

Electronic Supporting Information (ESI) for:

Homoleptic ruthenium(II) complexes bearing imidazol(in)ium-2-dithiocarboxylate ligands: synthesis, characterization, and redox properties

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Table of content

Part 1 – NMR spectra	4
Fig. S1. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a)	4
Fig. S2. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a)	4
Fig. S3. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a).....	5
Fig. S4. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b)	6
Fig. S5. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b).....	6
Fig. S6. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b)	7
Fig. S7. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c).....	8
Fig. S8. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c).....	8
Fig. S9. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c)	9
Fig. S10. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d).....	10
Fig. S11. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d).....	10
Fig. S12. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d)	11
Fig. S13. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (2e)	12
Fig. S14. $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (2e)	12
Fig. S15. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (2e).....	13
Part 2 – IR spectra	14
Fig. S16. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a)	14
Fig. S17. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b).....	15
Fig. S18. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c)	16
Fig. S19. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d).....	17
Fig. S20. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (2e).....	18
Part 3 – Mass spectra	19
Fig. S21. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a)	19
Fig. S22. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)	20
Fig. S23. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b)	21
Fig. S24. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)	22

Fig. S25. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c)	23
Fig. S26. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)	24
Fig. S27. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d)	25
Fig. S28. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)	26
Fig. S29. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (2e)	27
Fig. S30. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)	28
Part 4 – Cyclic voltammetry	29
Fig. S31. <i>Left</i> - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (2a) in CH_2Cl_2 at 25 °C. <i>Right</i> - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).....	29
Fig. S32. <i>Left</i> - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (2b) in CH_2Cl_2 at 25 °C. <i>Right</i> - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).....	29
Fig. S33. <i>Left</i> - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (2c) in CH_2Cl_2 at 25 °C. <i>Right</i> - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).....	30
Fig. S34. <i>Left</i> - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2d) in CH_2Cl_2 at 25 °C. <i>Right</i> - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).....	30
Fig. S35. <i>Left</i> - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (2e) in CH_2Cl_2 at 25 °C. <i>Right</i> - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).....	31
Fig. S36. Cyclic voltammogram of ferrocene in CH_2Cl_2 at 25 °C.....	31

Part 1 – NMR spectra

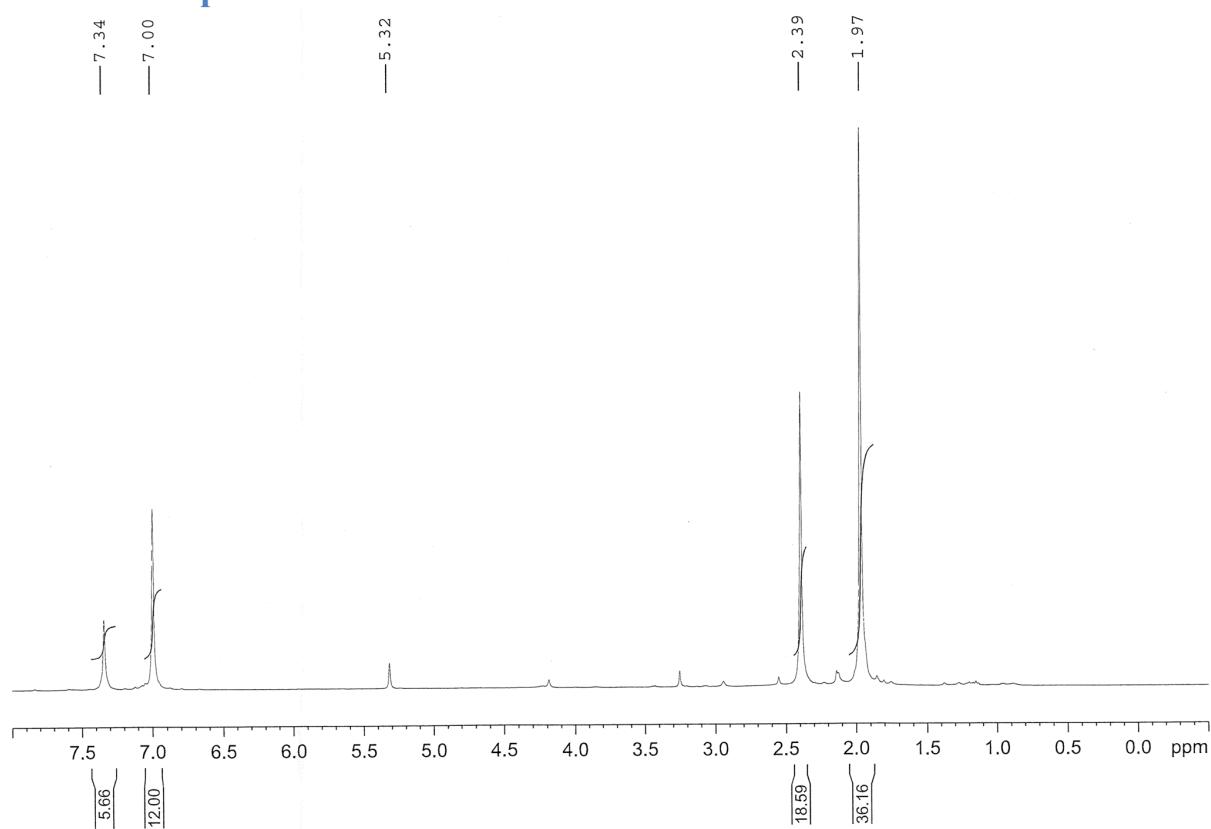


Fig. S1. ¹H NMR spectrum (400 MHz, CD₂Cl₂, 298 K) of [Ru(S₂C·IMes)₃](PF₆)₂ (**2a**)

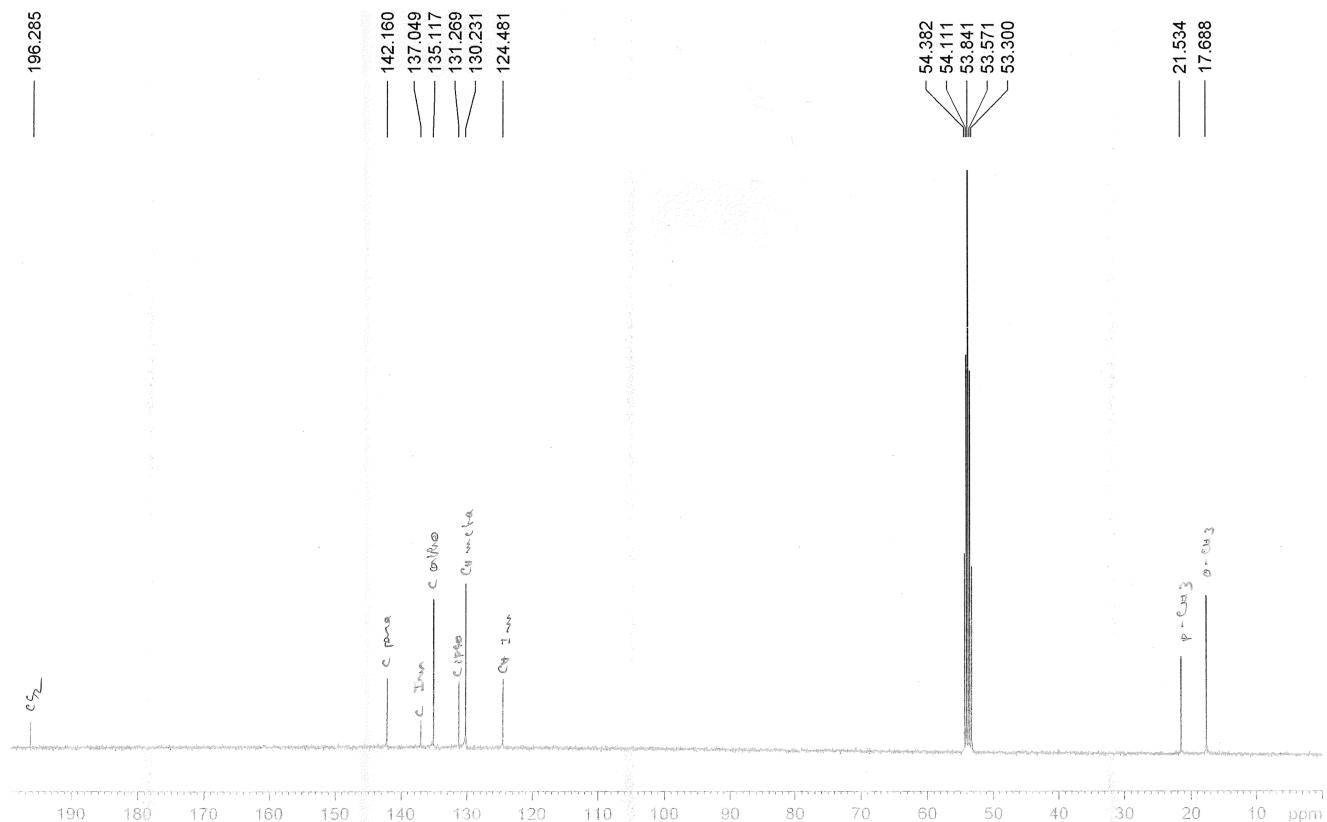


Fig. S2. ¹³C{¹H} NMR spectrum (101 MHz, CD₂Cl₂, 298 K) of [Ru(S₂C·IMes)₃](PF₆)₂ (**2a**)

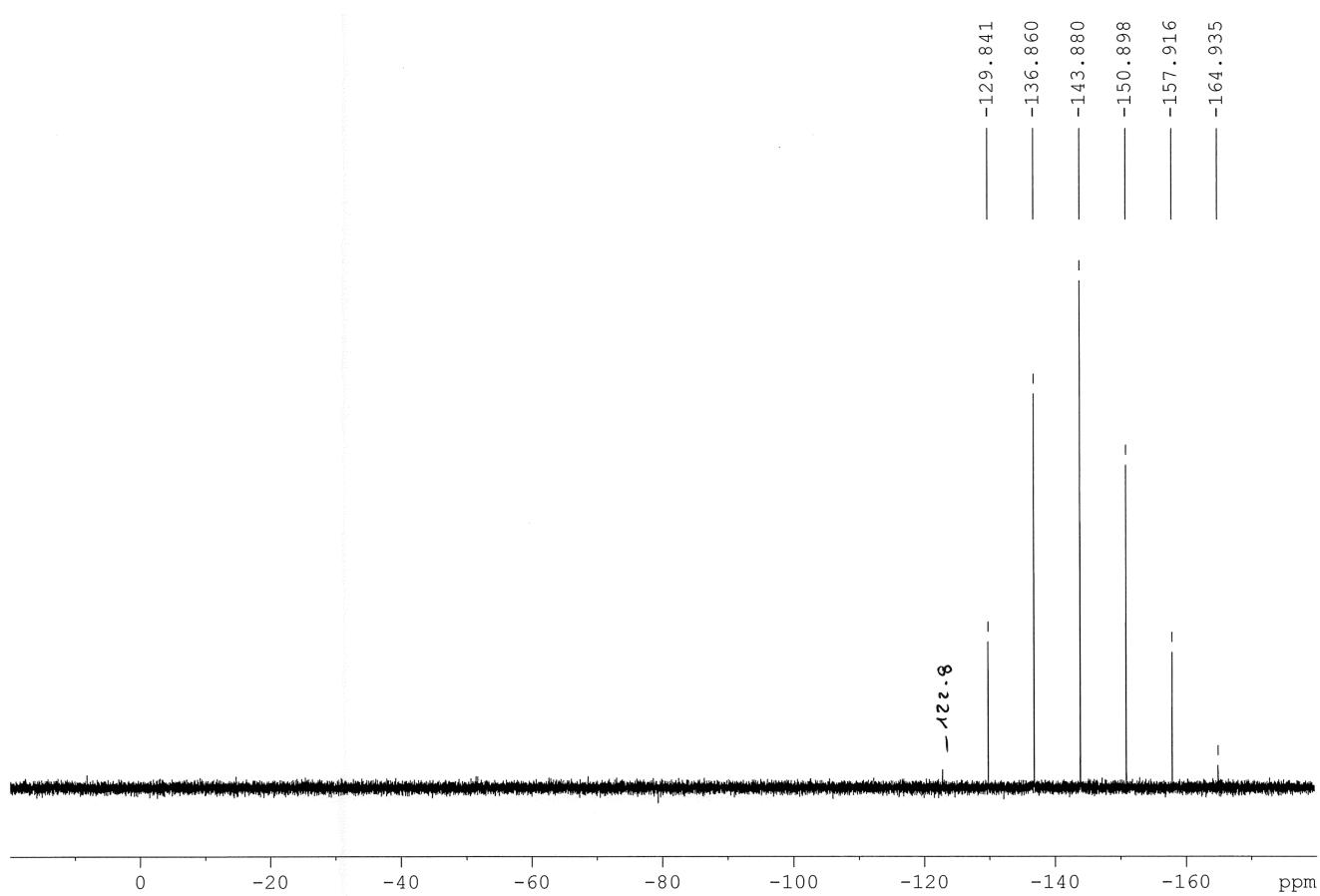


Fig. S3. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (**2a**)

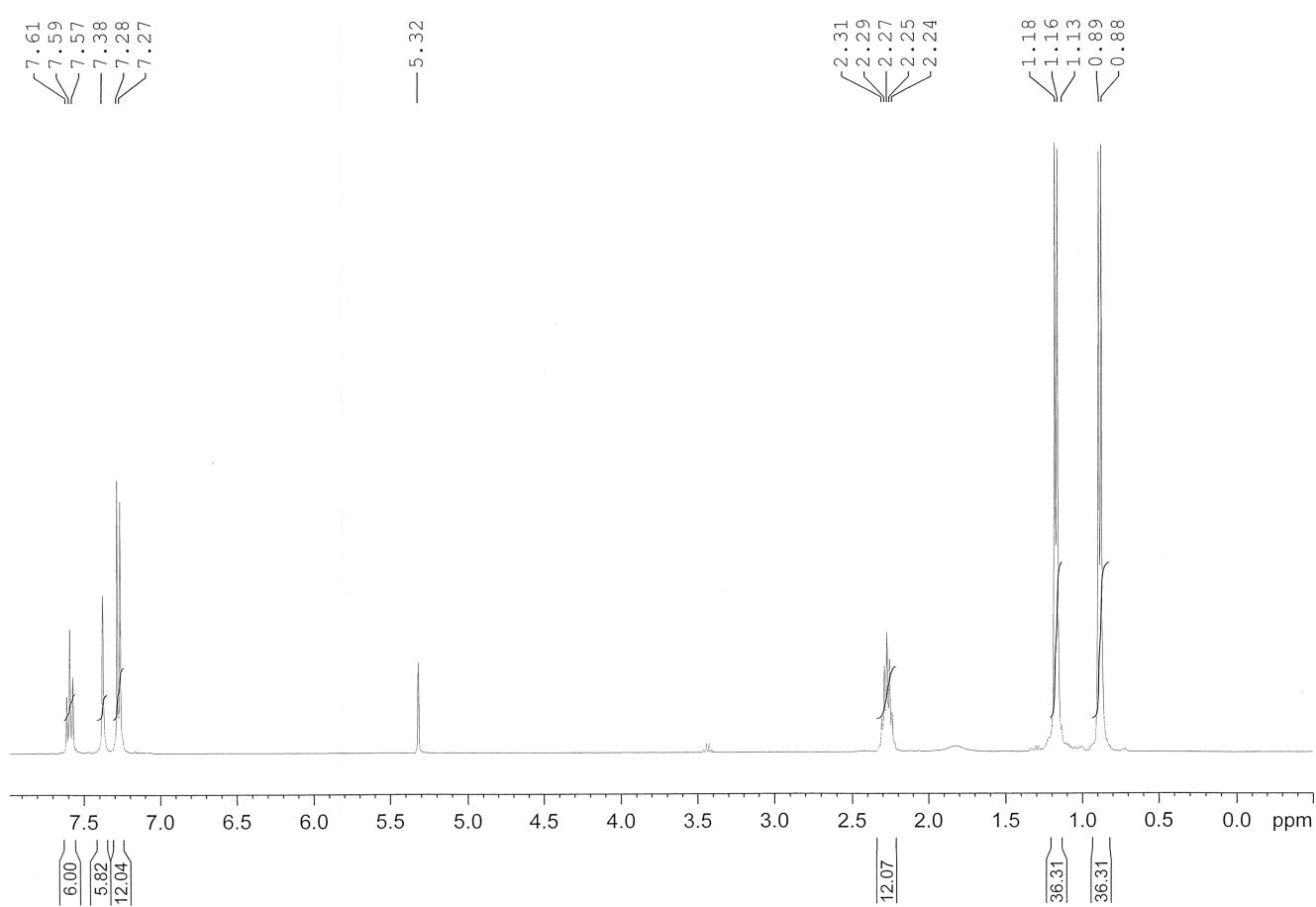


Fig. S4. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C-IDip})_3](\text{PF}_6)_2$ (**2b**)

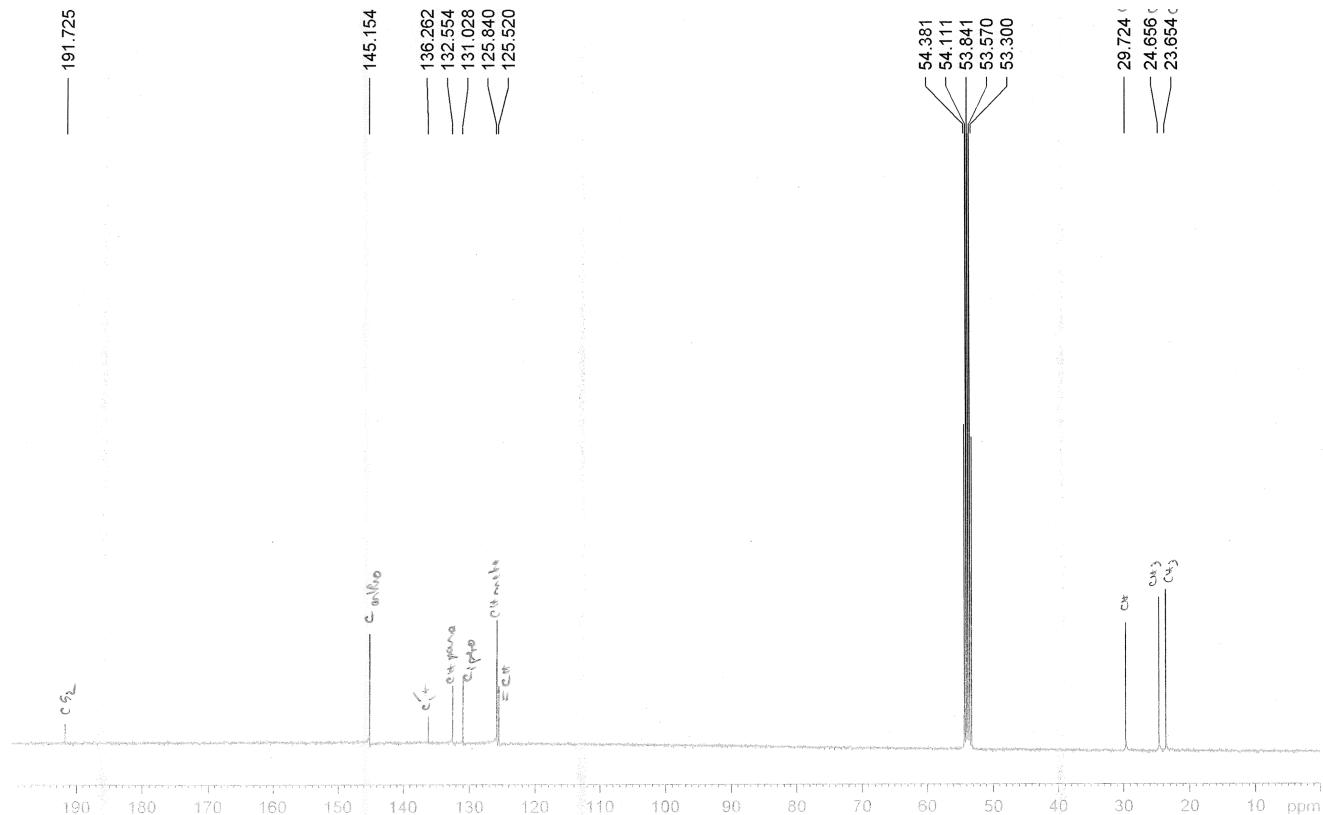


Fig. S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C-IDip})_3](\text{PF}_6)_2$ (**2b**)

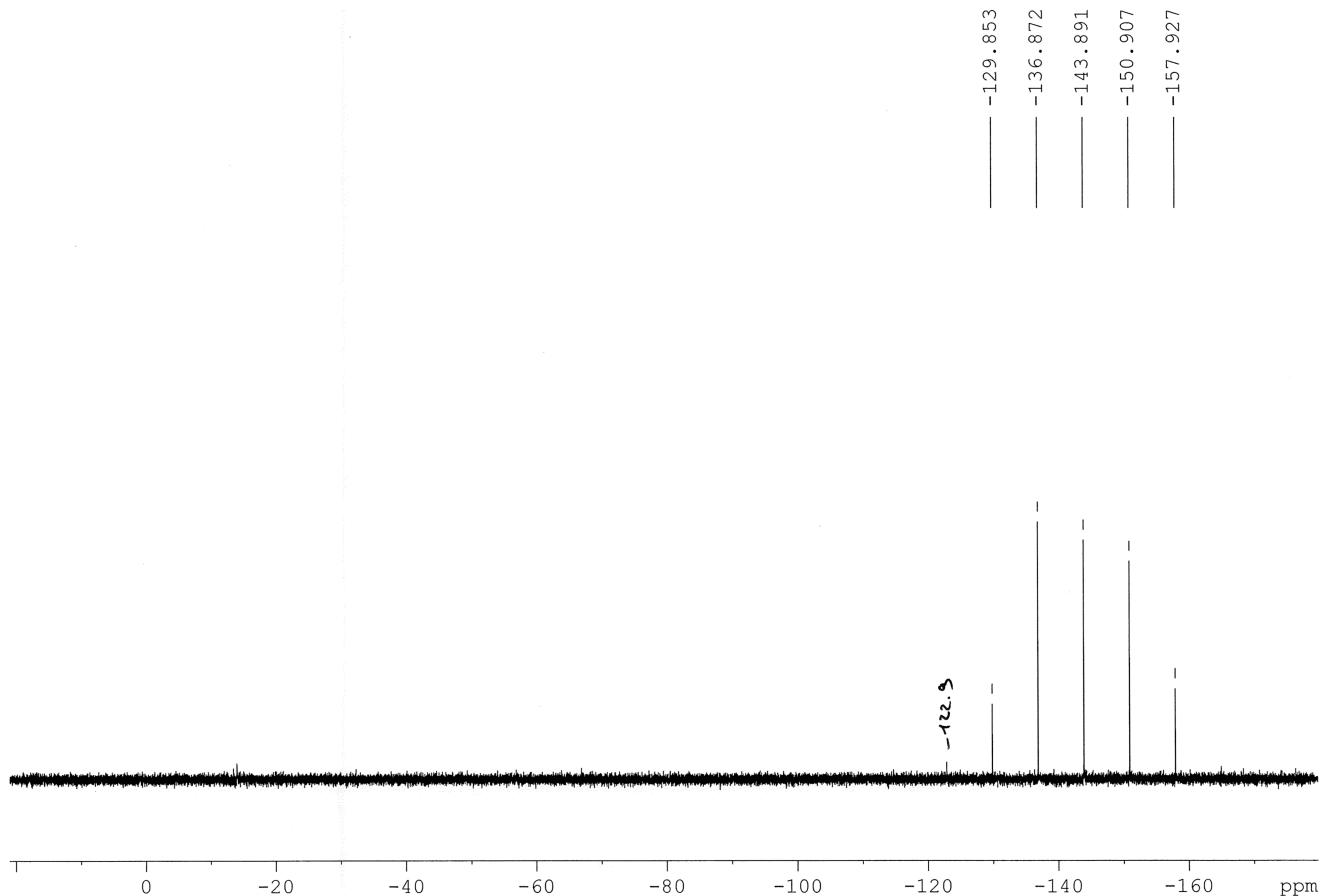


Fig. S6. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (**2b**)

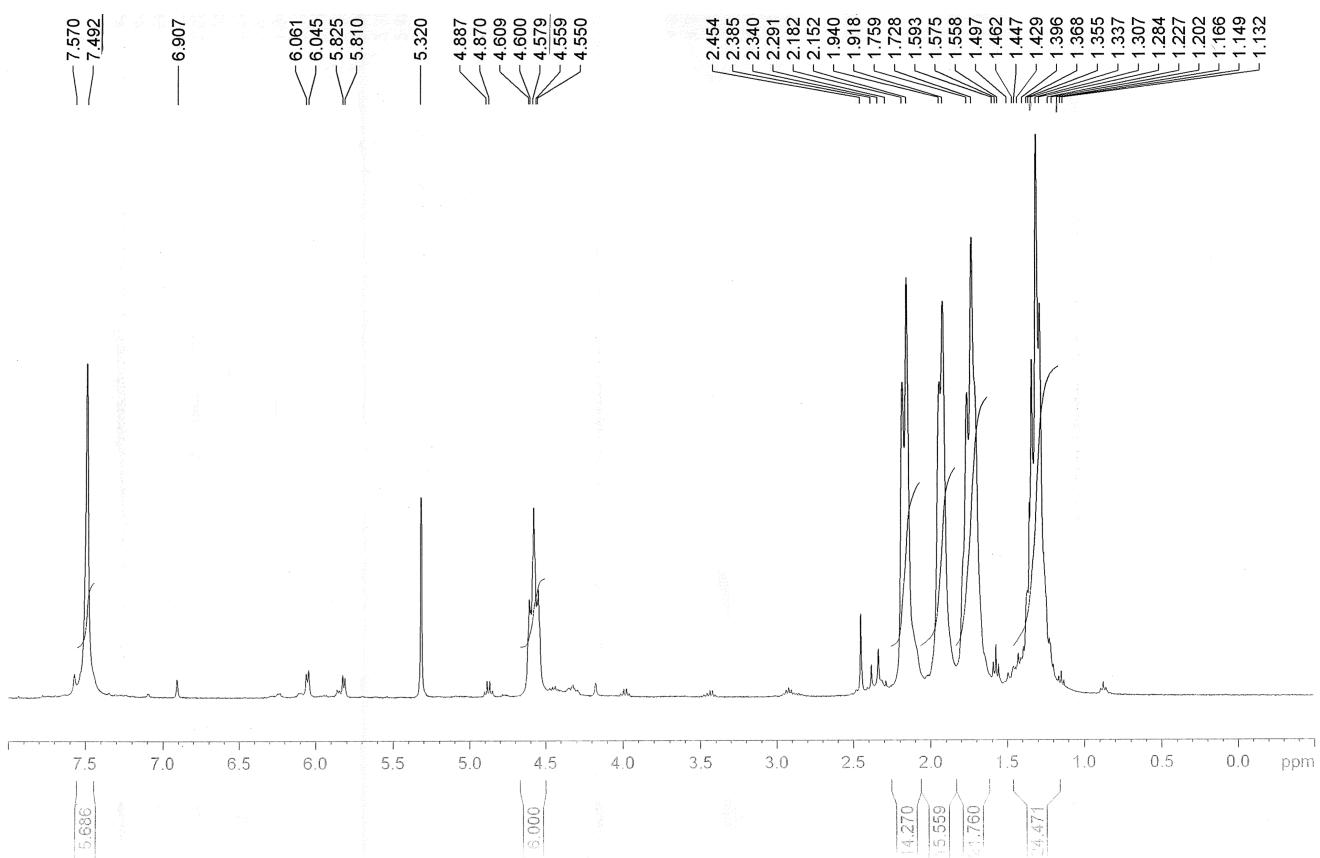


Fig. S7. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**)

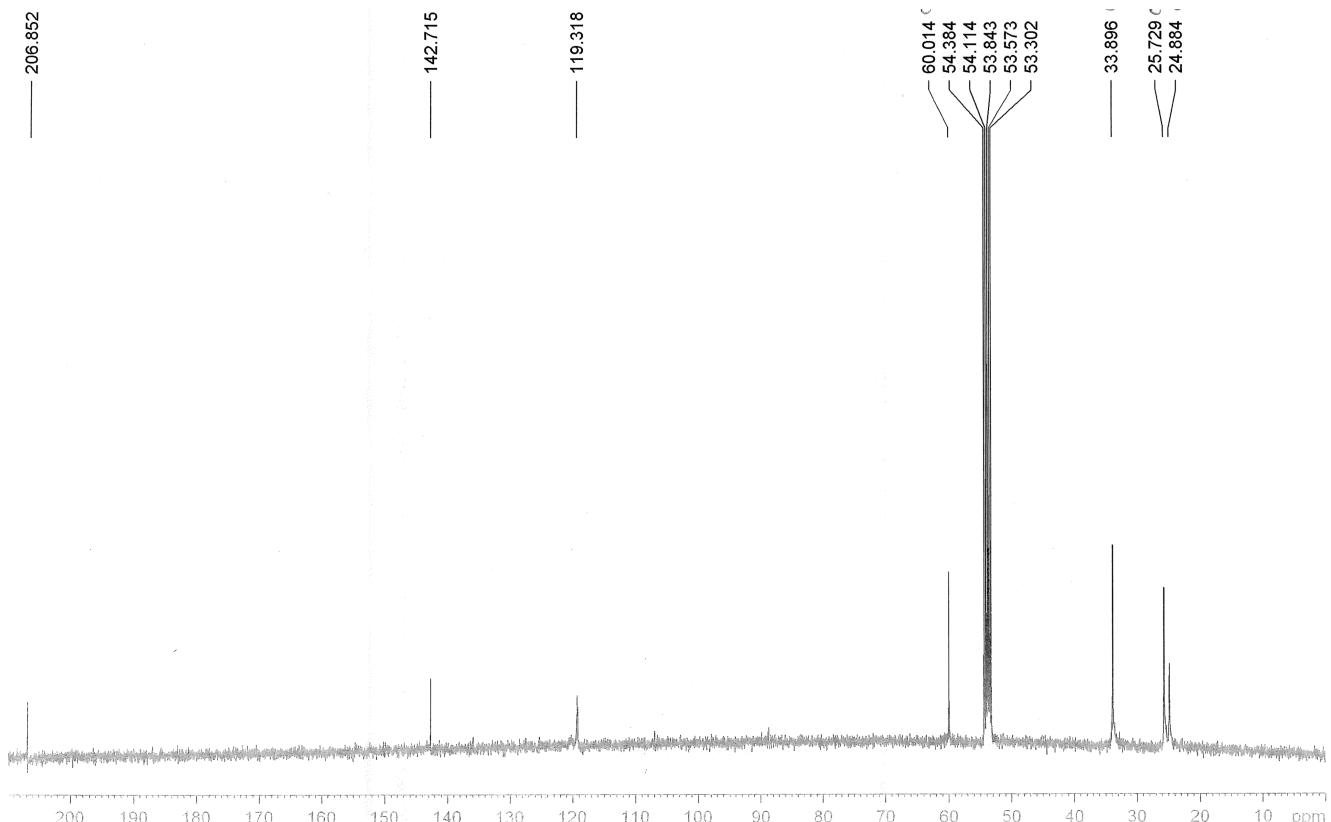


Fig. S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**)

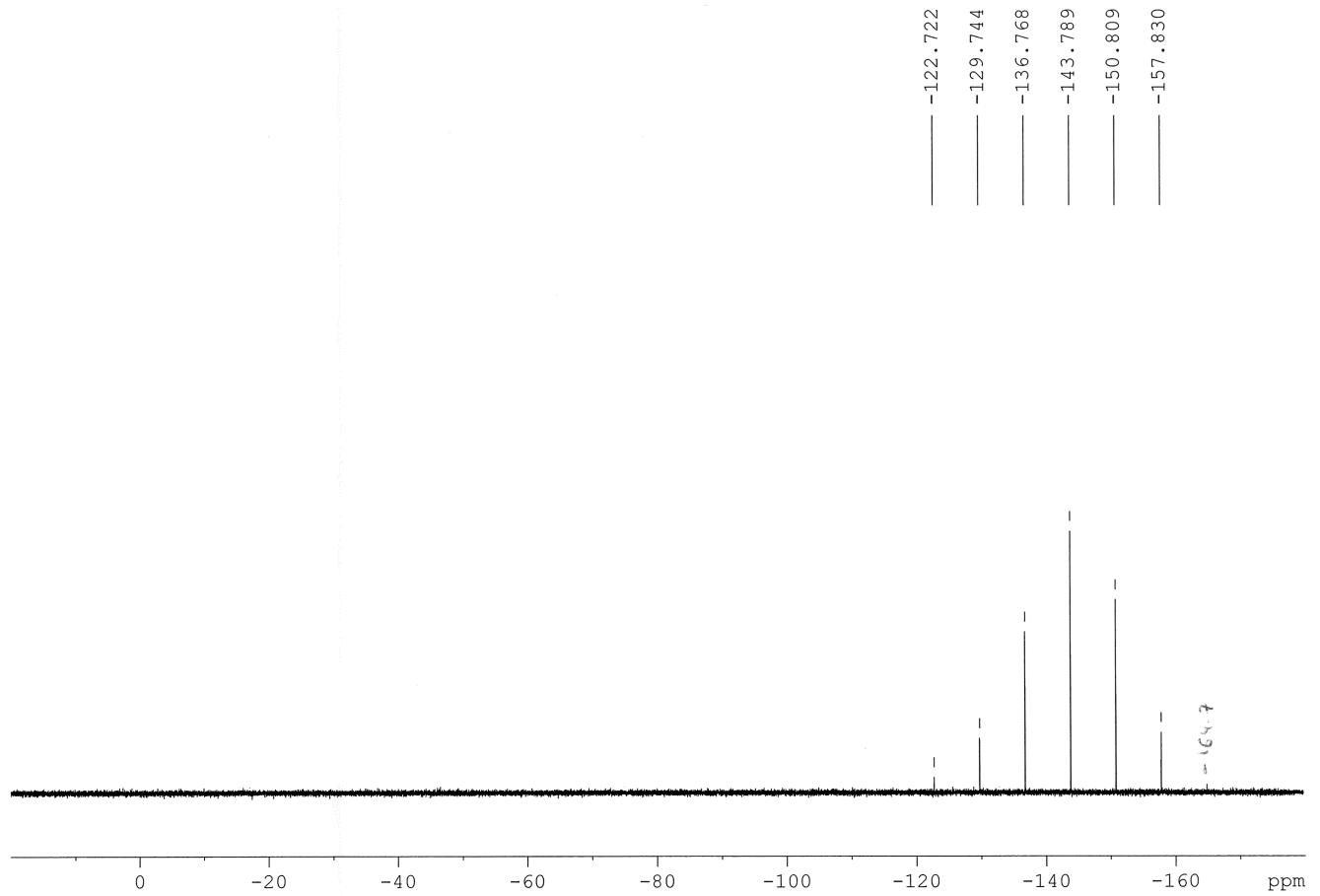


Fig. S9. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**)

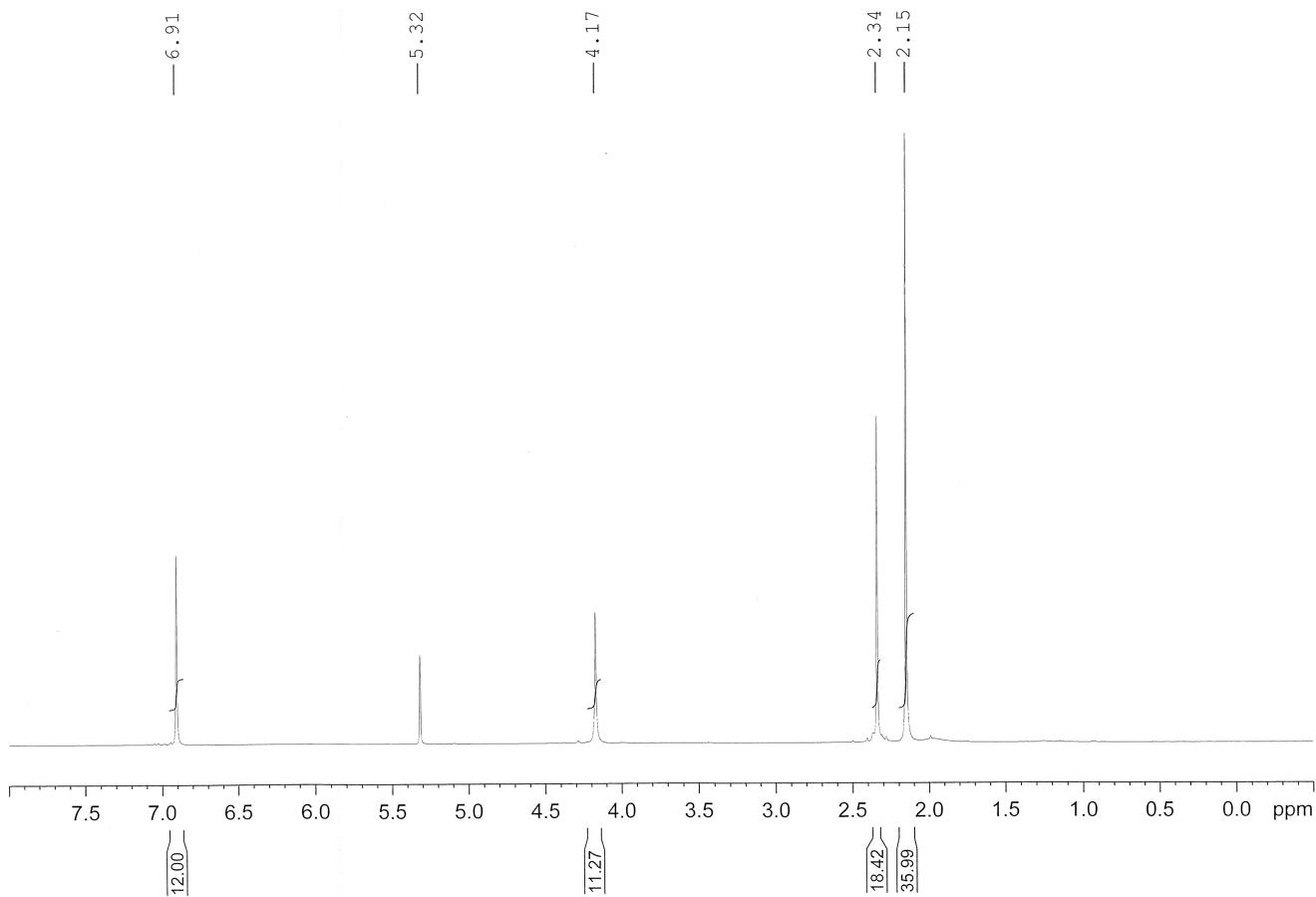


Fig. S10. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2d**)

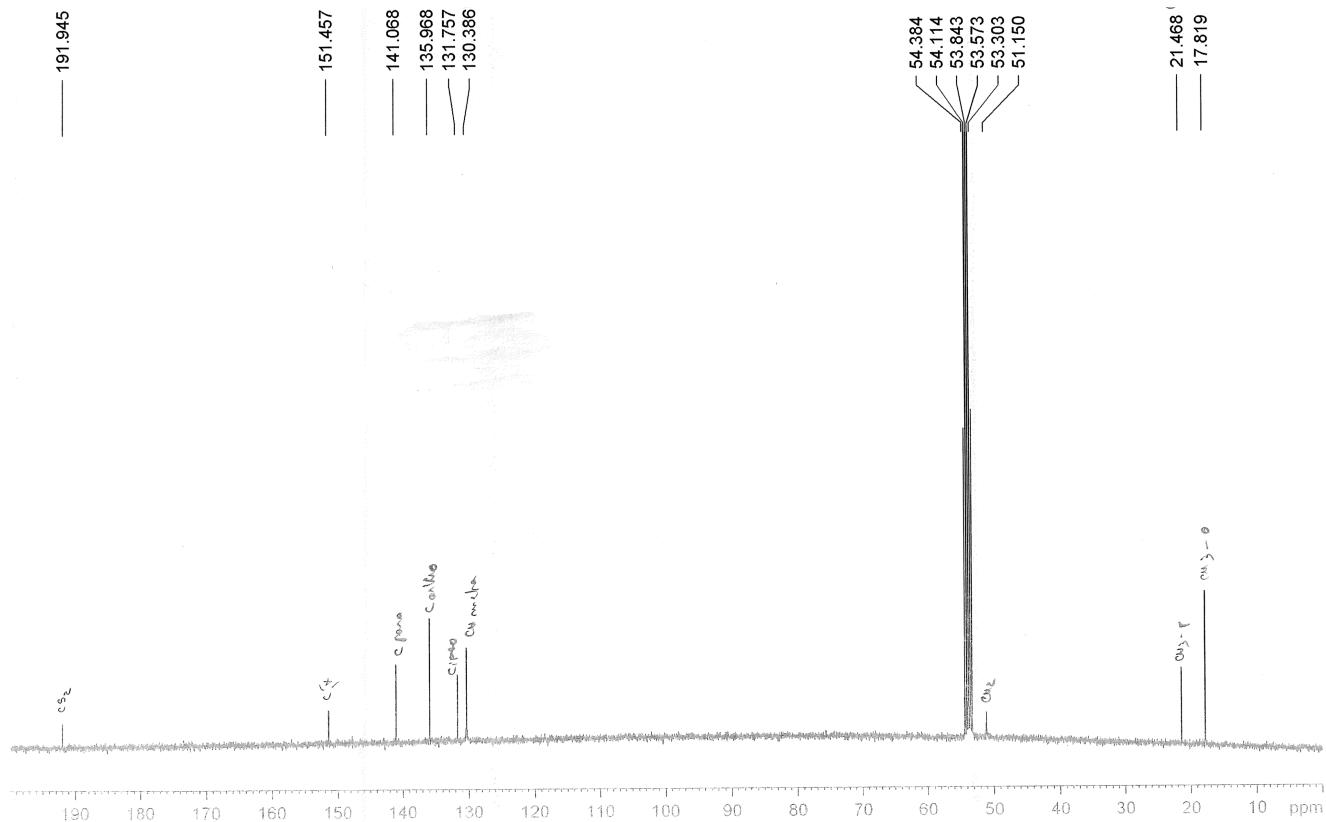


Fig. S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2d**)

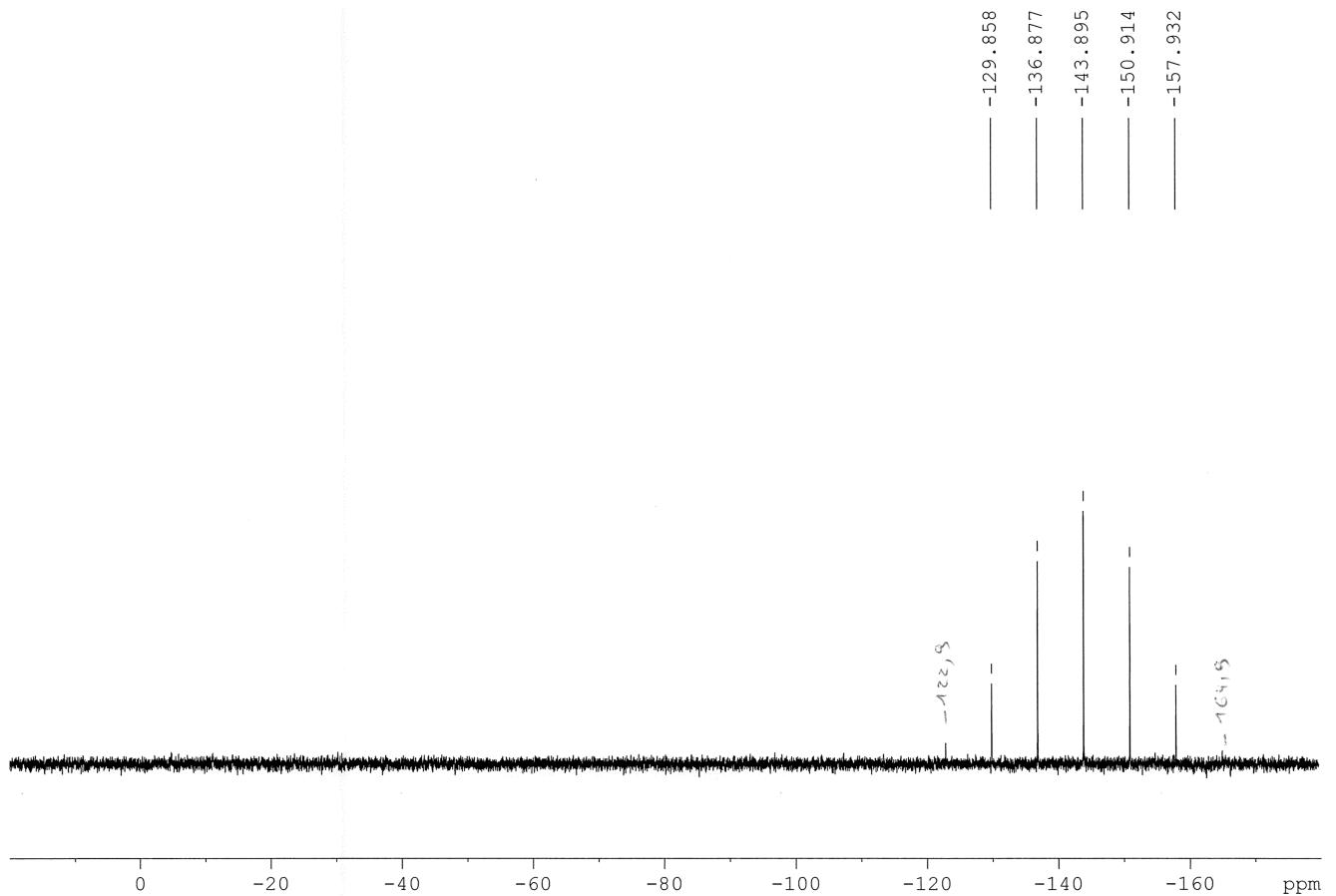


Fig. S12. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2d**)

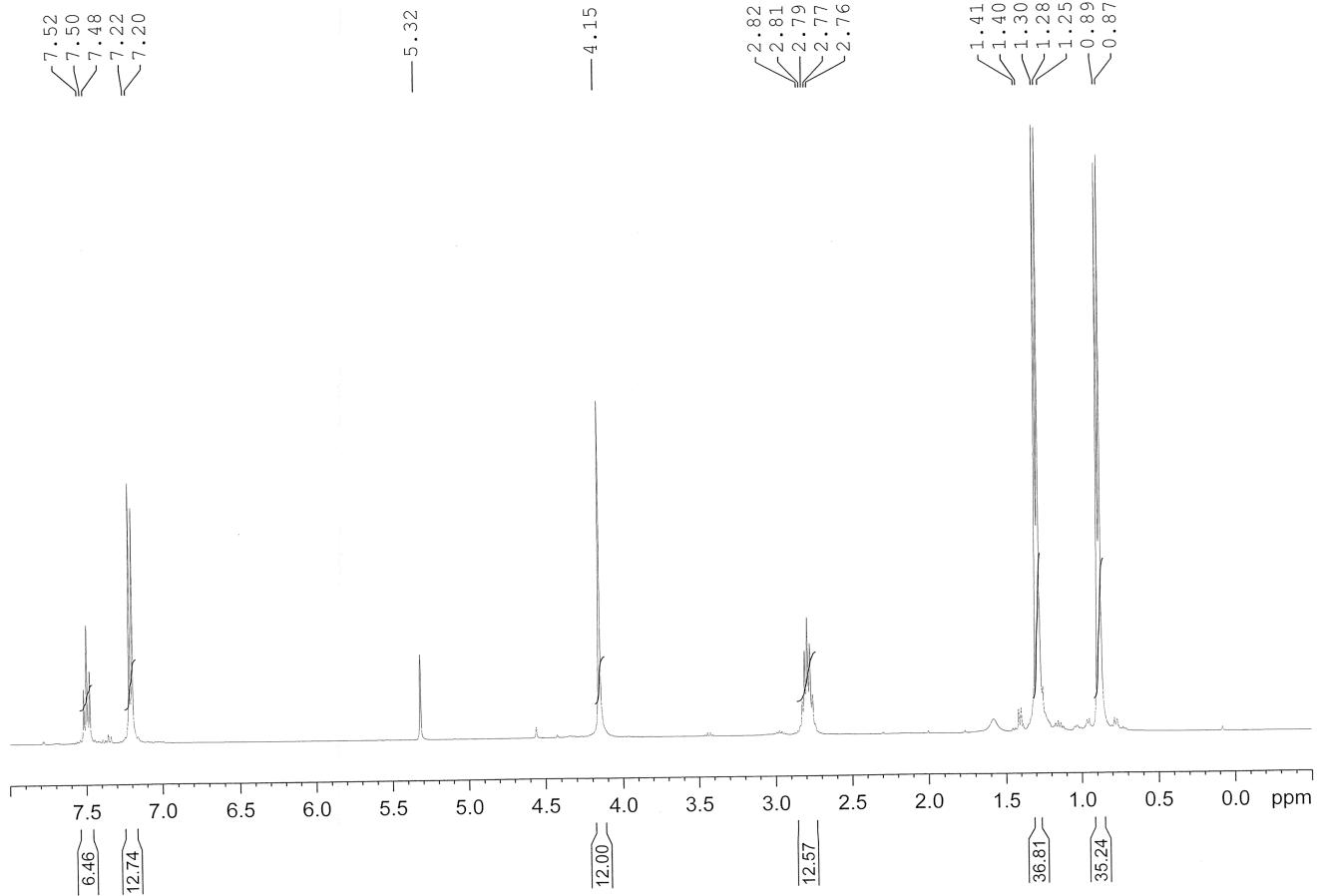


Fig. S13. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (**2e**)

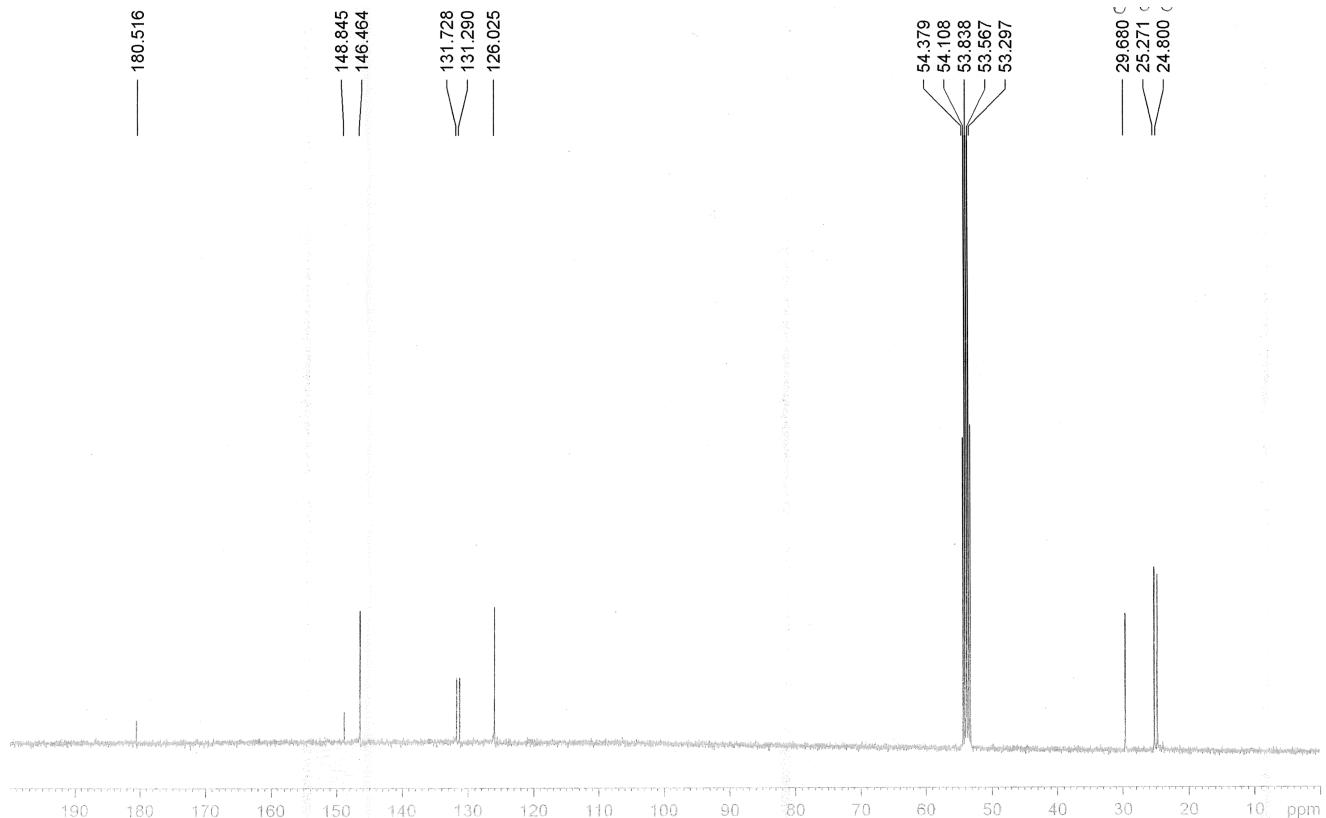


Fig. S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (**2e**)

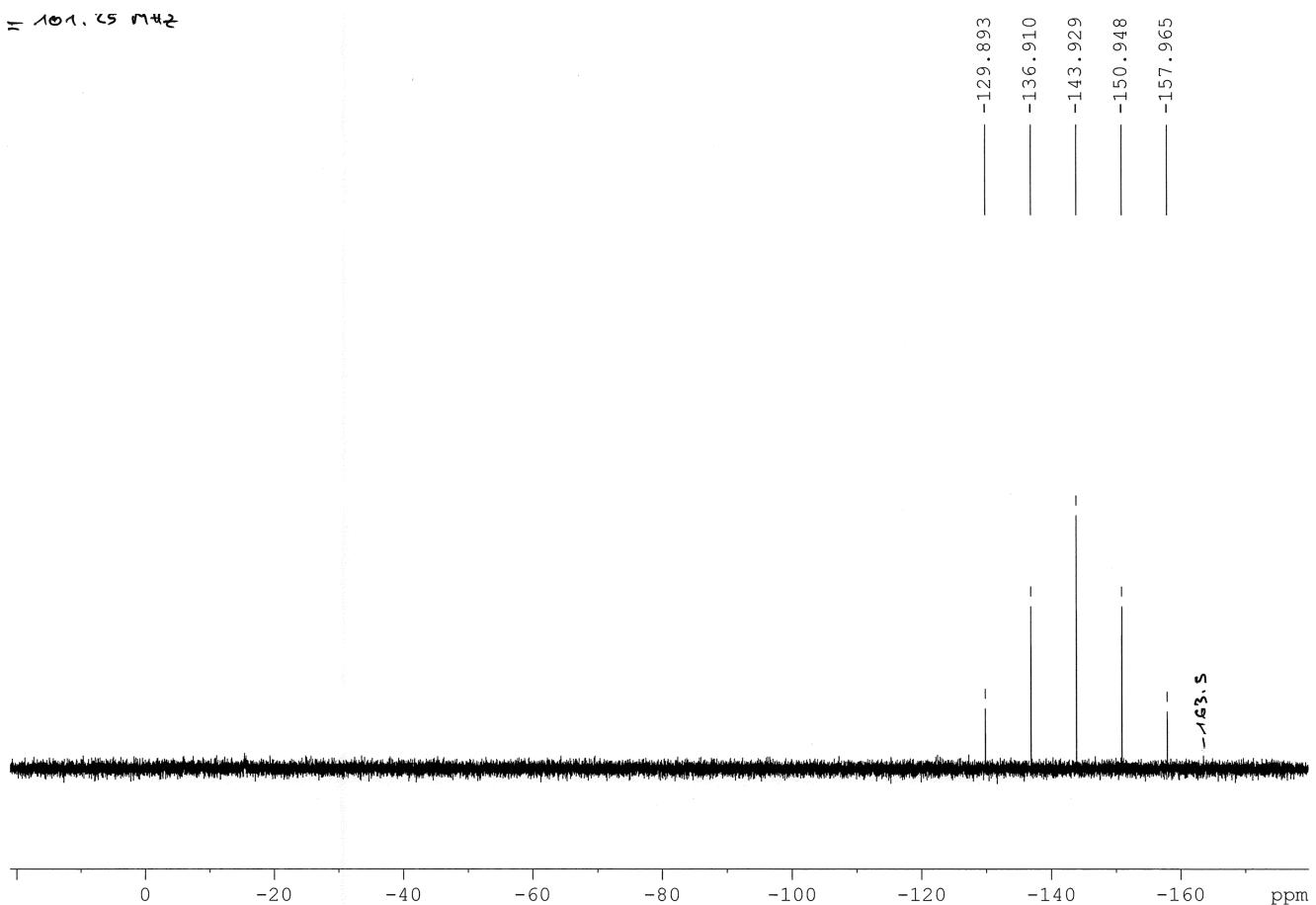


Fig. S15. ^{31}P NMR spectrum (101 MHz, CD_2Cl_2 , 298 K) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (**2e**)

Part 2 – IR spectra

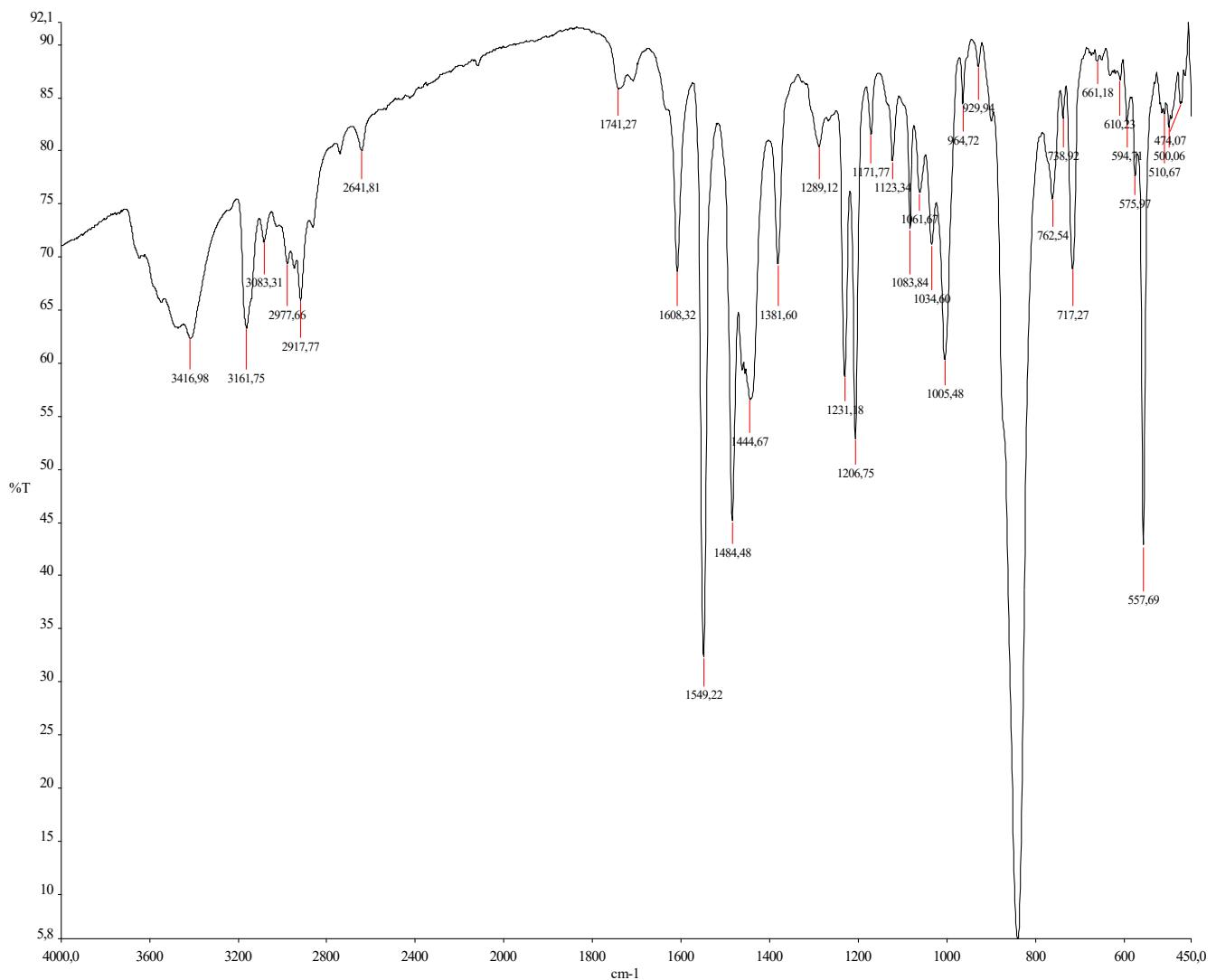


Fig. S16. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (**2a**)

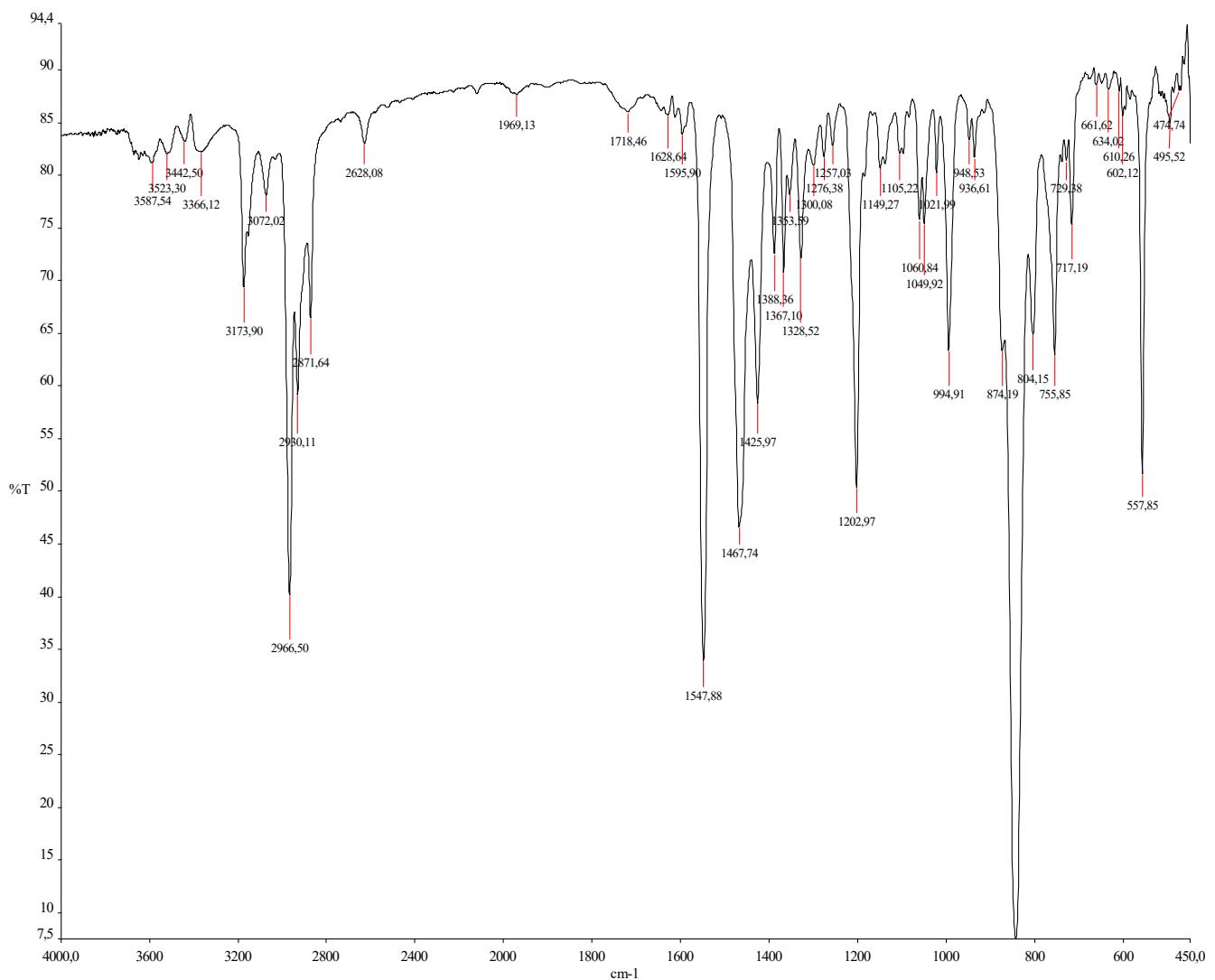


Fig. S17. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (**2b**)

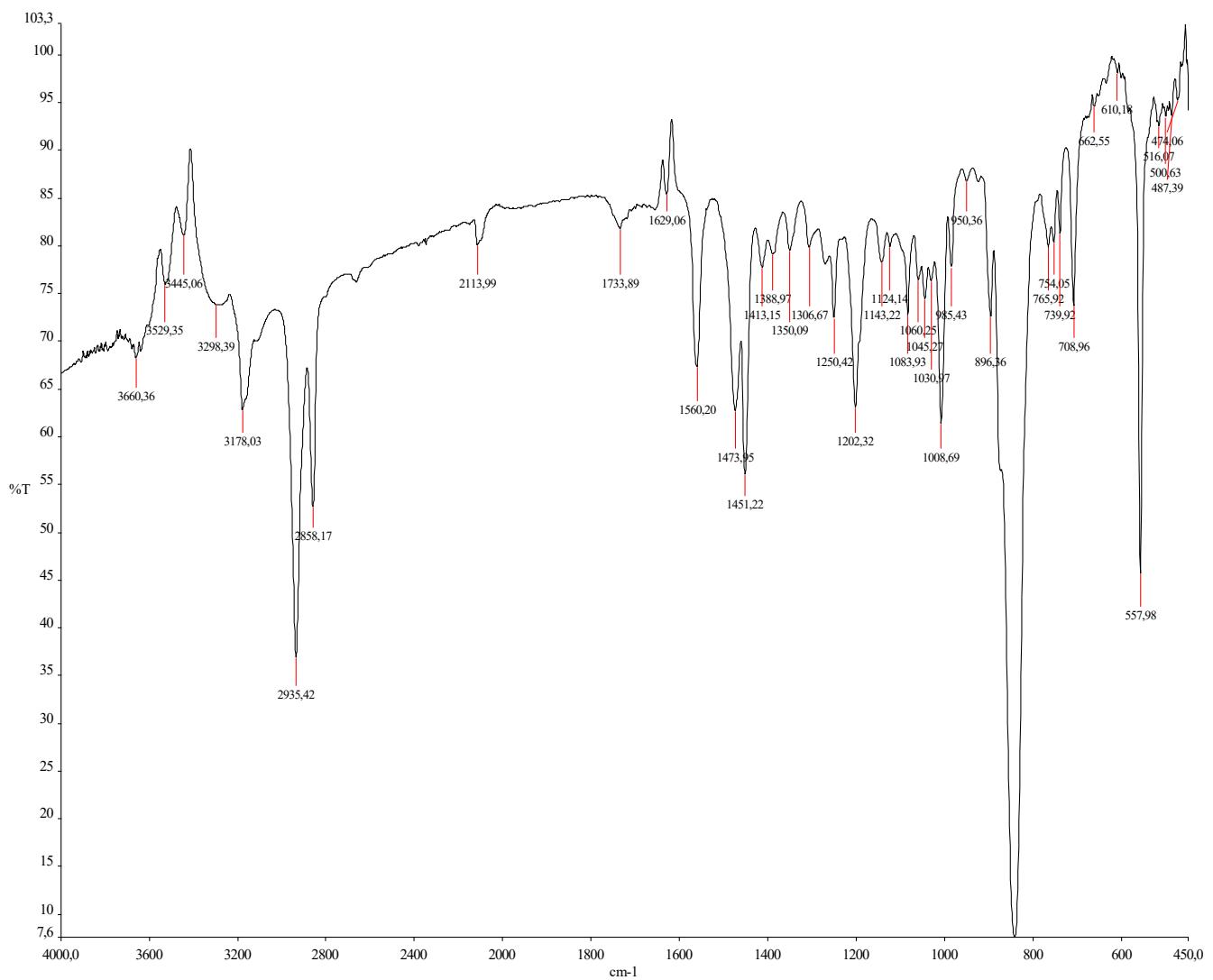


Fig. S18. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**)

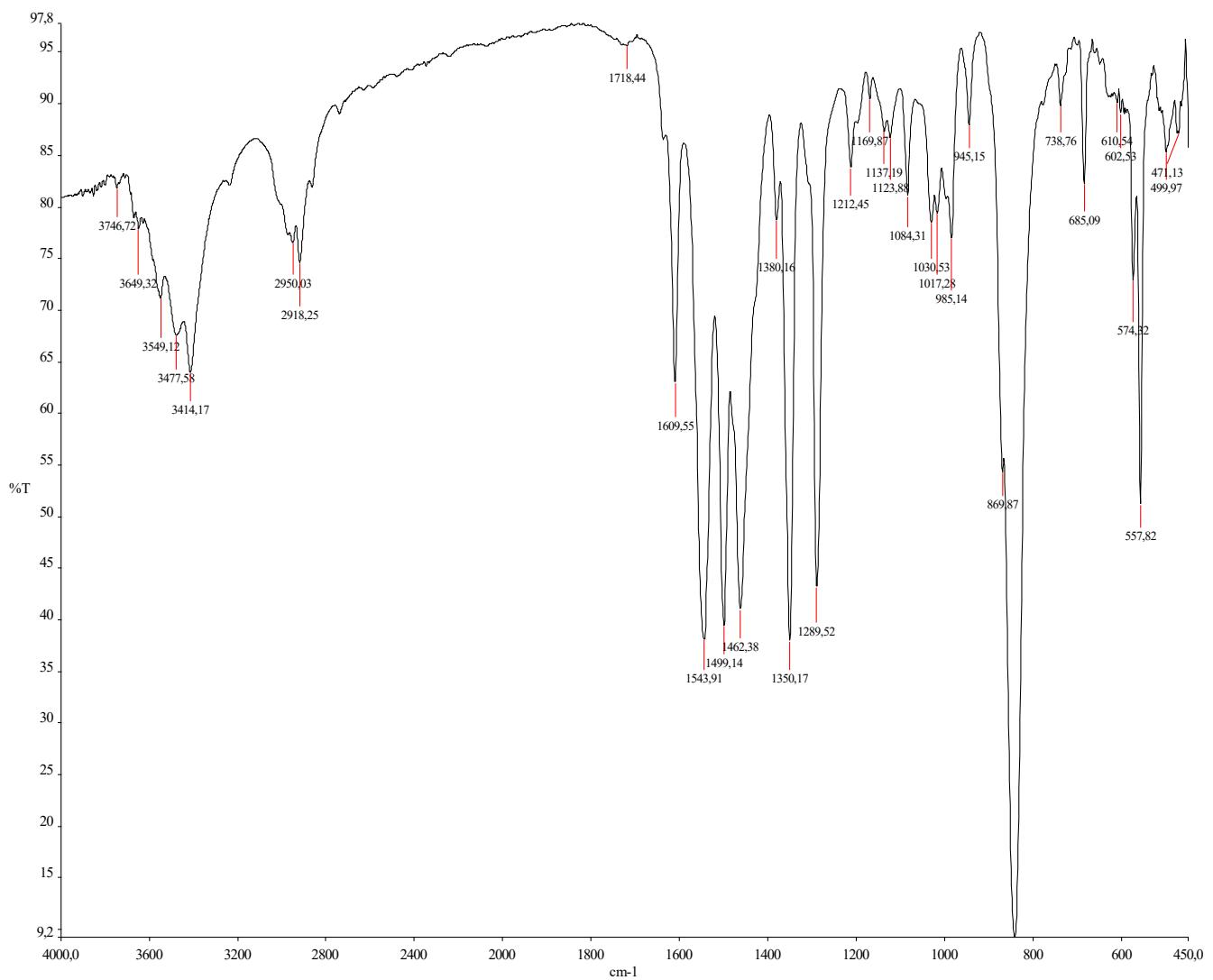


Fig. S19. FT-IR spectrum (KBr) of $[Ru(S_2C\cdot SIMes)_3](PF_6)_2$ (**2d**)

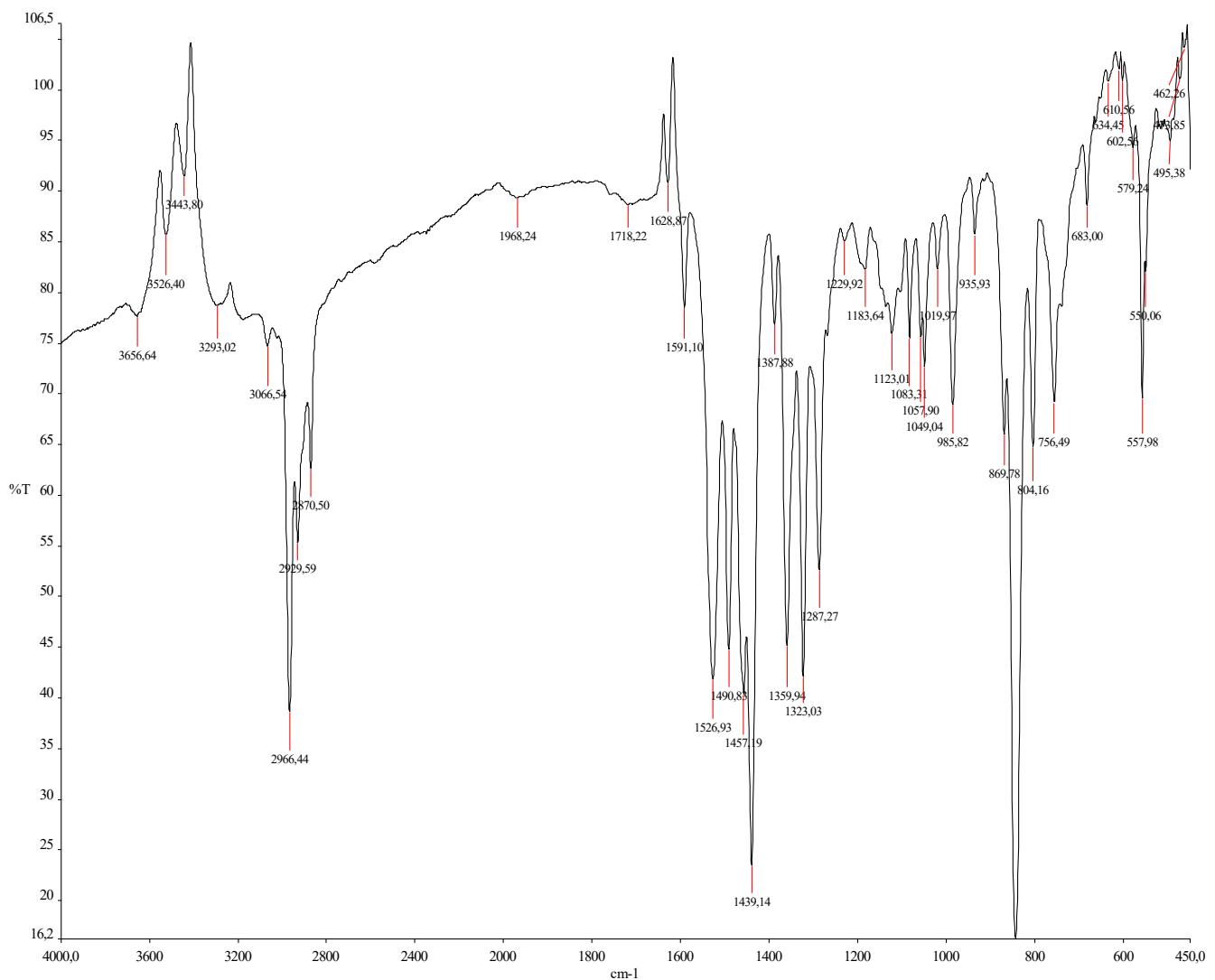


Fig. S20. FT-IR spectrum (KBr) of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (**2e**)

Part 3 – Mass spectra

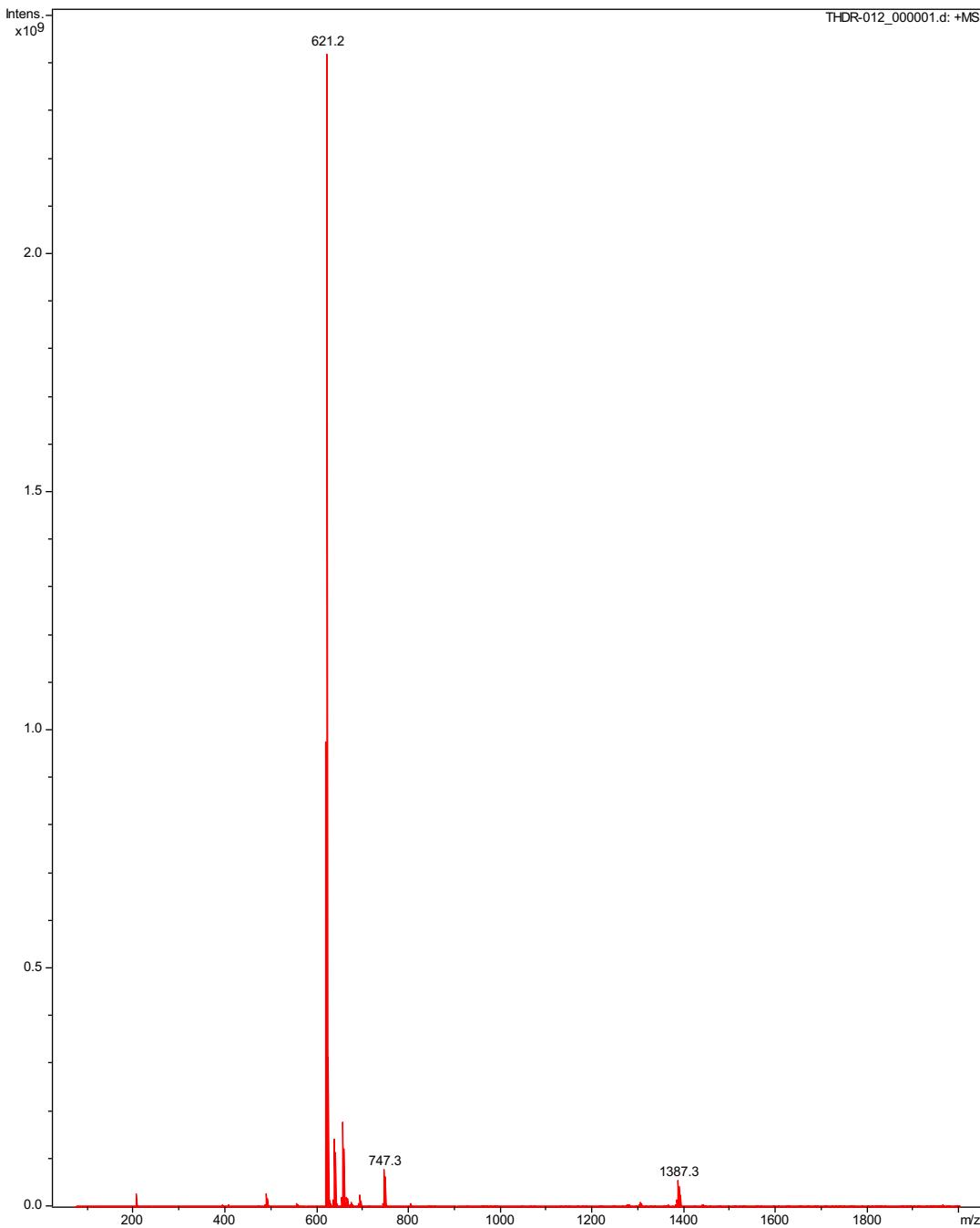


Fig. S21. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (**2a**)

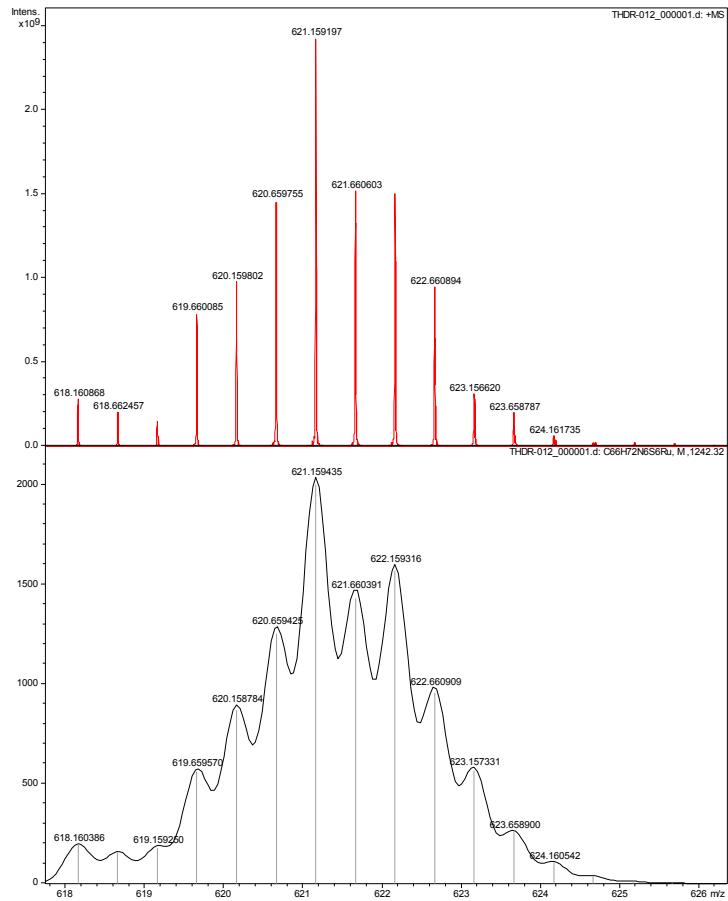


Fig. S22. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)

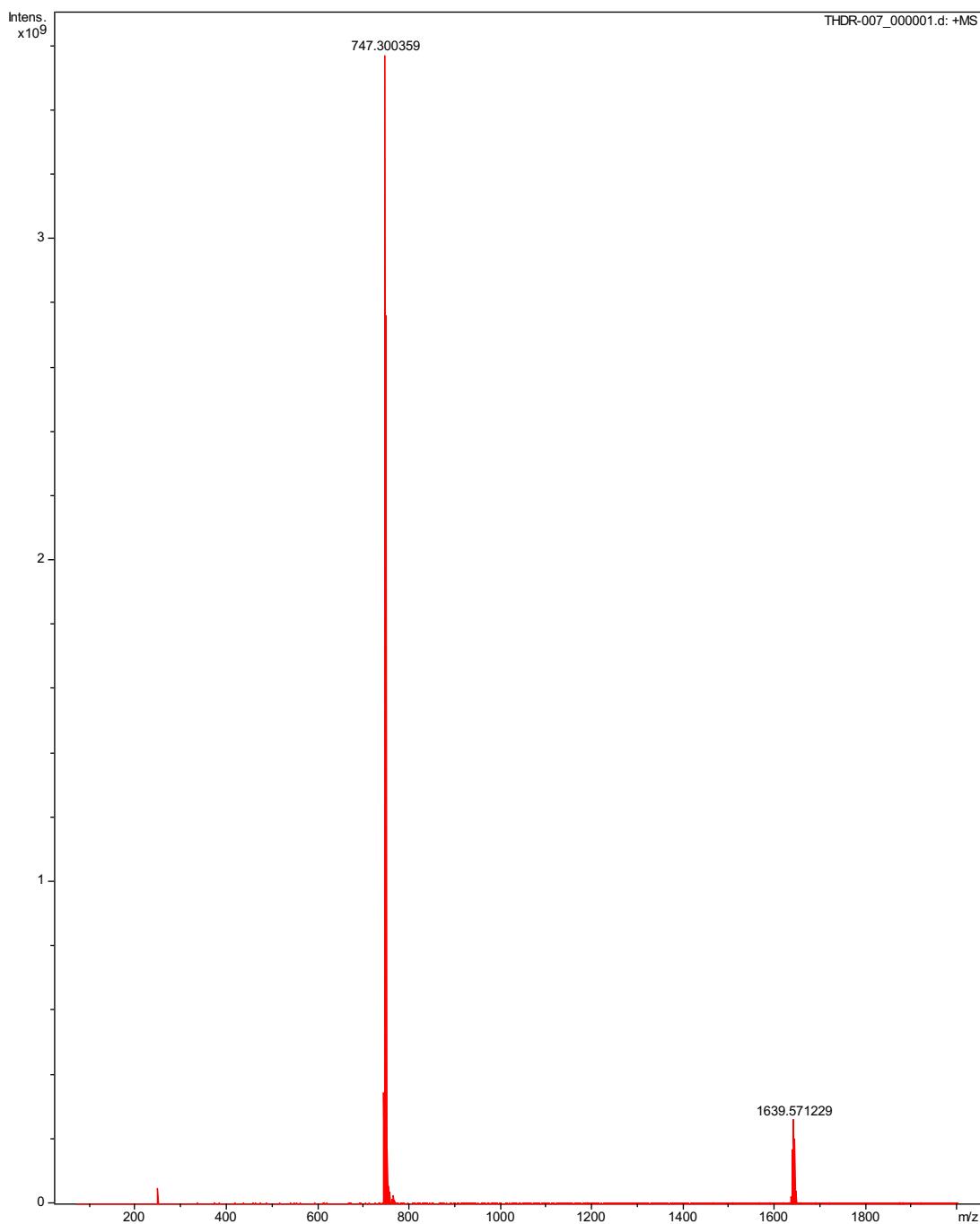


Fig. S23. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (**2b**)

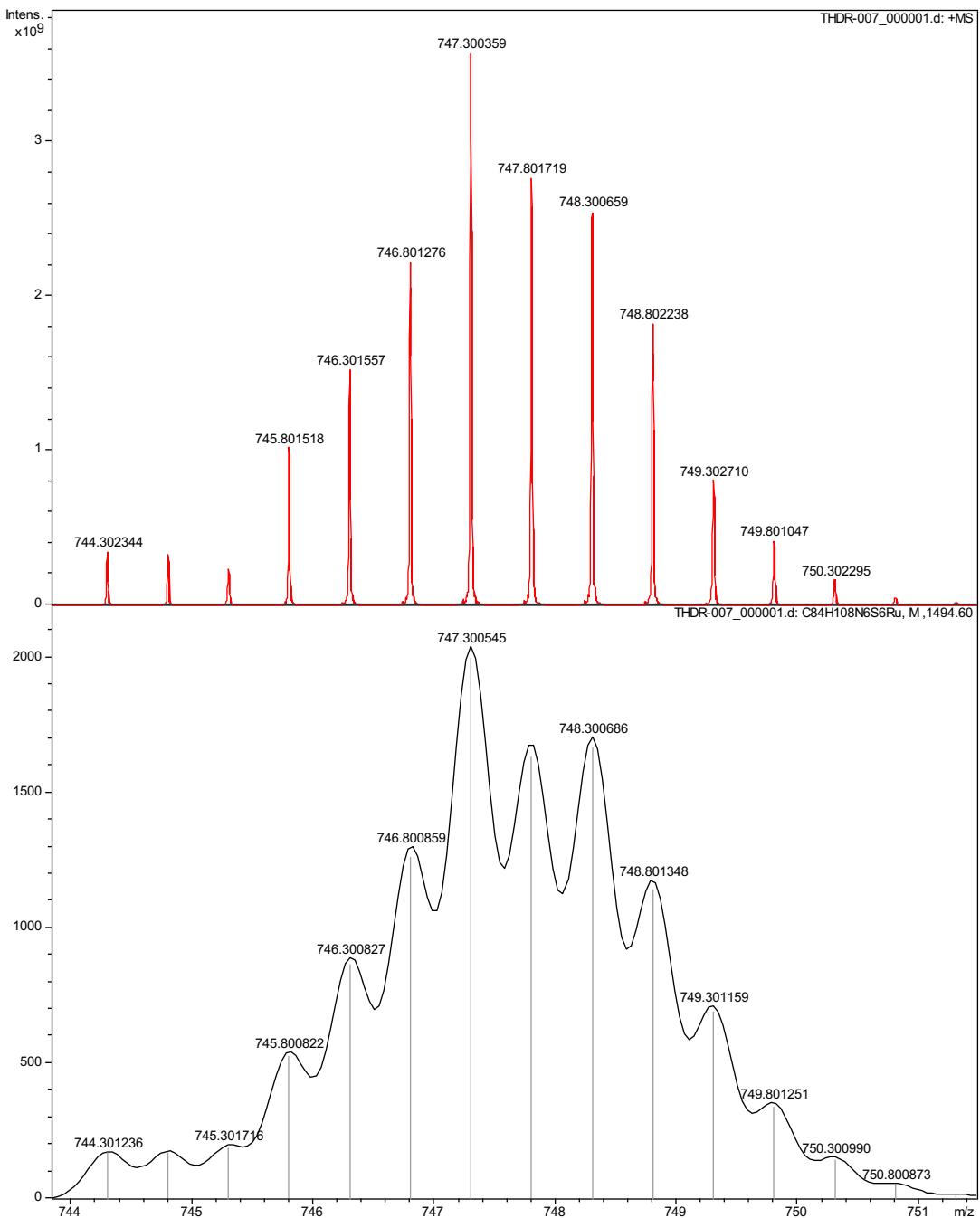


Fig. S24. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)

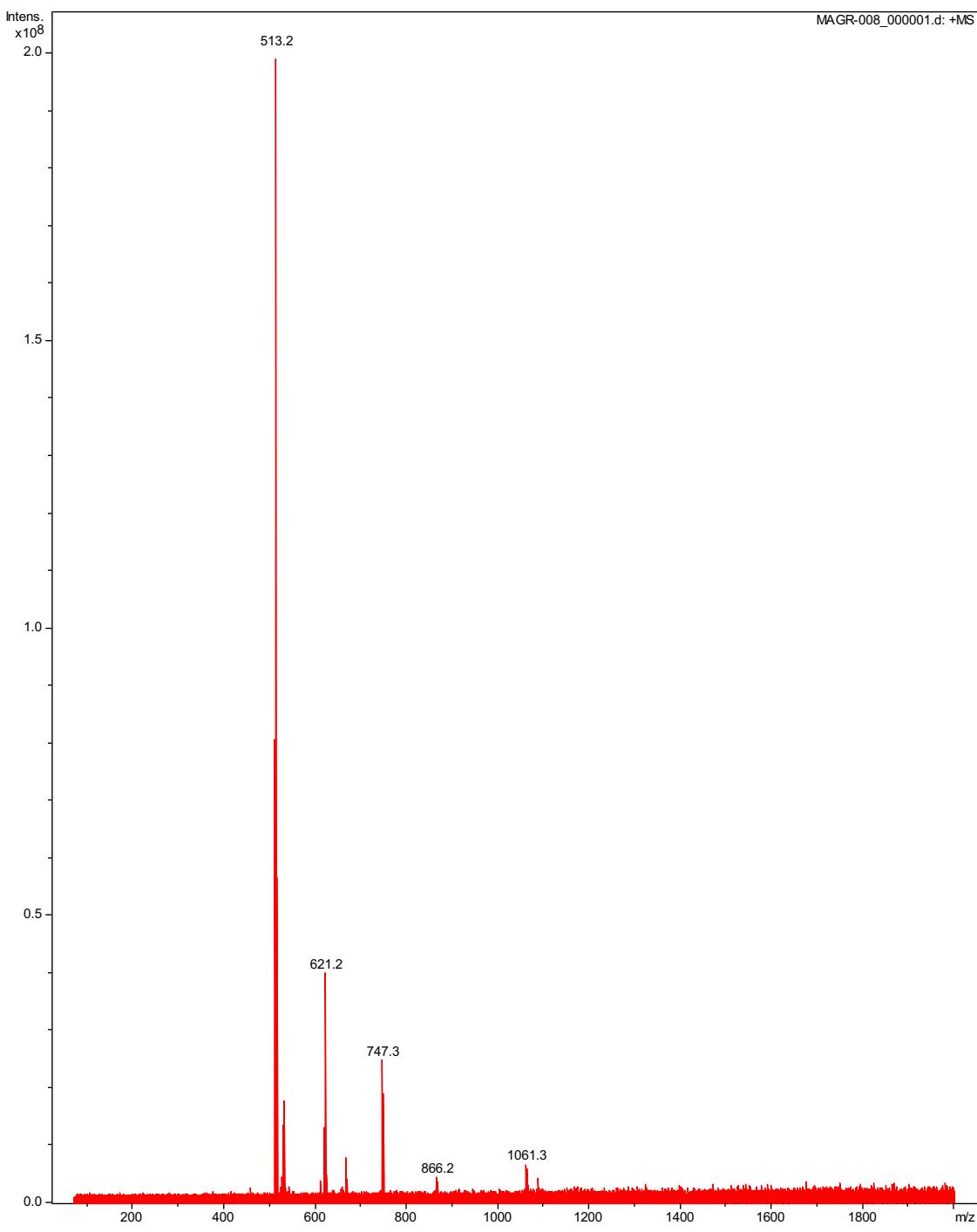


Fig. S25. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**)

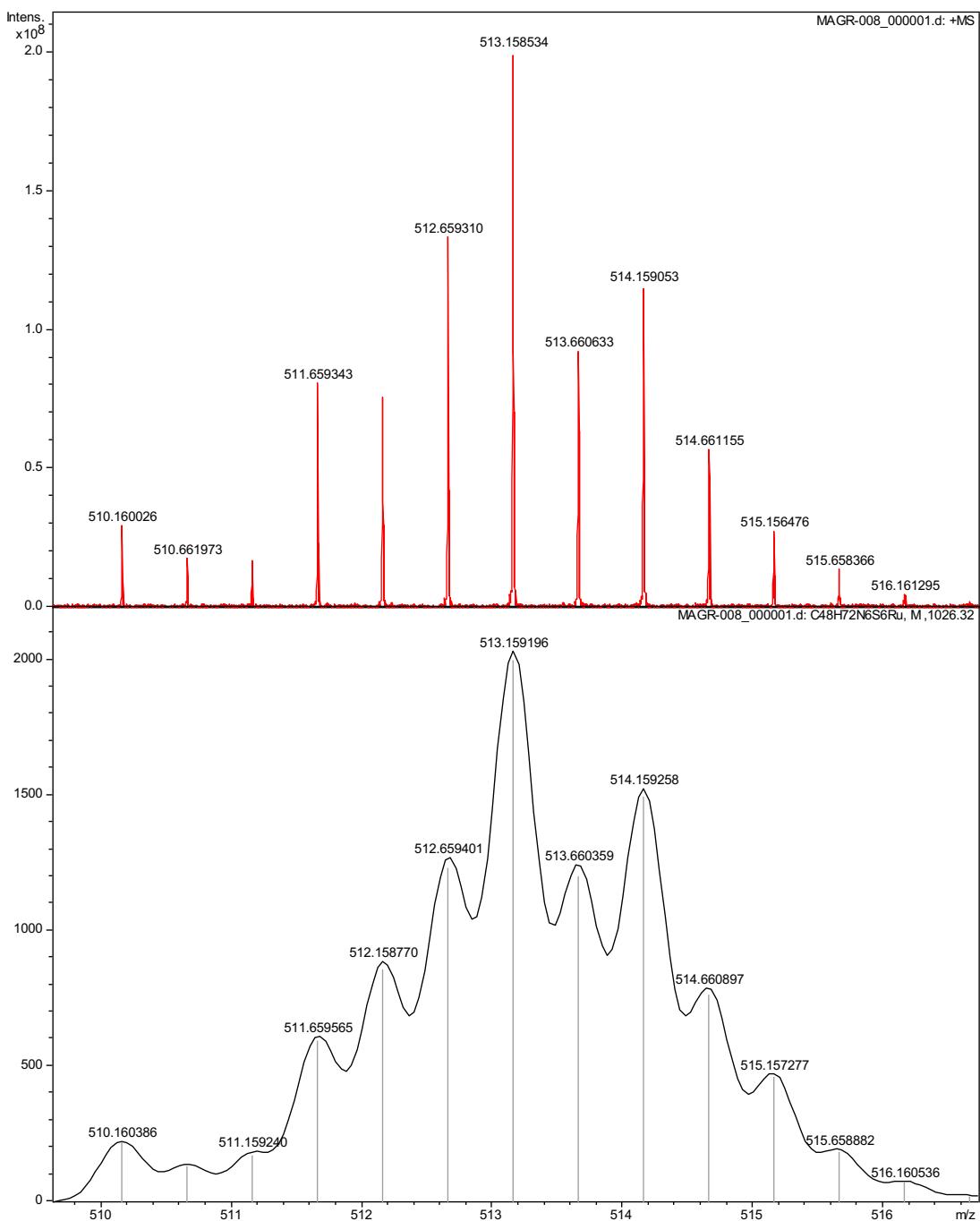


Fig. S26. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)

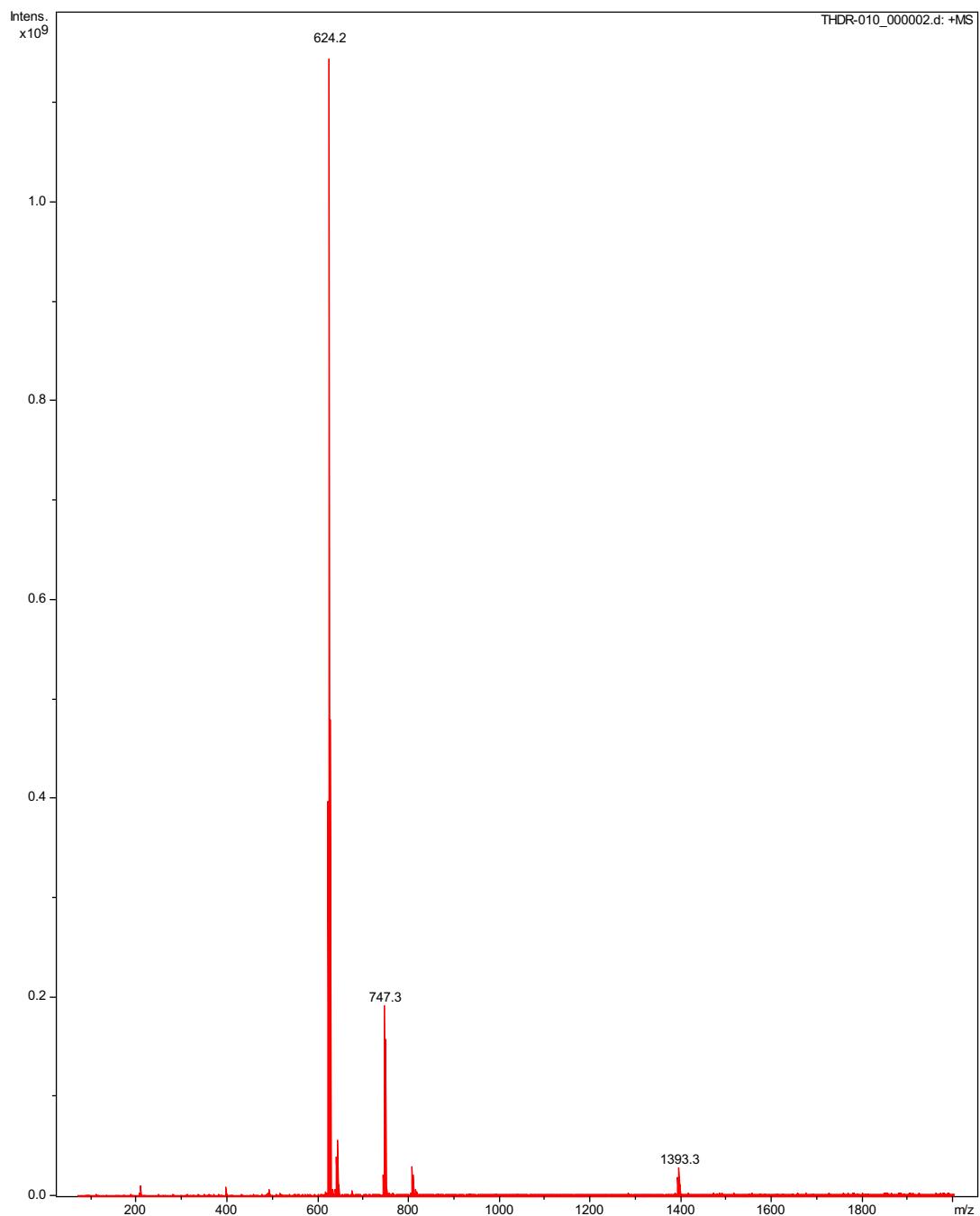


Fig. S27. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2d**)

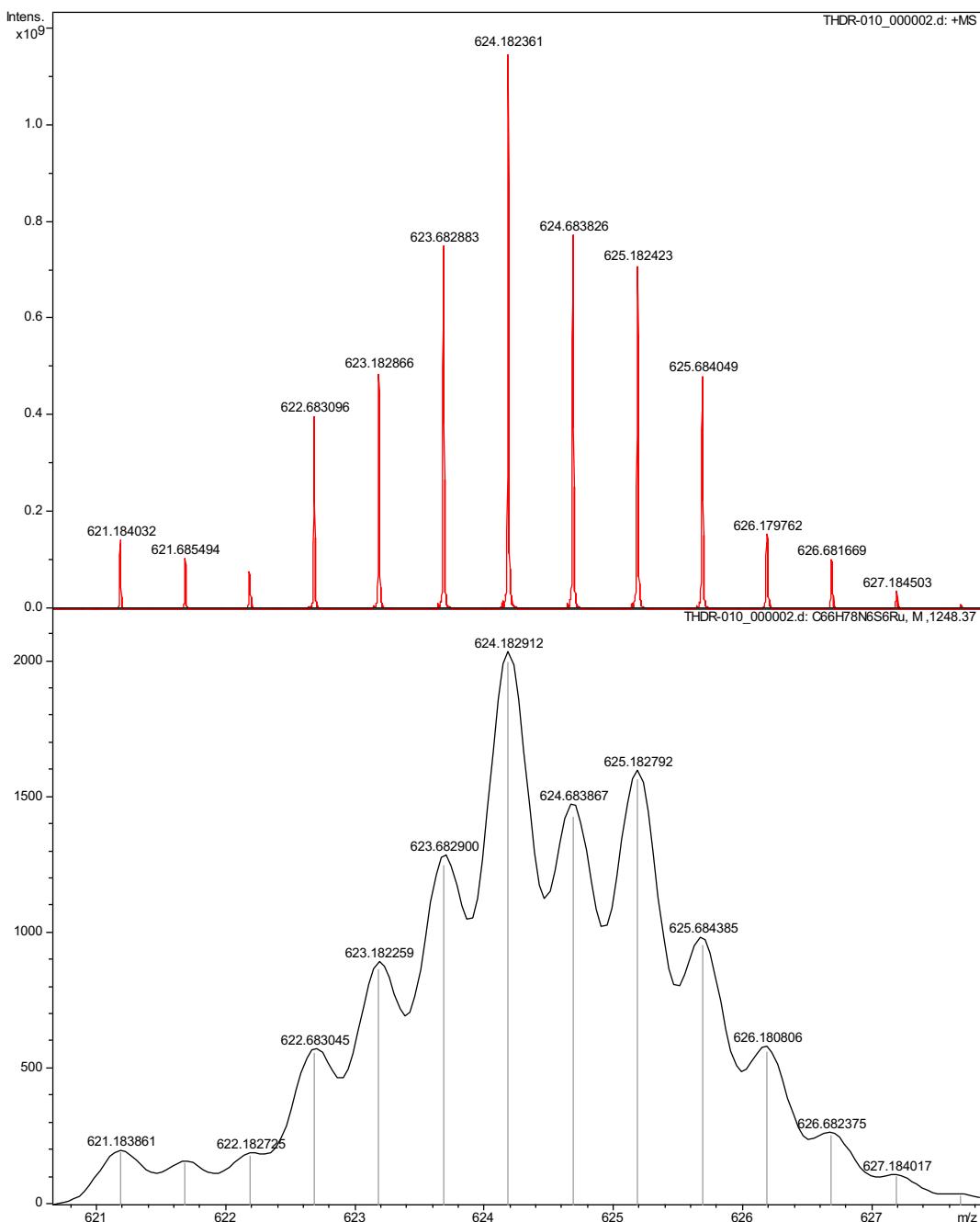


Fig. S28. Isotope profiles of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)

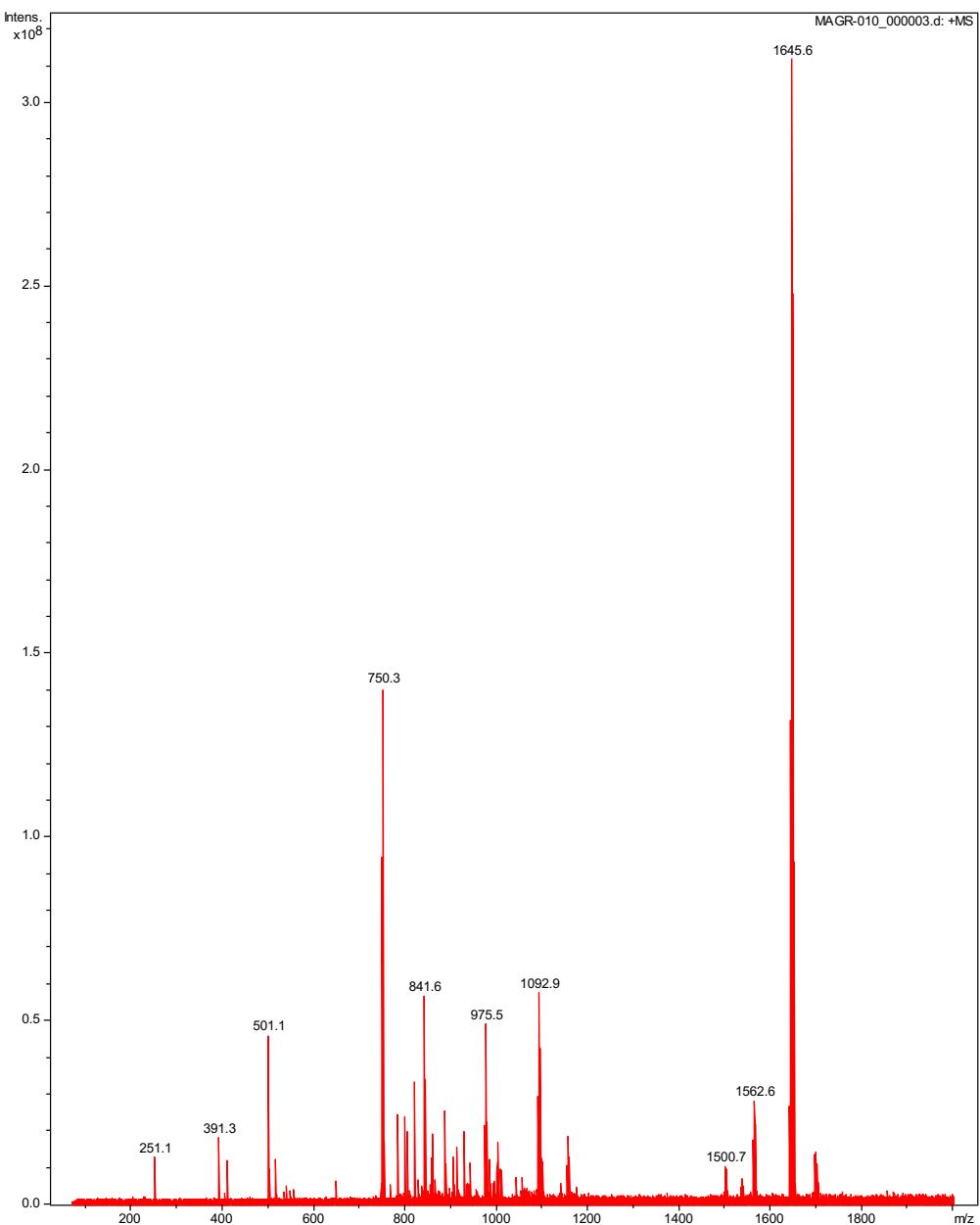


Fig. S29. ESI-MS spectrum of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIDip})_3](\text{PF}_6)_2$ (**2e**)

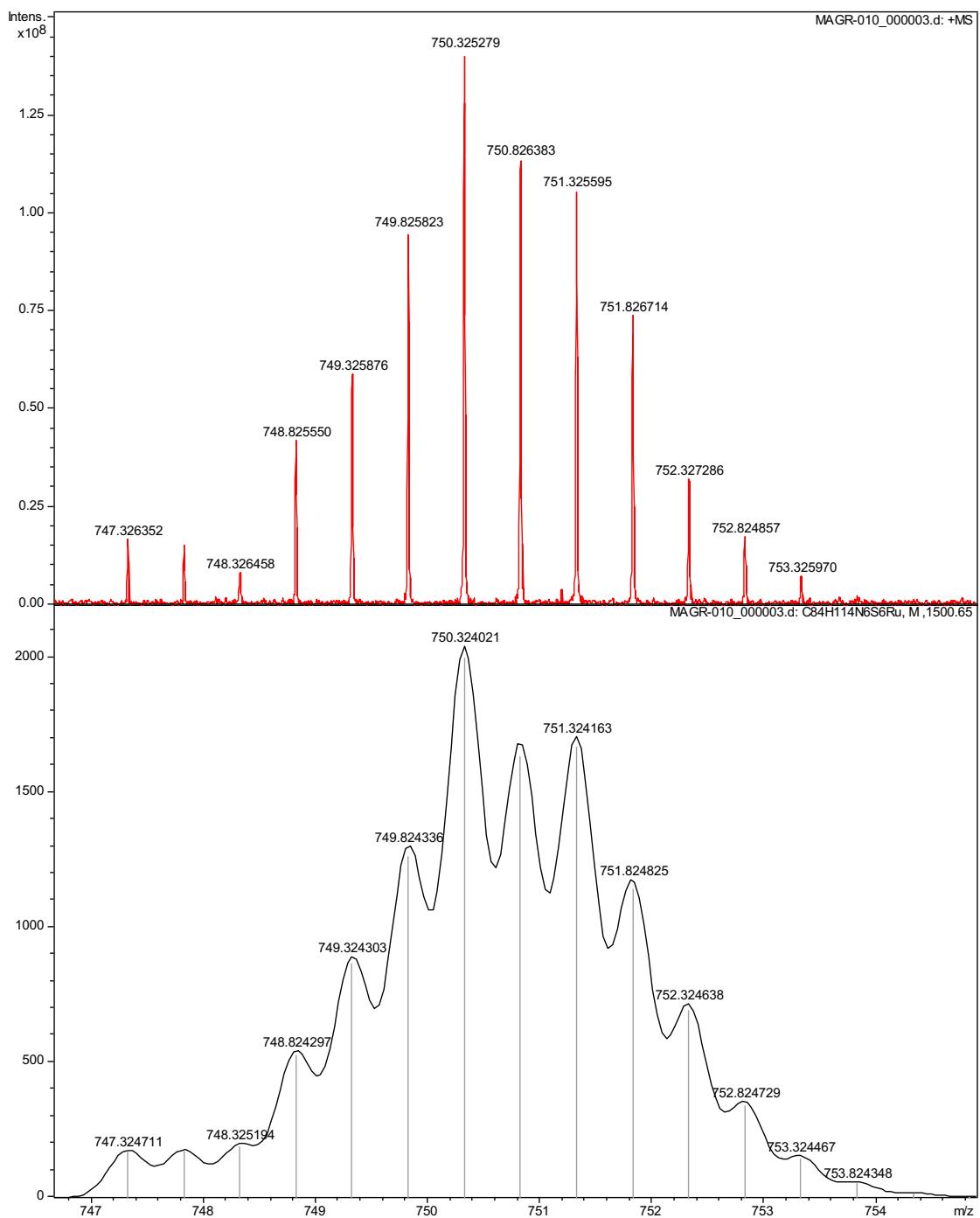


Fig. S30. Isotope profiles of $[Ru(S_2C \cdot SIDip)_3]^{2+}$ obtained by ESI-MS (in red) and simulated isotope patterns of the corresponding ion (in black)

Part 4 – Cyclic voltammetry

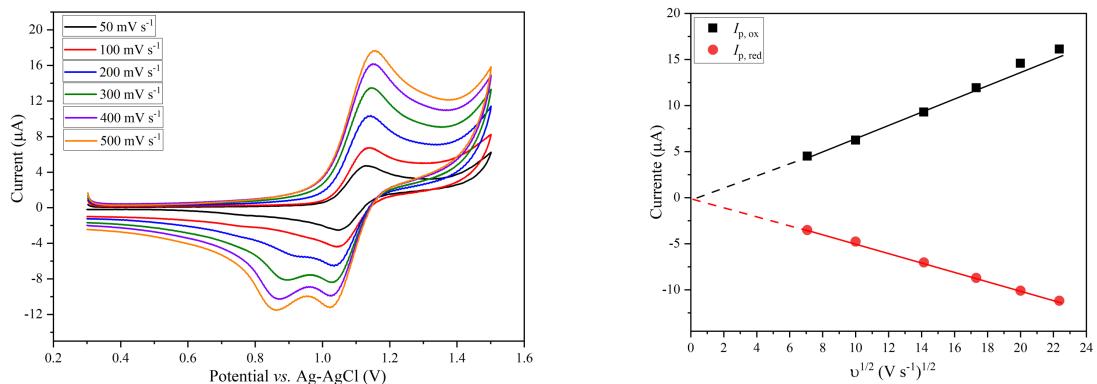


Fig. S31. *Left* - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IMes})_3](\text{PF}_6)_2$ (**2a**) in CH_2Cl_2 at 25 °C, scanning anodically at scan rates of 50, 100, 200, 300, 400 and 500 mV s⁻¹ ([Ru] = 1.0 mM, [*n*-Bu₄NPF₆] = 0.1 M). *Right* - Current (*I*) of the anodic (*I*_{p,ox}) and cathodic (*I*_{p,red}) processes vs. square root of the potential scan rate (ν).

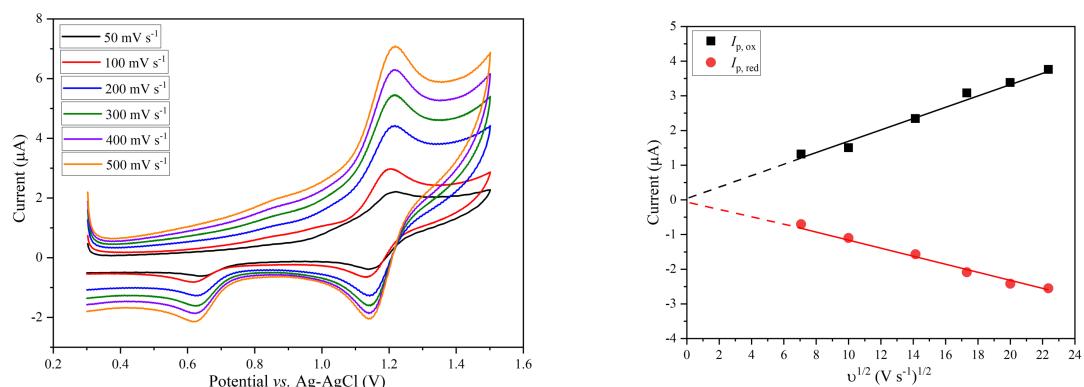


Fig. S32. *Left* - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{IDip})_3](\text{PF}_6)_2$ (**2b**) in CH_2Cl_2 at 25 °C, scanning anodically at scan rates of 50, 100, 200, 300, 400 and 500 mV s⁻¹ ([Ru] = 1.0 mM, [*n*-Bu₄NPF₆] = 0.1 M). *Right* - Current (*I*) of the anodic (*I*_{p,ox}) and cathodic (*I*_{p,red}) processes vs. square root of the potential scan rate (ν).

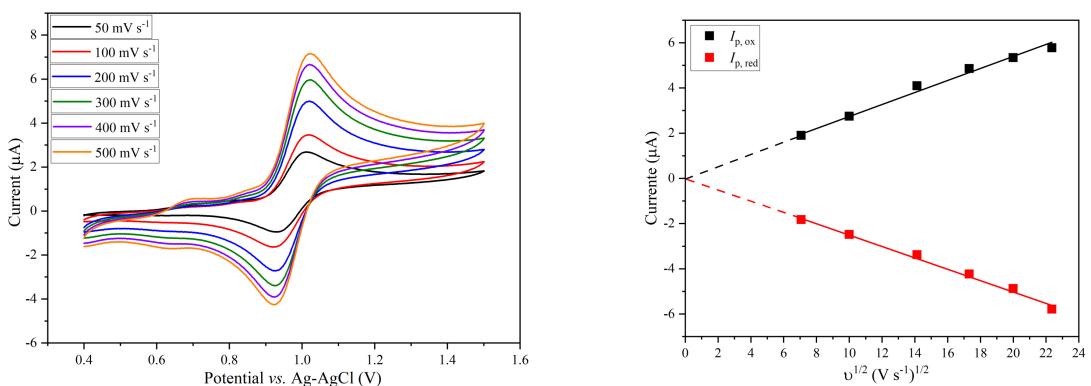


Fig. S33. *Left* - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{ICy})_3](\text{PF}_6)_2$ (**2c**) in CH_2Cl_2 at 25 °C, scanning anodically at scan rates of 50, 100, 200, 300, 400 and 500 mV s^{-1} ($[\text{Ru}] = 1.0 \text{ mM}$, $[n\text{-Bu}_4\text{NPF}_6] = 0.1 \text{ M}$). *Right* - Current (I) of the anodic ($I_{p,\text{ox}}$) and cathodic ($I_{p,\text{red}}$) processes vs. square root of the potential scan rate (v).

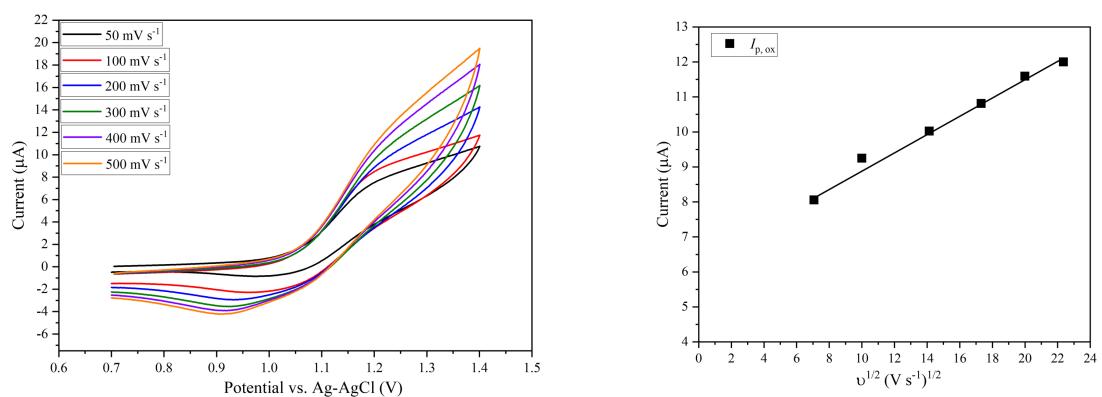


Fig. S34. *Left* - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2d**) in CH_2Cl_2 at 25 °C, scanning anodically at scan rates of 50, 100, 200, 300, 400 and 500 mV s^{-1} ($[\text{Ru}] = 1.0 \text{ mM}$, $[n\text{-Bu}_4\text{NPF}_6] = 0.1 \text{ M}$). *Right* - Current (I) of the anodic ($I_{p,\text{ox}}$) and cathodic ($I_{p,\text{red}}$) processes vs. square root of the potential scan rate (v).

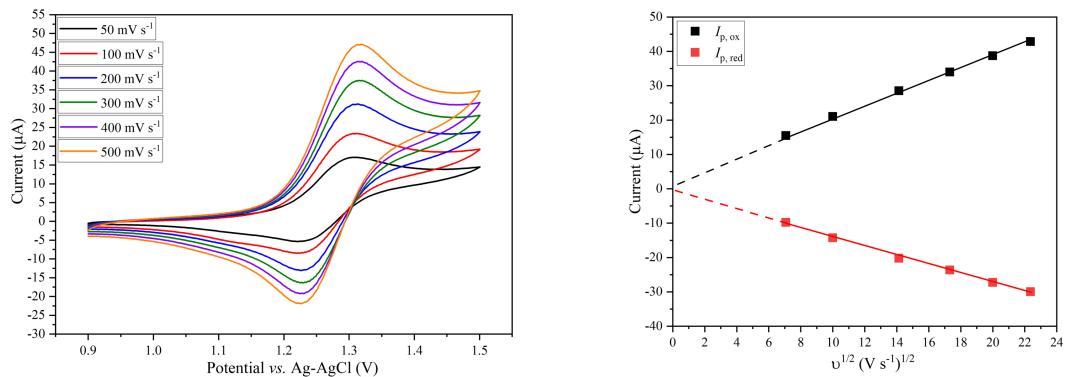


Fig. S35. *Left* - Cyclic voltammograms of $[\text{Ru}(\text{S}_2\text{C}\cdot\text{SIMes})_3](\text{PF}_6)_2$ (**2e**) in CH_2Cl_2 at 25 °C, scanning anodically at scan rates of 50, 100, 200, 300, 400 and 500 mV s^{-1} ($[\text{Ru}] = 1.0 \text{ mM}$, $[n\text{-Bu}_4\text{NPF}_6] = 0.1 \text{ M}$). *Right* - Current (I) of the anodic ($I_{\text{p,ox}}$) and cathodic ($I_{\text{p,red}}$) processes vs. square root of the potential scan rate (v).

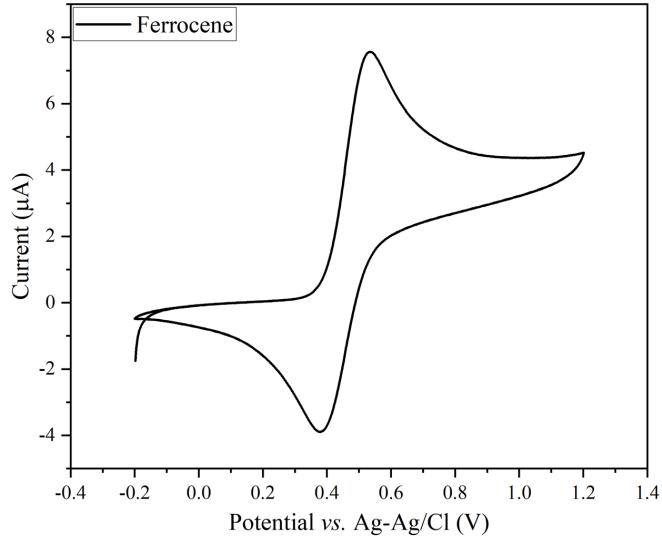


Fig. S36. Cyclic voltammogram of ferrocene in CH_2Cl_2 at 25 °C, scanning anodically from -0.2 to 1.2 V at scan rate of 100 mV s^{-1} ($[\text{Fc}] = 1.0 \text{ mM}$, $[n\text{-Bu}_4\text{NPF}_6] = 0.1 \text{ M}$).