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Synthesis of some ytterbium(III) tris-(perfluoroalkylsulfonyl)methides

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Abstract—Full experimental details are given for the preparation of highly active catalysts $Yb[C(SO_2C_4F_9)_3]_3$, $Yb[C(SO_2C_6F_{13})_3]_3$, and $Yb[C(SO_2C_6F_{13})_2SO_2C_8F_{17}]_3$. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Lanthanide(III) triflates and related species have enjoyed recent attention as catalysts for a wide range of reactions in organic synthesis.[1,2] The interest stems from their apparent ability to function as strong Lewis acids even in Lewis basic solvents such as THF and water, and by their relatively high turnover numbers compared to traditional Lewis acids.[3] For instance, ytterbium(III) triflate was found to catalyze the Mukaiyama aldol reaction of silylketene acetals with aqueous formaldehyde solution.[4] In the latter category, these compounds have been found to be effective catalysts (ca. 10 mol%) for Friedel–Crafts acylation reactions[5,6] where typically 'classical' Lewis acid catalysts must be used in at least stoichiometric quantities.[7] Notably, in many cases the lanthanide(III) triflate may be recovered from the reaction mixture by extracting into an aqueous phase and recycled after evaporation.

We have recently reported several novel catalytic applications of lanthanide(III) triflates including oxidation of benzylic alcohols with nitric acid,[8] the preparation of resorcinarenes,[9] and alcohol acetylation using acetic acid.[10] Of particular note is the use of catalytic quantities of lanthanide(III) triflates for the atom economic nitration of arenes using a single equivalent of nitric acid (and no sulfuric acid).[11] A mechanistic study revealed the crucial roles of both the metal[12] and the counterion[13] for efficient catalysis. The charge-to-size ratio of a given lanthanide(III) ion was found to be the determining factor for its catalytic activity, and the counterion must be the conjugate base of a strong acid ($pK_a < -12$). Based on these findings, we showed that the deliquescent hafnium(IV) and zirconium(IV), tetrapositive ions with high charge-to size ratios, triflates were excellent catalysts for the nitration of electron deficient arenes such as *o*-nitrotoluene.[14] Critically, the same high level of catalytic activity can be obtained with lanthanide(III) ions by utilizing the tris-(trifluoromethanesulfonyl)methide anion ($HCTf_3$:[15] pK_a ca. -18[16]). These salts are readily manipulated in air and are not deliquescent. Specifically, we introduced ytterbium(III) and scandium(III) tris-(trifluoromethanesulfonyl)methides ('triflides') $Yb(CTf_3)_3$ **1** and $Sc(CTf_3)_3$ **2** as catalysts for aromatic nitration.[17] We disclosed a novel route to the triflide ligand, the preparation of the ytterbium and scandium catalysts, X-ray crystal structures of both and their use for nitration. Along with all the other lanthanide(III) triflates, ytterbium and scandium salts **1** and **2** may be efficiently recycled repeatedly. We have also applied these catalysts for the nitration of perfluoroaromatics without complications from HF liberation.[18] More recently, we introduced a series of long-chain (C_4F_9, C_6F_{13}, C_8F_{17}) perfluorinated homologues of the triflide anion, the corresponding ytterbium(III) salts and their use for the first fluorous phase acylation with catalyst recycle.[19] It was found, in general, that as well as the long perfluorochains giving increased fluorous solubility, they also conferred higher catalytic activity to the metal complex. Mikami has also reported ytterbium and scandium tris-(nonafluorobutanesulfonyl)methides for Friedel–Crafts acylation[20] but failed to achieve a fluorous phase soluble catalyst. More recently, the same group reported on scandium(III) tris-(perfluorooctanesulfonyl)-methide for fluorous phase Friedel–Crafts acylation and other carbon–carbon bond forming reactions.[21] However, to date neither our group nor Mikami's have disclosed experimental procedures for the syntheses of these highly active catalysts. In this paper we give full experimental

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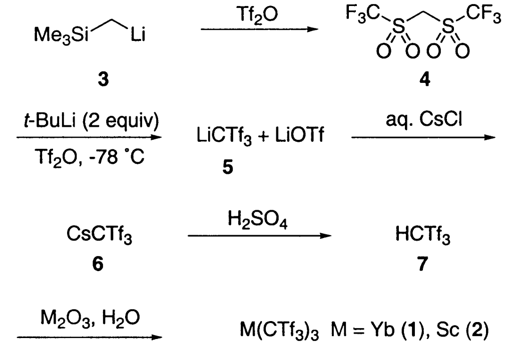


Scheme 1.

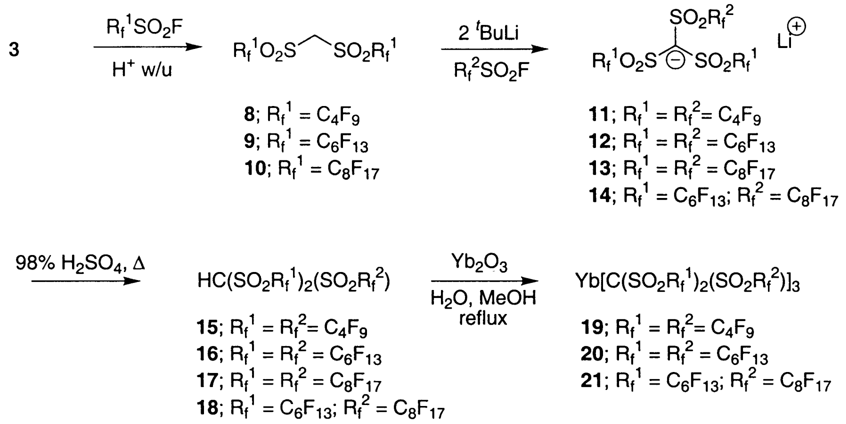
details for the preparation of these perfluorosulfonylmethide ligands and the corresponding ytterbium-(III) catalysts.

2. Results and discussion

The synthetic route to the perfluorinated methides is based on our previously published route to the triflide anion[17] but with significant modifications due to the changing solubility profiles of these heavily fluorinated materials. For the parent triflide ligand (Tf_3C^-), triflic anhydride was allowed to react with trimethylsilylmethyllithium **3** to give methyleneditriflone **4** after acidic work-up (Scheme 1). Double deprotonation with 2 equiv. of *tert*-butyllithium and addition of triflic anhydride gave lithium triflide **5**. This was separated from the side product lithium triflate by selective precipitation of cesium triflide **6**. Sublimation from concentrated sulfuric acid gave the free acid **7**, from which ytterbium(III) **1** or scandium(III) triflide **2** was conveniently prepared by treatment with ytterbium or scandium oxide respectively.

Unlike gaseous CF_3SO_2F, the long chain sulfonyl fluorides $C_4F_9SO_2F$, $C_6F_{13}SO_2F$ and $C_8F_{17}SO_2F$ are commercially available and convenient sources of the electrophile '$C_nF_{2n+1}SO_2^+$'. Trimethylsilylmethyllithium **3** was found to react to with these electrophiles to give the corresponding methylene compounds $(C_4F_9SO_2)_2CH_2$ (**8**) (Nf_2CH_2), $(C_6F_{13}SO_2)_2CH_2$ (**9**) (Tdf_2CH_2) and $(C_8F_{17}SO_2)_2CH_2$ (**10**) (Hdf_2CH_2), in 58, 39 and 29%, respectively, after acid–base work-up, and vacuum sublimation (Scheme 2). The methylene compound **10** was alternatively purified by simple trituration with diethyl ether at 0°C. We have found that these compounds display diagnostic signals in their ^{13}C and ^{19}F NMR. For example the ^{13}C NMR resonances (DMSO-d_6) for the central methylene bridge are found at 59.4, 59.8 and 59.0 ppm and the CF_2 units alpha to the sulphone give characteristic ^{19}F NMR resonances at −113.3, −113.1 and −113.8 ppm for **8**, **9** and **10**, respectively. Sulfone **8** was also characterized by X-ray crystallography after recrystallization from 1,1,1-trifluoroethanol (Fig. 1).[†]

Following the procedure for the preparation of the triflide salts, the methylene sulfones **8–10** were treated with 2 equiv. of *tert*-butyllithium to generate the dianions. These were quenched with the corresponding sulphonyl fluorides to generate the methide salts **11–13**, respectively. Additionally, the mixed lithium methide **14** was prepared by quenching the dianion of sulfone **9** with $C_8F_{17}SO_2F$. The procedure for the purification of triflidic acid necessitated selective precipitation with cesium salt. For the higher homologues it was found that acidification and extraction with diethyl ether, evaporation and water washing gave the pure lithium salts. The lithium methides show characteristic resonances for the formally negatively charged central carbon atom in the ^{13}C NMR at 88–89 ppm, and the flanking CF_2 units show diagnostic resonances at −107.2±0.1 ppm in their ^{19}F NMR spectra (DMSO-d_6). Sublimation from



Scheme 2.

[†] *Crystal data for* **8**: $C_9H_2O_4F_{18}S_2\cdot C_2H_3OF_3$, $M=680.3$, orthorhombic, space group $Pca2_1$ (no. 29), $a=28.074(3)$, $b=5.385(2)$, $c=16.588(2)$ Å, $V=2507.8(8)$ Å^3, $Z=4$, $D_c=1.802$ g cm^{-3}, μ(Cu K$_\alpha$)=3.65 mm^{-1}, $T=293$ K, colourless platy needles; 1937 independent measured reflections, F^2 refinement, $R_1=0.165$, $wR_2=0.381$, 1019 independent observed reflections [$|F_0|>4\sigma(|F_0|)$, $2\theta\leq120°$], 404 parameters. The high final value of R_1 is a consequence of extensive disorder throughout the structure. Two partial occupancy (70/30) orientations of both the bis-(nonafluorobutanesulfonyl)methane chain and the included 2,2,2-trifluoroethanol molecule were identified, though these had to be heavily constrained to idealized bond length and angle geometries; the gross structure is, however, chemically unambiguous. The polarity of the structure could not be established. Crystallographic data (excluding structure factors) for this structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 173483. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail:deposit@ccdc.cam.ac.uk].

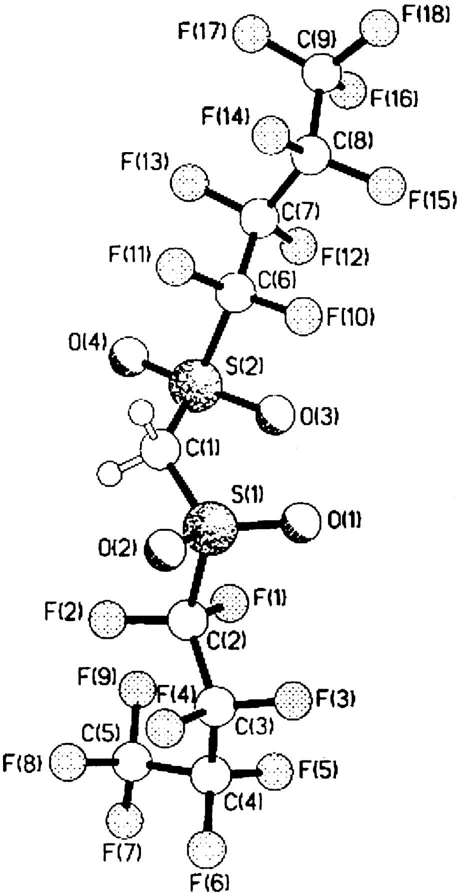


Figure 1. Major occupancy conformer in the solid state structure of **8**.

concentrated sulfuric acid delivered the free acids **15–18**. Finally, the ytterbium catalysts **19–21** were prepared by treating the corresponding free acids with ytterbium(III) oxide in aqueous ethanol.

We have already described the use of these catalysts for fluorous phase acylation reactions,[19] and we have shown the nonaflide catalyst **19** to operate at truly catalytic loadings (0.1–1 mol%) for Friedel–Crafts acylation under a suitable temperature and pressure regime.[22] The metal methide complexes **19–21** should find general use in diverse lanthanide catalyzed reactions.

3. Experimental

3.1. General

Trimethylsilylmethyllithium and *tert*-butyllithium were titrated immediately prior to use according to the procedure of Kofron.[23] Trimethylsilylmethyllithium was purchased from Aldrich as a 1.0 M solution and used without dilution. All reactions involving alkyllithiums were run under a nitrogen atmosphere. Et_2O was distilled from Na/benzophenone. Nonafluorobutanesulfonyl fluoride, tridecafluorohexanesufonyl fluoride and heptadecafluorooctanesulfonyl fluoride were purchased from Avocado, Lancaster and Fluka, respectively, and used as supplied. Vacuum sublimations were performed in a Kugelrohr apparatus. Ytterbium(III) oxide was purchased from Aldrich and used as supplied. All other reagents and solvents were supplied by Aldrich or BDH.

3.1.1. Bis-(nonafluorobutanesulfonyl)methane (8). Nonafluorobutanesulfonyl fluoride (13.5 mL, 75 mmol) was addded dropwise over 1 h to a stirred solution of Me_3SiCH_2Li in pentane (1.0 M, 150 mL, 150 mmol) at 2–5°C. The mixture was allowed to warm to room temperature, stirred for 60 h and quenched by the addition of saturated aqueous $NaHCO_3$ solution (150 mL). The pentane layer was separated and the aqueous layer extracted with CH_2Cl_2 (3×50 mL). The aqueous layer (containing a semi-solid foam) was acidified with concentrated HCl (ca. 60 mL) to pH 1 and extracted with Et_2O (3×50 mL). The combined ether extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to give a brown solid. Trituration with hexanes (3×100 mL) and vacuum sublimation (110°C, 0.3 mmHg) gave **8** (12.7 g, 58%) as a white solid: IR (KBr) 3000, 2928, 1389, 1354, 1296, 1218, 1185, 1140, 1113, 1032, 814, 722, 693 cm^{-1}; ^1H NMR (400 MHz, CD_3COCD_3) $\delta 6.43$ (br s); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 66.9 (br s, $(C_4F_9SO_2)_2\mathit{C}$), 106.1–122.6 (m, $(\mathit{C}_4F_9SO_2)_2C$); ^{19}F NMR (235 MHz, CD_3COCD_3) δ −125.6 (m, 4F), −120.7 (m, 4F), −109.5 (m, 4F), −80.7 (tt, J=9.8, 2.2 Hz, 6F); MS (FAB, negative ion) m/z 579 $[(Nf_2CH)^-$, 100%].

3.1.2. Bis-(tridecafluorohexanesulfonyl)methane (9). Tridecafluorohexanesulfonyl fluoride (5.74 mL, 25 mmol) was added dropwise over 2 h to a stirred solution of Me_3SiCH_2Li in pentane (1.0 M, 50 mL, 50 mmol) at 2–5°C. The mixture was allowed to warm to room temperature, stirred for 60 h and quenched by the addition of saturated aqueous $NaHCO_3$ solution (150 mL) and allowed to settle. The supernatants were decanted leaving a brown residue in the reaction vessel. The decanted pentane layer was separated from the aqueous phase and the latter extracted with CH_2Cl_2 (3×30 mL). The aqueous layer was acidified with concentrated HCl (ca. 30 mL) to pH 1, and extracted with Et_2O (3×30 mL). The reaction residue was forcibly mixed with saturated aqueous $NaHCO_3$ solution (60 mL) to give a cloudy suspension and acidified with concentrated HCl (ca. 30 mL), to pH 1. The resulting slurry was extracted with Et_2O (3×30 mL). The combined ethereal extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to give a brown solid. Trituration with CH_2Cl_2 followed by vacuum sublimation (160–170°C, 1.0 mmHg) gave **9** (3.8 g, 39%) as a white solid; ^1H NMR (400 MHz, DMSO-d_6) δ 7.34 (2H, s, $C\mathit{H}_2$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 59.8 (s, $(C_6F_{13}SO_2)_2\mathit{C}H_2$), 106.3–121.8 (m, $(\mathit{C}_6F_{13}SO_2)_2CH_2$); ^{19}F NMR (376 MHz, DMSO-d_6) δ −125.1 (4F, m), −121.9 (4F, m), −121.0 (4F, m), −119.1 (4F, m), −113.1 (4F, m), −79.7 (6F, m); MS (FAB, negative ion) m/z 1239 (100%), 779 ($M-H^+$, 70%).

3.1.3. Bis-(heptadecafluorooctanesulfonyl)methane (10). Heptadecafluorooctanesulfonyl fluoride (20.7 mL, 75 mmol) was added dropwise over 2.5 h to a stirred solution of Me_3SiCH_2Li in pentane (1.0 M, 150 mL, 150 mmol) at 3–5°C. The mixture was allowed to warm to room temperature, stirred for 60 h and quenched by the addition of saturated aqueous $NaHCO_3$ solution (150 mL) and allowed to settle. The supernatants were decanted leaving a brown residue in the reaction vessel. The decanted pentane layer was separated from the aqueous phase and the latter extracted with CH_2Cl_2 (3×50 mL). The aqueous layer was acidified with concentrated HCl (ca. 50 mL) to pH 1, and extracted with Et_2O (3×50 mL). The reaction residue was forcibly mixed with saturated aqueous $NaHCO_3$ solution (60 mL) to give a cloudy suspension and acidified with concentrated HCl (ca. 30 mL), to pH 1. The resulting slurry was extracted with Et_2O (3×30 mL). The combined ethereal extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to give a brown solid. Subsequent trituration with hexanes, CH_2Cl_2 and Et_2O at 0°C gave **10** (10.5 g, 29%) as a white solid; ^1H NMR (250 MHz, CD_3COCD_3) δ 5.55 (br s, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ 59.0 (s, $(C_8F_{17}SO_2)_3CH_2$), 107.4–120.9 (m, $(C_8F_{17}SO_2)_3CH_2$); ^{19}F NMR (235 MHz, CD_3COCD_3) δ −126.2 (4F, m), −122.7 (4F, m), −121.7 (12F, m), −119.6 (4F, m), −113.8 (4F, m), −81.2 (6F, m); MS (FAB, negative ion)*m/z* 980 (M, 30%), 559 (100).

3.1.4. Lithium tris-(nonafluorobutanesulfonyl)methide (11). *tert*-Butyllithium in pentane (1.4 M, 3.0 mL, 4.2 mmol) was added to a stirred solution of sulfone **8** (1.16 g, 2.0 mmol) in Et_2O (40 mL) at −20°C, and the mixture stirred for 1 h at −20°C. Nonafluorobutanesulfonyl fluoride (540 μL, 3.0 mmol) was added dropwise and the mixture was allowed to warm to room temperature and stirred for 24 h. The solvents were evaporated in vacuo and the residue quenched with saturated aqueous $NaHCO_3$ solution (100 mL). The aqueous layer was acidified with concentrated hydrochloric acid (ca. 50 mL) to pH 1, extracted with CH_2Cl_2 (3×30 mL) and Et_2O (3×30 mL). The combined ethereal extracts were evaporated in vacuo to furnish a pale yellow oil which was immediately taken into water (10 mL). A yellow–brown oil settled out, the water was removed and the oil was triturated with water (2×10 mL). Upon standing the oil solidified to yield **11** (1.15 g, 71%) as a dark yellow solid; IR (thin film) 3534, 1378, 1352, 1239, 1214, 1162, 1142, 1123, 1029, 972, 799, 737 cm^{-1}; ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.7 (s, $(C_4F_9SO_2)_3C$), 105.4–121.1 (m, $(C_4F_9SO_2)_3C$); ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.0 (6F, m), −120.6 (6F, m), −107.4 (6F, m), −79.8 (9F, m); MS (FAB, negative ion)*m/z* 861 [$(Nf_3C)^-$, 100%].

3.1.5. Lithium tris-(tridecafluorohexanesulfonyl)methide (12). *tert*-Butyllithium in pentane (1.7 M, 2.5 mL, 4.2 mmol) was added dropwise to a stirred solution of sulfone **9** (1.56 g, 2.0 mmol) in Et_2O (40 mL) at −78°C and the mixture was allowed to warm to −20°C over 1 h. Tridecafluorohexanesulfonyl fluoride (689 μL, 3.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The solvents were removed in vacuo and quenched with saturated aqueous $NaHCO_3$ solution (50 mL). The mixture acidified with concentrated hydrochloric acid (ca. 30 mL) to pH 1, and extracted with Et_2O (3×30 mL). The combined ethereal extracts were concentrated in vacuo to yield a pale yellow solid which was immediately taken into water (20 mL). A yellow–brown precipitate formed which was isolated by filtration and washed with water (2×20 mL). Trituration with Et_2O at −78°C gave **12** (1.68 g, 72%) as a dark yellow oil; ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.7 (s, $(C_6F_{13}SO_2)_3C$), 107.4–120.9 (m, $(C_6F_{13}SO_2)_3C$); ^{19}F NMR (376 MHz, DMSO-d_6) δ −125.5 (6F, m), −122.3 (6F, m), −121.2 (6F, m), −119.8 (6F, m), −107.3 (6F, m), −80.0 (9F, m); MS (FAB, negative ion) *m/z* 1161 [$(Tdf_3C)^-$, 100%].

3.1.6. Lithium tris-(heptadecafluorooctanesulfonyl)-methide (13). *tert*-Butyllithium in pentane (1.7 M, 1.25 mL, 2.1 mmol) was added dropwise to a stirred solution of sulfone **10** (980 mg, 1.0 mmol) at −78°C in Et_2O (30 mL) and allowed to warm to −20°C over 1 h. The resulting solution was re-cooled to −78°C and heptadecafluorohexanesulfonyl fluoride (415 μL, 1.5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 60 h. The solvents were removed in vacuo and quenched with saturated aqueous $NaHCO_3$ solution (50 mL). The mixture was acidified with concentrated hydrochloric acid (ca. 30 mL) to pH 1, and extracted with Et_2O (3×30 mL). The combined ethereal extracts were concentrated in vacuo to yield a pale yellow solid which was immediately taken into water (20 mL). A yellow–brown precipitate formed which was isolated by filtration and washed with water (2×20 mL). The resulting solid was subjected to vacuum sublimation (170–180°C, 0.4 mmHg) to remove unreacted starting material leaving **13** (220 mg, 15%) as a dark-brown glass; ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.4 (6F, m), −122.1 (6F, m), −121.2 (18F, m), −119.4 (6F, m), −107.3 (6F, m), −79.9 (9F, m); MS (FAB, negative ion) *m/z* 1461 [$(Hdf_3C)^-$, 50%].

3.1.7. Lithium tris-[heptadecafluorooctanesulfonyl-bis-(tridecafluorohexanesulfonyl)] methide (14). *tert*-Butyllithium in pentane (1.7 M, 2.5 mL, 4.2 mmol) was added dropwise to a stirred solution of sulfone **9** (1.56 g, 2.0 mmol) at −20°C in Et_2O (40 mL) and the reaction was stirred at −20°C for 1 h. Heptadecafluorooctanesulfonyl fluoride (826 μL, 3.0 mmol) was added dropwise, the mixture allowed to warm to room temperature and stirred for 24 h. The solvents were removed in vacuo and quenched with saturated aqueous $NaHCO_3$ solution (100 mL). The mixture was acidified with concentrated hydrochloric acid (ca. 50 mL) to pH 1, and extracted with Et_2O (3×30 mL). The combined ethereal extracts were concentrated in vacuo and the residue was taken immediately into water (10 mL). A yellow–brown precipitate formed which was isolated by filtration and washed with water (2×20 mL). Trituration with Et_2O at −78°C gave **14** (1.24 g, 49%) as a dark-yellow oily solid; ^{13}C NMR(100 MHz, DMSO-d_6) δ 88.8 (s, $(R_fSO_2)_3C$), 107.4–120.9 (m, $C_8F_{17}SO_2(C_6F_{13}SO_2)_2C$); ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.4 (6F, m), −122.1 (6F, m), −121.1 (10F, m), −119.7 (6F, m), −107.2 (6F, m), −80.0 (9F, m).

3.1.8. Tris-(nonafluorobutanesulfonyl)methane (15). A mixture of **11** (1.56 g, 1.8 mmol) and concentrated H_2SO_4 (1.0 mL, ca. 10 equiv.) was subjected to vacuum distillation (150–155°C, 0.4 mmHg) to give a white semi-solid mass. This was partitioned between Et_2O (10 mL) and water (10 mL) and treated with saturated aqueous barium chloride solution (20 mL). The ethereal layer was separated and the aqueous layer extracted with Et_2O (2×15 mL) and the combined ethereal extracts were concentrated in vacuo. Purification by vacuum distillation (150–155°C, 0.4 mmHg) gave **15** (1.48 g, 95%) as a white solid; ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.8 (s, $(C_4F_9SO_2)_3CH$), 107.8–121.2 (m, $(C_4F_9SO_2)_3CH$); ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.0 (6F, m), −120.6 (6F, m), −107.3 (6F, m), −79.8 (9F, m); MS (FAB, negative ion) *m/z* 861 [$(Nf_3C)^-$, 100%].

3.1.9. Tris-(tridecafluorohexanesulfonyl)methane (16). A mixture of **12** (1.65 g, 1.4 mmol) and concentrated H_2SO_4 (0.75 mL, ca. 10 equiv.) was subjected to vacuum distillation (150–155°C, 0.3 mmHg) to generate a white semi-solid mass. This was partitioned between Et_2O (10 mL) and water (10 mL) and treated with saturated aqueous barium chloride solution (20 mL). The ethereal layer was separated and the aqueous layer extracted with Et_2O (2×15 mL) and the combined ethereal extracts were concentrated in vacuo. Purification by vacuum distillation (150–155°C, 0.3 mmHg) gave **16** (1.52 g, 94%) as a colorless oil which solidified upon standing; ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.4 (6F, m), −122.2 (6F, m), −121.1 (6F, m), −119.7 (6F, m), −107.2 (6F, m), −79.9 (9F, m).

3.1.10. Tris-(heptadecafluorooctanesulfonyl)methane (17). A mixture of **13** (90 mg, 0.06 mmol) and concentrated H_2SO_4 (35 μL, ca. 10 equiv.) was subjected to vacuum distillation (150–160°C, 0.2 mmHg) to generated a white semi-solid mass. This was partitioned between Et_2O (5 mL) and water (5 mL) and treated with saturated aqueous barium chloride solution (7.5 mL). The ethereal layer was separated and the aqueous layer extracted with Et_2O (2×10 mL) and the combined ethereal extracts were concentrated in vacuo. Purification by vacuum distillation gave **17** (63 mg, 72%) as a colouless oil which solidified upon standing; ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.7 (6F, m), −122.4 (6F, m), −121.3 (18F, m), −119.9 (6F, m), −107.3 (6F, m), −80.3 (9F, m); MS (FAB, negative) *m/z* 1462 (M, 100%).

3.1.11. Tris-[heptadecafluorooctanesulfonyl-bis-(tridecafluorohexanesulfonyl)] methane (18). A mixture of **14** (1.08 g, 0.85 mmol) and concentrated H_2SO_4 (0.5 mL, ca. 10 equiv.) was subjected to vacuum distillation (160–170°C, 0.3 mmHg) to generate a white semi-solid mass. This was partitioned between Et_2O (10 mL) and water (10 mL) and treated with saturated aqueous barium chloride solution (15 mL). The ethereal layer was separated and the aqueous layer extracted with Et_2O (2×10 mL) and the combined ethereal extracts were concentrated in vacuo. Purification by vacuum distillation gave **18** (1.05 g, 95%) as a pale brown oil which solidified upon standing; ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.6 (6F, m), −122.3 (6F, m), −121.3 (10F, m), −119.9 (6F, m), −107.3 (6F, m), −80.1 (9F, m).

3.1.12. Ytterbium (III) tris-(nonafluorobutanesulfonyl)-methide (19). A suspension of Yb_2O_3 (34.5 mg, 0.088 mmol), acid **15** (431 mg, 0.5 mmol) in water (0.25 mL) and EtOH (0.25 mL) was heated at reflux for 24 h. The solution was cooled, diluted with EtOH (2 mL), filtered, concentrated in vacuo, and dried under high vacuum (0.1 mmHg) for 2 days to give **19** (441 mg, 96%) as a off-white glass: IR (thin film) 3500–3350, 1630, 1378, 1351, 1238, 1214, 1162, 1142, 1124, 1029, 971, 873, 737 cm^{-1}; ^{19}F NMR (235 MHz, DMSO-d_6) δ −124.9 (18F, m), −120.6 (18F, m), −107.3 (18F, m), −79.8 (27F, m).

3.1.13. Ytterbium (III) tris-(tridecafluorohexanesulfonyl)methide (20). A suspension of Yb_2O_3 (34.5 mg, 0.088 mmol), acid **15** (581 mg, 0.5 mmol) in water (0.3 mL) and EtOH (0.2 mL) was heated at reflux for 24 h. The solution was cooled, diluted with EtOH (2 mL), filtered, concentrated in vacuo, and dried under high vacuum (0.1 mmHg) for 2 days to give **20** (610 mg, 100%) as a off-white glass.

3.1.14. Ytterbium (III) tris-[heptadecafluorooctanesulfonyl-bis-(tridecafluorohexanesulfonyl)]methide (21). A suspension of Yb_2O_3 (13.8 mg, 0.035 mmol), acid **15** (252 mg, 0.2 mmol) in water (0.3 mL) and EtOH (0.3 mL) was heated at reflux for 24 h. The solution was cooled, diluted with EtOH (2 mL), filtered, concentrated in vacuo, and dried under high vacuum (0.1 mmHg) for 2 days to give **21** (258 mg, 98%) as a off-white glass: ^{19}F NMR (235 MHz, DMSO-d_6) δ −125.2 (18F, m), −122.0 (18F, m), −121.1 (30F, m), −119.6 (18F, m), −107.1 (18F, m), −79.7 (27F, m).

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