Supporting information

Cyclobutadiene Arene Complexes of Rhodium and Iridium

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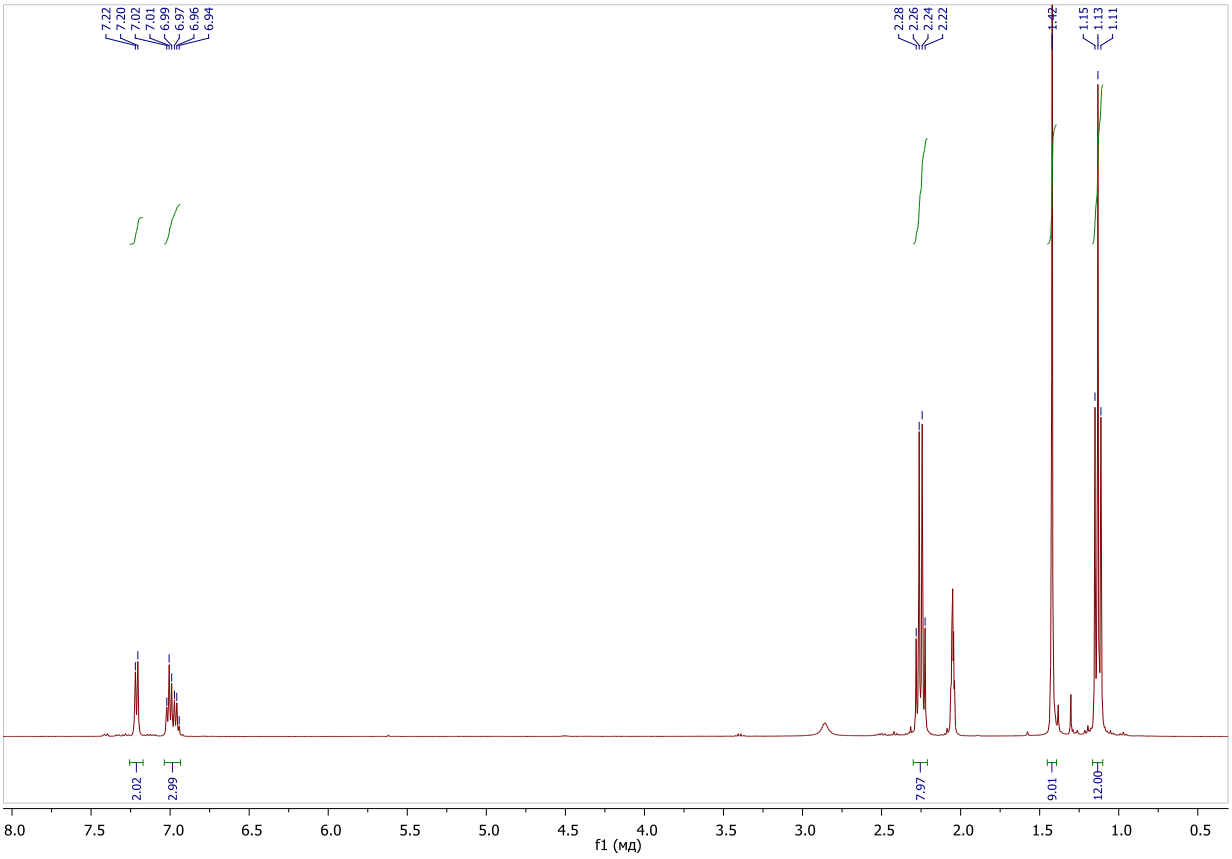
Details of X-ray diffraction experiments. Crystals of [**1d**]BF_4 ($C_{25}H_{38}BF_4O_2Rh$, M = 560.27) are triclinic, space group P-1, at 120 K: a = 8.8170(7), b = 8.9463(7), c = 18.1443(14) Å, α = 95.973(2), β = 95.706(2), γ = 110.448(2)°, V = 1319.52(18) $Å^3$, Z = 2, d_{calc} = 1.410 g cm^{-3}, μ(MoKα) = 6.94 cm^{-1}, F(000) = 580. Crystals of [**2**]PO_2F_2 ($C_{16}H_{26}F_2O_2PRh$, M = 422.25) are orthorhombic, space group $P2_12_12_1$, at 100 K: a = 8.3540(13), b = 9.2101(15), c = 21.622(3) Å, V = 1663.6(5) $Å^3$, Z = 4, d_{calc} = 1.686 g cm^{-3}, μ(MoKα) = 11.46 cm^{-1}, F(000) = 864. Intensities of 13855 and 19126 reflections for [**1d**]BF_4 and [**2**]PO_2F_2, respectively, were measured with Bruker APEX2 and APEX2 DUO diffractometers both using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). 5765 and 4001 independent reflections [R_{int} 0.0520 and 0.0569] were used in further refinement for [**1d**]BF_4 and [**2**]PO_2F_2, respectively. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation in riding model. For [**1d**]BF_4 the refinement converged to wR_2 = 0.0914 and GOF = 1.021 for all the independent reflections (R_1 = 0.0372 was calculated against F for 4921 observed reflections with I>2σ(I)). For [**2**]PO_2F_2 the refinement converged to wR_2 = 0.1589 and GOF = 1.093 for all the independent reflections (R_1 = 0.0578 was calculated against F for 3512 observed reflections with I>2σ(I)). All calculations were performed using the SHELXTL PLUS 5.0 software (G.M. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112–122.). CCDC 1473047 and 1473048 contain the supplementary crystallographic data for [**1d**]BF_4 and [**2**]PO_2F_2; those can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ^{1}H and ^{13}C NMR spectra of $[(C_4Et_4)Rh(\text{tert-butylbenzene})]PF_6$ ([**1b**]PF_6) in $(CD_3)_2CO$.



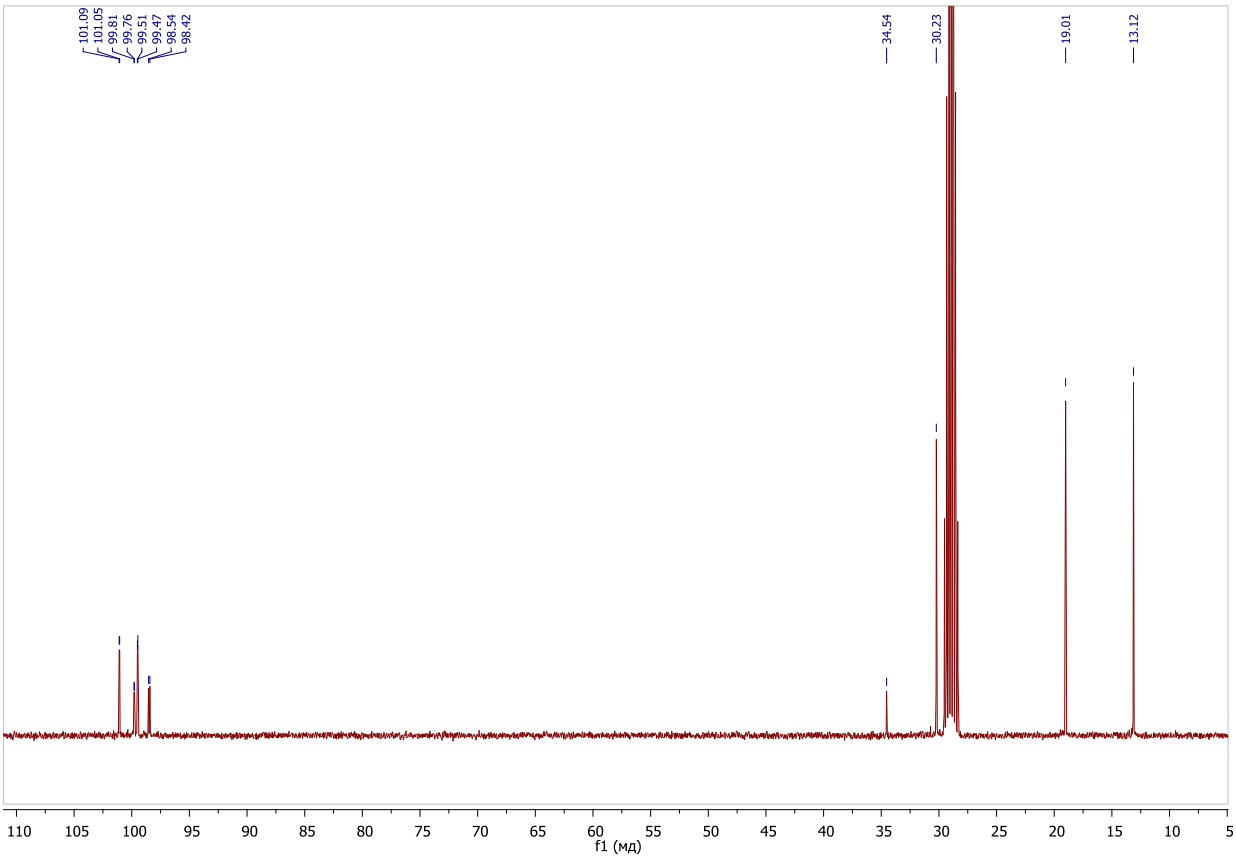
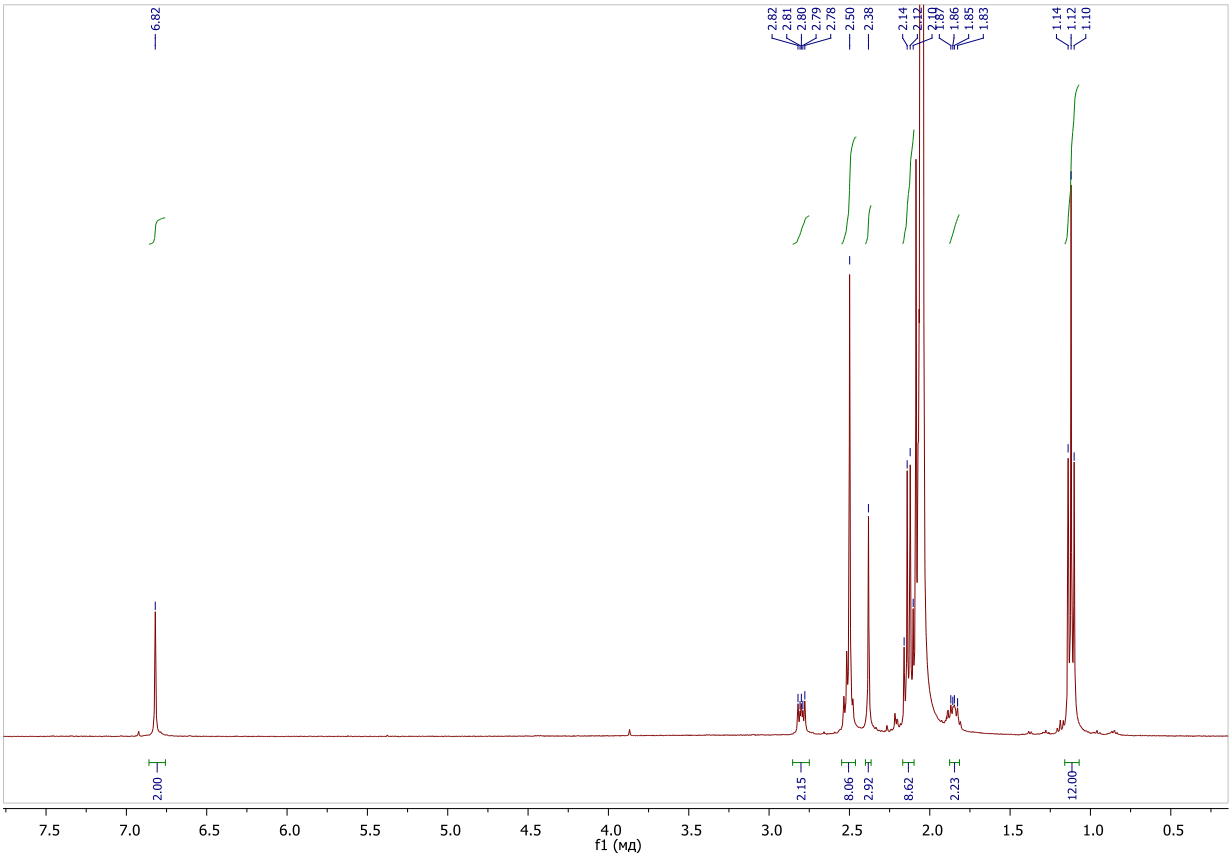


Figure S2. ^{1}H and ^{13}C NMR spectra and [(C_4Et_4)Rh(3-mesityl-propionic acid)]PF_6 ([**1d**]PF_6) in $(CD_3)_2CO$.



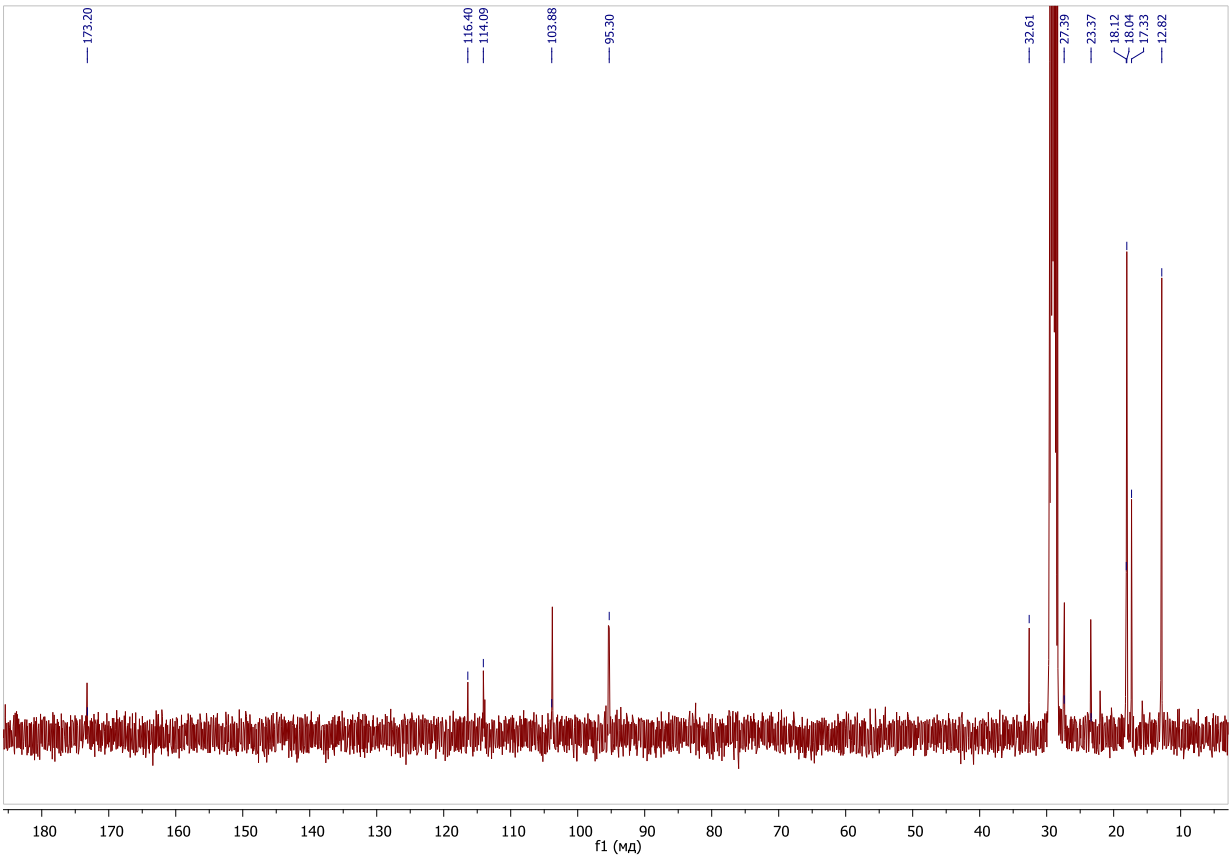
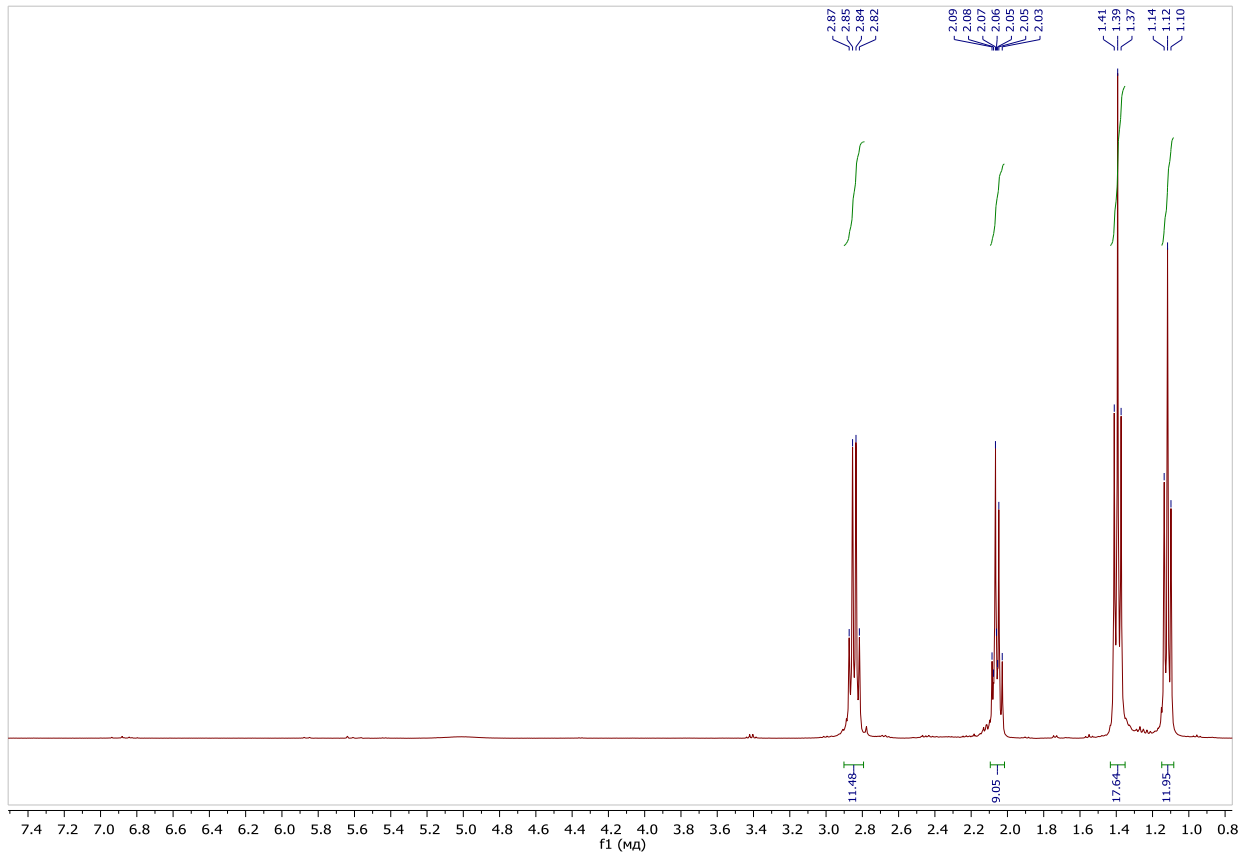


Figure S3. ^{1}H and ^{13}C NMR spectra of $[(C_4Et_4)Rh(C_6Et_6)]PF_6$ ([**1e**]PF_6) in $(CD_3)_2CO$.



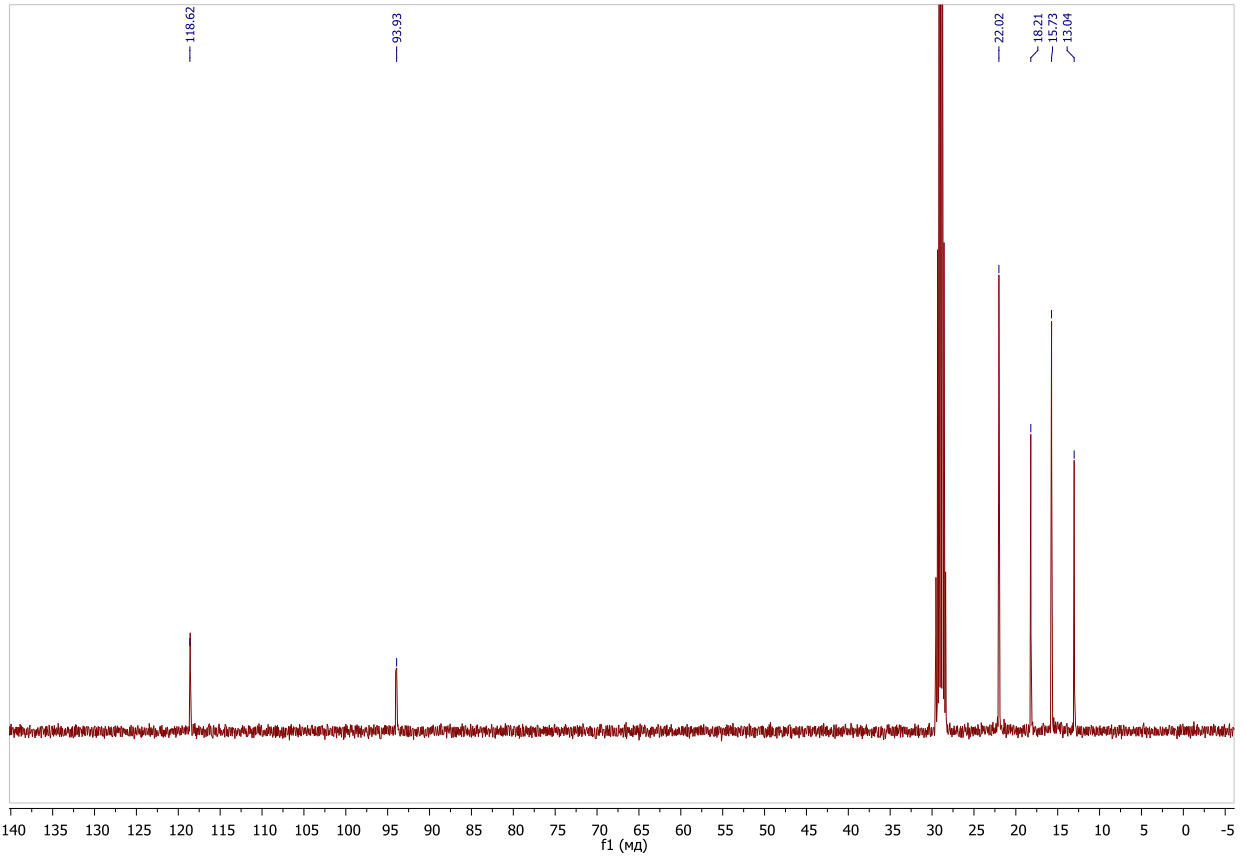
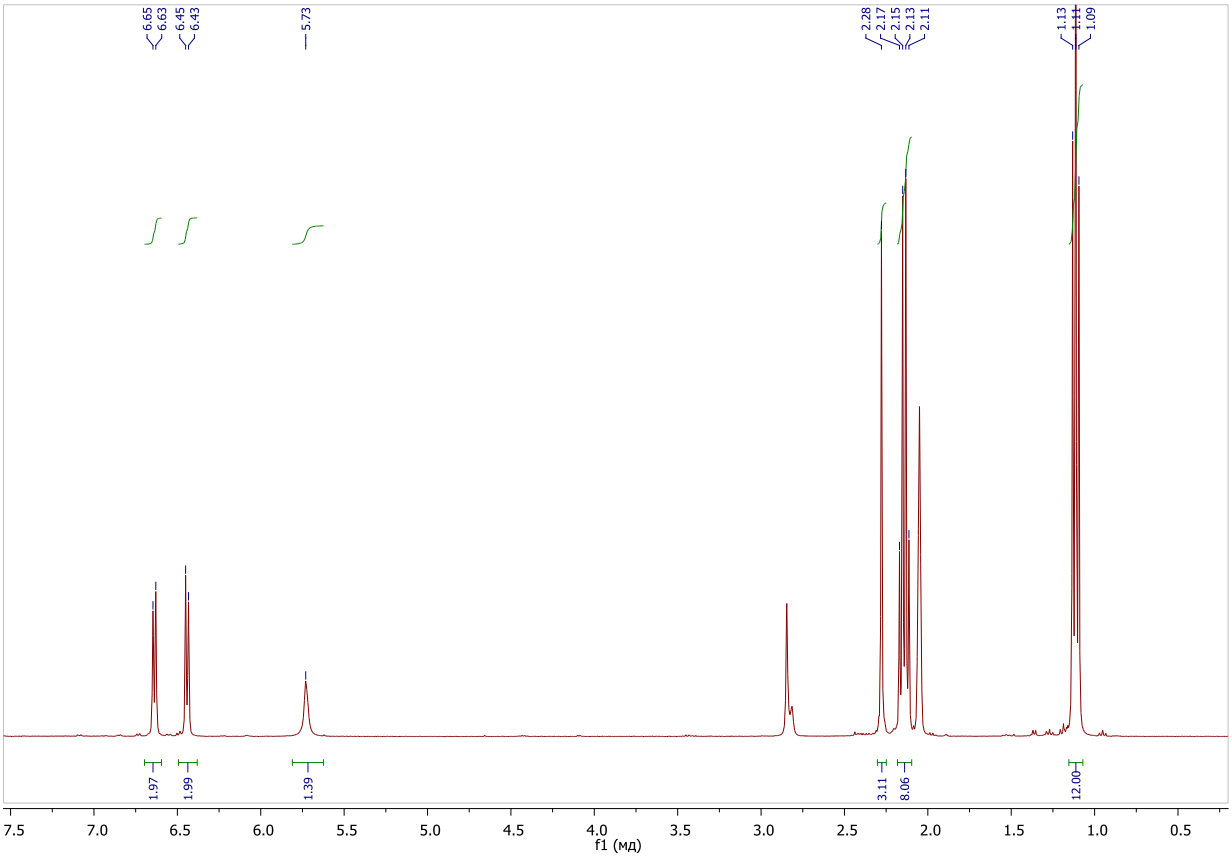


Figure S4. ^{1}H and ^{13}C NMR spectra of $[(C_4Et_4)Rh(p\text{-methylaniline})]PF_6$ ([**1f**]PF_6) in $(CD_3)_2CO$.



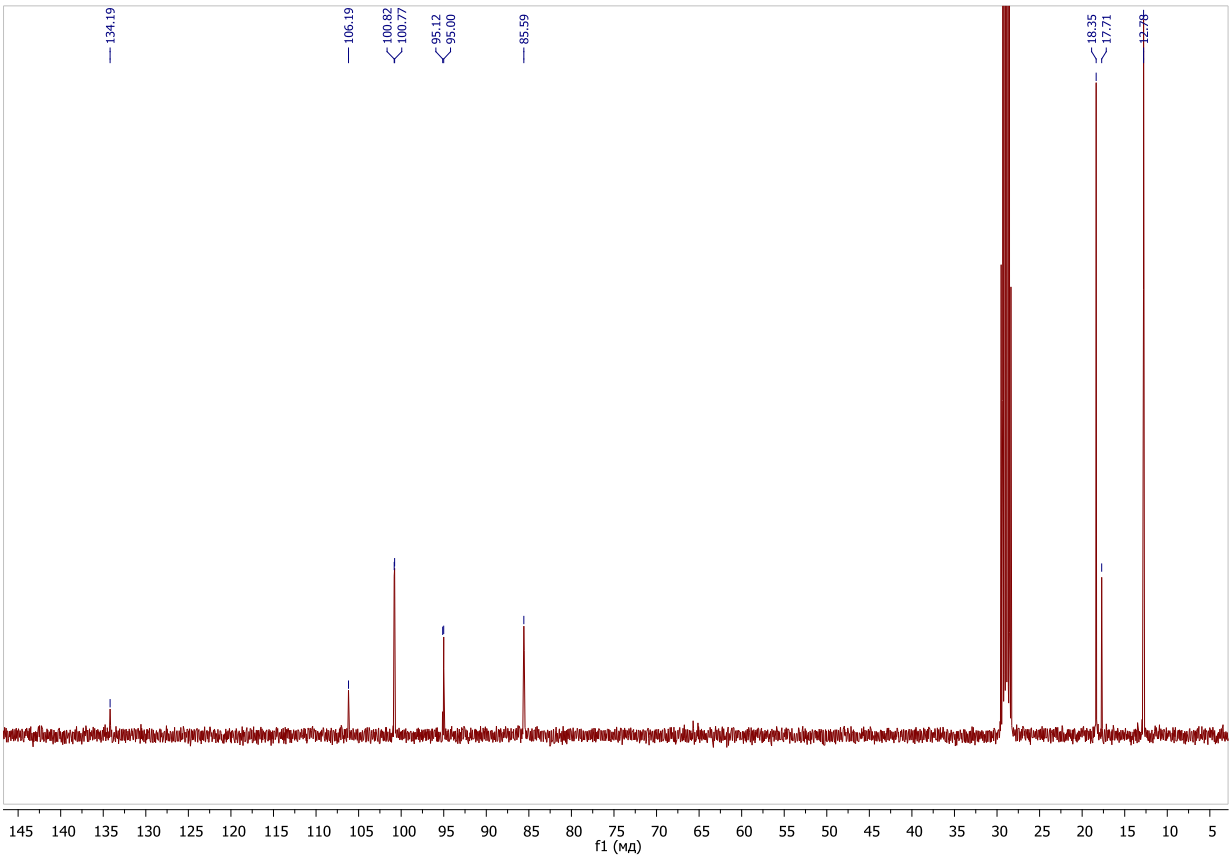
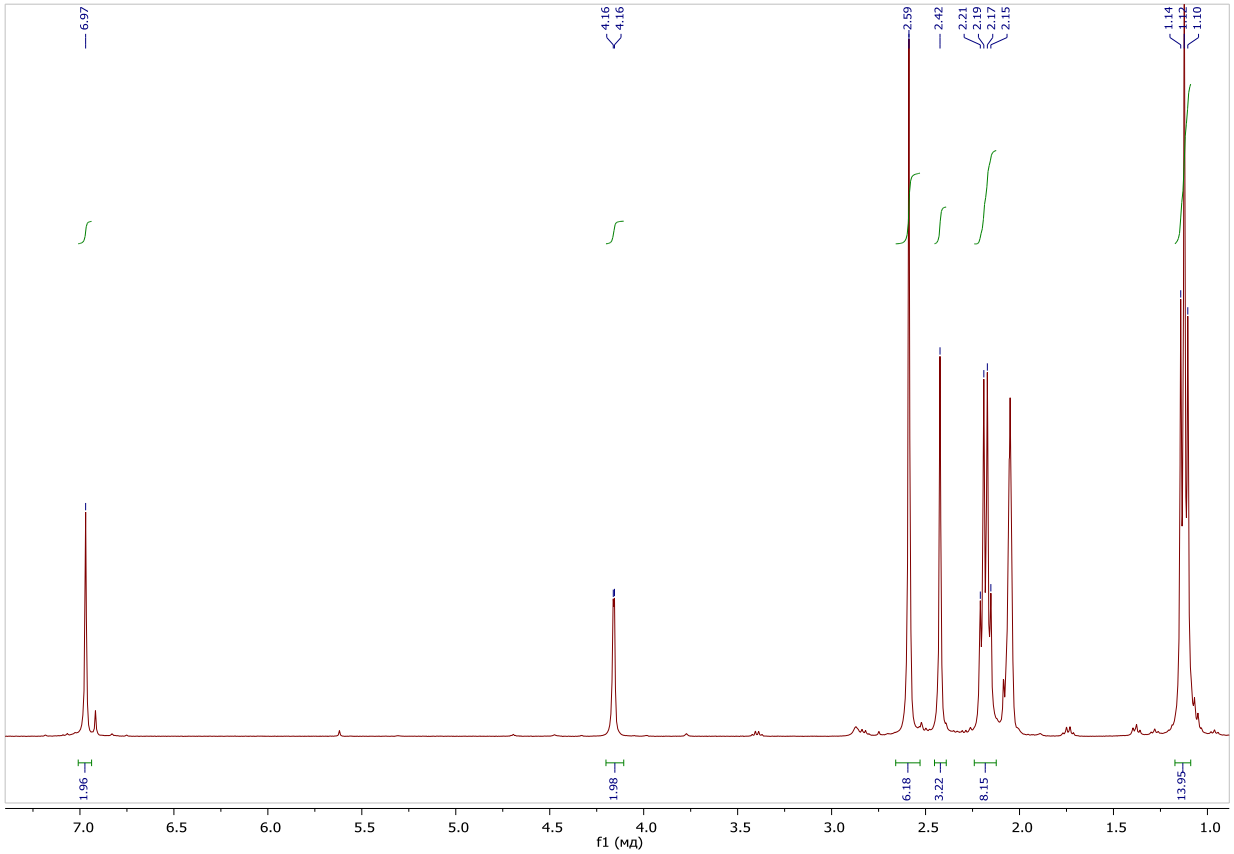


Figure S5. ^{1}H and ^{13}C NMR spectra of $[(C_4Et_4)Rh(2\text{-mesityl-acetonitrile})]PF_6$ ([**1g**]PF_6) in $(CD_3)_2CO$.



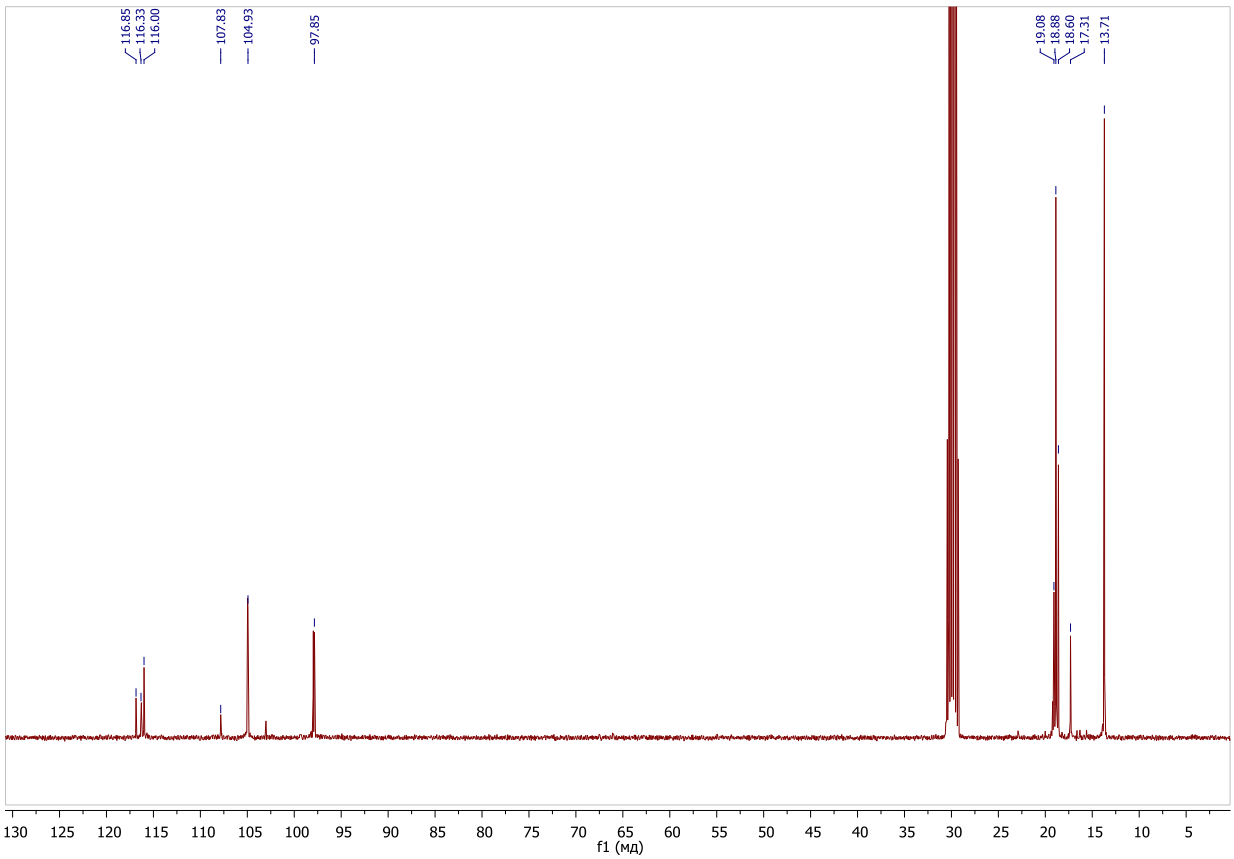


Figure S6. ^{1}H and ^{13}C NMR spectra of $[(coe)_2Rh(p\text{-xylene})]PF_6$ ([**3**]PF_6) in CD_3NO_2.

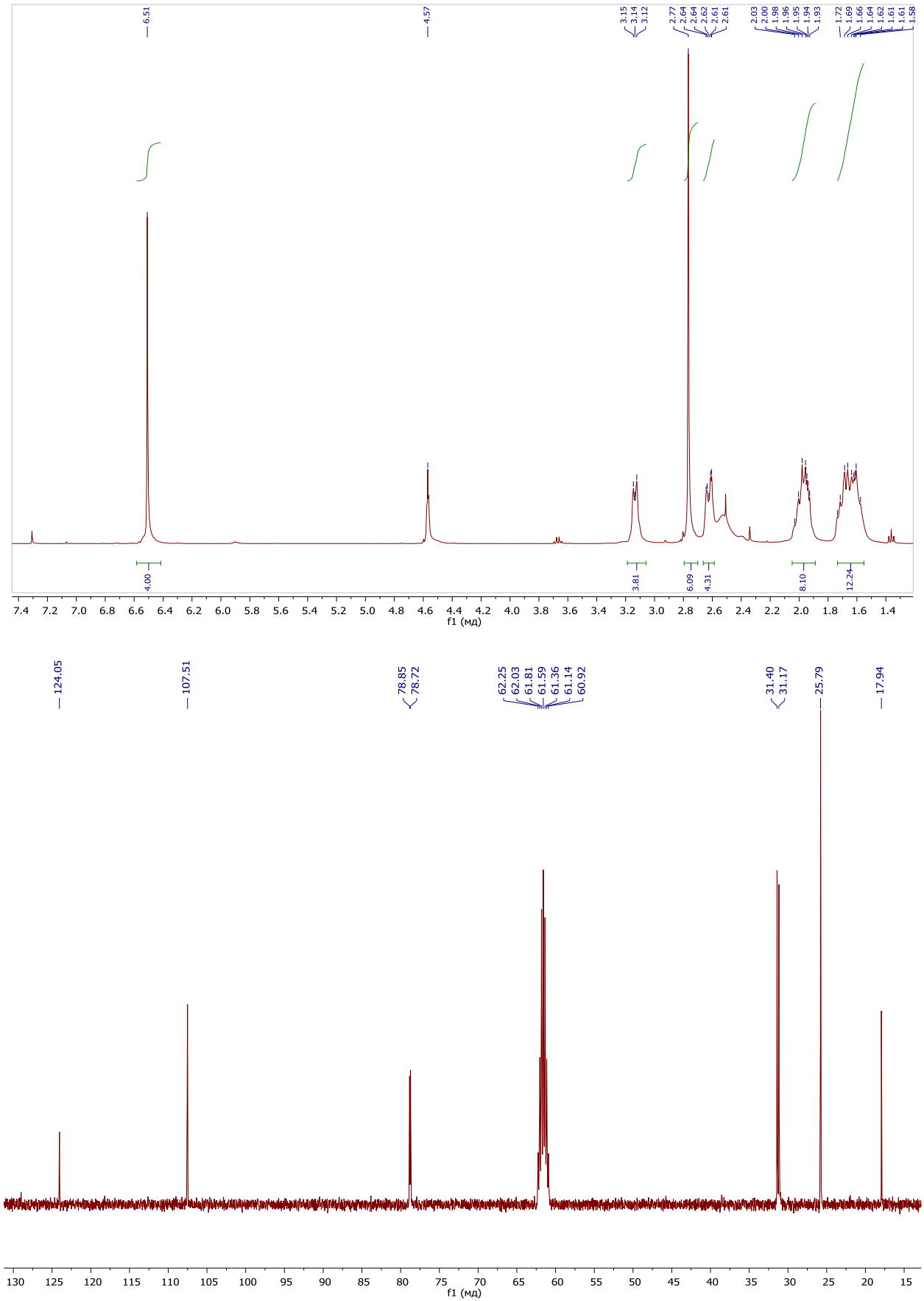
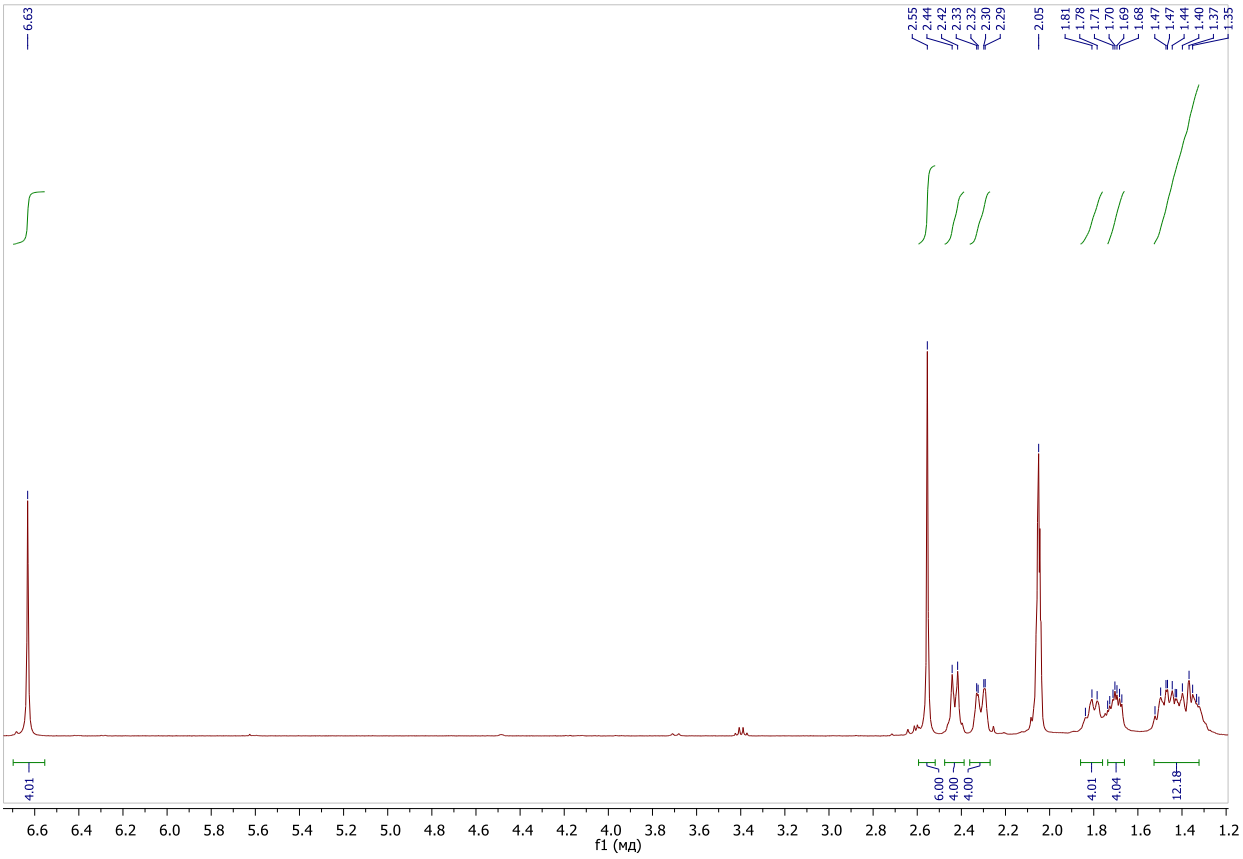


Figure S7. ^{1}H and ^{13}C NMR spectra of $[(coe)_2Ir(p\text{-xylene})]PF_6$ ([**4**]PF_6) in $(CD_3)_2CO$.



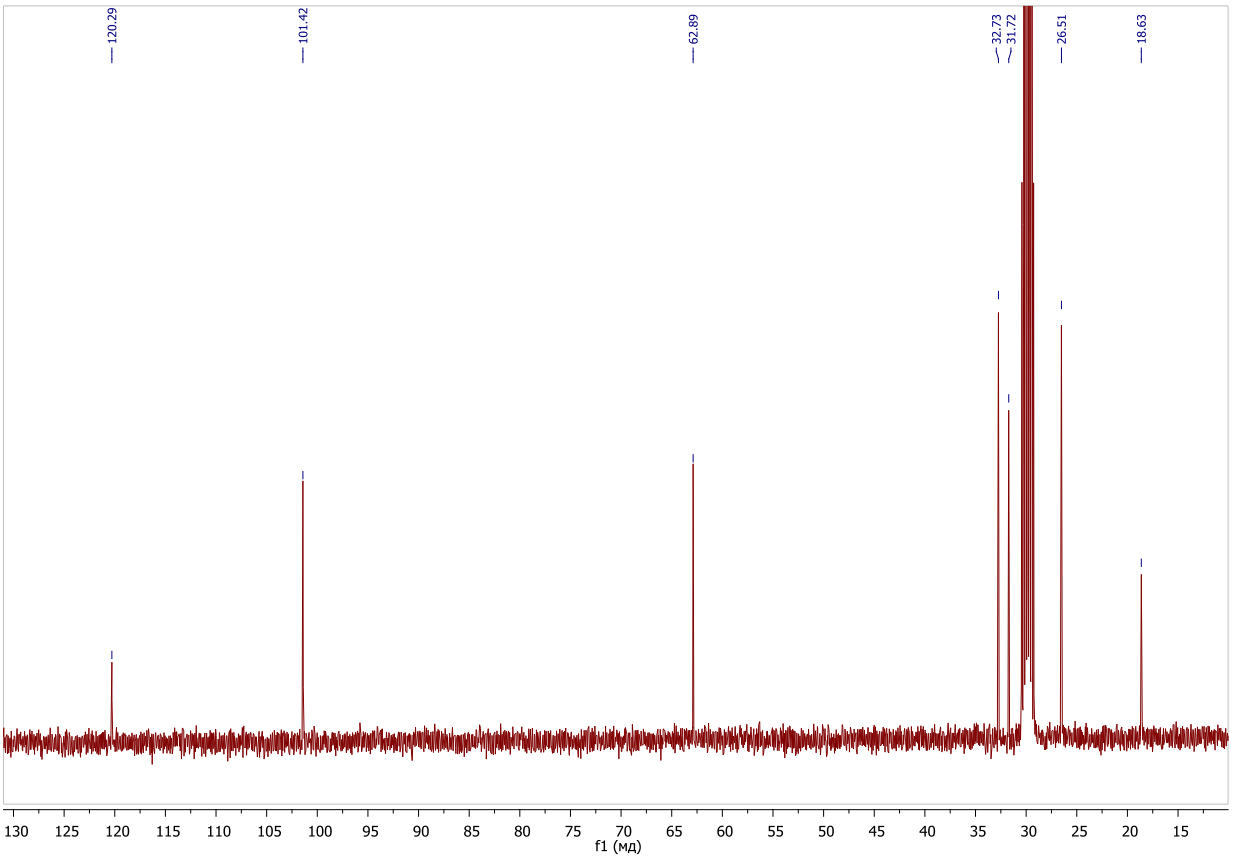
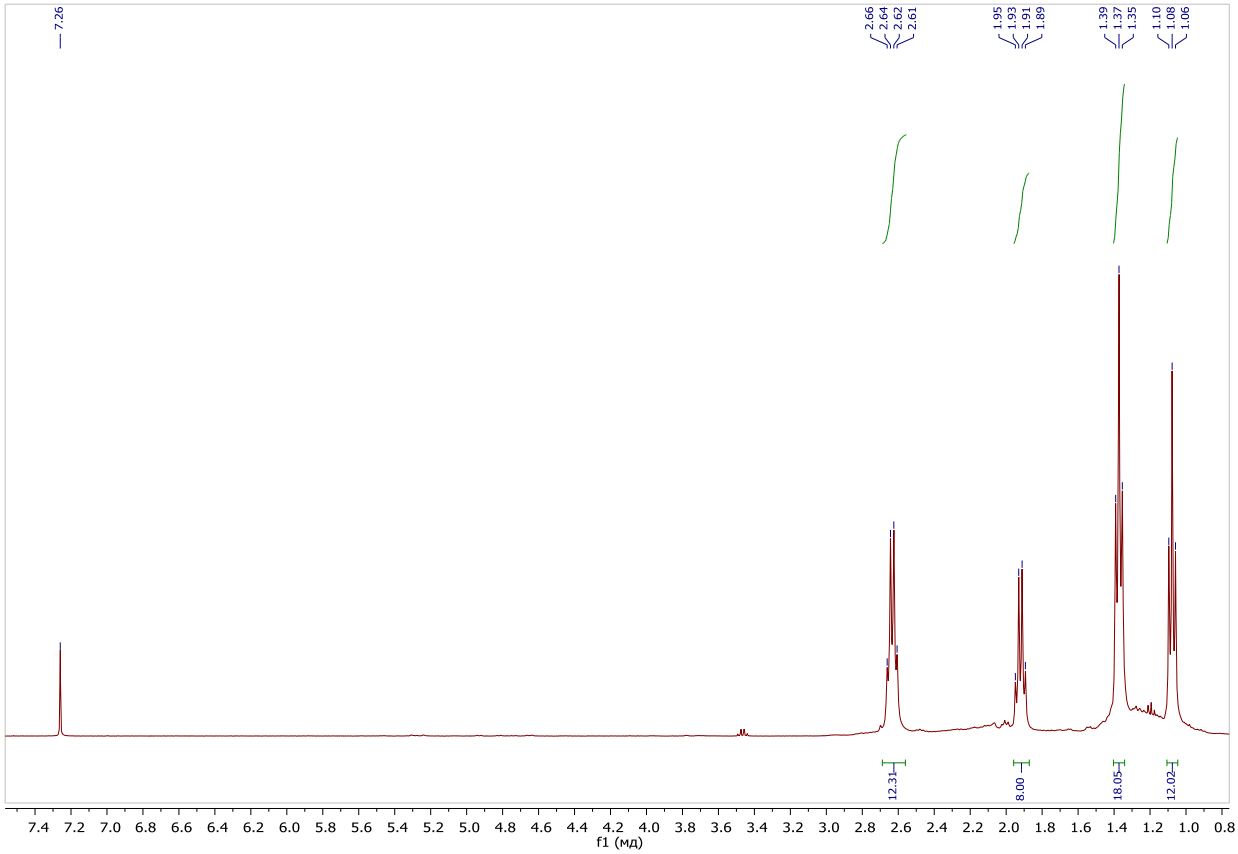


Figure S8. ^{1}H (in $CDCl_3$) and ^{13}C (in $(CD_3)_2CO$) NMR spectra of $[(C_4Et_4)Ir(C_6Et_6)]PF_6$ ([**5**]PF_6).



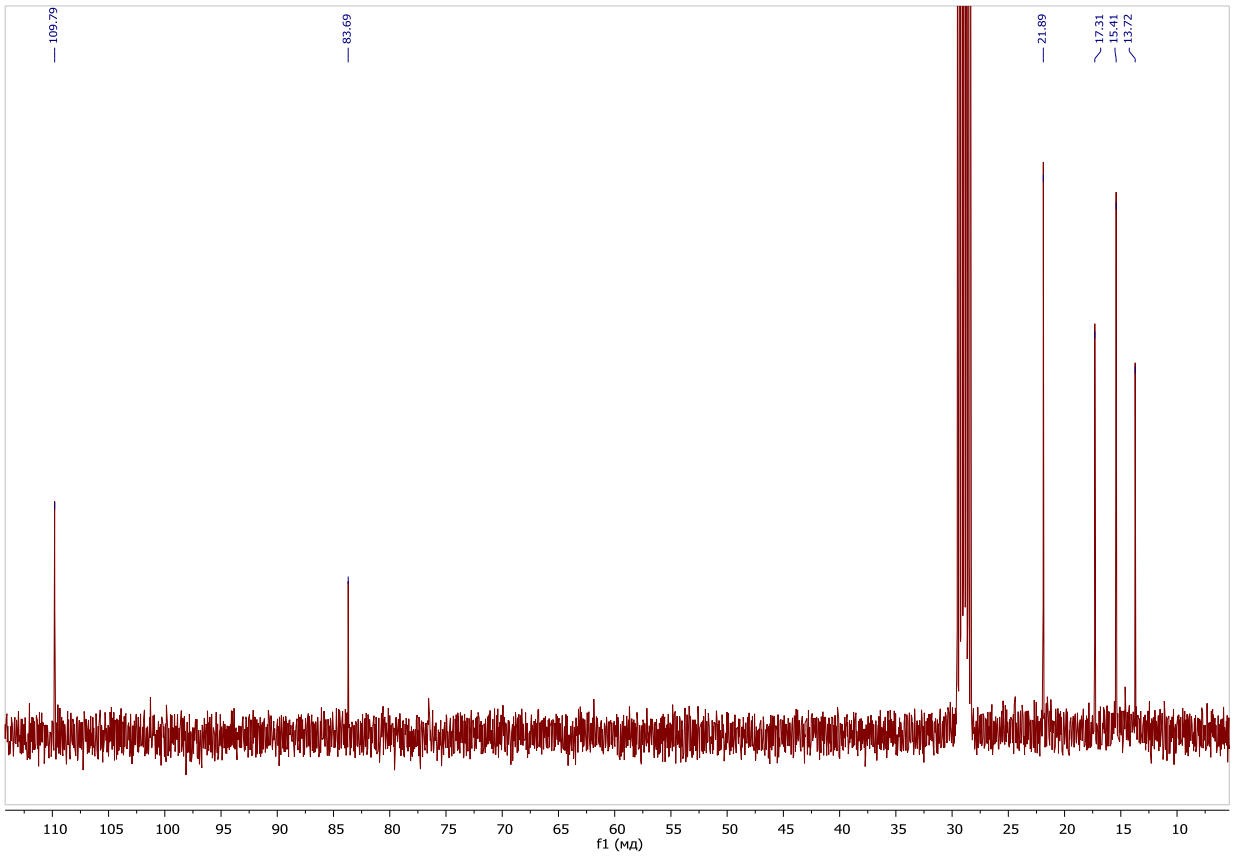


Figure S9. ^{1}H (in $(CD_3)_2CO$) and ^{13}C (in CD_3NO_2) NMR spectra of $[(C_4Ph_4)Ir(p\text{-xylene})]PF_6$ ([**6**]PF_6).