

Diastereoselective Attack on Chiral-at-Metal Ruthenium Allenylidene Complexes to Give Alkynyl Complexes

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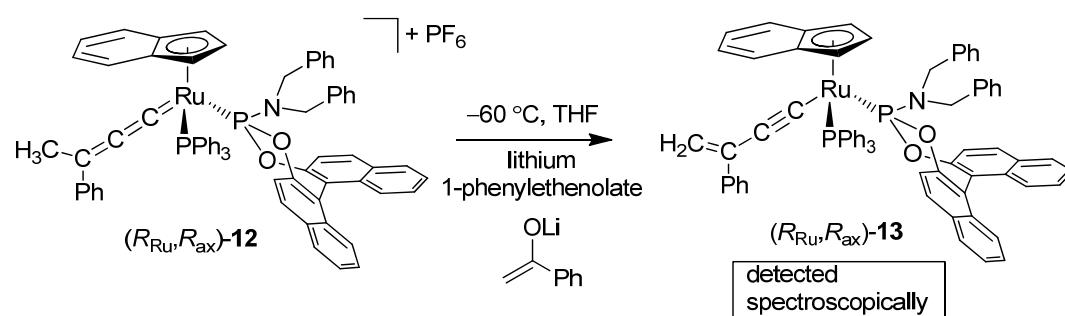
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1. Experimental and spectroscopic data for the generation of the enynyl complex (R_{Ru}, R_{ax})-**13**

The reaction between (R_{Ru}, R_{ax})-**12** and 1-phenylethenolate did not result in a nucleophilic attack at the C_γ atom, but resulted mainly in deprotonation of the methyl group to give the neutral enynyl complex (R_{Ru}, R_{ax})-**13** (Scheme S1).

Scheme S1. Enynyl formation.



The complex could not be isolated spectroscopically pure; the isolated material contained other, unidentified material. However, key NMR and IR data in addition to the FAB-MS of the crude material established the formation of (R_{Ru}, R_{ax})-**13**. The terminal $=CH_2$ unit gave two signals at 5.29 and 4.93 ppm in the 1H NMR and a diagnostic signal at 110.2 ppm in the $^{13}C\{^1H\}$ NMR in addition to signals at 113.6 and 112.1 ppm for the $Ru-C\equiv C$ carbon atoms. Also, bands at 2069 cm^{-1} and 2034 cm^{-1} were observed in the IR, while the band around 1950 cm^{-1} diagnostic for allenylidene complexes has disappeared. These spectroscopic data closely resemble those of previously synthesized enynyl complexes. It has previously been reported that hydrogens on carbon atoms in a position alpha to the C_γ atom of the allenylidene chain can be considerably acidic. Such protons can be removed by bases as weak as K_2CO_3 , as shown for an allenylidene

complex $[\text{Ru}(\text{Ind})(\text{PPh}_3)_2=\text{C}=\text{C}=\text{C}(\text{CH}_2)\text{R}]^+$ which gave upon deprotonation an enynyl complex (R denotes a cyclic steroid backbone, of which the CH_2 group is a member).

Generation of $(R_{\text{Ru}}, R_{\text{ax}})$ -[Ru(Ind)(PPh₃)(6){C≡C-C=(CH₂)Ph}]⁺ PF₆[−] [(R_{Ru}, R_{ax})-13]. A two neck round bottom flask was charged with acetophenone (0.277 g, 2.31 mmol) and THF (2 mL). The flask was then cooled to −60 °C followed by the rapid addition of freshly titrated LDA (5 mL, 0.46 M) and the solution was stirred at −60 °C for two hours and then warmed to room temperature. To a separate Schlenk tube was added $(R_{\text{Ru}}, R_{\text{ax}})$ -[Ru(Ind)(PPh₃)(6){C=C=C(CH₃)Ph}]⁺ PF₆[−] (0.232 g, 0.228 mmol) and THF (10 mL) and the solution was cooled to −60 °C for 10 minutes followed by the dropwise addition of the prepared acetophenone enolate (0.801 mL, 0.329 M, 0.341 mmol) over the course of 7 minutes. The solution was stirred at −60 °C for 2 hours and at room temperature for 2 hours. The solvent was removed by oil pump vacuum to yield the crude solid as a mixture of alkynyl-vinylidene and enolate attack products. The crude solid was purified by flash column chromatography (2 × 30 cm silica column, eluted with 2:1 v/v CH₂Cl₂/diethyl ether) to yield $(R_{\text{Ru}}, R_{\text{ax}})$ -13 as impure orange solid (0.129 g, 0.094 mmol, 42 %). Key NMR assignment data (δ, CDCl₃): ¹H 5.29 (s, 1H, C=CH), 4.93 (s, 1H, C=CH). ¹³C {¹H}: 113.6 (s, C_ω), 112.1 (s, C_β), 110.2 (s, PhC=CH₂). ³¹P {¹H}: 177.98 (d, ³J_{PP}=124.7 Hz, (R)-6), 55.55 (d, ³J_{PP}=123.9 Hz, PPh₃). IR (cm^{−1}, ATR): 3428(m), 3056(w), 2069(s), 2034(s), 1683(m), 1590(m), 1464(s), 1433(s), 1325(s), 1229(s), 1092(s), 952(s), 822(s), 743(s), 693(s). MS (FAB): 1116 ([$(R_{\text{Ru}}, R_{\text{ax}})$ -13]⁺, 35%), 988 ([$(R_{\text{Ru}}, R_{\text{ax}})$ -13 − C≡C-PhC=CH₂]⁺, 10%), 854 ([$(R_{\text{Ru}}, R_{\text{ax}})$ -13 − PPh₃]⁺, 60%).

2. Table S1 (Crystallographic Parameters)

	$[(R_{Ru}, R_{ax})\text{-11}]^+PF_6^- \cdot CH_2Cl_2$	$(R_{Ru}, R_{ax})\text{-17} \cdot \text{toluene}$
Empirical formula	$C_{79}H_{66}Cl_2F_6NO_2P_3Ru$	$C_{91}H_{73}NO_3P_2Ru$
Formula weight	1440.20	1391.51
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	P1	$P2_12_12_1$
Unit cell dimensions a, b, c [Å]	a = 11.1558(9) Å b = 11.8706(8) Å c = 14.5713(11) Å	a = 14.1888(4) Å b = 17.6625(5) Å c = 29.0539(9) Å
Unit cell dimensions α , β , γ [deg]	$\alpha = 110.713(4)^\circ$ $\beta = 96.502(4)^\circ$ $\gamma = 107.918(4)^\circ$	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume / Z	1663.0(2) Å ³ / 1	7281.2(4) Å ³ / 4
Density (calculated)	1.438 Mg/m ³	1.269 Mg/m ³
Absorption coefficient	0.455 mm ⁻¹	0.311 mm ⁻¹
F(000)	740	2896
Crystal size / mm ³	0.219 × 0.187 × 0.059	0.432 × 0.174 × 0.079
Theta range for data collection	1.945 to 28.356°	1.597 to 27.117°
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$	$-18 \leq h \leq 18$, $-14 \leq k \leq 22$, $-37 \leq l \leq 37$
Reflections collected	38508	148862
Independent reflections	15431 [R(int) = 0.0424]	16056 [R(int) = 0.0715]
Completeness to theta = 25.242°	99.9 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8621 and 0.7834	0.9281 and 0.8579
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	15431 / 589 / 798	16056 / 140 / 822
Goodness-of-fit on F2	1.024	1.050
Final R indices [I > 2sigma(I)]	R1 = 0.0477, wR2 = 0.1098	R1 = 0.0438, wR2 = 0.1142
R indices (all data)	R1 = 0.0550, wR2 = 0.1149	R1 = 0.0545, wR2 = 0.1222
Absolute structure parameter	-0.032(11)	-0.010(8)
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.726 and -0.769 e.Å ⁻³	0.964 and -0.416 e.Å ⁻³

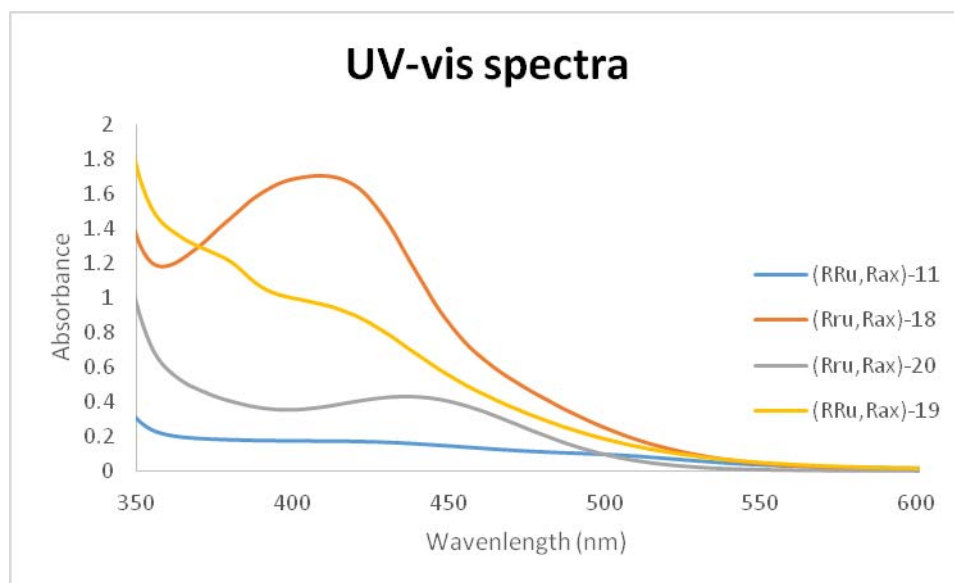
3. UV-vis spectra of selected complexes

(R_{Ru}, R_{ax})-**11** (blue)

(R_{Ru}, R_{ax})-**18** (orange)

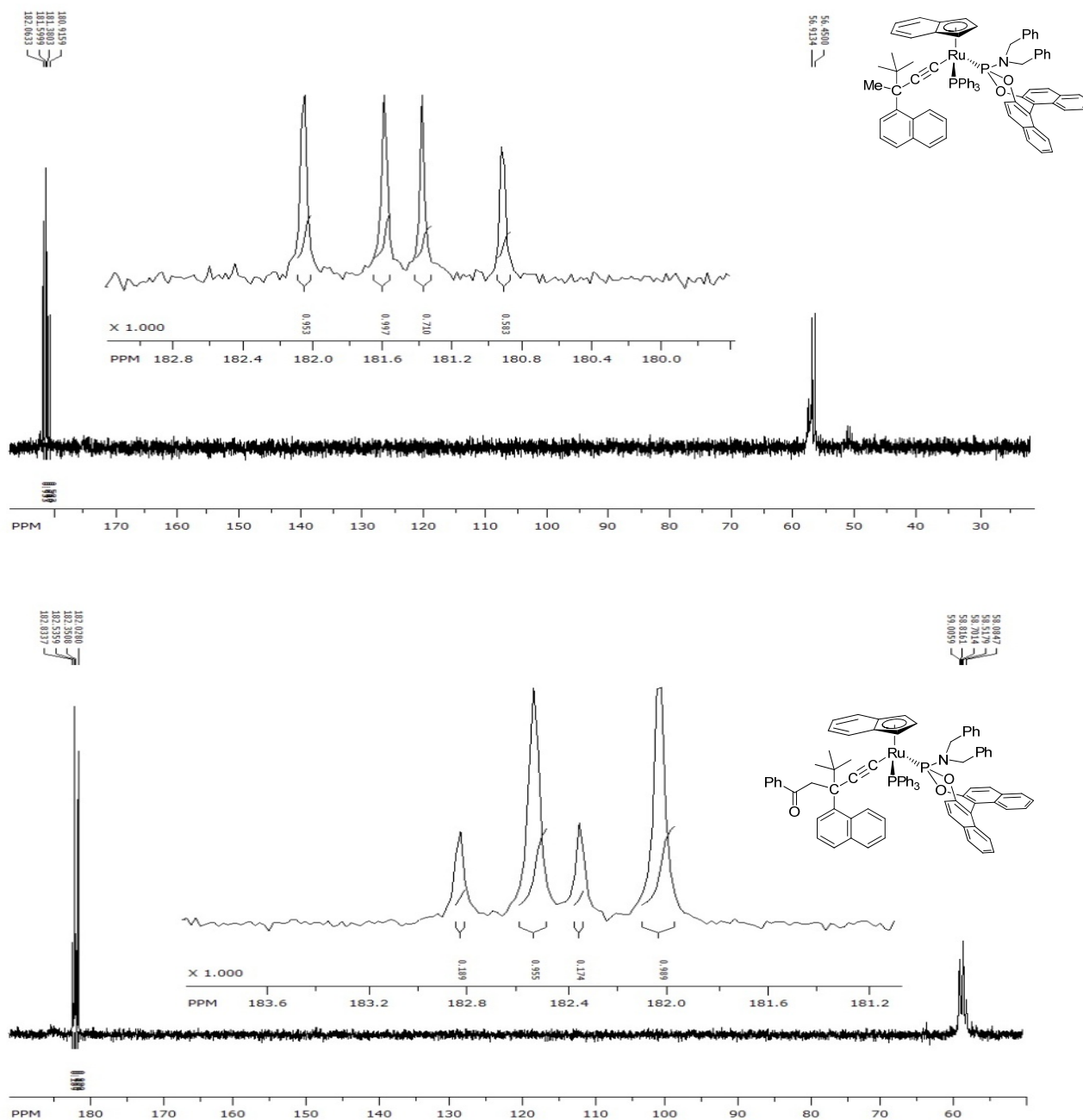
(R_{Ru}, R_{ax})-**19** (yellow)

(R_{Ru}, R_{ax})-**20** (grey)

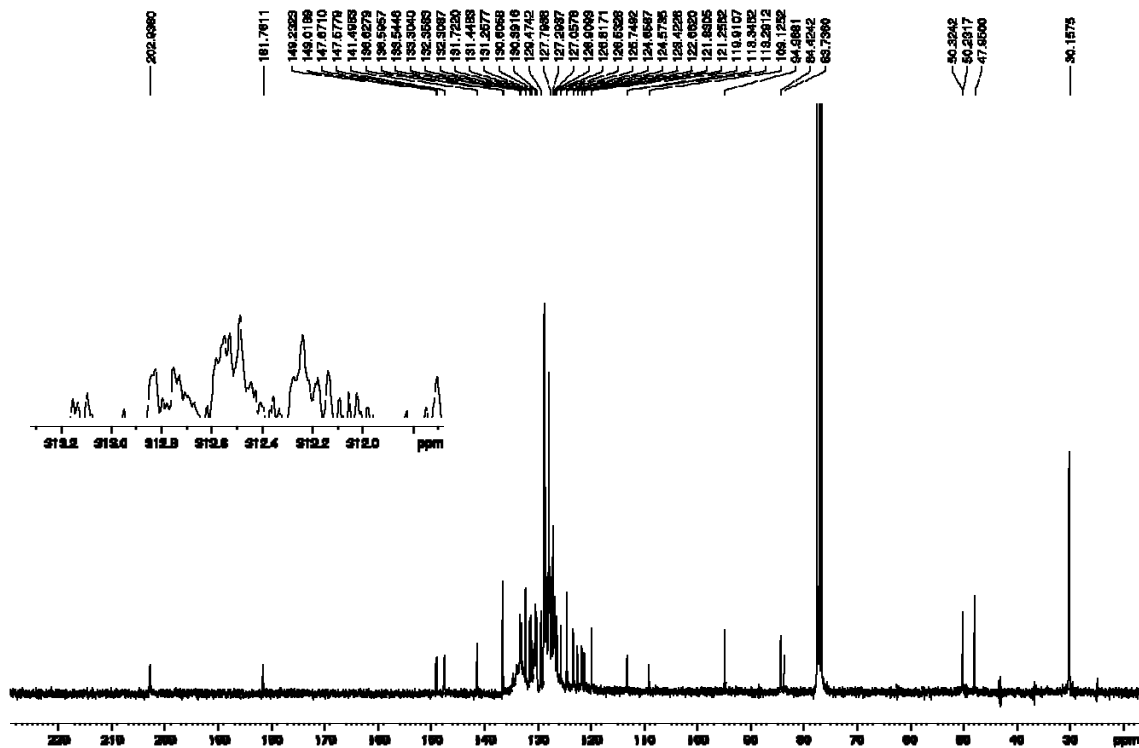
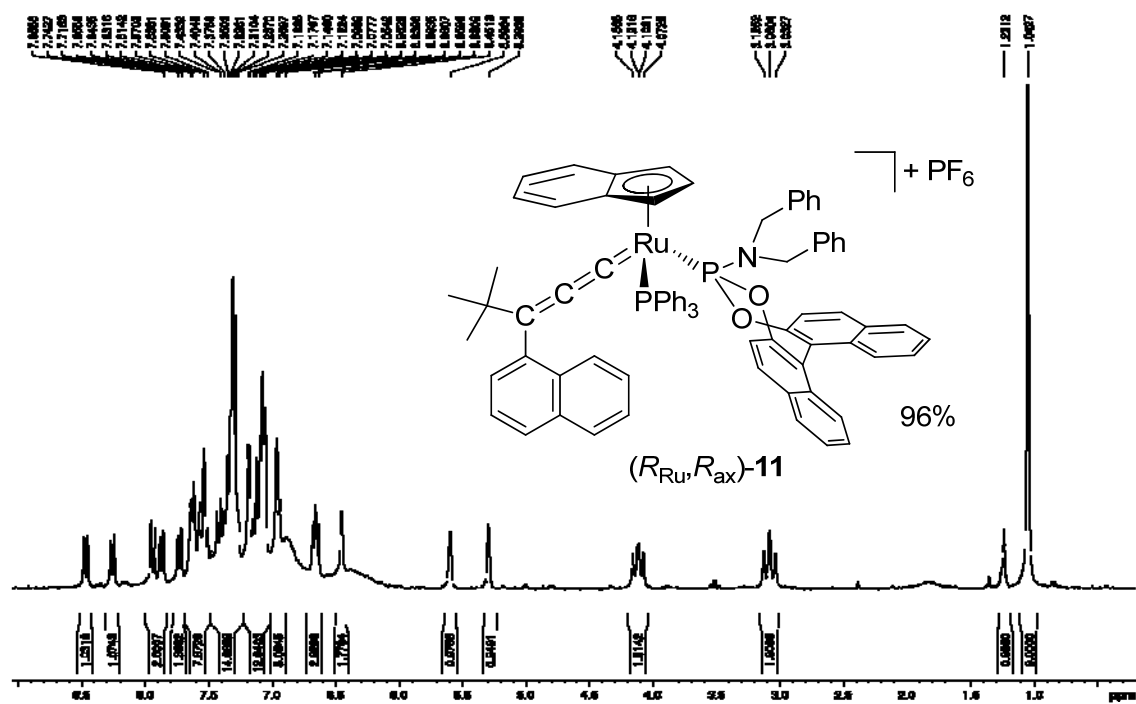


4. $^{31}\text{P}\{^1\text{H}\}$ NMR complexes for the determination of diastereomeric excesses

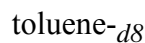
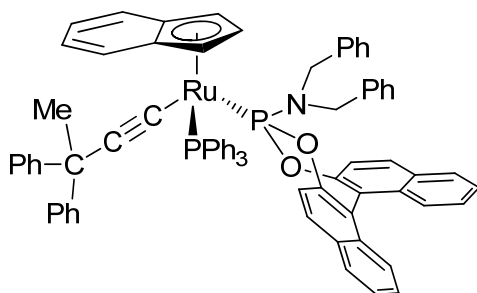
Integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of ($R_{\text{Ru}}, R_{\text{ax}}$)-**18** (top) and ($R_{\text{Ru}}, R_{\text{ax}}$)-**20** (bottom) for the determination of enantiomeric excesses.



^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $(R_{\text{Ru}}, R_{\text{ax}})\text{-[Ru(Ind)(PPh}_3\text{)(6)\{=C=C=C}(t\text{-Bu)(2-naphthyl)\}^+\text{PF}_6^-]$, $[(R_{\text{Ru}}, R_{\text{ax}})\text{-11}]$



[(R_{Ru} , R_{ax})-14]

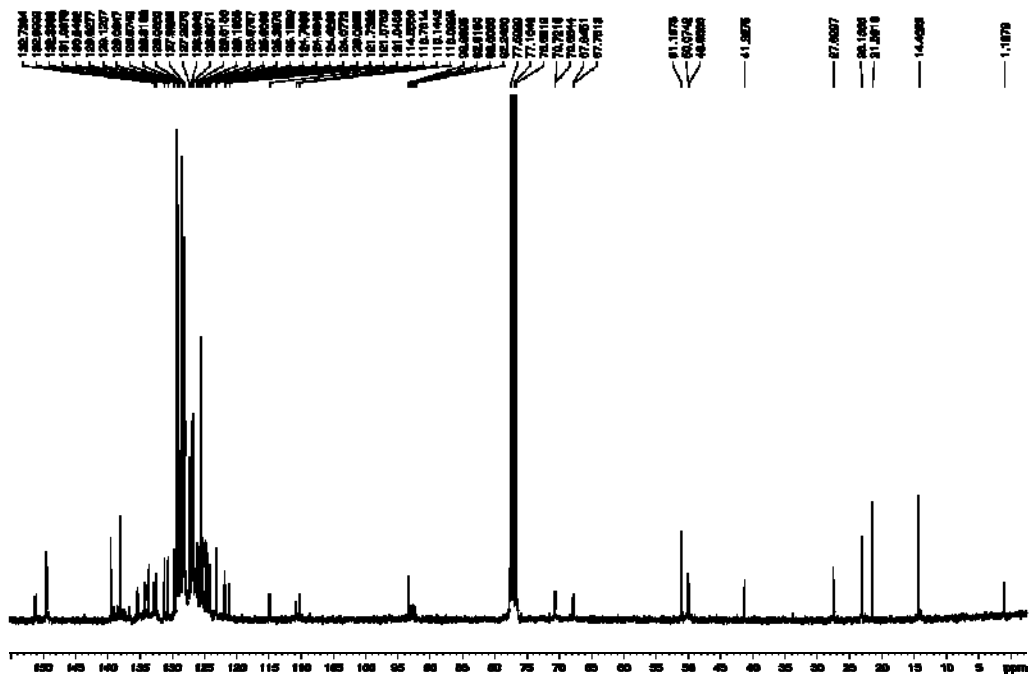


Chemical structure of the complex:

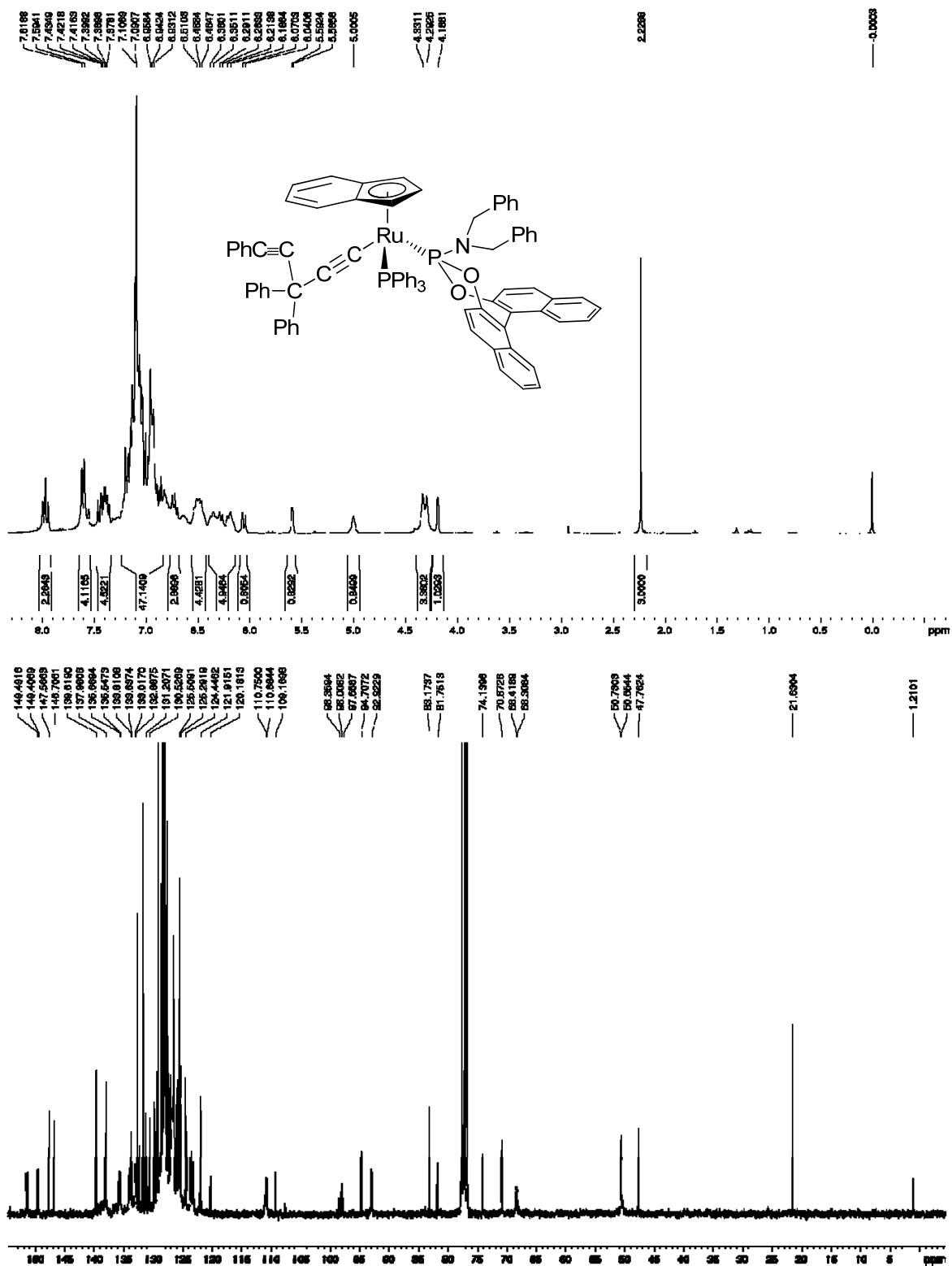
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¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The spectrum includes integration values below the baseline and chemical shift values above the peaks.

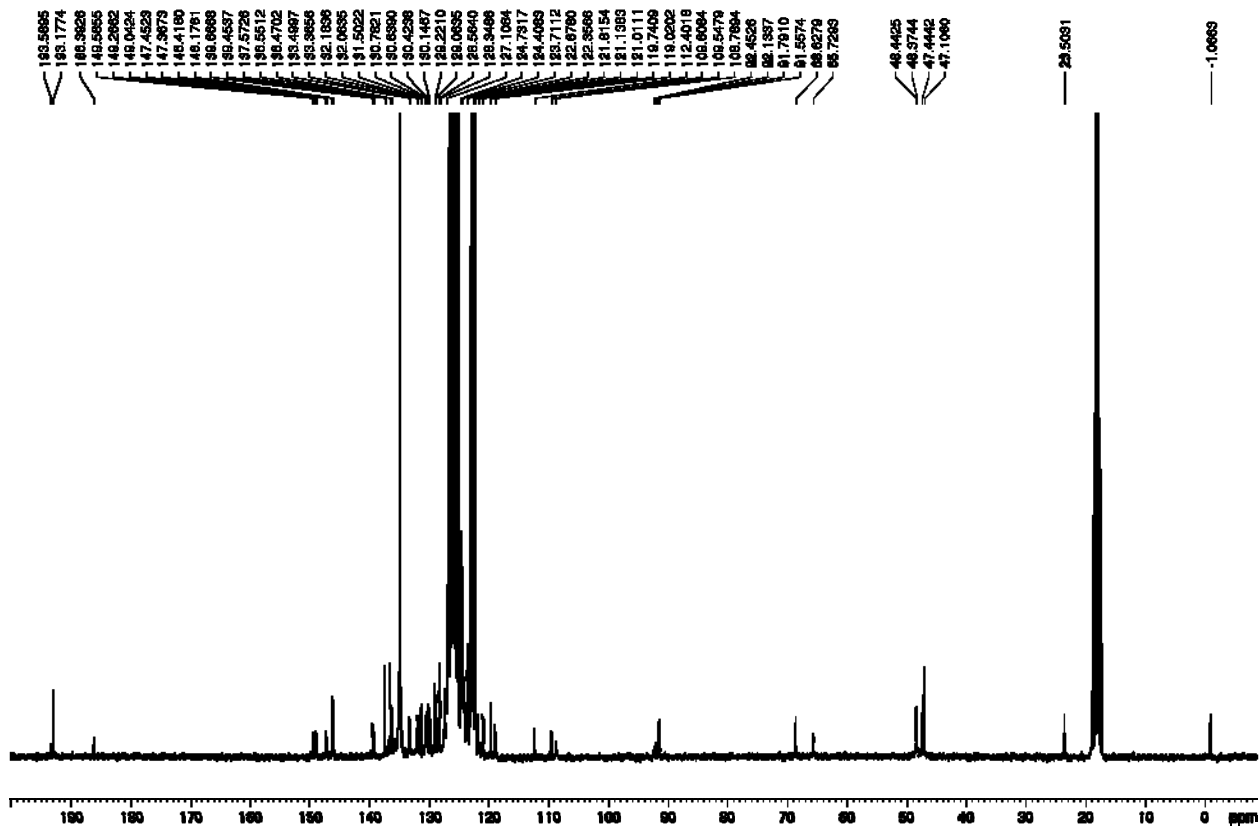
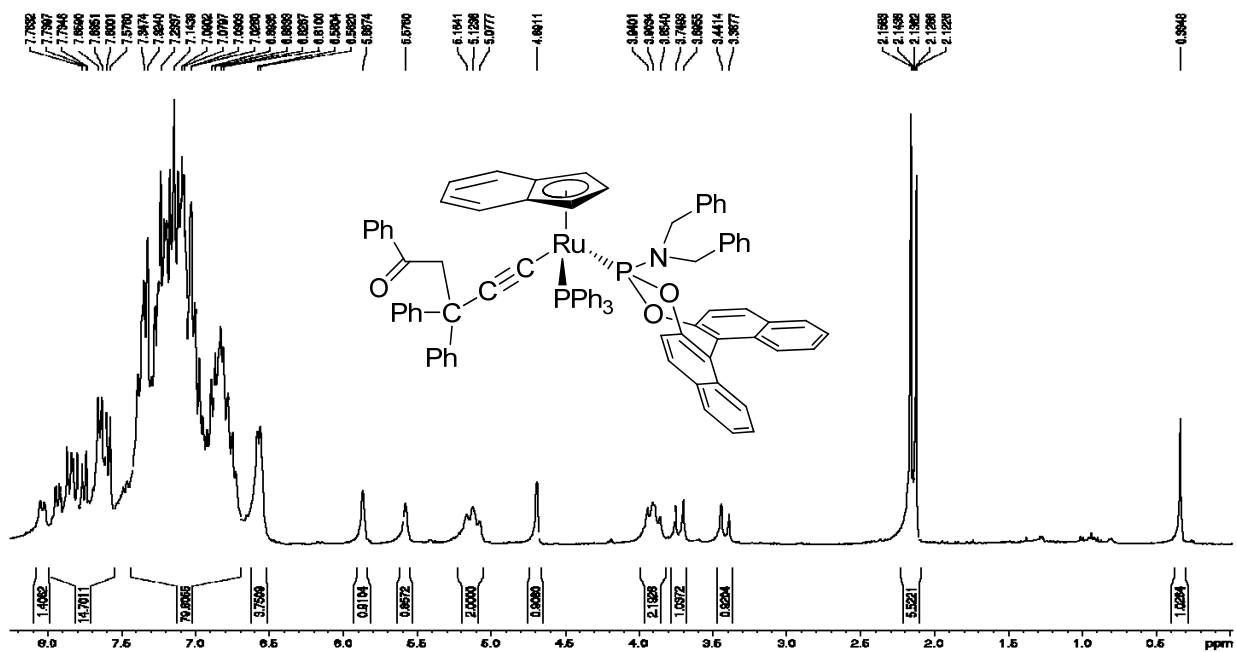
Chemical shift values (ppm): 7.4598, 7.4644, 7.4765, 7.5219, 7.5765, 7.5820, 7.5920, 7.6020, 7.6120, 7.6220, 7.6320, 7.6420, 7.6520, 7.6620, 7.6720, 7.6820, 7.6920, 7.7020, 7.7120, 7.7220, 7.7320, 7.7420, 7.7520, 7.7620, 7.7720, 7.7820, 7.7920, 7.8020, 7.8120, 7.8220, 7.8320, 7.8420, 7.8520, 7.8620, 7.8720, 7.8820, 7.8920, 7.9020, 7.9120, 7.9220, 7.9320, 7.9420, 7.9520, 7.9620, 7.9720, 7.9820, 7.9920, 8.0020, 8.0120, 8.0220, 8.0320, 8.0420, 8.0520, 8.0620, 8.0720, 8.0820, 8.0920, 8.1020, 8.1120, 8.1220, 8.1320, 8.1420, 8.1520, 8.1620, 8.1720, 8.1820, 8.1920, 8.2020, 8.2120, 8.2220, 8.2320, 8.2420, 8.2520, 8.2620, 8.2720, 8.2820, 8.2920, 8.3020, 8.3120, 8.3220, 8.3320, 8.3420, 8.3520, 8.3620, 8.3720, 8.3820, 8.3920, 8.4020, 8.4120, 8.4220, 8.4320, 8.4420, 8.4520, 8.4620, 8.4720, 8.4820, 8.4920, 8.5020, 8.5120, 8.5220, 8.5320, 8.5420, 8.5520, 8.5620, 8.5720, 8.5820, 8.5920, 8.6020, 8.6120, 8.6220, 8.6320, 8.6420, 8.6520, 8.6620, 8.6720, 8.6820, 8.6920, 8.7020, 8.7120, 8.7220, 8.7320, 8.7420, 8.7520, 8.7620, 8.7720, 8.7820, 8.7920, 8.8020, 8.8120, 8.8220, 8.8320, 8.8420, 8.8520, 8.8620, 8.8720, 8.8820, 8.8920, 8.9020, 8.9120, 8.9220, 8.9320, 8.9420, 8.9520, 8.9620, 8.9720, 8.9820, 8.9920, 9.0020, 9.0120, 9.0220, 9.0320, 9.0420, 9.0520, 9.0620, 9.0720, 9.0820, 9.0920, 9.1020, 9.1120, 9.1220, 9.1320, 9.1420, 9.1520, 9.1620, 9.1720, 9.1820, 9.1920, 9.2020, 9.2120, 9.2220, 9.2320, 9.2420, 9.2520, 9.2620, 9.2720, 9.2820, 9.2920, 9.3020, 9.3120, 9.3220, 9.3320, 9.3420, 9.3520, 9.3620, 9.3720, 9.3820, 9.3920, 9.4020, 9.4120, 9.4220, 9.4320, 9.4420, 9.4520, 9.4620, 9.4720, 9.4820, 9.4920, 9.5020, 9.5120, 9.5220, 9.5320, 9.5420, 9.5520, 9.5620, 9.5720, 9.5820, 9.5920, 9.6020, 9.6120, 9.6220, 9.6320, 9.6420, 9.6520, 9.6620, 9.6720, 9.6820, 9.6920, 9.7020, 9.7120, 9.7220, 9.7320, 9.7420, 9.7520, 9.7620, 9.7720, 9.7820, 9.7920, 9.8020, 9.8120, 9.8220, 9.8320, 9.8420, 9.8520, 9.8620, 9.8720, 9.8820, 9.8920, 9.9020, 9.9120, 9.9220, 9.9320, 9.9420, 9.9520, 9.9620, 9.9720, 9.9820, 9.9920, 10.0020, 10.0120, 10.0220, 10.0320, 10.0420, 10.0520, 10.0620, 10.0720, 10.0820, 10.0920, 10.1020, 10.1120, 10.1220, 10.1320, 10.1420, 10.1520, 10.1620, 10.1720, 10.1820, 10.1920, 10.2020, 10.2120, 10.2220, 10.2320, 10.2420, 10.2520, 10.2620, 10.2720, 10.2820, 10.2920, 10.3020, 10.3120, 10.3220, 10.3320, 10.3420, 10.3520, 10.3620, 10.3720, 10.3820, 10.3920, 10.4020, 10.4120, 10.4220, 10.4320, 10.4420, 10.4520, 10.4620, 10.4720, 10.4820, 10.4920, 10.5020, 10.5120, 10.5220, 10.5320, 10.5420, 10.5520, 10.5620, 10.5720, 10.5820, 10.5920, 10.6020, 10.6120, 10.6220, 10.6320, 10.6420, 10.6520, 10.6620, 10.6720, 10.6820, 10.6920, 10.7020, 10.7120, 10.7220, 10.7320, 10.7420, 10.7520, 10.7620, 10.7720, 10.7820, 10.7920, 10.8020, 10.8120, 10.8220, 10.8320, 10.8420, 10.8520, 10.8620, 10.8720, 10.8820, 10.8920, 10.9020, 10.9120, 10.9220, 10.9320, 10.9420, 10.9520, 10.9620, 10.9720, 10.9820, 10.9920, 11.0020, 11.0120, 11.0220, 11.0320, 11.0420, 11.0520, 11.0620, 11.0720, 11.0820, 11.0920, 11.1020, 11.1120, 11.1220, 11.1320, 11.1420, 11.1520, 11.1620, 11.1720, 11.1820, 11.1920, 11.2020, 11.2120, 11.2220, 11.2320, 11.2420, 11.2520, 11.2620, 11.2720, 11.2820, 11.2920, 11.3020, 11.3120, 11.3220, 11.3320, 11.3420, 11.3520, 11.3620, 11.3720, 11.3820, 11.3920, 11.4020, 11.4120, 11.4220, 11.4320, 11.4420, 11.4520, 11.4620, 11.4720, 11.4820, 11.4920, 11.5020, 11.5120, 11.5220, 11.5320, 11.5420, 11.5520, 11.5620, 11.5720, 11.5820, 11.5920, 11.6020, 11.6120, 11.6220, 11.6320, 11.6420, 11.6520, 11.6620, 11.6720, 11.6820, 11.6920, 11.7020, 11.7120, 11.7220, 11.7320, 11.7420, 11.7520, 11.7620, 11.7720, 11.7820, 11.7920, 11.8020, 11.8120, 11.8220, 11.8320, 11.8420, 11.8520, 11.8620, 11.8720, 11.8820, 11.8920, 11.9020, 11.9120, 11.9220, 11.9320, 11.9420, 11.9



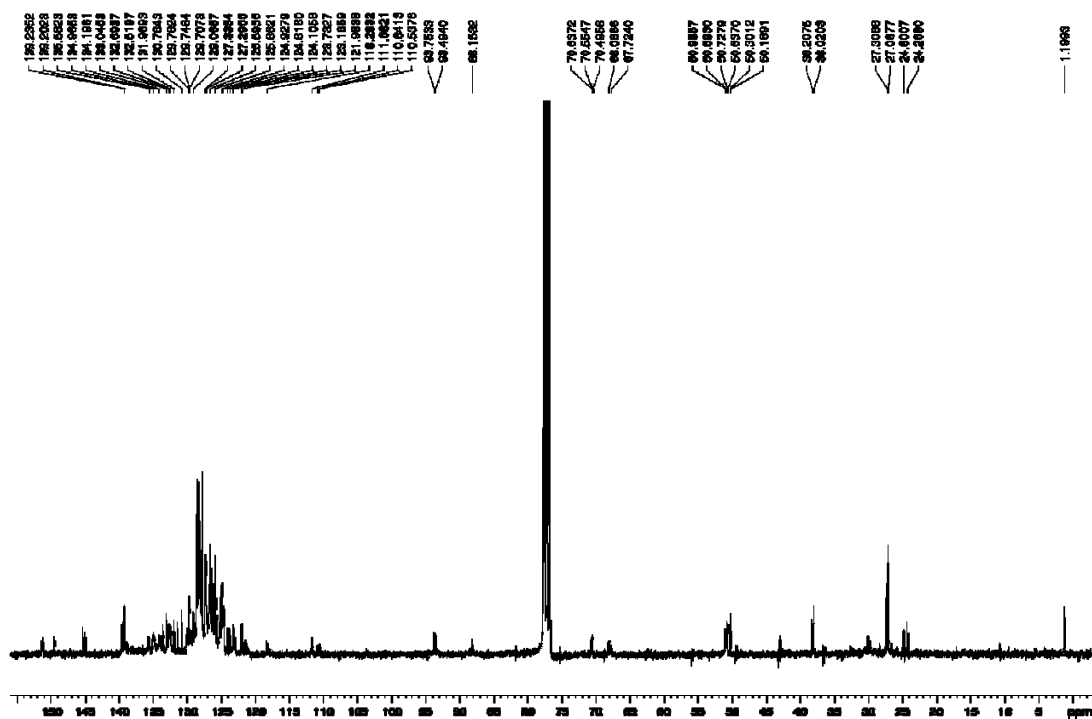
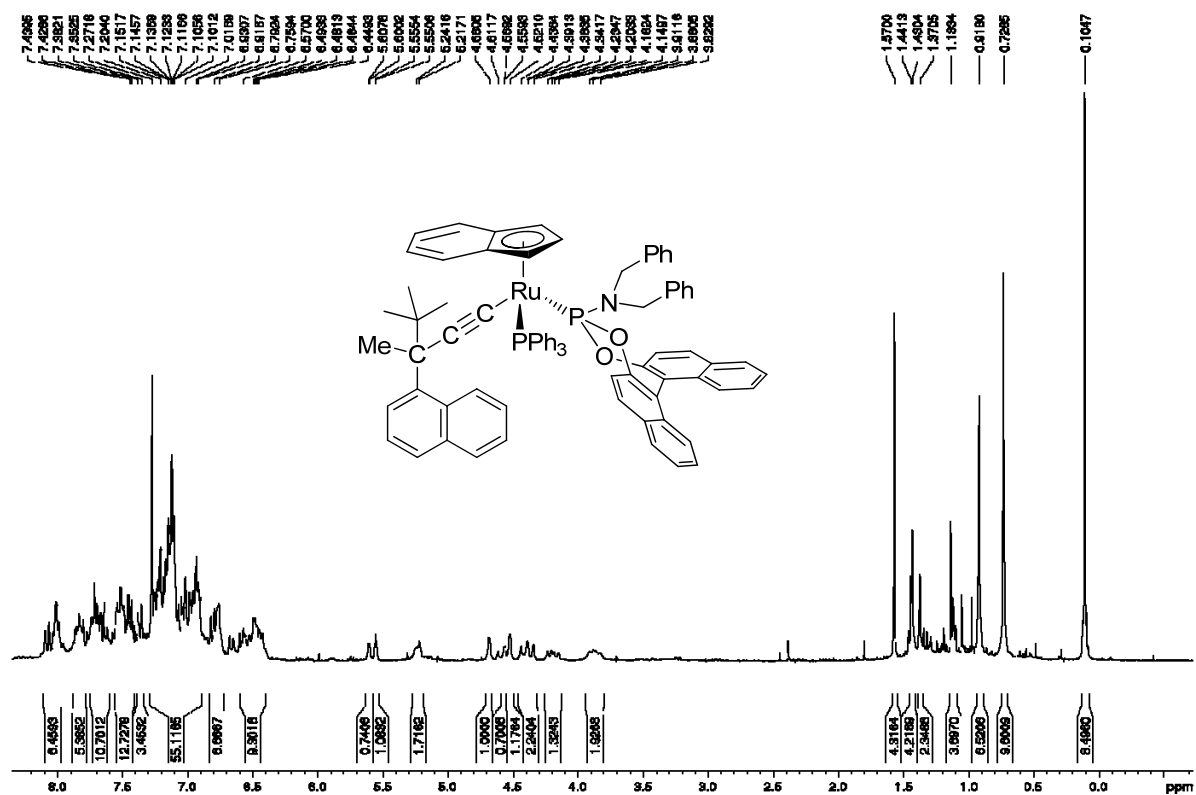
(R_{Ru}, R_{ax}) -[RuCl(Ind)(PPh₃)(6)(C≡C-CPh₂C≡CPh)], [(R_{Ru}, R_{ax})-**16**]



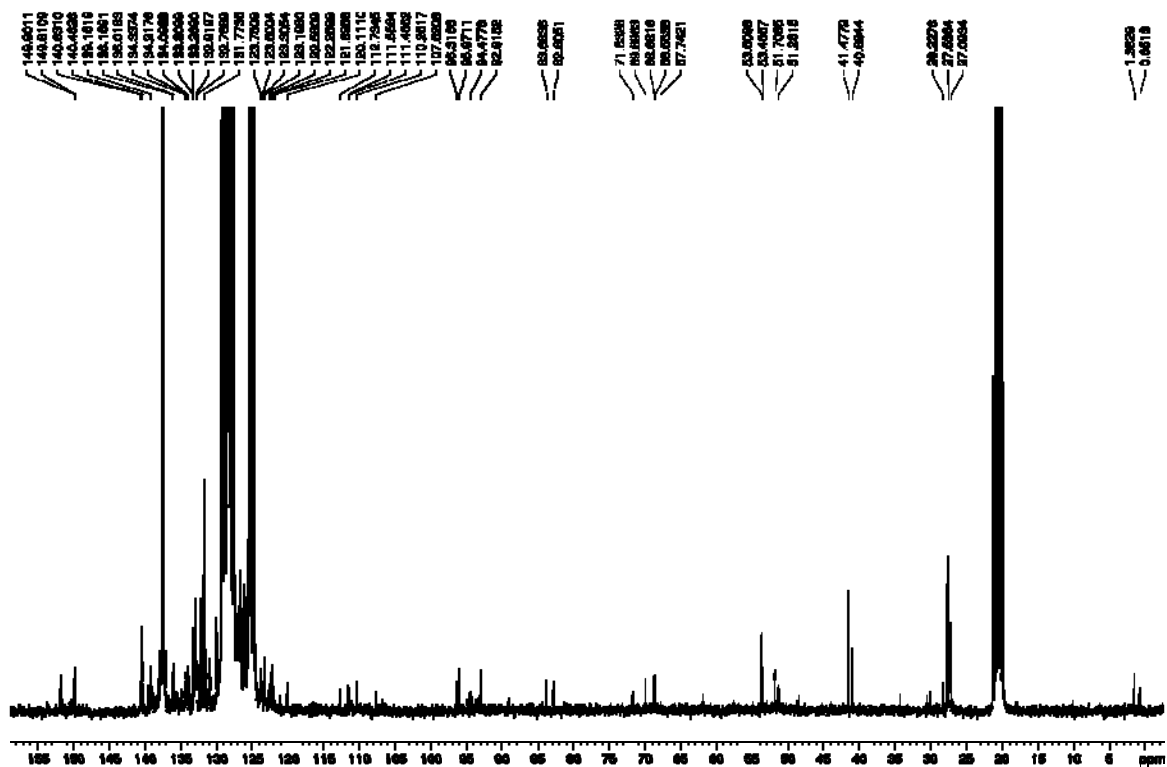
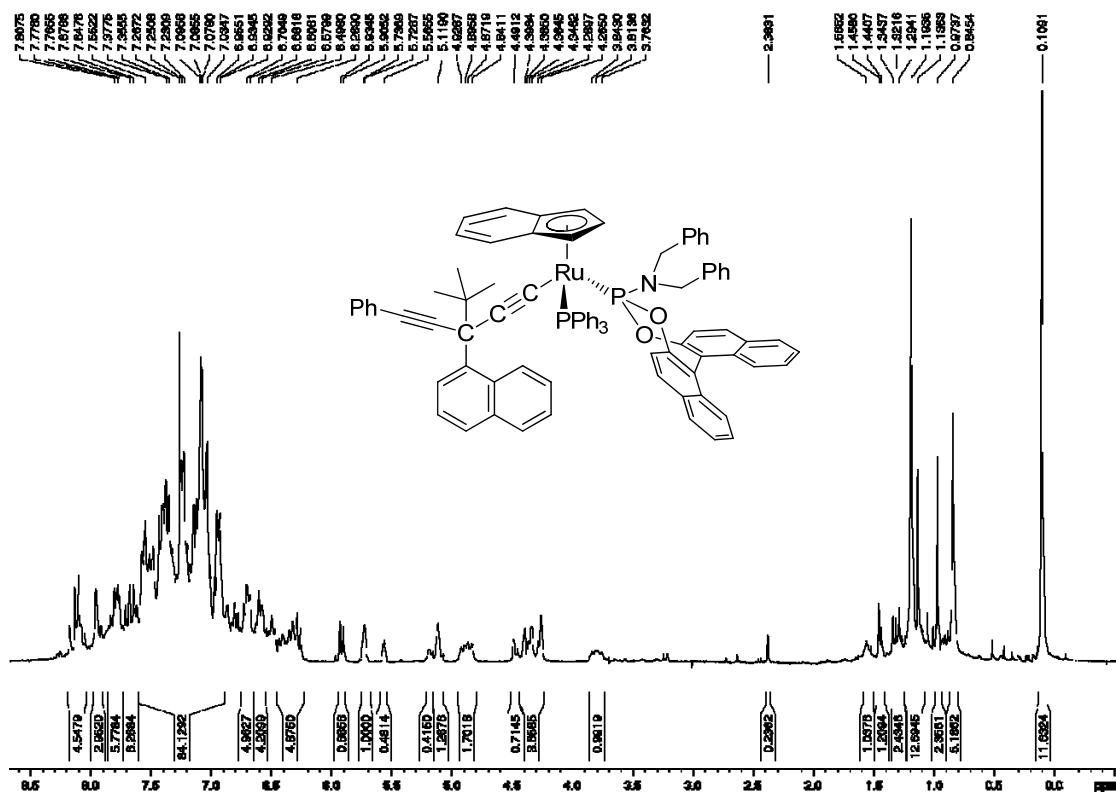
(R_{Ru}, R_{ax}) -[RuCl(Ind)(PPh₃)(6)]{C≡C-CPh₂CH₂C(O)Ph}, [(R_{Ru}, R_{ax})-17]



(R_{Ru}, R_{ax}) -[Ru(Ind)(PPh₃)(**6**){C≡C-C(*t*-Bu)(2-naphthyl)CH₃}], [(*R*_{Ru}, *R*_{ax})-**18**]



(R_{Ru}, R_{ax}) -[Ru(Ind)(PPh₃)(**6**){C≡C-C(*t*-Bu)(2-naphthyl)C≡CPh}], [(R_{Ru}, R_{ax})-**19**]



(R_{Ru}, R_{ax}) -[Ru(Ind)(PPh₃)(**6**){C≡C-C(*t*-Bu)(2-naphthyl)CH₂C(O)Ph}], [(R_{Ru}, R_{ax})-**20**]

