Supplementary Information (SI) for New Journal of Chemistry.




*Supporting Information*

# Ferrocene-containing Schiff bases and their Sn(IV) complexes with two non-conjugated redox-active fragments: dependence of spectroscopic and redox properties on complexation and solvent

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## NMR spectroscopy of 1a, 1b, and 2a

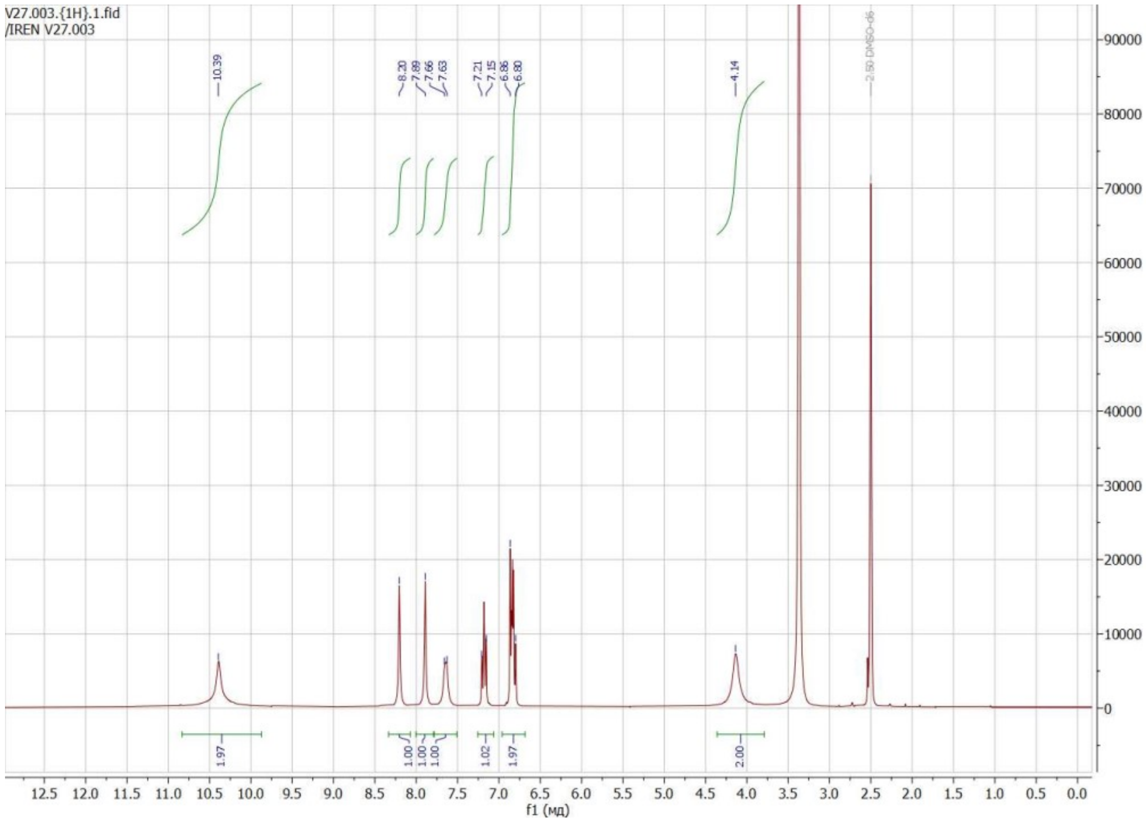



**Figure S1.** $^{1}$H NMR spectrum of **1a** in DMSO-d$_6$.

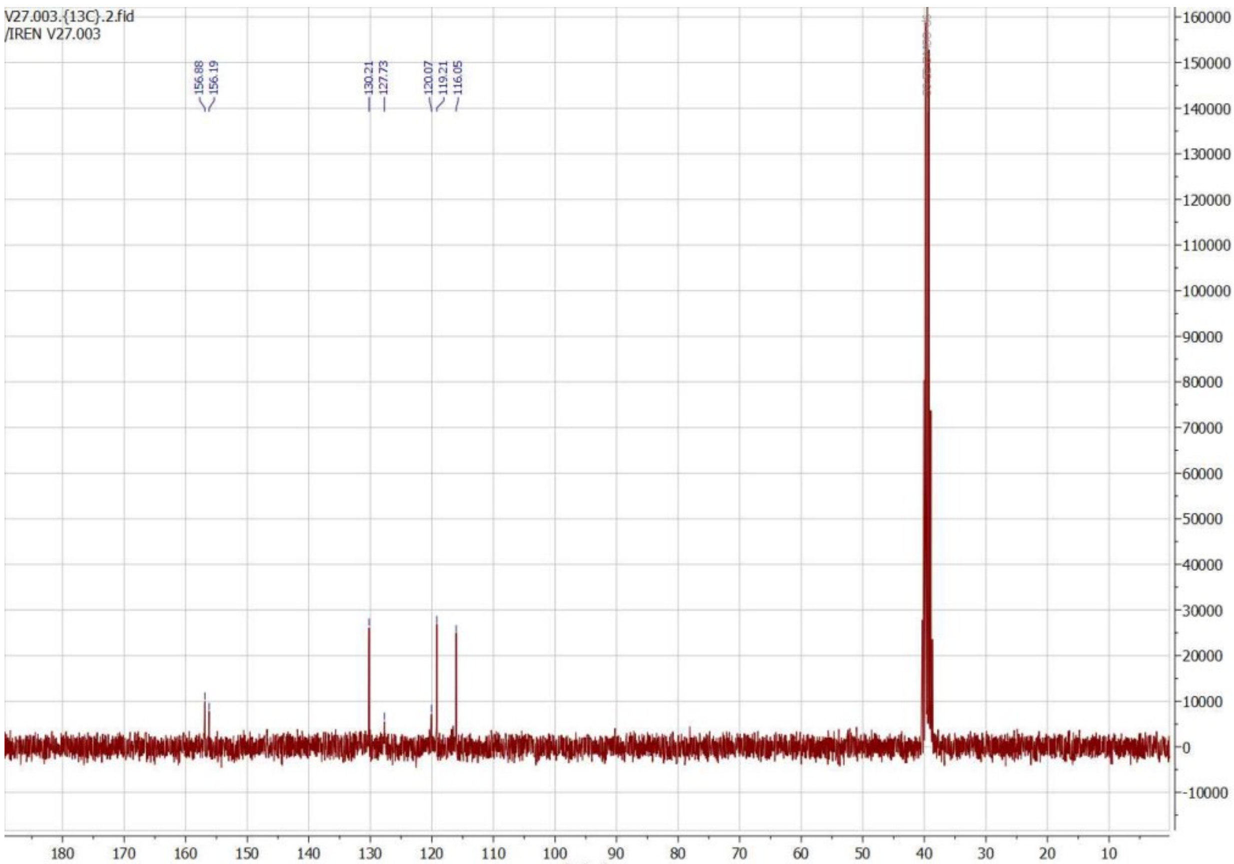



**Figure S2.** $^{13}$C NMR spectrum of **1a** in DMSO-d$_6$.

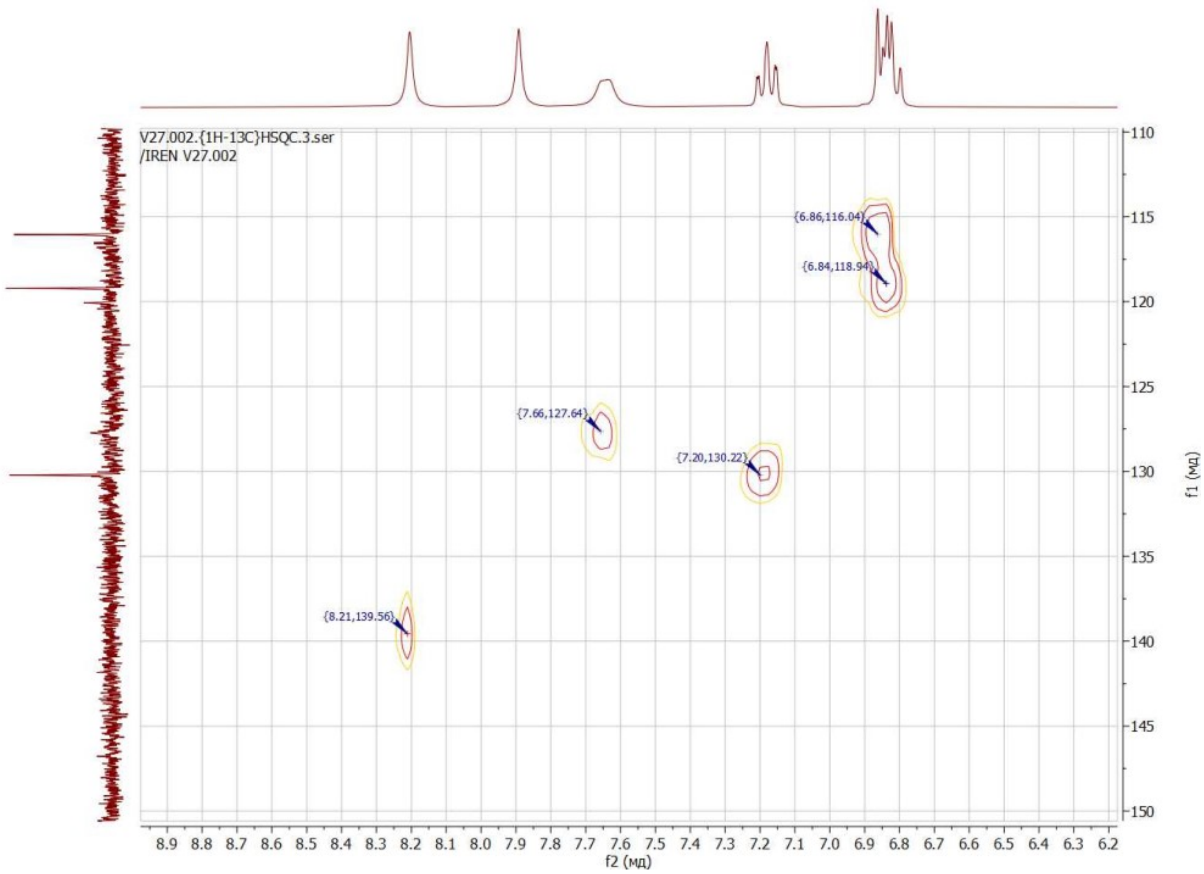



**Figure S3.** HSQC spectrum of **1a** in DMSO-$d_6$.

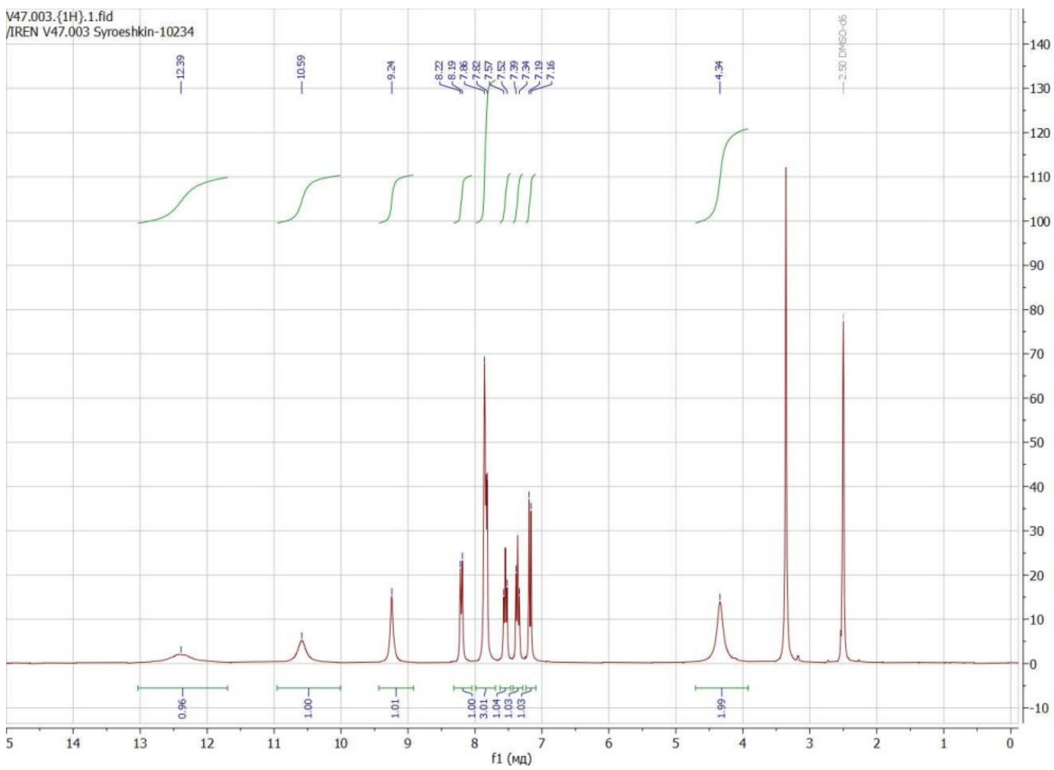



**Figure S4.** [1]H NMR spectrum of **1b** in DMSO-$d_6$.

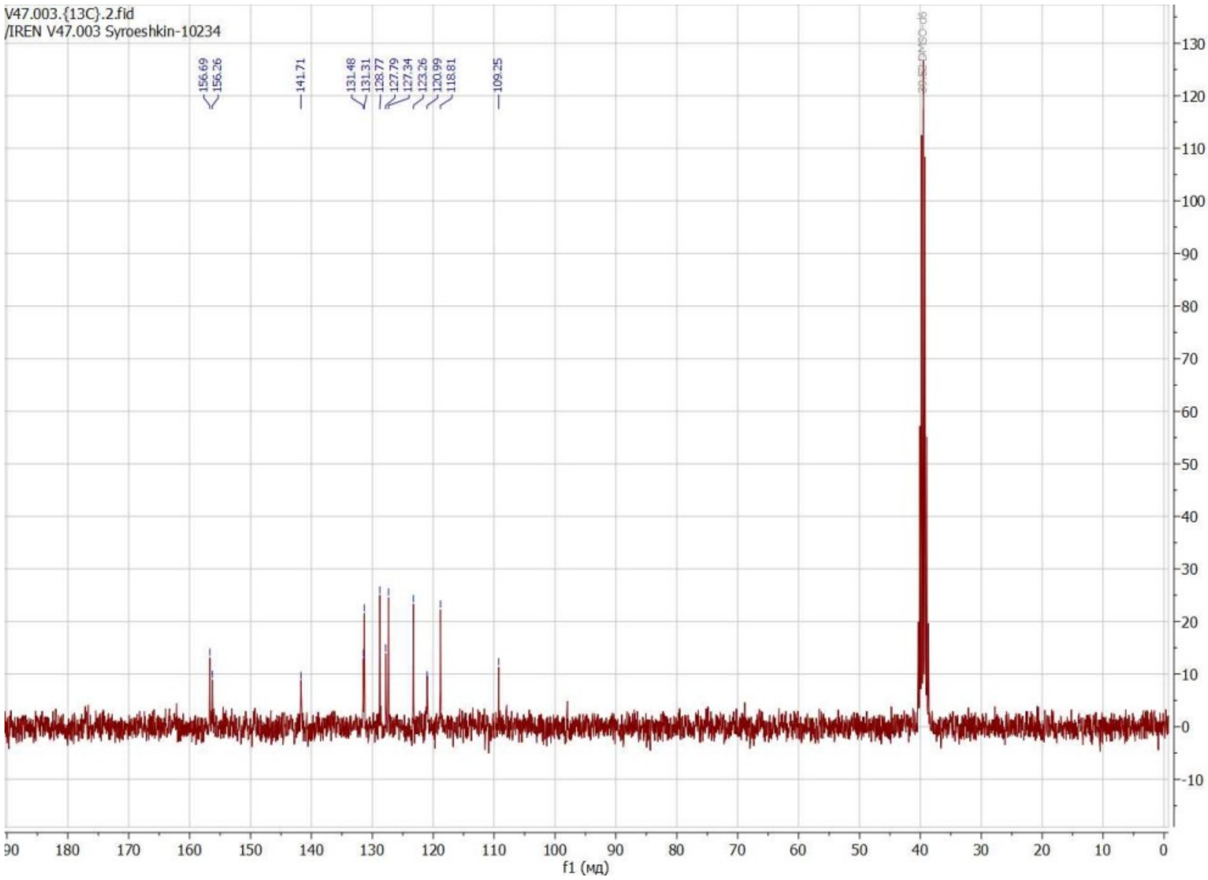



**Figure S5.** $^{13}C$ NMR spectrum of **1b** in DMSO-$d_6$.

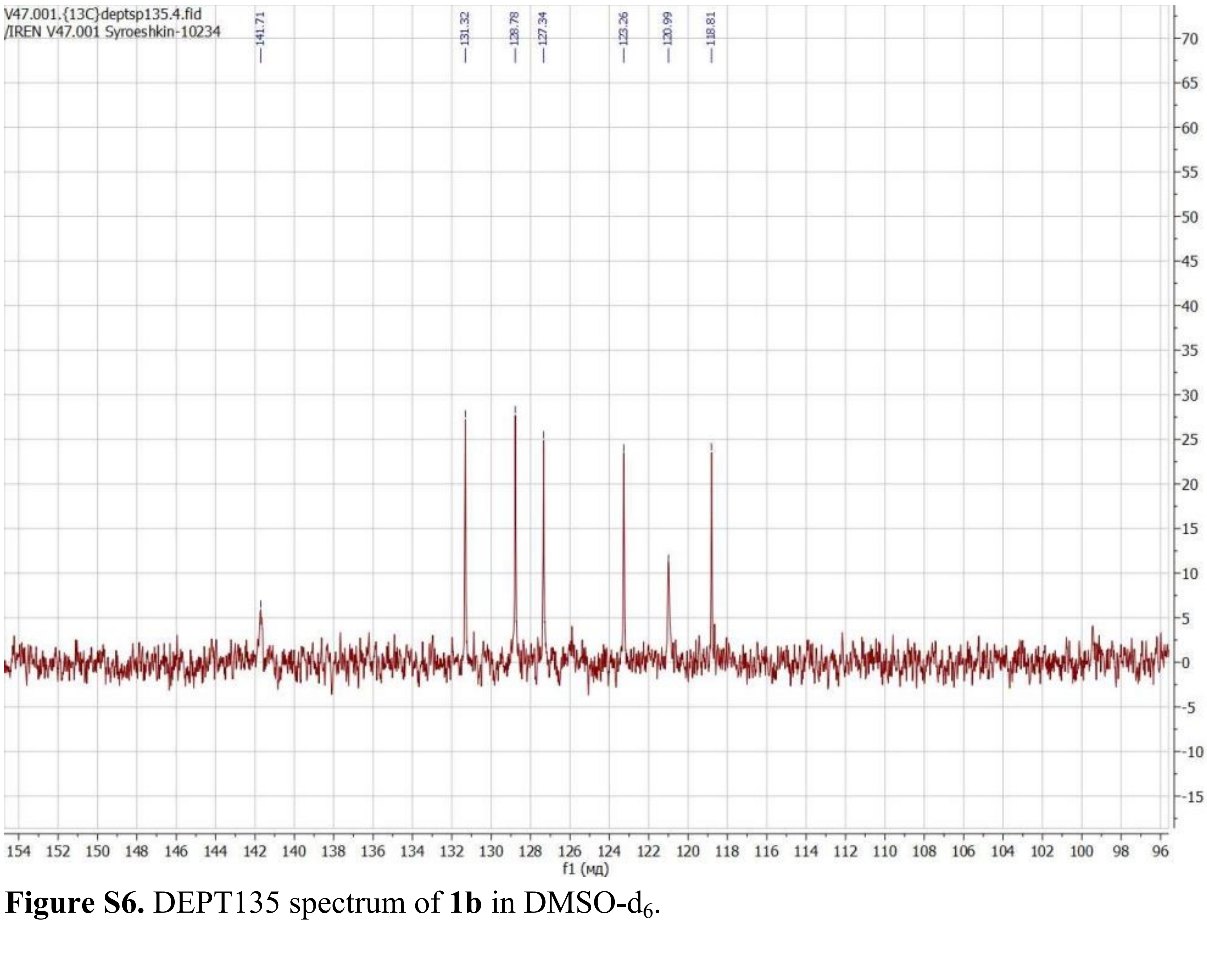



**Figure S6.** DEPT135 spectrum of **1b** in DMSO-$d_6$.

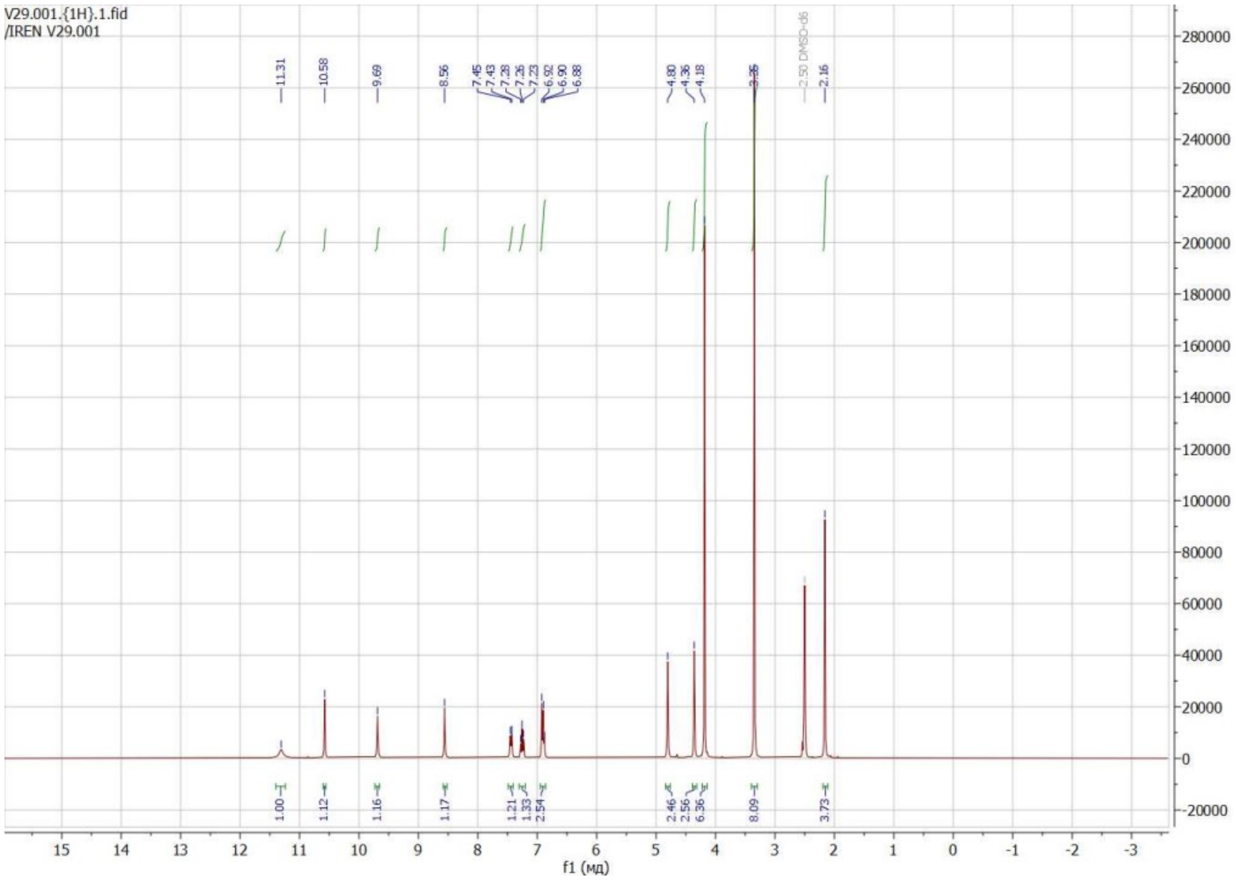


**Figure S7.** $^{1}$H NMR spectrum of **2a** in DMSO-d$_6$.

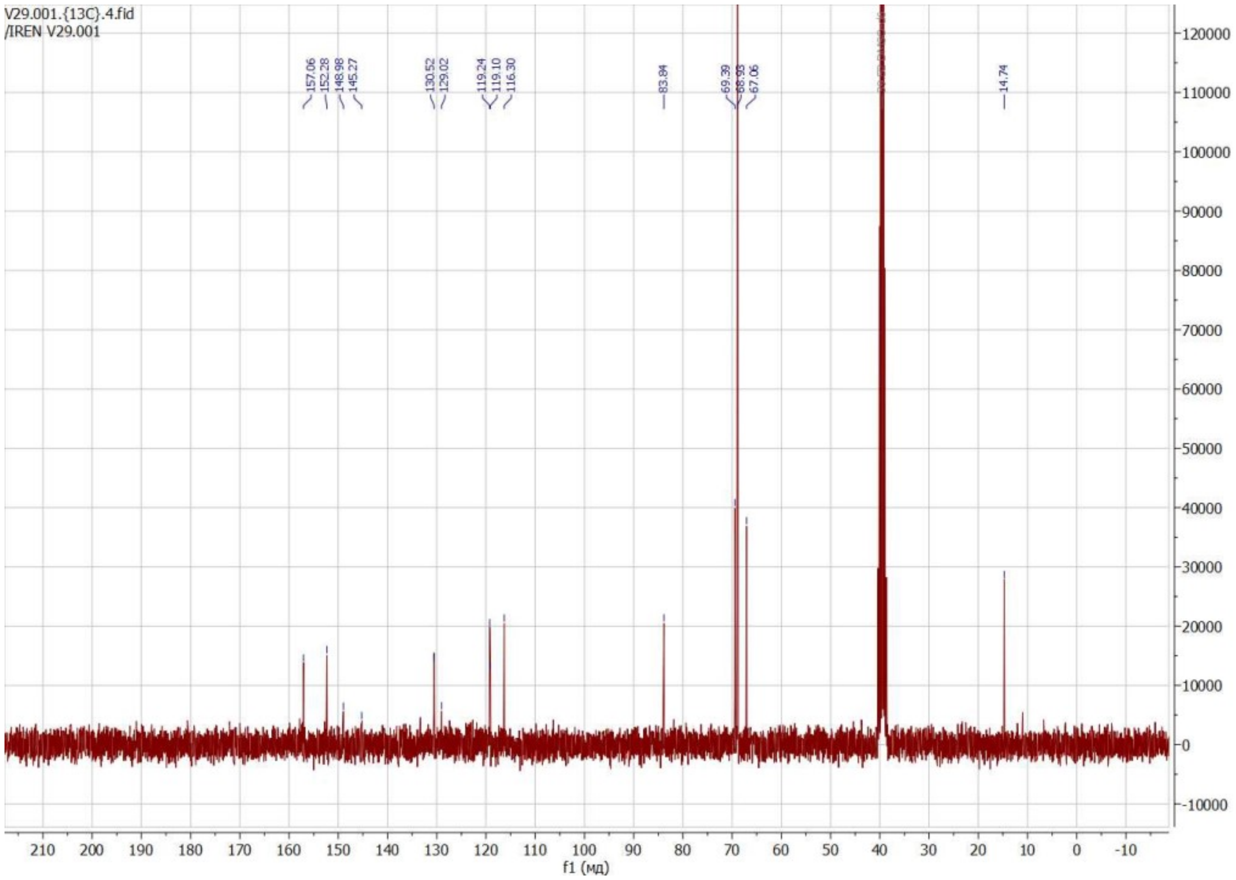


**Figure S8.** $^{13}$C NMR spectrum of **2a** in DMSO-d$_6$.

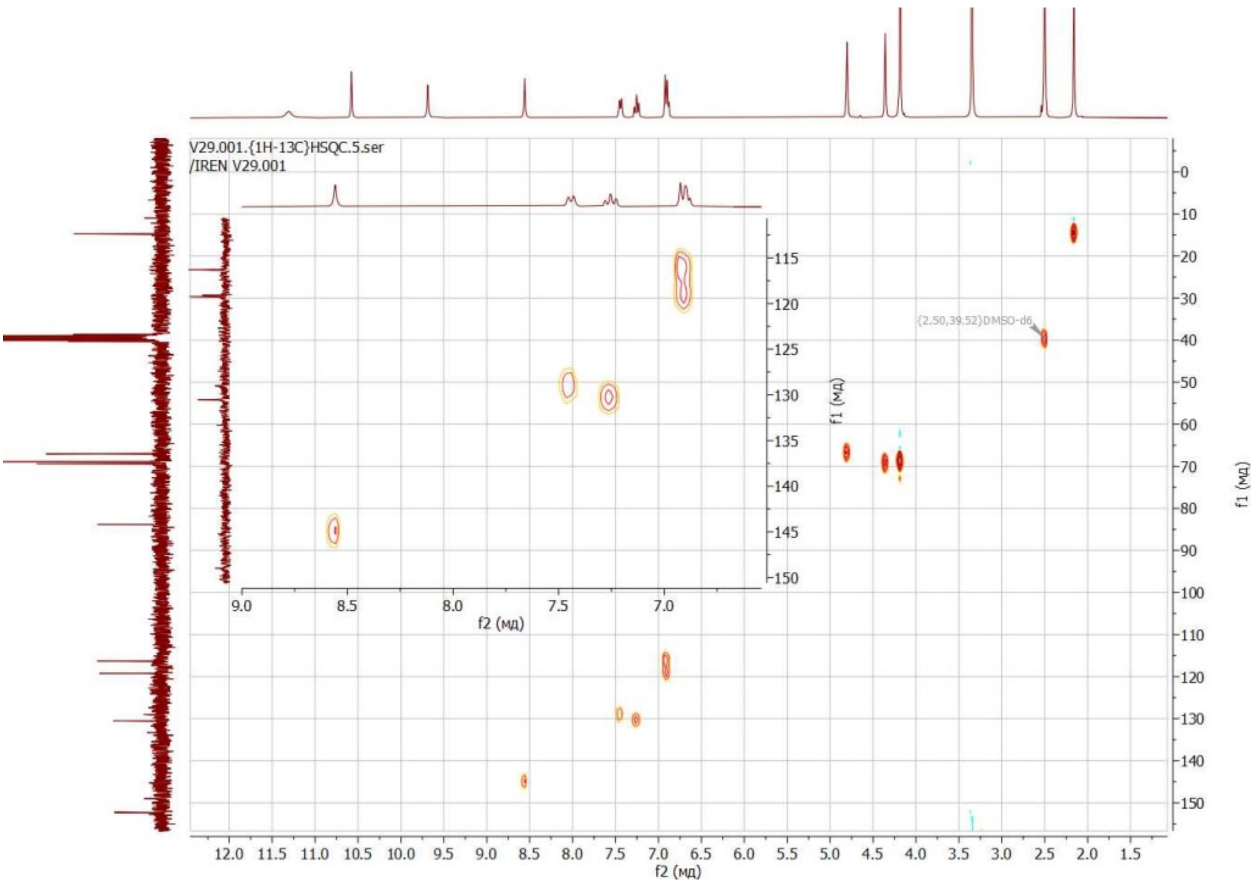



**Figure S9.** HSQC spectrum of **2a** in DMSO-d$_6$.

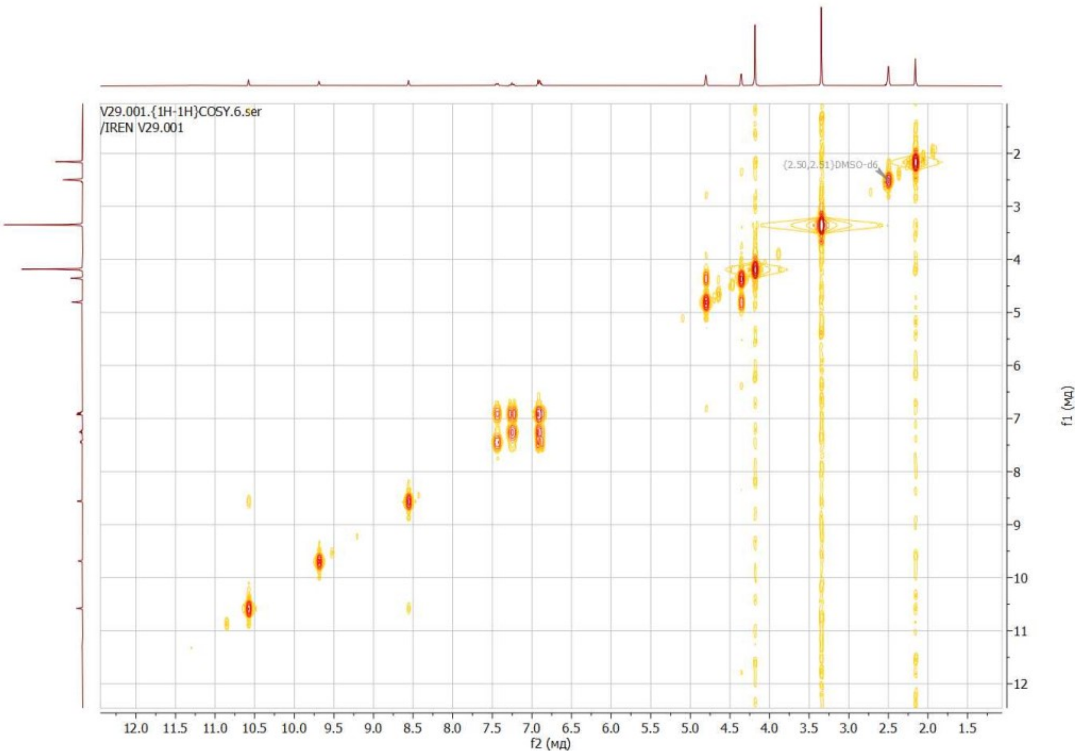



**Figure S10.** COSY spectrum of **2a** in DMSO-d$_6$.

## IR and mass-spectroscopy of 2a

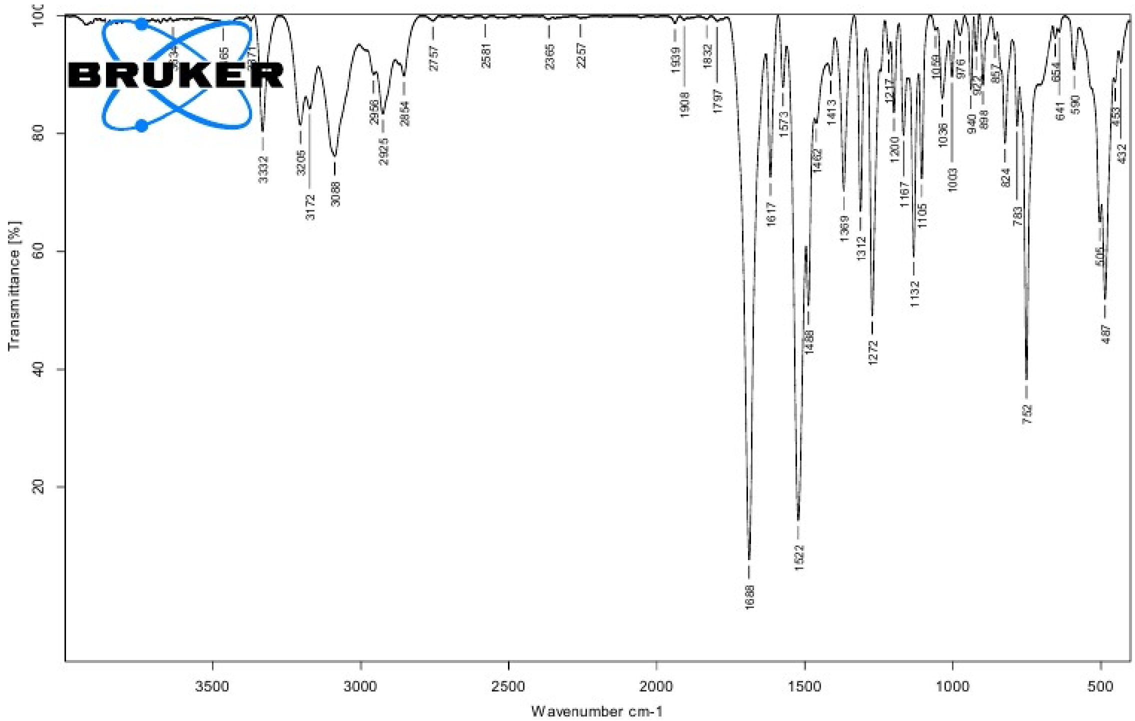



**Figure S11.** IR spectrum of **2a**.

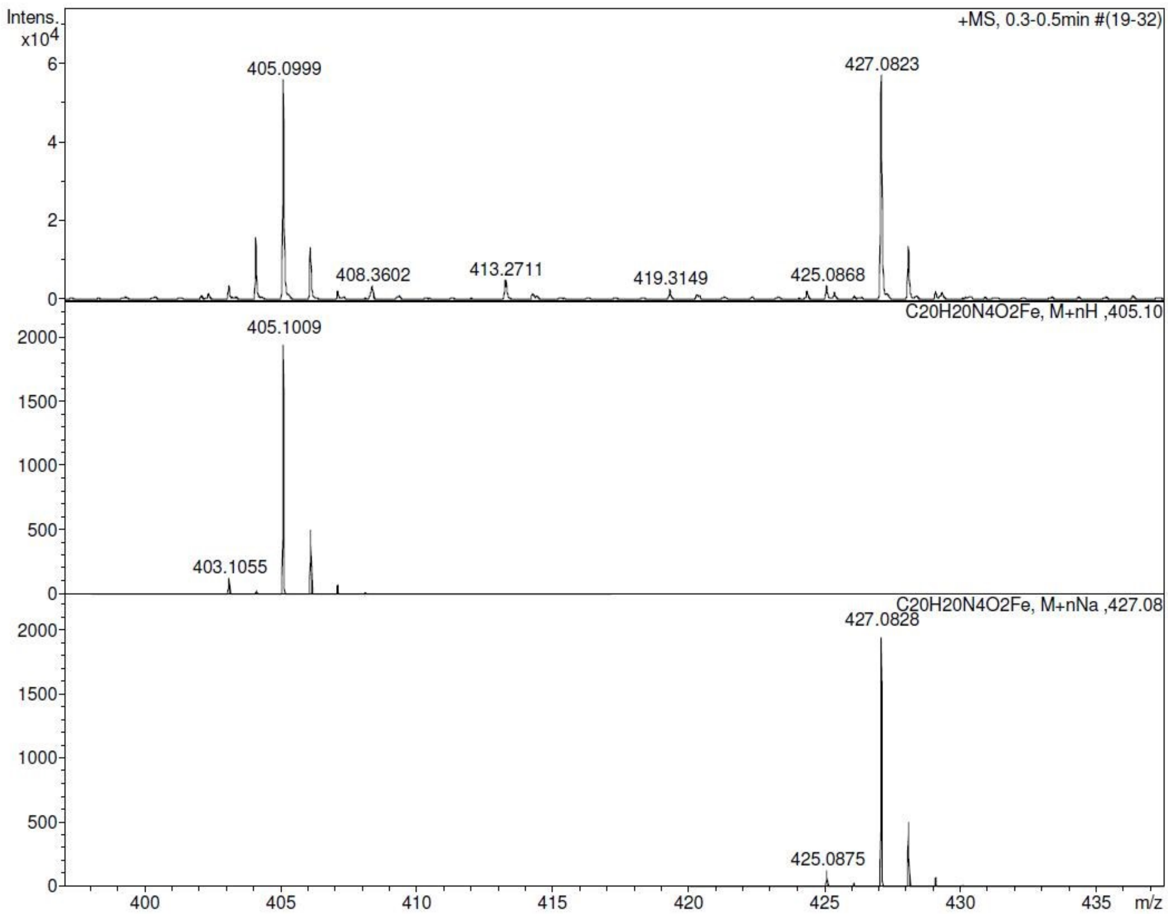



**Figure S12.** Molecular ion fragment of HRMS spectrum of **2a**.

# NMR, IR and mass-spectroscopy of 2b

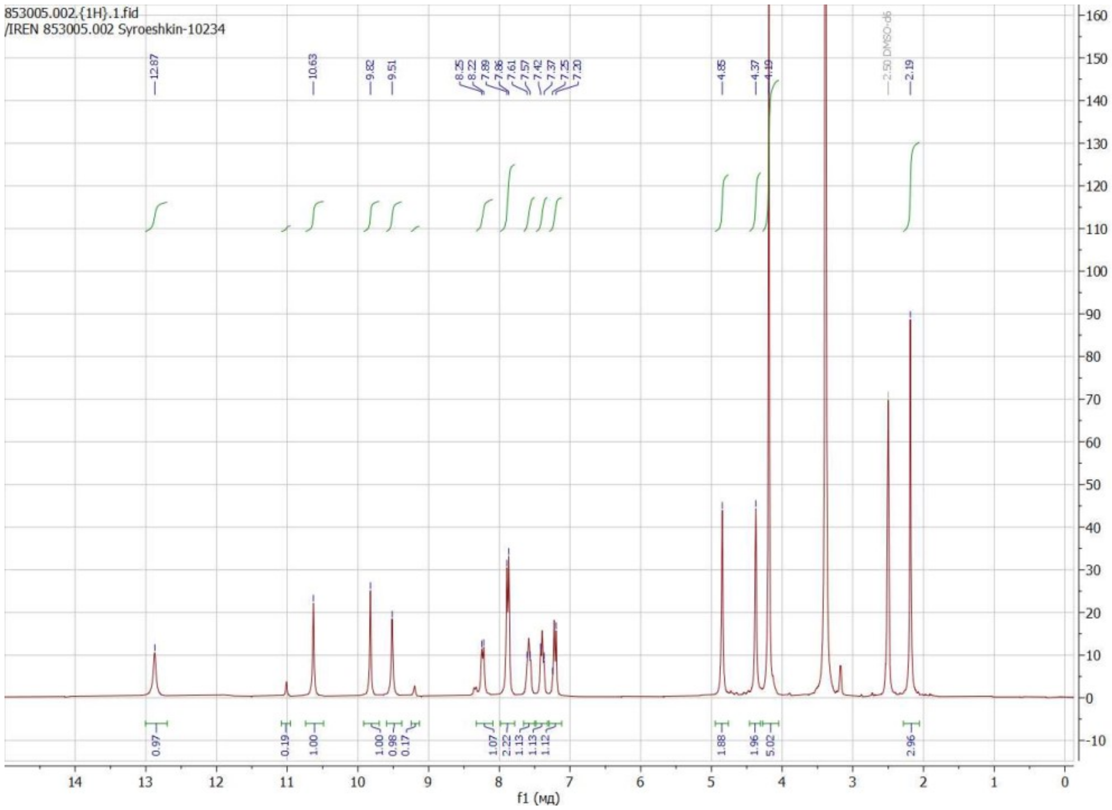



**Figure S13.** $^{1}H$ NMR spectrum of **2b** in DMSO-$d_6$.

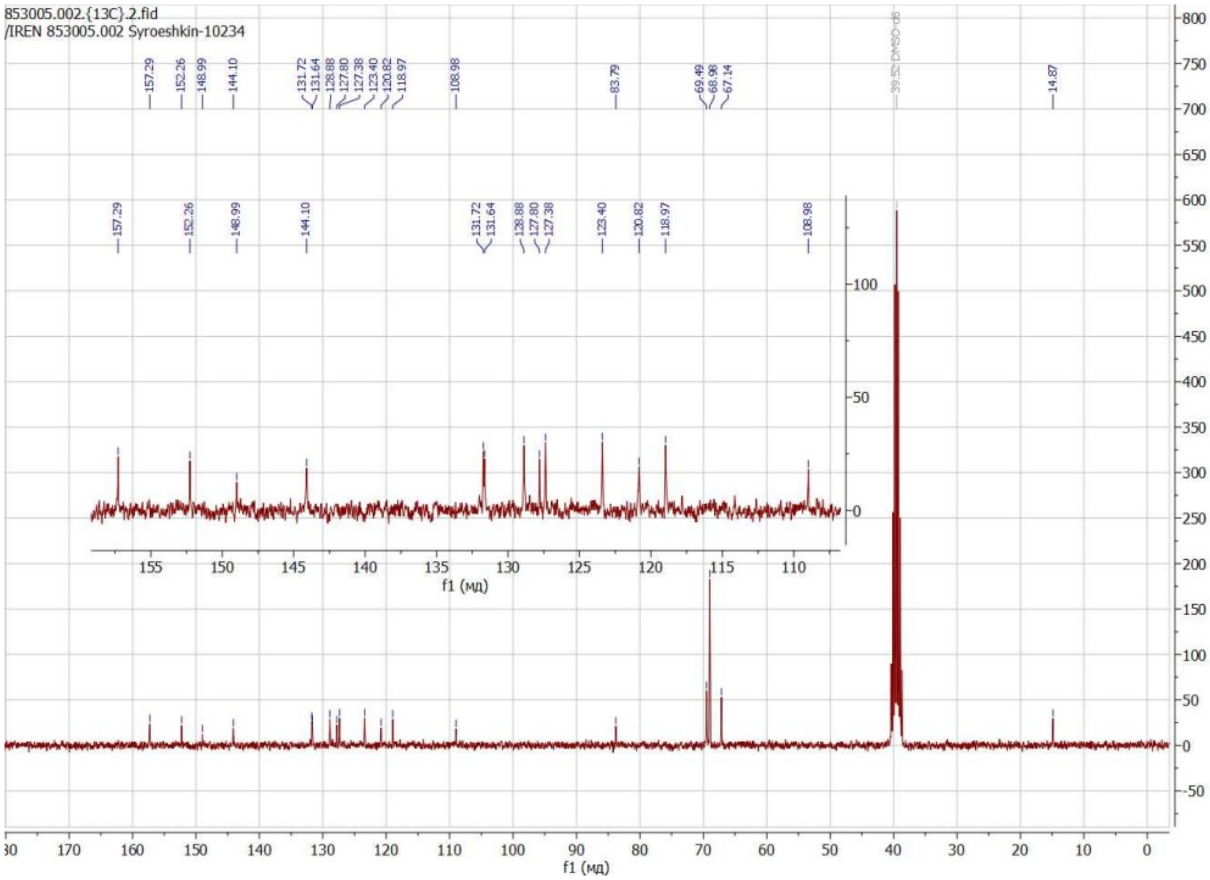



**Figure S14.** $^{13}C$ NMR spectrum of **2b** in DMSO-$d_6$.

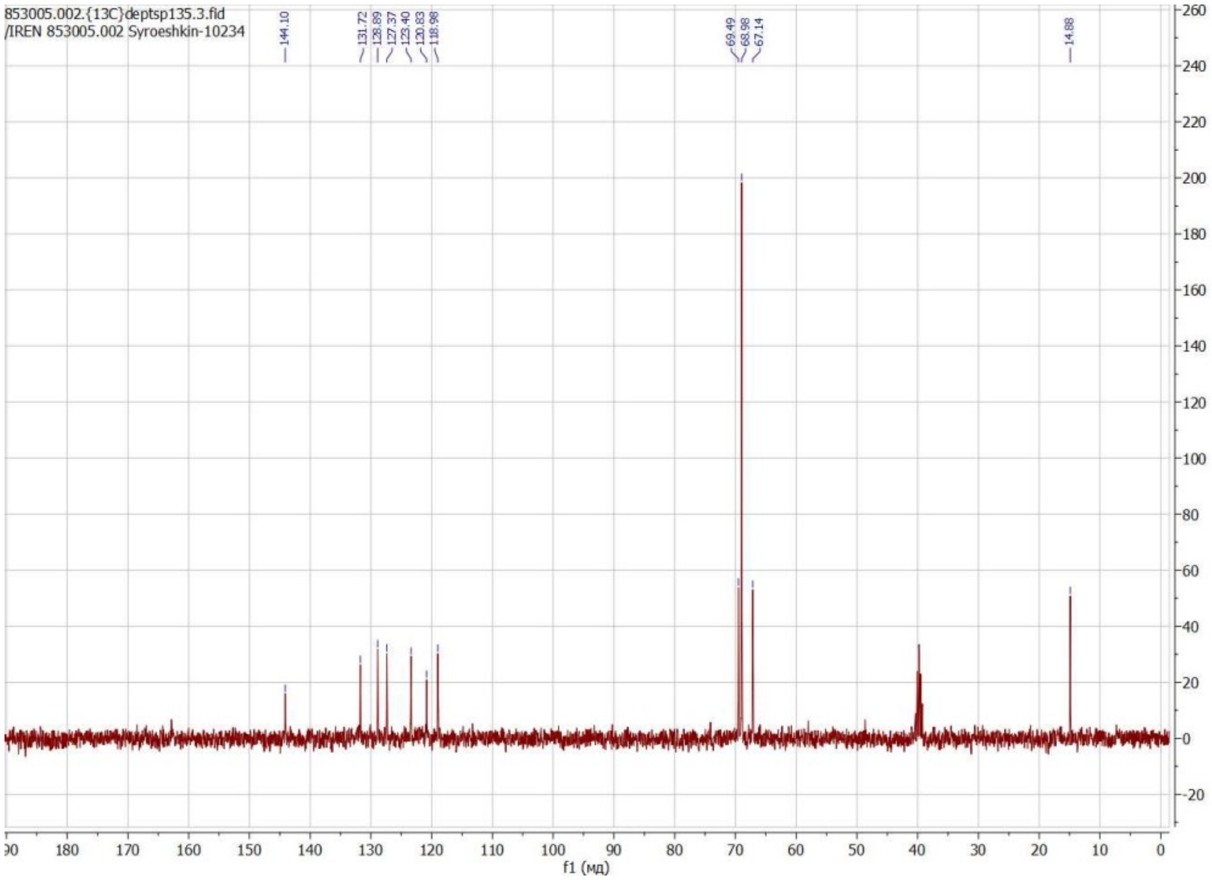



**Figure S15.** DEPT135 spectrum of **2b** in DMSO-$d_6$.

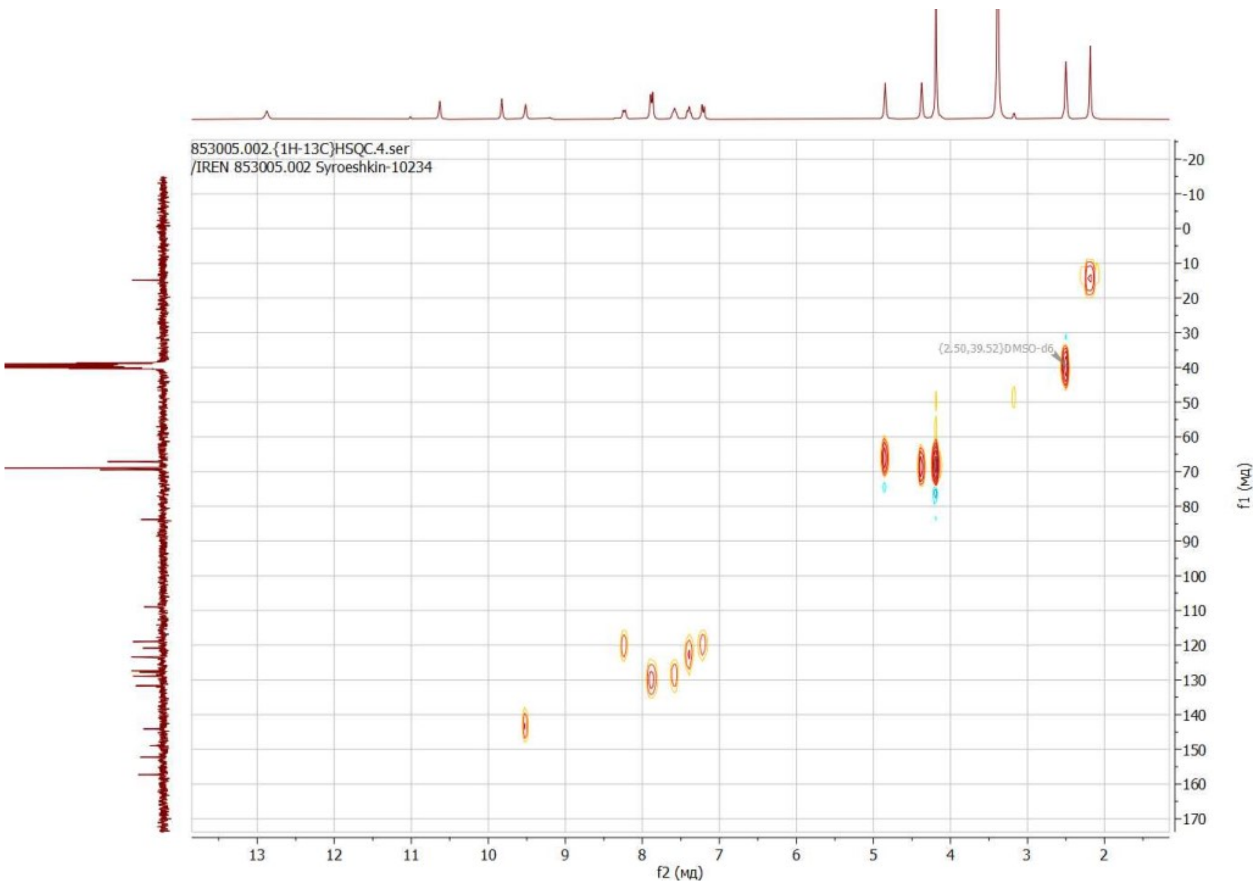



**Figure S16.** HSQC spectrum of **2b** in DMSO-$d_6$.

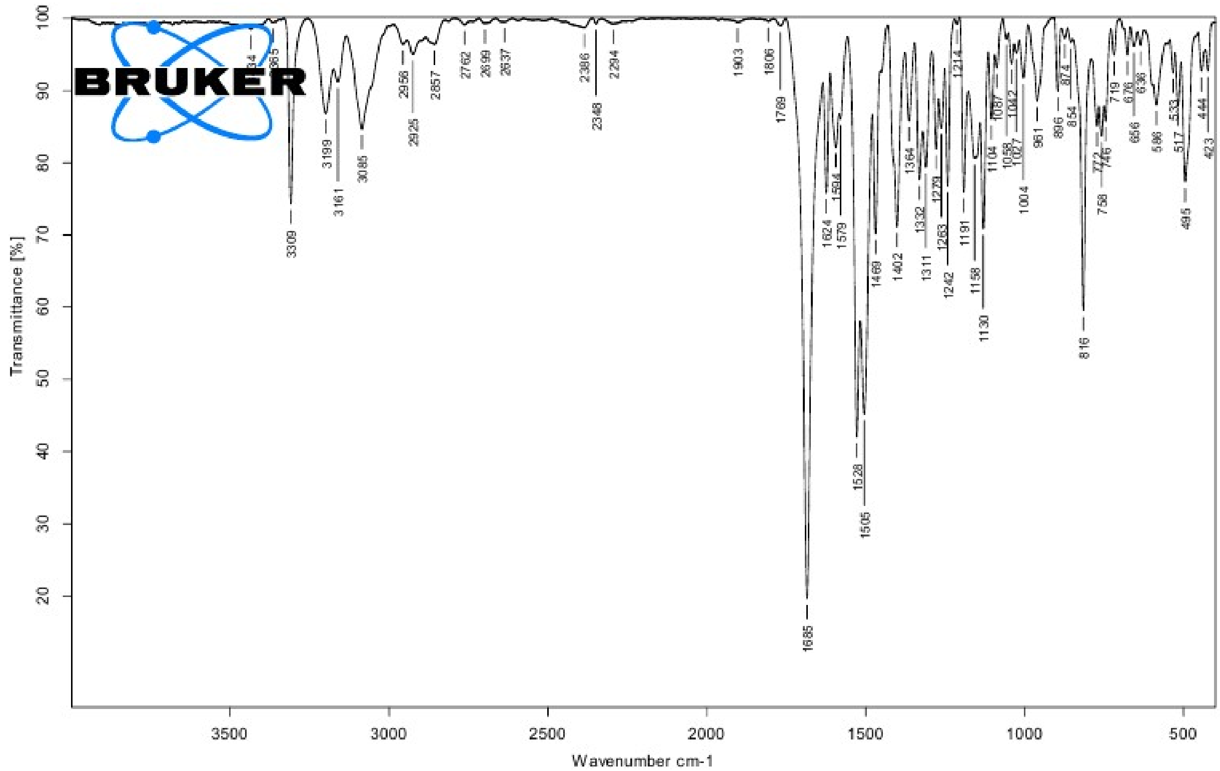



**Figure S17.** IR spectrum of **2b**.

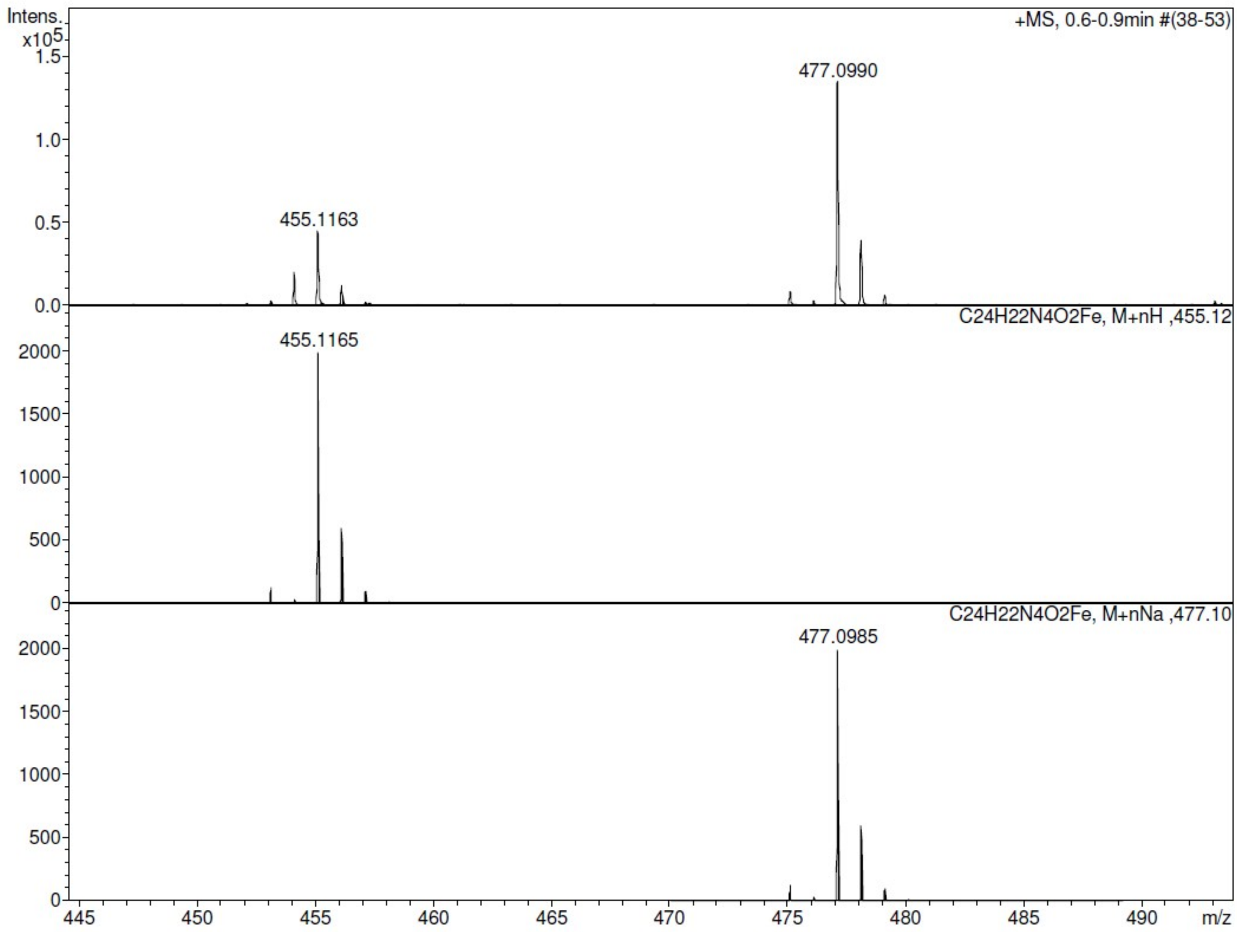



**Figure S18.** Molecular ion fragment of HRMS spectrum of **2b**.

## NMR, IR and mass-spectroscopy of 3a and 3b

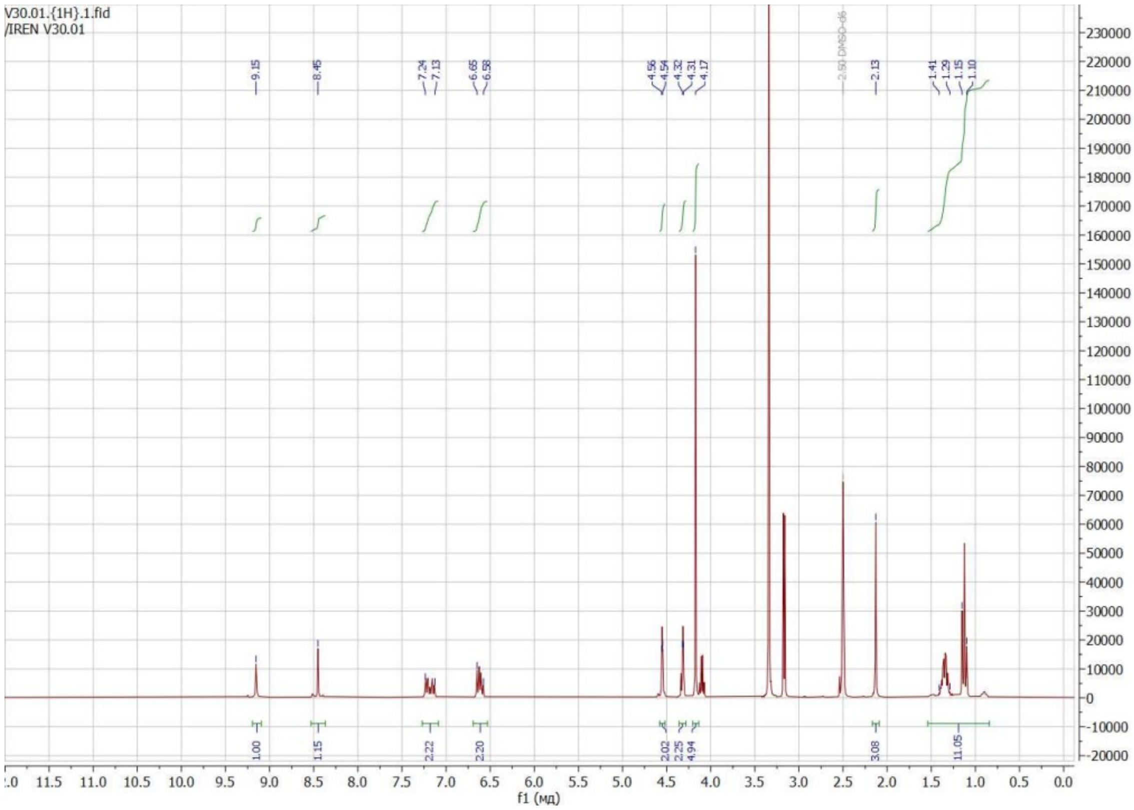



**Figure S19.** $^{1}H$ NMR spectrum of **3a** in DMSO-$d_6$.

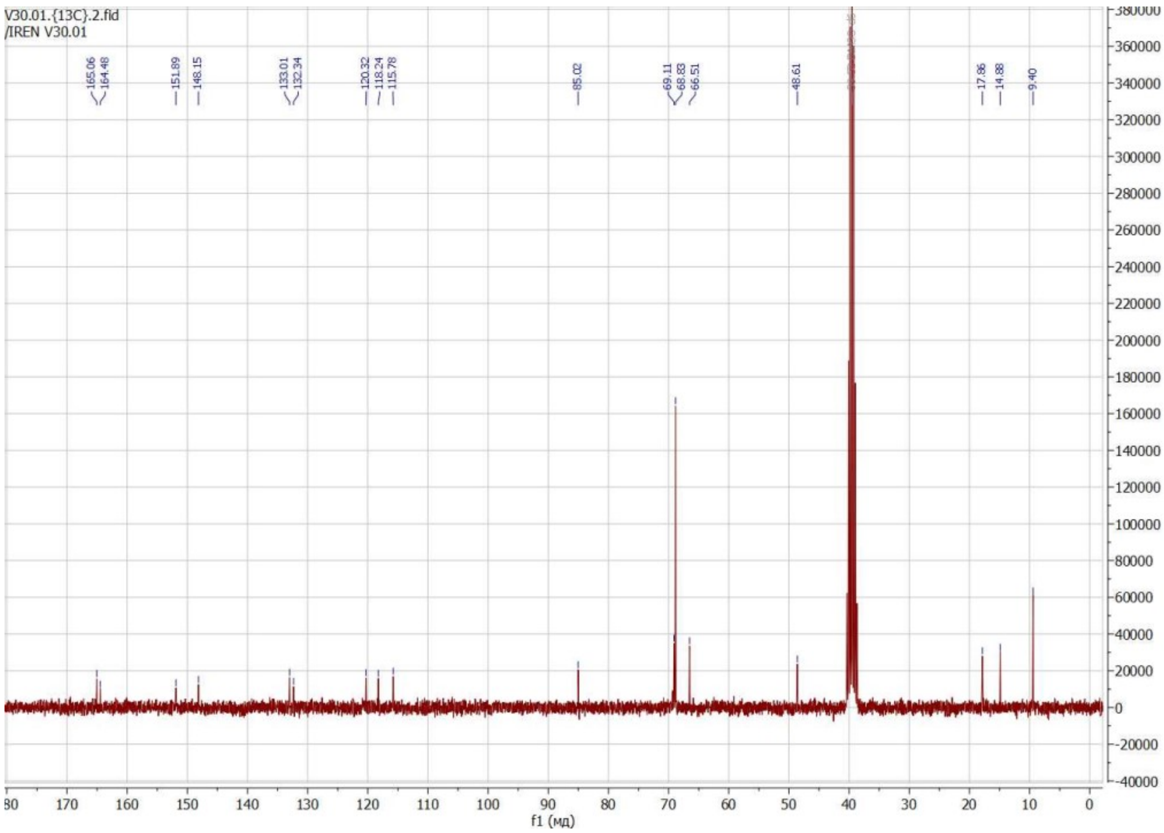



**Figure S20.** $^{13}C$ NMR spectrum of **3a** in DMSO-$d_6$.

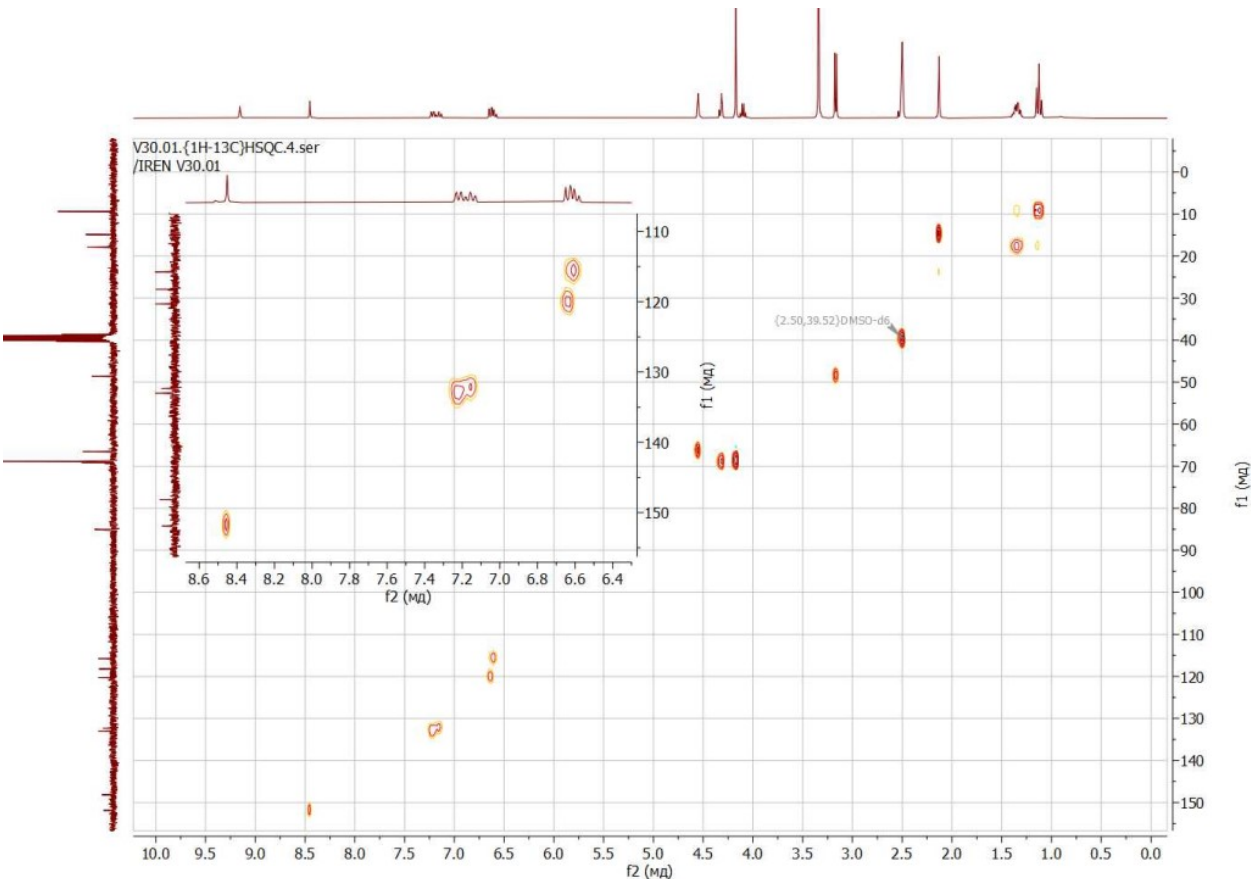



**Figure S21.** HSQC spectrum of **3a** in DMSO-$d_6$.

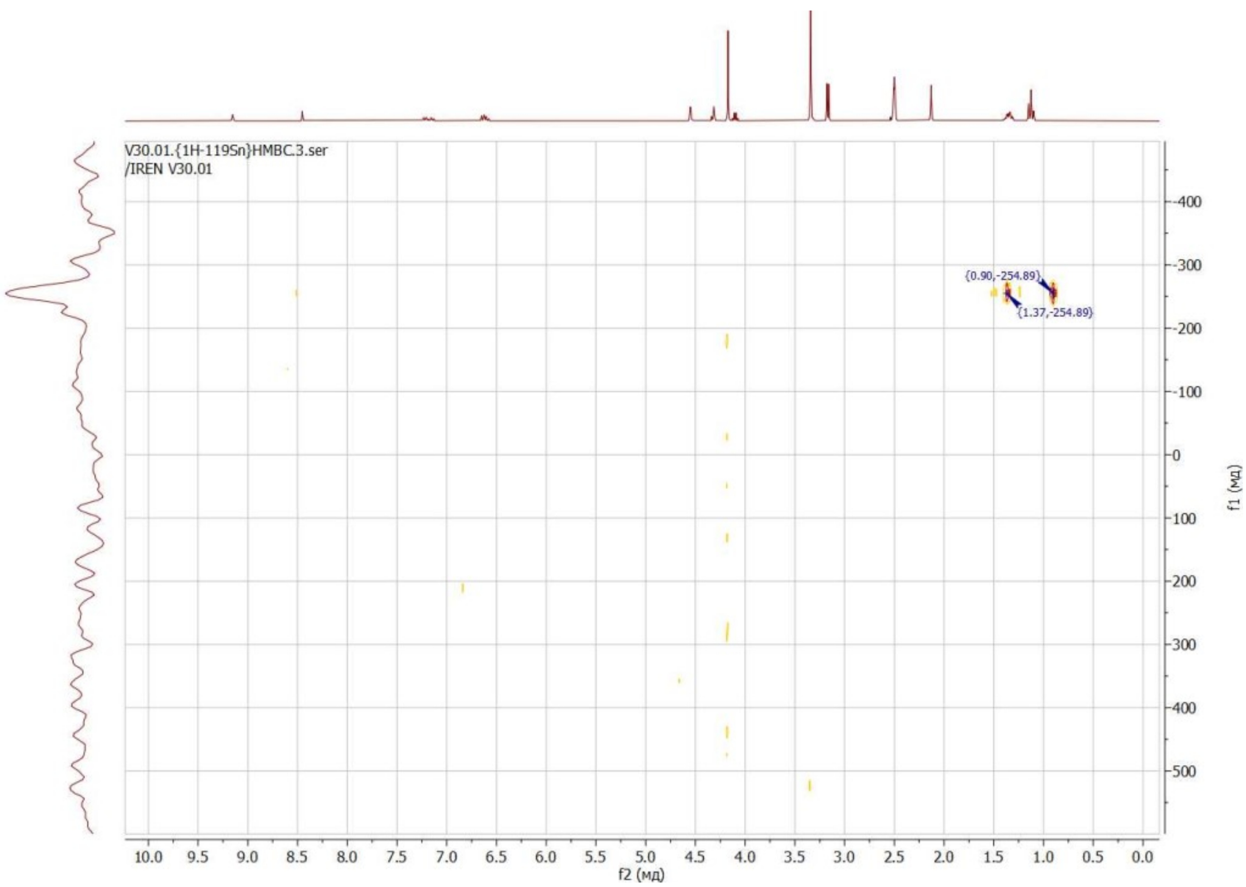



**Figure S22.** HMBC spectrum of **3a** in DMSO-$d_6$.

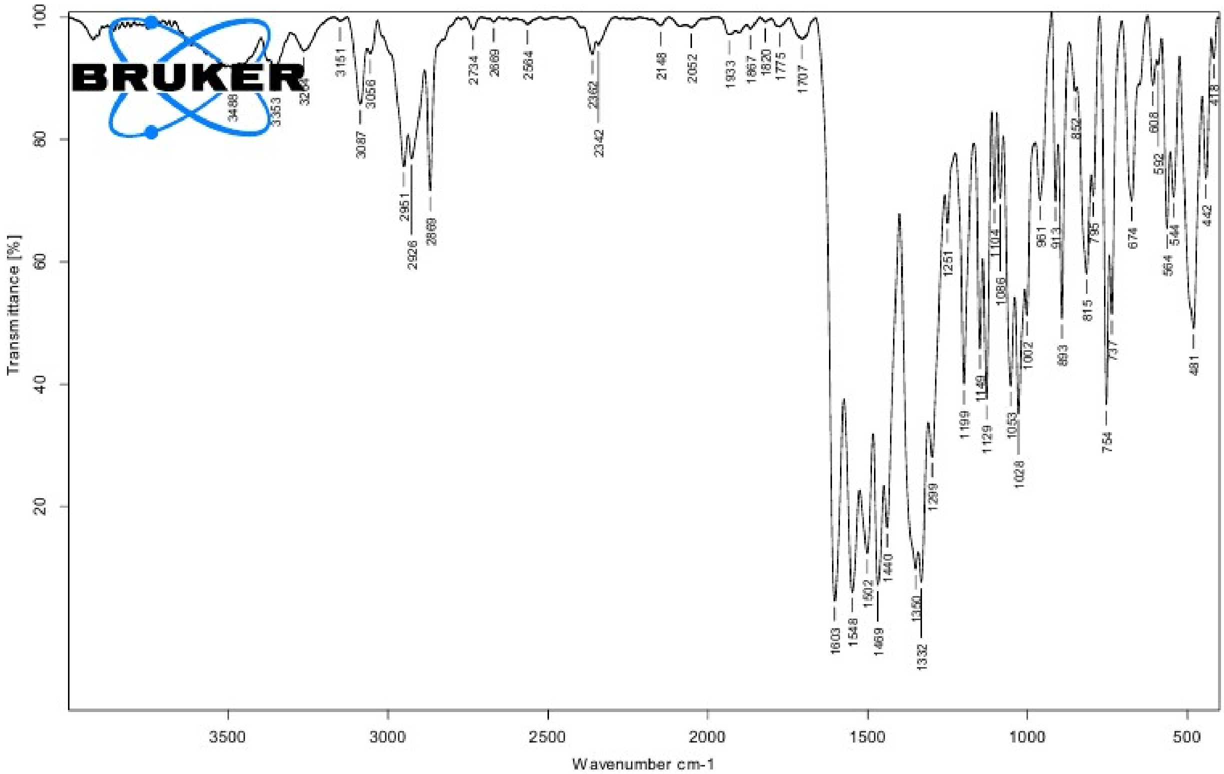



**Figure S23.** IR spectrum of **3a**.

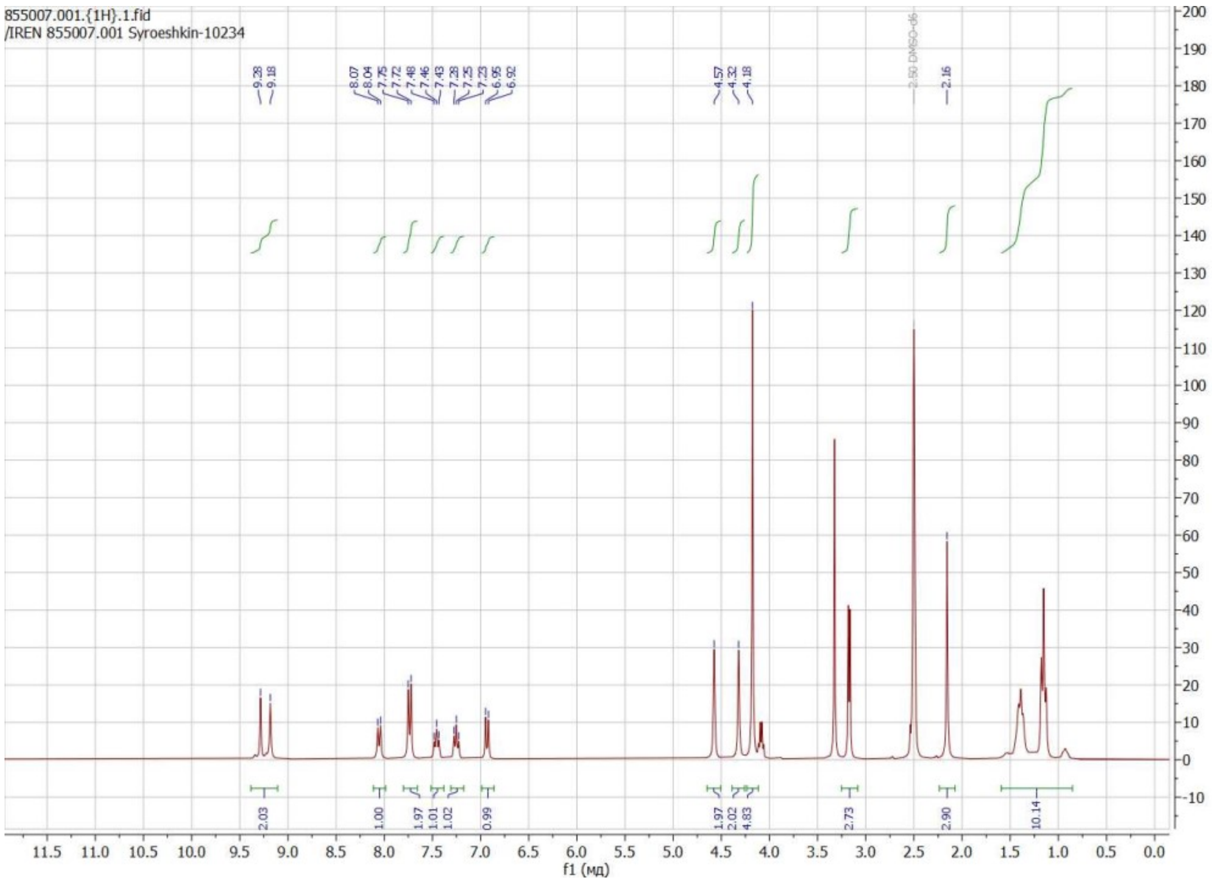



**Figure S24.** $^{1}$H NMR spectrum of **3b** in DMSO-d$_6$.

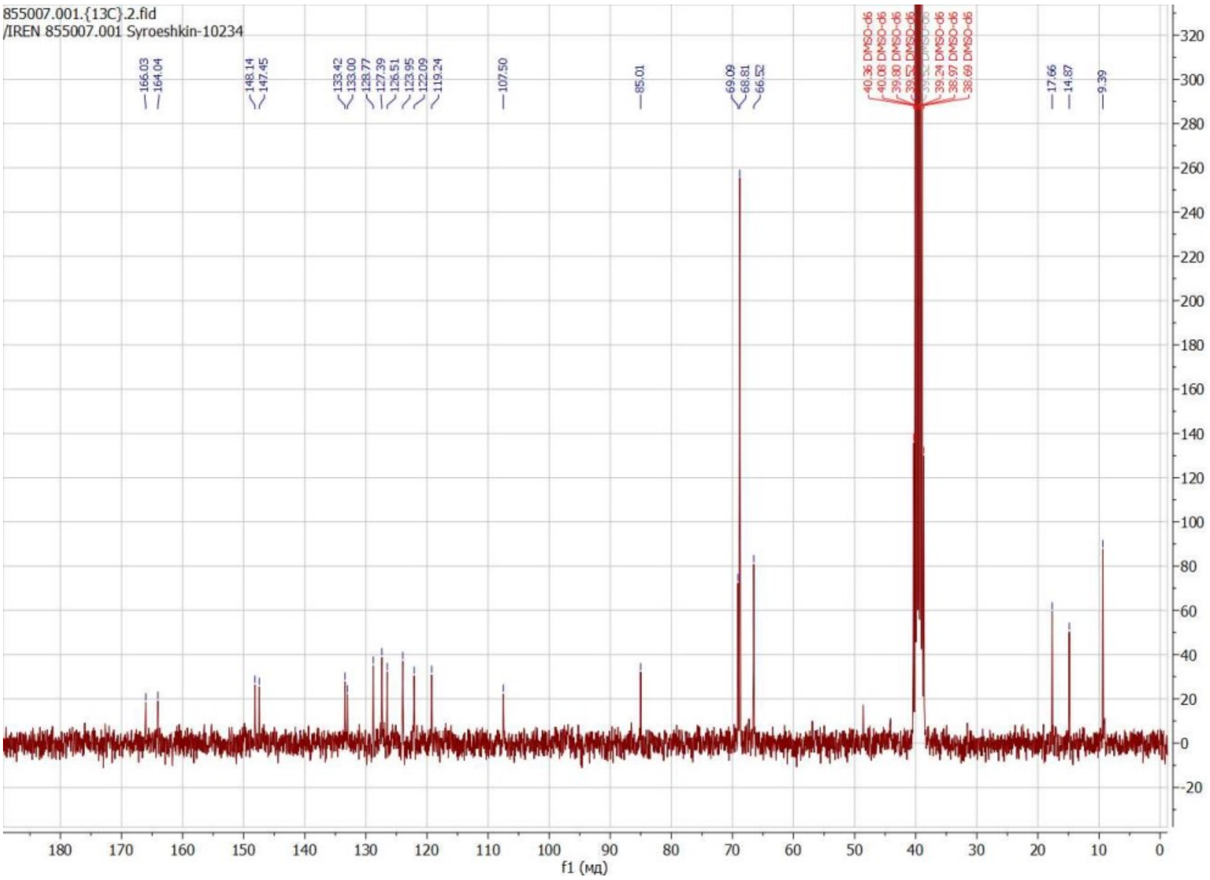



**Figure S25.** $^{13}C$ NMR spectrum of **3b** in DMSO-$d_6$.

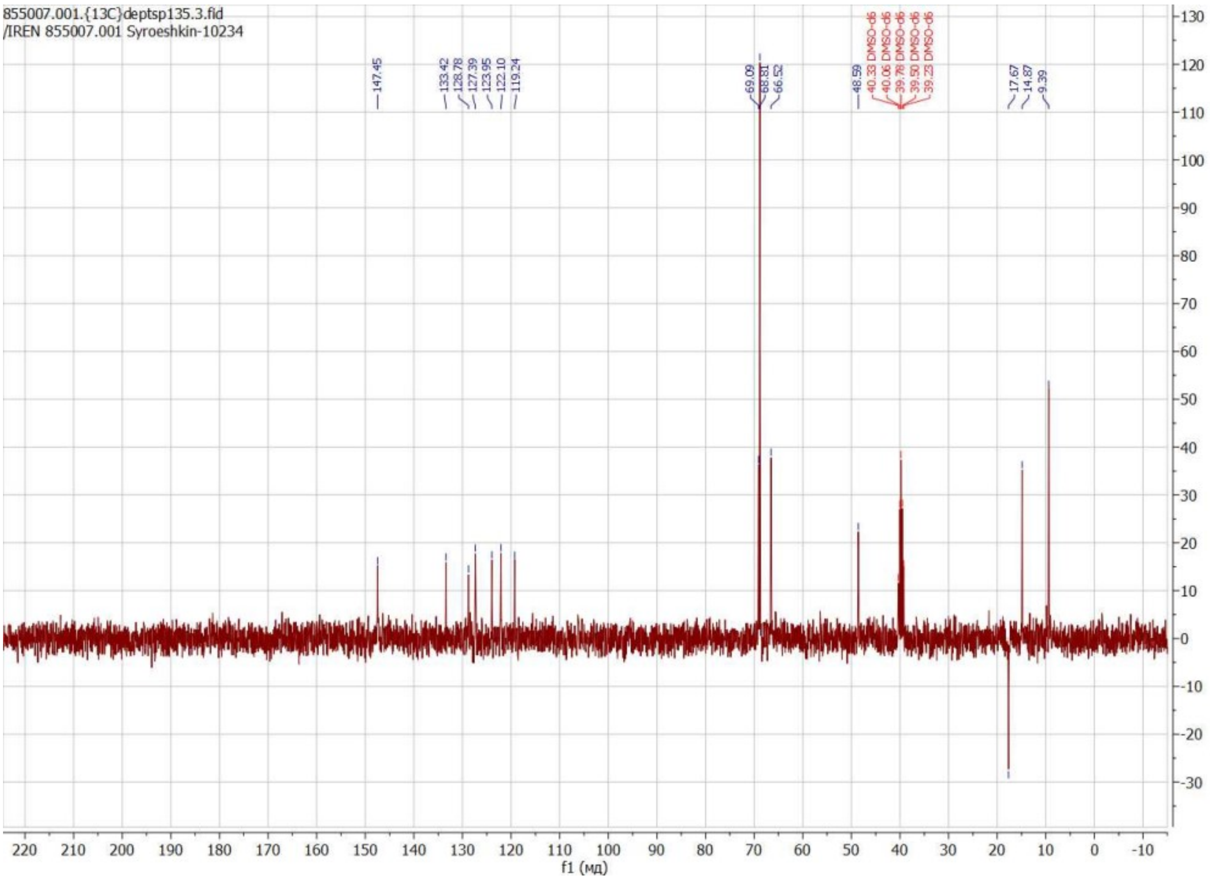



**Figure S26.** DEPT135 spectrum of **3b** in DMSO-$d_6$.

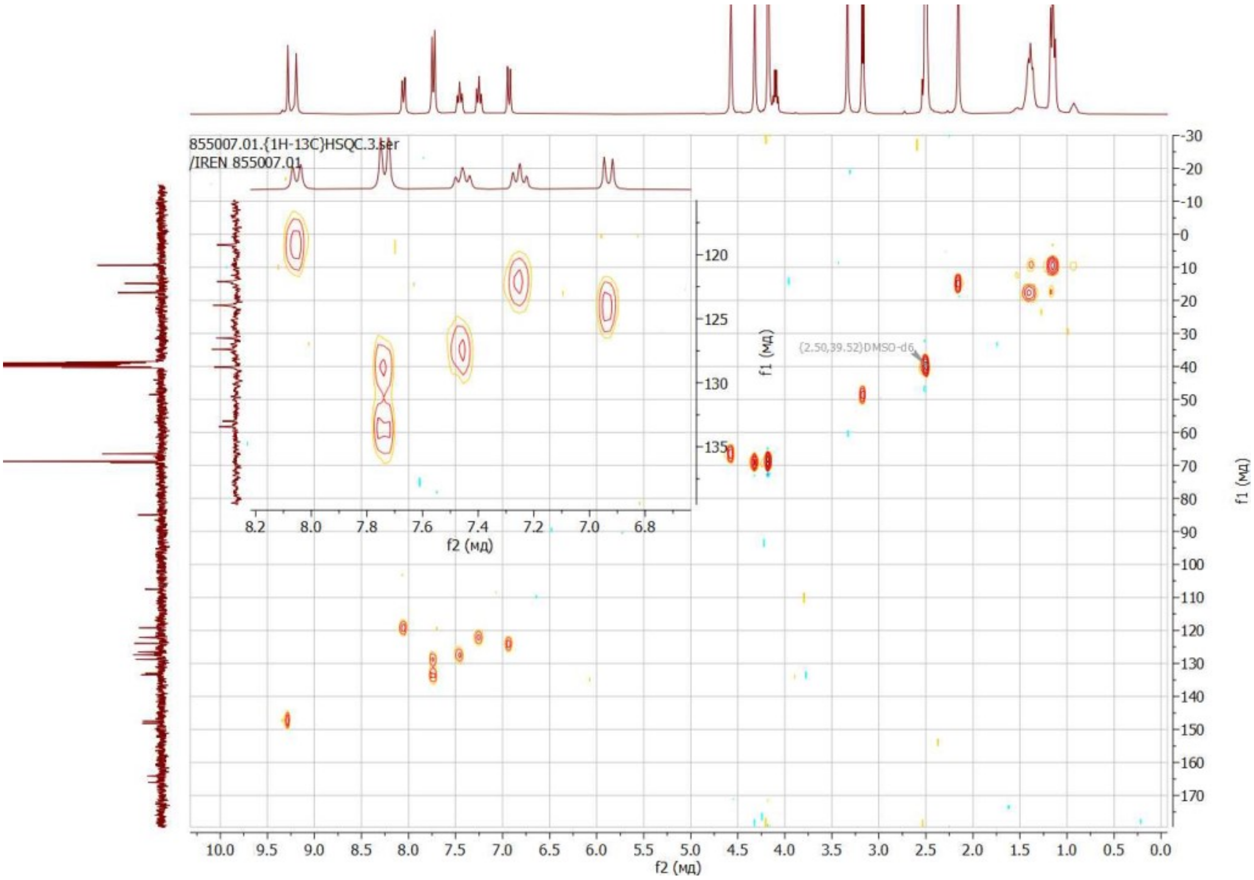


**Figure S27.** HSQC spectrum of **3b** in DMSO-$d_6$.

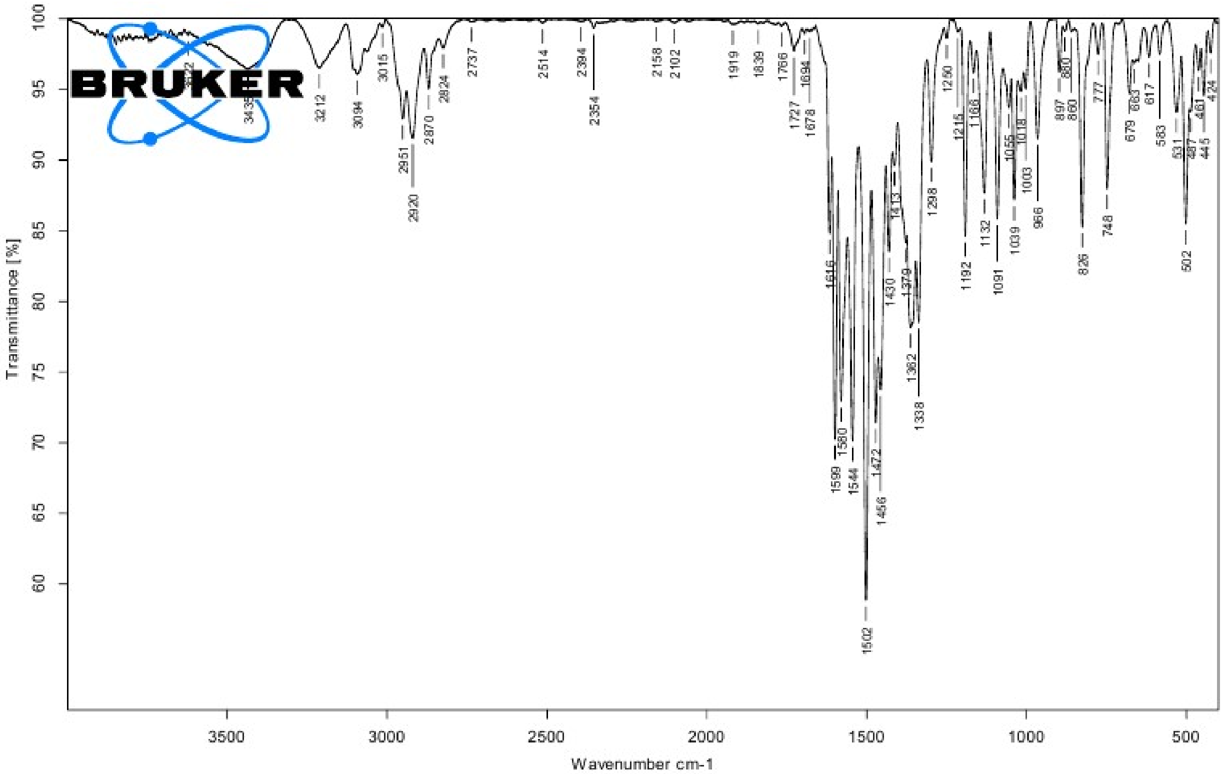


**Figure S28.** IR spectrum of **3b**.

## Crystal structures of 2b and 3a

X-ray diffraction data for **2b** and **3a**·4MeOH were collected at 100K on a four-circle Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu $K_{\alpha}$-radiation. The intensity data were integrated and analytically corrected (gaussian method) for absorption and decay by the CrysAlisPro program [1]. The structures were solved by dual methods using SHELXT-2014/5 [2] and refined by the full-matrix least-squares minimization method on $F^2$ using SHELXL-2018/3 [3] in the Olex2 program (ver.1.3 and 1.5) [4]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. For **2b**, locations of hydrogen atoms (H1, H2 and H3 at atoms O1, N2 and N3) were found from the electron density-difference map. For **3a**·4MeOH, positions of H2A, H4A, H4B and H5A (at N2, O4, O4A and O5, accordingly) were found from the electron density-difference map; the N-H and O-H distances were restrained to be 0.85(2)Å. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}$(H)=1.5$U_{eq}$(C) for methyl groups and $U_{iso}$(H)=1.2$U_{eq}$(C) otherwise. A rotating group model was applied for methyl groups in **2b** and **3a**·4MeOH and for hydroxyl groups O4-H4A and O5-H5A in **3a**·4MeOH. The *SHELXTL* program suite [5] was used for molecular graphics.

Crystal data, data collection and structure refinement details are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2475683 and 2475684; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/structures/

**Table S1.** Crystal data and structure refinement for **2b**.

| Identification code | **2b** | **3a**·4MeOH |
|---|---|---|
| Empirical formula | $C_{24}H_{22}FeN_4O_2$ | $C_{52}H_{72}Fe_2N_8O_8Sn_2$ |
| Formula weight | 454.30 | 1286.25 |
| Temperature, K | 100.0(1) | 100.0(1) |
| Wavelength, Å | 1.54184 | 1.54184 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | Pbca | $P\bar{1}$ |
| Unit cell dimensions | | |
| a, Å | 16.88798(12) | 7.63447(12) |
| b, Å | 11.87134(7) | 10.59566(18) |
| c, Å | 20.52860(14) | 17.0440(3) |
| α, ° | 90.0 | 97.9351(14) |
| β, ° | 90.0 | 90.0735(13) |
| γ, ° | 90.0 | 104.0650(14) |
| Volume, Å$^3$ | 4115.63(5) | 1323.72(4) |
| Z | 8 | 1 |
| Calcd. density, g·cm$^{-3}$ | 1.466 | 1.614 |
| Absorption coefficient (μ), mm$^{-1}$ | 6.118 | 12.218 |
| F(000) | 1888 | 656 |
| Crystal size, mm | 0.21 × 0.08 × 0.03 | 0.25 × 0.19 × 0.16 |
| θ range, ° | 4.307 - 80.015 | 4.346 - 80.409 |
| Index ranges | $-21 \le h \le 21$, | $-9 \le h \le 9$, |
| | $-12 \le k \le 15$, | $-13 \le k \le 13$, |
| | $-26 \le l \le 26$ | $-21 \le l \le 21$ |
| Reflections | | |
| Collected | 53108 | 10270* |
| Independent [$R_{int}$] | 4470 [0.0308] | 10270 [0*] |
| Observed with I>2σ(I) | 4141 | 10122 |
| Completeness to $\theta_{full}$ / $\theta_{max}$ | 1.000 / 0.994 | 0.999 / 0.992 |
| Max. / min. transmission | 1.000 / 0.450 | 0.379 / 0.200 |
| Data / restraints / parameters | 4470 / 0 / 290 | 10270 / 6 / 346 |
| Goodness-of-fit on $F^2$ | 1.093 | 1.067 |
| $R_1$ / $\omega R_2$ indices for I>2σ(I) | 0.0307 / 0.0877 | 0.0470 / 0.1328 |
| $R_1$ / $\omega R_2$ indices for all data | 0.0332 / 0.0896 | 0.0475 / 0.1331 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$, ē·Å$^{-3}$ | 0.365 / -0.603 | 1.787 / -1.108 |
| CCDC deposition number | 2475683 | 2475684 |

* The number of collected reflections are set equal to the number of independent reflections for **3a** due to conventional processing the X-ray data as for a non-merohedral twin. Therefore, $R_{int}$ is equal to zero.

**The structure of 2b**

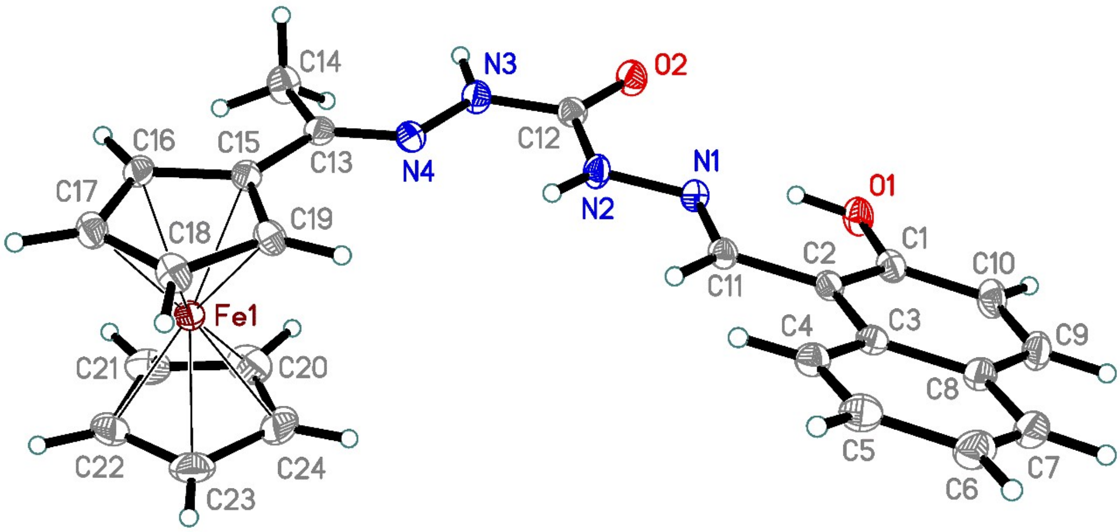



**Figure S29.** The structure of **2b**. The anisotropic thermal displacement ellipsoids for non-hydrogen atoms are set to a 50% probability level. Hydrogen bonds are not shown.

**Table S2.** Selected bond lengths [Å] for **2b**.

| | | | | | |
|---|---|---|---|---|---|
| Fe1-C15 | 2.0415(13) | N2-C12 | 1.3705(17) | C8-C9 | 1.419(2) |
| Fe1-C16 | 2.0473(14) | N3-N4 | 1.3895(15) | C9-C10 | 1.365(2) |
| Fe1-C17 | 2.0517(13) | N3-C12 | 1.3611(17) | C13-C14 | 1.5021(18) |
| Fe1-C18 | 2.0481(14) | N4-C13 | 1.2893(17) | C13-C15 | 1.4670(18) |
| Fe1-C19 | 2.0445(14) | C1-C2 | 1.3917(18) | C15-C16 | 1.4391(18) |
| Fe1-C20 | 2.0463(15) | C1-C10 | 1.4105(19) | C15-C19 | 1.4337(19) |
| Fe1-C21 | 2.0522(16) | C2-C3 | 1.4397(19) | C16-C17 | 1.424(2) |
| Fe1-C22 | 2.0483(14) | C2-C11 | 1.4535(18) | C17-C18 | 1.427(2) |
| Fe1-C23 | 2.0475(16) | C3-C4 | 1.4192(18) | C18-C19 | 1.4197(19) |
| Fe1-C24 | 2.0452(15) | C3-C8 | 1.4230(19) | C20-C21 | 1.419(3) |
| O1-C1 | 1.3604(17) | C4-C5 | 1.3713(19) | C20-C24 | 1.422(3) |
| O2-C12 | 1.2321(17) | C5-C6 | 1.408(2) | C21-C22 | 1.421(2) |
| N1-N2 | 1.3678(15) | C6-C7 | 1.369(2) | C22-C23 | 1.422(2) |
| N1-C11 | 1.2868(17) | C7-C8 | 1.420(2) | C23-C24 | 1.422(2) |

**Table S3.** Selected bond angles [°] for **2b**.

| | | | | | |
|---|---|---|---|---|---|
| C15-Fe1-C16 | 41.22(5) | C23-Fe1-C21 | 68.31(7) | N4-C13-C15 | 116.09(11) |
| C15-Fe1-C17 | 68.77(5) | C23-Fe1-C22 | 40.62(7) | C15-C13-C14 | 119.09(12) |
| C15-Fe1-C18 | 68.81(6) | C24-Fe1-C16 | 156.89(7) | C13-C15-Fe1 | 124.79(9) |
| C15-Fe1-C19 | 41.08(5) | C24-Fe1-C17 | 160.64(7) | C16-C15-Fe1 | 69.61(7) |
| C15-Fe1-C20 | 107.42(6) | C24-Fe1-C18 | 123.45(7) | C16-C15-C13 | 126.92(12) |
| C15-Fe1-C21 | 124.97(6) | C24-Fe1-C20 | 40.68(8) | C19-C15-Fe1 | 69.57(8) |
| C15-Fe1-C22 | 162.04(6) | C24-Fe1-C21 | 68.28(7) | C19-C15-C13 | 125.43(12) |
| C15-Fe1-C23 | 155.76(6) | C24-Fe1-C22 | 68.30(6) | C19-C15-C16 | 107.62(12) |
| C15-Fe1-C24 | 120.56(6) | C24-Fe1-C23 | 40.65(7) | C15-C16-Fe1 | 69.18(7) |
| C16-Fe1-C17 | 40.65(6) | C11-N1-N2 | 118.05(11) | C17-C16-Fe1 | 69.84(8) |
| C16-Fe1-C18 | 68.73(6) | N1-N2-C12 | 117.56(11) | C17-C16-C15 | 107.69(12) |
| C16-Fe1-C21 | 108.41(6) | C12-N3-N4 | 118.13(11) | C16-C17-Fe1 | 69.51(8) |
| C16-Fe1-C22 | 125.04(6) | C13-N4-N3 | 117.54(11) | C16-C17-C18 | 108.36(12) |
| C16-Fe1-C23 | 161.37(7) | O1-C1-C2 | 122.30(12) | C18-C17-Fe1 | 69.49(8) |
| C17-Fe1-C21 | 122.29(7) | O1-C1-C10 | 116.61(12) | C17-C18-Fe1 | 69.76(8) |
| C18-Fe1-C17 | 40.74(6) | C2-C1-C10 | 121.08(13) | C19-C18-Fe1 | 69.56(8) |
| C18-Fe1-C21 | 157.12(7) | C1-C2-C3 | 119.22(12) | C19-C18-C17 | 108.18(13) |
| C18-Fe1-C22 | 121.22(6) | C1-C2-C11 | 120.62(13) | C15-C19-Fe1 | 69.35(7) |
| C19-Fe1-C16 | 69.03(6) | C3-C2-C11 | 120.15(11) | C18-C19-Fe1 | 69.84(8) |
| C19-Fe1-C17 | 68.51(6) | C4-C3-C2 | 122.95(12) | C18-C19-C15 | 108.15(12) |
| C19-Fe1-C18 | 40.60(5) | C4-C3-C8 | 117.88(12) | C21-C20-Fe1 | 69.97(9) |
| C19-Fe1-C20 | 124.10(7) | C8-C3-C2 | 119.12(12) | C21-C20-C24 | 108.09(15) |
| C19-Fe1-C21 | 161.47(7) | C5-C4-C3 | 120.93(13) | C24-C20-Fe1 | 69.62(9) |
| C19-Fe1-C22 | 155.86(6) | C4-C5-C6 | 121.01(13) | C20-C21-Fe1 | 69.52(9) |
| C19-Fe1-C23 | 120.08(7) | C7-C6-C5 | 119.68(13) | C20-C21-C22 | 107.94(15) |
| C19-Fe1-C24 | 106.47(7) | C6-C7-C8 | 120.69(14) | C22-C21-Fe1 | 69.58(9) |
| C20-Fe1-C16 | 121.88(7) | C7-C8-C3 | 119.80(13) | C21-C22-Fe1 | 69.88(9) |
| C20-Fe1-C17 | 157.48(7) | C9-C8-C3 | 119.01(13) | C21-C22-C23 | 108.15(15) |
| C20-Fe1-C18 | 160.48(7) | C9-C8-C7 | 121.14(14) | C23-C22-Fe1 | 69.66(9) |
| C20-Fe1-C21 | 40.51(7) | C10-C9-C8 | 121.51(13) | C22-C23-Fe1 | 69.72(9) |
| C20-Fe1-C22 | 68.22(6) | C9-C10-C1 | 120.01(13) | C22-C23-C24 | 107.83(15) |
| C20-Fe1-C23 | 68.38(7) | N1-C11-C2 | 119.38(12) | C24-C23-Fe1 | 69.58(9) |
| C22-Fe1-C17 | 108.18(6) | O2-C12-N2 | 122.66(12) | C20-C24-Fe1 | 69.70(9) |
| C22-Fe1-C21 | 40.54(7) | O2-C12-N3 | 122.60(12) | C23-C24-Fe1 | 69.76(9) |
| C23-Fe1-C17 | 124.33(7) | N3-C12-N2 | 114.74(12) | C23-C24-C20 | 107.99(15) |
| C23-Fe1-C18 | 106.75(7) | N4-C13-C14 | 124.81(12) | | |

**Table S4.** Torsion angles [°] for **2b**.

| | | | |
|---|---|---|---|
| Fe1-C15-C16-C17 | 59.45(9) | C6-C7-C8-C9 | 175.98(14) |
| Fe1-C15-C19-C18 | -59.26(10) | C7-C8-C9-C10 | -176.91(14) |
| Fe1-C16-C17-C18 | 58.80(10) | C8-C3-C4-C5 | 0.53(19) |
| Fe1-C17-C18-C19 | 59.16(10) | C8-C9-C10-C1 | -0.3(2) |
| Fe1-C18-C19-C15 | 58.95(9) | C10-C1-C2-C3 | 2.4(2) |
| Fe1-C20-C21-C22 | -59.18(11) | C10-C1-C2-C11 | -178.33(12) |
| Fe1-C20-C24-C23 | 59.48(11) | C11-N1-N2-C12 | 178.50(12) |
| Fe1-C21-C22-C23 | -59.36(11) | C11-C2-C3-C4 | -4.1(2) |
| Fe1-C22-C23-C24 | -59.37(11) | C11-C2-C3-C8 | 178.66(12) |
| Fe1-C23-C24-C20 | -59.44(11) | C12-N3-N4-C13 | -172.57(12) |
| O1-C1-C2-C3 | -177.22(12) | C13-C15-C16-Fe1 | 118.82(13) |
| O1-C1-C2-C11 | 2.1(2) | C13-C15-C16-C17 | 178.28(12) |
| O1-C1-C10-C9 | 178.39(12) | C13-C15-C19-Fe1 | -118.83(13) |
| N1-N2-C12-O2 | -3.90(19) | C13-C15-C19-C18 | -178.09(12) |
| N1-N2-C12-N3 | 175.56(11) | C14-C13-C15-Fe1 | 83.73(14) |
| N2-N1-C11-C2 | 177.24(11) | C14-C13-C15-C16 | -5.8(2) |
| N3-N4-C13-C14 | -0.12(19) | C14-C13-C15-C19 | 172.16(13) |
| N3-N4-C13-C15 | 179.82(11) | C15-C16-C17-Fe1 | -59.03(9) |
| N4-N3-C12-O2 | -177.56(12) | C15-C16-C17-C18 | -0.24(15) |
| N4-N3-C12-N2 | 2.99(17) | C16-C15-C19-Fe1 | 59.44(9) |
| N4-C13-C15-Fe1 | -96.22(13) | C16-C15-C19-C18 | 0.18(15) |
| N4-C13-C15-C16 | 174.28(12) | C16-C17-C18-Fe1 | -58.80(9) |
| N4-C13-C15-C19 | -7.78(19) | C16-C17-C18-C19 | 0.35(16) |
| C1-C2-C3-C4 | 175.23(13) | C17-C18-C19-Fe1 | -59.28(10) |
| C1-C2-C3-C8 | -2.03(19) | C17-C18-C19-C15 | -0.33(16) |
| C1-C2-C11-N1 | -10.0(2) | C19-C15-C16-Fe1 | -59.42(9) |
| C2-C1-C10-C9 | -1.2(2) | C19-C15-C16-C17 | 0.03(15) |
| C2-C3-C4-C5 | -176.76(13) | C20-C21-C22-Fe1 | 59.14(11) |
| C2-C3-C8-C7 | 178.10(13) | C20-C21-C22-C23 | -0.21(17) |
| C2-C3-C8-C9 | 0.58(19) | C21-C20-C24-Fe1 | -59.62(11) |
| C3-C2-C11-N1 | 169.26(12) | C21-C20-C24-C23 | -0.14(18) |
| C3-C4-C5-C6 | -1.0(2) | C21-C22-C23-Fe1 | 59.49(11) |
| C3-C8-C9-C10 | 0.6(2) | C21-C22-C23-C24 | 0.13(17) |
| C4-C3-C8-C7 | 0.71(19) | C22-C23-C24-Fe1 | 59.45(11) |
| C4-C3-C8-C9 | -176.81(12) | C22-C23-C24-C20 | 0.01(18) |
| C4-C5-C6-C7 | 0.3(2) | C24-C20-C21-Fe1 | 59.40(11) |
| C5-C6-C7-C8 | 1.0(2) | C24-C20-C21-C22 | 0.22(17) |
| C6-C7-C8-C3 | -1.5(2) | | |

**Table S5.** Hydrogen bond parameters for **2b** [Å and °].

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O1-H1···N1 | 0.93(2) | 1.70(2) | 2.5410(15) | 149.7(17) |
| N2-H2···N4 | 0.84(2) | 2.217(18) | 2.5906(16) | 107.1(15) |
| N2-H2···O1#1 | 0.84(2) | 2.572(19) | 3.2706(15) | 141.6(16) |
| N3-H3···O2#2 | 0.85(2) | 2.02(2) | 2.8639(15) | 168.0(18) |

Symmetry transformations to generate equivalent atoms: #1 -x+3/2, y+1/2, z; #2 -x+1, -y+1, -z+1.

**The structure of 3a**·4MeOH

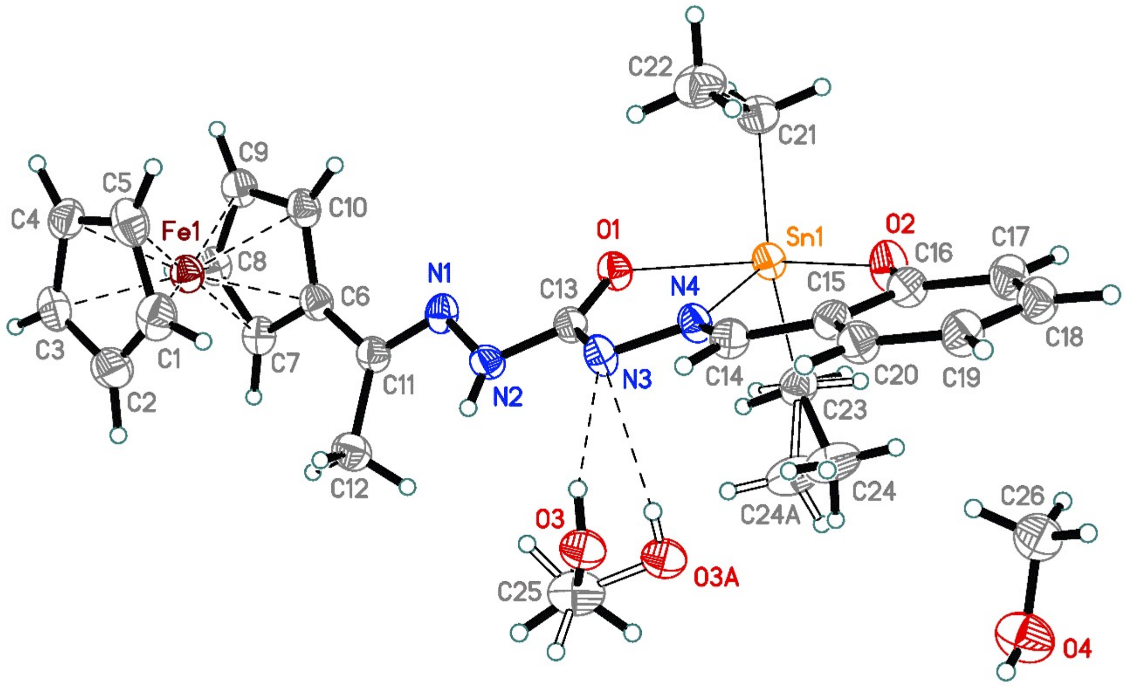



**Figure S30.** The asymmetric unit of the structure of **3a**·4MeOH. Minor components of the disorder are shown with open solid lines. The anisotropic thermal displacement ellipsoids for non-hydrogen atoms are set to a 50% probability level.

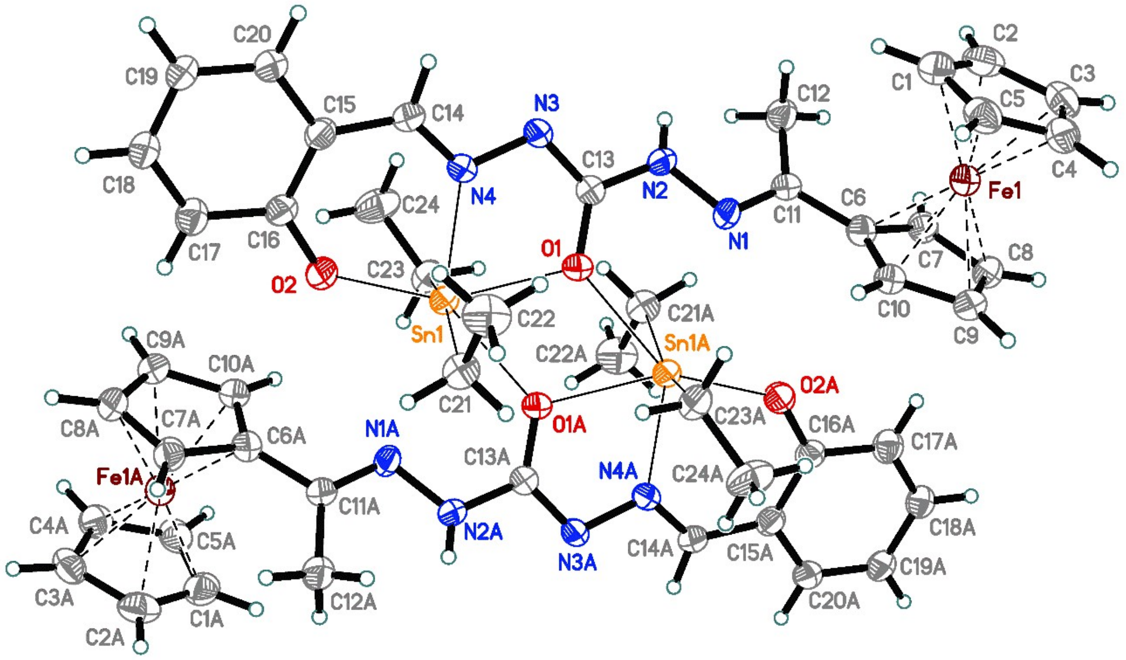



**Figure S31.** The structure of complex **3a**. Minor components of the disorder are omitted. The molecule is located at an inversion center. The anisotropic thermal displacement ellipsoids for non-hydrogen atoms are set to a 50% probability level.

**Table S6.** Selected bond lengths [Å] for **3a**.

| | | | | | |
|---|---|---|---|---|---|
| Sn1-O1#1 | 2.578(3) | O2-C16 | 1.311(6) | C9-C10 | 1.417(7) |
| Sn1-O1 | 2.269(3) | N1-N2 | 1.390(5) | C11-C12 | 1.499(7) |
| Sn1-O2 | 2.105(4) | N1-C11 | 1.296(6) | C14-C15 | 1.449(7) |
| Sn1-N4 | 2.261(4) | N2-C13 | 1.390(6) | C15-C16 | 1.415(7) |
| Sn1-C21 | 2.112(5) | N3-N4 | 1.399(5) | C15-C20 | 1.411(7) |
| Sn1-C23 | 2.114(5) | N3-C13 | 1.322(6) | C16-C17 | 1.430(7) |
| Fe1-C1 | 2.042(6) | N4-C14 | 1.287(6) | C17-C18 | 1.365(7) |
| Fe1-C2 | 2.010(6) | C1-C2 | 1.385(9) | C18-C19 | 1.394(8) |
| Fe1-C3 | 2.049(5) | C1-C5 | 1.420(9) | C19-C20 | 1.379(7) |
| Fe1-C4 | 2.057(5) | C2-C3 | 1.450(9) | C21-C22 | 1.526(7) |
| Fe1-C5 | 2.049(6) | C3-C4 | 1.430(8) | C23-C24 | 1.520(8) |
| Fe1-C6 | 2.044(5) | C4-C5 | 1.421(8) | C23-C24A | 1.520(9) |
| Fe1-C7 | 2.039(5) | C6-C7 | 1.436(7) | O3-C25 | 1.423(7) |
| Fe1-C8 | 2.047(5) | C6-C10 | 1.437(7) | O3A-C25 | 1.423(8) |
| Fe1-C9 | 2.054(5) | C6-C11 | 1.469(7) | O4-C26 | 1.416(8) |
| Fe1-C10 | 2.054(5) | C7-C8 | 1.418(7) | | |
| O1-C13 | 1.282(6) | C8-C9 | 1.432(8) | | |

Symmetry transformation: #1 -x+2, -y+1, -z+1

**Table S7.** Selected bond angles [°] for **3a**.

| | | | | | |
|---|---|---|---|---|---|
| O1-Sn1-O1#1 | 64.97(14) | C6-Fe1-C8 | 68.4(2) | C4-C3-C2 | 106.4(5) |
| O2-Sn1-O1#1 | 144.82(12) | C6-Fe1-C9 | 68.6(2) | C3-C4-Fe1 | 69.3(3) |
| O2-Sn1-O1 | 150.01(14) | C6-Fe1-C10 | 41.1(2) | C5-C4-Fe1 | 69.5(3) |
| O2-Sn1-N4 | 81.31(15) | C7-Fe1-C1 | 128.0(2) | C5-C4-C3 | 107.9(5) |
| O2-Sn1-C21 | 90.82(19) | C7-Fe1-C3 | 117.7(2) | C1-C5-Fe1 | 69.4(3) |
| O2-Sn1-C23 | 94.69(19) | C7-Fe1-C4 | 151.7(2) | C1-C5-C4 | 108.2(5) |
| N4-Sn1-O1 | 69.31(13) | C7-Fe1-C5 | 166.3(2) | C4-C5-Fe1 | 70.1(3) |
| N4-Sn1-O1#1 | 133.81(13) | C7-Fe1-C6 | 41.18(19) | C7-C6-Fe1 | 69.2(3) |
| C21-Sn1-O1#1 | 83.32(16) | C7-Fe1-C8 | 40.6(2) | C7-C6-C10 | 107.9(4) |
| C21-Sn1-O1 | 90.27(18) | C7-Fe1-C9 | 69.0(2) | C7-C6-C11 | 126.0(5) |
| C21-Sn1-N4 | 103.46(18) | C7-Fe1-C10 | 69.2(2) | C10-C6-Fe1 | 69.8(3) |
| C21-Sn1-C23 | 159.1(2) | C8-Fe1-C3 | 107.4(2) | C10-C6-C11 | 125.8(5) |
| C23-Sn1-O1 | 94.87(18) | C8-Fe1-C4 | 118.2(2) | C11-C6-Fe1 | 121.4(4) |
| C23-Sn1-O1#1 | 80.58(16) | C8-Fe1-C5 | 152.1(2) | C6-C7-Fe1 | 69.6(3) |
| C23-Sn1-N4 | 97.29(18) | C8-Fe1-C9 | 40.9(2) | C8-C7-Fe1 | 70.0(3) |
| C1-Fe1-C3 | 68.6(2) | C8-Fe1-C10 | 68.2(2) | C8-C7-C6 | 107.3(5) |
| C1-Fe1-C4 | 68.3(2) | C9-Fe1-C4 | 107.4(2) | C10-C9-Fe1 | 69.8(3) |
| C1-Fe1-C5 | 40.6(2) | C9-Fe1-C10 | 40.4(2) | C10-C9-C8 | 107.8(5) |
| C1-Fe1-C6 | 108.4(2) | C10-Fe1-C4 | 127.2(2) | C6-C10-Fe1 | 69.1(3) |
| C1-Fe1-C8 | 165.8(2) | Sn1-O1-Sn1#1 | 115.03(14) | C9-C10-Fe1 | 69.8(3) |
| C1-Fe1-C9 | 152.3(2) | C13-O1-Sn1 | 113.5(3) | C9-C10-C6 | 108.1(5) |
| C1-Fe1-C10 | 119.1(2) | C13-O1-Sn1#1 | 126.5(3) | N1-C11-C6 | 116.6(4) |
| C2-Fe1-C1 | 40.0(3) | C16-O2-Sn1 | 135.7(3) | N1-C11-C12 | 123.5(4) |
| C2-Fe1-C3 | 41.9(3) | C11-N1-N2 | 114.3(4) | C6-C11-C12 | 119.9(4) |
| C2-Fe1-C4 | 69.1(2) | N1-N2-C13 | 117.2(4) | O1-C13-N2 | 119.2(4) |
| C2-Fe1-C5 | 68.3(3) | C13-N3-N4 | 110.7(4) | O1-C13-N3 | 125.5(4) |
| C2-Fe1-C6 | 118.0(2) | N3-N4-Sn1 | 117.1(3) | N3-C13-N2 | 115.2(4) |
| C2-Fe1-C7 | 107.5(2) | C14-N4-Sn1 | 128.3(3) | N4-C14-C15 | 127.0(5) |
| C2-Fe1-C8 | 128.1(3) | C14-N4-N3 | 114.6(4) | C16-C15-C14 | 123.6(4) |
| C2-Fe1-C9 | 166.4(3) | C2-C1-Fe1 | 68.8(3) | C20-C15-C14 | 116.9(5) |
| C2-Fe1-C10 | 152.1(2) | C2-C1-C5 | 108.6(5) | C20-C15-C16 | 119.5(5) |
| C3-Fe1-C4 | 40.8(2) | C5-C1-Fe1 | 70.0(3) | O2-C16-C15 | 123.6(5) |
| C3-Fe1-C5 | 68.5(2) | C1-C2-Fe1 | 71.3(3) | O2-C16-C17 | 118.7(5) |
| C3-Fe1-C9 | 127.0(2) | C1-C2-C3 | 108.8(5) | C15-C16-C17 | 117.7(5) |
| C3-Fe1-C10 | 164.9(2) | C3-C2-Fe1 | 70.5(3) | C18-C17-C16 | 120.7(5) |
| C5-Fe1-C4 | 40.5(2) | C2-C3-Fe1 | 67.6(3) | C17-C18-C19 | 121.8(5) |
| C5-Fe1-C9 | 118.2(2) | C4-C3-Fe1 | 69.9(3) | C20-C19-C18 | 118.6(5) |
| C5-Fe1-C10 | 108.1(2) | C7-C8-Fe1 | 69.4(3) | C19-C20-C15 | 121.6(5) |

| | | | | | |
|---|---|---|---|---|---|
| C6-Fe1-C3 | 152.4(2) | C7-C8-C9 | 108.9(4) | C22-C21-Sn1 | 111.9(4) |
| C6-Fe1-C4 | 165.7(2) | C9-C8-Fe1 | 69.8(3) | C24-C23-Sn1 | 112.6(6) |
| C6-Fe1-C5 | 128.2(2) | C8-C9-Fe1 | 69.3(3) | C24A-C23-Sn1 | 117.5(15) |

Symmetry transformation to generate equivalent atoms: #1 -x+2, -y+1, -z+1

**Table S8.** Torsion angles [°] for **3a**.

| | | | |
|---|---|---|---|
| Sn1-O1-C13-N2 | -157.7(3) | C3-C4-C5-Fe1 | 58.8(4) |
| Sn1#1-O1-C13-N2 | -4.2(6) | C3-C4-C5-C1 | -0.3(6) |
| Sn1-O1-C13-N3 | 17.9(6) | C5-C1-C2-Fe1 | 58.8(4) |
| Sn1#1-O1-C13-N3 | 171.4(4) | C5-C1-C2-C3 | -2.1(7) |
| Sn1-O2-C16-C15 | 2.9(8) | C6-C7-C8-Fe1 | -59.8(3) |
| Sn1-O2-C16-C17 | -176.6(4) | C6-C7-C8-C9 | -1.1(6) |
| Sn1-N4-C14-C15 | -2.3(8) | C7-C6-C10-Fe1 | 59.0(3) |
| Fe1-C1-C2-C3 | -60.8(4) | C7-C6-C10-C9 | -0.2(6) |
| Fe1-C1-C5-C4 | 59.5(4) | C7-C6-C11-N1 | 160.3(5) |
| Fe1-C2-C3-C4 | -59.4(4) | C7-C6-C11-C12 | -20.6(8) |
| Fe1-C3-C4-C5 | -58.9(4) | C7-C8-C9-Fe1 | -58.5(4) |
| Fe1-C4-C5-C1 | -59.1(4) | C7-C8-C9-C10 | 1.0(6) |
| Fe1-C6-C7-C8 | 60.1(4) | C8-C9-C10-Fe1 | -59.2(4) |
| Fe1-C6-C10-C9 | -59.1(4) | C8-C9-C10-C6 | -0.5(6) |
| Fe1-C6-C11-N1 | -113.8(5) | C10-C6-C7-Fe1 | -59.3(4) |
| Fe1-C6-C11-C12 | 65.3(6) | C10-C6-C7-C8 | 0.8(6) |
| Fe1-C7-C8-C9 | 58.7(4) | C10-C6-C11-N1 | -27.2(8) |
| Fe1-C8-C9-C10 | 59.5(4) | C10-C6-C11-C12 | 152.0(5) |
| Fe1-C9-C10-C6 | 58.7(4) | C11-N1-N2-C13 | 173.4(4) |
| O2-C16-C17-C18 | -179.6(5) | C11-C6-C7-Fe1 | 114.4(5) |
| N1-N2-C13-O1 | -24.8(6) | C11-C6-C7-C8 | 174.5(5) |
| N1-N2-C13-N3 | 159.2(4) | C11-C6-C10-Fe1 | -114.7(5) |
| N2-N1-C11-C6 | 168.1(4) | C11-C6-C10-C9 | -173.9(5) |
| N2-N1-C11-C12 | -11.0(7) | C13-N3-N4-Sn1 | -12.5(5) |
| N3-N4-C14-C15 | 174.3(5) | C13-N3-N4-C14 | 170.6(4) |
| N4-N3-C13-O1 | -3.9(7) | C14-C15-C16-O2 | 4.4(8) |
| N4-N3-C13-N2 | 171.8(4) | C14-C15-C16-C17 | -176.1(5) |
| N4-C14-C15-C16 | -4.4(8) | C14-C15-C20-C19 | 175.7(5) |
| N4-C14-C15-C20 | 178.9(5) | C15-C16-C17-C18 | 0.8(8) |
| C1-C2-C3-Fe1 | 61.3(4) | C16-C15-C20-C19 | -1.0(8) |
| C1-C2-C3-C4 | 1.9(6) | C16-C17-C18-C19 | -1.7(9) |
| C2-C1-C5-Fe1 | -58.0(4) | C17-C18-C19-C20 | 1.2(8) |

| | | | |
|---|---|---|---|
| C2-C1-C5-C4 | 1.5(7) | C18-C19-C20-C15 | 0.2(8) |
| C2-C3-C4-Fe1 | 58.0(4) | C20-C15-C16-O2 | -179.0(5) |
| C2-C3-C4-C5 | -1.0(6) | C20-C15-C16-C17 | 0.5(7) |

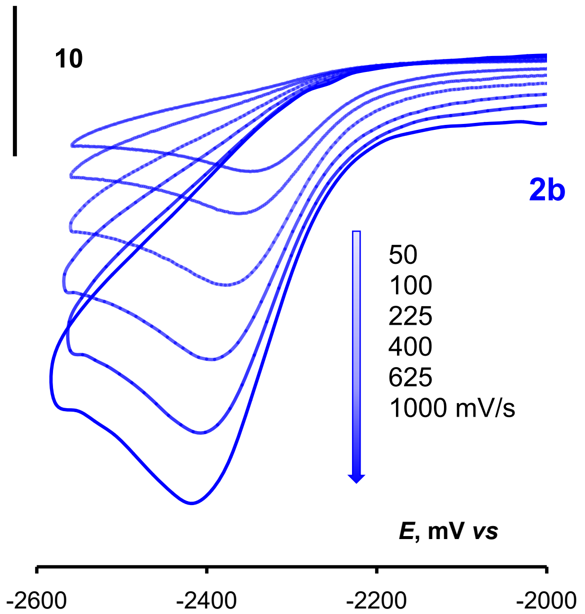
Symmetry transformation to generate equivalent atoms: #1 -x+2, -y+1, -z+1

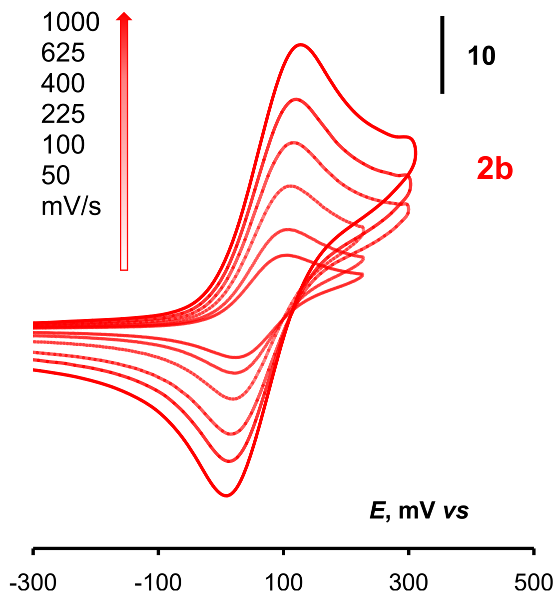
**Table S9.** Hydrogen bond parameters for **3a** [Å and °].

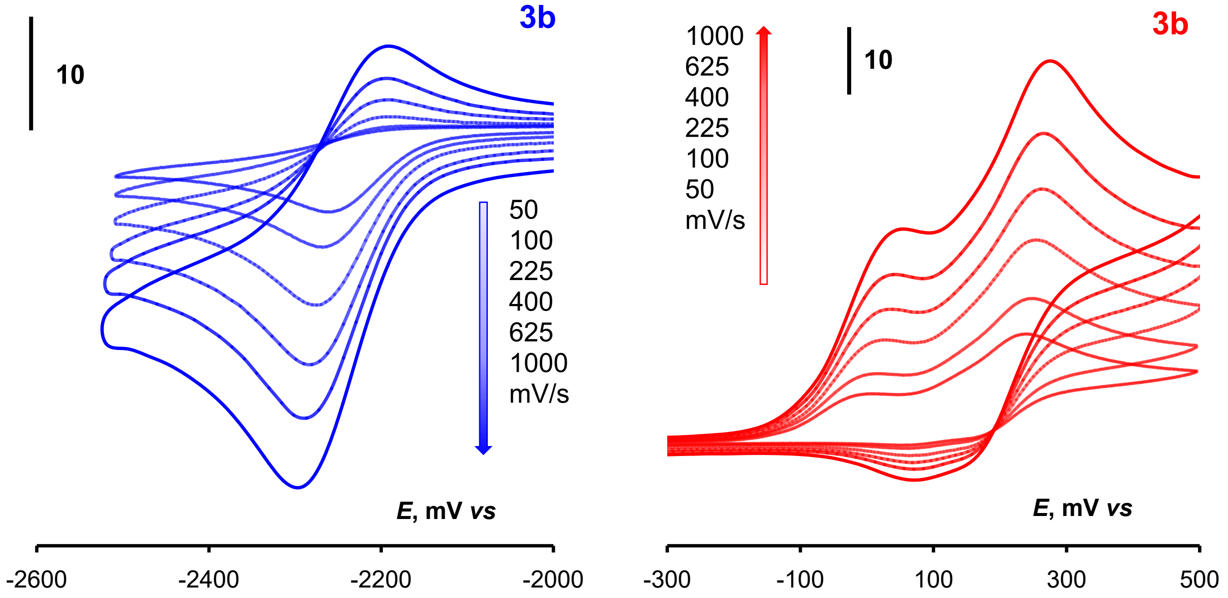
| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠(DHA) |
|---|---|---|---|---|
| N(2)-H(2)···O(3)#2 | 0.76 | 2.31 | 2.864(6) | 131.0 |
| O(3)-H(3A)···N(3) | 0.83 | 1.97 | 2.776(6) | 162.2 |
| O(3A)-H(3B)···N(3) | 0.84 | 2.32 | 2.95(10) | 131.8 |

Symmetry transformation to generate equivalent atoms: #2 -x+1, -y, -z+1

## Electrochemistry of 2b and 3b

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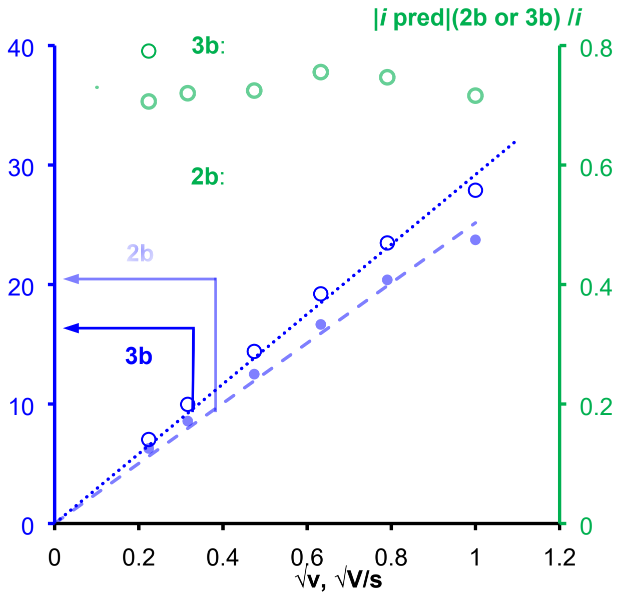
100
225
400
625
1000
mV/s
E, mV vs
-2600
-2400
-2200
-2000
3b
1000
625
400
225
100
50
mV/s
10
E, mV vs
-300
-100
100
300
500


|i pred|(2b or 3b) /i
3b:
2b:
2b
3b
40
30
20
10
0
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
√v, √V/s

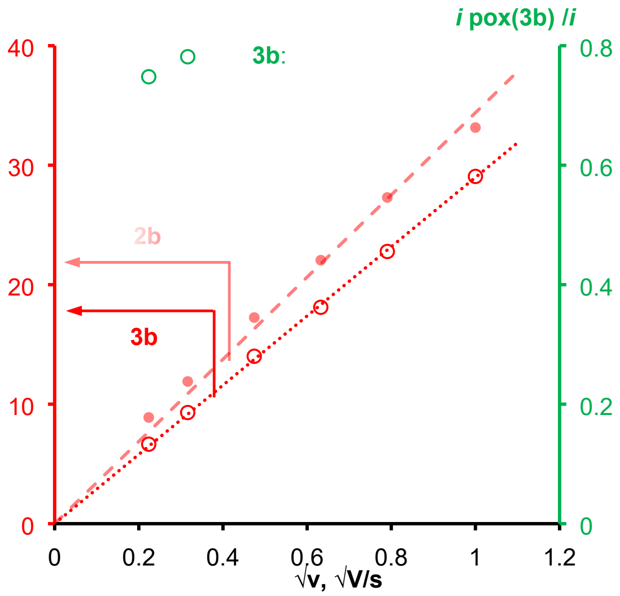

i pox(3b) /i
3b:
2b
3b
40
30
20
10
0
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
√v, √V/s

**Figure S32.** CV curves of reduction and oxidation of 2.5 mmol/L solutions of compounds **2b** (*top*) and **3b** (*middle*) in 0.1 M $Bu_4NPF_6$/DMF on a disk glassy carbon working electrode ($d$ = 1.7 mm) at potential scan rates of 50, 100, 225, 400, 625, and 1000 mV/s. Dependences of the peak currents (background corrected values were used) of the corresponding curves on the square root of the potential scan rate, as well as their values relative to the oxidation peak current of **2b** taken as the standard single-electron current under these conditions (*bottom*).

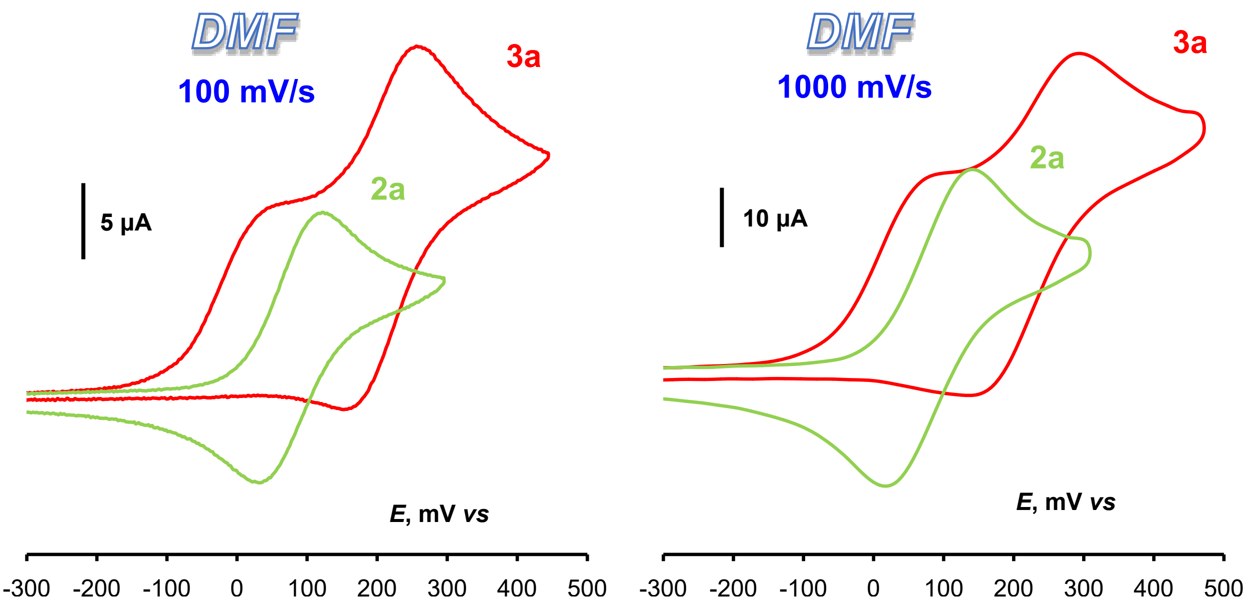



**Figure S33.** CV curves of oxidation of 2.5 mmol/L solutions of compounds **2a** and **3a** in 0.1 M $Bu_4NPF_6$/DMF on a disk glassy carbon working electrode ($d$ = 1.7 mm) at potential scan rates of 100 (*left*), and 1000 mV/s (*right*).

## EPR spectroscopy

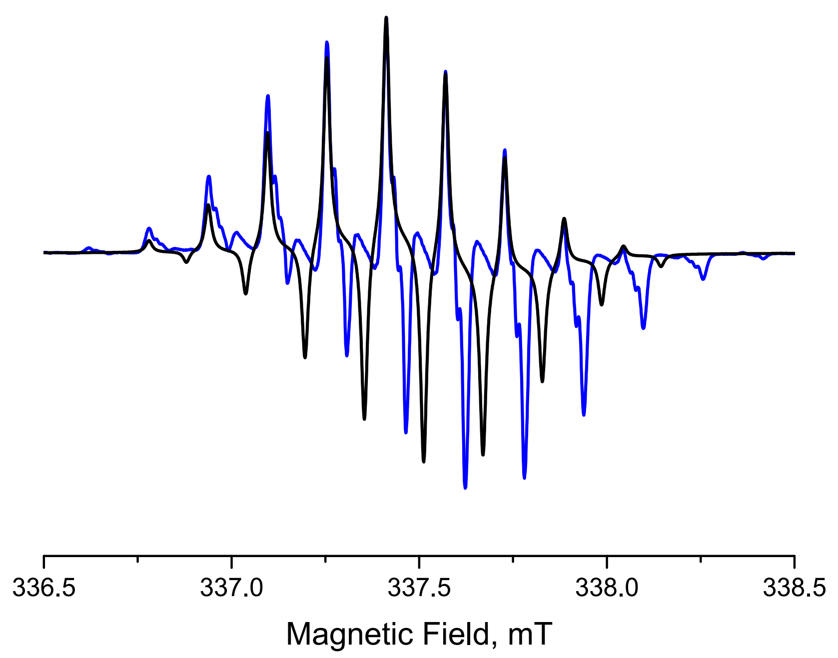



**Figure S34.** Experimental continuous-wave X-band EPR spectrum of reaction product formed upon oxidation of **3a** with an equivalent of TCNE in DCM (blue solid line). A simulated black solid line is a weighted superposition of two EPR spectra: with $g = 2.0024$ (85%, broad singlet) and with $g = 2.0030$, $a_{iso}(4\ ^{14}N) = 0.158$ mT, (15%, nine dominant lines). The difference between the experimental and calculated spectra is due to the presence of other non-identified radicals in the reaction mixture or an interaction of $TCNE^{-\bullet}$ with the oxidized Shiff-base moiety.

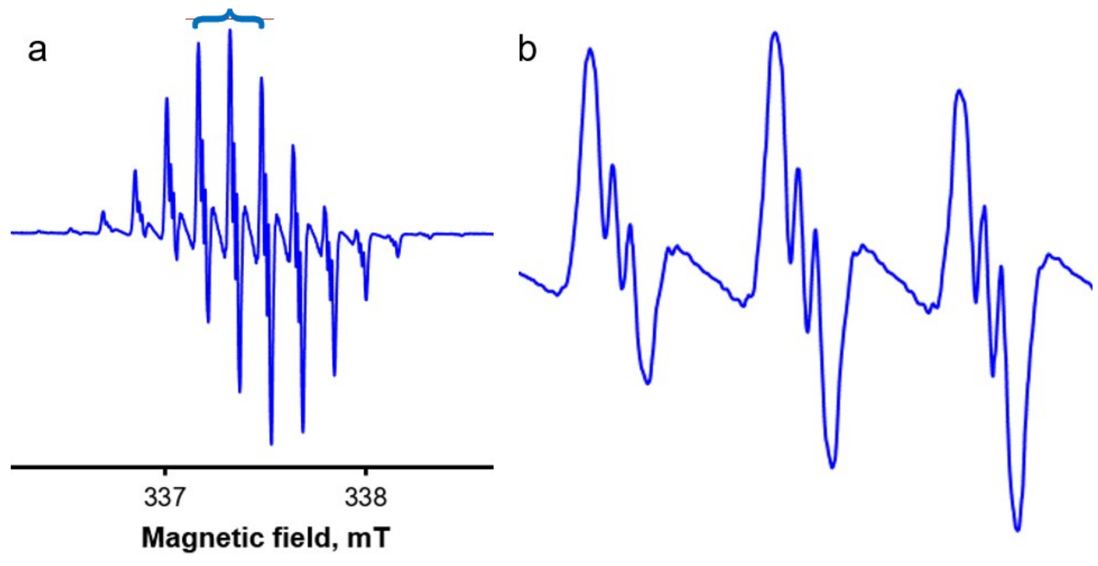



**Figure S35.** a) Experimental continuous-wave X-band EPR spectrum of reaction product formed upon oxidation of **3b** with an equivalent of TCNE in DCM; b) the central part of the same spectrum.

# Results of DFT calculations

***Methodology.*** To analyze results of the spectroscopic and electrochemical measurements, a series of calculations has been performed. First of all, we performed search for isomeric structures of ligand **2a** and complex **3a** using the conformer search procedure as implemented in the ORCA Global Optimizer Algorithm (GOAT) [6] at the GFN2-xTB level of theory [7]. Then using the geometries of isomeric structures, their optimization was performed at the B97-D3 level [8,9] with def2-TZVP basis set [10] in two solvents (DMF and DCM). Finally, geometries of the isomers of **2a** with lowest Gibbs free energy, as well as those of complex **3a**, dimer (**3a**)$_2$ and radical cations and dications of **2a**, **3a**, and (**3a**)$_2$ were optimized at the PBE0-D3/def2-TZVP level [8,10,11,12]; the influence of the solvent (DMF or DCM) was accounted for using the CPCM model [13]. Optimizations of the dimer dication geometry was performed for its triplet state, as the closed-shell singlet state was shown to be an excited state. The Becke–Johnson damping function was used in all dispersion corrected calculations [14]. Gibbs free energies were calculated in the RRHO approximation [15]. NBO analysis of coordination bonds and calculation of natural atomic charges were performed for optimized geometry of neutral **2a**, **3a** and (**3a**)$_2$ and their cations and dications using the NBO 7.0 program [16]; molecular orbitals (MOs) calculated at the PBE0/def2-TZVP level were used as input data for the NBO procedure. The orbital (or charge transfer, CT) contributions ($|E_{CT}|$) to the energies of the coordination Sn–O and Sn–N bonds were calculated within the NBO procedure using second-order perturbation theory:

$$\Delta E_{DA}^{(2)} = n_D \langle \Phi_D | \hat{F} | \Phi_A \rangle^2 / (\varepsilon_D - \varepsilon_A),$$

where $\Phi_D$ and $\Phi_A$ and $\varepsilon_D$ and $\varepsilon_A$ are the natural Lewis-type orbitals of the donor (D) and acceptor (A) and their energies, respectively; $n_D$ – the population of the natural orbital of the donor, and $\hat{F}$ – the Fock operator.

The ORCA 6.0.1 software package [17,18] was used for all calculations. To clarify the electronic structure of open-shell systems (radical cation and dication), CASSCF calculations [19] were also performed.

***Results of calculations of electronic structures of ligand 2a, complex 3a and its dimer (3a)$_2$.***

**Table S10**. Structures and relative Gibbs free energies of the neutral conformers and tautomers of **2a** optimized in DCM at different levels of theory: B97-D3/def2-TZVP and PBE0-D3/def2-TZVP.

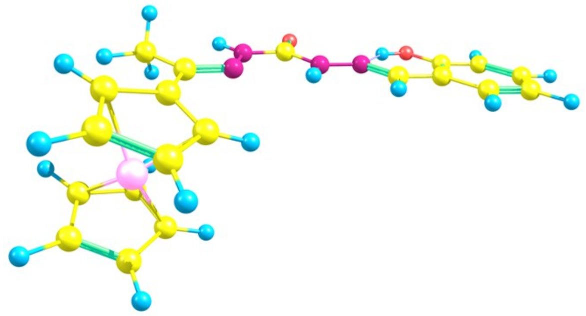
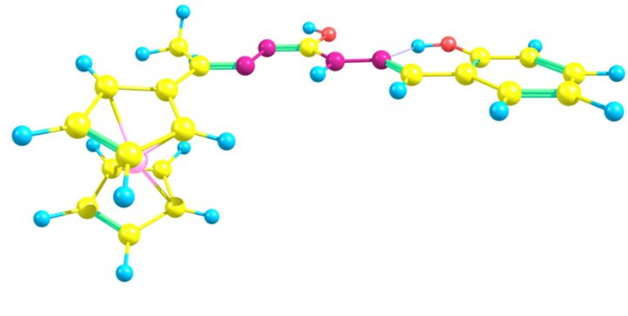
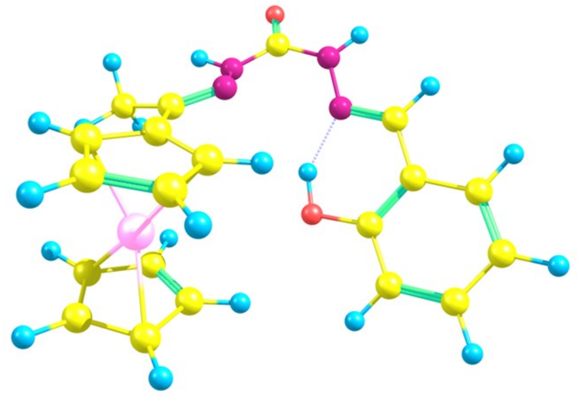
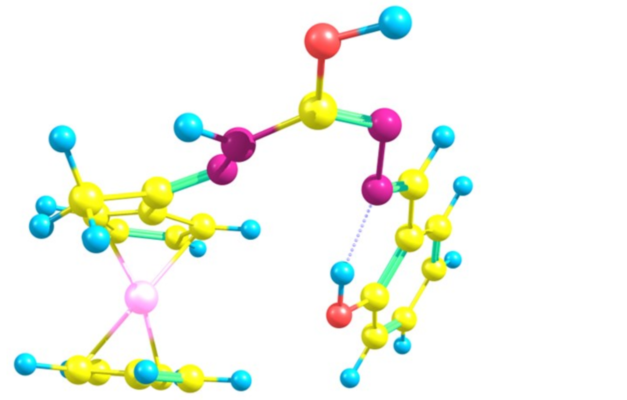
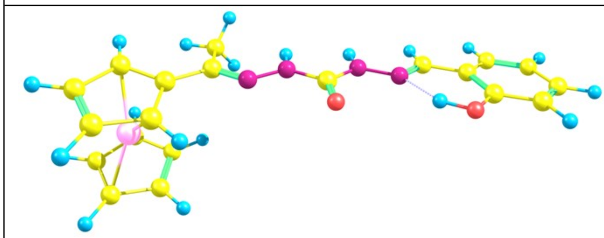
| **Keto-forms** | **Enol-forms** |
|---|---|
|  |  |
| **Keto-1, ΔG = 0.0 kcal/mol** | **Enol-1, ΔG= 15.6 (B97), 14.9 (PBE0) kcal/mol** |
|  |  |
| **Keto-2, ΔG = 3.3 (B97), 4.6 (PBE0) kcal/mol** | **Enol-2, ΔG= 16.2 (B97) kcal/mol** |
|  | |
| **Keto-3, ΔG = 3.8 (B97), 3.7 (PBE0) kcal/mol** | |

**Table S11**. Relative Gibbs free energies (ΔG) of the neutral conformers (keto-forms) and tautomers (enol-form) of **2a** optimized in DMF at different levels of theory: PBE0-D3/def2-TZVP and B97-D3/def2-TZVP.

| Conformer, tautomer | Keto-1 | Enol-1 | Keto-2 | Keto-3 |
|---|---|---|---|---|
| ΔG (PBE0-B3) | 0.0 | 15.4 | 2.9 | 5.9 |
| ΔG (B97-B3) | 0.0 | 11.0 | 2.6 | 4.5 |

The data in Tables 10 and 11 show that for both solvents (DCM and DMF) only the keto-form of **2a** is present in solution, the presence of significant amounts of the enol-form can be completely excluded. Moreover, in both solutions only one conformer of **2a** is present, in which the relative position of ferrocene and its substituent is similar to that of **2b** in the crystal.

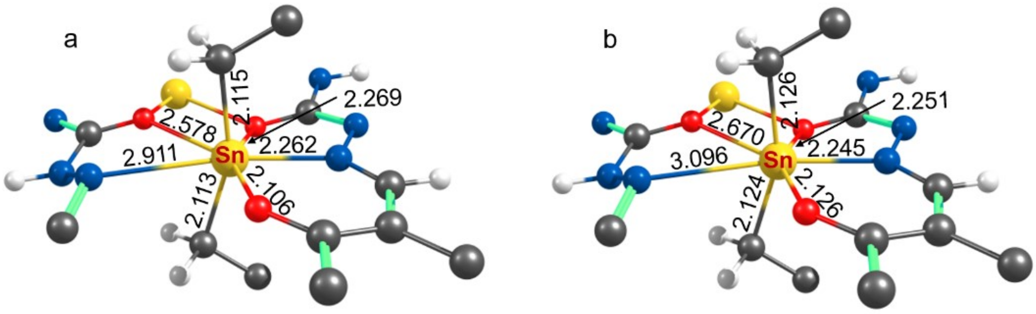
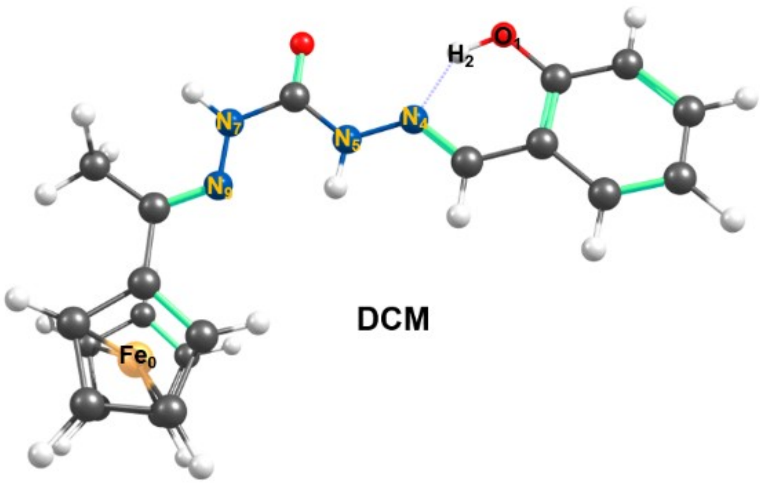



**Figure S36.** Bond lengths in the Sn coordination sphere of the $(\mathbf{3a})_2$ dimer in the crystalline state (*a*) and in the structure optimized in DMF solution at the PBE0-D3 level (*b*).

***Results of calculations of electronic structure and relative Gibbs Free Energies of Cations and Dications of Ligand 2a, Complex 3a and its Dimer (3a)₂.***

**Table S12**. Relative Gibbs free energies of cations and triplet dications of **2a**, and Mulliken atomic spin populations for them calculated in **DCM** at the (U)PBE0/def2-TZVP level of theory (geometry optimization performed using (U)PBE0-D3 functional).




| Comp. | Charge | ΔG, kcal/mol (eV) | ρ(Fe) | ρ($N_4$) | ρ($N_5$) | ρ($N_7$) | ρ($N_9$) | ρ(O) | $\sum\rho(N)$ | $\sum\rho(PhO)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Keto-1 | neutral | 0.00 | – | – | – | – | – | | | |
| | cation | 109.07 (4.73) | **1.31** | 0.000 | 0.000 | 0.002 | 0.000 | | | |
| | dication | 250.89 (10.88) | 1.28 | **0.182** | **0.188** | **0.051** | **–0.015** | **0.115** | **0.406** | **0.601** |
| Enol-1 | neutral | 14.92 | – | – | – | – | – | | | |
| | cation[a] | 121.78 (5.29) | **1.25** | 0.001 | 0.004 | 0.009 | 0.015 | | | |
| | dication[a] | 260.35 (11.29) | 1.31 | **0.087** | **0.247** | **0.311** | **0.052** | | | |
| Keto-2 | neutral | 3.69 | – | – | – | – | – | | | |
| | cation[a] | 111.38 (4.83) | 1.26 | 0.012 | 0.008 | 0.002 | 0.001 | | | |
| | dication[a] | 253.43 (10.99) | 1.29 | –0.029 | 0.064 | 0.208 | 0.168 | | | |
| Keto-3 | neutral | 4.63 | – | – | – | – | – | | | |
| | cation[a] | 112.07 (4.86) | 1.27 | –0.001 | 0.002 | 0.000 | 0.000 | | | |
| | dication[a] | 255.97 (11.10) | 1.27 | –0.004 | 0.021 | 0.201 | 0.184 | | | |

[a] Gibbs free energies of cation and dication relative to the corresponding neutral form.

**Table S13**. Relative Gibbs free energies of radical cation, triplet dication of the lowest conformer of **2a**, and Mulliken atomic spin populations (ρ) for them calculated **in DMF** at the (U)PBE0/def2-TZVP level of theory (geometry optimization performed using (U)PBE0-D3 functional).

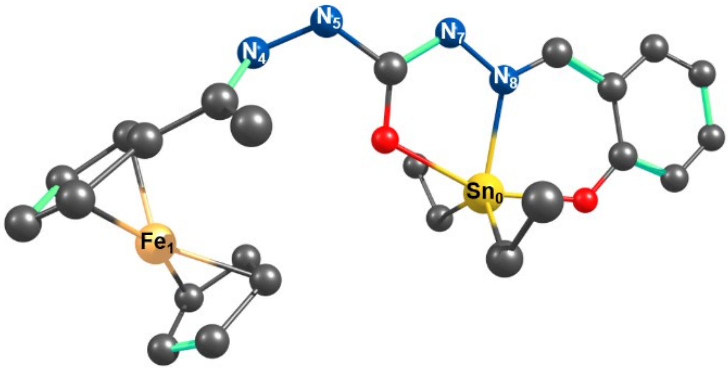
| Comp. | Charge | ΔG, kcal/mol (eV) | ρ(Fe) | $\rho(N_4)$ | $\rho(N_5)$ | $\rho(N_7)$ | $\rho(N_9)$ | $\rho(O_1)$ | $\sum\rho(N)$ | $\sum\rho(PhO)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| keto-1 | neutral | 0.00 | – | – | – | – | – | – | | |
| | cat. | **104.5 (4.53)** | **1.26** | 0.000 | 0.001 | 0.006 | 0.008 | 0.000 | | |
| | dicat. | 239.9 (10.40) | 1.28 | **0.204** | **0.230** | **0.044** | **–0.016** | **0.104** | **0.462** | **0.592** |

Results of Tables S12 and S13 demonstrate that electrochemical or chemical oxidation of free ligand **2a** in both solutions (in DCM and DMF) yields a radical cation with spin density localized almost exclusively on the ferrocenium fragment. The second electron in turn would be detached from the Schiff-base fragment, for which the spin density is localized mainly on the phenyl ring, as well as on O atom of OH group and on $N_4$ and $N_5$ nitrogen atoms.

**Table S14**. Relative Gibbs free energies (ΔG, kcal/mol) of conformers of **3a**, as well as Gibbs free energies of formation of radical cation **3a**$^{+\bullet}$ and dication **3a**$^{2+}$, E1 and E2 in eV. All optimizations and calculations of the Gibbs free energies were performed **in DCM** at the (U)B97-D3/def2-TZVP level.

| **3a** | ΔG | ΔG1(**3a** → **3a**$^{+\bullet}$) | ΔG2(**3a** → **3a**$^{2+}$) | ΔG3(**3a** + **3a** → (**3a**)$_2$) | E1= ΔG1/F | E2= ΔG2/F |
|---|---|---|---|---|---|---|
| conf. 1 | 0.00 | 108.2 | 235.1 | –6.00 | 4.69 | 11.0 |
| conf. 2 | 0.88 | 107.9 | 235.7 | –5.75 | 4.68 | 11.1 |
| conf. 3 | 1.27 | 108.2 | 235.0 | –8.53 | 4.69 | 11.0 |
| conf. 4 | 1.47 | 108.6 | 236.1 | –8.93 | 4.71 | 11.1 |

**Table S15**. Results of calculations at the (U)PBE0/def2-TZVP level in **DCM** for conformers of radical cations **3a**$^{+\bullet}$ and dications **3a**$^{2+}$: the ΔG values correspond to the reactions **3a** → **3a**$^{+\bullet}$ + **e** and **3a** → **3a**$^{2+}$ + **2e**, Mulliken atomic spin populations correspond to the radical cation **3a**$^{+\bullet}$ in the doublet state and the dication **3a**$^{2+}$ in the triplet state.




| | Charge | ΔG, kcal/mol (eV) | ρ(Fe) | ρ(Sn) | ρ(N$_4$) | ρ(N$_5$) | ρ(N$_7$) | ρ(N$_8$) | $\sum\rho(N)$ | $\sum\rho(PhO)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| conf. 1 | cat. | 109.1 (4.73) $\langle\tilde{S}^2\rangle = 0.774$ | 0.025 | –0.006 | **0.039** | **0.176** | **0.413** | **0.045** | **0.667** | **0.29** |
| | dicat. | 250.9 (10.88) $\langle\tilde{S}^2\rangle = 2.067$ | **1.329** | –0.008 | –0.004 | 0.129 | 0.395 | 0.086 | **0.606** | **0.343** |

**Table S16**. Results of calculations at the (U)PBE0/def2-TZVP level in **DMF** for conformers of radical cations **3a**$^{+\bullet}$ and dications **3a**$^{2+}$: the ΔG values correspond to the reactions **3a** → **3a**$^{+\bullet}$ + **e** and **3a** → **3a**$^{2+}$ + **2e.**

| **3a** | ΔG | ΔG1(**3a** → **3a**$^{+\bullet}$) | ΔG2(**3a** → **3a**$^{2+}$) | E1= ΔG1/F | E2= ΔG2/F |
|---|---|---|---|---|---|
| conf. 1 | 0.00 | 115.8 | 225.6 | 5.02 | 9.78 |
| conf. 2 | 0.28 | 117.5 | 227.0 | 5.10 | 9.82 |
| conf. 3 | 0.12 | 116.4 | 226.2 | 5.05 | 9.80 |
| conf. 4 | 0.89 | 116.8 | 226.4 | 5.07 | 9.82 |

**Table S17**. Results of calculations at the (U)PBE0/def2-TZVP level in **DMF** for conformers of radical cations **3a**$^{+\bullet}$ and dications **3a**$^{2+}$: Mulliken atomic spin populations correspond to the radical cation **3a**$^{+\bullet}$ in the doublet state and the dication **3a**$^{2+}$ in the triplet state.

| **3a** | Charge | ρ(Fe) | ρ (Sn) | $\rho(N_4)$ | $\rho(N_5)$ | $\rho(N_7)$ | $\rho(N_8)$ | $\rho(O_1)$ | $\sum\rho(N)$ | $\sum\rho(PhO)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| conf. 1 | cat. | 0.028 | –0.006 | **0.036** | **0.174** | **0.417** | **0.045** | **0.070** | **0.672** | **0.286** |
| | dicat. | **1.328** | –0.008 | -0.002 | 0.134 | 0.405 | 0.076 | **0.083** | **0.613** | **0.240** |
| conf. 2 | cat. | 0.025 | –0.006 | **0.039** | **0.176** | **0.413** | **0.045** | **0.71** | **0.657** | **0.289** |
| | dicat. | **1.330** | –0.009 | –0.002 | 0.134 | 0.402 | 0.077 | **0.083** | **0.611** | **0.328** |

Geometry of the (**3a**)$_2$ dimer, as well as those of its radical cation and dication, were optimized at the PBE0-D3/def2-TZVP level in DMF solution and their thermodynamic properties were calculated (Table S18). It turned out that the first step of ionization of (**3a**)$_2$ leads to the removal of an electron from one of the ferrocene centers of the (**3a**)$_2$ dimer. This is evidenced by the spin population of 1.32 of one of the iron cations, with 0.34 β-electron spin localized on the carbon atoms of the pentadienyl rings of this ferrocene center (Fig. S39). Thus, the entire spin density after ionization turns out to be on one of the ferrocene fragments.

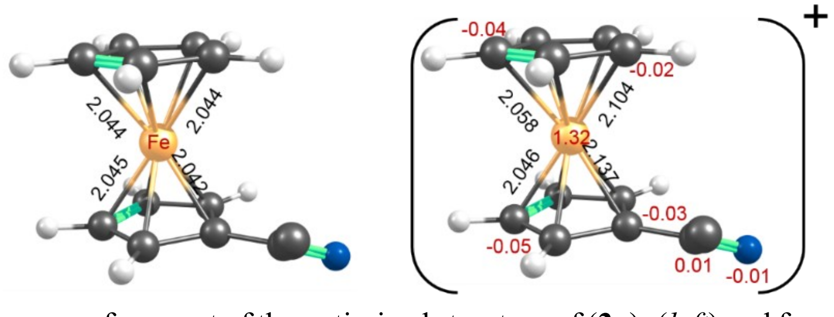



**Figure S37.** Ferrocene fragment of the optimized structure of (**3a**)$_2$ (*left*) and ferrocenium fragment of the optimized structure of the $(3a)_2^{+\cdot}$ radical cation with atomic spin population of the selected atoms (*right*).

Similarly, the second ionization step of the (**3a**)$_2$ dimer leads to the removal of an electron from the second ferrocene fragment. According to the calculations, the dication of the dimer is a species with an open-shell electronic configuration, similar to the dications of **2a** and **3a**. In the triplet state of the dication, the spin population on both iron cations is 1.32, and 0.34 of β–spin is localized on the carbon atoms of the Cp rings of each ferrocenium centers. Thus, upon ionization, electrons are removed first from one and then from the second ferrocene fragment. The exchange interaction between the ferrocenium fragments in dication is negligible, and the parameter $J$ is estimated as –0.02, 0.0, and –0.8 $cm^{-1}$ from BS-DFT, CASSCF(6,6), and CASSCF(6,6)/NEVPT2 calculations, respectively. Thus, the singlet and triplet state of dication are nearly degenerate.

**Table S18.** Results of calculations at the (U)PBE0-D3/def2-TZVP level in DMF for the (**3a**)$_2$ dimer, its radical cation and dication in the open-shell triplet and closed-shell singlet states.

| Charge | 0 | +1 | +2(open-shell) | +2 (closed-shell) |
|---|---|---|---|---|
| E | -5555.599281 | -5555.433681 | -5555.266665 | -5555.215125 |
| ZPE | 0.96091719 | 0.96173711 | 0.96245689 | 0.96323878 |
| H | -5554.638364 | -5554.471944 | -5554.304208 | -5554.251887 |
| ΔH, kcal/mol | 0.00 | 104.43 | 209.69 | 242.52 |
| G, Eh | -5554.728584 | -5554.563012 | -5554.395989 | -5554.340652 |
| ΔG, kcal/mol | 0 | 103.90 | 208.71 | 243.43 |
| ΔG, eV | **0** | **4.50** | **9.05** | **10.55** |

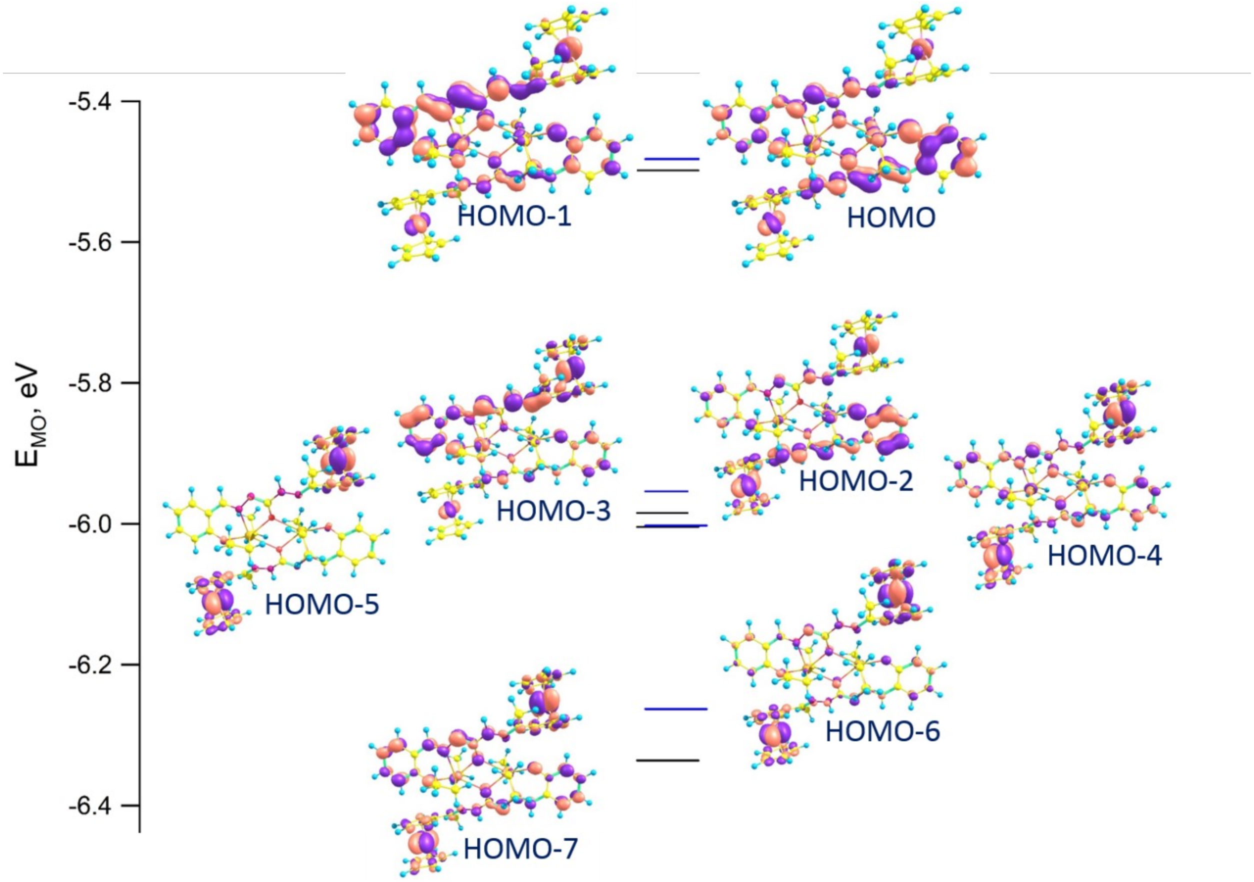



**Figure S38.** Diagram of the highest occupied molecular orbitals of the (**3a**)$_2$ dimer calculated at the PBE0/def2-TZVP level.

Figure S38 displays the series of highest occupied MOs of the (**3a**)$_2$ dimer. It can be seen that HOMO and HOMO-1 are very close in energy ($\Delta E \sim 0.02$ eV) and both are localized predominantly on the Schiff bases with a small contribution from the d-AOs of the Fe cations. The same is true for HOMO-2 and HOMO-3. In turn, HOMO-5 and HOMO-6 are localized almost exclusively on ferrocene fragments, while HOMO-4 and HOMO-7 are also localized predominantly on ferrocenes with a noticeable delocalization to the Schiff basis. Thus, based on the nature of the highest occupied orbitals, it is difficult to predict that the first and second oxidation steps will lead to the detachment of electrons from ferrocenes.

The observed difference in the electrochemical oxidation of ligand **2a** and its tin complex **3a** is based on two factors simultaneously. Firstly, it is most likely that in the case of complex **3a**, the Schiff-base/tin moiety is oxidized in the first step, whereas in the case of **2a**, the ferrocene moiety is oxidized first. Indeed, our DFT calculations predict that, unlike **2a**, the oxidation of **3a** leads to the formation of a radical cation with the spin density localized on the Schiff-base moiety, predominantly on the nitrogen atoms (Tables S15, S17). The second reason for the differences in the electrochemical oxidation of **2a** and **3a** is associated with the dimerization of complex **3a**, leading to the presence of two types of particles in the solution, **3a** and (**3a**)$_2$. Moreover, calculations predict that, unlike the monomer **3a**, oxidation of the dimer (**3a**)$_2$ should result in the removal of an electron from the ferrocene fragment. It is natural to assume that this process corresponds to a reversible wave, which is observed in the more anodic part of the CV.

As mentioned above, the presence of the (**3a**)$_2$ dimers is evident from the high-resolution mass spectra recorded using electrospray ionization and is confirmed by the results of our DFT calculations. Moreover, results of the DFT calculations predict that the oxidation of the dimer (**3a**)$_2$ leads to the formation of a radical cation with a spin density localized exclusively on the ferrocene fragment (Figure S41). Thus, based on DFT calculations, it is possible to give a consistent explanation for the unusual oxidation process of complex **3a**.

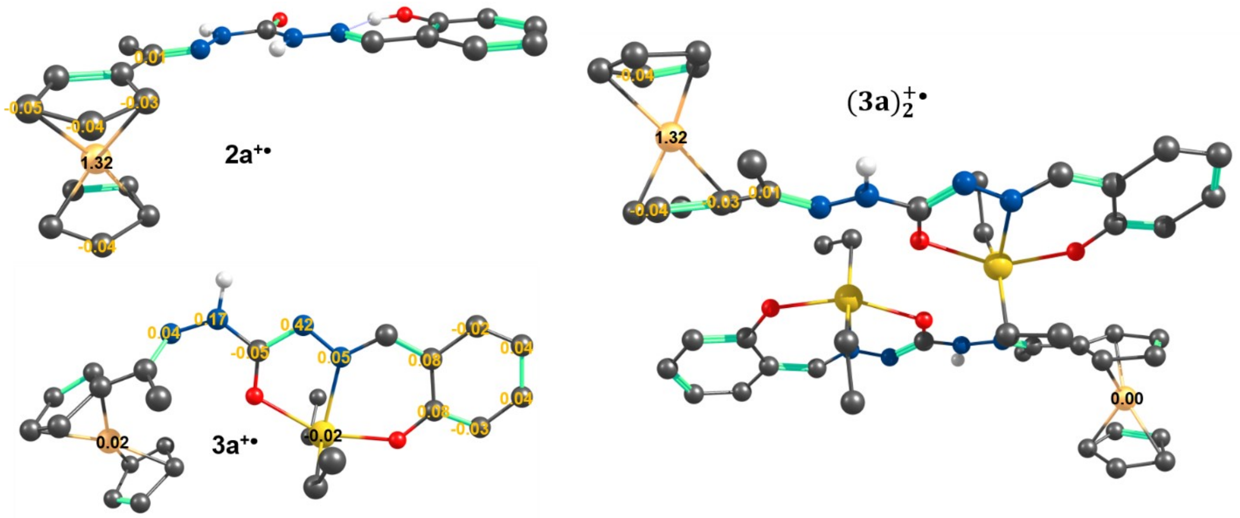



**Figure S39.** Atomic spin populations calculated at the UPBE0/def2-TZVP for radical cations of **2a**, **3a**, and (**3a**)$_2$ in DMF.

For compound **2a**, we calculated the electron structure of not only its radical cation but also its dication (Tables S12, S13). The dication **2a**$^{2+}$ is an open-shell species with one unpaired electron localized on ferrocene and the other on the Schiff base (Tables S12, S13); the exchange interaction between the radical centers is very weak ($J$ = 1.5 cm$^{-1}$ at the BS-UPBE0 level). The second unpaired electron is localized mainly on the phenyl ring and the O atom of OH group, as well as on the $N_4$ and $N_5$ nitrogen atoms of the Shiff base (see Table S12 for numbering). Note that for radical cation **3a**$^{+•}$, the spin density is localized predomonantly on the $N_7$ and $N_5$ atoms of the Shiff base (see Table S15 for numbering). Thus, the difference in the redox properties of compounds **2a** and **3a** are due to a significant difference in the electronic structure of the Shiff base radical fragments in their oxidized forms.

***The geometries of the calculated structures***

1. Neutral form of Schiff base **2a** in $CH_2Cl_2$
   E= –2406.31246300 Eh

| | | | |
|---|---|---|---|
| Fe | 11.179589 | 12.019319 | 12.373475 |
| O | 12.699373 | 3.816468 | 7.138080 |
| H | 12.256602 | 4.506887 | 7.691819 |
| O | 10.229894 | 5.334399 | 9.833686 |
| N | 12.125570 | 6.186036 | 8.059707 |
| N | 11.458110 | 7.014879 | 8.874764 |
| H | 11.618176 | 8.016649 | 8.860207 |
| N | 9.910481 | 7.475070 | 10.492650 |
| H | 9.208766 | 7.148715 | 11.143815 |
| N | 10.254020 | 8.776543 | 10.377318 |
| C | 13.563150 | 4.436892 | 6.324063 |
| C | 13.731276 | 5.837528 | 6.345493 |
| C | 14.649893 | 6.420596 | 5.467492 |
| C | 15.388814 | 5.655053 | 4.586884 |
| C | 15.212867 | 4.273765 | 4.577066 |
| H | 15.785621 | 3.659451 | 3.891370 |
| C | 14.311162 | 3.669627 | 5.435277 |
| H | 14.168799 | 2.595094 | 5.432818 |
| C | 12.981666 | 6.683625 | 7.246865 |
| H | 13.170588 | 7.759798 | 7.209184 |
| C | 10.520977 | 6.515256 | 9.732656 |
| C | 9.645245 | 9.637165 | 11.108197 |
| C | 8.553993 | 9.276340 | 12.063760 |
| H | 8.188848 | 10.146588 | 12.602135 |
| H | 8.916149 | 8.555006 | 12.803562 |
| H | 7.712266 | 8.814925 | 11.537599 |
| C | 10.078059 | 11.025078 | 10.978641 |
| C | 9.381176 | 12.185025 | 11.441862 |
| H | 8.420447 | 12.199414 | 11.932885 |
| C | 10.176820 | 13.322248 | 11.154007 |
| H | 9.931054 | 14.343524 | 11.403353 |
| C | 11.369048 | 12.878936 | 10.521629 |
| H | 12.192350 | 13.504865 | 10.211513 |
| C | 11.312954 | 11.467783 | 10.413820 |
| H | 12.079042 | 10.826128 | 10.007518 |
| C | 11.529563 | 10.723662 | 13.918611 |
| H | 11.183354 | 9.701139 | 13.949613 |
| C | 10.814526 | 11.862328 | 14.379163 |
| H | 9.832629 | 11.856030 | 14.828311 |
| C | 11.602931 | 13.013463 | 14.109573 |
| H | 11.323735 | 14.036032 | 14.315034 |
| C | 12.803272 | 12.586360 | 13.480526 |
| H | 13.596944 | 13.227302 | 13.126836 |
| C | 12.757772 | 11.170528 | 13.362595 |
| H | 13.510157 | 10.546896 | 12.903518 |
| H | 16.095468 | 6.123987 | 3.913318 |

| | | | |
|---|---|---|---|
| H | 14.772570 | 7.498772 | 5.490876 |

2. Neutral form of Schiff base **2a** in DMF
   E = –2406.31566679 Eh

| | | | |
|---|---|---|---|
| Fe | 11.179857 | 12.017036 | 12.370230 |
| O | 12.693145 | 3.822329 | 7.138186 |
| H | 12.254248 | 4.516802 | 7.691295 |
| O | 10.230091 | 5.334609 | 9.831644 |
| N | 12.125178 | 6.189034 | 8.061151 |
| N | 11.457425 | 7.017516 | 8.876650 |
| H | 11.620278 | 8.019045 | 8.864095 |
| N | 9.907989 | 7.474499 | 10.493064 |
| H | 9.207918 | 7.148357 | 11.146388 |
| N | 10.250515 | 8.776942 | 10.376604 |
| C | 13.561058 | 4.440426 | 6.324863 |
| C | 13.732991 | 5.840399 | 6.349512 |
| C | 14.654688 | 6.422488 | 5.474055 |
| C | 15.392475 | 5.655851 | 4.593033 |
| C | 15.212416 | 4.275147 | 4.580077 |
| H | 15.784260 | 3.660388 | 3.893985 |
| C | 14.307377 | 3.671985 | 5.436090 |
| H | 14.162171 | 2.597745 | 5.430934 |
| C | 12.984191 | 6.687214 | 7.251320 |
| H | 13.175669 | 7.762767 | 7.216597 |
| C | 10.519520 | 6.517892 | 9.732869 |
| C | 9.641751 | 9.636784 | 11.108659 |
| C | 8.552482 | 9.275940 | 12.066012 |
| H | 8.184626 | 10.146752 | 12.601558 |
| H | 8.918072 | 8.558210 | 12.807556 |
| H | 7.712371 | 8.809560 | 11.541721 |
| C | 10.074385 | 11.024736 | 10.977671 |
| C | 9.379049 | 12.184671 | 11.443567 |
| H | 8.419922 | 12.198821 | 11.937802 |
| C | 10.174630 | 13.321701 | 11.154512 |
| H | 9.930193 | 14.342897 | 11.405769 |
| C | 11.365209 | 12.878340 | 10.518690 |
| H | 12.188229 | 13.504123 | 10.207309 |
| C | 11.308230 | 11.467227 | 10.409751 |
| H | 12.073198 | 10.825778 | 10.000777 |
| C | 11.532442 | 10.719583 | 13.913092 |
| H | 11.184832 | 9.697425 | 13.943099 |
| C | 10.819170 | 11.858349 | 14.376504 |
| H | 9.837835 | 11.852123 | 14.827014 |
| C | 11.607750 | 13.009384 | 14.106153 |
| H | 11.329359 | 14.032032 | 14.312684 |
| C | 12.806498 | 12.582152 | 13.473776 |
| H | 13.599526 | 13.223039 | 13.118332 |
| C | 12.759816 | 11.166272 | 13.354618 |
| H | 13.510566 | 10.542710 | 12.892604 |
| H | 16.101620 | 6.123880 | 3.921396 |
| H | 14.780545 | 7.500210 | 5.499872 |

3. Cation of Schiff base **2a**$^+$ in $CH_2Cl_2$
   E = –2406.13759401 Eh

| | | | |
|---|---|---|---|
| Fe | 11.232797 | 12.004148 | 12.352496 |
| O | 12.618502 | 3.850902 | 7.046115 |
| H | 12.165802 | 4.523827 | 7.609951 |
| O | 10.084278 | 5.344350 | 9.726021 |
| N | 12.070743 | 6.197562 | 8.054390 |
| N | 11.382557 | 7.021629 | 8.863739 |
| H | 11.570462 | 8.017954 | 8.883079 |
| N | 9.777512 | 7.464401 | 10.443524 |
| H | 9.034842 | 7.118916 | 11.039403 |
| N | 10.124740 | 8.747594 | 10.389155 |
| C | 13.547812 | 4.480684 | 6.316378 |
| C | 13.757820 | 5.872111 | 6.415411 |
| C | 14.746268 | 6.465136 | 5.623354 |
| C | 15.513238 | 5.717002 | 4.753151 |
| C | 15.294273 | 4.344384 | 4.665373 |
| H | 15.888537 | 3.743861 | 3.985875 |
| C | 14.323652 | 3.731104 | 5.436667 |
| H | 14.148517 | 2.663475 | 5.372618 |
| C | 12.982440 | 6.701118 | 7.308825 |
| H | 13.202567 | 7.771950 | 7.324077 |
| C | 10.408534 | 6.514346 | 9.663456 |
| C | 9.493275 | 9.597056 | 11.117485 |
| C | 8.374896 | 9.234365 | 12.035233 |
| H | 8.000949 | 10.093477 | 12.585321 |
| H | 8.707529 | 8.489055 | 12.764813 |
| H | 7.541339 | 8.799478 | 11.474634 |
| C | 9.945680 | 10.977095 | 10.979237 |
| C | 9.318514 | 12.139901 | 11.505247 |
| H | 8.404843 | 12.166739 | 12.079297 |
| C | 10.115914 | 13.266984 | 11.181230 |
| H | 9.902701 | 14.289581 | 11.453471 |
| C | 11.254214 | 12.805178 | 10.462907 |
| H | 12.065154 | 13.414007 | 10.092808 |
| C | 11.155961 | 11.395776 | 10.354569 |
| H | 11.883835 | 10.736335 | 9.907976 |
| C | 11.778269 | 10.745299 | 13.977076 |
| H | 11.447865 | 9.721184 | 14.074510 |
| C | 11.084890 | 11.886234 | 14.444561 |
| H | 10.143845 | 11.880708 | 14.974374 |
| C | 11.807978 | 13.039446 | 14.039056 |
| H | 11.525078 | 14.064307 | 14.225966 |
| C | 12.951014 | 12.602329 | 13.310650 |
| H | 13.693780 | 13.235780 | 12.849916 |
| C | 12.925444 | 11.181016 | 13.274705 |
| H | 13.631722 | 10.545619 | 12.761362 |
| H | 16.274692 | 6.191582 | 4.146782 |
| H | 14.900488 | 7.536184 | 5.706899 |

4. Cation of Schiff base **2a**$^{+}$ in DMF
   E = –2406.14742970 Eh

| | | | |
|---|---|---|---|
| Fe | 11.224729 | 12.008736 | 12.350434 |
| O | 12.613092 | 3.862877 | 7.050498 |
| H | 12.164411 | 4.544919 | 7.610063 |
| O | 10.098991 | 5.339034 | 9.726627 |
| N | 12.069482 | 6.206674 | 8.048466 |
| N | 11.380465 | 7.026382 | 8.859151 |
| H | 11.566937 | 8.023411 | 8.884816 |
| N | 9.783805 | 7.458603 | 10.446928 |
| H | 9.055003 | 7.114185 | 11.060283 |
| N | 10.126615 | 8.745278 | 10.381673 |
| C | 13.543510 | 4.487472 | 6.315353 |
| C | 13.753757 | 5.879228 | 6.409066 |
| C | 14.741519 | 6.467884 | 5.613224 |
| C | 15.506981 | 5.715258 | 4.744741 |
| C | 15.287804 | 4.342457 | 4.662452 |
| H | 15.880972 | 3.738787 | 3.984690 |
| C | 14.317361 | 3.733193 | 5.438203 |
| H | 14.141835 | 2.665196 | 5.378784 |
| C | 12.979847 | 6.711690 | 7.301576 |
| H | 13.198528 | 7.782421 | 7.317540 |
| C | 10.413350 | 6.514234 | 9.665668 |
| C | 9.507802 | 9.593700 | 11.120168 |
| C | 8.409748 | 9.232459 | 12.062348 |
| H | 8.038776 | 10.095851 | 12.607725 |
| H | 8.764861 | 8.500824 | 12.795208 |
| H | 7.571338 | 8.781580 | 11.522208 |
| C | 9.957568 | 10.975402 | 10.972032 |
| C | 9.331605 | 12.140405 | 11.498354 |
| H | 8.416975 | 12.170237 | 12.070611 |
| C | 10.128613 | 13.266415 | 11.162985 |
| H | 9.916908 | 14.291395 | 11.427092 |
| C | 11.260978 | 12.797919 | 10.439682 |
| H | 12.075659 | 13.401961 | 10.069511 |
| C | 11.159268 | 11.391456 | 10.334489 |
| H | 11.886288 | 10.730268 | 9.888390 |
| C | 11.741991 | 10.744567 | 13.975307 |
| H | 11.402886 | 9.722442 | 14.063820 |
| C | 11.041510 | 11.891641 | 14.421006 |
| H | 10.089457 | 11.893065 | 14.930554 |
| C | 11.787516 | 13.039637 | 14.035514 |
| H | 11.511719 | 14.067587 | 14.215718 |
| C | 12.947170 | 12.589720 | 13.342976 |
| H | 13.704381 | 13.215679 | 12.895303 |
| C | 12.912385 | 11.171376 | 13.309896 |
| H | 13.626657 | 10.530925 | 12.813813 |
| H | 16.267867 | 6.187628 | 4.135749 |
| H | 14.896840 | 7.539112 | 5.692447 |

5. Dication of Schiff base **2a**$^{2+}$ in $CH_2Cl_2$
   E = –2405.91112963 Eh

| | | | |
|---|---|---|---|
| Fe | 11.166393 | 12.016244 | 12.410272 |
| O | 12.667967 | 3.913043 | 7.165824 |
| H | 12.232838 | 4.619081 | 7.722316 |
| O | 10.346864 | 5.344718 | 9.722658 |
| N | 12.174808 | 6.293232 | 8.020068 |
| N | 11.527695 | 7.088243 | 8.813904 |
| H | 11.672053 | 8.097830 | 8.821054 |
| N | 9.963534 | 7.456297 | 10.459580 |
| H | 9.257730 | 7.105558 | 11.098059 |
| N | 10.292049 | 8.757400 | 10.378635 |
| C | 13.516633 | 4.466436 | 6.350201 |
| C | 13.740009 | 5.900891 | 6.323441 |
| C | 14.677131 | 6.417738 | 5.406330 |
| C | 15.356958 | 5.586705 | 4.563873 |
| C | 15.128170 | 4.185563 | 4.602890 |
| H | 15.678597 | 3.543574 | 3.925381 |
| C | 14.232403 | 3.635000 | 5.472414 |
| H | 14.049158 | 2.568806 | 5.511056 |
| C | 13.050086 | 6.781531 | 7.180053 |
| H | 13.253883 | 7.851145 | 7.126124 |
| C | 10.580701 | 6.527680 | 9.683367 |
| C | 9.656215 | 9.591308 | 11.116717 |
| C | 8.556019 | 9.216874 | 12.050875 |
| H | 8.172676 | 10.077193 | 12.592549 |
| H | 8.912444 | 8.490925 | 12.788442 |
| H | 7.726744 | 8.758072 | 11.503941 |
| C | 10.082759 | 10.984424 | 10.984923 |
| C | 9.371590 | 12.147746 | 11.423719 |
| H | 8.414895 | 12.165650 | 11.922450 |
| C | 10.146074 | 13.286002 | 11.085545 |
| H | 9.896438 | 14.310964 | 11.316536 |
| C | 11.329069 | 12.842764 | 10.449568 |
| H | 12.149480 | 13.470234 | 10.133083 |
| C | 11.301329 | 11.435174 | 10.392328 |
| H | 12.085542 | 10.797732 | 10.013613 |
| C | 11.524923 | 10.761229 | 14.001716 |
| H | 11.185350 | 9.736667 | 14.033156 |
| C | 10.789086 | 11.904556 | 14.427177 |
| H | 9.791428 | 11.903091 | 14.839584 |
| C | 11.592659 | 13.051353 | 14.185754 |
| H | 11.302396 | 14.077471 | 14.356686 |
| C | 12.812880 | 12.620722 | 13.615586 |
| H | 13.607143 | 13.262630 | 13.263449 |
| C | 12.773854 | 11.211800 | 13.497852 |
| H | 13.540445 | 10.593159 | 13.055201 |
| H | 16.074801 | 5.988522 | 3.860285 |
| H | 14.843860 | 7.488197 | 5.384904 |

6. Dication of Schiff base **2a**$^{2+}$ in DMF
   E = –2405.93185976 Eh

| | | | |
|---|---|---|---|
| Fe | 11.192032 | 11.979002 | 12.357603 |
| O | 12.644897 | 3.926629 | 7.149304 |
| H | 12.193319 | 4.615726 | 7.710971 |
| O | 10.254989 | 5.328795 | 9.720655 |
| N | 12.118952 | 6.288741 | 8.051695 |
| N | 11.459251 | 7.073816 | 8.841791 |
| H | 11.609999 | 8.083445 | 8.869502 |
| N | 9.880009 | 7.440737 | 10.466461 |
| H | 9.171430 | 7.097092 | 11.105987 |
| N | 10.216975 | 8.739290 | 10.380812 |
| C | 13.516375 | 4.506726 | 6.372477 |
| C | 13.733123 | 5.939712 | 6.389315 |
| C | 14.697378 | 6.487528 | 5.515782 |
| C | 15.407339 | 5.684059 | 4.673671 |
| C | 15.182226 | 4.282836 | 4.668977 |
| H | 15.755378 | 3.659986 | 3.992313 |
| C | 14.261502 | 3.704302 | 5.495825 |
| H | 14.084126 | 2.636447 | 5.498064 |
| C | 13.017269 | 6.796928 | 7.243788 |
| H | 13.219143 | 7.867855 | 7.221479 |
| C | 10.496887 | 6.511535 | 9.693155 |
| C | 9.598643 | 9.581309 | 11.123663 |
| C | 8.509786 | 9.222465 | 12.076018 |
| H | 8.137624 | 10.090579 | 12.612873 |
| H | 8.875518 | 8.503453 | 12.815709 |
| H | 7.672072 | 8.760379 | 11.545146 |
| C | 10.040812 | 10.967899 | 10.977146 |
| C | 9.364964 | 12.143870 | 11.437567 |
| H | 8.428836 | 12.179289 | 11.973095 |
| C | 10.146475 | 13.267793 | 11.070999 |
| H | 9.925021 | 14.296422 | 11.314100 |
| C | 11.299010 | 12.804511 | 10.394582 |
| H | 12.120202 | 13.417330 | 10.052608 |
| C | 11.246171 | 11.397571 | 10.341053 |
| H | 12.006124 | 10.746707 | 9.936375 |
| C | 11.587454 | 10.719144 | 13.933085 |
| H | 11.228511 | 9.701570 | 13.975747 |
| C | 10.891510 | 11.875872 | 14.388762 |
| H | 9.910444 | 11.893028 | 14.838925 |
| C | 11.705869 | 13.007237 | 14.115287 |
| H | 11.439669 | 14.038726 | 14.292968 |
| C | 12.893301 | 12.554860 | 13.494982 |
| H | 13.681747 | 13.182765 | 13.106445 |
| C | 12.823431 | 11.146671 | 13.378591 |
| H | 13.557645 | 10.514624 | 12.901380 |
| H | 16.145502 | 6.106704 | 4.004261 |
| H | 14.856823 | 7.559207 | 5.532146 |

7. Neutral form of complex **3a** in $CH_2Cl_2$
   E= –2777.77974664 Eh

| | | | |
|---|---|---|---|
| Sn | 4.300425 | 3.273525 | 9.143311 |
| Fe | 4.087649 | 0.909779 | 3.562256 |
| O | 4.781307 | 1.489528 | 7.992934 |
| O | 4.141695 | 4.464547 | 10.853241 |
| N | 5.050112 | -0.948600 | 6.791139 |
| N | 5.393454 | -0.702347 | 8.115832 |
| H | 5.222491 | -1.508287 | 8.699665 |
| N | 4.954872 | 0.433478 | 10.039350 |
| N | 4.629091 | 1.646654 | 10.560334 |
| C | 3.490970 | 2.592860 | 2.566629 |
| H | 3.629598 | 2.764876 | 1.509756 |
| C | 4.413089 | 2.926844 | 3.595898 |
| H | 5.376079 | 3.395377 | 3.458468 |
| C | 3.865224 | 2.491708 | 4.832478 |
| H | 4.345803 | 2.546047 | 5.796977 |
| C | 2.605656 | 1.888965 | 4.569779 |
| H | 1.958097 | 1.431570 | 5.302856 |
| C | 2.374154 | 1.951690 | 3.168188 |
| H | 1.516482 | 1.552690 | 2.647610 |
| C | 5.239845 | -0.466654 | 4.520500 |
| C | 3.998528 | -1.049087 | 4.116788 |
| H | 3.257599 | -1.461603 | 4.782741 |
| C | 3.900254 | -0.945623 | 2.707933 |
| H | 3.063476 | -1.268854 | 2.107086 |
| C | 5.069412 | -0.295571 | 2.227430 |
| H | 5.278623 | -0.042875 | 1.198866 |
| C | 5.895216 | 0.005274 | 3.339176 |
| H | 6.842519 | 0.520297 | 3.299219 |
| C | 5.699156 | -0.293602 | 5.898107 |
| C | 6.878884 | 0.586539 | 6.137884 |
| H | 7.256662 | 0.467729 | 7.151250 |
| H | 6.613315 | 1.633992 | 5.986285 |
| H | 7.667449 | 0.338462 | 5.424746 |
| C | 5.021265 | 0.471398 | 8.719157 |
| C | 4.472000 | 1.708509 | 11.842655 |
| H | 4.618210 | 0.772317 | 12.379383 |
| C | 4.116344 | 2.851246 | 12.629739 |
| C | 3.956281 | 4.162125 | 12.113533 |
| C | 3.605332 | 5.184643 | 13.010469 |
| H | 3.484289 | 6.185060 | 12.610563 |
| C | 3.421438 | 4.931610 | 14.353857 |
| H | 3.149520 | 5.746824 | 15.015799 |
| C | 3.582897 | 3.643268 | 14.866344 |
| H | 3.440303 | 3.446015 | 15.921520 |
| C | 3.928080 | 2.627084 | 14.004531 |
| H | 4.060780 | 1.617107 | 14.379295 |
| C | 2.270427 | 3.316588 | 8.500131 |
| H | 1.804768 | 4.163919 | 9.007089 |
| H | 2.281607 | 3.531515 | 7.429159 |

| | | | |
|---|---|---|---|
| C | 1.545396 | 2.011437 | 8.793273 |
| H | 1.529159 | 1.787199 | 9.862778 |
| H | 2.019127 | 1.168424 | 8.285165 |
| H | 0.507596 | 2.060581 | 8.451126 |
| C | 6.043355 | 4.258550 | 8.428978 |
| H | 6.047577 | 4.144185 | 7.342824 |
| H | 5.928139 | 5.319343 | 8.659076 |
| C | 7.305567 | 3.681045 | 9.053823 |
| H | 8.195674 | 4.195312 | 8.679846 |
| H | 7.418805 | 2.619256 | 8.821315 |
| H | 7.299745 | 3.783804 | 10.141905 |

8. Neutral form of complex **3a** in DMF
   E = –2777.78197591 Eh

| | | | |
|---|---|---|---|
| Sn | 4.138954 | 3.377456 | 9.129201 |
| Fe | 4.187862 | 0.801167 | 3.407490 |
| O | 4.490380 | 1.564463 | 7.936709 |
| O | 3.975274 | 4.457818 | 10.934995 |
| N | 4.916743 | -0.917052 | 6.734695 |
| N | 5.038136 | -0.638152 | 8.061544 |
| H | 5.050795 | -1.441786 | 8.677328 |
| N | 4.744342 | 0.494860 | 9.982932 |
| N | 4.491900 | 1.676997 | 10.507618 |
| C | 3.555164 | 2.404046 | 2.307845 |
| H | 3.810413 | 2.575326 | 1.272791 |
| C | 4.299999 | 2.843543 | 3.436128 |
| H | 5.219971 | 3.408063 | 3.410358 |
| C | 3.645550 | 2.368190 | 4.603827 |
| H | 3.986322 | 2.495865 | 5.619909 |
| C | 2.498015 | 1.633987 | 4.200283 |
| H | 1.809863 | 1.121948 | 4.856084 |
| C | 2.442068 | 1.657205 | 2.779812 |
| H | 1.704909 | 1.162469 | 2.165291 |
| C | 5.351711 | -0.458229 | 4.494954 |
| C | 4.221635 | -1.158295 | 3.961634 |
| H | 3.455023 | -1.644610 | 4.543699 |
| C | 4.277418 | -1.064602 | 2.552214 |
| H | 3.549012 | -1.465570 | 1.863586 |
| C | 5.425332 | -0.303631 | 2.199166 |
| H | 5.720990 | -0.030874 | 1.197371 |
| C | 6.088581 | 0.078568 | 3.388667 |
| H | 6.981212 | 0.681257 | 3.449154 |
| C | 5.631610 | -0.234925 | 5.902351 |
| C | 6.729536 | 0.700319 | 6.271300 |
| H | 7.027727 | 0.583120 | 7.311426 |
| H | 6.408646 | 1.732412 | 6.114110 |
| H | 7.593196 | 0.518540 | 5.630877 |
| C | 4.744350 | 0.539661 | 8.618497 |
| C | 4.463574 | 1.701505 | 11.832441 |
| H | 4.643821 | 0.742770 | 12.313032 |
| C | 4.230311 | 2.805673 | 12.655091 |

| | | | |
|---|---|---|---|
| C | 3.995301 | 4.143864 | 12.180893 |
| C | 3.783649 | 5.156823 | 13.142775 |
| H | 3.608557 | 6.163140 | 12.782368 |
| C | 3.800168 | 4.871520 | 14.480562 |
| H | 3.633896 | 5.670280 | 15.195018 |
| C | 4.029380 | 3.560280 | 14.952766 |
| H | 4.037403 | 3.360388 | 16.016525 |
| C | 4.239349 | 2.558409 | 14.055208 |
| H | 4.418280 | 1.542836 | 14.390593 |
| C | 2.087987 | 3.487987 | 8.602863 |
| H | 1.774561 | 4.514625 | 8.799729 |
| H | 2.039257 | 3.314245 | 7.526316 |
| C | 1.256972 | 2.478925 | 9.381030 |
| H | 1.318188 | 2.648873 | 10.458616 |
| H | 1.577297 | 1.452874 | 9.184529 |
| H | 0.204833 | 2.555472 | 9.093902 |
| C | 5.969864 | 4.256028 | 8.518245 |
| H | 6.030672 | 4.110405 | 7.438074 |
| H | 5.880607 | 5.325289 | 8.717352 |
| C | 7.157366 | 3.638914 | 9.241490 |
| H | 8.086541 | 4.111708 | 8.912106 |
| H | 7.244923 | 2.569131 | 9.037736 |
| H | 7.085770 | 3.770020 | 10.323808 |

9. Cation of complex **3a** (**3a**$^+$) in $CH_2Cl_2$
   E = –2777.58985106 Eh

| | | | |
|---|---|---|---|
| Sn | 4.147235 | 3.385455 | 9.116498 |
| Fe | 4.188036 | 0.787967 | 3.382315 |
| O | 4.523853 | 1.580349 | 7.916723 |
| O | 3.952310 | 4.452521 | 10.925565 |
| N | 4.932767 | -0.913104 | 6.714653 |
| N | 5.060528 | -0.627094 | 8.038386 |
| H | 5.067482 | -1.428543 | 8.657008 |
| N | 4.763620 | 0.502123 | 9.959959 |
| N | 4.502376 | 1.681233 | 10.488697 |
| C | 3.626907 | 2.433409 | 2.306406 |
| H | 3.936478 | 2.636805 | 1.292290 |
| C | 4.317299 | 2.825723 | 3.485317 |
| H | 5.242231 | 3.381266 | 3.524911 |
| C | 3.598828 | 2.318657 | 4.601516 |
| H | 3.891065 | 2.402662 | 5.637159 |
| C | 2.466701 | 1.612007 | 4.114647 |
| H | 1.741016 | 1.085125 | 4.715840 |
| C | 2.484199 | 1.683789 | 2.694852 |
| H | 1.774445 | 1.219350 | 2.026929 |
| C | 5.351042 | -0.471602 | 4.468569 |
| C | 4.211881 | -1.168041 | 3.949986 |
| H | 3.447521 | -1.644957 | 4.542607 |
| C | 4.256760 | -1.085383 | 2.539778 |
| H | 3.520654 | -1.487150 | 1.859990 |
| C | 5.406754 | -0.335024 | 2.171413 |

| | | | |
|---|---|---|---|
| H | 5.696504 | -0.073312 | 1.165028 |
| C | 6.082477 | 0.052139 | 3.352084 |
| H | 6.980022 | 0.648610 | 3.399828 |
| C | 5.640422 | -0.236795 | 5.871230 |
| C | 6.739516 | 0.703174 | 6.225567 |
| H | 7.045029 | 0.594144 | 7.264461 |
| H | 6.414949 | 1.733128 | 6.062170 |
| H | 7.599385 | 0.518206 | 5.581016 |
| C | 4.770504 | 0.551956 | 8.596523 |
| C | 4.467079 | 1.699539 | 11.813494 |
| H | 4.652930 | 0.739649 | 12.289705 |
| C | 4.220075 | 2.797352 | 12.640394 |
| C | 3.971635 | 4.134773 | 12.170446 |
| C | 3.744476 | 5.141562 | 13.135071 |
| H | 3.559122 | 6.147002 | 12.777566 |
| C | 3.759263 | 4.851282 | 14.471636 |
| H | 3.581115 | 5.645277 | 15.188456 |
| C | 4.001629 | 3.540851 | 14.939879 |
| H | 4.007795 | 3.337113 | 16.002860 |
| C | 4.226295 | 2.544891 | 14.039637 |
| H | 4.415160 | 1.530285 | 14.372458 |
| C | 2.102525 | 3.484029 | 8.564476 |
| H | 1.779620 | 4.507792 | 8.761067 |
| H | 2.067112 | 3.313871 | 7.486820 |
| C | 1.267495 | 2.467766 | 9.328877 |
| H | 1.314424 | 2.634205 | 10.407719 |
| H | 1.594584 | 1.443775 | 9.132681 |
| H | 0.218583 | 2.540139 | 9.029558 |
| C | 5.977393 | 4.284050 | 8.532353 |
| H | 6.037932 | 4.178472 | 7.447515 |
| H | 5.888093 | 5.345585 | 8.769240 |
| C | 7.166927 | 3.643376 | 9.231264 |
| H | 8.095166 | 4.127861 | 8.916885 |
| H | 7.255440 | 2.581375 | 8.990455 |
| H | 7.098201 | 3.737028 | 10.317610 |

10. Cation of complex **3a** (**3a**$^{+}$) in DMF
E = –2777.59632851 Eh

| | | | |
|---|---|---|---|
| Sn | 4.138954 | 3.377456 | 9.129201 |
| Fe | 4.187862 | 0.801167 | 3.407490 |
| O | 4.490380 | 1.564463 | 7.936709 |
| O | 3.975274 | 4.457818 | 10.934995 |
| N | 4.916743 | -0.917052 | 6.734695 |
| N | 5.038136 | -0.638152 | 8.061544 |
| H | 5.050795 | -1.441786 | 8.677328 |
| N | 4.744342 | 0.494860 | 9.982932 |
| N | 4.491900 | 1.676997 | 10.507618 |
| C | 3.555164 | 2.404046 | 2.307845 |
| H | 3.810413 | 2.575326 | 1.272791 |
| C | 4.299999 | 2.843543 | 3.436128 |
| H | 5.219971 | 3.408063 | 3.410358 |

| | | | |
|---|---|---|---|
| C | 3.645550 | 2.368190 | 4.603827 |
| H | 3.986322 | 2.495865 | 5.619909 |
| C | 2.498015 | 1.633987 | 4.200283 |
| H | 1.809863 | 1.121948 | 4.856084 |
| C | 2.442068 | 1.657205 | 2.779812 |
| H | 1.704909 | 1.162469 | 2.165291 |
| C | 5.351711 | -0.458229 | 4.494954 |
| C | 4.221635 | -1.158295 | 3.961634 |
| H | 3.455023 | -1.644610 | 4.543699 |
| C | 4.277418 | -1.064602 | 2.552214 |
| H | 3.549012 | -1.465570 | 1.863586 |
| C | 5.425332 | -0.303631 | 2.199166 |
| H | 5.720990 | -0.030874 | 1.197371 |
| C | 6.088581 | 0.078568 | 3.388667 |
| H | 6.981212 | 0.681257 | 3.449154 |
| C | 5.631610 | -0.234925 | 5.902351 |
| C | 6.729536 | 0.700319 | 6.271300 |
| H | 7.027727 | 0.583120 | 7.311426 |
| H | 6.408646 | 1.732412 | 6.114110 |
| H | 7.593196 | 0.518540 | 5.630877 |
| C | 4.744350 | 0.539661 | 8.618497 |
| C | 4.463574 | 1.701505 | 11.832441 |
| H | 4.643821 | 0.742770 | 12.313032 |
| C | 4.230311 | 2.805673 | 12.655091 |
| C | 3.995301 | 4.143864 | 12.180893 |
| C | 3.783649 | 5.156823 | 13.142775 |
| H | 3.608557 | 6.163140 | 12.782368 |
| C | 3.800168 | 4.871520 | 14.480562 |
| H | 3.633896 | 5.670280 | 15.195018 |
| C | 4.029380 | 3.560280 | 14.952766 |
| H | 4.037403 | 3.360388 | 16.016525 |
| C | 4.239349 | 2.558409 | 14.055208 |
| H | 4.418280 | 1.542836 | 14.390593 |
| C | 2.087987 | 3.487987 | 8.602863 |
| H | 1.774561 | 4.514625 | 8.799729 |
| H | 2.039257 | 3.314245 | 7.526316 |
| C | 1.256972 | 2.478925 | 9.381030 |
| H | 1.318188 | 2.648873 | 10.458616 |
| H | 1.577297 | 1.452874 | 9.184529 |
| H | 0.204833 | 2.555472 | 9.093902 |
| C | 5.969864 | 4.256028 | 8.518245 |
| H | 6.030672 | 4.110405 | 7.438074 |
| H | 5.880607 | 5.325289 | 8.717352 |
| C | 7.157366 | 3.638914 | 9.241490 |
| H | 8.086541 | 4.111708 | 8.912106 |
| H | 7.244923 | 2.569131 | 9.037736 |
| H | 7.085770 | 3.770020 | 10.323808 |

11. Dication **3a**$^{2+}$ in $CH_2Cl_2$

E= –2777.40199356 Eh

| | | | |
|---|---|---|---|
| Sn | 4.184781 | 3.417469 | 9.127412 |

| | | | |
|---|---|---|---|
| Fe | 4.153466 | 0.767063 | 3.354828 |
| O | 4.573577 | 1.608864 | 7.909534 |
| O | 3.956090 | 4.467233 | 10.942224 |
| N | 4.919923 | -0.873679 | 6.695213 |
| N | 5.049094 | -0.611767 | 8.028263 |
| H | 4.983454 | -1.421993 | 8.631528 |
| N | 4.743300 | 0.517233 | 9.952732 |
| N | 4.496083 | 1.694054 | 10.484518 |
| C | 3.498592 | 2.488767 | 2.293505 |
| H | 3.798358 | 2.715675 | 1.280793 |
| C | 4.204884 | 2.845693 | 3.467593 |
| H | 5.124153 | 3.410911 | 3.506328 |
| C | 3.521796 | 2.279202 | 4.580110 |
| H | 3.824317 | 2.342570 | 5.614800 |
| C | 2.394514 | 1.567061 | 4.080999 |
| H | 1.689383 | 0.998369 | 4.668481 |
| C | 2.386704 | 1.700754 | 2.668532 |
| H | 1.689190 | 1.230526 | 1.991047 |
| C | 5.364448 | -0.458720 | 4.463401 |
| C | 4.255864 | -1.207438 | 3.951162 |
| H | 3.490226 | -1.681322 | 4.545189 |
| C | 4.331991 | -1.185138 | 2.540481 |
| H | 3.612573 | -1.620595 | 1.862695 |
| C | 5.462595 | -0.423203 | 2.166647 |
| H | 5.751808 | -0.174681 | 1.156017 |
| C | 6.101476 | 0.032184 | 3.340471 |
| H | 6.973556 | 0.667232 | 3.375050 |
| C | 5.656346 | -0.210856 | 5.879293 |
| C | 6.766217 | 0.713954 | 6.224555 |
| H | 7.058497 | 0.613790 | 7.267754 |
| H | 6.466006 | 1.749232 | 6.043612 |
| H | 7.629176 | 0.500815 | 5.591721 |
| C | 4.778723 | 0.573711 | 8.587852 |
| C | 4.448197 | 1.703588 | 11.811940 |
| H | 4.618283 | 0.737827 | 12.281592 |
| C | 4.208938 | 2.796308 | 12.643410 |
| C | 3.972170 | 4.143359 | 12.182256 |
| C | 3.750813 | 5.147461 | 13.152526 |
| H | 3.575042 | 6.156190 | 12.799909 |
| C | 3.759785 | 4.847332 | 14.484925 |
| H | 3.587013 | 5.636422 | 15.208254 |
| C | 3.989720 | 3.528745 | 14.944931 |
| H | 3.990949 | 3.319784 | 16.006889 |
| C | 4.207936 | 2.535571 | 14.042052 |
| H | 4.386573 | 1.517926 | 14.370520 |
| C | 2.149135 | 3.521344 | 8.542662 |
| H | 1.832330 | 4.549616 | 8.725019 |
| H | 2.129025 | 3.341998 | 7.466154 |
| C | 1.295920 | 2.519008 | 9.304941 |
| H | 1.328515 | 2.695940 | 10.382494 |
| H | 1.616298 | 1.490222 | 9.123460 |
| H | 0.252204 | 2.598134 | 8.989866 |

| | | | |
|---|---|---|---|
| C | 6.036686 | 4.300532 | 8.591037 |
| H | 6.113019 | 4.216473 | 7.505376 |
| H | 5.953798 | 5.357801 | 8.848372 |
| C | 7.205960 | 3.631698 | 9.297138 |
| H | 8.144189 | 4.111110 | 9.005858 |
| H | 7.285886 | 2.573232 | 9.038466 |
| H | 7.121324 | 3.707098 | 10.383659 |

12. Dication of complex **3a** (**3a**$^{2+}$) in DMF
E= –2777.42105793 Eh

| | | | |
|---|---|---|---|
| Sn | 4.189390 | 3.413188 | 9.142161 |
| Fe | 4.138761 | 0.780617 | 3.390531 |
| O | 4.575418 | 1.603299 | 7.933863 |
| O | 3.945608 | 4.465586 | 10.956225 |
| N | 4.917221 | -0.874094 | 6.718989 |
| N | 5.042956 | -0.617457 | 8.052807 |
| H | 4.980739 | -1.429171 | 8.654482 |
| N | 4.738307 | 0.512581 | 9.977912 |
| N | 4.494272 | 1.691273 | 10.506364 |
| C | 3.406094 | 2.443130 | 2.304715 |
| H | 3.645879 | 2.626796 | 1.267668 |
| C | 4.178239 | 2.850235 | 3.421783 |
| H | 5.095186 | 3.419081 | 3.386380 |
| C | 3.557984 | 2.331527 | 4.593621 |
| H | 3.915517 | 2.439048 | 5.606540 |
| C | 2.406110 | 1.601052 | 4.189002 |
| H | 1.741170 | 1.051701 | 4.838720 |
| C | 2.317058 | 1.675328 | 2.776965 |
| H | 1.585642 | 1.172304 | 2.161481 |
| C | 5.362337 | -0.441678 | 4.489956 |
| C | 4.264653 | -1.200682 | 3.969453 |
| H | 3.503184 | -1.688691 | 4.557410 |
| C | 4.341363 | -1.163698 | 2.559694 |
| H | 3.626617 | -1.600100 | 1.877587 |
| C | 5.460687 | -0.381370 | 2.193626 |
| H | 5.745367 | -0.117154 | 1.185776 |
| C | 6.092674 | 0.071466 | 3.372290 |
| H | 6.955027 | 0.719153 | 3.414211 |
| C | 5.653734 | -0.205179 | 5.907497 |
| C | 6.765498 | 0.714781 | 6.258941 |
| H | 7.054139 | 0.612560 | 7.302860 |
| H | 6.469543 | 1.751157 | 6.077143 |
| H | 7.628756 | 0.498711 | 5.627337 |
| C | 4.775858 | 0.567875 | 8.611993 |
| C | 4.449996 | 1.704915 | 11.833332 |
| H | 4.620145 | 0.740650 | 12.306067 |
| C | 4.216958 | 2.801757 | 12.661958 |
| C | 3.975794 | 4.145499 | 12.197464 |
| C | 3.762918 | 5.152900 | 13.166582 |
| H | 3.583510 | 6.160403 | 12.812006 |
| C | 3.784019 | 4.858016 | 14.500538 |

| | | | |
|---|---|---|---|
| H | 3.617799 | 5.650213 | 15.222165 |
| C | 4.017794 | 3.541933 | 14.963378 |
| H | 4.028619 | 3.336783 | 16.026113 |
| C | 4.227689 | 2.545656 | 14.061382 |
| H | 4.409397 | 1.528694 | 14.390396 |
| C | 2.160442 | 3.528844 | 8.538101 |
| H | 1.846686 | 4.557198 | 8.725481 |
| H | 2.154474 | 3.359420 | 7.459807 |
| C | 1.293349 | 2.522853 | 9.279535 |
| H | 1.313865 | 2.688714 | 10.359202 |
| H | 1.612988 | 1.495042 | 9.091680 |
| H | 0.254230 | 2.609638 | 8.951257 |
| C | 6.048092 | 4.290733 | 8.621231 |
| H | 6.132084 | 4.204622 | 7.536284 |
| H | 5.965553 | 5.348405 | 8.877063 |
| C | 7.209441 | 3.618137 | 9.336792 |
| H | 8.151281 | 4.095987 | 9.054258 |
| H | 7.288200 | 2.560143 | 9.076096 |
| H | 7.114853 | 3.691206 | 10.422760 |

13. Neutral form of dimer (**3a**)$_2$ in $CH_2Cl_2$
E = –5555.59570522 Eh

| | | | |
|---|---|---|---|
| Sn | 5.918065 | 3.628586 | 10.431029 |
| Fe | 3.202377 | 1.547120 | 2.360975 |
| O | 5.434487 | 2.922183 | 8.351019 |
| O | 5.551260 | 3.640256 | 12.523462 |
| N | 4.974208 | 1.690752 | 5.961724 |
| N | 4.917893 | 1.048754 | 7.151400 |
| H | 4.528210 | 0.117173 | 7.208871 |
| N | 4.526251 | 1.062006 | 9.373432 |
| N | 4.695092 | 1.754029 | 10.536670 |
| C | 1.731148 | 0.479579 | 3.295178 |
| H | 1.805499 | 0.073310 | 4.292775 |
| C | 2.128556 | -0.171433 | 2.095444 |
| H | 2.554724 | -1.160708 | 2.021389 |
| C | 1.902015 | 0.724648 | 1.015401 |
| H | 2.128468 | 0.536538 | -0.023421 |
| C | 1.367079 | 1.928870 | 1.548264 |
| H | 1.116808 | 2.815406 | 0.985100 |
| C | 1.261427 | 1.777258 | 2.957865 |
| H | 0.916219 | 2.527501 | 3.653314 |
| C | 4.811962 | 1.625895 | 3.616837 |
| C | 5.178138 | 1.062174 | 2.353539 |
| H | 5.580991 | 0.074519 | 2.189281 |
| C | 4.913941 | 2.025838 | 1.347933 |
| H | 5.066971 | 1.889598 | 0.287891 |
| C | 4.372367 | 3.180592 | 1.974279 |
| H | 4.036677 | 4.075767 | 1.472858 |
| C | 4.306954 | 2.935157 | 3.366603 |
| H | 3.911134 | 3.602474 | 4.113322 |
| C | 4.874527 | 0.955441 | 4.910246 |

| | | | |
|---|---|---|---|
| C | 4.792142 | -0.536449 | 4.965918 |
| H | 4.803851 | -0.969883 | 3.969588 |
| H | 3.862901 | -0.858117 | 5.449608 |
| H | 5.623935 | -0.948505 | 5.545221 |
| C | 4.963043 | 1.736869 | 8.331972 |
| C | 4.200690 | 1.198814 | 11.592629 |
| H | 3.682092 | 0.253670 | 11.431961 |
| C | 4.254433 | 1.670978 | 12.943549 |
| C | 4.919438 | 2.859917 | 13.346823 |
| C | 4.880832 | 3.196190 | 14.715033 |
| H | 5.391933 | 4.101831 | 15.020934 |
| C | 4.229187 | 2.403667 | 15.635132 |
| H | 4.224710 | 2.696542 | 16.679983 |
| C | 3.578715 | 1.232130 | 15.239144 |
| H | 3.068599 | 0.609844 | 15.963972 |
| C | 3.600845 | 0.884156 | 13.907531 |
| H | 3.101250 | -0.020320 | 13.573725 |
| C | 4.587064 | 5.272008 | 10.240727 |
| H | 4.747360 | 5.872637 | 11.137067 |
| H | 4.900619 | 5.857515 | 9.377999 |
| C | 3.144736 | 4.810209 | 10.123615 |
| H | 2.467393 | 5.666272 | 10.046880 |
| H | 2.836702 | 4.225766 | 10.994475 |
| H | 2.991776 | 4.189400 | 9.237343 |
| C | 7.833541 | 2.707547 | 10.526968 |
| Sn | 6.748843 | 4.192154 | 6.405610 |
| Fe | 9.448410 | 6.308204 | 14.474266 |
| O | 7.238408 | 4.901683 | 8.483677 |
| O | 7.103099 | 4.179866 | 4.311020 |
| N | 7.690553 | 6.145220 | 10.867741 |
| N | 7.748230 | 6.781940 | 9.675353 |
| H | 8.135771 | 7.714220 | 9.614518 |
| N | 8.148407 | 6.757442 | 7.454668 |
| N | 7.982926 | 6.059391 | 6.294523 |
| C | 10.919417 | 7.377670 | 13.541847 |
| H | 10.847465 | 7.779971 | 12.542465 |
| C | 10.514990 | 8.031657 | 14.737607 |
| H | 10.085016 | 9.019670 | 14.806351 |
| C | 10.740551 | 7.140408 | 15.821838 |
| H | 10.509421 | 7.331548 | 16.859079 |
| C | 11.281878 | 5.936152 | 15.295521 |
| H | 11.533140 | 5.052602 | 15.862926 |
| C | 11.392469 | 6.082953 | 13.885790 |
| H | 11.742973 | 5.331372 | 13.194446 |
| C | 7.844032 | 6.219532 | 13.212411 |
| C | 7.470678 | 6.785436 | 14.472580 |
| H | 7.063412 | 7.772039 | 14.632255 |
| C | 7.734761 | 5.825779 | 15.482077 |
| H | 7.577097 | 5.964541 | 16.541115 |
| C | 8.283491 | 4.671395 | 14.861300 |
| H | 8.620721 | 3.779020 | 15.366648 |
| C | 8.353344 | 4.912997 | 13.468499 |

| | | | |
|---|---|---|---|
| H | 8.754976 | 4.245292 | 12.725217 |
| C | 7.783614 | 6.885217 | 11.916377 |
| C | 7.860114 | 8.377208 | 11.855469 |
| H | 7.842211 | 8.814302 | 12.850133 |
| H | 8.790054 | 8.700979 | 11.374546 |
| H | 7.029081 | 8.783689 | 11.271159 |
| C | 7.708395 | 6.087492 | 8.498144 |
| C | 8.489597 | 6.603150 | 5.238567 |
| H | 9.016153 | 7.544383 | 5.396391 |
| C | 8.441955 | 6.121136 | 3.890803 |
| C | 7.759796 | 4.941154 | 3.489471 |
| C | 7.807276 | 4.593534 | 2.124264 |
| H | 7.283189 | 3.694847 | 1.819796 |
| C | 8.482175 | 5.367432 | 1.205104 |
| H | 8.492624 | 5.066294 | 0.162642 |
| C | 9.148066 | 6.531021 | 1.598911 |
| H | 9.676185 | 7.138944 | 0.874780 |
| C | 9.118099 | 6.889600 | 2.927568 |
| H | 9.628557 | 7.788691 | 3.259496 |
| C | 8.080273 | 2.548537 | 6.593381 |
| H | 7.909341 | 1.940404 | 5.704080 |
| H | 7.776457 | 1.970618 | 7.464706 |
| C | 9.524164 | 3.010162 | 6.689988 |
| H | 10.201716 | 2.154309 | 6.767253 |
| H | 9.822868 | 3.586140 | 5.810296 |
| H | 9.687573 | 3.639257 | 7.568549 |
| C | 4.839164 | 5.125814 | 6.316437 |
| H | 4.670245 | 5.523410 | 7.317489 |
| H | 4.121468 | 4.321087 | 6.161178 |
| C | 4.740755 | 6.208714 | 5.258893 |
| H | 3.739362 | 6.650128 | 5.252100 |
| H | 5.452986 | 7.016827 | 5.441073 |
| H | 4.938174 | 5.817307 | 4.259092 |
| H | 8.005292 | 2.304384 | 9.528570 |
| H | 8.545628 | 3.518157 | 10.677302 |
| C | 7.938429 | 1.632441 | 11.591861 |
| H | 8.942141 | 1.196395 | 11.600747 |
| H | 7.230394 | 0.819223 | 11.416139 |
| H | 7.739861 | 2.029843 | 12.589066 |

14. Neutral form of dimer (**3a**)$_2$ in DMF
E = –5555.59928073 Eh

| | | | |
|---|---|---|---|
| Sn | 5.940551 | 3.640631 | 10.432202 |
| Fe | 3.241522 | 1.499439 | 2.317761 |
| O | 5.433970 | 2.927821 | 8.357582 |
| O | 5.592132 | 3.657622 | 12.529777 |
| N | 4.941666 | 1.694166 | 5.971972 |
| N | 4.857733 | 1.064879 | 7.167336 |
| H | 4.451407 | 0.140707 | 7.229443 |
| N | 4.489606 | 1.093584 | 9.393882 |
| N | 4.681683 | 1.785697 | 10.554056 |

| | | | |
|---|---|---|---|
| C | 1.707801 | 0.516543 | 3.244844 |
| H | 1.713660 | 0.208170 | 4.279768 |
| C | 2.187631 | -0.243818 | 2.143281 |
| H | 2.620070 | -1.231838 | 2.194550 |
| C | 2.038609 | 0.543659 | 0.969295 |
| H | 2.339648 | 0.259338 | -0.027913 |
| C | 1.468962 | 1.790461 | 1.345615 |
| H | 1.261093 | 2.618481 | 0.684582 |
| C | 1.262989 | 1.772768 | 2.752310 |
| H | 0.870970 | 2.584452 | 3.346754 |
| C | 4.806373 | 1.610380 | 3.625216 |
| C | 5.221160 | 1.040045 | 2.379944 |
| H | 5.637846 | 0.054377 | 2.239482 |
| C | 4.978576 | 1.991429 | 1.357075 |
| H | 5.164638 | 1.846334 | 0.303486 |
| C | 4.401528 | 3.144666 | 1.954125 |
| H | 4.068694 | 4.029555 | 1.432863 |
| C | 4.295001 | 2.911794 | 3.346481 |
| H | 3.864995 | 3.580218 | 4.073638 |
| C | 4.836857 | 0.950808 | 4.926411 |
| C | 4.719456 | -0.538250 | 4.992229 |
| H | 4.755528 | -0.980730 | 4.000307 |
| H | 3.765541 | -0.831763 | 5.445091 |
| H | 5.520231 | -0.964381 | 5.603874 |
| C | 4.933085 | 1.754693 | 8.344519 |
| C | 4.183413 | 1.243196 | 11.615063 |
| H | 3.644882 | 0.307871 | 11.461549 |
| C | 4.252536 | 1.719835 | 12.964203 |
| C | 4.943473 | 2.897220 | 13.358815 |
| C | 4.911964 | 3.244167 | 14.724925 |
| H | 5.441636 | 4.141296 | 15.024305 |
| C | 4.246816 | 2.470682 | 15.651884 |
| H | 4.250250 | 2.771070 | 16.694697 |
| C | 3.573493 | 1.308749 | 15.264909 |
| H | 3.052490 | 0.701366 | 15.994691 |
| C | 3.585390 | 0.952211 | 13.934971 |
| H | 3.067361 | 0.055674 | 13.607657 |
| C | 4.625149 | 5.297534 | 10.238966 |
| H | 4.769344 | 5.885236 | 11.146650 |
| H | 4.961150 | 5.893151 | 9.391574 |
| C | 3.182096 | 4.850495 | 10.079515 |
| H | 2.515787 | 5.713570 | 9.986281 |
| H | 2.843458 | 4.265179 | 10.938295 |
| H | 3.050349 | 4.235041 | 9.186286 |
| C | 7.844787 | 2.697881 | 10.510328 |
| Sn | 6.752163 | 4.192360 | 6.400364 |
| Fe | 9.469900 | 6.277790 | 14.521616 |
| O | 7.251413 | 4.900220 | 8.477164 |
| O | 7.147906 | 4.167746 | 4.310986 |
| N | 7.754346 | 6.110576 | 10.873505 |
| N | 7.836411 | 6.749975 | 9.683431 |
| H | 8.238994 | 7.676143 | 9.628630 |

| | | | |
|---|---|---|---|
| N | 8.176811 | 6.751222 | 7.453173 |
| N | 7.976224 | 6.072786 | 6.286680 |
| C | 11.000594 | 7.262485 | 13.591635 |
| H | 10.989201 | 7.578390 | 12.559016 |
| C | 10.530399 | 8.016339 | 14.701815 |
| H | 10.101097 | 9.006195 | 14.660615 |
| C | 10.684325 | 7.219628 | 15.869037 |
| H | 10.390856 | 7.497602 | 16.870283 |
| C | 11.247339 | 5.973761 | 15.479783 |
| H | 11.456829 | 5.140242 | 16.133343 |
| C | 11.444367 | 6.001193 | 14.072000 |
| H | 11.829816 | 5.192695 | 13.468982 |
| C | 7.898392 | 6.177926 | 13.221605 |
| C | 7.491726 | 6.743678 | 14.471723 |
| H | 7.078538 | 7.729820 | 14.618923 |
| C | 7.736085 | 5.786680 | 15.488825 |
| H | 7.555322 | 5.927201 | 16.543951 |
| C | 8.306166 | 4.634463 | 14.883218 |
| H | 8.638522 | 3.745872 | 15.398508 |
| C | 8.406803 | 4.873586 | 13.491691 |
| H | 8.830223 | 4.206117 | 12.759897 |
| C | 7.864185 | 6.845567 | 11.924759 |
| C | 7.983908 | 8.334919 | 11.868366 |
| H | 7.952308 | 8.771228 | 12.863094 |
| H | 8.936558 | 8.629919 | 11.413813 |
| H | 7.181577 | 8.766228 | 11.262402 |
| C | 7.748977 | 6.074954 | 8.499047 |
| C | 8.430304 | 6.649374 | 5.223522 |
| H | 8.939754 | 7.600209 | 5.380833 |
| C | 8.340685 | 6.196168 | 3.867528 |
| C | 7.709914 | 4.985906 | 3.472745 |
| C | 7.713914 | 4.666491 | 2.100059 |
| H | 7.230418 | 3.743827 | 1.800424 |
| C | 8.296112 | 5.497324 | 1.166547 |
| H | 8.273296 | 5.217025 | 0.118415 |
| C | 8.910268 | 6.691273 | 1.553961 |
| H | 9.366419 | 7.343215 | 0.819201 |
| C | 8.925726 | 7.020978 | 2.890896 |
| H | 9.400471 | 7.940961 | 3.218795 |
| C | 8.067925 | 2.536870 | 6.597459 |
| H | 7.926322 | 1.951253 | 5.688105 |
| H | 7.731130 | 1.939076 | 7.442827 |
| C | 9.509519 | 2.987619 | 6.759389 |
| H | 10.179141 | 2.126523 | 6.847067 |
| H | 9.845361 | 3.579559 | 5.904004 |
| H | 9.639312 | 3.597931 | 7.656443 |
| C | 4.838017 | 5.114538 | 6.308320 |
| H | 4.658830 | 5.492380 | 7.315448 |
| H | 4.130578 | 4.305136 | 6.132958 |
| C | 4.735592 | 6.212793 | 5.267480 |
| H | 3.726879 | 6.636996 | 5.254988 |
| H | 5.431340 | 7.029970 | 5.471330 |

| | | | |
|---|---|---|---|
| H | 4.949873 | 5.840940 | 4.263409 |
| H | 8.032898 | 2.352071 | 9.493771 |
| H | 8.557630 | 3.494013 | 10.721023 |
| C | 7.924112 | 1.565168 | 11.515754 |
| H | 8.928545 | 1.130854 | 11.526803 |
| H | 7.223496 | 0.761762 | 11.276574 |
| H | 7.700054 | 1.907296 | 12.528297 |

15. Cation of dimer $(\mathbf{3a})_2^+$ in $CH_2Cl_2$
E = –5555.42475344 Eh

| | | | |
|---|---|---|---|
| Sn | 5.901754 | 3.621381 | 10.425891 |
| Fe | 3.247627 | 1.476238 | 2.384146 |
| O | 5.440552 | 2.920891 | 8.361216 |
| O | 5.603430 | 3.623114 | 12.534823 |
| N | 5.033320 | 1.678930 | 5.973337 |
| N | 5.000271 | 1.029593 | 7.161904 |
| H | 4.641154 | 0.085410 | 7.214770 |
| N | 4.598925 | 1.029715 | 9.384608 |
| N | 4.734004 | 1.735209 | 10.543564 |
| C | 1.821208 | 0.353686 | 3.324522 |
| H | 1.914951 | -0.051742 | 4.320888 |
| C | 2.235322 | -0.280316 | 2.121332 |
| H | 2.696181 | -1.253608 | 2.042771 |
| C | 1.969815 | 0.608721 | 1.044416 |
| H | 2.196616 | 0.430671 | 0.003862 |
| C | 1.394380 | 1.791623 | 1.582541 |
| H | 1.108427 | 2.669250 | 1.022309 |
| C | 1.302496 | 1.633904 | 2.992385 |
| H | 0.933438 | 2.369714 | 3.691111 |
| C | 4.861400 | 1.614920 | 3.628871 |
| C | 5.240859 | 1.067561 | 2.361960 |
| H | 5.681324 | 0.096803 | 2.192969 |
| C | 4.933307 | 2.022180 | 1.360294 |
| H | 5.084814 | 1.893855 | 0.299001 |
| C | 4.351719 | 3.154319 | 1.992183 |
| H | 3.978244 | 4.036412 | 1.494204 |
| C | 4.304510 | 2.904460 | 3.384393 |
| H | 3.886649 | 3.554389 | 4.134652 |
| C | 4.954850 | 0.943564 | 4.919722 |
| C | 4.924596 | -0.550355 | 4.970810 |
| H | 4.943520 | -0.979611 | 3.972875 |
| H | 4.010237 | -0.905213 | 5.459483 |
| H | 5.774253 | -0.935460 | 5.542592 |
| C | 5.014412 | 1.716182 | 8.341502 |
| C | 4.225440 | 1.192273 | 11.599168 |
| H | 3.721158 | 0.238734 | 11.444893 |
| C | 4.229534 | 1.700758 | 12.938469 |
| C | 4.892001 | 2.891200 | 13.341704 |
| C | 4.768435 | 3.279952 | 14.689912 |
| H | 5.256830 | 4.198280 | 14.993888 |
| C | 4.053732 | 2.527286 | 15.597443 |

| | | | |
|---|---|---|---|
| H | 3.984761 | 2.861050 | 16.627569 |
| C | 3.420402 | 1.345956 | 15.205641 |
| H | 2.862059 | 0.753668 | 15.919859 |
| C | 3.515023 | 0.952546 | 13.889888 |
| H | 3.023755 | 0.042820 | 13.558367 |
| C | 4.562023 | 5.261469 | 10.266512 |
| H | 4.735891 | 5.864899 | 11.158638 |
| H | 4.853956 | 5.847093 | 9.396160 |
| C | 3.120261 | 4.789617 | 10.179372 |
| H | 2.436956 | 5.641630 | 10.114252 |
| H | 2.832607 | 4.205506 | 11.057409 |
| H | 2.953312 | 4.166287 | 9.297443 |
| C | 7.859966 | 2.788086 | 10.506781 |
| Sn | 6.730848 | 4.219444 | 6.398830 |
| Fe | 9.456182 | 6.205117 | 14.485380 |
| O | 7.214358 | 4.963974 | 8.496149 |
| O | 7.080051 | 4.207100 | 4.309540 |
| N | 7.685145 | 6.273514 | 10.853550 |
| N | 7.795290 | 6.851444 | 9.663262 |
| H | 8.120666 | 7.805664 | 9.570553 |
| N | 8.105839 | 6.812558 | 7.437952 |
| N | 7.928843 | 6.110677 | 6.279793 |
| C | 11.179159 | 7.054340 | 13.580904 |
| H | 11.182823 | 7.467038 | 12.582367 |
| C | 10.828314 | 7.748884 | 14.764483 |
| H | 10.545362 | 8.789011 | 14.827472 |
| C | 10.869287 | 6.824051 | 15.844805 |
| H | 10.640106 | 7.040859 | 16.877115 |
| C | 11.240967 | 5.555974 | 15.315590 |
| H | 11.332628 | 4.635386 | 15.872130 |
| C | 11.430106 | 5.705319 | 13.917312 |
| H | 11.666604 | 4.913818 | 13.221519 |
| C | 7.760267 | 6.366391 | 13.184496 |
| C | 7.523099 | 6.979283 | 14.449020 |
| H | 7.286928 | 8.018884 | 14.617528 |
| C | 7.668206 | 5.994548 | 15.460823 |
| H | 7.549875 | 6.157220 | 16.521369 |
| C | 8.022907 | 4.770681 | 14.828447 |
| H | 8.232553 | 3.833607 | 15.321364 |
| C | 8.090160 | 5.006642 | 13.435623 |
| H | 8.396626 | 4.295776 | 12.687690 |
| C | 7.798323 | 7.033257 | 11.890951 |
| C | 7.990454 | 8.511763 | 11.811002 |
| H | 8.008176 | 8.972636 | 12.795054 |
| H | 8.940522 | 8.752243 | 11.320443 |
| H | 7.189833 | 8.975260 | 11.226299 |
| C | 7.693024 | 6.141394 | 8.485243 |
| C | 8.405095 | 6.670763 | 5.217037 |
| H | 8.913020 | 7.622716 | 5.370628 |
| C | 8.345589 | 6.193489 | 3.870754 |
| C | 7.695046 | 4.992376 | 3.478594 |
| C | 7.729833 | 4.648793 | 2.112044 |

| | | | |
|---|---|---|---|
| H | 7.230906 | 3.733989 | 1.813956 |
| C | 8.362278 | 5.447234 | 1.184657 |
| H | 8.364605 | 5.149098 | 0.141330 |
| C | 8.996558 | 6.632477 | 1.569154 |
| H | 9.490962 | 7.258132 | 0.836505 |
| C | 8.979688 | 6.987266 | 2.897722 |
| H | 9.466292 | 7.901697 | 3.223273 |
| C | 8.106703 | 2.614973 | 6.605251 |
| H | 7.975960 | 2.018667 | 5.701107 |
| H | 7.794514 | 2.012515 | 7.456787 |
| C | 9.534470 | 3.112467 | 6.748565 |
| H | 10.230674 | 2.272067 | 6.828190 |
| H | 9.841535 | 3.711468 | 5.887436 |
| H | 9.658955 | 3.728581 | 7.642514 |
| C | 4.802200 | 5.113385 | 6.327450 |
| H | 4.636594 | 5.515200 | 7.327413 |
| H | 4.100630 | 4.291993 | 6.186145 |
| C | 4.670639 | 6.185419 | 5.262365 |
| H | 3.660329 | 6.605698 | 5.264724 |
| H | 5.367777 | 7.009748 | 5.429624 |
| H | 4.863256 | 5.789787 | 4.263332 |
| H | 8.055436 | 2.435459 | 9.494139 |
| H | 8.543240 | 3.618207 | 10.688140 |
| C | 8.005065 | 1.672248 | 11.524815 |
| H | 9.029278 | 1.287392 | 11.530559 |
| H | 7.341962 | 0.834049 | 11.298888 |
| H | 7.769852 | 2.007739 | 12.537211 |

16. Cation of dimer $(\mathbf{3a})_2^+$ in DMF
E = –5555.43368118 Eh

| | | | |
|---|---|---|---|
| Sn | 5.925509 | 3.633225 | 10.447002 |
| Fe | 3.160744 | 1.637282 | 2.309148 |
| O | 5.418138 | 2.915828 | 8.355680 |
| O | 5.531124 | 3.642364 | 12.533381 |
| N | 4.922794 | 1.675020 | 5.977708 |
| N | 4.836305 | 1.055748 | 7.154152 |
| H | 4.516448 | 0.097466 | 7.216904 |
| N | 4.550823 | 1.042546 | 9.388235 |
| N | 4.742701 | 1.725002 | 10.556277 |
| C | 1.501367 | 0.697987 | 3.197769 |
| H | 1.481982 | 0.390565 | 4.233254 |
| C | 2.009150 | -0.062409 | 2.111279 |
| H | 2.418304 | -1.059693 | 2.170718 |
| C | 1.916605 | 0.739645 | 0.937763 |
| H | 2.241056 | 0.458615 | -0.052749 |
| C | 1.353525 | 1.990150 | 1.309867 |
| H | 1.195324 | 2.835454 | 0.656788 |
| C | 1.099355 | 1.959541 | 2.702159 |
| H | 0.728656 | 2.782832 | 3.295057 |
| C | 4.828734 | 1.646100 | 3.645014 |
| C | 5.162934 | 1.101478 | 2.370856 |

| | | | |
|---|---|---|---|
| H | 5.521073 | 0.100887 | 2.181671 |
| C | 4.927662 | 2.095154 | 1.383797 |
| H | 5.083724 | 1.979751 | 0.321956 |
| C | 4.422478 | 3.250560 | 2.041865 |
| H | 4.109519 | 4.169222 | 1.569193 |
| C | 4.356076 | 2.967136 | 3.424963 |
| H | 3.947596 | 3.612757 | 4.184422 |
| C | 4.837308 | 0.940993 | 4.920780 |
| C | 4.715641 | -0.546126 | 4.958374 |
| H | 4.759911 | -0.981920 | 3.963621 |
| H | 3.759181 | -0.843108 | 5.403888 |
| H | 5.514195 | -0.982403 | 5.565863 |
| C | 4.944259 | 1.734707 | 8.346120 |
| C | 4.312934 | 1.128823 | 11.619097 |
| H | 3.828710 | 0.165412 | 11.459410 |
| C | 4.401403 | 1.576692 | 12.974854 |
| C | 4.999090 | 2.803763 | 13.370578 |
| C | 4.994919 | 3.116379 | 14.744792 |
| H | 5.452706 | 4.051443 | 15.045753 |
| C | 4.445072 | 2.263265 | 15.677060 |
| H | 4.467204 | 2.538667 | 16.726461 |
| C | 3.864021 | 1.052405 | 15.288660 |
| H | 3.433792 | 0.383893 | 16.024047 |
| C | 3.848195 | 0.728716 | 13.951297 |
| H | 3.398409 | -0.202878 | 13.621289 |
| C | 4.575983 | 5.259488 | 10.247376 |
| H | 4.693296 | 5.836423 | 11.165725 |
| H | 4.912904 | 5.875115 | 9.415065 |
| C | 3.146603 | 4.780695 | 10.060737 |
| H | 2.461144 | 5.629431 | 9.976163 |
| H | 2.812432 | 4.170646 | 10.903907 |
| H | 3.040950 | 4.180439 | 9.153942 |
| C | 7.852890 | 2.738090 | 10.522321 |
| Sn | 6.716072 | 4.201664 | 6.413445 |
| Fe | 9.389480 | 6.369117 | 14.496900 |
| O | 7.221753 | 4.914439 | 8.473484 |
| O | 6.981192 | 4.184806 | 4.299099 |
| N | 7.686758 | 6.163398 | 10.847352 |
| N | 7.764954 | 6.792894 | 9.650532 |
| H | 8.162806 | 7.720788 | 9.588133 |
| N | 8.141703 | 6.753205 | 7.422556 |
| N | 7.964600 | 6.043495 | 6.270610 |
| C | 10.910296 | 7.372938 | 13.571540 |
| H | 10.895489 | 7.693826 | 12.540521 |
| C | 10.432413 | 8.116796 | 14.685327 |
| H | 9.993637 | 9.102674 | 14.648694 |
| C | 10.594940 | 7.316558 | 15.848775 |
| H | 10.298411 | 7.586647 | 16.851272 |
| C | 11.170541 | 6.078415 | 15.453792 |
| H | 11.388283 | 5.244006 | 16.103500 |
| C | 11.367170 | 6.114161 | 14.046155 |
| H | 11.761019 | 5.312311 | 13.439696 |

| | | | |
|---|---|---|---|
| C | 7.821999 | 6.249750 | 13.193416 |
| C | 7.407007 | 6.819359 | 14.439056 |
| H | 6.985956 | 7.803138 | 14.579493 |
| C | 7.656721 | 5.870288 | 15.462236 |
| H | 7.472259 | 6.015779 | 16.516040 |
| C | 8.238240 | 4.719351 | 14.865186 |
| H | 8.576438 | 3.836564 | 15.386519 |
| C | 8.340982 | 4.951362 | 13.472386 |
| H | 8.773111 | 4.284358 | 12.745304 |
| C | 7.784806 | 6.908672 | 11.892184 |
| C | 7.889241 | 8.398463 | 11.824973 |
| H | 7.853508 | 8.841529 | 12.816585 |
| H | 8.838993 | 8.699341 | 11.368291 |
| H | 7.082649 | 8.817090 | 11.215849 |
| C | 7.704678 | 6.096414 | 8.477772 |
| C | 8.488130 | 6.553540 | 5.206223 |
| H | 9.037050 | 7.484770 | 5.345743 |
| C | 8.449564 | 6.032670 | 3.871421 |
| C | 7.724440 | 4.873123 | 3.483366 |
| C | 7.818969 | 4.468357 | 2.136952 |
| H | 7.281366 | 3.574793 | 1.843156 |
| C | 8.563105 | 5.176473 | 1.217462 |
| H | 8.604978 | 4.831329 | 0.189551 |
| C | 9.258694 | 6.327708 | 1.594373 |
| H | 9.840459 | 6.885507 | 0.871032 |
| C | 9.193509 | 6.736075 | 2.907782 |
| H | 9.731710 | 7.622980 | 3.228357 |
| C | 8.036735 | 2.545084 | 6.579538 |
| H | 7.880185 | 1.957660 | 5.673631 |
| H | 7.717636 | 1.947126 | 7.431932 |
| C | 9.481151 | 2.996345 | 6.716378 |
| H | 10.149718 | 2.134412 | 6.802250 |
| H | 9.806326 | 3.579396 | 5.850927 |
| H | 9.625465 | 3.614454 | 7.605772 |
| C | 4.800280 | 5.125586 | 6.357694 |
| H | 4.626820 | 5.473498 | 7.375838 |
| H | 4.080516 | 4.329986 | 6.167111 |
| C | 4.700536 | 6.258091 | 5.353330 |
| H | 3.693111 | 6.685096 | 5.354394 |
| H | 5.398444 | 7.065475 | 5.586852 |
| H | 4.918441 | 5.921797 | 4.337440 |
| H | 8.025354 | 2.353910 | 9.516275 |
| H | 8.551314 | 3.558650 | 10.680967 |
| C | 7.981245 | 1.649873 | 11.570714 |
| H | 8.995913 | 1.240293 | 11.575149 |
| H | 7.295267 | 0.821460 | 11.379953 |
| H | 7.771756 | 2.025983 | 12.574104 |

17. Dication of dimer (**3a**)$_2^{2+}$ in $CH_2Cl_2$
E = –5555.24839602 Eh

| | | | |
|---|---|---|---|
| Sn | 5.921522 | 3.592584 | 10.430693 |
| Fe | 3.231754 | 1.558478 | 2.350604 |
| O | 5.454060 | 2.865212 | 8.350890 |
| O | 5.636848 | 3.599241 | 12.535364 |
| N | 5.018258 | 1.558574 | 5.989096 |
| N | 4.935440 | 0.965429 | 7.176974 |
| H | 4.632205 | 0.003254 | 7.262226 |
| N | 4.619030 | 0.987447 | 9.403853 |
| N | 4.772687 | 1.696197 | 10.560636 |
| C | 1.552828 | 0.612829 | 3.238351 |
| H | 1.563240 | 0.196982 | 4.235484 |
| C | 1.953089 | -0.056438 | 2.055432 |
| H | 2.295125 | -1.078563 | 1.991366 |
| C | 1.867078 | 0.868560 | 0.977608 |
| H | 2.116841 | 0.669531 | -0.053511 |
| C | 1.417787 | 2.110695 | 1.507690 |
| H | 1.278563 | 3.026675 | 0.953357 |
| C | 1.226040 | 1.945828 | 2.903339 |
| H | 0.938721 | 2.720288 | 3.599211 |
| C | 4.927192 | 1.481316 | 3.657897 |
| C | 5.202612 | 0.891573 | 2.390186 |
| H | 5.495510 | -0.132475 | 2.215325 |
| C | 5.009389 | 1.875627 | 1.385621 |
| H | 5.140796 | 1.728692 | 0.324325 |
| C | 4.587679 | 3.073839 | 2.026265 |
| H | 4.329270 | 4.001884 | 1.539341 |
| C | 4.528521 | 2.823688 | 3.416738 |
| H | 4.179510 | 3.510081 | 4.169394 |
| C | 4.921626 | 0.803477 | 4.947542 |
| C | 4.778466 | -0.681078 | 5.015983 |
| H | 4.770290 | -1.133495 | 4.027885 |
| H | 3.838992 | -0.955952 | 5.508907 |
| H | 5.596662 | -1.122954 | 5.592901 |
| C | 5.012070 | 1.670818 | 8.356542 |
| C | 4.289366 | 1.143389 | 11.623887 |
| H | 3.793704 | 0.184642 | 11.474912 |
| C | 4.312227 | 1.646888 | 12.962145 |
| C | 4.957634 | 2.850697 | 13.354061 |
| C | 4.851342 | 3.235424 | 14.704765 |
| H | 5.324775 | 4.163711 | 15.001209 |
| C | 4.171106 | 2.465628 | 15.623396 |
| H | 4.114656 | 2.796291 | 16.655223 |
| C | 3.555460 | 1.270487 | 15.242687 |
| H | 3.024544 | 0.666190 | 15.967518 |
| C | 3.631726 | 0.880910 | 13.925859 |
| H | 3.153394 | -0.038287 | 13.601946 |
| C | 4.553552 | 5.207539 | 10.259094 |
| H | 4.704309 | 5.803754 | 11.160264 |
| H | 4.848642 | 5.808538 | 9.400430 |

| | | | |
|---|---|---|---|
| C | 3.121630 | 4.712280 | 10.146302 |
| H | 2.425929 | 5.554076 | 10.081336 |
| H | 2.831533 | 4.113912 | 11.013756 |
| H | 2.977126 | 4.096612 | 9.255096 |
| C | 7.888338 | 2.780707 | 10.488394 |
| Sn | 6.750145 | 4.233059 | 6.402388 |
| Fe | 9.433035 | 6.277543 | 14.484248 |
| O | 7.218164 | 4.960779 | 8.481924 |
| O | 7.033557 | 4.226622 | 4.297471 |
| N | 7.651294 | 6.268870 | 10.843009 |
| N | 7.733687 | 6.861759 | 9.654993 |
| H | 8.034541 | 7.824659 | 9.569453 |
| N | 8.052243 | 6.838626 | 7.428293 |
| N | 7.899920 | 6.128880 | 6.271957 |
| C | 11.109023 | 7.232420 | 13.600126 |
| H | 11.098085 | 7.649946 | 12.603681 |
| C | 10.704565 | 7.898014 | 14.783613 |
| H | 10.358048 | 8.918580 | 14.848903 |
| C | 10.792897 | 6.971626 | 15.860003 |
| H | 10.540954 | 7.167996 | 16.891116 |
| C | 11.247853 | 5.732137 | 15.328456 |
| H | 11.390304 | 4.815890 | 15.881505 |
| C | 11.440692 | 5.900139 | 13.933248 |
| H | 11.732147 | 5.128109 | 13.236423 |
| C | 7.739328 | 6.346981 | 13.174159 |
| C | 7.458911 | 6.935575 | 14.441254 |
| H | 7.160988 | 7.958317 | 14.615444 |
| C | 7.655110 | 5.952666 | 15.446334 |
| H | 7.521260 | 6.099231 | 16.507394 |
| C | 8.083599 | 4.756327 | 14.806654 |
| H | 8.345412 | 3.829590 | 15.294201 |
| C | 8.144063 | 5.006569 | 13.416217 |
| H | 8.497565 | 4.321731 | 12.664252 |
| C | 7.743996 | 7.024578 | 11.884385 |
| C | 7.882220 | 8.509594 | 11.815890 |
| H | 7.887464 | 8.962178 | 12.803943 |
| H | 8.821468 | 8.787622 | 11.324297 |
| H | 7.063380 | 8.948616 | 11.237711 |
| C | 7.659000 | 6.155589 | 8.475756 |
| C | 8.385214 | 6.680244 | 5.208891 |
| H | 8.881601 | 7.638670 | 5.357598 |
| C | 8.363884 | 6.175256 | 3.871142 |
| C | 7.716477 | 4.972490 | 3.479312 |
| C | 7.824434 | 4.586071 | 2.129233 |
| H | 7.349350 | 3.658593 | 1.832876 |
| C | 8.508270 | 5.353240 | 1.211083 |
| H | 8.565923 | 5.021313 | 0.179736 |
| C | 9.125899 | 6.547388 | 1.591645 |
| H | 9.659567 | 7.149685 | 0.867180 |
| C | 9.047930 | 6.938621 | 2.907881 |
| H | 9.527667 | 7.857120 | 3.231708 |
| C | 8.118127 | 2.618074 | 6.573705 |

| | | | |
|---|---|---|---|
| H | 7.966575 | 2.021311 | 5.673021 |
| H | 7.823681 | 2.017655 | 7.432992 |
| C | 9.550174 | 3.113244 | 6.685028 |
| H | 10.245800 | 2.271402 | 6.750146 |
| H | 9.839720 | 3.710866 | 5.816875 |
| H | 9.695434 | 3.729618 | 7.575625 |
| C | 4.783734 | 5.046126 | 6.345533 |
| H | 4.597473 | 5.405442 | 7.357526 |
| H | 4.107891 | 4.207057 | 6.179036 |
| C | 4.615273 | 6.151677 | 5.319922 |
| H | 3.587234 | 6.525832 | 5.324787 |
| H | 5.272470 | 6.998590 | 5.529956 |
| H | 4.839974 | 5.809432 | 4.307535 |
| H | 8.074831 | 2.420604 | 9.476710 |
| H | 8.563700 | 3.620247 | 10.654316 |
| C | 8.057180 | 1.676126 | 11.514975 |
| H | 9.085221 | 1.301978 | 11.510075 |
| H | 7.399925 | 0.828988 | 11.305997 |
| H | 7.832895 | 2.019349 | 12.527105 |

18. Dication of dimer $(\mathbf{3a})_2^{2+}$ in DMF
E = –5555.26666460 Eh

| | | | |
|---|---|---|---|
| Sn | 5.939597 | 3.630471 | 10.436764 |
| Fe | 3.226272 | 1.545820 | 2.319919 |
| O | 5.427132 | 2.907641 | 8.364471 |
| O | 5.649081 | 3.651692 | 12.544545 |
| N | 4.961225 | 1.632674 | 6.006849 |
| N | 4.877417 | 1.023235 | 7.189569 |
| H | 4.564404 | 0.063245 | 7.261290 |
| N | 4.565243 | 1.045876 | 9.423059 |
| N | 4.740510 | 1.754089 | 10.578526 |
| C | 1.570401 | 0.572642 | 3.183142 |
| H | 1.542526 | 0.258796 | 4.216509 |
| C | 2.105026 | -0.172746 | 2.099486 |
| H | 2.530008 | -1.163385 | 2.159121 |
| C | 2.015823 | 0.634404 | 0.929398 |
| H | 2.357698 | 0.364142 | -0.058235 |
| C | 1.428001 | 1.873899 | 1.301151 |
| H | 1.264238 | 2.720160 | 0.650706 |
| C | 1.154969 | 1.830560 | 2.689710 |
| H | 0.762678 | 2.644027 | 3.282291 |
| C | 4.878849 | 1.586839 | 3.676141 |
| C | 5.237803 | 1.044409 | 2.408195 |
| H | 5.614994 | 0.049393 | 2.226760 |
| C | 4.996699 | 2.030833 | 1.415371 |
| H | 5.166879 | 1.915006 | 0.355746 |
| C | 4.462765 | 3.179076 | 2.063429 |
| H | 4.139397 | 4.090596 | 1.584001 |
| C | 4.384143 | 2.898119 | 3.446550 |
| H | 3.953305 | 3.536976 | 4.199536 |
| C | 4.888331 | 0.889062 | 4.956248 |

| | | | |
|---|---|---|---|
| C | 4.783050 | -0.598832 | 5.002879 |
| H | 4.836806 | -1.039765 | 4.010768 |
| H | 3.827688 | -0.902762 | 5.446010 |
| H | 5.583476 | -1.022757 | 5.616549 |
| C | 4.964570 | 1.721006 | 8.371171 |
| C | 4.261407 | 1.208314 | 11.646645 |
| H | 3.749393 | 0.256737 | 11.505068 |
| C | 4.310347 | 1.710288 | 12.986053 |
| C | 4.975081 | 2.906831 | 13.370187 |
| C | 4.892453 | 3.289420 | 14.723841 |
| H | 5.380903 | 4.211493 | 15.014955 |
| C | 4.218962 | 2.525196 | 15.652035 |
| H | 4.183893 | 2.854310 | 16.685393 |
| C | 3.584920 | 1.337109 | 15.278683 |
| H | 3.059403 | 0.736231 | 16.010390 |
| C | 3.636371 | 0.950281 | 13.959200 |
| H | 3.143167 | 0.037140 | 13.640138 |
| C | 4.598402 | 5.267800 | 10.259454 |
| H | 4.733255 | 5.847930 | 11.173477 |
| H | 4.922963 | 5.878501 | 9.418435 |
| C | 3.163336 | 4.796151 | 10.096777 |
| H | 2.483418 | 5.649282 | 10.013370 |
| H | 2.835536 | 4.196726 | 10.949928 |
| H | 3.041082 | 4.188493 | 9.197061 |
| C | 7.866736 | 2.730085 | 10.482354 |
| Sn | 6.724638 | 4.210709 | 6.396445 |
| Fe | 9.473026 | 6.244091 | 14.509995 |
| O | 7.233161 | 4.929687 | 8.471213 |
| O | 7.025585 | 4.192941 | 4.290325 |
| N | 7.711054 | 6.191858 | 10.834655 |
| N | 7.791834 | 6.806596 | 9.654631 |
| H | 8.107734 | 7.765881 | 9.586001 |
| N | 8.091427 | 6.796843 | 7.419727 |
| N | 7.912321 | 6.095183 | 6.260957 |
| C | 11.122635 | 7.242392 | 13.650908 |
| H | 11.135356 | 7.593969 | 12.629403 |
| C | 10.611192 | 7.950625 | 14.769041 |
| H | 10.191332 | 8.945145 | 14.751715 |
| C | 10.710990 | 7.100393 | 15.907057 |
| H | 10.388321 | 7.337839 | 16.909453 |
| C | 11.282155 | 5.869829 | 15.480331 |
| H | 11.452480 | 5.000081 | 16.097112 |
| C | 11.534425 | 5.963592 | 14.089635 |
| H | 11.911204 | 5.170656 | 13.460359 |
| C | 7.807773 | 6.227622 | 13.165782 |
| C | 7.464561 | 6.769680 | 14.437992 |
| H | 7.098951 | 7.767842 | 14.625848 |
| C | 7.703913 | 5.778421 | 15.426216 |
| H | 7.542964 | 5.893365 | 16.487379 |
| C | 8.221129 | 4.626420 | 14.771057 |
| H | 8.537664 | 3.709787 | 15.245206 |
| C | 8.291882 | 4.910879 | 13.387928 |

| | | | |
|---|---|---|---|
| H | 8.708835 | 4.269297 | 12.629639 |
| C | 7.794803 | 6.930136 | 11.888344 |
| C | 7.909659 | 8.417593 | 11.846827 |
| H | 7.866857 | 8.855303 | 12.840878 |
| H | 8.863196 | 8.717141 | 11.396940 |
| H | 7.106946 | 8.849345 | 11.241621 |
| C | 7.697048 | 6.115905 | 8.469560 |
| C | 8.377316 | 6.653846 | 5.193077 |
| H | 8.879775 | 7.610006 | 5.337766 |
| C | 8.323724 | 6.161667 | 3.850270 |
| C | 7.677431 | 4.956078 | 3.463564 |
| C | 7.755290 | 4.583998 | 2.106847 |
| H | 7.281563 | 3.654916 | 1.813810 |
| C | 8.405735 | 5.367120 | 1.177918 |
| H | 8.437415 | 5.045738 | 0.142024 |
| C | 9.020693 | 6.564413 | 1.553851 |
| H | 9.527926 | 7.180265 | 0.821700 |
| C | 8.974754 | 6.940745 | 2.876598 |
| H | 9.454180 | 7.860491 | 3.197680 |
| C | 8.067913 | 2.575691 | 6.574333 |
| H | 7.937765 | 1.998758 | 5.657606 |
| H | 7.740848 | 1.961168 | 7.411549 |
| C | 9.501340 | 3.049669 | 6.744234 |
| H | 10.182856 | 2.197647 | 6.825800 |
| H | 9.830610 | 3.653979 | 5.895086 |
| H | 9.619181 | 3.653228 | 7.647276 |
| C | 4.792010 | 5.098843 | 6.345579 |
| H | 4.631731 | 5.478936 | 7.354713 |
| H | 4.083528 | 4.284567 | 6.196665 |
| C | 4.655420 | 6.194759 | 5.305645 |
| H | 3.639302 | 6.600329 | 5.307896 |
| H | 5.338995 | 7.023787 | 5.502112 |
| H | 4.865531 | 5.830133 | 4.298021 |
| H | 8.024807 | 2.355070 | 9.471079 |
| H | 8.580476 | 3.538878 | 10.636088 |
| C | 7.996362 | 1.626517 | 11.515093 |
| H | 9.010227 | 1.215378 | 11.511495 |
| H | 7.308399 | 0.802740 | 11.311982 |
| H | 7.786960 | 1.985196 | 12.525045 |

# Electronic absorption spectroscopy of compounds 2a, 3a and $(3a)_2$

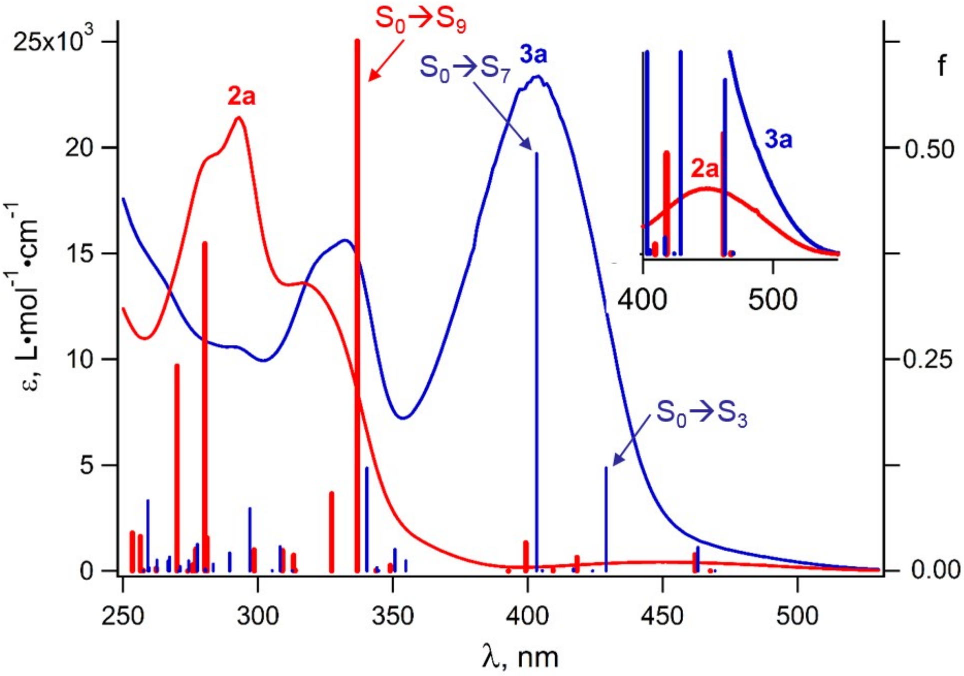



**Figure S40.** Experimental UV-Vis spectra of ligand **2a** (red curve) and complex **3a** (blue curve) in DCM. Positions and oscillator strengths (f) of the electronic transitions calculated at the TD-TPSSh/def2-TZVP level are depicted as red bars for **2a** and as blue bars for **3a**.

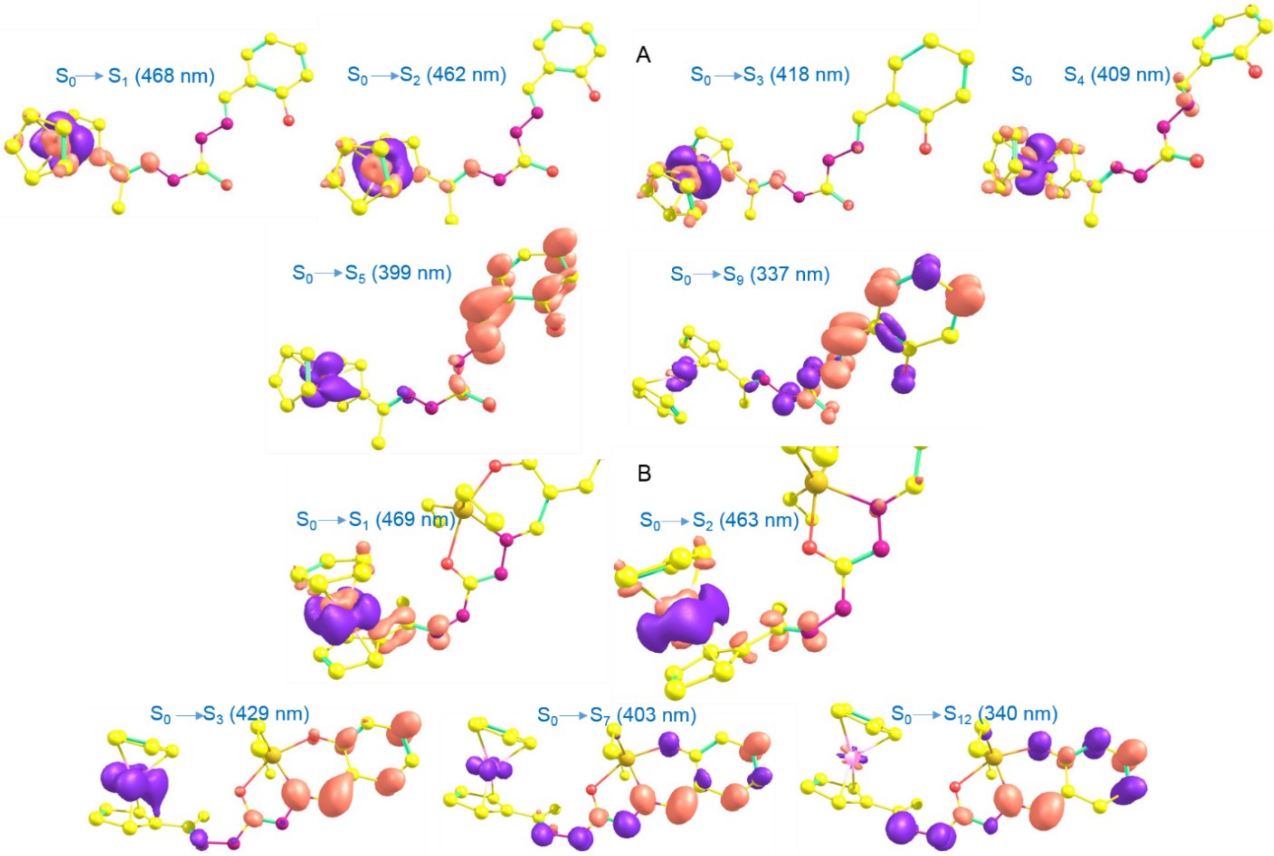



**Figure S41a.** Difference electron density maps (isosurfaces at 0.003 a.u., negative difference in purple, positive difference in orange) visualizing changes in the electron distribution between the excited and ground states of ligand **2a** (A) and complex **3a** (B).

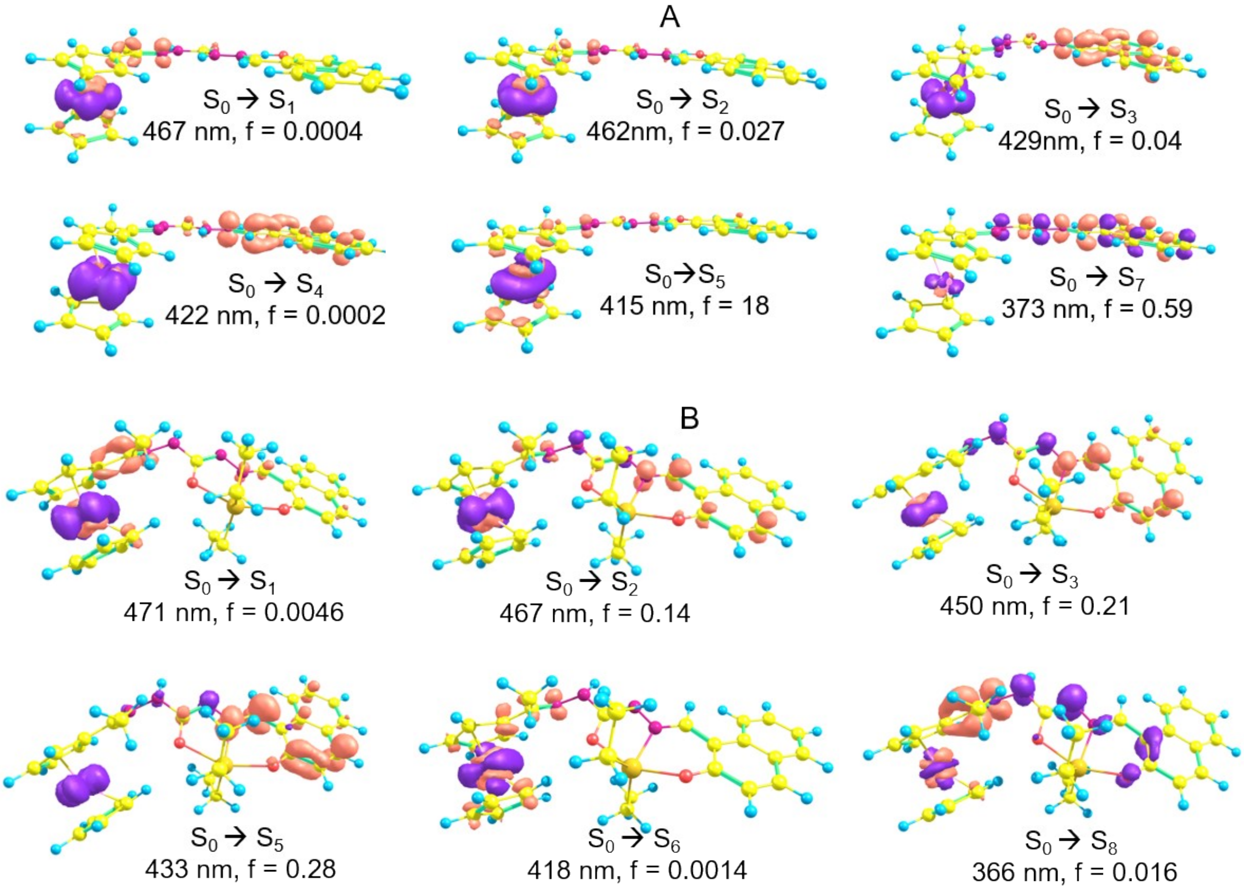



**Figure S41b.** Difference electron density maps (isosurfaces at 0.003 a.u., negative difference in purple, positive difference in orange) visualizing changes in the electron distribution between the excited and ground states of ligand **2b** (A) and complex **3b** (B).

Figure 41b shows that for the Schiff base with ferrocene group **2b** (A), the lowest-energy transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ are localized primarily on ferrocene and are d-d type transitions. The subsequent $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions are of metal-to-ligand charge transfer (MLCT) in nature, while the $S_0 \rightarrow S_5$ transition is primarily a $\pi$–$\pi$* transition of the Schiff base.

For tin complex **3b**, the lowest-energy transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ have a significant contribution of the d-d promotion, as well as the MLCT transitions for the first two and $\pi$–$\pi$* transition for the latter. The $S_0 \rightarrow S_5$ transition is predominately MLCT in character, while $S_0 \rightarrow S_6$ is predominately a d-d type transitions, and $S_0 \rightarrow S_8$ is a mixture of d-d transition and CT transition in the Schiff base ligand.

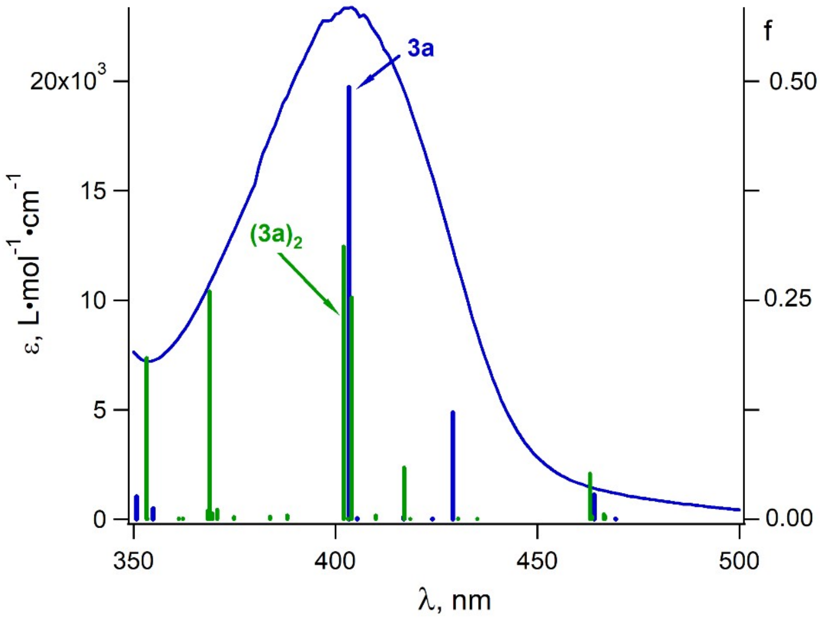



**Figure S42.** Experimental UV-Vis spectra of **3a** (blue curve) in DCM. Positions and oscillator strengths (f) of the electronic transitions calculated at the TD-TPSSh/def2-TZVP level are depicted as blue bars for **3a** and as green bars for its dimer (**3a**)$_2$.

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