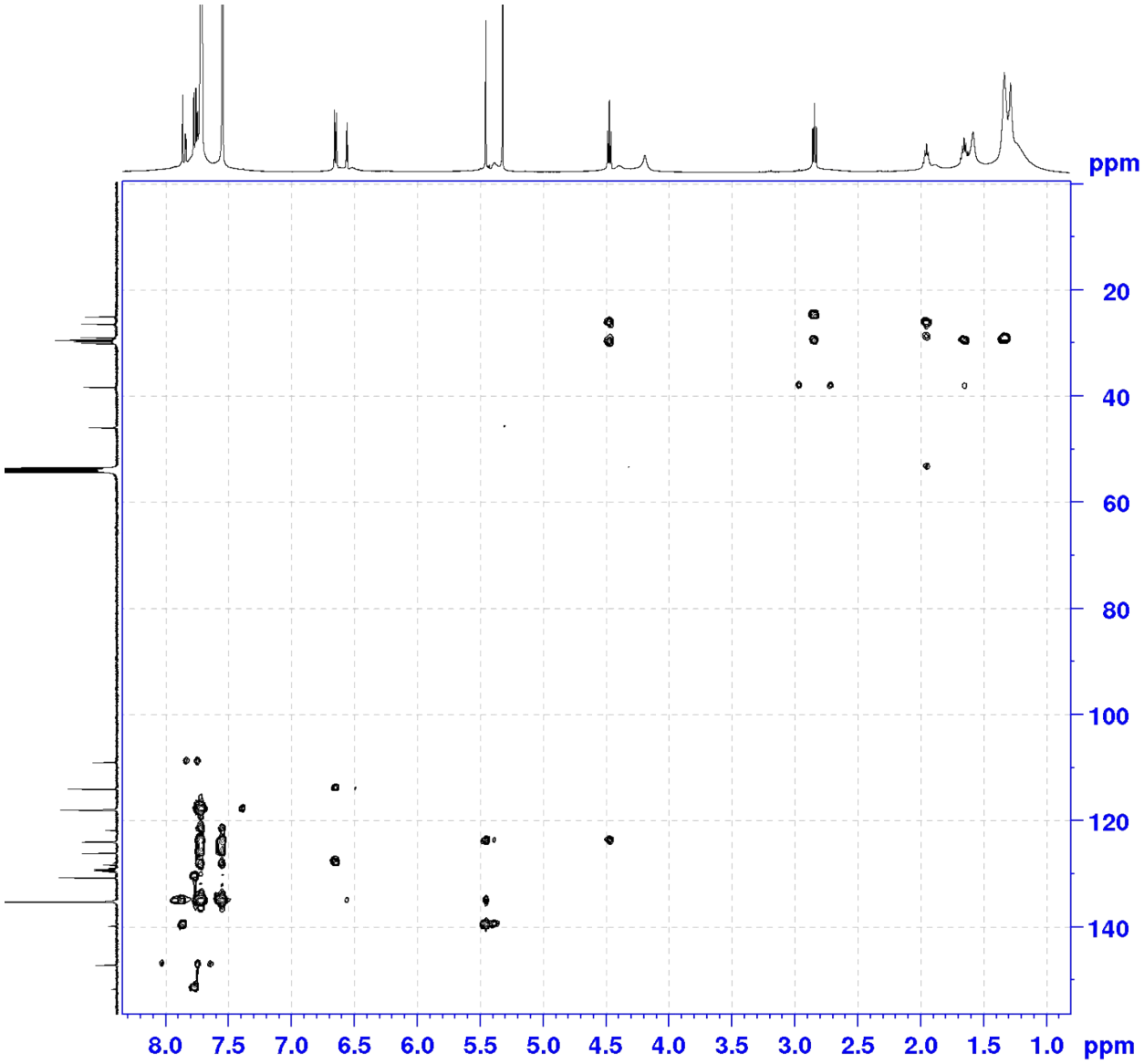
Current Data Parameters
NAME MR-104


199.34
183.21
182.51
182.39
181.69
162.94
162.70
162.53
162.45
162.37
162.20
162.04
161.95
161.87
161.71
161.46
151.85
147.12
147.11
200
190
180
170
160
ppm
147.12
147.11
147.2
ppm
108.88
108.87
109.0
ppm
129.78
129.50
129.47
129.19
129.16
128.87
128.85
127.83
126.40
124.03
123.69
120.99
117.99
117.95
117.92
114.04
108.88
108.87
130
125
120
115
110
ppm
53.40
45.79
38.34
30.01
29.71
29.69
29.49
29.43
28.97
26.40
25.17
55
50
45
40
35
30
ppm

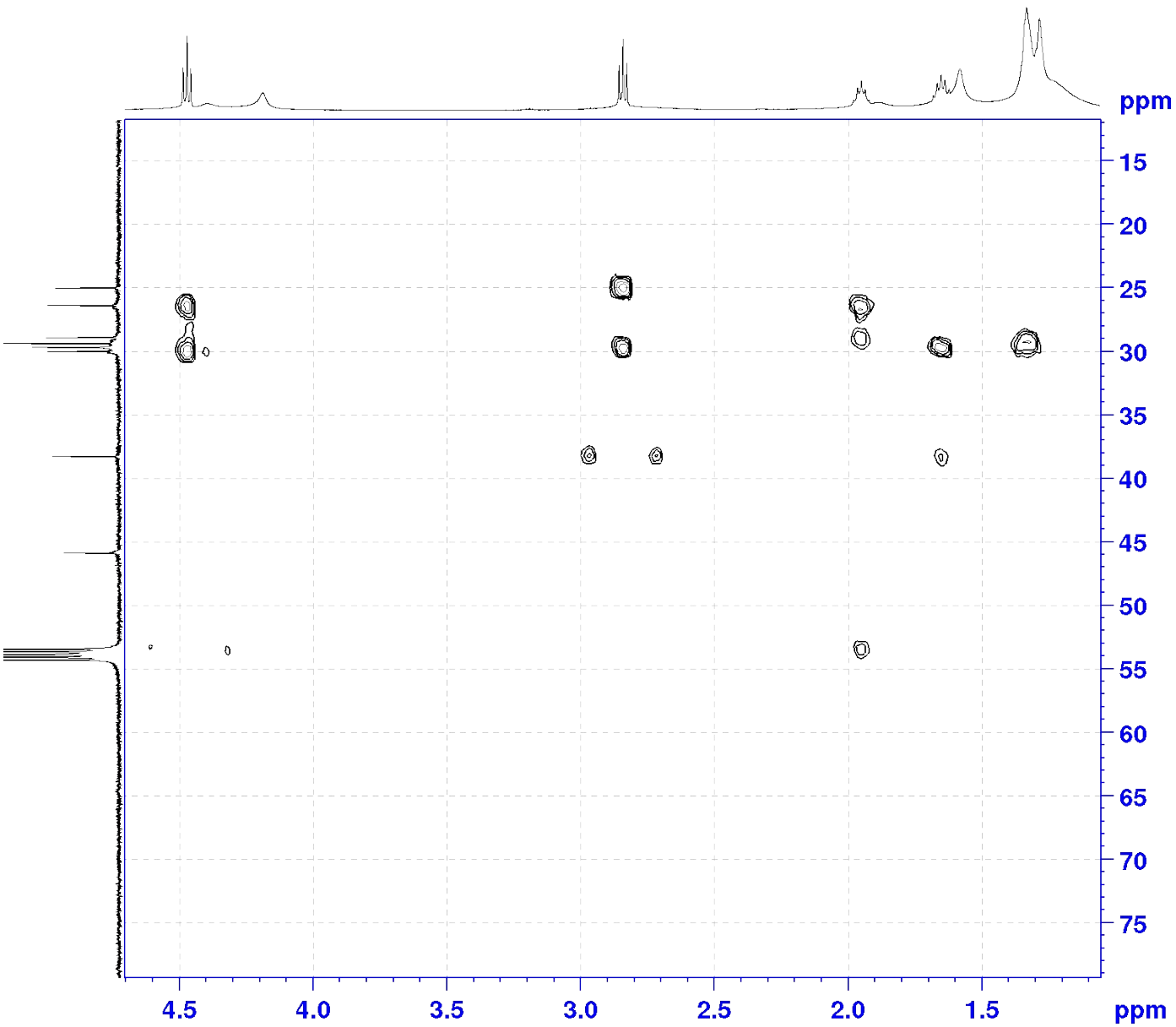




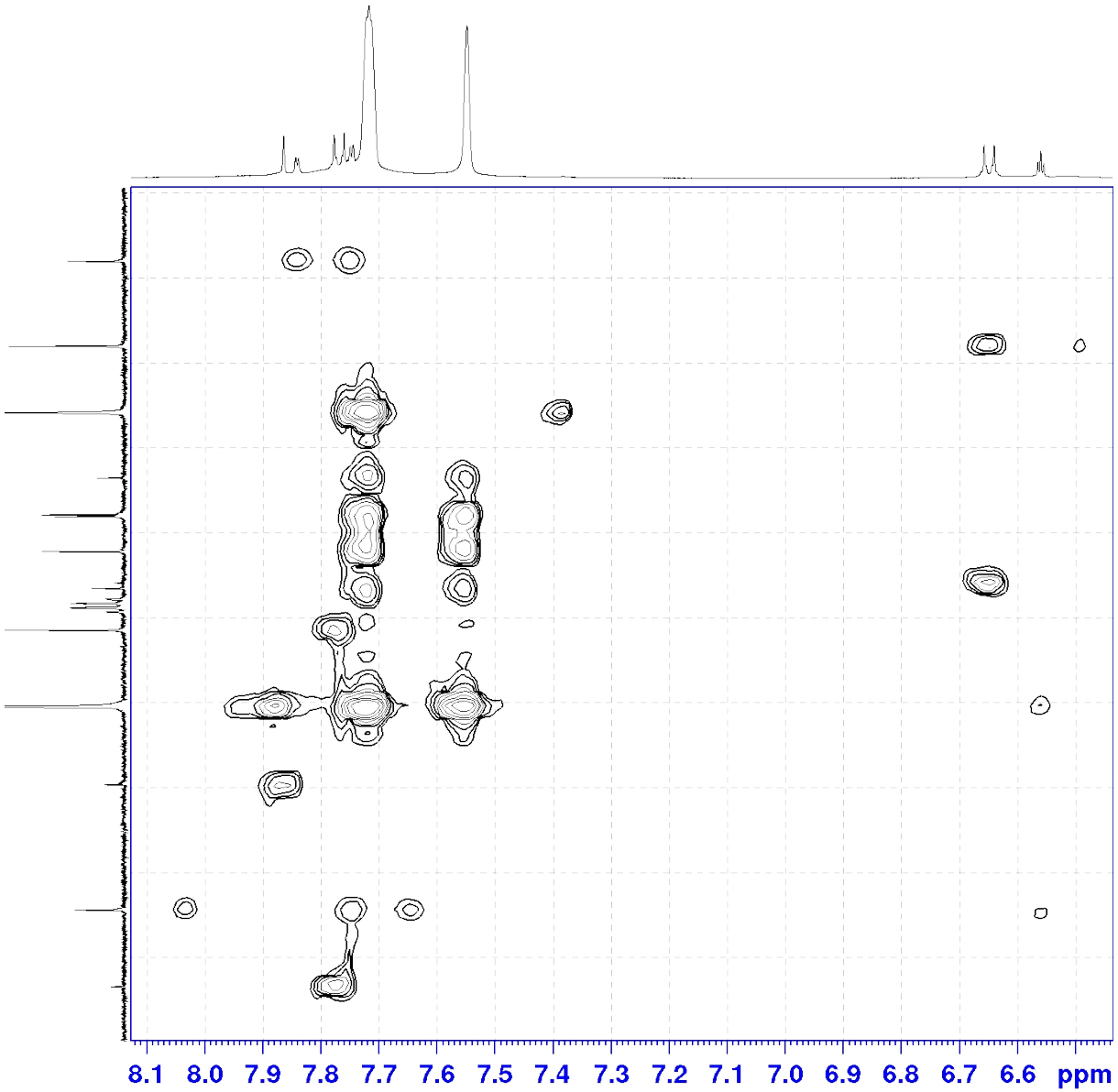
2D HSQC NMR spectrum of compound **Rh^{I}C$_{11}$** in CD_2Cl_2 assignment of ^{1}H (red) and ^{13}C (blue) NMR resonances.



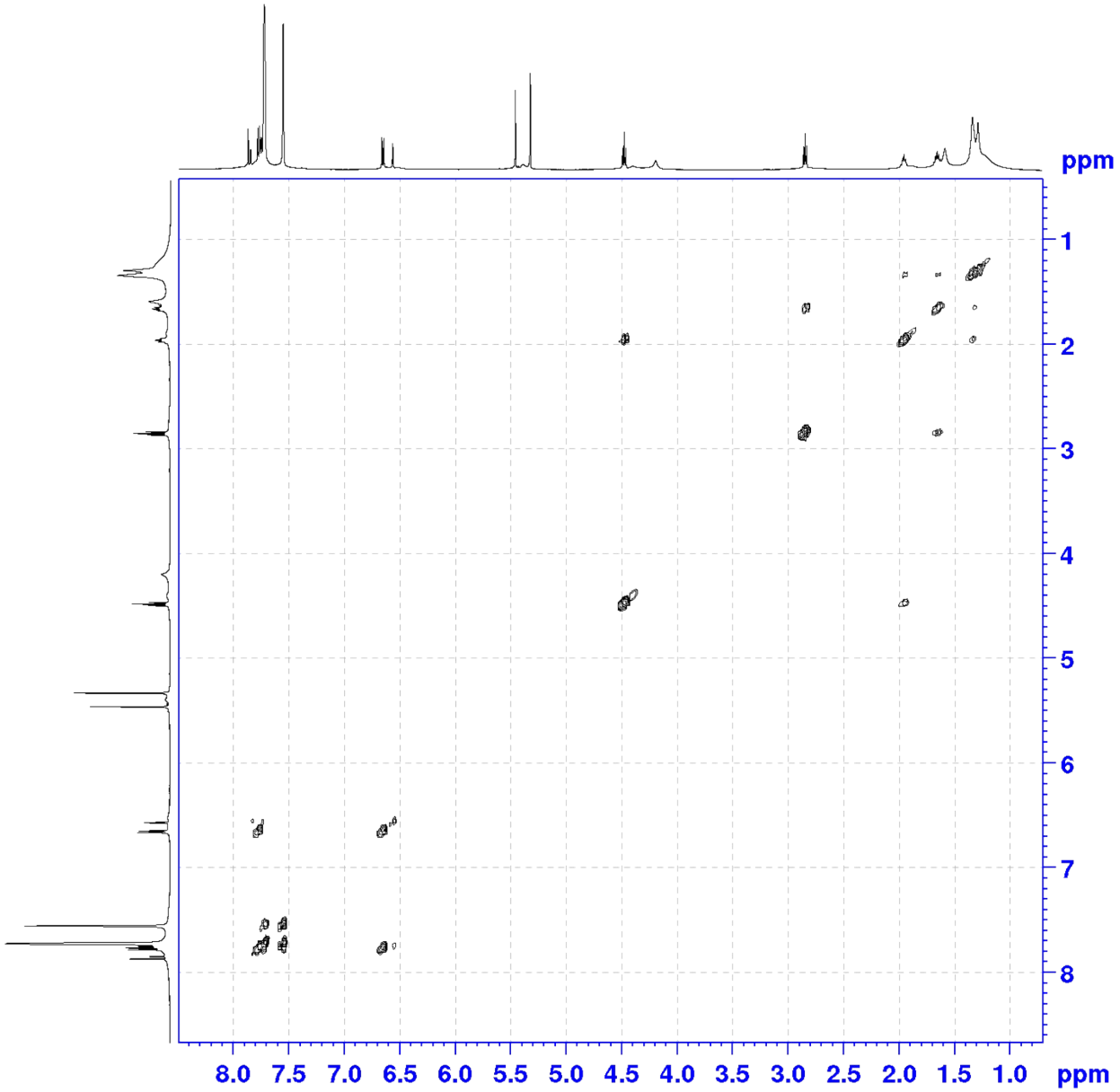
2D HMBC NMR spectrum of compound **Rh^{I}C$_{11}$** in CD_2Cl_2.



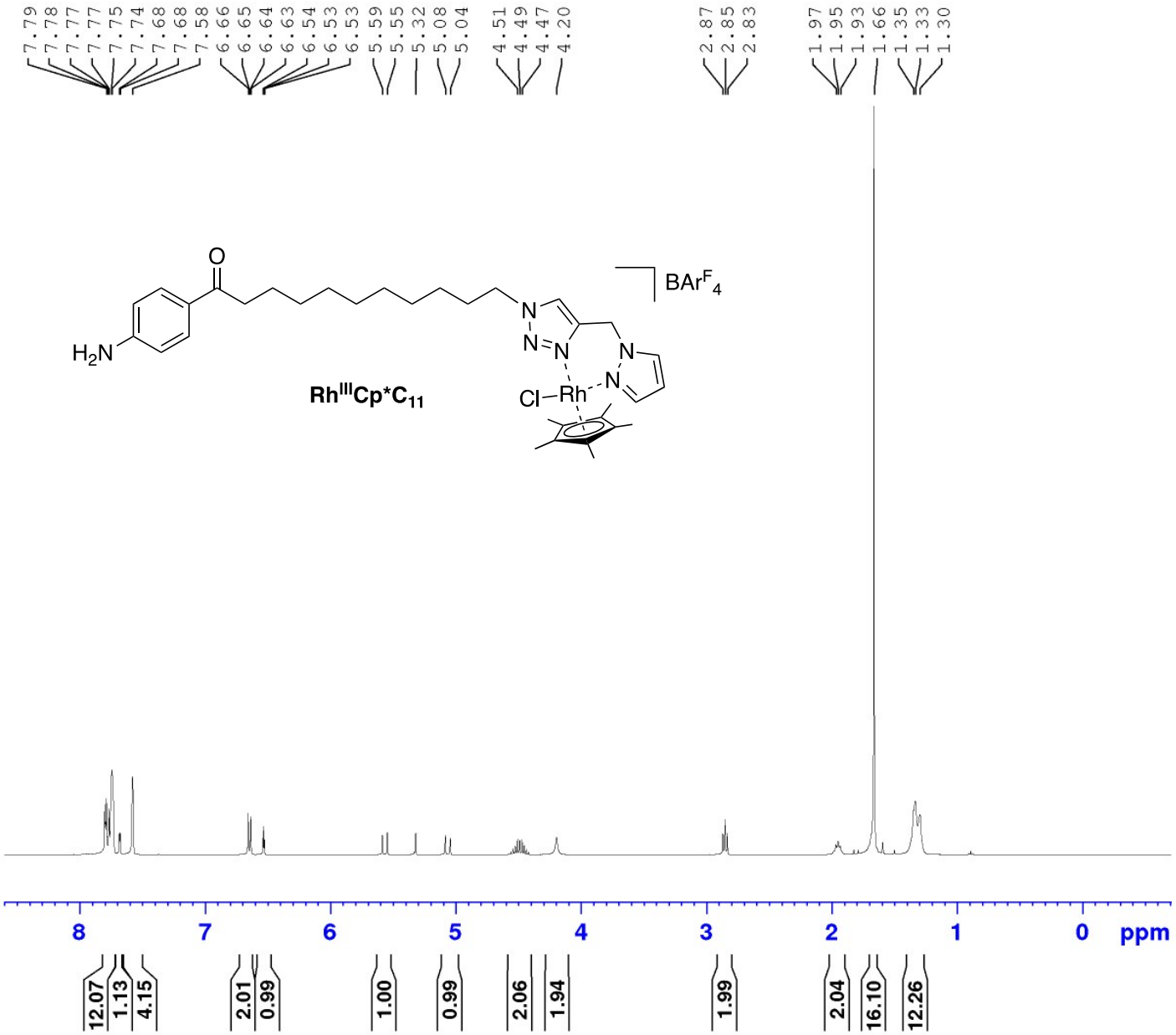
Selected range of the 2D HMBC NMR spectrum of compound **$Rh^{I}C_{11}$** in CD_2Cl_2.



Selected range of the 2D HMBC NMR spectrum of compound **Rh^{I}C$_{11}$** in CD_2Cl_2.



2D COSY NMR spectrum of compound **Rh^{I}C$_{11}$** in CD_2Cl_2.

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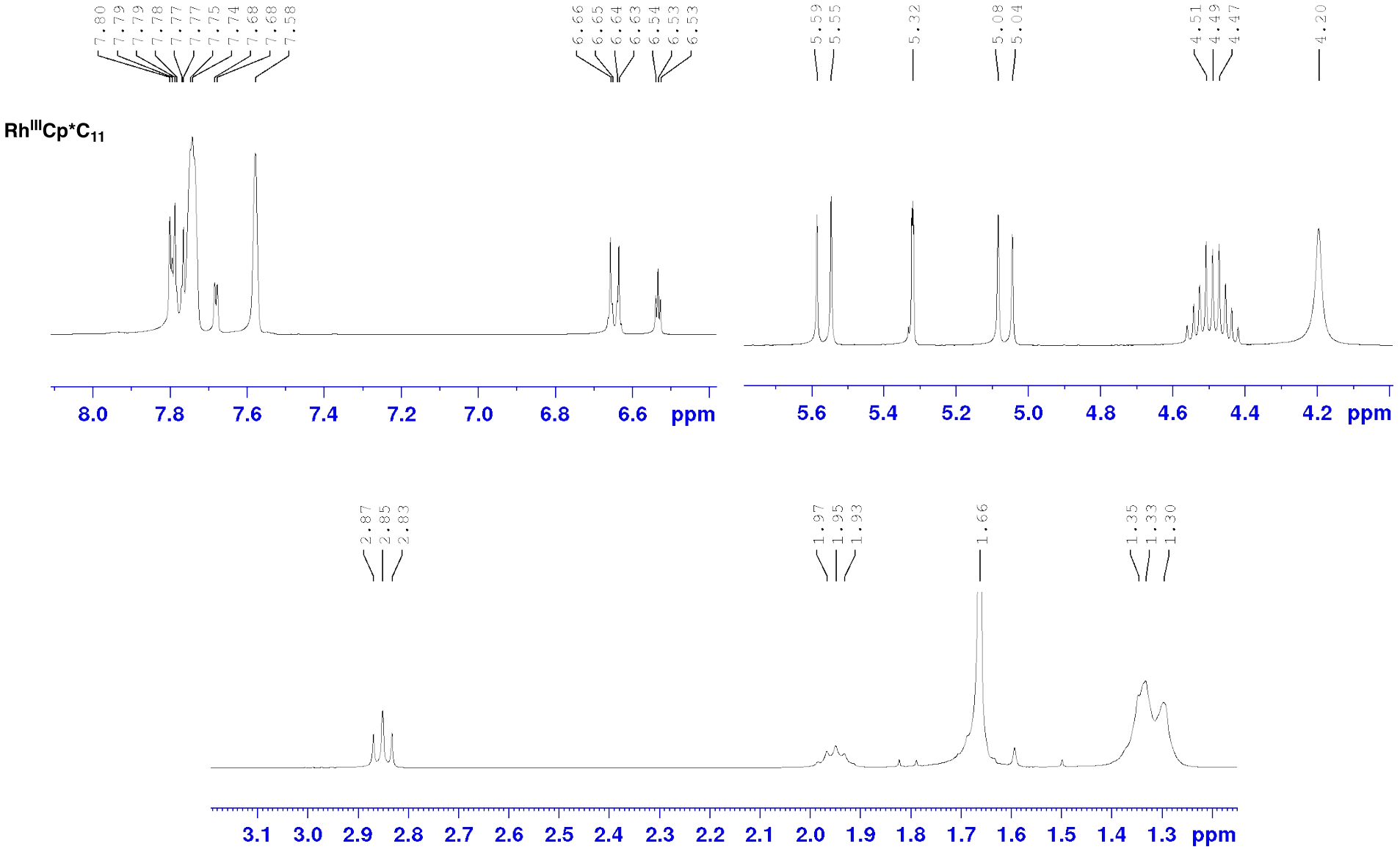
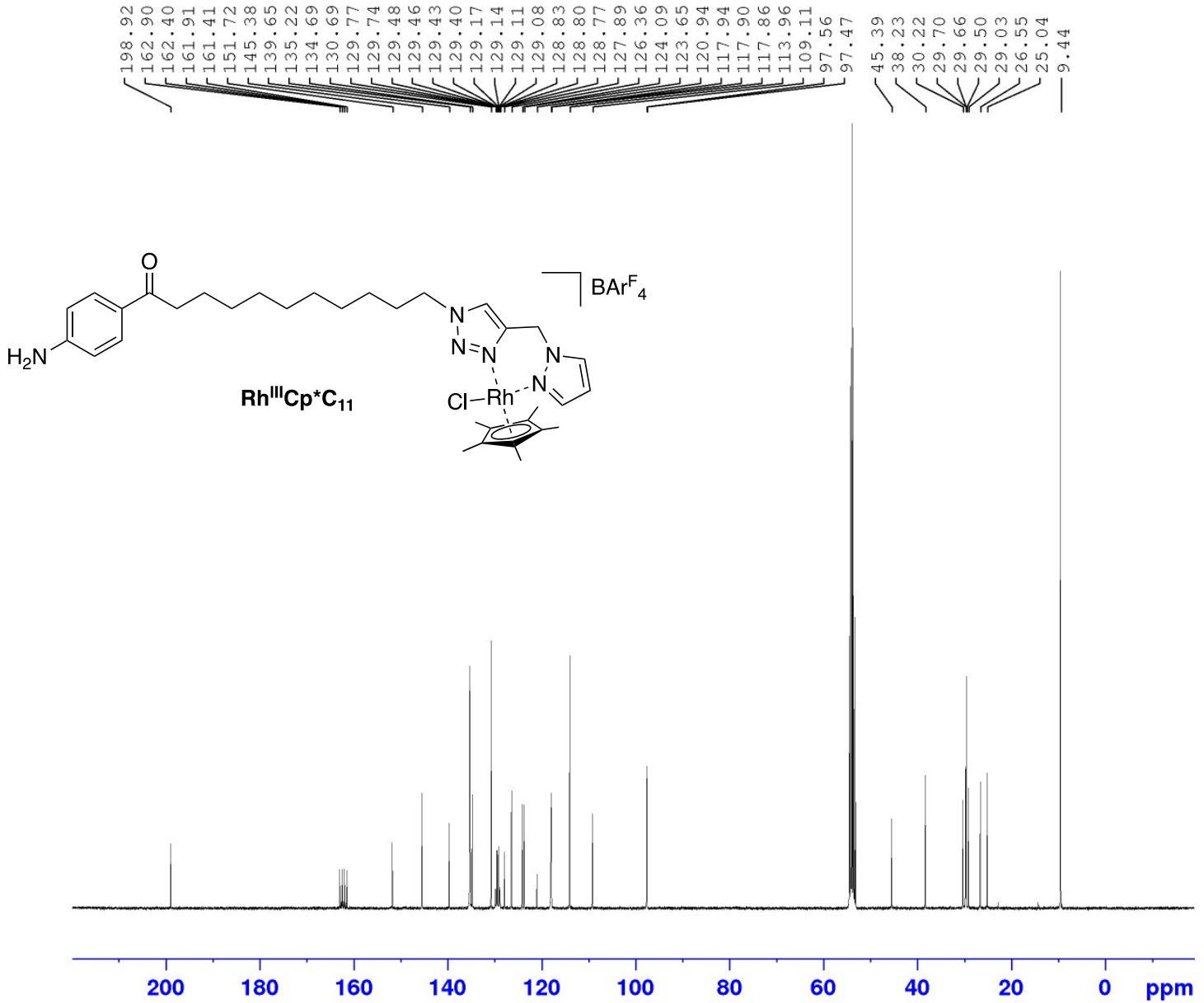
Current Data Parameters
NAME                  MR-230
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190819
Time                 16.32 h
INSTRUM              spect
PROBHD    Z116098_0573 (
PULPROG                zg30
TD                    65536
SOLVENT             CD2Cl2
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                      55.9
DW                    62.400 usec
DE                    12.00 usec
TE                    298.0 K
D1              2.50000000 sec
TD0                        1
SFO1           400.1524709 MHz
NUC1                      1H
P1                    10.00 usec
PLW1           15.75399971 W

F2 - Processing parameters
SI                        65536
SF             400.1500154 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```

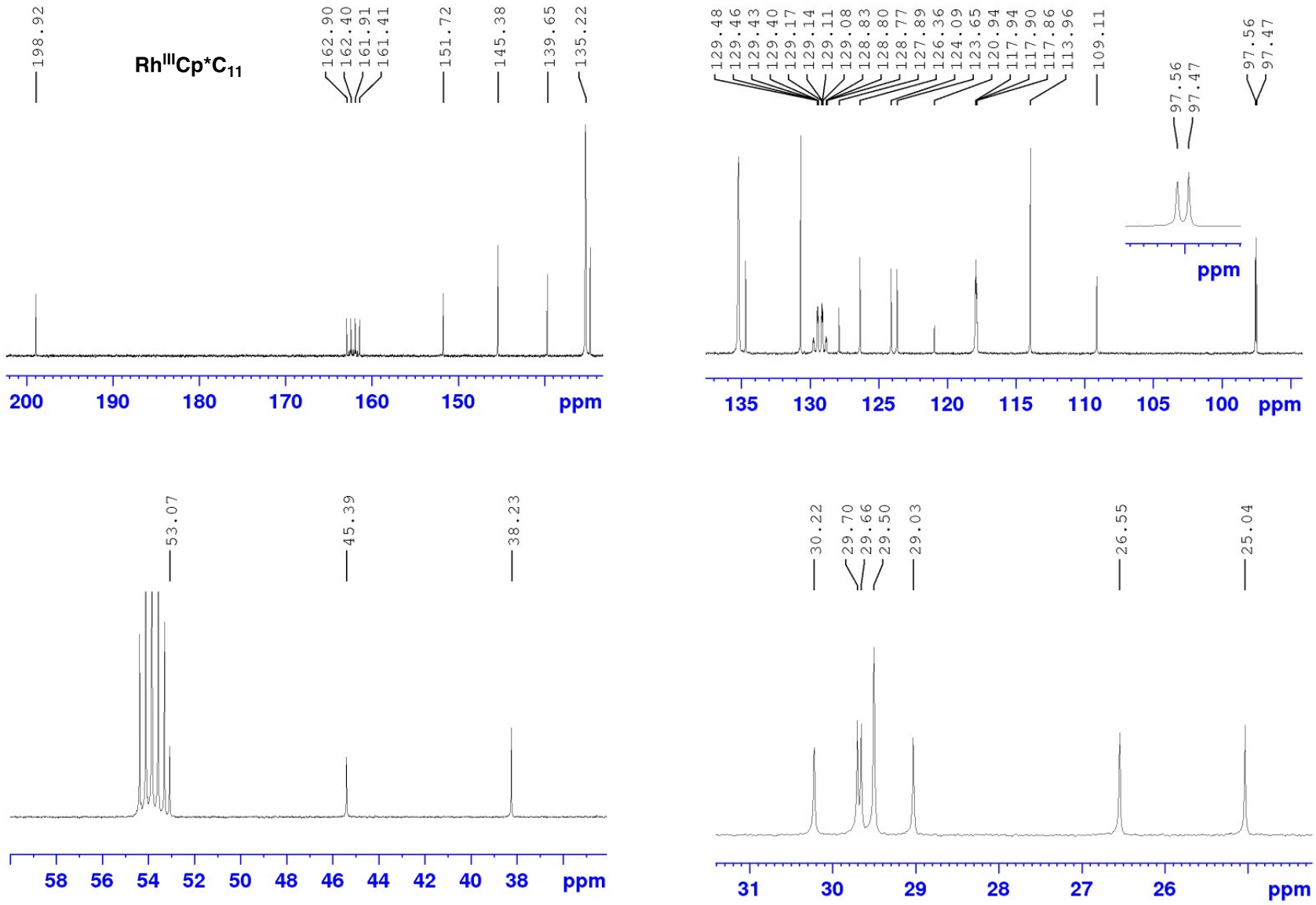

Rh^III Cp*C11
7.80
7.79
7.79
7.78
7.77
7.77
7.75
7.74
7.68
7.68
7.58
6.66
6.65
6.64
6.63
6.54
6.53
6.53
5.59
5.55
5.32
5.08
5.04
4.51
4.49
4.47
4.20
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
ppm
2.87
2.85
2.83
1.97
1.95
1.93
1.66
1.35
1.33
1.30
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
ppm

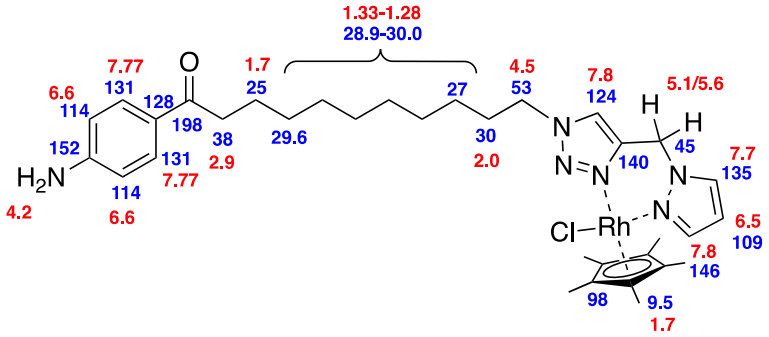



```
Current Data Parameters
NAME                  MR-230
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190820
Time                   0.48 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG               zgpg30
TD                     65536
SOLVENT               CD2Cl2
NS                       6000
DS                          4
SWH               24038.461 Hz
FIDRES             0.733596 Hz
AQ                 1.3631488 sec
RG                    198.41
DW                    20.800 usec
DE                     6.50 usec
TE                    298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1
SFO1            100.6278593 MHz
NUC1                     13C
P1                    10.00 usec
PLW1            80.53199768 W
SFO2            400.1516006 MHz
NUC2                     1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2            15.75399971 W
PLW12            0.19449000 W
PLW13            0.09782900 W

F2 - Processing parameters
SI                       32768
SF              100.6177559 MHz
WDW                         EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```


Rh^III Cp*C11
198.92
162.90
162.40
161.91
161.41
151.72
145.38
139.65
135.22
200 190 180 170 160 150 ppm
129.48
129.46
129.43
129.40
129.17
129.14
129.11
129.08
128.83
128.80
128.77
127.89
126.36
124.09
123.65
120.94
117.94
117.90
117.86
113.96
109.11
97.56
97.47
97.56
97.47
ppm
135 130 125 120 115 110 105 100 ppm
53.07
45.39
38.23
58 56 54 52 50 48 46 44 42 40 38 ppm
30.22
29.70
29.66
29.50
29.03
26.55
25.04
31 30 29 28 27 26 ppm

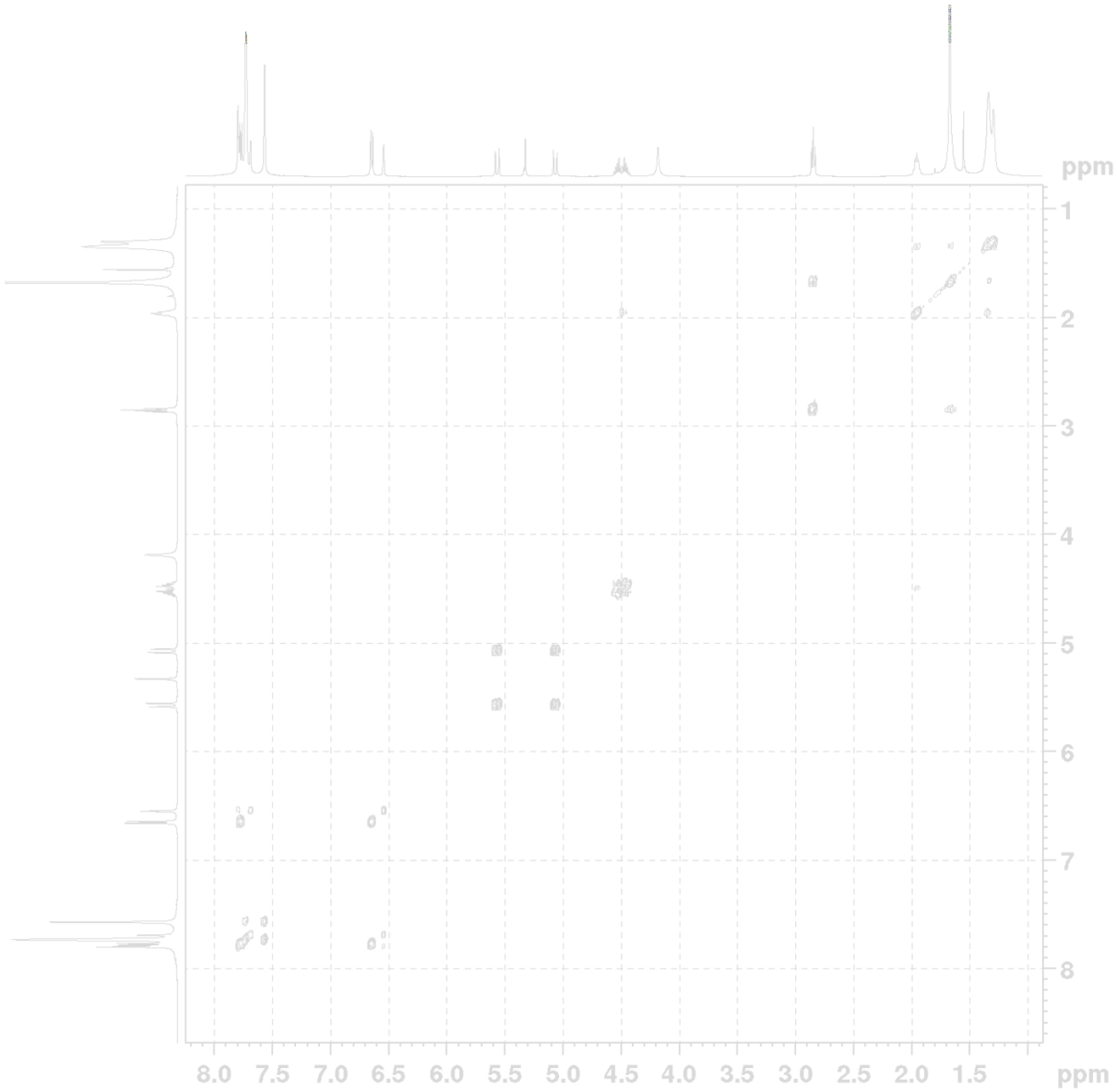


2D HSQC NMR spectrum of compound **$Rh^{III}C_{11}$** in CD_2Cl_2 and sssignment of ^{1}H (red) and ^{13}C (blue) NMR resonances.

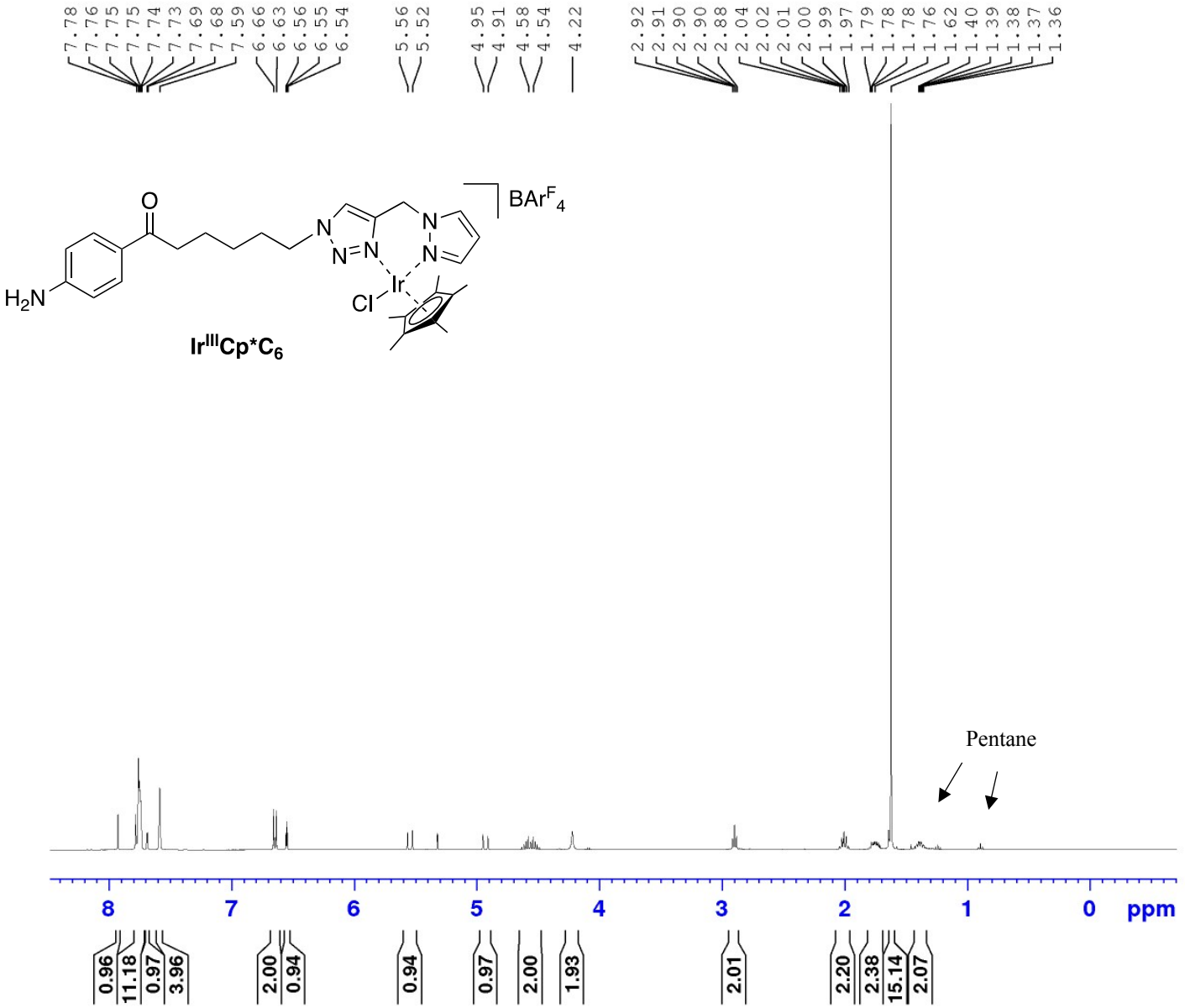
2D HMBC NMR spectrum of compound **$Rh^{III}C_{11}$** in CD_2Cl_2.

Selected range of the 2D HMBC NMR spectrum of compound **$Rh^{III}C_{11}$** in CD_2Cl_2.

Selected range of the 2D HMBC NMR spectrum of compound **$Rh^{III}C_{11}$** in CD_2Cl_2.



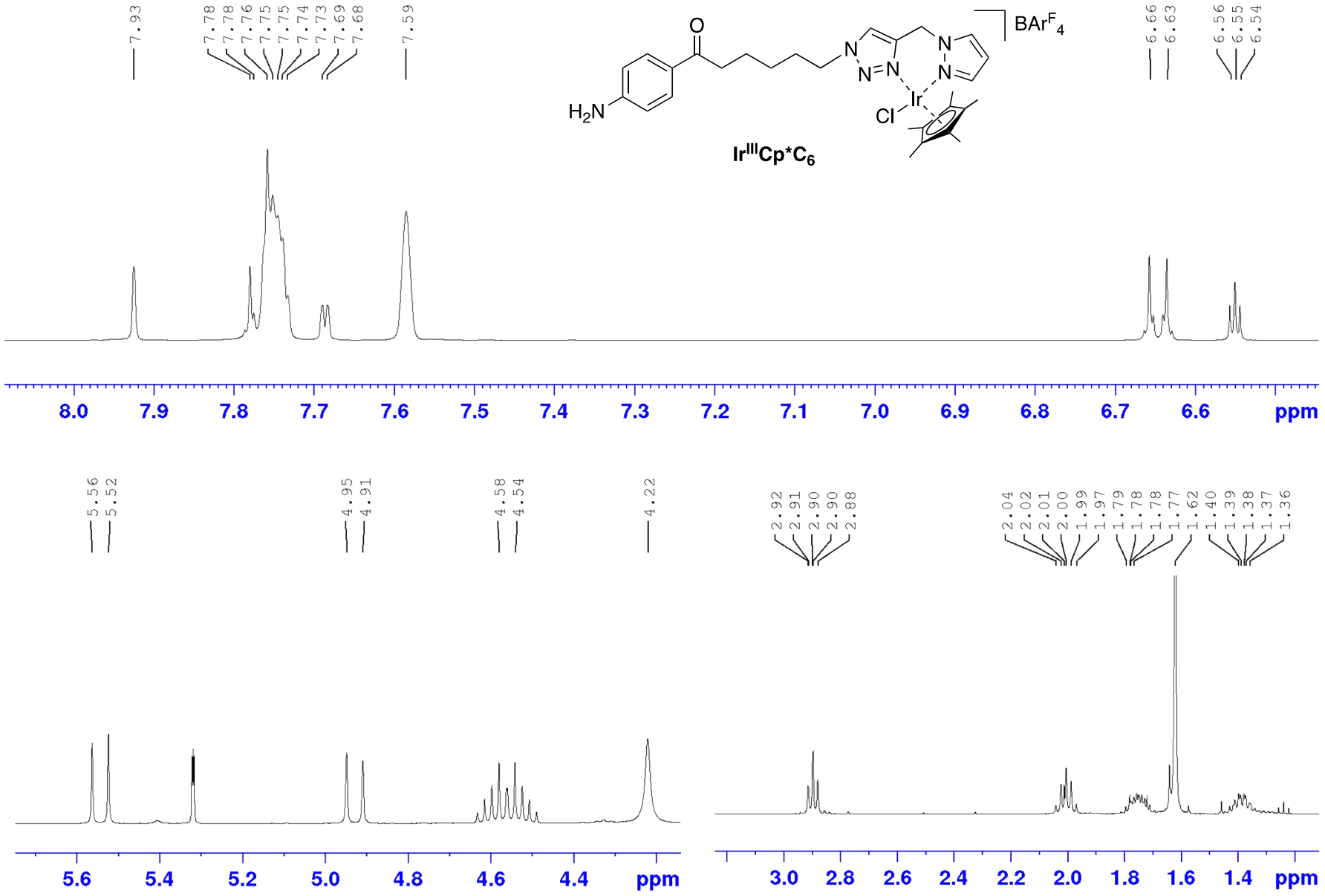
2D COSY NMR spectrum of compound **$Rh^{III}C_{11}$** in CD_2Cl_2.

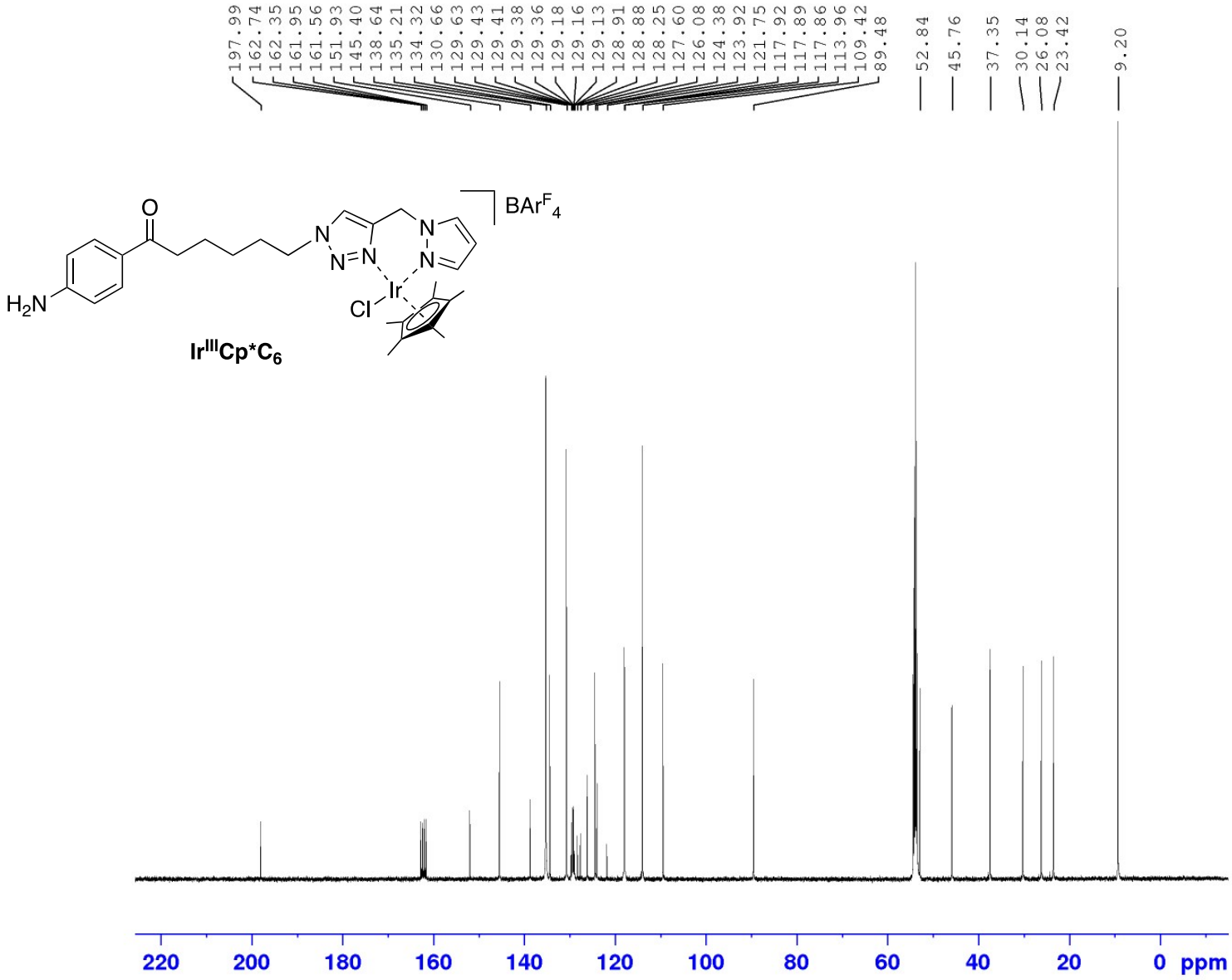



```
Current Data Parameters
NAME                  MR-97-3
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20190305
Time                    9.43 h
INSTRUM                 spect
PROBHD    Z116098_0573 (
PULPROG                 zg30
TD                     65536
SOLVENT             CD2Cl2
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.244532 Hz
AQ                  4.0894465 sec
RG                      49.89
DW                     62.400 usec
DE                     12.00 usec
TE                     298.0 K
D1                2.50000000 sec
TD0                         1
SFO1             400.1524709 MHz
NUC1                       1H
P1                     10.00 usec
PLW1             15.75399971 W

F2 - Processing parameters
SI                     65536
SF               400.1500154 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```


7.93
7.78
7.78
7.76
7.75
7.75
7.74
7.73
7.69
7.68
7.59
6.66
6.63
6.56
6.55
6.54
O
H2N
N
N=N
N
N
Ir
Cl
BArF4
IrIIICp*C6
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
5.56
5.52
4.95
4.91
4.58
4.54
4.22
2.92
2.91
2.90
2.90
2.88
2.04
2.02
2.01
2.00
1.99
1.97
1.79
1.78
1.78
1.77
1.62
1.40
1.39
1.38
1.37
1.36
5.6
5.4
5.2
5.0
4.8
4.6
4.4
ppm
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm




```
Current Data Parameters
NAME                   MR-97
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20200115
Time                  21.32 h
INSTRUM                spect
PROBHD    Z119470_0266 (
PULPROG                zgpg
TD                    65536
SOLVENT             CD2Cl2
NS                     6000
DS                        2
SWH               34090.910 Hz
FIDRES             1.040372 Hz
AQ                0.9611947 sec
RG                   187.37
DW                   14.667 usec
DE                    7.59 usec
TE                   298.2 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1            125.7804239 MHz
NUC1                    13C
P1                   10.00 usec
PLW1            98.23000336 W
SFO2            500.1632510 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2            25.00000000 W
PLW12            0.48129001 W
PLW13            0.24208000 W

F2 - Processing parameters
SI                    65536
SF              125.7652797 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

$Ir^{III}Cp^*C_6$

74
35
95
56

93

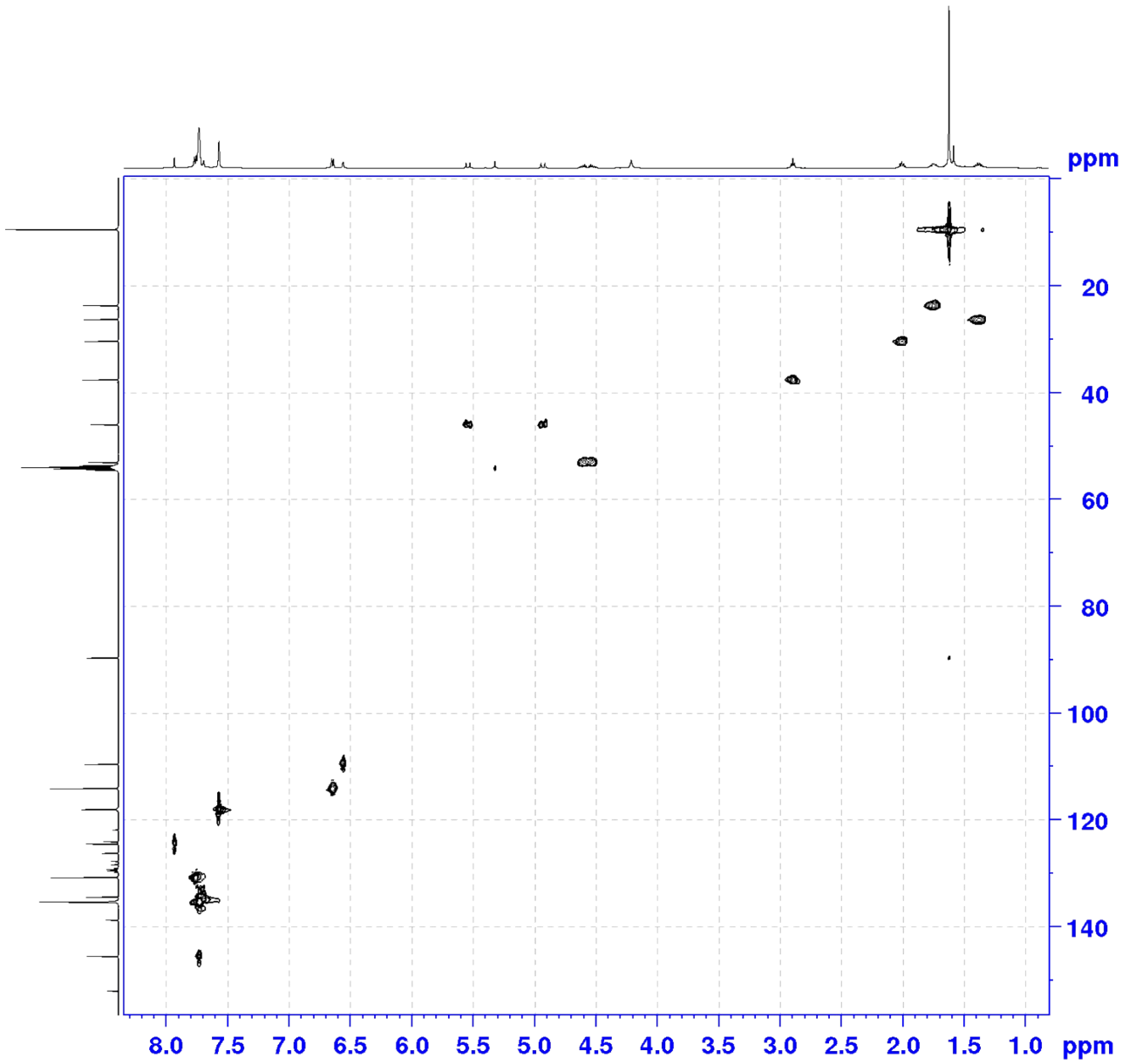
40

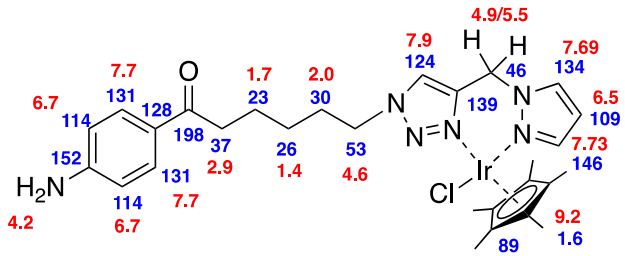
64

21
32

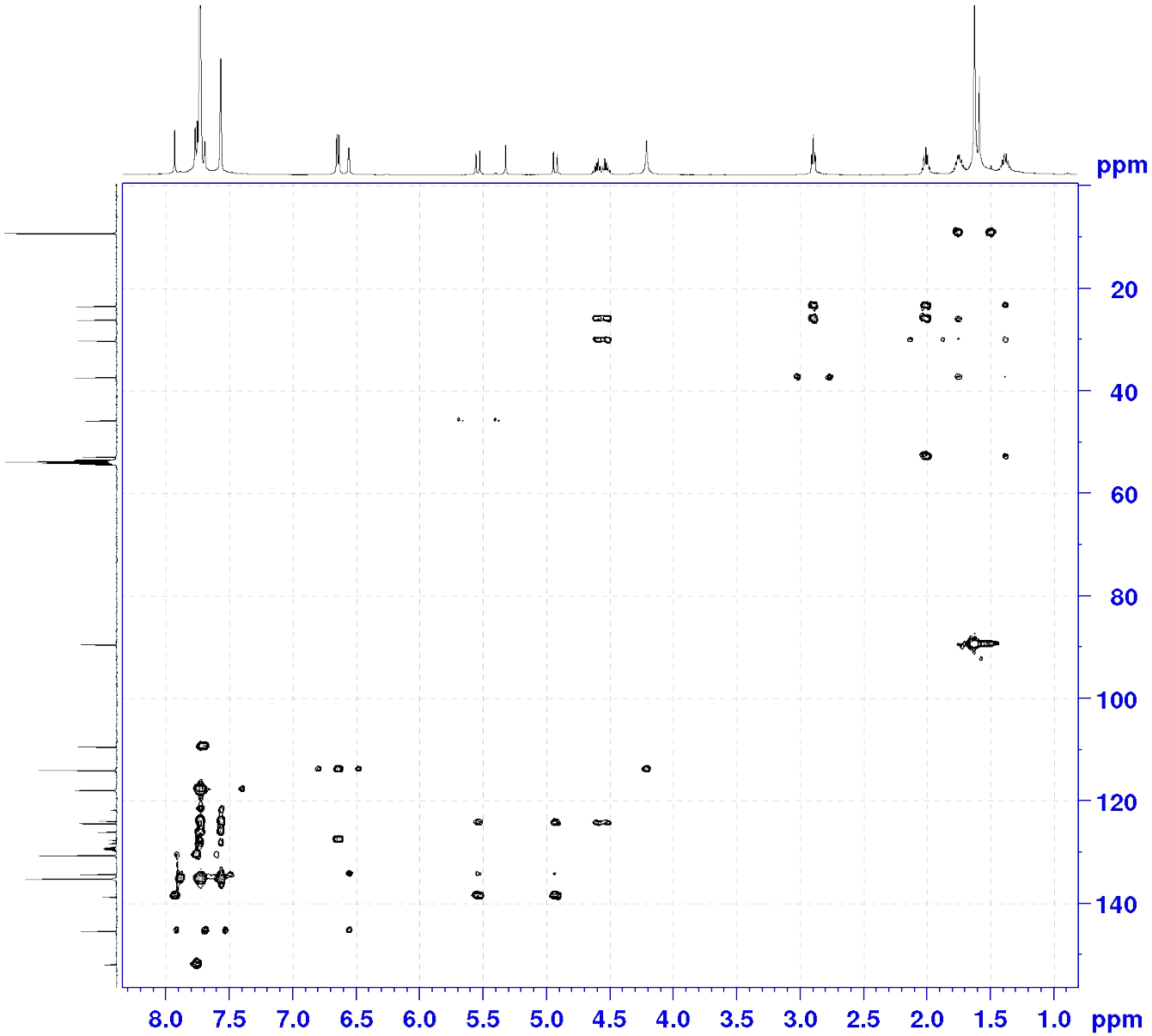
66
63
43
41
38
36
18
16
13
91
88
25
60
08
38
92

75

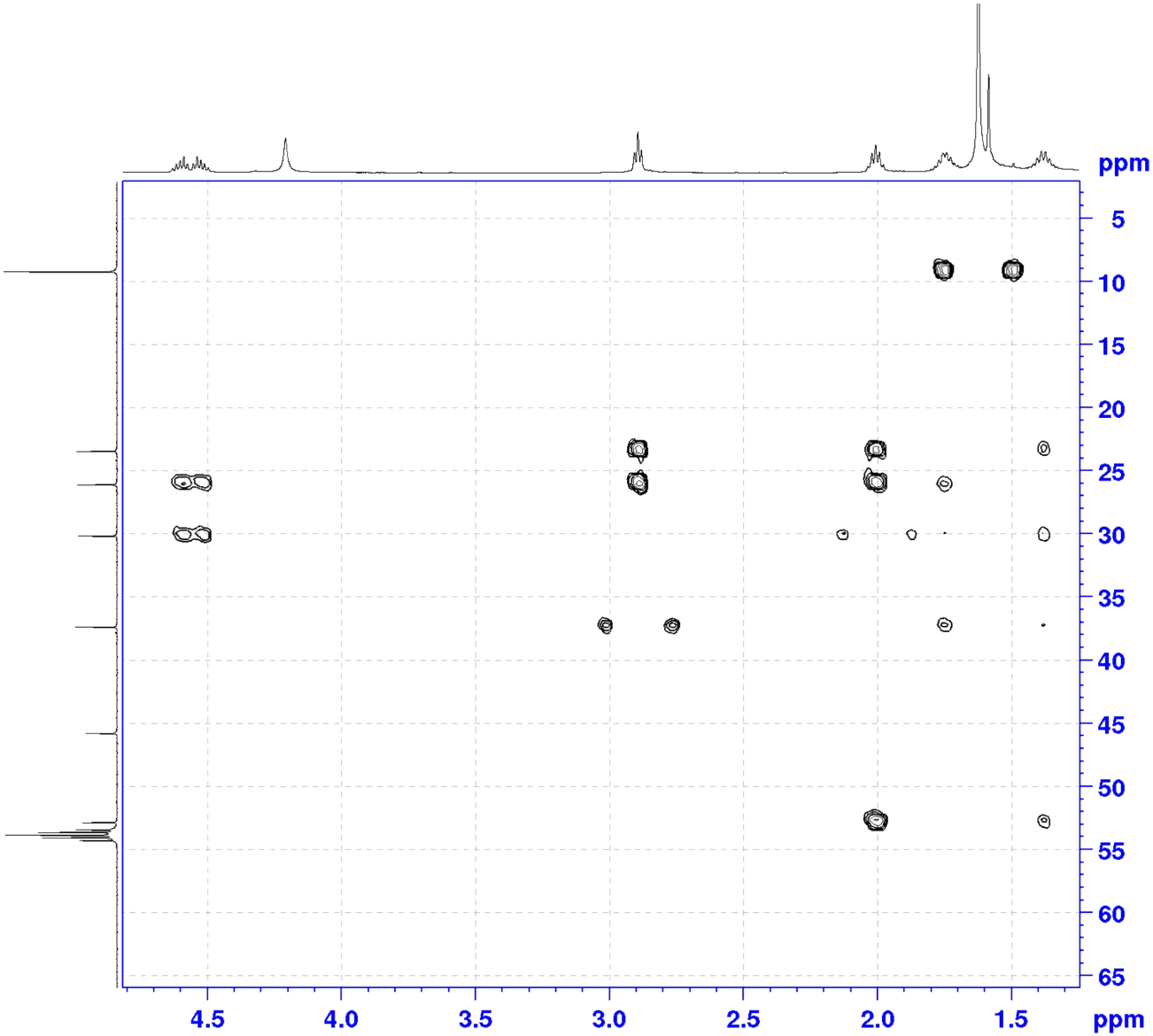




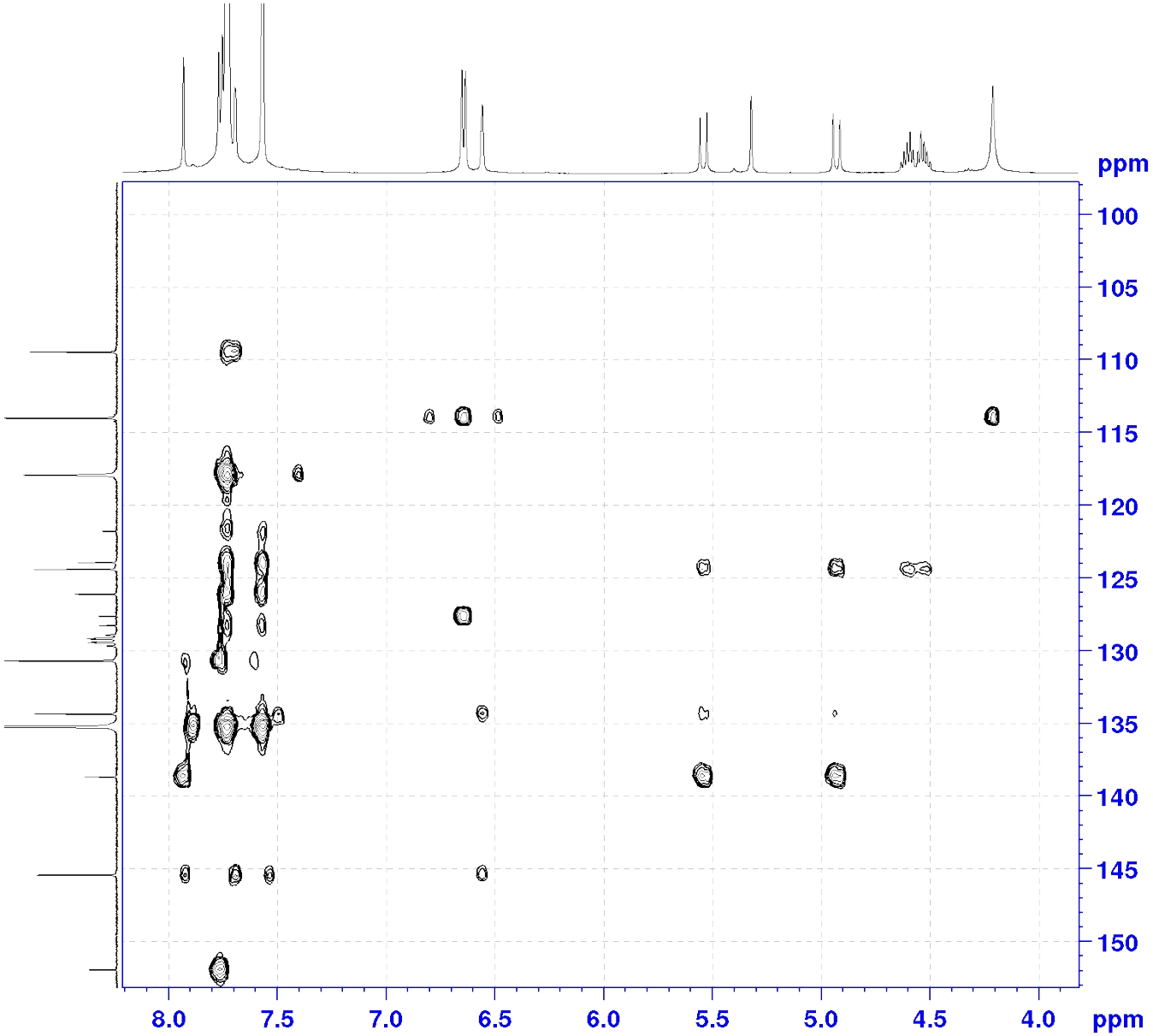
2D HSQC NMR spectrum of compound **Ir^{III}C$_6$** in CD_2Cl_2 and sssignment of ^{1}H (red) and ^{13}C (blue) NMR resonances.



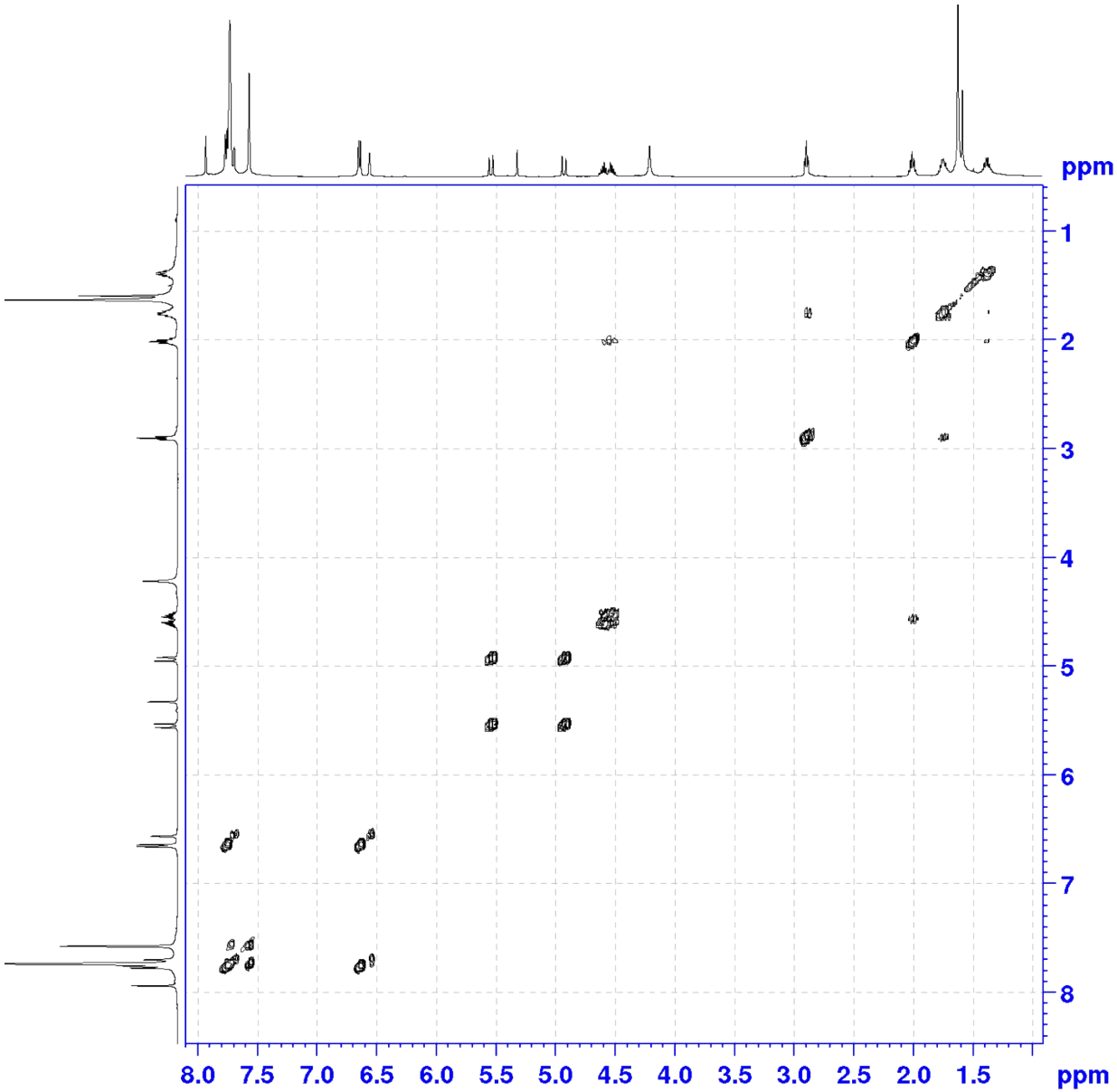
2D HMBC NMR spectrum of compound $\mathbf{Ir^{III}C_6}$ in CD_2Cl_2.



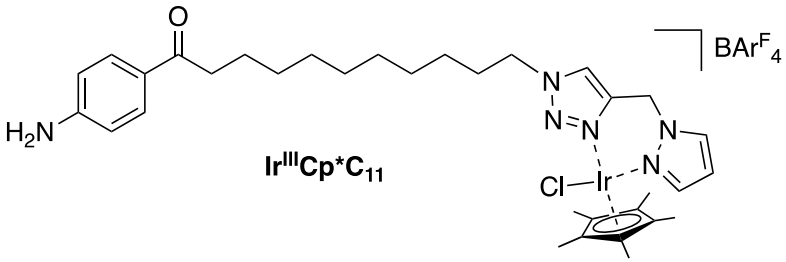
Selected ranges of the 2D HSQC NMR spectrum of compound $\mathbf{Ir^{III}C_6}$ in CD_2Cl_2.



Selected ranges of the 2D HSQC NMR spectrum of compound $\mathbf{Ir^{III}C_6}$ in CD_2Cl_2.



2D COSY NMR spectrum of compound $\mathbf{Ir^{III}C_6}$ in CD_2Cl_2.

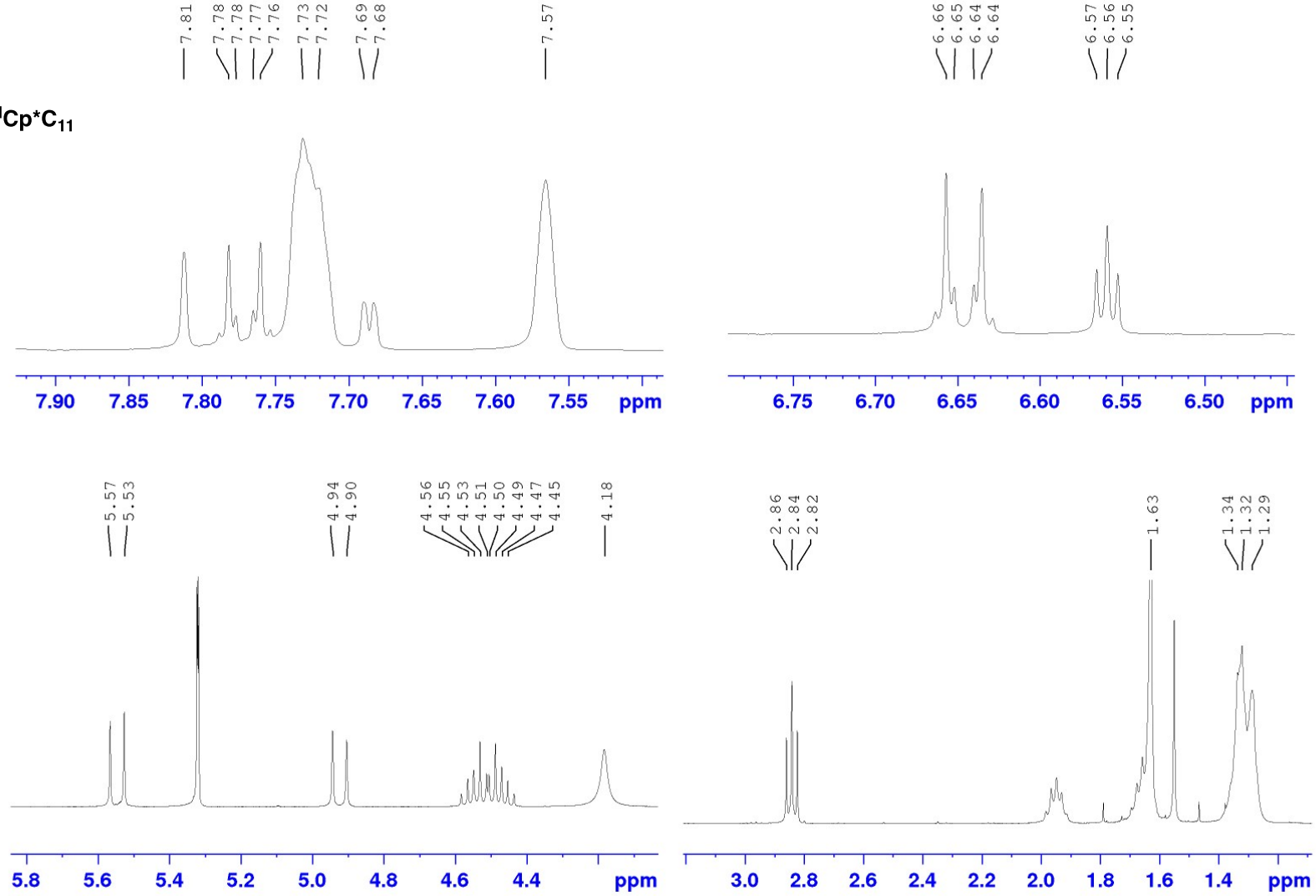


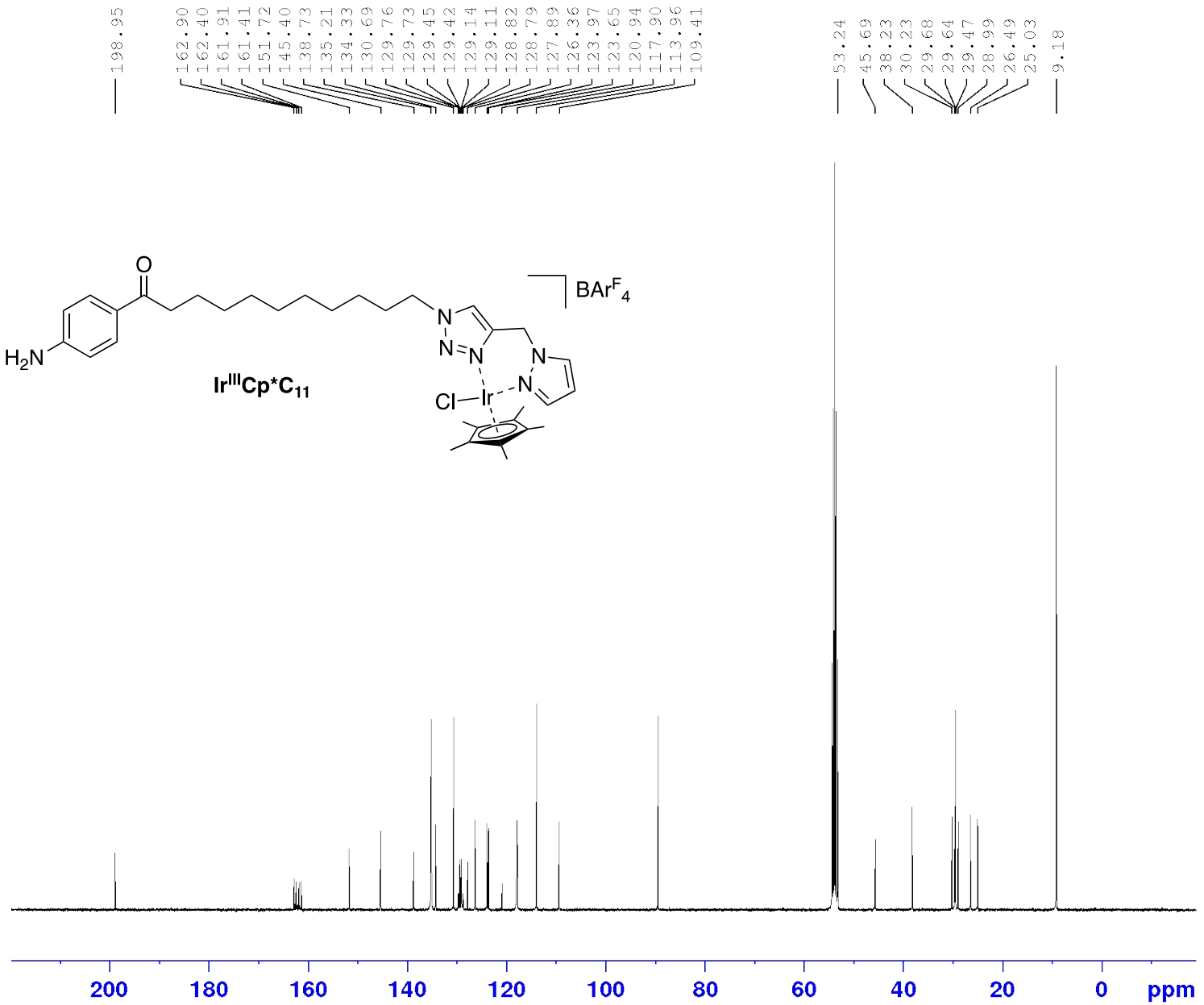
$Ir^{III}Cp^{*}C_{11}$

7.81
7.78
7.78
7.77
7.76
7.73
7.72
7.69
7.68
7.57
6.66
6.65
6.64
6.64
6.57
6.56
6.55
6.57
6.53
4.94
4.90
4.56
4.55
4.53
4.51
4.50
4.49
4.47
4.45
4.18
2.86
2.84
2.82
1.63
1.34
1.32
1.29

Current Data Parameters
NAME MB-131

$Ir^{III}Cp^*C_{11}$

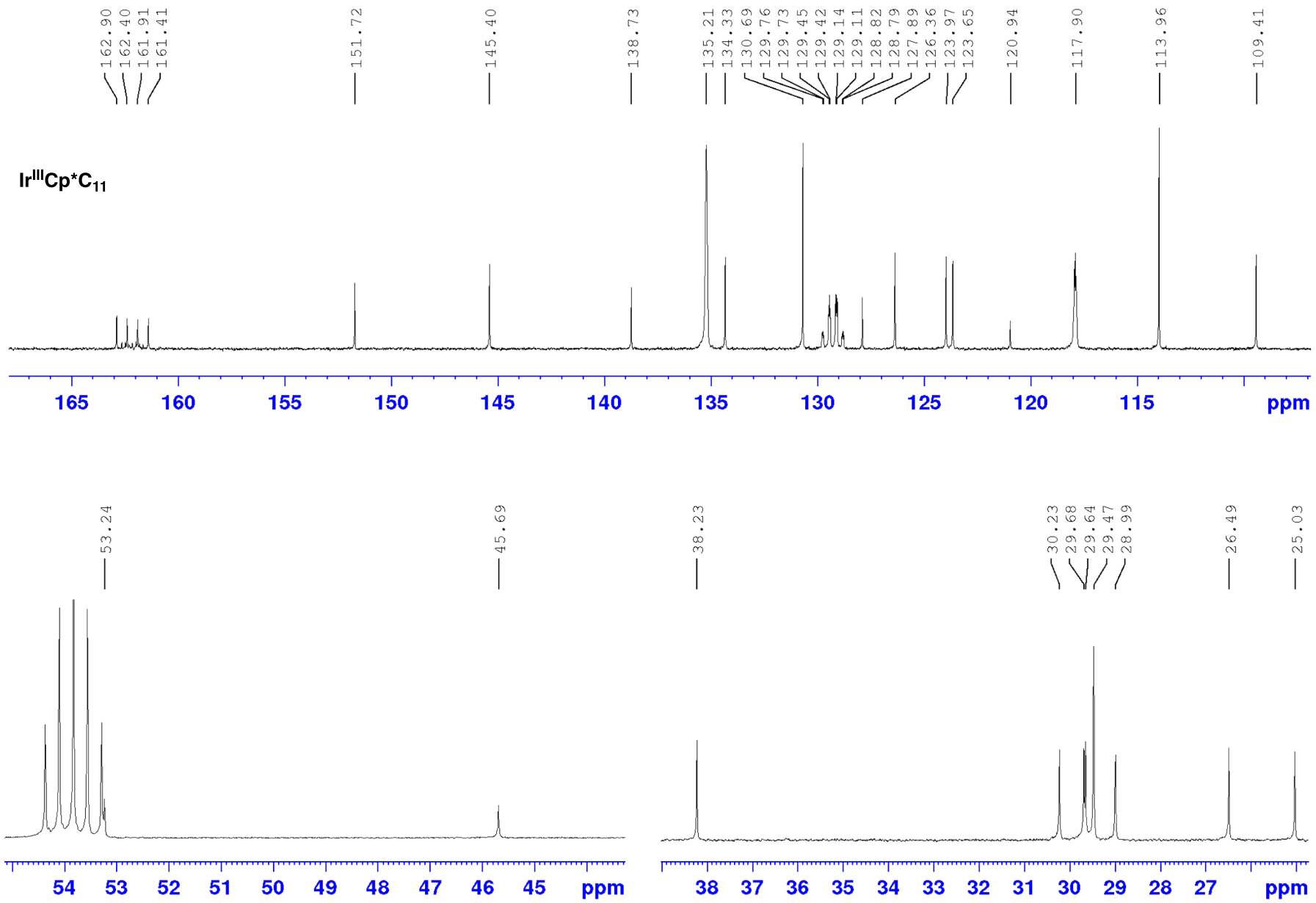

7.81
7.78
7.78
7.77
7.76
7.73
7.72
7.69
7.68
7.57
6.66
6.65
6.64
6.64
6.57
6.56
6.55
7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 ppm
6.75 6.70 6.65 6.60 6.55 6.50 ppm
5.57
5.53
4.94
4.90
4.56
4.55
4.53
4.51
4.50
4.49
4.47
4.45
4.18
2.86
2.84
2.82
1.63
1.34
1.32
1.29
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 ppm
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm

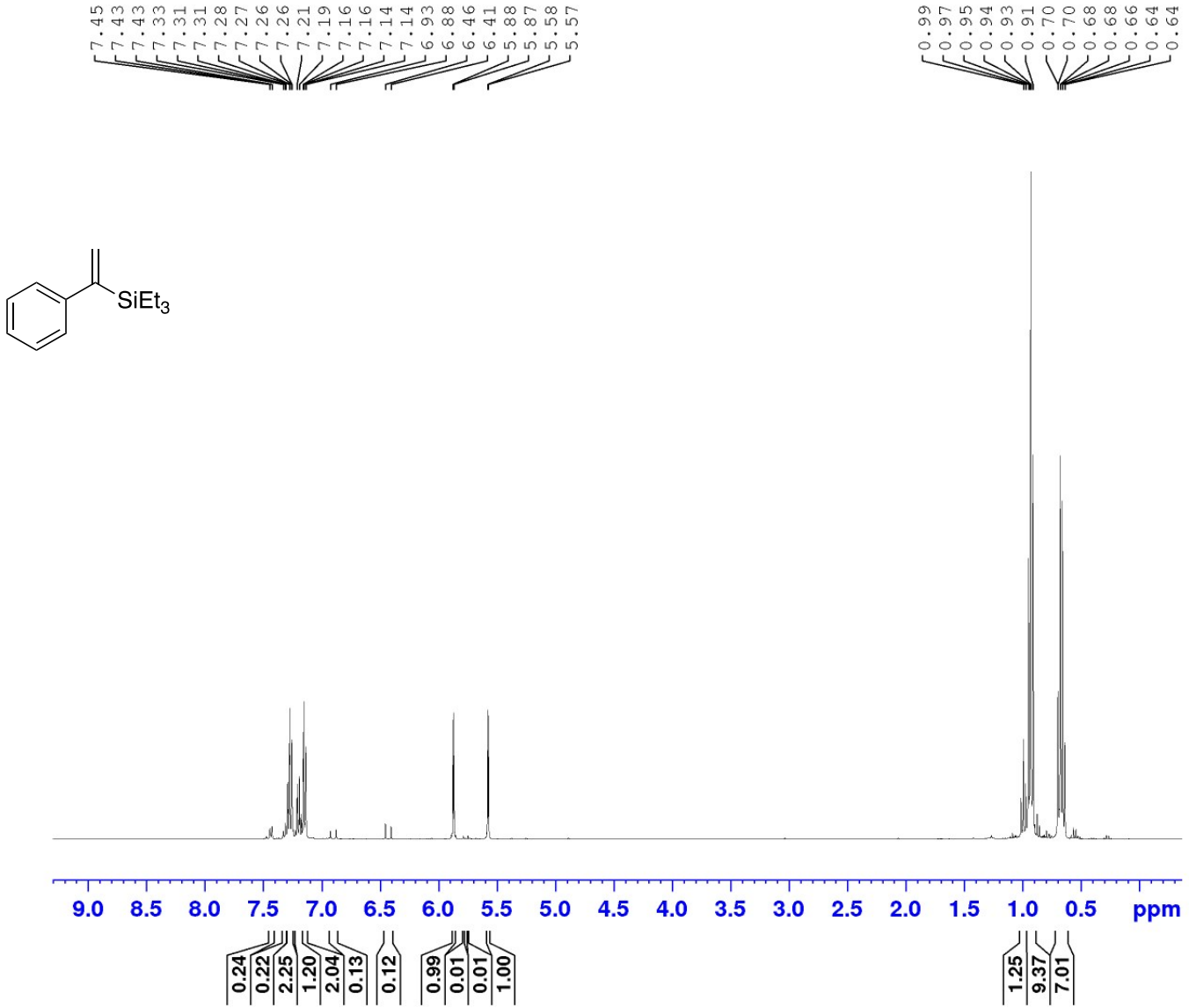



```
Current Data Parameters
NAME                  MR-131
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190406
Time                  3.09 h
INSTRUM               spect
PROBHD    Z116098_0573 (
PULPROG              zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                     6250
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   198.41
DW                  20.800 usec
DE                   6.50 usec
TE                  298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1
SFO1            100.6278593 MHz
NUC1                    13C
P1                   10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

F2 - Processing parameters
SI                     32768
SF              100.6177560 MHz
WDW                       EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

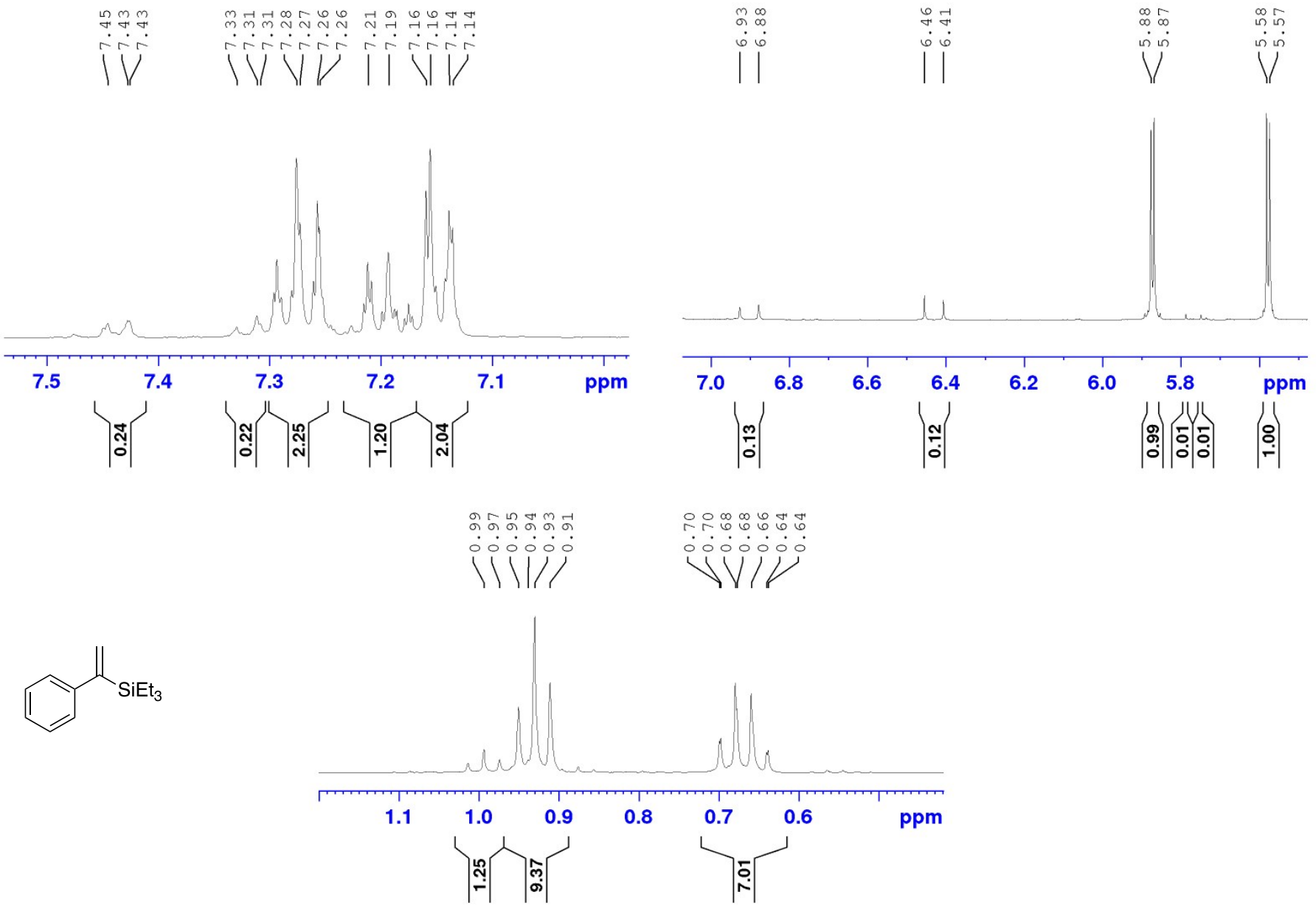

Ir^III Cp*C11
162.90
162.40
161.91
161.41
151.72
145.40
138.73
135.21
134.33
130.69
129.76
129.73
129.45
129.42
129.14
129.11
128.82
128.79
127.89
126.36
123.97
123.65
120.94
117.90
113.96
109.41
165 160 155 150 145 140 135 130 125 120 115 ppm
53.24
45.69
38.23
30.23
29.68
29.64
29.47
28.99
26.49
25.03
54 53 52 51 50 49 48 47 46 45 ppm
38 37 36 35 34 33 32 31 30 29 28 27 ppm

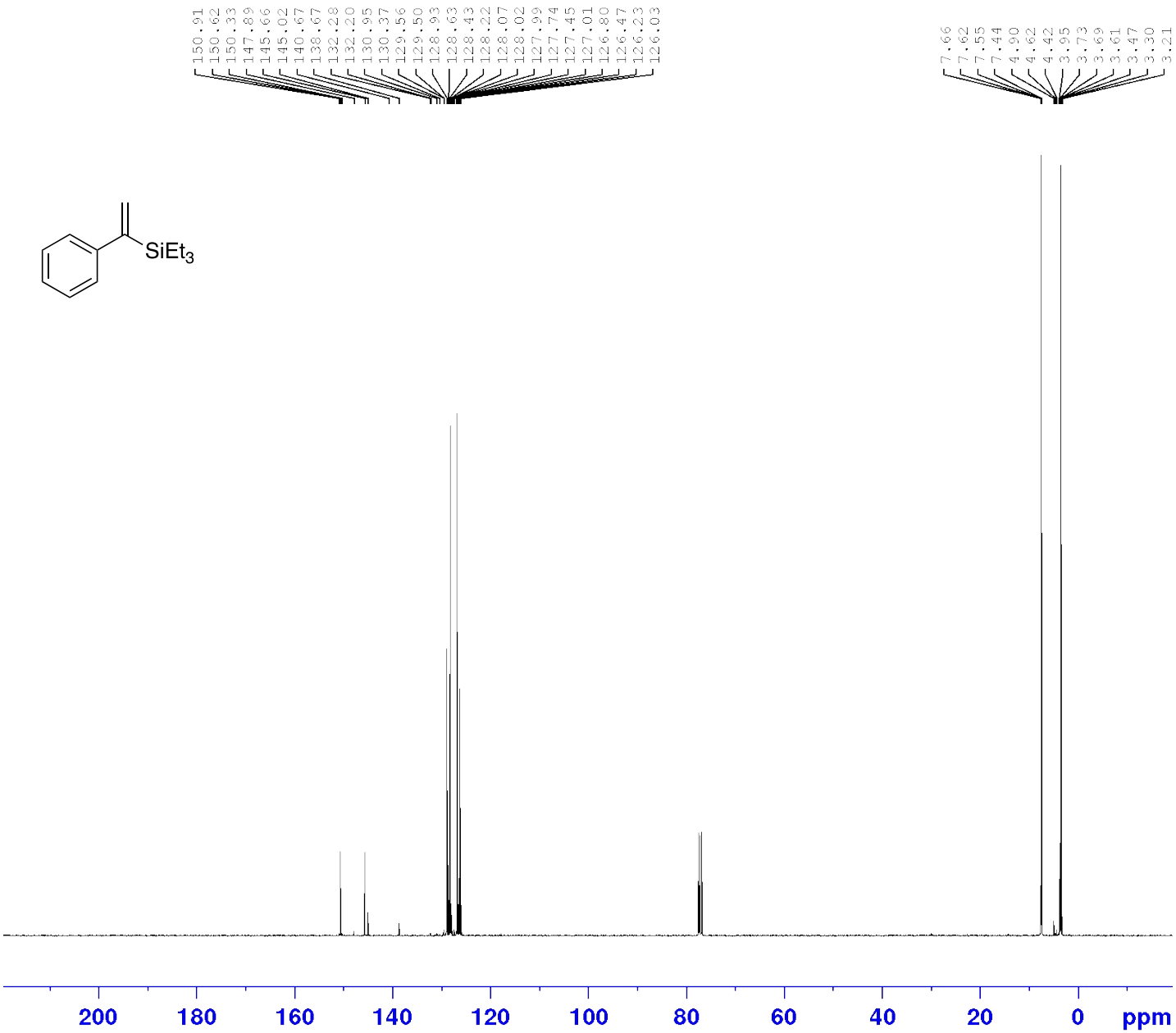



```
Current Data Parameters
NAME                  MR-316
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20191113
Time                 14.40 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8012.820 Hz
FIDRES            0.244532 Hz
AQ                4.0894465 sec
RG                    16.03
DW                   62.400 usec
DE                   12.00 usec
TE                   298.0 K
D1                2.50000000 sec
TD0                       1
SFO1           400.1524709 MHz
NUC1                     1H
P1                   10.00 usec
PLW1           15.75399971 W

F2 - Processing parameters
SI                    65536
SF             400.1500395 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

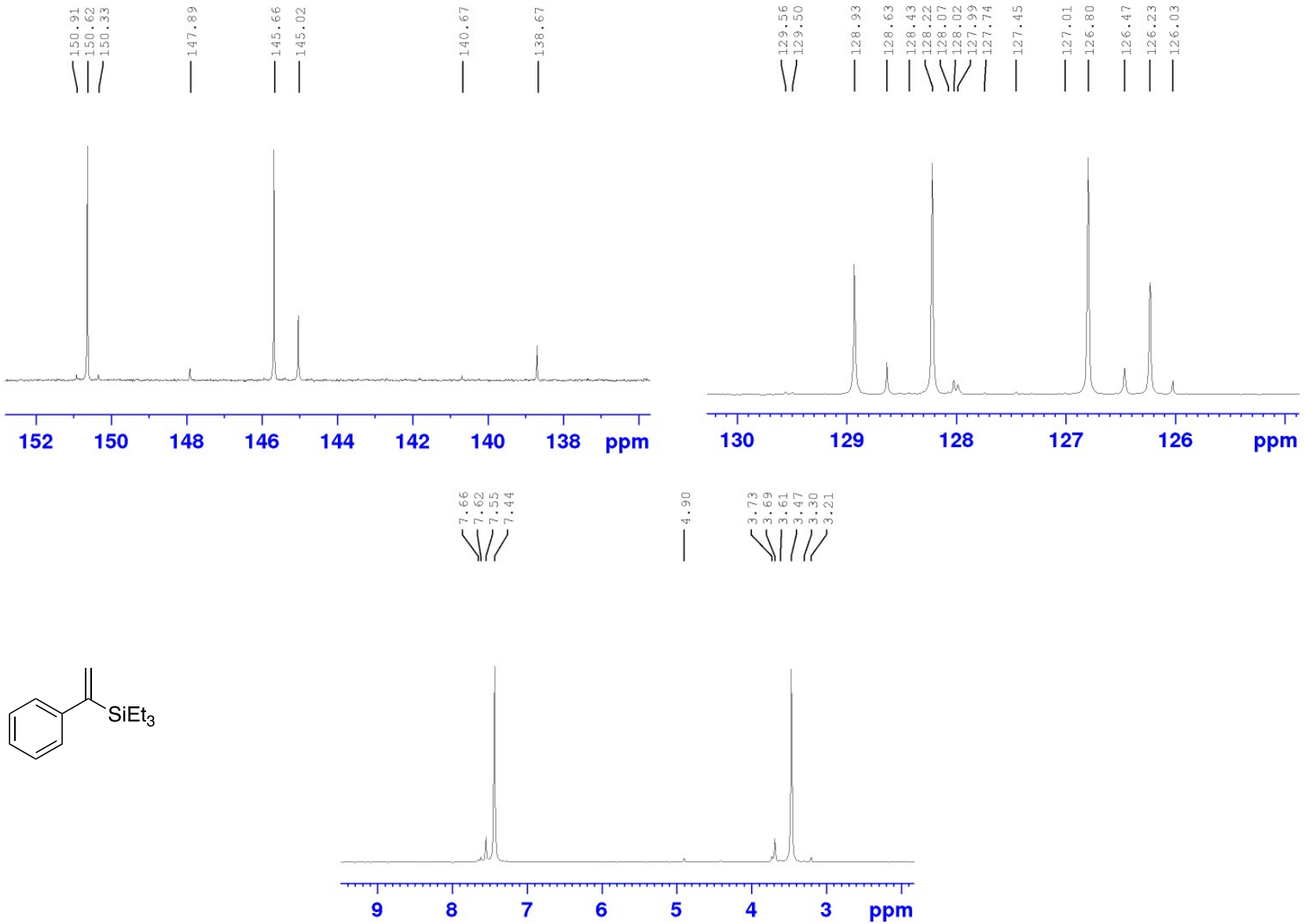

7.45
7.43
7.43
7.33
7.31
7.31
7.28
7.27
7.26
7.26
7.21
7.19
7.16
7.16
7.14
7.14
6.93
6.88
6.46
6.41
5.88
5.87
5.58
5.57
7.5
7.4
7.3
7.2
7.1
ppm
7.0
6.8
6.6
6.4
6.2
6.0
5.8
ppm
0.24
0.22
2.25
1.20
2.04
0.13
0.12
0.99
0.01
0.01
1.00
0.99
0.97
0.95
0.94
0.93
0.91
0.70
0.70
0.68
0.68
0.66
0.64
0.64
SiEt3
1.1
1.0
0.9
0.8
0.7
0.6
ppm
1.25
9.37
7.01

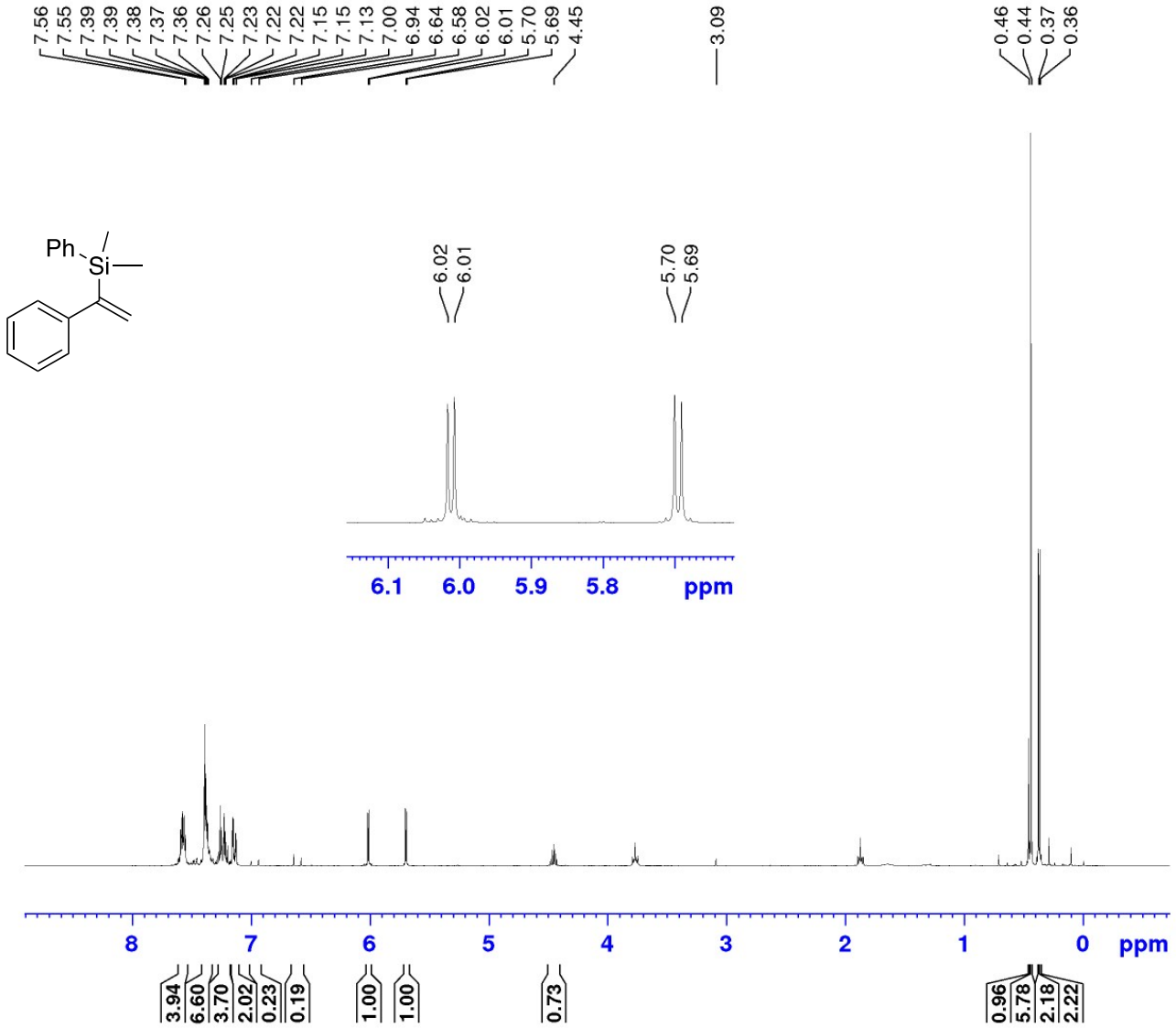



```
Current Data Parameters
NAME                  MR-316
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20191114
Time                   2.27 h
INSTRUM                spect
PROBHD    Z116098_0573 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2000
DS                        4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ                1.3631488 sec
RG                   198.41
DW                  20.800 usec
DE                   6.50 usec
TE                   298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           100.6278593 MHz
NUC1                    13C
P1                   10.00 usec
PLW1           80.53199768 W
SFO2           400.1516006 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           15.75399971 W
PLW12           0.19449000 W
PLW13           0.09782900 W

F2 - Processing parameters
SI                    32768
SF             100.6177888 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```


150.91
150.62
150.33
147.89
145.66
145.02
140.67
138.67
129.56
129.50
128.93
128.63
128.43
128.22
128.07
128.02
127.99
127.74
127.45
127.01
126.80
126.47
126.23
126.03
152
150
148
146
144
142
140
138
ppm
130
129
128
127
126
ppm
7.66
7.62
7.55
7.44
4.90
3.73
3.69
3.61
3.47
3.30
3.21
SiEt3
9
8
7
6
5
4
3
ppm




```
Current Data Parameters
NAME                  mr-66
EXPNO                     1
PROCNO                    1

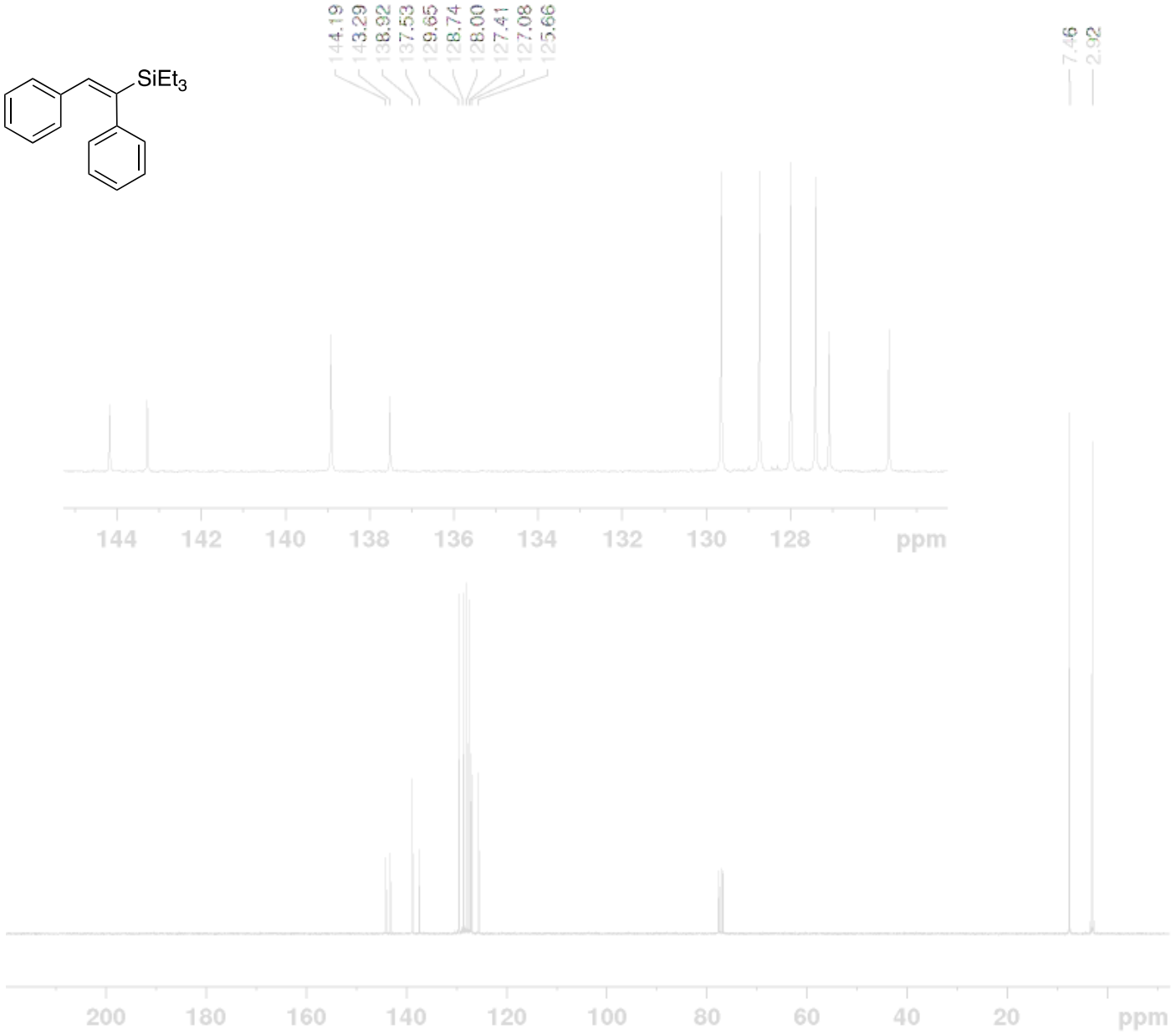
F2 - Acquisition Parameters
Date_              20200604
Time                 17.10 h
INSTRUM         NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                5882.353 Hz
FIDRES            0.179515 Hz
AQ                5.5705600 sec
RG                      101
DW                 85.000 usec
DE                   8.24 usec
TE                   -7.8 K
D1              2.00000000 sec
TD0                       1
SFO1           300.1319508 MHz
NUC1                     1H
P0                   4.67 usec
P1                  14.00 usec
PLW1            8.82489967 W

F2 - Processing parameters
SI                    65536
SF             300.1300073 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

7.40
7.37
7.19
7.19
7.18
7.17
7.14
7.14
7.11
7.11
7.09
6.90

1.11
1.08
1.06
0.79
0.78
0.76

Current Data Parameters
NAME mx-55




```
Current Data Parameters
NAME                  mr-55
EXPNO                     3
PROCNO                    1

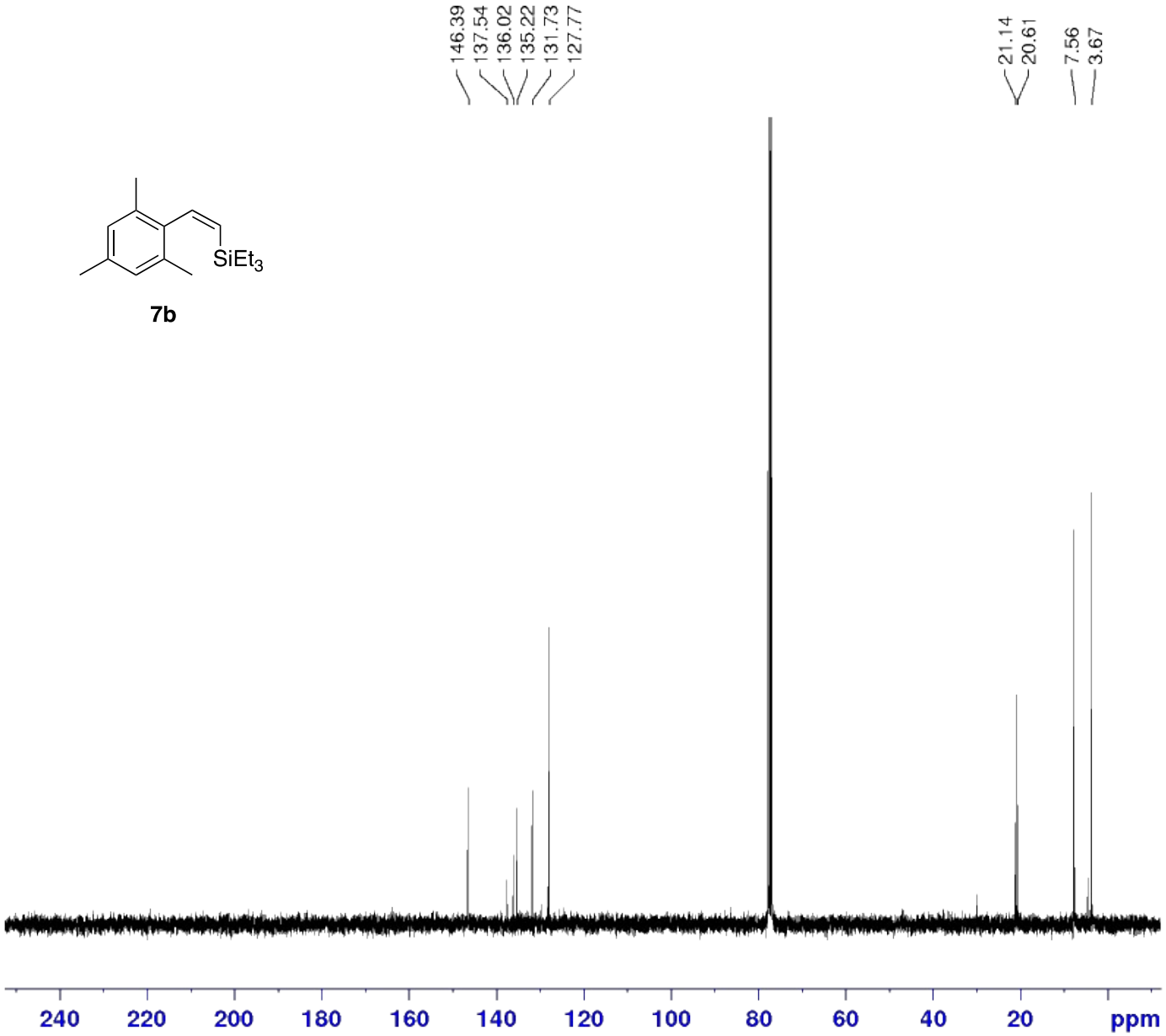
F2 - Acquisition Parameters
Date_              20200526
Time                 16.55 h
INSTRUM          NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        2
SWH              20000.000 Hz
FIDRES            0.610352 Hz
AQ                1.6384000 sec
RG                      101
DW                 25.000 usec
DE                  7.67 usec
TE                  298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1            75.4768047 MHz
NUC1                    13C
P0                   3.33 usec
P1                  10.00 usec
PLW1           34.53799820 W
SFO2          300.1319508 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2               90.00 usec
PLW2           8.82489967 W
PLW12          0.21354000 W
PLW13          0.10741000 W

F2 - Processing parameters
SI                    65536
SF              75.4677485 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

SiEt3

7b

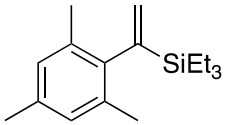
7.24
7.19
6.81
5.99
5.94
5.77
5.76
5.65
5.64
2.34
2.27
2.26
2.18
2.12
1.55
1.26
0.94
0.91
0.88
0.85
0.84
0.83
0.82
0.81
0.80
0.80
0.79
0.62
Current Data Parameters




```
Current Data Parameters
NAME                  mr-90_2
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20200624
Time                  14.45 h
INSTRUM            NEO_SPECT
PROBHD    Z104275_D460 (
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       450
DS                         2
SWH                20000.000 Hz
FIDRES             0.610352 Hz
AQ                 1.6384000 sec
RG                       101
DW                    25.000 usec
DE                     7.67 usec
TE                     -7.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1
SFO1               75.4768047 MHz
NUC1                      13C
P0                     3.33 usec
P1                    10.00 usec
PLW1              34.53799820 W
SFO2             300.1319508 MHz
NUC2                       1H
CPDPRG[2              waltz65
PCPD2                 90.00 usec
PLW2               8.82469967 W
PLW12              0.21354000 W
PLW13              0.10741000 W

F2 - Processing parameters
SI                     65536
SF                75.4677377 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```


SiEt3

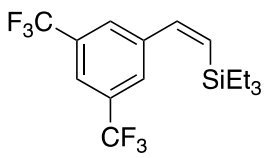
7c

6.84
6.84
5.79
5.78
5.67
5.66
2.27
2.14
0.96
0.95
0.93
0.93
0.90
0.67
0.67
0.64
0.64
0.62
0.59
0.59
Current Data Parameters

SiEt3

7c

151.11
141.85
134.75
134.06
129.49
128.12
21.01
7.45
7.41
Current Data Parameters
NAME mr-79



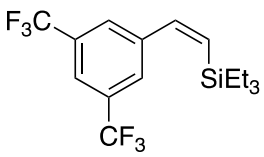
8b

7.77
7.73
7.46
7.42

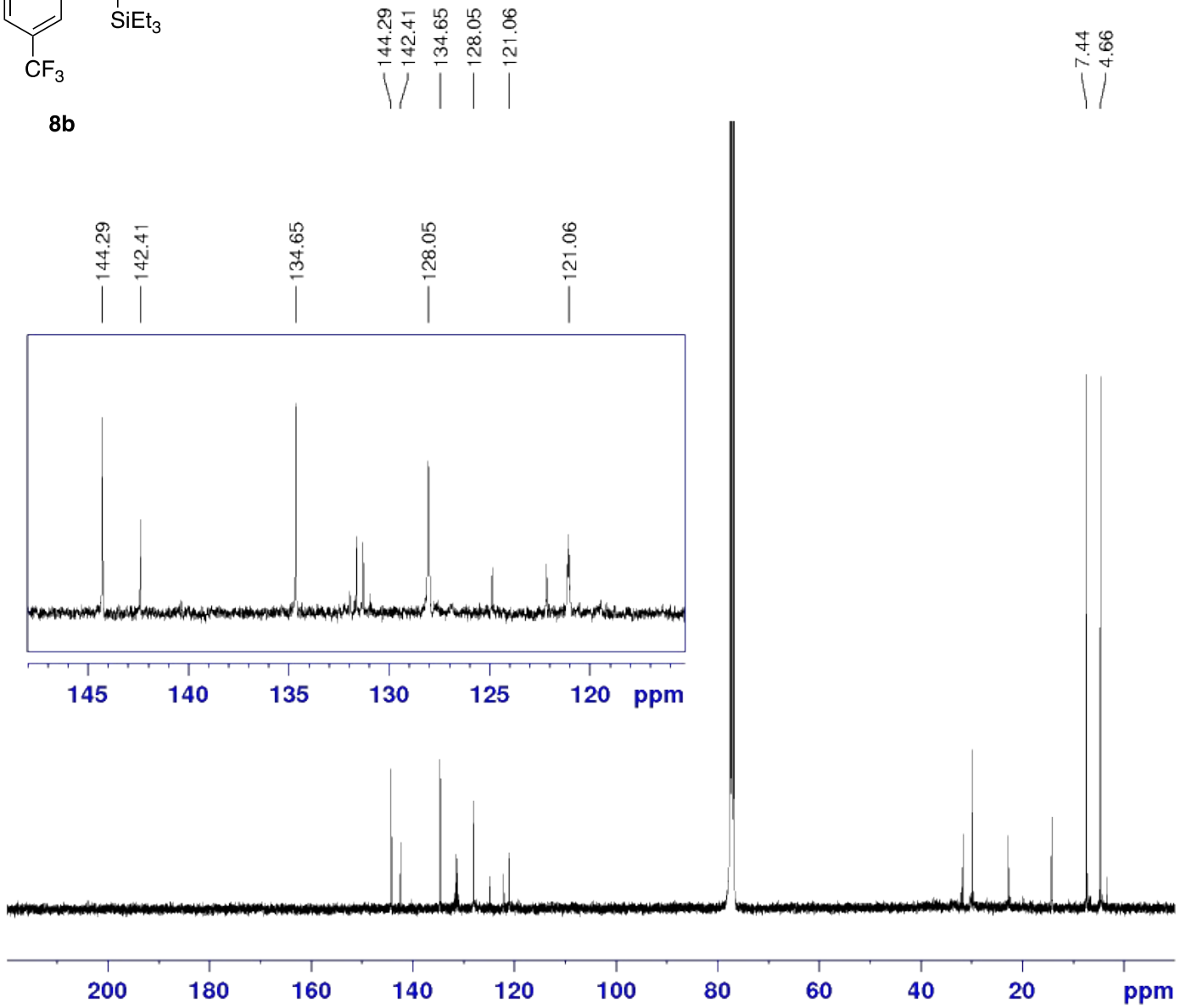
6.05
6.01

1.54
1.26
0.89
0.88
0.87
0.85
0.55
0.54

Current Data Parameters



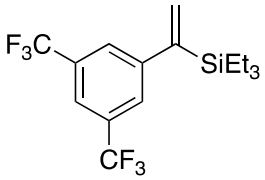
8b




```
Current Data Parameters
NAME                  mr-103
EXPNO                      3
PROCNO                     1

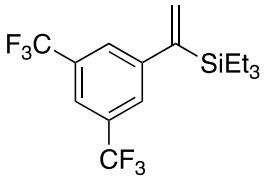
F2 - Acquisition Parameters
Date_               20200707
Time                   6.41 h
INSTRUM                spect
PROBHD    Z108618_0516 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    13312
DS                        2
SWH              27173.912 Hz
FIDRES           0.829282 Hz
AQ               1.2058624 sec
RG                      203
DW                 18.400 usec
DE                  8.65 usec
TE                  300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      13
SFO1           100.6248421 MHz
NUC1                    13C
P0                  3.27 usec
P1                  9.80 usec
PLW1           77.98300171 W
SFO2           400.1326008 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2               90.00 usec
PLW2           11.99499989 W
PLW12           0.32877001 W
PLW13           0.16537000 W

F2 - Processing parameters
SI                    65536
SF             100.6127518 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```


F3C
SiEt3
CF3

8c

7.84
7.73
7.56
6.97
6.90
6.66
6.60
5.95
5.95
5.74
5.73
0.96
0.94
0.91
0.71
0.71
0.69
0.68
0.66
Current Data Parameters

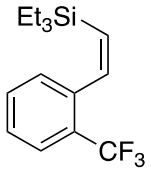


8c


```
Current Data Parameters
NAME                  mr-94_2
EXPNO                       1
PROCNO                      1

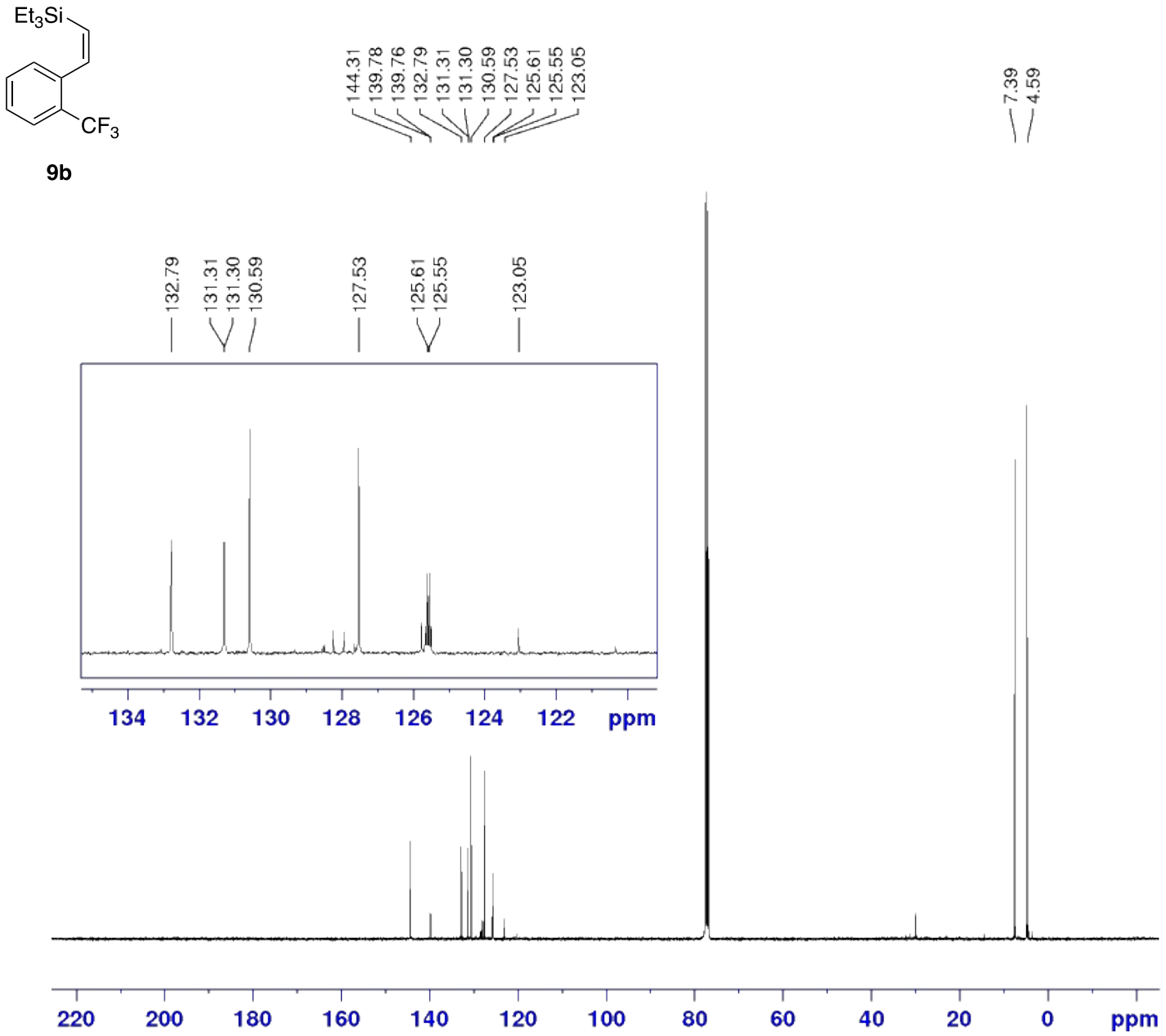
F2 - Acquisition Parameters
Date_              20200625
Time                  15.58 h
INSTRUM                spect
PROBHD    Z108618_0516 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      650
DS                        2
SWH               27173.912 Hz
FIDRES            0.829282 Hz
AQ                1.2058624 sec
RG                      203
DW                 18.400 usec
DE                  8.65 usec
TE                  300.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           100.6248421 MHz
NUC1                    13C
P0                   3.27 usec
P1                   9.80 usec
PLW1           77.98300171 W
SFO2           400.1326008 MHz
NUC2                    1H
CPDPRG[2            waltz65
PCPD2               90.00 usec
PLW2           11.99499989 W
PLW12           0.32877001 W
PLW13           0.16537000 W

F2 - Processing parameters
SI                    65536
SF             100.6127504 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```


Et3Si
CF3

9b

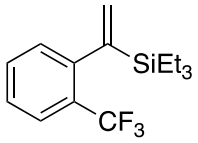
7.65
7.64
7.63
7.63
7.63
7.61
7.60
7.48
7.48
7.48
7.45
7.45
7.45
7.40
7.40
7.37
7.37
7.34
7.33
7.31
7.31
7.26
5.97
5.92
0.86
0.84
0.81
0.46
0.46
0.43
0.41
0.38
0.38
Current Data Parameters




```
Current Data Parameters
NAME                  MR-98
EXPNO                     2
PROCNO                    1

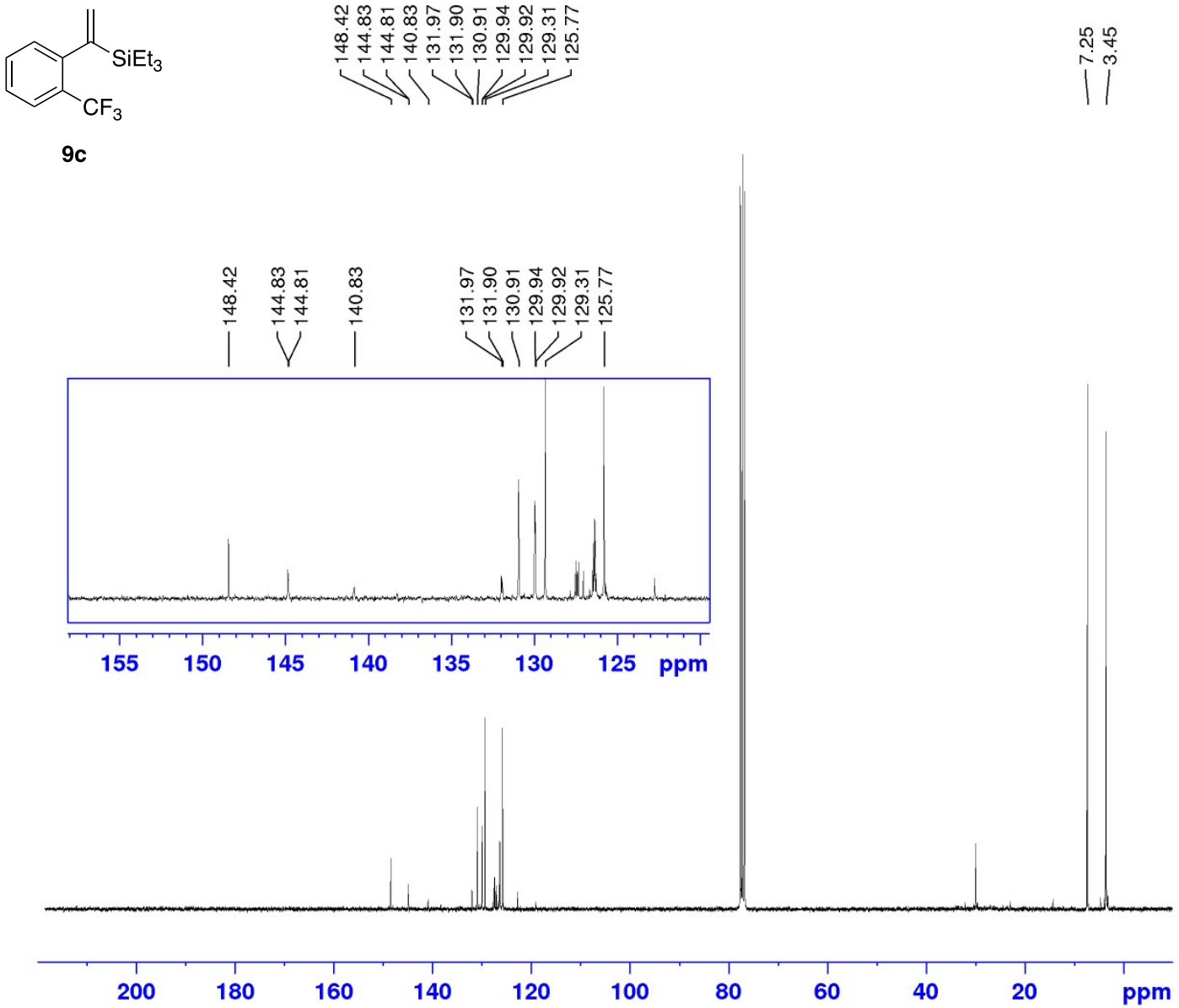
F2 - Acquisition Parameters
Date_              20200630
Time                  1.37 h
INSTRUM               spect
PROBHD    Z108618_0516 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    7168
DS                       4
SWH              25252.525 Hz
FIDRES            0.770646 Hz
AQ               1.2976128 sec
RG                     203
DW                  19.800 usec
DE                   6.50 usec
TE                  300.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      7
SFO1           100.6228303 MHz
NUC1                   13C
P0                   3.27 usec
P1                   9.80 usec
PLW1           77.98300171 W
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           11.99499989 W
PLW12           0.32877001 W
PLW13           0.16537000 W

F2 - Processing parameters
SI                   65536
SF             100.6127521 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```


SiEt3
CF3

9c

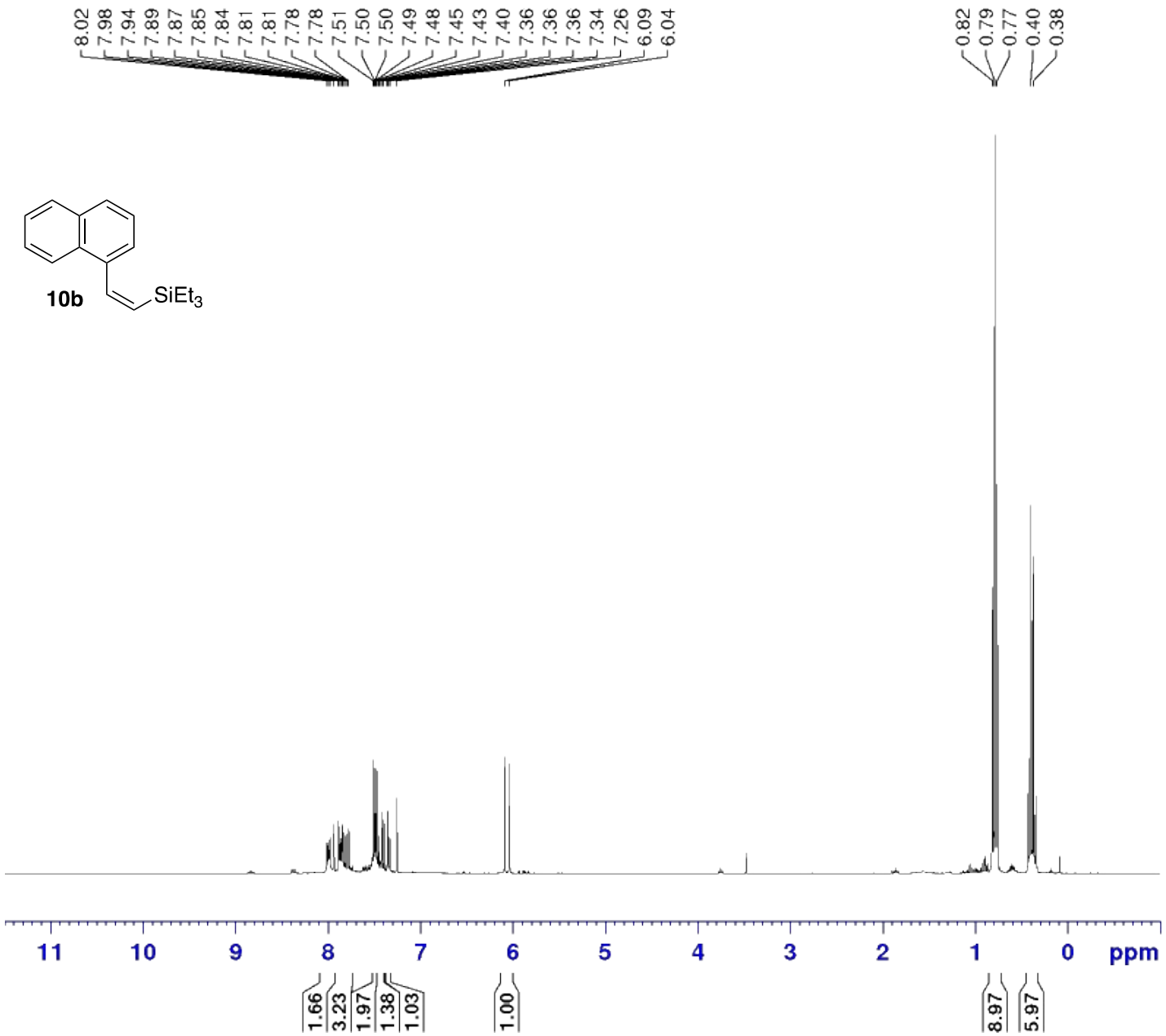
7.64
7.62
7.45
7.45
7.42
7.42
7.40
7.40
7.30
7.28
7.03
7.01
5.76
5.76
5.75
5.75
5.75
5.72
5.71
0.93
0.90
0.87
0.67
0.65
0.65
0.63
0.60
0.57
0.57
Current Data Parameters
NAME mr-63




```
Current Data Parameters
NAME                  mr-83_2
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20200618
Time                    0.30 h
INSTRUM            NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       6000
DS                          4
SWH                17857.143 Hz
FIDRES              0.544957 Hz
AQ                  1.8350080 sec
RG                        101
DW                     28.000 usec
DE                      6.50 usec
TE                      -7.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1
SFO1               75.4752953 MHz
NUC1                      13C
P0                      3.33 usec
P1                     10.00 usec
PLW1              34.53799820 W
SFO2             300.1312005 MHz
NUC2                      1H
CPDPRG[2              waltz65
PCPD2                  90.00 usec
PLW2               8.82489967 W
PLW12              0.21354000 W
PLW13              0.10741000 W

F2 - Processing parameters
SI                        32768
SF                 75.4677371 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```




```
Current Data Parameters
NAME                  mr-91
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20200622
Time                 15.50 h
INSTROM          NEO_SPECT
PROBHD    Z104275_046D (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               5882.353 Hz
FIDRES            0.179515 Hz
AQ                5.5705600 sec
RG                      101
DW                 85.000 usec
DE                  8.24 usec
TE                  -7.8 K
D1              2.00000000 sec
TD0                       1
SFO1           300.1319508 MHz
NUC1                    1H
P0                  4.67 usec
P1                 14.00 usec
PLW1            8.82489967 W

F2 - Processing parameters
SI                    65536
SF             300.1300073 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

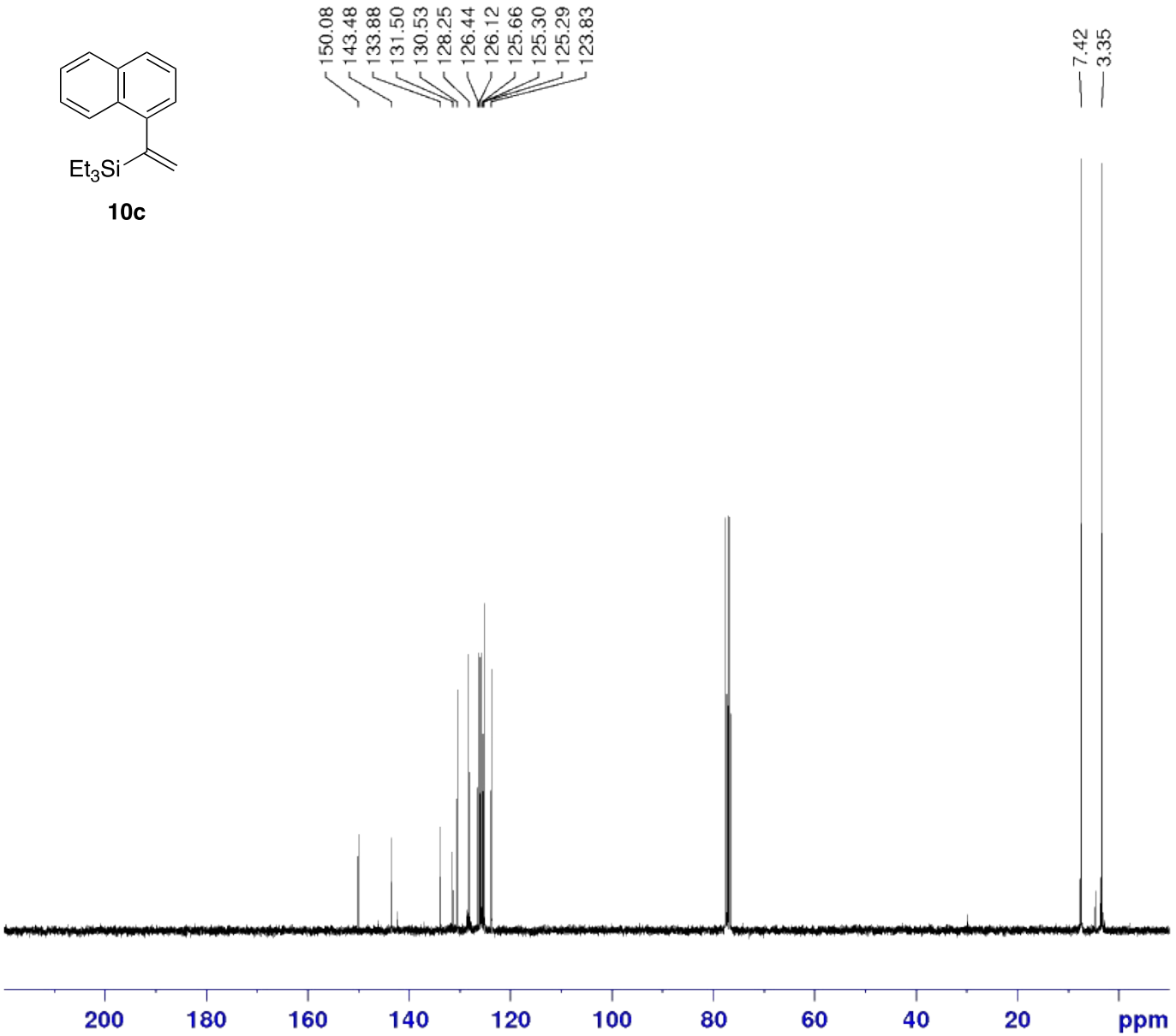
10b
SiEt3

8.19
8.52
8.33
1.93
1.76
8.39
7.96
5.93
5.89
5.65
5.32
5.19
Current Data Parameters

Et3Si

10c

7.98
7.98
7.96
7.95
7.86
7.85
7.83
7.73
7.70
7.48
7.47
7.46
7.44
7.42
7.42
7.39
7.10
7.10
7.08
7.07
6.55
6.48
6.10
6.05
5.95
5.94
5.89
5.88
1.10
1.07
1.05
0.95
0.93
0.90
0.80
0.77
0.75
0.67
0.66
0.64
0.61
0.59
Current Data Parameters




```
Current Data Parameters
NAME                  mr-77
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20200622
Time                 10.36 h
INSTRUM          NEO_SPECT
PROBHD     Z104275_0460 (
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     480
DS                       2
SWH              20000.000 Hz
FIDRES           0.610352 Hz
AQ               1.6384000 sec
RG                     101
DW                25.000 usec
DE                 7.67 usec
TE                 -7.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1            75.4768047 MHz
NUC1                   13C
P0                  3.33 usec
P1                 10.00 usec
PLW1           34.53799820 W
SFO2           300.1319508 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2              90.00 usec
PLW2            8.82489967 W
PLW12           0.21354000 W
PLW13           0.10741000 W

F2 - Processing parameters
SI                   65536
SF              75.4677400 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```

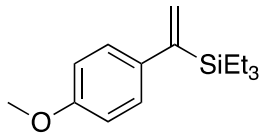
11b

7.41
7.36
7.24
7.21
6.88
6.86
6.83
6.81
6.29
6.22
5.68
5.63

3.82
3.82

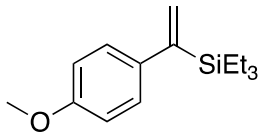
1.02
1.01
0.99
0.96
0.92
0.92
0.90
0.89
0.89
0.86
0.67
0.67
0.64
0.62
0.62
0.59

Current Data Parameters


SiEt3
O

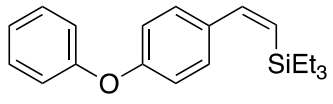
11c

7.41
7.38
7.13
7.10
6.86
6.83
6.29
6.23
5.87
5.86
5.53
5.52
3.82
3.81
0.96
0.94
0.91
0.72
0.71
0.69
0.66
0.64
0.63
Current Data Parameters
NAME mr-93

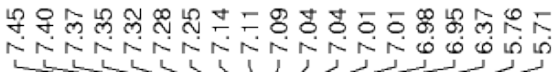

SiEt3
O

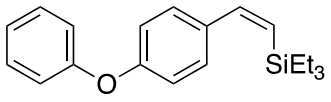
11c

159.66
133.36
129.63
114.35
113.00
113.07
77.81
77.67
73.18
54.03
53.67
29.35
Current Data Parameters


O
SiEt3

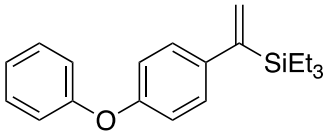
12b


7.45
7.40
7.37
7.35
7.32
7.28
7.25
7.14
7.11
7.09
7.04
7.04
7.01
7.01
6.98
6.95
6.37
5.76
5.71
0.92
0.89
0.87
0.62
0.59
0.57
Current Data Parameters
NAME mr-100

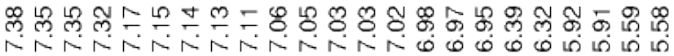

O
SiEt3

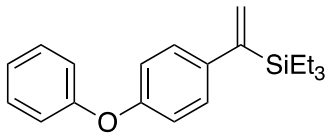
12b

157.42
156.72
147.01
135.90
129.89
129.45
128.96
127.84
123.38
119.03
119.00
118.97
118.46
77.64
74.93
Current Data Parameters
NAME mr-100

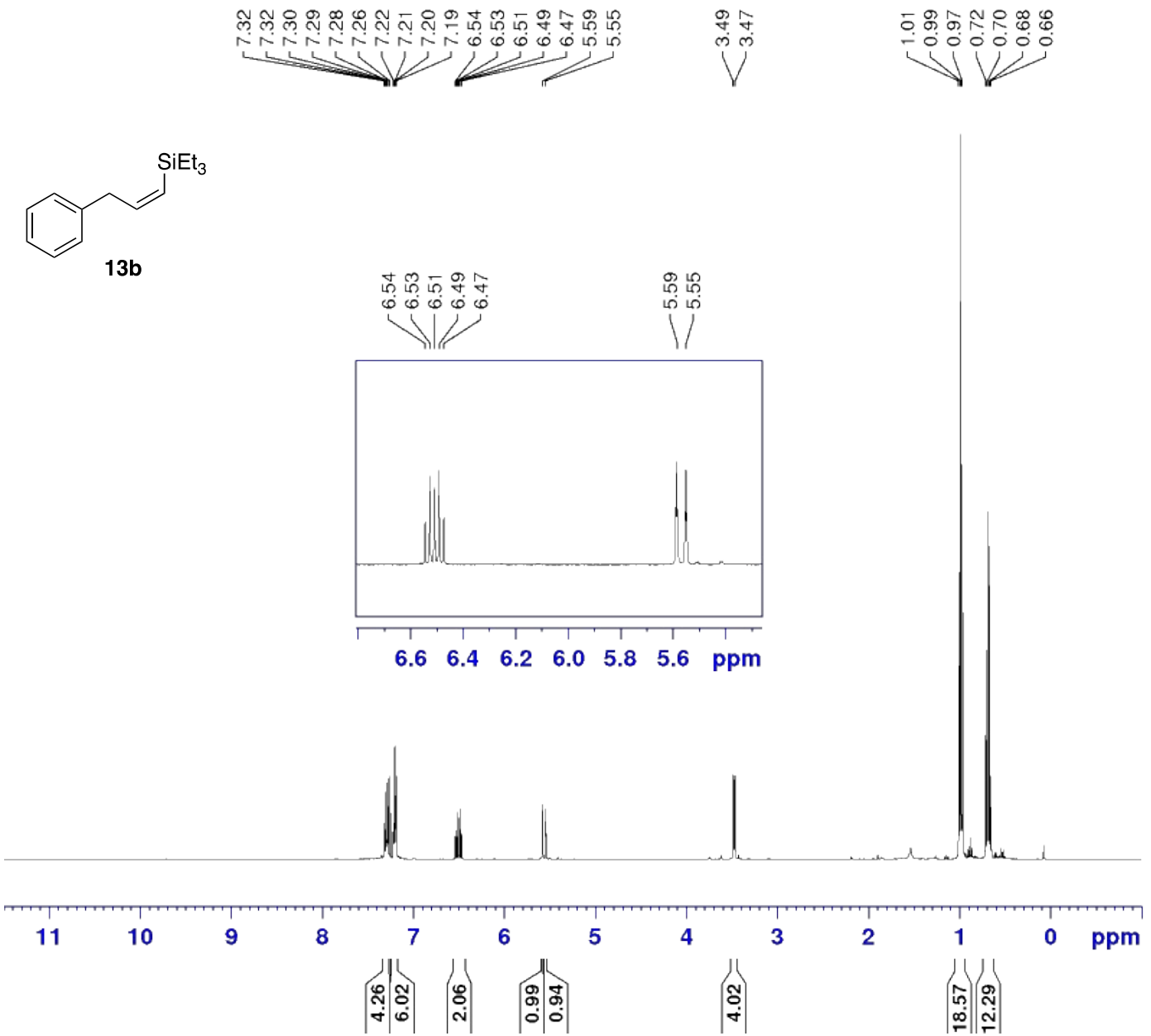

SiEt3
O

12c


7.38
7.35
7.35
7.32
7.17
7.15
7.14
7.13
7.11
7.06
7.05
7.03
7.03
7.02
6.98
6.97
6.95
6.39
6.32
5.92
5.91
5.59
5.58
1.29
0.99
0.96
0.94
0.74
0.74
0.72
0.71
0.69
0.66
0.66
0.11
Current Data Parameters



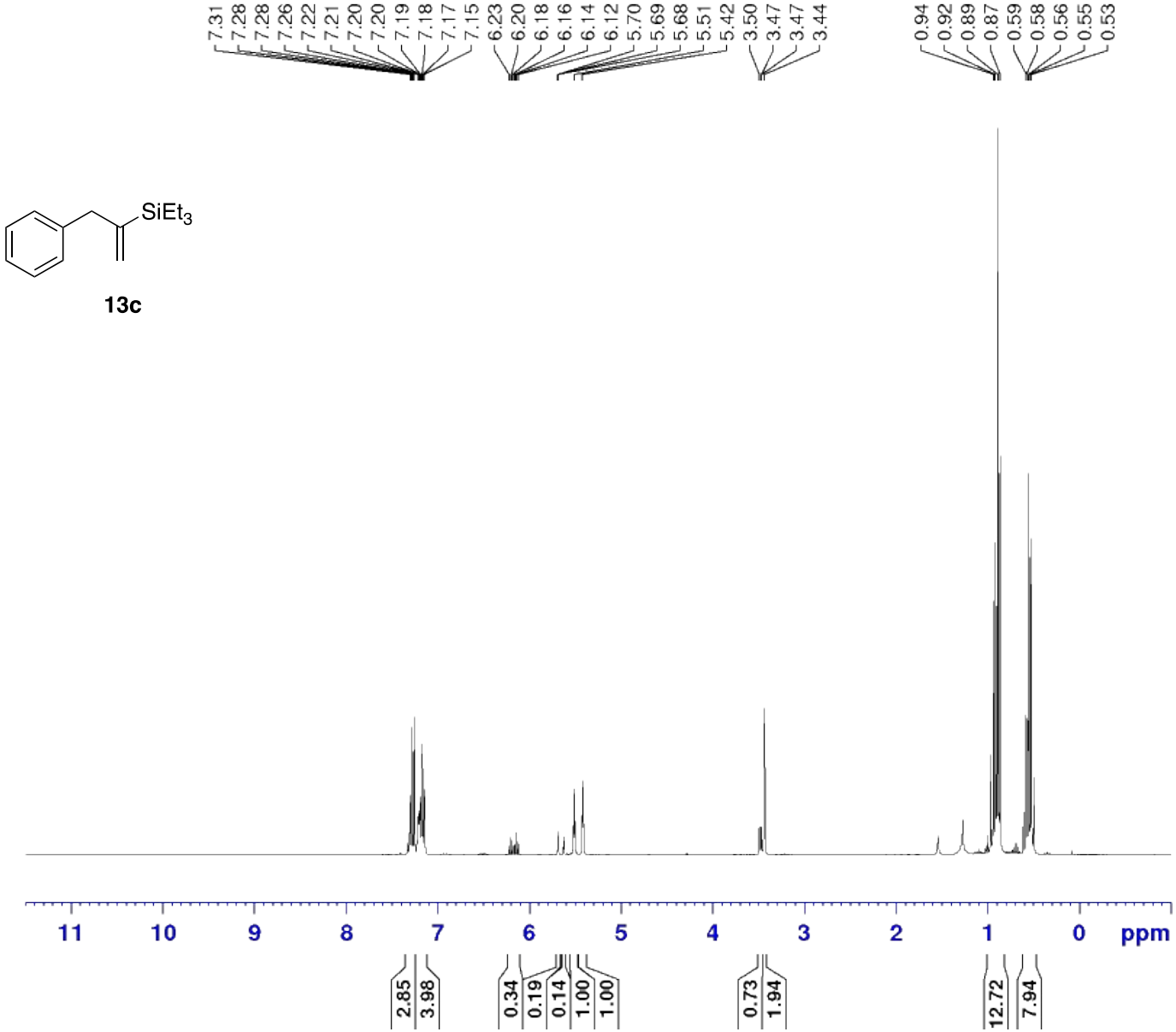
12c




```
Current Data Parameters
NAME                  mr-104
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20200706
Time                 18.24 h
INSTRUM                spect
PROBHD    Z108618_0516 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                      203
DW                   62.400 usec
DE                   16.93 usec
TE                   300.0 K
D1                 2.00000000 sec
TD0                        1
SFO1            400.1326008 MHz
NUC1                      1H
P0                    4.97 usec
P1                   14.90 usec
PLW1           11.99499989 W

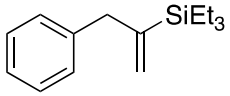
F2 - Processing parameters
SI                    65536
SF              400.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                  mr-95
EXPNO                     2
PROCNO                    1

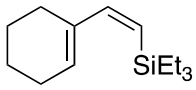
F2 - Acquisition Parameters
Date_              20200625
Time                 10.07 h
INSTRUM         NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               5882.353 Hz
FIDRES           0.179515 Hz
AQ               5.5705600 sec
RG                     101
DW                85.000 usec
DE                 8.24 usec
TE                 -7.8 K
D1             2.00000000 sec
TD0                      1
SFO1          300.1319508 MHz
NUC1                    1H
P0                 4.67 usec
P1                14.00 usec
PLW1           8.82489967 W

F2 - Processing parameters
SI                   65536
SF            300.1300072 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```


SiEt3

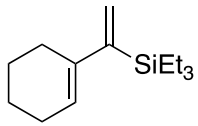
13c


148.36
146.53
140.32
140.18
129.47
128.80
128.51
128.24
127.97
127.40
126.09
126.03
43.70
43.16
7.52
7.39
3.65
2.99
Current Data Parameters
NAME mr-95


SiEt3

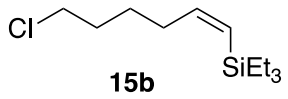
14b

6.76
6.76
6.72
6.72
5.65
5.65
5.35
5.31
2.09
2.04
1.65
1.64
1.64
1.63
1.62
1.58
1.57
1.57
1.54
0.95
0.93
0.91
0.61
0.59
Current Data Parameters


SiEt3

14c

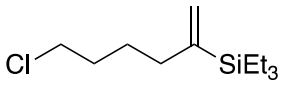
7.57
7.51
7.80
7.72
7.71
7.66
7.66
7.60
7.27
7.26
6.16
5.59
5.54
5.97
5.95
5.95
5.94
5.93
5.91
5.90
5.68
5.66
5.65
5.56
5.53
Current Data Parameters



15b

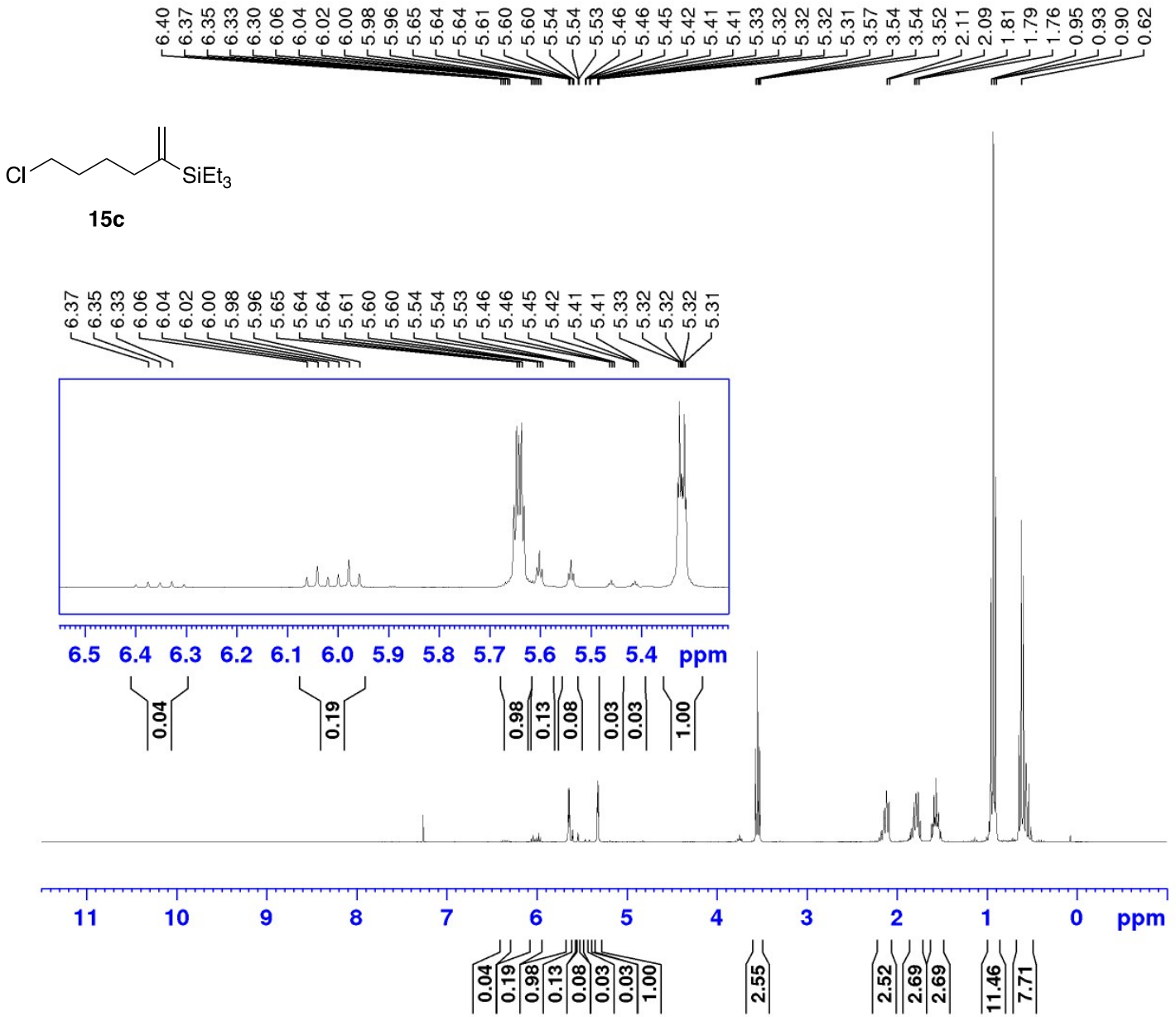
6.40
6.38
6.35
6.33
6.30
5.46
5.46
5.46
5.42
5.41
5.41
3.56
3.54
3.52
2.15
2.15
2.13
2.12
1.83
1.82
1.80
1.80
1.77
1.56
1.53
1.51
0.97
0.95
0.92
0.62
0.62
0.60

Current Data Parameters


Cl
SiEt3

15c

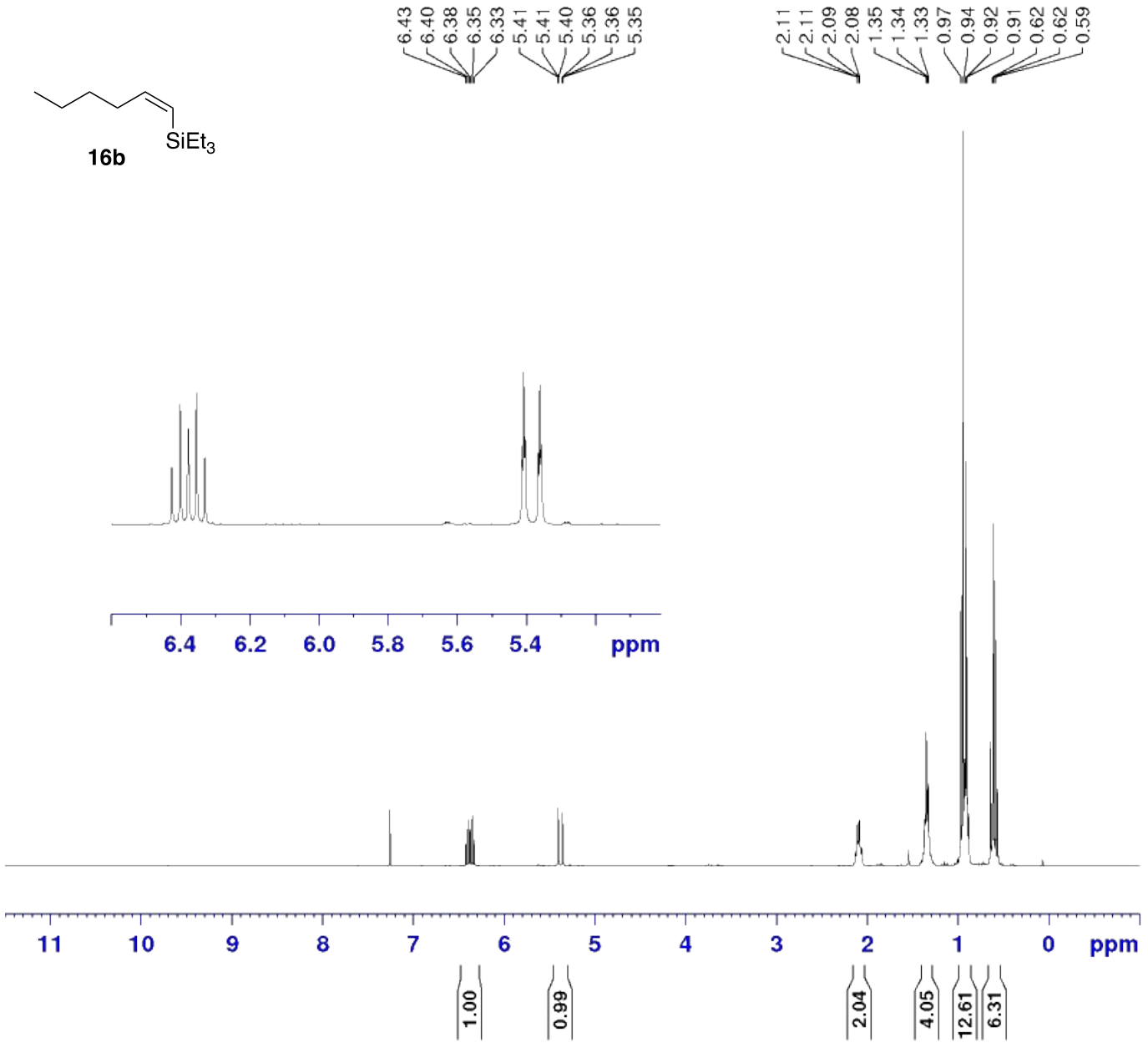
3.53
7.72
6.76
5.64
13
26
55
58
18
18
11
4
9
5
5
7
Current Data Parameters




```
Current Data Parameters
NAME                  mr-101
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20200701
Time                 16.01 h
INSTRUM          NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                5882.353 Hz
FIDRES             0.179515 Hz
AQ                 5.5705600 sec
RG                   47.4347
DW                    85.000 usec
DE                     8.24 usec
TE                    -7.8 K
D1              2.00000000 sec
TD0                       1
SFO1           300.1319508 MHz
NUC1                     1H
P0                     4.67 usec
P1                    14.00 usec
PLW1            8.82489967 W

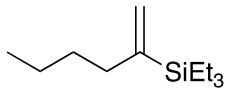
F2 - Processing parameters
SI                    65536
SF             300.1300072 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                  mr-62
EXPNO                     1
PROCNO                    1

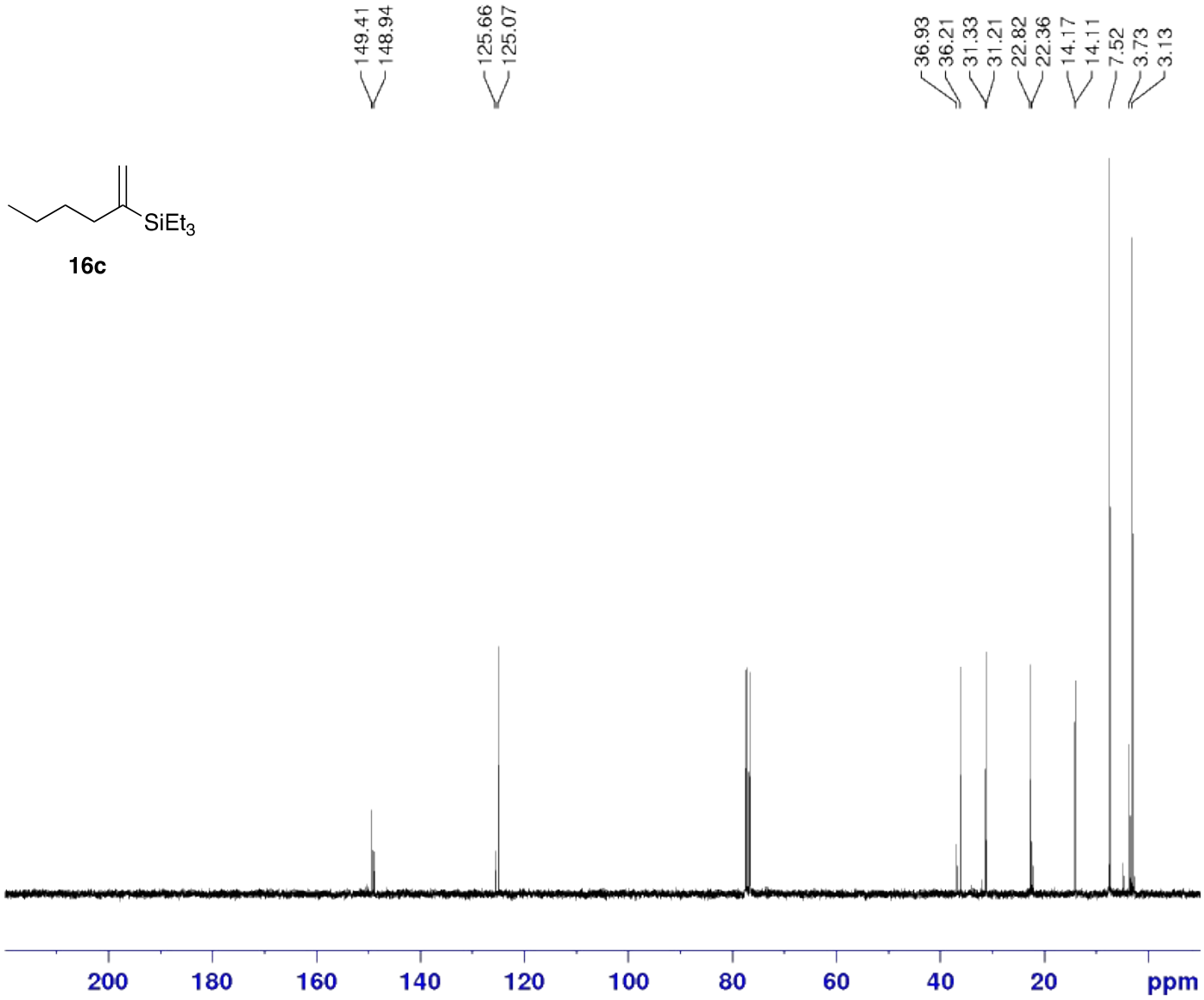
F2 - Acquisition Parameters
Date_              20200601
Time                 17.08 h
INSTRUM          NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               5882.353 Hz
FIDRES           0.179515 Hz
AQ               5.5705600 sec
RG                     90.5
DW                  85.000 usec
DE                   8.24 usec
TE                  296.0 K
D1               2.00000000 sec
TD0                       1
SFO1          300.1319508 MHz
NUC1                     1H
P0                    4.67 usec
P1                   14.00 usec
PLW1           8.82489967 W

F2 - Processing parameters
SI                    65536
SF            300.1300076 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```


SiEt3

16c

.41
.38
.36
.33
.09
.07
.05
.03
.01
.98
.64
.64
.63
.63
.62
.57
.51
.41
.37
.30
.29
.29
.29
.28
.28
.09
.37
.35
.35
.96
.93
.91
.91
.65
.64
.62
.62
.59




```
Current Data Parameters
NAME                  mr-102
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_              20200701
Time                 16.25 h
INSTRUM          NEO_SPECT
PROBHD    Z104275_0460 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      151
DS                        2
SWH               20000.000 Hz
FIDRES             0.610352 Hz
AQ                 1.6384000 sec
RG                      101
DW                   25.000 usec
DE                    7.67 usec
TE                    -7.8 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1            75.4768047 MHz
NUC1                    13C
P0                    3.33 usec
P1                   10.00 usec
PLW1           34.53799820 W
SFO2           300.1319508 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                90.00 usec
PLW2            8.82489967 W
PLW12           0.21354000 W
PLW13           0.10741000 W

F2 - Processing parameters
SI                    65536
SF              75.4677360 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```