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Synthesis and Characterization of Non-Chelating Ruthenium–Indenylidene Olefin Metathesis Catalysts Derived from Substituted 1,1-diphenyl-2-propyn-1-ols

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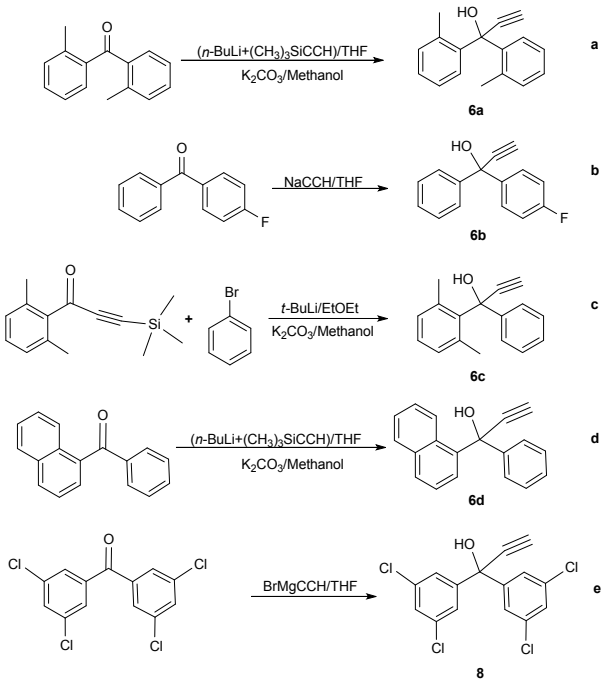
Supporting Information

Detailed synthesis procedure of the propargylic alcohols 6a-d, 8



Scheme S1 The general synthesis strategy of the ligands **6a-d** and **8**.

The synthesis of the compounds **6a** and **6d** were done by the addition of deprotonated ethynyltrimethylsilane using *n*-BuLi and followed by the deprotection of the trimethylsilyl group was carried out (Scheme S1, a, d). The propargylic alcohol **6b** was obtained by direct addition of the ethynyl group using a sodium salt according to the reported method in literature[1] (Scheme S1, b). For the synthesis of compound **8,** a similar procedure was followed as for **6b** while using BrMgCCH instead of NaCCH (Scheme S1, e). Finally, **6c** was prepared following the well-established method reported by the group of Bruneau (Scheme S1, c).[2] Single crystals suitable for x-ray diffraction of **6a** were obtained by slowly evaporation of **6a** in acetone solution.

X-ray data of 6a and 2

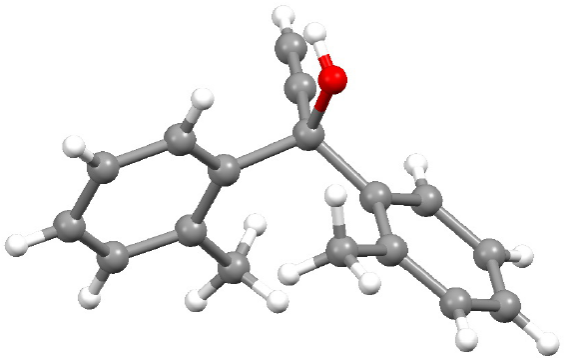


Fig. S1 Molecular structure of compound **6a**.

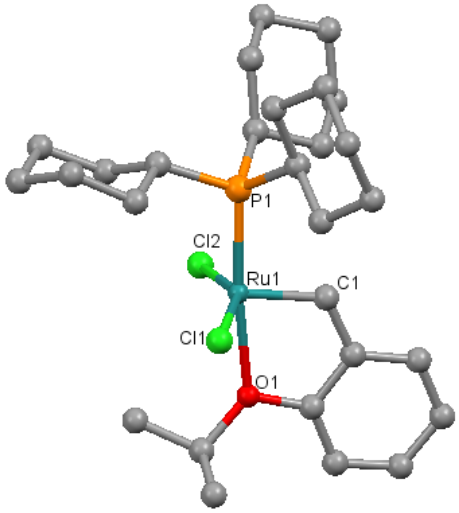
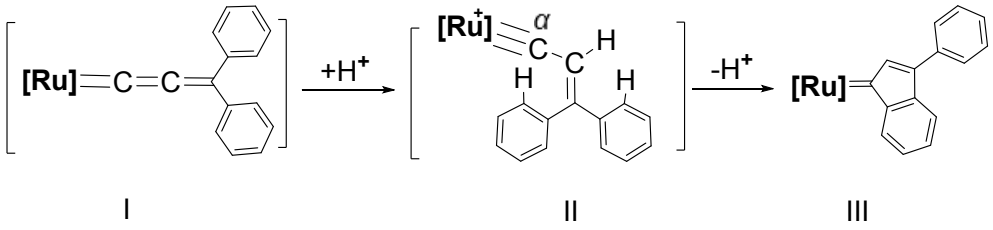


Fig. S2 Molecular structure of compound **2**, with atom labeling scheme of the hetero-atoms and carbon atom C1. Only one $RuCl_2$(2-*iso*-propoxybenzylidene)(PCy_3) molecule of the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.

Compound **6a** crystallized in the centro-symmetric monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. S1). Crystals of the complex **2** crystallized in the centro-symmetric monoclinic space group $P2_1/c$. The asymmetric unit of the structure consists of two, almost structurally identical $RuCl_2$(2-*iso*-propoxybenzylidene)(PCy_3) molecules (Fig. S2). In this case, the square-pyramidal geometry around the ruthenium atom is more distorted in comparison with **5a-d** and **3**, showing Ru-Cl bond lengths in the range of 2.330(1) and 2.344(1) Å, Ru-P bond lengths of 2.274(1) and 2.277(1) Å and Ru-O bond lengths of 2.258(3) and 2.285(3) Å, considering both molecules in the asymmetric unit. The Ru=C bond lengths are 1.832(5) and 1.841(4) Å. Especially the Ru-P bonds are considerably shorter in comparison with **5a-d** and **3**. Also, the Cl-Ru-Cl angles of 148.81(5) and 153.95(5)° and the P-Ru-O angles of 174.39(9) and 175.47(9)°, for both molecules, respectively, cause the ruthenium coordination polyheder to have a tendency towards a trigonal bipyramid. The 2-*iso*-propoxybenzylidene ligand is torsioned with respect to the P-Ru-O plane with O1-Ru1-C1-C2 torsion angles of -10.3(3) and 4.6(4)°, for both molecules, respectively.

Plausible mechanism for ruthenium indenyldene catalysts synthesis process



Scheme S2 Proposed mechanism for the formation of indenylidene complex **III** from allenylidene intermediates **I**.[3]

The mechanism for the formation of indenylidene species has been proposed and confirmed by several researchers (Scheme S2).[3] It is interesting to note that although two aromatic rings of the propargylic alcohols **6b,d** (one ring contains a substituent and the other ring is non-substituted) are available for reorganization through the allenylidene intermediate to indenylidene, only the non-substituted aromatic ring is suitable for reorganization, yielding a single compound **7b**,**d**, respectively. In the reports of Bruneau[2] and Schrödi[4], describing the synthesis of **4b** and its methoxy analogue, the reorganization occurred via the substituted aromatic ring. Although these results seem to be contradictory to each other, they are in good agreement with the assumption that the most electron rich aromatic ring will act to generate the five membered ring of the indenylidene part (III). This is in agreement with the proposed theory for the indenylidene formation from the reorganization of the allenylidene intermediate (from I to III).[3a] The *ortho*-proton from the electron-rich aromatic ring will be preferred by the electron deficient *α*-carbon from the protonated allenylidene intermediate (II). In general, when one of the two aromatic rings of the propargylic alcohol, contains one or more electron-donating substituents, this will be the employed aromatic ring to establish the reorganization for the formation of indenylidene.

Furthermore, it is noteworthy that during the ruthenium indenylidene formation process (Scheme 2), the formation of indenylidene moieties from substituted diphenyl propargylic alcohols could be inhibited by strong electron withdrawing substituents on the aromatic ring (*e.g.* 1,1-bis(3,5-dichlorophenyl)-2-propyn-1-ol (**8**), which could not generate an indenylidene moiety).

Single crystal X-ray diffraction

Crystal data for compound **2**. CCDC 986934, $C_{28}H_{45}Cl_2OPRu$, M = 600.58, monoclinic, space group $P2_1/c$ (No. 14), a = 11.4775(3) Å, b = 19.2194(5) Å, c = 25.7969(6) Å, β = 96.478(2)°, V = 5654.2(2) Å^3, Z = 8, T = 100 K, ρ_{calc} = 1.411 g cm^{-3}, μ(Mo-Kα) = 0.819 mm^{-1}, F(000) = 2512, 47765 reflections measured, 11553 unique (R_{int} = 0.1085) which were used in all calculations. The final R1 was 0.0543 ($I > 2\sigma(I)$) and wR2 was 0.1250 (all data). The asymmetric unit contains two structurally almost identical $RuCl_2$(2-*iso*-propoxybenzylidene)(PCy_3) molecules.

Crystal data for compound **3**. CCDC 986933, $C_{51}H_{76}Cl_2P_2Ru$, M = 923.03, trigonal, space group R-3 (No. 148), $a = b$ = 46.1591(18) Å, c = 13.9447(3) Å, V = 25731(2) Å^3, Z = 18, T = 100 K, ρ_{calc} = 1.072 g cm^{-3}, μ(Cu-Kα) = 3.804 mm^{-1}, F(000) = 8820, 35079 reflections measured, 11577 unique (R_{int} = 0.0915) which were used in all calculations. The final R1 was 0.0628 (I >2σ (I)) and wR2 was 0.1812 (all data). The 3-phenyl-1-indenylidene moiety was found disordered over two positions, rotated about 166° with respect to each other and refined with occupancy factors of 0.617(3) and 0.383(3), respectively.

Crystal data for compound **5a**. CCDC 986932, $C_{53}H_{80}Cl_2P_2Ru{+}CH_2Cl_2$, M = 1036.01, monoclinic, space group $P2_1/c$ (No. 14), a = 19.2677(13) Å, b = 14.6496(8) Å, c = 22.219(2) Å, β = 122.706(5)°, V = 5277.3(7) Å^3, Z = 4, T = 150 K, ρ_{calc} = 1.304 g cm^{-3}, μ(Mo-Kα) = 0.595 mm^{-1}, F(000) = 2192, 32170 reflections measured, 9032 unique (R_{int} = 0.0777) which were used in all calculations. The final R1 was 0.0634 ($I > 2\sigma(I)$) and wR2 was 0.1795 (all data). The 3-*o*-tolyl moiety was found disordered over two positions, rotated about 162° with respect to each other and was refined with occupancy factors of 0.433(11) and 0.567(11), respectively.

Crystal data for compound **5b**. CCDC 1005476, $C_{51}H_{75}Cl_2P_2Ru$, M = 941.02, trigonal, space group R-3 (No. 148), $a = b$ = 45.479(3) Å, c = 14.1790(5) Å, V = 25398(4) Å^3, Z = 18, T = 100 K, ρ_{calc} = 1.107 g cm^{-3}, μ(Cu-Kα) = 3.889 mm^{-1}, F(000) = 8964, 33760 reflections measured, 9865 unique (R_{int} = 0.1960) which were used in all calculations. The final R1 was 0.0916 ($I > 2\sigma(I)$) and wR2 was 0.2086 (all data).

Crystal data for compound **5c**. CCDC 1005474, $C_{53}H_{80}Cl_2P_2Ru$, M = 951.08, trigonal, space group R-3 (No. 148), $a = b$ = 47.1514(15) Å, c = 13.6692(3) Å, V = 26319(2) Å^3, Z = 18, T = 100 K, ρ_{calc} = 1.080 g cm^{-3}, μ(Cu-Kα) = 3.731 mm^{-1}, F(000) = 9108, 54435 reflections measured, 10305 unique (R_{int} = 0.1012) which were used in all calculations. The final R1 was 0.0720 ($I > 2\sigma(I)$) and wR2 was 0.1715 (all data). The 3-2,6-xylyl-1-indenylidene moiety was found disordered over two positions, rotated about 150° with respect to each other and was refined with occupancy factors of 0.434(4) and 0.566(4), respectively.

Crystal data for compound **5d**. CCDC 1005475, $C_{55}H_{78}Cl_2P_2Ru$, M = 973.08, trigonal, space group R-3 (No. 148), $a = b$ = 46.0420(17) Å, c = 14.0313(3) Å, V = 25760(2) Å^3, Z = 18, T = 100 K, ρ_{calc} = 1.129 g cm^{-3}, μ(Cu-Kα) = 3.825 mm^{-1}, F(000) = 9288, 35274 reflections measured, 10053 unique (R_{int} = 893) which were used in all calculations. The final R1 was 0.0968 ($I > 2\sigma(I)$) and wR2 was 0.2263 (all data). The 3-naphthyl-1-indenylidene moiety was found disordered over two positions, rotated about 163° with respect to each other and was refined with occupancy factors of 0.442(5) and 0.558(5), respectively.

Crystal data for compound **6a**. CCDC 1005473, $C_{17}H_{16}O_1$, M = 236.31, monoclinic, space group $P2_1/c$ (No. 14), a = 6.6764(2) Å, b = 16.5673(6) Å, c = 11.6107(2) Å, β = 92.308(3)°, V = 1283.22(7) Å^3, Z = 4, T = 100 K, ρ_{calc} = 1.223 g cm^{-3}, μ(Cu-Kα) = 0.574 mm^{-1}, F(000) = 504, 5337 reflections measured, 2252 unique (R_{int} = 0.0233) which were used in all calculations. The final R1 was 0.0383 ($I > 2\sigma(I)$) and wR2 was 0.1072 (all data).

Crystal data for compound **7a**. CCDC 1005472, $C_{53}H_{44}Cl_2P_2Ru$, M = 914.79, triclinic, space group P-1 (No. 2), a = 10.2241(8) Å, b = 12.7121(10) Å, c = 20.0557(16) Å, α = 72.940 (7)°, β = 122.706(5)°, γ= 81.407 (6)°, V = 2415.8(3) Å^3, Z = 2, T = 150 K, ρ_{calc} = 1.258 g cm^{-3}, μ(Mo-Kα) = 0.534 mm^{-1}, F(000) = 940, 15613 reflections measured, 7988 unique (R_{int} = 0.0717) which were used in all calculations. The final R1 was 0.0619 ($I > 2\sigma(I)$) and wR2 was 0.1767 (all data). For the structure of **7a**, the data was collected on a RU200 rotating anode with MAR345 image plate, only capable of using φ scans, which is not entirely sufficient to attain complete triclinic data, hence the lower completeness of 94%.

^{1}H, ^{13}C and ^{31}P NMR spectra

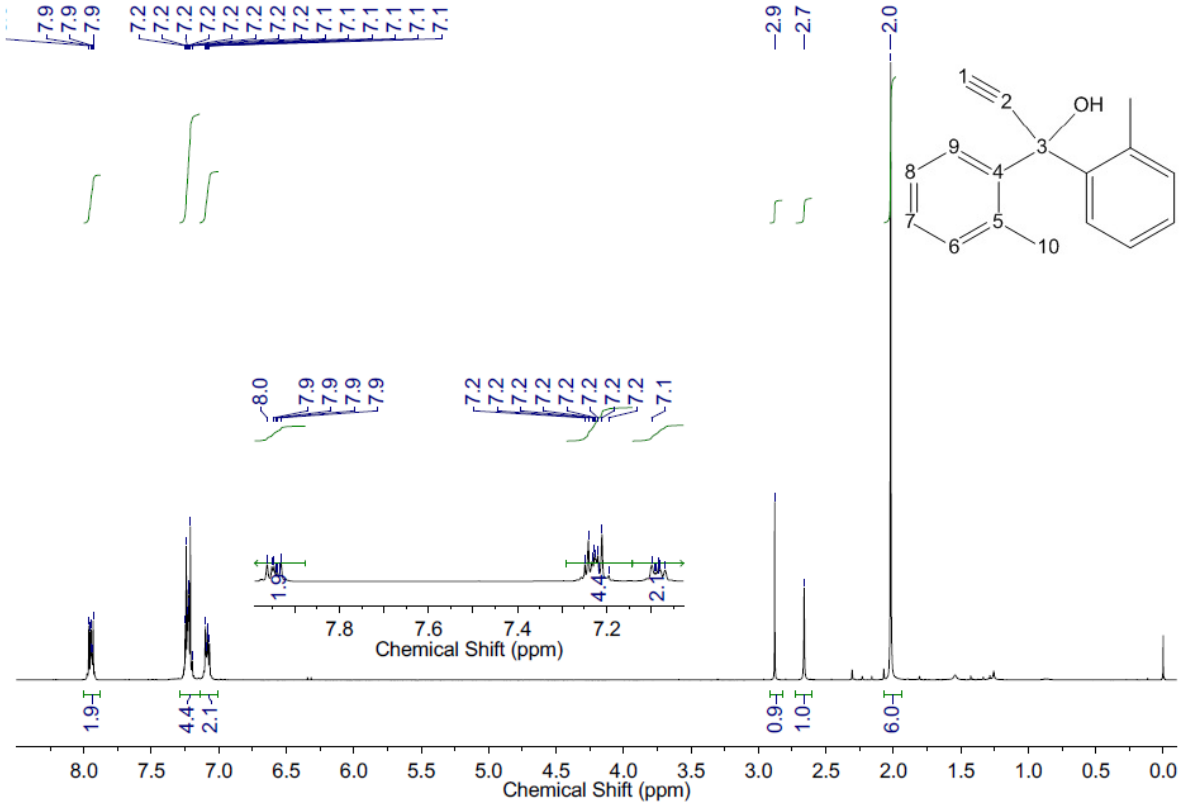


Fig. S3 ^{1}H NMR spectrum for **6a**.

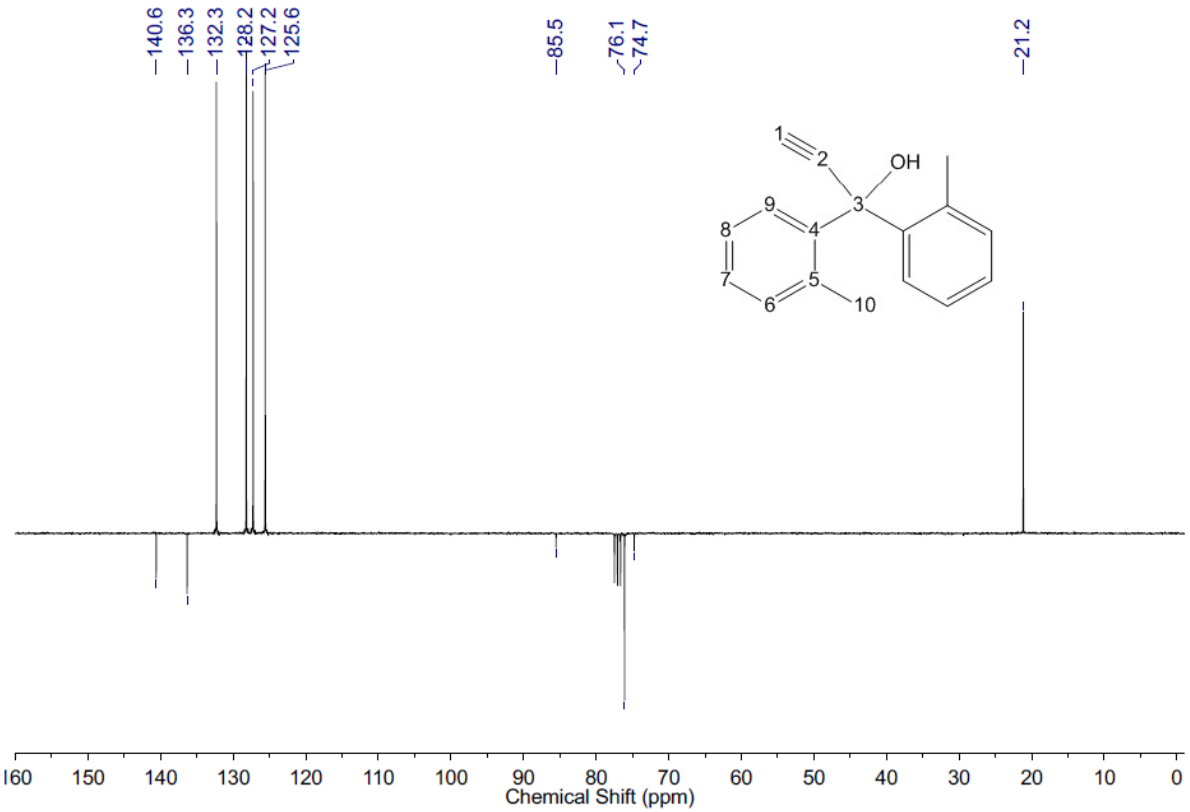


Fig. S4 ^{13}C{^{1}H} NMR spectrum for **6a**.

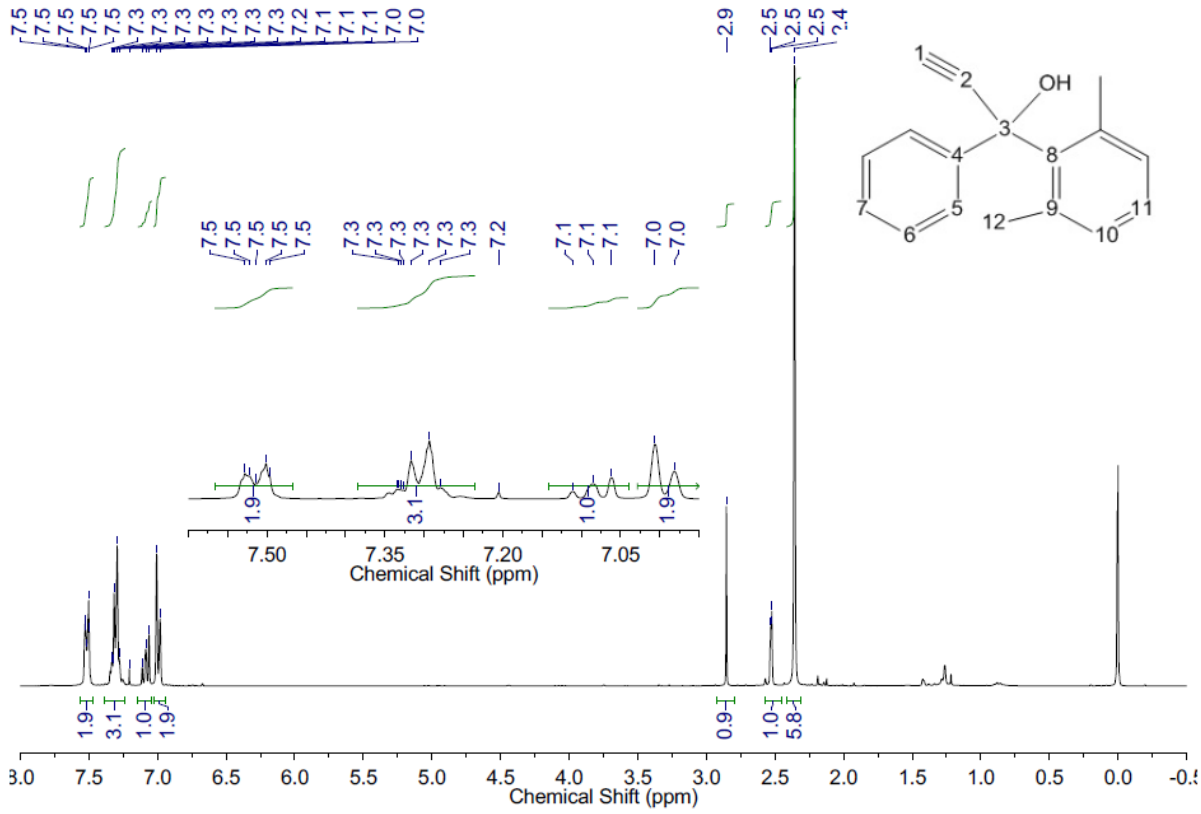


Fig. S5 ^{1}H NMR spectrum for **6c**.

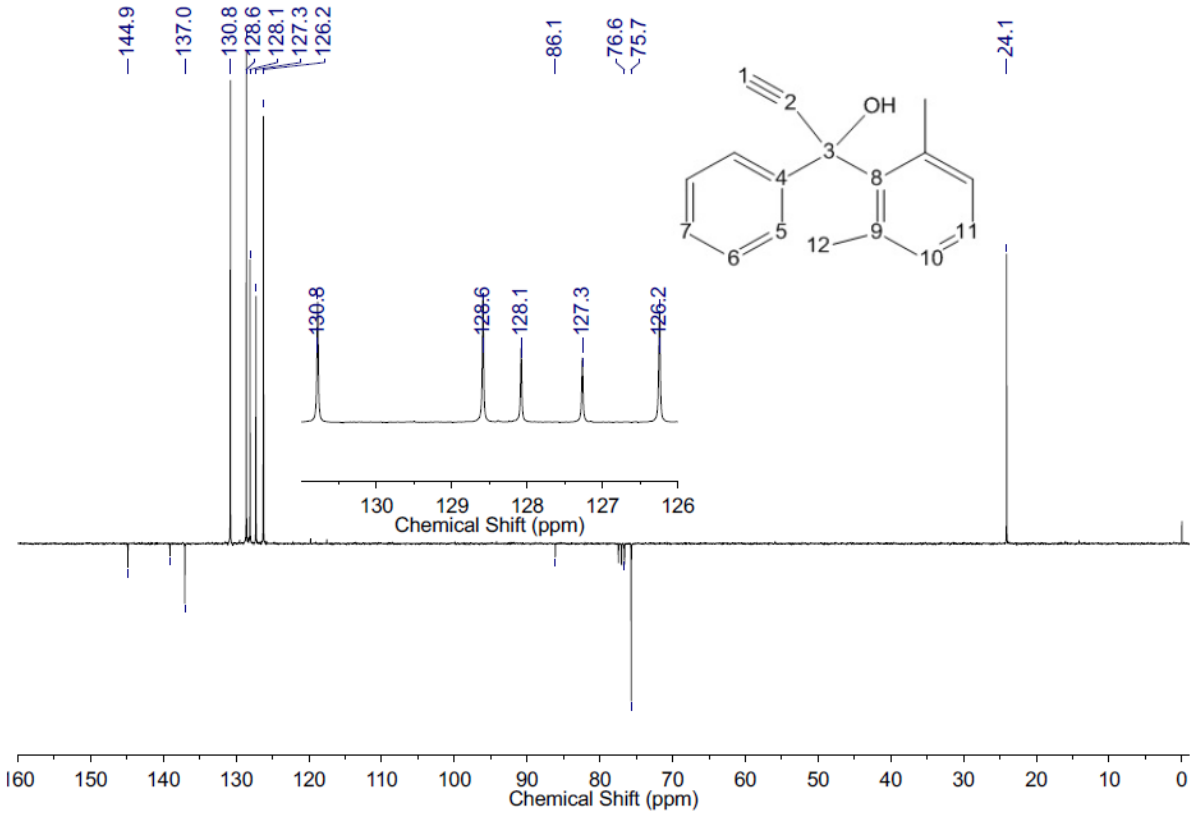


Fig. S6 ^{13}C{^{1}H} NMR spectrum for **6c**.

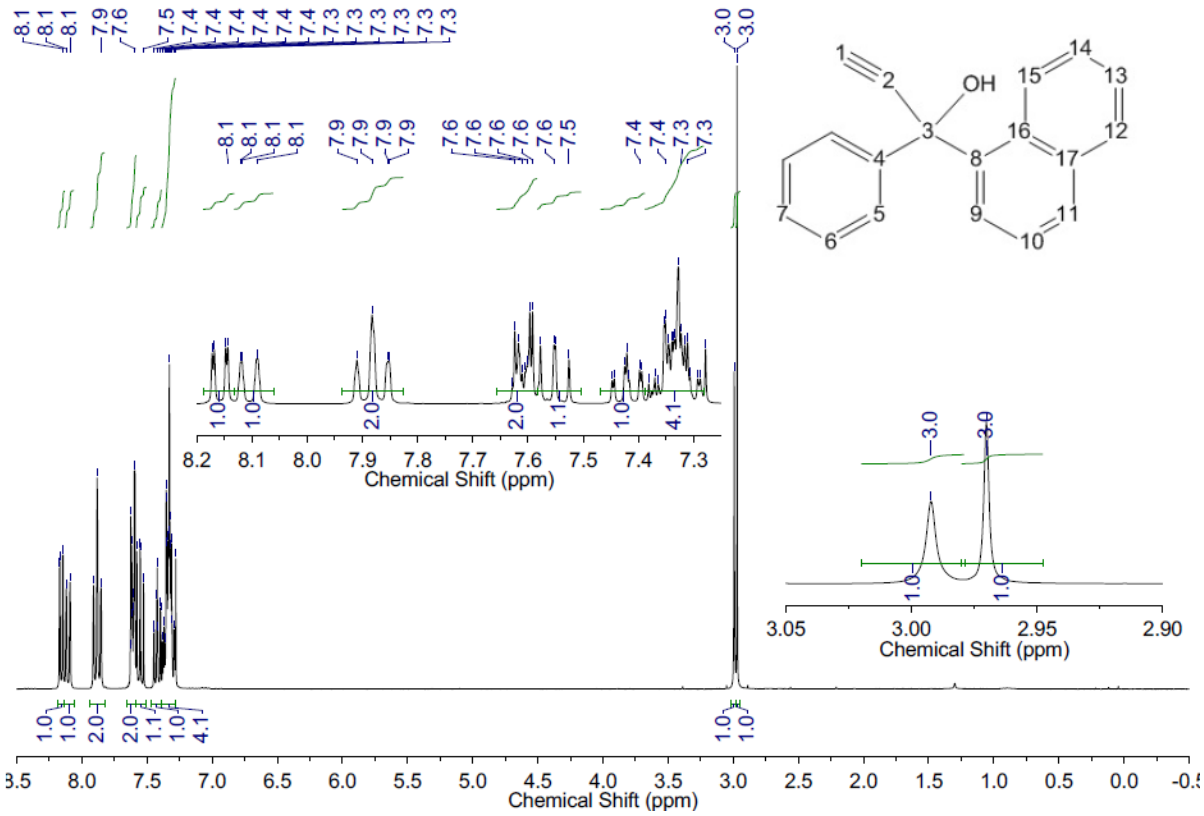


Fig. S7 ^{1}H NMR spectrum for **6d**.

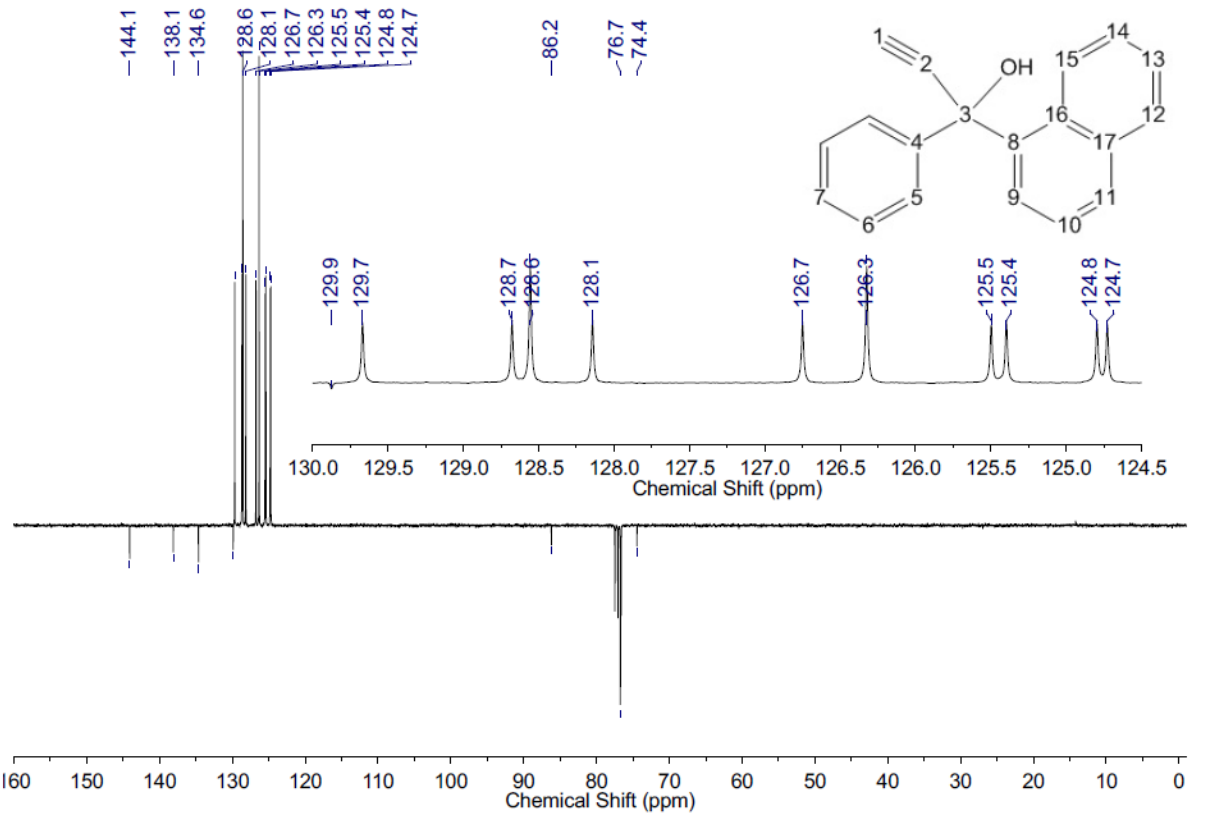


Fig. S8 ^{13}C{^{1}H} NMR spectrum for **6d**.

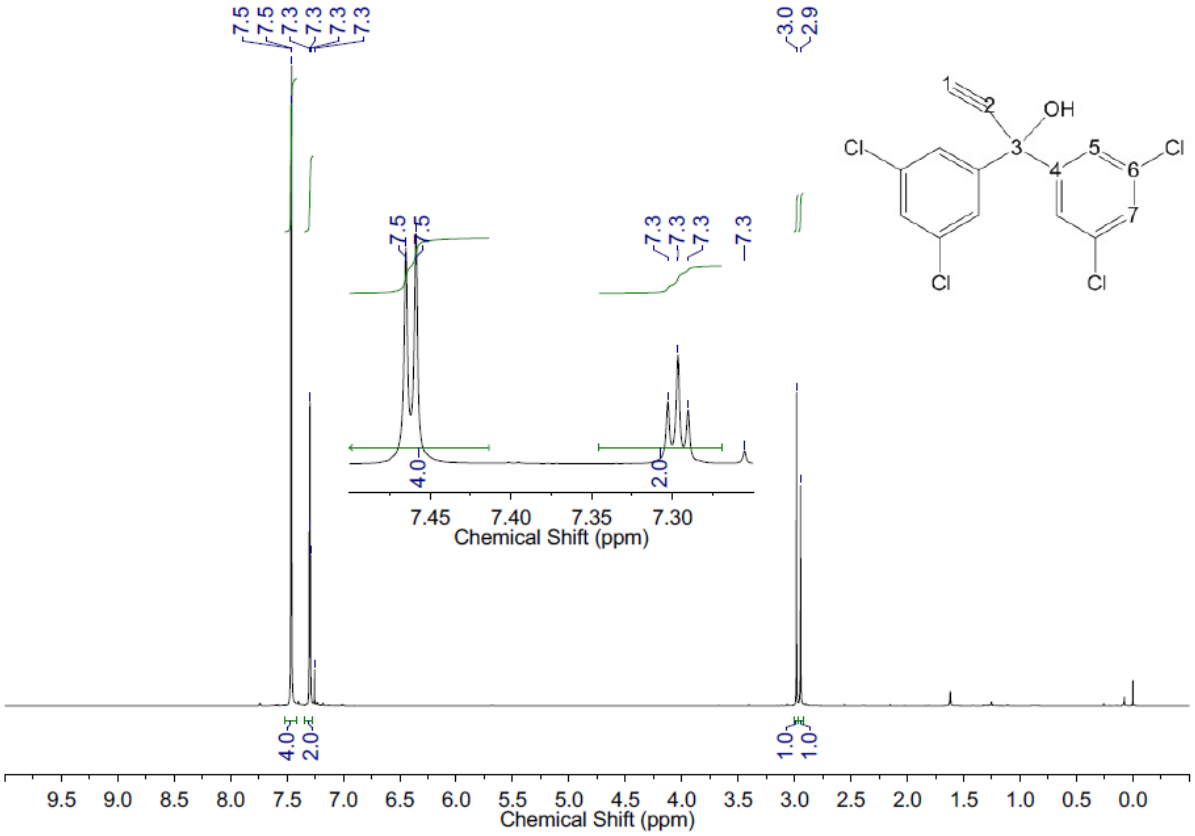


Fig. S9 ^{1}H NMR spectrum for **8**.

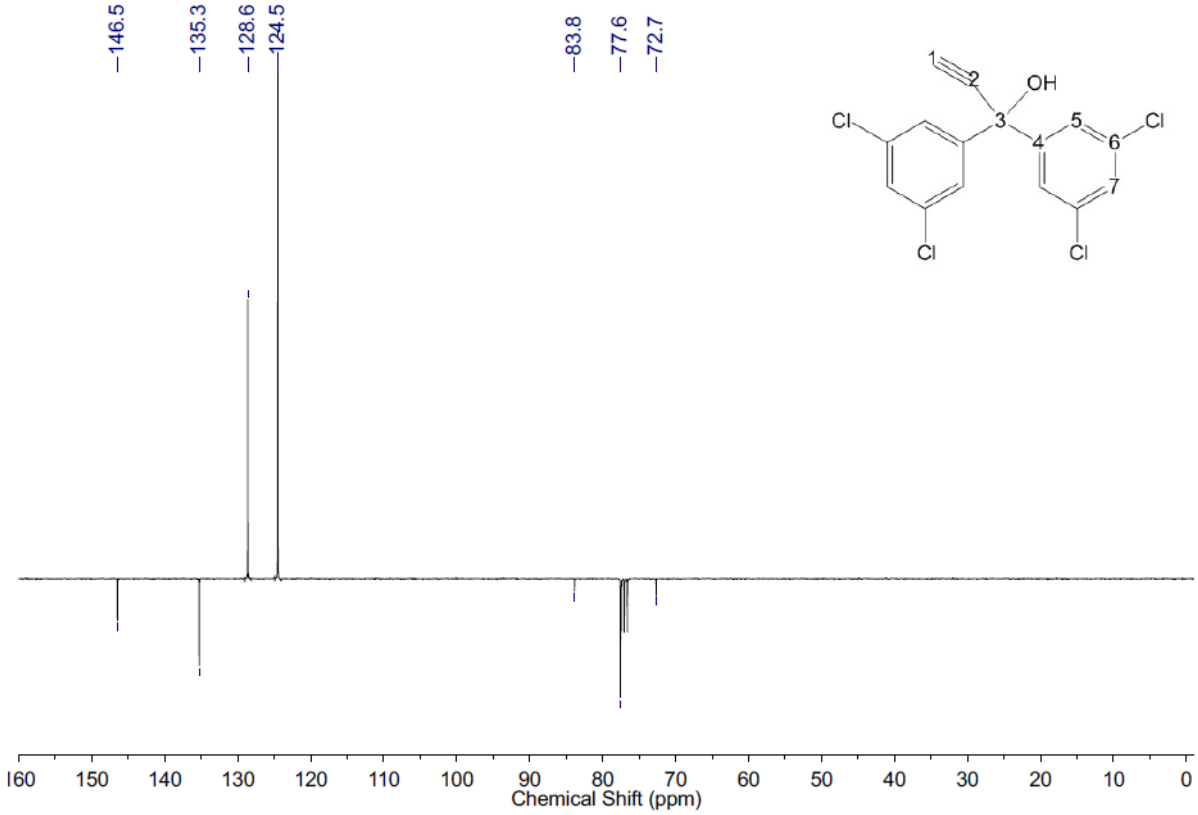


Fig. S10 ^{13}C{^{1}H} NMR spectrum for **8**.

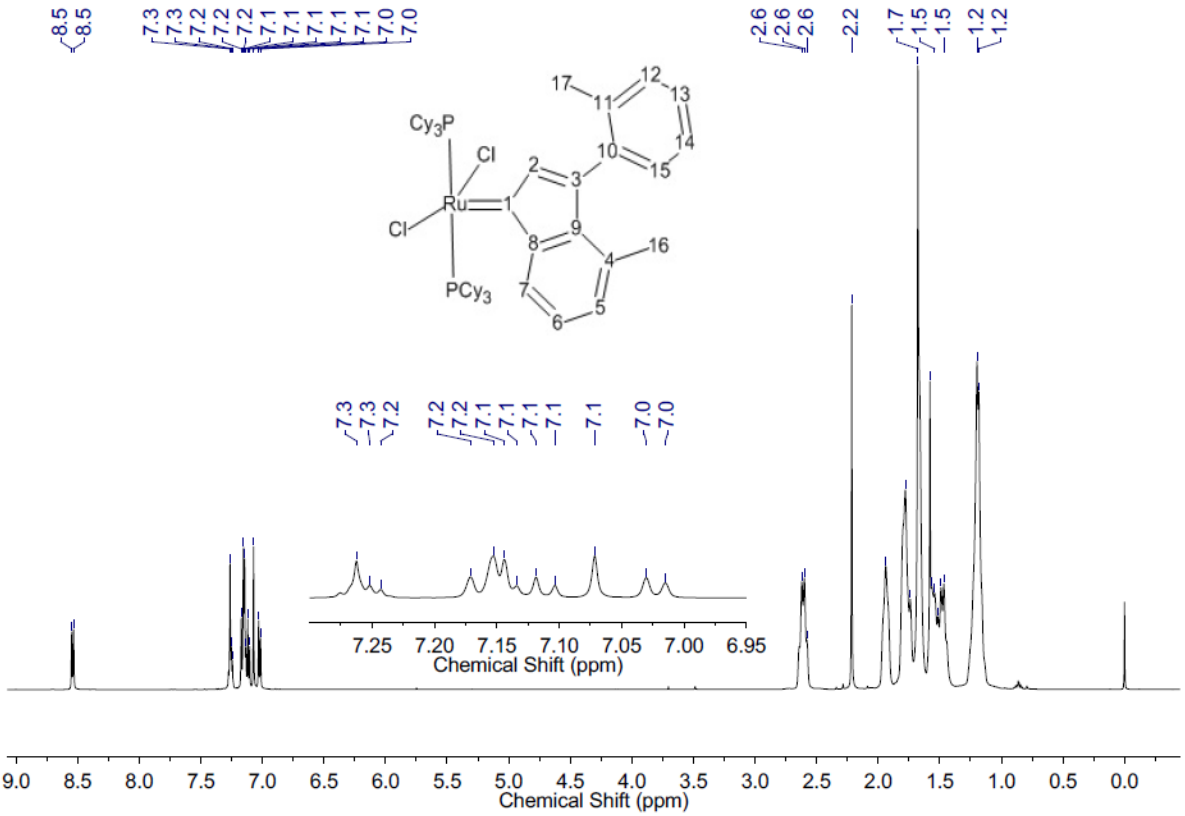


Fig. S11 ^{1}H NMR spectrum for **5a**.

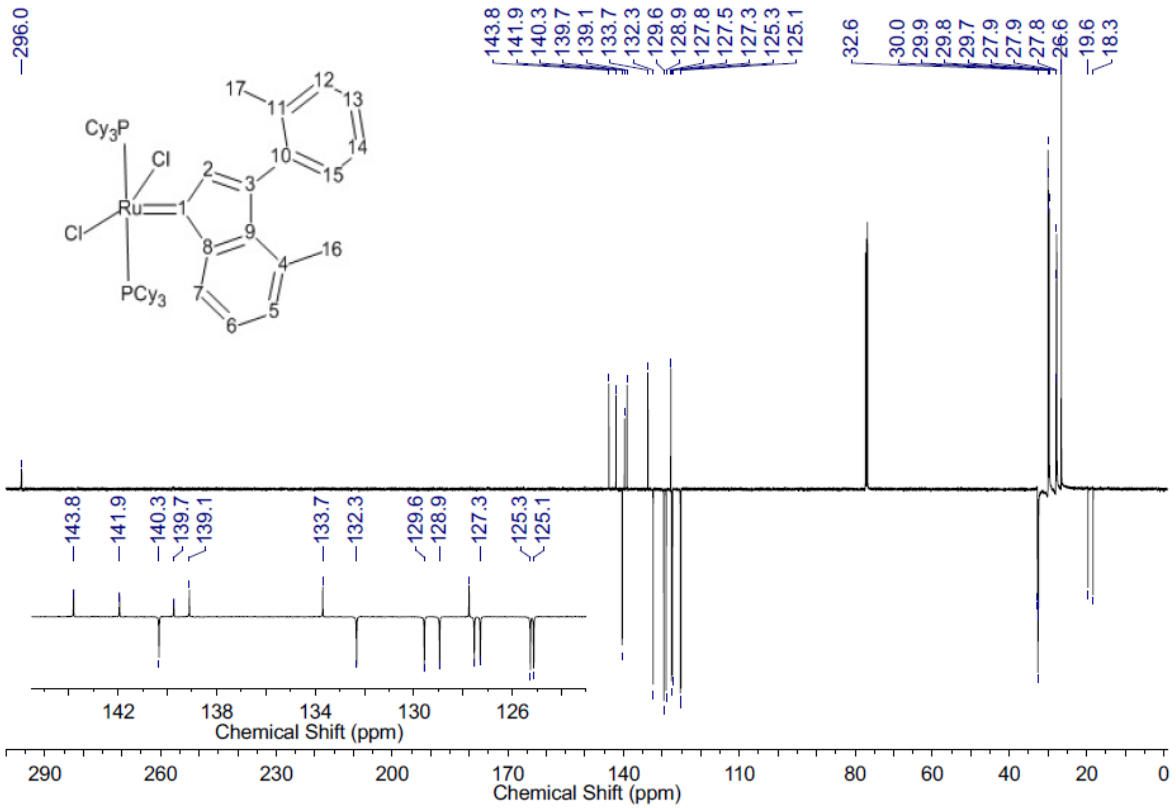


Fig. S12 ^{13}C{^{1}H} NMR spectrum for **5a**.

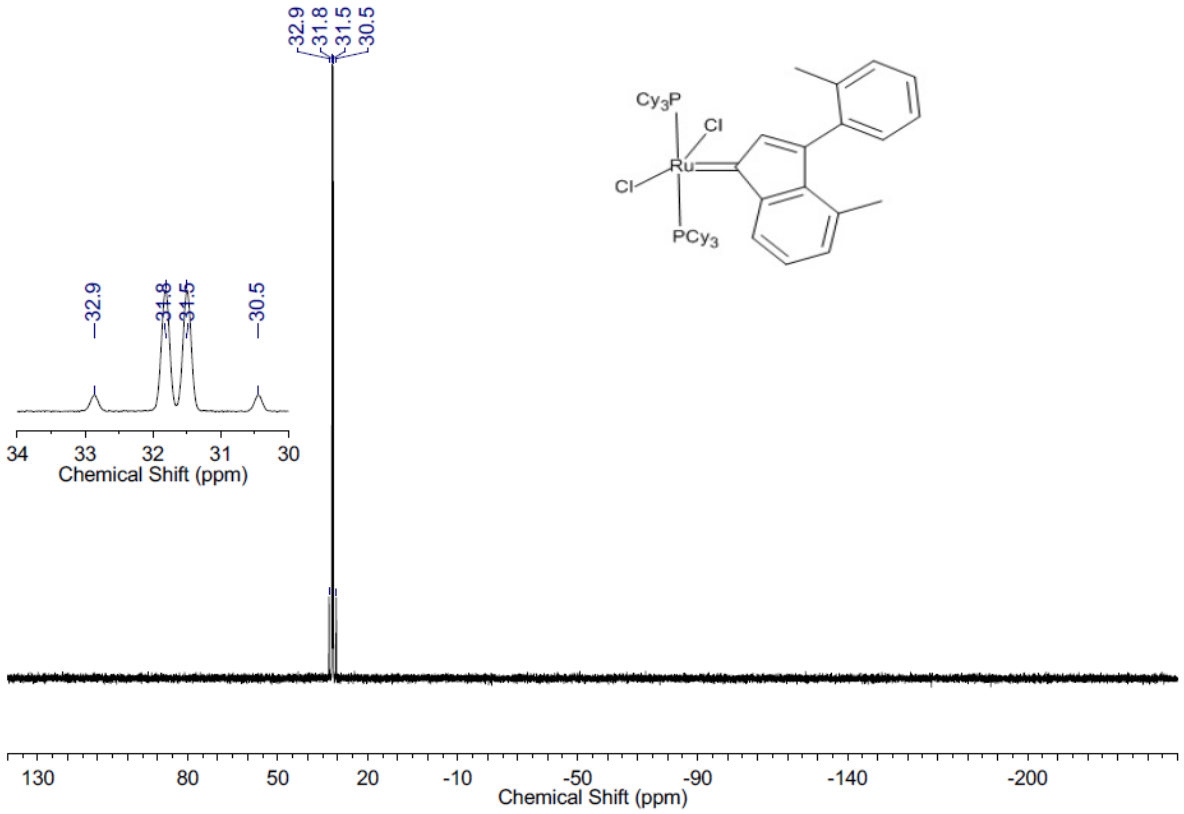


Fig. S13 $^{31}P\{^{1}H\}$ NMR spectrum for **5a**.

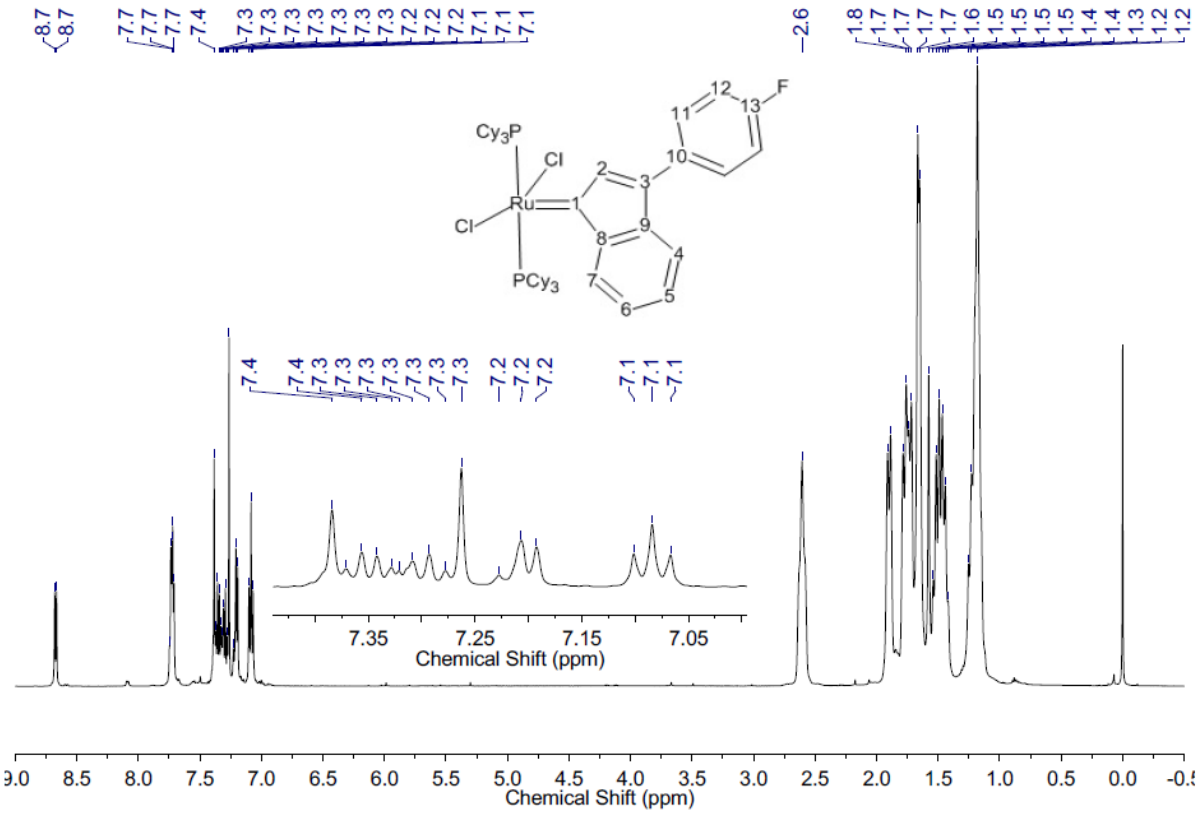


Fig. S14 ^{1}H NMR spectrum for **5b**.

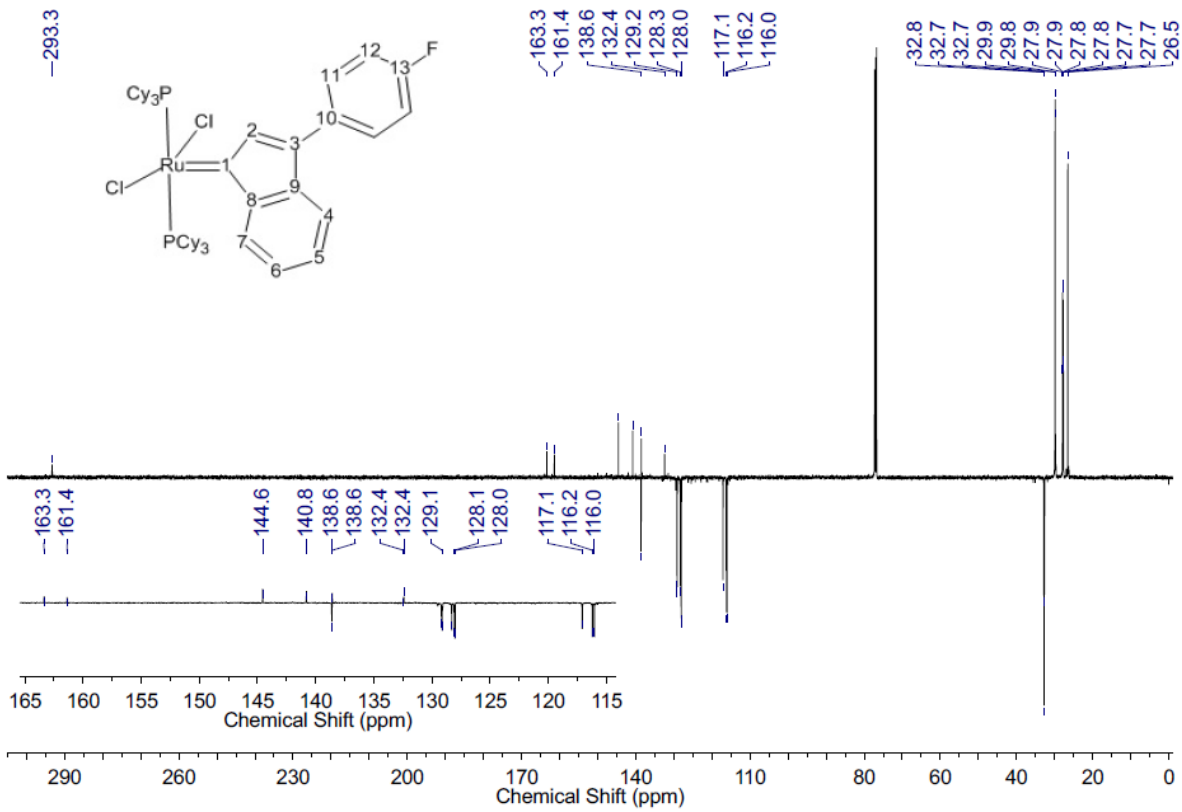


Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum for **5b**.

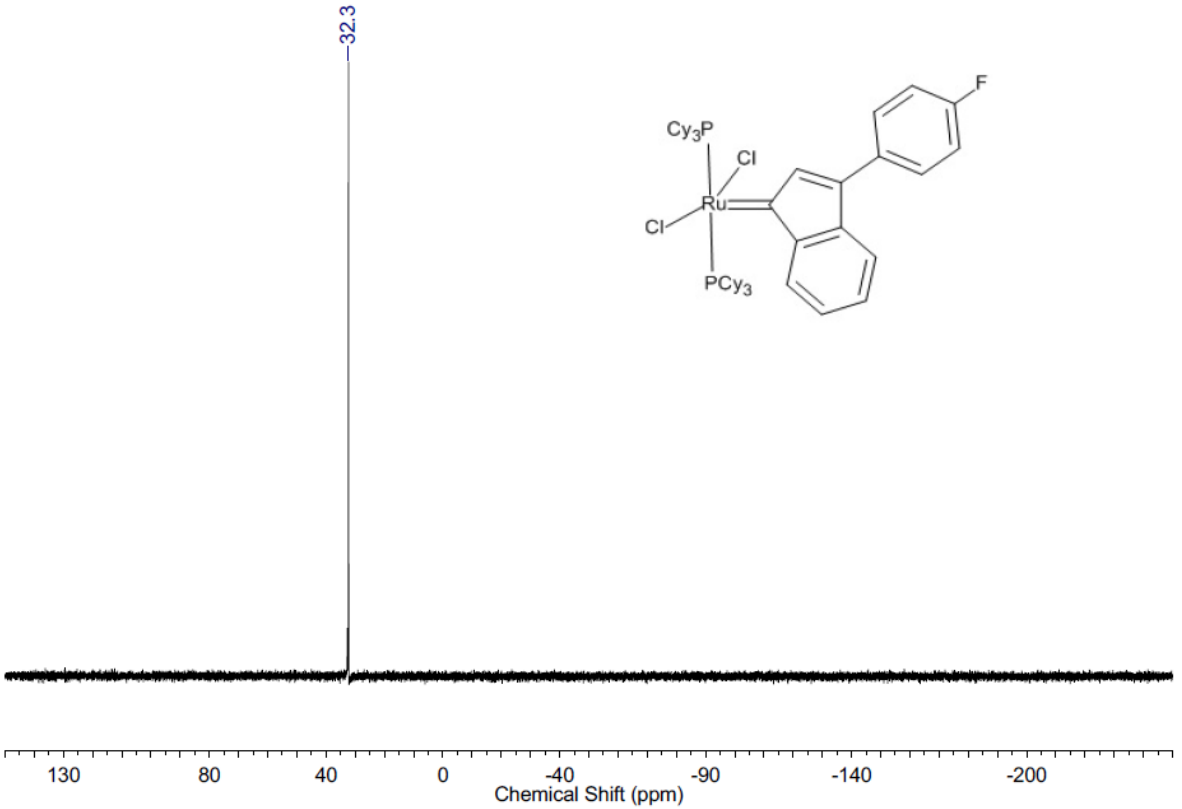


Fig. S16 $^{31}P\{^{1}H\}$ NMR spectrum for **5b**.

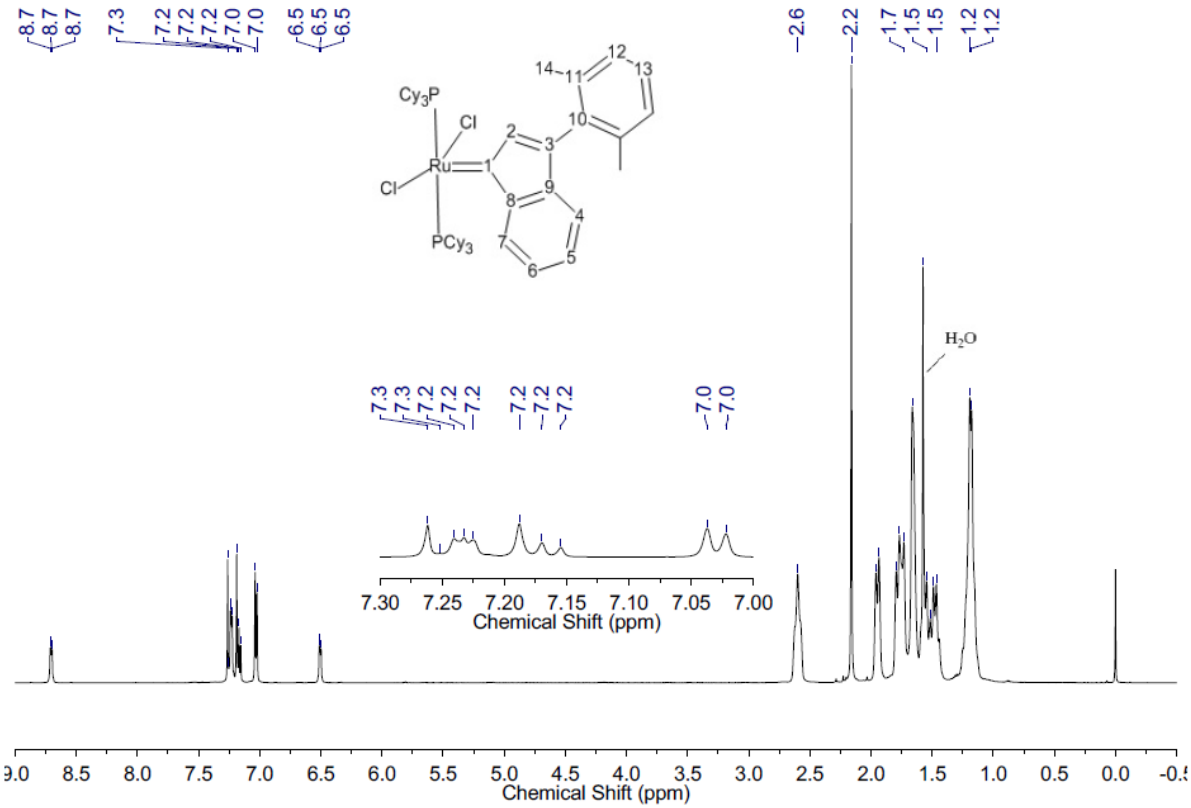


Fig. S17 ^{1}H NMR spectrum for **5c**.

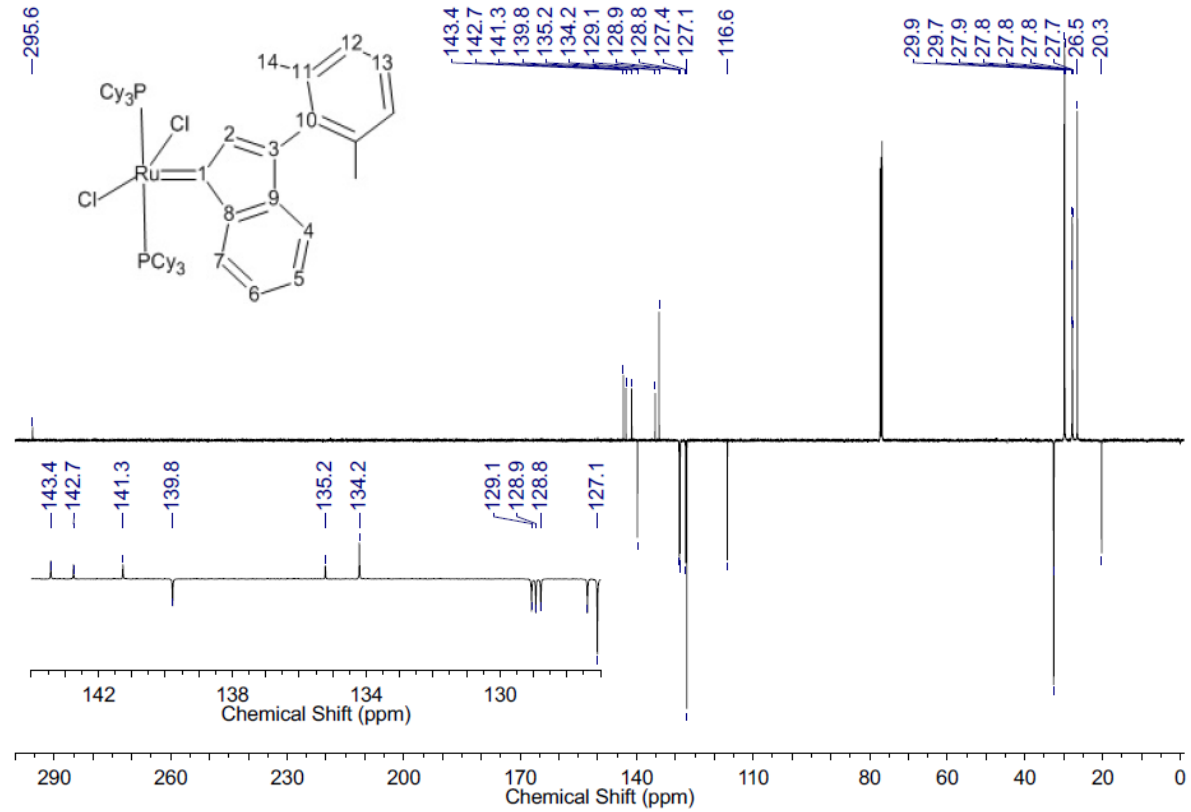


Fig. S18 $^{13}C\{^{1}H\}$ NMR spectrum for **5c**.

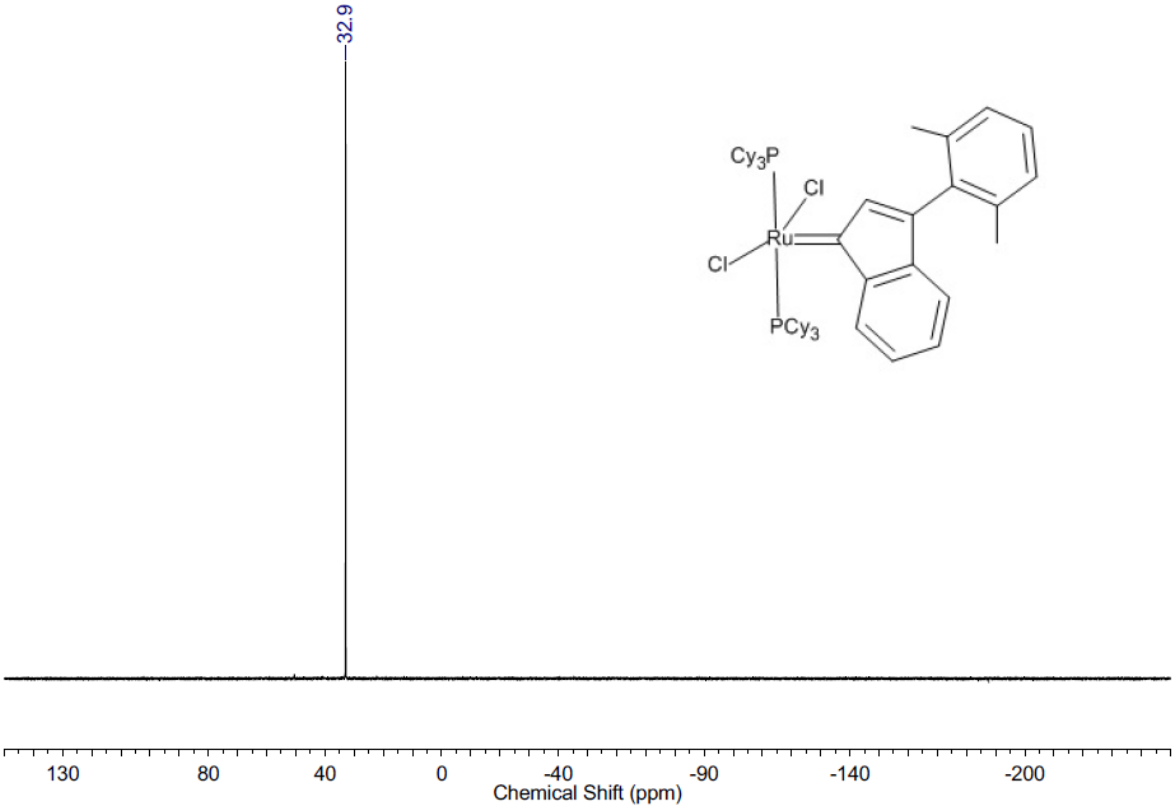


Fig. S19 $^{31}P\{^{1}H\}$ NMR spectrum for **5c**.

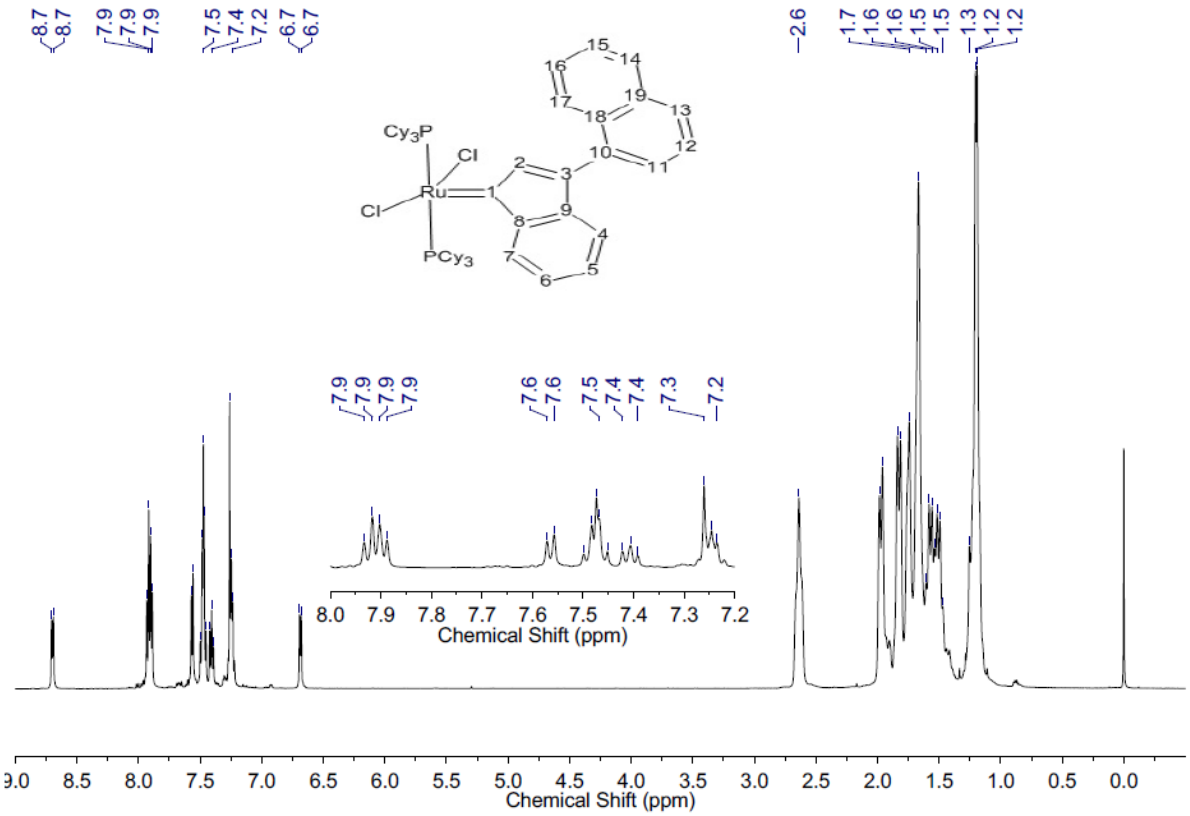


Fig. S20 ^{1}H NMR spectrum for **5d**.

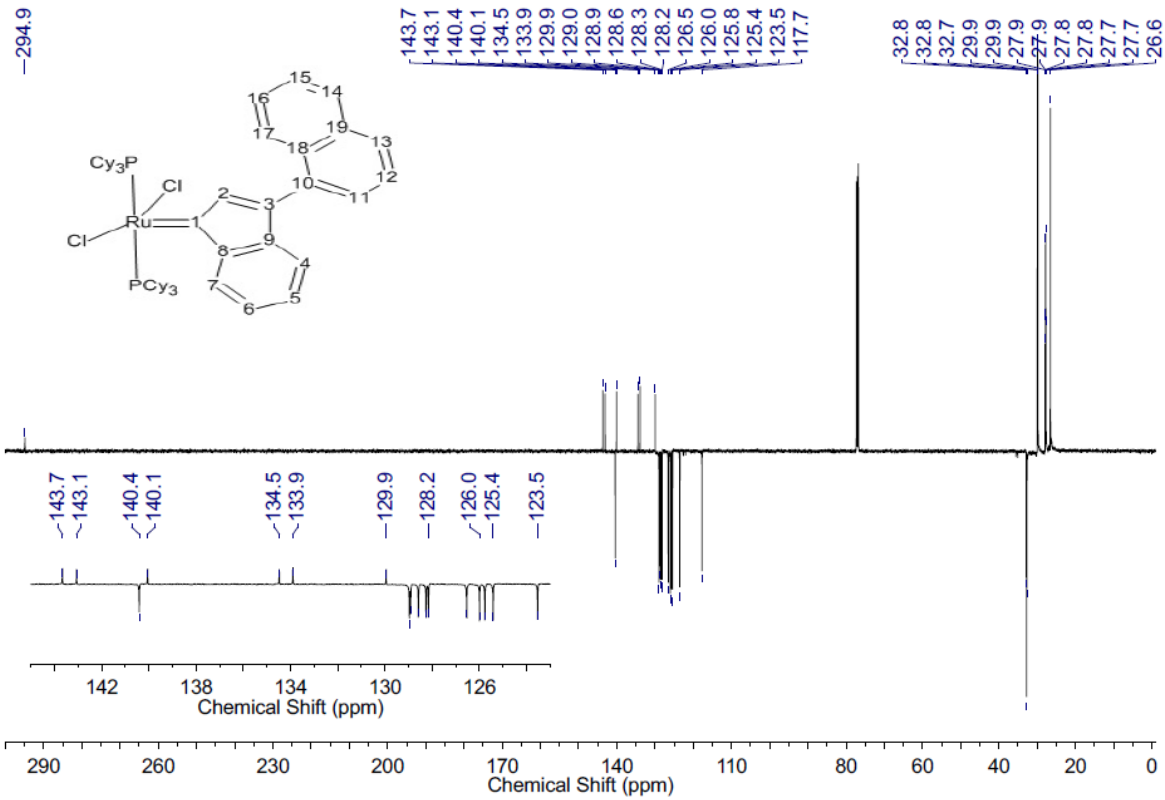


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum for **5d**.

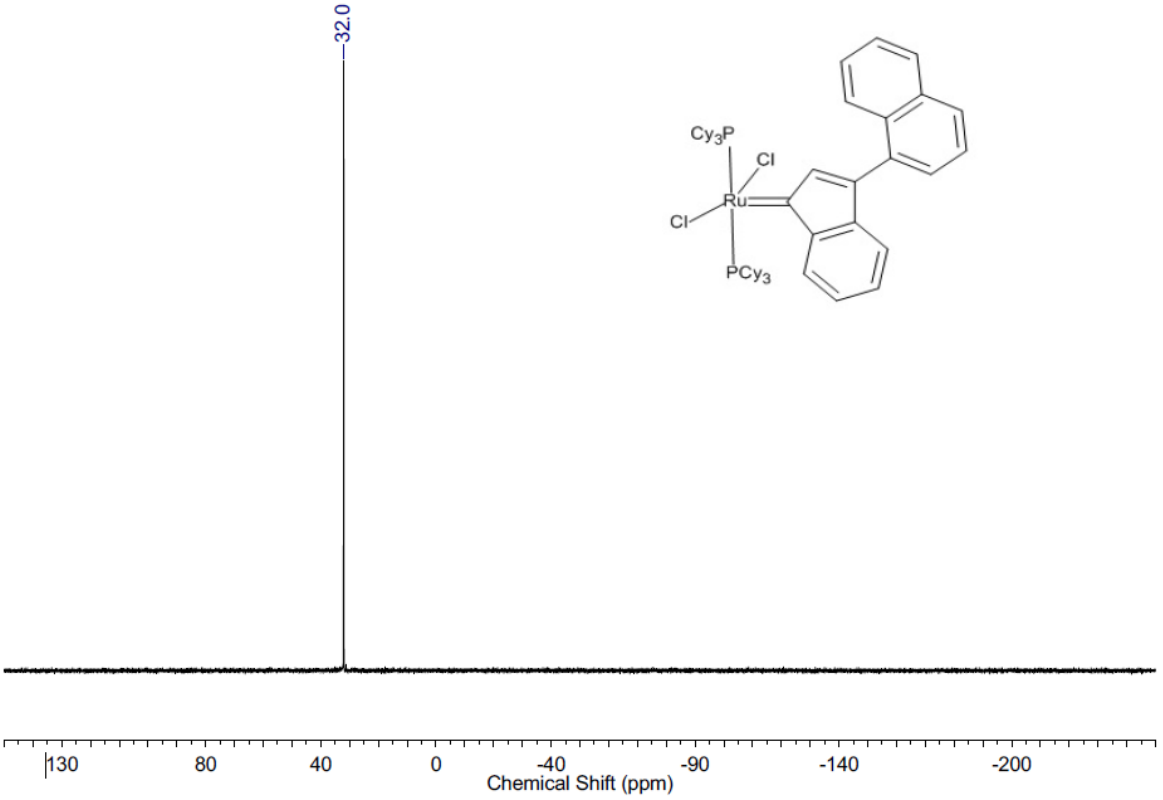


Fig. S22 $^{31}P\{^{1}H\}$ NMR spectrum for **5d**.

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