**Supporting Information for**

# Cycloruthenated Imines: A Step into the Nanomolar Region

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## Experimental details

### Single crystal X-ray crystallographic data and refinement details.

X-ray diffraction data for **2a**, **3e**, **3m** and **3o** were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K -radiation. The intensity data were integrated by the SAINT program [1] and were corrected for absorption and decay using SADABS [2]. The structure was solved by direct methods using SHELXT [3] and refined on $F^2$ using SHELXL-2018 [4] in the OLEX2 program [5]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite [1] was used for molecular graphics.

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K -radiation (for compounds **1n**, **2b**, **2d**, **2f**-**2l**, **2n**, **3a**, **3b**, **3f**, **3h**, **3j**) and using monochromatized Mo K -radiation (for compounds **2e**, **3c**). The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program [6]. The structure was solved by direct methods using SHELXT [3] and refined on $F^2$ using SHELXL-2018[4] in the OLEX2 program.[5] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite [1] was used for molecular graphics.

The structures of **2a**, **2b**, **3c** and **3m** contained unresolved/highly disordered acetonitrile and ether molecules in the crystal channels, which were removed by the SQUEEZE method [7] implemented in the OLEX2 program [5].

### Cyclic voltammetry

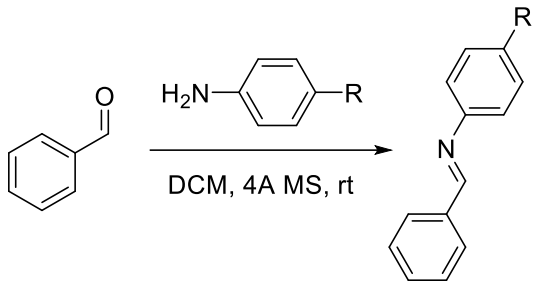
The electrochemical oxidation and reduction behavior of the compounds under discussion was investigated by cyclic voltammetry using an IPC-Pro-MF potentiostat from Econix. The preparation of solutions and all measurements were performed in an argon-filled glovebox at a water and oxygen level of no more than 0.1 ppm. Before use, acetonitrile (HPLC grade, Acros) with an initial water content of no more than 100 ppm was stored over molecular sieves (4 Å) pre-dried under oil pump vacuum at 200-250 °C for 4 h. $Bu_4NPF_6$ (Sigma Aldrich) was dried under oil pump vacuum at 80 °C for 4 h. The water content in the 0.1 M $Bu_4NPF_6$/acetonitrile system used did not exceed 20 ppm after that, which was monitored by Karl Fischer titration using a Mettler-Toledo C10SD titrator. The compounds dissolved in 5 ml of the background electrolyte were electrochemically analyzed in a standard conical three-electrode glass cell. The working electrode was a 1.7 mm diameter glassy carbon disk electrode placed in PTFE. Before use, it was polished with sandpaper and GOI paste until a mirror shine was achieved. The auxiliary electrode was a platinum wire pre-calcined in a gas burner flame. The potentials of the processes under study were measured relative to a silver wire coated with AgCl (achieved by galvanostatic anodizing in a 5% hydrochloric acid solution) separated from the main solution by an electrochemical bridge filled with an auxiliary electrolyte. Separately, under similar conditions, the oxidation curves of ferrocene were recorded, and the given values were corrected according to the oxidation potential of the latter.

### Cells and MTT assay.

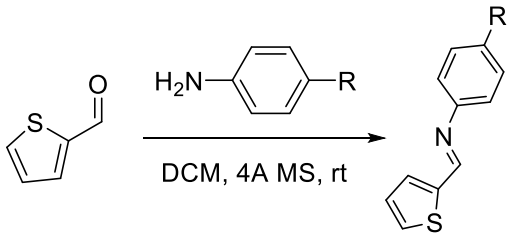
The human A2780 ovarian adenocarcinoma, A2780cis cisplatin resistant ovarian adenocarcinoma, HEK293 human embryonic kidney cell lines were obtained from the European collection of authenticated cell cultures (ECACC; Salisbury, UK). Cells were grown in a RPMI 1640 (Gibco™, Ireland) cell medium (A2780, A2780cis), or DMEM (Gibco™, Ireland) cell medium (HEK293) supplemented with 10% fetal bovine serum (Gibco™, Brazil). The cells were cultured in an incubator at 37 °C in a humidified 5% CO2 atmosphere and were subcultured two times a week. The antiproliferative activity was studied by MTT assays as published previously [8]

1. Bruker. APEX-III. *Bruker AXS Inc.*, Madison, Wisconsin, USA, **2019**.
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3. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71, 3-8. http://doi.org/10.1107/S2053273314026370
4. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3-8. http://doi.org/10.1107/S2053229614024218
5. Dolomanov O.V.; Bourhis L.J.; Gildea R.J.; Howard J.A.K.; Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42(2), 229-341. http://doi.org/10.1107/S0021889808042726
6. CrysAlisPro. Version 1.171.41. *Rigaku Oxford Diffraction*, **2021**.
7. Spek A. L., *Acta Cryst.*, 2015, **C71**, 9-18, http://dx.doi.org/10.1107/S2053229614024929
8. Nosova, Y.N.; Foteeva, L.S.; Zenin, I. V.; Fetisov, T.I.; Kirsanov, K.I.; Yakubovskaya, M.G.; Antonenko, T.A.; Tafeenko, V.A.; Aslanov, L.A.; Lobas, A.A.; et al. Enhancing the Cytotoxic Activity of Anticancer Pt IV Complexes by Introduction of Lonidamine as an Axial Ligand. *Eur. J. Inorg. Chem.* **2017**, *2017*, 1785–1791, http://dx.doi.org/10.1002/ejic.201600857

**Preparation of starting materials**




1a (R = H): 92%
1b (R = F): 94%
1c (R = Me): 99%
1d (R = Et): 96%
1e (R = tBu): 96%
1f (R = OMe): 95%
1g (R = COOEt): 91%
1h (R = $NO_2$): 90%
1i (R = $CF_3$): 90%




1j (R = F): 94%
1k (R = Me): 99%
1l (R = OMe): 96%
1m (R = COOEt): 94%
1n (R = $NO_2$): 85%
1o (R = $CF_3$): 77%

Scheme S1. Preparation of starting imines.

*General procedure for imines **1a**-**1o**.*

Equimolar amounts of corresponding aldehyde (2.5 mmol) and aniline (2.5 mmol) were stirred in dry DCM (7.8 ml) with 2.5 g of 4 Å molecular sieves (1 g/1 mmol) for 72 h in argon atmosphere, reaction mixture was filtered and evaporated. Product used without further purification.

## NMR spectra

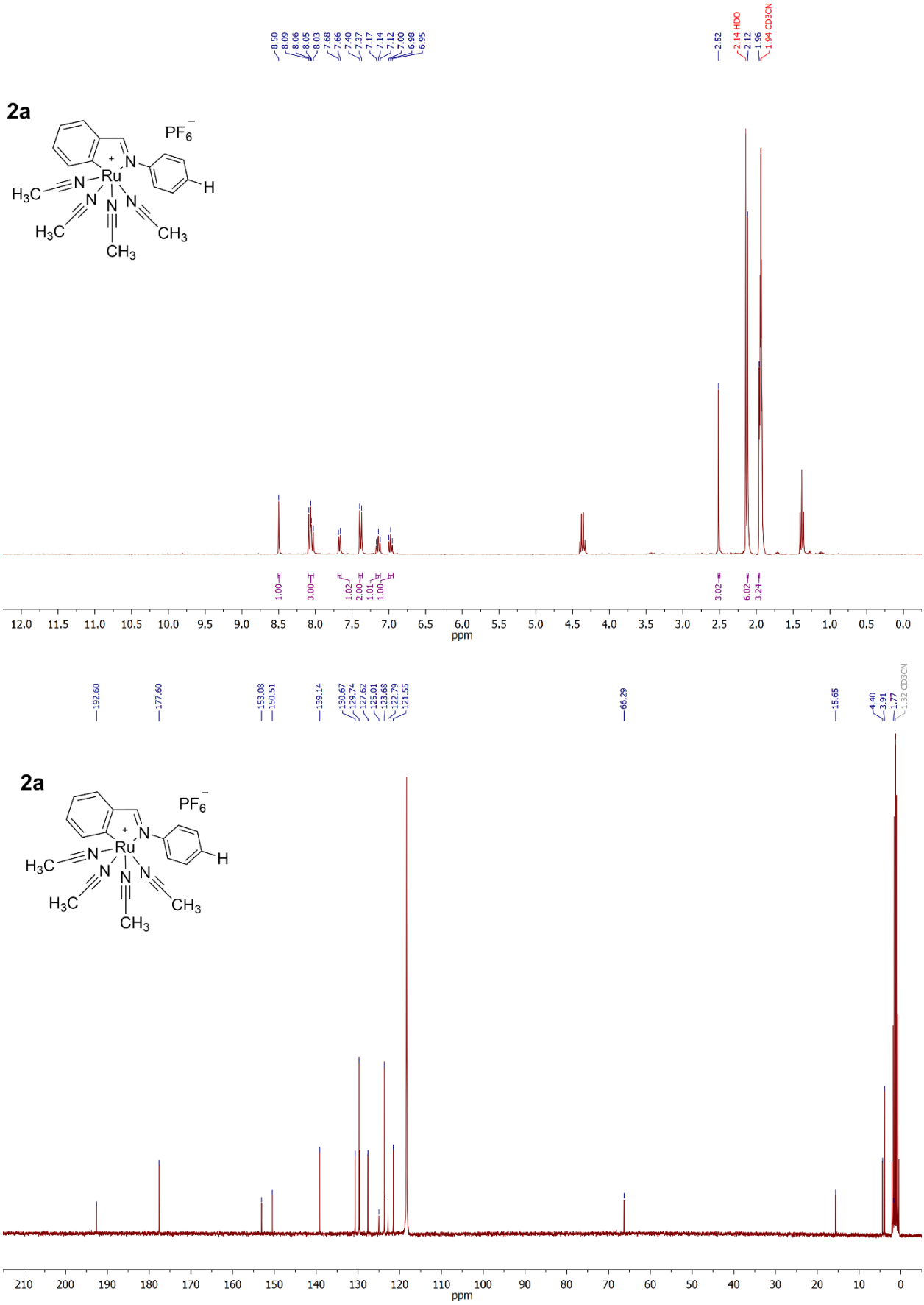



Figure S1. NMR spectra of **2a**.

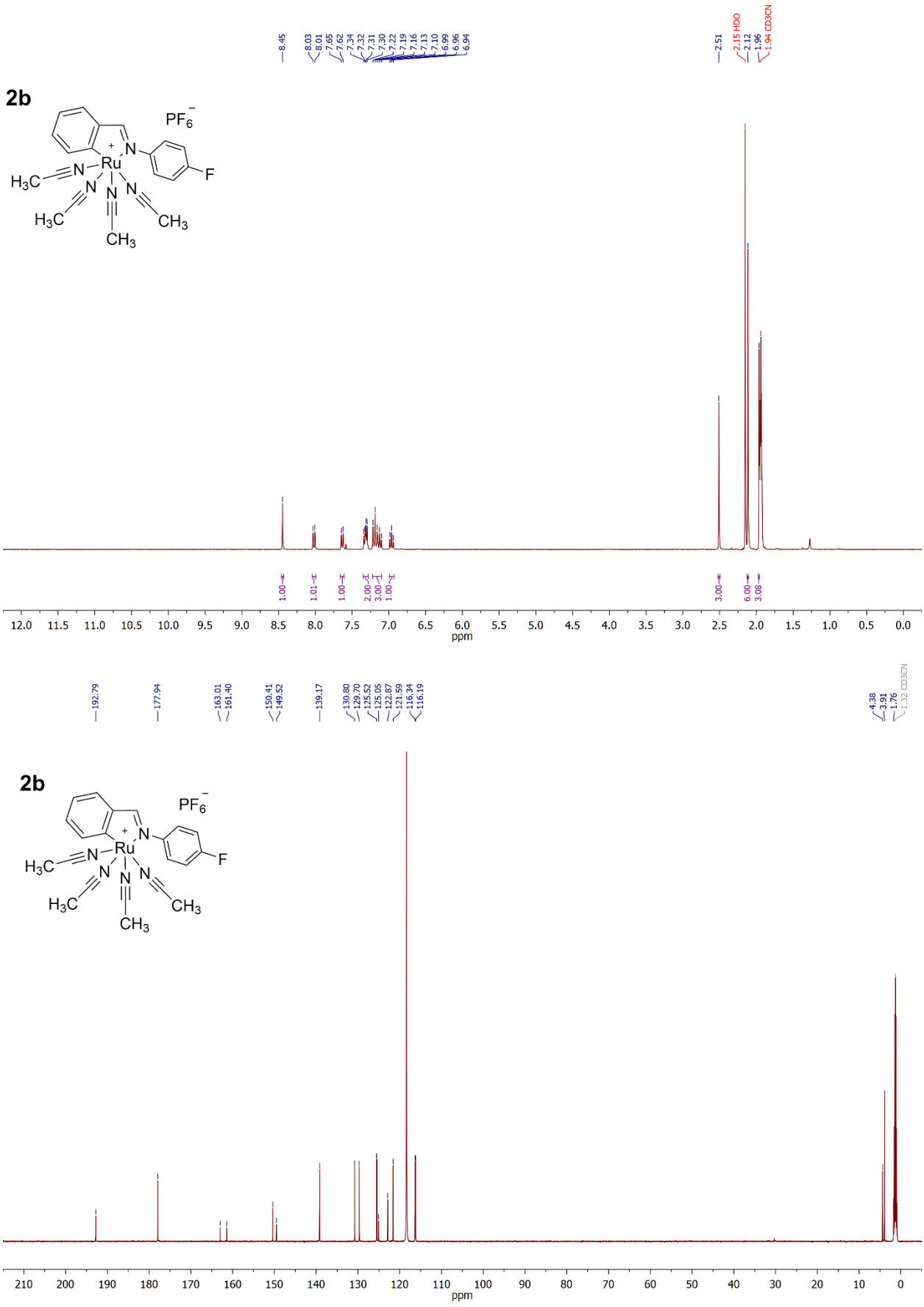



Figure S2. NMR spectra of **2b**.

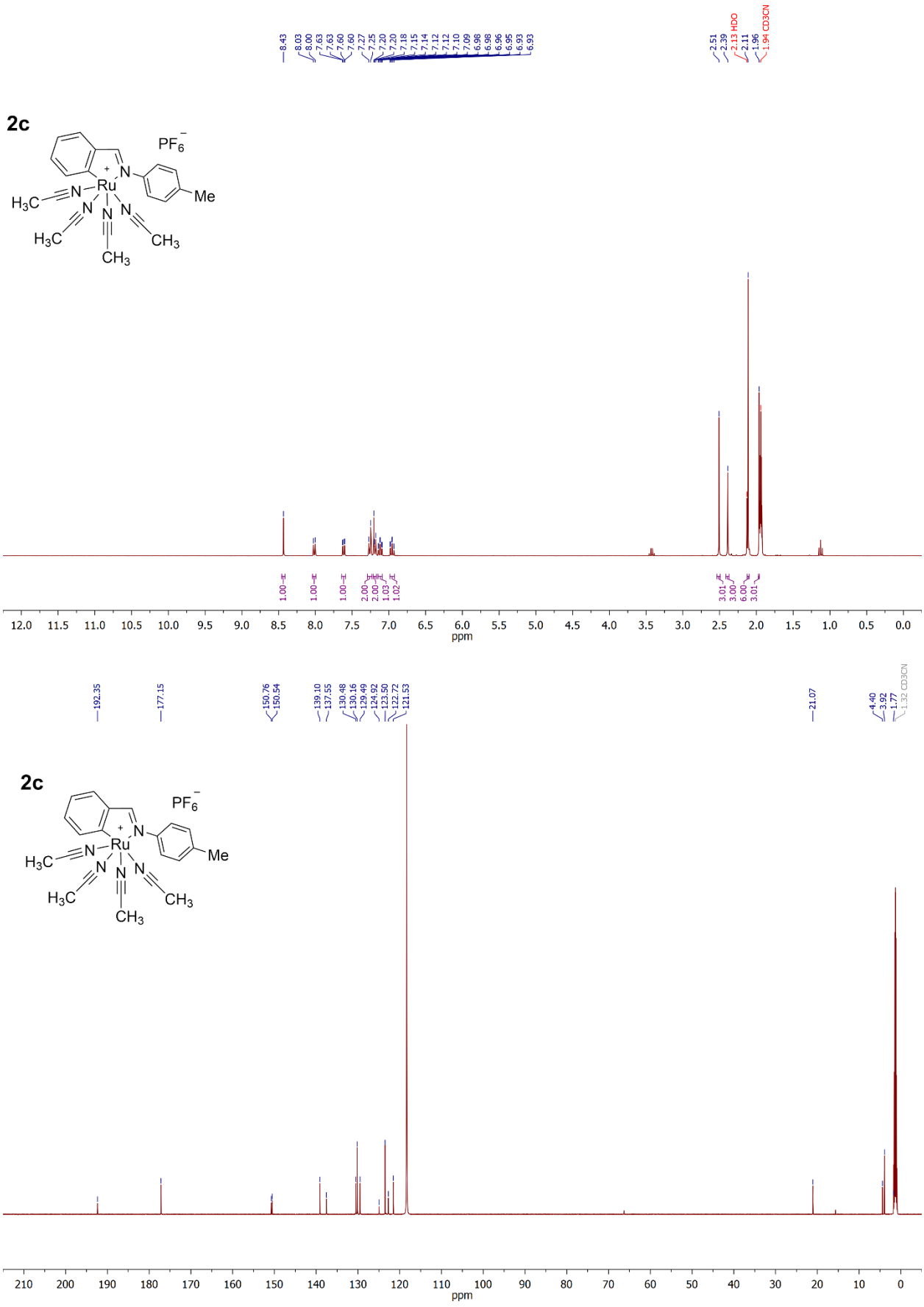



Figure S3. NMR spectra of **2c**.

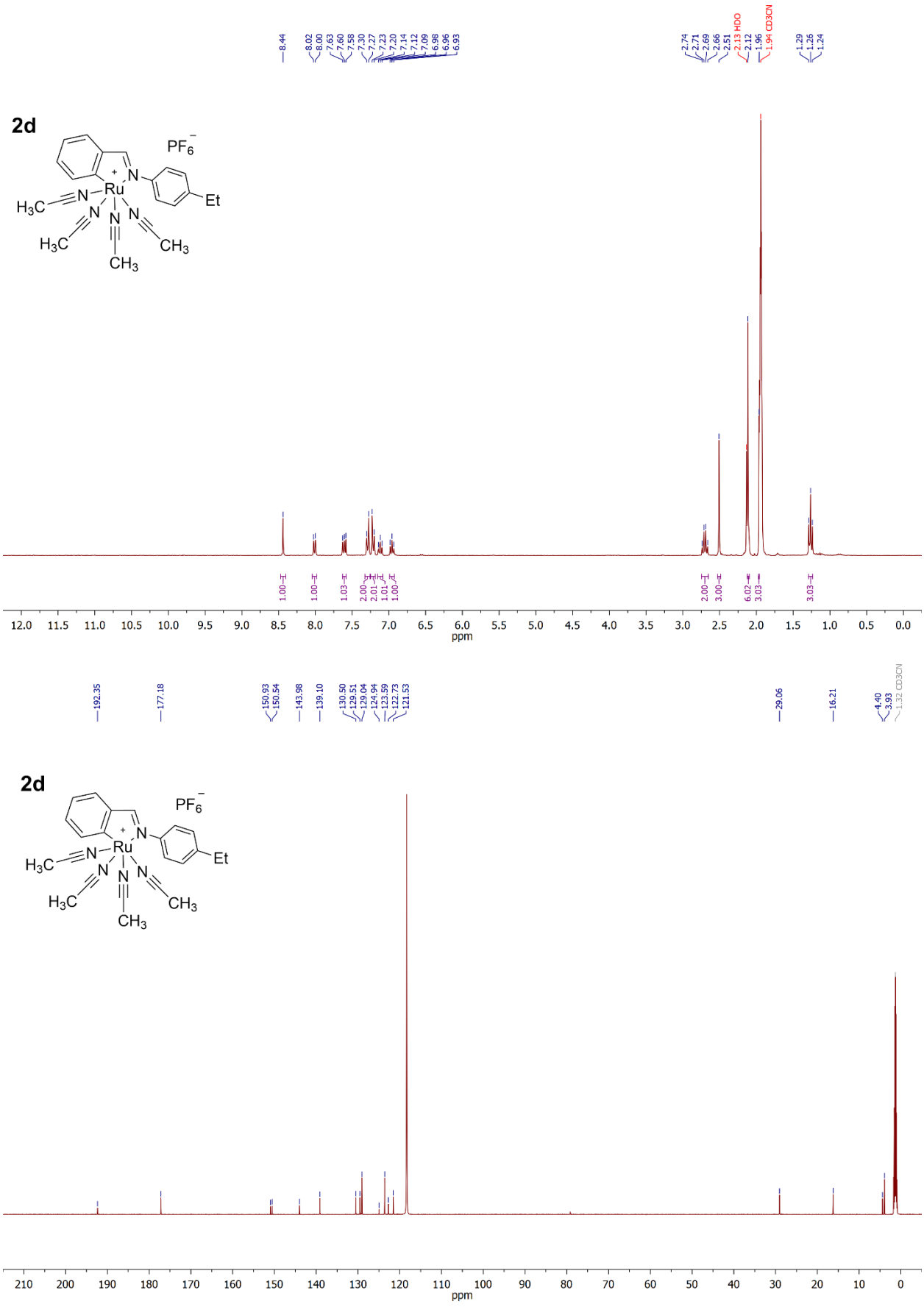



Figure S4. NMR spectra of **2d**.

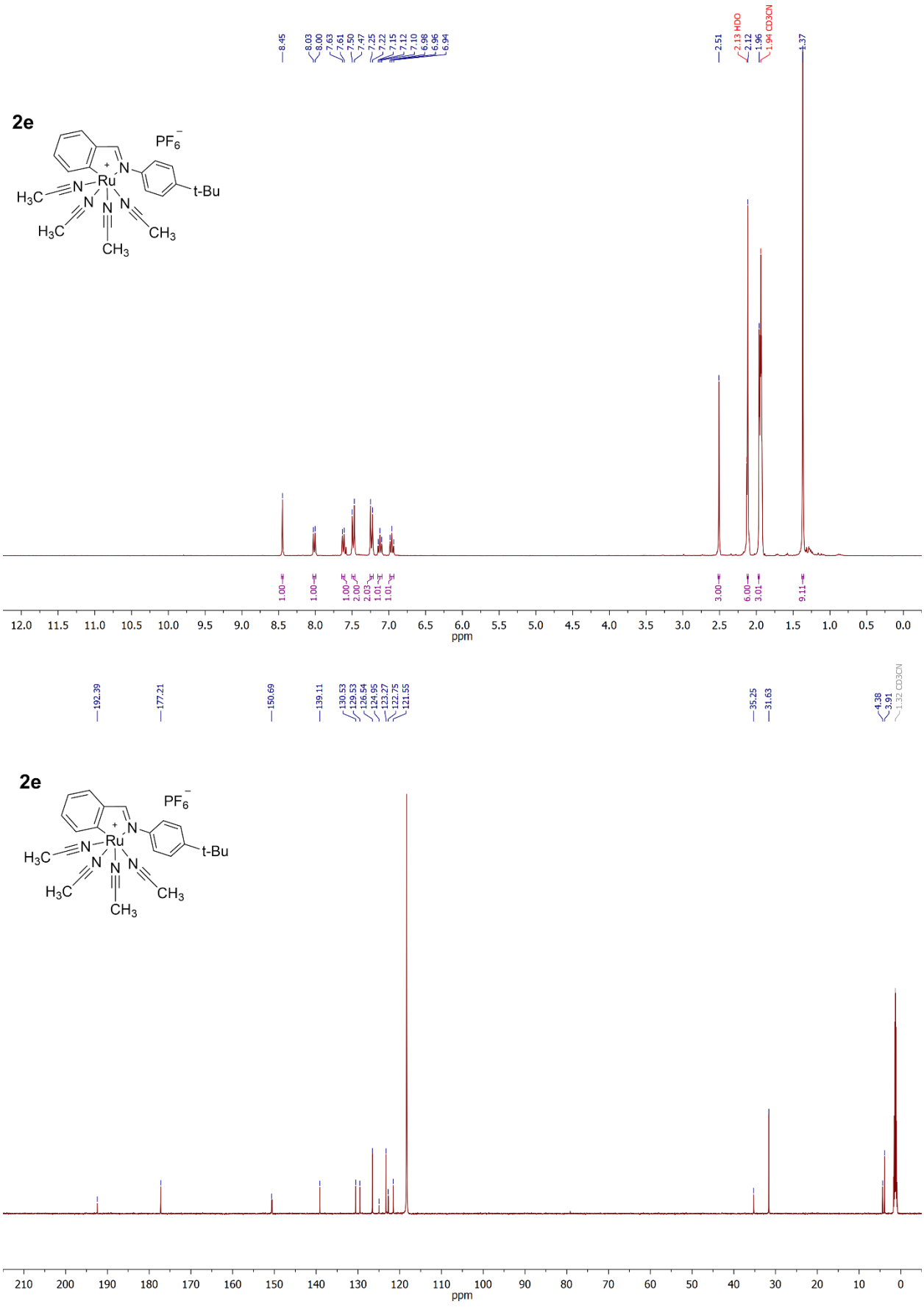



Figure S5. NMR spectra of **2e**.

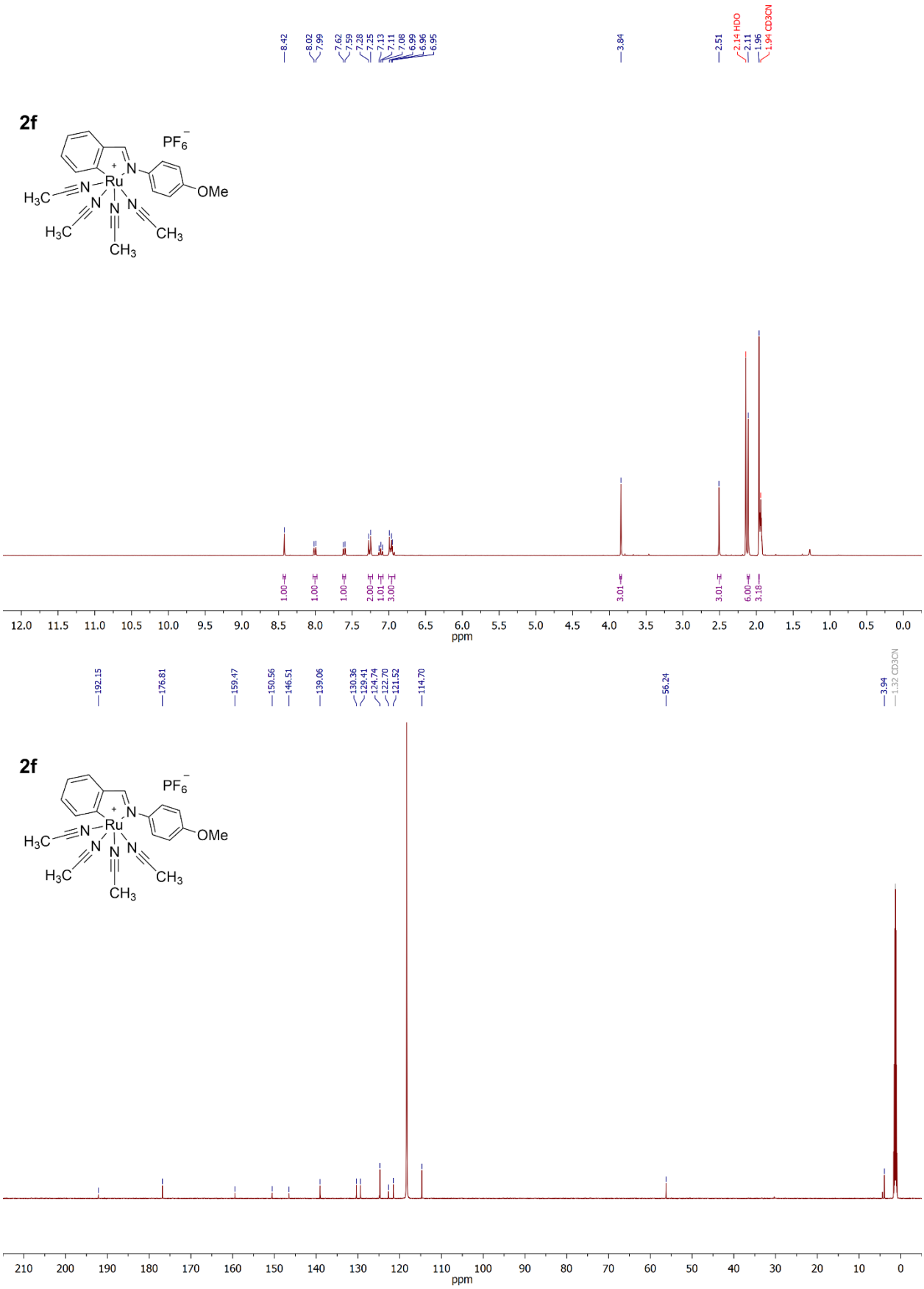



Figure S6. NMR spectra of **2f**.

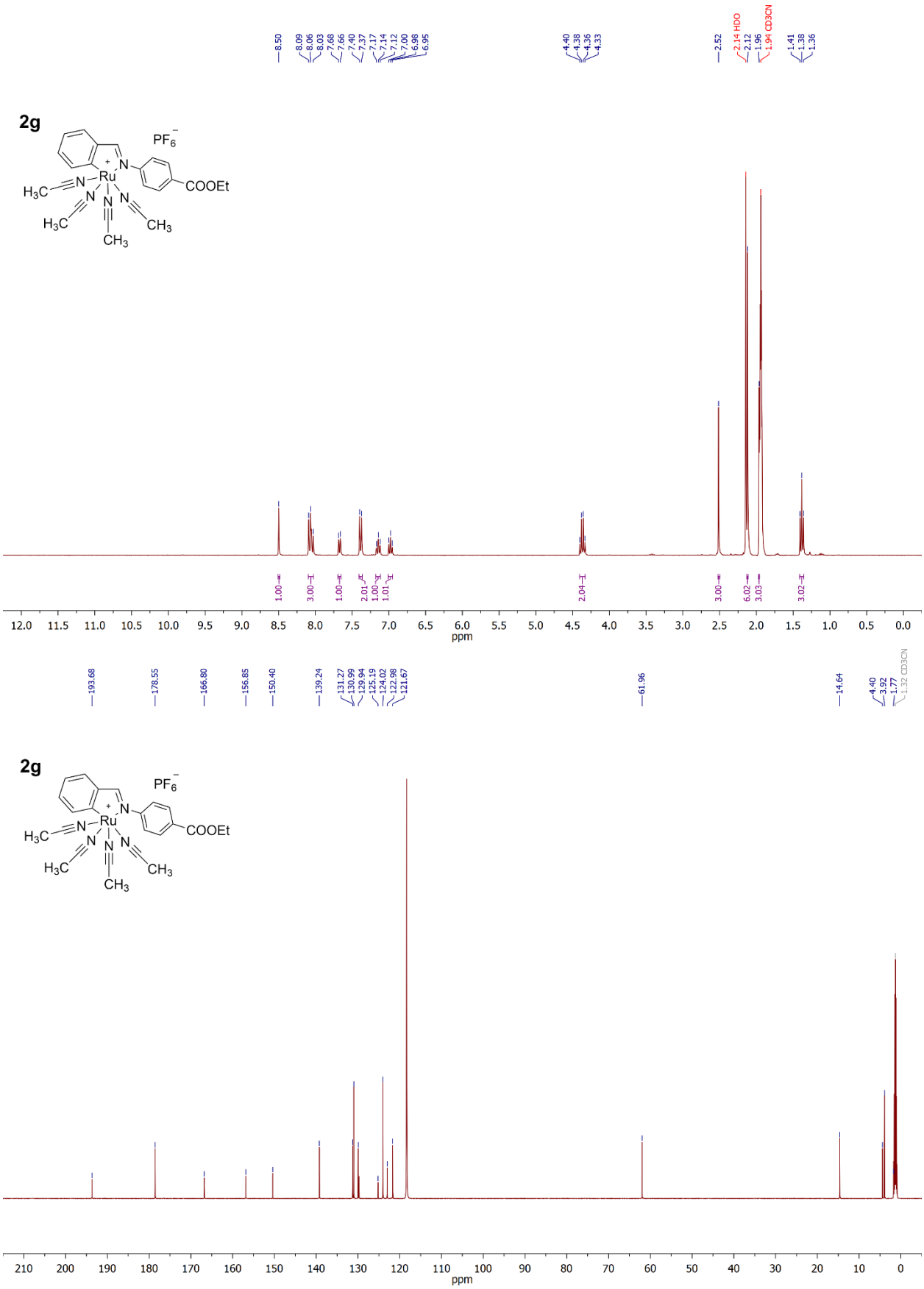



Figure S7. NMR spectra of **2g**.

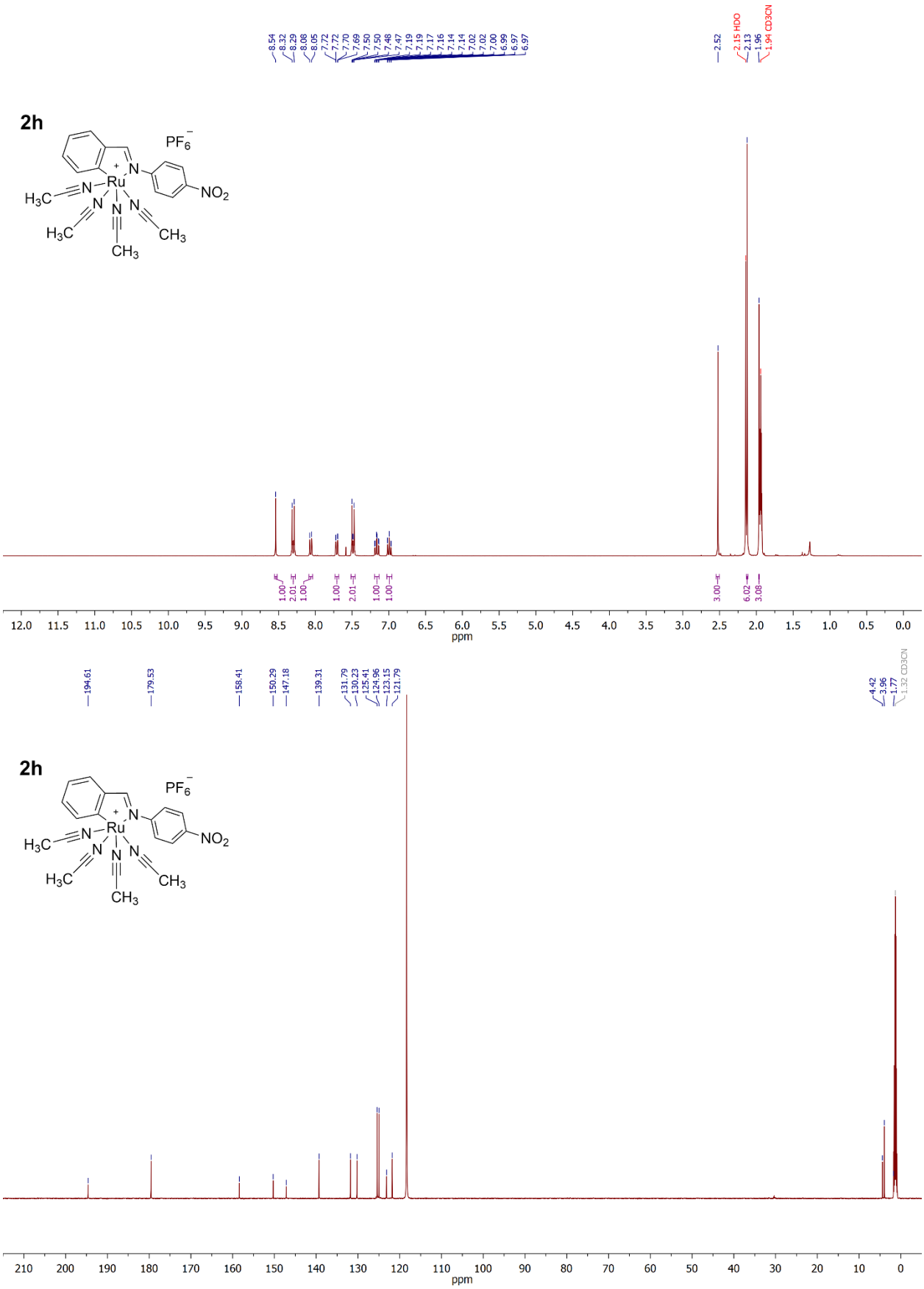



Figure S8. NMR spectra of **2h**.

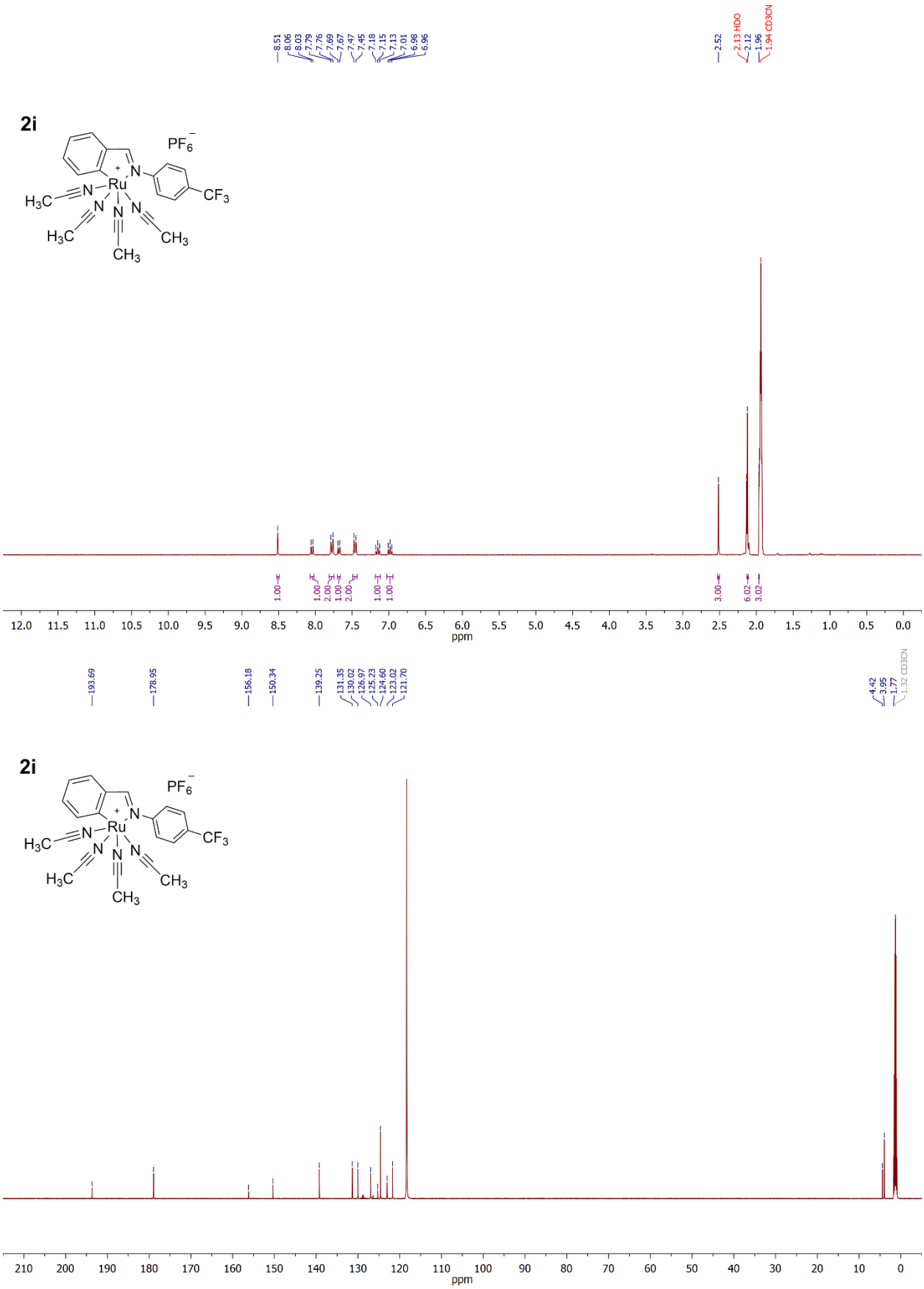



Figure S9. NMR spectra of **2i**.

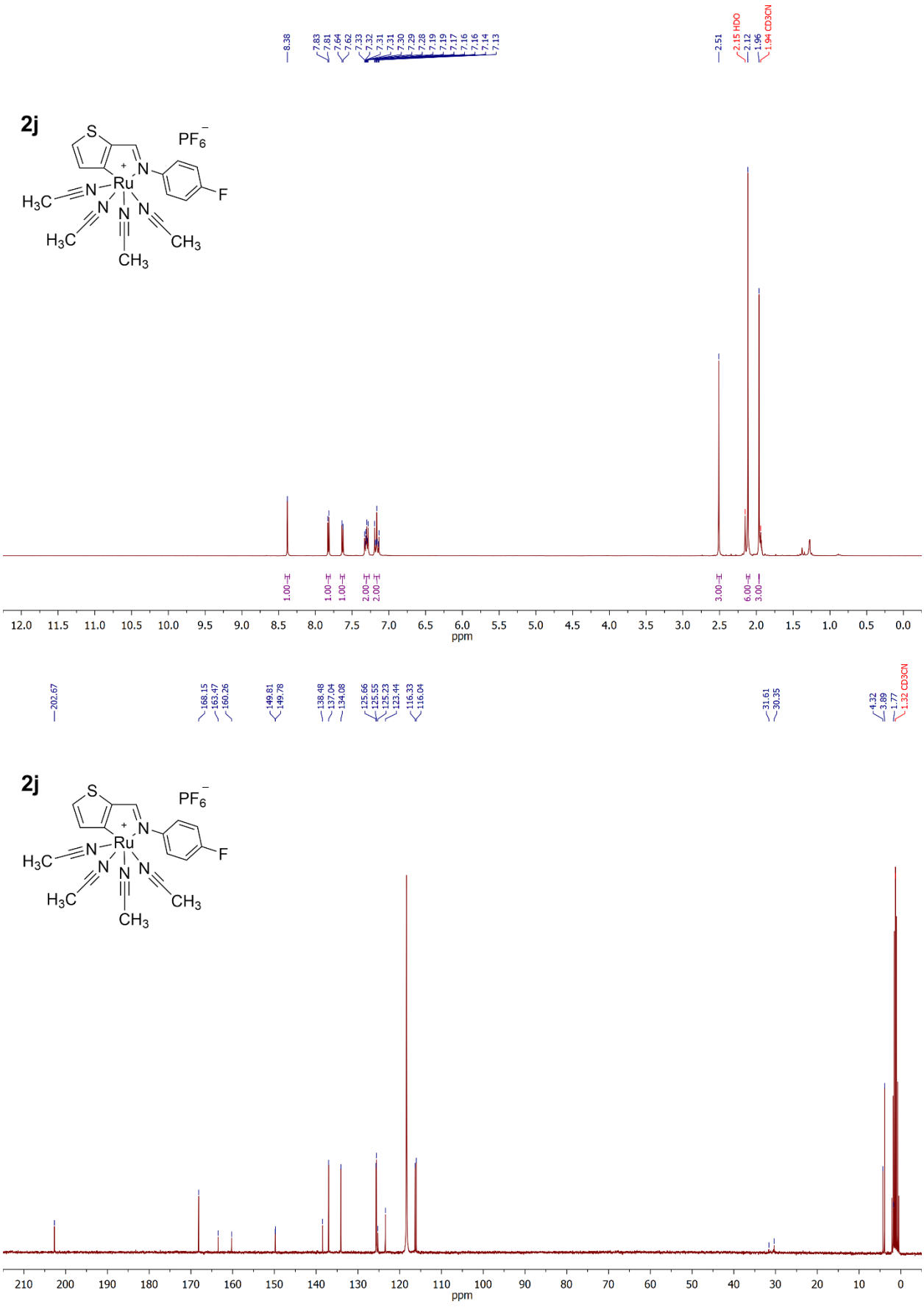



Figure S10. NMR spectra of **2j**.

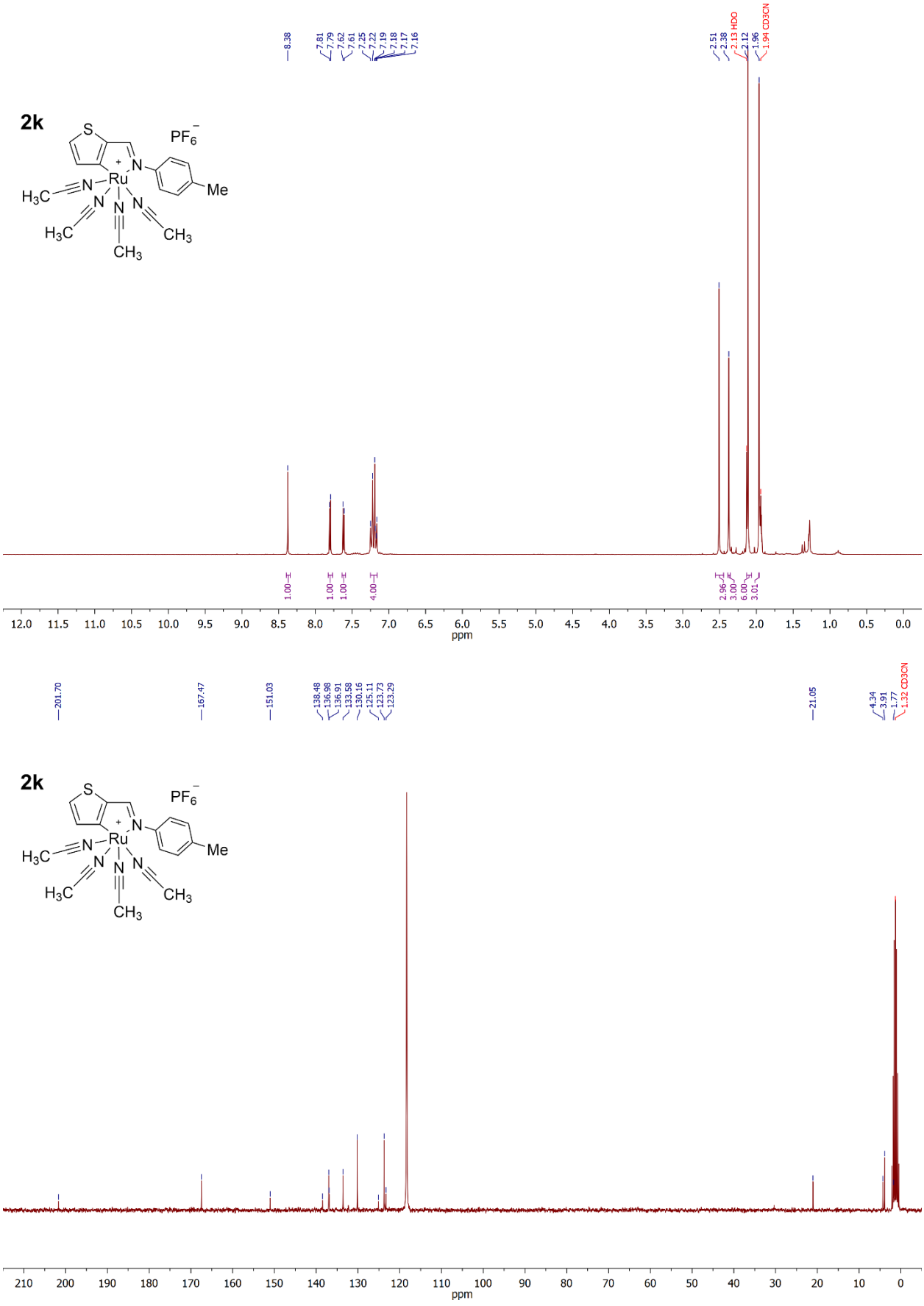



Figure S11. NMR spectra of **2k**.

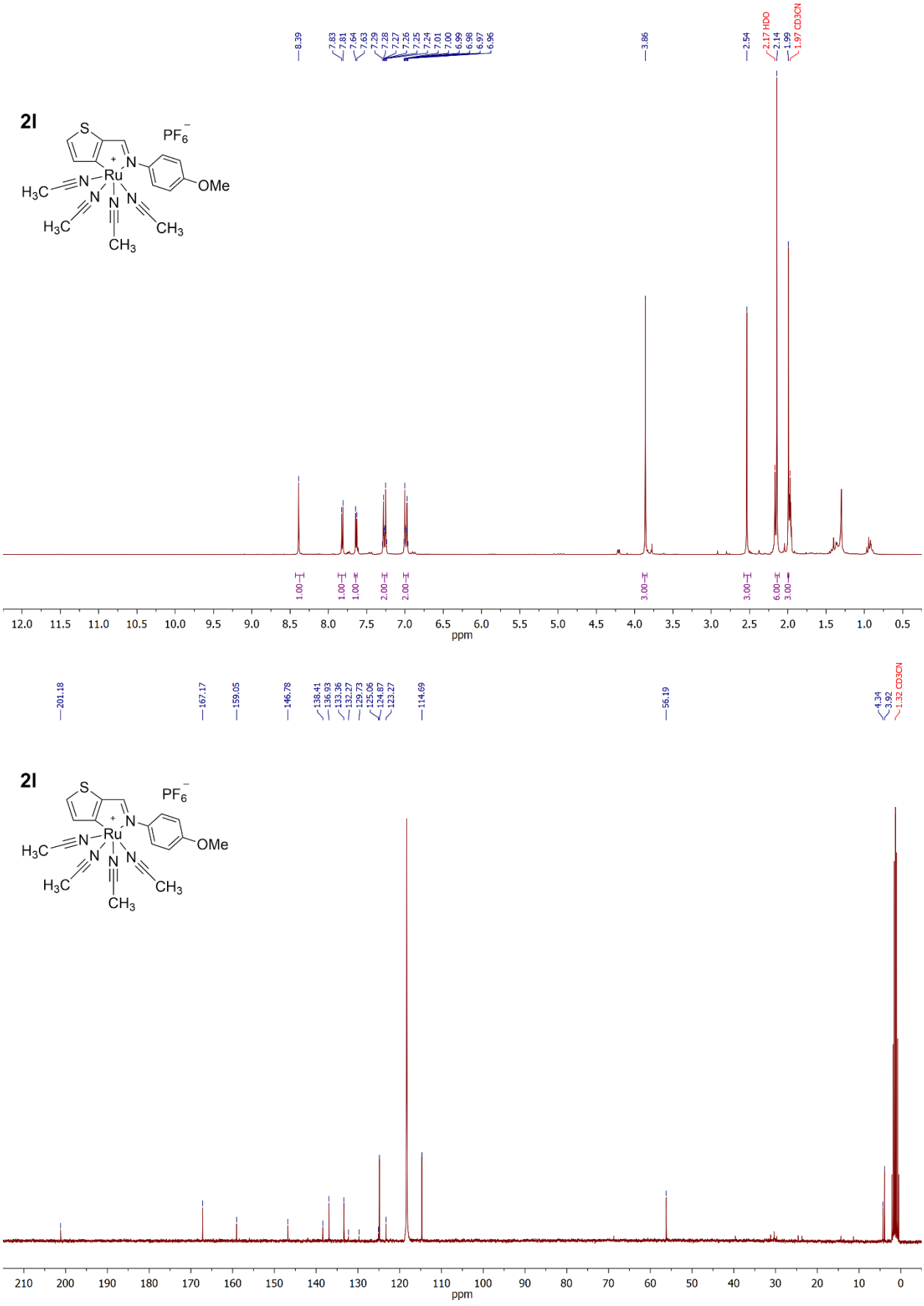



Figure S12. NMR spectra of **2l**.

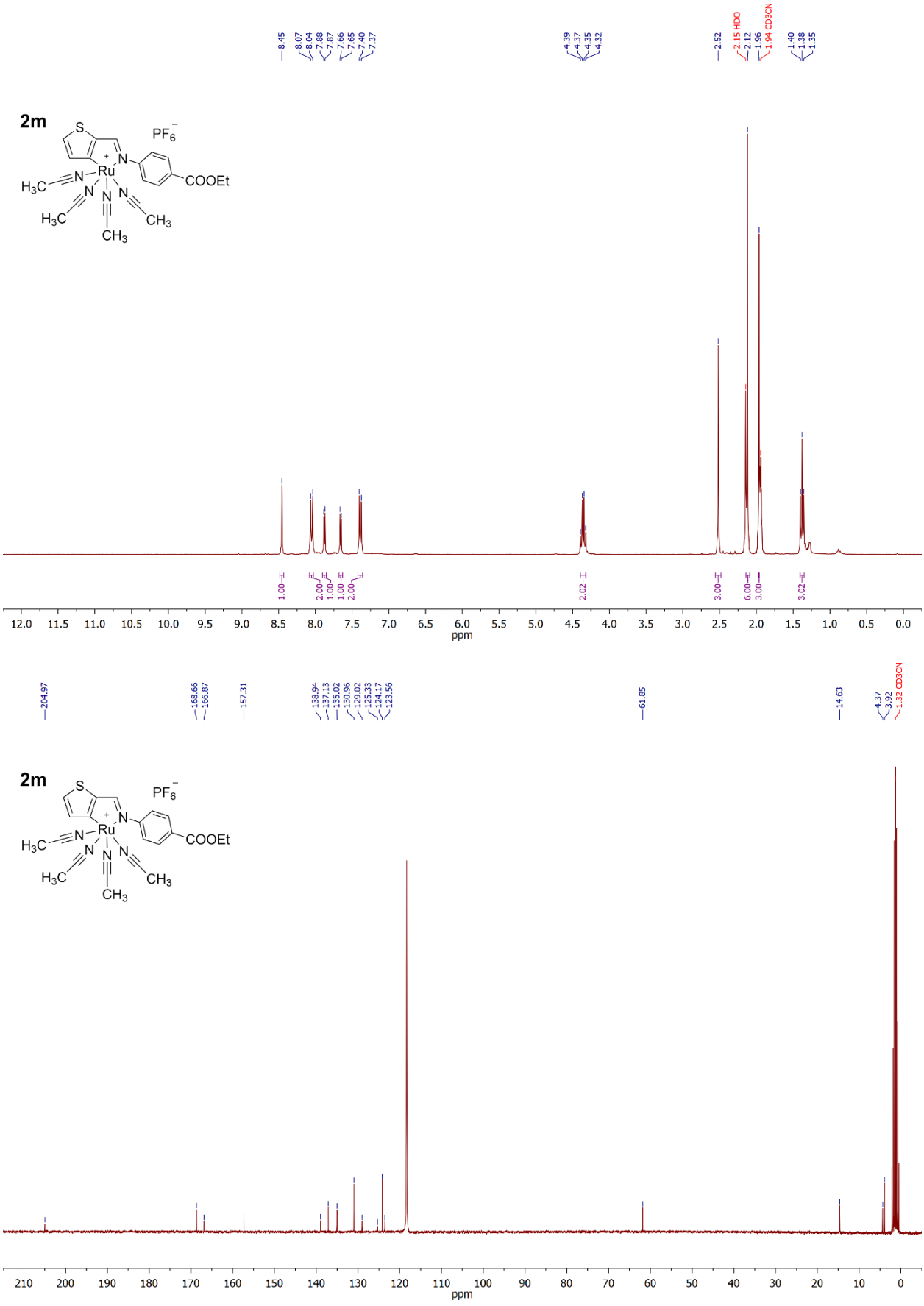



Figure S13. NMR spectra of **2m**.

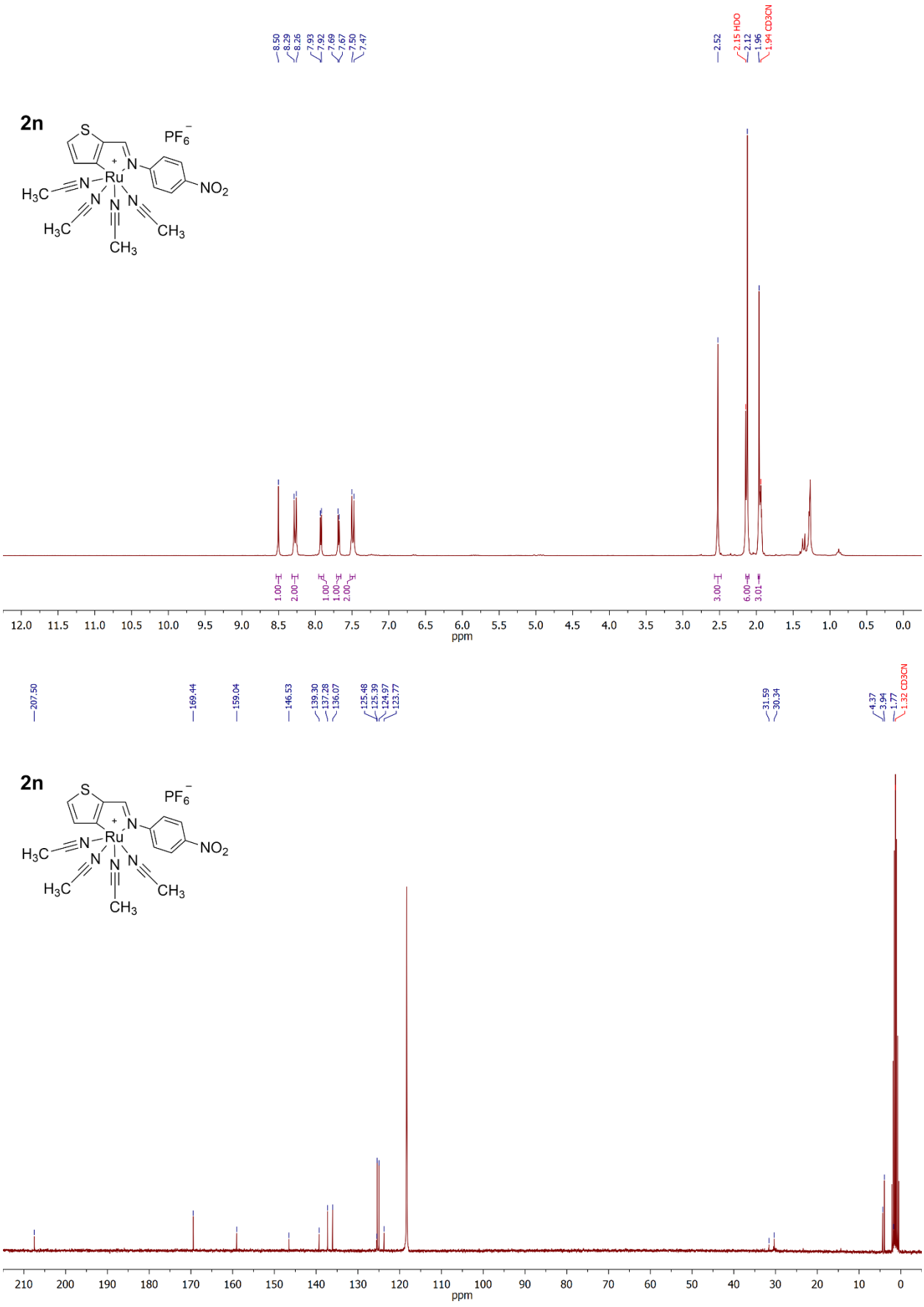



Figure S14. NMR spectra of **2n**.

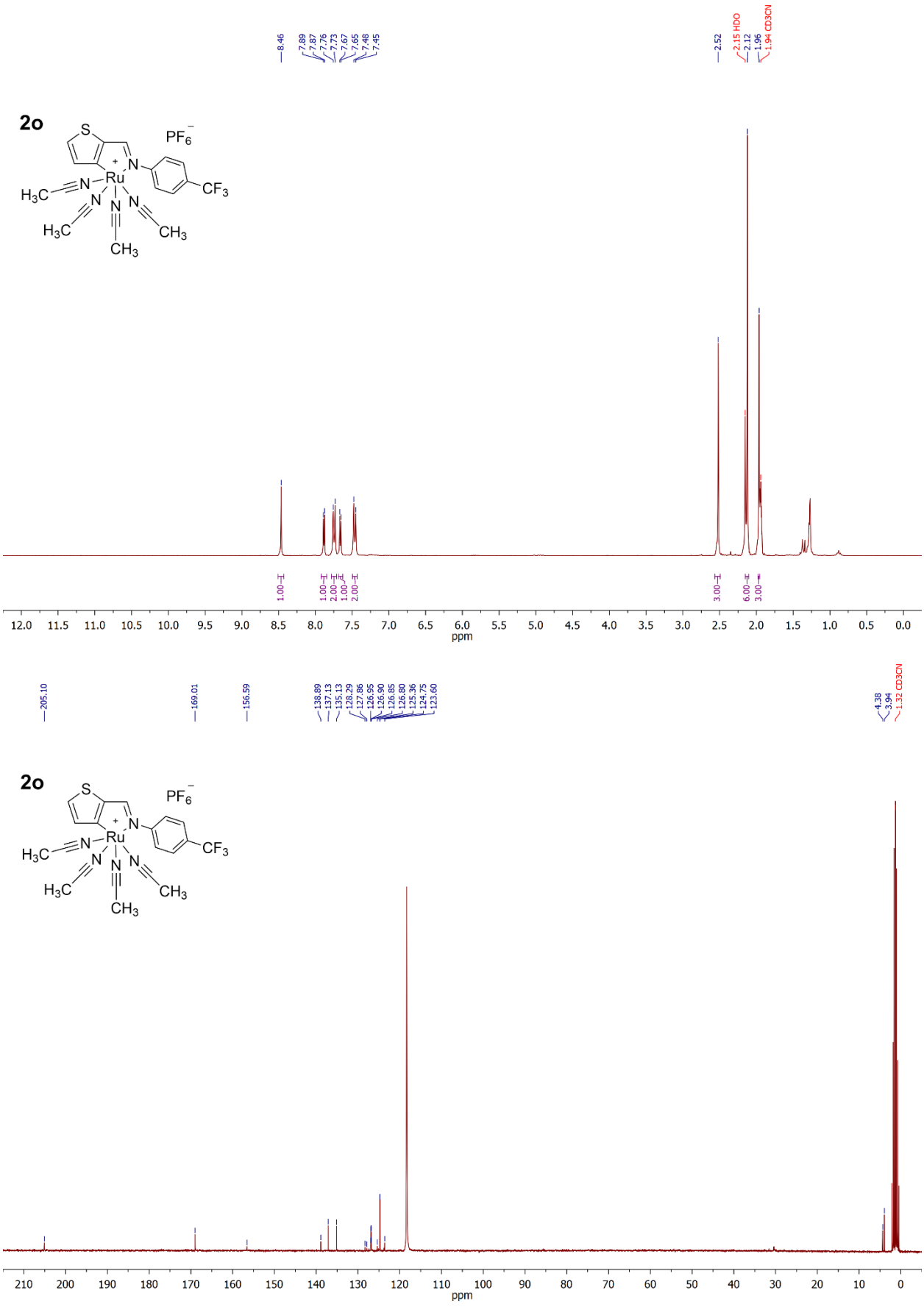



Figure S15. NMR spectra of **2o**.

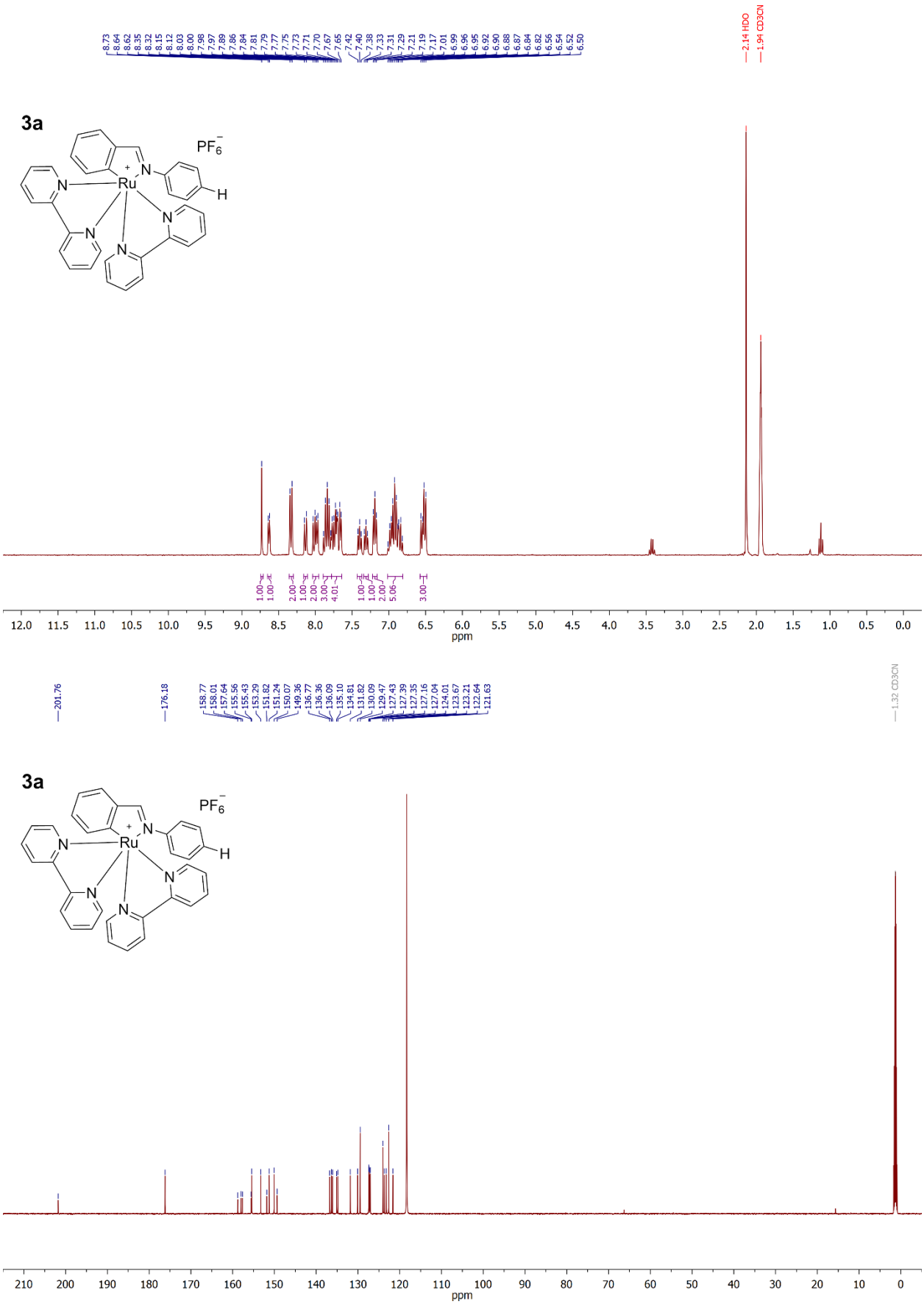



Figure S16. NMR spectra of **3a**.

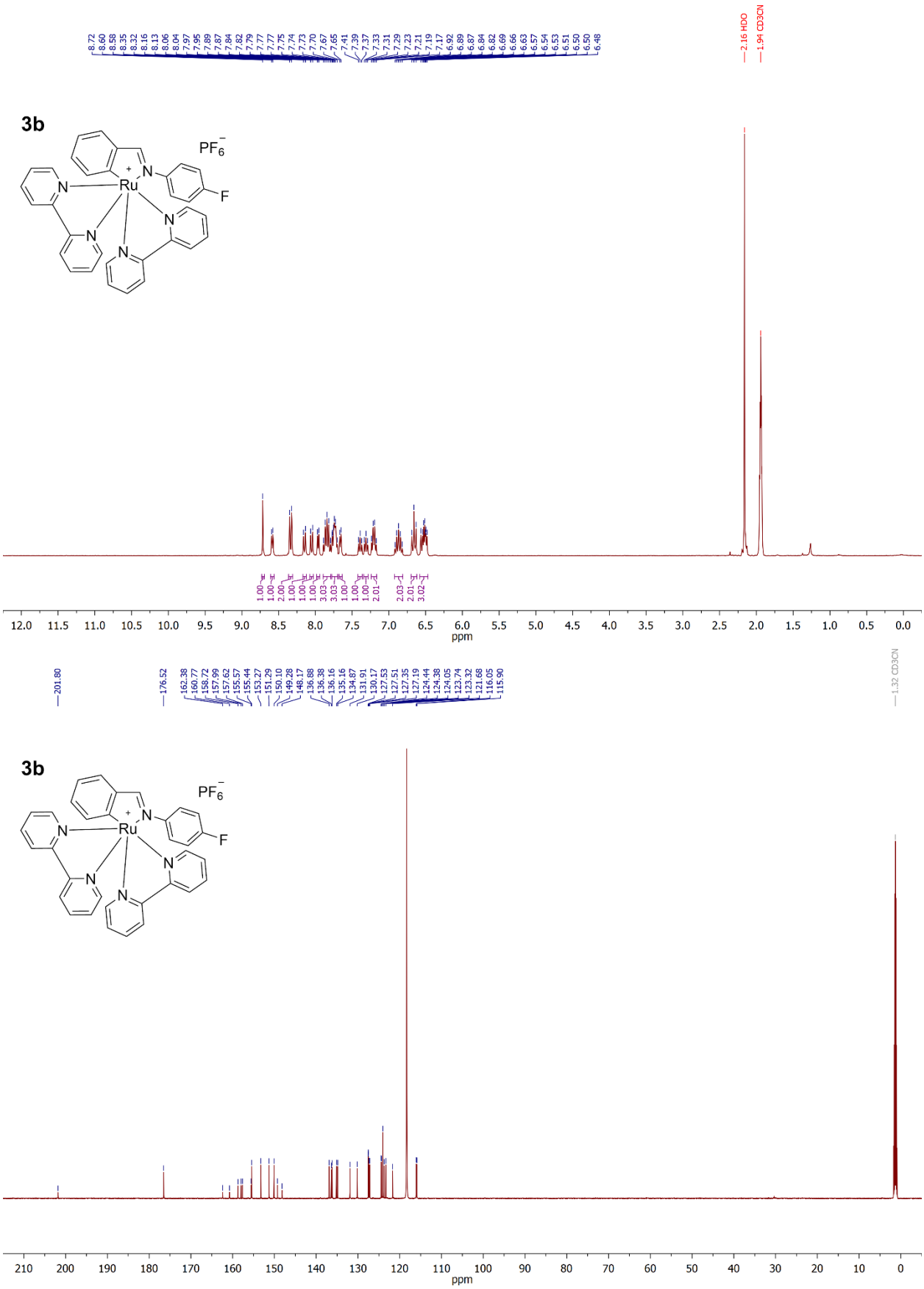



Figure S17. NMR spectra of **3b**.

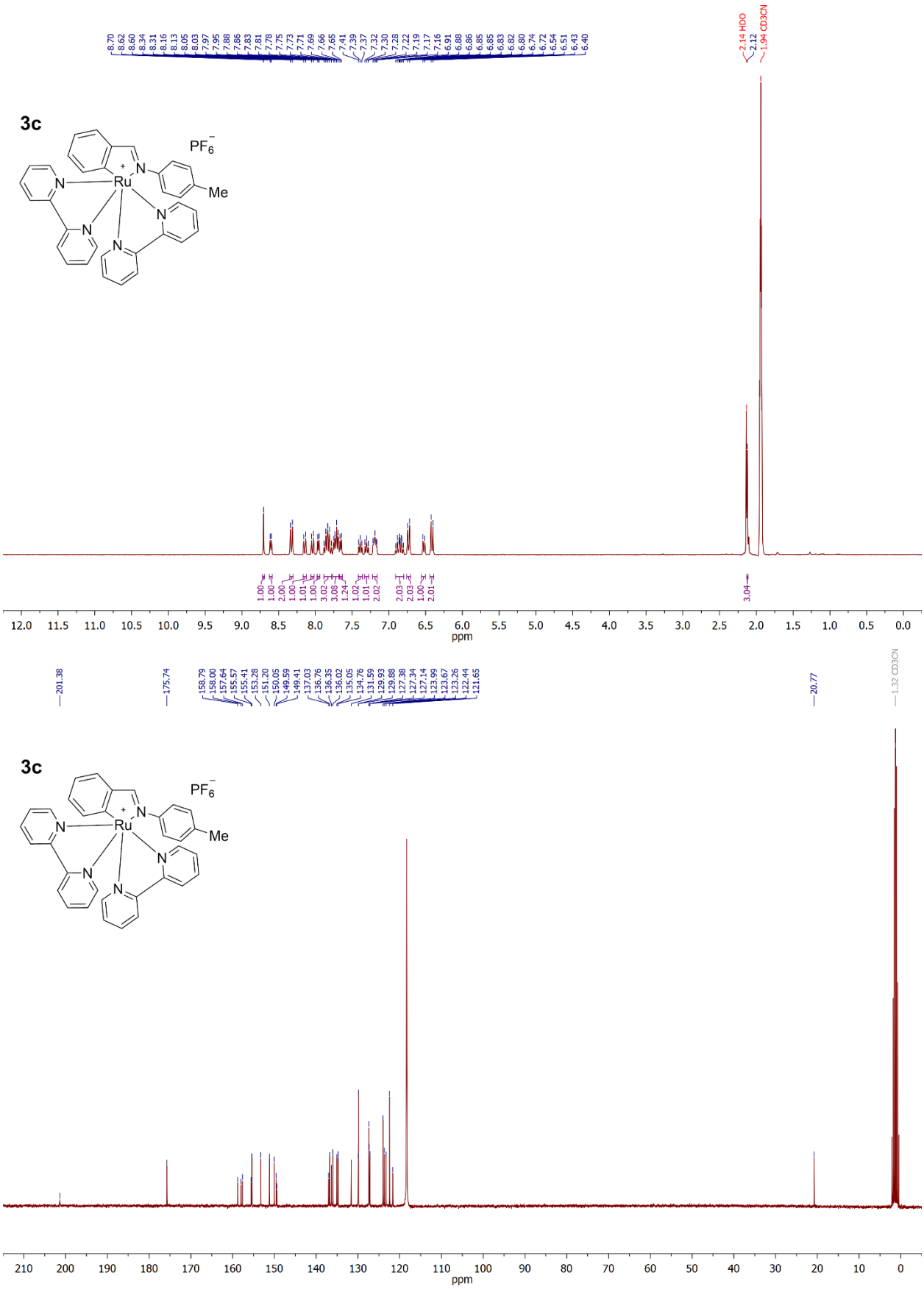



Figure S18. NMR spectra of **3c**.

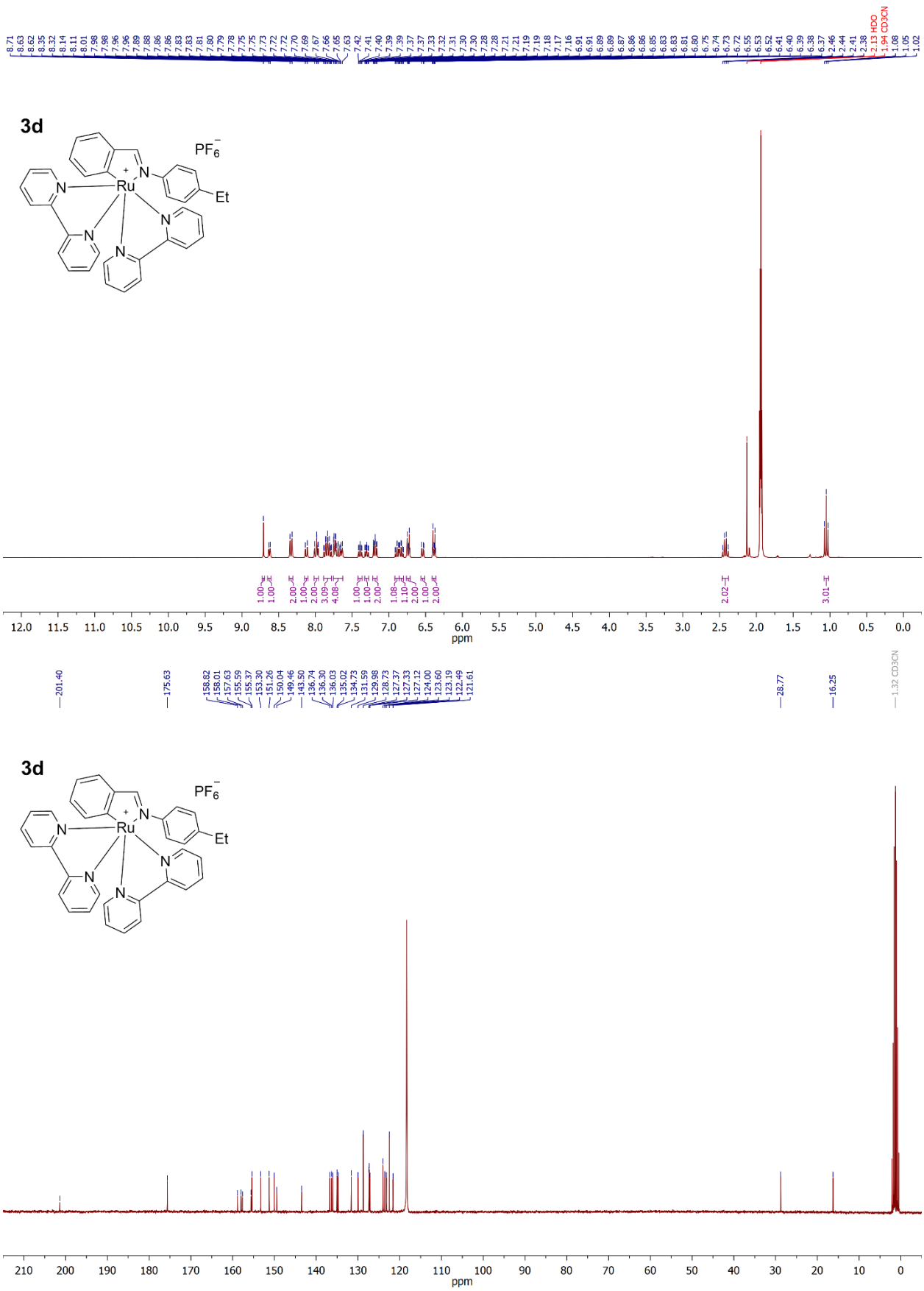



Figure S19. NMR spectra of **3d**.

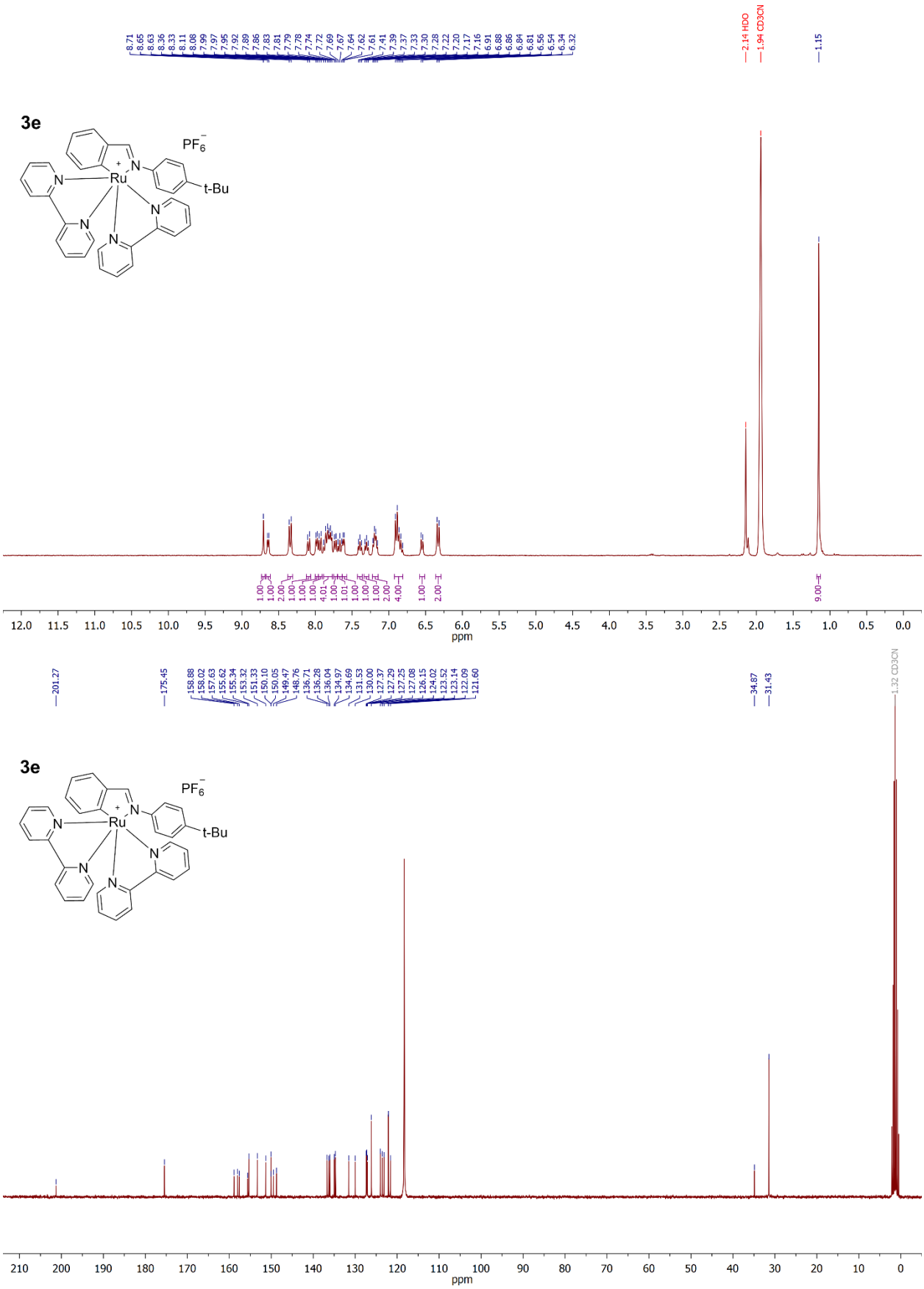



Figure S20. NMR spectra of **3e**.

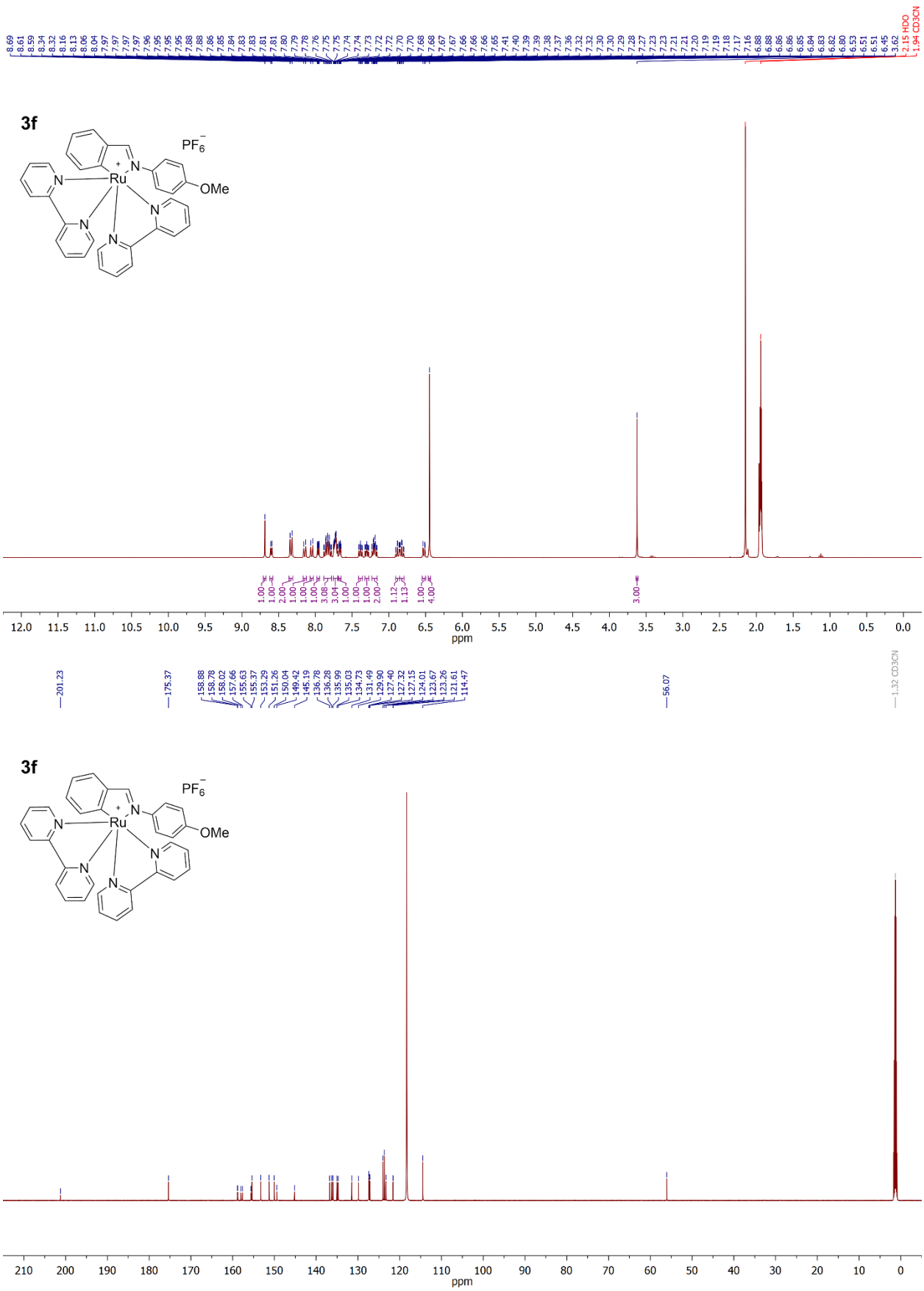



Figure S21. NMR spectra of **3f**.

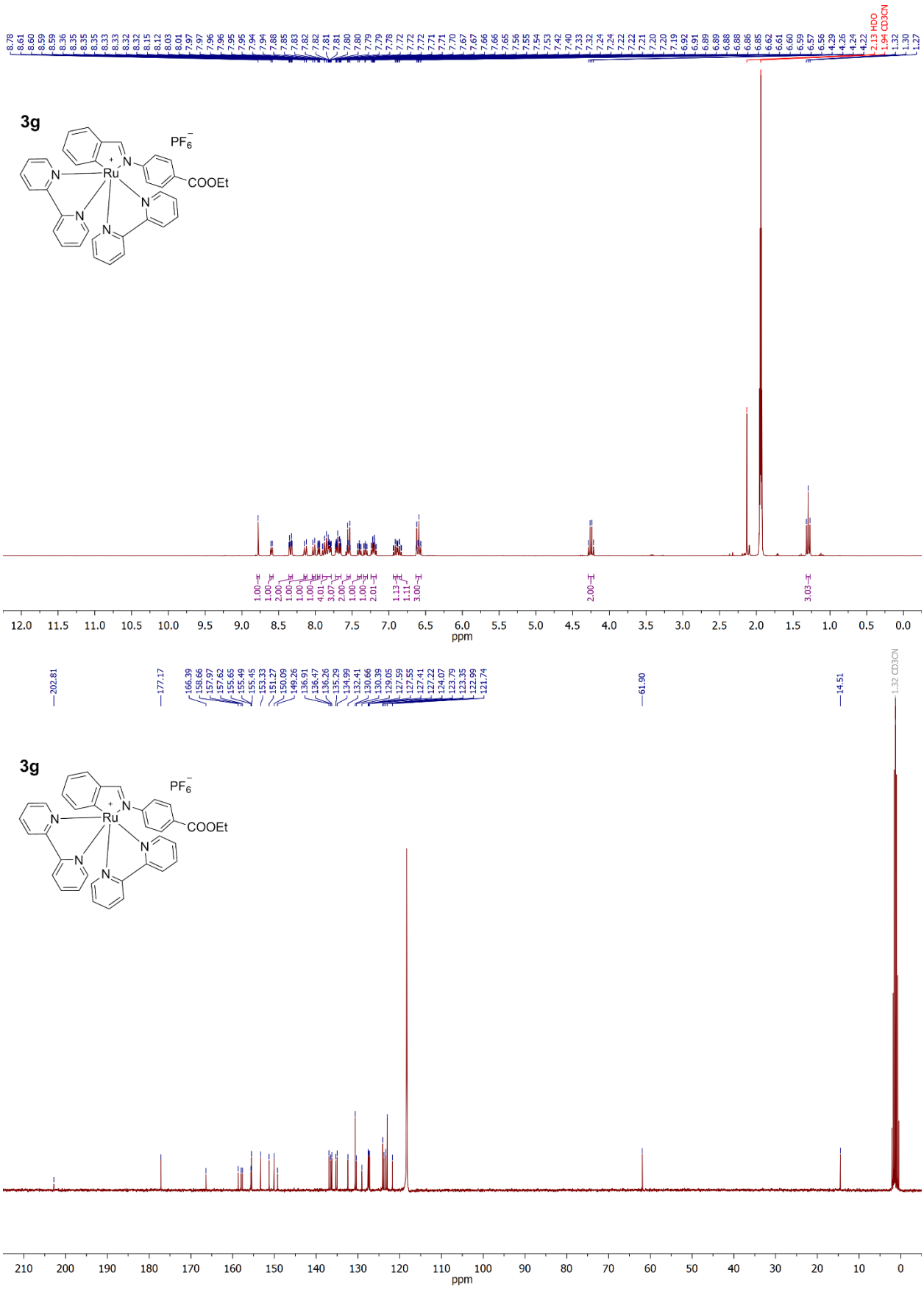



Figure S22. NMR spectra of **3g**.

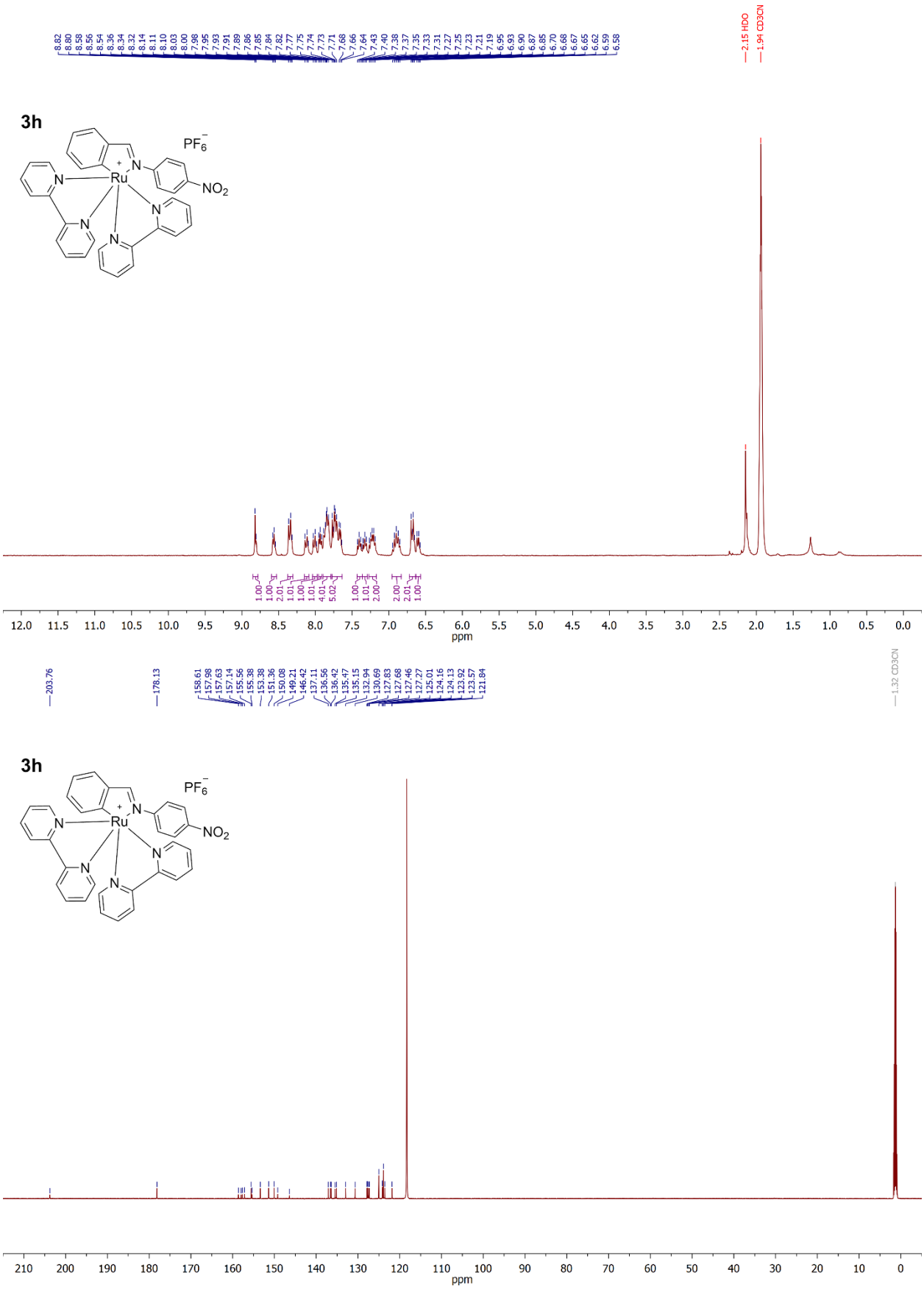



Figure S23. NMR spectra of **3h**.

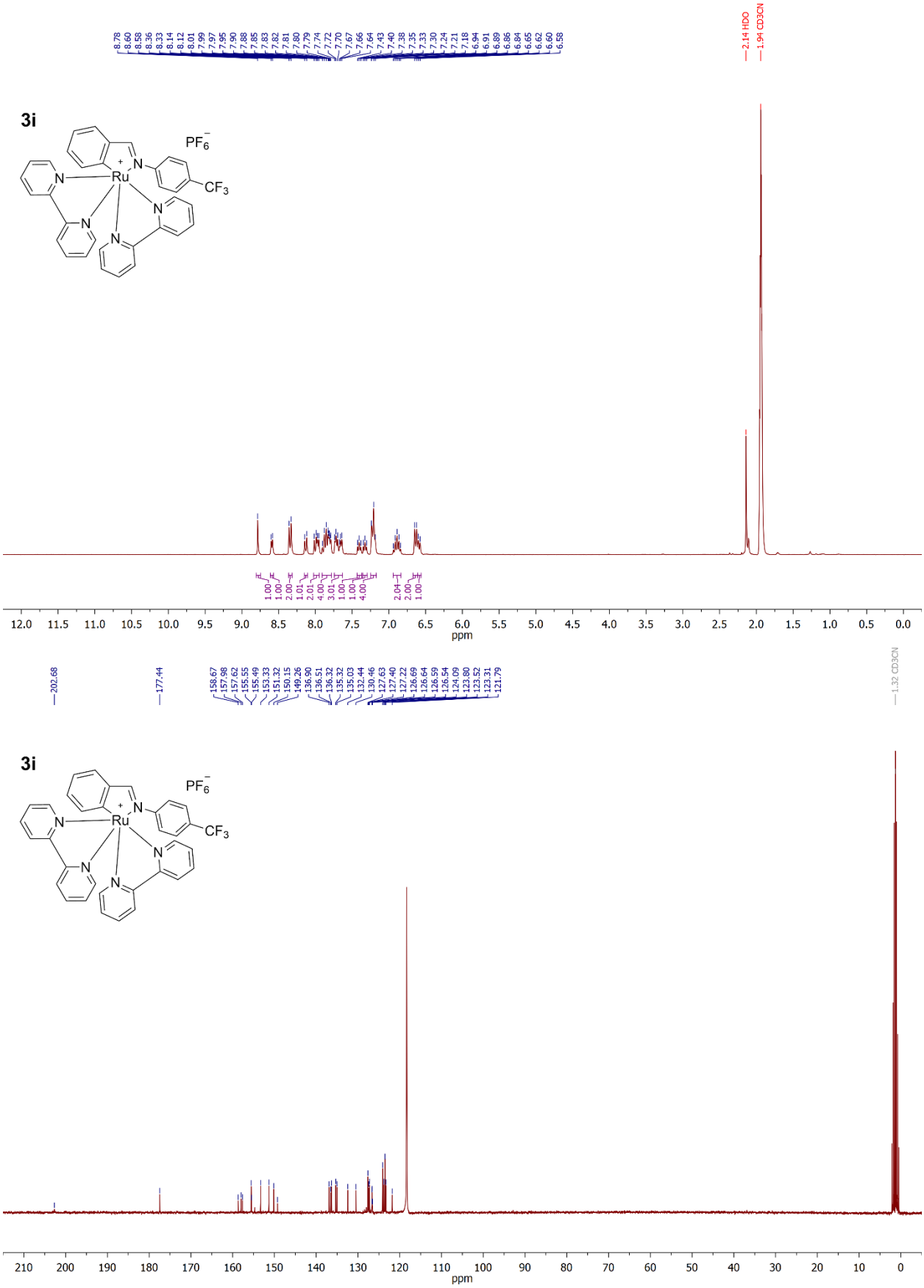



Figure S24. NMR spectra of **3i**.

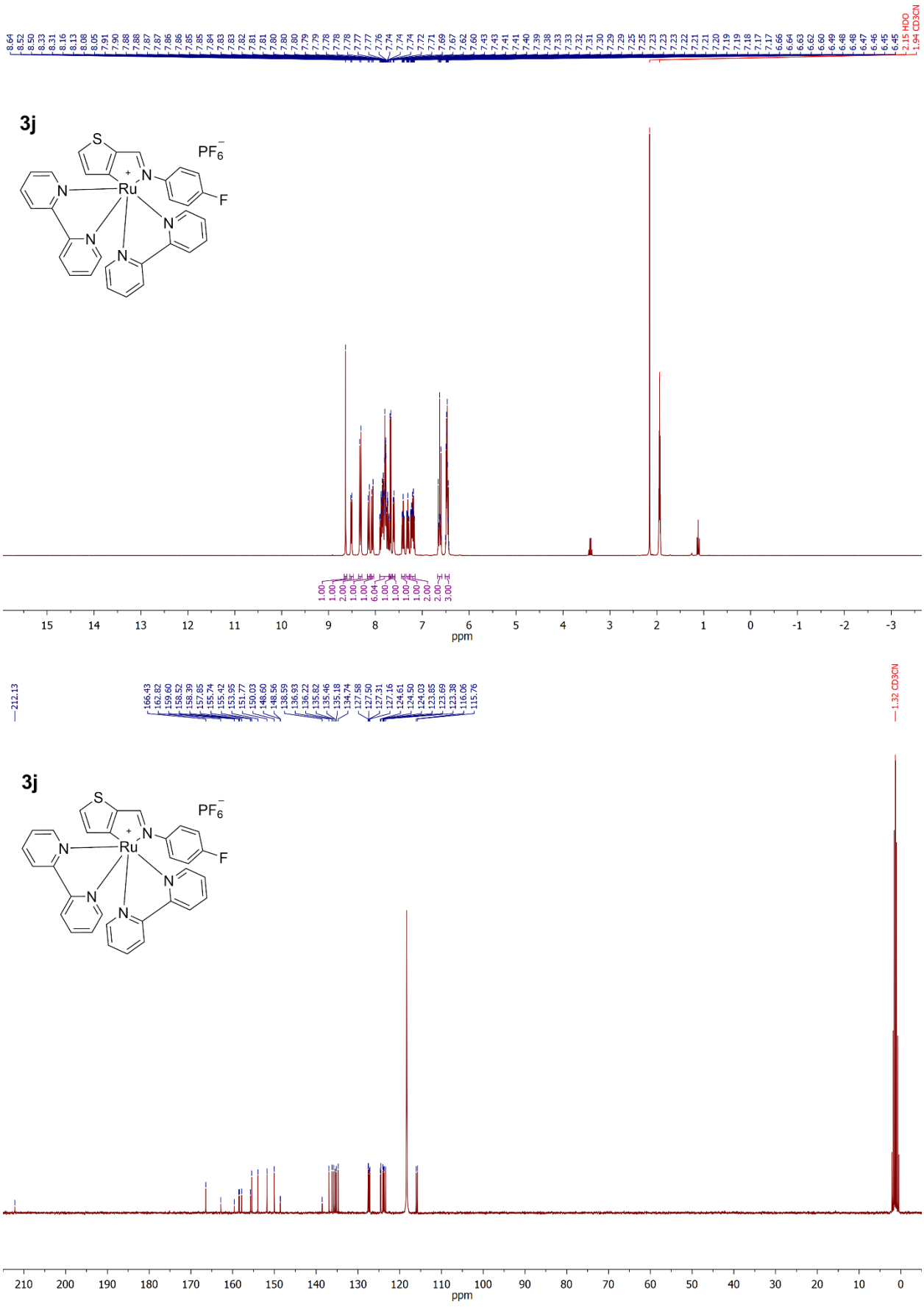



Figure S25. NMR spectra of **3j**.

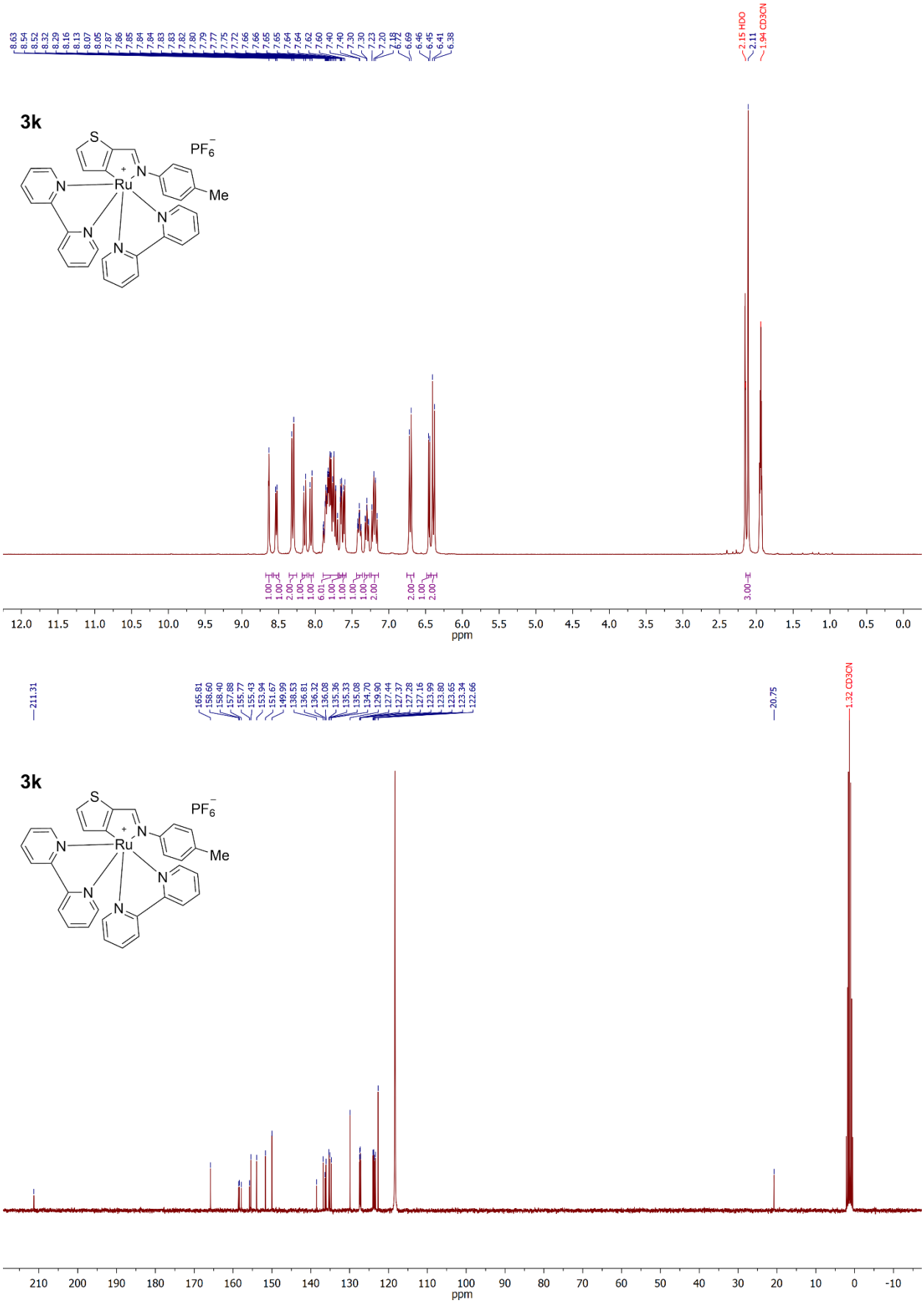



Figure S26. NMR spectra of **3k**.

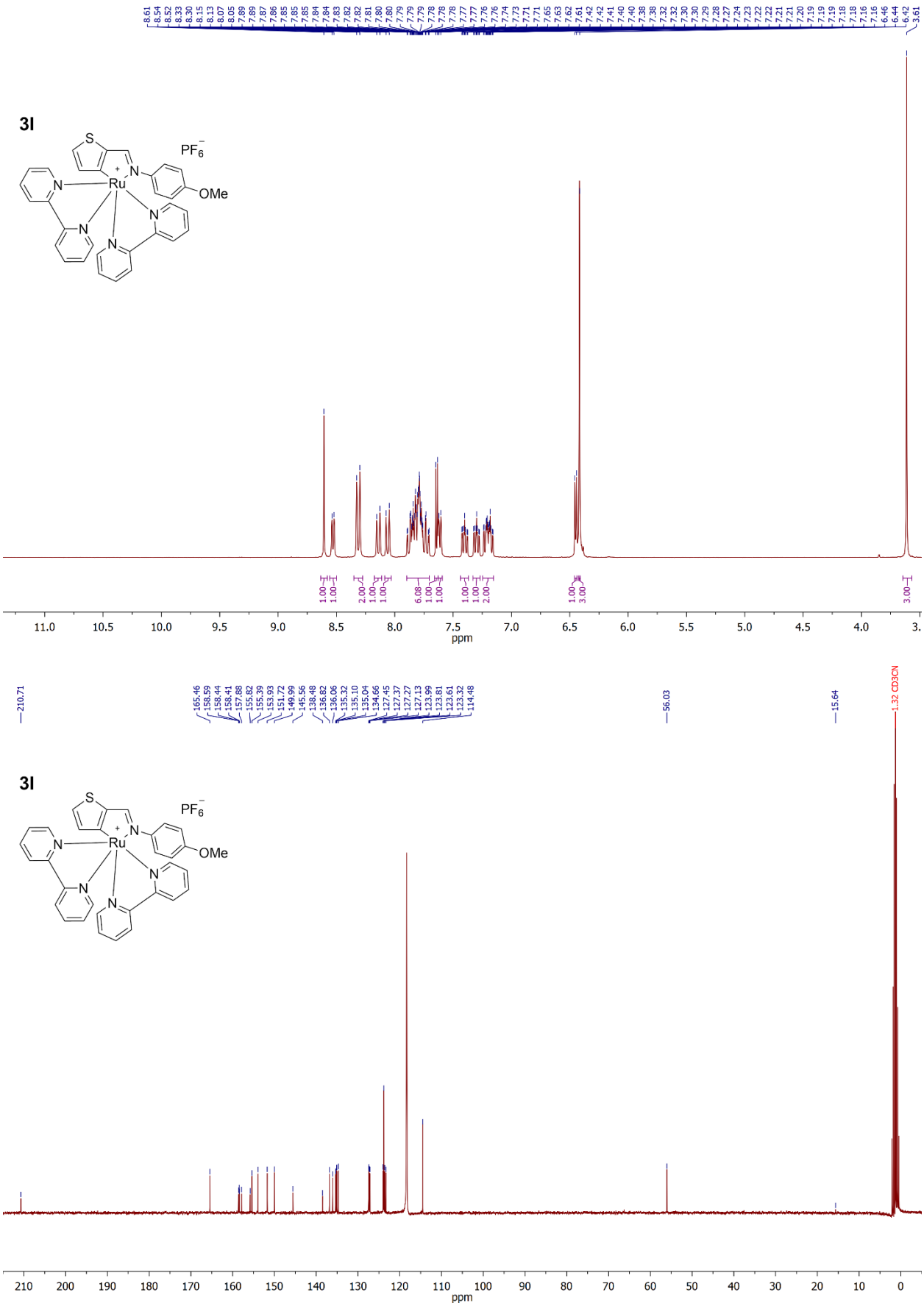



Figure S27. NMR spectra of **3l**.

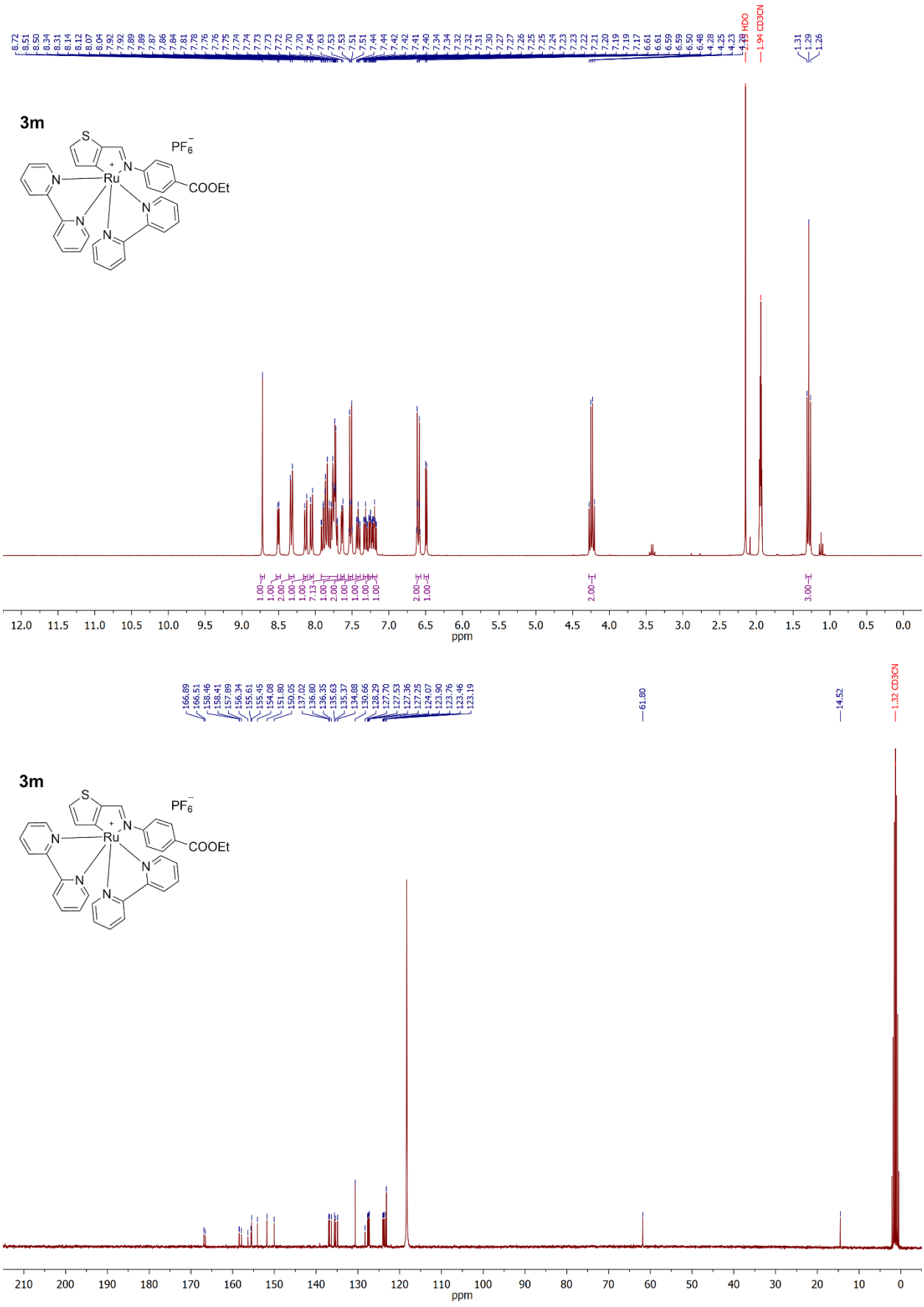



Figure S28. NMR spectra of **3m**.

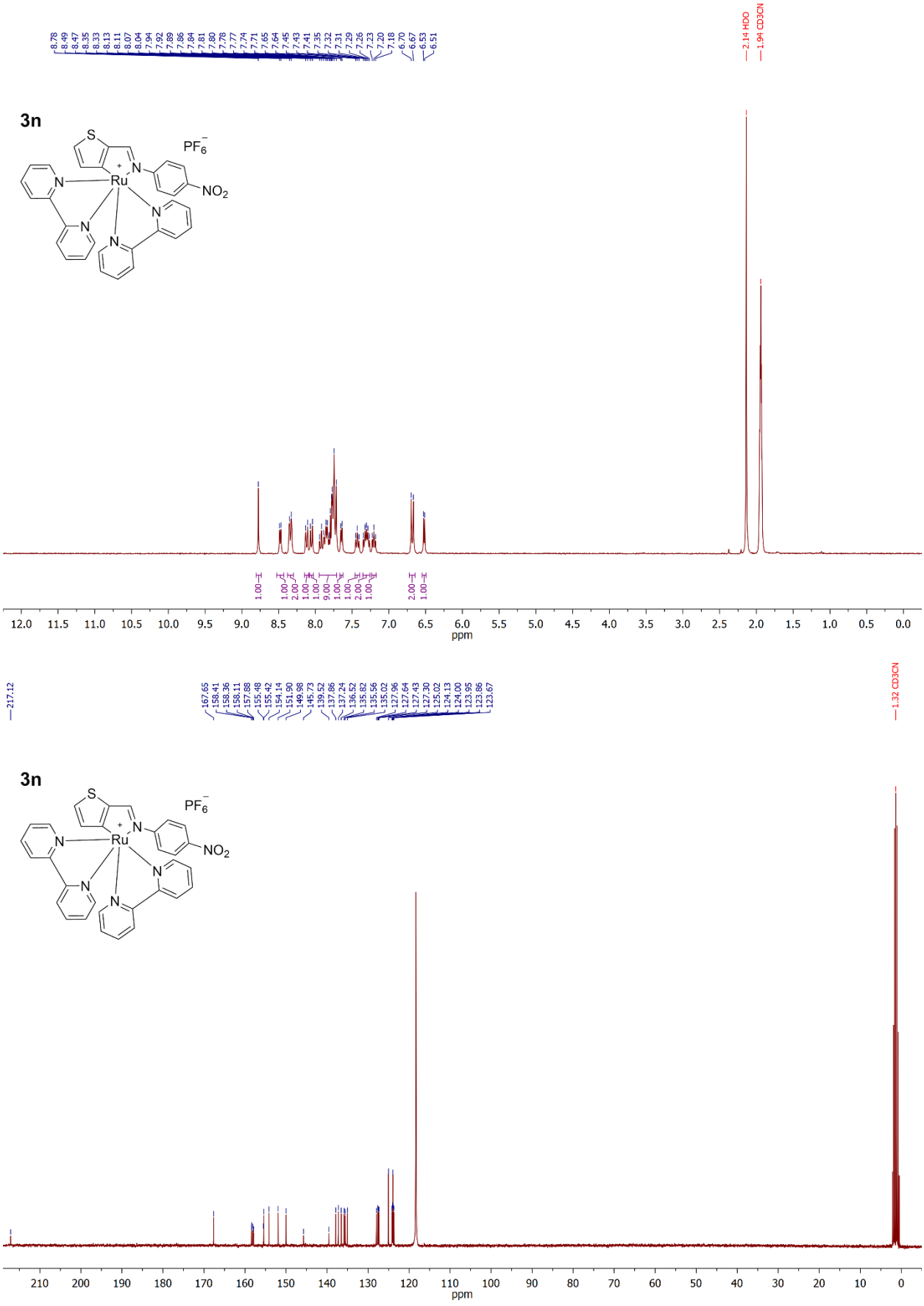



Figure S29. NMR spectra of **3n**.

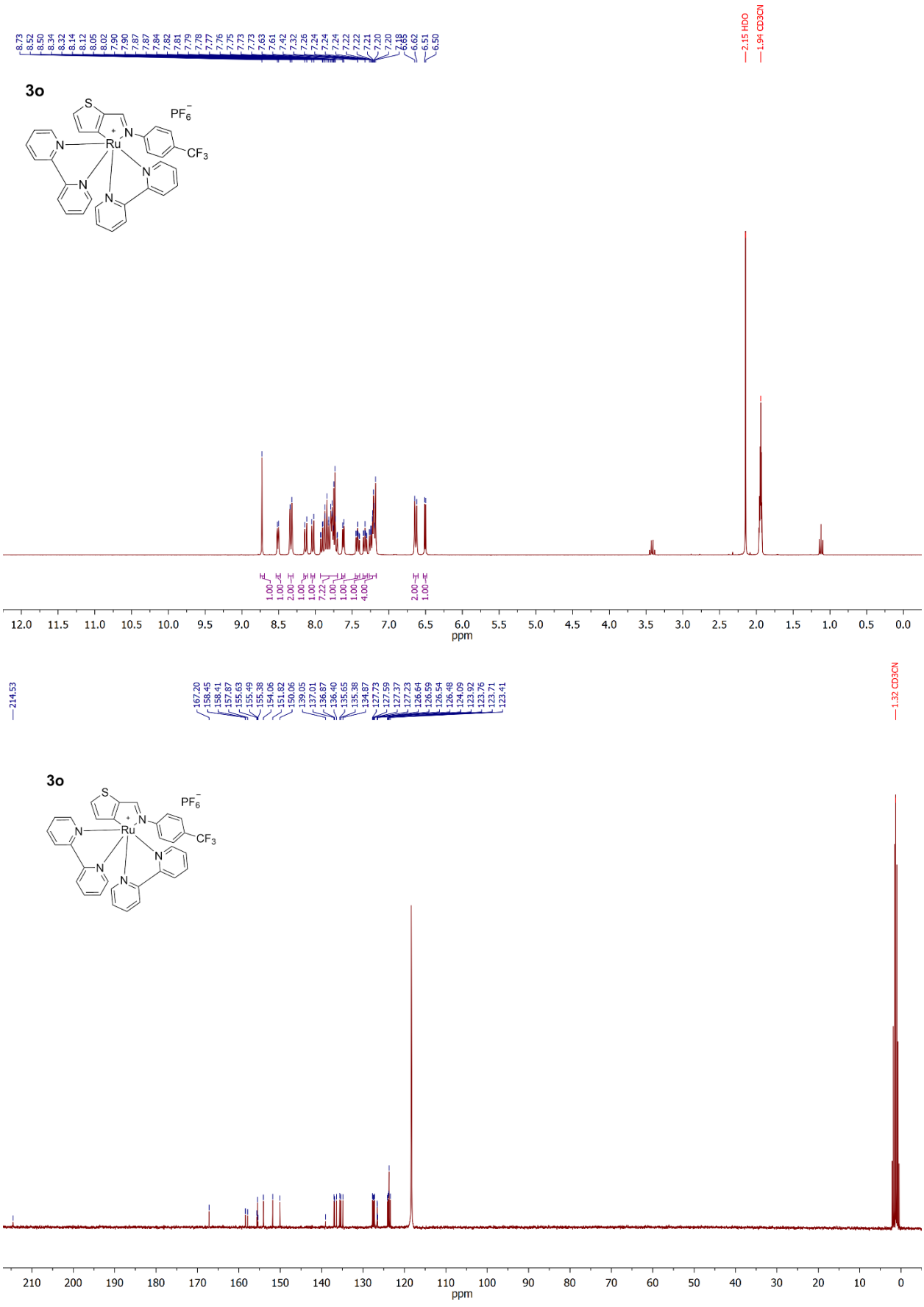



Figure S30. NMR spectra of **3o**.

**Table S1**. Structure parameters of ruthenium complexes

| | **2a***0.8$CH_3CN$ | **2b***$CH_3CN$ | **2d** | **2e** |
|---|---|---|---|---|
| Empirical formula | $C_{21.80}H_{23.20}F_6N_{5.40}PRu$ | $C_{22}H_{22.50}F_7N_{5.50}PRu$ | $C_{23}H_{26}F_6N_5PRu$ | $C_{25}H_{30}F_6N_5PRu$ |
| Formula weight | 606.90 | 628.99 | 618.53 | 646.58 |
| Temperature, K | 100.00 | 100.15 | | 100.15 |
| Wavelength, Å | 0.71073 | 1.54184 | 1.54184 | 0.71073 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Triclinic |
| Space group | P-1 | P-1 | P $2_1/c$ | P-1 |
| Unit cell dimensions | | | | |
| a, Å | 8.8365(3) | 8.8149(2) | 11.25950(10) | 8.45880(10) |
| b, Å | 11.6174(4) | 12.0070(2) | 21.85140(10) | 12.80830(10) |
| c, Å | 13.2729(5) | 13.4216(2) | 11.72570(10) | 13.41760(10) |
| $\alpha$, ° | 102.9410(10) | 104.459(2) | 90 | 92.1060(10) |
| $\beta$, ° | 102.1310(10) | 102.197(2) | 114.7490(10) | 101.5280(10) |
| $\gamma$, ° | 96.3880(10) | 99.947(2) | 90 | 99.9540(10) |
| Volume, $Å^3$ | 1280.25(8) | 1305.79(4) | 2619.96(4) | 1399.10(2) |
| Z | 2 | 2 | 4 | 2 |
| Density (calculated), $g/cm^3$ | 1.574 | 1.600 | 1.568 | 1.535 |
| Absorption coefficient, $mm^{-1}$ | 0.739 | 6.097 | 6.003 | 0.681 |
| F(000) | 610 | 630 | 1248 | 656 |
| Crystal size, $mm^3$ | 0.695 x 0.415 x 0.336 | 0.35 x 0.24 x 0.15 | 0.47 x 0.3 x 0.13 | 0.35 x 0.19 x 0.08 |
| Theta range for data collection | 2.543 to 33.175 | 3.529 to 80.124 | 4.046 to 80.037 | 2.159 to 35.304 |
| Reflections collected | 66386 | 34569 | 35764 | 66639 |
| Independent reflections | 9771 | 5649 | 5703 | 11863 |
| R(int) | 0.0261 | 0.0429 | 0.0405 | 0.0307 |
| Observed reflections | 9354 | 5539 | 5581 | 11024 |
| Data / restraints / parameters | 9771 / 784 / 326 | 5649 / 172 / 336 | 5703 / 131 / 368 | 11863 / 38 / 359 |
| Goodness-of-fit on $F^2$ | 1.054 | 1.036 | 1.051 | 1.041 |
| $R_1$ [I>2σ (I)] | 0.0288 | 0.0365 | 0.0301 | 0.0272 |
| $wR_2$ (all data) | 0.0766 | 0.0905 | 0.0753 | 0.0696 |
| Largest diff. peak and hole, e*$Å^3$ | 0.841 and -0.869 | 0.518 and -0.787 | 0.543 and -0.669 | 0.937 and -0.691 |
| CCDC number | 2502950 | 2502941 | 2502939 | 2502947 |

**Table S1** (continued). Structure parameters of ruthenium complexes

| | **2f** | **2g***0.5$Et_2O$*0.5$CH_3CN$ | **2h** | **2i** |
|---|---|---|---|---|
| Empirical formula | $C_{22}H_{24}F_6N_5OPRu$ | $C_{27}H_{32.50}F_6N_{5.50}O_{2.50}PRu$ | $C_{21}H_{21}F_6N_6O_2PRu$ | $C_{22}H_{21}F_9N_5PRu$ |
| Formula weight | 620.50 | 720.12 | 635.48 | 658.48 |
| Temperature, K | 99.99(10) | 99.97(18) | 100.15 | 99.98(13) |
| Wavelength, Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | P-1 | P c | P $2_1/c$ |
| Unit cell dimensions | | | | |
| a, Å | 8.64530(10) | 8.54460(10) | 11.61256(4) | 10.94550(10) |
| b, Å | 11.32120(10) | 17.28890(10) | 8.33269(3) | 21.59160(10) |
| c, Å | 13.8756(2) | 22.9894(2) | 26.25801(10) | 12.12600(10) |
| $\alpha$, ° | 107.6330(10) | 105.8030(10) | 90 | 90 |
| $\beta$, ° | 103.6220(10) | 96.5870(10) | 93.8689(3) | 114.8150(10) |
| $\gamma$, ° | 91.2860(10) | 101.5920(10) | 90 | 90 |
| Volume, $Å^3$ | 1251.40(3) | 3148.99(5) | 2535.036(16) | 2601.15(4) |
| Z | 2 | 4 | 4 | |
| Density (calculated), $g/cm^3$ | 1.647 | 1.519 | 1.665 | 1.681 |
| Absorption coefficient, $mm^{-1}$ | 6.318 | 5.148 | 6.298 | 6.262 |
| F(000) | 624 | 1464 | 1272 | 1312 |
| Crystal size, $mm^3$ | 0.88 x 0.53 x 0.2 | 0.59 x 0.45 x 0.06 | 0.442 x 0.216 x 0.104 | 0.28 x 0.27 x 0.16 |
| Theta range for data collection | 3.456 to 80.408 | 2.738 to 80.128 | 3.374 to 80.131 | 4.095 to 80.049 |
| Reflections collected | 33371 | 84174 | 66221 | 35846 |
| Independent reflections | 5411 | 13614 | 10703 | 5662 |
| R(int) | 0.0516 | 0.0435 | 0.0402 | 0.0376 |
| Observed reflections | 5386 | 13295 | 10675 | 5633 |
| Data / restraints / parameters | 5411 / 70 / 323 | 13614 / 99 / 834 | 10703 / 44 / 661 | 5662 / 24 / 338 |
| Goodness-of-fit on $F^2$ | 1.110 | 1.039 | 1.032 | 1.053 |
| $R_1$ [I>2σ (I)] | 0.0370 | 0.0344 | 0.0306 | 0.0338 |
| $wR_2$ (all data) | 0.0954 | 0.0888 | 0.0793 | 0.0797 |
| Largest diff. peak and hole, e*$Å^3$ | 0.974 and -1.046 | 0.871 and -0.791 | 0.715 and -0.699 | 0.912 and -0.967 |
| CCDC number | 2502937 | 2502951 | 2502949 | 2502940 |

**Table S1** (continued). Structure parameters of ruthenium complexes

| | **2j** | **2k** | **2l** | **2n** |
|---|---|---|---|---|
| Empirical formula | $C_{19}H_{19}F_7N_5PRuS$ | $C_{20}H_{22}F_6N_5PRuS$ | $C_{20}H_{22}F_6N_5OPRuS$ | $C_{19}H_{19}F_6N_6O_2PRuS$ |
| Formula weight | 614.49 | 610.52 | 626.52 | 641.50 |
| Temperature, K | 100.00(10) | 100.00(10) | 100.00(10) | 100.00(10) |
| Wavelength, Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 | P-1 |
| Unit cell dimensions | | | | |
| a, Å | 8.44380(10) | 8.49400(10) | 10.6030(2) | 8.4253(3) |
| b, Å | 11.21030(10) | 11.82980(10) | 10.8966(2) | 12.0245(4) |
| c, Å | 13.8196(2) | 13.85960(10) | 24.7104(3) | 13.6424(7) |
| $\alpha$, ° | 103.9940(10) | 107.1030(10) | 81.3310(10) | 107.573(4) |
| $\beta$, ° | 107.5030(10) | 107.5780(10) | 88.6410(10) | 106.241(4) |
| $\gamma$, ° | 95.7790(10) | 97.5610(10) | 63.214(2) | 97.271(3) |
| Volume, $Å^3$ | 1189.09(3) | 1231.22(2) | 2516.33(8) | 1230.96(9) |
| Z | 2 | 2 | 4 | 2 |
| Density (calculated), $g/cm^3$ | 1.716 | 1.647 | 1.654 | 1.731 |
| Absorption coefficient, $mm^{-1}$ | 7.472 | 7.150 | 7.045 | 7.263 |
| F(000) | 612 | 612 | 1256 | 640 |
| Crystal size, $mm^3$ | 0.42 x 0.157 x 0.143 | 0.316 x 0.126 x 0.027 | 0.772 x 0.489 x 0.365 | 0.224 x 0.199 x 0.04 |
| Theta range for data collection | 3.500 to 80.096 | 3.576 to 80.030 | 3.623 to 80.098 | 3.608 to 79.970 |
| Reflections collected | 31531 | 32933 | 67133 | 31040 |
| Independent reflections | 5148 | 5330 | 10879 | 5325 |
| R(int) | 0.0399 | 0.0370 | 0.0684 | 0.0371 |
| Observed reflections | 5098 | 5222 | 10569 | 5231 |
| Data / restraints / parameters | 5148 / 55 / 357 | 5330 / 127 / 350 | 10879 / 0 / 642 | 5325 / 557 / 373 |
| Goodness-of-fit on $F^2$ | 1.081 | 1.078 | 1.133 | 1.080 |
| $R_1$ [$I>2\sigma(I)$] | 0.0274 | 0.0318 | 0.0432 | 0.0347 |
| $wR_2$ (all data) | 0.0716 | 0.0809 | 0.1150 | 0.0917 |
| Largest diff. peak and hole, $e*Å^3$ | 0.624 and -0.637 | 0.737 and -0.729 | 1.388 and -1.622 | 0.897 and -0.981 |
| CCDC number | 2502936 | 2502938 | 2502948 | 2502935 |

**Table S1** (continued). Structure parameters of ruthenium complexes

| | **3a***CH3CN | **3b***$Et_2O$ | **3c***1.5$Et_2O$ | **3e***$CH_3CN$ |
|---|---|---|---|---|
| Empirical formula | $C_{35}H_{29}F_6N_6PRu$ | $C_{37}H_{35}F_7N_5OPRu$ | $C_{37}H_{35.50}F_6N_5O_{0.75}PRu$ | $C_{39}H_{37}F_6N_6PRu$ |
| Formula weight | 779.68 | 830.74 | 808.24 | 835.78 |
| Temperature, K | 99.97(13) | 99.97(15) | 100.0(2) | 100.00 |
| Wavelength, Å | 1.54184 | 1.54184 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | P $2_1$/n | P-1 | P-1 | P-1 |
| Unit cell dimensions | | | | |
| a, Å | 11.98880(10) | 12.4931(2) | 11.1184(2) | 11.7141(2) |
| b, Å | 13.08430(10) | 13.2824(2) | 12.9449(2) | 12.5133(2) |
| c, Å | 20.89010(10) | 13.5109(2) | 13.0295(2) | 12.9723(2) |
| $\alpha$, ° | 90 | 100.0660(10) | 83.2850(10) | 83.7450(10) |
| $\beta$, ° | 92.9950(10) | 116.292(2) | 75.7620(10) | 89.7810(10) |
| $\gamma$, ° | 90 | 111.075(2) | 71.9200(10) | 71.7860(10) |
| Volume, $Å^3$ | 3272.45(4) | 1719.56(6) | 1726.26(5) | 1794.56(5) |
| Z | 4 | 2 | 2 | 2 |
| Density (calculated), $g/cm^3$ | 1.583 | 1.604 | 1.555 | 1.547 |
| Absorption coefficient, $mm^{-1}$ | 4.959 | 4.813 | 0.571 | 0.551 |
| F(000) | 1576 | 844 | 823 | 852 |
| Crystal size, $mm^3$ | 0.631 x 0.256 x 0.146 | 0.63 x 0.33 x 0.19 | 0.61 x 0.28 x 0.1 | 0.423 x 0.318 x 0.214 |
| Theta range for data collection | 3.988 to 80.170 | 3.890 to 80.034 | 2.176 to 35.385 | 2.084 to 33.197 |
| Reflections collected | 45013 | 45842 | 82597 | 111797 |
| Independent reflections | 7134 | 7422 | 14589 | 13707 |
| R(int) | 0.0407 | 0.0499 | 0.0430 | 0.0348 |
| Observed reflections | 7008 | 7353 | 13128 | 12549 |
| Data / restraints / parameters | 7134 / 3 / 455 | 7422 / 21 / 463 | 14589 / 64 / 440 | 13707 / 0 / 482 |
| Goodness-of-fit on $F^2$ | 1.117 | 1.048 | 1.044 | 1.041 |
| $R_1$ [I>2σ (I)] | 0.0333 | 0.0404 | 0.0321 | 0.0239 |
| $wR_2$ (all data) | 0.0935 | 0.1060 | 0.0847 | 0.0590 |
| Largest diff. peak and hole, e*$Å^3$ | 1.044 and -1.356 | 1.355 and -1.200 | 1.440 and -0.664 | 0.551 and -0.675 |
| CCDC number | 2502943 | 2502942 | 2502952 | 2502954 |

**Table S1** (continued). Structure parameters of ruthenium complexes

| | **3f***$CH_3CN$ | **3h***$CH_3CN$ | **3j***$CH_3CN$ | **3l***$CH_3CN$ |
|---|---|---|---|---|
| Empirical formula | $C_{36}H_{31}F_6N_6OPRu$ | $C_{35}H_{28}F_6N_7O_2PRu$ | $C_{33}H_{26}F_7N_6PRuS$ | $C_{34}H_{29}F_6N_6OPRuS$ |
| Formula weight | 809.71 | 824.68 | 803.70 | 815.73 |
| Temperature, K | 99.98(13) | 100.15 | 100.00(10) | 100.00 |
| Wavelength, Å | 1.54184 | 1.54184 | 1.54184 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | P $2_1/n$ | P $2_1/n$ | P $2_1/n$ | P-1 |
| Unit cell dimensions | | | | |
| a, Å | 13.11770(6) | 13.04570(10) | 12.15020(10) | 11.1999(2) |
| b, Å | 11.20731(5) | 11.09040(10) | 13.10690(10) | 11.8657(2) |
| c, Å | 23.18196(9) | 23.69180(10) | 20.49870(10) | 13.0164(2) |
| $\alpha$, ° | 90 | 90 | 90 | 89.3440(10) |
| $\beta$, ° | 97.3765(4) | 99.6870(10) | 94.9890(10) | 75.8140(10) |
| $\gamma$, ° | 90 | 90 | 90 | 75.7930(10) |
| Volume, $Å^3$ | 3379.87(2) | 3378.90(4) | 3252.08(4) | 1623.58(5) |
| Z | 4 | 4 | 4 | 2 |
| Density (calculated), $g/cm^3$ | 1.591 | 1.621 | 1.641 | 1.669 |
| Absorption coefficient, $mm^{-1}$ | 4.848 | 4.895 | 5.640 | 0.671 |
| F(000) | 1640 | 1664 | 1616 | 824 |
| Crystal size, $mm^3$ | 0.274 x 0.222 x 0.077 | 0.5 x 0.28 x 0.11 | 0.56 x 0.406 x 0.319 | 0.449 x 0.314 x 0.172 |
| Theta range for data collection | 3.683 to 80.004 | 3.634 to 80.007 | 4.008 to 80.000 | 1.937 to 33.227 |
| Reflections collected | 47084 | 47102 | 44852 | 109729 |
| Independent reflections | 7341 | 7360 | 7076 | 12446 |
| R(int) | 0.0376 | 0.0341 | 0.0457 | 0.0362 |
| Observed reflections | 7125 | 7230 | 7005 | 11436 |
| Data / restraints / parameters | 7341 / 649 / 477 | 7360 / 784 / 486 | 7076 / 45 / 477 | 12446 / 623 / 468 |
| Goodness-of-fit on $F^2$ | 1.019 | 1.058 | 1.118 | 1.033 |
| $R_1$ [I>2σ (I)] | 0.0290 | 0.0328 | 0.0333 | 0.0258 |
| $wR_2$ (all data) | 0.0722 | 0.0835 | 0.0810 | 0.0630 |
| Largest diff. peak and hole, e*$Å^3$ | 0.663 and -0.629 | 0.676 and -0.845 | 0.720 and -0.697 | 0.777 and -0.676 |
| CCDC number | 2502946 | 2502945 | 2502944 | 2502953 |

**Table S1** (continued). Structure parameters of ruthenium complexes

| | **3m***1.25$CH_3CN$ | **3o** | **1n** |
|---|---|---|---|
| Empirical formula | $C_{35.24}H_{29.88}F_6N_{5.62}O_2PRuS$ | $C_{32}H_{23}F_9N_5PRuS$ | $C_{11}H_8N_2O_2S$ |
| Formula weight | 842.19 | 812.65 | 232.25 |
| Temperature, K | 100.00 | 100.00 | 100.00(10) |
| Wavelength, Å | 0.71073 | 0.71073 | 1.54184 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | P-1 | P-1 | C 2/c |
| Unit cell dimensions | | | |
| a, Å | 12.8277(5) | 9.9059(4) | 9.27410(10) |
| b, Å | 13.2553(5) | 12.5785(5) | 11.99550(10) |
| c, Å | 13.3198(5) | 13.7546(6) | 18.4996(2) |
| $\alpha$, ° | 118.3860(10) | 80.180(2) | 90 |
| $\beta$, ° | 114.0610(10) | 77.243(2) | 92.6890(10) |
| $\gamma$, ° | 91.9430(10) | 70.897(2) | 90 |
| Volume, $Å^3$ | 1744.75(12) | 1570.48(11) | 2055.77(4) |
| Z | 2 | 2 | 8 |
| Density (calculated), $g/cm^3$ | 1.603 | 1.719 | 1.501 |
| Absorption coefficient, $mm^{-1}$ | 0.629 | 0.704 | 2.692 |
| F(000) | 851 | 812 | 960 |
| Crystal size, $mm^3$ | 0.28 x 0.21 x 0.12 | 0.568 x 0.235 x 0.186 | 0.356 x 0.321 x 0.18 |
| Theta range for data collection | 2.175 to 33.194 | 1.723 to 33.324 | 4.786 to 80.024 |
| Reflections collected | 119201 | 112703 | 14187 |
| Independent reflections | 13338 | 12017 | 2247 |
| R(int) | 0.0349 | 0.0578 | 0.0356 |
| Observed reflections | 12367 | 10140 | 2184 |
| Data / restraints / parameters | 13338 / 1346 / 524 | 12017 / 0 / 442 | 2247 / 0 / 146 |
| Goodness-of-fit on $F^2$ | 1.042 | 1.039 | 1.071 |
| $R_1$ [I>2σ (I)] | 0.0321 | 0.0403 | 0.0336 |
| $wR_2$ (all data) | 0.0793 | 0.0982 | 0.0922 |
| Largest diff. peak and hole, e*$Å^3$ | 0.924 and -0.900 | 1.015 and -1.396 | 0.322 and -0.265 |
| CCDC number | 2502956 | 2502955 | 2502934 |

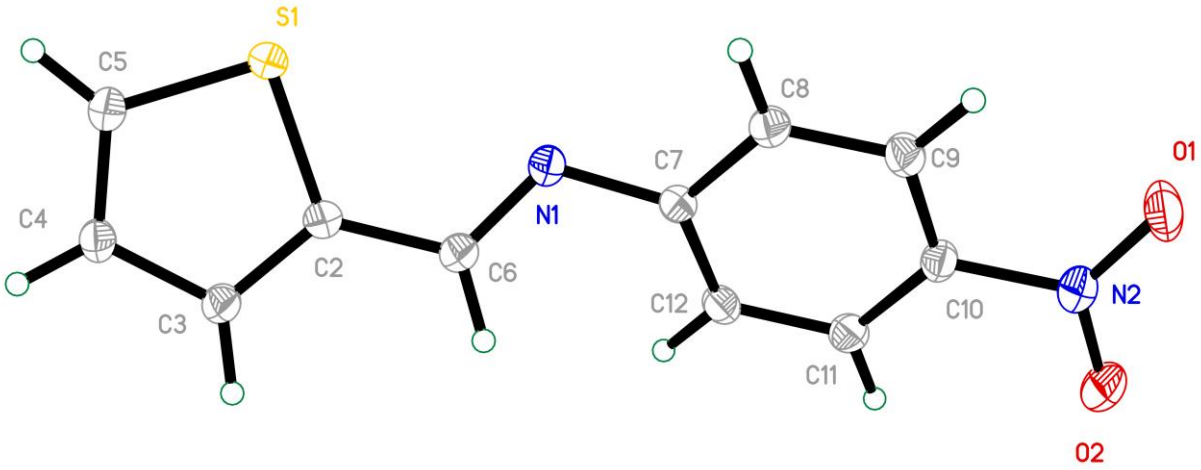



Figure S31. Crystal structure of **1n**.

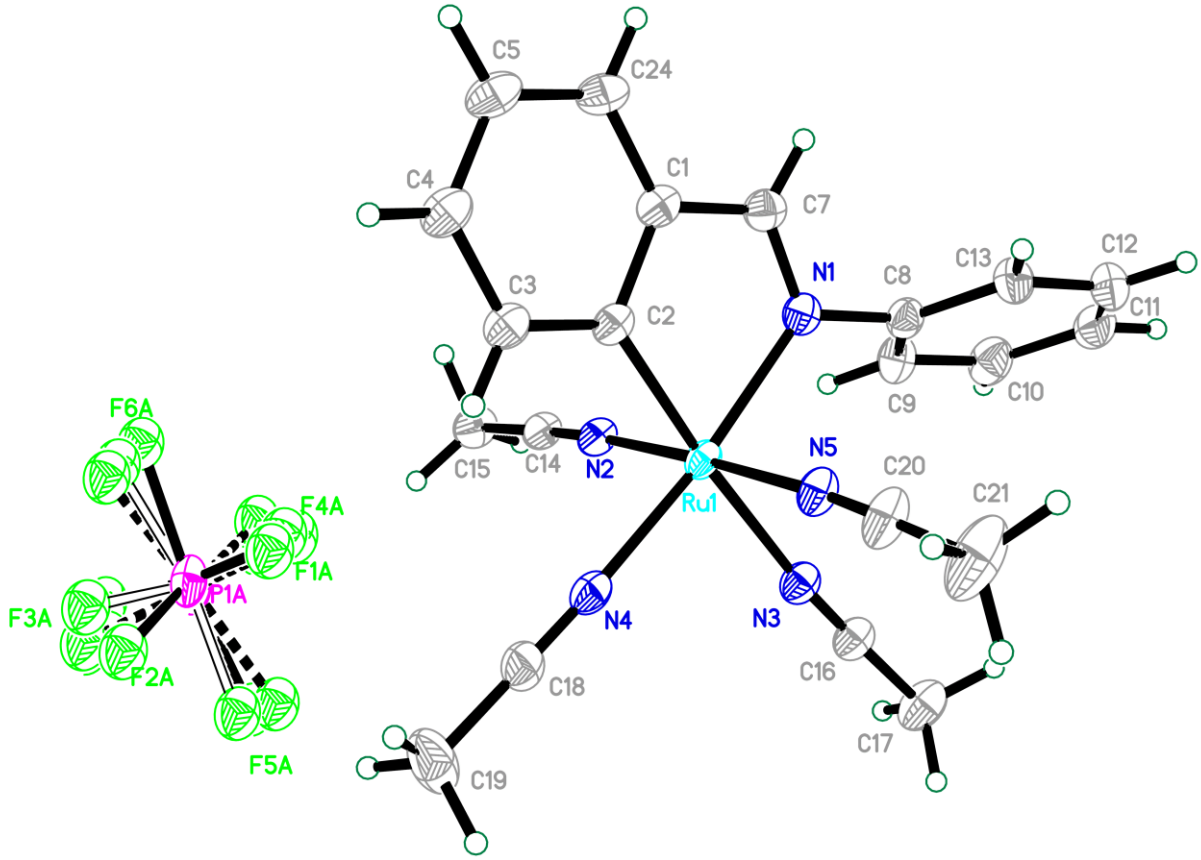



Figure S32. Crystal structure of **2a**.

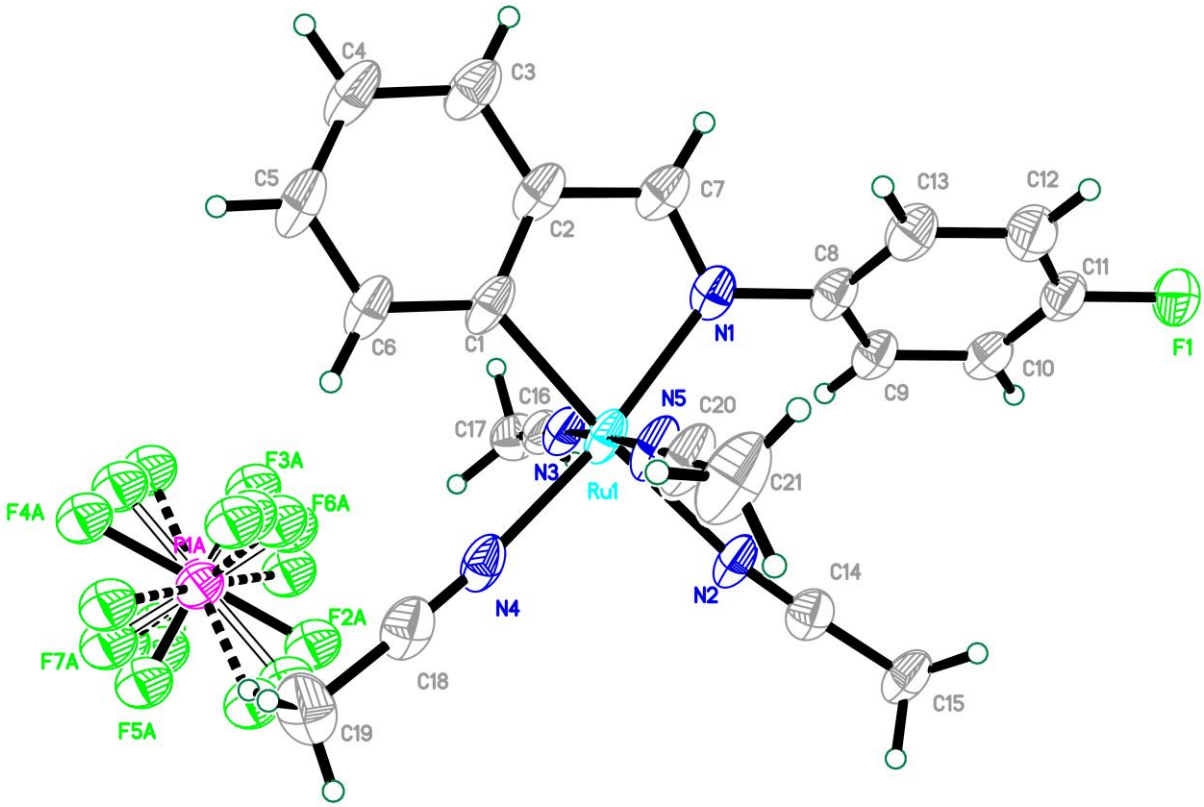



Figure S33. Crystal structure of **2b**.

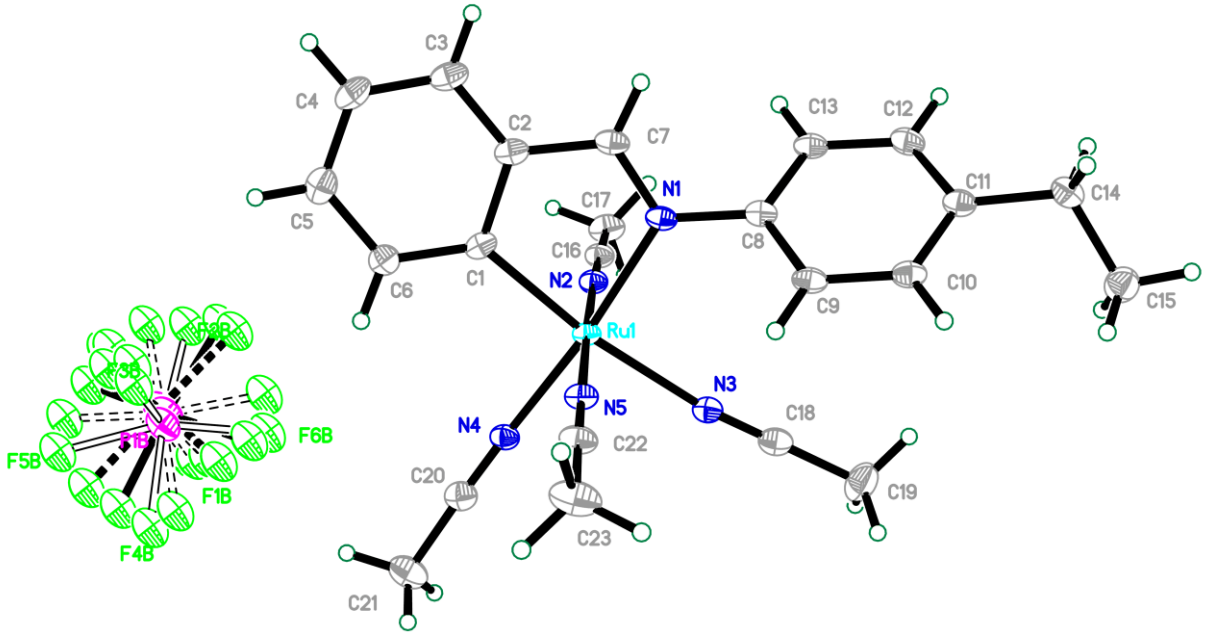



Figure S34. Crystal structure of **2d**.

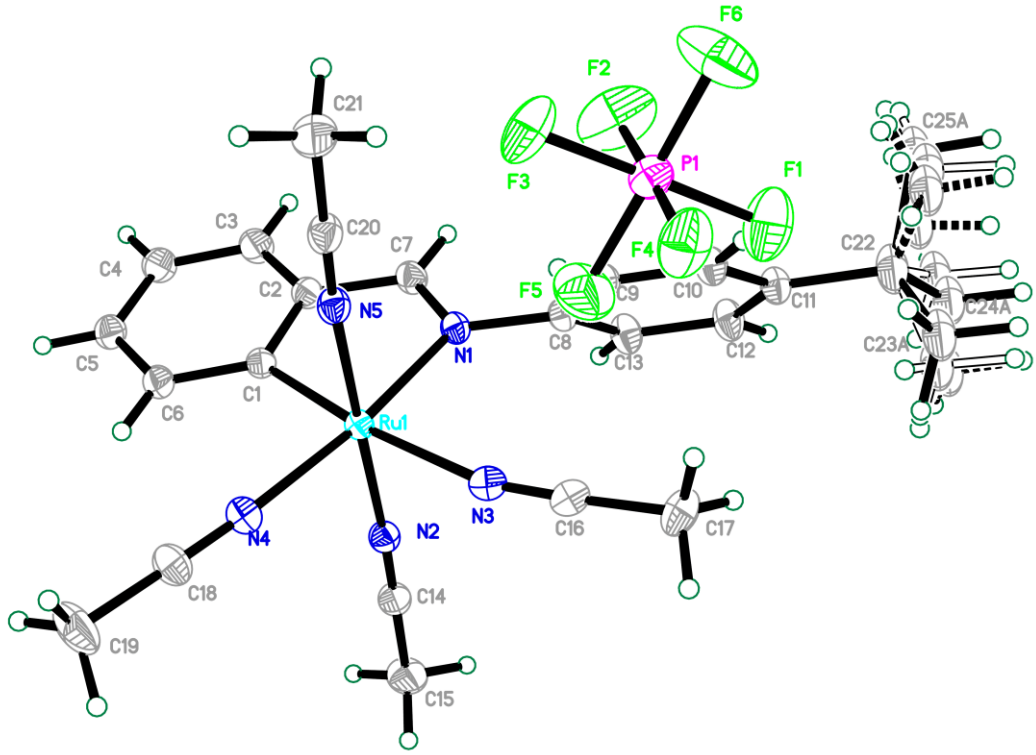



Figure S35. Crystal structure of **2e**.

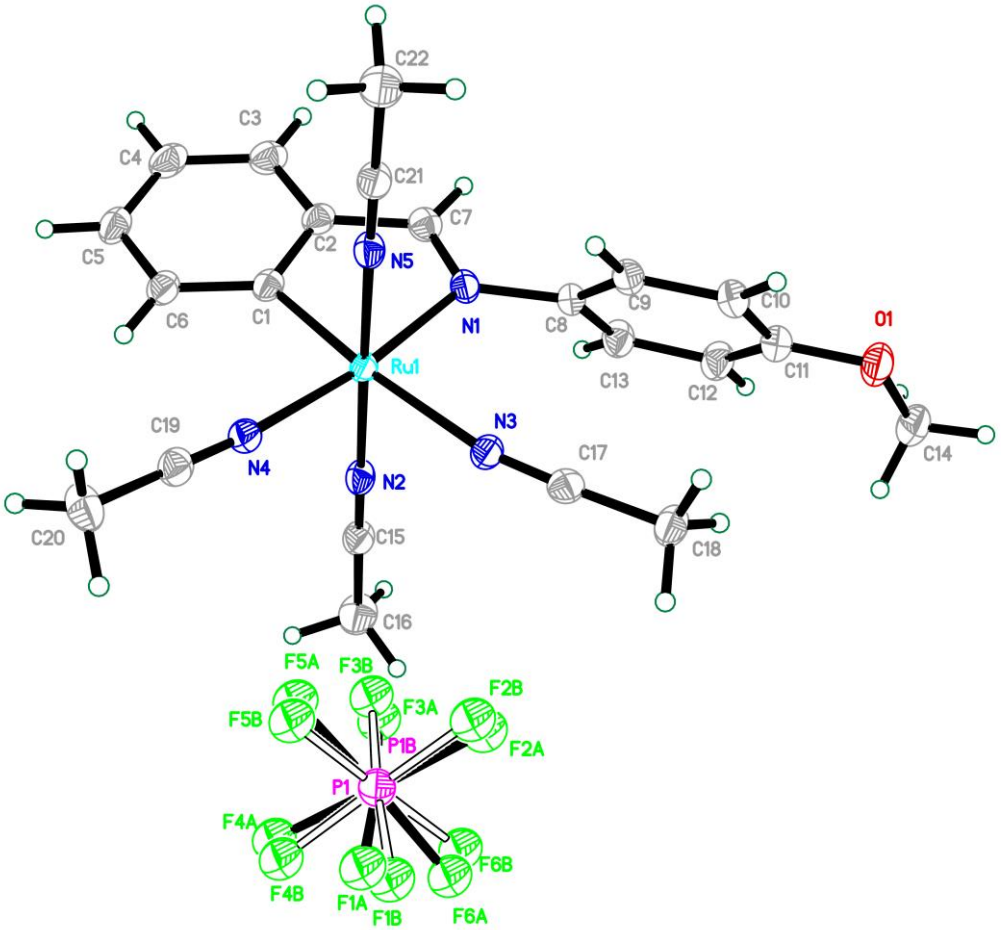



Figure S36. Crystal structure of **2f**.

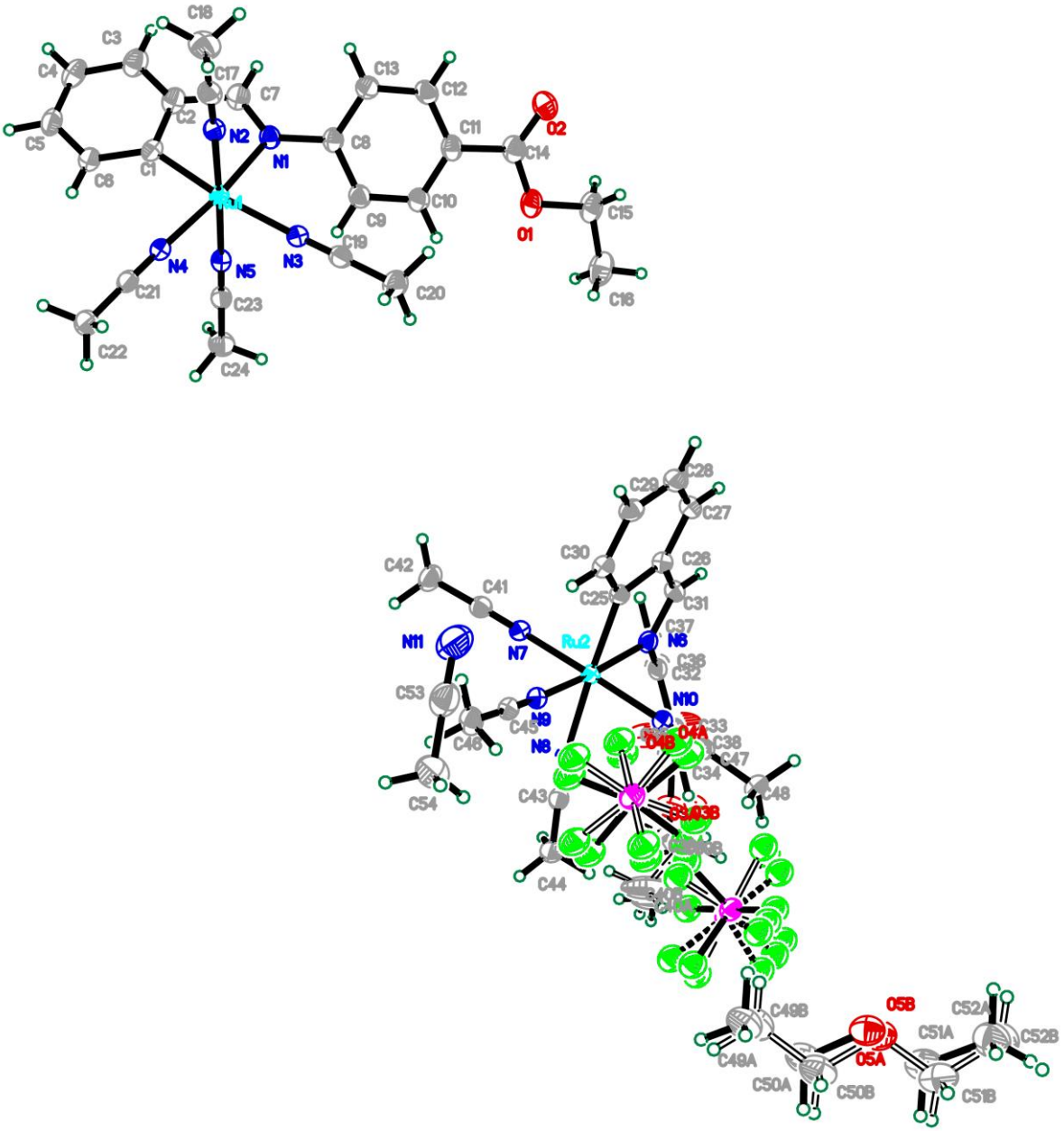



Figure S37. Crystal structure of **2g**.

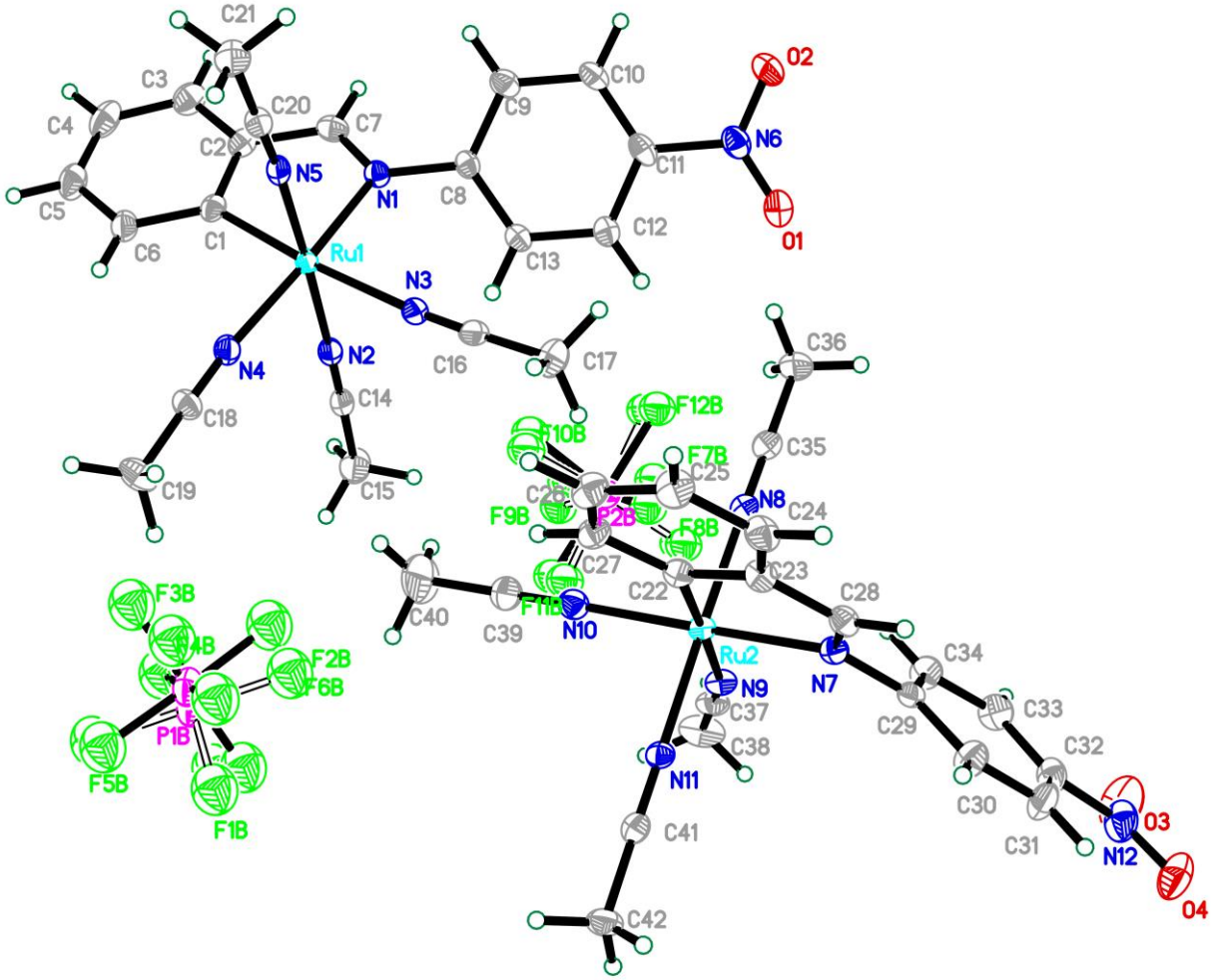



Figure S38. Crystal structure of **2h**.

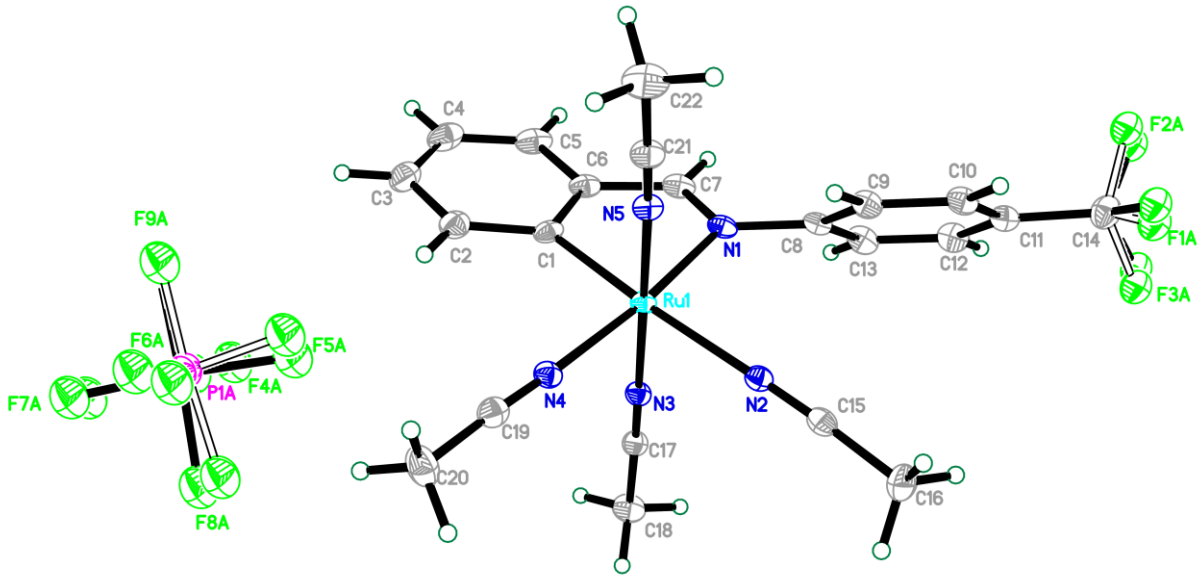



Figure S39. Crystal structure of **2i**.

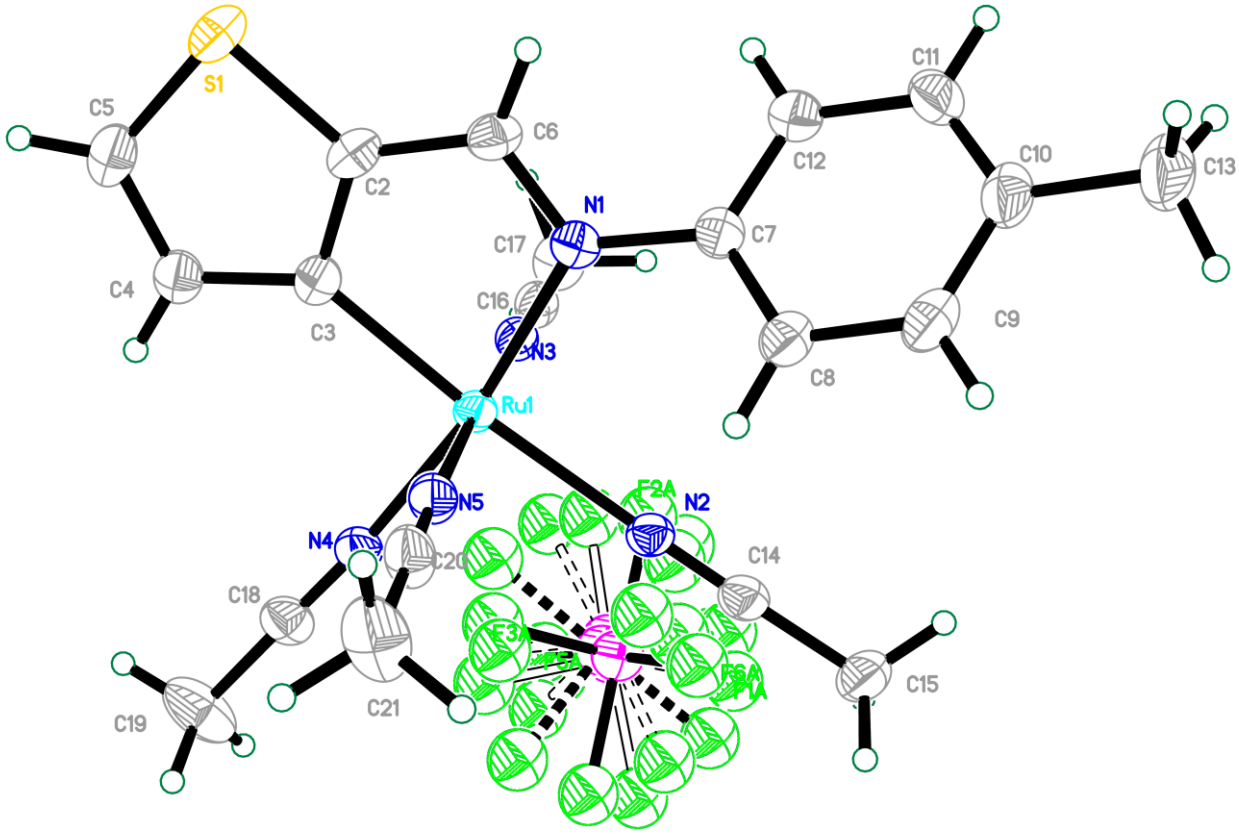



Figure S40. Crystal structure of **2k**.

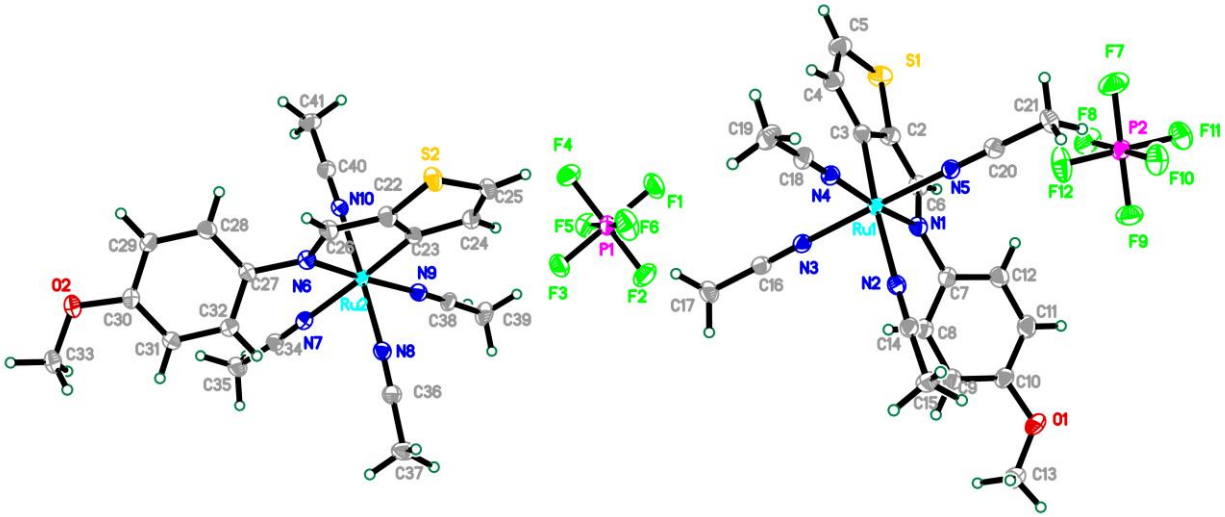



Figure S41. Crystal structure of **2l**.

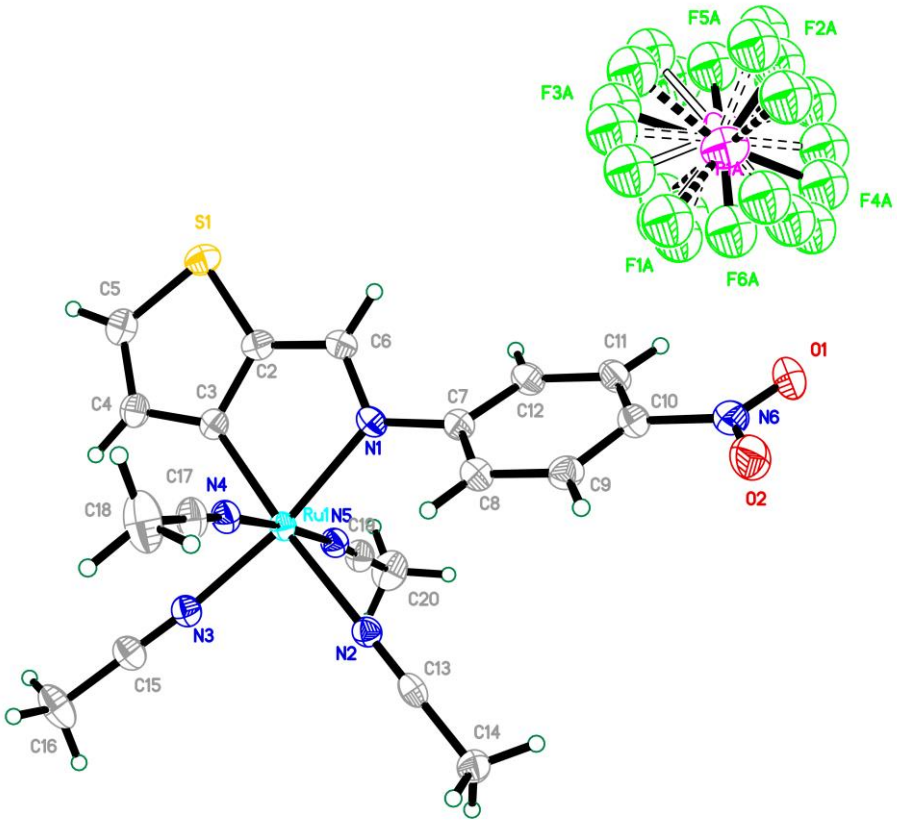



Figure S42. Crystal structure of **2m**.

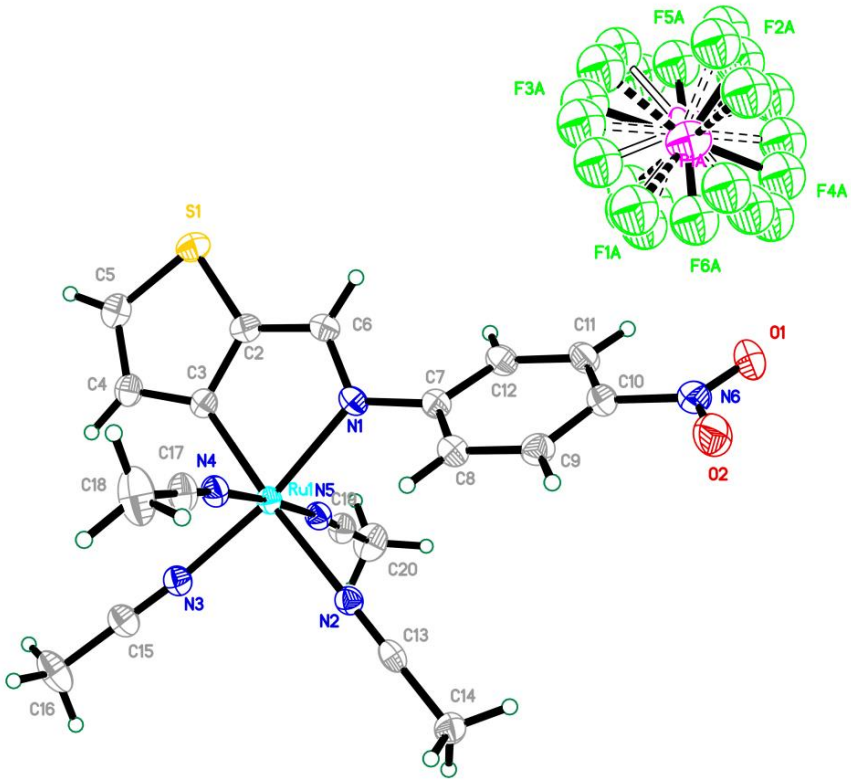



Figure S43. Crystal structure of **2n**.

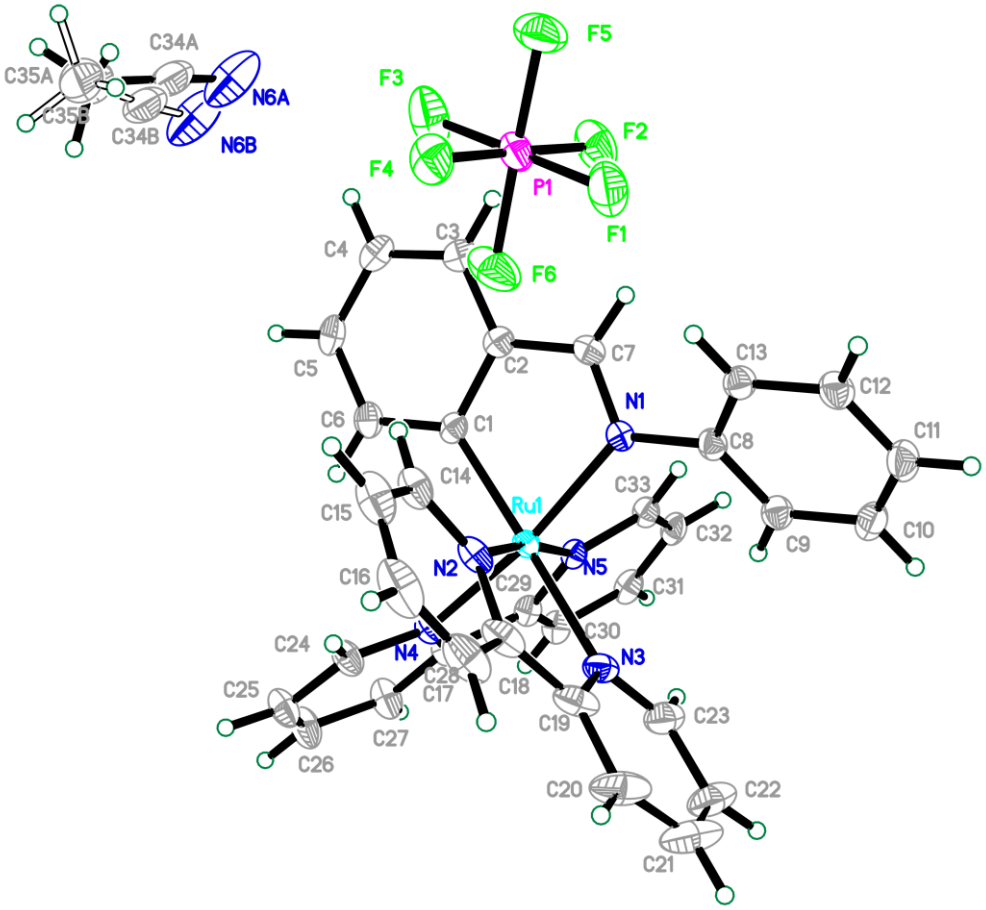



Figure S44. Crystal structure of **3a**.

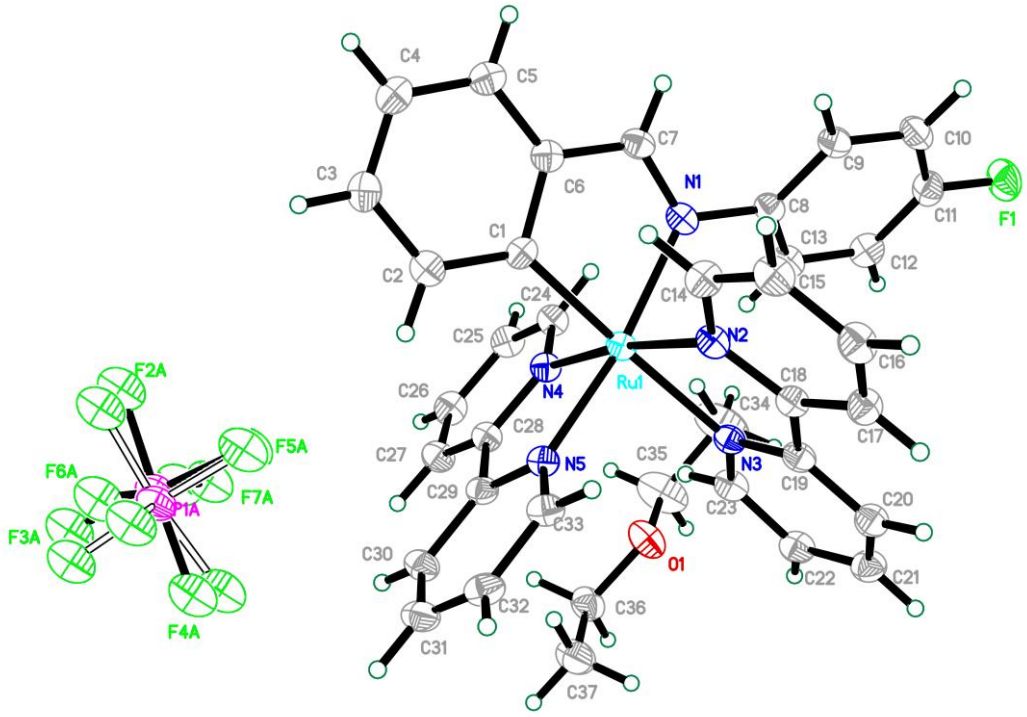



Figure S45. Crystal structure of **3b**.

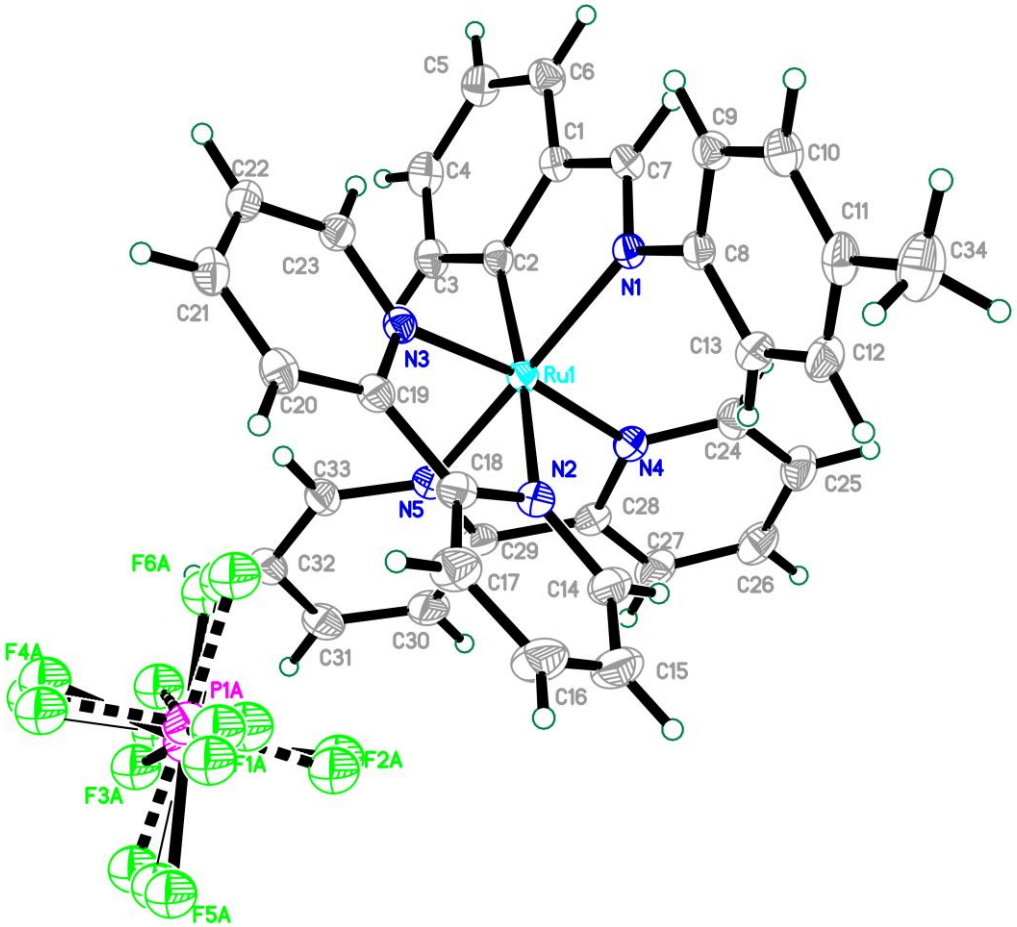



Figure S46. Crystal structure of **3c**.

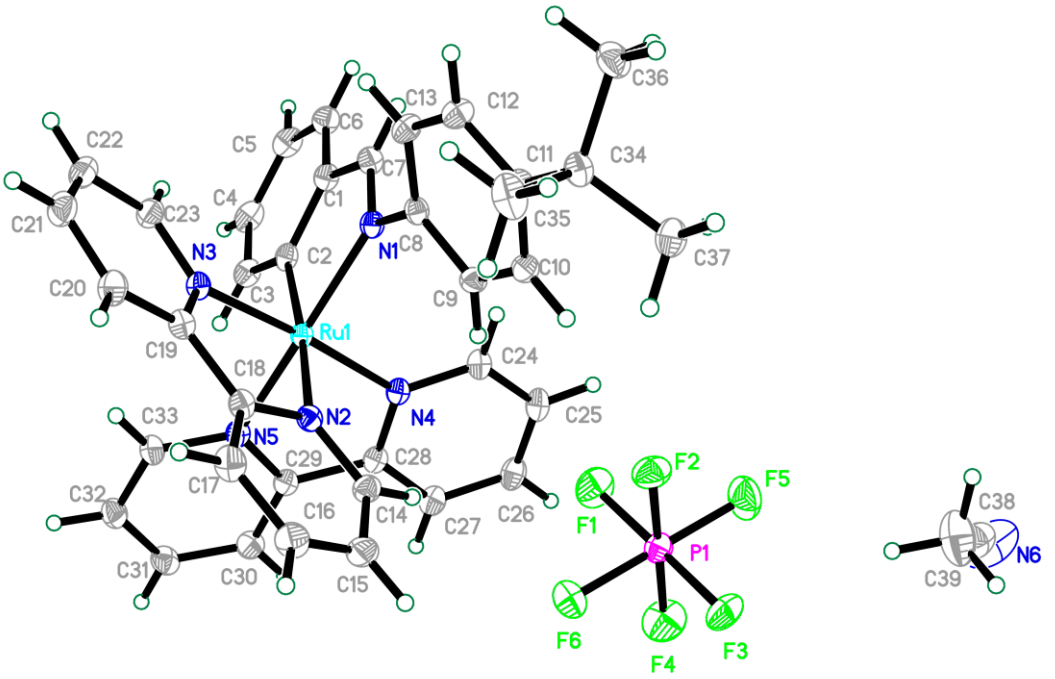



Figure S47. Crystal structure of **3e**.

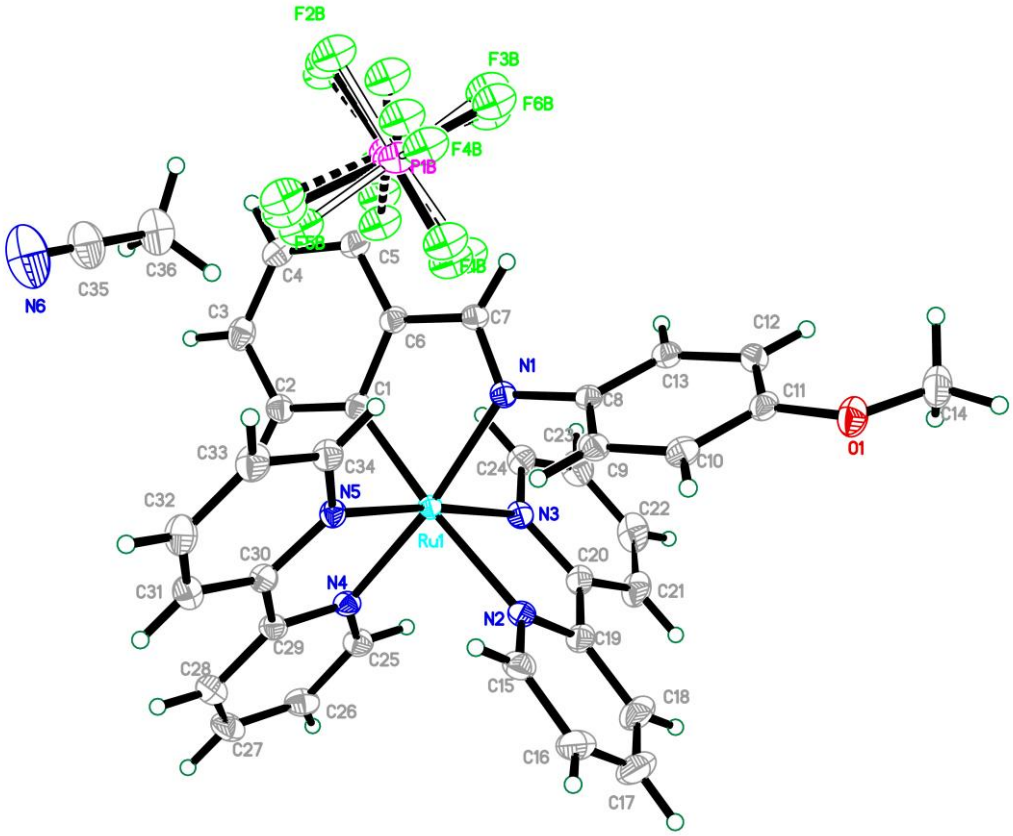



Figure S48. Crystal structure of **3f**.

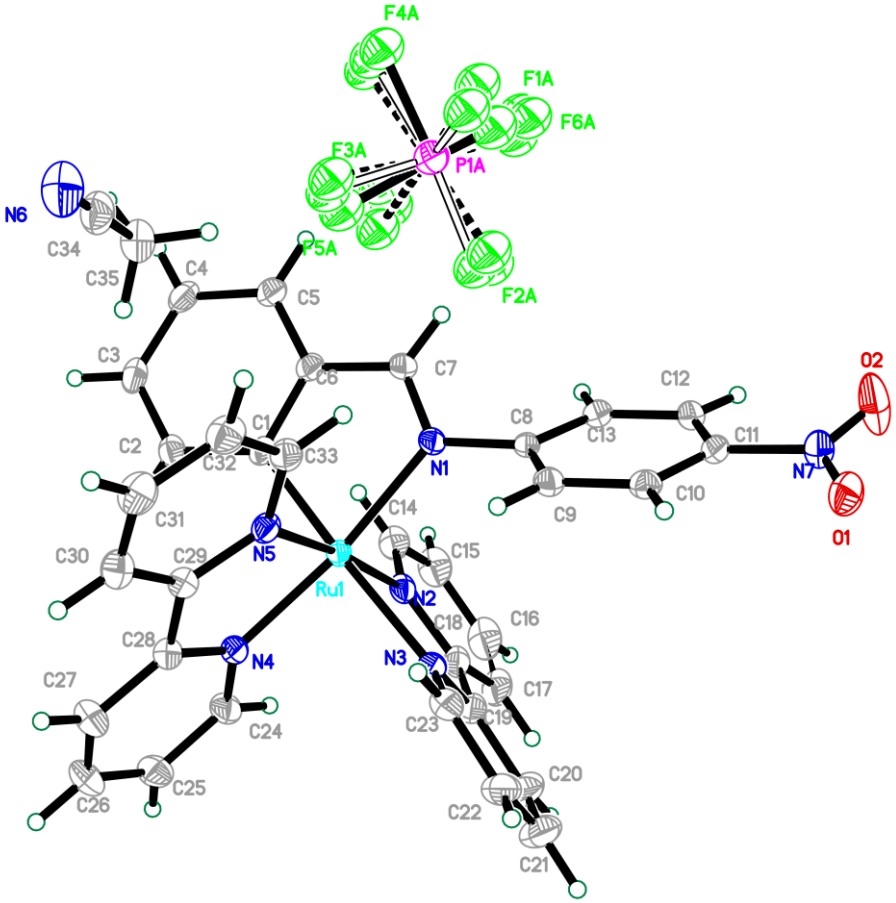



Figure S49. Crystal structure of **3h**.

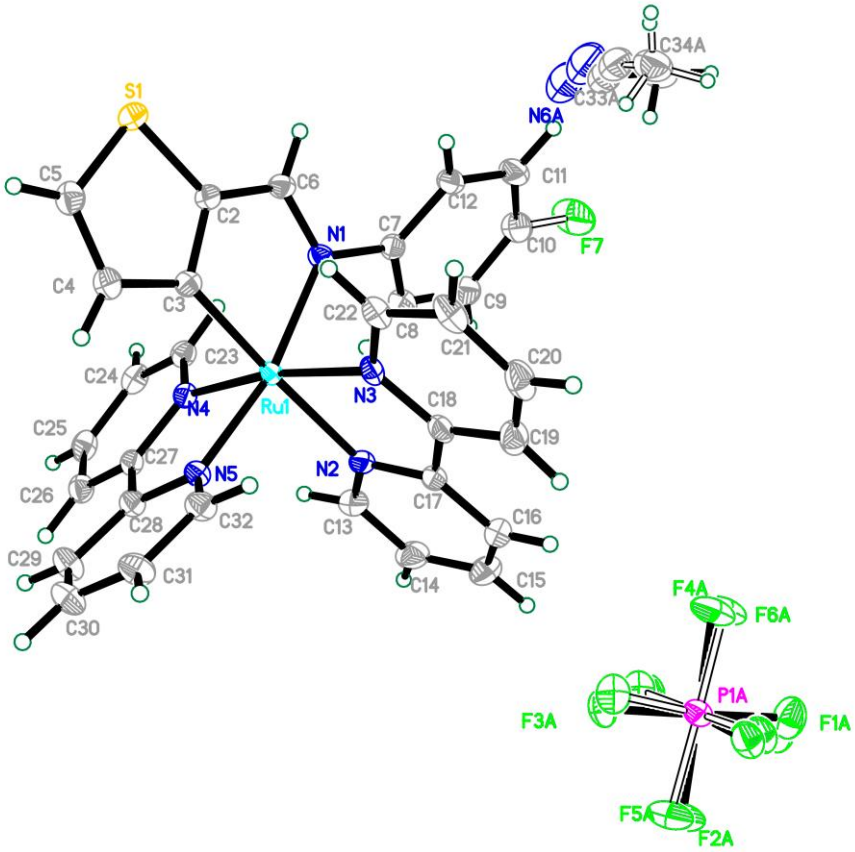



Figure S50. Crystal structure of **3j**.

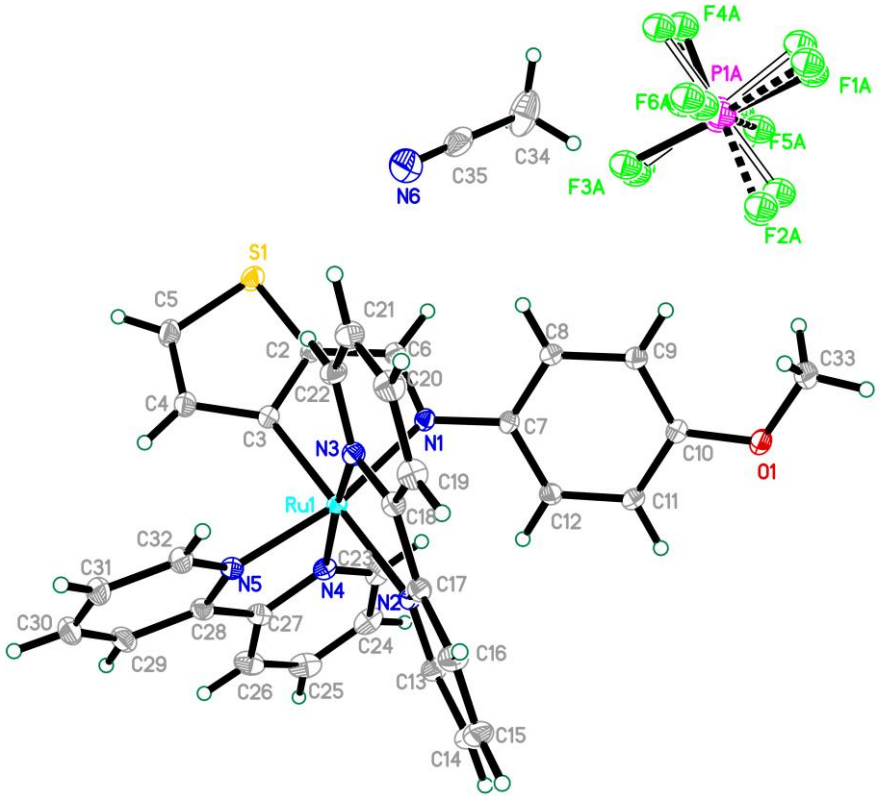



Figure S51. Crystal structure of **3l**.

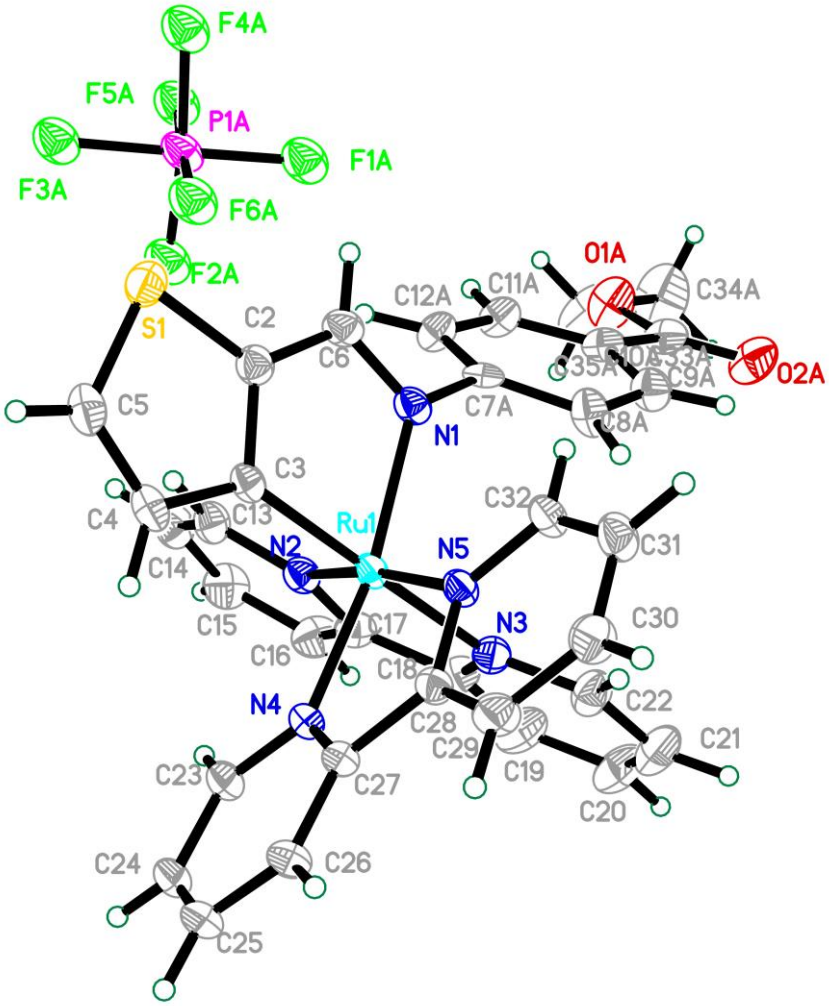



Figure S52. Crystal structure of **3m**.

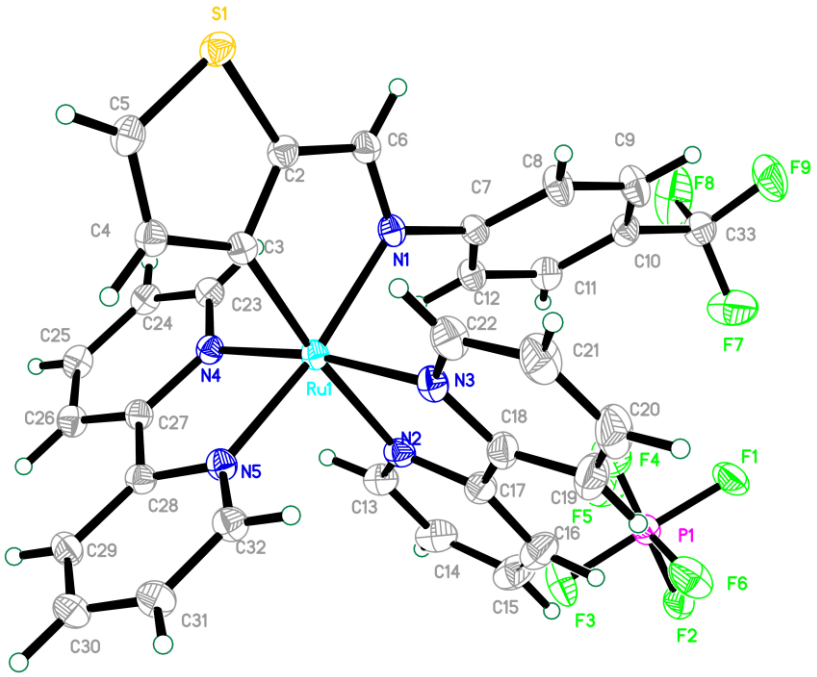



Figure S53. Crystal structure of **3o**.

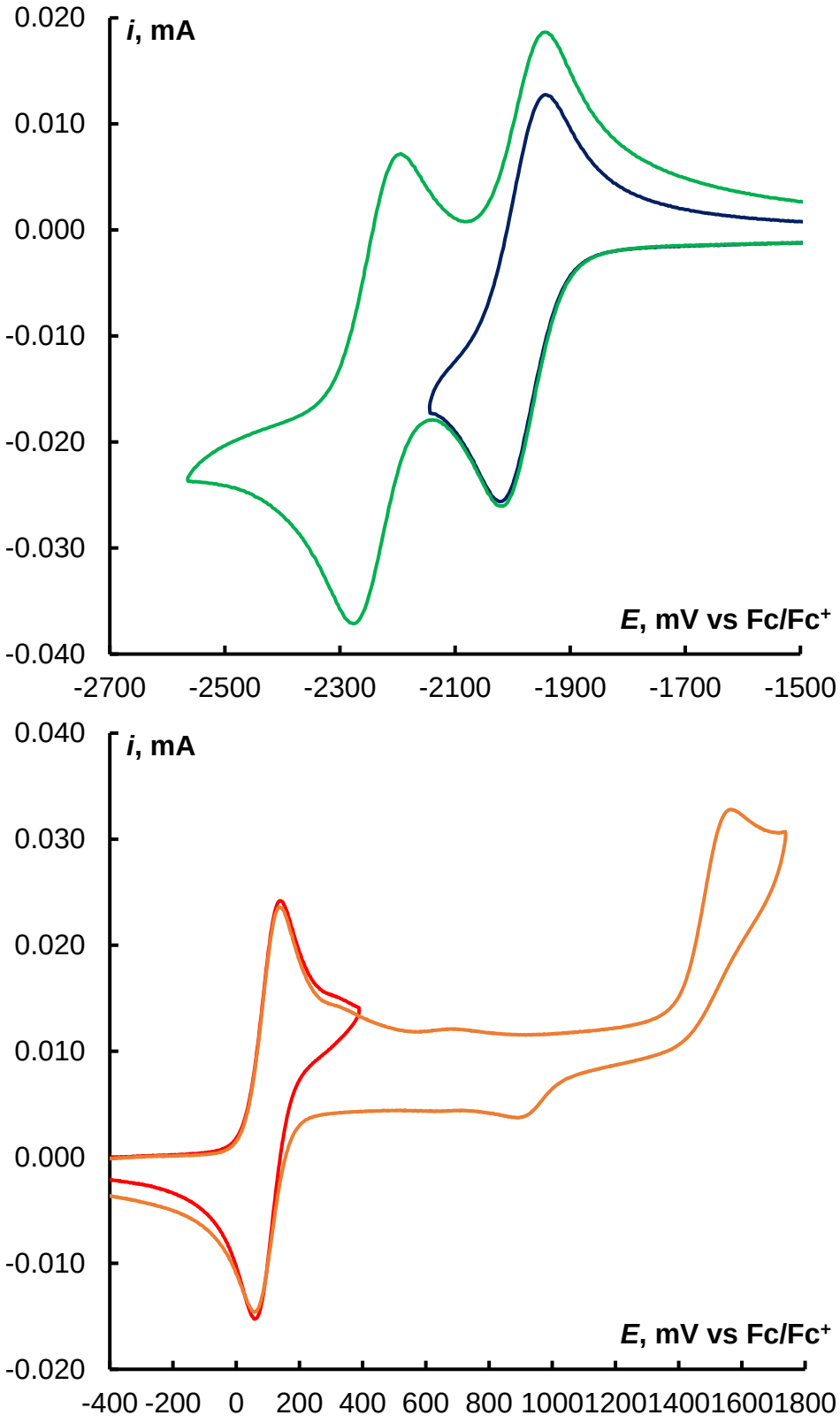



Figure S54. CV curves of **3a**.

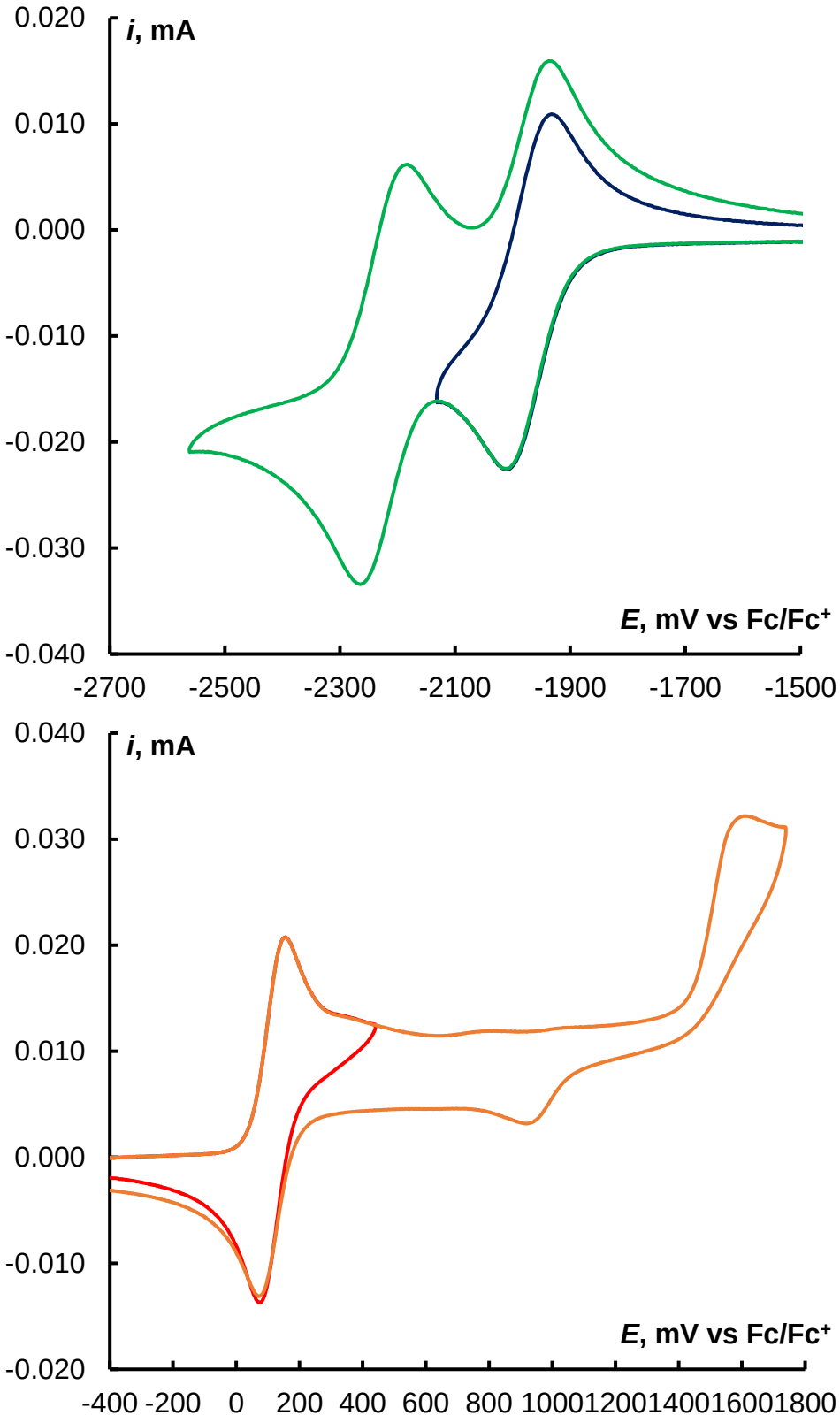



Figure S55. CV curves of **3b**.

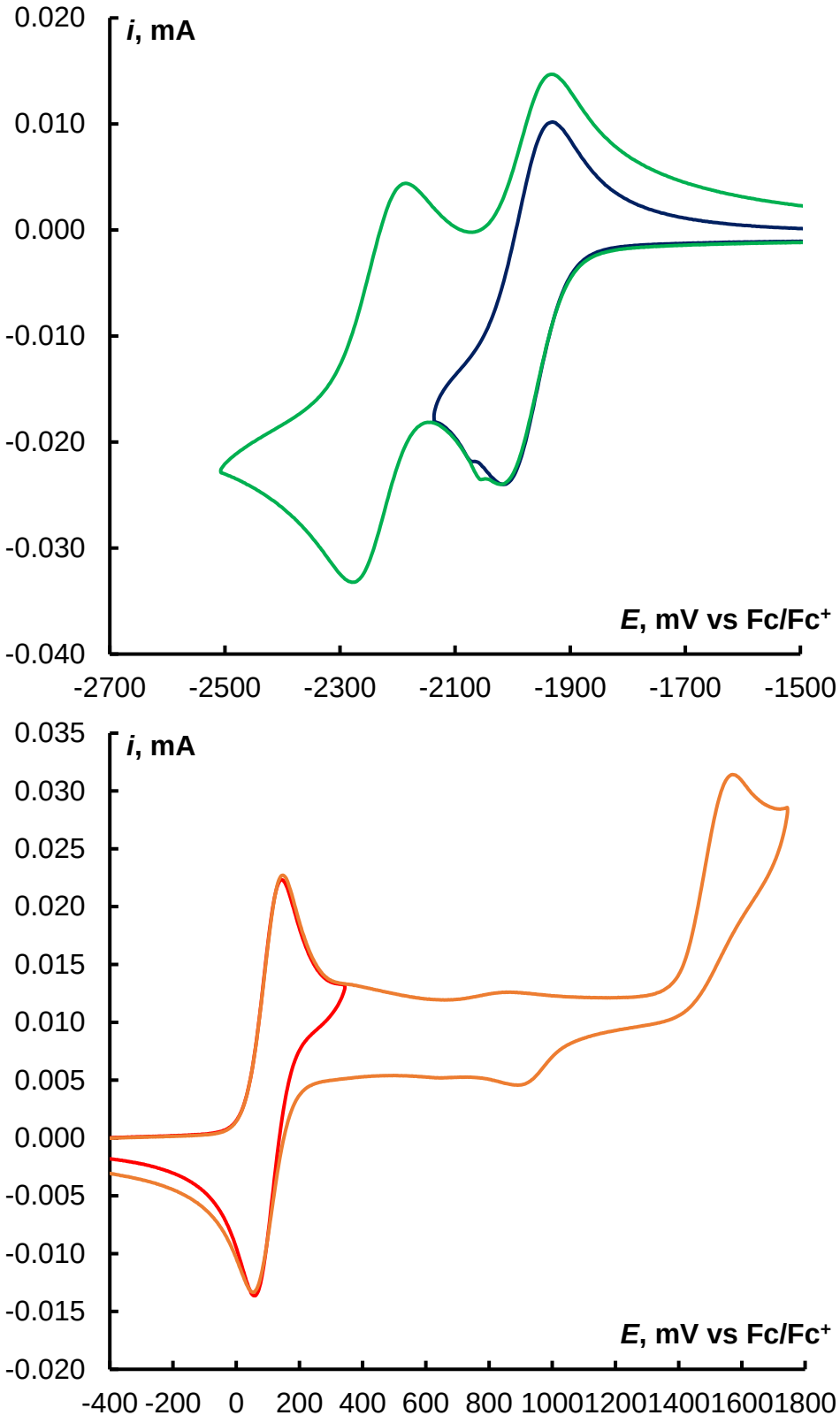



Figure S56. CV curves of **3c**.

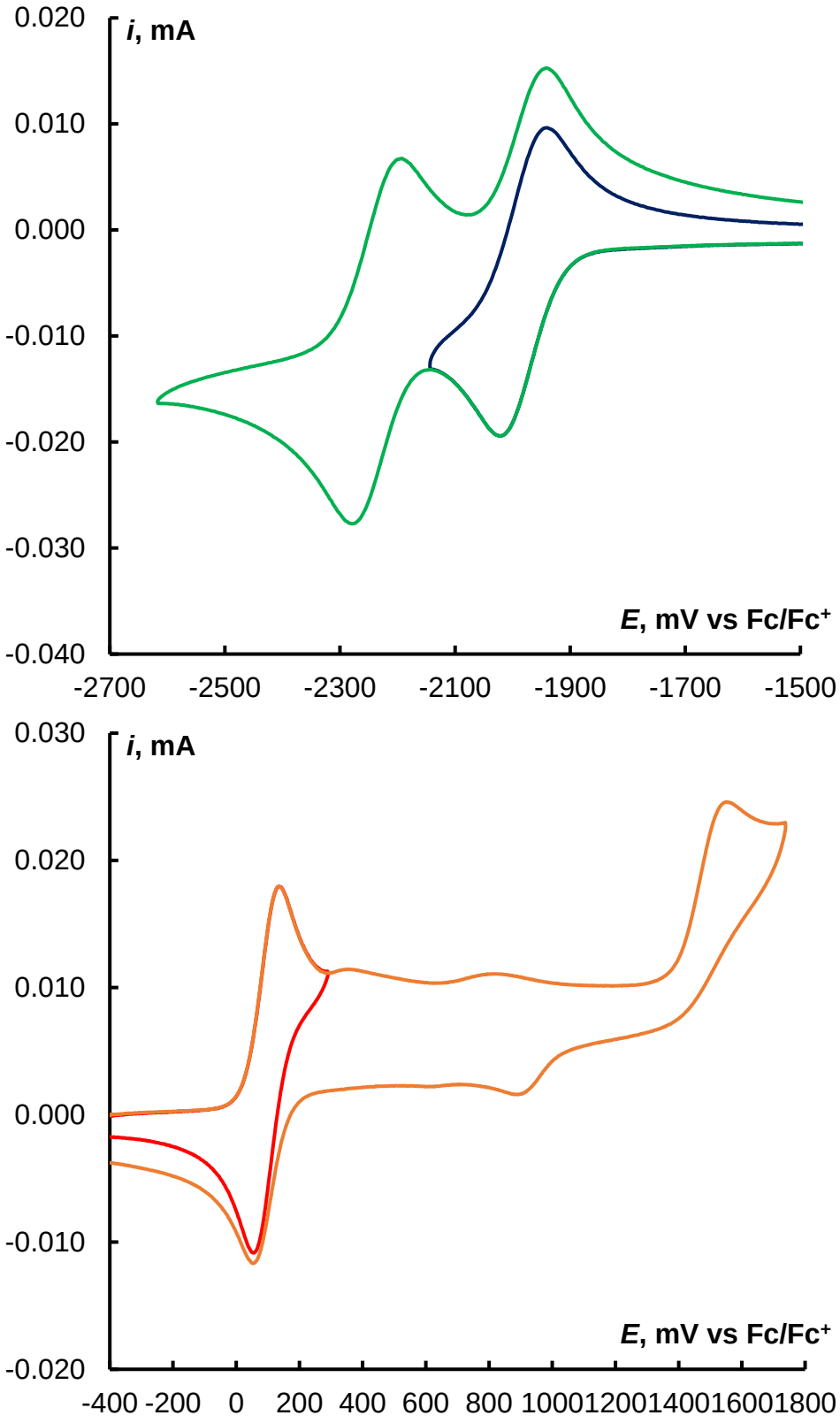



Figure S57. CV curves of **3d**.

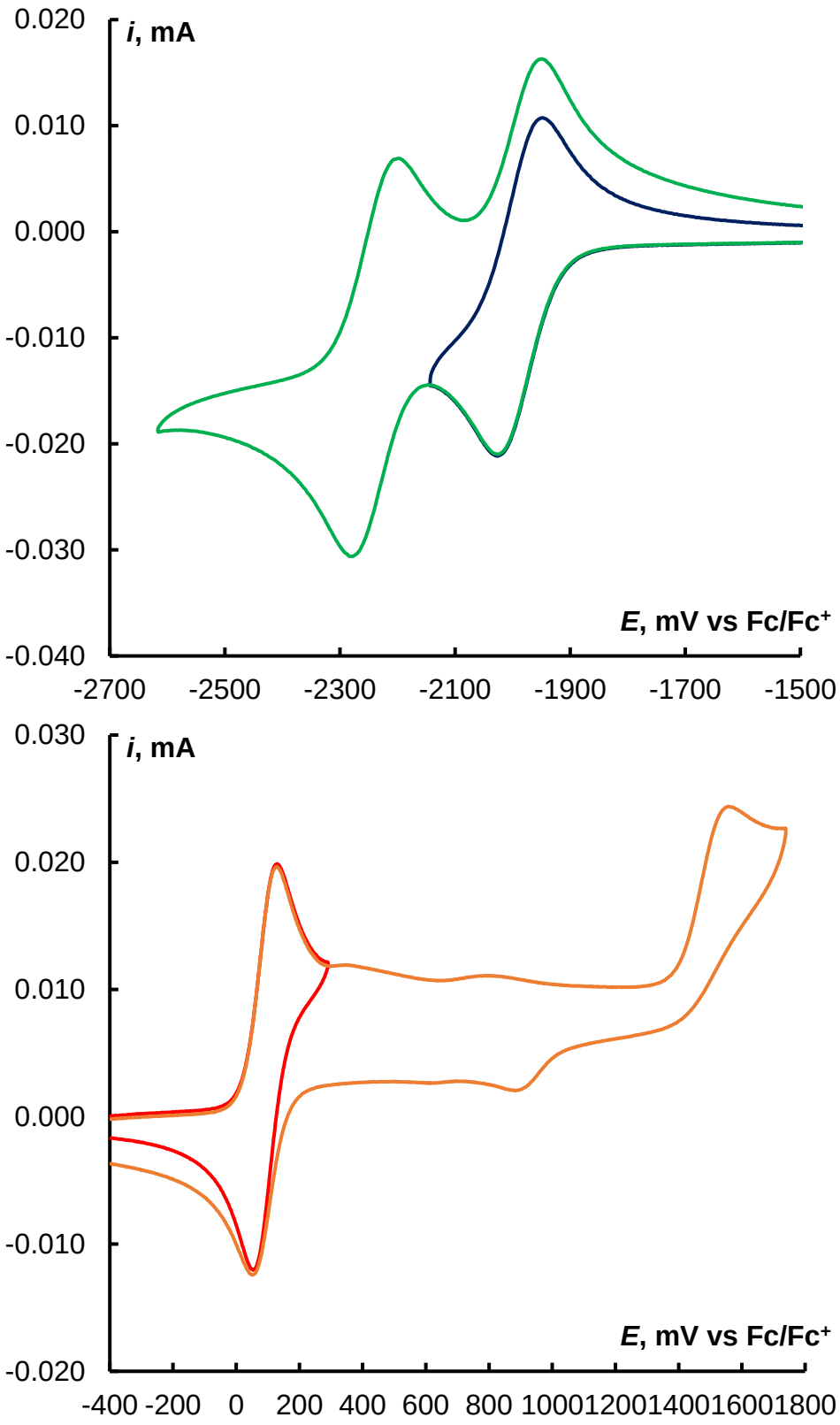



Figure S58. CV curves of **3e**.

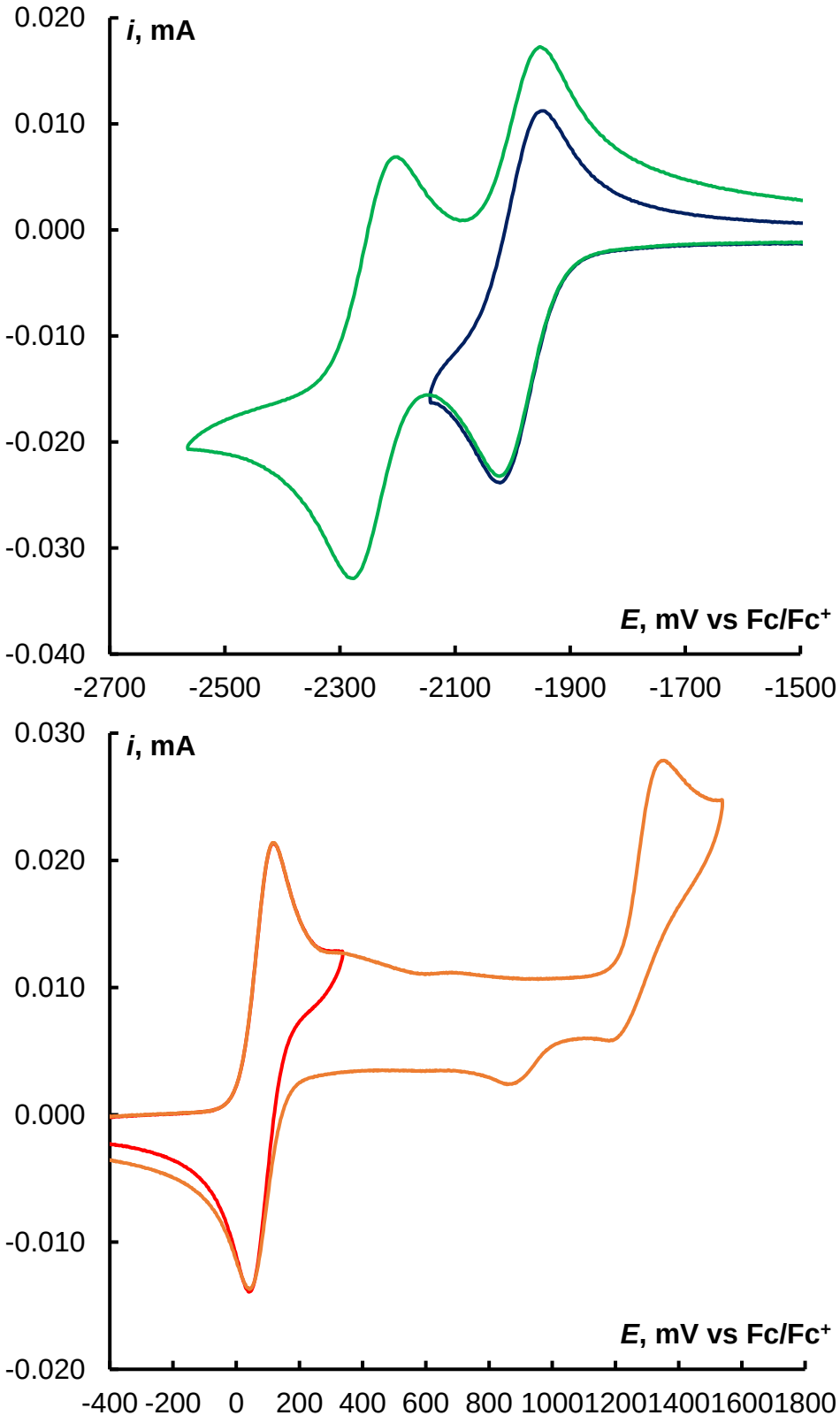



Figure S59. CV curves of **3f**.

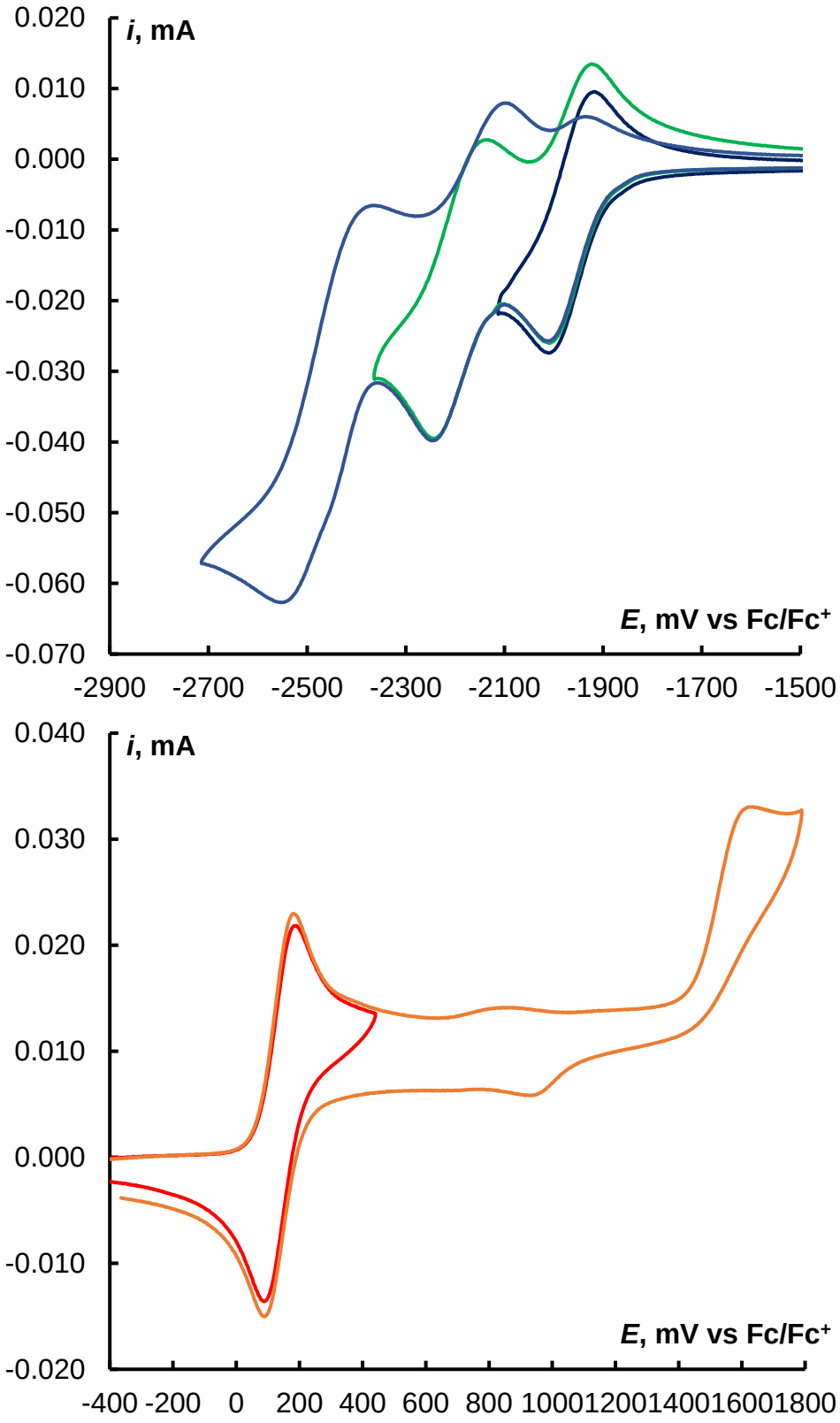



Figure S60. CV curves of **3g**.

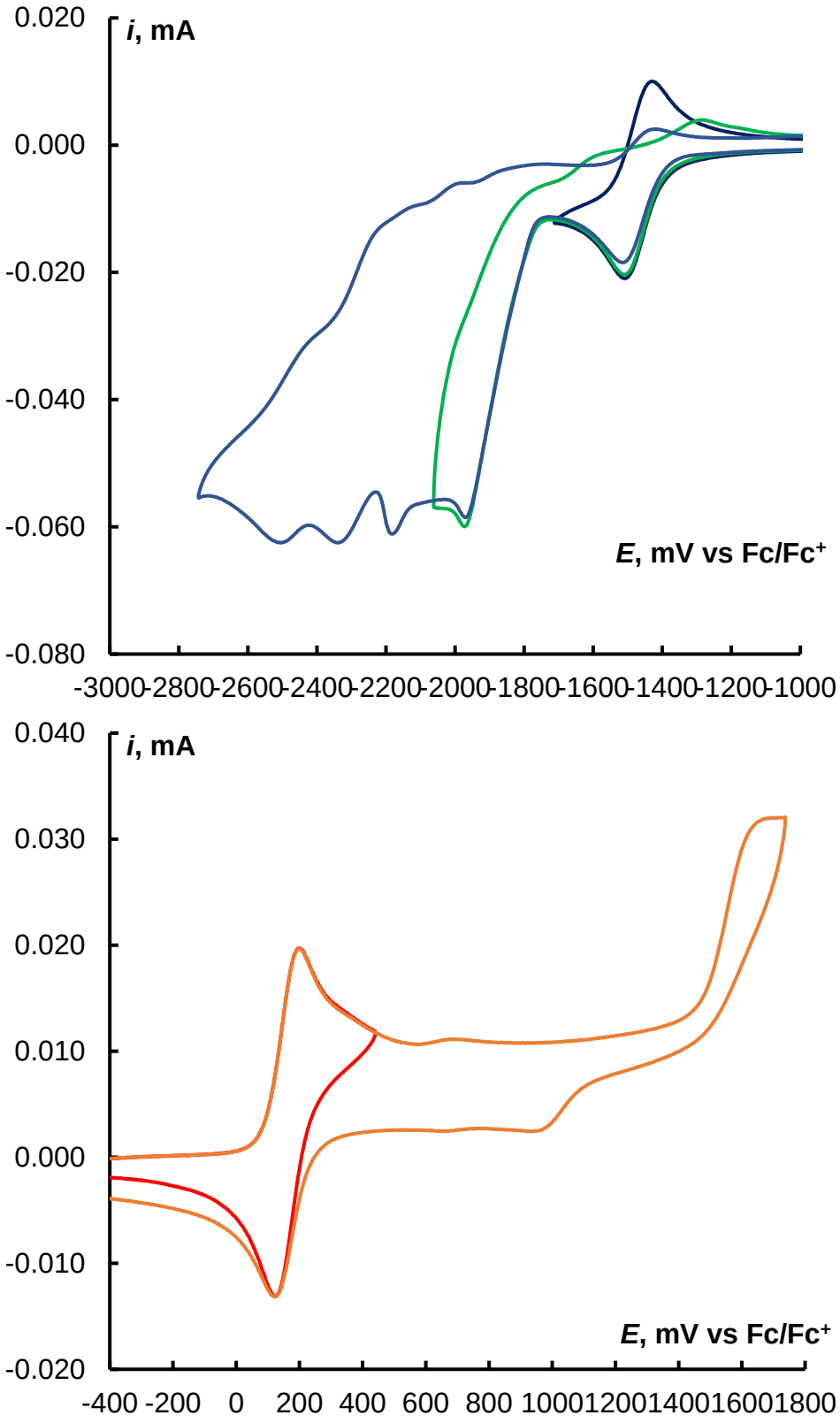



Figure S61. CV curves of **3h**.

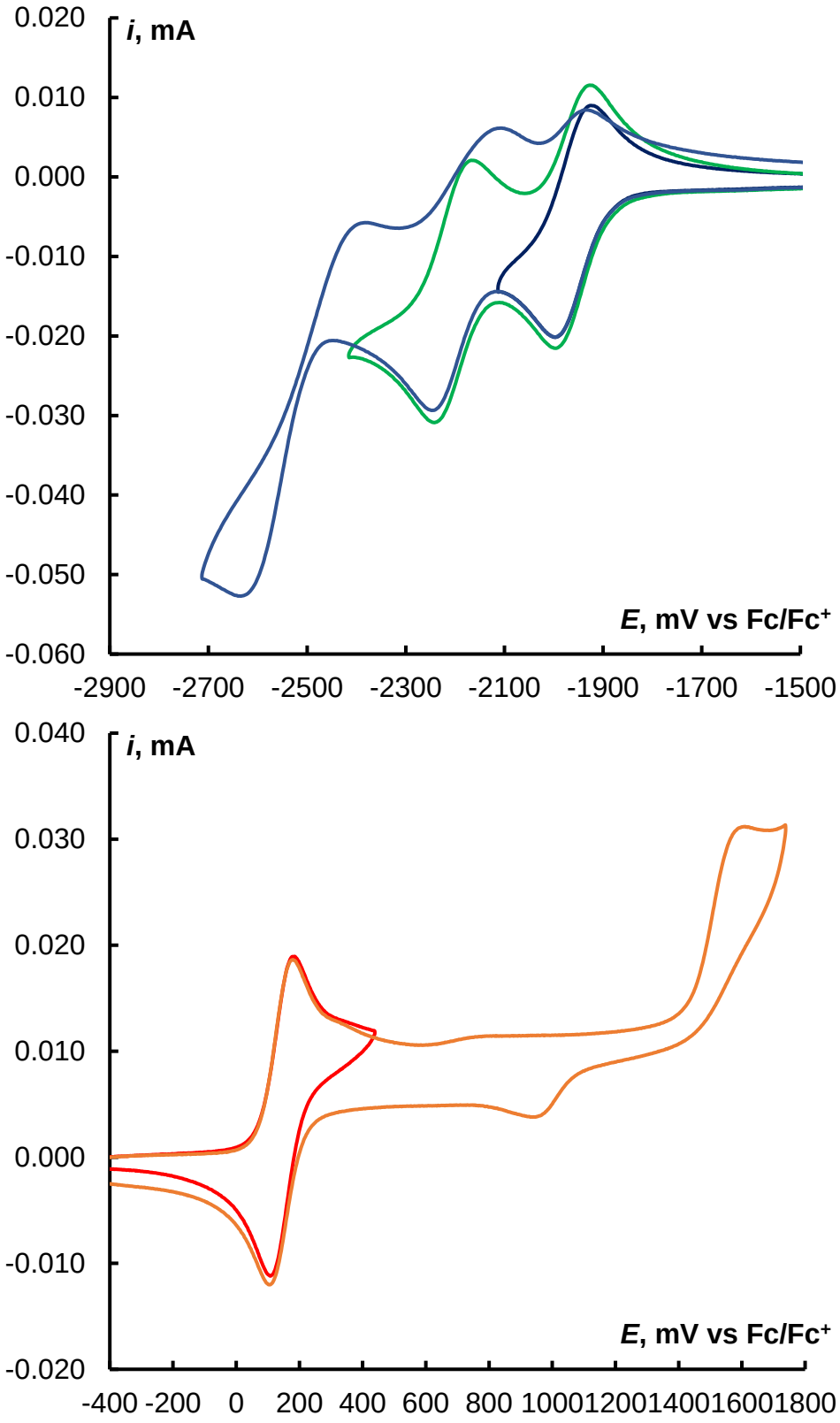



Figure S62. CV curves of **3i**.

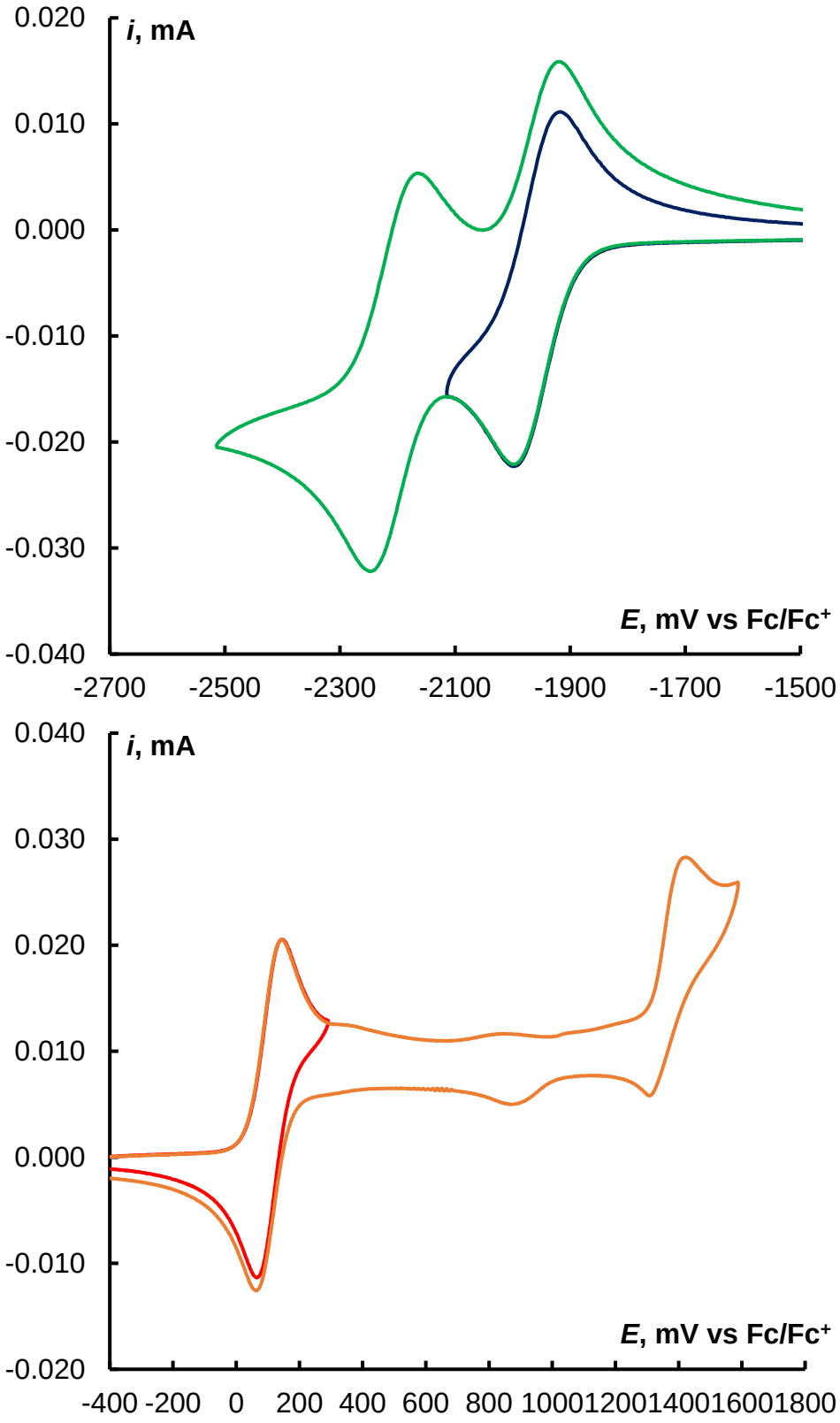



Figure S63. CV curves of **3j**.

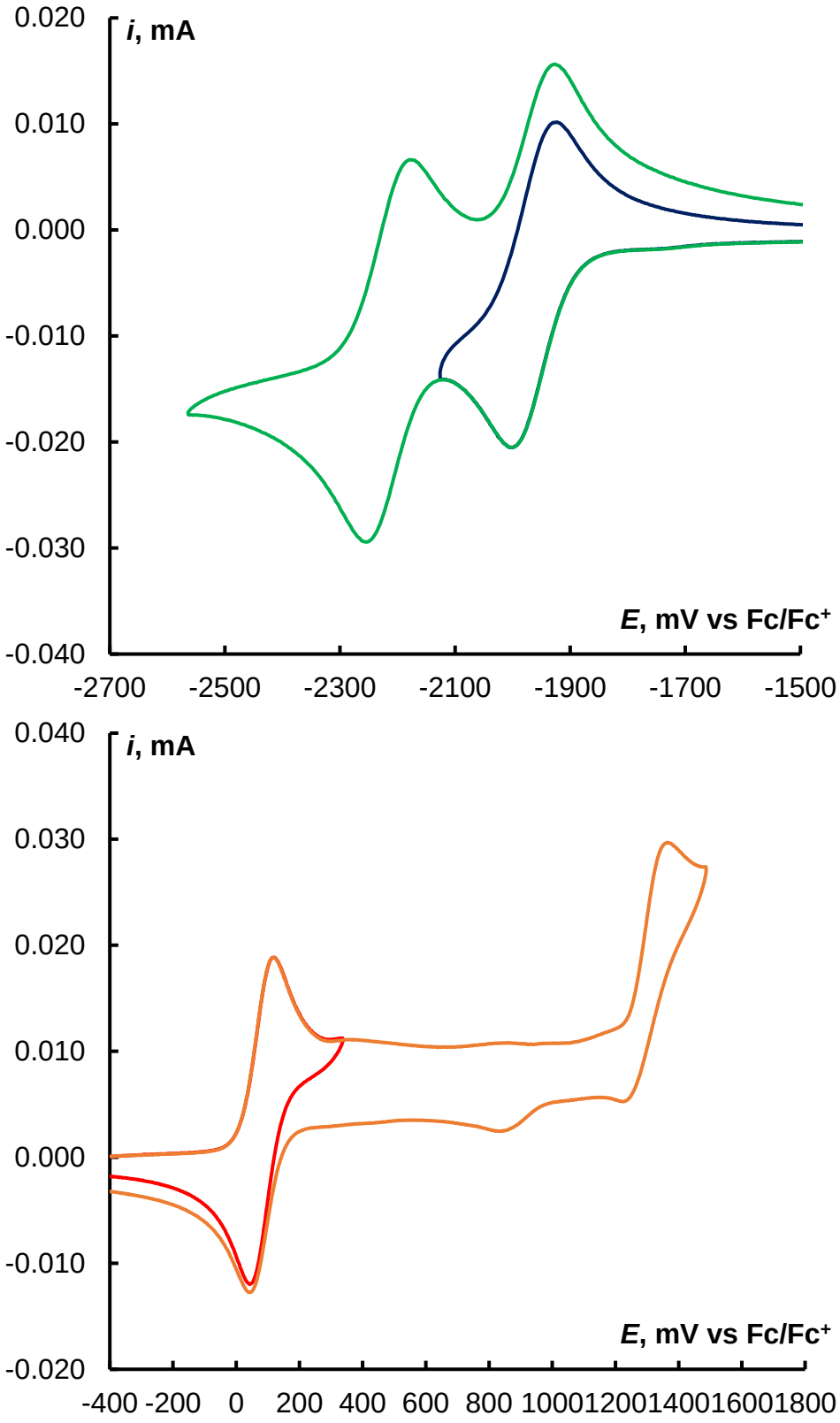



Figure S64. CV curves of **3k**.

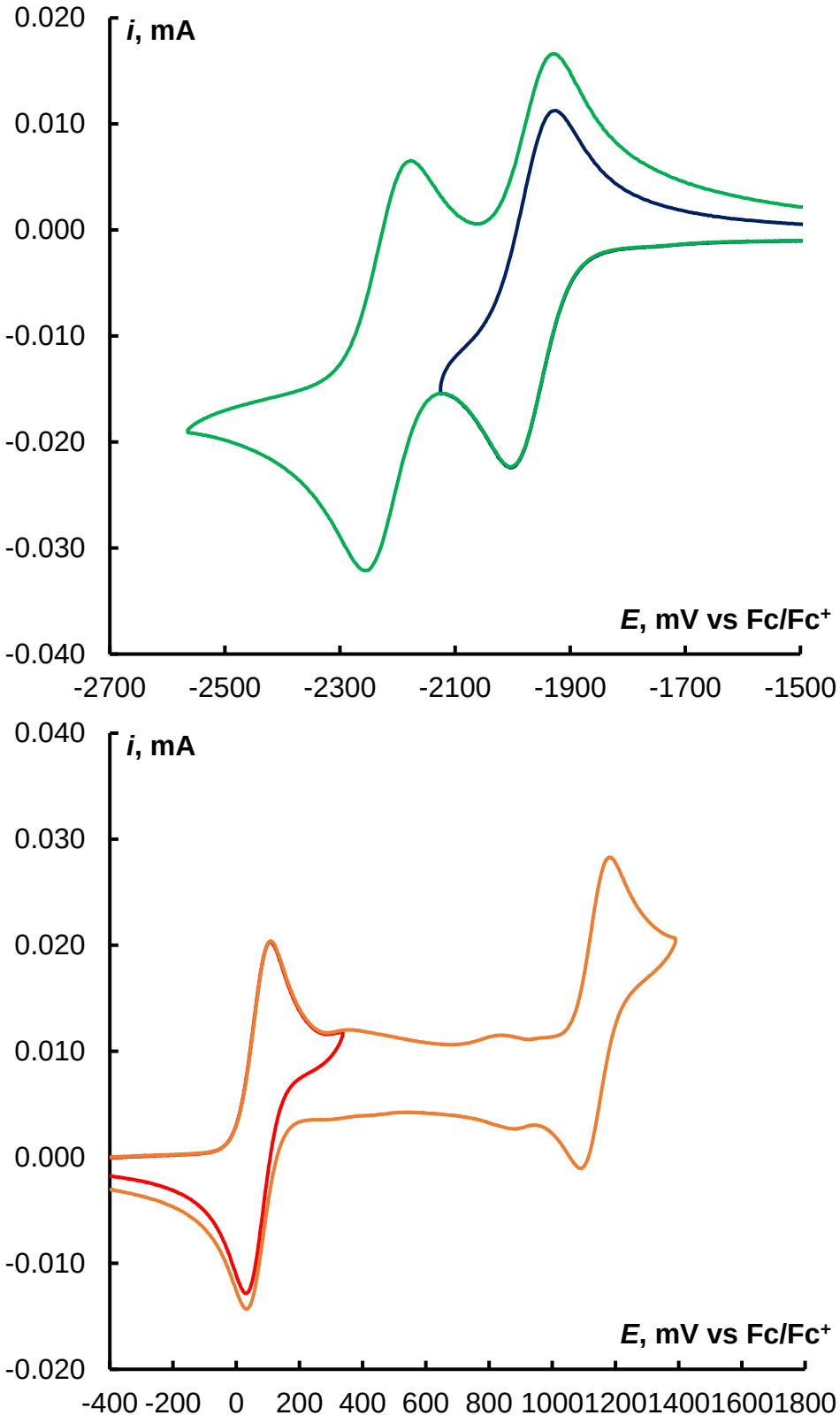



Figure S65. CV curves of **3l**.

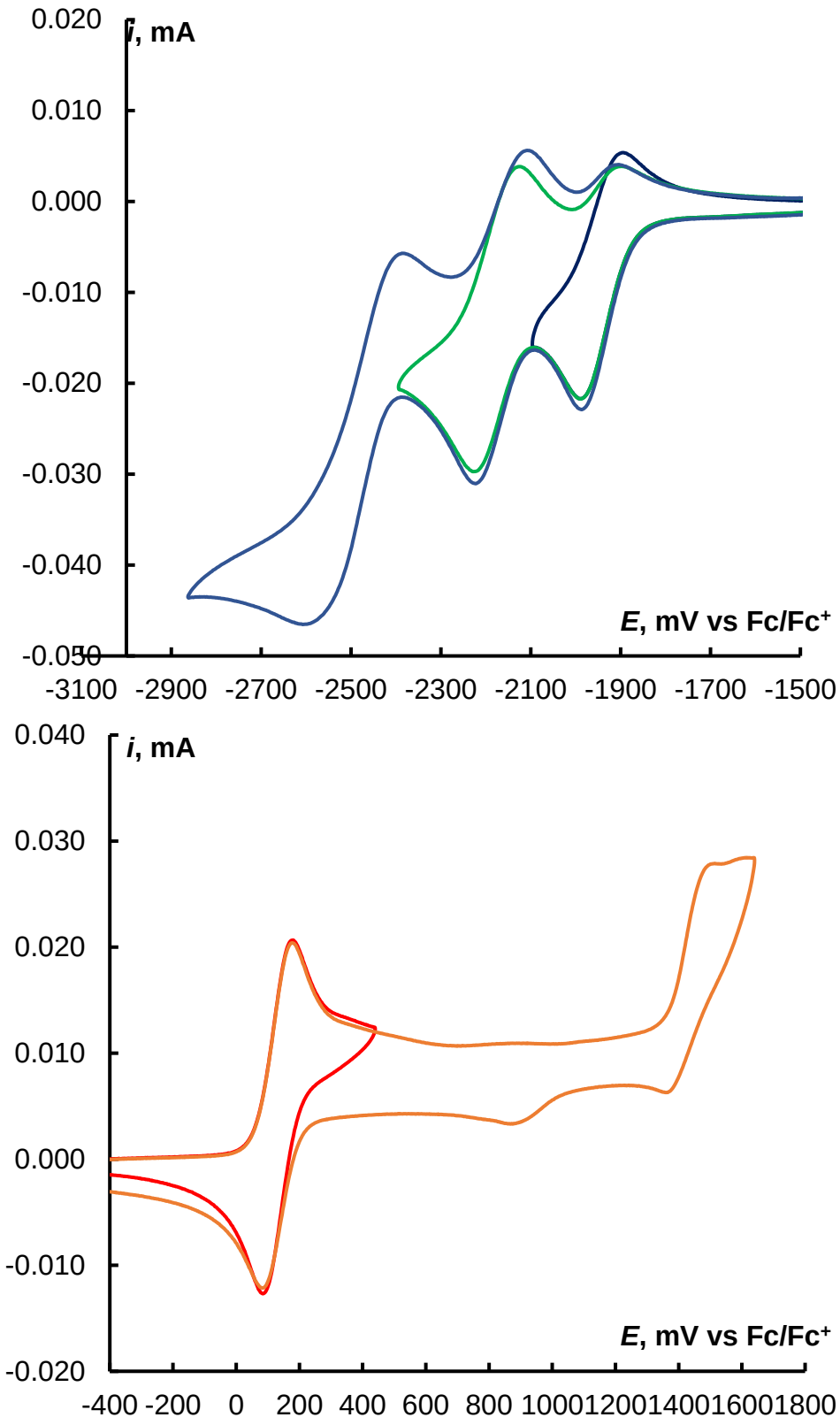



Figure S66. CV curves of **3m**.

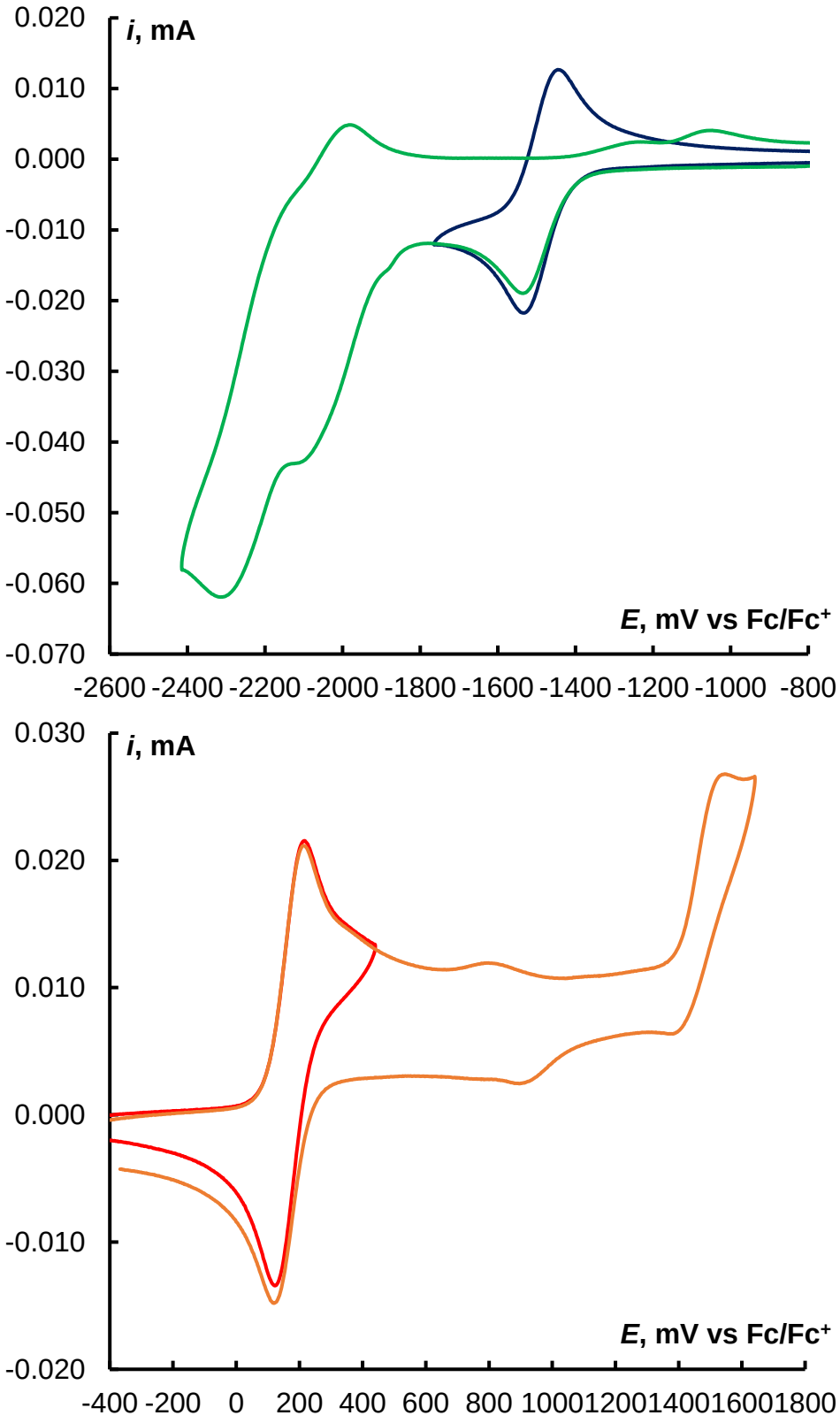



Figure S67. CV curves of **3n**.

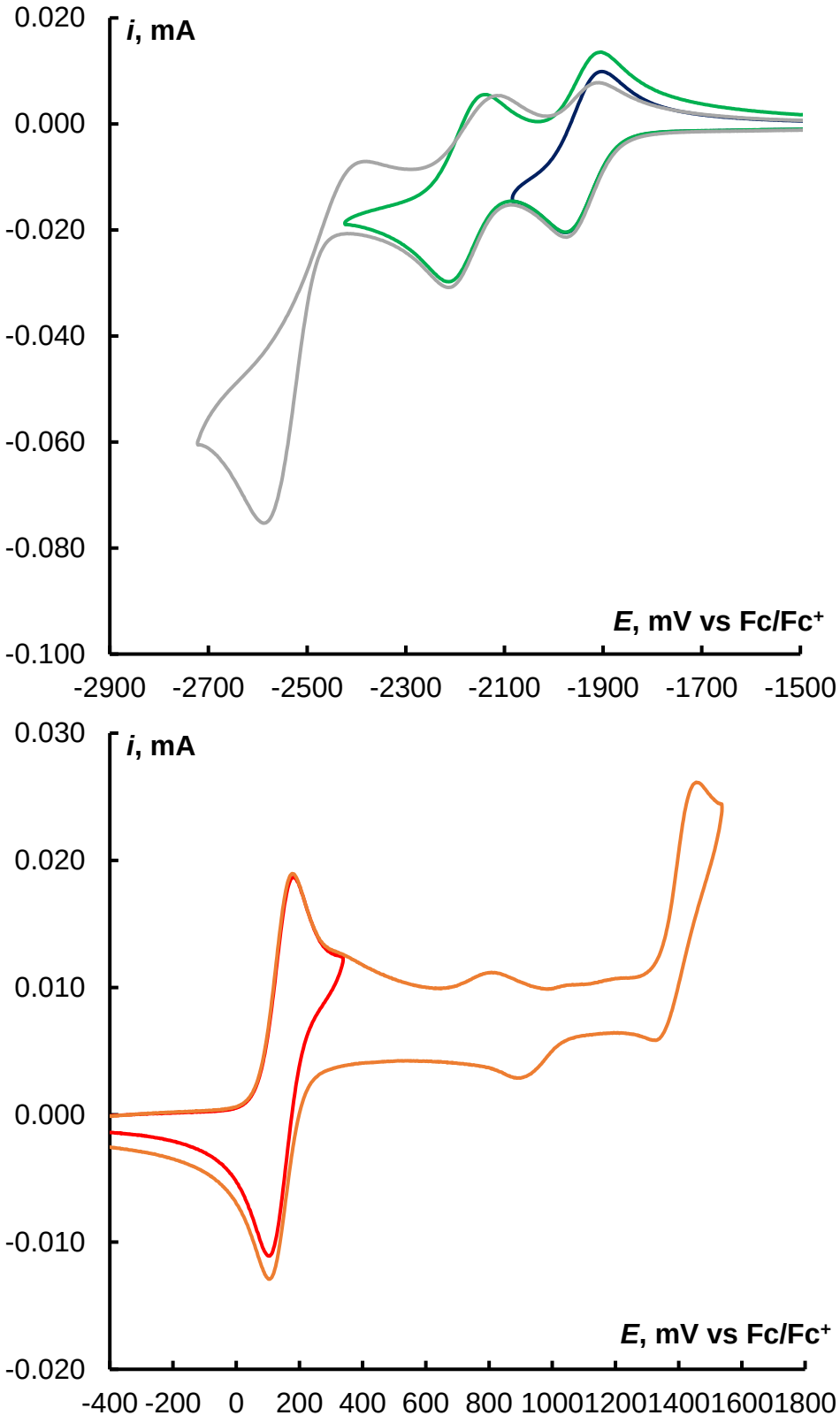
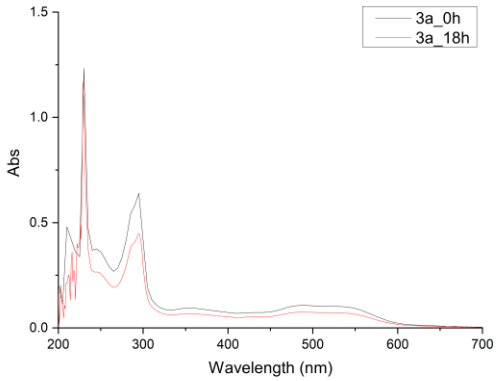
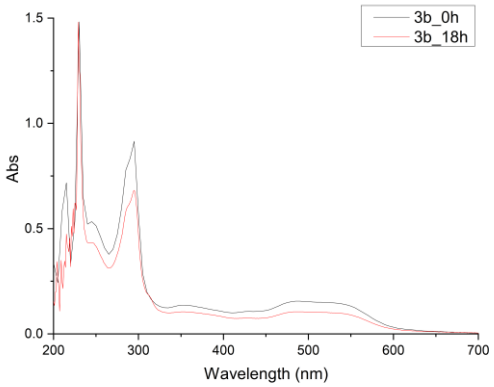
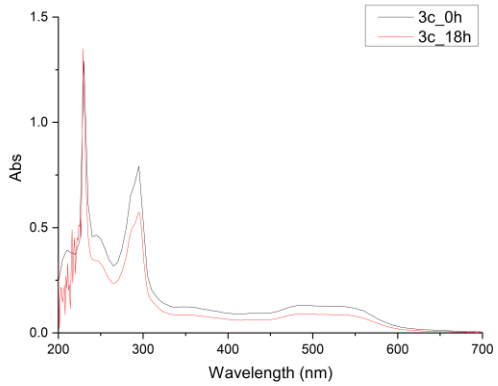
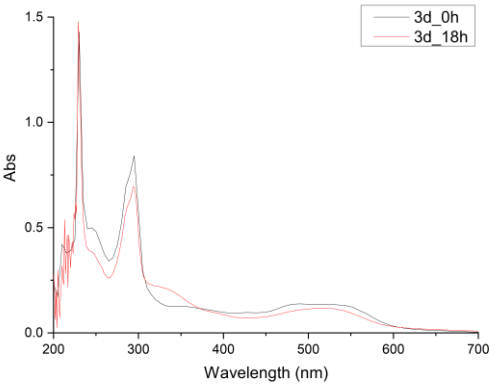


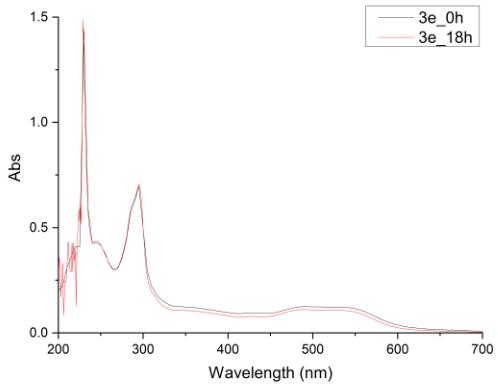

Figure S68. CV curves of **3o**.

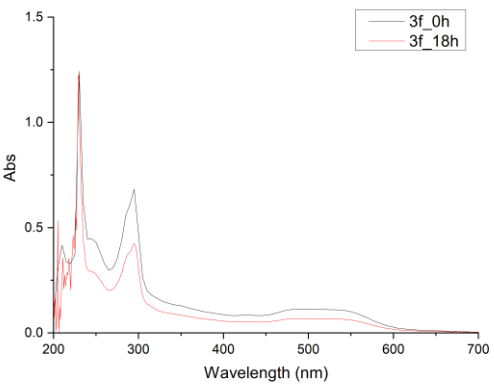

3a_0h
3a_18h
Abs
Wavelength (nm)


3b_0h
3b_18h
Abs
Wavelength (nm)


3c_0h
3c_18h
Abs
Wavelength (nm)


3d_0h
3d_18h
Abs
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3f_18h
Abs
Wavelength (nm)

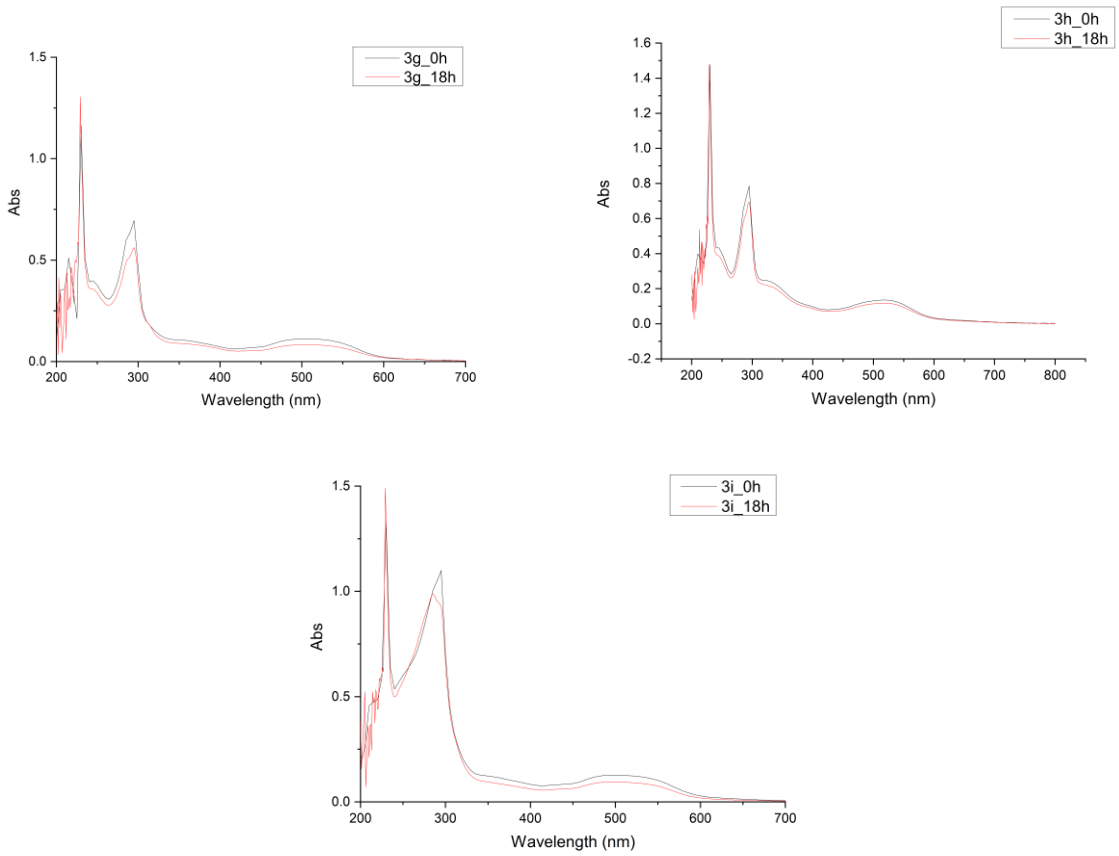



Figure S69. UV-vis spectra of **3a**-**3i** in PBS – 0.5% DMSO solution, concentration $1*10^{-5}$ M immediately after dissolution and after 18 h at room temperature.

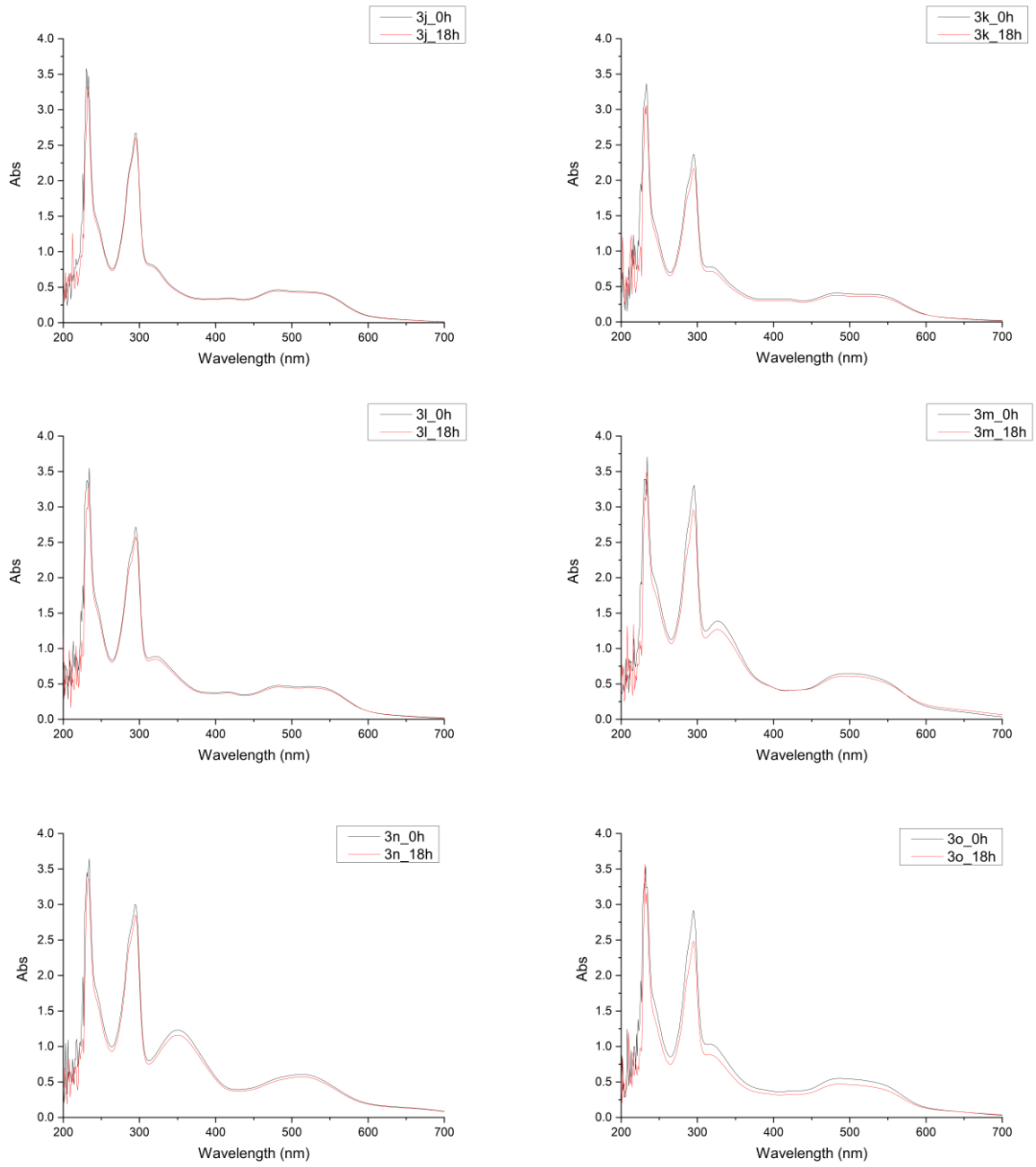



Figure S70. UV-vis spectra of **3j**-**3o** in PBS – 0.5% DMSO solution, concentration $5*10^{-5}$ M immediately after dissolution and after 18 h at room temperature.