Self-Assembly of Stereoselective, Mononuclear, Triple-Stranded Helicate Complexes ML_3 with Trivalent Scandium and Lanthanide Metal Ions − Quantitative Transmetallation of the Lanthanide(III) Ion by Sodium(I) Ions

Magdalena Capó,*[a] José Gonzalez,[a] and Harry Adams[b]

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Mononuclear triple-stranded helicate complexes ML_3 ($M = Sc^{3+}, La^{3+}, Sm^{3+}, Yb^{3+}$) were self-assembled and structurally characterized by NMR spectroscopy and high-resolution mass spectrometry. The solid-state structure of the ytterbium complex was determined by X-ray crystallography. The core lanthanide metal ion was replaced quantitatively by three sodium ions. Homo- and heterotrinuclear complexes containing the alkali metal ions Li^+ and Na^+ were obtained from the mononuclear lanthanide complexes.

Introduction

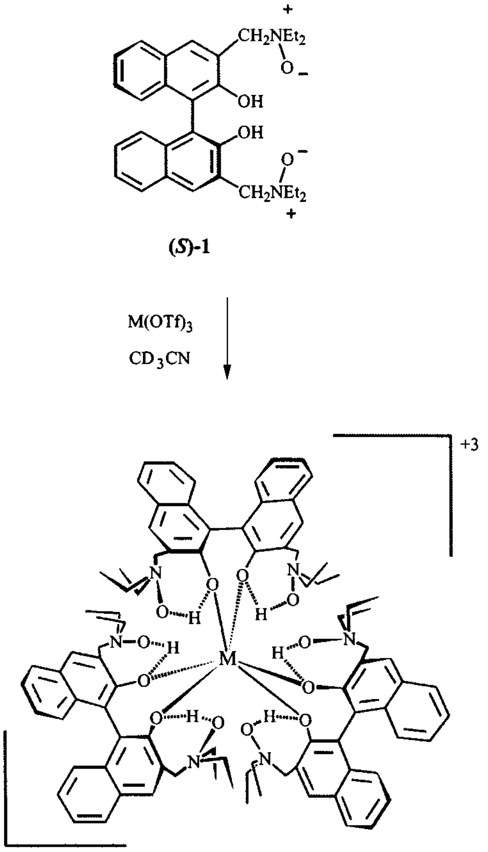
Helicate derivatives by self-assembly of multidentate organic ligands and metal ions have been a subject of current interest during the last two decades.[1] A tetradentate chiral ligand unit **1**[2] has been designed that self-assembles with lanthanide ions of different sizes to yield mononuclear triple-stranded helicates. The chiral ligand **1** in solution is able to form trinuclear helicates by self-assembly in the presence of sodium or lithium triflates[3] and mononuclear helicates in the presence of trivalent scandium or lanthanide triflates.

Here we report the formation of four stereoselective triple helices obtained quantitatively from the enantiomerically pure ligand (*S*)-**1**[4] and $M(OTf)_3$ (Scheme 1). The stoichiometry of the complexes has been determined by NMR titration experiments and mass spectrometry.

Results and Discussion

Treatment of $Sc(OTf)_3$ in acetonitrile with racemic or enantiopure (*S*)-**1** in the ratio 1:3 led to the formation of a single highly symmetrical metal complex, as demonstrated by the ^1H NMR spectrum, which contains a single set of resonances[5] (Figure 1).

A ^{45}Sc NMR spectrum was recorded to study the interaction between the ligand and the scandium ion. After



(*S*)-**1**

2 M = Sc^{+3}
3 M = La^{+3}
4 M = Sm^{+3}
5 M = Yb^{+3}

Scheme 1

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[a] Departament de Química, Universitat de les Illes Balears,
07071 Palma de Mallorca, Spain
Fax: (internat.) + 34-97-117-3426
E-mail: magdalena.capo@uib.es
[b] Department of Chemistry, University of Sheffield,
Sheffield, S3 7HT, UK

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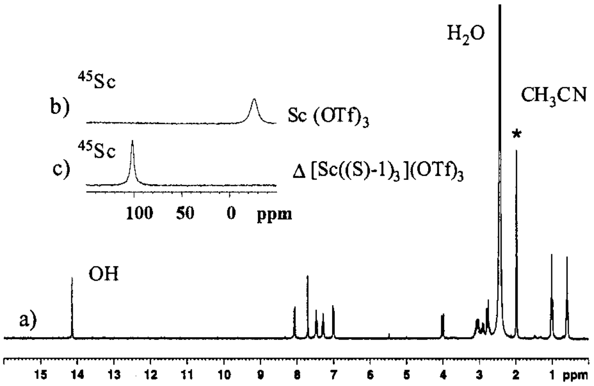


Figure 1. a) The ^{1}H NMR spectra of Δ-[Sc{(*S*)-**1**}$_3$](OTf)$_3$ (**2**) in CD$_3$CN solution; b) ^{45}Sc NMR spectra of scandium triflate; c) ^{45}Sc NMR spectra of complex Δ-[Sc{(*S*)-**1**}$_3$](OTf)$_3$ (**2**)

addition of 3 equiv. of the ligand (*S*)-**1** to a solution of Sc(OTf)$_3$ in acetonitrile, the ^{45}Sc NMR resonance of the bound cation undergoes a downfield shift to δ = 106 ppm. The presence of a sharp singlet evidences a magnetically equivalent arrangement around the scandium cation (Figure 1c). The ^{45}Sc NMR spectrum of free Sc(OTf)$_3$ shows a broad singlet at δ = −30 ppm. The diastereotopic benzilic protons were used as probe for the ^{1}H NMR analysis of the complexes **2**−**5**. The signals of the benzilic protons are largely split into two AB patterns, except for the ytterbium complex **5**, where they appear as a broad doublet at δ = 1.2−1.11 ppm (Figure 2). A characteristic NMR property of a paramagnetic lanthanide ion, such as Yb^{III}, is the large chemical-shift range usually shown by the ligand resonances.[6] These paramagnetically shifted resonances are highly sensitive to slight structural and electronic variations.

The appearance of ^{1}H NMR resonances with a large downfield shift [δ(OH) = 31.53 ppm], and aromatic and benzilic protons with large upfield shifts (δ = 4.53 and 1.2−1.01 ppm, respectively) is consistent with complexation of the ligand (*S*)-**1** by the paramagnetic ytterbium ion (Figure 2).

Due to the fact that the chemical shift in paramagnetic complexes is strongly temperature-dependent, significant changes in the proton resonances can be observed with small temperature variations for complex **5** (Figure 2). A 2D ^{1}H-^{1}H DQF-COSY (ESI) NMR experiment allowed the assignment of all peaks of complex **5**.

Single crystals of the ytterbium complex **5** suitable for an X-ray diffraction study could be obtained.[7] The crystal structure shows **5** to be mononuclear in the solid state[8] (Figure 3a). Each (*S*)-**1** ligand wraps around the metal ion. All the oxygen atoms are distributed in a tubular maner. In the center of the cavity the ytterbium ion is surrounded by six oxygen atoms, with Yb−O distances ranging from 2.208 to 2.248 Å (Figure 3b).

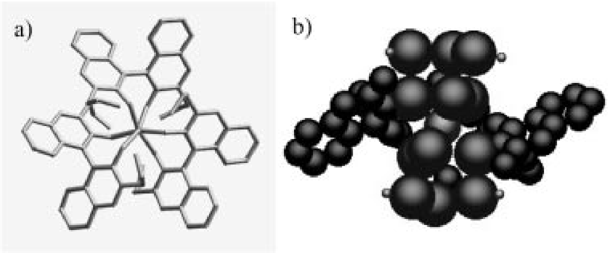


Figure 3. a) Molecular structure of Δ-[Yb{(*S*)-**1**}$_3$] (OTf)$_3$ (**5**) (top view); ethyl chains and triflates are omitted for clarity; b) space-filling representation; selected bond lengths [Å]: Yb(1)−O(1) 2.208, Yb(1)−O(2) 2.212, Yb(1)−O(3) 2.237, Yb(1)−O(4) 2.244, Yb(1)−O(5) 2.250, Yb(1)−O(6) 2.248, Yb(1)−O(7) 4.103, Yb(1)−O(8) 4.180, Yb(1)−O(9) 4.215, Yb(1)−O(10) 4.136, Yb(1)−O(11) 4.240, Yb(1)−O(12) 4.251

The selectivity of the ligand (*S*)-**1** with Ln^{III} ions in acetonitrile was monitored by ^{1}H NMR spectroscopy by adding a solution containing La/Sm/Yb in a 1:1:1 ratio to 3 equiv. of the ligand. The ^{1}H NMR spectrum shows the presence of a single metal complex corresponding to the ytterbium complex **5**.

The characterization of heteronuclear complexes bearing lanthanides is interesting because magnetic superexchange interactions between the bridged metal atoms may exist.[9] Further studies to obtain trinuclear dimetallic complexes Ln^{III}/2Na^I or Ln^{III}/2Li^I (Scheme 2) were therefore performed. Unfortunately, the addition of 2 equiv. of sodium or lithium triflate to the lanthanide complexes **3**−**5** to synthesize heterotrinuclear complexes failed, probably due to the repulsion between the lanthanide and the alkali ions. However, treatment of complexes LnL$_3$ with sodium acetate

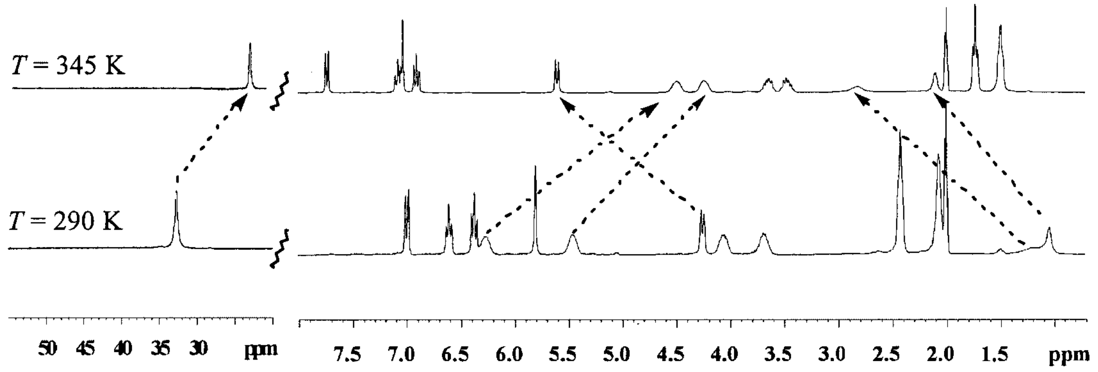
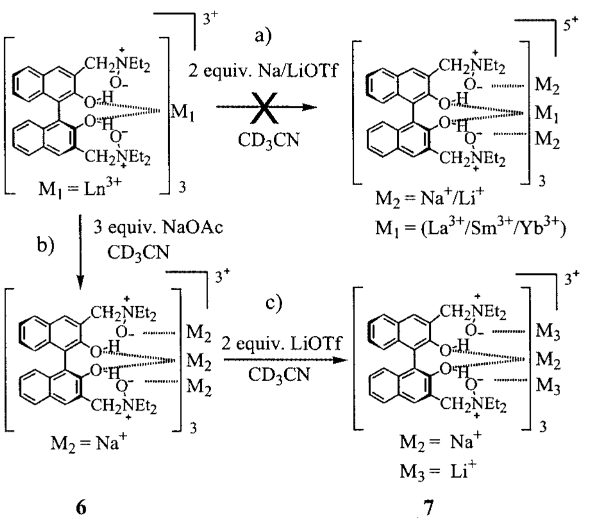


Figure 2. ^{1}H NMR spectra of complex **5**

resulted in spectral changes, completed by the addition of 3 equiv. of sodium acetate. As a result, the central Ln^{III} ion of the homonuclear complexes **3**−**5** was replaced quantitatively by the alkali metal ion, and ytterbium acetate was isolated by filtration as a white microcrystalline powder. Interestingly, the addition of sodium acetate to complexes **3**−**5** gave identical spectra to the trinuclear helicate **6** obtained from the ligand (*S*)-**1** and 3 equiv. of sodium triflate.[3] Finally, a heterotrinuclear complex **7** was obtained by substitution of the two external sodium ions by addition of 2 equiv. of lithium triflate to complex **6**.



Scheme 2

The exchange process was observed by ^7Li NMR spectroscopic studies in CD_3CN (Figure 4) where, if we compare the lithium spectrum of complex **7** with that of complex **8**, we can observe a signal at $\delta = 1.35$ ppm corresponding to the lithium ions placed at the external positions. The selective exchange of the two sodium ions at the apical positions by two lithium ions can be attributed to the fact that the size and shape of the sites are more suitable for the ionic radius and the coordination geometry of this ion. Evidence for this substitution was also observed in a ^7Li-^1H 2D HOESY NMR spectrum.

The formation of the homo- and heterotrinuclear complexes Δ-[Na_3{(*S*)-**1**}$_3$]$(OTf)_3$ (**6**) and Δ-[$LiNa_2${(*S*)-**1**}$_3$]$(OTf)_3$ (**7**) was further confirmed by ESI mass spectrometry {ESI-MS: *m*/*z* = 1832.6791 (calcd. for $C_{92}H_{108}F_6N_6Na_3O_{18}S_2$ [M − OTf]$^+$), found 1832.6344; MS (FAB^+): *m*/*z* = 1972 [MNa^+], 1956 [MLi^+], 1950 [MH^+], 1800 [M − OTf]}.

In summary, we have presented our efforts to prepare and characterize different stereoselective triple helical lanthanide complexes in solution and the solid state by the choice of a large La^{III}, a medium-sized Sm^{III} and a small Yb^{III} lanthanide ion. The recognition of one specific lanthanide ion (ytterbium) in the presence of others (lanthanum and samarium) is of great interest due to the minimal size differences of these ions and their similar chemical properties.

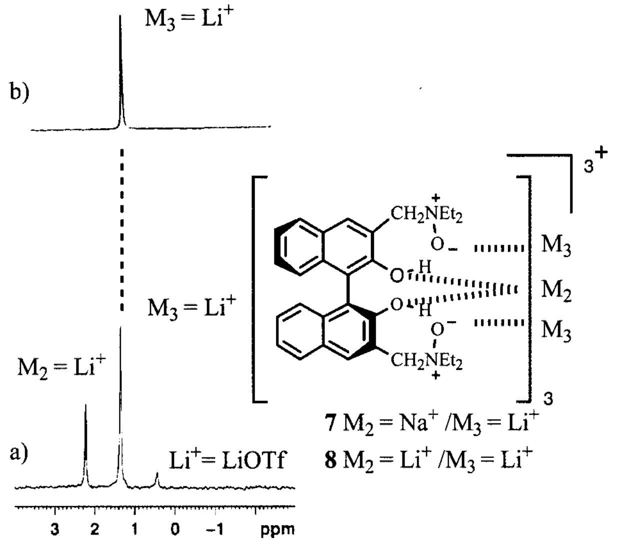


Figure 4. a) ^7Li NMR soectrum of complex **8** in CD_3CN solution; b) ^7Li NMR of complex **7** where there is only one signal corresponding to the lithium ions at the symmetrical external positions M_3

The homo- and heterotrinuclear complexes containing alkali atoms were obtained from the mononuclear lanthanide complexes. To the best of our knowledge this is the first case where a lanthanide(III) ion is replaced quantitatively by an alkali metal ion.

Experimental Section

General: The 1:3 complexes were prepared by mixing the ligand (*S*)-**1** with stoichiometric amounts of $M(OTf)_3$ in acetonitrile. The complexes were directly isolated in 70−80% yield by removing the solvent.

(*S*)-1: $[\alpha]^{25}_{589} = -186$ (*c* = 0.010, CH_3CN). ^1H NMR (CD_3CN, 300 MHz): δ = 16.40 (br. s, 2 H, OH), 7.90−788 (m, 2 H), 7.28−7.26 (m, 4 H), 7.14−7.12 (m, 2 H), 4.73 (m, 4 H), 3.39 (m, 8 H), 1.4 (t, *J* = 7.2 Hz, 12 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz) 156.5, 136.4, 132.8, 128.7, 127.8, 127.3, 125.3, 122.9, 122.0, 119.6, 69.5, 60.7, 60.3, 9.5, 9.2 ppm. MS (FAB^+): *m*/*z* = 489 [MH^+]. HRMS (FAB+): *m*/*z* = 489.2753 (calcd. for $C_{30}H_{37}$ N_2O_4), found 489.2741.

Δ-[Sc{(*S*)-1}$_3$](OTf)$_3$ (2): M.p. 256−257 °C. $[\alpha]^{25}_{589} = +190.8$ (*c* = 0.24, CH_2Cl_2). ^1H NMR (CD_3CN): δ = 14.16 (s, 6 H), 8.10 (d, *J* = 8.0 Hz, 6 H), 7.74 (s, 6 H), 7.50 (t, *J* = 7.5 Hz, 6 H), 7.31 (t, *J* = 7.7 Hz, 6 H), 7.03 (d, *J* = 8.4 Hz, 6 H), 4.03 (d, *J* = 13.5 Hz, 6 H), 3.13−2.76 (m, 24 H), 2.81 (d, *J* = 13.5 Hz, 6 H), 1.03 (t, *J* = 7.1 Hz, 18 H), 0.61 (t, *J* = 7.2 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 156.6, 135.9, 134.7, 128.8, 128.3, 127.5, 125.9, 123.7, 121.9, 119.8, 63.5, 60.8, 57.5, 7.4, 7.2 ppm. ^{45}Sc NMR (CD_3CN, 72 MHz): δ = 106 ppm. MS (FAB^+): *m*/*z* = 1980 [MNa^+], 1958 [MH^+], 1808 [M − OTf].

Δ-[La{(*S*)-1}$_3$](OTf)$_3$ (3): M.p. 243−244 °C. $[\alpha]^{25}_{589} = +79.2$ (*c* = 0.24, CH_2Cl_2). ^1H NMR (CD_3CN): δ = 14.64 (s, 6 H), 8.17 (d, *J* = 8.0 Hz, 6 H), 7.85 (s, 6 H), 7.52 (t, *J* = 7.4 Hz, 6 H), 7.34 (t, *J* = 7.6 Hz, 6 H), 6.93 (d, *J* = 8.4 Hz, 6 H), 3.92 (d, *J* = 13.7 Hz, 6 H), 3.14−2.88 (m, 24 H), 2.98 (d, *J* = 13.7 Hz, 6 H), 1.07 (t, *J* = 7.1 Hz, 18 H), 0.59 (t, *J* = 7.2 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 153.8, 135.8, 135.0, 128.7, 127.9, 124.8, 123.7, 121.5, 119.9, 64.0, 60.3, 58.8, 7.0, 6.8 ppm. MS (FAB$^+$): *m/z* = 2073 [MNa$^+$], 2051 [MH$^+$], 1902 [M − OTf].

Δ-[Sm{(*S*)-1}$_3$](OTf)$_3$ (4): M.p. 238−239 °C. $[\alpha]^{25}_{589}$ = +159 (*c* = 0.024, CD_3CN). ^{1}H NMR (CD_3CN): δ = 18.03 (s, 6 H), 7.86 (d, *J* = 6.9 Hz, 6 H), 7.38 (t, *J* = 7.3 Hz, 6 H),7.31(s, 6 H), 7.16 (t, *J* = 7.2 Hz, 6 H), 6.59 (d, *J* = 8.4 Hz, 6 H), 3.57 (d, *J* = 13.7 Hz, 6 H), 3.38−3.16 (m, 24 H), 2.65 (d, *J* = 13.7 Hz, 6 H), 1.27 (t, *J* = 6.9 Hz, 18 H), 0.86 (t, *J* = 6.9 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 155.5, 135.38, 134.36, 128.75, 127.81, 127.04, 124.65, 123.33, 119.75, 117.85, 64.02, 61.00, 58.94, 7.40, 7.28 ppm. ESI-MS: *m/z* = 1916.4758 [M − OTf].

Δ-[Yb{(*S*)-1}$_3$](OTf)$_3$ (5): M.p. 254−255 °C. $[\alpha]^{25}_{589}$ = +200.8 (*c* = 0.12, CH_2Cl_2). ^{1}H NMR (CD_3CN): δ = 31.53 (br. s, 6 H), 7.05 (d, *J* = 8.1 Hz, 6 H), 6.65 (t, *J* = 7.5 Hz, 6 H), 6.42 (t, *J* = 7.4 Hz, 6 H), 6.12 (br. s, 6 H), 5.89 (s, 6 H), 5.39 (br. s, 6 H), 4.35 (d, *J* = 8.4 Hz, 6 H), 4.07−4.01 (m, 6 H), 3.69−3.62 (m, 6 H), 2.36 (s, 18 H), 2.03 (s, 18 H), 1.38 (br. s, 6 H), 1.11 (s, 6 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 132.5, 129.8, 127.9, 127.3, 125.9, 125.7, 125.0, 124.0, 123.5, 119.9, 63.3, 61.4, 59.4, 8.8, 8.3 ppm. MS (FAB$^+$): *m/z* = 2109 [MNa$^+$], 2087 [MH$^+$], 1936 [M − OTf]. HRMS (FAB$^+$): *m/z* = 1936.64543 (calcd. for $C_{92}H_{108}F_6N_6O_{18}S_2Yb$ [M − HOTf + H$^+$]), found 1936.65769. Pale-yellow single crystals of **5** were obtained by the slow evaporation of the solvent from a CH_3CN solution.

Δ-[Na$_3${(*S*)-1}$_3$](OTf)$_3$ (6): $[\alpha]^{25}_{589}$ = +299 (*c* = 0.014, CH_3CN). ^{1}H NMR (CD_3CN, 300 MHz): δ = 16.01 (s, 6 H, OH), 8.14 (d, *J* = 5 Hz, 6 H), 7.68 (s, 6 H), 7.49 (t, *J* = 7 Hz, 6 H), 7.33 (t, *J* = 7 Hz, 6 H), 7.03 (d, *J* = 8.4 Hz, 6 H), 3.86 (d, *J* = 13.2 Hz, 6 H), 2.94 (m, 24 H), 2.72 (d, *J* = 13.2 Hz, 6 H), 1.02 (t, *J* = 6.9 Hz, 18 H), 0.5 (t, *J* = 6.9 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 154.05, 135.07, 133.64, 128.39, 128.06, 127.20, 124.93, 123.27, 122.25, 118.97, 65.62, 60.91, 58.00, 7.98, 7.21 ppm. ^{23}Na NMR (CD_3CN, 79 MHz): δ = 5.69, −1.06 ppm. ESI-MS: *m/z* = 1832.6791 (calcd. for $C_{92}H_{108}F_6N_6Na_3O_{18}S_2$ [M − OTf]$^+$); found 1832.6344.

Δ-[Li$_2$Na{(*S*)-1]$_3$}(OTf)$_3$ (7): ^{1}H NMR (CD_3CN, 300 MHz): δ = 15.66 (s, 6 H, OH), 8.08 (d, *J* = 5 Hz, 6 H), 7.53 (s, 6 H), 7.48 (t, *J* = 7 Hz, 6 H), 7.36(t, *J* = 7 Hz, 6 H), 7.08 (d, *J* = 8.4 Hz, 6 H), 4.11 (d, *J* = 13 Hz, 6 H), 3.03−2.83 (m, 24 H), 2.82 (d, *J* = 13 Hz, 6 H), 1.02 (t, *J* = 6.9 Hz, 18 H), 0.57 (t, *J* = 6.9 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 153.89, 135.91, 134.55, 129.41, 129.06, 128.39, 125.45, 124.39, 122.47, 119.70, 66.95, 61.72, 58.75, 9.46, 7.85 ppm. ^{7}Li NMR (CD_3CN, 116 MHz): δ = 1.32 ppm. MS (FAB$^+$): *m/z* = 1972 [MNa$^+$], 1956 (MLi$^+$), 1950 [MH$^+$], 1800 [M − OTf] ESI-MS: *m/z* = 1799.7284 (calcd. for $C_{92}H_{108}F_6Li_2N_6NaO_{18}S_2$ [M − OTf]$^+$); found 1799.7358.

Δ-[Li$_3${(*S*)-1}$_3$](OTf)$_3$ (8): $[\alpha]^{25}_{589}$ = +329 (*c* = 0.012, CH_3CN). ^{1}H NMR (CD_3CN, 300 MHz): δ = 15.36 (s, 6 H, OH), 8.08 (d, *J* = 5 Hz, 6 H), 7.50 (s, 6 H), 7.48 (t, *J* = 7 Hz, 6 H), 7.35(t, *J* = 7 Hz, 6 H), 7.08 (d, *J* = 8.4 Hz, 6 H), 3.89 (d, *J* = 13 Hz, 6 H), 3.05−2.87 (m, 24 H), 2.72 (d, *J* = 13 Hz, 6 H), 1.01 (t, *J* = 6.9 Hz, 18 H), 0.52 (t, *J* = 6.9 Hz, 18 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 153.25, 134.85, 133.88, 128.50, 128.37, 127.33, 125.18, 123.57, 122.18, 119.16, 65.35, 60.87, 57.26, 8.58, 6.88 ppm. ^{7}Li NMR (CD_3CN, 116 MHz): δ = 2.23, 1.35 ppm. HRMS (ES): *m/z* = 1783.7546 (calcd. for $C_{92}H_{108}F_6Li_3N_6O_{18}S_2$ [M − OTf]$^+$), found 1783.7593.

Acknowledgments

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