

SUPPLEMENTARY INFORMATION

Ruthenium-nickel heterobimetallic complex as a bifunctional catalyst for
ROMP of norbornene and ethylene polymerization

Gustavo H. C. Masson^a, Thaís R. Cruz^a, Patrik D. S. Gois^a, Daniele M. Martins^b,
Benedito, S. Lima-Neto^b, Guedmiller S. Oliveira^c, Antonio E. H. Machado^c, Katia
Bernardo-Gusmão^d, Beatriz E. Goi^a, Valdemiro P. Carvalho-Jr^{a*}

^aFaculdade de Ciências e Tecnologia, UNESP – Univ. Estadual Paulista, CEP 19060-900, Presidente Prudente, SP, Brazil

^bInstituto de Química de São Carlos, Universidade de São Paulo, CEP 13560-970, São Carlos, SP, Brazil

^cInstituto de Química, Universidade Federal de Uberlândia, P.O. Box 593, CEP 38400-089, Uberlândia, MG, Brazil

^dInstituto de Química, Universidade Federal do Rio Grande do Sul, P.O. Box 15003, CEP 91501-970, Porto Alegre, RS, Brazil

Correspondence to: Valdemiro P. Carvalho-Jr (E-mail: valdemiro.carvalho@unesp.br)

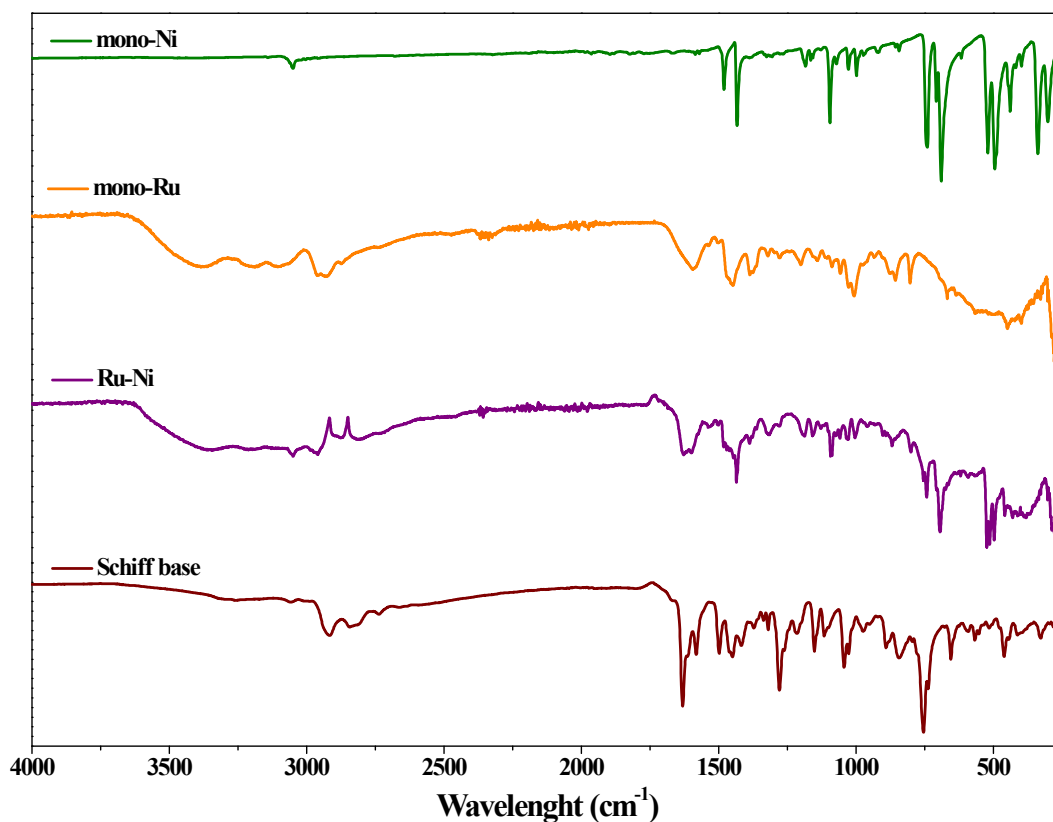


Fig. S1. FTIR spectra of Schiff base, **mono-Ru**, **mono-Ni**, and **Ru-Ni**.

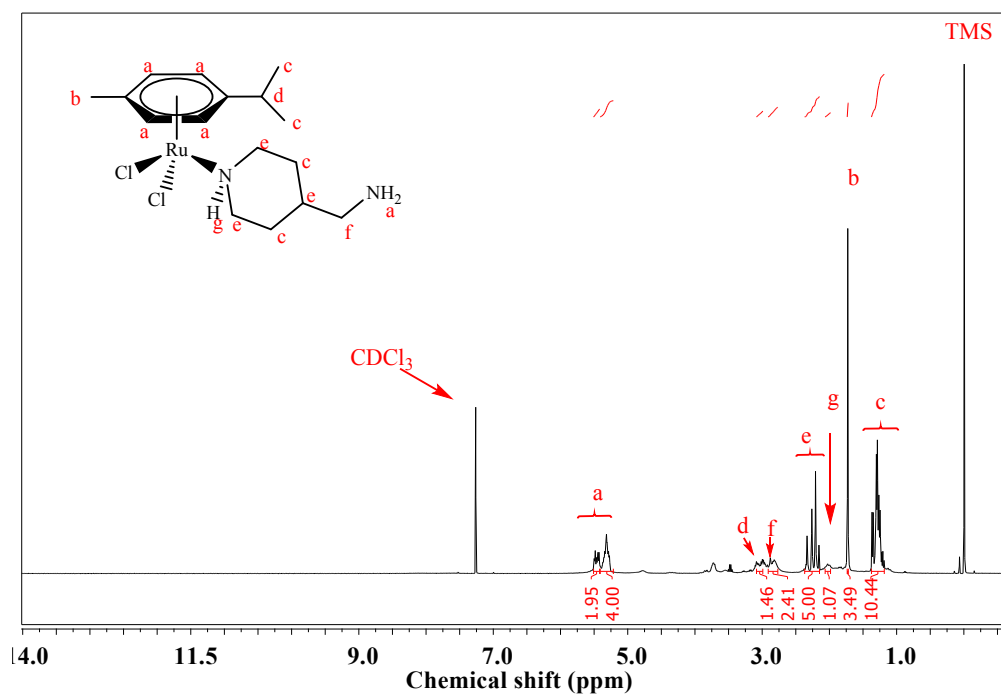


Fig. S2. ¹H NMR spectra of **mono-Ru** from CDCl₃ solutions (δ in ppm).

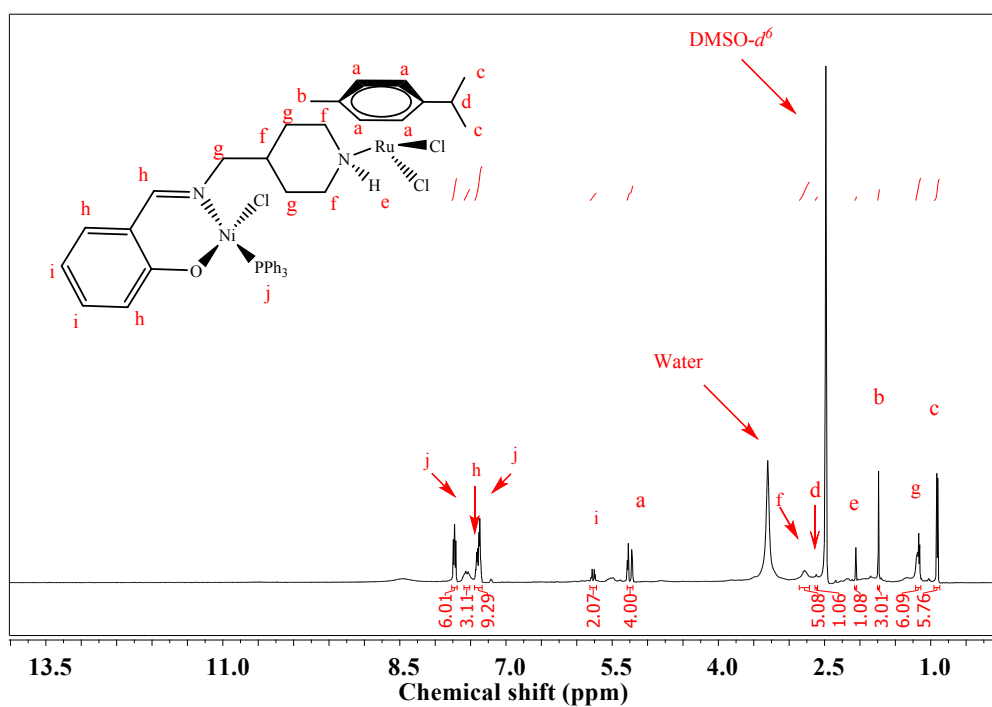


Fig. S3. ^1H NMR spectra of Ru-Ni from DMSO- d_6 solutions (δ in ppm).

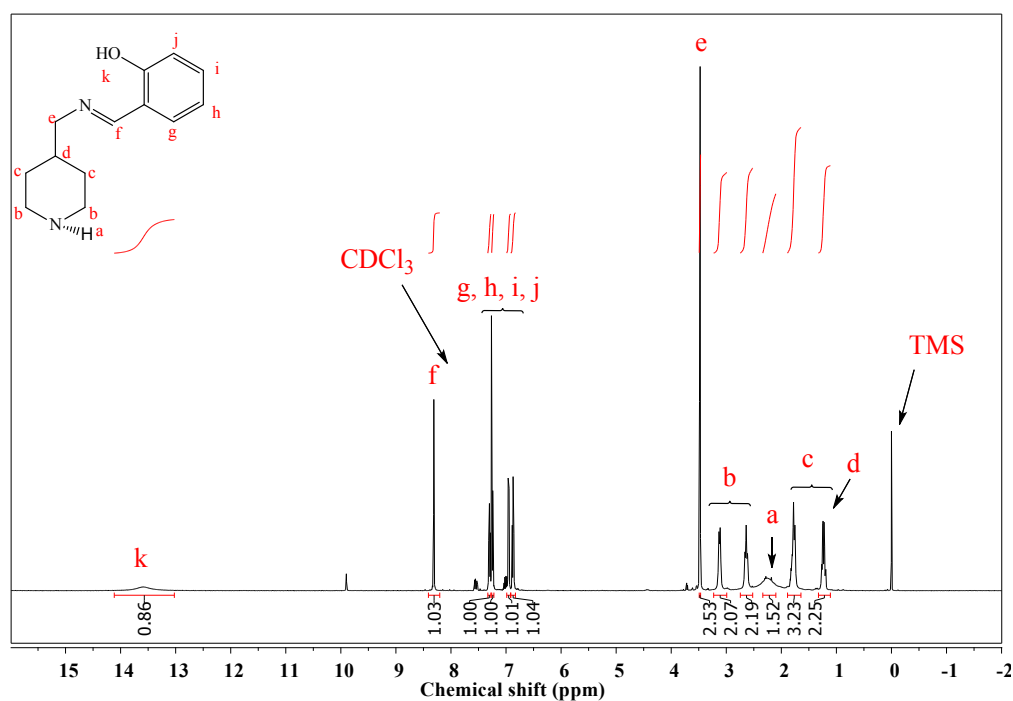


Fig. S4. ^1H NMR spectra of Schiff-pip from CDCl₃ solutions (δ in ppm).

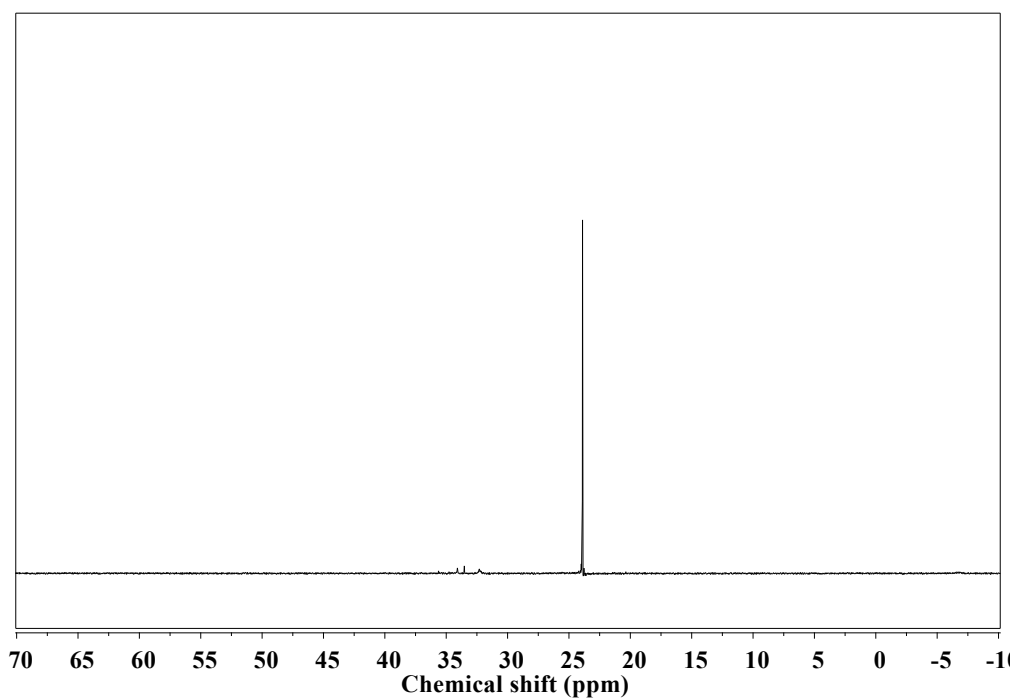


Fig. S5. ^{31}P { ^1H } NMR spectra of **Ru-Ni** from $\text{DMSO-}d^6$ solutions (δ in ppm).

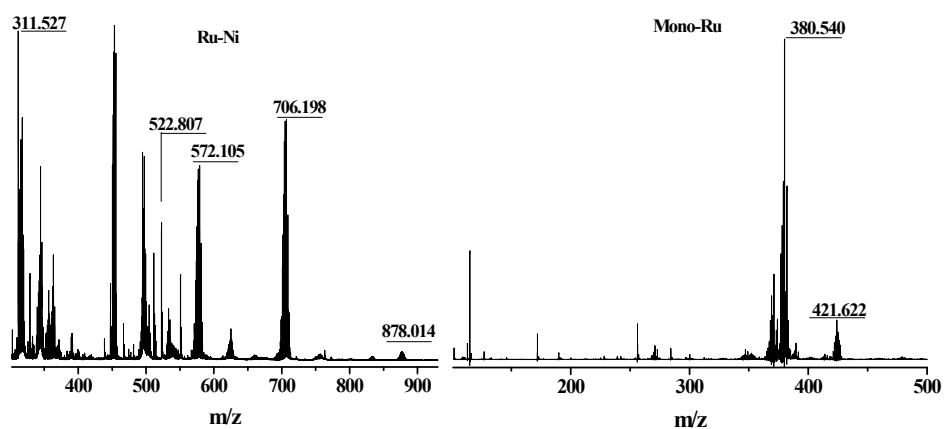


Fig. S6. MALDI-TOF spectrum of **Ru-Ni** and **mono-Ru** in MeOH.

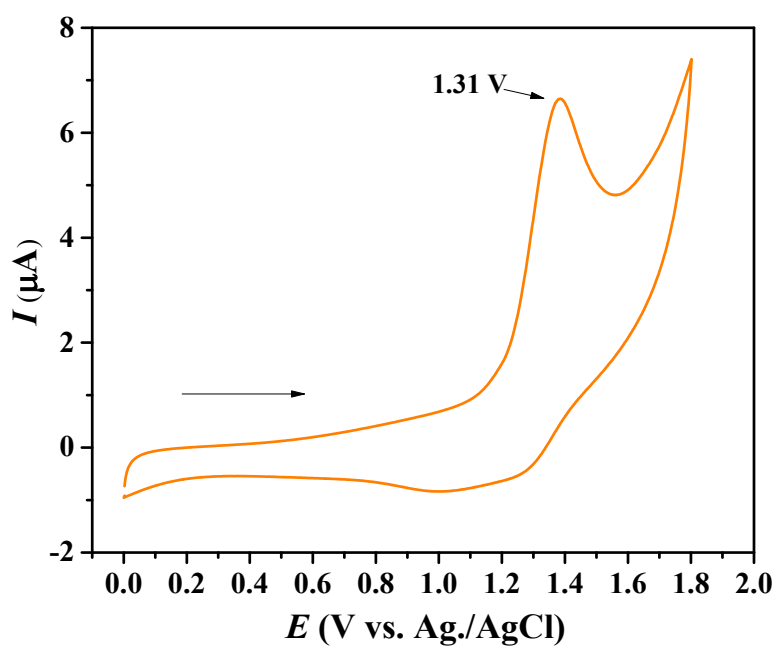


Fig. S7. Cyclic voltammogram of **mono-Ru** at $1.0 \cdot 10^{-3}$ M and $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ 0.1 M vs. Ag/AgCl; obtained at $100 \text{ mV} \cdot \text{s}^{-1}$.

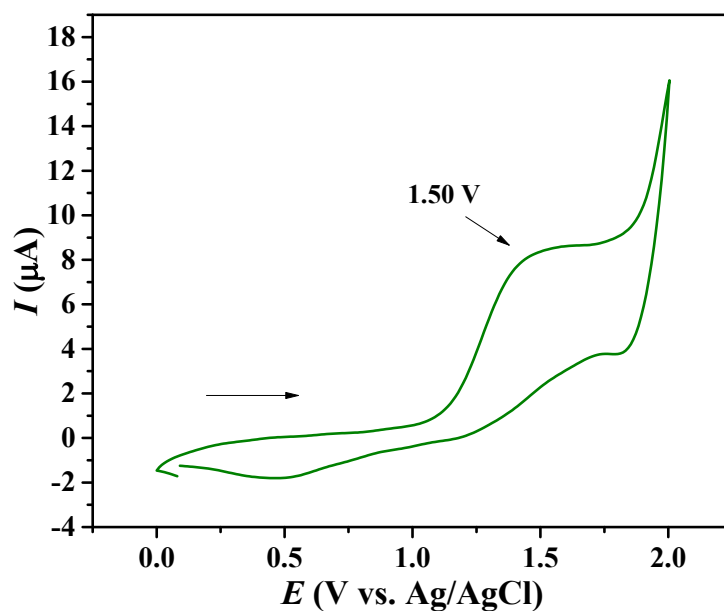


Fig. S8. Cyclic voltammogram of **mono-Ni** at $1.0 \cdot 10^{-3}$ M and $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ 0.1 M vs. Ag/AgCl; scanning anodically from 0.8 up to 1.6 V at $100 \text{ mV} \cdot \text{s}^{-1}$.

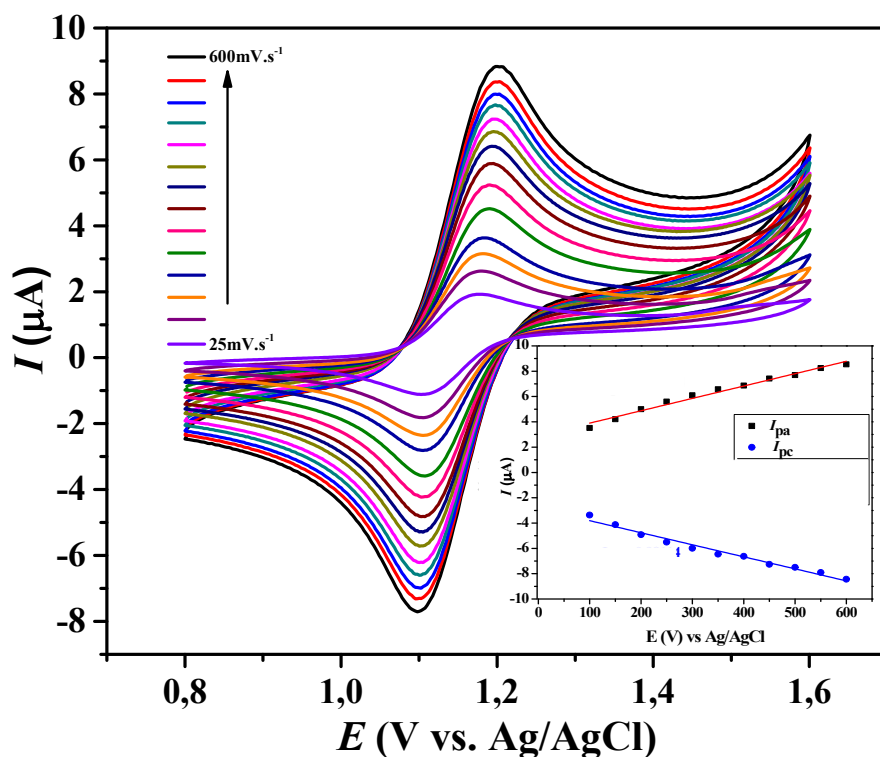


Fig. S9. Cyclic voltammogram of **Ru-Ni** at $1.0 \cdot 10^{-3}$ M and $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ 0.1 M vs. Ag/AgCl; scanning anodically from 0.8 up to 1.6 V at scan rates of 25, 50, 75, 100, 150, 175, 200, 300, 400 and 500 mV s^{-1} . *Insert* - Current (I) of the anodic (I_{pa}) and cathodic (I_{pc}) processes vs. square root of the potential scan rate (v).

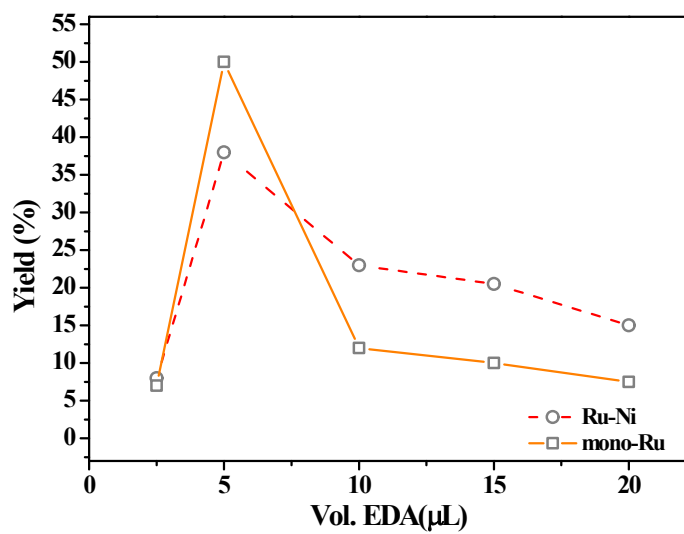


Fig S10. Dependence of yield as a function of the volume of EDA molar ratio for ROMP of NBE with **mono-Ru** and **Ru-Ni**; $[NBE]/[Ru] = 5000$ in $CHCl_3$ for 60 min.

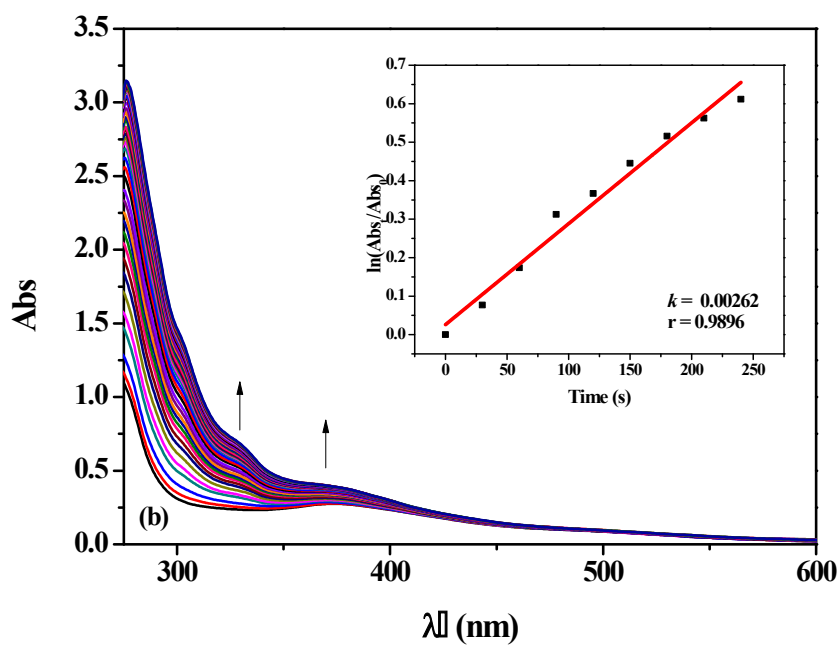
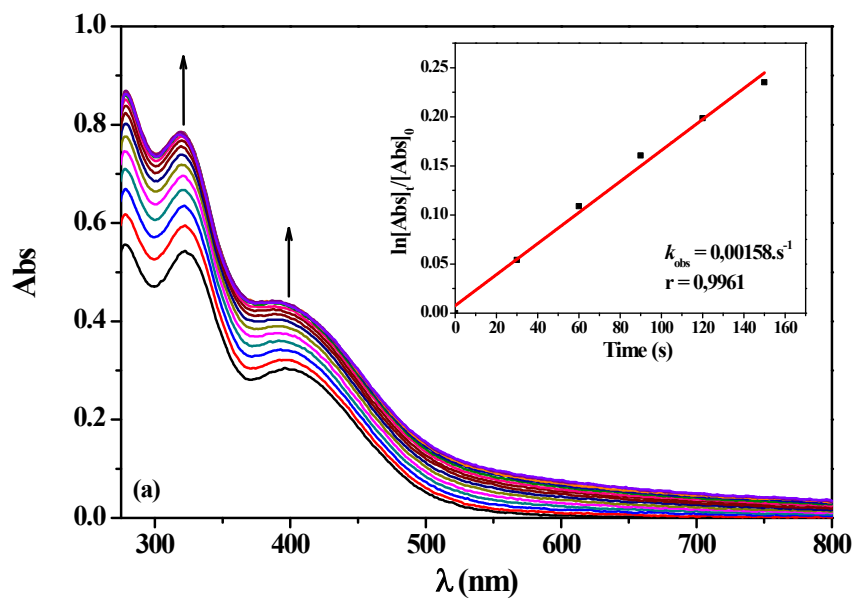


Fig. S11. Kinetic study of **mono-Ru** (a) and **Ru-Ni** (b) in presence of EDA monitored by electronic spectroscopy every 30 seconds and (*insert*) dependence of $\ln(\text{Abs}_t/\text{Abs}_0)$ as a function of time at 316 nm. $[\text{Ru}] = 1.0 \cdot 10^{-5} \text{ M}$; $[\text{EDA}] = 1.26 \cdot 10^{-5} \text{ mol L}^{-1}$ in CHCl_3 and 25 °C.

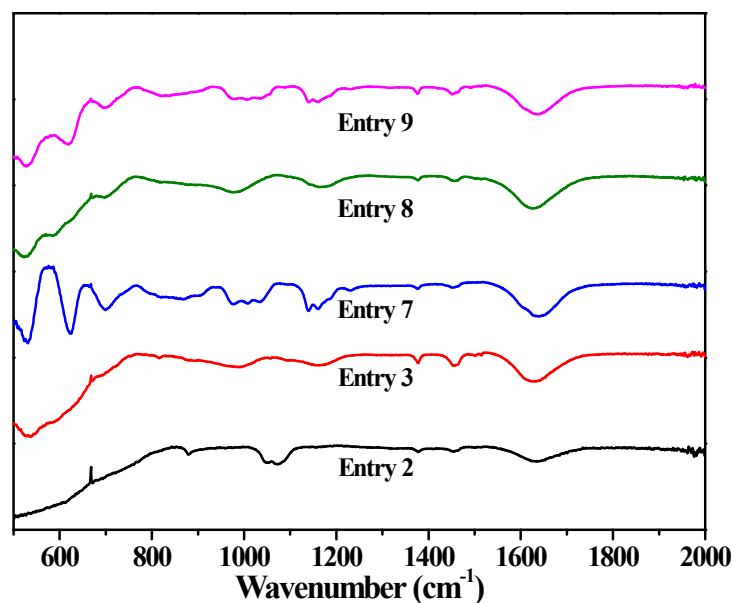


Fig. S12 FTIR spectra of polyethylene obtained from **Ru-Ni**.

Table S1 Peaks detected in the positive ion MALDI-TOF mass spectrum of the **Ru-Ni** and **mono-Ru** complex.

	Peak position (m/z)	m/z range	Peak assignment
	311.527	309.528-320.575	$[\text{NiCl}-(\text{N},\text{O})-(4\text{-aminomethyl})]^+$
	522.807	521.363-524.617	$[\text{RuCl}_2(p\text{-cymene})-(\text{N},\text{O})-(4\text{-aminomethyl})]^+$
Ru-Ni	572.105	570.192-583.116	$[\text{Ni}(\text{PPh}_3)\text{Cl}(\text{N},\text{O})-(4\text{-aminomethyl})]^+$
	706.198	696.905-712.930	$[\text{RuCl}_2(\mu\text{-Schiff-pip})\text{Ni}(\text{PPh}_3)]^+$
	878.014	869.625-883.558	$[\text{Ru-Ni}+\text{H}]^+$
	421.622	421.622-428.663	$[\text{Mono-Ru}+\text{H}]^+$
Mono-Ru	380.540	377.521-383.562	$[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})(\text{pipNH}_2)]^+\text{-isopropyl}$