Supporting Information

Table of contents

X-ray crystallography

General

Table S1: Details of XRD data refinement.

Compound	2	3	5a
Empirical formula	$C_{45}H_{18}F_{15}InN_6$	$C_{45}H_{18}F_{15}GaN_6$	$C_{57}H_{45}F_{12}GaN_6O_3$
Formula weight	1042.47	997.37	1159.71
Temperature/K	100.04	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	trigonal
Space group	$P2_1/n$	Pbca	$R\bar{3}$
a/Å	10.5034(8)	25.7650(8)	24.0883(10)
b/Å	13.5594(11)	8.8371(3)	24.0883(10)
c/Å	28.179(2)	35.7783(11)	15.2527(7)
α/°	90	90	90
β/°	93.7280(10)	90	90
γ/°	90	90	120
Volume/Å^3	4004.7(5)	8146.3(5)	7664.6(7)
Z	4	8	6
D_{calc} g/cm^3	1.729	1.626	1.508
μ/mm^{-1}	0.704	1.940	0.635
F(000)	2056.0	3968.0	3552.0
Crystal size/mm^3	0.34×0.11×0.1	0.37×0.16×0.09	0.5×0.08×0.08
Radiation	MoK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$
Wavelength/Å	0.71073	1.54178	0.71073
2θ/°	2.90-50.75	4.94-136.59	3.31-63.02
Reflections collected	49555	52826	93276
Independent reflections	7365	7436	5684
R_{int}	0.0162	0.0834	0.0443
R_{sigma}	0.0096	0.0519	0.0247
Restraints	0	0	0
Parameters	604	604	239
GooF	1.092	1.044	1.046
R_1 [$I \geq 2\sigma(I)$]	0.0204	0.477	0.341
wR_2 [$I \geq 2\sigma(I)$]	0.0460	0.1127	0.0710
R_1 [all data]	0.0220	0.0679	0.0528
wR_2 [all data]	0.0469	0.1234	0.0778
Largest peak/e Å^{-3}	0.31	0.59	0.45
Deepest hole/e Å^{-3}	-0.34	-0.44	-0.40

Table S2: Details of XRD data refinement.

Compound	**12c**	**13a**
Empirical formula	$C_{57}H_{45}F_{12}FeN_6O_3$	$C_{54}H_{33}F_{12}InN_6O_3$
Formula weight	1145.84	1156.68
Temperature/K	100.01	100(2)
Crystal system	trigonal	trigonal
Space group	$R\bar{3}$	$R\bar{3}$
a/Å	24.0020(11)	23.433(3)
b/Å	24.0020(11)	23.433(3)
c/Å	15.1852(9)	15.332(5)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å^3	7576.1(8)	7291(3)
Z	6	6
D_{calc} g/cm^3	1.507	1.581
μ/mm^{-1}	3.253	0.585
F(000)	3522.0	3480.0
Crystal size/mm^3	0.6×0.06×0.02	0.5×0.03×0.03
Radiation	CuK$_\alpha$	MoK$_\alpha$
Wavelength/Å	1.54178	0.71073
2θ/°	7.21-138.40	4.81-52.58
Reflections collected	31292	48936
Independent reflections	3129	3274
R_{int}	0.1428	0.0954
R_{sigma}	0.0980	0.0385
Restraints	0	0
Parameters	239	229
GooF	1.056	1.027
R_1 [I≥2σ (I)]	0.0605	0.0308
wR_2 [I≥2σ (I)]	0.1562	0.0591
R_1 [all data]	0.0739	0.0533
wR_2 [all data]	0.1686	0.0656
Largest peak/e Å^{-3}	0.47	0.33
Deepest hole/e Å^{-3}	-0.51	-0.42

Crystal Data for 2: $C_{45}H_{18}F_{15}InN_6$ (M =1042.47 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.5034(8) Å, b = 13.5594(11) Å, c = 28.179(2) Å, β = 93.7280(10)°, V = 4004.7(5) Å^3, Z = 4, T = 100.04 K, μ(MoK$_\alpha$) = 0.704 mm^{-1}, D_{calc} = 1.729 g/cm^3, 49555 reflections measured (2.896° ≤ 2θ ≤ 50.752°), 7365 unique (R_{int} = 0.0162, R_{sigma} = 0.0096) which were used in all calculations. The final R_1 was 0.0204 (I > 2σ(I)) and wR_2 was 0.0469 (all data). The C bound H atoms were placed in their expected calculated positions and refined as riding model: C–H = 0.95–0.99 Å, with U_{iso}(H) = 1.2 U_{eq} (C) for H atoms. No constraints or restraints were applied.

Crystal Data for 3: $C_{45}H_{18}F_{15}GaN_6$ (M =997.37 g/mol): orthorhombic, space group Pbca (no. 61), a = 25.7650(8) Å, b = 8.8371(3) Å, c = 35.7783(11) Å, V = 8146.3(5) Å^3, Z = 8, T = 100(2) K, $\mu(\mathrm{CuK}_\alpha)$ = 1.940 mm^{-1}, D_{calc} = 1.626 g/cm^3, 52826 reflections measured (4.94° ≤ 2θ ≤ 136.586°), 7436 unique (R_{int} = 0.0834, R_{sigma} = 0.0519) which were used in all calculations. The final R_1 was 0.0477 (I > 2σ(I)) and wR_2 was 0.1234 (all data). The C bound H atoms were placed in their expected calculated positions and refined as riding model: C–H = 0.95–0.99 Å, with U_{iso}(H) = 1.2 U_{eq} (C) for H atoms. No constraints or restraints were applied.

Crystal Data for 5a: $C_{57}H_{45}F_{12}GaN_6O_3$ (M =1159.71 g/mol): trigonal, space group R$\overline{3}$ (no. 148), a = 24.0883(10) Å, c = 15.2527(7) Å, V = 7664.6(7) Å^3, Z = 6, T = 100(2) K, $\mu(\mathrm{MoK}_\alpha)$ = 0.635 mm^{-1}, D_{calc} = 1.508 g/cm^3, 93276 reflections measured (3.308° ≤ 2θ ≤ 63.016°), 5684 unique (R_{int} = 0.0443, R_{sigma} = 0.0247) which were used in all calculations. The final R_1 was 0.0341 (I > 2σ(I)) and wR_2 was 0.0778 (all data). The C bound H atoms were placed in their expected calculated positions and refined as riding model: C–H = 0.95–0.98 Å, with U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq} (C) for all other atoms other H atoms. No constraints or restraints were applied.

Crystal Data for 12c: $C_{57}H_{45}F_{12}FeN_6O_3$ (M =1145.84 g/mol): trigonal, space group R$\overline{3}$ (no. 148), a = 24.0020(11) Å, c = 15.1852(9) Å, V = 7576.1(8) Å^3, Z = 6, T = 100.01 K, $\mu(\mathrm{CuK}_\alpha)$ = 3.253 mm^{-1}, D_{calc} = 1.507 g/cm^3, 31292 reflections measured (7.21° ≤ 2θ ≤ 138.4°), 3129 unique (R_{int} = 0.1428, R_{sigma} = 0.0980) which were used in all calculations. The final R_1 was 0.0605 (I > 2σ(I)) and wR_2 was 0.1686 (all data). The C bound H atoms were placed in their expected calculated positions and refined as riding model: C–H = 0.95–0.98 Å, with U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq} (C) for all other atoms other H atoms. No constraints or restraints were applied.

Crystal Data for 13a: $C_{54}H_{33}F_{12}InN_6O_3$ (M =1156.68 g/mol): trigonal, space group R$\overline{3}$ (no. 148), a = 23.433(3) Å, c = 15.332(5) Å, V = 7291(3) Å^3, Z = 6, T = 100(2) K, $\mu(\mathrm{MoK}_\alpha)$ = 0.585 mm^{-1}, D_{calc} = 1.581 g/cm^3, 48936 reflections measured (4.814° ≤ 2θ ≤ 52.582°), 3274 unique (R_{int} = 0.0954, R_{sigma} = 0.0385) which were used in all calculations. The final R_1 was 0.0308 (I > 2σ(I)) and wR_2 was 0.0656 (all data). The C bound H atoms were placed in their expected calculated positions and refined as riding model: C–H = 0.95–0.99 Å, with U_{iso}(H) = 1.2 U_{eq} (C) for H atoms. No constraints or restraints were applied.

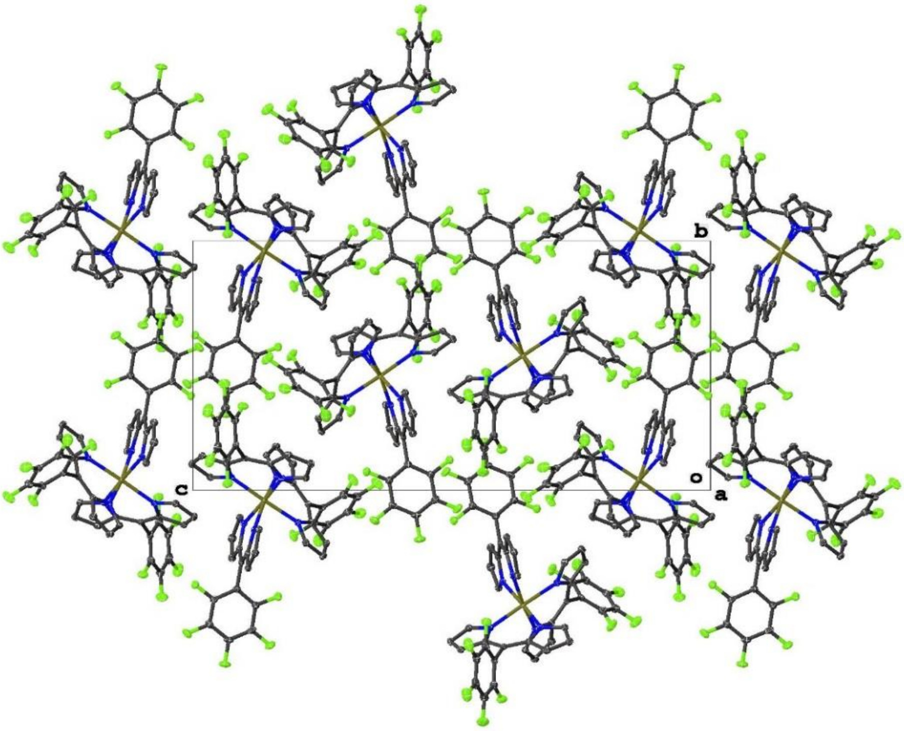


Figure S 1. View of the crystal packing of complex 2 along the a-axis. Hydrogens atoms and atom labels have been omitted for clarity.

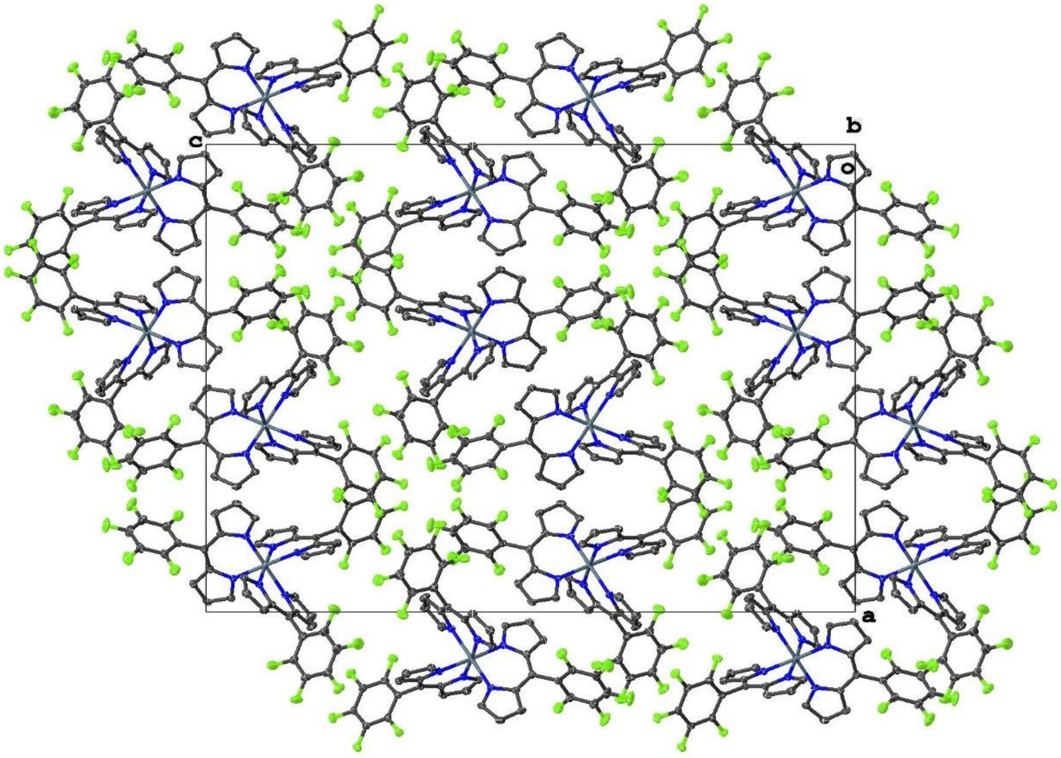


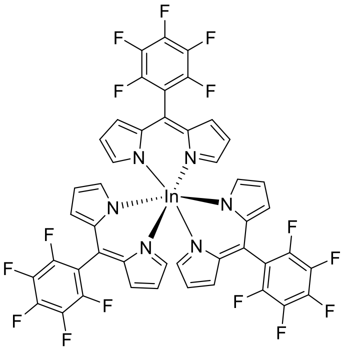
Figure S 2. View of the crystal packing of complex 3 along the b-axis. Hydrogens atoms and atom labels have been omitted for clarity.

Synthesis

General

The nomenclature and numbering (^{13}C and ^{19}F NMR spectra) are in accordance with IUPAC recommendations. THF and DMF used as solvents for the reactions were stored over molecular sieves. All liquid reagents were added through syringes. Purchased reagents were used as received without further purification. All reactions were monitored by TLC analysis. The preparative purification of mixtures by column chromatography was conducted on silica gel (60 M, 40-63 µm). The yields refer to analytically pure compounds. NMR spectra were recorded on a 400 and 500 MHz instrument, respectively. Chemical shifts are given in parts per million (ppm) relative to the resonance of the solvent. As deuterated solvents chloroform (δ = 7.26, 77.0 ppm) and methanol (δ = 3.31, 49.0 ppm) were used. Integrals are in accordance to assignments and coupling constants are given in hertz (Hz). All ^{13}C NMR spectra are proton–decoupled. The multiplicity is indicated as follows: s (singlet), br s (broad singlet), d (doublet), t (triplet), m (multiplet), m_c (centered multiplet) dd (doublet of doublets). The *ortho*- and *meta*-fluorine signals in the ^{19}F NMR spectra of the substituted tetrafluorophenyl moieties exhibit the A,A’B,B’ and A,A’X,X’ coupling pattern typical for *para*-substituted aromatic compounds, in the ^{19}F NMR spectra these signals are denoted as m_c. HRMS analyses were performed by ESI-TOF, the solvent flow rate was adjusted to 4 µL/min and spray voltage was set to 4 kV. Drying gas flow rate was set to 15 psi (1 bar) and all other parameters were adjusted for a maximum abundance of the respective $[M+H]^+$. The UV/Vis spectra were measured with a UV/Visible spectrometer using DCM as solvent and quartz cuvettes of 1 cm length (see also exemplary calculation given for compound **5b**). Emission spectra were recorded with a fluorescence spectrometer using quartz cuvettes of 1 cm length and DCM as a solvent. Melting points are uncorrected. Compound **1**[1], 5-{4-(*N*-hexylamino)-2,3-5,6-tetrafluorophenyl}dipyrrane[2], 5-{4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl}dipyrrane[2], 5-{4-(prop-2-ynyloxy)-2,3,5,6-Tetrafluorophenyl}-dipyrrin[3], 5-{4-(butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrane[3] and dichloro(*p*-cymen)ruthenium(II) dimer[4] **[16]** were prepared according to the literature.

Tris(5-pentafluorophenyl-dipyrrinato) indium(III) [2]



According to the general procedure for the synthesis of trisdipyrrinato complexes, PFP-dipyrrin **1** (100 mg, 0.32 mmol, 3.1 eq.) was dissolved in dry THF (10 mL), $InCl_3$ (23 mg, 0.10 mmol) and DIPEA (186 mg, 1.44 mmol, 14 eq.) were added and the mixture was refluxed for 6 h. The solvent was evaporated to dryness and the crude product was purified by column chromatography (silica gel, DCM). The purified and evaporated product was washed with pentane and dried *in vacuo*. The product was obtained as orange crystals (146 mg, 44%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.39 (dd, J = 4.2, 1.3 Hz, 6 H, H_{pyrrole}), 6.61 (d, J = 4.1 Hz, 6 H, H_{pyrrole}), 7.18-7.20 (m, 6 H, H_{pyrrole}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 113.63 (t, $J_{C\text{-}F}$ = 18.0 Hz, Ar-C_{ipso}), 118.63 (C_{pyrrole}), 132.43 (C_{pyrrole}), 136.24 (t, $J_{C\text{-}F}$ = 14.0 Hz, Ar-C_{para}), 138.26 (t, $J_{C\text{-}F}$ = 13.5 Hz, Ar-C_{para}), 139.74 (C_{meso}), 141.57 (d, $J_{C\text{-}F}$ = 259.5 Hz, Ar-C_{meta}), 144.72 (d, $J_{C\text{-}F}$ = 250.3 Hz, Ar-C_{ortho}), 151.52 (C_{pyrrole}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -161.22 – -161.06 (m, 6 F, Ar-F_{meta}), -152.66 (t, J = 20.8 Hz, 3 F, Ar-F_{para}), -139.06 (m_c, J = 23.5, 6.7 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{30}H_{12}F_{10}InN_4^+$ [M-L]$^+$ 732.9941, found 732.9961; *m/z* calc. for $C_{45}H_{18}F_{15}InKN_6^+$ [M+K]$^+$ 1081.0024, found 1081.0078.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 455 (5.17), 508 (4.94) nm.

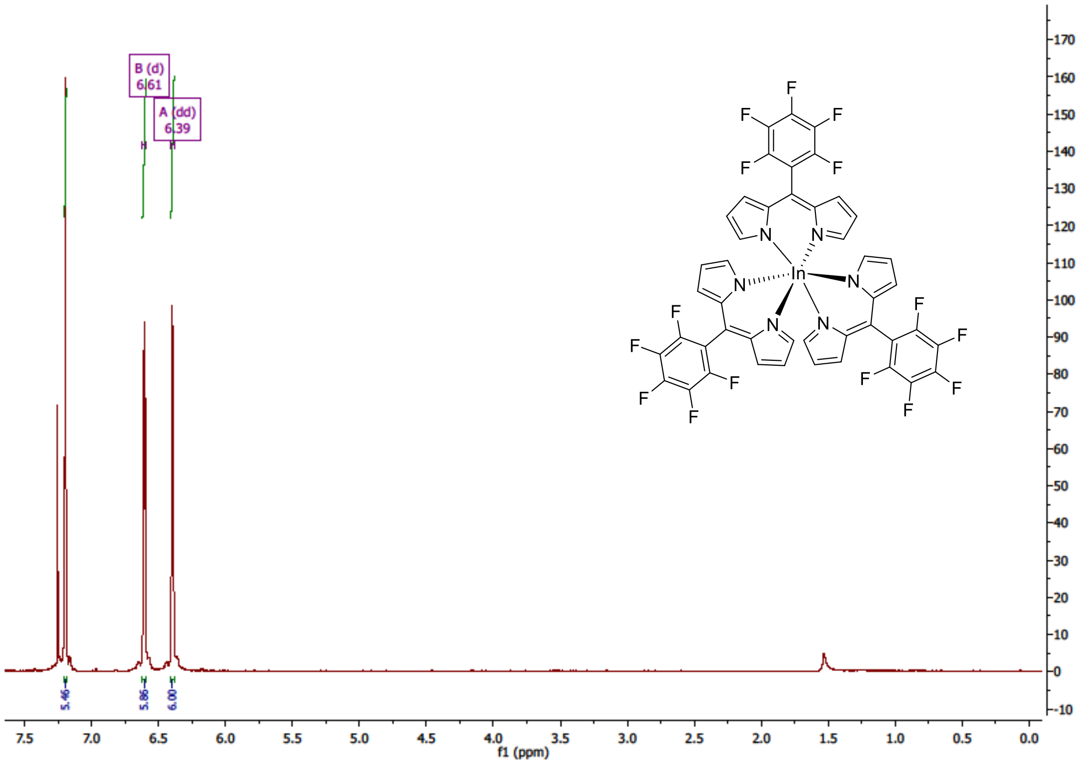


Figure S 3. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 2**

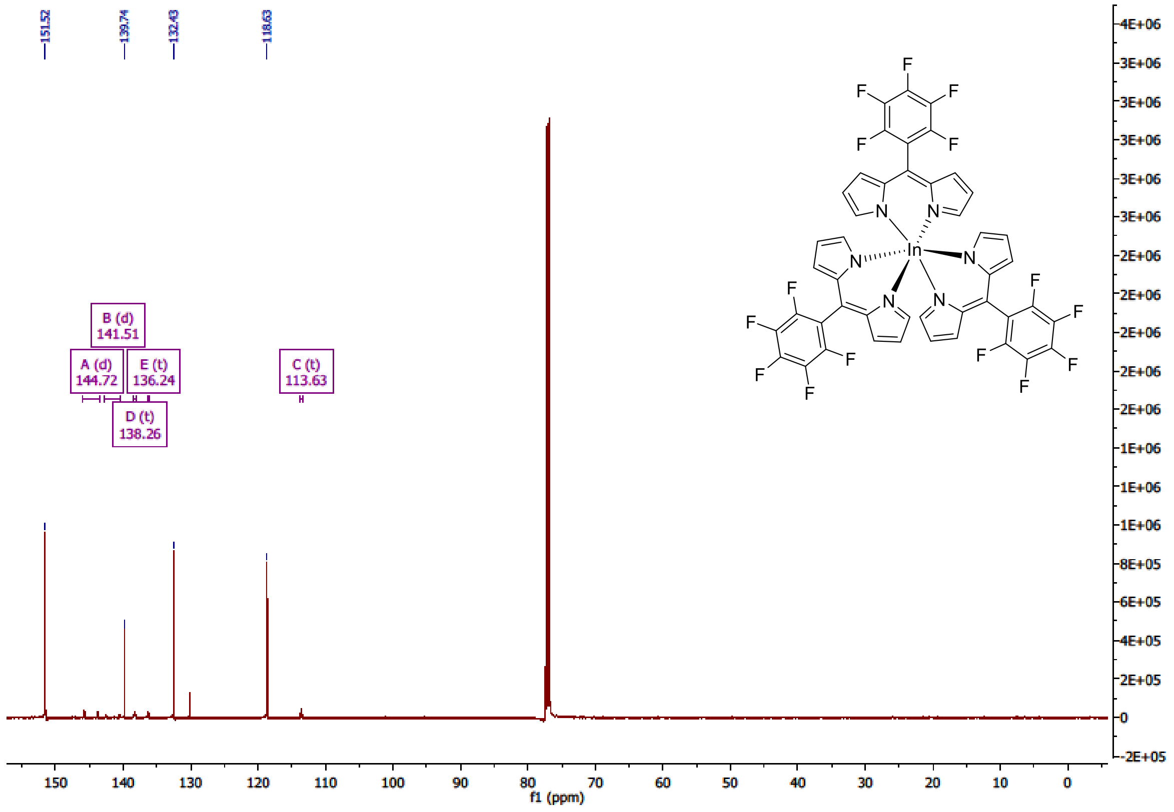


Figure S 4. **^{13}C NMR (126 MHz, $CDCl_3$) spectrum of complex 2.**

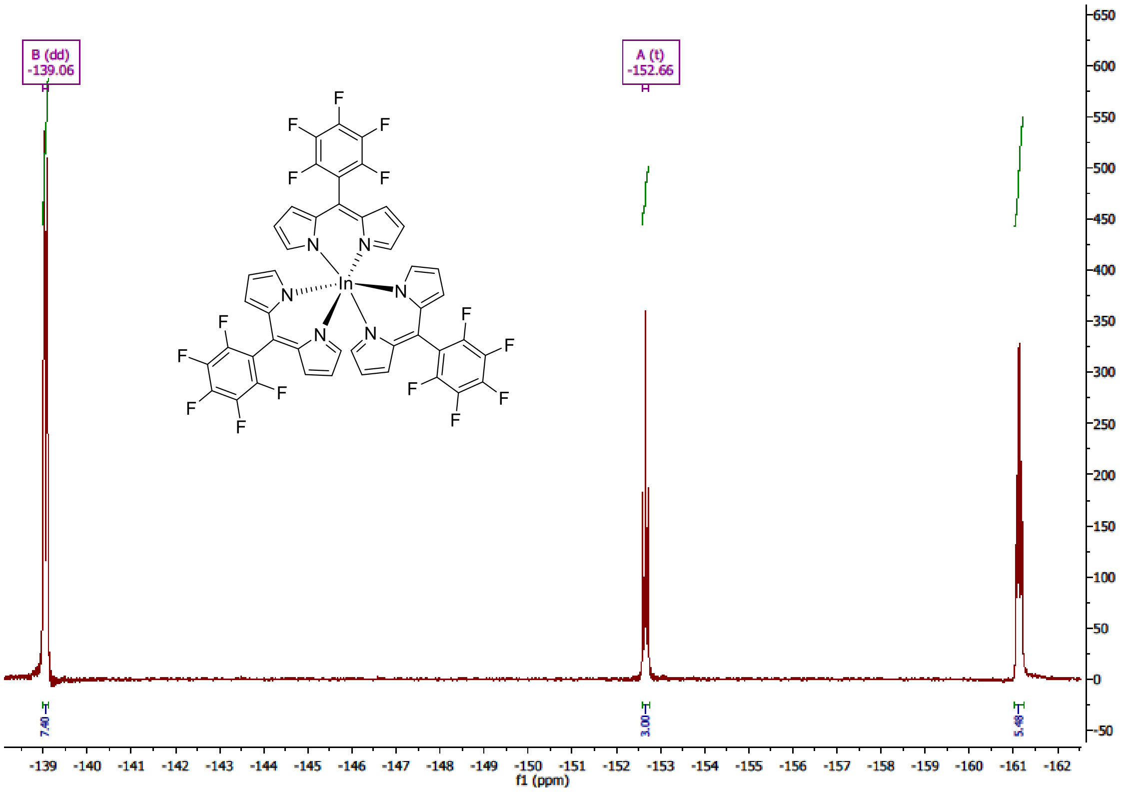


Figure S 5. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 2.

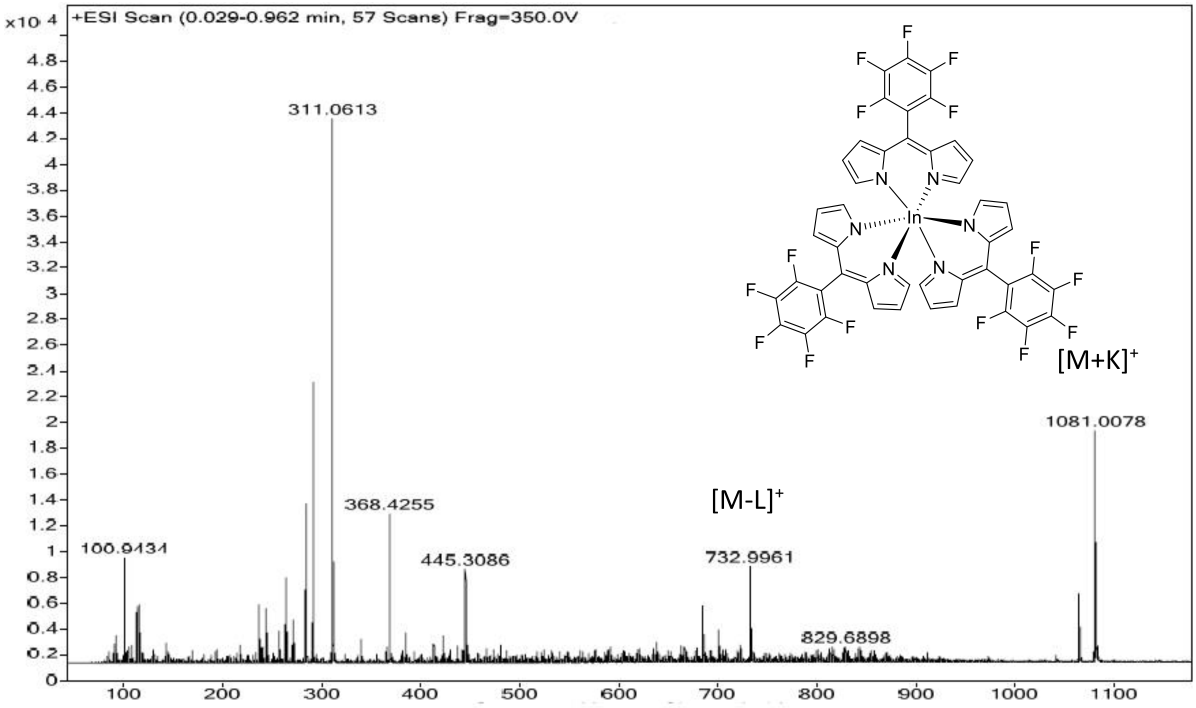


Figure S 6. HRMS (ESI-TOF) spectrum of complex 2.

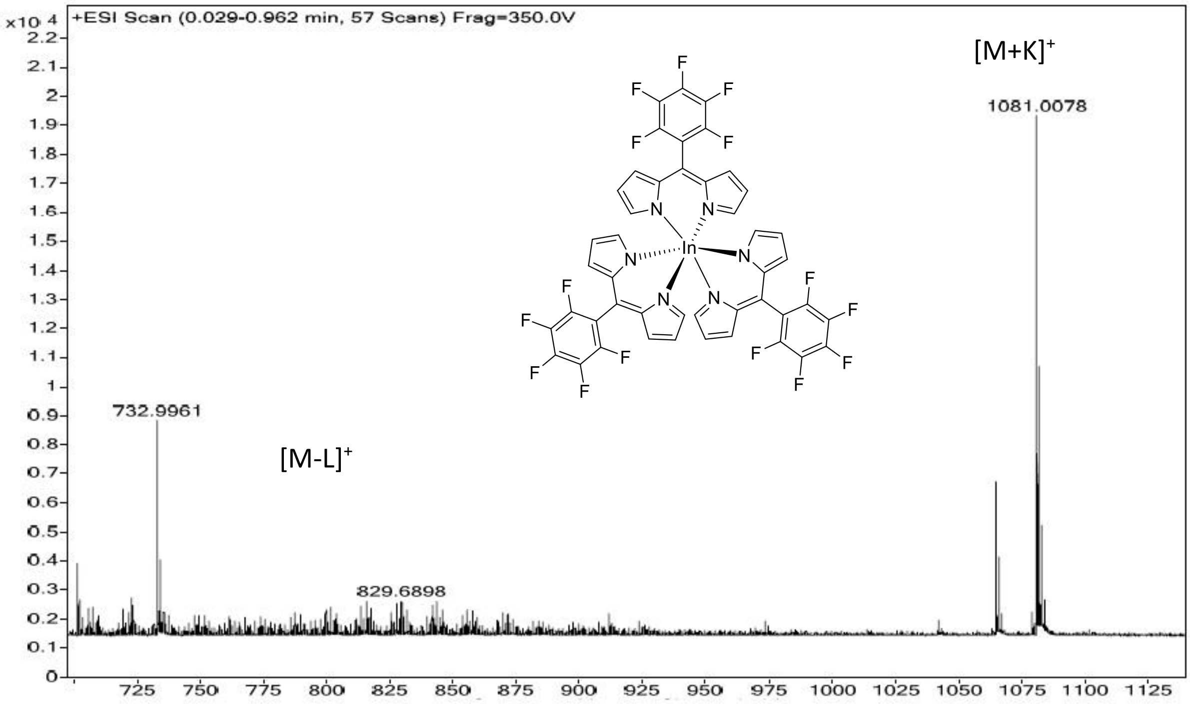


Figure S 7. HRMS (ESI-TOF) spectrum of complex

Tris(5-pentafluorophenyl-dipyrrinato) gallium(III) [3]

According to the general procedure for the synthesis of trisdipyrrinato complexes, PFP-dipyrrin **1** (486 mg, 1.56 mmol, 3.1 eq.) was dissolved in dry THF (10 mL), $GaCl_3$ (89 mg, 0.50 mmol) and DIPEA (2.3 mL, 7.00 mmol, 14 eq.) were added and the mixture was refluxed for 6 h. The solvent was evaporated to dryness and the crude product was purified by column chromatography (silica gel, DCM). The purified and evaporated product was washed with pentane and dried *in vacuo*. The product was obtained as orange crystals (311 mg, 48%).

Mp: 236-240 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.33 (dd, *J* = 4.2, 1.4 Hz, 6 H, H_{pyrrole}), 6.58 (d, *J* = 4.1 Hz, 6 H, H_{pyrrole}), 6.96-6.98 (m, 6 H, H_{pyrrole}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 112.93 (t, $J_{C\text{-}F}$ = 19.5 Hz, Ar-C_{ipso}), 118.10. (C_{pyrrole}), 131.23 (C_{pyrrole}), 136.31 (t, $J_{C\text{-}F}$ = 12.9 Hz, Ar-C_{para}), 138.33 (C_{meso}), 141.53 (d, $J_{C\text{-}F}$ = 255.5 Hz, Ar-C_{meta}), 144.68 (d, $J_{C\text{-}F}$ = 246.5 Hz, Ar-C_{ortho}), 150.40 (C_{pyrrole}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -161.15 — -161.00 (m, 6 F, Ar-F_{meta}), -152.50 (t, *J* = 20.8 Hz, 3 F, Ar-F_{para}), -139.05 – -138.90 (m_c, *J* = 15.3 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. $C_{45}H_{18}F_{15}GaKN_6^+$ $[M+K]^+$: 1035.0241, found 1035.0245; *m/z* calc. for $C_{30}H_{12}F_{10}GaN_4^+$ $[M-L]^+$ 687.0158, found 687.0165.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 457 (4.92), 509 (4.85) nm.

Elemental analysis $C_{45}H_{18}F_{15}GaN_6$ (996.0): calc. 54.19 (C), 1.82 (H), 8.43 (N), found 54.23 (C), 2.05 (H), 8.72 (N).

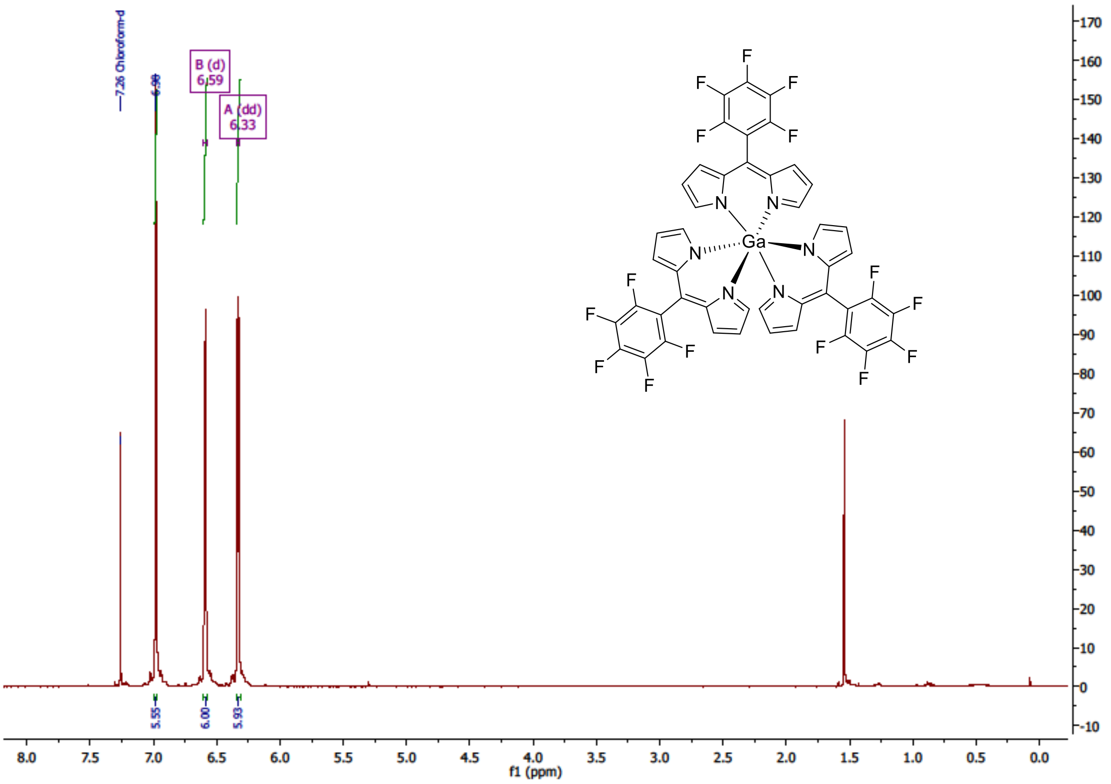


Figure S 8. ^1H **NMR (400 MHz,** $CDCl_3$**) spectrum of complex 3.**

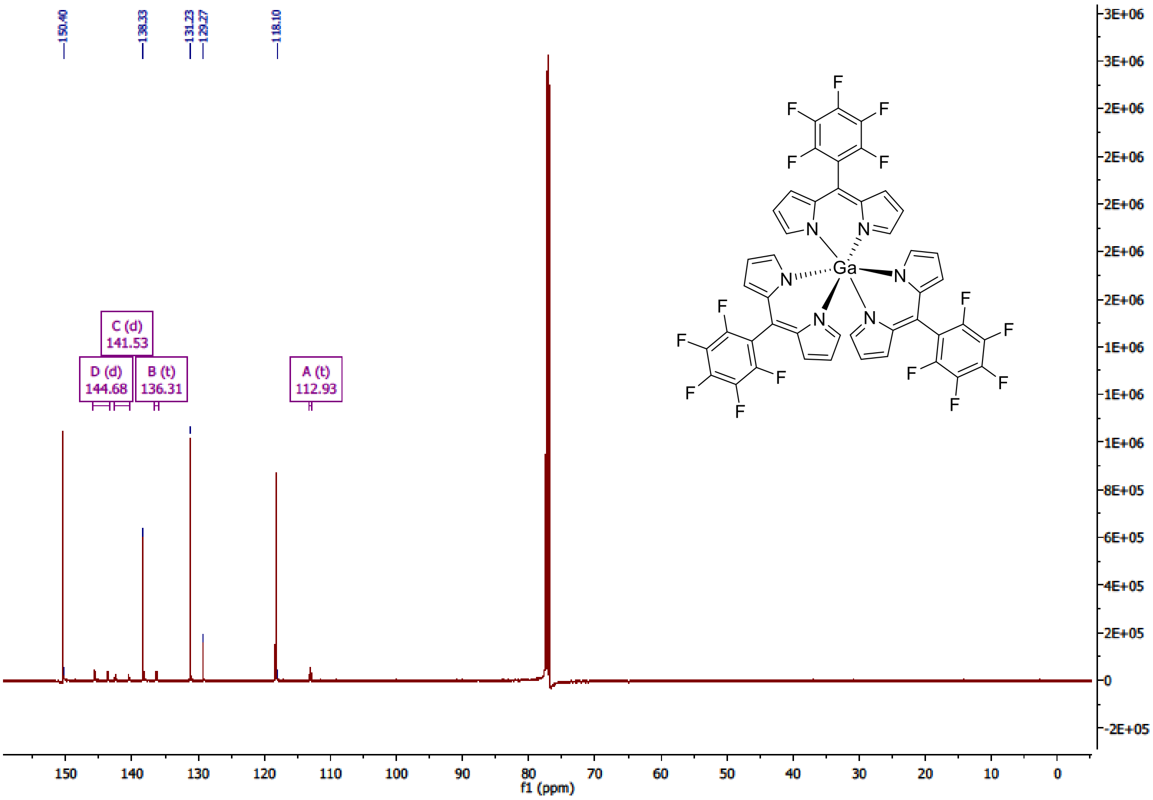


Figure S 9. **^{13}C NMR (126 MHz, $CDCl_3$) spectrum of complex 3.**

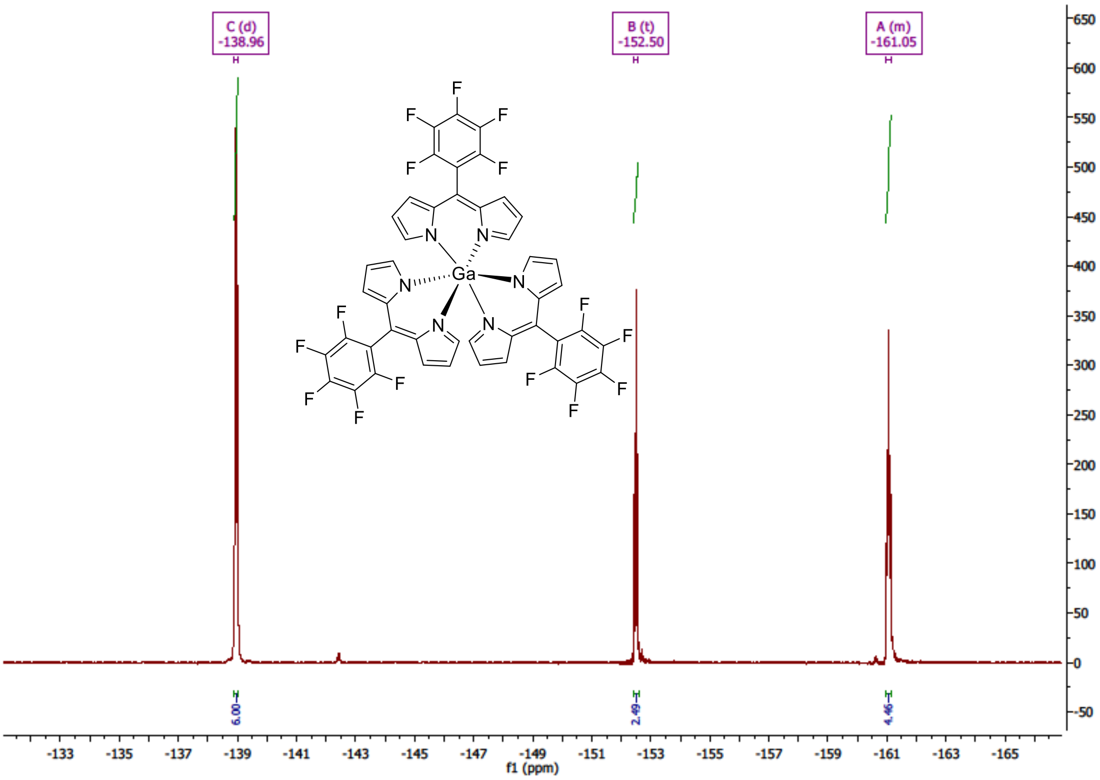


Figure S 10. **^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 3.**

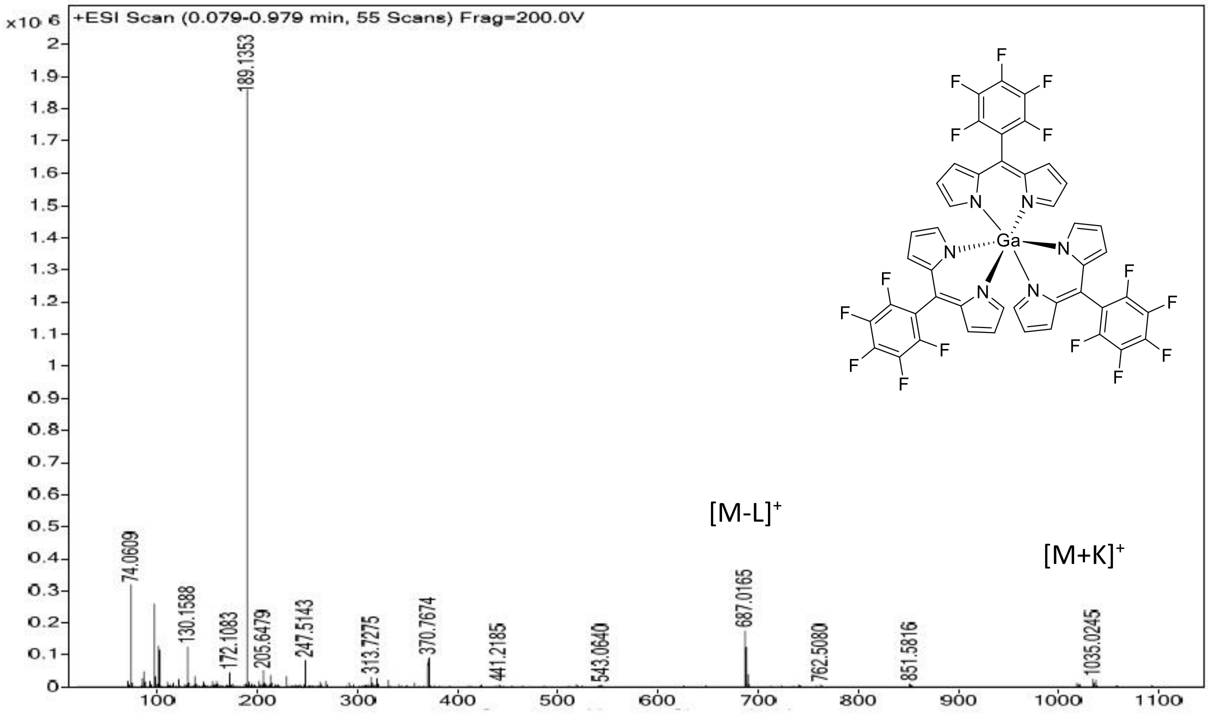


Figure S 11. HRMS (ESI-TOF) spectrum of complex 3.

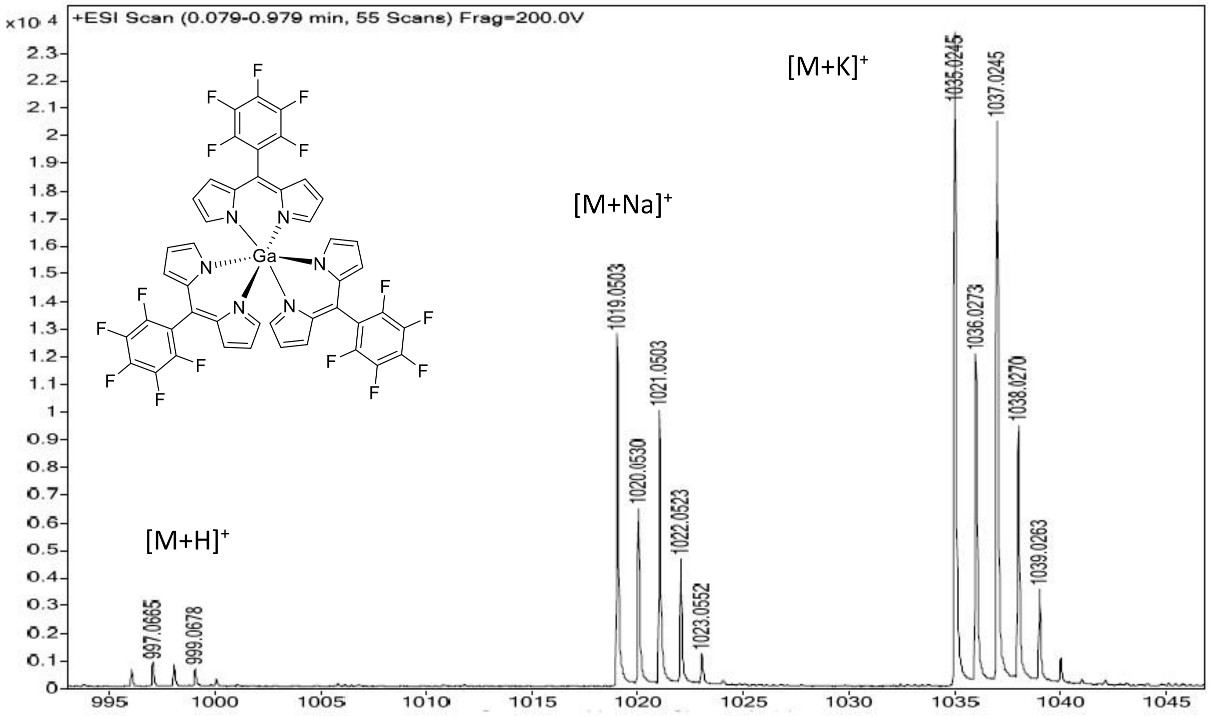
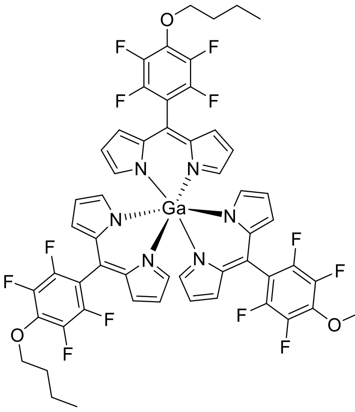


Figure S 12. HRMS (ESI-TOF) spectrum of complex 3.

Tris[5-{4-(butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [5a]



Method A: According to the general procedure for the post-functionalization with alcohols, a mixture of complex **3** (50 mg, 50 µmol), freshly powdered KOH (42 mg, 0.75 mmol, 15 eq.) and *n*-butane (90 µL, 74 mg, 1.00 mmol, 20 eq.) in dry THF (3 mL) were stirred for 16 h at rt. The mixture was diluted with DCM and washed several times with water. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2) and evaporated to dryness. After recrystallization (DCM/*n*-hexane) the product was obtained as an orange solid (29 mg, 50%).

Method B: According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **8** (130 mg, 0.357 mmol, 3.1 eq.) was dissolved in dry THF (10 mL), $GaCl_3$ (20 mg, 0.11 mmol) and DIPEA (40 µL, 46 mg, 0.35 mmol, 3.1 eq.) were added and the mixture was refluxed for 12 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and evaporated to dryness. After recrystallization (DCM/*n*-hexane) the product was obtained as an orange solid (38 mg, 30%).

Mp: 208-218 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.4 Hz, 9 H, CH_3), 1.50-1.58 (m, 6 H, CH_2), 1.78-1.86 (m, 6 H, CH_2), 4.33 (t, J = 6.4 Hz, 6 H, CH_2), 6.30 (dd, J = 4.2, 1.5 Hz, 6 H, $H_{pyrrole}$), 6.62 (d, J = 4.0 Hz, 6 H, $H_{pyrrole}$), 6.96-6.98 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.84 (CH_3), 18.91 (CH_2), 32.07 (CH_2), 75.26 (CH_2), 111.05 (t, $J_{C\text{-}F}$ = 19.6 Hz, Ar-C_{ipso}), 117.91 ($C_{pyrrole}$), 131.34 ($C_{pyrrole}$), 138.32 (t, $J_{C\text{-}F}$ = 13.5 Hz, Ar-C_{para}), 138.74 (C_{meso}), 140.79 (dd, $J_{C\text{-}F}$ = 249.2, 14.7 Hz, Ar-C_{meta}), 144.81 (d, $J_{C\text{-}F}$ = 235.3 Hz, Ar-C_{ortho}), 150.24 ($C_{pyrrole}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -156.93 (m$_c$, J = 21.4, 7.3 Hz, 6 F, Ar-C$_{meta}$), -141.05 (m$_c$, J = 21.7, 7.3 Hz, 6 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{30}F_8GaN_4O_2^+$ [M-L]$^+$ 795.1497, found 795.1492; *m/z* calc. for $C_{57}H_{45}F_{12}GaN_6NaO_3^+$ [M+Na]$^+$ 1181.2510, found 1181.2491.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 457 (4.95), 508 (4.86) nm.

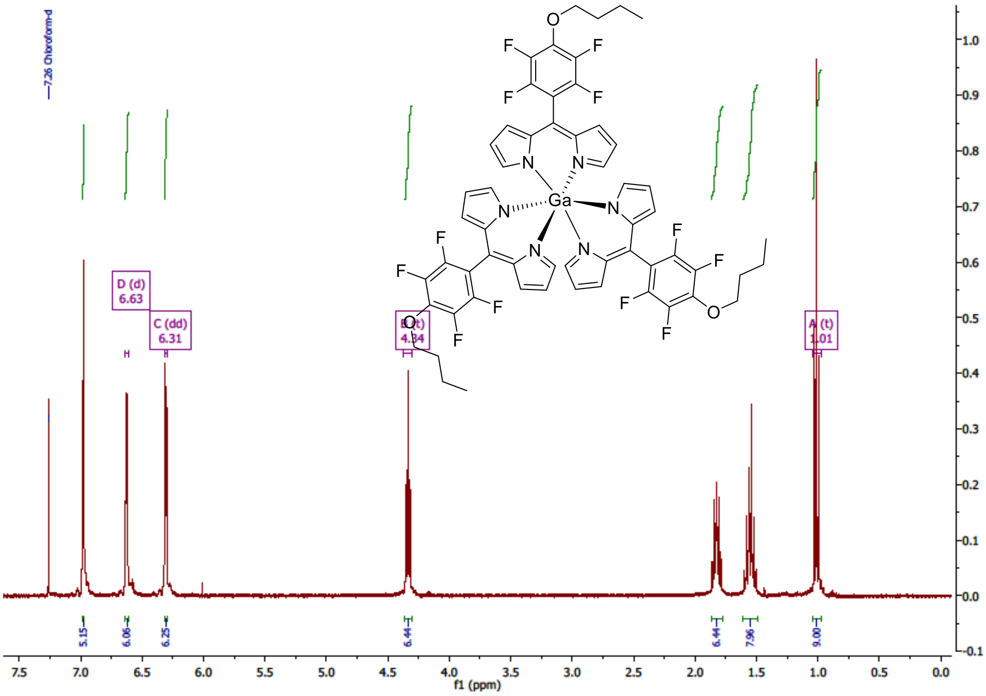


Figure S 13. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 5a.

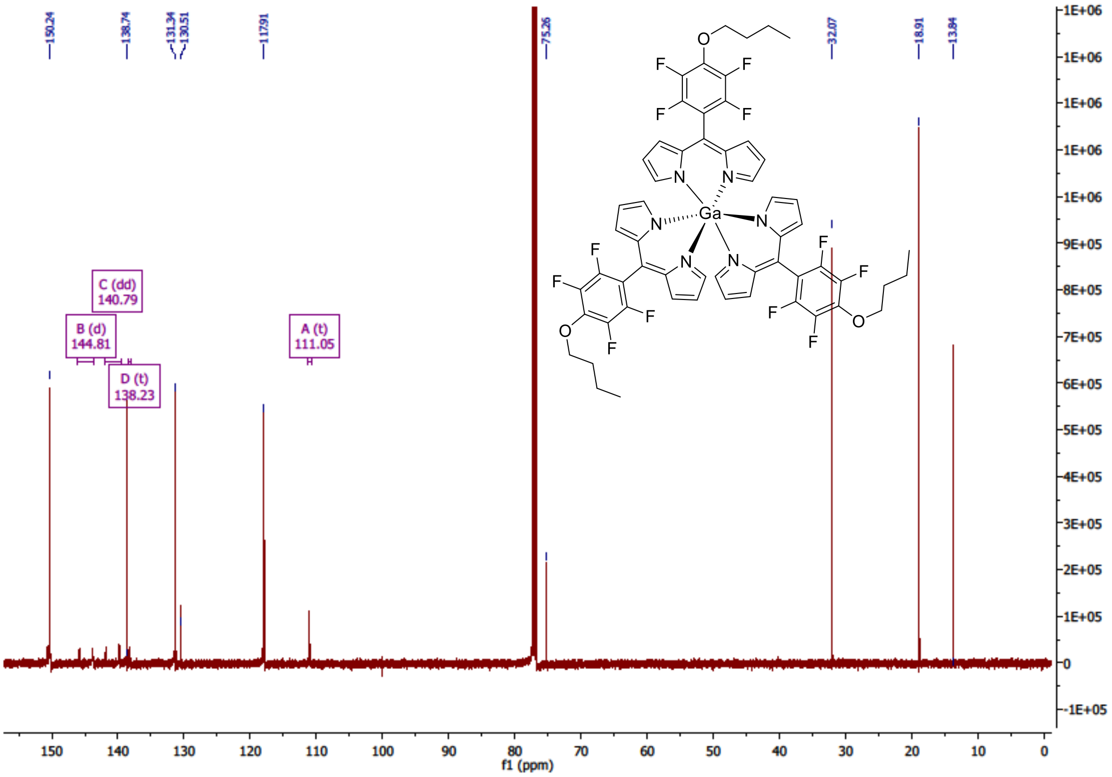


Figure S 14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of complex 5a

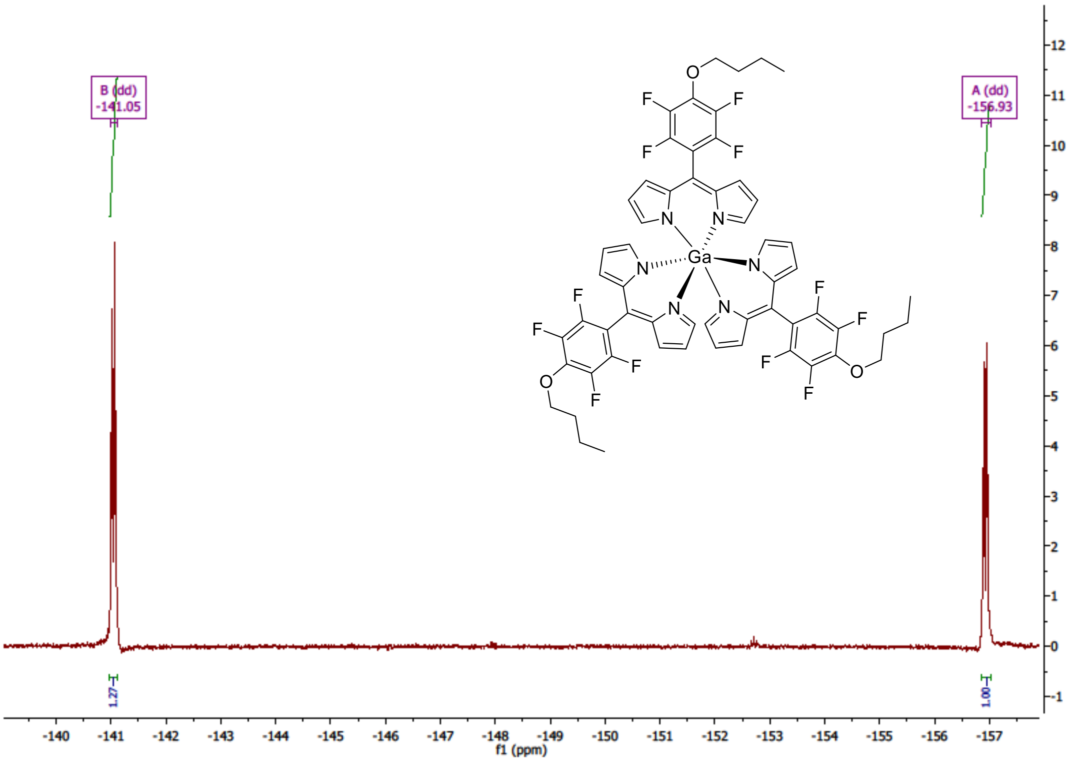


Figure S 15. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 5a.

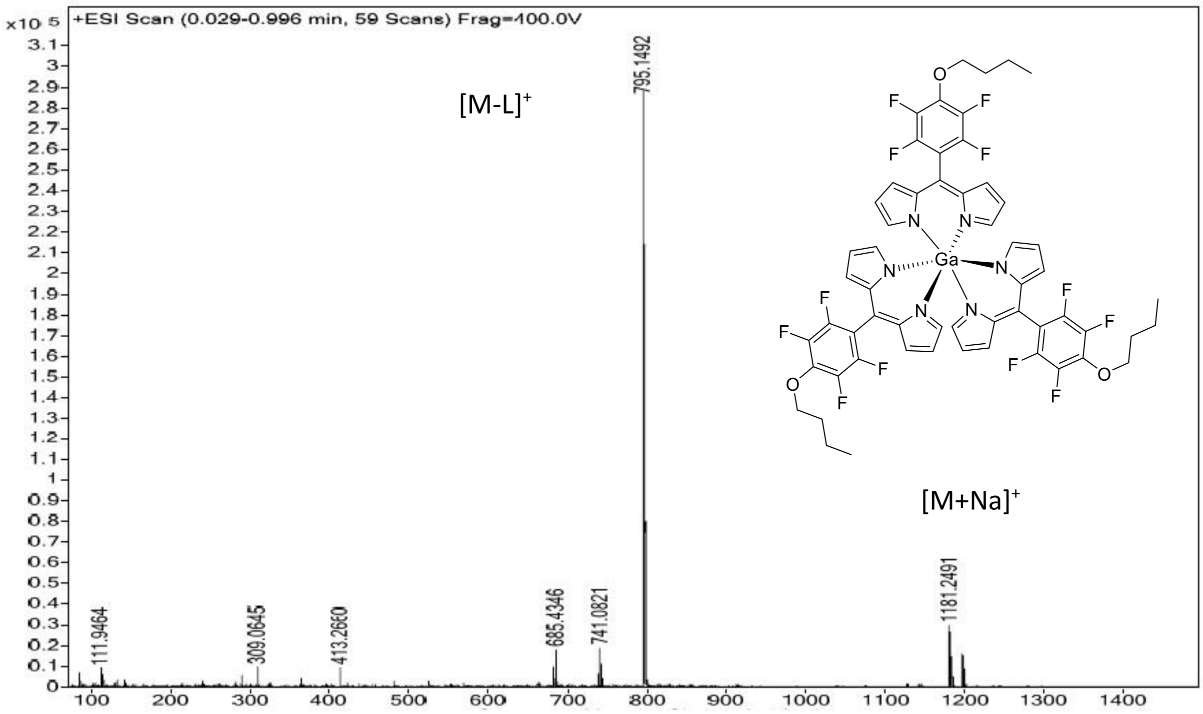


Figure S 16. HRMS (ESI-TOF) spectrum of complex 5a.

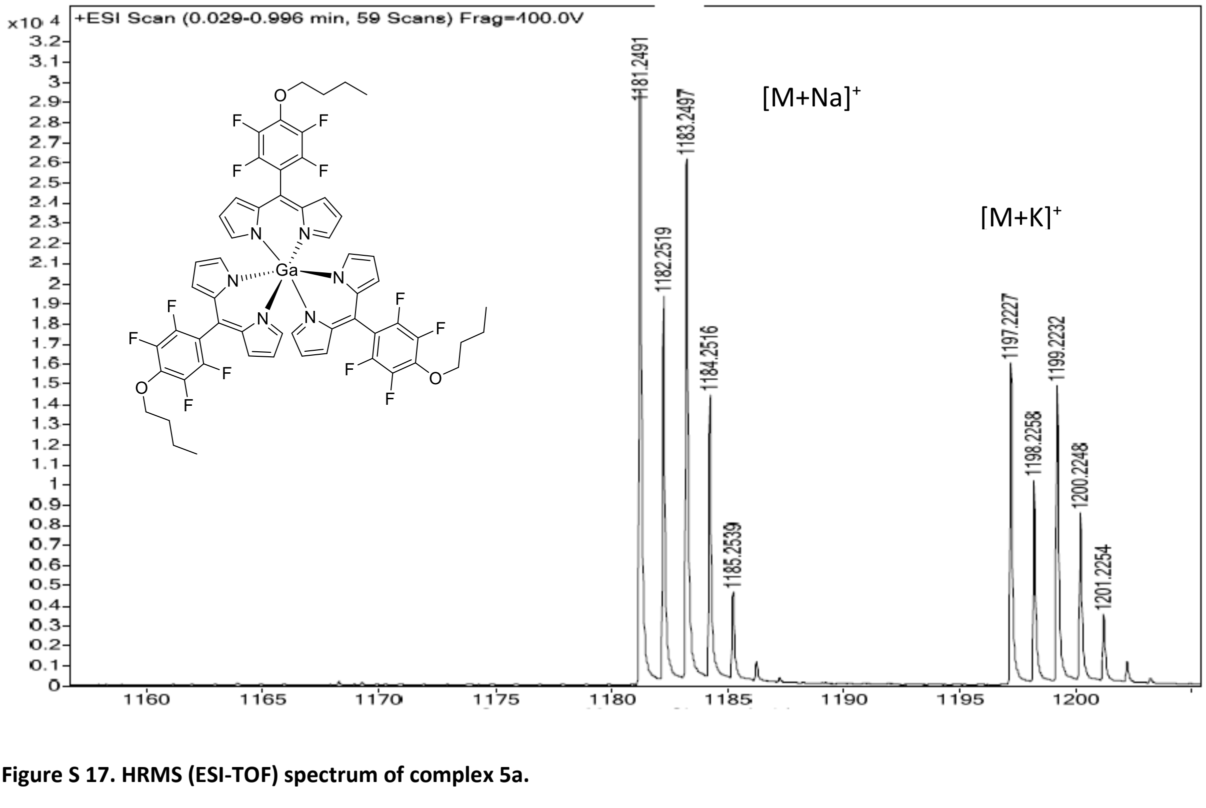
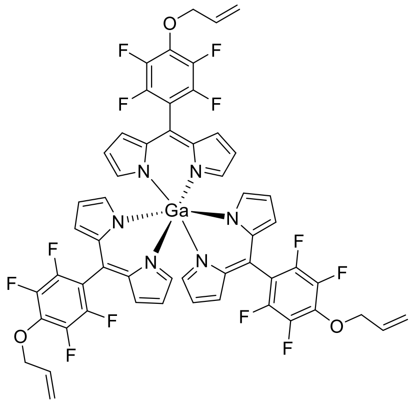


Figure S 17. HRMS (ESI-TOF) spectrum of complex 5a.

Tris[5-{4-(prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [5b]



Method A: According to the general procedure for the post-functionalization with alcohols, a mixture of complex **3** (50 mg, 50 µmol), freshly powdered KOH (26 mg, 1.5 mmol, 30 eq.) and allylic alcohol (68 µ, 58 mg, 1.0 mmol, 20 eq.) in dry THF (3 mL) were stirred at rt for 16 h. The mixture was diluted with DCM, washed several times with water and the organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1), evaporated to dryness, washed with pentane and dried *in vacuo*. The product was isolated as an orange solid (14 mg, 25%).

Method B: According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **9** (100 mg, 0.287 mmol, 3.1 eq.) was dissolved in dry THF (10 mL), $GaCl_3$ (16 mg, 0.09 mmol) and DIPEA (40 µL, 37 mg, 0.287 mmol, 3.1 eq) were added and the mixture was refluxed for 4 h. The mixture was diluted with DCM and washed with water several times, dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 3:1). The purified and evaporated product was washed with pentane and dried *in vacuo*. The product was obtained as orange crystals (58 mg, 57%).

Mp: 209-216 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (d, *J* = 6.0 Hz, 6 H, CH_2), 5.36 (dd, *J* = 10.3, 1.1 Hz, 3 H, $C{=}CH_2$), 5.45 (dd, *J* = 17.1, 1.4 Hz, 3 H, $C{=}CH_2$), 6.10-6.15 (m, 3 H, CH), 6.30 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.60 (d, *J* = 4.0 Hz, 6 H, $H_{pyrrole}$), 6.95-6.98 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ =75.53 (CH$_2$), 111.55 (t, $J_{C\text{-}F}$ = 19.5 Hz, Ar-C$_{ipso}$), 117.88 (C$_{\text{pyrrole}}$), 120.34 (C=CH$_2$), 131.29 (C$_{\text{pyrrole}}$), 132.23 (CH), 138.58 (C$_{meso}$), 137.27 (t, $J_{C\text{-}F}$ = 11.9 Hz, Ar-C$_{para}$), 140.91 (dd, $J_{C\text{-}F}$ = 249.1, 14.8 Hz, Ar-C$_{meta}$), 144.81 (d, $J_{C\text{-}F}$ = 247.6 Hz, Ar-C$_{ortho}$), 150.26 (C$_{\text{pyrrole}}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -156.04 (m$_c$, J = 22.4, 7.7 Hz, 6 F, Ar-F$_{meta}$), -140.90 (m$_c$, J = 23.1, 7.3 Hz, 6 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{33}F_{12}GaN_6NaO_3$+ [M+Na]$^+$ 1133.1571, found 1133.1576; *m/z* calc. for $C_{36}H_{22}F_8GaN_4O_2$ [M-L]$^+$ 763.0871, found 763.0891.

UV/Vis (DCM): λ$_{\text{max}}$ [log ε (dm^3·mol^{-1}·cm^{-1})] = 456 (4.94), 508 (4.89) nm.

Calculation for the absorption coefficient

Preparation of the stock solution:

Molar mass [g/mol]	Mass [g]	[mol]	Volume [L]	Concentration [mol/L]
1110.10	0.0019	$1.7117\cdot10^{-6}$	0.01	0.0002

The stock solution was prepared by dissolving 1.9 mg of the compound in 10 mL of DCM. Aliquots of this stock solution 25 µL, 50 µL, and 75 µL, respectively, were dissolved in 2 mL of DCM and the extinction of the respective solutions was determined with the UV/Vis spectrometer.

Calculation of the absorption coefficient:

$C_1 = 2.2242\cdot10^{-6}$

Wavelength λ [nm]	Extinction	ε [dm^3·mol^{-1}·cm^{-1}]
456	0.277424	124727
508	0.230954	103835

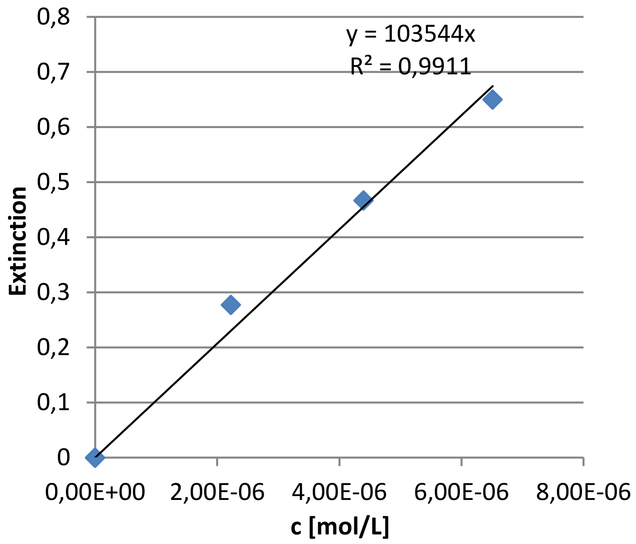
$C_2 = 4.3942\cdot10^{-6}$

Wavelength λ [nm]	Extinction	ε [dm^3·mol^{-1}·cm^{-1}]
456	0.466759	106221
508	0.389574	88656

$C_3 = 6.5119\cdot10^{-6}$

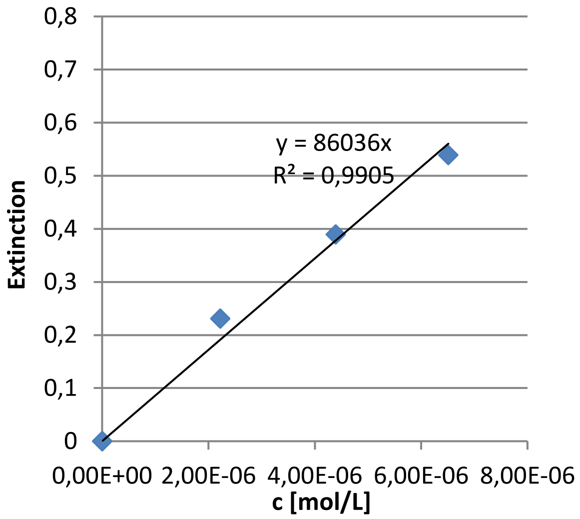
Wavelength λ [nm]	Extinction	ε [dm^3·mol^{-1}·cm^{-1}]
456	0.6502	99854
508	0.538972	82767

For λ= 456 nm



Log(103544) = 5.01

For λ=508 nm



Log(86036) = 4.93

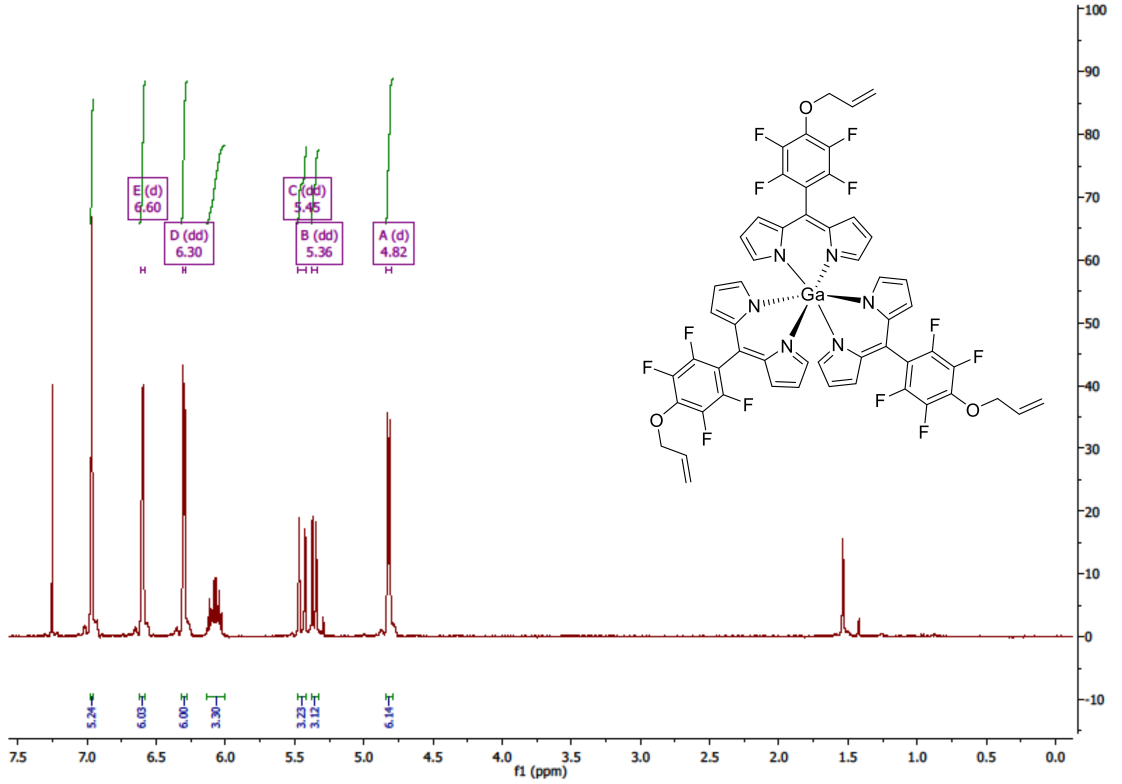


Figure S 18. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 5b.

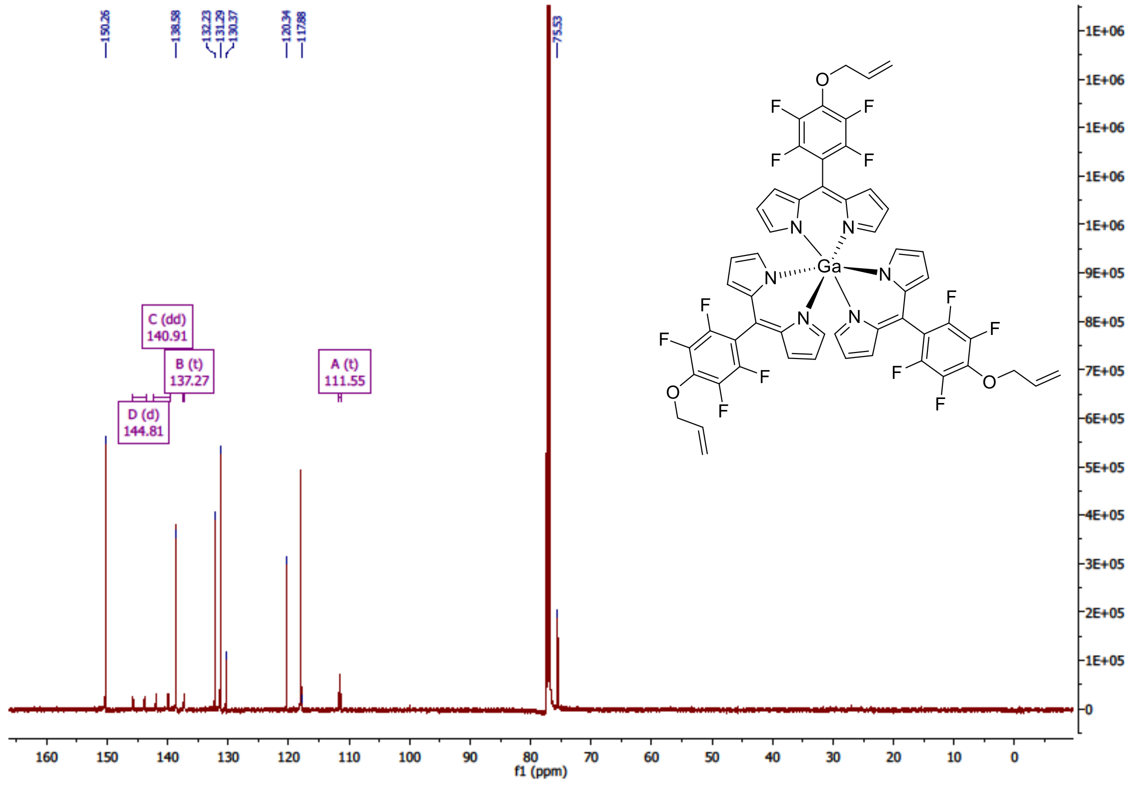


Figure S 19. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 5b.

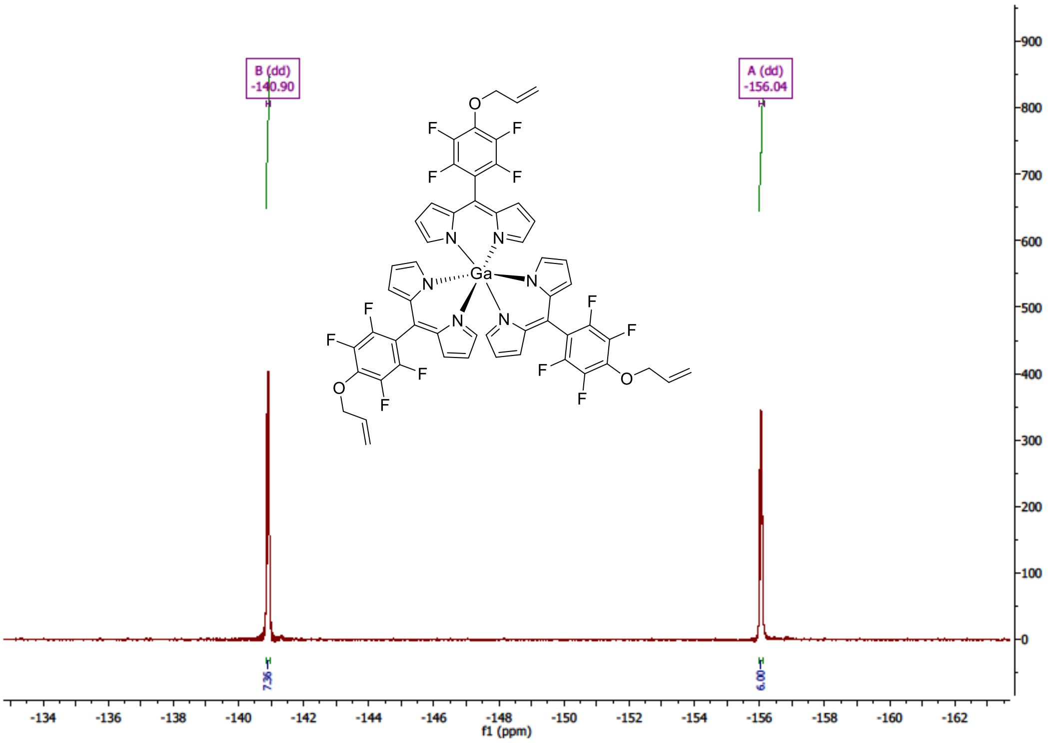


Figure S 20. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 5b.

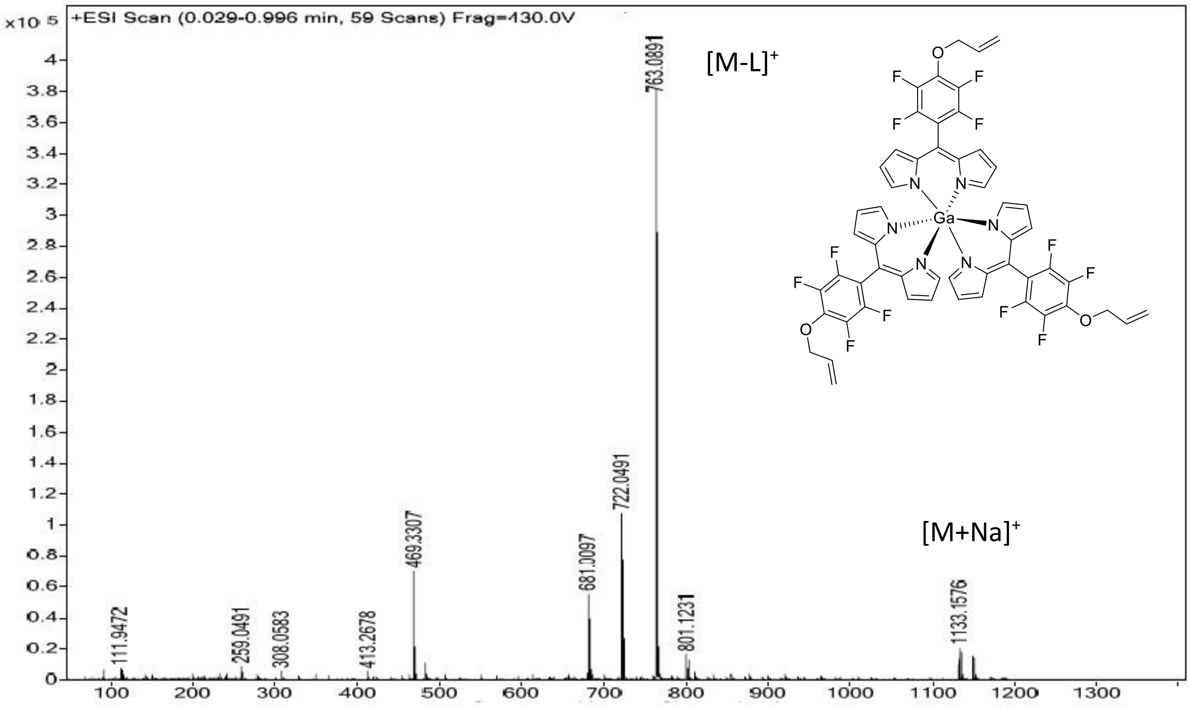


Figure S 21. HRMS (ESI-TOF) spectrum of complex 5b.

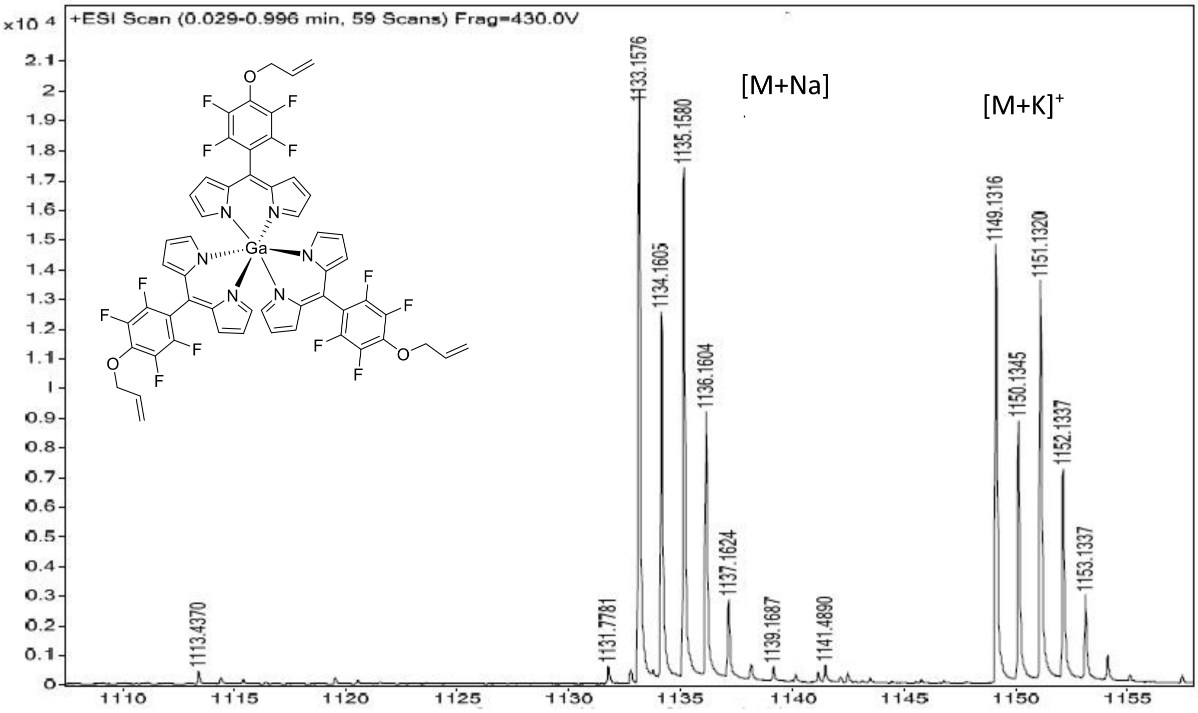


Figure S 22. HRMS (ESI-TOF) spectrum of complex 5b.

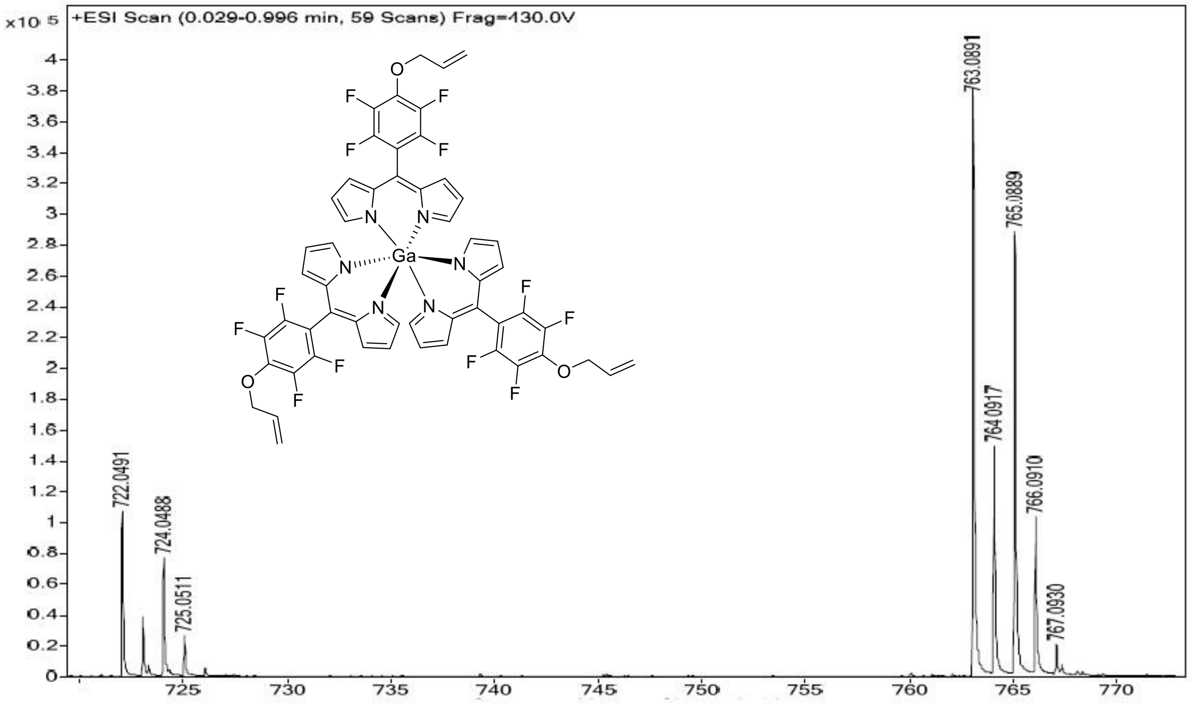
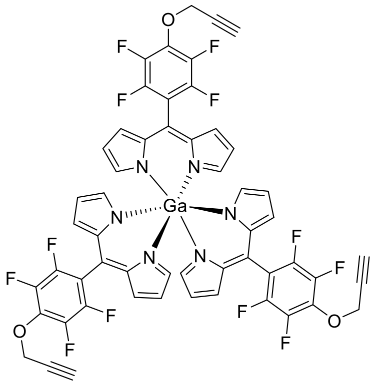


Figure S 23. HRMS (ESI-TOF) spectrum of complex 5b.

Tris[5-{4-(prop-2-ynyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [5c]



Method A: According to the general procedure for the post-functionalization with alcohols, a mixture of complex **3** (50 mg, 50 µmol), propargylic alcohol (0.10 mL, 105 mg, 210 µmol, 4.2 eq.) and freshly powdered KOH (10 mg, 170 µmol, 3.5 eq.) in dry THF (10 mL) was stirred under the exclusion of light for 16 h at rt. TLC shows three products, so more KOH (10 mg, 170 µmol, 3.5 eq) and alcohol (0.10 mL, 105 mg, 210 µmol, 4.2 eq.) were added and the mixture stirred for another 24 h. The mixture was diluted with DCM, washed with water several times, dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1). After evaporation to dryness, the product was washed with pentane and dried *in vacuo*. The product was isolated as orange crystals in 54 % (30 mg) yield.

Method B: According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of 5-{4-(prop-2-ynyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrin (100 mg, 0.28 mmol, 3.1 eq.), $GaCl_3$ (16 mg, 90 µmol) and DIPEA (37 mg, 40 µL, 288 µmol, 14 eq.) were dissolved in dry THF and refluxed for 12 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1), evaporated to dryness and washed with pentane. The product was obtained as orange crystals (23 mg, 23%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (t, J = 2.4 Hz, 3 H, CH), 5.25 (d, J = 2.4 Hz, 6 H, CH_2), 6.59 (dd, J = 4.1, 1.3 Hz, 6 H, $H_{pyrrole}$), 6.89 (d, J = 4.2 Hz, 6 H, $H_{pyrrole}$), 7.53-7.54 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 61.72 (CH_2), 76.91 (C≡CH), 77.63 (C≡CH), 112.59 (t, $J_{C\text{-}F'}$ = 19.5 Hz, Ar-C_{ipso}), 118.12 ($C_{pyrrole}$), 131.30 ($C_{pyrrole}$), 136.07 (m, Ar-C_{para}), 138.47 (C_{meso}), 141.22 (d, $J_{C\text{-}F}$ = 259.7 Hz, Ar-C$_{\mathit{meta}}$), 144.65 (d, $J_{C\text{-}F}$ = 240.2 Hz, Ar-C$_{\mathit{ortho}}$), 150.35 (C$_{\mathrm{pyrrole}}$) ppm.**^{19}F NMR (376 MHz, CDCl$_3$):** δ = -155.24 (m$_c$, J = 21.5, 7.2 Hz, 6 F, Ar-F$_{\mathit{meta}}$), -140.50 (m$_c$, J = 21.8, 7.3 Hz, 6 F, Ar-F$_{\mathit{ortho}}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{36}H_{18}F_8GaN_4O_2^+$ [M-L]$^+$ 759.0558, found 759.0551; *m/z* calc. for $C_{54}H_{27}F_{12}GaKN_6O_3^+$ [M+K]$^+$ 1143.0840, found 1143.0817.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 457 (5.09), 508 (5.05) nm.

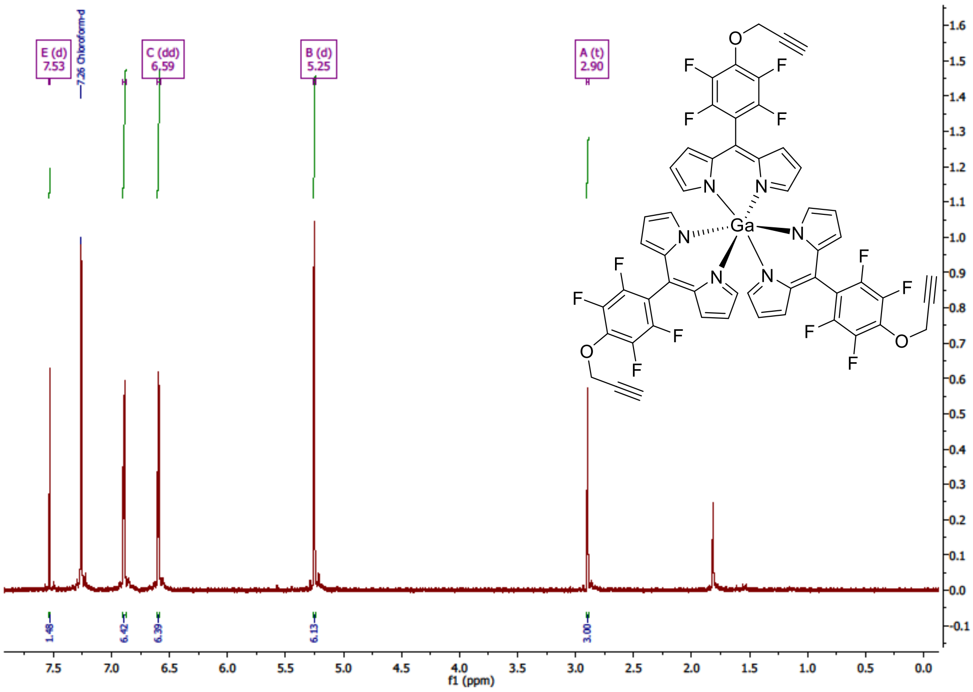


Figure S 24. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 5c.

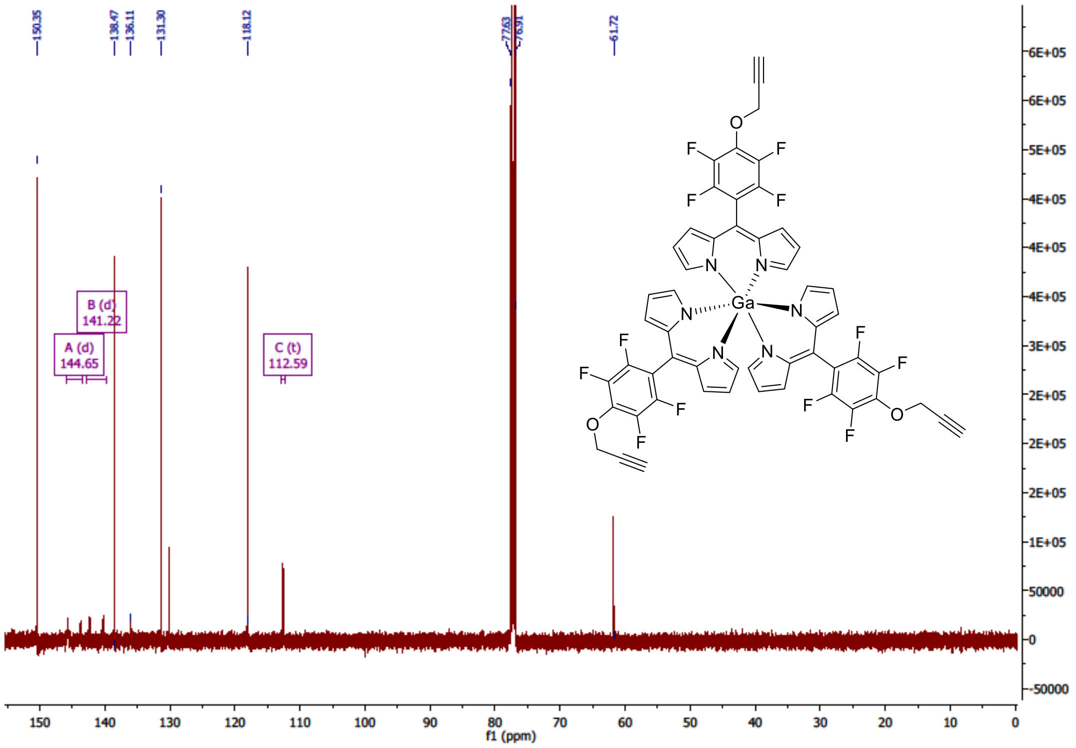


Figure S 25. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 5c.

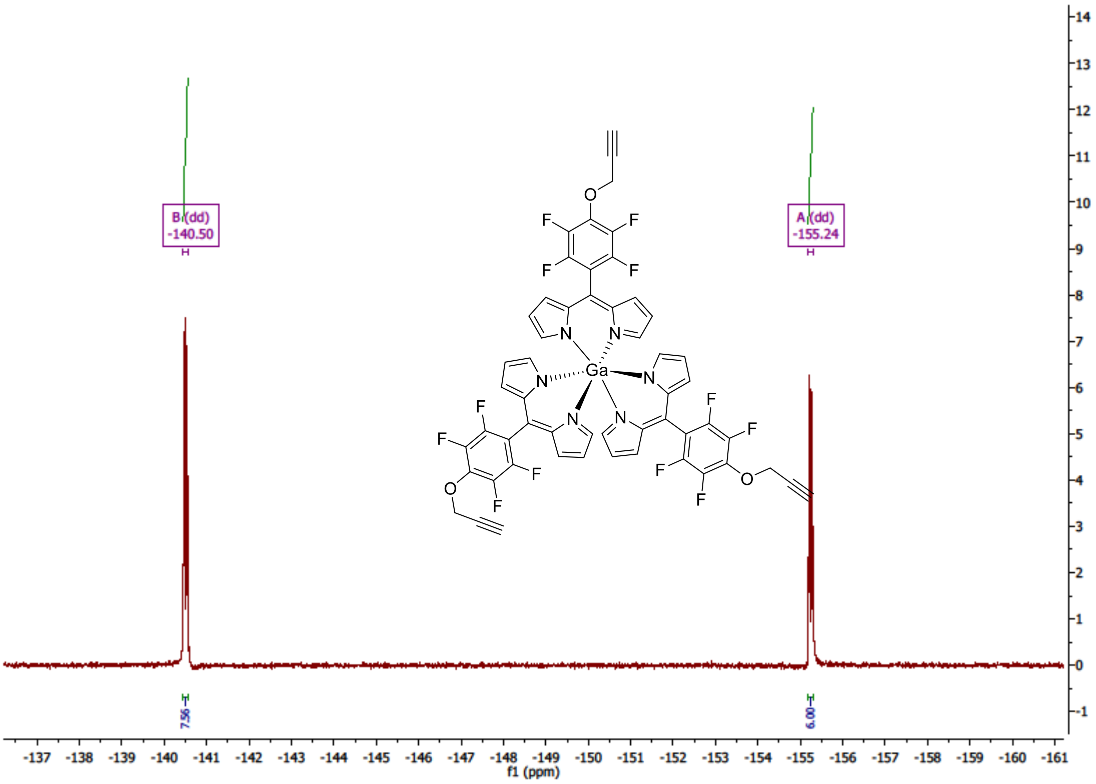


Figure S 26. ^{19}F NMR (376 MHz, CDCL$_3$) spectrum of complex 5c.

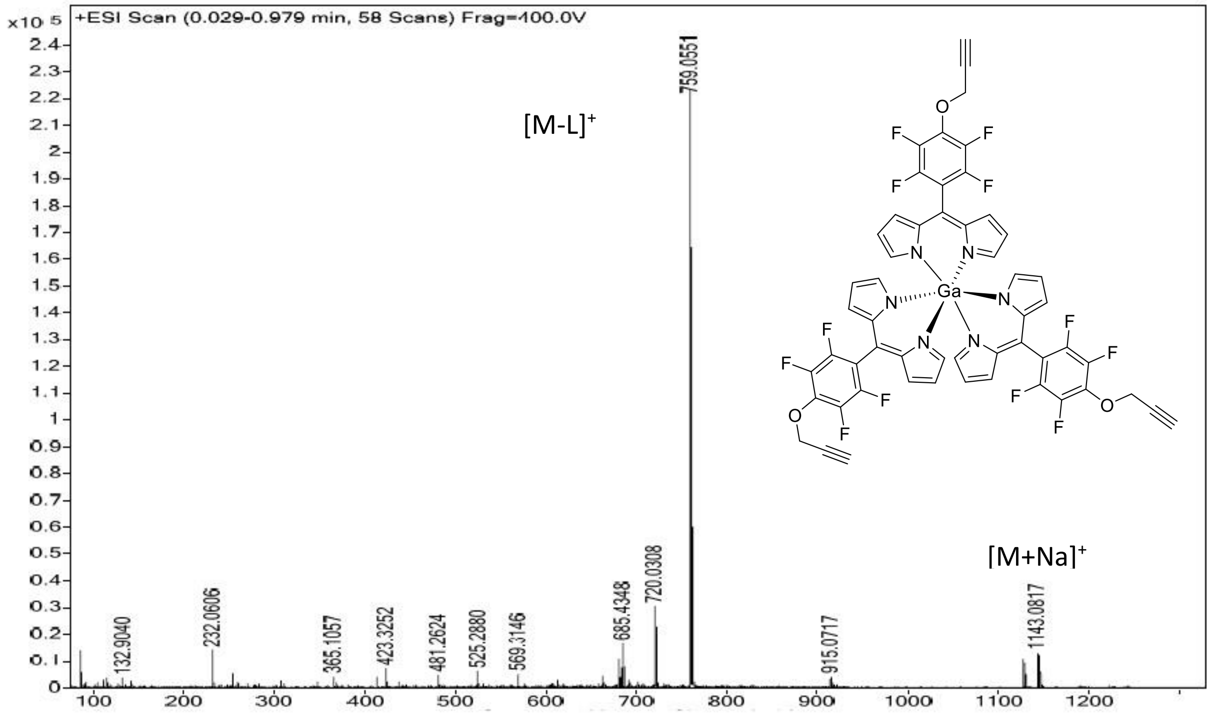


Figure S 27. HRMS (ESI-TOF) spectrum of complex 5c.

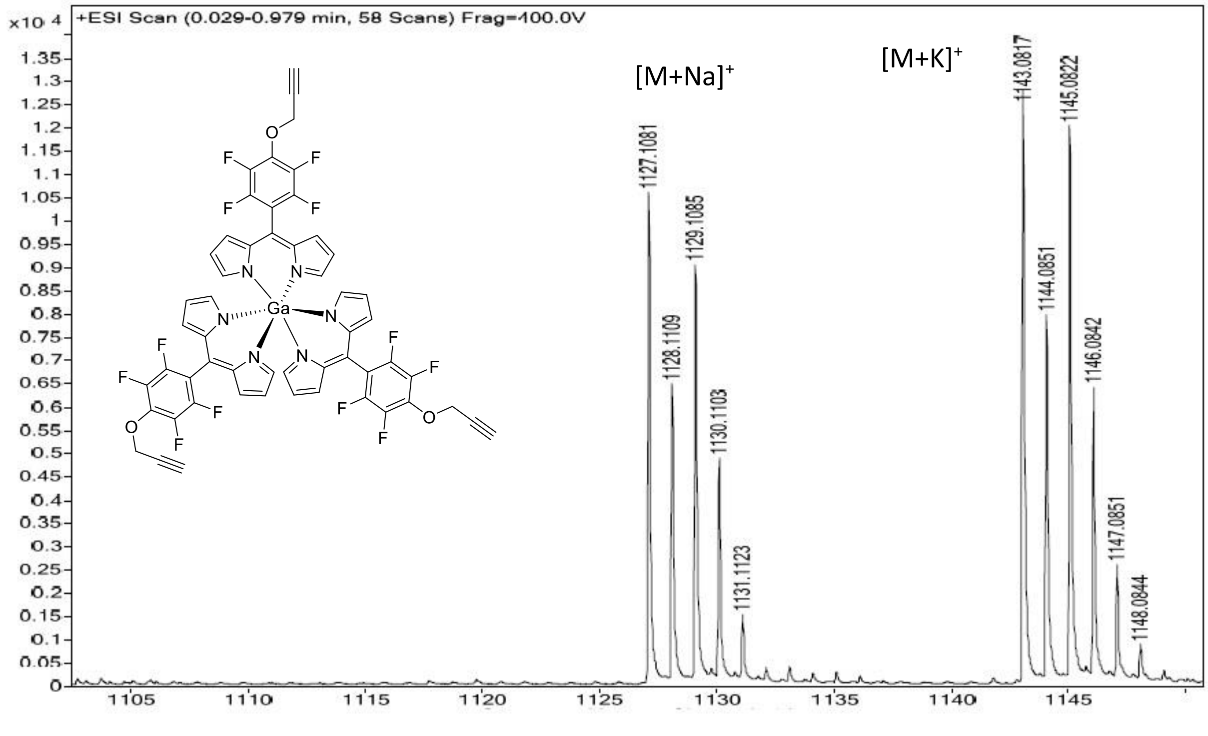


Figure S 28. HRMS (ESI-TOF) spectrum of complex 5c.

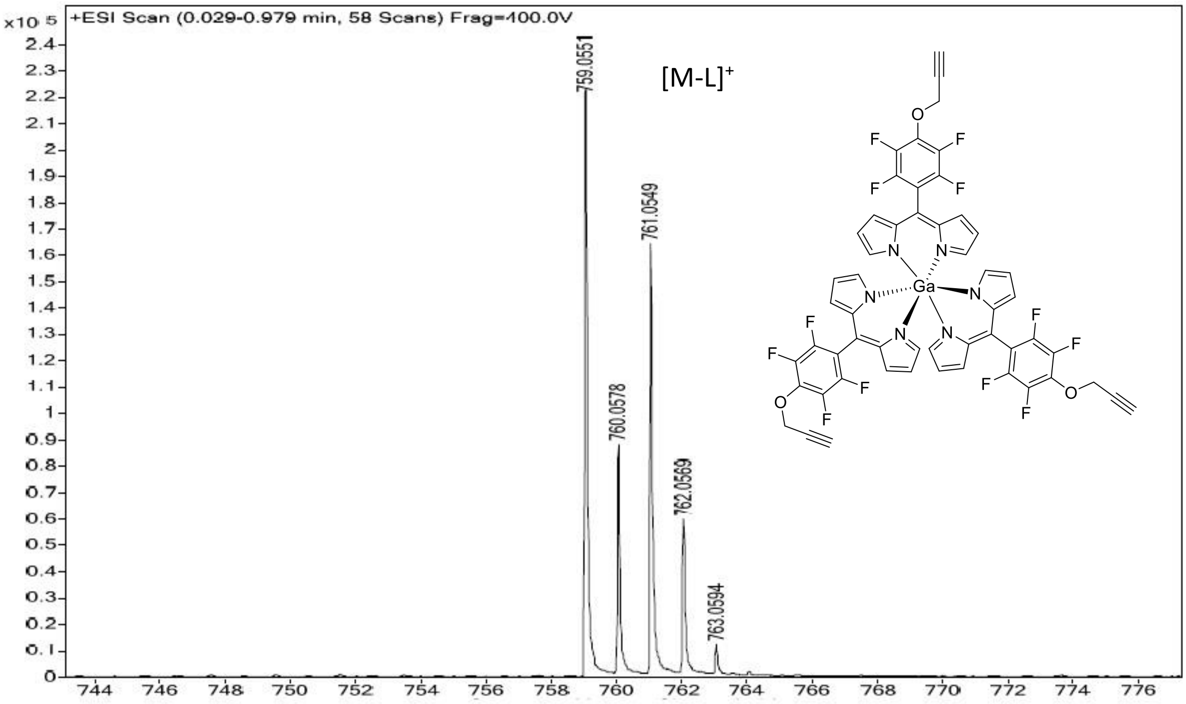
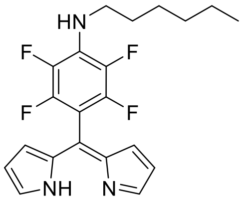


Figure S 29. HRMS (ESI-TOF) spectrum of complex 5c.

5-{4-(*N*-Hexylamino)-2,3,5,6-tetrafluorophenyl}dipyrrin [6]



According to the general procedure for the synthesis of *para*-phenyl-substituted PFP-dipyrrins, a mixture of 5-{4-(*N*-hexylamino)-2,3-5,6-tetrafluorophenyl}dipyrrane (603 mg, 1.53 mmol) and DDQ (452 mg, 1.99 mmol, 1.3 eq.) in THF (10 mL) was stirred for 20 min at rt. The mixture was filtered through silica gel and evaporated to dryness. Further purification was achieved by column chromatography (silica gel, DCM). After evaporation to dryness, the product was washed with pentane and dried *in vacuo* to obtain the product as a yellow solid (200 mg, 34%).

Mp: 55-57 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.92 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.30-1.45 (m, 6 H, CH_2), 1.60-1.70 (m, 2 H, CH_2), 3.44-3.51 (m, 2 H, CH_2), 3.95 (br s, 1 H, NH), 6.39 (dd, *J* = 4.2, 1.4 Hz, 2 H, $H_{pyrrole}$), 6.58 (d, *J* = 4.2 Hz, 2 H, $H_{pyrrole}$), 7.61-7.63 (m, 2 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.08 (CH_3), 22.66 (CH_2), 26.42 (CH_2), 30.92 (CH_2), 31.57 (CH_2), 45.94 (t, $J_{C\text{-}F}$ = 4.0 Hz, CH_2), 102.79 (t, $J_{C\text{-}F}$ = 19.3 Hz, Ar-C_{ipso}), 118.40 (C_{pyrrole}), 127.55 (C_{pyrrole}), 128.94 (t, $J_{C\text{-}F}$ = 11.4 Hz, Ar-C_{para}), 136.94 (dd, $J_{C\text{-}F}$ = 236.3, 13.1 Hz, Ar-C_{meta}), 141.11 (C_{meso}), 144.66 (C_{pyrrole}), 144.93 (d, $J_{C\text{-}F}$ = 243.6 Hz, Ar-C_{ortho}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -160.45 (m_c, *J* = 16.9 Hz, 2 F, Ar-F_{meta}), -141.70 (m_c, *J* = 15.8 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{21}H_{22}F_4N_3^+$ $[M+H]^+$ 392.1744, found 392.1739.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 433 (4.59) nm.

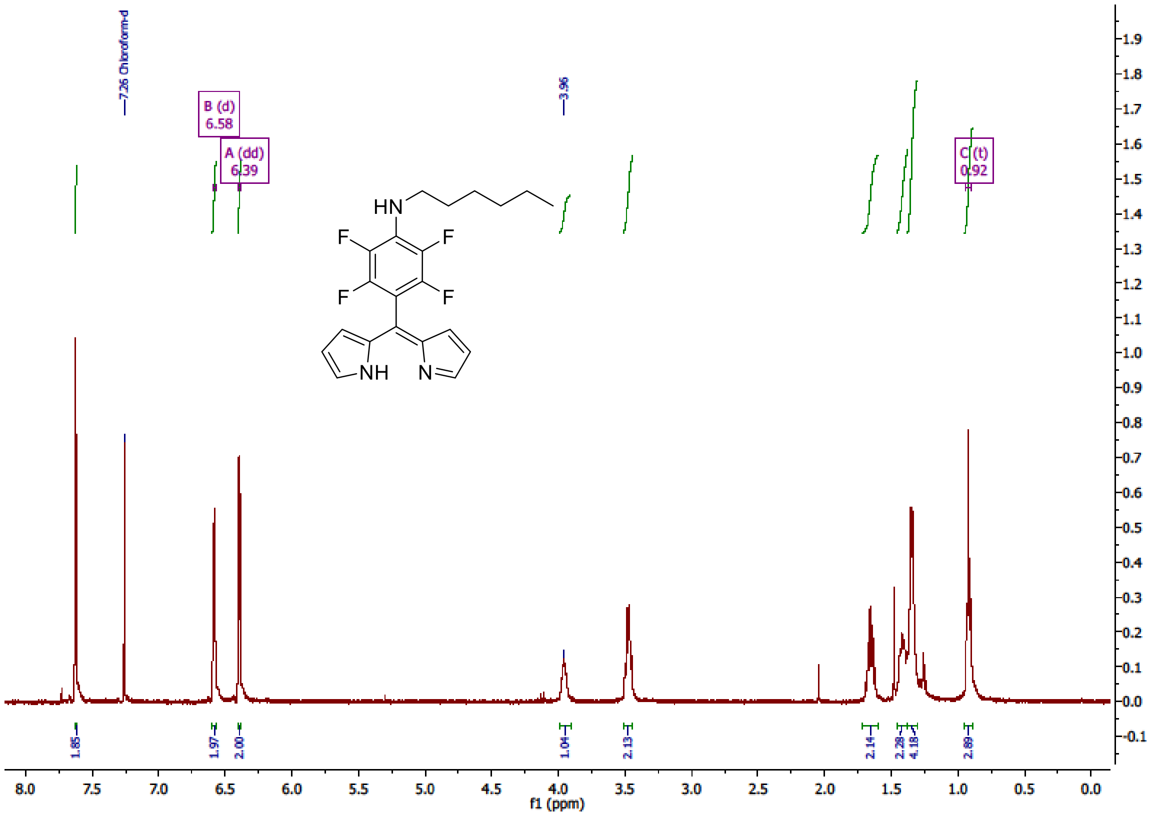


Figure S 30. ^1H **NMR (400 MHz,** $CDCl_3$**) spectrum of dipyrrin 6.**

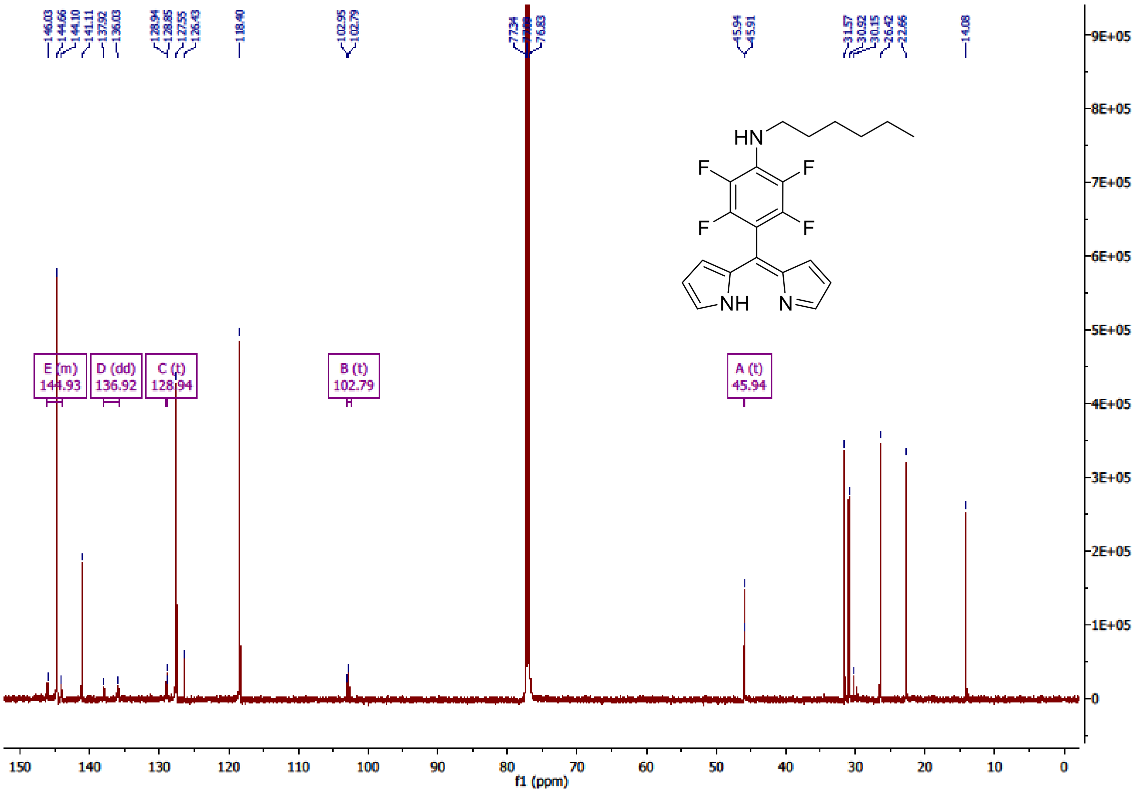


Figure S 31. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of dipyrrin 6.

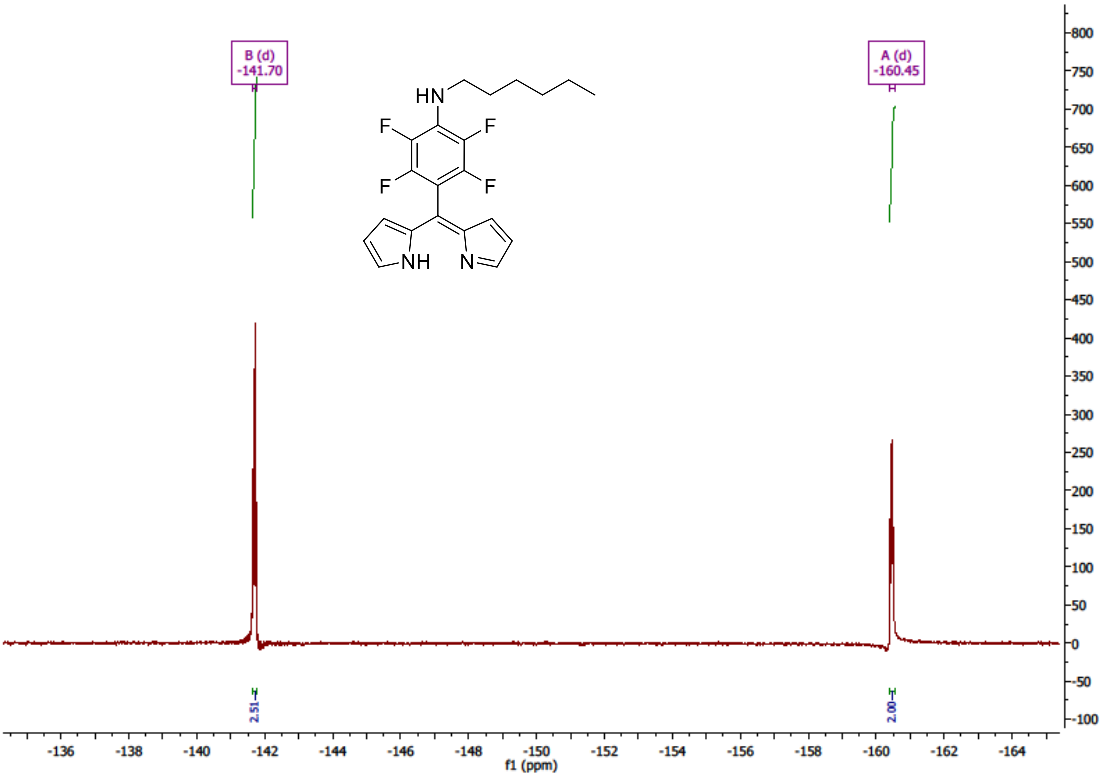


Figure S 32. ^{19}F NMR spectrum (376 MHz, CDCl$_3$) spectrum of dipyrrin 6.

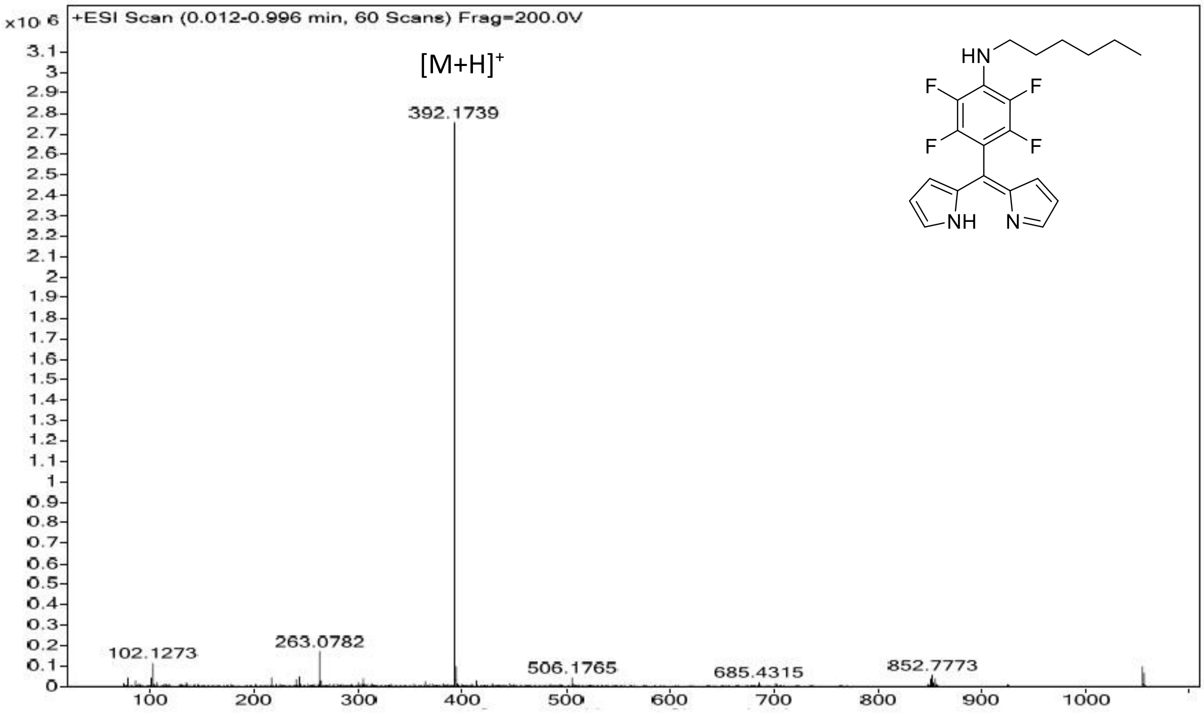


Figure S 33. HRMS (ESI-TOF) spectrum of dipyrrin 6.

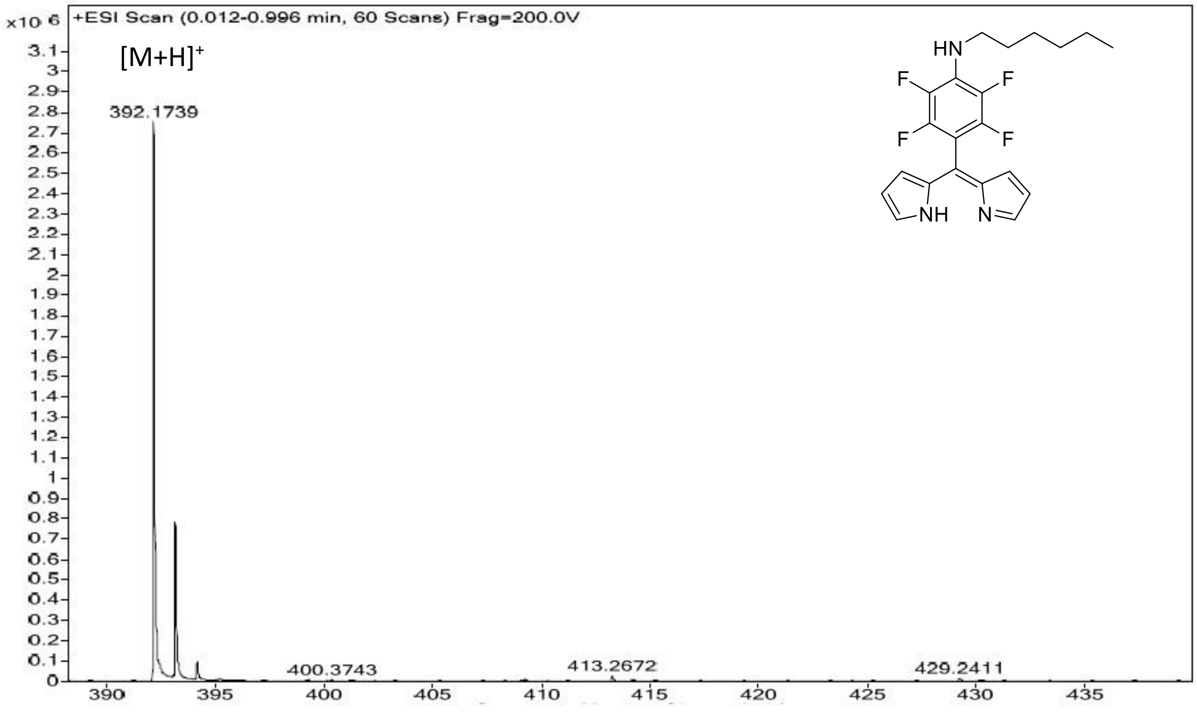
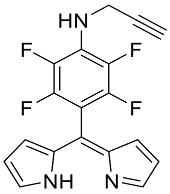


Figure S 34. HRMS (ESI-TOF) spectrum of dipyrrin 6.

5-{4-(*N*-Prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl}dipyrrin [7]



According the general procedure for the synthesis of *para-phenyl*-substituted PFP-dipyrrins, 5-{4-(*N*-Prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl}dipyrrane (913 mg, 2.63 mmol) was dissolved in THF (10 mL), DDQ (776 mg, 3.40 mmol, 1.3 eq.) was added and the mixture stirred for 15 min at rt. The mixture was filtered through silica gel, evaporated to dryness and purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1),evaporated to dryness, washed with pentane and dried *in vacuo* to obtain the product as a yellow oil (640 mg, 70%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.26 (t, *J* = 7.2 Hz, 1 H, C≡CH), 4.20-4.25 (m, 2 H, CH$_2$), 6.40 (dd, *J* = 4.20, 1.4 Hz, 2 H, H$_{pyrrole}$), 6.56 (d, *J* = 4.2 Hz, 2 H, H$_{pyrrole}$), 7.62-7.62 (m, 2 H, H$_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 35.30 (CH$_2$), 72.79 (C≡CH), 79.92 (C≡CH), 105.03 (m, Ar-C$_{ipso}$), 118.16 (C$_{pyrrole}$), 127.39 (C$_{pyrrole}$), 140.54 (C$_{meso}$), 144.78 (C$_{pyrrole}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -158.33 (m$_c$, *J* = 21.9, 7.7 Hz, 2 F, Ar-F$_{meta}$), -140.95 (dd, *J* = 21.2, 7.1 Hz, 2 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{18}H_{12}F_4N_3^+$ [M+H]$^+$ 346.0962, found 346.0973.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 432 (4.45) nm.

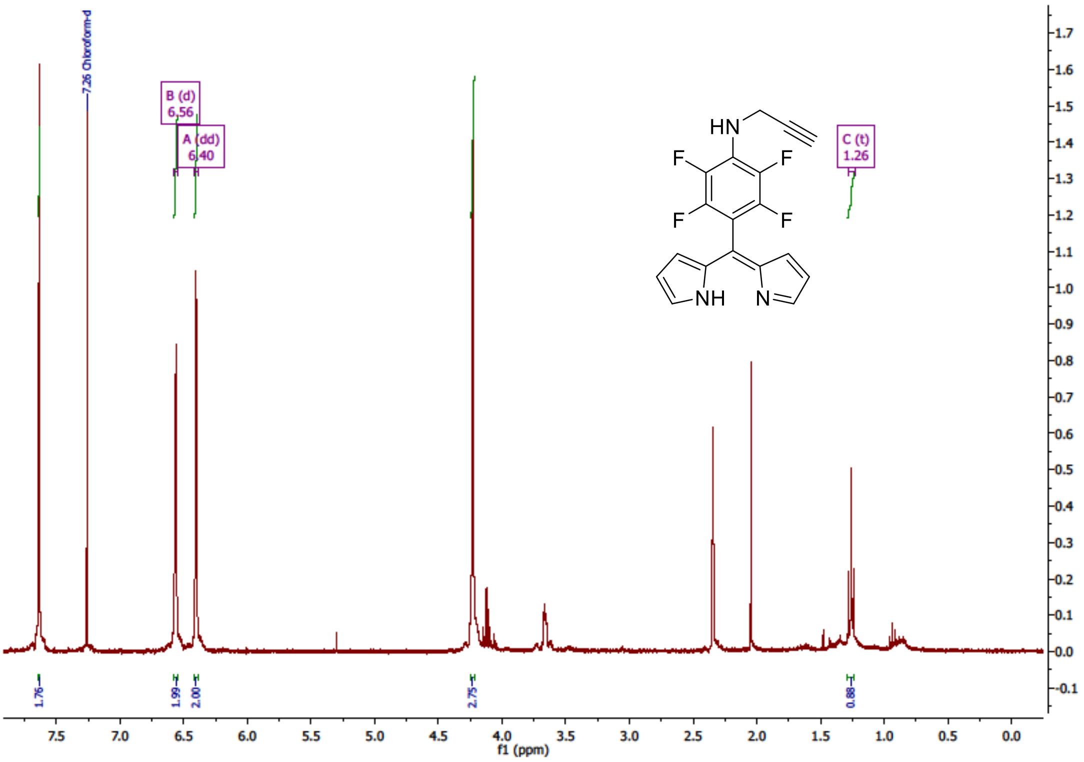


Figure S 35.^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of dipyrrin 7.**

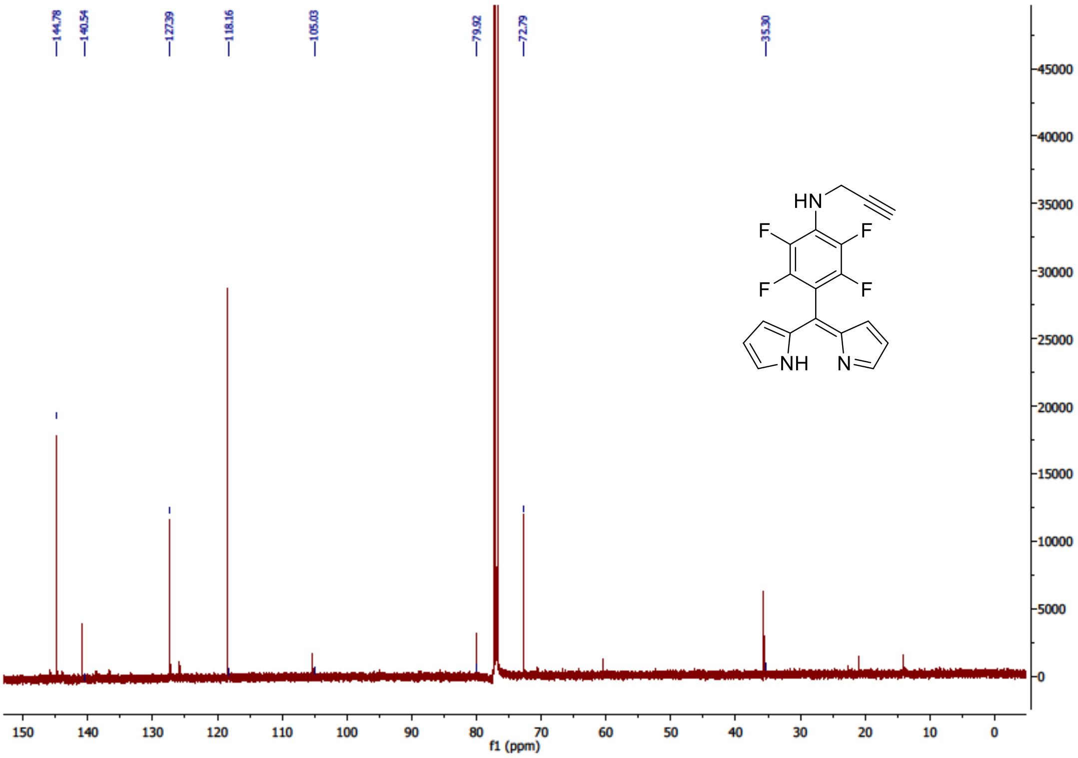


Figure S 36. ^{13}**C NMR (126 MHZ, CDCl$_3$) spectrum of dipyrrin 7.**

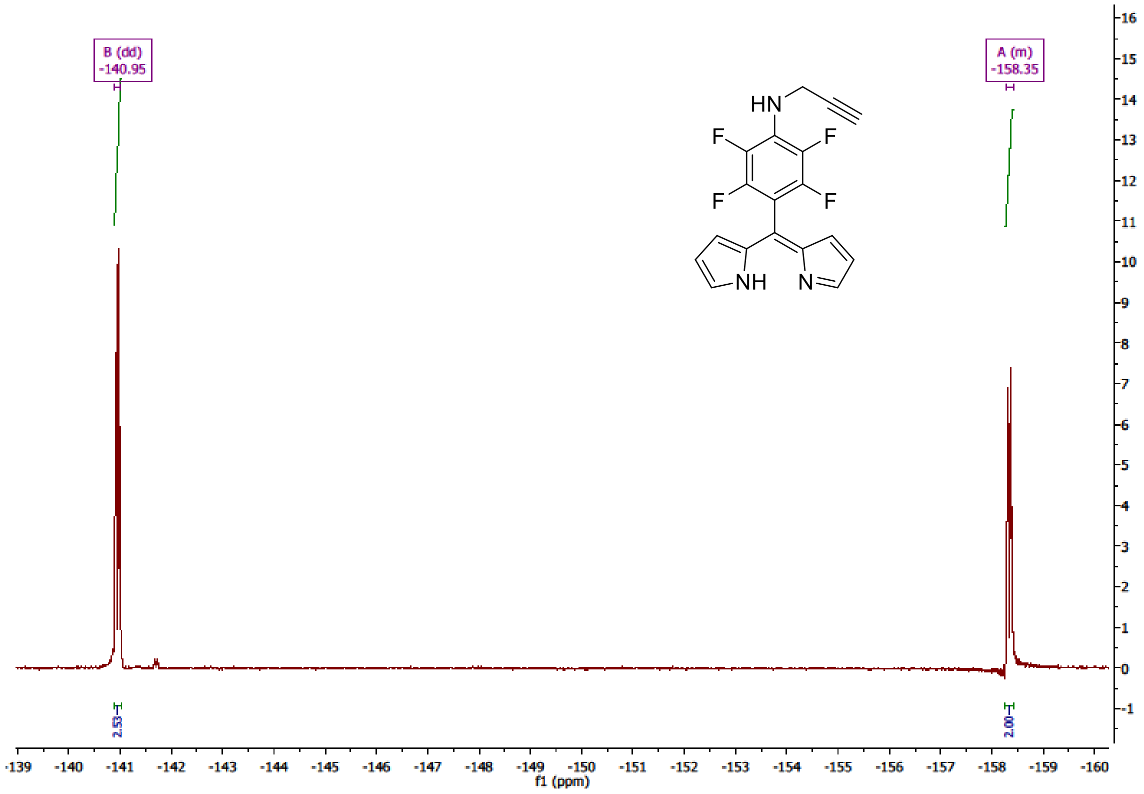


Figure S 37.^{19}**F NMR (376 MHz, CDCl**$_3$**) spectrum of dipyrrin 7.**

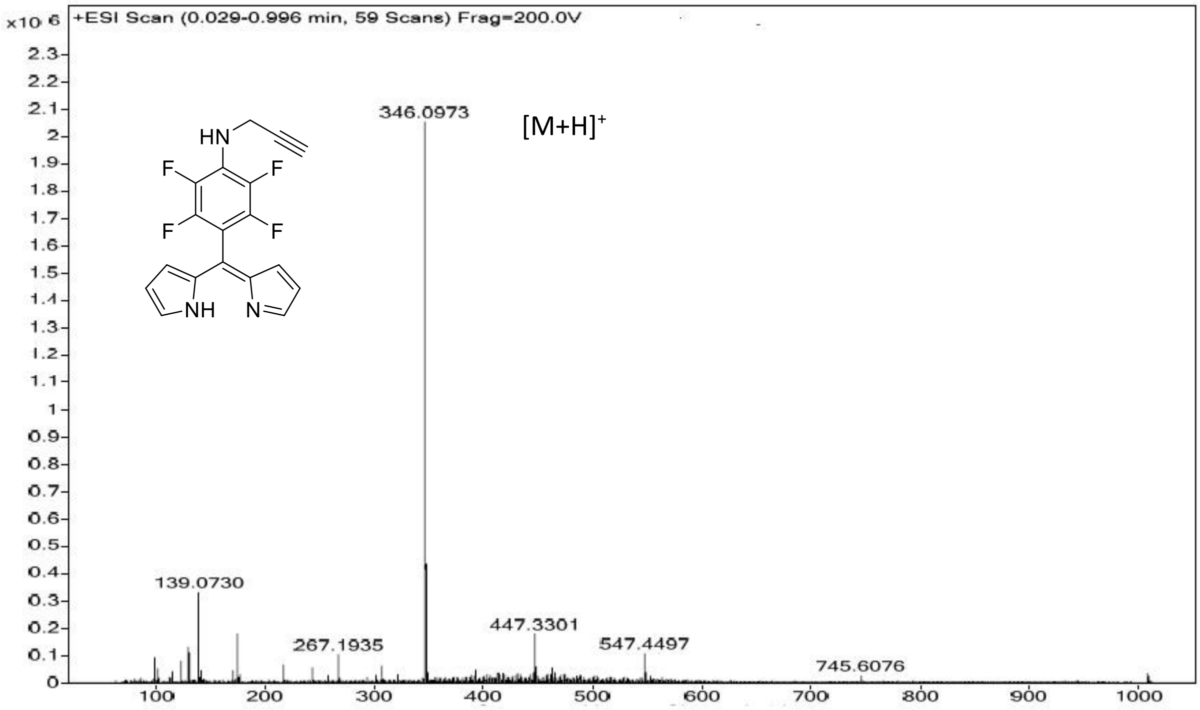


Figure S 38. HRMS (ESI-TOF) spectrum of dipyrrin 7.

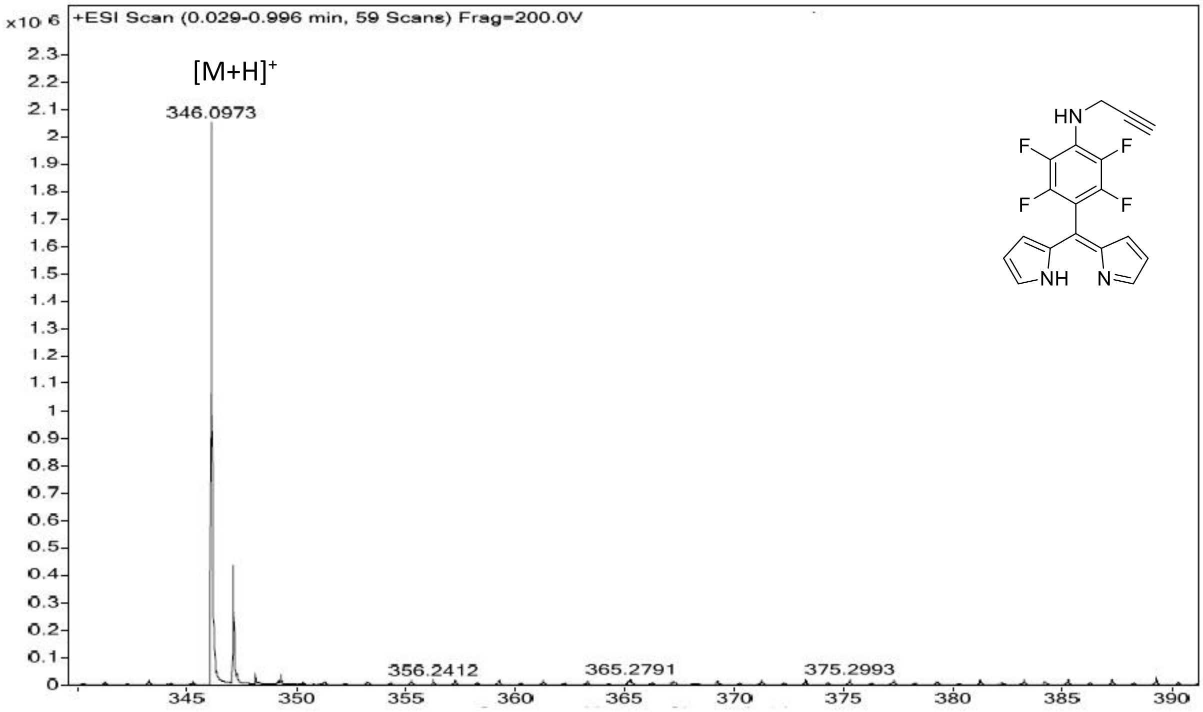
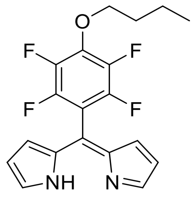


Figure S 39. HRMS (ESI-TOF) spectrum of dipyrrin 7.

5-{4-(Butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrin [8]



According the general procedure for the synthesis of *para-phenyl*-substituted PFP-dipyrrins, 5-{4-(Butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrane (654 mg, 1.78 mmol) was dissolved in THF (10 mL), DDQ (526 mg, 2.32 mg, 1.3 eq) was added and the mixture was stirred for 15 min at rt. The crude product was filtered through silica gel, evaporated to dryness and purified by column chromatography (silica gel, DCM). The product was evaporated to dryness and washed with pentane. The product was dried *in vacuo* and was isolated as a yellow oil (260 mg, 40%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.01 (t, *J* = 7.4 Hz, 3 H, CH$_3$), 1.50-1.60 (m, 2 H, CH$_2$), 1-78-1.88 (m, 2 H, CH$_2$), 4.34 (t, *J* = 6.5 Hz, 2 H, CH$_2$), 6.41 (dd, *J* = 4.2, 1.4 Hz, 2 H, H$_{pyrrole}$), 6.52 (d, *J* = 4.2 Hz, 2 H, H$_{pyrrole}$), 7.63-7.65 (m, 2 H, H$_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 13.79 (CH$_3$), 18.89 (CH$_2$), 32.06 (CH$_2$), 75.22 (CH$_2$), 109.54 (t, $J_{C\text{-}F}$ = 19.2 Hz, Ar-C$_{ipso}$), 118.74 (C$_{\text{pyrrole}}$), 127.27 (C$_{\text{pyrrole}}$), 138.42 (t, $J_{C\text{-}F}$ = 11.9 Hz, Ar-C$_{para}$), 145.09 (C$_{\text{pyrrole}}$), 140.95 (dd, $J_{C\text{-}F}$ = 248.5, 15.0 Hz, Ar-C$_{meta}$), 145.21 (d, $J_{C\text{-}F}$ = 249.0 Hz, Ar-C$_{ortho}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -156.54 (m$_c$, *J* = 14.3 Hz, 2 F, Ar-F$_{meta}$), -140.42 (m$_c$, *J* = 22.6, 7.9 Hz, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{19}H_{17}F_4N_2O^+$ [M+H]$^+$ 365.1272, found 365.1277.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 431 (4.62) nm.

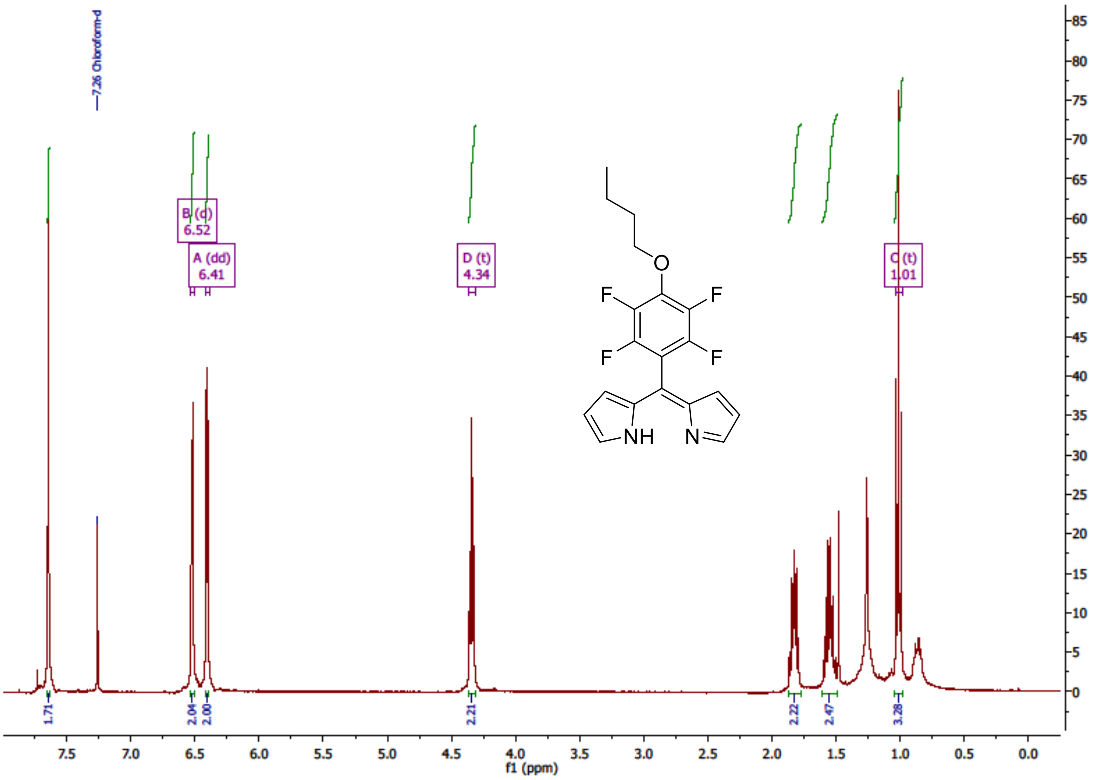


Figure S 40. **^{1}H NMR (400 MHz, CDCl$_3$) spectrum of dipyrrin 8.**

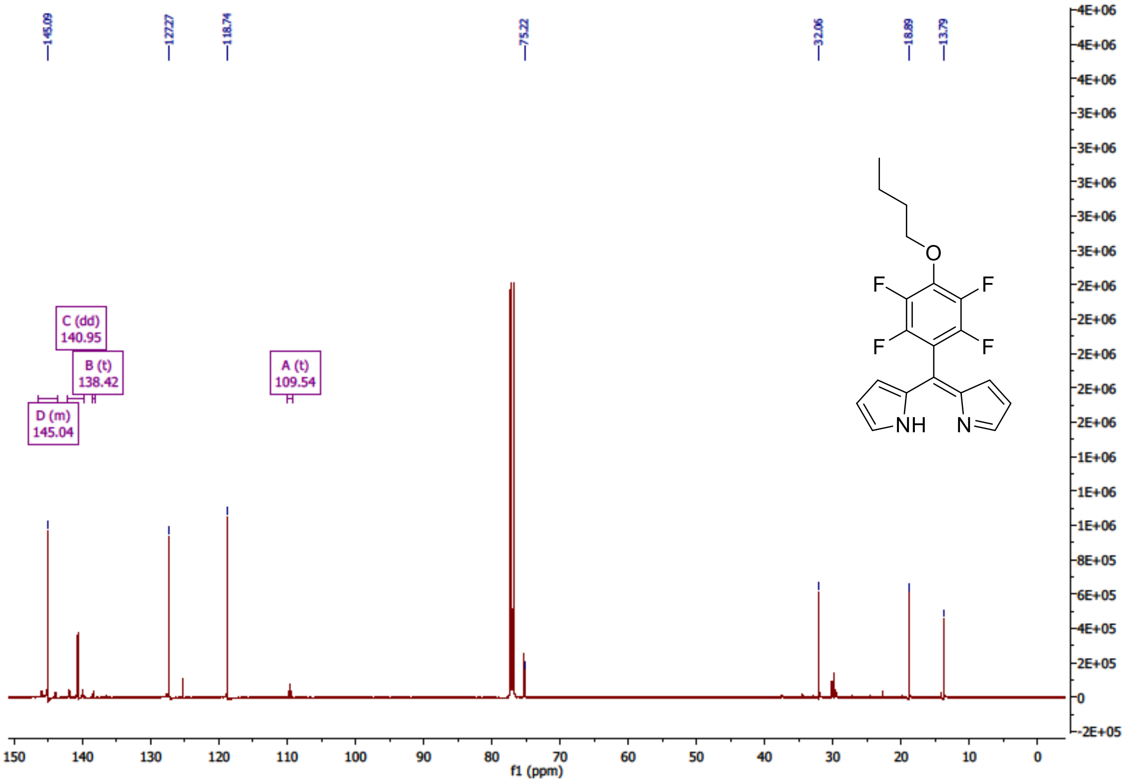


Figure S 41. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of dipyrrin 8.

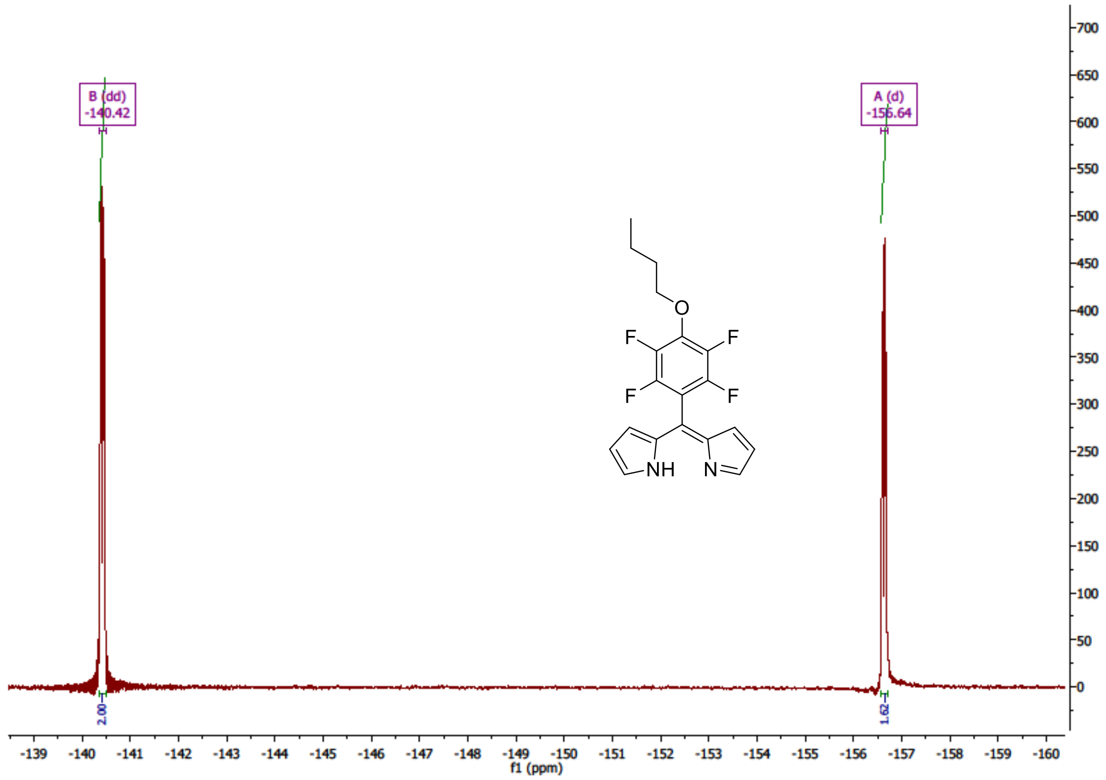


Figure S 42. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of dipyrrin 8.

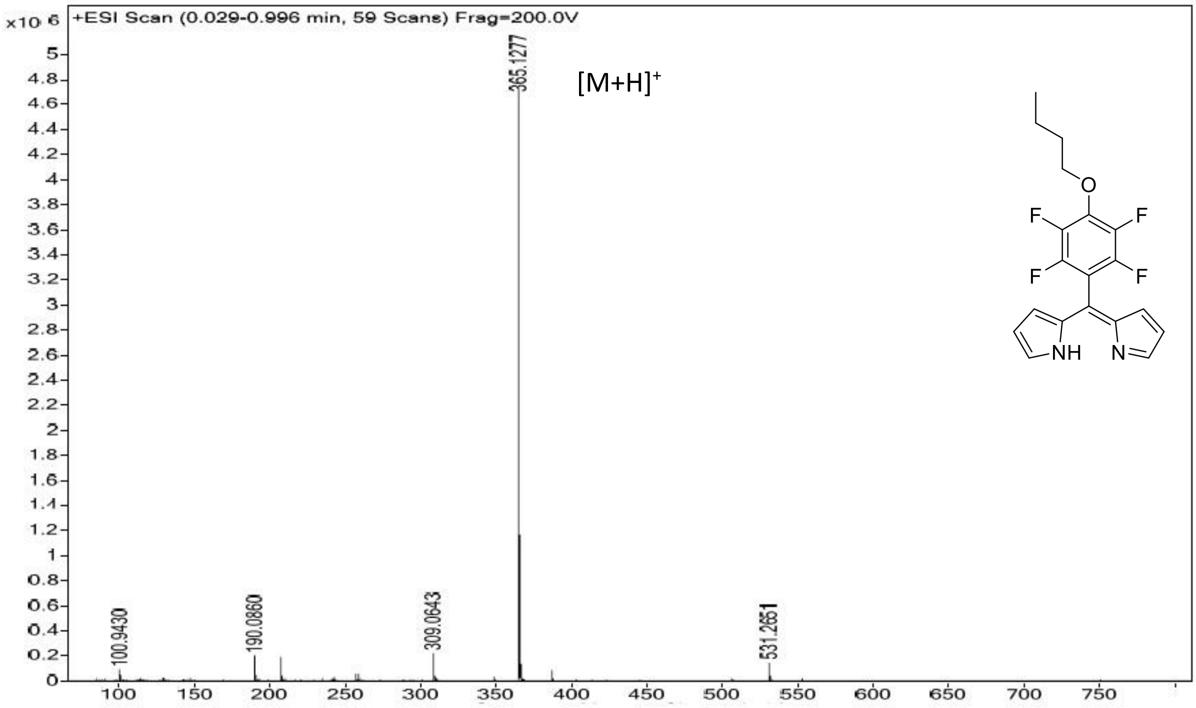


Figure S 43. HRMS (ESI-TOF) spectrum of dipyrrin 8.

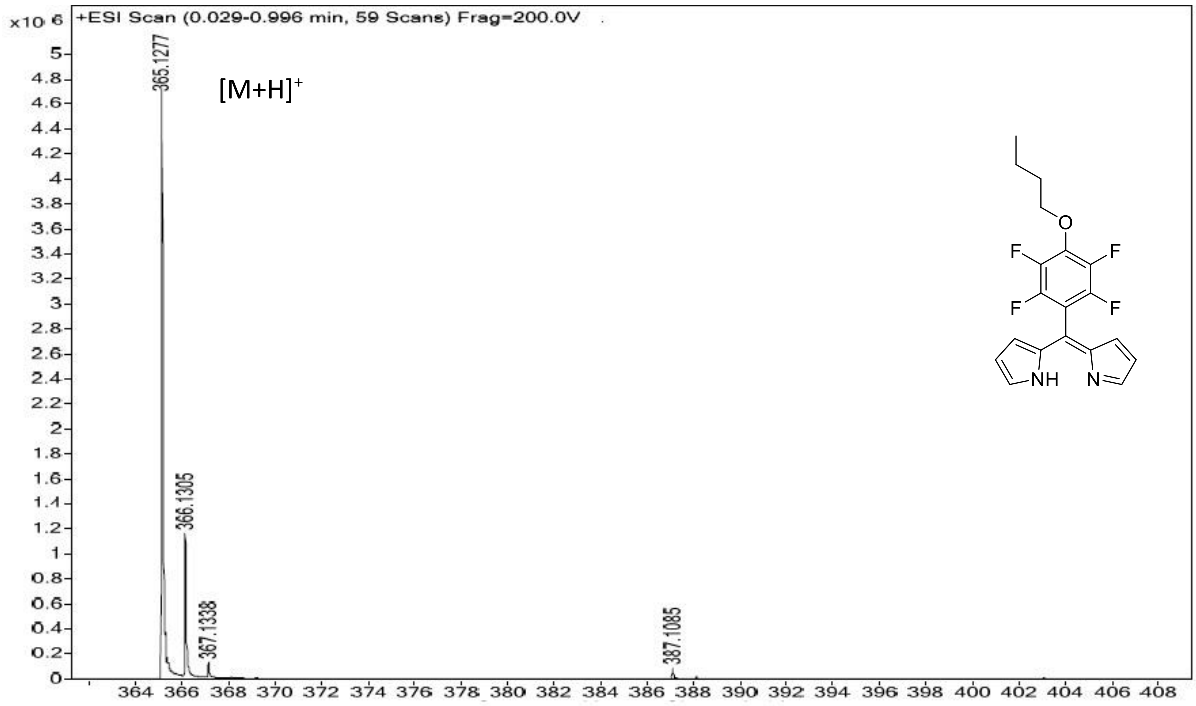
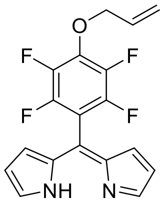


Figure S 44. HRMS (ESI-TOF) spectrum of dipyrrin 8.

5-{4-(Prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrin [9]



According the general procedure for the synthesis of *para-phenyl*-substituted PFP-dipyrrins, 5-{4-(Prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrane (372 mg, 1.07 mmol) was dissolved in THF (10 mL), DDQ (315 mg, 1.38 mmol, 1.3 eq.) was added and the mixture was stirred for 15 min at rt. The mixture was filtered through silica gel and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 3:1). After evaporation to dryness the product was washed with pentane. The product was isolated as a yellow oil (300 mg, 80%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.83 (d, *J* = 6.1 Hz, 2 H, CH$_2$), 5.37 (dd, *J* = 10.3,1.2 Hz, 1 H, C=CH$_2$), 5.46 (dd, *J* = 17.1, 1.4 Hz, 1 H, C=CH$_2$), 6.05-6.15 (m, 1 H, CH), 6.41 (dd, *J* = 4.2, 1.4 Hz, 2 H, H$_{\text{pyrrole}}$), 6.50 (d, *J* = 3.6 Hz, 2 H, H$_{\text{pyrrole}}$), 7.64 (t, *J* = 1.1 Hz, 2 H, H$_{\text{pyrrole}}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 75.45 (CH$_2$), 118.77 (C$_{\text{pyrrole}}$), 110.01 (t, $J_{C\text{-}F}$ = 19.2 Hz, Ar-C$_{ipso}$), 120.31 (C=*C*H$_2$), 127.11 (C$_{\text{pyrrole}}$), 132.16 (CH), 137.43 (C$_{meso}$), 137.34 (m, Ar-C$_{para}$), 141.01 (dd, $J_{C\text{-}F}$ = 248.6, 15.2 Hz, Ar-C$_{meta}$), 144.93 (d, $J_{C\text{-}F}$ = 243.9 Hz, Ar-C$_{ortho}$), 145.06 (C$_{\text{pyrrole}}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -155.08 (m$_c$, *J* = 22.4, 8.1 Hz, 2 F, Ar-F$_{meta}$), -140.28 (m$_c$, *J* = 21.9, 7.8 Hz, 2 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc for $C_{18}H_{13}F_4N_2O^+$ [M+H]$^+$ 349.0959, found 349.1002.

UV/Vis (DCM): λ$_{\text{max}}$ [log ε (dm^3·mol^{-1}·cm^{-1})] = 430 (4.65) nm.

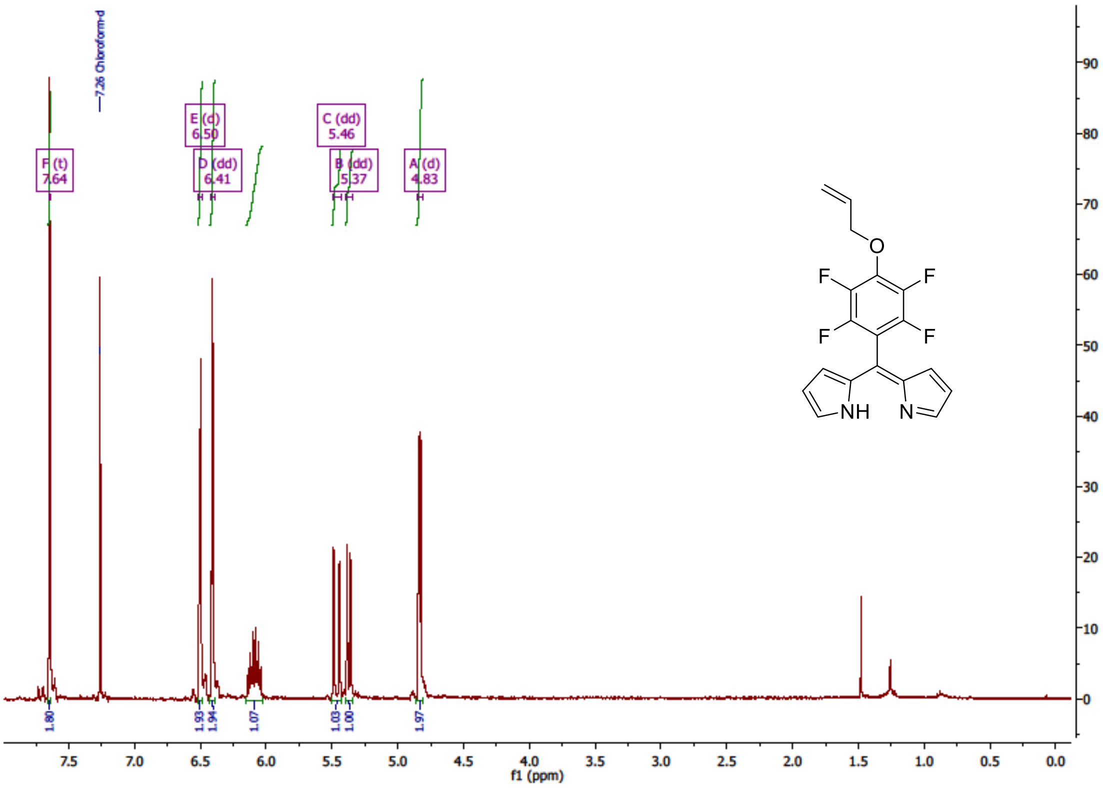


Figure S 45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dipyrrin 9.

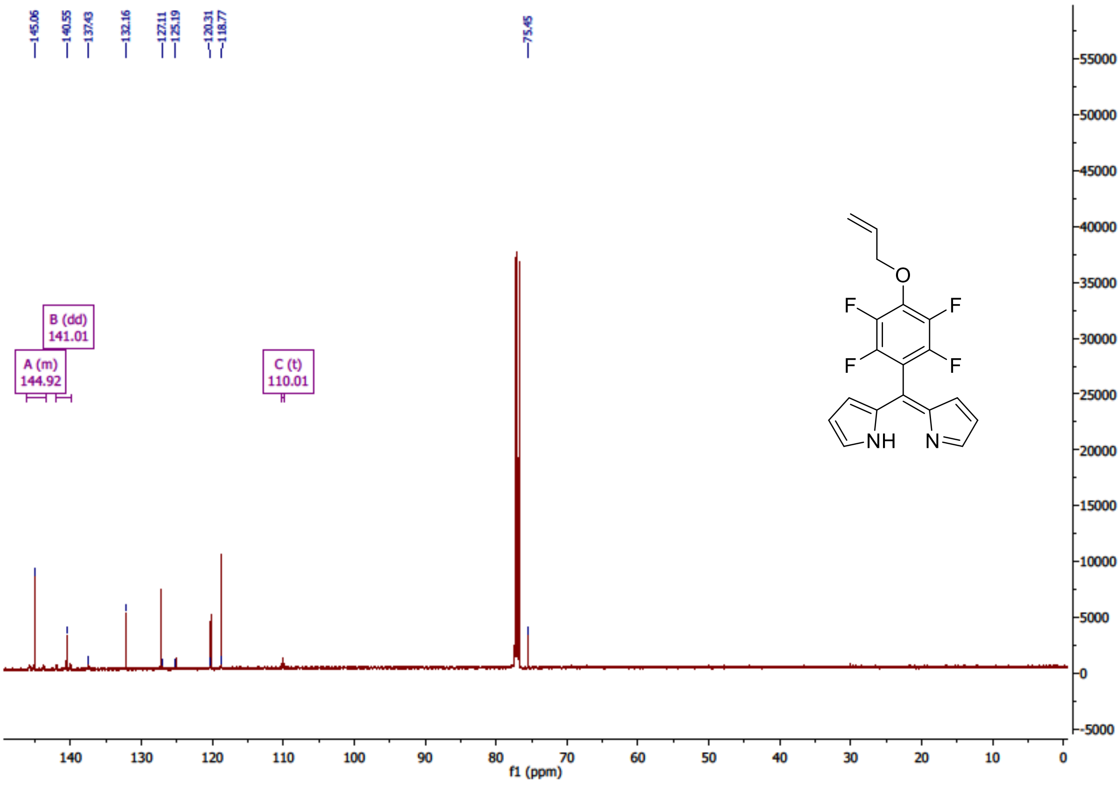


Figure S 46. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of dipyrrin 9.

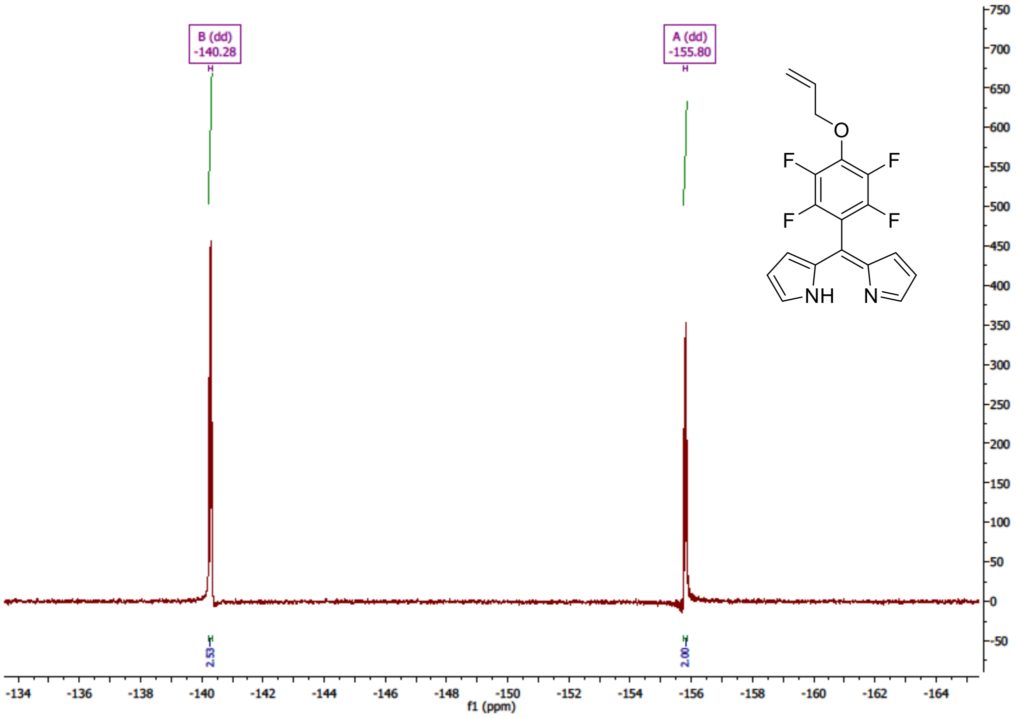


Figure S 47. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of dipyrrin 9.

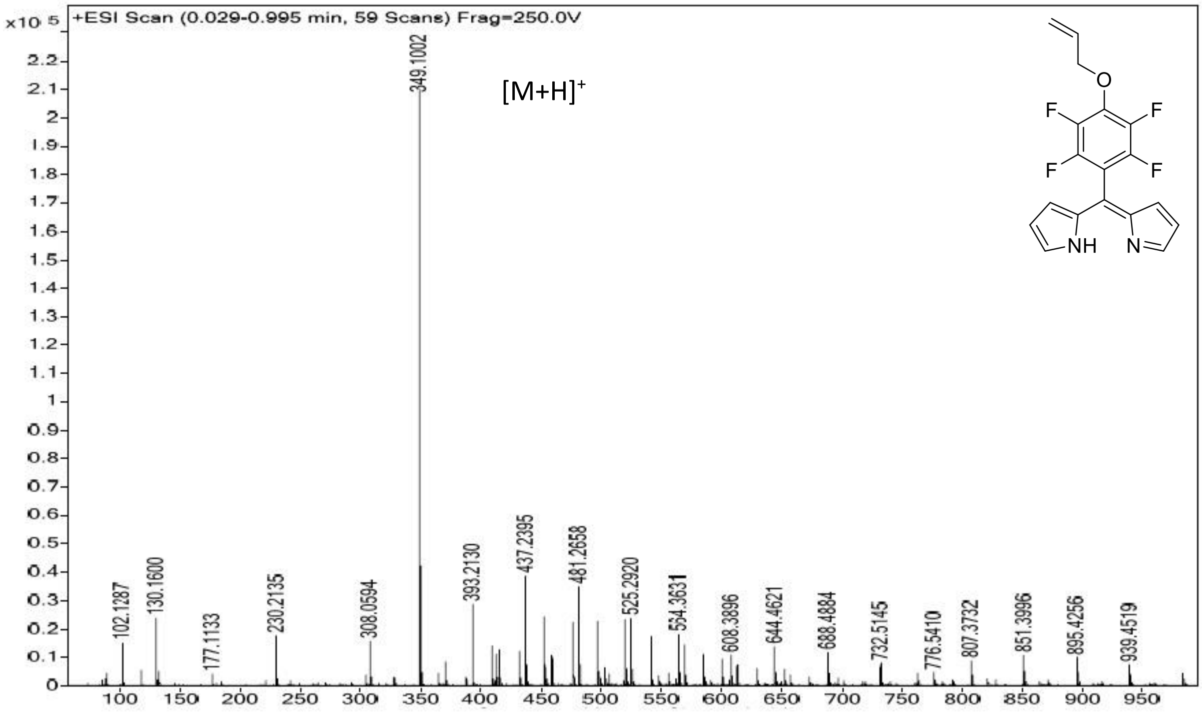


Figure S 48. HRMS (ESI-TOF) spectrum of dipyrrin 9.

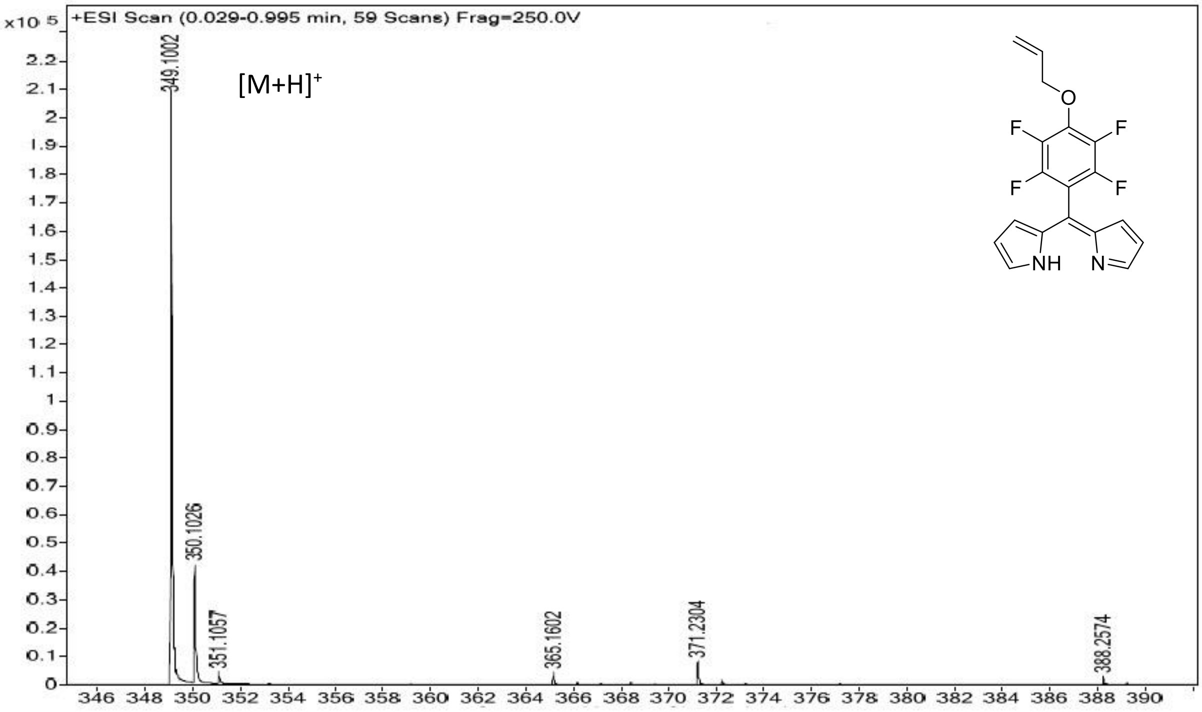
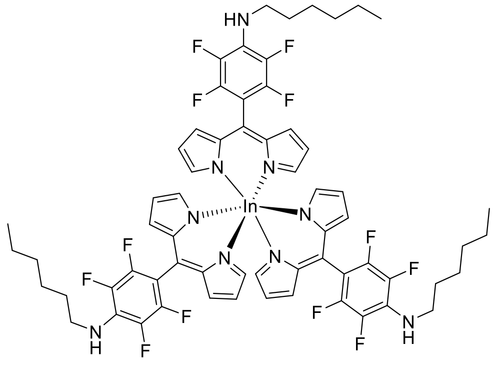


Figure S 49. HRMS (ESI-TOF) spectrum of dipyrrin 9.

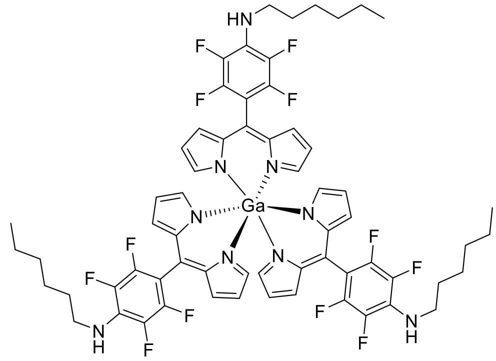
Tris[5-{4-(*N*-hexylamino)-2,3,5,6-tetrafluorophenyl}dipyrrinato] indium(III) [10a]



Method A: Under argon atmosphere complex **2** (70 mg, 67 µmol) was dissolved in dry DMSO (3 mL), *n*-Hexylamine (0.4 mL, 338 mg, 3.35 mmol. 50 eq.) was added and the mixture stirred at 80 °C. After 6 h a reaction control by TLC showed still starting material, so more amine was added (0.2 mL, 170 mg, 25 eq.) After 7 h at 80 °C, the reaction was stopped. The reaction mixture was diluted with DCM and washed several times. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. After purification by column chromatography traces of an inseparable mixture of different substituted In(DPM)$_3$-complexes as well as dipyrrin were isolated.

Method B: According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of dipyrrin **6** (100 mg, 0.25 mmol, 3.1 eq), $InCl_3$ (18 mg, 82 µmol) and DIPEA (40 µL, 32 mg, 0.25 mmol, 3.1 eq.) were dissolved in dry THF (3 mL) and the mixture was refluxed for 20 h. The mixture was diluted with DCM and washed the organic layer was washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. Further purification was achieved by column chromatography (silica gel, DCM/*n*-hexane =1:1). The desired product could not be isolated.

Tris[5-{4-(*N*-hexylamino)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [10b]



Method A: Under argon atmosphere complex **3** (70 mg, 70 µmol) was dissolved in dry DMSO (3 mL), *n*-hexylamine (0.18 mL, 142 mg, 1.40 mmol, 20 eq.) was added and the mixture stirred at 80 °C. After 48 h TLC still showed starting material, so that more amine (0.18 mL, 142 mg, 1.40 mmol, 20 eq.) was added. After 6 d at 80 °C and 3 d at 100 °C, the reaction was stopped. The desired product could not be isolated.

Method B: According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of dipyrrin **6** (100 mg, 0.25 mmol, 3.1 eq.), $GaCl_3$ (14 mg, 80 µmol) and DIPEA (22 mg, 0.25 mmol, 3.1 eq.) were dissolved in dry THF and the mixture was refluxed for 16 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1). After evaporation to dryness, the product was washed with pentane and dried *in vacuo* to obtain the product as an orange solid (121 mg, 97%).

Mp: 55-60 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.92 (t, *J* = 7.0 Hz, 9 H, CH$_3$), 1.30-1.45 (m, 18 H, CH$_2$), 1.60-1.70 (m, 6 H, CH$_2$), 3.43-3.51 (m, 6 H, CH$_2$), 6.39 (dd, *J* = 4.2, 1.4 Hz, 6 H, H$_{\text{pyrrole}}$), 6.59 (d, *J* = 4.2, 0.8 Hz, 6 H, H$_{\text{pyrrole}}$), 7.61-7.62 (m, 6 H, H$_{\text{pyrrole}}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 14.09 (CH$_3$), 22.68 (CH$_2$), 26.43 (CH$_2$), 30.82 (CH$_2$), 31.50 (CH$_2$), 45.99 (CH$_2$), 102.82 (t, $J_{C\text{-}F}$ = 19.2 Hz, Ar-C$_{ipso}$), 118.42 (C$_{\text{pyrrole}}$), 127.50 (C$_{\text{pyrrole}}$), 128.96 (t, $J_{C\text{-}F}$ = 11.3 Hz, Ar-C$_{para}$), 136.98 (dd, $J_{C\text{-}F}$ = 239.3, 16.4 Hz, Ar-C$_{meta}$), 141.20 (C$_{meso}$), 145.02 (d, $J_{C\text{-}F}$ = 245.7 Hz, Ar-C$_{ortho}$), 144.67 (C$_{\text{pyrrole}}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -160.45 (m$_c$, *J* = 16.8 Hz, Ar-C$_{meta}$), -141.70 (m$_c$, *J* = 14.9 Hz, Ar-C$_{ortho}$) ppm.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm $^{-1}$)] = 433 (4.96) nm.

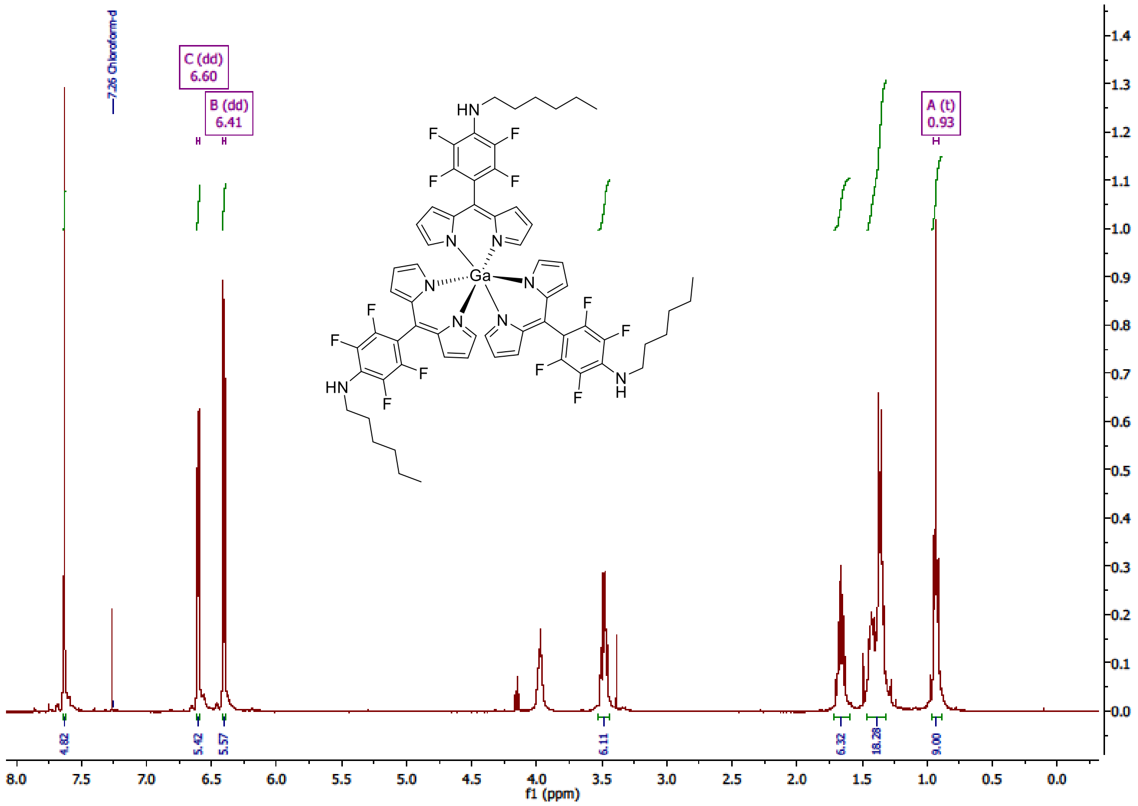


Figure S 50. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 10b.

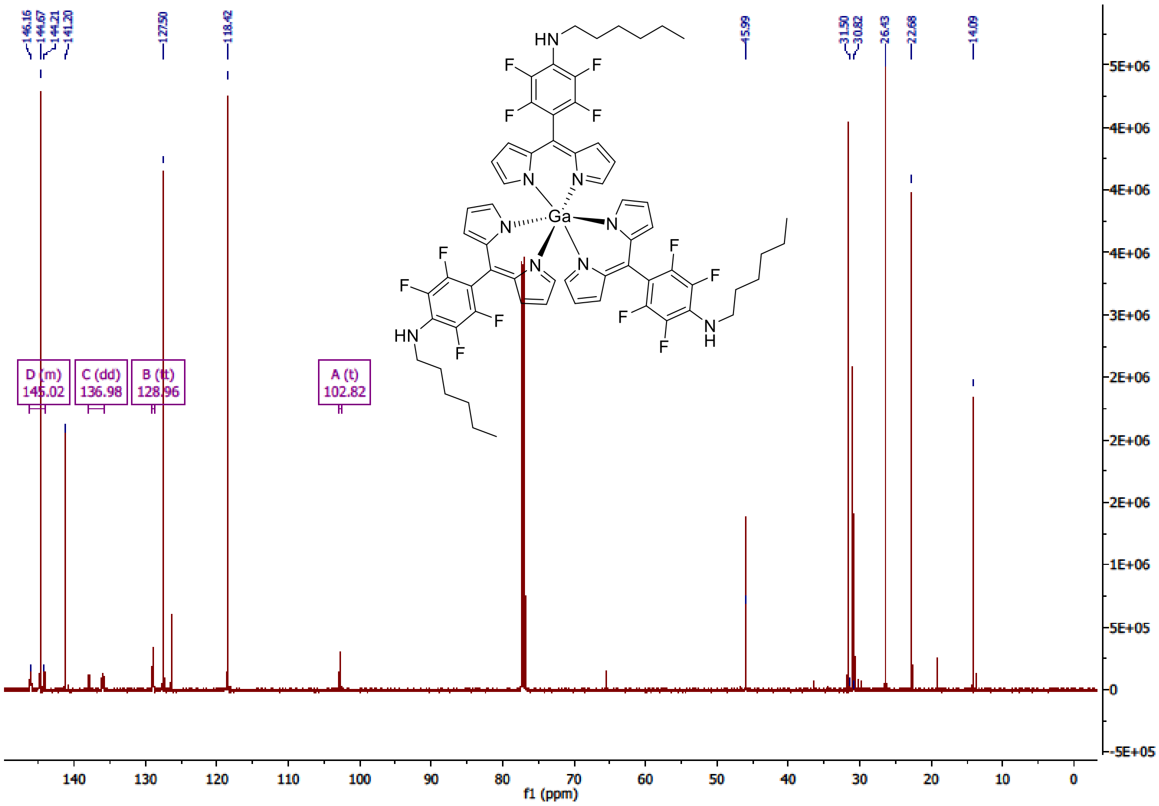


Figure S 51. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 10b.

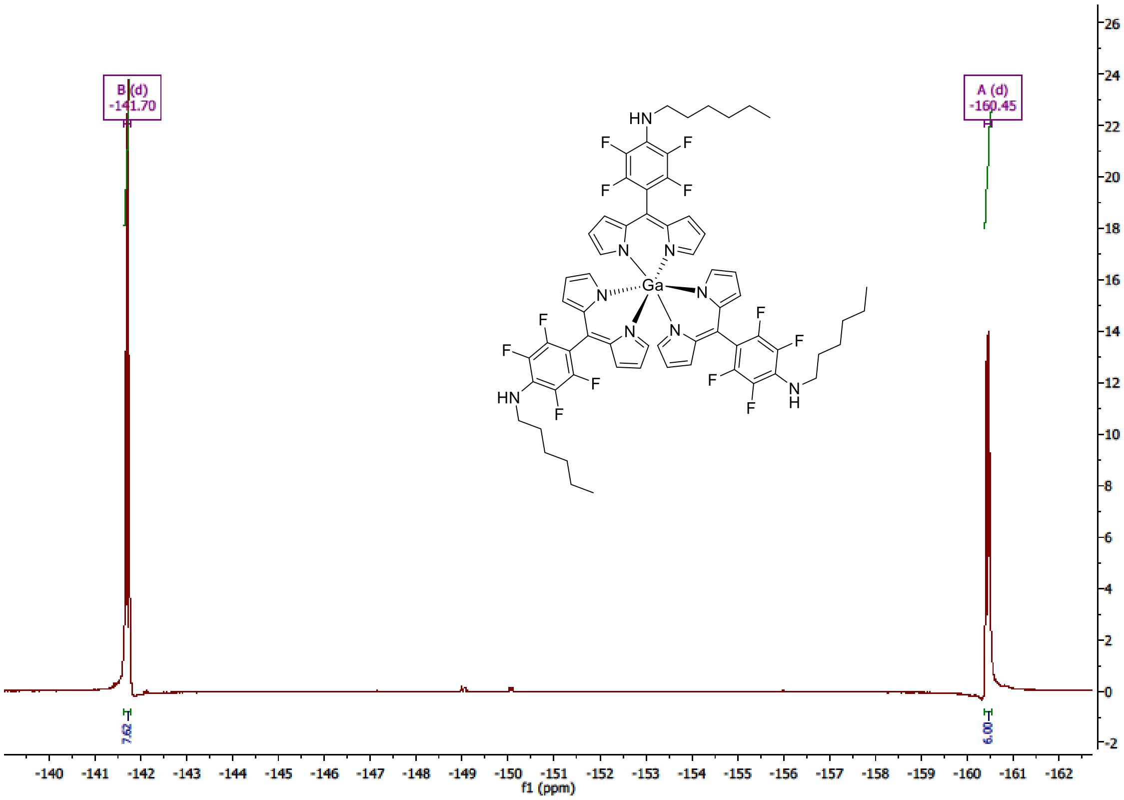
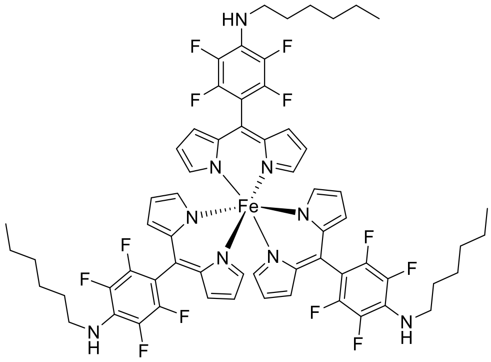


Figure S 52. ^{19}F NMR (376 MHZ, CDCl$_3$) spectrum of complex 10b.

Tris[5-{4-(*N*-hexylamino)-2,3,5,6-tetrafluorophenyl}dipyrrinato] iron(III) [10c]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of dipyrrin **6** (100 mg, 0.255 mmol, 3.1 eq.), $FeCl_3 \cdot 6H_2O$ (22 mg, 82 µmol) and DIPEA (0.19 mL, 1.14 mmol, 14 eq.) were dissolved in MeOH (3 mL) and stirred for 1.5 h at 50 °C. The mixture was evaporated to dryness and purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2). The product was dried *in vacuo*. The product was obtained as a black solid (24 mg, 21%).

Mp: 205-208 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = -29.55 (br s, 6 H, $H_{pyrrole}$), -7.44 (br s, 6 H, $H_{pyrrole}$), -6.43 (br s, 6 H, $H_{pyrrole}$), 1.18 (t, *J* = 7.1 Hz, 9 H, CH_3), 1.60-1.75 (m, 12 H, CH_2), 1.85-1.95 (m, 6 H, CH_2), 2.20-2.30 (m, 6 H, CH_2), 4.15-4.20 (m, 6 H, CH_2), 4.83 (br s, 3 H, NH) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -159.65 (m_c, *J* = 18.3 Hz, 6 F, Ar-F_{meta}), -138.52 (m_c, *J* = 16.5 Hz, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{42}H_{40}F_8FeN_6^+$ $[M-L]^+$ 836.2536, found 836.2548; *m/z* calc. for $C_{63}H_{60}F_{12}FeN_9Na$ $[M+Na]^+$ 1249.4027, found 1249.4057.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 449 (4.72), 500 (4.60) nm.

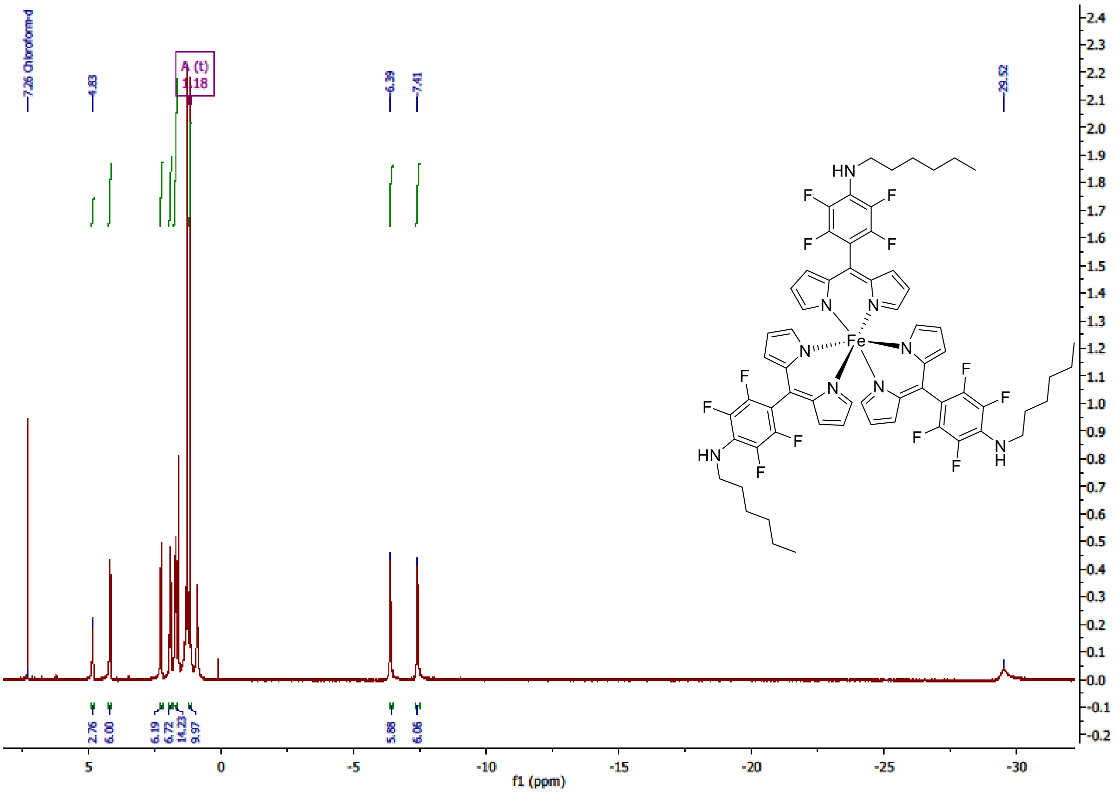


Figure S 53. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 10c.

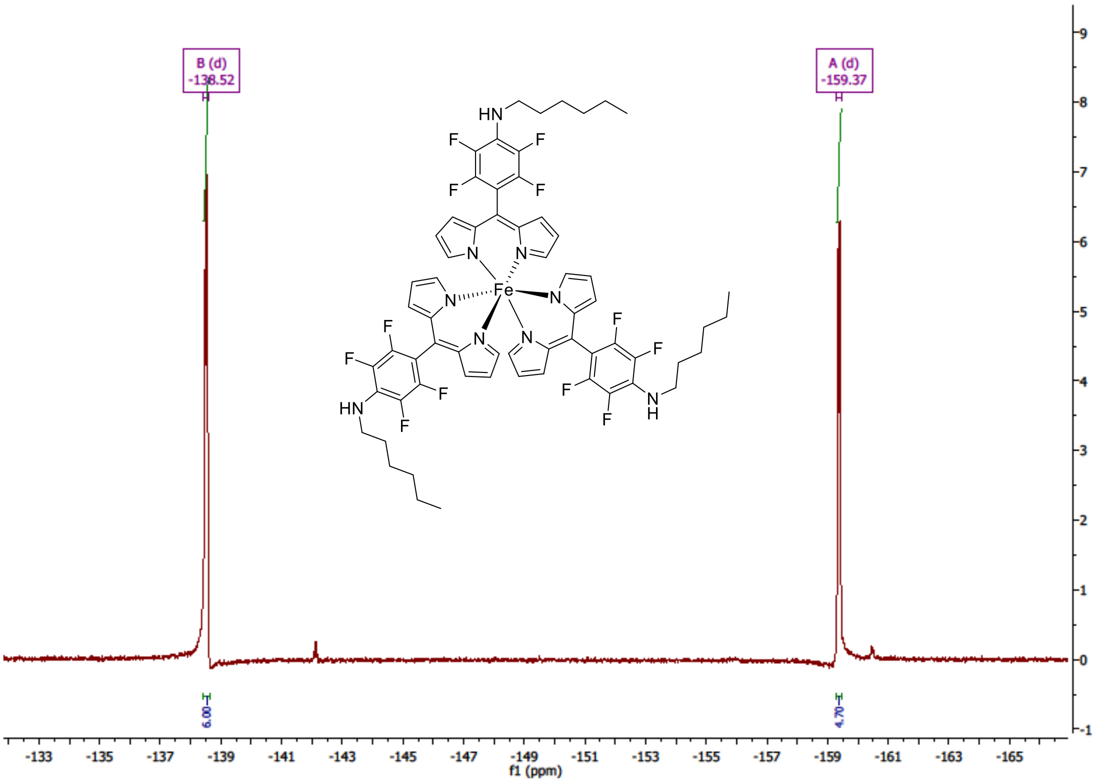


Figure S 54. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 10c.

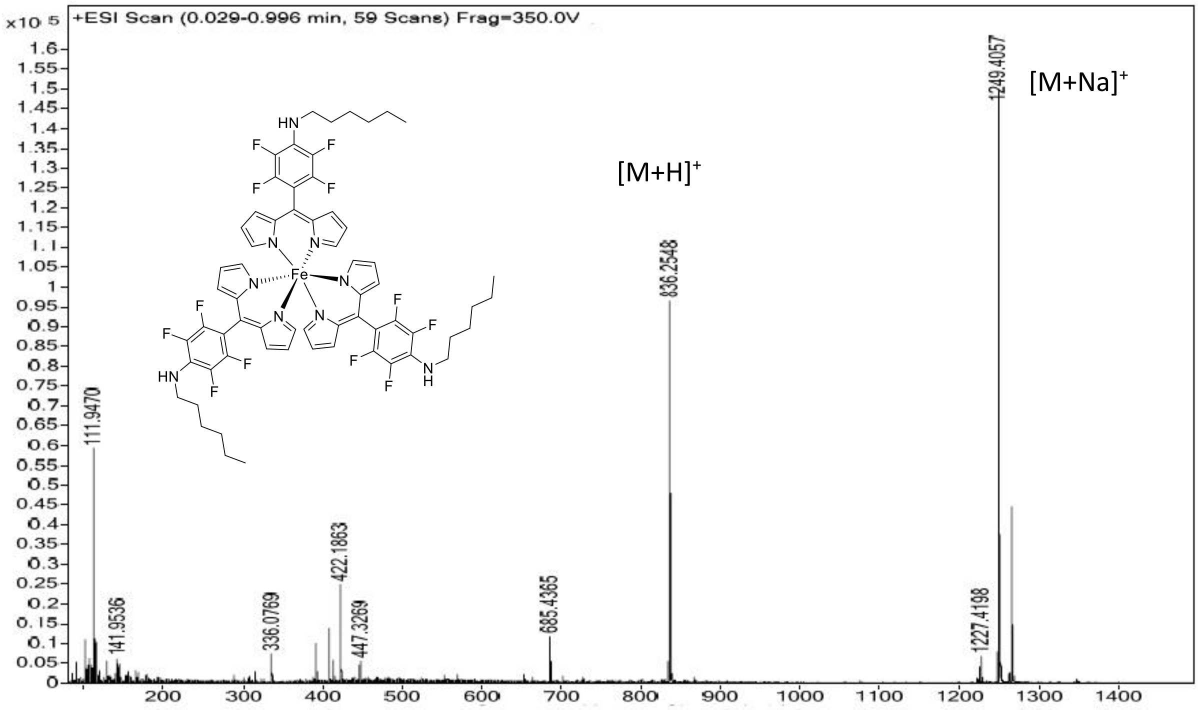


Figure S 55. HRMS (ESI-TOF) spectrum of complex 10c.

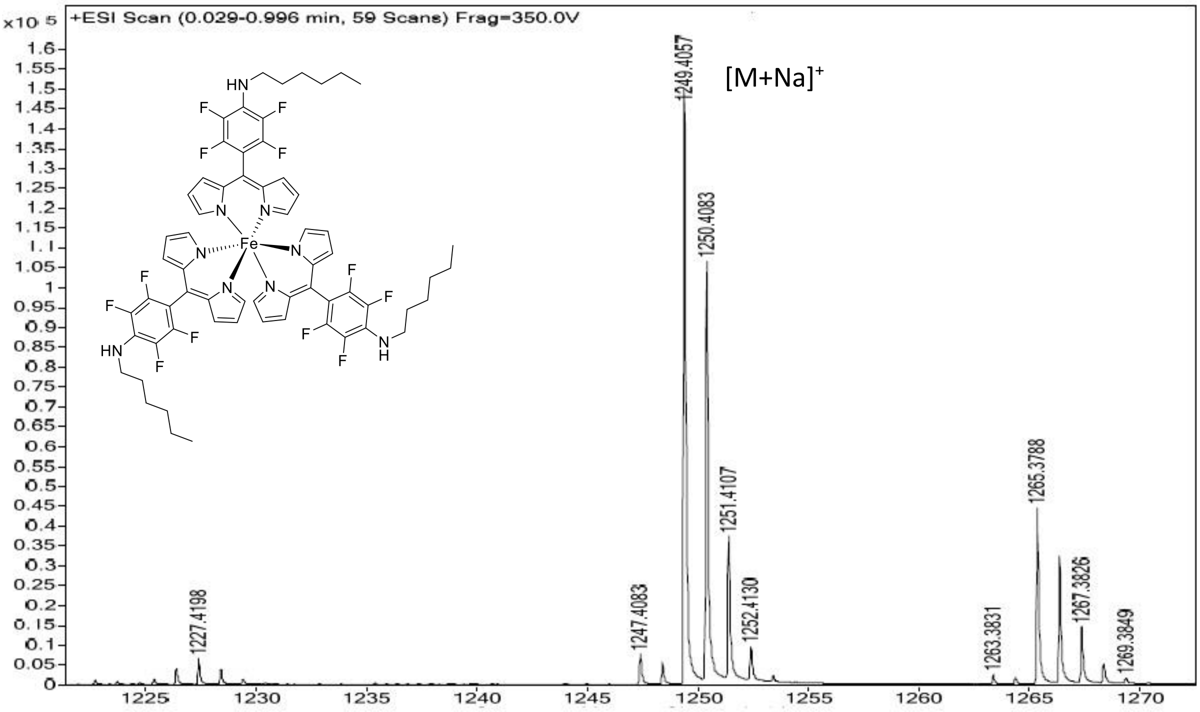
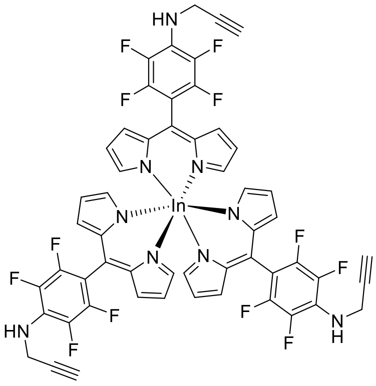


Figure S 56. HRMS (ESI-TOF) spectrum of complex 10c.

Tris[5-{4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorphenyl}dipyrrinato] indium(III) [11a]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **7** (120 mg, 0.34 mmol, 3.1 eq), $InCl_3$ (25 mg, 0.11 mmol) and DIPEA (60 µL, 44 mg, 0.34 mmol, 3.1 eq.) were dissolved in dry THF and refluxed for 24 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) to obtain the product as a red oil (100 mg, 79%).

^{1}H NMR (400 MHz, CDCl$_3$): δ =2.34-2.36 (m, 3 H, C≡CH), 4.20-4.25 (m, 6 H, CH_2), 6.41 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.57 (d, *J* = 4.2 Hz, 6 H, $H_{pyrrole}$), 7.63-7.65 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 35.47 (CH_2), 80.08 (C≡CH), 72.86 (C≡CH), 105.33 (t, $J_{C\text{-}F}$ = 19.1 Hz, Ar-C_{ipso}), 118.59 ($C_{pyrrole}$), 125.88 (t, $J_{C\text{-}F}$ = 2.0 Hz, Ar-C_{para}), 127.43 ($C_{pyrrole}$), 137.87 (d, $J_{C\text{-}F}$ = 241.2 Hz, Ar-C_{meta}), 141.06 (C_{meso}), 144.90 ($C_{pyrrole}$), 145.05 (d, $J_{C\text{-}F}$ = 246.4 Hz, Ar-C_{ortho}) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -158.33 (m_c, *J* = 21.3, 7.4 Hz, 6 F, Ar-F_{meta}), -140.95 (m_c, *J* = 13.5, 9.8 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{30}F_{12}InN_9Na^+$ [M+Na]$^+$ 1170.1364, found 1170.1367; *m/z* calc. for $C_{54}H_{30}F_{12}InKN_9^+$ [M+K]$^+$ 1186.1103, found 1186.1107.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 438 (5.06) nm.

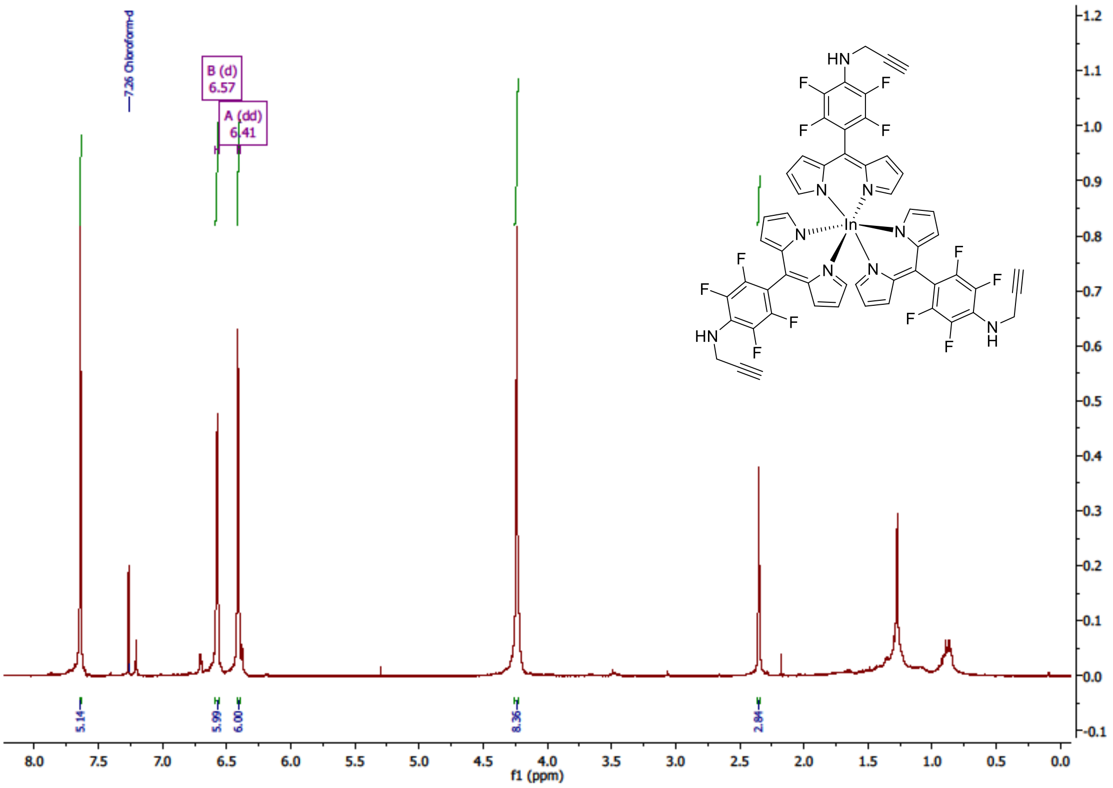


Figure S 57. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex **11a.**

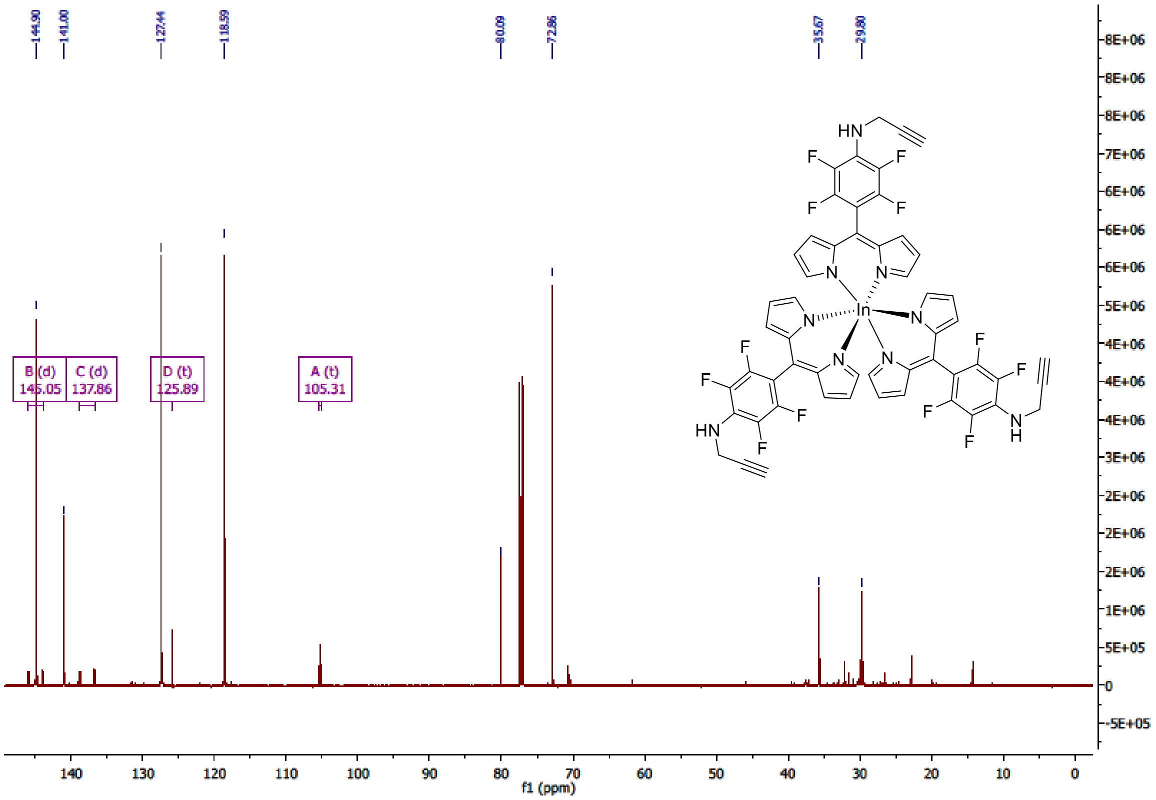


Figure S 58. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex **11a.**

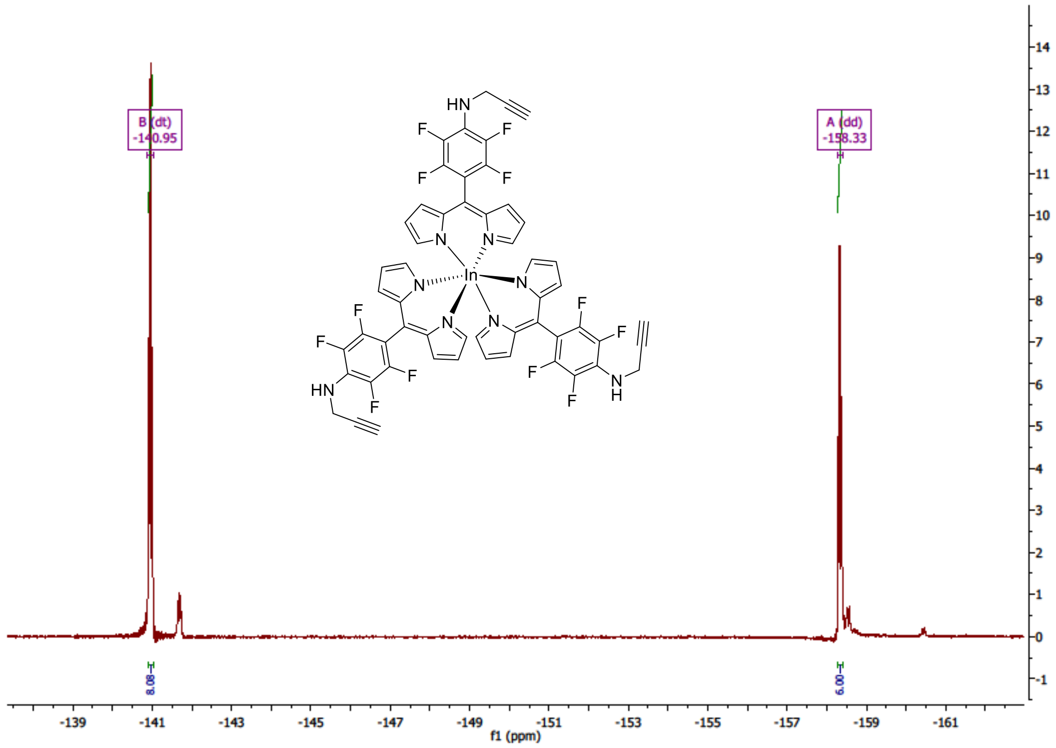


Figure S 59. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex **11a**.

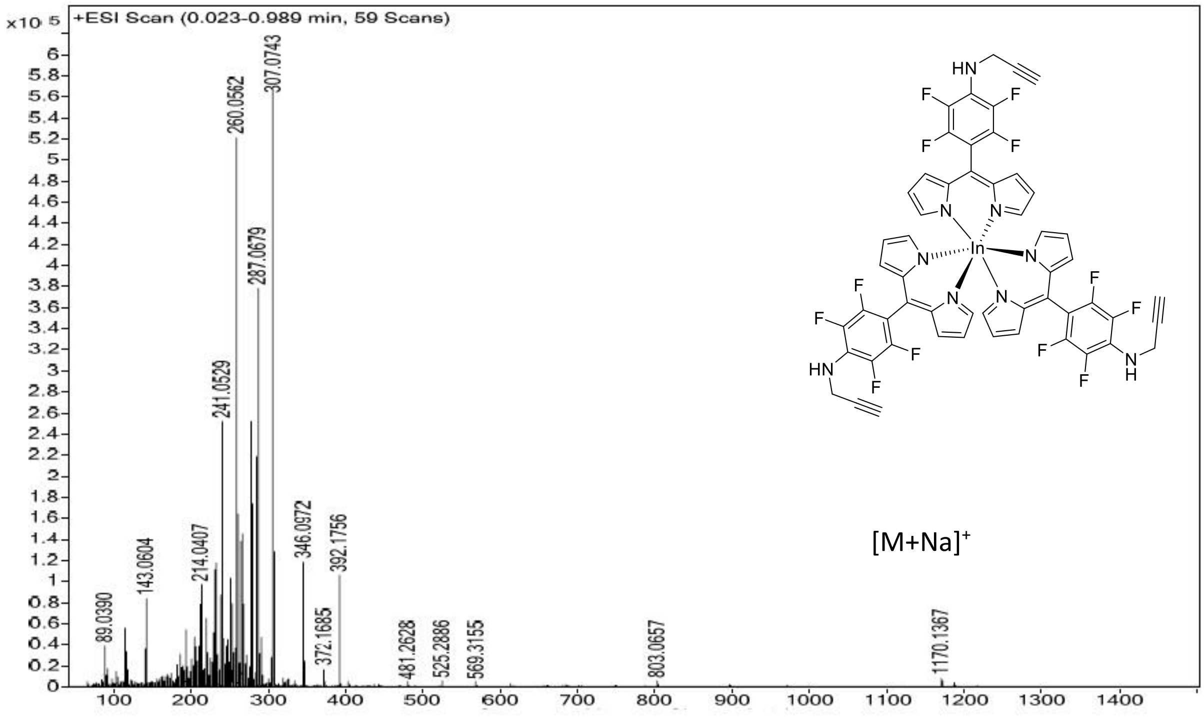


Figure S 60. HRMS (ESI-TOF) spectrum of complex **11a**.

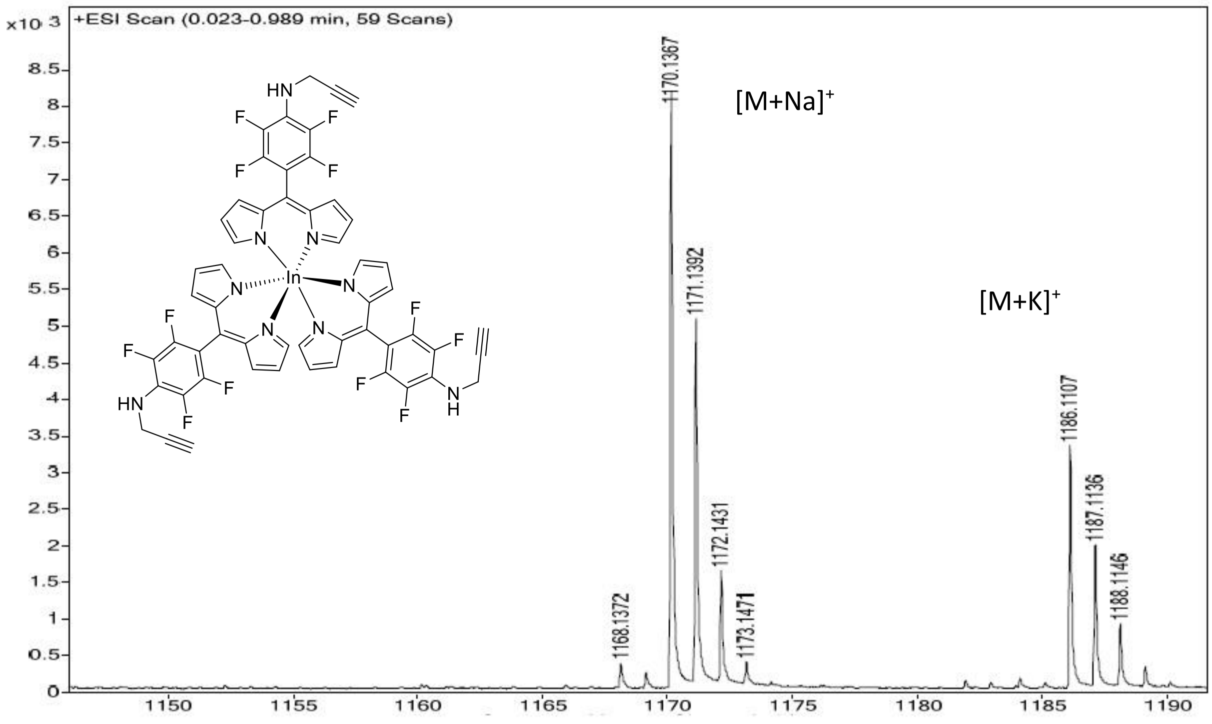
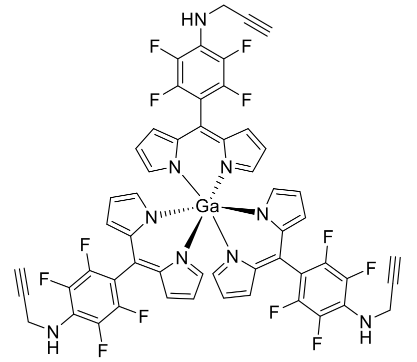


Figure S 61. HRMS (ESI-TOF) spectrum of complex 11a.

Tris[5-{4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [11b]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **7** (125 mg, 0.36 mmol, 3.1 eq.), $GaCl_3$ (20 mg, 0.11 mmol) and DIPEA (60 µL, 0.36 mmol, 3.1 eq.) were dissolved in dry THF and refluxed for 24 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) to obtain the product as a red oil (96 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (t, *J* = 2.3 Hz, 3 H, C≡CH), 4.20-4.24 (m, 6 H, CH_2), 6.41 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.58 (d, *J* = 4.1 Hz, 6 H, $H_{pyrrole}$), 7.62-7.64 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 35.67 (CH$_2$), 72.86 (C≡CH), 80.09 (C≡CH), 105.31 (t, $J_{\text{C-F}}$ =19.2 Hz, Ar-C$_{ipso}$), 118.59 (C$_{\text{pyrrole}}$), 125.89 (t, $J_{C\text{-}F}$ = 2.1 Hz, Ar-C$_{para}$), 127.44 (C$_{\text{pyrrole}}$), 137.86 (d, $J_{\text{C-F}}$ = 241.3 Hz, Ar-C$_{meta}$), 141.00 (C$_{meso}$), 144.90 (C$_{\text{pyrrole}}$), 145.05 (m, $J_{\text{C-F}}$ =246.4 Hz, Ar-C$_{ortho}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -158.33 (m$_c$, *J* = 22.2, 7.6 Hz, 6 F, Ar-F$_{meta}$), -140.97 (m$_c$, *J* = 21.9, 7.7 Hz, 6 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{30}F_{12}GaN_9Na^+$ [M+Na]$^+$ 1124.1581, found 1124.1566.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 455 (5.04), 511 (5.08) nm.

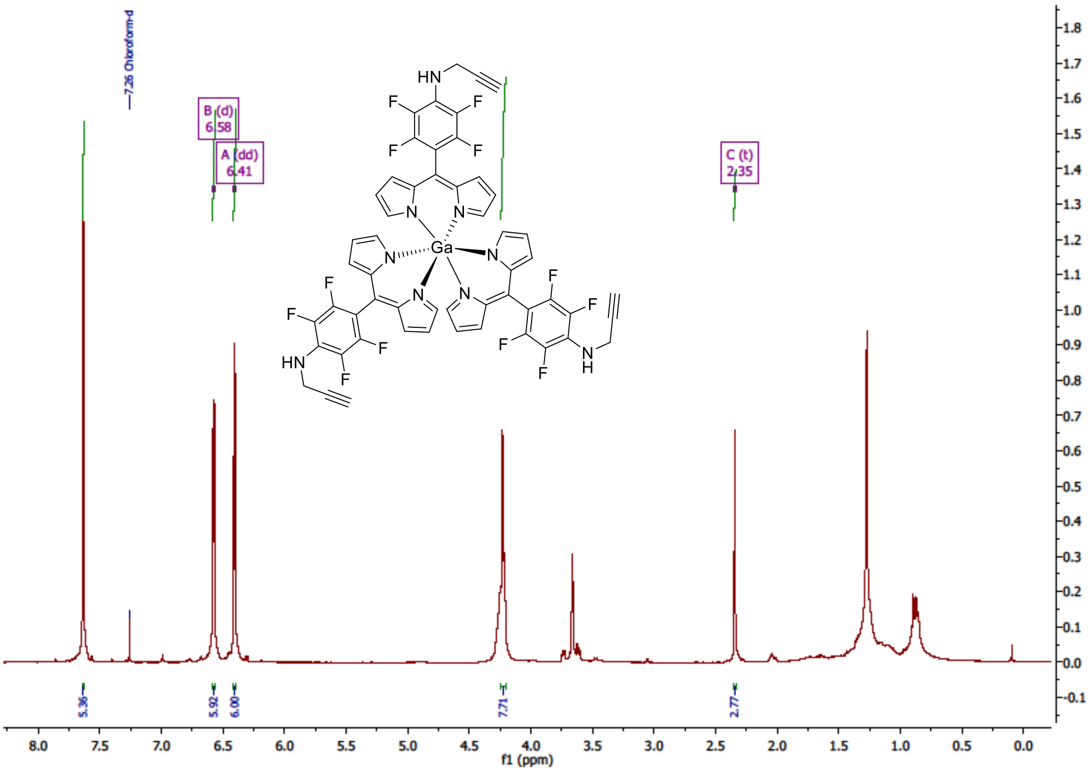


Figure S 62. ^{1}H NMR (400 MHz, CDCL$_3$) spectrum of complex 11b.

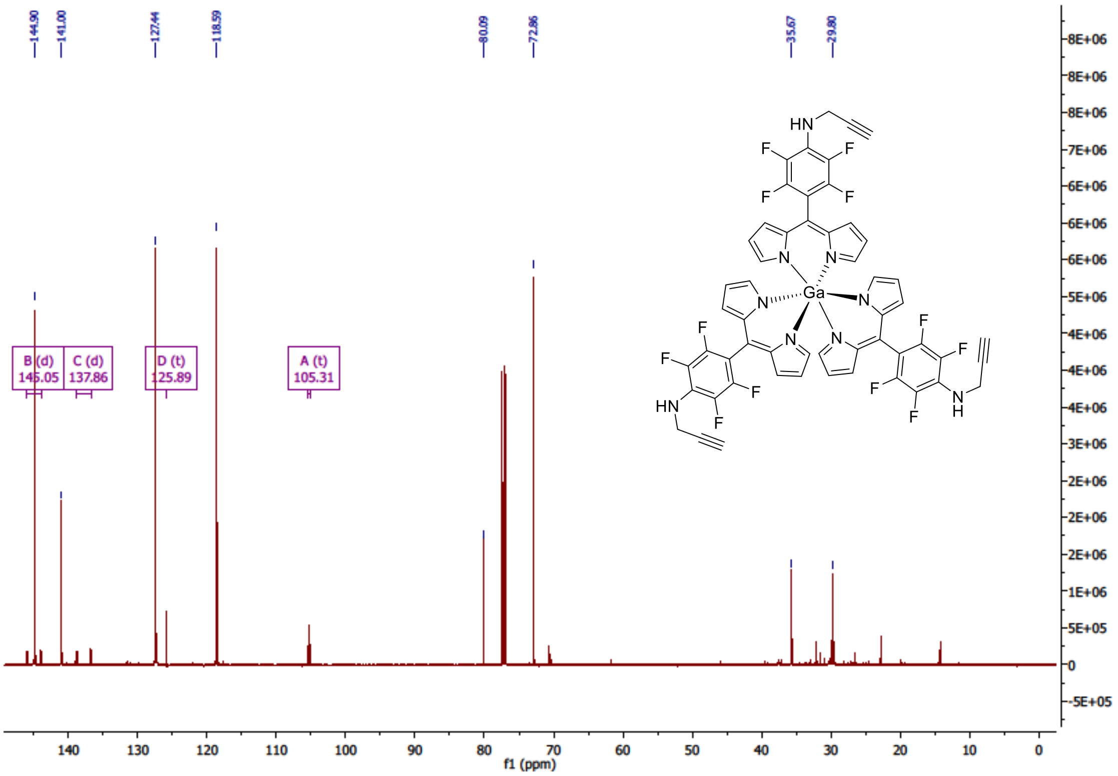


Figure S 63. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 11b.

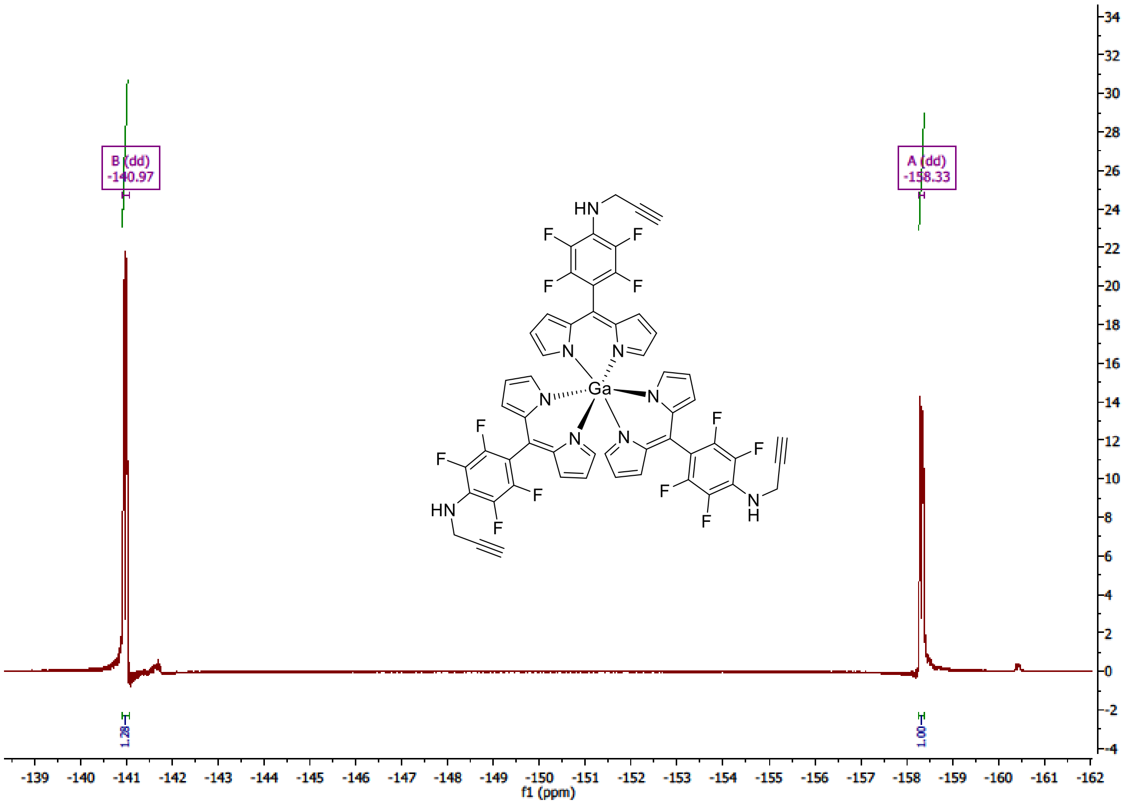


Figure S 64. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 11b.

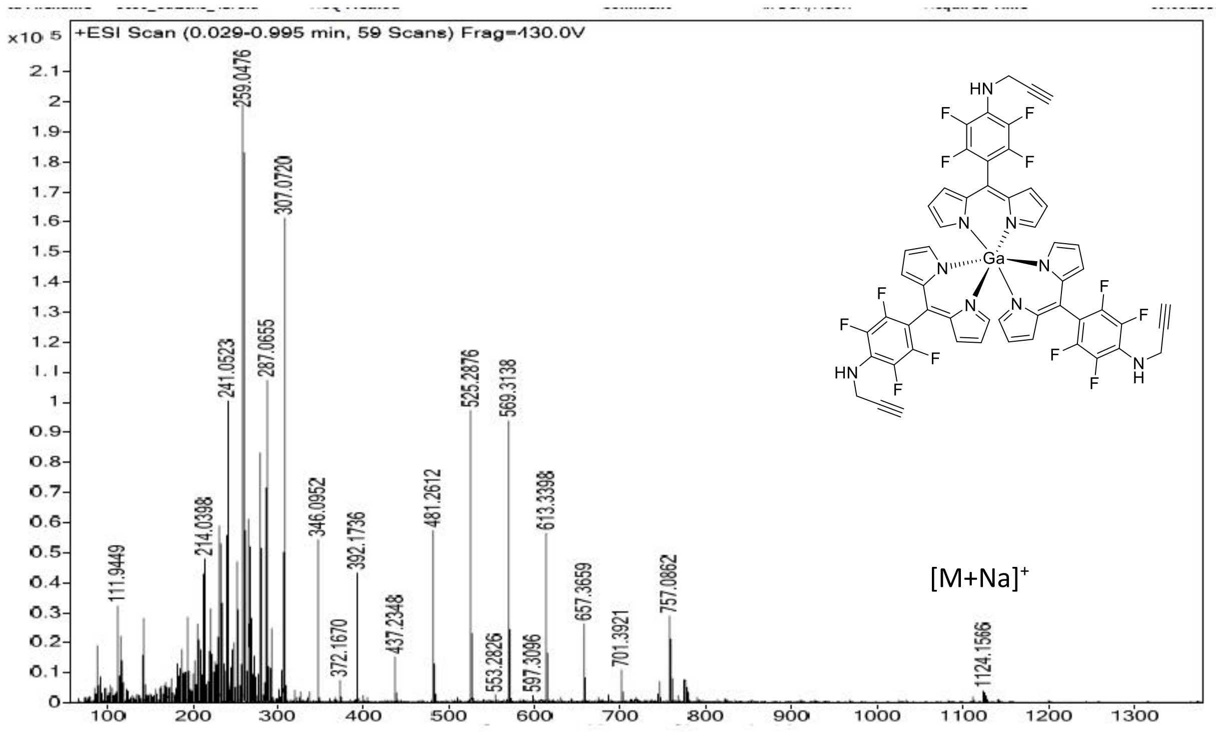


Figure S 65. HRMS (ESI-TOF) spectrum of complex 11b.

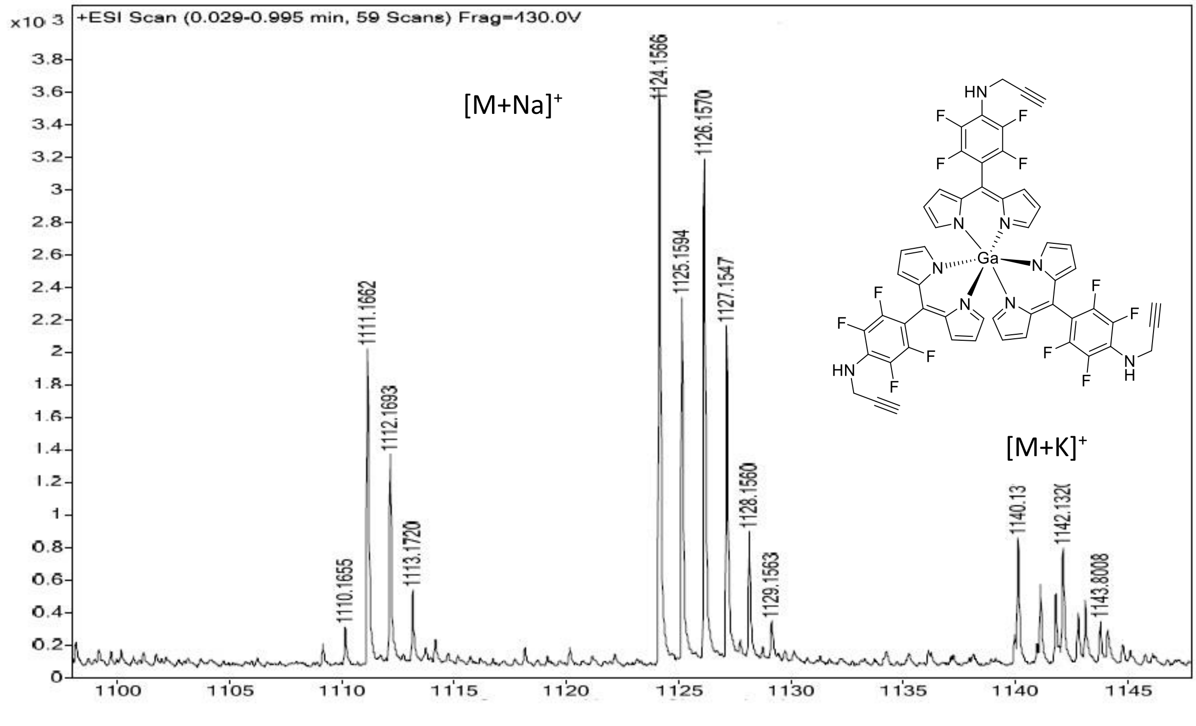
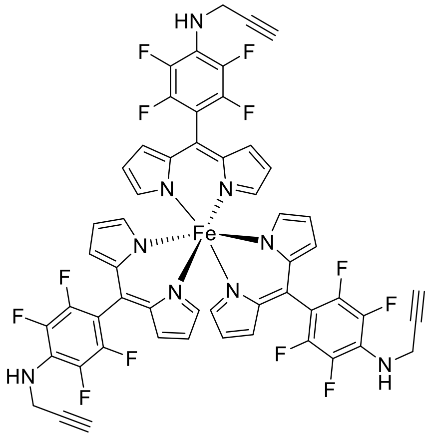


Figure S 66. HRMS (ESI-TOF) spectrum of complex 11b.

Tris[5-{4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl}-dipyrrinato] iron(III) [11c]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of dipyrrin **7** (130 mg, 0.37 mmol, 3.1 eq), DIPEA (0.28 mL, 216 mg, 1.68 mmol, 14 eq) and $FeCl_3 \cdot 6H_2O$ (32 mg, 0.12 mmol) in MeOH (5 mL) were stirred at 50 °C for 2 h. The mixture was evaporated to dryness and purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1), evaporated to dryness and washed with pentane. The product was dried *in vacuo* and was obtained as a red solid (27 mg, 66%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = -29.47 (br s, 6 H, $H_{pyrrole}$), -7.57 (m, 6 H, $H_{pyrrole}$), 6.36 (m, 6 H, $H_{pyrrole}$), 2.82 (t, *J* = 2.3 Hz, 3 H, C≡CH), 4.88-4.92 (m, 6 H, CH_2), 5.04-5.12 (m, 3 H, NH) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -157.20 (m_c, *J* = 18.2 Hz, 6 F, Ar-F_{meta}), -137.77 (m_c, *J* = 16.3 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{30}F_{12}FeN_9Na^+$ $[M+Na]^+$ 1111.1674, found 1111.1738; *m/z* calc. for $C_{54}H_{30}F_{12}FeKN_9^+$ $[M+K]^+$ 1127.1414, found 1127.1476.

UV/VIS (DCM): λ_{max}/nm [log (ε/L mol^{-1} cm^{-1})] = 448 (4.86), 500 (4.74) nm.

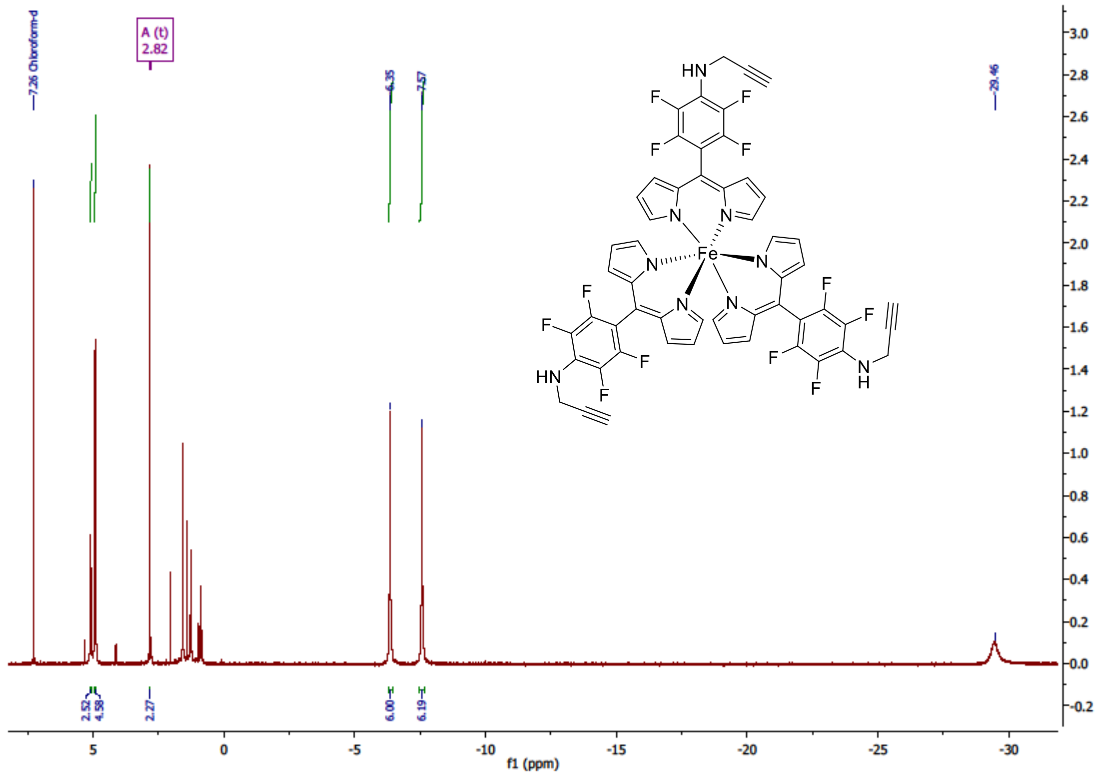


Figure S 67. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 11b.**

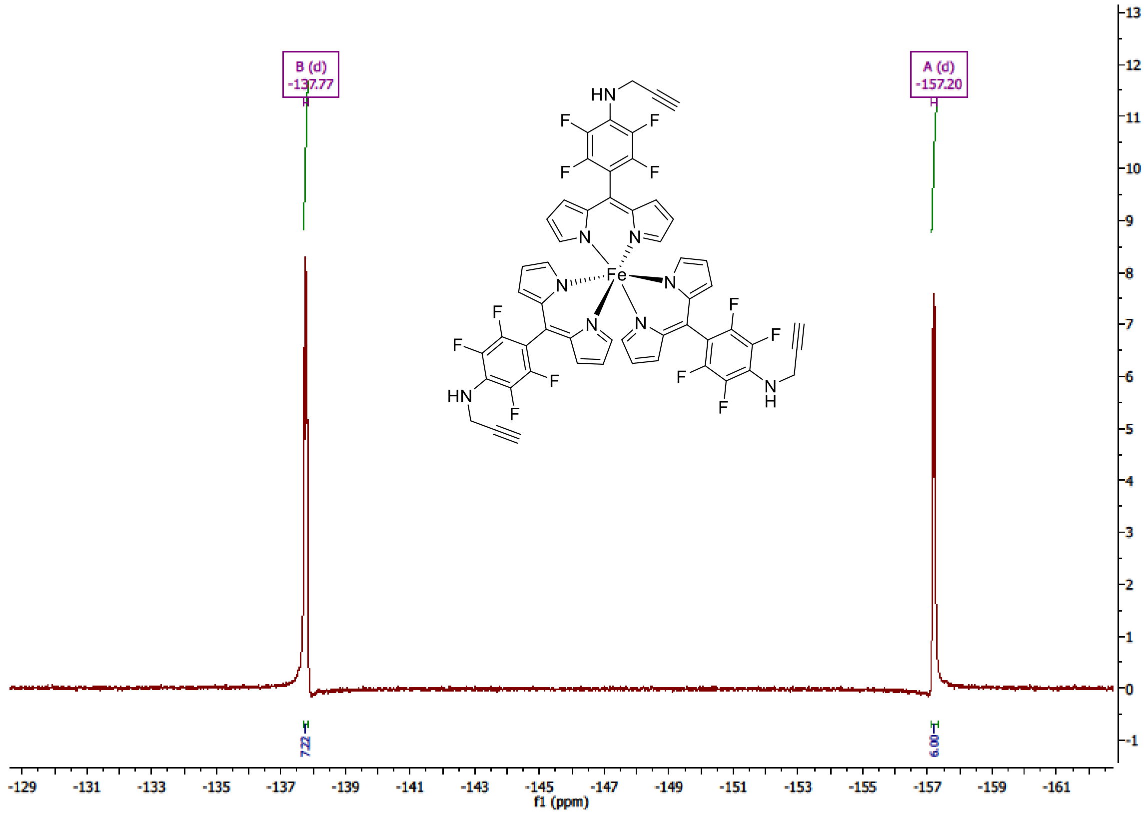


Figure S 68. **^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 11b.**

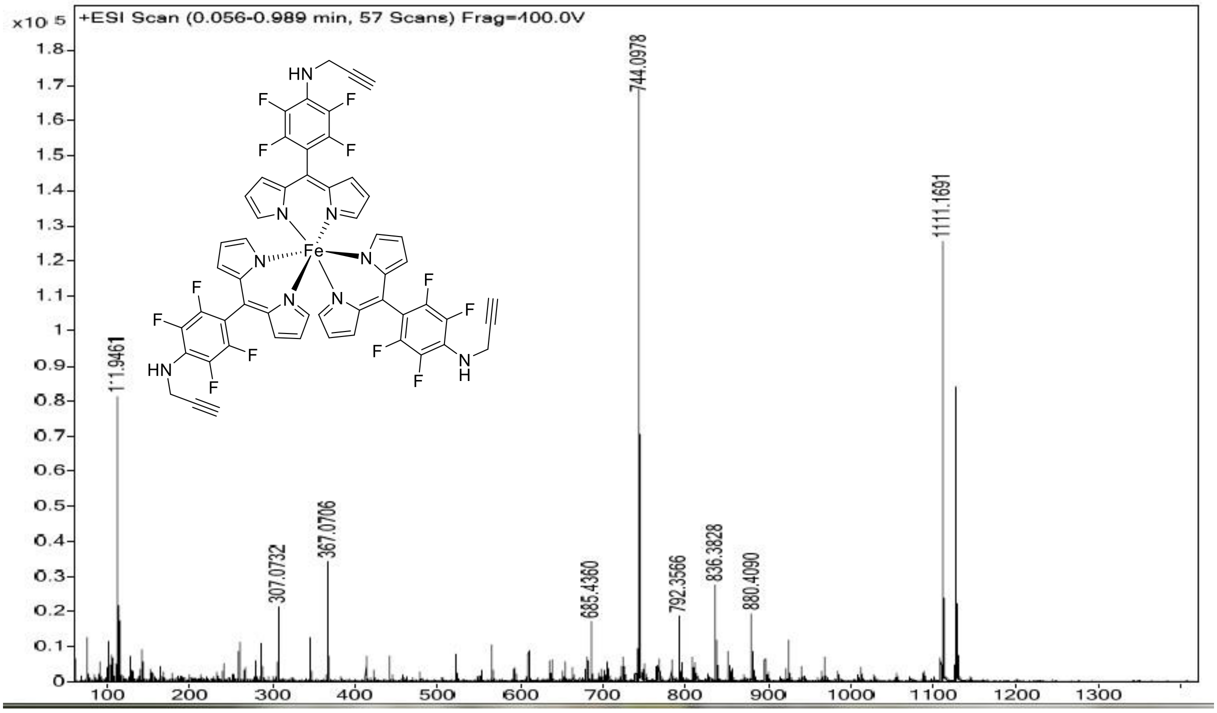


Figure S 69. HRMS (ESI-TOF) spectrum of complex 11b.

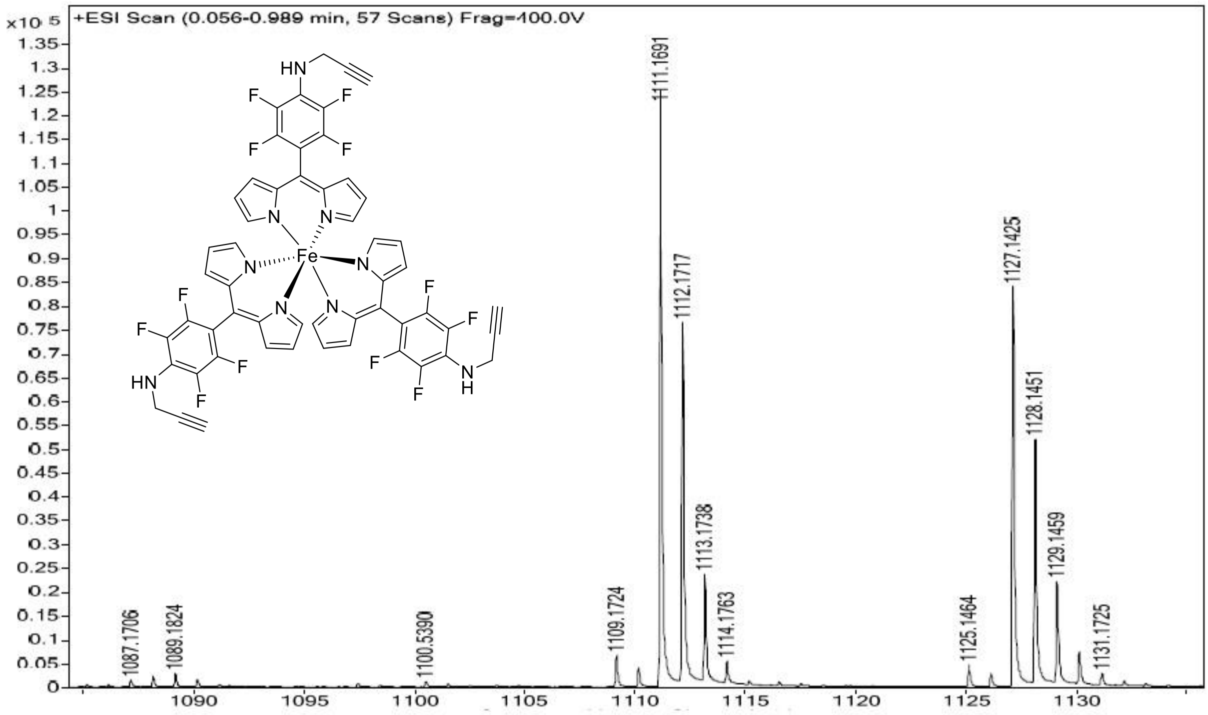
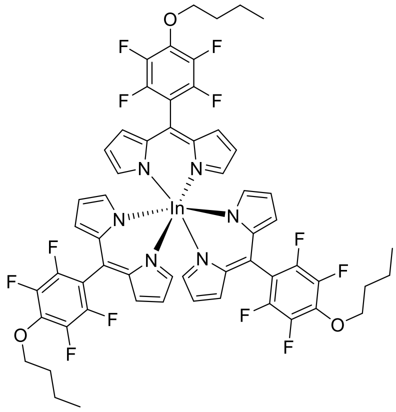


Figure S 70. HRMS (ESI-TOF) spectrum of complex 11b.

Tris[5-{4-(butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] indium(III) [12a]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, a mixture of dipyrrin **8** (116 mg, 0.31 mmol, 3.1 eq.), $InCl_3$ (22 mg, 0.10 mmol) and DIPEA (41 mg, 50 µL, 0.31 mmol, 3.1 eq) in dry THF (5 mL) was refluxed for 12 h. The mixture was diluted with DCM and washed several times with water. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallized (DCM/*n*-hexane). The product was obtained as an orange solid (8 mg, 6%).

Mp: 105-110 °C.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 9 H, CH_3), 1.50-1.60 (m, 6 H, CH_2), 1.79-1.84 (m, 6 H, CH_2), 4.33 (t, *J* = 6.6 Hz, 6 H, CH_2), 6.38 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.65 (d, *J* = 4.2 Hz, 6 H, $H_{pyrrole}$), 7.00-7.20 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (176 MHz, $CDCl_3$): The signal to noise ratio does not allow a meaningful interpretation.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -156.97 (m_c, *J* = 22.3, 7.9 Hz, 6 F, Ar-F_{meta}), -141.16 (m_c, *J* = 22.4, 8.1 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{57}H_{45}F_{12}InN_6NaO_3^+$ $[M+Na]^+$ 1227.2293, found 1227.2282; *m/z* calc for $C_{38}H_{30}F_8InN_4O_2^+$ $[M-L]^+$ calc. for 841.1280, found 841.1274.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 449 (4.67), 506 (4.51) nm.

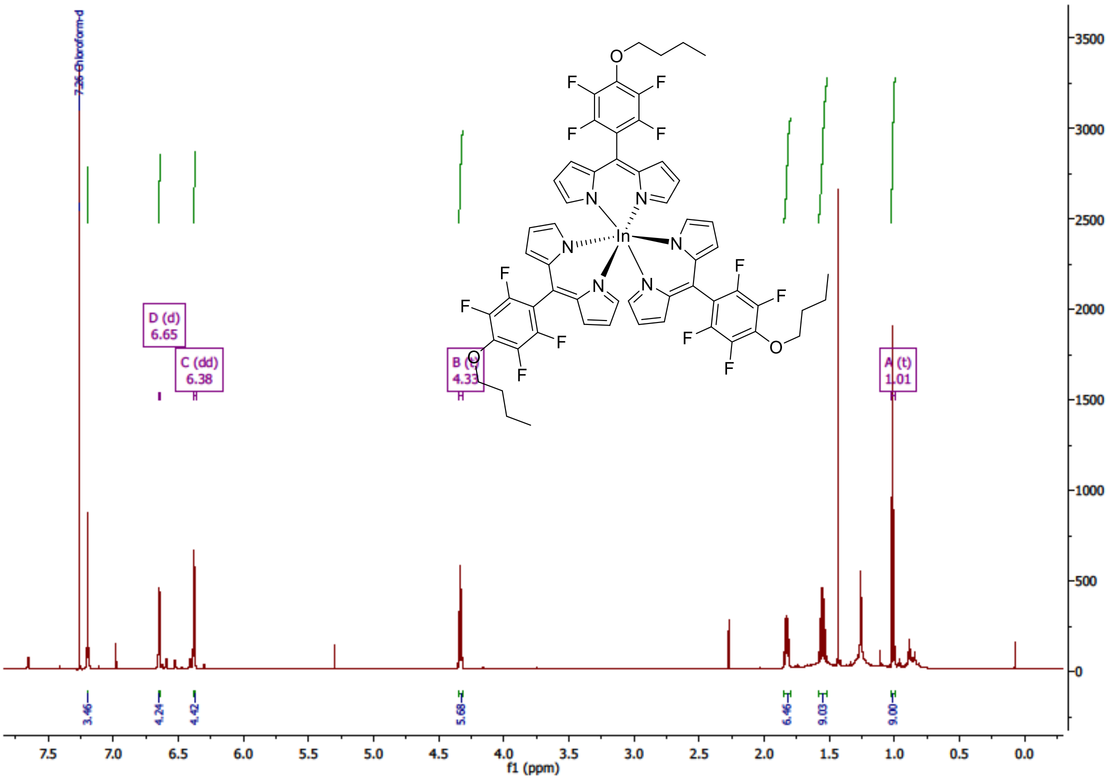


Figure S 71. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 12a.

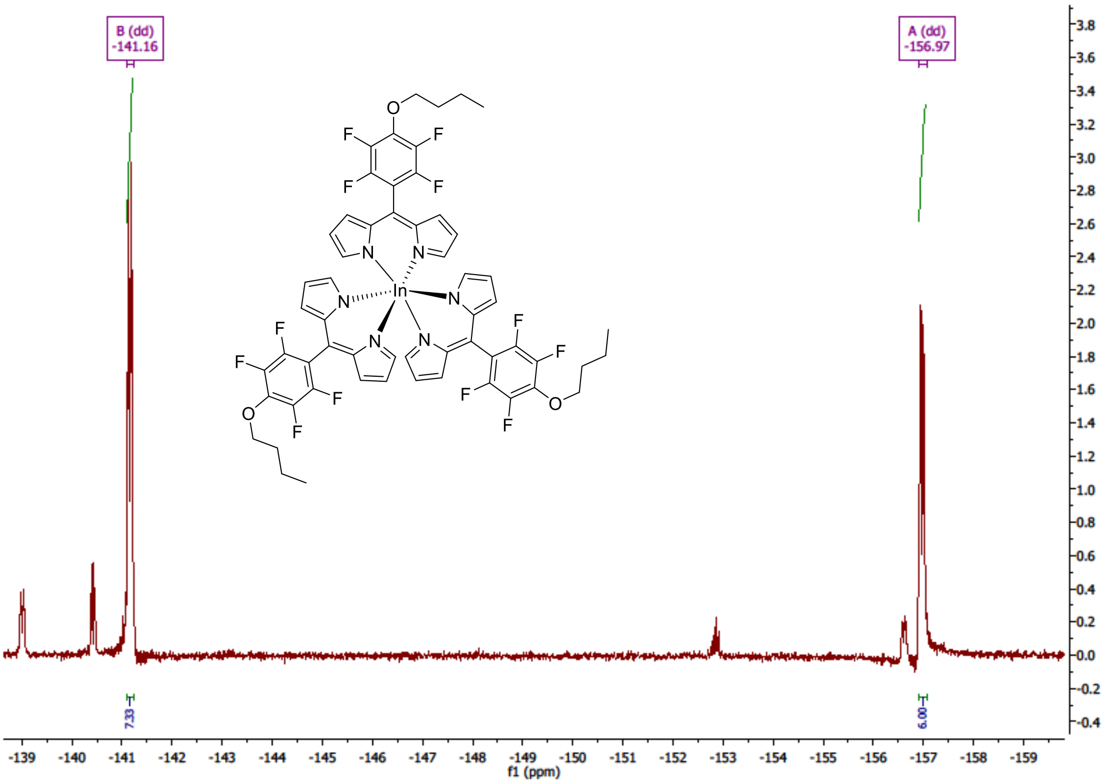


Figure S 72. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 12a.

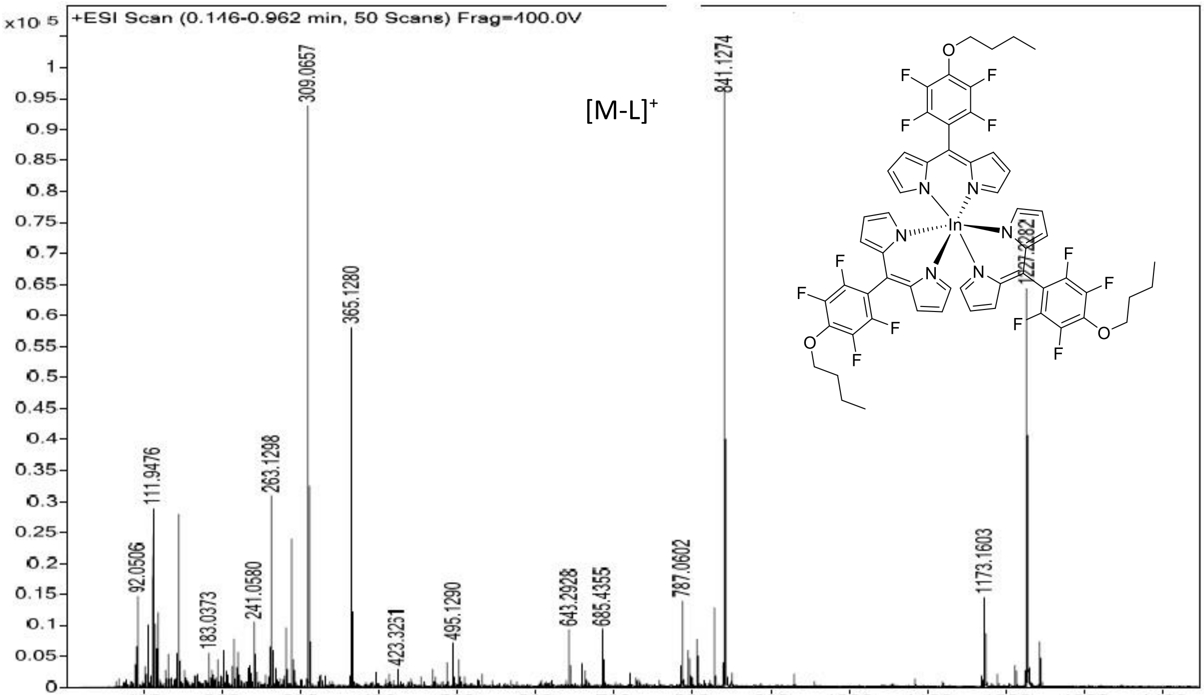


Figure S 73. HRMS (ESI-TOF) spectrum of complex 12a.

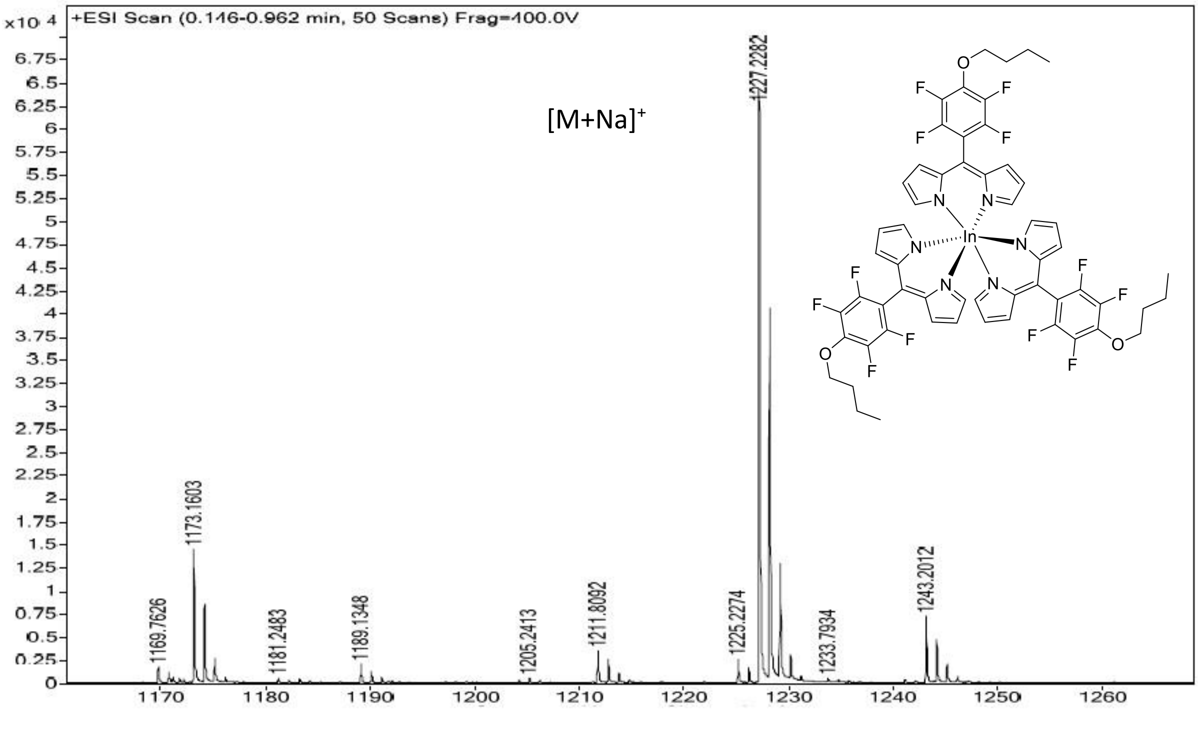
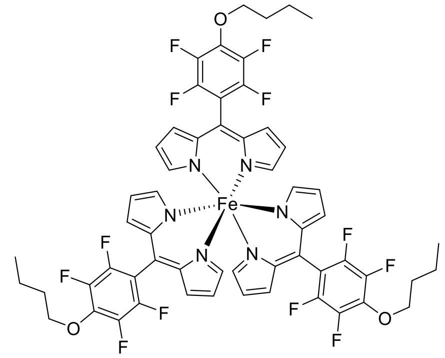


Figure S 74. HRMS (ESI-TOF) spectrum of complex 12a.

Tris[5-{4-(butyl-1-oxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] iron(III) [12c]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **8** (91 mg, 240 µmol, 3.1 eq.) was dissolved in dry MeOH (10 mL), $FeCl_3 \cdot 6H_2O$ (21 mg, 80 µmol) and DIPEA (0.6 mL, 1.12 mmol, 14 eq.) were added and the mixture was stirred for 30 min at 50 °C. The mixture was evaporated to dryness, purified by column chromatography (silica gel, DCM /*n*-hexane = 1:1), evaporated to dryness, washed with pentane and dried *in vacuo*. The product was isolated as a green solid (38 mg, 41%).

Mp: 235-238 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = -29.14 (br s, 6 H, $H_{pyrrole}$), -7.65 (br s, 6 H, $H_{pyrrole}$), -6.36 (br s, 6 H, $H_{pyrrole}$), 1.37 (t, J = 7.4 Hz, 9 H, CH_3), 1.98-2.10 (m, 6 H, CH_2), 2.34-2.42 (m, 6 H, CH_2), 5.10 (t, J = 6.4 Hz, 6 H, CH_2) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.20 (CH_3), 19.42 (CH_2), 32.62 (CH_2), 43.87 ($C_{pyrrole}$), 75.97 (CH_2), 108.31 (Ar-C_{ipso}), 126.28 (C_{meso}), 134.20 ($C_{pyrrole}$), 136.16 (Ar-C_{para}), 143.40 (dd, $J_{C\text{-}F}$ = 249.5, 54.7 Hz, Ar-C) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -155.62 (m_c, J = 18.0 Hz, 6 F, Ar-F_{meta}), -137.32 (m_c, J = 16.5 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{30}F_8FeN_4O_2^+$ $[M\text{-}L]^+$ 782.1590, found 782.1567; *m/z* calc. for $C_{57}H_{45}F_{12}FeN_6NaO_3^+$ $[M+Na]^+$ 1168.2603, found 1168.2582.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 451 (4.69), 505 (4.55) nm.

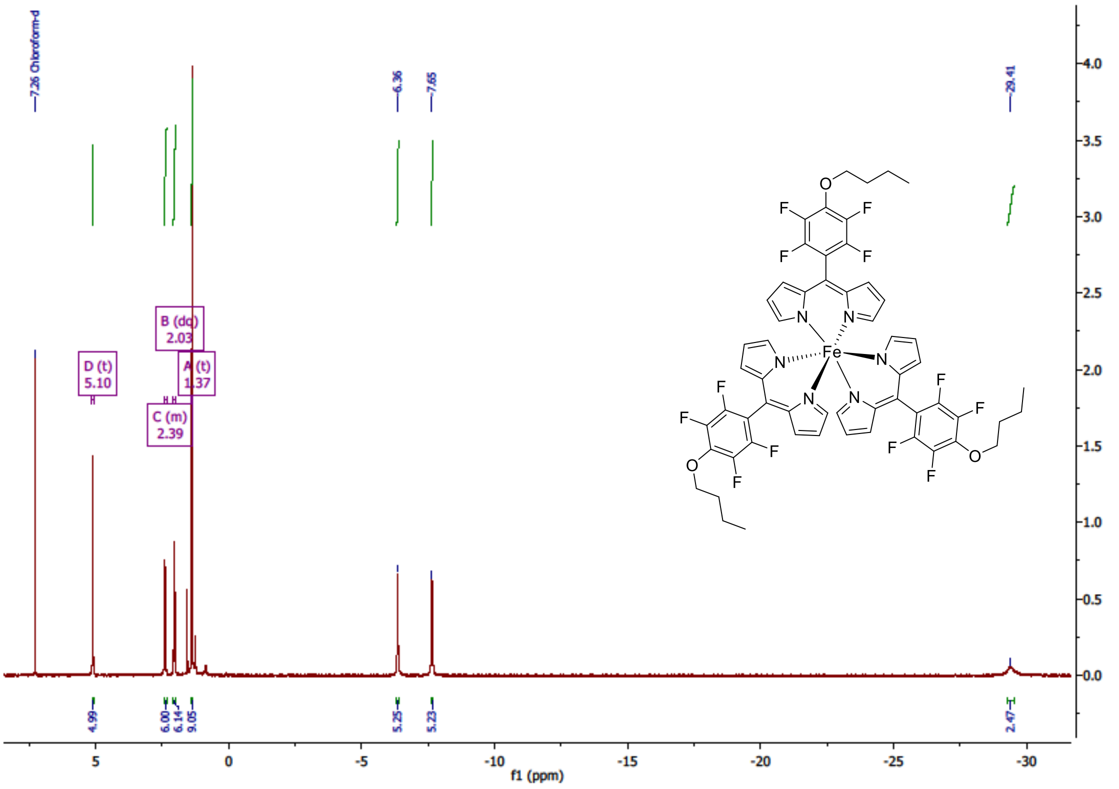


Figure S 75. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 12c.

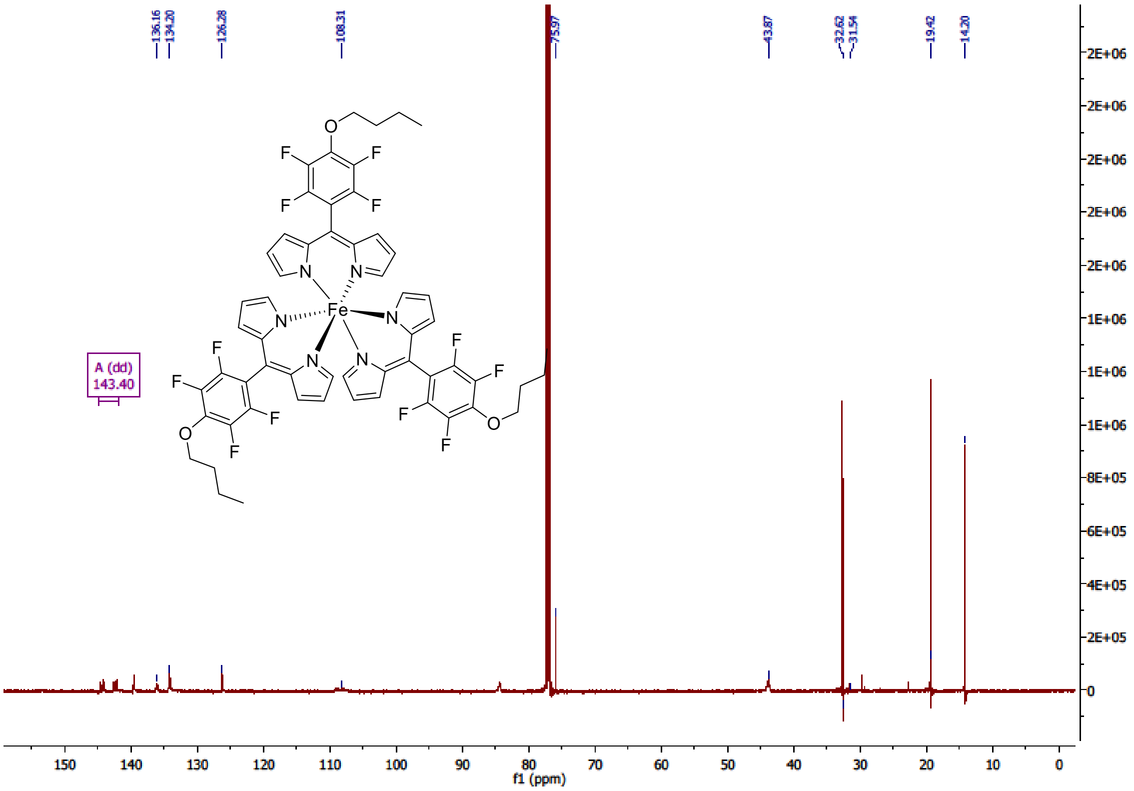


Figure S 76. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 12c.

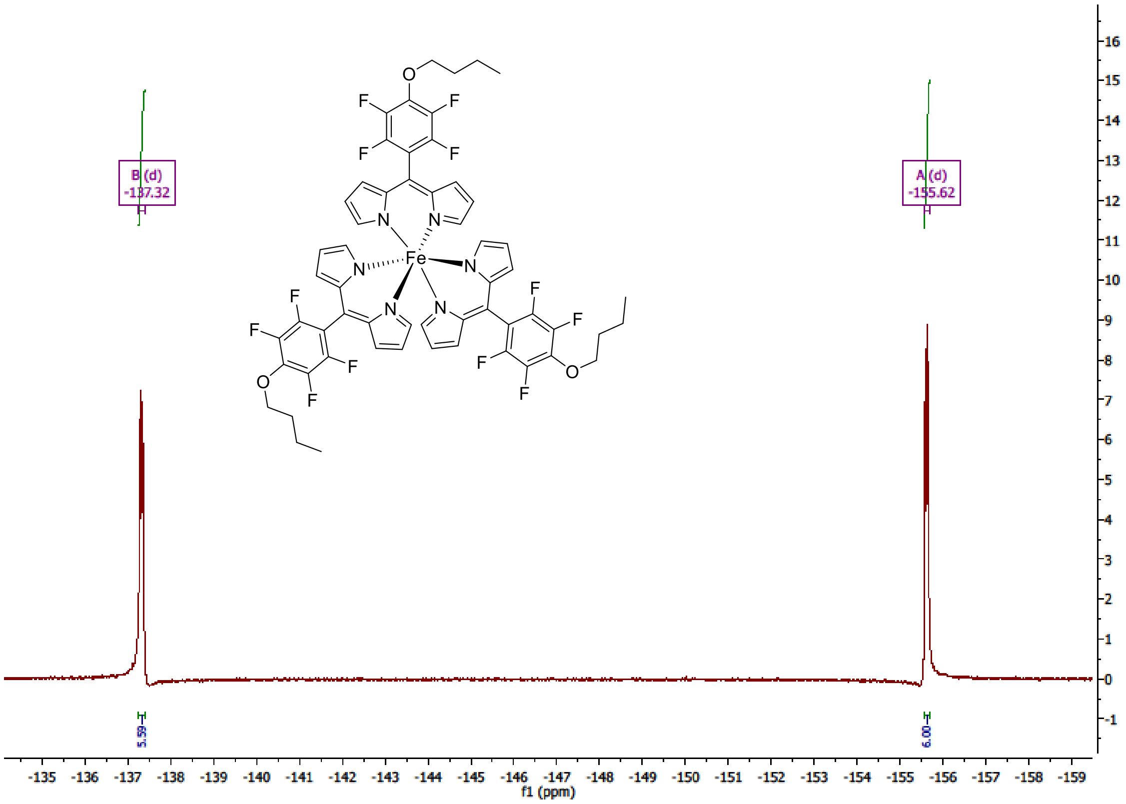


Figure S 77. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 12c.

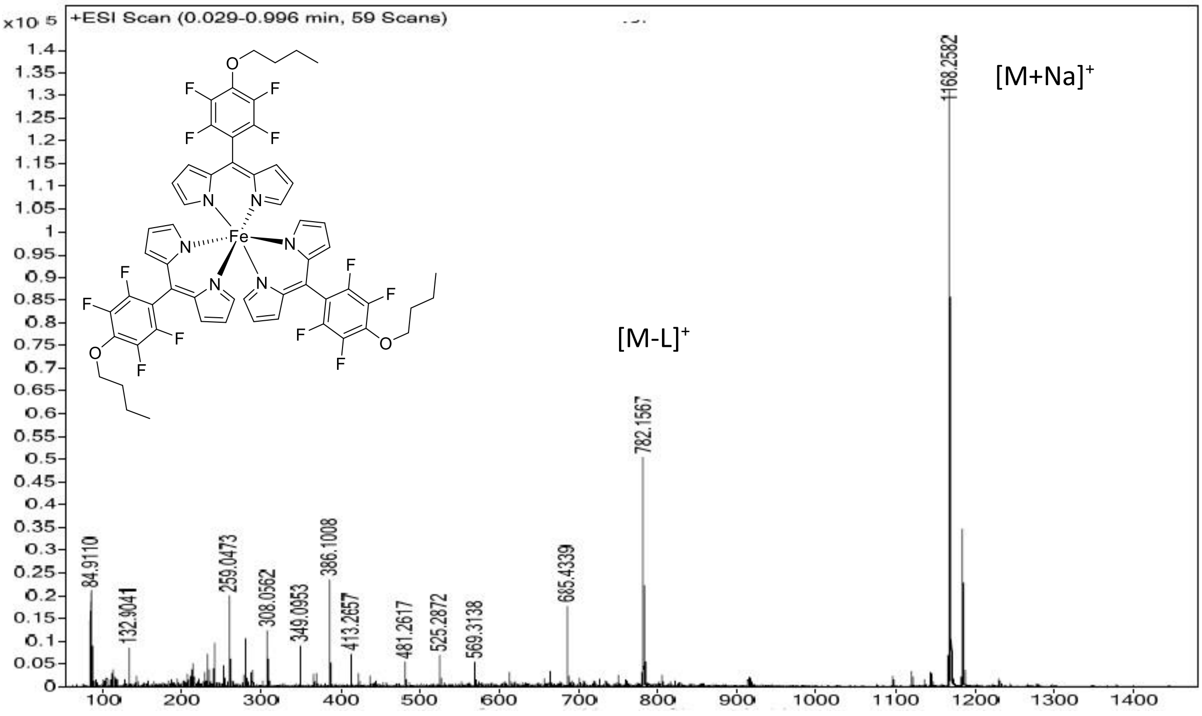


Figure S 78. HRMS (ESI-TOF) spectrum of complex 12c.

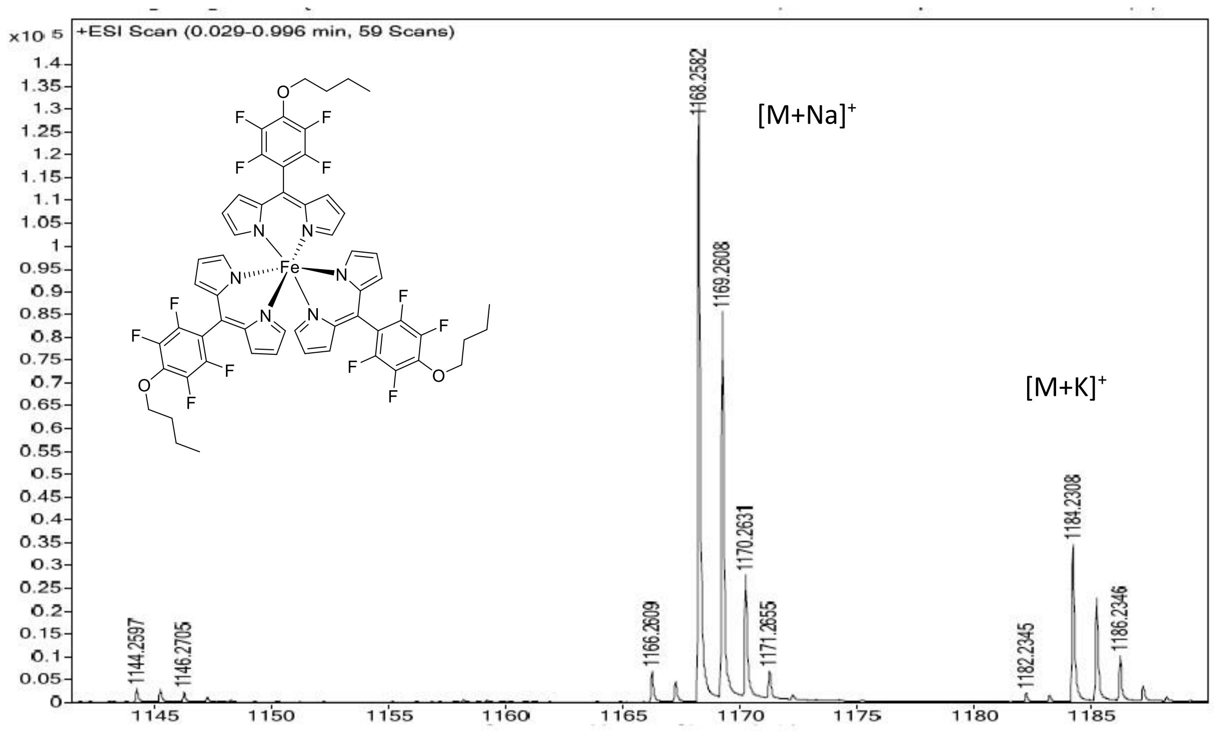
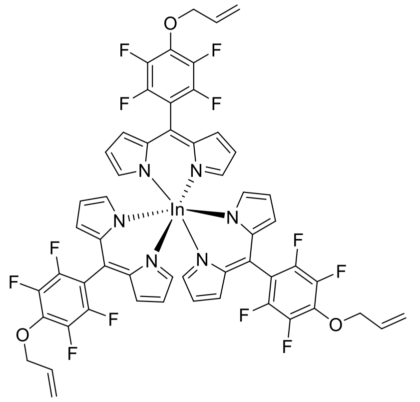


Figure S 79. HRMS (ESI-TOF) spectrum of complex 12c.

Tris[5-{4-(prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] indium(III) [13a]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **9** (50 mg, 0.14 mmol, 3.1 eq.), $InCl_3$ (10 mg, 0.04 mmol) and DIPEA (23 µmol, 0.14 mmol, 3.1 eq.) were dissolved in THF (10 mL) and refluxed for 4 h. The mixture was diluted with DCM and washed several times with water. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 3:1), evaporated to dryness and washed with pentane and dried *in vacuo* to obtain the product as orange crystals (30 mg, 56%).

Mp: 222-230 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (d, *J* = 6.2 Hz, 6 H, CH_2), 5.36 (dd, *J* = 10.3, 0.8 Hz, 6 H, $C{=}CH_2$), 5.45 (dd, *J* = 17.1, 1.4 Hz, 6 H, $C{=}CH_2$), 6.02-6.14 (m, 3 H, CH), 6.37 (dd, *J* = 4.2, 1.2 Hz, 6 H, H_{pyrrole}), 6.62 (d, *J* = 4.0 Hz, 6 H, H_{pyrrole}), 7.18-7.20 (m, 6 H, H_{pyrrole}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 75.53 (CH_2), 112.25 (t, $J_{C\text{-}F}$ = 19.5 Hz, Ar-F_{ipso}), 118.29 (C_{pyrrole}), 120.35 ($C{=}CH_2$), 132.23 (CH), 132.51 (C_{pyrrole}), 140.01 (C_{meso}), 151.23 (C_{pyrrole}), 137.21 (t, $J_{C\text{-}F}$ = 12.1 Hz, Ar-F_{para}), 140.69 (d, $J_{C\text{-}F}$ = 239.6 Hz, Ar-C_{meta}), 144.80 (d, $J_{C\text{-}F}$ = 243.0 Hz, Ar-F_{ortho}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -156.09 (m_c, *J* = 22.3, 7.4 Hz, 2 F, Ar-F_{meta}), -141.02 (m_c, *J* = 21.4, 7.2 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{33}F_{12}InN_6NaO_3^+$ $[M+Na]^+$ 1179.1354, found 1179.1337; *m/z* calc. for $C_{36}H_{22}F_8InN_4O_2^+$ $[M-L]^+$ 809.0654, found 809.0633.

UV/Vis (DCM): λ_{max} [log ε ($dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$)] = 455 (4.71), 507 (4.45) nm.

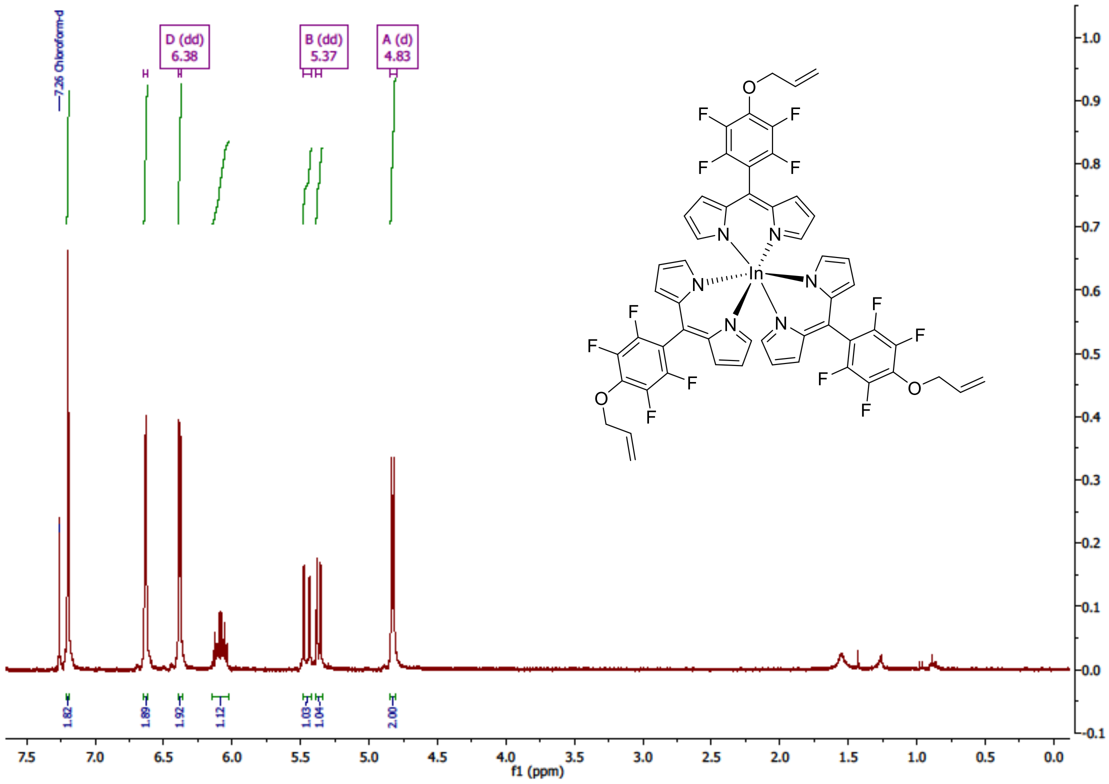


Figure S 80. **^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 13a.**

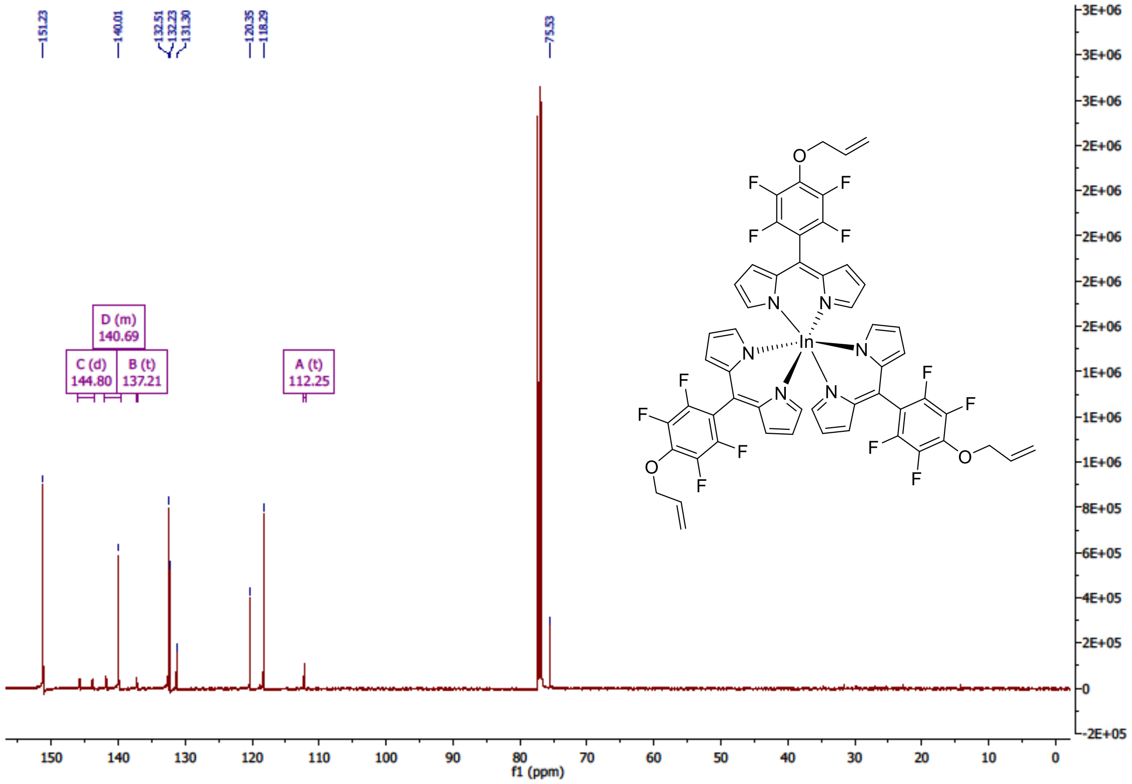


Figure S 81. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 13a.

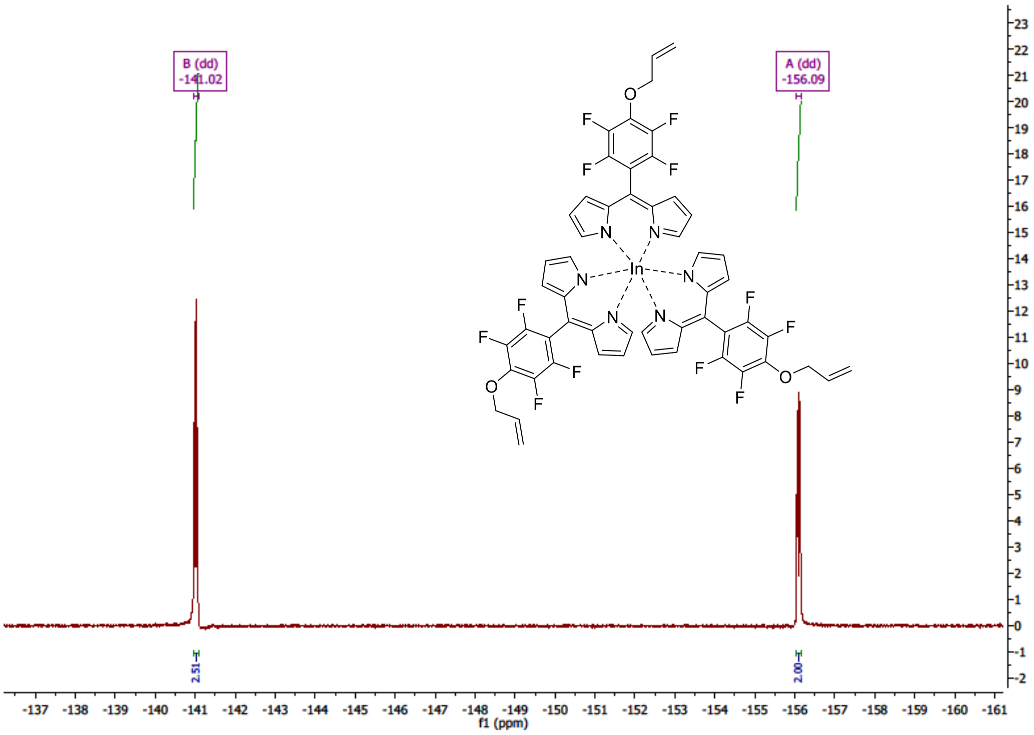


Figure S 82. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 13a.

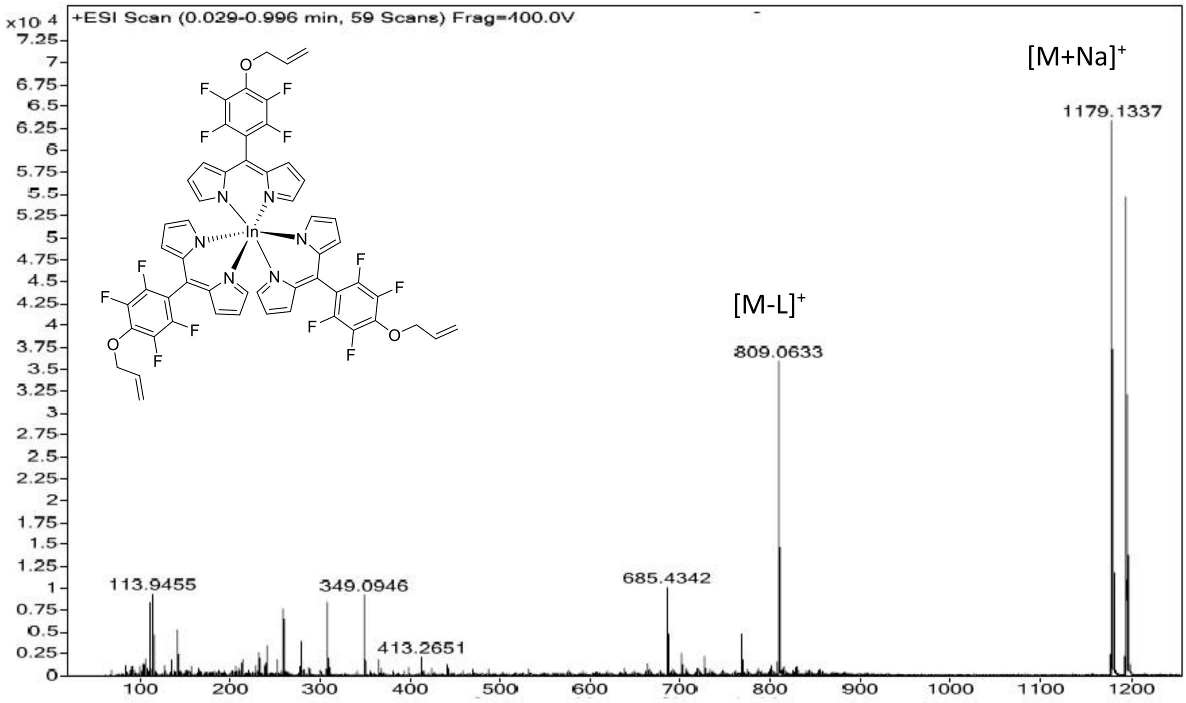


Figure S 83. HRMS (ESI-TOF) spectrum of complex 13a.

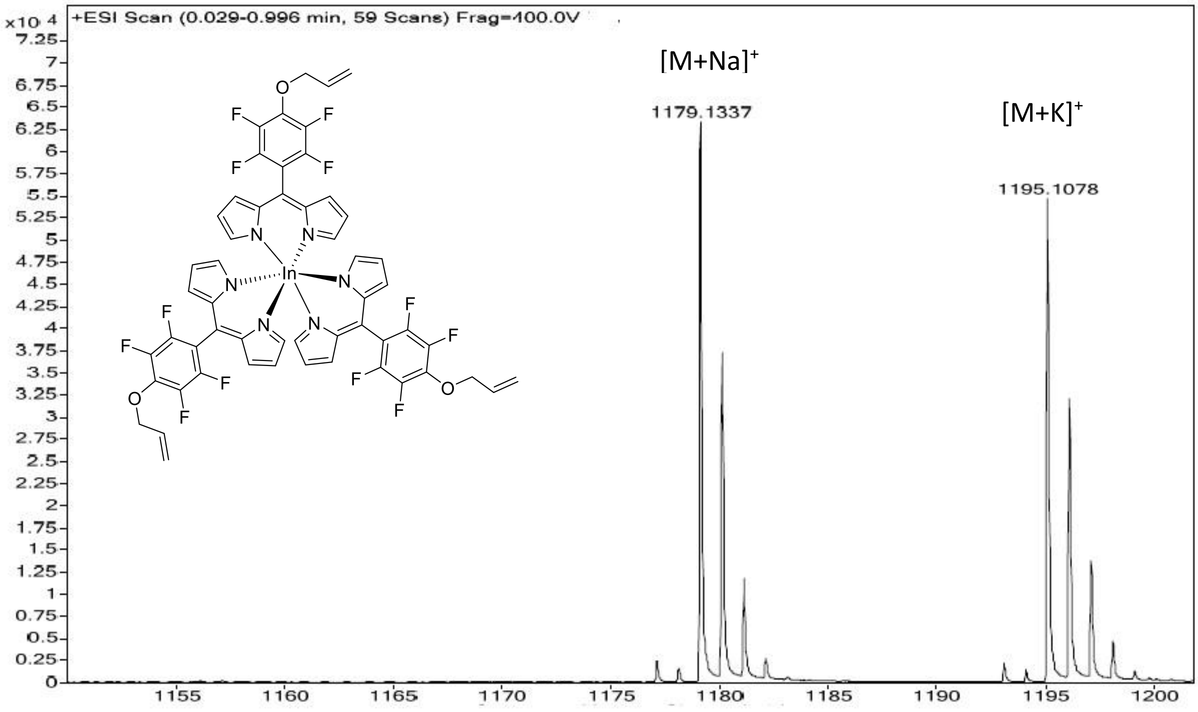
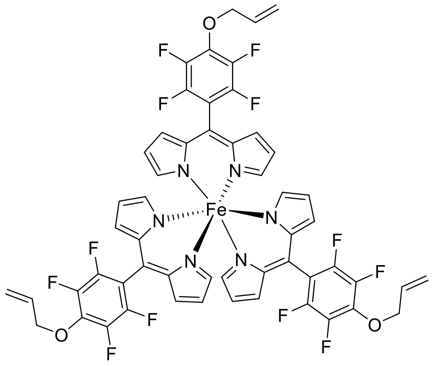


Figure S 84. HRMS (ES-TOF) spectrum of complex 13a.

Tris[5-{4-(prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl}dipyrrinato] iron(III) [13c]



According to the general procedure for the synthesis of tris(dipyrrinato) complexes starting from pre-functionalized dipyrrins, dipyrrin **9** (161 mg, 0.462 mmol, 3.1 eq.) was dissolved in MeOH (10 mL), $FeCl_3 \cdot 6H_2O$ (40 mg, 0.14 mmol) and DIPEA (20 µL, 16 mg, 2.08 mmol, 14 eq.) were added and the mixture was stirred at 50 °C for 1 h. The mixture was evaporated to dryness and purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2). The product was evaporated to dryness, washed with pentane and dried *in vacuo*. The product was obtained as green crystals (106 mg, 65%).

Mp: >300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = -29.54 (br s, 6 H, $H_{pyrrole}$), -7.72 (br s, 6 H, $H_{pyrrole}$), -6.39 (br s, 6 H, $H_{pyrrole}$), 5.58 (d, *J* = 6.0 Hz, 6 H, CH_2), 5.84 (dd, *J* = 17.2, 13 Hz, 3 H, $C=CH_2$), 6.04 (dd, *J* = 17.2, 13 Hz, 3 H, $C=CH_2$), 6.64-6.76 (m, 3 H, CH) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -154.72 (m_c, *J* = 17.7 Hz, 6 F, Ar-F_{meta}), -137.19 (m_c, *J* = 16.4 Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{54}H_{33}F_{12}FeKN_6O_3^+$ $[M+K]^+$ 1136.1404, found 1136.1371; *m/z* calc. for $C_{36}H_{22}F_8FeN_4O_2^+$ $[M-L]^+$ 750.0964, found 750.0938.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 450 (3.83) nm.

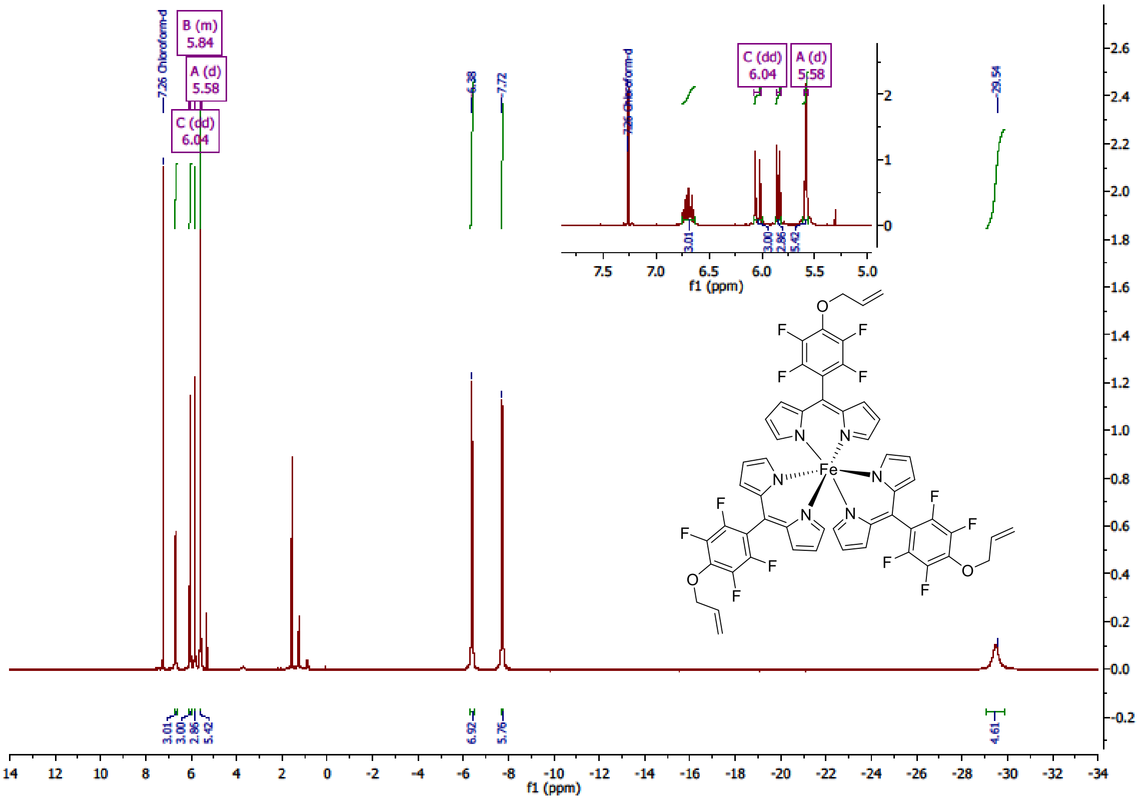


Figure S 85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 13c.

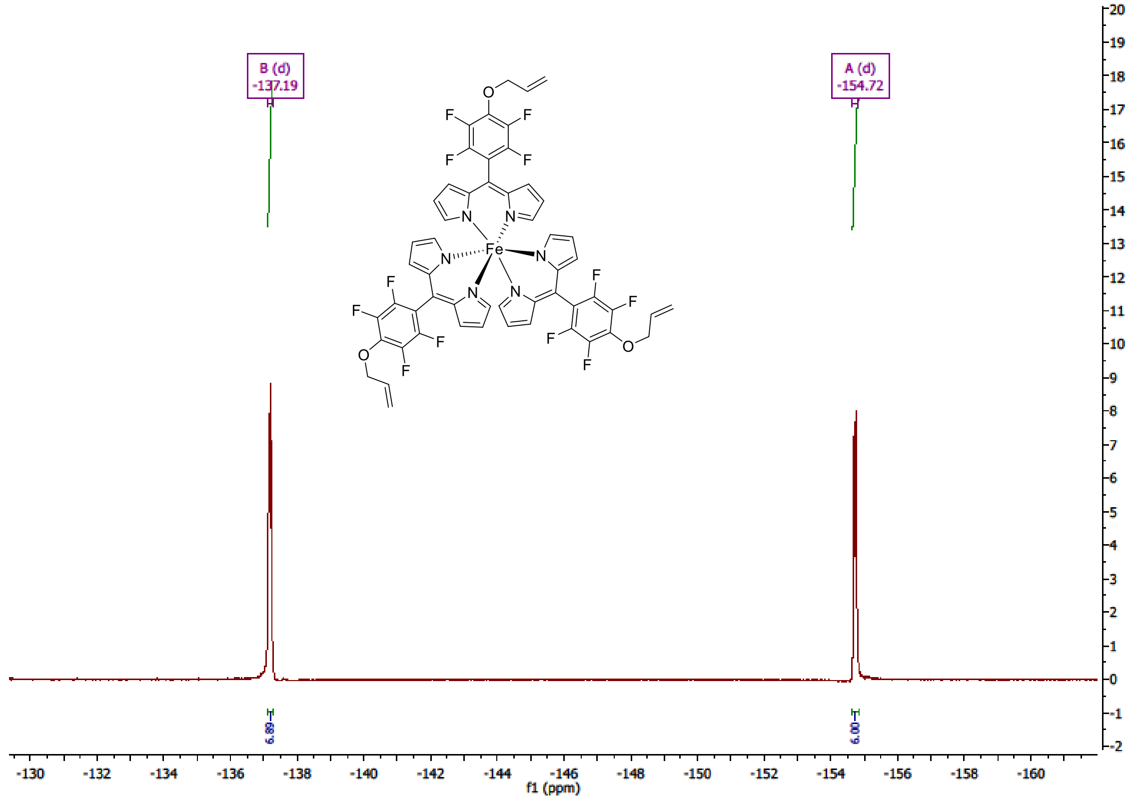


Figure S 86. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 13c.

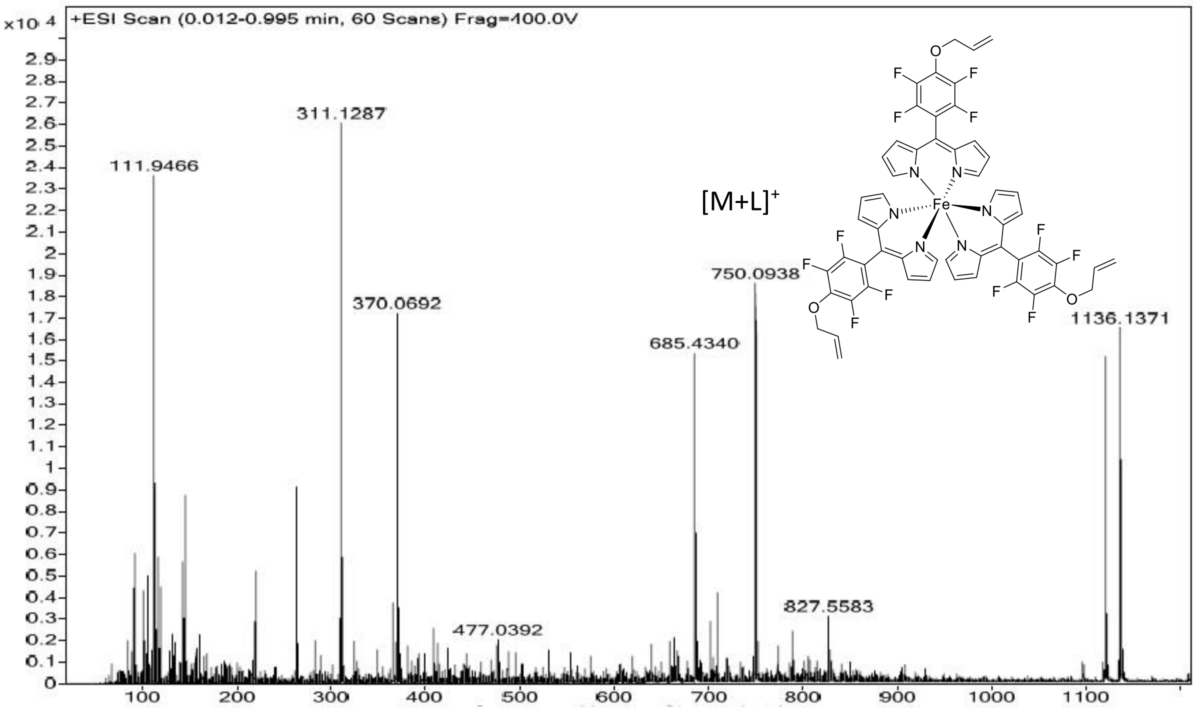


Figure S 87. HRMS (ESI-TOF) spectrum of complex 13c.

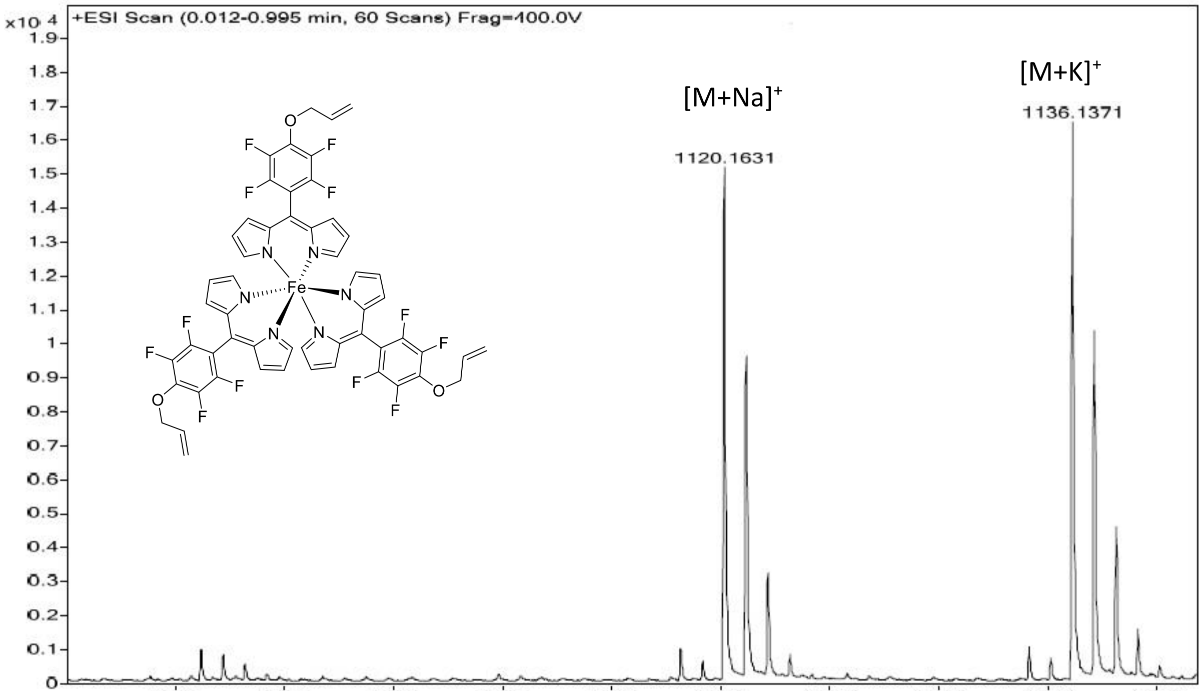
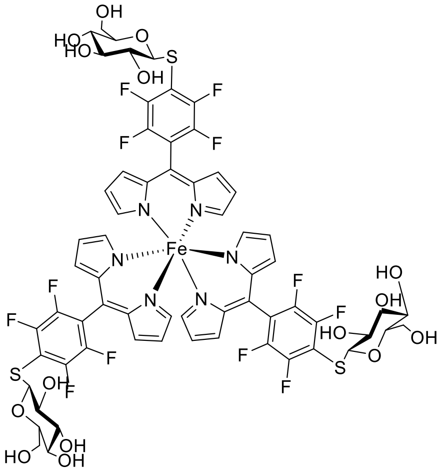


Figure S 88. HRMS (ES-TOF) spectrum of complex 13c.

Tris[5-{4-(β-D-thioglucosyl)-2,3,5,6-tetrafluorophenyl}dipyrrinato] iron(III) [14a]



According to the general procedure for the glycosylation of the metal complexes, complex **4** (61 mg, 62 µmol) was dissolved in dry DMF (5 mL), β-D-thio-glucose sodium salt (57 mg, 0.26 mmol, 4.2 eq.) was added and the mixture stirred for 40 min at rt. The mixture was evaporated to dryness and the crude product was purified by column chromatography (silica gel, DCM/MeOH = 85:15). The product was evaporated to dryness, washed with pentane and dried *in vacuo*. The product was obtained as a black solid (20 mg, 21%).

Mp: 175-180°C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = -26.88 (br s, 6 H, H$_{\mathrm{pyrrole}}$), -5.02 (d, *J* = 14.7 Hz, 6 H, H$_{\mathrm{pyrrole}}$), -4.18 (br s, 6 H, H$_{\mathrm{pyrrole}}$), 5.74-5.80 (m, 2 H, CH), 5.86-5.92 (m, 1 H, CH), 6.00-6.30 (m, 16 H, CH, OH), 6.40 -6.50 (m, 2 H, CH$_2$), 6.60-6.70 (m, 2 H, CH$_2$), 8.01-8.10 (m, 2 H, CH$_2$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -138.95 – -138.65 (m, 6 F, Ar-F$_{meta}$), -133.35 (m, 6 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{63}H_{51}F_{12}FeN_6NaO_{15}S_3^+$ [M+Na]$^+$ 1534.1630, found 1534.1611.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 453 (4.67), 500 (4.59) nm.

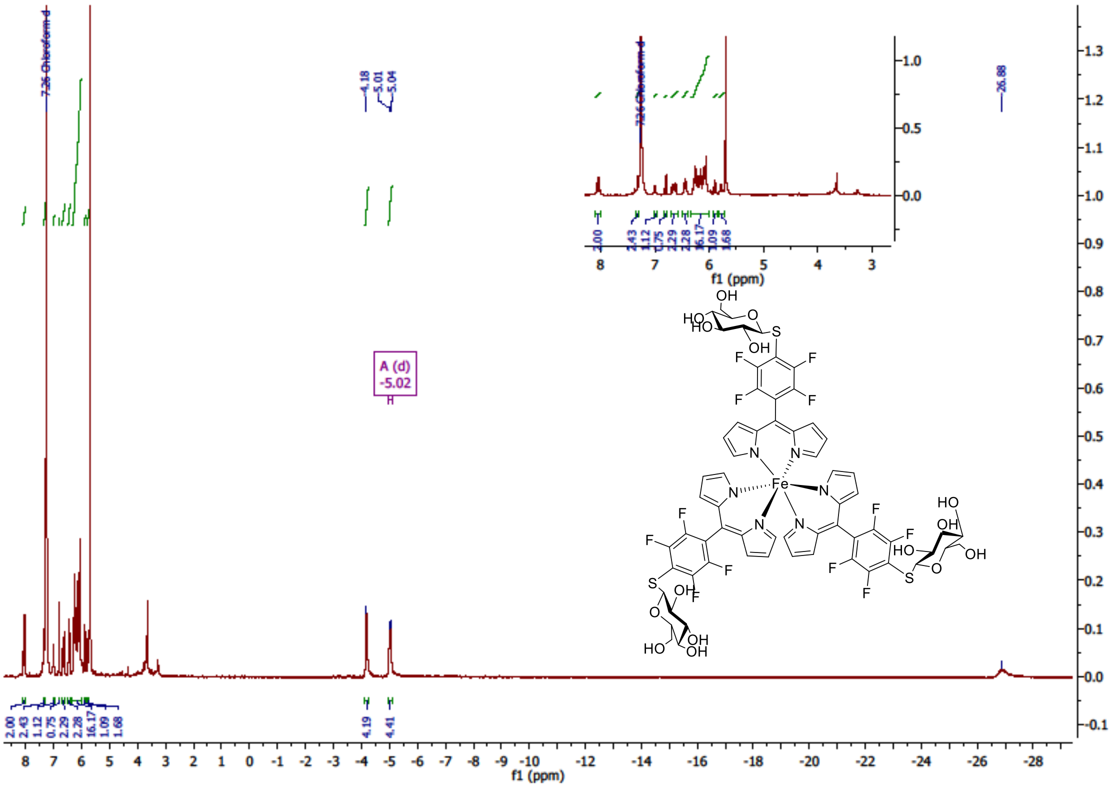


Figure S 89. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex 14a.

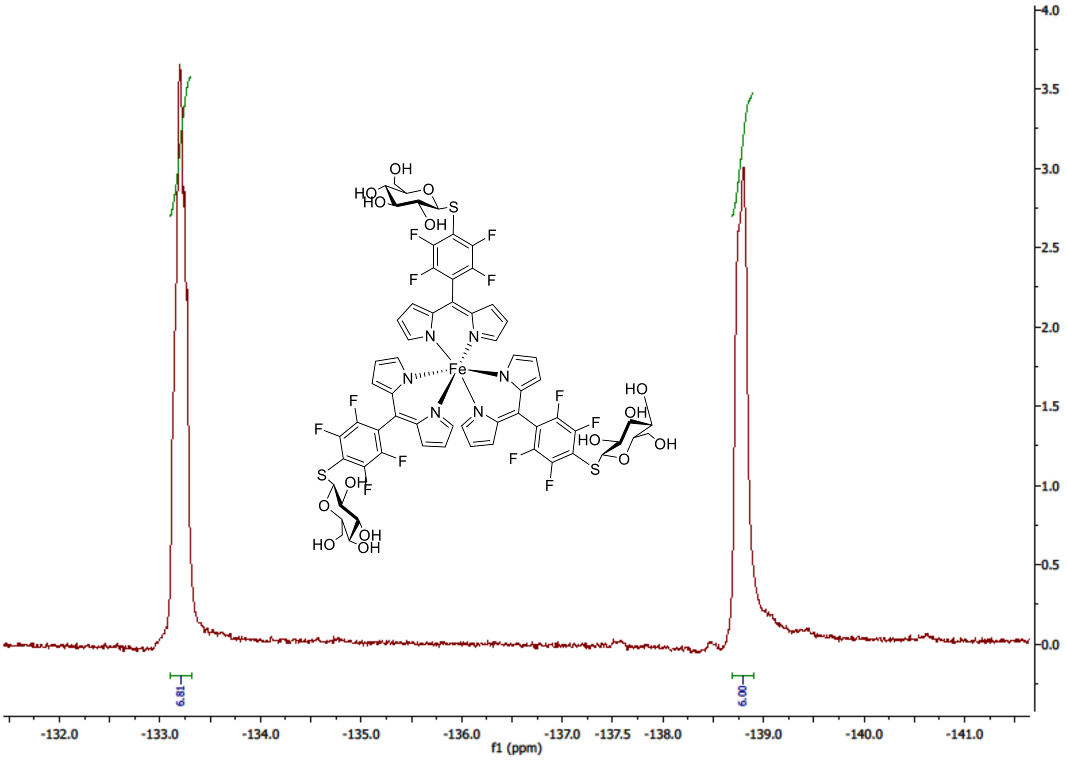


Figure S 90. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 14a.

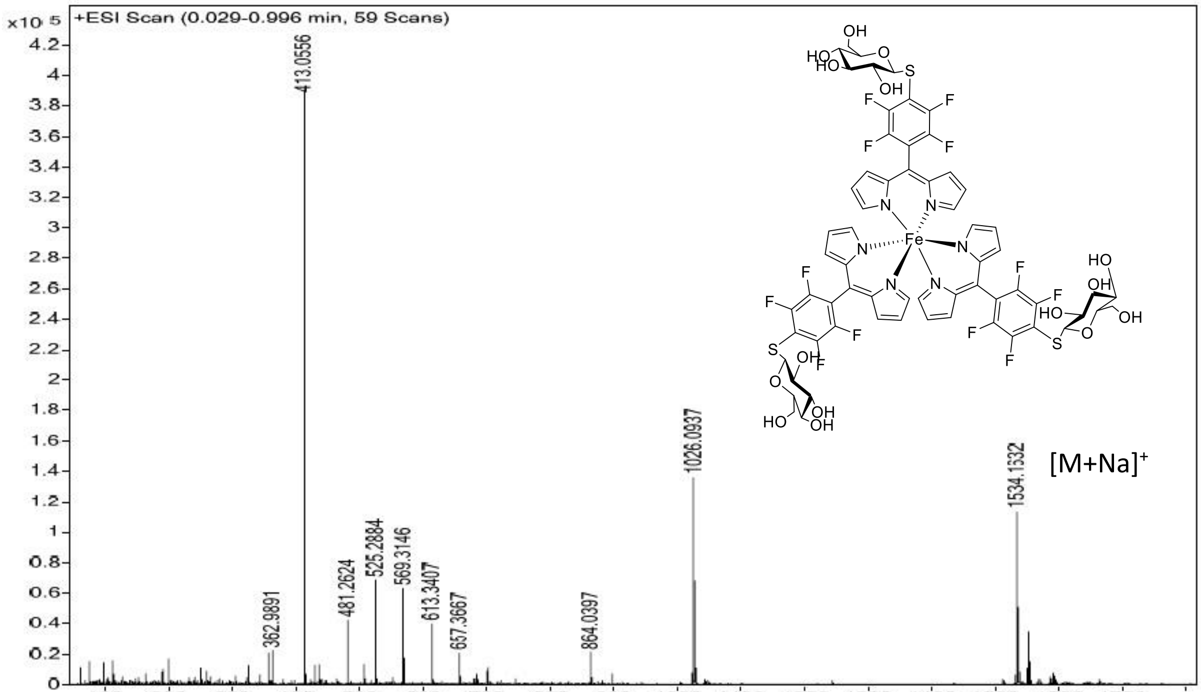


Figure S 91. HRMS (ESI-TOF) spectrum of complex 14a.

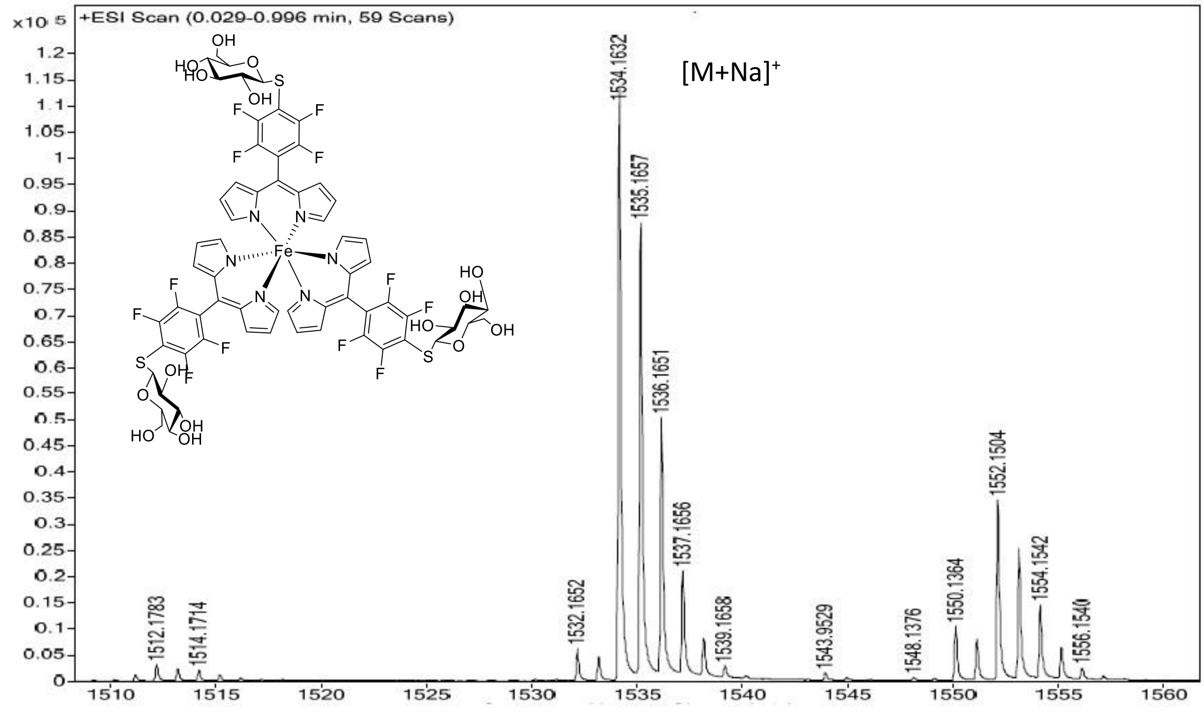
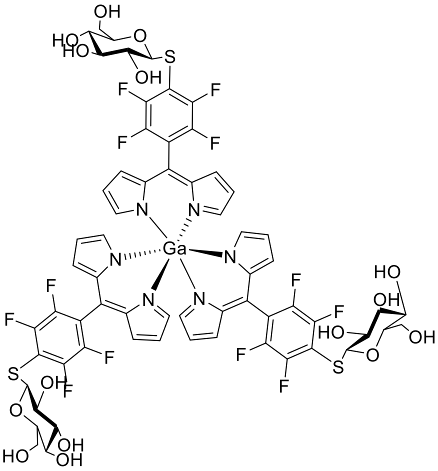


Figure S 92. HRMS (ESI-TOF) spectrum of complex 14a.

Tris[5-{4-(β-D-thioglucosyl)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [14b]



According to the general procedure for the glycosylation of the metal complexes, a mixture of complex **3** (67 mg, 67 µmol) and β-D-thioglucose sodium salt (55 mg, 0.25 mmol, 3.7 eq.) in dry DMF (5 mL) was stirred for 40 min at rt. The mixture was evaporated to dryness, purified by column chromatography (silica gel, DCM/MeOH = 8:2), washed with pentane and dried *in vacuo*. The product was obtained as a red solid (50 mg, 49%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, CD_3OD): δ = 3.25-3.45 (m, 22 H, $H_{glucose}$), 3.57-3.63 (m, 3 H, $H_{glucose}$), 3.77-3.79 (m, 2 H, $H_{glucose}$), 3.80-3.82 (m, 1 H, $H_{glucose}$), 4.90-4.94 (m, 6 H, CH_2), 6.32 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.71 (d, *J* = 4.1 Hz, $H_{pyrrole}$), 6.93-6.96 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CD_3OD): δ = 61.46 ($C_{glucose}$), 70.17 ($C_{glucose}$), 74.44 ($C_{glucose}$), 78.24 ($C_{glucose}$), 81.11 ($C_{glucose}$), 81.13 ($C_{glucose}$), 85.34 (CH_2), 85.42 (CH_2), 112.82 (Ar-C_{ipso}), 117.77 ($C_{pyrrole}$), 130.36 (Ar-C_{para}), 131.36, ($C_{pyrrole}$), 138.19 (C_{meso}), 144.37 (dd, *J* = 253.0, 16.4 Hz, Ar-C_{meta}), 146.93 (dd, *J* = 244.2, 16.9 Hz, Ar-C_{ortho}), 149.94 ($C_{pyrrole}$) ppm.

^{19}F NMR (376 MHz, CD_3OD): δ = -142.47 (m_c, *J* = 24.3, 11.3 Hz, 6 F, Ar-F_{meta}), -134.60 — -134.30 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{42}H_{34}F_8GaN_4O_{10}S_2^+$ $[M-L]^+$ 1039.0844, found 1039.0765; *m/z* calc. for $C_{63}H_{51}F_{12}GaN_6NaO_{15}S_3^+$ $[M+Na]^+$ 1547.1531; found 1547.1420.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 453 (4.89), 505 (4.82) nm.

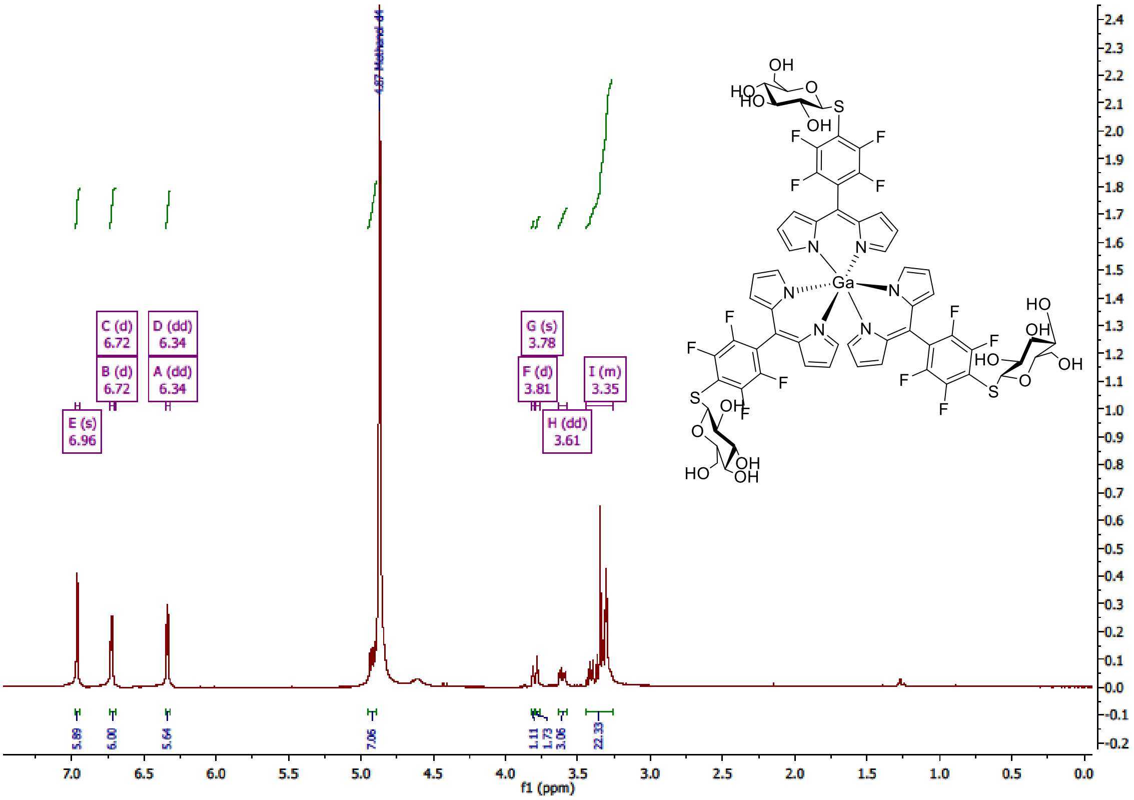


Figure S 93. ^{1}H **NMR (400 MHz,** CD_3OD**) spectrum of complex 14b.**

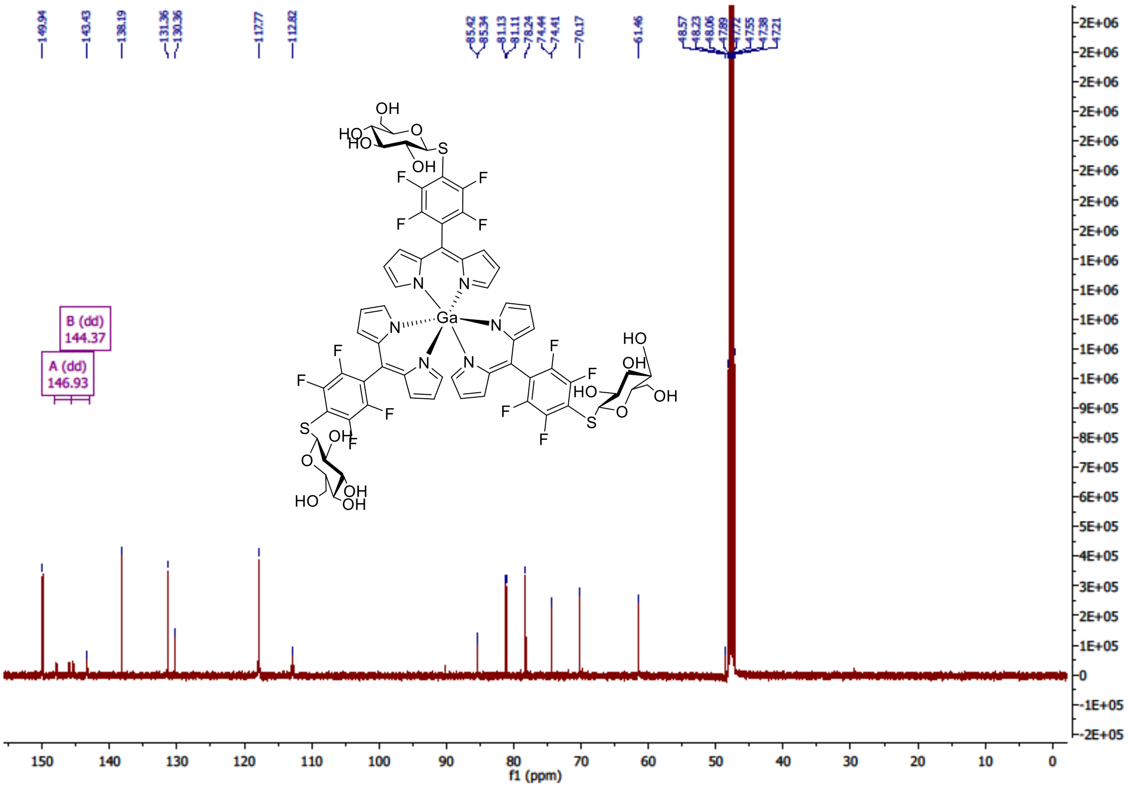


Figure S 94. ^{13}C **NMR (126 MHz,** CD_3OD**) spectrum of complex 14b.**

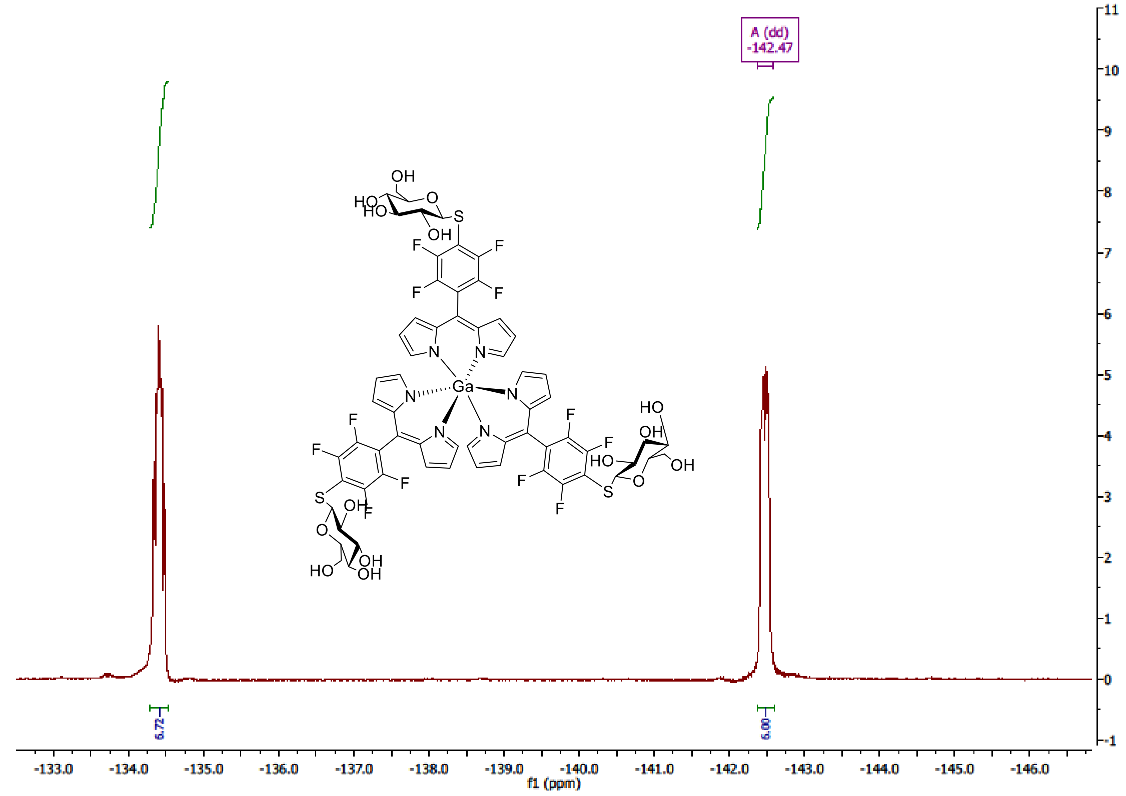


Figure S 95. ^{19}F NMR (376 MHz, CD_3OD) spectrum of complex 14b.

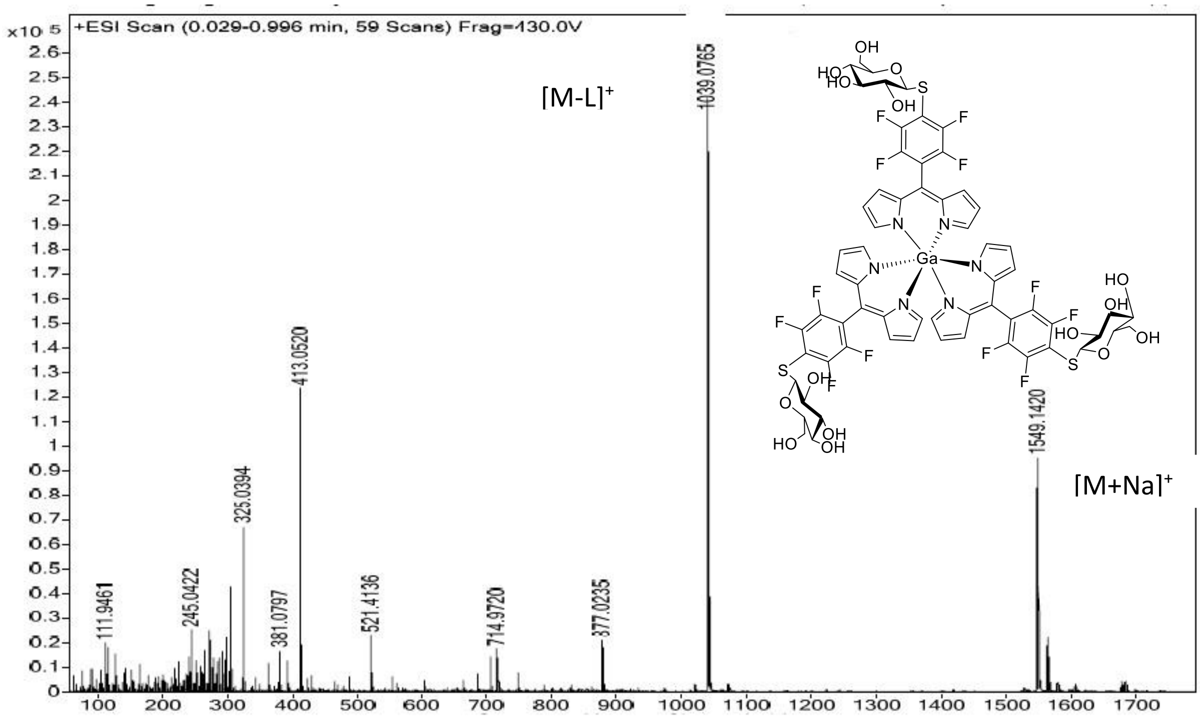


Figure S 96. HRMS (ESI-TOF) spectrum of complex 14b.

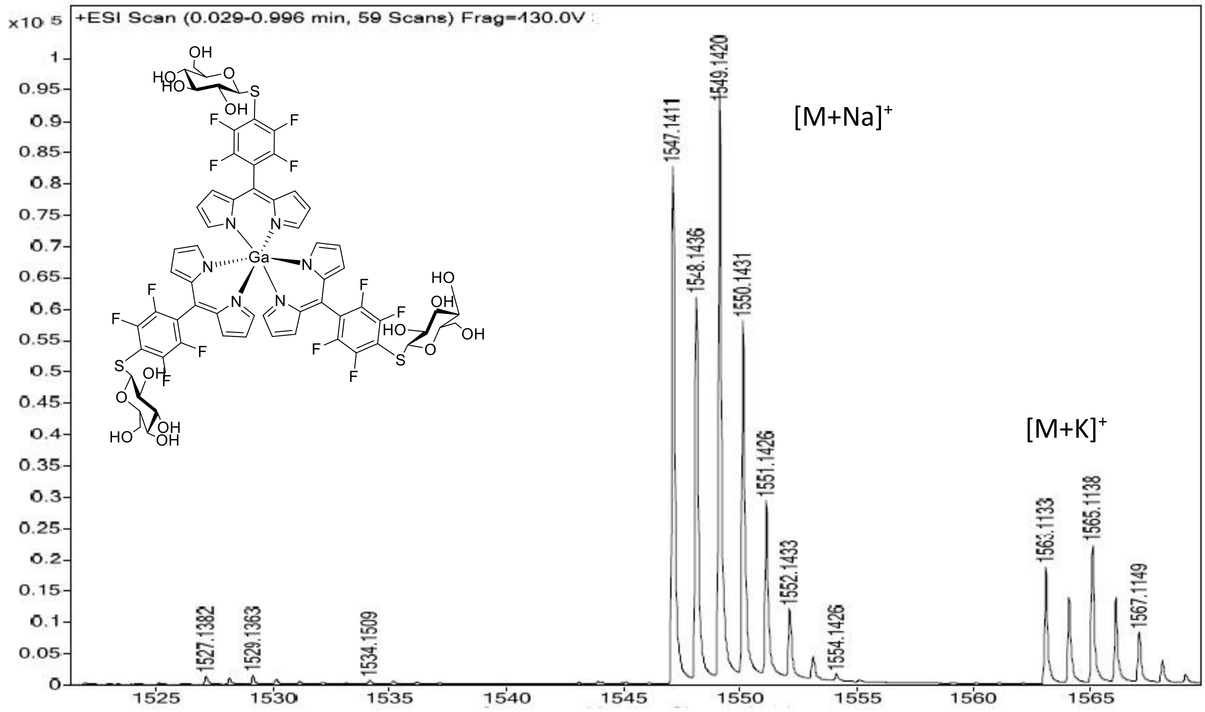
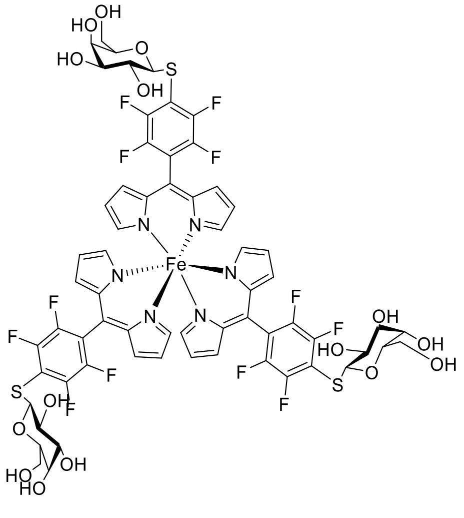


Figure S 97. HRMS (ESI-TOF) spectrum of complex 14b.

Tris[5-{4-(β-D-thiogalactosyl)-2,3,5,6-tetrafluorophenyl}dipyrrinato] iron(III) [15a]



According to the general procedure for the glycosylation of the metal complexes, complex **4** (100 mg, 0.10 mmol) was dissolved in dry DMF (5 mL), β-D-thiogalactose sodium salt (93 mg, 0.43 mmol, 4.5 eq.) was added and the mixture stirred for 3 h at rt. The mixture was evaporated to dryness and purified by column chromatography (silica gel, DCM/MeOH = 85:15). The product was evaporated to dryness, washed with pentane and dried *in vacuo*. The product was isolated as an orange solid (50 mg, 32%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = -29.19 (br s, 6 H, $H_{pyrrole}$), -7.41 (d, *J* = 17.0 Hz, 6 H, $H_{pyrrole}$), -6.55 (br s, 6 H, $H_{pyrrole}$), 3.48-3.51 (m, 4 H, $H_{galactoe}$), 3.56-3.59 (m, 4 H, $H_{galactose}$), 3.66-3.70 (m, 4 H, $H_{galactose}$), 4.40 (s, 2 H, CH_2), 4.42 (s, 2 H, CH_2), 4.57-4.59 (br s, 12 H, OH) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -138.87 (m$_c$, *J* = 18.5 Hz, 6 F, Ar-F$_{meta}$), -132.97 (m$_c$, *J* = 19.6 Hz, Ar-F$_{ortho}$) ppm.

HRMS (ESI-MS): *m/z* calc. for $C_{63}H_{51}F_{12}FeN_6NaO_{15}S_3^+$ [M+Na]$^+$ 1534.1625, found 1534.1659.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 455 (4.99), 508 (4.90) nm.

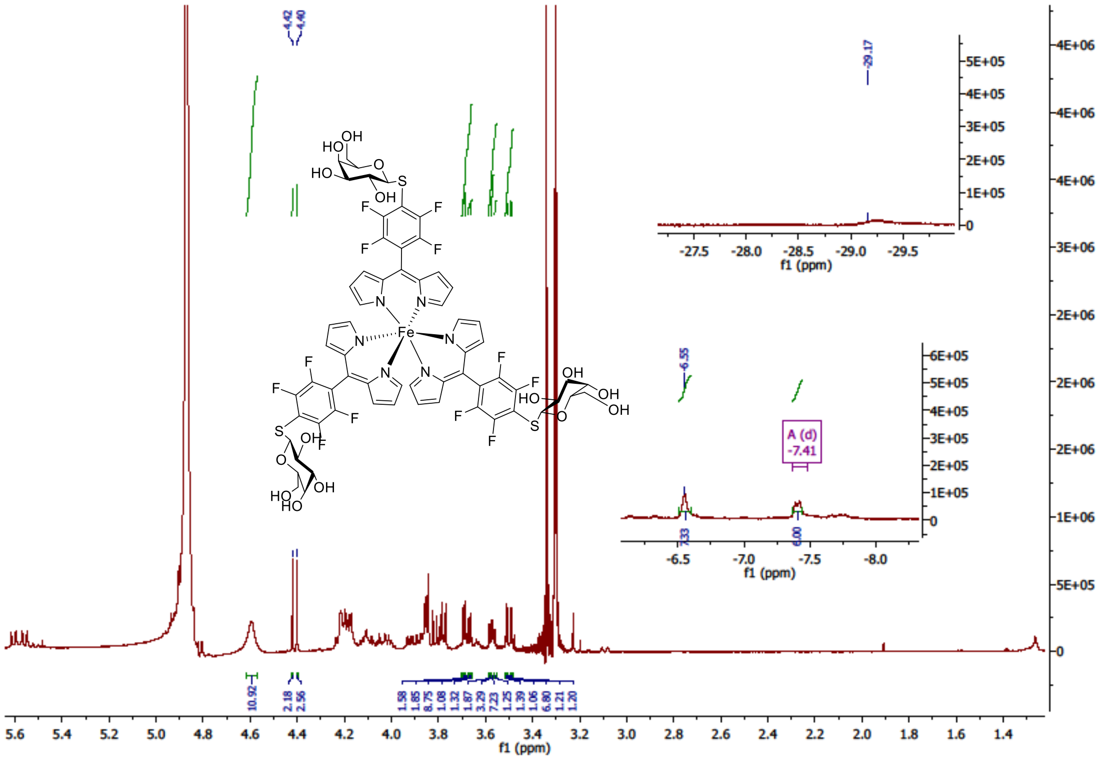


Figure S 98. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex **15a.**

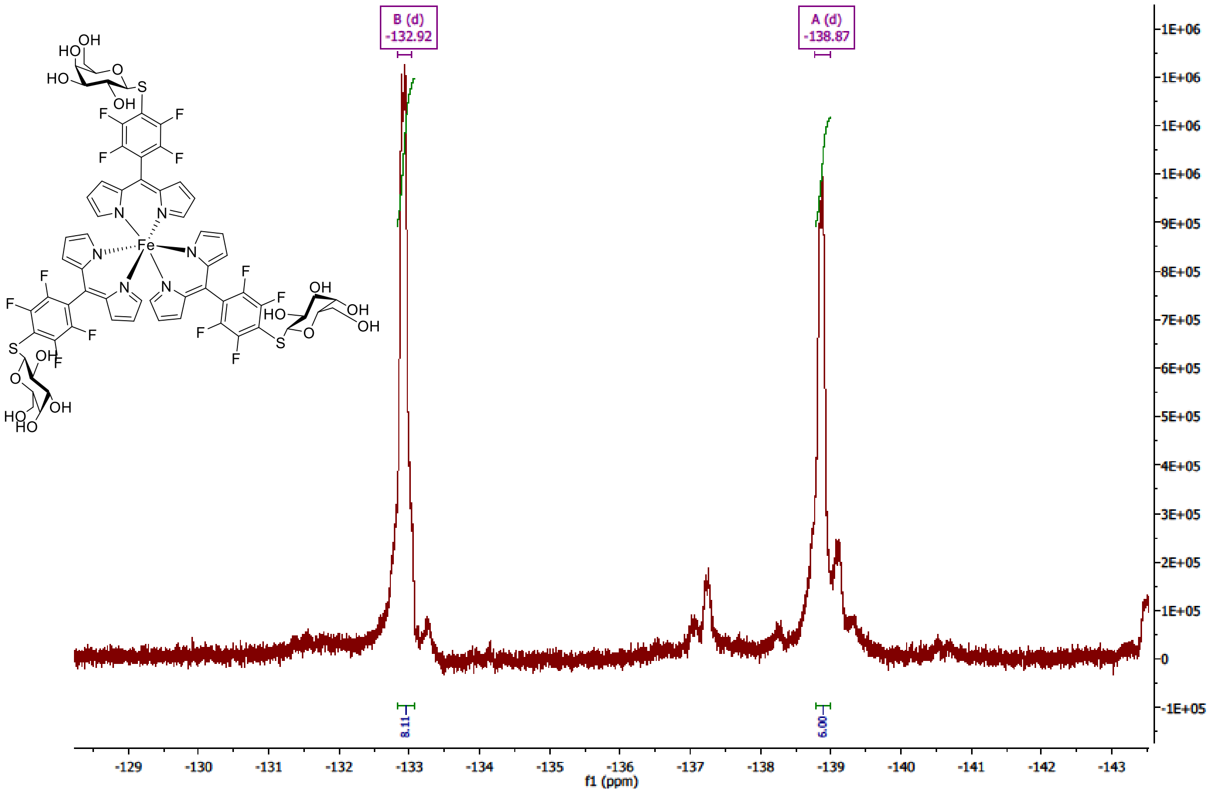


Figure S 99. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 15a.

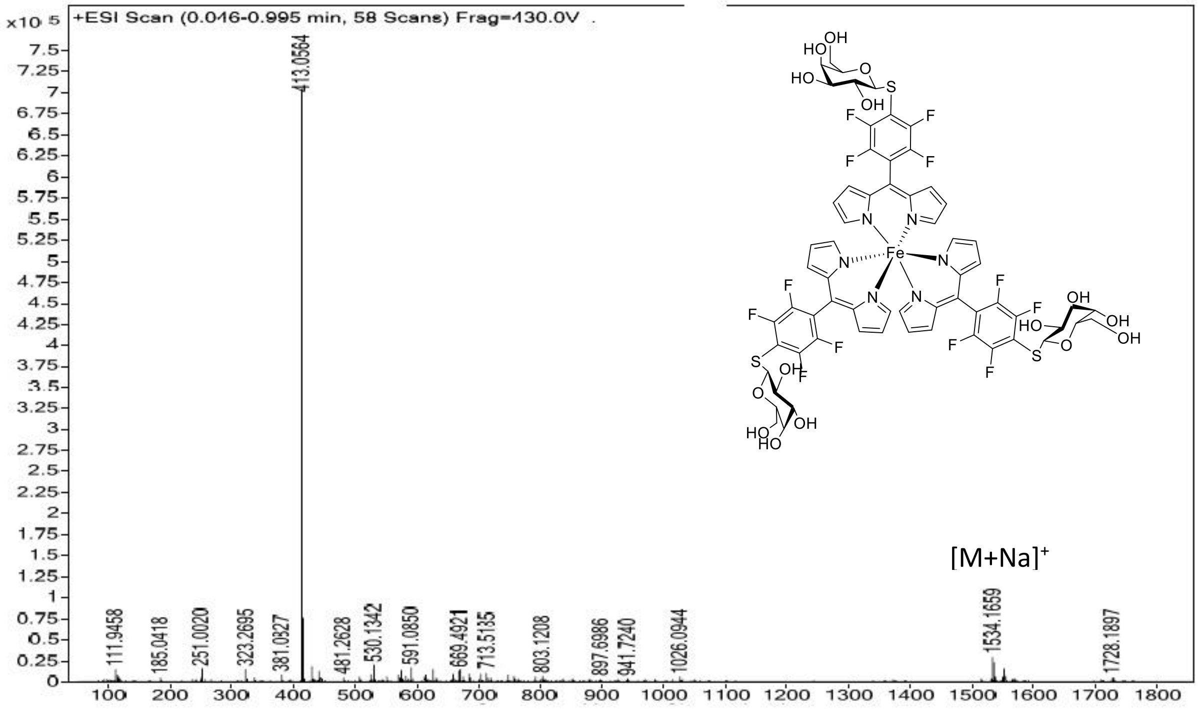


Figure S 100. HRMS (ESI-TOF) spectrum of complex 15a.

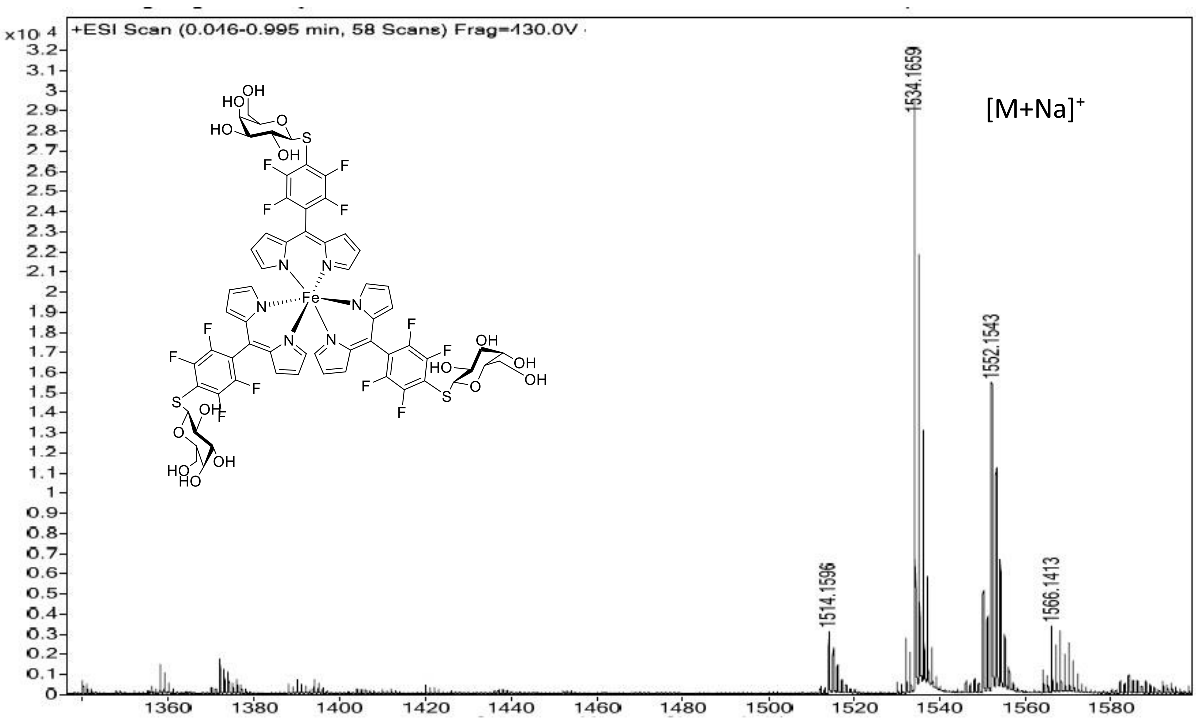
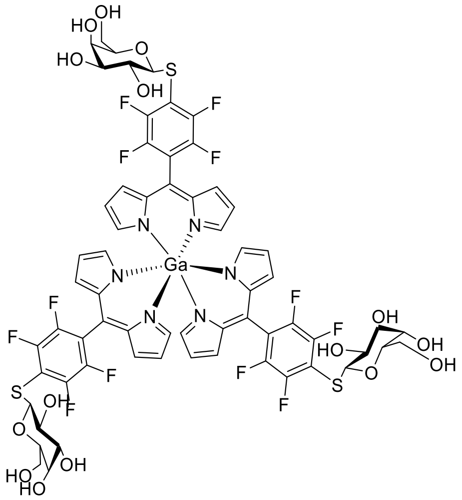


Figure S 101. HRMS (ESI-TOF) spectrum of complex 15a.

Tris[5-{4-(β-D-thiogalactosyl)-2,3,5,6-tetrafluorophenyl}dipyrrinato] gallium(III) [15b]



According to the general procedure for the glycosylation of the metal complexes, complex **3** (74 mg, 74 µmol) was dissolved in dry DMF (5 mL), β-D-thiogalactose sodium salt (73 mg, 0.33 mmol, 4.5 eq.) was added and the mixture stirred for 1.5 h at rt. The mixture was evaporated to dryness and purified by column chromatography (silica gel, DCM/MeOH = 85:15) to obtain the product as an orange solid (100 mg, 88%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, CD_3OD): δ = 2.81 (d, *J* = 0.6 Hz, 3 H, CH_2), 2.94 (d, *J* = 0.6 Hz, 3 H, CH_2), 3.26-3.28 (m, 3 H, $H_{galactose}$), 3.50-3.56 (m, 9 H, $H_{galactose}$), 3.62-3.65 (m, 9 H, $H_{galactose}$), 3.88-3.90 (m, 3 H, $H_{galactose}$), 6.30 (dd, *J* = 4.2, 1.4 Hz, 6 H, $H_{pyrrole}$), 6.69 (d, *J* = 4.1 Hz, 6 H, $H_{pyrrole}$), 6.90-6.92 (m, 6 H, $H_{pyrrole}$) ppm.

^{13}C NMR (126 MHz, CD_3OD): δ = 30.58 (CH_2), 35.90 (CH_2), 61.39 ($C_{galactose}$), 61.47 ($C_{galactose}$), 69.38 ($C_{galactose}$), 71.35 ($C_{galactose}$), 74.83 ($C_{galactose}$), 112.82 (t, $J_{C\text{-}F}$ = 20.5 Hz, Ar-C_{ipso}), 117.90 ($C_{pyrrole}$), 131.42 ($C_{pyrrole}$), 138.19 (C_{meso}), 144.32 (dd, $J_{C\text{-}F}$ = 248.5, 16.0 Hz, Ar-C_{meta}), 147.06 (dd, $J_{C\text{-}F}$ = 246.6, 13.6 Hz, Ar-C_{ortho}), 150.00 ($C_{pyrrole}$) ppm.

^{19}F NMR (376 MHz, CD_3OD): δ = -142.37 (m_c, *J* = 24.3, 11.1 Hz, 6 F, Ar-F_{meta}), -133.82 (m_c, *J* = 24.1, 11.1 Hz, 6 F, Ar-F_{meta}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{63}H_{51}F_{12}GaN_6NaO_{15}S_3^+$ $[M+K]^+$ 1547.1531, found 1547.1522.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 453 (5.02), 506 (4.99) nm.

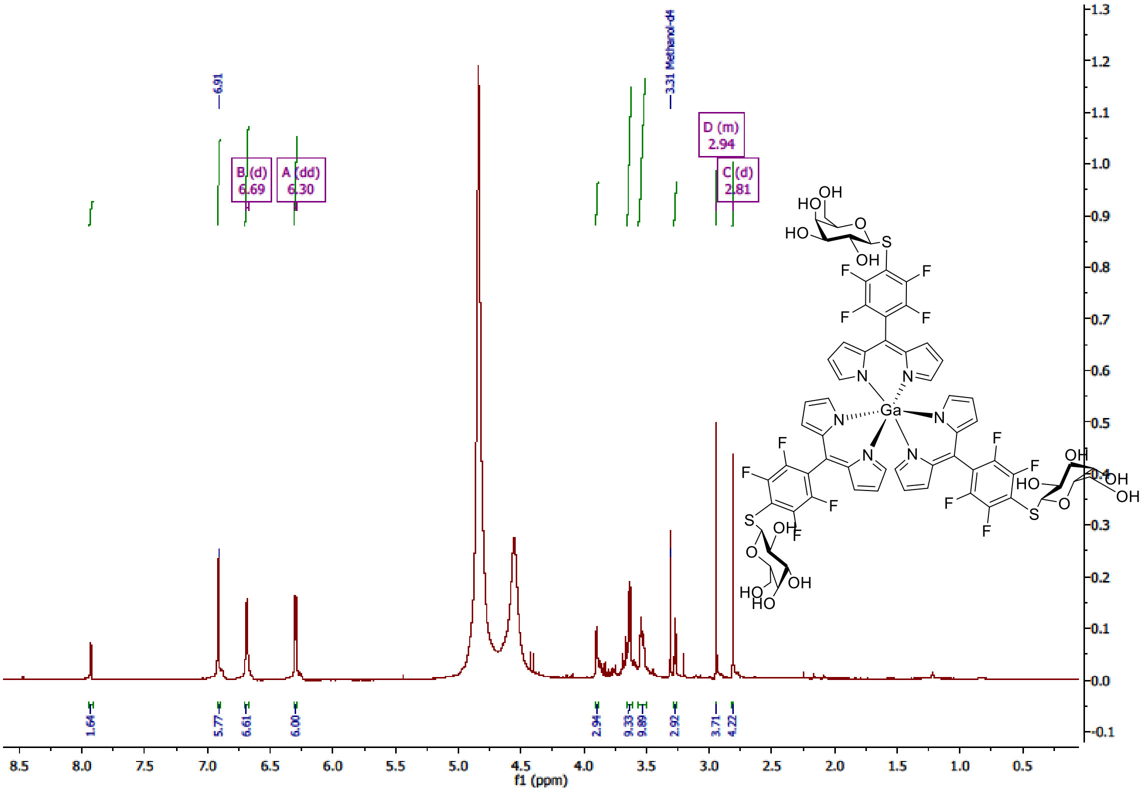


Figure S 102. ^{1}H NMR (400 MHz, CD_3OD) spectrum of complex 15b.

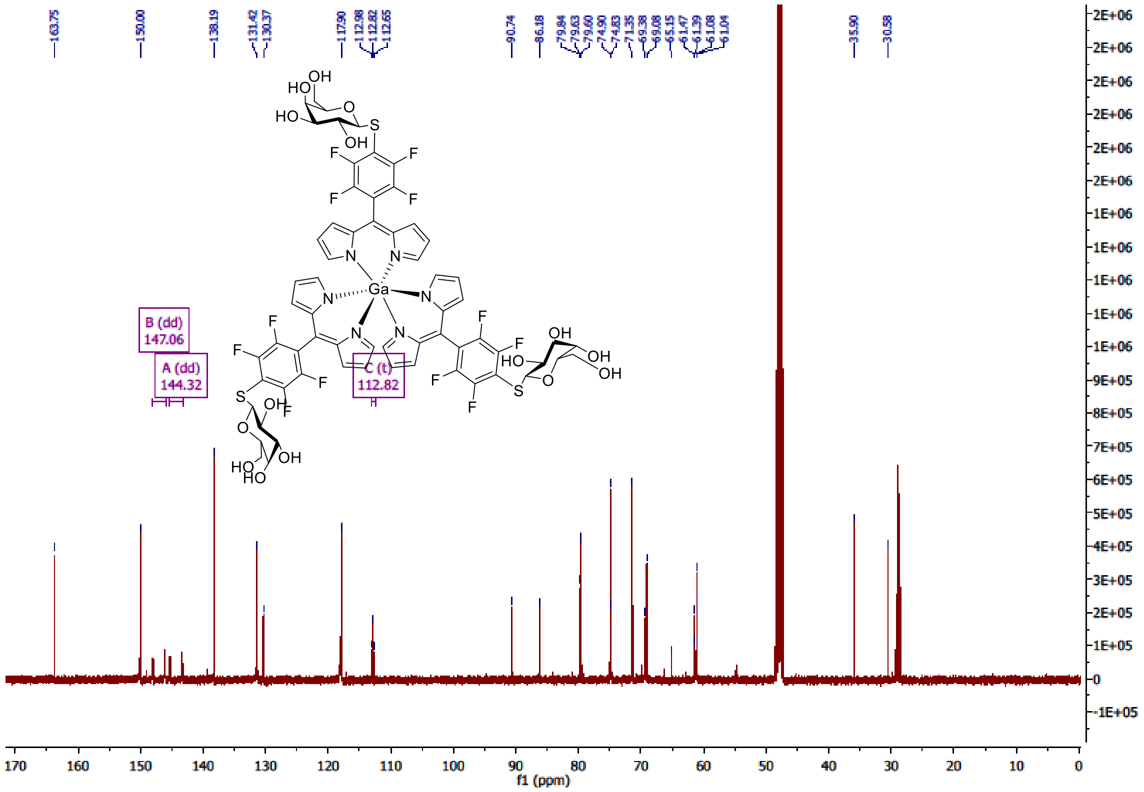


Figure S 103. ^{13}C NMR (126 MHz, CD_3OD) spectrum of complex 15b.

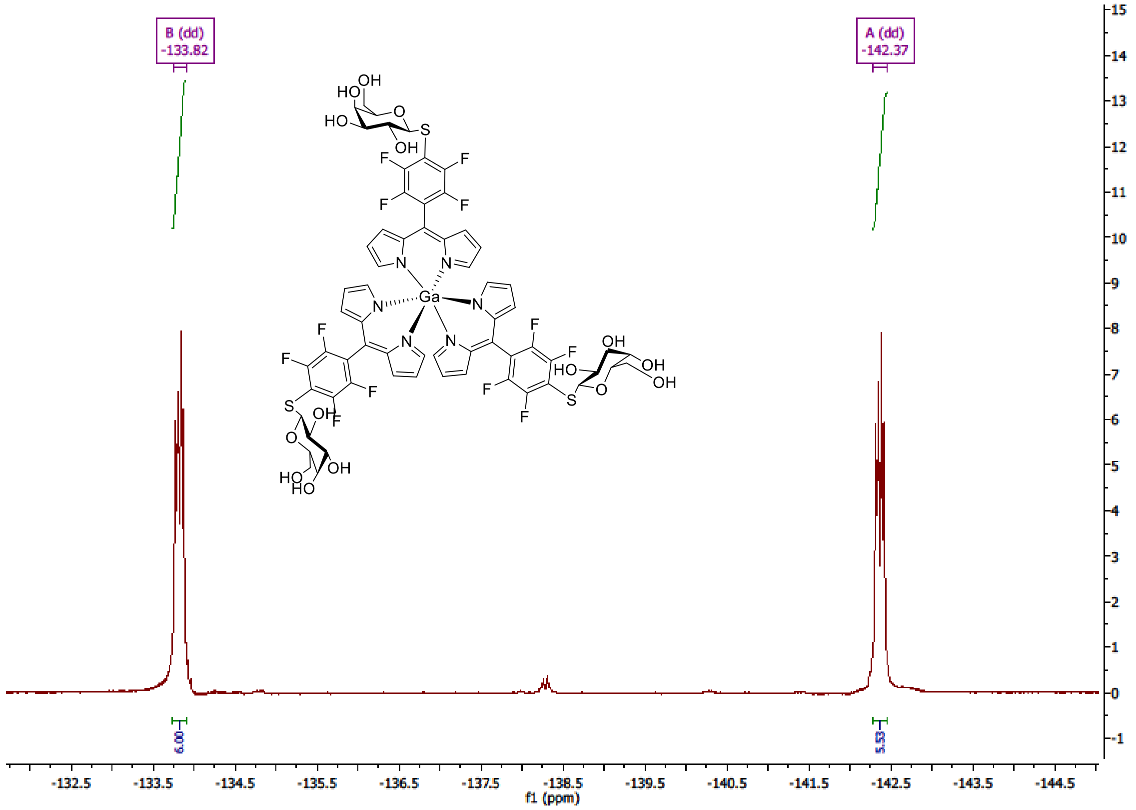


Figure S 104. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of complex 15b.

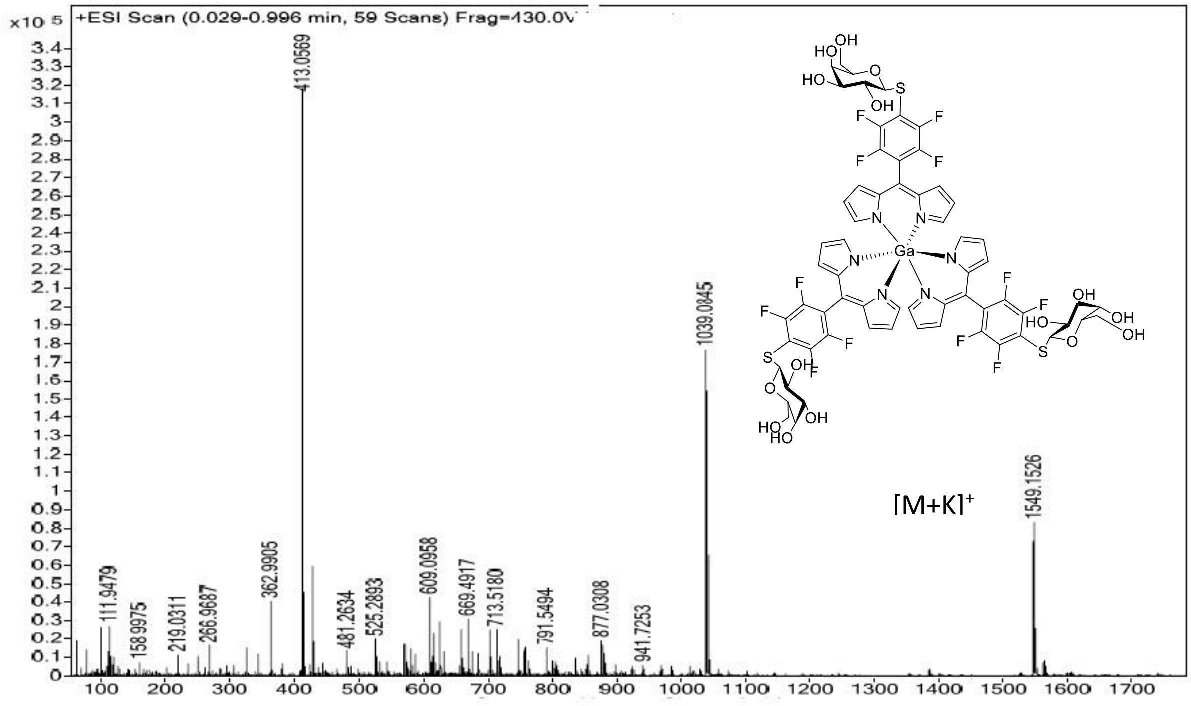


Figure S 105. HRMS (ESI-TOF) spectrum of complex 15b.

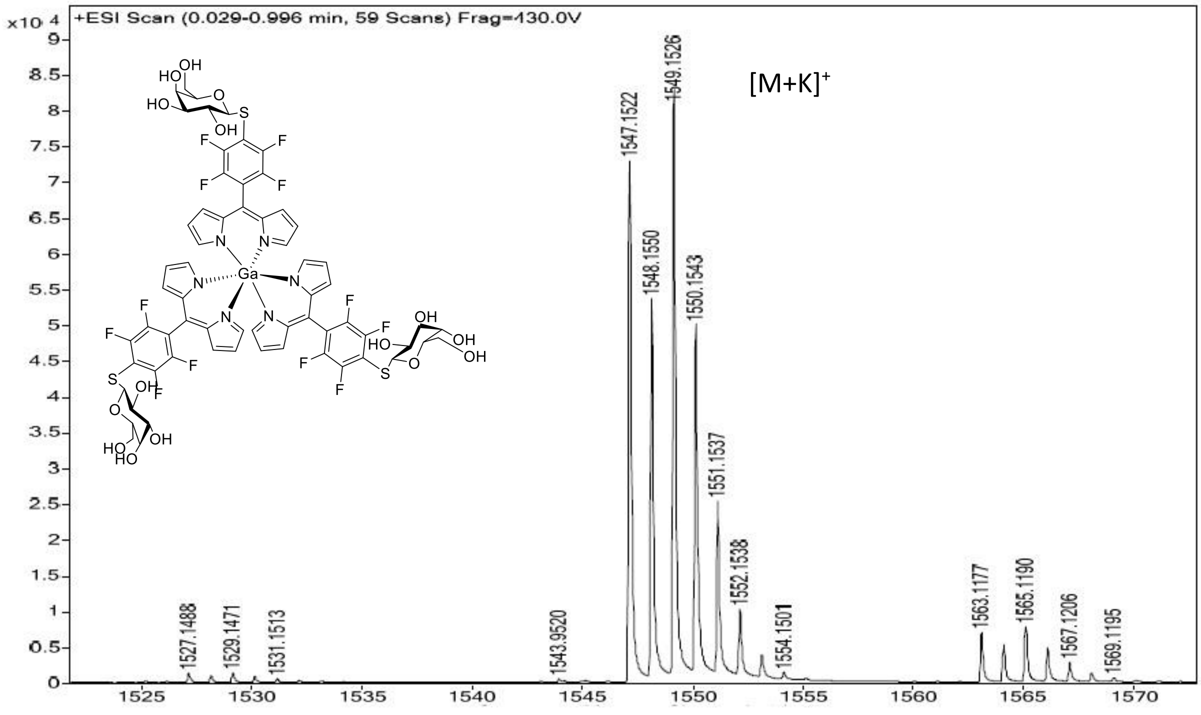
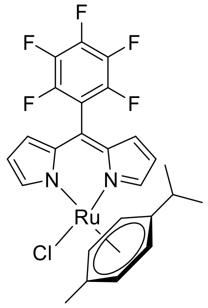


Figure S 106. HRMS (ESI-TOF) spectrum of complex 15b.

[(η^6-p-Cymen)ruthenium(Cl)(5-pentafluorophenyl)dipyrrin)] [17]



Under argon atmosphere and exclusion of light dichloro(p-cymen)ruthenium(II)dimer **16** (100 mg, 0.16 mmol) and PFP-dipyrrin **1** (100 mg, 0.326 mmol) were dissolved in DCM (3.0 mL). After the addition of DIPEA (2.0 mL, 1.14 mmol, 7 eq.) the reaction mixture was stirred for 24 h at rt. After the addition of water the mixture was washed several times with water. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. The crude product was recrystallised (DCM/*n*-pentane) to obtain the product as red crystals (180 mg, 94%).

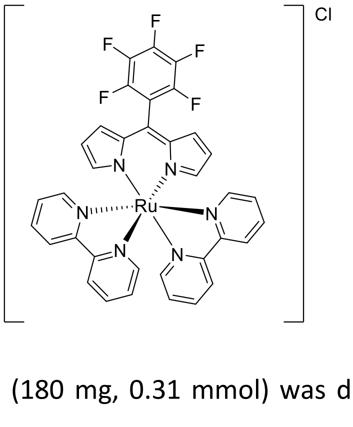
^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.07 (d, *J* = 6.9 Hz, 6 H, $C\mathit{H}_3CHC\mathit{H}_3$), 2.12 (s, 3 H, CH_3), 2.50-2.53 (m, 1 H, CH), 5.23-5.27 (m, 2 H, Ar-H), 5.31 (d, *J* = 6.1 Hz, 2 H, Ar-H), 6.48-6.50 (m, 2 H, $H_{pyrrole}$), 8.01-8.04 (m, 2 H, $H_{pyrrole}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -161.81 – -161.63 (m_c, *J* = 23.2, 9.1 Hz, 1 F, Ar-F_{meta}), -160.99 – -160.83 (m_c, *J* = 1 F, Ar-F_{meta}), 153.00 (m_c, *J* = 20.9 Hz, 1 F, Ar-F_{para}), -139.36 (m_c, *J* = 22.3 Hz, 1 F, Ar-F_{ortho}), 137.36 (m_c, *J* = 23.4 Hz, 1 F, Ar-F_{ortho}) ppm.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 454 (4.49), 504 (4.57) nm.

The spectroscopic data are in accordance with the literature.[5]

[Bis(2,2´-bipyridyl)-(5-pentafluorophenyl)dipyrrinato)] ruthenium(II) chloride [18]



Under argon atmosphere dipyrrin **1** (180 mg, 0.31 mmol) was dissolved in dry EtOH (20 mL), 2,2´-bipyridine (97 mg, 0.62 mmol, 2 eq.) was added and the mixture was refluxed for 24 h. The mixture was diluted with DCM and washed with water several times. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM to DCM/MeOH = 8:1), evaporated to dryness and washed with pentane and dried *in vacuo* to obtain the product as a black-green solid (160 mg, 68%).

Mp: 168-170 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.29 (dd, *J* = 4.4, 1.4 Hz, 2 H, H$_{\text{pyrrole}}$), 6.37 (t, *J* = 1.3 Hz, 2 H, H$_{\text{pyrrole}}$), 6.53 (d, *J* = 4.3 Hz, 2 H, H$_{\text{pyrrole}}$), 7.25-7.32 (m, 4 H, H$_{\text{bipyr}}$), 7.65 (dd, *J* = 5.6, 0.7 Hz, 2 H, H$_{\text{bipyr}}$), 7.89-7.95 (m, 4 H, H$_{\text{bipyr}}$), 7.97-8.02 (m, 2 H, H$_{\text{bipyr}}$), 8.71-8.79 (m, 4 H, H$_{\text{bipyr}}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 113.39 (t, $J_{\text{C-F}}$ = 19.3 Hz, Ar-C$_{ipso}$), 119.67 (C$_{\text{pyrrole}}$), 126.34 (C$_{\text{bipyr}}$), 126.81 (C$_{\text{bipyr}}$), 129.77 (C$_{\text{pyrrole}}$), 134.47 (C$_{meso}$), 136.18 (C$_{\text{bipyr}}$), 136.88 (C$_{\text{bipyr}}$), 138.32 (t, $J_{C\text{-}F}$ = 15.5 Hz, Ar-C$_{para}$), 141.33 (d, $J_{C\text{-}F}$ = 242.8 Hz, Ar-C$_{meta}$), 144.68 (d, $J_{C\text{-}F}$ = 244.9 Hz, Ar-C$_{ortho}$), 150.74 (C$_{\text{pyrrole}}$), 150.58 (C$_{\text{bipyr}}$), 151.82 (C$_{\text{bipyr}}$), 157.39 (C$_{\text{bipyr}}$), 158.17 (C$_{\text{bipyr}}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -161.20 – -161.00 (m, 2 F, Ar-F$_{meta}$), -152.91 (t, *J* = 20.8 Hz, 1 F, Ar-F$_{para}$), -139.88 – 139.76 (m$_c$, *J* = 23.1, 6.7 Hz, 2 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{35}H_{22}F_5N_6Ru^+$ [M]$^+$ 723.0864, found 723.0900.

UV/Vis (DCM): λ$_{\text{max}}$ [log ε (dm^3·mol^{-1}·cm^{-1})] = 471 (4.66), 513 (4.07) nm.

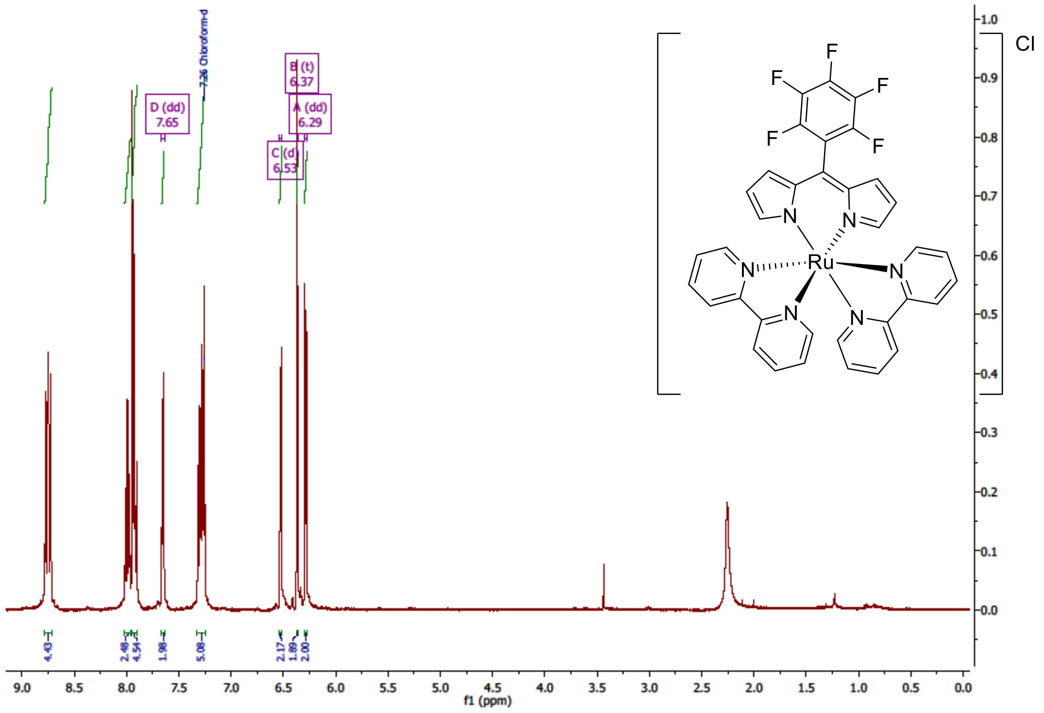


Figure S 107. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of complex **18**.

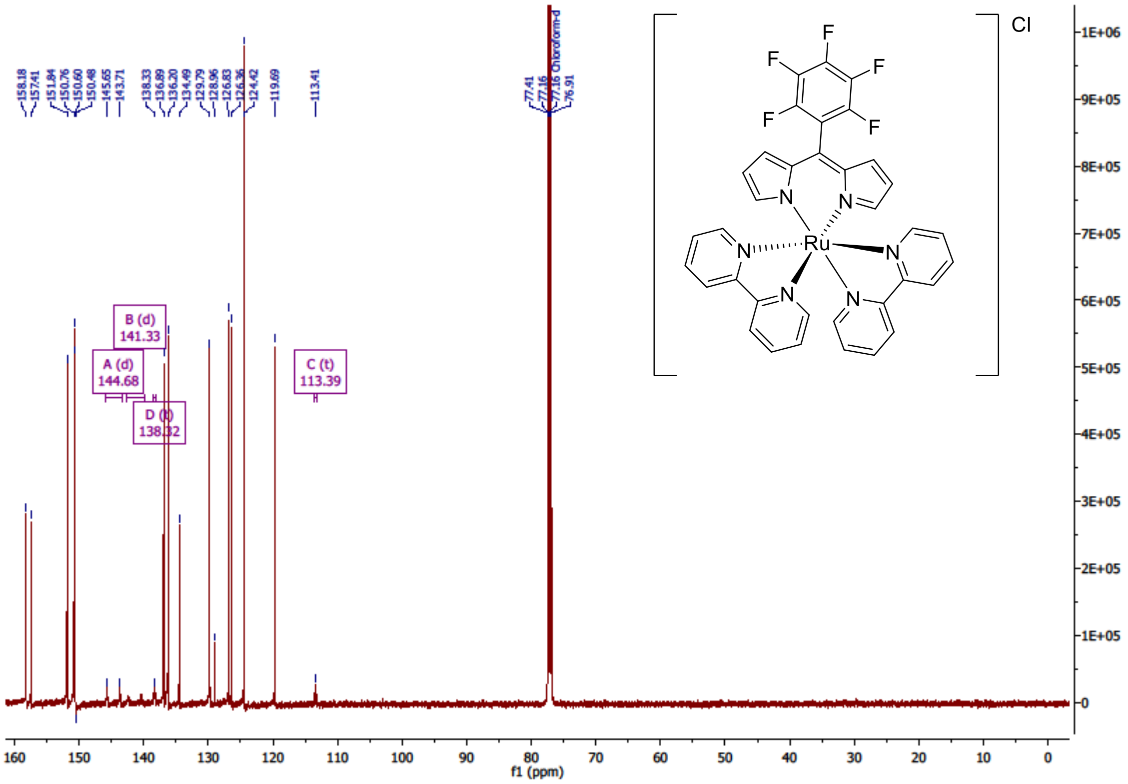


Figure S 108. **^{13}C NMR (126 MHz, CDCl$_3$) spectrum of cmplex 18.**

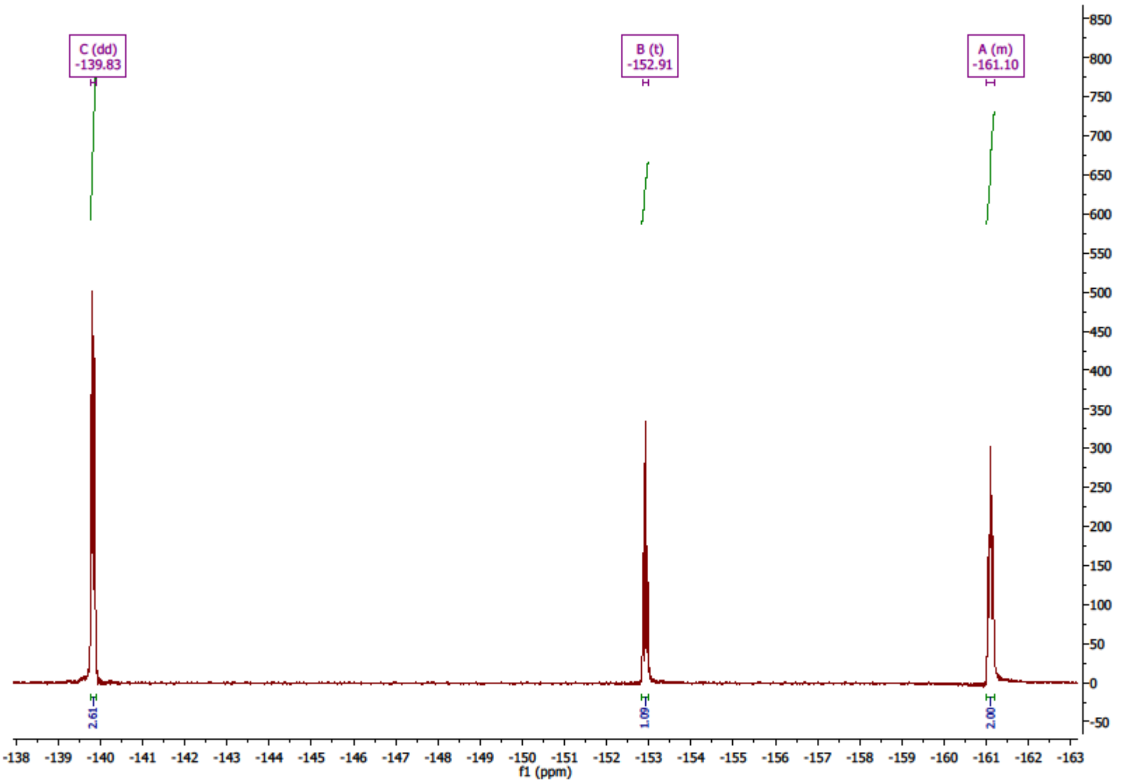


Figure S 109. **^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 18.**

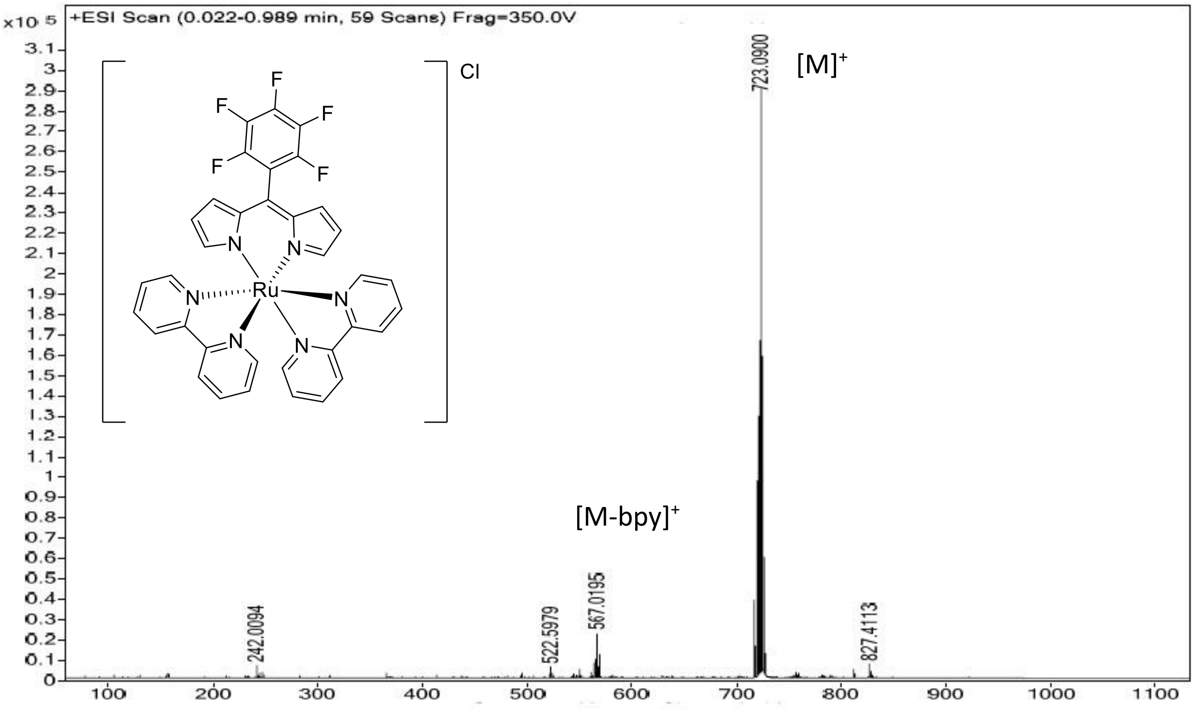


Figure S 110. HRMS (ESI-TOF) spectrum of complex 18.

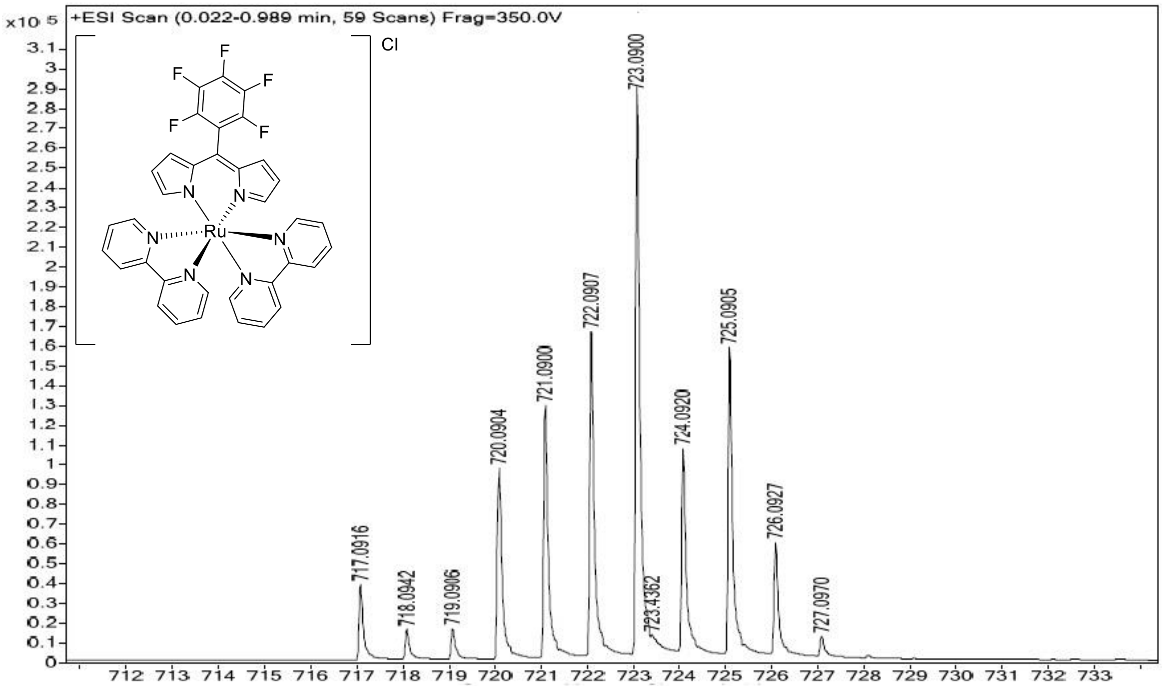
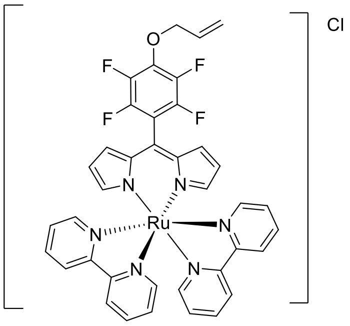


Figure S 111. HRMS (ESI-TOF) spectrum of complex 18.

[Bis(2,2´-bipyridyl(4-(prop-2-enyloxy)-2,3,5,6-tetrafluorophenyl)dipyrrinato)] ruthenium(II) chloride [19a]



According to the general procedure for the post-functionalization with alcohols, complex **18** (70 mg, 92 µmol) was dissolved in dry THF (3.0 mL), freshly powdered KOH (7 mg, 0.12 mmol, 1.3 eq.) and allylic alcohol (0.1 mL, 10 mg, 0.18 mmol, 2 eq.) were added and the mixture was stirred for 2 h at rt. The mixture was diluted with DCM and washed with water several times. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/MeOH = 85:15) and recrystallization (DCM/*n*-pentane) to obtain the product as a black solid (59 mg, 80%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (d, *J* = 6.1 Hz, 2 H, CH_2), 5.35 (dd, *J* = 10.3, 1.0 Hz, 1 H, $C{=}CH_2$), 5.44 (dd, *J* = 17.1, 1.3 Hz, 1 H, $C{=}CH_2$), 6.00-6.10 (m, 1 H, CH), 6.29 (dd, *J* = 4.4, 1.4 Hz, 2 H, $H_{pyrrole}$), 6.36-6.37 (m, 2 H, $H_{pyrrole}$), 6.57 (d, *J* = 4.3 Hz, 2 H, $H_{pyrrole}$), 7.26-7.33 (m, 4 H, H_{bipyr}), 7.67 (d, *J* = 5.5 Hz, 2 H, H_{bipyr}), 7.88-7.94 (m, 2 H, H_{bipyr}), 7.94-8.02 (m, 4 H, H_{bipyr}), 8.69-8.77 (m, 4 H, H_{bipyr}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 75.56 (CH_2), 111.87 (t, $J_{C\text{-}F}$ = 19.7 Hz, Ar-F_{para}), 119.38 ($C_{pyrrole}$), 120.32 ($C{=}CH_2$), 124.28 (C_{bipyr}), 124.32 (C_{bipyr}), 126.32 (C_{bipyr}), 126.80 (C_{bipyr}), 130.02 ($C_{pyrrole}$), 134.84 (C_{meso}), 136.05 (C_{bipyr}), 136.78 (C_{bipyr}), 137.17 (m, Ar-F_{para}), 140.95 (dd, $J_{C\text{-}F}$ = 250.0, 18.0 Hz, Ar-F_{meta}), 144.73 (d, $J_{C\text{-}F}$ = 249.0 Hz, Ar-F_{ortho}), 150.42 (C_{bipyr}), 150.60 ($C_{pyrrole}$), 157.39 (C_{bipyr}), 158.17 (C_{bipyr}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -156.10 – -155.95 (m_c, *J* = 22.6, 7.8 Hz, 2 F, Ar-F_{meta}), -141.84 – -141.72 (m_c, *J* = 23.1, 7.5 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{27}F_4N_6ORu^+$ $[M]^+$ 761.1220, found 761.1290.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 469 (4.85), 516 (4.26) nm.

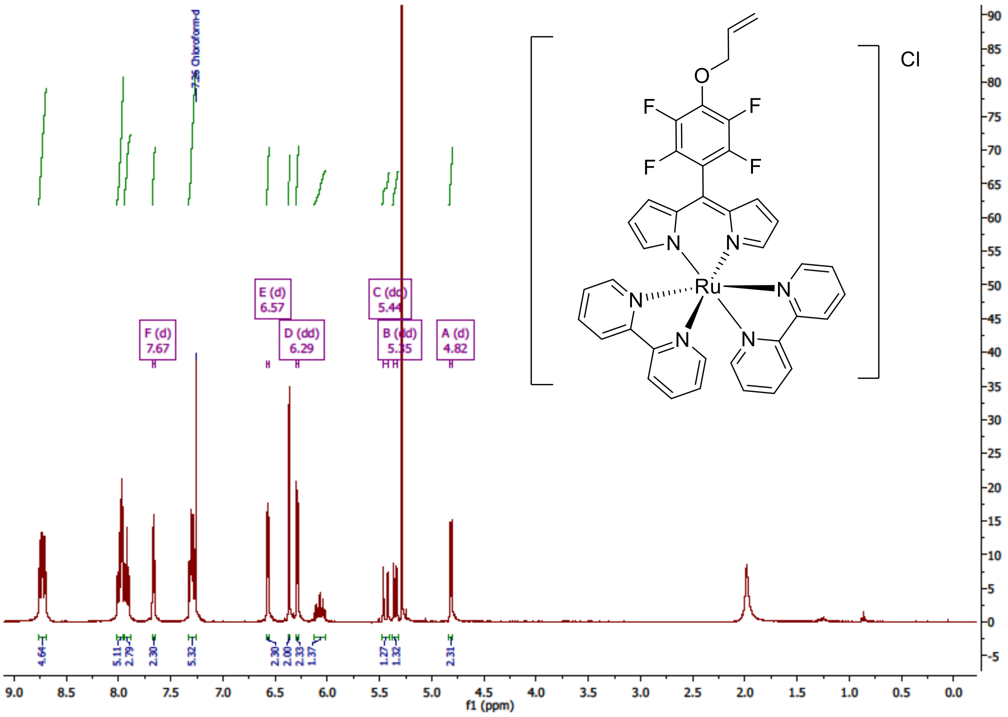


Figure S 112. ^{1}H NMR (400 MHz, CDCL$_3$) spectrum of complex 19a.

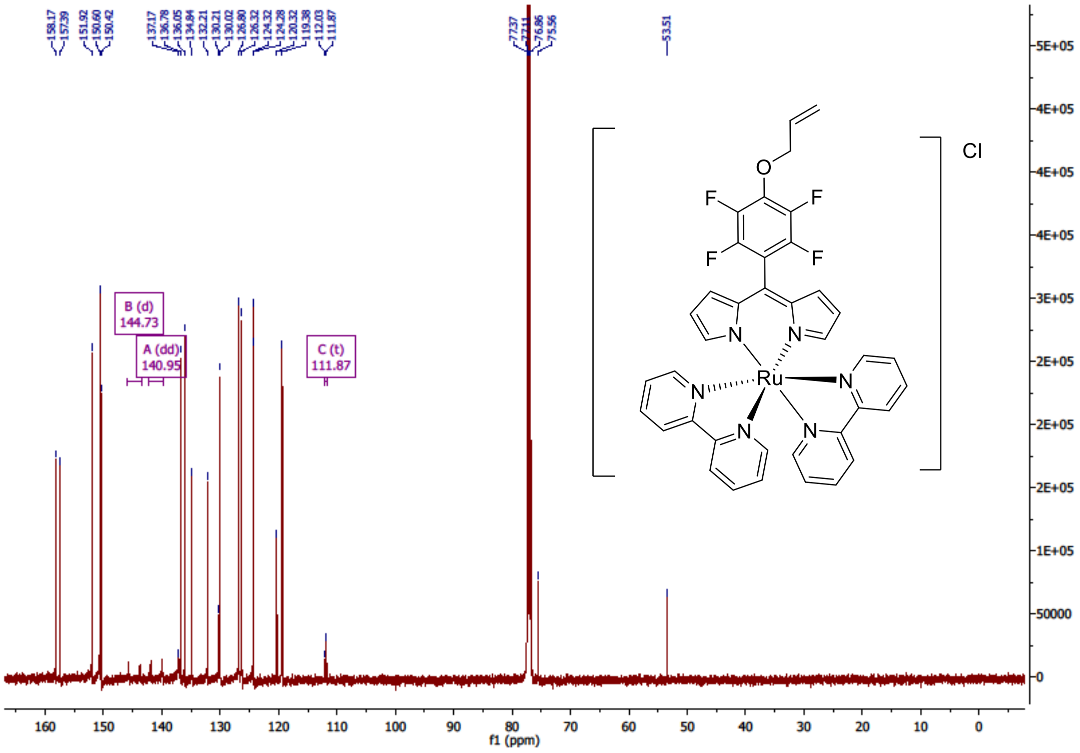


Figure S 113. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 19a.

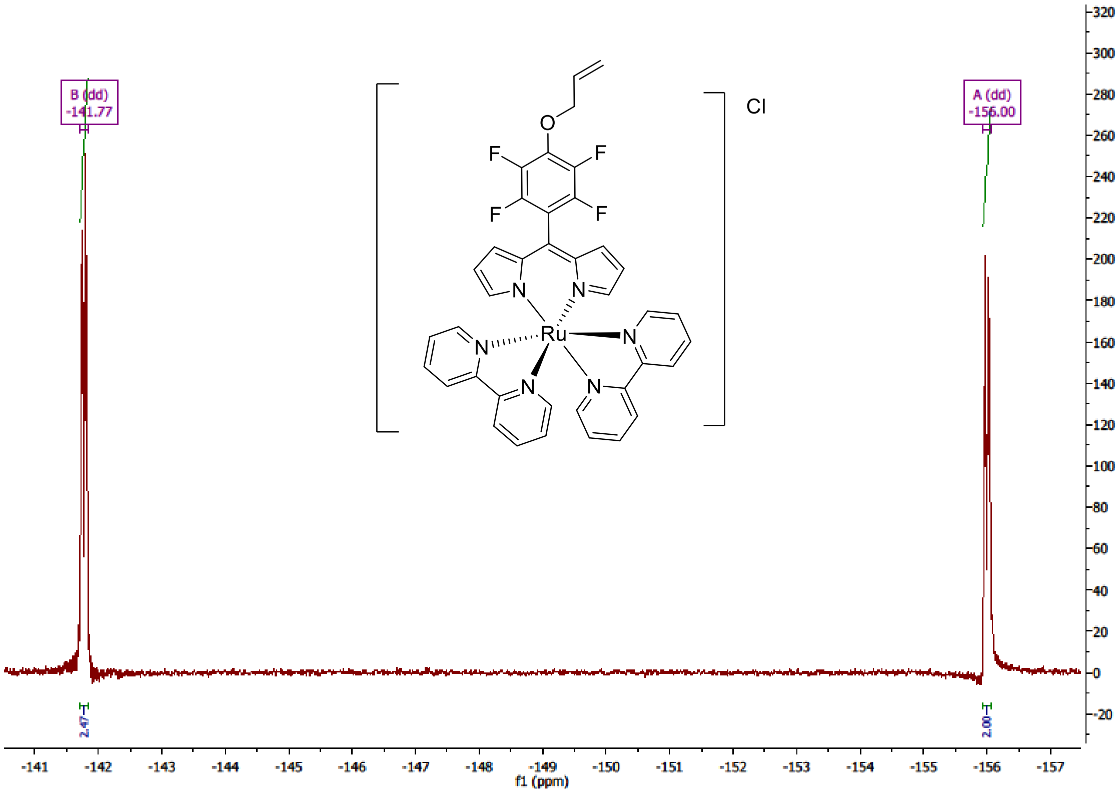


Figure S 114. ^{19}**F NMR (376 MHz, CDCL$_3$) spectrum of complex 19a.**

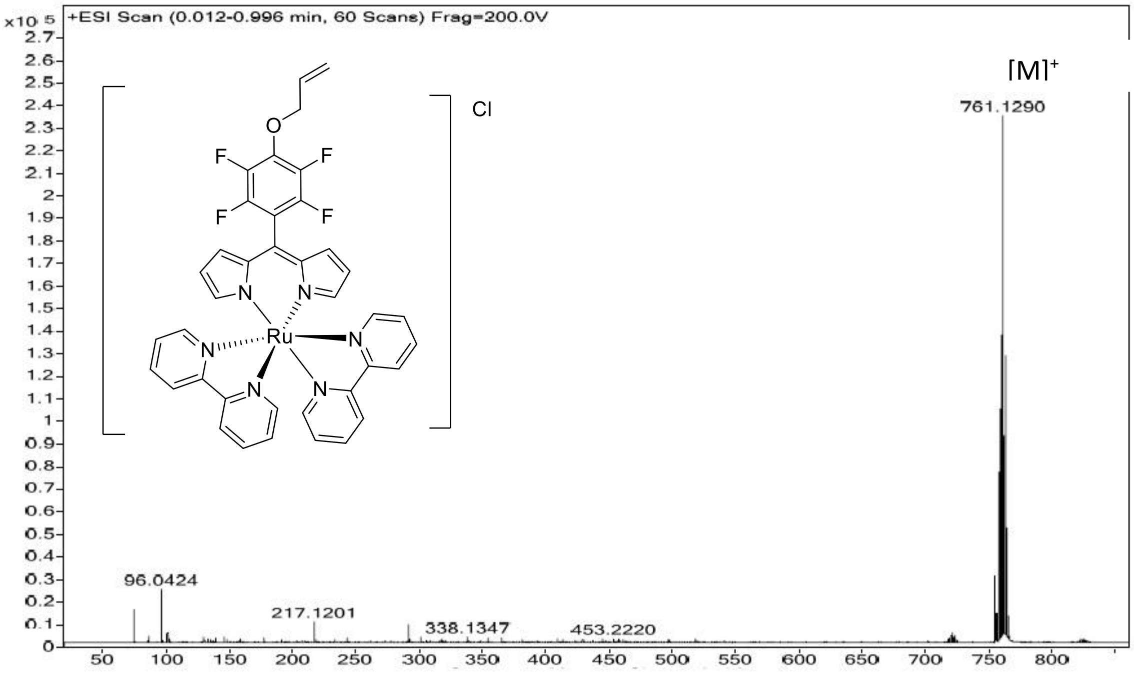


Figure S 115. HRMS (ESI-TOF) spectrum of complex 19a.

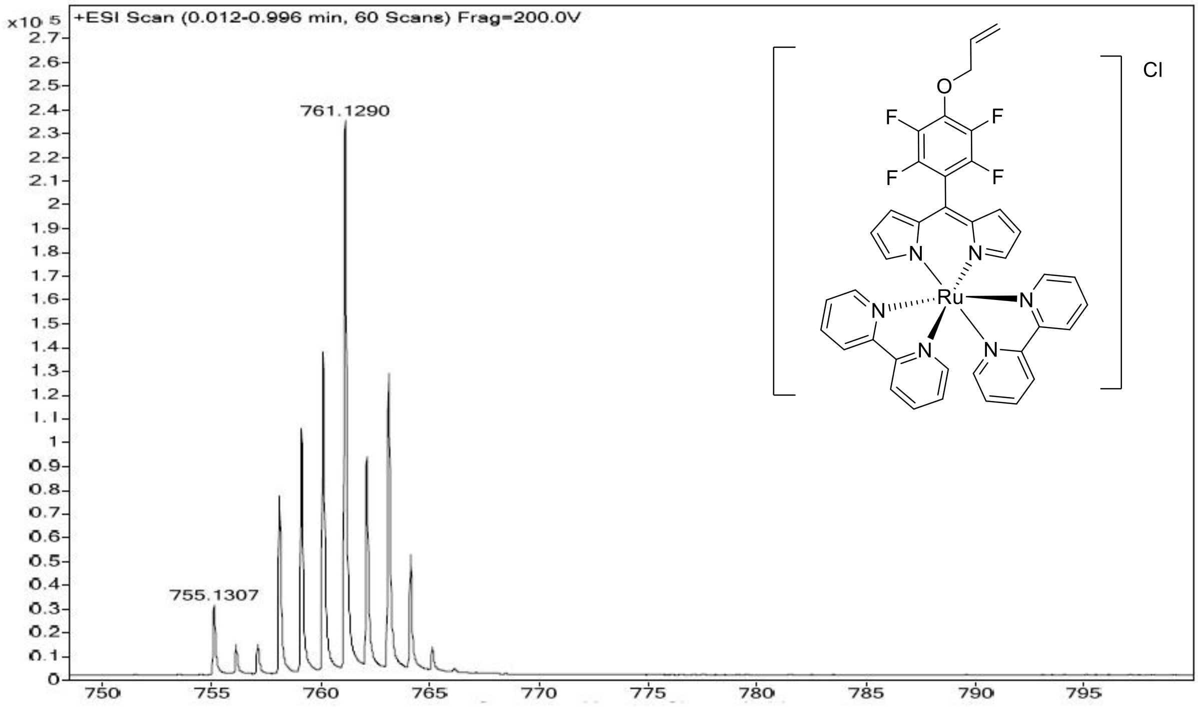
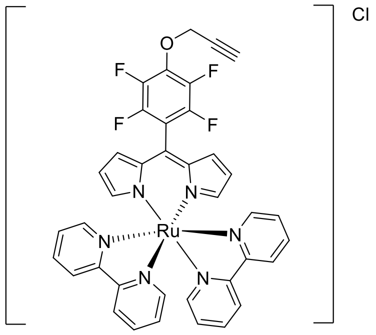


Figure S 116. HRMS (ESI-TOF) spectrum of complex 19a.

[Bis(2,2´-bipyridyl(4-(prop-2-ynyloxy)-2,3,5,6-tetrafluorophenyl)dipyrrinato)] ruthenium(II) chloride [19b]



According to the general procedure for the post-functionalization with alcohols, complex **18** (70 mg, 92 µmol) was dissolved in dry THF (3.0 mL), freshly powdered KOH (7 mg, 0.12 mmol, 1.3 eq.) and propargylic alcohol (0.1 mL, 100 mg, 0.18 mmol, 2 eq.) were added and the mixture was stirred for 5 h at rt. The mixture was diluted with DCM and washed with water several times. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. Further purification was achieved by column chromatography (silica gel, DCM/MeOH = 85:15) and recrystallization (DCM/*n*-pentane) to obtain the product as a black solid (45 mg, 62%).

Mp: >300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (t, *J* = 2.4 Hz, 1 H, CH), 4.99-5.00 (m, 2 H, CH_2), 6.30 (dd, *J* = 4.4, 1.4 Hz, 2 H, $H_{pyrrole}$), 6.37-6.39 (m, 2 H, $H_{pyrrole}$), 6.58 (d, *J* = 4.3 Hz, 2 H, $H_{pyrrole}$), 7.28-7.34 (m, 4 H, H_{bipyr}), 7.69 (d, *J* = 5.6 Hz, 2 H, H_{bipyr}), 7.88-7.95 (m, 2 H, H_{bipyr}), 7.95-8.01 (m, 4 H, H_{bipyr}), 8.62-8.69 (m, 4 H, H_{bipyr}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.32 (CH), 61.73 (CH_2), 119.38 ($C_{pyrrole}$), 124.06 (C_{bipyr}), 124.08 (C_{bipyr}), 126.25 (C_{bipyr}), 126.76 (C_{bipyr}), 129.91 ($C_{pyrrole}$), 134.67 (C_{meso}), 135.95 (C_{bipyr}), 136.67 (C_{bipyr}), 150.42 (C_{bipyr}), 150.63 ($C_{pyrrole}$), 151.88 (C_{bipr}), 157.33 (C_{bipyr}), 158.07 (C_{bipyr}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -155.21 (m_c, *J* = 22.7, 8.4 Hz, Ar-C_{meta}), -141.37 (m_c, *J* = 22.8, 8.2 Hz, Ar-C_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{26}F_4N_6ORu^{2+}$ $[M+H]^{2+}$ 760.1137, found 760.1109.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 469 (4.53), 518 (3.92) nm.

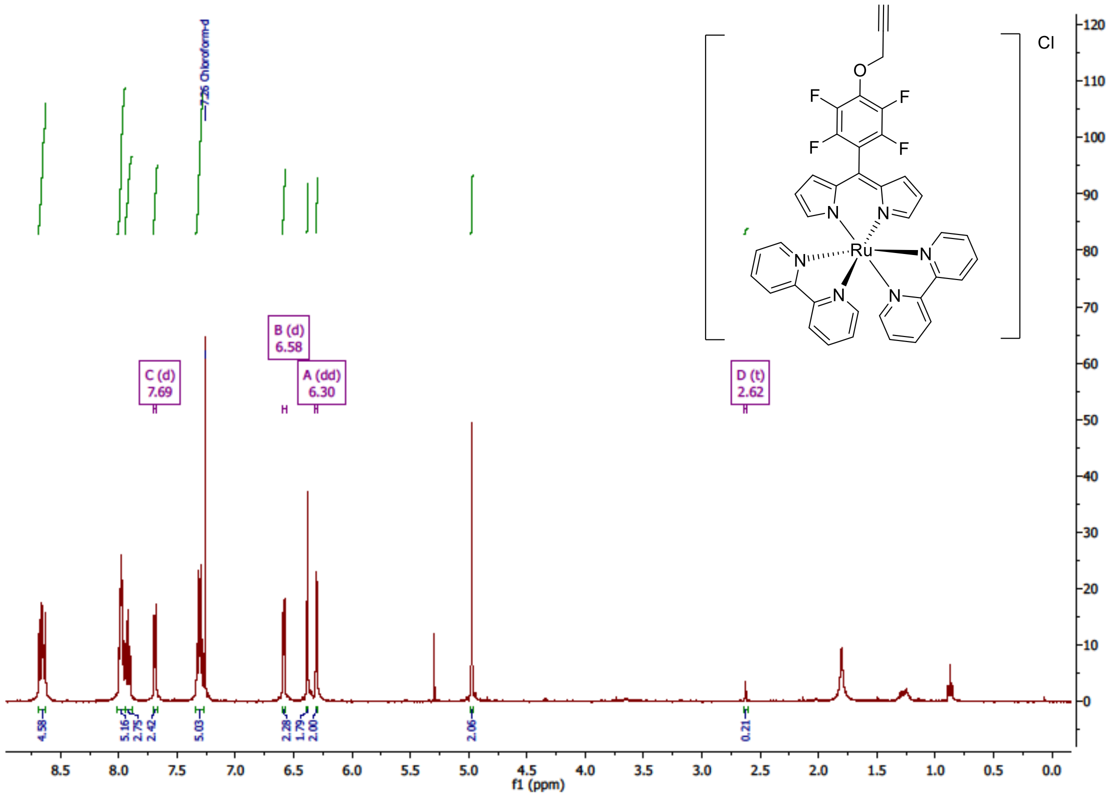


Figure S 117.^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 19b.

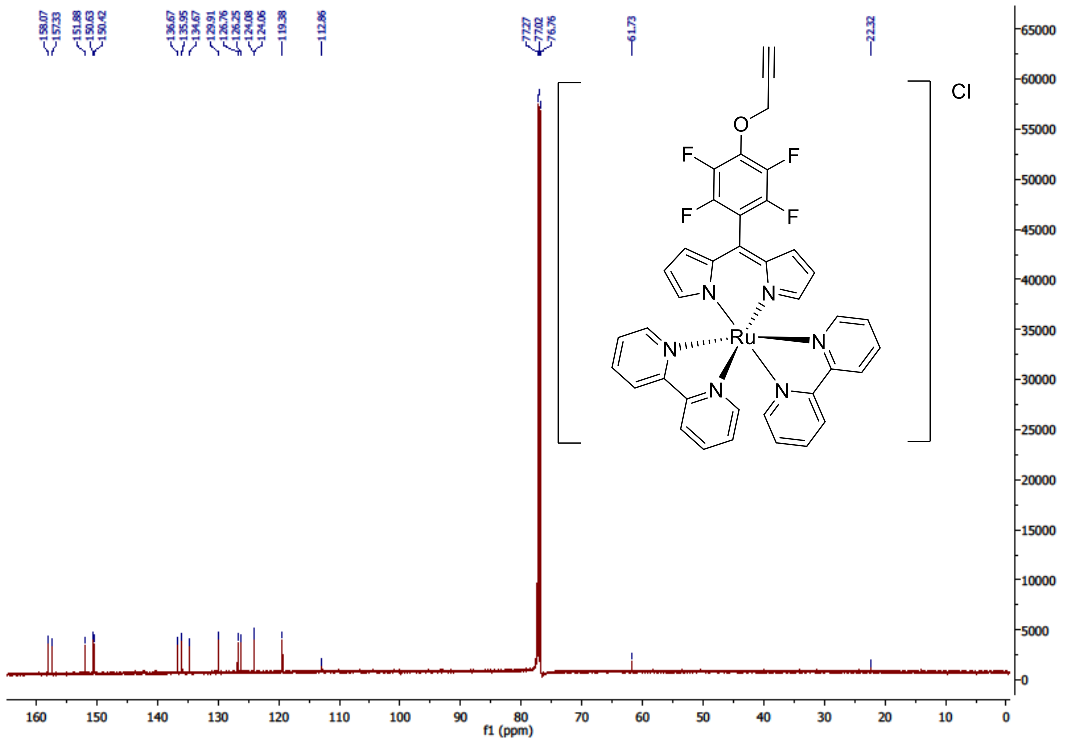


Figure S 118. ^{13}**C NMR (126 MHz, CDCl$_3$) spectrum of complex 19b.**

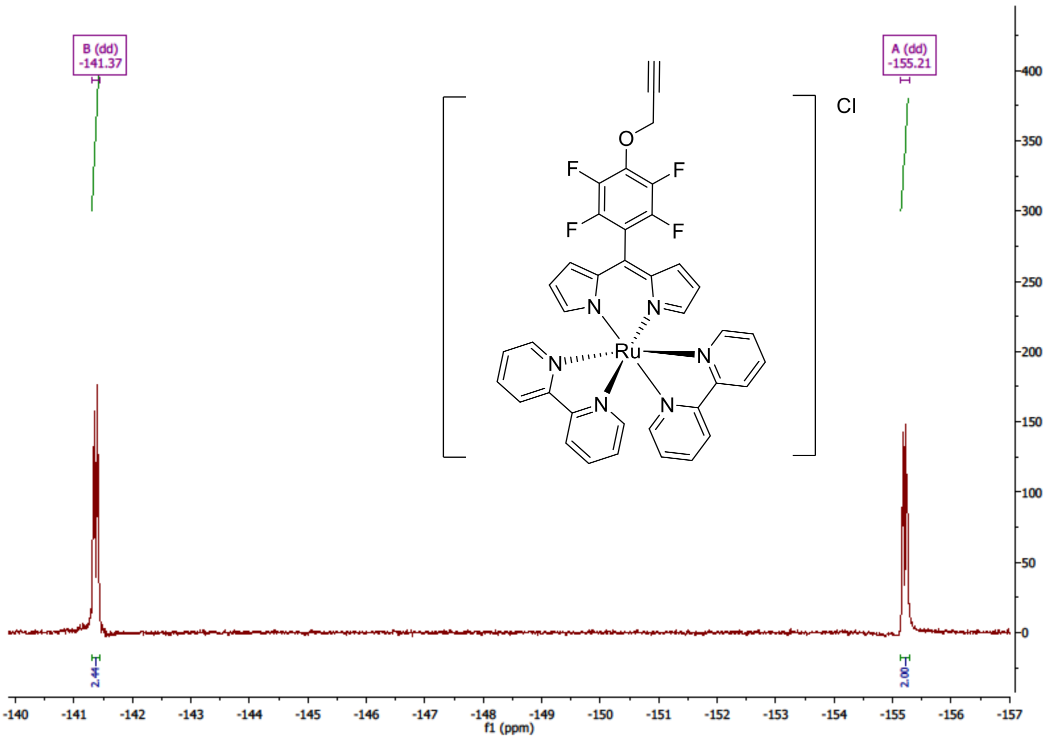


Figure S 119. ^{19} **F NMR (376 MHz, CDCl$_3$) spectrum of complex 19b.**

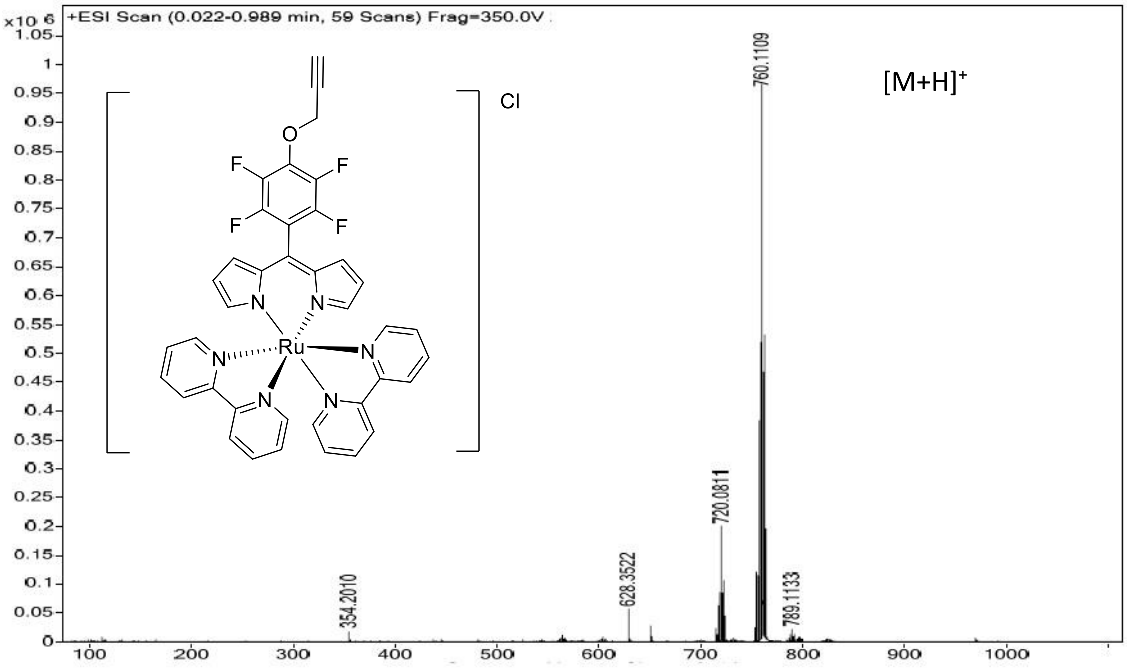


Figure S 120. HRMS (ESI-TOF) spectrum of complex 19b.

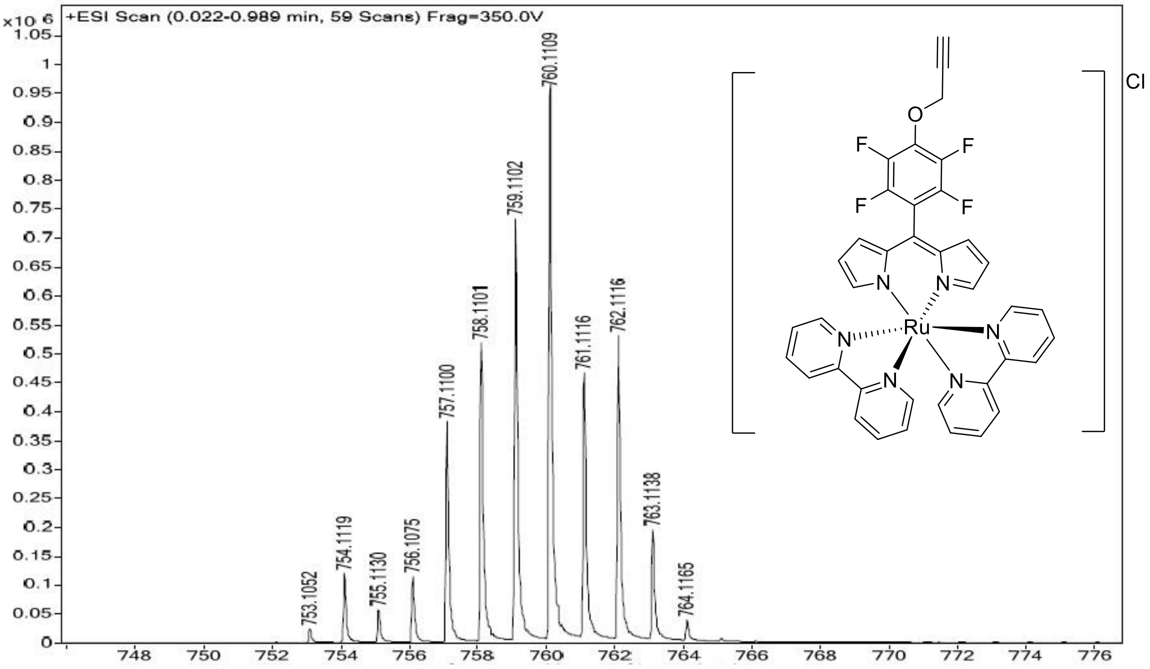
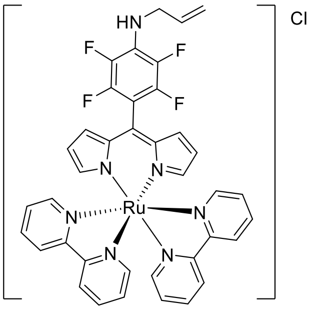


Figure S 121. HRMS (ESI-TOF) spectrum of complex 19b.

[Bis(2,2´-bipyridyl(4-(*N*-prop-2-enylamino)-2,3,5,6-tetrafluorophenyl)dipyrrinato)] ruthenium(II) chloride [20a]



According to the general procedure for the synthesis of post-functionalization with amines, complex **18** (70 mg, 90 µmol) was dissolved in DMSO (3.0 mL), allylamine (0.13 mL, 105 mg, 1.84 mmol, 20 eq.) was added and the mixture was stirred at 80 °C for 1 hour. The mixture was diluted with DCM and washed with water several times. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/MeOH = 85:15) and recrystallization (DCM/*n*-pentane) to obtain the product as black-green crystals (31 mg, 43%).

Mp: 172-175 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.04-4.16 (m, 2 H, CH$_2$), 5.21 (dd, *J* = 10.3, 0.9 Hz, 1 H, C=CH$_2$), 5.30 (dd, *J* = 17.1, 1.2 Hz, 1 H, C=CH$_2$), 5.92-6.02 (m, 1 H, CH), 6.27 (dd, *J* = 4.4, 1.2 Hz, 2 H, H$_{\text{pyrrole}}$), 6.33-6.35 (m, 2 H, H$_{\text{pyrrole}}$), 6.65 (d, *J* = 4.2 Hz, 2 H, H$_{\text{pyrrole}}$), 7.24-7.32 (m, 4 H, H$_{\text{bipyr}}$), 7.66 (d, *J* = 5.2 Hz, 2 H, H$_{\text{bipyr}}$), 7.89 (t, *J* = 7.6 Hz, 2 H, H$_{\text{bipyr}}$), 7.94-7.95 (m, 4 H, H$_{\text{bipyr}}$), 8.60-8.72 (m, 4 H, H$_{\text{bipyr}}$) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 48.16 (CH$_2$), 105.40 (t, $J_{C\text{-}F}$ = 20.0 Hz, Ar-C$_{ipso}$), 117.16 (C=*C*H$_2$), 119.07 (C$_{\text{pyrrole}}$), 124.12 (C$_{\text{bipyr}}$), 124.15 (C$_{\text{bipyr}}$), 126.30 (C$_{\text{bipyr}}$), 126.76 (C$_{\text{bipyr}}$), 128.05 (t, *J* = 11.8 Hz, Ar-C$_{para}$), 130.31 (C$_{\text{pyrrole}}$), 131.34 (C$_{\text{bipyr}}$), 135.03 (CH), 135.50 (C$_{meso}$), 135.93 (C$_{\text{bipyr}}$), 136.66 (C$_{\text{bipyr}}$), 136.95 (d, $J_{C\text{-}F}$ = 245.3 Hz, Ar-C$_{meta}$), 144.89 (d, $J_{C\text{-}F}$ = 243.5 Hz, Ar-C$_{ortho}$), 150.05 (C$_{\text{pyrrole}}$), 150.63 (C$_{\text{bipyr}}$), 151.98 (C$_{\text{bipyr}}$), 157.36 (C$_{\text{bipyr}}$), 158.17 (C$_{\text{bipyr}}$) ppm.

^{19}F NMR (376 MHz, CDCl$_3$): δ = -159.74 – -159.58 (m$_c$, *J* = 17.2 Hz, 2 F, Ar-F$_{meta}$), -143.21 – -143.00 (m$_c$, *J* = 15.6 Hz, 2 F, Ar-F$_{ortho}$) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{28}F_4N_7Ru^+$ [M]$^+$ 760.75, found 760.1416.

UV/Vis (DCM): $\lambda_{\max}$ [log ε (dm^3·mol^{-1}·cm^{-1})] = 469 (4.53), 518 (3.92) nm.

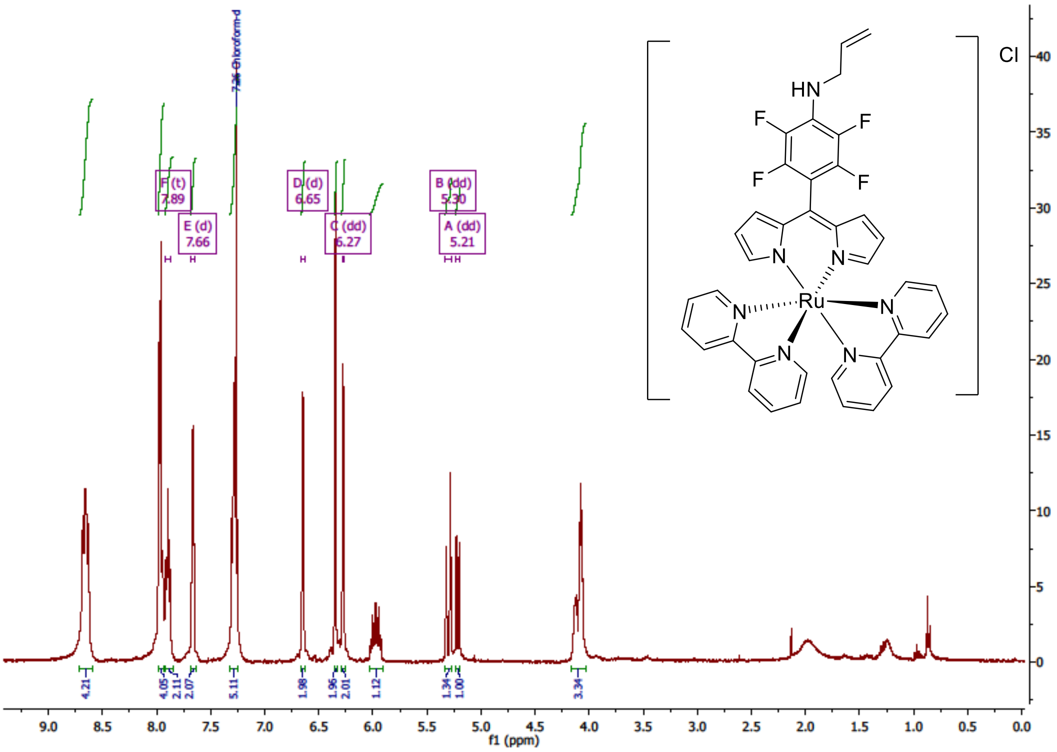


Figure S 122. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of complex 20a.**

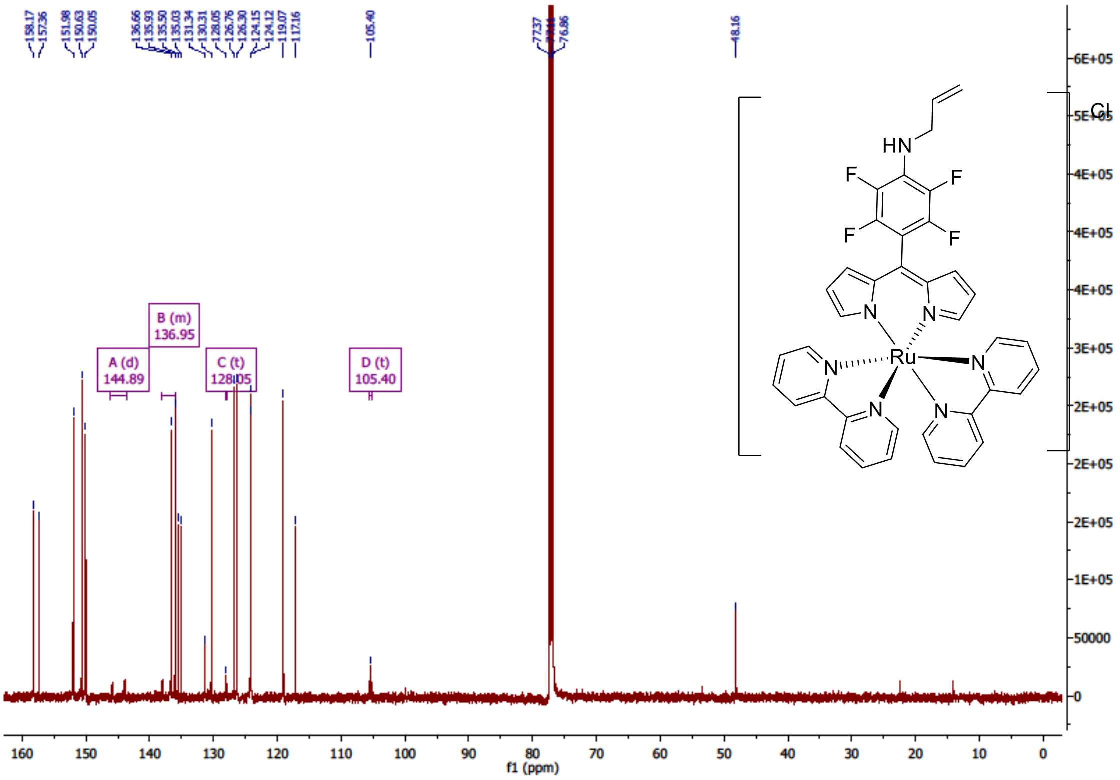


Figure S 123.^{13}**C NMR (126 MHz, CDCl$_3$) spectrum of complex 20a**.

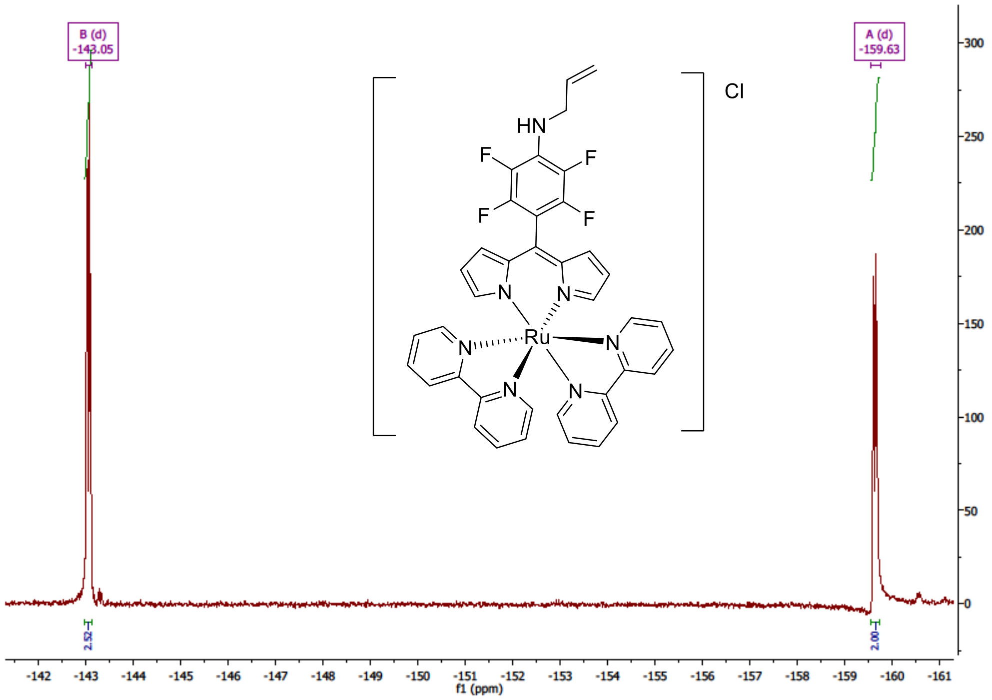


Figure S 124. ^{19}**F NMR (376 MHz, CDCl$_3$) spectrum of complex 20a.**

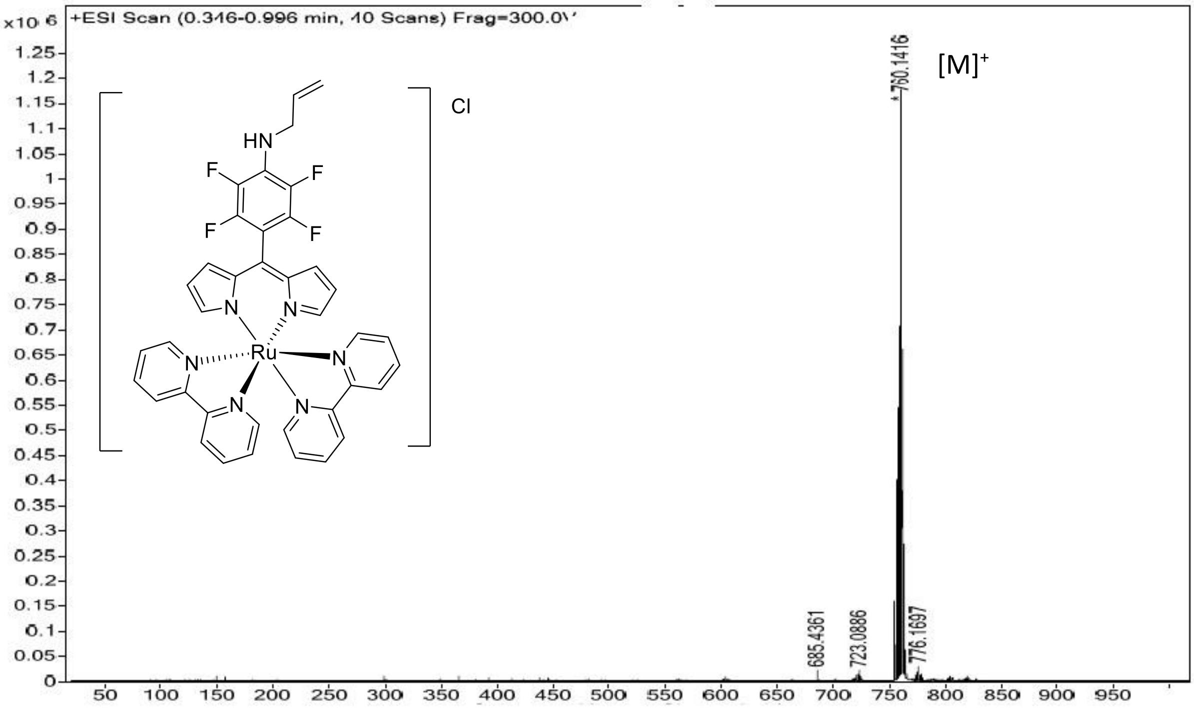


Figure S 125. HRMS (ESI-TOF) spectrum of complex 20a.

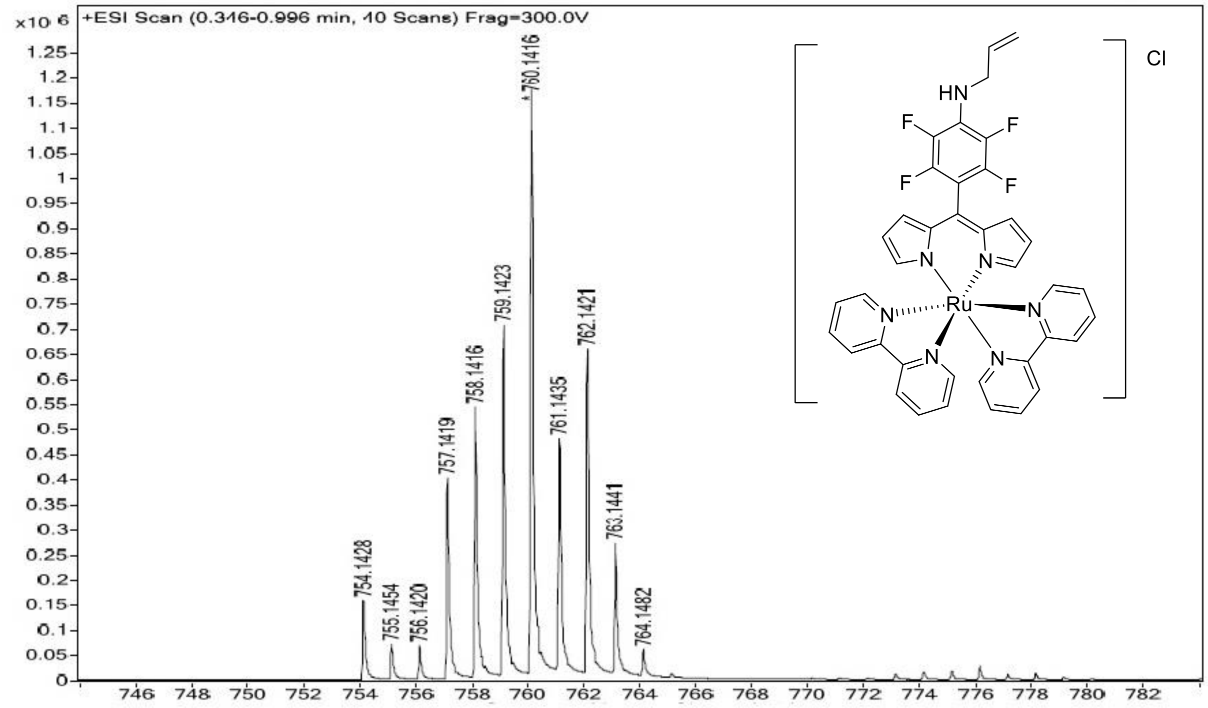
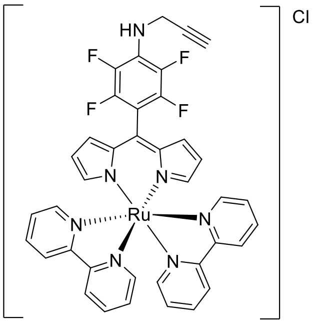


Figure S 126. HRMS (ESI-TOF) spectrum of complex 20a.

[Bis(2,2´-bipyridyl(4-(*N*-prop-2-ynylamino)-2,3,5,6-tetrafluorophenyl)dipyrrinato)] ruthenium(II) chloride [20b]



According to the general procedure for the synthesis of post-functionalization with amines, complex **18** (70 mg, 90 µmol) was dissolved in dry DMSO (3 mL), propargylamine (198 mg, 3.60 mmol, 0.23 mL, 40 eq.) was added and the mixture stirred for 7 h at 80 °C. The mixture was diluted with DCM and washed several times with water. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, DCM/MeOH = 85:15) and recrystallization (DCM/*n*-pentane) to obtain the product as black crystals (29 mg, 41%).

Mp: > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (t, *J* = 1.5 Hz, 1 H C≡CH), 4.22-4.24 (m, 2 H, CH_2), 6.29 (dd, *J* = 4.4, 1.4 Hz, 2 H, $H_{pyrrole}$), 6.36-6.38 (m, 2 H, $H_{pyrrole}$), 6.65 (d, *J* = 4.2 Hz, 2 H, $H_{pyrrole}$), 7.28-7.32 (m, 4 H, H_{bipyr}), 7.69 (d, *J* = 4.8 Hz, 2 H, H_{bipyr}), 7.90-7.95 (m, 2 H, H_{bipyr}), 7.96-8.01 (m, 4 H, H_{bipyr}), 8.63-8.70 (m, 4 H, H_{bipyr}) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 35.73 (CH_2), 72.81 (C≡*C*H), 80.07 (*C*≡CH), 119.17 ($C_{pyrrole}$), 124.17 (C_{bipyr}), 124.23 (C_{bipyr}), 126.31 (C_{bipyr}), 126.80 (C_{bipyr}), 130.27 ($C_{pyrrole}$), 131.02 (C_{bipyr}), 135.33 (C_{meso}), 135.93 (C_{bipyr}), 136.70 (C_{bipyr}), 150.17 ($C_{pyrrole}$), 150.62 (C_{bipyr}), 152.00 (C_{bipyr}), 157.39 (C_{bipyr}), 158.17 (C_{Bipyr}) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -158.50 – -158.36 (m, 2 F, Ar-F_{meta}), -142.58 – -142.46 (m, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calc. for $C_{38}H_{26}F_4N_7Ru^+[M]^+$ 758.1224, found 758.1291.

UV/Vis (DCM): λ_{max} [log ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)] = 469 (4.53), 518 (3.92) nm.

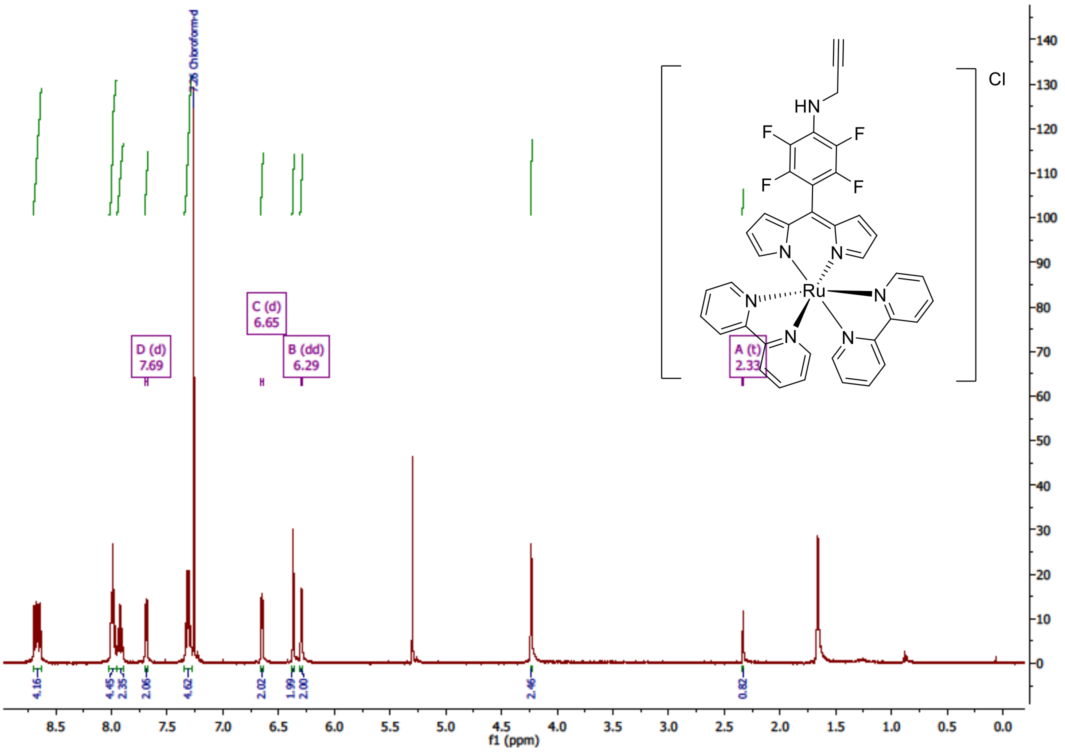


Figure S 127. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex 20b.

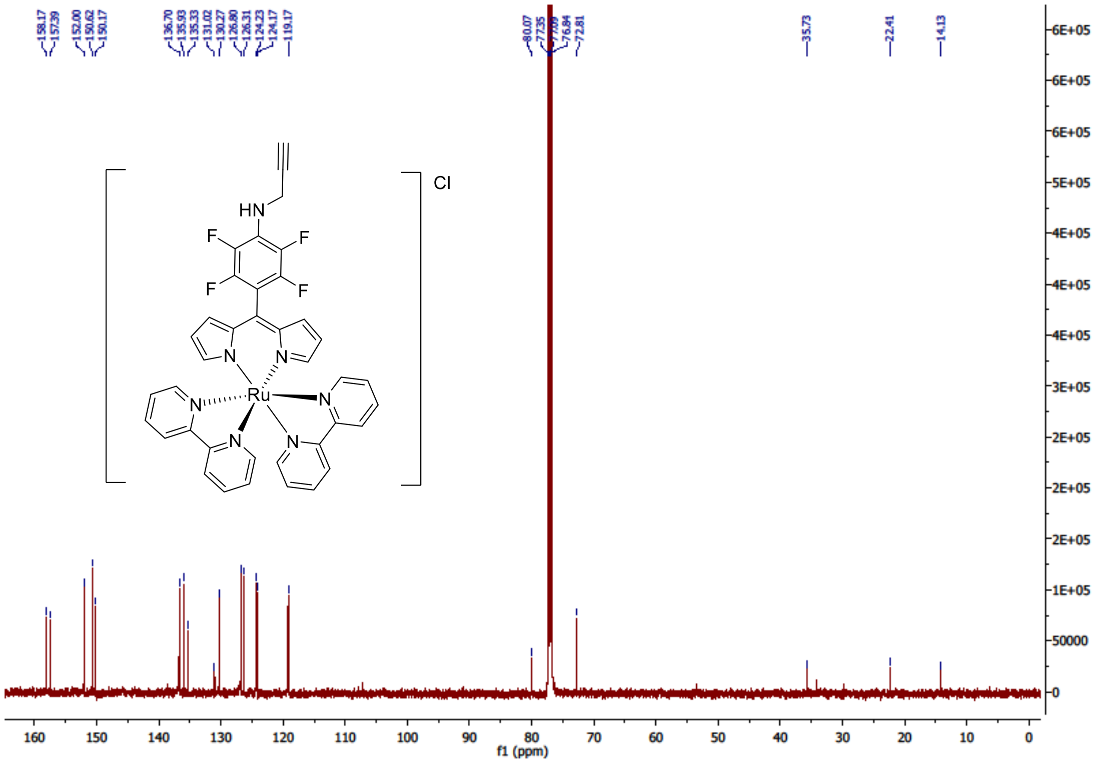


Figure S 128. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of complex 20b.

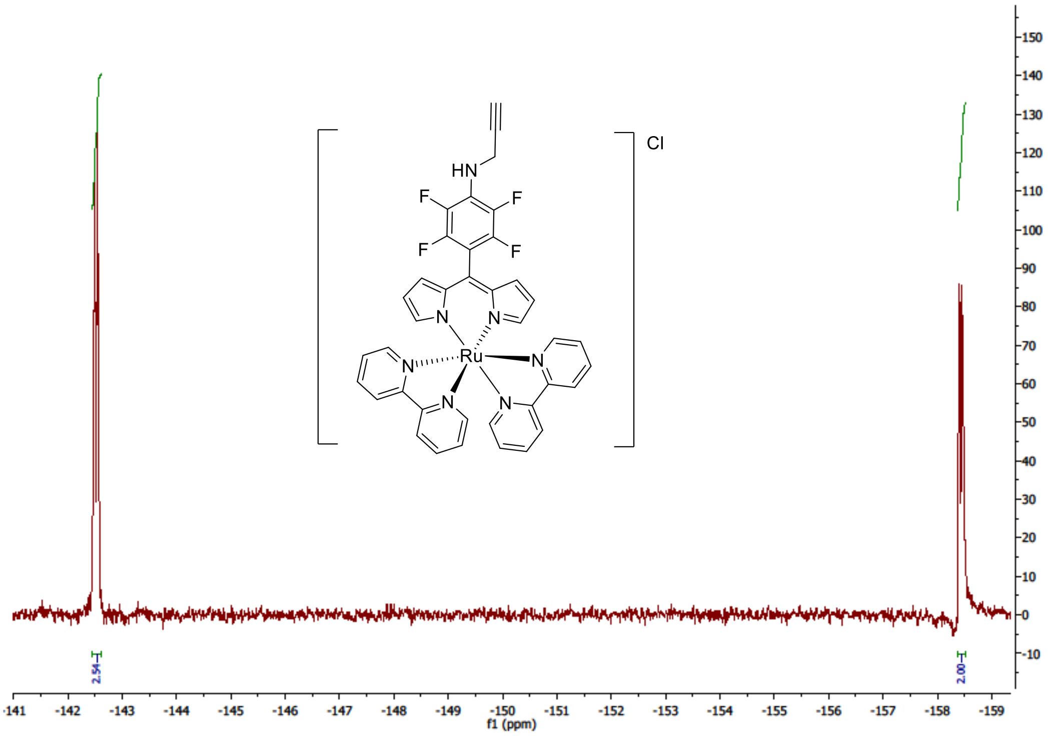


Figure S 129. ^{19}F NMR (376 MHz, CDCl$_3$) spectrum of complex 20b.

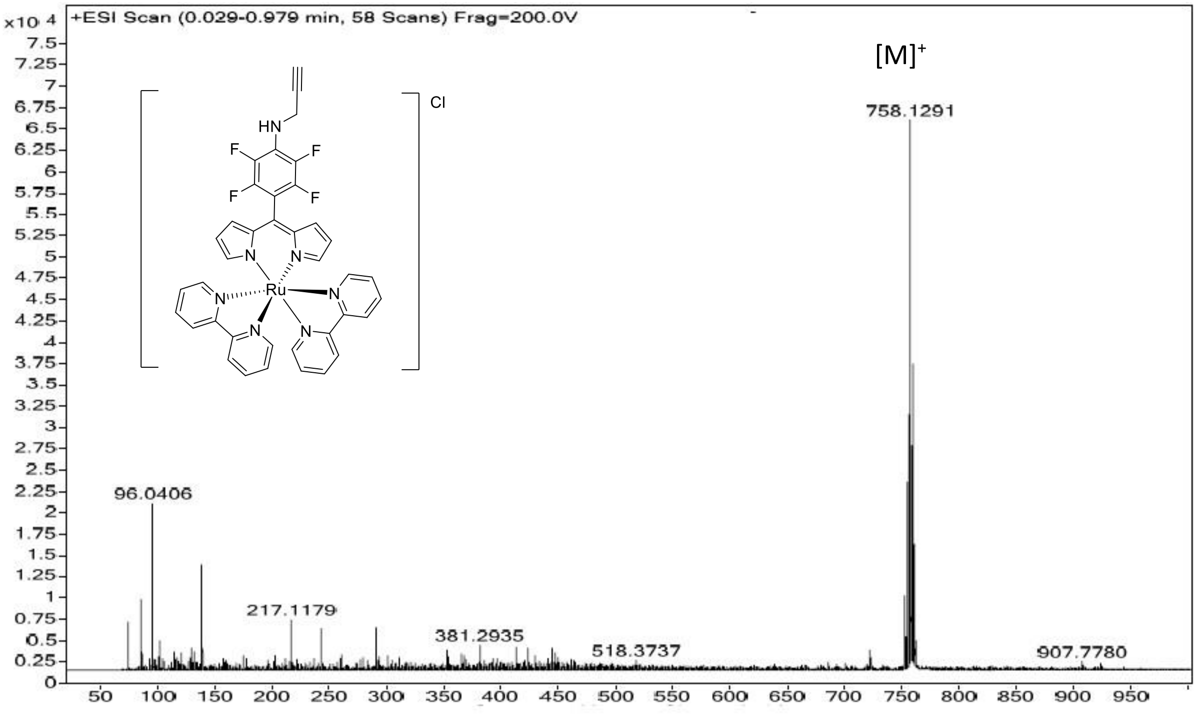


Figure S 130. HRMS (ESI-TOF) spectrum of complex 20b.

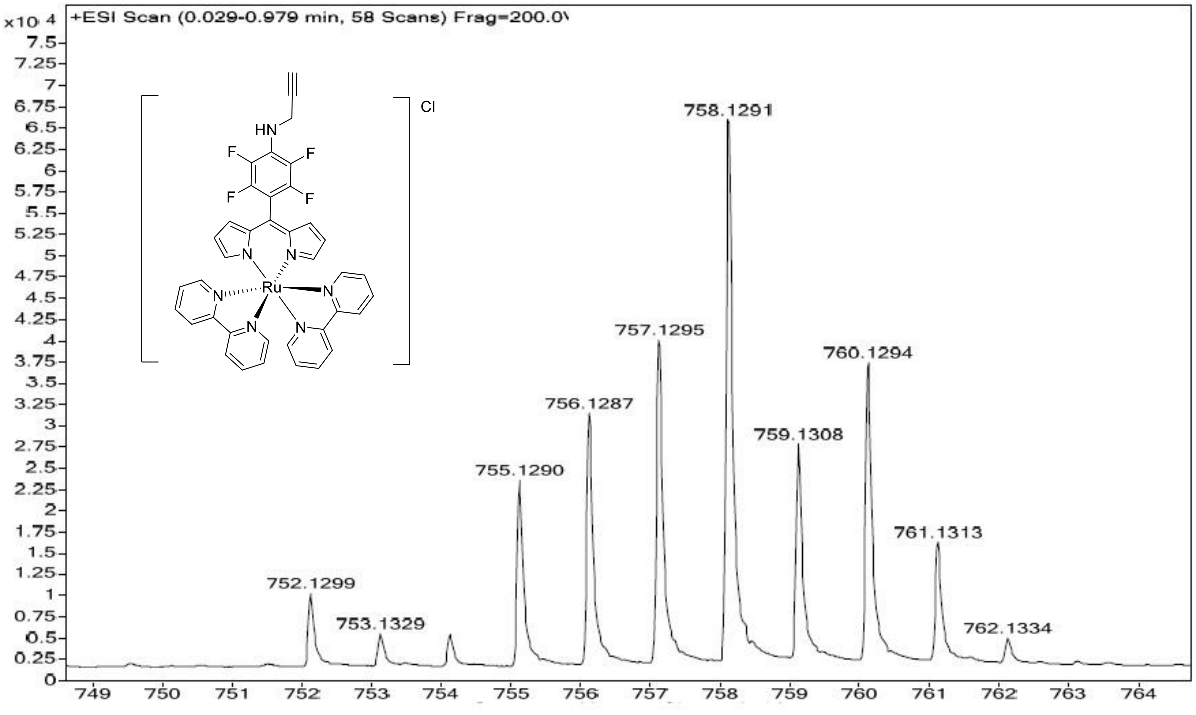
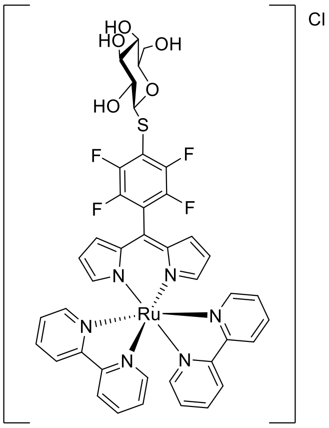


Figure S 131. HRMS (ESI-TOF) spectrum of complex 20b.

[Bis(2,2´-bipyridyl)-(1-thio-β-D-glucosyl)-2,3,5,6-tetrafluorophenyl)dipyrrinato)] ruthenium(II) chloride [21]



According to the general procedure for the glycosylation of the metal complexes, [Ru(dpm)(bipyr)$_2$] **18** (100 mg, 0.13 mmol) was dissolved in dry DMF (3 mL), 1-thio-β-D-glucose sodium salt hydrate (37 mg, 0.17 mmol, 1.3 eq.) was added and the mixture stirred for 10 min at rt. The mixture was evaporated to dryness and purified by column chromatography (DCM/MeOH = 85:15), evaporated to dryness and washed with pentane and dried *in vacuo* to obtain the product as a black solid (60 mg, 50%).

Mp: 220-223 °C.

^{1}H NMR (400 MHz, CD$_3$OD): δ = 3.32-3.38 (m, 2 H, $CH_{glucose}$), 3.40-3.46 (m, 1 H, $CH_{glucose}$), 3.58-3.63 (m, 1 H, $CH_{glucose}$), 4.90-4.96 (m, 2 H, CH_2), 6.31 (dd, J = 4.5, 1.3 Hz, 2 H, $H_{pyrrole}$), 6.44-6.45 (m, 2 H, $H_{pyrrole}$), 6.63 (d, J = 4.4 Hz, 2 H, $H_{pyrrole}$), 7.33-7.38 (m, 4 H, H_{bipyr}), 7.83 (d, J = 5.0 Hz, 2 H, H_{bipyr}), 7.90-8.05 (m, 6 H, H_{bipyr}), 8.58 (t, J = 8.2 Hz, 4 H, H_{bipyr}) ppm.

^{13}C NMR (126 MHz, CD$_3$OD): δ = 61.46 ($C_{glucose}$), 70.16 ($C_{glucose}$), 74.44 ($C_{glucose}$), 78.25 ($C_{glucose}$), 81.13 ($C_{glucose}$), 81.15 ($C_{glucose}$), 85.50 (CH_2), 112.46 (t, $J_{C\text{-}F}$ = 20.6 Hz, Ar-C_{ipso}), 119.31 ($C_{pyrrole}$), 126.20 (C_{bipyr}), 126.62 (C_{bipyr}), 129.75 ($C_{pyrrole}$), 134.37 (C_{meso}), 135.86 (C_{bipyr}), 136.40 (C_{bipyr}), 144.39 (dd, $J_{C\text{-}F}$ = 247.3, 15.8 Hz, Ar-C_{meta}), 146.91 (dd, $J_{C\text{-}F}$ = 247.0, 15.6 Hz, Ar-C_{ortho}), 150.44 ($C_{pyrrole}$), 150.94 (C_{bipyr}), 151.87 (C_{bipyr}), 157.54 (C_{bipyr}), 158.33 (C_{bipyr}) ppm.

^{19}F NMR (376 MHz, CD$_3$OD): δ = -142.96 (m_c, J = 24.3, 11.3 Hz, 2 F, Ar-F_{meta}), -134.40 – -134.22 (m, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calc. for $C_{41}H_{33}F_4N_6O_5RuS^+$ $[M]^+$ 899.1213, found 899.1230.

UV/Vis (DCM): λ_{max} [log ε (dm^3·mol^{-1}·cm^{-1})] = 440 (4.56), 468 (4.90) nm.

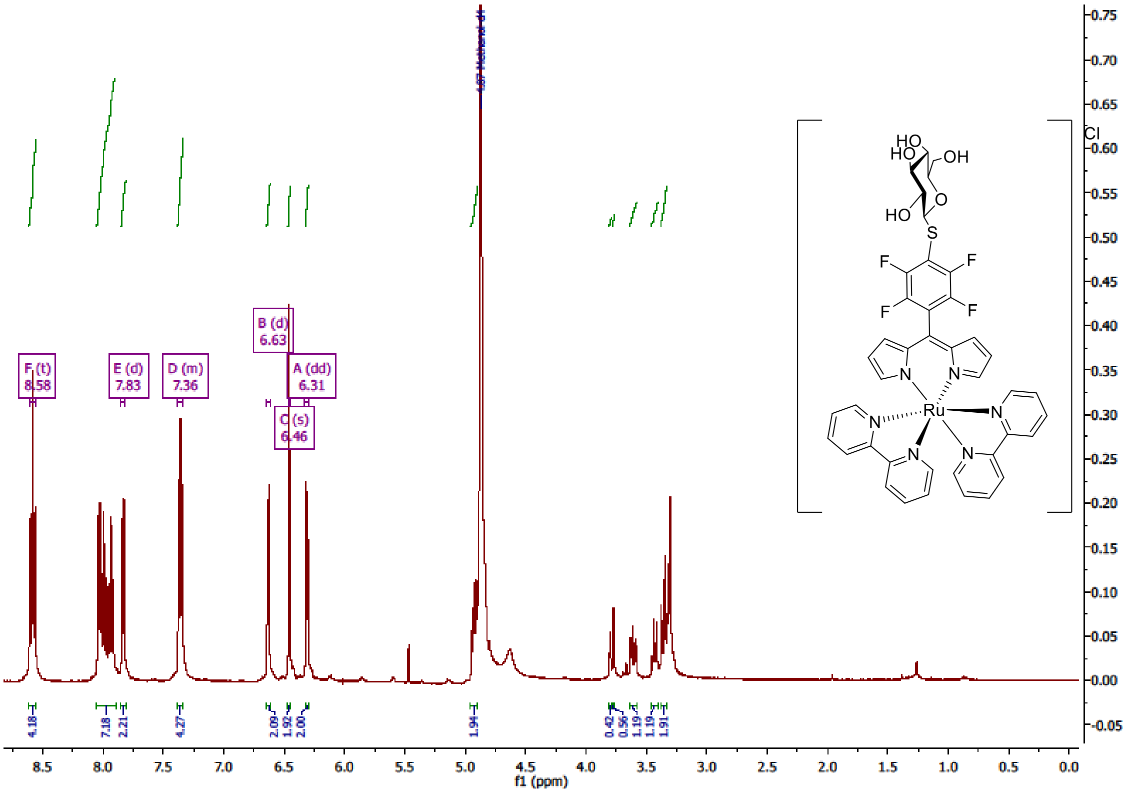


Figure S 132. ^{1}H NMR (400 MHz, CD$_3$OD) spectrum of complex 21.

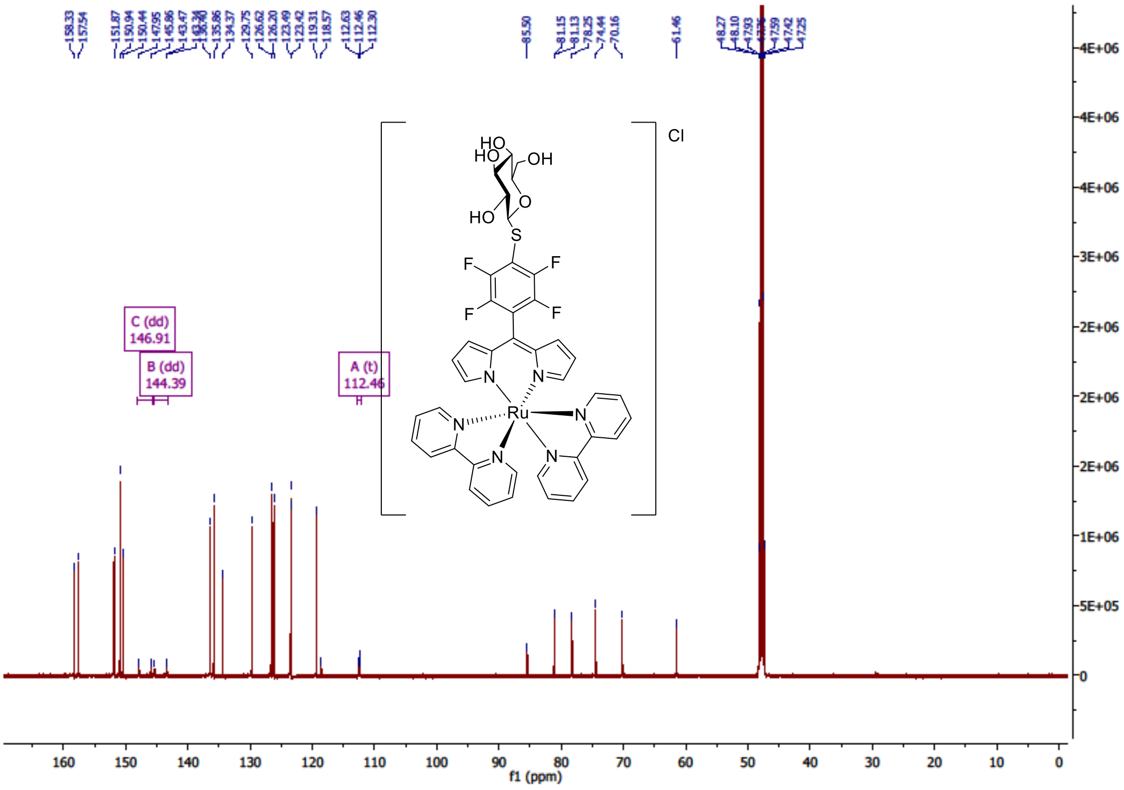


Figure S 133. ^{13}C NMR (126 MHz, CD$_3$OD) spectrum of complex 21.

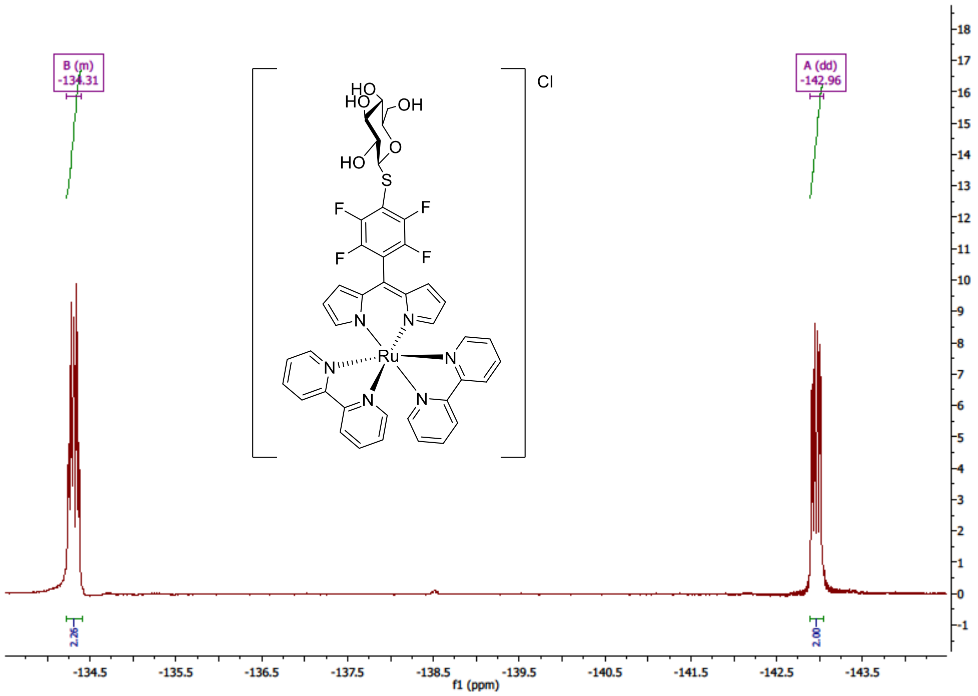


Figure S 134. ^{19}F **NMR (376 MHz,** CD_3OD**) spectrum of complex 21.**

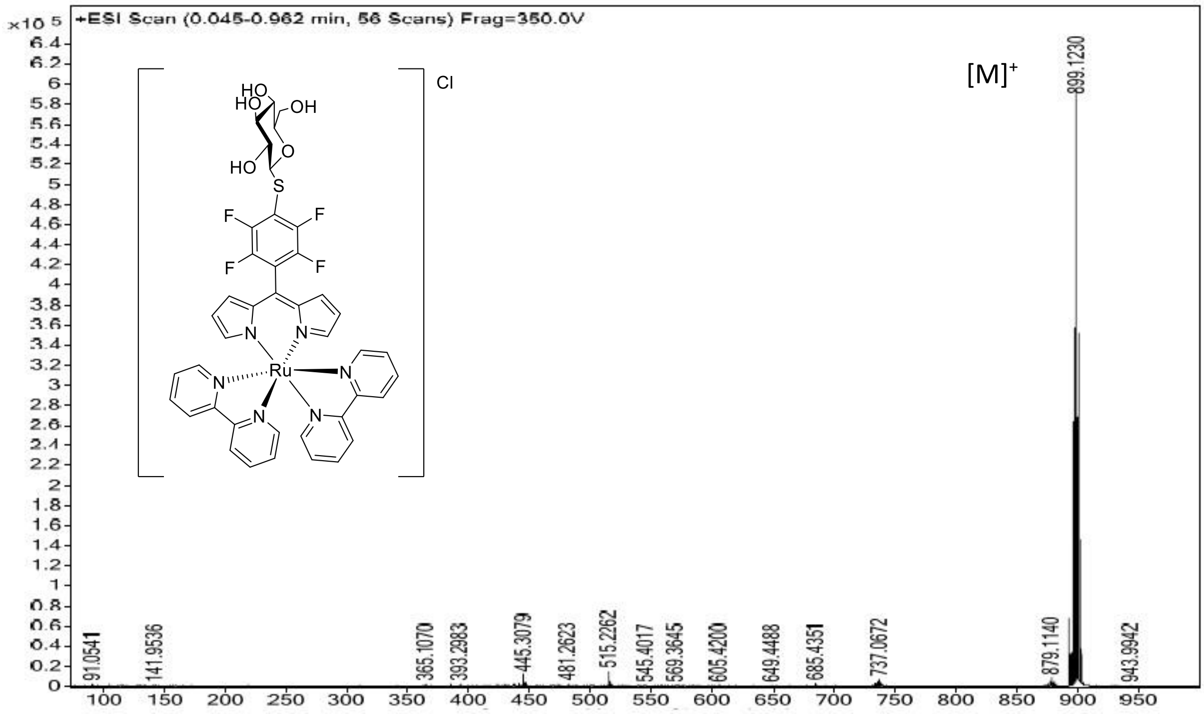


Figure S 135. HRMS (ESI-TOF) spectrum of complex 21.

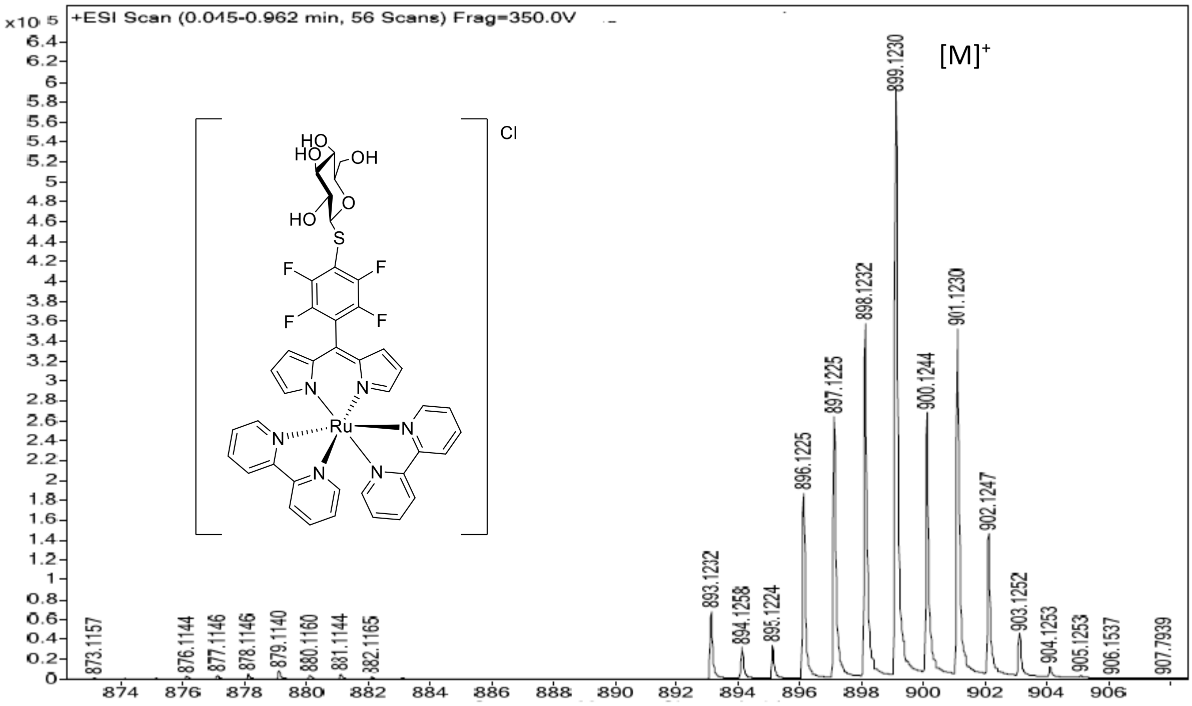


Figure S 136. HRMS (ESI-TOF) spectrum of complex 21.

P values for the cell testing experiments.

The results for untreated cells compared to those treated with the metal complexes, as well as those treated with light only compared to those treated with light and metal complexes have been analysed. A correction according to Bonferroni has been performed;[6] given are the adjusted p values ($p^*_i = p_i \times n$, $n = 4$). P values for the toxicities/phototoxicities lower than $p < 0.005$ are marked with an asterisk in the diagrams (Figures 12 and 13).

Compound 14a:

Cell line	p values (for toxicity/phototoxicity and substance concentration)			
	2 µM	10 µM	2 µM	10 µM
	Toxicity		Phototoxicity (Toxicity. with light)	
L929	8,31E-04	1,14E-03	4,96E-01	5,76E-01
HT29	3,03E-01	2,89E-01	1,42E+00	1,28E+00
A431	3,39E-01	5,26E-02	1,49E-01	2,01E-02
CAL27	9,36E-02	8,16E-04	2,11E-01	3,08E-01
A253	7,63E-01	1,61E-03	4,42E-01	1,61E-02

Compound 14b:

Cell line	p values (for toxicity/phototoxicity and substance concentration)			
	2 µM	10 µM	2 µM	10 µM
	Toxicity		Phototoxicity (Toxicity. with light)	
L929	8,83E-02	1,70E-01	1,09E-03	6,95E-04
HT29	1,69E-01	5,19E-02	4,18E-07	3,00E-06
A431	8,17E-01	2,40E-01	1,30E-04	5,07E-05
CAL27	9,12E-01	7,72E-01	1,92E-06	7,63E-07
A253	1,64E+00	7,38E-01	1,64E-04	4,14E-05

Compound 15a:

Cell line	p values (for toxicity/phototoxicity and substance concentration)			
	2 µM	10 µM	2 µM	10 µM
	Toxicity		Phototoxicity (Toxicity. with light)	
L929	5,40E-01	6,79E-01	5,99E-01	1,16E+00
HT29	4,78E-02	6,00E-03	1,61E-01	5,35E-03
A431	6,83E-03	6,39E-02	7,48E-01	5,45E-02
CAL27	6,55E-01	1,57E+00	1,01E+00	1,21E+00
A253	4,05E-01	6,14E-01	1,18E+00	1,78E+00

Compound 15b:

Cell line	p values (for toxicity/phototoxicity and substance concentration)			
	2 µM	10 µM	2 µM	10 µM
	Toxicity		Phototoxicity (Toxicity. with light)	
L929	3,12E-02	4,53E-03	7,46E-06	7,85E-09
HT29	7,69E-01	1,04E+00	1,51E-02	4,18E-03
A431	3,51E-01	5,14E-02	9,87E-07	7,43E-05
CAL27	2,47E-01	8,56E-02	4,74E-05	4,21E-05
A253	9,29E-03	9,46E-02	4,32E-07	2,98E-05

Compound 5b:

Cell line	p values (for toxicity/phototoxicity and substance concentration)			
	2 µM	10 µM	2 µM	10 µM
	Toxicity		Phototoxicity (Toxicity. with light)	
L929	4,84E-02	3,54E-03	3,25E-01	7,21E-02
HT29	4,64E-02	1,16E-01	1,37E+00	7,56E-02
A431	1,79E+00	7,59E-01	1,89E+00	1,28E+00
CAL27	4,86E-02	3,23E-02	1,72E-01	3,26E-01
A253	4,21E-01	8,58E-01	2,64E-02	1,82E-02

References

1 L. Yu, K. Muthukumaran, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, P. D. Boyle, D. F. Bocian, D. Holten and J. S. Lindsey, *Inorg. Chem.*, 2003, **42**, 6629–6647.

2 C. S. Gutsche, M. Ortwerth, S. Gräfe, K. J. Flanagan, M. O. Senge, H.-U. Reissig, N. Kulak and A. Wiehe, *Chem. Eur. J.*, 2016, **22**, 13953–13964.

3 H. R. A. Golf, H.-U. Reissig and A. Wiehe, *Org. Lett.*, 2015, **17**, 982−985.

4 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233–241.

5 G. Li, A.Yella, D. G. Brown, S. I Gorelsky, M. K. Nazeeruddin, M. Grätzel, C. P. Berlinguette and M.Shatruk, *Inorg. Chem,.* **2014**, *53*, 5417-5419.

6 K. Lesack and C. Naugler, *J. Pathol. Informatics*, **2011**, 2, 52.