SUPPORTING INFORMATION

Title: A Triarylated 1,2,3-Triazol-5-ylidene Ligand with a Redox-Active Ferrocenyl Substituent for Rhodium(I)-Catalyzed Hydroformylation of 1-Octene

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I. General considerations

Characterisation Techniques

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AVANCE-III-300 operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P and 282.40 MHz for ^{19}F; or AVANCE-III-400 operating at 400.21 MHz for ^{1}H, 100.64 MHz for ^{13}C, 162.01 MHz for ^{31}P and 376.57 MHz for ^{19}F. ^{1}H Chemical shifts are reported as δ (ppm) values downfield from Me_4Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD_2Cl_2, 5.32 ppm; $CDCl_3$, 7.26 ppm; C_6D_6, 7.16 ppm; CD_3CN, 1.94 ppm). $^{13}C\{^{1}H\}$ chemical shifts are also reported as δ (ppm) values downfield from Me_4Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD_2Cl_2, 54.0 ppm; $CDCl_3$, 77.16 ppm; C_6D_6, 128.06 ppm; CD_3CN, 118.26 ppm). The chemical shifts are given in ppm and the proton coupling constants (*J*) are given in Hz. The spectral coupling patterns are designated as follows: s - singlet; d - doublet; t - triplet; q - quartet; sept-septet; m - multiplet; br - broad signal. The assignment of the NMR for each complex follows the numbering scheme individually assigned for each compound illustrated on the respective NMR spectra below. An asterisk (*) denotes solvent contaminant in the NMR spectra. Chemical shift assignment in the ^{1}H NMR spectra is based on first-order analysis and when required were confirmed by two-dimensional (2D) (^{1}H-^{1}H) homonuclear chemical shift correlation (COSY) experiments. The ^{13}C shifts were obtained from proton-decoupled ^{13}C NMR spectra. Where necessary, the multiplicities of the ^{13}C signals were deduced from proton-decoupled DEPT-135 spectra. The resonances of the proton-bearing carbon atoms were correlated with specific proton resonances using 2D (^{13}C-^{1}H) heteronuclear single-quantum coherence (HSQC) experiments. Standard Bruker pulse programs were used in the experiments.

Single crystal X-ray diffraction data for **B** and **C** were collected on a Bruker Apex II-CCD detector using Mo-K_{α} radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2 at 150 K. Structures were solved and refined using Olex2 and SHELXTL.[1]

Solution IR spectra (ν(CO) were recorded on a Bruker ALPHA FT–IR spectrophotometer with a NaCl cell, using CH_2Cl_2 as solvent. The range of absorption measured was from 4000-600 cm^{-1}.

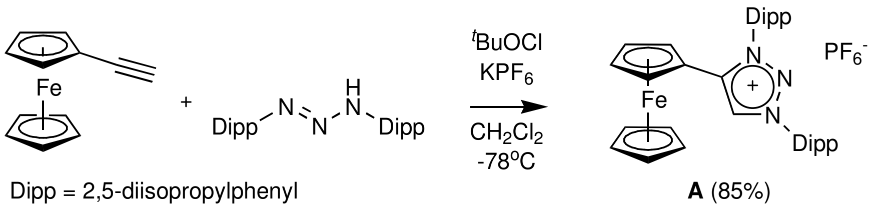
Mass spectral analyses were performed on a Waters Synapt G2 HDMS by direct infusion at *5* µL/min with positive electron spray as the ionization technique. The *m/z* values were measured in the range of

400-1500 with acetonitrile as solvent. Prior to analysis, a 5 mM sodium formate solution was used to calibrate the instrument in resolution mode.

Elemental analyses were carried out using a Thermo Flash 1112 Series CHNS-O Analyzer, and melting points were measured with a Stuart SMP10 melting point apparatus.

II. Synthesis and characterization of ligand precursors A – C

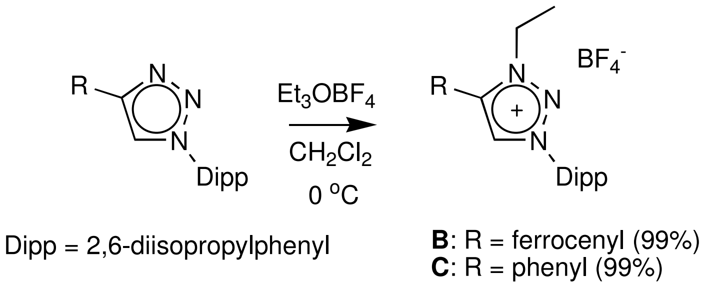
Synthesis of *1,3-bis(2,6-diisopropylphenyl)-4-ferrocenyl-1H-1,2,3-triazolium hexafluorophosphate(V)* (**A**).



*Scheme S1. Synthesis of triazolium salt **A***

An adapted procedure of the previously reported method for diarylated triazolium salt synthesis was followed.[2] Ethynylferrocene (1.00 g, 4.76 mmol), 2 equivalents of triazene (3.48 g, 9.52 mmol) and excess KPF_6 (2.00 g, 10.8 mmol) were added to a purged Schlenk vessel and dissolved in anhydrous dichloromethane (DCM). The solution was cooled to -78 °C and 2 equivalents of *tert*-butylhypochlorite (1.08 mL, 9.52 mmol) were added dropwise. The solution was kept cold for at least 5 hours and then left to warm up to room temperature overnight. After filtration, the filtrate was concentrated under reduced pressure and the solid was triturated with hexane and diethyl ether, affording **A** as an orange powder. Yield: 2.9 g (85%). M.p: 215–220 °C (decomp). ^{1}H NMR (300 MHz, CD_3CN) δ 9.06 (s, 1H, trz-**H, H-1**), 7.77 (t, *J* = 7.9 Hz, 2H, dipp-**H**, **H-2**), 7.56 (dd, *J* = 7.7, 6.0 Hz, 4H, dipp-**H**, **H-3**), 4.56 (m, 2H, Fc-**H**, **H-4**), 4.35 (m, 2H, Fc-**H**, **H-5**), 4.25 (s, 5H, Fc-**H**, **H-6**), 2.42 (dd, *J* = 13.6, 6.8 Hz, 2H, dipp(iso)-C**H**, **H-7**), 2.34 (dd, *J* = 13.1, 6.4 Hz, 2H,dipp(iso)-C**H**, **H-7**), 1.36 (d, *J* = 6.8 Hz, 6H, dipp(iso)-C**H**3, **H-8**), 1.23 (d, *J* = 6.8 Hz, 6H, dipp(iso)-C**H**3, **H-8**), 1.18 (d, *J* = 6.9 Hz, 6H, dipp(iso)-C**H**3, **H-8**), 1.15 (d, *J* = 6.9 Hz, 6H, dipp(iso)-C**H**3, **H-8**). ^{13}C {^{1}H} NMR (75 MHz, CD_3CN) δ 149.0 (Trz-**C**$_q$, **C-1**), 146.5 (dipp-**C**$_q$, **C-2**), 146.2 (dipp-C$_q$, **C-2**), 134.6 (dipp-C$_q$, **C-3**), 134.4 (dipp-C$_q$, **C-3**), 131.5 (Trz-**C**H, **C-4**), 131.3 (dipp-**C**H, **C-5**), 130.4 (dipp-CH, **C-5**), 126.5 (dipp-**C**H, **C-6**), 126.1 (dipp-**C**H, **C-6**), 73.2 (Fc-**C**H, **C-7**), 71.8 (Fc-**C**H, **C-8**), 70.4 (Fc-**C**H, **C-9**), 64.6 (Fc-C$_q$, **C-10**), 30.2 (dipp(iso)-**C**H, **C-11**), 25.2 (dipp(iso)-**C**H_3, **C-12**), 24.5 (dipp(iso)-**C**H_3, **C-12**), 24.1 (dipp(iso)-**C**H_3, **C-12**), 22.8 (dipp(iso)-**C**H_3, **C-12**). ^{31}P {^{1}H} NMR (121 MHz, CD_3CN) δ -144.61 (sept, *J* = 706.3 Hz, **P**F_6). ^{19}F

{^{1}H} NMR (282 MHz, CD_3CN) δ -72.95 (d, *J* = 706.3 Hz, P**F**$_6$). Anal. Calcd for $C_{36}H_{44}N_3FePF_6$: C 56.55, H 5.80, N 5.50. Found: C 56.19, H 5.51, N 5.50. ESI-HRMS (15 V, positive mode, m/z): calcd for $[M]^+$: 574.2884. Found: 574.2893.



*Scheme S2. Synthesis of triazolium salts **B** and **C**.*

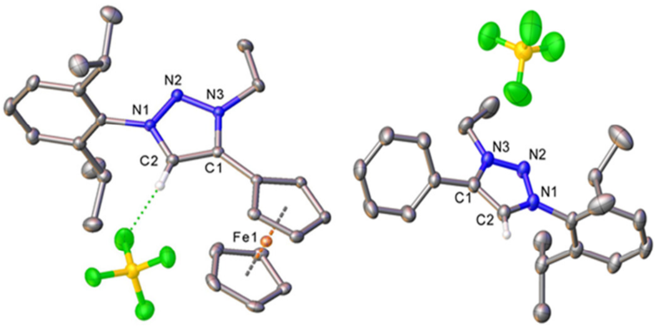
The precursor salts **B** and **C** were synthesized from their corresponding known precursor triazoles.[3] To a solution of the appropriate triazole derivative (2.4 mmol) in DCM, a solution of 3 equivalents of triethyloxonium tetrafluouroborate (7.2 mmol, 1.4 g), in *ca.* 10 mL of solvent DCM was added at -30 °C and left to reach room temperature overnight. After evaporation of the solvent, the solid was dissolved in minimum ethyl acetate (2 mL) after which diethyl ether (20 mL) was added and stirred for 1 hour. The precipitate was filtered and dried to yield the corresponding triazolium salt.

1-ethyl-3-(2,6-diisopropylphenyl)-4-ferrocenyl-1*H*-1,2,3-triazolium tetrafluoroborate(III) **B:** Orange powder. Yield: 1.3 mg (99 %). M.p. 194–198 °C (decomp). ^{1}H NMR (300 MHz, CD_3CN) δ 8.67 (s, 1H, trz-**H**, **H-1**), 7.72 (t, *J* = 7.8 Hz, 1H, dipp-**H**, **H-2**), 7.51 (d, *J* = 7.8 Hz, 2H, dipp-**H**, **H-3**), 4.90 (d, *J* = 1.7 Hz, 2H, Fc-**H**, **H-4**), 4.70 (m, *J* = 7.2 Hz, 4H, Fc-**H** (2H), **H-6** and CH_3C**H**$_2$ (2H), **H-5**), 4.30 (s, 5H, Fc-**H, H-7**), 2.30 (m, 2H, dipp(iso)-C**H**, **H-8**), 1.65 (t, *J* = 7.2 Hz, 3H, CH_2C**H**$_3$, **H-9**), 1.22 (dd, *J* = 20.4, 6.8 Hz, 12H, dipp(iso)-CH_3, **H-10**). ^{13}C {^{1}H} NMR (75 MHz, CD_3CN) δ 146.5 (dipp-**C**$_q$, **C-1**), 145.5 (dipp-**C**$_q$, **C-2**), 133.9 (dipp-**C**H, **C-3**), 131.9 (trz-**C**$_q$, **C-4**), 131.1 (trz-**C**H, **C-5**), 125.8 (dipp-**C**H, **C-6**), 72.6 (Fc-**C**H, **C-7**), 71.5 (Fc-**C**H, **C-8**), 70.6 (Fc-**C**H, **C-9**), 66.2 (Fc-C_q, **C-10**), 49.3 (-CH_3**C**H_2, **C-11**), 29.5 (dipp-(iso)-**C**H, **C-12**), 24.4 (dipp-(iso)-**C**H_3, **C-13**), 23.9 (dipp-(iso)-**C**H_3, **C-13**), 13.8 (-CH_2**C**H_3, **C-14**). ^{19}F NMR (282 MHz, CD_3CN) δ -151.69 (d, *J* = 15.0 Hz, B**F**$_4$). Anal. Calcd for $C_{26}H_{32}N_3FeBF_4$: C 58.41, H 6.03, N 7.86. Found: C 58.41, H 5.745, N 7.56. ESI-HRMS (15 V, positive mode, m/z): calcd for $[M]^+$: 442.1945. Found: 442.1904

1-ethyl-3-(2,6-diisopropylphenyl)-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate(III) **C:** White crystalline powder. Yield: 1.0 g, 99%. M.p. 94–98 °C. ^{1}H NMR (300 MHz, CD_3CN) δ 8.66 (s, 1H, trz-**H**, **H-1**), 7.75 (m, 5H, Ph-C**H**, **H-3** + m, 1H, dipp-C**H, H-2** at 7.72), 7.52 (d, *J* = 7.8 Hz, 2H, dipp-C**H**, **H-4**), 4.68 (q, *J* = 7.2 Hz, 2H, -C$H_2$$CH_3$, **H-5**), 2.40 (m, 2H, dipp-(iso)-C**H**, **H-6**), 1.62 (t, *J* = 7.2 Hz, 3H, -CH_2CH_3, **H-7**), 1.21 (dd, *J* = 15.0, 6.8 Hz, 12H, dipp-(iso)-CH_3, **H-8**). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN) δ 146.6 (dipp-C_q, **C-1**), 144.7 (dipp-C_q, **C-2**), 133.9 (dipp-**C**H, **C-3**), 132.9 (Ph-**C**H, **C-4**), 132.0 (Ph-C**H**, **C-4**) 131.9 (trz-C_q, **C-5**) 130.8 (trz-**C**H, **C-6**), 130.5 (Ph-**C**H, **C-4**), 125.8 (dipp-**C**H, **C-7**), 123.1 (Ph-C_q, **C-8**), 49.3 (-**C**$H_2$$CH_3$, **C-9**), 29.4 (dipp-(iso)-**C**H, **C-10**), 24.7 (dipp-(iso)-**C**H_3, **C-11**), 23.7 (dipp-(iso)-**C**H_3, **C-11**), 13.9 (-CH_2**C**H_3, **C-12**). ^{19}F NMR (282 MHz, CD_3CN) δ -151.82 (d, *J* = 15.0 Hz). Anal. Calcd for $C_{22}H_{28}N_3BF_4$: C 60.40 H 6.45 N 9.60. Found: C 60.61 H 6.20 N 9.46. ESI-HRMS (15 V, positive mode, m/z): calcd for $[M]^+$: 334.2283. Found: 334.2247.

Single crystal X-ray structures of compounds **B** and **C**

Suitable crystals of **B** and **C** for X-ray diffraction were obtained from a layered concentrated DCM solution and toluene (1:9).



B **C**

Figure S1. Molecular structures of triazolium salts **B** and **C**, showing 50% probability ellipsoids and partial atom-numbering scheme. Hydrogens (except for trz-H) are omitted for clarity.

Crystal data for compound **B**

$C_{26}H_{32}BF_4FeN_3$ (M = 529.20 g/mol): monoclinic, space group C2/c, a = 29.3111(19) Å, b = 9.0993(6) Å, c = 18.6543(12) Å, α = 90°, β = 90.198(3) °, γ = 90°, V = 4975.3(6) Å3, Z = 8, T = 150 K, Dcalc = 1.413 g/cm3, μ(MoKα) = 0.656 mm-1, 86054 reflections measured (4.368° ≤ 2Θ ≤ 52.91°), 5134 unique [R_{int} = 0.0323, R_{sigma} = 0.0133] which were used in all calculations. The final R_1 was 0.0293 (I > 2σ(I)) and wR_2 was 0.0705 (all data).

Crystal data for compound **C**

$C_{22}H_{28}BF_4N_3$ (M = 421.28 g/mol): monoclinic, space group CP2$_1$/c, a = 8.2036(7) Å, b = 12.5525(11) Å, c = 21.5301(17) Å, α = 90°, β = 92.659(4) °, γ = 90°, V = 2214.7(3) Å^3, Z = 4, T = 150 K, D_{calc} = 1.263 g/cm^3, μ(CuKα) = 0.822 mm^{-1}, 75653 reflections measured (4.368° ≤ 2Θ ≤ 52.91°), 4529 unique [R_{int} = 0.0596, R_{sigma} = 0.0255] which were used in all calculations. The final R_1 was 0.0607 (I > 2σ(I)) and wR_2 was 0.1544 (all data).

III. NMR spectra and atom numbering schemes of A – C and free MIC A'

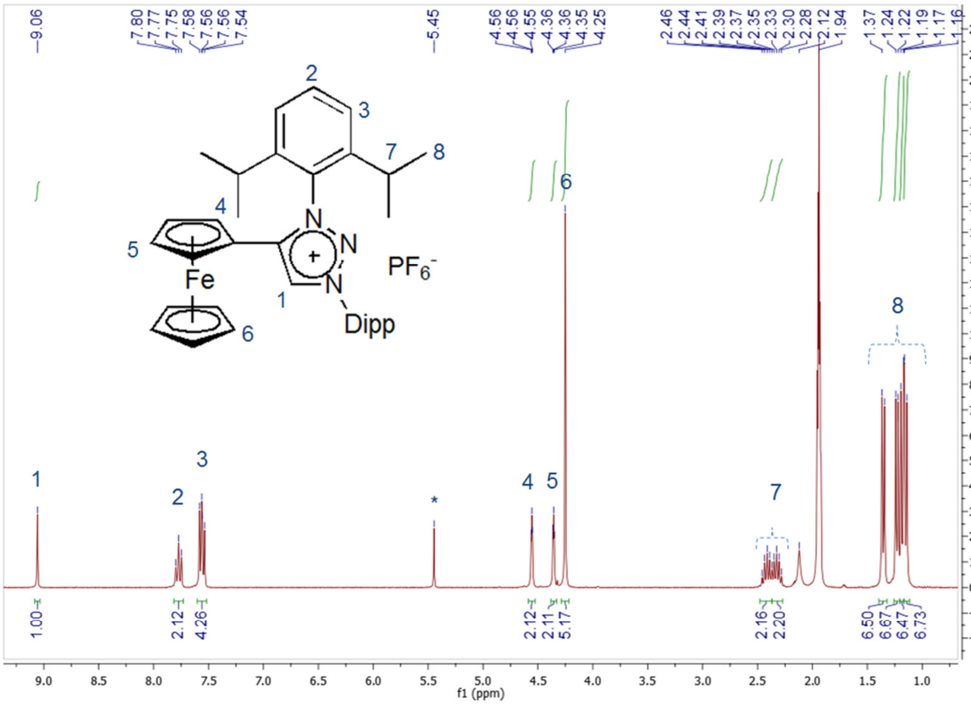


Figure S2. The ^1H NMR spectrum of **A** *in solvent CD_3CN.*

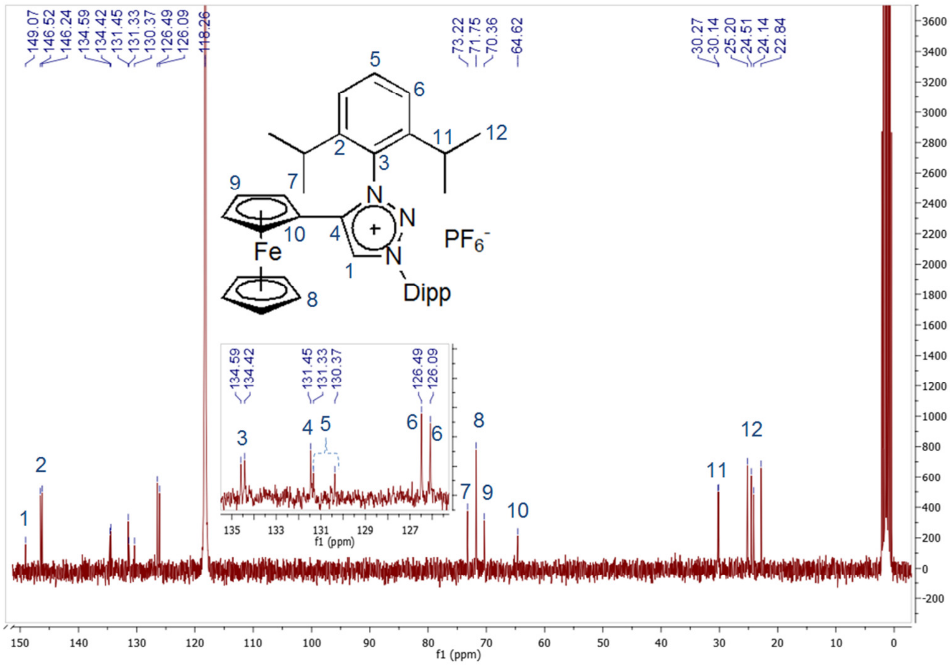


*Figure S3. The $^{13}C\{^{1}H\}$ NMR spectrum of **A** in solvent CD_3CN.*

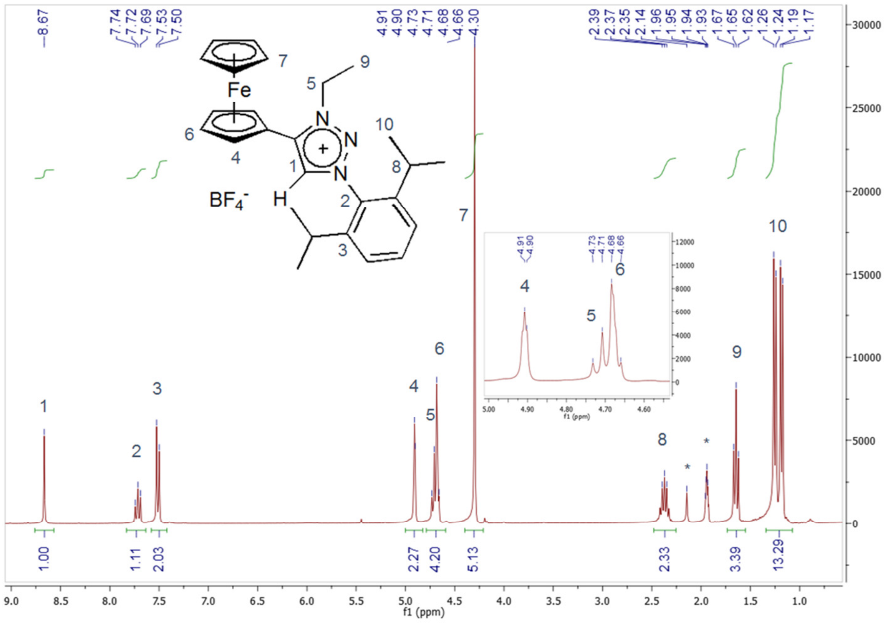


*Figure S4. The ^{1}H NMR spectrum of **B** in solvent CD_3CN.*

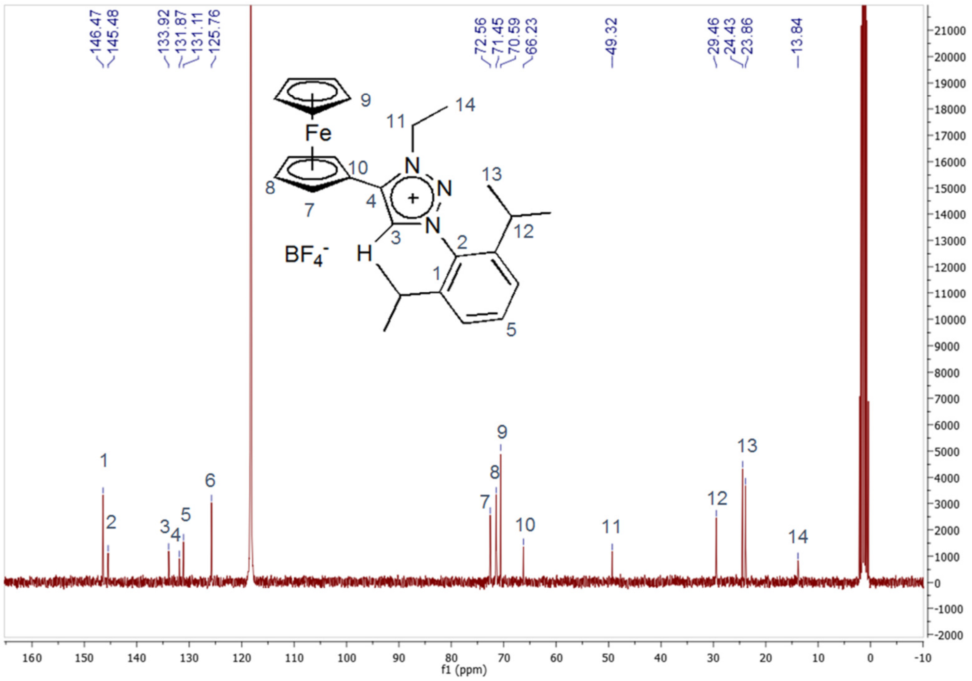


*Figure S5. The $^{13}C\{^1H\}$ NMR spectrum of **B** in solvent CD_3CN.*

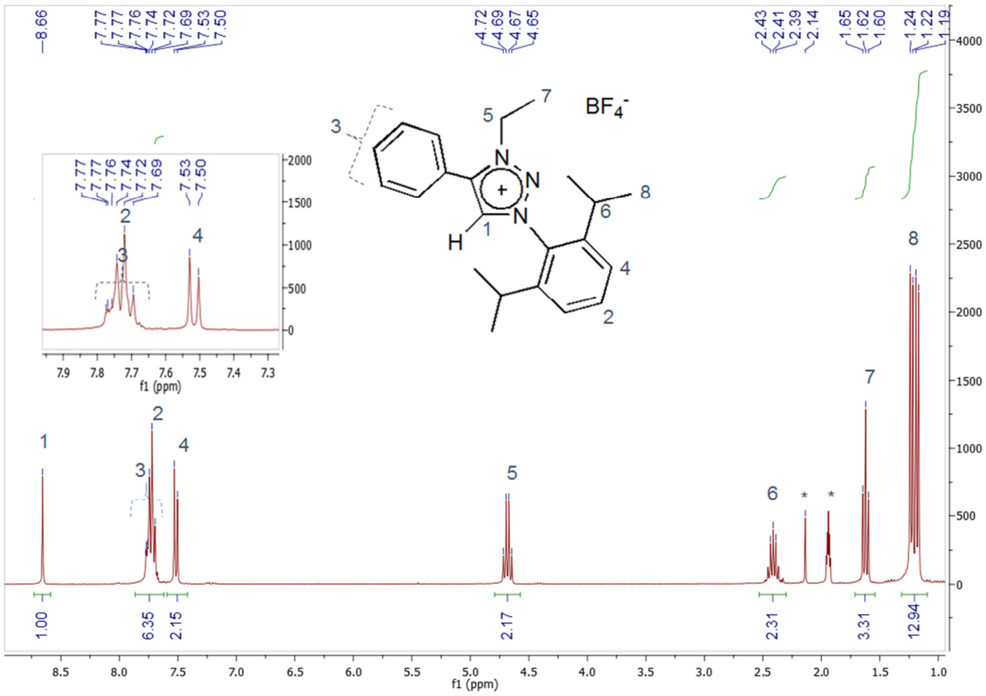


*Figure S6. The ^1H NMR spectrum of **C** in solvent CD_3CN.*

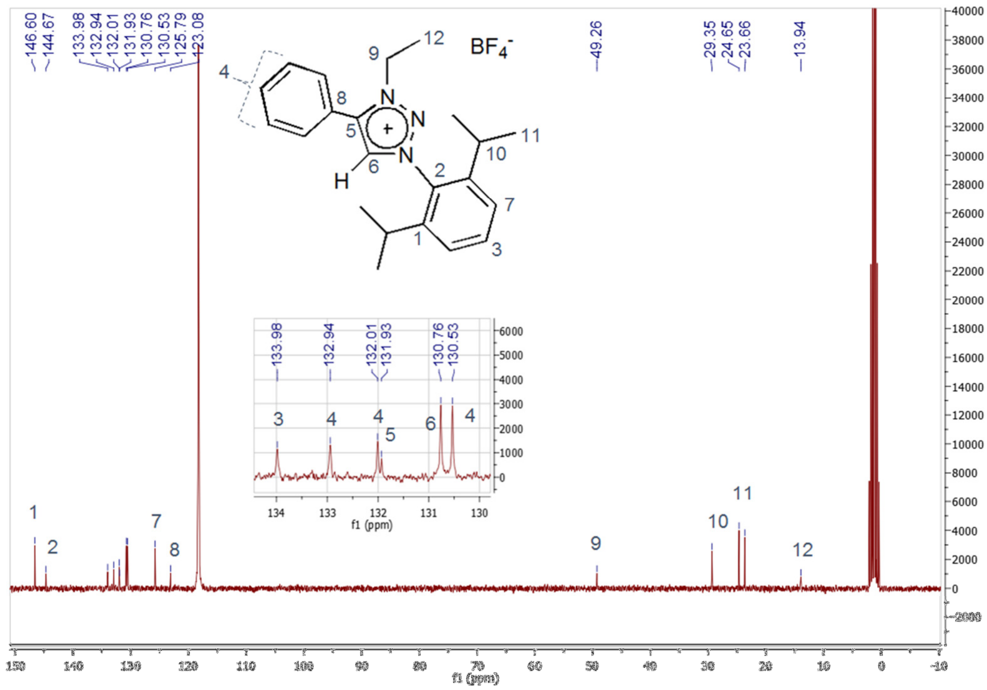


*Figure S7. The $^{13}C\{^1H\}$ NMR spectrum of **C** in solvent CD_3CN.*

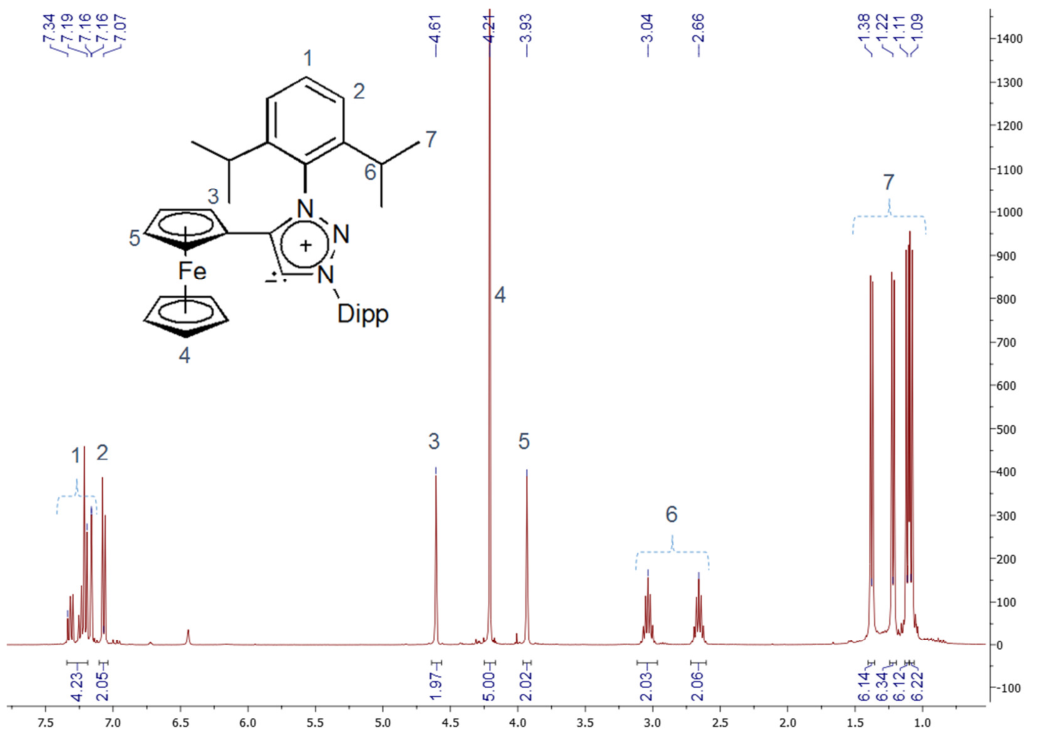


*Figure S8. The ^1H NMR spectrum of the free carbene **A'** in solvent C_6D_6.*

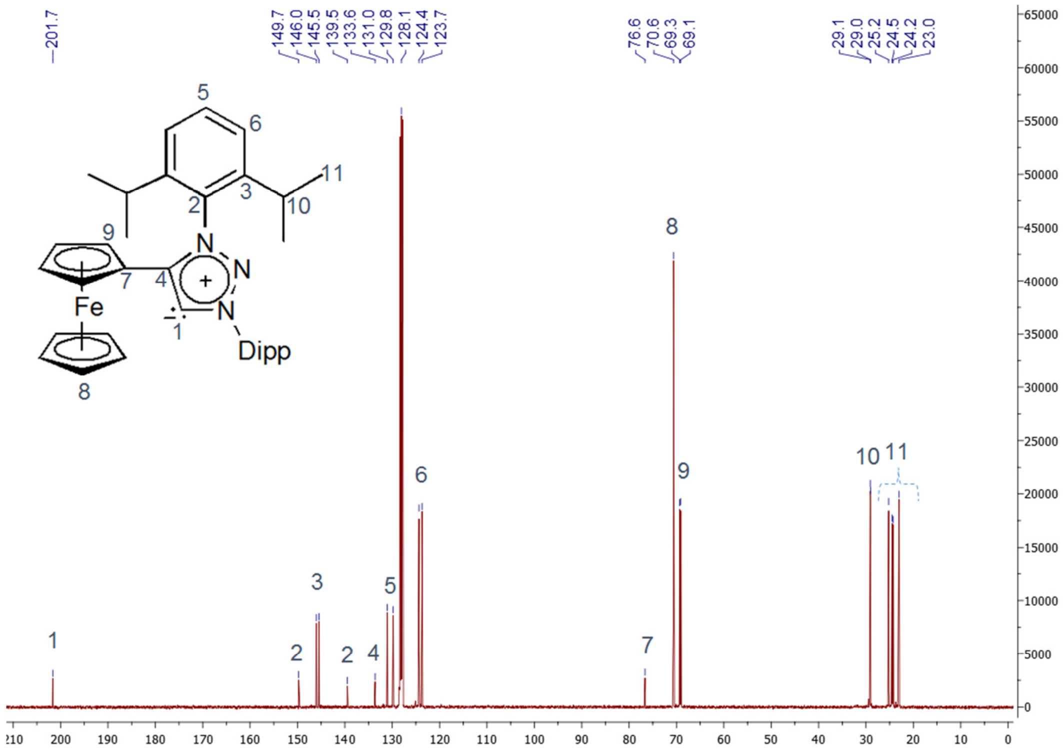


*Figure S9. The $^{13}C\ \{^{1}H\}$ NMR spectrum of the free carbene **A'** in solvent C_6D_6.*

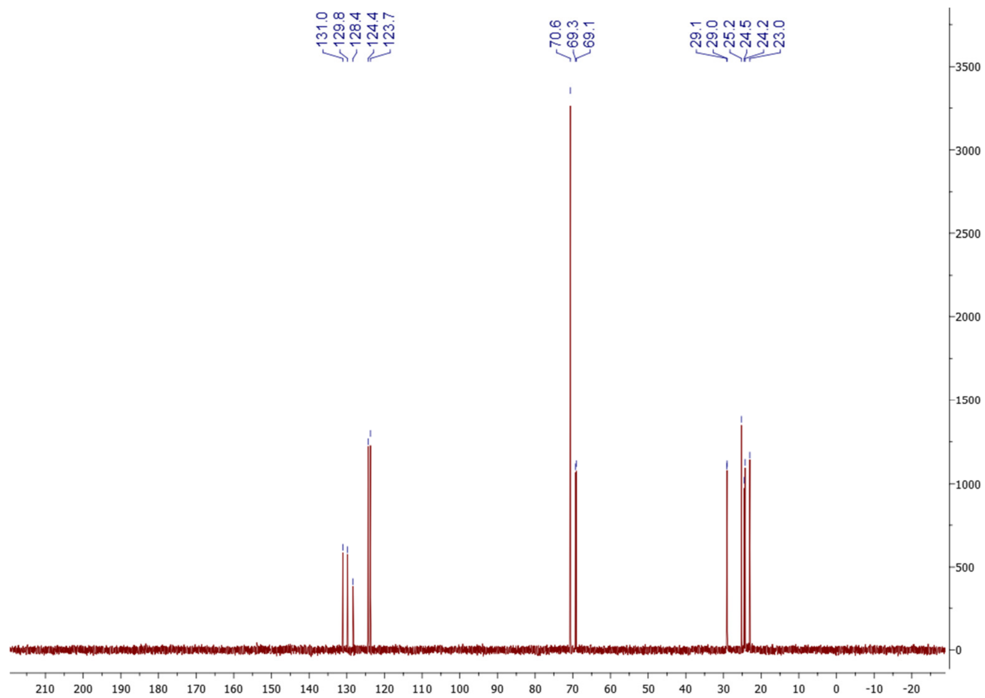


*Figure S10. The ^{13}C DEPT135 NMR spectrum of the free carbene **A'** in solvent C_6D_6.*

IV. NMR spectra and atom numbering schemes of complexes 1–7

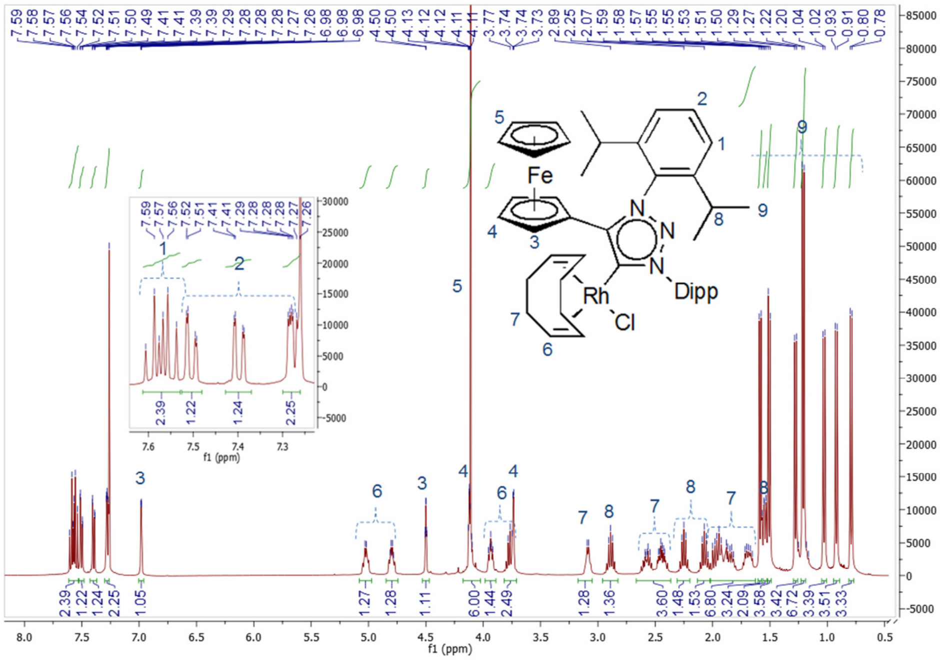


Figure S11. The [1]H NMR spectrum of ***1*** *in solvent $CDCl_3$.*

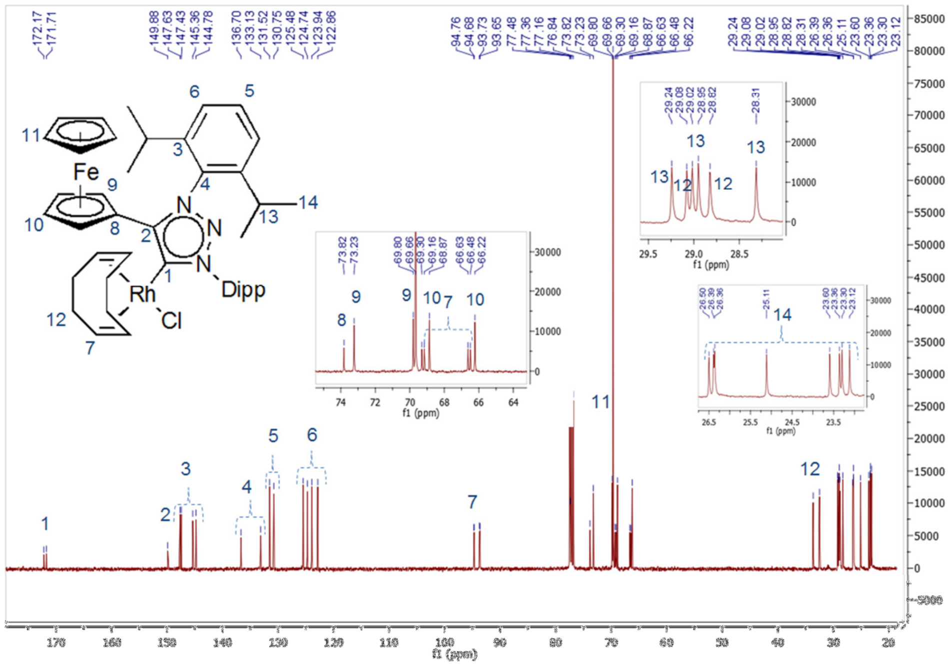


Figure S12. The [13]C {[1]H} NMR spectrum of ***1*** *in solvent $CDCl_3$.*

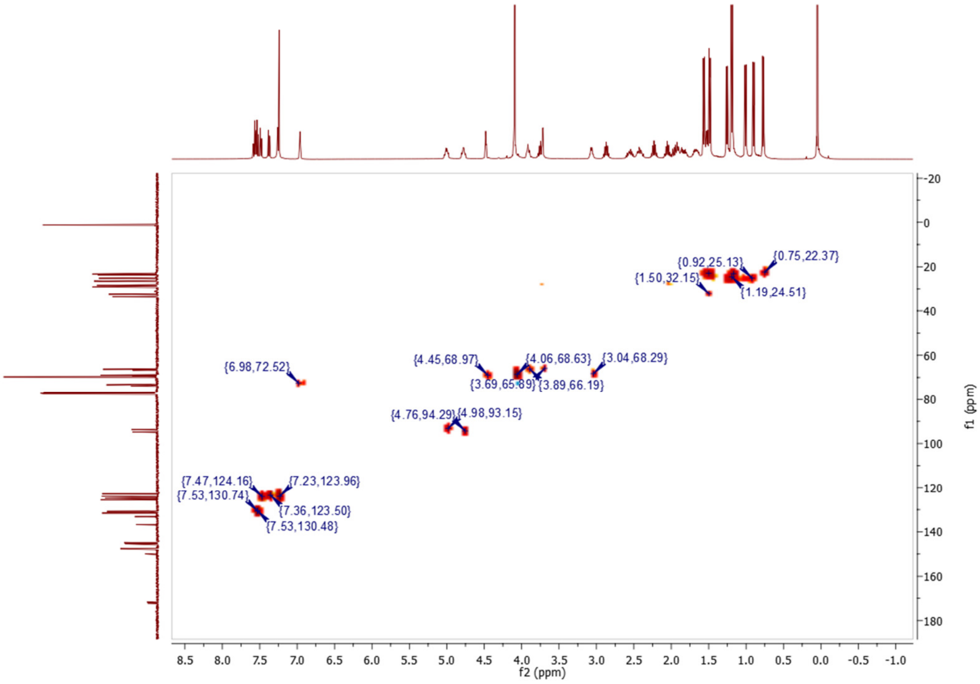


*Figure S13. The HSQC (2D-NMR) spectrum of **1** in solvent $CDCl_3$.*

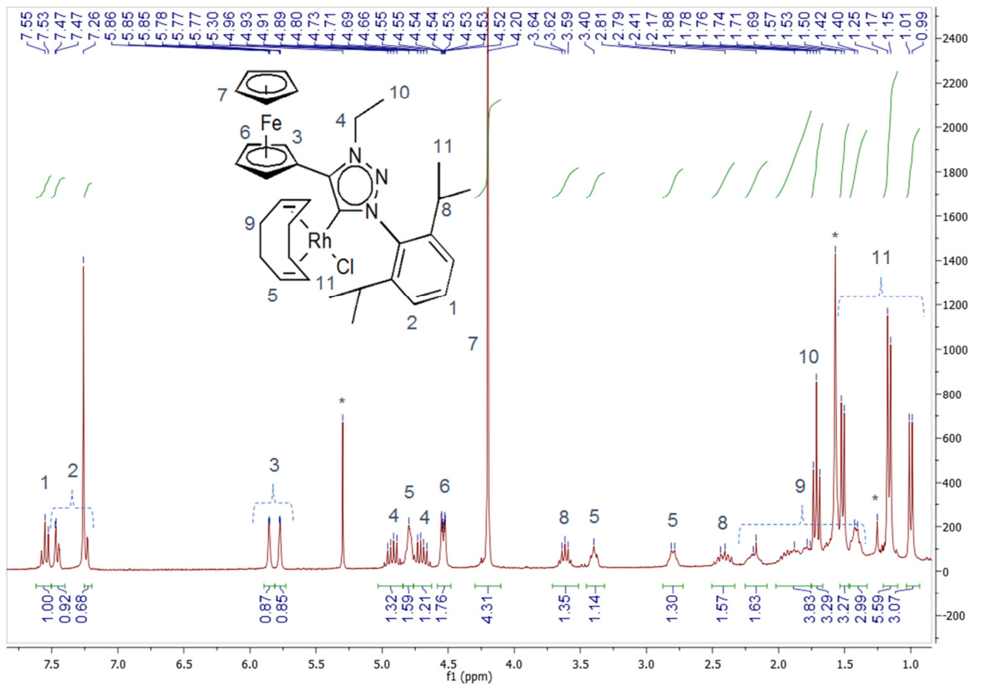


*Figure S14. The ^1H NMR spectrum of **2** in solvent $CDCl_3$.*

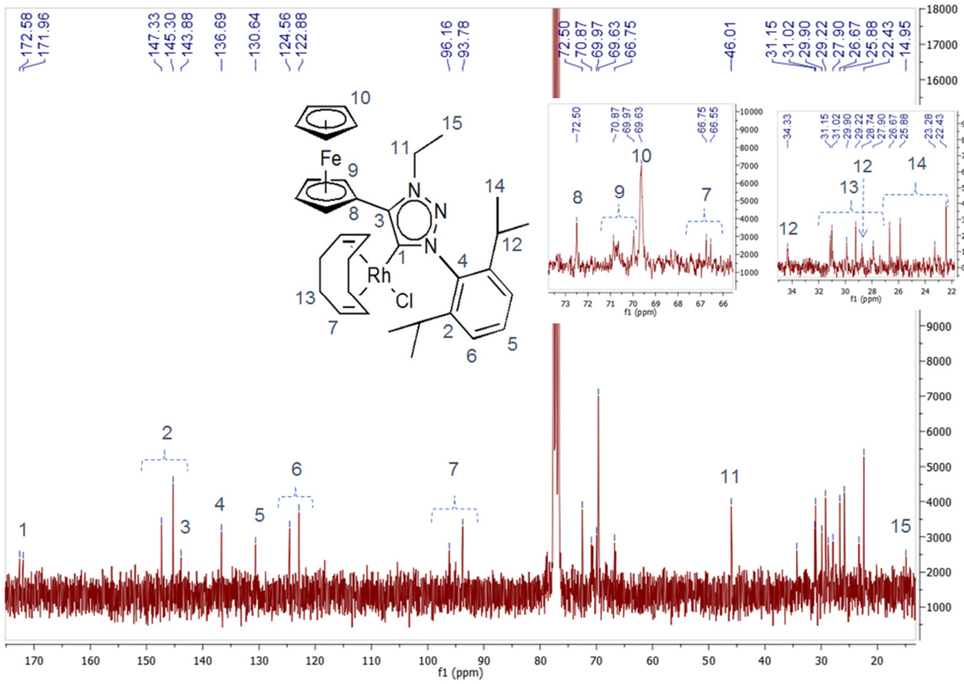


*Figure S15. The $^{13}C\{^{1}H\}$NMR spectrum of **2** in solvent $CDCl_3$.*

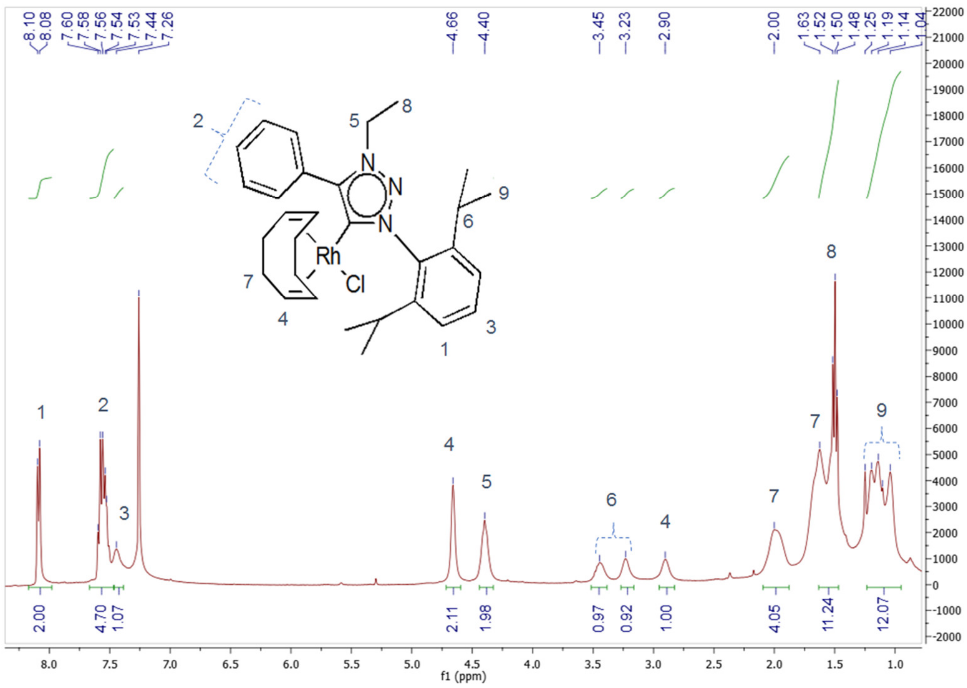


*Figure S16. The ^{1}H NMR spectrum of **3** in solvent $CDCl_3$.*

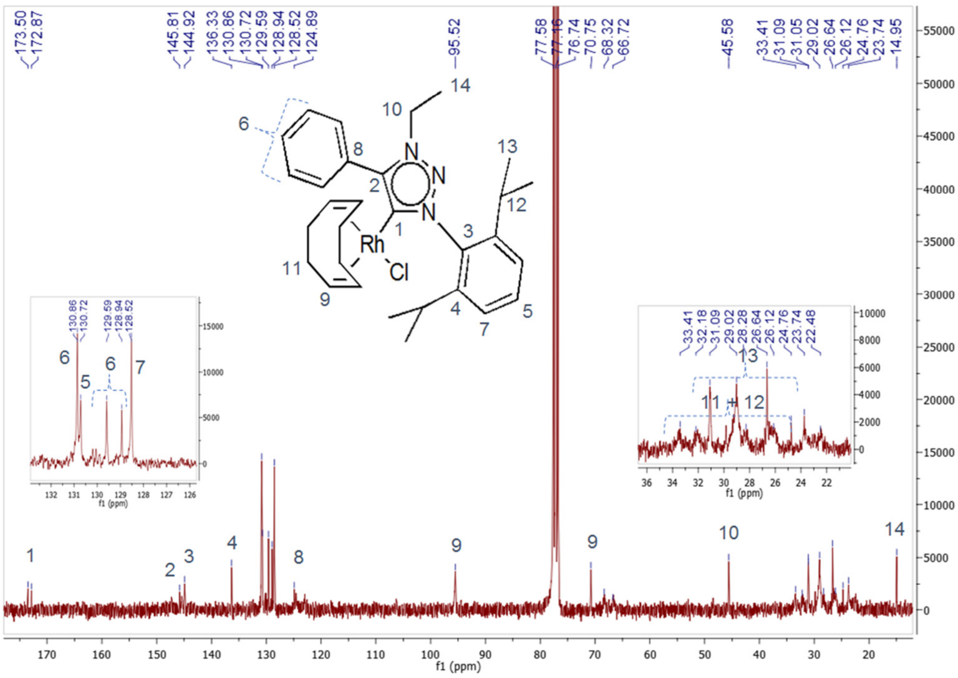


*Figure S17. The $^{13}C\{^{1}H\}$ NMR spectrum of **3** in solvent $CDCl_3$.*

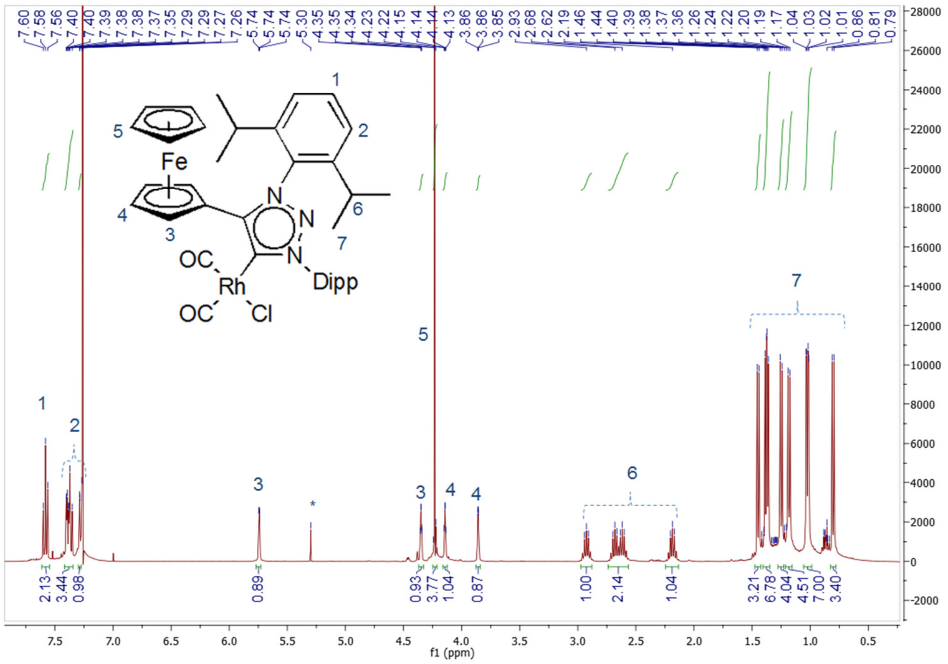


*Figure S18. The ^{1}H NMR spectrum of **4** in solvent $CDCl_3$.*

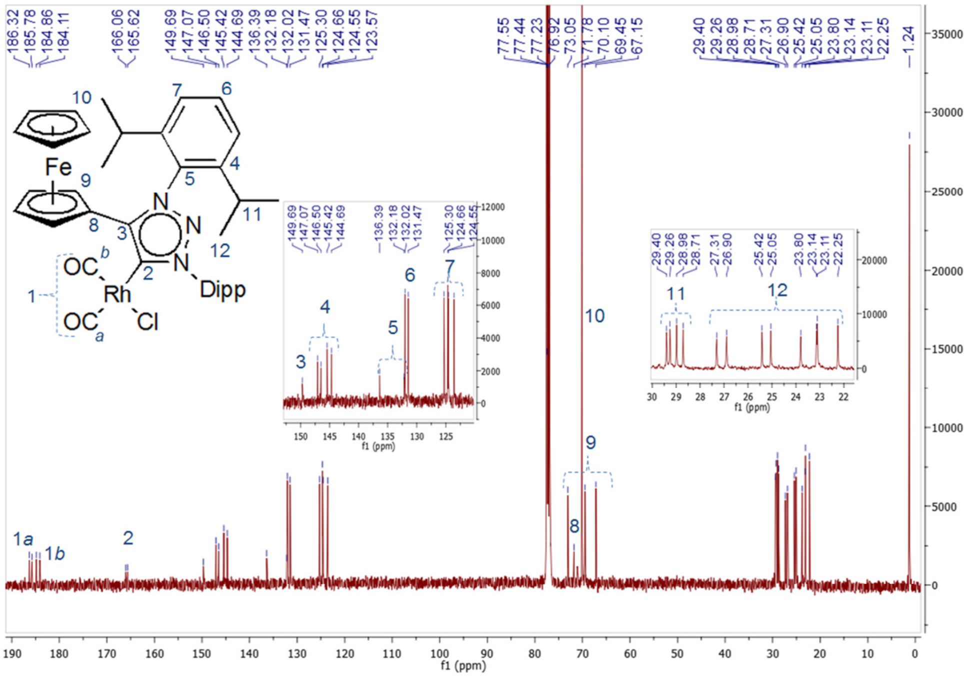


*Figure S19. The $^{13}C\{^{1}H\}$ NMR spectrum of **4** in solvent $CDCl_3$.*

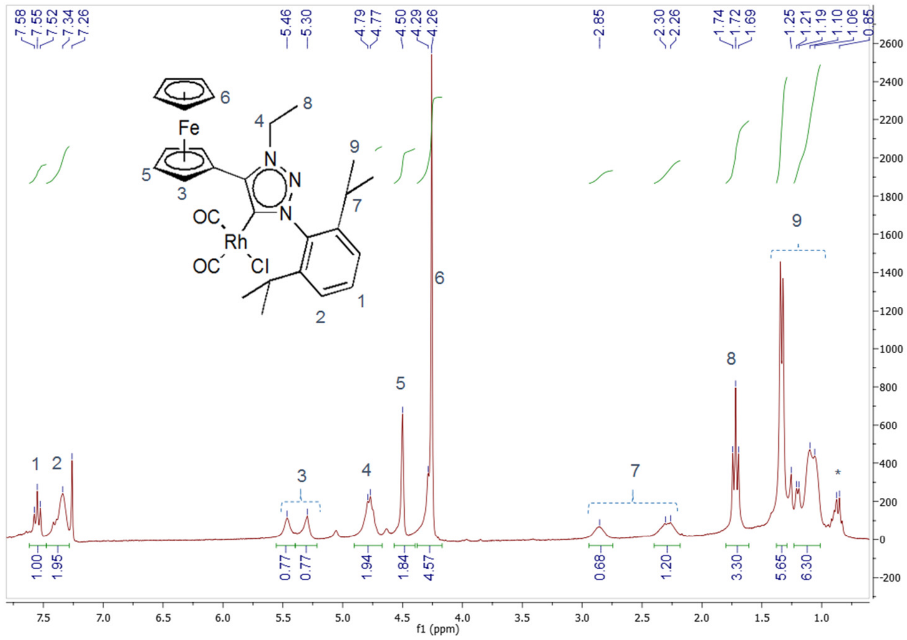


*Figure S20. The ^{1}H NMR spectrum of **5** in solvent $CDCl_3$.*

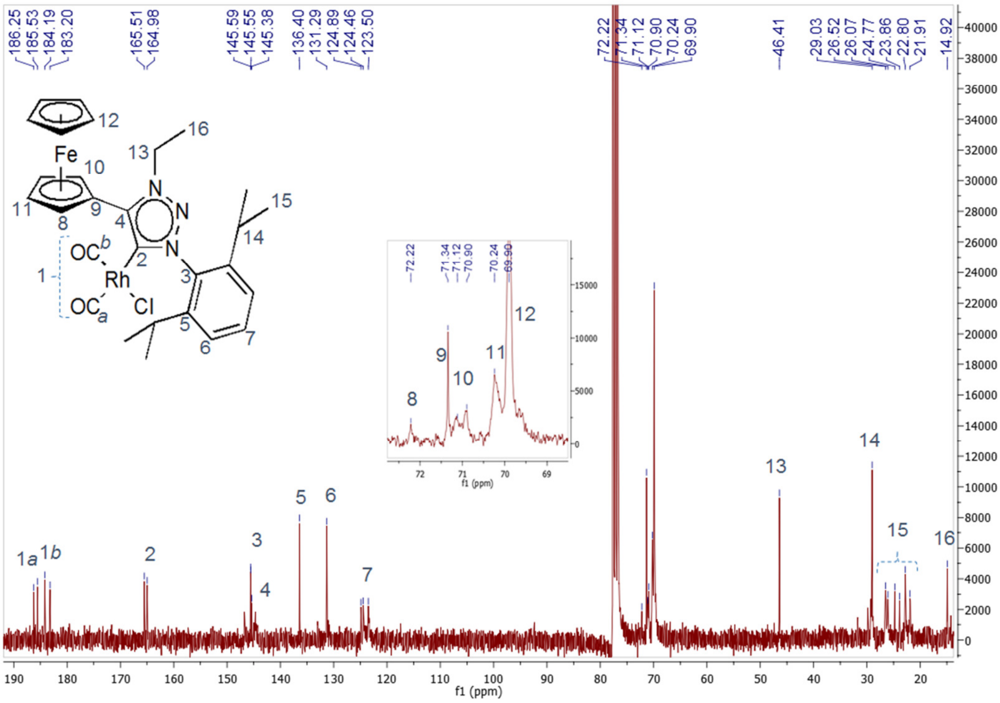


*Figure S21. The $^{13}C\{^{1}H\}$ NMR spectrum of **5** in solvent $CDCl_3$.*

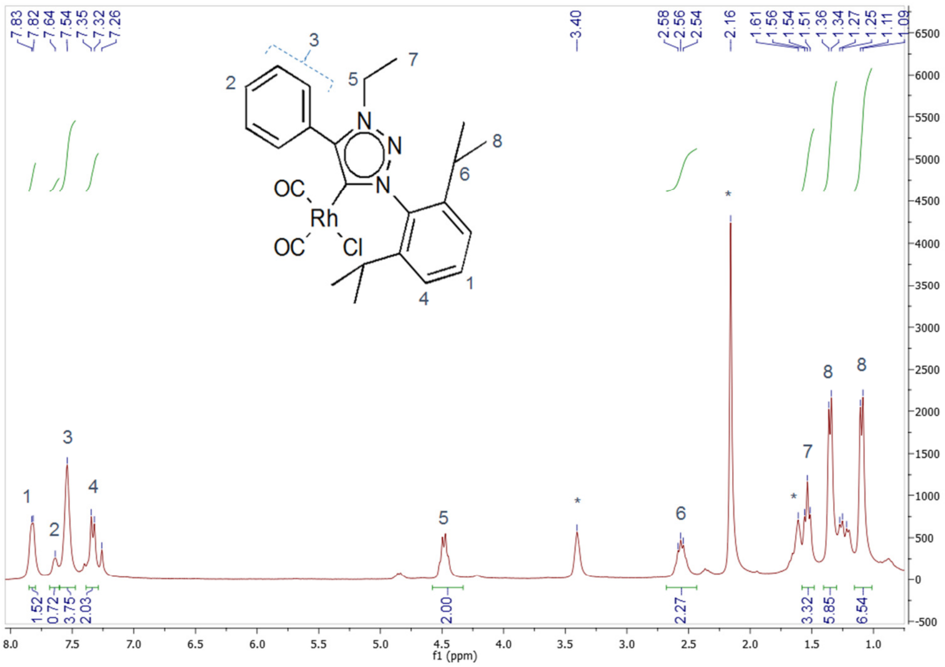


*Figure S22. The ^{1}H NMR spectrum of **6** in solvent $CDCl_3$.*

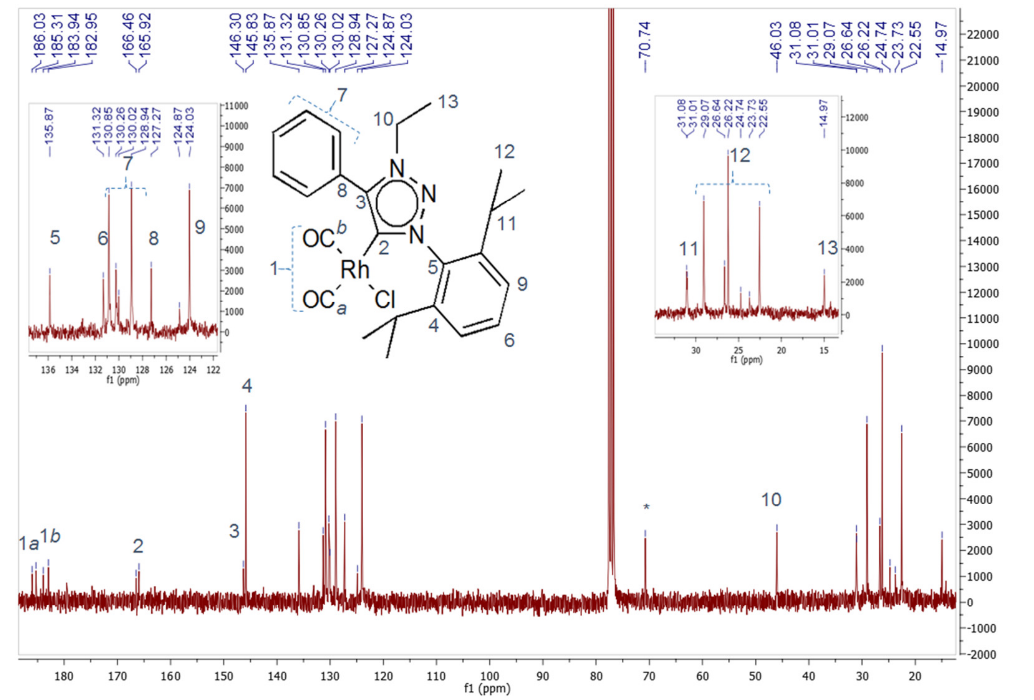


*Figure S23. The $^{13}C\{^{1}H\}$ NMR spectrum of **6** in solvent $CDCl_3$.*

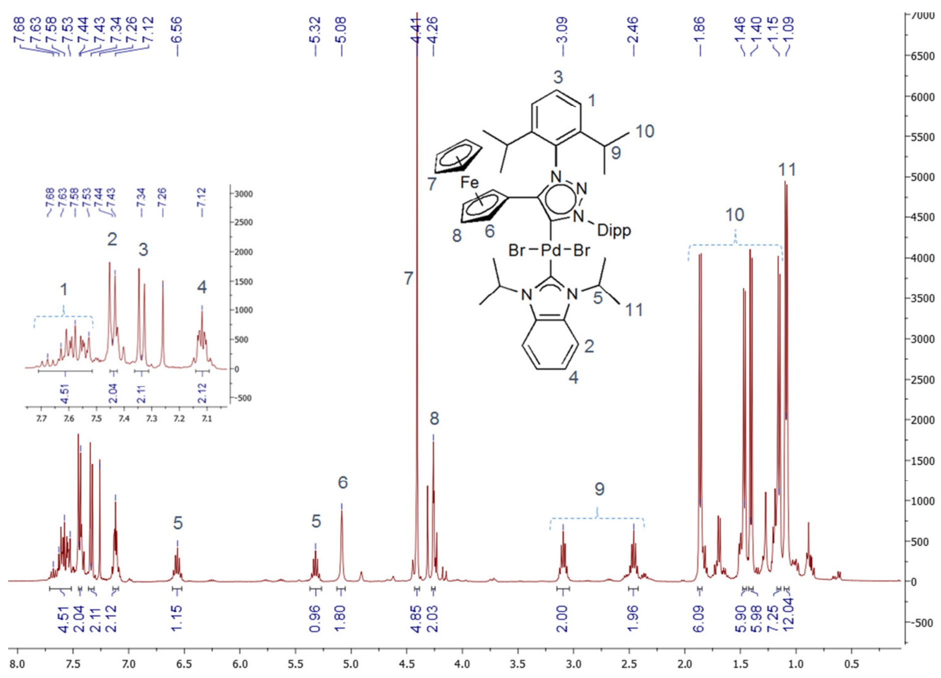


*Figure S24. The ^{1}H NMR spectrum of **7** in solvent $CDCl_3$.*

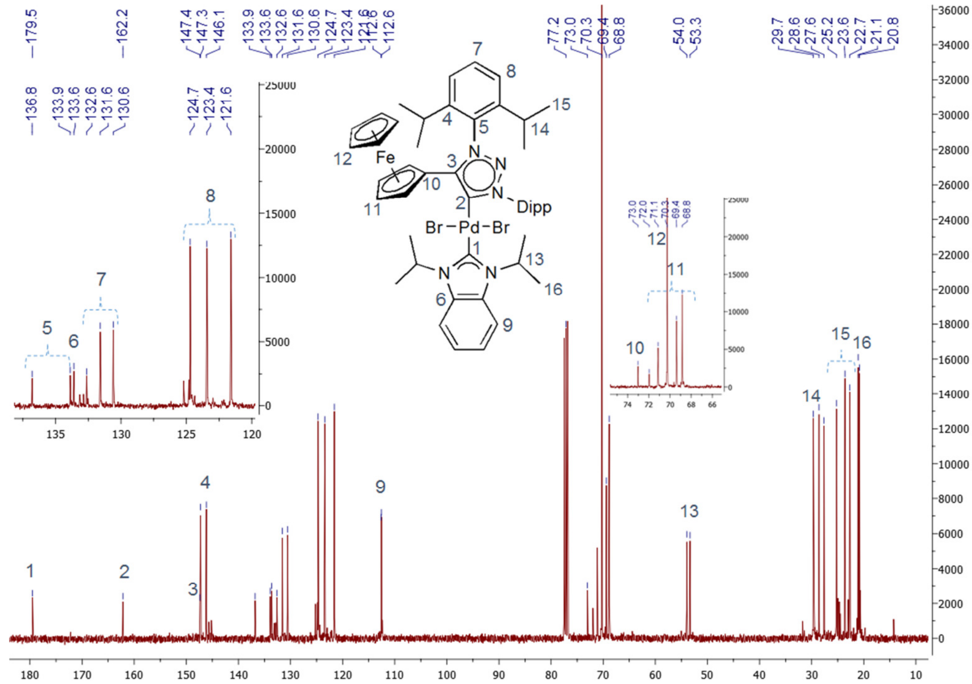


Figure S25. The ^{13}C {^{1}H} NMR spectrum of complex **7** in solvent $CDCl_3$.

V. ^{19}F NMR spectrum of A_{ox}

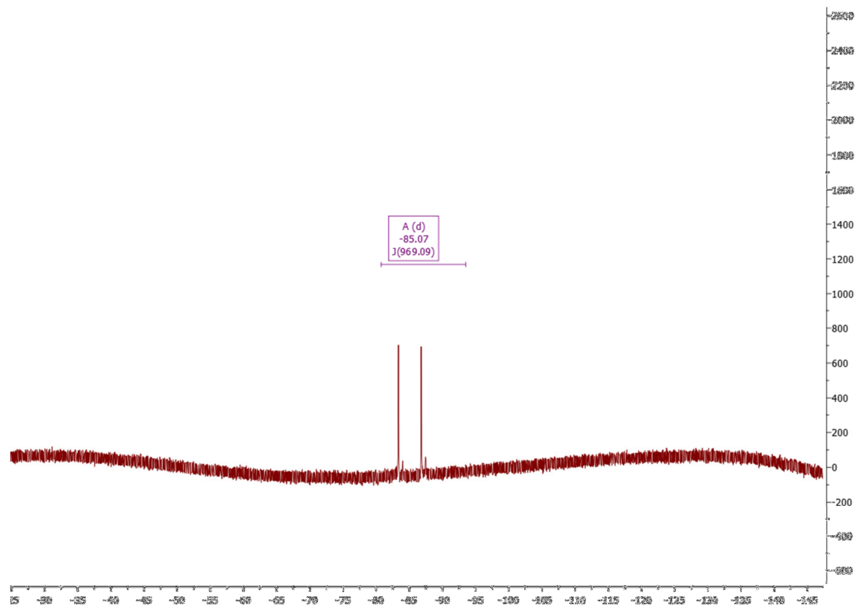


Figure S26. The ^{19}F NMR spectrum of $\boldsymbol{A_{ox}}$ in solvent CD_2Cl_2.

VI. Cyclic voltammograms of A, 1 and 4

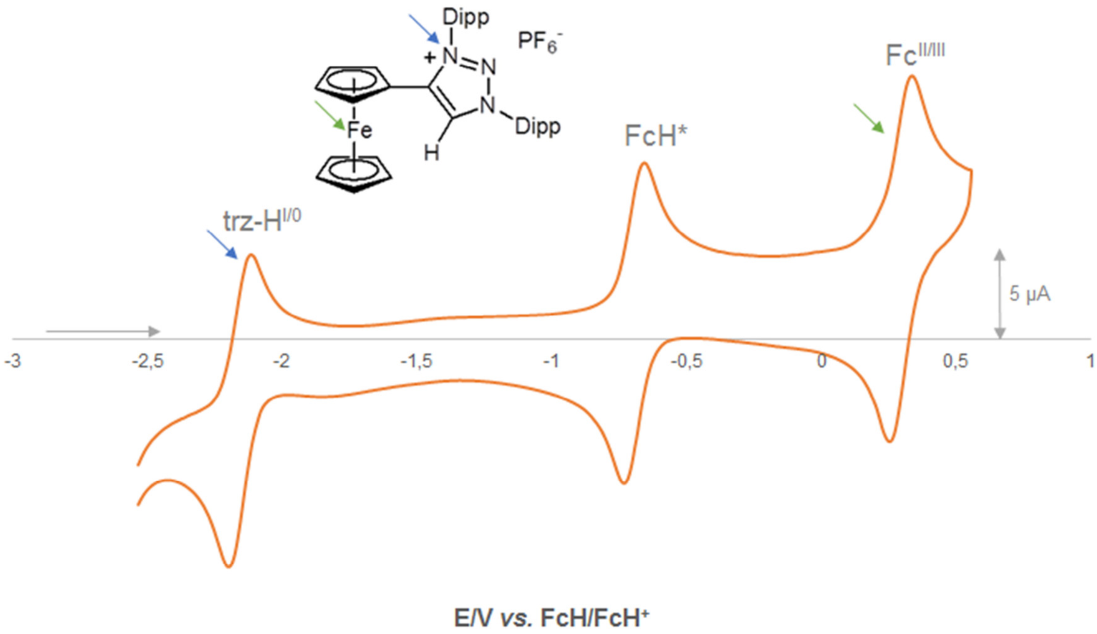


*Figure S27. The CV obtained of **A** at a glassy carbon electrode at a scan rate of 0.1 V. s^{-1} in CH_2Cl_2, with decamethylferrocene (FcH*) as internal standard.*

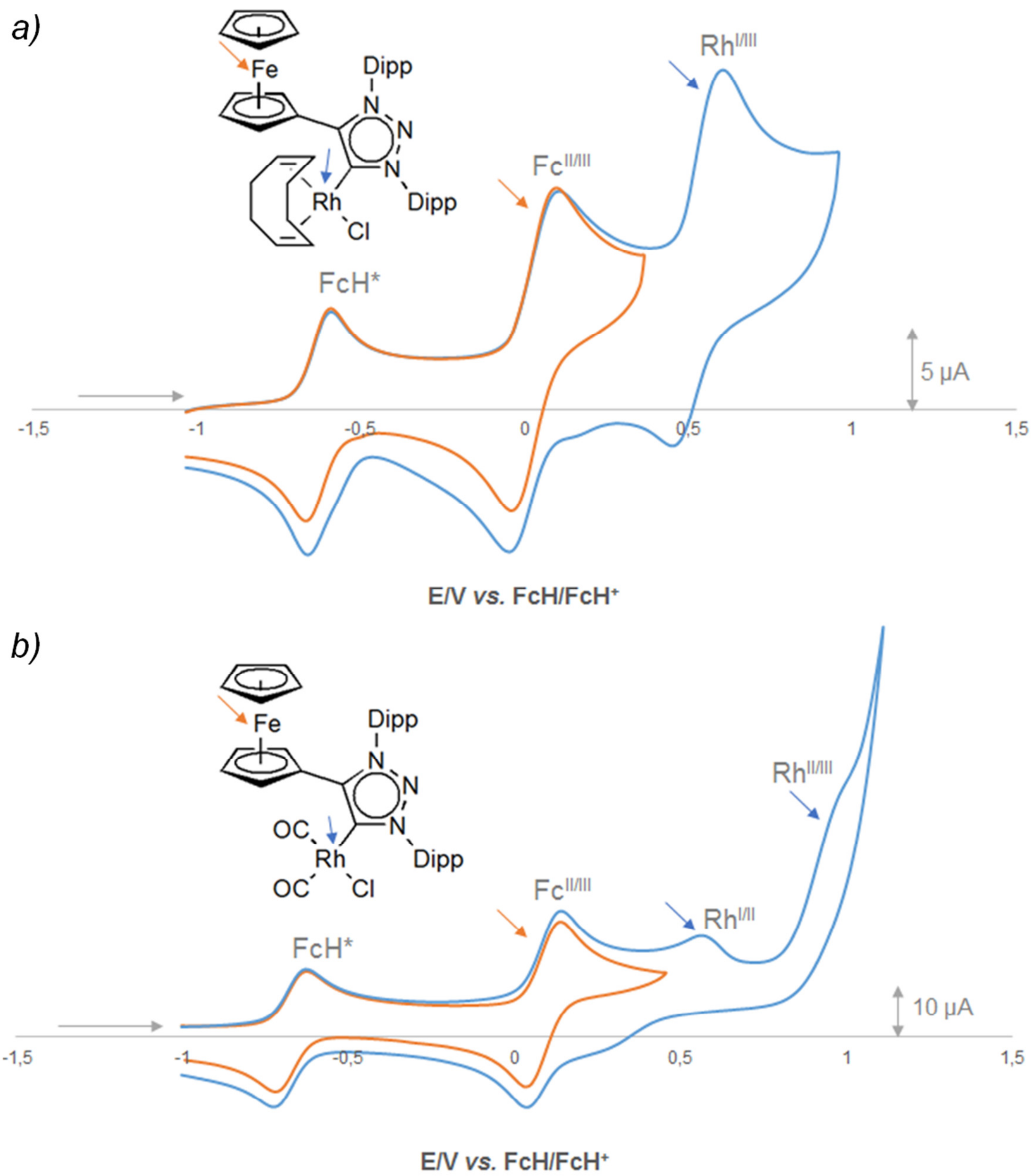


*Figure S28. The CVs obtained for (a) **1** and (b) **4** at a glassy carbon electrode at a scan rate of 0.1 V. s^{-1} in CH_2Cl_2, with decamethylferrocene (FcH*) as internal standard. In both cases, the redox event of the ferrocenyl moiety (after curtailing the scan at 0.5 V), is overlaid in orange.*

VII. IR data of 4 and 4_{ox}

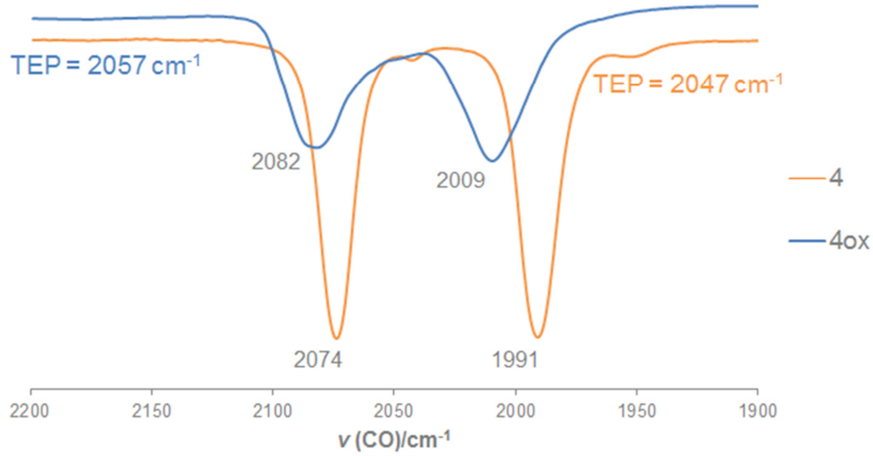


*Figure S29. The carbonyl stretching frequencies obtained from IR measurements in solvent DCM of the complexes **4** and $\mathbf{4}_{ox}$. The calculated TEP values in cm^{-1}, calculated as TEP (cm^{-1}) [Rh to Ni] = $0.8001\nu_{CO}^{av/Rh}$ + 420.0 (cm^{-1}),[4] are indicated.*

VIII. Optimization of hydroformylation catalytic reaction conditions for 1

*Table S1. Optimization results[a] of the hydroformylation of 1-octene with catalyst precursor **1**.*

Entry	Reaction conditions	% con-version	% Alde-hydes	% Iso-octene	% Non-anal	% Branched	TOF[b]	TON[c]	n/*iso*
Variation of syngas pressure and time. Temperature = 75 °C; [1]: 1-octene = 1:2500 (0.04 mol %)									
1	40 bar/ 4 hours	69.78 (6.48)	69.76 (4.42)	30.24 (4.42)	69.57 (0.44)	30.43 (0.44)	304.82 (42.40)	1219.30 (169.62)	2.29 (0.05)
2	40 bar/ 6 hours	85.12 (7.19)	67.48 (9.42)	32.52 (9.42)	68.61 (2.32)	31.39 (2.32)	237.57 (17.72)	1425.41 (106.32)	2.20 (0.24)
3	40 bar/ 8 hours	80.76 (8.59)	58.98 (7.91)	41.02 (7.91)	70.26 (2.64)	29.74 (2.64)	148.36 (21.23)	1186.86 (169.80)	2.38 (0.29)
4	50 bar/ 8 hours	85.93 (15.05)	71.15 (8.33)	28.85 (8.33)	65.88 (0.71)	34.12 (0.71)	188.57 (16.50)	1508.59 (132.04)	1.93 (0.06)
Variation of temperature. Syngas pressure = 40 bar; time = 8 hr; [1]: 1-octene = 1:1250 (0.08 mol %)									
5	55 °C	56.23 (20.33)	82.38 (16.12)	17.62 (16.12)	59.27 (1.28)	40.73 (1.28)	69.77 (19.74)	558.18 (157.96)	1.46 (0.08)
6	75 °C	95.83 (2.40)	66.57 (3.39)	33.43 (3.39)	70.59 (3.21)	29.41 (3.21)	99.73 (7.07)	797.85 (56.57)	2.43 (0.36)
7	95 °C	98.80 (0.40)	69.36 (3.56)	30.64 (3.56)	62.00 (1.76)	38.00 (1.76)	107.06 (5.17)	856.50 (41.39)	1.64 (0.12)
Variation of syngas pressure. Temperature = 75°C; time = 8 hr; [1]: 1-octene = 1:1250 (0.08 mol %)									
8	30 bar	74.77 (18.84)	65.35 (3.09)	34.65 (3.09)	69.82 (0.70)	30.18 (0.70)	75.77 (15.79)	606.17 (126.32)	2.31 (0.08)
9	50 bar	85.79 (7.56)	77.99 (4.10)	22.01 (4.10)	63.58 (2.81)	36.42 (2.81)	104.78 (13.61)	838.26 (108.88)	1.76 (0.21)

[a]Reactions carried out in triplicate, average of three runs given with standard deviation in parentheses.

[b]Turnover frequency, calculated as TOF = mol aldehydes/mol cat.h^{-1}

[c]Turnover number, calculated as TON = mol aldehydes/mol cat.

IX. References

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