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Supplementary Information

Synthesis and Characterization of Rhena[10]annulynes

Qiang Cao,[a] Ping Wang,[a] Yuanting Cai,[b] Yuhui Hua,[b] Shaohui Zheng,[a] Xu Cheng,[a] Guomei He,[a] Ting Bin Wen,[b] and Jiangxi Chen*[a]

[a]Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, People's Republic of China. E-mail: chenjx@xmu.edu.cn

[b]Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China.

*Corresponding author: chenjx@xmu.edu.cn

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1. Experimental Procedures

General Information: All manipulations were carried out under an argon atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (tetrahydrofuran) or calcium hydride (CH_2Cl_2). Reagents were used as received from commercial sources without further purification. $ReH_5(PMePh_2)_3$ (**1**),[1] alkynol **2** (**2a,** R = ^{t}Bu; **2b**, R = 1-Ad),[2-4] were prepared according to the previously published procedure. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra were collected on a Bruker AVIII-400 spectrometer at room temperature. ^{1}H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4. Two-dimensional and one-dimensional NMR spectra are abbreviated as HMBC (heteronuclear multiple bond coherence) and DEPT (distortionless enhancement by polarization transfer). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High resolution mass spectra (HRMS) experiments were recorded on an Agilent 1290-6545XT. Elemental analyses were performed on a Flash Smart CHNS/O elemental analyzer.

Synthesis and characterization of Complex 3a: The solution of rhenium hydride $ReH_5(PMePh_2)_3$ (1) (1.7054 g, 2.15 mmol) and alkynol (2a) (1.0645 g, 3.45 mmol) in dichloromethane (20 mL) was added with hydrogen chloride (2.0 M in diethyl ether, 3.2 mL, 6.4 mmol), and the mixture was stirred at room temperature for 12 h to obtain a green solution. The solvent of the reaction mixture was removed under vacuum. The residue was washed with methanol (2.5 mL × 1, 2 mL × 4) to give a green solid, which was collected by filtration and dried under vacuum. Yield, 2.2075 g, 89.3 %. ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ -10.73 (d, J_{PP} = 11.5 Hz, *P*MePh$_2$), -13.48 ppm (t, J_{PP} = 11.2 Hz, *P*MePh$_2$). ^{1}H NMR (400.0 MHz, CD_2Cl_2): 0.29 (s, 9 H, Si*Me*$_3$), 1.08 (s, 9 H, H15), 1.90 (d, J_{PH} = 9.3 Hz, 3 H, P*Me*Ph$_2$), 2.39 (br, 6 H, P*Me*Ph$_2$), 4.25 (br, 1 H, H2), 6.74 (dd, J_{PH} = 8.6 Hz, J_{HH} = 7.3 Hz, 4 H, *Ph*), 6.92 (t, J_{HH} = 6.9 Hz, 4 H, *Ph*), 7.02-7.22 (m, 8 H, *Ph*), 7.20-7.29 (m, 2 H, H11 and H12), 7.27-7.43 (m, 6 H, *Ph*), 7.50 (d, J_{HH} = 7.4 Hz, 1 H, H13), 7.52-7.76 (m, 8 H, *Ph*), 8.12 ppm (d, J_{HH} = 7.4 Hz, 1 H, H10). ^{13}C NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC): δ 262.2 (q, J_{PC} = 15.4 Hz, C1), 141.7 (d, J_{PC} = 2.2 Hz, C2), 139.6 (d, J_{PC} = 46.9 Hz, *Ph*), 139.6 (q, J_{PC} =

3.0 Hz, C3), 138.4 (t, J_{PC} = 20.3 Hz, *Ph*), 138.1 (t, J_{PC} = 22.8 Hz, *Ph*), 134.8 (s, C10), 133.9 (t, J_{PC} = 4.2 Hz, *Ph*), 133.5 (s, C13), 133.2 (t, J_{PC} = 4.6 Hz, *Ph*), 133.0 (d, J_{PC} = 9.1 Hz, *Ph*), 129.6 (s *Ph*), 129.4 (s *Ph*), 129.2 (s, C11), 129.1 (s, *Ph*), 128.7 (s, C12), 128.3 (t, J_{PC} = 3.9 Hz, *Ph*), 127.6-127.9 (m, *Ph*), 125.4 (s, C6), 125.3 (s, C7), 104.7 (s, C8), 99.0 (s, C5), 98.6 (s, C9), 94.9 (s, C4), 37.4 (s, C14), 29.0 (s, C15), 20.8 (d, J_{PC} = 35.8 Hz, P*Me*Ph_2), 17.5 (t, J_{PC} = 16.6 Hz, P*Me*Ph_2), 0.1 ppm (s, Si*Me*$_3$). Elemental analysis calcd (%) for $C_{59}H_{62}Cl_2P_3ReSi$: C, 61.66; H, 5.44. Found: C, 61.79; H, 5.49.

Synthesis and characterization of Complex 3b. The solution of rhenium hydride $ReH_5(PMePh_2)_3$ (1) (1.7785 g, 2.25 mmol) and alkynol (2b) (1.2998 g, 3.37 mmol) in dichloromethane (20 mL) was added with hydrogen chloride (2.0 M in diethyl ether, 3.2 mL, 6.4 mmol), and the mixture was stirred at room temperature for 12 h to obtain a green solution. The solvent of the reaction mixture was removed under vacuum. The residue was washed with methanol (4 mL × 5) to give a green solid, which was collected by filtration and dried under vacuum. Yield, 1.9261 g, 69.9 %.$^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ -10.38 (d, J_{PP} = 11.4 Hz, *P*$MePh_2$), -13.29 ppm (t, J_{PP} = 11.4 Hz, *P*$MePh_2$). ^1H NMR (400.0 MHz, CD_2Cl_2): 0.31 (s, 9 H, Si*Me*$_3$), 1.57-1.96 (m, 15 H, Ad), 2.05 (br, 3 H, P*Me*Ph_2), 2.36 (br, 6 H, P*Me*Ph_2), 4.28 (br, 1 H, H2), 6.78 (dd, J_{PH} = 8.4 Hz, J_{HH} = 7.1 Hz, 4 H, *Ph*), 6.95 (t, J_{HH} = 7.1 Hz, 4 H, *Ph*), 7.10-7.45 (m, 16 H, *Ph*), 7.51 (d, J_{HH} = 7.2 Hz, 1 H, H13), 7.55-7.77 (m, 8 H, *Ph*), 7.93 ppm (d, J_{HH} = 7.4 Hz, 1 H, H10). ^{13}C NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C DEPT-135, ^1H-^{13}C HSQC and ^1H-^{13}C HMBC): δ 262.2 (q, J_{PC} = 15.5 Hz, C1), 142.0 (d, J_{PC} = 3.7 Hz, C2), 139.5 (d, J_{PC} = 46.5 Hz, *Ph*), 139.5 (q, J_{PC} = 3.8 Hz, C3), 138.3 (t, J_{PC} = 20.5 Hz, *Ph*), 137.9 (t, J_{PC} = 22.8 Hz, *Ph*), 134.5 (s, C10), 133.8 (t, J_{PC} = 4.6 Hz, *Ph*), 133.6 (s, C13), 133.1 (t, J_{PC} = 4.8 Hz, *Ph*), 132.9 (d, J_{PC} = 8.7 Hz, *Ph*), 129.4 (s *Ph*), 129.2 (s *Ph*), 129.0 (s, *Ph*), 128.8 (s, C11), 128.5 (s, C12), 128.1 (t, J_{PC} = 4.2 Hz, *Ph*), 127.5-127.8 (m, *Ph*), 125.1 (s, C6), 124.8 (s, C7), 104.7 (s, C8), 98.7 (s, C5), 98.7 (s, C9), 94.2 (s, C4), 40.7 (s, Ad), 38.7 (s, Ad), 36.7 (s, Ad), 28.7 (s, Ad), 20.5 (d, J_{PC} = 35.6 Hz, P*Me*Ph_2), 17.3 (t, J_{PC} = 16.6 Hz, P*Me*Ph_2), 0.0 ppm (s, Si*Me*$_3$). Elemental analysis calcd (%) for $C_{65}H_{68}Cl_2P_3ReSi$: C, 63.61; H, 5.58. Found: C, 63.76; H, 5.59.

Synthesis and characterization of Complex 4a. To a solution of (**3a**) (0.3003 g, 0.26 mmol) in THF (6 mL) was added tetrabutylammonium flouride (TBAF) (1.0 M in THF, 0.32 mL, 0.32 mmol). The mixture was stirred at room temperature for 3 h to give a yellow green solution. The solvent of reaction mixture was dried under vacuum to give a solid. The resulting solid was dissolved in dichloromethane (1.5 mL) and then was loaded on a silica gel column. The column was flashed with dichloromethane and eluted with dichloromethane/tetrahydrofuran (20:1) to give an orange solution. The solvent of the orange solution was dried under vacuum to give an orange solid, which was washed with tetrahydrofuran (0.1 mL × 2) and hexane (0.6 mL × 4) and dried under vacuum. Yield, 139.9 mg, 61.0 %. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 1.12, -0.25 ppm (ABq, J_{AB} = 224.3 Hz, Re*P*MePh$_2$). ^{1}H NMR plus $^{1}H\{^{31}P\}$ (400.0 MHz, CD_2Cl_2): δ 1.08 (s, 9 H, H15), 2.10 (d, J_{PH} = 8.4 Hz, 3 H, P*Me*Ph$_2$), 2.41 (d, J_{PH} = 8.7 Hz, 3 H, P*Me*Ph$_2$), 5.10 (t, J_{PH} = 5.5 Hz, 1 H, H8), 5.86 (br, 1 H, H2), 6.83-7.89 (m, 24 H, *Ph*), 7.02 (t, J_{HH} = 7.0 Hz, 1 H, H12 mentioned above), 7.16 (t, J_{HH} = 7.5 Hz, 1 H, H11 mentioned above), 7.25 (d, J_{HH} = 9.0 Hz, 1 H, H13 mentioned above), 7.34 ppm (d, J_{HH} = 7.8 Hz, 1 H, H10 mentioned above). ^{13}C NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC): δ 332.6 (t, J_{PC} = 11.7 Hz, C1), 276.5 (t, J_{PC} = 13.7 Hz, C9), 156.3 (t, J_{PC} = 3.5 Hz, C3), 137.1 (s, C2), 135.5 (dt, J_1 = 43.2 Hz, J_2 = 9.2 Hz, *Ph*), 134.2 (dd, J_1 = 41.1 Hz, J_2 = 8.0 Hz, *Ph*), 133.6 (s, C7), 133.5 (d, J_{PC} = 8.8 Hz, *Ph*), 133.0 (d, J_{PC} = 7.8 Hz, *Ph*), 132.6 (d, J_{PC} = 16.5 Hz), 132.6 (s, *Ph*), 131.8 (s, C11), 130.5 (d, J_{PC} = 23.0 Hz, *Ph*), 130.3 (s, C12), 130.0 (s, *Ph*), 128.3 (dd, J_1 = 13.4 Hz, J_2 = 8.6 Hz *Ph*), 127.6 (dd, J_1 = 21.6 Hz, J_2 = 8.3 Hz, *Ph*), 127.2 (s, C13), 125.7 (s, C10), 121.6 (s, C6), 113.5 (s, C8), 104.3 (s, C5), 93.3 (s, C4), 36.4 (s, C14), 29.1 (s, C15), 15.0 (dd, J_1 = 30.4 Hz, J_2 = 5.5 Hz, P*Me*Ph$_2$), 12.8 ppm (dd, J_1 = 29.2 Hz, J_2 = 5.9 Hz, P*Me*Ph$_2$). Elemental analysis (%) calcd for $C_{43}H_{41}Cl_2P_2Re$: C 58.90, H 4.71; found: C 58.86, H 4.65.

Synthesis and characterization of Complex 4b. To a solution of (**3b**) (0.5000 g, 0.41 mmol) in THF (10 mL) was added tetrabutylammonium flouride (TBAF) (1.0 M in THF, 0.61 mL, 0.61 mmol). The mixture was stirred at room temperature for 3 h to give a yellow green solution. The solvent of reaction mixture was dried under vacuum to give a solid. The resulting solid was dissolved in dichloromethane (2 mL) and then was loaded on a

silica gel column. The column was flashed with dichloromethane and eluted with dichloromethane/tetrahydrofuran (20:1) to give an orange solution. The solvent of the orange solution was dried under vacuum to give an orange solid. The resulted solid was redissolved with tetrahydrofuran (1.5 mL) and then hexane (20 mL) was added to give an orange precipitate, which was collected by filtration, washed with hexane (3 mL × 2) and dried under vacuum. Yield, 175.4 mg, 45.0 %. $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 1.29, -0.60 ppm (ABq, J_{AB} = 224.6 Hz, Re*P*MePh$_2$). ^{1}H NMR plus $^{1}H\{^{31}P\}$ (400.0 MHz, CD_2Cl_2,): 1.56-1.80 (m, 12 H, Ad), 2.01 (br, 3 H, Ad), 2.07 (d, J_{PH} = 9.0 Hz, 3 H, P*Me*Ph$_2$), 2.38 (d, J_{PH} = 9.4 Hz, 3 H, P*Me*Ph$_2$), 5.04 (t, J_{PH} = 5.5 Hz, 1 H, H8), 5.82 (br, 1 H, H2), 6.83-7.89 (m, 24 H, *Ph*), 7.00 (t, J_{HH} = 7.0 Hz, 1 H, H12 mentioned above), 7.13 (t, J_{HH} = 7.4 Hz, 1 H, H11 mentioned above), 7.22 (d, J_{HH} = 8.0 Hz, 1 H, H13 mentioned above), 7.32 ppm (d, J_{HH} = 7.7 Hz, 1 H, H10 mentioned above). ^{13}C NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C DEPT-135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC): δ 332.6 (t, J_{PC} = 11.8 Hz, C1), 276.8 (t, J_{PC} = 13.1 Hz, C9), 156.2 (t, J_{PC} = 3.5 Hz, C3), 136.8 (s, C2), 135.5 (dt, J_1 = 45.9 Hz, J_2 = 4.9 Hz, *Ph*), 134.4 (dd, J_1 = 42.3 Hz, J_2 = 5.1 Hz, *Ph*), 134.2 (dd, J_1 = 43.1 Hz, J_2 = 5.4 Hz, *Ph*), 133.5 (s, C7), 133.3 (dd, J_1 = 53.0 Hz, J_2 = 8.3 Hz, *Ph*), 132.6 (t, J_{PC} = 8.0 Hz, *Ph*), 131.8 (s, C10), 130.5 (d, J_{PC} = 27.7 Hz, *Ph*), 130.2 (s, C12), 130.0 (d, J_{PC} =7.7 Hz, *Ph*), 128.3 (dd, J_1 = 15.9 Hz, J_2 = 9.0 Hz, *Ph*), 127.6 (dd, J_1 = 26.2 Hz, J_2 = 8.7 Hz, *Ph*), 127.1 (s, C13), 125.6 (s, C11), 121.5 (s, C6), 113.4 (s, C8), 104.6 (s, C5), 93.0 (s, C4), 41.3 (s, Ad), 38.3 (s, Ad), 36.6 (s, Ad), 28.8 (s, Ad), 14.9 (dd, J_1 = 32.2 Hz, J_2 = 3.4 Hz, P*Me*Ph$_2$), 12.8 ppm (dd, J_1 = 31.3 Hz, J_2 = 3.5 Hz, P*Me*Ph$_2$). Elemental analysis (%) calcd for $C_{49}H_{47}Cl_2P_2Re$: C 61.63, H 4.96; found: C 61.90, H 5.27.

2. X-ray Crystallographic Analysis

Single crystals of **3a** and **4a** suitable for X-ray diffraction were grown from dichloromethane (for **3a**) or toluene (for **4a**) solution layered with hexane. The single crystal X-ray diffraction data of **3a** was collected on a SuperNova Dual Cu at home/near Atlas diffractometer using Mo Kα radiation (λ = 0.71073 Å). The single crystal X-ray diffraction data of **4a** was collected on a XtaLAB Synergy Dualflex HyPix diffractometer using Cu Kα radiation (λ = 1.54184 Å). Using Olex2,[5] the structures of **3a** and **4a** were solved with the Shelxt[6] structure solution program using Intrinsic Phasing and refined

with the Shelxt[6] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Some of the solvent molecules and phenyl groups were disordered and refined with suitable restrains. The X-ray crystal structures have been deposited in the Cambridge Crystallographic Data Centre under the deposition numbers CCDC-2152928 (complex **3a**) and CCDC-2152927 (complex **4a**). The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

Table S1. Crystallographic data and refinement details for **3a** and **4a**.

	3a	**4a**
Empirical formula	$C_{60}H_{64}Cl_4P_3ReSi$	$C_{93.58}H_{90.67}Cl_4P_4Re_2$
Color & habit	pink, plate	yellow, block
Crystal size (mm^3)	0.12 x 0.11 x 0.05	0.1 x 0.08 x 0.05
Temperature (K)	100.00(10)	100.00(19)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pna2_1$
a (Å)	16.2507(3)	24.4910(4)
b (Å)	20.9637(2)	12.5355(2)
c (Å)	18.1840(3)	28.4851(5)
α (°)	90	90
β (°)	115.618(2)	90
γ (°)	90	90
V ($Å^3$), Z	5585.86(17), 4	8745.1(3), 4
D_{cal} (g/cm^3)	1.467	1.408
μ (mm^{-1})	2.512	7.472
2θ range for data collection (°)	6.786 to 61.03	6.206 to 130
Reflections collected	30022	40523
Indep. Reflection, R_{int}, R_{sigma}	14449, 0.0219, 0.0331	12591, 0.0468, 0.0477
Data/ restraints/ parameters	14449/0/631	12583/385/980
Goodness-of-fit on F^2	1.042	1.034
R_1 [I > 2sigma(I)], wR_2	0.0237, 0.0518	0.0414, 0.1105
R_1 (all data), wR_2	0.0275, 0.0537	0.0454, 0.1144
Largest diff. peak and hole ($e \cdot Å^{-3}$)	1.49/-1.22	1.45/-0.59

3. NMR and HRMS Spectra

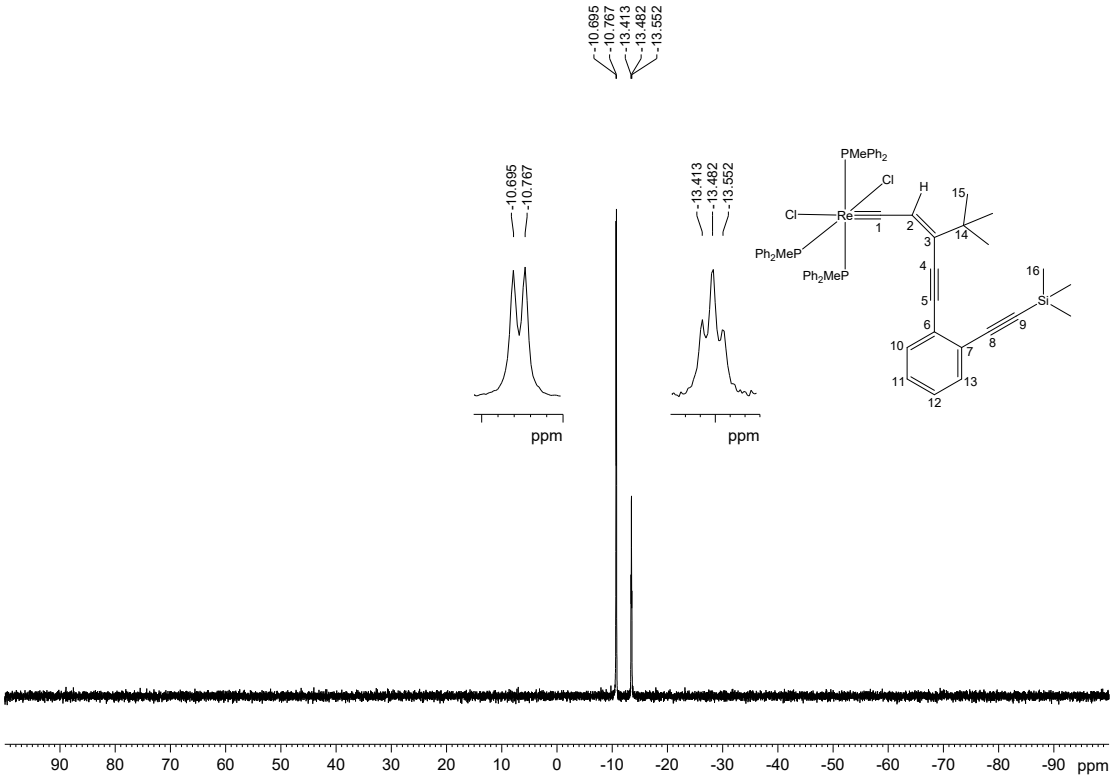


Figure S1. The $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz) of **3a** in CD_2Cl_2.

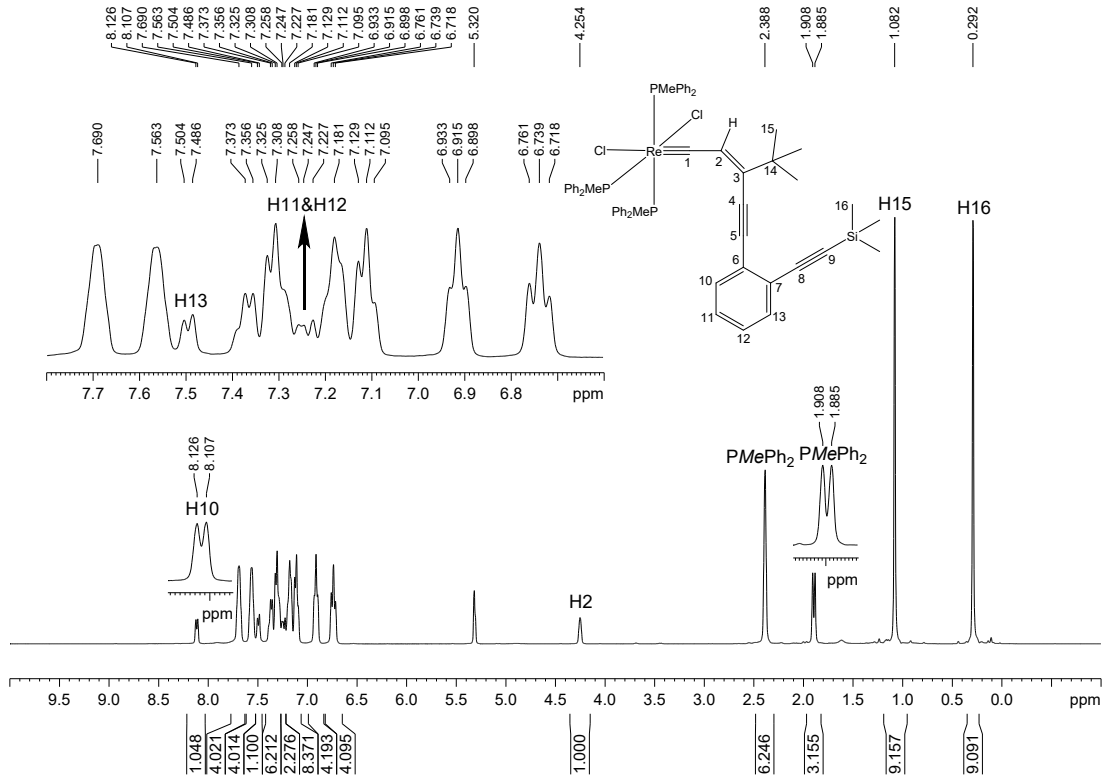


Figure S2. The ^{1}H NMR spectrum (400.0 MHz) of **3a** in CD_2Cl_2.

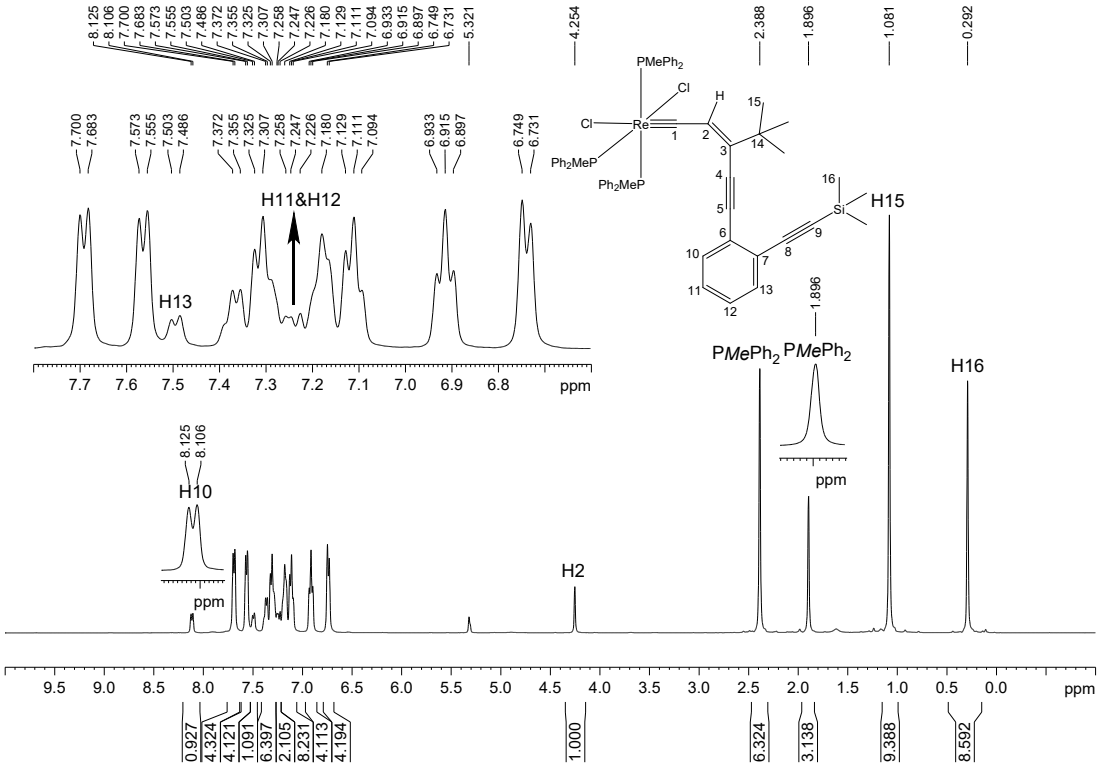


Figure S3. The $^{1}H\{^{31}P\}$ NMR spectrum (400.0 MHz) of **3a** in CD_2Cl_2.

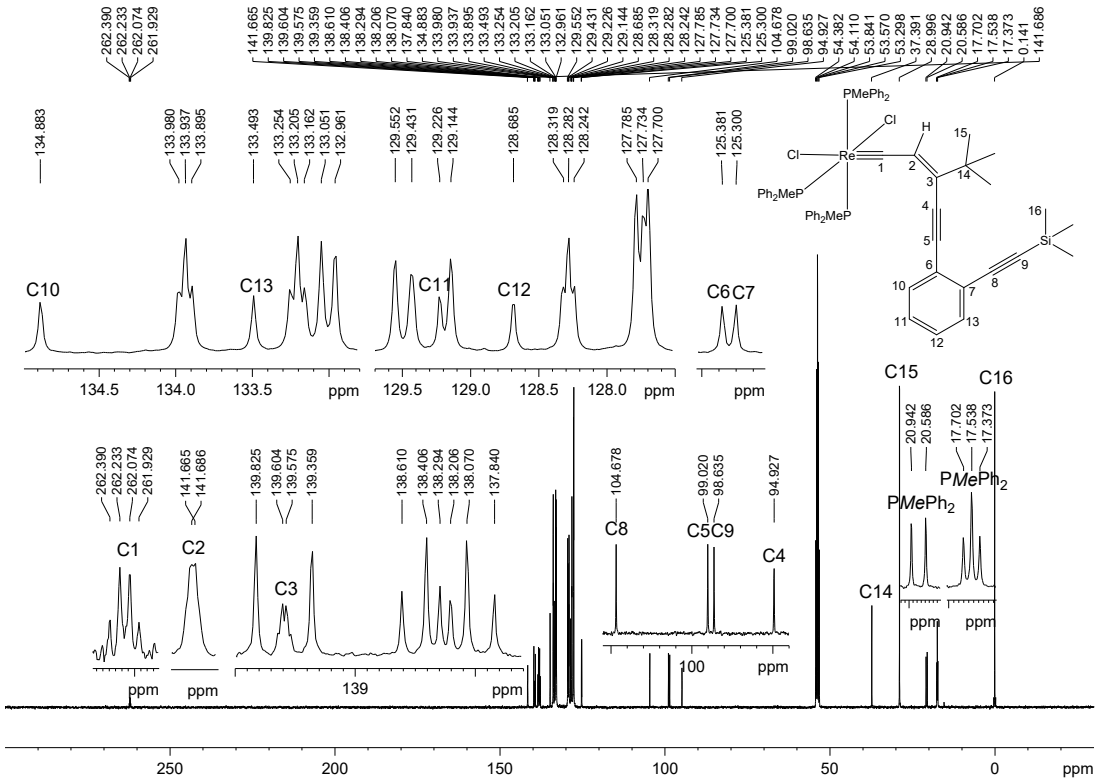


Figure S4. The $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of **3a** in CD_2Cl_2.

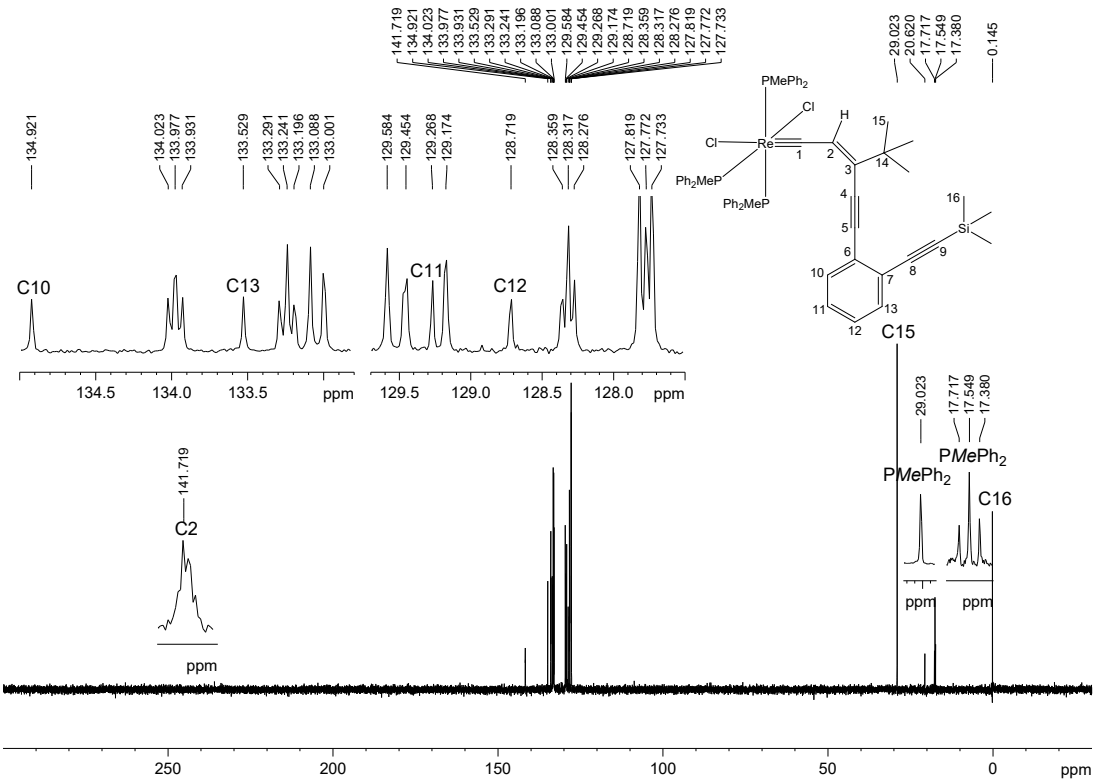


Figure S5. The ^{13}C DEPT135 NMR spectrum (100.6 MHz) of **3a** in CD_2Cl_2.

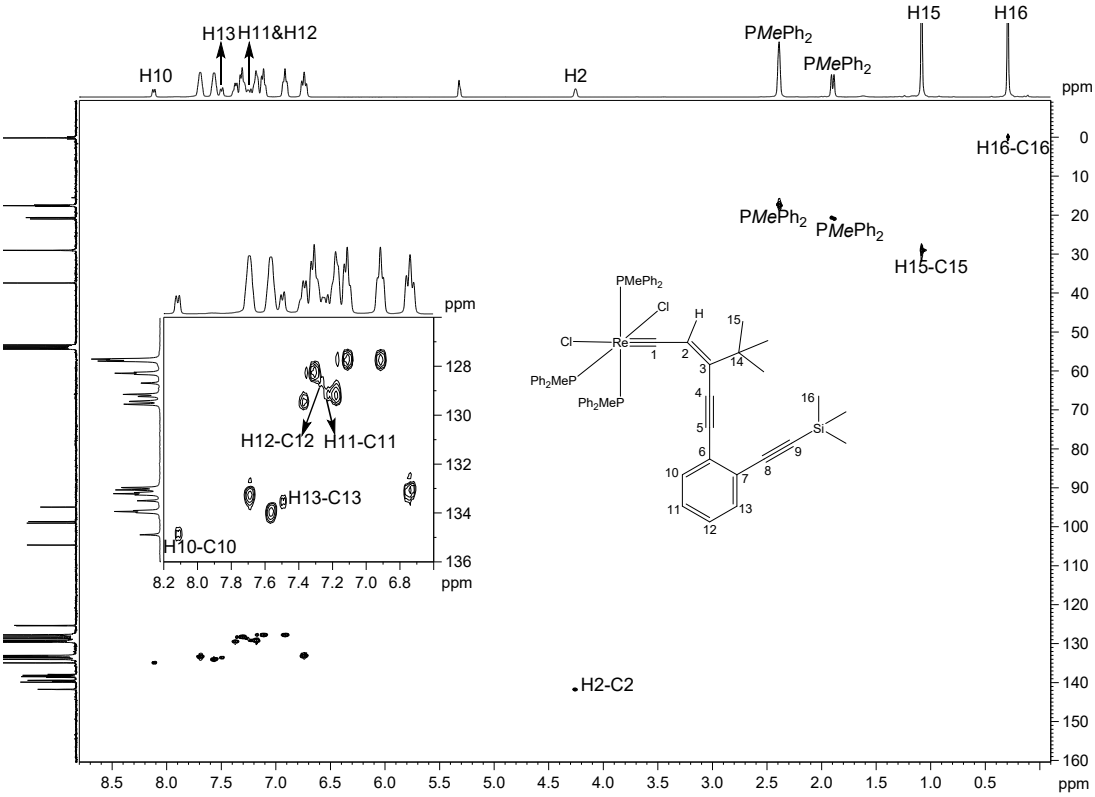


Figure S6. The ^{1}H-^{13}C HSQC spectrum of **3a** in CD_2Cl_2.

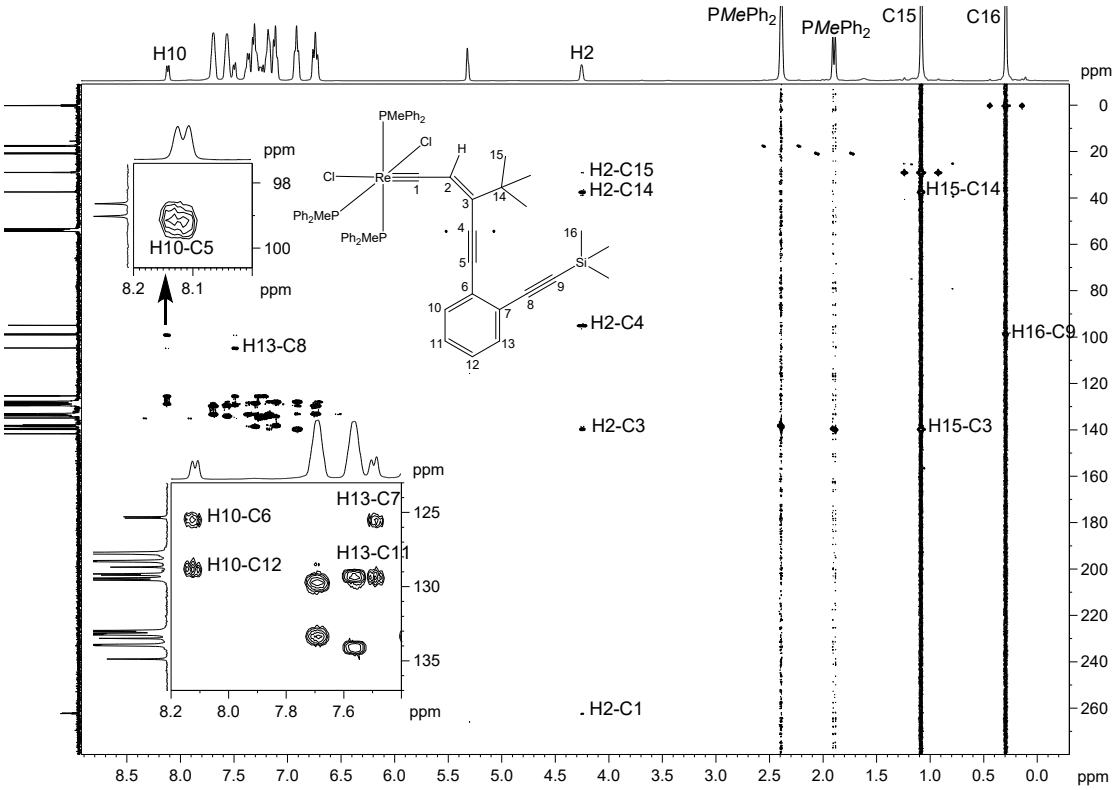


Figure S7. The ^{1}H-^{13}C HMBC spectrum of **3a** in CD_2Cl_2.

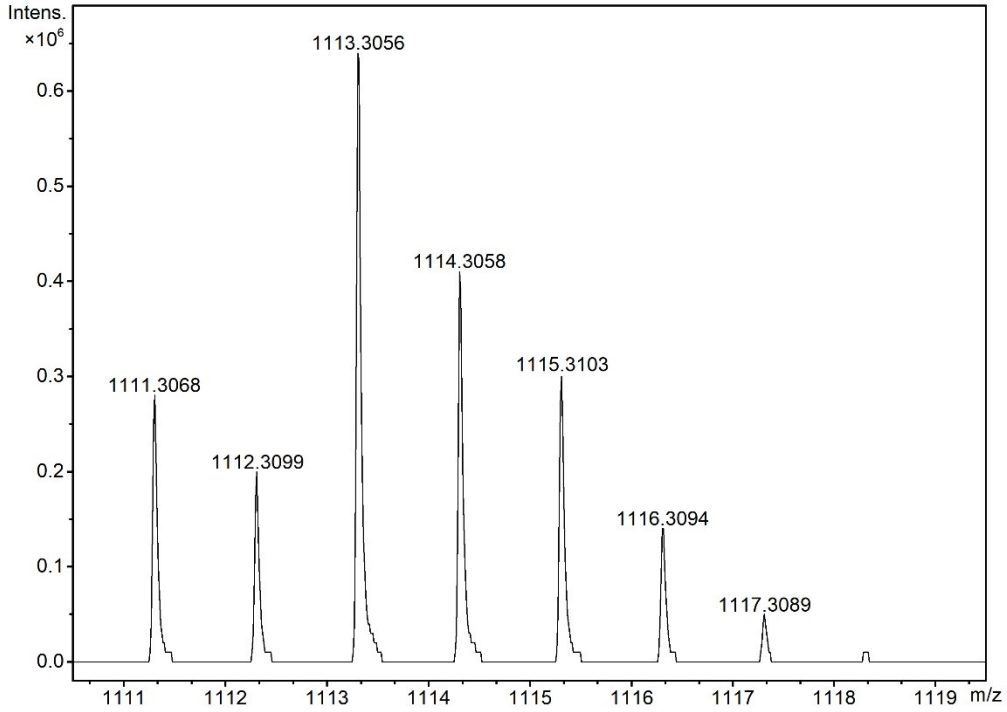


Figure S8. The HRMS spectrum of [**3a**-Cl]$^{+}$ measured in dichloromethane.

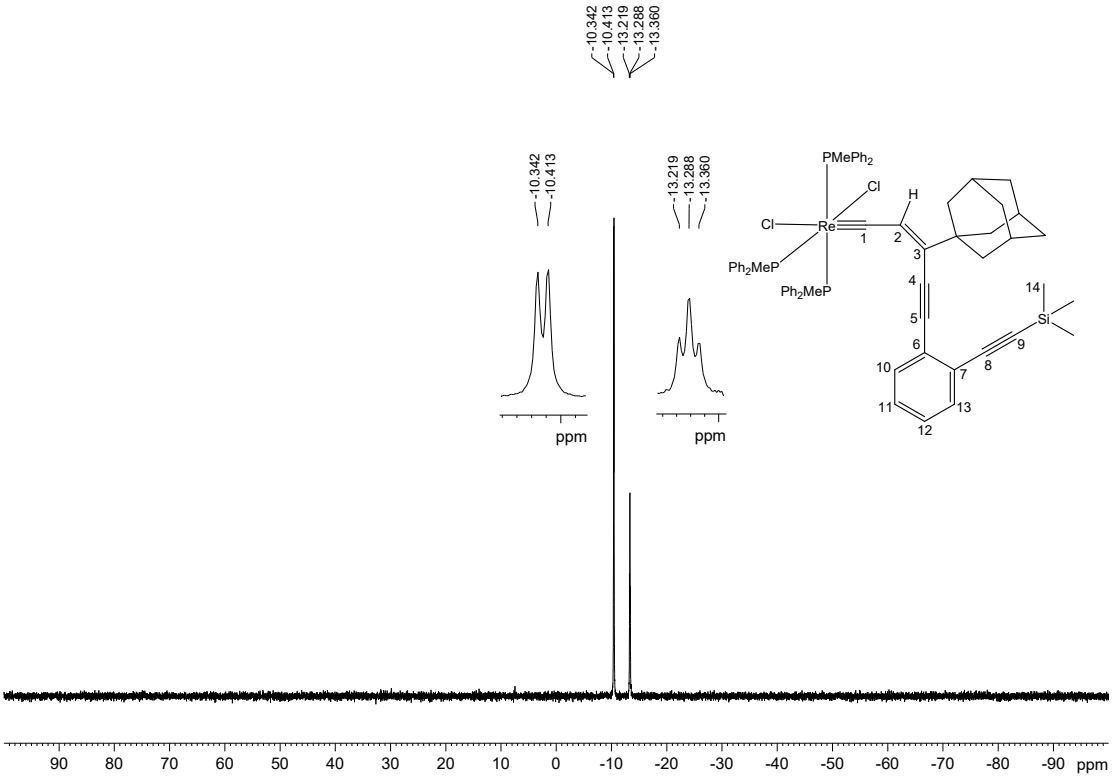


Figure S9. The $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz) of **3b** in CD_2Cl_2.

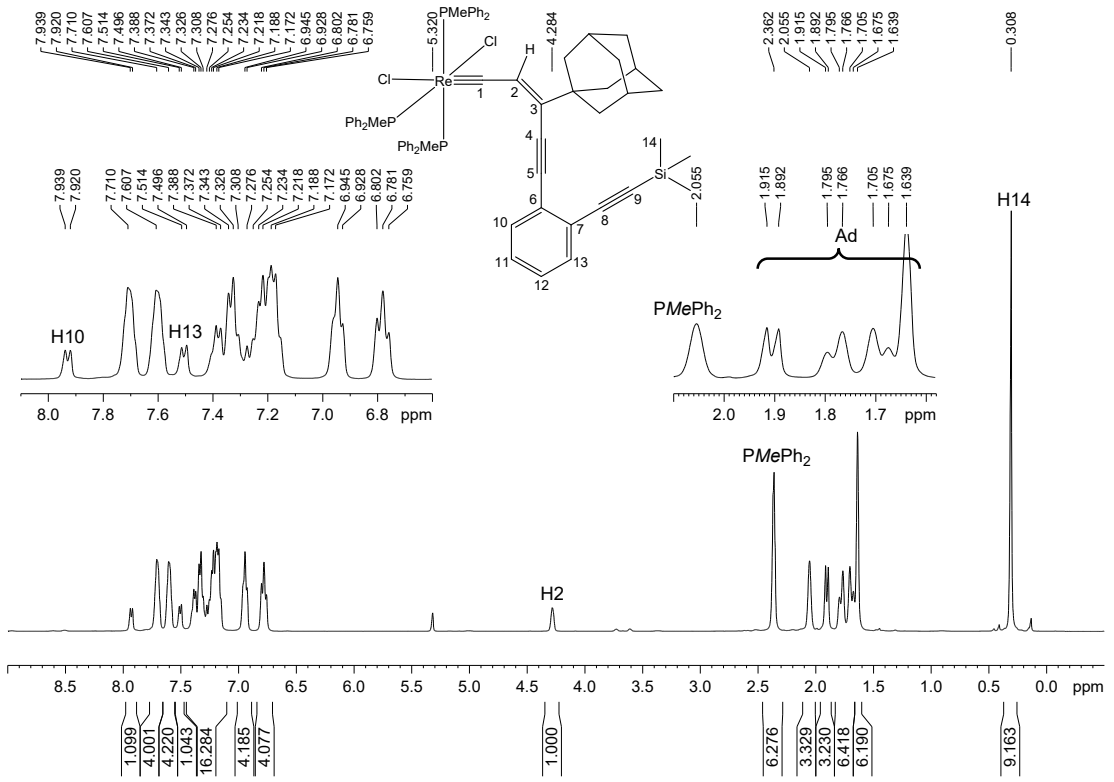


Figure S10. The ^{1}H NMR spectrum (400.0 MHz) of **3b** in CD_2Cl_2.

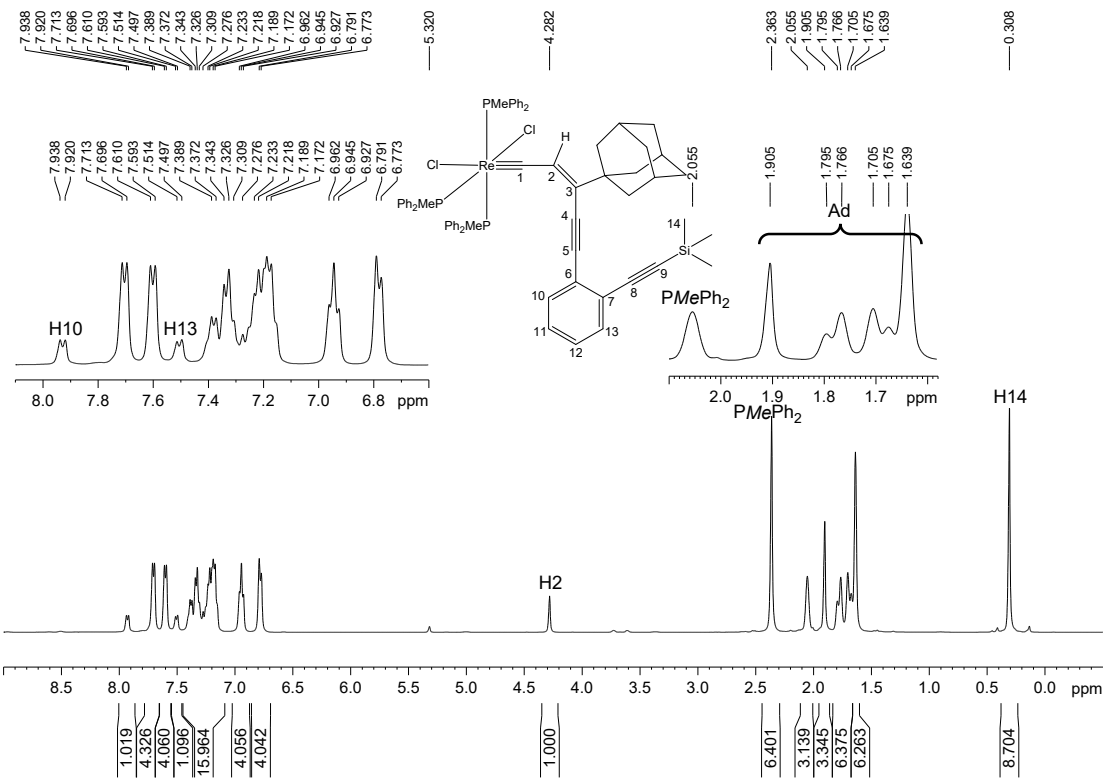


Figure S11. The $^{1}H\{^{31}P\}$ NMR spectrum (400.0 MHz) of **3b** in CD_2Cl_2.

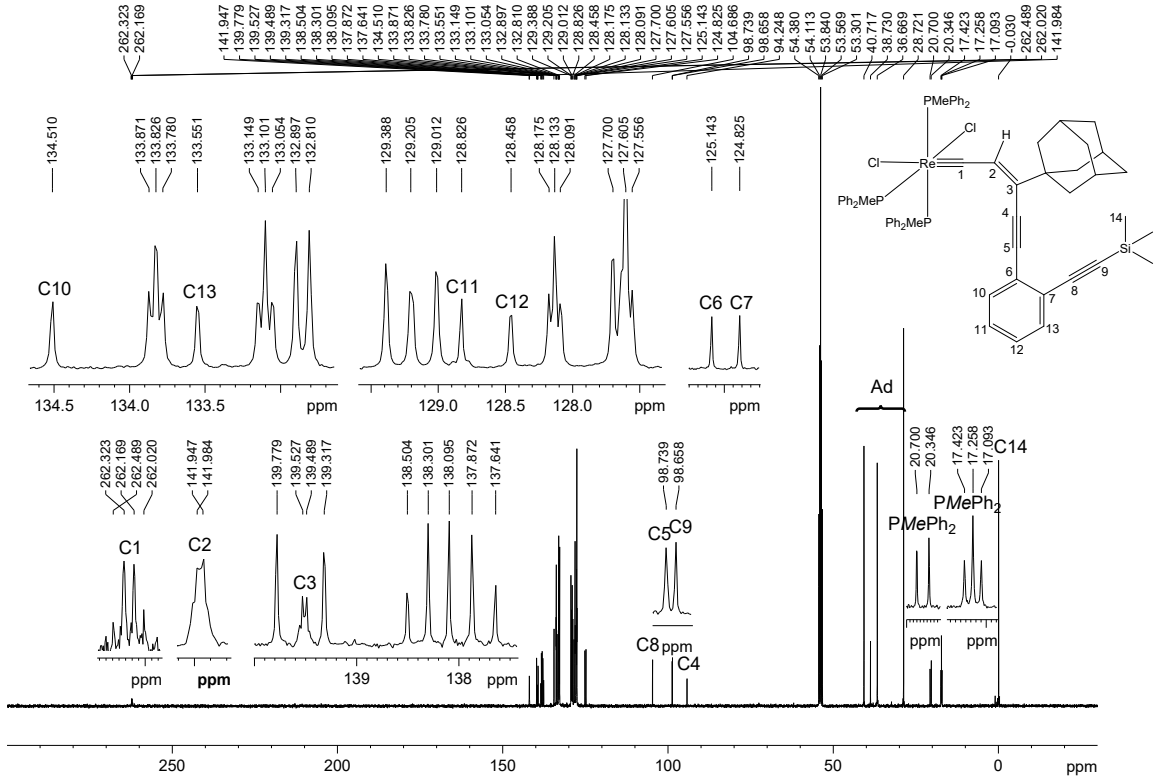


Figure S12. The $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of **3b** in CD_2Cl_2.

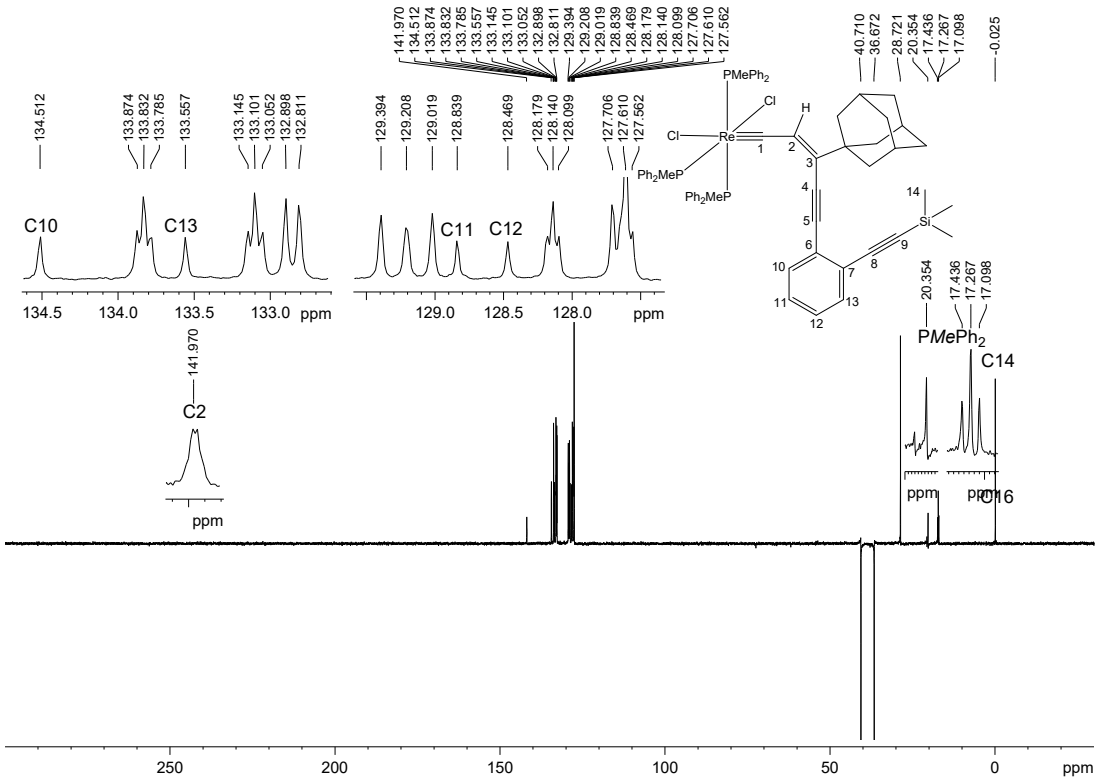


Figure S13. The ^{13}C DEPT135 NMR spectrum (100.6 MHz) of **3b** in CD_2Cl_2.

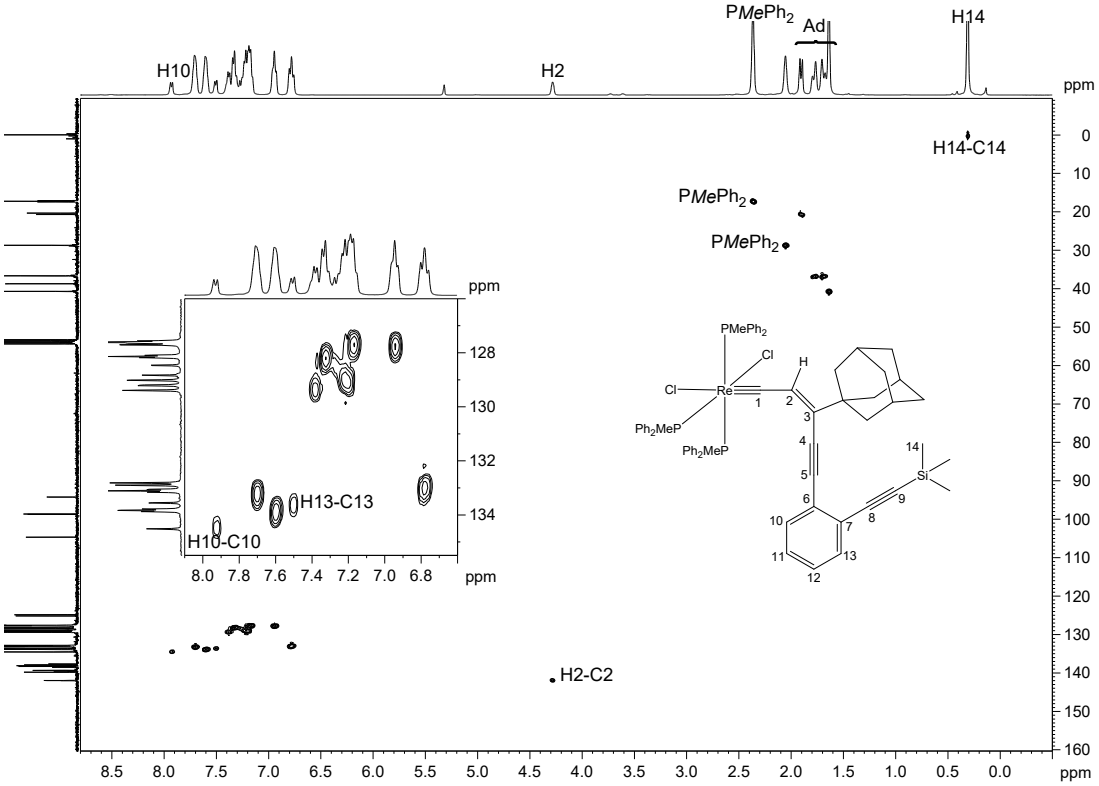


Figure S14. The ^{1}H-^{13}C HSQC spectrum of **3b** in CD_2Cl_2.

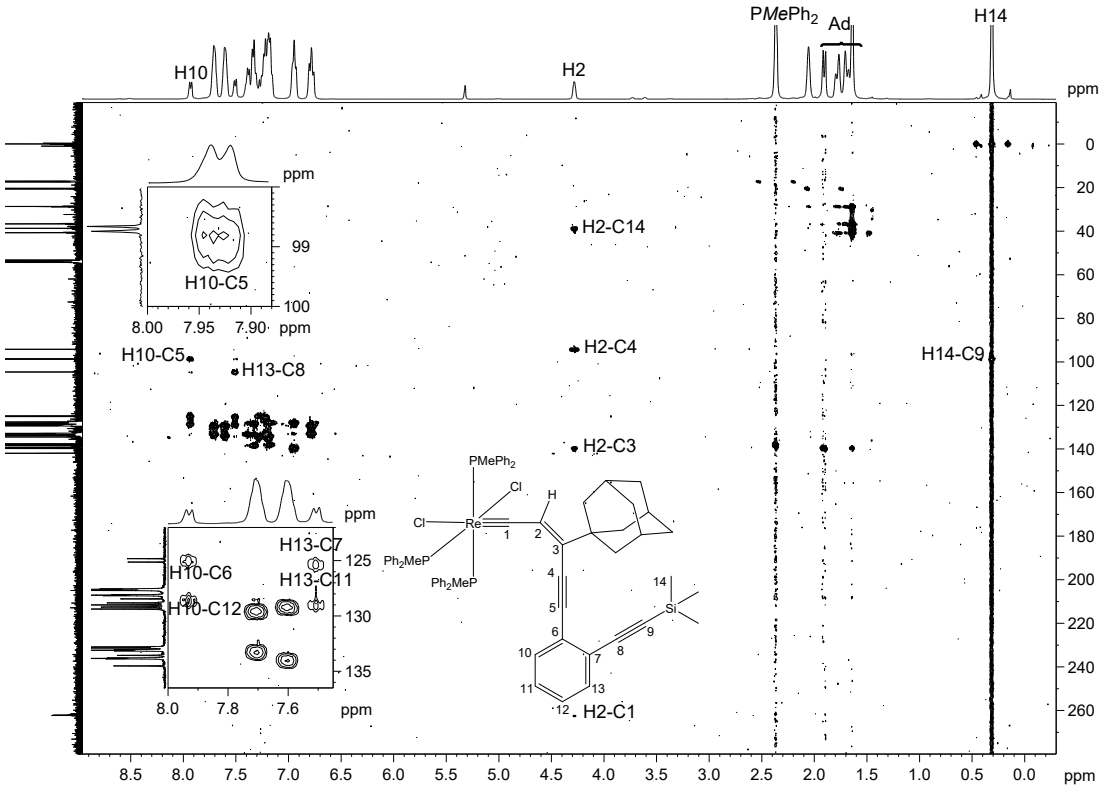


Figure S15. The ^{1}H-^{13}C HMBC spectrum of **3b** in CD_2Cl_2.

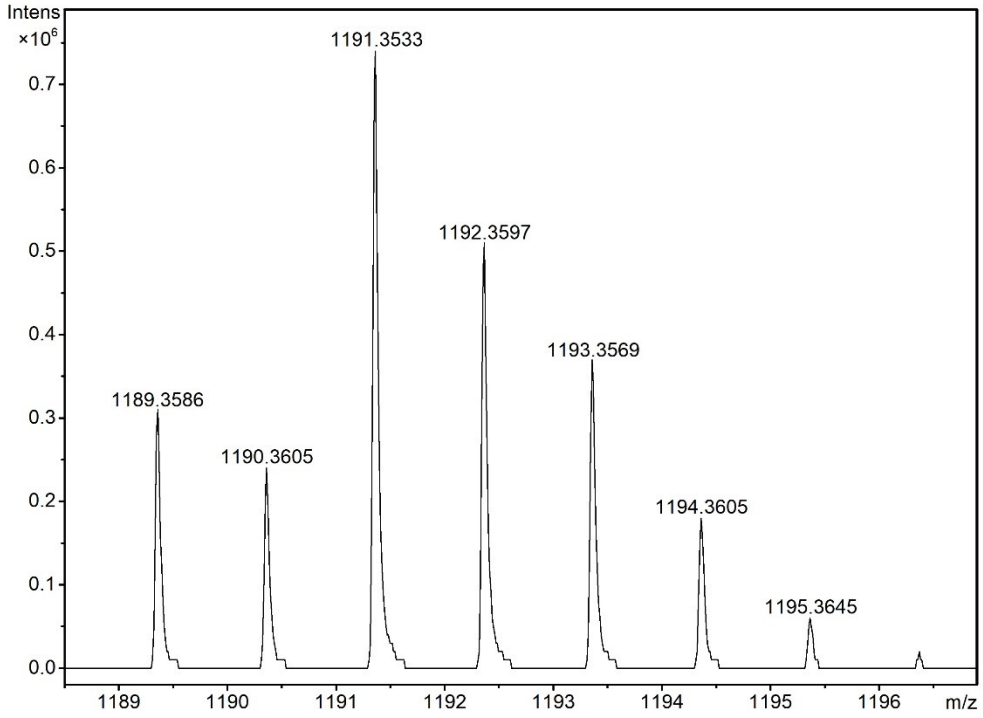


Figure S16. The HRMS spectrum of [**3b**-Cl]$^{+}$ measured in dichloromethane.

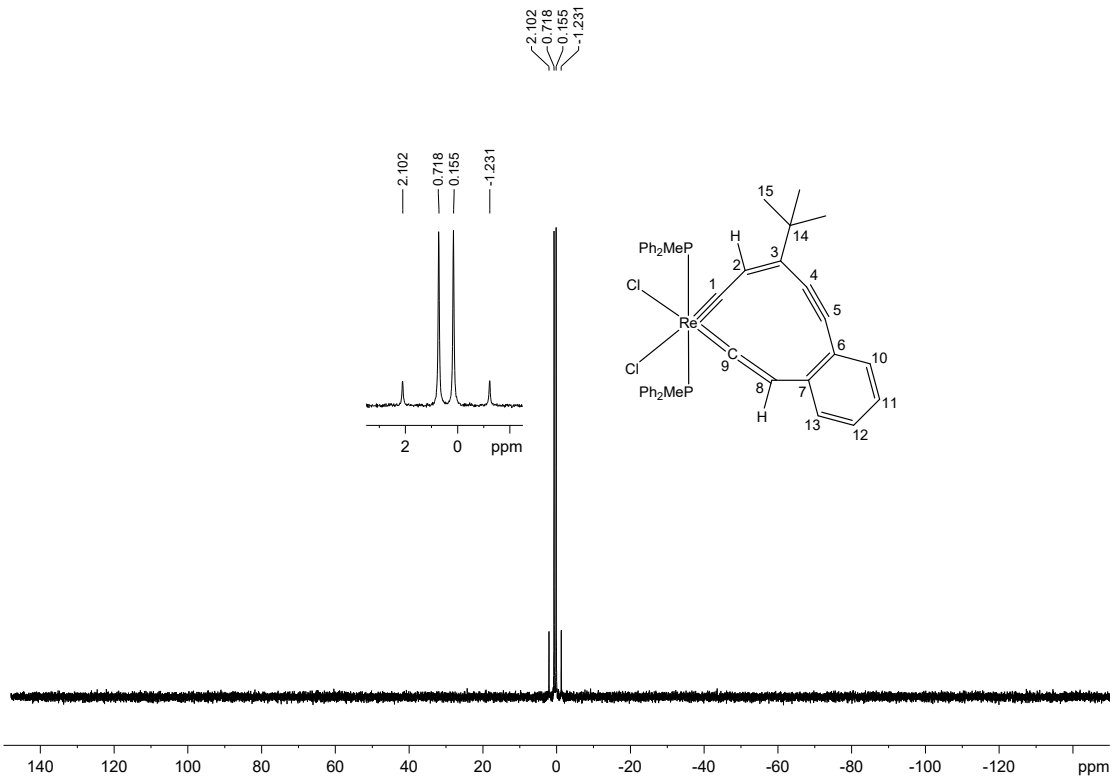


Figure 17. The $^{31}P\{^{1}H\}$ NMR spectrum (161.9 MHz) of **4a** in CD_2Cl_2.

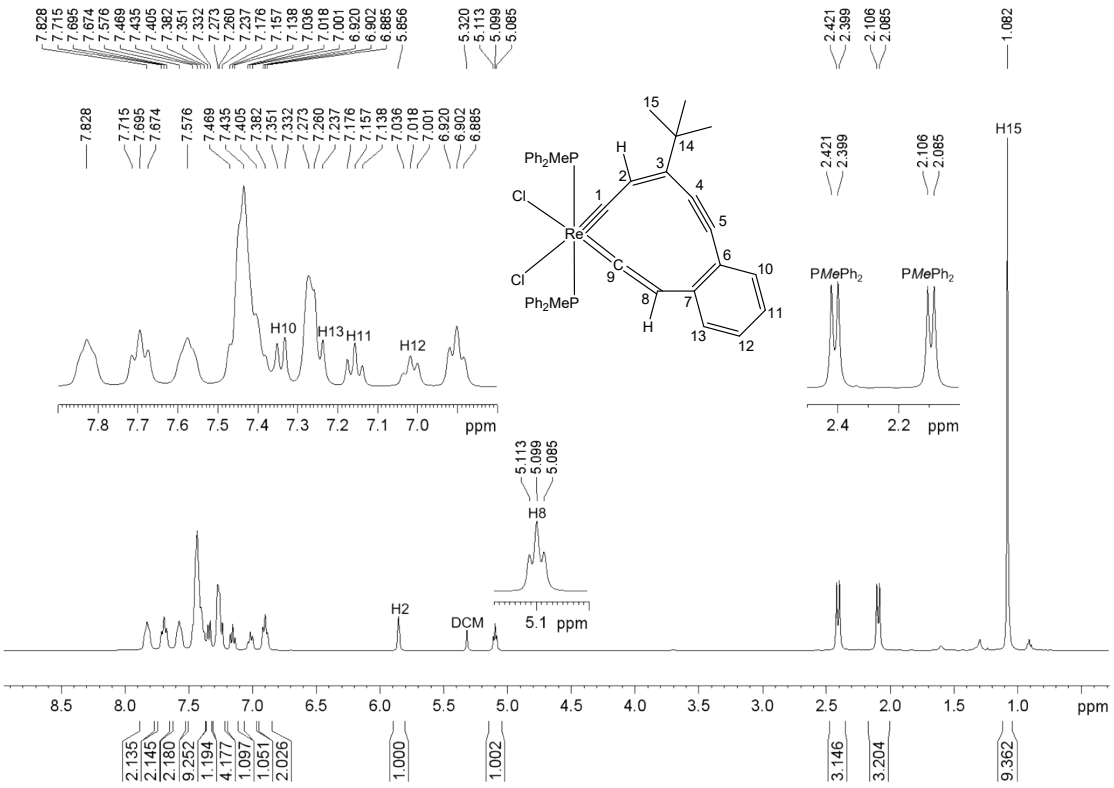


Figure S18. The ^{1}H NMR spectrum (400.0 MHz) of **4a** in CD_2Cl_2.

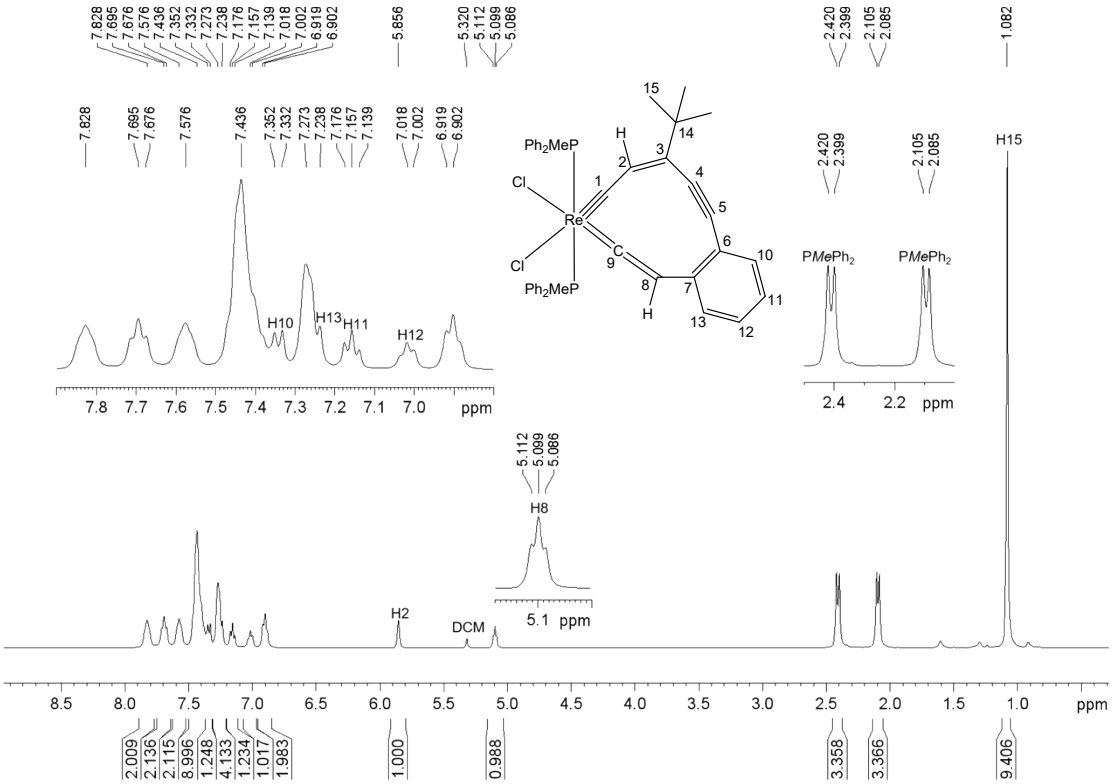


Figure S19. The ^{1}H $\{^{31}P\}$ NMR spectrum (400.0 MHz) of **4a** in CD_2Cl_2.

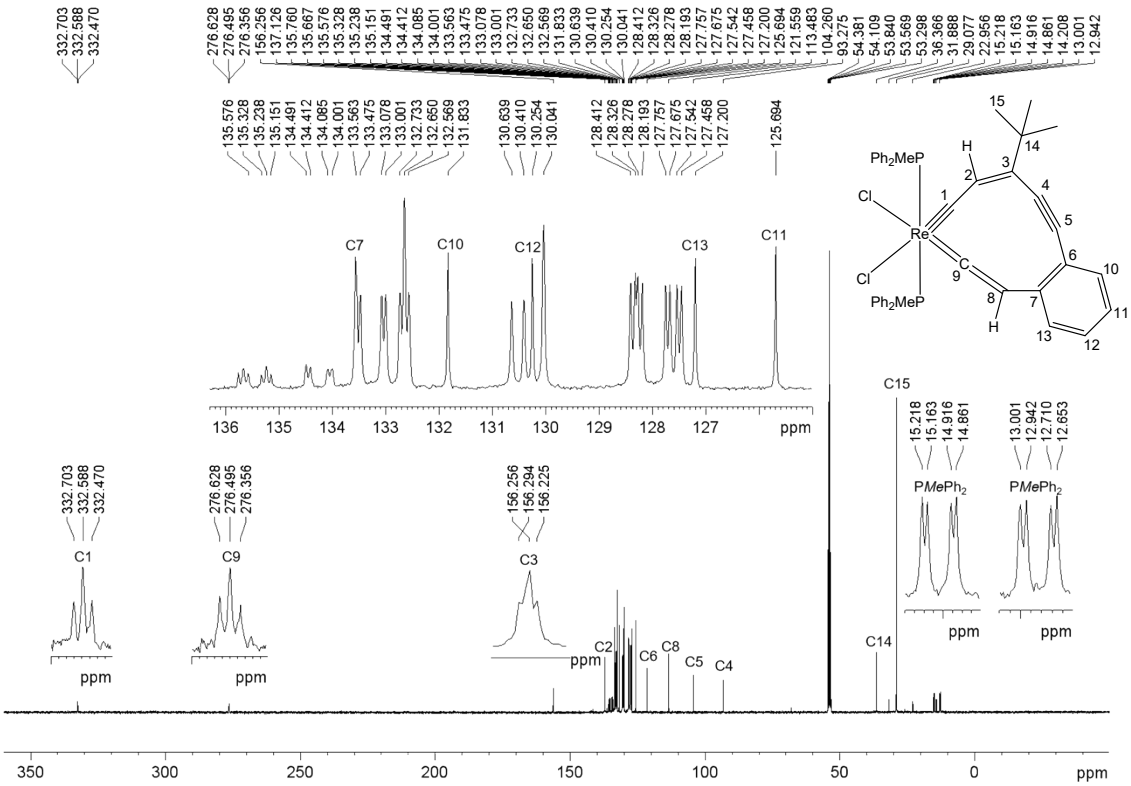


Figure S20. The $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of **4a** in CD_2Cl_2.

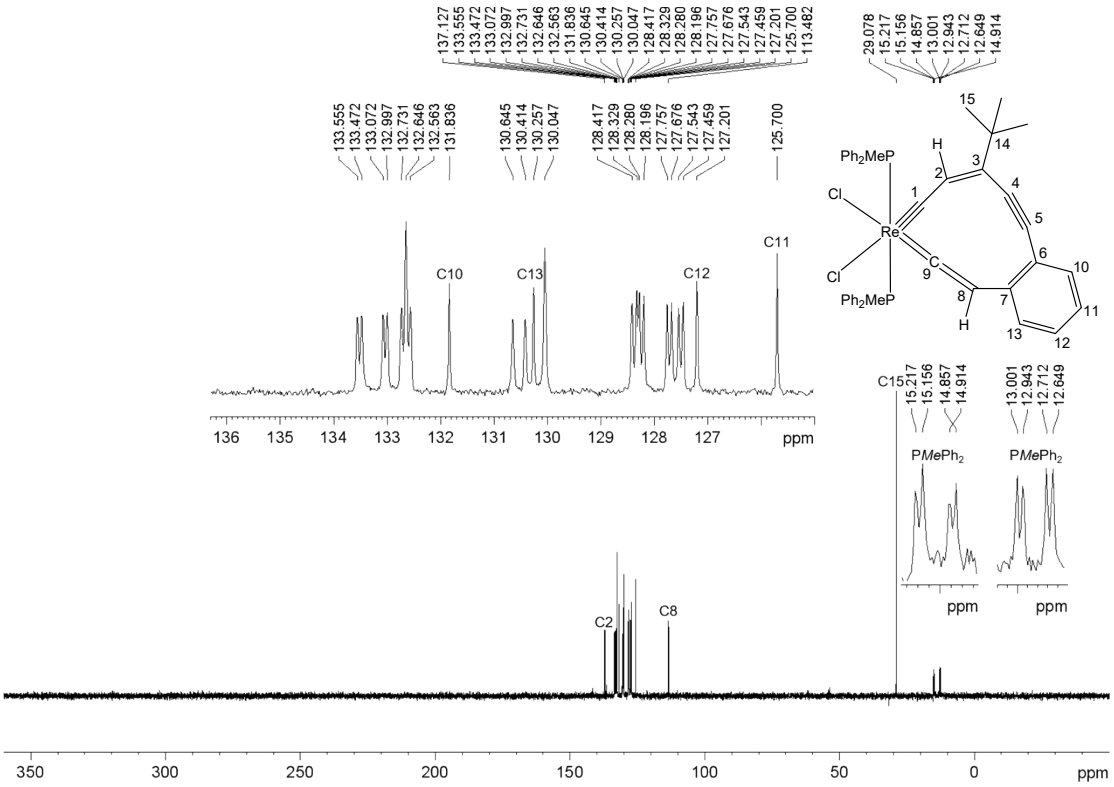


Figure S21. The ^{13}C DEPT135 NMR spectrum (100.6 MHz) of **4a** in CD_2Cl_2.

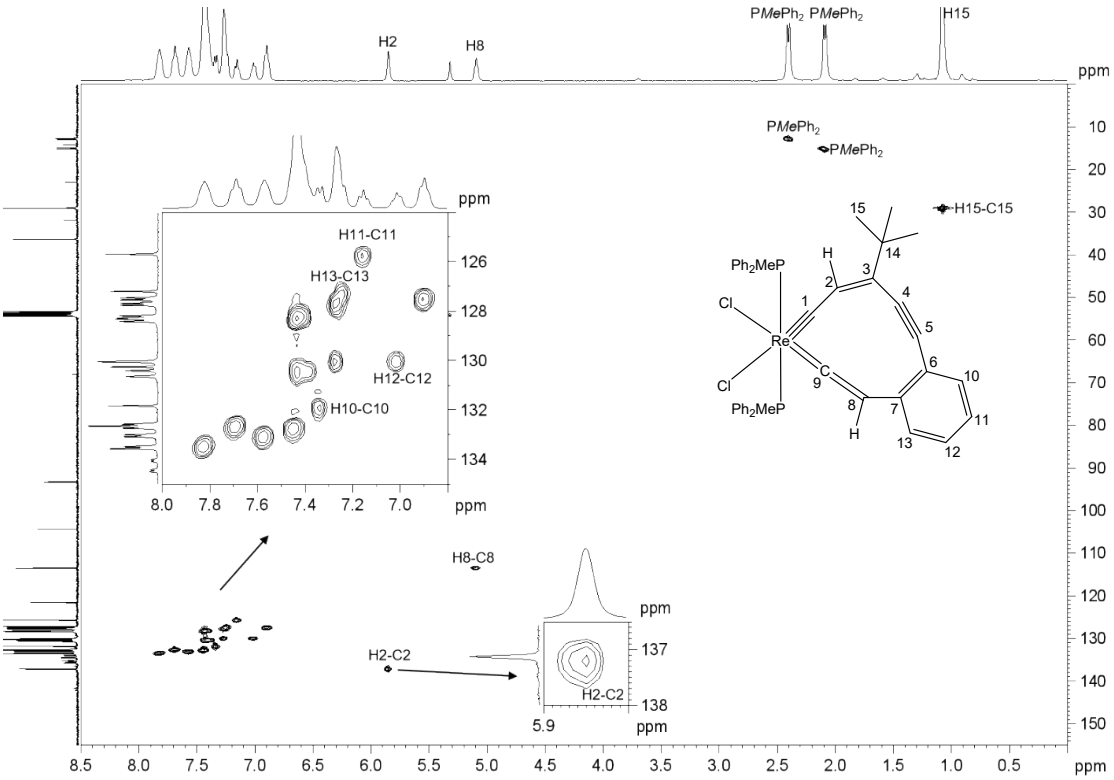


Figure S22. The ^{1}H-^{13}C HSQC spectrum of **4a** in CD_2Cl_2.

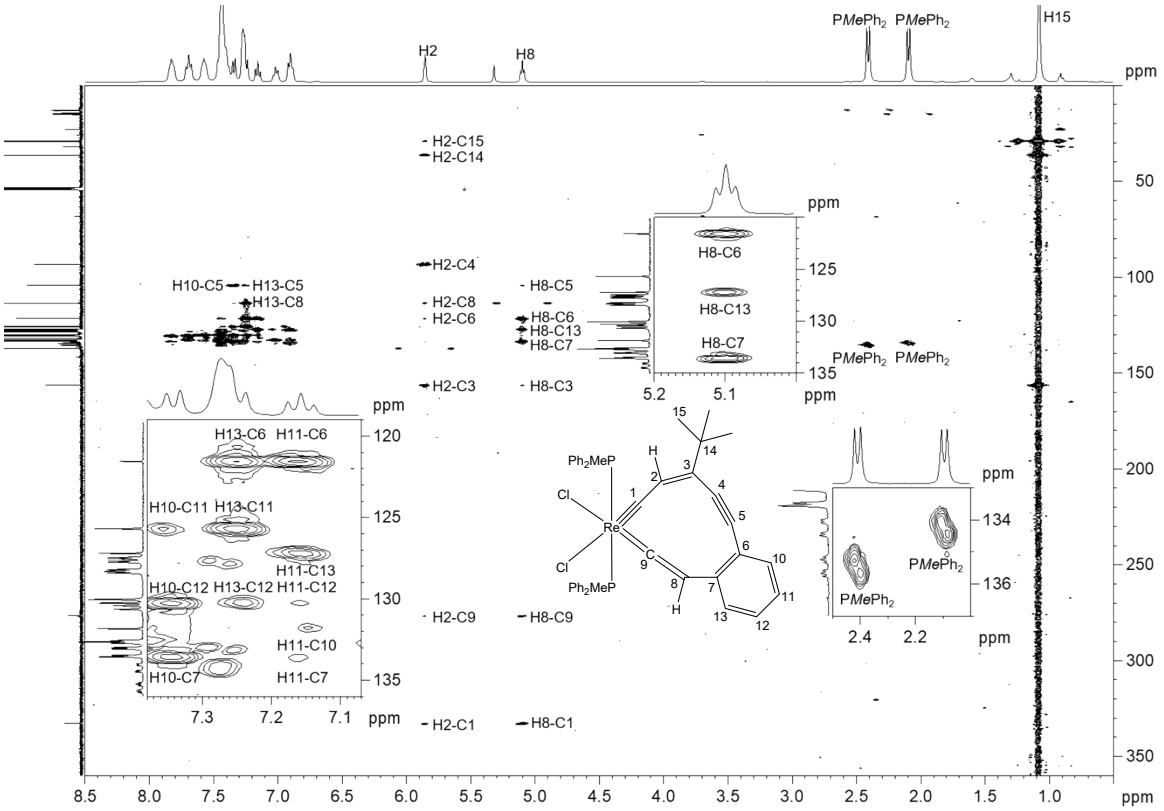


Figure S23. The ^{1}H-^{13}C HMBC spectrum of **4a** in CD_2Cl_2.

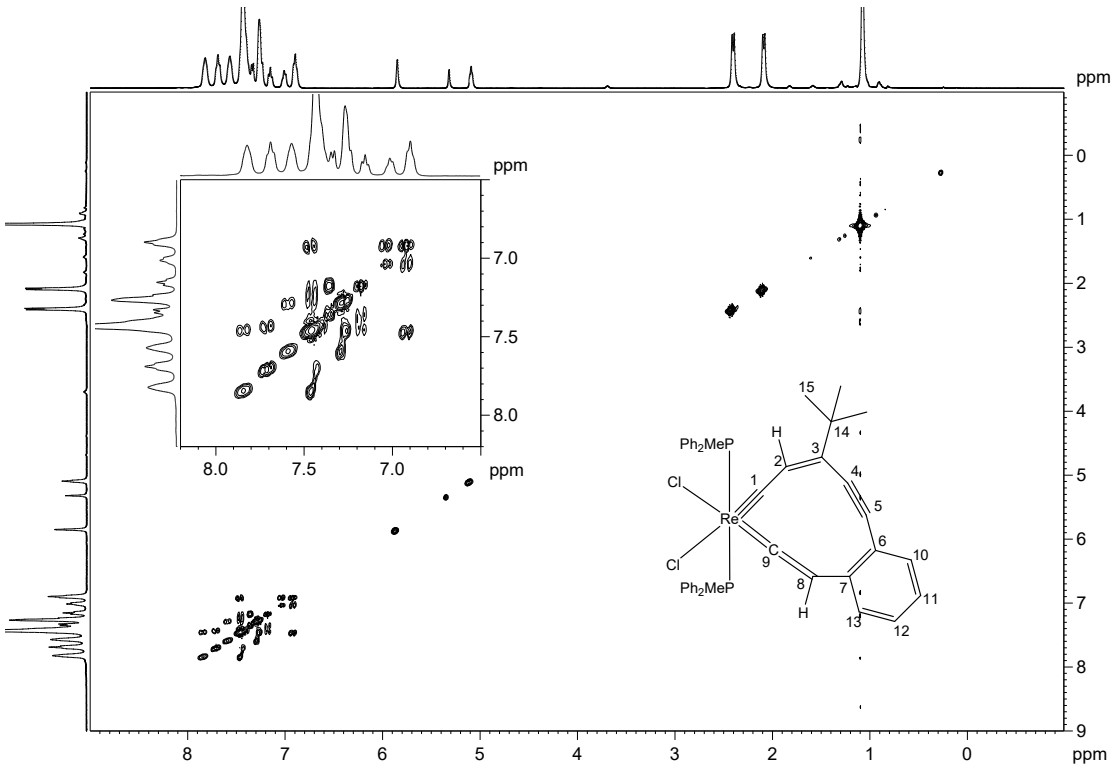


Figure S24. The ^{1}H-^{1}H COSY NMR spectrum of **4a** in CD_2Cl_2.

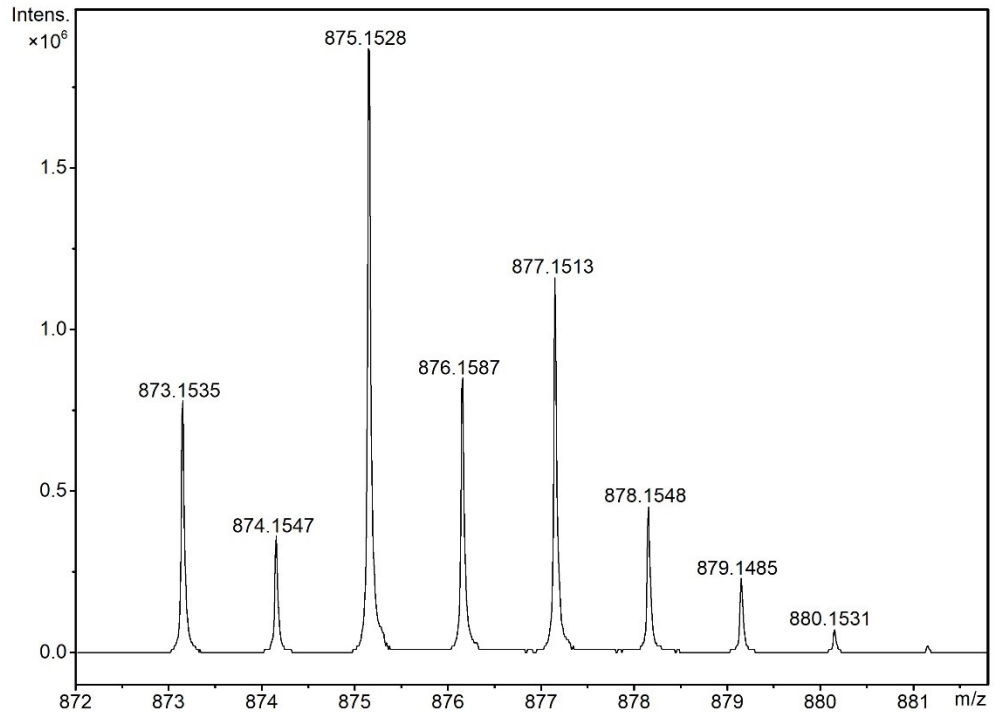


Figure S25. The HRMS spectrum of [**4a**-H]$^-$ measured in dichloromethane.

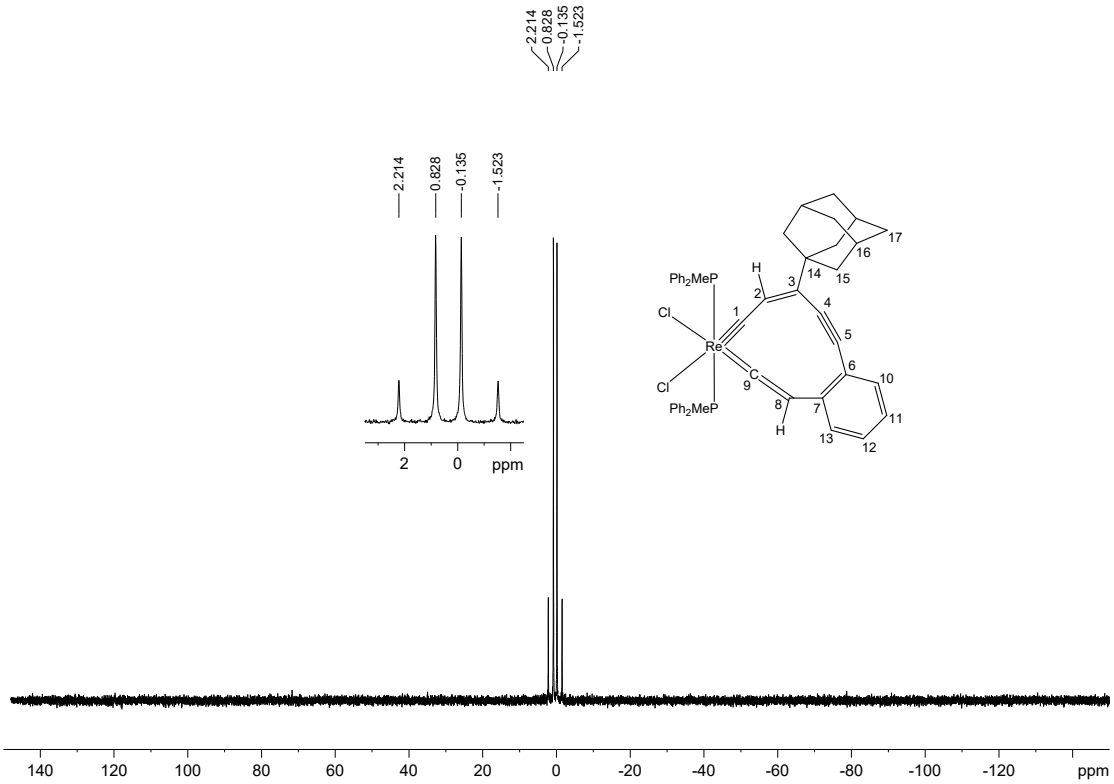


Figure S26. The $^{31}P\{^1H\}$ NMR spectrum (161.9 MHz) of **4b** in CD_2Cl_2.

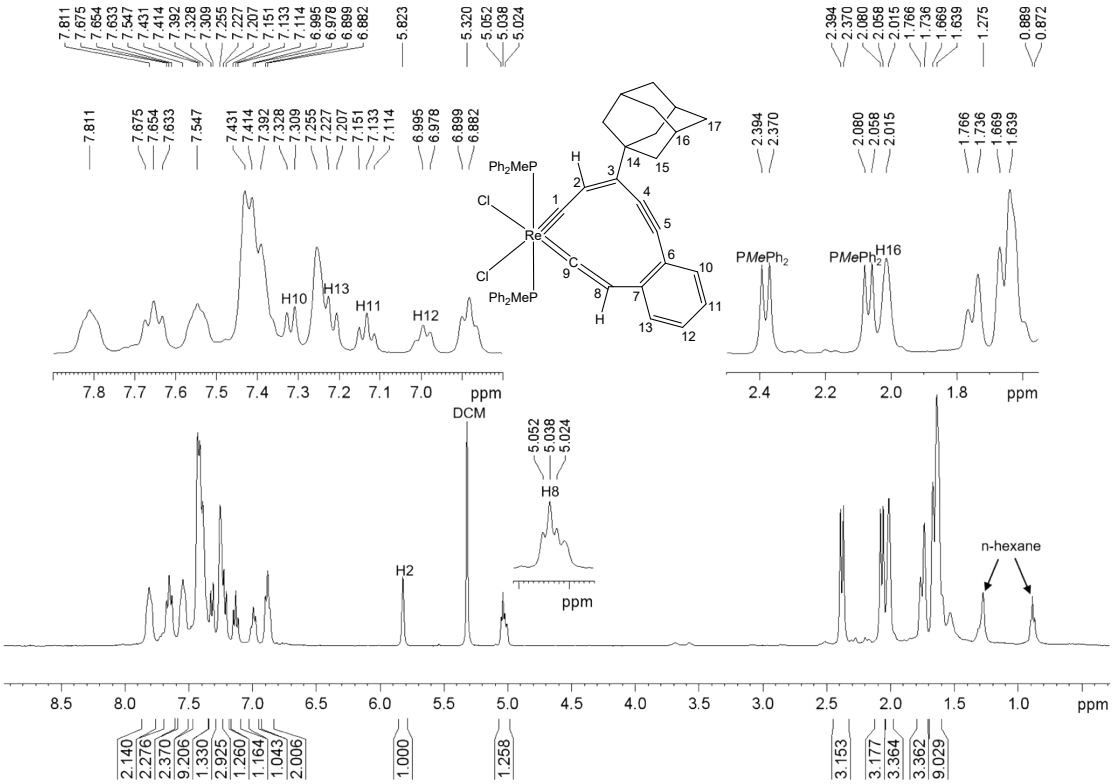


Figure S27. The ^{1}H NMR spectrum (400.0 MHz) of **4b** in CD_2Cl_2.

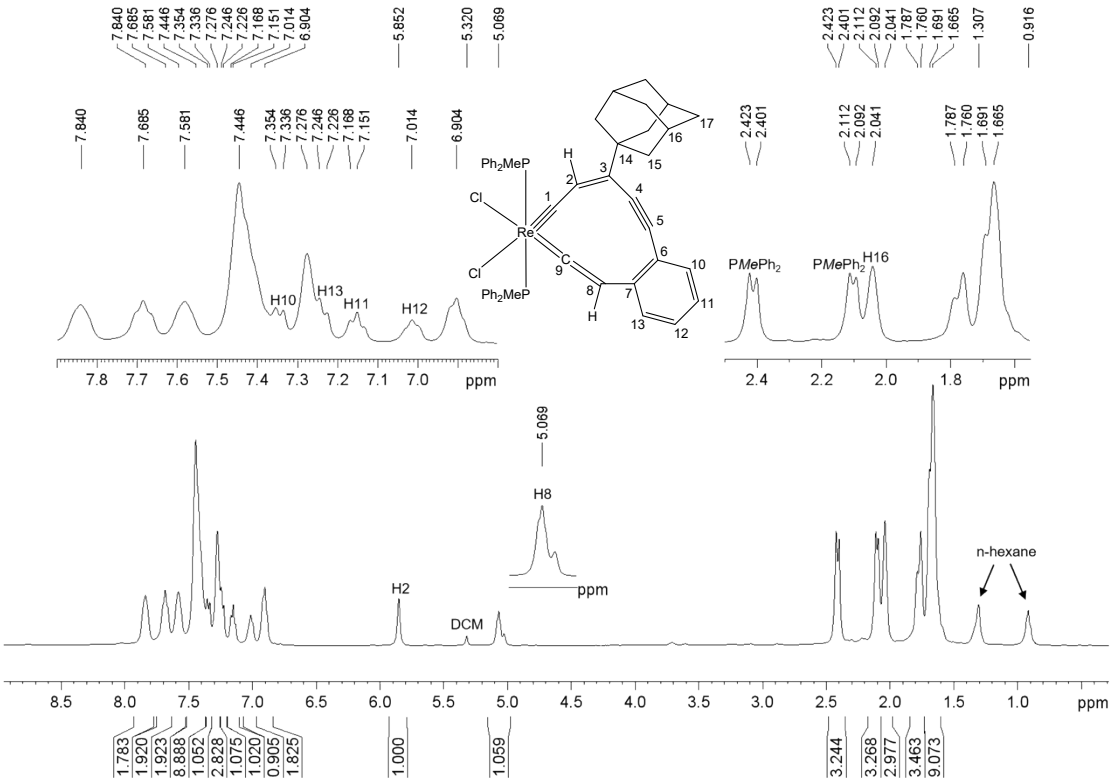


Figure S28. The $^{1}H\{^{31}P\}$ NMR spectrum (400.0 MHz) of **4b** in CD_2Cl_2.

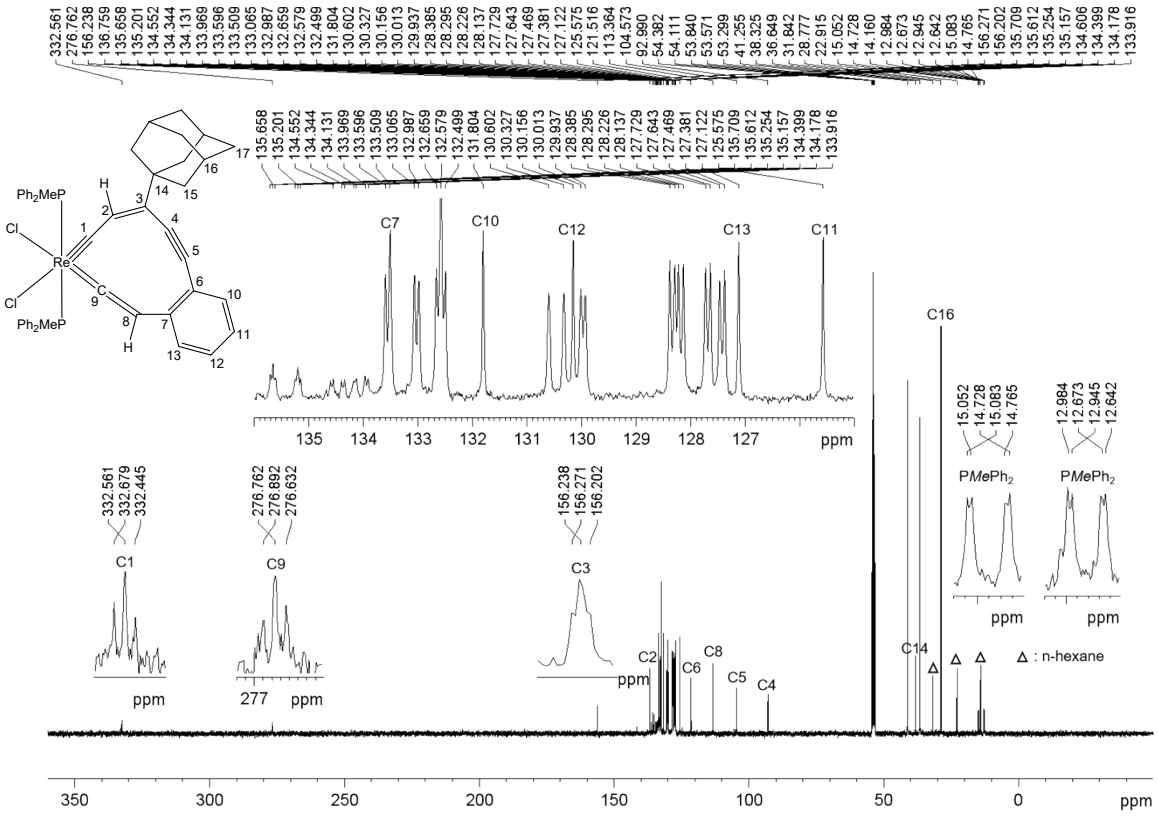


Figure S29. The $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz) of **4b** in CD_2Cl_2.

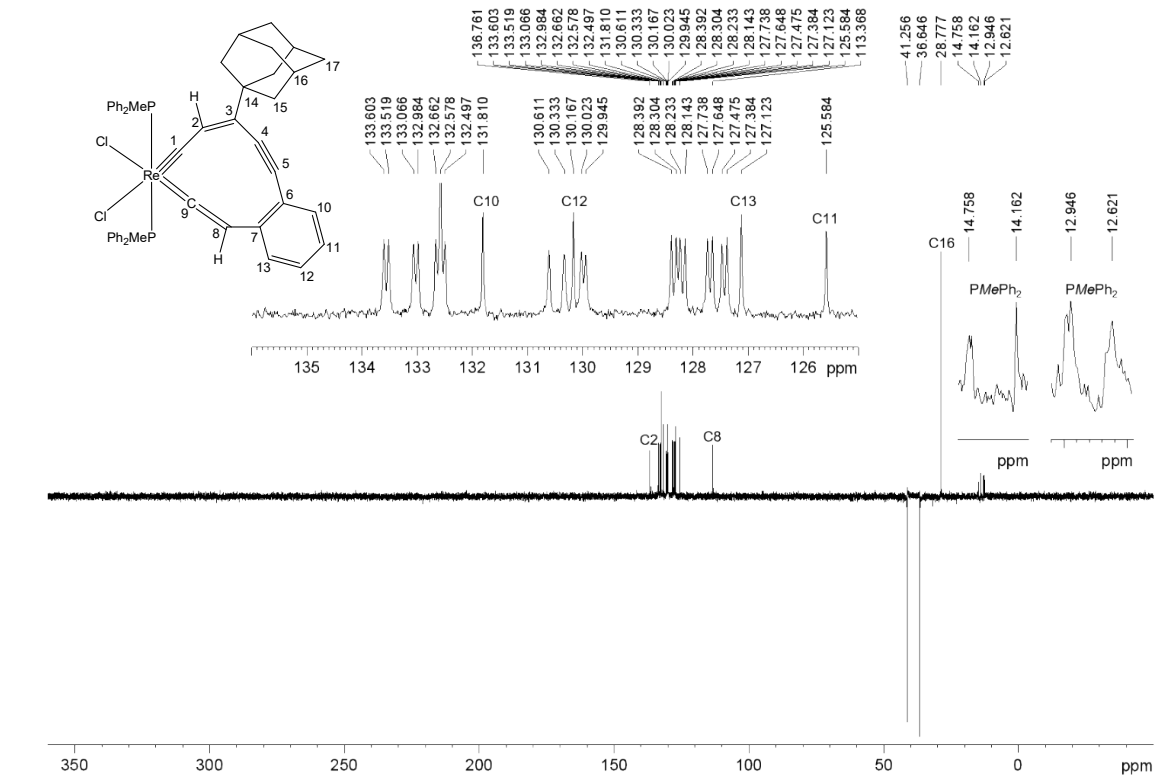


Figure S30. The ^{13}C DEPT135 NMR spectrum (100.6 MHz) of **4b** in CD_2Cl_2.

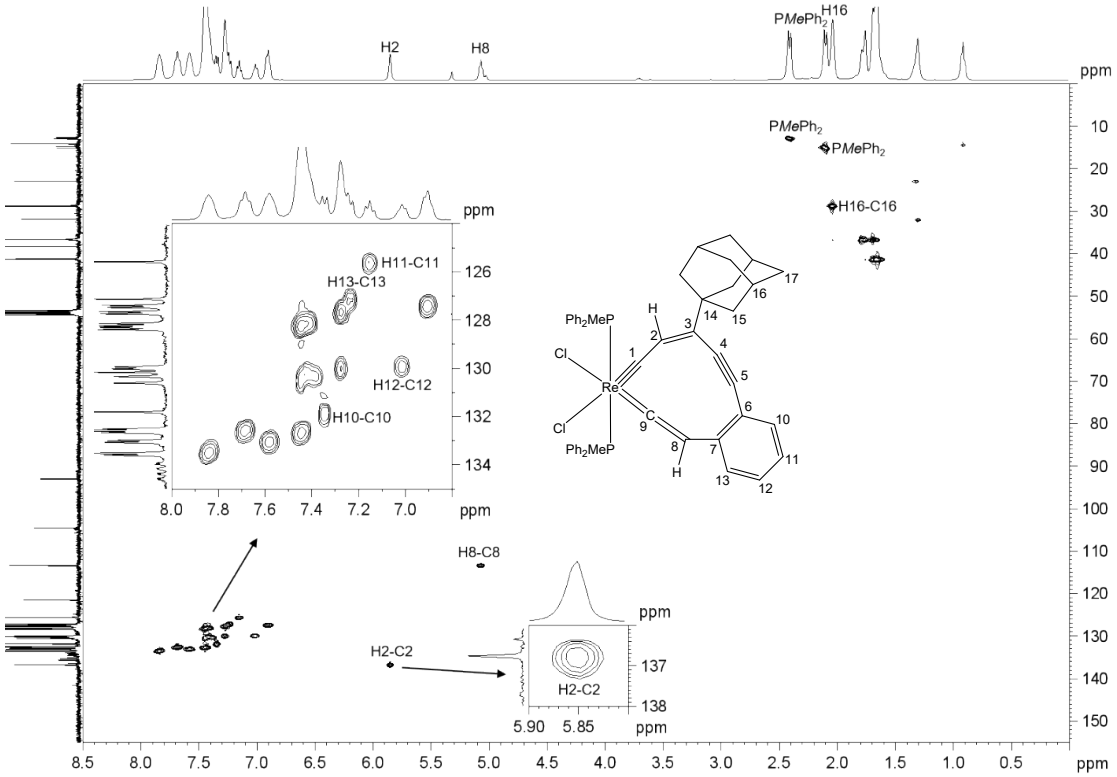


Figure S31. The ^{1}H-^{13}C HSQC spectrum of **4b** in CD_2Cl_2.

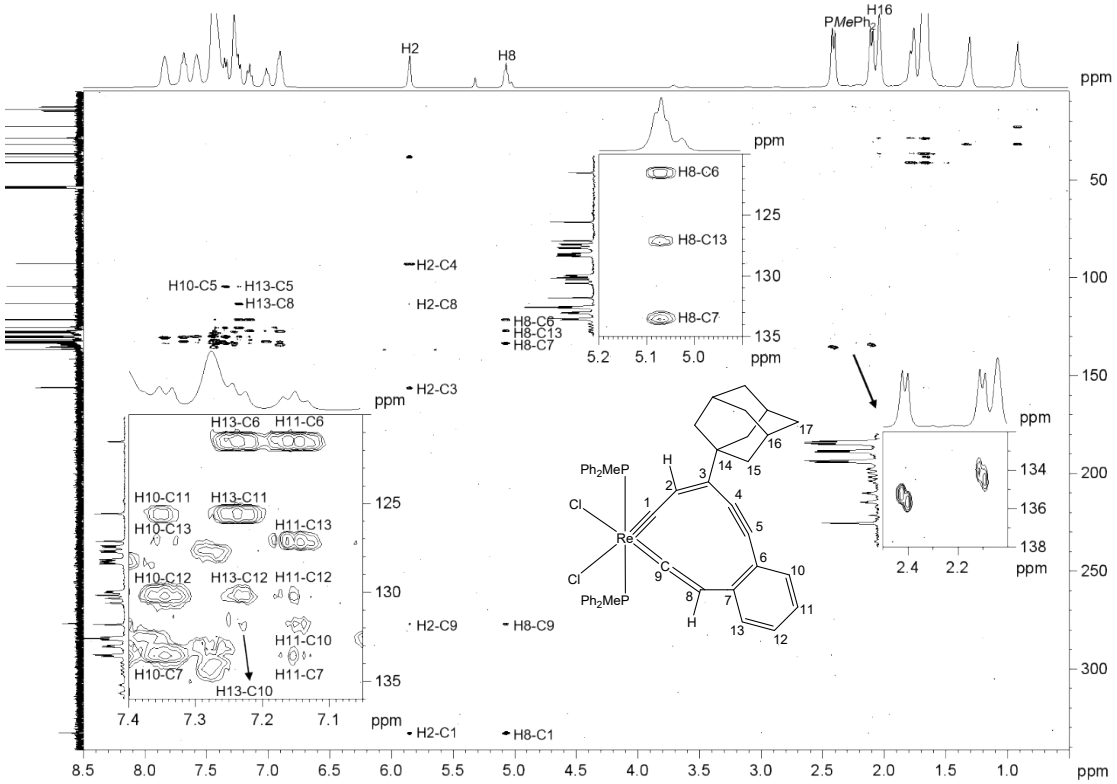


Figure S32. The ^{1}H-^{13}C HMBC spectrum of **4b** in CD_2Cl_2.

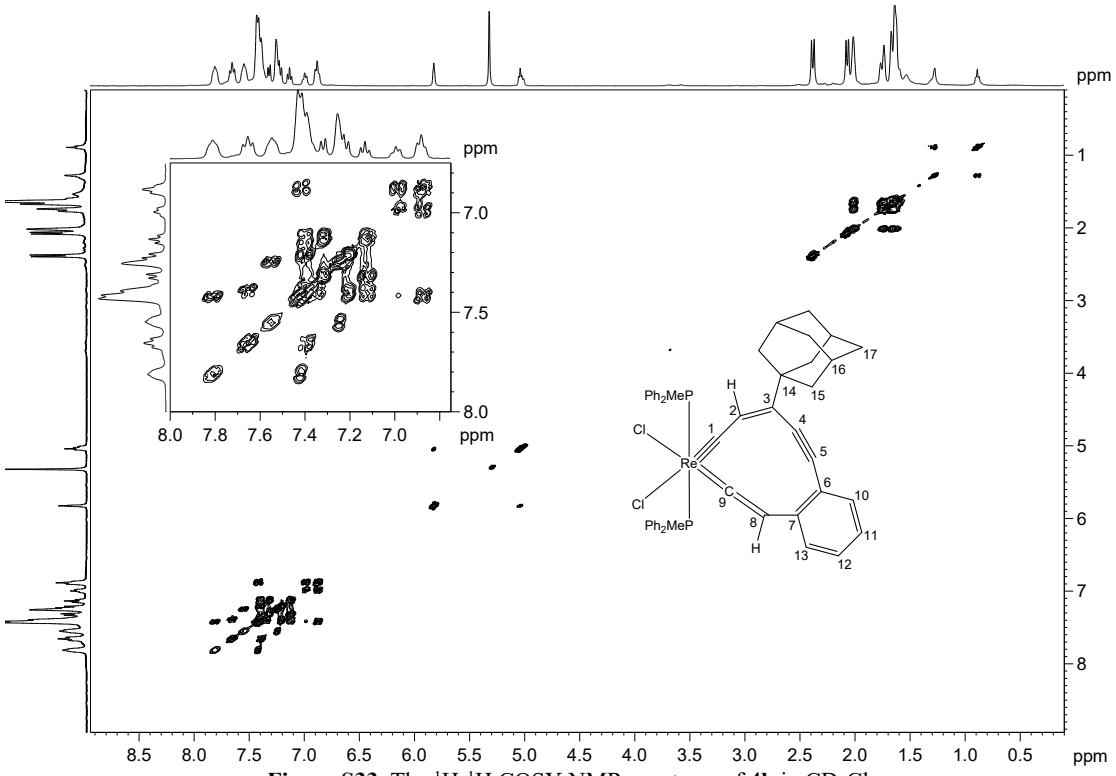


Figure S33. The ^{1}H-^{1}H COSY NMR spectrum of **4b** in CD_2Cl_2.

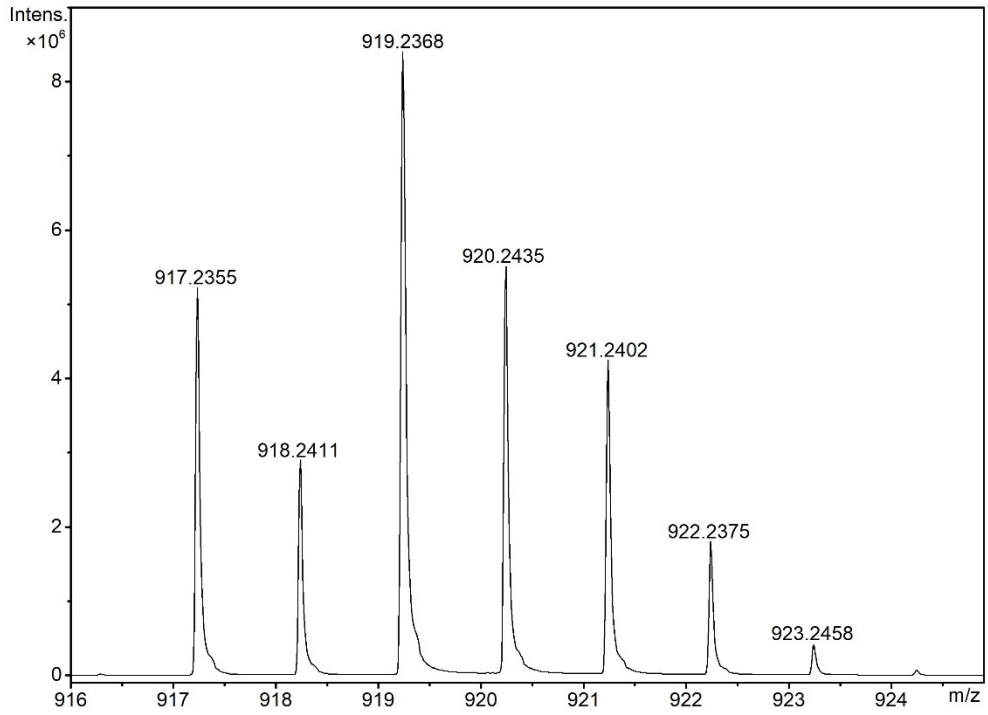
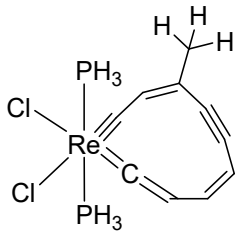


Figure S34. The HRMS spectrum of [**4b**-Cl]$^{+}$ measured in dichloromethane.

4. Computational Details

All the optimizations were performed with the Gaussian 16 Ver. C01 software package.[7] All of the structures evaluated were optimized at the B3LYP/def2-TZVP level of density functional theory (DFT).[8-11] The anisotropy of the induced current density (AICD) calculations were carried out with the AICD program.[12,13] The analysis of the iso-chemical shielding surfaces (ICSS)[14,15] and the π-type localized orbital locator (LOL-π)[16] were performed using the wavefunction analysis code Multiwfn 3.8[17] and the GaussView 6.1.1 software.[18]

5. The Calculated Cartesian Coordinates with Electronic Energies



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P	2.13922500	-0.47414000	-1.99602200
P	-0.12106000	0.22294700	2.21493700
C	-0.95444800	2.49541400	-1.15932100
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C	-3.21485900	-0.25400300	0.09883800
C	-1.81666800	-2.03051200	-0.66258900
H	-1.72175900	-3.02465000	-1.09099400
C	-3.21347800	0.96806500	0.16387200
C	-0.69234700	-1.24215800	-0.54513100
H	2.36757200	-1.81165200	-2.35446200
H	3.45114300	-0.02685300	-1.77854900
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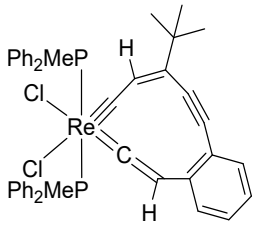
H	-4.49864100	-2.67270300	0.96912900
H	-5.09948500	-2.15296500	-0.59834700
H	-3.97591300	-3.52400300	-0.48859200



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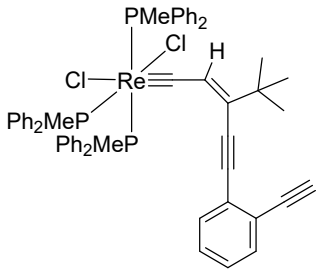

7a

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C	2.36043100	1.42888300	2.02508500

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C	1.11242500	-2.78011100	1.33568200
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H	4.63544600	0.38284100	2.40290100
C	2.73637900	-3.42296300	3.01855700
H	3.76072700	-3.65886400	3.27746500
C	-2.36678100	4.19116200	-2.00625900
H	-1.63950000	4.93426400	-2.30651500
C	0.86518500	5.59692200	0.58659400
H	0.63098800	5.90818200	1.59705600
C	1.70576900	6.37295500	-0.20635800
H	2.12910900	7.29041800	0.18272500
C	1.74280500	-3.45782600	3.98963900
H	1.98531800	-3.72625100	5.01028900
C	2.06726800	2.20767000	4.70901900
H	1.96087900	2.50601200	5.74448700
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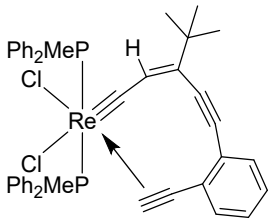
H	2.58351400	-3.84715300	-4.67715800
C	1.99397600	5.96340000	-1.50175300
H	2.64632900	6.55891900	-2.12827700
C	5.47057700	-1.98682500	-0.51666800
H	5.70365100	-2.64651700	-1.34311600
C	-4.40214500	1.53166600	3.15540400
H	-4.25603800	2.41616400	2.53253500
H	-4.86076100	1.84896600	4.09464700
H	-5.09853800	0.86725400	2.64532500
C	5.97397900	-1.09646200	1.65302800
H	6.60385700	-1.05669500	2.53340800
C	0.43448200	-3.14844700	3.63748900
H	-0.35140600	-3.17494300	4.38219600
C	6.28689200	-1.95671900	0.60729400
H	7.16162700	-2.59261900	0.66591200
C	-1.17574600	0.75757100	1.72188100
H	-0.60940800	1.39375500	2.39259100
C	-2.42799900	0.38473000	2.10900400
C	-3.23656700	-0.44302300	1.29379000
C	-3.99682400	-1.11689000	0.63395200
C	-4.85385500	-1.87461200	-0.20471100
C	-6.04297800	-2.46576400	0.29331000
C	-6.42128900	-2.33353800	1.65947200
C	-6.76939900	-2.24114300	2.80725400
C	-4.52701400	-2.03640100	-1.56056000
H	-3.61818200	-1.58420600	-1.93730800
C	-5.35246700	-2.76033200	-2.40502700
H	-5.08296700	-2.87106400	-3.44737700
C	-6.51915800	-3.34154000	-1.91549800
H	-7.16402000	-3.90899000	-2.57413900
C	4.34531800	-1.17290100	-0.59232600
H	3.73195200	-1.19597900	-1.48077500
C	-6.85888100	-3.19483300	-0.57982000
H	-7.76343300	-3.64357200	-0.19191100
C	-3.05888500	0.82976000	3.44278900
C	2.42560700	-3.08461700	1.70661000
H	3.21533000	-3.06657800	0.97035800
C	-2.16173300	1.79686800	4.22357800
H	-1.20372900	1.34851600	4.48959900

H	-2.66266000	2.07944800	5.15148300
H	-1.96725200	2.71304500	3.66279800
C	2.77356400	-5.36788800	-3.17135600
H	3.23492800	-6.08814600	-3.83575400
C	0.12266900	-2.81350200	2.32472400
H	-0.90336800	-2.57974800	2.07909100
C	-3.70595800	4.55018900	-1.94827400
H	-4.00283600	5.55808400	-2.21097200
Cl	2.22310800	0.21726000	-2.86446200
Cl	-1.08334000	-0.58796600	-2.66688100
P	-0.16673600	2.43993200	-1.83745900
P	2.58377400	0.87145900	0.27953000
P	0.65730900	-2.30801800	-0.39119600
Re	0.52372800	0.18068200	-0.90896000
H	-7.07341900	-2.15620800	3.82139800



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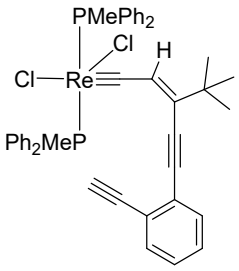
E = -3345.446529 a.u.

Re	0.28341300	-0.51735900	-0.64014900
Cl	0.83097100	0.38539400	-2.89907600
Cl	-0.08730300	-2.78968800	-1.93715700
P	2.77172900	-0.99264200	-0.79144900
P	-2.06143000	-0.01393500	-1.63764500
C	5.29447000	0.23237500	-0.80110500
H	5.66311700	-0.74077800	-0.50430600
C	3.92210400	0.43963200	-0.98620200
C	3.48417200	1.70919100	-1.36332800
H	2.43538900	1.87824800	-1.55347900
C	3.51808500	-1.85778800	0.64587300
C	-0.73973100	-1.48345300	1.06140400
C	6.20147100	1.26806500	-0.98066800
H	7.25841200	1.08637900	-0.83096000
C	5.75279300	2.53154300	-1.34926400
H	6.45891700	3.34040500	-1.48991500
C	0.17061100	2.51574300	2.09391900
C	-3.65179700	-2.22621900	-1.08498500
H	-2.79962100	-2.78651100	-1.45005900
C	4.39442300	2.74646900	-1.54117400
H	4.03553300	3.72328100	-1.84073200
C	-0.84342300	1.62549600	2.49788900
C	-5.90732500	-2.19264500	-0.23419300
H	-6.81238800	-2.71746900	0.04523900
C	0.80246000	3.35241300	4.35533900
H	1.71842400	2.75850400	4.36363900
H	0.00946000	2.75623100	4.80812900
H	0.96336600	4.23586600	4.97714200
C	-2.51327000	-2.83484100	2.10640100
H	-2.17036200	-3.66868600	1.50910200
C	-1.88212800	-1.59454600	1.94461800
C	-4.81289000	-2.89596100	-0.72568400
H	-4.85931700	-3.97317700	-0.82738100
C	0.88055800	2.15467300	0.97827700
H	1.70541200	2.77389000	0.64427700
C	0.43202000	3.77747500	2.91879200
C	1.56927800	4.62659000	2.33988800
H	1.34717300	4.96439400	1.32592600
H	2.51511300	4.08204100	2.32094700
H	1.71323900	5.51344300	2.95976000
C	-4.00836400	-1.92129000	3.76430500
H	-4.82956000	-2.04965700	4.45762600
C	-1.61582200	0.70763600	2.67206500
C	-2.32650200	-0.50768000	2.74605200
C	-3.57386900	-0.83257200	-0.97298900
C	-3.39215500	-0.69110800	3.64248300
H	-3.71419600	0.14808500	4.24502000
C	0.59973500	0.99926200	0.22351000
C	3.20171600	-2.03971700	-2.22564100
H	2.91643800	-1.48998600	-3.12006800
H	2.61702900	-2.95685600	-2.20000400
H	4.27125600	-2.24813100	-2.23872200
C	-2.47714700	1.77268100	-1.69243800
C	-2.58602500	2.50035800	-0.50449800
H	-2.40487500	2.01595200	0.44517700
C	-3.56041300	-2.99699600	2.99753500
H	-4.03469100	-3.96553700	3.09421600
C	-5.83078400	-0.81301900	-0.10233600
H	-6.67542300	-0.25459400	0.28178000
C	-2.20827300	-0.55917200	-3.38207700
H	-1.97194000	-1.61988100	-3.41374200
H	-1.48967300	-0.03873400	-4.00650200
H	-3.22854800	-0.38935900	-3.72497400
C	-4.67376400	-0.13497000	-0.47389000
H	-4.64527000	0.94149500	-0.38566700
C	-0.85488000	4.62568400	2.96084500
H	-1.69168100	4.05516500	3.36614100
H	-1.12683500	4.97008900	1.96166000
H	-0.70399000	5.50332900	3.59325100

C	-3.13884400	4.49701700	-1.73621800
H	-3.39741700	5.54841800	-1.75274400
C	-2.92606200	3.84671300	-0.52584600
H	-3.02124900	4.38815400	0.40670300
C	-2.68800400	2.43698300	-2.90322700
H	-2.59707100	1.90983900	-3.84104800
C	3.85184100	-3.21211800	0.60080800
H	3.70548900	-3.78171400	-0.30635700
C	-3.01069000	3.78942300	-2.92399500
H	-3.16390900	4.28648000	-3.87369100
C	3.69804900	-1.16200300	1.84611600
H	3.43073200	-0.11452200	1.90791600
C	4.21617300	-1.79931500	2.96419500
H	4.35132200	-1.24411300	3.88386100
C	4.36930200	-3.85185500	1.72419300
H	4.62417000	-4.90277600	1.67016200
C	4.55595100	-3.14800400	2.90600200
H	4.95879500	-3.64583200	3.77890300
C	0.45308900	-1.90133200	0.94791700
H	1.20958200	-2.51072500	1.40527800

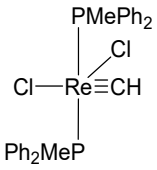


9

E = -3345.444504 a.u.

C	2.64862300	1.16467000	-1.32252700
H	2.82059000	0.14457100	-0.98182400
H	3.58838700	1.71323100	-1.37617300
H	2.20209100	1.11436200	-2.31388500
C	-3.95817700	-0.51653500	0.99085600
C	-3.30447700	-1.30321700	-1.71154500
C	1.50055200	3.72590200	-0.79040500
C	-2.38852400	-2.35778900	-1.65473500
H	-1.57173600	-2.32193900	-0.94597200
C	2.26339400	2.00349700	1.42847600
C	0.98889500	4.01965600	-2.05956700
H	0.56048900	3.23190200	-2.66713500
C	-4.26157000	1.38390000	-1.13874700
H	-4.19878100	2.22420800	-0.44831700
H	-5.29157500	1.03180400	-1.18335700
H	-3.93804000	1.71957100	-2.12452700
C	-4.73935300	-1.67487900	0.99943000
H	-4.84464900	-2.26646100	0.10066800
C	2.02854900	4.76327700	-0.02112100
H	2.42364700	4.56259500	0.96499600
C	-3.83546600	0.22117100	2.17358400
H	-3.22889600	1.11696500	2.18786500
C	-2.50027300	-3.44117000	-2.51553800
H	-1.77924400	-4.24678900	-2.45780000
C	-0.34558800	-0.39911700	0.74735200
C	-3.52144700	-3.48178200	-3.45952100
H	-3.60344600	-4.32239700	-4.13716200
C	2.05094500	6.06495000	-0.51129200
H	2.46222600	6.85875000	0.09992700
C	2.11963200	2.39693700	3.81348300
H	1.53209800	2.68365800	4.67684700
C	-4.32302400	-1.35278900	-2.66468000
H	-5.04225100	-0.54932100	-2.74262600
C	-5.38429900	-2.08529900	2.16166400
H	-5.98227800	-2.98818700	2.15037500
C	-5.26267100	-1.34266200	3.32920500
H	-5.76626300	-1.66222000	4.23307700
C	3.46042000	2.05859500	3.96248900
H	3.92279200	2.07973000	4.94154200
C	2.35855200	-2.92623400	3.77039800
H	3.19965600	-3.07619200	3.09370200
H	2.48701900	-3.59360600	4.62561000
H	2.39412600	-1.89678100	4.13169200
C	1.01846600	5.31904800	-2.54810100
H	0.61972400	5.52907400	-3.53278200
C	-4.48799000	-0.18763000	3.33018300
H	-4.38636900	0.39817400	4.23539700
C	1.00124500	-4.68322200	2.58331000
H	0.05237200	-4.92418500	2.09988100
H	1.13143500	-5.35943700	3.43110400
H	1.80239100	-4.87449600	1.86977200
C	4.20222200	1.69003200	2.84761100
H	5.24582100	1.42043700	2.95237900
C	-0.13723600	-1.37668100	1.75020800
H	-0.87912200	-1.34975100	2.54066400
C	0.87173900	-2.28213900	1.85397700
C	1.86932900	-2.42295400	0.85754400
C	2.75058200	-2.67133300	0.06427700
C	3.81778500	-2.99999800	-0.81239100
C	3.66939800	-2.95783100	-2.22216100
C	2.43688800	-2.57273100	-2.81590900
C	1.39781500	-2.23465200	-3.31766300
C	5.05369500	-3.39366400	-0.27409900

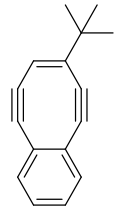
H	5.16285400	-3.42687900	0.80158700
C	6.11718300	-3.73049300	-1.09372400
H	7.06068500	-4.02879400	-0.65499600
C	5.96976700	-3.68549000	-2.47800200
H	6.79783500	-3.94852600	-3.12348800
C	4.75873000	-3.30469800	-3.03203000
H	4.63486100	-3.27003700	-4.10604000
C	1.01541100	-3.22005800	3.07109000
C	1.52287900	2.36361100	2.55960700
H	0.47717300	2.61985500	2.45542100
C	-0.11493200	-3.03682700	4.09168300
H	-0.13208800	-2.02749800	4.50649600
H	0.03643500	-3.73040200	4.92093200
H	-1.09477800	-3.24929000	3.66045700
C	1.54875900	6.34648000	-1.77507700
H	1.56630400	7.36038900	-2.15485500
C	3.60962000	1.66632900	1.58936300
H	4.20882100	1.37665600	0.73797000
C	-4.42919500	-2.43345700	-3.53470100
H	-5.22216200	-2.45157200	-4.27197100
Cl	-1.67546100	2.83912500	0.95292800
Cl	-0.56871000	0.64580700	-2.64205100
P	-3.11017900	0.08955300	-0.53041700
P	1.43970500	1.97854400	-0.21299000
Re	-0.81382100	0.95103200	-0.26591800
H	0.47533800	-1.89021200	-3.71888100



10

E = -2727.194394 a.u.

Re	-0.00000900	-0.00002400	-0.33625100
Cl	-0.09777600	2.16385100	-1.37952200
Cl	0.09770200	-2.16406800	-1.37917800
P	2.45251500	0.06533500	-0.54561200
P	-2.45254300	-0.06541800	-0.54547400
C	4.76599700	1.52575600	0.12215100
H	5.31444400	0.72969500	-0.36616900
C	3.37043500	1.46745100	0.20937600
C	2.69186800	2.49575600	0.86261800
H	1.61358900	2.46842500	0.92637100
C	3.33183000	-1.40173100	0.11496300
C	5.46504700	2.58987000	0.67381800
H	6.54496900	2.62054400	0.59987400
C	4.77872600	3.61198400	1.32347900
H	5.32384800	4.44257000	1.75440300
C	-2.69181400	-2.49564000	0.86311100
H	-1.61352900	-2.46830800	0.92678100
C	3.39445600	3.56190800	1.41680600
H	2.85387800	4.35477600	1.91830600
C	-4.77864700	-3.61178800	1.32427600
H	-5.32374400	-4.44231100	1.75535400
C	-3.39436900	-3.56171100	1.41749500
H	-2.85376200	-4.35451500	1.91906300
C	-3.37042100	-1.46741900	0.20977800
C	0.00004100	0.00011500	1.39445800
C	2.94239700	0.15027100	-2.31173700
H	2.56734000	1.09379400	-2.70742000
H	2.47107400	-0.66572700	-2.85837800
H	4.02364500	0.10422000	-2.43834300
C	-3.33182600	1.40174700	0.11492300
C	-3.60392600	1.47802900	1.48435100
H	-3.34934600	0.64892800	2.13270500
C	-5.46500700	-2.58975700	0.67452600
H	-6.54493500	-2.62043300	0.60066600
C	-2.94251800	-0.15062700	-2.31156000
H	-2.56747400	-1.09420700	-2.70711800
H	-2.47123100	0.66529100	-2.85835200
H	-4.02377300	-0.10460400	-2.43811500
C	-4.76599000	-1.52572400	0.12266200
H	-5.31446500	-0.72972600	-0.36572600
C	-4.54584200	3.67716200	1.20719200
H	-5.01720400	4.55601900	1.62882000
C	-4.20823600	2.60378500	2.02569800
H	-4.41660200	2.64293300	3.08764800
C	-3.66767900	2.48693400	-0.69642900
H	-3.45087900	2.46706800	-1.75490000
C	3.66760700	-2.48705600	-0.69623600
H	3.45072700	-2.46736000	-1.75469400
C	-4.27263700	3.61544200	-0.15271600
H	-4.52561300	4.44827100	-0.79679000
C	3.60403000	-1.47779100	1.48438300
H	3.34951200	-0.64858000	2.13262100
C	4.20836500	-2.60346700	2.02587000
H	4.41680900	-2.64244300	3.08781100
C	4.27259000	-3.61548300	-0.15238200
H	4.52550600	-4.44842100	-0.79633800
C	4.54589500	-3.67698300	1.20751500
H	5.01727700	-4.55577700	1.62925300
H	0.00007400	0.00036600	2.47535600



11

E = -618.197043 a.u

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C	-3.60793900	1.12609200	-0.00001100
C	-4.61571600	0.15382100	0.00001600
C	-4.28866600	-1.18859700	0.00004300
C	-2.94583100	-1.58585300	0.00004500
H	-3.86521500	2.17701100	-0.00003300
H	-5.65345000	0.46132500	0.00001400
H	-5.06792500	-1.93960000	0.00006400
H	-2.68898400	-2.63693300	0.00006600
C	-0.52275600	-0.91291200	0.00001800
C	0.65019800	-0.61407900	0.00001800
C	-1.14461700	1.64291000	-0.00003500
C	0.04141500	1.88704000	-0.00005000
C	1.78559800	0.27362900	-0.00001200
C	3.20183200	-0.27690800	-0.00000300
C	3.38707100	-1.15219100	1.25716200
C	3.38705900	-1.15226300	-1.25712000
C	4.25457100	0.83668300	-0.00004000
H	3.27571500	-0.55949500	2.16705500
H	2.65346900	-1.95927300	1.28768400
H	4.38392100	-1.59852500	1.25944700
H	3.27569400	-0.55962000	-2.16704700
H	4.38390900	-1.59859700	-1.25938900
H	2.65345700	-1.95934700	-1.28758800
H	5.25368600	0.39754100	-0.00003300
H	4.17234200	1.47023300	-0.88535200
H	4.17235100	1.47028400	0.88523500
C	1.43845700	1.59187700	-0.00004700
H	2.18246600	2.37471400	-0.00007200

$PMePh_2$

E = -844.7809647 a.u.

P	-0.03718200	1.35432600	-0.68591700
C	-1.38411200	-0.62959000	0.89811300
H	-0.47314600	-0.72146400	1.47664700
C	-1.43519700	0.25383900	-0.18458800
C	-2.61793400	0.33503500	-0.92369100
H	-2.66726900	1.00299200	-1.77577200
C	1.43178500	0.31832900	-0.28802600
C	-2.48742300	-1.40314700	1.23490900
H	-2.43050300	-2.08488100	2.07475800
C	-3.66312100	-1.30477100	0.49620500
H	-4.52201800	-1.90956600	0.75924200
C	-3.72708300	-0.43334400	-0.58366500
H	-4.63595800	-0.35615900	-1.16754200
C	-0.06652500	2.57473300	0.70688000
H	-1.00129800	3.13158300	0.63415300
H	0.75363500	3.28511100	0.59273900
H	-0.01245600	2.11154700	1.69352600
C	2.37990900	0.64215300	0.68519000
H	2.24467700	1.51327200	1.31222400
C	1.65923100	-0.81551300	-1.07933000
H	0.94739200	-1.07912200	-1.85333000
C	2.78055400	-1.60909600	-0.88831800
H	2.93057500	-2.48527700	-1.50704400
C	3.51313500	-0.14624600	0.86937400
H	4.23542800	0.12481100	1.62974200
C	3.71563100	-1.27544500	0.08801200
H	4.59558200	-1.88936300	0.23302400

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