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The perfluorinated trityl cation accessible as a triflate derivative

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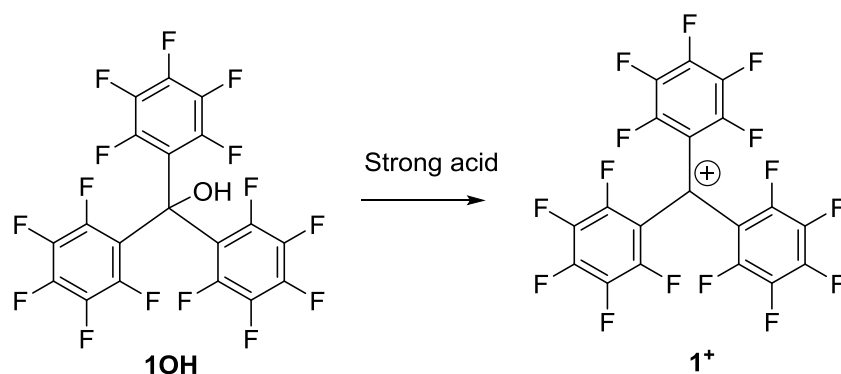
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ABSTRACT

While ultimately not isolable for X-ray structural characterization, the free perfluorinated trityl cation is shown to be observable in neat triflic acid, which represents milder conditions than previous reports of this cation in “magic acid” or oleum. A triflate-bound species can be generated in organic solvents using stoichiometric amounts of triflic acid and is shown to be synthetically viable for hydride abstraction from Et₃SiH. It is demonstrated that the *para* position on the –C₆F₅ rings is the primary point of attack for decomposition of the cation.

INTRODUCTION

The perfluorinated analogue of the trityl cation (1^+) was first observed in superacidic media¹ independently by Filler² and by Olah³ in the 1960s, generated by protonation of an alcohol precursor (**1OH**, Scheme 1). The stability of 1^+ was limited in oleum, better in “magic acid”, but no salt of the cation could be isolated.



Scheme 1. Generation of trityl cation 1^+ under superacidic conditions.

The electrophilicities of partially fluorinated trityl cations have been studied recently by Mayr and co-workers,^{4,5} but the fully fluorinated analogue was not included. Given the explosion in utility observed for the boron counterpart, trispentafluorophenyl borane,^{6,7} and the availability of new counterions for reactive cations^{8,9} we proposed in a theoretical paper in 2014 that it was time to revisit the fully fluorinated analogue of the trityl cation.¹⁰ We predicted that its fluoride and hydride affinities would be very high, much higher than those of trityl cation and trispentafluorophenyl borane. Stephan and co-workers studied the perfluorinated trityl cation as an extreme Lewis acid showing good correlation between predicted Global Electrophilicity Indexes and Lewis acidity.¹¹

Herein we report on our efforts to observe and isolate cation 1^+ as a triflate or carborane salt in non-superacidic media along with an exploration of its chemistry.

RESULTS AND DISCUSSION

Our initial goal was to prepare a halo derivative of **1OH** for use in halide abstraction routes to form **1⁺**. The starting alcohol **1OH** was initially synthesized by Filler *et al.* by reacting LiC_6F_5 with decafluorobenzophenone.² They reported being unable to synthesize a halogenated derivative. We repeated their synthesis of **1OH** and further verified its structure by X-ray (Figure 1). *Caution: in the course of a routine 2 g synthesis, we experienced an explosion from LiC_6F_5 despite the mixture being held in a dry-ice/ EtOH bath.* We subsequently found that replacing the lithium reagent with the Grignard reagent $\text{BrMg-C}_6\text{F}_5$, generated from Mg metal and $\text{Br-C}_6\text{F}_5$, provides a suitable alternative route to **1OH**, albeit with a somewhat lower yield.

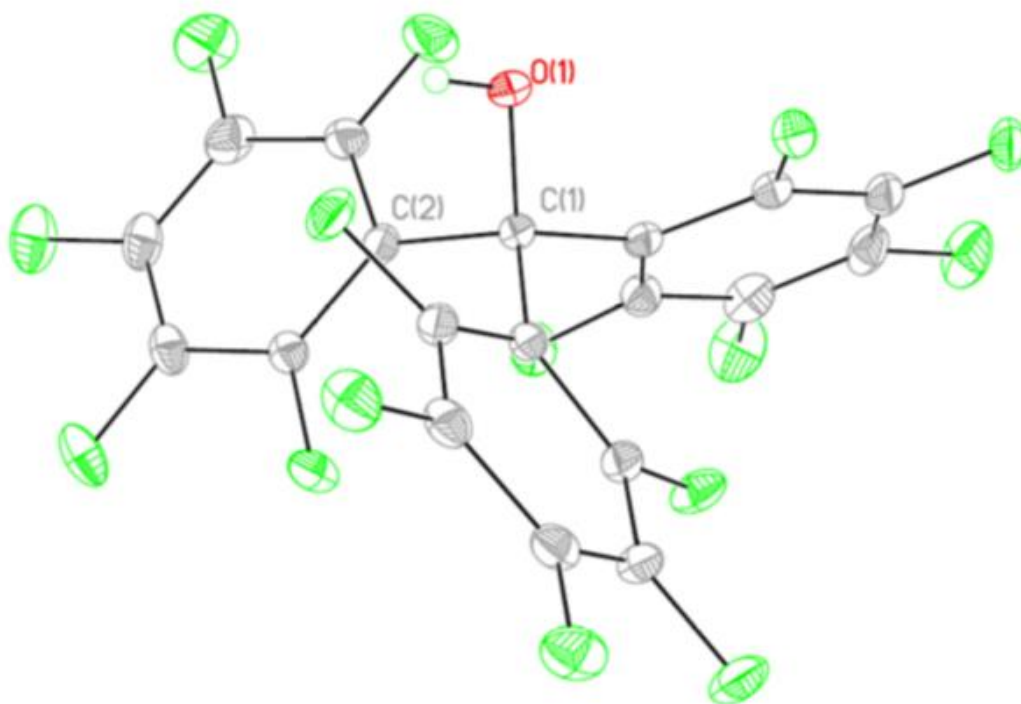


Figure 1. Solid-state structure of **1OH**. Thermal ellipsoids are depicted at the 50% probability level.

In an attempt to form the bromo derivative, **1OH** was reacted with neat acetyl bromide, following the reported procedure for the formation of trityl bromide from trityl alcohol.¹² Fluorine-19 NMR of the reaction mixture and isolated material gave the expected three resonances, shifted from those from **1OH**. However, X-ray studies revealed the presence of the acetate derivative, **1OAc**, rather than the targeted bromide (Figure 2). The ¹H NMR spectrum of the isolated powder contained a singlet, confirming identity of the bulk material with the single crystal.

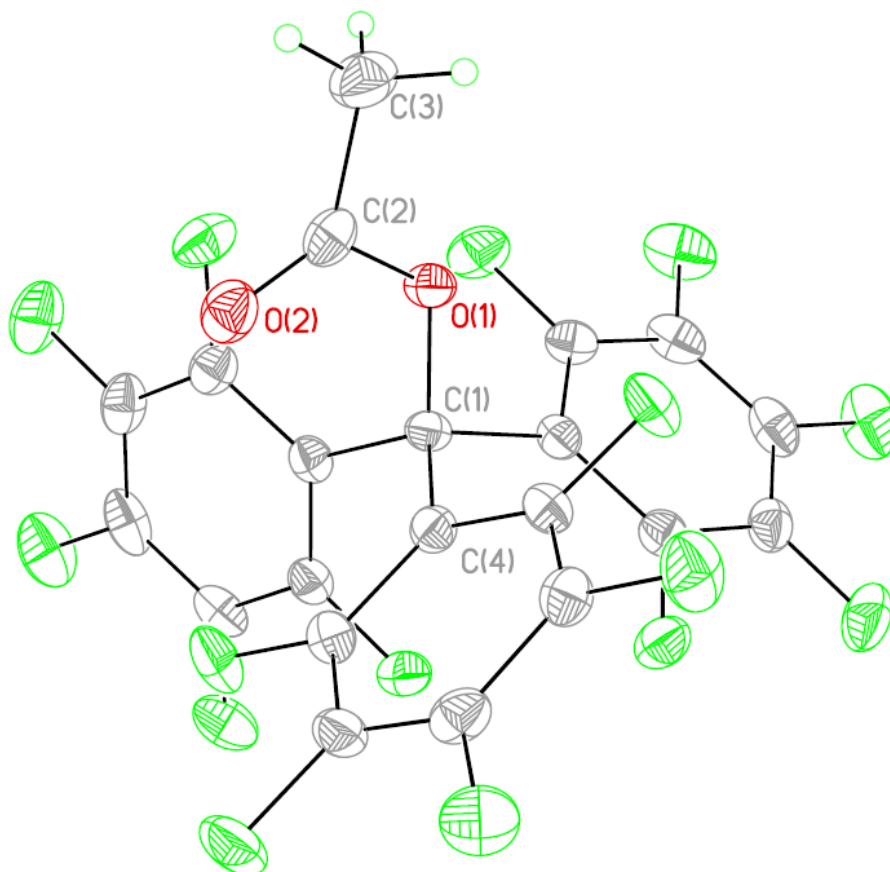
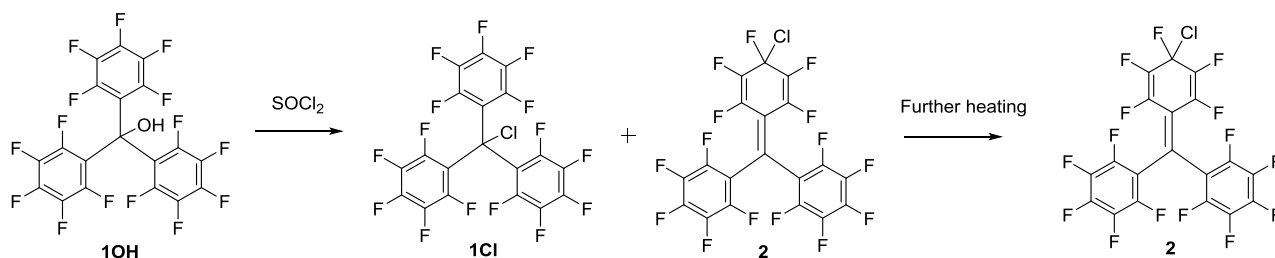


Figure 2. Solid-state structure of **1OAc**. Thermal ellipsoids are depicted at the 50% probability level.

We next used SOCl_2 to form the chloro derivative (Scheme 2). Reaction in *p*-xylene at 142 °C consistently resulted in a crude product showing nine ^{19}F NMR signals. The mixture could be chromatographically separated into two compounds, one showing six signals, the other showing the expected three signals from symmetric $-\text{C}_6\text{F}_5$ groups. X-ray diffraction revealed the latter structure to be the targeted chloroalkane **1Cl** (Figure 3). The former compound, with six ^{19}F signals, was revealed to be chlorinated at the *para*-position with sp^3 hybridized carbon, **2** (Figure 4). Heating **1Cl** to high temperatures results in transformation to **2**, presumably by attack from chlorine onto the *para* position, which is known to be a reactive site on $-\text{C}_6\text{F}_5$ rings with respect to nucleophilic attack.¹³ Efforts to minimize formation of this *para*-substituted isomer through various synthetic modifications (lower reaction temperatures, Vilsmeier-Haack chemistry or alternative chlorinating agents) failed to give better yields of the desired **1Cl**. Indeed, **2** often became the sole product. This suggests product formation is under kinetic control, favoring less sterically hindered attack of the chloride ion at the *para* position. Nevertheless, under milder reaction temperatures (≤ 80 °C approx.) **2** shows significantly reduced solubility relative to the desired chloroalkane, allowing isolation of **1Cl** in reasonable purity.



Scheme 2. Generation of chloro-derivatives **1Cl** and **2**.

Examination of the solid-state contacts in **1Cl** shows that the intermolecular contact for the chloride atom and the *para* carbon position is 3.35 Å, less than the sum of their Van der Waals radii of ~3.5

Å. These are the closest contacts for these atoms, indicative of the Lewis basic nature of the terminal chloride and more importantly, the Lewis acidic nature of the para carbon atom.

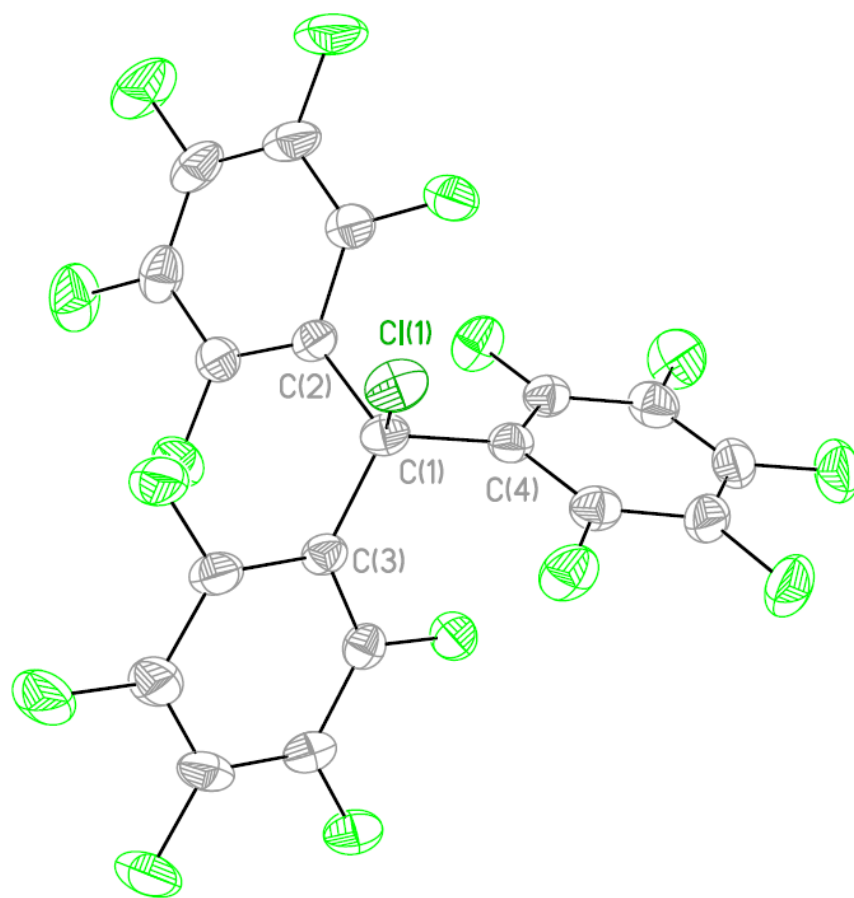


Figure 3. Solid-state structure of **1Cl**. Thermal ellipsoids are depicted at the 50% probability level.

Selected bond distances (Å): C(1)-Cl(1) 1.845(2), C(1)-C(4) 1.538(3).

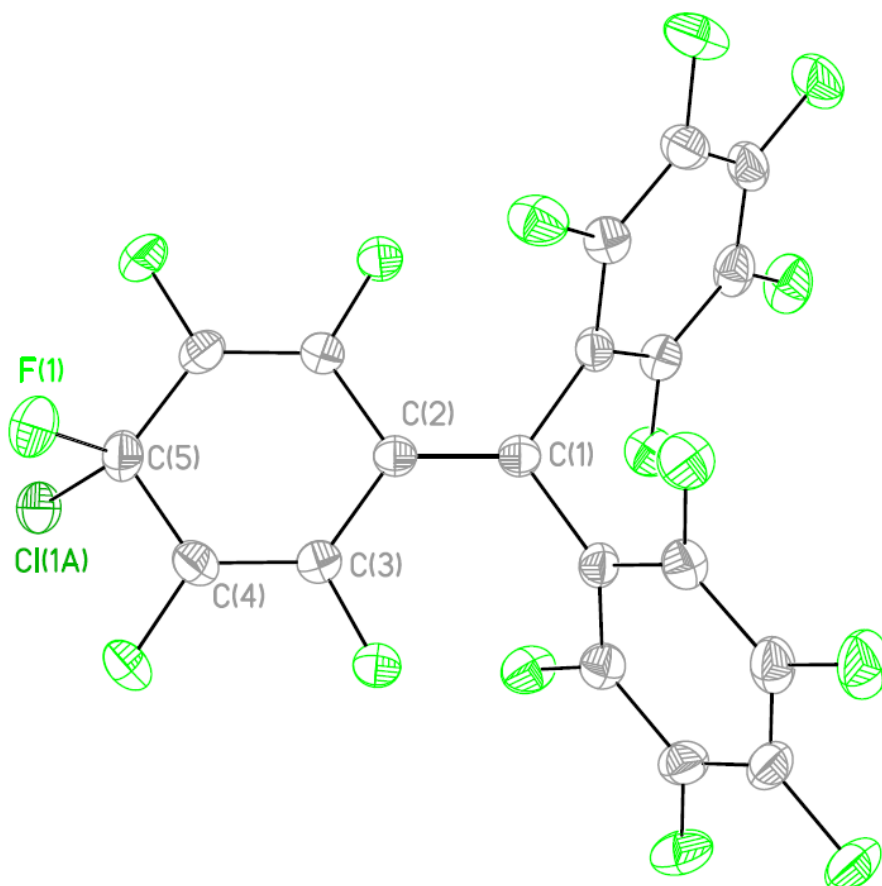
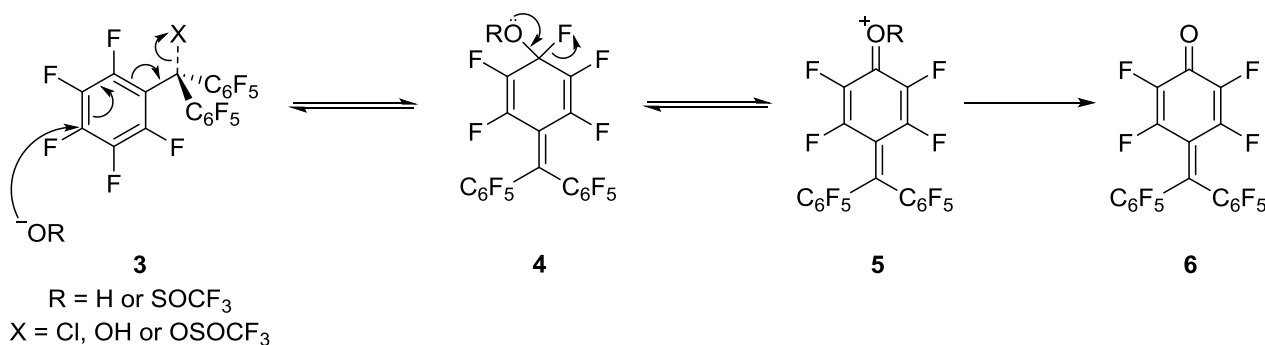


Figure 4. Solid-state structure of **2**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-Cl(1A) 1.727(3), C(5)-F(1) 1.415(5), C(4)-C(5) 1.484(2), C(3)-C(4) 1.327(2), C(2)-C(3) 1.466(2), C(1)-C(2) 1.355(3).

With the requisite chloroalkane in hand, we set about investigating its reaction with various halide abstraction agents. ^{19}F NMR analysis of a 1:1 mixture of **1Cl** and silver triflate (AgOTf) after stirring at ambient temperature for 20 hours in acetonitrile indicated formation of a new species having similar characteristics to the starting material. However, concentration of the colourless reaction mixture resulted in isolation of a new red solid whose ^{19}F NMR showed five new resonances. X-ray analysis revealed this compound to be the dienone **6** (Scheme 3, Figure 5), previously reported from quenching reactions between **1OH** and H_2SO_4 with water.¹⁴ Although

employing stringent anhydrous conditions, we surmised that trace amounts of water lead to its formation. Thus, despite all reasonable efforts to exclude water from the system, we continued to isolate **6** as the sole reaction product. The same outcome was observed when employing a stoichiometric amount of trimethylsilyl triflate (TMSOTf) instead of AgOTf. Attempts at using $\text{Ag}_2[\text{B}_{12}\text{Cl}_{12}]$ as a halide abstraction agent introducing the weakly coordinating $[\text{B}_{12}\text{Cl}_{12}]^{2-}$ anion¹⁵ resulted in no reaction.

A plausible reaction pathway to rationalize this reproducible formation of **6** is proposed in Scheme 3. In solution, chloroalkane **1Cl** undergoes gradual conversion to its *para*-chloro isomer **2** (*vide supra*). Similarly, the kinetically-controlled attack of a nucleophile (in this case, water or triflate anion) at the *para* position of one perfluorinated aryl ring results in formation of alkene **4** through loss of leaving group X. In this case, the leaving group may be a chloride ion or hydroxyl/triflate group (given the appearance of resonances correlating well to the perfluorinated alcohol in crude ^{19}F NMR spectra). Subsequent elimination of F^- yields the more stable conjugated dienone **6** *via* **5**.



Scheme 3. Proposed mechanism for the generation of ketone **6**.

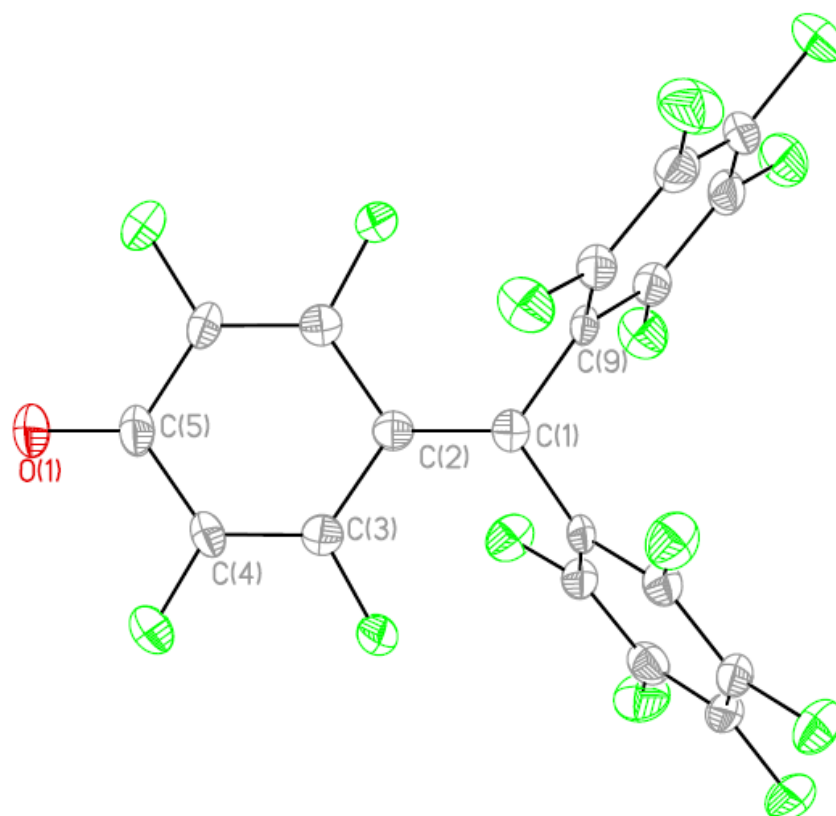
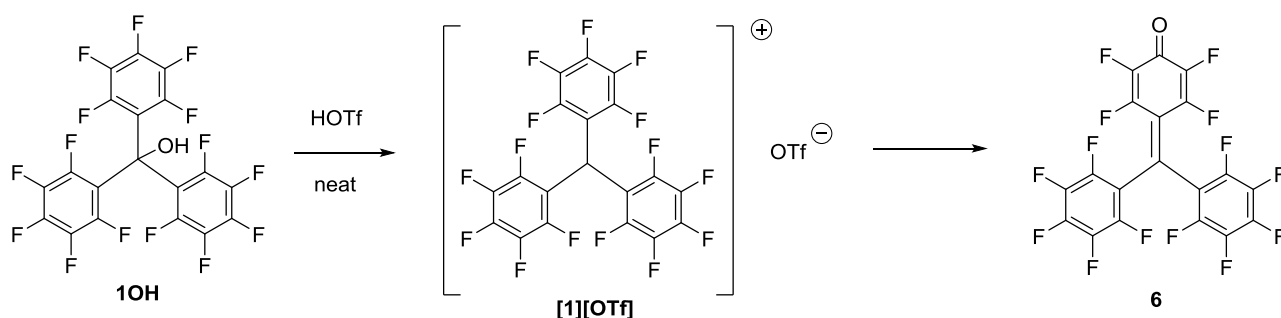


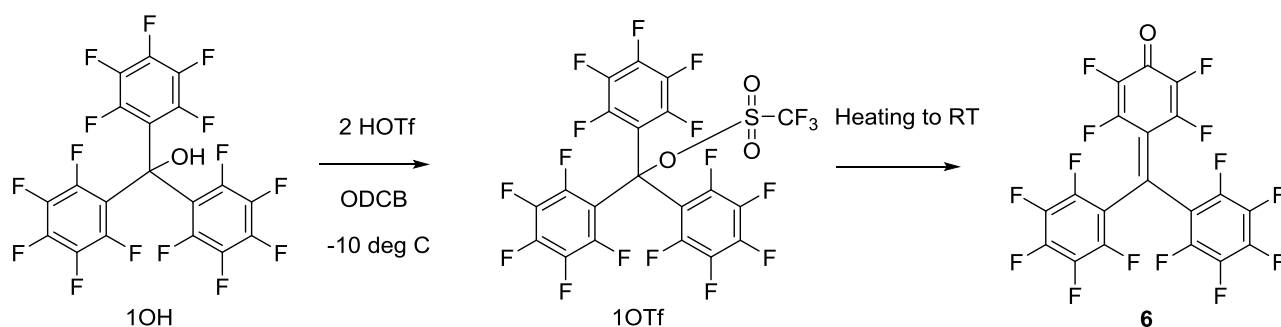
Figure 5. Solid-state structure of **6**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-O(1) 1.214(3), C(4)-C(5) 1.460(2), C(3)-C(4) 1.329(2), C(2)-C(3) 1.462(2), C(1)-C(2) 1.357(3), C(1)-C(9) 1.494(2).

The addition of neat triflic acid to solid **1OH** at -30 °C resulted in immediate generation of a deep maroon solution (Scheme 4). ^{19}F NMR spectroscopy of the solution with the NMR probe set at -30 °C revealed three signals at -115, -128, and -157 ppm. The strongly downfield shift of the *para* and *ortho* fluorine atoms is consistent with the observations of Olah and co-workers for ionized **1**⁺ in strongly acidic media.³ While this cation is stable for at least two hours at -30 °C, warming to room temperature results in decomposition, with ketone **6** being the main product after a sample was held overnight.



Scheme 4. Generation of 1^+ as a triflate salt in neat HOTf and decomposition to **6** upon warming.

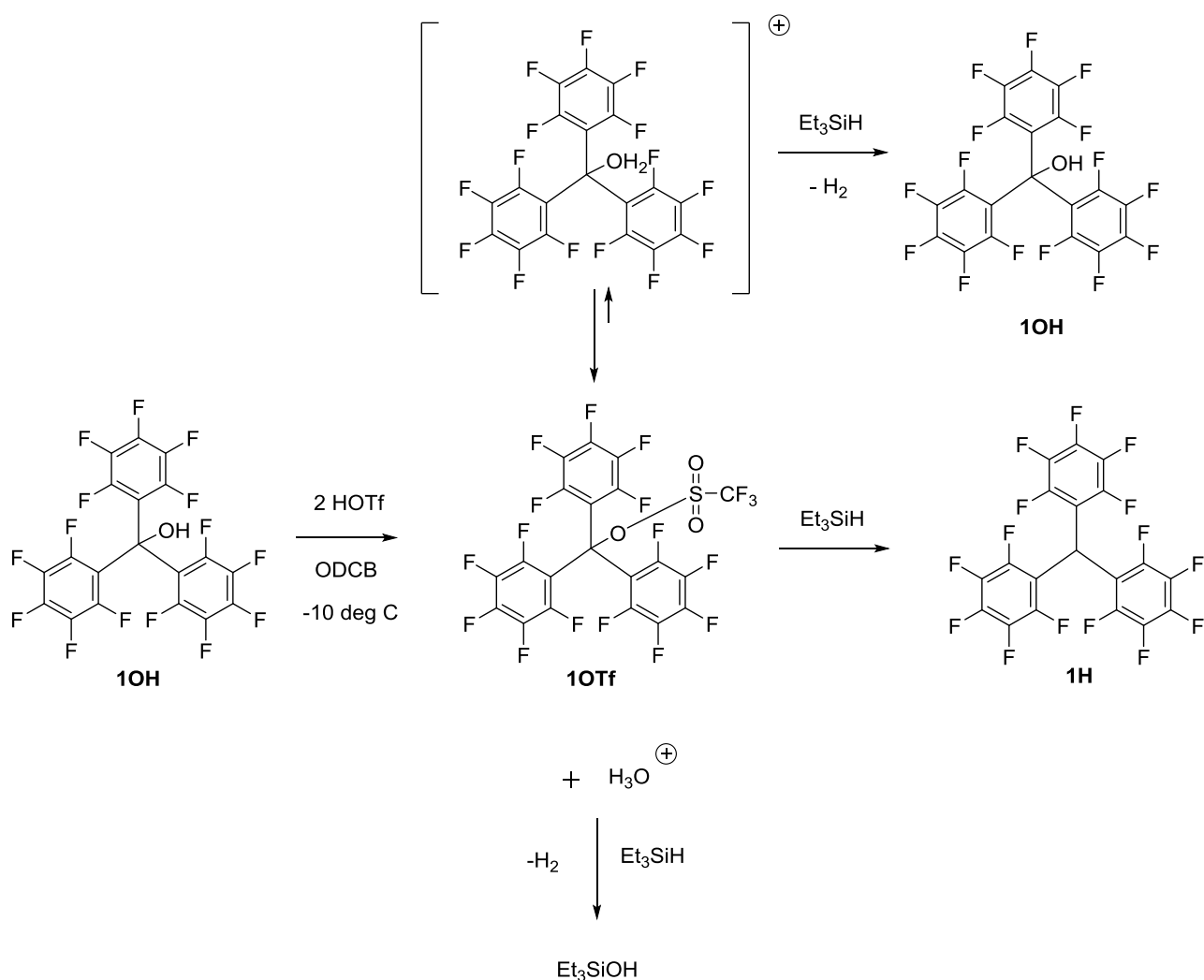
Neat triflic acid is a harsh medium and likely precludes the synthetic use of 1^+ . We therefore explored its formation in organic solvents. Reacting two equivalents of TfOH (one to protonate the alcohol, and the second to sequester the resulting equivalent of H_2O) with **1OH** in *ortho*-dichlorobenzene (ODCB) resulted in the immediate formation of a dark red colored solution (Scheme 5). The ^{19}F NMR spectrum of the reaction mixture at $-10\text{ }^\circ C$ was relatively clean, with three ^{19}F signals at -142.5 , -153.6 , and -162.8 ppm. These signals are distinctly different from those of **1OH** in the same solvent and far upfield to what is consistent with a free cation, as observed with neat triflic acid. Warming to room temperature resulted in decomposition of the mixture to signals consistent with **6** as the main product after 48 hours. The data is consistent with the formation of **1OTf**, with the triflate fragment remaining bound to the carbon centre.



Scheme 5. Generation of **1OTf** and decomposition to **6** upon warming.

To lend support to the proposed formation of **1OTf** and explore its synthetic utility, we explored its ability to act as a hydride acceptor. This is expected behavior, as triflate is an excellent leaving group bound to electron-deficient carbon.

Addition of Et₃SiH as a hydride donor to a solution of **1OTf** prepared from **1OH** and two equivalents of HOTf at -10 °C in *ortho*-dichlorobenzene (Scheme 6), resulted in an NMR spectrum consistent with the presence of two species, one the regenerated alcohol **1OH**, and the other as tris(pentafluorophenyl)methane **1H**.¹⁶ Performing the reaction in toluene at low temperature allowed for simpler isolation of **1H** in a pure form, because toluene is more easily removed under vacuum. We hypothesize that the competing reactions shown in Scheme 6 account for this distribution of products. Nevertheless, the generation of **1H** is supportive of the generation of **1OTf**. The anion is too strongly coordinating to allow ionization to **1**⁺ in low dielectric media.



Scheme 6. Reaction pathways of **1OTf** with hydride donor Et_3SiH .

Carborane anions are much less coordinating than triflate and often allow isolation of extremely reactive cations.⁸ To determine if the *closo*-carborane anion $[\text{HCB}_{11}\text{Cl}_{11}]^-$ might allow isolation of “free” $\mathbf{1}^+$ in non-super acidic media, solid alcohol **1OH** was mixed with two equivalents of solid $[\text{C}_6\text{H}_7][\text{HCB}_{11}\text{Cl}_{11}]$, the protonated benzene salt of the carborane. IR spectroscopy indicated that mixing the two solids did not result in any reaction but the addition of a drop of benzene resulted in the immediate generation of a maroon slurry, followed by immediate evaporation. IR spectroscopy of the resulting solid indicated loss of **1OH**. The vibrations associated with stretching of $\text{C}_{\text{central}}-\text{C}_{\text{ipso}}$ bonds are shifted to lower frequencies ($1604\text{--}1611\text{ cm}^{-1}$) compared to **1OH** (1653 cm^{-1}). For comparison, calculated vibration frequencies using B3LYP-D3(BJ)/def2-TZVPP give $1671\text{--}1678$

cm⁻¹ for **1OH** and 1667 cm⁻¹ for **1**⁺. For comparison, the IR spectrum for the trityl salt of the same carborane anion shows stretches associated with the central-ipso C-C bonds at 1577 cm⁻¹ while the computationally predicted vibration for the trityl cation is found at 1630 cm⁻¹. The blue shift for the perfluorinated compound is likely a result of a stronger C-C bond induced by the π donor ability of the fluorine atoms.

Despite this evidence for the existence of **1**⁺ in the solid state, it does not appear that the cation is stable in low polarity solvents. Although addition of 2 equivalents of [C₆H₇][CHB₁₁Cl₁₁] to a solution of **1OH** in a variety of arene solvents (toluene, benzene, *ortho*-dichlorobenzene) did result in the immediate formation of red solutions, they underwent decolorization within minutes and we were unable to identify any ¹⁹F NMR signals consistent with formation of **1**.

CONCLUSIONS

We have demonstrated that the perfluorinated trityl cation exists in neat triflic acid. In less polar organic solvents it exists with bound triflate but nevertheless shows reactivity as a hydride acceptor with silanes. The free cation appears to exist in the solid state when the counterion is switched to an ultra-inert carborane but intrinsic decomposition prevents its full characterization. It is apparent that the para-carbon position of the -C₆F₅ ring is the Achilles heel of this reactive species.

ASSOCIATED CONTENT

Supporting Information. Experimental details with associated ^1H , ^{19}F , IR spectra of synthesized compounds and reaction mixtures. Computational details and Cartesian coordinates for calculated species. X-ray crystallographic details in .cif format.

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ACKNOWLEDGMENT

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Supporting Information

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1 General Methods

Melting points were determined using a Gallenkamp standard melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker Avance III HD UltraShield Ascend 400 MHz (400.23 MHz) spectrometer using the solvent peak as internal reference (CDCl₃: δ H 7.26 and CD₃CN: δ H 1.94). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), app. t (apparent triplet); coupling constants (J) are in Hertz (Hz). Due to the highly fluorinated nature of all synthesised compounds, which results in extensive carbon-fluorine coupling, ¹³C NMR analysis was not recorded as it provides no distinctive resonances and hence no meaningful data. ¹⁹F NMR spectra were recorded on the previously mentioned instrument at 376.5 Hz. TLC analysis was performed on precoated 60F₂₅₄ slides, and visualised under a UV lamp. Flash chromatography was carried out using silica gel, particle size 0.2-0.063 mm and using the indicated mobile phase as correlated with TLC analysis.

All commercially available compounds were used as provided without further purification. THF, acetonitrile and toluene were dried using an Innovative Technology PureSolv 7 Solvent System and then stored over 3Å molecular sieves under N₂ for 24 hours if more stringent anhydrous conditions were required. *p*-Xylene was dried over CaH₂ overnight, filtered and stored over 3Å molecular sieves for 24 hours prior to use. Anhydrous *ortho*-dichlorobenzene was purchased from Sigma-Aldrich (1 L, lot number SHBH9726) and used as received.

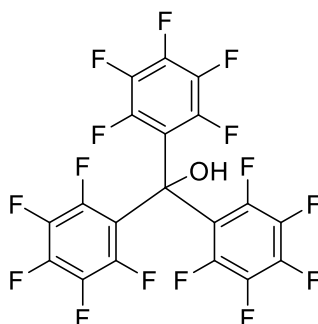
Ag₂[B₁₂Cl₁₂] was prepared according to the procedure employed by Ozerov *et al.*¹

[C₆H₇][CHB₁₁Cl₁₁] was prepared according to the procedure employed by Reed.²

2 Synthesis

Tris(perfluorophenyl)methanol (1OH)

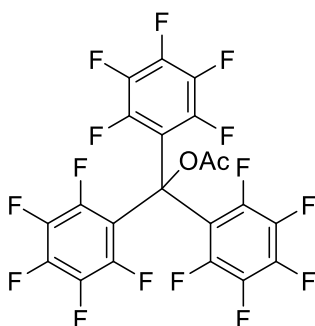
*Note: This compound can be synthesised, as previously described in the literature,³ using bromopentafluorobenzene and *n*-butyllithium to prepare lithium pentafluorobenzene in situ. However, LiC_6F_5 is prone to degrade explosively through elimination of LiF . Despite maintaining a cooling bath temperature of $-75\text{ }^\circ\text{C}$, we have experienced quite a violent explosion when preparing LiC_6F_5 on a 2 g scale. Therefore, we describe a safer, albeit lower yielding, procedure below utilising the more stable Grignard reagent.*



To an oven-dried two-necked 100 mL Schlenk flask equipped with a magnetic stirring bar and reflux condenser was added magnesium (292 mg, 12.0 mmol, 1.2 equiv.). The flask was sealed and evacuated/backflushed with N_2 x 3 before THF (26 mL) was added *via* syringe with stirring. 400 μL bromopentafluorobenzene was then also added *via* syringe and the suspension heated at $35 - 40\text{ }^\circ\text{C}$ (can be done by hand or using a heating bath) until an exotherm was observed. The vessel was then removed from heat and 100 μL aliquots of bromopentafluorobenzene were added periodically up to a total volume of 1.5 mL (12.0 mmol, 1.2 equiv.) over the course of 15 mins. Once addition was complete, the reaction mixture had developed the typical brown colour of a Grignard reagent. It was then heated to reflux for 1 hour before cooling to room temperature and subsequently to $0 - 5\text{ }^\circ\text{C}$ in an ice bath. After stirring on ice for 5 mins, a solution of decafluorobenzophenone (3.62 g, 10.0 mmol, 1.0 equiv.) in THF (7 mL) was added dropwise *via* syringe over 5 mins. No distinctive colour change was observed over the course of the addition. The reaction mixture was allowed to warm back to room temperature before stirring overnight. It was then quenched

through dropwise addition of 6M HCl (10 mL). 25 mL Et₂O was added and, after stirring at room temperature for 2 mins, the layers were separated. The aqueous layer was washed with 2 x 10 mL Et₂O, after which the combined organics were washed with 1 x 10 mL saturated aqueous bicarbonate solution and 2 x 20 mL H₂O. They were then dried over 6 g (~ 2 wts) MgSO₄, filtered and the filter cake washed with 2 x 5 mL Et₂O. The filtrate was concentrated under reduced pressure at 40 °C to obtain an orange oil. ¹⁹F NMR analysis of this oil showed it to be primarily the desired product with small unknown impurities. ¹H NMR analysis also showed residual THF present, which may prevent solidification. Therefore, *n*-hexane (20 mL) was added to the oil, which dissolved, before concentrating again under reduced pressure at 40 °C. Repeating this procedure thrice further yields an orange solid upon final concentration. This solid was covered with ~ 4 mL hexane and cooled to 0 -5 °C for 2 hours. The supernatant was then removed and the solid triturated with a further 2 mL cold hexane. Removing the supernatant once more and drying the solid under reduced pressure at room temperature overnight provided the title compound as a beige solid in 3.42 g (65%) yield. Crystals suitable for X-ray crystallography studies were grown from a concentrated solution of the material in *n*-hexane at -10 °C or *via* slow vapour diffusion from a concentrated CH₂Cl₂ solution into MeCN. M.p. 117 - 118 °C (lit.³ 116.5-117.5 °C). δ_H (400 MHz, CDCl₃): 4.26 (s, 1H). δ_F (376 MHz, CD₃CN): -140.17 (d, *J*_{FF} 18.70), -154.14 (t, *J*_{FF} 21.28), -163.20 (app. t.).

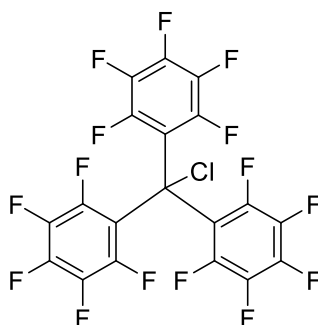
Tris(perfluorophenyl)methyl acetate (**10Ac**)



To a 5 mL round-bottom flask equipped with a magnetic stirring bar was charged tris(perfluorophenyl)methanol (**10H**, 90 mg, 0.17 mmol, 1.0 equiv.) and acetyl bromide (1 mL, 13.5 mmol, 79.4 equiv.). This mixture was refluxed for 16 hours before removing the excess acetyl bromide under reduced pressure at room temperature to give a light yellow

solid. This was purified further by flash column chromatography using *n*-hexane/CH₂Cl₂ (98:2) eluent. After concentrating the relevant fractions under reduced pressure at 40 °C, the title compound was obtained as a light yellow solid in 40 mg (41%) yield. Crystals suitable for X-ray crystallography studies were grown from a concentrated solution of the material in Et₂O at -10 °C. M.p. 152 – 155 °C. δ_{H} (400 MHz, CDCl₃): 2.17 (s). δ_{F} (376 MHz, CDCl₃): -137.90 (d, J_{FF} 19.5), -151.23 (t, J_{FF} 21.0), -160.84 (app. t.).

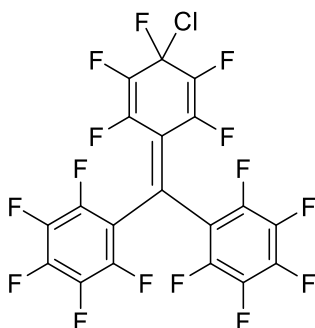
6,6',6''-(chloromethanetriyl)tris(1,2,3,4,5-pentafluorobenzene) (1Cl)



Prior to mixing the reactants, an oil bath was heated to 142.0 °C. Once at temperature, tris(pentafluorophenyl)methanol (**1OH**, 902 mg, 1.7 mmol, 1.0 equiv.) was charged to a 250 mL round-bottom flask equipped with a magnetic stirring bar. *p*-Xylene (60 mL) was added and the solid dissolved readily to form a pale yellow solution. Pyridine (13.7 μ L, 0.17 mmol, 0.1 equiv.) was added *via* micropipette with no change in the appearance of the reaction mixture. Thionyl chloride (9.0 mL, 124.2 mmol, 73.0 equiv.) was then charged in one portion and the flask equipped with a reflux condenser before being placed in the pre-heated oil bath. After approximately 3 mins, reflux was underway and after a further 3 mins the reaction mixture was observed to darken in colour to a pale brown-yellow. After heating for 24 hours, the vessel was allowed to cool to room temperature. The reaction mixture was observed to be orange-yellow at this point. It was concentrated under reduced pressure at 60 °C to obtain a brown-yellow residue that was dried further under hi-vacuum at room temperature. ¹⁹F NMR analysis of this residue showed it to be primarily the desired product with no starting material observed. TLC analysis revealed three primary components of this mixture, each separated by < 0.05 R_F value using a 100% hexane mobile phase. The least polar of these is 6,6'-((4-chloro-2,3,4,5,6-pentafluorocyclohexa-2,5-dien-1-ylidene)methylene)bis(1,2,3,4,5-pentafluorobenzene) (*para*-chloro isomer, **2**), while the most polar is a mix of 1-

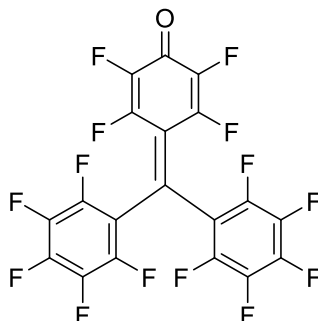
(chloromethyl)-4-methylbenzene and 1-(dichloromethyl)-4-methylbenzene, presumably formed through chlorination of the *p*-xylene solvent under the harsh reaction conditions. The middle spot is the desired product. To the crude material (crude weight: 1.67 g) was therefore charged 4 mL hexane to form a suspension which was filtered to remove the less soluble *para*-chloro isomer **2**. After concentrating the filtrate, the resulting residue was purified *via* flash column chromatography using a column 4 cm (d) x 33 cm (h) and 100% hexane as the eluent. Collecting ~12 mL fractions, the desired product eluted in fractions 29 – 37. Concentration of these fractions under reduced pressure at 40 °C followed by drying further under hi-vacuum at room temperature provided the title compound as a pale yellow solid in 337 mg (36%) yield. Crystal suitable for X-ray crystallography studies were grown from a concentrated solution of the material in CH₂Cl₂ at -10 °C or *via* slow vapour diffusion from a concentrated *n*-hexane solution into toluene. M.p. 104 - 106 °C. δ_F (376 MHz, CDCl₃): -135.50 (d, J_{FF} 18.29), -150.07 (app. t.), -160.38 (app. t.).

6,6'-((4-chloro-2,3,4,5,6-pentafluorocyclohexa-2,5-dien-1-ylidene)methylene)bis(1,2,3,4,5-pentafluorobenzene) (2)



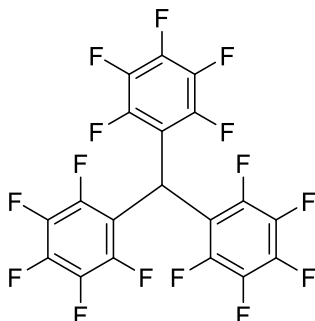
The title compound was isolated as described above as a white solid (yield not determined). Crystals suitable for X-ray crystallography studies were grown from a concentrated solution of the material in Et₂O at -10 °C. M.p. 204 – 205 °C. δ_F (376 MHz, CDCl₃): -104.72 (app. t), -139.42 (app. t), -145.65 (d, J_{FF} 33.24), -146.34 (s), -149.07 (app. t), -160.26 (s).

4-(bis(perfluorophenyl)methylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dien-1-one (6)



This compound was isolated as part of studies conducted into the reaction between tris(perfluorophenyl)methanol and methanesulfonic acid. To a 25 mL Schlenk flask equipped with a magnetic stirring bar was charged tris(perfluorophenyl)methanol (**1OH**, 59 mg, 0.11 mmol, 1.0 equiv.). The flask was sealed and evacuated/backflushed with N₂ x 3. Neat methanesulfonic acid (1.0 mL, 15.4 mmol, 140.0 equiv.) was added *via* syringe to form a suspension that was sonicated for 5 mins to disperse the solid. The flask was then equipped with a reflux condenser under a positive N₂ flow and the reaction mixture heated at 75.0 °C for 20 hours. Upon cooling, the reaction mixture was dark red with a solid present. This solid was filtered and washed with H₂O before pulling dry to give the title compound as a light tan solid in undetermined yield. Crystals suitable for X-ray crystallography studies were grown from a concentrated solution of the material in CH₂Cl₂ at -10 °C. δ_F (376 MHz, CDCl₃): -130.03 (s), -139.15 (d, J_{FF} 18.97), -147.05 (app. t), -147.45 (s), -159.38 (app. t).

Tris(perfluorophenyl)methane (1H)



Note: This compound was prepared in toluene rather than 1,2-dichlorobenzene due to the high boiling point of 1,2-dichlorobenzene (180.5 °C), which makes it difficult to remove during work-up.

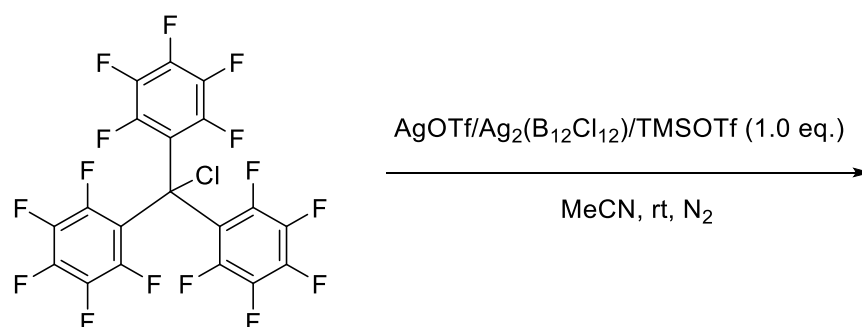
To an oven-dried 10 mL Schlenk flask equipped with a magnetic stirring bar was added tris(perfluorophenyl)methanol (**1OH**, 100 mg, 0.19 mmol, 1.0 equiv.). The flask was sealed and evacuated/backflushed with N₂ x 3. Toluene (2.0 mL, 20 vol.) was charged *via* syringe. The solid dissolves readily, forming a beige solution. The vessel was then cooled to -84 °C in a liquid N₂/EtOAc bath and stirred for 10 mins. Triflic acid (33.6 µL, 0.38 mmol, 2.0 equiv.) was then added under a positive flow of N₂ *via* micropipette. The reaction mixture turns a deep red immediately and solid of the same colour is seen to precipitate (some of which clumps together). This suspension was stirred at -84 °C for 2 mins before triethylsilane (60.8 µL, 0.38 mmol, 2.0 equiv.) was added under a positive flow of N₂ by micropipette. The colour of the reaction mixture lightens immediately to beige-orange, although some of the red solid remains clumped together. The vessel was allowed to warm naturally over the course of 1 hour before removing the cooling bath and allowing it to warm further to room temperature over a further 15 mins. The reaction mixture was then concentrated under reduced pressure at room temperature to obtain a beige solid which was dissolved in CH₂Cl₂ (5 mL). The resulting solution was washed with saturated aqueous bicarbonate solution (2 mL). After allowing the mixture to settle, it was charged to a separating funnel where good separation was observed between the layers. The organic layer was removed and the aqueous layer washed with CH₂Cl₂ (2 mL). The combined organic layers were then dried over 200 mg

MgSO₄ (2 wts) before filtering and washing the filter cake with 1 x 1 mL CH₂Cl₂. The filtrate was then concentrated under reduced pressure at 40 °C to obtain a beige solid which was dried further under hi-vacuum at room temperature. The vessel was then cooled to 0 – 5 °C in an ice/water bath and triturated with 400 µL cold hexane. The solid was then dried further under reduced pressure at 40 °C before sampling for NMR spectroscopy (CDCl₃, 10 mg/mL). ¹⁹F NMR showed the presence of two separate, symmetrical perfluorinated aromatic compounds, one of which corresponded to tris(perfluorophenyl)methanol. ¹H NMR showed a resonance at 6.22 ppm and tris(perfluorophenyl)methanol at 4.26 ppm. The presence of triethylsilane was also observed. The crude material was allowed to dry at room temperature under reduced pressure overnight before being sampled again for NMR analysis. ¹⁹F revealed no change, but ¹H showed the triethylsilane to have been removed while the resonances at 6.22 ppm and 4.26 ppm remained. The material was then purified further by flash column chromatography using a 97.5:2.5 hexane/EtOAc eluent (column radius: 0.75 cm, column height: 18 cm). 6 mL fractions were collected. The compound of interest eluted in fractions 2 – 4, which were then concentrated under a stream of N₂ before drying further under hi-vacuum at room temperature to provide tris(perfluorophenyl)methane as a white solid in 23 mg (24%) yield. M.p. 159 – 160 °C (lit.⁴ 158 – 159.5 °C). δ_H (400 MHz, CDCl₃): 6.22 (s, 1H). δ_F (376 MHz, CDCl₃): -141.54 (d, *J*_{FF} 19.56), -152.30 (app. t), -160.74 (t, *J*_{FF} 18.10).

3 General Procedures

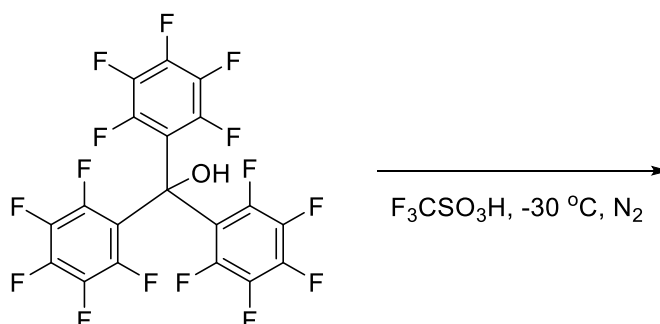
Note: all reactions involving non-acidic reagents were conducted in an N₂-filled glovebox.

Treatment of chloroalkane with halide abstraction agents



To a 20 mL vial equipped with a magnetic stirring bar was charged 6,6',6''-(chloromethanetriyl)tris(1,2,3,4,5-pentafluorobenzene) (**1Cl**, 50 mg, 0.091 mmol, 1.0 equiv.) and the relevant solid halide abstraction agent (AgOTf/Ag₂[B₁₂Cl₁₂], 0.091 mmol, 1.0 equiv.). This mixture was then suspended in acetonitrile (1.0 mL, 20 vol). In reactions utilising TMSOTf, this was then charged *via* micropipette in one portion. The vessel was sealed and stirred at room temperature. ¹⁹F NMR analysis of the crude reaction was performed by removing 250 μL of the reaction mixture and diluting with 250 μL CD₃CN.

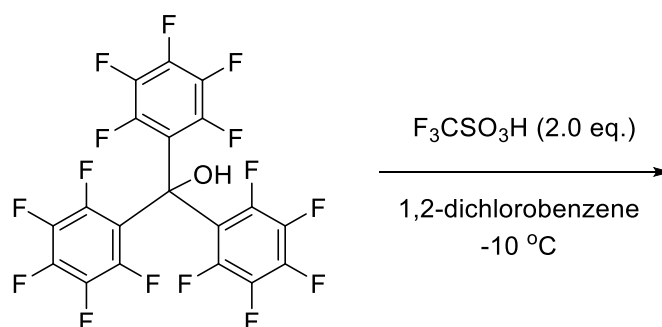
Reaction of tris(perfluorophenyl)methanol in neat triflic acid



To an NMR tube was charged triflic acid (1.0 mL) before sealing and cooling the tube to -30 °C. It was allowed to equilibrate for 10 mins. Tris(perfluorophenyl)methanol (**1OH**, 50 mg,

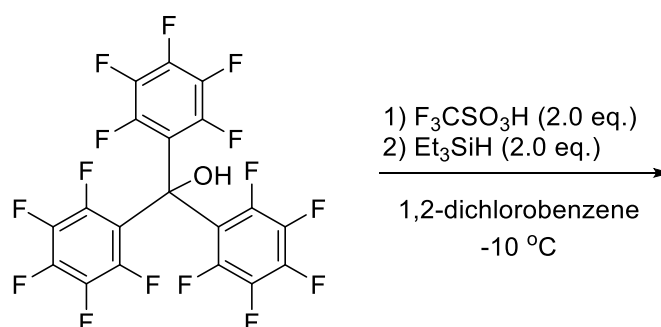
0.095 mmol,) was then charged in one portion. The reaction mixture turned from colourless to deep red immediately. It was agitated lightly by hand to ensure homogeneity before being allowed to stand at -30 °C for 10 mins. It was then analysed by ^{19}F NMR (neat) at -30 °C.

Reaction of tris(perfluorophenyl)methanol with triflic acid in 1,2-dichlorobenzene at -10 °C



To an NMR tube was charged tris(perfluorophenyl)methanol (**1OH**, 25 mg, 0.047 mmol, 1.0 equiv.) and 0.5 mL 1,2-dichlorobenzene (0.5 mL) to form a pale yellow solution. This was then cooled to -10 °C and allowed to equilibrate for 10 mins. Triflic acid (8.3 μL , 0.094 mmol, 2.0 equiv.) was then charged *via* micropipette in one portion. The pale yellow solution immediately turned a very deep red and was homogenous. The sample was subsequently analysed by ^{19}F NMR at -10 °C, which revealed the presence of a new symmetrical species (see NMR spectral data below). Upon allowing the sample to warm to ambient temperature and re-analysing by ^{19}F NMR, the resulting spectrum showed a complex mixture of resonances. Allowing the sample to stand at room temperature for 2 days and subsequently re-analysing by ^{19}F NMR revealed five primary aromatic resonances indicating degradation to the dienone **6**.

Reaction of tris(perfluorophenyl)methanol with 1) triflic acid and 2) triethylsilane in 1,2-dichlorobenzene at -10 °C



Tris(perfluorophenyl)methanol (**1OH**, 100 mg, 0.19 mmol, 1.0 equiv.) was charged to a 10 mL Schlenk flask equipped with a magnetic stirring bar. The flask was sealed and evacuated/backflushed with N₂ x 3. 1,2-dichlorobenzene (2.0 mL) was then charged *via* syringe to form a pale yellow solution which was then cooled to -10 °C and allowed to equilibrate for 10 mins with stirring. Triflic acid (33.6 μL, 0.38 mmol, 2.0 equiv.) was then charged dropwise *via* micropipette under a positive flow of N₂. The pale yellow solution immediately turned deep red and was homogenous. This mixture was stirred at -10 °C for 10 mins before triethylsilane (60.7 μL, 0.38 mmol, 2.0 equiv.) was charged dropwise *via* micropipette under a positive flow of N₂. The red colour of the reaction began to fade and gradually becomes orange/beige. However, a gummy red residue formed down the bottom of the flask which trapped the magnetic stirring bar and caused stirring to halt. The flask was therefore agitated by hand for ~ 5 mins to achieve homogeneity, by which point the red colour had disappeared and the stirring bar had loosened again. The reaction mixture was then stirred at -10 °C for 90 mins before sampling for ¹⁹F NMR analysis (neat). The resulting spectrum revealed the presence of tris(perfluorophenyl)methanol **1OH** and tris(perfluorophenyl)methane **1H** as the primary components of the mixture (see NMR spectral data below).

Protonation of tris(perfluorophenyl)methanol by [C₆H₇][CHB₁₁Cl₁₁]

The described manipulations and characterization via FT-IR were carried out in dry-boxes (H₂O, O₂ < 0.5 ppm) at room temperature. ATR-FT-IR characterization was carried out using an ABB MB3000 spectrometer in the 4000 – 525 cm⁻¹ frequency range using a diamond crystal. In a solvent free method of protonation, a 1 dram vial containing a teflon stir bar was

charged with approx. 30.0 mg freshly prepared $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$, and either approx. 26.5 or 13.2 mg **1OH** (0.05 mmol, 1.0 equiv.; or 0.025 mmol, 0.5 equiv.). The solids were allowed to thoroughly mix by stirring with no solvent added. Analysis of the solid suggests protonation of **1OH** was unsuccessful by this method indicated by the presence of the CH_2^+ symmetric stretch at approx. 2780 cm^{-1} . The second method of protonation considered the first method with **1OH** mixed with $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ in 1:1 and 1:2 ratios while mixing in approx. 0.5 mL of benzene. Partial dissolution of the solids was observed with a blue color persisting for minutes. Removal of volatiles under vacuum yielded a dark solid that appears stable at low temperature ($-38.5\text{ }^\circ\text{C}$). ATR-FT-IR analysis shown in Figures S2 and S3 suggests the presence of unreacted $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$, **1OH** (minimal), and a new material, potentially the perfluorotrityl cation, based on a comparative analysis to $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ described in Figure S4. Reactions between **1OH** and $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ in a 1:2 ratio mixing in toluene or 1,2-dichlorobenzene resulted in a maroon or green solution, respectively, though as above, the color persisted for only a short time in solution. Small plate-like crystals were obtained via slow cooling, though attempts to obtain diffraction data of the crystal proved unsuccessful during mounting.

4 Infrared data

Figure S1: tris(perfluorophenyl)methanol (**1OH**)

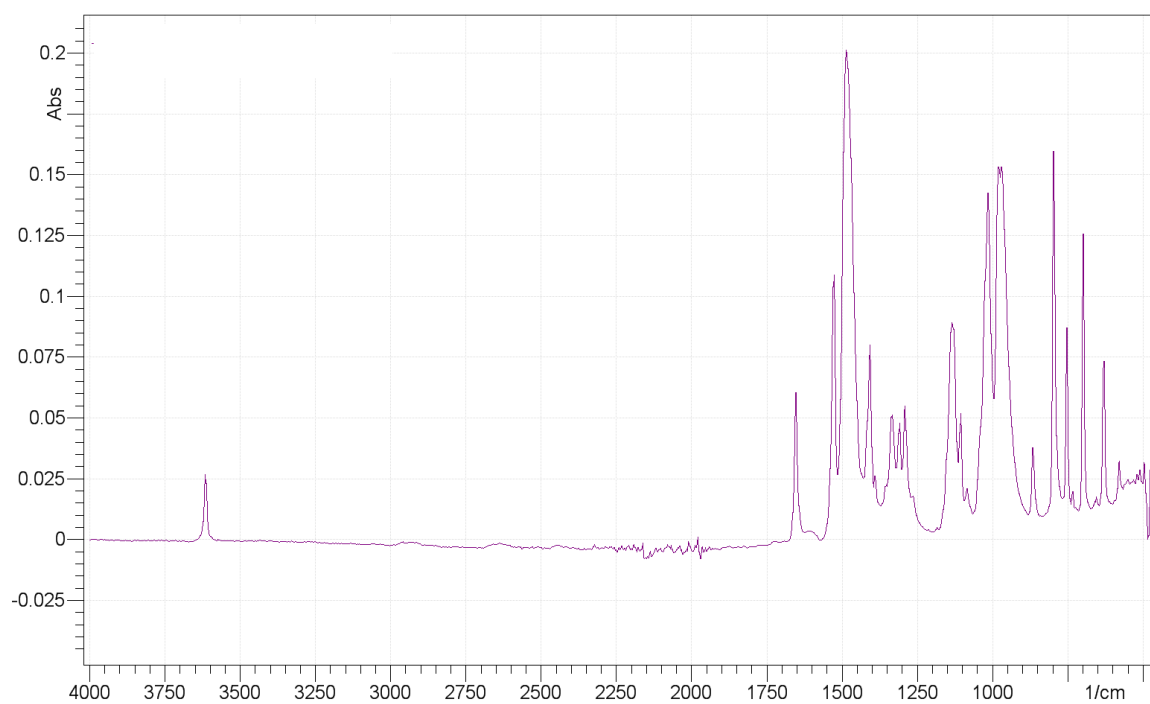


Figure S2: Rxn of tris(perfluorophenyl)methanol (**1OH**) + $[C_6H_7][CHB_{11}Cl_{11}]$ in benzene followed by evaporation

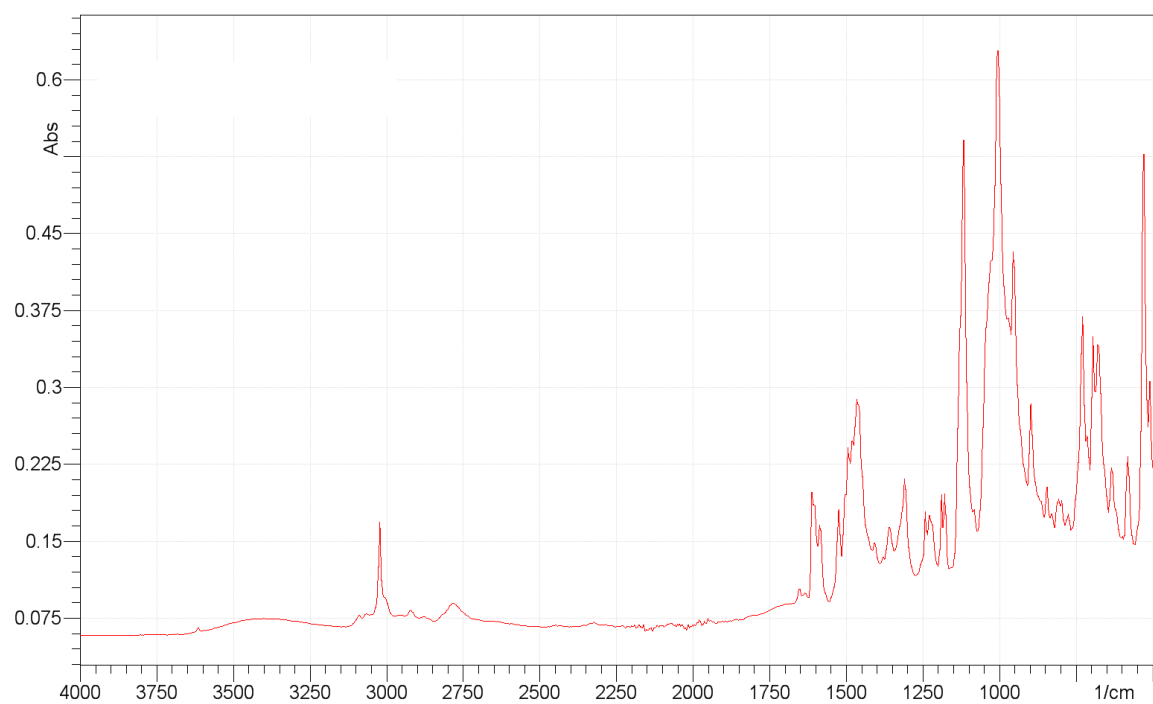


Figure S3: Expanded region of 1250 to 1700 cm^{-1} for overlay of FT-IR spectra for **1OH** (purple), $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ (blue), rxn of 1OH and $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ prior to solvent inclusion (black) and rxn of 1OH and $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ after mixing in benzene and subsequent evaporation (red).

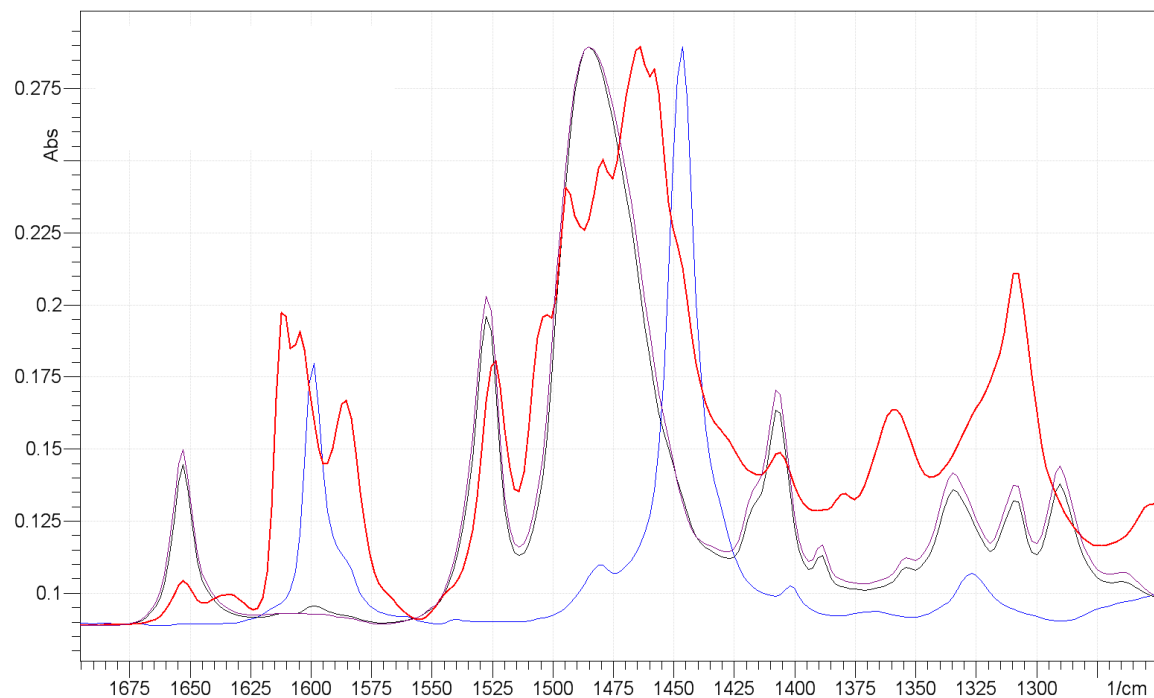
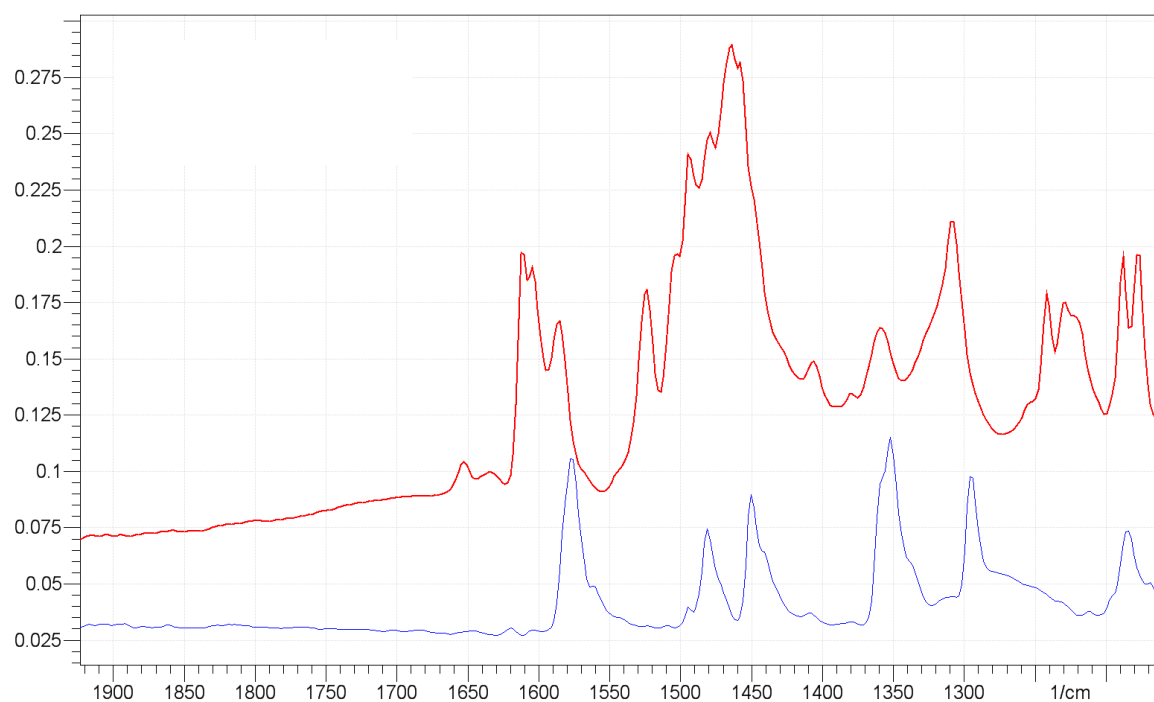


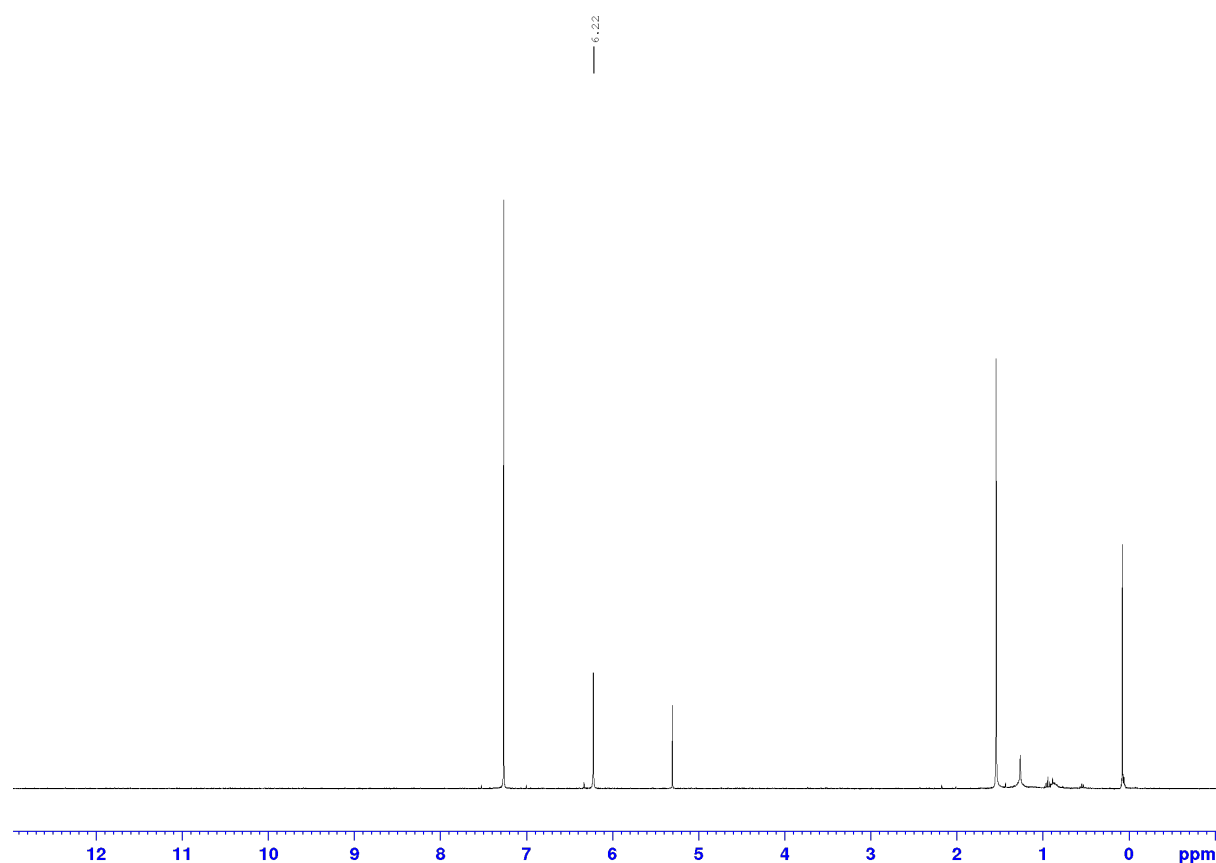
Figure S4: Expanded region of 1250 to 1900 cm^{-1} for overlay spectra of FT-IR for **1OH** mixed with $[\text{C}_6\text{H}_7][\text{CHB}_{11}\text{Cl}_{11}]$ after addition of benzene and subsequent evaporation (red). Known sample of $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ (blue).



5 ^1H NMR data for tris(perfluorophenyl)methane

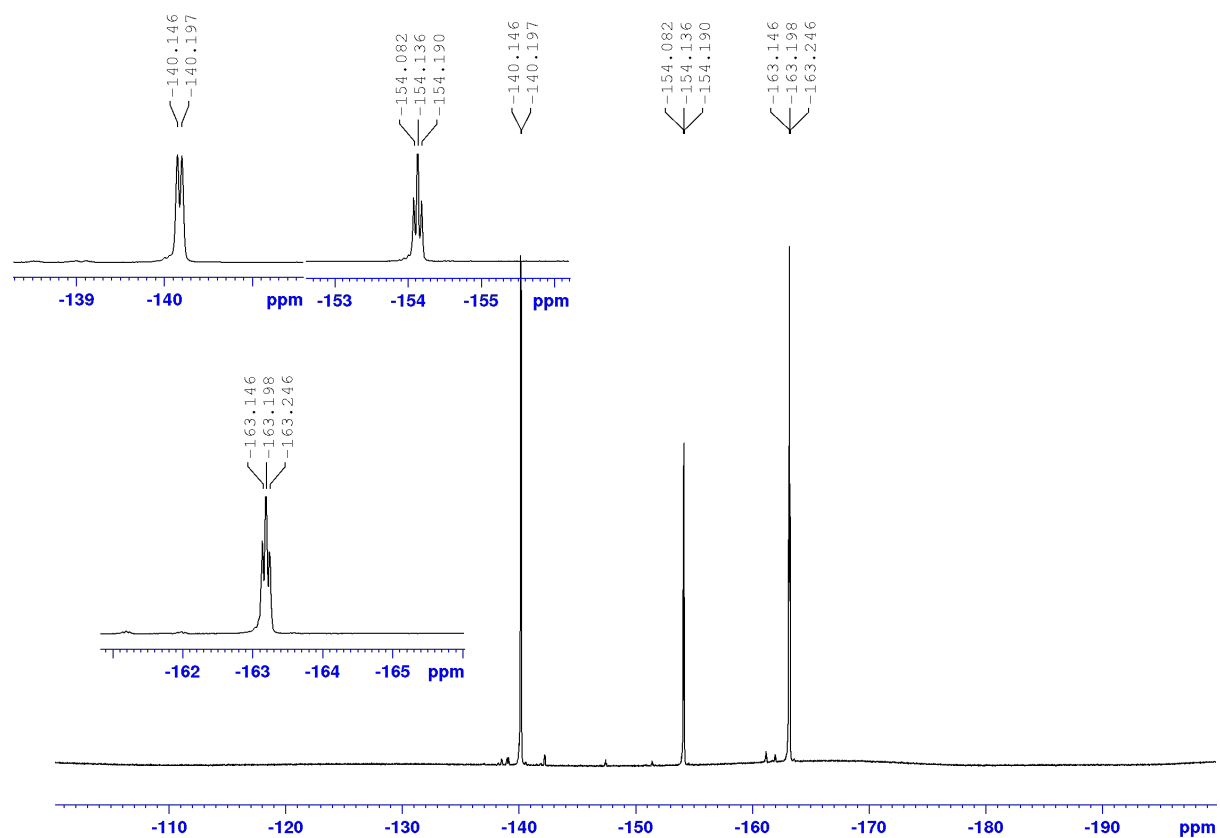
Note: the high molecular mass of tris(perfluorophenyl)methane and the fact that it contains only one proton means the resonance signal is very weak relative to the mass of material used to prepare a sample for NMR analysis. Trace impurities and residual solvents therefore appear much more prominent than is actually the case.

Tris(perfluorophenyl)methane (1H)

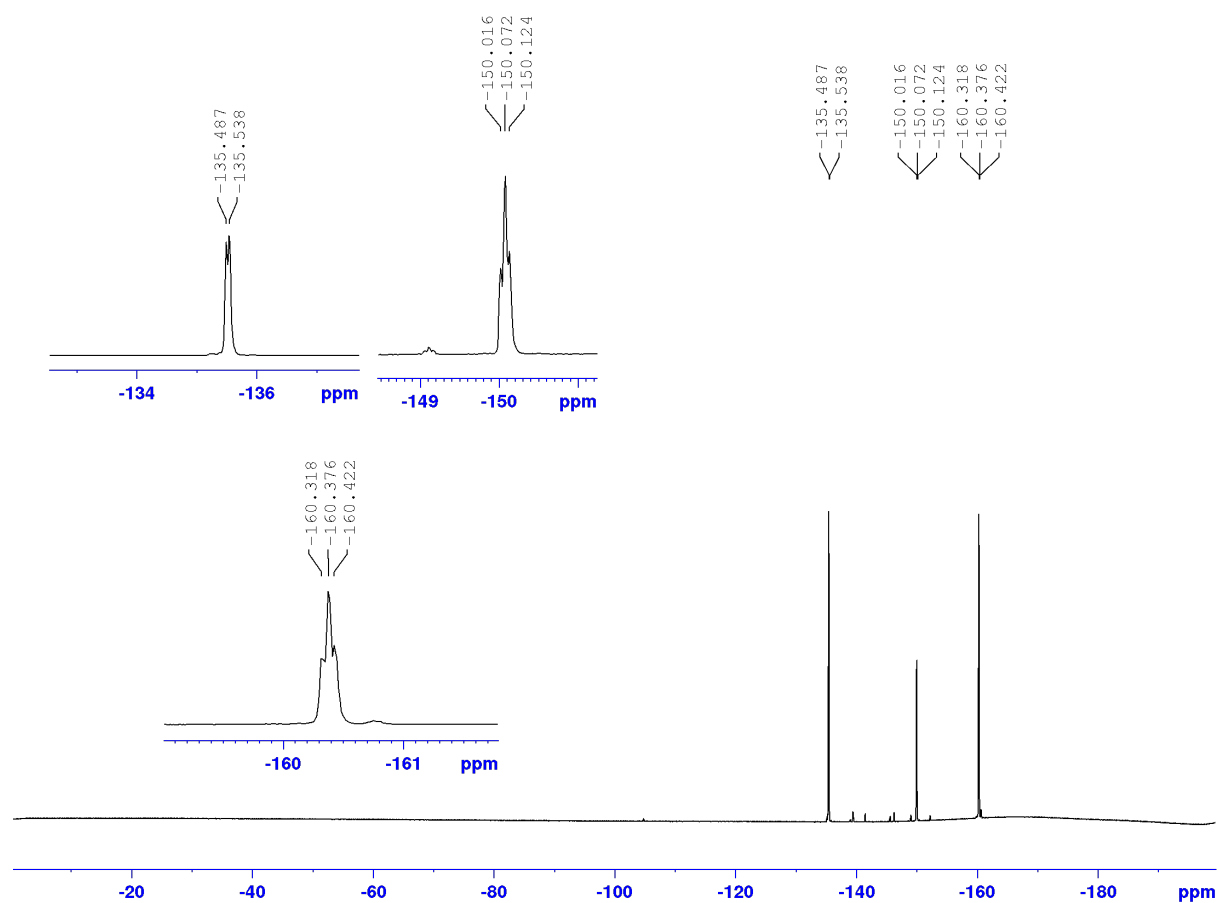


6 ^{19}F NMR data

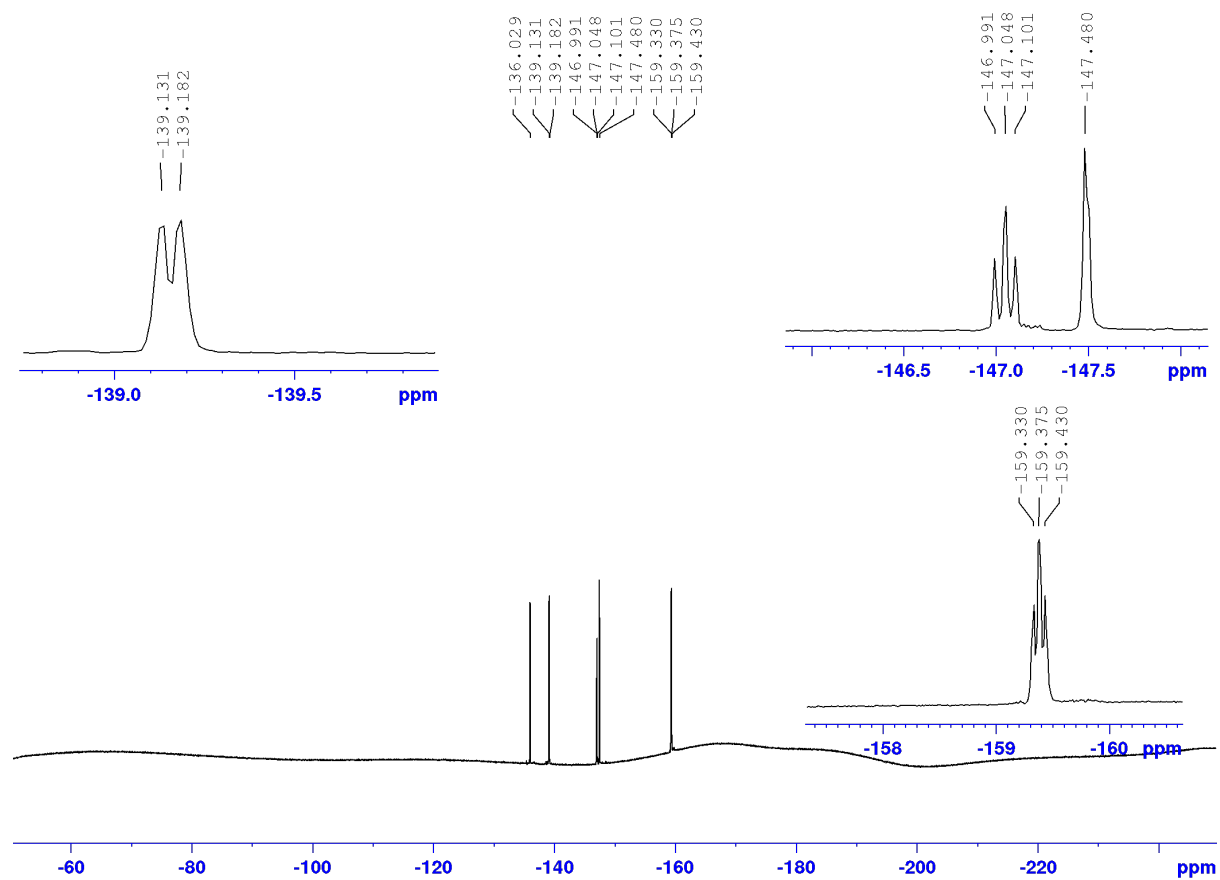
Tris(perfluorophenyl)methanol (10H)



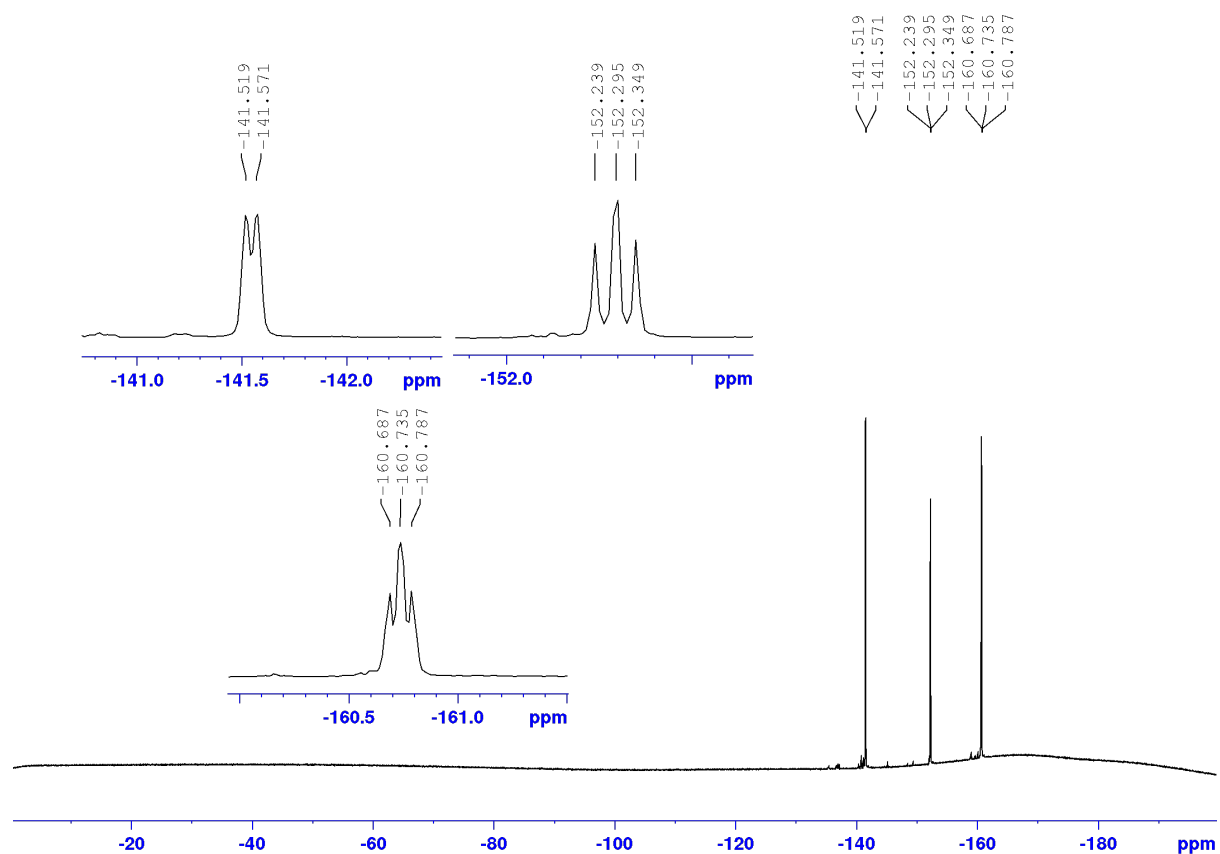
6,6',6''-(chloromethanetriyl)tris(1,2,3,4,5-pentafluorobenzene) (1Cl)



4-(bis(perfluorophenyl)methylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dien-1-one (2)

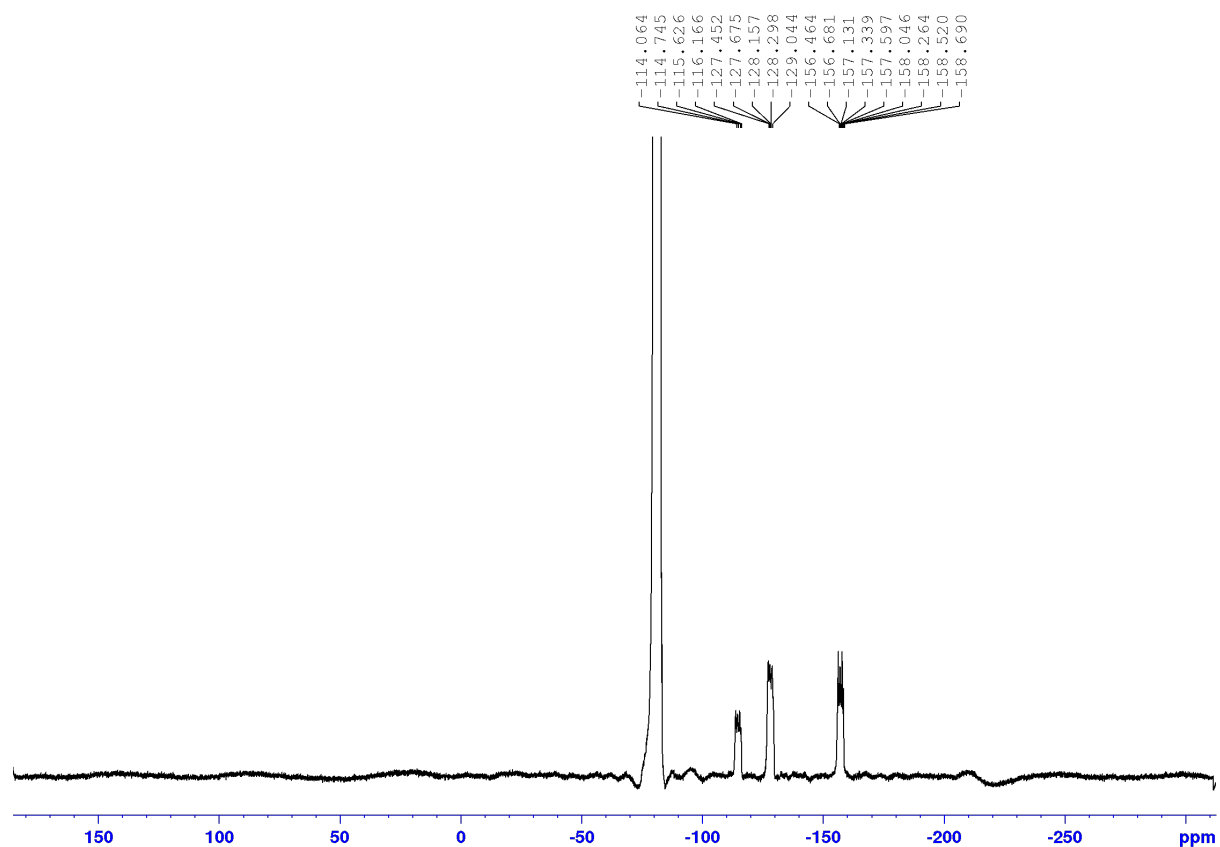


Tris(perfluorophenyl)methane (1H)



Reaction of tris(perfluorophenyl)methanol in neat triflic acid @ - 30 °C

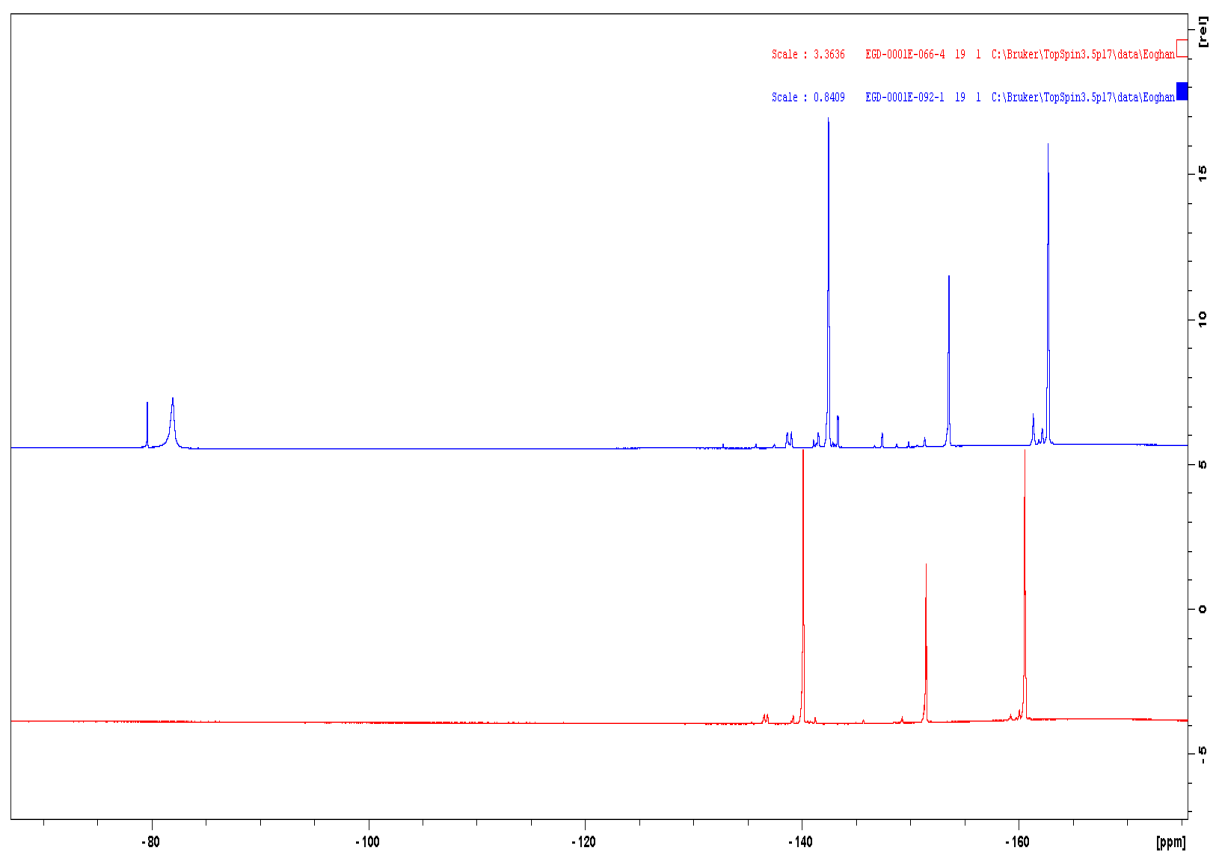
Note: this spectrum has been further baseline corrected post-automatic processing.



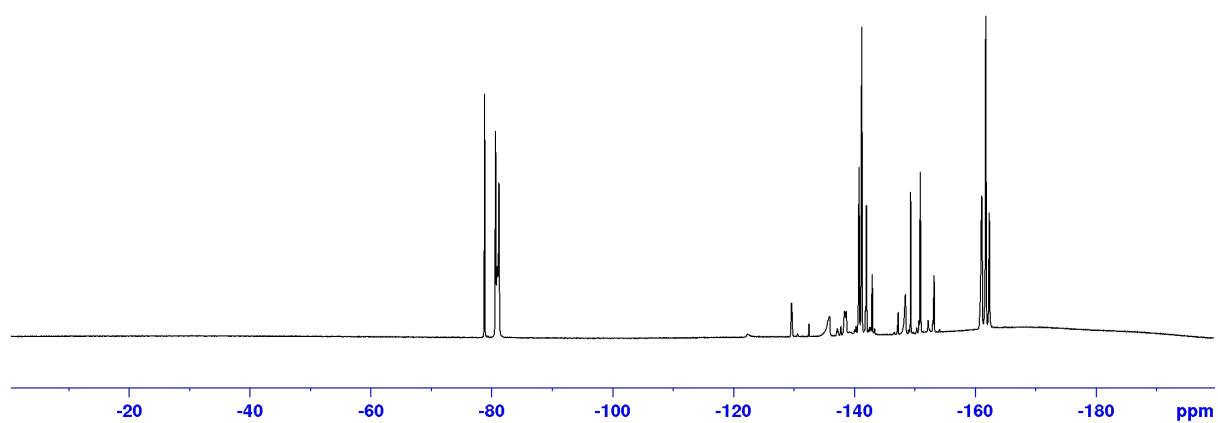
Reaction of tris(perfluorophenyl)methanol with triflic acid in 1,2-dichlorobenzene @ -10 °C

Blue = crude reaction mixture

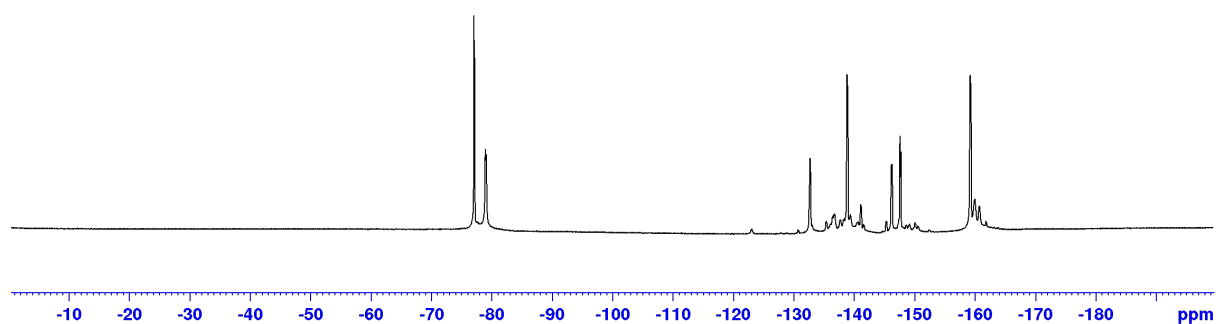
Red = tris(perfluorophenyl)methanol in 1,2-dichlorobenzene



After warming the above sample to ambient temperature and analysing immediately



Above sample after standing at room temperature for 2 days



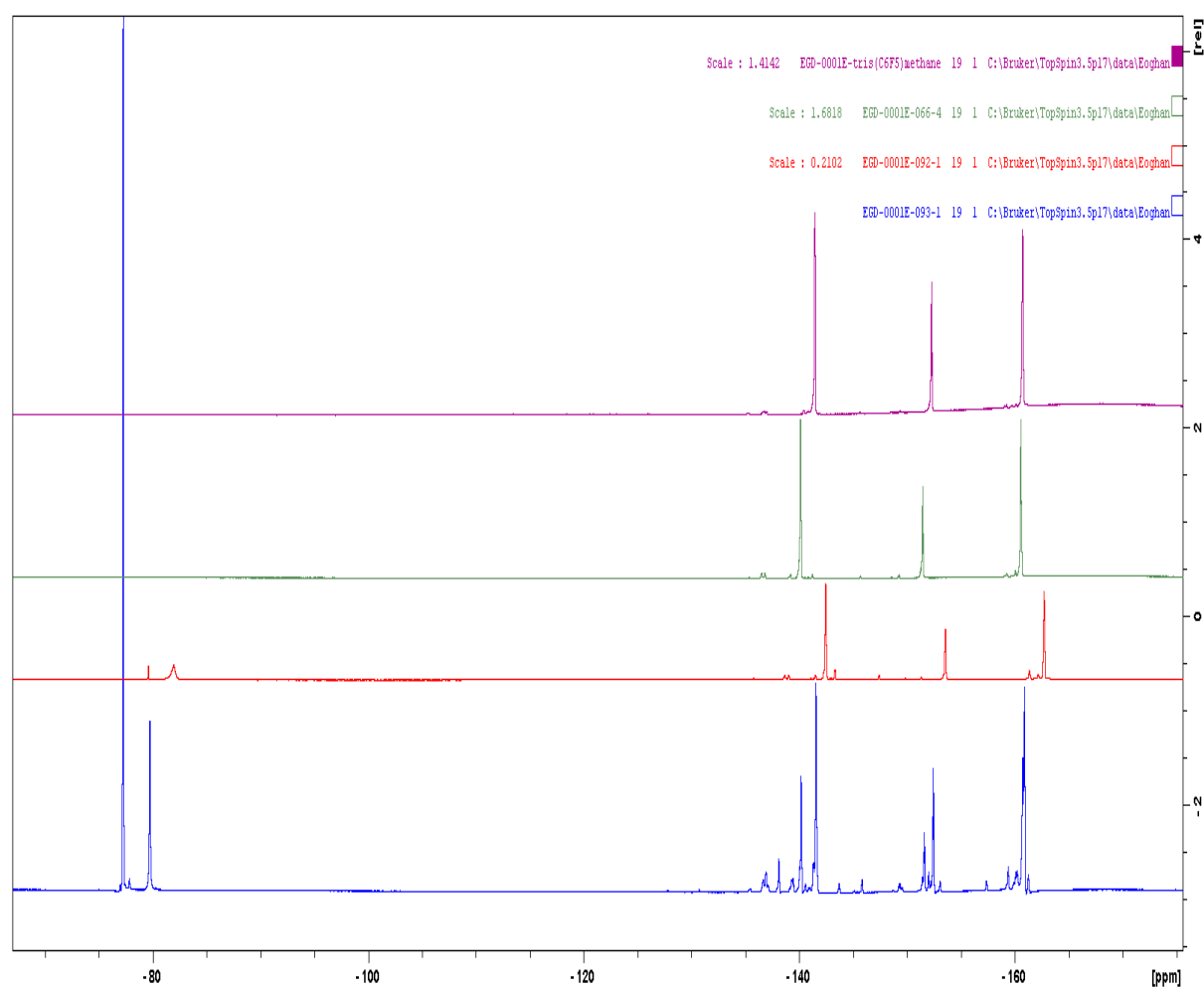
Reaction of tris(perfluorophenyl)methanol with 1) triflic acid and 2) triethylsilane in 1,2-dichlorobenzene @ -10 °C

Blue = crude reaction mixture after Et₃SiH addition

Red = crude reaction mixture before Et₃SiH addition

Green = tris(perfluorophenyl)methanol in 1,2-dichlorobenzene

Purple = tris(perfluorophenyl)methane in 1,2-dichlorobenzene



7. Computational Methods

All calculations were performed with Gaussian 09,⁵ with an ultrafine DFT integration grid. Geometry optimizations were carried out using the B3LYP density functional^{6,7} with the def2-TZVPP basis set.^{8,9} Dispersion was included with Grimme's D3 dispersion, including Becke-Johnson damping,¹⁰ denoted as B3LYP-D3(BJ). Stationary points were all characterized as minima by calculating the Hessian matrix analytically at the same level of theory.

8. Cartesian coordinates of optimized geometries

Trityl cation
C(Ph)₃

```
1 1
6    0.000000  0.000000  0.000000
6    0.000000  1.440415  0.000000
6   -1.011978  2.160237  0.672627
6    1.011978  2.160237 -0.672627
6   -0.998538  3.540843  0.683157
1   -1.767676  1.622616  1.225256
6    0.998538  3.540843 -0.683157
1    1.767676  1.622616 -1.225256
6    0.000000  4.232828  0.000000
1   -1.758784  4.083424  1.226453
1    1.758784  4.083424 -1.226453
1    0.000000  5.314109  0.000000
6    1.247436 -0.720207  0.000000
6    1.364831 -1.956518 -0.672627
6    2.376810 -0.203720  0.672627
6    2.567191 -2.635180 -0.683157
1    0.521389 -2.342160 -1.225256
6    3.565729 -0.905662  0.683157
1    2.289065  0.719544  1.225256
6    3.665737 -2.116414  0.000000
1    2.656957 -3.564863 -1.226453
1    4.415741 -0.518560  1.226453
1    4.602154 -2.657055  0.000000
6   -1.247436 -0.720207  0.000000
6   -1.364831 -1.956518  0.672627
6   -2.376810 -0.203720 -0.672627
6   -2.567191 -2.635180  0.683157
1   -0.521389 -2.342160  1.225256
6   -3.565729 -0.905662 -0.683157
1   -2.289065  0.719544 -1.225256
6   -3.665737 -2.116414  0.000000
```

1	-2.656957	-3.564863	1.226453
1	-4.415741	-0.518560	-1.226453
1	-4.602154	-2.657055	0.000000

C(C₆F₅)₃ cation

1	1		
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6	0.000000	1.438234	0.000000
6	-0.956903	2.184113	0.730216
6	0.956903	2.184113	-0.730216
6	-0.951001	3.561620	0.751340
9	-1.857921	1.562075	1.479733
6	0.951001	3.561620	-0.751340
9	1.857921	1.562075	-1.479733
6	0.000000	4.254843	0.000000
9	-1.830074	4.230083	1.473886
9	1.830074	4.230083	-1.473886
9	0.000000	5.562951	0.000000
6	1.245547	-0.719117	0.000000
6	1.413045	-1.920759	-0.730216
6	2.369949	-0.263354	0.730216
6	2.608953	-2.604401	-0.751340
9	0.423836	-2.390044	-1.479733
6	3.559954	-0.957219	0.751340
9	2.281757	0.827969	1.479733
6	3.684802	-2.127421	0.000000
9	2.748322	-3.699932	-1.473886
9	4.578396	-0.530151	1.473886
9	4.817657	-2.781476	0.000000
6	-1.245547	-0.719117	0.000000
6	-1.413045	-1.920759	0.730216
6	-2.369949	-0.263354	-0.730216
6	-2.608953	-2.604401	0.751340
9	-0.423836	-2.390044	1.479733
6	-3.559954	-0.957219	-0.751340
9	-2.281757	0.827969	-1.479733
6	-3.684802	-2.127421	0.000000
9	-2.748322	-3.699932	1.473886
9	-4.578396	-0.530151	-1.473886
9	-4.817657	-2.781476	0.000000

C(C₆F₅)₃OH

0	1		
6	0.028478	0.000058	-0.759341
6	1.421238	0.486264	-0.313035
6	1.669070	1.505162	0.603476
6	2.551973	-0.112568	-0.880725
6	2.953656	1.938469	0.907278
6	3.840281	0.303269	-0.592340

6	4.045727	1.341482	0.304210
6	-0.278333	-1.442464	-0.329407
6	-1.360568	-2.100138	-0.919843
6	0.436884	-2.167687	0.618089
6	-1.678903	-3.416125	-0.626376
6	0.134941	-3.486440	0.927638
6	-0.922686	-4.119145	0.298378
6	-1.097068	0.960385	-0.311023
6	-1.949707	0.728326	0.764628
6	-1.305096	2.155603	-0.995658
6	-2.977588	1.598367	1.101953
6	-2.319030	3.043124	-0.683546
6	-3.171327	2.758836	0.372424
9	-1.796444	-0.335954	1.562281
9	-3.770863	1.324113	2.135188
9	-4.150946	3.597607	0.688538
9	-2.468958	4.168171	-1.379145
9	-0.471251	2.525623	-1.991135
9	-2.174449	-1.462459	-1.763914
9	-2.719956	-4.002474	-1.215396
9	-1.220601	-5.380830	0.589313
9	0.857019	-4.140412	1.836781
9	1.443732	-1.620635	1.313146
9	2.430374	-1.162918	-1.694024
9	4.884034	-0.302495	-1.155233
9	5.277486	1.748593	0.588416
9	3.133522	2.926932	1.782244
9	0.679965	2.118696	1.268308
8	0.033610	-0.081784	-2.182724
1	0.205494	0.791575	-2.547193

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