

Original Article

# Application of Green Chemistry for the One-pot Preparation of Tris (4-bromophenyl) Chlorosilane

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**Abstract** - Among the twelve principles of green chemistry are the avoidance of waste, the use of benign chemicals, and the incorporation of the starting materials into the final product. To this end, a one-pot facile, more benign, less expensive and higher yield method has been used for the preparation of tris(4-bromophenyl)chlorosilane, which is a highly used precursor for the making of a rigid core carbosilane dendrimers. The reaction pathway for the synthesis of tris(4-bromophenyl)chlorosilane is similar to the procedure followed for synthesising similar compounds in the literature but with differences in starting materials and modifications in the workup processes. The tris(4-bromophenyl)chlorosilane in this work was prepared by the dissolution of 1,4-dibromobenzene in dry ether at -76 °C, followed by the slow addition/stirring of *n*-BuLi. After 1 h of stirring, tetrachlorosilane was slowly added at temperature range of -70 to -75 °C. The reaction setup was allowed to stir further to room temperature for 24 h. The reaction was stopped, followed by a workup to obtain a colourless powder product with an 82% yield. The colourless powder was characterised by melting point (123.4 °C) and elemental analysis (Anal. Calc for C<sub>18</sub>H<sub>12</sub>ClBr<sub>3</sub>Si: C, 40.67; H, 2.28; found: C, 40.80; H, 2.26; as well as <sup>1</sup>H NMR: δ (CDCl<sub>3</sub> 400 MHz) 7.44 (d, J = 8.4 Hz, 6H, Ar-H), 7.58 (d, J = 8.4 Hz, 6H, Ar-H); <sup>13</sup>C{<sup>1</sup>H}, NMR: δ (CDCl<sub>3</sub>, 101 MHz) 126.46, 130.66, 131.61, 136.53 ppm; <sup>29</sup>Si{<sup>1</sup>H}, NMR: δ (CDCl<sub>3</sub>, 79.5 MHz) 1.47 ppm. The results obtained from this one-pot synthetic method are in agreement with that reported in the literature for the multi-step pathway and more expensive starting materials.

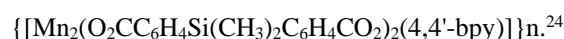
**Keywords** - Green chemistry, One-pot, Tris(4-bromophenyl)chlorosilane, *n*-BuLi, 1,4-dibromobenzene, Tetrachlorosilane.

## 1. Introduction

The traditional ways in which many chemical reactions are conducted are changing, especially as it relates to the overall greenness and sustainability of chemical processes. Chemistry is a dynamic science for which research chemists continue asking questions and experimenting to refine or replace existing methods and theories. This is most glaring for reactions with a wide range of applications constantly revisited, refined or modified to arrive at better methods or more benign products. Bridging ligands are important building units in the construction of Metal-Organic Frameworks (MOFs)<sup>1,2</sup> and Covalent Organic Frameworks (COFs)<sup>3</sup>. Hence, to control the structure of a MOF and or a COF material, the selection of rigid, organic linkers is one of the most crucial decisions.

For this reason, most of the organic linkers used in the construction of MOFs and COFs are usually molecules containing aromatic groups that give rigidity to MOF and COF networks. The functional groups in the aromatic organic ligand could be carboxylic acid (Davies et al., 2007, 2010; Guo et al., 2017; Li et al., 1999; Liu et al., 2017; Vlad et al., 2016; Wen et al., 2012) heterocyclic aromatic rings containing N atoms (pyridine)<sup>10-15</sup> or other coordinating functional groups such as phosphonates<sup>16-20</sup> and sulfonate<sup>21,22</sup>. In theory, the structure, as well as the properties of a MOF, can be pre-designed and systematically tuned using a suitable selection of the building blocks.

Dipyridyl linkers have also been used in the literature for the synthesis of MOF materials. However, as they are neutral components, another anionic ligand or counterion is required to balance out the positive charge on the metal centres. For example, Bunz and co-workers constructed a series of MOFs using the tetrahedral pyridine linker [tetrakis(4-(pyridin-4-ylethynyl)phenyl)silane].<sup>23</sup> This series of MOFs was reported to show a variety of topologies, interpenetrations as well as porosities. Mandal and co-workers used a carboxylate silicon-based linker, 4,4'-bipyridine as a co-connector and Mn(II) paddle-wheel subunit to construct



Mocanu *et al.*<sup>15</sup> used 1,3,5,7-tetrakis{4-(4-pyridyl)phenyl}adamantane and copper (II) ions to construct a 3-D MOF [CuL<sup>1</sup>(H<sub>2</sub>O)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O. This MOF was reported to show a 4-fold interpenetration with a pts topology. A zinc(II) MOF [Zn<sub>2</sub>(1 4-o-pda)<sub>2</sub>(1-abpy)]<sub>n</sub> based on flexible *o*-phenylenediacetate and rigid 4,4'-azobis(pyridine) ligands were constructed by Tabak and co-workers<sup>14</sup>. This MOF was reported to be thermally stable up to 300 °C.

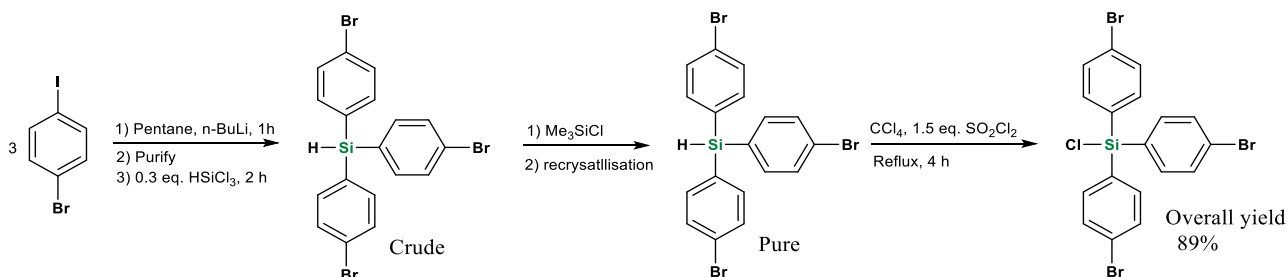
Most of the carboxylate and N-heterocyclic linkers used for the construction of MOF and COF materials are based on carbon centres as well as commercially available connectors. Silicon-based connecting units are scarce



compared to their carbon analogues, but silicon-centred linkers are more convenient to prepare through metathesis compared to their carbon analogues.<sup>25</sup> To this end, it is still desirable to design novel linkers with tailored dimensionality or pendant functional groups to have control of the physicochemical properties of the resultant framework materials. Several synthetic routes have been employed for the synthesis of varieties of rigid aryl systems based on silicon or boron centres with carboxylate or pyridyl pendants. (Amoroso et al., 1994; Baker et al., 2017; Beele et al., 2010; Davies et al., 2010; Delmas et al., 2017; Deshmukh et al., 2017; Gontarczyk et al., 2015; Kotha and

Shah, 2008; Liu 2017; Schüttrumpf et al., 2015; Wander et al., 2009; Wang et al., 2010; Wenzel et al., 2009; Yang et al., 2008; Zhang et al., 2013)

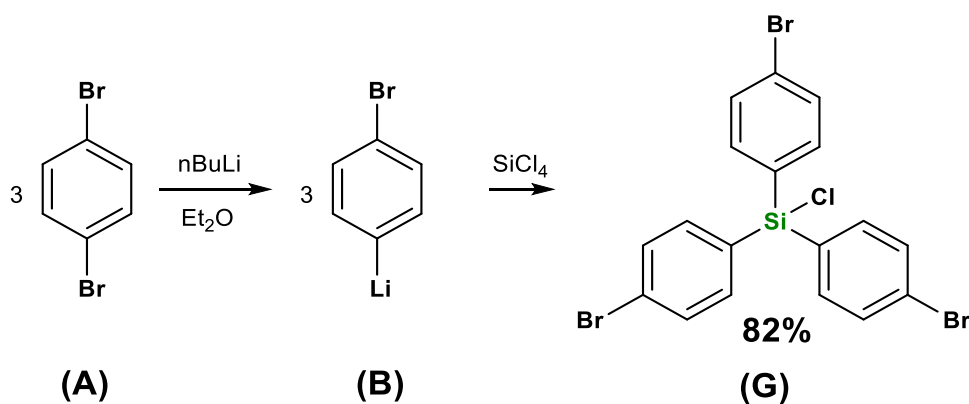
In this study, tris(4-bromophenyl)chlorosilane (G), a molecule usually utilised as a precursor for the formation of a rigid core carbosilane dendrimers, has been synthesised through a one-pot facile and straightforward technique. In the literature<sup>26</sup>, the preparation of compound (G) was carried out using several steps that involved the formation of tris(4-bromophenyl)silane followed by the addition of the other reagents to give the compound (G) as shown in Scheme 1



Scheme 1. Multi-step synthetic method for the preparation of tris(4-bromophenyl)chlorosilane (G), adapted from reference <sup>26</sup>.

The tris(4-bromophenyl)silane was thereafter chlorinated using reagents such as  $\text{Cl}_2$ ,  $\text{PCl}_5$ ,  $\text{CCl}_4$  or  $\text{SO}_2\text{Cl}_2$  to give (G). In addition to being a multi-step synthetic route which is time-consuming, the starting material, 1-bromo-4-iodo benzene, as well as some of the other reagents used in this protocol, are expensive, corrosive, pyrophoric and carcinogenic.

In this report, a straightforward and less expensive method is used for the synthesis of compound (G), as shown in Scheme 2



Scheme 2. Reaction method for the preparation of compound (G)

The reaction pathway for the synthesis of compound (G) is similar to the procedure followed for the synthesis of compounds of some similar molecules but with some modifications in the workup process. The workup for the making of compounds in the literature required the quenching of the reaction with water (details in experimental section), whereas, in the making of compound (G), the reaction was not quenched with water (to avoid hydrolysis of the remaining Si-Cl group) rather, more dry ether was added to partition all of the product into the organic layer and the formation of the colourless precipitate. The precipitate formed at the end of the reaction was filtered off, and the volatiles were removed using a rotary evaporator to give a colourless powder.

## 2. Materials and Method

### 2.1. Chemicals and Reagents

All chemicals, reagents and solvents were purchased from Sigma Aldrich or Alfa Aesar and used as received unless otherwise stated. Spectroscopy:  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{11}\text{B}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AVANCE III HD 400 MHz or 500 MHz spectrometers in  $\text{CDCl}_3$  solvent unless stated otherwise. The chemical shifts ( $\delta$ ) for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{29}\text{Si}\{^1\text{H}\}$ , and  $^{11}\text{B}\{^1\text{H}\}$ , are quoted in ppm with reference to  $\text{Me}_4\text{Si}$  and  $\text{BF}_3\text{OEt}_2$  respectively. Coupling constants are reported in Hz. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode. Elemental analysis was carried out by Stephen Boyer of London Metropolitan University, Uk.

In a three-neck round bottom flask equipped with a magnetic stirrer bar, 1,4-dibromobenzene (14.16 g, 60 mmol) was dissolved in dry Et<sub>2</sub>O (100 ml) under N<sub>2</sub> and then degassed. The degassed solution was cooled to -76 °C. <sup>n</sup>BuLi (2.5 M) in hexane (24 ml, 60 mmol) was added to the solution dropwise while stirring. After the addition of the <sup>n</sup>BuLi, the solution was slowly raised to room temperature and stirred for another 1 h. The solution was then cooled again to -75 °C, and then tetrachlorosilane (3.4 g, 2.3 ml, 20 mmol) was added slowly, keeping the temperature in the range of -70 to -75 °C. At the end of the addition, the reaction mixture was slowly raised to room temperature again and stirred overnight. The next day 30 ml of dry Et<sub>2</sub>O was added to the reaction mixture. Some white precipitates were observed (LiCl), and these were removed via filtration by the use of a Buchner funnel. The precipitate on the Buchner funnel was rinsed with (25 ml x 4) of dry Et<sub>2</sub>O.

The filtrate was transferred into a round bottom flask, and the solvent was removed using a rotary evaporator to give a crude powder product which was recrystallized from hexane (-40 to -50 °C) to give colourless powder which was stored under dry N<sub>2</sub> at 4 °C (8.73 g, 82%) yield (lit, 95%)<sup>26</sup>, Mp: 123.4 °C (lit, 123 °C)<sup>26</sup>; Anal. Calc for C<sub>18</sub>H<sub>12</sub>ClBr<sub>3</sub>Si:

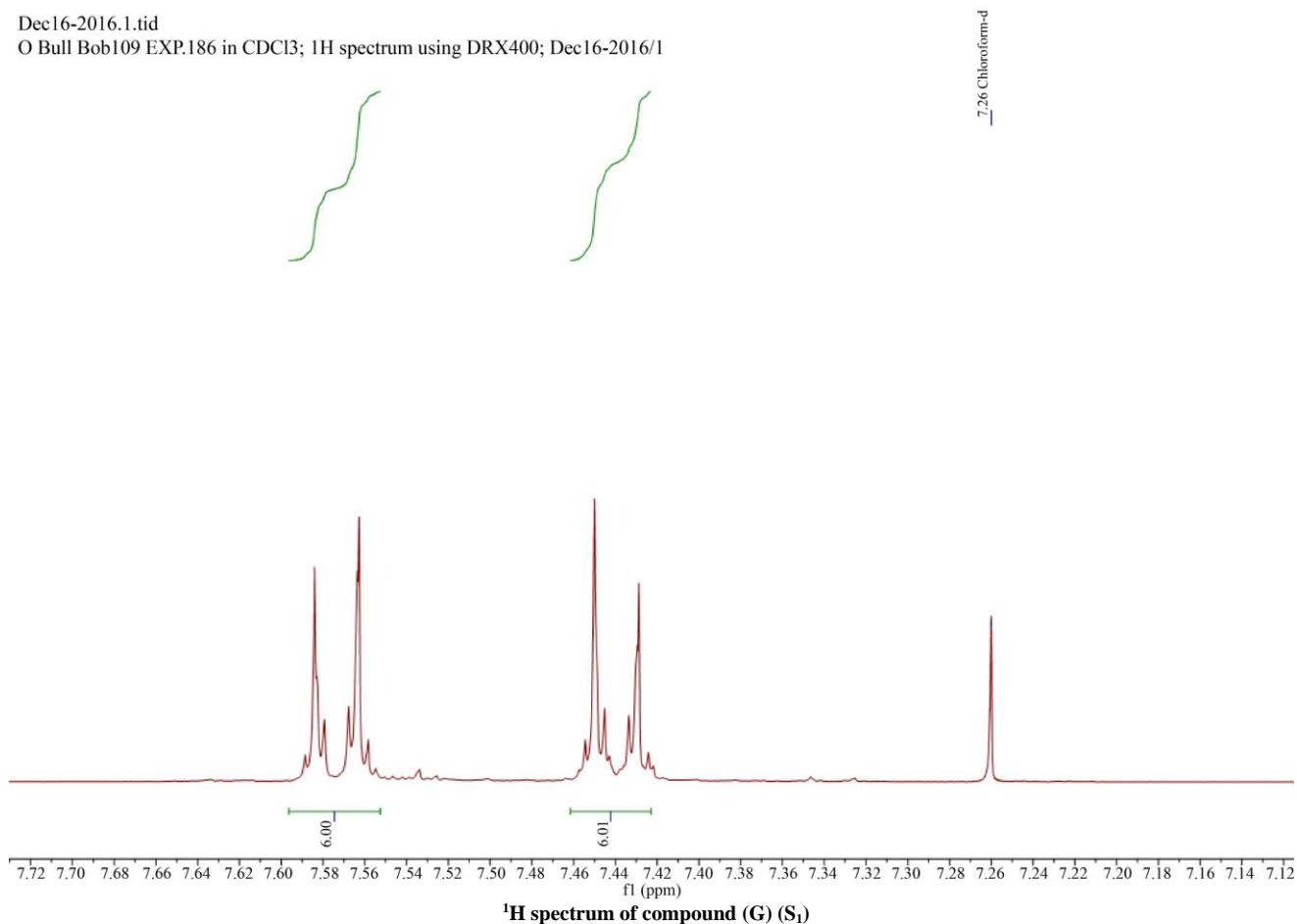
C, 40.67; H, 2.28; found: C, 40.80; H, 2.26; <sup>1</sup>H NMR: δ (CDCl<sub>3</sub> 400 MHz) 7.44 (d, *J* = 8.4 Hz, 6H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 6H, Ar-H); <sup>13</sup>C{<sup>1</sup>H}, NMR: δ (CDCl<sub>3</sub>, 101 MHz) 126.46, 130.66, 131.61, 136.53 ppm; <sup>29</sup>Si{<sup>1</sup>H}, NMR: δ (CDCl<sub>3</sub>, 79.5 MHz) 1.47 ppm.

### 3. Results and Discussion

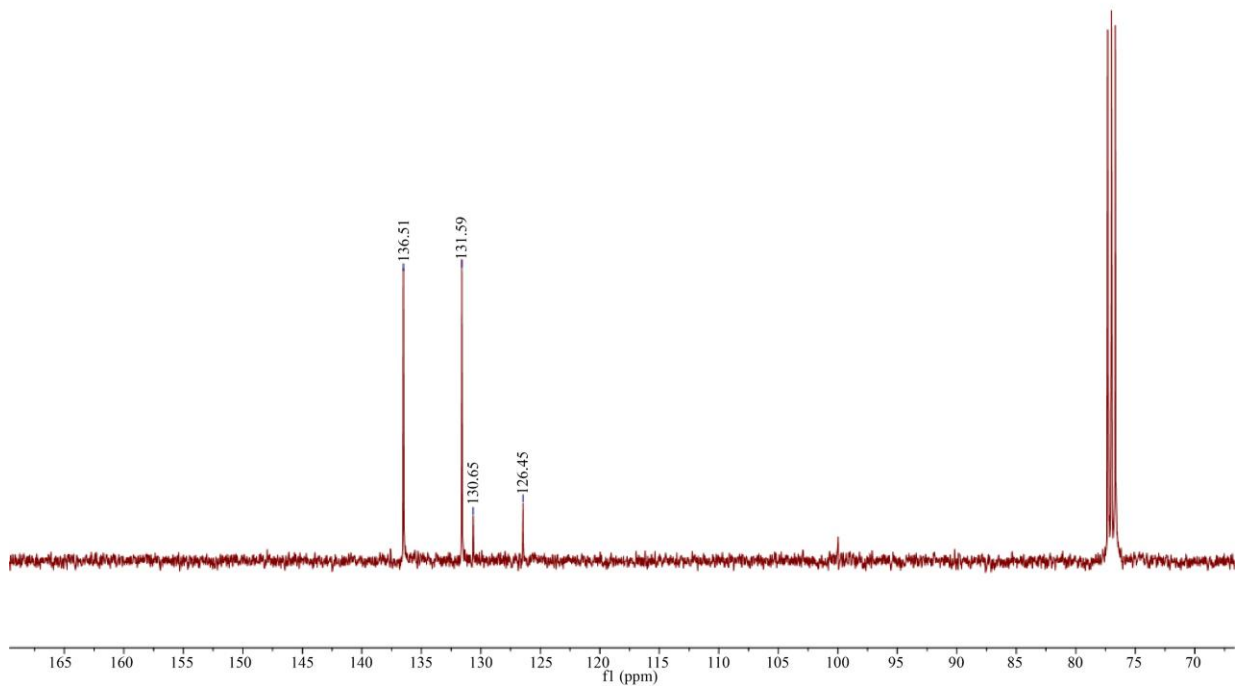
The results of the melting of the obtained products as well as the spectroscopic studies, show that tris(4-bromophenyl)chlorosilane has been prepared via a one-pot synthetic method. The final obtained powder was recrystallized from hexane, which resulted in the formation of compound (G) in 82% (M.p = 123.4 °C) (lit. overall yield, 89%, M.p = 123 °C).<sup>26</sup> The <sup>1</sup>H NMR of the compound (G) showed well-resolved resonances with aromatic proton signals found within the range δ = 7.44 - 7.58 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of (G) shows signals for the aromatic carbons in the range of 126.46-136.33 ppm. Furthermore, the <sup>29</sup>Si{<sup>1</sup>H} NMR of compound (G) shows a singlet at (1.47 ppm), (lit. 1.48 ppm).<sup>26</sup> The NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H}) spectra of compound (G) are provided as supplementary information (S<sub>1</sub>-S<sub>3</sub>, respectively).

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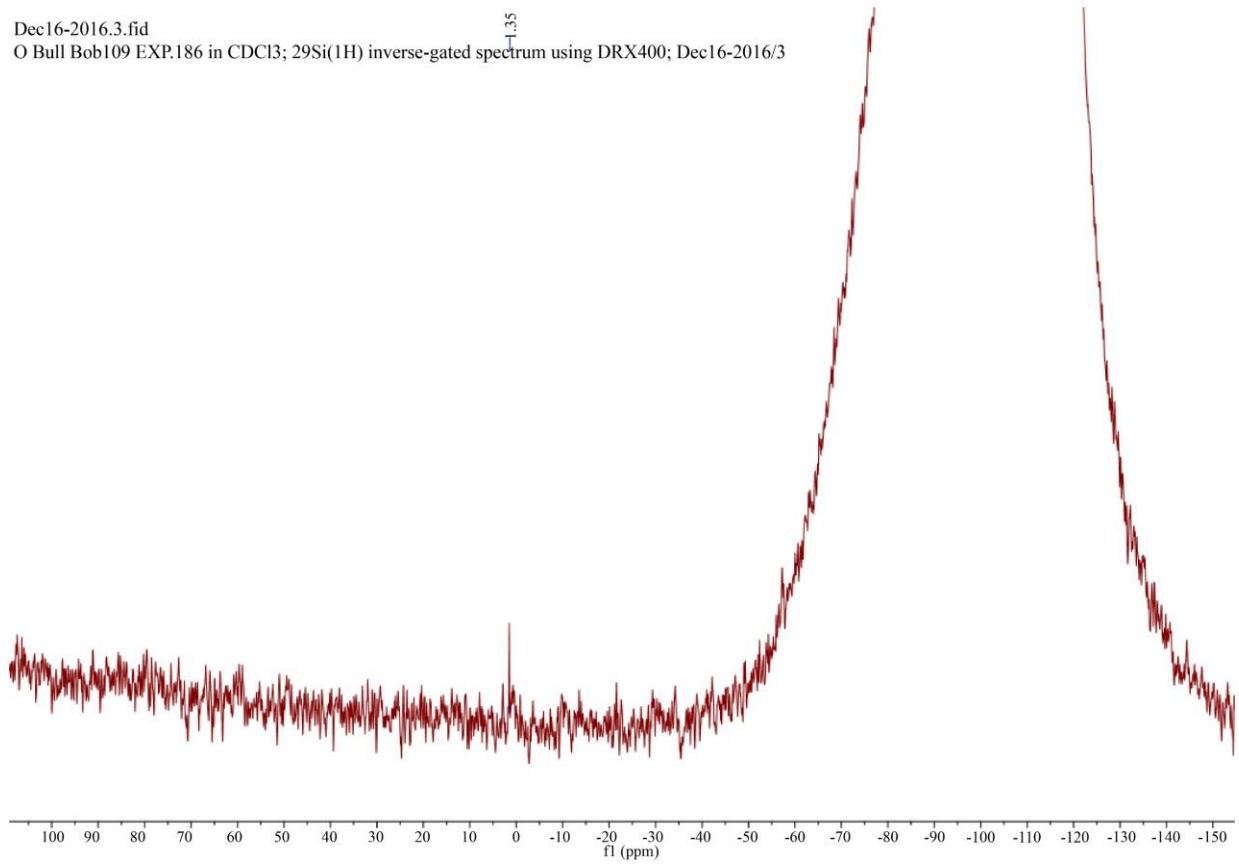
O Bull Bob109 EXP.186 in CDCl<sub>3</sub>; <sup>1</sup>H spectrum using DRX400; Dec16-2016/1



Dec16-2016.2.hid  
O Bull Bob109 EXP.136 in CDCl<sub>3</sub>; <sup>13</sup>C{<sup>1</sup>H} spectrum using DRX400; Dec16-2016/2



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O Bull Bob109 EXP.186 in CDCl<sub>3</sub>; <sup>29</sup>Si{<sup>1</sup>H} inverse-gated spectrum using DRX400; Dec16-2016/3



#### 4. Conclusion

A one-pot green synthetic method has been used to prepare tris(4-bromophenyl)chlorosilane- a widely used precursor for the making of rigid carbosilane dendrimers. This method is safe, less expensive, fast, high yielding and easy to replicate. Therefore it should be explored with more robust starting materials such as 4, 4'-dibromo-1,1'-biphenyl.

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