Supporting Information

Electron-Deficient Ru(II) Complexes as Catalyst Precursors for Ethylene Hydrophenylation

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NMR spectra of complexes 1-5

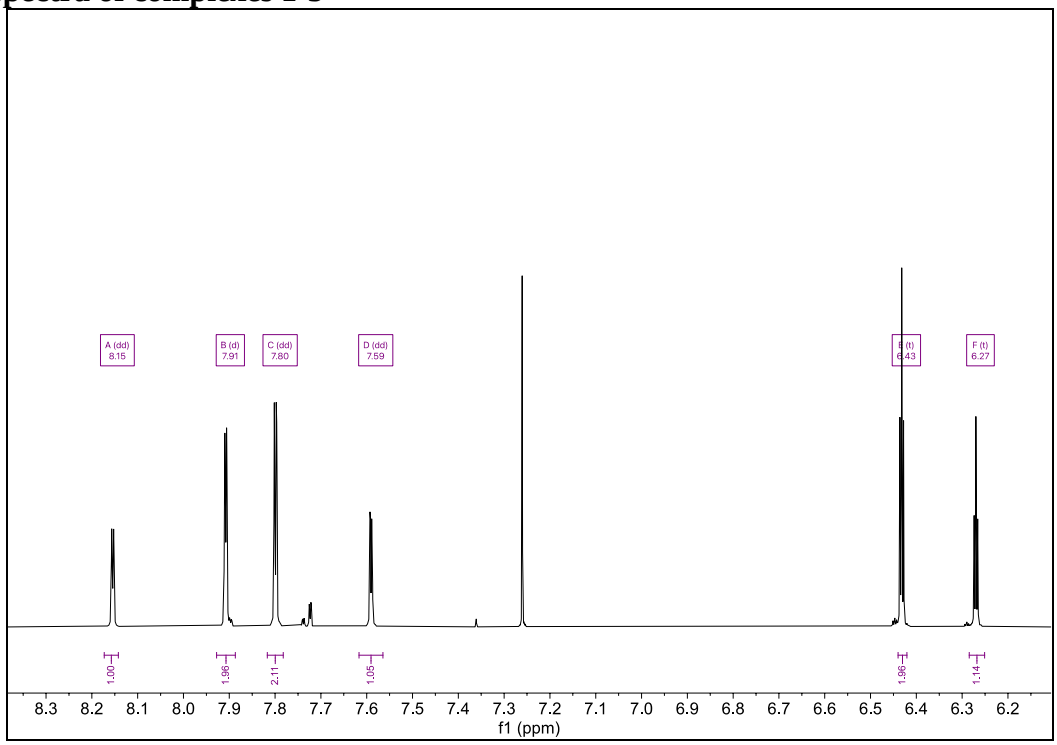


Figure S1. ^{1}H NMR spectrum of $TpRu(NO)Cl_2$ (**1**) in $CDCl_3$.

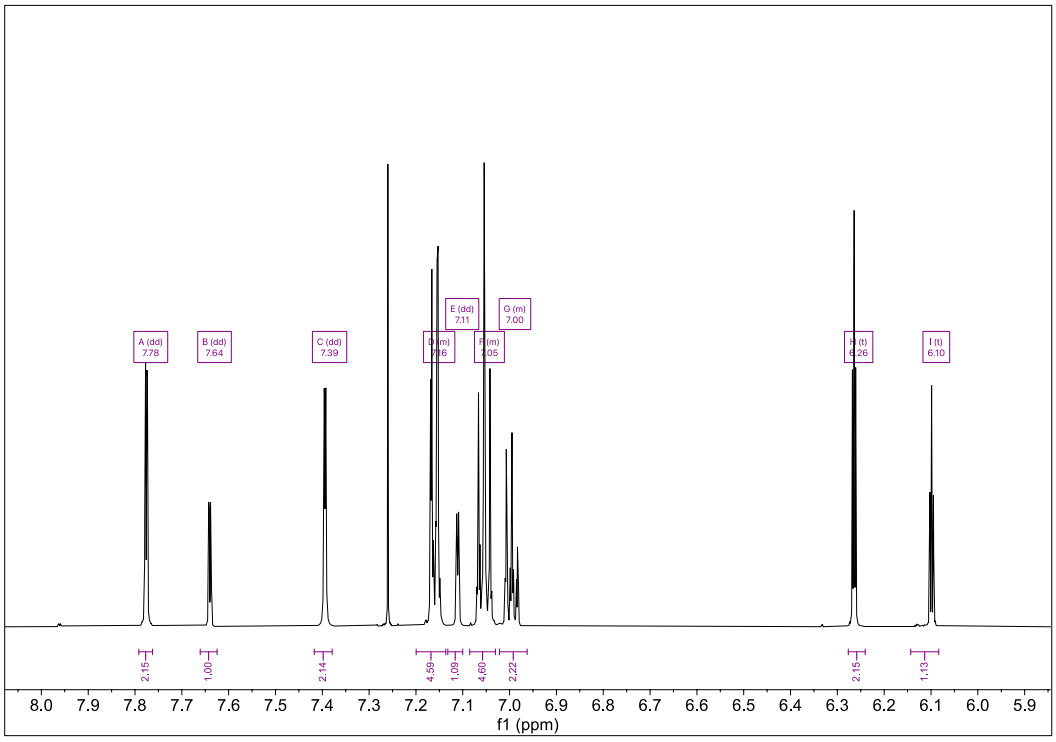


Figure S2. ^{1}H NMR spectrum of $TpRu(NO)Ph_2$ (**2**) in $CDCl_3$.

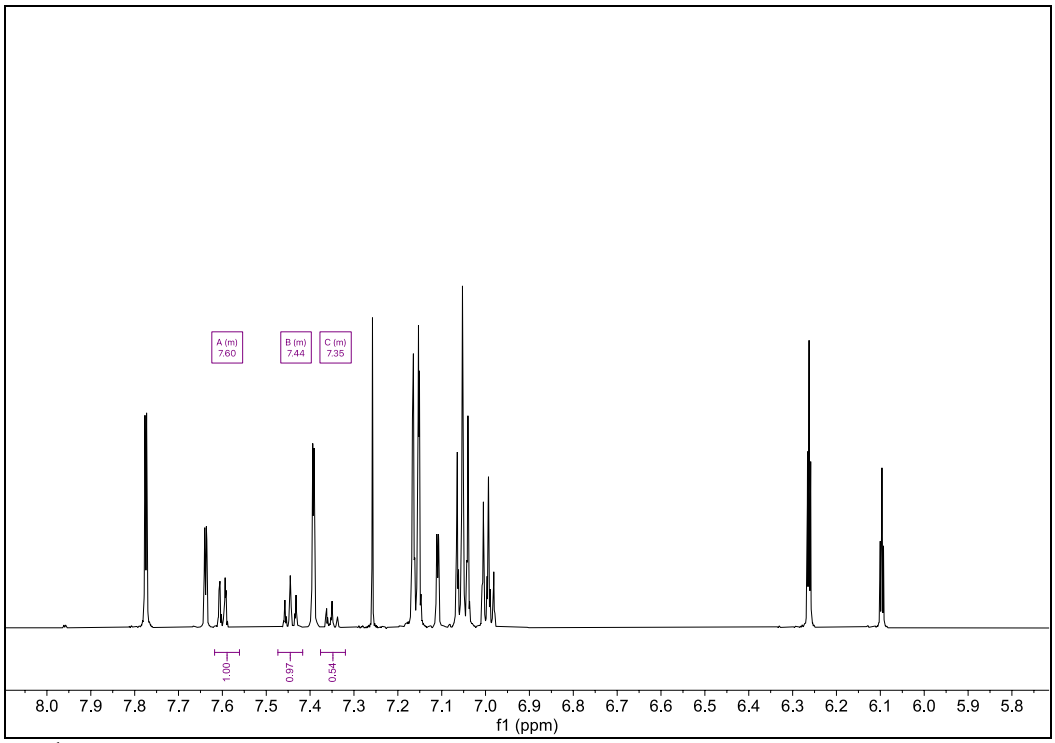


Figure S3. ^{1}H NMR spectrum of TpRu(NO)Ph$_2$ (**2**) in CDCl$_3$ after 24 hours at room temperature, the production of biphenyl (integrated) is observed.

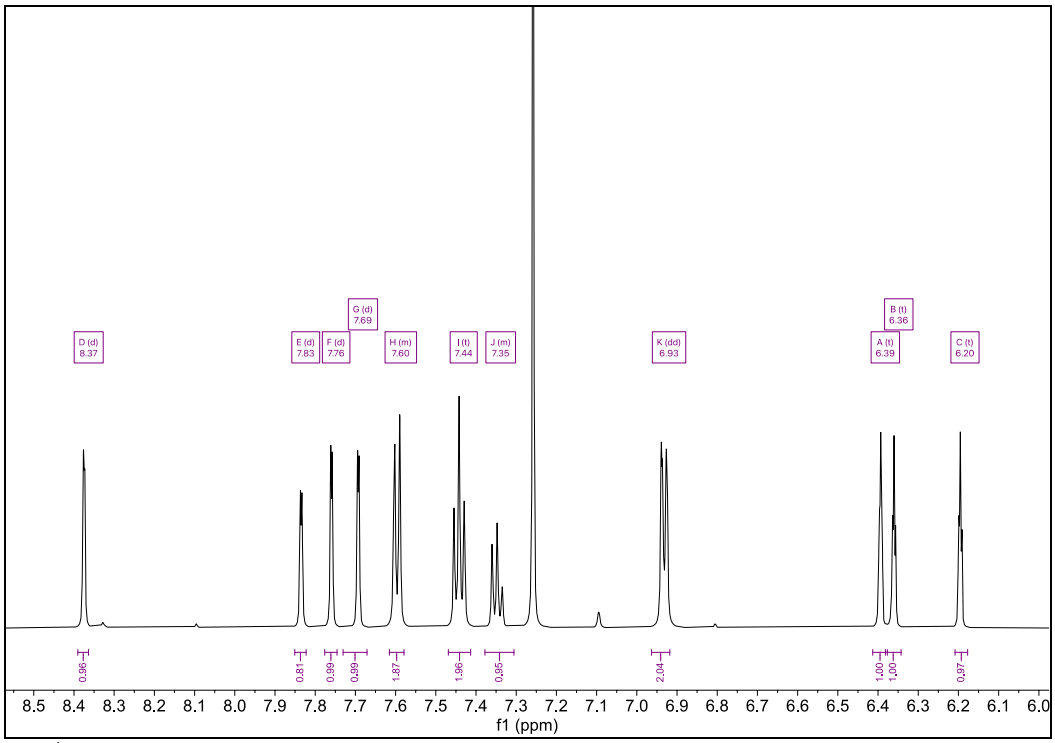


Figure S4. ^{1}H NMR spectrum of TpRu(NO)(OTf)Ph (**3**) in CDCl$_3$.

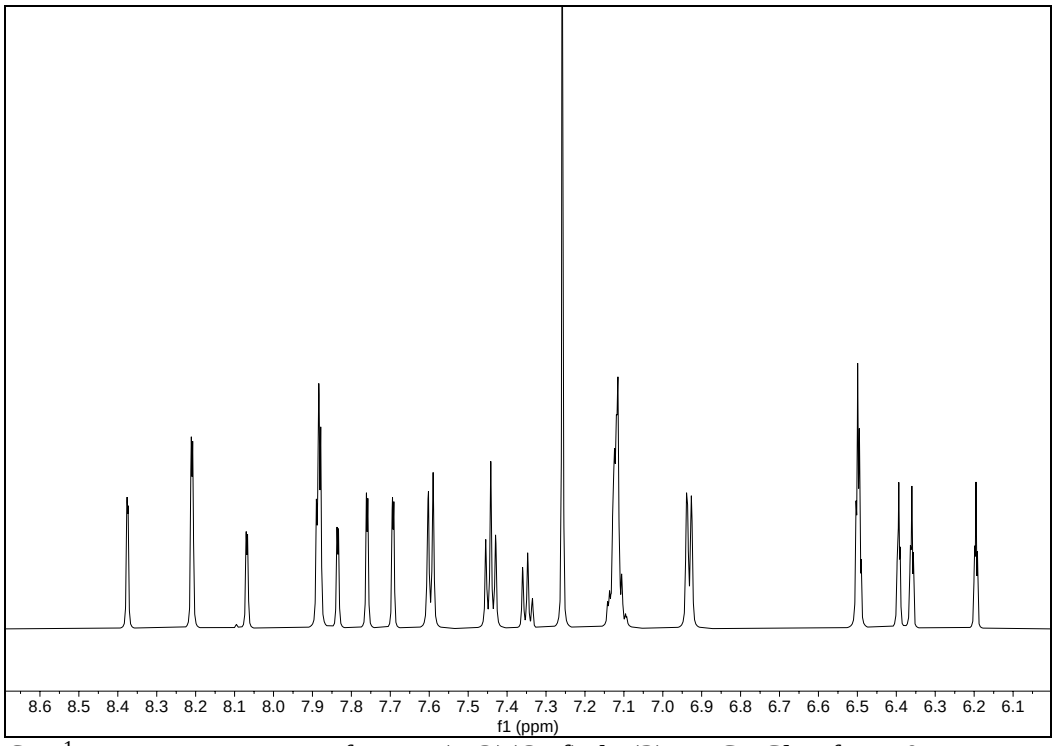


Figure S5. ^{1}H NMR spectrum of TpRu(NO)(OTf)Ph (**3**) in $CDCl_3$ after 10 minutes at room temperature.

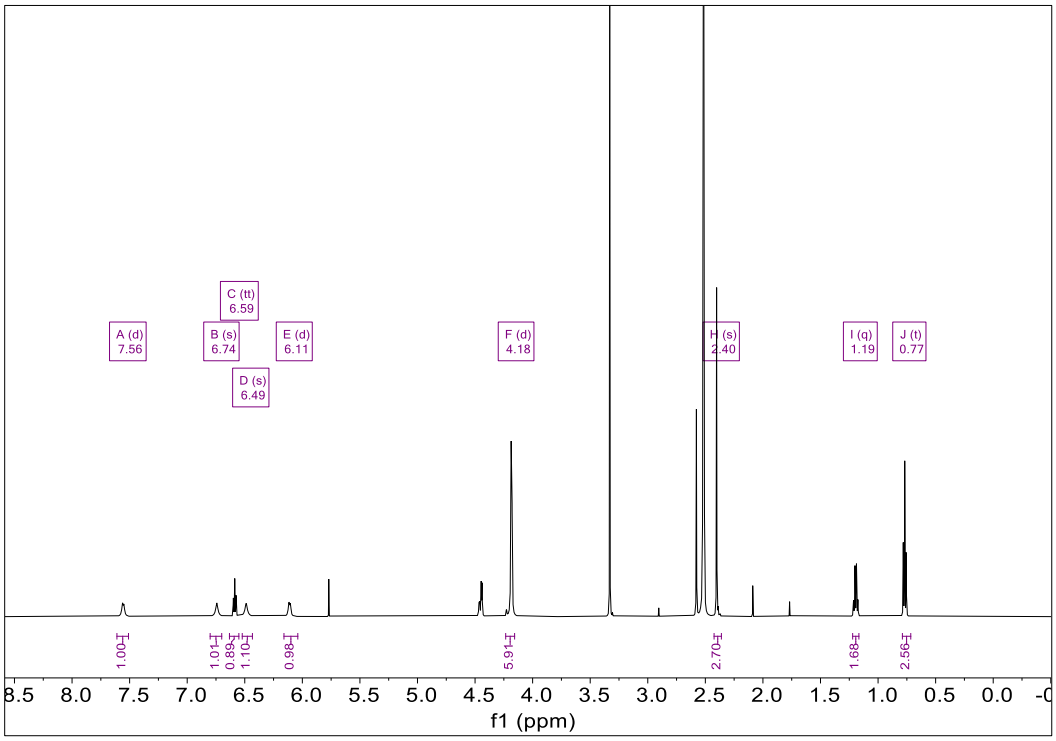


Figure S6. ^{1}H NMR spectrum of (Tp^{Br3})Ru P(OCH$_2$)$_3$CEt (NCMe)Ph (**4**) in DMSO-*d*$_6$.

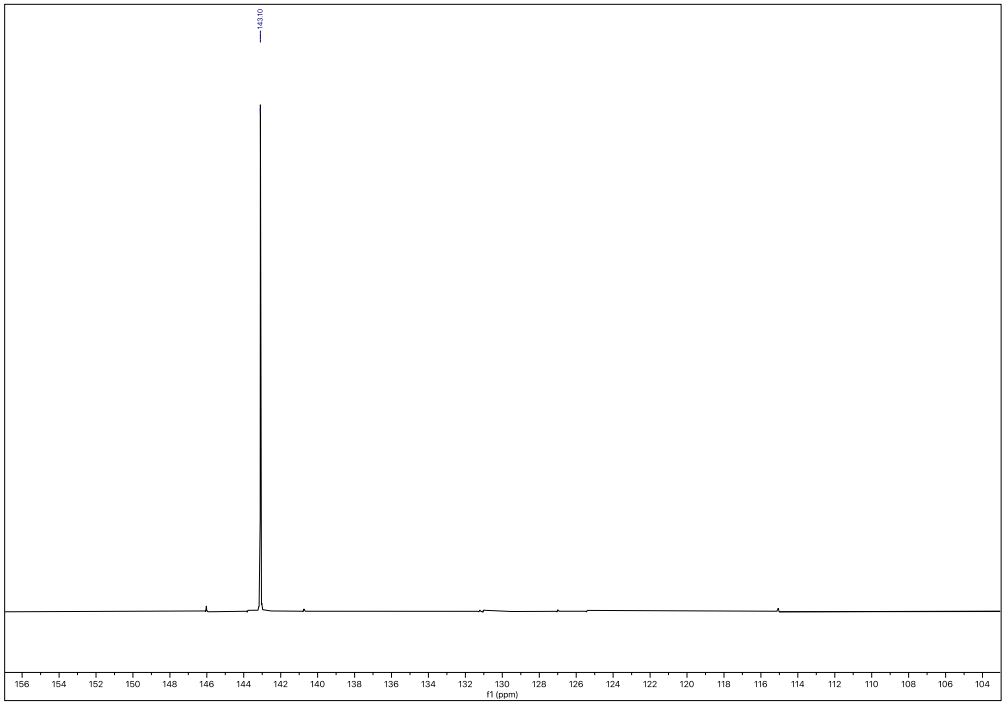


Figure S7. ^{31}P{^{1}H} NMR spectrum of (Tp^{Br3})Ru P(OCH$_2$)$_3$CEt (NCMe)Ph (**4**) in DMSO-*d*$_6$.

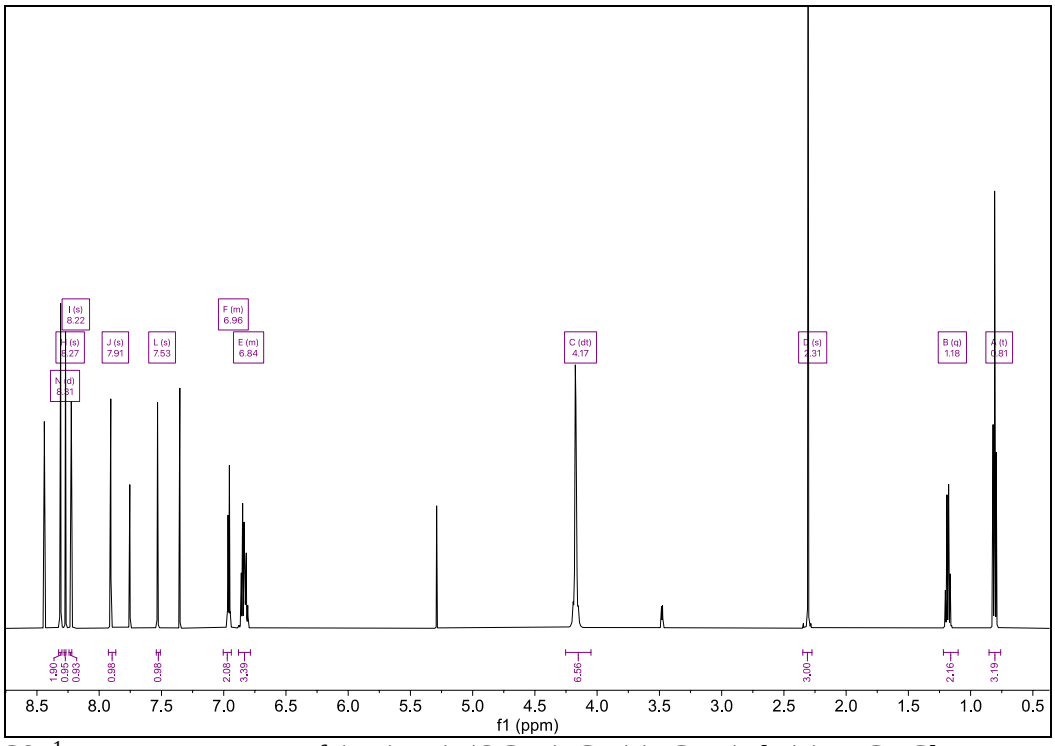


Figure S8. ^{1}H NMR spectrum of (Ttz)Ru(P(OCH_2)$_3$CEt)(NCMe)Ph (**5**) in $CDCl_3$.

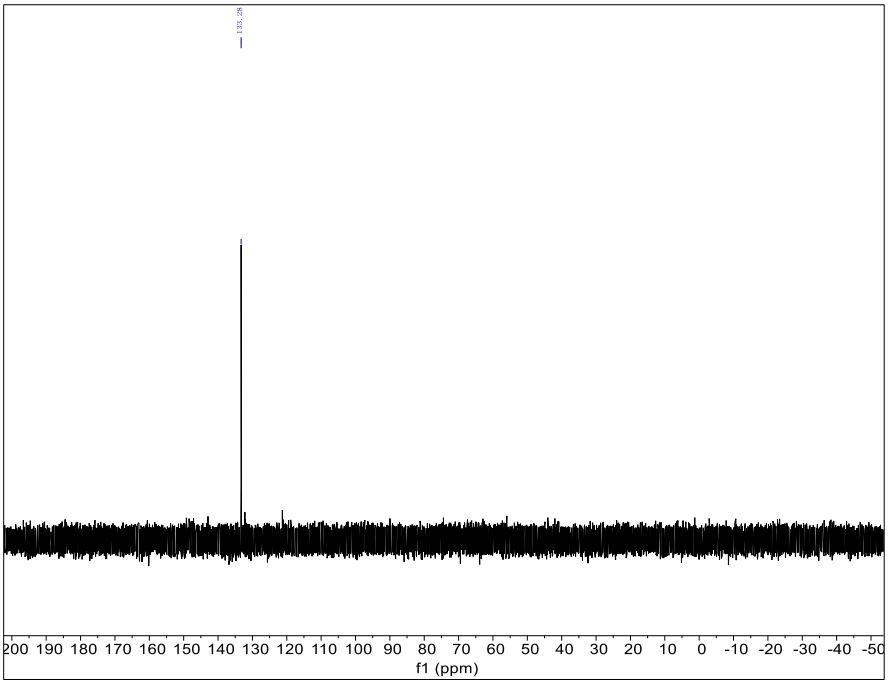


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of TtzRu(P(OCH_2)$_3$CEt)(NCMe)Ph (**5**) in $CDCl_3$.

IR Spectra of $TpRu(NO)Cl_2$ (**1**) and $TpRu(NO)Ph_2$ (**2**).

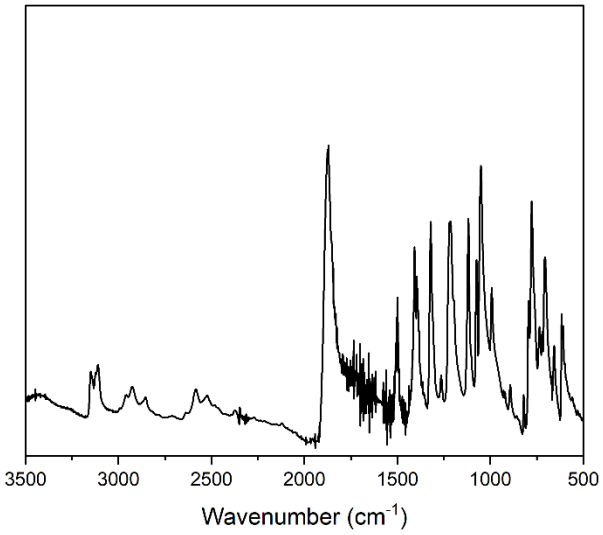


Figure S10. Solid state IR spectrum of $TpRu(NO)Cl_2$ (**1**).

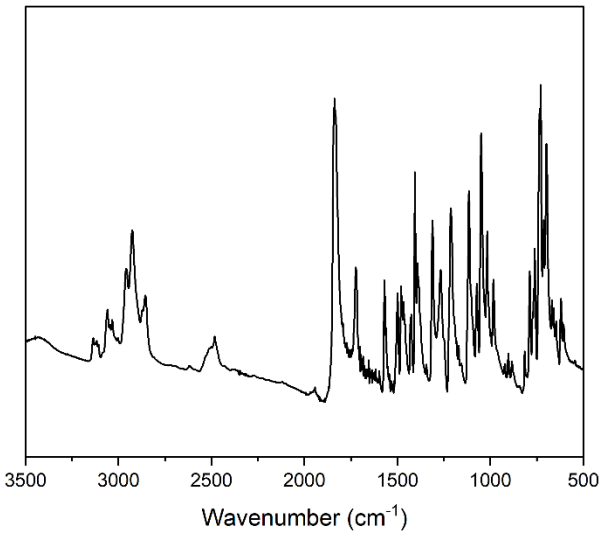
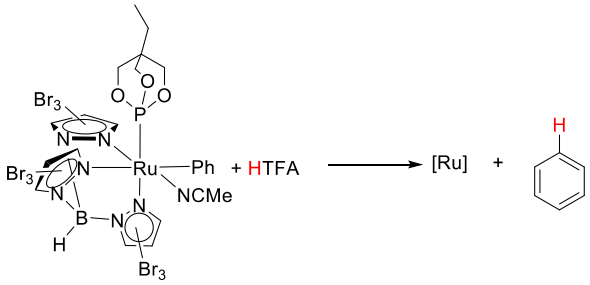


Figure S11. Solid state IR spectrum of $TpRu(NO)Ph_2$ (**2**).

Benzene releasing experiment from (Tp^{Br3})Ru $P(OCH_2)_3CEt$ (NCMe)Ph (4).



Scheme S1. Protonation of (Tp^{Br3})Ru $P(OCH_2)_3CEt$ (NCMe)Ph (**4**) by HTFA (trifluroracetic acid).

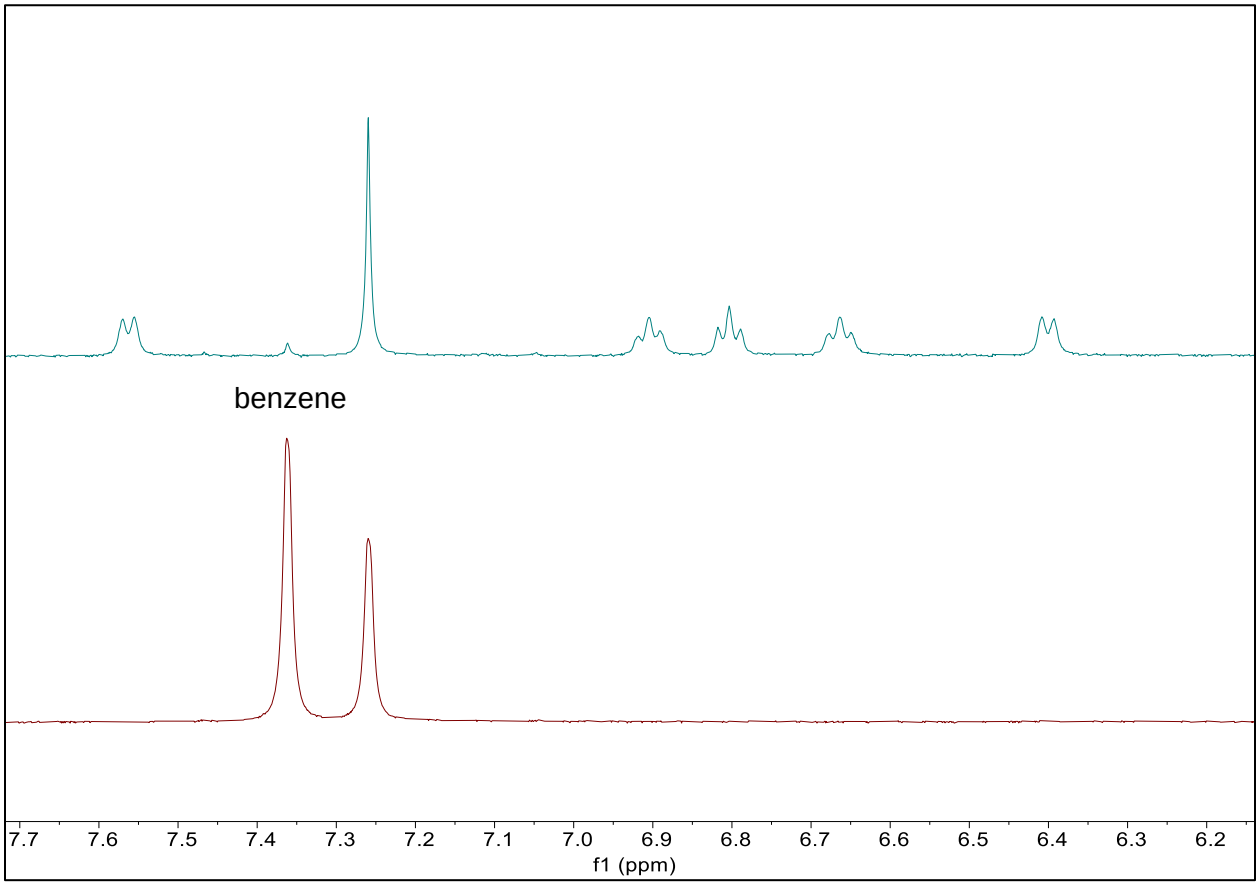


Figure S12. ^1H NMR spectra of protonation of (Tp^{Br3})Ru($P(OCH_2)_3CEt$)(NCMe)Ph (**4**) using HTFA. Top: ^1H NMR of **4** prior to acid addition. Bottom: ^1H NMR after acid addition.

Variable Temperature NMR Experiment of (Tp^{Br3})Ru $P(OCH_2)_3CEt$ (NCMe)Ph (4).

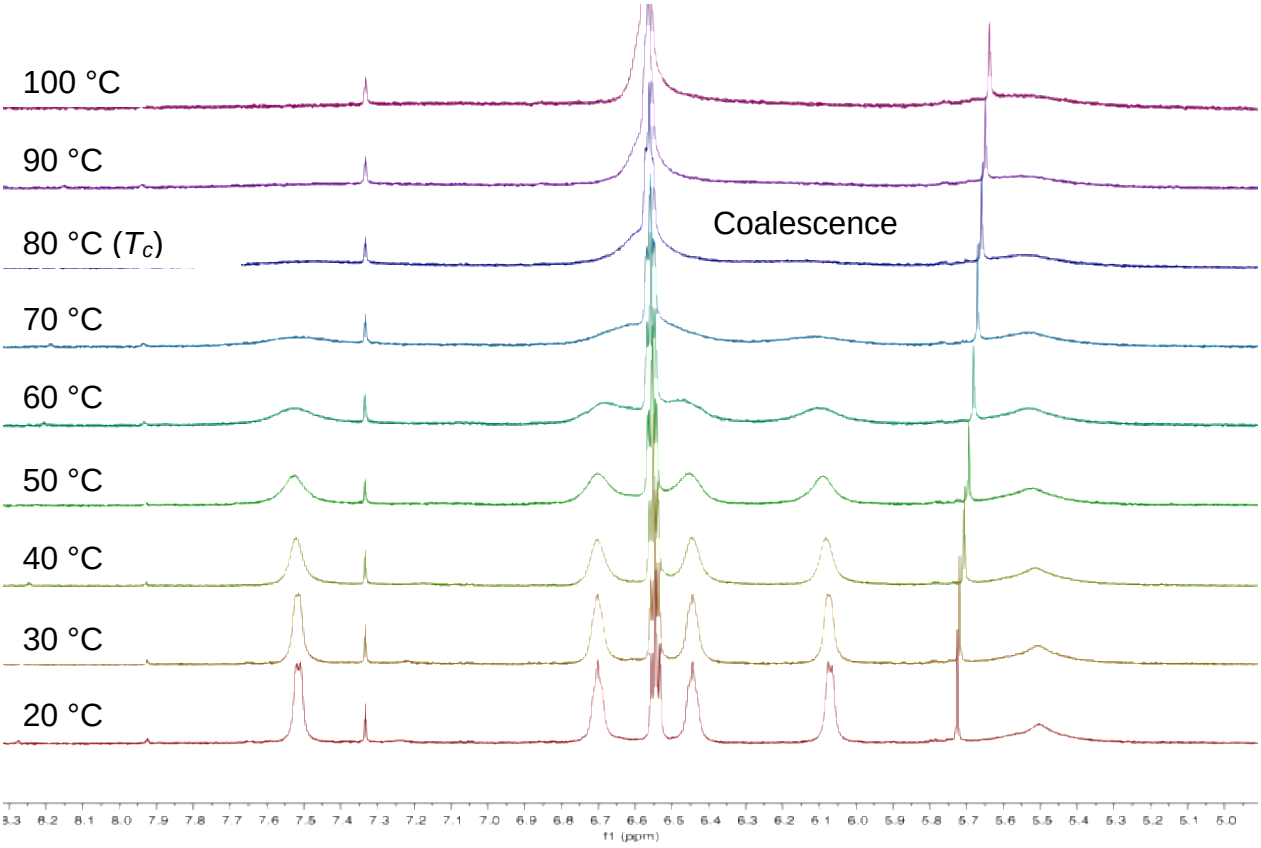


Figure S13. Variable temperature ^{1}H NMR spectra of (Tp^{Br3})Ru($P(OCH_2)_3CEt$)(NCMe)Ph (**4**) from 20 °C (bottom) to 100 °C (top) in DMSO-d_6.

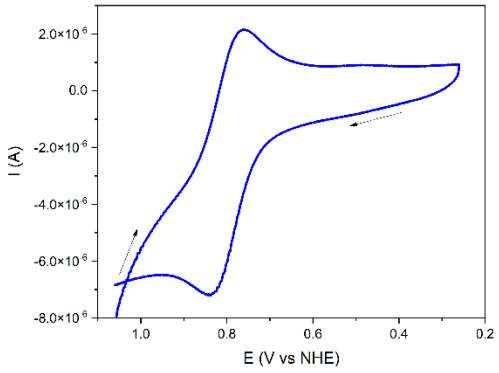


Figure S14. CV of (Ttz)Ru($P(OCH_2)_3CEt$)(NCMe)Ph (**5**) in NCMe.

Product Quantification of Catalytic Ethylene Hydrophenylation Reactions

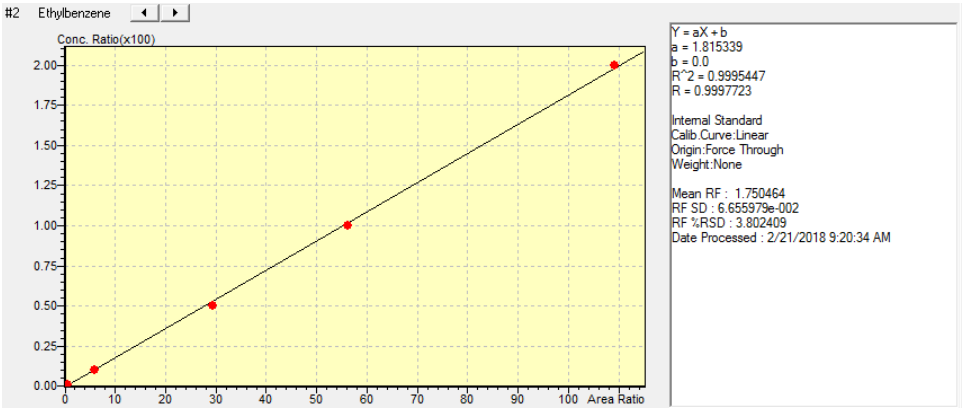


Figure S15. Calibration curve for ethylbenzene quantification on GC-FID, The slope, correlation coefficient and the response factor of the regression lines were 1.82, 0.99 and 1.75 for ethylbenzene respectively.

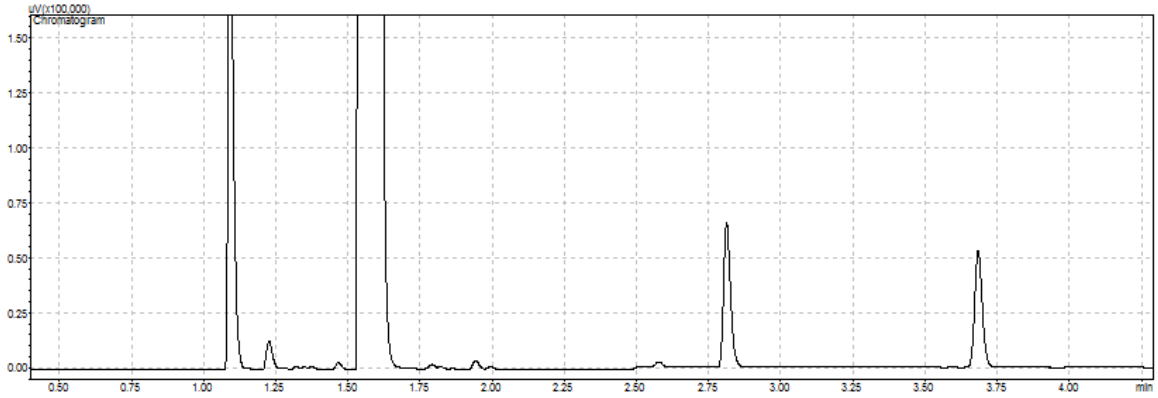


Figure S16. Representative GC-FID chromatogram of a reaction mixture from ethylene hydrophenylation reaction under anaerobic conditions. Peak assignments: 1-2 minutes dichloromethane, acetone and benzene; 2.81 minutes ethylbenzene; 3.69 minutes hexamethylbenzene (internal standard. Unidentified peaks are negligible and not included when calculating overall selectivity. GC-FID Parameters: starting temperature: 100 °C; time at starting temp: 2.5 min; ramp1: 40 °C/min up to 240 °C; hold for 2 min; flow rate (carrier): 3.01 mL/min (He); split ratio: 35:1; inlet temperature: 200 °C; detector temperature: 240 °C.

Single Crystal X-ray Diffraction

A dark-red block-like crystal of **2** was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a fine-focus sealed tube (Mo K_α, λ = 0.71073 Å) and a graphite monochromator. The frames were integrated with the Bruker SAINT software package[1] using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[1]

[1] Bruker (2012). *Saint; SADABS; APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.

The structure was solved and refined using the Bruker SHELXTL Software Package[2] within APEX3 [1] and OLEX2.[3] Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{equiv}$ of the parent atom. In one of the three chemically equivalent but crystallographically distinct molecules in the structure, there was disorder of the NO and one Ph group. The relative occupancy of the disordered positions was freely refined. Constraints and restraints were used on the anisotropic displacement parameters of the disordered atoms and the disordered bonds.

Table S1. Crystallographic data for $TpRu(NO)Ph_2$ (**2**).

	$TpRu(NO)Ph_2$ (**2**)
CCDC number	2170944
Formula	$C_{21}H_{20}BN_7ORu$
FW (g/mol)	498.32
Temp (K)	100(2)
λ (Å)	0.71073
Size (mm)	0.125 x 0.147 x 0.172
Crystal habit	dark red block
Crystal system	triclinic
Space group	P 1
a (Å)	9.7056(9)
b(Å)	10.5964(10)
c (Å)	16.2142(16)
α (°)	91.326(3)
β (°)	98.612(3)
γ (°)	103.202(3)
Volume ($Å^3$)	1602.3(3)
Z	3
Density (g/cm^3)	1.549
μ (mm^{-1})	0.762
F(000)	756
θ range (°)	1.27 to 29.62
Index ranges	$-13 \leq h \leq 13$ $-14 \leq k \leq 14$ $-22 \leq l \leq 22$
Reflns collected	75345
Independent reflns	18049 [$R_{int} = 0.0506$]
Data / restraints /parameters	18049 / 5 / 828
GOF on F^2	1.030
R_1 ($I>2\sigma(I)$)	0.0372
wR_2 (all data)	0.0759

[2] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.
[3] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.