General Procedures, Materials and Instrumentation

((Trimethylsilyl)ethynyl)ferrocene[1], $AuCl(SMe_2)$[2], TBTA[3], N-(2-Propyn-1-yl)benzamide[4], acetylferrocenium tetrafluoroborate[5], 2-azido-1,3,5-trimethylbenzene and 2-azido-1,3-diisopropylbenzene[6] were prepared as described previously in the literature. Commercially available chemicals were used as purchased, unless otherwise noted. The solvents used for metal complex synthesis, catalysis, cyclic voltammetry and UV/Vis spectroelectrochemistry measurements were dried and distilled under nitrogen and degassed by common techniques prior to use. Column chromatography was performed over Silica 60 M (0.04 – 0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded on a Jeol ECS 400 or Jeol ECX 400 spectrometer by using the chemical shift of the solvent as an internal standard. Mass spectrometry was performed on an Agilent 6210 ESI-TOF.

X-Ray data were collected on a Bruker Smart AXS, Bruker Kappa APEX II duo or Bruker D8 Venture system. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard 'ψ–ω scan techniques' and were scaled and reduced using Saint+software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2. If it is noted, bond length and angles were measured with Diamond Crystal and Molecular Structure Visualization Version 3.1.

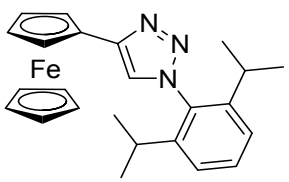
Cyclic voltammograms were recorded with a PAR VersaStat 4 potentiostat (Ametek) with a conventional three-electrode configuration consisting of a carbon working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode. The scan rate for each measurement is 100mV/s and at room temperature, unless otherwise noted. The experiments were carried out in absolute THF containing 0.1 M Bu_4NPF_6 (Fluka, ≥99.0 %, electrochemical grade) as the supporting electrolyte. UV/Vis spectra were recorded with an Avantes spectrometer consisting of a light source (AvaLight-DH-S-Bal), an UV/Vis detector (AvaSpec-ULS2048), and a NIR detector (AvaSpec-NIR256-TEC). UV/Vis spectroelectrochemistry measurements were carried out in an optically transparent thin-layer electrochemical (OTTLE) cell with a platinum-mesh working electrode, a platinum-mesh counter electrode, and a silver-foil pseudo reference. The experiments were carried out in absolute THF containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. Solvents used are equal for each compound which are used for the CV measurements.

The program package ORCA 3.0.0 was used for all DFT calculations.[7] The geometry optimization and single-point calculations were performed by the DFT method with BP86 and B3LYP functionals, respectively,[8] including relativistic effects in zero-order regular approximation (ZORA).[9] Convergence criteria for the geometry optimization were set to default values (OPT), and "tight" convergence criteria were used for SCF calculations (TIGHTSCF). Triple- ζ valence quality basis sets (def2-TZVP) were used for all atoms.[10] The resolution of the identity approximation (RIJCOSX) was employed[11,12] with matching auxiliary basis sets.[13] All spin densities were calculated according to Löwdin population analysis.[13] Spin densities were visualized via the program Molekel.[14]

General Procedure for the Preparation of 1-Substituted 4-Ferrocenyl 1*H*-1,2,3-Triazoles

To a solution of ((trimethylsilyl)ethynyl)ferrocene (1 equiv., 226 mg, 0.8 mmol) in methanol (2 mL) was added potassium fluoride (3 equiv., 134 mg, 2.4 mmol) and the reaction mixture was stirred for one hour at room temperature. Then the corresponding azide (2-azido-1,3,5-trimethylbenzene or 2-azido-1,3-diisopropylbenzene) (1 equiv., 0.8 mmol), copper(II) sulfate pentahydrate (0.05 equiv., 9 mg, 0.036 mmol), sodium ascorbate (0.01 equiv., 1.5 mg, 0.0075 mmol), TBTA (0.01 equiv., 4 mg, 0.0075 mmol) and a mixture of water/*tert*-butyl alcohol (6 mL: 6 mL) were added. The reaction mixture was heated overnight at 55 °C. After heating, a solution of EDTA sodium salt in water/ammonia (5 mL: 5mL) was added, and the product was extracted with dichloromethane (4 x 15 mL). The combined organic phases were dried with sodium sulfate, filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography over silica gel by using a gradient from 0 to 10% acetone in dichloromethane. Single crystals suitable for X-ray diffraction analysis were obtained by slow vaporizing from a concentrated solution of the triazole in diethyl ether at 8°C.

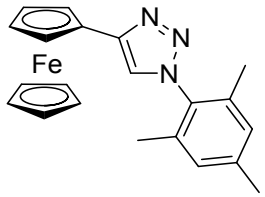
1-[1,3-diisopropylphenyl]-4-Ferrocenyl-1*H*-1,2,3-triazole 1a



The product was obtained as an orange solid in a yield of 37% (122.3 mg, 0.3 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.59 (s, 1H, Triazol-*5H*), 7.49 (t, *J* = 7.8 Hz, 1H, Aryl-*H*), 7.30 (d, *J* = 7.8 Hz, 2H, Aryl-*H*), 4.84 (t, *J* = 1.8 Hz, 2H, Fc-H_α), 4.34 (t, *J* = 1.8 Hz, 2H, Fc-H_β), 4.08 (s, 5H, Fc-Cp), 2.36 (hept, *J* = 6.8 Hz, 2H, 2xC*H*), 1.19 (d, *J* = 6.8 Hz, 6H, 2xCH_3), 1.16 (d, *J* = 6.9 Hz, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25°C) δ 146.7 (Triazol-*C*), 146.2, 133.5, 130.9, 124.0, 121.9 (all Aryl-*C*), 75.0, 69.8, 69.0, 66.8 (all Fc-*C*), 28.6, 24.4, 24.1 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for [$C_{24}H_{27}FeN_3$] ([M + H]$^+$) *m/z* 414.1627, found 414.1627.

1-[1,3,5-trimethylphenyl]-4-Ferrocenyl-1*H*-1,2,3-triazole 1b

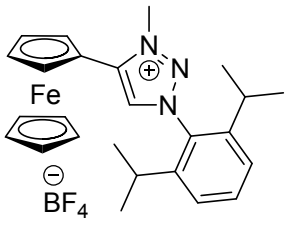


The product was obtained as an orange solid in a yield of 33% (96.1 mg, 0.26 mmol).
^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.53 (s, 1H, Triazol-*5H*), 6.99 (s, 2H, Aryl-*H*), 4.81 (t, J = 1.9 Hz, 2H, Fc-H_α), 4.32 (t, J = 1.9Hz, 2H, Fc-H_β), 4.07 (s, 5H, Fc-Cp), 2.35 (s, 3H, CH_3), 2.00 (s, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25°C) δ 146.7, 140.0, 135.1, 133.6, 129.1, 120.6 (all Aryl-*C*), 75.1, 69.6, 68.8, 66.7 (all Fc-*C*), 21.2, 17.3 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for [C21H21FeN$_3$] [(M +Na)$^+$] *m/z* 394.0983, found 394.0985.

General Procedure for the Preparation of 3-Methyl-1*H*-1,2,3-Triazolium Tetrafluoroborates

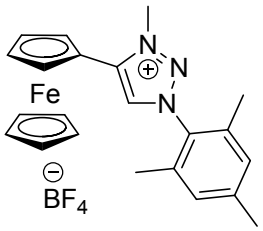
To a solution of the 1-substituted 4-ferrocenyl 1*H*-1,2,3-triazole (1 equiv., 0.5 mmol) in dichloromethane (5 mL) was added trimethyloxonium tetrafluoroborate (1.1 equiv., 81.4 mg, 0.55 mmol). After the reaction mixture was stirred at room temperature for three days, methanol (1 mL) was added and the solvent was removed in vacuum. Then the residue was re-resolved in dichloromethane (2 mL), precipitated with diethyl ether (50 mL) and filtered to give the pure product. Single crystals suitable for X-ray diffraction analysis were obtained by condensing diethyl ether onto a concentrated solution of the triazolium salt in dichloromethane at room temperature.

1-[1,3-diisopropylphenyl]-3-methyl-4-Ferrocenyl-1*H*-1,2,3-triazolium tetrafluoroborate [2a]BF_4



The product was obtained as an orange solid in a yield of 89% (229.3 mg, 0.445 mmol).
^{1}H NMR (400 MHz, CD_2Cl_2, 25°C) δ 8.53 (s, 1H, Triazolium-*5H*), 7.65 (t, J = 7.9 Hz, 1H, Aryl-*H*), 7.40 (d, J = 7.8 Hz, 2H, Aryl-*H*), 4.99 (t, J = 1.7 Hz, 2H, Fc-H_α), 4.67 (t, J = 1.7 Hz, 2H, Fc-H_β), 4.44 (s, 3H, N-CH_3), 4.28 (s, 5H, Fc-Cp), 2.25 (hept, J = 6.8 Hz, 2H, C*H*), 1.24 (d, J = 6.8 Hz, 6H, 2xCH_3), 1.18 (d, J = 6.8 Hz, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25°C) δ 145.7, 145.3, 133.0, 130.7, 129.6, 124.8 (all Aryl-*C*), 72.3, 70.7, 69.6, 64.5 (all Fc-*C*), 39.7 (N-*C*H_3), 29.0, 24.0, 23.6 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for $[C_{25}H_{30}FeN_3BF_4]$ $[(M - BF_4)^-]$ *m/z* 428.1784, found 428.1785.

1-[1,3,5-trimethylphenyl]-3-methyl-4-Ferrocenyl-1H-1,2,3-triazolium tetrafluoroborate [2b]BF_4

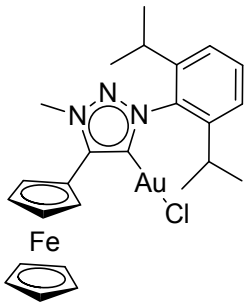


The product was obtained as a yellow solid in a yield of 92% (215.3 mg, 0.455 mmol).
^{1}H NMR (400 MHz, CD_2Cl_2, 25°C) δ 8.52 (s, 1H, Triazolium-*5H*), 7.11 (s, 2H, Aryl-*H*), 4.97 (t, J = 1.8 Hz, 2H, Fc-H_α), 4.66 (t, J = 1.8 Hz, 2H, Fc-H_β), 4.44 (s, 3H, N-CH_3), 4.30 (s, 5H, Fc-Cp), 2.40 (s, 3H, CH_3), 2.11 (s, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25°C) δ 145.5, 142.8, 134.4, 131.2, 129.9, 129.0 (all Aryl-*C*), 72.0, 70.6, 69.4, 64.8 (all Fc-*C*), 39.5 (N-*C*H_3), 21.0, 17.0 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for $[C_{22}H_{24}FeN_3BF_4]$ $[(M - BF_4)^-]$ *m/z* 386.1315, found 386.1324.

General Procedure for the Preparation of the gold carbene complexes

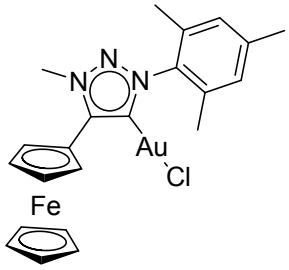
A mixture of 1-substituted 3-methyl 4-ferrocenyl -1*H*-1,2,3-triazolium tetrafluoroborate (1 equiv., 0.1 mmol), silver(I) oxide (1.5 equiv., 34.8 mg, 0.15 mmol), potassium chloride (2 equiv., 15.1 mg, 0.2 mmol) and caesium carbonate (3 equiv., 97.8 mg, 0.3 mmol) in absolute acetonitrile (10mL) was stirred at room temperature under exclusion of light. After the reaction was complete (this was detected by ^{1}H-NMR-spectroscopy) the reaction mixture was filtered over Celite under N_2-atmosphere and volatiles were removed under high vacuum. The residue was dissolved in absolute dichloromethane (10 mL) and AuCl(SMe_2) (1 equiv., 29.4 mg, 0.1 mmol) was added. After stirring over night at room temperature, the reaction mixture was filtered over Celite and the solvent was evaporated. The residue was re-resolved in dichloromethane (2 mL) and precipitated with pentane (50 mL) and filtered. The pure product was obtained from recrystallization in dichloromethane/hexane as red crystals. Single crystals suitable for X-ray diffraction analysis were obtained by condensing hexane onto a concentrated solution of the complex in dichloromethane at room temperature.

Complex 3a



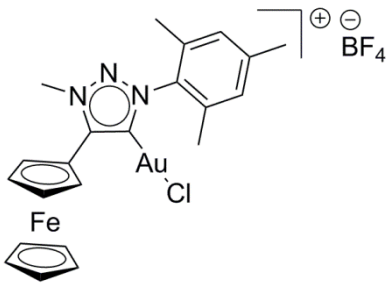
The product was obtained as red crystals in a yield of 33% (21.4 mg, 0.032 mmol).
^{1}H NMR (400 MHz, CD_2Cl_2, 25°C) δ 7.59 (t, J = 7.8 Hz, 1H, Aryl-*H*), 7.34 (d, J = 7.9 Hz, 2H, Aryl-*H*), 5.11 (t, J = 1.9 Hz, 2H, Fc-H_α), 4.52 (t, J = 1.9 Hz, 2H, Fc-H_β), 4.29 (s, 5H, Fc-Cp), 4.23 (s, 3H, N-CH_3), 2.31 (hept, J = 6.8 Hz, 1H, C*H*), 1.33 (d, J = 6.9 Hz, 6H, 2xCH_3), 1.13 (d, J = 6.9 Hz, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25°C) δ 161.9 (Carbene-*C*), 146.7, 145.6, 136.0, 131.9, 124.8 (all Aryl-*C*), 71.1, 70.8, 70.7, 70.0 (all Fc-*C*), 39.1 (N-*C*H_3), 29.2, 24.5, 24.4 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for [$C_{25}H_{29}AuFeN_3Cl$] [$(M - Cl)^-$] *m/z* 624.1376 found 624.1326.

Complex 3b



The product was obtained as red crystals in a yield of 36% (22.2 mg, 0.036 mmol).
^{1}H NMR (400 MHz, CD_2Cl_2, 25°C) δ 7.08 (s, 2H, Aryl-*H*), 5.10 (t, J = 1.8 Hz, 2H, Fc-H_α), 4.53 (t, J = 1.9 Hz, 2H, Fc-H_β), 4.32 (s, 5H, Fc-Cp), 4.24 (s, 3H, N-CH_3), 2.40 (s, 3H, CH_3), 2.08 (s, 6H, 2xCH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25°C) δ 160.4 (Carbene-*C*), 147.1, 141.4, 136.4, 134.8, 129.8 (all Aryl-*C*), 71.1, 71.0, 70.7, 70.0 (all Fc-*C*), 38.9 (N-*C*H$_3$), 21.6, 17.8 (all Alkyl-*C*) ppm. HRMS (ESI): calcd for [$C_{22}H_{23}AuFeN_3Cl$] [(M – Cl)$^+$] *m/z* 582.0907 found 582.0879.

Complex [3b]BF_4



Complex **3b** (see Figure S1: **a)**) (1 equiv., 17.05 mg, 0.0276 mmol) and acetylferrocenium tetrafluoroborate (1 equiv., 8.71 mg, 0.0276 mmol) were stirred in absolute dichloromethane (2.5 mL) for two hours at room temperature. Upon mixing, a color chance from yellow to green occurred immediately. Then absolute diethyl ether (6 mL) was added to precipitate the product and stirred for a few minutes. To remove the formed acetylferrocene which is soluble in diethyl ether (see Figure S1: **b)**), the solution was removed with a syringe. This was repeated four times to remove all acetylferrocene to obtain complex **[3b]BF_4** as green solid (see Figure S1: **c)**).
Anal. Calc. for $C_{22}H_{23}AuBClF_4FeN_3$: C 37.51; H 3.29; N 5.96 %; found: C 37.46; H 3.31; N 5.98 %. UV/Vis spectrum: See Figure S21.

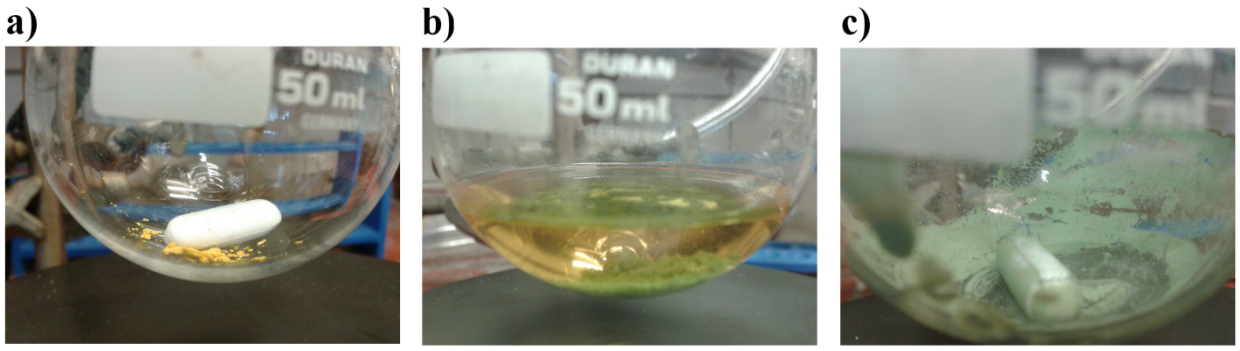
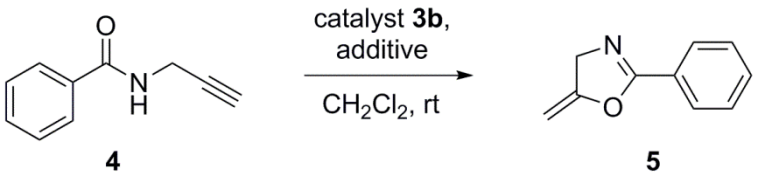


Figure S1: **a)** Complex **3b b)** Precipitated complex **[3b]BF_4** and solution of acetylferrocene **c)** Isolated and pure complex **[3b]BF_4**

Catalysis

General procedure for the catalytic cyclization reaction of *N*-propargylcarboxamide, 4 to 4,5-dihydrooxazole, 5



4 **5**

To a solution of catalyst **3b** (1 mol%) and for one case acetylferrocenium tetrafluoroborate (1.2 equiv. 1.2 mol%) in absolute dichloromethane (1 mL) was added N-(2-Propyn-1-yl)benzamide (0.1 mmol). The reaction mixture was stirred at room temperature for twenty-four hours. Hexadecane was also added to the reaction mixture. Samples were taken after different reaction times. For that, a little sample was taken with a glass pipette and filtered over a little plug of silica (also in a glass pipette) and eluted with dichloromethane. The solvent was removed and the conversions to the product 5-Methylene-2-phenyl-4,5-dihydrooxazole were detected by ^{1}H NMR spectroscopy with hexadecane as internal standard.

Table S1: Gold(I)-catalyzed formation of 4,5-dihydrooxazole **5**[1]

Entry	Catalyst	Additive	Reaction time / h	Conversion / %[2]
1	**3b**	-	2	0
		-	3	0
		-	5	0
		-	24	10
2	**3b**	$[FcOAc]BF_4$	1	10
		$[FcOAc]BF_4$	3	21
		$[FcOAc]BF_4$	5	40
		$[FcOAc]BF_4$	24	88

[1]Reaction conditions: N-(2-Propyn-1-yl)benzamide (0.1 mmol), catalyst **3b** (1 mol-%), for entry 2 acetylferrocenium tetrafluoroborate (1.2 mol%) and dichloromethane (1 mL), room temperature. [2] Determined by ^{1}H NMR spectroscopy with hexadecane as internal standard.

^{1}H and ^{13}C NMR

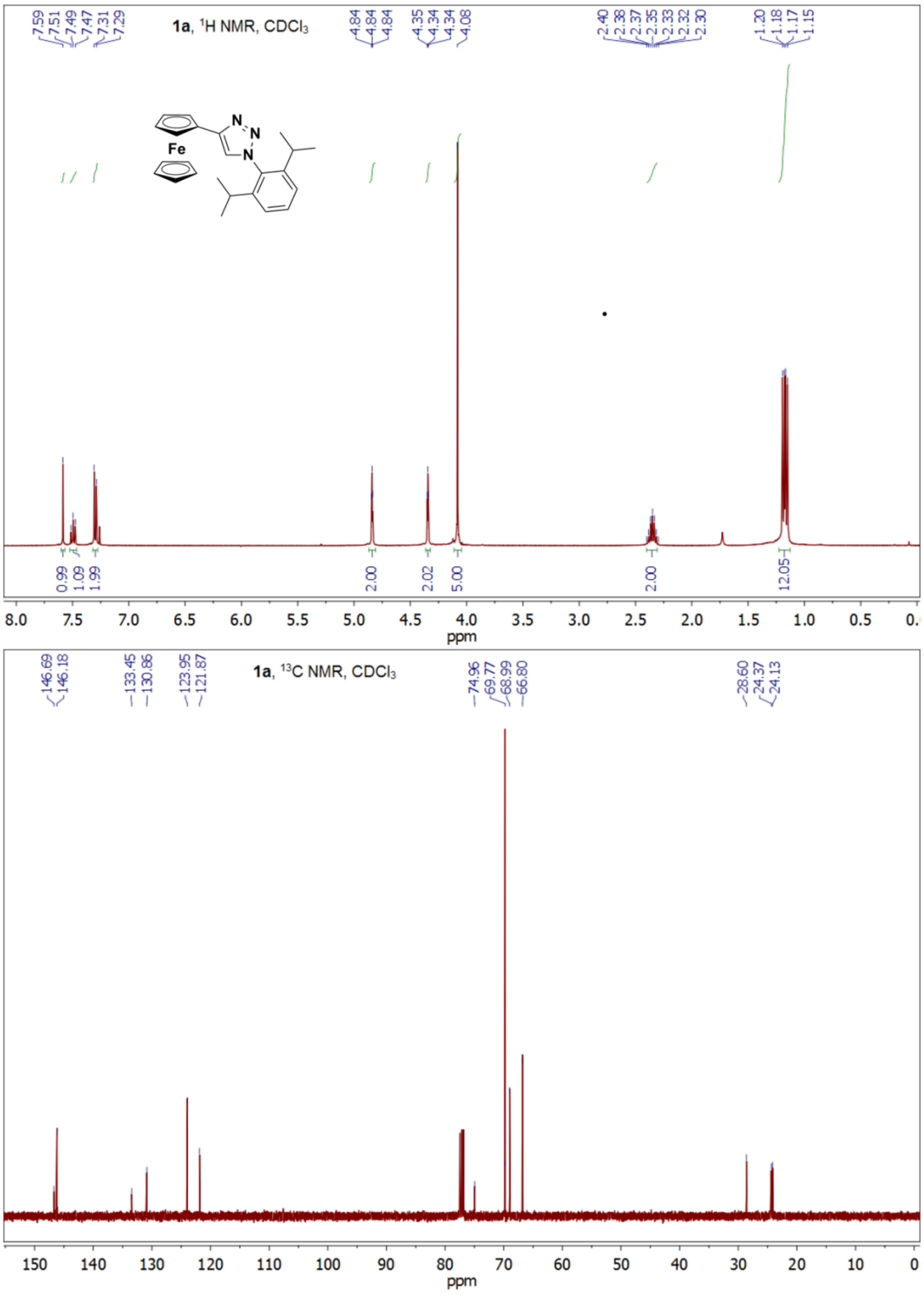


Figure S2: ^{1}H (top) and ^{13}C NMR (bottom) spectra of Compound **1a** in $CDCl_3$

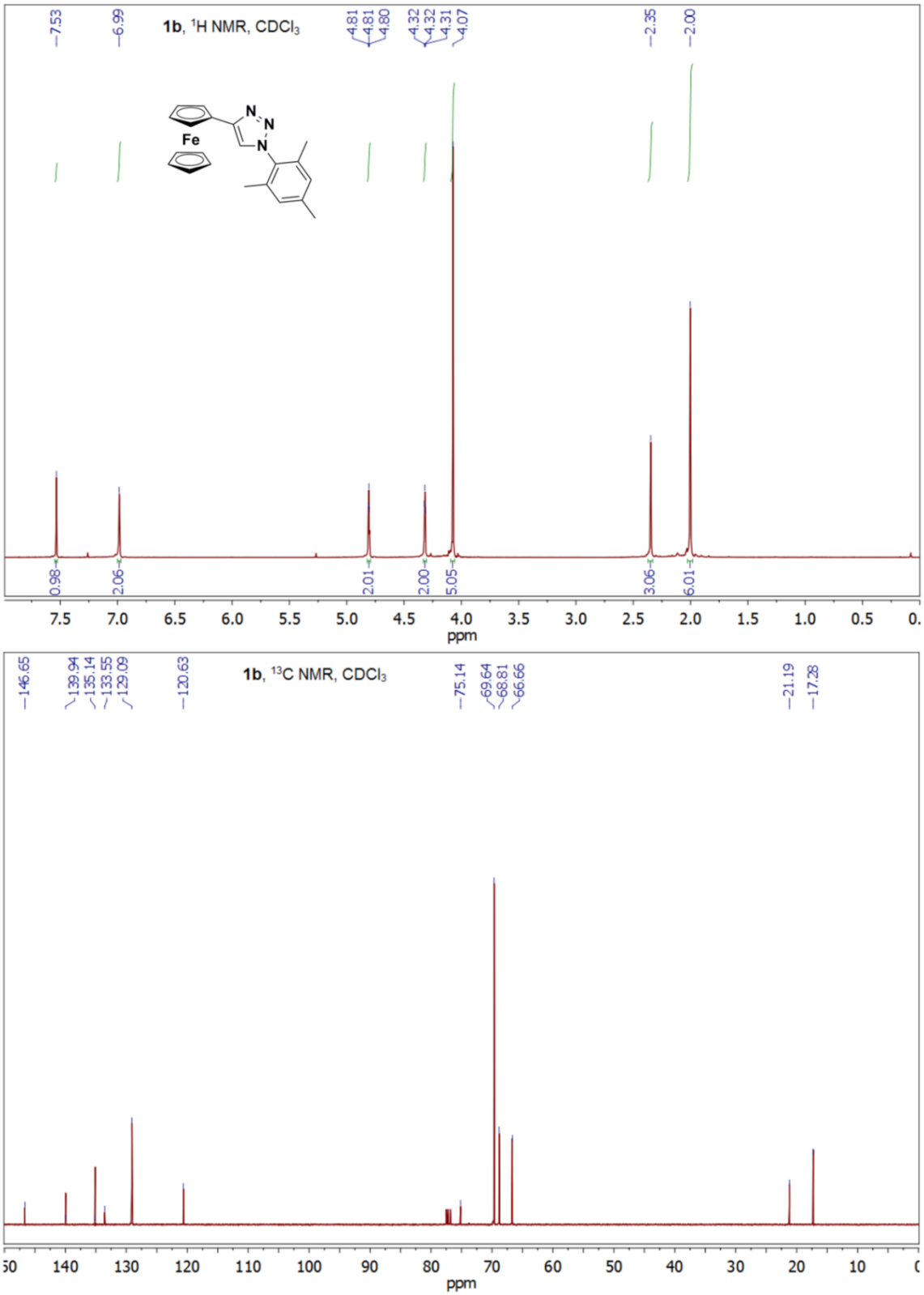


Figure S3: ^{1}H (top) and ^{13}C NMR (bottom) spectra of Compound **1b** in $CDCl_3$

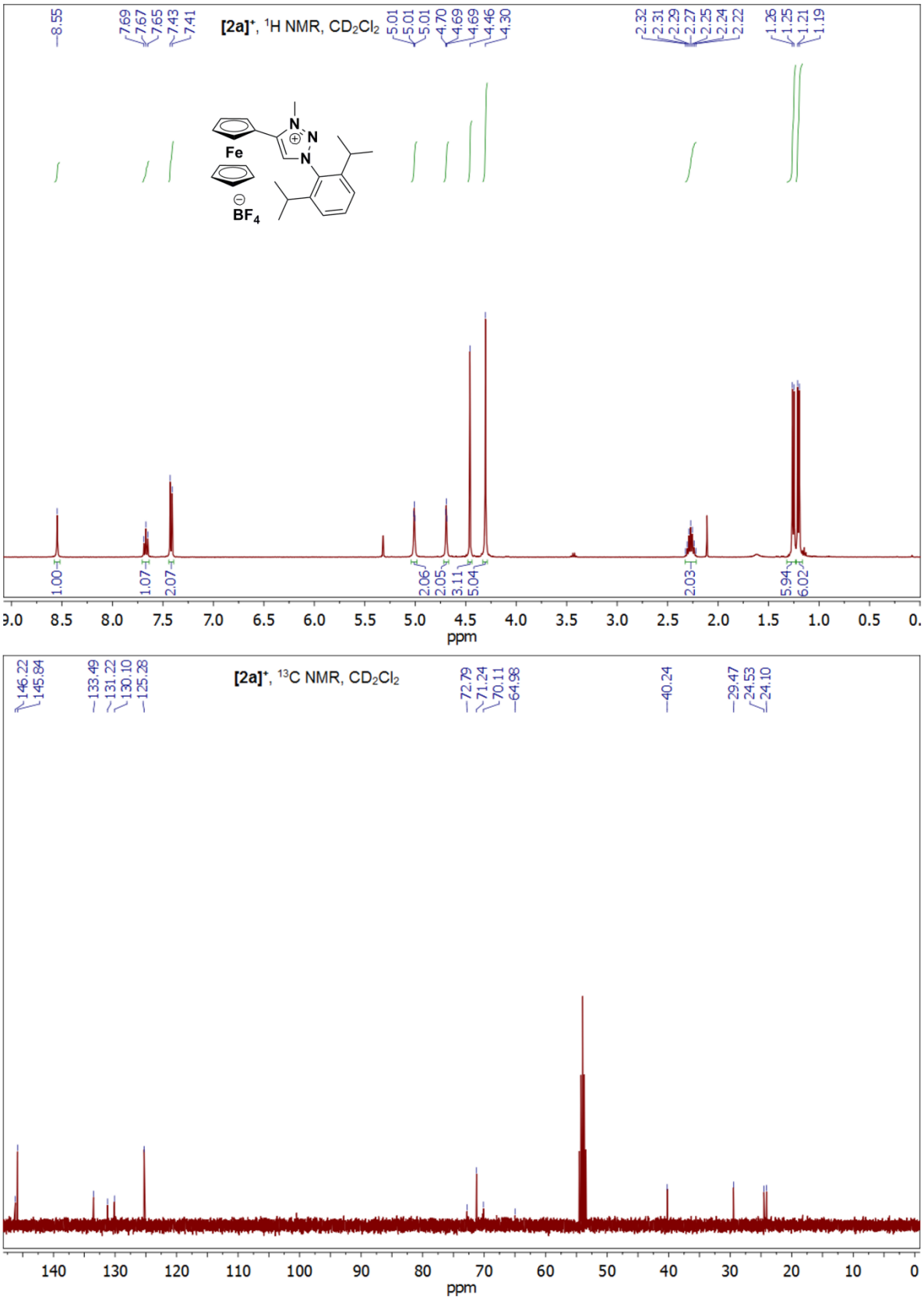


Figure S4: ^{1}H (top) and ^{13}C (bottom) NMR spectra of Compound **[2a]BF_4** in CD_2Cl_2

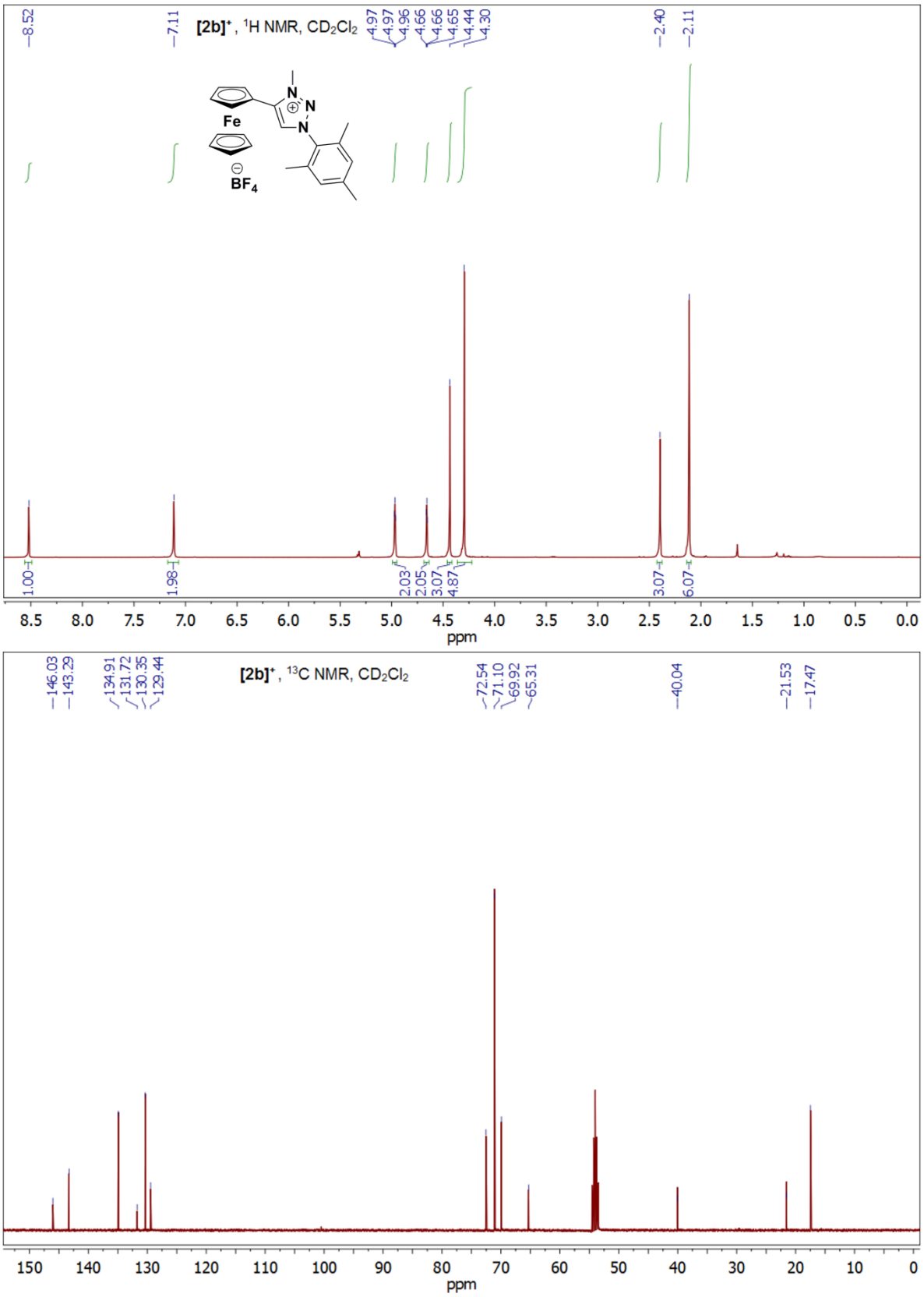


Figure S5: ^{1}H (top) and ^{13}C (bottom) NMR spectra of Compound **[2b]BF_4** in CD_2Cl_2

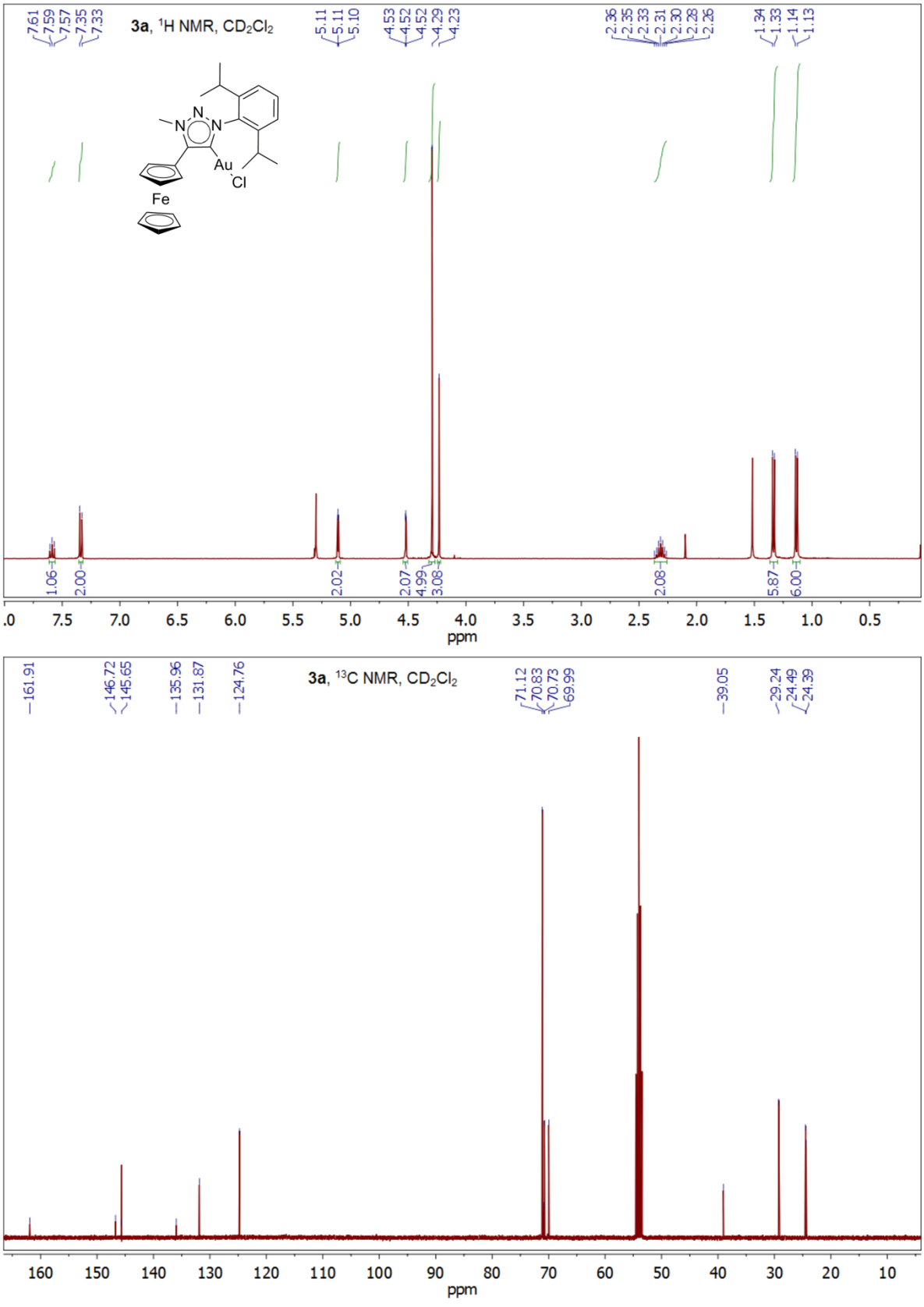


Figure S6: ^{1}H (top) and ^{13}C (bottom) NMR spectra of Compound **3a** in CD_2Cl_2

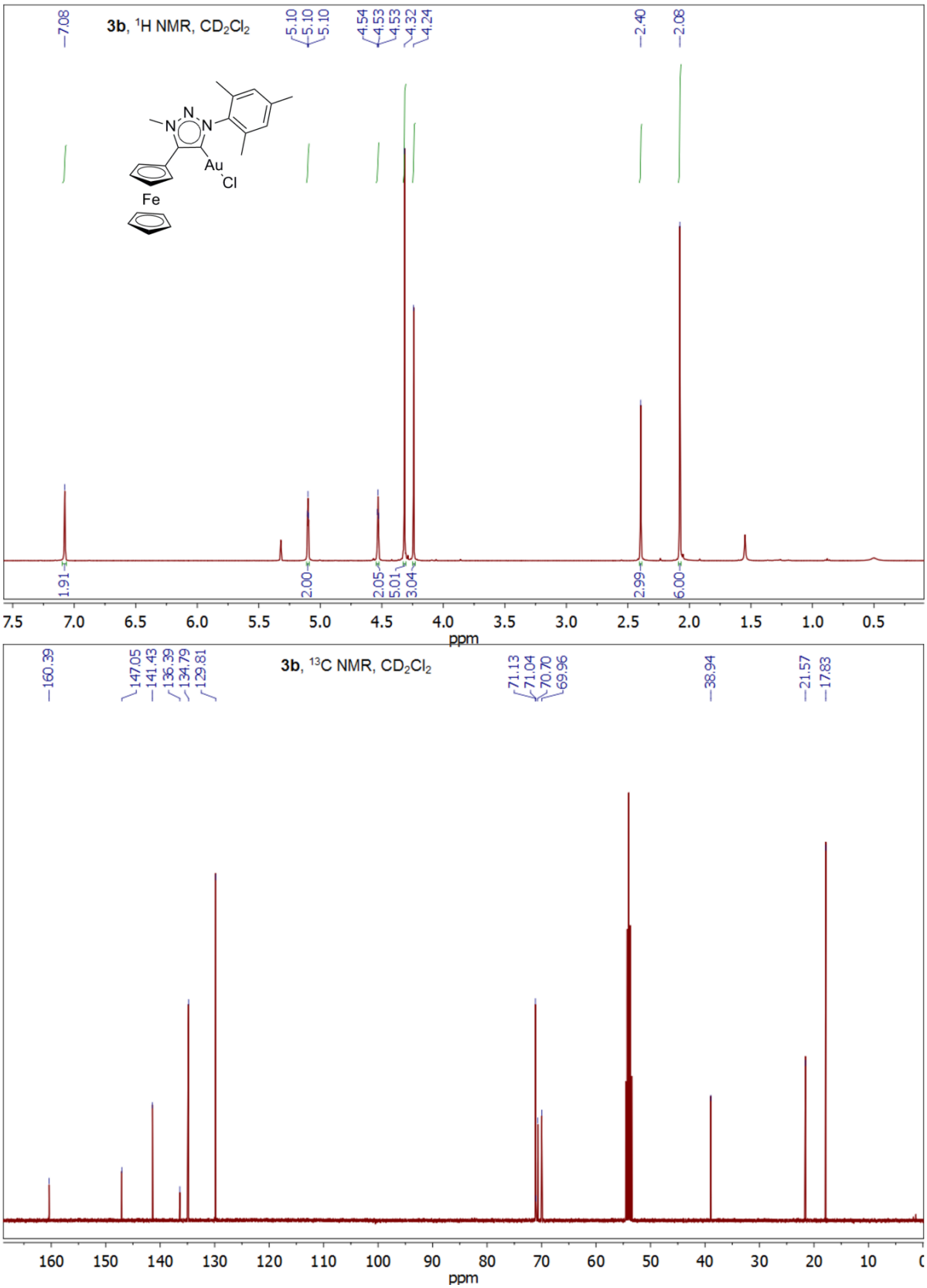


Figure S7: ^{1}H (top) and ^{13}C (bottom) NMR spectra of Compound **3b** in CD_2Cl_2

Cyclic Voltammetry

Table S2: Oxidation and reduction potentials ($E_{1/2}$), reduction peak potentials (E) and difference of the oxidation potentials (ΔE) of compounds **1a** – **3b**.[1]

	Oxidation		**Reduction**	
	$E_{1/2}$ / V	ΔE / V	E / V	$E_{1/2}$ / V
1a	0.05	0.12	-	-
1b	0.03	0.09	-	-
[2a]$^+$	0.23	0.12	-2.17	-
[2b]$^+$	0.23	0.09	-2.17	-
3a	0.12	0.14	-2.76	-
3a[2]	0.12	0.16	-	-2.70
3b	0.13	0.11	-2.73	-
3b[2]	0.13	0.26	-	-2.77

[1]Measured in absolute THF containing 0.1 M Bu_4NPF_6 as the supporting electrolyte with a scanrate of 100mV/s at room temperature. [2] Measured at -30°C.

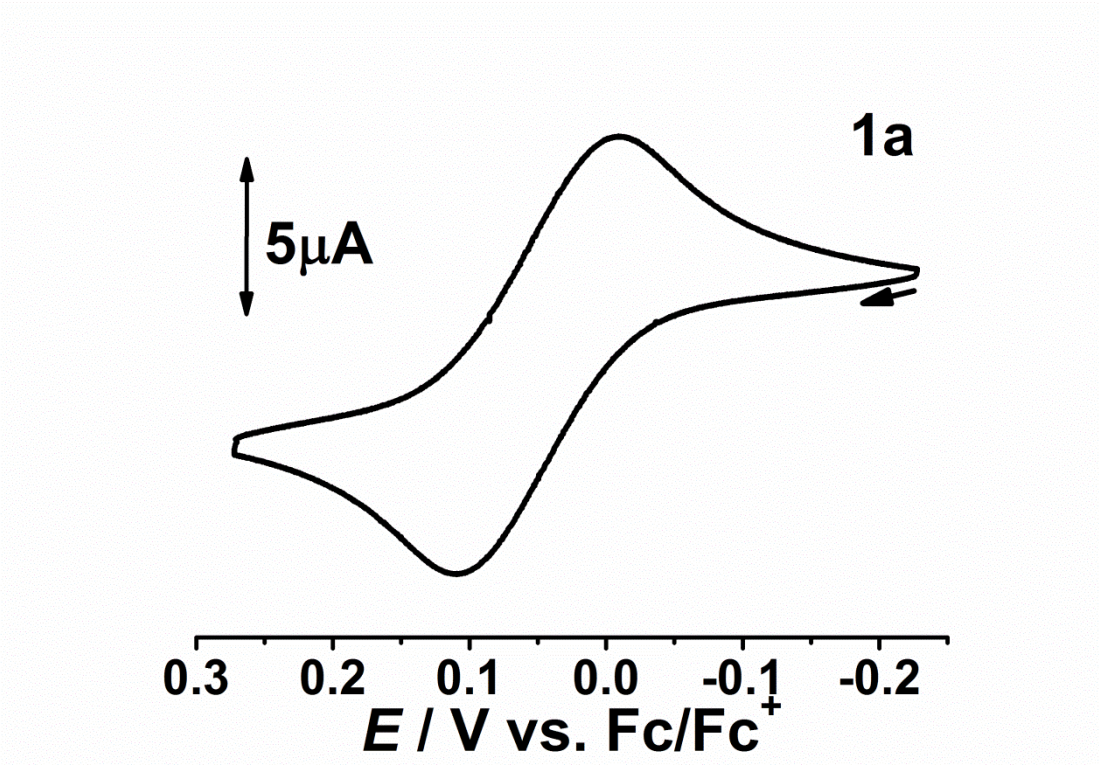


Figure S8: Cyclic Voltammogram of Compound **1a** in THF

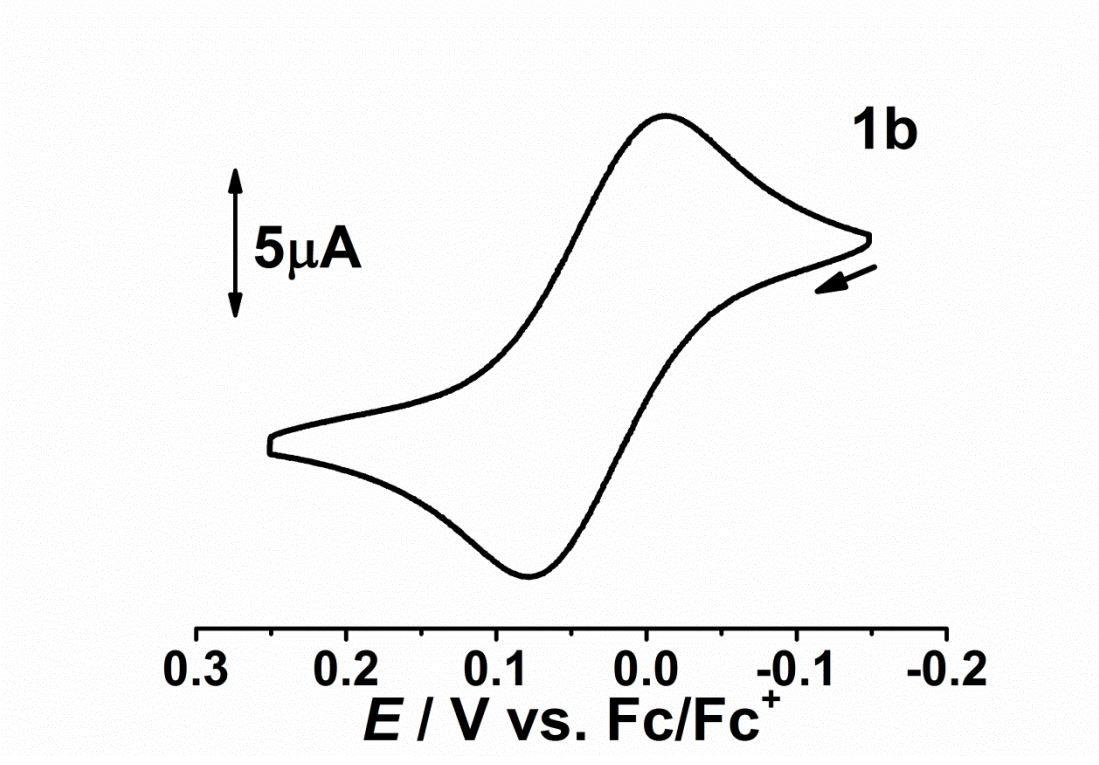


Figure S9: Cyclic Voltammogram of Compound **1b** in THF

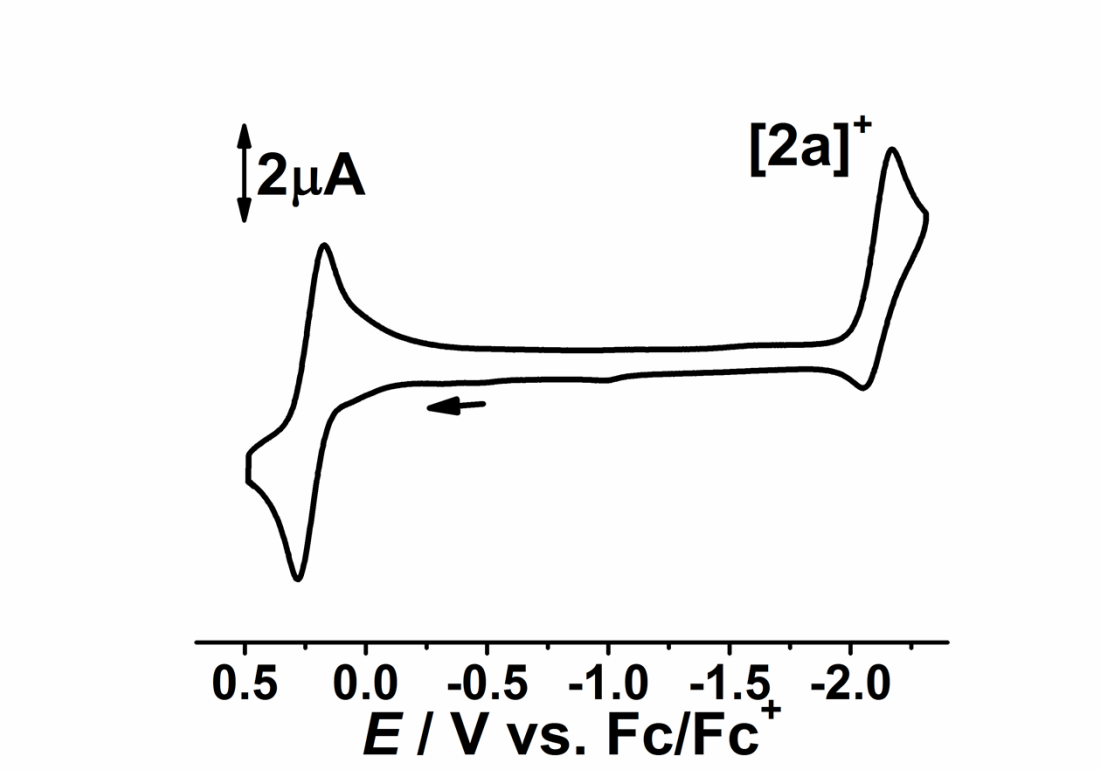


Figure S10: Cyclic Voltammogram of Compound **[2a]**$^{+}$ in THF

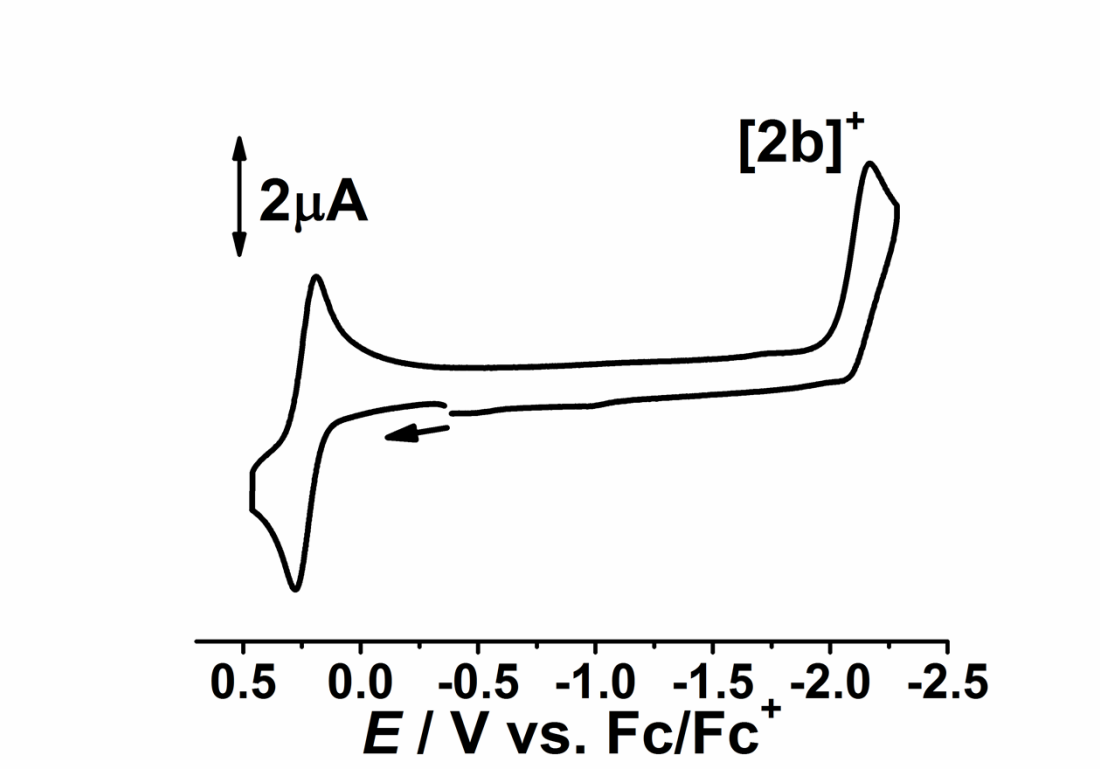


Figure S11: Cyclic Voltammogram of Compound **[2b]**$^{+}$ in THF

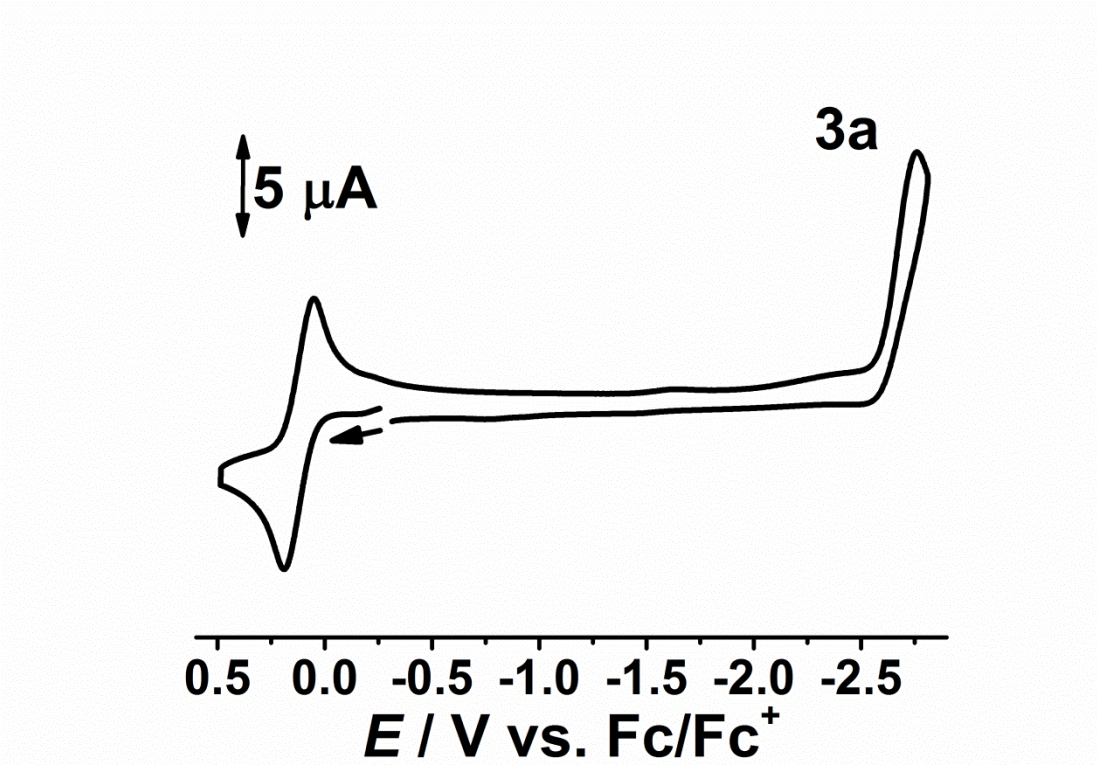


Figure S12: Cyclic Voltammogram of Compound **3a** in THF

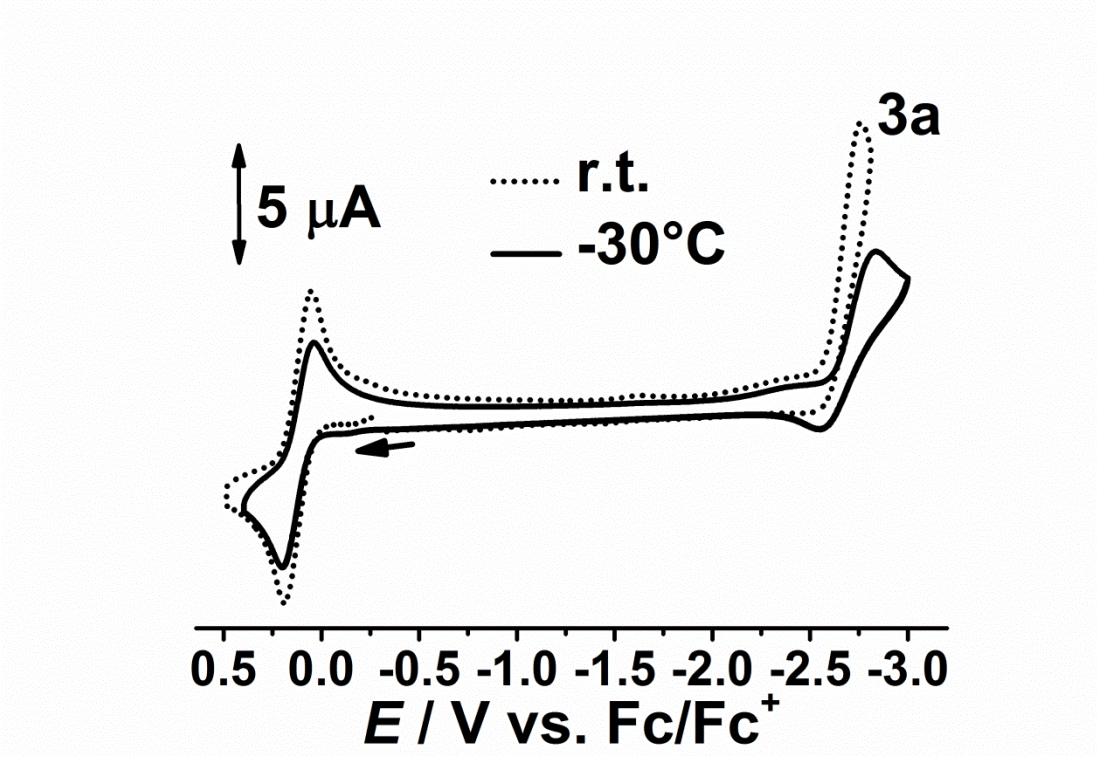


Figure S13: Cyclic Voltammograms of Compound **3a** at different temperatures in THF

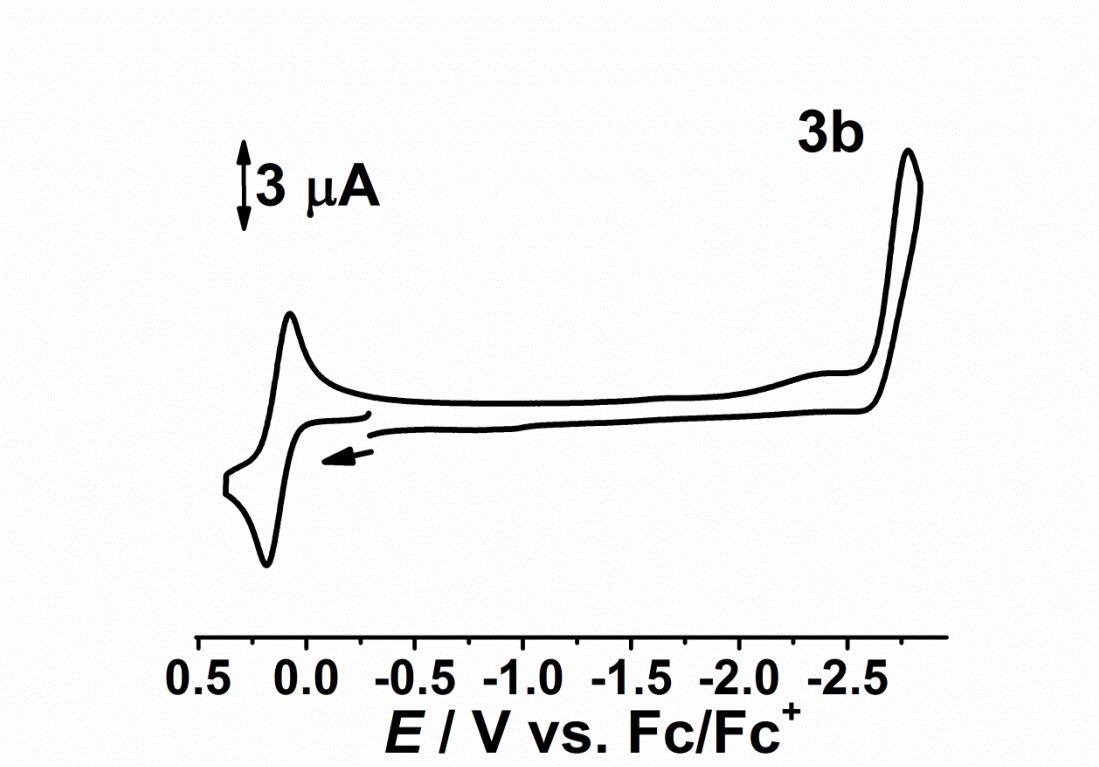


Figure S14: Cyclic Voltammogram of Compound **3b** in THF

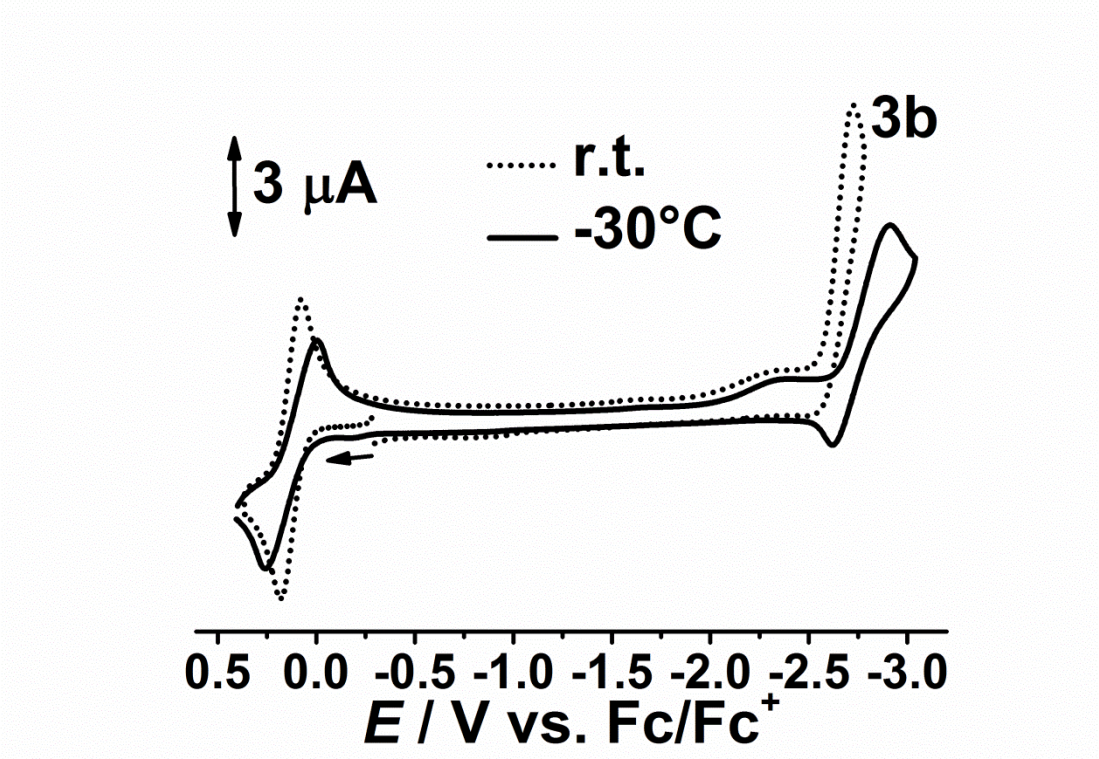


Figure S15: Cyclic Voltammograms of Compound **3b** at different temperatures in THF

UV/Vis Spectroscopy/Spectroelectrochemistry

Table S3: UV/Vis data of the native and the one-electron oxidized compounds **1a** – **3b**.[1]

	λ / nm (ε / $M^{-1}cm^{-1}$)
1a^0	216(33582), 225(31777), 270(11875)
[1a]$^{\bullet+}$	216(30435), 225(26397), 264(13229), 293(9856) sh, 750(450)
1b^0	217(34740), 226(36400),269(13180)
[1b]$^{\bullet+}$	217(30600), 225(29250), 258(15500) sh, 289(12870) sh, 732(350)
[2a]$^+$	216(29262), 225(26855), 272(16747), 364(879), 450(364)
[2a]$^{\bullet 2+}$	216(28059), 225(24010), 265(19404), 272(19096) sh, 645(84)
[2b]$^+$	217(22770), 226(23310), 273(14650), 365(1110) sh, 449(610) sh
[2b]$^{\bullet 2+}$	217(21360), 225(18790), 262(22810), 292(16370) sh, 643 (590)
3a^0	212(19348), 277(7567), 357(1135), 456(512)
[3a]$^{\bullet+}$	212(14389), 263(10951), 400(1166) sh, 708(353)
3b^0	212(18271), 277(7098), 364(763), 449(315)
[3b]$^{\bullet+}$	212(13952), 262(9850), 405(752) sh, 713(333)

[1]Measured in absolute THF containing 0.1 M Bu_4NPF_6 as the supporting electrolyte at room temperature.

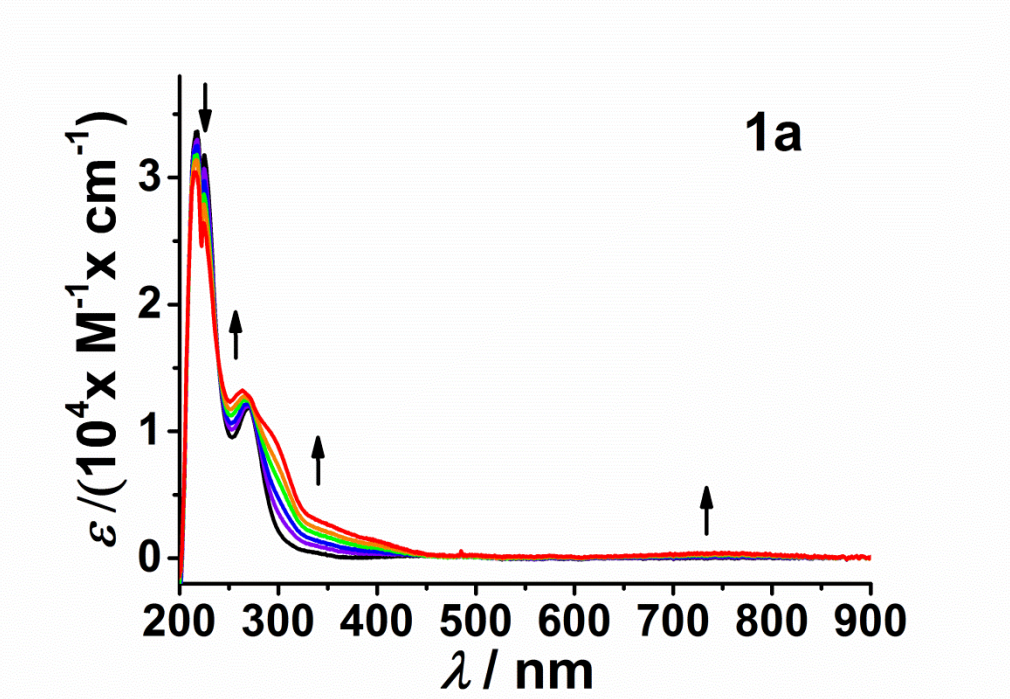


Figure S16: Change in the UV/Vis absorption of Compound **1a** in the course of a one-electron oxidation in THF

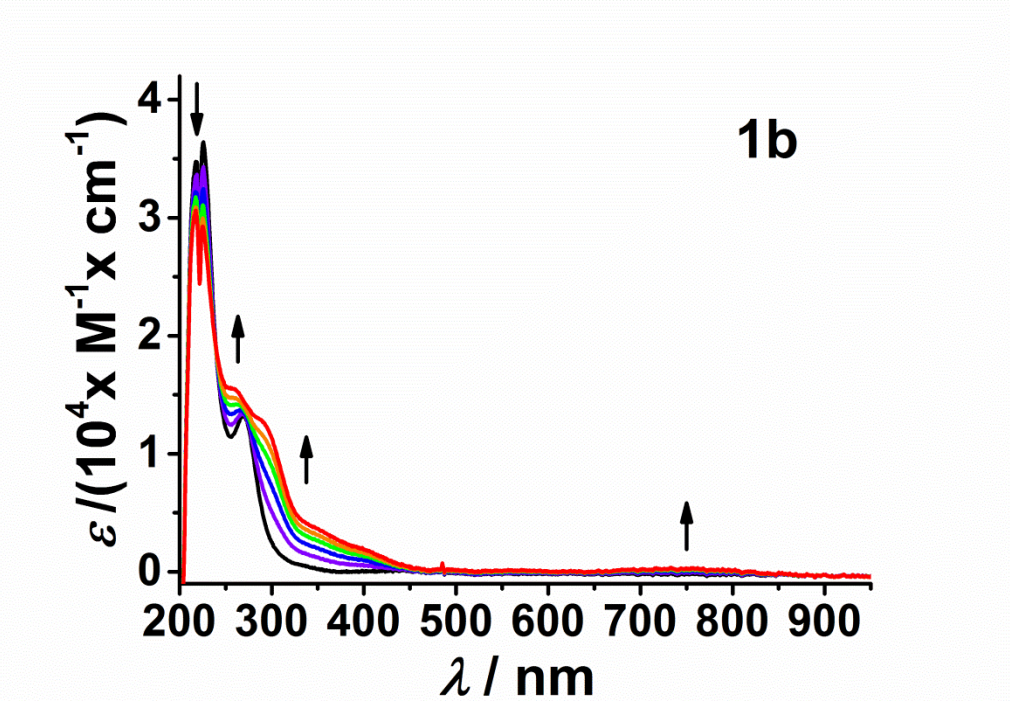


Figure S17: Change in the UV/Vis absorption of Compound **1b** in the course of a one-electron oxidation in THF

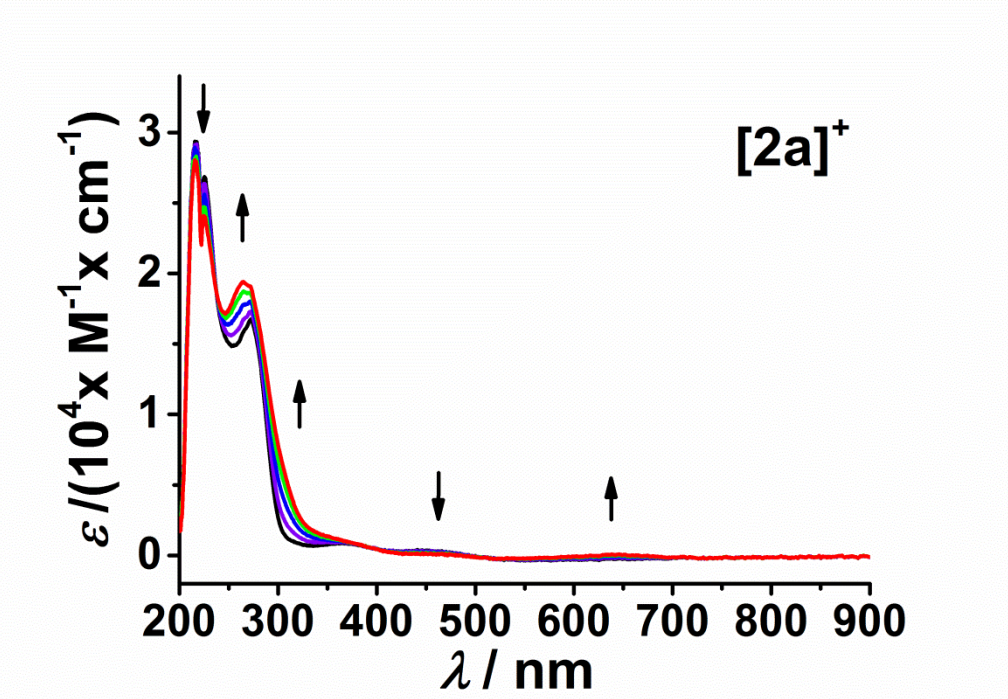


Figure S18: Change in the UV/Vis absorption of Compound **[2a]**$^{+}$ in the course of a one-electron oxidation in THF

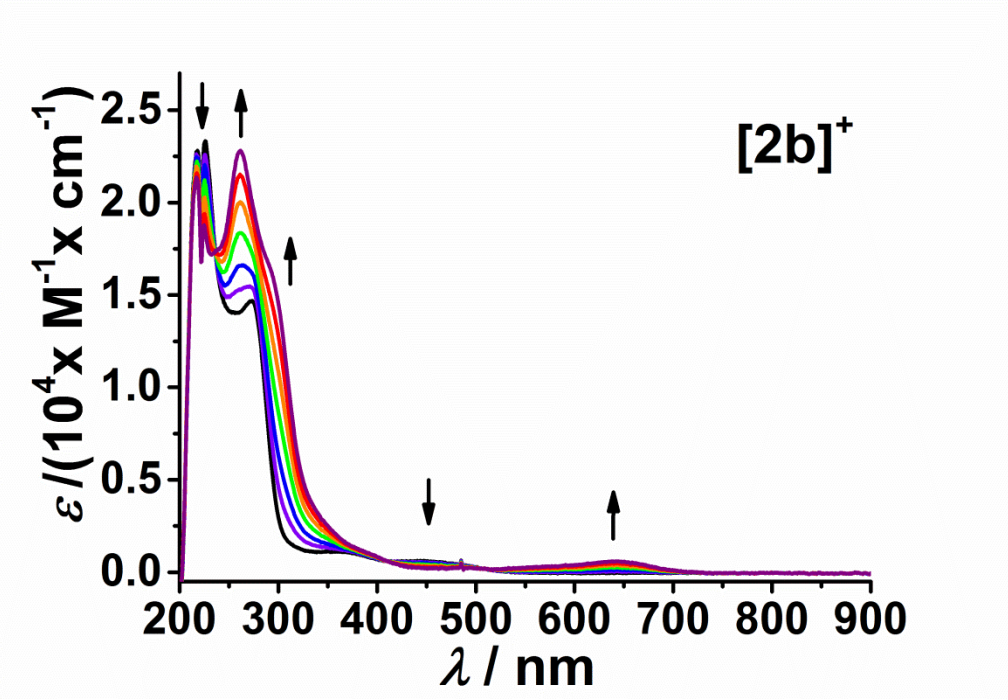


Figure S19: Change in the UV/Vis absorption of Compound **[2b]**$^{+}$ in the course of a one-electron oxidation in THF

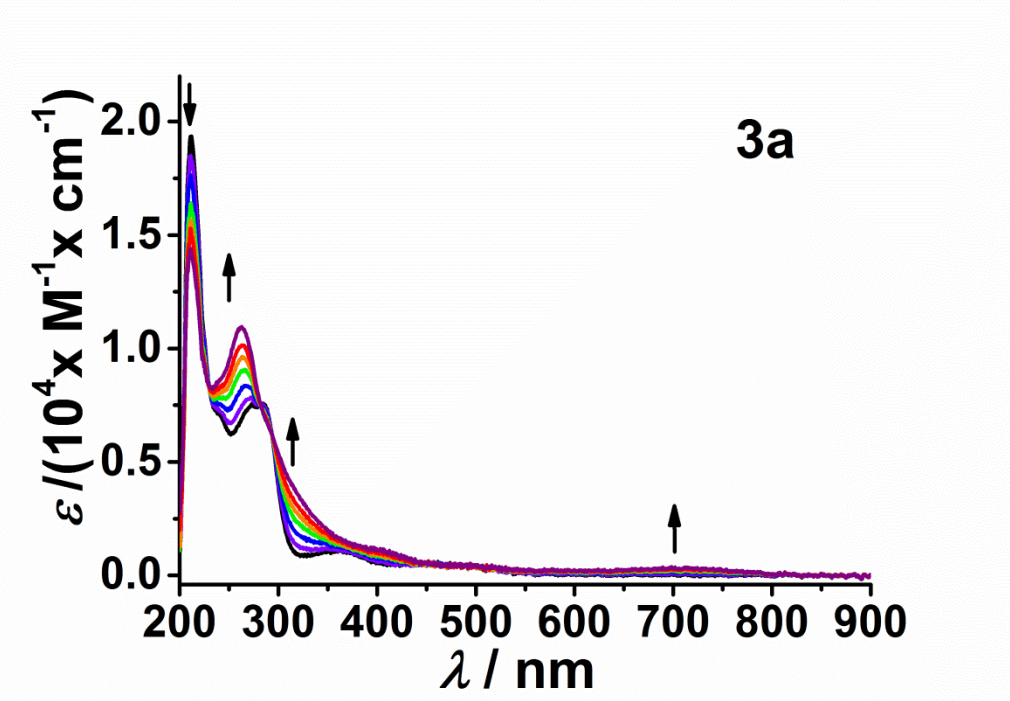


Figure S20: Change in the UV/Vis absorption of Compound **3a** in the course of a one-electron oxidation in THF

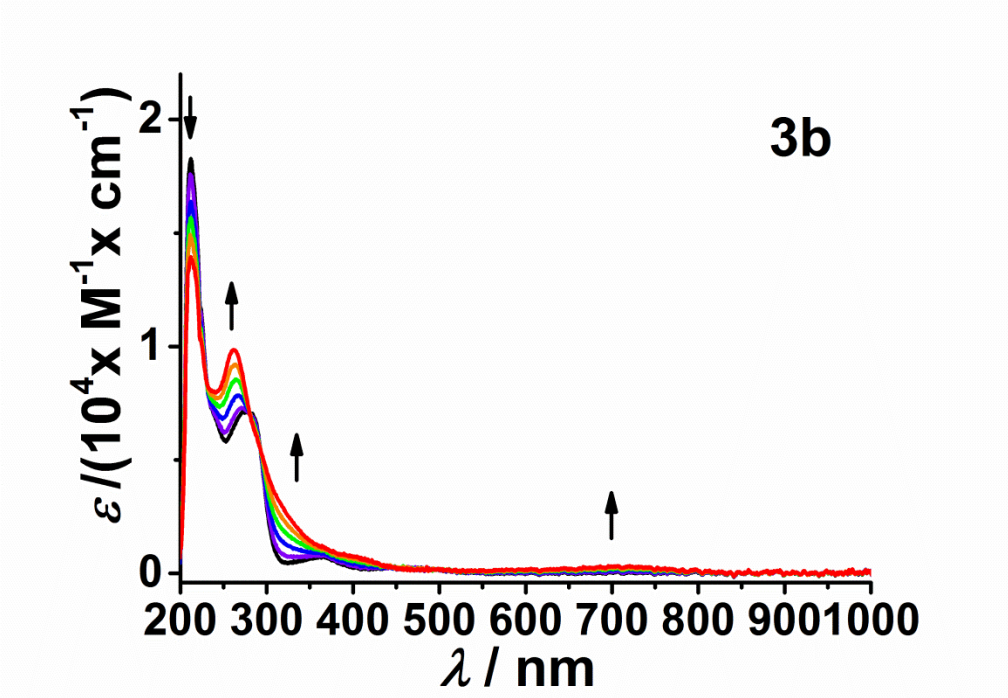


Figure S21: Change in the UV/Vis absorption of Compound **3b** in the course of a one-electron oxidation in THF

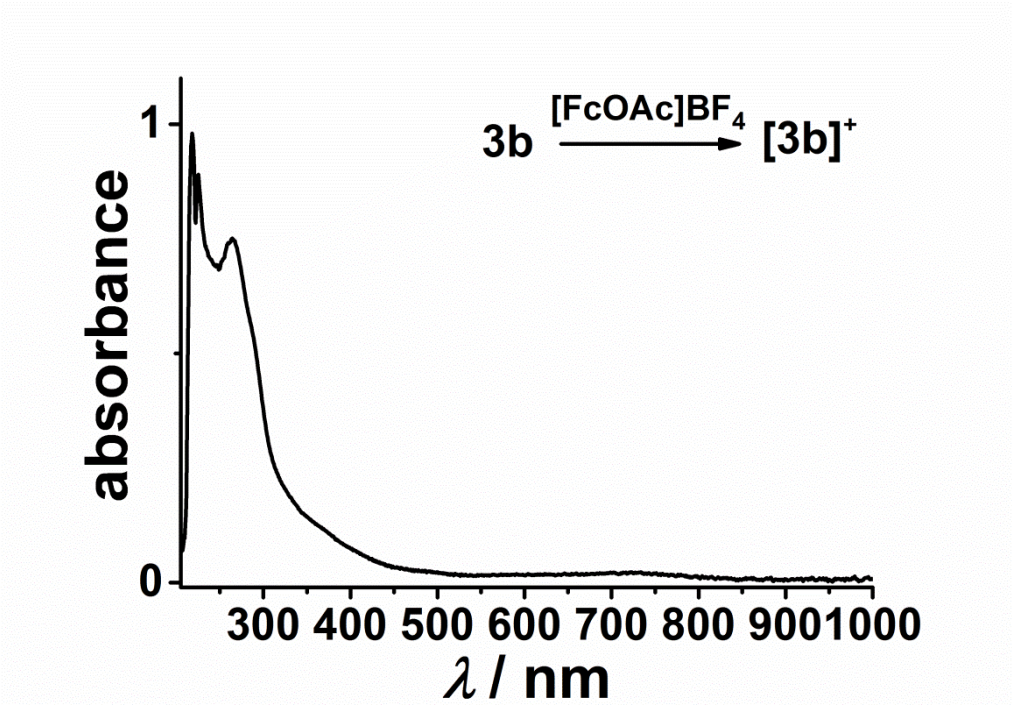


Figure S22: UV/Vis spectrum of Compound **[3b]**$^{\cdot+}$ (chemically oxidized) in THF

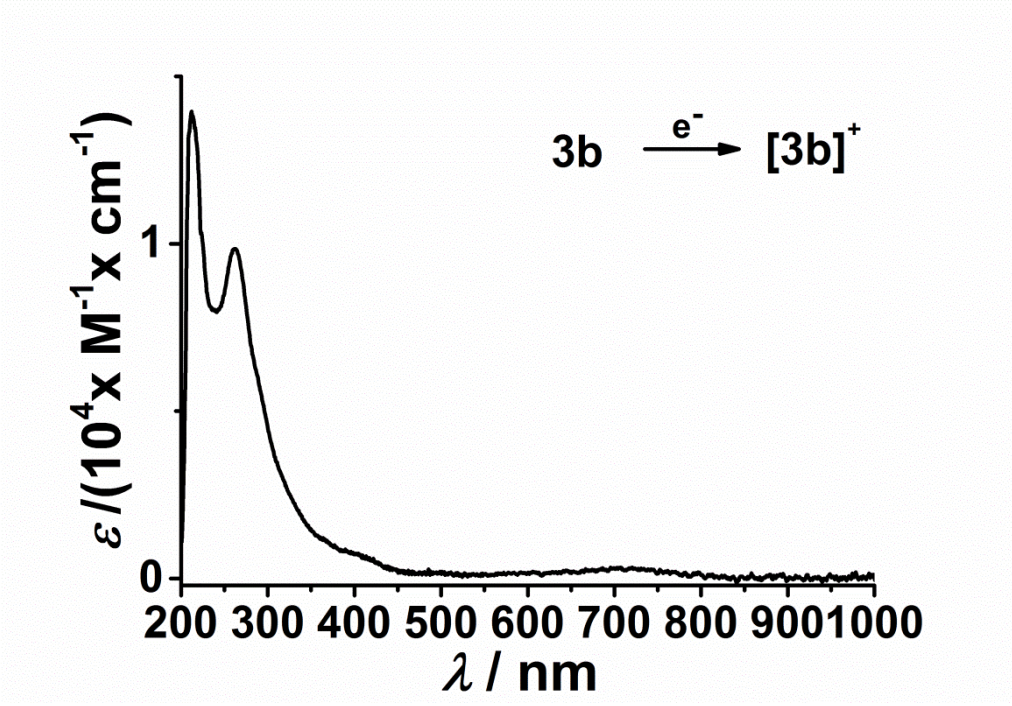


Figure S23: UV/Vis spectrum of Compound **[3b]**$^{\cdot+}$ (electrochemically oxidized) in THF

Crystal Structures

Table S4: Parameters for the Data Collection and Structure Refinement for Triazoles **1a**[1] and **1b**[2].

	1a	**1b**
Chemical formula	$C_{24}H_{27}FeN_3$	$C_{21}H_{21}FeN_3$
M_r	413.34	371.26
Crystal system, space group	orthorhombic, Fdd2	monoclinic, $P2_1/n$
Temperature (K)	110(2)	100(2)
a, *b*, *c* (Å)	21.0171(8), 49.949(3), 7.7045(3)	7.2798(15), 16.749(4), 14.796(3)
α, β, γ (°)	90, 90, 90	90, 103.923(4), 90
V (Å^3)	8088.0(6)	751.0(6)
Z	16	4
Density (g/cm^3)	1.358	1.408
F000	3488	776
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.760	0.869
Crystal size (mm)	0.16 x 0.15 x 0.10	0.23 x 0.18 x 0.05
meas. refl.	18835	22956
indep. ref.	4457	4039
obsvd. [I > 2σ(I)] refl.	3692	3395
R_{int}	0.0583	0.0251
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0390, 0.0635, 1.010	0.0380, 0.1051, 1.056
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.516, –0.411	0.656, –0.609
CCDC	965899	956900

[1] Collected on a Bruker Kappa APEX II duo using Mo *Kα* radiation (λ = 0.71073 Å) at 110(2) K.

[2] Collected on a Bruker Smart AXS using Mo *Kα* radiation (λ = 0.71073 Å) at 100(2) K.

Table S5: Parameters for the Data Collection and Structure Refinement for Triazolium salts [**2a**]BF_4[1] and [**2b**]BF_4[2].

	[**2a**]BF_4	[**2b**]BF_4
Chemical formula	$C_{25}H_{30}BF_4FeN_3$	$C_{22}H_{24}BF_4FeN_3$
M_r	515.18	473.10
Crystal system, space group	triclinic, P-1	orthorhombic, Pbca
Temperature (K)	100(2)	140(2)
a, *b*, *c* (Å)	8.5466(6), 9.9789(6), 14.7438(10)	9.213(5), 9.618(5), 47.215(5)
α, β, γ (°)	104.047(3), 91.109(4), 101.147(3)	90, 90, 90
V (Å^3)	1193.91(14)	4184(3)
Z	2	8
Density (g/cm^3)	1.433	1.502
F000	536	1952
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.681	0.770
Crystal size (mm)	0.38 x 0.11 x 0.06	0.26 x 0.24 x 0.22
meas. refl.	40810	21218
indep. ref.	6005	3659
obsvd. [I > 2σ(I)] refl.	5300	2201
R_{int}	0.0269	0.1311
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0445, 0.1290, 1.062	0.0696, 0.2027, 1.075
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.472, –0.456	0.637, –0.524
CCDC	965895	1015508

[1] Collected on a Bruker Kappa APEX II duo using Mo *Kα* radiation (λ = 0.71073 Å) at 100(2) K.

[2] Collected on a Bruker Smart AXS using Mo *Kα* radiation (λ = 0.71069 Å) at 140(2) K.

Table S6: S Parameters for the Data Collection and Structure Refinement for Complexes **3a** and **3b**.[1]

	3a	**3b**
Chemical formula	$C_{25}H_{29}AuClFeN_3$	$C_{22}H_{23}AuClFeN_3$
M_r	659.78	617.70
Crystal system, space group	monoclinic, C2/c	monoclinic, $P2_1/c$
Temperature (K)	100(2)	100(2)
a, *b*, *c* (Å)	29.3929(14), 9.2832(4), 17.3954(8)	24.435(5), 7.515(5), 11.492(5)
α, β, γ (°)	90.00, 90.428(2), 90.00	90.00, 93.546(5), 90.00
V (Å^3)	4746.4(4)	2106.2(17)
Z	8	4
Density (g/cm^3)	1.847	1.948
F000	2576	1192
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	6.916	7.785
Crystal size (mm)	0.80 x 0.12 x 0.10	0.22 x 0.17 x 0.02
meas. refl.	19765	20214
indep. ref.	4866	4298
obsvd. [I > 2σ(I)] refl.	4447	3163
R_{int}	0.0292	0.0501
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0170, 0.0349, 1.062	0.0283, 0.0566, 0.0495
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.402, –0.502	0.862, –1.188
CCDC	1022582	1022581

[1]Collected on a Bruker D8 Venture using Mo *Kα* radiation (**3a**: λ = 0.71073 Å; **3b**: λ = 0.71069 Å) at 100(2) K.

Table S7: Selected measured bond length in Å of compounds **1a** – **3b** and optimized structures (BP86) of **1b** – **3b** and [**1b**]$^{\cdot+}$ – [**3b**]$^{\cdot+}$.

				[**1b**]$^{\cdot+}_{calc}$				[**2b**]$^{\cdot 2+}_{calc}$				[**3b**]$^{\cdot+}_{calc}$
	1a	**1b**	**1b$_{calc.}$**	.	**[2a]$^{+}$**	**[2b]$^{+}$**	**[2b]$^{+}_{calc.}$**	.	**3a**	**3b**	**3b$_{calc.}$**	.
C1 - C2	1.365(3)	1.369(3)	1.388	1.392	1.376(3)	1.376(9)	1.389	1.385	1.397(3)	1.387(6)	1.406	1.405
C1 - N3	1.349(3)	1.352(3)	1.359	1.349	1.351(3)	1.341(8)	1.358	1.358	1.360(3)	1.370(5)	1.370	1.372
C2 - N1	1.365(3)	1.372(3)	1.374	1.377	1.363(3)	1.376(8)	1.377	1.376	1.362(3)	1.365(5)	1.373	1.375
N1 - N2	1.311(3)	1.310(3)	1.314	1.302	1.327(2)	1.318(7)	1.331	1.325	1.327(3)	1.327(5)	1.331	1.321
N2 - N3	1.346(3)	1.359(2)	1.363	1.377	1.330(2)	1.325(7)	1.328	1.329	1.338(3)	1.339(5)	1.339	1.339
C2 - C3	1.461(3)	1.453(3)	1.452	1.443	1.453(3)	1.452(8)	1.443	1.451	1.455(3)	1.457(6)	1.450	1.448
N3 - C14	1.436(3)	1.442(3)	1.433	1.435	1.451(3)	1.452(8)	1.444	1.446	1.453(3)	1.437(6)	1.439	1.441
N1 - C13	-	-	-	-	1.466(3)	1.452(8)	1.459	1.461	1.470(3)	1.455(5)	1.459	1.462
Au1 - C1	-	-	-	-	-	-	-	-	1.982(2)	1.992(5)	1.973	1.967
Au1 - Cl1	-	-	-	-	-	-	-	-	2.284(2)	2.288(2)	2.308	2.294
Fe1 - Cp_{cent}[1]	1.652(2)	1.643(2)	1.629	1.691	1.645(5)	1.639(2)	1.629	1.705	1.648(3)	1.642(2)	1.626	1.696
Fe1 - Cp'_{cent}[1,2]	1.653(2)	1.644(2)	1.634	1.699	1.649(3)	1.650(1)	1.641	1.703	1.651(3)	1.642(2)	1.637	1.698
Au1 - Fe1[1]	-	-	-	-	-	-	-	-	4.257(4)	4.244(2)	4.146	4.019

[1] Measured with the program Diamond 3.1. [2] Cp' = unsubstituted Cp-ring

Table S8: Selected measured bond angles in ° of compounds **1a** – **3b** and optimized structures (BP86) of **1b** – **3b** and [**1b**]$^{\cdot+}$ – [**3b**]$^{\cdot+}$.

	1a	**1b**	**1b$_{calc.}$**	**[1b]$^{\cdot+}_{calc.}$**	**[2a]$^{+}$**	**[2b]$^{+}$**	**[2b]$^{+}_{calc.}$**	**[2b]$^{\cdot2+}_{calc.}$**	**3a**	**3b**	**3b$_{calc.}$**	**[3b]$^{\cdot+}_{calc.}$**
C1 - C2 - N1	107.8(2)	108.3(2)	107.6	107.9	104.7(2)	103.9(5)	103.9	104.5	106.4(2)	105.7(4)	105.9	106.5
C2 - C1 - N3	105.2(2)	104.9(2)	104.9	104.8	105.6(2)	106.2(5)	106.1	105.9	102.8(2)	104.1(4)	103.0	102.7
C1 - N3 - N2	110.6(2)	110.8(2)	110.6	110.5	113.1(2)	113.1(5)	112.7	112.4	115.1(2)	113.8(4)	114.9	114.4
C2 - N1 - N2	109.1(2)	109.1(2)	109.6	109.4	113.1(2)	113.0(5)	113.0	112.6	112.9(2)	113.4(4)	113.0	112.3
N1 - N2 - N3	107.2(2)	106.9(3)	107.1	107.4	103.5(2)	103.8(5)	104.2	104.7	102.8(2)	103.1(3)	103.2	104.1
C1 - Au1 - Cl1	-	-	-	-	-	-	-	-	178.1(2)	176.5(2)	178.1	176.8

Table S9: Selected angles of mean planes[1] of the different rings in ° of compounds **1a** – **3b** and optimized structures (BP86) of **1b** – **3b** and [**1b**]$^{\cdot+}$ – [**3b**]$^{\cdot+}$.

	1a	**1b**	**1b$_{calc.}$**	**[1b]$^{\cdot+}_{calc.}$**	**[2a]$^{+}$**	**[2b]$^{+}$**	**[2b]$^{+}_{calc.}$**	**[2b]$^{\cdot2+}_{calc.}$**	**3a**	**3b**	**3b$_{calc.}$**	**[3b]$^{\cdot+}_{calc}$**
Trz - Ar	81.8(7)	87.3(7)	81.9	79.4	81.5(7)	71.3(2)	85.7	81.7	83.5(7)	81.9(1)	86.6	88.1
Cp - Trz	15.1(8)	14.0(8)	2.9	5.8	40.1(7)	19.2(2)	19.9	18.3	22.9(8)	23.5(1)	28.6	32.0
Cp - Cp'[2]	1.8(1)	2.9(9)	1.0	7.0	0.1(1)	2.1(3)	2.1	4.3	1.2(1)	1.9(2)	0.4	8.0
Cp - Ar	86.4(7)	75.6(8)	80.4	73.8	44.8(8)	87.6(2)	76.2	84.3	77.5(8)	75.7(2)	69.2	65.8
C3 - Cp$_{cent}$ - Cp'$_{cent}$ - C8[2,3]	15.2(2)	0.3(2)	0.5	-1.8	1.3(2)	0.8(4)	1.4	0.7	5.9(2)	3.1(3)	2.1	4.2

[1] Measured with the program Diamond 3.1. [2] Cp' = unsubstituted Cp-ring [3] Arrangement of the Cp-rings to each other.

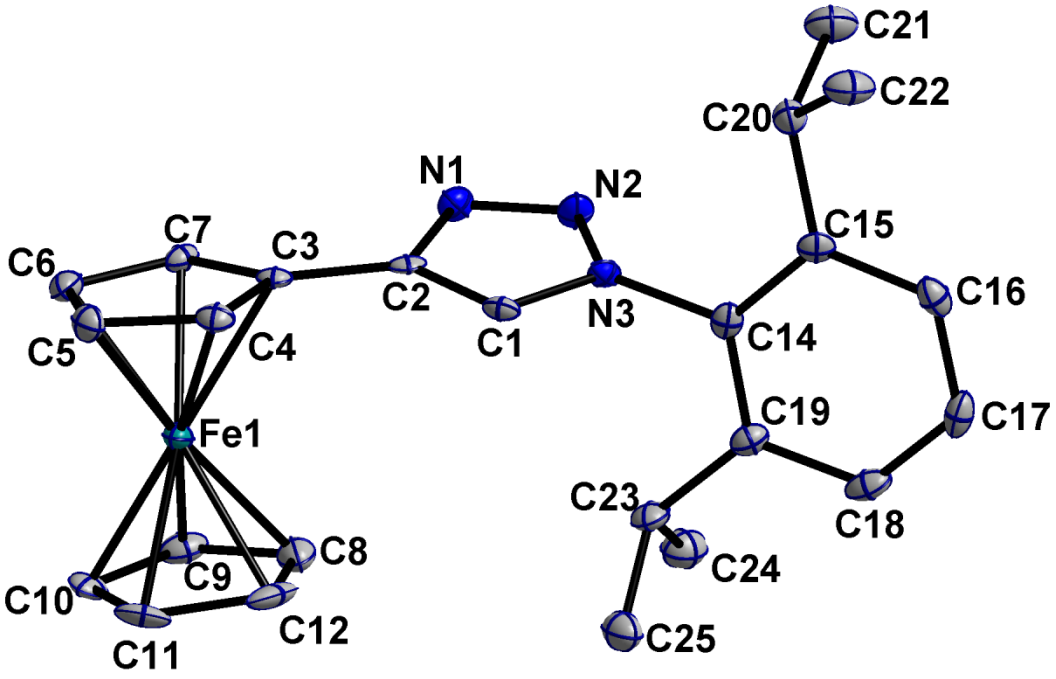


Figure S24: Crystal structure of **1a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

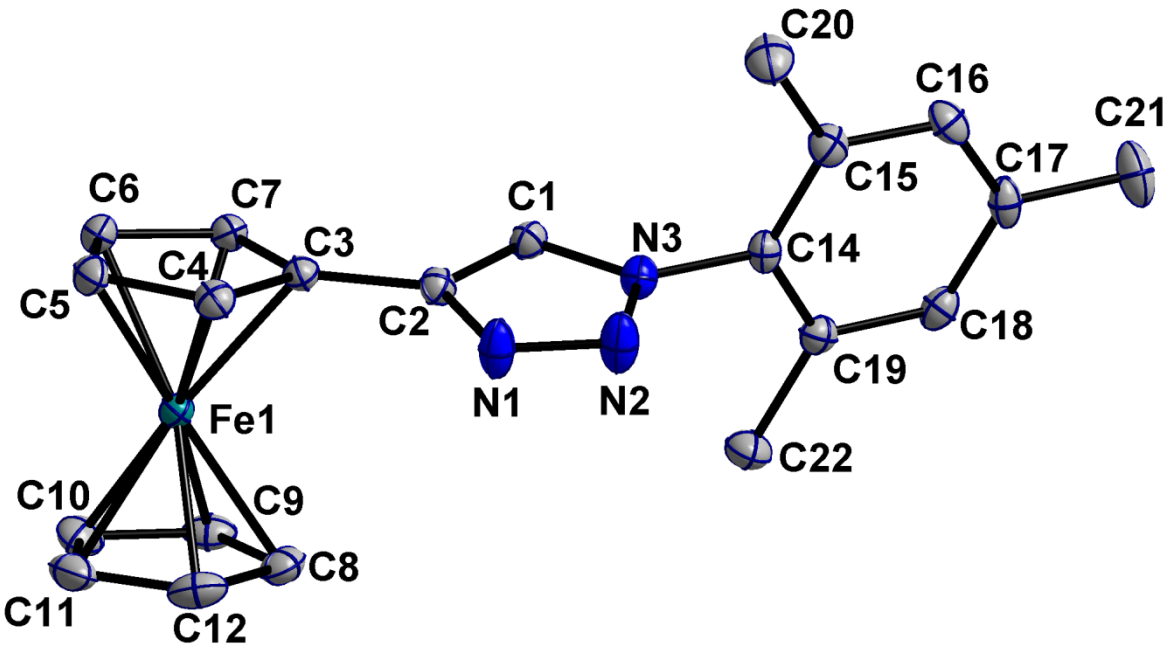


Figure S25: Crystal structure of **1b**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

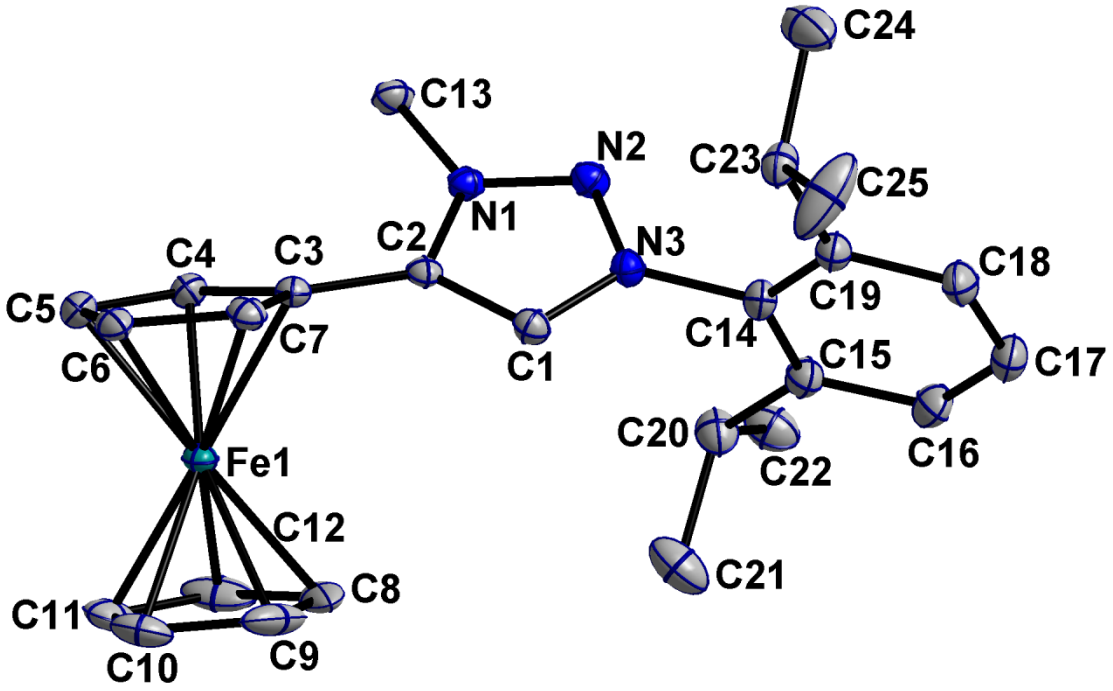


Figure S26: Crystal structure of **[2a]**$^{+}$. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and anions have been omitted for clarity.

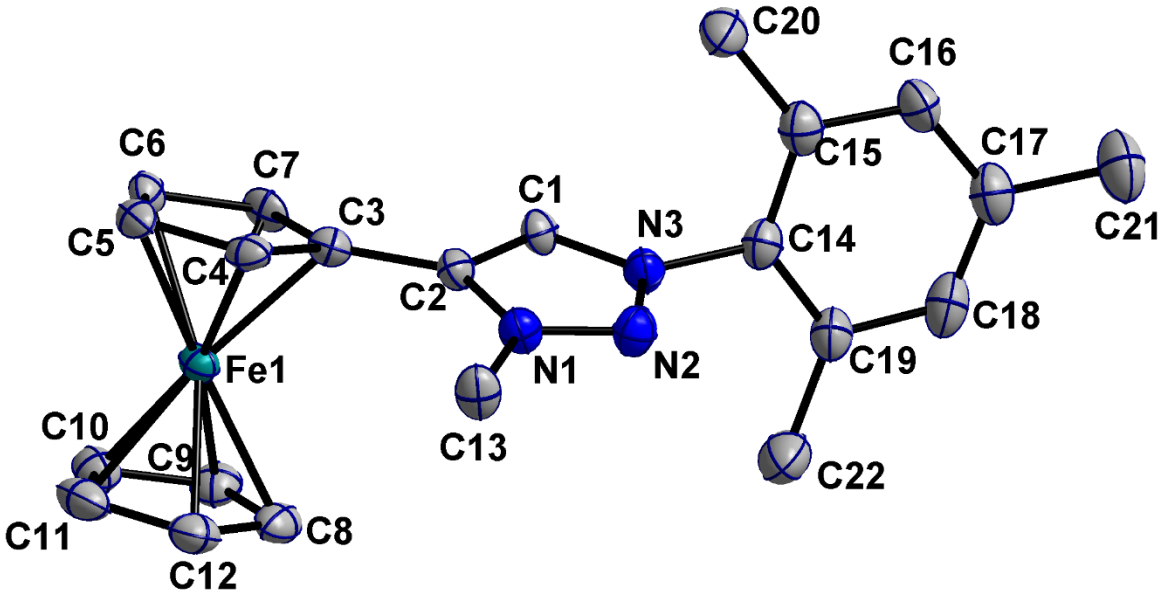


Figure S27: Crystal structure of **[2b]**$^{+}$. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and anions have been omitted for clarity.

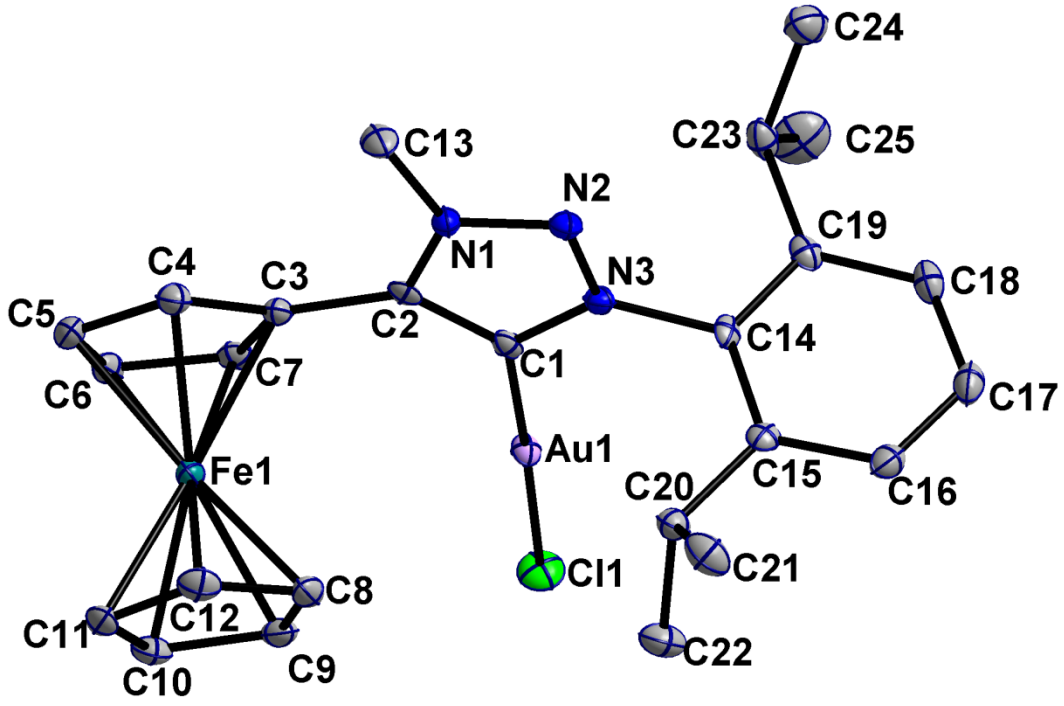


Figure S28: Crystal structure of **3a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

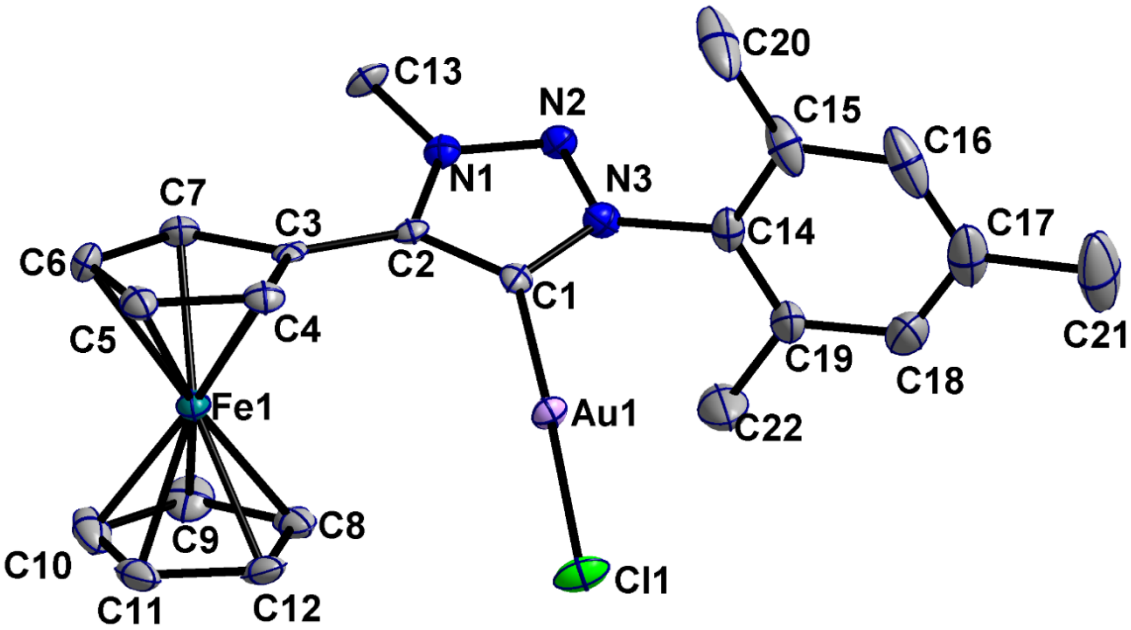


Figure S29: Crystal structure of **3b**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

DFT calculations

Table S10: Main absorption transitions and corresponding contributions of different molecular orbitals for **1b** and [**1b**]$^{\bullet+}$.

Compound	**Main contributing excitation (%)**	**Transition energy / nm**	**Oscillator strength**	λ_{exp} **/ nm**	ε_{exp} **/ M^{-1}cm^{-1}**
1b	-			217	34740
	-			226	36400
	HOMO -3 → LUMO +3 (15)	244.0	0.207	269	13180
	HOMO -2 → LUMO +3 (14)				
[1b]$^{\bullet+}$	-			217	30600
	-			225	29250
	HOMO -6(β) → LUMO +1(β) (15)	232.0	0.184	258	15500 sh
	HOMO -14(β) → LUMO (β) (18)				
	HOMO -2(β) → LUMO +1(β) (29)	287.8	0.094	289	12870 sh
	HOMO -2(β) → LUMO (β) (70)	591.9	0.034	732	350

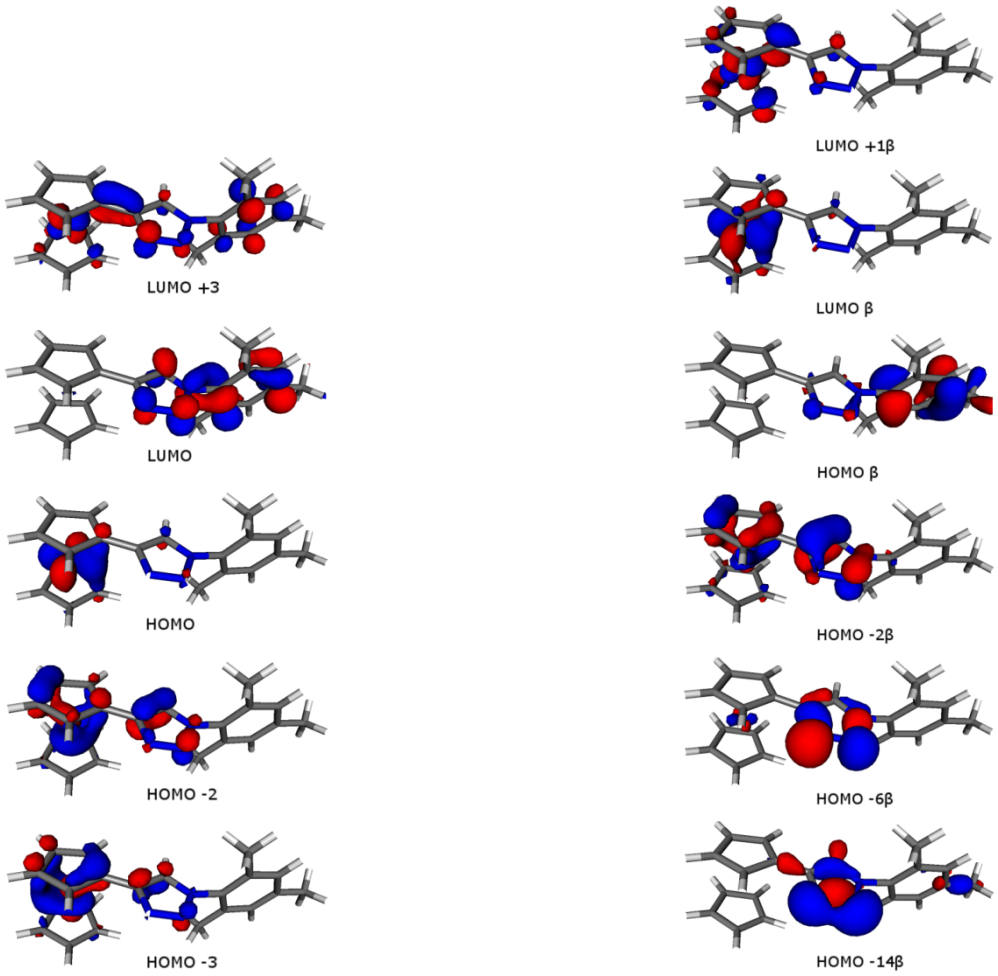


Figure S30: Contributing orbitals of **1b** (left) and [**1b**]$^{\bullet+}$ (right) for the main absorption transitions.

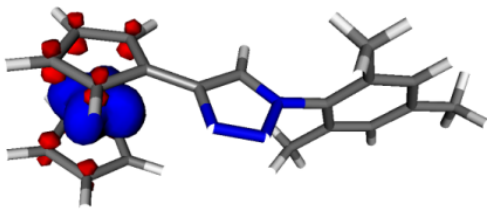


Figure S31: Spin-density distribution of [**1b**]$^{\bullet+}$.

Table S11: Main absorption transitions and corresponding contributions of different molecular orbitals for **[2b]$^{+}$** and **[2b]$^{\cdot 2+}$**.

Compound	**Main contributing excitation (%)**	**Transition energy / nm**	**Oscillator strength**	**λ_{exp} / nm**	**ε_{exp} / M^{-1}cm^{-1}**
[2b]$^{+}$	-			217	22770
	-			226	23310
	HOMO -7 → LUMO (67)	271.8	0.069	273	14650
	HOMO -6 → LUMO (27)	305.9	0.099	365	1110 sh
	HOMO -4 → LUMO (45)				
	HOMO → LUMO (62)	438.7	0.004	449	610 sh
[2b]$^{\cdot 2+}$	-			217	21360
	-			225	18790
	HOMO -2(α) → LUMO +2(α) (33)	250.9	0.118	262	22810
	HOMO -2(β) → LUMO +3(β) (14)				
	HOMO -2(β) → LUMO +1(β) (27)	272.3	0.112	292	16370 sh
	HOMO -2(β) → LUMO (β) (50)	448.8	0.002	643	590
	HOMO -4(α) → LUMO +1(α) (19)				

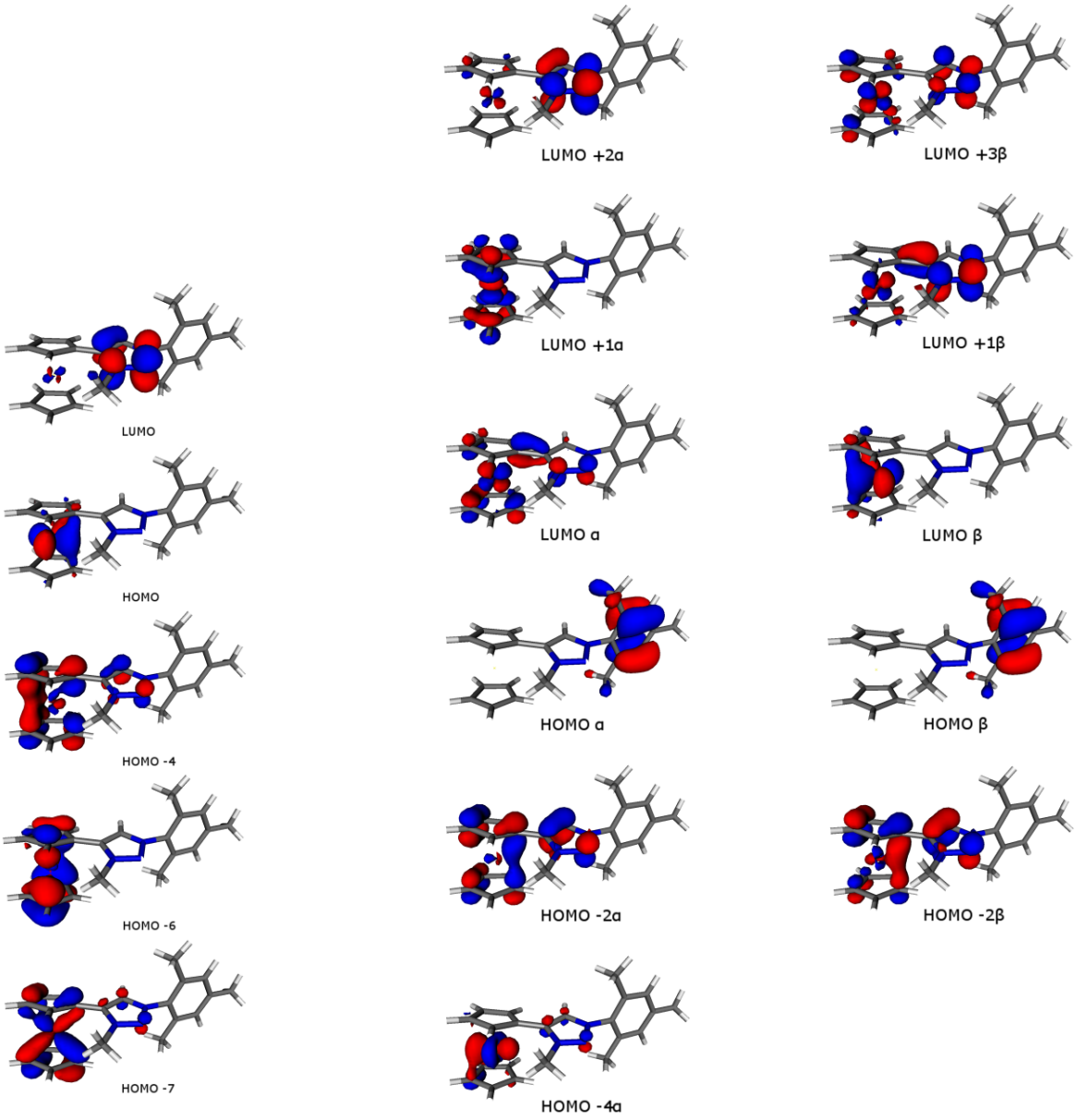


Figure S32: Contributing orbitals of [**2b**]$^{+}$ (left) and [**2b**]$^{\bullet 2+}$ (right) for the main absorption transitions.

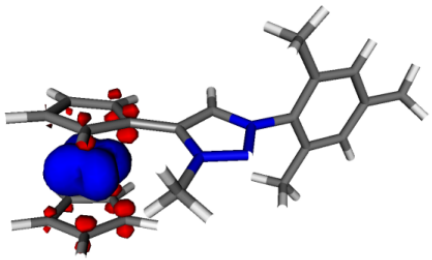


Figure S33: Spin-density distribution of [**2b**]$^{\bullet 2+}$.

Table S12: Main absorption transitions and corresponding contributions of different molecular orbitals for **3b** and [**3b**]$^{\bullet+}$.

Compound	**Main contributing excitation (%)**	**Transition energy / nm**	**Oscillator strength**	λ_{exp} **/ nm**	ε_{exp} **/ M^{-1}cm^{-1}**
3b	-			212	18271
	HOMO -5 → LUMO (20)	280.8	0.091	277	7098
	HOMO → LUMO +1 (18)				
	HOMO → LUMO +5 (27)				
	HOMO → LUMO (70)	387.7	0.020	364	763
	HOMO -1 → LUMO +4 (35)	491.0	0.002	449	315
	HOMO → LUMO +1 (27)				
	HOMO → LUMO +5 (22)				
[3b]$^{\bullet+}$	-			212	13952
	HOMO -5(β) → LUMO +1(β) (20)	273.2	0.078	262	9850
	HOMO -4(β) → LUMO +2(β) (18)				
	HOMO -12(α) → LUMO (α) (35)	426.2	0.014	405	752 sh
	HOMO -2(β) → LUMO (β) (79)	635.9	0.018	713	333

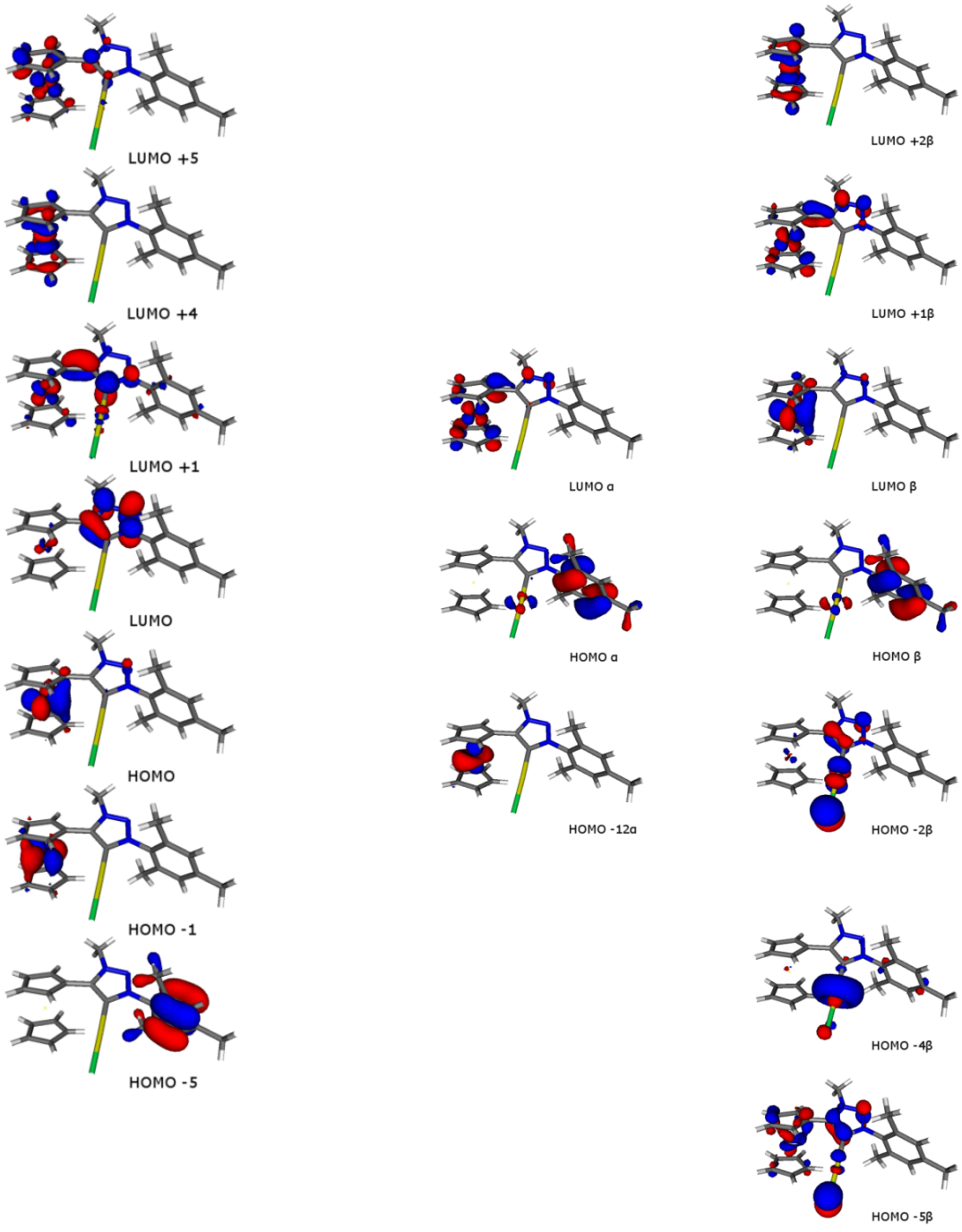


Figure S34: Contributing orbitals of **3b** (left) and $[\mathbf{3b}]^{\bullet+}$ (right) for the main absorption transitions.

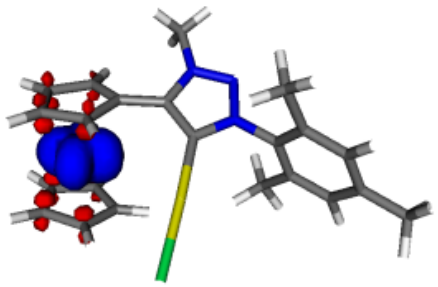


Figure S35: Spin-density distribution of [**3b**]$^{\bullet+}$.

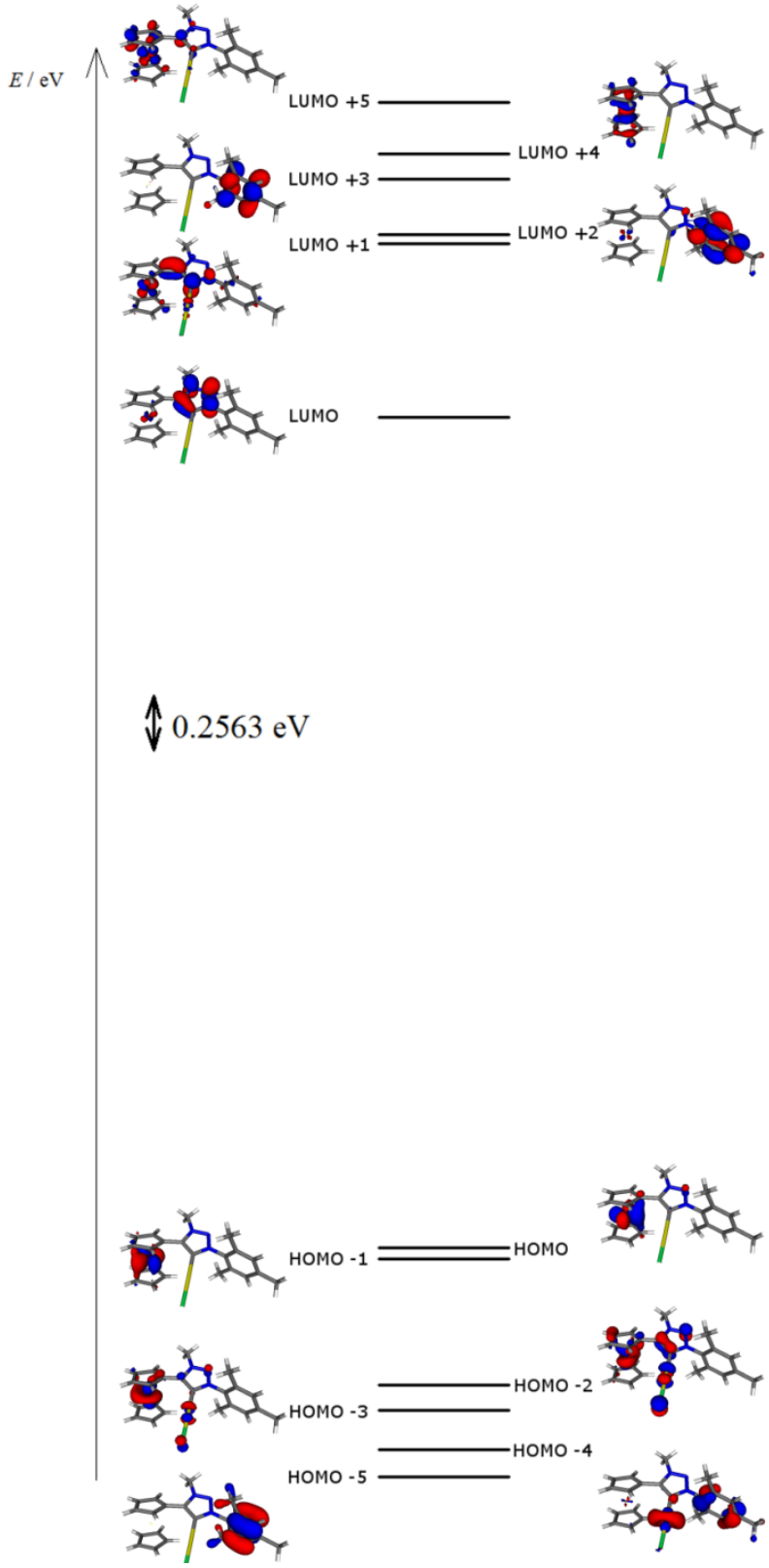


Figure S36: Molecular orbital scheme of complex **3b**. Canonical orbitals (B3LYP).

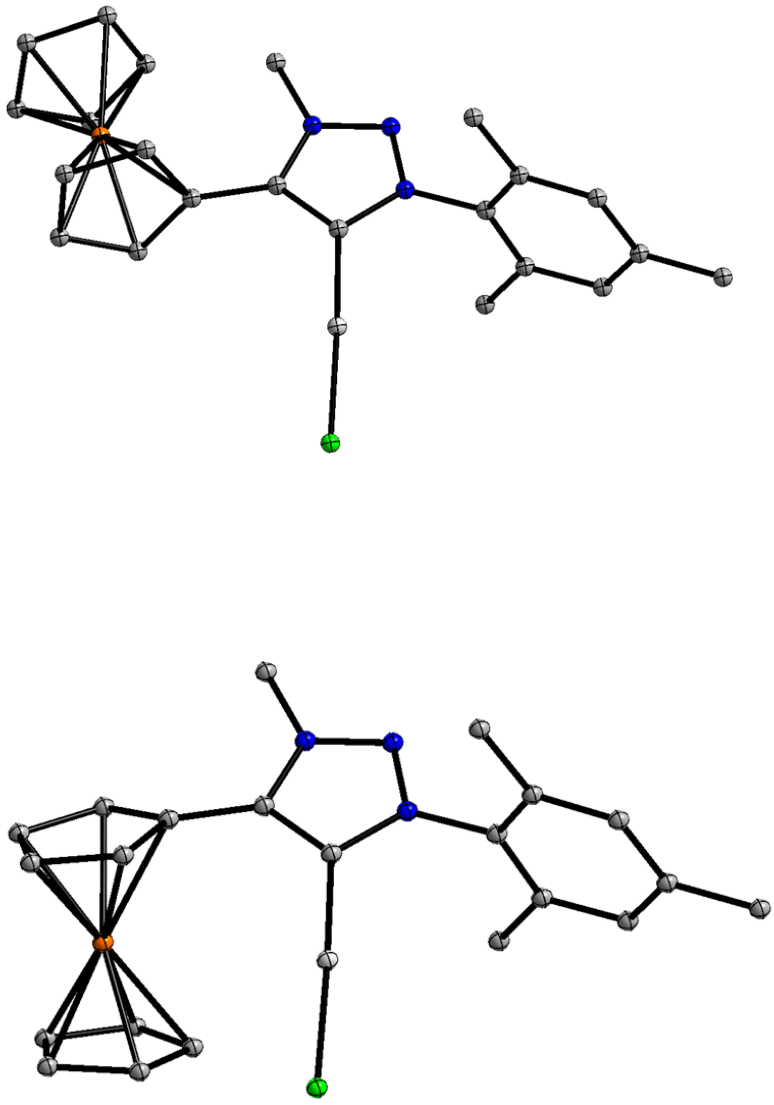


Figure S37: Rotated structure of [3b]•+ used as a starting point for DFT optimization (top) and structure obtained after geometry optimization (below).

Table S13: Geometry coordinates of **1b**.

Fe	-0.30741763765462	5.71749052011116	1.03981977152970
N	1.47152071218835	3.47174393548274	3.71511039003431
N	1.96280587883812	2.25903196157638	3.83442898599711
N	2.64891675597120	1.98803227944359	2.68853840173969
C	3.29063994616213	0.72221728607021	2.48742756664970
C	2.61785681865905	-0.25889048197539	1.74486031399632
C	4.56147666592047	0.51235267664582	3.04891024058445
C	4.52958057957816	-1.74447570178452	2.10223400559022
C	2.59087833874300	3.04329258616388	1.83486973842203
H	3.07685474815586	3.02945869887808	0.86719559772183
C	1.82769847388724	3.99611647178890	2.49574502605807
C	1.25308161516601	-0.00057245718096	1.16495965730091
H	0.56370742754462	0.39257331679166	1.92574569347905
H	0.82701807935150	-0.92420229512317	0.75519312953709
H	1.29663565865028	0.74137766129649	0.35330979932245
C	-2.07520136076473	4.82687774133268	1.53073164167616
H	-2.44368363613363	4.68158531517986	2.54222959113337
C	5.24562661009742	1.58965247290740	3.84579608022105
H	6.25999413025779	1.27918554762350	4.12366819191612
H	4.68794380197962	1.81574868863090	4.76631108411082
H	5.31364635774813	2.52777443225070	3.27548146169533
C	5.20401284103211	-3.07620750097909	1.90018211482336
H	4.58598943512593	-3.74836099852914	1.29143910680674
H	5.39890852786949	-3.56900242810936	2.86460838524818

H	6.17585270543858	-2.95459430501244	1.39871883888528
C	5.16172691476267	-0.73271586685217	2.84030976887754
H	6.15075170964804	-0.91651815670330	3.26665049374550
C	3.26254997441843	-1.48953181242547	1.56482939490766
H	2.75538873212753	-2.26997404115929	0.99311388904462
C	0.36527263112196	7.39352647870875	1.99017496435823
H	-0.23882699154260	8.25474206180564	2.26142010327009
C	-2.30408617598501	5.97872751081274	0.70435229529814
H	-2.87969209287911	6.85799247758163	0.98001598554778
C	-0.94456028212142	4.50865649807741	-0.47290091825122
H	-0.31001826997599	4.08085153489520	-1.24408741090813
C	-1.23639207281784	3.91965320933546	0.80211884553283
H	-0.84691217987857	2.97587440192485	1.17424368038837
C	1.40949165173151	5.31588187830373	2.05741143838923
C	1.05469405723062	7.20576752474073	0.74588935822950
H	1.06530117242419	7.89889666521648	-0.09057073089866
C	1.69617019091827	5.92475766062151	0.78165824204581
H	2.27948575367771	5.48004588809418	-0.01975229651318
C	0.57785139358365	6.23040505346087	2.79913827197849
H	0.17323338168470	6.04770072318165	3.78967935149126
C	-1.60524946932166	5.78241903420898	-0.53383289352498
H	-1.55971350261917	6.48646585269050	-1.36007664748823

Table S14: Geometry coordinates of [**1b**]$^{\bullet+}$.

Fe	-0.35817884777637	5.72848691216163	1.02504098022157
N	1.51334629355179	3.46167603217408	3.65208897077222
N	1.99258677334752	2.25909681183244	3.79003109086867
N	2.70261722138436	1.96487152944684	2.64736510346112
C	3.34570525444160	0.69260837211378	2.47921340637819
C	2.70464871152581	-0.28081521401070	1.69949880704892
C	4.58112075095925	0.47746829861082	3.11307098014311
C	4.58328127588984	-1.77884671453681	2.16419417511253
C	2.65880253888320	3.00131433952214	1.78478004305913
H	3.16407252263165	2.98054692361203	0.82657011787576
C	1.89338067823705	3.96848959566003	2.42948310569825
C	1.37540073879364	-0.01537700056312	1.04480678779831
H	0.64955616409602	0.39586976834476	1.76112941741506
H	0.96081113921114	-0.94129228996274	0.62919595369251
H	1.47071739445363	0.70802894755946	0.22049156025687
C	-2.21318788917287	4.92145510174884	1.57936690859319
H	-2.52347079489474	4.74614633628002	2.60519064011681
C	5.23001469276829	1.54963493977341	3.94502792700185
H	6.22734379756155	1.23237977696231	4.27139256494809
H	4.63102440273041	1.77582295428188	4.83934405313063
H	5.33446259810139	2.48867522656920	3.38139935266422
C	5.25801573188568	-3.11457097698723	2.00014823932332
H	4.66765261442563	-3.78560209615471	1.36378360693416
H	5.40221631416698	-3.60350744032996	2.97523059670226

H	6.25439655114607	-2.99893711733420	1.54807766763623
C	5.18144848497575	-0.77182420118171	2.93653401912797
H	6.14397296236614	-0.96280229645611	3.41624190515516
C	3.34981727493954	-1.51531423208035	1.55672283550567
H	2.86911184646667	-2.29271192770107	0.95914843224538
C	0.47001418905815	7.36417296192649	1.93957675907229
H	-0.09577292815814	8.24189844608710	2.23693030141459
C	-2.36135850479496	6.14765226439283	0.84799513607338
H	-2.82149641381775	7.05892116482525	1.21790730221014
C	-1.27033645365123	4.61686569284914	-0.51074818706946
H	-0.74103455483027	4.17205784409732	-1.34834984433723
C	-1.55516707723323	3.98308754302143	0.73258566653702
H	-1.24649889018252	2.98144001874866	1.02093757773749
C	1.50597822238231	5.28852301236730	1.99426336756108
C	1.07996279736596	7.14013196543706	0.65972588329546
H	1.06238857587939	7.81654641505431	-0.18941542420867
C	1.69871143589318	5.84984470413442	0.68733027385596
H	2.22107810904875	5.37617471560877	-0.13862540160451
C	0.71493290262179	6.21357415078718	2.75377176476651
H	0.36323650133651	6.05148056034788	3.76768627557883
C	-1.77509635056054	5.95817170740148	-0.44947669896683
H	-1.70941875745398	6.70031647355841	-1.23936400080321

Table S15: Geometry coordinates of **[2b]$^{+}$**.

Fe	8.83843066520552	1.86413593227904	2.28234409509762
N	10.57878374644798	2.48377792244123	5.63214026906768
C	9.86693845854015	0.94643812882426	3.76225321247593
C	9.31232494826992	0.82503621711271	6.25683985130742
H	8.69315014819543	-0.05484669309259	6.37391776896130
N	10.41930257492051	2.64164426901295	6.94372321314827
C	9.91967792392548	1.38034187280243	5.13774449034195
C	9.08025152164496	-0.12593385808781	1.85721976972167
H	8.46093555677578	-0.70855650236272	1.18186760005899
C	7.70771270597786	2.00971895046066	10.43472072982285
H	6.82198480195824	2.53759306746028	10.79442610613829
N	9.64375229829065	1.62568930106533	7.30290048183771
C	8.83087903554857	0.07747359330950	3.24825741770385
H	8.00040743671631	-0.32940123885088	3.81790161042414
C	9.55787256441205	0.51349125906227	10.83580565181424
H	10.12619770830144	-0.12952029170614	11.51065700594687
C	9.23414528976845	1.47970907427840	8.67982312598843
C	8.42591926950413	1.18499766626887	11.31387004526725
C	8.09210990059727	2.17769639643220	9.10213027773498
C	6.98108261520628	2.66898662480595	2.57169742624104
H	6.19150406951151	2.23357228863678	3.17744617662604
C	9.98994429118653	0.64264025301572	9.51033128965204
C	7.32256616631951	3.06841634726463	8.16539061551058
H	6.42072726998679	3.45301829678614	8.65514631698873

H	7.01208346445009	2.52952572184654	7.25761545998176
H	7.92922303728990	3.92867467816706	7.84508908960103
C	11.20901983541745	-0.08027329623652	9.00633453511021
H	11.94194531938379	0.61848499720503	8.57691887645695
H	10.95135981974029	-0.80698436794761	8.22103589460851
H	11.69535908479436	-0.62645791701068	9.82270210874539
C	11.37346399367759	3.46424627507579	4.90122234887737
H	11.49006607854878	4.34193642576157	5.54193835132497
H	10.83917545465854	3.72518934716599	3.98117197489033
H	12.35454273207650	3.03954274453525	4.66010711154339
C	7.21354530486599	2.41536424212844	1.17902855061856
H	6.63406696621266	1.74920878446247	0.54634024338550
C	7.98337241057924	1.03180893116265	12.74404600026979
H	8.63651792326327	0.34274578779428	13.29365434997046
H	6.95347400133604	0.64829257777655	12.79699771770602
H	7.99214376342655	2.00223315714553	13.26244244346312
C	8.37020673852416	3.16302700995730	0.77787464884829
H	8.81839033585588	3.16327385390512	-0.21154012964443
C	10.74641280876806	1.28042347759283	2.66005971135127
H	11.63453036670767	1.90111317091718	2.69994046103320
C	10.25566811379937	0.60910192502333	1.49769937820741
H	10.68879593215878	0.67518907155681	0.50402867283617
C	8.85223902589623	3.88129007464327	1.92142014895615
H	9.71999294021449	4.53500677031607	1.94230063232987
C	7.99288552431688	3.57537072696949	3.02840069856562

H	8.09855805682617	3.95099695286704	4.04313617308522

Table S16: Geometry coordinates of [**2b**]$^{\bullet 2+}$.

Fe	8.82400849876602	1.84497810490141	2.25290926668705
N	10.56718143235176	2.54726458564646	5.65639287099956
C	9.88870122270486	0.99732406145305	3.77729324115110
C	9.31545614436213	0.86686832975604	6.26589226946421
H	8.70143387050064	-0.01857021815361	6.37542601892232
N	10.40372001681123	2.68729351933012	6.96391180750360
C	9.91989422104585	1.43960987409077	5.15925092350927
C	9.24974378002493	-0.22385983015625	1.90907155721039
H	8.68409266758923	-0.86557721096837	1.23937515010893
C	7.75483717861825	2.06047928214148	10.47955565025413
H	6.90371922334891	2.62598200960385	10.86428910367728
N	9.63868516495696	1.66034797874324	7.31931811110965
C	8.92538644946855	0.04415877464414	3.26853542840540
H	8.09705597220679	-0.38905760519876	3.82177108165209
C	9.52228443246836	0.45131479658210	10.81707593120113
H	10.06102116376778	-0.24020856054091	11.46755430990616
C	9.23251990792869	1.49765502943521	8.69712116106877
C	8.43378764378985	1.17063462712511	11.32639425417858
C	8.13540047250917	2.24745608993631	9.14903488371844
C	6.89917148536800	2.59004138312986	2.47012342362649
H	6.12202867988138	2.10816327256655	3.05650277393272
C	9.94974001853673	0.59423644044012	9.49211028501076
C	7.40610120421760	3.20522508890839	8.24686774910382
H	6.51969864663754	3.60618946966991	8.75106427795358

H	7.07234895396194	2.71425524691210	7.31983848720355
H	8.04610471853570	4.05404777179563	7.96266287484646
C	11.12303108539846	-0.17928869962803	8.95582103193262
H	11.86989501687701	0.48557929329190	8.49746032463316
H	10.81355470735054	-0.90624560476470	8.18933121007441
H	11.61348735910042	-0.73584259938369	9.76239685294866
C	11.38002580430705	3.53218415916832	4.94593270654085
H	11.53812597322321	4.37608883450120	5.62187338474776
H	10.84314795873274	3.86302713325885	4.05038723143310
H	12.34166107145625	3.08353572392961	4.67303480407334
C	7.13619183121361	2.39420973312828	1.07481317656067
H	6.59424479871133	1.71004539478558	0.42750756990839
C	7.99749468086016	1.00089666399097	12.75569847304988
H	8.60265532778028	0.24618173077762	13.27258171308840
H	6.94190340993432	0.69614459285025	12.80977519096768
H	8.08657501722750	1.95004106761934	13.30510386323266
C	8.25506949805415	3.18770386197403	0.69573606951693
H	8.71336401127202	3.20961661553898	-0.28934861732146
C	10.78701070754497	1.31743492077724	2.68826488385590
H	11.63074012373667	1.99809585443116	2.71263830947252
C	10.38606458674447	0.55303575875646	1.55635781594014
H	10.83929416750537	0.60734368446997	0.57030131463504
C	8.72450073396073	3.88307904955769	1.85126436439797
H	9.57136183948139	4.56282788854554	1.88119874904607
C	7.88142415799677	3.51868859851793	2.95715689251706

H	7.95869296117175	3.89381403211154	3.97388979234283

Table S17: Geometry coordinates of **3b**.

Au	5.53820631060814	-5.39819762115826	6.62296015428634
Fe	2.23005951636722	-4.12938875040261	4.47007719893230
Cl	5.14333867066853	-7.37861798661199	7.73976150370242
C	2.73152756930840	-3.29721871511846	6.25224179791642
H	3.15019779567339	-3.81948796713381	7.10765675231186
N	5.73553488525262	-1.83500928724437	4.46289447054768
C	9.00749183090863	-3.47285598046130	6.69366350471750
C	10.21951469192780	-4.11451000167558	6.97605605693372
H	10.77020036507299	-3.82479474357028	7.87348809836657
N	7.06180728828046	-3.25196546773237	5.24295626694233
N	7.03443456410029	-2.11528688164532	4.53559884400222
C	7.99025282282227	-5.31211476253953	3.48253080123554
H	8.56295053807465	-6.01325785359386	2.86432944918648
H	7.69381189953105	-4.45758102793696	2.85780219430064
H	7.06534678037433	-5.81571335546310	3.80586264400667
C	3.50257135161283	-2.71203777809946	5.17726889305775
C	1.24335657779653	-2.36281571092077	4.73573936216849
H	0.32194539924004	-2.07024955899743	4.24072580741842
C	1.20023535231546	-5.88629554167857	4.33929475869074
H	0.34730923915206	-6.16035096231859	4.95361435715247
C	5.33232824502679	-0.61885592431706	3.76503973096496
H	6.20740376427024	0.03356649647427	3.70224908433815
H	4.53533111293072	-0.13090391229198	4.33496094976396
H	4.97782386068294	-0.86330900615734	2.75676508373591

C	1.34692347947724	-3.07149265092393	5.97764775281320
H	0.51707081552997	-3.40821883786636	6.59207696092414
C	8.79154545057491	-4.87890458098912	4.67832034231340
C	4.94848217476642	-2.76814636008145	5.09105638744481
C	8.32745352025843	-3.87118811719068	5.53648274562431
C	12.03770391142587	-5.79832947268243	6.47146836643060
H	12.47508954485360	-5.40190054209695	7.39646389954258
H	12.76740800864192	-5.66028450706693	5.65953073140725
H	11.89563747572032	-6.88229282905763	6.59586510409167
C	5.83290256716072	-3.72295630194831	5.62366548224221
C	2.57806983632494	-6.13686016269804	4.65150300078967
H	2.95969489164567	-6.62590335995855	5.54382529347346
C	10.73372864823301	-5.11820678679604	6.14643679459943
C	8.43716895666454	-2.42579739756914	7.60954434153216
H	9.11237771902780	-2.23982755811716	8.45294346312758
H	7.46435548876860	-2.74983174552644	8.01086449434322
H	8.26956975181832	-1.47479612584607	7.08355290533526
C	3.37511181040635	-5.57984241235433	3.59926091451900
H	4.46110514231098	-5.56660809170741	3.57062013438275
C	2.56587130700998	-2.14354671993804	4.23231697296476
H	2.80916191512854	-1.66190825161557	3.29124590063898
C	2.49578252366370	-4.98543340490052	2.63546168669229
H	2.79685484265677	-4.46078753386917	1.73310829156143
C	10.00648275600882	-5.48714665024301	5.00521878855494
H	10.39046751806643	-6.27523883657463	4.35362909340036

C	1.14850549268328	-5.17514868858839	3.09329153343655
H	0.24940401917451	-4.81759977319894	2.59918085313437

Table S18: Geometry coordinates of [**3b**]$^{\bullet+}$.

Au	5.49870084805830	-5.37748761300047	6.50839578225200
Fe	2.23486801936969	-4.18869200297785	4.48626240034898
Cl	4.99289064496153	-7.38830013015277	7.49084701557495
C	2.76933757941875	-3.20818041579631	6.22775400588426
H	3.18328612811061	-3.69078547587327	7.10833727707489
N	5.78263552085774	-1.75050220169582	4.47085910781293
C	8.99819089205226	-3.49194156577742	6.72544824429216
C	10.20049026877178	-4.15222458422429	7.00500109127794
H	10.73022777390017	-3.90786779966879	7.92804969481921
N	7.08890039740133	-3.19887601608512	5.23925310344481
N	7.06704348686388	-2.04176319744874	4.56636304462042
C	8.05784131265731	-5.16779148971470	3.39941946610751
H	8.62993733670622	-5.86879479711085	2.78085227554589
H	7.81757444570692	-4.28466158102220	2.78987228974058
H	7.10444937513084	-5.65096146781655	3.66714979046795
C	3.54198417951247	-2.63363265178078	5.15639952840140
C	1.29662178888198	-2.35090393632118	4.65722500399972
H	0.38425876800191	-2.08643296461184	4.13114753860653
C	1.09111874947743	-5.88410509680707	4.45510297470857
H	0.22101537210651	-6.03294893311124	5.08752245462834
C	5.39218497148314	-0.51446023555409	3.79516306978490
H	6.27448720393335	0.12891794563130	3.74726146248080

H	4.60097344763389	-0.02784118237760	4.37470397986835
H	5.04188262486214	-0.74165315959744	2.78165676226470
C	1.38382503902492	-3.01302393510500	5.92625335556575
H	0.55033333789155	-3.32354397142681	6.54887218866847
C	8.82802896053520	-4.80085834498972	4.63716348857825
C	4.98623426418674	-2.69357736932294	5.07651634990301
C	8.34898768196590	-3.83361056280445	5.53297315121342
C	12.02728566547754	-5.81307692516331	6.46139644622305
H	12.42546896376123	-5.48982224082251	7.43129705674748
H	12.78579398331092	-5.60440104121328	5.69183164000285
H	11.89034903572461	-6.90425395011925	6.49049349853208
C	5.85090380266052	-3.67111194913855	5.59576836383454
C	2.44194209365459	-6.24654312581643	4.77954186496047
H	2.78837126466787	-6.69717686996263	5.70672732641400
C	10.73189533756691	-5.11682095728971	6.14030598555239
C	8.41227141670925	-2.48286490288849	7.67333978113439
H	9.05922971946127	-2.35463102224572	8.54875869091935
H	7.41965880445012	-2.80455565787306	8.02520218088694
H	8.28541262640459	-1.50137238492309	7.19308281177226
C	3.26867325764868	-5.87395730211306	3.67911934213172
H	4.35156280618429	-5.96386960707055	3.64961006944394
C	2.62277182284655	-2.12824656476707	4.18002146434849
H	2.87923384620413	-1.69554928052921	3.21826255044255
C	2.45333474689285	-5.26803996540962	2.68244896531844
H	2.80229230860186	-4.84130847438221	1.74635068140231

C	10.03195708323374	-5.42880247597988	4.96503010719585
H	10.42988948522680	-6.18644872693865	4.28640758514251
C	1.10035088012369	-5.27470339145176	3.15363849487312
H	0.23995062972352	-4.87138844735789	2.62765919478456

Table S19: Rotated geometry coordinates of [**3b**]$^{\bullet+}$

Au	5.49870	-5.37749	6.50840
Fe	2.25844	-1.20897	4.20840
Cl	4.99289	-7.38830	7.49085
C	2.48892	-3.25630	4.39599
H	2.63758	-3.94154	3.56652
N	5.78264	-1.75050	4.47086
C	8.99819	-3.49194	6.72545
C	10.20049	-4.15222	7.00500
H	10.73023	-3.90787	7.92805
N	7.08890	-3.19888	5.23925
N	7.06704	-2.04176	4.56636
C	8.05784	-5.16779	3.39942
H	8.62994	-5.86879	2.78085
H	7.81757	-4.28466	2.78987
H	7.10445	-5.65096	3.66715
C	3.54198	-2.63363	5.15640
C	1.51252	-1.90863	6.00870
H	0.77737	-1.37766	6.60597
C	0.97310	-0.33865	2.87648

H	-0.02845	-0.70900	2.67916
C	5.39218	-0.51446	3.79516
H	6.27449	0.12892	3.74726
H	4.60097	-0.02784	4.37470
H	5.04188	-0.74165	2.78166
C	1.23741	-2.82277	4.93860
H	0.25584	-3.12856	4.58960
C	8.82803	-4.80086	4.63716
C	4.98623	-2.69358	5.07652
C	8.34899	-3.83361	5.53297
C	12.02729	-5.81308	6.46140
H	12.42547	-5.48982	7.43130
H	12.78579	-5.60440	5.69183
H	11.89035	-6.90425	6.49049
C	5.85090	-3.67111	5.59577
C	2.16755	-0.72315	2.17878
H	2.24381	-1.45154	1.37479
C	10.73190	-5.11682	6.14031
C	8.41227	-2.48286	7.67334
H	9.05923	-2.35463	8.54876
H	7.41966	-2.80456	8.02520
H	8.28541	-1.50137	7.19308
C	3.25747	-0.00597	2.75407
H	4.30246	-0.12791	2.48070
C	2.92843	-1.78464	6.13438

H	3.44157	-1.11996	6.82203
C	2.76004	0.80543	3.81212
H	3.35625	1.43344	4.46807
C	10.03196	-5.42880	4.96503
H	10.42989	-6.18645	4.28641
C	1.34312	0.60881	3.89170
H	0.67343	1.07779	4.60666

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