

Supporting Information

A Hemilabile and Cooperative N-Donor-Functionalized 1,2,3-Triazol-5-Ylidene Ligand for Alkyne Hydrothiolation Reactions

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I. General considerations

Standard Operating Procedure

All synthetic manipulations, unless otherwise stated, were performed under an N₂ gas or Ar gas atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids were stored and handled in a PureLab HE glove box. Preparation of NMR and crystallization samples that also require an inert atmosphere were done in the glove box.

Materials

Reagent ^tBuOCl was prepared according to the method of Mintz and Walling.ⁱ The precursor compound 1,3-bis-(2,6-di-*iso*-propylphenyl)triaz-1-ene was prepared as previously reported by us.ⁱⁱ All other reagents were obtained from commercial sources and were used without any further purification.

Unless otherwise stated, only anhydrous solvents were used during experimental procedures. Anhydrous THF and Et₂O were obtained after distillation over sodium and benzophenone under a N₂ gas atmosphere. Anhydrous PhMe and hexane were obtained after distillation over sodium under a N₂ gas atmosphere. Anhydrous CH₂Cl₂ was obtained after distillation over calcium hydride under a N₂ gas atmosphere. Deuterated benzene was dried over sodium and distilled under an Ar gas atmosphere.

Characterisation Techniques

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AVANCE-III-300 operating at 300.13 MHz for ¹H, 75.47 MHz for ¹³C, 121.49 MHz for ³¹P and 282.40 MHz for ¹⁹F; or AVANCE-III-400 operating at 400.21 MHz for ¹H, 100.64 MHz for ¹³C, 162.01 MHz for ³¹P and 376.57 MHz for ¹⁹F. ¹H Chemical shifts are reported as δ (ppm) values downfield from Me₄Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD₂Cl₂, 5.32 ppm; CDCl₃, 7.26 ppm; C₆D₆, 7.16 ppm). ¹³C chemical shifts are also reported as δ (ppm) values downfield from Me₄Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD₂Cl₂, 54.0 ppm; CDCl₃, 77.16 ppm; C₆D₆, 128.06 ppm). Proton coupling constants (*J*) are given in Hz. The spectral coupling patterns are designated as follows: s/S - singlet; d/D - doublet; t/T - triplet; q/Q - quartet; sept-septet; m - multiplet; br - broad signal.

Chemical shift assignment in the ¹H NMR spectra is based on first-order analysis and when required were confirmed by two-dimensional (2D) (¹H-¹H) 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 - ^1H) heteronuclear single-quantum coherence (HSQC) experiments. Standard Bruker pulse programs were used in the experiments.

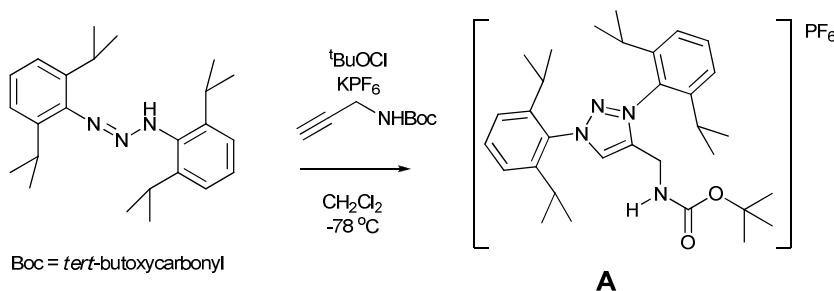
Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2 at 150 K. Structures were solved and refined using Olex2 and SHELXTL. A satisfactory refinement of the crystal structure of ligand salt **C** was only obtained after squeeze methodology was applied in order to eliminate residual electronic density of the solvent, which could not be refined otherwise^{iii-v}

Solution IR spectra ($\nu(\text{CO})$ and $\nu(\text{NH})$) 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 $4000\text{-}600 \text{ cm}^{-1}$.

Mass spectral analyses were performed on a Waters Synapt G2 HDMS by direct infusion at $5 \mu\text{L}/\text{min}$ with positive electron spray as the ionization technique. The m/z values were measured in the range of $400\text{-}1500$ with acetonitrile (dichloromethane for complexes **5** and **6**) as solvent. Prior to analysis, a 5 mM sodium formate solution was used to calibrate the instrument in resolution mode.

II. Synthesis and characterization of ligand precursors A – C

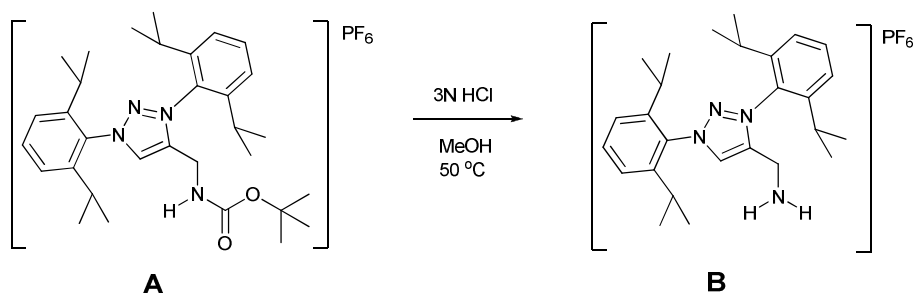
Synthesis of 4-(((tert-butoxycarbonyl)amino)methyl)-1,3-bis(2,6-diisopropylphenyl)-1,2,3-triazol-3-ium hexafluorophosphate (**A**)



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

N-Boc-propargylamine (5.00 g, 38.7 mmol), 1.3 eq. 1,3-bis-(2,6-di-*iso*-propylphenyl)triaz-1-eneⁱⁱ (15.1 g, 50.3 mmol), and 1.5 eq KPF₆ (10.7 g, 58.07 mmol) were dissolved in CH₂Cl₂ and cooled to -78 °C. *t*BuOCl (24 mmol, 2.73 mL) was added dropwise and the solution stirred overnight while slowly allowing to warm to room temperature. The resulting brown solution was frit filtered and subsequent solvent removal yields a light brown powder. Washing with 3 x 150 mL portions of hexane followed 2 x 150 mL portions of ether and ultimately trituration with acetone and ether yielded a white powder. Yield: 19.56 g, 76 %. HRMS (*m/z*): [M-PF₆]⁺ calculated: 519.3699; observed: 519.3610. FTIR (CH₂Cl₂, cm⁻¹): 1715 (ν_{CO}), 3442 (ν_{NH}). ¹H NMR (300MHz, CD₂Cl₂): δ 8.49 (br, 1H, H₅), 7.72, 7.69 (dd, 1H, *J* = 7.96 Hz, 7.86 Hz, H₉), 7.48, 7.44 (d, 2H, *J* = 7.87 Hz, 7.82 Hz, H_{8,10}), 5.73 (br, 1H, H_N) 4.32 (d, 2H, *J* = 5.9 Hz, H₁₆), 2.30 (m, 4H, H_{12,14}), 1.38 (s, 9H, H₁₉), 1.38, 1.29, 1.19, 1.14 (d, 24H, *J* = 6.43 Hz, 6.75 Hz, 6.83 Hz, 6.84 Hz, H_{13,15}). ¹³C NMR (75 MHz, CD₂Cl₂): δ 156.1 (C₁₇), 147.3 (C₄), 146.3, 145.9 (C_{7,11}), 134.1, 133.9 (C₉), 132.9 (C₅), 131.1, 128.6 (C₆), 125.9, 125.5 (C_{8,10}), 81.2 (C₁₈), 35.8 (C₁₆), 29.9, 29.7, 28.4 (C₁₉), 25.9, 24.9, 24.0, 22.9 (C_{13,15}). ³¹P NMR (121 MHz, CD₂Cl₂): δ -144.54 (sept, *J* = 711.2 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂) δ -72.95 (d, *J* = 711.2 Hz).

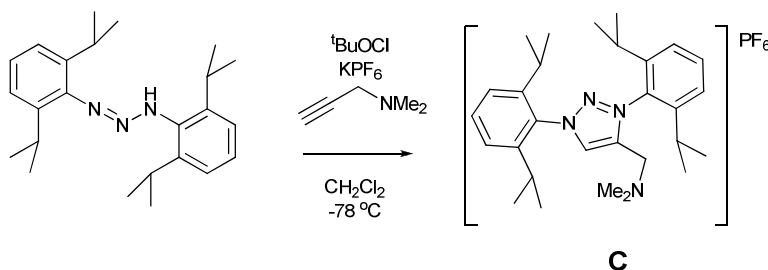
Synthesis of 4-((amino)methyl)-1,3-bis(2,6-diisopropylphenyl)-1,2,3-triazol-3-ium hexafluorophosphate (**B**)



Scheme S2. Synthesis of triazolium salt **B**

Compound **A** (8.0 g, 12.0 mmol) was treated with 50 mL, 3N HCl (methanolic) and stirred for 3 days at 50 °C. The solution was neutralised with saturated NaHCO₃ (aq) and the pH adjusted to pH 9 with KOH (aq). Repeated partitioning between CH₂Cl₂ and H₂O provides a yellow organic phase which is dried over MgSO₄ (s). Counterion exchange with 2 eq. (0.13 g, 24 mmol) KPF₆ in CH₂Cl₂ yields the white residue after frit filtration and solvent removal. The residue is washed with one 50 mL portion ether to yield a white powder (**2**). Yield: 6.0 g, 10.6 mmol, 88 %. HRMS (m/z): [M-PF₆]⁺ calculated: 419.3175; observed: 419.3138. FTIR (CH₂Cl₂, cm⁻¹): 3281, 3323 (ν_{NH}). ¹H NMR (300 MHz, CD₂Cl₂): δ 8.64 (s, 1H, H₅) 7.73, 7.70 (dd, 1H, *J* = 7.86 Hz, 7.88 Hz, H₉), 7.48, 7.45 (d, 2H, *J* = 7.87 Hz, 7.89 Hz, H_{8,10}), 3.94 (s, 2H) 2.29 (sept, 2H, *J* = 6.63 Hz, H_{12, 14}), 2.19 (sept, 2H, *J* = 6.81 Hz, H_{12,14}), 1.75 (br, 2H, NH), 1.34, 1.32, 1.19, 1.15 (d, 24H, *J* = 4.61 Hz, 4.62 Hz, 6.83 Hz, 6.86 Hz, H_{13,15}). ¹³C NMR (75 MHz, CD₂Cl₂): δ 146.0, 145.9 (C_{7,11}), 134.1, 133.8 (C₉), 132.6 (C₅), 131.1, 128.8 (C₆), 125.9, 125.5 (C_{8,10}), 36.6 (C₁₆), 30.0, 29.8 (C_{12,14}), 25.7, 25.1, 23.9, 23.2 (C_{13,15}). ³¹P NMR (121 MHz, CD₂Cl₂): δ -144.5 ppm (sept, *J* = 711.1 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -72.9 ppm (d, *J* = 711.2 Hz).

Synthesis of 1,3-bis(2,6-diisopropylphenyl)-4-((dimethylamino)methyl)-1,2,3-triazol-3-ium hexafluorophosphate (**C**)



Scheme S3. Synthesis of triazolium salt **C**

N-dimethylaminopropyne (3 mL, 27.9 mmol), 1.3 eq. 1,3-bis-(2,6-di-*iso*-propylphenyl)triaz-1-eneⁱⁱ (13.2 g, 36.2 mmol), and 1.5 eq KPF₆ (15.4 g, 41.8 mmol) were mixed in CH₂Cl₂ and cooled to -78 °C. 1.3 eq ^tBuOCl (2.73 mL, 36.2) was added dropwise in the dark and the solution stirred overnight while slowly allowing to room temperature. The resulting brown solution was frit filtered and subsequent solvent removal yielded a light brown powder. Washing with 3 x 150 mL portions of hexane followed by 2 x 150 mL portions of ether and ultimately trituration with acetone and ether yields a white powder (**C**). Yield: 13.0 g, 79%. HRMS (*m/z*): [M-PF₆]⁺ calculated: 447.3487; observed: 447.3475. ¹H NMR (300 MHz, CD₂Cl₂): δ 8.70 (s, 1H, H₅), 7.72 (td, 2H, *J*_{meta} = 3.67 Hz, *J*_{ortho} = 7.86 Hz, H₉), 7.48, 7.46 (d, 2H, *J* = 7.87 Hz, 7.88 Hz, H_{8,10}), 3.55 (s, 2H, H₁₆), 2.20 (m, (6H + 4H), H₁₇ + H_{12,14}), 1.33, 1.31, 1.21, 1.14 (d, 24H, *J* = 6.72, 6.78, 6.84, 6.86, H_{13,15}). ¹³C NMR (75 MHz, CD₂Cl₂): δ 146.0, 145.7 (C_{7,11}), 134.1, 133.9 (C₉), 133.5 (C₅), 130.9, 128.7 (C₆), 125.7, 125.6 (C_{8,10}), 51.5 (C₁₆), 45.4 (C₁₇), 30.3, 29.9 (C_{12,14}), 25.9, 24.7, 24.0, 22.7 (C_{13,15}). ³¹P NMR (121 MHz, CD₂Cl₂): δ -144.4 (sept, *J* = 711.1 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂) δ -72.6 (d, *J* = 711.2 Hz).

Single crystal X-ray structures of compounds **A** – **C**

Single crystals suitable for X-ray diffraction were obtained by crystallization of the triazolium precursor ligands via slow evaporation of a dichloromethane solution.

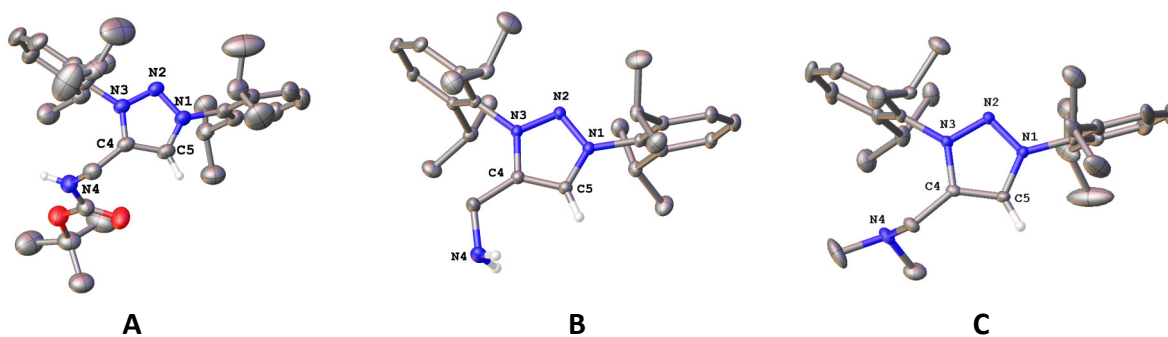


Figure S1. The solid-state structures of the three triazolium salts **A**, **B** and **C** with 50% probability ellipsoids. PF₆⁻ counterions and hydrogens (except for triazolium CH and NH functional groups) are omitted for clarity.

Crystal data for compound A

Crystal Data for $C_{32}H_{47}F_6N_4O_2P$ ($M=664.70$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 11.4306(8)$ Å, $b = 12.5316(8)$ Å, $c = 25.6776(19)$ Å, $\beta = 98.073(4)^\circ$, $V = 3641.7(4)$ Å³, $Z = 4$, $T = 296.15$ K, $\mu(\text{CuK}\alpha) = 1.217$ mm⁻¹, $D_{\text{calc}} = 1.212$ g/cm³, 82966 reflections measured ($6.954^\circ \leq 2\theta \leq 137.682^\circ$), 6684 unique ($R_{\text{int}} = 0.0811$, $R_{\text{sigma}} = 0.0325$) which were used in all calculations. The final R_1 was 0.0871 ($I > 2\sigma(I)$) and wR_2 was 0.2968 (all data).

Crystal data for compound B

Crystal Data for $C_{28}H_{41}N_4F_6PCl_2$ ($M=649.52$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 12.3690(4)$ Å, $b = 10.8982(3)$ Å, $c = 24.2256(7)$ Å, $\beta = 99.7060(13)^\circ$, $V = 3218.86(17)$ Å³, $Z = 4$, $T = 150.15$ K, $\mu(\text{CuK}\alpha) = 2.806$ mm⁻¹, $D_{\text{calc}} = 1.340$ g/cm³, 52070 reflections measured ($7.404^\circ \leq 2\theta \leq 158.072^\circ$), 6915 unique ($R_{\text{int}} = 0.0777$, $R_{\text{sigma}} = 0.0421$) which were used in all calculations. The final R_1 was 0.0721 ($I > 2\sigma(I)$) and wR_2 was 0.2091 (all data).

Crystal data for compound C

Crystal Data for $C_{29}H_{42}F_6N_4P$ ($M=591.63$ g/mol): triclinic, space group $P-1$ (no. 2), $a = 11.9695(11)$ Å, $b = 12.7036(10)$ Å, $c = 13.9642(12)$ Å, $\alpha = 65.772(3)^\circ$, $\beta = 64.835(3)^\circ$, $\gamma = 62.931(3)^\circ$, $V = 1648.2(3)$ Å³, $Z = 2$, $T = 150.0$ K, $\mu(\text{MoK}\alpha) = 0.140$ mm⁻¹, $D_{\text{calc}} = 1.192$ g/cm³, 61310 reflections measured ($4.294^\circ \leq 2\theta \leq 52.946^\circ$), 6784 unique ($R_{\text{int}} = 0.058$, $R_{\text{sigma}} = 0.0300$) which were used in all calculations. The final R_1 was 0.0714 ($I > 2\sigma(I)$) and wR_2 was 0.1966 (all data).

III. NMR spectra and atom numbering schemes of A – C and 1 – 6

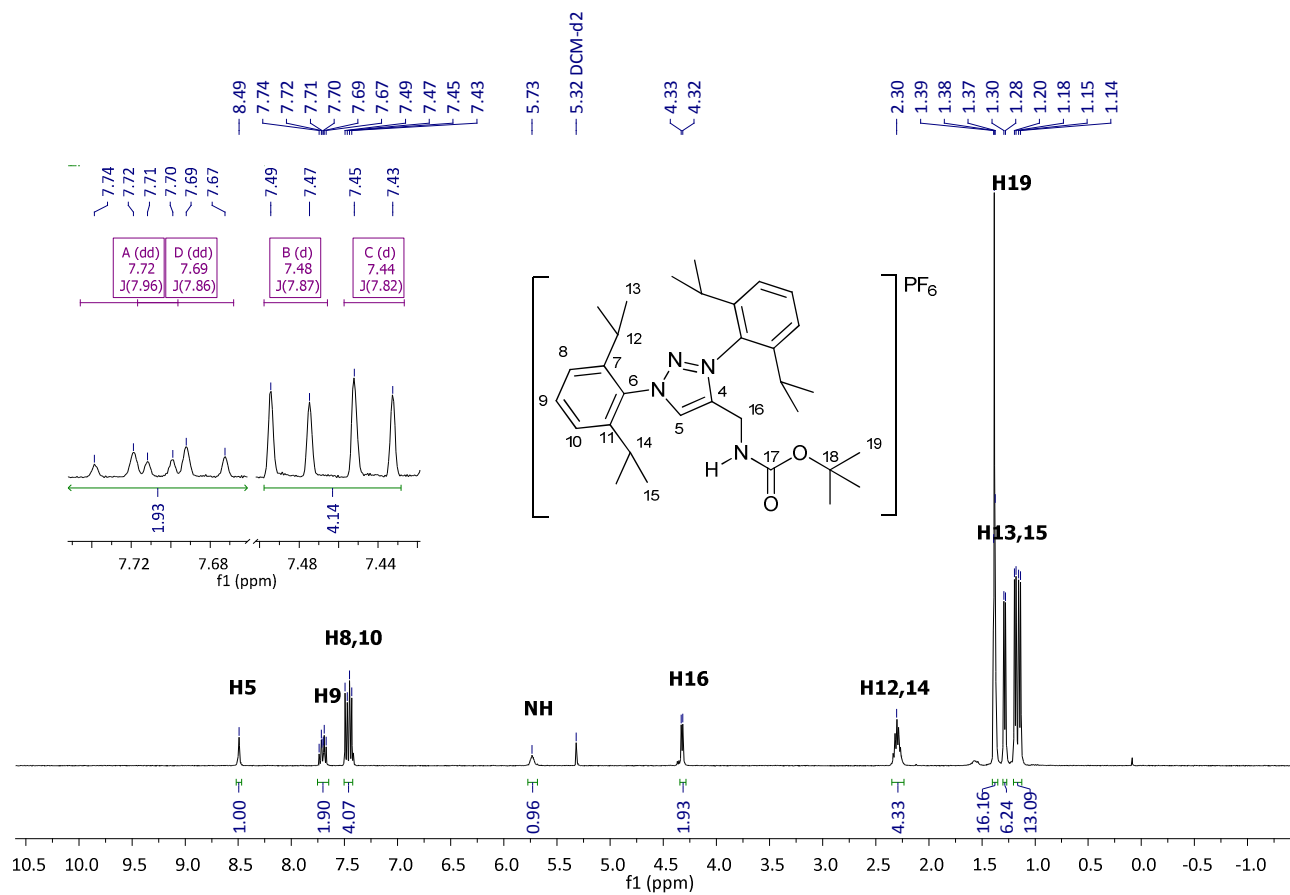


Figure S2. ¹H NMR spectrum of A in CD₂Cl₂

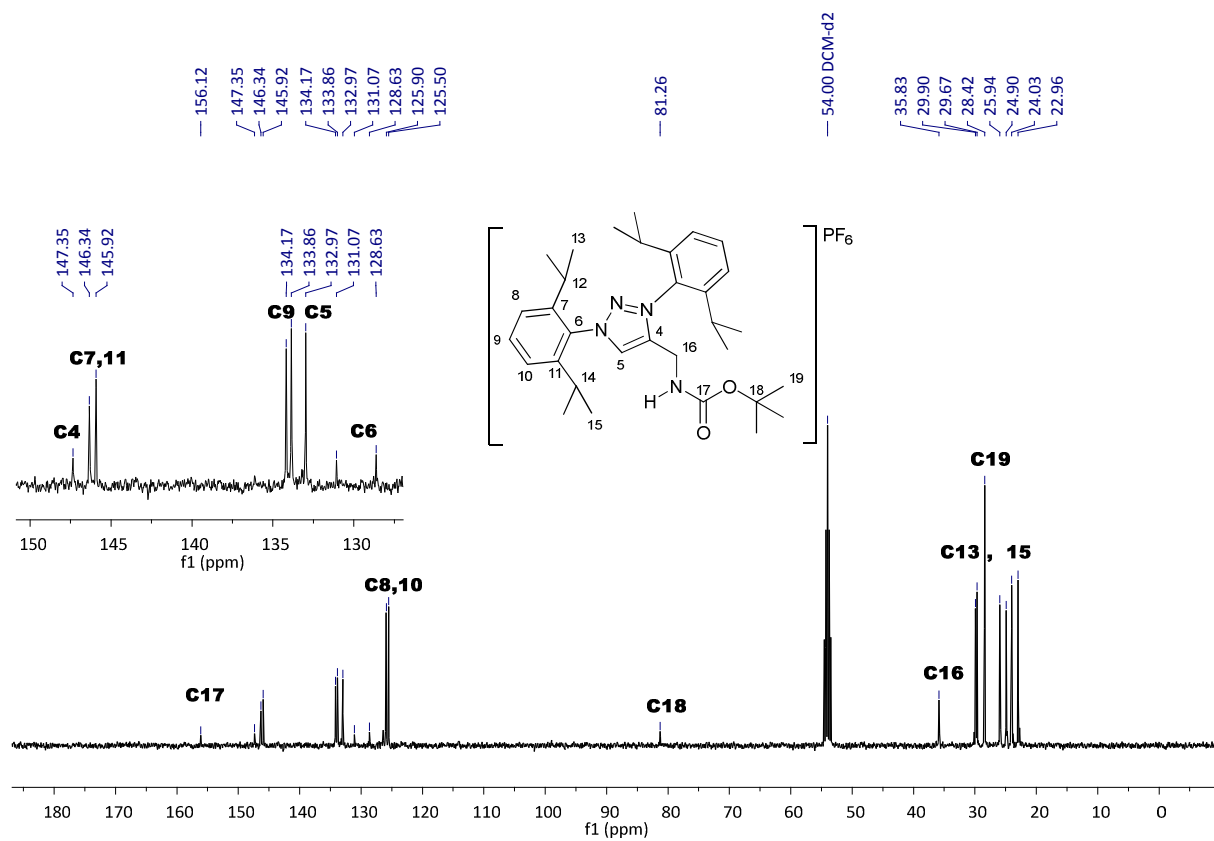


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **A** in CD_2Cl_2

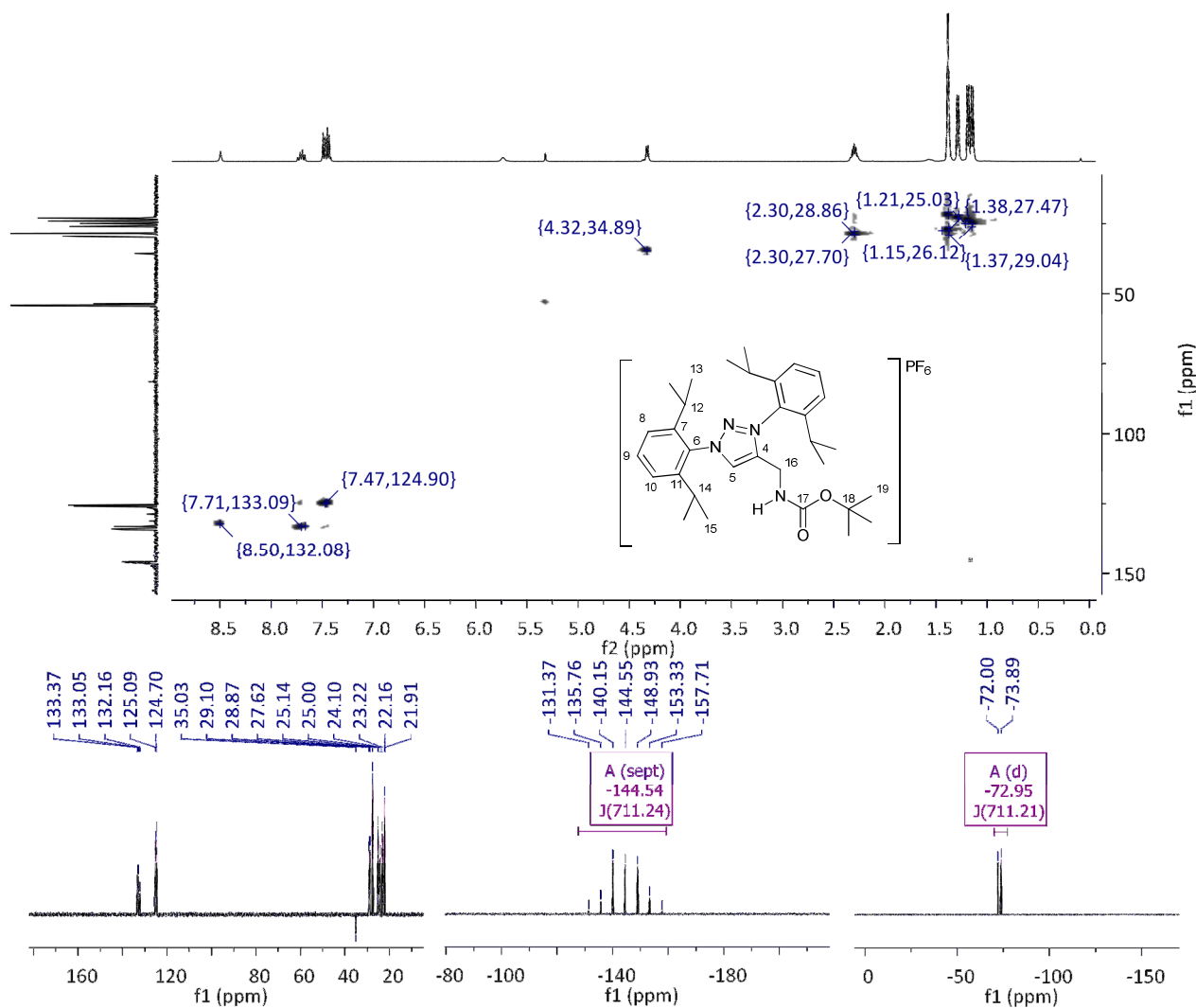


Figure S4. HSQC 2D spectrum (top), and the ^{13}C DEPT135 (bottom left), ^{31}P (bottom, centre) and ^{19}F (bottom, right) NMR spectra of **A** in CD_2Cl_2

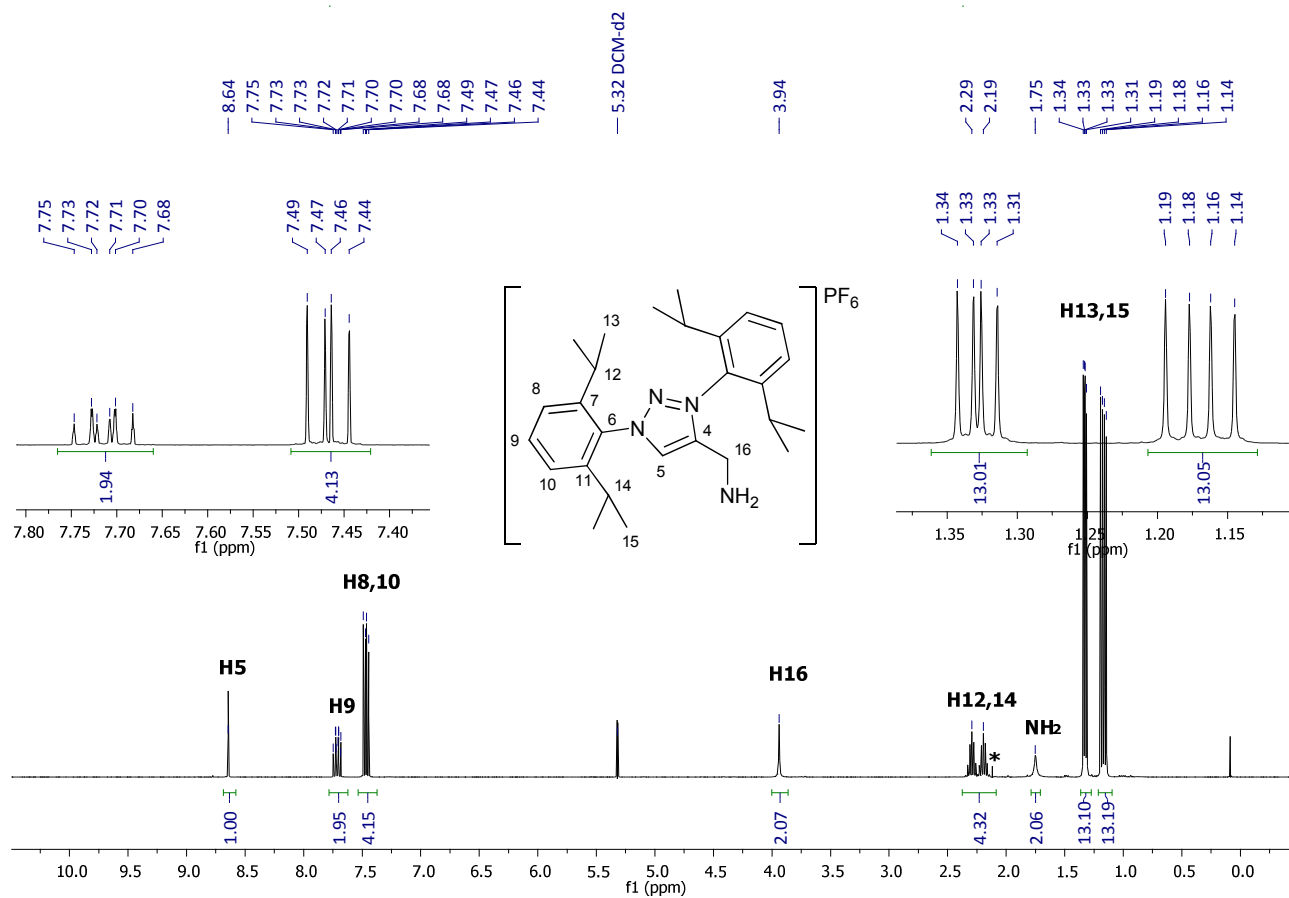


Figure S5. ^1H NMR spectrum of **B** in CD_2Cl_2

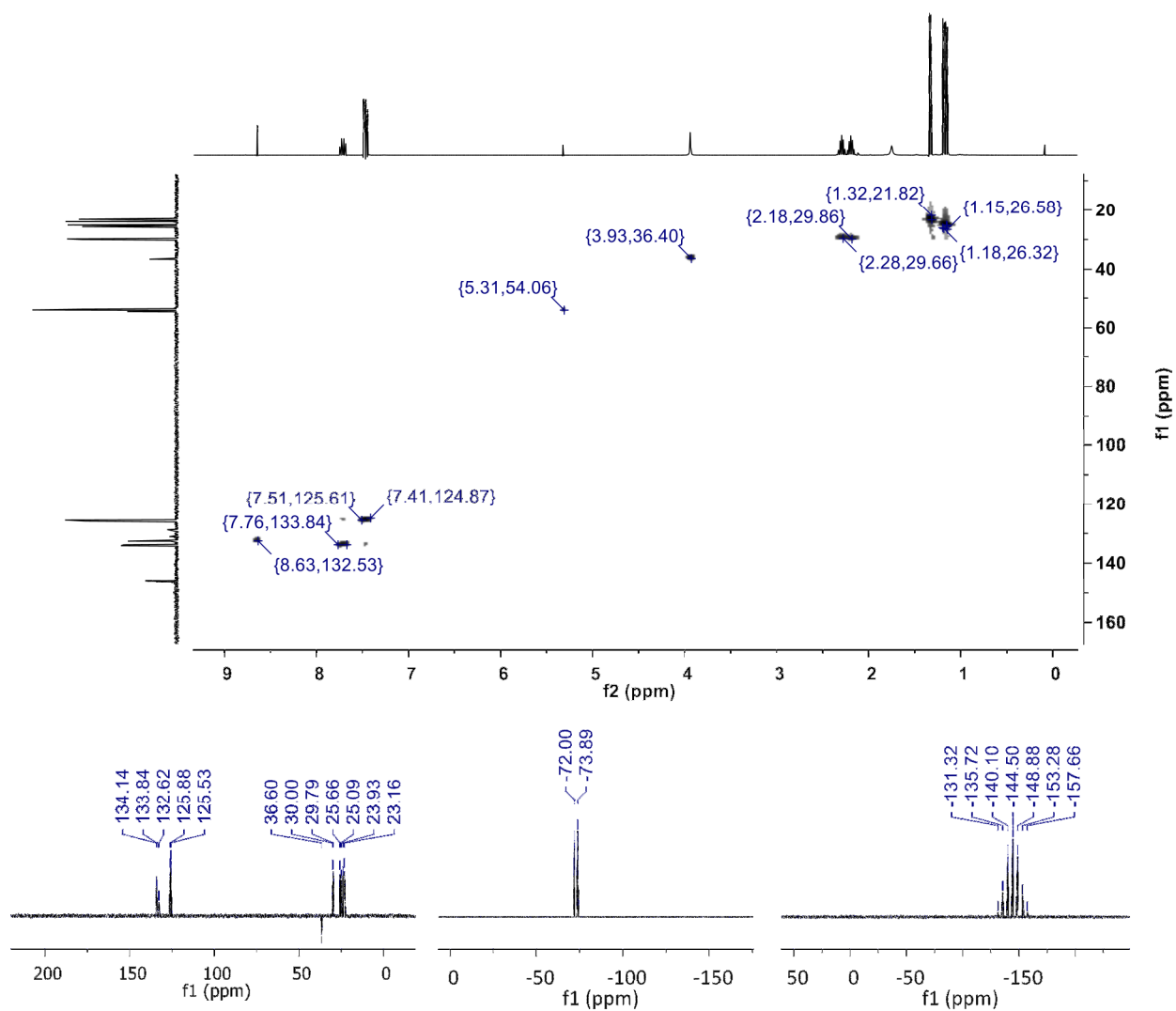


Figure S7. HSQC 2D spectrum (top), and the ^{13}C DEPT135 (bottom left), ^{19}F (bottom, centre) and ^{31}P (bottom, right) NMR spectra of **B** in CD_2Cl_2

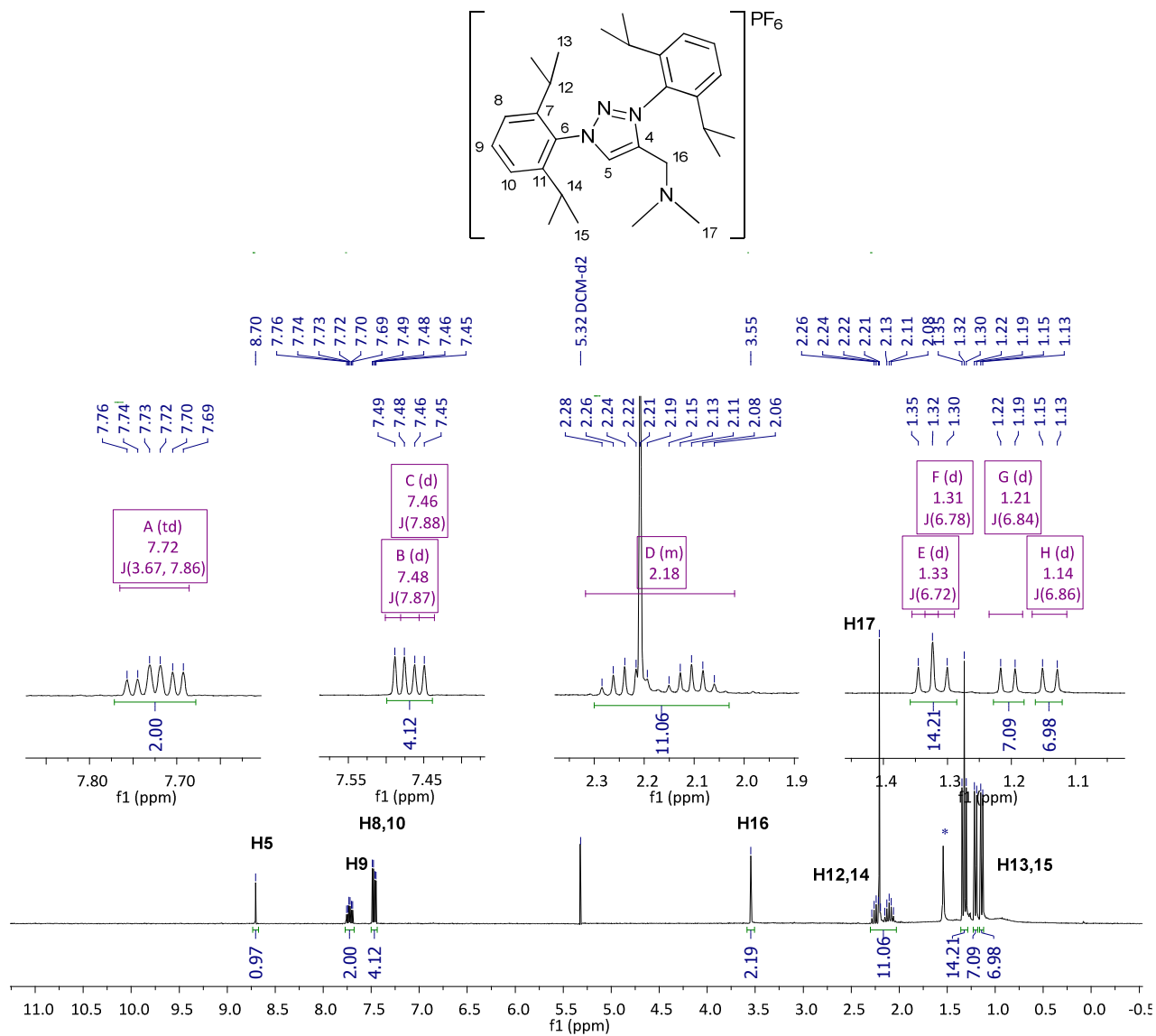


Figure S8. ^1H NMR spectrum of **C** in CD₂Cl₂

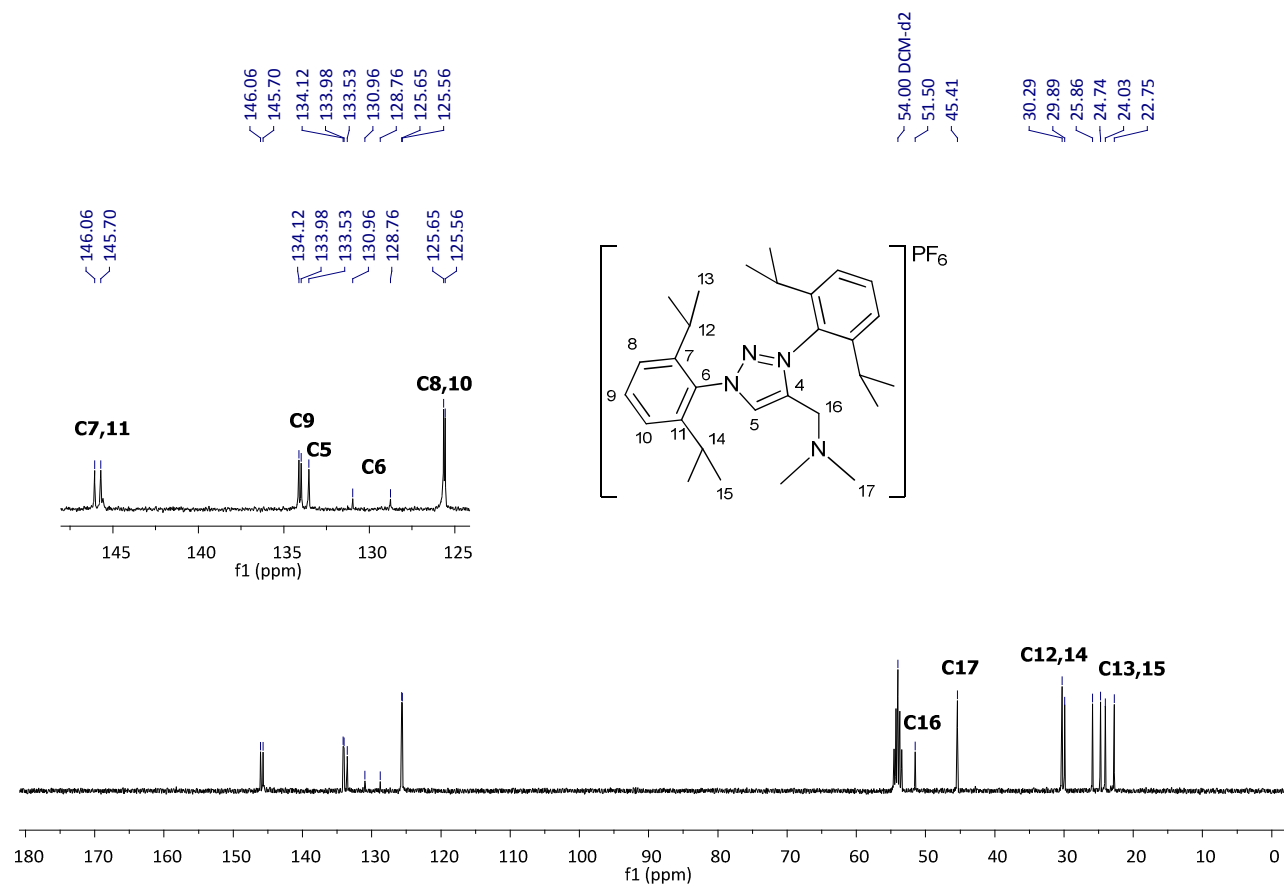


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **C** in CD_2Cl_2

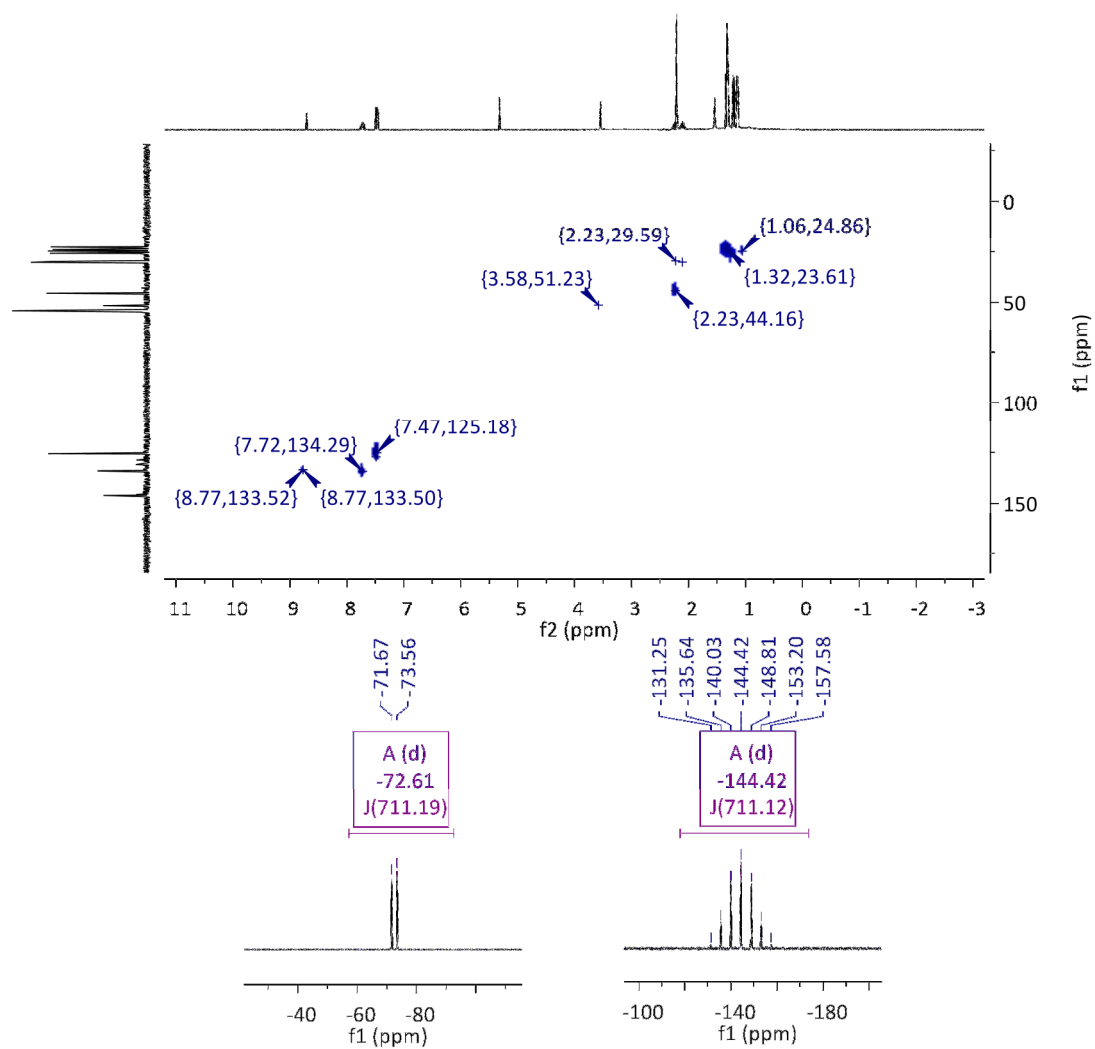


Figure S10. HSQC 2D spectrum (top), and ^{19}F (bottom, left) and ^{31}P (bottom, right) NMR spectra of **C** in CD_2Cl_2

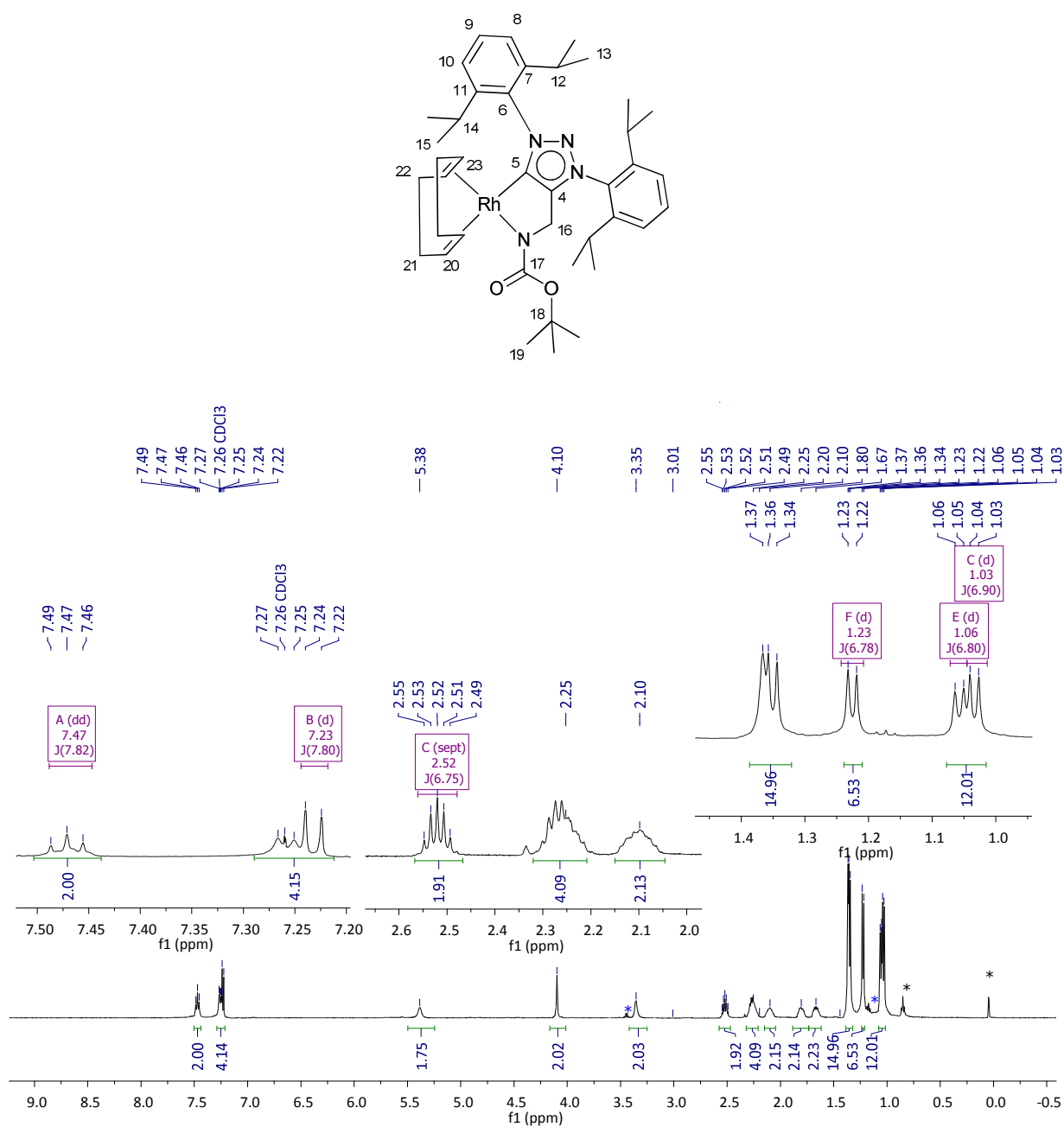


Figure S11. ^1H NMR spectrum of **1** in CDCl_3 . * annotates grease and diethyl ether.

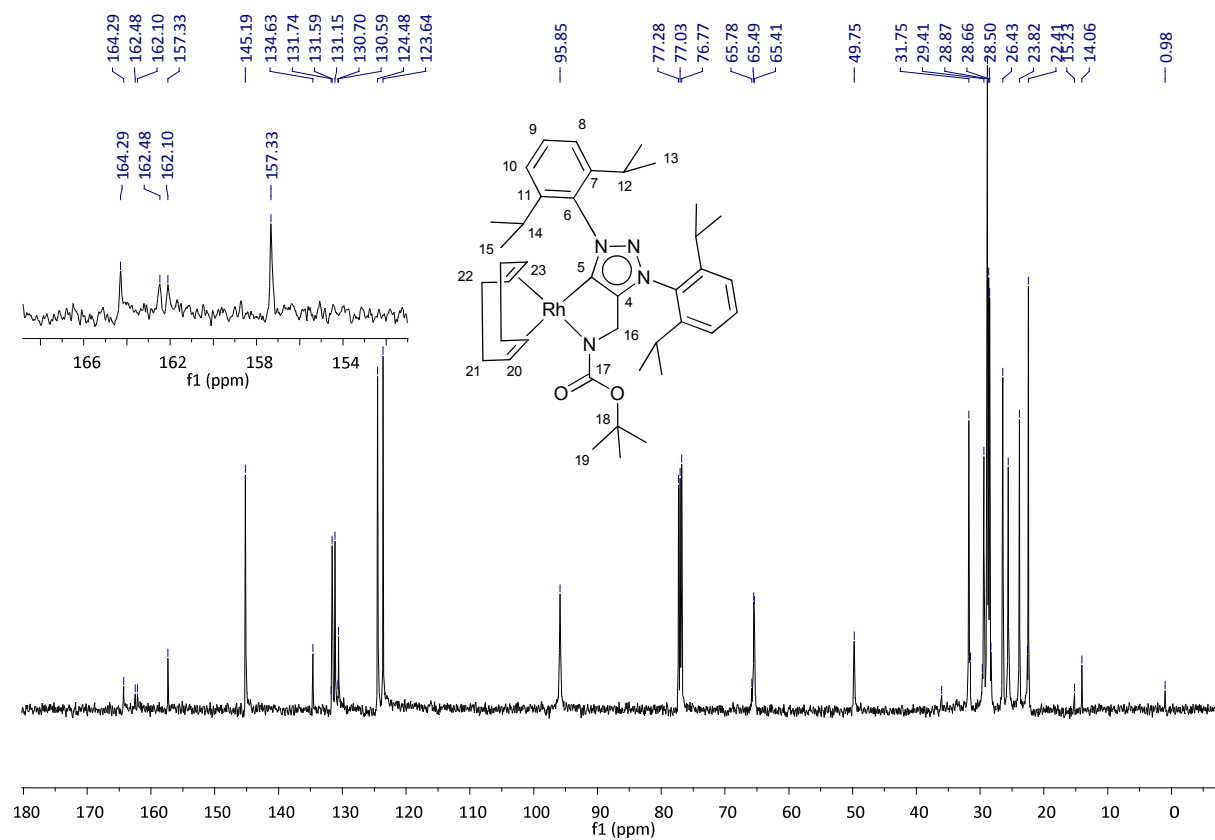


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 . * annotates grease and diethyl ether.

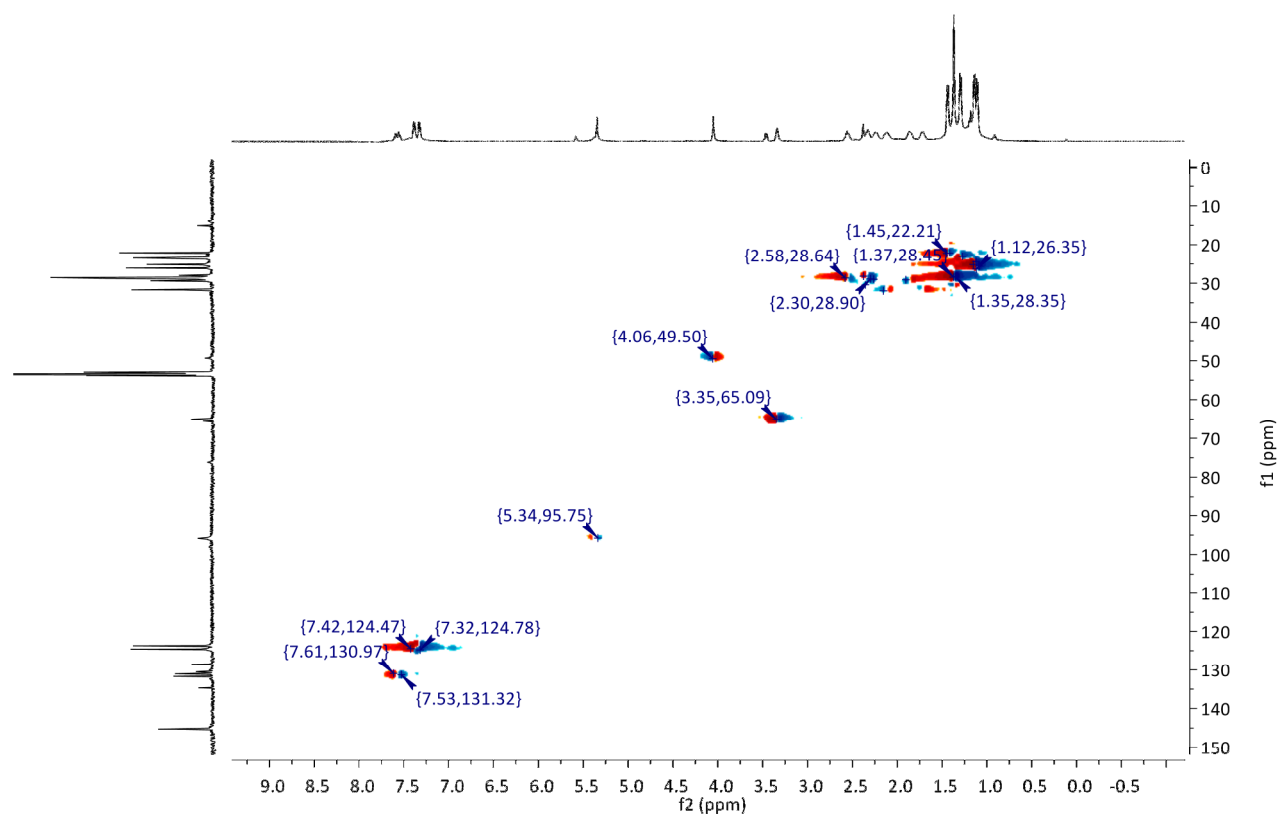


Figure S13. HSQC 2D NMR spectrum of **1** in CD_2Cl_2

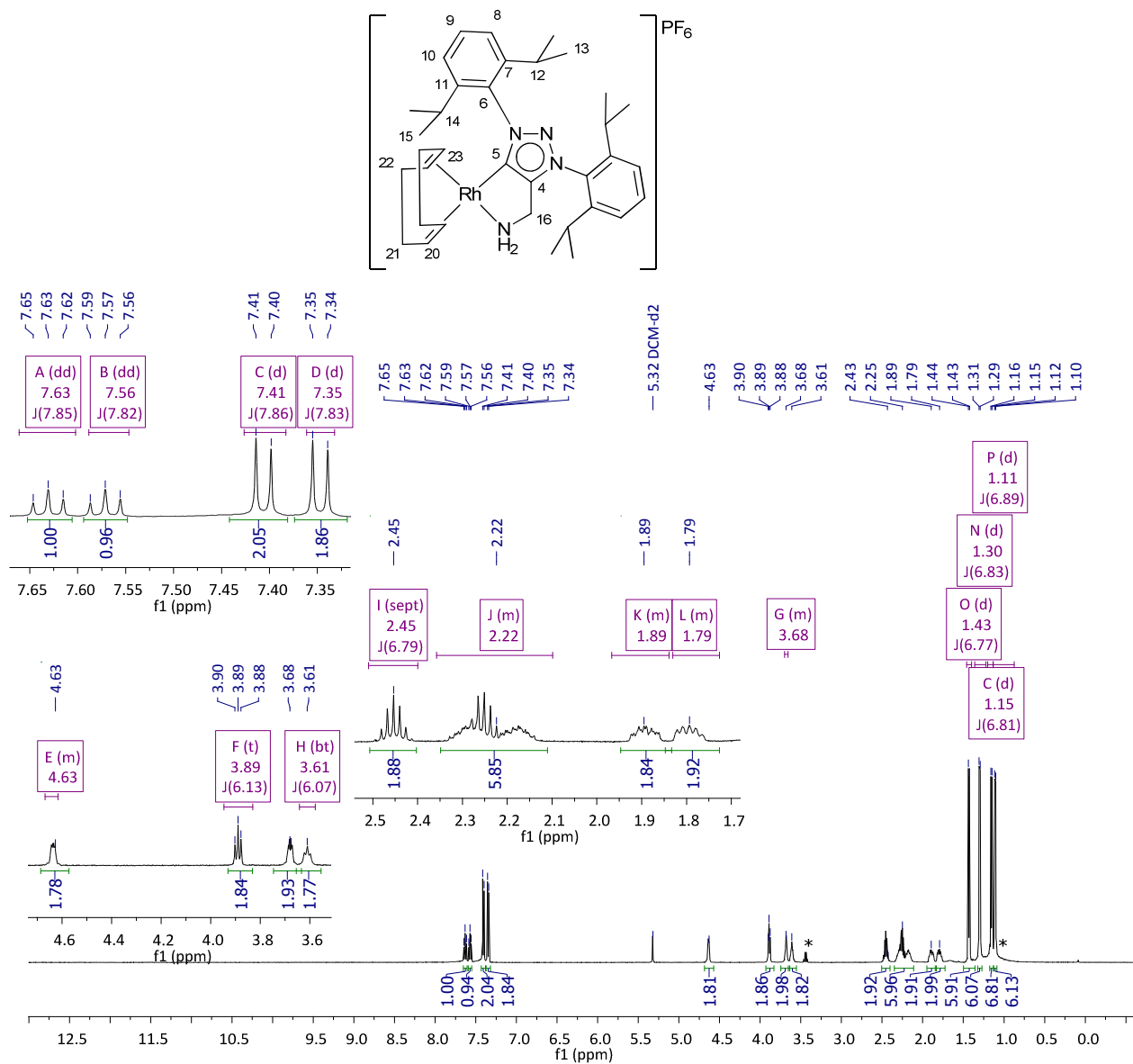


Figure S14. ¹H NMR spectrum of **2** in CD₂Cl₂

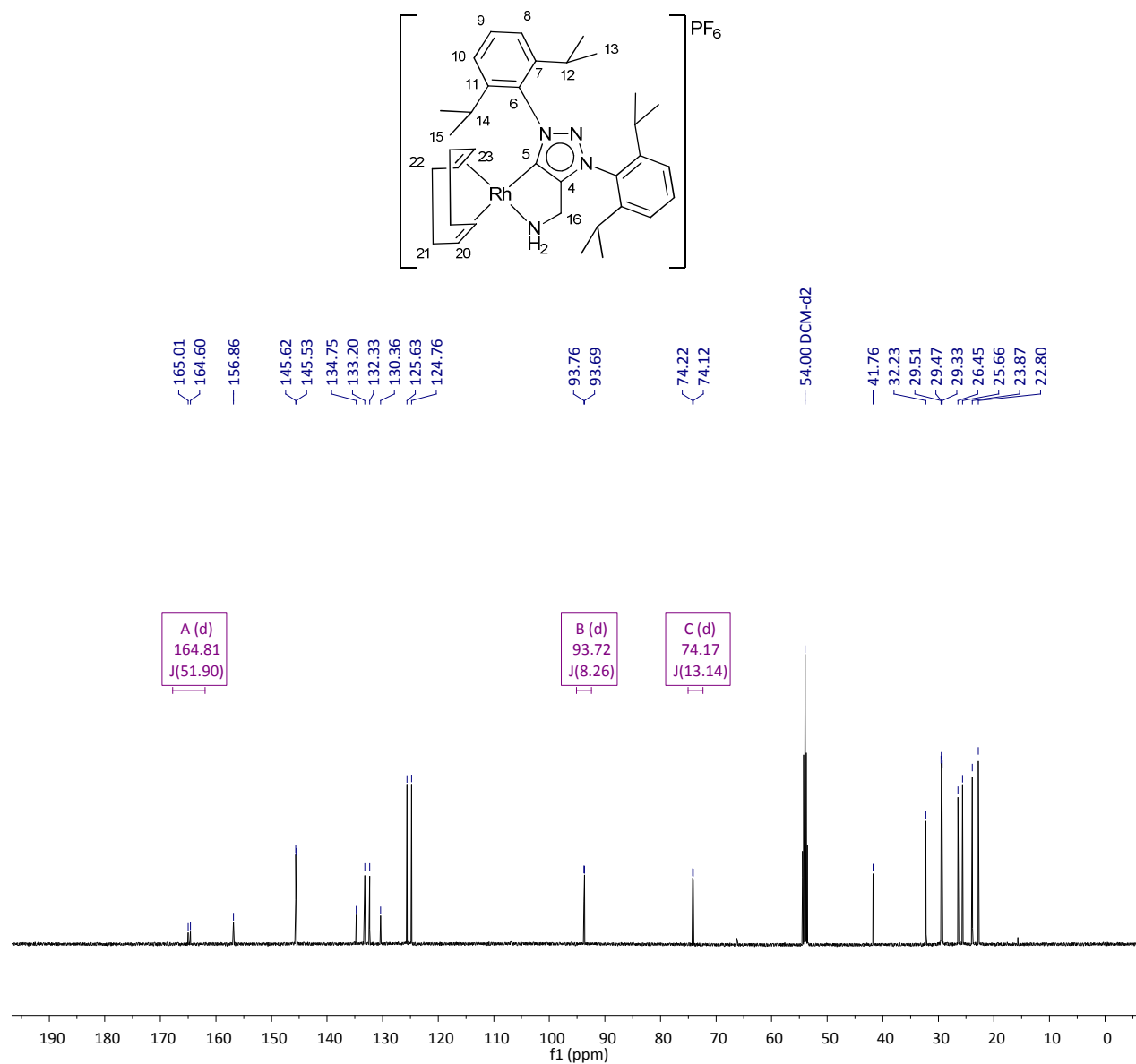


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2

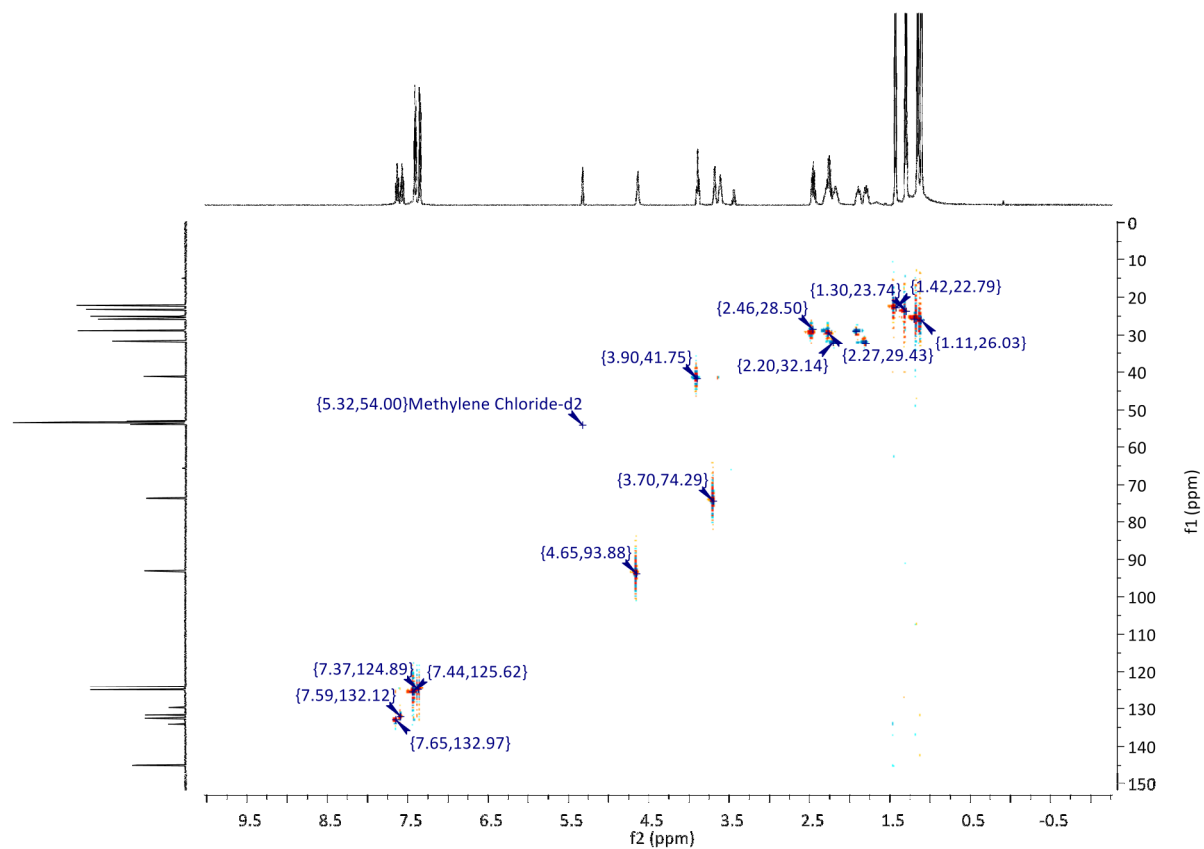


Figure S16. HSQC 2D NMR spectrum of **2** in CD_2Cl_2

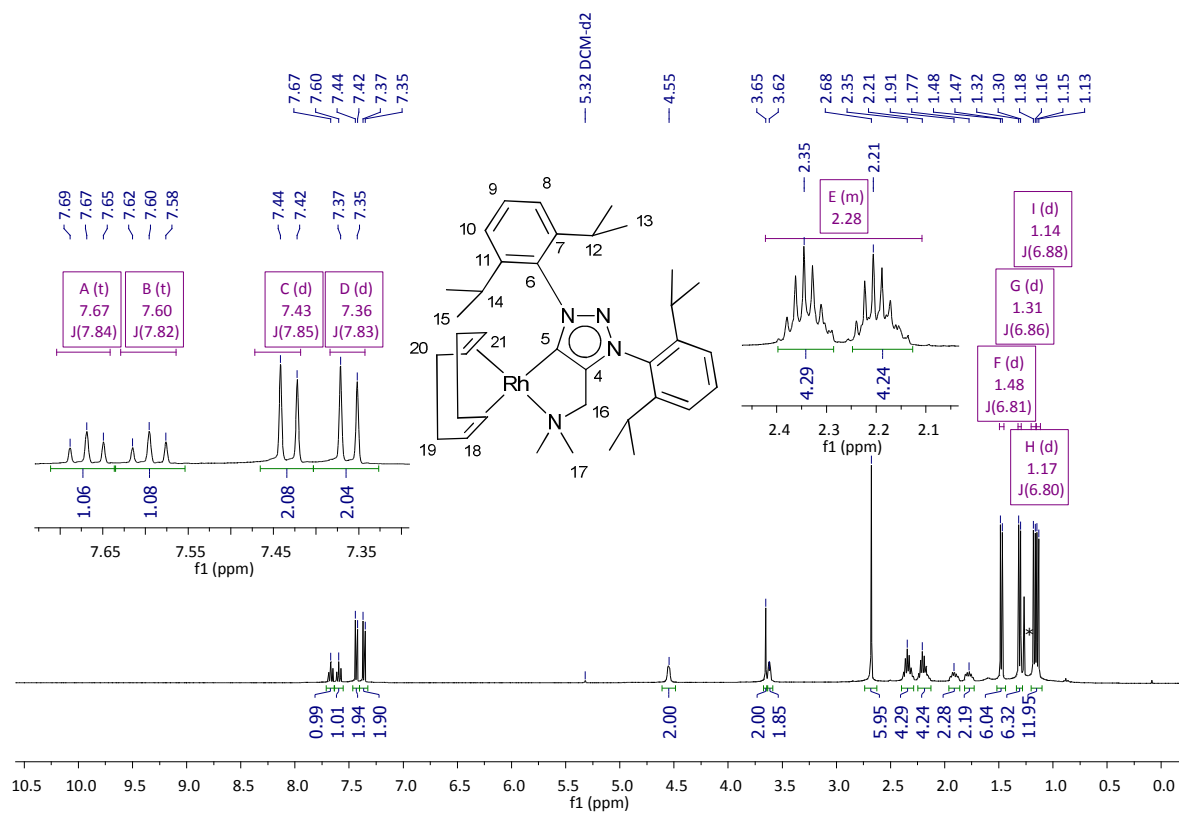


Figure S17. ¹H NMR spectrum of **3** in CD₂Cl₂

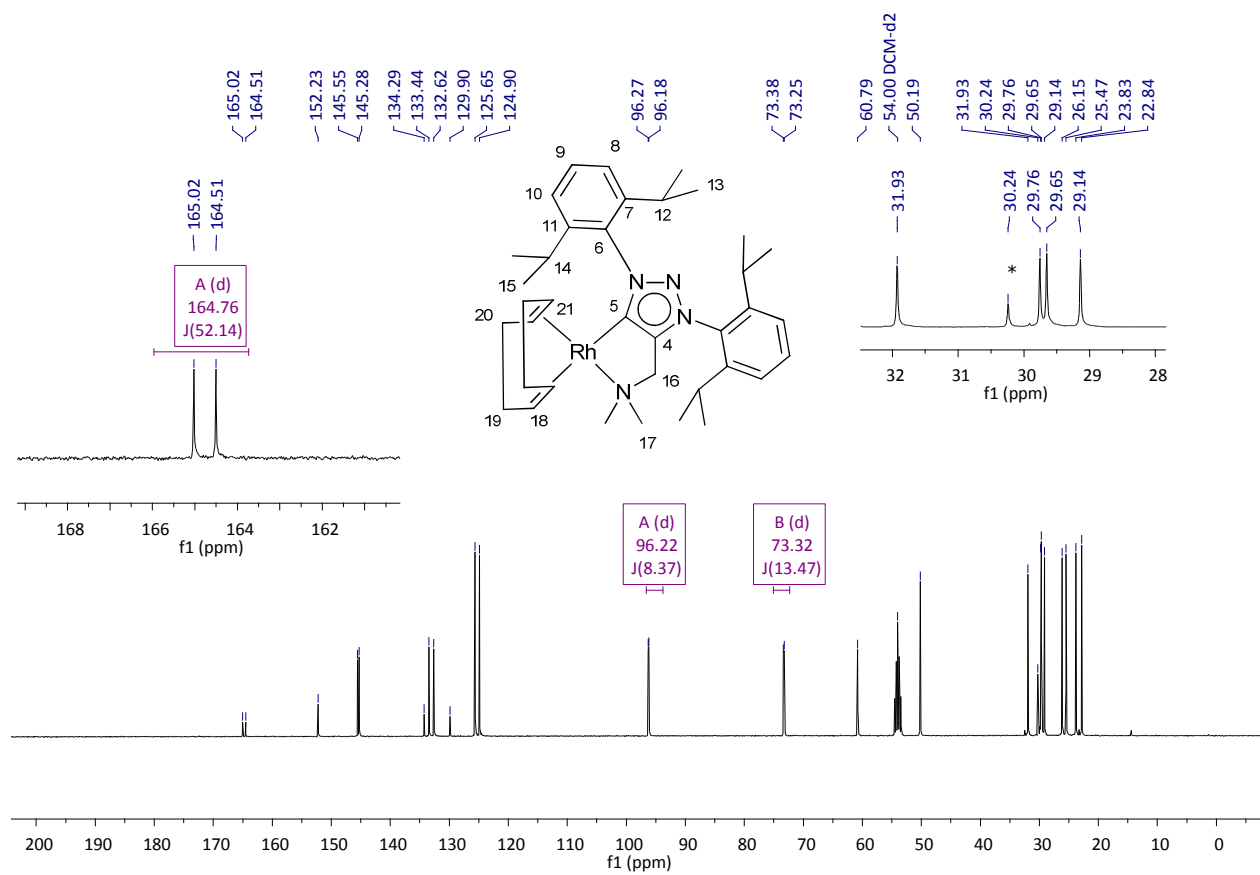


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 . * annotates grease

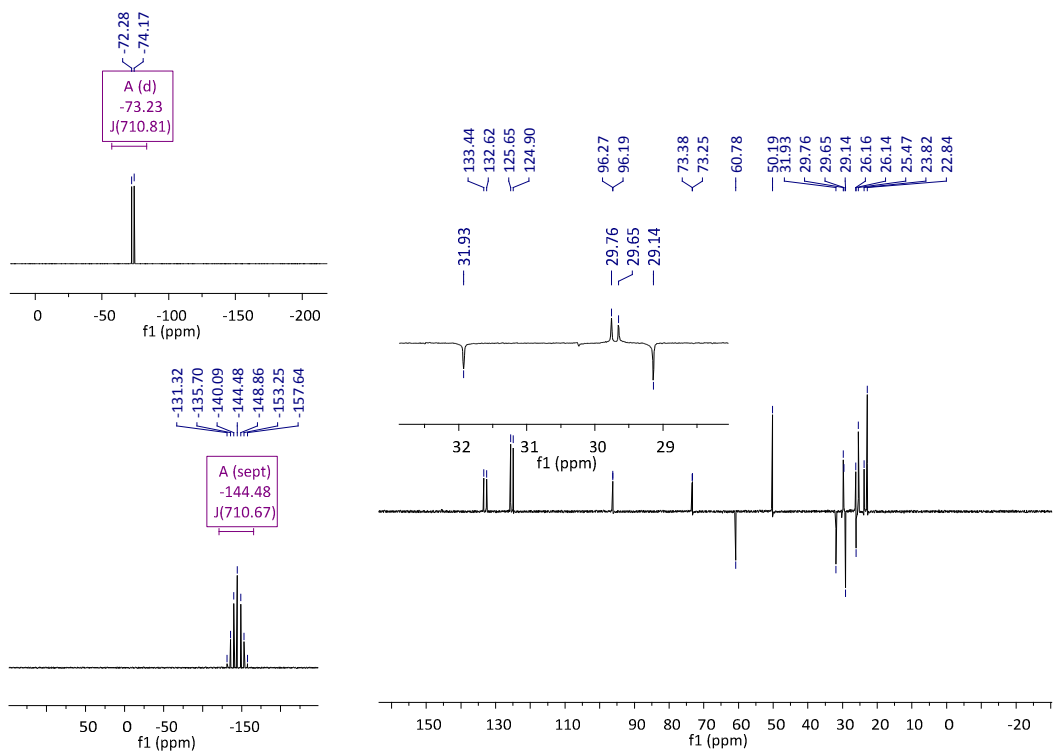


Figure S19. ^{19}F (top, left), ^{31}P (bottom, left) and ^{13}C DEPT135 (right), NMR spectra of **3** in CD_2Cl_2

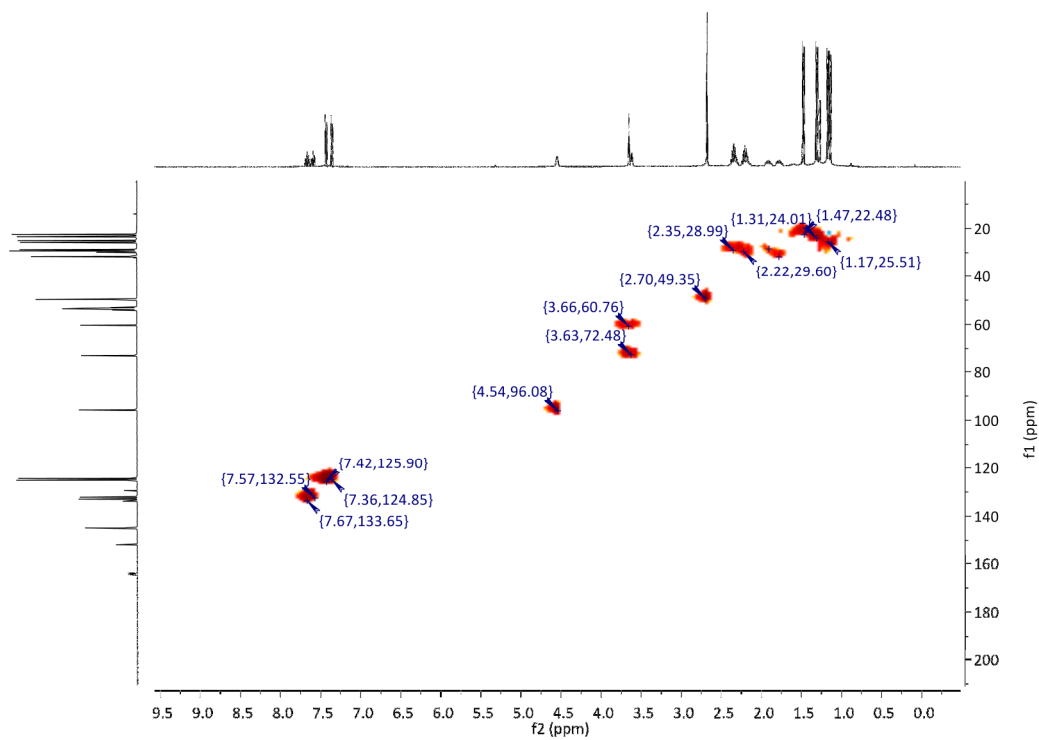


Figure S20. HSQC 2D NMR spectrum of **3** in CD_2Cl_2

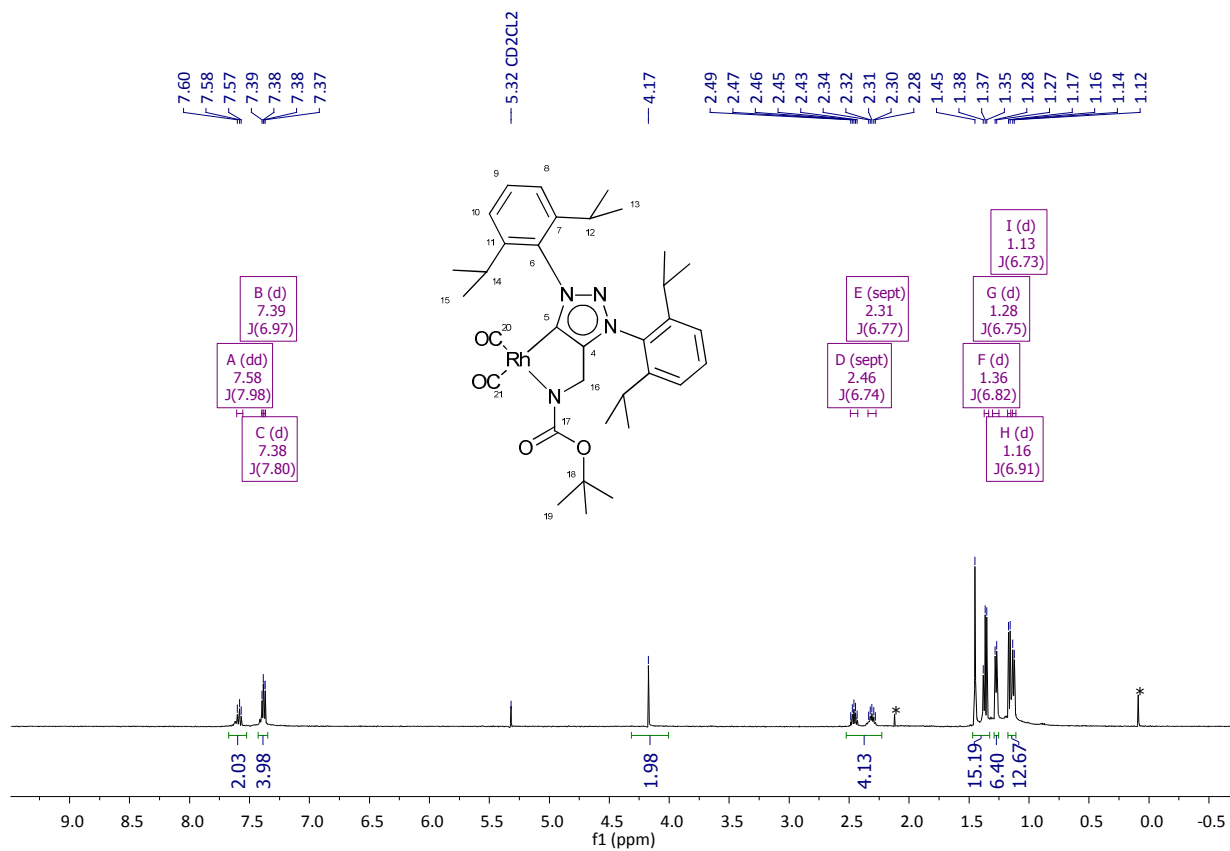


Figure S21. ¹H NMR spectrum of **4** in CD₂Cl₂

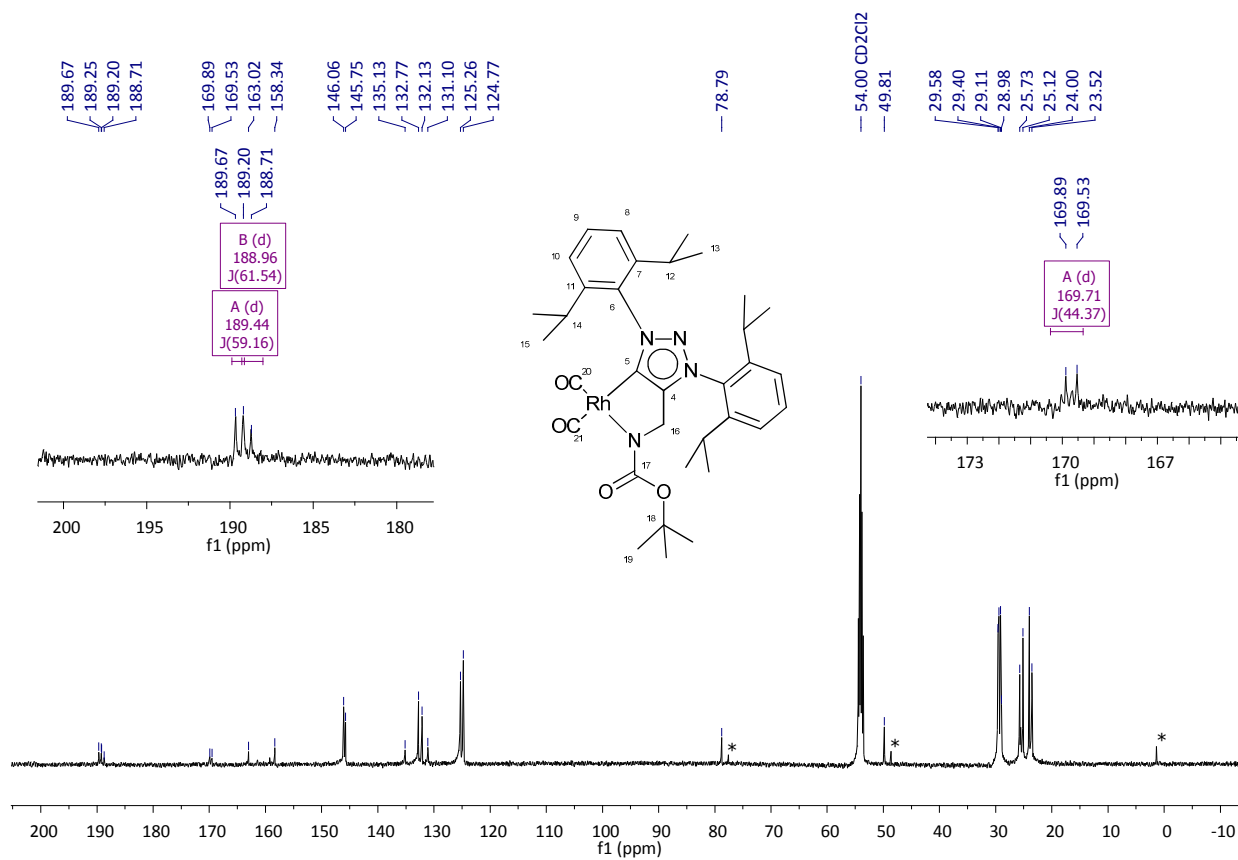


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 . *annotates a contaminant and grease

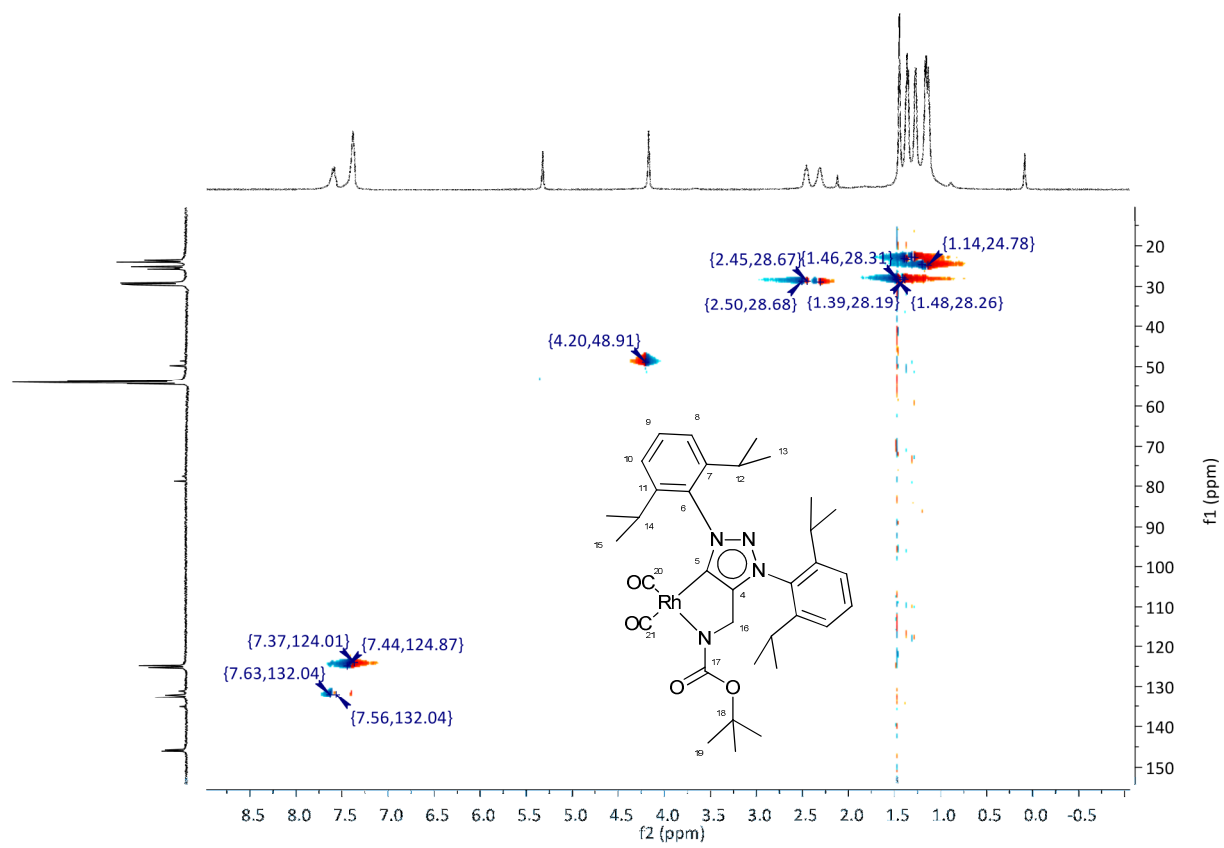


Figure S23. HSQC 2D NMR spectrum of **4** in CD_2Cl_2

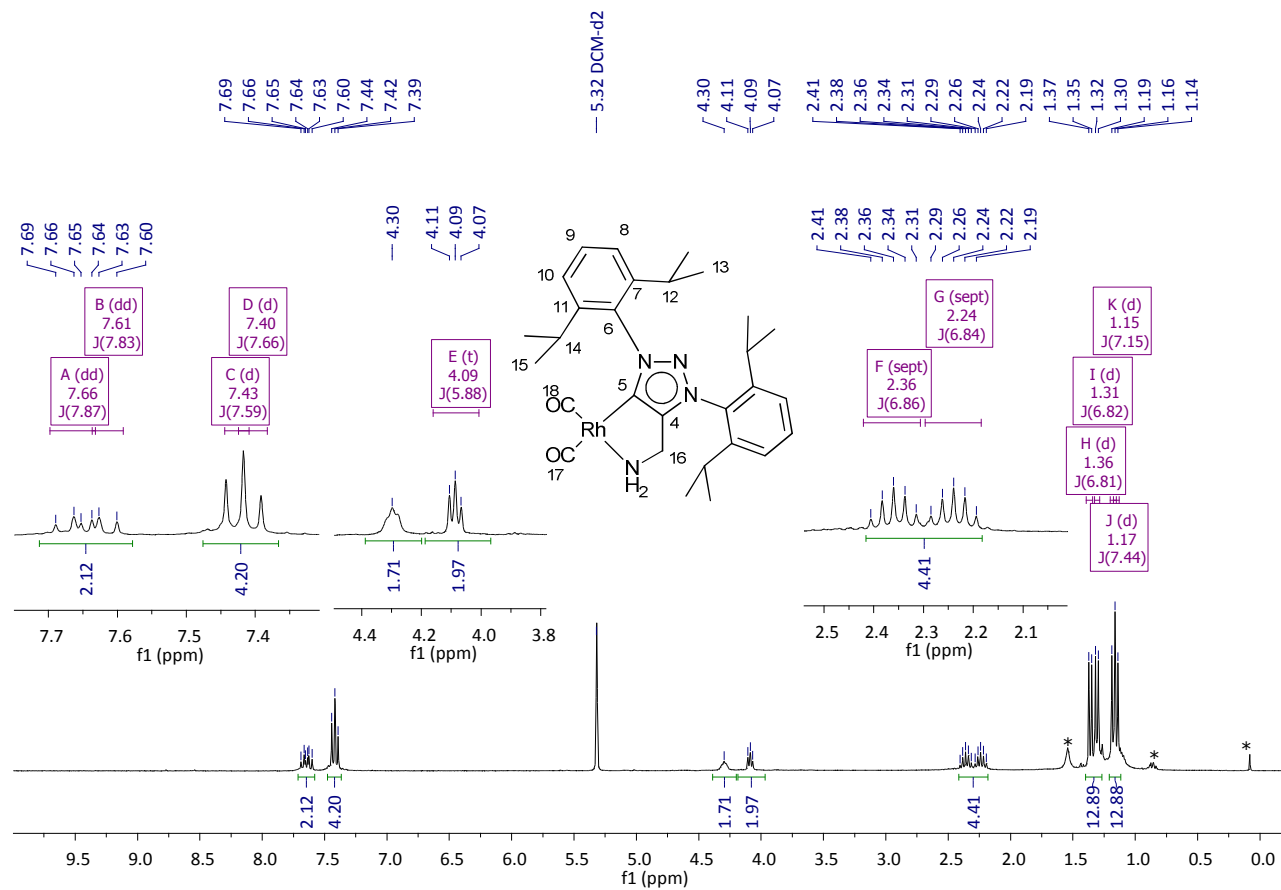


Figure S24. ¹H NMR spectrum of **5** in CD₂Cl₂. *annotates grease and water

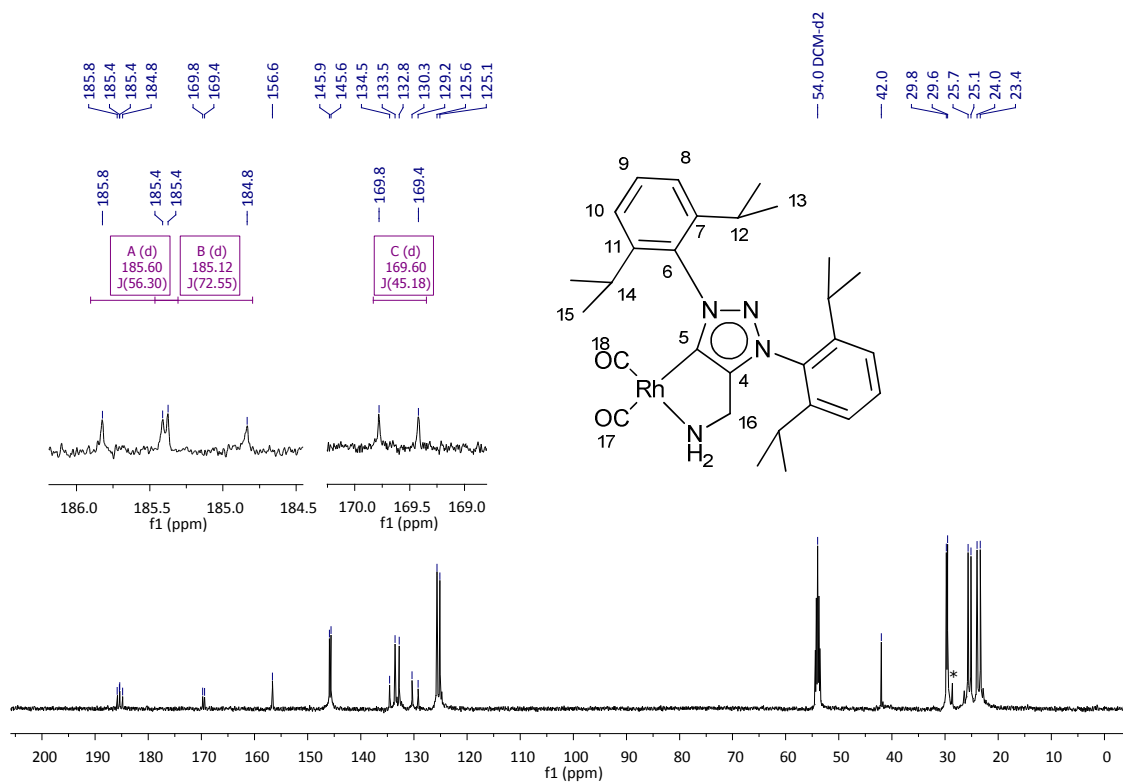


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in CD_2Cl_2 . * annotates grease

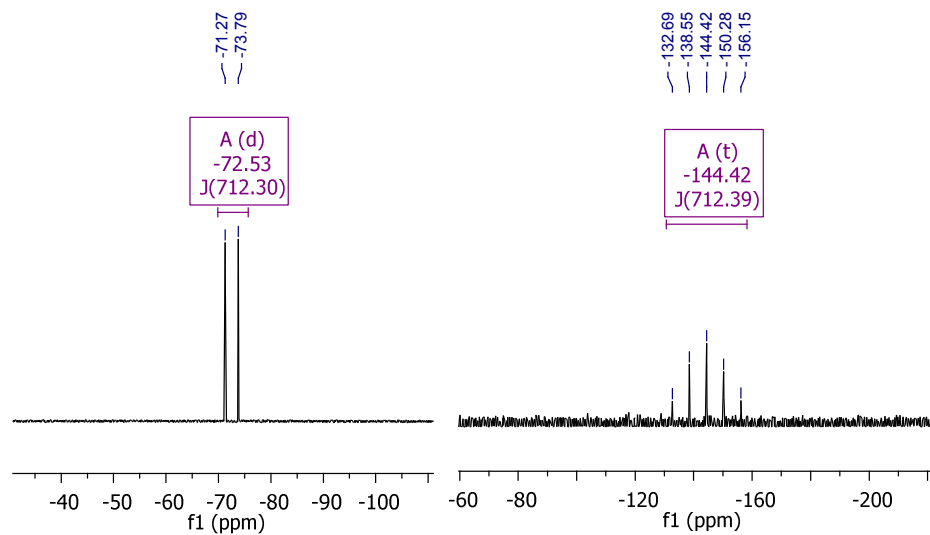


Figure S26. ^{19}F (left) and ^{31}P (right) NMR spectra of **5** in CD_2Cl_2

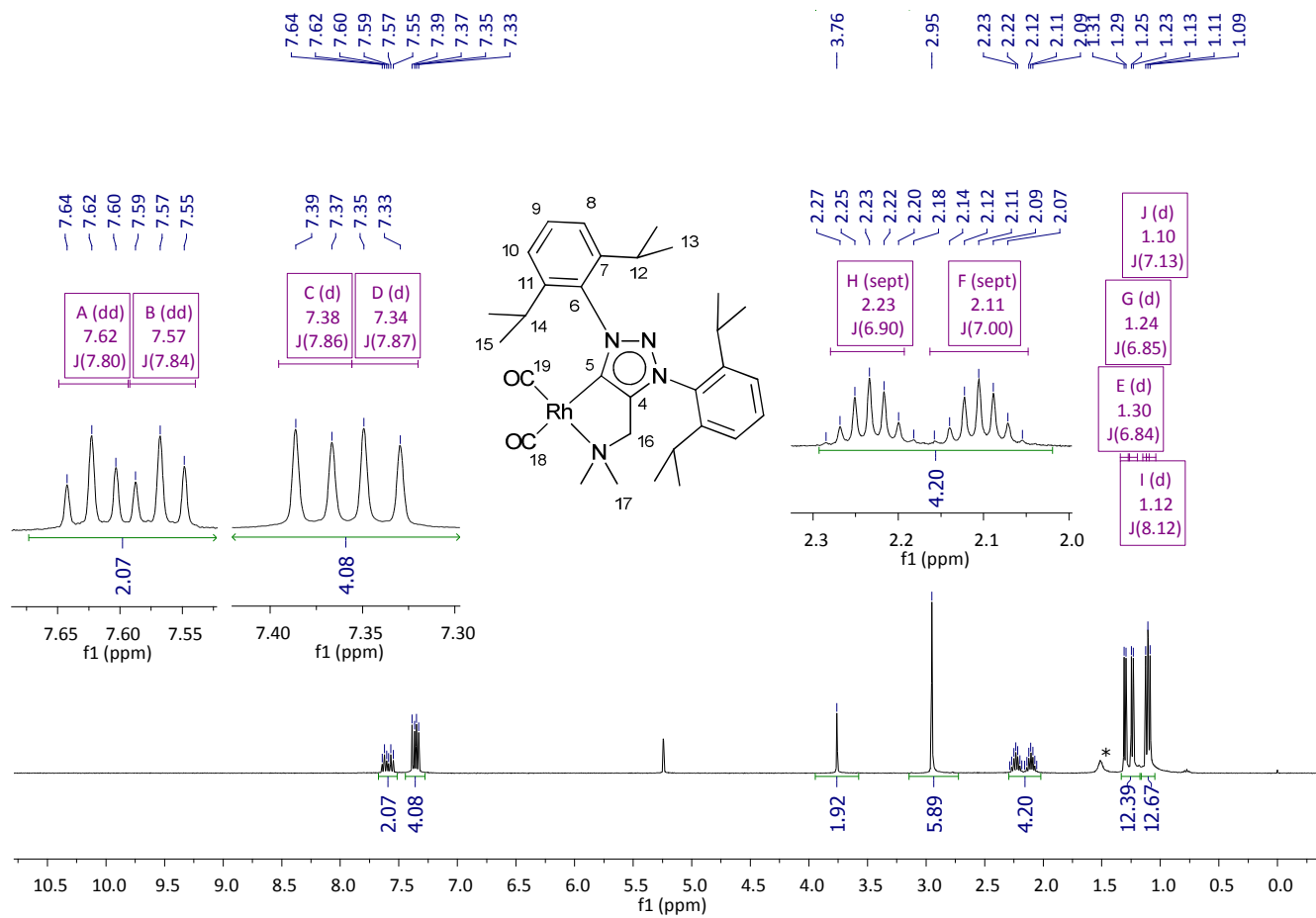


Figure S27. ^1H NMR spectrum of **6** in CD_2Cl_2 . * annotates water

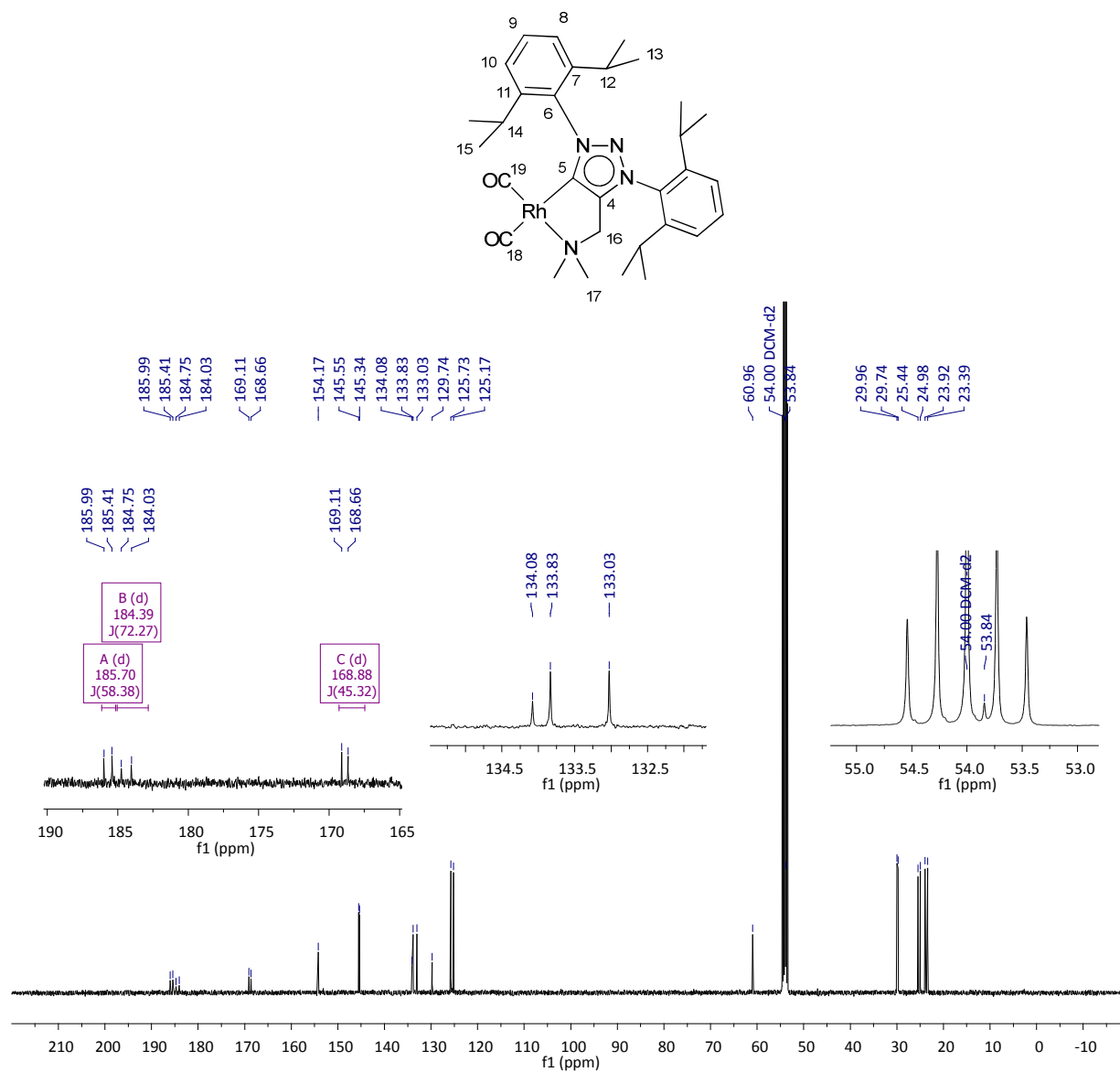


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6 in CD_2Cl_2 .

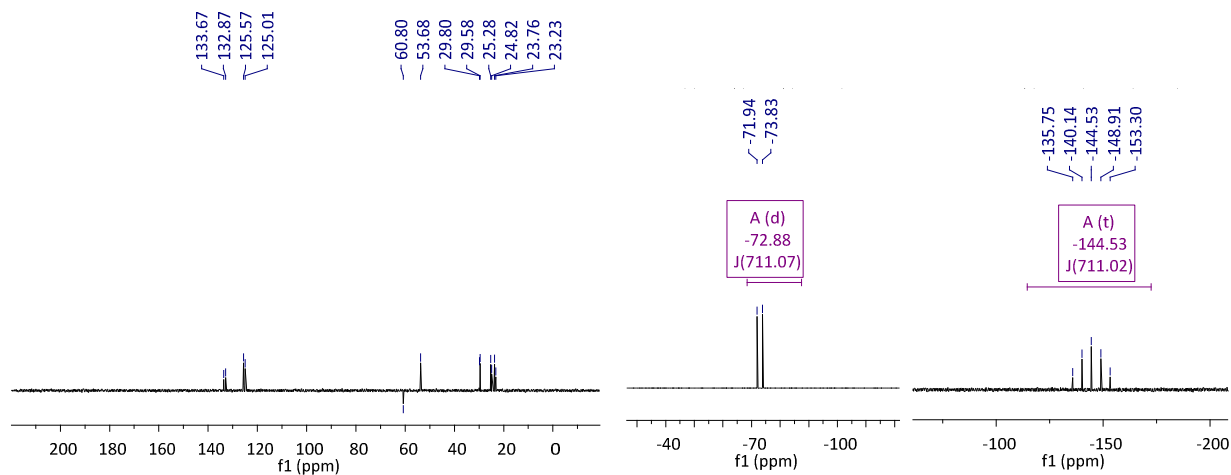


Figure S29. ^{13}C DEPT135 (left), ^{19}F (centre), ^{31}P (right) and NMR spectra of **6** in CD_2Cl_2

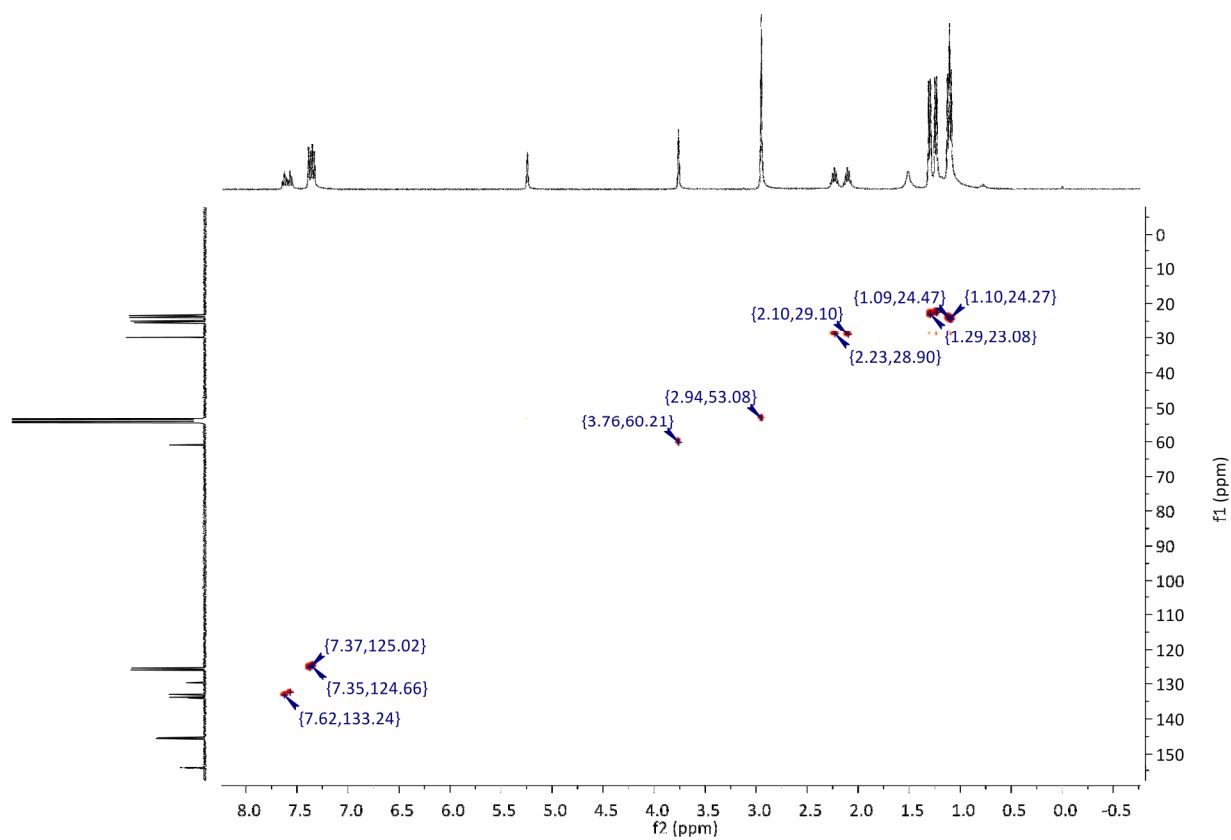


Figure S30. HSQC 2D NMR spectrum of **6** in CD_2Cl_2

IV. Single crystal X-ray structures of **1** and **3**

Single crystals suitable for X-ray diffraction were obtained by crystallization of the complexes **1** and **3** via slow evaporation of a dichloromethane solution. A satisfactory refinement of the crystal structure of complex **1** was only obtained after squeeze methodology was applied in order to eliminate residual electronic density of the solvent, which could not be refined otherwise.^{vi}

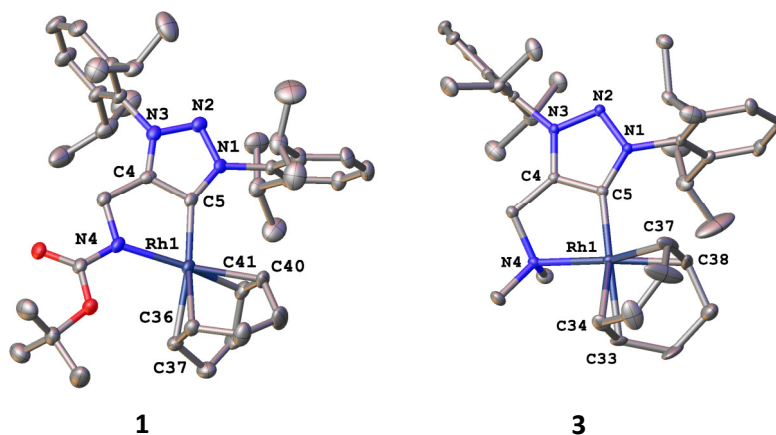


Figure S31. Solid-state structures of complexes **1** and **3** with 50% probability ellipsoids. The PF_6^- counterion (**3**) and hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: C5–Rh1 2.026(5); Rh1–N4 2.137(4); Rh1–C36 2.196(5); Rh1–C37 2.177(5); Rh1–C40 2.127(5); Rh1–C41 2.098(5); C5–Rh1–N4 79.36(16); C5–Rh1–C36 163.02(17); C5–Rh1–C37 159.99(17); C5–Rh1–C40 96.20(19); C5–Rh1–C41 94.3(2); for **3**: C5–Rh1 2.017(2); Rh1–N4 2.222(2); Rh1–C33 2.201(2); Rh1–C34 2.189(2); Rh1–C37 2.101(3); Rh1–C38 2.100(3); C5–Rh1–N4 78.44(8); C5–Rh1–C33 165.27(10); C5–Rh1–C34 157.69(11); C5–Rh1–C37 95.28(11); C5–Rh1–C38 98.30(10).

Crystal data for complex 1

$\text{C}_{40}\text{H}_{57}\text{N}_4\text{O}_2\text{Rh}$ ($M = 728.80$ g/mol): triclinic, space group P-1 (no. 2), $a = 14.5423(5)$ Å, $b = 15.9964(4)$ Å, $c = 19.7807(6)$ Å, $\alpha = 92.709(2)^\circ$, $\beta = 105.208(3)^\circ$, $\gamma = 105.446(3)^\circ$, $V = 4245.9(2)$ Å³, $Z = 4$, $T = 273$ K, $\mu(\text{MoK}\alpha) = 0.436$ mm⁻¹, $D_{\text{calc}} = 1.140$ g/cm³, 47216 reflections measured ($5.658^\circ \leq 2\theta \leq 52^\circ$), 16656 unique ($R_{\text{int}} = 0.0792$, $R_{\text{sigma}} = 0.0858$) which were used in all calculations. The final R_1 was 0.0686 ($I > 2\sigma(I)$) and wR_2 was 0.2112 (all data).

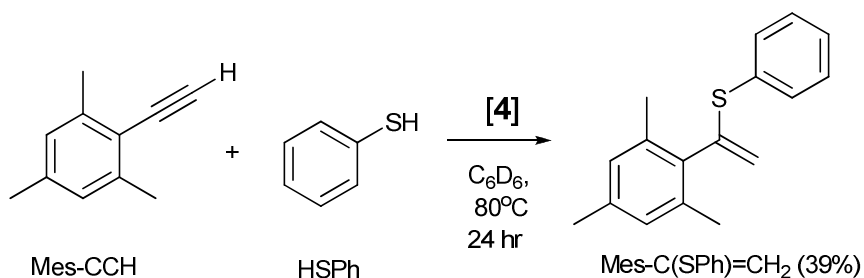
Crystal data for complex 3

$\text{C}_{38}\text{H}_{56}\text{Cl}_2\text{F}_6\text{N}_4\text{PRh}$ ($M = 887.64$ g/mol): triclinic, space group P-1 (no. 2), $a = 10.7013(6)$ Å, $b = 13.2201(7)$ Å, $c = 14.9440(7)$ Å, $\alpha = 87.018(2)^\circ$, $\beta = 83.658(2)^\circ$, $\gamma = 82.300(3)^\circ$, $V = 2080.79(19)$ Å³, $Z = 2$, $T = 150.0$ K, $\mu(\text{MoK}\alpha) = 0.636$ mm⁻¹, $D_{\text{calc}} = 1.417$ g/cm³, 90642

reflections measured ($4.498^\circ \leq 2\theta \leq 54.478^\circ$), 9271 unique ($R_{\text{int}} = 0.0604$, $R_{\text{sigma}} = 0.0302$) which were used in all calculations. The final R_1 was 0.0373 ($I > 2\sigma(I)$) and wR_2 was 0.0839 (all data).

V. Catalytic studies

Reactions were performed in duplicate, and the average yields and conversions reported. Standard operating procedure for hydrothiolation reactions: a high pressure NMR tube with a J. Young valve was loaded with 2 mol % catalyst (9.68 μmol), 2 mol % K_2CO_3 (1.33 mg, 9.68 μmol) and 1 equivalent of internal standard, anisole (25.7 μL , 237.2 μmol). To the mixture was added deuterated benzene (0.5 mL). One equivalent of terminal alkyne (237.2 μmol) and thiol (237.2 μmol) was added, and the NMR tube capped. ^1H NMR spectroscopy was performed at time 10 min after addition of the substrates. The reaction mixture was heated up to 80 $^\circ\text{C}$ and reacted for 24 hours. Upon cooling down to room temperature, ^1H NMR spectroscopy was performed at the final time. Conversions and calculated yields were determined from NMR analysis based on integration of alkyne and product, referenced to the internal standard. Product identity was confirmed by comparison with previously reported NMR spectra,^{vii} except for the reaction products of Table 2, entries 9–10. ^1H NMR data of these new vinyl sulfide products are given below in Schemes S4-S5, and Figures S32-S35.



Scheme S4. α -vinyl sulfide product Mes-C(SPh)=CH₂ from reaction in Table 2, entry 9 (Mes = 2,4,6-trimethylphenyl).

Product Table 2, entry 9: Mes-C(SPh)=CH₂

$^1\text{H}\{^{13}\text{C}\}$ NMR (300 MHz, C_6D_6): δ 7.53 (m, 2H, *o*-SPh), 6.66–7.12 (m, 5H, Ph-H and Mes-H, overlap), 4.95 (br s, 1H, CH₂), 4.88 (br s, 1H, CH₂), 2.46 (s, 6H, Mes-*o*-(CH₃)₂), 2.13 (s, 3H, Mes-*p*-CH₃).

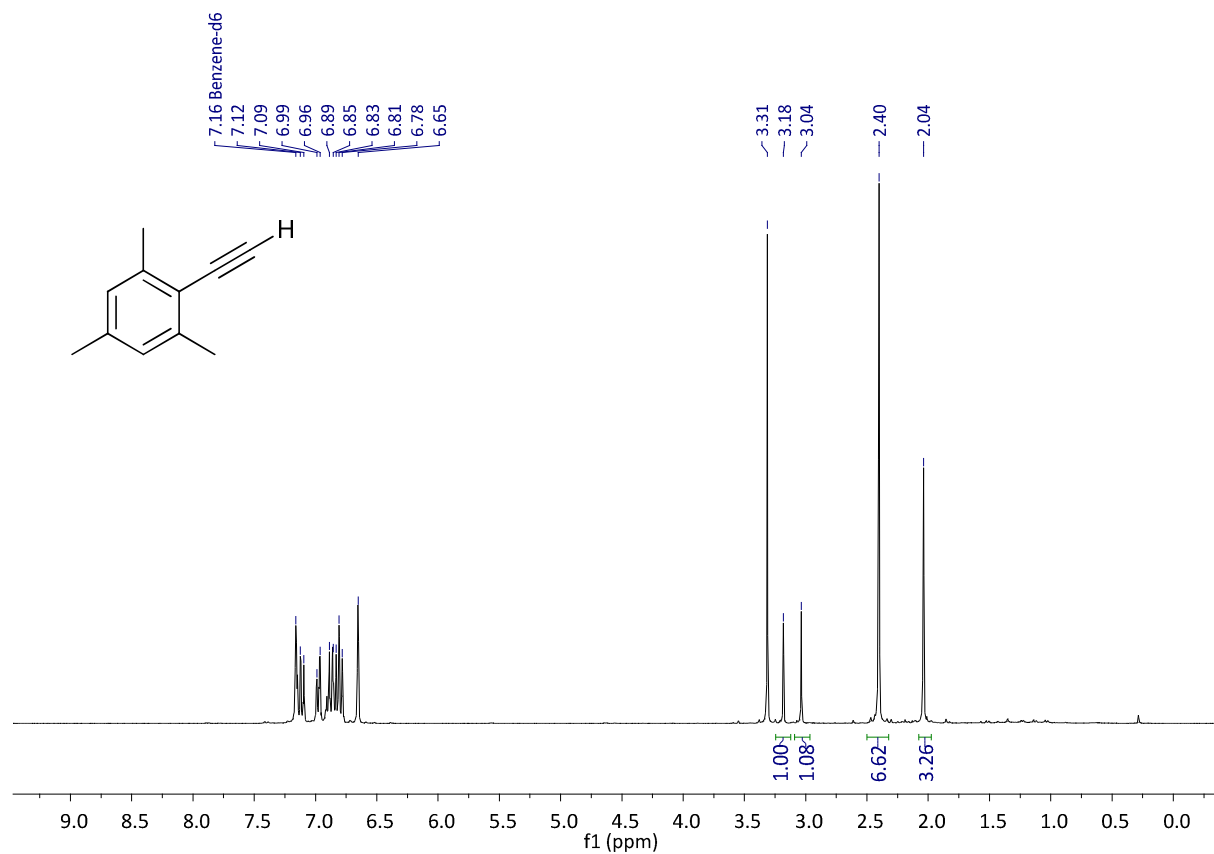


Figure S32. ¹H NMR spectrum of Mes-C≡CH (Mes = 2,4,6-trimethylphenyl), internal standard anisole and 2 mol % **4**, in C₆D₆ at t = 10 min.

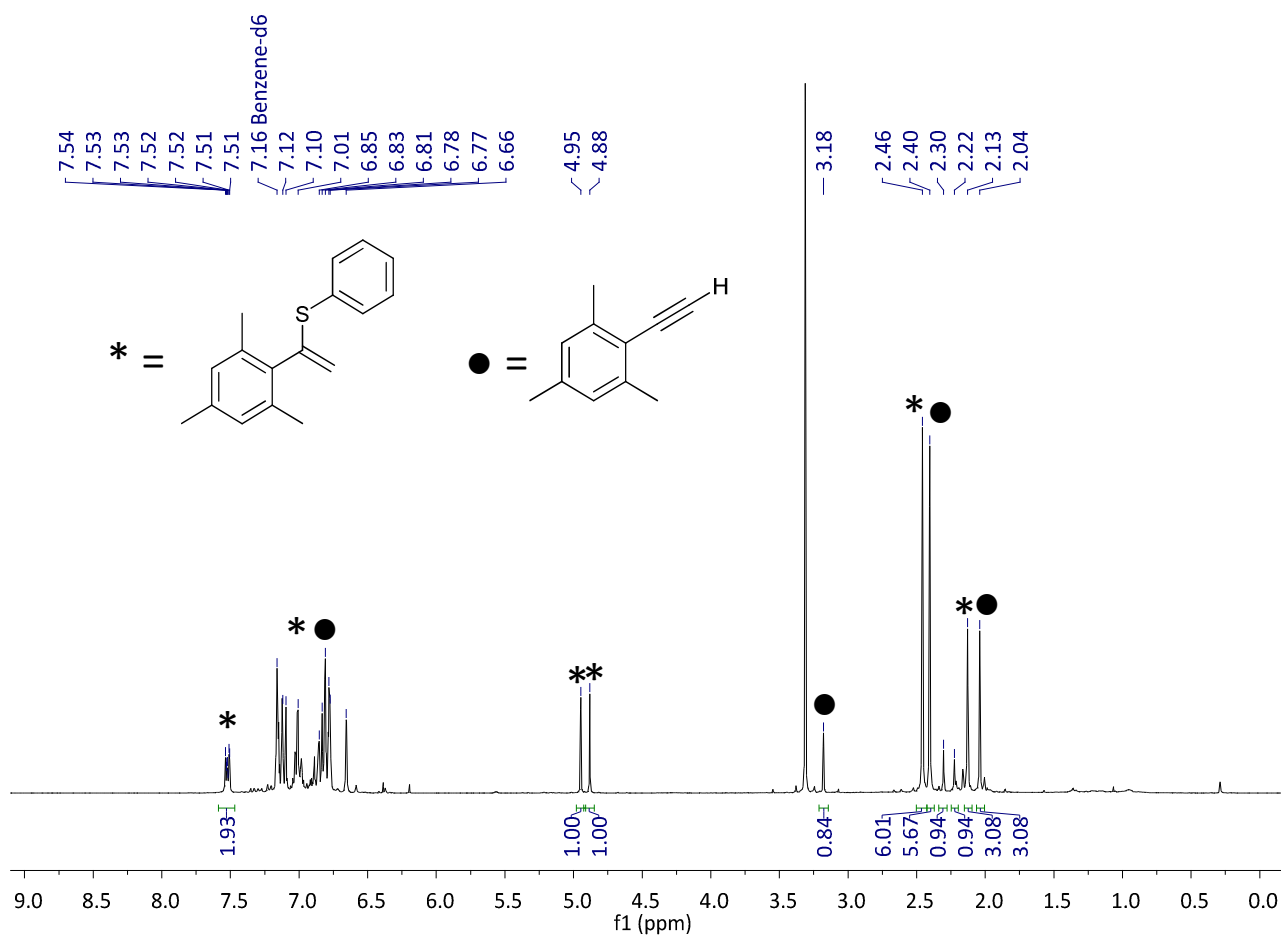
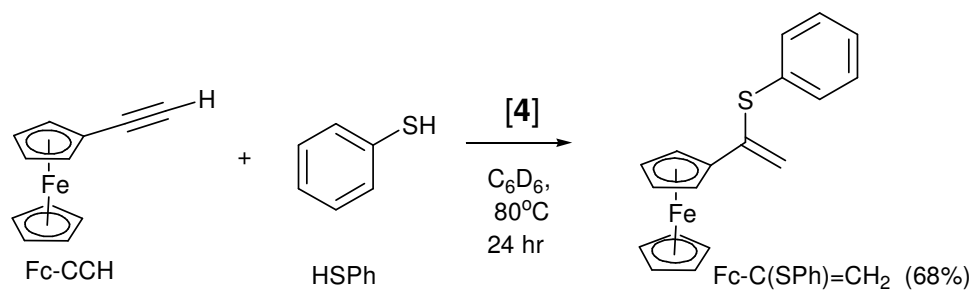


Figure S33. ^1H NMR spectrum of α -vinyl sulfide product $\text{Mes-C}(\text{SPh})=\text{CH}_2$ (*), unreacted $\text{Mes-C}\equiv\text{CH}$ (•) (Mes = 2,4,6-trimethylphenyl), internal standard anisole and 2 mol % **4**, in C_6D_6 at $t = 24$ hr with 49% conversion, 39 % yield.



Scheme S5. α -vinyl sulfide product Fc-C(SPh)=CH₂ from reaction in Table 2, entry 10.

Product Table 2, entry 10: Fc-C(SPh)=CH₂

¹H{¹³C} NMR (300 MHz, C₆D₆): δ 7.51 (m, 2H, *o*-SPh), 6.79-7.12 (m, 5H, Ph-H and Mes-H, overlap), 5.48 (br s, 1H, CH₂), 4.92 (br s, 1H, CH₂), 4.54 (br s, 2H, α -Cp'Fe), 4.12 (s, 5H, CpFe), 4.03 (br s, 2H, β -Cp'Fe).

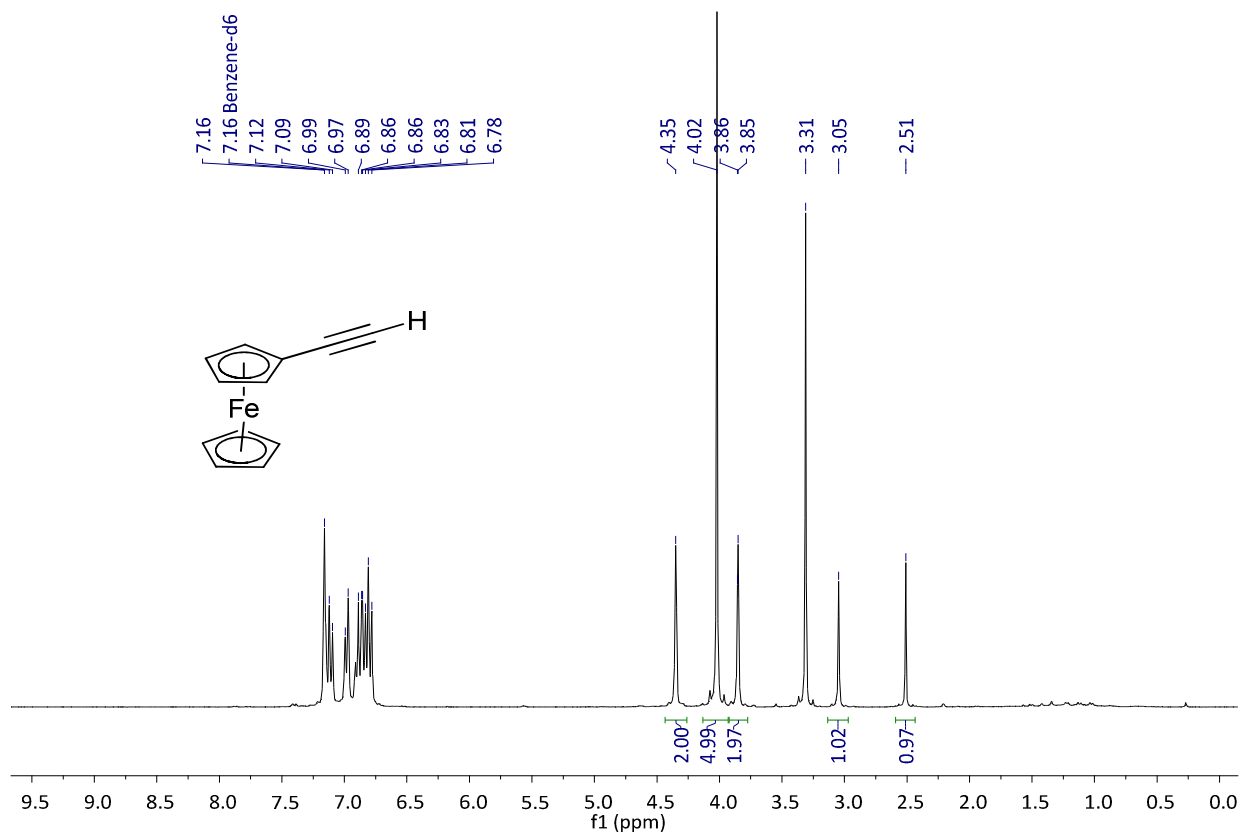


Figure S34. ¹H NMR spectrum of Fc-C≡CH (Fc = ferrocenyl), internal standard anisole and 2 mol % **4**, in C₆D₆ at t = 10 min.

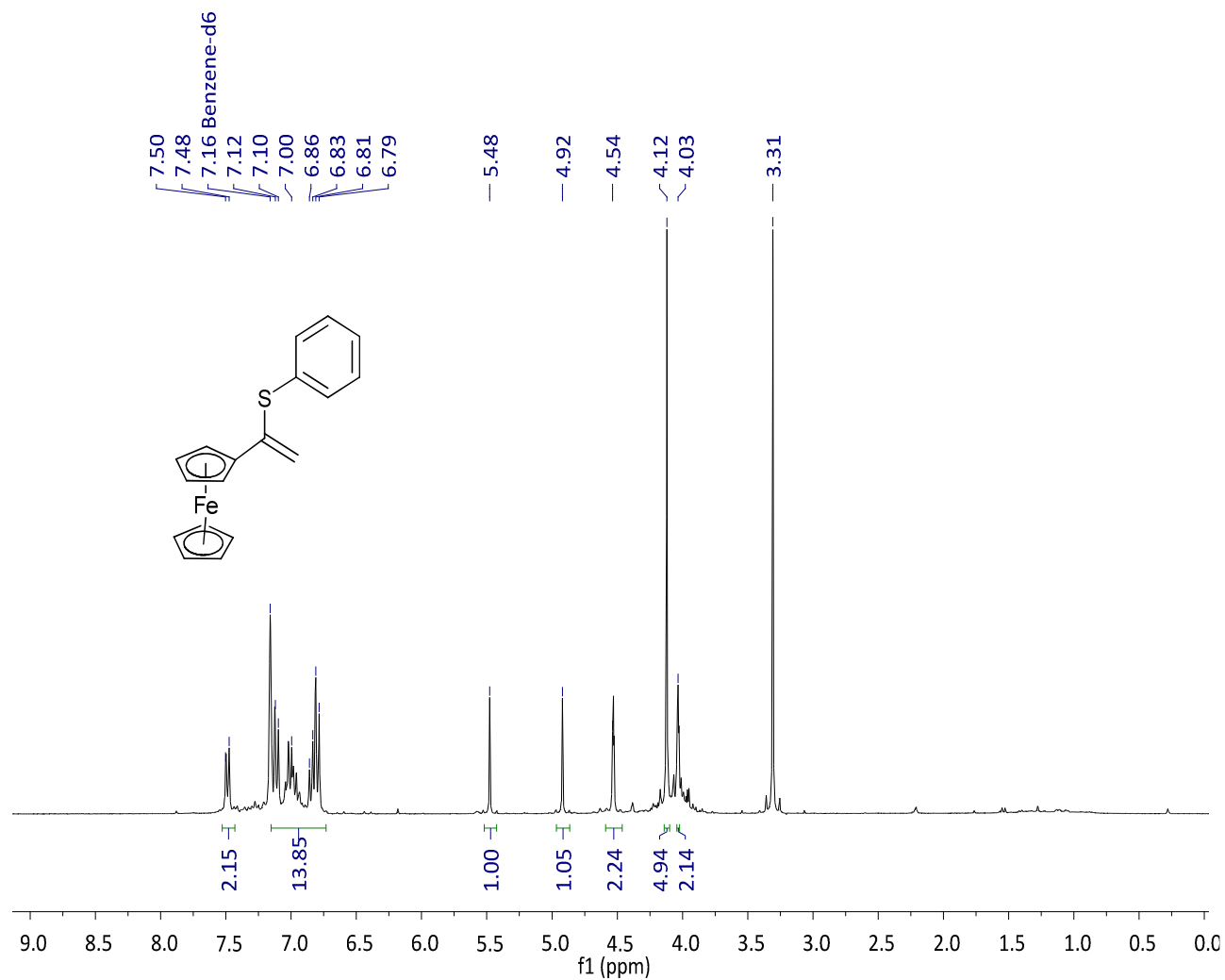


Figure S35. ^1H NMR spectrum of α -vinyl sulfide product Fc-C(SPh)=CH_2 , unreacted $\text{Fc-C}\equiv\text{CH}$, internal standard anisole and 2 mol % **4**, in C_6D_6 at $t = 24$ hr, with 95% conversion, 68 % yield (Fc = ferrocenyl).

VI. Stoichiometric Reactions

Stoichiometric tests were performed in the high pressure NMR tubes in conditions that mimic the catalytic runs.

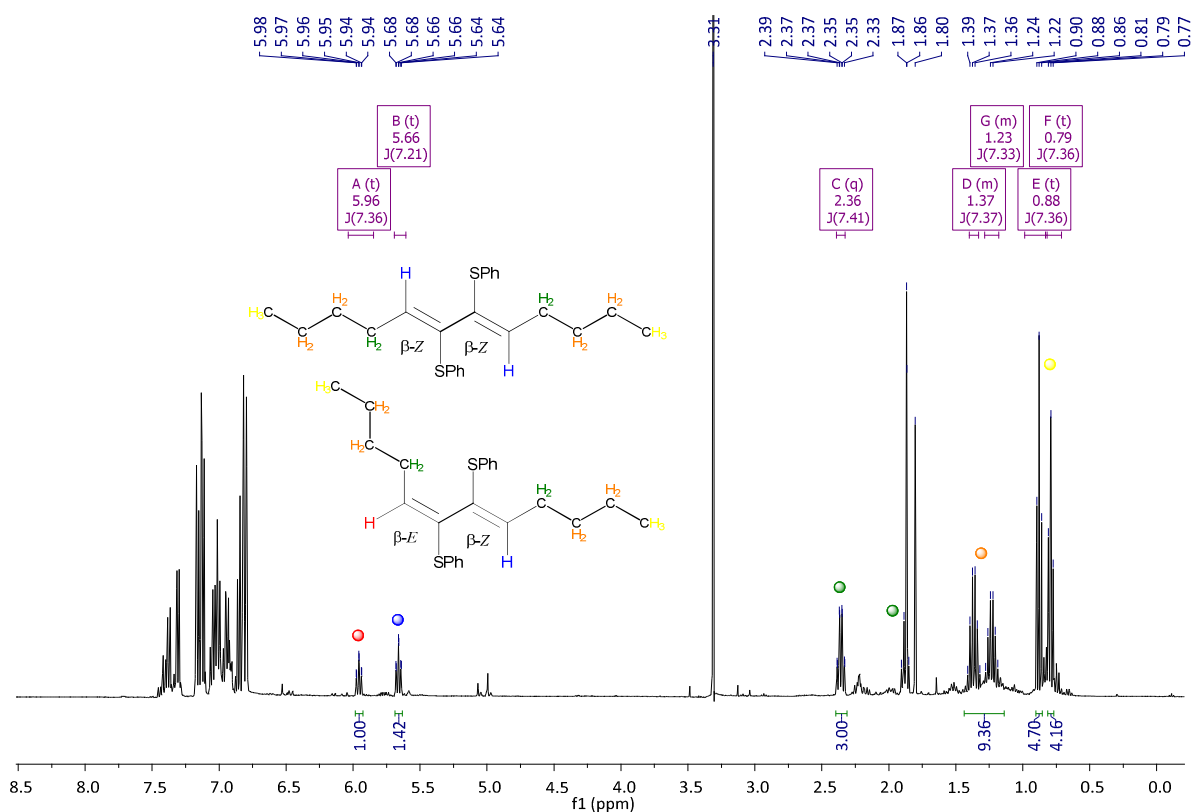


Figure S36. ¹H NMR spectrum of the coupled bis-β-E,β-Z and β-Z,β-Z vinyl sulfide products.

Stoichiometric reactions of 5 and 6

To test the hypothesis of a base-promoted deprotonation of the thiophenol, and coordination of the resultant thiolate with concomitant de-coordination of the NR₂ (R = H, Me), stoichiometric reactions were performed where 1 equivalent of thiophenol and K₂CO₃ was added to both complexes **5** and **6**. The FT-IR spectra of these complexes indicated a shift of the N-H stretching frequencies from 3331 and 3285 cm⁻¹ for **5**, to 3311 and 3240 cm⁻¹, indicating dissociation of the NH₂-moiety; while for the NMe₂-complex **6** the ν(CO) bands shifted from 2030 and 2090 cm⁻¹ to 2008 and 2076 cm⁻¹, more closely correlating with the carbonyl vibration bands observed for the neutral Rh(I) complex **4** (1993, 2068 cm⁻¹). In both cases,

these results point to the hemilabile action of the NR_2 -ligands of the cationic complexes, followed by coordination of the deprotonated thiol to yield a neutral $\text{Rh}(\text{I})$ intermediate. In addition, no Rh-H upfield shift was observed in the ^1H NMR spectra, nor was the $\nu(\text{Rh-H})$ vibration observed in the 2200 – 2300 cm^{-1} region in the IR spectra. This result was also supported by computational calculations (see SI, Figures S42-44); (c) deprotonation of the thiol by the weak base, with no N-H effect and solely a hemilabile function.

Stoichiometric reactions of 4

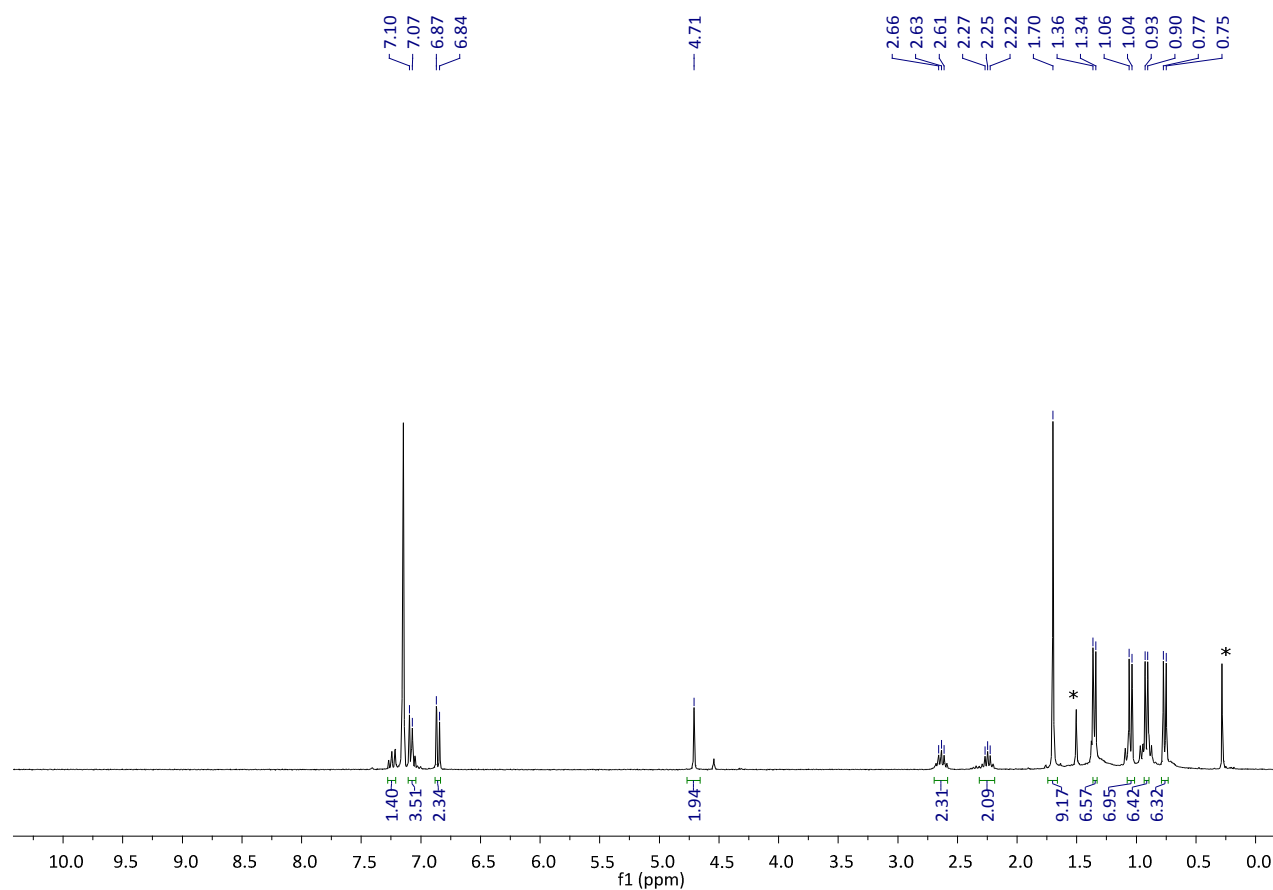


Figure S37. ^1H NMR spectrum of complex **4** before thiophenol addition in C_6D_6 .

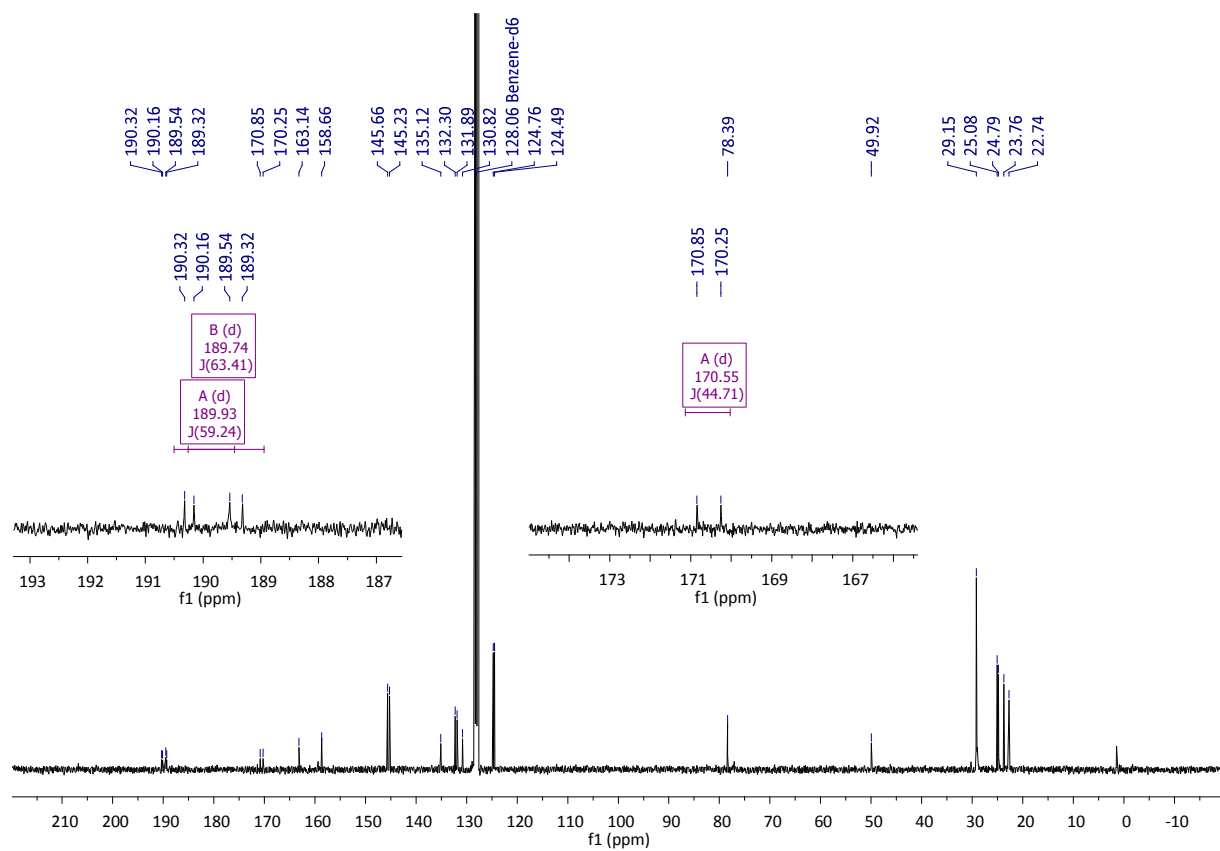


Figure S38. ^{13}C NMR spectrum of complex **4** prior to thiophenol addition in C_6D_6 .

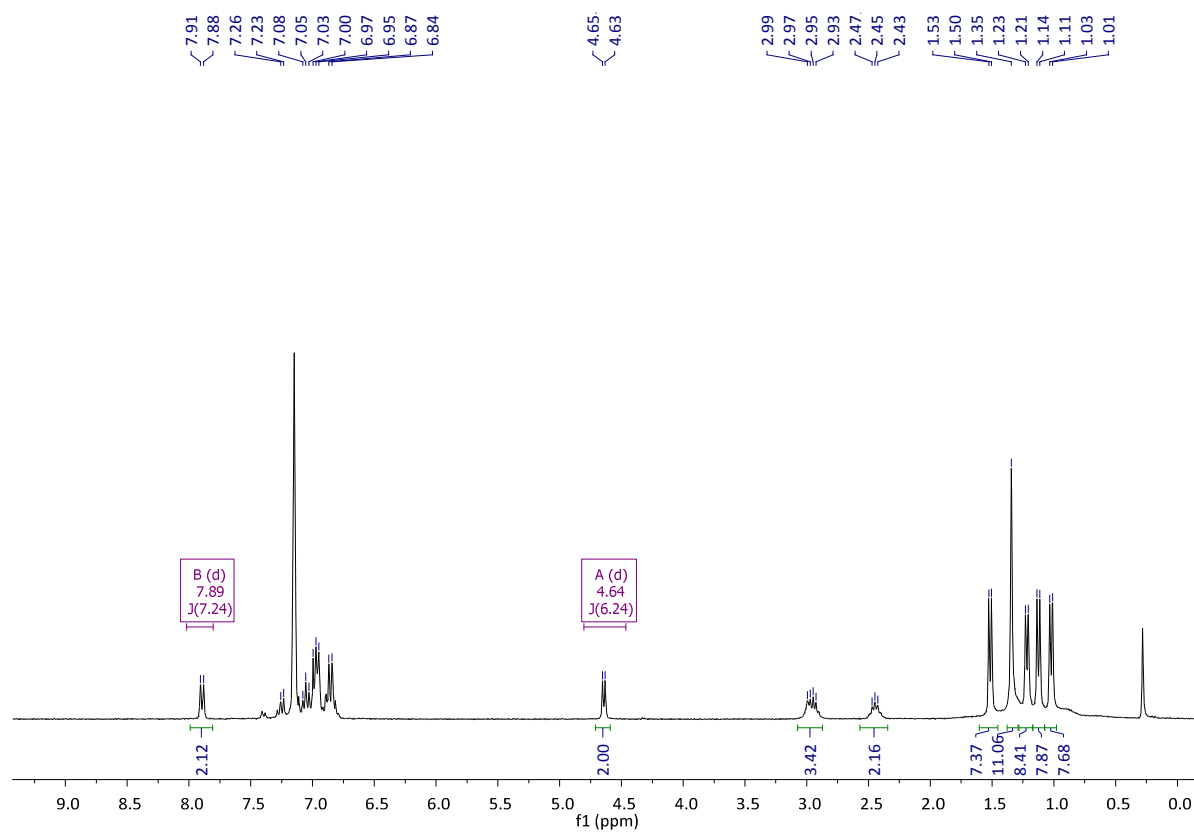


Figure S39. ^1H NMR spectrum of complex **4** after addition of 1 equivalent of thiophenol at room temperature, in the absence of base in C_6D_6 .

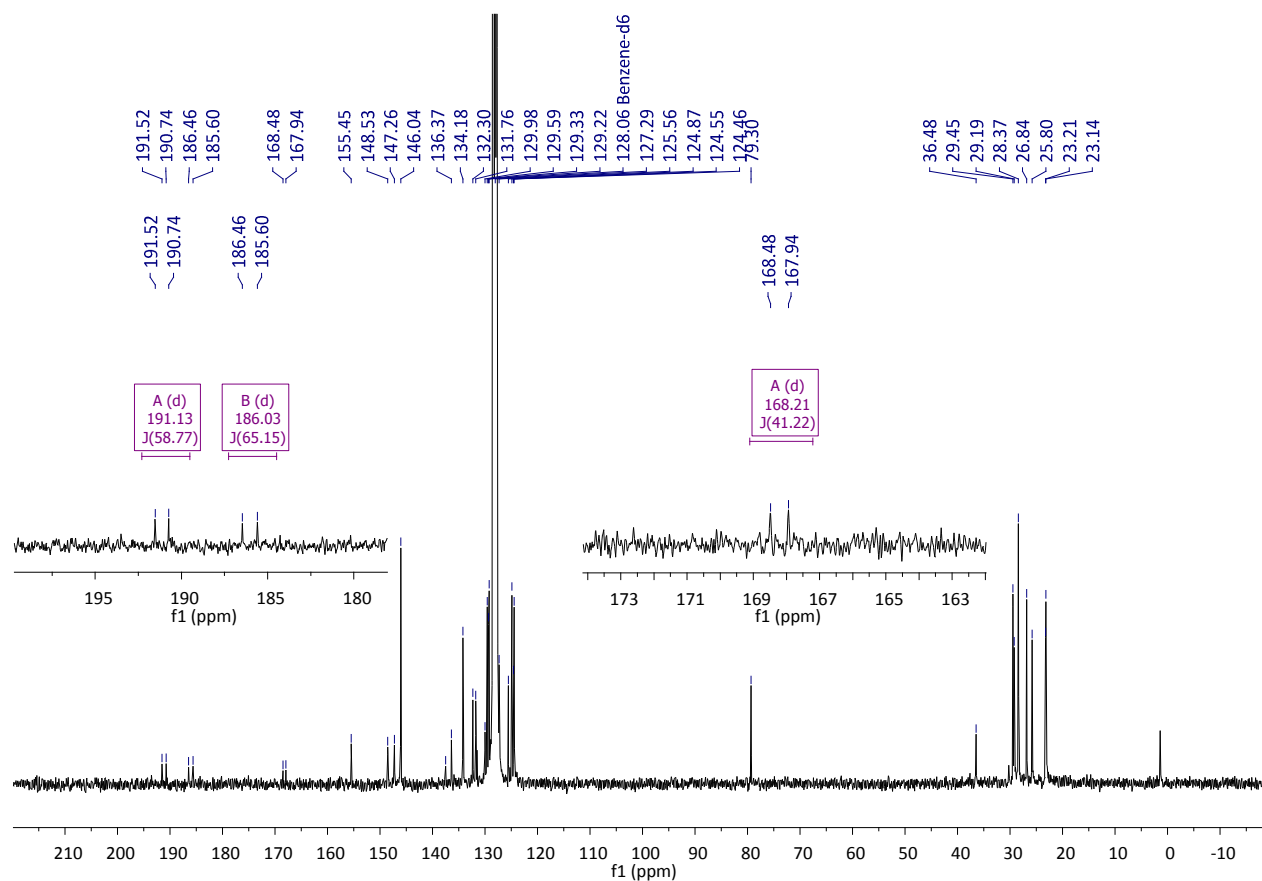


Figure S40. ^{13}C NMR spectrum of complex **4** after thiophenol addition (1 eq), at room temperature in C_6D_6 .

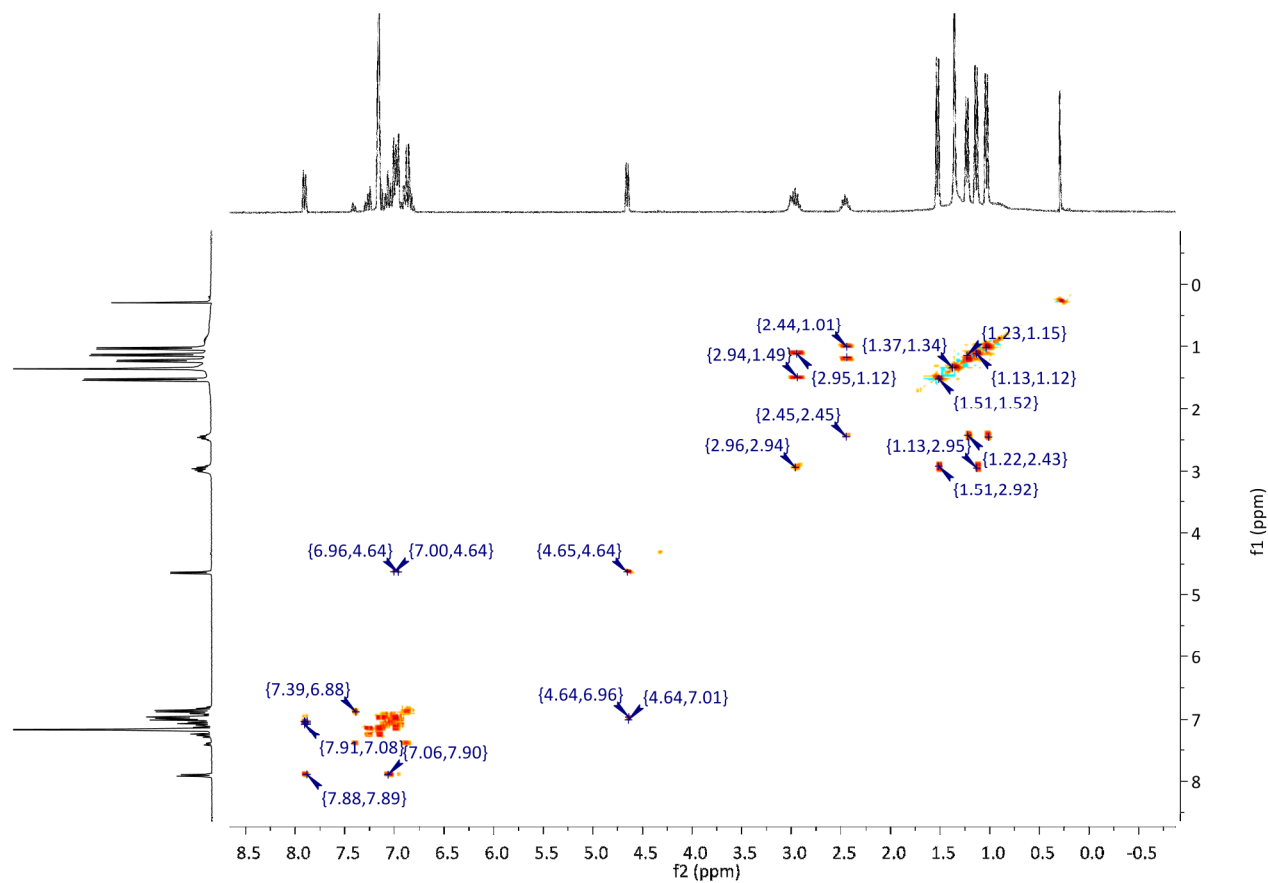


Figure S41. COSY 2D NMR spectrum of complex **4** after thiophenol addition in C_6D_6 .

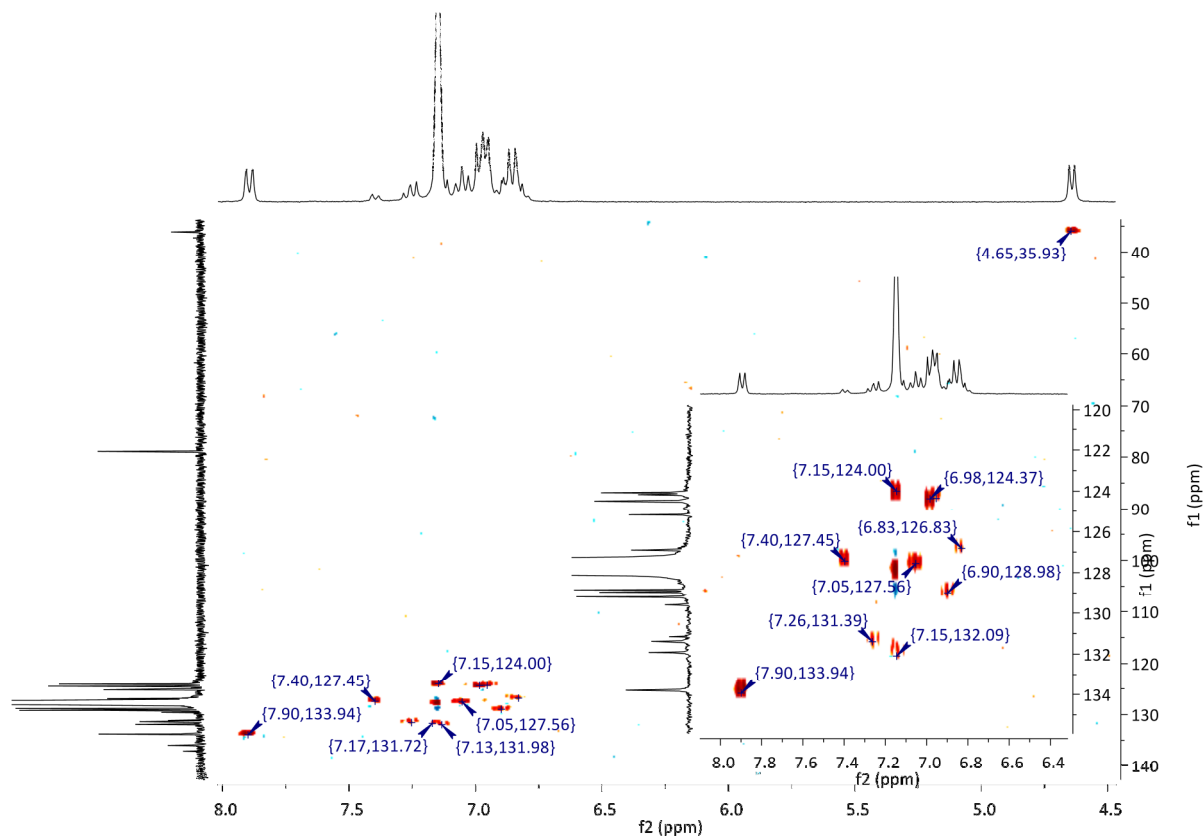


Figure S42. Selected regions of the HSQC 2D spectrum of complex **4** after thiophenol addition in C_6D_6 .

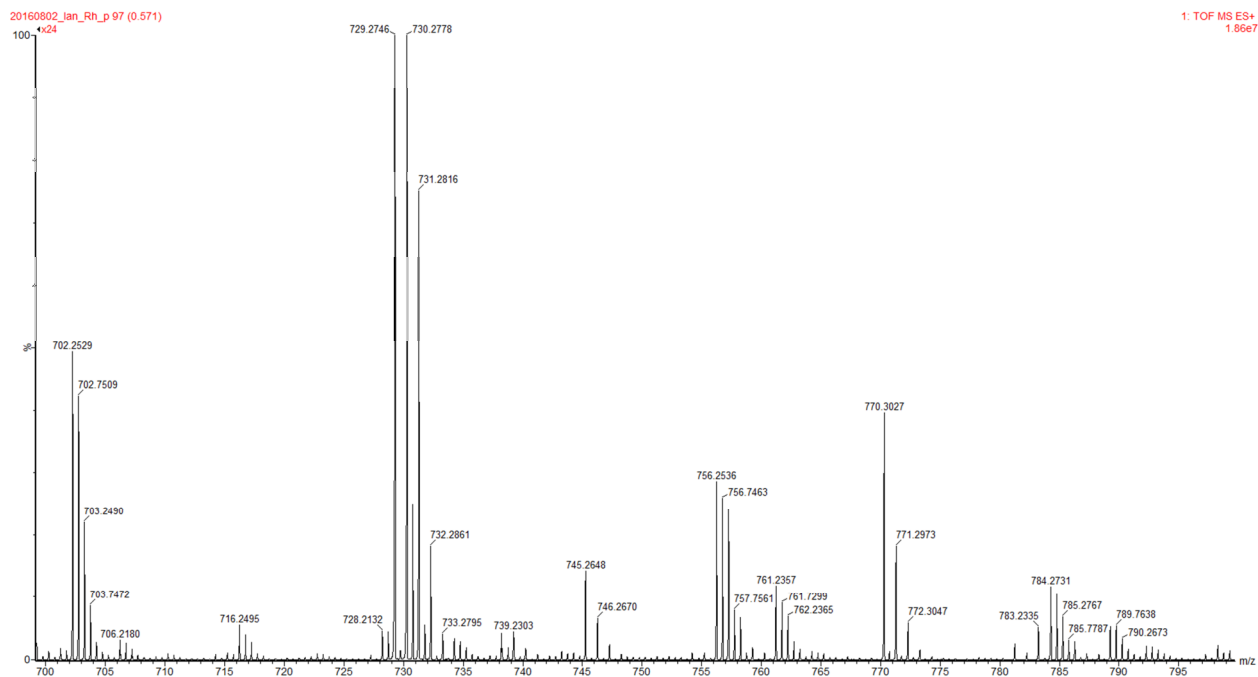


Figure S43. HRMS (ESI-FIA) spectrum of complex **4** + HSPH (INT2')

VII. Computational DFT studies

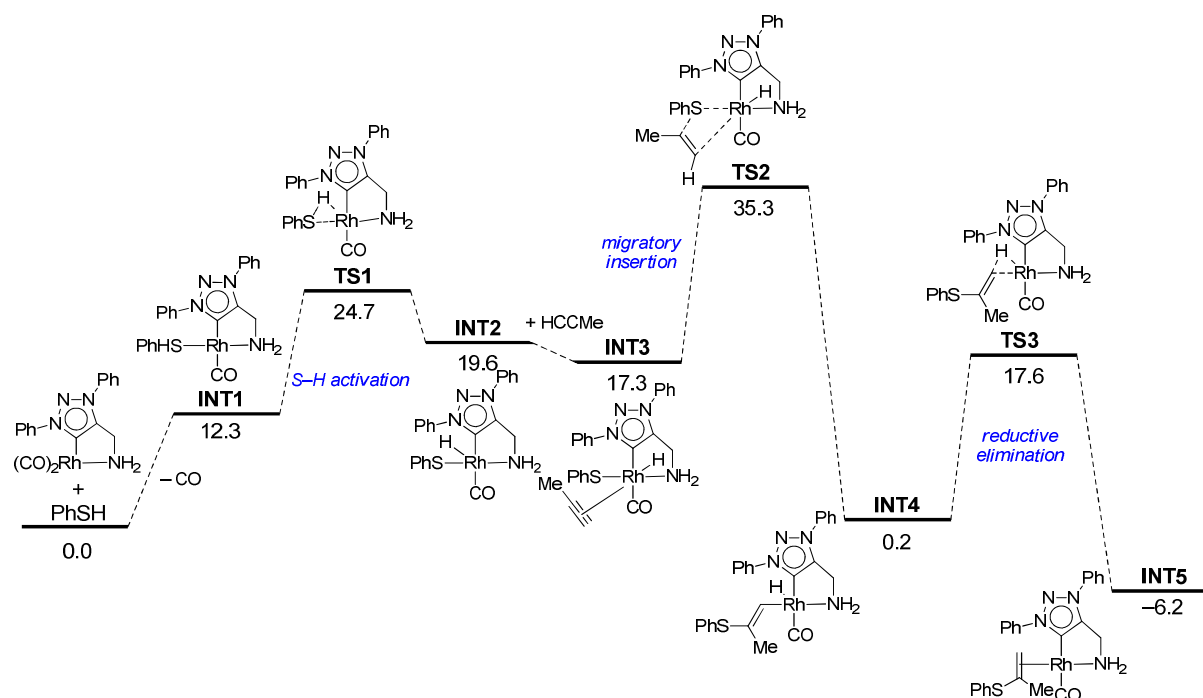


Figure S44. Pathway (a). A chelate complex was considered with a classical oxidative addition, migratory insertion and reductive elimination catalytic cycle. Charges omitted for clarity.

In pathway (a) (Figure S44), oxidative addition follows ligand association and S-H activation. The thiol substitutes the carbonyl *trans* to the amine group that shows a weaker *trans* effect than the carbene ligand to yield intermediate 1 (INT 1). Alkyne association occurs *trans* to the hydride since this is the only manner in which the selectivity for the α -vinyl sulphide can be obtained (M-H insertion is favoured over M-S insertion, M-H insertion yields β -isomers). The rate determining step was calculated as the migratory insertion step to yield transition state 2 (TS 2). Reductive elimination follows M-H activation.

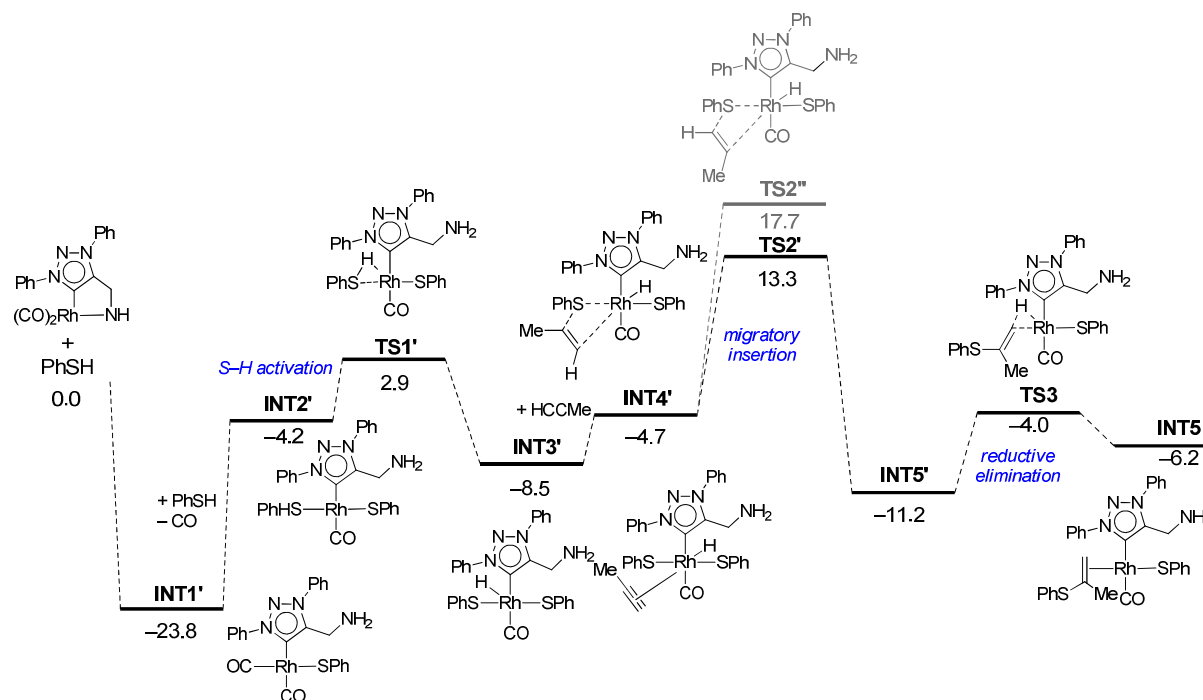


Figure S45. The N-H effect was considered which results in a bifunctional mechanism whereby the thiol is heterolytically cleaved across the M-N bond to yield a thiolate complex. Charges omitted for clarity.

As shown in Figure S45, a bifunctional heterolytic cleavage of the S-H bond was calculated to be a highly exergonic step to yield intermediate 1 (**INT1'**) in pathway (b). (It should be noted that the very high exergonicity can be a result of the calculations considering a gas phase reaction and a 1:1 interaction between isolated molecular entities). The thiolate ligand substitutes the aminyl function by deprotonation of the Rh-N bond. Subsequent substitution of a carbonyl ligand by the thiol leads to oxidative addition to yield intermediate 3 (**INT 3'**). Alkyne coordination is *trans* to the hydride to allow the observed selectivity. Migratory insertion was again calculated as the rate determining step with two possible intermediates. **TS 2''** is slightly higher in energy than **TS 2'**, which supports the observed selectivity towards the α -isomer.

Pathway (c) involves no N-H effect, and involves the formation of a thiolate complex (**INT 1'**) (Figure S46). The nucleophilic addition of the thiolate ligand was calculated as a highly exergonic step. Oxidative addition/reductive elimination cycles describe the catalytic process.

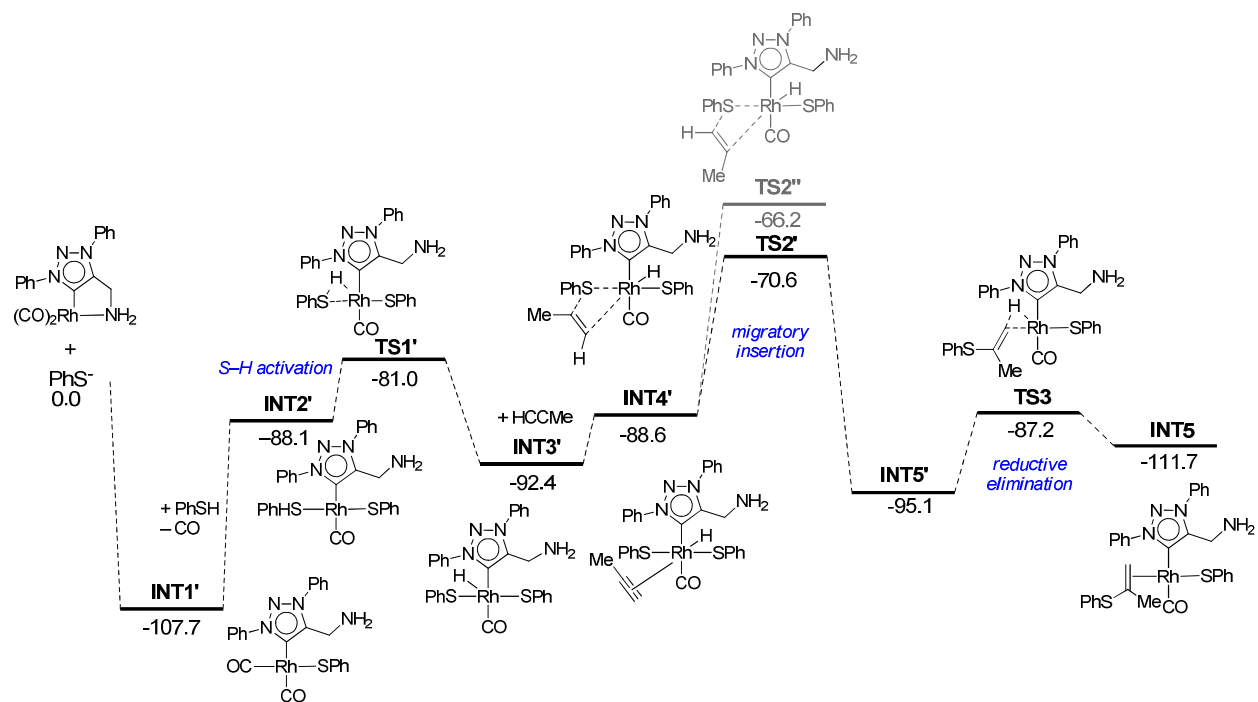


Figure S46. Pathway (c). A hemilabile function was considered without consideration of the N-H effect. Charges omitted for clarity.

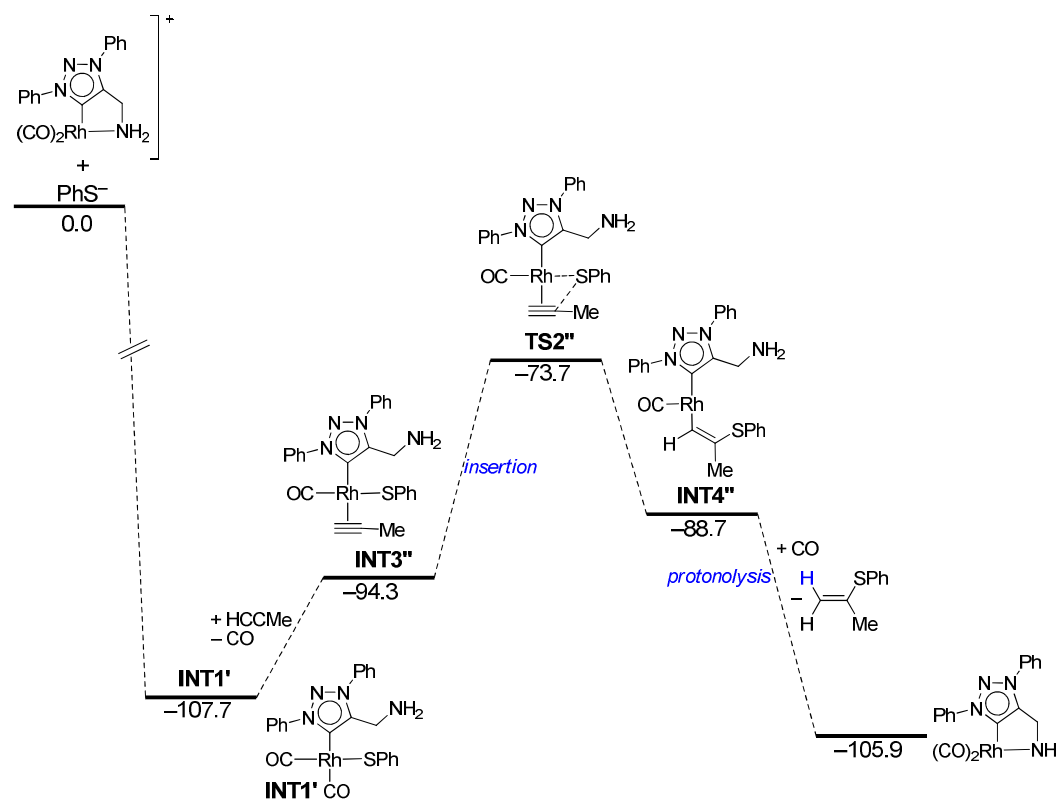


Figure S47. Pathway (d). A hemilabile function was considered without consideration of the N-H effect, and without oxidative addition of a second thiophenol molecule.

Pathway (d) (Figure S47) was calculated to demonstrate a similar mechanism for **5** as that displayed by complex **6**; namely substitution of the amine ligand by thiophenolate (**INT1'**), followed by substitution of the carbonyl ligand (*cis* to the thiolate) by the alkyne to yield **INT3'**. 1,2-Insertion of the alkyne into the Rh-S bond followed by protonolysis delivers the α -vinyl sulphide product in a more energetically favourable pathway as compared to (a) – (c) (Figures S44-S46).

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the main text. All calculations have been performed at the B3LYP-D3/def2-SVP level.

4M: E= -1480.258915

N	2.324488000	-0.548607000	-0.207236000
C	0.881906000	1.048582000	-0.078597000
C	0.968500000	-0.339239000	-0.123483000
N	2.159830000	1.532325000	-0.105362000
N	3.053330000	0.559824000	-0.197065000
Rh	-0.830573000	-1.282795000	0.245235000
C	-2.548440000	-1.942174000	0.782810000
O	-3.510746000	-2.407692000	1.188279000
C	-0.422342000	1.750525000	0.044159000
H	-0.439521000	2.387680000	0.951855000
H	-0.586682000	2.453100000	-0.792708000
N	-1.451794000	0.718186000	0.060660000
C	-0.114432000	-2.983041000	0.442280000
O	0.327095000	-4.036077000	0.590376000
C	3.009979000	-1.799918000	-0.328850000
C	4.124654000	-2.057890000	0.474777000
C	2.551361000	-2.736617000	-1.257963000
C	4.782897000	-3.282043000	0.347202000
C	3.213162000	-3.960226000	-1.370033000
C	4.327025000	-4.234542000	-0.570812000
H	4.459625000	-1.306418000	1.191009000
H	1.678500000	-2.506135000	-1.870094000
H	5.650857000	-3.495748000	0.975185000
H	2.853689000	-4.702360000	-2.086105000
H	4.840684000	-5.194529000	-0.661147000
C	2.621511000	2.884867000	-0.001193000
C	1.930782000	3.909189000	-0.655637000
C	3.763632000	3.155258000	0.761757000
C	2.387852000	5.223322000	-0.533434000

C	4.214011000	4.471588000	0.867625000
C	3.526857000	5.507450000	0.225402000
H	1.054508000	3.684204000	-1.262695000
H	4.283960000	2.337973000	1.261894000
H	1.849974000	6.026464000	-1.041908000
H	5.103774000	4.688943000	1.462937000
H	3.879756000	6.537211000	0.317167000
C	-2.689520000	1.260903000	-0.074921000
O	-2.910379000	2.467966000	-0.142622000
O	-3.669780000	0.319991000	-0.146869000
C	-5.068819000	0.692445000	-0.313014000
C	-5.264817000	1.454033000	-1.629489000
H	-4.871043000	0.859516000	-2.469019000
H	-6.338937000	1.626463000	-1.802805000
H	-4.744097000	2.418429000	-1.603261000
C	-5.547804000	1.502503000	0.896889000
H	-5.030003000	2.468048000	0.946714000
H	-6.633063000	1.677374000	0.825553000
H	-5.348202000	0.942884000	1.824283000
C	-5.791296000	-0.655387000	-0.372433000
H	-5.652821000	-1.215964000	0.562331000
H	-6.868819000	-0.498813000	-0.534222000
H	-5.396816000	-1.265655000	-1.199096000

INT1: E= -2110.351529

N	-1.836188000	1.775070000	-0.338924000
C	-0.981338000	-0.011816000	-1.179335000
C	-0.633565000	1.251184000	-0.721625000
N	-2.330216000	-0.120754000	-1.053152000
N	-2.872202000	0.966507000	-0.535142000
Rh	1.384730000	1.629824000	-0.702279000
C	3.304756000	1.749729000	-0.777725000
O	4.442214000	1.835932000	-0.833269000
C	0.039245000	-1.040917000	-1.519756000
H	-0.272754000	-2.044794000	-1.193065000
H	0.240695000	-1.094423000	-2.600956000
N	1.260122000	-0.593743000	-0.805659000
C	1.171461000	3.463241000	-0.617732000
O	1.010068000	4.598171000	-0.577934000
C	-2.024340000	2.996302000	0.389457000
C	-1.339044000	3.135238000	1.600261000
C	-2.858011000	3.996154000	-0.111825000
C	-1.484630000	4.326534000	2.314140000
C	-2.996430000	5.179803000	0.616934000
C	-2.307114000	5.346618000	1.823249000
H	-0.722033000	2.307627000	1.965039000
H	-3.380120000	3.845463000	-1.058310000
H	-0.956137000	4.453596000	3.261637000

H	-3.639745000	5.976843000	0.237212000
H	-2.414616000	6.277399000	2.385435000
C	-3.148262000	-1.263167000	-1.364461000
C	-3.654733000	-1.408474000	-2.658322000
C	-3.381905000	-2.208203000	-0.365718000
C	-4.423006000	-2.536159000	-2.955454000
C	-4.149611000	-3.332611000	-0.678233000
C	-4.668890000	-3.495828000	-1.966202000
H	-3.448667000	-0.647183000	-3.413493000
H	-2.961990000	-2.069799000	0.630845000
H	-4.829033000	-2.665509000	-3.961240000
H	-4.326952000	-4.081246000	0.096151000
H	-5.267282000	-4.378670000	-2.204137000
C	2.362047000	-1.461055000	-0.982973000
O	2.325019000	-2.463919000	-1.659629000
O	3.379297000	-1.024670000	-0.246546000
C	4.458458000	-1.915961000	0.211179000
C	5.323801000	-2.328575000	-0.979321000
H	5.707366000	-1.436015000	-1.497499000
H	6.183057000	-2.918007000	-0.623565000
H	4.746270000	-2.931856000	-1.691264000
C	3.832926000	-3.108868000	0.937457000
H	3.307344000	-3.772122000	0.237369000
H	4.620938000	-3.688989000	1.441140000
H	3.117335000	-2.748223000	1.692710000
C	5.227884000	-1.026317000	1.185551000
H	4.564699000	-0.699882000	2.000385000
H	6.075670000	-1.581300000	1.614475000
H	5.613596000	-0.134317000	0.670261000
H	1.042195000	-0.605292000	0.325368000
S	0.553266000	-0.501542000	2.117728000
C	-0.533869000	-1.889527000	2.157787000
C	-1.692567000	-1.884283000	2.973123000
C	-0.276325000	-3.071981000	1.418731000
C	-2.530535000	-2.998770000	3.056185000
C	-1.123837000	-4.179558000	1.495578000
C	-2.256460000	-4.158474000	2.318561000
H	-1.917270000	-0.985047000	3.551905000
H	0.620541000	-3.128313000	0.796813000
H	-3.410518000	-2.960116000	3.705323000
H	-0.888341000	-5.074382000	0.911868000
H	-2.909380000	-5.032065000	2.390567000

TS1: E= -2110.349331

N	2.918051000	-0.318846000	-0.155660000
C	1.462936000	1.043375000	-0.968988000
C	1.688901000	-0.311956000	-0.757753000
N	2.540429000	1.707485000	-0.471872000

N	3.448159000	0.885429000	0.024619000
Rh	0.036675000	-1.511816000	-0.959983000
C	-1.633623000	-2.436960000	-1.147645000
O	-2.623328000	-2.998105000	-1.259592000
C	0.180939000	1.578301000	-1.510855000
H	-0.038134000	2.590256000	-1.135926000
H	0.195326000	1.630551000	-2.609957000
N	-0.850932000	0.611070000	-1.090261000
C	1.011357000	-3.060475000	-1.145852000
O	1.638342000	-4.013622000	-1.279936000
C	3.587112000	-1.458745000	0.404813000
C	2.918005000	-2.196400000	1.385698000
C	4.868352000	-1.797749000	-0.032256000
C	3.553349000	-3.317343000	1.924223000
C	5.492191000	-2.918538000	0.520529000
C	4.833820000	-3.679731000	1.492530000
H	1.924193000	-1.878939000	1.715006000
H	5.359738000	-1.191933000	-0.795611000
H	3.044409000	-3.905942000	2.690837000
H	6.492918000	-3.200915000	0.185639000
H	5.323545000	-4.559279000	1.917399000
C	2.655572000	3.121065000	-0.236162000
C	3.570495000	3.887053000	-0.957779000
C	1.821847000	3.675626000	0.740471000
C	3.647531000	5.257753000	-0.696042000
C	1.906739000	5.048022000	0.985261000
C	2.815693000	5.835751000	0.269093000
H	4.208547000	3.413074000	-1.705873000
H	1.135629000	3.023348000	1.292346000
H	4.358667000	5.875331000	-1.249229000
H	1.266219000	5.500354000	1.745725000
H	2.879051000	6.908426000	0.467263000
C	-2.134614000	0.833198000	-1.648372000
O	-2.329775000	1.575340000	-2.582456000
O	-3.025836000	0.114471000	-0.979634000
C	-4.478018000	0.203980000	-1.235069000
C	-4.770240000	-0.256690000	-2.663582000
H	-4.362670000	-1.265794000	-2.827806000
H	-5.859620000	-0.297760000	-2.816524000
H	-4.334624000	0.430657000	-3.400017000
C	-4.940957000	1.637302000	-0.970217000
H	-4.498227000	2.338294000	-1.689963000
H	-6.036964000	1.688631000	-1.058345000
H	-4.661193000	1.936732000	0.050891000
C	-5.060655000	-0.760056000	-0.204845000
H	-4.761067000	-0.464817000	0.810088000
H	-6.159340000	-0.750670000	-0.268628000
H	-4.706685000	-1.783854000	-0.389367000
H	-0.862371000	0.586745000	-0.018624000

S	-0.164417000	0.248030000	1.867575000
C	-1.830247000	0.244168000	2.467913000
C	-2.628794000	1.408944000	2.407704000
C	-2.415906000	-0.915765000	3.021981000
C	-3.942846000	1.414148000	2.880973000
C	-3.730801000	-0.907759000	3.492210000
C	-4.506937000	0.255972000	3.428425000
H	-2.197736000	2.320040000	1.984034000
H	-1.818648000	-1.829020000	3.076821000
H	-4.532146000	2.334404000	2.822602000
H	-4.155473000	-1.823618000	3.914083000
H	-5.535431000	0.259362000	3.797871000

INT2: E= -2110.392139

N	2.294540000	-1.300409000	0.026615000
C	1.777567000	0.749902000	0.468859000
C	1.199909000	-0.461001000	0.085273000
N	3.125739000	0.515926000	0.583638000
N	3.452003000	-0.731845000	0.320042000
Rh	-0.777288000	-0.956019000	-0.418500000
C	-2.596426000	-1.343663000	-0.803680000
O	-3.690862000	-1.559170000	-1.062460000
C	1.190556000	2.123417000	0.707276000
H	1.370354000	2.412422000	1.755198000
H	1.724809000	2.850058000	0.075708000
N	-0.213688000	2.226208000	0.431458000
C	-0.226242000	-1.180825000	-2.191831000
O	0.146818000	-1.306362000	-3.272214000
C	2.294022000	-2.696740000	-0.304505000
C	1.325928000	-3.532984000	0.260266000
C	3.260583000	-3.189723000	-1.185590000
C	1.325564000	-4.887308000	-0.080298000
C	3.250912000	-4.547161000	-1.512336000
C	2.282902000	-5.395482000	-0.964327000
H	0.585848000	-3.123073000	0.949641000
H	4.001023000	-2.511193000	-1.611317000
H	0.571084000	-5.547372000	0.353438000
H	3.997779000	-4.940094000	-2.205988000
H	2.274695000	-6.455808000	-1.227993000
C	4.161976000	1.453455000	0.910510000
C	5.133680000	1.750510000	-0.048500000
C	4.178884000	2.048903000	2.174508000
C	6.139357000	2.666497000	0.267194000
C	5.185378000	2.969068000	2.476401000
C	6.163502000	3.277796000	1.525273000
H	5.091530000	1.267250000	-1.025938000
H	3.421546000	1.781899000	2.913884000
H	6.903461000	2.906761000	-0.475398000

H	5.208748000	3.439140000	3.462021000
H	6.949479000	3.997224000	1.766433000
C	-0.640938000	2.528731000	-0.835922000
O	0.086715000	2.920087000	-1.728520000
O	-1.973691000	2.352320000	-0.916741000
C	-2.721642000	2.625060000	-2.145104000
C	-2.227440000	1.725833000	-3.281642000
H	-2.304169000	0.668894000	-2.990439000
H	-2.853244000	1.884944000	-4.173474000
H	-1.183374000	1.946624000	-3.534666000
C	-2.605467000	4.111215000	-2.495965000
H	-1.571844000	4.370430000	-2.757808000
H	-3.259760000	4.343515000	-3.350547000
H	-2.922101000	4.728016000	-1.640437000
C	-4.157282000	2.265505000	-1.759967000
H	-4.491005000	2.874616000	-0.906145000
H	-4.832933000	2.450618000	-2.608629000
H	-4.231424000	1.205275000	-1.478077000
H	-0.825474000	1.643901000	1.008249000
S	-1.178518000	-0.625937000	1.934531000
C	-2.934413000	-0.448383000	2.241041000
C	-3.558774000	-1.258580000	3.205354000
C	-3.703116000	0.526233000	1.576880000
C	-4.919033000	-1.103991000	3.490350000
C	-5.062908000	0.669657000	1.859064000
C	-5.679471000	-0.142655000	2.817307000
H	-2.969668000	-2.017334000	3.726079000
H	-3.231622000	1.163796000	0.826955000
H	-5.388661000	-1.746493000	4.240614000
H	-5.644250000	1.425705000	1.323470000
H	-6.743977000	-0.027759000	3.037072000

INT3: E= -2113.674401

N	1.078474000	-1.057101000	-1.269093000
C	0.899316000	0.708439000	-0.035465000
C	0.280285000	-0.520239000	-0.281437000
N	1.984809000	0.770309000	-0.862912000
N	2.115207000	-0.299710000	-1.616108000
Rh	-1.365183000	-1.299085000	0.650016000
C	-3.218185000	-1.345582000	1.954950000
C	0.504198000	1.807630000	0.916167000
H	0.908923000	1.583788000	1.913423000
H	0.938380000	2.757100000	0.576346000
N	-0.927897000	1.961717000	1.028732000
C	-2.322472000	-1.229977000	-0.931165000
O	-2.913294000	-1.163142000	-1.921060000
C	0.933374000	-2.318577000	-1.934293000
C	0.454618000	-3.429340000	-1.231674000

C	1.287648000	-2.419075000	-3.284823000
C	0.320314000	-4.649378000	-1.898127000
C	1.153343000	-3.645800000	-3.936545000
C	0.667495000	-4.762184000	-3.247506000
H	0.176464000	-3.329879000	-0.180712000
H	1.659355000	-1.540079000	-3.811835000
H	-0.055141000	-5.517621000	-1.351720000
H	1.422997000	-3.725885000	-4.992227000
H	0.559457000	-5.719320000	-3.763296000
C	2.956112000	1.818799000	-0.965035000
C	3.174852000	2.430183000	-2.201842000
C	3.656636000	2.206357000	0.180183000
C	4.118686000	3.455150000	-2.289765000
C	4.592671000	3.238117000	0.079069000
C	4.824137000	3.861405000	-1.151490000
H	2.603315000	2.105470000	-3.072442000
H	3.485033000	1.688704000	1.125395000
H	4.297121000	3.943992000	-3.250178000
H	5.148785000	3.547780000	0.966800000
H	5.557884000	4.667688000	-1.224790000
C	-1.606936000	2.499016000	-0.034279000
O	-1.071401000	3.122445000	-0.930558000
O	-2.926023000	2.246322000	0.078598000
C	-3.900627000	2.790334000	-0.871837000
C	-3.607411000	2.295161000	-2.291244000
H	-3.557449000	1.197383000	-2.311912000
H	-4.418919000	2.617347000	-2.962521000
H	-2.658083000	2.700736000	-2.660835000
C	-3.895279000	4.318503000	-0.782376000
H	-2.932512000	4.723583000	-1.119999000
H	-4.695725000	4.731769000	-1.415474000
H	-4.073251000	4.640698000	0.255543000
C	-5.224028000	2.214725000	-0.367123000
H	-5.413963000	2.530906000	0.669895000
H	-6.055130000	2.564976000	-0.997496000
H	-5.200601000	1.114986000	-0.399498000
H	-1.404153000	1.234430000	1.558343000
S	-0.218997000	-1.285605000	2.777765000
C	1.529855000	-0.988367000	2.658651000
C	2.360759000	-1.671530000	1.745832000
C	2.139390000	-0.064204000	3.533537000
C	3.732200000	-1.418766000	1.687193000
C	3.516414000	0.175907000	3.485126000
C	4.322088000	-0.491944000	2.555920000
H	1.917145000	-2.413450000	1.081613000
H	1.515234000	0.466061000	4.257544000
H	4.346717000	-1.956852000	0.960154000
H	3.961560000	0.894619000	4.179415000
H	5.396761000	-0.298619000	2.512595000

C	-2.957580000	-2.516233000	1.643976000
H	-2.990707000	-3.590672000	1.559381000
C	-3.747716000	-0.103193000	2.525458000
H	-4.735747000	-0.278390000	2.983080000
H	-3.060416000	0.266017000	3.303785000
H	-3.839470000	0.677721000	1.756286000

TS2: E= -2113.644085

N	0.810527000	-0.520404000	1.285939000
C	-0.430954000	-1.038164000	-0.407622000
C	0.133108000	0.068930000	0.230345000
N	-0.041876000	-2.145570000	0.293036000
N	0.716346000	-1.846142000	1.320221000
Rh	0.172727000	1.981527000	-0.556857000
C	1.762559000	3.543452000	-1.988550000
C	-1.265230000	-1.040746000	-1.661125000
H	-0.619563000	-0.767961000	-2.508528000
H	-1.679738000	-2.037021000	-1.854038000
N	-2.337146000	-0.066724000	-1.596064000
C	-1.087610000	2.648787000	0.600229000
O	-1.922597000	3.047753000	1.296124000
C	1.601689000	0.092701000	2.318617000
C	1.890870000	1.459888000	2.275766000
C	2.096490000	-0.702288000	3.363364000
C	2.678101000	2.029832000	3.278479000
C	2.885033000	-0.119983000	4.355974000
C	3.181413000	1.246736000	4.320228000
H	1.499924000	2.063243000	1.450475000
H	1.865002000	-1.765583000	3.391575000
H	2.898960000	3.099205000	3.235953000
H	3.268269000	-0.743940000	5.167087000
H	3.798852000	1.696827000	5.101348000
C	-0.305071000	-3.530139000	0.021592000
C	-1.626611000	-3.976918000	-0.066751000
C	0.782263000	-4.393679000	-0.140963000
C	-1.853432000	-5.330290000	-0.333249000
C	0.536249000	-5.743582000	-0.398354000
C	-0.779240000	-6.211500000	-0.496439000
H	-2.448452000	-3.268372000	0.064235000
H	1.796044000	-3.995393000	-0.072602000
H	-2.880105000	-5.696576000	-0.406041000
H	1.375452000	-6.430997000	-0.528258000
H	-0.967320000	-7.268242000	-0.701629000
C	-3.321542000	-0.255558000	-0.662272000
O	-3.543453000	-1.327401000	-0.120359000
O	-3.986977000	0.886969000	-0.450221000
C	-5.037025000	1.005687000	0.565441000
C	-4.471834000	0.664011000	1.947806000

H	-3.586354000	1.282642000	2.154136000
H	-5.231510000	0.877915000	2.715736000
H	-4.193977000	-0.395379000	2.010569000
C	-6.221147000	0.113626000	0.185464000
H	-5.935581000	-0.945646000	0.214457000
H	-7.051742000	0.279538000	0.889138000
H	-6.572761000	0.360207000	-0.828533000
C	-5.410199000	2.486038000	0.488062000
H	-5.759996000	2.740662000	-0.523899000
H	-6.213190000	2.712424000	1.205916000
H	-4.535011000	3.108534000	0.723885000
H	-2.043034000	0.902755000	-1.724808000
S	1.521294000	1.152928000	-2.423246000
C	2.660643000	-0.015933000	-1.696300000
C	3.439589000	0.295715000	-0.567884000
C	2.750867000	-1.309598000	-2.242460000
C	4.260168000	-0.669237000	0.019085000
C	3.576812000	-2.271671000	-1.653316000
C	4.330080000	-1.960395000	-0.515953000
H	3.368874000	1.291282000	-0.127005000
H	2.156606000	-1.563875000	-3.123751000
H	4.836131000	-0.411382000	0.911637000
H	3.626314000	-3.274520000	-2.086855000
H	4.968137000	-2.716373000	-0.051698000
C	0.629244000	3.832641000	-1.487055000
H	0.112874000	4.779739000	-1.333534000
C	3.136247000	3.770754000	-2.449533000
H	3.340960000	4.855729000	-2.394232000
H	3.861833000	3.253968000	-1.801739000
H	3.290783000	3.419633000	-3.480525000

INT4: E= -2113.594634

N	-0.365572000	1.405305000	0.854293000
C	1.099406000	0.928536000	-0.656941000
C	0.051199000	0.348365000	0.061675000
N	1.216565000	2.226420000	-0.231753000
N	0.325175000	2.528036000	0.685068000
Rh	-0.734952000	-1.580718000	-0.298450000
C	-2.606269000	-2.666724000	-2.002077000
C	1.903839000	0.283140000	-1.757404000
H	1.241619000	0.133001000	-2.624155000
H	2.726042000	0.933745000	-2.078473000
N	2.427442000	-1.014277000	-1.382464000
C	0.214385000	-2.507261000	0.950136000
O	0.799334000	-3.113104000	1.745811000
C	-1.442924000	1.436385000	1.807754000
C	-2.211209000	0.291325000	2.034121000
C	-1.719740000	2.627122000	2.495889000

C	-3.259983000	0.340711000	2.953284000
C	-2.771066000	2.659827000	3.412187000
C	-3.545795000	1.518911000	3.646378000
H	-1.988194000	-0.627610000	1.479585000
H	-1.114571000	3.513639000	2.313178000
H	-3.861270000	-0.556190000	3.117006000
H	-2.983814000	3.588198000	3.947979000
H	-4.369528000	1.551321000	4.363617000
C	2.135296000	3.249639000	-0.647254000
C	3.509109000	2.990009000	-0.630783000
C	1.626218000	4.491814000	-1.040159000
C	4.383901000	4.003142000	-1.033705000
C	2.514959000	5.494796000	-1.430641000
C	3.892920000	5.250816000	-1.431269000
H	3.875216000	2.010816000	-0.311466000
H	0.548185000	4.660156000	-1.032518000
H	5.459639000	3.812851000	-1.026332000
H	2.128489000	6.468995000	-1.739121000
H	4.585388000	6.037346000	-1.740918000
C	3.408420000	-1.075347000	-0.428605000
O	4.073569000	-0.112264000	-0.077927000
O	3.528383000	-2.324841000	0.032980000
C	4.431184000	-2.672076000	1.135441000
C	4.051868000	-1.877032000	2.388284000
H	2.988689000	-2.032615000	2.622069000
H	4.651551000	-2.230434000	3.241455000
H	4.237386000	-0.804900000	2.246504000
C	5.881339000	-2.429345000	0.709893000
H	6.066233000	-1.360587000	0.543559000
H	6.562954000	-2.792806000	1.494653000
H	6.101631000	-2.977320000	-0.219564000
C	4.155248000	-4.161841000	1.336629000
H	4.379097000	-4.720844000	0.415373000
H	4.783790000	-4.556136000	2.149581000
H	3.097911000	-4.318498000	1.593044000
H	1.735216000	-1.765594000	-1.345581000
S	-2.230133000	-0.878884000	-2.184872000
C	-3.500628000	-0.000690000	-1.251624000
C	-4.507115000	-0.658324000	-0.534503000
C	-3.415680000	1.398562000	-1.222297000
C	-5.427243000	0.089010000	0.204797000
C	-4.329506000	2.134808000	-0.464785000
C	-5.340403000	1.483792000	0.248464000
H	-4.546015000	-1.748850000	-0.530883000
H	-2.623458000	1.908993000	-1.776848000
H	-6.209236000	-0.428115000	0.767021000
H	-4.246189000	3.223855000	-0.427829000
H	-6.050239000	2.060904000	0.845261000
C	-1.775275000	-3.158998000	-1.064978000

H	-1.792651000	-4.238238000	-0.856690000
C	-3.632352000	-3.283063000	-2.904093000
H	-3.716599000	-4.360200000	-2.689429000
H	-4.628673000	-2.826027000	-2.769644000
H	-3.363791000	-3.161145000	-3.968050000

VIII. References

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