True Blue: Blue-Emitting Al^{3+} Quinolinolate Complexes.

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Content:

1. *General*

Materials. Commercial solvents and reagents were used as received from the chemical suppliers. Reactions that required anhydrous conditions were carried out under inert atmosphere of argon in oven-dried glassware. Tetrahydrofuran (THF) was distilled from K-Na alloy under argon and dichloromethane (DCM) was distilled from CaH_2 under argon. All reactions were monitored using Whatman K6F Silica Gel 60Å analytical TLC plates by UV detection (254 and 365 nm). Silica gel (60Å, 32-63μm) was used for column chromatography.

Instrumentation. Melting points (uncorrected) were measured using Thomas Hoover capillary melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker 300 MHz spectrometer. ^{19}F NMR spectra were recorded using a Varian 400 MHz. The MALDI spectrum were recorded at a MALDTI-TOF Bruker Daltonics Omiflex using 9,10-dihydroxyanthracene as matrix assistant.

Absorption spectra were recorded using a Hitachi U-3010 double beam spectrophotometer, accurate to ± 0.3 nm. The light source consisted of Deuterium (D2) and Tungsten Iodide (50W) lamps for the ultraviolet and visible regions respectively. The concentration of the solutions was

adjusted so that the measured absorbances would range between 0.1 and 0.3 for the optical measurements.

Emission spectra were recorded using a spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). The fluorescence quantum yields of the luminophores were measured as a function of the excitation wavelength using quinine sulfate in 0.05 M H_2SO_4 as a standard (Φ_{QS}=0.546) by the method described by Crosby.[1]

2. *Theoretical calculations*

The choice of the theoretical methodology (DFT/B3LYP/6-31G*) was justified on its reliability reproducing the geometry and electronic properties of Alq_3.[2] Nevertheless, it is worthy to note that the HOMO value obtained with the best functional for Alq_3 is offset about 1eV from the ionization energies measured in condensed phase (6.35-6.65eV). In this case, large corrections must be included in order to compensate for the additional stabilization of the charged species in the solid state arising from polarization of neighboring molecules and vibronic relaxation.[3] The selection of the method was justifed by comparing our results with Wong and collaborators' report on similar systems.[4] In their work, the estimated energy levels for $2Meq_2AlOH$ were: -5.34eV and -5.52eV for HOMO and HOMO-1 orbitals; while for $2Meq_2AlOPh$ the obtained energies were: -5.29eV and -5.49eV for HOMO and HOMO-1 respectively. In order to validate our selection, we also estimated the HOMO level energy for $2Meq_2AlOH$, obtaining essentially the same results: -5.35eV (HOMO) and -5.51eV (HOMO-1). For the compound $2Meq_2AlOPh$ we obtained: -5.28eV and -5.46eV for HOMO and HOMO-1 energy levels in very good agreement with the previous study.

In general, the HOMO energy levels calculated for the compounds **1a-f** correlated with those estimated from the electrochemical measurement (see figure 1), supporting effective modification of the frontier orbital energy.

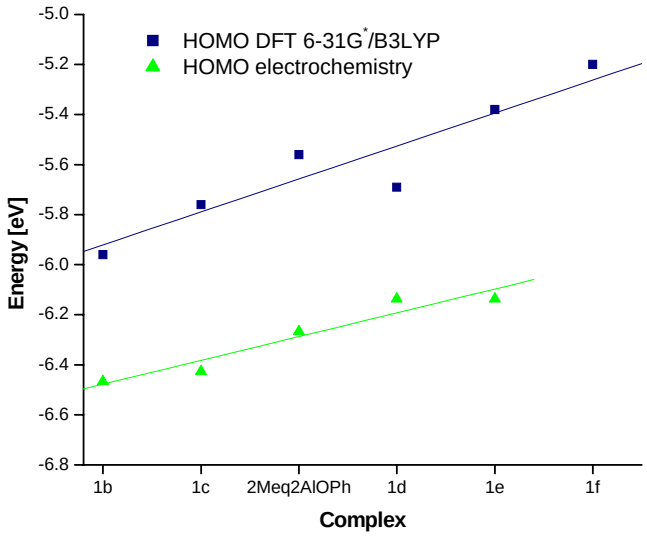

Figure S1 HOMO levels estimated from DFT calculations and HOMO values obtained from electrochemistry.

3. *Absorption and emission spectra of* 1a-f.

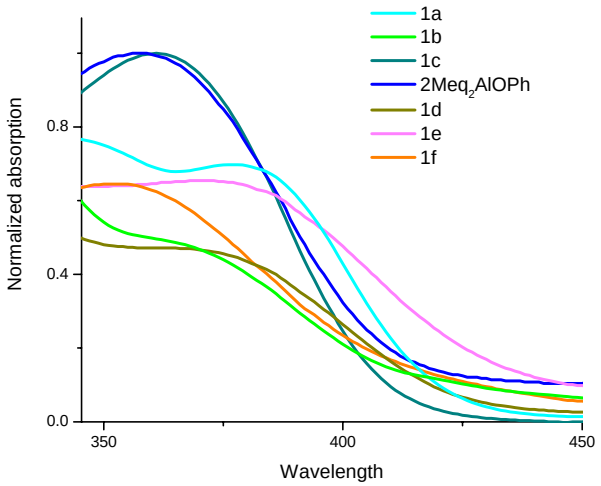

Figure S2 UV-Vis absorption spectra of complexes **1a-f** in dichloromethane.

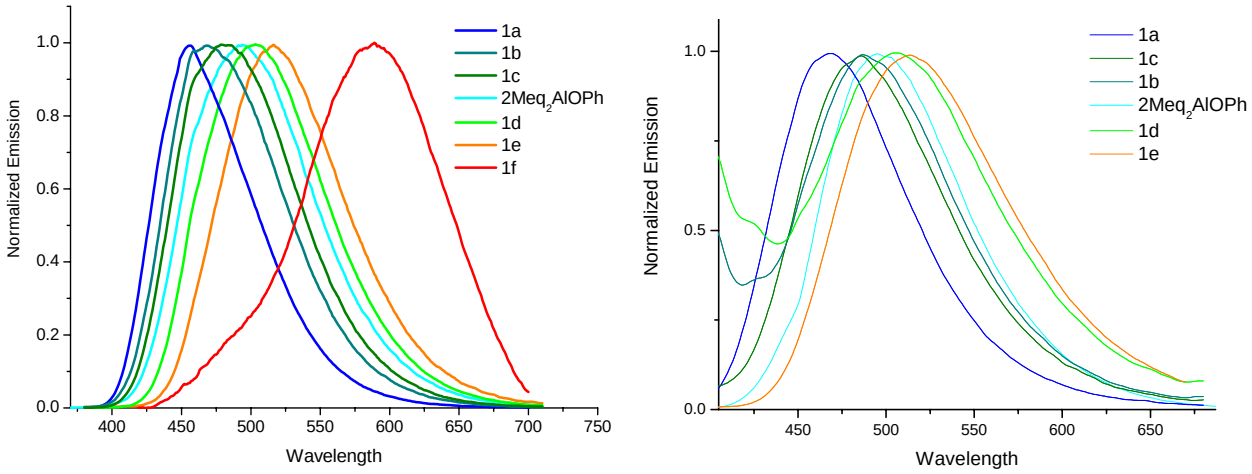

Figure S3 Left: Emission spectra of complexes **1a-f** in dichloromethane. Right: Emission spectra of complexes **1a-e** in PMMA 20% w/w in dichloromethane suspension.

4. Synthesis of quinolinolate derivatives and ligands used for preparation of 1a-f.

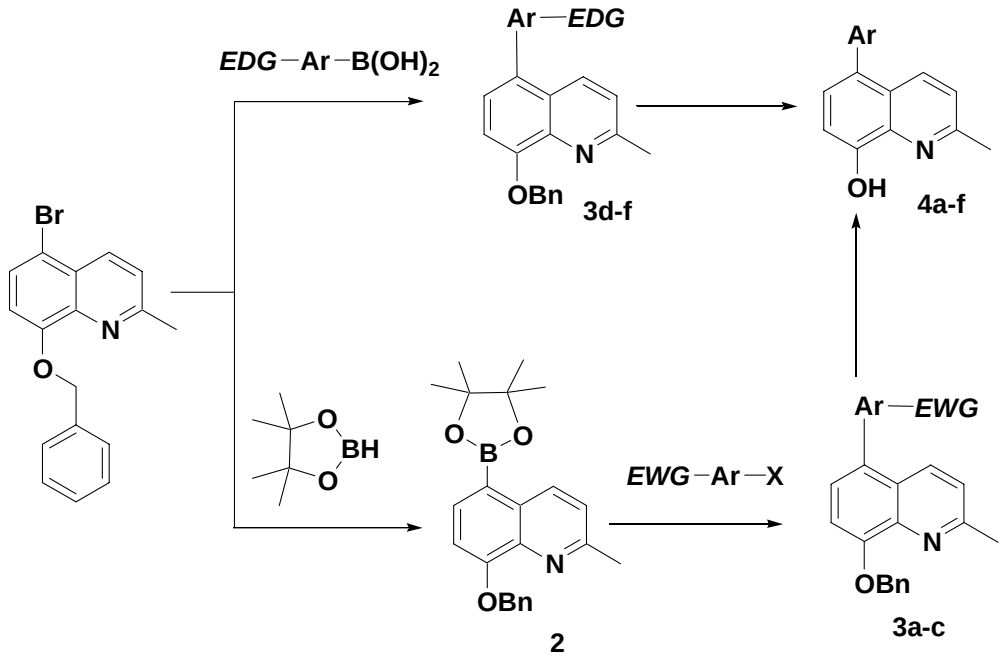

Figure S4 Synthetic scheme of quinolinolate derivatives and ligands.

Synthesis of 8-benzyloxy-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl-quinoline. (2) A solution of 8-benzyloxy-5-bromo-2-methyl-quinoline (8 g, 24.25 mmol) in THF (160 ml) was prepared. *Tetrakis*-triphenyl phosphine (800 mg, 0.69 mmol) was added under nitrogen atmosphere. The 4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (4 ml, 27.75 mmol) was added using a syringe and trimethyl amine (32 ml) was added after that. The solution was then stirred at 100 °C for 16 h. The solution was diluted with diethyl ether (250ml) and passed through a silica gel pad. The filtrate was evaporated and an orange oil was obtained. Then it was recrystallized from acetone/hexane. 7.73 g of a white solid were obtained in a 85% yield (mp 110 °C). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.37 (s, 12H); 2.80 (s, 3H); 5.48 (s, 2H); 6.98 (d, 1H, *J*= 7.8 Hz); 7.29 (t, 1H, *J*= 7.25, 4.57 Hz); 7.33 (d, 1H, *J*= 2.7 Hz); 7.35 (t, 2H, *J*= 2.7 Hz); 7.50 (d, 2H, *J*= 8.06 Hz); 7.91 (d, 1H, *J*= 7.79 Hz); 8.97 (d, 1H, *J*= 8.86 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 55.35 CH_3, 70.76 CH_2, 109.48 CH, 113.87 CH, 121.39 CH, 126.98 CH, 127.08 CH, 127.78 CH, 127.96 C, 128.62 CH, 131.13 CH, 131.79 CH, 132.22 CH, 134.34 CH, 137.08 C, 140.58 C, 149.09 CH, 153.50 C, 158.97 C. . EI/MS (DIP, 70 eV): m/z 375 (28) [M^+], 298 (33) [M-Ph^+], 269 (36) [M-$Benzaldehyde^+$], 91 (100) [$Tropylium^+$].

Synthesis of 8-benzyloxy-5-2-methyl-substituted quinoline. On the same way we have used in previous research in our group two methods were used depending on the nature of the substituents.[5]

For the electron-withdrawing groups a solution of 8-benzyloxy-2-methyl-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl-quinoline and the aromatic halide in toluene (20 ml) was prepared. The palladium catalyst (3% mol), phase transfer catalyst (10% mol), and 1 M K_2CO_3 aq (20 ml) were added after the solution was purged with argon for several minutes. The mixture was then stirred at 90 °C for 14 h. The solution was diluted with ethyl acetate (100 ml) and the organic components were extracted with toluene. The organic phase was washed with brine (50 ml) and water (100 ml). It was dried over Na_2SO_4, filtered and the filtrate was evaporated to yield an orange oil. The oil was then purified by column chromatography using acetone/hexane/DCM 2:7:1 as eluent.

8-(benzyloxy)-5-[2-(4,6-dimethoxy-1,3,5-triazinyl)]-2-methyl-quinoline (3a)

2-chloro-4,6-dimethoxy-1,3,5-triazine was used as a starting aryl halide. Mobile phase for chromatography: hexanes/acetone 7:3. Yield: 0.134 g (40%) of white solid. The analytical sample was obtained by crystallization from acetone-hexanes mixture to provide white crystals, mp 144-146 ^{o}C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.82 (s, 3H); 4.13 (s, 6H); 5.53 (m, 2H); 7.08 (d, 1H, *J* = 8.7 Hz); 7.31 (d, 1H, *J* = 7.4 Hz); 7.37 (m, 2H); 7.43 (d, 1H, *J* = 8.9 Hz); 7.52 (d, 2H, *J* = 8.1 Hz); 8.44 (d, 1H, *J* = 8.7 Hz); 9.57 (d, 1H, *J* = 8.7 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 25.58 CH_3, 55.23 CH_3, 70.83 CH_2, 109.13 CH, 123.43 CH, 123.54 CH, 124.07 C, 126.51 C, 126.85 CH, 128.66 CH, 131.42 CH, 134.77 CH, 136.57 C, 140.16 C, 157.36 C, 158.06 C, 172.43 C, 175.80 C. EI/MS (DIP, 70 eV): *m/z* 388 (54) [M^+], 311 (46) [M-Ph^+], 282 (46) [M^+-Benzaldehyde], 91 (100) [Tropylium$^+$].

8-(benzyloxy)-5-(2,3,5,6-tetrafluoro-4-pyridyl)-2-methyl-quinoline (3b)

4-bromo-2,3,5,6-tetrafluoro-pyridine was used as starting aryl halide. Mobile phase for chromatography: hexanes/ acetone 7:3. Yield: 0.332 g (80 %) of white solid. The analytical sample was obtained by crystallization from ethanol to provide white crystals, mp 168-170°C. ^{1}H NMR ($CDCl_3$),δ (ppm): 2.86 (s, 3H); 5.54 (s, 2H); 7.14 (d, 1H, *J* = 9.2 Hz); 7.33-7.46 (m, 5H); 7.56 (d, 2H, *J* = 9.4 Hz); 7.69 (d, 1H, *J* = 9.0 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 25.62 CH_3, 71.06 CH_2, 109.57 CH, 123.63 CH, 126.93 CH, 127.97 CH, 128.60 CH, 128.70 CH, 136.54 C, 156.00 C, 158.95 C. ^{19}F NMR ($CDCl_3$), δ (ppm): -91.59 (td, 2F, *J* = 12.7, 7.6, 12.7 Hz); -142.42 (td, 2F, *J* = 12.7, 7.6, 12.6 Hz). EI/MS (DIP, 70 eV): *m/z* 398 (20) [M^+], 321 (16) [M-Ph^+], 292 (26) [M^+-Benzaldehyde], 91 (100) [Tropylium$^+$].

8-(benzyloxy)-5-(2,3,4,5,6-pentafluoro)-2-methyl-quinoline (3c)

1,2,3,4,5-pentafluoro-6-iodo-benzene was used as starting aryl halide. Mobile phase for chromatography: hexanes/ acetone 7:3. Yield: 0.334 g (75 %) of white solid. The analytical sample was obtained by crystallization from hexanes/ acetone 8:2 to provide crystals, mp 138-140°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.84 (s, 3H); 5.52 (s, 2H); 7.10 (d, 1H, *J* = 8.3 Hz); 7.29-7.44 (m, 5H); 7.56 (d, 2H, *J* = 9.6 Hz); 7.66 (dt, 1H, J = 9.7 Hz). ^{13}C NMR APT ($CDCl_3$), δ (ppm): 25.66 CH_3, 70.99 CH_2, 109.74 CH, 126.88 CH, 127.85 CH, 128.66 CH, 133.02 CH, 136.82 CH, 155.27 C, 158.59 C. ^{19}F NMR ($CDCl_3$), δ (ppm): -140.35 (b, 2F); -153.14 (b, 1F); -

161.46 (b, 2F). EI/MS (DIP, 70 eV): *m/z* 415 (29) [M^+], 338 (17) [M-Ph^+], 309 (26) [M^+-Benzaldehyde], 91 (100) [$Tropylium^+$].

For the electron-donating groups, the screw cap flask was loaded with aryl boronic acids (1.0 mmol), the Pd catalyst (5% mol), KF (3.3 mmol), and $P(t\text{-}Bu)_3$ (1.2% mol) . A solution of 5-bromo-2-methyl-quinoline (0.95 mmol) in freshly distilled THF (5 ml) was prepared and the solution was purged with Ar. The solution was then stirred at 45 °C for 18 h under Ar. The reaction was diluted with diethyl ether (25 ml) and filtered through a silica gel pad. The filtrate was evaporated and a solid was obtained. The solid was recrystallized from hot ethanol and hexane.

8-(benzyloxy)-5-(4-cyanophenyl)-2-methyl-quinoline (3d)

4-cyano-phenylboronic acid was used as starting material for the cross coupling. The resulting compound was recrystallized from ethanol to give 0.469 g (yield 90%, mp 181-183 °C) of the product. ^1H NMR ($CDCl_3$), δ (ppm): 2.83 (s, 3H); 5.51 (s, 2H); 7.27 (d, 1H, *J* = 10.1 Hz); 7.28-7.41 (m, 5H); 7.50-7.57 (t, 4H, *J* = 8.1, 4.7 Hz); 7.75 (d, 2H, *J* = 9.23); 7.99 (d, 1H, *J* = 9.23 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 26.62 CH_3, 70.96 CH_2, 109.95 CH, 111.05 CH, 118.80 CH, 122.90 CH, 125.40 CH, 126.56 CH, 126.90 CH, 127.77 CH, 128.59 CH, 130.35 CH, 130.78 CH, 132.21 CH, 133.5 CH, 137.01 C, 140.22 C, 144.60 C, 154.19 C, 158.38 C. EI/MS (DIP, 70 eV): m/z 350 (30) [M^+], 273 (15) [M-Ph^+], 244 (30) [M-$Benzaldehyde^+$], 91 (100) [$Tropylium^+$].

8-(benzyloxy)-5-(phenyl)-2-methyl-quinoline (3e)

Phenyl boronic acid was used as starting material for the cross coupling. The resulting compound was recrystallized from ethanol and hexane to give 0.452 g (yield 90%, mp 153-155 °C) of the product. ^1H NMR ($CDCl_3$), δ (ppm): 2.81 (s, 3H); 5.50 (s, 2H); 7.04 (d, 1H, *J* = 8.8 Hz); 7.23-7.35 (m, 3H); 7.36-7.41 (m, 5H); 7.44-7.46 (m, 2H); 7.56 (d, 2H, *J* = 8.1 Hz); 8.08 (d, 1H, *J* = 9.4 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 25.64 CH_3, 70.8 CH_2, 110.02 CH, 122.40 CH, 126.15 CH, 126.91 CH, 127.16 CH, 127.64 CH, 128.36 CH, 128.54 CH, 130.12 CH, 134.41 CH. EI/MS (DIP, 70 eV): m/z 325 (30) [M^+], 248 (35) [M-Ph^+], 219 (38) [M-$Benzaldehyde^+$], 91 (100) [$Tropylium^+$].

8-(benzyloxy)-5-(4-dimethyl-amino-phenyl)-2-methyl-quinoline (3f)

4-dimethylamino-phenyl boronic acid was used as starting material for the cross coupling. The resulting solid was recrystallized from ethanol and hexanes to yield 0.238 g (75 %, mp 136-138 °C) of the product. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.81 (s, 3H); 3.02 (s, 6H), 5.49 (s, 2H); 6.83 (d, 2H, *J* = 8.3 Hz); 7.02 (d, 1H, *J* = 9.6 Hz); 7.22 (d, 1H, J = 10.5 Hz); 7.27-7.32 (m, 4H); 7.38 (t, 3H, *J* = 3.74, 8.6 Hz); 7.55 (d, 2H, *J* = 10.9 Hz); 8.18 (d, 1H, *J* = 11.1 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 25.59 CH_3, 40.59 CH_3, 70.97 CH_2, 110.39 CH, 112.36 CH, 122.09 CH, 125.81 CH, 126.27 CH, 126.94 CH, 127.58 CH, 127.71 CH, 128.51 CH, 130.80 CH, 132.95 C, 134.86 C, 137.52 C, 140.22 C, 149.74 C, 152.72 C, 157.66 C. EI/MS (DIP, 70 eV): m/z 368 (32) [M^+], 277 (60) [M-Ph^+], 249 (30) [M-$Benzaldehyde^+$], 91 (100) [$Tropylium^+$].

Deprotection of the benzyl derivative by catalytic transfer hydrogenation– A general method for the preparation of the ligands 4a-f:

A slightly modified published procedure of hydrogenolysis was employed.[3] To a mixture of the benzyl derivative 3a-f (1.80 mmol) and 10% Pd/C catalyst (300 mg) in degassed isopropanol (30 mL), 1,4-cyclohexadiene (0.500 mL, 5.4 mmol) was added in one portion. The mixture was heated at 110 °C for three hours in a screw-cap flask. The solution was cooled to room temperature and filtered over filter paper in order to remove the catalyst. The solvent was evaporated and the crude product was purified by recrystallization or column chromatography.

8-hydroxy-5-[2-(4,6-dimethoxy-1,3,5-triazinyl)]-2-methyl-quinoline (4a):

White solid, mp 147-149°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.74 (s, 3H); 4.14 (s, 6H); 7.21 (d, 1H, *J* = 8.6 Hz); 7.43 (d, 1H, *J* = 8.6 Hz); 8.66 (d, *J* = 8.6 Hz); 9.72 (d, *J* = 8.6 Hz). ^{13}C APT NMR ($CDCl_3$) δ (ppm): 24.64 CH_3, 55.18 CH_3, 109.08 CH, 121.99 C, 123.95 CH, 125.70 C, 132.92 CH, 135.82 CH, 137.64 C, 155.83 C, 156.77 C, 172.41 C. EI/MS (DIP, 70 eV): *m/z* 298 (100) [M^+], 283 (63) [M-CH_3^+], 226 (46).

8-hydroxy-5-(2, 3, 5, 6-tetrafluoro-4-pyridil-phenyl)-2-methyl-quinoline (4b):

White solid, mp 98-100°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.78 (s, 3H); 7.27 (d, 1H, *J* = 9.04 Hz); 7.38 (d, 1H, *J* = 8.85 Hz); 7.44 (d, 1H, *J* = 8.10 Hz); 7.73 (dt, 1H, *J* = 2.63, 2.2 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 24.90 CH_3, 109.30 CH, 123.89 C. ^{19}F NMR ($CDCl_3$), δ (ppm): -91.65

(td, 2F, ***J*** **=** 15.2, 15.2, 12.6 Hz); -142.72 (td, 2F, ***J*** **=** 15.2, 15.2, 12.6 Hz). EI/MS (DIP, 70 eV): *m/z* 308 (64) [M^+], 280 (100).

8-hydroxy-5-(2, 3, 4, 5, 6-pentafluorophenyl)-2-methyl-quinoline (4c):

Yellow solid, mp 118-120°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.76 (s, 3H); 7.21 (d, 1H, *J* = 8.10 Hz); 7.33 (d, 1H, *J* = 8.66 Hz); 7.38 (d, 1H, *J* = 7.72 Hz); 7.76 (d, 1H, *J* = 8.47 Hz). ^{13}C APT NMR ($CDCl_3$) δ (ppm): 24.61 CH_3, 109.90 CH, 122.58 CH, 123.38 CH, 130.09 CH, 134.32 CH, 150.12 C, 152.69 C,152.72 C, 157.19 C . ^{19}F NMR ($CDCl_3$), δ (ppm): -143.00 (dd, 2F, ***J*** = 10.1, 10.1 Hz); -152.72 (d, 1F, ***J*** **=** 10.1 Hz); -159.16 (dd, 2F, ***J*** **=** 10.1, 10.1 Hz). EI/MS (DIP, 70 eV): *m/z* 325 (100) [M^+], 297 (80), 207 (30).

8-hydroxy-5-(4-cyanophenyl)-2-methyl-quinoline (4d):

Yellow solid, mp 138-140°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.75 (s, 3H); 7.20 (d, 1H, *J* = 7.72 Hz); 7.31 (d, 1H, *J* = 8.66 Hz); 7.35(d, 1H, *J* = 7.91 Hz); 7.55 (dt, 2H, *J* = 1.69, 1.88 Hz); 7.77 (dt, 2H, *J* = 2.07, 1.88 Hz); 8.06 (d, 1H, *J* = 8.85 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 24.64 CH_3, 109.40 CH, 123.12 CH, 127.72 CH, 130.68 CH, 132.28 CH, 133.849 CH. EI/MS (DIP, 70 eV): *m/z* 260 (100) [M^+], 232 (30), 130 (20), 102 (19).

8-hydroxy-5-(phenyl)-2-methyl-quinoline (4e):

Yellow solid, mp 103-104°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.75 (s, 3H); 7.18 (d, 1H, *J* = 7.34 Hz); 7.28 (d, 1H, *J* = 8.47 Hz); 7.37(d, 1H, *J* = 8.10 Hz); 7.41-7.49 (m, 5H); 8.19 (d, 1H, *J* = 8.66 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 24.89 CH_3, 109.29 CH, 122.65 CH, 127.08 CH, 127.21 C, 128.42 CH,130.07 CH, 134.72 CH, 137.89 C, 139.40 C, 156.67 C. EI/MS (DIP, 70 eV): *m/z* 235 (100) [M^+], 207 (30).

8-hydroxy-5-(4-dimethyl-amino-phenyl)-2-methyl-quinoline (4f):

Orange solid, mp 160-162°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.72 (s, 3H); 3.02 (s, 6H); 6.84 (d, 2H, *J* = 9.23 Hz); 7.16 (d, 1H, *J* = 7.53 Hz); 7.27(d, 1H, *J* = 7.16 Hz); 7.32 (d, 3H, *J* = 8.30 Hz); 8.22 (d, 1H, *J* = 8.85 Hz). ^{13}C APT NMR ($CDCl_3$), δ (ppm): 24.65 CH_3, 40.62 CH_3, 122.44 CH, 122.31 CH, 126.77 CH, 130.74 CH. EI/MS (DIP, 70 eV): *m/z* 278 (100) [M^+], 263 (20), 233 (12), 204 (11), 139 (30), 117 (24).

Preparation of the Aluminum complexes. A general method for the preparation of 1a-f: Synthesis of bis-(5-substituted-2-methyl-quinolinato)(phenolato) Al $^{3+}$ complexes. A solution of the 5-substituted quinaldine ligand (0.34 mmol) and aluminum phenoxide (0.17 mmol) in ethanol (5 ml) was prepared. The solution was stirred for 4 h at 80 °C. After heating a precipitate was obtained, then filtered off and dried. All Al(III) complexes show low solubility in common solvents precluding recording ^{13}C-NMR spectra.

Bis-[2-methyl-8-quinolinolate]phenolato Aluminum (III) (H):

Yield: 0.526 g (70%) of gray solid, mp > 250 °C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.99 (s, 6H); 6.37 (d, 2H, *J* = 7.91 Hz); 6.52 (t, 1H, *J*= 6.41, 6.78 Hz); 6.84 (t, 2H, *J*= 10.55, 7.35 Hz), 7.10 (d, 2H, *J*= 7.92 Hz); 7.20 (d, 2H, *J*= 8.10 Hz); 7.34 (d, 2H, *J*= 8.29 Hz); 7.45 (t, 2H, *J*= 8.66, 6.59 Hz); 8.20 (d, 2H, *J* = 8.86 Hz). Calcd for $C_{26}H_{21}AlN_2O_3$: *m/z* 436.14. MALDI-TOF: Anal. Found *m/z* 343.15 [M-OPh^{+}]. Calcd for $C_{20}H_{15}AlN_2O_3$: *m/z* 343.10.

Bis-{5-[2-(4,6-dimethoxy-1,3,5-triazinyl)]-2-methyl-8-quinolinolate}phenolato Aluminum (III) (1a):

Yield: 0.106 g (70%) of yellow solid, mp > 250°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.73 (s, 6H); 4.14 (s, 12H); 6.77-6.95 (b, 5H); 7.21 (d, 2H, *J*= 8.47 Hz); 7.43 (d, 2H, *J*= 9.04 Hz), 8.66 (d, 2H, *J*= 8.66 Hz); 9.71 (d, 2H, *J*= 8.66 Hz). Calcd for $C_{36}H_{31}AlN_8O_7$: *m/z* 714.21. MALDI-TOF: Anal. Found *m/z* 621.72 [M-OPh^{+}]. Calcd for $C_{30}H_{26}AlN_8O_6$: *m/z* 621.18.

Bis-[5-(2,3,5,6-tetrafluoro-4-pyridyl]-2-methyl-8-quinolinolate)phenolato Aluminum (III) (1b):

Yield: 0.028g (80%), mp> 250°C, ^{1}H NMR ($CDCl_3$), δ (ppm): 2.77 (s, 6H); 6.77-6.91 (b, 5H); 7.30 (d, 2H, *J* = 9.41 Hz); 7.39 (d, 2H, *J* = 9.04 Hz); 7.45 (d, 2H, *J* = 8.28 Hz); 7.74 (d, 2H, *J* =9.04 Hz). Calcd for $C_{36}H_{19}AlF_8N_4O_3$: *m/z* 734.11. MALDI-TOF: No relevant peak observed.

Bis-[5-(2, 3, 4, 5, 6-pentafluorophenyl]-2-methyl-8-quinolinolate)phenolato Aluminum (III) (1c):

Yield: 0.042g (60%), mp > 250°C . ^{1}H NMR ($CDCl_3$), δ (ppm): unresolved. Calcd for $C_{38}H_{19}AlF_{10}N_2O_3$: *m/z* 768.11. MALDI-TOF: *m/z* 675.44 [M-OPh$^+$]. Calcd for $C_{32}H_{14}AlF_{10}N_2O_2$: *m/z* 675.07.

Bis[5-(4-cyanophenyl]-2-methyl-8-quinolinolate)phenolato Aluminum (III) (1d):

Yield: 0.034g (40%), mp > 250°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.74 (s, 6H); 6.77-6.90 (b, 5H); 7.21 (d, 2H, *J* = 7.91 Hz); 7.32 (d, 2H, *J*= 8.66 Hz); 7.36 (d, 2H, *J* = 7.72 Hz); 7.56 (d, 4H, J= 8.47 Hz); 7.77 (d, 4H, *J*= 8.28 Hz); 8.05 (d, 2H, *J*= 8.66 Hz). $C_{40}H_{27}AlN_4O_3$: *m/z* 638.19. MALDI-TOF: *m/z* 545.35 [M-OPh$^+$]. Calcd for $C_{36}H_{22}AlN_2O_2$: *m/z* 545.16.

Bis-(5-phenyl-2-methyl-8-quinolinolate)phenolato Aluminum (III) (1e):

Yield: 0.063g (90%), mp > 250°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.75 (s, 6H); 6.77-6.93 (b, 5H); 7.19 (d, 2H, *J* = 8.29 Hz); 7.28 (d, 2H, *J* = 8.85 Hz); 7.36 (d, 2H, *J*= 8.28 Hz); 7.41-7.52 (b, 10H); 8.15 (d, 2H, *J*= 8.85 Hz). $C_{38}H_{29}AlN_2O_3$: *m/z* 588.20. MALDI-TOF: *m/z* 495.31 [M-OPh$^+$]. Calcd for $C_{32}H_{24}AlN_2O_2$: *m/z* 495.16.

Bis-[5-(4-dimethylaminophenyl]-2-methyl-8-quinolinolate)phenolato Aluminum (III) (1f):

Yield: 0.054g (70%), mp > 250°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.74 (s, 6H); 3.04 (s, 12H); 6.83-6.91 (b, 5H); 7.19 (d, 2H, *J* = 8.12 Hz); 7.24 (d, 2H, *J* = 7.40 Hz); 7.31-7.37 (b, 8H); 7.43 (d, 2H, *J* = 7.49 Hz); 8.23 (d, 2H, *J* = 8.85 Hz). $C_{42}H_{39}AlN_4O_3$: *m/z* 674.28. MALDI-TOF: *m/z* 501.61 [M-OPh$^+$]. Calcd for $C_{36}H_{34}AlN_4O_2$: *m/z* 501.25.

5. [1]H NMR of the compounds

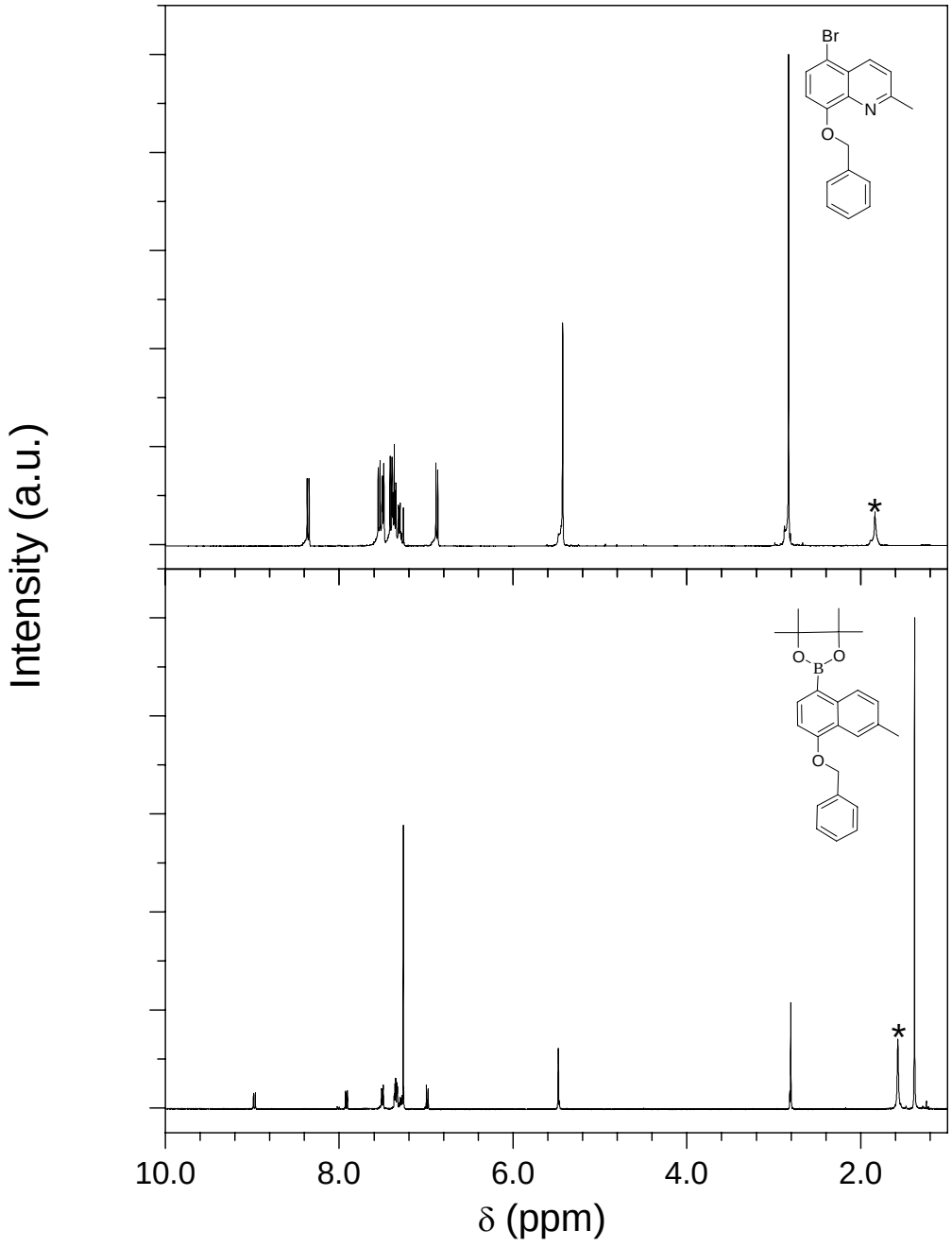

Figure S5 [1]H NMR spectrum of 8-benzyloxy-5-bromo-2-methyl-quinoline and 2 solutions in $CDCl_3$. *(water) in $CDCl_3$.[6]

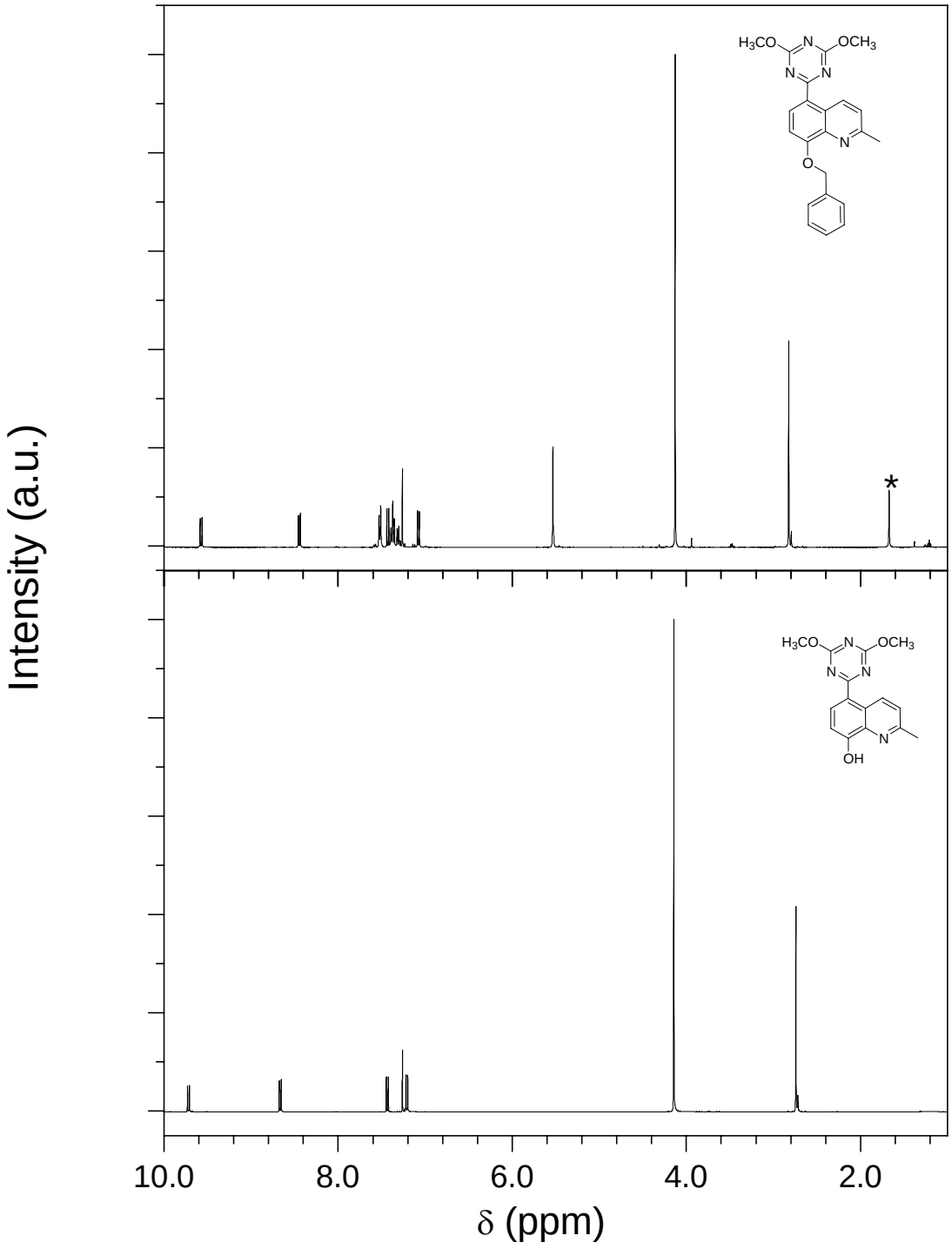

Figure S6 ^{1}H NMR spectrum of 3a (top) and 4a (bottom) solutions in $CDCl_3$. *(water) in $CDCl_3$.[6]

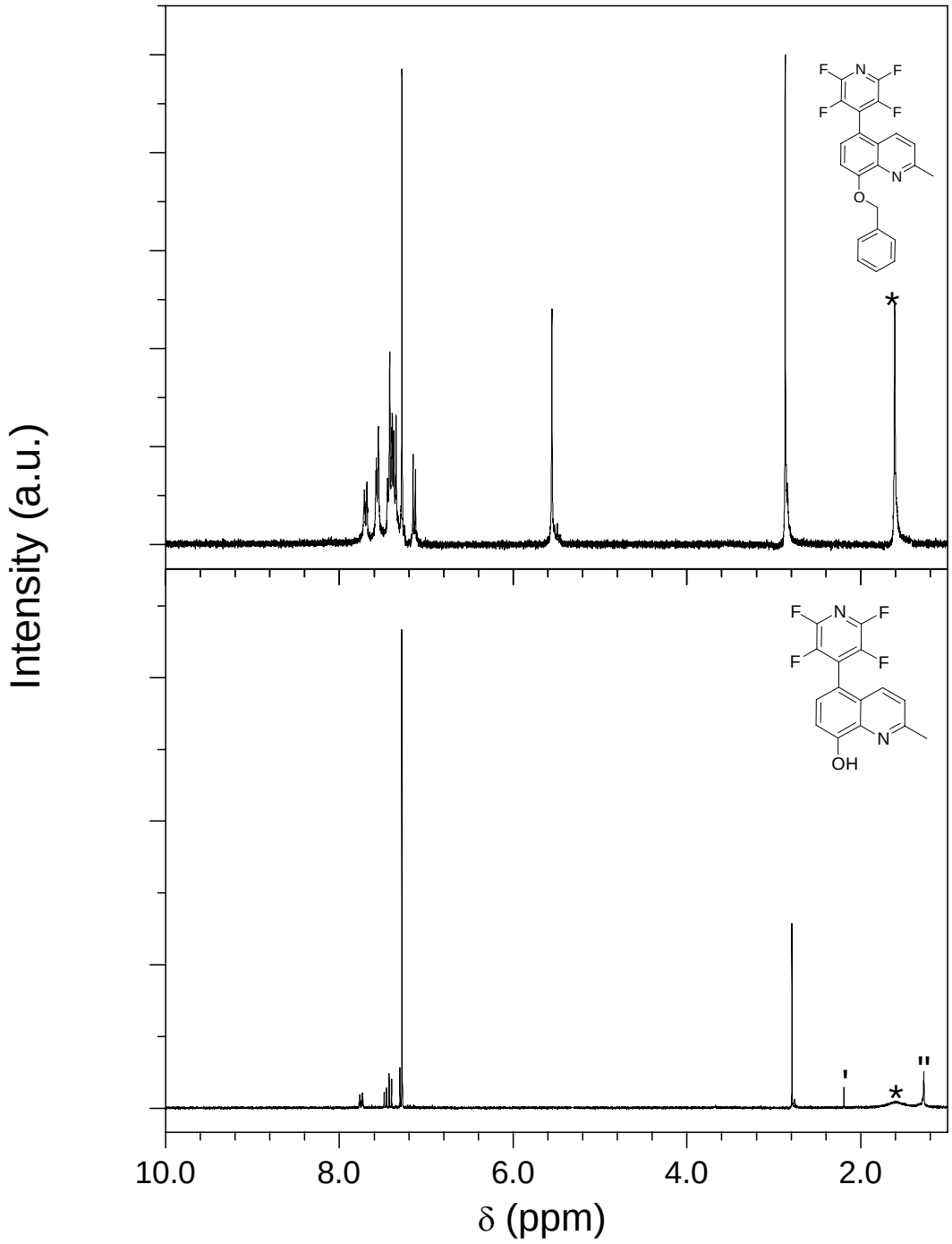

Figure S7 ^{1}H NMR spectrum of 3b (top) and 4b (bottom) solutions in $CDCl_3$. “(grease), *(water) and ‘(acetone) in $CDCl_3$.[6]

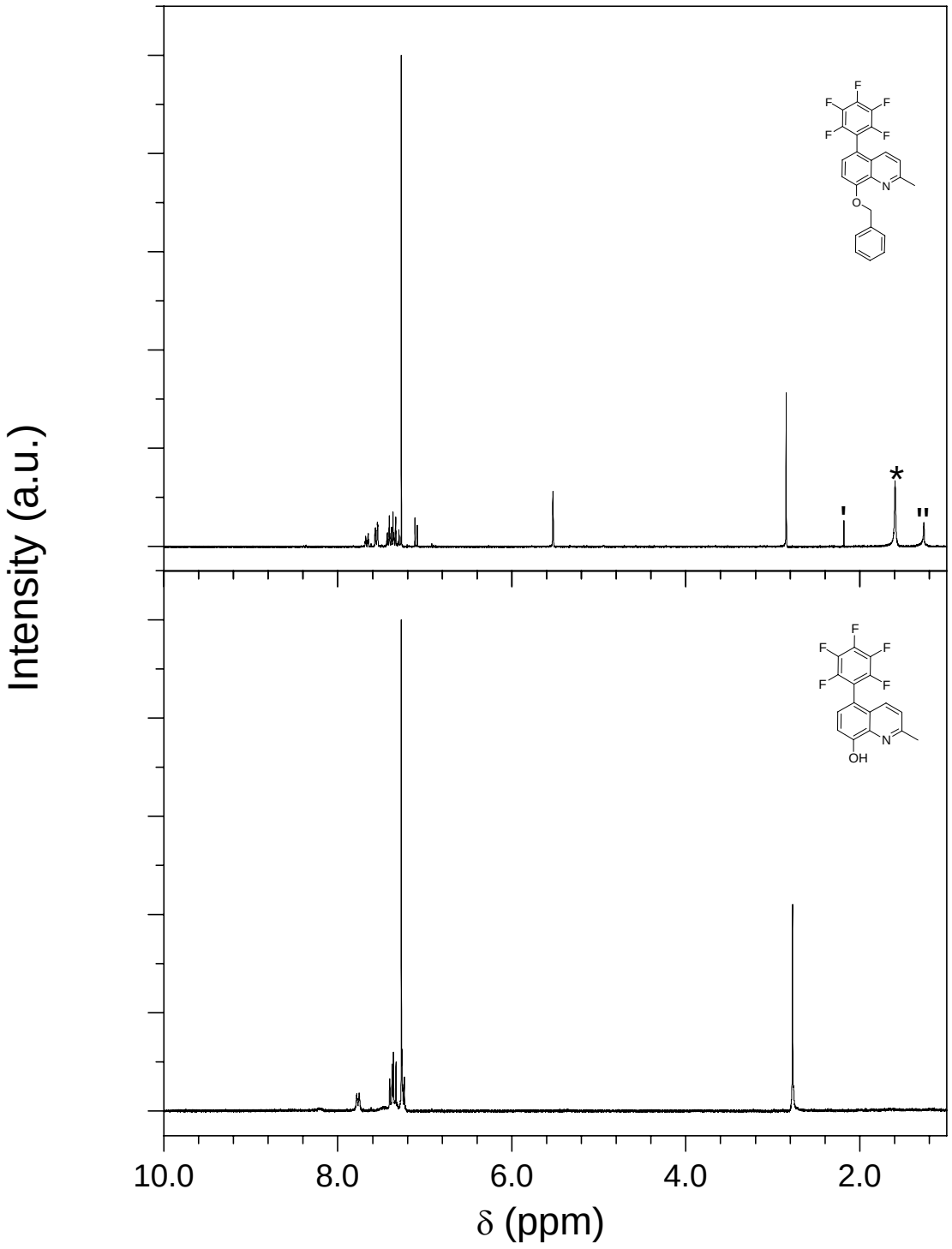

Figure S8 ^{1}H NMR spectrum of 3c (top) and 4c (bottom) solutions in $CDCl_3$. “(grease), *(water) and ‘(acetone) in $CDCl_3$.[6]

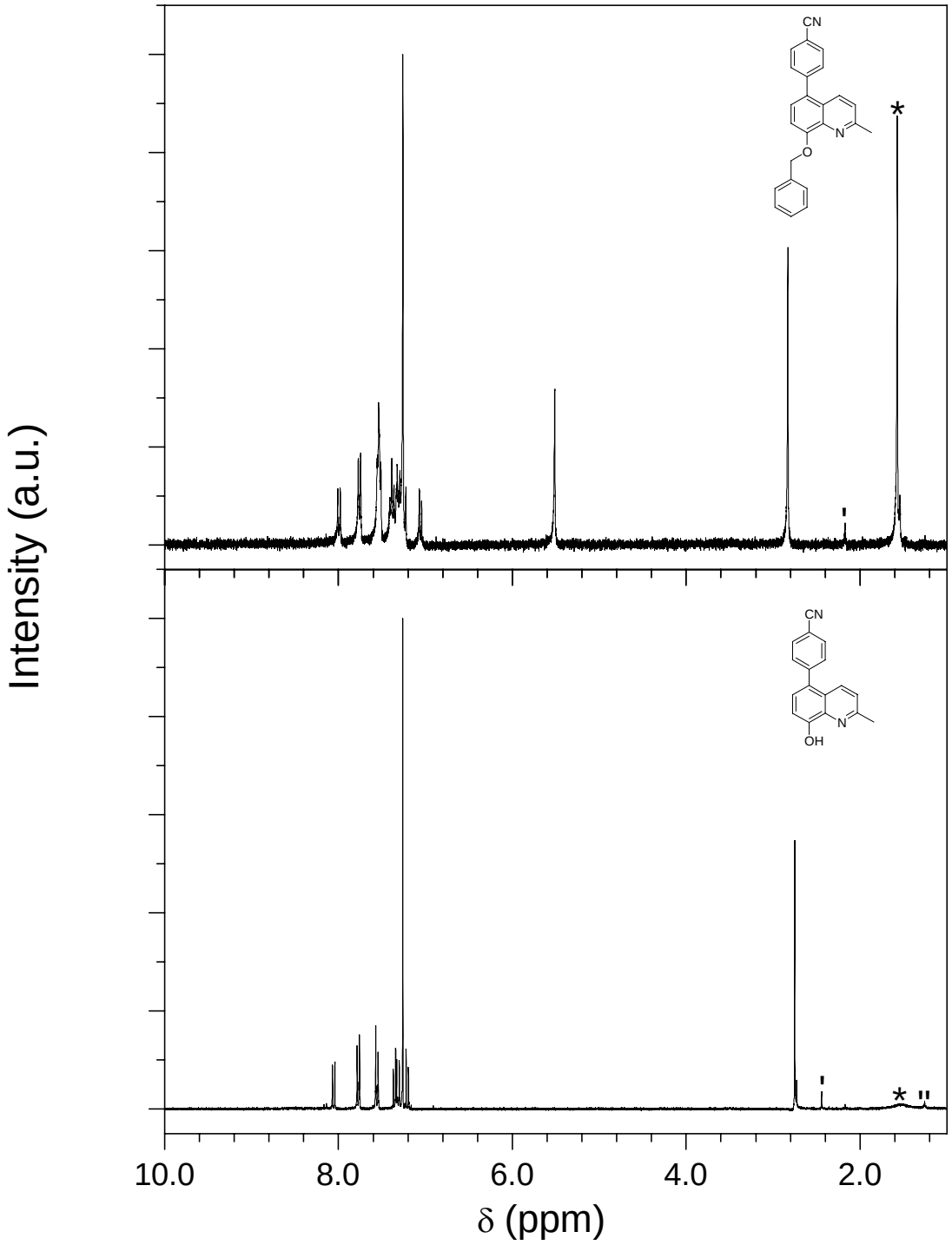

Figure S9 ^{1}H NMR spectrum of 3d (top) and 4d (bottom) solutions in $CDCl_3$. “(grease), *(water) and ‘(acetone) in $CDCl_3$.[6]

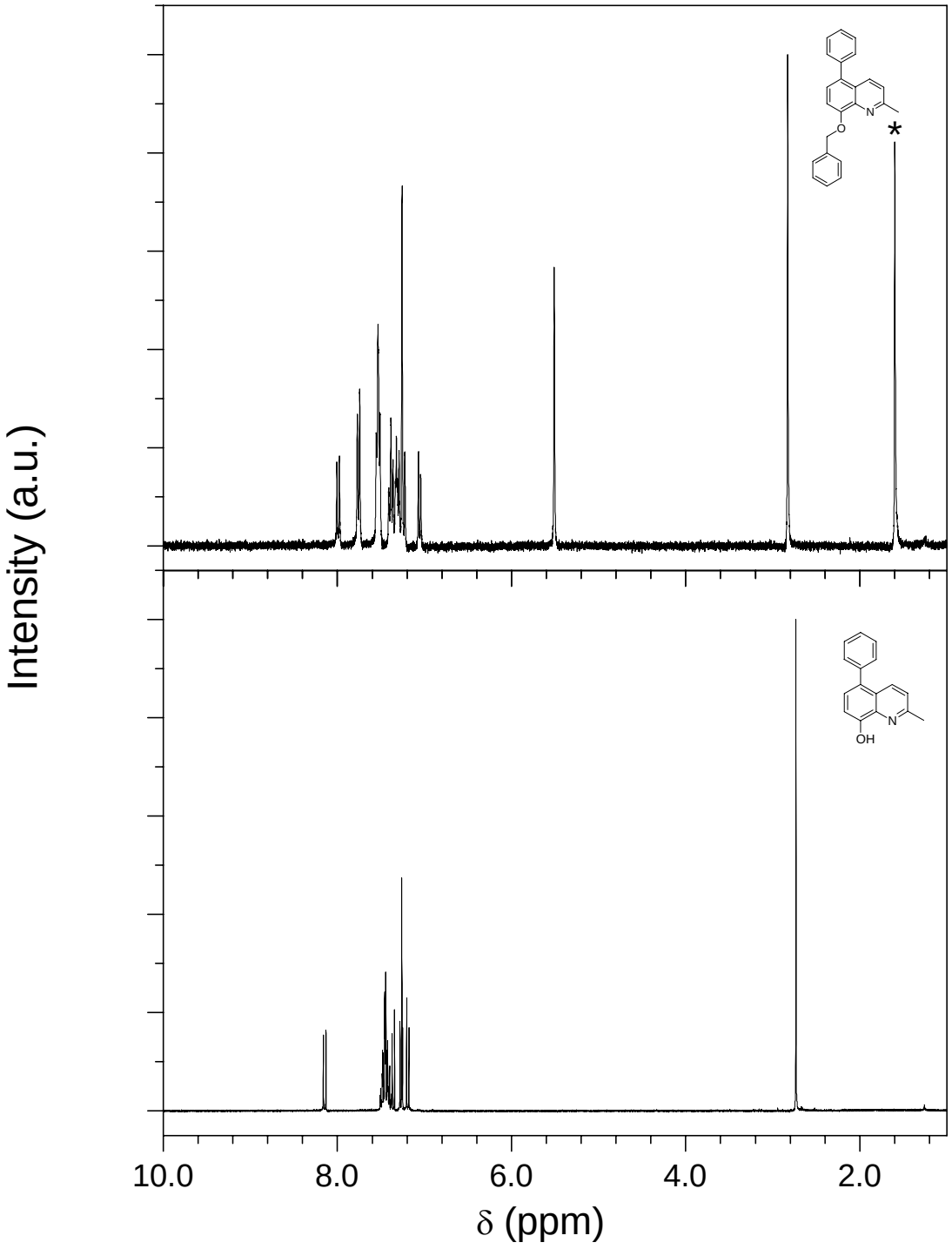

Figure S10 ^{1}H NMR spectrum of 3e (top) and 4e (bottom) solutions in $CDCl_3$.*(water) in $CDCl_3$.[6]

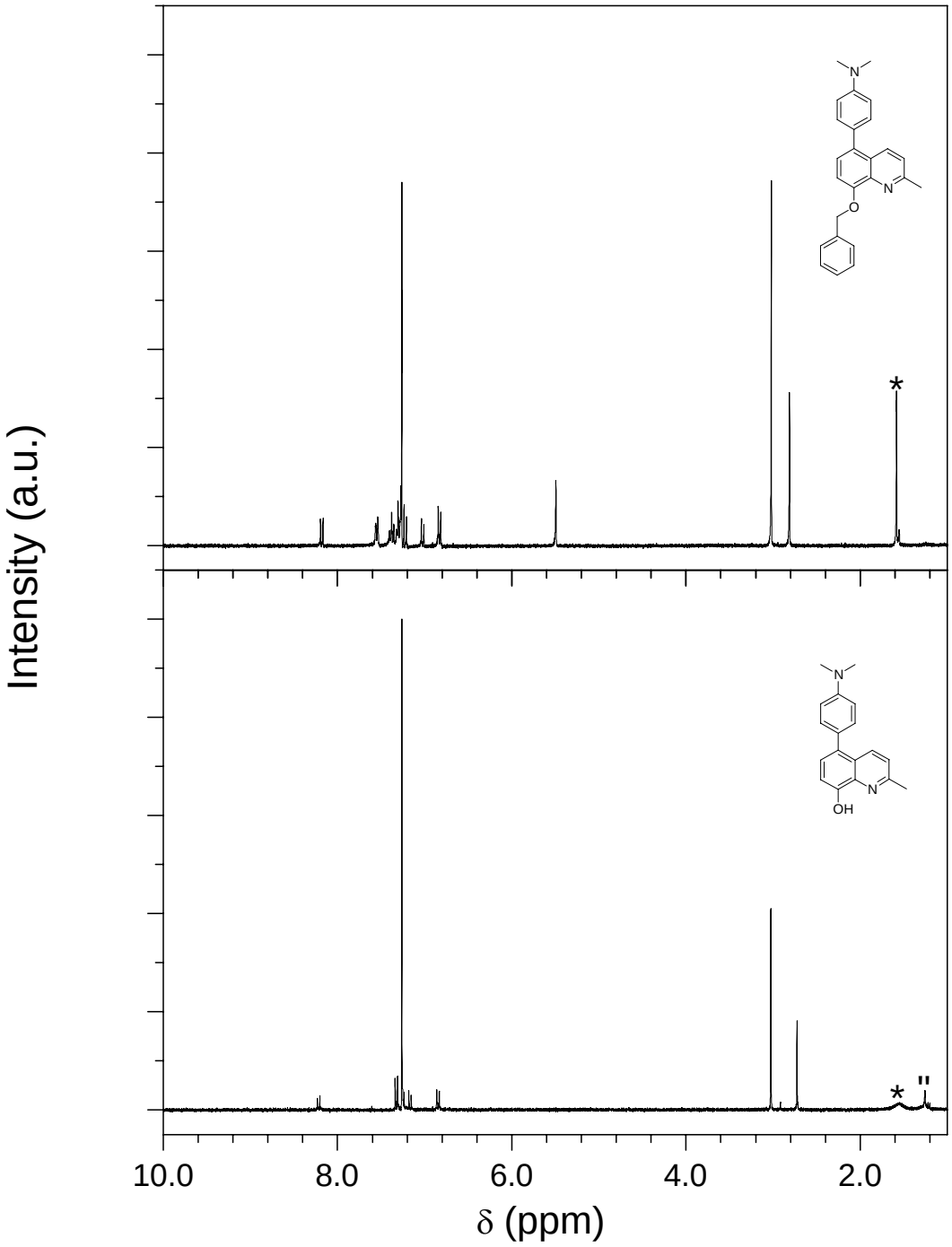

Figure S11 ^{1}H NMR spectrum of 3f (top) and 4f (bottom) solutions in $CDCl_3$. “(grease) and *(water) in $CDCl_3$.[6]

6. *Complexes' MALDI-TOF spectrum*

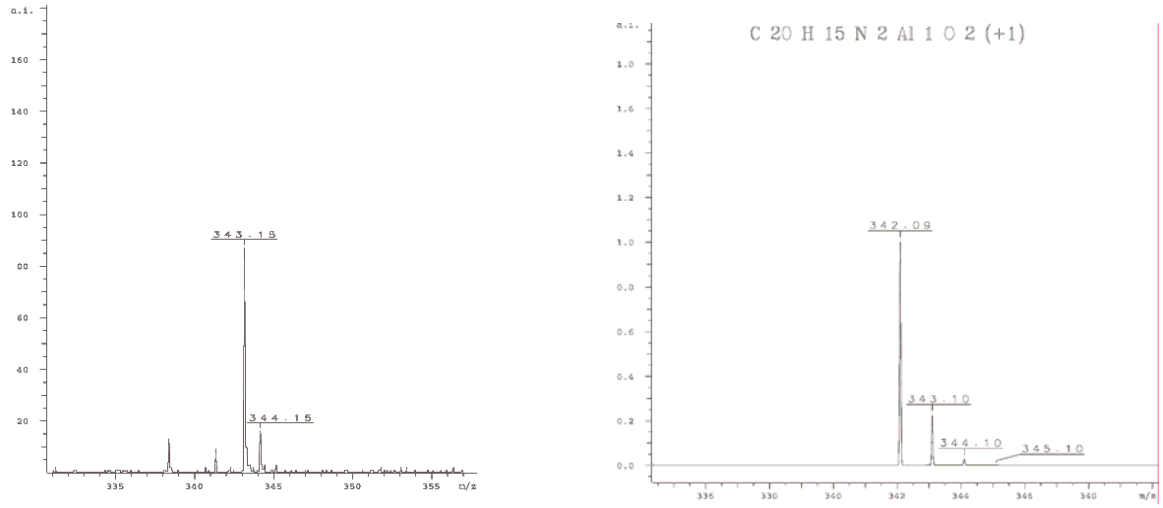

Figure S12 MALDI-TOF spectrum of **2Meq$_2$AlOPh**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{20}H_{15}N_2Al_1O_2$ (right).

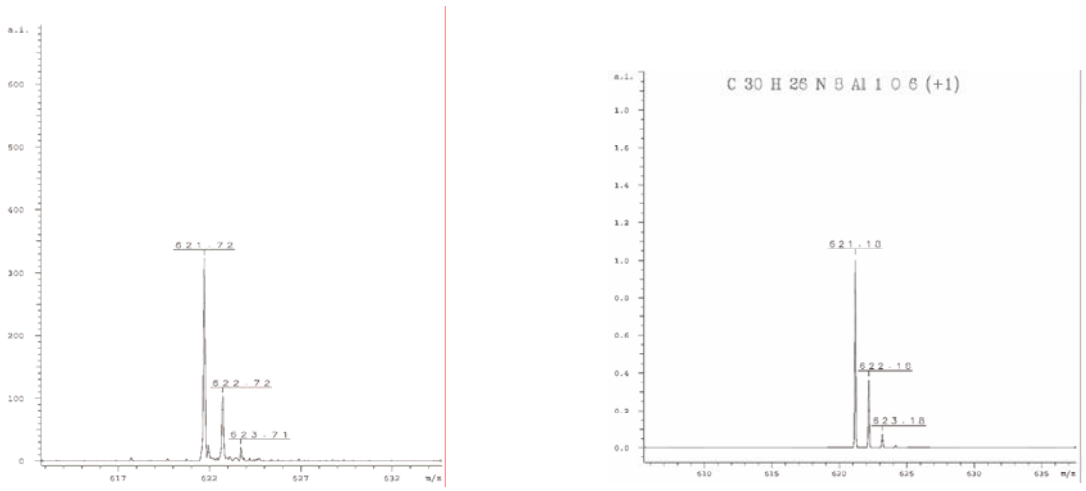

Figure S13 MALDI-TOF spectrum of **1a**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{30}H_{26}N_8Al_1O_6$ (right).

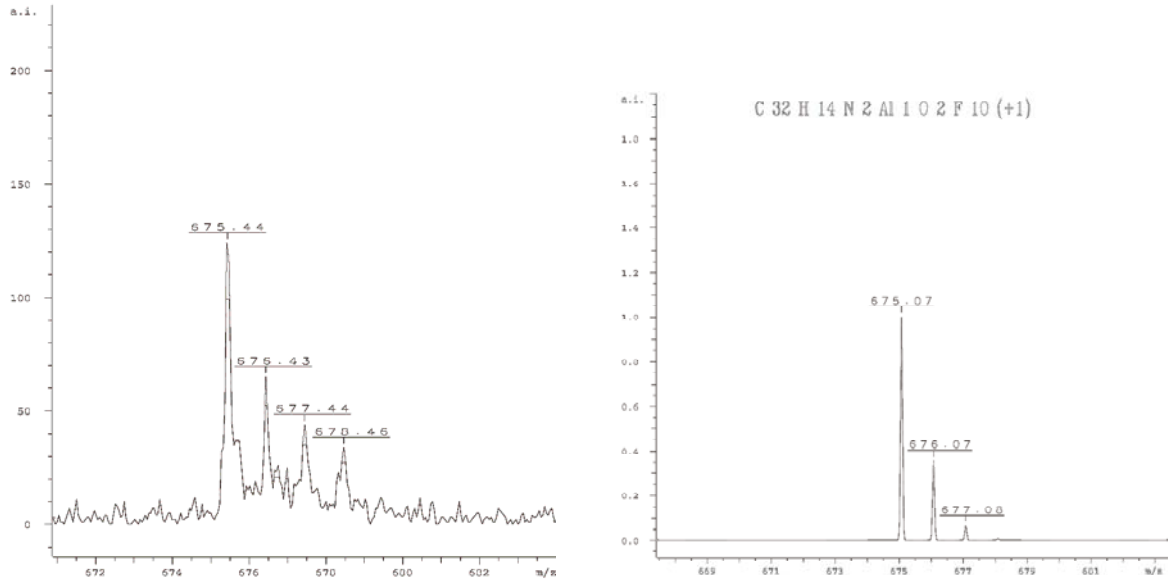

Figure S14 MALDI-TOF spectrum of **1c**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{32}H_{14}N_2Al_1O_2F_{10}$ (right).

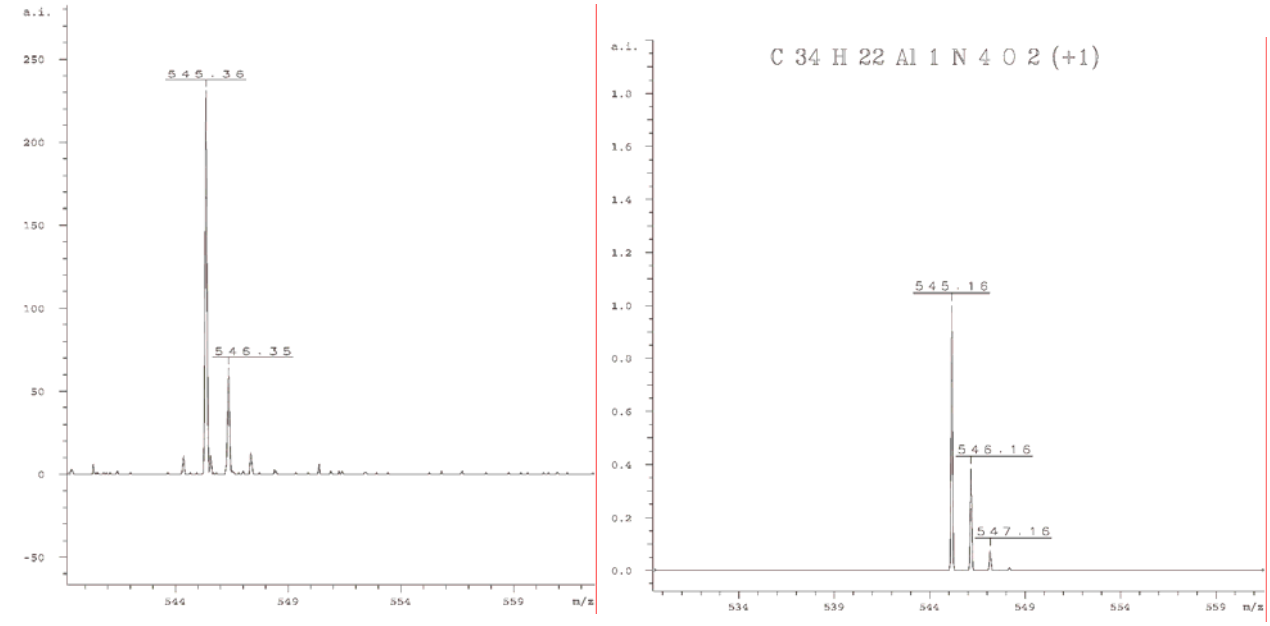

Figure S15 MALDI-TOF spectrum of **1d**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{34}H_{22}N_4Al_1O_2$ (right).

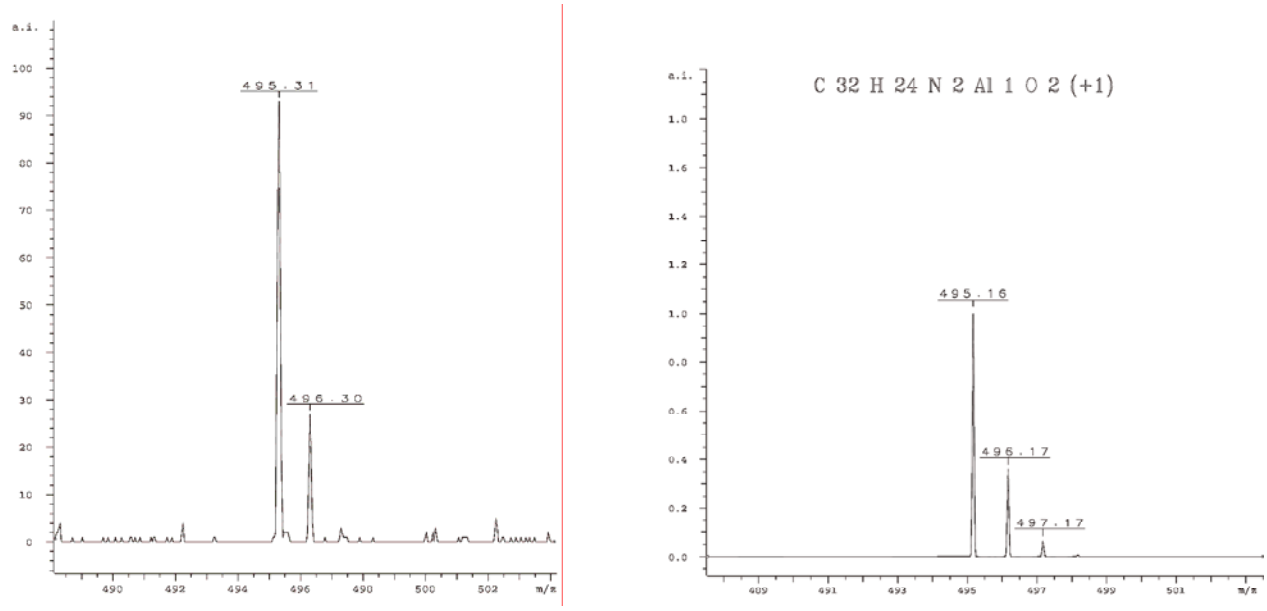

Figure S16 MALDI-TOF spectrum of **1e**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{32}H_{23}N_2Al_1O_2$ (right).

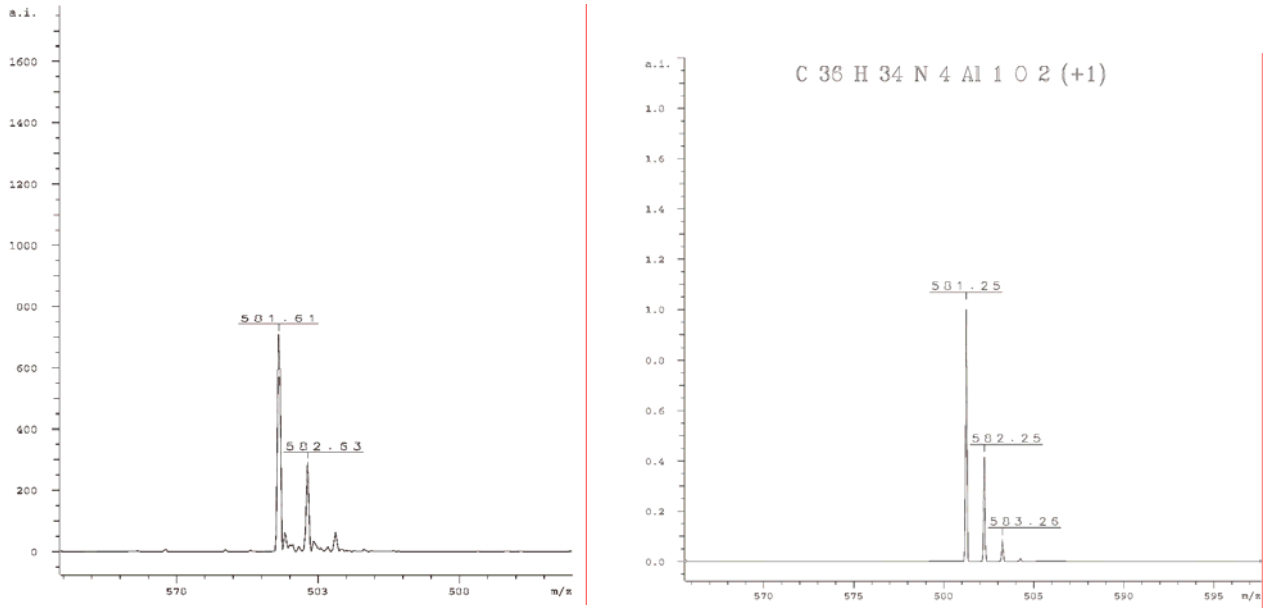

Figure S17 MALDI-TOF spectrum of **1f**. [M-OPh$^+$] (left) and theoretical isotopic distribution for $C_{36}H_{34}N_4Al_1O_2$ (right).

7. *Estimation of the HOMO-LUMO energy gap for the complexes*

The HOMO and LUMO energies were calculated by a procedure adapted from the report by Pommerehne and collaborators.[7] The value for Fc with respect to the zero vacuum level is estimated as –4.8 eV, determined from -4.6 eV for the standard electrode potential E° of normal hydrogen electrode (NHE) on the zero vacuum level, and 0.2 V for Fc *vs* NHE. Cyclic voltammetry measurements were carried out using an Electrochemical Workstation in a three-electrode cell (Pt working electrode) at room temperature. Millimolar DCM solutions of bis-(5-substituted-2-methyl-8-quinolinolato)(phenolato) Al^{3+}, containing 0.1M of recrystallized supporting electrolyte tetrabutylammonium perchlorate TBAP, were used. All potentials were referenced against the $Ag/AgNO_3$ reference electrode and each measurement was calibrated using a ferrocene/ferrocenium (Fc) redox system. Under these conditions the ferrocene/ferrocenium couple potential was determined to be +0.240 V *vs* $Ag/AgNO_3$. A scan rate of 100 mV was typically employed.

The electrochemistry of **1a-f** and **2Meq$_2$AlOPh** show oxidation and reduction processes for each of the two different kinds of ligand on the complexes. The reduction and oxidation potentials for the ligands of interest (quinolinolate like) were selected by comparison with the CV curve of Aluminum phenoxide. All those new peak different from the Aluminum phenoxide CV were selected. The oxidation and reduction peaks reported were measured at the half wave potential using a sygmoidal function and searching for waves at a potential range of 0.3V.

As it was described recently by Yang et al. in *Chem. Commun.*,[8] when oxidation peaks are not well defined on the CV, it is possible to note them in the 1st derivative of the curve. In the **2Meq$_2$AlOPh** CV in figure S18 the inflection point on the curve is not very clear. The 1st derivative of the curve is shown as a inset in the figure S18. In this curve is very clear where the minimum was positioned at.

The oxidation and reduction processes in the series are irreversible.

As described by Armstrong and collaborators, the cyclic voltammetry (CV) of Alq_3 in solution is characterized by irreversible single reduction and oxidation processes.[9] These peaks are chemically irreversible in the time scale of the experiment used (rate 100mV/s). However they showed that voltammetric experiments at significantly higher rate (2000 V/s) the one electron reduction process behaves essentially reversible.[9]

It is important to be very careful when the electrochemical behavior wants to be compared to the behavior of electronic processes in solid state. These electronic transitions occur on a different interface, essentially static. Also in solid state these transitions are several orders of magnitude faster than molecular diffusion.[10]

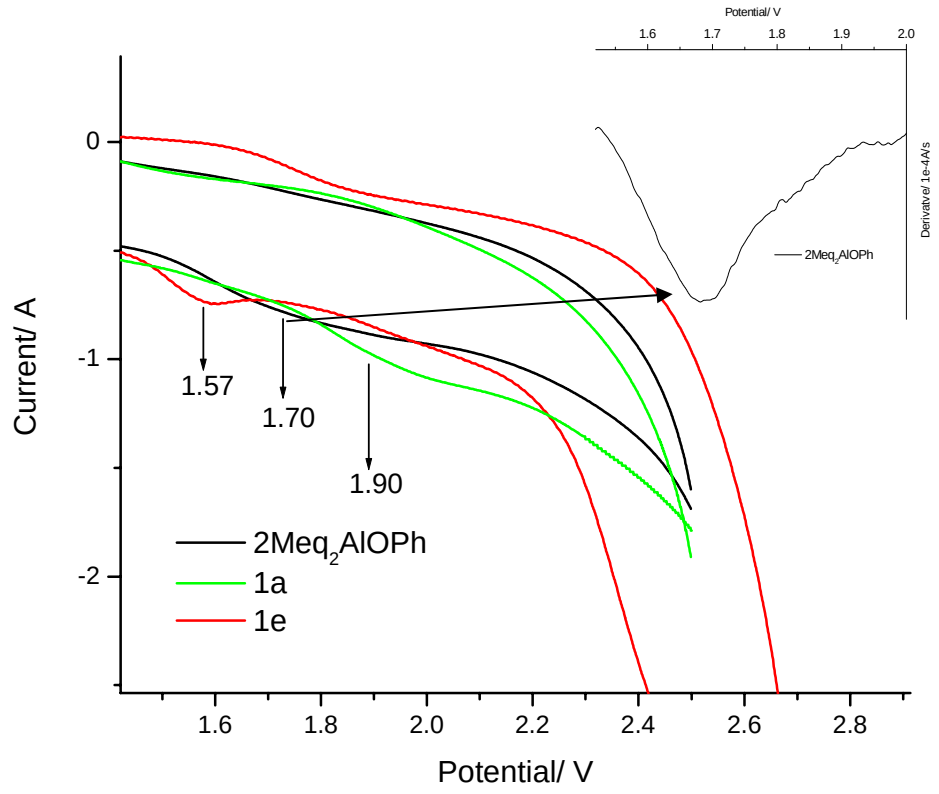

Figure S18 Oxidation peaks from cyclic voltammogram of $2Meq_2AlOPh$, 1a and 1e solution in CH_3CN. And the 1st differential curve of cyclic voltammogram of $2Meq_2AlOPh$ solution in CH_3CN.

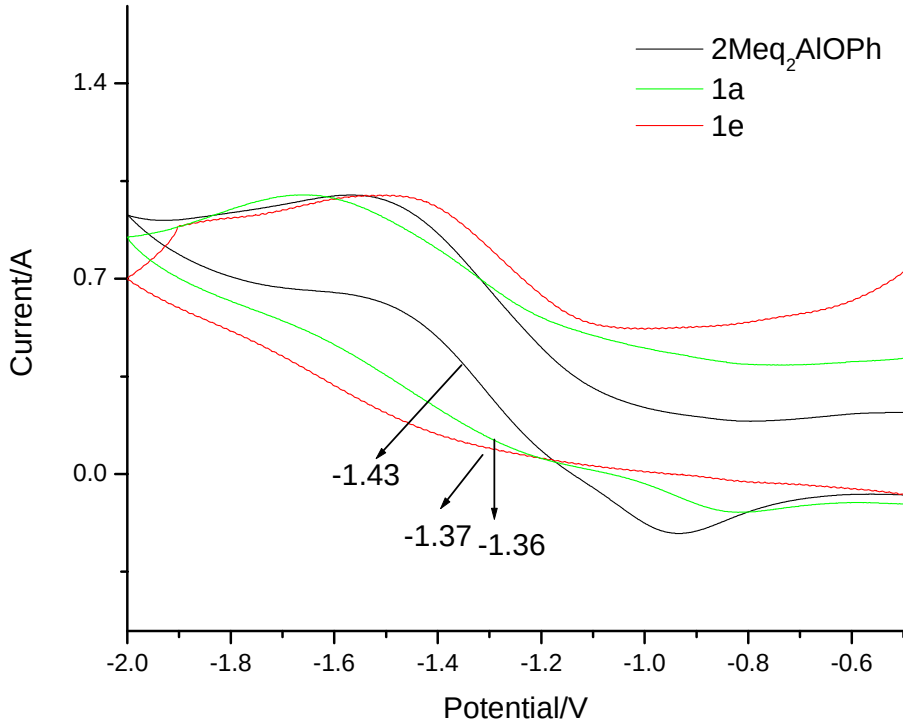

Figure S19 Reduction peaks from cyclic voltammogram of $2Meq_2AlOPh$, 1a and 1e solution in CH_3CN.

8. References

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